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# Functional Supramolecular Architectures: Mechanistic Analysis of Solid-State Colorimetric Switching and Creation of Novel Energy Conversion Materials 

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# Functional Supramolecular Architectures: Mechanistic Analysis of Solid-State Colorimetric Switching and Creation of Novel Energy Conversion Materials 

by

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## Dissertation

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## Dedication

Dedicated to Yogi and Allison. I love you both more than anything.
"I am among those who think that science has great beauty [she told her interlocutors.] A scientist in his laboratory is not only a technician: he is also a child placed before natural phenomena which impress him like a fairy tale."

- Marie Curie, Nobel Prize in Physics (1903), Nobel Prize in Chemistry (1911)

Excerpt from Madame Curie: a biography. By Eve Curie, translated by Vincent Sheean. Doubleday, Doran: New York, 1939

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# Abstract <br> Functional Supramolecular Architectures: Mechanistic Analysis of Solid-State Colorimetric Switching and Creation of Novel Energy Conversion Materials 

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There is still a great deal to learn about the assembly and dynamic properties of solid-state supramolecular architectures. The higher order structure of solids imposes severe limitations on molecular motion and dynamics. Yet, there is growing interest in creating dynamic solids that assemble in predictable ways for functional applications, including sensing and energy conversion. An understanding of the interplay between all of the relevant non-covalent interactions is fundamental for the rational design of such architectures. Electrostatic interactions of all types, including hydrogen bonding and van der Waals interactions, combine to determine the exact intermolecular geometries adopted by organic molecules and assemblies in solids, liquids, and mesophases.

A significant portion of work in the Iverson group has broadly focused on the self-assembly of aromatic units, both in solution and more recently, in the solid-state. This dissertation builds on this body of research and describes fundamental investigations into intermolecular interactions that give rise to functional supramolecular architectures, driven by the self-assembly of organic molecules in the solid-state. The majority of this vii
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Chapter 1 provides an introduction to non-covalent interactions, polymorphism, and stimuli-responsive materials. Chapter 2 describes the synthesis of 14 new MAN-NI dyads, and goes on to provide an in-depth structural and spectroscopic characterization illustrating the different polymorphs that can be formed by symmetric and asymmetric dyads, as well as the photophysical origins for the differences in color between various polymorphs. Chapter 3 details the stimuli-responsive properties of dyads, with particular focus on the thermochromic orange-to-yellow transition seen when dyads are heated. Detailed structural, spectroscopic, thermal, and morphological analyses are described in the context of characterizing the two different states. Chapter 4 goes on to describe the mechanistic analysis that uncovered the presumptive molecular switching mechanism, and the key interactions that enable polymorphic switching mechanisms. Chapter 5 details the application of aromatic interactions for the rational design of supramolecular assemblies in perylene diimides (PDI) for novel energy conversion materials.

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## CHAPTER 1

## Aromatic Interactions in Supramolecular Chemistry: Dynamics and Properties of Self-Assembled, Stimuli-Responsive Materials

### 1.1 NON-COVALENT Interactions

Non-covalent forces are a requirement for life as we know it. Hydrogen bonding between water molecules provides the solution that enables interactions between organic molecules and vital biological machinery. These hydrogen bonds also contribute to the stability of complementary double-stranded DNA (dsDNA) that allow for compact and valuable storage redundancy, yet are weak enough to allow the "unzipping" of dsDNA by topoisomerases, and the "reading and writing" of sequences by polymerases in growing or expressing cells.

Yet, the complexity seen in nature relies on an ensemble of dynamic intermolecular interactions, not just hydrogen bonds. Hydrophobic and entropic effects further help to keep DNA assembled, and as chemists, we have learned to better understand and characterize intermolecular interactions, including those that stabilize the double helix of DNA. Specifically, we can attribute stability of dsDNA to conformational preferences of the sugar phosphate backbone combined with aromatic interactions, an encompassing interaction including the hydrophobic effect, dispersive, and electrostatic interactions. Aromatic interactions between DNA bases provide favorable interbase interactions, while also minimizing the exposure of hydrophobic nucleobases to water, and maximizing the entropically favorable solvation of the sugar phosphate backbone.

Medicinal chemists have come to exploit the same aromatic interactions as a way to target DNA for pharmaceutical therapies. Aromatic interactions enable lifesaving chemotherapeutics like Doxorubicin to kill cancer cells by intercalating into dsDNA, blocking the unzipping action of topoisomerases as well as the reading and writing of DNA by polymerases. ${ }^{1}$ Driven by non-covalent interactions, the intercalating drug kills cancer cells by stopping the dynamic molecular machines required for life.

While individually weak and operating on the atomic scale, accumulation of various noncovalent interactions can create stable structures that can be visualized, as in the case of the microscopic supramolecular assemblies of DNA with various histone proteins that form chromosomes. Yet even larger manifestations of weak intermolecular interactions can be seen at the macroscopic level, as in the case of a gecko fixed to a vertical wall, held against gravity by van der Waals interactions. ${ }^{2}$

Although dispersive interactions are critical for the gecko to adhere, the interaction alone provides little benefit to its vitality without the dynamic ability to change it, for example, in order to avoid predation. The geckos' ability to run relies on the concerted and cooperative movements of myosin molecular machines along actin filaments, powered by ATP. Macroscopic movement is achieved when energy derived from ATP is coupled to the molecular machine, ${ }^{3}$ in turn driving collective and dynamic conformational changes between various forms, each being accessible by varying an ensemble of non-covalent interactions. While natural selection has had great success in manipulating numerous dynamic, non-covalent interactions that enable life, chemists are only beginning to combine non-covalent interactions in dynamic, supramolecular assemblies.

In organic molecules, the ability to rationally predict conformational preferences in solution, or packing geometries in the solid-state becomes increasingly difficult with size. An understanding of the interplay between covalent constraints and non-covalent interactions is fundamental for the rational design of molecules that interact with predictable geometries. In order to achieve the complexity observed in nature, we must not just learn to understand and
utilize the collective ensemble of non-covalent interactions, we must also learn how to alter and access various conformations through dynamic molecular motions.

### 1.2 Interactions Between Alkanes

Alkanes and other hydrophobic organic molecules are attracted to one another primarily through dispersion forces, as there is no permanent electrostatic attraction between alkanes. ${ }^{4}$ Specifically, London dispersion forces represent the attractive term in the interaction described by the van der Waals potential, ${ }^{5}$ and reflect induced dipole-induced dipole interactions that underlie favorable intermolecular interactions in polarizable alkanes.

The hydrophobic effect can also drive the association of hydrophobic, organic molecules in certain environments. The self-association of hydrophobic molecules in aqueous environments is known as the hydrophobic effect, and is primarily responsible for the folding of proteins, the assembly of phospholipids into membranes, and sometimes the binding of small molecules to receptors in water. ${ }^{4}$ The hydrophobic effect primarily arises from the exposed organic surface area and two primary mechanisms decrease exposed organic surface: self-aggregation of organics and shape changes to decrease hydrophobic surface area. Shape changes result from conformational rotations in simple alkanes, with changes from staggered-anti to gauche conformations decreasing the surface area presented by an alkane.

While other intermolecular effects are often invoked when rationalizing stability preferences (e.g. orbital interactions, aromatic interactions, etc.), it is valuable to note the strength of dispersion forces. For example, the most energetically favorable packing of $n$-pentane dimers has a binding energy of $3.6 \mathrm{kcal} \mathrm{mol}^{-1}$, significantly stronger than the binding of the benzene dimer $\left(2.7 \mathrm{kcal} \mathrm{mol}^{-1}\right) .{ }^{5}$ When packed as trans isomers in the solid-state that limit their conformational flexibility, alkanes are held together in part by homonuclear $\mathrm{R}-\mathrm{H} \cdots \mathrm{H}-\mathrm{R}$ dihydrogen interactions. ${ }^{6}$ While individually weak, accumulations in longer, rigid packed alkanes can yield significant association energies, as high as $4.6 \mathrm{kcal} \mathrm{mol}^{-1}$ in $n$-hexane, ${ }^{7}$ and
even higher in alkyl polyhedranes. ${ }^{6}$ These weak van der Waals interactions differ from weak hydrogen bonds as, unlike the latter, these induced dipole-induced dipole interactions do not have directionality requirements. ${ }^{6}$

An interesting phenomenon seen in alkanes is the "odd-even" effect, where the melting points of alkanes are seen to increase in a 'zig-zag' shape, rather than a continuous increase. ${ }^{8}$ While Baeyer noted this experimental observation in $1877,{ }^{9}$ the basis for this behavior was not understood fully until the start of the $21^{\text {st }}$ century. ${ }^{10}$ Single-crystal structures of $n$-alkanes longer than six carbons show characteristic differences in packing between even and odd numbered alkanes. In even numbered alkanes, methyl groups on each chain end have optimal intermolecular contacts to adjacent alkanes, whereas odd numbered chains have optimal distances only at one end of the chain, and longer distances at the other. Thus, a "packing effect" is seen to give rise to the odd-even effect, and can be explained by a simple geometric model for crystal packing, where odd alkanes have lower density, fewer intermolecular contacts, and thus have lower melting points.

### 1.3 AROMATIC INTERACTIONS \& AROMATIC SELF-ASSEMBLY

### 1.3.1 Modern Theory: Local, Direct Interaction Model

Interactions between aromatic units have been well known and increasingly studied over the last half-century. Our current understanding of aromatic interactions has enabled the application of this fundamental non-covalent interaction to numerous fields including catalyst design, ${ }^{11,12}$ optical monitoring and self-assembly, ${ }^{13}$ and molecular sensing. ${ }^{14}$

Yet, interactions between aromatic units have not been as widely studied as other noncovalent interactions. In 1960, Patrick and Rosser published a short report describing a 1:1 complex that formed when benzene and hexafluorobenzene are mixed. ${ }^{15}$ A model for understanding the formation of this complex as well as rationalizing the geometries adopted by interacting aromatic was put forth by Hunter and Sanders in $1990 .{ }^{16}$ This model, known as the
"polar $/ \pi$ model", is an often invoked rationale for understanding the relative geometries adopted by aromatic units. The "polar/ $\pi$ model" model rationalizes aromatic stacking as resulting from maximizing favorable quadrupole-quadrupole interactions between aromatic units ${ }^{16}$ and found apparent support in subsequent experimental work. ${ }^{17-19}$ Qualitatively, analysis of quadrupolequadrupole interactions can be visualized by comparing calculated electrostatic potential maps (ESPs) between the relevant aromatic units (Figure 1.1).




Common Aromatic Stacking Geometries


Offset Parallel, or
Offset Face-to-Face


Face-Centered, Sandwich Stacked, or Parallel Face-to-Face



Edge-to-Face, or Herringbone

Figure 1.1 Calculated electrostatic potential maps (ESPs) for the indicated molecules, scaled for relative comparison. Bottom: common aromatic stacking geometries and some of the descriptions often encountered to describe each.

Based on analysis of quadrupole moments, a molecular complex between benzene and hexafluorobenzene could be rationalized as having a 'face-centered' aromatic stacking geometry because complementary charges within each respective aromatic ring would be maximized in this geometry (Figure 1.1)

While the "polar/ $\pi$ model" provides a nice description for the face-to-face stacking interactions of complementary aromatic units, as in the case of benzene and hexafluorobenzene, the model does not accurately describe the favorable self-associations of electron rich aromatics. For example, the "polar/ $\pi$ model" would expect unfavorable face-to-face interactions between two methoxybenzene (anisole) molecules (top right Figure 1.1), as the methoxy group is a known electron donor, and the interaction of two electron rich aromatics based on quadrupolequadrupole interactions would thus be unfavorable. Yet, numerous examples have shown that all substituents stabilize the substituted benzene dimers in the gas phase, ${ }^{20-25}$ and a more accurate model to describe interactions between various aromatic units must account for such interactions.

Later work by Rashkin and Waters, ${ }^{26}$ as well as computational work by Wheeler and Houk, ${ }^{27,28}$ and more recently Wheeler, ${ }^{20,29-31}$ has provided strong evidence in favor of a different model, known as the "local, direct interaction" model. ${ }^{20}$ This model postulates that the substituents on aromatic rings dictate aromatic stacking geometries as a result of local, throughspace electrostatic interactions from polarized bonds. Whereas previous model has rationalized stacking geometry based on polarization of the $\pi$-electron cloud, the "local, direct interaction" model poses that aromatic geometry results from the local, direct interaction between substituents and the other ring. Said differently, strong electrostatic dipoles on the periphery of aromatic units dictate aromatic interaction geometries. This "local, direct interaction" model has since been expanded to include various interaction geometries, including edge-to-face interactions, as well as other aromatic interactions, including the cation $/ \pi^{28}$ and anion $/ \pi$ interactions. ${ }^{32}$

Elegant computational work supporting this model has been reported, and an example of such work is shown in Figure 1.2. Computational work revealed that the interaction in the
benzene dimer with varying substituents (e.g. $\mathrm{X}-\mathrm{C}_{6} \mathrm{H}_{5} \cdots \mathrm{C}_{6} \mathrm{H}_{6}$ ) can be modeled simply by the interaction between a hydrogen capped substituent and an aromatic ring, without the substituent being itself bound to an aromatic ring (e.g. (X-H $\left.{ }^{\cdots} \mathrm{C}_{6} \mathrm{H}_{6}\right)$. Shown in the top of Figure 1.2 is a plot of the computed interaction energy of dimers made between benzene and one of 25 different monosubstituted benzenes plotted versus the Hammet $\sigma_{\text {meta }}$ parameter, which is taken to reflect the inductive electron-donating or withdrawing ability of a given substituent. ${ }^{27}$ The overall correlation between $\sigma_{\text {meta }}$ and the relative interaction energy is taken to indicate that the interaction between aromatics can be qualitatively understood in terms of the electron donating or withdrawing characteristics of a given substitent. ${ }^{27}$

To understand the nature of this interaction, a simple change was made to the benzene dimer, where the benzene ring in the substituted benzene derivative was replaced with a simple hydrogen atom (e.g. $\mathrm{Cl}-\mathrm{C}_{6} \mathrm{H}_{5}$ becomes $\mathrm{Cl}-\mathrm{H}$ ). Shown in the bottom of Figure 1.2, a remarkably similar correlation exists is shown for the dimer formed from a hydrogen-capped substituentbenzene dimer ( $\mathrm{X}-\mathrm{H} \cdots \mathrm{C}_{6} \mathrm{H}_{6}$ ) and the substituted benzene-benzene dimer ( $\mathrm{X}-\mathrm{C}_{6} \mathrm{H}_{5} \cdots \mathrm{C}_{6} \mathrm{H}_{6}$ ) shown above. For the 25 different substituents in each case, a strong correlation is seen between the two different interaction energies $(r=0.91) .{ }^{27}$ This remarkable similarity was the basis for the "local, direct interaction" model, where the substituent effects can be described simply from the direct interaction between the substituent and the other ring, and did not need to involve the $\pi$-system of the substituted ring. ${ }^{27}$


Figure 1.2 The "local, direct interaction" model of aromatic interactions shows that the same relative interaction energy exists between a substituted benzene-benzene dimer, and a hydrogen bound substituent-benzene dimer when plotted against $\sigma_{\text {meta }}$. Reprinted with permission from Ref. ${ }^{30}$, https://pubs.acs.org/doi/10.1021/ar300109n .Copyright 2012 American Chemical Society.

### 1.3.1.1 Electrostatic Potential Maps and Aromatic Interactions

In the previous section, electrostatic potential maps (ESPs) were used in order to qualitatively understand interactions between aromatic units. As ESPs will be referenced throughout this dissertation, a few brief comments are necessary in order to clearly explain what they can and cannot tell us, as well as how they can be qualitatively 'predicted'.

Briefly, ESPs are a priori quantum mechanical calculations that reflect the attractive or repulsive force calculated from moving a positive point charge around the surface of a given molecule. ${ }^{4}$ In this work, all ESPs are calculated using an isodensity surface with an electronic distribution of 0.002 electrons $\mathrm{au}^{-3}$, corresponding to over $99.5 \%$ of total electron density. In plotted ESPs, the magnitude of the interaction (plotted as energy) between the point charge and the molecule is shown, and a red color will always refer to an attractive force.

Substitutions on benzene rings that result in changes to ESPs are often used to rationalize local changes to electronics following substitution. For example, addition of electron donating substituents resulting in changes to calculated ESPs are sometimes said to reflect a more "electron rich" system, when that is not necessarily the case. Wheeler and Houk have noted that ${ }^{33}$ "While negative ESPs often do correspond to electron-rich regions, the assumption that changes in ESPs necessarily indicate local changes in the electron density is incorrect.", and thus, caution must me made when evaluating ESPs. While the calculated ESP is a function of electron density in all surrounding space with an inverse dependence on distance, even small differences in charge distribution can have significant effects on calculated ESPs. For example, a charge of $0.1 e$ results in changes of over $10 \mathrm{kcal} \mathrm{mol}^{-1}$ to the ESP at a distance of $3 \AA \AA^{33}$ Wheeler has gone on to note that simply considering the sign of the ESP above the center of aromatic rings when trying to predict aromatic interactions may lead to conclusions that are not supported by accurate computational predictions, ${ }^{20}$ and that ESPs do not necessarily provide reliable indication of the strength of electrostatic components of stacking interactions. ${ }^{20}$ This is in agreement with our earlier discussion, noting that there is actually a favorable interaction in the formation of a methoxybenzene dimer, despite the red color central to the ESP shown in Figure
1.1. It is the C-O bond dipole of anisole that dictates the aromatic geometry adopted between the two units, and in a face-to-face dimer, the preferred interaction geometry for would avoid overlapping the strong C-O bond dipoles, either by adopting an off-set parallel geometry, or having rotational differences, such that the C-O bonds are oriented away from one another.

ESPs can provide a qualitative tool for understanding the interactions between substituted aromatic rings when used in appropriate ways, and can even be qualitatively envisioned in many simple cases with prior knowledge of certain reference ESPs. Wheeler and Houk have shown a valuable method for predicting ESPs for substituted benzenes by the additive construction from simpler ESP components. ${ }^{28}$ In this method, illustrated in Figure 1.3, the ESP for various substituted benzene derivatives are shown to be remarkably similar to the "additive ESPs" constructed by adding the individual benzene and substituent ESP together. This method shows that ESPs can be predicted from the addition of hydrogen-capped substituent ESPs to benzene, and allows for a quick 'back of the envelope' tool to quickly and qualitatively evaluate electrostatic charges on substituted aromatics that can be valuable when rationalizing aromatic interaction geometries.

Note the ESP for cyanobenzene (Figure 1.3) shows a more positive ESP compared to unsubstituted benzene (see Figure 1.1). As discussed above, the origins for this relative increase in positive ESP above the center of the cyanobenzene are not the result of a decrease in electron density of the pi-system from the cyano substituent. Rather, this effect to the ESP arises from through-space effects caused by the appended cyano group, whereby the positive local dipole from the CN substituent "overwhelms" the negative character provided by the aryl pi-system. Thus, changes in ESPs should not be taken as an indication of local changes in electron density. ${ }^{28,30}$


Figure 1.3 Calculated ESPs for substituted aromatics (top) strongly resemble ESPs generated by adding separately computed ESPs for benzene and each substituent (bottom). Reprinted with permission from Ref. ${ }^{30}$, https://pubs.acs.org/doi/10.1021/ar300109n .Copyright 2012 American Chemical Society

### 1.3.2 Aromatic Interactions in Solution

Aromatic interactions are derived from a combination of electrostatic, dispersive, and solvophobic interactions. ${ }^{34}$ Because of the combination of different physical interactions, aromatic interaction energetics can show large variation depending on the aromatics involved, as well as the surrounding conditions (e.g. water versus chloroform). Aromatic interactions have been experimentally studied in the solution using a number of different platforms that rely on the same basic premise: rigid systems that can force aromatic interactions, and measuring a distribution interacting and non-interacting geometries using ${ }^{1} \mathrm{H}$ NMR.

Work in the early 1990s by Cozzi, Siegel, and coworkers investigated the influence of substituent effects on solution-based aromatic interactions in cofacial 1,8-diarylnaphthalene
systems using ${ }^{1} \mathrm{H}$ NMR (Figure 1.4). ${ }^{17-19}$ In this rigid naphthyl framework, appended aromatic rings are be forced into a face-to-face type interaction which would be this lost based on rotation around the indicated biaryl-type bond (Figure 1.4). NMR was used to quantify the rotation barrier, which in turn was used as a proxy for the strength of the parallel interaction. The authors reported that polar $/ \pi$ electrostatic interactions were the determinant in understanding the geometry adopted by the two appended arenes, as opposed to charge-transfer based interactions. ${ }^{17-19}$ Rashkin and Waters ${ }^{26}$ went on to provide experimental work to explain that the magnitude of offset parallel interactions as resulting from orientational effects between substituents and hydrogen atoms on adjacent rings (Figure 1.4). More recent work by Shimizu and coworkers ${ }^{34-36}$ using atropisomeric molecular torsion balances have studied positional and additive substituent effects, and trends were found to agree with the "local, direct interaction" model put forth by Wheeler and Houk, yet could not definitively rule out indirect substituent effect interactions.


Cozzi and Siegel, 1993


Rashkin \& Waters, 2002


Shimizu, 2008

Figure 1.4. Examples of systems used to experimentally study aromatic interactions in solution.

Other strategies to study and quantify aromatic interactions in solution have been put forth by Cubberley and Iverson. Using aromatic donor 1,5-dihydroxynaphthalene (DAN) and acceptor 1,4,5,8-naphthalenetetracarboxylic diimide (NDI), association constants were determined for donor-acceptor complexes as well as respective self-association complexes in solvents of varying polarities, as measured by the empirical solvent parameter $\mathrm{E}_{\mathrm{T}}(30)$. Results
from ${ }^{1} \mathrm{H}$ NMR binding studies are shown in the top of Figure 1.5. In general, association constants are larger in solvents of increasing polarity for DAN-DAN, NDI-NDI, and DAN-NDI complexes. The increase in association constant as a function of solvent polarity was interpreted as a consequence of the hydrophobic effect, whereby the larger aromatic faces are driven to associate more in higher polarity solvents as a way of decreasing unfavorable exposure of aromatic surface area to the surrounding environment. Noteworthy, larger binding constants are seen for the NDI-NDI self-association complexes compared to the DAN-DAN complexes can be attributed in part to the larger NDI surface area, thus engendering a larger net hydrophobic effect. It is worth mentioning at this point that the strongly polarized carbonyls of NDI (Figure 1.6) distributed around the ring would allow for more favorable aromatic stacking geometries, for example in an off-set parallel stacking geometry, compared to DAN.

|  | Solvent | $K_{\mathrm{a}}\left(\mathbf{M}^{-1}\right)$ (donor-donor) | $K_{\mathrm{a}}\left(\mathbf{M}^{-1}\right)$ (acceptor-acceptor) | $\begin{gathered} K_{\mathrm{a}}\left(\mathbf{M}^{-1}\right) \\ \text { (donor-acceptor) } \end{gathered}$ | $-\Delta G^{\circ}(\mathrm{kcal} / \mathrm{mol})$ <br> (donor-acceptor) | $\begin{gathered} E_{\mathrm{T}(30)} \\ (\mathrm{kcal} / \mathrm{mol}) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{CDCl}_{3}$ | (1) | (1) | $2 \pm<0.5$ | 0.4 | 39.1 |
| 2 | acetone-d6 | $1 \pm<0.5$ | $1 \pm<0.5$ | $8 \pm<0.5$ | 1.2 | 42.2 |
| 3 | DMSO-d6 | $1 \pm 1$ | $2 \pm<0.5$ | $3 \pm<0.5$ | 0.7 | 45 |
| 4 | $\mathrm{CD}_{3} \mathrm{CN}$ | $1 \pm 1$ | $3 \pm<0.5$ | $11 \pm<0.5$ | 1.4 | 45.6 |
| 5 | $\mathrm{CD}_{3} \mathrm{OD}$ | $1 \pm<0.5$ | $8 \pm<0.5$ | $30 \pm<0.5$ | 2 | 55.5 |
| 6 | $3: 1 \mathrm{CD}_{3} \mathrm{OD} / \mathrm{D}_{2} \mathrm{O}$ | $1 \pm<0.5$ | $15 \pm<0.5$ | $63 \pm 2$ | 2.5 | 57 |
| 7 | $1: 1 \mathrm{CD}_{3} \mathrm{OD} / \mathrm{D}_{2} \mathrm{O}$ | $2 \pm<0.5$ | $28 \pm 2$ | $254 \pm 41$ | 3.3 | 58.9 |
| 8 | $1: 3 \mathrm{CD}_{3} \mathrm{OD} / \mathrm{D}_{2} \mathrm{O}$ | $10 \pm 2$ | $101 \pm 28$ | $952 \pm 64$ | 4.1 | 60.8 |
| 9 | $\mathrm{D}_{2} \mathrm{O}$ | $20 \pm 4$ | $245 \pm 101$ | $2045 \pm 63$ | 4.5 | 63 |



Donor



Figure 1.5. Electron rich DAN and electron deficient NDI association constants as measured by ${ }^{1} \mathrm{H}$ NMR in indicated solvents. Plotted is the measured free energy for the $1: 1$ NDI:DAN complex versus solvent polarity, with stronger complex formation being observed in increasingly polar solvents. Adapted with permission from Ref. ${ }^{37}$ Copyright 2001 American Chemical Society.

### 1.3.3 Supramolecular Self-Assembly of DAN-NDI in Foldamers

### 1.3.3.1 Lokey's AEDAMER

The aforementioned association constants computed for DAN and NDI followed early work by the Iverson group to use complementary aromatic units as a means to assemble the first abiotic foldamers, that is, molecules that would spontaneously fold into an ordered structure in water. In 1995, Lokey and Iverson reported the first aromatic electron donor-acceptor foldamer (aedamer) (Figure 1.6). ${ }^{38}$ The foldamer design was built around a DAN-NDI co-crystal having alternating face-centered stacking of DAN-NDI units. Molecular mechanics modeling assisted the design of a semi-rigid hydrophilic peptide back bone in between complementary DAN and NDI shown in Figure 1.6. Once synthesized, proof of the folded complex came from NMR spectral studies and an observed broad charge-transfer (CT) band that was seen, resulting in a characteristic plum color due to electronic donor-acceptor interactions between the high lying HOMO of DAN, and the low-lying LUMO of NDI.


Figure 1.6. Lokey and Iverson foldamer seen to fold into a pleated secondary structure in aqueous media. ${ }^{38}$ ESPs for dimethyl DAN and NDI are shown (B3LYP, 6-31G*).

### 1.3.3.2 Irreversible Foldamer to Amyloid Fibril - Nguyen, Bradford, and Peebles

Following this initial foldamer, subsequent work in the Iverson group investigated additional secondary structures that could be assembled based on the complementary interactions of DAN and NDI. ${ }^{39-42}$ Nguyen and Iverson ${ }^{43}$ introduced amphiphilicity into the peptide backbone, by replacing a single aspartic acid with leucine, conceptually similar to the biologically relevant leucine zipper motif. While the molecule still folded into a pleated structure in water, a unique, irreversible conformational change was noticed after the foldamer was heated to $80^{\circ} \mathrm{C}$, resulting in a gel that persisted indefinitely. The formation of an irreversible aggregate was thought to result from a mechanism initially involving unfolding, followed by a kinetically irreversible conversion to a tangled aggregate.

In 2008, Bradford and Iverson ${ }^{44}$ reported a follow-up report on a structure activity relationship of a series of amphiphilic aedamers, with variation in side chains. Notably, the leucine introduced by Nguyen was replaced with other hydrophobic residues, including norleucine, isoleucine, and valine. Upon heating, the three leucine isomers were found to form hydrogels following irreversible aggregation. Characterization of the aggregates using rheology, circular dichroism, and scanning electron microscopy revealed that the aggregates were actually highly ordered intermolecular assemblies, analogous to amyloid formation in proteins. Further, the three different leucine isomers formed assemblies with significant differences in hydrogel properties, while the valine derivative did not form a hydrogel. Taken together, the differences in supramolecular aggregate formation and hydrogel properties were reported to reflect the sensitivity of the nature and geometry of intermolecular interactions adopted by the selfassembled aggregates.

A follow up report by Peebles and Iverson ${ }^{45}$ sought to better characterize the nature of the intermolecular interactions that gave rise to the highly ordered aggregate formed upon heating. Upon heating the amphiphilic, alternating DAN-NDI foldamer shown in Figure 1.7 generated a highly ordered amyloid like fiber as previously observed. ${ }^{43-45}$ Structural characterization of the fibrils using transmission electron microscopy (TEM) and atomic force microscopy (AFM)
revealed the width of the fibrils was equal to the length of the extended, unfolded molecule. Further, AFM measurements revealed a helical pitch, consistent with previous observations for 1-dimensional fibers seen formed from the offset face-to-face self-stacking of NDI. ${ }^{46}$



Figure 1.7. Transformation of a kinetically stable, soluble foldamer to an irreversible aggregate from upon heating, driven by conformational switching of alternating DAN-NDI aromatic stacking to NDI-NDI stacking geometries. Adapted from Ref. ${ }^{45}$, Reprinted with permission from ${ }^{47}$ Copyright 2013 WILEY-VCH Verlag GmbH \& Co. KGaA, Weinheim.

A conformational change from the soluble, kinetically stable folded state to a more thermodynamically stable fibril aggregate was found to result from NDI moieties switching from DAN-NDI alternating stacking in the folded state to NDI off-set self-stacking in the aggregate. ${ }^{45}$

An understanding of the conformational change could not be explained using the polar $/ \pi$ model, as it would predict a repulsive interaction between two NDI units based on quadrupolequadrupole repulsion. On the other hand, using the local, direct interaction model, one can rationalize NDI offset self-stacking as a favorable electrostatic interaction resulting from the
overlap of the electron rich carbonyl oxygen atom of one NDI molecule with the electron deficient carbonyl carbon atom of an adjacent NDI. Previously not resolved, an understanding of the mechanism of conformational switching in this foldamer-to-aggregate transformation helped illuminate aromatic packing modes that can be accessed by NDI.

### 1.3.3.3 Ikkanda's Nucleotidomimetic DNA, DAN, \& NDI Foldamers

Following success using NDI as a threading intercalator for binding of DNA sequences, ${ }^{48-57}$ subsequent investigations sought to explore and quantify aromatic interactions between NDI, DAN, and DNA in the context of nucleic acid containing foldamers. These nucleotidomimetic foldamers have the same sugar-phosphate backbone of DNA and assemble into a double helical heteroduplex in solution, thus falling under the umbrella 'foldamer' classification. ${ }^{58}$ In 2014, Ikkanda and Iverson ${ }^{59}$ reported a nucleotidomimetic foldamer assembly where several internal bases were replaced with DAN and NDI (Figure 1.8). In order to maintain the double helical backbone, a spacer was introduced on the complementary strand, opposite of DAN/NDI, such that for the 6 total bases replaced across the two strands, three were spacers, and the other three were combinations of DAN and NDI derivatives. The general trends for the DAN-DAN-DAN and NDI-NDI-NDI duplexes shown in Figure 1.8 track with self-stacking preferences reported by Cubberley and Iverson ${ }^{37}$ previously discussed (section 1.3.2), and further highlight the ability of DNA to have favorable aromatic stacking interactions with other aromatic molecules.


Figure 1.8 DAN and NDI directed assembly of nucleic acid showing an internal NDI-DANNDI sequences has similar melting points to the same sequence with three A-T base pairs. Adapted with permission from Ref. ${ }^{59}$
https://pubs.acs.org/doi/10.1021/jo402704z Copyright 2014 American Chemical Society.

### 1.3.4 Solid-State Supramolecular Assemblies of DAN \& NDI

Previously described work highlighted the ability for DAN and NDI to have favorable aromatic interactions in solution. Other work in the Iverson group explored the ability for these aromatic units to assemble in the solid-state. Early work by Reczek and coworkers ${ }^{60}$ explored the ability for DAN and NDI derivatives to assemble into columns with alternating DAN-NDI facecentered stacking in the solid-state. Alkyl substituted DAN and NDI derivatives were found to
form stable mesophases, as well as soft/plastic crystals, and derivates with liquid-crystalline properties made from alternating DAN-NDI stacks within columns. Later work by Alvey and coworkers ${ }^{61}$ explored a structure activity relationship related to thermal properties, and reported controllable thermochromism in the mixtures based on side chain substitution

Both of these works using alkyl substituted DAN and NDI derivatives revealed thermochromic changes that accompany the reorganization of some DAN and NDI mixtures. ${ }^{60-62}$ Shown in Figure 1.9, cooling of certain DAN and NDI mixtures from the isotropic phase produced a deep red colored mesophase, attributed to the formation of a CT complex, with DAN-NDI adopting an alternating face-centered stacking geometry. Even more interesting, a dramatic thermochromic change occurred in some derivatives with additional cooling, when the red mesophase cooled to form a yellow crystalline solid (Figure 1.9), with the color change taken as an indication that CT interactions were lost upon crystallization. Various structural, optical, and thermal characterizations indicated this color change was the result of the self-sorting of NDI and DAN. Meaning, during cooling, the alternating face-centered NDI-DAN stacking geometries switched to NDI off-set parallel self-stacking and DAN self-stacking in a herringbone geometry (Figure 1.9). Unique to this system, little observable morphological change was seen following this self-sorting behavior.



DAN-DAN

Figure 1.9 Cooling of a 1:1 isotropic melt of certain DAN and NDI derivatives would initially form a maroon mesophase that would turn into a yellow crystalline solid upon cooling, with retention of the overall crystalline morphology. The process was shown to be due to self-sorting of alternating DAN and NDI monomers, shown by representative crystal structures, showing alternating DAN-NDI face-centered stacking switching to NDI-NDI offset parallel self-stacking and DAN-DAN edge-to-face (herringbone) self-stacking. ${ }^{60}$

### 1.3.5 Variation in Solid-State Packing Geometries: DAN and NDI

The polar $/ \pi$ model does provide an intuitive rationale for the face-centered stacking geometry adopted by the relatively electron rich 1,5-dialkoxylnaphthalene (DAN) and relatively electron poor 1,4,5,8-naphthalenetetracarboxylic diimide (NDI) pioneered by our group in the context of aqueous foldamers (Figure 1.10). ${ }^{37-45}$ Contrary to what the polar/ $\pi$ model would
predict but consistent with the local, direct interaction model and previously described results, NDI has been shown to exhibit highly favorable NDI-NDI associations in solution, ${ }^{37}$ as well as adopt NDI offset self-stacking in a variety of contexts (Figure 1.10). ${ }^{45,46,60-65}$
a) ND





DAN

d)


Figure 1.10 a) NDI and DAN with calculated electrostatic potentials (B3LYP, 6-31G*). Bottom, representative crystal structures of DAN and NDI stacking modes with hydrogen atoms omitted for clarity ${ }^{60}$ b) Alternating DAN-NDI face-centered stacking. c) NDI-NDI offset parallel self-stacking d) DAN-DAN self-stacking in an edge-toface stacking geometry. Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

The favorable self-stacking of NDI can be thought of as being derived from its strong carbonyl C-O bond dipoles (Figure 1.10). As predicted by the "local, direct interaction model", aromatic stacking geometries adopted by NDI are expected to result from the favorable direct, through space interactions of polarized groups. Note the positive charge shown on the ESP in between each carbonyl. Off-set NDI-NDI self-stacking that places the electronegative carbonyl oxygen in this very location, making for an energetically favorable interaction. Shown in the
crystal structure in Figure 1.10c, the measured intermolecular distance between a carbonyl oxygen of one NDI molecule and the carbonyl carbon of an adjacent NDI measures $3.30 \AA$, indicative of a very close intermolecular contact for two face-to-face stacked aromatics. It is this type of interaction between the most polarized carbonyl groups that is believed to underlie the favorable self-stacking of NDI in the thermochromic mesophases, as well as the previously described foldamer forming fibrils. Thus, NDI can be thought of as having a "split personality" in terms of its favorable stacking modes: alternating face-centered stacking with electron rich aromatics like DAN, and offset NDI self-stacking.

### 1.4 POLYMORPHISM

Polymorphism is defined as the ability of a single chemical entity to exist in the solidstate in multiple different crystalline structures, and is a commonly occurring property among organic molecules. ${ }^{67-71}$ While made of the same chemical components, polymorphism can enable a single molecule to form materials with different properties, ${ }^{72}$ including different solubilities, ${ }^{73}$ melting points, ${ }^{63}$ crystalline morphologies, ${ }^{66}$ as well as differences in electronic, ${ }^{74}$ optical, ${ }^{75}$ and mechanical properties. ${ }^{76}$ The ability to access different properties from a single chemical entity have resulted in an increase in research into polymorphism as a functional tool for materials applications. ${ }^{68,74}$ Yet, despite the vast improvements in our understanding of polymorphism, targeted polymorphism still remains a highly desirable goal. ${ }^{70}$

While a newer area of research in the functional materials community, research into polymorphism has been a long standing area of research interest in metallurgy ${ }^{77}$ and the pharmaceutical industry. ${ }^{78}$ Pharmaceutical interests in polymorphism stem from the different physical properties between polymorphs and the effects different polymorphs have on the use and efficacy of a drug. Different polymorphs can dramatically change the properties of a drug and change how a given drug is manufactured, influence its chemical stability and shelf-life, and
arguably most important, determine how the drug behaves inside the body, including the rate and extent to which the drug is absorbed. ${ }^{69,72}$

One of the most famous examples of polymorphism affecting the pharmaceutical industry came in the summer of 1998 with the antiretroviral drug ritnovair, marketed under the name Norvir, used for the treatment of Acquired Immunodeficiency Syndrome (AIDS). ${ }^{73}$ Only being bioavailable in the solution phase, ritnovair was packaged as a liquid and semi-solid capsules with the drug dissolved in an ethanol/water mixture. It was not until after drug development and manufacture that various batches of the pharmaceutical failed dissolution tests. A second, previously unobserved polymorph was seen to precipitate out that was significantly less soluble than the previously known crystalline form, and this ultimately resulted in the product's recall. ${ }^{73}$

### 1.4.1 Time-Dependent Polymorphism in Monoalkoxynaphthalene-Naphthalimide DonorAcceptor Dyad

Most often, different polymorphs are found by varying crystallization parameters, including different methods for crystal growth, specific crystallization conditions, and even time. The presence of multiple polymorphs can sometimes be detected through optical analyses looking for different crystalline morphologies, but more definitive proof can come from quantitative spectroscopic or structural characterization methods.

In 2014, Peebles, Iverson, and coworkers reported the time-dependent polymorphism in a series of conjugated monoalkoxynaphthalene-naphthalimide (MAN-NI) donor-acceptor dyads (Figure 1.11). ${ }^{63}$ While different packing modes were observed, aromatic dyad cores were found to stack in columns in all polymorphs, as is often the case with aromatic molecules.


1: $\mathrm{R}=\mathrm{CH}_{3}$
2: $\mathrm{R}=\left(\mathrm{CH}_{2}\right)_{7} \mathrm{CH}_{3}$


3: $\mathrm{R}=\mathrm{CH}_{3}$
4: $\mathrm{R}=\left(\mathrm{CH}_{2}\right)_{7} \mathrm{CH}_{3}$


1


3


2


4

Figure 1.11 Structures and electrostatic potential maps of monoalkoxynaphthalenenaphthalimide (MAN-NI) donor acceptor dyads, with corresponding ESPs (B3LYP, 6-31G*). Reprinted with permission from Ref ${ }^{63}$. Copyright 2014 American Chemical Society.

In contrast to independent DAN and NDI units described previously, the covalently linked conjugated MAN-NI dyads do not have C2 symmetry, and thus the conjugated aromatic dyad core has directionality. Within a column, adjacent dyads can be stacked in one of two general ways. If adjacent aromatic cores align in the same orientation (e.g. MAN unit above another MAN unit) the stacking can be referred to as having a head-to-head (NI-NI, or MANMAN) stacking geometry. On the other hand, if adjacent dyads within a column are in opposite orientations, they are said to a head-to-tail (NI-MAN) stacking geometry.

Several of these MAN-NI dyads showed a difference in solid-state packing between relatively faster (yellow crystals) and slower (orange crystals) evaporation times from solution. While the photophysical basis for differences in color was unclear, analysis of single-crystal Xray diffraction structures and powder X-ray diffraction (PXRD) patterns indicated that the differences in optical properties resulted from differences in head-to-head and head-to-tail packing.

Rationalizing these two different polymorphs can be done using the same "local, direct interaction" model introduced earlier in this chapter. It is critical to note the most polarized
bonds present in the aromatic dyad core, as shown by the electrostatic potential map in Figure 1.11, are as predicted from previous discussions involving NDI. In an analogous manner, the carbonyl C-O bonds have the strongest dipole, and so each NI component can be thought of having favorable interactions between other adjacent NI units, when stacked in an off-set parallel fashion (similar to NDI-NDI offset stacking). Conversely, alternating face-centered stacking between the MAN core and an adjacent NI unit in the case of head-to-tail stacking is favored because of the general electrostatic complementarity of the MAN and NI core (similar to DANNDI face centered stacking).

### 1.4.2 Mechanisms of Polymorphic Transitions

In the previous example, polymorphs were said to have different optical properties, yet they were accessed by varying crystallization parameters. An ability to access different colored polymorphs, by transforming one polymorph into the other with the application of an external stimulus, could enable different colored polymorphs to become a colorimetric sensor. As mentioned at the beginning of section 1.4, numerous different properties beyond color (electrical, physical, etc.) can change between two given polymorphs. Thus, polymorphism can become a functional design principle for materials when combined with the ability to form and interconvert various polymorphs, ${ }^{68}$ where dynamic materials can be formed from simply the interconversion of individual chemical entities.

A number of different classification systems exist ${ }^{69,} 79$ to characterize and describe polymorphic transitions, that is, the interconversion of multiple polymorphs, and a few of these systems will be described for the sake of completeness. In the late $19^{\text {th }}$ century, Lehmann characterized two different types of polymorphism: "Monotropic" polymorphism, was said to be when one polymorph irreversibly transforms to a second and "enantiotropic" polymorphism, is when two polymorphs can undergo a reversible phase transition. ${ }^{72}$ Ehrenfest's classifications ${ }^{80}$ are instead based on thermodynamic quantities (e.g. entropy), and how those quantities change
during the polymorphic transitions. First order transitions are defined as those that have entropy, or volume changes and are further characterized by having an infinite heat capacity at the transition point, as all energy being added to the system is driving the transition, as opposed to increasing the temperature of the system. ${ }^{69}$ Second order transitions do not involve entropy or volume changes, and have a continuous first order derivative of free energy, but do have second order discontinuities in heat capacity, thermal expansivity, and compressibility. ${ }^{69}$ Other classifications put forth are based on structural relationships between the two phases, or the continuity of phase transitions. In the latter, put forth by Ubbelohde, ${ }^{79}$ continuous transitions are those that have continuous, "smooth" transitions from one phase to the other, while discontinuous transitions are just that. ${ }^{69}$ A final note on terminology, this dissertation treats the terms polymorphic transition and polymorphic transformation as synonymous and will use them interchangeably, following the work of Anwar and Zahn. ${ }^{69}$

While previously mentioned classification systems provide a very brief introduction to terms used to classify polymorphic transitions throughout the literature, a different type of classification dominates the most recent descriptions of polymorphic transitions in functional materials. In materials related fields, polymorphic transitions are divided into two general transition types: either nucleation and growth transitions, or cooperative/martensitic transitions. Martensitic transitions are named after the transition that accompanies the rapid cooling of the austenite form of iron to yield the hard steel known as martensite. ${ }^{81}$ This transition is a rapid, diffusionless, first-order transition that is accompanied by the cooperative movement of atoms ${ }^{82}$ and may also be referred to as a displacive or cooperative transformations. ${ }^{69,83}$

Most phase transitions are believed to begin through initiation mechanisms that, in general, resemble nucleation and growth processes. ${ }^{69,82}$ In martensitic transitions, the transition initiates in an activated process displaying first order kinetics. ${ }^{82,} 84$ Nucleation and growth transitions operate similarly to the nucleation of crystals in solution, where nucleation of a 'daughter' phase in the solid-state initiates polymorphic phase transitions. ${ }^{85,86}$ Nucleation mostly occurs at 'preferred sites', that in general provide accessible degrees of freedom in the form of
edges, surfaces, grain boundaries, or point defects in a solid ${ }^{69}$ and growth of this nucleated phase is noted to often disrupt the integrity of the initial crystal. ${ }^{83}$

In general, polymorphic transitions are believed to operate at a phase contact interface, that involves the simple relocation of molecules from the parent phase to the new daughterphase, where the movement occurs between a small gap between phases, and not through an intermediate amorphous layer (Figure 1.12). ${ }^{69,} 85,86$ However, polymorphic crystal-to-crystal transitions that do proceed through a transient amorphous phase have been reported. ${ }^{87}$

Daughter Phase


Parent Phase

Figure 1.12 General scheme for polymorphic transitions operating at a transition interface, where by simple translational and rotational movements allow for molecule by molecule transition. A single molecule highlighted in green is seen detaching from the parent phase then reattaching and aligning to the growing daughter phase. ${ }^{81}$

Recent work has shed light on the variable nature of phase transition interfaces and these interfaces are noted to vary in nature. In some cases, transitions are sharp boundaries, modeled to operate on length scales of $0.1-1 \mathrm{~nm}$, with an average transition front of approximately half a molecular layer. ${ }^{69}$ However, more diffuse transition boundaries have been proposed in the past two decades. Molecular dynamics (MD) simulations of phase transitions in ionic compounds, have been reported to propagate through the "liquid-like" movement of individual components, followed by "freezing" the newly formed daughter phase expanding through multiple molecular layers. ${ }^{88}$ While shown in ionic compounds involved in high pressure simulations, these more diffuse transition phase boundaries seem plausible with the conditions that can favor the liquidlike movement of individual species.

Support for transition boundaries that expand length scales beyond 10 nm have found support from in recent MD simulations for organic molecules in the phase transition seen in DLnorleucine. ${ }^{89}$ In 2013, Zahn and Anwar used MD simulations to show that the $\beta \rightarrow \alpha$ phase transition in DL-norleucine crystals involved concerted molecular displacements, and not a nucleation and growth mechanism. The authors reported that the mechanism was likely to involve a compression wave that has a wavelength larger than the 10 nm simulation cell, and that the length scale for other molecular displacements would have a dependence "on the compressibility of all the molecules along the displacement direction and be limited by defects within the crystal structure." ${ }^{89}$

An excellent summary detailing the key differences between the two polymorphic transition mechanisms (nucleation and growth or cooperative/martensitic) is shown in Figure 1.13. Martensitic (cooperative) transitions can be characterized by fully cooperative, diffusionless transitions that proceeds in a layer-by-layer manner, moving very fast (rates of $10^{3}$ $-10^{7} \mathrm{~mm} \mathrm{~s}^{-1}$ ) with near perfect correspondence in orientation between the parent and daughter phases and often small changes in lattice parameters between the two phases. In contrast, nucleation and growth transitions operate through significantly slower, diffusion-based reorganizations that move through the material in a molecule-by-molecule fashion, with relatively large overall changes in packing, and no orientational relationship between the parent and daughter phase.


Figure 1.13 General properties seen in the two different polymorphic transition mechanisms encountered in polymorphic materials literature. Republished with permission of Royal Society of Chemistry from Ref ${ }^{82}$; permission conveyed through Copyright Clearance Center, Inc.

Park and Diao have classified ${ }^{82}$ the relatively small changes seen in Martensitic transitions as being translational, conformational, or rotational in nature, and as shown in Figure 1.14, the daughter phase produced after the transition shows strong similarities to the parent phase.


Figure 1.14 Three different types of changes give rise to Martensitic (cooperative) polymorphic transitions, all of which result in relatively small changes to the unit cell parameters. Republished with permission of Royal Society of Chemistry from Ref ${ }^{82}$; permission conveyed through Copyright Clearance Center, Inc.

It is worth noting that, Christian ${ }^{77}$ and others have noted that many transitions do not cleanly fit into this binary nomenclature created to describe transitions very different than that seen in metallurgic contexts. Additional nomenclatures have been employed across the literature, and this dissertation does not serve as a comprehensive review. Yet one important example is worthy of being mentioned. Transformations that have correspondence between the parent and daughter lattice (a martensitic property) but also operate through long range diffusion (a nucleation and growth property) have been observed, and can be referred to as diffusional displacive transformations. ${ }^{77,90}$

While a vast majority of polymorphic transition research is focused on materials applications, it is valuable to note biological examples of polymorphic transformations. Arguably the most interesting example is the martensitic transformation of the T4 bacteriophage virus, ${ }^{91} \mathrm{a}$ double stranded DNA tailed virus that infects $E$. coli, and is said to be "one of the most complex viruses". ${ }^{92}$ The virus has a long viral sheath made up of six interacting helices, where each helix is assembled by monomeric gp18 proteins (Figure 1.15), and this viral sheath has two different conformations. In the elongated conformation, gp18 protein monomers that make up the viral sheath store energy like a stretched spring (Figure 1.15). ${ }^{92}$ Compression of the outer viral sheath utilizes the rapid rotation and radial expansion of gp18 monomers that make up the sheath, releasing $25 \mathrm{kcal} \mathrm{mol}^{-1}$ of energy per monomer. ${ }^{92}$ The cooperative, martensitic transformation of this viral sheath enables a rapid compression of the cylindrical viral sheath, shrinking it from 925 to $420 \AA$ in length. ${ }^{93}$ This transition drives a rigid, viral DNA containing central tube, surrounded by the viral sheath, through the bacterial outer membrane, and enabling the viral DNA delivery and subsequent infection.


Figure 1.15 The T4 bacteriophage viral sheath contracts following a martensitic transformation, resulting in compression of the viral sheath, enabling the delivery of viral DNA to the host. Gp18 proteins in three of the six helices shown in pink, blue, and green. Reprinted with permission from Ref. ${ }^{93}$ Copyright 2009 European Molecular Biology Organization.

### 1.5 Polymorphic Stimuli-Responsive Materials

Many materials exploit polymorphism as a functional property that allows some form of reporting. ${ }^{68}$ Polymorphic phase transitions have been thoroughly reviewed ${ }^{82}$ including in experimental, ${ }^{94}$ computational, ${ }^{69}$ and theoretical contexts. ${ }^{95}$ Stimuli induced polymorphic color switching has been achieved in the solid-state following the application of various types of external stimuli including heat, ${ }^{64}$ pressure, ${ }^{96}$ mechanical force, ${ }^{87, ~ 97-99}$ electric potential, ${ }^{100}$ and exposure to various analytes including salts ${ }^{101}$ and solvent. ${ }^{102}$ Stimuli-responsive materials that induce macroscopic and photophysical changes have been extensively investigated and reviewed, ${ }^{103-105}$ and show promise for mechanical applications including actuators ${ }^{106-109}$ and self-
healing materials. ${ }^{110,111}$ Covalent modifications of polymorphic systems have been effectively used to impart tunability in various color changing, stimuli-responsive systems. ${ }^{60,112}$

Computational efforts have successfully modeled polymorphic transformations, but have been limited to small molecules ${ }^{81,109,113}$ or larger, rigid systems ${ }^{107}$. Experimental insights into the mechanisms by which polymorphs interconvert would better inform the future design of novel polymorphic systems. While numerous examples for color changing materials that rely on polymorphism exist, elucidating the molecular mechanisms by which these materials change is experimentally challenging because many experimental techniques employed only provide a time and space average of structural information. ${ }^{69}$ Application of external stimuli to polymorphic systems containing flexible substituents (e.g. alky chains) often involve switching between crystalline and non-crystalline states, with structures of the latter often being inferred from structural information like powder XRD. ${ }^{64,}{ }^{101}$ A subset of reports on polymorphic transitions have been able to correlate macroscopic changes to specific nanoscopic reorganization. ${ }^{83,84,}$, 109, 111, 114-120

A recent example of this was when Ito and co-workers correlated molecular rearrangements to macroscopic mechanical motion from the anisotropic strain release in thermosalient crystals. ${ }^{120}$ This thermosalient effect is a rapid, cooperative displacement of molecules, and thus falls within the class of martensitic (or displacive, cooperative) transformations. ${ }^{69,83}$

### 1.5.1 Amphiphilic Dipolar Luminescent Materials via Metastable States

Although it is the aromatic $\pi$-system that directly influences the electronic and photophysical properties of the system, substituents appended to aromatic molecules are a critical and determining factor in the solid-state electronic, ${ }^{121}$ spectroscopic and stimuliresponsive properties of solid-state stimuli-responsive systems. ${ }^{122}$ An example of utilizing substituents on aromatic systems to influence photophysical properties in the solid-state came
from Yagai, Ito, and co-workers, presenting a design principle for stimuli-responsive color switching materials that exploit polymorphism through competing interactions between aromatic lumiphores and appended side-chains (Figure 1.16). ${ }^{101}$ By constructing amphiphilic and dipolar characteristics into a single molecule, different metastable polymorphic states were stabilized through competing intermolecular interactions of the dipolar aromatic core, a hydrophilic sidechain, and a hydrophobic sidechain. It is worth noting that this system self-assembled through the formation of alternating aromatic, hydrophilic, and hydrophobic layers. The same group has also reported stimuli-responsive systems that exploit the switching between multiple accessible polymorphs through mechanically induced crystal-to-crystal transformations. ${ }^{87,} 94,99$,



Figure 1.16 Structures representative of Ito's amphiphilic dipolar luminescent materials ${ }^{101}$ and Lam's fused ladder thioarenes, ${ }^{118}$ both of which show thermally induced polymorphic phase transitions.

### 1.5.2 Reversible Crystal-to-Crystal Transition in Ladder Thienoarenes

Abe, Lam, and coworkers ${ }^{118}$ characterized reversible crystal-to-crystal transitions involving two distinct reorganizations in donor dithienocyclopenta-thieno-[3,2-b]thiophene (DTCTT) derivatives with variable side chains (Figure 1.16). Their work highlighted the influence of multiple different intermolecular interactions on thermally induced polymorphic transitions, specifically noting the role of side chain size and flexibility as well as the influence of heteroatoms in this polymorphic system.

Disc shaped DTCTT derivatives were seen to assemble as 1-dimensional columns, and certain derivatives were seen to undergo reversible crystal-to-crystal transitions when heated. Upon heating the di(HTh2BT)DTCTT derivative, shown in Figure 1.16, a continuous reorganization between columns was seen to precede a second, discontinuous phase transition, characterized by a change in DTCTT aromatic stacking and further intercolumnar reorganizations. The multiple transitions observed in the di(HTh2BT)DTCTT derivative (Figure 1.16) was attributed to a complex interplay between various intermolecular interactions, including stabilizing aromatic and S-S interactions between adjacent stacked DTCTT cores, competing with repulsive interactions derived from bulky spirocyclic phenyl groups, and rotationally flexible benzo-[2,1,3]thiadiazole (BT) and thiophene (Th) end groups.

In contrast to the reversible transition in the dithiophene containing derivative di(HTh2BT)DTCTT in Figure 1.16, a derivative only differing by a single thiophene unit in each side chain (diHThBT side chains) did not show reversible solid-state polymorphism. This difference in transition behavior was reported to reflect the critical role of side chains for imparting the structural flexibility required for this solid-state polymorphic transition, highlighting the role that small structural changes can impart on polymorphic transitions.

### 1.5.3 Alkyl Rotor Driven Crystal Deformation

Systems containing alkyl groups are noted to be instrumental for many thermally induced polymorphic transitions. In the previous example, aromatic and alkyl side chains provided the flexibility for imparting polymorphic transition behavior. Yet in other systems, polymorphic transitions have been attributed to rotational motion of relatively small alkyl chains, with possible applications as molecular rotors. Su , Sato, and coworkers reported single crystals capable of reversible and repeatable crystal expansion and contraction by exploiting thermally induced rotational isomerization of an $n$-butyl ester containing cobalt (II) complex (Figure 1.17). ${ }^{116}$ Analysis of single-crystal structures showed that the $\mathrm{Co}(\mathrm{II})$ complex formed 1D columns stabilized by aromatic and shape-complementary van der Waals interactions, and 3D molecular packing was dominated by non-conventional $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonding. Heating of this complex resulted in rotational isomerization of the butyl side-chain, form anti in the lower temperature polymorph to a gauche conformation in the higher temperature polymorph (Figure 1.17). Increased intermolecular repulsion following isomerization resulted in positive thermal expansion of the crystal, and cooling reverted the isomerization, causing contraction about the crystal long axis in a repeatable fashion.


Figure 1.17 Anisotropic crystal expansion seen following conformational isomerization of an $n$ butyl ester cobalt complex, with reversible and repeatable cycling in successive heating-cooling cycles. Adapted from Ref. ${ }^{116}$

### 1.5.4 Peebles' Donor-Acceptor MAN-NI Dyads

As part of the Iverson groups comprehensive supramolecular program focused on NDI and its analogs and introduced previously, a series of molecules were synthesized incorporating naphthalene monoimides (NI) covalently linked via an alkyne to monoalkoxynaphthalenes (MAN) with $n$-alkyl side chains (Figure 1.18). As noted previously, several of these MAN-NI donor-acceptor dyads showed a dramatic difference in solid-state color between solids created from relatively faster (yellow, Figure 1.18 g ) and slower (orange, Figure 1.18f) evaporation from solution. ${ }^{63}$ However, in addition to these different optical properties, interesting color changing properties were found when external stimuli was applied.
a)


1: $\quad \mathrm{R}=\mathrm{CH}_{3}$
2. $\mathrm{R}=\left(\mathrm{CH}_{2}\right)_{7} \mathrm{CH}_{3}$


3: $\quad \mathrm{R}=\mathrm{CH}_{3}$
4: $\mathrm{R}=\left(\mathrm{CH}_{2}\right)_{7} \mathrm{CH}_{3}$
b) Yellow crystals of 1 f

c) Yellow-orange crystals of $1 \mathbf{s}$

d) Orange crystals of $\mathbf{4 s}$

e) Proposed packing model for $\mathbf{4 f}$

g)
h)



Figure 1.18 Proposed packing of MAN-NI dyad polymorphs with different optical properties and the formation of different polymorphs of $\mathbf{4}$ shown in the bottom, either grown as an orange solid with red emission when grown by slower evaporation (panel f), or grown as a yellow solid with green emission from faster evaporation (panel g). Reproduced from Ref. ${ }^{64}$ with permission from The Royal Society of Chemistry.

In the solid-state, one of the dyads (dyad $\mathbf{4}$ in Figure 1.18a) was found to change color in response to grinding (orange to yellow, Figure 1.19a-b), heating (orange to yellow, Figure 1.20), and vapor fuming (yellow to orange, Figure 1.19c-e), with repeatable cycles of color changing. ${ }^{64}$


Figure 1.19 Mechanochromic and halochromic -responsive properties of the octyl MAN-NI dyad. a) grinding of the letters "UT" convert the drop cast orange material yellow, and b) vapor fuming with DCM reverts back to the orange form. c-e) POM images show thermally heated yellow material return to an orange form following exposure to DCM vapor. Reproduced from Ref. ${ }^{64}$ with permission from The Royal Society of Chemistry.

Similar to the thermochromic behavior of independent DAN and NDI mixtures previously described, the change in color was determined to result from a conformational change of the aromatic units. Based upon single crystal data, X-ray diffraction (XRD) patterns, and modeling, the stimuli-responsive behavior was reported to result from a conformational switch between the two stable polymorphs previously accessed by varying crystal growth time (section 1.4.1).

When ground or heated, the orange crystalline form, possessing a head-to-head (NI-NI) stacking geometry (Figure 1.19d), interconverted to a yellow soft crystalline mesophase with a head-to-tail (NI-MAN) stacking geometry (Figure 1.19e) that persisted at room temperature in the absence of solvent vapor, an indication that both packing geometries have kinetic stability. Figure 1.20 shows the conversion of the orange crystalline form to the yellow soft crystalline mesophase, while maintaining macroscopic morphology, when heated at $110^{\circ} \mathrm{C}$ for 30 seconds. Interestingly, and in contrast to many of the polymorphic systems previously described, the stimuli-induced thermochromic transition of this MAN-NI dyad proceeded without altering the microscopic morphology of the original crystal (Figure 1.20).


Figure 1.20 Overall proposed dyad packing and stimuli-responsive properties seen in the octyl MAN-NI dyad. Adapted from Ref. ${ }^{64}$ with permission from The Royal Society of Chemistry.

From this initial dyad series, it was clear that both substitution position and side chain identity played a role in the stimuli-responsive properties, as only the 1,4 -substituted MAN with n-Octyl chains (dyad 4, Figure 1.18) was capable of stimuli-responsive colorimetric switching behavior. However, the photophysical basis for the differences in polymorph color as well as the
structural basis for stimuli-responsive colorimetric switching was unclear, as a single-crystal structure of the yellow polymorph was not yet solved.

### 1.6 Influence of Molecular Packing on Spectroscopic and Stimuli-Responsive Properties

Variations in optical and spectroscopic properties in different polymorphs arise from various photophysical processes. Differences in color of aromatic molecules packed in the solidstate are often attributed to general differences in intermolecular packing and specific photophysical origins for these differences have been reported to arise from numerous different mechanisms. Photophysical origins for differences in color have been in hundreds of examples and have been attributed to changes in types and extent of and intermolecular charge-transfer complex formation, ${ }^{60,61,124-127}$ changes to $\mathrm{H} / \mathrm{J}$ aggregate formation, ${ }^{123,} 101,128$ on-off switching of FRET in bicomponent mixtures, ${ }^{129}$ excimer ${ }^{98}$ and exciplex formation, ${ }^{130}$ changes to aurophilic interactions in organo-gold complexes, ${ }^{87,131}$ aggregation induced emission (AIE) ${ }^{96,132}$, as well as being attributed to general conformational or packing differences between the two states that change overlap of $\pi$-systems. ${ }^{98,133-136,}$

In contrast to intermolecular mechanisms that give rise to different optical properties, intramolecular processes can also change optical properties, including from intramolecular charge-transfer mechanisms ${ }^{137}$ as well as conformational based changes. For example, Minakata and co-workers reported a tri-color mechanically responsive polymorphic system that had multiple colors resulting from changes in rotations of terminal donor units within a three component donor-acceptor-donor complex. ${ }^{138}$ Rotations of these terminal units resulted in changes in the relative energies of frontier orbitals, and the different colors were attributed to these changes in frontier orbital energies.

In the solid-state, slight changes in molecular packing can dramatically alter the optical and electronic properties of conjugated materials through various mechanisms that can operate in
isolation or parallel. ${ }^{139-141}$ For example, long-range electronic coupling between molecules, that is dependent on the alignment of transition dipole moments, can alter the spectroscopic properties of solid-state systems compared to free molecules. ${ }^{141}$ In addition, short-range intermolecular interactions that manifest through direct orbital overlap, especially through LUMO-LUMO and HOMO-HOMO overlap, can facilitate the delocalization of locally excited states into delocalized excitonic charge-transfer (CT) states. ${ }^{140,141}$ While these intermolecular excitonic interactions are distinct, the net electronic coupling experienced is a product of the interference between short- and long-range coupling. ${ }^{141}$

### 1.6.1 Chung's Switch in Mechanism of Polymorphic Switching: Cooperative or Nucleation and Growth Mechanisms

Previously, side chain size was shown to influence the reversibility of polymorphic transitions in fused ladder thienoarenes. In addition to the influence side chains can have on accessing various polymorphs, size chain differences can alter the mechanisms by which polymorphs interconvert.

Chung, Diao, and coworkers have investigated cooperative polymorphic transitions in single crystals of ditert-butyl [1] benzothieno[3,2-b][1]1benzothiophene (ditBu-BTBT) and 13bis(triisopropylsilylethnyl) pentacene (TIPS-pentacene). ${ }^{119}$ Single crystals of either semiconductor were shown to undergo a reversible, thermally induced phase transitions characterized by a rapid, concerted movement of the polymorphic phase boundary through the crystal, resulting in a small shape change. In ditBu-BTBT crystals, the cooperative phase transition initiated from rotation of the tert-butyl side chains and, interestingly, was seen to move through crystals two distinct pathways, moving either parallel or perpendicular to the (001) crystal face. Using TIPS-pentacene, they showed a similar martensitic transition took place, and concluded
that rotational motion caused by the order to disorder transition of bulky tert-butyl side chains was a generalizable mechanism to induce cooperative transitions.

Follow-up work by the same group highlighted the sensitivity of the transition mechanism. ${ }^{83}$, 142 A single atom substitution in BTBT side chains, from tert-butyl to trimethylsilyl (TMS), changed the mechanism from a cooperative, rapid transition (average transition speed $176 \mu \mathrm{~m} \mathrm{~s}^{-1}$ ) to a slower nucleation and growth mechanism (average transition speed $\left.1.8 \mu \mathrm{~m} \mathrm{~s}^{-1}\right)$ (Figure 1.21).


Figure 1.21 Different side chains on BTBT derivatives yield materials that have polymorphic transitions that proceed through different transition mechanisms. Nucleation and growth mechanisms proceed in variable orientations, at rates 2 orders of magnitude slower. Adapted with permission from Ref. ${ }^{83}$ Copyright 2019 American Chemical Society.

Changes to unit cells following the nucleation and growth transition in the TMS derivative, and the cooperative transition in the tert-butyl derivative are shown in Figure 1.22a and 1.22 b , respectively. Importantly, the cooperative transition involving the tert-butyl derivative is seen to result in smaller changes to unit cell parameters, as well as a smaller change in the edge-to-face interaction angle between BTBT cores when compared to the nucleation and growth pathway (Figure 1.22a-1.22b).


Figure 1.22 Different side chains on BTBT have polymorphic transitions that proceed through different transition mechanisms. Nucleation and growth mechanisms in TMS side chain derivatives. show larger unit cell changes with interlocked side chains. Cooperative transitions (martensitic) reveal $t$-butyl side chains with rotational motion and no contacts to adjacent neighbors. Adapted with permission from Ref. ${ }^{83}$ Copyright 2019 American Chemical Society.

As expected, the larger silicone atom and longer bonds in the TMS group result in a ca. $15 \%$ increase in the side chain radius compared to the tert-butyl group. The larger TMS group packs closer to adjacent molecules with short contacts to adjacent molecules, whereas no short contacts exist to the tert-butyl side chain. These differences prevent the TMS side chain from rotating freely (Figure 1.22 c ), while allowing rotational motion of the smaller tert-butyl side chain to rotate (Figure 1.22d).

As described previously, the trigger to initiate this rapid, cooperative transition was attributed to cooperative rotations of the bulky side chains appended to aromatic cores. Nucleation and growth pathways were reported from bulkier side chains, and attributed to decreased rotational motion thereby disfavoring the cooperative transition pathway. Further, the bulkier TMS groups decreased overall crystal packing density, which was said to in turn allow for multiple thermally accessible packing orientations, favoring nucleation and growth pathways. In contrast, cooperative transitions were said to arise from polymorphs with more dense packing that can allow for rotational motion, and said to be favored when changes in herringbone packing geometry are minimized between two polymorphs. Taken together, these works highlight the sensitivity of polymorphic transitions mechanisms to subtle structural modifications and underscore the role that thermal motion and side chain flexibility have on enabling various polymorphic transition pathways.

## CHAPTER 2

## Monoalkoxynaphthalene-Naphthalimide Donor-Acceptor Dyads: Synthesis, Structural and Spectroscopic Characterization ${ }^{1}$

### 2.1 CHAPTER SUMMARY

### 2.1.1 Introduction

Previous work on conjugated monoalkoxynaphthalene-naphthalimide (MAN-NI) donoracceptor dyads revealed multiple polymorphs that could be accessed by varying crystal growth parameters, and further, that stimuli-responsive properties could be achieved with certain sidechain substituents. Only one dyad in the initial series (symmetric, $n$-octyl side-chains) demonstrated dynamic and reversible stimuli-responsive behavior in the solid-state: colorimetric switching from orange to yellow when heated (thermochromic) or ground (mechanochromic), and reversal from yellow to orange following exposure to solvent vapor (solvatochromic). Previous comparative structural and spectroscopic studies led to the conclusion that the structure of both the grown and thermally generated yellow material had head-to-tail packing although the structure of the yellow polymorph was unknown. Key questions remained: can the amount of stimuli that induces the colorimetric switch be tuned by changing side-chain lengths, and what is the photophysical basis for the two differently colored polymorphs? This chapter describes the synthesis and characterization of new dyad derivatives, the materials they form in the solid-state,

[^0]and the photophysical origins for the differences in color displayed by various colored polymorphs.

### 2.1.2 Scientific Questions

This work sought to answer the questions: What is the definitive structure of the yellow polymorph? Can other dyad derivatives with different side-chain lengths form polymorphic materials? What are the photophysical origins of the differences in color between polymorphs? What colors are possible? Understanding these effects will better elucidate the intermolecular interactions that help enable the emergence of stimuli-responsive properties and inform the design and synthesis of new solid-state materials with desirable properties, including tunable stimuli-responsive and colorimetric properties.

### 2.1.3 Approach

The goal of this work was to investigate a structure activity relationship (SAR) of new MAN-NI dyads with varying alkyl chain lengths. This SAR would first investigate the ability of various MAN-NI dyads to form polymorphs before later evaluating how different side chains affect stimuli responsive properties (Chapter 3). The MAN-NI dyads explored were focused around the most promising MAN-NI dyad from the initial series: the 1,4 -substituted MAN with $n$-octyl alkyl chains that showed promising stimuli-responsive behavior. As such, the SAR was focused around making derivatives with side chains longer and shorter than the octyl derivative. In addition, asymmetric dyads were explored to further investigate the role of side chain variation in polymorphic and stimuli responsive systems. This SAR involved the synthesis of various derivatives in order to solve single-crystal structures of the materials, something that had not previously been achieved. The overarching goals of this work were to understand what structural features in MAN-NI dyads (1) enable derivatives to form various colored polymorphs and (2) what is the structural and photophysical basis for the differences in color.


## Symmetric Dyad Series

R, R' = Methyl $\quad 1$
$\mathrm{R}, \mathrm{R}^{\prime}=n$-Hexyl $\underline{\underline{6}}$
$\mathrm{R}, \mathrm{R}^{\prime}=n$-Heptyl $\quad \underline{\mathbf{7}}$
$\mathrm{R}, \mathrm{R}^{\prime}=n$-Octyl $\underline{\underline{8}}$
$\mathrm{R}, \mathrm{R}^{\prime}=n$-Nonyl $\quad \underline{9}$
$\mathrm{R}, \mathrm{R}^{\prime}=n$-Decyl $\quad 10$
$\mathrm{R}, \mathrm{R}^{\prime}=n$-Dodecyl $\quad 12$
R, $\mathrm{R}^{\prime}=n$-Hexadecyl $\underline{16}$

## Asymmetric Dyad Series

$\mathrm{R}=n$-Hexyl R' $=n$-Octyl $\quad$ M6N8
R $=$ n-Octyl $\quad \mathrm{R}^{\prime}=n$-Hexyl $\quad$ M8N6
$R=n$-Octyl $\quad R^{\prime}=n$-Decyl $\quad$ M8N10
$R=n$-Decyl R' $=$ n-Octyl $\quad$ M10N8

Asymmetric Naming Convention: MRNR'

Symmetric Naming Convention: $\underline{\mathbf{R}}$

Figure 2.1 Structure-activity relationship for investigating new monoalkoxynaphthalenenaphthalimide (MAN-NI) donor-acceptor dyads.

### 2.1.4 Results

A structure activity relationship study with 10 new MAN-NI dyads was carried out in order to better understand polymorphism in this series of molecules. Following synthesis, reproducible methods to readily grow crystals for nine derivatives were found, including accessing multiple polymorphs for four different symmetric dyad derivatives. Structural characterization using single-crystal X-ray diffraction allowed for eleven single-crystal structures to be solved for nine derivatives (eleven symmetric dyad crystals: 1 bright orange, 5 orange, 5
yellow; three asymmetric dyad crystals: 1 yellow-orange, 1 gold, 1 yellow). Spectroscopic analysis of dyads in solution and in the solid-state was completed. The photophysical basis for the various colored dyads was determined based on a combination of structural, theoretical, and spectroscopic analyses.

### 2.2 RESULTS

### 2.2.1 Synthesis of Dyads

Dyads were synthesized following previously reported procedures. ${ }^{63}$ A synthetic scheme detailing intermediates and dyads synthesized is shown in Scheme 2.1. General information and detailed synthetic procedures and characterizations for each dyad and intermediate can be found in sections 2.5.1 and 2.5.6, respectively.

Access to 4-bromo-1-naphthol could be achieved on a 30 g scale in decent yield. From this common intermediate, the MAN portion (Figure 2.1) of each dyad could be accessed in 3 steps: alkylation with Williamson ether synthesis, Sonogashira cross-coupling to install the alkyne coupling partner, and deprotection to afford the terminal alkyne MAN unit. On the other side of the dyad, the NI portion was accessed in a single step from commercially available 4-bromo-1,8-naphthalic anhydride.



Scheme 2.1 Synthetic scheme for the synthesis of all dyads. Note, dyads with symmetric alkyl side chains are named with a single number (e.g. 6, for hexyl side-chains), while asymmetric dyads are named according to the length of alkyl chain on the Monoalkoxynaphthalene unit as well as the side chain on the Naphthalimide (e.g. M6N8, see Figure 2.1). 3

### 2.2.2 Crystal Growth

Consistent with initial reports of MAN-NI dyads, several of the dyads in this study crystallized as orange ( $\mathbf{0}$ ) or yellow ( $\mathbf{y}$ ) polymorphs, and different crystallization methods were employed to grow either the orange or yellow crystals. High-quality X-ray diffraction capable single crystals were grown primarily using slow-evaporation or vapor diffusion. Crystal growth conditions for crystals that resulted in single-crystal structures are shown in Scheme 2.2.


Scheme 2.2 Crystal growth conditions that formed crystals yielding single-crystal structures with the exception of $\mathbf{8 0}$. Crystal structure previously reported ${ }^{64}$ and grown via indicated slow conditions. Vapor diffusion conditions provide the same 80 polymorph.


Figure 2.2 Top: Side-by-side pictures of yellow, orange, and bright orange crystals grown from solution highlight color differences between individual crystalline samples. Bottom: Z-stacked optical micrographs of various derivatives representative of yellow and orange polymorphs.

Pictures and Z-stacked optical micrographs of various crystals are shown in Figure 2.2. A side-by-side comparison of crystal colors shown at the top highlights the subtle variation in colors that exists in yellow symmetric crystals $\mathbf{6 y}, \mathbf{7 y}$, and $\mathbf{8 y}$. Note that $\mathbf{1 b o}$ has both a very unique orange color compared to other dyad crystals, and also it forms characteristic thread like needles, in stark contrast to all orange crystals with two dimensions of obvious growth. Symmetric orange crystals had nearly identical color to the naked eye, although larger orange crystals often appeared more red when compared to smaller crystals.

Hundreds of different crystal growth conditions were screened during the course of this work, and a few general trends stand out. Orange crystals were best formed using vapor diffusion methods, and a single method could be used to form all orange crystals: vapor diffusion of the dyad in a solvent of $p$-xylenes with acetonitrile as the precipitant. In general, for a given symmetric dyad, orange crystals grew as shorter and wider crystals that had more structural integrity compared to their longer, more brittle, needle-like yellow counterparts. However, symmetric orange crystals tended to become shorter and narrower as alkyl side chain length increased: crystals of $\mathbf{6 0}$ over 1 cm in length could be consistently prepared using the conditions shown in Scheme 2.2. In contrast, and despite a variety of conditions, variations in concentration, and crystal growth temperature, most crystals of $\mathbf{1 0 0}$ and $\mathbf{1 2 0}$ were smaller than 1 mm in their longest dimension. Uniquely, and despite examining dozens of growth conditions, $\mathbf{1}$ only crystallized as a single polymorph (1bo), forming bright orange needles (Figure 2.2).

Yellow crystals could be formed by a combination of slow evaporation and vapor diffusion methods. Slow evaporation often yielded crystals with multiple different colors and morphologies, a likely indication of the formation of multiple different polymorphs within a single crystal growth vial. Symmetric yellow crystals were exceptionally brittle for derivatives with alkyl chains longer than heptyl. Yellow crystals of $\mathbf{9}$ and $\mathbf{1 0}$ were formed using slow evaporation methods, but even the slightest manipulation of these soft crystals would bend/break them.

Symmetric orange crystals grown from solution were better diffracting, higher quality crystals with smaller R-factors and no atoms with multiple site occupancies. In contrast, yellow symmetric polymorphs had more disorder, especially in alkyl side chains. Asymmetric dyad crystals displayed dramatic differences in optical and microscopic characteristics between the M6N8/M8N10 derivatives and M8N6/M10N8 derivatives, yet certain similarities were observed within each set of derivatives. The M8N6 and M10N8 derivatives grew crystals that had colors of gold and yellow-orange, respectively, although liquid and plastic crystals of these could be formed in several solvent conditions. Both of these derivatives with the longer alkyl chain on the

MAN unit grew more structurally robust crystals than most yellow symmetric crystals, and had more structural integrity than most orange crystals with side chains longer than 8 carbons. Between M8N6 and M10N8, the M8N6 crystals consistently had more growth in two dimensions compared to M10N8 derivatives. While not as big, M10N8 was able to form several subtly different colored crystals ranging from canary yellow to yellow-orange; however, characterization of yellow-most derivatives was not possible, as these crystals were extremely flexible and would easily bend/break when a small amount of pressure was applied.

Within the asymmetric series shown at the bottom of Figure 2.2, M8N6 and M10N8 are noted to have formed sturdy gold and yellow-orange crystals, respectively. These crystals were both different in color and had more structural integrity compared to symmetric yellow crystals and yellow crystals of M6N8. In contrast to all three other asymmetric derivates that formed materials with yellow hues, M8N10 was unique in the asymmetric series: it would only grow as very small (ca. $100 \mu \mathrm{~m}$ ) flexible, thread like needles that were orange to red-orange in color.

### 2.2.3 Single-Crystal Structures

In addition to the single-crystal structure of $\mathbf{8 0}$ previously reported, ${ }^{64} 14$ additional unique crystal structures were solved for the 12 dyads in this study by means of single-crystal Xray diffraction analysis. A summary of the crystallographic data for all dyad single-crystal structures is presented in Table 2.1 (orange and bright orange) and Table 2.2 (yellow and asymmetric). Before commencing a discussion of crystal packing and features of different dyad crystals, descriptors that will be used to describe dyad packing in the solid-state will be described.

|  | Dyad Crystal Structure |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 60 | 70 | 80 | 90 | 100 | 120 | 1bo |
| a ( $\AA$ ) | 4.69 | 4.68 | 4.67 | 4.67 | 4.67 | 4.67 | 17.81 |
| b ( $\AA$ ) | 38.87 | 41.44 | 43.93 | 46.58 | 49.08 | 54.24 | 26.10 |
| c ( $\AA$ ) | 15.56 | 15.42 | 15.52 | 15.39 | 16.71 | 15.48 | 3.85 |
| $\alpha$ (deg) | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| $\beta$ (deg) | 96.18 | 94.88 | 96.88 | 94.23 | 112.97 | 96.01 | 90.00 |
|  | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| Volume [ $\AA^{3}$ ] | 2,818 | 2,978 | 3,163 | 3,340 | 3,524 | 3,896 | 1,790 |
| Space Group | Cc | C c | Cc | C c | Cc | Cc | Pna $2_{1}$ |
| Chemical Formula | $\mathrm{C}_{36} \mathrm{H}_{3} \mathrm{NO}_{3}$ | $\mathrm{C}_{38} \mathrm{H}_{41} \mathrm{NO}_{3}$ | $\mathrm{C}_{40} \mathrm{H}_{45} \mathrm{NO}_{3}$ | $\mathrm{C}_{42} \mathrm{H}_{49} \mathrm{NO}_{3}$ | $\mathrm{C}_{44} \mathrm{H}_{53} \mathrm{NO}_{3}$ | $\mathrm{C}_{48} \mathrm{H}_{61} \mathrm{NO}_{3}$ | $\mathrm{C}_{26} \mathrm{H}_{16} \mathrm{NO}_{3}$ |
| $\begin{gathered} \mathrm{MW} \\ {\left[\mathrm{~g} \mathrm{~mol}^{-1}\right]} \end{gathered}$ | 531.67 | 559.72 | 587.77 | 615.82 | 643.87 | 699.98 | 391.41 |
| Density <br> [ $\mathrm{g} \mathrm{cm}^{-3}$ ] | 1.253 | 1.248 | 1.235 | 1.225 | 1.214 | 1.193 | 1.452 |
| Z | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| $\begin{gathered} \mathrm{R} \\ \text { (reflections) } \\ {[\%]} \end{gathered}$ | 5.09 | 6.26 | 19.05 | 6.84 | 9.47 | 8.17 | 11.72 |
| $\begin{gathered} \text { wR2 } \\ \text { (reflections) } \\ \text { [\%] } \end{gathered}$ | 11.96 | 17.58 | 33.77 | 21.19 | 29.52 | 20.03 | 35.40 |

Table 2.1 Crystallographic information for all orange and bright orange dyad single-crystal structures.


Table 2.2 Crystallographic information for all yellow and asymmetric dyad single-crystal structures.

### 2.2.3.1 Descriptors for Dyad Packing in the Solid-State

In general, polycyclic aromatic molecule stack together in the solid-state in a way that maximizes aromatic interactions. As such, in the solid-state, MAN-NI dyads form 1-dimensional columns (or stacks) from the stacking of aromatic dyad cores. It is useful to describe the stacking of dyads using two different terminologies to describe both the orientational and translational relationship between adjacent dyads within columns.

Dyad cores are asymmetric with a long and short molecular axis. Adjacent dyads within a column are always seen to stack with alignment of long and short molecular axes, respectively. Thus, two different orientations of dyad stacking are possible: head-to-head, with adjacent NI-NI
stacking, or head-to-tail, with adjacent NI-MAN stacking. Figure 2.3 shows a cartoon depiction of these two dyad aromatic stacking geometries. It is worthwhile to note that despite the relatively low rotation barrier around the internal alkyne, all crystal structures were solved with the two naphthyl rings of the aromatic core in the trans conformation.

## a) Describing How Dyads Pack in Columns



Figure 2.3 Aromatic stacking geometries and molecular slip are two ways to describe how dyad cores stack in columns.

A second description to describe stacking geometry is based on the translational relationship between adjacent dyads (top right of Figure 2.3). Translational movements of adjacent dyads that maintain alignment of the respective molecular axes will be discussed as having a 'molecular slip' or having an 'offset slip-stacking geometry'. Molecular slip for dyad crystal structures was calculated using a MATLAB script that involves the input of crystallographic parameters, defining a crystallographic coordinate system, and calculating centroids for each dyad core, as shown in in Figure 2.3.

In order for molecular slip calculations to be comparable, a consistent coordinate system must be defined, as shown in Figure 2.3. The long axis slip was defined by an axis made from the atoms ' X 1 ' and ' X 2 ' of the NI unit. The short axis was defined by the carbon atoms labeled 'Y1' and 'Y2'. As the dyad is not symmetric about the defined axis, an arbitrary designation was chosen for orienting the reference dyad in order to consistently define positive and negative slip values (unambiguously highlighted by the distorted perspective shown in Figure 2.3). After defining a coordinate system and the reference dyad, the last necessary task is to define a centroid for both dyads, which was chosen to be defined by the 39 atoms of each aromatic dyad core. Finally, the translational slip can then be calculated for the dyad above the reference dyad, based on the relative translation displacement between the two centroids.

This calculation also yields the distance between dyad cores ( Z axis displacement), although this dimension was the most consistent packing dimension for all dyad crystals. The spacing between aromatic cores is similar in all crystals, with an average distance of $3.36 \pm 0.05$ $\AA$ for all 14 crystal structures. The major differences in crystal packing have to do with translations about the long and short molecular axis, and orientation differences, which are discussed in detail in the following sections.

### 2.2.3.2 Symmetric Dyad Crystal Structures

Symmetric Crystal Packing Overview: Orange is Head-to-Head, Yellow is Head-to-
Tail. For the derivatives $\mathbf{6}, \mathbf{7}$, and $\mathbf{8}$, multiple polymorphs were found. For these three molecules, two general packing motifs were consistently observed: orange crystals (O) were always observed to be stacked with the dyad cores in a head-to-head geometry and yellow crystals ( $\mathbf{Y}$ ) were always observed to be stacked with the dyad cores in a head-to-tail geometry. Two structures were solved for yellow hexyl ( $\mathbf{6 y}$ and $\mathbf{6 y}$ ') and heptyl ( $\mathbf{7 y}$ and $7 \mathbf{y}^{\prime}$ ) polymorphs, with each set of polymorphs having similar packing of aromatic cores and the largest differences
being manifest in side-chain packing. It is critical to note that all of the solved crystal structures only contain the pure dyad; solvent was never observed within the crystalline lattice.

Orange Symmetric Dyad Crystals. With the notable exception of 1, all symmetric dyads formed orange crystals with strikingly similar packing features that will be discussed in terms of the three special dimensions. In all six orange crystals ( $\mathbf{6 0}, \mathbf{7 0}, \mathbf{8 0}, \mathbf{9 0}, \mathbf{1 0 0}$, and $\mathbf{1 2 0}$ ), dyads were found to adopt a head-to-head stacking geometry with remarkably similar slipstacking: an average long axis displacement of $3.07 \pm 0.03 \AA$ and a short axis displacement of $1.0 \pm 0.1 \AA$ (Figure 2.4). Alkyl side-chains in these crystals were found to be exclusively in the staggered-anti conformation (torsional angles of $180 \pm 5^{\circ}$ ) of with one notable exception. The side chain adopts a gauche conformation coming off of the MAN oxygen atom, with the O-C-CC dihedral angle (shown in magenta in Figure 2.4) averaging $72 \pm 3^{\circ}$ for all six crystal structures.


Figure 2.4 Single-crystal structures of $\mathbf{6 0}, \mathbf{7 0}, \mathbf{8 0}, \mathbf{9 0}, \mathbf{1 0 0}$, and $\mathbf{1 2 0}$ shown as head-to-head stacked dimers. Side-chains are exclusively in staggered-anti conformations, except the $\mathrm{C}-\mathrm{C}$ bond extending off of the MAN oxygen atom.

In the six orange polymorph crystals, adjacent columns are nearly perpendicular about the long axis of the dyad (Figure 2.5). Columns have intercolumnar angles of $87.53^{\circ}$ for $\mathbf{6 0}$, $86.97^{\circ}$ for $\mathbf{7 0}, 87.66^{\circ}$ for $\mathbf{8 0}, 87.03^{\circ}$ for $\mathbf{9 0}, 87.81^{\circ}$ for $\mathbf{1 0 0}$, and $87.42^{\circ}$ for $\mathbf{1 2 0}$, and an average intercolumnar angle of $87.5 \pm 0.4^{\circ}$ for all six orange crystals (Figure 2.5). As shown in the upper portion of Figure 2.5, side chains (pointing up) are seen to pack in close proximity with side chains of dyads in adjacent columns in one direction of the column.


Figure 2.5 Dyads stack in one-dimensional columns, and in all orange crystals, adjacent columns are roughly orthogonal. A single dyad has aromatic contacts to four other dyads (blue dashed lines), and a unique $-\mathrm{OCH}_{2}$ - to carbonyl oxygen hydrogen bond shown in the top right (green dashed line). Hydrogen atoms are omitted for clarity.

Several short-range contacts exist between adjacent columns and are believed to stabilize the orthogonal intercolumnar relationship. In the orange crystals, a single dyad molecule has
short contacts ( $2.45-2.65 \AA$ ) to four different dyads, in two adjacent columns (shown in Figure 2.5 as blue dashed lines for $\mathbf{6 0}$ ). For a single molecule, each NI carbonyl oxygen interacts with C-H bond(s) on adjacent MAN units in two different columns, and each side of the MAN unit has C-H contact(s) to NI units in adjacent contacts. Thus, these four contacts stabilize a given dyad in two dimensions and help enable the assembly of columns into layers. Within individual layers, three sub-layers exist: two alkyl chain layers on each side of a central aromatic layer.

In addition to interactions with four adjacent aromatic cores, unique non-typical hydrogen bonds are seen in all orange dyad crystals between alkoxy C-H bonds of alkoxy $\mathrm{O}-\mathrm{CH}_{2}$ - groups and adjacent NI carbonyl oxygens. As shown in the top right of Figure 2.5, the previously mentioned gauche conformation involving the MAN unit puts one hydrogen atom of the $-\mathrm{OCH}_{2}-$ methylene unit in close proximity to the carbonyl oxygen of a dyad in the adjacent column. This short-range interaction is consistent in all orange crystals, with an average separation of $2.63 \pm$ $0.03 \AA$. The interaction is the most notable intermolecular contact between dyads and adjacent columns, and is believed to stabilize the interaction between adjacent columns, by 'locking' potentially rotationally flexible side chains into a static conformation. Freezing of these side chains aids in assembly in the third dimension required for crystal packing: the assembly of 2dimensional layers into 3-dimensional 'stacks' of layers.

Beyond the rotational 'locking' of the alkyl side chain, the gauche conformation forces the side-chain to 'turn' with the adjacent column, and allows for intimate side chain packing within layers.


Figure 2.6 Single-crystal structures of the indicated dyad derivatives with Hydrogen atoms omitted for clarity. In all orange crystals, alternating alkyl and aromatic layers are formed. The single gauche conformation in orange crystal side chains allows for the are interdigitation with the dyad side chains in the layer above and below, in a 'cork' and 'bottle' fashion. Hydrogen atoms are omitted for clarity.

As shown in Figure 2.6, side chain interactions between adjacent layers give rise to alternating alkyl and aromatic layers. A directionality in side chain packing is apparent when looking at two columns from above, as shown by the crystal structures in the upper portion of Figure 2.6. One side of the dyad long axis has side chains packed towards a specific column, and the other alkyl side chain then packs towards the opposite column. In doing so, the side chains can interdigitate with adjacent dyad layers, in a 'cork' and 'bottle' type analogy (shown in the top left of Figure 2.6) that allows side chains to 'zip up'. The dominant staggered-anti
conformations of side chains maximize alkyl side chain van der Waals contact between adjacent columns and further stabilizes the third dimension of crystal growth.

Figure 2.7 shows an overlay of four orange polymorphs - 70, 90, 100, and $\mathbf{1 2 0}$ - both as trimers and as two columns of trimers. Despite the dramatic difference of 10 carbon atoms, $7 \mathbf{0}$ and $\mathbf{1 2 0}$ have nearly identical packing within columns, highlighted by the hexamer overlay on the right of Figure 2.7.


Figure 2.7 Overlay of $\mathbf{7 0}, \mathbf{9 0}, \mathbf{1 0 0}$, and $\mathbf{1 2 0}$ single crystals shows the remarkable similarity in 2D packing, with a common offset along the long-axis much like the offset of stairs in a stair case. Crystal structures shown as displacement ellipsoids set to the $50 \%$ probability level, and hydrogen atoms are omitted for clarity.

## Yellow Dyad Crystals.

Yellow symmetric dyad crystals were all found to have dyads packing in a head-to-tail geometry with two molecules in the asymmetric unit of the unit cell and similar molecular slip stacking geometries, as shown in Figure 2.8.


Figure 2.8 Symmetric dyads that form yellow crystals are shown to pack in one-dimensional columns with head-to-tail stacking geometries. Crystal structures shown as displacement ellipsoids set to the $50 \%$ probability level with multiple side chain occupancy shown as free carbon atoms. Hydrogen atoms are omitted for clarity.

In head-to-tail Y polymorphs, slip-stacking can be calculated relative to either one of the two molecules in the asymmetric unit. As discussed in section 2.2.3.1, the method for calculating molecular slip requires defining a coordinate system and a single reference dyad. Thus, yellow symmetric crystals with two molecules in the asymmetric unit will have at least two slip stacking geometry values, because each molecule can be defined as the reference dyad for calculating the slip of the other. To complicate things further, symmetry operations that define each unit cell can add additional slip stacking possibilities. For example, triclinic cells with the P-1 space group (the space group for $\mathbf{6 y}, \mathbf{6} \mathbf{y}^{\prime}$, and M6N8) possess a center of inversion and have a total of four different unique slip stacking geometries for the two dyads of the asymmetric unit.

In light of multiple calculated slip-stacking geometries for several head-to-tail polymorphs, a new convention is needed to minimize the number of molecular slips that describe the overall column orientation and make results comparable across derivatives. The reason for the need to simplify is because the dyad is asymmetric about the long axis and the translational displacement between two centroids in head-to-tail stacking geometries is not an ideal indicator of the general way the column packs. Restated, head-to-tail stacked dyads can have calculated slips that are not reflective of the overall stacking within the column. The goal of this convention
is to yield a minimum number of calculated molecular slips that provide insight into how dyads stack overall as they build within columns. This new convention for molecular slip in head-totail dyads will provide comparative metrics for how dyads are assembled within columns, rather than how each individual dyad sits above another as determined by translational displacements of the centroid.

Shown in Figure 2.9 is a column made from stacked derivatives of $\mathbf{6 y}$, and going across the figure to the right, the column is sequentially rotated in $90^{\circ}$ increments, showing all 4 sides of the column. With a goal of understanding how slip is calculated and the need for a new convention in head-to-tail dyads, we begin by first choosing the reference for the measurement. The initial choice for which dyad to begin calculating slip stacking geometry is arbitrary; the only requirement is the orientation requirement defined previously (MAN unit on left, NI on right, MAN unit projecting toward the observer, see Figure 2.3). Shown on the bottom of the left most column is a red colored dyad fulfilling this requirement.


Figure 2.9 Dyads packed in head-to-tail columns have challenges associated with calculating slip values that easily convey overall column orientation and yield values that are comparable across different derivatives. A convention for reporting head-to-tail molecular slip is defined to address these challenges.

Before a discussion of calculating dyad slip, qualitative comments on the column orientation are relevant. In the left most column, the red dyad could function as a reference for calculating slip for the above dyad. In this same column, the green dyad cannot itself function as a reference because the dyad does not have the correct orientation for the convention used to define positive and negative slip. When using the red dyad as a reference and the convention for positive and negative slip already defined, the long axis is noted to have a negative slip, and the short axis is seen to have a positive slip.

Note that a simple $180^{\circ}$ rotation about the Y-axis of the first column is all that is required to make the green dyad properly oriented to function as a reference. Also note that the qualitative view of dyads stacking within the column is exactly the opposite if the green dyad was used as a reference instead (shown in the right two columns of Figure 2.8).

Consider again the red reference dyad of $\mathbf{6 y}$ in the left most column, and note that centroids for each dyad are shown for the bottom four dyads of each column, represented by black spheres near the alkyne. The molecular slip for the dyad above the red reference dyad can be calculated by the translational displacement between the two centroids. Note that, qualitatively, the slip is expected to be negative along the long axis, and positive along the short axis. Quantitative results of this agree with the prediction, as shown for the calculated molecular slip labeled as "1" in Figure 2.9. In order to calculate the next slip moving up the column, the green dyad must now become the reference, and thus be oriented following the defined reference convention. Thus, in the third column, the green dyad is then in the right orientation to be used as a reference for the calculation of the slip labeled by " 2 ". The calculated slip maintains a negative long axis slip, however the short axis slip value has the opposite sign from the first slip calculation. Continuing this process of defining a new reference and calculating the additional unique molecular slips in the column (" 3 " and " 4 ") yield unique slips with similar alternating values as slip " 1 " and " 2 ". Thus, even though the column orientation never changed, the convention for how slip is defined and calculated using translational displacements of centroids creates slip values that have varying sign, yet describe the same overall column. This challenge in slip calculation for head-to-tail derivatives is further compounded with the use of a centroid defined for an asymmetric dyad core, and also the use of the NI core (that can have small variations out of planarity) to define the axes.

In light of this, a new convention is defined in order to (1) describe the overall orientation of dyad packing within head-to-tail columns and (2) enable the relative comparison of packing between different head-to-tail derivatives. Because the original convention consistently defines the correct value for long axis slip, the long axis slip will be reported as the simple average of all unique long axis molecular slips. In contrast, the short axis slip was seen to vary as the reference changed. In light of this, the convention takes an "orientation average", meaning that this average will describe the overall column structure by alternating the sign of alternating short axis slip values in order to maintain the overall column structure. To clarify, in Figure 2.9, the short
axis slip starting with the red reference dyad is clearly consistently positive to the naked eye, yet the calculations varied between positive and negative values by convention. So, this orientation average will multiply the second and fourth short axis value by negative one to have all short axis slips have the same sign prior to averaging. In doing so, the average of the four unique short axis slips becomes representative of the overall column orientation.

Because the choice of reference is arbitrary and the presence of an inversion center allows for equal and opposite slips to be calculated, the convention further details the average for both perspectives. Therefore, two different values will be used to describe slip stacking for head-to-tail polymorphs in order to make comparisons across derivatives clear. With a detailed understanding of how slip stacking is calculated for these more challenging head-to-tail derivatives, the slip stacking geometry for yellow symmetric derivatives can now be discussed and is shown in Figure 2.10.


Figure 2.10 Slip stacking of symmetric dyads that form yellow crystals, packing in a head-totail fashion. Bottom: overlay of $\mathbf{7 y}$ and $\mathbf{7 y}$ ' single-crystal structures shows remarkable similarities in packing of cores despite variation in side chain packing. Crystal structures shown as displacement ellipsoids set to the $50 \%$ probability level with multiple side chain occupancy shown as free carbon atoms. Hydrogen atoms are omitted for clarity.

As briefly mentioned at the beginning of this section describing yellow symmetric dyad crystals, there is similar slip-stacking within all yellow polymorphs, with an average long axis displacement of $1.11 \pm 0.09 \AA$ and a short axis displacement of $-1.47 \pm 0.06 \AA$. All five polymorphs are closely grouped, and further grouping within each set can be seen (Figure 2.10).

This is especially pronounced for the two heptyl polymorphs, $\mathbf{7 y}$ and $\mathbf{7 y}$ ', which also have remarkable similarity in packing, including the alignment of alkyl side chains on the overlaid trimer of $7 \mathbf{y}$ and $7 \mathbf{y}$ ' shown in the bottom left of Figure 2.10. Similar molecular slip stacking is seen between both yellow polymorphs and that of $\mathbf{8 y}$. Greater variation is seen in the two hexyl polymorphs. Yet, general to all five symmetric yellow polymorphs, derivatives with the same side chain length have nearly identical packing along the short axis, and the majority of difference between individual polymorphs in packing manifests along the dyad the long axis.


Figure 2.11 Symmetric dyads that form yellow crystals have variable intercolumnar relationships, with adjacent columns being either parallel ( $\mathbf{6 y}$ and $\mathbf{6 y}$ ') or rotated about the short axis of the dyad between $48-49^{\circ}\left(\mathbf{7 y}, 7 \mathbf{y}^{\prime}, \mathbf{8 y}\right)$. Reprinted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

In stark contrast to orange crystals with perpendicular columns about the long axis, aromatic cores in adjacent columns of $\mathbf{Y}$ crystals are either parallel or rotated about the short axis of the dyad (Figure 2.11). Adjacent columns are parallel to one another in both polymorphs of $\mathbf{6}$, while adjacent columns are rotated about the short-axis in $7 \mathbf{y}\left(48.570-48.98^{\circ}\right), 7 \mathbf{y}^{\prime}(48.09-$ $48.10^{\circ}$ ), and $8 \mathbf{y}\left(48.45-48.59^{\circ}\right)$.


Figure 2.12 View from above dyad columns in yellow crystals (4 dyads/column). Symmetric dyads that form yellow crystals have alternating aromatic and aliphatic layers, with segregated side-chains that have increasing disorder further from dyad cores.
Crystal structures shown as displacement ellipsoids set to the $50 \%$ probability level. Multiple side chain occupancy in $\mathbf{6 y}, \mathbf{7 y}$, and $\mathbf{7 y}$ ' shown as free carbon atoms. Hydrogen atoms are omitted for clarity.

As shown in Figure 2.12, alternating alkyl and aromatic layers are formed in all yellow crystals, similar to orange crystals, but with key differences. Side chains within the alkyl layer adopt staggered-anti and gauche conformations. Further, side chains in between layers are segregated and not interdigitated, as was the case with orange crystals. All yellow side-chains have increasing disorder in their side-chains with increased distance from the dyad core. It is important to note that $\mathbf{6 y}, \mathbf{7 y}$, and $7 \mathbf{y}^{\prime}$ had side chains with multiple site-occupancy in terminal carbon atoms of the alkyl chains (additional details in Table 2.2), indicating that disorder was present within the alkyl layers.


Figure 2.13 Single-crystal structure of $\mathbf{1 b o}$ as viewed from various perspectives indicated. In a) and c), crystal structures shown as displacement ellipsoids set to the $50 \%$ probability level. Hydrogen atoms omitted in b) for clarity.

Bright Orange Dyad Crystals. The methyl dyad 1 was only found to crystallize as bright orange needles. Denoted as being bright orange (bo), this derivative had many differences compared to symmetric orange crystals and as such is put in a category of its own. The only commonality between 1bo and the other orange derivatives was head-to-head stacking. However, the slip stacking was significantly different. Orange crystals were slipped $\sim 3 \AA$ along the long axis of the dyad, and $\sim 1 \AA$ along the short axis; 1bo was found to have shorter offset along the long axis $(0.8078 \AA)$ and a longer offset along the short axis ( $-1.695 \AA$ ). Unique in 1bo, two different packing motifs are seen in adjacent columns, where adjacent columns have interactions between either the short- or long-axis of dyads in a given adjacent column. Most
notable, 1bo does not form alternating alkyl and aromatic sheets (Figure 2.13c) in contrast to all other crystals in this report. While $\mathbf{1 b o}$ stacks in a head-to-head geometry, it has a unique slipstacking geometry with its largest offset along the short axis of the dyad, in contrast to the head-to-head stacked $\mathbf{O}$ dyads ( $\mathbf{6 0}, \mathbf{7 0}, \mathbf{8 0}$ ).

### 2.2.3.3 Asymmetric Dyad Single-Crystal Structures

Three high-quality asymmetric dyad single-crystal structures were solved. These structures had several distinct differences compared to all symmetric dyads, with a few common features. In common with their symmetric counterparts, all asymmetric dyads stacked in onedimensional columns, either in head-to-head or head-to-tail geometries as shown in Figure 2.14. Unique to the asymmetric series, altering the position of asymmetric alkyl substituents resulted in a change in aromatic stacking geometries, with head-to-tail packing in M6N8 and head-tohead packing in M8N6 (Figure 2.14).

M6N8 was the single asymmetric dyad that exhibited a head-to-tail stacking geometry. As was the case with $\mathbf{6 y}$ and $\mathbf{6 y}$, M6N8 had two molecules in the asymmetric unit, and four different possible column packing motifs: two different dimers of M6N8 are shown in Figure 2.14. It should be noted, a single M10N8 yellow crystal was found to have head-to-tail packing, but a refined single-crystal structure could not be solved for this derivative. A large enough data set was collected to conclusively determine head-to-tail packing of the aromatic core, but limited resolution and the absence of a number of reflections made refinement of a resolved, publishable structure impossible.


Figure 2.14 Asymmetric dyads form crystals that span from yellow to gold. Dyad molecules are shown to pack in columns with both head-to-head and head-to-tail stacking geometries. Crystal structures shown as displacement ellipsoids set to the 50\% probability level with hydrogen atoms omitted for clarity.

Nevertheless, M10N8 and its shorter counterpart, M8N6, were able to grow high-quality yellow-orange and gold crystals, respectively, and single-crystal structures of each were solved. Both of these structures had unique head-to-head packing, distinctly different from orange polymorphs and 1bo. Both M10N8 and M8N6 exhibited remarkably similar molecular slips with an average long axis displacement of $0.78 \pm 0.01 \AA$ and a short axis displacement of $3.69 \pm 0.08$ Å.


Figure 2.15 Single-crystal structures of asymmetric dyad crystals reveal various intercolumnar relationships, with adjacent columns being either parallel (M6N8) or rotated about the short axis of the dyad between 84-85 (M8N6, and M10N8).

Adjacent columns are parallel to one another in the structure of M6N8, reminiscent of $\mathbf{6 y}$ and 6y'. The other asymmetric derivatives had adjacent columns that were rotated almost perpendicular about the short-axis in M8N6 (85.15 ) and M10N8 (84.10 $)$. Similar to orange head-to-head polymorphs that were stabilized by four different dyads (two stabilizing MAN, two stabilizing NI units), M10N8 and M8N6 had intermolecular contacts (intermolecular contacts here are defined by Mercury software as being shorter than the sum of the van der Waals Radii) to five adjacent aromatic units due to close proximity in packing that accompanied herringbone, also called "edge-to-face", type aromatic interactions. Also similar, the nonconventional alkoxy $\mathrm{OCH}_{2}$ - to carbonyl oxygen hydrogen bond was present in both derivatives, with an average length of $2.50 \pm 0.06 \AA$. The torsional angle of the alkyl chain coming off the MAN unit (O-C-CC torsion) was also in a gauche conformation in these two derivatives, with an average torsion of $56 \pm 6^{\circ}$. In the shorter M8N6, the rest of the side chain exists in a staggered-anti conformation,
whereas in M10N8, each alkyl side chain has a gauche conformation part way down the alkyl chain.


Figure 2.16 Asymmetric dyad crystals form alternating aromatic and alkyl layers, but alkyl layers can have complete segregation of side-chains between layers (M6N8), or a mix of interdigitated and segregated side-chains (M8N6 and M10N8). Crystal structures shown as displacement ellipsoids set to the $50 \%$ probability level with hydrogen atoms omitted for clarity.

Asymmetric dyads all formed alkyl and aromatic layers in the third dimension of crystal packing. Interestingly, among M10N8 and M8N6 there was a mix of interdigitated and segregated side chains. Uniquely, asymmetric M10N8 and M8N6 form a unique hybrid alkyl/aromatic sublayer due to the offset of adjacent aromatic cores, and this hybrid sublayer has the net effect of decreasing the overall width of the alkyl layer. In contrast, side chains of M6N8 were entirely segregated from the adjacent layer.

An overlay of M10N8 and M8N6 shown in Figure 2.17 highlights the remarkable similarity in packing of the aromatic cores and the NI side chains between the two derivatives. These NI side chains are the segregated side chains seen in between interdigitated pairs in Figure 2.16. While the first carbon atoms of the MAN side-chain have similar placement, deviation occurs between more terminal atoms of MAN alkyl chains.


Figure 2.17 Similar crystal packing seen in single-crystal structures of M10N8 and M8N6. a) Overlay of single-crystal structures of M10N8 (green) and M8N6 (gold) with accompanying cartoon depicting the perspective being viewed. b) Similar sidechain packing seen in both derivatives, with a mix of interdigitated and segregated side chain packing between layers. In all cases, crystal structures shown as displacement ellipsoids set to the $50 \%$ probability level with hydrogen atoms omitted for clarity.

A single-crystal structure for M8N10 was never obtained, as this dyad would always crystallize as small, flexible crystalline needles/threads within polycrystalline aggregates despite efforts to grow crystals under numerous different crystal growth methods and conditions. In light of this, powder X-ray diffraction (PXRD) was carried out to gain structural insight into the packing of M8N10 crystals grown via vapor diffusion (toluene, acetonitrile). Shown in the top of Figure 2.18 is a crystal structure of $\mathbf{9 0}$ with select crystallographic planes shown in magenta and unit cell axes shown in black. In the bottom of Figure 2.18, normalized PXRD for M8N10, 9o, and 80 are shown, where the PXRD patterns for $\mathbf{8 0}$ and 90 shown are the calculated powder patterns based the respective single-crystal structure.


Figure 2.18 Crystal structure of $\mathbf{9 0}$ with certain crystallographic planes indicated by magenta colored lines. Hydrogen atoms omitted for clarity. Bottom: stacked normalized PXRD spectra with calculated spectra for $\mathbf{9 0}$ and $\mathbf{8 0}$.

A visual comparison of M8N10 and 9o PXRD shows several peaks with similar spacing. The low angle peak for M8N10 falls in between the low angle peak for $\mathbf{9 o}$ and $8 \mathbf{8 0}$. This low angle peak corresponds to the largest crystallographic spacing in the crystal. The observed peak in between that of $\mathbf{8 0}$ and $\mathbf{9 0}$ supports a proposed packing model for M8N10 that has interlayer spacing (e.g. length of alkyl chain layer) at a value between that of $\mathbf{8 0}$ and $\mathbf{9 0}$. The broad peak
width for the M8N10 low angle peak may be an indication of variation in interlayer spacing across the sample or within different crystalline domains.

Correspondence between the (002) and (022) crystallographic planes of $\mathbf{9 0}$ and $\mathbf{8 0}$ can also be seen. Note the (002) and the (022) plane in the $\mathbf{9 0}$ crystal structure shown in the top of Figure 2.18. The (002) plane passes through the alkyne of dyads in columns with the same displacement along the $b$-axis of the crystal but occupies different layers. The (022) plane passes a dyad also a layer above, but in the adjacent column (e.g. b-axis offset). Thus, taken together, these two planes provide an indication of the relationship between columns within the crystal. A correspondence in peak location for the (002) and (022) planes of $\mathbf{9 0}$ and $\mathbf{8 0}$ and peaks seen in the PXRD spectrum of M8N10 is believed to reflect a similar relationship between columns in M8N10. The broad peaks seen in the M8N10 spectra could be an indication of slight variation in crystal packing dimensions for the given planes across the polycrystalline sample, or even within different crystalline domains. The lack of an appreciable (061) plane in M8N10, may indicate variation in interlayer spacing and/or the absence of longer-range order in M8N10 crystals. While it is possible this peak is not observed in the PXRD of M8N10 due to preferred orientation effects, its absence could arise from variation in alkyl chain packing, causing changes in interlayer spacing within a single layer while maintaining order between adjacent columns within individual layers. Thus, it is believed from PXRD analysis that M8N10 has packing that is similar to its constitutional isomer, $\mathbf{9 0}$, with similar ordering between adjacent columns, and similar interlayer spacing. In agreement with observations that M8N10 forms small needles, the lack of appreciable crystal growth in three dimensions could result from variability in the packing of the side chains in the alkyl layer, or a lack of stabilizing intercolumnar interactions.

### 2.2.3.4 Comparison of Dyad Slip Stacking

A single combined plot of all different dyad slip stacking geometries is shown in Figure 2.19. Grouping can be observed between all orange dyads (squares), asymmetric M10N8 and

M8N6 (blue and purple diamonds), as well as yellow symmetric (circles) and asymmetric M6N8 (yellow diamond) head-to-tail crystals. Packed in a head-to-head fashion unlike yellow crystals with similar stacking, 1bo has its own very unique molecular slip.


Figure 2.19 Calculated molecular slip for all dyad crystals.

### 2.2.3.5 Preferred Orientation

With an understanding of how dyads stack in three dimensions in the crystalline state, analyses of the molecular orientations within crystals was carried out in an effort to understand how various crystal packing forces manifest as observable microscopic differences in crystal growth.


Figure 2.20 Preferred orientation for dyad molecules in symmetric orange crystals based on BFDH morphology calculations using single-crystal data.

Orientations of dyad molecules in the crystals was determined using Bravais, Friedel, Donnay, and Harker (BFDH) calculations from single crystal data and is shown in Figures 2.20 and 2.21. In all cases, molecular orientation of dyad molecules corresponds to the direction of aromatic stacking of dyads within columns.

As stated previously, the longest dimension of all crystals was the direction of aromatic stacking. In 60, the thinnest crystal dimension was found to arise from the relationship between columns, and the dimension from side-chain interactions is the second largest dimension. The preferred orientation for $\mathbf{6 0}$ shown in Figure 2.20 was calculated from the crystal dimensions that yielded the $\mathbf{6 0}$ single-crystal structure, where the thinnest crystal dimension to be made from interactions between column (e.g. rectangular prism). Other $\mathbf{6 0}$ crystals were seen that had nearly identical dimensions in the two smaller crystal axes (e.g. square prism). In longer derivatives, there is a reversal in the preferred orientation shown for 60 in Figure 2.20: longer derivatives form wider and thinner crystals, in which the width is made from the interactions of columns, and the height is made from the stacking of layers held together by alkyl chains.


Figure 2.21 Preferred orientation for dyad molecules in symmetric yellow crystals and M10N8 based on BFDH morphology calculations using single-crystal data.

### 2.2.4 Thin Films

Thin Films. Dyads were deposited onto quartz substrates using physical vapor deposition. During deposition, copper tape was used to hold the quartz substrates upside-down during the sublimation process, resulting in areas around the perimeter of films not having deposited material. These vacancies can be seen on all corners of the thin films shown in Figure 2.22, and create unique crystal boundaries that will be discussed later.

Sublimation of all deposited dyads (1, 7, and 10) generated amorphous yellow thin films (Figure 2.22a, c). Vapor annealing of yellow thin films in a fuming chamber with dichloromethane (DCM) yielded polycrystalline orange thin films (Figure 2.22d) and displayed orange emissions when irradiated with 365 nm light (Figure 2.22e). Vapor fuming of yellow films had slight variation in the amount of time required for the film to fully convert. Shown in Figure 2.22 e, an initially yellow film of $\mathbf{1 0}$ fully converts to an orange film over two days. Films would almost always begin on a film boundary, and proceed inward.

It is important to note the fine balance that must be present when fuming these dyad films. If the chamber was not tightly sealed, DCM would evaporate quickly, and the film would not convert without continual replenishment of DCM. If too much DCM was present in a sealed chamber, DCM would visibly condense on the film surface, causing it to fully dissolve and concentrate into a single spot in the middle of the substrate. In general, films would be fumed in a non-sealed cylindrical chamber (diameter and height ca. 10 cm ) with DCM (ca. 10 mL ) that was replenished roughly every 24 hours until complete conversion occurred.

Using fuming chambers, polycrystalline thin films made of discrete microcrystals were characterized by structural, optical, and spectroscopic measurements. GIWAXS of a $7 \boldsymbol{o}$ thin film (Figure 2.22 f ) showed that polycrystalline orange thin films had diffraction spots matching single-crystal structures, while also informing about preferred orientation of thin film samples. The location for diffraction spots can be calculated based on input of crystallographic parameters and GIWAXS parameters (e.g. sample-detector distance, wavelength) in a reported MATLAB script: GIXSGUI. ${ }^{143}$ The calculated spots for 70 match a preferred orientation of $7 \boldsymbol{0}$ to have the
long molecular axis of the crystal perpendicular to the substrate, ${ }^{144}$ indicated by the presence of the in-plane (020) reflection.


Figure 2.22 Dyad thin film preparation, structure, and optical properties. a) Dyad 7 seen deposited as a yellow material inside the physical vapor deposition chamber following sublimation. b) GIWAXS of 7 o thin film shows a polycrystalline thin film with calculated reflections that match $7 \mathbf{0}$ and show preferred orientation with the crystallographic long axis (020) perpendicular to the substrate. c) Methyl dyad $\mathbf{1}$ deposited as an amorphous yellow film. d) Polycrystalline 70 thin film formed following exposure of 7 to DCM vapor in a fuming chamber. e) UV irradiation shows fluorescence of a $\mathbf{1 0 0}$ film. f) From left-to-right: an amorphous, yellow thin film of $\mathbf{1 0}$ converts to $\mathbf{1 0 0}$ over two days when exposed to DCM vapor in a fuming chamber.

Optical micrographs of a 7 o thin film on quartz are shown in Figure 2.23 with varying magnification. Note that on the film boundaries, individual crystals can be distinguished.


Figure 2.23 Optical micrographs of 70 thin film shows a polycrystalline surface with distinguishable individual crystals seen on boundaries.

### 2.2.5 Spectroscopic Characterization

### 2.2.5.1 Solution Phase Spectroscopic Properties

In solution, all dyads had nearly identical spectroscopic properties, as the alkyl side chains do not affect electronic properties of the aromatic cores, exhibiting significant solvatochromism (Figure 2.24), with a strong bathochromic shift with solvents of increasing polarity (hexanes $\lambda_{\text {em-max }}=444 \mathrm{~nm}$, acetonitrile, $\lambda_{\mathrm{em}-\max }=593 \mathrm{~nm}$, Figure 2.24 ). This shift is consistent with a highly charge-separated excited state due to electron transfer from the electron rich MAN core, where the HOMO is primarily localized, to the electron deficient NI core, where the LUMO is localized (Figure 2.24a). This is further supported by 7 having a calculated excited state dipole of 14.64 Debye in the first electronically excited state, compared to just 7.21 Debye in the ground state ( $\omega$ B97X-D, $6-311+G^{* *}$ ).


Figure 2.24 (a) Calculated dyad electrostatic potential, molecular dipole, HOMO, and LUMO of 7 ( $\omega$ B97X-D, 6-311+G**). (b) 7 in solvents of increasing polarity from left to right. Bottom: UV irradiated samples, showing positive solvatochromism. Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

Absorbance and emission of Dyad 7 in a variety of solvents is shown in Figure 2.25. Absorbance profiles are similar for dyads in each solvent, with a range in the observed
absorbance max of 15 nm (hexanes $\lambda_{\text {abs-max }}=408 \mathrm{~nm}$, DCM $\lambda_{\text {abs-max }}=423 \mathrm{~nm}$ ). Vibronic peaks are only observed for 7 in hexanes. A shift in emission wavelength is seen when the solvent polarity increases from non-polar hexanes to polar acetonitrile (hexanes $\lambda_{\text {em-max }}=444 \mathrm{~nm}$, acetonitrile $\lambda_{\text {em-max }}=593 \mathrm{~nm}$ ). Plotting emission maxima versus $\mathrm{ET}(30)$, an empirically derived solvent polarity parameter, shows a general trend of increasing emission wavelength in more polar solvents.



Figure 2.25 Normalized absorbance and emission spectra for 7 in a variety of solvents and emission max plotted versus solvent polarity ( $\mathrm{E}_{\mathrm{T}}(30)$ ). Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

In addition to changes in emission wavelength with varying solvent, other shifts are seen in emission wavelength when even small amounts of polar solvent are added to a dyad in nonpolar solvent. Shown in Figure 2.26, as ethanol is added to dyad 7 dissolved in hexanes, the initial emission maxima of 444 nm shifts dramatically to $551 \mathrm{~nm}(\Delta=107 \mathrm{~nm})$ once the solution is $50 \%$ ethanol by volume. A 44 nm shift ( $37 \%$ increase) in the emission wavelength was seen with only $2.0 \%$ ethanol by volume.


Figure 2.26 Absorbance and emission spectra of 7 in mixtures of hexanes and ethanol.

A summary of dyad spectroscopic properties in solution, including quantum yields and fluorescence lifetimes, can be found in Table 2.3. Additional experimental details for solutionbased measurements can be found in section 2.5.3. Dyads are strong absorbers $\left(\varepsilon>10^{4} \mathrm{M}^{-1} \mathrm{~cm}^{-1}\right)$
and have high quantum yields in non-polar solvents. Quantum yields (QY) were determined using the relative determination method following reported protocols, ${ }^{145}$ using a Coumarin-153 standard. To calculate molar absorption coefficients, concentration dependent measurements (3, $5,10,25,50 \mu \mathrm{M})$ of each dyad in a given solvent were carried out. Molar absorption coefficients were calculated by the slope made from plotting the absorbance value (at $\lambda_{\text {abs-max }}$ ) versus concentration. The molar absorption coefficient for 7 in acetonitrile is not shown because limited solubility in higher concentrations hindered concentration-based measurements.

| Solvent | $\boldsymbol{\lambda}_{\text {abs-max }}(\mathrm{nm})$ | $\boldsymbol{\varepsilon}\left(\mathrm{M}^{-1} \mathrm{~cm}^{-1}\right)$ | $\boldsymbol{\lambda}_{\text {em-Max }}(\mathrm{nm})$ | FLT $(\mathrm{ns})$ | QY |
| :--- | :---: | :---: | :---: | :---: | :---: |
| EtOAc | 417 | $2.36 \times 10^{4}$ | 538 | 3.96 | 0.68 |
| PhMe | 414 | $1.97 \times 10^{4}$ | 489 | 2.58 | 0.73 |
| Hexanes | 408 | $2.57 \times 10^{4}$ | 444 | 2.34 | 0.73 |
| DCM | 426 | $2.27 \times 10^{4}$ | 558 | 4.40 | 0.68 |
| Acetone | 419 | $2.46 \times 10^{4}$ | 587 | 2.00 | 0.22 |
| MeCN | 418 | - | 593 | 0.94 | 0.07 |

Table 2.3 Summary of spectroscopic data for 7 in a variety of solvents. Absorbance maxima ( $\boldsymbol{\lambda}_{\text {abs-max }}$ ), emission maxima ( $\boldsymbol{\lambda}_{\text {em-max }}$ ), fluorescence lifetime (FLT) and fluorescence quantum yield (QY). FLT was determined from fitting the sample decay to a singleexponential function.

Time-correlated single photon counting measurements were conducted in order to determine solvent effects on fluorescence lifetime (FLT) of dyads in solution. A plot of the decay for 7 in a variety of solvents is shown in Figure 2.27, and the calculated FLT based upon of fitting a single exponential function to the decay is shown in Table 2.3. While 7 had the two shortest FLTs in the most polar solvents used, acetonitrile and acetone, the least polar solvents used, hexanes and toluene, had FLTs in the middle of the distribution. Chlorinated solvents gave rise to the longest FLTs, with DCM having the longest measured FLT ( 4.40 ns ), and $\mathrm{CHCl}_{3}$ (not shown) having a measured FLT of 3.94 ns , nearly identical to that of ethyl acetate ( 3.96 ns ).


Figure 2.27 Fluorescence lifetime of 7 in various solvents as measured by time-correlated single photon counting (TCSPC).

### 2.2.5.2 Solid-State Spectroscopic Properties

Shown in Figure 2.28 are pictures of crystals viewed under ambient visible light and also when irradiated by a 365 nm lamp. Crystals are shown in groups, where pictures were taken side-by-side to allow for comparison of symmetric orange, symmetric yellow, bright orange 1bo, and the four asymmetric derivatives.

Spectroscopic characterization of solids was completed by carefully sandwiching the solid material between two cleaned quartz slides. Absorbance of solids was calculated by measuring both diffuse reflectance and transmittance of the quartz 'sandwich'. Measurement of the quartz sandwich without material allowed a blank absorbance for the quartz holder to be calculated, and this blank absorbance was subtracted from sample data. Solid fluorescence emissions were collected using a front facing accessory that enabled the light source to be perpendicular to the sample, and emission to be collected at $22.5^{\circ}$ relative to the light source in order to reduce reflected light from the material surface. Additional information including instrumentation, and additional parameters for data collection can be found in section 2.5.4.

## Symmetric Orange Crystals



## Symmetric Yellow Crystals



Asymmetric Crystals


Figure 2.28 Color of all crystals under visible light and when irradiated at 365 nm .


Figure 2.29 Solid-state absorbance and emission for symmetric orange crystals grown from solution. Inset near the legend is the respective emission maxima (nm).

All orange crystals had very similar color to the naked eye under visible light and when irradiated with a 365 nm lamp (Figure 2.28) absorbance and emission of these crystals are indeed similar (Figure 2.29). All orange crystals have similar red shifted absorbance and emission profiles compared to yellow crystals, which are shown in Figure 2.30. Note that the exact emission maxima of orange crystals showed variability that appears correlated to crystal size to at least some extent, with some observed red-shifting as crystal size increases (Table 2.4).

| Compound | $\lambda_{\text {abs-Max }}(\mathrm{nm})$ | $\lambda_{\text {em-Max }}(\mathrm{nm})$ |
| :--- | :--- | :--- |
| 1bo | 371 | 590 |
| $\mathbf{6 o}$ | 371 | 625 |
| $\mathbf{7 o}$ | 360 | 617 |
| $\mathbf{8 o}$ | 296 | 613 |
| $\mathbf{9 o}$ | 428 | 624 |
| $\mathbf{1 0 0}$ | 357 | 615 |
| $\mathbf{1 2 0}$ | 359 | 615 |
| $\mathbf{6 y}$ | 392 | 569 |
| 7y | 390 | 554 |
| $\mathbf{8 y}$ | 395 | 554 |
| M6N8 | 293 | 561 |
| M8N6 | 357 | 568 |
| M8N10 | 430 | 616 |
| M10N8 | 402 | 564 |

Table 2.4 Solid-state absorbance and emission for dyad derivatives.


Figure 2.30 Solid-state absorbance and emission for symmetric yellow crystals grown from solution. Inset near the legend is the respective emission maxima (nm).

In general, all three symmetric yellow crystals had similar color judged by the naked eye; however, $\mathbf{6 y}$ did appear to have a slight orange hue compared to $\mathbf{7 y}$ and $\mathbf{8 y}$ when irradiated with a 365 nm lamp (Figure 2.28). Spectroscopically, $7 \mathbf{y}$ and $\mathbf{8 y}$ showed nearly identical absorbance and emission spectra (Figure 2.30, Table 2.4). In comparison, the emission of $\mathbf{6 y}$ has a small bathochromic shift relative to $\mathbf{7 y}$ and $\mathbf{8 y}$, as would be expected from the observed yellow-orange hue upon excitation with longwave UV light.


Figure 2.31 Solid-state absorbance and emission for asymmetric crystals, with colors ranging from yellow to orange-red grown from solution. Inset near the legend is the respective emission maxima (nm).

Asymmetric dyads had large variation in absorbance and emission profiles compared to the respective orange and yellow symmetric derivatives as shown in Figure 2.31. Three distinct absorbance profiles can be seen on the red-edge of the absorbance profiles, with similarity between M8N6 and M10N8. In comparison to these two derivatives, M6N8 had a hypsochromic shift in both absorbance and emission profiles, and M8N10 displayed bathochromic shifts in both its absorbance edge and the emission profiles.


Figure 2.32 Comparison of solid-state absorbance and emission crystals grown from solution, where overlap between certain asymmetric derivatives is seen. Inset near the legend is the respective emission maxima (nm).

A comparison of several selected derivatives is shown in Figure 2.32 in order to highlight a few commonalities. Not all derivatives are shown in order to provide clarity. Nevertheless, it is hoped that the following discussion will describe trends across all of the derivatives, even if each spectra is not shown in Figure 2.32. Head-to-tail derivatives, which includes yellow symmetric crystals $\mathbf{6 y}, 7 \mathbf{y}$, and $\mathbf{8 y}$, as well as M6N8, are seen to have similar absorbance and emission profiles, with the most blue-shifted absorbance edges of all crystals. Unlike the similarity in head-to-tail derivatives, the three different groups of head-to-head derivatives were all distinct. Head-to-head M6N8 and M8N10 have a unique absorbance edge, although emission profiles for these two derivatives fall within the range of yellow symmetric crystals. Similar to how 1bo had a molecular slip unlike all other derivatives, the absorbance and emission of $\mathbf{1 b o}$ is also truly unique, with an emission in between yellow and orange derivatives. Further, all symmetric
orange derivatives had similar spectroscopic behavior to one another, and uniquely, M8N10 displayed nearly identical absorbance and emission profiles.


Figure 2.33 Comparison of $\mathbf{7 y}$ and $\mathbf{7 o}$ absorbance and emission spectra relative to thin films of $\mathbf{7}$ either yellow ( $\mathbf{7} \mathbf{y}_{\text {Thin }}$ Film) or orange ( $\mathbf{7 o}_{\text {Thin Film }}$ ) in color.

Finally, a spectroscopic comparison was carried out between crystals grown from solution and thin films produced via physical vapor deposition. The $\mathbf{7 y}$ thin film shown in Figure 2.33 is an amorphous film of 7 following deposition via sublimation. The 70 thin film was formed from vapor annealing of a $\mathbf{7 y}$ thin film with DCM, as discussed previously. Thin films of 7 had differences in absorbance compared to their crystal counterparts. Despite these differences in absorbance spectra, similar emission profiles were seen between crystals and thin films of 7 in their yellow and orange forms, respectively.

### 2.3 DISCUSSION

### 2.3.1 Dyad Packing in the Solid-State

Dyad Packing. The dyads described in this chapter all pack in stacked columns, but they exhibit diversity in terms of both translational molecular slip and packing orientation (head-tohead versus head-to-tail). The geometries adopted by dyads within columns are in part due to aromatic stacking interactions, which are primarily guided by electrostatic, through-space interactions between the relatively strong dipoles on the periphery of the aromatic core, ${ }^{30}$ with a smaller dispersive component also contributing to the stability of aromatic stacks. ${ }^{146}$

Before a discussion on how aromatic interactions result in different geometries, the role of van der Waals, i.e. dispersive interactions, should be considered. Dispersive forces play a major role in stabilizing alkyl chains on adjacent dyads in the solid-state. The staggered-anti geometry of alkyl chains in the orange crystals maximizes the surface area and thus provide a large number of relatively weak dispersive forces that can stabilize all three dimensions of crystal packing. In contrast to the orange forms, a larger number of gauche conformations decreases side chains surface area in the yellow and asymmetric derivatives. This loss of surface area results in a decrease in dispersive interactions. Further, an analysis of voids in the orange and yellow crystals shows more empty space (voids) within the yellow crystals, specifically in locations adjacent to side-chain gauche conformations. For example, calculating the volume of a unit cell that has room to fit a $1 \AA$ spherical "probe" shows that $2.0 \%$ of the $7 \mathbf{y}$ unit cell can fit 1 $\AA$ probes, and they are all localized near gauche interactions close to the aromatic core. In contrast, none of these $1 \AA$ probes can fit within the unit cell of $7 \mathbf{0}$.

Multiple side chain occupancy sites ( $\mathbf{6 y}, 7 \mathbf{7}, 7 \mathbf{7}$ ') further hinder three-dimensional growth and add to the number of voids. For example, calculating the number of probes that can fit in $\mathbf{7 y}$ after removing atoms that have multiple site occupancy further increases the number of voids to $2.4 \%$ of the unit cell. The voids likely decrease stability of the crystal as well by allowing more accessible degrees of freedom thereby reducing contact surface area.

These vacancies also likely hinder three-dimensional growth for the same reason. While molecular geometric constraints can limit what atomic configurations are possible for a given molecule in the solid-state, other configurations that maximize alkyl side chain surface area may improve three-dimensional growth. For example, the other yellow polymorph, 7y', had a calculated void volume of $0.5 \%$ of the unit cell. While not indicative of stability in three dimensions, the crystal that yielded the structure of $\mathbf{7 y}$ ' was 0.83 mm in length, over three times longer than any other yellow crystal that yielded a single-crystal structure. Additionally, minimal side chain overlap in 1bo (Figure 2.13 ) provides a plausible explanation for 1 dimensional, needle-like crystal growth observed (Figure 2.2).

As discussed previously, the long axis of the crystal corresponds to the axis of aromatic stacking interactions. Therefore, on average longer yellow crystals may be an indication that aromatic interactions between yellow crystals are stronger than those in orange. Aromatic interactions between dyad cores have dominant energetic interactions based on the local, direct, through-space interactions of bond dipoles. In chapter 1, a discussion of relevant dyad bond dipoles highlighted differences between dipoles on the MAN and NI unit of the dyad, and an electrostatic potential map of 7 is shown in Figure 2.34 for convenience. Briefly, on the NI unit, the two strong carbonyl C-O bond dipoles, and to a lesser extent, five C-H bonds on the aromatic ring periphery influence stacking geometry. The C-H bonds on the MAN unit can also influence aromatic stacking geometry, as these bonds are noted to have significantly stronger bond dipoles than NI C-H bonds. In addition to the five aromatic C-H bonds the one alkoxy C-O bond on the MAN unit also has a significant bond dipole and will influence aromatic stacking geometries in accordance with modern theory.


Figure 2.34 Calculated electrostatic potential map of $\mathbf{7}$ in the conformation from the $\mathbf{7 o}$ singlecrystal structure ( $\omega$ B97X-D, $6-311+\mathrm{G}^{* *}$ ). Note the most polarized bonds are on the periphery of the aromatic core, as well as the alkoxy bound methylene unit.

The NI carbonyl is believed to have the strongest single bond dipole in the dyad, and thus, should have the largest single effect on aromatic stacking geometry. The offset selfstacking of NI units in head-to-head geometries of orange crystals places adjacent dyads with an average of a $3.1 \AA$ offset along the long axis and $1.0 \AA$ on the short axis. This placement aligns one of the NI carbonyls above the electron deficient NI aromatic core, with the oxygen atom roughly above the NI carbon-1. The other carbonyl is positioned slightly off-set (ca. $0.1 \AA$ ) from the C-H bond coming off of the NI carbon-7. This same carbonyl oxygen sits directly above a CH bond coming off of the imide ${\mathrm{N}-\mathrm{CH}_{2}-\text {, and while not a true aromatic-aromatic interaction, this }}_{\text {, }}$ is believed to be a stabilizing force that helps maintain the relative translational slip of the dyad. On the other side of the dyad core, the MAN unit with a $3.1 \AA$ offset positions the second ring (carbons 5-8) roughly over the alkyne linker of the dyad below. This positions C-H bonds of the MAN carbon-6 and carbon-8 near C-H bonds on the adjacent NI carbon-3 and MAN carbon-6,
although the angle adopted by each respective pair approximates $\sim 120^{\circ}$. Most notable however is the relative position of the C-H bonds on the MAN carbon- 8 with the adjacent MAN unit carbon5 C-H bond. These two bonds align almost directly on top of each other, and are exactly $180^{\circ}$ in opposition, in perfect alignment for a strong intermolecular interaction. In these orange symmetric crystals, the ensemble of interactions between aromatic cores is believed to stabilize cores within a column.

In other head-to-head derivatives, dramatic differences in translational displacement exist. For example, $\mathbf{1 b o}$ had a smaller long axis offset $(0.81 \AA)$ and a longer offset along the short axis (-1.7 $\AA$ ). In this stacking geometry, the larger short axis offset perfectly positions the carbonyls in the ideal geometry to interact favorably with carbonyls on a single adjacent dyad. Thus, within a column, each NI has strong dipolar interactions with four other NI carbonyls, where one carbonyl oxygen will sit between two carbonyl carbons. Beyond just aromaticaromatic interactions, the slip in 1bo places the alkoxy oxygen directly above a C - H bond of the methyl ether, and the NI carbonyl oxygen directly above a C-H bond of the N-Methyl imide, further stabilizing this conformation.

The head-to-head M6N8, and M10N8, as discussed earlier, have an average long axis slip of $0.8 \AA$ and a short axis displacement of $3.7 \AA$. This short axis offset is dictated by the intercolumnar packing in these asymmetric derivatives, where columns are roughly orthogonal about the short axis of the dyad (see Figure 2.15). In this geometry, a given dyad has a dyad from an adjacent column interacting in an edge-to-face geometry on one side of that dyad. In this way, any dyad that is stacked on top of the original dyad will be offset at least the width of the dyad ( $\sim 3.4 \AA$ ). The relative increase in short axis slip compared to $\mathbf{1 b o}$ results in the loss of each NI carbonyl interacting with carbonyls on adjacent dyads. In this geometry, a single NI carbonyl oxygen is favorably positioned over a single electron deficient NI carbonyl carbon. This larger short axis slipped geometry results in new interactions between two head-to-head MAN units. The $3.7 \AA$ slip along the short axis puts the second MAN ring of one dyad half-way over the
adjacent MAN unit. In this configuration, the alkoxy C-O bond is positioned in between the carbon-6 and carbon-7 C-H bonds.

Importantly, all of the interactions described above for these head-to-head geometries are dependent on translational slip. In all cases, stabilizing interactions were described related to the stability brought about specific, often NI carbonyl dipoles. Calculated slip stacking geometries for head-to-head stacks showed three different translational slips that were found, and of those with multiple geometries (all symmetric orange, and M8N6/M10N8), tight grouping was observed with minimal offset in aromatic slip stacking geometry (see Figure 2.19).

While geometric constraints can always minimize the number of possible orientations that a molecule can stably adopt in the solid state, the tight grouping of head-to-head packing and crystal structures that lack multiple side-chain occupancies is perhaps a result of a narrow packing range for these geometries. Said differently, perturbation of the NI-NI stacking geometry is likely to result in a strong energetic penalty when considering dipolar interactions, especially of the carbonyl. Small shifts in translational displacement would result in the loss of favorable interactions, and often times an increase in repulsive interactions, highlighting our groups previous reports on the role of the NI carbonyl as a dictating force in aromatic stacking geometry. ${ }^{47,60,61, ~ 63, ~ 64, ~} 66$

In contrast to the strongly polarized NI carbonyls localized on one side of the NI core, the MAN aromatic core has a larger number of strong bond dipoles oriented all around both rings. This is believed to allow for the MAN unit to have greater flexibility in terms of the geometry that can be adopted when stacked with NI units. For example, the average offset of $1.1 \AA$ and $1.5 \AA$ along the long and short axis, respectively, result in each unit being slightly offset along the short axis relative to the adjacent dyad. Perturbations in short axis offset would be energetically costly, as the alkoxy oxygen would come in proximity to the NI carbonyl; however, these would not be nearly as energetically costly as translation of a carbonyl oxygen above another carbonyl oxygen. In addition, as the MAN unit has many more strong dipoles, small
translations along either axis would still retain some degree of favorable dipolar interactions, whereas loss of stabilizing NI-NI dipolar interactions could occur with similar translations.

While head-to-tail yellow crystals are seen to also have clustered molecular slip stacking geometries, a greater deviation is seen in long axis slip ( $0.09 \AA$ in the yellow crystals versus $0.03 \AA$ in the orange crystals). In addition, three different crystal structures with multiple side chain occupancies and minimal side chain interactions between adjacent layers is taken as evidence that side-chain interactions are not a necessary component of head-to-tail stacking. The wide variation in side-chain packing that exists in all yellow structures (see Figure 2.12) is believed to reflect the role of aromatic interactions guiding crystal growth, rather than from sidechain packing.

The existence of multiple diverse intercolumnar relationships (parallel columns or rotated $\sim 45^{\circ}$ along the short axis) that exist around similar translational geometries is taken further to indicate that head-to-tail stacking geometries are able to allow for greater translational diversity in solid-state packing motifs.

In contrast, the conserved nearly perpendicular relationship between columns in all orange crystals appear to be stabilized through a combination of favorable side chain packing and electrostatic interactions between the most polarized bonds in the dyads, namely the imide carbonyl $\mathrm{C}-\mathrm{O}$ bonds and the $\mathrm{C}-\mathrm{H}$ bonds of alkoxy $\mathrm{O}-\mathrm{CH}_{2}$ groups (dashed green lines in Figure 2.4). An average distance of $\sim 2.6 \AA$ is indicative of a weak hydrogen bond, with an energy of less than $4 \mathrm{kcal} \mathrm{mol}^{-1}$ and contributions from both electrostatic and dispersive interactions likely. ${ }^{147}$ This conserved intercolumnar feature further introduces stability into higher order structures, and is believed to enable the growth of large, three-dimensional, macroscopic crystals. As noted earlier, this non-conventional hydrogen bond is one of four significant contacts each orange dyad makes with adjacent columns on either side. These four contacts are believed to lock the dyad in place and prevent any motion that may result in translational movements.

Previously, it was noted that the single-crystal structure of M8N10 (orange-red) was never obtained, as the dyad would crystallize out as orange-red polycrystalline needles/threads.

Crystal packing of M8N10 was proposed to be similar to 90 based on indexing of the M8N10 PXRD, and comparison to the 90 single-crystal structure derived PXRD pattern (Figure 2.18). The growth of thin, thread like crystals, morphologically similar to that seen in $\mathbf{1 b o}$ is attributed to variation in side chain packing within the layer, or a lack of stabilizing intercolumnar interactions, including the aforementioned non-conventional hydrogen bond.

Different crystal growth methods should be able to provide insight into the role of side chain packing in dyad crystal growth of orange and yellow polymorphs. Yellow symmetric crystals could be grown using slow evaporation or vapor diffusion. When grown by slow evaporation, the dyad crystals would almost always grow along the wall of the vial as the solvent level decreased. In contrast, orange crystals grown using slow evaporation would grow in solution the vast majority of the time, rarely adhering to the outer walls as evaporation progressed. This is very similar to how orange crystals are produced using vapor diffusion. Yellow crystals could also be grown via vapor diffusion, and it is noted that sometimes a single condition can yield orange or yellow polymorphs, often exclusively in each individual batch. The emergence of both polymorphs in a single vial may reflect the stochastic process of crystal growth, and following nucleation, the derivative that has been nucleated continues to grow in the most favorable way.

As previously noted, orange crystals almost always grew in solution. Further, for many longer derivatives, a single vapor diffusion solvent system would enable the formation of orange crystals: $p$-xylenes as the solvent, and acetonitrile as the precipitant. It is valuable to note the fact that the solvents hexanes and acetonitrile are immiscible under standard conditions. This helps inform how the process for orange crystal growth may begin: Nucleation in solution occurs as the concentration of acetonitrile increases, thereby causing alkyl side chains to decrease their solubility. When controlled, the slow increase in acetonitrile concentrations would allow for a dynamic equilibrium to allow for the assembly and subsequent dissolution of derivatives that do not pack in the most favorable ways. Only once thermodynamically stable packing motifs are formed, for example with all alkyl side chains in staggered-anti conformations, the dynamic
equilibrium shifts so that crystal growth is favored as the acetonitrile is not capable of dissolving the stable structure. This perspective for acetonitrile driving orange crystal growth by driving alkyl side chain appended dyads out of solution is also supported by the observation that longer dyads form many more, smaller crystals (see Figure 2.3). Longer derivatives have lower solubility in similar acetonitrile concentrations, and perhaps result in the kinetics for nucleation exceeding the kinetics for crystal growth.

In contrast to the dynamic sampling of crystal packing enabled by crystal growth in solution, crystal growth down the vial wall following decreasing solvent levels are not afforded the same ability. As the solvent level decreases and the concentration of dissolved dyad increases, solubility limits drive dyads out of solution and into packing motifs that are stable when not given chances to reorganize. In this way, head-to-tail packing produced from slow evaporation can be rationalized as allowing thermodynamically stable crystals to form in spite of not having all of the higher order stability requirements needed for orange crystal growth (e.g. intercolumnar packing, interlayer side chain interdigitation). Fewer intermolecular interactions may enable head-to-tail crystal growth from solution, supported by the more flexible aromatic stacking geometry afforded in head-to-tail packed dyads.

Interestingly, dimensional changes were seen in the preferred orientation of crystals as side chain lengths increased, with derivatives with longer side chains in general being seen to have a relative increase in crystal width (made from intercolumnar stacking) and a relative decrease in crystal height (made from the stacking of layers) (Figure $2.20 \& 2.2$ ). This morphological shift in crystal growth patterns may reflect a difference in intercolumnar and interlayer stabilization provided by longer side chains (thermodynamic) or change growth rates of different crystal faces. In agreement with these observations, it is possible that longer side chains may better stabilize adjacent columns (increasing crystal width) more than they stabilize adjacent layers, despite the presumed benefit that longer side chains would increase stability of interlayer, 'cork' and 'bottle', packing (Figure 2.6). While longer side chains presumably have more thermodynamically favorable 'cork' and 'bottle' packing, longer side chains likely
significantly decrease the rate for layered crystal growth, due to a greater extent of side chain order required for the 'cork' and 'bottle' packing of longer, more flexible side chains.

In summary, a stable head-to-head stacking geometry in orange crystals of symmetric dyads is seen to have maximized van der Waals interactions between the perfectly ordered and close-packed staggered-anti, interdigitated alkyl chains, and is thought to be the more thermodynamically stable form overall. It is believed that aromatic stacking interactions are slightly more favorable in the head-to-tail yellow form, stabilized by more complementary electrostatic interactions on the periphery of the aromatic units. Yet in the head-to-tail yellow crystals, the alkyl chains are no longer all staggered-anti, highly ordered, close-packed, or interdigitated. The bottom line is that there is an energetic and structural trade-off between the two forms; more stable side chain packing but less stable aromatic stacking geometry in the orange form, yet more stable aromatic stacking geometry with less favorable alkyl chain packing in the yellow form. Finally, the head-to-tail form is also believed to be more 'forgiving' of slight translational motion within columns, where aromatic stacking interaction as a function of translational motion can be thought of as having a broader potential well, compared to a steeper potential well in the head-to-head orange form. A steeper potential well in head-to-head symmetric dyad orange crystals is reflective of a presumptive larger energetic penalty for slight translational perturbations in stacking geometry, a consequence of the fine balance of through space interactions observed in the consistent geometries of self-stacking NI units.

### 2.3.2 Photophysical Properties in Solution

All dyads have nearly identical photophysical properties in solution, as differences in dyads are not on the aromatic core. Absorbance of visible light by a dyad molecule results in the intramolecular electron transfer from the HOMO, centered largely on the electron rich MAN unit (see Figure 2.24) to the LUMO, centered largely on the electron deficient NI unit. In so doing. a
large excited state dipole moment forms, explaining the striking solvatochromic behavior of the dyads in solvents of different polarities and is expected for such highly polarized excited states.

As the process for absorption of a photon is much faster $\left(10^{-15} \mathrm{sec}\right)$ than solvent reorganization $\left(10^{-10} \mathrm{sec}\right)$, the ground and excited states are not significantly affected by solvent polarity, as a molecule experiences the same local environment before and after absorption of a photon. This nicely explains the small 15 nm range in solution-state absorbance maxima, shown seen in Figure 2.25 (hexanes $\lambda_{\text {abs-max }}=408 \mathrm{~nm}$, DCM $\lambda_{\text {abs-max }}=423 \mathrm{~nm}$ ). In stark contrast, the fluorescence emissions showed far greater sensitivity to solvent polarity (Figure 2.26), with emission maxima spanning 149 nm (hexanes $\lambda_{\text {em-max }}=444 \mathrm{~nm}$, acetonitrile $\lambda_{\text {em-max }}=593 \mathrm{~nm}$ ).

On the other hand, fluorescence emissions are far more sensitive to solvent polarity and viscosity compared to absorption processes because of the longer fluorescence lifetimes ( $10^{-8}-10^{-}$ $\left.{ }^{9} \mathrm{sec}\right)$. Such a slow process means the solvent can 'relax' around the excited state and stabilize it, resulting the red-shifted emission (smaller energy gap).

Stabilization of the large excited state dipole moment by bulk solvent molecules is considered a general solvent effect, whereby the overall solvent polarity and refractive index of the solvent stabilize the excited state, and thus cause a red shift in emission. This type of general solvent effect does not explain the dramatic shift in emission seen for dyad 7 upon adding small additions of ethanol (Figure 2.20). The addition of $2 \%$ ethanol caused a shift in emission from 444 nm to 488 nm , while a further increase to $50 \%$ ethanol shifted the emission further to 551 nm . The addition of only $2 \%$ ethanol in conjunction with a bathochromic shift of 44 nm is thus attributed to specific solvent interactions that stabilize the dyad excited state likely through hydrogen bonding, as $2 \%$ is too small of a volume to alter bulk solvent properties. ${ }^{148}$

### 2.3.3 Photophysical Basis for Different Colored Solid-State Materials

The key structural difference in solid-state between symmetric orange and yellow polymorphs is the orientation of adjacent dyads within a given aromatic stack. Adjacent dyads in
orange polymorphs have offset head-to-head stacking geometries, while yellow polymorphs exhibit head-to-tail stacking geometries. In other words, in the dyad stacks of orange polymorphs, a given MAN unit is situated above and below MAN units of adjacent dyads, and NI units are adjacent to NI units on adjacent molecules. In this head-to-head packing arrangement, there is a small short-axis offset and a larger $\sim 3 \AA$ offset along the long axis of the molecule, where dyads shift unidirectionally in a column, much like the offset of stairs in a staircase (Figures 2.19, 2.4-2.7). The offset head-to-head stacking geometry in the orange form will lead to mixing of LUMO orbitals since orbital lobes of similar phase are in close proximity (Figure 2.35). This LUMO mixing can facilitate the dissociation of an initial locally excited state into charge-transfer states, where electrons and holes are delocalized onto multiple molecules. This is believed to be the basis for the red-shift seen in all orange crystals. At the quantitative level, differences in the precise geometry of LUMO orbital overlap due to slightly different displacements along the short and long molecular axes can be used to explain subtle differences between the optical properties of orange polymorphs.


Figure 2.35 Overlay of calculated LUMO of a 7 monomer ( $\omega$ B97X-D, $6-31 \mathrm{G}^{*}$ ) with the $\mathbf{7 o}$ crystal structure. A long-axis slip of $3 \AA \AA$ in all orange polymorphs allows for favorable orbital overlap in the NI-localized LUMO, as seen by a match in orbital phasing with adjacent dyads. Reprinted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

While dipolar coupling may be in play, it is not expected to be the basis for the red-shift seen with orange crystals, and this is rationalized by comparisons of head-to-head crystal structures for 1bo (Figure 2.13), asymmetric M8N6 (gold crystals) and M10N8 (yellow-orange) (Figure 2.17) and all orange polymorphs (Figures 2.4-2.7). Across these three groups, a larger slip along the short axis is correlated to smaller extent of red shifting compared to yellow polymorphs. Compared to all orange polymorphs (short axis slips of $1.0 \AA$ ), the smaller red-shift in $\mathbf{1 b} \mathbf{b o}$ is attributed to a decrease in short-range coupling derived from orbital overlap. The $1.7 \AA$ short axis slip in 1bo still allows for the possibility of orbital overlap, as ca. $3 \AA$ of overlap is present between adjacent NI unites. In contrast to 1bo, a $3.7 \AA$ short axis slip in head-to-head
stacked M8N6 (gold crystals) and M10N8 (yellow-orange) has smaller ( $\sim 1.5 \AA$ ) overlap between head-to-head stacked NI units, yet these asymmetric dyads are still seen to have a significant red shift compared to yellow, head-to-tail polymorphs (Figure 2.32).

The observable red-shift in 1bo, as well as M8N6 and M10N8, compared to all head-totail yellow polymorphs is believed to result from a combination of dipolar coupling within head-to-head stacked crystals and/or orbital overlap effects, with a larger orbital mixing component possible in 1bo compared to the two asymmetric head-to-head dyads. Computational efforts would be required in order to resolve the respective contributions.

All yellow polymorphs exhibit head-to-tail stacking geometries and show greater variation in slip-stacking geometry compared to the orange polymorphs (Figure 2.19). The absence of a red shift in yellow polymorphs is interpreted to indicate that MAN-NI dyads do not form CT complexes in head-to-tail packing geometries, almost certainly due to energetic differences that minimize HOMO-LUMO orbital mixing.

While no single-crystal structure was solved, indexing of the M8N10 (orange-red) PXRD pattern revealed similar packing to $\mathbf{9 0}$, and the red shift in emission is consistent with head-tohead packing similar to symmetric orange derivatives. Differences in optical properties between symmetric orange crystals (Figure 2.29) were attributed to small differences in slip stacking geometries (Figure 2.19). Thus, the red hue seen in M8N10 could be the result of small (ca. 0.1 Å) differences in dyad slip stacking compared to symmetric orange crystals.

### 2.4 CONCLUSION

Small changes in packing resulted in shifts in spectroscopic properties, and an understanding of the differences in dyad solid-state color was put forth. In the solid-state, dyads were crystallized in multiple different polymorphs, and a detailed understanding of their crystalline morphologies has been described. A qualitative understanding of the thermodynamics of dyad packing was proposed, in agreement with modern theory and prior results. A model to
understand differences in crystal growth propensities as a function of method was put forth, and in agreement with changes in preferred orientation changes seen in dyads with different side chain lengths.

MAN-NI donor-acceptor dyads are incredibly sensitive to their surrounding environment, and as such, make appealing candidates for future study. Solution-phase spectroscopic measurements showed that dyad fluorescence operates through an electron-transfer process that makes the dyad highly sensitive to the surrounding solvent environment, through both general (e.g. polarity) and specific (e.g. hydrogen-bonding) solvent-solute interactions.

### 2.5 EXPERIMENTAL

### 2.5.1 General Methods

All reagents were purchased from commercial vendors and used without further purification unless otherwise noted. NMR solvents were purchased from Cambridge Isotope Laboratories and used as received. All NMRs were completed in $\mathrm{CDCl}_{3}$ and the chemical shift in parts per million ( $\delta$ ) is referenced relative to the residual solvent peak: 7.26 ppm for ${ }^{1} \mathrm{H}-\mathrm{NMR}$ and 77.16 for ${ }^{13} \mathrm{C}-$ NMR. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMRs were obtained using a Bruker AVIII HD 500 with a BBFO Prodigy liquid nitrogen CryoProbe or an Agilent MR 400 MHz NMR spectrometer. Highresolution mass spectrometry was performed using a either a Waters AutoSpec GC/MS for chemical ionization (CI) or an Agilent Q-TOF LC/MS for atmospheric pressure chemical ionization (APCI).

### 2.5.2 X-ray Crystallography

Single-crystal structure data for $\mathbf{6 y}, \mathbf{6 y}^{\prime}, \mathbf{7 y}^{\prime}, \mathbf{8 y}, \mathbf{1 b o}, \mathbf{6 o}, \mathbf{7 0}, \mathbf{9 0}, \mathbf{1 0 0}$, and $\mathbf{1 2 0}$ was collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus Cu
$\mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA$ ) with collimating mirror monochromators. The data were collected at 100 K using an Oxford Cryostream low temperature device.

Single-crystal structure data for $\mathbf{7 y}$ was collected on Beamline 5.0.1 at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The synchrotron beamline produced a wavelength of $0.97741 \AA$. The data were collected at 100 K using an Oxford Cryostream low temperature device.

### 2.5.3 Solution-State Spectroscopy

Absorbance measurements in solution were made using a Cary 100 UV-Vis spectrophotometer. Steady-state fluorescence measurements were collected on a Horiba Jobin Yvon Fluorolog3. Time resolved fluorescence measurements were made using Horiba NanoLEDs (402 nm or 442 nm ) on a Horiba Jobin Jyvon Fluorolog3. FLT was calculated from fitting the sample decay to a single-exponential function. QY was determined relative to a Coumarin-153 standard solution following established protocols ${ }^{145}$, with maximum absorbance values at or below 0.1 absorbance units.

### 2.5.4 Solid-State Spectroscopy

Spectroscopic characterization of solid material was completed by very carefully sandwiching the solid between cleaned quartz (fused quartz microscope slides, 1 mm thick, Technical Glass Products, Inc.). Two cleaned quartz substrates were sandwiched together and the absorbance and emission spectra of this blank was subtracted from the sample data.

Solid-state absorbance measurements were made using Shimadzu UV-2600 UV-vis spectrometer with an integrating sphere attachment. Absorbance of solid-state samples were calculated from diffuse reflectance and transmittance measurements and calculated using the following formula,

$$
A=2-\log _{10}(R+T)
$$

where A is absorbance, R is reflectance (\%), and T is transmittance (\%).
Absorbance of thin-films was calculated using the same formula, except specular reflectance was measured instead of diffuse reflectance. Solid-state emission spectra were collected using the front-facing accessory on a Horiba Jobin Yvon Fluorolog3 and collected $22.5^{\circ}$ from the incident beam.

### 2.5.5 Thin Film Deposition

Thin films were made via physical vapor deposition (AMOD Thermal Deposition System, Ångstrom Engineering Inc.) onto rigorously cleaned quartz substrates. All films were deposited in order to achieve 100 nm thick thin films. Vapor annealing of thin films were done in sealed fuming chambers with volumes of DCM between $150 \mu \mathrm{~L}$ (using a hermetically sealed chamber) and 10 mL (using a non-sealed chamber) to generate the orange film.

### 2.5.6 Synthetic Procedures and Characterizations

4-bromonaphthalen-1-ol (4-bromo-1-naphthol): To a solution of 1-naphthol (20.8 g, 144 $\mathrm{mmol})$ in dry acetonitrile ( 145 mL ) was added freshly recrystallized NBS ( $27.0 \mathrm{~g}, 152 \mathrm{mmol}$ ) in several portions at room temperature over 30 min . After complete addition of the NBS, the reaction was allowed to stir at room temperature for an addition 4 hours. The reaction solution was then poured into $\mathrm{H}_{2} \mathrm{O}(100 \mathrm{~mL})$ and extracted with diethyl ether twice ( $2 \times 100 \mathrm{~mL}$ ). The organic layers were then combined and washed with $\mathrm{H}_{2} \mathrm{O}(3 \times 500 \mathrm{~mL})$ and sat. $\mathrm{NaCl}(3 \times 500$ mL ) and dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$. Filtration and removal of diethyl ether by rotary evaporation yielded the crude product which was then subjected to column chromatography $(20 \% / 80 \%$ DCM/hexanes to $100 \% \mathrm{DCM}$ ) to yield 4-bromo-1-naphthol as an off-white powder after rotary evaporation ( $22.3 \mathrm{~g}, 99.8 \mathrm{mmol}, 69 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.19(\mathrm{t}, J=9.5 \mathrm{~Hz}$, $2 \mathrm{H}), 7.66-7.57(\mathrm{~m}, 2 \mathrm{H}), 7.55(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.71(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.26(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (126 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 151.38,132.87,129.53,128.02,127.22,126.18,125.75,122.30$, 113.61, 109.31. HRMS (CI, positive): Calc. for $\mathrm{C}_{10} \mathrm{H}_{7} \mathrm{BrO}[\mathrm{M}]^{+}$221.9680, found 221.9674.

1-bromo-4-methoxynaphthalene (MAN 1.1): To a solution of 4-bromo-1-naphthol (3.0 g, 13.4 $\mathrm{mmol})$ in dry acetonitrile ( 80 mL ) was added dry $\mathrm{K}_{2} \mathrm{CO}_{3}(5.5 \mathrm{~g}, 39.8 \mathrm{mmol})$ and methyl iodide $(1.2 \mathrm{~mL}, 19.3 \mathrm{mmol})$ and the solution was heated to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM ( 100 mL ) and the $\mathrm{K}_{2} \mathrm{CO}_{3}$ removed using a celite plug, which was then rinsed with DCM ( 500 mL ). The crude solution was then absorbed onto silica, which was then then subjected to column chromatography ( $100 \%$ hexanes) to yield MAN 1.1 as a clear oil ( $2.15 \mathrm{~g}, 9.07 \mathrm{mmol}, 67.4 \%$ yield). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.30(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.19(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.67(\mathrm{~d}, J$ $=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.62(\mathrm{ddd}, J=8.4,6.8,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.54(\mathrm{ddd}, J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.67(\mathrm{~d}, J$ $=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.98(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 155.35,132.53,129.57,127.87$, 126.97, 126.91, 126.06, 122.54, 113.35, 104.61, 55.78. HRMS (CI, positive): Calc. for $\mathrm{C}_{11} \mathrm{H}_{9} \mathrm{BrO}[\mathrm{M}]^{+}$235.9837, found 235.9835 .

4-(4-methoxynaphthalen-1-yl)-2-methylbut-3-yn-2-ol (MAN 1.2): To a stirring solution of MAN $1.1(1.65 \mathrm{~g}, 6.96 \mathrm{mmol})$ in triethylamine $(70 \mathrm{~mL})$ was added 2-methyl-3-butyn-2-ol (2.05 $\mathrm{mL}, 20.9 \mathrm{mmol}$ ) and Nitrogen was bubbled through the solution for 10 min . After degassing the solution, $\mathrm{CuI}(66 \mathrm{mg}, 5 \mathrm{~mol} \%), \mathrm{PPh}_{3}(91 \mathrm{mg}, 5 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(244 \mathrm{mg}, 5 \mathrm{~mol} \%)$ were added and the reaction was brought to $90^{\circ} \mathrm{C}$ and left to reflux overnight. The reaction was then filtered, washed with diethyl ether $(100 \mathrm{~mL})$ and concentrated by rotary evaporation. DCM was then added $(300 \mathrm{~mL})$ and the organic solution was washed with $\mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL}), 1 \mathrm{~N} \mathrm{HCl}$ $(3 \times 300 \mathrm{~mL}), \mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL})$ and sat. $\mathrm{NaCl}(3 \times 300 \mathrm{~mL})$. The organic layer was then dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography ( $50 \% / 50 \%$ DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 1.2 as a yellow-white solid ( $851 \mathrm{mg}, 3.54 \mathrm{mmol}, 50.1 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.25(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.22(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.62-7.55(\mathrm{~m}$, $2 \mathrm{H}), 7.51(\mathrm{ddd}, J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.76(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.01(\mathrm{~s}, 3 \mathrm{H}), 2.10(\mathrm{~s}, 1 \mathrm{H}), 1.72$ ( $\mathrm{s}, 6 \mathrm{H}$ ). ${ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 156.11,134.33,131.16,127.42,125.93,125.83,125.48$, $122.39,112.51,103.58,97.22,80.58,66.10,55.76,31.92$. HRMS (CI, positive): Calc. for $\mathrm{C}_{16} \mathrm{H}_{1602}[\mathrm{M}]^{+} 240.1150$, found 240.1156 .

1-ethynyl-4-methoxynaphthalene (MAN 1.3): To a round bottom flask containing MAN 1.2 ( $850 \mathrm{mg}, 3.54 \mathrm{mmol}$ ) was added finely ground $\mathrm{KOH}(595 \mathrm{mg}, 10.6 \mathrm{mmol})$ and toluene ( 35 mL ). The reaction was then refluxed for 6 hours and upon cooling, the KOH was filtered, and washed with DCM until the filtrate was colorless ( $\sim 100 \mathrm{~mL}$ ). The solution was concentrated under reduced pressure and subsequent purification of the crude material by column chromatography ( $50 \% / 50 \%$ DCM/Hexanes) yielded MAN 1.3 as a brown oil ( $511 \mathrm{mg}, 2.80 \mathrm{mmol}, 79.2 \%$ yield). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.33-8.25(\mathrm{~m}, 2 \mathrm{H}), 7.68(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.60(\mathrm{ddd}, J=8.3$, $6.9,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.52(\mathrm{ddd}, J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.77(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.02(\mathrm{~s}, 3 \mathrm{H}), 3.38$ $(\mathrm{s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 156.47,134.57,132.05,127.58,125.98,125.92,125.44$,

6-bromo-2-methyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (NI 1): To a solution of 4-bromo-1,8-naphthalic anhydride ( $1.0 \mathrm{~g}, 3.6 \mathrm{mmol}$ ) was added Methylamine ( $40 \mathrm{wt} . \%$ in $\mathrm{H}_{2} \mathrm{O} ; 10 \mathrm{~mL}$ ) and 5 mL of Ethanol to aid in the dissolution of starting materials. The vial was purged with Nitrogen, then briefly sonicated before leaving the solution to stir at $35^{\circ} \mathrm{C}$ overnight. After the reaction was deemed complete by TLC the following morning, 5 mL of cold ethanol was added. The reaction was then filtered and the filtered solids were washed with $\mathrm{H}_{2} \mathrm{O}$ until the filtrate was colorless. To recrystallize the crude product, the washed solid was dissolved in boiling ethanol, then left to cool at room temperature for 3 hours, before being moved to the freezer to sit overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 1 as pale-yellow needles ( $0.69 \mathrm{~g}, 2.4 \mathrm{mmol}, 66 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.61(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.52(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.37(\mathrm{~d}, J=7.8$ $\mathrm{Hz}, 1 \mathrm{H}), 8.00(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.81(\mathrm{t}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.54(\mathrm{~s}, 3 \mathrm{H}){ }^{13} \mathrm{C}$ NMR ( 126 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 163.94,163.91,133.38,132.11,131.29,131.20,130.68,130.40,128.91,128.17$, 123.06, 122.19, 27.22. HRMS (CI, negative): Calc. for $\mathrm{C}_{13} \mathrm{H}_{8} \mathrm{BrNO}_{2}$ [M] 288.9738, found 288.9737.

## 6-((4-methoxynaphthalen-1-yl)ethynyl)-2-methyl- 1 H -benzo[de]isoquinoline-1,3(2H)-dione

(1): To an oven-dried three neck flask containing NI $1(1.12 \mathrm{~g}, 3.85 \mathrm{mmol})$ and MAN 1.3 (540 $\mathrm{mg}, 2.96 \mathrm{mmol})$ was added dry triethylamine $(30 \mathrm{~mL})$ and toluene $(30 \mathrm{~mL})$ and the solution was degassed for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing $\mathrm{PPh}_{3}(39 \mathrm{mg}, 5 \mathrm{~mol} \%)$, $\mathrm{CuI}(28 \mathrm{mg}, 5 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(104 \mathrm{mg}, 5 \mathrm{~mol} \%)$. The reaction solution was purged with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to $90^{\circ} \mathrm{C}$ and left to stir overnight. After allowing the reaction to cool, the reaction was filtered to
obtain the product which was rinsed with $\mathrm{H}_{2} \mathrm{O}(150 \mathrm{~mL})$ and dried under vacuum. Recrystallization of the crude product in toluene yielded $\mathbf{1}$ as a bright, neon orange crystals ( 865 $\mathrm{mg}, 2.21 \mathrm{mmol}, 74.7 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.88$ (dd, $J=8.4,1.3 \mathrm{~Hz}, 1 \mathrm{H}$ ), 8.68 (dd, $J=7.2,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.61(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.44(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.35(\mathrm{~d}, J=8.4$ $\mathrm{Hz}, 1 \mathrm{H}), 8.06(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.91-7.84(\mathrm{~m}, 2 \mathrm{H}), 7.70(\mathrm{ddd}, J=8.4,6.9,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.59$ (ddd, $J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.89(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.09(\mathrm{~s}, 3 \mathrm{H}), 3.59(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (126 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 164.56,164.29,157.25,134.27,132.81,132.47,131.78,131.75,130.72$, $128.58,128.28,128.01,127.57,126.23,125.85,125.63,123.07,122.78,121.75,112.09,103.92$, 98.37, 90.01, 55.95, 27.24. HRMS (CI, negative): Calc. for $\mathrm{C}_{26} \mathrm{H}_{17} \mathrm{NO}_{3}[\mathrm{M}]^{-} 391.1208$, found 391.1212.

1-bromo-4-(hexyloxy)naphthalene (MAN 6.1) : To a solution of 4-bromo-1-naphthol (4.0 g, $17.9 \mathrm{mmol})$ in dry acetonitrile ( 106 mL ) was added dry $\mathrm{K}_{2} \mathrm{CO}_{3}(7.4 \mathrm{~g}, 53.7 \mathrm{mmol})$ and 1bromohexane ( $3.02 \mathrm{~mL}, 21.5 \mathrm{mmol}$ ) and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM ( $\sim 100 \mathrm{~mL}$ ) and the $\mathrm{K}_{2} \mathrm{CO}_{3}$ removed using a celite plug which was then rinsed with DCM till the filtrate was colorless ( $\sim 500 \mathrm{~mL}$ ). The crude solution was then adsorbed onto silica, which was then subjected to column chromatography ( $100 \%$ hexanes) to yield MAN 6.1 as a white solid ( $4.32 \mathrm{~g}, 14.1 \mathrm{mmol}, 78.4 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.30(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.16$ (d, $J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.64(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.60(\mathrm{ddd}, J=8.4,6.8,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.52(\mathrm{ddd}, J=$ $8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.67(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.11(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.97-1.88(\mathrm{~m}, 2 \mathrm{H}), 1.60$ $-1.52(\mathrm{~m}, 2 \mathrm{H}), 1.44-1.32(\mathrm{~m}, 4 \mathrm{H}), 0.93(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $154.73,132.50,129.60,127.71,127.03,126.86,125.84,122.62,112.93,105.23,68.37,31.73$, 29.25, 26.01, 22.75, 14.20. HRMS (CI, positive): Calc. for $\mathrm{C}_{16} \mathrm{H}_{19} \mathrm{BrO}$ [M] ${ }^{+} 306.0619$, found 306.0612.

4-(4-(hexyloxy)naphthalen-1-yl)-2-methylbut-3-yn-2-ol (MAN 6.2): To a stirring solution of MAN $6.1(2.5 \mathrm{~g}, 8.1 \mathrm{mmol})$ in triethylamine ( 62 mL ) was added 2-methyl-3-butyn-2-ol ( 1.1 mL , 11.4 mmol ) and Argon was bubbled through the solution for 10 min . After degassing the solution, $\mathrm{CuI}(154 \mathrm{mg}, 10 \mathrm{~mol} \%), \mathrm{PPh}_{3}(212 \mathrm{mg}, 10 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(569 \mathrm{mg}, 10 \mathrm{~mol}$ $\%$ ) were added and the reaction was brought to $90^{\circ} \mathrm{C}$ and left for 20 hrs . The reaction was allowed to cool and then the solids were filtered, washed with diethyl ether $(2 \times 100 \mathrm{~mL})$ and concentrated by rotary evaporation. DCM was then added ( 300 mL ) and the organic solution was washed with $\mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL}), 1 \mathrm{NHCl}(3 \times 300 \mathrm{~mL}), \mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL})$ and brine ( $3 \times 300 \mathrm{~mL}$ ). The organic layer was then dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography ( $50 \% / 50 \%$ DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 6.2 as a brown oil (1.023 $\mathrm{g}, 3.3 \mathrm{mmol}, 40.8 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.30(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.22(\mathrm{~d}, J=$ $8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.60-7.54(\mathrm{~m}, 2 \mathrm{H}), 7.50(\mathrm{ddd}, J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, $4.14(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.08(\mathrm{~s}, 1 \mathrm{H}), 1.97-1.88(\mathrm{~m}, 2 \mathrm{H}), 1.72(\mathrm{~s}, 6 \mathrm{H}), 1.61-1.54(\mathrm{~m}, 2 \mathrm{H}), 1.45$ $-1.32(\mathrm{~m}, 4 \mathrm{H}), 0.93(\mathrm{t}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (126 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 155.62,134.37,131.25$, $127.34,125.90,125.70,125.63,122.51,112.14,104.28,97.11,80.67,68.45,66.11,31.93,31.76$, 29.32, 26.07, 22.77, 14.20. HRMS (CI, positive): Calc. for $\mathrm{C}_{21} \mathrm{H}_{2602}$ [M] ${ }^{+} 310.1933$, found 310.1936.

1-ethynyl-4-(hexyloxy)naphthalene (MAN 6.3): To a round bottom flask containing MAN 6.2 $(0.913 \mathrm{~g}, 2.9 \mathrm{mmol})$ was added finely ground $\mathrm{KOH}(0.460 \mathrm{~g}, 8.2 \mathrm{mmol})$ and toluene $(22 \mathrm{~mL})$. The reaction was then refluxed overnight. The next morning, the reaction was cooled and the KOH was filtered and washed with DCM until the filtrate was colorless, before being concentrated under reduced pressure. Purification of the crude material by column chromatography ( $50 \% / 50 \%$ DCM/Hexanes) yielded MAN 6.3 as a brown oil ( $0.647 \mathrm{~g}, 2.6$ mmol, $87 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.33-8.27(\mathrm{~m}, 2 \mathrm{H}), 7.66(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, $7.59(\mathrm{ddd}, J=8.4,6.8,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.51(\mathrm{ddd}, J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.75(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H})$,
$4.15(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 3.38(\mathrm{~s}, 1 \mathrm{H}), 1.93(\mathrm{p}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.56(\mathrm{dd}, J=10.6,4.7 \mathrm{~Hz}, 2 \mathrm{H})$, $1.45-1.32(\mathrm{~m}, 4 \mathrm{H}), 0.93(\mathrm{t}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 155.98,134.63$, $132.14,127.50,125.95,125.79,125.59,122.53,111.61,104.22,82.33,80.28,68.49,31.75$, 29.30, 26.06, 22.77, 14.20. HRMS (CI, positive): Calc. for $\mathrm{C}_{18} \mathrm{H}_{20} \mathrm{O}[\mathrm{M}]^{+} 252.1514$, found 252.1516.

6-bromo-2-hexyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (NI 6): To a solution of 4-bromo-1,8-naphthalic anhydride ( $1.0 \mathrm{~g}, 3.6 \mathrm{mmol}$ ) in ethanol $(10 \mathrm{~mL})$ was added 1-hexyylamine $(0.57$ $\mathrm{mL}, 4.3 \mathrm{mmol}$ ). The vial was purged with Nitrogen, sealed, and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered to remove unwanted, insoluble by-products, and washed with hot ethanol ( 50 mL ). To recrystallize the product, the filtrate was then heated while additional ethanol was added, until the contents were completely dissolved. The flask was allowed to cool at room temperature for 3 hours, before being moved to the freezer where it was stored overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 6 as offwhite needles ( $0.367 \mathrm{~g}, 1.0 \mathrm{mmol}, 28 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.66$ (dd, $J=7.3$, $1.1 \mathrm{~Hz}, 1 \mathrm{H}), 8.57(\mathrm{dd}, J=8.4,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 8.42(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 8.04(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H})$, $7.85(\mathrm{dd}, J=8.5,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.16(\mathrm{t}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 1.72(\mathrm{q}, J=7.9,7.3 \mathrm{~Hz}, 2 \mathrm{H}), 1.46-1.29$ $(\mathrm{m}, 6 \mathrm{H}), 0.89(\mathrm{t}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 163.78,163.76,133.36,132.16$, $131.35,131.24,130.80,130.33,129.19,128.23,123.35,122.49,40.78,31.69,28.18,26.93$, 22.71, 14.20. HRMS (CI, negative): Calc. for $\mathrm{C}_{18} \mathrm{H}_{18} \mathrm{BrNO}_{2}$ [M] 359.0521, found 359.0513.

## 2-hexyl-6-((4-(hexyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione

(6): To an oven-dried three neck flask containing NI $6(241 \mathrm{mg}, 0.955 \mathrm{mmol})$ and MAN 6.3 ( 515 $\mathrm{mg}, 1.43 \mathrm{mmol}$ ) was added dry triethylamine $(25 \mathrm{~mL})$ and the solution Nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing $\mathrm{PPh}_{3}(25 \mathrm{mg}, 10 \mathrm{~mol} \%), \mathrm{CuI}(18 \mathrm{mg}, 10 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(67 \mathrm{mg}, 10$
mol \%). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to $90^{\circ} \mathrm{C}$ and left to stir for 18 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with $\mathrm{H}_{2} \mathrm{O}(100 \mathrm{~mL})$ and dried under vacuum. Purification of the crude product via column chromatography (50\%/50\% DCM/Hexanes) to yield 6 as a yellow solid ( $421 \mathrm{mg}, 0.792 \mathrm{mmol}, 82.9 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.87(\mathrm{dd}, J=8.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.66(\mathrm{dd}, J=7.3,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.59(\mathrm{~d}, J=7.6 \mathrm{~Hz}$, $1 \mathrm{H}), 8.44(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.37(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.04(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.90-7.83(\mathrm{~m}$, 2 H ), 7.69 (ddd, $J=8.2,6.7,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.58$ (ddd, $J=8.3,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.87(\mathrm{~d}, J=8.1 \mathrm{~Hz}$, $1 \mathrm{H}), 4.25-4.16(\mathrm{~m}, 4 \mathrm{H}), 2.02-1.93(\mathrm{~m}, 2 \mathrm{H}), 1.80-1.70(\mathrm{~m}, 2 \mathrm{H}), 1.65-1.55(\mathrm{~m}, 2 \mathrm{H}), 1.49-$ $1.28(\mathrm{~m}, 10 \mathrm{H}), 0.94(\mathrm{t}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}), 0.90(\mathrm{t}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $164.26,164.00,156.76,134.33,132.69,132.57,131.72,130.66,128.49,128.38,127.94,127.53$, $126.10,125.83,125.77,123.23,122.88,121.88,111.74,104.60,98.44,90.01,68.68,40.74$, 31.76, 31.73, 29.30, 28.25, 26.98, 26.08, 22.79, 22.73, 14.23, 14.21. (CI, negative): Calc. for $\mathrm{C}_{36} \mathrm{H}_{37} \mathrm{NO}_{3}[\mathrm{M}]^{-}$531.2773, found 531.2786.

1-bromo-4-(heptyloxy)naphthalene (MAN 7.1): To a solution of 4-bromo-1-naphthol (3.72 g, $16.7 \mathrm{mmol})$ in dry acetonitrile ( 80 mL ) was added dry $\mathrm{K}_{2} \mathrm{CO}_{3}(6.9 \mathrm{~g}, 49.9 \mathrm{mmol})$ and 1bromoheptane ( $3.4 \mathrm{~mL}, 21.7 \mathrm{mmol}$ ) and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM $(100 \mathrm{~mL})$ and the $\mathrm{K}_{2} \mathrm{CO}_{3}$ removed using a celite plug which was then rinsed with DCM (500 mL ). The crude solution was then absorbed onto silica, which was then then subjected to column chromatography ( $100 \%$ hexanes) to yield MAN 7.1 as a white solid $(4.189 \mathrm{~g}, 13.0 \mathrm{mmol}, 78.1 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.31(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.17(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.64(\mathrm{~d}$, $J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.61(\mathrm{ddd}, J=8.4,6.8,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.53(\mathrm{ddd}, J=8.2,6.8,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.66(\mathrm{~d}$, $J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.11(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.93(\mathrm{p}, J=7.3,6.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.56(\mathrm{p}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H})$, $1.47-1.30(\mathrm{~m}, 6 \mathrm{H}), 0.93(\mathrm{t}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 154.86, 132.59,
$129.65,127.80,127.13,126.95,125.95,122.67,113.03,105.38,68.55,31.95,29.35,29.24$, 26.36, 22.78, 14.25. HRMS (CI, positive): Calc. for $\mathrm{C}_{17} \mathrm{H}_{21} \mathrm{BrO}[\mathrm{M}]^{+} 320.0776$, found 320.0767 .

4-(4-(heptyloxy)naphthalen-1-yl)-2-methylbut-3-yn-2-ol (MAN 7.2): To a stirring solution of MAN 7.1 ( $3.692 \mathrm{~g}, 11.5 \mathrm{mmol}$ ) in triethylamine $(88 \mathrm{~mL})$ was added 2-methyl-3-butyn-2-ol (1.45 $\mathrm{mL}, 14.9 \mathrm{mmol}$ ) and Argon was bubbled through the solution for 10 min . After degassing the solution, $\mathrm{CuI}(110 \mathrm{mg}, 5 \mathrm{~mol} \%), \mathrm{PPh}_{3}(152 \mathrm{mg}, 5 \mathrm{~mol} \%)$, and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(407 \mathrm{mg}, 5 \mathrm{~mol} \%)$ were added and the reaction was brought to $90^{\circ} \mathrm{C}$ and left for 23 hrs . The reaction was then filtered, washed with diethyl ether ( 100 mL ) and concentrated by rotary evaporation. DCM was then added $(300 \mathrm{~mL})$ and the organic solution was washed with $\mathrm{H} 2 \mathrm{O}(3 \mathrm{x} 300 \mathrm{~mL}), 1 \mathrm{~N} \mathrm{HCl}(3 \mathrm{x}$ $300 \mathrm{~mL}), \mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL})$ and sat. $\mathrm{NaCl}(3 \times 300 \mathrm{~mL})$. The organic layer was then dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography ( $50 \% / 50 \%$ DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 7.2 as brown oil ( $1.815 \mathrm{mg}, 5.59 \mathrm{mmol}, 48.7 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.31(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.23(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.61-7.54(\mathrm{~m}, 2 \mathrm{H}), 7.50$ (ddd, $J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.73(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.13(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.23(\mathrm{~s}, 1 \mathrm{H})$, $1.93(\mathrm{p}, J=7.5,6.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.73(\mathrm{~s}, 6 \mathrm{H}), 1.60-1.51(\mathrm{~m}, 2 \mathrm{H}), 1.46-1.29(\mathrm{~m}, 6 \mathrm{H}), 0.92(\mathrm{t}, J=$ $6.6 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (126 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 155.58,134.36,131.24,127.32,125.89,125.67$, $125.60,122.49,112.14,104.27,97.13,80.65,68.42,66.07,31.94,31.91,29.34,29.24,26.34$, 22.77, 14.23. HRMS (CI, positive): Calc. for $\mathrm{C}_{22} \mathrm{H}_{2802}[\mathrm{M}]^{+} 324.2089$, found 324.2085.

1-ethynyl-4-(heptyloxy)naphthalene (MAN 7.3): To a round bottom flask containing MAN 7.2 $(1.510 \mathrm{~g}, 4.65 \mathrm{mmol})$ was added finely ground KOH pellets ( $784 \mathrm{mg}, 14 \mathrm{mmol}$ ) and toluene ( 36 mL ). The reaction was then refluxed for 12 hrs and upon cooling the KOH was filtered, washed using DCM, and concentrated under reduced pressure. Purification of the crude material by column chromatography ( $50 \% / 50 \% \mathrm{DCM} /$ Hexanes) yielded MAN 7.3 as an amber-brown oil $\left(1.220 \mathrm{~g}, 4.58 \mathrm{mmol}, 98.5 \%\right.$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.33-8.27(\mathrm{~m}, 2 \mathrm{H}), 7.66(\mathrm{~d}, J$
$=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.59(\mathrm{t}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.51(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.75(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.15(\mathrm{t}$, $J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 3.38(\mathrm{~s}, 1 \mathrm{H}), 1.98-1.89(\mathrm{~m}, 2 \mathrm{H}), 1.61-1.51(\mathrm{~m}, 2 \mathrm{H}), 1.45-1.29(\mathrm{~m}, 6 \mathrm{H})$, $0.91(\mathrm{t}, J=6.6 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 155.97,134.62,132.14,127.50,125.94$, $125.78,125.58,122.53,111.60,104.21,82.33,80.28,68.48,31.95,29.33,29.24,26.35,22.78$, 14.24. HRMS (CI, positive): Calc. for $\mathrm{C}_{19} \mathrm{H}_{22} \mathrm{O}[\mathrm{M}]^{+} 266.1671$, found 266.1670.

6-bromo-2-heptyl- $\mathbf{1 H}$-benzo[de]isoquinoline-1,3(2H)-dione (NI 7): To a solution of 4-bromo-1,8-naphthalic anhydride ( $1.0 \mathrm{~g}, 3.6 \mathrm{mmol}$ ) in ethanol $(10 \mathrm{~mL})$ was added 1-heptylamine $(0.64$ $\mathrm{mL}, 4.3 \mathrm{mmol}$ ). The vial was purged with Nitrogen and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered and washed with hot ethanol $(50 \mathrm{~mL})$ to remove unwanted, insoluble by-products. To recrystallize the product, the filtrate was then heated and additional ethanol was added until the contents were completely dissolved. The flask was cooled to room temperature for 3 hours, before then being moved to the freezer, where it was stored overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 7 as off-white needles ( 0.515 g , $1.38 \mathrm{mmol}, 38.1 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.65(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.55(\mathrm{~d}, J=$ $8.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.40(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 8.03(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.84(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.16(\mathrm{t}, J$ $=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.72(\mathrm{p}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.46-1.26(\mathrm{~m}, 8 \mathrm{H}), 0.87(\mathrm{t}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (126 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 163.75,163.72,133.33,132.13,131.33,131.22,130.77,130.30,129.15$, 128.21, 123.33, 122.46, 40.78, 31.90, 29.17, 28.23, 27.23, 22.75, 14.22. HRMS (CI, negative): Calc. for $\mathrm{C}_{19} \mathrm{H}_{20} \mathrm{BrNO}_{2}[\mathrm{M}]^{-} 373.0667$, found 373.0668.

## 2-heptyl-6-((4-(heptyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-

dione (7): To a solution of NI $7(1.04 \mathrm{mg}, 2.78 \mathrm{mmol})$ in dry triethylamine ( 75 mL ) was added $\mathrm{PPh}_{3}(57 \mathrm{mg}, 5 \mathrm{~mol} \%)$ and MAN 7.3 ( $1.158 \mathrm{mg}, 4.34 \mathrm{mmol}$ ). Argon was bubbled through the solution for 10 min . To this solution was added $\mathrm{CuI}(41 \mathrm{mg}, 5 \mathrm{~mol} \%), \mathrm{PPh}_{3}(57 \mathrm{mg}, 5 \mathrm{~mol} \%$ ) and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(152 \mathrm{mg}, 5 \mathrm{~mol} \%)$ and the reaction was heated to $90^{\circ} \mathrm{C}$ for 12 hrs . After
allowing the reaction to cool, the reaction was filtered to obtain the product which was rinsed with $\mathrm{H}_{2} \mathrm{O}$ and dried under vacuum. Purification of the crude material by column chromatography ( $50 \% / 50 \% \mathrm{DCM} /$ Hexanes) yielded 7 as a yellow-orange solid ( $893 \mathrm{mg}, 1.60 \mathrm{mmol}, 57.4 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.87$ (d, $\left.J=8.4 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.67$ (d, $\left.J=7.3 \mathrm{~Hz}, 1 \mathrm{H}\right), 8.60(\mathrm{~d}$, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.44(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.37(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.05(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.90$ - $7.83(\mathrm{~m}, 2 \mathrm{H}), 7.69(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.58(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.87(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.25-$ $4.16(\mathrm{~m}, 4 \mathrm{H}), 1.98(\mathrm{p}, J=7.6,6.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.75(\mathrm{p}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 1.59(\mathrm{p}, J=7.8,7.3 \mathrm{~Hz}$, $2 \mathrm{H}), 1.46-1.26(\mathrm{~m}, 14 \mathrm{H}), 0.92(\mathrm{t}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}), 0.88(\mathrm{t}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 126 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 164.26,164.00,156.76,134.33,132.69,132.57,131.72,130.67,128.49,128.39$, 127.93, 127.53, 126.10, 125.83, 125.77, 123.23, 122.89, 121.88, 111.74, 104.60, 98.44, 90.00, $68.69,40.75,31.96,31.93,29.34,29.26,29.22,28.32,27.28,26.37,22.80,22.77,14.26$, 14.24.HRMS (CI, negative): Calc. for $\mathrm{C}_{38} \mathrm{H}_{41} \mathrm{NO}_{3}[\mathrm{M}]^{-} 559.3086$, found 559.3094.

1-bromo-4-(octyloxy)naphthalene (MAN 8.1): To a solution of 4-bromo-1-naphthol (4.0 g, $17.9 \mathrm{mmol})$ in dry acetonitrile $(100 \mathrm{~mL})$ was added dry $\mathrm{K}_{2} \mathrm{CO}_{3}(7.42 \mathrm{~g}, 53.7 \mathrm{mmol})$ and 1bromooctane ( $4.0 \mathrm{~mL}, 23.3 \mathrm{mmol}$ ) and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM $(100 \mathrm{~mL})$ and the $\mathrm{K}_{2} \mathrm{CO}_{3}$ removed using a celite plug which was then rinsed with DCM (500 mL ). The crude solution was then absorbed onto silica, which was then then subjected to column chromatography ( $100 \%$ hexanes) to yield MAN 8.1 as a white solid ( $4.2 \mathrm{~g}, 12.5 \mathrm{mmol}, 70 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.29(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 8.15(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.64(\mathrm{~d}$, $J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.60(\mathrm{ddd}, J=8.4,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.52(\mathrm{td}, J=7.6,6.9,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.67(\mathrm{~d}, J$ $=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.12(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.92(\mathrm{p}, J=7.3,6.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.60-1.53(\mathrm{~m}, 2 \mathrm{H}), 1.45-$ $1.27(\mathrm{~m}, 8 \mathrm{H}), 0.89(\mathrm{t}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 154.88,132.60,129.66$, $127.82,127.14,126.97,125.96,122.68,113.04,105.41,68.58,31.98,29.53,29.41,29.35,26.40$, 22.82, 14.26. HRMS (CI, positive): Calc. for $\mathrm{C}_{18} \mathrm{H}_{23} \mathrm{BrO}[\mathrm{M}]^{+} 334.0932$, found 334.0923.

2-methyl-4-(4-(octyloxy)naphthalen-1-yl)but-3-yn-2-ol (MAN 8.2): To an oven-dried three neck flask containing MAN $8.1(3.24 \mathrm{~g}, 9.66 \mathrm{mmol})$ in triethylamine ( 78 mL ) was added 2-methyl-3-butyn-2-ol ( $1.42 \mathrm{~mL}, 14.6 \mathrm{mmol}$ ) and Nitrogen was bubbled through the solution for 10 min. The three-neck flask was then equipped with a solid addition funnel containing $\mathrm{PPh}_{3}$ (274 mg, $10 \mathrm{~mol} \%$ ), $\mathrm{CuI}\left(199 \mathrm{mg}, 10 \mathrm{~mol} \%\right.$ ) and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(730 \mathrm{mg}, 10 \mathrm{~mol} \%)$. The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to $90^{\circ} \mathrm{C}$ and left to stir overnight. The reaction was allowed to cool and then the solids were filtered, washed with diethyl ether ( $2 \times 100 \mathrm{~mL}$ ) and concentrated by rotary evaporation. DCM was then added ( 300 mL ) and the organic solution was washed with $\mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL}), 1 \mathrm{~N} \mathrm{HCl}(3 \mathrm{x}$ $300 \mathrm{~mL}), \mathrm{H}_{2} \mathrm{O}(3 \mathrm{x} 300 \mathrm{~mL})$ and brine ( $3 \times 300 \mathrm{~mL}$ ). The organic layer was then dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography ( $50 \% / 50 \%$ DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 8.2 as a brown oil ( $1.23 \mathrm{~g}, 3.63 \mathrm{mmol}, 35.0 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.30(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.22(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.60-7.55(\mathrm{~m}, 2 \mathrm{H}), 7.50$ (ddd, $J=8.2,6.7,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.14(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.11(\mathrm{~s}, 1 \mathrm{H})$, $1.97-1.88(\mathrm{~m}, 2 \mathrm{H}), 1.72(\mathrm{~s}, 6 \mathrm{H}), 1.58-1.53(\mathrm{~m}, 2 \mathrm{H}), 1.42-1.29(\mathrm{~m}, 8 \mathrm{H}), 0.90(\mathrm{t}, J=6.7 \mathrm{~Hz}$, $3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 155.62,134.37,131.25,127.34,125.89,125.70,125.62$, $122.51,112.14,104.28,97.11,80.67,68.45,66.10,31.98,31.93,29.85,29.53,29.40,29.35$, 26.39, 22.82, 14.26. HRMS (CI, positive): Calc. for $\mathrm{C}_{23} \mathrm{H}_{30} \mathrm{O}_{2}[\mathrm{M}]^{+} 338.2246$, found 338.2244.

1-ethynyl-4-(octyloxy)naphthalene (MAN 8.3): To a round bottom flask containing MAN 8.2 ( $0.693 \mathrm{~g}, 2.05 \mathrm{mmol}$ ) was added finely ground KOH pellets ( $345 \mathrm{mg}, 6.15 \mathrm{mmol}$ ) and toluene $(16 \mathrm{~mL})$. The reaction was then refluxed for 12 hrs and upon cooling the KOH was filtered, washed using DCM, and concentrated under reduced pressure. Purification of the crude material by column chromatography ( $50 \% / 50 \% \mathrm{DCM} /$ Hexanes) yielded MAN 8.3 as a brown oil ( 0.549 g, $1.96 \mathrm{mmol}, 95.5 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.33-8.27(\mathrm{~m}, 2 \mathrm{H}), 7.66(\mathrm{~d}, J=8.0$
$\mathrm{Hz}, 1 \mathrm{H}), 7.59(\mathrm{ddd}, J=8.4,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.51(\mathrm{ddd}, J=8.1,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.75(\mathrm{~d}, J=8.0$ $\mathrm{Hz}, 1 \mathrm{H}), 4.15(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 3.38(\mathrm{~s}, 1 \mathrm{H}), 1.93(\mathrm{p}, J=7.4,6.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.61-1.51(\mathrm{~m}, 2 \mathrm{H})$, $1.45-1.28(\mathrm{~m}, 8 \mathrm{H}), 0.90(\mathrm{t}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 155.98,134.62$, 132.14, 127.50, 125.94, 125.78, 125.58, 122.54, 111.60, 104.22, 82.33, 80.28, 68.49, 31.98, 29.53, 29.41, 29.32, 26.38, 22.82, 14.26. HRMS (CI, positive): Calc. for $\mathrm{C}_{20} \mathrm{H}_{24} \mathrm{O}[\mathrm{M}]^{+}$ 280.1827, found 280.1820 .

6-bromo-2-octyl-1 $\boldsymbol{H}$-benzo[de]isoquinoline-1,3(2H)-dione (NI 8): To a solution of 4-bromo-1,8-naphthalic anhydride ( $3.0 \mathrm{~g}, 10.8 \mathrm{mmol}$ ) in ethanol ( 30 mL ) was added 1-octylamine ( 2.50 $\mathrm{mL}, 15.1 \mathrm{mmol}$ ). The vial was purged with Nitrogen and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered and washed with hot ethanol ( 50 mL ) to remove unwanted, insoluble by-products. To recrystallize the product, the filtrate was then heated and additional ethanol was added until the contents were completely dissolved. The flask was cooled to room temperature for 3 hours, before then being moved to the freezer, where it was stored overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 8 as pale-yellow needles ( 2.346 g , $6.05 \mathrm{mmol}, 56 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.65(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.55(\mathrm{~d}, J=8.5$ $\mathrm{Hz}, 1 \mathrm{H}), 8.40(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 8.03(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.84(\mathrm{t}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 4.15(\mathrm{t}, J=$ $7.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.72(\mathrm{p}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.46-1.23(\mathrm{~m}, 10 \mathrm{H}), 0.87(\mathrm{t}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 163.74,163.72,133.32,132.13,131.33,131.22,130.76,130.30,129.15$, 128.20 , 123.32, 122.46, 40.78, 31.96, 29.47, 29.36, 28.23, 27.28, 22.78, 14.23. HRMS (CI, negative): Calc. for $\mathrm{C}_{20} \mathrm{H}_{22} \mathrm{BrNO}_{2}[\mathrm{M}]^{-} 387.0834$, found 387.0826 .

## 2-octyl-6-((4-(octyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione

(8): To an oven-dried three neck flask containing NI 8 ( $296 \mathrm{mg}, 0.76 \mathrm{mmol}$ ) and MAN 8.3 (165 $\mathrm{mg}, 0.59 \mathrm{mmol}$ ) was added dry triethylamine ( 15 mL ) and the solution Nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition
funnel containing $\mathrm{PPh}_{3}(16 \mathrm{mg}, 10 \mathrm{~mol} \%), \mathrm{CuI}(11 \mathrm{mg}, 10 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(42 \mathrm{mg}, 10$ mol \%). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to $90^{\circ} \mathrm{C}$ and left to stir for xx hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with $\mathrm{H}_{2} \mathrm{O}$ and dried under vacuum. Purification of the crude product via column chromatography ( $50 \% / 50 \%$ DCM/Hexanes) yielded 8 as a yellow solid ( $241 \mathrm{mg}, 0.41 \mathrm{mmol}, 69.7 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.87(\mathrm{~d}, J$ $=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.67(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.59(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.44(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.37$ (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.05(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.90-7.83(\mathrm{~m}, 2 \mathrm{H}), 7.69(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.58$ (t, $J=7.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.87(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.25-4.16(\mathrm{~m}, 4 \mathrm{H}), 1.97(\mathrm{p}, J=7.8,6.7 \mathrm{~Hz}, 2 \mathrm{H})$, $1.75(\mathrm{p}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.59(\mathrm{p}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.49-1.22(\mathrm{~m}, 18 \mathrm{H}), 0.94-0.85(\mathrm{~m}, 6 \mathrm{H}){ }^{13} \mathrm{C}$ NMR (126 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 164.26,164.00,156.76,134.33,132.69,132.57,131.72,130.67$, $128.49,128.39,127.93,127.53,126.09,125.83,125.77,123.23,122.89,121.88,111.73,104.60$, $98.44,90.01,68.69,40.75,31.99,29.54,29.52,29.42,29.39,29.33,28.32,27.33,26.40,22.83$, 22.80, 14.27, 14.25. HRMS (CI, negative): Calc. for $\mathrm{C}_{40} \mathrm{H}_{45} \mathrm{NO}_{3}$ [M] ${ }^{-} 587.3399$, found 587.3413 .

1-bromo-4-(nonyloxy)naphthalene (MAN 9.1): To a solution of 4-bromo-1-naphthol (1.94 g, $8.7 \mathrm{mmol})$ in dry acetonitrile ( 51 mL ) was added dry $\mathrm{K}_{2} \mathrm{CO}_{3}(3.6 \mathrm{~g}, 26 . \mathrm{mmol})$ and 1bromononane ( $2.16 \mathrm{~mL}, 11.3 \mathrm{mmol}$ ) and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM $(\sim 100 \mathrm{~mL})$ and the $\mathrm{K}_{2} \mathrm{CO}_{3}$ removed using a celite plug which was then rinsed with DCM till the filtrate was colorless ( $\sim 500 \mathrm{~mL}$ ). The crude solution was then adsorbed onto silica, which was then subjected to column chromatography ( $100 \%$ hexanes) to yield MAN 9.1 as a white solid $\left(2.32 \mathrm{~g}, 6.6 \mathrm{mmol}, 77 \%\right.$ yield). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{cdcl}_{3}$ ) $\delta 8.32$ (ddd, $J=8.4,1.4,0.7 \mathrm{~Hz}, 1 \mathrm{H}$ ), 8.17 (ddd, $J=8.4,1.3,0.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.68-7.57(\mathrm{~m}, 2 \mathrm{H}), 7.53(\mathrm{ddd}, J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H})$, $6.66(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.10(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.93(\mathrm{p}, J=8.0,6.8,6.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.56(\mathrm{p}, J=$ 7.4, $6.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.47-1.25(\mathrm{~m}, 10 \mathrm{H}), 0.91(\mathrm{t}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.101 \mathrm{MHz}, \mathrm{cdcl}_{3}\right) \delta$
$154.85,132.59,129.65,127.80,127.12,126.96,125.94,122.67,113.02,105.37,68.54,32.04,29.71$, 29.57, 29.43, 29.34, 26.38, 22.84, 14.27. (CI, positive): Calc. for $\mathrm{C}_{19} \mathrm{H}_{25} \mathrm{OBr}[\mathrm{M}]^{+} 348.1089$, found 348.1088.

2-methyl-4-(4-(nonyloxy)naphthalen-1-yl)but-3-yn-2-ol (MAN 9.2): To a stirring solution of MAN $9.1(1.81 \mathrm{~g}, 5.2 \mathrm{mmol})$ in triethylamine ( 40 mL ) was added 2-methyl-3-butyn-2-ol ( 0.71 $\mathrm{mL}, 7.25 \mathrm{mmol}$ ) and Argon was bubbled through the solution for 10 min . After degassing the solution, $\mathrm{CuI}(49.5 \mathrm{mg}, 5 \mathrm{~mol} \%), \mathrm{PPh}_{3}(68.2 \mathrm{mg}, 5 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(182 \mathrm{mg}, 5 \mathrm{~mol} \%)$ were added and the reaction was brought to $90^{\circ} \mathrm{C}$ and left for 20 hrs . The reaction was allowed to cool and then the solids were filtered, washed with diethyl ether ( 2 x 100 mL ) and concentrated by rotary evaporation. DCM was then added ( 300 mL ) and the organic solution was washed with $\mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL}), 1 \mathrm{~N} \mathrm{HCl}(3 \times 300 \mathrm{~mL}), \mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL})$ and brine ( $3 \times 300 \mathrm{~mL}$ ). The organic layer was then dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography (50\%/50\% DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 9.2 as a brown oil ( 0.707 $\mathrm{g}, 2.01 \mathrm{mmol}, 38.6 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{cdcl}_{3}$ ) $\delta 8.30$ (ddd, $J=8.3,1.5,0.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 8.23 (ddd, $J=8.3,1.4,0.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.62-7.55(\mathrm{~m}, 2 \mathrm{H}), 7.50(\mathrm{ddd}, J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H})$, $6.73(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.12(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.23(\mathrm{~s}, 1 \mathrm{H}), 1.92(\mathrm{p}, J=7.6,7.0,6.5,6.5 \mathrm{~Hz}$, $2 \mathrm{H}), 1.73(\mathrm{~s}, 6 \mathrm{H}), 1.60-1.52(\mathrm{~m}, 2 \mathrm{H}), 1.43-1.25(\mathrm{~m}, 10 \mathrm{H}), 0.90(\mathrm{t}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\operatorname{cdcl}_{3}$ ) $\delta 155.51,134.33,131.21,127.28,125.87,125.63,125.56,122.46,112.13$, $104.23,97.16,80.60,77.48,77.16,76.84,68.36,66.01,53.52,32.00,31.88,29.66,29.54,29.39$, 29.29, 26.34, 22.80, 14.23. (CI, positive): Calc. for $\mathrm{C}_{24} \mathrm{H}_{32} \mathrm{O}_{2}[\mathrm{M}]^{+} 352.2402$, found 352.2399 .

1-ethynyl-4-(nonyloxy)naphthalene (MAN 9.3): To a round bottom flask containing MAN 9.2 $(0.555 \mathrm{~g}, 1.6 \mathrm{mmol})$ was added finely ground $\mathrm{KOH}(0.265 \mathrm{~g}, 4.8 \mathrm{mmol})$ and toluene $(12.3 \mathrm{~mL})$. The reaction was then refluxed overnight. The next morning, the reaction was cooled and the KOH was filtered and washed with DCM until the filtrate was colorless, before being
concentrated under reduced pressure. Purification of the crude material by column chromatography ( $50 \% / 50 \%$ DCM/Hexanes) yielded MAN 9.3 as a brown oil ( $0.357 \mathrm{~g}, 1.21$ mmol, $77.0 \%$ yield). 1H NMR ( 400 MHz , cdcl3) $\delta 8.41-8.33(\mathrm{~m}, 2 \mathrm{H}), 7.70(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, 7.64 (ddd, J = 8.2, 6.8, $1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.56$ (ddd, J = 8.3, 6.8, $1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.73(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, $4.12(\mathrm{t}, \mathrm{J}=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 3.44(\mathrm{~s}, 1 \mathrm{H}), 1.94(\mathrm{p}, \mathrm{J}=7.9,7.3,6.6,6.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.64-1.52(\mathrm{~m}, 2 \mathrm{H})$, $1.48-1.30(\mathrm{~m}, 10 \mathrm{H}), 0.96(\mathrm{t}, \mathrm{J}=6.8 \mathrm{~Hz}, 3 \mathrm{H}) .13 \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{cdcl} 3$ ) $\delta 155.90$, 134.59, $132.11,127.45,125.92,125.73,125.54,122.52,111.58,104.14,82.32,80.30,68.38,32.03$, 29.70, 29.56, 29.43, 29.29, 26.35, 22.84, 14.27. (CI, positive): Calc. for C21H26O [M]+ 294.1984, found 294.1981.

6-bromo-2-nonyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (NI 9): To a solution of 4-bromo-1,8-naphthalic anhydride ( $2.15 \mathrm{~g}, 7.8 \mathrm{mmol}$ ) in ethanol $(21.5 \mathrm{~mL})$ was added n -nonylamine ( 1.7 $\mathrm{mL}, 9.3 \mathrm{mmol}$ ). The vial was purged with Nitrogen, sealed, and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered to remove unwanted, insoluble by-products, and washed with hot ethanol. To recrystallize the product, the filtrate was then heated while additional ethanol was added, until the contents were completely dissolved. The flask was allowed to cool at room overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 9 as yellowwhite needles $(2.463 \mathrm{~g}, 6.12 \mathrm{mmol}, 78.9 \%$ yield). 1 H NMR ( $400 \mathrm{MHz}, \operatorname{cdcl} 3$ ) $\delta 8.64(\mathrm{dt}, \mathrm{J}=7.3$, $1.1 \mathrm{~Hz}, 1 \mathrm{H}), 8.54(\mathrm{dt}, \mathrm{J}=8.5,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.39(\mathrm{dd}, \mathrm{J}=7.8,1.0 \mathrm{~Hz}, 1 \mathrm{H}), 8.02(\mathrm{dd}, \mathrm{J}=7.8,1.0$ $\mathrm{Hz}, 1 \mathrm{H}), 7.83(\mathrm{ddd}, \mathrm{J}=8.4,7.3,0.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.15(\mathrm{t}, \mathrm{J}=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.71(\mathrm{p}, \mathrm{J}=7.5 \mathrm{~Hz}, 2 \mathrm{H})$, $1.45-1.22(\mathrm{~m}, 12 \mathrm{H}), 0.86(\mathrm{t}, \mathrm{J}=7.0 \mathrm{~Hz}, 3 \mathrm{H}) .13 \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 163.76,163.74$, 133.34, 132.15, 131.34, 131.23, 130.79, 130.31, 129.17, 128.22, 123.34, 122.48, 40.79, 32.00, 29.65, 29.51, 29.41, 28.24, 27.28, 22.81, 14.25. (CI, positive): Calc. for $\mathrm{C}_{21} \mathrm{H}_{24} \mathrm{BrNO}_{2}[\mathrm{M}]^{+} 401.0990$, found 401.0996.

## 2-nonyl-6-((4-(nonyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione

 (9): To an oven-dried three neck flask containing NI 9 ( $718 \mathrm{mg}, 1.8 \mathrm{mmol}$ ) and MAN 9.3 (350 $\mathrm{mg}, 1.2 \mathrm{mmol}$ ) was added dry triethylamine ( 30 mL ) and nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing PPh3 (16 mg, $5 \mathrm{~mol} \%$ ), $\mathrm{CuI}(11 \mathrm{mg}, 5 \mathrm{~mol} \%)$ and $\mathrm{PdCl} 2(\mathrm{PPh} 3) 2(42 \mathrm{mg}, 5 \mathrm{~mol} \%)$. The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to $90^{\circ} \mathrm{C}$ and left to stir for 17 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with H 2 O and dried under vacuum. Purification of the crude product via column chromatography (50\%/50\% DCM/Hexanes) to yield 9 as an orange-yellow solid ( $569 \mathrm{mg}, 0.92 \mathrm{mmol}, 77.7 \%$ yield). 1 H NMR ( 400 MHz , cdcl3) $\delta$ 8.82 (dd, J = 8.4, 1.2 Hz, 1H), 8.63 (dd, J = 7.3, $1.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 8.55 (d, J = $7.7 \mathrm{~Hz}, 1 \mathrm{H}), 8.40$ (dt, J $=8.3,0.9 \mathrm{~Hz}, 1 \mathrm{H}), 8.35(\mathrm{dt}, \mathrm{J}=8.2,1.0 \mathrm{~Hz}, 1 \mathrm{H}), 8.00(\mathrm{~d}, \mathrm{~J}=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.86-7.80(\mathrm{~m}, 2 \mathrm{H})$, $7.67(\mathrm{ddd}, \mathrm{J}=8.3,6.8,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.57(\mathrm{ddd}, \mathrm{J}=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.83(\mathrm{~d}, \mathrm{~J}=8.1 \mathrm{~Hz}, 1 \mathrm{H})$, $4.23-4.14(\mathrm{~m}, 4 \mathrm{H}), 1.96(\mathrm{dt}, \mathrm{J}=14.2,6.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.74(\mathrm{p}, \mathrm{J}=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.63-1.54(\mathrm{~m}$, $2 H), 1.47-1.25(\mathrm{~m}, 22 \mathrm{H}), 0.94-0.84(\mathrm{~m}, 6 \mathrm{H}) .13 \mathrm{C}$ NMR (101 MHz, cdcl3) $\delta 164.19,163.92$, $156.73,134.29,132.60,132.55,131.64,130.60,128.44,128.32,127.90,127.46,126.06,125.80$, $125.74,123.19,122.87,121.83,111.73,104.58,98.43,90.03,68.68,40.73,32.04,32.02,29.71$, 29.68, 29.58, 29.55, 29.43, 29.34, 28.31, 27.34, 26.40, 22.84, 22.82, 14.26. (CI, positive): Calc. for $\mathrm{C} 42 \mathrm{H} 49 \mathrm{NO} 3[\mathrm{M}]+615.3712$, found 615.3721 .1-bromo-4-(decyloxy)naphthalene (MAN 10.1): To a solution of 4-bromo-1-naphthol (4.00 g, $17.9 \mathrm{mmol})$ in dry acetonitrile ( 100 mL ) was added dry $\mathrm{K}_{2} \mathrm{CO}_{3}(7.42 \mathrm{~g}, 53.7 \mathrm{mmol})$ and 1bromodecane ( $4.82 \mathrm{~mL}, 23.3 \mathrm{mmol}$ ) and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM $(\sim 100 \mathrm{~mL})$ and the $\mathrm{K}_{2} \mathrm{CO}_{3}$ removed using a celite plug which was then rinsed with DCM till the filtrate was colorless ( $\sim 500 \mathrm{~mL}$ ). The crude solution was then adsorbed onto silica, which was
then subjected to column chromatography ( $100 \%$ hexanes) to yield MAN $\mathbf{1 0 . 1}$ as an oily white solid ( $3.62 \mathrm{~g}, 9.96 \mathrm{mmol}, 56 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.31$ (dd, $J=8.4,1.3 \mathrm{~Hz}$, $1 \mathrm{H}), 8.16(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.66-7.58(\mathrm{~m}, 2 \mathrm{H}), 7.52(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.67(\mathrm{~d}, J=8.2 \mathrm{~Hz}$, $1 \mathrm{H}), 4.11(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.93(\mathrm{p}, J=7.7,7.3,6.7,6.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.56(\mathrm{p}, J=7.8,7.3 \mathrm{~Hz}, 2 \mathrm{H})$, $1.43-1.27(\mathrm{~m}, 12 \mathrm{H}), 0.89(\mathrm{t}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 154.87, 132.60, $129.66,127.81,127.14,126.97,125.95,122.68,113.04,105.40,68.57,32.06,29.74,29.72$, 29.56, 29.48, 29.34, 26.39, 22.84, 14.27. (CI, positive): Calc. for $\mathrm{C}_{20} \mathrm{H}_{2} 7 \mathrm{BrO}[\mathrm{M}]^{+} 362.1245$, found 362.1240 .

4-(4-(decyloxy)naphthalen-1-yl)-2-methylbut-3-yn-2-ol (MAN 10.2): To a stirring solution of MAN $10.1(2.50 \mathrm{~g}, 6.9 \mathrm{mmol})$ in triethylamine $(53 \mathrm{~mL})$ was added 2-methyl-3-butyn-2-ol ( 0.95 $\mathrm{mL}, 9.7 \mathrm{mmol}$ ) and Argon was bubbled through the solution for 10 min . After degassing the solution, $\mathrm{CuI}(131 \mathrm{mg}, 10 \mathrm{~mol} \%), \mathrm{PPh}_{3}(181 \mathrm{mg}, 10 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(484 \mathrm{mg}, 10 \mathrm{~mol}$ $\%$ ) were added and the reaction was brought to $90^{\circ} \mathrm{C}$ and left for 23 hrs . The reaction was allowed to cool and then the solids were filtered, washed with diethyl ether ( $2 \times 100 \mathrm{~mL}$ ) and concentrated by rotary evaporation. DCM was then added ( 300 mL ) and the organic solution was washed with $\mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL}), 1 \mathrm{~N} \mathrm{HCl}(3 \times 300 \mathrm{~mL}), \mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL})$ and brine ( $3 \times 300 \mathrm{~mL}$ ). The organic layer was then dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography (50\%/50\% DCM/Hexanes) and concentrated by rotary evaporation to yield MAN $\mathbf{1 0 . 2}$ as a brown oil ( 1.085 $\mathrm{g}, 2.96 \mathrm{mmol}, 42.8 \%$ yield $).{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.29(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.22(\mathrm{~d}, J=$ $7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.60-7.54(\mathrm{~m}, 2 \mathrm{H}), 7.50(\mathrm{ddd}, J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, $4.14(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.08(\mathrm{~s}, 1 \mathrm{H}), 1.93(\mathrm{dt}, J=14.6,6.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.72(\mathrm{~s}, 6 \mathrm{H}), 1.62-1.50$ $(\mathrm{m}, 2 \mathrm{H}), 1.42-1.26(\mathrm{~m}, 12 \mathrm{H}), 0.88(\mathrm{t}, J=7.1,6.6 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $155.63,134.39,131.25,127.34,125.90,125.70,122.52,112.01,104.30,97.12,80.68,68.47$, $66.11,32.06,31.93,29.86,29.74,29.72,29.57,29.48,29.35,26.39,22.83,14.26$. (CI, positive): Calc. for $\mathrm{C}_{25} \mathrm{H}_{34} \mathrm{O}_{2}[\mathrm{M}]^{+} 366.2559$, found 366.2572 .

1-(decyloxy)-4-ethynylnaphthalene (MAN 10.3): To a round bottom flask containing MAN $10.2(1.00 \mathrm{~g}, 2.7 \mathrm{mmol})$ was added finely ground $\mathrm{KOH}(0.459 \mathrm{~g}, 8.2 \mathrm{mmol})$ and toluene $(21 \mathrm{~mL})$. The reaction was then refluxed overnight. The next morning, the reaction was cooled and the KOH was filtered and washed with DCM until the filtrate was colorless, before being concentrated under reduced pressure. Purification of the crude material by column chromatography ( $50 \% / 50 \% \mathrm{DCM} /$ Hexanes) yielded MAN 10.3 as a brown solid ( $0.813 \mathrm{~g}, 2.64$ mmol, $96.6 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.34-8.29(\mathrm{~m}, 2 \mathrm{H}), 7.67(\mathrm{~d}, J=8.0 \mathrm{~Hz}$, $1 \mathrm{H}), 7.60(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.52(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.75(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.14(\mathrm{t}, J=6.4$ $\mathrm{Hz}, 2 \mathrm{H}), 3.39$ ( $\mathrm{s}, 1 \mathrm{H}$ ), 1.93 (dt, $J=14.4,6.7 \mathrm{~Hz}, 2 \mathrm{H}), 1.56(\mathrm{p}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 1.43-1.26$ (m, $12 \mathrm{H}), 0.90(\mathrm{t}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 155.97,134.62,132.13,127.49$, 125.94, 125.77, 125.58, 122.54, 111.60, 104.21, 82.33, 80.28, 68.47, 32.06, 29.74, 29.72, 29.56, 29.48, 29.32, 26.37, 22.84, 14.27. (CI, positive): Calc. for $\mathrm{C}_{22} \mathrm{H}_{28} \mathrm{O}[\mathrm{M}]^{+}$308.2140, found 308.2133.

6-bromo-2-decyl-1H-benzo[de $]$ isoquinoline-1,3(2H)-dione (NI 10): To a solution of 4-bromo-1,8-naphthalic anhydride ( $2.150 \mathrm{~g}, 7.76 \mathrm{mmol}$ ) in ethanol ( 33 mL ) was added n -decylamine ( 2.00 $\mathrm{mL}, 9.90 \mathrm{mmol}$ ). The vial was purged with Nitrogen, sealed, and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered to remove unwanted, insoluble by-products, and washed with hot ethanol. To recrystallize the product, the filtrate was then heated while additional ethanol was added, until the contents were completely dissolved. The flask was allowed to cool at room temperature overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 10 as fluffy yellow needles ( $2.386 \mathrm{~g}, 5.73 \mathrm{mmol}, 73.9 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $8.65(\mathrm{~d}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.56(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 8.41(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 8.03(\mathrm{~d}, J=7.8 \mathrm{~Hz}$, $1 \mathrm{H}), 7.84(\mathrm{dd}, J=8.5,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.16(\mathrm{t}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.72(\mathrm{p}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.45-1.22$ $(\mathrm{m}, 14 \mathrm{H}), 0.87(\mathrm{t}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 163.76,163.73,133.33$,
$132.14,131.34,131.23,130.78,130.31,129.16,128.21,123.34,122.48,40.79,32.03,29.70$, 29.51, 29.44, 28.23, 27.28, 22.82, 14.26. (CI, positive): Calc. for $\mathrm{C}_{22} \mathrm{H}_{26} \mathrm{BrNO}_{2}[\mathrm{M}]^{+} 415.1147$, found 415.1135 .

## 2-decyl-6-((4-(decyloxy)naphthalen-1-yl)ethynyl)-1 H -benzo[de]isoquinoline-1,3(2H)-dione

 (10): To an oven-dried three neck flask containing NI 10 ( $572 \mathrm{mg}, 1.37 \mathrm{mmol}$ ) and MAN $\mathbf{1 0 . 3}$ ( $305 \mathrm{mg}, 0.989 \mathrm{mmol}$ ) was added dry triethylamine $(33 \mathrm{~mL})$ and nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing $\mathrm{PPh}_{3}(26 \mathrm{mg}, 10 \mathrm{~mol} \%), \mathrm{CuI}(19 \mathrm{mg}, 10 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(70 \mathrm{mg}, 10 \mathrm{~mol}$ \%). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to $90^{\circ} \mathrm{C}$ and left to stir for 21 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with $\mathrm{H}_{2} \mathrm{O}$ and dried under vacuum. Purification of the crude product via column chromatography ( $50 \% / 50 \% \mathrm{DCM} /$ Hexanes) to yield 10 as a yellow-orange solid ( $564 \mathrm{mg}, 0.876 \mathrm{mmol}, 89 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $8.87(\mathrm{dd}, J=8.3,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.67(\mathrm{dd}, J=7.2,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.60(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.44(\mathrm{~d}, J$ $=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.38(\mathrm{dd}, J=8.4,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 8.05(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.90-7.83(\mathrm{~m}, 2 \mathrm{H}), 7.69$ (ddd, $J=8.3,6.8,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.58(\mathrm{ddd}, J=8.3,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.87(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.25$ $-4.16(\mathrm{~m}, 4 \mathrm{H}), 1.97(\mathrm{p}, J=6.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.75(\mathrm{dt}, J=15.3,7.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.59(\mathrm{p}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H})$, $1.46-1.24(\mathrm{~m}, 26 \mathrm{H}), 0.92-0.85(\mathrm{~m}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 164.25, 163.99, $156.76,134.34,132.68,132.57,131.71,130.66,128.49,128.39,127.93,127.52,126.09,125.83$, $125.79,123.24,122.89,121.89,111.75,104.61,98.44,90.01,68.70,40.75,32.07,32.05,29.75$, 29.73, 29.57, 29.55, 29.49, 29.46, 29.33, 28.32, 27.33, 26.40, 22.84, 14.27. (CI, Negative) Calc. for $\mathrm{C}_{44} \mathrm{H}_{53} \mathrm{NO}_{3}\left[\mathrm{M}^{-}\right] 643.4025$, found 643.4024.1-bromo-4-(dodecyl)naphthalene (MAN 12.1): To a solution of 4-bromo-1-naphthol (2.00 g, $8.97 \mathrm{mmol})$ in dry acetonitrile ( 70 mL ) was added dry $\mathrm{K}_{2} \mathrm{CO}_{3}(3.27 \mathrm{~g}, 26.9 \mathrm{mmol})$ and 1-
bromododecane $(2.80 \mathrm{~mL}, 11.7 \mathrm{mmol})$ and the solution was allowed to reflux overnight. After removing the acetonitrile by rotary evaporation, the crude mixture was dissolved in DCM ( $\sim 100 \mathrm{~mL}$ ) and the $\mathrm{K}_{2} \mathrm{CO}_{3}$ removed using a celite plug which was then rinsed with DCM till the filtrate was colorless ( $\sim 500 \mathrm{~mL}$ ). The crude solution was then adsorbed onto silica, which was then subjected to column chromatography ( $100 \%$ hexanes) to yield MAN $\mathbf{1 2 . 1}$ as a white solid $\left(3.10 \mathrm{~g}, 7.92 \mathrm{mmol}, 88.3 \%\right.$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.30(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.16$ (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.67-7.58(\mathrm{~m}, 2 \mathrm{H}), 7.52(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.67(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.11$ $(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.92(\mathrm{p}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.60-1.53(\mathrm{~m}, 2 \mathrm{H}), 1.43-1.24(\mathrm{~m}, 16 \mathrm{H}), 0.88(\mathrm{t}, J$ $=6.8 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 154.89,132.62,129.66,127.82,127.16,126.98$, $125.96,122.68,113.05,105.42,68.59,32.07,29.82,29.80,29.76,29.74,29.56,29.50,29.35$, 26.39, 22.84, 14.27. (APCI, positive): Calc. for $\mathrm{C}_{22} \mathrm{H}_{31} \mathrm{BrO}[\mathrm{M}+\mathrm{H}]^{+} 391.1631$, found 391.1643.

4-(4-(dodecyloxy)naphthalen-1-yl)-2-methylbut-3-yn-2-ol (MAN 12.2): To a stirring solution of MAN $12.1(1.70 \mathrm{~g}, 4.34 \mathrm{mmol})$ in triethylamine ( 77 mL ) was added 2-methyl-3-butyn-2-ol ( $0.55 \mathrm{~mL}, 5.6 \mathrm{mmol}$ ) and Argon was bubbled through the solution for 10 min . After degassing the solution, $\mathrm{CuI}(83 \mathrm{mg}, 10 \mathrm{~mol} \%), \mathrm{PPh}_{3}(106 \mathrm{mg}, 10 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(316 \mathrm{mg}, 10$ mol \%) were added and the reaction was brought to $90^{\circ} \mathrm{C}$ and left for 16 hrs . The reaction was allowed to cool and then the solids were filtered, washed with diethyl ether ( $2 \times 100 \mathrm{~mL}$ ) and concentrated by rotary evaporation. DCM was then added ( 300 mL ) and the organic solution was washed with $\mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL}), 1 \mathrm{NHCl}(3 \times 300 \mathrm{~mL}), \mathrm{H}_{2} \mathrm{O}(3 \times 300 \mathrm{~mL})$ and brine ( $3 \times 300 \mathrm{~mL}$ ). The organic layer was then dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, loaded onto silica and concentrated by rotary evaporation. The crude material was purified by column chromatography ( $50 \% / 50 \%$ DCM/Hexanes) and concentrated by rotary evaporation to yield MAN 12.2 as a brown oil ( 0.583 $\mathrm{g}, 1.48 \mathrm{mmol}, 34.0 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.29(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 1 \mathrm{H}), 8.22(\mathrm{~d}, J=$ $8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.60-7.54(\mathrm{~m}, 2 \mathrm{H}), 7.50(\mathrm{ddd}, J=8.2,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.74(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, $4.14(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.10(\mathrm{~s}, 1 \mathrm{H}), 1.93(\mathrm{p}, J=7.7,7.2,6.6,6.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.72(\mathrm{~s}, 6 \mathrm{H}), 1.59-$ $1.52(\mathrm{~m}, 2 \mathrm{H}), 1.43-1.25(\mathrm{~m}, 16 \mathrm{H}), 0.88(\mathrm{t}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $\left.126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$
$155.62,134.37,131.25,127.34,125.90,125.69,125.63,122.51,112.14,104.28,97.11,80.67$, $68.45,66.10,32.07,31.93,29.85,29.82,29.80,29.76,29.74,29.57,29.50,29.35,26.38,22.84$, 14.27. (ESI, positive): Calc. for $\mathrm{C}_{27} \mathrm{H}_{38} \mathrm{O}_{2}[\mathrm{M}+\mathrm{Na}]^{+} 417.2764$, found 417.2764 .

1-(dodecyloxy)-4-ethynylnaphthalene (MAN 12.3): To a round bottom flask containing MAN $12.2(0.300 \mathrm{~g}, 0.760 \mathrm{mmol})$ was added finely ground $\mathrm{KOH}(0.127 \mathrm{~g}, 2.28 \mathrm{mmol})$ and toluene ( 6.3 mL ). The reaction was then refluxed overnight. The next morning, the reaction was cooled and the KOH was filtered and washed with DCM a colorless, before being concentrated under reduced pressure. Purification of the crude material by column chromatography (50\%/50\% DCM/Hexanes) yielded MAN 12.3 as a brown oil ( $0.214 \mathrm{~g}, 0.636 \mathrm{mmol}, 83.7 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.33-8.27(\mathrm{~m}, 2 \mathrm{H}), 7.66(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.59(\mathrm{ddd}, J=8.4,6.7,1.3$ $\mathrm{Hz}, 1 \mathrm{H}), 7.51(\mathrm{ddd}, J=8.1,6.7,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.75(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.15(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H})$, $3.38(\mathrm{~s}, 0 \mathrm{H}), 1.93(\mathrm{dt}, J=14.4,6.7 \mathrm{~Hz}, 2 \mathrm{H}), 1.60-1.53(\mathrm{~m}, 2 \mathrm{H}), 1.42-1.25(\mathrm{~m}, 16 \mathrm{H}), 0.88(\mathrm{t}, J$ $=6.8 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 155.99,134.64,132.14,127.50,125.96,125.79$, $125.61,122.55,111.63,104.23,82.34,80.27,68.50,32.08,29.86,29.82,29.80,29.77,29.74$, 29.56, 29.51, 29.33, 26.38, 22.84, 14.27. (CI, positive): Calc. for $\mathrm{C}_{42} \mathrm{H}_{32}[\mathrm{M}]^{+} 336.2453$, found 336.24540

6-bromo-2-dodecyl-1H-benzo[de $]$ isoquinoline-1,3(2H)-dione (NI 12): To a solution of 4-bromo-1,8-naphthalic anhydride ( $2.00 \mathrm{~g}, 7.22 \mathrm{mmol}$ ) in ethanol ( 30 mL ) was added n dodecylamine ( $1.74 \mathrm{~g}, 9.4 \mathrm{mmol}$ ). The vial was purged with Nitrogen, sealed, and the solution was refluxed overnight. After the reaction was deemed completed by TLC, the reaction was filtered to remove unwanted, insoluble by-products, and washed with hot ethanol. To recrystallize the product, the filtrate was then heated while additional ethanol was added, until the contents were completely dissolved. The flask was allowed to cool at room temperature overnight. The following day, the crystallized product was filtered, washed with cold ethanol, and dried under vacuum to give NI 12 as an off-white powder ( $1.92 \mathrm{~g}, 4.32 \mathrm{mmol}, 59.8 \%$ yield $)$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.66(\mathrm{dd}, J=7.3,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.57(\mathrm{dd}, J=8.5,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.42$ (d, $J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 8.04(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.85(\mathrm{dd}, J=8.5,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.16(\mathrm{t}, J=7.7 \mathrm{~Hz}$, $2 \mathrm{H}), 1.72(\mathrm{p}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.46-1.22(\mathrm{~m}, 19 \mathrm{H}), 0.88(\mathrm{t}, J=6.9 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (126 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 163.79,163.77,133.36,132.16,131.36,131.25,130.82,130.32,129.21,128.23$, $123.38,122.52,40.80,32.07,29.79,29.77,29.75,29.70,29.52,29.50,28.25,27.28,22.84$, 14.26. (ESI, positive): Calc. for $\mathrm{C}_{24} \mathrm{H}_{30} \mathrm{BrNO}_{2}[\mathrm{M}+\mathrm{Na}]^{+} 466.1352$, found 466.1352 .

## 2-dodecyl-6-((4-(dodecyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de] isoquinoline-1,3(2H)-

 dione (12): To an oven-dried three neck flask containing NI 12 ( $423 \mathrm{mg}, 0.951 \mathrm{mmol}$ ) and MAN 12.3 ( $214 \mathrm{mg}, 0.634 \mathrm{mmol}$ ) was added dry triethylamine ( 63 mL ) and Nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing $\mathrm{PPh}_{3}(17 \mathrm{mg}, 10 \mathrm{~mol} \%), \mathrm{CuI}(12 \mathrm{mg}, 10 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(45 \mathrm{mg}, 10$ mol \%). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to $90^{\circ} \mathrm{C}$ and left to stir for 24 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with $\mathrm{H}_{2} \mathrm{O}(50 \mathrm{~mL})$ and dried under vacuum. Purification of the crude product via column chromatography ( $50 \% / 50 \%$ DCM/Hexanes) yielded 12 as an orange solid ( $294 \mathrm{mg}, 0.420 \mathrm{mmol}, 66.2 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.87$ (dd, $J=8.3,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.67$ (dd, $J=7.3,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.59(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.44(\mathrm{~d}, J=8.3$ $\mathrm{Hz}, 1 \mathrm{H}), 8.38(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.05(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.90-7.82(\mathrm{~m}, 2 \mathrm{H}), 7.69(\mathrm{ddd}, J=$ $8.3,6.8,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.58(\mathrm{ddd}, J=8.3,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.87(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.25-4.15$ (m, 4H), 1.97 (dt, $J=14.4,6.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.75(\mathrm{p}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.59(\mathrm{p}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 1.47-$ $1.24(\mathrm{~m}, 34 \mathrm{H}), 0.88(\mathrm{td}, J=6.9,3.5 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 164.22,163.96$, $156.73,134.29,132.64,132.56,131.68,131.66,130.63,128.46,128.33,127.91,127.48,126.07$, $125.80,125.73,123.18,122.87,121.82,111.71,104.58,98.43,90.01,68.67,40.73,32.07,29.82$, 29.80, 29.78, 29.77, 29.75, 29.72, 29.57, 29.55, 29.50, 29.32, 28.30, 27.33, 26.39, 22.84, 14.27. (ESI, positive): Calc. for $\mathrm{C}_{48} \mathrm{H}_{61} \mathrm{NO}_{3}[\mathrm{M}+\mathrm{Na}]^{+} 722.4544$, found 722.4557.6-((4-(hexyloxy)naphthalen-1-yl)ethynyl)-2-octyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (M6N8): To an oven-dried three neck flask containing NI 8 ( $174 \mathrm{mg}, 0.449 \mathrm{mmol}$ ) and MAN 6.3 ( $136 \mathrm{mg}, 0.539 \mathrm{mmol}$ ) was added dry triethylamine $(10 \mathrm{~mL})$ and the solution Nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing $\mathrm{PPh}_{3}(5.9 \mathrm{mg}, 5 \mathrm{~mol} \%)$, $\mathrm{CuI}(4.3 \mathrm{mg}, 5 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}$ ( $15.8 \mathrm{mg}, 5 \mathrm{~mol} \%$ ). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to $90^{\circ} \mathrm{C}$ and left to stir for 14 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with $\mathrm{H}_{2} \mathrm{O}$ and dried under vacuum. Purification of the crude product via column chromatography (50\%/50\% DCM/Hexanes) to yield M6N8 as a bright yellow-orange solid ( $232 \mathrm{mg}, 0.414 \mathrm{mmol}, 92.3 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{cdcl}_{3}$ ) $\delta 8.85(\mathrm{dd}, J=8.4,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.64(\mathrm{dd}, J=7.3,1.2 \mathrm{~Hz}, 1 \mathrm{H})$, $8.57(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.42(\mathrm{ddd}, J=8.3,1.3,0.7 \mathrm{~Hz}, 1 \mathrm{H}), 8.35(\mathrm{ddd}, J=8.3,1.4,0.7 \mathrm{~Hz}, 1 \mathrm{H})$, 8.02 (d, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.90-7.78(\mathrm{~m}, 2 \mathrm{H}), 7.67(\mathrm{ddd}, J=8.3,6.8,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.56$ (ddd, $J=$ 8.2, 6.8, 1.3 Hz, 1H), $6.85(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.24-4.11(\mathrm{~m}, 4 \mathrm{H}), 1.96(\mathrm{p}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H})$, 1.73 (p, $J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.58(\mathrm{p}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.45-1.23(\mathrm{~m}, 14 \mathrm{H}), 0.93(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H})$, $0.86(\mathrm{t}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 164.22,163.96,156.74,134.31,132.64$, $132.56,131.68,130.63,128.46,128.35,127.91,127.49,126.08,125.81,125.76,123.21,122.87$, $121.85,111.74,104.59,98.43,90.02,68.68,40.74,31.98,31.76,29.51,29.39,29.30,28.31$, 27.33, 26.07, 22.80, 22.78, 14.24, 14.20. (CI, Negative) Calc. for $\mathrm{C}_{38} \mathrm{H}_{41} \mathrm{NO}_{3}\left[\mathrm{M}^{-}\right] 559.3086$, found 559.3107.

## 2-hexyl-6-((4-(octyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione

 (M8N6): To an oven-dried three neck flask containing NI $6(139 \mathrm{mg}, 0.386 \mathrm{mmol})$ and MAN $8.3(130 \mathrm{mg}, 0.464 \mathrm{mmol})$ was added dry triethylamine $(10 \mathrm{~mL})$ and the solution Nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solidaddition funnel containing $\mathrm{PPh}_{3}(5.0 \mathrm{mg}, 5 \mathrm{~mol} \%)$, $\mathrm{CuI}(3.7 \mathrm{mg}, 5 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}$ ( $13.3 \mathrm{mg}, 5 \mathrm{~mol} \%$ ). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to $95^{\circ} \mathrm{C}$ and left to stir for 16 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with $\mathrm{H}_{2} \mathrm{O}(50 \mathrm{~mL})$ and dried under vacuum. Purification of the crude product via column chromatography (50\%/50\% DCM/Hexanes) to yield M8N6 as an orange-yellow solid ( $201 \mathrm{mg}, 0.359 \mathrm{mmol}, 93.1 \%$ yield). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{cdcl}_{3}\right) \delta 8.87(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.66(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.59(\mathrm{~d}, J=7.6$ $\mathrm{Hz}, 1 \mathrm{H}), 8.44(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.37(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.04(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.91-7.83$ (m, 2H), $7.69(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.58(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.87(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.26-4.13$ (m, 4H), 1.97 (p, $J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.75$ (p, $J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 1.59(\mathrm{p}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 1.49-1.29$ $(\mathrm{m}, 14 \mathrm{H}), 0.93-0.87(\mathrm{~m}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 164.26, 164.00, 156.77, 134.34, $132.69,132.57,131.72,130.67,128.50,128.40,127.94,127.53,126.10,125.84,125.79,123.25$, $122.90,121.90,111.75,104.62,98.45,90.01,68.70,40.74,31.99,31.73,29.54,29.41,29.33$, 28.26, 26.98, 26.40, 22.83, 22.73, 14.26, 14.22. (CI, negative): Calc. for $\mathrm{C}_{38} \mathrm{H}_{41} \mathrm{NO}_{3}[\mathrm{M}]^{+}$ 599.3086, found 599.3083

## 6-((4-(decyloxy)naphthalen-1-yl)ethynyl)-2-octyl-1H-benzo[de]isoquinoline-1,3(2H)-dione

 (M10N8): To an oven-dried three neck flask containing NI 8 ( $296 \mathrm{mg}, 0.76 \mathrm{mmol}$ ) and MAN $\mathbf{1 0 . 3}$ ( $181 \mathrm{mg}, 0.59 \mathrm{mmol}$ ) was added dry triethylamine ( 15 mL ) and nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing $\mathrm{PPh}_{3}(16 \mathrm{mg}, 10 \mathrm{~mol} \%), \mathrm{CuI}(11 \mathrm{mg}, 10 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(42 \mathrm{mg}, 10$ mol \%). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to $90^{\circ} \mathrm{C}$ and left to stir for 17 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with $\mathrm{H}_{2} \mathrm{O}(50 \mathrm{~mL})$ and dried under vacuum. Purification of the crude product via column chromatography ( $50 \% / 50 \% \mathrm{DCM} /$ Hexanes ) to yieldM10N8 as a yellow-orange solid ( $254 \mathrm{mg}, 0.412 \mathrm{mmol}, 70.3 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\operatorname{cdcl}_{3}\right) \delta 8.85(\mathrm{dd}, J=8.3,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.65(\mathrm{dd}, J=7.3,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.58(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H})$, $8.46-8.33(\mathrm{~m}, 2 \mathrm{H}), 8.03$ (dd, $J=7.8,0.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.90-7.80(\mathrm{~m}, 2 \mathrm{H}), 7.68$ (ddd, $J=8.3,6.8$, $1.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.57$ (ddd, $J=8.3,6.9,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.86(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.25-4.11(\mathrm{~m}, 4 \mathrm{H})$, $2.03-1.91(\mathrm{~m}, 2 \mathrm{H}), 1.81-1.67(\mathrm{~m}, 2 \mathrm{H}), 1.65-1.53(\mathrm{~m}, 2 \mathrm{H}), 1.47-1.25(\mathrm{~m}, 22 \mathrm{H}), 0.93-0.83$ $(\mathrm{m}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 164.26,164.00,156.77,134.34,132.68,132.57,131.72$, $130.66,128.49,128.39,127.93,127.52,126.09,125.83,125.79,123.24,122.89,121.89,111.75$, $104.61,98.45,90.01,68.70,40.75,32.07,31.99,29.75,29.73,29.57,29.51,29.49,29.39,29.33$, 28.32, 27.34, 26.40, 22.84, 22.80, 14.27, 14.24. (CI, negative): Calc. for $\mathrm{C}_{42} \mathrm{H}_{49} \mathrm{NO}_{3}[\mathrm{M}]^{+}$ 615.3712, found 615.3726.

## 2-decyl-6-((4-(octyloxy)naphthalen-1-yl)ethynyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione

 (M8N10) :To an oven-dried three neck flask containing NI 10 ( $316 \mathrm{mg}, 0.76 \mathrm{mmol}$ ) and MAN $8.3(163 \mathrm{mg}, 0.58 \mathrm{mmol})$ was added dry triethylamine ( 15 mL ) and nitrogen was bubbled through the solution for 5 minutes. The three-neck flask was then equipped with a solid addition funnel containing $\mathrm{PPh}_{3}(16 \mathrm{mg}, 10 \mathrm{~mol} \%), \mathrm{CuI}(11 \mathrm{mg}, 10 \mathrm{~mol} \%)$ and $\mathrm{PdCl}_{2}\left(\mathrm{PPh}_{3}\right)_{2}(42 \mathrm{mg}, 10$ mol \%). The reaction solution was degassed with Nitrogen for an additional 10 minutes. Next, the contents of the solid addition funnel were added to the reaction solution and the solution was brought to $90^{\circ} \mathrm{C}$ and left to stir for 21 hours. After allowing the reaction to cool, the reaction was filtered to obtain the crude product which was rinsed with $\mathrm{H}_{2} \mathrm{O}(50 \mathrm{~mL})$ and dried under vacuum. Purification of the crude product via column chromatography ( $50 \% / 50 \%$ DCM/Hexanes) to yield M8N10 as a yellow-orange solid ( $271 \mathrm{mg}, 0.440 \mathrm{mmol}, 75.7 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 8.86(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.66(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.58(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 8.43(\mathrm{~d}, J=$ $8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.37(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 8.04(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.89-7.82(\mathrm{~m}, 2 \mathrm{H}), 7.69(\mathrm{t}, J=$ $7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.58(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.86(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.20(\mathrm{dt}, J=14.5,7.0 \mathrm{~Hz}, 4 \mathrm{H})$, $1.97(\mathrm{p}, J=6.7 \mathrm{~Hz}, 2 \mathrm{H}), 1.75(\mathrm{p}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.59(\mathrm{p}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 1.48-1.25(\mathrm{~m}, 22 \mathrm{H})$, $0.89(\mathrm{dt}, J=14.3,6.7 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(126 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 164.25,163.98,156.76,134.33$,$132.67,132.56,131.70,130.65,128.48,128.38,127.93,127.51,126.09,125.83,125.78,123.23$, $122.89,121.88,111.74,104.61,98.44,90.01,68.70,40.75,32.05,31.99,29.72,29.55,29.46$, 29.41, 29.33, 28.32, 27.33, 26.40, 22.83, 14.26. (CI, negative): Calc. for $\mathrm{C}_{42} \mathrm{H}_{49} \mathrm{NO}_{3}[\mathrm{M}]^{+}$ 615.3712, found 615.3709.

## CHAPTER 3

## Stimuli-Responsive Properties and Self-Assembly of MonoalkoxynaphthaleneNaphthalimide Donor-Acceptor Dyads ${ }^{1}$

### 3.1 CHAPTER SUMMARY

### 3.1.1 Introduction

Previous comparative spectroscopic and structural characterizations led to the conclusion that dyad stimuli-responsive properties were the result of polymorphic conformational switching. However, no direct structural comparison could be made between yellow crystals grown from solution and thermally generated yellow solids in 1,4-monoalkynaphthalene-naphthalimide donor-acceptor dyads. Further, previous work showed that the thermochromic transitions did not significantly change the surface morphology despite dramatic structural reorganization.

Enabled by a detailed understanding of dyad packing and the photophysical origins for differences in solid-state color as described in Chapter 2, investigations into the stimuliresponsive properties of dyads materials in the solid-state were carried out. The thermochromic orange-to-yellow transition was viewed as the most unique stimuli-responsive behavior in our dyad system, as the overall morphology of the crystals did not change following the application of a stimulus, unlike the case when orange crystals materials were mechanically sheared. Further, microscopic observations during heating allowed for the most convenient characterization of both initiation and propagation of the transition process, especially compared to the yellow-to-

[^1]orange transition that occurs in the presence of solvent vapor. Thus, characterization of the stimuli-responsive properties in the dyad materials was focused on characterizing the thermochromic orange-to-yellow transition.

Detailed optical, spectroscopic, thermal, and structural characterizations of thermally generated polymorphs were pursued in order to determine the structure of the yellow stimuliproduced polymorph. Following fundamental investigations into the structure, quantitative investigations into material changes after thermal conversion were explored. Analysis of asymmetric stimuli responsive properties was completed using analogous characterization methods. Finally, the ability to tune the stimuli-responsive properties of the system (e.g. transition temperature) were explored.

### 3.1.2 Scientific Questions

After investigating the polymorphic abilities of dyads in Chapter 2, the work described here sought to answer key questions related to the stimuli-responsive behavior of dyad materials, by trying to answer both fundamental and also specific, application-based questions. Specifically: What is the structure of the thermally-generated polymorph? How will differences in side chain identity influence stimuli responsive properties? What is the role of side-chain length on stimuli-induced transition properties (e.g. orange to yellow transition temperature)? Can the stimuli-responsive properties be tuned? What micro- and/or nanoscopic changes occur to dyad materials following thermally induced orange-to-yellow changes? What will the introduction of asymmetric side chains do to the stimuli-responsive properties?

### 3.1.3 Approach

In order to answer the questions defined above, comprehensive optical, spectroscopic, and structural analyses were completed on orange materials, the thermally generated materials
derived from them, as well as asymmetric derivatives that were heated. Characterization of the dynamic transition process was utilized heating polarized optical microscopy (POM), differential scanning calorimetry (DSC), in situ heating X-ray diffraction (XRD). Optical profilometry and non-contact atomic force microscopy (AFM) measurements were made in order to quantify surface and morphological changes following thermal conversion. Solid-state absorbance and emission measurements were made to provide spectroscopic comparisons to known dyad crystals. Grazing-incidence wide-angle X-ray scattering (GIWAXS) and well in situ heating single-crystal XRD experiments were employed in order to further elucidate the structure of the yellow material.

### 3.1.4 Results

All symmetric, head-to-head packed orange polymorphs in the study showed the same orange-to-yellow thermochromic and mechanochromic behavior, as well as the same yellow-toorange solvatochromic behavior previously reported for $8 .{ }^{64}$ The thermochromic orange-toyellow crystal-to-mesophase transition was repeatedly observed to move as a transition wavefront through orange crystals, adopting a characteristic angle relative to the long axis of the crystal. In symmetric orange dyad crystals, the orange-to-yellow transition temperatures and transition enthalpies were not clearly correlated with side-chain length, however, these transition parameters were found to be reproducibly influenced by crystal size.

All symmetric yellow head-to-tail packed dyad crystals and two of the four asymmetric dyad yellow crystals, M6N8 (yellow, head-to-tail) and M8N6 (gold, head-to-head) were found to have a single thermally induced melting transition without a color change. The other two asymmetric derivatives with the longest side chains, M8N10 (orange-red, head-to-head) and M10N8 (yellow-orange, head-to-head), were found to have two thermally induced transitions. Further, of these asymmetric derivatives with the longest side chains, only M8N10 had an
orange-to-yellow color change, M10N8 had an observable but colorless transition prior to melting.

Formed from the heating of symmetric dyad orange crystals, thermally generated yellow material was found to have similar solid-state packing as yellow crystals grown from solution based on spectroscopic and structural characterization. Microscopic morphology of dyad materials was confirmed to not change significantly following heating, although for the first time nanoscopic surface changes were seen to accompany the thermal transitions.

### 3.2 RESULTS

### 3.2.1 Stimuli-Responsive Behavior

Consistent with previous reports, ${ }^{63,64}$ and as discussed in chapter 2, many dyads in this study could crystalize as orange (' $\mathbf{O}$ ', or ' $\mathbf{o}$ ') or yellow (' $\mathbf{Y}$ ' or ' $\mathbf{y}$ ') polymorphs. When symmetric orange crystals of $\mathbf{6}, \mathbf{7}, \mathbf{8}, \mathbf{9}, \mathbf{1 0}$, and $\mathbf{1 2}$ referred to here as $\mathbf{6 0}, \mathbf{7 0}, \mathbf{8 0}, \mathbf{9 0}, \mathbf{1 0 0}$, and 120, respectively, are heated beyond $100^{\circ} \mathrm{C}$, the orange crystals transition to a soft-crystalline yellow material that persists indefinitely upon cooling. Reversal back to the orange crystalline phase occurs in less than 24 hours when exposed to DCM vapor in a fuming chamber. ${ }^{64}$ Further, all aforementioned symmetric orange dyad crystals were seen to be mechanochromic displaying an orange to yellow transition when a shearing force was applied.

When heated, $\mathbf{1 b o}$ crystals do not form a yellow material, and directly sublime at $284^{\circ} \mathrm{C}$. The two longer asymmetric dyad derivatives, M8N10 (orange-red) and M10N8 (yellow-orange) were seen to undergo thermally induced transitions: M8N10 had an orange to yellow transition, while M10N8 had an observable, yet colorless, transition prior to subsequent melting. Of the asymmetric derivatives, only M8N10 showed mechanochromic behavior, with a transition to a yellow material when a shearing force was applied.

### 3.2.2 Symmetric Dyad Stimuli-Responsive Properties and Thermochromic Orange-toYellow Transition

### 3.2.2.1 Optical Characterization: Polarized Optical Microscopy

Color Switching Moves Most Quickly as a Wavefront Through the Crystal. When symmetric orange dyad crystals are heated, they transform to a yellow material (designated as ' $\mathbf{Y}^{*}$ ' or ' $\mathbf{y}$ *' in the following discussion) prior to melting. Examination of this thermochromic orange-to-yellow conversion under a POM equipped with a heating stage revealed that thermally generated yellow material retains the overall microscopic morphology of the starting orange crystal (Figure 3.1 \& 3.2, Movie 3.1 \& 3.2). Details regarding heating POM experiments, including equipment used, heating protocols, and data acquisition parameters, can be found in section 3.5.1.

Numerous heating experiments of orange crystals under a POM verified that the thermochromic transition proceeds as one or more wavefronts moving through the orange crystal. It is assumed that a structural transition is occurring at the orange-yellow wavefront interface. The transition generally is observed to start at a crystal edge or a small crack/defect in the crystals.

While the overall crystal morphology is retained following thermal conversion, molecules within the thermally generated material have various degrees of freedom that will be described in the sections that follow. Thus, this thermal conversion is not a single-crystal to single-crystal transition; it is best characterized as a crystal-to-mesophase transition, where the yellow material $\left(\mathbf{Y}^{*}\right)$ is characterized as a soft crystalline mesophase.


Figure 3.1 Visualized under a microscope equipped with a heating stage, a single 7 o orange crystal is heated at $2^{\circ} \mathrm{C} \mathrm{min}^{-1}$ to form a yellow material, $7 \mathbf{y}^{*}$, that persists indefinitely after cooling. Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

In Figure 3.1, there are a series of POM images showing a single 70 crystal being heated at a heating rate of $2^{\circ} \mathrm{C} \mathrm{min}^{-1}$ to form a yellow mesophase, $7 \mathbf{y}^{*}$ (see Movie 3.1). As temperature increases, a series of relatively fast moving wavefronts can be seen moving down the length of the crystal, and as the wave passes, the color of the crystal changes to some extent. When viewed from above, a single point in the crystal may have multiple wavefronts pass through, presumably at different layers within the thickness of the crystal. Slower moving waves can also be seen moving up from the bottom of the long axis of the crystal. Between the fifth and sixth image in Figure 3.1, the bottom of the crystal is seen to go out of focus: the bottom of the crystal bent slightly out of the field of view, and this bending movement was noted to correlate with the movement of the faster, downward moving wave.

To gain additional insight into changes that occur during the transition, heating experiments were carried out under cross polarized conditions. Shown in Figure 3.2 (Movie 3.2), a large ( $\sim 1 \mathrm{~mm}$ long) single $\mathbf{6 0}$ crystal is heated to the corresponding $\mathbf{6 y *}$.


Figure 3.2 A single $\mathbf{6 0}$ crystal is heated under a cross polarized microscope at $5^{\circ} \mathrm{C} \mathrm{min}^{-1}$ to form $6 \mathbf{6}$ *. Bottom: Cartoon depiction of thermally induced changes occurring during the 60 to $\mathbf{6 y *}$ transition in the corresponding images above with the wavefront speed shown in white [ $\mu \mathrm{m} \mathrm{sec}^{-1}$ ] and the angle relative to the indicated crystal long axis shown in blue. Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

Similar to the thermal conversion of $\mathbf{7 0}$ shown in Figure 3.1, the thermochromic conversion of $\mathbf{6 0}$ to $\mathbf{6 y *}$ proceeds following a series of wavefronts that move through the crystal
without visibly disrupting the overall morphology of the crystal. The fastest moving orange-toyellow wavefronts proceed parallel to the long axis of the crystal (see Movie 3.2).

To better visualize how the transition moves through $\mathbf{6 0}$ in Figure 3.2, a cartoon depiction of thermally induced changes occurring during the $\mathbf{6 0}$ to $\mathbf{6 y *}$ transition is shown below each image. The yellow coloring denotes complete transition to the yellow form through all layers of the crystal. Inside the cartoon in white, arrows show the direction of wavefront movement and adjacent values representing the speed of the wavefront in $\mu \mathrm{m} \mathrm{sec}^{-1}$. The angle of the wavefront relative to the indicated long axis of the crystal is shown in blue.

Shown in Figure 3.2, the widest and fastest moving of these wavefronts move at speeds on the order of $12 \mu \mathrm{~m} \mathrm{~s}^{-1}$ and are generally diagonal in nature, exhibiting an average angle of 38 $\pm 4^{\circ}$ relative to the long edge of the crystal. When viewed from above the crystal, horizontal wavefronts are also seen that move parallel to either the long or short axis of the crystal, and proceed slower through the crystal with speeds on the order of $0.2-0.5 \mu \mathrm{~m} \mathrm{~s}^{-1}$. Importantly, the slower horizontal waves have been observed to turn, and as the angle becomes more pronounced the wavefront speed also increases. Note the lower portion of the $\mathbf{6 0}$ crystal in Figure 3.2. In images 2-4, the transition can be seen moving perpendicular to the long axis of the crystal. In the fifth image, two different wavefront speeds are shown, indicating the wave is beginning to adopt an angle that becomes pronounced in the sixth and seventh crystal images.

As the wavefront passes, the surface features and overall dimensions of the material only change slightly. For the $\mathbf{6 0}$ crystal shown in Figure 3.2 after heating from orange to yellow the average dimensions of the crystal grew $2.04 \mu \mathrm{~m}(0.21 \%)$ in length, $2.05 \mu \mathrm{~m}(1.1 \%)$ in width, and $0.21 \mu \mathrm{~m}(2.8 \%)$ in height, all while maintaining similar microscopic features.

In thicker crystals, multiple wavefronts are generally seen, apparently caused by multiple wavefronts moving through different horizontal layers within the crystal. Thicker crystals exhibited more of these waves. Thinner crystals appear to have only one or a few transition layers. Thicker crystals were also noted to deform or bend less during the thermal transition as compared to thinner crystals, as previously noted for the $7 \mathbf{o}$ crystal shown in Figure 3.1.

### 3.2.2.2 Spectroscopic Characterization: UV/vis and Fluorescence

Steady state absorbance and fluorescence measurements of thermally generated yellow material were made in an identical fashion to measurements of crystalline samples previously described (see sections 2.3.5.2 and 2.6.4). A comparison of solid-state absorbance and emission spectra between the $\mathbf{O}, \mathbf{Y}$, and $\mathbf{Y}^{*}$ forms for $\mathbf{6}, \mathbf{7}$, and $\mathbf{8}$, respectively, is shown in Figure 3.3, and a summary of absorbance ( $\lambda_{\text {abs-Max }}$ ) and emission maxima ( $\lambda_{\text {em-max }}$ ) is present in Table 3.1. Spectroscopic measurements of $\mathbf{9} \mathbf{y *}, \mathbf{1 0} \mathbf{y}$ *, and $\mathbf{1 2 y *}$ are not shown, as yellow crystals for those derivatives could never be grown and thus compared.

In general, $\mathbf{Y}$ and $\mathbf{Y}^{*}$ have closely matching absorption and emission spectra for each of the three derivatives. For $\mathbf{7}$ and $\mathbf{8 ,} \mathbf{Y}^{*}$ emission profiles have a small bathochromic shift compared to their $\mathbf{Y}$ counterparts, while $\mathbf{6 y *}$ shows a small hypsochromic shift in comparison to $\mathbf{6 y}$ (Figure 3.3).


Figure 3.3 Solid-state absorbance and emission comparing orange $(\mathbf{O})$ and yellow $(\mathbf{Y})$ crystals grown in solution to thermally produced yellow ( $\mathbf{Y}^{*}$ ) derivatives of $\mathbf{6}$ (top), 7 (middle), and 8 (bottom). Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

| Compound | $\lambda_{\text {abs-max }}(\mathrm{nm})$ | $\lambda_{\text {em-max }}(\mathrm{nm})$ |
| :---: | :---: | :---: |
| $\mathbf{6 y}$ | 392 | 569 |
| $\mathbf{7 y}$ | 390 | 554 |
| $\mathbf{8 y}$ | 395 | 554 |
| $\mathbf{6 y *}$ | 393 | 561 |
| $\mathbf{7} \mathbf{y}^{*}$ | 392 | 566 |
| $\mathbf{8 y}$ | 392 | 563 |

Table 3.1 Solid-state absorbance and emission parameters for dyad derivatives.

Orange thin films generated from vapor annealing (see section 2.3.4) showed similar behavior to orange crystals. Heating of orange thin films resulted in a blue-shift in both absorbance and emission profiles, as shown in the top of Figure 3.4. Emission maxima is 613 nm for 70 Thin Film and 562 nm for $\mathbf{7 y *}$ Thin Film, compared to 617 nm and 566 nm for 7 o and $7 \mathrm{y}^{*}$, respectively. Heating of $\mathbf{7 o}$ and $\mathbf{1 0 0}$ thin films at temperatures ranging from $105-120^{\circ} \mathrm{C}$ for $25-$ 120 seconds resulted in the thermal conversion to a yellow film, as shown in the bottom of Figure 3.4. Similar to the heating of 1bo crystals, no visible change was seen for thin films of 1bo when heated at $150^{\circ} \mathrm{C}$ for 10 minutes.


Figure 3.4 Absorbance and emission and side by side comparison of a 7 o thin film (left) and a $\mathbf{7} \mathbf{y}^{*}$ thin film (right). $\mathbf{7 y *}$ thin films were generated from heating 7 o thin films for 2 minutes at $120^{\circ} \mathrm{C}$. Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

### 3.2.2.3 Thermal Characterization: Differential Scanning Calorimetry

DSC Thermal Transition Characterization - Experimental Setup. Differential scanning calorimetry (DSC) was used in order to quantify thermally induced phase transitions. Shown in Figure 3.5 are two successive DSC heating-cooling cycles, starting with representative
symmetric orange ( $\mathbf{7 0}$ ) and yellow ( $\mathbf{6 y}$ ) crystals. In each of the two cycles, the temperature is ramped up at a rate of $5^{\circ} \mathrm{C} \mathrm{min}^{-1}$ from $40^{\circ} \mathrm{C}$ to $200^{\circ} \mathrm{C}$, held at $200^{\circ} \mathrm{C}$ for 5 minutes, cooled at $5^{\circ} \mathrm{C}$ $\min ^{-1}$ to $40^{\circ} \mathrm{C}$, followed by a 5 minute hold at $40^{\circ} \mathrm{C}$ to end the first heating-cooling cycle. This cycle is then repeated a second time in order to provide information about the material that forms when cooled from the isotropic melt (Iso).


Figure 3.5 Representative DSC measurements for symmetric orange (O) and yellow (Y) crystals in successive heating-cooling cycles. Values near peaks show the corresponding peak temperature $\left({ }^{\circ} \mathrm{C}\right)$, bracketed values represent the integrated transition enthalpy $\left[\mathrm{kJ} \mathrm{mol}^{-1}\right]$ for thermal transitions during the first heating-cooling cycle.

For the initial heating of $7 \mathbf{7 0}$ (trace shown as a solid black line), two endothermic peaks are seen during initial heating, corresponding to the observed thermal transition of $\mathbf{7 o}$ to $7 \mathbf{y}^{*}$, and the subsequent melting of $7 \mathbf{y}$ * to the isotropic phase. The 7 o to $7 \mathbf{y}^{*}$ transition has a peak temperature of $107.7^{\circ} \mathrm{C}$ with an integrated transition enthalpy of $42.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$, and the $7 \mathbf{y}^{*}$ to isotropic transition occurs at $140.9^{\circ} \mathrm{C}$ with a transition enthalpy of $23.6 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Subsequent cooling from the isotropic phase generates a collection of non-resolvable exothermic peaks, with a peak temperature of $125.7^{\circ} \mathrm{C}$ and transition enthalpy of $23.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Immediate reheating of this same, initially orange, material in a second identical heating-cooling cycle shows a change in thermal properties compared to the starting sample. Most notably, a single endothermic peak is seen in the second heating cycle that coincides with the initial $7 \mathbf{y} *$ to isotropic transition. This peak also has a nearly identical peak temperature of $141.0^{\circ} \mathrm{C}$ and a transition enthalpy of 22.5 kJ $\mathrm{mol}^{-1}$. The strong similarity in endothermic peaks near $141^{\circ} \mathrm{C}$ for both heating cycles is indicative that the material formed from cooling the isotropic phase is structurally similar to $7 \mathbf{y}$ * produced by the heating of $7 \mathbf{y}^{*}$.

In contrast to the heating of $\mathbf{7 0}$, the heating of a typical yellow derivative shows only one large endothermic peak in the first heating cycle (Figure 3.5). A single large endothermic peak at $150.2^{\circ} \mathrm{C}$ with a transition enthalpy of $26.3 \mathrm{~kJ} \mathrm{~mol}^{-1}$ corresponds to POM observations for the melting of $\mathbf{6 y}$ to the isotropic phase. Cooling of this isotropic phase shows a single exothermic cooling peak with a peak temperature of $124.4^{\circ} \mathrm{C}$ and a transition enthalpy of $24.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$. This exothermic cooling peak is in line with POM observations of $\mathbf{6 0}$ showing a single crystallization event when the isotropic phase solidifies into a yellow material. During subsequent reheating in the second heating cycle, a single endothermic peak is seen at a slightly lower temperature, with a lower peak temperature of $147.1^{\circ} \mathrm{C}$ and a smaller transition enthalpy of $23.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$. A consistent decrease in endothermic peak temperature and transition enthalpy in the second heating cycle of $\mathbf{Y}$ crystals may indicate that the yellow material formed from the cooling of the isotropic phase has less structural integrity compared to the yellow crystalline starting material,
while also having some general structural similarities. A reasonable conclusion is that some structural differences exist between $\mathbf{Y}$ and $\mathbf{Y}^{*}$ forms.

It is useful to note that in some yellow crystals, a second, small endothermic peak was occasionally seen during the initial heating. Note the small peak in the first heating cycle of $\mathbf{6 y}$ with a peak temperature of $127.5^{\circ} \mathrm{C}$ and a transition enthalpy of $2.6 \mathrm{~kJ} \mathrm{~mol}^{-1}$, roughly an order of magnitude smaller than all other phase transitions enthalpies observed. This peak may correlate to fast moving often colorless transitions occasionally seen in POM experiments that could be observed using polarizers, but often not observed under brightfield, non-polarized conditions. This relatively small peak that did not cause observable microscopic changes is attributed to relatively small molecular movements within the crystal prior to melting.

Thermal Transition Characterization - Symmetric Dyad Crystals. DSC was used to characterize the orange-to-yellow transition for $\mathbf{6 0}, \mathbf{7 0}, \mathbf{8 0}, \mathbf{9 0}, \mathbf{1 0 0}$, and $\mathbf{1 2 0}$. A comparison of two successive DSC heating-cooling cycles for all orange crystals is shown in Figure 3.6, with respective peak temperatures and transition enthalpies shown. Overall, the DSC traces of each derivative show two endothermic peaks corresponding to the $\mathbf{O}$ to $\mathbf{Y}^{*}$ phase transition and the subsequent melting of $\mathbf{Y}^{*}$ to the isotropic phase (Figure 3.6).

Cooling from the isotropic phase generates a yellow material that is believed to be structurally similar to thermally generated $\mathbf{Y}^{*}$, as shown by successive heating-and-cooling cycles (Figure 3.6). Heating of the yellow material that solidified from cooling of the isotropic phase shows an endothermic transition with nearly identical peak temperatures and transition enthalpies, shown inside the dashed boxes in Figure 3.6.


Figure 3.6. DSC heating and cooling experiments for all orange crystals (rates of $5^{\circ} \mathrm{C} \mathrm{min}^{-1}$ ) shows the presence of two endothermic transitions for all orange crystals during the first heating-cooling cycle (solid line) and one endothermic peak during the second (dashed line). Values near or within peaks show the corresponding peak temperature ( ${ }^{\circ} \mathrm{C}$ ), bracketed values represent integrated transition enthalpy $\left[\mathrm{kJ} \mathrm{mol}^{-}\right.$ ${ }^{1}$ ] for thermal transitions during the first heating-cooling cycle. Values inside dashed boxes represent the corresponding values for peaks in the second heating cycle.

Several unique features of these transitions should be noted. Most importantly, once heated to $\mathbf{Y}^{*}$, this form persists indefinitely for each derivative, even when cooled extremely slowly. For example, when 7 o was heated to produce $7 \mathbf{y}^{*}$, the $7 \mathbf{y}^{*}$ form persisted even when cooled at the slowest obtainable rate of $0.1^{\circ} \mathrm{C} \mathrm{min}^{-1}$. Further, holding orange crystals at temperatures slightly below the transition temperature for extended periods was not seen to result in significant thermally induced conversion of $\mathbf{O}$ to $\mathbf{Y}^{*}$. Note the transition temperature range of $100.9-115.3^{\circ} \mathrm{C}$ for the conversion of 7 o to $7 \mathbf{y}^{*}$ shown in Figure 3.6. When 7 o crystals were heated to $94^{\circ} \mathrm{C}$ (rate at $2^{\circ} \mathrm{C} \mathrm{min}^{-1}$ ) and held at that temperature for 4 hours, additional heating after the four hour isotherm showed two endothermic transitions, with the first transition having an integrated transition enthalpy of $37.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$. While slightly less than the previously reported transition enthalpy for 70 to $7 \mathbf{y}^{*}\left(42.2 \mathrm{~kJ} \mathrm{~mol}^{-1}\right.$, Figure 3.6$)$, the presence of the thermal transition indicates that orange material was present to a significant extent following the prolonged heating at $94^{\circ} \mathrm{C}$, or at the very least, that prolonged heating did not result in the same extent of structural reorganization that accompanies the $\mathbf{O}$ to $\mathbf{Y}^{*}$ conversion.

A comparison of transition onset and peak temperatures, as well as transition enthalpies for all orange and yellow crystals, is provided in Table 3.2. In general, when the respective orange crystals of similar size are heated for the different derivatives, the longer the side chains, the larger the enthalpy of transition for the $\mathbf{O}$ to $\mathbf{Y}^{*}$ conversion. In addition, similarly-sized yellow crystals grown from derivatives with longer side chains melt to the isotropic phase with increasing enthalpies of transition ranging from 24.10 to $34.69 \mathrm{~kJ} \mathrm{~mol}^{-1}$ for $\mathbf{6 y} \mathbf{- 8 y}$, respectively (Table 3.2). Importantly, compared to the grown yellow crystals ( $\mathbf{Y}$ ), thermally generated $\mathbf{Y}^{*}$ melts to the isotopic phase with less energy as shown by comparatively lower transition enthalpies for longer chain derivatives $\mathbf{7}$ and $\mathbf{8}$. In contrast, thermally generated $\mathbf{6 y *}$ has a larger transition enthalpy when heated to the isotropic phase compared to the same transition for $\mathbf{6 y}$.

|  | $\mathrm{O} \rightarrow \mathrm{Y}^{*}$ |  |  | $\mathbf{Y}^{*} \rightarrow$ Iso |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Onset <br> Temp <br> ( ${ }^{\circ} \mathrm{C}$ ) | Peak Temp ( ${ }^{\circ} \mathrm{C}$ ) | Transition Enthalpy ( $\mathrm{kJ} \mathrm{mol}^{-1}$ ) | Onset <br> Temp <br> $\left({ }^{\circ} \mathrm{C}\right)$ | Peak <br> Temp <br> ( ${ }^{\circ} \mathrm{C}$ ) | Transition Enthalpy ( $\mathrm{kJ} \mathrm{mol}^{-1}$ ) |
| 60 Larger Crystals | 97.17 | 105.24 | 32.24 | 147.50 | 148.94 | 28.78 |
| 60 Smaller Crystals | 98.94 | 110.43 | 35.10 | 147.23 | 149.31 | 31.11 |
| 70 | 100.86 | 107.7 | 42.16 | 138.20 | 140.91 | 23.61 |
| 80 | 97.03 | 99.78 | 53.12 | 133.83 | 136.72 | 27.07 |
| 90 | 104.07 | 108.68 | 56.10 | 132.82 | 135.04 | 26.75 |
| 100 | 103.87 | 105.90 | 55.18 | 125.53 | 130.56 | 21.53 |
| 120 | 105.90 | 107.81 | 69.97 | 124.37 | 1274.07 | 26.93 |
|  |  |  |  | $\mathrm{Y} \rightarrow$ Iso |  |  |
|  |  |  |  | Onset Temp $\left({ }^{\circ} \mathrm{C}\right)$ | Peak <br> Temp <br> ( ${ }^{\circ} \mathrm{C}$ ) | Transition Enthalpy ( $\mathrm{kJ} \mathrm{mol}^{-1}$ ) |
|  |  |  | 6y | 145.45 | 150.27 | 24.10 |
|  |  |  | 7 y | 126.62 | 142.75 | 32.90 |
|  |  |  | 8 y | 141.56 | 144.35 | 34.69 |

Table 3.2 Summary of symmetric dyad phase transitions measured by DSC at a heating rate of $5^{\circ} \mathrm{C} \mathrm{min}^{-1}$ for all samples. "O" represents Orange crystals grown from solution, " $\mathbf{Y}$ "" represents thermally generated yellow material from heating orange crystals (O), "Iso" represents the isotropic phase, and " $\mathbf{Y}$ " represents yellow crystals grown from solution.

However, care must be taken when interpreting the differences between derivatives, as we observed that crystal size influences the transition temperature and transition enthalpies measured for both the $\mathbf{O}$ to $\mathbf{Y}$ transition and the $\mathbf{Y}^{*}$ to the isotropic phase transition. For example, as shown in Figure 3.7, larger $\mathbf{6 0}$ crystals ( $\mathbf{6 0} \mathbf{L a r g e r}$ ) transformed to $\mathbf{Y}^{*}$ at higher temperatures, with larger enthalpies of transition, compared to smaller $\mathbf{6 0}$ crystals ( $\mathbf{6 0} \mathbf{s m a l l e r}$ ). For comparison, $7 \boldsymbol{0}$ is also shown in Figure 3.7, and the peak temperature for the $\mathbf{O}$ to $\mathbf{Y}^{*}$ transition in 70 is noted to fall between differently sized $\mathbf{6 0}$ crystals. Melting of $\mathbf{6 y *}$ to the isotropic phase followed the same size dependent trend. The $\mathbf{6 0}$ crystals used in DSC experiments were significantly larger than the $\mathbf{6 y}$ crystals used, and as such, the thermally generated $\mathbf{6 y *}$ crystals
were significantly larger than $\mathbf{6 y}$ (as overall morphology of crystals was seen to be retained when transitioning from $\mathbf{O}$ to $\mathbf{Y}^{*}$, see section 3.3.2.1).


Figure 3.7 Crystal size dependence in thermal transitions of orange crystals. Larger $\mathbf{6 0}$ crystals ( $60_{\text {Larger }}$ ) are seen to transition from orange-to-yellow at higher temperatures and require more energy than smaller $\mathbf{6 0}$ crystals ( $\mathbf{6 0 S m a l l e r}$ ). Heated at $5^{\circ} \mathrm{C} \mathrm{min}^{-1}$, DSC curves show orange crystals ( $\mathbf{O}$ ) being thermally converted to a yellow material $\left(\mathbf{Y}^{*}\right)$ prior to melting to the isotropic phase (Iso). Values near peaks show the corresponding peak temperature ( ${ }^{\circ} \mathrm{C}$ ), bracketed values represent integrated transition enthalpy [ $\mathrm{kJ} \mathrm{mol}^{-1}$ ]. Adapted with permission from Ref. ${ }^{66}$ Copyright 2020 American Chemical Society.

### 3.2.2.4 Morphological Characterization: Optical Profilometry

Crystal Size Changes Following Heating. Microscopic observation of the thermal transition of orange crystals to the soft crystalline mesophase saw overall retention of crystal shape following heating (Figure $3.1 \& 3.2$, Movie $3.1 \& 3.2$ ). However, small changes to crystal dimensions were observed in numerous heating experiments. Accurately quantifying these small changes using a POM proved difficult due to the small size of uniform crystals combined with POM imaging limitations (e.g. image resolution, depth of field limitations). Quantitative measurements of crystal size changes were investigated with optical profilometry in order to circumvent the aforementioned limitations. Details regarding equipment, sample preparation, measurement, and data analysis can be found in section 3.5.5.

The calculated density of $7 \boldsymbol{0}$ and both $7 \mathbf{y}$ polymorphs, as determined from single-crystal structures, are 1.25 and $1.22 \mathrm{~g} \mathrm{~cm}^{-3}$, respectively (Table $2.1 \& 2.2$ ). Based on the differences in density of $7 \mathbf{0}$ and either $7 \mathbf{y}$ polymorph, a hypothetical single-crystal-to-single-crystal transition from the more dense $7 \mathbf{7}$ to the less dense $7 \mathbf{y}$ would theoretically cause an increase in volume of $\sim 2.5 \%$ (see Theoretical $\Delta$ Volume $\mathbf{7 o} \rightarrow \mathbf{7 y} / \mathbf{7} \mathbf{y}$, Table 3.3). In contrast, the $\mathbf{6 0}$ polymorph is slightly less dense than both $\mathbf{6 y}$ polymorphs, and so a conversion of $\mathbf{6 0}$ to either $\mathbf{6 y}$ polymorph would result in a theoretical decrease in crystal size of $\sim 0.2 \%$ (see Theoretical $\Delta$ Volume $\mathbf{6 0} \rightarrow$ $\mathbf{6 y / 6 y}$, Table 3.3).

Optical profilometer measurements of individual $\mathbf{O}$ crystals before and after heating to $\mathbf{Y}^{*}$ were used to quantify volume changes after the transition in crystals of $\mathbf{6}$ and 7 (Table 3.3). Crystals of 70 adsorbed onto a silicon substrate showed a $4.4 \pm 0.5 \%$ increase in crystal volume after heating 7 o crystals to 7 y * similar to that expected based on 7 y crystal structures. In comparison, crystals of 6 showed a $3 \pm 1 \%$ increase in size.

| $\begin{gathered} \text { Dyad } \\ \text { Crystal } \end{gathered}$ | $\mathrm{O}_{\text {Volume }}\left(\boldsymbol{\mu} \mathrm{m}^{\mathbf{3}}\right.$ ) | $\mathbf{Y}$ *Volume ( $\mu^{\text {m }}$ ) | $\begin{aligned} & \Delta \text { Volume from O to } \mathrm{Y}^{*} \\ & (\%) \end{aligned}$ |
| :---: | :---: | :---: | :---: |
| 6 | 148,831 | 154,043 | 3.5\% |
| 6 | 133,792 | 138,275 | 3.4\% |
| 6 | 416,397 | 434,147 | 4.3\% |
| 6 | 188,562 | 190,711 | 1.1\% |
|  |  | Average $\triangle$ Volume $\mathbf{6 0} \rightarrow \mathbf{6 y *}$ | +3 $\pm 1 \%$ |
|  |  | Theoretical $\Delta$ Volume $\mathbf{6 0} \rightarrow \mathbf{6 y}$ | -0.32\% |
|  |  | Theoretical $\Delta$ Volume $\mathbf{6 0} \rightarrow \mathbf{6} \mathbf{y}^{\prime}$ | -0.08\% |
| 7 | 2,887 | 3,018 | 4.6\% |
| 7 | 1,025 | 1,074 | 4.7\% |
| 7 | 627 | 651 | 3.8\% |
|  |  | Average $\Delta$ Volume $\mathbf{7 o} \rightarrow \mathbf{7} \mathbf{y}^{*}$ | $+4.4 \pm 0.5 \%$ |
|  |  | Theoretical $\Delta$ Volume 7o $\rightarrow \mathbf{7 y}$ | +2.25\% |
|  |  | Theoretical $\Delta$ Volume $7 \mathbf{7} \rightarrow \mathbf{7} \mathbf{y}^{\prime}$ | +2.61\% |

Table 3.3 Optical profilometry volume measurements of individual crystals following the thermal conversion from $\mathbf{O}$ to $\mathbf{Y}^{*}$ with the corresponding percent change in volume, as measured by optical profilometry. "Theoretical $\Delta$ Volume" is the calculated percent change in volume expected for the given transformation, based on the density determined from the single-crystal structures (see Table $2.1 \& 2.2$ ). Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

While optical profilometry provided an easy way to quantify volume changes in crystals, the technique had two major pitfalls. Profilometry measurements were made using a focused 404 nm laser that would quickly scan the crystal surface. When the laser intensity was too high, as was often required for measuring smaller samples, the laser would 'write' in the surface as it scanned and measured the crystal, and the crystal surface was noticeable changed during the measurement process, as shown in Figure 3.8. While the surface changes were not observed to cause significant morphological change, it was anticipated that these surface changes were local surface melting or transformations of $\mathbf{O}$ to $\mathbf{Y}^{*}$ that could decrease accuracy of volume measurements.


Figure 3.8 Laser based optical profilometry measurements can transform the crystal, but also reveal morphological changes on the sub-micrometer scale that cannot be resolved, shown as the dark region indicated by the arrow in the lower panel.

A second major challenge occurred when trying to make volume measurements on glass or quartz substrates. The instrument would inconsistently and often inaccurately determine the location of the glass substrate relative to the sample, a result of the transparent nature of the substrate and how the instrument determines the three dimensional location of individual components within the viewing frame. Transparent substrates were frequently seen to have oscillating variations in the baseline, with amplitudes as large as $2 \mu \mathrm{~m}$. This deviation made the accurate measurement of small crystals on transparent substrates impossible. For example, the 70 crystal shown in Figure 3.1 has dimensions of a typical small orange dyad crystal, and has an estimated height relative to substrate of $\sim 8 \mu \mathrm{~m}$. Because baseline variations on transparent substrates were on the same order as crystal dimensions, crystals used in transmission POM
measurements (e.g. Figure $3.1 \& 3.2$ ) were not included in volume change measurements shown in Table 3.3.

Despite the limitations related to quantitative measurements of crystals on glass slides, measuring crystal dimensions on transparent substrates could be achieved when the relevant dimensions were easily distinguished from the substrate. Shown in Figure 3.8, the large 60 crystal previously shown in Figure 3.2 possesses distinct crystal faces that allow for individual crystal dimensions to be measured (e.g., average length profile of $\mathbf{6 0}$ and corresponding $\mathbf{6 y *}$ at the top of the crystal are 957.93 and $959.97 \mu \mathrm{~m}$, respectively). As noted previously, after heating the $\mathbf{6 0}$ crystal shown in Figure 3.8 (and Figure 3.2) average dimensions of the crystal grew 2.04 $\mu \mathrm{m}(0.21 \%)$ in length, $2.05 \mu \mathrm{~m}(1.1 \%)$ in width, and $0.21 \mu \mathrm{~m}$ (2.8\%) in height

Optical profilometry measurements allowed for micrometer scale measurement resolution, enabling accurate measurements of specific crystal dimensions and, when on the appropriate substrate, volume. These measurements further verified the POM observations that indicated changes in crystal dimensions were on the order of $1 \%$ and revealed that, while on average, individual dimensions changed little, specific regions of crystals can have larger than average changes. The arrow shown in the bottom left of Figure 3.8 indicates a region that was seen to develop rough surface features and the loss of previously protruding features following heating. Quantification of these sub-micron surface changes was not resolved using profilometry due to resolution limits, and alternative methods of nanometer scale surface characterization were explored.

### 3.2.2.5 Topological Characterization: Atomic Force Microscopy

Quantifying Nanoscopic Changes - Atomic Force Microscopy (AFM). Nanometer scale morphological changes accompanying the thermal conversion of $\mathbf{O}$ to $\mathbf{Y}^{*}$ were investigated using non-contract AFM. Non-contact AFM imaging of a single $7 \boldsymbol{o}$ orange crystal found on a $7 \boldsymbol{o}$ polycrystalline thin film reveals clean, sharp edges on an isolated single-crystals formed from the
fuming of a thin film of 7 (Figure 3.9). Thermal conversion of this single crystal to $7 \mathbf{y}^{*}$ and subsequent imaging shows the general crystalline shape is maintained following conversion, while the surface has nanoscopic feature changes including the formation of numerous ridges/steps. Shown alongside each AFM image is an optical micrograph at the indicated magnification that highlights the resolution achieved by AFM, especially in comparison to microscope-based measurements.


Figure 3.9 Non-contact AFM generated 3D profiles of the same crystal before and after heating, showing retention of overall shape with nanoscopic surface changes. Top: AFM image of 7 o crystal before heating, right: optical micrograph of corresponding 70 crystal. Bottom: Image of the same crystal following thermal conversion to $7 \mathbf{y}^{*}$, right: optical micrograph of corresponding $7 \mathbf{y}^{*}$ crystal. Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

Additional polycrystalline thin films were imaged to further characterize and resolve morphological changes following thermal conversion. Imaging of 70 thin films proved
challenging because of nearly vertical crystal boundaries with large step heights in most crystals. For example, the $7 \boldsymbol{0}$ crystal shown in Figure 3.10 had a step height of $\sim 40 \mathrm{~nm}$, while the adjacent crystals shown in the corresponding micrograph had step heights of over 500 nm . Film edges near the edge of the substrate were observed to have crystals with the smallest step heights, yet were challenging to image due to the presence of dust and other debris that would move with the AFM tip. The ideal location for imaging was found to be small inverted 'islands' within the film, as shown in Figure 3.10 (film shown previously in Figure 2.23). These crater like regions within the film are surrounded on all side by crystals, which are thought to minimize the amount of debris that collects near crystals within these crater-like depressions. Further, multiple crystals with step heights of less than 100 nm are often observed in these regions. Larger step heights can be imaged, although scans must be significantly slowed to enable the AFM tip to traverse large vertical boundary to remain in non-contact mode. While orange crystals were structured and not measurably changed when imaged in separate contact mode imaging experiments, samples of soft crystalline $7 \mathbf{y}^{*}$ were seen to have altered surface features following contact-mode measurements.

Multiple different regions, defined and shown in Figure 3.10, were imaged before and after heating. Three different sub-regions, named region "A", "B", and "C", were identified and imaged within a $400 \mu \mathrm{~m}^{2}$ area, referred to as the " $20 \mu \mathrm{~m}$ AFM Region". Each of the three subregions had distinct morphological features and were chosen in order to investigate how different crystalline features change following heating, and each of these regions will be described individually.


Figure 3.10 Protected regions within thin films show ideal properties for AFM imaging, with minimal step heights and protection from dust. Top: Optical micrographs of 7 o and the regions imaged by AFM, shown in Figures $3.11 \& 3.12$. Bottom: AFM images of a $20 \mu \mathrm{~m}$ AFM region for 7 o (left) and 7y* (right). These images show the 4 areas that were imaged using non-contact AFM for both $7 \mathbf{o}$ and $7 \mathbf{y *}$ show in Figure 3.11 \& 3.12. Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.


Figure 3.11 AFM images for $7 \mathbf{0}$ and their thermally generated 7y* counterparts. Side-by-side non-contact AFM generated 3D profiles comparing 7 o (left) and $7 \mathrm{y}^{*}$ (right) for the region specified above each image and defined in Figure 3.10. Arrows point to the same location on each film by referencing the indicated surface features. Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

Shown in Figure 3.11 are comparisons of 7 o (left) and $7 \mathbf{y}^{*}$ (right) forms for the $20 \mu \mathrm{~m}$ AFM region, Region A, and Region B. Note that surface features (e.g. dust specs, etches in quartz) can be seen in both $\mathbf{O}$ and $\mathbf{Y}^{*}$ images. Direct comparisons of the same location can be made before and after heating by referencing surface features (e.g., bumps, etches in the quartz) that were seen to not change their relative locations before and after heating.

Initial comparison of the $20 \mu \mathrm{~m}$ region shown in the top of Figure 3.11 reveals several general morphological similarities between the two polymorphs. In both cases, most long crystal edges are intact and traverse the same path. Moreover, in general, features that were raised in the $\mathbf{O}$ form are raised to a similar extent in the $\mathbf{Y}^{*}$ form. However, sharp edges and clearly defined crystal boundaries seen between individual crystal domains in the bottom of the $7 \mathrm{o} 20 \mu \mathrm{~m}$ region are no longer differentiable in the 7y* image.

The arrow shown in Region A of both 7o and 7y* (Figure 3.11) is in the same location in each image, based on identifying and overlapping distinct surface features. The arrow in $7 \mathbf{0}$ Region A points to a tall, fin-like feature, that extends 30 nm above the rest of the crystal, with a width of $\sim 175 \mathrm{~nm}$. After heating, the general shape of Region A remains the same, with noticeable changes to smaller surface ridges. The fin-like feature was seen to shrink 15 nm in height while increasing in width. Additional smaller steps are noted to emerge in the same location as the fin following the heating.

Indicated by the arrow in 7 o Region B (Figure 3.11) is a $\sim 110 \mathrm{~nm}$ gap between two individual crystals, with the gap being between the middle segment of one crystal and the terminal segment of another. Following heating, the terminal gap between the two crystals is no longer separated, and the previously point-like crystal terminus is seen to have retracted and are seen to be more rounded, with general changes to surface features similar to those previously noted.

The most resolved imaging was seen in the $4 \mu \mathrm{~m}^{2}$ Region C, as shown in Figure 3.12. Non-contact AFM measurements of $\mathbf{7 o}$ in Region C indicated the presence of lamellar structures with a step height of $\sim 1.3 \mathrm{~nm}$ (green profile, Figure 3.13 ) roughly the height of the aromatic core
in the dyad molecule ( 1.36 nm ). The general dimensions and lamellar structure are maintained following heating, however, nanoscopic changes to the shape of individual layers were observed (Figure 3.12). The differences in layer shapes after heating are interpreted to indicate that the layers underwent structural transitions somewhat independently from each other. Step height profiles passing through the same spatial location on the substrate, as indicated by the reference circles, are shown for $7 \mathbf{7 o}$ (blue trace) and $7 \mathbf{y}^{*}$ (black trace). Comparison of the profiles reveal that significant reorganization took place at that location, where five identifiable layers in $7 \mathbf{0}$ (green trace) were later seen to have only two layers in $7 \mathbf{y}^{*}$ (gold trace). While the location of individual layers changes, a detailed comparison of each AFM image shows 10 recognizable layers in each image at similar heights above the surface. The general morphology of the layers changed from longer, narrow to shorter and wider layers with discontinuities. In contrast to the layers in $7 \mathbf{o}$ with frequent step changes, layers observed in $7 \mathbf{y}^{*}$ were seen to have rounded edges, and noted to more frequently 'flow' down with changes in step height, having significantly more curvature than the sharper edges seen in $7 \mathbf{0}$.

Taken together, non-contact AFM imaging of $7 \mathbf{0}$ and $7 \mathbf{y}^{*}$ support previous imaging findings that show retention in much of the original crystalline boundaries and overall morphology following thermal conversion. However, AFM has uniquely shown that while there is, at least to a small extent, change occurring between individual layers, the overall lamellar structure is retained following thermal conversion.


Figure 3.12 Non-contact 3D AFM image of single 7 crystal before and after heating showing nanoscopic surface changes following heating. Top left: 3D image of a single 7 o crystal. Top right: Step-height profile of the blue trace (top) and the inset green trace (bottom) in the adjacent 7 o AFM image. Bottom left: 3D image of the same region above, after conversion to $7 \mathbf{y}^{*}$. Bottom right: Step-height profile of the black trace (top) and the inset yellow trace (bottom) in the adjacent 7y* AFM image. Adapted with permission from $\operatorname{Ref}{ }^{66}$. Copyright 2020 American Chemical Society.

### 3.2.2.6 Structural Characterization: Molecular Orientation

To explain the molecular movements that take place during the heating process, an understanding of the molecular orientation in each polymorph is necessary. As discussed in Chapter 2, dyad crystals were found to have a preferred orientation within crystals, with the long axis of all crystals shown to correspond to the direction of aromatic stacking (see section 2.3.3.5). The two smaller crystal dimensions were made from either interactions between columns, or interactions between adjacent side chain layers, and this dimensional preference varied with different derivatives and crystals (see Figure 2.20, section 2.3.3.5).

Using grazing-incidence wide-angle X-ray scattering (GIWAXS), preferred orientation of 7 o thin films was previously shown (see Figure 2.22 f , section 2.3.4) to have a dominant orientation preference for the long crystallographic axis (010) to be normal to the quartz substrate. The combination of GIWAXS scattering data and non-contact AFM indicate $7 \boldsymbol{0}$ thin films formed a bilayer type, lamellar structure with alternating alkyl and aromatic layers parallel to the substrate, similar to the preferred orientation seen in orange crystals (see Figure 2.6). Thus, dyad molecules in 70 thin films are oriented as shown in Figure 3.14, with the crystal long axis made from stacked dyad cores, and the height of the crystal made from stacks of dyad layers. These measurements confirm that individual layers of 70 imaged in AFM experiments (Figure 3.12) were individual layers of dyad molecules.


Figure 3.13 Preferred orientation of $\mathbf{7 o}$ in polycrystalline thin films as determined by GIWAXS measurements.

In agreement with the thermochromic conversion of a single crystal of $\mathbf{7 o}$ to $7 \mathbf{y}^{*}$, heating of a 70 polycrystalline thin film generated the corresponding $7 \mathbf{y}^{*}$ thin film as confirmed by spectroscopic measurements previously described (see Figure 3.4). GIWAXS measurements of the thermally generated $\mathbf{7 y *}$ thin film reveals that the structure of $7 \mathbf{y *}$ is not crystalline following thermal conversion, but is best described as a soft- or liquid-crystalline mesophase (Figure 3.15).

Shown in Figure 3.14 is a comparison of GIWAXS scattering data for 7 o and $\mathbf{7 y *}$ thin films. Inside each diffraction pattern, white circles show the calculated diffraction spots ${ }^{143}$ (transmission) and corresponding Miller indices based on lattice parameters from single-crystal structure data for $\mathbf{7 0}$ (top) and $\mathbf{7 y}$ (bottom), with preferred orientation where the crystallographic long axis is perpendicular to the substrate.


Figure 3.14 GIWAXS scattering pattern for thin films of 7 on a quartz substrate before and after heating. Top: Scattering of 7 o polycrystalline thin film. Bottom: Scattering of 7y* thin film produced from heating the $7 \boldsymbol{o}$ thin film shown above. White circles show the calculated diffraction spots (transmission) and corresponding Miller indices based on lattice parameters from single-crystal structure data for $7 \mathbf{o}$ (top) and $\mathbf{7 y}$ (bottom). Data collected at room temperature. Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

The lower panel of Figure 3.14 shows scattering of the $\mathbf{7 y}$ * thin film with in-plane (e.g. directly above the center of the beam) diffractions that correspond to the (200) crystallographic axis perpendicular to the substrate. Note that by convention, the long crystallographic axis is defined as the b-axis (010) for $\mathbf{7 0}$, whereas the long axis is the a-axis (100) in $7 \mathbf{y}$; the c -axis (001)
represents the packing of columns in both structures. The other diffuse diffraction spots seen in the $7 \mathbf{y *}$ * scattering data match the expected location calculated ${ }^{143}$ for the (20-2) and (40-2) crystallographic planes of $\mathbf{7 y}$. As shown in Figure 3.15, the (20-2) and (40-2) planes pass through columns of the aromatic cores and observed scattering in these locations is interpreted to represent periodic order within columns. Other (h0l) planes, including the partially inverted (202) and (402) planes also reflect columnar ordering in the crystal. Taken together, this structural data reveals that the $\mathbf{7 y}$ * thin film has the same lamellar structure as 7o, and that there is periodic order within columns of dyads. This columnar order seen in $7 \mathbf{y}^{*}$ is taken to indicate a significant reorganization of intercolumnar geometry following heating: columns packed roughly perpendicular about the dyad long axis in 70 (see Figure 2.5) reorganized to become roughly parallel about the long axis, while adopting a short axis rotation, as seen in yellow crystals of 7 (see Figure 2.11).

An increase in amorphous scattering at larger scattering angles in $7 \mathbf{y} *$ thin films, as well as more diffuse diffraction spots indicates that some disorder is present in $\mathbf{7 y *}$. In-plane scattering from 7y* thin films in the ( $h 00$ ) plane occurs at a smaller scattering angle than would occur for $7 \mathbf{y}$ based on calculated diffraction spots from the 7 y crystal structure. This smaller observed scattering angle of the ( $h 00$ ) planes in the $7 \mathbf{y}$ * thin film is indicative of a slightly larger ( $\sim 3 \AA$ ) lamellar spacing in $7 \mathbf{y}^{*}$ as compared to $7 \mathbf{y}$ and can be partially attributed to positive thermal expansion. ${ }^{114}$

Yellow crystals of symmetric dyads were previously shown to have segregated side chains (see Figure 2.12), and so the increase in increase in lamellar spacing seen following heating of $\mathbf{7 0}$ to $7 \mathbf{y}^{*}$ is believed to reflect the fact that the interdigitated side chains in $\mathbf{7 o}$ (see Figure 2.6) became segregated during the transition to $7 \mathbf{y}^{*}$, possible to a larger extent than in $\mathbf{7 y}$. The overall correspondence between calculated diffraction patterns of $7 \mathbf{y}$ and observed scattering of $7 \mathbf{y}$ * reflect similar packing motifs between the two species, and the proposed molecular packing for $7 \mathbf{y}^{*}$ is shown in Figure 3.15.


Figure 3.15 The proposed molecular packing of $\mathbf{7 y *}$ is believed to be similar to that of $\mathbf{7 y}$, with a lamellar structure and some columnar and intercolumnar order, however $7 \mathbf{y}$ * lacks long range crystalline order seen in $\mathbf{7 y}$. The proposed $\mathbf{7 y *}$ structure shown is the single-crystal structure of $\mathbf{7 y}$, with select $\mathbf{7 y}$ crystallographic planes shown in green.

One final addition must be noted for the proposed structure of $\mathbf{7 y *}$ that has not been addressed and is not accounted for in Figure 3.15: a variable tilt in lamellae of $7 \mathbf{y}$ * observed in several different X-ray scattering experiments. In one experiment, a single 70 crystal was heated to the corresponding $7 \mathbf{y}$ * form. Following conversion, a WAXS transmission experiment was performed in an end-on geometry, as shown at the top of Figure 3.16. In this geometry, the crystal was oriented such that the incoming X-ray beam will run parallel to, and through, the long axis of the crystal. The diffraction from this $\mathbf{7} \mathbf{y}^{*}$ sample is shown in Figure 3.16. Shown in the raw detector image and the polar transformation are equally spaced rings, that correspond to the ( $h 00$ ) planes formed from lamellar packing. Specific planes are indicated in the polar transformed diffraction pattern shown on the right hand side of the figure that has been corrected
to take the Ewald sphere into account. Diffraction from the (h00) planes in circular rings is an indication that multiple sets of equally spaced crystallographic planes are oriented in variable angles relative to the substrate. ${ }^{144}$ The strongest scattering, represented by the darkest color, is seen in-plane and is taken to indicate that the dominant orientation of lamellae are oriented parallel to the substrate. The lower intensity scattering seen moving away from in-plane scattering is taken to indicate that lamellae oriented parallel to the surface are the most common orientation of crystalline lamellae present. Other peaks observed are derived from ordering between lamellae, most notably a diffraction peak with spacing of $4.3 \AA\left(\mathrm{q}=1.47 \AA^{-1}\right)$ is seen, corresponding to spacing of crystalline packing in alkyl side chains. ${ }^{101}$ The presence of this peak supports the notion that some side chains are packed in the solid-state, however, other measurements observed variable extents of alkane packing, and as such, $7 \mathbf{y}^{*}$ is believed to have a mix of ordered, crystalline and disordered alkyl side chains across the sample.


Figure 3.16 End on transmission WAXS measurement of 7y* following the heating of a single 70 crystal shows scattering from lamellar packing with orientations in all directions, as seen by the circular diffraction rings. The strongest intensity scattering is seen inplane, originating from lamellae oriented parallel to the substrate. Data collected at room temperature.

### 3.2.2.7 Structural Characterization: In Situ Heating X-ray Diffraction

## Structural Changes During Polymorphic Transitions in Polycrystalline Samples. In

 an effort to elucidate the structural changes that accompany the real-time transition from $\mathbf{O}$ to $\mathbf{Y}$, in-situ heating X-ray diffraction (XRD) experiments were conducted. While typical real time experiments are done using more intense synchrotron radiation sources, large crystals werefound to diffract well from lab X-ray sources to gather structural information in short exposures (e.g. 9-30 seconds).

Numerous attempts to induce a single-crystal-to-single-crystal transition in crystals of $\mathbf{6 0}$ and 70 were unsuccessful, as variable orientations were seen for individual crystallographic planes, similar to that seen in Figure 3.16. In these attempted single-crystal-to-single-crystal experiments, the crystal was heated with a stream of hot nitrogen gas. The soft crystal was noted to physically deform with movement of the goniometer in the gas stream, and these deformations consistently resulted in loss of all diffraction spots. In order to circumvent these limitations, new experimental methods were devised to keep the crystal in place during heating and X-ray exposure.

The overall experimental setup for in situ heating XRD experiments is shown in Figure 3.17. A single orange crystal is placed in sandwiched between two thin, $5-7 \mu \mathrm{~m}$, mica sheets, and placed on a stationary heating stage in line with an X-ray source. Using this set up, numerous $\mathbf{6 0}$ and 70 crystals were heated while short transmission X-ray exposures (e.g. 30 seconds) were taken during heating in order to understand structural changes to crystals as they undergo the $\mathbf{O}$ to $\mathbf{Y}^{*}$ polymorphic transition. Shown in the bottom of Figure 3.17 is the $7 \mathbf{o}$ crystal over the beamline before, and the $7 \mathbf{y}^{*}$ soft-crystalline mesophase seen after heating, and again, the microscopic morphology of the crystal is noted to not change following heating.


Figure 3.17 Heating XRD experimental setup and single crystal of $7 \boldsymbol{o}$ shown before and after in situ heating to generate $\mathbf{7 y}$ *. Top left: Optical micrograph of initial 70 crystal. Top Right: Macroscopic perspective of 7 o on the heating stage shown in the bottom left. Bottom let: Optical micrograph of 70 crystal on top of heating stage mounted over the X-ray transmission hole. Crystal is held in place two pieces of mica sheets. Bottom right: Optical micrograph of $7 \mathbf{y}^{*}$ on heating stage directly following heating XRD-experiment.

The cross section of the X-ray beam is much larger than all transition wavefronts seen visualized by POM, meaning that these exposures are more of a bulk measurement that includes the $\mathbf{O}$ to $\mathbf{Y}^{*}$ transition wavefront, as well as regions of growing $\mathbf{Y}^{*}$ and shrinking $\mathbf{O}$. Despite these challenges, these measurements support the hypothesis that the transition from $\mathbf{O}$ to $\mathbf{Y}^{*}$ proceed through an amorphous transition state. ${ }^{69}$

Shown in Figure 3.18 are the 2D and 1D diffraction patterns showing the changes that accompanied the 7 o to $7 \mathbf{y}^{*}$ transition of the crystal shown in Figure 3.17. In the experiment, the crystal is heated from room temperature to $95^{\circ} \mathrm{C}$ at $5^{\circ} \mathrm{C} \mathrm{min}{ }^{-1}$, then ramped at $2^{\circ} \mathrm{C} \mathrm{min}^{-1}$ to $120^{\circ} \mathrm{C}$ and held at $120^{\circ} \mathrm{C}$ for 2 minutes before ramping $10^{\circ} \mathrm{C} \mathrm{min}{ }^{-1}$ to $90^{\circ} \mathrm{C}$, at which time the final exposure ( 1200 seconds) was captured. During heating beyond $95^{\circ} \mathrm{C}, 30$ second exposures were collected, and the time and temperature at the start of each exposure are embedded within the 2D scattering patterns shown in Figure 3.18. Time, $t=0 \mathrm{~s}$, was defined to start with the initiation of heating from $95^{\circ} \mathrm{C}$.

As 70 is heated, the few spots that satisfy the Bragg condition are seen to weaken in intensity before disappearing. Quickly following the gradual disappearance of 7 o diffraction spots, diffraction spots from 7y* appear in rapid succession, with scattering from 7y* lamellar spacing being observed before scattering from dyad stacks (Figure 3.18). The emergence of a low angle peak at $3.38^{\circ}$ two-theta (blue traces) correspond to lamellar spacing from the (200) plane that appears before other $(h 00)$ planes, and before the planes near $12.2^{\circ}$ and $13.7^{\circ}$ two-theta (green traces). The peak seen at $12.20^{\circ}$ is attributed to columnar order in $7 \mathbf{y}^{*}$ and can be assigned to the (202) plane. The peak observed at $13.74^{\circ}$ is attributed to the overlap of the (800) and (402) planes, the latter of which also represents columnar order. Note the spots seen in the bottom of the 2D diffraction patterns are attributed to diffraction caused by the mica sheets used to hold the crystal in place.


Figure 3.18 In situ heating XRD of the 7 o crystal shown in Figure 3.17 as it is heated to generate $7 \mathbf{y}^{*}$, shows the emergence of new diffraction patterns. Bottom: 1D traces from transformed 2D diffraction patterns shown above.

### 3.2.3 Asymmetric Dyad Stimuli-Responsive Properties

Optical Changes. The two shorter asymmetric derivatives M6N8 (yellow) and M8N6 (gold) did not have any observable optical transitions when heated prior to melting. Only the two longer asymmetric dyad derivatives, M8N10 (orange-red) and M10N8 (yellow-orange) were seen to undergo thermally induced transitions. Orange-red M8N10 had an orange-red-to-yellow transition that was observed to initiate all around the crystal edge and move towards the interior, creating small pixelated domains throughout the transformed yellow material. In contrast, M10N8 (yellow-orange) had an observable, yet colorless, transition prior to subsequent melting. Following heating, the thermally generated mesophase persists once cooled back to room temperature. Of the asymmetric derivatives, only M8N10 (orange-red) showed mechanochromic behavior, with a transition to a soft liquid-crystalline like yellow material when a shearing force was applied.

Thermal Transition Characterization - Asymmetric Dyad Crystals. Shown in Figure 3.8 are successive heating-cooling DSC measurements for asymmetric dyad derivatives. Peak transition temperatures and enthalpies of transition for these four derivatives are provided within Figure 3.20 and in Table 3.4. Interestingly, the existence of two endothermic transitions was seen not seen to correlate with head-to-head stacking geometry, but did occur in the two longer side chain derivatives. As noted in section 2.3.3.3, M8N6 (gold) M10N8 (yellow-orange) had similar head-to-head stacking geometries, M6N8 (yellow) was shown to have head-to-tail stacking geometry, and while no crystal structure was solved for M8N10 (orange-red), it is believed to have packing similar to $\mathbf{9 0}$ and thus pack in a head-to-head geometry (see Figure 2.18).

The two shorter derivatives, M8N6 (gold, head-to-head) and M6N8 (yellow, head-totail), are seen to have a single endothermic peak in the first heating that corresponds to POM observations for direct melting to the isotropic phase. Subsequent cooling of the isotropic phase generates a solid that, when reheated, has a lower transition temperature compared to each initial crystalline sample (Figure 3.20).

In contrast, the two longer asymmetric derivatives, M10N8 (yellow-orange, head-tohead) and M8N10 (orange-red, head-to-head), are seen to have two endothermic transitions, at $102.3^{\circ}$ and $107.1^{\circ}$, respectively, before melting to the isotropic phase. The integrated enthalpy of transition was different for both derivatives, with measured transition enthalpies of 16.2 and 48.0 $\mathrm{kJ} \mathrm{mol}^{-1}$ for M10N8 (yellow-orange) and M8N10, respectively. In contrast, a smaller difference was observed for the transition enthalpy corresponding to melting to the isotropic phase, with transition enthalpies of 19.8 and $25.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$ for M10N8 (yellow-orange) and M8N10 (orangered), respectively.

In comparison to the two transitions seen in orange symmetric crystals (Figure 3.6 and Table 3.2), M10N8 (yellow-orange) had the smallest transition enthalpy of all crystalline to mesophase transitions measured. In contrast, M8N10 (orange-red), had a crystal to mesophase transition enthalpy of $48.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$, most comparable to the transition enthalpy measured for the conversion of $\mathbf{8 0}$ to $\mathbf{8 \mathbf { y } ^ { * }}\left(53.1 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, and less than its constitutional isomer, $\mathbf{9 0}$, with a transition enthalpy of $56.1 \mathrm{~kJ} \mathrm{~mol}^{-1}$.

In comparison to the crystal-to-isotropic transition seen in yellow symmetric crystals (Figure 3.5, Table 3.2), head-to-head stacked M8N6 (gold) was seen to have the largest transition enthalpy measured $\left(42.2 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, for derivatives with a single thermal transition. The largest symmetric yellow crystal-to-isotropic transition was shown to be in $\mathbf{8 y}$, with transition temperature of $144.4^{\circ} \mathrm{C}$ and a transition enthalpy of $34.7 \mathrm{~kJ} \mathrm{~mol}^{-1}$. However, as discussed in section 3.2.2.3, crystal size was seen to influence transition temperatures and transition enthalpies. The larger three dimensional growth of M8N6 compared to symmetric yellow crystals (Figure 2.2) hinders meaningful thermodynamic comparisons between head-to-head and head-to-tail polymorphs that display a single thermal transition. Comparison of head-to-tail stacked M6N8 and its constitutional isomer 7y and 7y' reveal similar transition temperatures and enthalpies (see Table 3.2) between the three derivatives with similar packing geometries (see Figure 2.19). However, the parallel intercolumnar relationship between M6N8 (Figure 2.15)
resembles that of $\mathbf{6 y} / \mathbf{6 y}$ ', in contrast to the $49^{\circ}$ short-axis rotation seen between dyads in adjacent columns of $\mathbf{7 y} / 7 \mathbf{y}^{\prime}$ (Figure 2.11).


Figure 3.19 Successive DSC heating and cooling experiments for all asymmetric dyad crystals shows the presence of two endothermic transitions for longer M10N8 (yelloworange) and M8N10 (orange-red) derivatives, while only a single transition is seen for shorter derivatives. Values near peaks show the corresponding peak temperature $\left({ }^{\circ} \mathrm{C}\right)$, bracketed values represent integrated transition enthalpy $\left[\mathrm{kJ} \mathrm{mol}^{-1}\right]$.

| Sample | Lower Temperature Transition, if Present |  |  | Higher Temperature Transition |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Onset <br> Temp <br> $\left({ }^{\circ} \mathrm{C}\right)$ | Peak <br> Temp <br> $\left({ }^{\circ} \mathrm{C}\right)$ | Transition Enthalpy ( $\mathrm{kJ} \mathrm{mol}^{-1}$ ) | Onset <br> Temp <br> $\left({ }^{\circ} \mathrm{C}\right)$ | Peak <br> Temp <br> $\left({ }^{\circ} \mathrm{C}\right)$ | Transition Enthalpy ( $\mathrm{kJ} \mathrm{mol}^{-1}$ ) |
| M6N8 | - | - | - | 137.76 | 142.44 | 30.93 |
| M8N10 | 102.08 | 107.08 | 47.98 | 128.01 | 132.32 | 25.53 |
| M8N6 | - | - | - | 140.26 | 143.66 | 42.23 |
| M10N8 | 100.71 | 102.30 | 16.24 | 122.70 | 127.80 | 19.81 |

Table 3.4 Summary of asymmetric dyad phase transitions measured by DSC at a heating rate of $5^{\circ} \mathrm{C} \mathrm{min}^{-1}$ for all samples.

### 3.2.4 Self-Assembly From Isotropic Cooling

Previously, all orange symmetric dyads were shown to have the same general properties when heated, regardless of side chain length: initial thermal conversion into a yellow softcrystalline mesophase, and continued heating would result in melting to the isotropic phase. Shown in Figure 3.6 is an alkyl chain length dependent behavior for dyads when cooled from the isotropic phase, exhibiting differences in the patterns of exothermic cooling peaks.

When shorter derivatives 6, 7, and $\mathbf{8}$ were cooled from the isotropic phase, exothermic peaks were seen that cannot be individually resolved (e.g. the signal does not return completely to baseline). In contrast, cooling from the isotropic phase of derivatives $\mathbf{9 , 1 0}$, and $\mathbf{1 2}$ show two distinct exothermic peaks (or sets of peaks). Investigation of this phenomenon using a heating stage equipped POM shows optical differences are observed when 7 and 9 are cooled at $5^{\circ} \mathrm{C} \mathrm{min}^{-}$ ${ }^{1}$ from the isotropic phase.

Shown in Figure 3.20 is the cooling of 7 from the isotropic phase at $1^{\circ} \mathrm{C} \mathrm{min}^{-1}$ when viewed under cross polarized and brightfield conditions in separate, successive cooling experiments. The phase transition from the isotropic melt occurs over a period of 171-181 seconds in the two experiments, and is seen to follow the classical nucleation and growth crystallization pathways. The initial appearance and growth of the long rectangular domains resembles the smectic bâtonnets, ${ }^{149}$ suggesting a single transition from isotropic to a smectic, soft crystalline mesophase.


Figure 3.20 Self-assembly of 7 when cooled from the isotropic phase at $5^{\circ} \mathrm{C} \mathrm{min}^{-1}$ as viewed under cross polarized and brightfield conditions shows the initial formation of long rectangular bâtonnet like solids, indicative of an Iso-Sm like transition.

In contrast to 7, and in agreement with two exothermic peaks seen in DSC (Figure 3.6) cooling of 9 from the isotropic phase at $1{ }^{\circ} \mathrm{C} \mathrm{min}^{-1}$ shows the emergence of two distinct molecular species (Figure 3.21). Initial cooling from the isotropic phase generates small, randomly dispersed anisotropic circles that resemble fan-shaped focal conic domains (FCD), a well-known
smectic A defect, once cooled below $139.6^{\circ} \mathrm{C}$. The number and size of these FCDs were seen to increase as the sample was further cooled to $134.1^{\circ} \mathrm{C}$. Holding the temperature at this point was noted to not change the optical characteristics. The presence of concentric rings, four extinction brushes in the shape of a cross with a central hedgehog point defect are indicative of smectic phase under hybrid anchoring conditions. ${ }^{150-152}$ The emergence of FCD reflect the self-assembly of $\mathbf{9}$ into domains that have overall orientational order, with the dyads likely assembling within large cylindrical columns with the long axis of dyads oriented radially.

Continued cooling at a rate of $1^{\circ} \mathrm{C} \mathrm{min}^{-1}$ shows no further changes until the second transition temperature of $121.4^{\circ} \mathrm{C}, \sim 1,100$ seconds after the FCDs were observed. Once this lower transition temperature is reached, a relatively fast moving transition wave is seen to move through the remaining isotropic melt over a period of 10-15 seconds. The wave initiates near the edge of the isotropic melt, and moves radially outward, creating a series of concentric ridge-like rings in the material. Movement of this transition wave was seen to move through previously self-assembled FCD. As shown by the last three brightfield images, the FCDs were still visible after the wave-like transition. Further characterization of this solid using optical profilometry reveals the focal conic holes are still intact after the fast wave-like transition (Figure S3). Combined, the emergence of FCD and wave-like transition suggests 9 underwent an isotropicsmectic to a smectic, soft crystalline mesophase. transition.


Figure 3.21 Self-assembly of $\mathbf{9}$ when cooled from the isotropic phase at $5^{\circ} \mathrm{C} \mathrm{min}^{-1}$ viewed under cross polarized and brightfield conditions, showing the formation of two different phases over different timescales, initial formation of focal conic disc-like domains at higher temperatures before the movement of a faster wave like transition.

### 3.3 DISCUSSION

### 3.3.1 Self-Assembly From the Isotropic Melt

During cooling from the isotropic phase, varying extents of self-assembly are observed for different derivatives as a function of temperature. In the isotropic melt, the side-chain movements keep dyad molecules separated and prevents any anisotropic ordering. Upon cooling, the first molecular associations to occur are expected to be aromatic interactions between dyad cores, associating to form columnar stacks, while flexible alkyl side remain fluid, as previously
seen in mixtures of DAN and NDI. ${ }^{60,}{ }^{61}$ Once below a side chain dependent threshold temperature, it is thought that the attractive interactions between dyad cores can overcome thermal motion within side chains, thus nucleating columnar growth. Above this threshold temperature, interactions between dyad cores in nucleation processes are overcome by thermal motion of the side chains, while below the threshold temperature, growth from templated columns is likely. Continued cooling would be expected to reduce side-chain flexibility until they solidify into the final soft crystalline mesophase.

However, these two distinct self-assembly processes are not observed in all derivatives, and variations in side-chain length were correlated with different optical characteristics during the cooling process, as shown in Figure 3.20 and 3.21. Because shorter side-chains have less degree of freedom, 7 is expected to be able to nucleate successful columnar growth at higher temperatures compared to $\mathbf{9}$, as was observed (onset for $7148.5^{\circ} \mathrm{C}$, for $9139.6^{\circ} \mathrm{C}$, Figure 3.20 \& 3.21). The two-step, discrete self-assembly process observed in $\mathbf{9}$ is taken as an indication that once columnar stacks form, there is still significant side chain mobility, as seen by observed smectic A FCDs. Subsequent observable changes were only seen with additional cooling below a second transition temperature, at which point a fast moving wave-like transition moved through the sample. Once cooled past the second transition temperature, side chains in $\mathbf{9}$ are no longer able to remain fluid, and freeze out in a rapid nucleation and growth type process, as seen by the fast moving wave-like transition.

In contrast to $\mathbf{9}$, it is thought that the shorter side chains in $\mathbf{7}$ do not have enough thermal motion to maintain fluidity once assembled into columns. Thus, heptyl side chains become ordered as columns are formed, leading to the multidimensional growth observed in Figure 3.21, in a single self-assembly process. This postulated mechanism is further supported by the trends seen when all derivatives are cooled from the isotropic phase, as measured by DSC (Figure 3.6). Shorter derivatives $\mathbf{6}$ and 7 have a single exothermic transition, whereas derivatives $\mathbf{8}, \mathbf{9}, \mathbf{1 0}$, and 12 have two discrete exothermic transitions. These longer derivatives are also seen to have a final transition at successively lower temperatures, attributed to increasing thermal disorder in
derivatives with longer side that impede the complete self-assembly process until thermal motion can no longer overcome associations between side chains.

### 3.4 CONCLUSIONS

In summary, all symmetric orange dyads investigated were found to have thermochromic, transitions upon heating, with orange crystals transforming into a yellow material. The structure of the yellow material was determined to be a soft crystalline mesophase based on spectroscopic, structural, and thermal characterization methods. The thermally produced soft crystalline mesophase was shown to have similar molecular packing to yellow symmetric crystals grown from solution: head-to-tail dyad packing, columnar and intercolumnar order, with segregated side chains, yet differing from yellow crystals by having a decrease in long range order, a mix of order and disorder in side chains, and variably tilted lamellae.

When heated, 1bo crystals were found to directly sublime, and the two shorter asymmetric derivatives were seen to melt directly to the isotropic phase. The two longer asymmetric dyad derivatives, M8N10 (orange-red) and M10N8 (yellow-orange) were seen to undergo thermally induced transitions prior to melting, and only M8N10 had a thermochromic transition.

Visualized by POM, this thermochromic transition was seen to move as a wavefront through orange crystals. Repeatable observations revealed the fastest transitions move down the long axis of the crystal, and are observed to move at a $38^{\circ}$ angle, on average, relative to the long axis. Thermal analysis with DSC revealed that the orange-to-yellow transition temperature is influenced by crystal size in addition to side chain length, and a thus the tunability of the system is multivariable in nature. Micro- and nanoscopic measurements of crystals before and after heating confirm POM observations that the overall morphology of the material does not significantly change following the transition. A slightly larger change in crystal volume
following heating, compared to theoretical changes based on single-crystal structures, supports the proposed structure of the soft crystalline mesophase. High resolution AFM imaging of orange and yellow materials revealed a lamellar structure, with general retention of layers following transition, providing support for a transition mechanism operating largely within individual layers. Our proposed molecular mechanism(s) by which dyad packing switches from head-tohead to head-to-tail during the orange-to-yellow transition must account for the observed altered columnar and side chain packing. Further, any proposed mechanism must explain why the transition wavefront was seen to move at an angle, and how different layers within the crystal transition.

### 3.5 EXPERIMENTAL

### 3.5.1 Heating Microscopy

The heating microscopy experiments were carried out on a Zeiss Axio Scope A. 1 microscope equipped with a Linkam LTS420 thermal stage with either a $10 \mathrm{x} N$-Acroplan or 20 x N-Acroplan objective, with the ability to image under linear polarized, cross polarized, or unpolarized light. The chamber was closed during the experiment. The heating was controlled by Linkam add-on in the ZEN Core. Micrographs were taken every second ( 1 fps ) during the heating interval from $100^{\circ} \mathrm{C}$ to $120^{\circ} \mathrm{C}$. Time and temperature for each frame were determined by the Linkam software.

Protocol for heating of $7 \mathbf{0}$ to $7 \mathbf{y *}$ in Movie 3.1 and Figure 3.1 using 20x N-Acroplan objective: Heating from room temperature (RT) to $90^{\circ} \mathrm{C}$ at $20^{\circ} \mathrm{C} \mathrm{min}^{-1}$, then $10^{\circ} \mathrm{C} \mathrm{min}{ }^{-1}$ to $100^{\circ} \mathrm{C}$. The crystal was held at $100^{\circ} \mathrm{C}$ for 30 seconds, then heated at $2^{\circ} \mathrm{C} \mathrm{min}^{-1}$ to $120^{\circ} \mathrm{C}$, and directly was cooled to RT at a rate of $10^{\circ} \mathrm{C} \mathrm{min}^{-1}$.

Protocol for heating of $\mathbf{6 0}$ to $\mathbf{6 y *}$ in Movie 3.2 and Figure 3.2 using 10x N-Acroplan: Heating from room temperature to $90^{\circ} \mathrm{C}$ at $20^{\circ} \mathrm{C} \mathrm{min}^{-1}$, then $10^{\circ} \mathrm{C} \mathrm{min}^{-1}$ to $100^{\circ} \mathrm{C}$. The crystal was held at $100^{\circ} \mathrm{C}$ for 30 seconds, then heated at $5^{\circ} \mathrm{C} \mathrm{min}{ }^{-1}$ to $120^{\circ} \mathrm{C}$, held at $120^{\circ} \mathrm{C}$ for 1 min , then cooled to RT at $10^{\circ} \mathrm{C} \mathrm{min}^{-1}$. In the lower panel of Figure 3.2, wavefront speed was calculated as the distance the wave traveled perpendicular to the closest crystal long axes between the three frames (three seconds) before and three frames after the given frame.

### 3.5.2 Grazing-Incidence Wide Angle X-ray Scattering and Wide-Angle X-ray Scattering

Two-dimensional wide-angle X-ray scattering (WAXS) measurements and GrazingIncidence Wide Angle X-ray Scattering (GIWAXS) were made using a SAXSLabs Ganesha and analyzed using SAXSGUI and GIXSGUI ${ }^{3}$. The SAXSLAB Ganesha has a $\mathrm{Cu} \mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA$ ) with a Pilatus 300 detector (pixel size $0.172 \times 0.172 \mathrm{~mm}$ ). Sample
detector distance for wide angle measurements was $140.8143 \mathrm{~mm}, 3$ aperture GIWAXS mode, all horizontal and vertical guards set to 0.7 mm . Heating experiments inside were performed using a Linkam heating stage. Crystals were sandwiched between two thin Mica sheets ( 10 mm Mica Windows for Sandwich Cell (5-7 micron thick), SAXSLABS U.S., Inc.), on top of the Linkam stage and held in place with two 'lollipop' holders (see top right of Figure 3.17)

### 3.5.3 Atomic Force Microscopy

Non-Contact Atomic Force Microscopy (AFM) measurements were made on Park Scientific Instruments XE-100 and analyzed using Gwyiddon ${ }^{153}$. Following thermal conversion, the material was allowed to rest at room temperature for two days prior to subsequent imaging.

### 3.5.4 Thin Film Preparation

Thin films were made via physical vapor deposition (AMOD Thermal Deposition System, Ångstrom Engineering Inc.) onto quartz substrates. Vapor annealing of thin films were done in sealed fuming chambers with volumes of DCM between $700 \mu \mathrm{~L}$ and 2.0 mL to generate the orange form.

### 3.5.5 Optical Profilometry

Crystal size was quantitatively determined using a Keyence VK-X1100 Optical Profilometer and analyzed using VK-X1Series MultiFileAnalyzer software. To measure the change in crystal volume, orange crystals were adsorbed onto a cleaned silicon wafer by placing a single $\mathbf{6 0}$ or $\mathbf{7 o}$ crystal onto the wafer and dispensing $1 \mu \mathrm{~L}$ of cold methanol next to the crystal using an Eppendorf autopipette before gently moving the crystal into the methanol. Cold methanol was shown to not dissolve the crystals while allowing crystals to evenly adhere onto the surface as the small volume evaporated. After adsorption, crystals were left at room
temperature for at least 24 hours before $\mathbf{O}_{\text {volume }}$ was measured. $\mathbf{O}$ crystals were next heated at $120^{\circ} \mathrm{C}$ for 2 minutes, and then measured again to determine $\mathbf{Y}^{*}$ Volume. Volume was determined using Keyence VK-X Series MultiFileAnalyzer software following flattening of the substrate baseline and defining the boundary of the crystal. Silicon wafers were viewed as instrumental to volumetric analyses, as they consistently had a flat baseline measurement, in contrast to glass substrates which yielded inconsistent baseline measurements.

### 3.5.6 Information on Supplementary Movies 3.1 - 3.2

Movie 3.1. Movie of the heating of $7 \boldsymbol{0}$ to $7 \mathbf{y}^{*}$ as viewed under a 20 x objective equipped POM with a heating stage. Images acquired at 1 fps and stitched together to generate the following movie. Heating program: room temperature (RT) to $90^{\circ} \mathrm{C}$ at $20^{\circ} \mathrm{C} \mathrm{min}{ }^{-1}$, then $10^{\circ} \mathrm{C}$ $\mathrm{min}^{-1}$ to $100^{\circ} \mathrm{C}$. The crystal was held at $100^{\circ} \mathrm{C}$ for 30 seconds, then heated at $2^{\circ} \mathrm{C} \mathrm{min}^{-1}$ to $120^{\circ} \mathrm{C}$, then directly was cooled to RT at a rate of $10^{\circ} \mathrm{C} \mathrm{min}^{-1}$.

Movie 3.2. Movie of the heating of $\mathbf{6 0}$ to $\mathbf{6 y *}$ as viewed under a 10 x objective equipped cross polarized POM with a heating stage. Images acquired at 1 fps and stitched together to generate the following movie. Heating from room temperature to $90^{\circ} \mathrm{C}$ at $20^{\circ} \mathrm{C} \mathrm{min}{ }^{-1}$, then $10^{\circ} \mathrm{C}$ $\min ^{-1}$ to $100^{\circ} \mathrm{C}$. The crystal was held at $100^{\circ} \mathrm{C}$ for 30 seconds, then underwent $5^{\circ} \mathrm{C} \mathrm{min}^{-1}$ to $120^{\circ} \mathrm{C}$, held at $120^{\circ} \mathrm{C}$ for 1 min , then cooled to RT at $10^{\circ} \mathrm{C} \mathrm{min}^{-1}$.

## CHAPTER 4

## Mechanistic Analysis of Polymorphic Switching in MonoalkoxynaphthaleneNaphthalimide Donor-Acceptor Dyads ${ }^{1}$

### 4.1 ChAPTER SUMMARY

### 4.1.1 Introduction

In chapter 3, thermally induced polymorphic switching was described in both symmetric and asymmetric dyad derivatives. Heating of symmetric dyad orange crystals (head-to-head packing, orthogonal columns about the long molecular axis, and interdigitated side chains) were shown to form a yellow soft-crystalline mesophase (head-to-tail packing, parallel columns about the long molecular axis, and segregated side chains) that persists indefinitely after heating and in the absence of organic solvent vapor. Transitions were observed to start on crystal borders and defects, initially proceeding as slow moving transition waves that that formed dark, "pixelated" regions. In symmetric dyad orange crystals, a size dependency in transition temperature was observed, and transition wavefronts were repeatably observed to move 1-2 orders of magnitude faster than the slower transitions, always observed to be moving down the long axis of the crystal at $38^{\circ}$ angle on average. In asymmetric dyad derivatives, a variety of different thermally induced behaviors were observed. In longer asymmetric derivatives, both thermochromic and colorless transitions were observed, yet in both cases, no angled wavefront transition behavior was

[^2]observed, and transitions were seen to proceed in all directions at similar rates and form similar "pixelated" regions. Unique to asymmetric dyads, two dyads with the same features (head-tohead, columns orthogonal about the short molecular axis, mix of segregated and interdigitated side chains) showed diverging behavior, with one having a crystal-to-mesophase transition, and the other melting directly to the isotropic phase with the only apparent difference being side chain length. Key questions related to the mechanism and thermodynamics of the transformation remain.

### 4.1.2 Goals

This chapter seeks to answer: What is the molecular mechanism for the orange-to-yellow transition in orange crystals of symmetric dyads? Why does the transition consistently move at an angle in orange crystals of symmetric dyads? Why does crystal size affect the transition? Why do thermally induced transitions in asymmetric dyads not move at an angle? Why are some asymmetric dyad crystal-to-mesophase transitions thermochromic, and others do not have a color change? What is the thermodynamic basis for the transition, and how does the crystal remain intact during the transition and not melt? Why does the transition not reverse when cooled down to room temperature? What are the "pixelated" regions observed in asymmetric dyad crystals, and at the start of symmetric transitions before the emergence of an angled wavefront?

### 4.1.3 Results

Herein we report the first molecular-level mechanistic picture of the polymorphic transition that describes the molecular level movements that take place in thermochromic transition of symmetric MAN-NI dyads, as well as the thermochromic and colorless (or color neutral) transitions of asymmetric MAN-NI dyads. In contrast to previously reported
polymorphic systems with alkyl chains, ${ }^{83,116,118,119}$ the stimuli-induced thermochromic transition of symmetric MAN-NI dyads proceeded without altering the microscopic morphology of the original crystal while simultaneously exhibiting a dramatic visible color change in symmetric derivatives. Comprehensive standard and in situ heating XRD, grazing-incidence wide-angle Xray scattering (GIWAXS), non-contact atomic force microscopy (AFM), polarized optical microscopy (POM), spectroscopy, and differential scanning calorimetry (DSC) analyses were used to develop a full picture of the polymorphic switching process. Our analysis revealed that the MAN-NI dyads appear to be the first example of a polymorphic system involving a nucleation and growth mechanism that converts to a faster cooperative mechanism during a transition. The transition critically depends upon a complex interplay between the overall layered structure of the starting crystal, the thermodynamics of the two different polymorphs, and similar densities of the interconverting polymorphs.

### 4.2 DISCUSSION

### 4.2.1 Aliphatic Layer Packing Differences.

In all polymorphs except 1bo, dyads assemble to create an alternating bilayer type structure, with alternating alkyl and aromatic layers (Figure 4.1). However, the nature of alkyl chain packing differs markedly between the symmetric $\mathbf{O}$, symmetric $\mathbf{Y}$, and asymmetric polymorphs. Crystal structures of all head-to-head $\mathbf{O}$ polymorphs have alkyl chains in predominantly anti-staggered conformations, with side chains from adjacent layers interdigitating, forming a close-packed 'cork' and 'bottle' like structure (Figure 4.1, Figure 2.6). Alkyl side chains in head-to-tail Y crystals show more disorder and adopt mixtures of staggeredanti and gauche conformations and have segregated (i.e. not interdigitated) side chains (Figure 4.1, Figure 2.12). Disorder in $\mathbf{Y}$ side chains is seen by larger thermal displacement ellipsoids associated with side chains of $\mathbf{Y}$ crystals and multiple site occupancies for some alkyl chain atoms in $\mathbf{6 y}, \mathbf{7 y}$, and $7 \mathbf{y}^{\prime}$ (Figure 2.8, Table 2.2).

Importantly, in $\mathbf{O}$ crystals, the orientation of the dyad cores alternates in adjacent columns as shown in Figure 4.1. In other words, if a given aromatic stack in an $\mathbf{O}$ crystal has the NI units of the dyads oriented "up" in the crystal, both adjacent columns within the same layer will have the NI units oriented "down", and vice versa.


Figure 4.1 Crystal structures of $\mathbf{7 o}$ and $\mathbf{7 y}$ highlight the differences in all three packing dimensions, when viewed from two orthogonal perspectives. Top: Crystal structure of 70 showing head-to-head aromatic stacking geometry, perpendicular columns relative to the long axis of the dyad aromatic core, and interdigitated side chains. Bottom: Crystal structure of $7 \mathbf{y}$ showing head-to-tail dyad stacking geometry, adjacent columns tilted $49^{\circ}$ relative to the short axis of the aromatic dyad core, and segregated side chains. Previously, $7 \mathbf{y}^{*}$ was shown to have the same three dimensions of packing as $7 \mathbf{y}$, with the major difference being lack of long range crystalline order.

The nearly perpendicular relationship between columns in all $\mathbf{O}$ crystals appear to be stabilized through a combination of favorable side-chain packing and electrostatic interactions between the most polarized bonds in the dyads, namely the imide carbonyl C-O bonds and the CH bonds of alkoxy $\mathrm{O}-\mathrm{CH}_{2}$ groups of the MAN units as shown by dashed green lines in Figure 4.2a (section 2.4.1). These proposed $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ non-conventional hydrogen bonds create a zig-zag
network of connected dyads in the same layer of the crystal, and as seen in Figure 4.2b, the molecules linked in this way trace out an angle between $37-38^{\circ}$, relative to the long axis of the aromatic stacks, in $\mathbf{6 0}, \mathbf{7 0}$, and $\mathbf{8 0}$.


Figure 4.2 (a) Single-crystal structure of $7 \boldsymbol{o}$ illustrating intermolecular $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds (dashed green lines) between adjacent columns. Terminal side-chain atoms removed for clarity. (b) Cartoon depiction of typical orange crystal dimensions with preferred orientation: crystal long-axis is made from dyads stacked in columns, while the height of the crystal is made from alternating aromatic and alkyl layers. Projecting out of the cartoon is the 70 crystal structure as viewed from each unique crystal face, with H -atoms omitted on the line structures for clarity. Shown in space filling mode, six dyad molecules connected through the intercolumnar C-H $\cdots \mathrm{O}$ hydrogen bonding network shown in a). Top Right in magenta: When viewed from above the crystal, this intermolecular H-bonding network creates an angle relative to the long axis of the crystal of $37.5^{\circ}$ in $7 \mathbf{o}$ (shown in magenta), and $37.2^{\circ}$ in $\mathbf{6 0}$. Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

Asymmetric head-to-head packed M10N8 (yellow-orange crystals) and M8N6 (gold crystals) have unique alkyl layer packing, possessing a mix of interdigitated and segregated sidechain packing (Figure 4.3, Figure 2.16). Segregated NI side chains seen in Figure 4.3b decrease the interaction between adjacent layers in both derivatives, however a second subtle effect also decreases stability between layers. Unique to these two asymmetric derivatives is a hybrid alkyl/aromatic sublayer bordering both sides of each alkyl layer. Highlighted in Figure 4.3a, this hybrid sublayer contains alkyl and aromatic components across columns. This sublayer results in a decrease in the width of respective aromatic and the alkyl layers due to the staggered nature of asymmetric dyad packing.

b)




Figure 4.3 a) Packing of asymmetric M10N8 (yellow-orange crystals) and M8N6 (gold crystals) is characterized by head-to-head packing, adjacent columns rotated roughly orthogonal about the short axis of the dyad aromatic core, and a mixture of interdigitated and segregated side chains that result in hybrid alkyl and aromatic containing sublayers. b) Similar side chain packing in both derivatives, with a mix of interdigitated and segregated side chain packing between layers. Crystal structures shown as displacement ellipsoids set to the $50 \%$ probability level with hydrogen atoms omitted for clarity.

### 4.2.2 Orientations of Dyad Molecules in Crystals

Through a combination of transmission and GIWAXS experiments, done on both single and polycrystalline samples, as well as prediction of crystal morphology using Bravais, Friedel, Donnay, and Harker (BFDH) calculations from single-crystal data, the orientation of dyad molecules in each polymorph was determined (Figure 4.4a, section 2.3.3.5). In all dyad crystals, the long axis of the crystal is made from dyad aromatic stacking.

A schematic for orange dyad crystal packing is shown in Figure 4.4b. Orange crystals of symmetric dyads ( $\mathbf{6 0}, \mathbf{7 0}, \mathbf{8 0}, \mathbf{9 0}, \mathbf{1 0 0}$, and $\mathbf{1 2 0}$ ) are structurally analogous to a nice lasagna, with the relatively thick "noodle" layers comprised of highly ordered, closely packed alkyl side chains from adjacent layers, interdigitated in a 'cork' and 'bottle' fashion (Figures 2.4-2.7). The "meat/cheese/sauce" layers have the head-to-head aromatic dyad units stacked with the direction of stacking parallel to the long axis of the crystal (Figure $4.2 \& 4.4$ ).


Figure 4.4. Comparison of $\mathbf{7 o}$ and $\mathbf{7 y}$. (a) Cartoon illustrating preferred orientation, with alkyl and aromatic layers parallel to the substrate. Crystal structure of $7 \boldsymbol{o}$ showing head-to-head dyad core stacking geometry, perpendicular columns relative to the long axis of the dyad aromatic core, and interdigitated side chains (b) Schematic of 7 o packing. (c) Cartoon illustrating preferred orientation of $\mathbf{Y}$ crystals, with aromatic layers parallel to the substrate. Crystal structure of $7 \mathbf{y}$ showing head-to-tail dyad core stacking geometry, adjacent columns tilted $49^{\circ}$ relative to the short axis of the dyad aromatic core, and segregated side chains. Select crystallographic planes of $7 \mathbf{y}$ seen in 7y* are shown in green. (d) Schematic of 7y packing. Adapted with permission from Ref ${ }^{66}$. Copyright 2020 American Chemical Society.

The yellow material is also structured like a molecular lasagna (Figure 4.3d), but with important differences compared to the orange polymorph. In the yellow polymorph, the alkyl chains show more disorder, have a larger proportion of gauche conformations, and are no longer interdigitated between layers (Figure 4.3c \& 4.1). Similar to the orange material, however, the head-to-tail stacked aromatic dyad units of the yellow material are also stacked with the direction of stacking parallel to the long axis of the crystal.

As discussed in chapter 3, the general features of yellow material produced in various ways are consistent, especially with respect to dyad head-to-tail packing geometries, yet specific differences are present. Yellow crystals grown directly from solution (Y) exhibit a high level of short- and long-range order as indicated from single-crystal structures. On the other hand, thermally generated yellow material derived from orange crystals $\left(\mathbf{Y}^{*}\right)$ is best described as a soft-crystalline mesophase owing to long-range disorder and multiple variably oriented crystalline domains not seen in yellow crystals grown from solution (section 3.2.2.6).

### 4.2.3 Transition Moves Through the Orange Crystal as a Wavefront

When heated, we always observed the crystal-to-mesophase transition starting on the crystal boundary, or at a crystal defect, with the majority of a given orange-to-yellow transition sweeping along the long axis of the crystal (direction of stacking) as a wavefront, and different individual layers moving at slightly different rates (Figure $3.1 \& 3.2$, Movie $3.1 \& 3.2$ ). The wavefronts from each end meet in the interior of the solid to complete the conversion of the entire crystal. Using in situ heating transmission XRD, we could not detect any crystalline intermediate states during the transition process. In agreement with many proposed polymorphic transition mechanisms, ${ }^{69,86}$ we believe the transition wavefront represents an amorphous, fluidlike transition state between $\mathbf{O}$ and $\mathbf{Y}^{*}$ that enables the conformational switching from $\mathbf{O}$ to $\mathbf{Y}^{*}$ at this wavefront interface. Interestingly, the fastest wavefronts move at an approximately $38 \pm$
$4^{\circ}$ angle relative to the crystal long axis in what behaves like a highly cooperative or concerted process.

### 4.2.4 Structural Transition "Trigger"

So, what triggers the structural transition from the orange to the yellow polymorph prior to symmetric dyad crystals melting entirely? We propose that upon heating of the orange crystal, the structural transition "trigger" involves the local melting of the interdigitated alkyl chain layer, likely initiating through rotational isomerization of the alkyl side chains. Conformational isomerization of alkyl side chains would break the 'cork' and 'bottle' interaction between interdigitated side chains, resulting in an increase in disorder in the alkyl chain layer. This increase in disorder would allow for some translational movement within the alkyl chain layer, analogous to the fluidity exhibited within biological membranes. This flexibility and fluidity enables translational and/or rotational motion that has been seen in other alkyl chain containing polymorphic materials. ${ }^{83,116,118,119}$ The proposed triggering event, initiated by local melting of alkyl layers, does not disrupt the overall crystal morphology, apparently still held together by the stacked aromatics in between fluid alkyl layers as well as being confined by layers that have already transitioned, or are still in their orange crystalline form.

Importantly, we are assuming that the fluidity in alkyl side chains does allow the dyad molecules to move laterally within the layers of the material, to at least a limited extent. Even with fluidity in the alkyl chain layer, how do all of the molecules reorganize from head-to-head (O) to head-to-tail $\left(\mathbf{Y}^{*}\right)$ as the wavefront passes through the material without disrupting the overall crystal morphology? With the single exception of $\mathbf{1 b o}$, all symmetric dyad polymorphs have lamellar structures with consistent phase separation of alkyl and aromatic layers. A vertical "flip" of a single dyad within an $\mathbf{O}$ stack would convert the head-to-head packing into the head-to-tail packing seen in $\mathbf{Y}^{*}$. However, this vertical "flip" of the molecules is highly improbable as the phase separation would be lost during a "flipping" transition. The lowest energy transition
pathway that maintains the microscopic morphology of the crystal is thus expected to maintain this bilayer structure, with the majority of the reorganization happening within 2D dyad layers.

The head-to-head to head-to-tail stacking reorganization can readily occur with a limited lateral motion between adjacent layers of the dyads. Note in the structure of the orange material in Figure 4.1, the polarities of the adjacent head-to-head stacks of the dyads are exactly inverted with respect to each other in alternating fashion. Meaning, that if a given dyad molecule moves laterally into either adjacent stack in the solid, it will essentially be switching from the head-tohead orientation in its own stack to a head-to-tail orientation in the adjacent stack!

### 4.2.5 Both Faster and Slower Wavefronts are Seen in Orange Crystals of Symmetric Dyads

Slower transition wavefronts move in variable directions, however all share the same feature that they begin at an edge or crack and propagate away from regions that have already transitioned. The slowest transition wavefronts in symmetric crystals move parallel to horizontal crystal boundaries (Figure 3.2) while the fastest wavefronts move at an angle (Movie $3.1 \& 3.2$ ).

Analogous to growth of a new crystalline phase from a liquid phase, most phase transitions are believed to begin through initiation mechanisms that, in general, resemble nucleation and growth processes of crystals from solution. ${ }^{69,82}$ Initiation of all thermal transitions and the subsequent propagation of the slower transition wavefronts are believed to operate through these nucleation and growth mechanism. A crystal edge provides opportunity for dyad translational movement that does not exist in the packed crystal interior. ${ }^{69}$ Local melting of the alkyl chain layer allows for mobility within layers, and lateral motion within layers can allow for conformational sampling through translational movements without disrupting the crystal morphology. Conformational sampling on the crystal edges leads to nucleation of $\mathbf{Y}^{*}$ that then templates subsequent $\mathbf{Y}^{*}$ growth within the same layer. As multiple nucleation sites can emerge at different locations around a single crystal, and nucleation sights can have differences in orientation, multiple transitions across a single crystal give rise to numerous soft, polycrystalline
$\mathbf{Y}^{*}$ domains, and contributes to the observation that no SCSC transition was observed, despite numerous attempts. The darker "pixelated" region that makes up the majority of $\mathbf{Y}$ * in the first four images shown Figure 3.2 is attributed to these soft polycrystalline domains with variable orientations that formed from a nucleation and growth mechanism, the major transition observed at the start of transitions, and next to crystal edges and cracks, when dyads are not confined in all three crystallographic dimensions.

### 4.2.6 Why Do the Fastest Wavefronts Move at an Angle in Orange Crystals?

Interestingly, the fastest wavefronts move at an angle, and slower moving wavefronts speed up as an angled wavefront emerges. Because these fastest wavefronts move in a single direction through the crystal at speeds $1-2$ orders of magnitude faster than the slower wavefronts, the molecular rearrangements resulting in the transition along the wavefront are likely to be more or less concerted. A reasonable mechanistic hypothesis for the orange to yellow transition also needs to explain the observed $38 \pm 4^{\circ}$ angle of the transition wavefront relative to the long axis of the crystal, noting that this angle is the same as the proposed strongest intermolecular interaction between adjacent aromatic stacks in orange crystals, the proposed C$\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds (see Figure 4.2). We therefore propose that once one of the molecules in the $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonding network moves, the hydrogen bond to an adjacent molecule is disrupted. The loss of this hydrogen bond, that we believe stabilizes the geometry between columns, results in increased motion of the adjacent molecule, enabling its movement, and the disruption of the hydrogen bond to its adjacent molecule, and so on right down the entire $38^{\circ}$ line of hydrogen bonded molecules at the wavefront. This wavefront then moves down the crystal long axis, with a cooperative motion that turns the perpendicular dyad stacks parallel through a concerted "push", where successive dyads turn like individual pages when quickly flipping through a book. To the best of our knowledge, the observation of both thermally induced transition mechanisms operating in tandem and the switch from a nucleation and growth
mechanism on crystal edges to a cooperative mechanism in the crystal interior during a transition has not previously been reported.

### 4.2.7 Thermodynamic Balancing Act

DSC measurements confirmed that the orange material is the more stable at room temperature (and below) presumably because of the combination of a reasonably stable head-tohead stacking geometry, along with maximum van der Waals interactions between the perfectly ordered and close-packed staggered-anti, interdigitated alkyl chains. In the yellow form, stabilized by slightly more favorable electrostatic interactions on the periphery of the aromatic units, the presumably more stable head-to-tail stacking geometry is present, but the alkyl chains are no longer all staggered-anti, highly ordered, close-packed, or interdigitated. Importantly, modeling indicates that for geometric reasons, the dyad molecules cannot assemble in the more stable head-to-tail aromatic stacking orientation of the yellow solid and simultaneously accommodate the close-packed, staggered-anti, interdigitated alkyl chain layer seen in the orange crystal. The bottom line is that there is an energetic and structural trade-off between the two forms; more stable side chain packing but less stable aromatic stacking geometry in the orange form, yet more stable aromatic stacking geometry with less favorable alkyl chain packing in the yellow form. Affecting this balance, there is a dominating influence of entropy so that temperature becomes determinant of stability.

As mentioned above, the more highly ordered orange material is more stable at lower temperature because of larger surface area of contact and therefore an overall increased van der Waals attraction between adjacent molecules. However, at higher temperature, where $\Delta \mathrm{S}$ becomes more dominant, the yellow material is now more stable because of the more robust aromatic stacking geometry accompanied by a decrease in overall order (so an increase in intrinsic $\Delta \mathrm{S}$ ) of the alkyl chains. Serendipitously, the temperature at which the yellow form
becomes more stable than the orange form occurs for our dyad derivatives before the melting temperature of either the orange or the yellow material is reached.

Significantly, once the transition wavefront has gone through the heated crystal, cooling the solid does not bring back the orange material because the alkyl chains do not have the opportunity to repack, and so the material stays yellow. On the other hand, adding organic solvent vapor allows the surface alkyl chains to reorder at room temperature, regenerating the orange material only at the solid-air surface. Once reorganized on the surface back to the orange structure, the reorganization is propagated through the entire solid in a functional, or possibly mechanistic, reverse of the process observed upon heating.

### 4.2.8 Additional Evidence for Colorimetric Switching Mechanism

One expected consequence of the proposed mechanism is that each layer reorganizes more or less independently. As the alkyl bilayer becomes more fluid, associations between molecules in different layers are lost. In other words, once alkyl chains are no longer interdigitated, the proposed mechanism would predict that lateral diffusion of dyads and realignment to give head-to-tail stacking can occur at different rates in adjacent layers. Close inspection using optical analysis of extremely thin crystals undergoing the orange-to-yellow transition indicated that indeed the lower layers, closer to the heated surface, transitioned to yellow first, apparently independently from layers farther from the heated surface, that soon followed.

Side chain packing is expected to be critical for propagating the transition through the height of the crystal (e.g. through dyad layers). Local melting of a single alkyl layer disrupts stabilizing interactions in the adjacent aromatic layer, likely resulting in melting of the alkyl layer on the other side of this aromatic layer. Propagation of this disruption of alkyl-aromaticalkyl layers can thus be expected to enable the transition to proceed through dyad layers within
the crystal, in an analogous fashion to how cooperative transitions were previously described to propagate between columns.

The proposed mechanism would predict that the number of molecules in each layer would remain the same before and after the orange to yellow transition, but the morphology of each layer might change slightly as the molecules can diffuse laterally to some extent. Such minor changes in layer morphology, while maintaining overall layer volume, was indeed seen in the high-resolution AFM images of Figure 3.12. Further, similar densities of orange and yellow polymorphs support the small volume changes measured before and after heating (section 3.2.2.4).

Non-contact AFM of $7 \mathbf{7}$ * thin films observed the presence of more curved lamellae compared to $7 \boldsymbol{0}$ (Figure 3.12) and WAXS characterization of $7 \mathbf{y}^{*}$ generated from a heating single 70 crystal observed diffractions from lamellae with variable orientations (Figure 3.17). The presence of more curved lamellae in $7 \mathbf{y}^{*}$ thin films is an expected consequence for exposed surface layers that are observed to have significant morphological changes following heating which likely influence transitions in other adjacent, surface layers not confined in three dimensions (Figure 3.12). As discussed previously (section 4.2.4), multiple nucleation sites for $\mathbf{Y}^{*}$ were observed to form at various crystal edges/defects, and seen to give rise to multiple different transition wavefronts within individual crystals (Figure 3.2). Thus, individual $\mathbf{O}$ to $\mathbf{Y}^{*}$ transition waves propagating from differently oriented $\mathbf{Y}$ * nucleate lamellar growth with variable orientations, giving rise to variably orientated lamellae observed in non-contact AFM and WAXS experiments. The initiation of the transition in multiple individual locations provides a fitting explanation for why for why no single-crystal-to-single-crystal (SCSC) transition was observed. Further, it is known that SCSC transitions are often limited to small or nanocrystals ${ }^{69}$ and are often composed of rigid molecules that lack flexible alkyl chain substituents. ${ }^{97, ~ 99, ~ 108, ~ 110, ~}$ 131, 136

Methyl dyad 1 was synthesized before our detailed transition model was developed. Upon prolonged heating, crystals of dyad 1 remain bright orange and do not undergo a thermally
induced phase transition prior to sublimation $\left(284^{\circ} \mathrm{C}\right)$. In light of the proposed mechanism, this is as predicted. The methyl groups of $\mathbf{1}$ do not form a highly ordered, interdigitated alky chain bilayer (Figure 2.13), so there can be no triggering of a transition that would allow lateral motion of dyads in the solid state, as required in the other derivatives as the orange-to-yellow transition is triggered.

Crystal Size Dependent Transitions. In Chapter 3, the orange to yellow transition temperature was noted to have a dependence on size, where larger crystals transition at higher temperatures compared to smaller crystals (Figure 3.7). Physical size has been shown to influence the phase transition temperatures in a number of materials, most commonly nanomaterials including nanocrystals ${ }^{154,155}$ and nanorods, ${ }^{156}$ and more recently in perovskites. ${ }^{157}$ In these systems, a size dependence results from differences in surface energy and internal energy of each different crystal phase. ${ }^{156}$ Fewer reports exist for size-dependent transitions in organic, small molecule systems, however size-dependent differences in the glass transition temperatures of polymer films have been reported. ${ }^{158}$ The observation that larger crystals require more energy to transition, as measured by larger transition enthalpies, and the size-dependent variation in transition temperature supports the cooperative nature of the transition mechanism. On the other hand, it is possible that larger crystals, with a smaller surface area to volume ratio, had relatively fewer defects to nucleate growth of the new $\mathbf{Y}^{*}$ phase, and so kinetic effects cannot be definitively ruled out.

### 4.2.9 Asymmetric Dyad Materials

Asymmetric, head-to-head stacked M10N8 (yellow-orange crystals) and M8N6 (gold crystals) have the same preferred orientation features seen in symmetric dyad orange and yellow materials previously, with the long molecular axis being made of stacked aromatic dyad cores, and the height of crystals being made from alternating alkyl and aromatic sublayers (Figure 4.5). Both M10N8 (yellow-orange) and M8N6 (gold) have the structure of a molecular lasagna,
however, it deviates from the pristine molecular lasagnas of orange and yellow derivatives previously described. The formation of a hybrid alkyl and aromatic sublayer is better represented by an authentic lasagna, with intrusions between "noodle" and "meat/cheese/sauce" layers. On the molecular level, this intrusion manifests itself by the presence of alkyl and aromatic components within a defined region parallel to the substrate, highlighted in Figure 4.5.


Figure 4.5 Head-to-head stacked asymmetric M10N8 (yellow-orange crystals) and M8N6 (gold crystals) have preferred orientation with the same dimensional features orange and yellow crystals of symmetric dyads, but have a unique combination of interdigitated and segregated side chain packing that results in a hybrid alkyl and aromatic sublayer highlighted in beige.

Like orange crystals of symmetric dyads, asymmetric M10N8 (yellow-orange) and M8N6 (gold) are also seen to have a similar non-conventional $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds stabilizing adjacent columns, with an important difference resulting from adjacent columns being rotated roughly $90^{\circ}$ about the short dyad molecular axis. In contrast to the hydrogen bonded
network in orange crystals that trace out $\mathrm{a} \sim 38^{\circ}$ angle when viewed from above (Figure 4.2), the network of hydrogen bonds that link individual M10N8 (yellow-orange) and M8N6 (gold) dyads between adjacent columns trace out a line roughly perpendicular to the long axis of the crystal when viewed from above.

In an analogous manner, head-to-head stacked asymmetric dyads M10N8 (yelloworange) and M8N6 (gold) have the structural requirements believed to enable the head-to-head to head-to-tail polymorphic transition seen in orange crystals of symmetric dyads (Figure 4.3). Comparison of symmetric dyad orange (Figure 4.1) and yellow-orange M10N8 (Figure 4.3) crystal structures shows the similar existence of separate alkyl and aromatic layers, and adjacent columns with inverted polarities, such that head-to-head to head-to-tail switching could occur with limited lateral movement of dyads into adjacent columns. The two most significant differences seen between symmetric dyad orange crystals and asymmetric M10N8 (yelloworange) and M8N6 (gold) is a different intercolumnar geometry, and the presence of a hybrid alkyl/aromatic layer previously noted to decrease the overall width of the alkyl layer in asymmetric derivatives. The difference in column geometry between head-to-head symmetric and asymmetric dyad crystals would still allow for the head-to-head to head-to-tail intralayer switching in asymmetric crystals, and would require a smaller extent of columnar reorganization, and analogous local melting of the asymmetric alkyl layers.

Single-crystal structures of M8N6 (gold) and M10N8 (yellow-orange) reveal head-tohead stacking geometries with a dominant short-axis offset (Figure 2.17). This short-axis offset is in contrast to the dominant long-axis offset seen in orange crystals of symmetric dyads, which was previously shown to result in significant orbital overlap. This overlap was shown to be the photophysical basis for the red shift seen in orange crystals in the solid-state (section 2.4.3) and noted to be sensitive to small changes in molecular slip. While no single-crystal structure was solved, indexing of the M8N10 (orange-red) PXRD pattern revealed similar packing to 90, and the similar orange-red color and observed red shift is consistent with head-to-head packing similar to in symmetric dyads that form orange crystals.

While the three aforementioned asymmetric derivatives had head-to-head stacking, only M8N10 (orange-red) was seen to go through a thermochromic orange-red-to-yellow color change upon heating, which is as predicted based on proposed packing. However, the transition was observed to move through crystals from initiation locations all over the crystal surface, with no discernable cooperative movements observed in the thermochromic transition, and wavefronts proceeding parallel to all crystal dimensions at similar rates (section 3.2.3). With similar packing to orange crystals, the polymorphic switching in M8N10 is expected to occur through the same mechanism as seen in orange crystals, with local melting of the alkyl layer followed by conformational switching from head-to-head to head-to-tail, resulting in the observed orange-toyellow color change. As discussed previously (section 2.3.3.3), it is likely that variation in M8N10 side chain packing prevents the formation of the hydrogen bonding network seen in orange crystals, yet, the side chains still pack and allow for local melting of the alkyl layer. Observed transitions that initiate and propagate with no observed cooperative transition behavior is believed reflect the absence of long-range hydrogen bonded network previously shown to give rise to the cooperative transitions in orange crystals, but could also reflect differences in alkyl layer dynamics caused by packing of asymmetric side chains. Taken together, the thermochromic transition in M8N10 (orange-red-to-yellow) follows the same nucleation and growth transition pathway observed in orange crystals, yet differences in side chain packing compared to orange crystals prevent a cooperative thermochromic transition in M8N10.

In contrast to M8N10 (orange-red), the two other head-to-head packed asymmetric derivatives M10N8 (yellow-orange) and M8N6 (gold) had no clearly observable thermochromic transition prior to melting. Interestingly, despite having the same aromatic and side chain geometry, the same combination of interdigitated and segregated side chain packing, and the same hybrid alkyl/aromatic layer (Figure $4.3 \& 2.17$ ), only M10N8 (yellow-orange) was seen to have two thermal transitions; M8N6 (gold) melted directly to the isotropic phase when heated (Figure 3.19).

Why then does M10N8 have a thermal phase transition prior to melting, while M8N6 (gold) directly melts to the isotropic phase when heated? M10N8 (yellow-orange) was observed to have a colorless transition prior to melting, optically similar to the progression of the thermal transition seen in M8N10 (orange-red), with no discernable cooperative movements accompanying the formation of numerous "pixelated" regions. Further, M10N8 (yellow-orange) was found to have the lowest transition enthalpy for all crystal-to-mesophase transitions measured, with a measured enthalpy of $16.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (Table 3.4), roughly half that of the next smallest crystal-to-mesophase transition measured ( $\mathbf{6 0}, 32.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$, Table 3.2). The smallest crystal-to-mesophase transition enthalpy measured in M10N8 (yellow-orange) may reflect weaker interactions between side chains that are already partially segregated, and/or may reflect the smaller structural reorganization that would accompany a crystal-to-mesophase transition following a similar mechanism seen in orange crystals, as columns in M10N8 are already parallel about the long axis (Figure 2.15). Both M10N8 (yellow-orange) and M8N6 (gold) are noted to have a hybrid alkyl/aromatic layer, previously noted to decrease the net overlap between alkyl chains from dyads adjacent layers (Figures $4.3 \& 4.5$ ). The major difference between the two results from the interactions between side chains of adjacent layers. The shorter side chains in M8N6 (gold) have less overlap between interdigitated side chains compared to longer side chains in M10N8 (yellow-orange). Thus, while both had similar head-to-head stacking, intercolumnar, and side chain orientations, there is a decrease in interactions between side chains of adjacent layers in M8N6 (gold) compared to M10N8 (yellow-orange).

The difference in behavior when M10N8 (yellow-orange) and M8N6 (gold) are heated is believed to reflect a critical requirement for side chain overlap between adjacent layers, where sufficient overlap is required to enable local melting between adjacent layers, thus allowing for polymorphic switching to occur. Direct melting of M8N6 (gold) when heated can be attributed to a smaller overlap between side chains in adjacent layers that in turn prevents polymorphic switching to the corresponding mesophase at higher temperatures. During heating, thermal energy is thought to exceed the stabilizing interactions between M8N6 (gold) side chains within
individual alkyl layers, causing it to directly melt to the isotropic phase. In contrast, M10N8 (yellow-orange) crystals, with a larger extent of side chain overlap tip the balance by having sufficient side chain overlap to allow for local melting of the alkyl layer, and thus enable conformational sampling and switching to a metastable head-to-tail mesophase at higher temperatures, without melting of the solid.

In contrast to the orthogonal relationship between dyad long axes in orange crystals, the orthogonal relationship about the dyad short axis in M10N8 (yellow-orange) did not prevent a thermally induced crystal-to-mesophase transition. The colorless M10N8 (yellow-orange) crystal-to-mesophase was observed to proceed by a nucleation and growth type mechanism without observed cooperative transition behavior or significant differences in transition rates along different crystalline axes. This observation, combined with previously discussed nucleation and growth transitions in M8N10 (orange-red) further supports the role of side chain packing in enabling a cooperative transition.

Taken together, column orientation alone does not appear to dictate polymorphic switching behavior. In contrast, side chain packing appears to be the most critical factor in this stimuli-responsive transition, both enabling this dynamic process to occur, and also being critical for the emergence of observed cooperative transitions.

### 4.3 CONCLUSIONS

Symmetric Dyads. In conclusion, symmetric dyad orange crystals adopt a lamellar, layered structure, alternating between a highly ordered, interdigitated alkyl chain layer and stacked aromatic dyad cores, with the stacks aligned along the long axis of the crystals. Upon heating, the transition initiates when the alkyl chain layers become disordered, allowing for some degree of lateral diffusion and conformational sampling for dyads at a crystal phase boundary and within their own layer. Moving to either adjacent stack in the same layer allows a dyad to exchange a head-to-head stacking geometry (orange form) for a head-to-tail stacking geometry
(yellow form). The transition often initiates as a nucleation and growth mechanism that can transform to a cooperative transition wavefront that propagates through the interior of the crystal. The fastest moving wavefronts have an approximately $38^{\circ}$ angle with respect to the long axis of the crystal, corresponding to a C-H $\cdots \mathrm{O}$ hydrogen bond network of dyad molecules in adjacent stacks of the orange crystals.

In all transitions, the driving force for the crystal-to-mesophase transition appears to be that at lower temperature, the more highly ordered head-to-head form is lower in energy due to maximized van der Waals contacts, while at higher temperature, less ordered head-to-tail packing with disordered side chains is lower in energy, dictated in part by the increased importance of entropy at higher temperature. Once formed, the disordered, head-to-tail form becomes kinetically trapped and will persist in the absence of solvent vapor. Remarkably, the crystal-to-mesophase transition is apparently triggered at a temperature that is very close to the temperature at which the head-to-head and head-to-tail forms exchange as the most stable form. Just as remarkably, the transition occurs at a temperature that is lower than the melting point of the original head-to-head, or final head-to-tail solid.

Asymmetric Dyads. In asymmetric dyads, crystals exhibiting head-to-head stacking geometry are observed to have both thermochromic and non-thermochromic crystal-tomesophase, dependent on the initial dyad stacking geometry. In asymmetric dyads, transitions proceed exclusively through nucleation and growth pathways and are attributed to differences in side chain packing in asymmetric derivatives that prevent cooperative transitions seen in symmetric dyads. Side chain overlap between adjacent layers was shown to be the determinant factor for the emergence of polymorphic switching behavior in asymmetric dyads.

## CHAPTER 5

# Synthesis and Self-Assembly Properties of Symmetric and Asymmetric Perylene Diimides (PDIs) for Energy Conversion Applications 

### 5.1 CHAPTER SUMMARY

### 5.1.1 Introduction

Perylene diimides (PDIs) are widely used as dyes and pigments due to their electronic and structural properties: they strongly absorb light and have high photo and thermal stability. PDIs can also enable electronic energy conversion through spin allowed processes both in the solid-state and when interfaced with other materials (e.g. quantum dots). Theoretical calculations show that PDIs can be used for photon downconversion when certain slip stacking geometries are adopted. However, control over supramolecular assembly in PDI materials is not well understood. Deriving principles for the rational supramolecular assembly of PDI derivatives in the solid-state, with control over slip stacking geometry, is still a challenge despite a plethora of PDI crystal structures being reported. In addition, PDI derivatives have the potential to be useful for photon downconversion purposes, although synthetic challenges exist for making soluble PDI derivatives that can be interfaced with inorganic nanocrystals.

### 5.1.2 Scientific Questions

This chapter seeks to answer: How will varying substitutions on imide substituents change solid-state packing of PDI derivatives? How will different regioisomeric substitution patterns affect solid-state PDI assemblies? Can solid-state packing of PDI derivatives be rationalized by modern aromatic interaction theory? Can general procedures allow for the synthesis and purification of asymmetric PDIs with variable carboxylic acid linkers?

### 5.1.3 Approach

In symmetric PDI derivatives, derivatives were synthesized using commercially available benzylic amines with different regioisomeric substitution patterns to explore the influence of substitution pattern and position on solid-state self-assembly of PDI derivatives. Crystals were grown and single crystal structures solved that allowed for structural evaluation. Asymmetric PDIs would be synthesized following established protocols, with a goal being to create general synthetic procedures for the synthesis of asymmetric PDIs with variable carboxylic acid linkers.

### 5.1.4 Results

Analysis of reported crystal structures provided insight on determinants of PDI selfassembly, and are in line with modern aromatic interaction theory. A strategy for the rational design of new PDI N -imide substituents allowing for access to new slip stacking geometries was developed following the analysis. Three new symmetric PDI derivatives were synthesized using regioisomers that allowed for evaluation of the design strategy, and single-crystal structures were solved. Regioisomeric substitutions were found to alter optical properties, where 2,6-difluoroPDI was found to form a red solid, and 3,5-difluoro-PDI was found to form a black solid. Calculation of molecular slips verified the strategy as a means for accessing new symmetric PDIs for singlet fission materials. Characterization of symmetric PDIs is reported using low-resolution and high-resolution mass spectrometry, and reaction by-products and MS fragments are
identified. Asymmetric PDIs were successfully synthesized and purified, and a generalizable purification procedure as well as strategies for working with notoriously insoluble PDIs is reported.

### 5.2 BACKGROUND

### 5.2.1 Structural Modifications and Self-Assembly of PDI Derivatives

Structurally similar to NDI, perylene-3,4,9,10-perylene tetracarboxylic acid diimides (PDIs) are a related diimide with a five-ring perylene core. The presence of a strongly polarizing diimides on the peri positions of the perylene core (Figure 5.1) allow for useful comparisons to be made between assemblies made from PDI and NDI derivatives. As such, many of the aromatic interactions discussed in chapter 1 will be useful for understanding and rationalizing the self-assembly and solid-state packing of PDI derivatives described in this chapter. Synthetic modifications of perylene diimides ${ }^{159-163}$ can alter optical and energetic properties either through direct modifications of the perylene core that directly change energy of the frontier orbitals, ${ }^{164}$ or through substitutions to the imide position ${ }^{121,160}$ that change how PDI derivatives pack in the solid-state ${ }^{165-167}$ or self-assemble ${ }^{168-172}$ in solution. Modifications to ortho ${ }^{164,173,174}$ and bay ${ }^{175-177}$ positions are well documented, with the latter known to cause twisting of PDI cores, ${ }^{178}$ resulting in changes in optical and energy conversion properties.


Figure 5.1 Positions where PDIs can be functionalized. ${ }^{159}$

Recent reports of bay substituted PDIs shows differences in self-assembly properties. In 2021, Shang and coworkers reported three different bay substituted PDI derivatives with different bay substitution patterns. ${ }^{179}$ A single-crystal structure of a PDI derivative fluorinated on the 1- and 7-position of the perylene core are seen to pack in columns, and the strong C-F bond dipole (fluorine Pauling electronegativity is 4.0 ) is seen to either be localized behind an adjacent C-F bond, or position the fluorine atom above the imide carbonyl carbon. In both cases, the C-F bond can be thought of as contributing to the orientation of PDI self-assembly. Similar directing effects were shown with other polar, electron withdrawing groups. One derivative with a single cyano substitution on the bay position shows strong through space interactions between the electron withdrawing cyano group (group electronegativity of 3.3 , scaled to be comparable to Pauling scale ${ }^{4}$ ) and the imide carbonyl carbon of the adjacent PDI core. A final derivative brominated on the 1- and 7-position of the perylene core are noted to have twisted aromatic cores, resulting from the steric clash between each bromine and the opposite bay hydrogen atom. This twisting clearly will affect both the energy of the frontier orbitals, as well as influence the
degree of wavefunction overlap that can exist between adjacent PDI cores when packed in the solid-state.

In 2020, Sharber and Thomas showed that regioisomeric changes to fluorinated benzene side chains (Figure 5.2) result in changes in self-assembly and gave rise to variations in optical and stimuli-responsive (mechanochromic) properties (Figure 9). ${ }^{180}$ Importantly, simply by changing the fluorine substitution pattern on side chains between the three regioisomers shown in Figure 9, different solid-state packing was achieved and resulted in the observed differences in optical and stimuli-responsive properties.


Tetrafluoroinated Regioisomers

Figure 5.2 Regioisomeric substitution changes on tetrafluorinated benzene side chains enable differences in solid-state packing, resulting in different optical and stimuliresponsive that were attributed to the $\mathrm{C}-\mathrm{F}$ and $\mathrm{C}-\mathrm{H}$ bonds within the pendant side chains. ${ }^{180}$

### 5.2.2 PDI for Energy Conversion Applications

Singlet exciton fission is a photon down conversion process where a high energy excited state can be used to produce two separate, spin paired, electronically excited states. This process begins with the absorption of a photon by a molecule, resulting in the formation of an
electronically excited state. During this absorption process, spin is conserved, and thus the excitation results in a spin paired singlet excited state. Once excited, a number of different pathways are possible including fluorescence or radiationless internal conversion, where the excitation energy is lost as thermal energy.

In certain molecules, including polycyclic aromatics like tetracene ${ }^{181}$ and pentacene, ${ }^{182}$ the excited state energy can be efficiently transferred to adjacent molecules, and this process can favorable in the solid-state. Relaxation of the single spin-paired excited state can form two spin aligned triplet states when energy is conserved, namely when the triplet energies are half that of the singlet energy. Conservation of spin can be achieved when two molecules are involved, and thus this process can readily occur on faster time scales than could occur without flipping of spin, as in the case of intersystem crossing, typically a slow process in organic molecules.


Figure 5.3 The process for singlet fission can have both spin and energy conservation when two molecules are involved, and operate through successive electron and hole transfer. Reprinted with permission from Ref ${ }^{121}$. Copyright 2017 American Chemical Society.

Shown in Figure 5.3 is one of the postulated mechanisms showing how a two molecule, four electron system can create two spin aligned triplet excited states, following the excitation of one molecule to a spin paired, singlet excited state. The initial excitation on molecule "A" creates an electronically excited state when an electron is excited from the HOMO to the LUMO, with conservation of spin. This movement of the single electron creates a vacancy, or a 'hole' on
the HOMO of "A", and this electron and hole are then referred to as an exciton. The conservation of spin following the initial excitation is more specifically referred to as a singlet exciton. Transfer of the excited electron on "A" to the adjacent molecule "B" can create an ionic charge transfer state. This exciton is capable of migrating onto an adjacent molecule through an electron transfer process, when an electron is transferred from the HOMO of "B" to the LUMO of "A". The transfer of an electron with the opposite spin as the initially excited electron necessitates that this electron transferred must end up in a different orbital than the single electron in the HOMO of "A", as to not violate the Pauli exclusion principle. Energy can be conserved in this process when the initial excited state has double the energy of each triplet state. Thus, the generation of the two triplet excitons can form through processes that conserve energy and spin. Importantly, this process results in the creation of two different excited electronic states, yet only required a single electronic excitation.

Two major challenges for the application of this technology have proven to be the efficient absorption and production of triplet states and the efficient extraction of triplets once they are made. In 2013, Baldo and coworkers ${ }^{182}$ showed that singlet fission in pentacene films could form solar cells with quantum efficiencies above $100 \%$, showing that single photon absorption events can generate more than one charge carrier. While acenes are attractive because of their high charge-carrier mobility, ${ }^{183}$ they are known to be more reactive with increasing the number of rings ${ }^{184}$, and are known to undergo [4+2] cycloadditions with oxygen ${ }^{185}$ and this instability limits applications.

Perylene diimides (PDIs) appear to be valuable candidates for singlet fission applications. ${ }^{121,186}$ Since the 1950s, PDIs have found widespread use as dyes and pigments, especially in original automotive finishes, ${ }^{187}$ in part because of their high thermal, oxidative, and photostable properties. ${ }^{172,188}$ Beyond being more chemically stable, PDI derivatives have larger molar absorption coefficients $\left(\varepsilon>10^{4} \mathrm{M}^{-1} \cdot \mathrm{~cm}^{-1}\right)^{121,159,174,186}$ compared to acene based organic dyes ${ }^{189,190}$ which could allow for the use of less material and the production of thinner films.

In 2018, Roberts and coworkers ${ }^{121}$ showed that the rate of singlet fission can be predicted based on Redfield theory calculations as a function of slip stacking geometry in a series of PDI derivatives. The strong dependence for singlet fission rate on slip stacking geometries of PDI films is shown in Figure 5.4. Changes in slip stacking geometry are known to change the excitonic structure of PDIs in the solid-state, as excitations are delocalized over multiple PDI molecules ${ }^{167}$ where excited states are able to interact through short range orbital effects (e.g. HOMO-HOMO and LUMO-LUMO overlap), and longer range dipolar coupling mechanisms. ${ }^{141,}$ 191



Figure 5.4 Singlet fission rate in PDI materials is seen to depend on the slip stacking geometry of adjacent dyads. Reprinted with permission from Ref. ${ }^{121}$. Copyright 2017 American Chemical Society.

Theoretical calculations predicted that expanding into new slip stacking geometries would enable more functional singlet fission materials when singlet fission rate is maximized while the rate of triplet decay is minimized, by for example changing the binding interaction of the spin correlated triplet pair. As tuning of the imide substituent has been shown to change the
solid-state packing of PDI derivatives, ${ }^{165,166,192}$ PDI derivatives were sought that could expand into this unique slip-stacking space.

Photon upconversion is the functional the reverse process of singlet fission, the photon downconversion previously described. Typical organic molecules are not able to absorb light and generate an excited triplet state, as spin must be conserved, and the intersystem crossing that give rise to an excited triplet state is a slow process. As described previously, coupling of singlet excitons can give rise to triplet states, as in the case of PDIs in the solid state, with conservation of energy and spin.

Inorganic compounds are more effective at producing triplet states than many organics because of heavy atom effects that can induce strong spin-orbit coupling. ${ }^{193}$ In this process, coupling of electron spin and orbital angular momentum enhances the rate of intersystem crossing, while conserving energy and angular momentum, and thus increases the rate of triplet formation. ${ }^{193,194}$

It has also been shown that nanocrystal systems can sensitize (e.g., promote) the formation of triplet states. In some photon upconversion systems, ${ }^{190} \mathrm{PbS}$ nanocrystals have been shown to absorb lower energy photons (e.g. infrared), and generate excitons on nanocrystals. Following excitation, these nanocrystal systems can transfer multiple, lower energy triplets from nanocrystals to appended organic molecules (Figure 5.5) where lower energy excitons can be recombined, and result in the emission of a higher energy photon (e.g. visible).

Work by Roberts and coworkers ${ }^{190}$ has characterized the triplet energy transfer to surface bound carboxylic acid functionalized TIPS-pentacene (6,13-bis(triisopropylsilylethynyl)pentacene) ligands and showed the formation of intermediate triplet states localized on the nanocrystal surface, before being transferred to the acene derivative. This work highlighted the role the nanocrystal surface has in mediating energy transfer to appended ligands and the interactions between the nanocrystal and ligand as being influential for nanocrystal-based materials for photon upconversion purposes. For the same limitations
previously highlighted in the acene family (e.g. stability) investigations into photon upconversion using PDI functionalized nanocrystals is a worthy endeavor.


Figure 5.5 Functionalization of nanocrystals with organic molecules (e.g. TIPS-pentacene) can allow for energy conversion where triplets formed on PbS nanocrystals can be transferred to pentacene derivatives and recombined. Reprinted with permission from Ref. ${ }^{190}$ Copyright 2018 American Chemical Society.

### 5.3 Results

### 5.3.1 Literature Analysis of Symmetric PDI Crystal Packing

In order to rationally control the packing between PDI monomers in the solid-state to allow for maximal triplet exciton production while facilitating their extraction, an understanding of the non-covalent interactions that govern PDI packing is necessary. Following the established
notion that substitution of the imide side chains ${ }^{195,196}$ and PDI core ${ }^{178,} 197$ influences PDI packing, a survey of reported PDI crystal structures ${ }^{165,166,192}$ was completed.

This search focused on PDI derivatives with various N -imide substituents, and without any core functionalization. Shown in Figure 5.6 is a plot of the slip stacking geometries seen in 23 reported PDI crystal structures, grouped based off of general characteristics side chain identity (e.g. aliphatic versus aromatic). Five of these crystal structures had two different slip stacking geometries, due to multiple packing orientations in the crystal, and both reported slip stacking geometries are shown in Figure 5.6.


Figure 5.6: Slip-stacking geometries for reported PDI crystal structures ${ }^{165,166,192}$ shows the most variation in slip stacking comes from aromatic side chain-containing derivatives.

The largest variation in PDI slip stacking geometry is seen in derivatives with aromatic side chains, whereas many of aliphatic side chains display similar slip stacking geometries. Aliphatic chains with four or fewer carbons are seen to have a large variation in slip stacking.

Notably, there is clustering seen in longer aliphatic side chains possessing a $\sim 3 \AA$ long axis slip, and a shorter slip along the short axis (Figure 5.6 inset). The two aromatic derivatives seen with these stacking geometries have are pure hydrocarbons, being either a benzyl or m-xylenes side chain. It is worth pointing out that this $\sim 3 \AA$ long axis slip has a very similar geometry to that seen in the MAN-NI dyads described in chapters 2-4, which also contain an imide moiety. The outlier among aliphatic side chains has a long axis slip of $5.45 \AA$ and comes from a PDI with a branched sec-butyl side chain.
a)

b)

c)



Figure 5.7 Reported PDI crystal structure with key intermolecular interactions shown. ${ }^{166}$ a) PDI derivative with single-crystal structure shown in other panels. b) Distance between aromatic units of side-chain phenyl rings shown in green. c) Distance between H atoms and adjacent O atoms indicative of Hydrogen bonding that stabilize adjacent PDI columns. CCDC deposition number 1140280.

This survey identified the most relevant non-covalent interactions that should be manipulated in order to engineer new PDI derivatives that pack in predicted geometries. Analysis of published PDI crystal structures leads to the conclusion that aromatic side chains (Figure 5.6) and those capable of hydrogen bonding (Figure 5.7) allow for the greatest control over PDI packing morphologies in the solid-state. As shown in Figure 5.7, a methoxy benzyl side chain is seen to have aromatic interactions between adjacent benzyl side chains, and complementary hydrogen bonding between the methyl ethers.

### 5.3.2 Design \& Synthesis of Symmetric PDIs for Singlet Fission Purposes

As shown in Figure 5.7, the aromatic side chains play a role in PDI packing and in turn the slipped geometry adopted by the PDI cores. It is postulated that manipulation of the intermolecular interactions between aromatic side chains would influence the aromatic stacking geometry of the side chains, which would collectively influence the PDI cores stack relative to one another. In agreement with the aforementioned theory of aromatic interactions, we propose that substituting the $2,6 \mathrm{and} /$ or 3,5 position of the phenyl ring with more electronegative halogen atoms should increase the strength of this side chain interaction, yet in different ways for different regioisomers. It is further proposed that changing the strength of side chain interactions would in turn change the geometries adopted by the PDI cores as the side chains intermolecular interactions vary. In addition, the size and electronegativity of the substituted atom (e.g., Cl vs. F) should also change the geometry adopted, as both steric and dipolar changes would result.

Aromatic N -imide substituents were previously shown to have the largest range in slip stacking geometries and thus were chosen to explore other PDI chemical space. Several additional criteria were added in order to simplify the process. Aniline based amines were avoided, as imide formation with anilines requires more forcing conditions and often producing lower yields. Further, aniline derived imides have an orthogonal relationship between the PDI cores and the aromatic rings of the aniline side chains, and coplanarity of these moieties is not
seen due to the adjacent carbonyls. Benzyl amines and phenethyl amines would be explored, specifically those containing bonds that can direct the supramolecular assembly of PDIs, namely including strong bond dipoles in the form of fluorinated derivatives, and hydrogen bonding units like methoxy substituted derivatives. Further exploration of fluorinated derivatives would look at differences in assembly based on regioisomeric changes in fluorine substitution patterns (e.g. 2,6- versus 3,5-difluoro).

Guided by computational ${ }^{20,} 27,29-31$ and experimental ${ }^{34}$ theory regarding aromatic interactions, PDI derivatives with benzyl sidechains were synthesized in one step following established synthetic protocols ${ }^{160}$ using commercially available benzylic amines. Benzylic amines containing fluorines, chlorines, bromines, and methyl ethers were chosen based because of the strong influence they can exert on aromatic packing through hydrogen bonding and strong, through space dipolar interactions, as well as differences in steric size amongst the halogens. Each derivative was prepared on a 100 mg scale in a microwave reactor using the general procedure described in section 5.6.1. A general reaction scheme for symmetric PDI synthesis is shown below in Scheme 5.1.


Scheme 5.1 Example synthetic scheme for PDI synthesis, showing formation of the desired product and the undesired monoimide-monoanhydride by-product.

As symmetric PDI derivatives are sparingly soluble in organic solvents, purification of unreacted perylene dianhydride and the monoimide-monoanhydride adduct was achieved by stirring the crude reaction product in $10 \% \mathrm{KOH}$ (aq.). Unreported results showed that anhydrides were saponified in these conditions within seconds at room temperature. However, due to the insoluble nature of PDI derivatives, samples were stirred for 2-12 hours and frequently agitated in order to try and saponify all unreacted anhydride. Filtration of the desired product and washing with copious amounts of water removed carboxylate byproducts, affording the final products as solids with colors ranging from black to red. Shown in the bottom of Figure 5.8, filtering of crude products for the 3,5-difluoro-PDI yielded a red solid, while 2,6-difluoro-PDI yielded a black solid.


Figure 5.8 Crystal growth of indicated PDI derivatives shows variations in 1- and 2dimensional growth with various N-substituted benzylamine side-chains. Crystals shown grown from slow cooling of a saturated nitrobenzene solution. Bottom: different difluorobenzylamine regioisomers are seen to give rise to different optical properties as solids following purification.

### 5.3.3 PDI Single-Crystal Growth and Single-Crystal X-ray Diffraction Structures

Growth of PDI crystals was attempted using vapor diffusion, sublimation, and slow cooling of concentrated PDI solutions. The only solvent that yielded X-ray quality PDI symmetric crystals came from slow cooling of PDI derivatives dissolved in hot nitrobenzene, insulated to allow for slow cooling over periods of 24-48 hours, and crystals formed from this method are shown in the top of Figure 5.8.

High-quality single-crystals suitable for X-ray diffraction analysis were obtained using a recently reported microspace in-air sublimation method. ${ }^{198}$ In this method, crystals sublime at atmospheric pressure when heated on a hotplate at $350^{\circ} \mathrm{C}$ for periods of $1-5$ days and are grown on a cleaned glass substrate $\sim 100-200 \mu \mathrm{~m}$ above the sample. Only fluorinated PDI derivatives grew high quality single crystals by sublimation, and all fluorinated crystals were noted to be the largest crystals obtained and had the most structural integrity compared to other derivatives. Methoxy, and brominated derivatives sublimed but deposited as amorphous aggregates. Chlorinated derivatives were seen to grow 2-dimensional crystals, although the slightest manipulation resulted in bending of the crystal, after which time no diffraction could be observed.

Single crystal structures three different difluorinated PDI derivatives were obtained. A summary of crystallographic information for the three structures are provided in Table 5.1, and additional crystallographic information can be found in the Appendix. Interestingly, the three different crystals were found to have different space groups.

|  | PDI Crystal Structures |  |  |
| :---: | :---: | :---: | :---: |
|  | 2,6-difluoro-PDI | 3,5-difluoro-PDI | 3,4-difluoro-PDI |
| a ( $\AA$ ) | 4.89 | 28.58 | 6.73 |
| b (A) | 29.95 | 4.38 | 7.69 |
| c ( $\AA$ ) | 9.24 | 22.10 | 13.51 |
| $\alpha$ (deg) | 90 | 90 | 80.06 |
| $\beta$ (deg) | 105.04 | 103.684 | 85.94 |
| $\gamma$ (deg) | 90 | 90 | 73.35 |
| Volume [ $\AA^{3}$ ] | 1,306 | 2,684 | 659 |
| Space Group | P $121 / n 1$ | C $12 / \mathrm{c} 1$ | P-1 |
| Chemical Formula | $\mathrm{C}_{38} \mathrm{H}_{18} \mathrm{~F}_{4} \mathrm{~N}_{2} \mathrm{O}_{4}$ | $\mathrm{C}_{38} \mathrm{H}_{18} \mathrm{~F}_{4} \mathrm{~N}_{2} \mathrm{O}_{4}$ | $\mathrm{C}_{38} \mathrm{H}_{18} \mathrm{~F}_{4} \mathrm{~N}_{2} \mathrm{O}_{4}$ |
| $\underset{\left[\mathrm{g} \mathrm{~mol}^{-1}\right]}{\mathbf{M W}}$ | 642.54 | 642.54 | 642.54 |
| Density [ $\mathrm{g} \mathrm{cm}^{-3}$ ] | 1.634 | 1.590 | 1.619 |
| Z | 2 | 4 | 1 |
| $\begin{gathered} \mathbf{R} \\ \text { (reflections) } \\ {[\%]} \end{gathered}$ | 7.53 | 5.71 | 8.82 |
| $\begin{gathered} \text { wR2 } \\ \text { (reflections) } \\ {[\%]} \end{gathered}$ | 22.05 | 15.22 | 24.23 |
| Multiple Side Chain Occupancy | N/A | N/A | One benzyl ring has two site occupancies for all atoms bound to and in the ring; occupancy distribution 69:31 |

Table 5.1 Summary of crystallographic parameters for PDI single-crystal structures.
Calculation of slip stacking geometries for the three solved crystal structures shows a wide range of crystal slip stacking geometries that are achieved by the fluorinated side chain derivatives. Plotting of these slip stacking geometries alongside previous slip stacking geometry is shown in Figure 5.9, with abbreviations for each of the three structures inset. In order to make sense of the wide distribution seen in these three regioisomeric PDI derivatives, a closer inspection of each crystal structure is required.


Figure 5.9 Calculated slip stacking geometries of the three solved PDI crystal structures alongside previously shown slip stacking geometries (Figure 5.6).

Shown in Figure 5.10 are each of crystal structure shown as the single molecule making up the asymmetric unit. An angle can be defined that can describe the rotation seen in the benzylic side chain, where the angle is made from the intersection of the long axis of the PDI with a line that goes through the 2 and 6 carbons of each benzylic ring when viewed from above the PDI (shown in the top view of Figure 5.10). A similar angle is seen in benzylic side chains of the 2,6 and 3,5-difluoro derivatives, with a slightly larger torsion in the 2,6-derivative. The larger torsion in the 2,6 derivative may be due to an interesting electrostatic interaction between the fluorine and the carbonyl carbon, having a short measured distance of $3.099 \AA$. In comparison, the angle between the benzyl ring and the PDI long axis in the 3,4 derivative is ca. $90^{\circ}$. In order to understand the difference in these side chain orientations, packing must be taken into consideration.







Figure 5.10 Single-crystal structure of the three different PDI derivatives shows variable orientations of difluorobenzyl sidechains, with similarity seen in 2,6-difluoro-PDI and 3,5-difluoro-PDI. Multiple side chain occupancies shown in. Crystal structures shown as displacement ellipsoids set to the $50 \%$ probability level. Hydrogen atoms are omitted for clarity in some images. Note larger thermal ellipsoids in 3,5-difluoro-PDI are a result of the 5.0.1 beamline set up at the ALS (Lawrence Berkeley National Laboratory) where the data was collected by Dr. Vince Lynch, and can be attributed to limitations to the detector distance that limit resolution capabilities.

Shown in Figure 5.11 are trimers for each of the crystal structures based on packing of adjacent side chains. The $5.69 \AA$ long axis slip in the 3,4 derivative is clearly visible and results from the interdigitation of benzyl rings from adjacent PDI columns. The 3,4 derivative was seen to have a side chain in two site occupancies (details in Table 5.1) that can be seen in Figure 5.10, with slight rotational differences between the two conformations visible. The larger angle previously referenced in the 2,6 derivative is seen to result in the longer long axis slip ( $3.42 \AA$ ), compared to the 3,5 derivative $(1.38 \AA$ ) and is attributed to the 2,6 -difluoro substituents relative to the aromatic PDI cores, as well as interactions between adjacent side chains.


Figure 5.11 Single-crystal structures of trimers shown in space filling mode show how the different column morphologies that result across the three derivatives. Bottom: PDI derivatives stack in columns, view looking down sets of columns shows diversity of packing in various PDI derivatives.

Also shown in Figure 5.11 is the perspective when looking down on packed unit cells of each derivative. As expected for flat aromatic molecules, the PDI cores stack in columns, and the long axis of the crystals they form (Figure 5.8) is likely to be from this strong aromatic stacking interaction. It is interesting to note the different columnar orientations observed for each of the three derivatives.

### 5.3.4 Design and Synthesis of Asymmetric PDIs

A desire to covalently tether PDIs to lead-sulfide nanocrystal exists as described previously. In order to append PDIs to nanocrystals, a PDI should contain a carboxylic acid that can bind to the quantum dot surface. While symmetric, dicarboxylic acid PDI derivatives (e.g. N substituted glycine on each side of the PDI) would be suitable for this purpose, their extremely poor solubility in organic solvents limits their efficacy, as they require dissolution to engage in a ligand exchange and bind to the nanocrystal surface.

While synthetic modifications can be made at the ortho and bay positions of PDIs, (see Figure 5.1) these substitutions are well known to influence the electronic properties of PDI cores. The synthesis of asymmetric PDIs has been reported for various purposes ${ }^{199}$ including the study of interfacial electron transfer ${ }^{200}$ and the self-assembly of PDI nanobelts. ${ }^{201}$ Commonly in asymmetric PDI derivatives where solubility is desirable, "swallowtails" ${ }^{199}$ are introduced that enhance solubility, enabling chromatographic separation as well as the solution based exchange of carboxylic acid functionalized PDI derivatives onto surfaces, including ITO (tin-doped indium oxide). ${ }^{200}$

Experimental protocols and characterizations for all asymmetric PDI derivatives can be found in section 5.6.2. Briefly, dihexyl amine was accessed in excellent yield from the reductive amination of dihexylketone, and used directly to make PDI-Symmetric-Greasy. Desymmetrization of the PDI-Symmetric-Greasy in KOH afforded the monoimidemonoanhydride (MIMA) that was reacted with each amino acid to afford the asymmetric PDI derivatives.



Scheme 5.2 Synthetic scheme for the synthesis of asymmetric PDI derivatives.

### 5.4 DISCUSSION

### 5.4.1 Self-Assembly and Solid-State Packing of Symmetric PDI Derivatives

In the analysis of reported PDI crystal structures previously discussed, clustering of aliphatic PDI derivatives was shown (Figure 5.6) and is taken to reflect a small determinant influence of aliphatic side chain packing on PDI slip stacking geometry. In line with modern interaction theory introduced in chapter $1,20,27,29-31,33$ the clustering can be rationalized as having slip stacking geometry determined simply by the polarized PDI carbonyl bonds. Since these aliphatic side chains do not have strong dipoles present, they have little influence on packing geometries adopted by aromatic PDI cores, and as such, all aliphatic PDI derivatives are driven to assemble in the same general slip stacking geometry. This is further supported by previous observations of other imide containing molecules with comparable $\sim 3 \AA$ long axis slips, detailed in chapter 2 (see Figure 2.19), and said to be the result of imide determinant self-stacking.

Fluorinated benzyl amine side chains yielded single crystal structures and were noted to be the easiest to grow and easy to characterize. Short packing distances between side chains and differences in crystal structure match expectations based on the assumption that strong bond dipoles will determine aromatic stacking geometry.

Shown in Figure 5.12 are calculated ESPs for the different difluorobenzyl amines used as the side chains in the three PDI crystal structures. As expected, the fluorine atoms are seen to create strong C-F bond dipoles, and nearby C-H bond dipoles are shown to have complementary electrostatic potentials. It is interesting to note the change in electrostatic potential of the benzylic methylene unit in between the two fluorines of 2,6 difluorobenzyl amine derivative, compared to the other derivatives.




0


Figure 5.12 Calculated ESPs for different benzyl amines show strong C-F and C-H dipoles ( $\omega$ B97X-D, $6-311+\mathrm{G}^{* *}$ ).

Analysis of these difluorobenzyl side chains can lead to predictions about how various side chains will pack when appended to PDI cores. Shown in Figure 5.13 is a perspective view of the 2,6-difluoro-PDI crystal structure, with all short contacts measured, and categorized either based on the interaction type or the interaction geometry. As would be expected, the various C-H bond dipoles of the difluorobenzyl amine side chain make contacts to regions of high electron density, namely the carbonyl oxygen of adjacent PDI cores. On the other hand, fluorines are seen to make bidentate edge-to-face contacts with hydrogen atoms on the bay position of the PDI core, as well as having an interesting dipole interaction that aligns C-F dipoles opposite to one another in a face-to-face geometry (see $3.10 \AA$ contact in Figure 5.13).


Figure 5.13 Single-crystal structure of 2,6-difluoro-PDI with intermolecular contacts showing all the short contacts to a single 2,6-difluorobenzylamine side chain in the solidstate. Contacts are classified as either the interaction geometry or the type of interaction.

A similar analysis for the 3,5-difluoro-PDI derivative is shown in Figure 5.14, and while different individual contacts are observed, the same types of contacts are seen: C-H bonds interacting with imide carbonyl oxygens and fluorine atoms, and C-F bonds interacting with C-H bonds of other fluorinated side chains, as well as PDI hydrogens of the PDI core in a bidentate fashion.


Figure 5.14 Single-crystal structure of 3,5-difluoro-PDI showing close contacts to one difluorobenzyl ring making contacts to adjacent C-H bonds of PDI cores, difluorobenzyl rings, as well as contacts from C-F and carbonyl C-O bonds.

An analysis of ESPs of the three different PDIs is shown in Figure 5.15 in order to make sense of the repeated observations of fluorine atoms interacting with hydrogens in the bay positions of PDI cores. Similar to ESPs calculated for naphthalimides shown in chapter 1 and 2, the strongly polarizing carbonyls are seen to compliment the positive electrostatic potential seen on the aromatic hydrogen atoms of the PDI core. It is interesting to note that the polarized bonds appear to be the carbonyls, and the C-H bonds of the PDI core, as oppose to the C-F bonds of the side chains. While the C-F bonds may not be as strong of bond dipoles compared to imide C-O bonds, they clearly are able to have a dramatic effect on the self-assembly of PDI derivatives in the solid-state, and warrant further investigations as a tool for manipulating the self-assembly and energy conversion properties seen in PDIs.


Figure 5.15 Calculated ESPs for the three indicated PDI derivates using conformations found in single-crystal structures reveal similarities in electrostatics of PDI cores, and significant differences in electrostatic potentials of the various side chains based off of fluorine substitution position.

### 5.4.2 Synthesis of Asymmetric PDI Derivatives

Notably, the introduction of "swallowtails" on PDI imide positions has helps improve the poor solubility seen in symmetric PDI derivatives. This is expected and in agreement with literature reports, where branching of the side chain is known to help prevent coplanar, face-toface aggregation of PDI derivatives, due to the out of plane packing from the branched "swallowtails" (Scheme 5.2). ${ }^{159,172}$ Different synthetic routes have been reported for accessing asymmetric PDI derivatives, ${ }^{159}$ yet the formation of the symmetric PDI-Symmetric-Greasy prior to desymmeterization was found to result in the easiest chromatographic purifications.

As such, asymmetric PDIs were synthesized following the method outlined in Scheme 5.2, and chromatographic separations after each step allowed for access to a pure final asymmetric PDI. While the dihexylamine helped improve solubility of PDI derivatives, the large aromatic core still hinders solubility and can result in incomplete chromatographic purification. Dry loading of crude reaction mixtures was observed to greatly improve the efficacy and ease of chromatographic separations. Column chromatography using a series of mobile phase gradients, detailed in section 5.6.2, were found to allow for effective separations of various byproducts in the final step, and allow access to pure asymmetric PDI products. Noteworthy, gradients of DCM with increasing polarity from the addition of acetone helped to slowly elute by products, yet not move the desired PDI starting material. PDIs were effectively mobilized with acetic acid, likely through hydrogen bonding to the carbonyls. The same use of acetic acid and DCM mixtures is also noted to effectively dissolve PDI derivatives and intermediates, allowing for easy removal from filter papers. To make working with derivatives easier, intermediates and final PDI products were freeze dried (lyophilized) from benzene, following previous reports. ${ }^{202}$

### 5.4.3 Characterization of PDI Derivatives

Poor solubility for symmetric benzylic side chain derivatives precluded characterization using NMR spectroscopy, and as such, the majority of the products were characterized using mass spectrometry (MS). Initial characterization and synthetic procedure optimization utilized Fourier-transform infrared spectroscopy (FTIR). Using FTIR, the starting material and product could be easily visualized from quick FTIR spectral analysis of the crude sample in the solidstate. Differentiation of the starting anhydride and the final imide product was seen based on changes to the carbonyl $\mathrm{C}=\mathrm{O}$ stretching frequency, ${ }^{160,203}$ with the starting anhydride carbonyl having strong peaks at 1766 and $1730 \mathrm{~cm}^{-1}$ while the final diimide product had observed peaks at 1690 and $1655 \mathrm{~cm}^{-1}$ with no prominent peaks observed above $1700 \mathrm{~cm}^{-1}$.

A number of undesired masses were seen in low-resolution MS experiments, many of which are exemplified in Figure 5.16. The spectrum shown is that of the symmetrically substituted 3,5-difluoro-PDI, and the parent mass is observed as [M] at $642 \mathrm{~m} / \mathrm{z}$. The other prominent peaks in the spectrum are attributed to fragments from the desired symmetrically substituted PDI product, the undesired monoimide-monoanhydride by-product, and interestingly, nucleophilic aromatic substitutions seen between fluorinated benzylic amine side chains. These structures of ions that are believed to give rise to several of these peaks are shown in Figure 5.17.


Figure 5.16 Low-resolution mass spectra for example PDI derivative (3,5-difluoro) shows the parent ion as $[\mathrm{M}]^{-}$at $642 \mathrm{~m} / \mathrm{z}$. Peaks at 405 and 517 are believed to result from fragmentation and 266 is believed to be a byproduct of side-chain reactions.


Figure 5.17 Potential structures that give rise to ions shown in Figure 5.16.

Fragmentation between the imide and the benzene ring, either the $\mathrm{C}_{\text {Aromatic }} \mathrm{C}_{\text {Benzylic }}$ or $\mathrm{C}_{\text {Benzylic }}-\mathrm{N}_{\text {Imide }}$ bond is possible in chemical ionization (CI) methods, and would generate two different ions separated by 12 mass units. Interestingly, a feature seen during synthesis of fluorinated PDI derivatives was a prominent ion at $266 \mathrm{~m} / \mathrm{z}$ with certain side chains. In the reaction conditions for PDI formation $\left(165^{\circ} \mathrm{C}, 1 \mathrm{hr}\right.$, base), nucleophilic aromatic substitution of one benzylic amine on another is a reasonable mechanism for the formation of the $266 \mathrm{~m} / \mathrm{z}$ by product. This putative species is not removed during the standard aqueous workup procedure, but could be removed with acidic washing.

One final note on interpretation of PDI mass spectrum: the monoimide-monoanhydride byproduct and the fragmentation of the desired PDI product on the $\mathrm{C}_{\text {Benzylic }}-\mathrm{N}_{\text {Imide }}$ bond are separated by a single mass unit. Note in Figure 5.18 the inclusion of a larger peak at 517 and a smaller at $516 \mathrm{~m} / \mathrm{z}$. The peak at $517 \mathrm{~m} / \mathrm{z}$ correspond to the monoimide-monoanhydride byproduct with no ${ }^{13} \mathrm{C}$ atoms, while the peak at 518 corresponds to the byproduct with one ${ }^{13} \mathrm{C}$ atom. The peak at 516 is not from this byproduct; this peak is attributed to fragmentation of the desired PDI product along the $\mathrm{C}_{\text {Benzylic }}-\mathrm{N}_{\text {Imide }}$ bond, initially forming the resonance stabilized benzylic fragment.
MSF20-1385_IrCIneg1 \#6819-6824 RT: 28.38-28.40 AV: 6 NL: 3.70E7
T: - c CI Q1MS [100.000-900.000]



Exact Mass: 517.1


Figure 5.18 Low-resolution mass spectrum of 2,6-difluoro PDI following workup.

### 5.5 CONCLUSIONS

An analysis of known PDI crystal structures revealed that, in line with modern aromatic interaction theory, N-substituted PDI crystals with aliphatic side chains that lack strong dipoles self-assemble with little variation in stacking geometry. As predicted by this theory, aromatic stacking geometry in these derivatives is determined by the interaction of strong dipoles, namely the imide C-O and C-H bond dipoles, and these interactions result in the consistent geometry observed across aliphatic side chain containing derivatives. Further along these lines, aromatic interactions were seen to influence the aromatic stacking geometry in the same analysis of reported structures. Thus, a design strategy for accessing new PDI slip stacking modes was put forth in line with modern aromatic theory. PDI slip stacking geometry was confirmed to be tightly influenced by aromatic interactions, and regioisomeric substitutions were found to allow access to a wide variety of slip stacking modes previously not observed. Taken together, this work showed that strong dipoles in aromatic side chains can be used as a design strategy for the self-assembly of PDIs for energy conversion purposes. Work in asymmetric PDI synthesis was successful, and two different asymmetric derivatives with varying carboxylic acid linkers were achieved, and a general synthetic and purification strategy to access these might allow structure activity relationships investigating the role of side chain length on PDI-nanocrystal assemblies for photon upconversion purposes to be carried out.

### 5.6 EXPERIMENTAL

### 5.6.1 Symmetric PDI Synthesis

## General Reaction For Symmetric PDI Derivatives:

Adapted from ref. ${ }^{160}$. To a 10 mL microwave tube with a stir-bar is added $100 \mathrm{mg}(0.25 \mathrm{mmol})$ of perylene-3,4,9,10-tetracarboxylic dianhydride (PDA), 4 equivalents ( 1 mmol ) of the benzylic amine, 5 mL DMF, and $50 \mu \mathrm{~L}$ of triethylamine (TEA). The bright red microwave tube is then
briefly stirred and sonicated for 5 minutes to aid in dissolution of starting material. The reaction is then heated in a microwave reactor $\left(\mathrm{T}_{\mathrm{Max}}=165^{\circ} \mathrm{C}\right.$, Power $=80 \mathrm{~W}$, Duration $=60 \mathrm{~min}$, high stirring) until the protocol is finished, at which time the microwave vial was cooled prior to removal and noted to be significantly darker in color. The microwave vial is then emptied into an Erlenmeyer flask, and the microwave tube is rinsed with DMF ( $2 \times 1 \mathrm{~mL}$ ) and $10 \%$ aq. KOH ( 3 x 1 mL ). An additional 50 mL of $10 \% \mathrm{aq} . \mathrm{KOH}$ is added to the reaction mixture and is stirred for 2-12 hours at room temperature. The reaction mixture was then filtered and washed abundantly with water until the filtrate was colorless and the filtrate reached pH 7 . The solid-product was then dried under vacuum to yield the corresponding symmetric perylene-3,4,9,10-tetracarboxylic diimide (PDI).

2,9-bis(2,6-difluorobenzyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (2,6-difluoro-PDI): HRMS (CI, Positive) Calc. for $\mathrm{C}_{38} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{~F}_{4}\left[\mathrm{M}^{+}\right]$642.1203, found 642.1207.

2,9-bis(3,5-difluorobenzyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (3,5-difluoro-PDI):
HRMS (CI, Positive) Calc. for $\mathrm{C}_{38} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{~F}_{4}\left[\mathrm{M}^{+}\right]$642.1203, found 642.1185.

2,9-bis(3,4-difluorobenzyl)anthra[2,1,9-def:6,5,10-d'e'f'] diisoquinoline-1,3,8,10(2H,9H)-tetraone (3,4-difluoro-PDI):
HRMS (CI, Negative) Calc. for $\mathrm{C}_{38} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{~F}$ [M-] 642.1203, found 642.1201.

### 5.6.2 Asymmetric PDI Synthesis

Tridecan-7-amine (dihexylamine): Adapted from Ref. ${ }^{200}$ To an oven dried RBF with a stir bar is added tridecan-7-one $(10.00 \mathrm{~g}, 50.42 \mathrm{mmol})$, ammonium acetate $(38.88 \mathrm{~g}, 504 \mathrm{mmol})$ and $\mathrm{NaBH}_{3} \mathrm{CN}(2.20 \mathrm{~g}, 35.7 \mathrm{mmol})$ and was dissolved in dried methanol $(108 \mathrm{~mL})$. The reaction was monitored by GCMS, and upon completion after 24 hours, the reaction was quenched by the $10 \%$ aq. KOH to pH 12 . The reaction mixture was then extracted with $\mathrm{DCM}(50 \mathrm{~mL} \mathrm{x} \mathrm{4})$. Organic fractions were then combined and washed with brine ( $100 \mathrm{~mL} \times 2$ ), dried with $\mathrm{Na}_{2} \mathrm{SO}_{4}$,
and reduced under vacuum to afford tridecan-7-amine as a clear oil $(9.59 \mathrm{~g}, 48.1 \mathrm{mmol}, 95.4 \%$ yield) that was used without further purification. Note: Caution must be taken when dealing with cyanide containing mixtures. Oxidation of the sodium cyanide salt in the aqueous layer following the reaction was done in an ice-cooled bath by the slow addition of bleach, following standard protocols. ${ }^{204}{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 2.65(\mathrm{dt}, J=7.3,3.6 \mathrm{~Hz}, 1 \mathrm{H}), 1.39-1.20(\mathrm{~m}, 20 \mathrm{H})$, $1.08(\mathrm{~s}, 2 \mathrm{H}), 0.87(\mathrm{t}, J=6.8 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 51.36,38.36,32.02$, 29.64, 26.29, 22.77, 14.21. HRMS (ESI, positive): Calc. for $\mathrm{C}_{13} \mathrm{H}_{29} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+}$200.2373, found 200.2368 .

## 2,9-di(tridecan-7-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone

(PDI-Symmetric-Greasy): Procedure adapted from Ref. ${ }^{200}$. In an oven dried 250 mL RBF with a stir bar is added perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) ( $1.12 \mathrm{~g}, 2.85 \mathrm{mmol}$ ), tridecan-7-amine ( $1.42 \mathrm{~g}, 7.13 \mathrm{mmol}$ ), and imidazole ( $4.86 \mathrm{~g}, 71.3 \mathrm{mmol}$ ). The solids reaction mixture was stirred and heated to $180^{\circ} \mathrm{C}$ for 4 hours. The reaction was then allowed to cool to room temperature. Then 30 mL of ethanol was added to the reaction mixture, which was then transferred to an Erlenmeyer flask, and the RBF was washed out with IPA ( $\sim 10 \mathrm{~mL}$ ) and $\mathrm{H}_{2} \mathrm{O}$ ( $\sim 10 \mathrm{~mL}$ ) to help remove all the product. To this flask was then added $125 \mathrm{~mL} 2 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}$. The reaction mixture was then stirred overnight at room temperature. The next day, the solid crude product was filtered and rinsed with $\mathrm{H}_{2} \mathrm{O}(\sim 500 \mathrm{~mL})$ and dried under vacuum. The crude material was then loaded onto silica using DCM, reduced, and dried under vacuum. The crude material adsorbed onto silica was then purified via column chromatography ( $2: 1$ (v/v) DCM:hexanes) and concentrated under vacuum to yield PDI-Symmetric-Greasy as a dark red oily solid ( $1.54 \mathrm{~g}, 2.04 \mathrm{mmol}, 71.6 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.74-8.58(\mathrm{~m}, 8 \mathrm{H})$, $5.19(\mathrm{tt}, J=9.2,5.8 \mathrm{~Hz}, 2 \mathrm{H}), 2.25(\mathrm{dtd}, J=14.1,9.7,4.8 \mathrm{~Hz}, 4 \mathrm{H}), 1.91-1.80(\mathrm{~m}, 4 \mathrm{H}), 1.39-$ $1.16(\mathrm{~m}, 33 \mathrm{H}), 0.82(\mathrm{t}, J=6.8 \mathrm{~Hz}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 134.69,132.06,131.30$, 129.77, 126.63, 123.19, 54.92, 32.53, 31.91, 29.37, 27.08, 22.73, 14.19. HRMS (CI, negative): Calc. for $\mathrm{C}_{50} \mathrm{H}_{62} \mathrm{~N}_{2} \mathrm{O}_{4}[\mathrm{M}]^{-} 754.4710$, found 754.4733.

9-(tridecan-7-yl)-1H-isochromeno $\left[6^{\prime}, 5^{\prime}, 4^{\prime}: 10,5,6\right]$ anthra $[2,1,9-$ def $]$ isoquinoline-1,3,8,10(9H)tetraone (MIMA, monoimide-monoanhydride): Adapted from Ref. ${ }^{202}$. To a 230 mL 3-neck RBF with a stir bar was added 2,9-di(tridecan-7-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline1,3,8,10( $2 \mathrm{H}, 9 \mathrm{H}$ )-tetraone (PDI-Symmetric-Greasy) ( $1.03 \mathrm{~g}, 1.37 \mathrm{mmol}$ ), freshly ground KOH $(0.383 \mathrm{~g}, 6.83 \mathrm{mmol}, 5$ equiv.), and $t-\mathrm{BuOH}(35 \mathrm{~mL})$. The mixture was stirred and heated to reflux, and monitored via TLC. Disappearance of the starting PDI material was observed after 1.75 hours, at which time the reaction mixture was cooled and poured into a stirring flask containing 35 mL AcOH and 15 mL 2 M HCl , which continued to stir for 1 hour following the addition. The mixture was then filtered and the solid was washed with copious amounts of water until the filtrate was colorless and pH 7 then the crude solid was dried under vacuum. The crude material was loaded onto silica using 10:1 DCM: $\mathrm{AcOH}(\mathrm{v} / \mathrm{v}$ ), concentrated, and dried under vacuum. The crude material adsorbed onto silica was then purified via column chromatography (10:1 (v/v) DCM:AcOH) and concentrated under vacuum to yield MIMA as a red solid ( 397 mg $0.692 \mathrm{mmol}, 50.6 \%$ yield). To aid in future reactions, MIMA was freeze dried from benzene with $1 \%$ AcOH to yield MIMA as a fluffy dark red powder. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{cdcl}_{3}\right) \delta 8.77-$ $8.64(\mathrm{~m}, 8 \mathrm{H}), 5.18(\mathrm{tt}, J=9.4,5.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.24(\mathrm{dtd}, J=14.0,9.7,4.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.91-1.81(\mathrm{~m}$, $2 \mathrm{H}), 1.34-1.20(\mathrm{~m}, 16 \mathrm{H}), 0.82(\mathrm{t}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $126 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 160.15$, $136.62,133.75,132.08,129.69,127.03,126.76,124.09,123.33,119.23,55.08,32.51,31.90$, 29.34, 27.07, 22.72, 14.18. (HRMS (CI, Negative) Calc. for $\mathrm{C}_{37} \mathrm{H}_{35} \mathrm{~N}_{2} \mathrm{O}_{5}$ 573.2515, found 573.2528.

## 3-(1,3,8,10-tetraoxo-9-(tridecan-7-yl)-3,8,9,10-tetrahydroanthra[2,1,9-def:6,5,10-

$\boldsymbol{d}^{\prime} \boldsymbol{e}^{\prime} \boldsymbol{f}^{\prime} \mid$ diisoquinolin-2(1H)-yl)propanoic acid (PDI-Beta-Alanine): To a 10 mL microwave tube with a stir-bar is added MIMA $(12.9 \mathrm{mg}, 0.0224 \mathrm{mmol})$, beta-Alanine $(8.01 \mathrm{mg}, 0.0899$ mmol, 4 equivalents), 1.5 mL DMF, and $25 \mu \mathrm{~L}$ of triethylamine (TEA). The microwave tube is then sonicated briefly. The reaction is then heated in a microwave reactor $\left(\mathrm{T}_{\text {Max }}=165^{\circ} \mathrm{C}\right.$, Power
$=80 \mathrm{~W}$, Duration $=60 \mathrm{~min}$ ) until the protocol is finished and the microwave tube is then allowed to cool. The microwave tube is then emptied into an Erlenmeyer flask, and rinsed with DMF ( 2 x 0.5 mL ) and $10 \%$ aq. $\mathrm{KOH}(2 \times 1 \mathrm{~mL})$. An additional 30 mL of $10 \%$ aq. KOH is added to the reaction mixture and is stirred for 2 hours at room temperature. The mixture was then acidified using 1 M HCl to pH 1 . The solid product was then filtered and washed with water ( 100 mL ) and dried under vacuum. The crude product was then extracted off the dried filter paper by shaking the paper in a vial of 5 mL of $95 / 5(\mathrm{v} / \mathrm{v}) \mathrm{DCM} /$ acetic acid for 5 minutes. The isolated crude product was then reduced and dried under vacuum. Purification of the crude product by column chromatography was achieved using gradients to remove unwanted products starting with $100 \%$ DCM. Mobile phase gradients were then run as follows: $100 / 0 / 0$ to $80 / 20 / 0(\mathrm{v} / \mathrm{v})$ of DCM/acetone/acetic acid, a return to $100 \%$ DCM, then a slow increase from $100 / 0 / 0$ to $95 / 0 / 5$ DCM/acetone/acetic acid, and finally a slow increase in acetone from 95/0/5 to 90/5/5 DCM/acetone/acetic acid to elute the entire product band. Product fractions were combined, reduced, and dried under vacuum. The final product was then freeze-dried from benzene to yield the PDI-Beta-Alanine product as a dark-red fluffy solid ( $9.3 \mathrm{mg}, 0.014 \mathrm{mmol}, 64 \%$ ). HRMS (ESI, negative): Calc. for $\mathrm{C}_{40} \mathrm{H}_{40} \mathrm{~N}_{2} \mathrm{O}_{6}[\mathrm{M}]^{+}$643.2814, found 643.2820.

## 6-(1,3,8,10-tetraoxo-9-(tridecan-7-yl)-3,8,9,10-tetrahydroanthra[2,1,9-def:6,5,10-

$d^{\prime} e^{\prime} f^{\prime} \mid$ diisoquinolin-2(1H)-yl)hexanoic acid (PDI-Hexanoic Acid): To a 10 mL microwave tube with a stir-bar is added MIMA ( $10.0 \mathrm{mg}, 0.0174 \mathrm{mmol}$ ), 6 -aminohexanoic acid $(9.15 \mathrm{mg}$, 0.0697 mmol , 4 equivalents), 1.5 mL DMF, and $25 \mu \mathrm{~L}$ of triethylamine (TEA). The microwave tube is then sonicated briefly. The reaction is then heated in a microwave reactor $\left(\mathrm{T}_{\text {Max }}=165^{\circ} \mathrm{C}\right.$, Power $=80 \mathrm{~W}$, Duration $=60 \mathrm{~min}$ ) until the protocol is finished and the microwave tube is then allowed to cool. The microwave tube is then emptied into an Erlenmeyer flask, and rinsed with DMF ( $2 \times 0.5 \mathrm{~mL}$ ) and $10 \%$ aq. $\mathrm{KOH}(2 \times 1 \mathrm{~mL})$. An additional 30 mL of $10 \%$ aq. KOH is added to the reaction mixture, which is stirred for 2 hours at room temperature. The mixture was then
acidified using 1 M HCl to pH 1 . The solid product was then filtered and washed with water (100 mL ) and dried under vacuum. The crude product was then extracted off the dried filter paper by shaking the paper in a vial of 5 mL of $95 / 5(\mathrm{v} / \mathrm{v}) \mathrm{DCM} /$ acetic acid for 5 minutes. The isolated crude product was then reduced and dried under vacuum. Purification of the crude product by column chromatography was achieved using gradients to remove unwanted products starting with $100 \%$ DCM. Mobile phase gradients were then run as follows: $100 / 0 / 0$ to $80 / 20 / 0(\mathrm{v} / \mathrm{v})$ of DCM/acetone/acetic acid, a return to $100 \%$ DCM, then a slow increase from $100 / 0 / 0$ to $95 / 0 / 5$ DCM/acetone/acetic acid, and finally a slow increase in acetone from 95/0/5 to 90/5/5 DCM/acetone/acetic acid to elute the entire product band. Product fractions were combined, reduced, and dried under vacuum. The final product was then freeze-dried from benzene to yield the PDI-Hexanoic Acid product as a dark-red fluffy solid ( $7.5 \mathrm{mg}, 0.0109 \mathrm{mmol}, 62.8 \%$ ). HRMS (ESI, negative): Calc. for $\mathrm{C}_{43} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{O}_{6}$ [M] ${ }^{+}$686.3361, found 686.3341 .

## APPENDIX

## Single-Crystal X-ray Diffraction Data

Single-Crystal X-ray Diffraction information for Dyads 6y, 6y', 7y, 7y', 8y, 1bo, 6o, 7o, 80, 90, 100, 120, M6N8, M8N6, M10N8, and for PDI derivatives PDI-26F, PDI-34F, PDI-35F.

## CRYSTALLOGRAPHIC INFORMATION FOR 6Y

## Crystallographic Material for 6Y (6y).

X-ray Experimental.
Table 6Y.1. Crystallographic Data for 6Y.
Table 6Y.2. Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the non-hydrogen atoms of $6 \mathbf{Y}$.

Table 6Y.3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of $\mathbf{6 Y}$.
Table 6Y.4. Anisotropic thermal parameters for the non-hydrogen atoms of $6 \mathbf{Y}$.
Table 6Y.5. Fractional coordinates and isotropic thermal parameters $\left(\AA^{2}\right)$ for the hydrogen atoms of $\mathbf{6 Y}$.

Table 6Y.6. Torsion Angles $\left({ }^{(0)}\right.$ for the non-hydrogen atoms of $\mathbf{6 Y}$.

X-ray Experimental for complex $\mathrm{C}_{36} \mathrm{H}_{37} \mathrm{NO}_{3}(\mathbf{6 Y})$ : Crystals grew as long, yellow needles by slow evaporation from 1:1:1 Toluene:MeOH:EtOAc in a vial with the cap resting on top. The data crystal was cut from a much longer crystal and had approximate dimensions; $0.26 \times 0.06 \mathrm{x}$ 0.03 mm . The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{Cu} \mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA$ ) with collimating mirror monochromators. A total of 1032 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 15 seconds per frame with a detector offset of $+/-40.8^{\circ}$ and 46 seconds per frame with a detector offset of $+/-108.3^{\circ}$. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.' The structure was solved by direct methods using SuperFlip ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.3 Structure analysis was
aided by use of the programs PLATON98 ${ }^{4}$ and WinGX. ${ }^{5}$ The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

There are two molecules in the asymmetric unit. A portion of the $n$-hexyl side chain on one molecule was disordered about two primary conformations. The disorder was modeled by assigning the variable x to the site occupancy of one of the components and (1-x) to the alternate component of the disorder. A common isotropic displacement parameter was refined while refining x . The geometry of the two components was restrained to be equivalent throughout the refinement process.

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.0767 * \mathrm{P})^{2}+\right.$ $(0.4225 * \mathrm{P})]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)$ refined to 0.161 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0546 and a goodness of fit, $\mathrm{S},=0.991$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, $S$, are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. ${ }^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.37.31.
2) SuperFlip. Palatinus, L. Chapuis, G. (2007). J. Appl. Cryst. 40, 786-790.
3) Sheldrick, G. M. (2015). SHELXL-2013. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{W}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}} \mathrm{I}-\right| \mathrm{F}_{\mathrm{C}} \mathrm{l}\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 6Y. 1 Crystal data and structure refinement for $\mathbf{6 Y}$.

Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume
Z
Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=67.684^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices $[\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})]$
R indices (all data)
Extinction coefficient
Largest diff. peak and hole

C36 H37 N O3
531.66

100(2) K
$1.54184 \AA$
triclinic
P-1
$\mathrm{a}=8.7840(5) \AA \quad \alpha=88.389(4)^{\circ}$.
$b=13.4586(7) \AA \quad \beta=87.333(4)^{\circ}$.
$\mathrm{c}=24.0283(12) \AA \quad \gamma=81.921(4)^{\circ}$.
2808.7(3) $\AA^{3}$

4
$1.257 \mathrm{Mg} / \mathrm{m}^{3}$
$0.619 \mathrm{~mm}^{-1}$
1136
$0.260 \times 0.060 \times 0.030 \mathrm{~mm}^{3}$
3.317 to $74.321^{\circ}$.
$-10<=\mathrm{h}<=10,-16<=\mathrm{k}<=13,-20<=1<=29$
16816
$10845[\mathrm{R}($ int $)=0.0292]$
98.7 \%

Semi-empirical from equivalents
1.00 and 0.804

Full-matrix least-squares on $\mathrm{F}^{2}$
10845/3/755
0.991
$\mathrm{R} 1=0.0546, \mathrm{wR} 2=0.1381$
$\mathrm{R} 1=0.0855, \mathrm{wR} 2=0.1611$
n/a
0.372 and -0.238 e. $\AA^{-3}$

Table 6Y.2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $6 \mathbf{Y} . \mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $U^{\mathrm{ij}}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| N1 | 6021(2) | 4759(1) | 7638(1) | 20(1) |
| O1 | 3488(2) | 4749(1) | 7481(1) | 29(1) |
| O2 | 8540(2) | 4806(1) | 7800(1) | 27(1) |
| O3 | 10086(2) | 7626(1) | 2528(1) | 21(1) |
| C1 | 4755(2) | 4884(2) | 7298(1) | 20(1) |
| C2 | 5061(2) | 5166(1) | 6706(1) | 18(1) |
| C3 | 6549(2) | 5341(1) | 6514(1) | 16(1) |
| C4 | 7778(2) | 5232(1) | 6882(1) | 17(1) |
| C5 | 7514(2) | 4919(1) | 7469(1) | 20(1) |
| C6 | 3873(2) | 5249(1) | 6347(1) | 19(1) |
| C7 | 4130(2) | 5510(1) | 5785(1) | 20(1) |
| C8 | 5558(2) | 5704(1) | 5589(1) | 18(1) |
| C9 | 6803(2) | 5622(1) | 5947(1) | 17(1) |
| C10 | 8319(2) | 5806(1) | 5764(1) | 18(1) |
| C11 | 9491(2) | 5683(1) | 6135(1) | 18(1) |
| C12 | 9227(2) | 5403(1) | 6694(1) | 20(1) |
| C13 | 8618(2) | 6115(1) | 5199(1) | 19(1) |
| C14 | 8869(2) | 6394(1) | 4730(1) | 18(1) |
| C15 | 9175(2) | 6706(1) | 4166(1) | 18(1) |
| C16 | 8028(2) | 6803(1) | 3790(1) | 18(1) |
| C17 | 8284(2) | 7091(1) | 3228(1) | 19(1) |
| C18 | 9714(2) | 7308(1) | 3050(1) | 17(1) |
| C19 | 10950(2) | 7216(1) | 3423(1) | 16(1) |
| C20 | 12437(2) | 7412(1) | 3240(1) | 19(1) |
| C21 | 13621(2) | 7305(1) | 3599(1) | 20(1) |
| C22 | 13360(2) | 7019(1) | 4159(1) | 20(1) |
| C23 | 11929(2) | 6821(1) | 4348(1) | 19(1) |
| C24 | 10686(2) | 6909(1) | 3984(1) | 16(1) |
| C25 | 5796(2) | $4438(2)$ | 8226(1) | 24(1) |
| C26 | 6295(2) | $3316(2)$ | 8315(1) | 22(1) |
| C27 | 5169(2) | 2657(2) | 8110(1) | 24(1) |


| C28 | 5721(2) | 1529(2) | 8158(1) | 25(1) |
| :---: | :---: | :---: | :---: | :---: |
| C29 | 5985(2) | 1129(2) | 8752(1) | 25(1) |
| C30 | 6322(3) | -17(2) | 8772(1) | 30(1) |
| C31 | 8931(2) | 7715(2) | 2118(1) | 21(1) |
| C32 | 9660(2) | 8108(2) | 1588(1) | 23(1) |
| C33 | 8495(2) | 8466(2) | 1151(1) | 24(1) |
| C34 | 9278(3) | 8796(2) | 610(1) | 29(1) |
| C35 | 8151(3) | 9275(2) | 180(1) | 31(1) |
| C36 | 7380(3) | 10330(2) | 324(1) | 36(1) |
| N2 | 8951(2) | 10554(1) | 2300(1) | 22(1) |
| O4 | 11444(2) | 10628(1) | 2481(1) | 29(1) |
| O5 | 6455(2) | 10464(1) | 2115(1) | 26(1) |
| O6 | 4989(2) | 7448(1) | 7356(1) | 23(1) |
| C37 | 10196(2) | 10402(2) | 2643(1) | 21(1) |
| C38 | 9921(2) | 9984(1) | 3213(1) | 19(1) |
| C39 | 8438(2) | 9768(1) | 3385(1) | 17(1) |
| C40 | 7224(2) | 9916(1) | 3016(1) | 18(1) |
| C41 | 7473(2) | 10325(2) | 2444(1) | 21(1) |
| C42 | 11109(2) | 9856(1) | 3572(1) | 20(1) |
| C43 | 10852(2) | 9521(2) | 4124(1) | 21(1) |
| C44 | 9422(2) | 9310(1) | 4303(1) | 21(1) |
| C45 | 8182(2) | 9424(1) | 3941(1) | 18(1) |
| C46 | 6665(2) | 9228(1) | 4111(1) | 18(1) |
| C47 | 5504(2) | 9374(1) | 3736(1) | 20(1) |
| C48 | 5776(2) | 9713(1) | 3187(1) | 20(1) |
| C49 | 6353(2) | 8890(1) | 4667(1) | 20(1) |
| C50 | 6099(2) | 8618(1) | 5137(1) | 20(1) |
| C51 | 5813(2) | 8313(1) | 5702(1) | 19(1) |
| C52 | 6983(2) | 8225(1) | 6070(1) | 19(1) |
| C53 | 6757(2) | 7952(1) | 6634(1) | 21(1) |
| C54 | 5332(2) | 7734(1) | 6822(1) | 19(1) |
| C55 | 4076(2) | 7806(1) | 6459(1) | 18(1) |
| C56 | 2604(2) | 7600(1) | 6652(1) | 21(1) |
| C57 | 1403(2) | 7696(2) | 6301(1) | 22(1) |
| C58 | 1634(2) | 7987(2) | 5739(1) | 22(1) |
| C59 | 3056(2) | 8191(1) | 5541(1) | 22(1) |


| C60 | $4309(2)$ | $8107(1)$ | $5895(1)$ | $18(1)$ |
| :--- | ---: | ---: | ---: | ---: |
| C61 | $9167(2)$ | $11061(2)$ | $1754(1)$ | $25(1)$ |
| C62 | $8973(2)$ | $12199(2)$ | $1813(1)$ | $25(1)$ |
| C63 | $9076(2)$ | $12759(2)$ | $1255(1)$ | $26(1)$ |
| C64 | $9010(3)$ | $13891(2)$ | $1333(1)$ | $31(1)$ |
| C65 | $9178(4)$ | $14481(2)$ | $790(1)$ | $51(1)$ |
| C66 | $9275(6)$ | $15588(2)$ | $900(1)$ | $94(2)$ |
| C67 | $6116(2)$ | $7500(2)$ | $7763(1)$ | $22(1)$ |
| C68 | $5385(2)$ | $7272(2)$ | $8325(1)$ | $25(1)$ |
| C69 | $6551(3)$ | $7148(2)$ | $8777(1)$ | $34(1)$ |
| C70 | $5592(8)$ | $6876(6)$ | $9329(2)$ | $32(1)$ |
| C71 | $6638(6)$ | $6557(4)$ | $9803(2)$ | $37(1)$ |
| C72 | $5702(8)$ | $6469(5)$ | $10352(2)$ | $47(2)$ |
| C70A | $6004(8)$ | $7209(4)$ | $9380(3)$ | $33(1)$ |
| C71A | $5269(6)$ | $6280(4)$ | $9545(2)$ | $40(1)$ |
| C72A | $4587(8)$ | $6320(5)$ | $10142(2)$ | $55(2)$ |

Table 6Y.3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for $6 \mathbf{Y}$.

| N1-C1 | 1.400(3) | C18-C19 | 1.429(3) |
| :---: | :---: | :---: | :---: |
| N1-C5 | 1.399(2) | C19-C20 | 1.416(3) |
| N1-C25 | 1.477(2) | C19-C24 | 1.418(3) |
| O1-C1 | 1.214(2) | C20-C21 | 1.371(3) |
| O2-C5 | 1.221(3) | C20-H20 | 0.95 |
| O3-C18 | 1.356(2) | C21-C22 | 1.407(3) |
| O3-C31 | 1.438(2) | C21-H21 | 0.95 |
| C1-C2 | 1.484(3) | C22-C23 | 1.375(3) |
| C2-C6 | 1.376(3) | C22-H22 | 0.95 |
| C2-C3 | 1.414(3) | C23-C24 | 1.419(3) |
| C3-C4 | 1.416(3) | C23-H23 | 0.95 |
| C3-C9 | 1.421(3) | C25-C26 | 1.525(3) |
| C4-C12 | 1.379(3) | C25-H25A | 0.99 |
| C4-C5 | 1.477(3) | C25-H25B | 0.99 |
| C6-C7 | 1.401(3) | C26-C27 | 1.525(3) |
| C6-H6 | 0.95 | C26-H26A | 0.99 |
| C7-C8 | 1.376(3) | C26-H26B | 0.99 |
| C7-H7 | 0.95 | C27-C28 | 1.530(3) |
| C8-C9 | 1.412(3) | C27-H27A | 0.99 |
| C8-H8 | 0.95 | C27-H27B | 0.99 |
| C9-C10 | 1.435(3) | C28-C29 | 1.526(3) |
| C10-C11 | 1.383(3) | C28-H28A | 0.99 |
| C10-C13 | 1.430(3) | C28-H28B | 0.99 |
| C11-C12 | 1.402(3) | C29-C30 | 1.530(3) |
| C11-H11 | 0.95 | C29-H29A | 0.99 |
| C12-H12 | 0.95 | C29-H29B | 0.99 |
| C13-C14 | 1.200(3) | C30-H30A | 0.98 |
| C14-C15 | 1.432(3) | C30-H30B | 0.98 |
| C15-C16 | 1.374(3) | C30-H30C | 0.98 |
| C15-C24 | 1.438(2) | C31-C32 | 1.514(3) |
| C16-C17 | 1.411(3) | C31-H31A | 0.99 |
| C16-H16 | 0.95 | C31-H31B | 0.99 |
| C17-C18 | 1.376(3) | C32-C33 | 1.522(3) |
| C17-H17 | 0.95 | C32-H32A | 0.99 |


| C32-H32B | 0.99 | C47-C48 | 1.403(3) |
| :---: | :---: | :---: | :---: |
| C33-C34 | 1.527(3) | C47-H47 | 0.95 |
| C33-H33A | 0.99 | C48-H48 | 0.95 |
| C33-H33B | 0.99 | C49-C50 | 1.197(3) |
| C34-C35 | 1.529(3) | C50-C51 | 1.429(3) |
| C34-H34A | 0.99 | C51-C52 | 1.378(3) |
| C34-H34B | 0.99 | C51-C60 | 1.441(3) |
| C35-C36 | 1.526(3) | C52-C53 | 1.406(3) |
| C35-H35A | 0.99 | C52-H52 | 0.95 |
| C35-H35B | 0.99 | C53-C54 | 1.378(3) |
| C36-H36A | 0.98 | C53-H53 | 0.95 |
| C36-H36B | 0.98 | C54-C55 | 1.429(3) |
| C36-H36C | 0.98 | C55-C56 | 1.415(3) |
| N2-C37 | 1.389(3) | C55-C60 | 1.417(3) |
| N2-C41 | 1.401(2) | C56-C57 | 1.371(3) |
| N2-C61 | 1.479(2) | C56-H56 | 0.95 |
| O4-C37 | 1.222(2) | C57-C58 | 1.409(3) |
| O5-C41 | 1.213(3) | C57-H57 | 0.95 |
| O6-C54 | 1.361(2) | C58-C59 | 1.377(3) |
| O6-C67 | 1.434(2) | C58-H58 | 0.95 |
| C37-C38 | 1.487(3) | C59-C60 | 1.412(3) |
| C38-C42 | 1.373(3) | C59-H59 | 0.95 |
| C38-C39 | $1.415(3)$ | C61-C62 | 1.526(3) |
| C39-C40 | 1.407(3) | C61-H61A | 0.99 |
| C39-C45 | 1.421(3) | C61-H61B | 0.99 |
| C40-C48 | 1.380(3) | C62-C63 | 1.525(3) |
| C40-C41 | 1.484(3) | C62-H62A | 0.99 |
| C42-C43 | 1.409(3) | C62-H62B | 0.99 |
| C42-H42 | 0.95 | C63-C64 | 1.533(3) |
| C43-C44 | 1.373(3) | C63-H63A | 0.99 |
| C43-H43 | 0.95 | C63-H63B | 0.99 |
| C44-C45 | 1.414(3) | C64-C65 | 1.520(3) |
| C44-H44 | 0.95 | C64-H64A | 0.99 |
| C45-C46 | 1.433(3) | C64-H64B | 0.99 |
| C46-C47 | 1.382(3) | C65-C66 | 1.536(4) |
| C46-C49 | 1.426(3) | C65-H65A | 0.99 |


| C65-H65B | 0.99 | C70-H70A | 0.99 |
| :---: | :---: | :---: | :---: |
| C66-H66A | 0.98 | C70-H70B | 0.99 |
| C66-H66B | 0.98 | C71-C72 | 1.534(6) |
| C66-H66C | 0.98 | C71-H71A | 0.99 |
| C67-C68 | 1.511(3) | C71-H71B | 0.99 |
| C67-H67A | 0.99 | C72-H72A | 0.98 |
| C67-H67B | 0.99 | C72-H72B | 0.98 |
| C68-C69 | 1.517(3) | C72-H72C | 0.98 |
| C68-H68A | 0.99 | C70A-C71A | 1.520(6) |
| C68-H68B | 0.99 | C70A-H70C | 0.99 |
| C69-C70A | 1.506(7) | C70A-H70D | 0.99 |
| C69-C70 | 1.598(7) | C71A-C72A | 1.527(6) |
| C69-H69C | 0.96 | C71A-H71C | 0.99 |
| C69-H69D | 0.96 | C71A-H71D | 0.99 |
| C69-H69A | 0.96 | C72A-H72D | 0.98 |
| C69-H69B | 0.96 | C72A-H72E | 0.98 |
| C70-C71 | 1.512(6) | C72A-H72F | 0.98 |
| C1-N1-C5 | 125.12(16) | N1-C5-C4 | 117.35(17) |
| C1-N1-C25 | 118.79(16) | C2-C6-C7 | 119.97(18) |
| C5-N1-C25 | 116.09(16) | C2-C6-H6 | 120.0 |
| C18-O3-C31 | 118.45(14) | C7-C6-H6 | 120.0 |
| O1-C1-N1 | 120.93(18) | C8-C7-C6 | 120.63(18) |
| O1-C1-C2 | 122.61(19) | C8-C7-H7 | 119.7 |
| N1-C1-C2 | 116.45(16) | C6-C7-H7 | 119.7 |
| C6-C2-C3 | 120.70(17) | C7-C8-C9 | 120.74(17) |
| C6-C2-C1 | 118.76(17) | C7-C8-H8 | 119.6 |
| C3-C2-C1 | 120.53(18) | C9-C8-H8 | 119.6 |
| C2-C3-C4 | 120.52(17) | C8-C9-C3 | 118.68(17) |
| C2-C3-C9 | 119.26(18) | C8-C9-C10 | 123.06(17) |
| C4-C3-C9 | 120.22(17) | C3-C9-C10 | 118.26(17) |
| C12-C4-C3 | 120.28(17) | C11-C10-C13 | 120.07(17) |
| C12-C4-C5 | 119.76(18) | C11-C10-C9 | 119.75(17) |
| C3-C4-C5 | 119.95(17) | C13-C10-C9 | 120.19(18) |
| O2-C5-N1 | 120.34(17) | C10-C11-C12 | 121.40(17) |
| O2-C5-C4 | 122.32(18) | C10-C11-H11 | 119.3 |


| C12-C11-H11 | 119.3 | N1-C25-C26 | 112.10(17) |
| :---: | :---: | :---: | :---: |
| C4-C12-C11 | 120.07(18) | N1-C25-H25A | 109.2 |
| C4-C12-H12 | 120.0 | C26-C25-H25A | 109.2 |
| C11-C12-H12 | 120.0 | N1-C25-H25B | 109.2 |
| C14-C13-C10 | 178.7(2) | C26-C25-H25B | 109.2 |
| C13-C14-C15 | 178.9(2) | H25A-C25-H25B | 107.9 |
| C16-C15-C14 | 120.14(17) | C25-C26-C27 | 114.13(17) |
| C16-C15-C24 | 119.31(17) | C25-C26-H26A | 108.7 |
| C14-C15-C24 | 120.54(17) | C27-C26-H26A | 108.7 |
| C15-C16-C17 | 122.11(17) | C25-C26-H26B | 108.7 |
| C15-C16-H16 | 118.9 | C27-C26-H26B | 108.7 |
| C17-C16-H16 | 118.9 | H26A-C26-H26B | 107.6 |
| C18-C17-C16 | 119.35(18) | C26-C27-C28 | 114.32(17) |
| C18-C17-H17 | 120.3 | C26-C27-H27A | 108.7 |
| C16-C17-H17 | 120.3 | C28-C27-H27A | 108.7 |
| O3-C18-C17 | 124.87(17) | C26-C27-H27B | 108.7 |
| O3-C18-C19 | 114.32(16) | C28-C27-H27B | 108.7 |
| C17-C18-C19 | 120.80(17) | H27A-C27-H27B | 107.6 |
| C20-C19-C24 | 119.45(18) | C29-C28-C27 | 114.83(18) |
| C20-C19-C18 | 121.23(17) | C29-C28-H28A | 108.6 |
| C24-C19-C18 | 119.31(17) | C27-C28-H28A | 108.6 |
| C21-C20-C19 | 120.76(17) | C29-C28-H28B | 108.6 |
| C21-C20-H20 | 119.6 | C27-C28-H28B | 108.6 |
| C19-C20-H20 | 119.6 | H28A-C28-H28B | 107.5 |
| C20-C21-C22 | 120.09(17) | C28-C29-C30 | 111.45(18) |
| C20-C21-H21 | 120.0 | C28-C29-H29A | 109.3 |
| C22-C21-H21 | 120.0 | C30-C29-H29A | 109.3 |
| C23-C22-C21 | 120.39(18) | C28-C29-H29B | 109.3 |
| C23-C22-H22 | 119.8 | C30-C29-H29B | 109.3 |
| C21-C22-H22 | 119.8 | H29A-C29-H29B | 108.0 |
| C22-C23-C24 | 120.88(17) | C29-C30-H30A | 109.5 |
| C22-C23-H23 | 119.6 | C29-C30-H30B | 109.5 |
| C24-C23-H23 | 119.6 | H30A-C30-H30B | 109.5 |
| C19-C24-C23 | 118.42(17) | C29-C30-H30C | 109.5 |
| C19-C24-C15 | 119.09(17) | H30A-C30-H30C | 109.5 |
| C23-C24-C15 | 122.49(17) | H30B-C30-H30C | 109.5 |


| O3-C31-C32 | 106.37(15) | C37-N2-C41 | 125.22(16) |
| :---: | :---: | :---: | :---: |
| O3-C31-H31A | 110.5 | C37-N2-C61 | 117.55(16) |
| C32-C31-H31A | 110.5 | C41-N2-C61 | 117.10(17) |
| O3-C31-H31B | 110.5 | C54-O6-C67 | 117.76(15) |
| C32-C31-H31B | 110.5 | O4-C37-N2 | 120.55(18) |
| H31A-C31-H31B | 108.6 | O4-C37-C38 | 122.40(19) |
| C31-C32-C33 | 112.99(16) | N2-C37-C38 | 117.03(16) |
| C31-C32-H32A | 109.0 | C42-C38-C39 | 121.13(18) |
| C33-C32-H32A | 109.0 | C42-C38-C37 | 118.82(17) |
| C31-C32-H32B | 109.0 | C39-C38-C37 | 119.98(18) |
| C33-C32-H32B | 109.0 | C40-C39-C38 | 120.65(17) |
| H32A-C32-H32B | 107.8 | C40-C39-C45 | 120.37(17) |
| C32-C33-C34 | 111.61(17) | C38-C39-C45 | 118.95(18) |
| C32-C33-H33A | 109.3 | C48-C40-C39 | 120.43(18) |
| C34-C33-H33A | 109.3 | C48-C40-C41 | 119.19(18) |
| C32-C33-H33B | 109.3 | C39-C40-C41 | 120.34(17) |
| C34-C33-H33B | 109.3 | O5-C41-N2 | 120.99(18) |
| H33A-C33-H33B | 108.0 | O5-C41-C40 | 122.27(18) |
| C33-C34-C35 | 113.70(18) | N2-C41-C40 | 116.73(17) |
| C33-C34-H34A | 108.8 | C38-C42-C43 | 119.91(18) |
| C35-C34-H34A | 108.8 | C38-C42-H42 | 120.0 |
| C33-C34-H34B | 108.8 | C43-C42-H42 | 120.0 |
| C35-C34-H34B | 108.8 | C44-C43-C42 | 120.17(19) |
| H34A-C34-H34B | 107.7 | C44-C43-H43 | 119.9 |
| C36-C35-C34 | 114.1(2) | C42-C43-H43 | 119.9 |
| C36-C35-H35A | 108.7 | C43-C44-C45 | 121.19(18) |
| C34-C35-H35A | 108.7 | C43-C44-H44 | 119.4 |
| C36-C35-H35B | 108.7 | C45-C44-H44 | 119.4 |
| C34-C35-H35B | 108.7 | C44-C45-C39 | 118.64(17) |
| H35A-C35-H35B | 107.6 | C44-C45-C46 | 123.18(18) |
| C35-C36-H36A | 109.5 | C39-C45-C46 | 118.17(18) |
| C35-C36-H36B | 109.5 | C47-C46-C49 | 120.15(18) |
| H36A-C36-H36B | 109.5 | C47-C46-C45 | 119.82(18) |
| C35-C36-H36C | 109.5 | C49-C46-C45 | 120.03(18) |
| H36A-C36-H36C | 109.5 | C46-C47-C48 | 121.34(17) |
| H36B-C36-H36C | 109.5 | C46-C47-H47 | 119.3 |


| C48-C47-H47 | 119.3 | N2-C61-C62 | 111.00(17) |
| :---: | :---: | :---: | :---: |
| C40-C48-C47 | 119.86(18) | N2-C61-H61A | 109.4 |
| C40-C48-H48 | 120.1 | C62-C61-H61A | 109.4 |
| C47-C48-H48 | 120.1 | N2-C61-H61B | 109.4 |
| C50-C49-C46 | 179.1(2) | C62-C61-H61B | 109.4 |
| C49-C50-C51 | 178.6(2) | H61A-C61-H61B | 108.0 |
| C52-C51-C50 | 119.74(17) | C63-C62-C61 | 112.94(17) |
| C52-C51-C60 | 119.34(17) | C63-C62-H62A | 109.0 |
| C50-C51-C60 | 120.92(18) | C61-C62-H62A | 109.0 |
| C51-C52-C53 | 122.15(17) | C63-C62-H62B | 109.0 |
| C51-C52-H52 | 118.9 | C61-C62-H62B | 109.0 |
| C53-C52-H52 | 118.9 | H62A-C62-H62B | 107.8 |
| C54-C53-C52 | 119.15(18) | C62-C63-C64 | 111.46(18) |
| C54-C53-H53 | 120.4 | C62-C63-H63A | 109.3 |
| C52-C53-H53 | 120.4 | C64-C63-H63A | 109.3 |
| O6-C54-C53 | 124.22(18) | C62-C63-H63B | 109.3 |
| O6-C54-C55 | 114.56(16) | C64-C63-H63B | 109.3 |
| C53-C54-C55 | 121.22(17) | H63A-C63-H63B | 108.0 |
| C56-C55-C60 | 119.44(18) | C65-C64-C63 | 113.6(2) |
| C56-C55-C54 | 121.49(18) | C65-C64-H64A | 108.8 |
| C60-C55-C54 | 119.06(17) | C63-C64-H64A | 108.8 |
| C57-C56-C55 | 120.73(19) | C65-C64-H64B | 108.8 |
| C57-C56-H56 | 119.6 | C63-C64-H64B | 108.8 |
| C55-C56-H56 | 119.6 | H64A-C64-H64B | 107.7 |
| C56-C57-C58 | 119.95(18) | C64-C65-C66 | 111.1(2) |
| C56-C57-H57 | 120.0 | C64-C65-H65A | 109.4 |
| C58-C57-H57 | 120.0 | C66-C65-H65A | 109.4 |
| C59-C58-C57 | 120.39(19) | C64-C65-H65B | 109.4 |
| C59-C58-H58 | 119.8 | C66-C65-H65B | 109.4 |
| C57-C58-H58 | 119.8 | H65A-C65-H65B | 108.0 |
| C58-C59-C60 | 120.81(19) | C65-C66-H66A | 109.5 |
| C58-C59-H59 | 119.6 | C65-C66-H66B | 109.5 |
| C60-C59-H59 | 119.6 | H66A-C66-H66B | 109.5 |
| C59-C60-C55 | 118.68(17) | C65-C66-H66C | 109.5 |
| C59-C60-C51 | 122.28(18) | H66A-C66-H66C | 109.5 |
| C55-C60-C51 | 119.04(18) | H66B-C66-H66C | 109.5 |


| O6-C67-C68 | 107.28(16) | H70A-C70-H70B | 108.0 |
| :---: | :---: | :---: | :---: |
| O6-C67-H67A | 110.3 | C70-C71-C72 | 110.9(5) |
| C68-C67-H67A | 110.3 | C70-C71-H71A | 109.5 |
| O6-C67-H67B | 110.3 | C72-C71-H71A | 109.5 |
| C68-C67-H67B | 110.3 | C70-C71-H71B | 109.5 |
| H67A-C67-H67B | 108.5 | C72-C71-H71B | 109.5 |
| C67-C68-C69 | 111.74(18) | H71A-C71-H71B | 108.1 |
| C67-C68-H68A | 109.3 | C71-C72-H72A | 109.5 |
| C69-C68-H68A | 109.3 | C71-C72-H72B | 109.5 |
| C67-C68-H68B | 109.3 | H72A-C72-H72B | 109.5 |
| C69-C68-H68B | 109.3 | C71-C72-H72C | 109.5 |
| H68A-C68-H68B | 107.9 | H72A-C72-H72C | 109.5 |
| C70A-C69-C68 | 119.7(3) | H72B-C72-H72C | 109.5 |
| C68-C69-C70 | 104.5(3) | C69-C70A-C71A | 109.3(4) |
| C70A-C69-H69C | 107.0 | C69-C70A-H70C | 109.8 |
| C68-C69-H69C | 107.3 | C71A-C70A-H70C | 109.8 |
| C70A-C69-H69D | 107.5 | C69-C70A-H70D | 109.8 |
| C68-C69-H69D | 107.6 | C71A-C70A-H70D | 109.8 |
| C70-C69-H69D | 98.4 | H70C-C70A-H70D | 108.3 |
| H69C-C69-H69D | 107.1 | C70A-C71A-C72A | 112.4(5) |
| C68-C69-H69A | 110.7 | C70A-C71A-H71C | 109.1 |
| C70-C69-H69A | 111.4 | C72A-C71A-H71C | 109.1 |
| C70A-C69-H69B | 115.3 | C70A-C71A-H71D | 109.1 |
| C68-C69-H69B | 110.8 | C72A-C71A-H71D | 109.1 |
| C70-C69-H69B | 110.4 | H71C-C71A-H71D | 107.9 |
| H69A-C69-H69B | 109.0 | C71A-C72A-H72D | 109.5 |
| C71-C70-C69 | 111.4(5) | C71A-C72A-H72E | 109.5 |
| C71-C70-H70A | 109.4 | H72D-C72A-H72E | 109.5 |
| C69-C70-H70A | 109.4 | C71A-C72A-H72F | 109.5 |
| C71-C70-H70B | 109.4 | H72D-C72A-H72F | 109.5 |
| C69-C70-H70B | 109.4 | H72E-C72A-H72F | 109.5 |

Table 6Y.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $6 Y$. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| N1 | 20(1) | 23(1) | 16(1) | 4(1) | 2(1) | -4(1) |
| O1 | 18(1) | 39(1) | 28(1) | 10(1) | 6(1) | -6(1) |
| O2 | 24(1) | 37(1) | 23(1) | 8(1) | -5(1) | -12(1) |
| O3 | 18(1) | 31(1) | 15(1) | 8(1) | -2(1) | -6(1) |
| C1 | 18(1) | 21(1) | 22(1) | 3(1) | 2(1) | -3(1) |
| C2 | 18(1) | 16(1) | 20(1) | 2(1) | 2(1) | -2(1) |
| C3 | 17(1) | 13(1) | 19(1) | 2(1) | $0(1)$ | -4(1) |
| C4 | 20(1) | 15(1) | 17(1) | 3(1) | 1(1) | -4(1) |
| C5 | 20(1) | 19(1) | 21(1) | 2(1) | -1(1) | -6(1) |
| C6 | 15(1) | 17(1) | 25(1) | 2(1) | 2(1) | -3(1) |
| C7 | 18(1) | 19(1) | 24(1) | 1(1) | -4(1) | -2(1) |
| C8 | 20(1) | 17(1) | 18(1) | 2(1) | $0(1)$ | -2(1) |
| C9 | 18(1) | 12(1) | 20(1) | 2(1) | 1(1) | -2(1) |
| C10 | 20(1) | 15(1) | 18(1) | 3(1) | 3(1) | -3(1) |
| C11 | 15(1) | 18(1) | 23(1) | 4(1) | 3(1) | -5(1) |
| C12 | 17(1) | 19(1) | 24(1) | 3(1) | -3(1) | -4(1) |
| C13 | 16(1) | 18(1) | 23(1) | 3(1) | 1(1) | -3(1) |
| C14 | 15(1) | 18(1) | 21(1) | 3(1) | 2(1) | -4(1) |
| C15 | 19(1) | 14(1) | 19(1) | 2(1) | 3(1) | -4(1) |
| C16 | 16(1) | 17(1) | 22(1) | 3(1) | 3(1) | -4(1) |
| C17 | 17(1) | 21(1) | 20(1) | 4(1) | -3(1) | -3(1) |
| C18 | 19(1) | 17(1) | 16(1) | 3(1) | -1(1) | -3(1) |
| C19 | 17(1) | 13(1) | 18(1) | 2(1) | $0(1)$ | -3(1) |
| C20 | 19(1) | 17(1) | 21(1) | 4(1) | 2(1) | -3(1) |
| C21 | 14(1) | 20(1) | 25(1) | 3(1) | 1(1) | -5(1) |
| C22 | 18(1) | 18(1) | 24(1) | 1(1) | -4(1) | -1(1) |
| C23 | 22(1) | 17(1) | 18(1) | 2(1) | 1(1) | -3(1) |
| C24 | 17(1) | 13(1) | 19(1) | 2(1) | $0(1)$ | -2(1) |
| C25 | 26(1) | 30(1) | 16(1) | $6(1)$ | 3(1) | -6(1) |
| C26 | 19(1) | 28(1) | 20(1) | 7(1) | $0(1)$ | -5(1) |
| C27 | 20(1) | 29(1) | 24(1) | 8(1) | -1(1) | -6(1) |


| C28 | $23(1)$ | $29(1)$ | $22(1)$ | $5(1)$ | $-2(1)$ | $-7(1)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C29 | $23(1)$ | $29(1)$ | $23(1)$ | $7(1)$ | $-2(1)$ | $-6(1)$ |
| C30 | $29(1)$ | $31(1)$ | $29(1)$ | $8(1)$ | $-5(1)$ | $-4(1)$ |
| C31 | $20(1)$ | $26(1)$ | $17(1)$ | $4(1)$ | $-4(1)$ | $-4(1)$ |
| C32 | $18(1)$ | $32(1)$ | $20(1)$ | $6(1)$ | $-2(1)$ | $-4(1)$ |
| C33 | $22(1)$ | $31(1)$ | $19(1)$ | $7(1)$ | $-1(1)$ | $-5(1)$ |
| C34 | $25(1)$ | $38(1)$ | $22(1)$ | $10(1)$ | $0(1)$ | $-5(1)$ |
| C35 | $34(1)$ | $38(1)$ | $20(1)$ | $10(1)$ | $-4(1)$ | $-5(1)$ |
| C36 | $37(1)$ | $40(1)$ | $28(1)$ | $11(1)$ | $-3(1)$ | $-1(1)$ |
| N2 | $21(1)$ | $25(1)$ | $21(1)$ | $3(1)$ | $1(1)$ | $-7(1)$ |
| O4 | $20(1)$ | $40(1)$ | $28(1)$ | $6(1)$ | $4(1)$ | $-12(1)$ |
| O5 | $24(1)$ | $31(1)$ | $24(1)$ | $8(1)$ | $-6(1)$ | $-8(1)$ |
| O6 | $21(1)$ | $30(1)$ | $18(1)$ | $4(1)$ | $-2(1)$ | $-9(1)$ |
| C37 | $20(1)$ | $22(1)$ | $21(1)$ | $1(1)$ | $1(1)$ | $-7(1)$ |
| C38 | $19(1)$ | $17(1)$ | $20(1)$ | $1(1)$ | $1(1)$ | $-4(1)$ |
| C39 | $18(1)$ | $14(1)$ | $21(1)$ | $1(1)$ | $0(1)$ | $-3(1)$ |
| C40 | $19(1)$ | $14(1)$ | $23(1)$ | $2(1)$ | $0(1)$ | $-3(1)$ |
| C41 | $20(1)$ | $20(1)$ | $23(1)$ | $2(1)$ | $-1(1)$ | $-4(1)$ |
| C42 | $15(1)$ | $19(1)$ | $27(1)$ | $-1(1)$ | $0(1)$ | $-4(1)$ |
| C43 | $20(1)$ | $21(1)$ | $23(1)$ | $2(1)$ | $-4(1)$ | $-2(1)$ |
| C44 | $22(1)$ | $19(1)$ | $23(1)$ | $2(1)$ | $-2(1)$ | $-2(1)$ |
| C45 | $20(1)$ | $13(1)$ | $22(1)$ | $1(1)$ | $0(1)$ | $-2(1)$ |
| C46 | $19(1)$ | $14(1)$ | $22(1)$ | $2(1)$ | $1(1)$ | $-2(1)$ |
| C47 | $16(1)$ | $17(1)$ | $26(1)$ | $3(1)$ | $0(1)$ | $-5(1)$ |
| C48 | $18(1)$ | $17(1)$ | $26(1)$ | $1(1)$ | $-5(1)$ | $-4(1)$ |
| C49 | $16(1)$ | $19(1)$ | $26(1)$ | $2(1)$ | $0(1)$ | $-4(1)$ |
| C50 | $18(1)$ | $17(1)$ | $24(1)$ | $2(1)$ | $0(1)$ | $-4(1)$ |
| C51 | $20(1)$ | $16(1)$ | $21(1)$ | $1(1)$ | $2(1)$ | $-3(1)$ |
| C52 | $15(1)$ | $19(1)$ | $24(1)$ | $1(1)$ | $3(1)$ | $-4(1)$ |
| C53 | $18(1)$ | $21(1)$ | $23(1)$ | $2(1)$ | $-3(1)$ | $-4(1)$ |
| C54 | $21(1)$ | $17(1)$ | $18(1)$ | $0(1)$ | $0(1)$ | $-4(1)$ |
| C55 | $18(1)$ | $15(1)$ | $22(1)$ | $-2(1)$ | $2(1)$ | $-2(1)$ |
| C56 | $21(1)$ | $18(1)$ | $24(1)$ | $-1(1)$ | $4(1)$ | $-4(1)$ |
| C57 | $17(1)$ | $20(1)$ | $32(1)$ | $-4(1)$ | $2(1)$ | $-5(1)$ |
| C58 | $17(1)$ | $19(1)$ | $30(1)$ | $-2(1)$ | $-5(1)$ | $-2(1)$ |
| C59 | $22(1)$ | $18(1)$ | $24(1)$ | $1(1)$ | $-1(1)$ | $-1(1)$ |
|  |  |  |  |  |  |  |


| C60 | $18(1)$ | $13(1)$ | $22(1)$ | $0(1)$ | $0(1)$ | $-2(1)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| C61 | $24(1)$ | $30(1)$ | $21(1)$ | $6(1)$ | $1(1)$ | $-7(1)$ |
| C62 | $24(1)$ | $28(1)$ | $22(1)$ | $4(1)$ | $1(1)$ | $-6(1)$ |
| C63 | $24(1)$ | $29(1)$ | $23(1)$ | $6(1)$ | $-1(1)$ | $-5(1)$ |
| C64 | $34(1)$ | $30(1)$ | $29(1)$ | $6(1)$ | $1(1)$ | $-6(1)$ |
| C65 | $90(2)$ | $31(1)$ | $32(1)$ | $11(1)$ | $-5(1)$ | $-11(1)$ |
| C66 | $206(5)$ | $30(2)$ | $45(2)$ | $15(1)$ | $4(3)$ | $-25(2)$ |
| C67 | $19(1)$ | $26(1)$ | $21(1)$ | $3(1)$ | $-1(1)$ | $-4(1)$ |
| C68 | $25(1)$ | $28(1)$ | $21(1)$ | $5(1)$ | $1(1)$ | $-4(1)$ |
| C69 | $35(1)$ | $40(1)$ | $23(1)$ | $3(1)$ | $-3(1)$ | $7(1)$ |
| C70 | $31(4)$ | $42(4)$ | $20(3)$ | $-1(3)$ | $1(2)$ | $1(3)$ |
| C71 | $40(3)$ | $47(3)$ | $24(2)$ | $0(2)$ | $-2(2)$ | $-7(2)$ |
| C72 | $69(4)$ | $50(3)$ | $22(2)$ | $1(2)$ | $4(3)$ | $-9(3)$ |
| C70A | $40(4)$ | $35(4)$ | $23(3)$ | $-1(2)$ | $-11(2)$ | $-3(2)$ |
| C71A | $57(3)$ | $44(3)$ | $20(2)$ | $4(2)$ | $5(2)$ | $-14(2)$ |
| C72A | $67(4)$ | $73(4)$ | $28(3)$ | $0(3)$ | $7(3)$ | $-25(3)$ |

Table 6Y.5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $6 Y$.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| H6 | 2878 | 5129 | 6479 | 23 |
| H7 | 3311 | 5553 | 5537 | 24 |
| H8 | 5709 | 5896 | 5209 | 22 |
| H11 | 10497 | 5792 | 6009 | 22 |
| H12 | 10046 | 5330 | 6943 | 24 |
| H16 | 7030 | 6672 | 3913 | 22 |
| H17 | 7477 | 7134 | 2975 | 23 |
| H20 | 12616 | 7619 | 2864 | 23 |
| H21 | 14619 | 7425 | 3469 | 23 |
| H22 | 14178 | 6962 | 4408 | 24 |
| H23 | 11771 | 6622 | 4726 | 23 |
| H25A | 4695 | 4604 | 8342 | 29 |
| H25B | 6396 | 4815 | 8464 | 29 |
| H26A | 6429 | 3177 | 8718 | 26 |
| H26B | 7308 | 3129 | 8120 | 26 |
| H27A | 4973 | 2834 | 7714 | 29 |
| H27B | 4179 | 2808 | 8326 | 29 |
| H28A | 4950 | 1165 | 7995 | 30 |
| H28B | 6696 | 1376 | 7934 | 30 |
| H29A | 5059 | 1350 | 8992 | 30 |
| H29B | 6862 | 1412 | 8900 | 30 |
| H30A | 5455 | -299 | 8627 | 45 |
| H30B | 6471 | -251 | 9159 | 45 |
| H30C | 7258 | -237 | 8545 | 45 |
| H31A | 8018 | 8186 | 2242 | 25 |
| H31B | 8605 | 7053 | 2056 | 25 |
| H32A | 10429 | 7569 | 1430 | 28 |
| H32B | 10210 | 8672 | 1680 | 28 |
| H33A | 7765 | 9036 | 1298 | 29 |
| H33B | 7900 | 7916 | 1073 | 29 |


| H34A | 9918 | 8205 | 444 | 35 |
| :---: | :---: | :---: | :---: | :---: |
| H34B | 9973 | 9284 | 698 | 35 |
| H35A | 8710 | 9305 | -186 | 37 |
| H35B | 7344 | 8840 | 143 | 37 |
| H36A | 6804 | 10308 | 682 | 54 |
| H36B | 6674 | 10586 | 33 | 54 |
| H36C | 8167 | 10773 | 349 | 54 |
| H42 | 12102 | 9993 | 3447 | 24 |
| H43 | 11670 | 9440 | 4374 | 25 |
| H44 | 9263 | 9083 | 4676 | 25 |
| H47 | 4502 | 9241 | 3851 | 23 |
| H48 | 4965 | 9804 | 2935 | 24 |
| H52 | 7976 | 8352 | 5939 | 23 |
| H53 | 7575 | 7917 | 6881 | 25 |
| H56 | 2447 | 7393 | 7029 | 25 |
| H57 | 415 | 7566 | 6437 | 27 |
| H58 | 804 | 8042 | 5495 | 26 |
| H59 | 3196 | 8391 | 5162 | 26 |
| H61A | 8407 | 10884 | 1496 | 30 |
| H61B | 10210 | 10824 | 1594 | 30 |
| H62A | 7961 | 12424 | 2000 | 30 |
| H62B | 9779 | 12373 | 2052 | 30 |
| H63A | 8214 | 12636 | 1026 | 31 |
| H63B | 10051 | 12499 | 1052 | 31 |
| H64A | 8015 | 14149 | 1524 | 38 |
| H64B | 9841 | 14005 | 1578 | 38 |
| H65A | 8284 | 14435 | 561 | 61 |
| H65B | 10119 | 14184 | 579 | 61 |
| H66A | 8375 | 15870 | 1130 | 140 |
| H66B | 9298 | 15962 | 545 | 140 |
| H66C | 10214 | 15638 | 1096 | 140 |
| H67A | 6431 | 8178 | 7757 | 26 |
| H67B | 7039 | 7004 | 7682 | 26 |
| H68A | 4915 | 6648 | 8305 | 30 |
| H68B | 4556 | 7824 | 8423 | 30 |
| H69C | 7209 | 7655 | 8711 | 41 |


| H69D | 7179 | 6510 | 8729 | 41 |
| :--- | :---: | :---: | :---: | :---: |
| H69A | 6982 | 7758 | 8818 | 41 |
| H69B | 7367 | 6615 | 8692 | 41 |
| H70A | 4851 | 7469 | 9439 | 38 |
| H70B | 4999 | 6326 | 9250 | 38 |
| H71A | 7354 | 7055 | 9840 | 44 |
| H71B | 7258 | 5901 | 9719 | 44 |
| H72A | 5076 | 7115 | 10432 | 71 |
| H72B | 6403 | 6282 | 10655 | 71 |
| H72C | 5028 | 5953 | 10321 | 71 |
| H70C | 5245 | 7818 | 9436 | 40 |
| H70D | 6885 | 7252 | 9617 | 40 |
| H71C | 6054 | 5679 | 9508 | 48 |
| H71D | 4446 | 6214 | 9287 | 48 |
| H72D | 5418 | 6284 | 10403 | 82 |
| H72E | 4015 | 5752 | 10214 | 82 |
| H72F | 3890 | 6950 | 10192 | 82 |

Table 6Y.6. Torsion angles [ ${ }^{\circ}$ ] for $\mathbf{6 Y}$.

| C5-N1-C1-O1 | -178.46(19) | C8-C9-C10-C11 | -178.23(18) |
| :---: | :---: | :---: | :---: |
| C25-N1-C1-O1 | $1.2(3)$ | C3-C9-C10-C11 | 1.5(3) |
| C5-N1-C1-C2 | 2.7(3) | C8-C9-C10-C13 | 1.8(3) |
| C25-N1-C1-C2 | -177.56(17) | C3-C9-C10-C13 | -178.42(17) |
| O1-C1-C2-C6 | -2.0(3) | C13-C10-C11-C12 | 178.54(18) |
| N1-C1-C2-C6 | 176.76(18) | C9-C10-C11-C12 | -1.4(3) |
| O1-C1-C2-C3 | 178.36(19) | C3-C4-C12-C11 | -0.1(3) |
| N1-C1-C2-C3 | -2.9(3) | C5-C4-C12-C11 | 178.92(17) |
| C6-C2-C3-C4 | -178.50(18) | C10-C11-C12-C4 | 0.7(3) |
| C1-C2-C3-C4 | 1.1(3) | C14-C15-C16-C17 | -178.76(18) |
| C6-C2-C3-C9 | 1.2(3) | C24-C15-C16-C17 | 0.4(3) |
| C1-C2-C3-C9 | -179.21(17) | C15-C16-C17-C18 | -1.7(3) |
| C2-C3-C4-C12 | 179.99(18) | C31-O3-C18-C17 | -2.3(3) |
| C9-C3-C4-C12 | 0.3(3) | C31-O3-C18-C19 | 178.24(16) |
| C2-C3-C4-C5 | 0.9(3) | C16-C17-C18-O3 | -177.50(17) |
| C9-C3-C4-C5 | -178.75(17) | C16-C17-C18-C19 | $2.0(3)$ |
| C1-N1-C5-O2 | 178.74(19) | O3-C18-C19-C20 | -2.2(3) |
| C25-N1-C5-O2 | -1.0(3) | C17-C18-C19-C20 | 178.30(18) |
| C1-N1-C5-C4 | -0.8(3) | O3-C18-C19-C24 | 178.64(16) |
| C25-N1-C5-C4 | 179.49(16) | C17-C18-C19-C24 | -0.9(3) |
| C12-C4-C5-O2 | 0.3(3) | C24-C19-C20-C21 | 0.2(3) |
| C3-C4-C5-O2 | 179.33(19) | C18-C19-C20-C21 | -178.95(18) |
| C12-C4-C5-N1 | 179.79(18) | C19-C20-C21-C22 | -1.4(3) |
| C3-C4-C5-N1 | -1.1(3) | C20-C21-C22-C23 | 1.6(3) |
| C3-C2-C6-C7 | -0.1(3) | C21-C22-C23-C24 | -0.6(3) |
| C1-C2-C6-C7 | -179.73(17) | C20-C19-C24-C23 | 0.7(3) |
| C2-C6-C7-C8 | -1.2(3) | C18-C19-C24-C23 | 179.91(17) |
| C6-C7-C8-C9 | 1.5(3) | C20-C19-C24-C15 | -179.67(17) |
| C7-C8-C9-C3 | -0.4(3) | C18-C19-C24-C15 | -0.5(3) |
| C7-C8-C9-C10 | 179.32(18) | C22-C23-C24-C19 | -0.5(3) |
| C2-C3-C9-C8 | -0.9(3) | C22-C23-C24-C15 | 179.87(18) |
| C4-C3-C9-C8 | 178.77(17) | C16-C15-C24-C19 | 0.7(3) |
| C2-C3-C9-C10 | 179.34(17) | C14-C15-C24-C19 | 179.86(17) |
| C4-C3-C9-C10 | -1.0(3) | C16-C15-C24-C23 | -179.69(18) |


| C14-C15-C24-C23 | -0.5(3) | C39-C38-C42-C43 | -1.1(3) |
| :---: | :---: | :---: | :---: |
| C1-N1-C25-C26 | 99.2(2) | C37-C38-C42-C43 | 176.04(17) |
| C5-N1-C25-C26 | -81.1(2) | C38-C42-C43-C44 | 0.8(3) |
| N1-C25-C26-C27 | -75.7(2) | C42-C43-C44-C45 | -0.1(3) |
| C25-C26-C27-C28 | 175.67(17) | C43-C44-C45-C39 | -0.3(3) |
| C26-C27-C28-C29 | 61.7(2) | C43-C44-C45-C46 | -179.01(18) |
| C27-C28-C29-C30 | 172.33(17) | C40-C39-C45-C44 | -178.37(17) |
| C18-O3-C31-C32 | 178.49(16) | C38-C39-C45-C44 | 0.0(3) |
| O3-C31-C32-C33 | -167.10(17) | C40-C39-C45-C46 | 0.4(3) |
| C31-C32-C33-C34 | -176.48(18) | C38-C39-C45-C46 | 178.78(17) |
| C32-C33-C34-C35 | -173.4(2) | C44-C45-C46-C47 | 178.83(18) |
| C33-C34-C35-C36 | 73.1(3) | C39-C45-C46-C47 | 0.2(3) |
| C41-N2-C37-O4 | -179.83(19) | C44-C45-C46-C49 | -0.7(3) |
| C61-N2-C37-O4 | -4.3(3) | C39-C45-C46-C49 | -179.36(17) |
| C41-N2-C37-C38 | -1.5(3) | C49-C46-C47-C48 | 179.44(18) |
| C61-N2-C37-C38 | 174.13(17) | C45-C46-C47-C48 | -0.1(3) |
| O4-C37-C38-C42 | 0.6(3) | C39-C40-C48-C47 | 1.0(3) |
| N2-C37-C38-C42 | -177.74(18) | C41-C40-C48-C47 | -176.80(17) |
| O4-C37-C38-C39 | 177.82(19) | C46-C47-C48-C40 | -0.5(3) |
| N2-C37-C38-C39 | -0.5(3) | C50-C51-C52-C53 | 178.37(18) |
| C42-C38-C39-C40 | 179.12(18) | C60-C51-C52-C53 | -0.9(3) |
| C37-C38-C39-C40 | 2.0(3) | C51-C52-C53-C54 | 2.1(3) |
| C42-C38-C39-C45 | 0.7(3) | C67-O6-C54-C53 | 8.4(3) |
| C37-C38-C39-C45 | -176.45(17) | C67-O6-C54-C55 | -171.08(16) |
| C38-C39-C40-C48 | -179.36(18) | C52-C53-C54-O6 | 178.94(17) |
| C45-C39-C40-C48 | -1.0(3) | C52-C53-C54-C55 | -1.6(3) |
| C38-C39-C40-C41 | -1.5(3) | O6-C54-C55-C56 | 0.6(3) |
| C45-C39-C40-C41 | 176.85(17) | C53-C54-C55-C56 | -178.96(18) |
| C37-N2-C41-O5 | -178.58(19) | O6-C54-C55-C60 | 179.53(16) |
| C61-N2-C41-O5 | 5.8(3) | C53-C54-C55-C60 | 0.0(3) |
| C37-N2-C41-C40 | 1.9(3) | C60-C55-C56-C57 | -0.5(3) |
| C61-N2-C41-C40 | -173.73(17) | C54-C55-C56-C57 | 178.45(18) |
| C48-C40-C41-O5 | -2.0(3) | C55-C56-C57-C58 | 1.0(3) |
| C39-C40-C41-O5 | -179.86(19) | C56-C57-C58-C59 | -1.0(3) |
| C48-C40-C41-N2 | 177.53(18) | C57-C58-C59-C60 | 0.4(3) |
| C39-C40-C41-N2 | -0.3(3) | C58-C59-C60-C55 | 0.1(3) |


| C58-C59-C60-C51 | $179.89(18)$ | C61-C62-C63-C64 | $-175.26(18)$ |
| :--- | :---: | :--- | :---: |
| C56-C55-C60-C59 | $0.0(3)$ | C62-C63-C64-C65 | $177.5(2)$ |
| C54-C55-C60-C59 | $-179.03(17)$ | C63-C64-C65-C66 | $-174.0(3)$ |
| C56-C55-C60-C51 | $-179.86(17)$ | C54-O6-C67-C68 | $172.96(16)$ |
| C54-C55-C60-C51 | $1.1(3)$ | O6-C67-C68-C69 | $171.21(17)$ |
| C52-C51-C60-C59 | $179.46(18)$ | C67-C68-C69-C70A | $162.8(3)$ |
| C50-C51-C60-C59 | $0.2(3)$ | C67-C68-C69-C70 | $-178.0(3)$ |
| C52-C51-C60-C55 | $-0.7(3)$ | C68-C69-C70-C71 | $170.5(4)$ |
| C50-C51-C60-C55 | $-179.98(17)$ | C69-C70-C71-C72 | $170.5(5)$ |
| C37-N2-C61-C62 | $-82.0(2)$ | C68-C69-C70A-C71A | $70.9(5)$ |
| C41-N2-C61-C62 | $93.9(2)$ | C69-C70A-C71A-C72A | $-176.1(5)$ |
| N2-C61-C62-C63 | $-176.02(17)$ |  |  |

End of crystallographic info for $\mathbf{6 Y}$.

## CRystallographic Material for 6y ${ }^{\text {º }}$

## Crystallographic Material for $\mathbf{6 y}{ }^{\mathbf{\prime}}$

X-ray Experimental.
Table $\mathbf{6 y}$ '.1. Crystallographic Data for $\mathbf{6 y}{ }^{\prime}$.

Table $6 y^{\prime}$.2 . Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the non-hydrogen atoms of $\mathbf{6 y}$ '.

Table $\mathbf{6} \mathbf{y}^{\prime} .3$. Bond Lengths $(\AA \AA)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of $\mathbf{6 y}{ }^{\prime}$.

Table 6y'.4. Anisotropic thermal parameters for the non-hydrogen atoms of $\mathbf{6 y}$ '.

Table 6y'.5. Fractional coordinates and isotropic thermal parameters ( $\AA^{2}$ ) for the hydrogen atoms of $\mathbf{6 y}$ '.

Table $\mathbf{6 y}$ '. 6 . Torsion Angles $\left({ }^{(0}\right)$ for the non-hydrogen atoms of $\mathbf{6 y}$ '.

Crystallographic Material for 6Y':
X-ray Experimental for complex $\mathrm{C}_{36} \mathrm{H}_{37} \mathrm{NO}_{3}\left(6 \mathbf{Y}^{\prime}\right)$ : Crystals grew as long, yellow needles by slow evaporation from EtOAc The data crystal was cut from a longer crystal and had approximate dimensions; $0.26 \times 0.06 \times 0.03 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{CuK} \alpha$ radiation source ( $\lambda=1.5418 \AA$ ) with collimating mirror monochromators. A total of 1251 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 8 seconds per frame with a detector offset of $+/-40.8^{\circ}$ and 28 seconds per frame with a detector offset of $+/-108.3^{\circ}$. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31. ${ }^{1}$ The structure was solved by direct methods using SuperFlip ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7. ${ }^{3}$ Structure analysis was aided by use of the programs PLATON $98^{4}$ and WinGX. ${ }^{5}$ The
hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms).

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{Fo}_{\mathrm{o}}\right|^{2}-\left|\mathrm{Fc}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.1327 * \mathrm{P})^{2}+\right.$ $\left.\left(1.4735^{*} \mathrm{P}\right)\right]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{C}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)$ refined to 0.234 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0772 and a goodness of fit, $\mathrm{S},=1.03$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S , are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. ${ }^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.37.31.
2) SuperFlip. Palatinus, L. Chapuis, G. (2007). J. Appl. Cryst. 40, 786-790.
3) Sheldrick, G. M. (2015). SHELXL-2013. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\mid \mathrm{F}_{\mathrm{C}}\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 6Y'.1. Crystal data and structure refinement for $\mathbf{6 Y} Y^{\prime}$.

Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume
Z
Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=67.684^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole

C36 H37 N O3
531.66

100(2) K
$1.54184 \AA$
triclinic
P-1
$a=10.7586(4) \AA \quad \alpha=95.314(3)^{\circ}$.
$b=10.7921(4) \AA \quad \beta=98.742(3)^{\circ}$.
$\mathrm{c}=24.7104(9) \AA \quad \gamma=93.190(3)^{\circ}$.
2816.46(18) $\AA^{3}$

4
$1.254 \mathrm{Mg} / \mathrm{m}^{3}$
$0.617 \mathrm{~mm}^{-1}$
1136
$0.260 \times 0.063 \times 0.025 \mathrm{~mm}^{3}$
3.639 to $74.236^{\circ}$.
$-12<=\mathrm{h}<=13,-9<=\mathrm{k}<=13,-30<=1<=23$
20035
$10747[\mathrm{R}($ int $)=0.0267]$
97.7 \%

Semi-empirical from equivalents
1.00 and 0.777

Full-matrix least-squares on $\mathrm{F}^{2}$
10747 / 0 / 725
1.029
$R 1=0.0772, w R 2=0.2077$
$\mathrm{R} 1=0.1010, \mathrm{wR} 2=0.2345$
n/a
0.793 and $-0.315 \mathrm{e} . \AA^{-3}$

Table $\mathbf{6 Y} Y^{\prime}$.2. Atomic coordinates $\left(\times 10^{4}\right)$ and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $6 Y^{\prime} . U(e q)$ is defined as one third of the trace of the orthogonalized $U^{\text {ij }}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| C1 | 5649(2) | 5487(2) | 2814(1) | 20(1) |
| C2 | 5637(2) | 6137(2) | 3367(1) | 16(1) |
| C3 | 4579(2) | 6771(2) | 3483(1) | 15(1) |
| C4 | 3529(2) | 6822(2) | 3068(1) | 16(1) |
| C5 | 3514(2) | 6169(2) | 2512(1) | 20(1) |
| C6 | 6662(2) | 6087(2) | 3773(1) | 17(1) |
| C7 | 6655(2) | 6648(2) | 4307(1) | 18(1) |
| C8 | 5635(2) | 7273(2) | 4432(1) | 16(1) |
| C9 | 4576(2) | 7355(2) | 4024(1) | 15(1) |
| C10 | 3489(2) | 7994(2) | 4131(1) | 15(1) |
| C11 | 2484(2) | 8025(2) | 3709(1) | 16(1) |
| C12 | 2502(2) | 7441(2) | 3182(1) | 17(1) |
| C13 | 3479(2) | 8590(2) | 4671(1) | 16(1) |
| C14 | 3546(2) | 9059(2) | 5139(1) | 15(1) |
| C15 | 3726(2) | 9545(2) | 5704(1) | 16(1) |
| C16 | 4855(2) | 9371(2) | 6034(1) | 17(1) |
| C17 | 5101(2) | 9798(2) | 6596(1) | 16(1) |
| C18 | 4204(2) | 10432(2) | 6832(1) | 15(1) |
| C19 | 3037(2) | 10665(2) | 6508(1) | 15(1) |
| C20 | 2125(2) | 11333(2) | 6741(1) | 16(1) |
| C21 | 1001(2) | 11540(2) | 6430(1) | 17(1) |
| C22 | 746(2) | 11079(2) | 5867(1) | 17(1) |
| C23 | 1615(2) | 10422(2) | 5629(1) | 16(1) |
| C24 | 2791(2) | 10204(2) | 5942(1) | 15(1) |
| C25 | 4496(2) | 4797(2) | 1884(1) | 24(1) |
| C26 | 3701(2) | 3560(2) | 1842(1) | 26(1) |
| C27 | 3518(3) | 2883(3) | 1264(1) | 33(1) |
| C28 | 2550(3) | 1755(3) | 1186(1) | 33(1) |
| C29 | 2355(3) | 1066(3) | 609(1) | 41(1) |
| C30 | 1452(4) | -82(3) | 547(2) | 53(1) |
| C31 | 5351(2) | 10454(3) | 7746(1) | 25(1) |


| C32 | 5021(2) | 10683(3) | 8319(1) | 29(1) |
| :---: | :---: | :---: | :---: | :---: |
| C33 | 4918(2) | 12048(2) | 8503(1) | 27(1) |
| C34 | 4482(2) | 12233(3) | 9065(1) | 29(1) |
| C35 | 4308(3) | 13594(3) | 9250(1) | 32(1) |
| C36 | 3753(3) | 13750(3) | 9780(1) | 36(1) |
| C37 | -727(2) | 9445(2) | 7178(1) | 18(1) |
| C38 | -678(2) | 8832(2) | 6624(1) | 16(1) |
| C39 | 396(2) | 8220(2) | 6513(1) | 14(1) |
| C40 | 1436(2) | 8175(2) | 6932(1) | 16(1) |
| C41 | 1422(2) | 8799(2) | 7491(1) | 17(1) |
| C42 | -1688(2) | 8887(2) | 6214(1) | 17(1) |
| C43 | -1662(2) | 8340(2) | 5678(1) | 18(1) |
| C44 | -632(2) | 7725(2) | 5561(1) | 16(1) |
| C45 | 419(2) | 7651(2) | 5972(1) | 15(1) |
| C46 | 1516(2) | 7022(2) | 5868(1) | 15(1) |
| C47 | 2520(2) | 7003(2) | 6292(1) | 17(1) |
| C48 | 2482(2) | 7579(2) | 6821(1) | 17(1) |
| C49 | 1538(2) | 6430(2) | 5330(1) | 17(1) |
| C50 | 1462(2) | 5962(2) | 4859(1) | 16(1) |
| C51 | 1278(2) | 5473(2) | 4294(1) | 16(1) |
| C52 | 157(2) | 5653(2) | 3962(1) | 17(1) |
| C53 | -92(2) | 5204(2) | 3402(1) | 16(1) |
| C 54 | 789(2) | 4543(2) | 3173(1) | 15(1) |
| C55 | 1965(2) | 4324(2) | 3498(1) | 15(1) |
| C56 | 2873(2) | 3641(2) | 3268(1) | 16(1) |
| C57 | 3995(2) | 3442(2) | 3582(1) | 17(1) |
| C58 | 4254(2) | 3922(2) | 4141(1) | 17(1) |
| C59 | 3389(2) | 4591(2) | 4375(1) | 16(1) |
| C60 | 2215(2) | 4805(2) | 4062(1) | 15(1) |
| C61 | 355(2) | 10109(2) | 8118(1) | 23(1) |
| C62 | 1022(2) | 11408(2) | 8147(1) | 26(1) |
| C63 | 965(2) | 12198(3) | 8688(1) | 29(1) |
| C64 | -297(2) | 12784(3) | 8715(1) | 30(1) |
| C65 | -320(3) | 13533(3) | 9266(1) | 34(1) |
| C66 | -1542(3) | 14166(3) | 9292(1) | 39(1) |
| C67 | -465(2) | 4304(2) | 2276(1) | 22(1) |


| C68 | $-386(2)$ | $3632(3)$ | $1718(1)$ | $26(1)$ |
| :--- | ---: | ---: | ---: | ---: |
| C69 | $-1645(2)$ | $3538(3)$ | $1329(1)$ | $31(1)$ |
| C70 | $-1565(3)$ | $2868(3)$ | $766(1)$ | $35(1)$ |
| C71 | $-2856(3)$ | $2469(3)$ | $421(1)$ | $40(1)$ |
| C72 | $-3492(3)$ | $1313(3)$ | $609(1)$ | $45(1)$ |
| N1 | $4569(2)$ | $5517(2)$ | $2425(1)$ | $19(1)$ |
| N2 | $340(2)$ | $9407(2)$ | $7577(1)$ | $19(1)$ |
| O1 | $6547(2)$ | $4932(2)$ | $2698(1)$ | $27(1)$ |
| O2 | $2628(2)$ | $6177(2)$ | $2141(1)$ | $27(1)$ |
| O3 | $4331(1)$ | $10865(2)$ | $7372(1)$ | $20(1)$ |
| O4 | $-1639(2)$ | $9978(2)$ | $7293(1)$ | $27(1)$ |
| O5 | $2296(2)$ | $8789(2)$ | $7868(1)$ | $24(1)$ |
| O6 | $648(1)$ | $4052(2)$ | $2639(1)$ | $19(1)$ |

Table $\mathbf{6} \mathbf{Y}^{\prime} \cdot 3$. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for $\mathbf{6} \mathbf{Y}^{\prime}$.

| C1-O1 | 1.220(3) | C19-C24 | 1.421(3) |
| :---: | :---: | :---: | :---: |
| C1-N1 | 1.395(3) | C20-C21 | 1.373(3) |
| C1-C2 | 1.479 (3) | C20-H20 | 0.95 |
| C2-C6 | 1.381(3) | C21-C22 | 1.413(3) |
| C2-C3 | 1.412 (3) | C21-H21 | 0.95 |
| C3-C4 | 1.413(3) | C22-C23 | 1.373(3) |
| C3-C9 | 1.425(3) | C22-H22 | 0.95 |
| C4-C12 | 1.374(3) | C23-C24 | 1.422(3) |
| C4-C5 | 1.481(3) | C23-H23 | 0.95 |
| C5-O2 | 1.218(3) | C25-N1 | 1.472(3) |
| C5-N1 | 1.402(3) | C25-C26 | 1.531(3) |
| C6-C7 | 1.402(3) | C25-H25A | 0.99 |
| C6-H6 | 0.95 | C25-H25B | 0.99 |
| C7-C8 | 1.378 (3) | C26-C27 | 1.522(4) |
| C7-H7 | 0.95 | C26-H26A | 0.99 |
| C8-C9 | 1.414(3) | C26-H26B | 0.99 |
| C8-H8 | 0.95 | C27-C28 | 1.535(4) |
| C9-C10 | $1.436(3)$ | C27-H27A | 0.99 |
| C10-C11 | 1.387(3) | C27-H27B | 0.99 |
| C10-C13 | 1.430 (3) | C28-C29 | 1.525(4) |
| C11-C12 | 1.398 (3) | C28-H28A | 0.99 |
| C11-H11 | 0.95 | C28-H28B | 0.99 |
| C12-H12 | 0.95 | C29-C30 | 1.513(4) |
| C13-C14 | 1.208(3) | C29-H29A | 0.99 |
| C14-C15 | 1.426 (3) | C29-H29B | 0.99 |
| C15-C16 | 1.390 (3) | C30-H30A | 0.98 |
| C15-C24 | 1.430(3) | C30-H30B | 0.98 |
| C16-C17 | 1.401(3) | C30-H30C | 0.98 |
| C16-H16 | 0.95 | C31-O3 | 1.441(3) |
| C17-C18 | 1.382(3) | C31-C32 | 1.512(4) |
| C17-H17 | 0.95 | C31-H31A | 0.99 |
| C18-O3 | 1.358(3) | C31-H31B | 0.99 |
| C18-C19 | 1.430 (3) | C32-C33 | 1.516(4) |
| C19-C20 | 1.410(3) | C32-H32A | 0.99 |


| C32-H32B | 0.99 | C49-C50 | 1.216(3) |
| :---: | :---: | :---: | :---: |
| C33-C34 | 1.532(4) | C50-C51 | 1.425(3) |
| C33-H33A | 0.99 | C51-C52 | 1.385(3) |
| C33-H33B | 0.99 | C51-C60 | $1.430(3)$ |
| C34-C35 | 1.527(4) | C52-C53 | 1.403(3) |
| C34-H34A | 0.99 | C52-H52 | 0.95 |
| C34-H34B | 0.99 | C53-C54 | 1.376 (3) |
| C35-C36 | 1.519(4) | C53-H53 | 0.95 |
| C35-H35A | 0.99 | C54-O6 | 1.358(3) |
| C35-H35B | 0.99 | C54-C55 | 1.435(3) |
| C36-H36A | 0.98 | C55-C56 | 1.411(3) |
| C36-H36B | 0.98 | C55-C60 | 1.423(3) |
| C36-H36C | 0.98 | C56-C57 | 1.373(3) |
| C37-O4 | 1.220(3) | C56-H56 | 0.95 |
| C37-N2 | 1.401(3) | C57-C58 | 1.409(3) |
| C37-C38 | 1.473(3) | C57-H57 | 0.95 |
| C38-C42 | 1.377(3) | C58-C59 | 1.373(3) |
| C38-C39 | 1.413(3) | C58-H58 | 0.95 |
| C39-C40 | 1.411(3) | C59-C60 | 1.419(3) |
| C39-C45 | 1.421(3) | C59-H59 | 0.95 |
| C40-C48 | 1.377(3) | C61-N2 | 1.471(3) |
| C40-C41 | 1.481(3) | C61-C62 | 1.529(3) |
| C41-O5 | 1.220(3) | C61-H61A | 0.99 |
| C41-N2 | 1.402(3) | C61-H61B | 0.99 |
| C42-C43 | $1.405(3)$ | C62-C63 | 1.530(4) |
| C42-H42 | 0.95 | C62-H62A | 0.99 |
| C43-C44 | 1.376(3) | C62-H62B | 0.99 |
| C43-H43 | 0.95 | C63-C64 | 1.537(4) |
| C44-C45 | 1.413(3) | C63-H63A | 0.99 |
| C44-H44 | 0.95 | C63-H63B | 0.99 |
| C45-C46 | $1.439(3)$ | C64-C65 | 1.523(4) |
| C46-C47 | 1.388(3) | C64-H64A | 0.99 |
| C46-C49 | $1.424(3)$ | C64-H64B | 0.99 |
| C47-C48 | 1.402(3) | C65-C66 | 1.523(4) |
| C47-H47 | 0.95 | C65-H65A | 0.99 |
| C48-H48 | 0.95 | C65-H65B | 0.99 |


| C66-H66A | 0.98 | C69-H69A | 0.99 |
| :---: | :---: | :---: | :---: |
| C66-H66B | 0.98 | C69-H69B | 0.99 |
| C66-H66C | 0.98 | C70-C71 | 1.531(4) |
| C67-06 | 1.438(2) | C70-H70A | 0.99 |
| C67-C68 | 1.513(4) | C70-H70B | 0.99 |
| C67-H67A | 0.99 | C71-C72 | 1.532(4) |
| C67-H67B | 0.99 | C71-H71A | 0.99 |
| C68-C69 | 1.530(3) | C71-H71B | 0.99 |
| C68-H68A | 0.99 | C72-H72A | 0.98 |
| C68-H68B | 0.99 | C72-H72B | 0.98 |
| C69-C70 | 1.525(4) | C72-H72C | 0.98 |
| O1-C1-N1 | 120.7(2) | C8-C9-C3 | 118.8(2) |
| O1-C1-C2 | 122.4(2) | C8-C9-C10 | 123.0(2) |
| N1-C1-C2 | 116.9(2) | C3-C9-C10 | 118.3(2) |
| C6-C2-C3 | 120.4(2) | C11-C10-C13 | 121.7(2) |
| C6-C2-C1 | 119.0(2) | C11-C10-C9 | 119.5(2) |
| C3-C2-C1 | 120.6(2) | C13-C10-C9 | 118.79(19) |
| C2-C3-C4 | 120.5(2) | C10-C11-C12 | 121.4(2) |
| C2-C3-C9 | 119.4(2) | C10-C11-H11 | 119.3 |
| C4-C3-C9 | 120.2(2) | C12-C11-H11 | 119.3 |
| C12-C4-C3 | 120.3(2) | C4-C12-C11 | 120.4(2) |
| C12-C4-C5 | 119.7(2) | C4-C12-H12 | 119.8 |
| C3-C4-C5 | 119.9(2) | C11-C12-H12 | 119.8 |
| O2-C5-N1 | 120.2(2) | C14-C13-C10 | 175.5(2) |
| O2-C5-C4 | 122.5(2) | C13-C14-C15 | 174.6(2) |
| N1-C5-C4 | 117.2(2) | C16-C15-C14 | 118.5(2) |
| C2-C6-C7 | 120.3(2) | C16-C15-C24 | 118.9(2) |
| C2-C6-H6 | 119.8 | C14-C15-C24 | 122.56(19) |
| C7-C6-H6 | 119.8 | C15-C16-C17 | 122.3(2) |
| C8-C7-C6 | 120.5(2) | C15-C16-H16 | 118.9 |
| C8-C7-H7 | 119.8 | C17-C16-H16 | 118.9 |
| C6-C7-H7 | 119.8 | C18-C17-C16 | 119.42(19) |
| C7-C8-C9 | 120.7(2) | C18-C17-H17 | 120.3 |
| C7-C8-H8 | 119.7 | C16-C17-H17 | 120.3 |
| C9-C8-H8 | 119.7 | O3-C18-C17 | 124.40(19) |


| O3-C18-C19 | 114.88(19) | C28-C27-H27B | 109.0 |
| :---: | :---: | :---: | :---: |
| C17-C18-C19 | 120.7(2) | H27A-C27-H27B | 107.8 |
| C20-C19-C24 | 119.5(2) | C29-C28-C27 | 113.6(2) |
| C20-C19-C18 | 121.3(2) | C29-C28-H28A | 108.8 |
| C24-C19-C18 | 119.2(2) | C27-C28-H28A | 108.8 |
| C21-C20-C19 | 121.0(2) | C29-C28-H28B | 108.8 |
| C21-C20-H20 | 119.5 | C27-C28-H28B | 108.8 |
| C19-C20-H20 | 119.5 | H28A-C28-H28B | 107.7 |
| C20-C21-C22 | 119.8(2) | C30-C29-C28 | 112.9(3) |
| C20-C21-H21 | 120.1 | C30-C29-H29A | 109.0 |
| C22-C21-H21 | 120.1 | C28-C29-H29A | 109.0 |
| C23-C22-C21 | 120.47(19) | C30-C29-H29B | 109.0 |
| C23-C22-H22 | 119.8 | C28-C29-H29B | 109.0 |
| C21-C22-H22 | 119.8 | H29A-C29-H29B | 107.8 |
| C22-C23-C24 | 120.8(2) | C29-C30-H30A | 109.5 |
| C22-C23-H23 | 119.6 | C29-C30-H30B | 109.5 |
| C24-C23-H23 | 119.6 | H30A-C30-H30B | 109.5 |
| C19-C24-C23 | 118.4(2) | C29-C30-H30C | 109.5 |
| C19-C24-C15 | 119.45(19) | H30A-C30-H30C | 109.5 |
| C23-C24-C15 | 122.2(2) | H30B-C30-H30C | 109.5 |
| N1-C25-C26 | 112.2(2) | O3-C31-C32 | 106.95(19) |
| N1-C25-H25A | 109.2 | O3-C31-H31A | 110.3 |
| C26-C25-H25A | 109.2 | C32-C31-H31A | 110.3 |
| N1-C25-H25B | 109.2 | O3-C31-H31B | 110.3 |
| C26-C25-H25B | 109.2 | C32-C31-H31B | 110.3 |
| H25A-C25-H25B | 107.9 | H31A-C31-H31B | 108.6 |
| C27-C26-C25 | 111.9(2) | C31-C32-C33 | 113.7(2) |
| C27-C26-H26A | 109.2 | C31-C32-H32A | 108.8 |
| C25-C26-H26A | 109.2 | C33-C32-H32A | 108.8 |
| C27-C26-H26B | 109.2 | C31-C32-H32B | 108.8 |
| C25-C26-H26B | 109.2 | C33-C32-H32B | 108.8 |
| H26A-C26-H26B | 107.9 | H32A-C32-H32B | 107.7 |
| C26-C27-C28 | 112.9(2) | C32-C33-C34 | 112.2(2) |
| C26-C27-H27A | 109.0 | C32-C33-H33A | 109.2 |
| C28-C27-H27A | 109.0 | C34-C33-H33A | 109.2 |
| C26-C27-H27B | 109.0 | C32-C33-H33B | 109.2 |


| C34-C33-H33B | 109.2 | C38-C42-H42 | 119.8 |
| :---: | :---: | :---: | :---: |
| H33A-C33-H33B | 107.9 | C43-C42-H42 | 119.8 |
| C35-C34-C33 | 113.4(2) | C44-C43-C42 | 120.1(2) |
| C35-C34-H34A | 108.9 | C44-C43-H43 | 119.9 |
| C33-C34-H34A | 108.9 | C42-C43-H43 | 119.9 |
| C35-C34-H34B | 108.9 | C43-C44-C45 | 120.8(2) |
| C33-C34-H34B | 108.9 | C43-C44-H44 | 119.6 |
| H34A-C34-H34B | 107.7 | C45-C44-H44 | 119.6 |
| C36-C35-C34 | 112.8(2) | C44-C45-C39 | 118.9(2) |
| C36-C35-H35A | 109.0 | C44-C45-C46 | 122.7(2) |
| C34-C35-H35A | 109.0 | C39-C45-C46 | 118.43(19) |
| C36-C35-H35B | 109.0 | C47-C46-C49 | 121.8(2) |
| C34-C35-H35B | 109.0 | C47-C46-C45 | 119.4(2) |
| H35A-C35-H35B | 107.8 | C49-C46-C45 | 118.83(19) |
| C35-C36-H36A | 109.5 | C46-C47-C48 | 121.3(2) |
| C35-C36-H36B | 109.5 | C46-C47-H47 | 119.4 |
| H36A-C36-H36B | 109.5 | C48-C47-H47 | 119.4 |
| C35-C36-H36C | 109.5 | C40-C48-C47 | 120.4(2) |
| H36A-C36-H36C | 109.5 | C40-C48-H48 | 119.8 |
| H36B-C36-H36C | 109.5 | C47-C48-H48 | 119.8 |
| O4-C37-N2 | 120.4(2) | C50-C49-C46 | 174.7(2) |
| O4-C37-C38 | 122.8(2) | C49-C50-C51 | 175.0(2) |
| N2-C37-C38 | 116.86(19) | C52-C51-C50 | 118.8(2) |
| C42-C38-C39 | 120.4(2) | C52-C51-C60 | 119.3(2) |
| C42-C38-C37 | 118.9(2) | C50-C51-C60 | 121.89(19) |
| C39-C38-C37 | 120.7(2) | C51-C52-C53 | 122.2(2) |
| C40-C39-C38 | 120.4(2) | C51-C52-H52 | 118.9 |
| C40-C39-C45 | 120.3(2) | C53-C52-H52 | 118.9 |
| C38-C39-C45 | 119.3(2) | C54-C53-C52 | 119.49(19) |
| C48-C40-C39 | 120.2(2) | C54-C53-H53 | 120.3 |
| C48-C40-C41 | 119.7(2) | C52-C53-H53 | 120.3 |
| C39-C40-C41 | 120.1(2) | O6-C54-C53 | 124.80(19) |
| O5-C41-N2 | 120.2(2) | O6-C54-C55 | 114.48(19) |
| O5-C41-C40 | 122.7(2) | C53-C54-C55 | 120.7(2) |
| N2-C41-C40 | 117.10(19) | C56-C55-C60 | 119.6(2) |
| C38-C42-C43 | 120.5(2) | C56-C55-C54 | 121.2(2) |


| C60-C55-C54 | 119.2(2) | C63-C64-H64A | 109.1 |
| :---: | :---: | :---: | :---: |
| C57-C56-C55 | 120.7(2) | C65-C64-H64B | 109.1 |
| C57-C56-H56 | 119.7 | C63-C64-H64B | 109.1 |
| C55-C56-H56 | 119.7 | H64A-C64-H64B | 107.9 |
| C56-C57-C58 | 120.1(2) | C64-C65-C66 | 113.2(2) |
| C56-C57-H57 | 119.9 | C64-C65-H65A | 108.9 |
| C58-C57-H57 | 119.9 | C66-C65-H65A | 108.9 |
| C59-C58-C57 | 120.43(19) | C64-C65-H65B | 108.9 |
| C59-C58-H58 | 119.8 | C66-C65-H65B | 108.9 |
| C57-C58-H58 | 119.8 | H65A-C65-H65B | 107.8 |
| C58-C59-C60 | 120.8(2) | C65-C66-H66A | 109.5 |
| C58-C59-H59 | 119.6 | C65-C66-H66B | 109.5 |
| C60-C59-H59 | 119.6 | H66A-C66-H66B | 109.5 |
| C59-C60-C55 | 118.4(2) | C65-C66-H66C | 109.5 |
| C59-C60-C51 | 122.5(2) | H66A-C66-H66C | 109.5 |
| C55-C60-C51 | 119.10(19) | H66B-C66-H66C | 109.5 |
| N2-C61-C62 | 111.2(2) | O6-C67-C68 | 106.61(19) |
| N2-C61-H61A | 109.4 | O6-C67-H67A | 110.4 |
| C62-C61-H61A | 109.4 | C68-C67-H67A | 110.4 |
| N2-C61-H61B | 109.4 | O6-C67-H67B | 110.4 |
| C62-C61-H61B | 109.4 | C68-C67-H67B | 110.4 |
| H61A-C61-H61B | 108.0 | H67A-C67-H67B | 108.6 |
| C61-C62-C63 | 112.5(2) | C67-C68-C69 | 112.3(2) |
| C61-C62-H62A | 109.1 | C67-C68-H68A | 109.1 |
| C63-C62-H62A | 109.1 | C69-C68-H68A | 109.1 |
| C61-C62-H62B | 109.1 | C67-C68-H68B | 109.1 |
| C63-C62-H62B | 109.1 | C69-C68-H68B | 109.1 |
| H62A-C62-H62B | 107.8 | H68A-C68-H68B | 107.9 |
| C62-C63-C64 | 114.4(2) | C70-C69-C68 | 112.4(2) |
| C62-C63-H63A | 108.7 | C70-C69-H69A | 109.1 |
| C64-C63-H63A | 108.7 | C68-C69-H69A | 109.1 |
| C62-C63-H63B | 108.7 | C70-C69-H69B | 109.1 |
| C64-C63-H63B | 108.7 | C68-C69-H69B | 109.1 |
| H63A-C63-H63B | 107.6 | H69A-C69-H69B | 107.9 |
| C65-C64-C63 | 112.4(2) | C69-C70-C71 | 113.4(2) |
| C65-C64-H64A | 109.1 | C69-C70-H70A | 108.9 |


| C71-C70-H70A | 108.9 | H72A-C72-H72B | 109.5 |
| :--- | :--- | :--- | :--- |
| C69-C70-H70B | 108.9 | C71-C72-H72C | 109.5 |
| C71-C70-H70B | 108.9 | H72A-C72-H72C | 109.5 |
| H70A-C70-H70B | 107.7 | H72B-C72-H72C | 109.5 |
| C70-C71-C72 | $112.8(3)$ | C1-N1-C5 | $124.8(2)$ |
| C70-C71-H71A | 109.0 | C1-N1-C25 | $118.76(19)$ |
| C72-C71-H71A | 109.0 | C5-N1-C25 | $116.45(19)$ |
| C70-C71-H71B | 109.0 | C37-N2-C41 | $124.8(2)$ |
| C72-C71-H71B | 109.0 | C37-N2-C61 | $117.66(19)$ |
| H71A-C71-H71B | 107.8 | C41-N2-C61 | $117.48(19)$ |
| C71-C72-H72A | 109.5 | C18-O3-C31 | $118.22(18)$ |
| C71-C72-H72B | 109.5 | C54-O6-C67 | $117.96(17)$ |

Table 6Y'.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $6 Y^{\prime}$. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | 17(1) | 21(1) | 22(1) | 4(1) | 6(1) | 4(1) |
| C2 | 14(1) | 16(1) | 18(1) | 3(1) | 4(1) | 2(1) |
| C3 | 12(1) | 15(1) | 19(1) | 4(1) | 3(1) | -1(1) |
| C4 | 15(1) | 16(1) | 18(1) | 4(1) | 2(1) | 2(1) |
| C5 | 19(1) | 21(1) | 19(1) | 2(1) | 2(1) | 3(1) |
| C6 | 11(1) | 17(1) | 26(1) | 7(1) | 4(1) | 3(1) |
| C7 | 11(1) | 20(1) | 23(1) | 4(1) | -2(1) | $0(1)$ |
| C8 | 14(1) | 17(1) | 18(1) | 2(1) | 0 (1) | $0(1)$ |
| C9 | 11(1) | 16(1) | 19(1) | 3(1) | 4(1) | $0(1)$ |
| C10 | 12(1) | 15(1) | 18(1) | 2(1) | 4(1) | 1(1) |
| C11 | 10(1) | 16(1) | 23(1) | 2(1) | 4(1) | 3(1) |
| C12 | 11(1) | 20(1) | 20(1) | 4(1) | -2(1) | 2(1) |
| C13 | 11(1) | 18(1) | 20(1) | 2(1) | 4(1) | 3(1) |
| C14 | 12(1) | 17(1) | 18(1) | 3(1) | 3(1) | 3(1) |
| C15 | 14(1) | 15(1) | 18(1) | 4(1) | 3(1) | $0(1)$ |
| C16 | 13(1) | 18(1) | 20(1) | 2(1) | 4(1) | 4(1) |
| C17 | 11(1) | 18(1) | 20(1) | 3(1) | 2(1) | 3(1) |
| C18 | 14(1) | 16(1) | 15(1) | 3(1) | 3(1) | 2(1) |
| C19 | 12(1) | 16(1) | 17(1) | 4(1) | 3(1) | 1(1) |
| C20 | 14(1) | 18(1) | 18(1) | 4(1) | 3(1) | 3(1) |
| C21 | 12(1) | 18(1) | 22(1) | 4(1) | 5(1) | 4(1) |
| C22 | 11(1) | 20(1) | 21(1) | 5(1) | 1(1) | 3(1) |
| C23 | 13(1) | 18(1) | 18(1) | 3(1) | 2(1) | 1(1) |
| C24 | 12(1) | 14(1) | 19(1) | 5(1) | 3(1) | 1(1) |
| C25 | 26(1) | 29(1) | 17(1) | $0(1)$ | 7(1) | $5(1)$ |
| C26 | 31(1) | 25(1) | 21(1) | $0(1)$ | 6(1) | 5(1) |
| C27 | 43(2) | 30(1) | 26(1) | -1(1) | 11(1) | 2(1) |
| C28 | 30(1) | 33(1) | 36(2) | 2(1) | $5(1)$ | 7(1) |
| C29 | 44(2) | 38(2) | 40(2) | -1(1) | 9(1) | -2(1) |
| C30 | 57(2) | 50(2) | 49(2) | -9(2) | 12(2) | -11(2) |
| C31 | 19(1) | 34(1) | 22(1) | 3(1) | -3(1) | 11(1) |


| C32 | 28(1) | 35(1) | 24(1) | 4(1) | -1(1) | 8(1) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C33 | 22(1) | 30(1) | 30(1) | 5(1) | 1(1) | 2(1) |
| C34 | 26(1) | 32(1) | 28(1) | 3(1) | 1(1) | 4(1) |
| C35 | 30(1) | 34(1) | 32(2) | -1(1) | 6(1) | 1(1) |
| C36 | 30(1) | 42(2) | 37(2) | -2(1) | 7(1) | 3(1) |
| C37 | 16(1) | 20(1) | 20(1) | 3(1) | 5(1) | 3(1) |
| C38 | 12(1) | 16(1) | 20(1) | 3(1) | 4(1) | 1(1) |
| C39 | 11(1) | 14(1) | 17(1) | 5(1) | 3(1) | $0(1)$ |
| C40 | 13(1) | 16(1) | 19(1) | 3(1) | 3(1) | 1(1) |
| C41 | 16(1) | 16(1) | 19(1) | 3(1) | 1(1) | 2(1) |
| C42 | 11(1) | 16(1) | 23(1) | 4(1) | 3(1) | 3(1) |
| C43 | 11(1) | 19(1) | 22(1) | 4(1) | -2(1) | 0(1) |
| C44 | 13(1) | 17(1) | 17(1) | 2(1) | 0 (1) | -1(1) |
| C45 | 11(1) | 15(1) | 18(1) | 3(1) | 3(1) | $0(1)$ |
| C46 | 12(1) | 14(1) | 18(1) | 4(1) | 4(1) | $0(1)$ |
| C47 | 10(1) | 18(1) | 24(1) | 4(1) | 4(1) | 4(1) |
| C48 | 12(1) | 18(1) | 20(1) | 5(1) | -2(1) | 0 (1) |
| C49 | 11(1) | 19(1) | 21(1) | 3(1) | 4(1) | 2(1) |
| C50 | 12(1) | 17(1) | 19(1) | 3(1) | 4(1) | 2(1) |
| C51 | 14(1) | 15(1) | 18(1) | 4(1) | 4(1) | 1(1) |
| C52 | 12(1) | 18(1) | 22(1) | 2(1) | 7(1) | 3(1) |
| C53 | 12(1) | 17(1) | 19(1) | 4(1) | 2(1) | 2(1) |
| C54 | 14(1) | 18(1) | 14(1) | 4(1) | 3(1) | 2(1) |
| C55 | 14(1) | 15(1) | 17(1) | 4(1) | 3(1) | 1(1) |
| C56 | 14(1) | 17(1) | 20(1) | 3(1) | 5(1) | 2(1) |
| C 57 | 13(1) | 18(1) | 22(1) | 2(1) | 6(1) | 4(1) |
| C 58 | 11(1) | 19(1) | 22(1) | 6(1) | 1(1) | 2(1) |
| C 59 | 13(1) | 19(1) | 17(1) | 3(1) | 2(1) | 1(1) |
| C60 | 11(1) | 15(1) | 19(1) | 4(1) | 2(1) | 1(1) |
| C61 | 27(1) | 26(1) | 15(1) | -2(1) | 5(1) | 2(1) |
| C62 | 26(1) | 26(1) | 25(1) | -1(1) | 5(1) | 3(1) |
| C63 | 30(1) | 30(1) | 25(1) | -2(1) | 3(1) | 2(1) |
| C64 | 25(1) | 32(1) | 32(2) | 2(1) | 2(1) | 5(1) |
| C65 | 34(1) | 36(2) | 32(2) | -2(1) | 2(1) | 8(1) |
| C66 | 36(2) | 49(2) | 33(2) | -3(1) | 7(1) | 11(1) |
| C67 | 15(1) | 30(1) | 21(1) | 5(1) | -3(1) | 7(1) |


| C68 | $21(1)$ | $35(1)$ | $24(1)$ | $5(1)$ | $3(1)$ | $6(1)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| C69 | $26(1)$ | $36(1)$ | $30(1)$ | $7(1)$ | $-2(1)$ | $6(1)$ |
| C70 | $30(1)$ | $44(2)$ | $30(2)$ | $7(1)$ | $3(1)$ | $1(1)$ |
| C71 | $40(2)$ | $44(2)$ | $32(2)$ | $7(1)$ | $-4(1)$ | $1(1)$ |
| C72 | $40(2)$ | $52(2)$ | $39(2)$ | $-2(2)$ | $2(1)$ | $-9(1)$ |
| N1 | $20(1)$ | $22(1)$ | $17(1)$ | $2(1)$ | $3(1)$ | $4(1)$ |
| N2 | $18(1)$ | $22(1)$ | $17(1)$ | $2(1)$ | $3(1)$ | $4(1)$ |
| O1 | $25(1)$ | $33(1)$ | $26(1)$ | $1(1)$ | $9(1)$ | $14(1)$ |
| O2 | $27(1)$ | $34(1)$ | $20(1)$ | $-1(1)$ | $-4(1)$ | $9(1)$ |
| O3 | $16(1)$ | $28(1)$ | $14(1)$ | $2(1)$ | $-2(1)$ | $9(1)$ |
| O4 | $22(1)$ | $33(1)$ | $28(1)$ | $0(1)$ | $6(1)$ | $13(1)$ |
| O5 | $23(1)$ | $29(1)$ | $17(1)$ | $1(1)$ | $-4(1)$ | $5(1)$ |
| O6 | $13(1)$ | $28(1)$ | $16(1)$ | $1(1)$ | $0(1)$ | $7(1)$ |
|  |  |  |  |  |  |  |

Table 6Y'.5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $6 Y^{\prime}$.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H6 | 7375 | 5669 | 3690 | 21 |
| H7 | 7358 | 6598 | 4586 | 22 |
| H8 | 5642 | 7651 | 4795 | 20 |
| H11 | 1768 | 8452 | 3781 | 20 |
| H12 | 1800 | 7473 | 2900 | 21 |
| H16 | 5483 | 8948 | 5874 | 20 |
| H17 | 5877 | 9653 | 6812 | 20 |
| H20 | 2292 | 11645 | 7119 | 20 |
| H21 | 395 | 11993 | 6592 | 20 |
| H22 | -32 | 11224 | 5652 | 21 |
| H23 | 1429 | 10110 | 5252 | 19 |
| H25A | 5359 | 4625 | 1819 | 28 |
| H25B | 4126 | 5301 | 1593 | 28 |
| H26A | 4120 | 3018 | 2106 | 31 |
| H26B | 2867 | 3724 | 1945 | 31 |
| H27A | 4337 | 2597 | 1186 | 39 |
| H27B | 3237 | 3475 | 995 | 39 |
| H28A | 2832 | 1166 | 1455 | 39 |
| H28B | 1732 | 2043 | 1265 | 39 |
| H29A | 2025 | 1641 | 340 | 49 |
| H29B | 3179 | 816 | 521 | 49 |
| H30A | 1793 | -675 | 798 | 80 |
| H30B | 1341 | -473 | 167 | 80 |
| H30C | 635 | 157 | 636 | 80 |
| H31A | 6151 | 10929 | 7722 | 30 |
| H31B | 5450 | 9556 | 7655 | 30 |
| H32A | 5673 | 10348 | 8582 | 35 |
| H32B | 4207 | 10217 | 8330 | 35 |
| H33A | 4313 | 12404 | 8227 | 33 |
| H33B | 5750 | 12506 | 8523 | 33 |


| H34A | 3673 | 11736 | 9049 | 35 |
| :---: | :---: | :---: | :---: | :---: |
| H34B | 5110 | 11910 | 9344 | 35 |
| H35A | 5136 | 14075 | 9304 | 39 |
| H35B | 3746 | 13943 | 8955 | 39 |
| H36A | 2925 | 13290 | 9727 | 54 |
| H36B | 3661 | 14637 | 9879 | 54 |
| H36C | 4315 | 13423 | 10076 | 54 |
| H42 | -2406 | 9299 | 6293 | 20 |
| H43 | -2357 | 8393 | 5395 | 21 |
| H44 | -628 | 7346 | 5198 | 19 |
| H47 | 3246 | 6593 | 6222 | 20 |
| H48 | 3182 | 7558 | 7105 | 20 |
| H52 | -463 | 6095 | 4118 | 20 |
| H53 | -863 | 5355 | 3184 | 19 |
| H56 | 2706 | 3317 | 2891 | 20 |
| H57 | 4599 | 2979 | 3423 | 21 |
| H58 | 5032 | 3781 | 4357 | 20 |
| H59 | 3578 | 4915 | 4752 | 19 |
| H61A | 792 | 9645 | 8409 | 27 |
| H61B | -522 | 10191 | 8185 | 27 |
| H62A | 627 | 11842 | 7836 | 31 |
| H62B | 1916 | 11321 | 8107 | 31 |
| H63A | 1647 | 12874 | 8746 | 35 |
| H63B | 1128 | 11668 | 8994 | 35 |
| H64A | -453 | 13339 | 8418 | 36 |
| H64B | -986 | 12115 | 8651 | 36 |
| H65A | 394 | 14177 | 9337 | 41 |
| H65B | -197 | 12970 | 9561 | 41 |
| H66A | -1725 | 14645 | 8975 | 59 |
| H66B | -1455 | 14729 | 9632 | 59 |
| H66C | -2234 | 13532 | 9286 | 59 |
| H67A | -499 | 5212 | 2252 | 27 |
| H67B | -1231 | 3993 | 2413 | 27 |
| H68A | -117 | 2782 | 1767 | 32 |
| H68B | 261 | 4082 | 1550 | 32 |
| H69A | -2291 | 3085 | 1496 | 37 |


| H69B | -1917 | 4389 | 1283 | 37 |
| :--- | ---: | ---: | ---: | :--- |
| H70A | -1087 | 2119 | 817 | 42 |
| H70B | -1092 | 3427 | 561 | 42 |
| H71A | -2752 | 2291 | 31 | 48 |
| H71B | -3410 | 3167 | 445 | 48 |
| H72A | -2952 | 615 | 583 | 67 |
| H72B | -4307 | 1093 | 373 | 67 |
| H72C | -3623 | 1492 | 992 | 67 |

Table $\mathbf{6 Y} Y^{\prime}$.6. Torsion angles [ ${ }^{\circ}$ ] for $\mathbf{6 Y} Y^{\prime}$.

| O1-C1-C2-C6 | -1.9(4) | C10-C11-C12-C4 | -0.2(3) |
| :---: | :---: | :---: | :---: |
| N1-C1-C2-C6 | 177.1(2) | C14-C15-C16-C17 | -178.8(2) |
| O1-C1-C2-C3 | 179.9(2) | C24-C15-C16-C17 | 1.2(3) |
| N1-C1-C2-C3 | -1.2(3) | C15-C16-C17-C18 | -1.0(3) |
| C6-C2-C3-C4 | -179.9(2) | C16-C17-C18-O3 | 178.7(2) |
| C1-C2-C3-C4 | -1.6(3) | C16-C17-C18-C19 | -0.6(3) |
| C6-C2-C3-C9 | -0.2(3) | O3-C18-C19-C20 | 2.0(3) |
| C1-C2-C3-C9 | 177.99(19) | C17-C18-C19-C20 | -178.6(2) |
| C2-C3-C4-C12 | -179.9(2) | O3-C18-C19-C24 | -177.46(18) |
| C9-C3-C4-C12 | 0.5(3) | C17-C18-C19-C24 | $1.9(3)$ |
| C2-C3-C4-C5 | 2.2(3) | C24-C19-C20-C21 | 0.3(3) |
| C9-C3-C4-C5 | -177.47(19) | C18-C19-C20-C21 | -179.2(2) |
| C12-C4-C5-O2 | 1.5(4) | C19-C20-C21-C22 | 0.0(3) |
| C3-C4-C5-O2 | 179.5(2) | C20-C21-C22-C23 | 0.1(3) |
| C12-C4-C5-N1 | -177.8(2) | C21-C22-C23-C24 | -0.6(3) |
| C3-C4-C5-N1 | 0.1(3) | C20-C19-C24-C23 | -0.8(3) |
| C3-C2-C6-C7 | 1.0(3) | C18-C19-C24-C23 | 178.71(19) |
| C1-C2-C6-C7 | -177.3(2) | C20-C19-C24-C15 | 178.89(19) |
| C2-C6-C7-C8 | -1.0(3) | C18-C19-C24-C15 | -1.6(3) |
| C6-C7-C8-C9 | 0.2(3) | C22-C23-C24-C19 | 1.0(3) |
| C7-C8-C9-C3 | 0.5(3) | C22-C23-C24-C15 | -178.7(2) |
| C7-C8-C9-C10 | 180.0(2) | C16-C15-C24-C19 | 0.1(3) |
| C2-C3-C9-C8 | -0.5(3) | C14-C15-C24-C19 | -179.88(19) |
| C4-C3-C9-C8 | 179.12(19) | C16-C15-C24-C23 | 179.8(2) |
| C2-C3-C9-C10 | -179.99(19) | C14-C15-C24-C23 | -0.2(3) |
| C4-C3-C9-C10 | -0.4(3) | N1-C25-C26-C27 | 174.1(2) |
| C8-C9-C10-C11 | -179.5(2) | C25-C26-C27-C28 | -170.5(2) |
| C3-C9-C10-C11 | 0.0(3) | C26-C27-C28-C29 | 180.0(2) |
| C8-C9-C10-C13 | 1.0(3) | C27-C28-C29-C30 | 176.9(3) |
| C3-C9-C10-C13 | -179.58(19) | O3-C31-C32-C33 | -63.0(3) |
| C13-C10-C11-C12 | 179.9(2) | C31-C32-C33-C34 | 175.5(2) |
| C9-C10-C11-C12 | 0.3(3) | C32-C33-C34-C35 | -177.2(2) |
| C3-C4-C12-C11 | -0.2(3) | C33-C34-C35-C36 | 174.3(2) |
| C5-C4-C12-C11 | 177.8(2) | O4-C37-C38-C42 | 1.8(3) |


| N2-C37-C38-C42 | -177.5(2) | C51-C52-C53-C54 | 1.1(3) |
| :---: | :---: | :---: | :---: |
| O4-C37-C38-C39 | -179.6(2) | C52-C53-C54-O6 | 179.3(2) |
| N2-C37-C38-C39 | 1.1(3) | C52-C53-C54-C55 | -0.9(3) |
| C42-C38-C39-C40 | 179.3(2) | O6-C54-C55-C56 | -0.5(3) |
| C37-C38-C39-C40 | 0.7(3) | C53-C54-C55-C56 | 179.7(2) |
| C42-C38-C39-C45 | -0.6(3) | O6-C54-C55-C60 | 179.52(18) |
| C37-C38-C39-C45 | -179.21(19) | C53-C54-C55-C60 | -0.4(3) |
| C38-C39-C40-C48 | -179.9(2) | C60-C55-C56-C57 | -0.2(3) |
| C45-C39-C40-C48 | 0.1(3) | C54-C55-C56-C57 | 179.8(2) |
| C38-C39-C40-C41 | -1.7(3) | C55-C56-C57-C58 | -0.2(3) |
| C45-C39-C40-C41 | 178.29(19) | C56-C57-C58-C59 | 0.0(3) |
| C48-C40-C41-O5 | -1.6(3) | C57-C58-C59-C60 | 0.5(3) |
| C39-C40-C41-O5 | -179.9(2) | C58-C59-C60-C55 | -0.8(3) |
| C48-C40-C41-N2 | 179.0(2) | C58-C59-C60-C51 | 178.5(2) |
| C39-C40-C41-N2 | 0.7(3) | C56-C55-C60-C59 | 0.7(3) |
| C39-C38-C42-C43 | -0.2(3) | C54-C55-C60-C59 | -179.29(19) |
| C37-C38-C42-C43 | 178.4(2) | C56-C55-C60-C51 | -178.69(19) |
| C38-C42-C43-C44 | 1.0(3) | C54-C55-C60-C51 | 1.3(3) |
| C42-C43-C44-C45 | -1.0(3) | C52-C51-C60-C59 | 179.6(2) |
| C43-C44-C45-C39 | 0.2(3) | C50-C51-C60-C59 | -0.4(3) |
| C43-C44-C45-C46 | -179.8(2) | C52-C51-C60-C55 | -1.1(3) |
| C40-C39-C45-C44 | -179.36(19) | C50-C51-C60-C55 | 178.98(19) |
| C38-C39-C45-C44 | 0.6(3) | N2-C61-C62-C63 | 175.6(2) |
| C40-C39-C45-C46 | 0.7(3) | C61-C62-C63-C64 | -79.0(3) |
| C38-C39-C45-C46 | -179.38(19) | C62-C63-C64-C65 | 178.5(2) |
| C44-C45-C46-C47 | 179.1(2) | C63-C64-C65-C66 | 177.6(3) |
| C39-C45-C46-C47 | -0.9(3) | O6-C67-C68-C69 | 165.6(2) |
| C44-C45-C46-C49 | -1.1(3) | C67-C68-C69-C70 | 179.7(2) |
| C39-C45-C46-C49 | 178.86(19) | C68-C69-C70-C71 | 165.4(2) |
| C49-C46-C47-C48 | -179.3(2) | C69-C70-C71-C72 | -76.4(3) |
| C45-C46-C47-C48 | 0.4(3) | O1-C1-N1-C5 | -177.4(2) |
| C39-C40-C48-C47 | -0.6(3) | C2-C1-N1-C5 | 3.6(3) |
| C41-C40-C48-C47 | -178.80(19) | O1-C1-N1-C25 | 4.0(3) |
| C46-C47-C48-C40 | 0.3(3) | C2-C1-N1-C25 | -174.99(19) |
| C50-C51-C52-C53 | 179.8(2) | O2-C5-N1-C1 | 177.5(2) |
| C60-C51-C52-C53 | -0.2(3) | C4-C5-N1-C1 | -3.1(3) |


| O2-C5-N1-C25 | $-3.8(3)$ | O5-C41-N2-C61 | $5.1(3)$ |
| :--- | :---: | :--- | :---: |
| C4-C5-N1-C25 | $175.52(19)$ | C40-C41-N2-C61 | $-175.52(19)$ |
| C26-C25-N1-C1 | $100.5(2)$ | C62-C61-N2-C37 | $-94.7(2)$ |
| C26-C25-N1-C5 | $-78.2(3)$ | C62-C61-N2-C41 | $82.3(3)$ |
| O4-C37-N2-C41 | $178.5(2)$ | C17-C18-O3-C31 | $-11.7(3)$ |
| C38-C37-N2-C41 | $-2.1(3)$ | C19-C18-O3-C31 | $167.6(2)$ |
| O4-C37-N2-C61 | $-4.7(3)$ | C32-C31-O3-C18 | $-160.6(2)$ |
| C38-C37-N2-C61 | $174.64(19)$ | C53-C54-O6-C67 | $4.1(3)$ |
| O5-C41-N2-C37 | $-178.2(2)$ | C55-C54-O6-C67 | $-175.79(19)$ |
| C40-C41-N2-C37 | $1.2(3)$ | C68-C67-O6-C54 | $-178.99(19)$ |

End of Crystallographic info for $\mathbf{6 Y}{ }^{\prime}$

## Crystallographic Material for 7y

Crystallographic Material for 7y (7Y).

X-ray Experimental.
Table 7y.1. Crystallographic Data for $7 \mathbf{y}$.

Table $7 \mathbf{y}$.2. Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the nonhydrogen atoms of $7 \mathbf{y}$.

Table $7 \mathbf{y} .3$. Bond Lengths $(\AA)$ and Angles $\left(\left(^{\circ}\right)\right.$ for the non-hydrogen atoms of $7 \mathbf{y}$.
Table 7y.4. Anisotropic thermal parameters for the non-hydrogen atoms of $\mathbf{7 y}$.
Table 7y.5. Fractional coordinates and isotropic thermal parameters ( $\AA^{2}$ ) for the hydrogen atoms of $7 \mathbf{y}$.

Table 7y.6. Torsion Angles $\left(^{(0)}\right.$ for the non-hydrogen atoms of $\mathbf{7 y}$.

Crystallographic Material for 7y:
X-ray Experimental for $\mathrm{C}_{38} \mathrm{H}_{41} \mathrm{NO}_{3}$ : (7y) Crystals grew as long, yellow laths by vapor-vapor diffusion of Toluene and MeCN. The data crystal was cut from a larger crystal and had an approximate maximum dimensions of $0.15 \times 0.10 \times 0.04 \mathrm{~mm}$. The data were collected on Beamline 5.0.1 at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The synchrotron beamline produced a wavelength $=0.97741 \AA$. A total of 190 frames of data were collected using $\phi$-scans with a scan range of $1^{\circ}$ and a counting time of 4 seconds per frame for frames collected with a detector offset of $0.0^{\circ}$. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection was performed using the Beamline Operating Software, BOS/B3. The unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.40.53.' The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement
parameters for the non-H atoms using SHELXL-2016/6. ${ }^{\text {. }}$ Structure analysis was aided by use of the programs PLATON ${ }^{4}$, OLEX2 ${ }^{5}$ and WinGX. ${ }^{6}$ The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). There are two molecules in the asymmetric unit. In one molecule, one of the heptyl side chains was disordered. The disorder affected the last six carbon atoms of the n-heptyl group.

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.1262 * \mathrm{P})^{2}+\right.$ $(4.9486 * P)]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.175 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0573 and a goodness of fit, $\mathrm{S},=0.948$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S, are given below. ${ }^{7}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{8}$ All figures were generated using SHELXTL/PC. 9

## References

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2) SHELXT. (2015). G. M. Sheldrick. A program for crystal structure solution. Acta Cryst. A71, 3-8.
3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
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5) OLEX2. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. and Puschmann, H. A Complete Structure Solution, Refinement and Analysis Program. J. Appl. Cryst. 42, 339-341.
6) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
7) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \sum \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\left|\mathrm{F}_{\mathrm{c}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\mathrm{LW}_{\mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
8) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
9) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 7Y.1. Crystal data and structure refinement for 7Y.

| Empirical formula | C38 H41 N O3 |
| :---: | :---: |
| Formula weight | 559.72 |
| Temperature | 100.15 K |
| Wavelength | 0.97741 Å |
| Crystal system | monoclinic |
| Space group | P $121 / \mathrm{c} 1$ |
| Unit cell dimensions | $\mathrm{a}=53.0277(7) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=7.43870(10) \AA \quad \beta=94.613(2)^{\circ}$. |
|  | $\mathrm{c}=15.4897(3) \AA \quad \gamma=90^{\circ}$. |
| Volume | 6090.23(17) $\AA^{3}$ |
| Z | 8 |
| Density (calculated) | $1.221 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.174 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 2400 |
| Crystal size | $0.15 \times 0.1 \times 0.04 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.120 to $26.304^{\circ}$. |
| Index ranges | $-43<=\mathrm{h}<=47,-6<=\mathrm{k}<=6,-13<=\mathrm{l}<=13$ |
| Reflections collected | 7445 |
| Independent reflections | $3474[\mathrm{R}(\mathrm{int})=0.0175]$ |
| Completeness to theta $=26.304^{\circ}$ | 73.0 \% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00 and 0.210 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 3474 / 1246 / 822 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.048 |
| Final R indices [ $\mathrm{I} \times 2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0573, \mathrm{wR} 2=0.1593$ |
| R indices (all data) | $\mathrm{R} 1=0.0637, \mathrm{wR} 2=0.1754$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.282 and -0.193 e. $\AA^{-3}$ |

Table 7Y.2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $7 \mathbf{Y}$. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $U^{\mathrm{ij}}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| O1 | 3614(1) | 3397(4) | 10047(2) | 50(1) |
| O2 | 3795(1) | 5776(4) | 7472(2) | 51(1) |
| O3 | 1373(1) | 2849(4) | 5337(2) | 38(1) |
| N1 | 3705(1) | 4638(5) | 8767(3) | 40(1) |
| C1 | 3540(1) | 3790(6) | 9308(4) | 40(1) |
| C2 | 3278(1) | 3434(6) | 8937(3) | 30(1) |
| C3 | 3110(1) | 2655(5) | 9449(3) | 32(1) |
| C4 | 2861(1) | 2355(5) | 9124(3) | 33(1) |
| C5 | 2783(1) | 2784(5) | 8292(3) | 32(1) |
| C6 | 2950(1) | 3597(6) | 7740(3) | 29(1) |
| C7 | 2877(1) | 4113(6) | 6878(3) | 32(1) |
| C8 | 3052(1) | 4906(5) | 6385(3) | 32(1) |
| C9 | 3301(1) | 5178(5) | 6720(3) | 32(1) |
| C10 | 3379(1) | 4721(6) | 7550(3) | 28(1) |
| C11 | 3635(1) | 5077(6) | 7911(4) | 37(1) |
| C12 | 3204(1) | 3908(5) | 8081(3) | 30(1) |
| C13 | 2620(1) | 3855(6) | 6524(3) | 37(1) |
| C14 | 2405(1) | 3649(5) | 6258(3) | 36(1) |
| C15 | 2142(1) | 3419(6) | 5995(3) | 29(1) |
| C16 | 1990(1) | 2649(5) | 6572(3) | 32(1) |
| C17 | 1730(1) | 2449(5) | 6372(3) | 30(1) |
| C18 | 1621(1) | 2962(5) | 5587(3) | 29(1) |
| C19 | 1774(1) | 3681(5) | 4945(3) | 27(1) |
| C20 | 1670(1) | 4169(6) | 4116(3) | 34(1) |
| C21 | 1816(1) | 4896(5) | 3526(3) | 34(1) |
| C22 | 2074(1) | 5166(5) | 3739(3) | 33(1) |
| C23 | 2182(1) | 4711(5) | 4540(3) | 31(1) |
| C24 | 2035(1) | 3934(5) | 5161(3) | 28(1) |
| C25 | 3957(1) | 5028(7) | 9151(3) | 51(1) |
| C26 | 3973(1) | 6685(7) | 9712(3) | 55(1) |
| C27 | 4232(1) | 6891(8) | 10170(3) | 70(2) |


| C28 | 4257(1) | 8318(8) | 10853(3) | 74(2) |
| :---: | :---: | :---: | :---: | :---: |
| C29 | 4511(1) | 8341(9) | 11375(4) | 86(2) |
| C30 | 4536(1) | 9612(9) | 12116(4) | 91(2) |
| C31 | 4789(1) | 9563(11) | 12631(4) | 122(3) |
| C32 | 1203(1) | 2463(6) | 6004(3) | 39(1) |
| C33 | 942(1) | 2914(6) | 5620(3) | 39(1) |
| C34 | 854(1) | 1852(6) | 4828(3) | 41(1) |
| C35 | 599(1) | 2410(6) | 4405(3) | 45(1) |
| C36 | 521(1) | 1503(6) | 3553(3) | 46(1) |
| C37 | 272(1) | 2147(7) | 3128(3) | 60(2) |
| C38 | 203(1) | 1350(8) | 2250(3) | 72(2) |
| O4 | 1400(1) | 9576(4) | 2838(2) | 54(1) |
| O5 | 1166(1) | 7153(4) | 5329(2) | 53(1) |
| O6 | 3589(1) | 9873(4) | 7771(2) | 47(1) |
| N2 | 1286(1) | 8302(5) | 4075(3) | 35(1) |
| C39 | 1462(1) | 9106(6) | 3580(4) | 37(1) |
| C48 | 1593(1) | 8024(6) | 5337(3) | 28(1) |
| C57 | 3187(1) | 8884(6) | 8066(3) | 32(1) |
| C50 | 1780(1) | 8774(5) | 4843(3) | 30(1) |
| C56 | 3344(1) | 9658(6) | 7461(3) | 34(1) |
| C44 | 2035(1) | 8968(6) | 5214(3) | 35(1) |
| C55 | 3248(1) | 10113(5) | 6654(3) | 34(1) |
| C62 | 2929(1) | 8591(6) | 7806(3) | 34(1) |
| C40 | 1719(1) | 9322(6) | 3992(3) | 32(1) |
| C49 | 1337(1) | 7775(6) | 4931(3) | 38(1) |
| C46 | 1912(1) | 7650(5) | 6529(3) | 34(1) |
| C53 | 2831(1) | 9075(6) | 6968(3) | 35(1) |
| C45 | 2092(1) | 8394(6) | 6061(3) | 40(1) |
| C58 | 3281(1) | 8406(6) | 8902(3) | 38(1) |
| C43 | 2216(1) | 9722(5) | 4675(3) | 35(1) |
| C61 | 2775(1) | 7806(6) | 8422(3) | 40(1) |
| C52 | 2572(1) | 8817(6) | 6691(3) | 44(1) |
| C60 | 2876(1) | 7375(6) | 9229(3) | 45(1) |
| C54 | 2991(1) | 9849(5) | 6413(3) | 38(1) |
| C42 | 2144(1) | 10219(6) | 3857(3) | 44(1) |
| C51 | 2354(1) | 8596(6) | 6440(3) | 45(1) |


| C68 | $456(1)$ | $7918(7)$ | $501(3)$ | $51(1)$ |
| :--- | ---: | ---: | ---: | ---: |
| C67 | $491(1)$ | $6714(6)$ | $1273(3)$ | $48(1)$ |
| C59 | $3132(1)$ | $7645(6)$ | $9473(3)$ | $45(1)$ |
| C41 | $1900(1)$ | $10042(6)$ | $3506(3)$ | $40(1)$ |
| C47 | $1660(1)$ | $7472(5)$ | $6175(3)$ | $37(1)$ |
| C63 | $1035(1)$ | $7956(6)$ | $3645(3)$ | $49(1)$ |
| C66 | $731(1)$ | $7107(7)$ | $1873(3)$ | $48(1)$ |
| C64 | $1024(1)$ | $6174(6)$ | $3172(3)$ | $47(1)$ |
| C70 | $3768(1)$ | $10319(9)$ | $7154(4)$ | $57(2)$ |
| C65 | $770(1)$ | $5913(6)$ | $2641(3)$ | $52(1)$ |
| C69 | $222(1)$ | $7573(7)$ | $-91(3)$ | $67(2)$ |
| C71 | $4037(2)$ | $9966(19)$ | $7459(8)$ | $57(4)$ |
| C72 | $4116(2)$ | $11156(12)$ | $8208(6)$ | $54(3)$ |
| C73 | $4386(2)$ | $10806(14)$ | $8557(7)$ | $63(3)$ |
| C74 | $4478(2)$ | $12040(15)$ | $9296(7)$ | $55(3)$ |
| C75 | $4741(2)$ | $11690(20)$ | $9681(9)$ | $67(4)$ |
| C76 | $4823(4)$ | $12910(30)$ | $10437(11)$ | $91(6)$ |
| C71A | $4010(2)$ | $10310(30)$ | $7808(10)$ | $61(5)$ |
| C72A | $4234(2)$ | $11008(16)$ | $7412(7)$ | $58(3)$ |
| C73A | $4483(2)$ | $10756(18)$ | $7944(8)$ | $64(4)$ |
| C74A | $4509(3)$ | $11750(20)$ | $8790(9)$ | $61(5)$ |
| C75A | $4767(3)$ | $11580(30)$ | $9272(10)$ | $62(5)$ |
| C76A | $4799(5)$ | $12690(40)$ | $10080(12)$ | $64(6)$ |

Table 7Y.3. Bond lengths $[\AA]$ and angles [ $\left.{ }^{\circ}\right]$ for $7 \mathbf{Y}$.

| O1-C1 | $1.216(5)$ | C18-C19 | $1.435(6)$ |
| :---: | :---: | :---: | :---: |
| O2-C11 | 1.240(5) | C19-C20 | 1.404(6) |
| O3-C18 | 1.341(5) | C19-C24 | 1.411(6) |
| O3-C32 | $1.455(5)$ | C20-H20 | 0.95 |
| N1-C1 | $1.406(6)$ | C20-C21 | 1.358(6) |
| N1-C11 | 1.386(6) | C21-H21 | 0.95 |
| N1-C25 | $1.451(5)$ | C21-C22 | 1.395(5) |
| C1-C2 | 1.482(6) | C22-H22 | 0.95 |
| C2-C3 | 1.370(6) | C22-C23 | 1.368(5) |
| C2-C12 | $1.399(6)$ | C23-H23 | 0.95 |
| C3-H3 | 0.95 | C23-C24 | 1.409(6) |
| C3-C4 | 1.391(5) | C25-H25A | 0.99 |
| C4-H4 | 0.95 | C25-H25B | 0.99 |
| C4-C5 | 1.360(5) | C25-C26 | 1.506(6) |
| C5-H5 | 0.95 | C26-H26A | 0.99 |
| C5-C6 | 1.415(6) | C26-H26B | 0.99 |
| C6-C7 | 1.413(6) | C26-C27 | 1.503(6) |
| C6-C12 | $1.426(6)$ | C27-H27A | 0.99 |
| C7-C8 | 1.379(6) | C27-H27B | 0.99 |
| C7-C13 | 1.441(6) | C27-C28 | 1.497(7) |
| C8-H8 | 0.95 | C28-H28A | 0.99 |
| C8-C9 | $1.393(5)$ | C28-H28B | 0.99 |
| C9-H9 | 0.95 | C28-C29 | 1.513(7) |
| C9-C10 | 1.361(6) | C29-H29A | 0.99 |
| C10-C11 | 1.454(6) | C29-H29B | 0.99 |
| C10-C12 | $1.424(6)$ | C29-C30 | 1.485(7) |
| C13-C14 | 1.193(6) | C30-H30A | 0.99 |
| C14-C15 | $1.428(6)$ | C30-H30B | 0.99 |
| C15-C16 | 1.377(6) | C30-C31 | 1.505(7) |
| C15-C24 | $1.422(6)$ | C31-H31A | 0.98 |
| C16-H16 | 0.95 | C31-H31B | 0.98 |
| C16-C17 | $1.395(5)$ | C31-H31C | 0.98 |
| C17-H17 | 0.95 | C32-H32A | 0.99 |
| C17-C18 | 1.359(6) | C32-H32B | 0.99 |


| C32-C33 | $1.499(5)$ | C44-C45 | 1.390(6) |
| :---: | :---: | :---: | :---: |
| C33-H33A | 0.99 | C44-C43 | 1.436(6) |
| C33-H33B | 0.99 | C55-H55 | 0.95 |
| C33-C34 | 1.502(6) | C55-C54 | 1.398(6) |
| C34-H34A | 0.99 | C62-C53 | 1.406(6) |
| C34-H34B | 0.99 | C62-C61 | 1.429(6) |
| C34-C35 | 1.510(6) | C40-C41 | 1.377(6) |
| C35-H35A | 0.99 | C46-H46 | 0.95 |
| C35-H35B | 0.99 | C46-C45 | 1.360(6) |
| C35-C36 | 1.511(6) | C46-C47 | 1.412(6) |
| C36-H36A | 0.99 | C53-C52 | 1.421(6) |
| C36-H36B | 0.99 | C53-C54 | 1.380(6) |
| C36-C37 | 1.503(6) | C45-C51 | 1.470(7) |
| C37-H37A | 0.99 | C58-H58 | 0.95 |
| C37-H37B | 0.99 | C58-C59 | 1.356(6) |
| C37-C38 | 1.502(6) | C43-H43 | 0.95 |
| C38-H38A | 0.98 | C43-C42 | 1.343(6) |
| C38-H38B | 0.98 | C61-H61 | 0.95 |
| C38-H38C | 0.98 | C61-C60 | 1.358(6) |
| O4-C39 | 1.222(5) | C52-C51 | 1.203(6) |
| O5-C49 | $1.229(5)$ | C60-H60 | 0.95 |
| O6-C56 | 1.354(5) | C60-C59 | 1.393(6) |
| O6-C70 | $1.438(6)$ | C54-H54 | 0.95 |
| N2-C39 | 1.393(6) | C42-H42 | 0.95 |
| N2-C49 | 1.389(6) | C42-C41 | 1.370(6) |
| N2-C63 | $1.460(5)$ | C68-H68A | 0.99 |
| C39-C40 | $1.465(6)$ | C68-H68B | 0.99 |
| C48-C50 | 1.417(6) | C68-C67 | 1.493(6) |
| C48-C49 | 1.459(6) | C68-C69 | 1.505(6) |
| C48-C47 | 1.380(6) | C67-H67A | 0.99 |
| C57-C56 | $1.425(6)$ | C67-H67B | 0.99 |
| C57-C62 | $1.415(6)$ | C67-C66 | 1.542(6) |
| C57-C58 | 1.396 (6) | C59-H59 | 0.95 |
| C50-C44 | $1.430(6)$ | C41-H41 | 0.95 |
| C50-C40 | 1.393(6) | C47-H47 | 0.95 |
| C56-C55 | $1.354(6)$ | C63-H63A | 0.99 |


| C63-H63B | 0.99 | C74-H74B | 0.99 |
| :---: | :---: | :---: | :---: |
| C63-C64 | 1.513(6) | C74-C75 | $1.496(12)$ |
| C66-H66A | 0.99 | C75-H75A | 0.99 |
| C66-H66B | 0.99 | C75-H75B | 0.99 |
| C66-C65 | 1.486(6) | C75-C76 | 1.520(14) |
| C64-H64A | 0.99 | C76-H76A | 0.98 |
| C64-H64B | 0.99 | C76-H76B | 0.98 |
| C64-C65 | 1.530(6) | C76-H76C | 0.98 |
| C70-C71 | 1.493(11) | C71A-H71C | 0.99 |
| C70-C71A | 1.570(14) | C71A-H71D | 0.99 |
| C70-H70A | 1.03(4) | C71A-C72A | 1.478(15) |
| C70-H70B | 1.09(5) | C72A-H72C | 0.99 |
| C65-H65A | 0.99 | C72A-H72D | 0.99 |
| C65-H65B | 0.99 | C72A-C73A | 1.509(11) |
| C69-H69A | 0.98 | C73A-H73C | 0.99 |
| C69-H69B | 0.98 | C73A-H73D | 0.99 |
| C69-H69C | 0.98 | C73A-C74A | 1.500(14) |
| C71-H71A | 0.99 | C74A-H74C | 0.99 |
| C71-H71B | 0.99 | C74A-H74D | 0.99 |
| C71-C72 | 1.491(12) | C74A-C75A | 1.509(15) |
| C72-H72A | 0.99 | C75A-H75C | 0.99 |
| C72-H72B | 0.99 | C75A-H75D | 0.99 |
| C72-C73 | 1.516(10) | C75A-C76A | 1.501(16) |
| C73-H73A | 0.99 | C76A-H76D | 0.98 |
| C73-H73B | 0.99 | C76A-H76E | 0.98 |
| C73-C74 | 1.516(12) | C76A-H76F | 0.98 |
| C74-H74A | 0.99 |  |  |
| C18-O3-C32 | 117.2(3) | C3-C2-C12 | 120.5(4) |
| C1-N1-C25 | 116.3(4) | C12-C2-C1 | 120.4(5) |
| C11-N1-C1 | 123.1(4) | C2-C3-H3 | 119.9 |
| C11-N1-C25 | 120.6(4) | C2-C3-C4 | 120.2(4) |
| O1-C1-N1 | 120.1(4) | C4-C3-H3 | 119.9 |
| O1-C1-C2 | 122.7(5) | C3-C4-H4 | 119.6 |
| N1-C1-C2 | 117.1(5) | C5-C4-C3 | 120.8(4) |
| C3-C2-C1 | 119.1(4) | C5-C4-H4 | 119.6 |


| C4-C5-H5 | 119.5 | O3-C18-C19 | 114.6(4) |
| :---: | :---: | :---: | :---: |
| C4-C5-C6 | 121.0(4) | C17-C18-C19 | 120.0(4) |
| C6-C5-H5 | 119.5 | C20-C19-C18 | 121.9(4) |
| C5-C6-C12 | 117.6(4) | C20-C19-C24 | 119.2(4) |
| C7-C6-C5 | 123.5(4) | C24-C19-C18 | 118.9(4) |
| C7-C6-C12 | 118.9(4) | C19-C20-H20 | 119.5 |
| C6-C7-C13 | 120.0(4) | C21-C20-C19 | 121.0(4) |
| C8-C7-C6 | 119.8(4) | C21-C20-H20 | 119.5 |
| C8-C7-C13 | 120.2(4) | C20-C21-H21 | 120.0 |
| C7-C8-H8 | 119.5 | C20-C21-C22 | 120.0(4) |
| C7-C8-C9 | 120.9(4) | C22-C21-H21 | 120.0 |
| C9-C8-H8 | 119.5 | C21-C22-H22 | 119.7 |
| C8-C9-H9 | 119.3 | C23-C22-C21 | 120.6(4) |
| C10-C9-C8 | 121.5(4) | C23-C22-H22 | 119.7 |
| C10-C9-H9 | 119.3 | C22-C23-H23 | 119.8 |
| C9-C10-C11 | 121.5(5) | C22-C23-C24 | 120.5(4) |
| C9-C10-C12 | 119.3(4) | C24-C23-H23 | 119.8 |
| C12-C10-C11 | 119.2(4) | C19-C24-C15 | 119.6(4) |
| O2-C11-N1 | 118.9(4) | C23-C24-C15 | 121.8(4) |
| O2-C11-C10 | 121.5(5) | C23-C24-C19 | 118.6(4) |
| N1-C11-C10 | 119.5(5) | N1-C25-H25A | 108.8 |
| C2-C12-C6 | 119.8(5) | N1-C25-H25B | 108.8 |
| C2-C12-C10 | 120.5(4) | N1-C25-C26 | 113.9(4) |
| C10-C12-C6 | 119.7(4) | H25A-C25-H25B | 107.7 |
| C14-C13-C7 | 177.8(5) | C26-C25-H25A | 108.8 |
| C13-C14-C15 | 176.4(5) | C26-C25-H25B | 108.8 |
| C16-C15-C14 | 118.2(4) | C25-C26-H26A | 109.4 |
| C16-C15-C24 | 119.2(4) | C25-C26-H26B | 109.4 |
| C24-C15-C14 | 122.6(4) | H26A-C26-H26B | 108.0 |
| C15-C16-H16 | 119.3 | C27-C26-C25 | 111.1(4) |
| C15-C16-C17 | 121.4(4) | C27-C26-H26A | 109.4 |
| C17-C16-H16 | 119.3 | C27-C26-H26B | 109.4 |
| C16-C17-H17 | 119.6 | C26-C27-H27A | 108.4 |
| C18-C17-C16 | 120.8(4) | C26-C27-H27B | 108.4 |
| C18-C17-H17 | 119.6 | H27A-C27-H27B | 107.4 |
| O3-C18-C17 | 125.3(4) | C28-C27-C26 | 115.6(4) |


| C28-C27-H27A | 108.4 | C34-C33-H33A | 108.5 |
| :---: | :---: | :---: | :---: |
| C28-C27-H27B | 108.4 | C34-C33-H33B | 108.5 |
| C27-C28-H28A | 108.7 | C33-C34-H34A | 108.6 |
| C27-C28-H28B | 108.7 | C33-C34-H34B | 108.6 |
| C27-C28-C29 | 114.3(5) | C33-C34-C35 | 114.8(4) |
| H28A-C28-H28B | 107.6 | H34A-C34-H34B | 107.5 |
| C29-C28-H28A | 108.7 | C35-C34-H34A | 108.6 |
| C29-C28-H28B | 108.7 | C35-C34-H34B | 108.6 |
| C28-C29-H29A | 108.3 | C34-C35-H35A | 108.4 |
| C28-C29-H29B | 108.3 | C34-C35-H35B | 108.4 |
| H29A-C29-H29B | 107.4 | C34-C35-C36 | 115.5(4) |
| C30-C29-C28 | 116.1(5) | H35A-C35-H35B | 107.5 |
| C30-C29-H29A | 108.3 | C36-C35-H35A | 108.4 |
| C30-C29-H29B | 108.3 | C36-C35-H35B | 108.4 |
| C29-C30-H30A | 108.6 | C35-C36-H36A | 108.7 |
| C29-C30-H30B | 108.6 | C35-C36-H36B | 108.7 |
| C29-C30-C31 | 114.5(5) | H36A-C36-H36B | 107.6 |
| H30A-C30-H30B | 107.6 | C37-C36-C35 | 114.3(4) |
| C31-C30-H30A | 108.6 | C37-C36-H36A | 108.7 |
| C31-C30-H30B | 108.6 | C37-C36-H36B | 108.7 |
| C30-C31-H31A | 109.5 | C36-C37-H37A | 108.7 |
| C30-C31-H31B | 109.5 | C36-C37-H37B | 108.7 |
| C30-C31-H31C | 109.5 | H37A-C37-H37B | 107.6 |
| H31A-C31-H31B | 109.5 | C38-C37-C36 | 114.4(4) |
| H31A-C31-H31C | 109.5 | C38-C37-H37A | 108.7 |
| H31B-C31-H31C | 109.5 | C38-C37-H37B | 108.7 |
| O3-C32-H32A | 110.5 | C37-C38-H38A | 109.5 |
| O3-C32-H32B | 110.5 | C37-C38-H38B | 109.5 |
| O3-C32-C33 | 106.2(4) | C37-C38-H38C | 109.5 |
| H32A-C32-H32B | 108.7 | H38A-C38-H38B | 109.5 |
| C33-C32-H32A | 110.5 | H38A-C38-H38C | 109.5 |
| C33-C32-H32B | 110.5 | H38B-C38-H38C | 109.5 |
| C32-C33-H33A | 108.5 | C56-O6-C70 | 117.0(4) |
| C32-C33-H33B | 108.5 | C39-N2-C63 | 116.9(4) |
| C32-C33-C34 | 115.1(4) | C49-N2-C39 | 123.8(4) |
| H33A-C33-H33B | 107.5 | C49-N2-C63 | 119.2(4) |


| O4-C39-N2 | 119.8(4) | C44-C45-C51 | 118.2(5) |
| :---: | :---: | :---: | :---: |
| O4-C39-C40 | 123.5(5) | C46-C45-C44 | 121.3(4) |
| N2-C39-C40 | 116.7(5) | C46-C45-C51 | 120.5(5) |
| C50-C48-C49 | 119.0(4) | C57-C58-H58 | 119.1 |
| C47-C48-C50 | 119.1(4) | C59-C58-C57 | 121.8(4) |
| C47-C48-C49 | 121.8(5) | C59-C58-H58 | 119.1 |
| C62-C57-C56 | 118.6(4) | C44-C43-H43 | 119.8 |
| C58-C57-C56 | 122.0(4) | C42-C43-C44 | 120.4(4) |
| C58-C57-C62 | 119.4(5) | C42-C43-H43 | 119.8 |
| C48-C50-C44 | 120.2(4) | C62-C61-H61 | 119.8 |
| C40-C50-C48 | 120.4(4) | C60-C61-C62 | 120.3(4) |
| C40-C50-C44 | 119.4(5) | C60-C61-H61 | 119.8 |
| O6-C56-C57 | 114.0(4) | C51-C52-C53 | 178.7(5) |
| C55-C56-O6 | 125.2(5) | C61-C60-H60 | 119.3 |
| C55-C56-C57 | 120.8(4) | C61-C60-C59 | 121.4(5) |
| C50-C44-C43 | 117.3(4) | C59-C60-H60 | 119.3 |
| C45-C44-C50 | 118.4(5) | C55-C54-H54 | 119.1 |
| C45-C44-C43 | 124.4(4) | C53-C54-C55 | 121.8(4) |
| C56-C55-H55 | 120.1 | C53-C54-H54 | 119.1 |
| C56-C55-C54 | 119.8(4) | C43-C42-H42 | 118.9 |
| C54-C55-H55 | 120.1 | C43-C42-C41 | 122.1(5) |
| C57-C62-C61 | 117.7(4) | C41-C42-H42 | 118.9 |
| C53-C62-C57 | 119.9(5) | C52-C51-C45 | 175.0(5) |
| C53-C62-C61 | 122.3(4) | H68A-C68-H68B | 107.5 |
| C50-C40-C39 | 121.2(5) | C67-C68-H68A | 108.4 |
| C41-C40-C39 | 118.0(5) | C67-C68-H68B | 108.4 |
| C41-C40-C50 | 120.8(4) | C67-C68-C69 | 115.4(4) |
| O5-C49-N2 | 119.2(5) | C69-C68-H68A | 108.4 |
| O5-C49-C48 | 122.0(5) | C69-C68-H68B | 108.4 |
| N2-C49-C48 | 118.7(5) | C68-C67-H67A | 108.7 |
| C45-C46-H46 | 119.6 | C68-C67-H67B | 108.7 |
| C45-C46-C47 | 120.9(4) | C68-C67-C66 | 114.3(4) |
| C47-C46-H46 | 119.6 | H67A-C67-H67B | 107.6 |
| C62-C53-C52 | $121.2(5)$ | C66-C67-H67A | 108.7 |
| C54-C53-C62 | 118.9(4) | C66-C67-H67B | 108.7 |
| C54-C53-C52 | 119.8(5) | C58-C59-C60 | 119.3(5) |


| C58-C59-H59 | 120.3 | C66-C65-H65A | 108.6 |
| :---: | :---: | :---: | :---: |
| C60-C59-H59 | 120.3 | C66-C65-H65B | 108.6 |
| C40-C41-H41 | 120.0 | C64-C65-H65A | 108.6 |
| C42-C41-C40 | 120.0(5) | C64-C65-H65B | 108.6 |
| C42-C41-H41 | 120.0 | H65A-C65-H65B | 107.6 |
| C48-C47-C46 | 120.1(4) | C68-C69-H69A | 109.5 |
| C48-C47-H47 | 119.9 | C68-C69-H69B | 109.5 |
| C46-C47-H47 | 119.9 | C68-C69-H69C | 109.5 |
| N2-C63-H63A | 109.2 | H69A-C69-H69B | 109.5 |
| N2-C63-H63B | 109.2 | H69A-C69-H69C | 109.5 |
| N2-C63-C64 | 112.0(3) | H69B-C69-H69C | 109.5 |
| H63A-C63-H63B | 107.9 | C70-C71-H71A | 109.7 |
| C64-C63-H63A | 109.2 | C70-C71-H71B | 109.7 |
| C64-C63-H63B | 109.2 | H71A-C71-H71B | 108.2 |
| C67-C66-H66A | 108.5 | C72-C71-C70 | 110.0(9) |
| C67-C66-H66B | 108.5 | C72-C71-H71A | 109.7 |
| H66A-C66-H66B | 107.5 | C72-C71-H71B | 109.7 |
| C65-C66-C67 | 115.2(4) | C71-C72-H72A | 109.2 |
| C65-C66-H66A | 108.5 | C71-C72-H72B | 109.3 |
| C65-C66-H66B | 108.5 | C71-C72-C73 | 111.8(8) |
| C63-C64-H64A | 109.2 | H72A-C72-H72B | 107.9 |
| C63-C64-H64B | 109.2 | C73-C72-H72A | 109.2 |
| C63-C64-C65 | 111.8(4) | C73-C72-H72B | 109.2 |
| H64A-C64-H64B | 107.9 | C72-C73-H73A | 108.8 |
| C65-C64-H64A | 109.2 | C72-C73-H73B | 108.8 |
| C65-C64-H64B | 109.2 | H73A-C73-H73B | 107.7 |
| O6-C70-C71 | 114.5(7) | C74-C73-C72 | 113.7(8) |
| O6-C70-C71A | 96.8(6) | C74-C73-H73A | 108.8 |
| O6-C70-H70A | 113(2) | C74-C73-H73B | 108.8 |
| O6-C70-H70B | 108(2) | C73-C74-H74A | 108.4 |
| C71-C70-H70A | 112(2) | C73-C74-H74B | 108.4 |
| C71-C70-H70B | 104(2) | H74A-C74-H74B | 107.5 |
| C71A-C70-H70A | 109(2) | C75-C74-C73 | 115.3(9) |
| C71A-C70-H70B | 126(3) | C75-C74-H74A | 108.4 |
| H70A-C70-H70B | 104(3) | C75-C74-H74B | 108.4 |
| C66-C65-C64 | 114.6(4) | C74-C75-H75A | 108.8 |


| C74-C75-H75B | 108.8 | C72A-C73A-H73D | 108.4 |
| :--- | :--- | :--- | :--- |
| C74-C75-C76 | $113.7(12)$ | H73C-C73A-H73D | 107.4 |
| H75A-C75-H75B | 107.7 | C74A-C73A-C72A | $115.7(10)$ |
| C76-C75-H75A | 108.8 | C74A-C73A-H73C | 108.4 |
| C76-C75-H75B | 108.8 | C74A-C73A-H73D | 108.4 |
| C75-C76-H76A | 109.5 | C73A-C74A-H74C | 108.7 |
| C75-C76-H76B | 109.5 | C73A-C74A-H74D | 108.7 |
| C75-C76-H76C | 109.5 | C73A-C74A-C75A | $114.1(11)$ |
| H76A-C76-H76B | 109.5 | H74C-C74A-H74D | 107.6 |
| H76A-C76-H76C | 109.5 | C75A-C74A-H74C | 108.7 |
| H76B-C76-H76C | 109.5 | C75A-C74A-H74D | 108.7 |
| C70-C71A-H71C | 109.2 | C74A-C75A-H75C | 108.8 |
| C70-C71A-H71D | 109.2 | C74A-C75A-H75D | 108.8 |
| H71C-C71A-H71D | 107.9 | H75C-C75A-H75D | 107.7 |
| C72A-C71A-C70 | $112.0(11)$ | C76A-C75A-C74A | $113.8(14)$ |
| C72A-C71A-H71C | 109.2 | C76A-C75A-H75C | 108.8 |
| C72A-C71A-H71D | 109.2 | C76A-C75A-H75D | 108.8 |
| C71A-C72A-H72C | 108.5 | C75A-C76A-H76D | 109.5 |
| C71A-C72A-H72D | 108.5 | C75A-C76A-H76E | 109.5 |
| C71A-C72A-C73A | $115.2(10)$ | C75A-C76A-H76F | 109.5 |
| H72C-C72A-H72D | 107.5 | H76D-C76A-H76E | 109.5 |
| C73A-C72A-H72C | 108.5 | H76D-C76A-H76F | 109.5 |
| C73A-C72A-H72D | 108.5 | H76E-C76A-H76F | 109.5 |
| C72A-C73A-H73C | 108.4 |  |  |

Table 7Y.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathbf{7 Y}$. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| O1 | 44(2) | 64(2) | 41(2) | $9(2)$ | -7(2) | 1(2) |
| O2 | 36(2) | 64(2) | 52(2) | 1(2) | 1(2) | -11(2) |
| O3 | 24(2) | 48(2) | 40(2) | 2(2) | -5(2) | -2(2) |
| N1 | 26(2) | 56(3) | 36(3) | 5(2) | -11(2) | -1(2) |
| C1 | 37(3) | 40(3) | 44(3) | $0(3)$ | 3(3) | 6(2) |
| C2 | 33(3) | 28(3) | 30(3) | 1(2) | 2(3) | 3(2) |
| C3 | 40(3) | 29(3) | 25(3) | -1(2) | -1(3) | 3(2) |
| C4 | 32(3) | 30(3) | 37(3) | -2(2) | -1(3) | 4(2) |
| C5 | 23(3) | 35(3) | 36(3) | -4(2) | -3(3) | 1(2) |
| C6 | 30(3) | 27(3) | 30(3) | -3(2) | 2(3) | 3(2) |
| C7 | 40(3) | 28(3) | 29(3) | -3(2) | 2(3) | 5(2) |
| C8 | 41(3) | 31(3) | 21(3) | 2(2) | -6(3) | 7(2) |
| C9 | 35(3) | 30(3) | 31(3) | -1(2) | -3(3) | 5(2) |
| C10 | 27(3) | 32(3) | 24(3) | -2(2) | -11(2) | 3(2) |
| C11 | 33(3) | 40(3) | 37(3) | -4(3) | -6(3) | 5(2) |
| C12 | 38(3) | 20(3) | 33(3) | -1(2) | 6(3) | 4(2) |
| C13 | 42(3) | 32(3) | 36(3) | $0(2)$ | -2(3) | 6(3) |
| C14 | 41(3) | 28(3) | 36(3) | 1(2) | -4(3) | 7(2) |
| C15 | 28(3) | 27(3) | 28(3) | -5(2) | -8(3) | 4(2) |
| C16 | 37(3) | 28(3) | 29(3) | -1(2) | -6(3) | 8(2) |
| C17 | 30(3) | 24(3) | 37(3) | -1(2) | 1(3) | 3(2) |
| C18 | 27(3) | 22(3) | 37(3) | -1(2) | -6(3) | 2(2) |
| C19 | 21(3) | 25(3) | 34(3) | -3(2) | -6(3) | 1(2) |
| C20 | 33(3) | 30(3) | 37(3) | $0(2)$ | -9(3) | 2(2) |
| C21 | 38(3) | 31(3) | 32(3) | -3(2) | -8(3) | 0 (2) |
| C22 | 41(3) | 28(3) | 29(3) | -2(2) | 3(3) | -1(2) |
| C23 | 25(3) | 27(3) | 39(3) | -6(2) | -2(3) | 2(2) |
| C24 | 33(3) | 24(3) | 25(3) | -5(2) | -1(3) | 4(2) |
| C25 | 23(3) | 76(4) | 52(3) | 3(3) | -12(3) | -5(2) |
| C26 | 44(3) | 66(4) | 52(3) | 10(3) | -17(3) | -18(3) |
| C27 | 50(3) | 107(4) | 53(3) | -4(3) | -6(3) | -32(3) |


| C28 | $52(3)$ | $101(4)$ | $66(4)$ | $-4(3)$ | $-7(3)$ | $-41(3)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C29 | $56(3)$ | $135(5)$ | $67(4)$ | $-25(4)$ | $6(3)$ | $-39(3)$ |
| C30 | $70(4)$ | $130(5)$ | $71(4)$ | $-22(4)$ | $-6(3)$ | $-25(4)$ |
| C31 | $78(4)$ | $197(7)$ | $89(5)$ | $-64(5)$ | $-17(4)$ | $-21(4)$ |
| C32 | $28(3)$ | $47(3)$ | $42(3)$ | $-3(2)$ | $-5(3)$ | $0(2)$ |
| C33 | $37(3)$ | $44(3)$ | $37(3)$ | $-4(2)$ | $2(2)$ | $-4(2)$ |
| C34 | $28(3)$ | $49(3)$ | $44(3)$ | $2(3)$ | $-5(2)$ | $-1(2)$ |
| C35 | $36(3)$ | $51(3)$ | $48(3)$ | $-6(3)$ | $-2(3)$ | $0(2)$ |
| C36 | $30(3)$ | $56(3)$ | $50(3)$ | $-5(3)$ | $-10(3)$ | $-4(2)$ |
| C37 | $40(3)$ | $80(4)$ | $56(4)$ | $-7(3)$ | $-7(3)$ | $0(3)$ |
| C38 | $50(3)$ | $92(4)$ | $69(4)$ | $-12(3)$ | $-26(3)$ | $4(3)$ |
| O4 | $64(2)$ | $60(2)$ | $38(2)$ | $6(2)$ | $-7(2)$ | $7(2)$ |
| O5 | $41(2)$ | $58(2)$ | $61(2)$ | $-7(2)$ | $14(2)$ | $-7(2)$ |
| O6 | $36(2)$ | $49(2)$ | $54(2)$ | $2(2)$ | $-7(2)$ | $-2(2)$ |
| N2 | $24(2)$ | $46(2)$ | $33(3)$ | $-4(2)$ | $-11(2)$ | $2(2)$ |
| C39 | $45(3)$ | $33(3)$ | $33(3)$ | $-2(3)$ | $-6(3)$ | $8(2)$ |
| C48 | $32(3)$ | $29(3)$ | $22(3)$ | $-4(2)$ | $-8(3)$ | $5(2)$ |
| C57 | $36(3)$ | $30(3)$ | $29(3)$ | $-2(2)$ | $-6(3)$ | $5(2)$ |
| C50 | $35(3)$ | $23(3)$ | $33(3)$ | $-4(2)$ | $2(3)$ | $7(2)$ |
| C56 | $38(3)$ | $34(3)$ | $27(3)$ | $-3(2)$ | $-12(3)$ | $5(2)$ |
| C44 | $43(3)$ | $29(3)$ | $33(3)$ | $-6(2)$ | $-2(3)$ | $7(2)$ |
| C55 | $36(3)$ | $32(3)$ | $35(3)$ | $-2(2)$ | $3(3)$ | $-1(2)$ |
| C62 | $39(3)$ | $27(3)$ | $34(3)$ | $-6(2)$ | $-1(3)$ | $7(2)$ |
| C40 | $40(3)$ | $29(3)$ | $26(3)$ | $-2(2)$ | $4(3)$ | $3(2)$ |
| C49 | $47(3)$ | $35(3)$ | $32(3)$ | $-7(3)$ | $4(3)$ | $5(3)$ |
| C46 | $53(3)$ | $28(3)$ | $18(3)$ | $-1(2)$ | $-14(3)$ | $5(2)$ |
| C53 | $31(3)$ | $28(3)$ | $45(3)$ | $-7(3)$ | $-11(3)$ | $-1(2)$ |
| C45 | $52(3)$ | $30(3)$ | $38(3)$ | $-5(3)$ | $1(3)$ | $2(2)$ |
| C58 | $45(3)$ | $34(3)$ | $34(3)$ | $-4(3)$ | $-3(3)$ | $6(2)$ |
| C43 | $24(3)$ | $29(3)$ | $51(3)$ | $-4(3)$ | $-5(3)$ | $2(2)$ |
| C61 | $34(3)$ | $31(3)$ | $53(3)$ | $-6(3)$ | $-1(3)$ | $3(2)$ |
| C52 | $48(3)$ | $30(3)$ | $54(4)$ | $-5(3)$ | $-5(3)$ | $-2(3)$ |
| C60 | $56(3)$ | $30(3)$ | $51(3)$ | $-1(3)$ | $7(3)$ | $9(2)$ |
| C54 | $52(3)$ | $25(3)$ | $34(3)$ | $-4(2)$ | $-7(3)$ | $3(2)$ |
| C42 | $49(3)$ | $39(3)$ | $44(3)$ | $-2(3)$ | $0(3)$ | $5(2)$ |
| C51 | $56(3)$ | $29(3)$ | $50(4)$ | $-2(3)$ | $-2(3)$ | $1(3)$ |
|  |  |  |  |  |  |  |


| C68 | $45(3)$ | $65(3)$ | $44(3)$ | $2(3)$ | $-4(3)$ | $3(3)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| C67 | $38(3)$ | $57(3)$ | $51(3)$ | $4(3)$ | $2(3)$ | $4(2)$ |
| C59 | $62(3)$ | $38(3)$ | $33(3)$ | $-4(3)$ | $-2(3)$ | $12(3)$ |
| C41 | $46(3)$ | $35(3)$ | $38(3)$ | $-7(2)$ | $1(3)$ | $5(2)$ |
| C47 | $51(3)$ | $26(3)$ | $34(3)$ | $-4(2)$ | $4(3)$ | $2(2)$ |
| C63 | $34(3)$ | $57(3)$ | $53(3)$ | $-13(3)$ | $-11(3)$ | $7(2)$ |
| C66 | $30(3)$ | $66(3)$ | $46(3)$ | $12(3)$ | $-1(3)$ | $1(2)$ |
| C64 | $36(3)$ | $55(3)$ | $49(3)$ | $-7(3)$ | $-12(3)$ | $1(2)$ |
| C70 | $39(3)$ | $58(4)$ | $74(4)$ | $5(4)$ | $0(3)$ | $-9(3)$ |
| C65 | $51(3)$ | $50(3)$ | $54(3)$ | $-3(3)$ | $-3(3)$ | $-1(2)$ |
| C69 | $57(3)$ | $91(4)$ | $51(4)$ | $5(3)$ | $-13(3)$ | $4(3)$ |
| C71 | $48(5)$ | $56(7)$ | $70(7)$ | $-6(6)$ | $13(5)$ | $-11(5)$ |
| C72 | $44(5)$ | $59(6)$ | $60(6)$ | $-5(5)$ | $2(5)$ | $1(5)$ |
| C73 | $54(6)$ | $66(6)$ | $69(6)$ | $8(5)$ | $-3(5)$ | $-2(5)$ |
| C74 | $42(5)$ | $62(6)$ | $60(6)$ | $8(5)$ | $0(5)$ | $1(5)$ |
| C75 | $54(6)$ | $76(8)$ | $69(9)$ | $3(7)$ | $-9(6)$ | $7(6)$ |
| C76 | $76(9)$ | $98(10)$ | $95(13)$ | $-17(10)$ | $-15(9)$ | $-11(8)$ |
| C71A | $57(6)$ | $70(10)$ | $57(9)$ | $-17(8)$ | $10(6)$ | $-14(7)$ |
| C72A | $52(5)$ | $59(7)$ | $61(7)$ | $1(6)$ | $-2(5)$ | $-8(6)$ |
| C73A | $51(6)$ | $72(8)$ | $67(7)$ | $2(6)$ | $-7(6)$ | $3(6)$ |
| C74A | $49(7)$ | $63(8)$ | $68(8)$ | $4(7)$ | $-7(7)$ | $14(7)$ |
| C75A | $53(7)$ | $71(8)$ | $60(9)$ | $-2(8)$ | $-5(6)$ | $18(6)$ |
| C76A | $74(13)$ | $63(13)$ | $53(12)$ | $8(9)$ | $-6(9)$ | $16(10)$ |
|  |  |  |  |  |  |  |

Table 7Y.5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 7Y.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H3 | 3163 | 2319 | 10027 | 38 |
| H4 | 2744 | 1844 | 9488 | 40 |
| H5 | 2613 | 2534 | 8078 | 38 |
| H8 | 3002 | 5272 | 5809 | 38 |
| H9 | 3419 | 5693 | 6361 | 39 |
| H16 | 2063 | 2245 | 7117 | 38 |
| H17 | 1629 | 1948 | 6789 | 36 |
| H20 | 1494 | 3988 | 3966 | 40 |
| H21 | 1743 | 5221 | 2968 | 41 |
| H22 | 2175 | 5671 | 3322 | 39 |
| H23 | 2357 | 4920 | 4680 | 37 |
| H25A | 4072 | 5181 | 8681 | 61 |
| H25B | 4019 | 3985 | 9504 | 61 |
| H26A | 3933 | 7758 | 9348 | 66 |
| H26B | 3846 | 6602 | 10145 | 66 |
| H27A | 4282 | 5726 | 10441 | 85 |
| H27B | 4353 | 7158 | 9732 | 85 |
| H28A | 4123 | 8143 | 11253 | 88 |
| H28B | 4229 | 9505 | 10572 | 88 |
| H29A | 4546 | 7113 | 11600 | 103 |
| H29B | 4643 | 8636 | 10980 | 103 |
| H30A | 4403 | 9338 | 12508 | 109 |
| H30B | 4506 | 10847 | 11893 | 109 |
| H31A | 4923 | 9763 | 12244 | 184 |
| H31B | 4813 | 8386 | 12911 | 184 |
| H31C | 4795 | 10506 | 13074 | 184 |
| H32A | 1247 | 3203 | 6525 | 47 |
| H32B | 1214 | 1179 | 6170 | 47 |
| H33A | 937 | 4208 | 5469 | 47 |
| H33B | 822 | 2720 | 6067 | 47 |


| H34A | 845 | 567 | 4990 | 49 |
| :---: | :---: | :---: | :---: | :---: |
| H34B | 981 | 1968 | 4398 | 49 |
| H35A | 602 | 3726 | 4309 | 54 |
| H35B | 469 | 2160 | 4813 | 54 |
| H36A | 654 | 1706 | 3151 | 55 |
| H36B | 510 | 192 | 3652 | 55 |
| H37A | 137 | 1857 | 3510 | 71 |
| H37B | 279 | 3471 | 3071 | 71 |
| H38A | 327 | 1727 | 1849 | 108 |
| H38B | 34 | 1768 | 2034 | 108 |
| H38C | 203 | 36 | 2293 | 108 |
| H55 | 3355 | 10612 | 6253 | 41 |
| H46 | 1957 | 7244 | 7102 | 41 |
| H58 | 3455 | 8620 | 9077 | 46 |
| H43 | 2386 | 9871 | 4897 | 42 |
| H61 | 2601 | 7585 | 8267 | 48 |
| H60 | 2771 | 6878 | 9635 | 54 |
| H54 | 2925 | 10211 | 5853 | 45 |
| H42 | 2268 | 10710 | 3512 | 53 |
| H68A | 605 | 7793 | 162 | 62 |
| H68B | 451 | 9178 | 706 | 62 |
| H67A | 498 | 5454 | 1071 | 58 |
| H67B | 341 | 6831 | 1613 | 58 |
| H59 | 3201 | 7300 | 10033 | 54 |
| H41 | 1856 | 10416 | 2927 | 48 |
| H47 | 1536 | 6971 | 6513 | 44 |
| H63A | 991 | 8935 | 3227 | 58 |
| H63B | 909 | 7958 | 4082 | 58 |
| H66A | 880 | 7006 | 1529 | 57 |
| H66B | 723 | 8366 | 2077 | 57 |
| H64A | 1049 | 5186 | 3598 | 57 |
| H64B | 1162 | 6117 | 2782 | 57 |
| H65A | 758 | 4648 | 2443 | 62 |
| H65B | 632 | 6122 | 3022 | 62 |
| H69A | 220 | 8377 | -593 | 101 |
| H69B | 71 | 7794 | 222 | 101 |


| H69C | 221 | 6321 | -289 | 101 |
| :---: | :---: | :---: | :---: | :---: |
| H71A | 4058 | 8692 | 7635 | 69 |
| H71B | 4146 | 10194 | 6982 | 69 |
| H72A | 4002 | 10954 | 8675 | 65 |
| H72B | 4098 | 12428 | 8024 | 65 |
| H73A | 4401 | 9545 | 8760 | 76 |
| H73B | 4498 | 10951 | 8080 | 76 |
| H74A | 4469 | 13296 | 9084 | 66 |
| H74B | 4361 | 11933 | 9759 | 66 |
| H75A | 4860 | 11838 | 9226 | 81 |
| H75B | 4753 | 10424 | 9881 | 81 |
| H76A | 4996 | 12614 | 10658 | 136 |
| H76B | 4817 | 14169 | 10242 | 136 |
| H76C | 4709 | 12753 | 10899 | 136 |
| H71C | 3978 | 11048 | 8319 | 73 |
| H71D | 4044 | 9061 | 8010 | 73 |
| H72C | 4209 | 12309 | 7299 | 69 |
| H72D | 4245 | 10410 | 6845 | 69 |
| H73C | 4506 | 9457 | 8064 | 76 |
| H73D | 4621 | 11143 | 7593 | 76 |
| H74C | 4381 | 11294 | 9163 | 73 |
| H74D | 4474 | 13038 | 8678 | 73 |
| H75C | 4796 | 10298 | 9429 | 75 |
| H75D | 4897 | 11932 | 8882 | 75 |
| H76D | 4970 | 12519 | 10359 | 96 |
| H76E | 4775 | 13966 | 9930 | 96 |
| H76F | 4674 | 12330 | 10478 | 96 |
| H70A | 3744(7) | 11600(60) | 6900(20) | 47(14) |
| H70B | 3732(8) | 9450(70) | 6590(30) | 81(17) |

Table 7Y.6. Torsion angles [ ${ }^{[ }$] for $\mathbf{7 Y}$.

| O1-C1-C2-C3 | 1.1(6) | C11-N1-C1-O1 | 178.1(4) |
| :---: | :---: | :---: | :---: |
| O1-C1-C2-C12 | -179.7(4) | C11-N1-C1-C2 | -2.6(6) |
| O3-C18-C19-C20 | -1.8(5) | C11-N1-C25-C26 | 101.1(5) |
| O3-C18-C19-C24 | 177.0(3) | C11-C10-C12-C2 | -0.8(6) |
| O3-C32-C33-C34 | 60.8(5) | C11-C10-C12-C6 | 178.3(3) |
| N1-C1-C2-C3 | -178.2(4) | C12-C2-C3-C4 | -1.1(6) |
| N1-C1-C2-C12 | 1.0(6) | C12-C6-C7-C8 | -0.2(6) |
| N1-C25-C26-C27 | 173.4(4) | C12-C6-C7-C13 | -178.5(3) |
| C1-N1-C11-O2 | -177.9(4) | C12-C10-C11-O2 | 179.7(4) |
| C1-N1-C11-C10 | 2.5(6) | C12-C10-C11-N1 | -0.7(6) |
| C1-N1-C25-C26 | -79.6(5) | C13-C7-C8-C9 | 179.5(4) |
| C1-C2-C3-C4 | 178.1(4) | C14-C15-C16-C17 | 177.4(4) |
| C1-C2-C12-C6 | -178.5(3) | C14-C15-C24-C19 | -179.5(4) |
| C1-C2-C12-C10 | 0.7(6) | C14-C15-C24-C23 | -0.1(6) |
| C2-C3-C4-C5 | 1.7(6) | C15-C16-C17-C18 | 2.0(6) |
| C3-C2-C12-C6 | 0.7(6) | C16-C15-C24-C19 | 1.3(6) |
| C3-C2-C12-C10 | 179.8(3) | C16-C15-C24-C23 | -179.3(4) |
| C3-C4-C5-C6 | -1.9(6) | C16-C17-C18-O3 | -179.0(3) |
| C4-C5-C6-C7 | -178.4(4) | C16-C17-C18-C19 | 1.4(6) |
| C4-C5-C6-C12 | 1.5(6) | C17-C18-C19-C20 | 177.7(4) |
| C5-C6-C7-C8 | 179.7(4) | C17-C18-C19-C24 | -3.4(6) |
| C5-C6-C7-C13 | 1.4(6) | C18-O3-C32-C33 | 164.5(3) |
| C5-C6-C12-C2 | -0.9(6) | C18-C19-C20-C21 | 178.1(4) |
| C5-C6-C12-C10 | 179.9(3) | C18-C19-C24-C15 | 2.0(6) |
| C6-C7-C8-C9 | 1.2(6) | C18-C19-C24-C23 | -177.4(3) |
| C7-C6-C12-C2 | 179.0(3) | C19-C20-C21-C22 | 0.1(6) |
| C7-C6-C12-C10 | -0.2(6) | C20-C19-C24-C15 | -179.1(3) |
| C7-C8-C9-C10 | -1.9(6) | C20-C19-C24-C23 | 1.5(6) |
| C8-C9-C10-C11 | -177.2(4) | C20-C21-C22-C23 | -0.2(6) |
| C8-C9-C10-C12 | 1.6(6) | C21-C22-C23-C24 | 1.0(6) |
| C9-C10-C11-O2 | -1.5(6) | C22-C23-C24-C15 | 178.9(4) |
| C9-C10-C11-N1 | 178.1(4) | C22-C23-C24-C19 | -1.7(6) |
| C9-C10-C12-C2 | -179.7(4) | C24-C15-C16-C17 | -3.4(6) |
| C9-C10-C12-C6 | -0.5(6) | C24-C19-C20-C21 | -0.8(6) |


| C25-N1-C1-O1 | -1.2(6) | C50-C48-C49-N2 | -0.7(6) |
| :---: | :---: | :---: | :---: |
| C25-N1-C1-C2 | 178.1(4) | C50-C48-C47-C46 | -0.3(6) |
| C25-N1-C11-O2 | 1.4(6) | C50-C44-C45-C46 | 0.6(6) |
| C25-N1-C11-C10 | -178.2(3) | C50-C44-C45-C51 | 180.0(3) |
| C25-C26-C27-C28 | -170.5(4) | C50-C44-C43-C42 | 0.1(6) |
| C26-C27-C28-C29 | 172.9(4) | C50-C40-C41-C42 | 0.3(6) |
| C27-C28-C29-C30 | -174.1(5) | C56-O6-C70-C71 | -161.3(6) |
| C28-C29-C30-C31 | 178.7(5) | C56-O6-C70-C71A | -177.1(9) |
| C32-O3-C18-C17 | 12.0(5) | C56-C57-C62-C53 | -0.5(6) |
| C32-O3-C18-C19 | -168.5(3) | C56-C57-C62-C61 | 179.7(4) |
| C32-C33-C34-C35 | -175.5(4) | C56-C57-C58-C59 | -179.0(4) |
| C33-C34-C35-C36 | 173.4(4) | C56-C55-C54-C53 | -2.2(6) |
| C34-C35-C36-C37 | -177.3(4) | C44-C50-C40-C39 | 178.5(3) |
| C35-C36-C37-C38 | 175.6(4) | C44-C50-C40-C41 | 0.1(6) |
| O4-C39-C40-C50 | 179.6(4) | C44-C43-C42-C41 | 0.3(6) |
| O4-C39-C40-C41 | -2.1(6) | C62-C57-C56-O6 | -179.6(3) |
| O6-C56-C55-C54 | -179.1(3) | C62-C57-C56-C55 | 0.4(6) |
| O6-C70-C71-C72 | -64.8(11) | C62-C57-C58-C59 | 0.8(6) |
| O6-C70-C71A-C72A | -170.9(13) | C62-C53-C54-C55 | 2.0(6) |
| N2-C39-C40-C50 | -1.1(6) | C62-C61-C60-C59 | -1.3(6) |
| N2-C39-C40-C41 | 177.3(4) | C40-C50-C44-C45 | -179.3(4) |
| N2-C63-C64-C65 | -173.6(4) | C40-C50-C44-C43 | -0.3(6) |
| C39-N2-C49-O5 | 176.5(4) | C49-N2-C39-O4 | -178.0(4) |
| C39-N2-C49-C48 | -1.8(6) | C49-N2-C39-C40 | 2.7(6) |
| C39-N2-C63-C64 | 86.1(5) | C49-N2-C63-C64 | -92.1(5) |
| C39-C40-C41-C42 | -178.1(4) | C49-C48-C50-C44 | -177.5(3) |
| C48-C50-C44-C45 | 0.4(6) | C49-C48-C50-C40 | 2.2(6) |
| C48-C50-C44-C43 | 179.4(4) | C49-C48-C47-C46 | 176.6(4) |
| C48-C50-C40-C39 | -1.3(6) | C53-C62-C61-C60 | -179.4(4) |
| C48-C50-C40-C41 | -179.6(4) | C45-C44-C43-C42 | 179.1(4) |
| C57-C56-C55-C54 | 0.9(6) | C45-C46-C47-C48 | 1.3(6) |
| C57-C62-C53-C52 | -179.2(4) | C58-C57-C56-O6 | 0.2(6) |
| C57-C62-C53-C54 | -0.6(6) | C58-C57-C56-C55 | -179.9(4) |
| C57-C62-C61-C60 | 0.3(6) | C58-C57-C62-C53 | 179.7(4) |
| C57-C58-C59-C60 | -1.8(6) | C58-C57-C62-C61 | -0.1(6) |
| C50-C48-C49-O5 | -179.0(4) | C43-C44-C45-C46 | -178.3(4) |


| C43-C44-C45-C51 | $1.0(6)$ | C63-N2-C39-C40 | $-175.3(3)$ |
| :--- | :---: | :--- | :---: |
| C43-C42-C41-C40 | $-0.5(6)$ | C63-N2-C49-O5 | $-5.5(6)$ |
| C61-C62-C53-C52 | $0.5(6)$ | C63-N2-C49-C48 | $176.2(3)$ |
| C61-C62-C53-C54 | $179.1(4)$ | C63-C64-C65-C66 | $69.6(5)$ |
| C61-C60-C59-C58 | $2.1(6)$ | C70-O6-C56-C57 | $168.5(4)$ |
| C52-C53-C54-C55 | $-179.4(4)$ | C70-O6-C56-C55 | $-11.5(6)$ |
| C68-C67-C66-C65 | $-179.4(4)$ | C70-C71-C72-C73 | $178.4(9)$ |
| C67-C66-C65-C64 | $173.3(4)$ | C70-C71A-C72A-C73A | $-170.2(11)$ |
| C47-C48-C50-C44 | $-0.6(6)$ | C69-C68-C67-C66 | $-179.5(4)$ |
| C47-C48-C50-C40 | $179.2(4)$ | C71-C72-C73-C74 | $177.6(9)$ |
| C47-C48-C49-O5 | $4.1(6)$ | C72-C73-C74-C75 | $177.7(11)$ |
| C47-C48-C49-N2 | $-177.6(4)$ | C73-C74-C75-C76 | $-178.2(13)$ |
| C47-C46-C45-C44 | $-1.4(6)$ | C71A-C72A-C73A-C74A | $-64.6(18)$ |
| C47-C46-C45-C51 | $179.2(4)$ | C73AA-C74A-C75A-C76A | $175.2(17)$ |
| C63-N2-C39-O4 | $4.0(6)$ |  |  |

End of crystallographic info for $\mathbf{7 y}$.

## Crystallographic Material for 7Y'

## Crystallographic Material for 7Y':

X-ray Experimental for complex $\mathrm{C}_{38} \mathrm{H}_{41} \mathrm{NO}_{3}\left(7 \mathbf{Y}^{\prime}\right)$ : Crystals grew as very long, very thin, yellow laths by slow evaporation from vapor:vapor diffusion Benzene:Dioxane. The data crystal was cut from a larger crystal and had approximate dimensions; $0.83 \times 0.07 \times 0.03 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$ focus $\mathrm{CuK} \alpha$ radiation source $(\lambda=1.5418 \AA)$ with collimating mirror monochromators. A total of 1088 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 30 seconds per frame with a detector offset of $+/-39.8^{\circ}$ and 90 seconds per frame with a detector offset of $+/-110.7^{\circ}$. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.38.43f. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6. ${ }^{3}$ Structure analysis was aided by use of the programs PLATON98 ${ }^{4}$ and WinGX. ${ }^{5}$ The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms).

There are two molecules in the asymmetric unit. For each molecule, one of the heptyl side chains was disordered. The molecules stack in a head to tail manner with the lactam component of one molecule oriented on top of the ether end of an adjacent molecule. This stacking occurs in the b -axis direction. The disordered n -heptyl groups are intermingled with the disordered n -heptyl groups of adjacent molecules near inversion centers at $\mathrm{c}=1 / 2$.

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+\left(0.2^{*} \mathrm{P}\right)^{2}\right]$ and P $=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.576 , with $\mathrm{R}(\mathrm{F})$ equal to 0.222 and a goodness of fit, $\mathrm{S},=$ 1.87. Definitions used for calculating $R(F), R_{w}\left(F^{2}\right)$ and the goodness of fit, $S$, are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. ${ }^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.38.43f.
2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\left|\mathrm{F}_{\mathrm{C}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{W}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 7Y'.1. Crystal data and structure refinement for 7Y'.

Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume
Z
Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=67.684^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole

C38 H41 N O3
559.72

100(2) K
$1.54184 \AA$
monoclinic
I $2 / \mathrm{a}$

$$
\begin{array}{ll}
\mathrm{a}=15.5987(11) \AA & \alpha=90^{\circ} . \\
\mathrm{b}=7.4380(5) \AA & \beta=90.956(6)^{\circ} . \\
\mathrm{c}=105.361(8) \AA & \gamma=90^{\circ} .
\end{array}
$$

16
$1.217 \mathrm{Mg} / \mathrm{m}^{3}$
$0.593 \mathrm{~mm}^{-1}$
4800
$0.83 \times 0.074 \times 0.027 \mathrm{~mm}^{3}$
2.517 to $76.550^{\circ}$.
$-18<=\mathrm{h}<=19,-9<=\mathrm{k}<=7,-131<=1<=124$
36582
$12317[\mathrm{R}($ int $)=0.1155]$
100.0 \%

Semi-empirical from equivalents
1.00 and 0.438

Full-matrix least-squares on $\mathrm{F}^{2}$
12317 / 1654 / 859
1.870
$R 1=0.2225, w R 2=0.5382$
$R 1=0.2532, w R 2=0.5759$
n/a
0.644 and -0.608 e. $\AA^{-3}$

Table 7Y'.2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $7 Y^{\prime} . \mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| O1 | $9142(5)$ | $-3270(10)$ | $4412(1)$ | 55(2) |
| O2 | $11759(5)$ | $-951(10)$ | $4317(1)$ | $54(2)$ |
| O3 | 7548(4) | $-369(8)$ | $3192(1)$ | $36(1)$ |
| N1 | $10449(6)$ | $-2117(12)$ | $4364(1)$ | $51(2)$ |
| C1 | 9579(6) | $-2593(12)$ | 4333(1) | 42(2) |
| $\mathrm{C} 2$ | 9308(6) | $-2222(10)$ | 4201(1) | $36(2)$ |
| C3 | $8469(6)$ | $-2672(11)$ | 4163(1) | $37(2)$ |
| $\mathrm{C} 4$ | $8217(5)$ | -2404(10) | 4039(1) | 32(2) |
| C5 | 8747(6) | $-1603(10)$ | 3949(1) | 34(2) |
| C6 | $9608(5)$ | -1113(10) | 3987(1) | $33(1)$ |
| C7 | 10175(6) | $-307(10)$ | 3902(1) | $34(2)$ |
| C8 | 11006(6) | 144(10) | 3940(1) | $37(2)$ |
| C9 | 11263(6) | $-163(10)$ | $4067(1)$ | $36(2)$ |
| $\mathrm{C} 10$ | $10712(5)$ | $-956(10)$ | $4150(1)$ | $35(2)$ |
| C11 | $11028(7)$ | $-1316(13)$ | $4282(1)$ | $47(2)$ |
| $\mathrm{C} 12$ | $9855(5)$ | -1418(10) | 4113(1) | 33(2) |
| C13 | 8458(5) | -1367(10) | 3821(1) | 32(2) |
| C14 | $8229(5)$ | -1165(10) | 3711(1) | $33(2)$ |
| $\mathrm{C} 15$ | 8040(6) | -920(10) | 3580(1) | 34(2) |
| C16 | 8644(6) | -166(11) | 3502(1) | 35(2) |
| $\mathrm{C} 17$ | 8514(5) | 28(10) | 3372(1) | 33(2) |
| $\mathrm{C} 18$ | 7736(5) | -481(10) | 3317(1) | 31(1) |
| C19 | 7066(5) | -1195(10) | 3394(1) | 33(2) |
| $\mathrm{C} 20$ | 6262(5) | -1681(11) | 3342(1) | 35(2) |
| C21 | 5653(6) | -2372(11) | 3415(1) | 36(2) |
| C22 | 5786(6) | -2667(10) | 3546(1) | 37(2) |
| C23 | 6572(6) | -2207(10) | 3600(1) | 36(2) |
| C24 | 7235(6) | -1448(10) | 3526(1) | 34(2) |
| C25 | 10791(9) | -2660(17) | 4490(1) | 75(3) |
| C26 | 11230(30) | -4510(30) | 4472(2) | 85(3) |
| C27 | 11580(20) | -5360(30) | 4595(2) | 91(3) |


| C28 | 12060(20) | -7160(30) | 4575(2) | 101(4) |
| :---: | :---: | :---: | :---: | :---: |
| C29 | 12571(15) | -7800(30) | 4693(2) | 110(4) |
| C30 | 12010(20) | -8640(50) | 4797(2) | 118(5) |
| C31 | 11350(30) | -10010(60) | 4746(4) | 141(9) |
| C26A | 11330(30) | -4390(40) | 4501(2) | 86(3) |
| C27A | 11710(20) | -4680(30) | 4636(2) | 93(4) |
| C28A | 12170(20) | -6510(30) | 4651(2) | 103(4) |
| C29A | 12410(15) | -6950(30) | 4791(2) | 112(4) |
| C30A | 13186(18) | -5850(50) | 4841(3) | 116(6) |
| C31A | 14018(18) | -6220(60) | 4768(4) | 122(8) |
| C32 | 8251(6) | 51(12) | 3105(1) | 37(2) |
| C33 | 7925(6) | -430(11) | 2973(1) | 38(2) |
| C34 | 7137(6) | 648(12) | 2930(1) | 44(2) |
| C35 | 6772(6) | 79(13) | 2802(1) | 44(2) |
| C36 | 5940(6) | 1014(13) | 2763(1) | 43(2) |
| C37 | 5587(8) | 340(17) | 2636(1) | 61(3) |
| C38 | 4682(9) | 1110(20) | 2603(1) | 74(3) |
| O4 | 7551(5) | 5320(9) | 3082(1) | 53(2) |
| O5 | 5027(5) | 2940(10) | 3203(1) | 55(2) |
| O6 | 9465(5) | 2588(9) | 4301(1) | 51(2) |
| N2 | 6262(5) | 4193(9) | 3144(1) | 42(2) |
| C39 | 7124(6) | 4660(11) | 3167(1) | 41(2) |
| C40 | 7473(6) | 4476(10) | 3297(1) | 36(2) |
| C41 | 8308(6) | 5022(11) | 3329(1) | 44(2) |
| C42 | 8597(6) | 4851(11) | 3456(1) | 44(2) |
| C43 | 8115(6) | 4110(10) | 3550(1) | 40(2) |
| C44 | 7260(6) | 3554(11) | 3521(1) | 41(2) |
| C45 | 6693(6) | 2801(10) | 3613(1) | 40(2) |
| C46 | 5887(7) | 2274(11) | 3580(1) | 45(2) |
| C47 | 5595(7) | 2458(12) | 3455(1) | 44(2) |
| C48 | 6107(6) | 3152(9) | 3365(1) | 35(2) |
| C49 | 5752(7) | 3385(11) | 3233(1) | 44(2) |
| C50 | 6961(6) | 3725(10) | 3393(1) | 35(2) |
| C 51 | 8423(6) | 3942(11) | 3679(1) | 42(2) |
| C 52 | 8630(6) | 3702(12) | 3787(1) | 43(2) |
| C 53 | 8838(6) | 3424(12) | 3919(1) | 44(2) |


| C54 | 8251(6) | 2659(12) | 4002(1) | 43(2) |
| :---: | :---: | :---: | :---: | :---: |
| C55 | 8407(6) | 2394(12) | 4130(1) | 45(2) |
| C56 | 9218(6) | 2802(11) | 4180(1) | 42(2) |
| C57 | 9847(6) | 3600(11) | 4101(1) | 41(2) |
| C58 | 10686(6) | 4058(12) | 4148(1) | 48(2) |
| C59 | 11274(7) | 4835(12) | 4073(1) | 50(2) |
| C60 | 11099(7) | 5151(12) | 3946(1) | 49(2) |
| C61 | 10309(7) | 4696(12) | 3895(1) | 46(2) |
| C62 | 9668(6) | 3890(11) | 3973(1) | 40(2) |
| C63 | 5906(6) | 4558(12) | 3017(1) | 44(2) |
| C64 | 5432(7) | 6385(12) | 3014(1) | 49(2) |
| C65 | 4952(7) | 6624(14) | 2887(1) | 53(2) |
| C66 | 4191(7) | 5391(14) | 2866(1) | 52(2) |
| C67 | 3669(7) | 5804(15) | 2745(1) | 51(2) |
| C68 | 2877(7) | 4561(15) | 2729(1) | 54(2) |
| C69 | 2365(8) | 4893(18) | 2611(1) | 64(3) |
| C70 | 8803(9) | 2143(15) | 4391(1) | 61(2) |
| C71 | 9166(11) | 2340(20) | 4522(1) | 83(3) |
| C72 | 9803(18) | 1060(40) | 4577(2) | 91(4) |
| C73 | 9960(20) | 1260(30) | 4716(2) | 98(4) |
| C74 | 10392(19) | -350(30) | 4775(2) | 108(5) |
| C75 | 10920(20) | 30(40) | 4891(2) | 115(6) |
| C76 | 11590(20) | -1350(50) | 4919(3) | 128(9) |
| C72A | 8678(19) | 1270(30) | 4615(2) | 94(4) |
| C73A | 9010(20) | 1460(30) | 4749(1) | 100(4) |
| C74A | 9050(30) | 3360(30) | 4793(2) | 110(5) |
| C75A | 9370(30) | 3580(30) | 4926(2) | 115(6) |
| C76A | 9360(30) | 5480(40) | 4973(3) | 128(9) |

Table $7 \mathbf{Y}^{\prime} \cdot 3$. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for $7 \mathbf{Y}^{\prime}$.

| O1-C1 | 1.195(11) | C18-C19 | 1.438(11) |
| :---: | :---: | :---: | :---: |
| O2-C11 | 1.223(13) | C19-C20 | 1.408(12) |
| O3-C18 | 1.348(9) | C19-C24 | 1.421(10) |
| O3-C32 | 1.472(9) | C20-C21 | 1.332(12) |
| N1-C11 | 1.395(13) | C20-H20 | 0.95 |
| N1-C1 | 1.434 (13) | C21-C22 | 1.407(11) |
| N1-C25 | 1.479(12) | C21-H21 | 0.95 |
| C1-C2 | 1.471(11) | C22-C23 | 1.387(13) |
| C2-C12 | 1.403(11) | C22-H22 | 0.95 |
| C2-C3 | 1.404(13) | C23-C24 | 1.422(12) |
| C3-C4 | 1.374(11) | C23-H23 | 0.95 |
| C3-H3 | 0.95 | C25-C26A | 1.542(11) |
| C4-C5 | 1.398(11) | C25-C26 | 1.552(11) |
| C4-H4 | 0.95 | C25-H25A | 0.99 |
| C5-C13 | 1.424(11) | C25-H25B | 0.99 |
| C5-C6 | 1.440(12) | C26-C27 | 1.538(12) |
| C6-C7 | 1.401(11) | C26-H26A | 0.99 |
| C6-C12 | $1.402(11)$ | C26-H26B | 0.99 |
| C7-C8 | 1.392(12) | C27-C28 | 1.546(12) |
| C7-H7 | 0.95 | C27-H27A | 0.99 |
| C8-C9 | 1.407(12) | C27-H27B | 0.99 |
| C8-H8 | 0.95 | C28-C29 | 1.544(11) |
| C9-C10 | 1.369(11) | C28-H28A | 0.99 |
| C9-H9 | 0.95 | C28-H28B | 0.99 |
| C10-C12 | 1.428(12) | C29-C30 | 1.543(11) |
| C10-C11 | 1.492(12) | C29-H29A | 0.99 |
| C13-C14 | 1.214(11) | C29-H29B | 0.99 |
| C14-C15 | 1.419(11) | C30-C31 | 1.544(12) |
| C15-C16 | 1.382(12) | C30-H30A | 0.99 |
| C15-C24 | 1.426(12) | C30-H30B | 0.99 |
| C16-C17 | 1.391(10) | C31-H31A | 0.98 |
| C16-H16 | 0.95 | C31-H31B | 0.98 |
| C17-C18 | 1.388(11) | C31-H31C | 0.98 |
| C17-H17 | 0.95 | C26A-C27A | 1.550(11) |


| C26A-H26C | 0.99 | C38-H38B | 0.98 |
| :---: | :---: | :---: | :---: |
| C26A-H26D | 0.99 | C38-H38C | 0.98 |
| C27A-C28A | 1.547(12) | O4-C39 | $1.232(10)$ |
| C27A-H27C | 0.99 | O5-C49 | 1.217(12) |
| C27A-H27D | 0.99 | O6-C56 | 1.333(11) |
| C28A-C29A | 1.552(11) | O6-C70 | 1.455(13) |
| C28A-H28C | 0.99 | N2-C49 | 1.379(12) |
| C28A-H28D | 0.99 | N2-C39 | 1.407(13) |
| C29A-C30A | 1.546(12) | N2-C63 | 1.466(12) |
| C29A-H29C | 0.99 | C39-C40 | $1.472(12)$ |
| C29A-H29D | 0.99 | C40-C41 | 1.400(13) |
| C30A-C31A | 1.544(12) | C40-C50 | $1.413(11)$ |
| C30A-H30C | 0.99 | C41-C42 | 1.407(13) |
| C30A-H30D | 0.99 | C41-H41 | 0.95 |
| C31A-H31D | 0.98 | C42-C43 | 1.367(12) |
| C31A-H31E | 0.98 | C42-H42 | 0.95 |
| C31A-H31F | 0.98 | C43-C44 | $1.425(14)$ |
| C32-C33 | 1.514(10) | C43-C51 | 1.440 (13) |
| C32-H32A | 0.99 | C44-C50 | 1.424(12) |
| C32-H32B | 0.99 | C44-C45 | $1.439(12)$ |
| C33-C34 | 1.530(13) | C45-C46 | 1.357(14) |
| C33-H33A | 0.99 | C45-H45 | 0.95 |
| C33-H33B | 0.99 | C46-C47 | 1.393(13) |
| C34-C35 | 1.521(12) | C46-H46 | 0.95 |
| C34-H34A | 0.99 | C47-C48 | 1.350(12) |
| C34-H34B | 0.99 | C47-H47 | 0.95 |
| C35-C36 | 1.520(13) | C48-C50 | 1.424(13) |
| C35-H35A | 0.99 | C48-C49 | $1.494(13)$ |
| C35-H35B | 0.99 | C51-C52 | $1.193(13)$ |
| C36-C37 | 1.527(13) | C52-C53 | $1.436(13)$ |
| C36-H36A | 0.99 | C53-C54 | $1.401(14)$ |
| C36-H36B | 0.99 | C53-C62 | 1.447(13) |
| C37-C38 | 1.558(17) | C54-C55 | 1.374(13) |
| C37-H37A | 0.99 | C54-H54 | 0.95 |
| C37-H37B | 0.99 | C55-C56 | 1.398(13) |
| C38-H38A | 0.98 | C55-H55 | 0.95 |


| C56-C57 | 1.429(13) | C71-C72 | 1.484(13) |
| :---: | :---: | :---: | :---: |
| C57-C62 | 1.390(13) | C71-C72A | 1.488(13) |
| C57-C58 | 1.433(13) | C71-H71A | 0.99 |
| C58-C59 | 1.350(14) | C71-H71B | 0.99 |
| C58-H58 | 0.95 | C72-C73 | 1.495(13) |
| C59-C60 | 1.388(14) | C72-H72A | 0.99 |
| C59-H59 | 0.95 | C72-H72B | 0.99 |
| C60-C61 | 1.378(15) | C73-C74 | $1.496(14)$ |
| C60-H60 | 0.95 | C73-H73A | 0.99 |
| C61-C62 | 1.438(13) | C73-H73B | 0.99 |
| C61-H61 | 0.95 | C74-C75 | 1.488(14) |
| C63-C64 | 1.546(12) | C74-H74A | 0.99 |
| C63-H63A | 0.99 | C74-H74B | 0.99 |
| C63-H63B | 0.99 | C75-C76 | 1.497(13) |
| C64-C65 | 1.528(14) | C75-H75A | 0.99 |
| C64-H64A | 0.99 | C75-H75B | 0.99 |
| C64-H64B | 0.99 | C76-H76A | 0.98 |
| C65-C66 | 1.515(15) | C76-H76B | 0.98 |
| C65-H65A | 0.99 | C76-H76C | 0.98 |
| C65-H65B | 0.99 | C72A-C73A | $1.498(13)$ |
| C66-C67 | 1.532(14) | C72A-H72C | 0.99 |
| C66-H66A | 0.99 | C72A-H72D | 0.99 |
| C66-H66B | 0.99 | C73A-C74A | 1.494(13) |
| C67-C68 | 1.550(15) | C73A-H73C | 0.99 |
| C67-H67A | 0.99 | C73A-H73D | 0.99 |
| C67-H67B | 0.99 | C74A-C75A | 1.490(14) |
| C68-C69 | 1.483(15) | C74A-H74C | 0.99 |
| C68-H68A | 0.99 | C74A-H74D | 0.99 |
| C68-H68B | 0.99 | C75A-C76A | 1.493(13) |
| C69-H69A | 0.98 | C75A-H75C | 0.99 |
| C69-H69B | 0.98 | C75A-H75D | 0.99 |
| C69-H69C | 0.98 | C76A-H76D | 0.98 |
| C70-C71 | 1.483(17) | C76A-H76E | 0.98 |
| C70-H70A | 0.99 | C76A-H76F | 0.98 |
| C70-H70B | 0.99 |  |  |


| C18-O3-C32 | 117.9(7) | N1-C11-C10 | 116.6(9) |
| :---: | :---: | :---: | :---: |
| C11-N1-C1 | 125.7(8) | C6-C12-C2 | 122.5(8) |
| C11-N1-C25 | 116.5(10) | C6-C12-C10 | 117.3(7) |
| C1-N1-C25 | 117.6(9) | C2-C12-C10 | 120.1(7) |
| O1-C1-N1 | 119.6(8) | C14-C13-C5 | 178.6(9) |
| O1-C1-C2 | 125.2(10) | C13-C14-C15 | 174.9(9) |
| N1-C1-C2 | 115.2(8) | C16-C15-C14 | 120.0(8) |
| C12-C2-C3 | 119.0(7) | C16-C15-C24 | 118.5(7) |
| C12-C2-C1 | 122.3(9) | C14-C15-C24 | 121.5(7) |
| C3-C2-C1 | 118.7(8) | C15-C16-C17 | 122.8(8) |
| C4-C3-C2 | 119.4(8) | C15-C16-H16 | 118.6 |
| C4-C3-H3 | 120.3 | C17-C16-H16 | 118.6 |
| C2-C3-H3 | 120.3 | C18-C17-C16 | 119.7(7) |
| C3-C4-C5 | 122.7(8) | C18-C17-H17 | 120.2 |
| C3-C4-H4 | 118.6 | C16-C17-H17 | 120.2 |
| C5-C4-H4 | 118.6 | O3-C18-C17 | 124.4(7) |
| C4-C5-C13 | 120.6(8) | O3-C18-C19 | 115.4(7) |
| C4-C5-C6 | 118.8(7) | C17-C18-C19 | 120.2(7) |
| C13-C5-C6 | 120.5(7) | C20-C19-C24 | 119.8(8) |
| C7-C6-C12 | 120.6(8) | C20-C19-C18 | 121.6(7) |
| C7-C6-C5 | 122.0(7) | C24-C19-C18 | 118.6(8) |
| C12-C6-C5 | 117.4(7) | C21-C20-C19 | 120.9(8) |
| C8-C7-C6 | 120.9(7) | C21-C20-H20 | 119.6 |
| C8-C7-H7 | 119.5 | C19-C20-H20 | 119.6 |
| C6-C7-H7 | 119.5 | C20-C21-C22 | 121.8(9) |
| C7-C8-C9 | 119.0(8) | C20-C21-H21 | 119.1 |
| C7-C8-H8 | 120.5 | C22-C21-H21 | 119.1 |
| C9-C8-H8 | 120.5 | C23-C22-C21 | 118.8(8) |
| C10-C9-C8 | 120.3(8) | C23-C22-H22 | 120.6 |
| C10-C9-H9 | 119.9 | C21-C22-H22 | 120.6 |
| C8-C9-H9 | 119.9 | C22-C23-C24 | 121.1(7) |
| C9-C10-C12 | 121.8(7) | C22-C23-H23 | 119.4 |
| C9-C10-C11 | 118.1(8) | C24-C23-H23 | 119.4 |
| C12-C10-C11 | 120.1(8) | C19-C24-C23 | 117.5(8) |
| O2-C11-N1 | 121.2(8) | C19-C24-C15 | 120.2(8) |
| O2-C11-C10 | 122.1(9) | C23-C24-C15 | 122.3(7) |


| N1-C25-C26A | 118.7(11) | H30A-C30-H30B | 107.7 |
| :---: | :---: | :---: | :---: |
| N1-C25-C26 | 106.4(10) | C30-C31-H31A | 109.5 |
| N1-C25-H25A | 110.4 | C30-C31-H31B | 109.5 |
| C26-C25-H25A | 110.4 | H31A-C31-H31B | 109.5 |
| N1-C25-H25B | 110.4 | C30-C31-H31C | 109.5 |
| C26-C25-H25B | 110.4 | H31A-C31-H31C | 109.5 |
| H25A-C25-H25B | 108.6 | H31B-C31-H31C | 109.5 |
| C27-C26-C25 | 114.3(10) | C25-C26A-C27A | 112.4(10) |
| C27-C26-H26A | 108.7 | C25-C26A-H26C | 109.1 |
| C25-C26-H26A | 108.7 | C27A-C26A-H26C | 109.1 |
| C27-C26-H26B | 108.7 | C25-C26A-H26D | 109.1 |
| C25-C26-H26B | 108.7 | C27A-C26A-H26D | 109.1 |
| H26A-C26-H26B | 107.6 | H26C-C26A-H26D | 107.8 |
| C26-C27-C28 | 114.0(11) | C28A-C27A-C26A | 112.6(11) |
| C26-C27-H27A | 108.7 | C28A-C27A-H27C | 109.1 |
| C28-C27-H27A | 108.7 | C26A-C27A-H27C | 109.1 |
| C26-C27-H27B | 108.7 | C28A-C27A-H27D | 109.1 |
| C28-C27-H27B | 108.7 | C26A-C27A-H27D | 109.1 |
| H27A-C27-H27B | 107.6 | H27C-C27A-H27D | 107.8 |
| C29-C28-C27 | 113.7(11) | C27A-C28A-C29A | 112.6(10) |
| C29-C28-H28A | 108.8 | C27A-C28A-H28C | 109.1 |
| C27-C28-H28A | 108.8 | C29A-C28A-H28C | 109.1 |
| C29-C28-H28B | 108.8 | C27A-C28A-H28D | 109.1 |
| C27-C28-H28B | 108.8 | C29A-C28A-H28D | 109.1 |
| H28A-C28-H28B | 107.7 | H28C-C28A-H28D | 107.8 |
| C30-C29-C28 | 114.0(10) | C30A-C29A-C28A | 112.7(10) |
| C30-C29-H29A | 108.8 | C30A-C29A-H29C | 109.0 |
| C28-C29-H29A | 108.8 | C28A-C29A-H29C | 109.0 |
| C30-C29-H29B | 108.8 | C30A-C29A-H29D | 109.0 |
| C28-C29-H29B | 108.8 | C28A-C29A-H29D | 109.0 |
| H29A-C29-H29B | 107.6 | H29C-C29A-H29D | 107.8 |
| C29-C30-C31 | 113.8(10) | C31A-C30A-C29A | 113.2(11) |
| C29-C30-H30A | 108.8 | C31A-C30A-H30C | 108.9 |
| C31-C30-H30A | 108.8 | C29A-C30A-H30C | 108.9 |
| C29-C30-H30B | 108.8 | C31A-C30A-H30D | 108.9 |
| C31-C30-H30B | 108.8 | C29A-C30A-H30D | 108.9 |


| H30C-C30A-H30D | 107.7 | H36A-C36-H36B | 107.9 |
| :---: | :---: | :---: | :---: |
| C30A-C31A-H31D | 109.5 | C36-C37-C38 | 112.7(9) |
| C30A-C31A-H31E | 109.5 | C36-C37-H37A | 109.0 |
| H31D-C31A-H31E | 109.5 | C38-C37-H37A | 109.0 |
| C30A-C31A-H31F | 109.5 | C36-C37-H37B | 109.0 |
| H31D-C31A-H31F | 109.5 | C38-C37-H37B | 109.0 |
| H31E-C31A-H31F | 109.5 | H37A-C37-H37B | 107.8 |
| O3-C32-C33 | 106.1(7) | C37-C38-H38A | 109.5 |
| O3-C32-H32A | 110.5 | C37-C38-H38B | 109.5 |
| C33-C32-H32A | 110.5 | H38A-C38-H38B | 109.5 |
| O3-C32-H32B | 110.5 | C37-C38-H38C | 109.5 |
| C33-C32-H32B | 110.5 | H38A-C38-H38C | 109.5 |
| H32A-C32-H32B | 108.7 | H38B-C38-H38C | 109.5 |
| C32-C33-C34 | 113.9(7) | C56-O6-C70 | 117.1(9) |
| C32-C33-H33A | 108.8 | C49-N2-C39 | 123.4(8) |
| C34-C33-H33A | 108.8 | C49-N2-C63 | 119.3(8) |
| C32-C33-H33B | 108.8 | C39-N2-C63 | 117.3(7) |
| C34-C33-H33B | 108.8 | O4-C39-N2 | 119.9(9) |
| H33A-C33-H33B | 107.7 | O4-C39-C40 | 121.5(9) |
| C35-C34-C33 | 114.0(7) | N2-C39-C40 | 118.4(7) |
| C35-C34-H34A | 108.8 | C41-C40-C50 | 118.4(8) |
| C33-C34-H34A | 108.8 | C41-C40-C39 | 121.8(8) |
| C35-C34-H34B | 108.8 | C50-C40-C39 | 119.7(8) |
| C33-C34-H34B | 108.8 | C40-C41-C42 | 119.1(8) |
| H34A-C34-H34B | 107.7 | C40-C41-H41 | 120.4 |
| C36-C35-C34 | 114.4(7) | C42-C41-H41 | 120.4 |
| C36-C35-H35A | 108.6 | C43-C42-C41 | 123.4(9) |
| C34-C35-H35A | 108.6 | C43-C42-H42 | 118.3 |
| C36-C35-H35B | 108.6 | C41-C42-H42 | 118.3 |
| C34-C35-H35B | 108.6 | C42-C43-C44 | 119.1(8) |
| H35A-C35-H35B | 107.6 | C42-C43-C51 | 122.6(9) |
| C35-C36-C37 | 112.1(8) | C44-C43-C51 | 118.3(8) |
| C35-C36-H36A | 109.2 | C50-C44-C43 | 117.9(8) |
| C37-C36-H36A | 109.2 | C50-C44-C45 | 118.6(9) |
| C35-C36-H36B | 109.2 | C43-C44-C45 | 123.5(8) |
| C37-C36-H36B | 109.2 | C46-C45-C44 | 120.9(8) |


| C46-C45-H45 | 119.5 | C57-C58-H58 | 119.2 |
| :---: | :---: | :---: | :---: |
| C44-C45-H45 | 119.5 | C58-C59-C60 | 120.9(10) |
| C45-C46-C47 | 120.2(9) | C58-C59-H59 | 119.6 |
| C45-C46-H46 | 119.9 | C60-C59-H59 | 119.6 |
| C47-C46-H46 | 119.9 | C61-C60-C59 | 119.9(10) |
| C48-C47-C46 | 120.8(10) | C61-C60-H60 | 120.1 |
| C48-C47-H47 | 119.6 | C59-C60-H60 | 120.1 |
| C46-C47-H47 | 119.6 | C60-C61-C62 | 120.2(9) |
| C47-C48-C50 | 122.0(8) | C60-C61-H61 | 119.9 |
| C47-C48-C49 | 118.7(9) | C62-C61-H61 | 119.9 |
| C50-C48-C49 | 119.2(7) | C57-C62-C61 | 119.4(9) |
| O5-C49-N2 | 119.1(9) | C57-C62-C53 | 120.5(9) |
| O5-C49-C48 | 122.6(8) | C61-C62-C53 | 120.1(9) |
| N2-C49-C48 | 118.4(8) | N2-C63-C64 | 110.9(7) |
| C40-C50-C48 | 120.6(8) | N2-C63-H63A | 109.5 |
| C40-C50-C44 | 122.0(9) | C64-C63-H63A | 109.5 |
| C48-C50-C44 | 117.4(7) | N2-C63-H63B | 109.5 |
| C52-C51-C43 | 174.9(10) | C64-C63-H63B | 109.5 |
| C51-C52-C53 | 177.3(10) | H63A-C63-H63B | 108.0 |
| C54-C53-C52 | 121.7(9) | C65-C64-C63 | 110.5(8) |
| C54-C53-C62 | 116.2(8) | C65-C64-H64A | 109.6 |
| C52-C53-C62 | 122.1(9) | C63-C64-H64A | 109.6 |
| C55-C54-C53 | 124.3(9) | C65-C64-H64B | 109.6 |
| C55-C54-H54 | 117.9 | C63-C64-H64B | 109.6 |
| C53-C54-H54 | 117.9 | H64A-C64-H64B | 108.1 |
| C54-C55-C56 | 119.1(9) | C66-C65-C64 | 115.5(8) |
| C54-C55-H55 | 120.4 | C66-C65-H65A | 108.4 |
| C56-C55-H55 | 120.4 | C64-C65-H65A | 108.4 |
| O6-C56-C55 | 125.7(9) | C66-C65-H65B | 108.4 |
| O6-C56-C57 | 114.7(9) | C64-C65-H65B | 108.4 |
| C55-C56-C57 | 119.5(9) | H65A-C65-H65B | 107.5 |
| C62-C57-C56 | 120.3(9) | C65-C66-C67 | 113.9(8) |
| C62-C57-C58 | 117.8(9) | C65-C66-H66A | 108.8 |
| C56-C57-C58 | 121.8(9) | C67-C66-H66A | 108.8 |
| C59-C58-C57 | 121.7(10) | C65-C66-H66B | 108.8 |
| C59-C58-H58 | 119.2 | C67-C66-H66B | 108.8 |


| H66A-C66-H66B | 107.7 | C73-C72-H72B | 108.5 |
| :---: | :---: | :---: | :---: |
| C66-C67-C68 | 112.6(8) | H72A-C72-H72B | 107.5 |
| C66-C67-H67A | 109.1 | C72-C73-C74 | 113.3(14) |
| C68-C67-H67A | 109.1 | C72-C73-H73A | 108.9 |
| C66-C67-H67B | 109.1 | C74-C73-H73A | 108.9 |
| C68-C67-H67B | 109.1 | C72-C73-H73B | 108.9 |
| H67A-C67-H67B | 107.8 | C74-C73-H73B | 108.9 |
| C69-C68-C67 | 114.2(9) | H73A-C73-H73B | 107.7 |
| C69-C68-H68A | 108.7 | C75-C74-C73 | 114.8(15) |
| C67-C68-H68A | 108.7 | C75-C74-H74A | 108.6 |
| C69-C68-H68B | 108.7 | C73-C74-H74A | 108.6 |
| C67-C68-H68B | 108.7 | C75-C74-H74B | 108.6 |
| H68A-C68-H68B | 107.6 | C73-C74-H74B | 108.6 |
| C68-C69-H69A | 109.5 | H74A-C74-H74B | 107.5 |
| C68-C69-H69B | 109.5 | C74-C75-C76 | 113.9(14) |
| H69A-C69-H69B | 109.5 | C74-C75-H75A | 108.8 |
| C68-C69-H69C | 109.5 | C76-C75-H75A | 108.8 |
| H69A-C69-H69C | 109.5 | C74-C75-H75B | 108.8 |
| H69B-C69-H69C | 109.5 | C76-C75-H75B | 108.8 |
| O6-C70-C71 | 108.6(11) | H75A-C75-H75B | 107.7 |
| O6-C70-H70A | 110.0 | C75-C76-H76A | 109.5 |
| C71-C70-H70A | 110.0 | C75-C76-H76B | 109.5 |
| O6-C70-H70B | 110.0 | H76A-C76-H76B | 109.5 |
| C71-C70-H70B | 110.0 | C75-C76-H76C | 109.5 |
| H70A-C70-H70B | 108.4 | H76A-C76-H76C | 109.5 |
| C70-C71-C72 | 122.9(13) | H76B-C76-H76C | 109.5 |
| C70-C71-C72A | 111.6(13) | C71-C72A-C73A | 113.7(13) |
| C70-C71-H71A | 109.3 | C71-C72A-H72C | 108.8 |
| C72A-C71-H71A | 109.3 | C73A-C72A-H72C | 108.8 |
| C70-C71-H71B | 109.3 | C71-C72A-H72D | 108.8 |
| C72A-C71-H71B | 109.3 | C73A-C72A-H72D | 108.8 |
| H71A-C71-H71B | 108.0 | H72C-C72A-H72D | 107.7 |
| C71-C72-C73 | 115.2(14) | C74A-C73A-C72A | 113.4(13) |
| C71-C72-H72A | 108.5 | C74A-C73A-H73C | 108.9 |
| C73-C72-H72A | 108.5 | C72A-C73A-H73C | 108.9 |
| C71-C72-H72B | 108.5 | C74A-C73A-H73D | 108.9 |


| C72A-C73A-H73D | 108.9 | C76A-C75A-H75C | 108.8 |
| :--- | :--- | :--- | :--- |
| H73C-C73A-H73D | 107.7 | C74A-C75A-H75D | 108.8 |
| C75A-C74A-C73A | $114.2(15)$ | C76A-C75A-H75D | 108.8 |
| C75A-C74A-H74C | 108.7 | H75C-C75A-H75D | 107.6 |
| C73A-C74A-H74C | 108.7 | C75A-C76A-H76D | 109.5 |
| C75A-C74A-H74D | 108.7 | C75A-C76A-H76E | 109.5 |
| C73A-C74A-H74D | 108.7 | H76D-C76A-H76E | 109.5 |
| H74C-C74A-H74D | 107.6 | C75A-C76A-H76F | 109.5 |
| C74A-C75A-C76A | $114.0(14)$ | H76D-C76A-H76F | 109.5 |
| C74A-C75A-H75C | 108.8 | H76E-C76A-H76F | 109.5 |

Table 7Y'.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $7 \mathbf{Y}^{\prime}$. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| O1 | 56(4) | 80(5) | 28(3) | 8(3) | 3(3) | -12(3) |
| O2 | 49(4) | 71(4) | 41(3) | 8(3) | -10(3) | -11(3) |
| O3 | 34(3) | 50(3) | 24(2) | $0(2)$ | 7(2) | 2(2) |
| N1 | 56(4) | 65(4) | 33(3) | 3(3) | -5(3) | -12(3) |
| C1 | 42(4) | 52(4) | 33(3) | 3(3) | 5(3) | 6(3) |
| C2 | 40(4) | 36(4) | 33(3) | 2(3) | 3(3) | 5(3) |
| C3 | 38(4) | 41(4) | 32(3) | -1(3) | 9(3) | 5(3) |
| C4 | 33(4) | 29(3) | 35(3) | -2(2) | 3(3) | -2(3) |
| C5 | 41(4) | 32(3) | 30(3) | -6(2) | 1(3) | -6(3) |
| C6 | 34(3) | 33(3) | 32(3) | -6(2) | 3(2) | 2(3) |
| C7 | 43(4) | 36(3) | 25(3) | -3(2) | 3(3) | -2(3) |
| C8 | 36(4) | 33(3) | 42(3) | -2(3) | 7(3) | 2(3) |
| C9 | 35(4) | 31(3) | 42(3) | -2(3) | 3(3) | -4(3) |
| C10 | 33(3) | 35(3) | 36(3) | 1(3) | 1(3) | 2(3) |
| C11 | 50(4) | 55(4) | 37(3) | $0(3)$ | -4(3) | -1(3) |
| C12 | 33(3) | 36(3) | 31(3) | -6(2) | 3(2) | $0(3)$ |
| C13 | 35(4) | 32(3) | 29(3) | -2(2) | 2(2) | $0(3)$ |
| C14 | 31(4) | 38(3) | 29(3) | -2(3) | 4(2) | -5(3) |
| C15 | 40(4) | 31(3) | 30(3) | -3(2) | -1(2) | 7(3) |
| C16 | 35(4) | 38(4) | 32(3) | 1(3) | -6(3) | 5(3) |
| C17 | 32(3) | 35(3) | 31(3) | -3(3) | 5(3) | $0(3)$ |
| C18 | 33(3) | 33(3) | 28(3) | -7(2) | 3(2) | 2(3) |
| C19 | 30(3) | 39(3) | 30(3) | -2(3) | 3(2) | 3(3) |
| C20 | 31(3) | 42(4) | 33(3) | -2(3) | -2(3) | 7(3) |
| C21 | 30(4) | 39(4) | 38(3) | -4(3) | 3(3) | 8(3) |
| C22 | 41(4) | 29(3) | 40(3) | -3(3) | 6(3) | 2(3) |
| C23 | 43(4) | 31(3) | 33(3) | -3(3) | $0(3)$ | $5(3)$ |
| C24 | 41(4) | 36(3) | 26(3) | -7(2) | 0 (2) | 4(3) |
| C25 | 75(5) | 95(5) | 56(4) | 20(4) | -15(4) | -18(4) |
| C26 | 85(6) | 95(5) | 75(5) | 19(5) | -10(5) | -10(5) |
| C27 | 92(5) | 97(5) | 84(5) | 14(4) | -9(5) | -6(4) |


| C28 | 101(6) | 104(6) | 98(6) | 8(5) | -5(5) | $0(5)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C29 | 110(6) | 113(6) | 107(6) | 10(5) | -5(5) | 5(5) |
| C30 | 120(7) | 120(7) | 114(7) | 8(6) | -1(6) | 2(6) |
| C31 | 138(14) | 139(14) | 147(15) | 5(12) | 1(12) | -15(11) |
| C26A | 86(6) | 96(5) | 77(5) | 21(5) | -10(5) | -10(5) |
| C27A | 92(6) | 101(6) | 85(5) | 16(5) | -7(5) | -6(5) |
| C28A | 103(6) | 107(5) | 100(5) | 12(5) | -3(5) | 1(5) |
| C29A | 113(6) | 116(6) | 107(6) | $8(5)$ | -3(5) | 3(5) |
| C30A | 116(8) | 123(8) | 110(8) | 0(7) | 0(6) | -1(7) |
| C31A | 119(11) | 136(15) | 112(14) | -2(12) | -1(11) | 4(12) |
| C32 | 39(4) | 47(4) | 26(3) | $5(3)$ | 4(3) | $0(3)$ |
| C33 | 40(4) | 49(4) | 27(3) | -1(3) | 4(3) | $0(3)$ |
| C34 | 47(4) | 52(4) | 33(3) | 1(3) | -2(3) | 6(4) |
| C35 | 45(4) | 59(4) | 30(3) | -5(3) | 5(3) | 11(4) |
| C36 | 42(4) | 58(4) | 30(3) | 3(3) | 5(3) | 3(3) |
| C37 | 61(5) | 83(6) | 37(4) | -9(4) | -3(4) | 12(5) |
| C38 | 70(7) | 108(9) | 44(5) | -3(5) | -13(5) | 19(7) |
| O4 | 62(4) | 57(4) | 42(3) | 4(3) | 23(3) | 2(3) |
| O5 | 45(4) | 65(4) | 55(4) | -5(3) | -1(3) | -8(3) |
| O6 | 54(4) | 51(3) | 48(3) | -1(3) | $0(3)$ | 2(3) |
| N2 | 45(3) | 41(3) | 40(3) | -2(3) | 5(3) | 3(3) |
| C39 | 47(4) | 35(3) | 39(3) | $0(3)$ | 9(3) | -1(3) |
| C40 | 38(4) | 29(3) | 42(3) | 4(3) | 7(3) | 0 (3) |
| C41 | 40(4) | 37(4) | 54(4) | -1(3) | 14(3) | 2(3) |
| C42 | 35(4) | 39(4) | 58(4) | -1(3) | 1(3) | -1(3) |
| C43 | 45(4) | 29(3) | 47(3) | -4(3) | 4(3) | 3(3) |
| C44 | 41(4) | 40(4) | 42(3) | -2(3) | 1(3) | 8(3) |
| C45 | 54(4) | 29(3) | 35(3) | 1(3) | 1(3) | 7(3) |
| C46 | 49(4) | 39(4) | 47(4) | -1(3) | 11(3) | 5(3) |
| C47 | 42(4) | 42(4) | 47(4) | 2(3) | 11(3) | 4(3) |
| C48 | 41(4) | 23(3) | 42(3) | 2(3) | 9(3) | 2(3) |
| C49 | 46(4) | 39(4) | 47(4) | -2(3) | $0(3)$ | -7(3) |
| C50 | 39(4) | 30(3) | 36(3) | -1(3) | 6(3) | 5(3) |
| C51 | 38(4) | 36(4) | 51(3) | -7(3) | 2(3) | -2(3) |
| C52 | 32(4) | 45(4) | 52(3) | 0 (3) | 2(3) | $0(3)$ |
| C53 | 42(4) | 42(4) | 49(4) | -7(3) | -2(3) | 1(3) |


| C54 | $37(4)$ | $41(4)$ | $51(4)$ | $-8(3)$ | $-7(3)$ | $0(3)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| C55 | $33(4)$ | $48(4)$ | $54(4)$ | $-4(3)$ | $6(3)$ | $0(3)$ |
| C56 | $38(4)$ | $40(4)$ | $48(3)$ | $-6(3)$ | $0(3)$ | $1(3)$ |
| C57 | $36(4)$ | $36(4)$ | $52(4)$ | $-10(3)$ | $-1(3)$ | $-1(3)$ |
| C58 | $42(4)$ | $37(4)$ | $64(5)$ | $-9(3)$ | $-4(3)$ | $-2(3)$ |
| C59 | $40(4)$ | $36(4)$ | $74(4)$ | $-12(3)$ | $-1(3)$ | $-9(3)$ |
| C60 | $40(4)$ | $33(4)$ | $75(4)$ | $-8(3)$ | $10(4)$ | $3(3)$ |
| C61 | $42(4)$ | $41(4)$ | $54(4)$ | $-3(3)$ | $6(3)$ | $3(3)$ |
| C62 | $36(4)$ | $32(3)$ | $53(4)$ | $-12(3)$ | $5(3)$ | $6(3)$ |
| C63 | $45(5)$ | $47(4)$ | $41(4)$ | $-7(3)$ | $5(3)$ | $1(3)$ |
| C64 | $57(5)$ | $47(4)$ | $44(4)$ | $-3(3)$ | $5(3)$ | $6(4)$ |
| C65 | $50(5)$ | $62(5)$ | $46(4)$ | $1(4)$ | $3(3)$ | $-2(4)$ |
| C66 | $54(5)$ | $60(5)$ | $41(4)$ | $0(3)$ | $7(3)$ | $-9(4)$ |
| C67 | $49(5)$ | $70(5)$ | $35(4)$ | $0(4)$ | $8(3)$ | $-7(4)$ |
| C68 | $53(5)$ | $64(5)$ | $45(4)$ | $1(4)$ | $6(4)$ | $-2(4)$ |
| C69 | $51(6)$ | $89(7)$ | $52(5)$ | $5(5)$ | $6(4)$ | $-7(5)$ |
| C70 | $69(6)$ | $56(5)$ | $59(4)$ | $-1(4)$ | $11(4)$ | $3(5)$ |
| C71 | $95(7)$ | $85(7)$ | $69(5)$ | $3(5)$ | $-4(5)$ | $-7(6)$ |
| C72 | $93(7)$ | $94(7)$ | $84(6)$ | $4(6)$ | $1(6)$ | $0(6)$ |
| C73 | $101(7)$ | $105(6)$ | $89(6)$ | $4(5)$ | $2(5)$ | $2(5)$ |
| C74 | $108(8)$ | $115(7)$ | $99(7)$ | $6(6)$ | $1(6)$ | $6(6)$ |
| C75 | $116(9)$ | $122(9)$ | $106(8)$ | $3(7)$ | $-3(7)$ | $5(7)$ |
| C76 | $125(14)$ | $136(14)$ | $121(14)$ | $6(12)$ | $-9(11)$ | $12(11)$ |
| C72A | $97(7)$ | $101(7)$ | $85(6)$ | $10(5)$ | $6(6)$ | $-2(6)$ |
| C73A | $102(7)$ | $107(6)$ | $91(6)$ | $7(5)$ | $4(5)$ | $0(6)$ |

Table 7Y'.5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 7Y'.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H3 | 8080 | -3158 | 4222 | 44 |
| H4 | 7659 | -2777 | 4012 | 39 |
| H7 | 9990 | -64 | 3817 | 41 |
| H8 | 11394 | 650 | 3882 | 44 |
| H9 | 11820 | 182 | 4095 | 43 |
| H16 | 9170 | 238 | 3539 | 42 |
| H17 | 8955 | 507 | 3321 | 39 |
| H20 | 6153 | -1514 | 3254 | 42 |
| H21 | 5115 | -2674 | 3377 | 43 |
| H22 | 5346 | -3171 | 3595 | 44 |
| H23 | 6668 | -2404 | 3688 | 43 |
| H25A | 10321 | -2765 | 4552 | 90 |
| H25B | 11209 | -1762 | 4522 | 90 |
| H26A | 10816 | -5346 | 4432 | 102 |
| H26B | 11713 | -4355 | 4412 | 102 |
| H27A | 11099 | -5575 | 4653 | 109 |
| H27B | 11978 | -4499 | 4637 | 109 |
| H28A | 11642 | -8092 | 4550 | 121 |
| H28B | 12465 | -7010 | 4504 | 121 |
| H29A | 12998 | -8706 | 4667 | 132 |
| H29B | 12888 | -6770 | 4730 | 132 |
| H30A | 11699 | -7662 | 4841 | 142 |
| H30B | 12384 | -9241 | 4860 | 142 |
| H31A | 11013 | -10487 | 4816 | 212 |
| H31B | 10961 | -9421 | 4684 | 212 |
| H31C | 11647 | -11002 | 4704 | 212 |
| H26C | 11804 | -4332 | 4439 | 104 |
| H26D | 10966 | -5437 | 4478 | 104 |
| H27C | 12123 | -3703 | 4656 | 111 |
| H27D | 11244 | -4612 | 4698 | 111 |


| H28C | 12703 | -6496 | 4600 | 124 |
| :---: | :---: | :---: | :---: | :---: |
| H28D | 11797 | -7473 | 4616 | 124 |
| H29C | 11909 | -6697 | 4845 | 135 |
| H29D | 12543 | -8247 | 4798 | 135 |
| H30C | 13049 | -4555 | 4835 | 140 |
| H30D | 13286 | -6139 | 4932 | 140 |
| H31D | 14485 | -5494 | 4804 | 183 |
| H31E | 14166 | -7501 | 4775 | 183 |
| H31F | 13929 | -5916 | 4678 | 183 |
| H32A | 8767 | -662 | 3127 | 45 |
| H32B | 8399 | 1344 | 3110 | 45 |
| H33A | 7780 | -1725 | 2972 | 46 |
| H33B | 8390 | -229 | 2912 | 46 |
| H34A | 6686 | 517 | 2994 | 53 |
| H34B | 7294 | 1937 | 2926 | 53 |
| H35A | 7204 | 325 | 2736 | 53 |
| H35B | 6671 | -1235 | 2803 | 53 |
| H36A | 6042 | 2326 | 2758 | 52 |
| H36B | 5509 | 805 | 2830 | 52 |
| H37A | 5555 | -989 | 2638 | 73 |
| H37B | 5988 | 682 | 2568 | 73 |
| H38A | 4282 | 785 | 2670 | 111 |
| H38B | 4478 | 610 | 2522 | 111 |
| H38C | 4715 | 2424 | 2597 | 111 |
| H41 | 8674 | 5502 | 3267 | 52 |
| H42 | 9155 | 5272 | 3478 | 53 |
| H45 | 6885 | 2672 | 3699 | 47 |
| H46 | 5521 | 1778 | 3642 | 54 |
| H47 | 5030 | 2090 | 3432 | 52 |
| H54 | 7709 | 2299 | 3968 | 52 |
| H55 | 7970 | 1940 | 4182 | 54 |
| H58 | 10831 | 3808 | 4234 | 58 |
| H59 | 11816 | 5170 | 4108 | 60 |
| H60 | 11522 | 5680 | 3894 | 59 |
| H61 | 10188 | 4917 | 3807 | 55 |
| H63A | 5502 | 3587 | 2992 | 53 |


| H63B | 6375 | 4572 | 2955 | 53 |
| :---: | :---: | :---: | :---: | :---: |
| H64A | 5021 | 6441 | 3084 | 59 |
| H64B | 5852 | 7372 | 3025 | 59 |
| H65A | 4750 | 7884 | 2881 | 63 |
| H65B | 5361 | 6430 | 2818 | 63 |
| H66A | 3809 | 5485 | 2940 | 62 |
| H66B | 4398 | 4135 | 2862 | 62 |
| H67A | 4042 | 5663 | 2671 | 61 |
| H67B | 3475 | 7070 | 2747 | 61 |
| H68A | 3074 | 3295 | 2729 | 65 |
| H68B | 2502 | 4722 | 2803 | 65 |
| H69A | 2217 | 6171 | 2606 | 96 |
| H69B | 1838 | 4175 | 2613 | 96 |
| H69C | 2701 | 4551 | 2537 | 96 |
| H70A | 8604 | 893 | 4378 | 73 |
| H70B | 8306 | 2959 | 4380 | 73 |
| H71A | 9155 | 3622 | 4546 | 100 |
| H71B | 9772 | 1938 | 4523 | 100 |
| H72A | 10353 | 1228 | 4533 | 109 |
| H72B | 9603 | -177 | 4560 | 109 |
| H73A | 9410 | 1460 | 4759 | 118 |
| H73B | 10327 | 2327 | 4732 | 118 |
| H74A | 9946 | -1240 | 4797 | 129 |
| H74B | 10765 | -909 | 4711 | 129 |
| H75A | 10534 | 127 | 4964 | 138 |
| H75B | 11202 | 1215 | 4880 | 138 |
| H76A | 11909 | -1016 | 4996 | 191 |
| H76B | 11313 | -2524 | 4932 | 191 |
| H76C | 11983 | -1434 | 4848 | 191 |
| H72C | 8702 | -17 | 4591 | 113 |
| H72D | 8070 | 1645 | 4612 | 113 |
| H73C | 8626 | 776 | 4806 | 120 |
| H73D | 9585 | 917 | 4756 | 120 |
| H74C | 9436 | 4039 | 4736 | 132 |
| H74D | 8475 | 3905 | 4786 | 132 |
| H75C | 9968 | 3127 | 4932 | 138 |


| H75D | 9017 | 2831 | 4983 | 138 |
| :--- | :--- | :--- | :--- | :--- |
| H76D | 9573 | 5515 | 5061 | 192 |
| H76E | 9719 | 6225 | 4920 | 192 |
| H76F | 8766 | 5929 | 4970 | 192 |

Table $\mathbf{7} \mathbf{Y}^{\mathbf{}}$.6. Torsion angles [ ${ }^{[ }$] for $\mathbf{7} \mathbf{Y}^{\mathbf{}}$.

| C11-N1-C1-O1 | -179.7(10) | C5-C6-C12-C10 | 179.1(7) |
| :---: | :---: | :---: | :---: |
| C25-N1-C1-O1 | 6.0(15) | C3-C2-C12-C6 | -2.8(12) |
| C11-N1-C1-C2 | 1.6(14) | C1-C2-C12-C6 | 178.0(7) |
| C25-N1-C1-C2 | -172.7(9) | C3-C2-C12-C10 | -179.7(7) |
| O1-C1-C2-C12 | 179.8(9) | C1-C2-C12-C10 | 1.1(12) |
| N1-C1-C2-C12 | -1.6(12) | C9-C10-C12-C6 | 3.2(11) |
| O1-C1-C2-C3 | 0.6(14) | C11-C10-C12-C6 | -177.5(7) |
| N1-C1-C2-C3 | 179.2(8) | C9-C10-C12-C2 | -179.7(7) |
| C12-C2-C3-C4 | 3.4(12) | C11-C10-C12-C2 | -0.4(12) |
| C1-C2-C3-C4 | -177.3(7) | C14-C15-C16-C17 | 176.8(7) |
| C2-C3-C4-C5 | -3.6(12) | C24-C15-C16-C17 | -2.9(12) |
| C3-C4-C5-C13 | 179.5(7) | C15-C16-C17-C18 | 2.7(12) |
| C3-C4-C5-C6 | 2.9(11) | C32-O3-C18-C17 | 10.0(11) |
| C4-C5-C6-C7 | 180.0(7) | C32-O3-C18-C19 | -169.7(7) |
| C13-C5-C6-C7 | 3.4(11) | C16-C17-C18-O3 | -179.2(7) |
| C4-C5-C6-C12 | -2.1(11) | C16-C17-C18-C19 | 0.4(11) |
| C13-C5-C6-C12 | -178.7(7) | O3-C18-C19-C20 | -2.0(11) |
| C12-C6-C7-C8 | 2.6(12) | C17-C18-C19-C20 | 178.4(7) |
| C5-C6-C7-C8 | -179.5(7) | O3-C18-C19-C24 | 176.5(7) |
| C6-C7-C8-C9 | -2.3(12) | C17-C18-C19-C24 | -3.1(11) |
| C7-C8-C9-C10 | 2.5(12) | C24-C19-C20-C21 | 0.2(12) |
| C8-C9-C10-C12 | -3.1(12) | C18-C19-C20-C21 | 178.7(7) |
| C8-C9-C10-C11 | 177.6(7) | C19-C20-C21-C22 | -0.8(12) |
| C1-N1-C11-O2 | 179.8(9) | C20-C21-C22-C23 | 0.6(12) |
| C25-N1-C11-O2 | -5.9(15) | C21-C22-C23-C24 | 0.2(11) |
| C1-N1-C11-C10 | -1.0(14) | C20-C19-C24-C23 | 0.5(11) |
| C25-N1-C11-C10 | 173.3(9) | C18-C19-C24-C23 | -178.1(7) |
| C9-C10-C11-O2 | -1.2(14) | C20-C19-C24-C15 | -178.5(7) |
| C12-C10-C11-O2 | 179.5(9) | C18-C19-C24-C15 | 2.9(11) |
| C9-C10-C11-N1 | 179.7(8) | C22-C23-C24-C19 | -0.7(11) |
| C12-C10-C11-N1 | 0.4(12) | C22-C23-C24-C15 | 178.3(7) |
| C7-C6-C12-C2 | -179.9(7) | C16-C15-C24-C19 | 0.0(11) |
| C5-C6-C12-C2 | 2.1(11) | C14-C15-C24-C19 | -179.6(7) |
| C7-C6-C12-C10 | -2.9(11) | C16-C15-C24-C23 | -179.0(7) |


| C14-C15-C24-C23 | 1.4(11) | C42-C43-C44-C45 | -178.4(8) |
| :---: | :---: | :---: | :---: |
| C11-N1-C25-C26A | -77(2) | C51-C43-C44-C45 | -1.2(12) |
| C1-N1-C25-C26A | 97(2) | C50-C44-C45-C46 | -0.4(12) |
| C11-N1-C25-C26 | -82(2) | C43-C44-C45-C46 | -179.2(8) |
| C1-N1-C25-C26 | 93(2) | C44-C45-C46-C47 | -0.1(12) |
| N1-C25-C26-C27 | -176(3) | C45-C46-C47-C48 | 0.3(13) |
| C25-C26-C27-C28 | -177(3) | C46-C47-C48-C50 | 0.0(12) |
| C26-C27-C28-C29 | 168(3) | C46-C47-C48-C49 | -177.7(8) |
| C27-C28-C29-C30 | 76(3) | C39-N2-C49-O5 | -176.1(8) |
| C28-C29-C30-C31 | 47(4) | C63-N2-C49-O5 | 2.4(13) |
| N1-C25-C26A-C27A | 175(2) | C39-N2-C49-C48 | 6.0(12) |
| C25-C26A-C27A-C28A | 174(3) | C63-N2-C49-C48 | -175.5(7) |
| C26A-C27A-C28A-C29A | -170(3) | C47-C48-C49-O5 | -1.5(13) |
| C27A-C28A-C29A-C30A | -75(3) | C50-C48-C49-O5 | -179.4(8) |
| C28A-C29A-C30A-C31A | -62(3) | C47-C48-C49-N2 | 176.2(8) |
| C18-O3-C32-C33 | 164.1(6) | C50-C48-C49-N2 | -1.6(11) |
| O3-C32-C33-C34 | 61.5(9) | C41-C40-C50-C48 | 179.8(7) |
| C32-C33-C34-C35 | -176.0(8) | C39-C40-C50-C48 | -0.4(11) |
| C33-C34-C35-C36 | 174.4(8) | C41-C40-C50-C44 | 1.7(11) |
| C34-C35-C36-C37 | -177.9(9) | C39-C40-C50-C44 | -178.5(7) |
| C35-C36-C37-C38 | 173.1(10) | C47-C48-C50-C40 | -178.8(7) |
| C49-N2-C39-O4 | 177.4(8) | C49-C48-C50-C40 | -1.1(11) |
| C63-N2-C39-O4 | -1.2(11) | C47-C48-C50-C44 | -0.6(11) |
| C49-N2-C39-C40 | -7.4(12) | C49-C48-C50-C44 | 177.2(7) |
| C63-N2-C39-C40 | 174.0(7) | C43-C44-C50-C40 | -2.2(11) |
| O4-C39-C40-C41 | -0.7(13) | C45-C44-C50-C40 | 179.0(7) |
| N2-C39-C40-C41 | -175.8(7) | C43-C44-C50-C48 | 179.6(7) |
| O4-C39-C40-C50 | 179.5(8) | C45-C44-C50-C48 | 0.7(11) |
| N2-C39-C40-C50 | 4.4(11) | C52-C53-C54-C55 | -178.6(8) |
| C50-C40-C41-C42 | -1.7(12) | C62-C53-C54-C55 | 2.3(13) |
| C39-C40-C41-C42 | 178.5(8) | C53-C54-C55-C56 | -4.1(14) |
| C40-C41-C42-C43 | 2.6(13) | C70-O6-C56-C55 | -9.5(13) |
| C41-C42-C43-C44 | -3.1(13) | C70-O6-C56-C57 | 167.3(8) |
| C41-C42-C43-C51 | 179.8(8) | C54-C55-C56-O6 | -178.9(8) |
| C42-C43-C44-C50 | 2.8(12) | C54-C55-C56-C57 | 4.4(13) |
| C51-C43-C44-C50 | -180.0(7) | O6-C56-C57-C62 | 179.8(7) |


| C55-C56-C57-C62 | $-3.1(13)$ |
| :--- | :---: |
| O6-C56-C57-C58 | $2.5(12)$ |
| C55-C56-C57-C58 | $179.5(8)$ |
| C62-C57-C58-C59 | $3.5(13)$ |
| C56-C57-C58-C59 | $-179.1(8)$ |
| C57-C58-C59-C60 | $-2.8(14)$ |
| C58-C59-C60-C61 | $1.1(14)$ |
| C59-C60-C61-C62 | $-0.2(13)$ |
| C56-C57-C62-C61 | $180.0(8)$ |
| C58-C57-C62-C61 | $-2.6(12)$ |
| C56-C57-C62-C53 | $1.4(12)$ |
| C58-C57-C62-C53 | $178.9(7)$ |
| C60-C61-C62-C57 | $1.1(12)$ |
| C60-C61-C62-C53 | $179.6(8)$ |
| C54-C53-C62-C57 | $-0.9(12)$ |
| C52-C53-C62-C57 | $180.0(8)$ |
| C54-C53-C62-C61 | $-179.5(8)$ |
| C52-C53-C62-C61 | $1.5(12)$ |


| C49-N2-C63-C64 | $86.0(10)$ |
| :--- | :---: |
| C39-N2-C63-C64 | $-95.4(9)$ |
| N2-C63-C64-C65 | $-171.6(8)$ |
| C63-C64-C65-C66 | $68.8(12)$ |
| C64-C65-C66-C67 | $173.8(8)$ |
| C65-C66-C67-C68 | $-178.0(9)$ |
| C66-C67-C68-C69 | $-178.8(9)$ |
| C56-O6-C70-C71 | $-168.3(9)$ |
| O6-C70-C71-C72 | $-72(2)$ |
| O6-C70-C71-C72A | $-157.7(16)$ |
| C70-C71-C72-C73 | $-168(2)$ |
| C71-C72-C73-C74 | $163(2)$ |
| C72-C73-C74-C75 | $153(3)$ |
| C73-C74-C75-C76 | $-158(4)$ |
| C70-C71-C72A-C73A | $-178.5(19)$ |
| C71-C72A-C73A-C74A | $55(4)$ |
| C72A-C73A-C74A-C75A | $180(3)$ |
| C73A-C74A-C75A-C76A | $-176(4)$ |

End of crystallographic info for $\mathbf{7} \mathbf{Y}^{\prime}$

## Crystallographic Material for 8y

## Crystallographic Material for $\mathbf{8 Y}$.

X-ray Experimental.
Table 8Y.1. Crystallographic Data for $\mathbf{8 Y}$.
Table 8Y.2. Fractional coordinates and equivalent isotropic thermal parameters ( $\AA^{2}$ ) for the non-hydrogen atoms of $\mathbf{8 Y}$.

Table 8Y.3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of $\mathbf{8 Y}$.

Table 8Y.4. Anisotropic thermal parameters for the non-hydrogen atoms of $\mathbf{8 Y}$.

Table 8Y.5. Fractional coordinates and isotropic thermal parameters $\left(\AA^{2}\right)$ for the hydrogen atoms of $\mathbf{8 Y}$.

X-ray Experimental for complex $\mathrm{C}_{40} \mathrm{H}_{45} \mathrm{NO}_{2}(\mathbf{8 Y})$ : Crystals grew as long yellow needles by vapor diffusion of Toluene in a jar of MeCN . The data crystal had approximate dimensions; 0.28 x $0.033 \times 0.024 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{Cu} \mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA)$ with collimating mirror monochromators. A total of 670 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 20 seconds per frame with a detector offset of $+/-38.1^{\circ}$ and 60 seconds per frame with a detector offset of $+/-107.8^{\circ}$. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7. ${ }^{3}$ Structure analysis was aided by use of the programs PLATON98 ${ }^{4}$ and WinGX. ${ }^{5}$ The hydrogen
atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.077 * \mathrm{P})^{2}\right]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.290 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0989 and a goodness of fit, $\mathrm{S},=1.12$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S , are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. 8 Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.37.31.
2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
3) Sheldrick, G. M. (2015). SHELXL-2013. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \sum \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\left|\mathrm{F}_{\mathrm{c}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\mathrm{Lw}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 8Y.1. Crystal data and structure refinement for $\mathbf{8 Y}$.

| Empirical formula | C40 H45 N O3 |
| :---: | :---: |
| Formula weight | 587.77 |
| Temperature | 100(2) K |
| Wavelength | $1.54184 \AA$ |
| Crystal system | monoclinic |
| Space group | C c |
| Unit cell dimensions | $\begin{array}{ll} \mathrm{a}=56.522(6) \AA & \alpha=90^{\circ} . \\ \mathrm{b}=7.4288(11) \AA & \beta=95.814(10)^{\circ} . \\ \mathrm{c}=15.489(2) \AA & \gamma=90^{\circ} . \end{array}$ |
| Volume | 6470.4(16) $\AA^{3}$ |
| Z | 8 |
| Density (calculated) | $1.207 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.582 \mathrm{~mm}^{-1}$ |
| F(000) | 2528 |
| Crystal size | $0.280 \times 0.033 \times 0.024 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 5.742 to $58.927^{\circ}$. |
| Index ranges | $-62<=\mathrm{h}<=62,-8<=\mathrm{k}<=8,-12<=\mathrm{l}<=17$ |
| Reflections collected | 8294 |
| Independent reflections | $5494[\mathrm{R}(\mathrm{int})=0.0796]$ |
| Completeness to theta $=58.927^{\circ}$ | 99.6 \% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00 and 0.136 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 5494 / $530 / 797$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.123 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0989, \mathrm{wR} 2=0.2201$ |
| R indices (all data) | $\mathrm{R} 1=0.1765, \mathrm{wR} 2=0.2905$ |
| Absolute structure parameter | -0.6(10) |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.379 and -0.460 e. $\AA^{-3}$ |

Table 8Y.2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathbf{8 Y}$. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $U^{\mathrm{ij}}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| C1 | 6100(3) | 4680(20) | 4644(10) | 44(4) |
| C2 | 5856(2) | 4470(20) | 4872(9) | 38(4) |
| C3 | 5793(3) | 5000(20) | 5683(11) | 51(4) |
| C4 | 5556(2) | 4860(20) | 5867(9) | 42(4) |
| C5 | 5383(3) | 4060(20) | 5299(10) | 45(4) |
| C6 | 5441(2) | 3480(20) | 4456(10) | 40(4) |
| C7 | 5273(3) | 2750(20) | 3833(10) | 44(4) |
| C8 | 5339(3) | 2280(20) | 3040(11) | 49(4) |
| C9 | 5572(3) | 2450(20) | 2845(11) | 47(4) |
| C10 | 5735(2) | 3140(20) | 3450(9) | 38(4) |
| C11 | 5985(3) | 3400(20) | 3198(9) | 42(4) |
| C12 | 5680(2) | 3690(20) | 4258(9) | 37(4) |
| C13 | 5142(3) | 3910(20) | 5492(11) | 52(4) |
| C14 | 4935(3) | 3680(20) | 5615(10) | 43(4) |
| C15 | 4691(3) | 3430(20) | 5734(10) | 40(4) |
| C16 | 4539(3) | 2670(20) | 5101(10) | 41(4) |
| C17 | 4300(2) | 2410(20) | 5174(9) | 37(4) |
| C18 | 4209(2) | 2800(20) | 5955(10) | 38(4) |
| C19 | 4361(2) | 3590(20) | 6635(9) | 40(4) |
| C20 | 4270(2) | 4100(20) | 7464(9) | 40(4) |
| C21 | 4413(3) | 4870(20) | 8098(10) | 45(4) |
| C22 | 4655(3) | 5110(20) | $7994(10)$ | 47(4) |
| C23 | $4749(3)$ | $4750(20)$ | $7243(10)$ | 40(4) |
| C24 | 4601(2) | $3910(20)$ | 6554(9) | 36(4) |
| C25 | 6382(2) | $4560(20)$ | $3512(11)$ | 52(4) |
| C26 | $6378(3)$ | $6450(20)$ | 3042(11) | 51(4) |
| C27 | 6620(2) | $6800(20)$ | 2683(10) | 52(4) |
| C28 | 6665(3) | $5660(30)$ | 1922(11) | 59(5) |
| C29 | 6898(2) | $6150(20)$ | $1560(10)$ | 50(4) |
| C30 | 6954(3) | $5000(20)$ | $770(10)$ | 54(4) |
| C31 | 7187(3) | 5500(30) | 410(11) | 60(5) |


| C32 | 7249(3) | 4340(30) | -349(11) | 71(6) |
| :---: | :---: | :---: | :---: | :---: |
| C33 | 3811(3) | 2060(20) | 5391(10) | 48(4) |
| C34 | 3568(3) | 2000(20) | 5764(11) | 52(4) |
| C35 | 3375(2) | 1230(20) | 5139(10) | 53(4) |
| C36 | 3133(3) | 1230(20) | 5465(11) | 60(5) |
| C37 | 3113(3) | -70(20) | 6236(12) | 58(5) |
| C38 | 2872(3) | 30(30) | 6627(11) | 64(5) |
| C39 | 2863(3) | -1260(30) | 7373(12) | 66(5) |
| C40 | 2641(3) | -1120(30) | 7835(13) | 77(6) |
| C41 | 3929(3) | 7380(20) | 6179(10) | 42(4) |
| C42 | 4177(3) | 7770 (20) | 5995(9) | 40(4) |
| C43 | 4251(2) | 7320 (20) | 5215(10) | 38(4) |
| C44 | 4487(3) | 7620(20) | 5029(11) | 50(4) |
| C45 | 4647(2) | 8390(20) | 5651(9) | 35(4) |
| C46 | 4574(2) | 8910(20) | 6483(9) | 35(4) |
| C47 | 4734(3) | 9700(20) | 7132(9) | 40(4) |
| C48 | 4654(3) | 10150(20) | 7938(10) | 42(4) |
| C49 | 4417(3) | 9870(20) | 8082(10) | 46(4) |
| C50 | 4265(2) | 9070(20) | 7460(9) | 36(4) |
| C51 | 4016(3) | 8690(20) | 7651(10) | 47(4) |
| C52 | 4336(2) | 8590(20) | 6638(10) | 39(4) |
| C53 | 4887(2) | 8670(20) | 5461(9) | 37(4) |
| C54 | 5092(3) | 8880(20) | 5330(10) | 43(4) |
| C55 | 5338(2) | 9090(20) | 5230(9) | 35(4) |
| C56 | 5485(2) | 9850(20) | 5881(9) | 40(4) |
| C57 | 5730(3) | 10040(20) | 5842(9) | 43(4) |
| C58 | 5831(2) | 9540(20) | 5104(9) | 36(4) |
| C59 | 5685(2) | 8820(20) | 4379(9) | 36(4) |
| C60 | 5782(2) | 8330(20) | 3597(9) | 42(4) |
| C61 | 5638(3) | $7580(20)$ | 2915(10) | 41(4) |
| C62 | 5396(3) | 7370 (20) | 2981(10) | 48(4) |
| C63 | 5297(3) | 7770 (20) | 3739(11) | 48(4) |
| C64 | 5436(2) | 8560(20) | 4441(10) | 40(4) |
| C65 | 3625(2) | $7310(20)$ | 7230(10) | 49(4) |
| C66 | 3624(3) | 5520(20) | 7712(10) | 50(4) |
| C67 | 3378(3) | 5050(30) | 7919(11) | 58(5) |


| C68 | $3378(3)$ | $3340(20)$ | $8445(12)$ | $60(5)$ |
| :--- | ---: | ---: | ---: | ---: |
| C69 | $3121(3)$ | $2830(30)$ | $8641(12)$ | $63(5)$ |
| C70 | $3030(3)$ | $4060(30)$ | $9345(11)$ | $64(5)$ |
| C71 | $2785(3)$ | $3430(30)$ | $9584(12)$ | $66(5)$ |
| C72 | $2691(3)$ | $4630(30)$ | $10298(13)$ | $78(6)$ |
| C73 | $6234(3)$ | $9980(20)$ | $5767(10)$ | $50(4)$ |
| C74 | $6479(2)$ | $9550(20)$ | $5549(10)$ | $53(4)$ |
| C75 | $6557(3)$ | $10640(30)$ | $4808(11)$ | $56(4)$ |
| C76 | $6800(3)$ | $10100(30)$ | $4528(10)$ | $54(4)$ |
| C77 | $6869(3)$ | $11130(20)$ | $3734(10)$ | $52(4)$ |
| C78 | $7098(3)$ | $10480(30)$ | $3380(11)$ | $59(5)$ |
| C79 | $7145(3)$ | $11480(30)$ | $2585(11)$ | $65(5)$ |
| C80 | $7363(3)$ | $10830(30)$ | $2168(12)$ | $76(6)$ |
| N1 | $6148(2)$ | $4216(19)$ | $3803(8)$ | $45(3)$ |
| N2 | $3868(2)$ | $7838(19)$ | $7018(8)$ | $44(3)$ |
| O1 | $6261(2)$ | $5320(18)$ | $5148(7)$ | $58(3)$ |
| O2 | $6040(2)$ | $2893(18)$ | $2483(7)$ | $61(3)$ |
| O3 | $3980(2)$ | $2586(16)$ | $6121(6)$ | $46(3)$ |
| O4 | $3785(2)$ | $6684(17)$ | $5642(6)$ | $52(3)$ |
| O6 | $3944(2)$ | $9033(18)$ | $8364(7)$ | $60(3)$ |
|  | $6066(2)$ | $9610(15)$ | $4994(6)$ | $43(3)$ |

Table 8Y.3. Bond lengths $[\AA]$ and angles [ ${ }^{\circ}$ ] for $\mathbf{8 Y}$.

| C1-O1 | $1.234(18)$ | $\mathrm{C} 19-\mathrm{C} 20$ | $1.481(19)$ |
| :--- | :--- | :--- | :--- |
| C1-N1 | $1.40(2)$ | $\mathrm{C} 20-\mathrm{C} 21$ | $1.33(2)$ |
| C1-C2 | $1.46(2)$ | $\mathrm{C} 20-\mathrm{H} 20$ | 0.95 |
| C2-C3 | $1.40(2)$ | $\mathrm{C} 21-\mathrm{C} 22$ | $1.41(2)$ |
| C2-C12 | $1.429(19)$ | $\mathrm{C} 21-\mathrm{H} 21$ | 0.95 |
| C3-C4 | $1.40(2)$ | $\mathrm{C} 22-\mathrm{C} 23$ | $1.36(2)$ |
| C3-H3 | 0.95 | $\mathrm{C} 22-\mathrm{H} 22$ | 0.95 |
| C4-C5 | $1.38(2)$ | $\mathrm{C} 23-\mathrm{C} 24$ | $1.43(2)$ |
| C4-H4 | 0.95 | $\mathrm{C} 23-\mathrm{H} 23$ | 0.95 |
| C5-C13 | $1.43(2)$ | $\mathrm{C} 25-\mathrm{N} 1$ | $1.461(19)$ |
| C5-C6 | $1.45(2)$ | $\mathrm{C} 25-\mathrm{C} 26$ | $1.58(2)$ |
| C6-C7 | $1.40(2)$ | $\mathrm{C} 25-\mathrm{H} 25 \mathrm{~A}$ | 0.99 |
| C6-C12 | $1.420(19)$ | $\mathrm{C} 25-\mathrm{H} 25 \mathrm{~B}$ | $0.92-\mathrm{C}$ |


| C33-O3 | 1.457(17) | C46-C47 | 1.41(2) |
| :---: | :---: | :---: | :---: |
| C33-C34 | 1.55(2) | C46-C52 | 1.411(19) |
| C33-H33A | 0.99 | C47-C48 | 1.41(2) |
| C33-H33B | 0.99 | C47-H47 | 0.95 |
| C34-C35 | 1.493(19) | C48-C49 | 1.40(2) |
| C34-H34A | 0.99 | C48-H48 | 0.95 |
| C34-H34B | 0.99 | C49-C50 | 1.36(2) |
| C35-C36 | 1.51(2) | C49-H49 | 0.95 |
| C35-H35A | 0.99 | C50-C52 | $1.420(19)$ |
| C35-H35B | 0.99 | C50-C51 | 1.49 (2) |
| C36-C37 | 1.55(2) | C51-O5 | $1.243(18)$ |
| C36-H36A | 0.99 | C51-N2 | $1.379(19)$ |
| C36-H36B | 0.99 | C53-C54 | 1.207(19) |
| C37-C38 | 1.54(2) | C54-C55 | $1.424(19)$ |
| C37-H37A | 0.99 | C55-C56 | $1.36(2)$ |
| C37-H37B | 0.99 | C55-C64 | $1.45(2)$ |
| C38-C39 | 1.51(2) | C56-C57 | 1.40(2) |
| C38-H38A | 0.99 | C56-H56 | 0.95 |
| C38-H38B | 0.99 | C57-C58 | 1.38(2) |
| C39-C40 | 1.51(2) | C57-H57 | 0.95 |
| C39-H39A | 0.99 | C58-O6 | $1.355(17)$ |
| C39-H39B | 0.99 | C58-C59 | 1.430(19) |
| C40-H40A | 0.98 | C59-C60 | 1.42(2) |
| C40-H40B | 0.98 | C59-C64 | 1.437(18) |
| C40-H40C | 0.98 | C60-C61 | 1.38(2) |
| C41-O4 | 1.216(17) | C60-H60 | 0.95 |
| C41-N2 | 1.419(19) | C61-C62 | $1.39(2)$ |
| C41-C42 | 1.49 (2) | C61-H61 | 0.95 |
| C42-C43 | 1.36(2) | C62-C63 | 1.38(2) |
| C42-C52 | 1.41(2) | C62-H62 | 0.95 |
| C43-C44 | 1.41(2) | C63-C64 | 1.40(2) |
| C43-H43 | 0.95 | C63-H63 | 0.95 |
| C44-C45 | 1.38(2) | C65-N2 | 1.494(17) |
| C44-H44 | 0.95 | C65-C66 | 1.52(2) |
| C45-C53 | 1.429(19) | C65-H65A | 0.99 |
| C45-C46 | $1.45(2)$ | C65-H65B | 0.99 |


| C66-C67 | 1.50(2) | C73-H73A | 0.99 |
| :---: | :---: | :---: | :---: |
| C66-H66A | 0.99 | C73-H73B | 0.99 |
| C66-H66B | 0.99 | C74-C75 | 1.51(2) |
| C67-C68 | 1.51(2) | C74-H74A | 0.99 |
| C67-H67A | 0.99 | C74-H74B | 0.99 |
| C67-H67B | 0.99 | C75-C76 | 1.54(2) |
| C68-C69 | 1.56(2) | C75-H75A | 0.99 |
| C68-H68A | 0.99 | C75-H75B | 0.99 |
| C68-H68B | 0.99 | C76-C77 | 1.53(2) |
| C69-C70 | 1.55(2) | C76-H76A | 0.99 |
| C69-H69A | 0.99 | C76-H76B | 0.99 |
| C69-H69B | 0.99 | C77-C78 | 1.53(2) |
| C70-C71 | 1.54(2) | C77-H77A | 0.99 |
| C70-H70A | 0.99 | C77-H77B | 0.99 |
| C70-H70B | 0.99 | C78-C79 | 1.49(2) |
| C71-C72 | 1.55(2) | C78-H78A | 0.99 |
| C71-H71A | 0.99 | C78-H78B | 0.99 |
| C71-H71B | 0.99 | C79-C80 | 1.52(2) |
| C72-H72A | 0.98 | C79-H79A | 0.99 |
| C72-H72B | 0.98 | C79-H79B | 0.99 |
| C72-H72C | 0.98 | C80-H80A | 0.98 |
| C73-06 | 1.475(16) | C80-H80B | 0.98 |
| C73-C74 | 1.49(2) | C80-H80C | 0.98 |
| O1-C1-N1 | 118.8(14) | C4-C5-C13 | 122.0(16) |
| O1-C1-C2 | 122.8(14) | C4-C5-C6 | 119.3(14) |
| N1-C1-C2 | 118.3(13) | C13-C5-C6 | 118.6(15) |
| C3-C2-C12 | 119.3(14) | C7-C6-C12 | 119.3(14) |
| C3-C2-C1 | 121.1(14) | C7-C6-C5 | 122.4(13) |
| C12-C2-C1 | 119.6(13) | C12-C6-C5 | 118.3(14) |
| C2-C3-C4 | 119.8(15) | C8-C7-C6 | 119.4(14) |
| C2-C3-H3 | 120.1 | C8-C7-H7 | 120.3 |
| C4-C3-H3 | 120.1 | C6-C7-H7 | 120.3 |
| C5-C4-C3 | 122.2(15) | C7-C8-C9 | 121.7(16) |
| C5-C4-H4 | 118.9 | C7-C8-H8 | 119.2 |
| C3-C4-H4 | 118.9 | C9-C8-H8 | 119.2 |


| C10-C9-C8 | 118.8(15) | C23-C22-H22 | 118.5 |
| :---: | :---: | :---: | :---: |
| C10-C9-H9 | 120.6 | C21-C22-H22 | 118.5 |
| C8-C9-H9 | 120.6 | C22-C23-C24 | 118.5(14) |
| C9-C10-C12 | 122.5(13) | C22-C23-H23 | 120.7 |
| C9-C10-C11 | 117.4(13) | C24-C23-H23 | 120.7 |
| C12-C10-C11 | 119.9(13) | C19-C24-C23 | 120.5(13) |
| O2-C11-N1 | 121.8(14) | C19-C24-C15 | 117.6(13) |
| O2-C11-C10 | 121.1(13) | C23-C24-C15 | 121.8(13) |
| N1-C11-C10 | 117.1(13) | N1-C25-C26 | 108.9(12) |
| C10-C12-C6 | 118.2(13) | N1-C25-H25A | 109.9 |
| C10-C12-C2 | 121.0(13) | C26-C25-H25A | 109.9 |
| C6-C12-C2 | 120.9(14) | N1-C25-H25B | 109.9 |
| C14-C13-C5 | 175.2(19) | C26-C25-H25B | 109.9 |
| C13-C14-C15 | 178.4(18) | H25A-C25-H25B | 108.3 |
| C16-C15-C14 | 120.8(15) | C27-C26-C25 | 110.2(12) |
| C16-C15-C24 | 118.6(13) | C27-C26-H26A | 109.6 |
| C14-C15-C24 | 120.5(14) | C25-C26-H26A | 109.6 |
| C15-C16-C17 | 123.6(15) | C27-C26-H26B | 109.6 |
| C15-C16-H16 | 118.2 | C25-C26-H26B | 109.6 |
| C17-C16-H16 | 118.2 | H26A-C26-H26B | 108.1 |
| C16-C17-C18 | 119.5(14) | C28-C27-C26 | 114.3(14) |
| C16-C17-H17 | 120.3 | C28-C27-H27A | 108.7 |
| C18-C17-H17 | 120.3 | C26-C27-H27A | 108.7 |
| O3-C18-C17 | 125.7(14) | C28-C27-H27B | 108.7 |
| O3-C18-C19 | 115.4(13) | C26-C27-H27B | 108.7 |
| C17-C18-C19 | 118.8(13) | H27A-C27-H27B | 107.6 |
| C24-C19-C18 | 121.8(14) | C27-C28-C29 | 112.1(14) |
| C24-C19-C20 | 117.5(13) | C27-C28-H28A | 109.2 |
| C18-C19-C20 | 120.7(13) | C29-C28-H28A | 109.2 |
| C21-C20-C19 | 120.6(13) | C27-C28-H28B | 109.2 |
| C21-C20-H20 | 119.7 | C29-C28-H28B | 109.2 |
| C19-C20-H20 | 119.7 | H28A-C28-H28B | 107.9 |
| C20-C21-C22 | 119.7(16) | C28-C29-C30 | 114.4(14) |
| C20-C21-H21 | 120.2 | C28-C29-H29A | 108.7 |
| C22-C21-H21 | 120.2 | C30-C29-H29A | 108.7 |
| C23-C22-C21 | 122.9(15) | C28-C29-H29B | 108.7 |


| C30-C29-H29B | 108.7 | C36-C35-H35B | 108.7 |
| :---: | :---: | :---: | :---: |
| H29A-C29-H29B | 107.6 | H35A-C35-H35B | 107.6 |
| C31-C30-C29 | 114.0(14) | C35-C36-C37 | 113.4(14) |
| C31-C30-H30A | 108.7 | C35-C36-H36A | 108.9 |
| C29-C30-H30A | 108.7 | C37-C36-H36A | 108.9 |
| C31-C30-H30B | 108.7 | C35-C36-H36B | 108.9 |
| C29-C30-H30B | 108.7 | C37-C36-H36B | 108.9 |
| H30A-C30-H30B | 107.6 | H36A-C36-H36B | 107.7 |
| C30-C31-C32 | 114.6(15) | C38-C37-C36 | 114.0(14) |
| C30-C31-H31A | 108.6 | C38-C37-H37A | 108.7 |
| C32-C31-H31A | 108.6 | C36-C37-H37A | 108.7 |
| C30-C31-H31B | 108.6 | C38-C37-H37B | 108.7 |
| C32-C31-H31B | 108.6 | C36-C37-H37B | 108.7 |
| H31A-C31-H31B | 107.6 | H37A-C37-H37B | 107.6 |
| C31-C32-H32A | 109.5 | C39-C38-C37 | 111.8(14) |
| C31-C32-H32B | 109.5 | C39-C38-H38A | 109.3 |
| H32A-C32-H32B | 109.5 | C37-C38-H38A | 109.3 |
| C31-C32-H32C | 109.5 | C39-C38-H38B | 109.3 |
| H32A-C32-H32C | 109.5 | C37-C38-H38B | 109.3 |
| H32B-C32-H32C | 109.5 | H38A-C38-H38B | 107.9 |
| O3-C33-C34 | 104.7(12) | C38-C39-C40 | 114.7(15) |
| O3-C33-H33A | 110.8 | C38-C39-H39A | 108.6 |
| C34-C33-H33A | 110.8 | C40-C39-H39A | 108.6 |
| O3-C33-H33B | 110.8 | C38-C39-H39B | 108.6 |
| C34-C33-H33B | 110.8 | C40-C39-H39B | 108.6 |
| H33A-C33-H33B | 108.9 | H39A-C39-H39B | 107.6 |
| C35-C34-C33 | 112.6(13) | C39-C40-H40A | 109.5 |
| C35-C34-H34A | 109.1 | C39-C40-H40B | 109.5 |
| C33-C34-H34A | 109.1 | H40A-C40-H40B | 109.5 |
| C35-C34-H34B | 109.1 | C39-C40-H40C | 109.5 |
| C33-C34-H34B | 109.1 | H40A-C40-H40C | 109.5 |
| H34A-C34-H34B | 107.8 | H40B-C40-H40C | 109.5 |
| C34-C35-C36 | 114.1(14) | O4-C41-N2 | 121.5(14) |
| C34-C35-H35A | 108.7 | O4-C41-C42 | 121.8(14) |
| C36-C35-H35A | 108.7 | N2-C41-C42 | 116.8(13) |
| C34-C35-H35B | 108.7 | C43-C42-C52 | 120.0(14) |


| C43-C42-C41 | 120.3(14) | C54-C55-C64 | 121.7(14) |
| :---: | :---: | :---: | :---: |
| C52-C42-C41 | 119.7(13) | C55-C56-C57 | 122.7(14) |
| C42-C43-C44 | 121.8(15) | C55-C56-H56 | 118.6 |
| C42-C43-H43 | 119.1 | C57-C56-H56 | 118.6 |
| C44-C43-H43 | 119.1 | C58-C57-C56 | 120.3(14) |
| C45-C44-C43 | 119.4(16) | C58-C57-H57 | 119.8 |
| C45-C44-H44 | 120.3 | C56-C57-H57 | 119.8 |
| C43-C44-H44 | 120.3 | O6-C58-C57 | 126.0(13) |
| C44-C45-C53 | 119.2(14) | O6-C58-C59 | 114.2(13) |
| C44-C45-C46 | 120.5(13) | C57-C58-C59 | 119.8(13) |
| C53-C45-C46 | 120.3(13) | C60-C59-C58 | 121.6(13) |
| C47-C46-C52 | 120.1(14) | C60-C59-C64 | 119.0(13) |
| C47-C46-C45 | 121.9(13) | C58-C59-C64 | 119.4(13) |
| C52-C46-C45 | 118.0(13) | C61-C60-C59 | 120.4(13) |
| C48-C47-C46 | 119.5(14) | C61-C60-H60 | 119.8 |
| C48-C47-H47 | 120.2 | C59-C60-H60 | 119.8 |
| C46-C47-H47 | 120.2 | C60-C61-C62 | 119.7(14) |
| C49-C48-C47 | 120.2(15) | C60-C61-H61 | 120.2 |
| C49-C48-H48 | 119.9 | C62-C61-H61 | 120.2 |
| C47-C48-H48 | 119.9 | C63-C62-C61 | 121.5(15) |
| C50-C49-C48 | 120.0(15) | C63-C62-H62 | 119.3 |
| C50-C49-H49 | 120.0 | C61-C62-H62 | 119.3 |
| C48-C49-H49 | 120.0 | C62-C63-C64 | 120.6(15) |
| C49-C50-C52 | 122.0(14) | C62-C63-H63 | 119.7 |
| C49-C50-C51 | 118.8(14) | C64-C63-H63 | 119.7 |
| C52-C50-C51 | 119.1(13) | C63-C64-C59 | 118.6(14) |
| O5-C51-N2 | 119.6(14) | C63-C64-C55 | 122.5(13) |
| O5-C51-C50 | 122.7(14) | C59-C64-C55 | 118.8(13) |
| N2-C51-C50 | 117.6(13) | N2-C65-C66 | 112.7(12) |
| C46-C52-C42 | 120.3(14) | N2-C65-H65A | 109.0 |
| C46-C52-C50 | 118.1(13) | C66-C65-H65A | 109.0 |
| C42-C52-C50 | 121.6(13) | N2-C65-H65B | 109.0 |
| C54-C53-C45 | 177.5(16) | C66-C65-H65B | 109.0 |
| C53-C54-C55 | 176.3(16) | H65A-C65-H65B | 107.8 |
| C56-C55-C54 | 119.5(14) | C67-C66-C65 | 111.0(13) |
| C56-C55-C64 | 118.8(13) | C67-C66-H66A | 109.4 |


| C65-C66-H66A | 109.4 | H72A-C72-H72B | 109.5 |
| :---: | :---: | :---: | :---: |
| C67-C66-H66B | 109.4 | C71-C72-H72C | 109.5 |
| C65-C66-H66B | 109.4 | H72A-C72-H72C | 109.5 |
| H66A-C66-H66B | 108.0 | H72B-C72-H72C | 109.5 |
| C66-C67-C68 | 111.3(13) | O6-C73-C74 | 108.2(13 |
| C66-C67-H67A | 109.4 | O6-C73-H73A | 110.1 |
| C68-C67-H67A | 109.4 | C74-C73-H73A | 110.1 |
| C66-C67-H67B | 109.4 | O6-C73-H73B | 110.1 |
| C68-C67-H67B | 109.4 | C74-C73-H73B | 110.1 |
| H67A-C67-H67B | 108.0 | H73A-C73-H73B | 108.4 |
| C67-C68-C69 | 111.2(14) | C73-C74-C75 | 113.9(14 |
| C67-C68-H68A | 109.4 | C73-C74-H74A | 108.8 |
| C69-C68-H68A | 109.4 | C75-C74-H74A | 108.8 |
| C67-C68-H68B | 109.4 | C73-C74-H74B | 108.8 |
| C69-C68-H68B | 109.4 | C75-C74-H74B | 108.8 |
| H68A-C68-H68B | 108.0 | H74A-C74-H74B | 107.7 |
| C70-C69-C68 | 112.1(15) | C74-C75-C76 | 114.6(14 |
| C70-C69-H69A | 109.2 | C74-C75-H75A | 108.6 |
| C68-C69-H69A | 109.2 | C76-C75-H75A | 108.6 |
| C70-C69-H69B | 109.2 | C74-C75-H75B | 108.6 |
| C68-C69-H69B | 109.2 | C76-C75-H75B | 108.6 |
| H69A-C69-H69B | 107.9 | H75A-C75-H75B | 107.6 |
| C71-C70-C69 | 111.1(15) | C77-C76-C75 | 114.1(14 |
| C71-C70-H70A | 109.4 | C77-C76-H76A | 108.7 |
| C69-C70-H70A | 109.4 | C75-C76-H76A | 108.7 |
| C71-C70-H70B | 109.4 | C77-C76-H76B | 108.7 |
| C69-C70-H70B | 109.4 | C75-C76-H76B | 108.7 |
| H70A-C70-H70B | 108.0 | H76A-C76-H76B | 107.6 |
| C70-C71-C72 | 112.1(15) | C76-C77-C78 | 115.1(14 |
| C70-C71-H71A | 109.2 | C76-C77-H77A | 108.5 |
| C72-C71-H71A | 109.2 | C78-C77-H77A | 108.5 |
| C70-C71-H71B | 109.2 | C76-C77-H77B | 108.5 |
| C72-C71-H71B | 109.2 | C78-C77-H77B | 108.5 |
| H71A-C71-H71B | 107.9 | H77A-C77-H77B | 107.5 |
| C71-C72-H72A | 109.5 | C79-C78-C77 | 111.6(15 |
| C71-C72-H72B | 109.5 | C79-C78-H78A | 109.3 |


| C77-C78-H78A | 109.3 | H80A-C80-H80B | 109.5 |
| :--- | :--- | :--- | :--- |
| C79-C78-H78B | 109.3 | C79-C80-H80C | 109.5 |
| C77-C78-H78B | 109.3 | H80A-C80-H80C | 109.5 |
| H78A-C78-H78B | 108.0 | H80B-C80-H80C | 109.5 |
| C78-C79-C80 | $114.4(16)$ | C11-N1-C1 | $123.9(13)$ |
| C78-C79-H79A | 108.7 | C11-N1-C25 | $115.3(13)$ |
| C80-C79-H79A | 108.7 | C1-N1-C25 | $120.8(13)$ |
| C78-C79-H79B | 108.7 | C51-N2-C41 | $125.1(12)$ |
| C80-C79-H79B | 108.7 | C41-N2-C65 | $118.0(13)$ |
| H79A-C79-H79B | 107.6 | C18-O3-C33 | $116.8(12)$ |
| C79-C80-H80A | 109.5 | C58-O6-C73 | $116.6(12)$ |
| C79-C80-H80B | 109.5 |  | $117.5(11)$ |

Table 8Y.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathbf{8 Y}$. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | 27(7) | 63(9) | 42(7) | -7(7) | -1(6) | -5(6) |
| C2 | 27(6) | 54(8) | 34(7) | -5(6) | 6(5) | 7(6) |
| C3 | 37(7) | 55(8) | 59(8) | 6(7) | -3(7) | -4(7) |
| C4 | 35(7) | 54(8) | 39(7) | -3(7) | 10(6) | -3(6) |
| C5 | 41(7) | 53(8) | 41(7) | 2(7) | 9(6) | 0 (7) |
| C6 | 22(6) | 49(8) | 47(7) | 7(7) | 2(6) | $0(6)$ |
| C7 | 22(6) | 60(9) | 51(8) | 1(7) | 5(6) | 5(6) |
| C8 | 31(7) | 62(9) | 53(8) | 1(7) | -6(6) | 5(7) |
| C9 | 34(7) | 61(9) | 46(7) | -9(7) | 4(6) | 0(7) |
| C10 | 22(6) | 50(8) | 40(7) | -3(7) | 4(6) | -8(6) |
| C11 | 33(7) | 57(8) | 36(7) | -5(7) | 1(6) | 2(6) |
| C12 | 22(6) | 50(8) | 41(7) | -10(6) | 4(6) | 0(6) |
| C13 | 39(8) | 60(9) | 56(8) | 4(7) | 4(7) | 3(7) |
| C14 | 26(7) | 54(8) | 49(7) | -1(7) | 6(6) | 1(6) |
| C15 | 28(6) | 44(8) | 50(7) | 3(7) | 10(6) | -1(6) |
| C16 | 40(7) | 45(8) | 40(7) | 0(7) | 10(6) | 3(6) |
| C17 | 27(6) | 56(8) | 30(6) | -2(6) | 8(6) | 2(6) |
| C18 | 22(6) | 44(8) | 49(7) | 5(7) | 2(6) | 1(6) |
| C19 | 27(6) | 55(8) | 37(7) | 3(7) | 2(6) | -1(6) |
| C20 | 22(6) | 54(8) | 45(7) | -4(7) | 6(6) | 1(6) |
| C21 | 42(7) | 49(8) | 46(7) | 1(7) | 8(6) | 7(7) |
| C22 | 38(7) | 59(8) | 43(7) | -1(7) | -4(6) | 0(7) |
| C23 | 28(6) | 44(8) | 47(7) | 5(7) | -3(6) | 3(6) |
| C24 | 32(7) | 44(8) | 32(7) | 1(6) | 4(6) | 3(6) |
| C25 | 21(6) | 69(9) | 64(8) | 5(8) | $0(6)$ | 7(6) |
| C26 | 29(6) | 67(9) | 59(8) | 9(7) | 17(6) | 10(7) |
| C27 | 25(6) | 74(9) | 57(8) | -9(7) | 3(6) | -4(7) |
| C28 | 30(7) | 81(10) | 66(9) | $-1(8)$ | -5(6) | -8(7) |
| C29 | 20(6) | $70(9)$ | 59(8) | -11(7) | 0 (6) | 3(6) |
| C30 | $33(7)$ | 69(9) | 58(8) | 0(7) | -2(6) | 2(7) |


| C31 | 28(7) | 90(10) | 61(8) | 2(8) | 2(6) | 1(7) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C32 | 34(8) | 105(14) | 75(11) | -10(11) | 14(8) | -6(9) |
| C33 | 32(7) | 58(8) | 54(8) | -6(7) | 1(6) | -7(7) |
| C34 | 25(6) | 68(9) | 62(8) | -18(7) | -4(6) | 11(7) |
| C35 | 32(7) | 67(9) | 58(8) | -17(7) | -2(6) | -4(7) |
| C36 | 40(7) | 70(9) | 71(9) | -1(8) | 7(7) | 0 (7) |
| C37 | 35(7) | 68(9) | 72(9) | -4(8) | 6(7) | -4(7) |
| C38 | 37(7) | 79(10) | 75(9) | -5(8) | -2(7) | 5(7) |
| C39 | 38(7) | 86(10) | 74(9) | 5(8) | 0(7) | -3(7) |
| C40 | 47(9) | 99(14) | 88(12) | 3(12) | 15(9) | -6(10) |
| C41 | 31(7) | 51(8) | 45(7) | -16(7) | 1(6) | 2(6) |
| C42 | 30(7) | 54(8) | 39(7) | -4(7) | 7(6) | -2(6) |
| C43 | 18(6) | 52(8) | 43(7) | 4(7) | -7(5) | -3(6) |
| C44 | 32(7) | 65(9) | 53(8) | -3(7) | 5(6) | 1(7) |
| C45 | 24(6) | 46(8) | 35(6) | 7(6) | 2(5) | -5(6) |
| C46 | 20(6) | 44(8) | 39(7) | -5(6) | 0(5) | 1(6) |
| C47 | 28(6) | 47(8) | 45(7) | 1(7) | 2(6) | -4(6) |
| C48 | 32(6) | 55(8) | 39(7) | 1(7) | -1(6) | -5(6) |
| C49 | 30(7) | 63(9) | 46(7) | 2(7) | 7(6) | 3(7) |
| C50 | 32(7) | 48(8) | 28(6) | 2(6) | 6(5) | 4(6) |
| C 51 | 28(7) | 62(9) | 51(8) | -4(7) | 6(6) | 3(7) |
| C52 | 23(6) | 48(8) | 46(7) | 8(7) | 2(6) | 3(6) |
| C53 | 17(6) | 56(8) | 39(7) | -1(6) | 6(5) | 2(6) |
| C54 | 29(7) | 49(8) | 49(7) | 1(7) | 0 (6) | 6 (6) |
| C55 | 18(6) | 53(8) | 33(6) | 6(6) | 5(5) | -4(6) |
| C56 | 27(6) | 49(8) | 44(7) | 0(7) | 10(6) | $0(6)$ |
| C 57 | 28(6) | 64(9) | 39(7) | 5(7) | 8(6) | 1(6) |
| C58 | 24(6) | 47(8) | 36(7) | 6(6) | 2(6) | -3(6) |
| C59 | 26(6) | 53(8) | 28(6) | 6(6) | 1(5) | -1(6) |
| C60 | 26(6) | 58(9) | 43(7) | 7(7) | 7(6) | 1(6) |
| C61 | 30(7) | 50(8) | 43(7) | -6(7) | 6(6) | 4(6) |
| C62 | 33(7) | 72(9) | 38(7) | 0(7) | -1(6) | 14(7) |
| C63 | 32(7) | 52(8) | 62(8) | 1(7) | 5(6) | 3(7) |
| C64 | 20(6) | 53(8) | 49(7) | 0 (7) | 8(6) | -5(6) |
| C65 | 25(6) | 74(9) | 48(7) | -3(7) | 7(6) | 8(7) |
| C66 | 32(7) | 65(9) | 53(8) | 5(7) | 12(6) | 6 (7) |


| C67 | $30(7)$ | $76(9)$ | $68(8)$ | $1(8)$ | $5(6)$ | $13(7)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| C68 | $41(7)$ | $71(9)$ | $68(8)$ | $-7(8)$ | $7(7)$ | $6(7)$ |
| C69 | $45(8)$ | $77(10)$ | $71(9)$ | $-20(8)$ | $22(7)$ | $3(7)$ |
| C70 | $42(7)$ | $80(10)$ | $70(9)$ | $-11(8)$ | $10(7)$ | $0(7)$ |
| C71 | $45(8)$ | $79(10)$ | $75(9)$ | $-4(8)$ | $11(7)$ | $3(7)$ |
| C72 | $49(10)$ | $94(14)$ | $94(13)$ | $-16(11)$ | $24(9)$ | $-15(10)$ |
| C73 | $38(7)$ | $67(9)$ | $45(7)$ | $-8(7)$ | $-6(6)$ | $-10(7)$ |
| C74 | $27(6)$ | $67(9)$ | $64(8)$ | $4(7)$ | $0(6)$ | $-5(7)$ |
| C75 | $32(7)$ | $76(9)$ | $61(8)$ | $2(8)$ | $8(6)$ | $-2(7)$ |
| C76 | $31(7)$ | $66(9)$ | $65(8)$ | $0(7)$ | $8(6)$ | $-3(7)$ |
| C77 | $32(7)$ | $70(9)$ | $56(8)$ | $9(7)$ | $12(6)$ | $-13(7)$ |
| C78 | $33(7)$ | $82(10)$ | $63(8)$ | $7(8)$ | $13(6)$ | $-1(7)$ |
| C79 | $51(8)$ | $75(10)$ | $68(9)$ | $-4(8)$ | $8(7)$ | $-5(8)$ |
| C80 | $48(9)$ | $99(14)$ | $84(12)$ | $8(11)$ | $23(9)$ | $-2(10)$ |
| N1 | $21(5)$ | $67(8)$ | $48(6)$ | $-11(6)$ | $3(5)$ | $-2(5)$ |
| N2 | $19(5)$ | $70(8)$ | $44(6)$ | $5(6)$ | $9(5)$ | $-5(6)$ |
| O1 | $31(5)$ | $82(9)$ | $60(7)$ | $-6(7)$ | $3(5)$ | $-9(6)$ |
| O2 | $34(6)$ | $92(10)$ | $57(7)$ | $-3(7)$ | $4(5)$ | $-6(6)$ |
| O3 | $24(5)$ | $74(7)$ | $42(5)$ | $-6(5)$ | $4(4)$ | $10(5)$ |
| O4 | $28(5)$ | $78(8)$ | $49(6)$ | $-6(6)$ | $8(5)$ | $-7(6)$ |
| O5 | $28(5)$ | $87(9)$ | $66(7)$ | $-8(7)$ | $8(5)$ | $1(6)$ |
| O6 | $22(4)$ | $65(6)$ | $41(5)$ | $-6(5)$ | $2(4)$ | $-3(5)$ |

Table 8Y.5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathbf{8 Y}$.

|  | X | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H3 | 5911 | 5454 | 6108 | 61 |
| H4 | 5513 | 5323 | 6400 | 51 |
| H7 | 5113 | 2576 | 3961 | 53 |
| H8 | 5222 | 1824 | 2611 | 59 |
| H9 | 5615 | 2085 | 2294 | 56 |
| H16 | 4600 | 2307 | 4580 | 50 |
| H17 | 4198 | 1963 | 4695 | 45 |
| H20 | 4108 | 3877 | 7546 | 48 |
| H21 | 4351 | 5251 | 8616 | 54 |
| H22 | 4757 | 5557 | 8472 | 57 |
| H23 | 4910 | 5033 | 7176 | 48 |
| H25A | 6421 | 3598 | 3106 | 62 |
| H25B | 6505 | 4556 | 4015 | 62 |
| H26A | 6249 | 6464 | 2559 | 61 |
| H26B | 6346 | 7406 | 3457 | 61 |
| H27A | 6627 | 8084 | 2511 | 62 |
| H27B | 6749 | 6594 | 3153 | 62 |
| H28A | 6532 | 5811 | 1461 | 71 |
| H28B | 6670 | 4381 | 2100 | 71 |
| H29A | 7030 | 6011 | 2027 | 60 |
| H29B | 6892 | 7433 | 1386 | 60 |
| H30A | 6961 | 3719 | 944 | 65 |
| H30B | 6822 | 5136 | 304 | 65 |
| H31A | 7318 | 5415 | 883 | 72 |
| H31B | 7177 | 6776 | 217 | 72 |
| H32A | 7251 | 3068 | -177 | 106 |
| H32B | 7405 | 4682 | -512 | 106 |
| H32C | 7129 | 4516 | -846 | 106 |
| H33A | 3852 | 858 | 5169 | 58 |
| H33B | 3810 | 2943 | 4914 | 58 |


| H34A | 3582 | 1267 | 6301 | 63 |
| :---: | :---: | :---: | :---: | :---: |
| H34B | 3523 | 3238 | 5922 | 63 |
| H35A | 3418 | -19 | 5002 | 63 |
| H35B | 3367 | 1936 | 4593 | 63 |
| H36A | 3013 | 893 | 4982 | 72 |
| H36B | 3095 | 2470 | 5648 | 72 |
| H37A | 3136 | -1316 | 6037 | 70 |
| H37B | 3242 | 205 | 6697 | 70 |
| H38A | 2848 | 1277 | 6832 | 77 |
| H38B | 2742 | -248 | 6172 | 77 |
| H39A | 3003 | -1039 | 7799 | 80 |
| H39B | 2875 | -2498 | 7152 | 80 |
| H40A | 2634 | 70 | 8106 | 116 |
| H40B | 2644 | -2052 | 8284 | 116 |
| H40C | 2501 | -1288 | 7417 | 116 |
| H43 | 4141 | 6791 | 4784 | 46 |
| H44 | 4534 | 7291 | 4479 | 60 |
| H47 | 4894 | 9934 | 7027 | 48 |
| H48 | 4762 | 10652 | 8384 | 51 |
| H49 | 4362 | 10235 | 8615 | 55 |
| H56 | 5418 | 10278 | 6381 | 47 |
| H57 | 5828 | 10501 | 6327 | 52 |
| H60 | 5946 | 8516 | 3545 | 50 |
| H61 | 5704 | 7212 | 2403 | 49 |
| H62 | 5296 | 6937 | 2495 | 58 |
| H63 | 5135 | 7508 | 3785 | 58 |
| H65A | 3518 | 7219 | 6685 | 59 |
| H65B | 3562 | 8262 | 7591 | 59 |
| H66A | 3685 | 4562 | 7350 | 60 |
| H66B | 3731 | 5605 | 8257 | 60 |
| H67A | 3273 | 4901 | 7372 | 69 |
| H67B | 3314 | 6050 | 8250 | 69 |
| H68A | 3480 | 3497 | 8998 | 72 |
| H68B | 3445 | 2345 | 8121 | 72 |
| H69A | 3013 | 2924 | 8101 | 76 |
| H69B | 3120 | 1561 | 8840 | 76 |


| H70A | 3146 | 4041 | 9870 | 77 |
| :---: | :---: | :---: | :---: | :---: |
| H70B | 3018 | 5310 | 9127 | 77 |
| H71A | 2797 | 2166 | 9792 | 79 |
| H71B | 2669 | 3454 | 9058 | 79 |
| H72A | 2813 | 4727 | 10791 | 117 |
| H72B | 2547 | 4081 | 10491 | 117 |
| H72C | 2653 | 5827 | 10061 | 117 |
| H73A | 6194 | 9232 | 6260 | 61 |
| H73B | 6224 | 11263 | 5934 | 61 |
| H74A | 6486 | 8256 | 5400 | 63 |
| H74B | 6592 | 9758 | 6070 | 63 |
| H75A | 6562 | 11923 | 4978 | 67 |
| H75B | 6436 | 10511 | 4304 | 67 |
| H76A | 6923 | 10320 | 5018 | 65 |
| H76B | 6799 | 8799 | 4399 | 65 |
| H77A | 6887 | 12415 | 3887 | 63 |
| H77B | 6736 | 11025 | 3266 | 63 |
| H78A | 7233 | 10640 | 3830 | 70 |
| H78B | 7084 | 9177 | 3243 | 70 |
| H79A | 7167 | 12772 | 2734 | 78 |
| H79B | 7004 | 11381 | 2153 | 78 |
| H80A | 7505 | 10987 | 2579 | 114 |
| H80B | 7380 | 11539 | 1643 | 114 |
| H80C | 7344 | 9559 | 2015 | 114 |

End of Crystallographic material for $\mathbf{8 Y}$.

## Crystallographic Material for 1bo

## Crystallographic Material for 1BO.

X-ray Experimental.
Table 1BO.1. Crystallographic Data for 1BO.
Table 1BO.2. Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the non-hydrogen atoms of $\mathbf{1 B O}$.

Table 1BO.3. Bond Lengths $\left(\AA^{\circ}\right)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of 1BO.

Table 1BO.4. Anisotropic thermal parameters for the non-hydrogen atoms of 1BO.

Table 1BO.5. Fractional coordinates and isotropic thermal parameters $\left(\AA^{2}\right)$ for the hydrogen atoms of $\mathbf{1}$.

Table 1BO.6. Torsion Angles $\left(^{(0)}\right.$ for the non-hydrogen atoms of 1BO.

X-ray Experimental for complex $\mathrm{C}_{26} \mathrm{H}_{17} \mathrm{NO}_{3}(\mathbf{1 B O})$ Crystals grew as long, very thin orange needles by slow evaporation from $\mathrm{CHCl}_{3}$. The data crystal was cut from a larger crystal and had approximate dimensions; $0.45 \times 0.030 \times 0.018 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{Cu} \mathrm{K} \alpha$ radiation source ( $\lambda$ $=1.5418 \AA$ ) with collimating mirror monochromators. A total of 375 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 32 seconds per frame with a detector offset of $+/-41.6^{\circ}$ and 90.5 seconds per frame with a detector offset of $110.7^{\circ}$. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.40.37a. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the nonH atoms using SHELXL-2016/6. ${ }^{3}$ Structure analysis was aided by use of the programs

PLATON ${ }^{4}$ and WinGX. ${ }^{5}$ The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms).

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.099 * \mathrm{P})^{2}\right]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3$. $\mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.354 , with $\mathrm{R}(\mathrm{F})$ equal to 0.117 and a goodness of fit, $S,=1.10$. Definitions used for calculating $R(F), R_{w}\left(F^{2}\right)$ and the goodness of fit, $S$, are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. ${ }^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro V 1.171.40.37a (2019). Rigaku Oxford Diffraction, Tokyo, Japan.
2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
4) Spek, A. L. (2009). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands. Acta Cryst. D65, 148-155.
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\sum \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\mid \mathrm{F}_{\mathrm{O}}\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\mid \mathrm{F}_{\mathrm{C}}\right) / \Sigma\left|\mathrm{F}_{\mathrm{o}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 1BO.1. Crystal data and structure refinement for 1BO.

Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume
Z
Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=67.684^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices $[\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})]$
R indices (all data)
Absolute structure parameter
Extinction coefficient
Largest diff. peak and hole

C26 H17 N O3
391.40

100(2) K
$1.54184 \AA$
orthorhombic
Pna 21
$\mathrm{a}=17.809(4) \AA \quad \alpha=90^{\circ}$.
$\mathrm{b}=26.103(6) \AA \quad \beta=90^{\circ}$.
$\mathrm{c}=3.8515(15) \AA \quad \gamma=90^{\circ}$.
1790.4(9) $\AA^{3}$

4
$1.452 \mathrm{Mg} / \mathrm{m}^{3}$
$0.767 \mathrm{~mm}^{-1}$
816
$0.450 \times 0.030 \times 0.018 \mathrm{~mm}^{3}$
3.004 to $75.312^{\circ}$.
$-11<=\mathrm{h}<=21,-19<=\mathrm{k}<=32,-3<=\mathrm{l}<=4$
3667
$2417[\mathrm{R}(\mathrm{int})=0.1310]$
98.9 \%

Gaussian and multi-scan
1.00 and 0.433

Full-matrix least-squares on $\mathrm{F}^{2}$
2417 / 181/273
1.096
$R 1=0.1172, w R 2=0.2640$
$R 1=0.2026, w R 2=0.3540$
-1.6(10)
n/a
0.474 and -0.437 e. $\AA^{-3}$

Table 1BO.2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathbf{1 B O} . U(e q)$ is defined as one third of the trace of the orthogonalized $U^{i j}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| C1 | 1428(6) | 5130(4) | 2280(40) | 30(3) |
| C2 | 2128(6) | 5416(4) | 3140(40) | 28(3) |
| C3 | 2194(6) | 5912(5) | 2200(40) | 33(3) |
| C4 | 2853(6) | 6194(4) | 2980(50) | 34(3) |
| C5 | 3449(6) | 5973(4) | 4680(40) | 29(3) |
| C6 | 3380(6) | 5445(4) | 5690(50) | 31(3) |
| C7 | 3974(7) | 5189(5) | 7490(50) | 41(4) |
| C8 | 3892(7) | 4687(5) | 8470(50) | 40(3) |
| C9 | 3221(5) | 4415(5) | 7690(40) | 32(3) |
| C10 | 2649(6) | 4659(4) | 6020(40) | 28(3) |
| C11 | 1959(6) | 4369(4) | 5160(40) | 30(3) |
| C12 | 2710(5) | 5169(4) | 4930(40) | 27(3) |
| C13 | 4113(6) | 6261(5) | 5440(50) | 35(3) |
| C14 | 4662(6) | 6507(4) | 5990(50) | 31(3) |
| C15 | 5330(6) | 6807(4) | 6600(40) | 28(3) |
| C16 | 5948(6) | 6573(5) | 8110(40) | 34(3) |
| C17 | 6633(6) | 6843(4) | 8550(40) | 31(3) |
| C18 | 6675(6) | 7338(5) | 7580(50) | 30(3) |
| C19 | 6036(6) | 7606(4) | 6130(40) | 29(3) |
| C20 | 6064(6) | 8121(5) | 5270(50) | 36(3) |
| C21 | 5457(6) | 8361(4) | 3820(50) | 34(3) |
| C22 | 4792(7) | 8086(5) | 3280(50) | 39(3) |
| C23 | 4755(6) | 7580(4) | 4120(40) | 31(3) |
| C24 | 5366(6) | 7317(4) | 5630(40) | 29(3) |
| C25 | 716(6) | 4337(5) | 2430(50) | 36(3) |
| C26 | 7964(6) | 7386(5) | 9270(50) | 43(4) |
| N1 | 1396(5) | 4626(4) | 3390(40) | 33(3) |
| O1 | 916(4) | 5326(3) | 670(40) | 45(3) |
| O2 | 1872(4) | 3923(3) | 6040(40) | 38(3) |
| O3 | 7306(4) | 7632(3) | 7910(30) | 35(2) |

Table 1BO.3. Bond lengths $[\AA]$ and angles [ ${ }^{\circ}$ ] for 1BO.

| C1-O1 | 1.216(17) | C15-C16 | 1.387(17) |
| :---: | :---: | :---: | :---: |
| C1-N1 | $1.385(15)$ | C16-C17 | 1.420 (14) |
| C1-C2 | 1.491(15) | C16-H16 | 0.95 |
| C2-C3 | 1.349(16) | C17-C18 | 1.347(17) |
| C2-C12 | $1.402(18)$ | C17-H17 | 0.95 |
| C3-C4 | $1.418(16)$ | C18-O3 | 1.368(12) |
| C3-H3 | 0.95 | C18-C19 | $1.446(17)$ |
| C4-C5 | 1.374(19) | C19-C20 | 1.387(17) |
| C4-H4 | 0.95 | C19-C24 | $1.425(14)$ |
| C5-C13 | 1.432(16) | C20-C21 | 1.367(17) |
| C5-C6 | 1.437(16) | C20-H20 | 0.95 |
| C6-C12 | 1.424(15) | C21-C22 | 1.402(15) |
| C6-C7 | 1.429(19) | C21-H21 | 0.95 |
| C7-C8 | 1.373(18) | C22-C23 | 1.362(17) |
| C7-H7 | 0.95 | C22-H22 | 0.95 |
| C8-C9 | 1.423(16) | C23-C24 | 1.413(17) |
| C8-H8 | 0.95 | C23-H23 | 0.95 |
| C9-C10 | 1.362(18) | C25-N1 | 1.473(15) |
| C9-H9 | 0.95 | C25-H25A | 0.98 |
| C10-C12 | 1.400(16) | C25-H25B | 0.98 |
| C10-C11 | 1.481(15) | C25-H25C | 0.98 |
| C11-O2 | $1.222(14)$ | C26-O3 | 1.434(16) |
| C11-N1 | $1.385(17)$ | C26-H26A | 0.98 |
| C13-C14 | 1.189(16) | C26-H26B | 0.98 |
| C14-C15 | $1.444(15)$ | C26-H26C | 0.98 |
| C15-C24 | 1.383(16) |  |  |
| O1-C1-N1 | 121.9(11) | C2-C3-H3 | 119.5 |
| O1-C1-C2 | 121.9(12) | C4-C3-H3 | 119.5 |
| N1-C1-C2 | 116.2(12) | C5-C4-C3 | 121.5(12) |
| C3-C2-C12 | 120.6(11) | C5-C4-H4 | 119.3 |
| C3-C2-C1 | 119.6(12) | C3-C4-H4 | 119.3 |
| C12-C2-C1 | 119.8(11) | C4-C5-C13 | 121.0(12) |
| C2-C3-C4 | 120.9(13) | C4-C5-C6 | 117.8(10) |


| C13-C5-C6 | 121.2(12) | O3-C18-C19 | 114.3(11) |
| :---: | :---: | :---: | :---: |
| C12-C6-C7 | 118.9(11) | C20-C19-C24 | 120.7(11) |
| C12-C6-C5 | 120.0(12) | C20-C19-C18 | 122.2(10) |
| C7-C6-C5 | 121.0(11) | C24-C19-C18 | 117.1(11) |
| C8-C7-C6 | 120.0(12) | C21-C20-C19 | 121.0(11) |
| C8-C7-H7 | 120.0 | C21-C20-H20 | 119.5 |
| C6-C7-H7 | 120.0 | C19-C20-H20 | 119.5 |
| C7-C8-C9 | 120.5(14) | C20-C21-C22 | 119.6(12) |
| C7-C8-H8 | 119.7 | C20-C21-H21 | 120.2 |
| C9-C8-H8 | 119.7 | C22-C21-H21 | 120.2 |
| C10-C9-C8 | 119.6(12) | C23-C22-C21 | 120.1(12) |
| C10-C9-H9 | 120.2 | C23-C22-H22 | 119.9 |
| C8-C9-H9 | 120.2 | C21-C22-H22 | 119.9 |
| C9-C10-C12 | 121.9(11) | C22-C23-C24 | 122.2(11) |
| C9-C10-C11 | 119.1(11) | C22-C23-H23 | 118.9 |
| C12-C10-C11 | 118.8(12) | C24-C23-H23 | 118.9 |
| O2-C11-N1 | 120.3(11) | C15-C24-C23 | 122.9(11) |
| O2-C11-C10 | 122.0(13) | C15-C24-C19 | 120.8(11) |
| N1-C11-C10 | 117.7(10) | C23-C24-C19 | 116.4(11) |
| C10-C12-C2 | 121.9(10) | N1-C25-H25A | 109.5 |
| C10-C12-C6 | 118.9(12) | N1-C25-H25B | 109.5 |
| C2-C12-C6 | 119.2(11) | H25A-C25-H25B | 109.5 |
| C14-C13-C5 | 178.2(19) | N1-C25-H25C | 109.5 |
| C13-C14-C15 | 179.0(19) | H25A-C25-H25C | 109.5 |
| C24-C15-C16 | 120.0(10) | H25B-C25-H25C | 109.5 |
| C24-C15-C14 | 121.1(11) | O3-C26-H26A | 109.5 |
| C16-C15-C14 | 118.8(11) | O3-C26-H26B | 109.5 |
| C15-C16-C17 | 120.8(11) | H26A-C26-H26B | 109.5 |
| C15-C16-H16 | 119.6 | O3-C26-H26C | 109.5 |
| C17-C16-H16 | 119.6 | H26A-C26-H26C | 109.5 |
| C18-C17-C16 | 119.4(12) | H26B-C26-H26C | 109.5 |
| C18-C17-H17 | 120.3 | C1-N1-C11 | 125.6(10) |
| C16-C17-H17 | 120.3 | C1-N1-C25 | 116.2(11) |
| C17-C18-O3 | 123.9(12) | C11-N1-C25 | 118.1(10) |
| C17-C18-C19 | 121.8(10) | C18-O3-C26 | 117.0(11) |

Table 1BO.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 1BO. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | $14(5)$ | 31(5) | 45(8) | -1(6) | 10(5) | -6(4) |
| C2 | $15(5)$ | 30(5) | 38(7) | -3(5) | 8(5) | -6(4) |
| C3 | $21(5)$ | 34(5) | 45(7) | -4(6) | 3(6) | -2(5) |
| C4 | $25(5)$ | 27(5) | 50(8) | -9(6) | 4(6) | 4(4) |
| C5 | $14(5)$ | 30(5) | 45(7) | -4(5) | 7(5) | -6(4) |
| C6 | 18(5) | 30(5) | 45(7) | -8(6) | 1(6) | 0 (4) |
| C7 | $22(5)$ | 48(6) | 52(8) | -2(7) | 6(6) | -3(5) |
| C8 | $34(6)$ | 35(5) | 49(8) | -3(6) | 11(6) | 6(5) |
| C9 | 12(5) | 37(5) | 46(7) | 9(6) | 13(6) | 2(4) |
| $\mathrm{C} 10$ | $13(5)$ | 28(5) | 43(7) | 0(5) | 19(5) | -2(4) |
| C11 | 18(5) | 28(5) | 45(8) | -2(5) | 16(5) | -3(4) |
| C12 | 8(4) | 28(5) | 44(7) | 0(5) | 9(5) | -1(4) |
| C13 | 16(5) | 47(6) | 42(7) | -3(6) | 6(6) | -1(5) |
| C14 | 23(5) | 32(5) | 39(7) | 2(5) | 3(6) | -1(4) |
| C15 | 12(5) | 28(5) | 45(7) | -1(5) | 1(5) | -3(4) |
| C16 | 23(5) | 32(5) | 46(7) | -7(6) | 5(6) | -5(5) |
| C17 | 16(5) | 29(5) | 48(7) | -3(6) | $0(6)$ | -4(4) |
| C18 | 7(4) | 37(5) | 47(7) | -5(6) | 7(5) | -6(4) |
| C19 | 15(5) | 31(5) | 42(7) | 0(5) | 2(5) | -3(4) |
| C20 | 18(5) | 35(5) | 54(8) | 2(6) | -2(6) | 1(4) |
| C21 | 23(5) | 27(5) | 51(8) | -4(5) | 2(6) | -4(4) |
| C22 | 22(5) | 46(6) | 49(8) | 2(6) | $0(6)$ | 2(5) |
| C23 | 16(5) | 38(6) | 40(7) | 6(6) | 0(5) | -6(4) |
| C24 | 15(5) | 31(5) | 40(7) | -6(6) | -3(5) | -2(4) |
| C25 | 15(5) | 44(7) | 50(9) | 13(6) | 19(6) | -2(5) |
| C26 | 20(6) | 62(8) | 47(9) | -19(8) | 6(7) | -5(6) |
| N1 | 17(4) | 31(4) | 50(7) | 4(5) | 1(5) | -4(4) |
| O1 | 17(4) | 42(5) | 76(8) | 4(6) | -3(5) | -2(4) |
| O2 | 19(4) | 33(4) | 63(7) | 7(5) | 5(5) | -4(3) |
| O3 | 8(3) | 39(4) | 58(6) | -5(5) | 0(4) | -1(3) |

Table 1BO.5. Hydrogen coordinates ( $\mathrm{x} 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 1BO.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H3 | 1793 | 6074 | 1002 | 40 |
| H4 | 2884 | 6543 | 2308 | 41 |
| H7 | 4426 | 5367 | 7998 | 49 |
| H8 | 4286 | 4520 | 9688 | 47 |
| H9 | 3172 | 4065 | 8319 | 38 |
| H16 | 5912 | 6227 | 8862 | 40 |
| H17 | 7059 | 6676 | 9508 | 37 |
| H20 | 6511 | 8310 | 5679 | 43 |
| H21 | 5487 | 8712 | 3191 | 40 |
| H22 | 4365 | 8253 | 2327 | 47 |
| H23 | 4304 | 7397 | 3666 | 38 |
| H25A | 461 | 4219 | 4540 | 55 |
| H25B | 857 | 4040 | 1011 | 55 |
| H25C | 378 | 4559 | 1104 | 55 |
| H26A | 7887 | 7306 | 11725 | 64 |
| H26B | 8396 | 7616 | 9024 | 64 |
| H26C | 8059 | 7070 | 7973 | 64 |

Table 1BO.6. Torsion angles [ ${ }^{\circ}$ ] for 1BO.

| O1-C1-C2-C3 | 2(2) | C5-C6-C12-C2 | 1(2) |
| :---: | :---: | :---: | :---: |
| N1-C1-C2-C3 | -178.7(15) | C24-C15-C16-C17 | -3(2) |
| O1-C1-C2-C12 | -178.5(14) | C14-C15-C16-C17 | 175.8(15) |
| N1-C1-C2-C12 | 1(2) | C15-C16-C17-C18 | 2(2) |
| C12-C2-C3-C4 | 0 (2) | C16-C17-C18-O3 | 179.6(15) |
| C1-C2-C3-C4 | 180.0(15) | C16-C17-C18-C19 | 0 (2) |
| C2-C3-C4-C5 | 1(2) | C17-C18-C19-C20 | 177.3(18) |
| C3-C4-C5-C13 | 179.8(16) | O3-C18-C19-C20 | -2(2) |
| C3-C4-C5-C6 | -1(2) | C17-C18-C19-C24 | -2(2) |
| C4-C5-C6-C12 | 0 (2) | O3-C18-C19-C24 | 178.3(14) |
| C13-C5-C6-C12 | 179.5(15) | C24-C19-C20-C21 | -2(3) |
| C4-C5-C6-C7 | -179.7(16) | C18-C19-C20-C21 | 178.4(16) |
| C13-C5-C6-C7 | 0 (2) | C19-C20-C21-C22 | 1(3) |
| C12-C6-C7-C8 | -1(2) | C20-C21-C22-C23 | -1(3) |
| C5-C6-C7-C8 | 179.1(17) | C21-C22-C23-C24 | 2(3) |
| C6-C7-C8-C9 | 1(3) | C16-C15-C24-C23 | -179.3(15) |
| C7-C8-C9-C10 | -2(2) | C14-C15-C24-C23 | 2(2) |
| C8-C9-C10-C12 | 3(2) | C16-C15-C24-C19 | 1(2) |
| C8-C9-C10-C11 | 178.7(15) | C14-C15-C24-C19 | -177.9(15) |
| C9-C10-C11-O2 | 4(2) | C22-C23-C24-C15 | 177.8(18) |
| C12-C10-C11-O2 | 179.9(15) | C22-C23-C24-C19 | -2(2) |
| C9-C10-C11-N1 | -178.5(15) | C20-C19-C24-C15 | -177.9(16) |
| C12-C10-C11-N1 | -2.2(19) | C18-C19-C24-C15 | 2(2) |
| C9-C10-C12-C2 | 178.3(15) | C20-C19-C24-C23 | 2(2) |
| C11-C10-C12-C2 | 2(2) | C18-C19-C24-C23 | -178.1(14) |
| C9-C10-C12-C6 | -3(2) | O1-C1-N1-C11 | 178.2(15) |
| C11-C10-C12-C6 | -178.7(14) | C2-C1-N1-C11 | -1(2) |
| C3-C2-C12-C10 | 178.0(16) | O1-C1-N1-C25 | 2(2) |
| C1-C2-C12-C10 | -2(2) | C2-C1-N1-C25 | -177.7(13) |
| C3-C2-C12-C6 | -1(2) | O2-C11-N1-C1 | 179.6(16) |
| C1-C2-C12-C6 | 179.4(16) | C10-C11-N1-C1 | 2(2) |
| C7-C6-C12-C10 | 1(2) | O2-C11-N1-C25 | -4(2) |
| C5-C6-C12-C10 | -178.3(15) | C10-C11-N1-C25 | 178.4(14) |
| C7-C6-C12-C2 | -179.3(15) | C17-C18-O3-C26 | 2(2) |

End of 1BO crystallographic info

## Crystallographic Material for 60

## Crystallographic Material for 60.

X-ray Experimental.
Table 60.1. Crystallographic Data for 60.
Table 60.2. Fractional coordinates and equivalent isotropic thermal parameters ( $\AA^{2}$ ) for the non-hydrogen atoms of $\mathbf{6 0}$.

Table 60.3. Bond Lengths $(\AA)$ and Angles $\left({ }^{( }\right)$for the non-hydrogen atoms of $\mathbf{6 0}$

Table 60.4. Anisotropic thermal parameters for the non-hydrogen atoms of $\mathbf{6 0 .}$

Table 60.5. Fractional coordinates and isotropic thermal parameters ( $\AA^{2}$ ) for the hydrogen atoms of $6 \mathbf{0}$.

Table 60.6. Torsion Angles $\left(^{( }\right)$for the non-hydrogen atoms of $\mathbf{6 0}$.

X-ray Experimental for $\mathrm{C}_{36} \mathrm{H}_{37} \mathrm{NO}_{3}$ : (6O) Crystals grew as very, long orange laths by vapor:vapor diffusion from ( $30 \%$ Toluene, $70 \%$ Xylenes) in a jar of MeCN. The data crystal was cut from a larger crystal and had approximate dimensions; $0.41 \times 0.037 \times 0.020 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{Cu} \mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA$ ) with collimating mirror monochromators. A total of 762 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 15 seconds per frame for frames collected with a detector offset of $+/-41.6^{\circ}$ and 60 seconds per frame with frames collected with a detector offset of $+/-112.0^{\circ}$. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.39.46. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-
squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL$2016 / 6 .{ }^{3}$ Structure analysis was aided by use of the programs PLATON ${ }^{4}$ and WinGX. ${ }^{5}$ The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms). The absolute structure could not be reliably determined using either the method of Flack ${ }^{6}$ or the Hooft y-parameter method. ${ }^{7}$

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.0395 * \mathrm{P})^{2}\right]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}} \mathrm{I}^{2}+2\right| \mathrm{F}_{\mathrm{c}} \mathrm{l}^{2}\right) / 3 . \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.120 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0509 and a goodness of fit, $\mathrm{S},=1.00$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S , are given below. ${ }^{8}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{9}$ All figures were generated using SHELXTL/PC. ${ }^{10}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

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8) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \sum \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\left|\mathrm{F}_{\mathrm{C}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\mathrm{LW}_{\mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(\mathrm{n}-\mathrm{p})}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
9) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
10) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 60.1. Crystal data and structure refinement for 60.

Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume

Z

Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=67.684^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Absolute structure parameter
Extinction coefficient
Largest diff. peak and hole
shelx
C36 H37 N O3
531.66

100(2) K
$1.54184 \AA$
monoclinic
C c
$a=4.6867(4) \AA \quad \alpha=90^{\circ}$.
$b=38.869(4) \AA \quad \beta=96.175(10)^{\circ}$.
$\mathrm{c}=15.557(2) \AA \quad \gamma=90^{\circ}$.
2817.5(5) $\AA^{3}$

4
$1.253 \mathrm{Mg} / \mathrm{m}^{3}$
$0.617 \mathrm{~mm}^{-1}$
1136
$0.410 \times 0.037 \times 0.020 \mathrm{~mm}^{3}$
2.273 to $68.306^{\circ}$.
$-5<=\mathrm{h}<=3,-42<=\mathrm{k}<=46,-17<=1<=18$
5693
$2975[\mathrm{R}(\mathrm{int})=0.0535]$
97.0 \%

Semi-empirical from equivalents
1.00 and 0.750

Full-matrix least-squares on $\mathrm{F}^{2}$
2975 / 2 / 363
1.003
$R 1=0.0509, w R 2=0.1070$
$\mathrm{R} 1=0.0791, \mathrm{wR} 2=0.1196$
0.3(4)
n/a
0.232 and $-0.232 \mathrm{e} . \AA^{-3}$

Table 60.2. Atomic coordinates $\left(\times 10^{4}\right)$ and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $1 . U(e q)$ is defined as one third of the trace of the orthogonalized $U^{i j}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| C1 | -2524(8) | 5808(1) | 6029(3) | 17(1) |
| C2 | -544(8) | 5537(1) | 5784(3) | 14(1) |
| C3 | 1174(8) | 5366(1) | 6419(3) | 20(1) |
| C4 | 3082(8) | 5107(1) | 6196(3) | 20(1) |
| C5 | 3251(8) | 5022(1) | 5348(4) | 18(1) |
| C6 | 1471(8) | 5194(1) | 4669(3) | 18(1) |
| C7 | 1506(9) | 5112(1) | 3783(3) | 19(1) |
| C8 | -231(9) | 5282(1) | 3158(3) | 21(1) |
| C9 | -2106(9) | 5546(1) | 3384(3) | 21(1) |
| C10 | -2193(8) | 5627(1) | 4242(3) | 16(1) |
| C11 | -4172(8) | 5904(1) | 4467(3) | 18(1) |
| C12 | -432(8) | 5454(1) | 4897(3) | 16(1) |
| C13 | 5203(9) | 4766(1) | 5124(3) | 19(1) |
| C14 | 6872(9) | 4550(1) | 4927(3) | 18(1) |
| C15 | 8856(8) | 4296(1) | 4691(3) | 18(1) |
| C16 | 9180(8) | 4235(1) | 3835(3) | 20(1) |
| C17 | 11116(9) | 3984(1) | 3580(3) | 18(1) |
| C18 | 12672(8) | 3794(1) | 4208(3) | 18(1) |
| C19 | 12456(8) | 3849(1) | 5109(3) | 19(1) |
| C20 | 14161(8) | 3661(1) | 5761(3) | 20(1) |
| C21 | 13944(9) | 3725(1) | 6620(4) | 22(1) |
| C22 | 11981(9) | 3973(1) | 6861(3) | 22(1) |
| C23 | 10315(9) | 4159(1) | 6240(3) | 21(1) |
| C24 | 10529(8) | 4104(1) | 5354(3) | 16(1) |
| C25 | -6125(8) | 6253(1) | 5582(3) | 17(1) |
| C26 | -4513(9) | 6596(1) | 5600(3) | 21(1) |
| C27 | -6412(9) | 6904(1) | 5777(3) | 20(1) |
| C28 | $-4806(9)$ | 7244(1) | 5733(3) | 22(1) |
| C29 | -6605(10) | 7564(1) | 5888(4) | 24(1) |
| C30 | -4885(11) | 7893(2) | 5828(4) | 34(1) |
| C31 | 14873(9) | 3463(1) | 3152(3) | 24(1) |


| C32 | $16561(9)$ | $3129(1)$ | $3143(3)$ | $23(1)$ |
| :--- | :--- | :--- | :--- | :--- |
| C33 | $14825(10)$ | $2815(1)$ | $3354(4)$ | $25(1)$ |
| C34 | $16383(10)$ | $2473(2)$ | $3292(3)$ | $26(1)$ |
| C35 | $14502(11)$ | $2162(2)$ | $3435(4)$ | $31(1)$ |
| C36 | $16007(14)$ | $1817(2)$ | $3346(4)$ | $38(1)$ |
| N1 | $-4236(7)$ | $5969(1)$ | $5353(3)$ | $17(1)$ |
| O1 | $-2683(6)$ | $5893(1)$ | $6777(2)$ | $25(1)$ |
| O2 | $-5660(7)$ | $6066(1)$ | $3925(2)$ | $28(1)$ |
| O3 | $14491(6)$ | $3531(1)$ | $4039(2)$ | $22(1)$ |

Table 60.3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for $6 \mathbf{O}$.

| C1-O1 | 1.221(7) | C19-C20 | 1.425(7) |
| :---: | :---: | :---: | :---: |
| C1-N1 | 1.400(6) | C20-C21 | 1.374(8) |
| C1-C2 | 1.479(7) | C20-H20 | 0.95 |
| C2-C3 | 1.377(7) | C21-C22 | 1.411(7) |
| C2-C12 | 1.424(7) | C21-H21 | 0.95 |
| C3-C4 | 1.414(7) | C22-C23 | 1.381(8) |
| C3-H3 | 0.95 | C22-H22 | 0.95 |
| C4-C5 | 1.372(7) | C23-C24 | 1.409(7) |
| C4-H4 | 0.95 | C23-H23 | 0.95 |
| C5-C13 | 1.420(7) | C25-N1 | 1.482(6) |
| C5-C6 | 1.438(7) | C25-C26 | 1.532(7) |
| C6-C7 | 1.416(7) | C25-H25A | 0.99 |
| C6-C12 | 1.418(7) | C25-H25B | 0.99 |
| C7-C8 | 1.370(7) | C26-C27 | 1.532(7) |
| C7-H7 | 0.95 | C26-H26A | 0.99 |
| C8-C9 | 1.418(7) | C26-H26B | 0.99 |
| C8-H8 | 0.95 | C27-C28 | 1.526(7) |
| C9-C10 | $1.376(7)$ | C27-H27A | 0.99 |
| C9-H9 | 0.95 | C27-H27B | 0.99 |
| C10-C12 | 1.412(7) | C28-C29 | 1.536(7) |
| C10-C11 | $1.486(7)$ | C28-H28A | 0.99 |
| C11-O2 | 1.213(6) | C28-H28B | 0.99 |
| C11-N1 | 1.405(7) | C29-C30 | 1.521(8) |
| C13-C14 | 1.208(7) | C29-H29A | 0.99 |
| C14-C15 | 1.431(7) | C29-H29B | 0.99 |
| C15-C16 | 1.376(7) | C30-H30A | 0.98 |
| C15-C24 | 1.437(7) | C30-H30B | 0.98 |
| C16-C17 | 1.417(7) | C30-H30C | 0.98 |
| C16-H16 | 0.95 | C31-O3 | $1.435(6)$ |
| C17-C18 | 1.371(7) | C31-C32 | 1.521(7) |
| C17-H17 | 0.95 | C31-H31A | 0.99 |
| C18-O3 | $1.375(6)$ | C31-H31B | 0.99 |
| C18-C19 | 1.432(7) | C32-C33 | 1.524(8) |
| C19-C24 | 1.420(7) | C32-H32A | 0.99 |


| C32-H32B | 0.99 | C35-C36 | 1.528(8) |
| :---: | :---: | :---: | :---: |
| C33-C34 | 1.525(7) | C35-H35A | 0.99 |
| C33-H33A | 0.99 | C35-H35B | 0.99 |
| C33-H33B | 0.99 | C36-H36A | 0.98 |
| C34-C35 | $1.525(8)$ | C36-H36B | 0.98 |
| C34-H34A | 0.99 | C36-H36C | 0.98 |
| C34-H34B | 0.99 |  |  |
| O1-C1-N1 | 120.3(4) | C9-C10-C11 | 118.7(4) |
| O1-C1-C2 | 122.9(4) | C12-C10-C11 | 120.4(4) |
| N1-C1-C2 | 116.7(4) | O2-C11-N1 | 121.2(4) |
| C3-C2-C12 | 120.4(4) | O2-C11-C10 | 122.6(5) |
| C3-C2-C1 | 119.6(4) | N1-C11-C10 | 116.2(4) |
| C12-C2-C1 | 120.1(4) | C10-C12-C6 | 119.7(5) |
| C2-C3-C4 | 120.3(5) | C10-C12-C2 | 120.7(4) |
| C2-C3-H3 | 119.9 | C6-C12-C2 | 119.6(4) |
| C4-C3-H3 | 119.9 | C14-C13-C5 | 179.3(5) |
| C5-C4-C3 | 120.8(5) | C13-C14-C15 | 179.8(6) |
| C5-C4-H4 | 119.6 | C16-C15-C14 | 120.6(5) |
| C3-C4-H4 | 119.6 | C16-C15-C24 | 119.8(4) |
| C4-C5-C13 | 120.8(5) | C14-C15-C24 | 119.6(5) |
| C4-C5-C6 | 120.3(4) | C15-C16-C17 | 122.0(5) |
| C13-C5-C6 | 118.9(5) | C15-C16-H16 | 119.0 |
| C7-C6-C12 | 118.4(5) | C17-C16-H16 | 119.0 |
| C7-C6-C5 | 123.0(4) | C18-C17-C16 | 118.7(5) |
| C12-C6-C5 | 118.6(5) | C18-C17-H17 | 120.7 |
| C8-C7-C6 | 121.1(4) | C16-C17-H17 | 120.7 |
| C8-C7-H7 | 119.5 | C17-C18-O3 | 124.0(5) |
| C6-C7-H7 | 119.5 | C17-C18-C19 | 121.9(4) |
| C7-C8-C9 | 120.6(5) | O3-C18-C19 | 114.1(4) |
| C7-C8-H8 | 119.7 | C24-C19-C20 | 119.4(5) |
| C9-C8-H8 | 119.7 | C24-C19-C18 | 118.8(4) |
| C10-C9-C8 | 119.4(5) | C20-C19-C18 | 121.8(4) |
| C10-C9-H9 | 120.3 | C21-C20-C19 | 120.4(4) |
| C8-C9-H9 | 120.3 | C21-C20-H20 | 119.8 |
| C9-C10-C12 | 120.9(4) | C19-C20-H20 | 119.8 |


| C20-C21-C22 | $120.1(5)$ | C30-C29-C28 | $111.6(4)$ |
| :--- | :--- | :--- | :--- |
| C20-C21-H21 | 120.0 | C30-C29-H29A | 109.3 |
| C22-C21-H21 | 120.0 | C28-C29-H29A | 109.3 |
| C23-C22-C21 | $120.5(5)$ | C30-C29-H29B | 109.3 |
| C23-C22-H22 | 119.7 | C28-C29-H29B | 109.3 |
| C21-C22-H22 | 119.7 | H29A-C29-H29B | 108.0 |
| C22-C23-C24 | $120.8(5)$ | C29-C30-H30A | 109.5 |
| C22-C23-H23 | 119.6 | C29-C30-H30B | 109.5 |
| C24-C23-H23 | 119.6 | H30A-C30-H30B | 109.5 |
| C23-C24-C19 | $118.9(5)$ | C29-C30-H30C | 109.5 |
| C23-C24-C15 | $122.2(4)$ | H30B-C30-H30C | 109.5 |
| C19-C24-C15 | $118.9(4)$ | O3-C31-C32 | 109.5 |
| N1-C25-C26 | $110.3(3)$ | O3-C31-H31A | $109-\mathrm{C}$ |


| C34-C35-C36 | $113.7(5)$ | H36A-C36-H36B | 109.5 |
| :--- | :--- | :--- | :--- |
| C34-C35-H35A | 108.8 | C35-C36-H36C | 109.5 |
| C36-C35-H35A | 108.8 | H36A-C36-H36C | 109.5 |
| C34-C35-H35B | 108.8 | H36B-C36-H36C | 109.5 |
| C36-C35-H35B | 108.8 | C1-N1-C11 | $125.8(4)$ |
| H35A-C35-H35B | 107.7 | C1-N1-C25 | $117.6(4)$ |
| C35-C36-H36A | 109.5 | C11-N1-C25 | $116.5(4)$ |
| C35-C36-H36B | 109.5 | C18-O3-C31 | $117.6(4)$ |

Table 60.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 60. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | 10(2) | 19(3) | 22(3) | 2(2) | -2(2) | 0(2) |
| C2 | 10(2) | 14(2) | 18(2) | -1(2) | 1(2) | $0(2)$ |
| C3 | 12(2) | 28(3) | 20(2) | -2(2) | $0(2)$ | $0(2)$ |
| C4 | 14(2) | 19(3) | 26(3) | 3(2) | 1(2) | 3(2) |
| C5 | 9(2) | 18(3) | 28(3) | -3(2) | 4(2) | 1(2) |
| C6 | 15(2) | 13(2) | 25(2) | 2(2) | 4(2) | -3(2) |
| C7 | 18(2) | 18(3) | 21(2) | -1(2) | 4(2) | 3(2) |
| C8 | 23(2) | 24(3) | 18(2) | -4(2) | 5(2) | -3(2) |
| C9 | 22(2) | 18(3) | 23(3) | 2(2) | 4(2) | $0(2)$ |
| C10 | 13(2) | 14(2) | 22(2) | 0 (2) | 3(2) | $0(2)$ |
| C11 | 16(2) | 16(2) | 22(2) | -3(2) | -3(2) | $0(2)$ |
| C12 | 13(2) | 16(3) | 20(2) | 1(2) | 5(2) | -2(2) |
| C13 | 17(2) | 18(3) | 21(2) | 2(2) | 1(2) | -2(2) |
| C14 | 15(2) | 17(2) | 23(2) | -2(2) | 4(2) | -3(2) |
| C15 | 13(2) | 17(2) | 24(3) | -1(2) | 2(2) | $0(2)$ |
| C16 | 15(2) | 20(3) | 25(3) | 1(2) | $0(2)$ | $0(2)$ |
| C17 | 22(2) | 18(3) | 15(2) | -1(2) | 2(2) | -1(2) |
| C18 | 14(2) | 18(3) | 22(3) | -3(2) | 5(2) | 2(2) |
| C19 | 12(2) | 16(2) | 28(3) | -1(2) | 2(2) | -2(2) |
| C20 | 14(2) | 20(3) | 24(3) | 2(2) | -1(2) | $0(2)$ |
| C21 | 19(2) | 19(3) | 27(3) | 3(2) | -4(2) | 2(2) |
| C22 | 23(2) | 27(3) | 17(2) | -1(2) | 4(2) | -2(2) |
| C23 | 18(2) | 22(3) | 23(3) | -4(2) | 4(2) | -1(2) |
| C24 | 14(2) | 15(2) | 21(2) | -3(2) | $0(2)$ | -3(2) |
| C25 | 16(2) | 17(3) | 20(2) | -3(2) | 5(2) | 2(2) |
| C26 | 15(2) | 23(3) | 25(3) | -2(2) | 1(2) | 1(2) |
| C27 | 21(2) | 20(3) | 20(2) | 0 (2) | 3(2) | -1(2) |
| C28 | 20(2) | 24(3) | 21(2) | -3(2) | $0(2)$ | 2(2) |
| C29 | 25(2) | 17(3) | 31(3) | -1(2) | 6(2) | $0(2)$ |
| C30 | 34(3) | 20(3) | 47(3) | 0 (3) | -2(3) | 2(2) |
| C31 | 23(2) | 24(3) | 25(3) | -5(2) | 6 (2) | 5(2) |


| C32 | $19(2)$ | $27(3)$ | $22(3)$ | $-3(2)$ | $5(2)$ | $4(2)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| C33 | $25(2)$ | $24(3)$ | $26(3)$ | $-4(2)$ | $7(2)$ | $5(2)$ |
| C34 | $26(2)$ | $30(3)$ | $23(3)$ | $-3(2)$ | $5(2)$ | $9(2)$ |
| C35 | $38(3)$ | $24(3)$ | $32(3)$ | $0(2)$ | $10(2)$ | $12(2)$ |
| C36 | $56(3)$ | $23(3)$ | $36(3)$ | $3(3)$ | $13(3)$ | $12(3)$ |
| N1 | $17(2)$ | $13(2)$ | $21(2)$ | $-4(2)$ | $5(2)$ | $1(2)$ |
| O1 | $26(2)$ | $29(2)$ | $18(2)$ | $-2(2)$ | $3(1)$ | $5(2)$ |
| O2 | $30(2)$ | $30(2)$ | $21(2)$ | $-2(2)$ | $-2(2)$ | $9(2)$ |
| O3 | $22(1)$ | $23(2)$ | $21(2)$ | $-2(2)$ | $0(1)$ | $6(1)$ |
|  |  |  |  |  |  |  |

Table 60.5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 60.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| H3 | 1078 | 5422 | 7009 | 24 |
| H4 | 4261 | 4991 | 6640 | 24 |
| H7 | 2753 | 4937 | 3620 | 23 |
| H8 | -177 | 5224 | 2567 | 26 |
| H9 | -3294 | 5664 | 2948 | 25 |
| H16 | 8074 | 4365 | 3402 | 24 |
| H17 | 11331 | 3949 | 2986 | 22 |
| H20 | 15455 | 3490 | 5601 | 24 |
| H21 | 15116 | 3602 | 7052 | 27 |
| H22 | 11804 | 4012 | 7456 | 27 |
| H23 | 9009 | 4326 | 6411 | 25 |
| H25A | -6777 | 6208 | 6156 | 21 |
| H25B | -7841 | 6265 | 5152 | 21 |
| H26A | -3745 | 6631 | 5038 | 26 |
| H26B | -2864 | 6587 | 6054 | 26 |
| H27A | -8127 | 6906 | 5346 | 24 |
| H27B | -7071 | 6879 | 6357 | 24 |
| H28A | -4109 | 7264 | 5156 | 27 |
| H28B | -3105 | 7240 | 6169 | 27 |
| H29A | -8310 | 7570 | 5454 | 29 |
| H29B | -7284 | 7548 | 6468 | 29 |
| H30A | -3136 | 7881 | 6234 | 51 |
| H30B | -6043 | 8090 | 5975 | 51 |
| H30C | -4367 | 7920 | 5238 | 51 |
| H31A | 15943 | 3654 | 2911 | 28 |
| H31B | 12990 | 3440 | 2803 | 28 |
| H32A | 18284 | 3146 | 3568 | 27 |
| H32B | 17218 | 3099 | 2564 | 27 |
| H33A | 13034 | 2809 | 2954 | 30 |
| H33B | 14278 | 2840 | 3948 | 30 |


| H34A | 17070 | 2454 | 2714 | 31 |
| :--- | :--- | :--- | :--- | :--- |
| H34B | 18085 | 2469 | 3728 | 31 |
| H35A | 12768 | 2171 | 3012 | 37 |
| H35B | 13868 | 2177 | 4021 | 37 |
| H36A | 16495 | 1791 | 2752 | 57 |
| H36B | 14726 | 1630 | 3479 | 57 |
| H36C | 17764 | 1809 | 3748 | 57 |

Table 60.6. Torsion angles [ ${ }^{\circ}$ ] for 60.

| O1-C1-C2-C3 | 1.4(7) | C1-C2-C12-C6 | -179.9(4) |
| :---: | :---: | :---: | :---: |
| N1-C1-C2-C3 | -179.3(4) | C14-C15-C16-C17 | -179.7(4) |
| O1-C1-C2-C12 | -179.0(4) | C24-C15-C16-C17 | 0.5(7) |
| N1-C1-C2-C12 | 0.4(6) | C15-C16-C17-C18 | 1.0(7) |
| C12-C2-C3-C4 | 0.4(7) | C16-C17-C18-O3 | 176.2(4) |
| C1-C2-C3-C4 | -179.9(4) | C16-C17-C18-C19 | -1.9(7) |
| C2-C3-C4-C5 | -0.1(7) | C17-C18-C19-C24 | 1.2(7) |
| C3-C4-C5-C13 | 178.9(4) | O3-C18-C19-C24 | -177.0(4) |
| C3-C4-C5-C6 | -0.3(7) | C17-C18-C19-C20 | -177.4(4) |
| C4-C5-C6-C7 | -178.8(4) | O3-C18-C19-C20 | 4.4(6) |
| C13-C5-C6-C7 | 2.1(7) | C24-C19-C20-C21 | 0.1(7) |
| C4-C5-C6-C12 | 0.5(6) | C18-C19-C20-C21 | 178.7(4) |
| C13-C5-C6-C12 | -178.7(4) | C19-C20-C21-C22 | 1.3(7) |
| C12-C6-C7-C8 | 0.7(7) | C20-C21-C22-C23 | -1.6(7) |
| C5-C6-C7-C8 | 179.9(4) | C21-C22-C23-C24 | 0.3(7) |
| C6-C7-C8-C9 | 0.1(7) | C22-C23-C24-C19 | 1.1(7) |
| C7-C8-C9-C10 | -0.6(7) | C22-C23-C24-C15 | -179.2(4) |
| C8-C9-C10-C12 | 0.2(7) | C20-C19-C24-C23 | -1.3(6) |
| C8-C9-C10-C11 | 180.0(4) | C18-C19-C24-C23 | -179.9(4) |
| C9-C10-C11-O2 | -1.9(7) | C20-C19-C24-C15 | 179.0(4) |
| C12-C10-C11-O2 | 177.8(5) | C18-C19-C24-C15 | 0.3(6) |
| C9-C10-C11-N1 | 178.0(4) | C16-C15-C24-C23 | 179.1(4) |
| C12-C10-C11-N1 | -2.2(6) | C14-C15-C24-C23 | -0.7(7) |
| C9-C10-C12-C6 | 0.6(7) | C16-C15-C24-C19 | -1.2(7) |
| C11-C10-C12-C6 | -179.2(4) | C14-C15-C24-C19 | 179.1(4) |
| C9-C10-C12-C2 | -179.5(4) | N1-C25-C26-C27 | 176.4(4) |
| C11-C10-C12-C2 | 0.8(6) | C25-C26-C27-C28 | -176.2(4) |
| C7-C6-C12-C10 | -1.0(6) | C26-C27-C28-C29 | 179.0(4) |
| C5-C6-C12-C10 | 179.7(4) | C27-C28-C29-C30 | -179.6(5) |
| C7-C6-C12-C2 | 179.1(4) | O3-C31-C32-C33 | 70.3(5) |
| C5-C6-C12-C2 | -0.2(6) | C31-C32-C33-C34 | 176.2(4) |
| C3-C2-C12-C10 | 179.8(4) | C32-C33-C34-C35 | -175.3(5) |
| C1-C2-C12-C10 | 0.2(6) | C33-C34-C35-C36 | 178.1(5) |
| C3-C2-C12-C6 | -0.2(6) | O1-C1-N1-C11 | 177.3(4) |


| $\mathrm{C} 2-\mathrm{C} 1-\mathrm{N} 1-\mathrm{C} 11$ | $-2.1(6)$ | $\mathrm{C} 10-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 25$ | $177.8(4)$ |
| :--- | :---: | :--- | :---: |
| $\mathrm{O} 1-\mathrm{C} 1-\mathrm{N} 1-\mathrm{C} 25$ | $2.5(6)$ | $\mathrm{C} 26-\mathrm{C} 25-\mathrm{N} 1-\mathrm{C} 1$ | $88.2(5)$ |
| $\mathrm{C} 2-\mathrm{C} 1-\mathrm{N} 1-\mathrm{C} 25$ | $-176.9(4)$ | $\mathrm{C} 26-\mathrm{C} 25-\mathrm{N} 1-\mathrm{C} 11$ | $-87.1(5)$ |
| $\mathrm{O} 2-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 1$ | $-177.1(4)$ | $\mathrm{C} 17-\mathrm{C} 18-\mathrm{O} 3-\mathrm{C} 31$ | $3.0(7)$ |
| $\mathrm{C} 10-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 1$ | $3.0(6)$ | $\mathrm{C} 19-\mathrm{C} 18-\mathrm{O} 3-\mathrm{C} 31$ | $-178.8(4)$ |
| $\mathrm{O} 2-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 25$ | $-2.2(6)$ | $\mathrm{C} 32-\mathrm{C} 31-\mathrm{O} 3-\mathrm{C} 18$ | $-170.9(4)$ |

End of 60 data.

## Crystallographic Material for 7o

Crystallographic Material for 70.
X-ray Experimental.
Table 70.1. Crystallographic Data for 70.
Table 70.2. Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the non-hydrogen atoms of 70.

Table 70.3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of 70.
Table 70.4. Anisotropic thermal parameters for the non-hydrogen atoms of 70.

Table 70.5. Fractional coordinates and isotropic thermal parameters $\left(\AA^{2}\right)$ for the hydrogen atoms of 70.

Table 70.6. Torsion Angles $\left(^{(0)}\right.$ for the non-hydrogen atoms of 70.

X-ray Experimental for complex $\mathrm{C}_{38} \mathrm{H}_{41} \mathrm{NO}_{3}$ : (70) Crystals grew as very long, orange laths by precipitation from a 1.0 mM solution of 7 in Acetone. The data crystal was cut from a longer crystal and had approximate dimensions; $0.28 \times 0.089 \times 0.031 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{Cu} \mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA$ ) with collimating mirror monochromators. A total of 1007 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 26 seconds per frame with a detector offset of $+/-41.9^{\circ}$ and 90 seconds per frame with a detector offset of $+/-110.4^{\circ}$. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.' The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6. ${ }^{3}$ Structure analysis was aided by use of
the programs PLATON98 ${ }^{4}$ and WinGX. ${ }^{5}$ The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms).

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{O}}\right)\right)^{2}+(0.098 * \mathrm{P})^{2}\right]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.176 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0626 and a goodness of fit, $\mathrm{S},=1.02$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S , are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. ${ }^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.37.31.
2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\left|\mathrm{F}_{\mathrm{c}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 70.1. Crystal data and structure refinement for 70.

| Empirical formula | C38 H41 N O3 |
| :---: | :---: |
| Formula weight | 559.72 |
| Temperature | 100(2) K |
| Wavelength | 1.54184 £ |
| Crystal system | monoclinic |
| Space group | Cc |
| Unit cell dimensions | $a=4.6766(7) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=41.435(3) \AA \quad \beta=94.880(10)^{\circ}$. |
|  | $\mathrm{c}=15.4245(15) \AA \quad \gamma=90^{\circ}$. |
| Volume | 2978.0(6) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.248 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.608 \mathrm{~mm}^{-1}$ |
| F(000) | 1200 |
| Crystal size | $0.28 \times 0.089 \times 0.031 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 3.581 to $76.009^{\circ}$. |
| Index ranges | $-5<=\mathrm{h}<=5,-47<=\mathrm{k}<=51,-18<=1<=19$ |
| Reflections collected | 8683 |
| Independent reflections | 4179 [ $\mathrm{R}(\mathrm{int}$ ) $=0.0878]$ |
| Completeness to theta $=67.684^{\circ}$ | 100.0 \% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00 and 0.457 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 4179 / 578 / 381 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.021 |
| Final R indices [ $1>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0626, \mathrm{wR} 2=0.1627$ |
| R indices (all data) | $\mathrm{R} 1=0.0774, \mathrm{wR} 2=0.1758$ |
| Absolute structure parameter | 0.0(4) |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.318 and -0.351 e. $\AA^{-3}$ |

Table 7O.2. Atomic coordinates $\left(\times 10^{4}\right)$ and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 70. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $U^{\mathrm{ij}}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| C1 | -4827(9) | 5838(1) | 6958(3) | 17(1) |
| C2 | -2880(9) | 5578(1) | 6725(3) | 17(1) |
| C3 | -2793(10) | 5492(1) | 5865(3) | 20(1) |
| C4 | -940(10) | 5247(1) | 5623(3) | 21(1) |
| C5 | 816(10) | 5091(1) | 6245(3) | 20(1) |
| C6 | 804(9) | 5175(1) | 7132(3) | 17(1) |
| C7 | 2602(9) | 5017(1) | 7805(3) | 18(1) |
| C8 | 2466(10) | 5105(1) | 8666(3) | 20(1) |
| C9 | 570(10) | 5351(1) | 8896(3) | 20(1) |
| C10 | -1185(9) | 5505(1) | 8261(3) | 17(1) |
| C11 | -3154(9) | 5762(1) | 8510(3) | 18(1) |
| C12 | -1098(9) | 5418(1) | 7373(3) | 17(1) |
| C13 | 4557(9) | 4772(1) | 7587(3) | 19(1) |
| C14 | 6234(9) | 4568(1) | 7389(3) | 18(1) |
| C15 | 8221(9) | 4328(1) | 7168(3) | 18(1) |
| C16 | 8650(10) | 4266(1) | 6304(3) | 20(1) |
| C17 | 10592(10) | 4029(1) | 6070(3) | 19(1) |
| C18 | 12088(9) | 3847(1) | 6706(3) | 17(1) |
| C19 | 11793(9) | 3909(1) | 7606(3) | 16(1) |
| C20 | 13416(10) | 3736(1) | 8267(3) | 21(1) |
| C21 | 13116(10) | 3798(1) | 9132(3) | 23(1) |
| C22 | 11165(10) | 4037(1) | 9364(3) | 24(1) |
| C23 | 9571(10) | 4207(1) | 8734(3) | 20(1) |
| C24 | 9837(9) | 4149(1) | 7840(3) | 16(1) |
| C25 | -6722(9) | 6180(1) | 8081(3) | 18(1) |
| C26 | -5019(10) | 6494(1) | 8082(3) | 22(1) |
| C27 | -6853(10) | 6792(1) | 8245(3) | 20(1) |
| C28 | -5092(10) | 7102(1) | 8227(3) | 22(1) |
| C29 | -6890(10) | 7409(1) | 8291(3) | 21(1) |
| C30 | -5088(11) | 7716(1) | 8265(3) | 26(1) |
| C31 | -6924(12) | 8021(1) | 8289(4) | 32(1) |


| C32 | $14430(10)$ | $3541(1)$ | $5654(3)$ | $21(1)$ |
| :--- | :--- | :--- | :--- | :--- |
| C33 | $16275(10)$ | $3240(1)$ | $5647(3)$ | $21(1)$ |
| C34 | $14580(10)$ | $2929(1)$ | $5783(3)$ | $22(1)$ |
| C35 | $16411(10)$ | $2625(1)$ | $5754(3)$ | $21(1)$ |
| C36 | $14641(10)$ | $2315(1)$ | $5802(3)$ | $22(1)$ |
| C37 | $16421(11)$ | $2007(1)$ | $5790(3)$ | $25(1)$ |
| C38 | $14612(12)$ | $1702(1)$ | $5831(3)$ | $30(1)$ |
| N1 | $-4880(8)$ | $5906(1)$ | $7851(2)$ | $17(1)$ |
| O1 | $-6348(8)$ | $5987(1)$ | $6424(2)$ | $27(1)$ |
| O2 | $-3263(7)$ | $5847(1)$ | $9268(2)$ | $25(1)$ |
| O3 | $13906(7)$ | $3603(1)$ | $6543(2)$ | $21(1)$ |

Table 70. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for 70.

| C1-O1 | 1.211(6) | C19-C24 | 1.419(6) |
| :---: | :---: | :---: | :---: |
| C1-N1 | $1.409(5)$ | C20-C21 | 1.377(6) |
| C1-C2 | $1.476(6)$ | C20-H20 | 0.95 |
| C2-C3 | 1.378(6) | C21-C22 | 1.411(6) |
| C2-C12 | 1.409(6) | C21-H21 | 0.95 |
| C3-C4 | 1.404(6) | C22-C23 | 1.369(7) |
| C3-H3 | 0.95 | C22-H22 | 0.95 |
| C4-C5 | 1.371(7) | C23-C24 | 1.415(6) |
| C4-H4 | 0.95 | C23-H23 | 0.95 |
| C5-C6 | 1.412(6) | C25-N1 | 1.485(5) |
| C5-H5 | 0.95 | C25-C26 | 1.526(5) |
| C6-C12 | 1.414(6) | C25-H25A | 0.99 |
| C6-C7 | 1.437(6) | C25-H25B | 0.99 |
| C7-C8 | $1.385(6)$ | C26-C27 | $1.536(5)$ |
| C7-C13 | 1.424(6) | C26-H26A | 0.99 |
| C8-C9 | 1.416(6) | C26-H26B | 0.99 |
| C8-H8 | 0.95 | C27-C28 | 1.529(6) |
| C9-C10 | $1.378(6)$ | C27-H27A | 0.99 |
| C9-H9 | 0.95 | C27-H27B | 0.99 |
| C10-C12 | 1.420(6) | C28-C29 | 1.530(6) |
| C10-C11 | 1.480(5) | C28-H28A | 0.99 |
| C11-O2 | 1.226(6) | C28-H28B | 0.99 |
| C11-N1 | $1.380(6)$ | C29-C30 | 1.529(6) |
| C13-C14 | 1.212(6) | C29-H29A | 0.99 |
| C14-C15 | 1.422(6) | C29-H29B | 0.99 |
| C15-C16 | $1.388(6)$ | C30-C31 | 1.529(6) |
| C15-C24 | $1.436(6)$ | C30-H30A | 0.99 |
| C16-C17 | 1.407(6) | C30-H30B | 0.99 |
| C16-H16 | 0.95 | C31-H31A | 0.98 |
| C17-C18 | $1.378(6)$ | C31-H31B | 0.98 |
| C17-H17 | 0.95 | C31-H31C | 0.98 |
| C18-O3 | 1.359(5) | C32-O3 | $1.437(5)$ |
| C18-C19 | 1.430(6) | C32-C33 | 1.516(6) |
| C19-C20 | 1.414(6) | C32-H32A | 0.99 |


| C32-H32B | 0.99 | C36-C37 | 1.528(6) |
| :---: | :---: | :---: | :---: |
| C33-C34 | 1.535(6) | C36-H36A | 0.99 |
| C33-H33A | 0.99 | C36-H36B | 0.99 |
| C33-H33B | 0.99 | C37-C38 | 1.524(6) |
| C34-C35 | 1.528(6) | C37-H37A | 0.99 |
| C34-H34A | 0.99 | C37-H37B | 0.99 |
| C34-H34B | 0.99 | C38-H38A | 0.98 |
| C35-C36 | $1.532(6)$ | C38-H38B | 0.98 |
| C35-H35A | 0.99 | C38-H38C | 0.98 |
| C35-H35B | 0.99 |  |  |
| O1-C1-N1 | 120.3(4) | C10-C9-H9 | 119.9 |
| O1-C1-C2 | 123.1(4) | C8-C9-H9 | 119.9 |
| N1-C1-C2 | 116.6(4) | C9-C10-C12 | 120.3(4) |
| C3-C2-C12 | 119.9(4) | C9-C10-C11 | 119.6(4) |
| C3-C2-C1 | 119.5(4) | C12-C10-C11 | 120.1(4) |
| C12-C2-C1 | 120.6(4) | O2-C11-N1 | 120.5(4) |
| C2-C3-C4 | 120.7(4) | O2-C11-C10 | 122.2(4) |
| C2-C3-H3 | 119.6 | N1-C11-C10 | 117.3(4) |
| C4-C3-H3 | 119.6 | C2-C12-C6 | 119.6(4) |
| C5-C4-C3 | 120.1(4) | C2-C12-C10 | 120.2(4) |
| C5-C4-H4 | 119.9 | C6-C12-C10 | 120.2(4) |
| C3-C4-H4 | 119.9 | C14-C13-C7 | 178.7(4) |
| C4-C5-C6 | 120.7(4) | C13-C14-C15 | 179.2(5) |
| C4-C5-H5 | 119.7 | C16-C15-C14 | 120.6(4) |
| C6-C5-H5 | 119.7 | C16-C15-C24 | 119.2(4) |
| C5-C6-C12 | 119.0(4) | C14-C15-C24 | 120.2(4) |
| C5-C6-C7 | 122.4(4) | C15-C16-C17 | 121.6(4) |
| C12-C6-C7 | 118.6(4) | C15-C16-H16 | 119.2 |
| C8-C7-C13 | 119.8(4) | C17-C16-H16 | 119.2 |
| C8-C7-C6 | 120.0(4) | C18-C17-C16 | 120.0(4) |
| C13-C7-C6 | 120.2(4) | C18-C17-H17 | 120.0 |
| C7-C8-C9 | 120.8(4) | C16-C17-H17 | 120.0 |
| C7-C8-H8 | 119.6 | O3-C18-C17 | 124.2(4) |
| C9-C8-H8 | 119.6 | O3-C18-C19 | 115.2(4) |
| C10-C9-C8 | 120.1(4) | C17-C18-C19 | 120.6(4) |


| C20-C19-C24 | 119.4(4) | C27-C28-C29 | 113.4(4) |
| :---: | :---: | :---: | :---: |
| C20-C19-C18 | 121.4(4) | C27-C28-H28A | 108.9 |
| C24-C19-C18 | 119.3(4) | C29-C28-H28A | 108.9 |
| C21-C20-C19 | 120.7(4) | C27-C28-H28B | 108.9 |
| C21-C20-H20 | 119.7 | C29-C28-H28B | 108.9 |
| C19-C20-H20 | 119.7 | H28A-C28-H28B | 107.7 |
| C20-C21-C22 | 119.9(4) | C30-C29-C28 | 112.5(4) |
| C20-C21-H21 | 120.0 | C30-C29-H29A | 109.1 |
| C22-C21-H21 | 120.0 | C28-C29-H29A | 109.1 |
| C23-C22-C21 | 120.3(4) | C30-C29-H29B | 109.1 |
| C23-C22-H22 | 119.8 | C28-C29-H29B | 109.1 |
| C21-C22-H22 | 119.8 | H29A-C29-H29B | 107.8 |
| C22-C23-C24 | 121.1(4) | C31-C30-C29 | 112.0(4) |
| C22-C23-H23 | 119.4 | C31-C30-H30A | 109.2 |
| C24-C23-H23 | 119.4 | C29-C30-H30A | 109.2 |
| C23-C24-C19 | 118.6(4) | C31-C30-H30B | 109.2 |
| C23-C24-C15 | 122.1(4) | C29-C30-H30B | 109.2 |
| C19-C24-C15 | 119.3(4) | H30A-C30-H30B | 107.9 |
| N1-C25-C26 | 109.8(3) | C30-C31-H31A | 109.5 |
| N1-C25-H25A | 109.7 | C30-C31-H31B | 109.5 |
| C26-C25-H25A | 109.7 | H31A-C31-H31B | 109.5 |
| N1-C25-H25B | 109.7 | C30-C31-H31C | 109.5 |
| C26-C25-H25B | 109.7 | H31A-C31-H31C | 109.5 |
| H25A-C25-H25B | 108.2 | H31B-C31-H31C | 109.5 |
| C25-C26-C27 | 112.8(3) | O3-C32-C33 | 107.4(3) |
| C25-C26-H26A | 109.0 | O3-C32-H32A | 110.2 |
| C27-C26-H26A | 109.0 | C33-C32-H32A | 110.2 |
| C25-C26-H26B | 109.0 | O3-C32-H32B | 110.2 |
| C27-C26-H26B | 109.0 | C33-C32-H32B | 110.2 |
| H26A-C26-H26B | 107.8 | H32A-C32-H32B | 108.5 |
| C28-C27-C26 | 111.4(3) | C32-C33-C34 | 112.8(4) |
| C28-C27-H27A | 109.4 | C32-C33-H33A | 109.0 |
| C26-C27-H27A | 109.4 | C34-C33-H33A | 109.0 |
| C28-C27-H27B | 109.4 | C32-C33-H33B | 109.0 |
| C26-C27-H27B | 109.4 | C34-C33-H33B | 109.0 |
| H27A-C27-H27B | 108.0 | H33A-C33-H33B | 107.8 |


| C35-C34-C33 | $113.0(4)$ | H36A-C36-H36B | 107.7 |
| :--- | :--- | :--- | :--- |
| C35-C34-H34A | 109.0 | C38-C37-C36 | $112.8(4)$ |
| C33-C34-H34A | 109.0 | C38-C37-H37A | 109.0 |
| C35-C34-H34B | 109.0 | C36-C37-H37A | 109.0 |
| C33-C34-H34B | 109.0 | C38-C37-H37B | 109.0 |
| H34A-C34-H34B | 107.8 | C36-C37-H37B | 109.0 |
| C34-C35-C36 | $112.5(4)$ | H37A-C37-H37B | 107.8 |
| C34-C35-H35A | 109.1 | C37-C38-H38A | 109.5 |
| C36-C35-H35A | 109.1 | H38A-C38-H38B | 109.5 |
| C34-C35-H35B | 109.1 | H38A-C38-H38C | 109.5 |
| C36-C35-H35B | 109.1 | H38B-C38-H38C | 109.5 |
| H35A-C35-H35B | 107.8 | C11-N1-C1 | 109.5 |
| C37-C36-C35 | $113.8(4)$ | C11-N1-C25 | 109.5 |
| C37-C36-H36A | 108.8 | C1-N1-C25 | $125.1(4)$ |
| C35-C36-H36A | 108.8 | C18-O3-C32 | $118.0(3)$ |
| C37-C36-H36B | 108.8 | 108.8 |  |

Table 70.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 7O. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | 26(2) | 12(2) | 13(2) | -2(1) | -4(2) | -3(2) |
| C2 | 24(2) | 11(2) | 14(2) | -4(1) | -2(2) | -3(1) |
| C3 | 27(2) | 16(2) | 17(2) | 1(2) | -5(2) | -1(2) |
| C4 | 32(2) | 16(2) | 14(2) | -4(2) | -3(2) | -1(2) |
| C5 | 30(2) | 12(2) | 17(2) | -2(1) | 1(2) | 0 (2) |
| C6 | 21(2) | 11(2) | 18(2) | -1(1) | -2(2) | -2(1) |
| C7 | 22(2) | 11(2) | 19(2) | $0(1)$ | -1(2) | -3(2) |
| C8 | 25(2) | 16(2) | 18(2) | 3(2) | -7(2) | 2(2) |
| C9 | 25(2) | 16(2) | 18(2) | 0 (2) | -4(2) | -2(2) |
| C10 | 22(2) | 11(2) | 17(2) | $0(1)$ | $0(2)$ | -1(2) |
| C11 | 25(2) | 12(2) | 17(2) | 1(1) | -4(2) | -1(2) |
| C12 | 21(2) | 10(2) | 19(2) | -1(1) | -2(2) | -2(1) |
| C13 | 22(2) | 16(2) | 18(2) | 1(2) | -2(2) | -2(2) |
| C14 | 20(2) | 13(2) | 20(2) | 2(1) | -5(2) | 0 (2) |
| C15 | 21(2) | 12(2) | 20(2) | -2(2) | -2(2) | $0(1)$ |
| C16 | 26(2) | 12(2) | 20(2) | $0(1)$ | -7(2) | 3(2) |
| C17 | 29(2) | 14(2) | 14(2) | -2(1) | -2(2) | 0 (2) |
| C18 | 21(2) | 10(2) | 20(2) | -3(1) | -3(2) | -2(1) |
| C19 | 22(2) | 9(2) | 17(2) | -2(1) | -5(2) | -4(1) |
| C20 | 27(2) | 14(2) | 21(2) | -1(2) | -4(2) | 2(2) |
| C21 | 28(2) | 20(2) | 19(2) | 2(2) | -5(2) | 0 (2) |
| C22 | 33(2) | 20(2) | 17(2) | -1(2) | $0(2)$ | -2(2) |
| C23 | 26(2) | 14(2) | 20(2) | -6(2) | $0(2)$ | -1(2) |
| C24 | 22(2) | 10(2) | 17(2) | -2(1) | -5(2) | -3(1) |
| C25 | 22(2) | 13(2) | 18(2) | -1(1) | -3(2) | 5(2) |
| C26 | 25(2) | 12(2) | 28(2) | -2(2) | -1(2) | 2(2) |
| C27 | 26(2) | 13(2) | 21(2) | -2(2) | -6(2) | 5(2) |
| C28 | 33(2) | 13(2) | 20(2) | 0 (2) | -2(2) | 1(2) |
| C29 | 27(2) | 13(2) | 22(2) | -2(2) | -6(2) | 3(2) |
| C30 | 33(2) | 16(2) | 26(2) | 1(2) | -6(2) | 2(2) |
| C31 | 44(3) | 13(2) | 36(3) | -2(2) | -12(2) | 1(2) |


| C32 | $31(2)$ | $16(2)$ | $15(2)$ | $-2(2)$ | $-2(2)$ | $2(2)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C33 | $28(2)$ | $14(2)$ | $21(2)$ | $-3(2)$ | $-2(2)$ | $0(2)$ |
| C34 | $29(2)$ | $14(2)$ | $21(2)$ | $-2(2)$ | $-3(2)$ | $-1(2)$ |
| C35 | $29(2)$ | $16(2)$ | $18(2)$ | $1(1)$ | $-4(2)$ | $1(2)$ |
| C36 | $30(2)$ | $17(2)$ | $18(2)$ | $1(2)$ | $-3(2)$ | $2(2)$ |
| C37 | $32(2)$ | $18(2)$ | $24(2)$ | $0(2)$ | $-4(2)$ | $4(2)$ |
| C38 | $44(3)$ | $14(2)$ | $31(3)$ | $1(2)$ | $-4(2)$ | $2(2)$ |
| N1 | $22(2)$ | $11(1)$ | $16(2)$ | $-1(1)$ | $-3(1)$ | $0(1)$ |
| O1 | $38(2)$ | $21(2)$ | $18(2)$ | $1(1)$ | $-9(1)$ | $9(1)$ |
| O2 | $37(2)$ | $20(1)$ | $18(2)$ | $-4(1)$ | $-2(1)$ | $5(1)$ |
| O3 | $33(2)$ | $15(1)$ | $16(2)$ | $-3(1)$ | $0(1)$ | $6(1)$ |
|  |  |  |  |  |  |  |

Table 70.5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 70.

|  | X | y | Z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| H3 | -3999 | 5600 | 5430 | 24 |
| H4 | -904 | 5190 | 5028 | 25 |
| H5 | 2054 | 4925 | 6078 | 23 |
| H8 | 3659 | 5000 | 9108 | 24 |
| H9 | 508 | 5411 | 9489 | 24 |
| H16 | 7608 | 4388 | 5860 | 24 |
| H17 | 10872 | 3994 | 5475 | 23 |
| H20 | 14727 | 3575 | 8114 | 25 |
| H21 | 14222 | 3681 | 9571 | 27 |
| H22 | 10957 | 4079 | 9960 | 28 |
| H23 | 8264 | 4366 | 8899 | 24 |
| H25A | -7400 | 6143 | 8664 | 21 |
| H25B | -8422 | 6194 | 7654 | 21 |
| H26A | -4203 | 6518 | 7514 | 26 |
| H26B | -3402 | 6482 | 8539 | 26 |
| H27A | -8486 | 6803 | 7793 | 24 |
| H27B | -7641 | 6771 | 8818 | 24 |
| H28A | -4129 | 7109 | 7680 | 26 |
| H28B | -3582 | 7099 | 8718 | 26 |
| H29A | -8408 | 7413 | 7803 | 25 |
| H29B | -7839 | 7404 | 8841 | 25 |
| H30A | -3625 | 7717 | 8768 | 31 |
| H30B | -4072 | 7717 | 7728 | 31 |
| H31A | -7759 | 8034 | 8850 | 47 |
| H31B | -8466 | 8013 | 7818 | 47 |
| H31C | -5725 | 8211 | 8215 | 47 |
| H32A | 15435 | 3726 | 5411 | 26 |
| H32B | 12594 | 3507 | 5297 | 26 |
| H33A | 17861 | 3258 | 6112 | 26 |
| H33B | 17134 | 3227 | 5083 | 26 |


| H34A | 13761 | 2941 | 6353 | 26 |
| :--- | :--- | :--- | :--- | :--- |
| H34B | 12964 | 2915 | 5326 | 26 |
| H35A | 17913 | 2629 | 6247 | 25 |
| H35B | 17382 | 2624 | 5208 | 25 |
| H36A | 13642 | 2319 | 6343 | 27 |
| H36B | 13158 | 2311 | 5305 | 27 |
| H37A | 17430 | 2002 | 5251 | 30 |
| H37B | 17893 | 2009 | 6290 | 30 |
| H38A | 13249 | 1690 | 5313 | 45 |
| H38B | 13558 | 1708 | 6354 | 45 |
| H38C | 15867 | 1512 | 5854 | 45 |

Table 70.6. Torsion angles [ ${ }^{\circ}$ ] for 70.

| O1-C1-C2-C3 | -1.2(6) | C11-C10-C12-C6 | 179.3(4) |
| :---: | :---: | :---: | :---: |
| N1-C1-C2-C3 | 178.0(4) | C14-C15-C16-C17 | -179.7(4) |
| O1-C1-C2-C12 | 178.2(4) | C24-C15-C16-C17 | 1.2(6) |
| N1-C1-C2-C12 | -2.6(5) | C15-C16-C17-C18 | 1.0(7) |
| C12-C2-C3-C4 | -0.1(6) | C16-C17-C18-O3 | 176.8(4) |
| C1-C2-C3-C4 | 179.4(4) | C16-C17-C18-C19 | -3.1(6) |
| C2-C3-C4-C5 | -0.2(7) | O3-C18-C19-C20 | 3.2(6) |
| C3-C4-C5-C6 | -0.5(6) | C17-C18-C19-C20 | -176.9(4) |
| C4-C5-C6-C12 | 1.4(6) | O3-C18-C19-C24 | -177.0(3) |
| C4-C5-C6-C7 | 179.8(4) | C17-C18-C19-C24 | 2.9(6) |
| C5-C6-C7-C8 | -178.9(4) | C24-C19-C20-C21 | -0.1(6) |
| C12-C6-C7-C8 | -0.5(6) | C18-C19-C20-C21 | 179.8(4) |
| C5-C6-C7-C13 | 2.0(6) | C19-C20-C21-C22 | 0.2(7) |
| C12-C6-C7-C13 | -179.6(4) | C20-C21-C22-C23 | -0.2(7) |
| C13-C7-C8-C9 | 179.0(4) | C21-C22-C23-C24 | -0.1(7) |
| C6-C7-C8-C9 | -0.1(6) | C22-C23-C24-C19 | 0.3(6) |
| C7-C8-C9-C10 | 0.5(6) | C22-C23-C24-C15 | -179.0(4) |
| C8-C9-C10-C12 | -0.3(6) | C20-C19-C24-C23 | -0.2(6) |
| C8-C9-C10-C11 | -179.9(4) | C18-C19-C24-C23 | 180.0(4) |
| C9-C10-C11-O2 | 0.8(6) | C20-C19-C24-C15 | 179.1(4) |
| C12-C10-C11-O2 | -178.8(4) | C18-C19-C24-C15 | -0.7(5) |
| C9-C10-C11-N1 | -179.5(4) | C16-C15-C24-C23 | 178.0(4) |
| C12-C10-C11-N1 | 0.8(5) | C14-C15-C24-C23 | -1.2(6) |
| C3-C2-C12-C6 | 1.1(6) | C16-C15-C24-C19 | -1.3(6) |
| C1-C2-C12-C6 | -178.4(4) | C14-C15-C24-C19 | 179.5(4) |
| C3-C2-C12-C10 | -179.8(4) | N1-C25-C26-C27 | 175.5(3) |
| C1-C2-C12-C10 | 0.8(6) | C25-C26-C27-C28 | -179.1(4) |
| C5-C6-C12-C2 | -1.7(6) | C26-C27-C28-C29 | 173.9(4) |
| C7-C6-C12-C2 | 179.9(4) | C27-C28-C29-C30 | -179.5(4) |
| C5-C6-C12-C10 | 179.1(4) | C28-C29-C30-C31 | 177.5(4) |
| C7-C6-C12-C10 | 0.7(6) | O3-C32-C33-C34 | 75.0(4) |
| C9-C10-C12-C2 | -179.5(4) | C32-C33-C34-C35 | 178.6(4) |
| C11-C10-C12-C2 | 0.1(6) | C33-C34-C35-C36 | -174.5(3) |
| C9-C10-C12-C6 | -0.3(6) | C34-C35-C36-C37 | -179.1(4) |


| C35-C36-C37-C38 | $-179.6(4)$ | O1-C1-N1-C25 | $-4.0(6)$ |
| :--- | :---: | :--- | :---: |
| O2-C11-N1-C1 | $176.7(4)$ | C2-C1-N1-C25 | $176.8(3)$ |
| C10-C11-N1-C1 | $-2.9(6)$ | C26-C25-N1-C11 | $85.7(4)$ |
| O2-C11-N1-C25 | $3.8(6)$ | C26-C25-N1-C1 | $-87.9(4)$ |
| C10-C11-N1-C25 | $-175.9(3)$ | C17-C18-O3-C32 | $3.6(6)$ |
| O1-C1-N1-C11 | $-177.0(4)$ | C19-C18-O3-C32 | $-176.5(3)$ |
| C2-C1-N1-C11 | $3.8(6)$ | $\mathrm{C} 33-\mathrm{C} 32-\mathrm{O} 3-\mathrm{C} 18$ | $-174.6(3)$ |

End of crystallographic data for 70.

## Crystallographic Material for 9o

Crystallographic Material for 90 .
X-ray Experimental.
Table 90.1. Crystallographic Data for 90.
Table 90.2. Fractional coordinates and equivalent isotropic thermal parameters ( $\AA^{2}$ ) for the nonhydrogen atoms of $\mathbf{9 0}$.

Table 90.3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of 90.
Table 90.4. Anisotropic thermal parameters for the non-hydrogen atoms of $\mathbf{9 0}$.

Table 90.5. Fractional coordinates and isotropic thermal parameters ( $\AA^{2}$ ) for the hydrogen atoms of 90 .

Table 90.6. Torsion Angles $\left(^{( }\right)$for the non-hydrogen atoms of 90.

X-ray Experimental for complex $\mathrm{C}_{42} \mathrm{H}_{49} \mathrm{NO}_{3}(\mathbf{9 0})$ : Crystals grew as long, orange laths by vapor diffusion (solvent $=\mathrm{p}$-xylenes, precipitant $=$ acetonitrile). The data crystal was cut from a larger crystal and had approximate dimensions; $0.29 \times 0.09 \times 0.03 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{Cu} \mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA)$ with collimating mirror monochromators. A total of 1015 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 30 seconds per frame with a detector offset of $+/-41.9^{\circ}$ and 80 seconds per frame with a detector offset of $+/-$ $110.4^{\circ}$. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.38.43f. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6. ${ }^{3}$ Structure analysis was aided by use of the programs PLATON98 ${ }^{4}$ and WinGX. ${ }^{5}$ The hydrogen atoms were calculated in ideal positions
with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms).

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.1329 * \mathrm{P})^{2}+\right.$ $(0.9071 * \mathrm{P})]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)$ refined to 0.212 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0684 and a goodness of fit, $\mathrm{S},=1.06$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S, are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. ${ }^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.38.43f.
2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\left|\mathrm{F}_{\mathrm{c}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{W}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 90.1. Crystal data and structure refinement for 90 .

| Empirical formula | C42 H49 N O3 |
| :---: | :---: |
| Formula weight | 615.82 |
| Temperature | 100(2) K |
| Wavelength | 1.54184 £ |
| Crystal system | monoclinic |
| Space group | Cc |
| Unit cell dimensions | $\mathrm{a}=4.6726(4) \AA \quad \alpha=90^{\circ}$. |
|  | $\mathrm{b}=46.582(3) \AA \quad \beta=94.233(7)^{\circ}$. |
|  | $\mathrm{c}=15.3879(11) \AA \quad \gamma=90^{\circ}$. |
| Volume | $3340.1(4) \AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.225 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.586 \mathrm{~mm}^{-1}$ |
| F(000) | 1328 |
| Crystal size | $0.290 \times 0.090 \times 0.030 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 3.449 to $75.634^{\circ}$. |
| Index ranges | $-5<=\mathrm{h}<=5,-49<=\mathrm{k}<=58,-18<=1<=19$ |
| Reflections collected | 9974 |
| Independent reflections | $4830[\mathrm{R}(\mathrm{int})=0.0689]$ |
| Completeness to theta $=67.684^{\circ}$ | 99.9 \% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00 and 0.591 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 4830 / 278 / 417 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.061 |
| Final R indices [ $1>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0684, \mathrm{wR} 2=0.1928$ |
| R indices (all data) | $\mathrm{R} 1=0.0774, \mathrm{wR} 2=0.2119$ |
| Absolute structure parameter | -0.3(4) |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.314 and $-0.353 \mathrm{e} . \AA^{-3}$ |

Table 90.2. Atomic coordinates ( $\mathrm{x} 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $90 . \mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| C1 | -2950(9) | 5680(1) | 6030(3) | 20(1) |
| C2 | -957(9) | 5450(1) | 5781(3) | 20(1) |
| C3 | 775(10) | 5314(1) | 6405(3) | 23(1) |
| C4 | 2676(10) | 5095(1) | 6187(3) | 23(1) |
| C5 | 2820(10) | 5016(1) | 5322(3) | 21(1) |
| C6 | 1043(9) | 5154(1) | 4655(3) | 19(1) |
| C7 | 1061(10) | 5076(1) | 3759(3) | 23(1) |
| C8 | -721(11) | 5214(1) | 3144(3) | 24(1) |
| C9 | -2594(10) | 5434(1) | 3378(3) | 22(1) |
| C10 | -2644(10) | 5513(1) | 4240(3) | 19(1) |
| C11 | -4632(10) | 5744(1) | 4476(3) | 19(1) |
| C12 | -879(9) | 5372(1) | 4892(3) | 17(1) |
| C13 | 4796(10) | 4796(1) | 5100(3) | 21(1) |
| C14 | 6455(10) | 4614(1) | 4906(3) | 21(1) |
| C15 | 8438(9) | 4400(1) | 4688(3) | 19(1) |
| C16 | 8877(10) | 4342(1) | 3826(3) | 22(1) |
| C17 | 10823(10) | 4128(1) | 3588(3) | 22(1) |
| C18 | 12307(9) | 3972(1) | 4217(3) | 19(1) |
| C19 | 12023(10) | 4024(1) | 5124(3) | 19(1) |
| C20 | 13658(10) | 3876(1) | 5782(3) | 24(1) |
| C21 | 13359(10) | 3936(1) | 6643(3) | 25(1) |
| C22 | 11392(10) | 4146(1) | 6874(3) | 23(1) |
| C23 | 9805(10) | 4299(1) | 6255(3) | 22(1) |
| C24 | 10061(9) | 4241(1) | 5358(3) | 18(1) |
| C25 | -6517(10) | 6051(1) | 5604(3) | 21(1) |
| C26 | -4836(10) | 6329(1) | 5597(3) | 23(1) |
| C27 | -6676(10) | 6595(1) | 5762(3) | 22(1) |
| C28 | -4930(10) | 6870(1) | 5742(3) | 23(1) |
| C29 | -6726(11) | 7143(1) | 5809(3) | 23(1) |
| C30 | $-4909(10)$ | 7416(1) | 5783(3) | 23(1) |
| C31 | -6673(11) | 7692(1) | 5804(3) | 23(1) |


| C32 | $-4859(11)$ | $7963(1)$ | $5774(3)$ | $26(1)$ |
| :--- | :--- | :--- | :--- | :--- |
| C33 | $-6641(12)$ | $8237(1)$ | $5782(4)$ | $33(1)$ |
| C34 | $14656(10)$ | $3694(1)$ | $3170(3)$ | $22(1)$ |
| C35 | $16511(10)$ | $3427(1)$ | $3160(3)$ | $24(1)$ |
| C36 | $14828(10)$ | $3153(1)$ | $3295(3)$ | $24(1)$ |
| C37 | $16673(11)$ | $2880(1)$ | $3274(3)$ | $22(1)$ |
| C38 | $14896(11)$ | $2604(1)$ | $3318(3)$ | $25(1)$ |
| C39 | $16690(11)$ | $2330(1)$ | $3287(3)$ | $24(1)$ |
| C40 | $14889(11)$ | $2056(1)$ | $3310(3)$ | $25(1)$ |
| C41 | $16644(11)$ | $1781(1)$ | $3296(3)$ | $27(1)$ |
| C42 | $14814(12)$ | $1510(1)$ | $3333(3)$ | $32(1)$ |
| N1 | $-4677(8)$ | $5808(1)$ | $5372(2)$ | $19(1)$ |
| O1 | $-3065(8)$ | $5757(1)$ | $6787(2)$ | $27(1)$ |
| O2 | $-6124(8)$ | $5876(1)$ | $3942(2)$ | $29(1)$ |
| O3 | $14133(7)$ | $3752(1)$ | $4059(2)$ | $23(1)$ |

Table 90.3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for 90.

| C1-O1 | 1.225(6) | C19-C24 | 1.426(6) |
| :---: | :---: | :---: | :---: |
| C1-N1 | 1.382(6) | C20-C21 | 1.371(6) |
| C1-C2 | 1.487(6) | C20-H20 | 0.95 |
| C2-C3 | 1.365(6) | C21-C22 | 1.408(6) |
| C2-C12 | 1.418(6) | C21-H21 | 0.95 |
| C3-C4 | 1.409(6) | C22-C23 | 1.364(7) |
| C3-H3 | 0.95 | C22-H22 | 0.95 |
| C4-C5 | 1.389(6) | C23-C24 | 1.420(6) |
| C4-H4 | 0.95 | C23-H23 | 0.95 |
| C5-C6 | $1.426(6)$ | C25-N1 | 1.482(5) |
| C5-C13 | 1.435(6) | C25-C26 | 1.516(6) |
| C6-C12 | 1.421(6) | C25-H25A | 0.99 |
| C6-C7 | $1.426(6)$ | C25-H25B | 0.99 |
| C7-C8 | 1.374(7) | C26-C27 | 1.540(5) |
| C7-H7 | 0.95 | C26-H26A | 0.99 |
| C8-C9 | 1.408(6) | C26-H26B | 0.99 |
| C8-H8 | 0.95 | C27-C28 | 1.518(6) |
| C9-C10 | 1.379(6) | C27-H27A | 0.99 |
| C9-H9 | 0.95 | C27-H27B | 0.99 |
| C10-C12 | 1.410(6) | C28-C29 | 1.533(6) |
| C10-C11 | $1.486(6)$ | C28-H28A | 0.99 |
| C11-O2 | 1.205(6) | C28-H28B | 0.99 |
| C11-N1 | 1.410(5) | C29-C30 | 1.532(6) |
| C13-C14 | 1.205(6) | C29-H29A | 0.99 |
| C14-C15 | 1.416(6) | C29-H29B | 0.99 |
| C15-C16 | 1.384(6) | C30-C31 | 1.527(6) |
| C15-C24 | 1.439(6) | C30-H30A | 0.99 |
| C16-C17 | 1.413(6) | C30-H30B | 0.99 |
| C16-H16 | 0.95 | C31-C32 | 1.524(6) |
| C17-C18 | 1.362(6) | C31-H31A | 0.99 |
| C17-H17 | 0.95 | C31-H31B | 0.99 |
| C18-O3 | 1.364(5) | C32-C33 | 1.525(6) |
| C18-C19 | 1.433(6) | C32-H32A | 0.99 |
| C19-C20 | $1.406(6)$ | C32-H32B | 0.99 |


| C33-H33A | 0.98 | C38-C39 | 1.527(6) |
| :---: | :---: | :---: | :---: |
| C33-H33B | 0.98 | C38-H38A | 0.99 |
| C33-H33C | 0.98 | C38-H38B | 0.99 |
| C34-O3 | $1.432(5)$ | C39-C40 | 1.533(6) |
| C34-C35 | 1.517(6) | C39-H39A | 0.99 |
| C34-H34A | 0.99 | C39-H39B | 0.99 |
| C34-H34B | 0.99 | C40-C41 | 1.522(6) |
| C35-C36 | 1.521(6) | C40-H40A | 0.99 |
| C35-H35A | 0.99 | C40-H40B | 0.99 |
| C35-H35B | 0.99 | C41-C42 | 1.527(7) |
| C36-C37 | $1.539(6)$ | C41-H41A | 0.99 |
| C36-H36A | 0.99 | C41-H41B | 0.99 |
| C36-H36B | 0.99 | C42-H42A | 0.98 |
| C37-C38 | $1.535(6)$ | C42-H42B | 0.98 |
| C37-H37A | 0.99 | C42-H42C | 0.98 |
| C37-H37B | 0.99 |  |  |
| O1-C1-N1 | 120.4(4) | C8-C7-H7 | 120.0 |
| O1-C1-C2 | 122.0(4) | C6-C7-H7 | 120.0 |
| N1-C1-C2 | 117.6(4) | C7-C8-C9 | 121.3(4) |
| C3-C2-C12 | 120.3(4) | C7-C8-H8 | 119.4 |
| C3-C2-C1 | 120.2(4) | C9-C8-H8 | 119.4 |
| C12-C2-C1 | 119.6(4) | C10-C9-C8 | 119.7(4) |
| C2-C3-C4 | 121.3(4) | C10-C9-H9 | 120.1 |
| C2-C3-H3 | 119.3 | C8-C9-H9 | 120.1 |
| C4-C3-H3 | 119.3 | C9-C10-C12 | 120.6(4) |
| C5-C4-C3 | 119.8(4) | C9-C10-C11 | 119.0(4) |
| C5-C4-H4 | 120.1 | C12-C10-C11 | 120.4(4) |
| C3-C4-H4 | 120.1 | O2-C11-N1 | 120.8(4) |
| C4-C5-C6 | 120.2(4) | O2-C11-C10 | 122.8(4) |
| C4-C5-C13 | 119.7(4) | N1-C11-C10 | 116.4(4) |
| C6-C5-C13 | 120.1(4) | C10-C12-C2 | 120.8(4) |
| C12-C6-C5 | 119.0(4) | C10-C12-C6 | 119.7(4) |
| C12-C6-C7 | 118.6(4) | C2-C12-C6 | 119.5(4) |
| C5-C6-C7 | 122.4(4) | C14-C13-C5 | 179.3(5) |
| C8-C7-C6 | 120.0(4) | C13-C14-C15 | 179.1(5) |


| C16-C15-C14 | 120.7(4) | C25-C26-C27 | 113.0(4) |
| :---: | :---: | :---: | :---: |
| C16-C15-C24 | 118.5(4) | C25-C26-H26A | 109.0 |
| C14-C15-C24 | 120.8(4) | C27-C26-H26A | 109.0 |
| C15-C16-C17 | 122.0(4) | C25-C26-H26B | 109.0 |
| C15-C16-H16 | 119.0 | C27-C26-H26B | 109.0 |
| C17-C16-H16 | 119.0 | H26A-C26-H26B | 107.8 |
| C18-C17-C16 | 119.8(4) | $\mathrm{C} 28-\mathrm{C} 27-\mathrm{C} 26$ | 111.5(4) |
| C18-C17-H17 | 120.1 | C28-C27-H27A | 109.3 |
| C16-C17-H17 | 120.1 | C26-C27-H27A | 109.3 |
| C17-C18-O3 | 124.5(4) | C28-C27-H27B | 109.3 |
| C17-C18-C19 | 121.4(4) | C26-C27-H27B | 109.3 |
| O3-C18-C19 | 114.0(4) | H27A-C27-H27B | 108.0 |
| C20-C19-C24 | 119.5(4) | C27-C28-C29 | 113.6(4) |
| C20-C19-C18 | 122.1(4) | C27-C28-H28A | 108.8 |
| C24-C19-C18 | 118.4(4) | C29-C28-H28A | 108.8 |
| C21-C20-C19 | 120.4(4) | C27-C28-H28B | 108.8 |
| C21-C20-H20 | 119.8 | C29-C28-H28B | 108.8 |
| C19-C20-H20 | 119.8 | H28A-C28-H28B | 107.7 |
| C20-C21-C22 | 120.1(4) | C30-C29-C28 | 112.4(4) |
| C20-C21-H21 | 120.0 | C30-C29-H29A | 109.1 |
| C22-C21-H21 | 120.0 | C28-C29-H29A | 109.1 |
| C23-C22-C21 | 121.3(4) | C30-C29-H29B | 109.1 |
| C23-C22-H22 | 119.4 | C28-C29-H29B | 109.1 |
| C21-C22-H22 | 119.4 | H29A-C29-H29B | 107.9 |
| C22-C23-C24 | 119.9(4) | C31-C30-C29 | 113.3(4) |
| C22-C23-H23 | 120.1 | C31-C30-H30A | 108.9 |
| C24-C23-H23 | 120.1 | C29-C30-H30A | 108.9 |
| C23-C24-C19 | 118.8(4) | C31-C30-H30B | 108.9 |
| C23-C24-C15 | 121.3(4) | C29-C30-H30B | 108.9 |
| C19-C24-C15 | 119.9(4) | H30A-C30-H30B | 107.7 |
| N1-C25-C26 | 110.0(4) | C32-C31-C30 | 113.2(4) |
| N1-C25-H25A | 109.7 | C32-C31-H31A | 108.9 |
| C26-C25-H25A | 109.7 | C30-C31-H31A | 108.9 |
| N1-C25-H25B | 109.7 | C32-C31-H31B | 108.9 |
| C26-C25-H25B | 109.7 | C30-C31-H31B | 108.9 |
| H25A-C25-H25B | 108.2 | H31A-C31-H31B | 107.8 |


| C31-C32-C33 | 112.9(4) | H37A-C37-H37B | 107.8 |
| :---: | :---: | :---: | :---: |
| C31-C32-H32A | 109.0 | C39-C38-C37 | 113.4(4) |
| C33-C32-H32A | 109.0 | C39-C38-H38A | 108.9 |
| C31-C32-H32B | 109.0 | C37-C38-H38A | 108.9 |
| C33-C32-H32B | 109.0 | C39-C38-H38B | 108.9 |
| H32A-C32-H32B | 107.8 | C37-C38-H38B | 108.9 |
| C32-C33-H33A | 109.5 | H38A-C38-H38B | 107.7 |
| C32-C33-H33B | 109.5 | C38-C39-C40 | 113.0(4) |
| H33A-C33-H33B | 109.5 | C38-C39-H39A | 109.0 |
| C32-C33-H33C | 109.5 | C40-C39-H39A | 109.0 |
| H33A-C33-H33C | 109.5 | C38-C39-H39B | 109.0 |
| H33B-C33-H33C | 109.5 | C40-C39-H39B | 109.0 |
| O3-C34-C35 | 107.6(3) | H39A-C39-H39B | 107.8 |
| O3-C34-H34A | 110.2 | C41-C40-C39 | 113.9(4) |
| C35-C34-H34A | 110.2 | C41-C40-H40A | 108.8 |
| O3-C34-H34B | 110.2 | C39-C40-H40A | 108.8 |
| C35-C34-H34B | 110.2 | C41-C40-H40B | 108.8 |
| H34A-C34-H34B | 108.5 | C39-C40-H40B | 108.8 |
| C34-C35-C36 | 112.6(4) | H40A-C40-H40B | 107.7 |
| C34-C35-H35A | 109.1 | C40-C41-C42 | 113.0(4) |
| C36-C35-H35A | 109.1 | C40-C41-H41A | 109.0 |
| C34-C35-H35B | 109.1 | C42-C41-H41A | 109.0 |
| C36-C35-H35B | 109.1 | C40-C41-H41B | 109.0 |
| H35A-C35-H35B | 107.8 | C42-C41-H41B | 109.0 |
| C35-C36-C37 | 113.3(4) | H41A-C41-H41B | 107.8 |
| C35-C36-H36A | 108.9 | C41-C42-H42A | 109.5 |
| C37-C36-H36A | 108.9 | C41-C42-H42B | 109.5 |
| C35-C36-H36B | 108.9 | H42A-C42-H42B | 109.5 |
| C37-C36-H36B | 108.9 | C41-C42-H42C | 109.5 |
| H36A-C36-H36B | 107.7 | H42A-C42-H42C | 109.5 |
| C38-C37-C36 | 112.7(4) | H42B-C42-H42C | 109.5 |
| C38-C37-H37A | 109.0 | C1-N1-C11 | 125.2(4) |
| C36-C37-H37A | 109.0 | C1-N1-C25 | 118.1(3) |
| C38-C37-H37B | 109.0 | C11-N1-C25 | 116.5(4) |
| C36-C37-H37B | 109.0 | C18-O3-C34 | 117.8(3) |

Table 90. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 90 . The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | 21(2) | 16(2) | 23(2) | $0(2)$ | -1(2) | -3(2) |
| C2 | 20(2) | 14(2) | 26(2) | 1(2) | 3(2) | -3(2) |
| C3 | 24(2) | 26(2) | 18(2) | 1(2) | 1(2) | -1(2) |
| C4 | 25(2) | 19(2) | 24(2) | 2(2) | -3(2) | 1(2) |
| C5 | 21(2) | 19(2) | 24(2) | 3(2) | 4(2) | -3(2) |
| C6 | 17(2) | 19(2) | 23(2) | 1(2) | 5(2) | -3(2) |
| C7 | 29(2) | 16(2) | 23(2) | -1(1) | 4(2) | 0(2) |
| C8 | 26(2) | 25(2) | 21(2) | -2(2) | 4(2) | -1(2) |
| C9 | 22(2) | 21(2) | 22(2) | 1(2) | -4(2) | -1(2) |
| C10 | 21(2) | 15(2) | 21(2) | -2(1) | 1(2) | -2(2) |
| C11 | 23(2) | 13(2) | 21(2) | -2(1) | -2(2) | -3(2) |
| C12 | 19(2) | 11(2) | 22(2) | $0(1)$ | 1(2) | -2(1) |
| C13 | 24(2) | 21(2) | 20(2) | 3(2) | -1(2) | $0(2)$ |
| C14 | 23(2) | 17(2) | 22(2) | 2(1) | -4(2) | 0 (2) |
| C15 | 19(2) | 14(2) | 24(2) | -3(1) | $0(2)$ | $0(2)$ |
| C16 | 21(2) | 22(2) | 21(2) | 2(2) | -6(2) | 3(2) |
| C17 | 25(2) | 20(2) | 21(2) | -4(2) | -1(2) | 2(2) |
| C18 | 18(2) | 14(2) | 23(2) | -5(1) | -1(2) | -1(2) |
| C19 | 22(2) | 10(2) | 24(2) | -3(1) | 1(2) | -4(2) |
| C20 | 23(2) | 21(2) | 27(2) | $0(2)$ | -1(2) | 5(2) |
| C21 | 25(2) | 25(2) | 23(2) | 2(2) | -4(2) | 2(2) |
| C22 | 27(2) | 24(2) | 19(2) | -3(2) | 1(2) | -3(2) |
| C23 | 24(2) | 20(2) | 24(2) | -5(2) | 3(2) | -2(2) |
| C24 | 19(2) | 16(2) | 20(2) | -4(1) | 1(2) | -2(2) |
| C25 | 22(2) | 17(2) | 26(2) | 2(2) | 1(2) | 4(2) |
| C26 | 21(2) | 19(2) | 30(2) | -2(2) | -1(2) | 2(2) |
| C27 | 23(2) | 19(2) | 24(2) | $0(2)$ | 1(2) | 3(2) |
| C28 | 25(2) | 20(2) | 23(2) | $0(2)$ | 0 (2) | 0(2) |
| C29 | 27(2) | 19(2) | 24(2) | $0(2)$ | -1(2) | 3(2) |
| C30 | 24(2) | 22(2) | 22(2) | $0(2)$ | -2(2) | 0(2) |
| C31 | 26(2) | 22(2) | 22(2) | $0(2)$ | 1(2) | 3(2) |


| C32 | $28(2)$ | $20(2)$ | $30(2)$ | $1(2)$ | $-3(2)$ | $1(2)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C33 | $35(3)$ | $24(2)$ | $37(3)$ | $2(2)$ | $-8(2)$ | $2(2)$ |
| C34 | $25(2)$ | $22(2)$ | $19(2)$ | $0(2)$ | $-2(2)$ | $0(2)$ |
| C35 | $23(2)$ | $21(2)$ | $27(2)$ | $-3(2)$ | $2(2)$ | $2(2)$ |
| C36 | $24(2)$ | $24(2)$ | $23(2)$ | $-2(2)$ | $3(2)$ | $0(2)$ |
| C37 | $24(2)$ | $20(2)$ | $23(2)$ | $-1(2)$ | $2(2)$ | $-2(2)$ |
| C38 | $25(2)$ | $24(2)$ | $26(2)$ | $2(2)$ | $2(2)$ | $-2(2)$ |
| C39 | $26(2)$ | $19(2)$ | $26(2)$ | $1(2)$ | $1(2)$ | $-2(2)$ |
| C40 | $24(2)$ | $26(2)$ | $26(2)$ | $1(2)$ | $2(2)$ | $-2(2)$ |
| C41 | $30(2)$ | $24(2)$ | $27(2)$ | $3(2)$ | $2(2)$ | $1(2)$ |
| C42 | $34(3)$ | $26(2)$ | $37(3)$ | $3(2)$ | $-2(2)$ | $3(2)$ |
| N1 | $21(2)$ | $18(2)$ | $18(2)$ | $-1(1)$ | $3(1)$ | $-2(1)$ |
| O1 | $32(2)$ | $25(1)$ | $22(2)$ | $-2(1)$ | $0(1)$ | $7(1)$ |
| O2 | $34(2)$ | $30(2)$ | $22(2)$ | $2(1)$ | $-2(1)$ | $7(1)$ |
| O3 | $27(2)$ | $21(1)$ | $21(2)$ | $-2(1)$ | $0(1)$ | $6(1)$ |

Table 90.5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ For 90 .

|  | X | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| H3 | 697 | 5369 | 6998 | 27 |
| H4 | 3855 | 5002 | 6632 | 27 |
| H7 | 2304 | 4929 | 3588 | 27 |
| H8 | -689 | 5161 | 2549 | 29 |
| H9 | -3818 | 5526 | 2945 | 26 |
| H16 | 7839 | 4448 | 3380 | 26 |
| H17 | 11095 | 4095 | 2990 | 27 |
| H20 | 14980 | 3732 | 5629 | 29 |
| H21 | 14481 | 3835 | 7084 | 29 |
| H22 | 11165 | 4182 | 7472 | 28 |
| H23 | 8531 | 4444 | 6423 | 27 |
| H25A | -7200 | 6019 | 6190 | 26 |
| H25B | -8214 | 6063 | 5180 | 26 |
| H26A | -4015 | 6350 | 5025 | 28 |
| H26B | -3221 | 6320 | 6050 | 28 |
| H27A | -8300 | 6605 | 5312 | 26 |
| H27B | -7477 | 6577 | 6338 | 26 |
| H28A | -3957 | 6875 | 5192 | 27 |
| H28B | -3427 | 6866 | 6230 | 27 |
| H29A | -8232 | 7147 | 5322 | 28 |
| H29B | -7691 | 7139 | 6361 | 28 |
| H30A | -3464 | 7415 | 6287 | 28 |
| H30B | -3865 | 7414 | 5246 | 28 |
| H31A | -8122 | 7692 | 5301 | 28 |
| H31B | -7711 | 7694 | 6342 | 28 |
| H32A | -3799 | 7960 | 5241 | 31 |
| H32B | -3430 | 7964 | 6282 | 31 |
| H33A | -7995 | 8242 | 5264 | 49 |
| H33B | -5368 | 8404 | 5778 | 49 |
| H33C | -7705 | 8241 | 6307 | 49 |


| H34A | 15652 | 3858 | 2918 | 27 |
| :--- | :--- | :--- | :--- | :--- |
| H34B | 12819 | 3662 | 2821 | 27 |
| H35A | 18083 | 3442 | 3625 | 28 |
| H35B | 17388 | 3415 | 2595 | 28 |
| H36A | 13238 | 3139 | 2835 | 29 |
| H36B | 13972 | 3164 | 3864 | 29 |
| H37A | 17688 | 2878 | 2732 | 27 |
| H37B | 18140 | 2883 | 3772 | 27 |
| H38A | 13898 | 2605 | 3864 | 30 |
| H38B | 13413 | 2602 | 2824 | 30 |
| H39A | 18142 | 2330 | 3790 | 28 |
| H39B | 17725 | 2331 | 2749 | 28 |
| H40A | 13824 | 2057 | 3842 | 30 |
| H40B | 13460 | 2056 | 2801 | 30 |
| H41A | 18092 | 1781 | 3800 | 32 |
| H41B | 17682 | 1777 | 2759 | 32 |
| H42A | 13640 | 1521 | 3834 | 49 |
| H42B | 16068 | 1341 | 3393 | 49 |
| H42C | 13561 | 1494 | 2796 | 49 |

Table 90.6. Torsion angles [ ${ }^{\circ}$ ] for 90 .

| O1-C1-C2-C3 | 1.3(6) | C7-C6-C12-C2 | 179.1(4) |
| :---: | :---: | :---: | :---: |
| N1-C1-C2-C3 | -179.2(4) | C14-C15-C16-C17 | -179.5(4) |
| O1-C1-C2-C12 | -178.9(4) | C24-C15-C16-C17 | 1.1(7) |
| N1-C1-C2-C12 | 0.5(5) | C15-C16-C17-C18 | 0.7(7) |
| C12-C2-C3-C4 | 0.1(6) | C16-C17-C18-O3 | 176.9(4) |
| C1-C2-C3-C4 | 179.8(4) | C16-C17-C18-C19 | -2.3(6) |
| C2-C3-C4-C5 | 0.4(7) | C17-C18-C19-C20 | -176.3(4) |
| C3-C4-C5-C6 | -0.2(6) | O3-C18-C19-C20 | 4.4(6) |
| C3-C4-C5-C13 | 178.8(4) | C17-C18-C19-C24 | 2.1(6) |
| C4-C5-C6-C12 | -0.4(6) | O3-C18-C19-C24 | -177.2(3) |
| C13-C5-C6-C12 | -179.5(4) | C24-C19-C20-C21 | 0.5(6) |
| C4-C5-C6-C7 | -178.5(4) | C18-C19-C20-C21 | 178.9(4) |
| C13-C5-C6-C7 | 2.4(6) | C19-C20-C21-C22 | 0.4(7) |
| C12-C6-C7-C8 | 1.1(6) | C20-C21-C22-C23 | -1.7(7) |
| C5-C6-C7-C8 | 179.2(4) | C21-C22-C23-C24 | 1.9(7) |
| C6-C7-C8-C9 | -0.2(7) | C22-C23-C24-C19 | -0.9(6) |
| C7-C8-C9-C10 | 0.3(7) | C22-C23-C24-C15 | -179.4(4) |
| C8-C9-C10-C12 | -1.3(6) | C20-C19-C24-C23 | -0.3(6) |
| C8-C9-C10-C11 | 179.9(4) | C18-C19-C24-C23 | -178.7(4) |
| C9-C10-C11-O2 | -3.3(6) | C20-C19-C24-C15 | 178.2(4) |
| C12-C10-C11-O2 | 177.9(4) | C18-C19-C24-C15 | -0.3(6) |
| C9-C10-C11-N1 | 177.3(4) | C16-C15-C24-C23 | 177.1(4) |
| C12-C10-C11-N1 | -1.5(6) | C14-C15-C24-C23 | -2.2(6) |
| C9-C10-C12-C2 | -179.0(4) | C16-C15-C24-C19 | -1.3(6) |
| C11-C10-C12-C2 | -0.2(6) | C14-C15-C24-C19 | 179.3(4) |
| C9-C10-C12-C6 | 2.2(6) | N1-C25-C26-C27 | 175.5(3) |
| C11-C10-C12-C6 | -179.0(4) | C25-C26-C27-C28 | -179.4(4) |
| C3-C2-C12-C10 | -179.6(4) | C26-C27-C28-C29 | 174.1(4) |
| C1-C2-C12-C10 | 0.7(6) | C27-C28-C29-C30 | -179.8(3) |
| C3-C2-C12-C6 | -0.7(6) | C28-C29-C30-C31 | 177.2(3) |
| C1-C2-C12-C6 | 179.5(4) | C29-C30-C31-C32 | -179.8(4) |
| C5-C6-C12-C10 | 179.7(4) | C30-C31-C32-C33 | 179.1(4) |
| C7-C6-C12-C10 | -2.1(6) | O3-C34-C35-C36 | 75.9(4) |
| C5-C6-C12-C2 | 0.9(6) | C34-C35-C36-C37 | 179.2(4) |


| $\mathrm{C} 35-\mathrm{C} 36-\mathrm{C} 37-\mathrm{C} 38$ | $-174.2(4)$ | $\mathrm{O} 2-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 1$ | $-176.5(4)$ |
| :--- | :---: | :--- | :---: |
| $\mathrm{C} 36-\mathrm{C} 37-\mathrm{C} 38-\mathrm{C} 39$ | $179.3(3)$ | $\mathrm{C} 10-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 1$ | $2.9(6)$ |
| $\mathrm{C} 37-\mathrm{C} 38-\mathrm{C} 39-\mathrm{C} 40$ | $-178.6(4)$ | $\mathrm{O} 2-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 25$ | $-3.2(6)$ |
| $\mathrm{C} 38-\mathrm{C} 39-\mathrm{C} 40-\mathrm{C} 41$ | $-178.9(4)$ | $\mathrm{C} 10-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 25$ | $176.2(3)$ |
| $\mathrm{C} 39-\mathrm{C} 40-\mathrm{C} 41-\mathrm{C} 42$ | $179.1(4)$ | $\mathrm{C} 26-\mathrm{C} 25-\mathrm{N} 1-\mathrm{C} 1$ | $85.6(4)$ |
| O1-C1-N1-C11 | $177.1(4)$ | $\mathrm{C} 26-\mathrm{C} 25-\mathrm{N} 1-\mathrm{C} 11$ | $-88.2(4)$ |
| C2-C1-N1-C11 | $-2.4(6)$ | $\mathrm{C} 17-\mathrm{C} 18-\mathrm{O} 3-\mathrm{C} 34$ | $3.8(6)$ |
| O1-C1-N1-C25 | $3.8(6)$ | $\mathrm{C} 19-\mathrm{C} 18-\mathrm{O} 3-\mathrm{C} 34$ | $-177.0(3)$ |
| C2-C1-N1-C25 | $-175.6(3)$ | $\mathrm{C} 35-\mathrm{C} 34-\mathrm{O} 3-\mathrm{C} 18$ | $-174.8(3)$ |

End crystallographic info for 90 .

## Crystallographic Material for 100

Crystallographic Material for $\mathbf{1 0 0}$.
X-ray Experimental.
Table 100.1. Crystallographic Data for $\mathbf{1 0 0}$.
Table 100.2. Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the non-hydrogen atoms of $\mathbf{1 0 0}$.

Table 100.3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of $\mathbf{1 0 0}$.

Table 100.4. Anisotropic thermal parameters for the non-hydrogen atoms of $\mathbf{1 0 0}$.

Table 100.5. Fractional coordinates and isotropic thermal parameters $\left(\AA^{2}\right)$ for the hydrogen atoms of $\mathbf{1 0 0}$.

Table 100.6. Torsion Angles $\left(^{(0)}\right.$ for the non-hydrogen atoms of $\mathbf{1 0 0}$.

X-ray Experimental for complex $\mathrm{C}_{44} \mathrm{H}_{53} \mathrm{NO}_{3}$ (100): Crystals grew as long, orange laths by vapor diffusion (solvent $=\mathrm{p}$-xylenes, precipitant $=$ acetonitrile). The data crystal was cut from a larger crystal and had approximate dimensions; $0.28 \times 0.06 \times 0.02 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{Cu} \mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA)$ with collimating mirror monochromators. A total of 581 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 25 seconds per frame with a detector offset of $+/-40.3^{\circ}$ and 75 seconds per frame with a detector offset of $+/-$ $110.0^{\circ}$. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.38.43f. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6. ${ }^{3}$ Structure analysis was aided by use of the programs PLATON9 $8^{4}$ and WinGX. ${ }^{5}$ The hydrogen atoms were calculated in ideal positions
with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms).

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.1829 * \mathrm{P})^{2}+\right.$ $(0.4842 * \mathrm{P})]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.295 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0947 and a goodness of fit, $\mathrm{S},=1.04$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S, are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. ${ }^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.38.43f.
2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\left|\mathrm{F}_{\mathrm{C}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{W}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 100.1 Crystal data and structure refinement for $\mathbf{1 0 0}$.

| Identification code | shelx |
| :---: | :---: |
| Empirical formula | C44 H53 N O3 |
| Formula weight | 643.87 |
| Temperature | 100(2) K |
| Wavelength | $1.54184 \approx$ |
| Crystal system | monoclinic |
| Space group | C c |
| Unit cell dimensions | $\begin{array}{ll} \mathrm{a}=4.6678(13) \approx & \alpha=90 \infty . \\ \mathrm{b}=49.083(9) \approx & \beta=112.97(3) \infty . \\ \mathrm{c}=16.707(4) \approx & \gamma=90 \infty . \end{array}$ |
| Volume | 3524.4(16) $\approx^{3}$ |
| Z | 4 |
| Density (calculated) | $1.213 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.576 \mathrm{~mm}^{-1}$ |
| F(000) | 1392 |
| Crystal size | $0.280 \times 0.062 \times 0.023 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 3.391 to $74.798 \times 0$. |
| Index ranges | $-5<=\mathrm{h}<=5,-55<=\mathrm{k}<=60,-10<=1<=20$ |
| Reflections collected | 5696 |
| Independent reflections | $3928[\mathrm{R}(\mathrm{int})=0.0658]$ |
| Completeness to theta $=67.684 \infty$ | 98.4 \% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00 and 0.564 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 3928 / 290 / 435 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.045 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0947, \mathrm{wR} 2=0.2648$ |
| R indices (all data) | $\mathrm{R} 1=0.1159, \mathrm{wR} 2=0.2952$ |
| Absolute structure parameter | -0.5(7) |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.671 and -0.442 e. $\sim^{-3}$ |

Table 2.100. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for $\mathbf{1 0 0} . U(e q)$ is defined as one third of the trace of the orthogonalized $U^{i j}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| C1 | -4104(18) | 8206(1) | 4479(5) | 24(1) |
| C2 | -2379(17) | 7994(1) | 4233(5) | 22(1) |
| C3 | -3175(18) | 7931(2) | 3373(5) | 25(1) |
| C4 | -1540(18) | 7726(2) | 3135(5) | 26(2) |
| C5 | 872(19) | 7590(1) | 3765(5) | 26(2) |
| C6 | 1748(17) | 7647(1) | 4660(5) | 20(1) |
| C7 | 4190(17) | 7508(1) | 5329(5) | 22(1) |
| C8 | 4872(18) | 7577(2) | 6187(5) | 26(2) |
| C9 | 3182(17) | 7782(2) | 6422(5) | 24(1) |
| C10 | 821(17) | 7915(1) | 5774(4) | 21(1) |
| C11 | -923(16) | 8127(1) | 6032(5) | 22(1) |
| C12 | 44(16) | 7855(1) | 4892(5) | 21(1) |
| C13 | 5958(17) | 7308(2) | 5112(5) | 24(1) |
| C14 | 7444(19) | 7140(2) | 4913(5) | 26(2) |
| C15 | 9172(17) | 6939(1) | 4690(5) | 23(1) |
| C16 | 8705(17) | 6894(2) | 3826(5) | 25(2) |
| C17 | 10427(17) | 6698(2) | 3589(5) | 23(1) |
| C18 | 12561(17) | 6542(1) | 4215(5) | 23(1) |
| C19 | 13215(17) | 6585(1) | 5113(5) | 23(1) |
| C20 | 15507(18) | 6434(2) | 5775(5) | 28(2) |
| C21 | 16145(18) | 6481(2) | 6634(5) | 29(2) |
| C22 | 14393(19) | 6674(2) | 6871(5) | 29(2) |
| C23 | 12134(18) | 6824(1) | 6245(5) | 25(2) |
| C24 | 11494(16) | 6785(1) | 5353(5) | 22(1) |
| C25 | -5003(18) | 8478(2) | 5596(5) | 28(2) |
| C26 | -3389(18) | 8752(1) | 5618(5) | 25(2) |
| C27 | -5176(18) | 8992(2) | 5790(5) | 26(2) |
| C28 | -3508(18) | 9263(1) | 5766(5) | 25(2) |
| C29 | -5277(18) | 9514(1) | 5875(5) | 24(1) |
| C30 | -3611(19) | 9776(1) | 5807(5) | 27(2) |
| C31 | $-5270(19)$ | 10037(2) | 5890(5) | 27(2) |


| C32 | $-3562(19)$ | $10292(2)$ | $5791(5)$ | $29(2)$ |
| :--- | ---: | ---: | :--- | :--- |
| C33 | $-5200(20)$ | $10556(2)$ | $5868(6)$ | $31(2)$ |
| C34 | $-3470(20)$ | $10810(2)$ | $5760(7)$ | $40(2)$ |
| C35 | $13781(18)$ | $6286(2)$ | $3171(5)$ | $27(2)$ |
| C36 | $15609(19)$ | $6026(2)$ | $3158(5)$ | $30(2)$ |
| C37 | $14066(19)$ | $5771(2)$ | $3342(5)$ | $28(2)$ |
| C38 | $15720(20)$ | $5509(2)$ | $3299(5)$ | $31(2)$ |
| C39 | $14030(20)$ | $5254(2)$ | $3411(5)$ | $29(2)$ |
| C40 | $15550(20)$ | $4988(2)$ | $3335(5)$ | $29(2)$ |
| C41 | $13770(20)$ | $4737(2)$ | $3433(5)$ | $32(2)$ |
| C42 | $15205(19)$ | $4466(2)$ | $3335(5)$ | $29(2)$ |
| C43 | $13350(20)$ | $4220(2)$ | $3431(5)$ | $32(2)$ |
| C44 | $14760(30)$ | $3952(2)$ | $3316(6)$ | $42(2)$ |
| N1 | $-3338(15)$ | $8260(1)$ | $5363(4)$ | $22(1)$ |
| O1 | $-6155(14)$ | $8341(1)$ | $3935(4)$ | $34(1)$ |
| O2 | $-321(14)$ | $8194(1)$ | $6785(3)$ | $31(1)$ |
| O3 | $14249(13)$ | $6336(1)$ | $4051(3)$ | $28(1)$ |

Table 100.3. Bond lengths [ $\approx$ ] and angles [ $\infty$ ] for $\mathbf{1 0 0}$.

| C1-O1 | 1.227(10) |
| :---: | :---: |
| C1-N1 | 1.402(9) |
| C1-C2 | 1.471(9) |
| C2-C3 | 1.370(10) |
| C2-C12 | 1.408(10) |
| C3-C4 | $1.413(10)$ |
| C3-H3 | 0.9500 |
| C4-C5 | $1.375(11)$ |
| C4-H4 | 0.9500 |
| C5-C6 | 1.417(10) |
| C5-H5 | 0.9500 |
| C6-C7 | $1.423(10)$ |
| C6-C12 | 1.437(9) |
| C7-C8 | 1.383(10) |
| C7-C13 | 1.416(10) |
| C8-C9 | $1.425(10)$ |
| C8-H8 | 0.9500 |
| C9-C10 | $1.372(10)$ |
| C9-H9 | 0.9500 |
| C10-C12 | 1.403(9) |
| C10-C11 | 1.487(9) |
| C11-O2 | 1.222(9) |
| C11-N1 | 1.401(9) |
| C13-C14 | 1.204(11) |
| C14-C15 | 1.414(10) |
| C15-C16 | 1.391(10) |
| C15-C24 | 1.427(11) |
| C16-C17 | 1.408(10) |
| C16-H16 | 0.9500 |
| C17-C18 | $1.363(11)$ |
| C17-H17 | 0.9500 |
| C18-O3 | 1.373(9) |
| C18-C19 | $1.426(10)$ |
| C19-C20 | $1.413(11)$ |


| C19-C24 | 1.422(10) |
| :---: | :---: |
| C20-C21 | 1.367(11) |
| C20-H20 | 0.9500 |
| C21-C22 | $1.405(11)$ |
| C21-H21 | 0.9500 |
| C22-C23 | $1.372(12)$ |
| C22-H22 | 0.9500 |
| C23-C24 | $1.413(10)$ |
| C23-H23 | 0.9500 |
| C25-N1 | 1.463(9) |
| C25-C26 | $1.534(10)$ |
| C25-H25A | 0.9900 |
| C25-H25B | 0.9900 |
| C26-C27 | 1.534(9) |
| C26-H26A | 0.9900 |
| C26-H26B | 0.9900 |
| C27-C28 | 1.549(10) |
| C27-H27A | 0.9900 |
| C27-H27B | 0.9900 |
| C28-C29 | 1.534(10) |
| C28-H28A | 0.9900 |
| C28-H28B | 0.9900 |
| C29-C30 | 1.528(9) |
| C29-H29A | 0.9900 |
| C29-H29B | 0.9900 |
| C30-C31 | 1.532(10) |
| C30-H30A | 0.9900 |
| C30-H30B | 0.9900 |
| C31-C32 | 1.529(11) |
| C31-H31A | 0.9900 |
| C31-H31B | 0.9900 |
| C32-C33 | $1.535(10)$ |
| C32-H32A | 0.9900 |
| C32-H32B | 0.9900 |
| C33-C34 | $1.529(11)$ |
| C33-H33A | 0.9900 |


| C33-H33B | 0.9900 |
| :---: | :---: |
| C34-H34A | 0.9800 |
| C34-H34B | 0.9800 |
| C34-H34C | 0.9800 |
| C35-O3 | 1.422(8) |
| C35-C36 | 1.540(10) |
| C35-H35A | 0.9900 |
| C35-H35B | 0.9900 |
| C36-C37 | 1.534(11) |
| C36-H36A | 0.9900 |
| C36-H36B | 0.9900 |
| C37-C38 | 1.517(10) |
| C37-H37A | 0.9900 |
| C37-H37B | 0.9900 |
| C38-C39 | $1.525(11)$ |
| C38-H38A | 0.9900 |
| C38-H38B | 0.9900 |
| C39-C40 | $1.515(10)$ |
| C39-H39A | 0.9900 |
| C39-H39B | 0.9900 |
| C40-C41 | 1.531(11) |
| C40-H40A | 0.9900 |
| C40-H40B | 0.9900 |
| C41-C42 | 1.527(10) |
| C41-H41A | 0.9900 |
| C41-H41B | 0.9900 |
| C42-C43 | 1.530(11) |
| C42-H42A | 0.9900 |
| C42-H42B | 0.9900 |
| C43-C44 | 1.519(11) |
| C43-H43A | 0.9900 |
| C43-H43B | 0.9900 |
| C44-H44A | 0.9800 |
| C44-H44B | 0.9800 |
| C44-H44C | 0.9800 |


| O1-C1-N1 | 118.9(6) |
| :---: | :---: |
| O1-C1-C2 | 122.0(7) |
| N1-C1-C2 | 119.1(7) |
| C3-C2-C12 | 121.2(6) |
| C3-C2-C1 | 119.9(7) |
| C12-C2-C1 | 118.9(6) |
| C2-C3-C4 | 120.0(7) |
| C2-C3-H3 | 120.0 |
| C4-C3-H3 | 120.0 |
| C5-C4-C3 | 120.1(7) |
| C5-C4-H4 | 120.0 |
| C3-C4-H4 | 120.0 |
| C4-C5-C6 | 121.7(7) |
| C4-C5-H5 | 119.2 |
| C6-C5-H5 | 119.2 |
| C5-C6-C7 | 123.1(6) |
| C5-C6-C12 | 117.6(7) |
| C7-C6-C12 | 119.2(6) |
| C8-C7-C13 | 120.9(7) |
| C8-C7-C6 | 119.0(7) |
| C13-C7-C6 | 120.0(6) |
| C7-C8-C9 | 122.0(7) |
| C7-C8-H8 | 119.0 |
| C9-C8-H8 | 119.0 |
| C10-C9-C8 | 118.7(7) |
| C10-C9-H9 | 120.7 |
| C8-C9-H9 | 120.7 |
| C9-C10-C12 | 121.9(6) |
| C9-C10-C11 | 117.8(6) |
| C12-C10-C11 | 120.3(6) |
| O2-C11-N1 | 119.1(6) |
| O2-C11-C10 | 123.8(7) |
| N1-C11-C10 | 117.1(6) |
| C10-C12-C2 | 121.3(6) |
| C10-C12-C6 | 119.2(7) |
| C2-C12-C6 | 119.5(6) |


| C14-C13-C7 | 178.9(8) |
| :---: | :---: |
| C13-C14-C15 | 178.8(8) |
| C16-C15-C14 | 120.7(7) |
| C16-C15-C24 | 119.0(7) |
| C14-C15-C24 | 120.2(7) |
| C15-C16-C17 | 121.8(7) |
| C15-C16-H16 | 119.1 |
| C17-C16-H16 | 119.1 |
| C18-C17-C16 | 119.6(6) |
| C18-C17-H17 | 120.2 |
| C16-C17-H17 | 120.2 |
| C17-C18-O3 | 124.3(6) |
| C17-C18-C19 | 121.1(6) |
| O3-C18-C19 | 114.5(6) |
| C20-C19-C24 | 118.7(7) |
| C20-C19-C18 | 122.1(7) |
| C24-C19-C18 | 119.1(7) |
| C21-C20-C19 | 121.4(7) |
| C21-C20-H20 | 119.3 |
| C19-C20-H20 | 119.3 |
| C20-C21-C22 | 119.8(7) |
| C20-C21-H21 | 120.1 |
| C22-C21-H21 | 120.1 |
| C23-C22-C21 | 120.3(7) |
| C23-C22-H22 | 119.8 |
| C21-C22-H22 | 119.8 |
| C22-C23-C24 | 121.0(7) |
| C22-C23-H23 | 119.5 |
| C24-C23-H23 | 119.5 |
| C23-C24-C19 | 118.6(7) |
| C23-C24-C15 | 122.1(7) |
| C19-C24-C15 | 119.2(6) |
| N1-C25-C26 | 110.0(6) |
| N1-C25-H25A | 109.7 |
| C26-C25-H25A | 109.7 |
| N1-C25-H25B | 109.7 |


| C26-C25-H25B | 109.7 |
| :---: | :---: |
| H25A-C25-H25B | 108.2 |
| C27-C26-C25 | 112.3(6) |
| C27-C26-H26A | 109.1 |
| C25-C26-H26A | 109.1 |
| C27-C26-H26B | 109.1 |
| C25-C26-H26B | 109.1 |
| H26A-C26-H26B | 107.9 |
| C26-C27-C28 | 109.8(6) |
| C26-C27-H27A | 109.7 |
| C28-C27-H27A | 109.7 |
| C26-C27-H27B | 109.7 |
| C28-C27-H27B | 109.7 |
| H27A-C27-H27B | 108.2 |
| C29-C28-C27 | 112.8(6) |
| C29-C28-H28A | 109.0 |
| C27-C28-H28A | 109.0 |
| C29-C28-H28B | 109.0 |
| C27-C28-H28B | 109.0 |
| H28A-C28-H28B | 107.8 |
| C30-C29-C28 | 110.7(6) |
| C30-C29-H29A | 109.5 |
| C28-C29-H29A | 109.5 |
| C30-C29-H29B | 109.5 |
| C28-C29-H29B | 109.5 |
| H29A-C29-H29B | 108.1 |
| C29-C30-C31 | 113.9(6) |
| C29-C30-H30A | 108.8 |
| C31-C30-H30A | 108.8 |
| C29-C30-H30B | 108.8 |
| C31-C30-H30B | 108.8 |
| H30A-C30-H30B | 107.7 |
| C32-C31-C30 | 111.9(6) |
| C32-C31-H31A | 109.2 |
| C30-C31-H31A | 109.2 |
| C32-C31-H31B | 109.2 |


| C30-C31-H31B | 109.2 |
| :---: | :---: |
| H31A-C31-H31B | 107.9 |
| C31-C32-C33 | 112.7(6) |
| C31-C32-H32A | 109.0 |
| C33-C32-H32A | 109.0 |
| C31-C32-H32B | 109.0 |
| C33-C32-H32B | 109.0 |
| H32A-C32-H32B | 107.8 |
| C34-C33-C32 | 112.0(7) |
| C34-C33-H33A | 109.2 |
| C32-C33-H33A | 109.2 |
| C34-C33-H33B | 109.2 |
| C32-C33-H33B | 109.2 |
| H33A-C33-H33B | 107.9 |
| C33-C34-H34A | 109.5 |
| C33-C34-H34B | 109.5 |
| H34A-C34-H34B | 109.5 |
| C33-C34-H34C | 109.5 |
| H34A-C34-H34C | 109.5 |
| H34B-C34-H34C | 109.5 |
| O3-C35-C36 | 107.1(6) |
| O3-C35-H35A | 110.3 |
| C36-C35-H35A | 110.3 |
| O3-C35-H35B | 110.3 |
| C36-C35-H35B | 110.3 |
| H35A-C35-H35B | 108.5 |
| C37-C36-C35 | 111.6(6) |
| C37-C36-H36A | 109.3 |
| C35-C36-H36A | 109.3 |
| C37-C36-H36B | 109.3 |
| C35-C36-H36B | 109.3 |
| H36A-C36-H36B | 108.0 |
| C38-C37-C36 | 113.4(7) |
| C38-C37-H37A | 108.9 |
| C36-C37-H37A | 108.9 |
| C38-C37-H37B | 108.9 |


| C36-C37-H37B | 108.9 |
| :---: | :---: |
| H37A-C37-H37B | 107.7 |
| C37-C38-C39 | 113.2(7) |
| C37-C38-H38A | 108.9 |
| C39-C38-H38A | 108.9 |
| C37-C38-H38B | 108.9 |
| C39-C38-H38B | 108.9 |
| H38A-C38-H38B | 107.8 |
| C40-C39-C38 | 114.6(7) |
| C40-C39-H39A | 108.6 |
| C38-C39-H39A | 108.6 |
| C40-C39-H39B | 108.6 |
| C38-C39-H39B | 108.6 |
| H39A-C39-H39B | 107.6 |
| C39-C40-C41 | 113.3(7) |
| C39-C40-H40A | 108.9 |
| C41-C40-H40A | 108.9 |
| C39-C40-H40B | 108.9 |
| C41-C40-H40B | 108.9 |
| H40A-C40-H40B | 107.7 |
| C42-C41-C40 | 114.2(7) |
| C42-C41-H41A | 108.7 |
| C40-C41-H41A | 108.7 |
| C42-C41-H41B | 108.7 |
| C40-C41-H41B | 108.7 |
| H41A-C41-H41B | 107.6 |
| C41-C42-C43 | 112.6(7) |
| C41-C42-H42A | 109.1 |
| C43-C42-H42A | 109.1 |
| C41-C42-H42B | 109.1 |
| C43-C42-H42B | 109.1 |
| H42A-C42-H42B | 107.8 |
| C44-C43-C42 | 112.2(7) |
| C44-C43-H43A | 109.2 |
| C42-C43-H43A | 109.2 |
| C44-C43-H43B | 109.2 |


| C42-C43-H43B | 109.2 |
| :--- | :--- |
| H43A-C43-H43B | 107.9 |
| C43-C44-H44A | 109.5 |
| C43-C44-H44B | 109.5 |
| H44A-C44-H44B | 109.5 |
| C43-C44-H44C | 109.5 |
| H44A-C44-H44C | 109.5 |
| H44B-C44-H44C | 109.5 |
| C11-N1-C1 | $123.2(6)$ |
| C11-N1-C25 | $118.3(6)$ |
| C1-N1-C25 | $118.4(6)$ |
| C18-O3-C35 | $117.7(6)$ |

Symmetry transformations used to generate equivalent atoms:

Table 100.4. Anisotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for $\mathbf{1 0 0}$. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | 28(3) | 27(3) | 18(3) | -5(3) | 11(3) | -3(3) |
| C2 | 30(4) | 24(3) | 14(3) | -4(2) | 11(3) | 3(3) |
| C3 | 31(4) | 29(3) | 18(3) | 1(3) | 12(3) | 1(3) |
| C4 | 29(4) | 37(4) | 16(3) | -1(3) | 12(3) | $0(3)$ |
| C5 | 35(4) | 24(3) | 22(3) | $0(3)$ | 12(3) | 0 (3) |
| C6 | 24(3) | 22(3) | 18(3) | 1(2) | 14(3) | -1(2) |
| C7 | 26(3) | 25(3) | 20(3) | $0(3)$ | 13(3) | -2(3) |
| C8 | 25(3) | 31(3) | 22(3) | -2(3) | 10(3) | 1(3) |
| C9 | 22(3) | 27(3) | 23(3) | -3(3) | 10(3) | $0(3)$ |
| C10 | 27(3) | 22(3) | 18(3) | -2(3) | 12(3) | 1(3) |
| C11 | 22(3) | 25(3) | 18(3) | -3(3) | 7(3) | 1(3) |
| C12 | 21(3) | 25(3) | 21(3) | -6(3) | 12(3) | -3(2) |
| C13 | 20(3) | 32(3) | 21(3) | 1(3) | 11(3) | -2(3) |
| C14 | 32(4) | 26(3) | 22(3) | $0(3)$ | 12(3) | -2(3) |
| C15 | 21(3) | 26(3) | 22(3) | -3(3) | 8(3) | -1(3) |
| C16 | 23(3) | 32(3) | 19(3) | -1(3) | 8(3) | 3(3) |
| C17 | 25(3) | 28(3) | 17(3) | -4(3) | 9(3) | -3(3) |
| C18 | 27(4) | 21(3) | 20(3) | -6(3) | 8(3) | 0 (2) |
| C19 | 30(4) | 19(3) | 19(3) | -3(2) | 11(3) | -2(2) |
| C20 | 30(4) | 28(3) | 22(3) | -2(3) | 7(3) | 2(3) |
| C21 | 31(4) | 34(3) | 20(3) | 4(3) | 7(3) | 1(3) |
| C22 | 30(4) | 41(4) | 18(3) | -3(3) | 11(3) | -4(3) |
| C23 | 30(4) | 28(3) | 20(3) | -6(3) | 11(3) | -3(3) |
| C24 | 25(3) | 24(3) | 18(3) | -5(3) | $9(3)$ | -6(3) |
| C25 | 27(4) | 27(3) | 29(4) | -2(3) | 8(3) | 2(3) |
| C26 | 28(3) | 24(3) | 25(3) | -4(3) | 11(3) | 3(3) |
| C27 | 23(3) | 30(3) | 25(3) | 2(3) | $9(3)$ | 1(3) |
| C28 | 28(4) | 27(3) | 20(3) | $0(3)$ | 10(3) | 1(3) |
| C29 | 24(3) | 27(3) | 21(3) | -3(3) | 8(3) | -1(2) |
| C30 | 29(4) | 29(3) | 22(3) | -4(3) | 10(3) | -4(3) |
| C31 | 29(4) | 32(3) | 21(3) | -4(3) | 13(3) | -2(3) |


| C32 | $30(4)$ | $30(3)$ | $22(3)$ | $3(3)$ | $5(3)$ | $4(3)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| C33 | $35(4)$ | $26(3)$ | $32(4)$ | $-1(3)$ | $12(3)$ | $4(3)$ |
| C34 | $42(5)$ | $28(3)$ | $47(5)$ | $3(4)$ | $16(4)$ | $-2(3)$ |
| C35 | $30(4)$ | $34(4)$ | $14(3)$ | $-5(3)$ | $5(3)$ | $3(3)$ |
| C36 | $33(4)$ | $35(4)$ | $22(3)$ | $-8(3)$ | $10(3)$ | $1(3)$ |
| C37 | $30(4)$ | $34(4)$ | $19(3)$ | $-4(3)$ | $8(3)$ | $3(3)$ |
| C38 | $37(4)$ | $29(3)$ | $22(3)$ | $2(3)$ | $9(3)$ | $5(3)$ |
| C39 | $31(4)$ | $31(3)$ | $21(3)$ | $0(3)$ | $5(3)$ | $6(3)$ |
| C40 | $36(4)$ | $30(3)$ | $20(3)$ | $1(3)$ | $8(3)$ | $5(3)$ |
| C41 | $36(4)$ | $36(4)$ | $19(3)$ | $-1(3)$ | $7(3)$ | $5(3)$ |
| C42 | $30(4)$ | $35(4)$ | $22(3)$ | $-4(3)$ | $10(3)$ | $6(3)$ |
| C43 | $36(4)$ | $40(4)$ | $22(3)$ | $2(3)$ | $13(3)$ | $3(3)$ |
| C44 | $58(6)$ | $36(4)$ | $34(5)$ | $-2(4)$ | $18(4)$ | $7(4)$ |
| N1 | $30(3)$ | $19(2)$ | $14(3)$ | $-2(2)$ | $5(2)$ | $0(2)$ |
| O1 | $38(3)$ | $37(3)$ | $17(2)$ | $0(2)$ | $0(2)$ | $10(2)$ |
| O2 | $34(3)$ | $38(3)$ | $16(2)$ | $-5(2)$ | $6(2)$ | $4(2)$ |
| O3 | $34(3)$ | $31(2)$ | $18(2)$ | $-2(2)$ | $9(2)$ | $7(2)$ |
|  |  |  |  |  |  |  |

Table 100.5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\approx^{2} \times 10^{3}\right)$ for $\mathbf{1 0 0}$.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H3 | -4825 | 8026 | 2937 | 31 |
| H4 | -2107 | 7681 | 2540 | 32 |
| H5 | 1978 | 7455 | 3595 | 32 |
| H8 | 6518 | 7485 | 6633 | 31 |
| H9 | 3680 | 7825 | 7015 | 29 |
| H16 | 7184 | 6998 | 3385 | 30 |
| H17 | 10103 | 6674 | 2995 | 28 |
| H20 | 16628 | 6296 | 5621 | 33 |
| H21 | 17768 | 6384 | 7070 | 35 |
| H22 | 14775 | 6701 | 7467 | 35 |
| H23 | 10982 | 6955 | 6414 | 31 |
| H25A | -5044 | 8440 | 6173 | 34 |
| H25B | -7178 | 8486 | 5165 | 34 |
| H26A | -1266 | 8746 | 6079 | 30 |
| H26B | -3193 | 8781 | 5055 | 30 |
| H27A | -5288 | 8970 | 6367 | 31 |
| H27B | -7326 | 8996 | 5344 | 31 |
| H28A | -1402 | 9261 | 6236 | 30 |
| H28B | -3263 | 9276 | 5205 | 30 |
| H29A | -7412 | 9514 | 5420 | 29 |
| H29B | -5436 | 9507 | 6448 | 29 |
| H30A | -3403 | 9777 | 5239 | 32 |
| H30B | -1487 | 9775 | 6268 | 32 |
| H31A | -7412 | 10037 | 5438 | 32 |
| H31B | -5417 | 10040 | 6465 | 32 |
| H32A | -3405 | 10288 | 5217 | 34 |
| H32B | -1422 | 10291 | 6243 | 34 |
| H33A | -7340 | 10557 | 5418 | 38 |
| H33B | -5336 | 10562 | 6444 | 38 |
| H34A | -1334 | 10807 | 6196 | 60 |


| H34B | -4539 | 10973 | 5838 | 60 |
| :---: | :---: | :---: | :---: | :---: |
| H34C | -3441 | 10811 | 5177 | 60 |
| H35A | 14546 | 6442 | 2933 | 32 |
| H35B | 11539 | 6260 | 2813 | 32 |
| H36A | 15732 | 6008 | 2583 | 36 |
| H36B | 17756 | 6042 | 3602 | 36 |
| H37A | 14018 | 5787 | 3927 | 34 |
| H37B | 11888 | 5761 | 2914 | 34 |
| H38A | 17843 | 5512 | 3760 | 37 |
| H38B | 15920 | 5499 | 2732 | 37 |
| H39A | 13908 | 5262 | 3988 | 35 |
| H39B | 11879 | 5257 | 2966 | 35 |
| H40A | 17688 | 4983 | 3788 | 35 |
| H40B | 15706 | 4981 | 2761 | 35 |
| H41A | 13660 | 4742 | 4013 | 38 |
| H41B | 11612 | 4746 | 2992 | 38 |
| H42A | 17353 | 4455 | 3780 | 35 |
| H42B | 15322 | 4460 | 2757 | 35 |
| H43A | 13262 | 4224 | 4014 | 39 |
| H43B | 11187 | 4233 | 2992 | 39 |
| H44A | 14901 | 3949 | 2746 | 64 |
| H44B | 13451 | 3801 | 3355 | 64 |
| H44C | 16851 | 3933 | 3773 | 64 |

Table 100.6. Torsion angles $[\infty]$ for $\mathbf{1 0 0}$.

| O1-C1-C2-C3 | -3.9(12) |
| :---: | :---: |
| N1-C1-C2-C3 | 177.6(7) |
| O1-C1-C2-C12 | 177.0(7) |
| N1-C1-C2-C12 | -1.5(10) |
| C12-C2-C3-C4 | -0.4(11) |
| C1-C2-C3-C4 | -179.4(7) |
| C2-C3-C4-C5 | -0.7(11) |
| C3-C4-C5-C6 | 1.3(12) |
| C4-C5-C6-C7 | 178.7(7) |
| C4-C5-C6-C12 | -0.7(11) |
| C5-C6-C7-C8 | -179.7(7) |
| C12-C6-C7-C8 | -0.3(10) |
| C5-C6-C7-C13 | 2.6(11) |
| C12-C6-C7-C13 | -178.0(6) |
| C13-C7-C8-C9 | 178.3(7) |
| C6-C7-C8-C9 | 0.7(11) |
| C7-C8-C9-C10 | -0.4(11) |
| C8-C9-C10-C12 | -0.3(11) |
| C8-C9-C10-C11 | 179.8(6) |
| C9-C10-C11-O2 | 1.9(11) |
| C12-C10-C11-O2 | -178.1(7) |
| C9-C10-C11-N1 | -179.6(7) |
| C12-C10-C11-N1 | 0.4(10) |
| C9-C10-C12-C2 | -179.8(7) |
| C11-C10-C12-C2 | 0.1(10) |
| C9-C10-C12-C6 | 0.6(10) |
| C11-C10-C12-C6 | -179.5(6) |
| C3-C2-C12-C10 | -178.6(7) |
| C1-C2-C12-C10 | 0.4(10) |
| C3-C2-C12-C6 | 1.0(11) |
| C1-C2-C12-C6 | 180.0(6) |
| C5-C6-C12-C10 | 179.2(6) |
| C7-C6-C12-C10 | -0.3(9) |
| $\mathrm{C} 5-\mathrm{C} 6-\mathrm{C} 12-\mathrm{C} 2$ | -0.4(10) |


| $\mathrm{C} 7-\mathrm{C} 6-\mathrm{C} 12-\mathrm{C} 2$ | -179.9(7) |
| :---: | :---: |
| C14-C15-C16-C17 | 179.1(7) |
| C24-C15-C16-C17 | $1.0(11)$ |
| C15-C16-C17-C18 | 1.6(11) |
| C16-C17-C18-O3 | 176.6(7) |
| C16-C17-C18-C19 | -3.7(11) |
| C17-C18-C19-C20 | -177.4(7) |
| O3-C18-C19-C20 | 2.3(10) |
| C17-C18-C19-C24 | 3.2(11) |
| O3-C18-C19-C24 | -177.1(6) |
| C24-C19-C20-C21 | -1.8(11) |
| C18-C19-C20-C21 | 178.8(7) |
| C19-C20-C21-C22 | 3.3(12) |
| C20-C21-C22-C23 | -2.8(12) |
| C21-C22-C23-C24 | $0.7(12)$ |
| C22-C23-C24-C19 | $0.8(11)$ |
| C22-C23-C24-C15 | -179.6(7) |
| C20-C19-C24-C23 | -0.3(10) |
| C18-C19-C24-C23 | 179.2(6) |
| C20-C19-C24-C15 | -179.9(7) |
| C18-C19-C24-C15 | -0.5(10) |
| C16-C15-C24-C23 | 178.8(7) |
| C14-C15-C24-C23 | 0.8(11) |
| C16-C15-C24-C19 | -1.6(10) |
| C14-C15-C24-C19 | -179.6(6) |
| N1-C25-C26-C27 | 175.6(6) |
| C25-C26-C27-C28 | -177.6(6) |
| C26-C27-C28-C29 | 176.3(6) |
| C27-C28-C29-C30 | -177.5(6) |
| C28-C29-C30-C31 | 178.8(6) |
| C29-C30-C31-C32 | -178.3(6) |
| C30-C31-C32-C33 | 179.7(6) |
| C31-C32-C33-C34 | -179.5(7) |
| O3-C35-C36-C37 | 71.7(8) |
| C35-C36-C37-C38 | 177.6(6) |
| C36-C37-C38-C39 | -175.4(6) |


| C37-C38-C39-C40 | $177.6(6)$ |
| :--- | :---: |
| C38-C39-C40-C41 | $-179.0(6)$ |
| C39-C40-C41-C42 | $178.4(6)$ |
| C40-C41-C42-C43 | $-179.6(6)$ |
| C41-C42-C43-C44 | $179.0(7)$ |
| O2-C11-N1-C1 | $177.0(7)$ |
| C10-C11-N1-C1 | $-1.6(10)$ |
| O2-C11-N1-C25 | $1.2(10)$ |
| C10-C11-N1-C25 | $-177.3(6)$ |
| O1-C1-N1-C11 | $-176.4(7)$ |
| C2-C1-N1-C11 | $2.2(10)$ |
| O1-C1-N1-C25 | $-0.7(11)$ |
| C2-C1-N1-C25 | $177.9(6)$ |
| C26-C25-N1-C11 | $89.4(8)$ |
| C26-C25-N1-C1 | $-86.5(8)$ |
| C17-C18-O3-C35 | $1.3(11)$ |
| C19-C18-O3-C35 | $-178.4(6)$ |
| C36-C35-O3-C18 | $-173.0(6)$ |

Symmetry transformations used to generate equivalent atoms:

End of crystallographic info for $\mathbf{1 0 0}$.

## Crystallographic Material for 120

Crystallographic Material for $\mathbf{1 2 0}$.
X-ray Experimental.
Table 120.1. Crystallographic Data for $\mathbf{1 2 0}$.
Table 120.2. Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the non-hydrogen atoms of $\mathbf{1 2 0}$.

Table 120.3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of $\mathbf{1 2 0}$.

Table 120.4. Anisotropic thermal parameters for the non-hydrogen atoms of $\mathbf{1 2 0}$.

Table 120.5. Fractional coordinates and isotropic thermal parameters $\left(\AA^{2}\right)$ for the hydrogen atoms of $\mathbf{1 2 0}$.

Table 120.6. Torsion Angles $\left(^{(0)}\right.$ for the non-hydrogen atoms of $\mathbf{1 2 0}$.

X-ray Experimental for complex $\mathrm{C}_{48} \mathrm{H}_{61} \mathrm{NO}_{3}$ (120): Crystals grew as very thin, orange laths by vapor diffusion (p-xylenes, acetonitrile) The data crystal had approximate dimensions; 0.21 x $0.05 \times 0.03 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{Cu} \mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA)$ with collimating mirror monochromators. A total of 448 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 45 seconds per frame with a detector offset of $0.0^{\circ}$ and 74 seconds per frame with a detector offset of $+/-72.3^{\circ}$. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.38.46. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6. ${ }^{3}$ Structure analysis was aided by use of the programs PLATON ${ }^{4}$ and WinGX. ${ }^{5}$ The hydrogen atoms were calculated in
ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.0422 * \mathrm{P})^{2}\right]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.200 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0817 and a goodness of fit, $\mathrm{S},=1.00$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S , are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. 8 Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

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5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{W}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\mid \mathrm{F}_{\mathrm{C}}\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 120. Crystal data and structure refinement for $\mathbf{1 2 0}$.

| Empirical formula | C48 H61 N O3 |
| :---: | :---: |
| Formula weight | 699.97 |
| Temperature | 100(2) K |
| Wavelength | $1.54184 \AA$ |
| Crystal system | monoclinic |
| Space group | C c |
| Unit cell dimensions | $\begin{array}{ll} \mathrm{a}=4.6653(8) \AA & \alpha=90^{\circ} . \\ \mathrm{b}=54.243(7) \AA & \beta=96.006(15)^{\circ} . \\ \mathrm{c}=15.4813(18) \AA & \gamma=90^{\circ} . \end{array}$ |
| Volume | 3896.2(10) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.193 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.559 \mathrm{~mm}^{-1}$ |
| $F(000)$ | 1520 |
| Crystal size | $0.210 \times 0.050 \times 0.030 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 5.747 to $56.765^{\circ}$. |
| Index ranges | $-4<=\mathrm{h}<=5,-46<=\mathrm{k}<=58,-12<=\mathrm{l}<=16$ |
| Reflections collected | 5754 |
| Independent reflections | $3982[\mathrm{R}(\mathrm{int})=0.1110]$ |
| Completeness to theta $=56.765^{\circ}$ | 93.7 \% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00 and 0.181 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 3982 / 314 / 471 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 0.995 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0817, \mathrm{wR} 2=0.1564$ |
| R indices (all data) | $\mathrm{R} 1=0.1484, \mathrm{wR} 2=0.2003$ |
| Absolute structure parameter | 0.1(10) |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.263 and -0.269 e. $\AA^{-3}$ |

Table 120.2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathbf{1 2 0} . U(e q)$ is defined as one third of the trace of the orthogonalized $U^{i j}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| C1 | -4150(20) | 5639(2) | 4473(8) | 31(3) |
| C2 | -2170(20) | 5446(2) | 4247(7) | 26(3) |
| C3 | -2130(20) | 5387(2) | 3374(7) | 28(3) |
| C4 | -210(30) | 5202(2) | 3138(8) | 36(3) |
| C5 | 1510(30) | 5079(2) | 3767(7) | 30(3) |
| C6 | 1510(20) | 5136(2) | 4647(8) | 29(3) |
| C7 | 3260(30) | 5010(2) | 5338(8) | 28(3) |
| C8 | 3110(20) | 5074(2) | 6189(7) | 32(3) |
| C9 | 1140(20) | 5258(2) | 6413(8) | 37(3) |
| C10 | -570(20) | 5377(2) | 5788(7) | 24(3) |
| C11 | -2560(20) | 5568(2) | 6033(8) | 29(3) |
| C12 | -460(20) | 5322(2) | 4900(7) | 23(3) |
| C13 | 5240(20) | 4827(2) | 5114(7) | 29(3) |
| C14 | 6940(20) | 4672(2) | 4904(7) | 26(3) |
| C15 | 8950(20) | 4493(2) | 4677(7) | 31(3) |
| C16 | 9300(20) | 4447(2) | 3830(8) | 31(3) |
| C17 | 11300(20) | 4266(2) | 3588(7) | 28(3) |
| C18 | 12790(20) | 4134(2) | 4230(7) | 28(3) |
| C19 | 12550(20) | 4168(2) | 5121(7) | 27(3) |
| C20 | 14130(20) | 4039(2) | 5793(8) | 34(3) |
| C21 | 13890(20) | 4081(2) | 6633(8) | 36(3) |
| C22 | 11940(30) | 4258(2) | 6862(8) | 36(3) |
| C23 | 10330(20) | 4390(2) | 6241(7) | 33(3) |
| C24 | 10570(20) | 4354(2) | 5361(7) | 28(3) |
| C25 | -6190(20) | 5890(2) | 5598(7) | 28(3) |
| C26 | -4680(20) | 6132(2) | 5621(8) | 33(3) |
| C27 | -6630(30) | 6349(2) | 5796(8) | 35(3) |
| C28 | -5050(20) | 6592(2) | 5773(8) | 38(3) |
| C29 | -6900(30) | 6821(2) | 5907(8) | 36(3) |
| C30 | -5190(30) | 7060(2) | 5836(8) | 34(3) |
| C31 | -6960(30) | 7293(2) | 5925(8) | 37(3) |


| C32 | $-5190(30)$ | $7528(2)$ | $5830(8)$ | $39(3)$ |
| :--- | :--- | :--- | :--- | :--- |
| C33 | $-6880(30)$ | $7765(2)$ | $5900(8)$ | $37(3)$ |
| C34 | $-5050(20)$ | $7996(2)$ | $5797(8)$ | $35(3)$ |
| C35 | $-6670(30)$ | $8239(2)$ | $5872(8)$ | $44(4)$ |
| C36 | $-4780(30)$ | $8464(2)$ | $5761(9)$ | $53(4)$ |
| C37 | $15090(30)$ | $3898(2)$ | $3173(7)$ | $35(3)$ |
| C38 | $16910(30)$ | $3668(2)$ | $3163(8)$ | $39(3)$ |
| C39 | $15300(30)$ | $3436(2)$ | $3364(8)$ | $34(3)$ |
| C40 | $17030(30)$ | $3198(2)$ | $3299(8)$ | $33(3)$ |
| C41 | $15230(30)$ | $2966(2)$ | $3420(8)$ | $35(3)$ |
| C42 | $16870(30)$ | $2725(2)$ | $3347(8)$ | $34(3)$ |
| C43 | $15030(30)$ | $2497(2)$ | $3434(8)$ | $36(3)$ |
| C44 | $16600(30)$ | $2254(2)$ | $3350(8)$ | $36(3)$ |
| C45 | $14750(30)$ | $2027(2)$ | $3443(8)$ | $34(3)$ |
| C46 | $16250(30)$ | $1780(2)$ | $3332(7)$ | $35(3)$ |
| C47 | $14310(30)$ | $1556(2)$ | $3436(8)$ | $40(3)$ |
| C48 | $15780(30)$ | $1311(2)$ | $3309(8)$ | $51(4)$ |
| N1 | $-4292(19)$ | $5685(2)$ | $5370(6)$ | $26(2)$ |
| O1 | $-2690(18)$ | $5629(1)$ | $6800(5)$ | $39(2)$ |
| O3 | $-5689(19)$ | $5754(2)$ | $3938(5)$ | $47(2)$ |

Table 120.3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for $\mathbf{1 2 0}$.

| C1-O2 | $1.214(13)$ | $\mathrm{C} 19-\mathrm{C} 24$ | $1.443(15)$ |
| :--- | :--- | :--- | :--- |
| C1-N1 | $1.420(14)$ | $\mathrm{C} 20-\mathrm{C} 21$ | $1.337(14)$ |
| C1-C2 | $1.462(15)$ | $\mathrm{C} 20-\mathrm{H} 20$ | 0.95 |
| C2-C3 | $1.391(14)$ | $\mathrm{C} 21-\mathrm{C} 22$ | $1.393(16)$ |
| C2-C12 | $1.391(14)$ | $\mathrm{C} 21-\mathrm{H} 21$ | 0.95 |
| C3-C4 | $1.416(15)$ | $\mathrm{C} 22-\mathrm{C} 23$ | $1.361(15)$ |
| C3-H3 | 0.95 | $\mathrm{C} 22-\mathrm{H} 22$ | 0.95 |
| C4-C5 | $1.369(15)$ | $\mathrm{C} 23-\mathrm{C} 24$ | $1.393(15)$ |
| C4-H4 | 0.95 | $\mathrm{C} 23-\mathrm{H} 23$ | 0.95 |
| C5-C6 | $1.396(15)$ | $\mathrm{C} 25-\mathrm{N} 1$ | $1.489(13)$ |
| C5-H5 | 0.95 | $\mathrm{C} 25-\mathrm{C} 26$ | $1.491(14)$ |
| C6-C7 | $1.447(15)$ | $\mathrm{C} 25-\mathrm{H} 25 \mathrm{~A}$ | 0.99 |
| C6-C12 | $1.451(14)$ | $\mathrm{C} 25-\mathrm{H} 25 \mathrm{~B}$ | $0.992-\mathrm{C}$ |


| C33-C34 | 1.534(15) | C41-C42 | 1.524(14) |
| :---: | :---: | :---: | :---: |
| C33-H33A | 0.99 | C41-H41A | 0.99 |
| C33-H33B | 0.99 | C41-H41B | 0.99 |
| C34-C35 | 1.531(15) | C42-C43 | 1.523(14) |
| C34-H34A | 0.99 | C42-H42A | 0.99 |
| C34-H34B | 0.99 | C42-H42B | 0.99 |
| C35-C36 | $1.525(16)$ | C43-C44 | 1.520(14) |
| C35-H35A | 0.99 | C43-H43A | 0.99 |
| C35-H35B | 0.99 | C43-H43B | 0.99 |
| C36-H36A | 0.98 | C44-C45 | 1.516(15) |
| C36-H36B | 0.98 | C44-H44A | 0.99 |
| C36-H36C | 0.98 | C44-H44B | 0.99 |
| C37-O3 | 1.429(13) | C45-C46 | 1.527(14) |
| C37-C38 | 1.508(15) | C45-H45A | 0.99 |
| C37-H37A | 0.99 | C45-H45B | 0.99 |
| C37-H37B | 0.99 | C46-C47 | 1.533(14) |
| C38-C39 | 1.516 (15) | C46-H46A | 0.99 |
| C38-H38A | 0.99 | C46-H46B | 0.99 |
| C38-H38B | 0.99 | C47-C48 | 1.519(15) |
| C39-C40 | 1.532(14) | C47-H47A | 0.99 |
| C39-H39A | 0.99 | C47-H47B | 0.99 |
| C39-H39B | 0.99 | C48-H48A | 0.98 |
| C40-C41 | $1.535(15)$ | C48-H48B | 0.98 |
| C40-H40A | 0.99 | C48-H48C | 0.98 |
| C40-H40B | 0.99 |  |  |
| O2-C1-N1 | 119.3(11) | C5-C4-H4 | 120.0 |
| O2-C1-C2 | 123.5(11) | C3-C4-H4 | 120.0 |
| N1-C1-C2 | 117.1(10) | C4-C5-C6 | 121.8(11) |
| C3-C2-C12 | 122.1(11) | C4-C5-H5 | 119.1 |
| C3-C2-C1 | 117.9(10) | C6-C5-H5 | 119.1 |
| C12-C2-C1 | 119.9(10) | C5-C6-C7 | 124.2(11) |
| C2-C3-C4 | 119.0(10) | C5-C6-C12 | 118.8(10) |
| C2-C3-H3 | 120.5 | C7-C6-C12 | 116.9(11) |
| C4-C3-H3 | 120.5 | C8-C7-C13 | 120.7(11) |
| C5-C4-C3 | 120.0(11) | C8-C7-C6 | 120.6(11) |


| C13-C7-C6 | 118.5(11) | C20-C21-C22 | 119.3(12) |
| :---: | :---: | :---: | :---: |
| C7-C8-C9 | 120.7(11) | C20-C21-H21 | 120.4 |
| C7-C8-H8 | 119.6 | C22-C21-H21 | 120.4 |
| C9-C8-H8 | 119.6 | C23-C22-C21 | 120.7(12) |
| C10-C9-C8 | 120.4(12) | C23-C22-H22 | 119.7 |
| C10-C9-H9 | 119.8 | C21-C22-H22 | 119.7 |
| C8-C9-H9 | 119.8 | C22-C23-C24 | 121.5(12) |
| C9-C10-C12 | 121.4(11) | C22-C23-H23 | 119.2 |
| C9-C10-C11 | 119.5(11) | C24-C23-H23 | 119.2 |
| C12-C10-C11 | 119.1(9) | C23-C24-C19 | 117.9(10) |
| O1-C11-N1 | 120.3(10) | C23-C24-C15 | 123.8(11) |
| O1-C11-C10 | 122.0(10) | C19-C24-C15 | 118.3(10) |
| N1-C11-C10 | 117.7(10) | N1-C25-C26 | 111.8(10) |
| C2-C12-C10 | 122.1(10) | N1-C25-H25A | 109.2 |
| C2-C12-C6 | 118.0(11) | C26-C25-H25A | 109.2 |
| C10-C12-C6 | 119.9(10) | N1-C25-H25B | 109.2 |
| C14-C13-C7 | 178.6(12) | C26-C25-H25B | 109.2 |
| C13-C14-C15 | 178.7(13) | H25A-C25-H25B | 107.9 |
| C16-C15-C14 | 120.7(11) | C25-C26-C27 | 113.1(10) |
| C16-C15-C24 | 120.5(11) | C25-C26-H26A | 109.0 |
| C14-C15-C24 | 118.8(11) | C27-C26-H26A | 109.0 |
| C15-C16-C17 | 121.5(11) | C25-C26-H26B | 109.0 |
| C15-C16-H16 | 119.2 | C27-C26-H26B | 109.0 |
| C17-C16-H16 | 119.2 | H26A-C26-H26B | 107.8 |
| C18-C17-C16 | 118.0(11) | C28-C27-C26 | 111.4(10) |
| C18-C17-H17 | 121.0 | C28-C27-H27A | 109.3 |
| C16-C17-H17 | 121.0 | C26-C27-H27A | 109.3 |
| C17-C18-O3 | 122.0(10) | C28-C27-H27B | 109.3 |
| C17-C18-C19 | 124.1(10) | C26-C27-H27B | 109.3 |
| O3-C18-C19 | 113.9(9) | H27A-C27-H27B | 108.0 |
| C20-C19-C18 | 124.8(11) | C27-C28-C29 | 114.8(10) |
| C20-C19-C24 | 117.5(11) | C27-C28-H28A | 108.6 |
| C18-C19-C24 | 117.7(10) | C29-C28-H28A | 108.6 |
| C21-C20-C19 | 123.1(12) | C27-C28-H28B | 108.6 |
| C21-C20-H20 | 118.5 | C29-C28-H28B | 108.6 |
| C19-C20-H20 | 118.5 | H28A-C28-H28B | 107.5 |


| C30-C29-C28 | 111.7(10) | C36-C35-C34 | 112.5(11) |
| :---: | :---: | :---: | :---: |
| C30-C29-H29A | 109.3 | C36-C35-H35A | 109.1 |
| C28-C29-H29A | 109.3 | C34-C35-H35A | 109.1 |
| C30-C29-H29B | 109.3 | C36-C35-H35B | 109.1 |
| C28-C29-H29B | 109.3 | C34-C35-H35B | 109.1 |
| H29A-C29-H29B | 107.9 | H35A-C35-H35B | 107.8 |
| C31-C30-C29 | 113.9(10) | C35-C36-H36A | 109.5 |
| C31-C30-H30A | 108.8 | C35-C36-H36B | 109.5 |
| C29-C30-H30A | 108.8 | H36A-C36-H36B | 109.5 |
| C31-C30-H30B | 108.8 | C35-C36-H36C | 109.5 |
| C29-C30-H30B | 108.8 | H36A-C36-H36C | 109.5 |
| H30A-C30-H30B | 107.7 | H36B-C36-H36C | 109.5 |
| C30-C31-C32 | 112.3(10) | O3-C37-C38 | 107.4(9) |
| C30-C31-H31A | 109.2 | O3-C37-H37A | 110.2 |
| C32-C31-H31A | 109.2 | C38-C37-H37A | 110.2 |
| C30-C31-H31B | 109.2 | O3-C37-H37B | 110.2 |
| C32-C31-H31B | 109.2 | C38-C37-H37B | 110.2 |
| H31A-C31-H31B | 107.9 | H37A-C37-H37B | 108.5 |
| C33-C32-C31 | 114.2(11) | C37-C38-C39 | 113.0(10) |
| C33-C32-H32A | 108.7 | C37-C38-H38A | 109.0 |
| C31-C32-H32A | 108.7 | C39-C38-H38A | 109.0 |
| C33-C32-H32B | 108.7 | C37-C38-H38B | 109.0 |
| C31-C32-H32B | 108.7 | C39-C38-H38B | 109.0 |
| H32A-C32-H32B | 107.6 | H38A-C38-H38B | 107.8 |
| C32-C33-C34 | 112.9(11) | C38-C39-C40 | 114.3(10) |
| C32-C33-H33A | 109.0 | C38-C39-H39A | 108.7 |
| C34-C33-H33A | 109.0 | C40-C39-H39A | 108.7 |
| C32-C33-H33B | 109.0 | C38-C39-H39B | 108.7 |
| C34-C33-H33B | 109.0 | C40-C39-H39B | 108.7 |
| H33A-C33-H33B | 107.8 | H39A-C39-H39B | 107.6 |
| C35-C34-C33 | 114.3(10) | C39-C40-C41 | 112.6(10) |
| C35-C34-H34A | 108.7 | C39-C40-H40A | 109.1 |
| C33-C34-H34A | 108.7 | C41-C40-H40A | 109.1 |
| C35-C34-H34B | 108.7 | C39-C40-H40B | 109.1 |
| C33-C34-H34B | 108.7 | C41-C40-H40B | 109.1 |
| H34A-C34-H34B | 107.6 | H40A-C40-H40B | 107.8 |


| C42-C41-C40 | 114.0(10) | C46-C45-H45A | 108.5 |
| :---: | :---: | :---: | :---: |
| C42-C41-H41A | 108.8 | C44-C45-H45B | 108.5 |
| C40-C41-H41A | 108.8 | C46-C45-H45B | 108.5 |
| C42-C41-H41B | 108.8 | H45A-C45-H45B | 107.5 |
| C40-C41-H41B | 108.8 | C45-C46-C47 | 113.7(10) |
| H41A-C41-H41B | 107.7 | C45-C46-H46A | 108.8 |
| C43-C42-C41 | 113.5(10) | C47-C46-H46A | 108.8 |
| C43-C42-H42A | 108.9 | C45-C46-H46B | 108.8 |
| C41-C42-H42A | 108.9 | C47-C46-H46B | 108.8 |
| C43-C42-H42B | 108.9 | H46A-C46-H46B | 107.7 |
| C41-C42-H42B | 108.9 | C48-C47-C46 | 113.7(11) |
| H42A-C42-H42B | 107.7 | C48-C47-H47A | 108.8 |
| C44-C43-C42 | 114.7(10) | C46-C47-H47A | 108.8 |
| C44-C43-H43A | 108.6 | C48-C47-H47B | 108.8 |
| C42-C43-H43A | 108.6 | C46-C47-H47B | 108.8 |
| C44-C43-H43B | 108.6 | H47A-C47-H47B | 107.7 |
| C42-C43-H43B | 108.6 | C47-C48-H48A | 109.5 |
| H43A-C43-H43B | 107.6 | C47-C48-H48B | 109.5 |
| C45-C44-C43 | 114.2(10) | H48A-C48-H48B | 109.5 |
| C45-C44-H44A | 108.7 | C47-C48-H48C | 109.5 |
| C43-C44-H44A | 108.7 | H48A-C48-H48C | 109.5 |
| C45-C44-H44B | 108.7 | H48B-C48-H48C | 109.5 |
| C43-C44-H44B | 108.7 | C11-N1-C1 | 124.0(10) |
| H44A-C44-H44B | 107.6 | C11-N1-C25 | 118.6(9) |
| C44-C45-C46 | 115.3(10) | C1-N1-C25 | 117.1(9) |
| C44-C45-H45A | 108.5 | C18-O3-C37 | 118.6(9) |

Table 120.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathbf{1 2 0}$. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | 26(6) | 34(7) | 30(7) | 3(6) | $-9(5)$ | -5(5) |
| C2 | 40(7) | 18(6) | 21(6) | -2(5) | 4(5) | 0(5) |
| C3 | 34(7) | 25(6) | 24(6) | 7(5) | $0(5)$ | 4(5) |
| C4 | 52(8) | 29(7) | 27(7) | 5(6) | 10(6) | 3(6) |
| C5 | 45(7) | 26(6) | 21(6) | -10(5) | 8(5) | -1(5) |
| C6 | 27(6) | 21(6) | 37(7) | 6(5) | -5(5) | -4(5) |
| C7 | 44(7) | 16(6) | 22(6) | -4(5) | $0(5)$ | -3(5) |
| C8 | 42(7) | 23(6) | 29(7) | 11(5) | -5(5) | 8(5) |
| C9 | 36(7) | 40(7) | 35(7) | 5(6) | 6(6) | -1(6) |
| C10 | 37(7) | 16(6) | 20(6) | 6(5) | 4(5) | 6(5) |
| C11 | 33(7) | 29(7) | 24(7) | -8(6) | -2(5) | -1(5) |
| C12 | 32(6) | 17(6) | 23(6) | 12(5) | 11(5) | -4(5) |
| C13 | 32(7) | 24(6) | 32(7) | 6(5) | 8(5) | -8(5) |
| C14 | 34(6) | 18(6) | 28(7) | 5(5) | 6(5) | $0(5)$ |
| C15 | 34(7) | 28(6) | 29(7) | 0 (5) | -3(5) | 4(5) |
| C16 | 31(7) | 27(6) | 33(7) | 0 (5) | -3(5) | -4(5) |
| C17 | 35(7) | 21(6) | 29(7) | -10(5) | 7(5) | 1(5) |
| C18 | 35(7) | 20(6) | 26(7) | 4(5) | -7(5) | 5(5) |
| C19 | 34(7) | 20(6) | 28(7) | 2(5) | $5(5)$ | 8(5) |
| C20 | 38(7) | 29(6) | 34(7) | 3(6) | -2(6) | 2(5) |
| C21 | 38(7) | 36(7) | 32(7) | -5(6) | -4(5) | 3(5) |
| C22 | 44(7) | 37(7) | 28(7) | 1(6) | 7(6) | -3(6) |
| C23 | 42(7) | 27(6) | 30(7) | -1(5) | 4(6) | 3(5) |
| C24 | 27(6) | 29(6) | 27(7) | 1(5) | 1(5) | -3(5) |
| C25 | 37(7) | 13(6) | 36(7) | -4(5) | 5(5) | 7(5) |
| C26 | 41(7) | 22(6) | 37(7) | -3(5) | 3(5) | 2(5) |
| C27 | 50(7) | 22(6) | 33(7) | 3(5) | 5(6) | -3(5) |
| C28 | 42(7) | 31(7) | 42(7) | 6(6) | 7(6) | 4(5) |
| C29 | 43(7) | 28(6) | 35(7) | 2(5) | -4(5) | 2(5) |
| C30 | 54(7) | 21(6) | 28(7) | 3(5) | 2(6) | -4(5) |
| C31 | 53(8) | 24(6) | 33(7) | 4(5) | -1(6) | 0(5) |


| C32 | $49(7)$ | $32(7)$ | $35(7)$ | $1(6)$ | $0(6)$ | $4(5)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| C33 | $58(8)$ | $17(6)$ | $34(7)$ | $3(5)$ | $0(6)$ | $3(5)$ |
| C34 | $46(7)$ | $25(6)$ | $34(7)$ | $6(5)$ | $4(6)$ | $2(5)$ |
| C35 | $62(8)$ | $25(7)$ | $46(7)$ | $-2(6)$ | $5(6)$ | $1(6)$ |
| C36 | $65(10)$ | $27(7)$ | $66(9)$ | $4(7)$ | $0(7)$ | $-5(7)$ |
| C37 | $45(7)$ | $31(7)$ | $32(7)$ | $-6(6)$ | $14(6)$ | $2(5)$ |
| C38 | $50(7)$ | $27(6)$ | $40(7)$ | $-5(6)$ | $1(6)$ | $-3(6)$ |
| C39 | $44(7)$ | $23(6)$ | $36(7)$ | $-4(5)$ | $9(5)$ | $12(5)$ |
| C40 | $42(7)$ | $16(6)$ | $40(7)$ | $-6(5)$ | $2(6)$ | $3(5)$ |
| C41 | $47(7)$ | $18(6)$ | $39(7)$ | $-1(5)$ | $1(6)$ | $6(5)$ |
| C42 | $53(7)$ | $19(6)$ | $30(7)$ | $4(5)$ | $7(6)$ | $5(5)$ |
| C43 | $52(7)$ | $21(6)$ | $32(7)$ | $1(5)$ | $-6(5)$ | $3(5)$ |
| C44 | $50(7)$ | $24(6)$ | $34(7)$ | $3(5)$ | $3(6)$ | $3(5)$ |
| C45 | $42(7)$ | $24(6)$ | $34(7)$ | $3(5)$ | $0(5)$ | $5(5)$ |
| C46 | $52(7)$ | $23(6)$ | $31(7)$ | $5(5)$ | $14(6)$ | $9(5)$ |
| C47 | $60(8)$ | $21(6)$ | $40(7)$ | $6(5)$ | $9(6)$ | $4(6)$ |
| C48 | $78(10)$ | $28(8)$ | $47(9)$ | $3(6)$ | $7(7)$ | $5(7)$ |
| N1 | $36(5)$ | $24(5)$ | $18(5)$ | $3(4)$ | $1(4)$ | $9(4)$ |
| O1 | $54(5)$ | $31(5)$ | $30(5)$ | $-1(4)$ | $-2(4)$ | $18(4)$ |
| O2 | $60(6)$ | $43(5)$ | $35(5)$ | $-4(4)$ | $-6(4)$ | $13(5)$ |
| O3 | $57(5)$ | $25(4)$ | $30(5)$ | $1(4)$ | $8(4)$ | $6(4)$ |

Table 120.5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for $\mathbf{1 2 0}$.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H3 | -3373 | 5469 | 2943 | 33 |
| H4 | -112 | 5164 | 2543 | 43 |
| H5 | 2727 | 4951 | 3600 | 36 |
| H8 | 4330 | 4995 | 6634 | 38 |
| H9 | 1023 | 5298 | 7006 | 44 |
| H16 | 8189 | 4538 | 3389 | 37 |
| H17 | 11566 | 4238 | 2996 | 34 |
| H20 | 15444 | 3916 | 5646 | 41 |
| H21 | 15042 | 3992 | 7069 | 43 |
| H22 | 11730 | 4286 | 7458 | 43 |
| H23 | 9008 | 4509 | 6413 | 40 |
| H25A | -6858 | 5857 | 6174 | 34 |
| H25B | -7913 | 5897 | 5166 | 34 |
| H26A | -3897 | 6159 | 5058 | 40 |
| H26B | -3032 | 6128 | 6080 | 40 |
| H27A | -8323 | 6350 | 5353 | 42 |
| H27B | -7338 | 6328 | 6372 | 42 |
| H28A | -4265 | 6607 | 5206 | 46 |
| H28B | -3397 | 6590 | 6230 | 46 |
| H29A | -8593 | 6822 | 5466 | 43 |
| H29B | -7602 | 6812 | 6488 | 43 |
| H30A | -3538 | 7060 | 6293 | 41 |
| H30B | -4406 | 7062 | 5266 | 41 |
| H31A | -7706 | 7293 | 6501 | 45 |
| H31B | -8635 | 7292 | 5476 | 45 |
| H32A | -3534 | 7528 | 6285 | 47 |
| H32B | -4416 | 7524 | 5259 | 47 |
| H33A | -7645 | 7770 | 6472 | 44 |
| H33B | -8539 | 7766 | 5446 | 44 |
| H34A | -3377 | 7993 | 6247 | 42 |


| H34B | -4295 | 7990 | 5224 | 42 |
| :---: | :---: | :---: | :---: | :---: |
| H35A | -8348 | 8244 | 5424 | 53 |
| H35B | -7410 | 8247 | 6448 | 53 |
| H36A | -3093 | 8459 | 6195 | 80 |
| H36B | -5884 | 8615 | 5839 | 80 |
| H36C | -4144 | 8463 | 5177 | 80 |
| H37A | 16083 | 4038 | 2927 | 42 |
| H37B | 13217 | 3872 | 2820 | 42 |
| H38A | 18620 | 3687 | 3595 | 47 |
| H38B | 17609 | 3651 | 2583 | 47 |
| H39A | 13522 | 3425 | 2958 | 41 |
| H39B | 14723 | 3449 | 3960 | 41 |
| H40A | 18709 | 3200 | 3748 | 39 |
| H40B | 17775 | 3191 | 2724 | 39 |
| H41A | 14508 | 2973 | 3998 | 42 |
| H41B | 13537 | 2966 | 2977 | 42 |
| H42A | 17660 | 2721 | 2777 | 41 |
| H42B | 18524 | 2722 | 3804 | 41 |
| H43A | 14270 | 2501 | 4007 | 43 |
| H43B | 13366 | 2503 | 2982 | 43 |
| H44A | 17354 | 2248 | 2775 | 43 |
| H44B | 18277 | 2247 | 3798 | 43 |
| H45A | 13044 | 2037 | 3007 | 40 |
| H45B | 14054 | 2031 | 4025 | 40 |
| H46A | 17961 | 1769 | 3766 | 42 |
| H46B | 16934 | 1775 | 2748 | 42 |
| H47A | 13660 | 1560 | 4024 | 48 |
| H47B | 12584 | 1569 | 3009 | 48 |
| H48A | 16355 | 1302 | 2718 | 76 |
| H48B | 14450 | 1176 | 3398 | 76 |
| H48C | 17499 | 1297 | 3729 | 76 |

Table 120.6. Torsion angles [ ${ }^{\circ}$ ] for $\mathbf{1 2 0}$.

| O2-C1-C2-C3 | -2.3(17) | C7-C6-C12-C10 | 1.3(15) |
| :---: | :---: | :---: | :---: |
| N1-C1-C2-C3 | 175.9(9) | C14-C15-C16-C17 | -179.3(10) |
| O2-C1-C2-C12 | 179.8(11) | C24-C15-C16-C17 | -1.3(17) |
| N1-C1-C2-C12 | -1.9(16) | C15-C16-C17-C18 | 2.0 (16) |
| C12-C2-C3-C4 | -2.8(17) | C16-C17-C18-O3 | 176.6(9) |
| C1-C2-C3-C4 | 179.4(11) | C16-C17-C18-C19 | -1.6(17) |
| C2-C3-C4-C5 | 2.2(17) | C17-C18-C19-C20 | -177.9(11) |
| C3-C4-C5-C6 | -2.5(17) | O3-C18-C19-C20 | 3.8(16) |
| C4-C5-C6-C7 | 179.5(11) | C17-C18-C19-C24 | 0.6(17) |
| C4-C5-C6-C12 | 3.1(16) | O3-C18-C19-C24 | -177.8(9) |
| C5-C6-C7-C8 | -179.0(11) | C18-C19-C20-C21 | 178.4(12) |
| C12-C6-C7-C8 | -2.6(15) | C24-C19-C20-C21 | -0.1(17) |
| C5-C6-C7-C13 | 4.1(16) | C19-C20-C21-C22 | 1.3(18) |
| C12-C6-C7-C13 | -179.5(10) | C20-C21-C22-C23 | -1.3(18) |
| C13-C7-C8-C9 | 179.6(11) | C21-C22-C23-C24 | 0.0(18) |
| C6-C7-C8-C9 | 2.7(17) | C22-C23-C24-C19 | 1.3(17) |
| C7-C8-C9-C10 | -1.5(18) | C22-C23-C24-C15 | -178.7(11) |
| C8-C9-C10-C12 | 0.2(17) | C20-C19-C24-C23 | -1.2(16) |
| C8-C9-C10-C11 | -179.3(10) | C18-C19-C24-C23 | -179.8(10) |
| C9-C10-C11-O1 | 1.7(17) | C20-C19-C24-C15 | 178.7(10) |
| C12-C10-C11-O1 | -177.9(10) | C18-C19-C24-C15 | 0.2(16) |
| C9-C10-C11-N1 | -179.7(10) | C16-C15-C24-C23 | -179.8(11) |
| C12-C10-C11-N1 | 0.8(15) | C14-C15-C24-C23 | -1.8(17) |
| C3-C2-C12-C10 | -178.0(11) | C16-C15-C24-C19 | 0.2(17) |
| C1-C2-C12-C10 | -0.3(16) | C14-C15-C24-C19 | 178.2(10) |
| C3-C2-C12-C6 | $3.4(16)$ | N1-C25-C26-C27 | 176.2(9) |
| C1-C2-C12-C6 | -178.8(10) | C25-C26-C27-C28 | -177.4(10) |
| C9-C10-C12-C2 | -178.7(12) | C26-C27-C28-C29 | 177.7(9) |
| C11-C10-C12-C2 | 0.9(15) | C27-C28-C29-C30 | -177.5(10) |
| C9-C10-C12-C6 | -0.2(16) | C28-C29-C30-C31 | 177.5(9) |
| C11-C10-C12-C6 | 179.4(10) | C29-C30-C31-C32 | -178.8(9) |
| C5-C6-C12-C2 | -3.5(15) | C30-C31-C32-C33 | 179.0(9) |
| C7-C6-C12-C2 | 179.9(10) | C31-C32-C33-C34 | -179.8(10) |
| C5-C6-C12-C10 | 177.9(9) | C32-C33-C34-C35 | -179.5(10) |


| $\mathrm{C} 33-\mathrm{C} 34-\mathrm{C} 35-\mathrm{C} 36$ | $-179.6(10)$ |
| :--- | :---: |
| $\mathrm{O} 3-\mathrm{C} 37-\mathrm{C} 38-\mathrm{C} 39$ | $71.0(13)$ |
| $\mathrm{C} 37-\mathrm{C} 38-\mathrm{C} 39-\mathrm{C} 40$ | $176.1(10)$ |
| $\mathrm{C} 38-\mathrm{C} 39-\mathrm{C} 40-\mathrm{C} 41$ | $-174.4(10)$ |
| $\mathrm{C} 39-\mathrm{C} 40-\mathrm{C} 41-\mathrm{C} 42$ | $179.2(10)$ |
| $\mathrm{C} 40-\mathrm{C} 41-\mathrm{C} 42-\mathrm{C} 43$ | $-177.8(10)$ |
| $\mathrm{C} 41-\mathrm{C} 42-\mathrm{C} 43-\mathrm{C} 44$ | $179.1(10)$ |
| $\mathrm{C} 42-\mathrm{C} 43-\mathrm{C} 44-\mathrm{C} 45$ | $179.6(10)$ |
| $\mathrm{C} 43-\mathrm{C} 44-\mathrm{C} 45-\mathrm{C} 46$ | $178.1(9)$ |
| $\mathrm{C} 44-\mathrm{C} 45-\mathrm{C} 46-\mathrm{C} 47$ |  |
| $\mathrm{C} 45-\mathrm{C} 46-\mathrm{C} 47-\mathrm{C} 48$ | $179.7(10)$ |
| $\mathrm{O} 1-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 1$ | $178.9(10)$ |
| $\mathrm{C} 10-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 1$ | $175.5(11)$ |
| $\mathrm{O} 1-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 25$ | $-3.1(15)$ |
| $\mathrm{C} 10-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 25$ | $2.5(16)$ |
| $\mathrm{O} 2-\mathrm{C} 1-\mathrm{N} 1-\mathrm{C} 11$ | $-176.2(10)$ |
| $\mathrm{C} 2-\mathrm{C} 1-\mathrm{N} 1-\mathrm{C} 11$ | $-177.9(10)$ |
| O2-C1-N1-C25 | $3.7(16)$ |
| C2-C1-N1-C25 | $-4.8(16)$ |
| C26-C25-N1-C11 | $176.9(9)$ |
| C26-C25-N1-C1 | $87.8(12)$ |
| C17-C18-O3-C37 | $-85.8(12)$ |
| C19-C18-O3-C37 | $2.6(16)$ |
| C38-C37-O3-C18 | $-179.0(10)$ |
|  |  |

End crystallographic info for $\mathbf{1 2 0}$.

## Crystallographic Material for M6N8

Crystallographic Material for M6N8.

X-ray Experimental.
Table M6N8.1. Crystallographic Data for M6N8.
Table M6N8.2. Fractional coordinates and equivalent isotropic thermal parameters ( $\AA^{2}$ ) for the non-hydrogen atoms of M6N8.

Table M6N8.3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of M6N8.

Table M6N8.4. Anisotropic thermal parameters for the non-hydrogen atoms of M6N8.

Table M6N8.5. Fractional coordinates and isotropic thermal parameters $\left(\AA^{2}\right)$ for the hydrogen atoms of M6N8.

Table M6N8.6. Torsion Angles $\left(^{\circ}\right)$ for the non-hydrogen atoms of M6N8.

X-ray Experimental for complex $\mathrm{C}_{38} \mathrm{H}_{41} \mathrm{NO}_{3}$ (M6N8): Crystals grew as long, yellow laths by vapor diffusion (xylenes, ethanol). The data crystal was cut from a larger crystal and had approximate dimensions; $0.36 \times 0.14 \times 0.04 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus Cu K $\alpha$ radiation source ( $\lambda$ $=1.5418 \AA$ ) with collimating mirror monochromators. A total of 974 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 12.5 seconds per frame with a detector offset of $+/-39.8^{\circ}$ and 45 seconds per frame with a detector offset of $+/-112.0^{\circ}$. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.39.46. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement
parameters for the non-H atoms using SHELXL-2016/6. ${ }^{3}$ Structure analysis was aided by use of the programs PLATON ${ }^{4}$ and WinGX. ${ }^{5}$ The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms).

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{O}}\right)\right)^{2}+(0.1211 * \mathrm{P})^{2}\right]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.333 , with $\mathrm{R}(\mathrm{F})$ equal to 0.1078 and a goodness of fit, $\mathrm{S},=1.04$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S , are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC..$^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

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2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
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4) Spek, A. L. (2009). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands. Acta Cryst. D65, 148-155.
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection. $\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{o}}\right|-\left|\mathrm{F}_{\mathrm{C}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{o}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\mathrm{L} \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table M6N8.1. Crystal data and structure refinement for M6N8.

| Empirical formula | C38 H41 N O3 |
| :---: | :---: |
| Formula weight | 559.72 |
| Temperature | 100(2) K |
| Wavelength | $1.54184 \AA$ |
| Crystal system | triclinic |
| Space group | P-1 |
| Unit cell dimensions | $a=10.7618(17) \AA$ 没 $\quad \alpha=85.568(9)^{\circ}$. |
|  | $\mathrm{b}=10.7781(11) \AA \quad \beta=85.579(12)^{\circ}$. |
|  | $\mathrm{c}=26.506(3) \AA \quad \gamma=87.082(11)^{\circ}$. |
| Volume | 3053.1(7) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.218 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.593 \mathrm{~mm}^{-1}$ |
| F(000) | 1200 |
| Crystal size | $0.360 \times 0.140 \times 0.044 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 3.354 to $68.202^{\circ}$. |
| Index ranges | $-9<=\mathrm{h}<=12,-12<=\mathrm{k}<=12,-31<=\mathrm{l}<=31$ |
| Reflections collected | 15978 |
| Independent reflections | $10441[\mathrm{R}(\mathrm{int})=0.0729]$ |
| Completeness to theta $=67.684^{\circ}$ | 93.9 \% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00 and 0.360 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 10441 / 0 / 761 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.042 |
| Final R indices [I $>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.1074, \mathrm{wR} 2=0.2601$ |
| R indices (all data) | $\mathrm{R} 1=0.1840, \mathrm{wR} 2=0.3333$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.488 and -0.340 e. $\AA^{-3}$ |

Table M6N8.2. Atomic coordinates $\left(\times 10^{4}\right)$ and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for M6N8. U(eq) is defined as one third of the trace of the orthogonalized $U^{i j}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| C1 | $2879(5)$ | $4055(5)$ | 7274(2) | 29(1) |
| C2 | $2466(4)$ | $3939(4)$ | 6757(2) | $23(1)$ |
| C3 | 1895(4) | $2851(4)$ | 6664(2) | $26(1)$ |
| $\mathrm{C} 4$ | $1515(4)$ | $2721(4)$ | 6176(2) | $26(1)$ |
| C5 | $1680(4)$ | $3623(4)$ | 5789(2) | 26(1) |
| C6 | $2260(4)$ | $4761(4)$ | 5873(2) | $23(1)$ |
| C7 | $2496(4)$ | $5710(5)$ | 5493(2) | 27(1) |
| C8 | 3073(4) | 6770(4) | 5592(2) | 26(1) |
| C9 | $3408(4)$ | $6909(5)$ | $6090(2)$ | 28(1) |
| $\mathrm{C} 10$ | $3216(4)$ | $5990(4)$ | $6469(2)$ | 23(1) |
| C11 | $3602(4)$ | $6165(5)$ | 6979(2) | 28(1) |
| $\mathrm{C} 12$ | $2646(4)$ | 4884(4) | $6371(2)$ | 22(1) |
| C13 | $1290(4)$ | 3486(4) | $5296(2)$ | 25(1) |
| C14 | 994(4) | 3486(4) | 4860(2) | 24(1) |
| C15 | $734(4)$ | 3583(4) | 4341(2) | 25(1) |
| C16 | 1032(4) | 4664(5) | 4040(2) | 27(1) |
| C17 | 809(4) | 4830(4) | 3530(2) | 26(1) |
| C18 | $230(4)$ | 3931(4) | 3301(2) | 26(1) |
| C19 | -100(4) | 2798(4) | 3593(2) | 24(1) |
| $\mathrm{C} 20$ | -693(4) | 1854(5) | 3368(2) | 26(1) |
| C21 | -1006(4) | 764(5) | 3653(2) | 27(1) |
| C22 | -770(4) | 598(4) | 4169(2) | 27(1) |
| C23 | -189(4) | 1504(4) | 4385(2) | 26(1) |
| C24 | 153(4) | 2628(4) | 4115(2) | 23(1) |
| C25 | 3855(5) | 5307(5) | 7851(2) | 32(1) |
| C26 | 5123(5) | 4638(5) | 7907(2) | 37(1) |
| C27 | 5573(5) | 4731(6) | 8440(2) | 40(1) |
| C28 | 6561(5) | 3755(5) | 8587(2) | 38(1) |
| C29 | 6914(5) | 3843(5) | 9134(2) | 41(1) |
| C30 | 7889(5) | 2837(6) | 9308(2) | 44(1) |
| C31 | 7448(6) | 1524(6) | 9306(3) | 49(2) |


| C32 | 8336(6) | 541(7) | 9546(3) | 58(2) |
| :---: | :---: | :---: | :---: | :---: |
| C33 | 359(5) | 5098(5) | 2494(2) | 31(1) |
| C34 | -55(5) | 5002(5) | 1972(2) | 35(1) |
| C35 | 617(5) | 3988(5) | 1677(2) | 38(1) |
| C36 | 74(5) | 3853(6) | 1171(2) | 42(1) |
| C37 | 763(5) | 2929(6) | 841(2) | 42(1) |
| C38 | 66(6) | 2718(7) | 378(3) | 52(2) |
| C39 | 7863(4) | 9018(5) | 7291(2) | 28(1) |
| C40 | 7452(4) | 8904(5) | 6776(2) | 25(1) |
| C41 | 6870(4) | 7847(4) | 6672(2) | 28(1) |
| C42 | 6496(4) | 7726(4) | 6183(2) | 26(1) |
| C43 | 6675(4) | 8628(4) | 5793(2) | 24(1) |
| C44 | 7286(4) | 9749(4) | 5889(2) | 21(1) |
| C45 | 7517(4) | 10720(4) | 5509(2) | 26(1) |
| C46 | 8110(4) | 11754(4) | 5615(2) | 25(1) |
| C47 | 8439(4) | 11887(5) | 6111(2) | 27(1) |
| C48 | 8229(4) | 10959(4) | 6488(2) | 24(1) |
| C49 | 8624(4) | 11115(5) | 7002(2) | 28(1) |
| C50 | 7648(4) | 9870(4) | 6388(2) | 24(1) |
| C51 | 6292(4) | 8503(4) | 5301(2) | 24(1) |
| C52 | 5995(4) | 8493(4) | 4867(2) | 24(1) |
| C53 | 5729(4) | 8564(4) | 4346(2) | 25(1) |
| C54 | 6027(4) | 9630(5) | 4039(2) | 25(1) |
| C55 | 5795(4) | 9779(4) | 3526(2) | 27(1) |
| C56 | 5208(4) | 8876(4) | 3311(2) | 25(1) |
| C 57 | 4885(4) | 7745(4) | 3608(2) | 24(1) |
| C58 | 4304(4) | 6793(4) | 3389(2) | 27(1) |
| C59 | 3989(4) | 5716(5) | 3677(2) | 27(1) |
| C60 | 4252(4) | 5569(4) | 4193(2) | 25(1) |
| C61 | 4813(4) | 6476(5) | 4409(2) | 28(1) |
| C62 | 5144(4) | 7607(4) | 4122(2) | 24(1) |
| C63 | 8938(5) | 10227(5) | 7864(2) | 34(1) |
| C64 | 10308(5) | 9717(5) | 7856(2) | 37(1) |
| C65 | 10918(5) | 9887(6) | 8346(2) | 39(1) |
| C66 | 11089(5) | 11222(6) | 8457(2) | 40(1) |
| C67 | 11919(5) | 11330(6) | 8896(2) | 41(1) |


| C68 | $12025(5)$ | $12666(6)$ | $9030(2)$ | $43(1)$ |
| :--- | ---: | ---: | ---: | ---: |
| C69 | $12940(6)$ | $12794(6)$ | $9433(3)$ | $50(2)$ |
| C70 | $12929(6)$ | $14113(7)$ | $9610(3)$ | $54(2)$ |
| C71 | $5300(4)$ | $9983(5)$ | $2492(2)$ | $30(1)$ |
| C72 | $4843(5)$ | $9855(5)$ | $1976(2)$ | $32(1)$ |
| C73 | $5045(5)$ | $11002(5)$ | $1613(2)$ | $37(1)$ |
| C74 | $4604(6)$ | $10889(7)$ | $1096(2)$ | $50(2)$ |
| C75 | $4751(7)$ | $12035(7)$ | $738(3)$ | $56(2)$ |
| C76 | $6061(8)$ | $12460(8)$ | $628(3)$ | $72(2)$ |
| N1 | $3416(4)$ | $5192(4)$ | $7349(2)$ | $26(1)$ |
| N2 | $8430(4)$ | $10136(4)$ | $7366(2)$ | $28(1)$ |
| O1 | $2761(3)$ | $3257(3)$ | $7616(1)$ | $34(1)$ |
| O2 | $4079(3)$ | $7111(4)$ | $7080(2)$ | $38(1)$ |
| O3 | $-41(3)$ | $4002(3)$ | $2814(1)$ | $29(1)$ |
| O4 | $7723(3)$ | $8218(3)$ | $7628(1)$ | $34(1)$ |
| O5 | $9119(4)$ | $12044(4)$ | $7104(2)$ | $40(1)$ |
| O6 | $4910(3)$ | $8924(3)$ | $2823(1)$ | $29(1)$ |

Table M6N8.3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for M6N8.

| C1-O1 | 1.204(7) | C19-C24 | 1.426(7) |
| :---: | :---: | :---: | :---: |
| C1-N1 | $1.415(6)$ | C20-C21 | 1.388(7) |
| C1-C2 | 1.489(7) | C20-H20 | 0.95 |
| C2-C12 | 1.397(7) | C21-C22 | 1.408(7) |
| C2-C3 | 1.399(6) | C21-H21 | 0.95 |
| C3-C4 | 1.404(7) | C22-C23 | 1.369(6) |
| C3-H3 | 0.95 | C22-H22 | 0.95 |
| C4-C5 | $1.366(8)$ | C23-C24 | 1.410(7) |
| C4-H4 | 0.95 | C23-H23 | 0.95 |
| C5-C13 | 1.423(7) | C25-N1 | 1.463(6) |
| C5-C6 | $1.445(6)$ | C25-C26 | 1.522(8) |
| C6-C7 | 1.398(7) | C25-H25A | 0.9900 |
| C6-C12 | 1.429(7) | C25-H25B | 0.9900 |
| C7-C8 | 1.379(6) | C26-C27 | 1.541(7) |
| C7-H7 | 0.95 | C26-H26A | 0.9900 |
| C8-C9 | 1.416(7) | C26-H26B | 0.9900 |
| C8-H8 | 0.95 | C27-C28 | 1.508(8) |
| C9-C10 | 1.367(7) | C27-H27A | 0.9900 |
| C9-H9 | 0.95 | C27-H27B | 0.9900 |
| C10-C12 | 1.418(6) | C28-C29 | 1.538(8) |
| C10-C11 | 1.472(7) | C28-H28A | 0.9900 |
| C11-O2 | 1.222(6) | C28-H28B | 0.9900 |
| C11-N1 | 1.390(7) | C29-C30 | 1.539(9) |
| C13-C14 | 1.223(7) | C29-H29A | 0.9900 |
| C14-C15 | 1.419(7) | C29-H29B | 0.9900 |
| C15-C16 | 1.397(7) | C30-C31 | 1.516(9) |
| C15-C24 | 1.424(6) | C30-H30A | 0.9900 |
| C16-C17 | 1.388(7) | C30-H30B | 0.9900 |
| C16-H16 | 0.95 | C31-C32 | 1.524(10) |
| C17-C18 | 1.380(6) | C31-H31A | 0.9900 |
| C17-H17 | 0.95 | C31-H31B | 0.9900 |
| C18-O3 | 1.342(6) | C32-H32A | 0.98 |
| C18-C19 | $1.439(7)$ | C32-H32B | 0.98 |
| C19-C20 | 1.419(6) | C32-H32C | 0.98 |


| C33-O3 | 1.463(6) | C47-C48 | 1.371(7) |
| :---: | :---: | :---: | :---: |
| C33-C34 | 1.500(7) | C47-H47 | 0.95 |
| C33-H33A | 0.9900 | C48-C50 | 1.409(6) |
| C33-H33B | 0.9900 | C48-C49 | 1.484(7) |
| C34-C35 | 1.513(7) | C49-O5 | 1.216(6) |
| C34-H34A | 0.9900 | C49-N2 | 1.387(7) |
| C34-H34B | 0.9900 | C51-C52 | 1.219(7) |
| C35-C36 | 1.525(8) | C52-C53 | 1.428(7) |
| C35-H35A | 0.9900 | C53-C54 | 1.392(7) |
| C35-H35B | 0.9900 | C53-C62 | 1.423(6) |
| C36-C37 | 1.505(8) | C54-C55 | 1.395(7) |
| C36-H36A | 0.9900 | C54-H54 | 0.95 |
| C36-H36B | 0.9900 | C55-C56 | 1.369(6) |
| C37-C38 | 1.524(8) | C55-H55 | 0.95 |
| C37-H37A | 0.9900 | C56-O6 | 1.355(6) |
| C37-H37B | 0.9900 | C56-C57 | 1.442(7) |
| C38-H38A | 0.98 | C57-C62 | 1.408(7) |
| C38-H38B | 0.98 | C57-C58 | 1.412(6) |
| C38-H38C | 0.98 | C58-C59 | 1.382(7) |
| C39-O4 | 1.200(7) | C58-H58 | 0.95 |
| C39-N2 | 1.413(6) | C59-C60 | 1.412(7) |
| C39-C40 | 1.482(7) | C59-H59 | 0.95 |
| C40-C41 | 1.384(6) | C60-C61 | 1.359(6) |
| C40-C50 | 1.417(7) | C60-H60 | 0.95 |
| C41-C42 | $1.405(7)$ | C61-C62 | 1.432(7) |
| C41-H41 | 0.95 | C61-H61 | 0.95 |
| C42-C43 | 1.372(7) | C63-N2 | 1.479(6) |
| C42-H42 | 0.95 | C63-C64 | 1.545(7) |
| C43-C51 | 1.415(7) | C63-H63A | 0.9900 |
| C43-C44 | 1.453(6) | C63-H63B | 0.9900 |
| C44-C45 | 1.414(7) | C64-C65 | 1.527(7) |
| C44-C50 | 1.425(7) | C64-H64A | 0.9900 |
| C45-C46 | 1.369(7) | C64-H64B | 0.9900 |
| C45-H45 | 0.95 | C65-C66 | 1.513(8) |
| C46-C47 | 1.409(7) | C65-H65A | 0.9900 |
| C46-H46 | 0.95 | C65-H65B | 0.9900 |


| C66-C67 | 1.537(8) | C71-H71A | 0.9900 |
| :---: | :---: | :---: | :---: |
| C66-H66A | 0.9900 | C71-H71B | 0.9900 |
| C66-H66B | 0.9900 | C72-C73 | 1.520(8) |
| C67-C68 | 1.521(8) | C72-H72A | 0.9900 |
| C67-H67A | 0.9900 | C72-H72B | 0.9900 |
| C67-H67B | 0.9900 | C73-C74 | 1.500(8) |
| C68-C69 | 1.527(8) | C73-H73A | 0.9900 |
| C68-H68A | 0.9900 | C73-H73B | 0.9900 |
| C68-H68B | 0.9900 | C74-C75 | 1.506(10) |
| C69-C70 | 1.531(9) | C74-H74A | 0.9900 |
| C69-H69A | 0.9900 | C74-H74B | 0.9900 |
| C69-H69B | 0.9900 | C75-C76 | 1.505(10) |
| C70-H70A | 0.98 | C75-H75A | 0.9900 |
| C70-H70B | 0.98 | C75-H75B | 0.9900 |
| C70-H70C | 0.98 | C76-H76A | 0.98 |
| C71-06 | $1.444(6)$ | C76-H76B | 0.98 |
| C71-C72 | 1.506(7) | C76-H76C | 0.98 |
| O1-C1-N1 | 120.7(5) | C8-C7-C6 | 121.1(5) |
| O1-C1-C2 | 123.6(5) | C8-C7-H7 | 119.4 |
| N1-C1-C2 | 115.7(4) | C6-C7-H7 | 119.4 |
| C12-C2-C3 | 120.3(4) | C7-C8-C9 | 119.3(5) |
| C12-C2-C1 | 121.4(4) | C7-C8-H8 | 120.3 |
| C3-C2-C1 | 118.4(4) | C9-C8-H8 | 120.3 |
| C2-C3-C4 | 119.0(4) | C10-C9-C8 | 121.1(4) |
| C2-C3-H3 | 120.5 | C10-C9-H9 | 119.4 |
| C4-C3-H3 | 120.5 | C8-C9-H9 | 119.4 |
| C5-C4-C3 | 122.3(4) | C9-C10-C12 | 120.1(4) |
| C5-C4-H4 | 118.9 | C9-C10-C11 | 119.2(4) |
| C3-C4-H4 | 118.9 | C12-C10-C11 | 120.6(4) |
| C4-C5-C13 | 122.0(4) | O2-C11-N1 | 120.2(5) |
| C4-C5-C6 | 120.1(5) | O2-C11-C10 | 122.6(5) |
| C13-C5-C6 | 117.9(5) | N1-C11-C10 | 117.2(4) |
| C7-C6-C12 | 119.3(4) | C2-C12-C10 | 120.0(4) |
| C7-C6-C5 | 123.5(5) | C2-C12-C6 | 121.1(4) |
| C12-C6-C5 | 117.2(4) | C10-C12-C6 | 118.9(4) |


| C14-C13-C5 | 173.6(5) | C26-C25-H25B | 109.3 |
| :---: | :---: | :---: | :---: |
| C13-C14-C15 | 174.3(4) | H25A-C25-H25B | 108.0 |
| C16-C15-C14 | 119.2(4) | C25-C26-C27 | 111.6(5) |
| C16-C15-C24 | 118.2(5) | C25-C26-H26A | 109.3 |
| C14-C15-C24 | 122.5(4) | C27-C26-H26A | 109.3 |
| C17-C16-C15 | 122.7(4) | C25-C26-H26B | 109.3 |
| C17-C16-H16 | 118.6 | C27-C26-H26B | 109.3 |
| C15-C16-H16 | 118.6 | H26A-C26-H26B | 108.0 |
| C18-C17-C16 | 120.4(4) | C28-C27-C26 | 114.4(5) |
| C18-C17-H17 | 119.8 | C28-C27-H27A | 108.7 |
| C16-C17-H17 | 119.8 | C26-C27-H27A | 108.7 |
| O3-C18-C17 | 125.3(4) | C28-C27-H27B | 108.7 |
| O3-C18-C19 | 115.3(4) | C26-C27-H27B | 108.7 |
| C17-C18-C19 | 119.3(5) | H27A-C27-H27B | 107.6 |
| C20-C19-C24 | 119.6(4) | C27-C28-C29 | 112.0(5) |
| C20-C19-C18 | 120.7(5) | C27-C28-H28A | 109.2 |
| C24-C19-C18 | 119.8(4) | C29-C28-H28A | 109.2 |
| C21-C20-C19 | 120.2(5) | C27-C28-H28B | 109.2 |
| C21-C20-H20 | 119.9 | C29-C28-H28B | 109.2 |
| C19-C20-H20 | 119.9 | H28A-C28-H28B | 107.9 |
| C20-C21-C22 | 120.4(4) | C28-C29-C30 | 114.0(5) |
| C20-C21-H21 | 119.8 | C28-C29-H29A | 108.8 |
| C22-C21-H21 | 119.8 | C30-C29-H29A | 108.8 |
| C23-C22-C21 | 119.4(4) | C28-C29-H29B | 108.8 |
| C23-C22-H22 | 120.3 | C30-C29-H29B | 108.8 |
| C21-C22-H22 | 120.3 | H29A-C29-H29B | 107.7 |
| C22-C23-C24 | 122.6(5) | C31-C30-C29 | 113.2(5) |
| C22-C23-H23 | 118.7 | C31-C30-H30A | 108.9 |
| C24-C23-H23 | 118.7 | C29-C30-H30A | 108.9 |
| C23-C24-C15 | 122.8(5) | C31-C30-H30B | 108.9 |
| C23-C24-C19 | 117.7(4) | C29-C30-H30B | 108.9 |
| C15-C24-C19 | 119.5(4) | H30A-C30-H30B | 107.8 |
| N1-C25-C26 | 111.5(4) | C30-C31-C32 | 113.1(5) |
| N1-C25-H25A | 109.3 | C30-C31-H31A | 109.0 |
| C26-C25-H25A | 109.3 | C32-C31-H31A | 109.0 |
| N1-C25-H25B | 109.3 | C30-C31-H31B | 109.0 |


| C32-C31-H31B | 109.0 | C38-C37-H37B | 109.2 |
| :---: | :---: | :---: | :---: |
| H31A-C31-H31B | 107.8 | H37A-C37-H37B | 107.9 |
| C31-C32-H32A | 109.5 | C37-C38-H38A | 109.5 |
| C31-C32-H32B | 109.5 | C37-C38-H38B | 109.5 |
| H32A-C32-H32B | 109.5 | H38A-C38-H38B | 109.5 |
| C31-C32-H32C | 109.5 | C37-C38-H38C | 109.5 |
| H32A-C32-H32C | 109.5 | H38A-C38-H38C | 109.5 |
| H32B-C32-H32C | 109.5 | H38B-C38-H38C | 109.5 |
| O3-C33-C34 | 108.4(4) | O4-C39-N2 | 121.2(5) |
| O3-C33-H33A | 110.0 | O4-C39-C40 | 122.7(4) |
| C34-C33-H33A | 110.0 | N2-C39-C40 | 116.1(4) |
| O3-C33-H33B | 110.0 | C41-C40-C50 | 119.6(4) |
| C34-C33-H33B | 110.0 | C41-C40-C39 | 119.8(5) |
| H33A-C33-H33B | 108.4 | C50-C40-C39 | 120.6(4) |
| C33-C34-C35 | 115.2(5) | C40-C41-C42 | 120.0(5) |
| C33-C34-H34A | 108.5 | C40-C41-H41 | 120.0 |
| C35-C34-H34A | 108.5 | C42-C41-H41 | 120.0 |
| C33-C34-H34B | 108.5 | C43-C42-C41 | 122.7(4) |
| C35-C34-H34B | 108.5 | C43-C42-H42 | 118.7 |
| H34A-C34-H34B | 107.5 | C41-C42-H42 | 118.7 |
| C34-C35-C36 | 112.8(5) | C42-C43-C51 | 122.4(4) |
| C34-C35-H35A | 109.0 | C42-C43-C44 | 118.7(4) |
| C36-C35-H35A | 109.0 | C51-C43-C44 | 118.9(4) |
| C34-C35-H35B | 109.0 | C45-C44-C50 | 119.3(4) |
| C36-C35-H35B | 109.0 | C45-C44-C43 | 122.5(4) |
| H35A-C35-H35B | 107.8 | C50-C44-C43 | 118.2(4) |
| C37-C36-C35 | 115.4(5) | C46-C45-C44 | 120.5(5) |
| C37-C36-H36A | 108.4 | C46-C45-H45 | 119.8 |
| C35-C36-H36A | 108.4 | C44-C45-H45 | 119.8 |
| C37-C36-H36B | 108.4 | C45-C46-C47 | 120.1(4) |
| C35-C36-H36B | 108.4 | C45-C46-H46 | 119.9 |
| H36A-C36-H36B | 107.5 | C47-C46-H46 | 119.9 |
| C36-C37-C38 | 112.1(5) | C48-C47-C46 | 120.6(4) |
| C36-C37-H37A | 109.2 | C48-C47-H47 | 119.7 |
| C38-C37-H37A | 109.2 | C46-C47-H47 | 119.7 |
| C36-C37-H37B | 109.2 | C47-C48-C50 | 120.6(5) |


| C47-C48-C49 | 119.1(4) | C62-C61-H61 | 119.5 |
| :---: | :---: | :---: | :---: |
| C50-C48-C49 | 120.3(5) | C57-C62-C53 | 120.6(4) |
| O5-C49-N2 | 120.6(5) | C57-C62-C61 | 117.9(4) |
| O5-C49-C48 | 122.3(5) | C53-C62-C61 | 121.5(5) |
| N2-C49-C48 | 117.1(4) | N2-C63-C64 | 110.7(4) |
| C48-C50-C40 | 120.4(4) | N2-C63-H63A | 109.5 |
| C48-C50-C44 | 118.8(5) | C64-C63-H63A | 109.5 |
| C40-C50-C44 | 120.8(4) | N2-C63-H63B | 109.5 |
| C52-C51-C43 | 174.7(5) | C64-C63-H63B | 109.5 |
| C51-C52-C53 | 174.9(4) | H63A-C63-H63B | 108.1 |
| C54-C53-C62 | 117.7(5) | C65-C64-C63 | 113.0(4) |
| C54-C53-C52 | 118.9(4) | C65-C64-H64A | 109.0 |
| C62-C53-C52 | 123.4(4) | C63-C64-H64A | 109.0 |
| C53-C54-C55 | 122.7(4) | C65-C64-H64B | 109.0 |
| C53-C54-H54 | 118.7 | C63-C64-H64B | 109.0 |
| C55-C54-H54 | 118.7 | H64A-C64-H64B | 107.8 |
| C56-C55-C54 | 120.0(4) | C66-C65-C64 | 115.6(5) |
| C56-C55-H55 | 120.0 | C66-C65-H65A | 108.4 |
| C54-C55-H55 | 120.0 | C64-C65-H65A | 108.4 |
| O6-C56-C55 | 125.5(4) | C66-C65-H65B | 108.4 |
| O6-C56-C57 | 114.5(4) | C64-C65-H65B | 108.4 |
| C55-C56-C57 | 120.0(5) | H65A-C65-H65B | 107.4 |
| C62-C57-C58 | 120.3(4) | C65-C66-C67 | 113.0(5) |
| C62-C57-C56 | 119.0(4) | C65-C66-H66A | 109.0 |
| C58-C57-C56 | 120.7(5) | C67-C66-H66A | 109.0 |
| C59-C58-C57 | 120.3(5) | C65-C66-H66B | 109.0 |
| C59-C58-H58 | 119.8 | C67-C66-H66B | 109.0 |
| C57-C58-H58 | 119.8 | H66A-C66-H66B | 107.8 |
| C58-C59-C60 | 119.7(4) | C68-C67-C66 | 113.1(5) |
| C58-C59-H59 | 120.2 | C68-C67-H67A | 109.0 |
| C60-C59-H59 | 120.2 | C66-C67-H67A | 109.0 |
| C61-C60-C59 | 120.7(4) | C68-C67-H67B | 109.0 |
| C61-C60-H60 | 119.6 | C66-C67-H67B | 109.0 |
| C59-C60-H60 | 119.6 | H67A-C67-H67B | 107.8 |
| C60-C61-C62 | 121.1(5) | C67-C68-C69 | 113.4(5) |
| C60-C61-H61 | 119.5 | C67-C68-H68A | 108.9 |


| C69-C68-H68A | 108.9 | C72-C73-H73A | 108.8 |
| :---: | :---: | :---: | :---: |
| C67-C68-H68B | 108.9 | C74-C73-H73B | 108.8 |
| C69-C68-H68B | 108.9 | C72-C73-H73B | 108.8 |
| H68A-C68-H68B | 107.7 | H73A-C73-H73B | 107.7 |
| C68-C69-C70 | 113.0(6) | C73-C74-C75 | 114.7(5) |
| C68-C69-H69A | 109.0 | C73-C74-H74A | 108.6 |
| C70-C69-H69A | 109.0 | C75-C74-H74A | 108.6 |
| C68-C69-H69B | 109.0 | C73-C74-H74B | 108.6 |
| C70-C69-H69B | 109.0 | C75-C74-H74B | 108.6 |
| H69A-C69-H69B | 107.8 | H74A-C74-H74B | 107.6 |
| C69-C70-H70A | 109.5 | C76-C75-C74 | 115.8(7) |
| C69-C70-H70B | 109.5 | C76-C75-H75A | 108.3 |
| H70A-C70-H70B | 109.5 | C74-C75-H75A | 108.3 |
| C69-C70-H70C | 109.5 | C76-C75-H75B | 108.3 |
| H70A-C70-H70C | 109.5 | C74-C75-H75B | 108.3 |
| H70B-C70-H70C | 109.5 | H75A-C75-H75B | 107.4 |
| O6-C71-C72 | 108.2(4) | C75-C76-H76A | 109.5 |
| O6-C71-H71A | 110.1 | C75-C76-H76B | 109.5 |
| C72-C71-H71A | 110.1 | H76A-C76-H76B | 109.5 |
| O6-C71-H71B | 110.0 | C75-C76-H76C | 109.5 |
| C72-C71-H71B | 110.0 | H76A-C76-H76C | 109.5 |
| H71A-C71-H71B | 108.4 | H76B-C76-H76C | 109.5 |
| C71-C72-C73 | 113.1(4) | C11-N1-C1 | 125.1(4) |
| C71-C72-H72A | 109.0 | C11-N1-C25 | 118.5(4) |
| C73-C72-H72A | 109.0 | C1-N1-C25 | 116.3(4) |
| C71-C72-H72B | 109.0 | C49-N2-C39 | 125.4(4) |
| C73-C72-H72B | 109.0 | C49-N2-C63 | 117.4(4) |
| H72A-C72-H72B | 107.8 | C39-N2-C63 | 117.0(4) |
| C74-C73-C72 | 113.9(5) | C18-O3-C33 | 117.2(4) |
| C74-C73-H73A | 108.8 | C56-06-C71 | 117.5(4) |

Table M6N8.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for M6N8. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | $31(3)$ | 26(3) | 31(3) | -6(2) | -3(2) | 3(2) |
| C2 | $16(2)$ | 25(2) | 30(2) | -8(2) | -4(2) | 2(2) |
| C3 | $26(2)$ | $13(2)$ | $38(3)$ | -1(2) | -1(2) | 6(2) |
| C4 | $21(2)$ | $16(2)$ | $43(3)$ | -9(2) | -5(2) | 0(2) |
| C5 | $19(2)$ | 20(2) | 40(3) | -10(2) | -5(2) | 1(2) |
| C6 | $14(2)$ | $13(2)$ | $43(3)$ | -6(2) | -6(2) | 7(2) |
| C7 | 22(2) | 22(2) | 37(3) | -11(2) | -4(2) | 3(2) |
| C8 | 22(2) | 16(2) | 38(3) | -1(2) | -2(2) | 4(2) |
| C9 | 21(2) | 19(2) | 44(3) | -8(2) | -9(2) | 4(2) |
| C10 | 16(2) | 20(2) | 34(2) | -7(2) | -3(2) | 7(2) |
| C11 | 26(2) | 26(3) | 33(3) | -6(2) | -5(2) | 1(2) |
| C12 | 20(2) | 13(2) | 32(2) | -4(2) | -6(2) | 4(2) |
| C13 | 24(2) | 15(2) | 38(3) | -4(2) | -6(2) | 2(2) |
| C14 | 25(2) | 12(2) | 35(3) | -5(2) | -3(2) | -2(2) |
| C15 | 18(2) | 20(2) | 38(3) | -9(2) | -3(2) | 4(2) |
| C16 | 26(2) | 20(2) | 36(3) | -12(2) | 1(2) | -6(2) |
| C17 | 26(2) | 15(2) | 37(3) | -2(2) | -4(2) | -3(2) |
| C18 | 20(2) | 20(2) | 37(3) | -4(2) | -1(2) | $0(2)$ |
| C19 | 18(2) | 18(2) | 35(3) | -7(2) | -2(2) | 3(2) |
| C20 | 20(2) | 19(2) | 39(3) | -8(2) | -2(2) | 7(2) |
| C21 | 20(2) | 19(2) | 45(3) | -10(2) | -5(2) | $0(2)$ |
| C22 | 23(2) | 15(2) | 42(3) | -2(2) | -4(2) | 1(2) |
| C23 | 24(2) | 20(2) | 35(3) | -6(2) | -4(2) | 5(2) |
| C24 | 12(2) | 21(2) | 36(3) | -7(2) | -2(2) | 5(2) |
| C25 | 33(3) | 30(3) | 33(3) | -7(2) | -8(2) | 1(2) |
| C26 | 36(3) | 34(3) | 43(3) | -9(2) | -12(2) | 1(2) |
| C27 | 44(3) | 36(3) | 43(3) | -4(2) | -9(2) | -1(2) |
| C28 | 37(3) | 34(3) | 44(3) | 1(2) | -8(2) | -6(2) |
| C29 | 40(3) | 31(3) | 55(3) | -6(2) | -14(2) | -2(2) |
| C30 | 36(3) | 45(4) | 51(3) | -7(3) | -6(2) | $0(3)$ |
| C31 | 60(4) | 33(3) | 56(4) | $-2(3)$ | -13(3) | -2(3) |


| C32 | 54(4) | 50(4) | 69(5) | 0(3) | -12(3) | 4(3) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C33 | 34(3) | 19(2) | 40(3) | 1(2) | -2(2) | -3(2) |
| C34 | 35(3) | 31(3) | 38(3) | 1(2) | -5(2) | 1(2) |
| C35 | 32(3) | 30(3) | 50(3) | -3(2) | -5(2) | 2(2) |
| C36 | 41(3) | 39(3) | 48(3) | -4(2) | -10(2) | 3(2) |
| C37 | 46(3) | 36(3) | 44(3) | -4(2) | -7(2) | -4(2) |
| C38 | 58(4) | 49(4) | 51(4) | -17(3) | -5(3) | -5(3) |
| C39 | 28(2) | 24(3) | 35(3) | -8(2) | -4(2) | O(2) |
| C40 | 21(2) | 25(2) | 30(2) | -5(2) | -4(2) | -2(2) |
| C41 | 30(2) | 18(2) | 35(3) | -1(2) | -3(2) | 3(2) |
| C42 | 21(2) | 16(2) | 43(3) | -10(2) | -6(2) | 1(2) |
| C43 | 21(2) | 15(2) | 37(3) | -4(2) | -5(2) | 3(2) |
| C44 | 13(2) | 17(2) | 34(2) | -6(2) | -10(2) | 7(2) |
| C45 | 18(2) | 20(2) | 38(3) | -4(2) | -6(2) | 8(2) |
| C46 | 21(2) | 16(2) | 37(3) | 0 (2) | -4(2) | 7(2) |
| C47 | 25(2) | 19(2) | 38(3) | -10(2) | -4(2) | 1(2) |
| C48 | 15(2) | 18(2) | 38(3) | -7(2) | -6(2) | 4(2) |
| C49 | 27(2) | 20(2) | 38(3) | -7(2) | -6(2) | 2(2) |
| C50 | 21(2) | 18(2) | 34(3) | -7(2) | -2(2) | 5(2) |
| C51 | 21(2) | 10(2) | 43(3) | -11(2) | -7(2) | 6(2) |
| C52 | 21(2) | 13(2) | 40(3) | -5(2) | -4(2) | -1(2) |
| C53 | 19(2) | 16(2) | 40(3) | -4(2) | -7(2) | 6(2) |
| C54 | 17(2) | 20(2) | 40(3) | -11(2) | -4(2) | 2(2) |
| C55 | 21(2) | 17(2) | 43(3) | -4(2) | -4(2) | 0 (2) |
| C56 | 22(2) | 20(2) | 33(3) | -7(2) | 1(2) | 3(2) |
| C57 | 19(2) | 15(2) | 39(3) | -5(2) | -3(2) | 3(2) |
| C58 | 16(2) | 18(2) | 46(3) | -2(2) | -9(2) | 4(2) |
| C59 | 24(2) | 22(2) | 36(3) | -14(2) | -4(2) | -1(2) |
| C60 | 19(2) | 17(2) | 40(3) | -4(2) | -2(2) | $0(2)$ |
| C61 | 26(2) | 24(2) | 32(2) | -2(2) | -1(2) | 0 (2) |
| C62 | 18(2) | 15(2) | 38(3) | -6(2) | -3(2) | 3(2) |
| C63 | 38(3) | 34(3) | 33(3) | -6(2) | -12(2) | -3(2) |
| C64 | 34(3) | 35(3) | 45(3) | -13(2) | -12(2) | 5(2) |
| C65 | 34(3) | 37(3) | 49(3) | -11(2) | -13(2) | 1(2) |
| C66 | 36(3) | 42(3) | 45(3) | -6(2) | -8(2) | -9(2) |
| C67 | 31(3) | 39(3) | 56(4) | -8(3) | -12(2) | -4(2) |


| C68 | $42(3)$ | $36(3)$ | $52(3)$ | $-3(2)$ | $-9(2)$ | $-5(2)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C69 | $43(3)$ | $47(4)$ | $60(4)$ | $-10(3)$ | $-9(3)$ | $-10(3)$ |
| C70 | $60(4)$ | $49(4)$ | $55(4)$ | $-10(3)$ | $-6(3)$ | $-13(3)$ |
| C71 | $29(2)$ | $23(2)$ | $39(3)$ | $-1(2)$ | $-4(2)$ | $-2(2)$ |
| C72 | $35(3)$ | $28(3)$ | $34(3)$ | $-5(2)$ | $-7(2)$ | $4(2)$ |
| C73 | $28(3)$ | $32(3)$ | $51(3)$ | $-3(2)$ | $-5(2)$ | $-4(2)$ |
| C74 | $57(4)$ | $45(4)$ | $52(4)$ | $-7(3)$ | $-10(3)$ | $-11(3)$ |
| C75 | $69(4)$ | $47(4)$ | $55(4)$ | $-11(3)$ | $-16(3)$ | $0(3)$ |
| C76 | $99(6)$ | $60(5)$ | $59(4)$ | $3(4)$ | $-12(4)$ | $-23(4)$ |
| N1 | $26(2)$ | $22(2)$ | $33(2)$ | $-6(2)$ | $-2(2)$ | $-3(2)$ |
| N2 | $28(2)$ | $24(2)$ | $34(2)$ | $-8(2)$ | $-5(2)$ | $-3(2)$ |
| O1 | $40(2)$ | $24(2)$ | $39(2)$ | $0(2)$ | $-7(2)$ | $-2(2)$ |
| O2 | $40(2)$ | $29(2)$ | $47(2)$ | $-6(2)$ | $-13(2)$ | $-13(2)$ |
| O3 | $32(2)$ | $20(2)$ | $37(2)$ | $-5(1)$ | $-5(1)$ | $-1(1)$ |
| O4 | $37(2)$ | $26(2)$ | $39(2)$ | $1(2)$ | $-7(2)$ | $-5(2)$ |
| O5 | $46(2)$ | $32(2)$ | $45(2)$ | $-8(2)$ | $-14(2)$ | $-15(2)$ |
| O6 | $31(2)$ | $23(2)$ | $36(2)$ | $-3(1)$ | $-7(1)$ | $-2(1)$ |
|  |  |  |  |  |  |  |

Table M6N8.5. Hydrogen coordinates ( $\mathrm{x} 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \mathrm{x} 10^{3}\right)$ for M6N8.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| H3 | 1767 | 2209 | 6926 | 31 |
| H4 | 1129 | 1979 | 6114 | 32 |
| H7 | 2254 | 5624 | 5161 | 32 |
| H8 | 3245 | 7399 | 5328 | 31 |
| H9 | 3772 | 7654 | 6162 | 33 |
| H16 | 1404 | 5311 | 4191 | 32 |
| H17 | 1056 | 5568 | 3337 | 31 |
| H20 | -877 | 1969 | 3023 | 31 |
| H21 | -1382 | 126 | 3498 | 33 |
| H22 | -1011 | -136 | 4366 | 32 |
| H23 | -8 | 1369 | 4731 | 31 |
| H25A | 3243 | 4950 | 8114 | 38 |
| H25B | 3917 | 6199 | 7906 | 38 |
| H26A | 5739 | 5009 | 7650 | 45 |
| H26B | 5066 | 3750 | 7844 | 45 |
| H27A | 5907 | 5564 | 8456 | 49 |
| H27B | 4847 | 4659 | 8692 | 49 |
| H28A | 7314 | 3858 | 8351 | 45 |
| H28B | 6251 | 2918 | 8554 | 45 |
| H29A | 6151 | 3774 | 9366 | 49 |
| H29B | 7244 | 4673 | 9162 | 49 |
| H30A | 8661 | 2917 | 9081 | 53 |
| H30B | 8096 | 2984 | 9655 | 53 |
| H31A | 7355 | 1337 | 8952 | 59 |
| H31B | 6617 | 1477 | 9493 | 59 |
| H32A | 9153 | 562 | 9356 | 87 |
| H32B | 8000 | -284 | 9537 | 87 |
| H32C | 8425 | 714 | 9898 | 87 |
| H33A | 1278 | 5137 | 2480 | 38 |
| H33B | -16 | 5865 | 2637 | 38 |


| H34A | 63 | 5811 | 1775 | 42 |
| :---: | :---: | :---: | :---: | :---: |
| H34B | -959 | 4854 | 2001 | 42 |
| H35A | 569 | 3186 | 1885 | 45 |
| H35B | 1509 | 4178 | 1615 | 45 |
| H36A | -799 | 3604 | 1239 | 51 |
| H36B | 55 | 4679 | 979 | 51 |
| H37A | 883 | 2126 | 1043 | 50 |
| H37B | 1598 | 3236 | 728 | 50 |
| H38A | -763 | 2420 | 489 | 78 |
| H38B | 533 | 2095 | 180 | 78 |
| H38C | -20 | 3503 | 169 | 78 |
| H41 | 6723 | 7202 | 6932 | 33 |
| H42 | 6103 | 6990 | 6119 | 32 |
| H45 | 7259 | 10656 | 5177 | 31 |
| H46 | 8300 | 12382 | 5353 | 30 |
| H47 | 8809 | 12627 | 6186 | 32 |
| H54 | 6405 | 10282 | 4184 | 30 |
| H55 | 6043 | 10508 | 3327 | 32 |
| H58 | 4129 | 6893 | 3042 | 32 |
| H59 | 3597 | 5077 | 3530 | 32 |
| H60 | 4034 | 4829 | 4391 | 30 |
| H61 | 4988 | 6357 | 4756 | 33 |
| H63A | 8429 | 9746 | 8130 | 41 |
| H63B | 8894 | 11108 | 7948 | 41 |
| H64A | 10336 | 8819 | 7798 | 45 |
| H64B | 10794 | 10148 | 7568 | 45 |
| H65A | 10404 | 9486 | 8633 | 47 |
| H65B | 11746 | 9442 | 8331 | 47 |
| H66A | 10261 | 11629 | 8540 | 48 |
| H66B | 11466 | 11674 | 8147 | 48 |
| H67A | 11572 | 10832 | 9199 | 50 |
| H67B | 12764 | 10973 | 8803 | 50 |
| H68A | 11191 | 12997 | 9153 | 51 |
| H68B | 12296 | 13180 | 8719 | 51 |
| H69A | 13792 | 12558 | 9295 | 59 |
| H69B | 12728 | 12206 | 9730 | 59 |


| H70A | 13055 | 14711 | 9314 | 80 |
| :--- | ---: | ---: | ---: | ---: |
| H70B | 13601 | 14168 | 9836 | 80 |
| H70C | 12124 | 14307 | 9792 | 80 |
| H71A | 6221 | 10010 | 2466 | 36 |
| H71B | 4946 | 10764 | 2629 | 36 |
| H72A | 3942 | 9696 | 2015 | 39 |
| H72B | 5283 | 9125 | 1827 | 39 |
| H73A | 4601 | 11729 | 1763 | 44 |
| H73B | 5946 | 11163 | 1578 | 44 |
| H74A | 3712 | 10691 | 1134 | 61 |
| H74B | 5073 | 10181 | 943 | 61 |
| H75A | 4418 | 11873 | 413 | 67 |
| H75B | 4230 | 12726 | 881 | 67 |
| H76A | 6364 | 12738 | 938 | 108 |
| H76B | 6069 | 13151 | 365 | 108 |
| H76C | 6604 | 11768 | 510 | 108 |

Table M6N8.6. Torsion angles $\left[{ }^{\circ}\right]$ for M6N8.

| O1-C1-C2-C12 | -178.8(5) | C5-C6-C12-C10 | -179.8(4) |
| :---: | :---: | :---: | :---: |
| N1-C1-C2-C12 | 2.2(7) | C14-C15-C16-C17 | 180.0(4) |
| O1-C1-C2-C3 | 0.8(8) | C24-C15-C16-C17 | -1.3(7) |
| N1-C1-C2-C3 | -178.2(4) | C15-C16-C17-C18 | 2.4(8) |
| C12-C2-C3-C4 | 0.4(7) | C16-C17-C18-O3 | 179.4(5) |
| C1-C2-C3-C4 | -179.2(4) | C16-C17-C18-C19 | -2.2(7) |
| C2-C3-C4-C5 | -0.2(7) | O3-C18-C19-C20 | -1.3(7) |
| C3-C4-C5-C13 | -179.9(4) | C17-C18-C19-C20 | -179.8(4) |
| C3-C4-C5-C6 | -0.2(7) | O3-C18-C19-C24 | 179.8(4) |
| C4-C5-C6-C7 | 178.0(4) | C17-C18-C19-C24 | 1.2(7) |
| C13-C5-C6-C7 | -2.2(7) | C24-C19-C20-C21 | -1.1(7) |
| C4-C5-C6-C12 | 0.2(7) | C18-C19-C20-C21 | 180.0(4) |
| C13-C5-C6-C12 | 180.0(4) | C19-C20-C21-C22 | 1.7(7) |
| C12-C6-C7-C8 | -1.1(7) | C20-C21-C22-C23 | -2.2(7) |
| C5-C6-C7-C8 | -178.8(4) | C21-C22-C23-C24 | 2.1(7) |
| C6-C7-C8-C9 | -1.4(7) | C22-C23-C24-C15 | 178.7(4) |
| C7-C8-C9-C10 | 2.8(7) | C22-C23-C24-C19 | -1.4(7) |
| C8-C9-C10-C12 | -1.5(7) | C16-C15-C24-C23 | -179.8(5) |
| C8-C9-C10-C11 | 178.7(4) | C14-C15-C24-C23 | -1.2(7) |
| C9-C10-C11-O2 | 0.8(7) | C16-C15-C24-C19 | 0.3(6) |
| C12-C10-C11-O2 | -178.9(5) | C14-C15-C24-C19 | 178.9(4) |
| C9-C10-C11-N1 | -178.4(4) | C20-C19-C24-C23 | 0.9(6) |
| C12-C10-C11-N1 | 1.8(7) | C18-C19-C24-C23 | 179.9(4) |
| C3-C2-C12-C10 | 179.5(4) | C20-C19-C24-C15 | -179.2(4) |
| C1-C2-C12-C10 | -1.0(7) | C18-C19-C24-C15 | -0.2(6) |
| C3-C2-C12-C6 | -0.3(7) | N1-C25-C26-C27 | -178.6(4) |
| C1-C2-C12-C6 | 179.2(4) | C25-C26-C27-C28 | 159.8(5) |
| C9-C10-C12-C2 | 179.1(4) | C26-C27-C28-C29 | -176.5(4) |
| C11-C10-C12-C2 | -1.1(7) | C27-C28-C29-C30 | 178.1(5) |
| C9-C10-C12-C6 | -1.1(7) | C28-C29-C30-C31 | -61.5(7) |
| C11-C10-C12-C6 | 178.7(4) | C29-C30-C31-C32 | -172.1(6) |
| C7-C6-C12-C2 | -177.9(4) | O3-C33-C34-C35 | -69.4(5) |
| C5-C6-C12-C2 | 0.0(6) | C33-C34-C35-C36 | 174.5(4) |
| C7-C6-C12-C10 | 2.3(7) | C34-C35-C36-C37 | 175.4(5) |


| C35-C36-C37-C38 | 172.1(5) | C62-C53-C54-C55 | -1.1(7) |
| :---: | :---: | :---: | :---: |
| O4-C39-C40-C41 | 0.6(8) | C52-C53-C54-C55 | -179.7(4) |
| N2-C39-C40-C41 | -179.0(4) | C53-C54-C55-C56 | 2.5(7) |
| O4-C39-C40-C50 | -179.5(5) | C54-C55-C56-O6 | 178.6(4) |
| N2-C39-C40-C50 | 0.9(7) | C54-C55-C56-C57 | -2.9(7) |
| C50-C40-C41-C42 | 1.1(7) | O6-C56-C57-C62 | -179.3(4) |
| C39-C40-C41-C42 | -179.0(4) | C55-C56-C57-C62 | 2.0(7) |
| C40-C41-C42-C43 | -0.4(8) | O6-C56-C57-C58 | 0.0(7) |
| C41-C42-C43-C51 | -179.8(4) | C55-C56-C57-C58 | -178.6(4) |
| C41-C42-C43-C44 | 0.6(7) | C62-C57-C58-C59 | -0.2(7) |
| C42-C43-C44-C45 | 179.5(4) | C56-C57-C58-C59 | -179.5(4) |
| C51-C43-C44-C45 | -0.2(7) | C57-C58-C59-C60 | -0.1(7) |
| C42-C43-C44-C50 | -1.3(6) | C58-C59-C60-C61 | -0.1(7) |
| C51-C43-C44-C50 | 179.0(4) | C59-C60-C61-C62 | 0.5(7) |
| C50-C44-C45-C46 | 1.6(7) | C58-C57-C62-C53 | -180.0(4) |
| C43-C44-C45-C46 | -179.2(4) | C56-C57-C62-C53 | -0.7(7) |
| C44-C45-C46-C47 | -3.3(7) | C58-C57-C62-C61 | 0.7(7) |
| C45-C46-C47-C48 | 3.4(7) | C56-C57-C62-C61 | 180.0(4) |
| C46-C47-C48-C50 | -1.9(7) | C54-C53-C62-C57 | 0.2(7) |
| C46-C47-C48-C49 | 178.1(4) | C52-C53-C62-C57 | 178.8(4) |
| C47-C48-C49-O5 | 0.6(8) | C54-C53-C62-C61 | 179.5(4) |
| C50-C48-C49-O5 | -179.4(5) | C52-C53-C62-C61 | -1.9(7) |
| C47-C48-C49-N2 | -178.0(4) | C60-C61-C62-C57 | -0.8(7) |
| C50-C48-C49-N2 | 2.0(7) | C60-C61-C62-C53 | 179.8(4) |
| C47-C48-C50-C40 | 179.0(4) | N2-C63-C64-C65 | 175.1(5) |
| C49-C48-C50-C40 | -1.0(7) | C63-C64-C65-C66 | -65.7(7) |
| C47-C48-C50-C44 | 0.2(7) | C64-C65-C66-C67 | -169.2(5) |
| C49-C48-C50-C44 | -179.7(4) | C65-C66-C67-C68 | -176.3(5) |
| C41-C40-C50-C48 | 179.5(4) | C66-C67-C68-C69 | -174.8(5) |
| C39-C40-C50-C48 | -0.5(7) | C67-C68-C69-C70 | -173.3(5) |
| C41-C40-C50-C44 | -1.9(7) | O6-C71-C72-C73 | 172.2(4) |
| C39-C40-C50-C44 | 178.2(4) | C71-C72-C73-C74 | 179.6(5) |
| C45-C44-C50-C48 | -0.1(6) | C72-C73-C74-C75 | 177.7(6) |
| C43-C44-C50-C48 | -179.3(4) | C73-C74-C75-C76 | 59.4(9) |
| C45-C44-C50-C40 | -178.8(4) | O2-C11-N1-C1 | -179.7(5) |
| C43-C44-C50-C40 | 2.0(7) | C10-C11-N1-C1 | -0.5(7) |


| O2-C11-N1-C25 | $-2.7(7)$ | O4-C39-N2-C49 | $-179.5(5)$ |
| :--- | :---: | :--- | :---: |
| C10-C11-N1-C25 | $176.5(4)$ | C40-C39-N2-C49 | $0.1(7)$ |
| O1-C1-N1-C11 | $179.5(5)$ | O4-C39-N2-C63 | $5.2(7)$ |
| C2-C1-N1-C11 | $-1.5(7)$ | C40-C39-N2-C63 | $-175.2(4)$ |
| O1-C1-N1-C25 | $2.4(7)$ | C64-C63-N2-C49 | $-86.8(6)$ |
| C2-C1-N1-C25 | $-178.5(4)$ | C64-C63-N2-C39 | $88.9(5)$ |
| C26-C25-N1-C11 | $-97.6(5)$ | C17-C18-O3-C33 | $2.8(7)$ |
| C26-C25-N1-C1 | $79.7(5)$ | C34-C33-O3-C18 | $-175.7(4)$ |
| O5-C49-N2-C39 | $179.9(5)$ | C55-C56-O6-C71 | $-178.9(4)$ |
| C48-C49-N2-C39 | $-1.6(7)$ | C57-C56-O6-C71 | $3.6(7)$ |
| O5-C49-N2-C63 | $-4.8(7)$ | C72-C71-O6-C56 | $-175.0(4)$ |
| C48-C49-N2-C63 | $173.7(4)$ | $-178.6(4)$ |  |

End crystallographic info for M6N8.

## Crystallographic Material for M8N6

Crystallographic Material for M8N6.

X-ray Experimental.
Table M8N6.1. Crystallographic Data for M8N6.
Table M8N6.2. Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the non-hydrogen atoms of M8N6.

Table M8N6.3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of M8N6.

Table M8N6.4. Anisotropic thermal parameters for the non-hydrogen atoms of M8N6.
Table M8N6.5. Fractional coordinates and isotropic thermal parameters $\left(\AA^{2}\right)$ for the hydrogen atoms of M8N6.

Table M8N6.6. Torsion Angles $\left(^{\circ}\right)$ for the non-hydrogen atoms of M8N6.

X-ray Experimental for complex $\mathrm{C}_{38} \mathrm{H}_{41} \mathrm{NO}_{3}$ (M8N6): Crystals grew as long, thin needles by slow evaporation from 1:1:1 dichloromethane:acetonitrile:chloroform. The data crystal was cut from a longer crystal and had approximate dimensions; $0.61 \times 0.04 \times 0.03 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus Cu K $\alpha$ radiation source $(\lambda=1.5418 \AA)$ with collimating mirror monochromators. A total of 790 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 15 seconds per frame with a detector offset of $+/-42.2^{\circ}$ and 50 seconds per frame with a detector offset of $+/-110.4^{\circ}$. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.39.46. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6. ${ }^{3}$ Structure analysis was aided by use of
the programs PLATON ${ }^{4}$ and WinGX. ${ }^{5}$ The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms).

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.12 * \mathrm{P})^{2}\right]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.413 , with $\mathrm{R}(\mathrm{F})$ equal to 0.155 and a goodness of fit, S , $=1.35$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S , are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC..$^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.39.46.
2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
4) Spek, A. L. (2009). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands. Acta Cryst. D65, 148-155.
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{O}}\right|-\left|\mathrm{F}_{\mathrm{c}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table M8N6.1. Crystal data and structure refinement for M8N6.


Table M8N6.2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for M8N6. U(eq) is defined as one third of the trace of the orthogonalized $U^{i j}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| C1 | 6490(4) | $7700(20)$ | 1740(2) | 44(3) |
| C2 | 6208(4) | 7280(20) | 1970(2) | 36(3) |
| C3 | 5768(4) | 8800(20) | 2001(2) | 43(3) |
| C4 | 5508(4) | 8470(20) | 2223(2) | 43(3) |
| C5 | 5711(4) | 6580(20) | 2415(2) | 46(3) |
| C6 | 6152(4) | 4856(19) | 2389(2) | 35(3) |
| C7 | 6382(4) | 2840(20) | 2584(2) | 39(3) |
| C8 | 6793(4) | 1250(20) | 2541(2) | 43(3) |
| C9 | 7049(4) | 1680(20) | 2316(2) | 41(3) |
| C10 | 6865(4) | 3680(20) | 2133(2) | 37(3) |
| C11 | 7144(4) | 4090(20) | 1901(2) | 36(2) |
| C12 | 6411(4) | 5220(20) | 2160(2) | 34(2) |
| C13 | 6141(4) | 2470(20) | 2814(2) | 41(3) |
| C14 | 5923(4) | 2210(20) | 3008(2) | 43(3) |
| C15 | 5679(4) | 2000(20) | 3242(2) | 43(3) |
| C16 | 5258(4) | 3730(20) | 3266(2) | 47(3) |
| C17 | 5001(4) | 3610(20) | 3493(2) | 46(3) |
| C18 | 5194(4) | 1830(20) | 3695(2) | 44(3) |
| C19 | 5642(4) | 60(20) | 3683(2) | 34(2) |
| C20 | 5845(5) | -1710(20) | 3892(2) | 52(3) |
| C21 | 6271(4) | -3380(20) | 3880(2) | 52(3) |
| C22 | 6498(4) | -3320(30) | 3643(2) | 53(3) |
| C23 | 6323(4) | -1710(20) | 3440(2) | 45(3) |
| C24 | 5883(4) | 160(20) | 3452(2) | 37(3) |
| C25 | 7263(4) | 6910(20) | 1520(2) | 51(3) |
| C26 | 7084(5) | 5440(30) | 1261(2) | 60(3) |
| C27 | 7419(5) | 6350(30) | 1046(2) | 56(3) |
| C28 | 7290(6) | 4810(30) | 784(2) | 73(4) |
| C29 | 7619(6) | 5800(30) | 583(3) | 75(4) |
| C30 | 7507(6) | 4230(30) | 318(3) | 80(4) |
| C31 | 4504(5) | 3220(30) | 3938(2) | 61(3) |


| C32 | $4358(8)$ | $3010(40)$ | $4204(4)$ | $115(6)$ |
| :--- | ---: | ---: | ---: | ---: |
| C33 | $4307(8)$ | $480(40)$ | $4307(4)$ | $124(7)$ |
| C34 | $4117(9)$ | $180(40)$ | $4589(4)$ | $127(7)$ |
| C35 | $4238(8)$ | $-1640(40)$ | $4754(4)$ | $119(6)$ |
| C36 | $4026(7)$ | $-1830(40)$ | $5008(3)$ | $103(5)$ |
| C37 | $4189(9)$ | $-3700(50)$ | $5192(4)$ | $143(8)$ |
| C38 | $3956(7)$ | $-4210(40)$ | $5435(3)$ | $104(6)$ |
| N1 | $6948(3)$ | $6233(17)$ | $1728(2)$ | $37(2)$ |
| O1 | $6322(3)$ | $9499(18)$ | $1569(2)$ | $60(2)$ |
| O2 | $7536(3)$ | $2772(16)$ | $1868(1)$ | $49(2)$ |
| O3 | $4979(3)$ | $1643(18)$ | $3925(2)$ | $64(2)$ |

Table M8N6.3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for M8N6.

| C1-O1 | 1.256(13) | C19-C24 | 1.414(14) |
| :---: | :---: | :---: | :---: |
| C1-N1 | 1.357(14) | C20-C21 | 1.349(16) |
| C1-C2 | 1.483(14) | C20-H20 | 0.95 |
| C2-C3 | 1.357(14) | C21-C22 | 1.421(15) |
| C2-C12 | 1.421(14) | C21-H21 | 0.95 |
| C3-C4 | 1.414(14) | C22-C23 | 1.304(15) |
| C3-H3 | 0.95 | C22-H22 | 0.95 |
| C4-C5 | 1.369(15) | C23-C24 | 1.438(15) |
| C4-H4 | 0.95 | C23-H23 | 0.95 |
| C5-C6 | 1.409(15) | C25-N1 | 1.470(13) |
| C5-H5 | 0.95 | C25-C26 | 1.486(15) |
| C6-C7 | 1.439(14) | C25-H25A | 0.99 |
| C6-C12 | $1.443(13)$ | C25-H25B | 0.99 |
| C7-C8 | $1.335(15)$ | C26-C27 | 1.557(15) |
| C7-C13 | $1.419(15)$ | C26-H26A | 0.99 |
| C8-C9 | $1.424(14)$ | C26-H26B | 0.99 |
| C8-H8 | 0.95 | C27-C28 | 1.507(16) |
| C9-C10 | 1.371(15) | C27-H27A | 0.99 |
| C9-H9 | 0.95 | C27-H27B | 0.99 |
| C10-C12 | 1.388(14) | C28-C29 | 1.506(17) |
| C10-C11 | 1.486(14) | C28-H28A | 0.99 |
| C11-O2 | 1.204(12) | C28-H28B | 0.99 |
| C11-N1 | 1.400(14) | C29-C30 | 1.524(17) |
| C13-C14 | 1.218(14) | C29-H29A | 0.99 |
| C14-C15 | 1.436(15) | C29-H29B | 0.99 |
| C15-C16 | 1.371(15) | C30-H30A | 0.98 |
| C15-C24 | 1.413(15) | C30-H30B | 0.98 |
| C16-C17 | 1.417(14) | C30-H30C | 0.98 |
| C16-H16 | 0.95 | C31-O3 | 1.421(14) |
| C17-C18 | 1.363(15) | C31-C32 | $1.465(18)$ |
| C17-H17 | 0.95 | C31-H31A | 0.99 |
| C18-O3 | 1.378(12) | C31-H31B | 0.99 |
| C18-C19 | 1.420(14) | C32-C33 | 1.37(2) |
| C19-C20 | $1.390(15)$ | C32-H32A | 0.99 |


| C32-H32B | 0.99 | C36-C37 | 1.32(3) |
| :---: | :---: | :---: | :---: |
| C33-C34 | 1.59(2) | C36-H36A | 0.99 |
| C33-H33A | 0.99 | C36-H36B | 0.99 |
| C33-H33B | 0.99 | C37-C38 | 1.48(2) |
| C34-C35 | 1.23(2) | C37-H37A | 0.99 |
| C34-H34A | 0.99 | C37-H37B | 0.99 |
| C34-H34B | 0.99 | C38-H38A | 0.98 |
| C35-C36 | 1.49(2) | C38-H38B | 0.98 |
| C35-H35A | 0.99 | C38-H38C | 0.98 |
| C35-H35B | 0.99 |  |  |
| O1-C1-N1 | 120.9(9) | C10-C9-H9 | 119.7 |
| O1-C1-C2 | 120.0(10) | C8-C9-H9 | 119.7 |
| N1-C1-C2 | 119.0(10) | C9-C10-C12 | 119.8(9) |
| C3-C2-C12 | 120.3(9) | C9-C10-C11 | 119.3(9) |
| C3-C2-C1 | 121.4(10) | C12-C10-C11 | 120.9(9) |
| C12-C2-C1 | 118.2(9) | O2-C11-N1 | 120.9(9) |
| C2-C3-C4 | 121.7(10) | O2-C11-C10 | 123.0(9) |
| C2-C3-H3 | 119.1 | N1-C11-C10 | 116.0(9) |
| C4-C3-H3 | 119.1 | C10-C12-C2 | 120.8(9) |
| C5-C4-C3 | 119.0(10) | C10-C12-C6 | 120.4(9) |
| C5-C4-H4 | 120.5 | C2-C12-C6 | 118.7(9) |
| C3-C4-H4 | 120.5 | C14-C13-C7 | 178.1(11) |
| C4-C5-C6 | 122.0(9) | C13-C14-C15 | 177.4(11) |
| C4-C5-H5 | 119.0 | C16-C15-C24 | 120.0(9) |
| C6-C5-H5 | 119.0 | C16-C15-C14 | 118.4(10) |
| C5-C6-C7 | 124.5(9) | C24-C15-C14 | 121.5(10) |
| C5-C6-C12 | 118.2(9) | C15-C16-C17 | 120.9(10) |
| C7-C6-C12 | 117.3(9) | C15-C16-H16 | 119.5 |
| C8-C7-C13 | 120.8(10) | C17-C16-H16 | 119.5 |
| C8-C7-C6 | 120.7(9) | C18-C17-C16 | 119.1(10) |
| C13-C7-C6 | 118.4(9) | C18-C17-H17 | 120.5 |
| C7-C8-C9 | 120.9(10) | C16-C17-H17 | 120.5 |
| C7-C8-H8 | 119.6 | C17-C18-O3 | 122.8(10) |
| C9-C8-H8 | 119.6 | C17-C18-C19 | 121.9(9) |
| C10-C9-C8 | 120.6(10) | O3-C18-C19 | 115.3(9) |


| C20-C19-C24 | $120.2(10)$ | C29-C28-C27 | $112.5(11)$ |
| :--- | :--- | :--- | :--- |
| C20-C19-C18 | $121.7(9)$ | C29-C28-H28A | 109.1 |
| C24-C19-C18 | $118.1(9)$ | C27-C28-H28A | 109.1 |
| C21-C20-C19 | $121.3(10)$ | C29-C28-H28B | 109.1 |
| C21-C20-H20 | 119.4 | C27-C28-H28B | 109.1 |
| C19-C20-H20 | 119.4 | H28A-C28-H28B | 107.8 |
| C20-C21-C22 | $118.0(11)$ | C28-C29-C30 | $113.6(12)$ |
| C20-C21-H21 | 121.0 | C28-C29-H29A | 108.8 |
| C22-C21-H21 | 121.0 | C30-C29-H29A | 108.8 |
| C23-C22-C21 | $123.4(11)$ | C28-C29-H29B | 108.8 |
| C23-C22-H22 | 118.3 | C30-C29-H29B | 108.8 |
| C21-C22-H22 | 118.3 | C39A-C29-H29B | 107.7 |
| C22-C23-C24 | $119.9(10)$ | C29-C30-H30A | 109.5 |
| C22-C23-H23 | 120.1 | C29-C33-H30B | $1093-\mathrm{C}$ |


| C35-C34-C33 | $127(2)$ | H36A-C36-H36B | 106.6 |
| :--- | :--- | :--- | :--- |
| C35-C34-H34A | 105.5 | C36-C37-C38 | $126(2)$ |
| C33-C34-H34A | 105.5 | C36-C37-H37A | 105.8 |
| C35-C34-H34B | 105.5 | C38-C37-H37A | 105.8 |
| C33-C34-H34B | 105.5 | C36-C37-H37B | 105.8 |
| H34A-C34-H34B | 106.1 | C38-C37-H37B | 105.8 |
| C34-C35-C36 | $123.7(19)$ | H37A-C37-H37B | 106.2 |
| C34-C35-H35A | 106.4 | C37-C38-H38A | 109.5 |
| C36-C35-H35A | 106.4 | C37-C38-H38B | 109.5 |
| C34-C35-H35B | 106.4 | H38A-C38-H38C | 109.5 |
| C36-C35-H35B | 106.4 | H38B-C38-H38C | 109.5 |
| H35A-C35-H35B | 106.5 | C1-N1-C11 | 109.5 |
| C37-C36-C35 | $122.8(18)$ | C1-N1-C25 | $124.6(8)$ |
| C37-C36-H36A | 106.6 | C11-N1-C25 | $118.4(9)$ |
| C35-C36-H36A | 106.6 | C18-O3-C31 | $117.0(9)$ |
| C37-C36-H36B | 106.6 | 106.6 | $117.4(9)$ |
| C35-C36-H36B |  |  |  |

Table M8N6.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for M8N6. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | $48(6)$ | 34(5) | 50(6) | -8(5) | 12(5) | -5(5) |
| C2 | $27(5)$ | $33(5)$ | 47(5) | 2(4) | 5(4) | -1(4) |
| C3 | $45(6)$ | 34(5) | 49(5) | 3(5) | 5(5) | -2(5) |
| C4 | $33(5)$ | $40(6)$ | 54(6) | 1(5) | 4(5) | 0(4) |
| C5 | $44(6)$ | 54(6) | 43(5) | -8(5) | 13(5) | -13(5) |
| C6 | $39(5)$ | 24(5) | 41(5) | -1(4) | 8(4) | -12(4) |
| C7 | 33(5) | 43(6) | 43(5) | -7(4) | 14(4) | -2(5) |
| C8 | $41(5)$ | 37(6) | 49(6) | 6(5) | 5(5) | -7(5) |
| C9 | 27(5) | 41(6) | 54(6) | -2(5) | 2(5) | -9(4) |
| C10 | 39(5) | 30(5) | 41(5) | 7(4) | 4(4) | -6(4) |
| C11 | 26(5) | 32(5) | 49(6) | 5(5) | 4(4) | 0(4) |
| C12 | 32(5) | 27(5) | 43(5) | -4(4) | 9(4) | -7(4) |
| C13 | 34(5) | 35(5) | 53(6) | 8(4) | 4(5) | 1(4) |
| C14 | 30(5) | 36(5) | 61(6) | -4(5) | 3(5) | -7(4) |
| C15 | 39(5) | 48(6) | 43(5) | -2(5) | 12(5) | -6(5) |
| C16 | 49(6) | 38(6) | 56(6) | 6(5) | 13(5) | -5(5) |
| C17 | 33(5) | 53(6) | 50(6) | -4(5) | 2(5) | 9(5) |
| C18 | 31(5) | 48(6) | 52(6) | 0(5) | $7(5)$ | 0(5) |
| C19 | 32(5) | 32(5) | 38(5) | 1(4) | 5(4) | -4(4) |
| C20 | 47(6) | 64(7) | 46(6) | 2(5) | 11(5) | 7(5) |
| C21 | 40(6) | 59(6) | 55(6) | -3(5) | 3(5) | -4(5) |
| C22 | 37(5) | 56(6) | 65(7) | 0(6) | 7(5) | 6(5) |
| C23 | 42(6) | 50(6) | 44(5) | -2(5) | 13(5) | -10(5) |
| C24 | 30(5) | 36(5) | 46(6) | -1(4) | 8(4) | 1(4) |
| C25 | 43(6) | 47(6) | 62(6) | 2(5) | 8(5) | -3(5) |
| C26 | 57(6) | 64(7) | 56(6) | 13(5) | 7(5) | -13(5) |
| C27 | 47(6) | 64(6) | 54(6) | 5(5) | 4(5) | -3(5) |
| C28 | 81(7) | 77(7) | 67(7) | -2(6) | 33(6) | -16(6) |
| C29 | 72(7) | 82(8) | 72(7) | 0(6) | 20(6) | 4(6) |
| C30 | 90(10) | 82(9) | 71(8) | -16(7) | 25(7) | -16(8) |
| C31 | 58(7) | 79(8) | 51(6) | 14(5) | 21(5) | 10(6) |


| C32 | $113(9)$ | $121(10)$ | $119(9)$ | $25(8)$ | $42(8)$ | $24(8)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| C33 | $119(10)$ | $126(11)$ | $146(10)$ | $21(8)$ | $68(8)$ | $26(8)$ |
| C34 | $133(10)$ | $137(11)$ | $123(10)$ | $24(8)$ | $55(8)$ | $17(8)$ |
| C35 | $123(10)$ | $123(10)$ | $117(10)$ | $16(8)$ | $39(8)$ | $16(8)$ |
| C36 | $104(9)$ | $101(9)$ | $114(9)$ | $23(8)$ | $47(7)$ | $14(7)$ |
| C37 | $136(11)$ | $165(12)$ | $137(11)$ | $19(9)$ | $47(9)$ | $22(9)$ |
| C38 | $99(11)$ | $130(13)$ | $87(10)$ | $21(9)$ | $31(9)$ | $13(10)$ |
| N1 | $37(5)$ | $38(5)$ | $37(4)$ | $1(4)$ | $12(4)$ | $-7(4)$ |
| O1 | $57(5)$ | $67(6)$ | $55(5)$ | $22(4)$ | $14(4)$ | $15(4)$ |
| O2 | $51(5)$ | $50(5)$ | $48(4)$ | $-4(4)$ | $18(4)$ | $0(4)$ |
| O3 | $64(5)$ | $78(6)$ | $54(4)$ | $5(4)$ | $23(4)$ | $22(4)$ |
|  |  |  |  |  |  |  |

Table M8N6.5. Hydrogen coordinates ( $\mathrm{x} 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \mathrm{x} 10^{3}\right)$ for M8N6.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H3 | 5632 | 10133 | 1869 | 52 |
| H4 | 5197 | 9533 | 2240 | 52 |
| H5 | $5549$ | 6421 | 2570 | 55 |
| H8 | 6917 | -185 | 2663 | 51 |
| H9 | 7349 | 567 | 2292 | 49 |
| H16 | 5138 | 5027 | 3129 | 57 |
| H17 | 4698 | 4755 | 3504 | 55 |
| H20 | 5680 | -1752 | 4047 | 63 |
| H21 | 6415 | -4558 | 4025 | 62 |
| H22 | 6793 | -4520 | 3631 | 64 |
| H23 | 6486 | -1766 | 3285 | 53 |
| H25A | 7657 | 6500 | 1590 | 61 |
| H25B | 7232 | 8876 | 1484 | 61 |
| H26A | 6687 | 5786 | 1192 | 72 |
| H26B | 7133 | 3474 | 1292 | 72 |
| H27A | 7347 | 8296 | 1007 | 67 |
| H27B | 7816 | 6151 | 1123 | 67 |
| H28A | 7369 | 2869 | 821 | 87 |
| H28B | 6892 | 4993 | 706 | 87 |
| H29A | 8017 | 5661 | 663 | 89 |
| H29B | 7534 | 7731 | 544 | 89 |
| H30A | 7681 | 2445 | 346 | 120 |
| H30B | 7660 | 5225 | 182 | 120 |
| H30C | 7108 | 4014 | 257 | 120 |
| H31A | 4191 | 2586 | 3798 | 74 |
| H31B | 4576 | 5135 | 3899 | 74 |
| H32A | 4641 | 4002 | 4333 | 138 |
| H32B | 4004 | 3971 | 4196 | 138 |
| H33A | 4668 | -435 | 4324 | 149 |
| H33B | 4041 | -542 | 4172 | 149 |


| H34A | 4234 | 1876 | 4688 | 152 |
| :--- | ---: | ---: | :--- | :--- |
| H34B | 3709 | 226 | 4546 | 152 |
| H35A | 4646 | -1643 | 4806 | 143 |
| H35B | 4135 | -3357 | 4656 | 143 |
| H36A | 4101 | -60 | 5100 | 123 |
| H36B | 3620 | -1992 | 4956 | 123 |
| H37A | 4588 | -3375 | 5258 | 172 |
| H37B | 4160 | -5437 | 5093 | 172 |
| H38A | 4254 | -4228 | 5594 | 156 |
| H38B | 3767 | -5960 | 5418 | 156 |
| H38C | 3693 | -2775 | 5454 | 156 |
|  |  |  |  |  |

Table M8N6.6. Torsion angles [ ${ }^{\circ}$ ] for M8N6..

| O1-C1-C2-C3 | -0.1(16) | C7-C6-C12-C2 | -177.5(9) |
| :---: | :---: | :---: | :---: |
| N1-C1-C2-C3 | 176.0(9) | C24-C15-C16-C17 | -3.7(16) |
| O1-C1-C2-C12 | 180.0(10) | C14-C15-C16-C17 | 179.8(10) |
| N1-C1-C2-C12 | -3.9(14) | C15-C16-C17-C18 | 3.1(17) |
| C12-C2-C3-C4 | 1.8(16) | C16-C17-C18-O3 | 177.9(10) |
| C1-C2-C3-C4 | -178.1(10) | C16-C17-C18-C19 | -0.8(17) |
| C2-C3-C4-C5 | $1.0(16)$ | C17-C18-C19-C20 | 178.7(11) |
| C3-C4-C5-C6 | -3.6(16) | O3-C18-C19-C20 | -0.1(15) |
| C4-C5-C6-C7 | -179.9(10) | C17-C18-C19-C24 | -1.0(16) |
| C4-C5-C6-C12 | 3.4(15) | O3-C18-C19-C24 | -179.7(9) |
| C5-C6-C7-C8 | 178.7(10) | C24-C19-C20-C21 | -0.3(17) |
| C12-C6-C7-C8 | -4.6(14) | C18-C19-C20-C21 | -180.0(11) |
| C5-C6-C7-C13 | 2.0(15) | C19-C20-C21-C22 | -1.6(18) |
| C12-C6-C7-C13 | 178.7(9) | C20-C21-C22-C23 | 1.4(19) |
| C13-C7-C8-C9 | -177.6(10) | C21-C22-C23-C24 | 0.9(18) |
| C6-C7-C8-C9 | 5.8(15) | C16-C15-C24-C19 | 1.8(16) |
| C7-C8-C9-C10 | -2.1(16) | C14-C15-C24-C19 | 178.3(9) |
| C8-C9-C10-C12 | -2.9(15) | C16-C15-C24-C23 | -180.0(10) |
| C8-C9-C10-C11 | 179.5(9) | C14-C15-C24-C23 | -3.5(16) |
| C9-C10-C11-O2 | -1.7(16) | C20-C19-C24-C15 | -179.2(10) |
| C12-C10-C11-O2 | -179.3(10) | C18-C19-C24-C15 | 0.5(15) |
| C9-C10-C11-N1 | -177.6(9) | C20-C19-C24-C23 | 2.5(15) |
| C12-C10-C11-N1 | 4.8(14) | C18-C19-C24-C23 | -177.8(9) |
| C9-C10-C12-C2 | -179.0(9) | C22-C23-C24-C15 | 179.0(11) |
| C11-C10-C12-C2 | -1.4(15) | C22-C23-C24-C19 | -2.8(16) |
| C9-C10-C12-C6 | 3.9(15) | N1-C25-C26-C27 | 177.5(10) |
| C11-C10-C12-C6 | -178.5(9) | C25-C26-C27-C28 | 175.7(11) |
| C3-C2-C12-C10 | -179.1(10) | C26-C27-C28-C29 | 179.2(12) |
| C1-C2-C12-C10 | 0.8(14) | C27-C28-C29-C30 | 178.7(12) |
| C3-C2-C12-C6 | -2.0(14) | O3-C31-C32-C33 | -51(2) |
| C1-C2-C12-C6 | 177.9(9) | C31-C32-C33-C34 | -176.7(15) |
| C5-C6-C12-C10 | 176.6(9) | C32-C33-C34-C35 | -151(3) |
| C7-C6-C12-C10 | -0.3(14) | C33-C34-C35-C36 | -177.5(19) |
| C5-C6-C12-C2 | -0.5(13) | C34-C35-C36-C37 | -175(3) |


| C35-C36-C37-C38 | $-173(2)$ |
| :--- | :---: |
| O1-C1-N1-C11 | $-175.8(10)$ |
| C2-C1-N1-C11 | $8.1(15)$ |
| O1-C1-N1-C25 | $3.7(15)$ |
| C2-C1-N1-C25 | $-172.3(9)$ |
| O2-C11-N1-C1 | $175.6(10)$ |
| C10-C11-N1-C1 | $-8.4(14)$ |
| O2-C11-N1-C25 | $-4.0(14)$ |
| C10-C11-N1-C25 | $172.0(9)$ |
| C26-C25-N1-C1 | $-89.6(13)$ |
| C26-C25-N1-C11 | $90.0(12)$ |
| C17-C18-O3-C31 | $5.9(17)$ |
| C19-C18-O3-C31 | $-175.4(10)$ |
| C32-C31-O3-C18 | $-174.4(13)$ |

End crystallographic info for M8N6.

## Crystallographic Material for M10N8

## Crystallographic Material for M10N8.

X-ray Experimental.
Table M10N8.1. Crystallographic Data for M10N8.
Table M10N8.2. Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the non-hydrogen atoms of M10N8.

Table M10N8.3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of M10N8.
Table M10N8.4. Anisotropic thermal parameters for the non-hydrogen atoms of M10N8.

Table M10N8.5. Fractional coordinates and isotropic thermal parameters $\left(\AA^{2}\right)$ for the hydrogen atoms of M10N8.

Table M10N8.6. Torsion Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of M10N8.

X-ray Experimental for complex $\mathrm{C}_{42} \mathrm{H}_{49} \mathrm{NO}_{3}$ (M10N8): Crystals grew as long, yellow-orange needles by vapor diffusion (benzene, cyclohexane). The data crystal was cut from a larger crystal and had approximate dimensions; $0.37 \times 0.05 \times 0.02 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{Cu} \mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA)$ with collimating mirror monochromators. A total of 917 frames of data were collected using $\omega$-scans with a scan range of $1^{\circ}$ and a counting time of 23 seconds per frame with a detector offset of $+/-36.2^{\circ}$ and 75 seconds per frame with a detector offset of $+/-$ $83.0^{\circ}$. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6. ${ }^{3}$ Structure analysis was aided by use of
the programs PLATON98 ${ }^{4}$ and WinGX. ${ }^{5}$ The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms).

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.1179 * \mathrm{P})^{2}+\right.$ $(7.3878 * \mathrm{P})]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)$ refined to 0.444 , with $\mathrm{R}(\mathrm{F})$ equal to 0.166 and a goodness of fit, $\mathrm{S},=1.17$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S, are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. ${ }^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Agilent Technologies (2013). Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.37.31.
2) SHELXT. Sheldrick, G. M. (2015) Acta. Cryst. A71, 3-8.
3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 9-18.
4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.
5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. J. Appl. Cryst. 32. 837-838.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection. $\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{o}}\right|-\left|\mathrm{F}_{\mathrm{C}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{o}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\mathrm{L} \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table M10N8.1. Crystal data and structure refinement for M10N8.

Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume
Z
Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=58.932^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2$ sigma $(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole

C42 H49 N O3
615.82

100(2) K
$1.54184 \AA$
monoclinic
C 2/c
$\mathrm{a}=24.607(11) \AA \quad \alpha=90^{\circ}$.
$\mathrm{b}=5.034(3) \AA$
$\mathrm{c}=56.37(2) \AA$
$\beta=99.55(4)^{\circ}$.
$\gamma=90^{\circ}$.
6885(6) $\AA^{3}$
8
$1.188 \mathrm{Mg} / \mathrm{m}^{3}$
$0.569 \mathrm{~mm}^{-1}$
2656
$0.37 \times 0.05 \times 0.02 \mathrm{~mm}^{3}$
4.211 to $58.932^{\circ}$.
$-15<=\mathrm{h}<=26,-5<=\mathrm{k}<=5,-62<=\mathrm{l}<=62$
14214
$4874[\mathrm{R}(\mathrm{int})=0.2411]$
98.4 \%

Semi-empirical from equivalents
1.00 and 0.576

Full-matrix least-squares on $\mathrm{F}^{2}$
4874 / 276 / 417
1.170
$R 1=0.1655, w R 2=0.3600$
$\mathrm{R} 1=0.2967, \mathrm{wR} 2=0.4440$
n/a
0.633 and $-0.394 \mathrm{e} . \AA^{-3}$

Table M10N8.2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for M10N8. U(eq) is defined as one third of the trace of the orthogonalized $U^{i j}$ tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| C1 | 6545(4) | -860(20) | 1824(2) | 43(3) |
| C2 | 6237(4) | -300(20) | 2032(2) | 40(3) |
| C3 | 5794(5) | -1970(20) | 2056(2) | 53(3) |
| C4 | 5522(5) | -1550(20) | 2260(2) | 51(3) |
| C5 | 5699(4) | 300(19) | 2425(2) | 42(3) |
| C6 | 6148(4) | 1990(20) | 2406(2) | 42(3) |
| C7 | 6354(4) | 3968(19) | 2572(2) | 40(3) |
| C8 | 6787(4) | 5590(20) | 2540(2) | 44(3) |
| C9 | 7052(4) | 5210(20) | 2339(2) | 42(3) |
| C10 | 6885(4) | 3285(17) | 2178(2) | 33(2) |
| C11 | 7196(4) | 2790(20) | 1970(2) | 42(3) |
| C12 | 6433(4) | 1636(19) | 2198(2) | 39(3) |
| C13 | 6093(5) | 4360(20) | 2783(2) | 55(3) |
| C14 | 5871(5) | 4600(20) | 2961(2) | 53(3) |
| C15 | 5601(4) | 4850(20) | 3168(2) | 41(3) |
| C16 | 5167(4) | 3190(20) | 3195(2) | 48(3) |
| C17 | 4903(4) | 3360(20) | 3394(2) | 44(3) |
| C18 | 5063(5) | 5200(20) | 3569(2) | 53(3) |
| C19 | 5522(4) | 6930(20) | 3558(2) | 43(3) |
| C20 | 5734(4) | 8700(20) | 3736(2) | 49(3) |
| C21 | 6158(4) | 10420(20) | 3717(2) | 51(3) |
| C22 | 6409(4) | 10260(20) | 3510(2) | 47(3) |
| C23 | 6237(5) | 8520(20) | 3331(2) | 50(3) |
| C24 | 5791(4) | 6700(20) | 3347(2) | 43(3) |
| C25 | 7356(4) | 10(20) | 1633(2) | 48(3) |
| C26 | 7202(5) | 1540(30) | 1401(2) | 62(3) |
| C27 | 7531(5) | 490(20) | 1210(2) | 57(3) |
| C28 | 7502(5) | 2120(20) | 987(2) | 62(3) |
| C29 | 7847(6) | 1050(30) | 805(2) | 68(3) |
| C30 | 7893(6) | 2790(30) | 593(2) | 84(4) |
| C31 | 7360(7) | 3250(30) | 422(3) | 91(5) |


| C32 | $7437(7)$ | $5110(40)$ | $214(3)$ | $104(5)$ |
| :--- | ---: | ---: | ---: | ---: |
| C33 | $4344(5)$ | $4050(30)$ | $3789(2)$ | $64(3)$ |
| C34 | $4187(7)$ | $4600(40)$ | $4025(3)$ | $104(5)$ |
| C35 | $4089(7)$ | $7260(30)$ | $4067(3)$ | $106(5)$ |
| C36 | $3880(7)$ | $8120(40)$ | $4309(3)$ | $103(5)$ |
| C37 | $4216(7)$ | $7180(40)$ | $4540(3)$ | $109(5)$ |
| C38 | $4022(7)$ | $8320(30)$ | $4762(3)$ | $98(5)$ |
| C39 | $4316(9)$ | $7420(50)$ | $4989(4)$ | $144(7)$ |
| C40 | $4151(7)$ | $8190(40)$ | $5213(3)$ | $107(5)$ |
| C41 | $4432(9)$ | $7300(50)$ | $5447(4)$ | $151(8)$ |
| C42 | $4276(8)$ | $7760(40)$ | $5665(3)$ | $135(7)$ |
| N1 | $7008(4)$ | $692(17)$ | $1820(2)$ | $47(2)$ |
| O1 | $6391(3)$ | $-2528(16)$ | $1675(1)$ | $58(2)$ |
| O2 | $7590(3)$ | $4148(15)$ | $1942(1)$ | $55(2)$ |
| O3 | $4848(3)$ | $5498(17)$ | $3775(1)$ | $65(2)$ |

Table M10N8.3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for M10N8.

| C1-O1 | 1.203(12) | C19-C24 | 1.459(13) |
| :---: | :---: | :---: | :---: |
| C1-N1 | 1.386(13) | C20-C21 | 1.373(15) |
| C1-C2 | 1.526(14) | C20-H20 | 0.95 |
| C2-C3 | 1.401(14) | C21-C22 | 1.410(14) |
| C2-C12 | 1.381(14) | C21-H21 | 0.95 |
| C3-C4 | $1.436(14)$ | C22-C23 | 1.347(15) |
| C3-H3 | 0.95 | C22-H22 | 0.95 |
| C4-C5 | 1.339(14) | C23-C24 | 1.440(15) |
| C4-H4 | 0.95 | C23-H23 | 0.95 |
| C5-C6 | 1.415(13) | C25-N1 | 1.504(11) |
| C5-H5 | 0.95 | C25-C26 | 1.512(15) |
| C6-C7 | 1.401(14) | C25-H25A | 0.99 |
| C6-C12 | 1.471(13) | C25-H25B | 0.99 |
| C7-C8 | 1.377(14) | C26-C27 | 1.543(14) |
| C7-C13 | 1.455(14) | C26-H26A | 0.99 |
| C8-C9 | 1.410(13) | C26-H26B | 0.99 |
| C8-H8 | 0.95 | C27-C28 | 1.494(16) |
| C9-C10 | 1.348(13) | C27-H27A | 0.99 |
| C9-H9 | 0.95 | C27-H27B | 0.99 |
| C10-C12 | 1.408(13) | C28-C29 | 1.532(15) |
| C10-C11 | 1.522(13) | C28-H28A | 0.99 |
| C11-O2 | 1.219(11) | C28-H28B | 0.99 |
| C11-N1 | 1.383(13) | C29-C30 | 1.501(17) |
| C13-C14 | $1.226(13)$ | C29-H29A | 0.99 |
| C14-C15 | 1.439(13) | C29-H29B | 0.99 |
| C15-C16 | 1.383(14) | C30-C31 | 1.51(2) |
| C15-C24 | $1.400(14)$ | C30-H30A | 0.99 |
| C16-C17 | 1.394(13) | C30-H30B | 0.99 |
| C16-H16 | 0.95 | C31-C32 | 1.534(19) |
| C17-C18 | 1.359(15) | C31-H31A | 0.99 |
| C17-H17 | 0.95 | C31-H31B | 0.99 |
| C18-O3 | 1.360(12) | C32-H32A | 0.98 |
| C18-C19 | 1.439(15) | C32-H32B | 0.98 |
| C19-C20 | 1.378(15) | C32-H32C | 0.98 |


| C33-O3 | 1.452(13) | C38-C39 | 1.44(2) |
| :---: | :---: | :---: | :---: |
| C33-C34 | 1.475(17) | C38-H38A | 0.99 |
| C33-H33A | 0.99 | C38-H38B | 0.99 |
| C33-H33B | 0.99 | C39-C40 | 1.44(2) |
| C34-C35 | 1.39(2) | C39-H39A | 0.99 |
| C34-H34A | 0.99 | C39-H39B | 0.99 |
| C34-H34B | 0.99 | C40-C41 | 1.46(3) |
| C35-C36 | 1.60(2) | C40-H40A | 0.99 |
| C35-H35A | 0.99 | C40-H40B | 0.99 |
| C35-H35B | 0.99 | C41-C42 | 1.37(2) |
| C36-C37 | 1.50(2) | C41-H41A | 0.99 |
| C36-H36A | 0.99 | C41-H41B | 0.99 |
| C36-H36B | 0.99 | C42-H42A | 0.98 |
| C37-C38 | 1.52(2) | C42-H42B | 0.98 |
| C37-H37A | 0.99 | C42-H42C | 0.98 |
| C37-H37B | 0.99 |  |  |
| O1-C1-N1 | 123.3(9) | C8-C7-C13 | 118.8(9) |
| O1-C1-C2 | 121.8(9) | C6-C7-C13 | 118.9(9) |
| N1-C1-C2 | 115.0(9) | C7-C8-C9 | 119.8(9) |
| C3-C2-C12 | 123.2(8) | C7-C8-H8 | 120.1 |
| C3-C2-C1 | 117.2(9) | C9-C8-H8 | 120.1 |
| C12-C2-C1 | 119.3(9) | C10-C9-C8 | 120.5(9) |
| C2-C3-C4 | 117.5(10) | C10-C9-H9 | 119.8 |
| C2-C3-H3 | 121.2 | C8-C9-H9 | 119.8 |
| C4-C3-H3 | 121.2 | C9-C10-C12 | 121.9(8) |
| C5-C4-C3 | 121.2(10) | C9-C10-C11 | 120.1(8) |
| C5-C4-H4 | 119.4 | C12-C10-C11 | 118.1(9) |
| C3-C4-H4 | 119.4 | O2-C11-N1 | 122.7(9) |
| C4-C5-C6 | 122.3(9) | O2-C11-C10 | 121.5(9) |
| C4-C5-H5 | 118.9 | N1-C11-C10 | 115.9(9) |
| C6-C5-H5 | 118.9 | C2-C12-C10 | 123.6(8) |
| C5-C6-C7 | 125.1(9) | C2-C12-C6 | 117.8(8) |
| C5-C6-C12 | 117.9(9) | C10-C12-C6 | 118.6(9) |
| C7-C6-C12 | 116.9(8) | C14-C13-C7 | 177.8(12) |
| C8-C7-C6 | 122.2(8) | C13-C14-C15 | 178.9(13) |


| C16-C15-C24 | 119.6(8) | C25-C26-C27 | 110.2(10) |
| :---: | :---: | :---: | :---: |
| C16-C15-C14 | 120.3(10) | C25-C26-H26A | 109.6 |
| C24-C15-C14 | 120.1(9) | C27-C26-H26A | 109.6 |
| C15-C16-C17 | 121.6(10) | C25-C26-H26B | 109.6 |
| C15-C16-H16 | 119.2 | C27-C26-H26B | 109.6 |
| C17-C16-H16 | 119.2 | H26A-C26-H26B | 108.1 |
| C18-C17-C16 | 120.6(10) | C28-C27-C26 | 116.2(10) |
| C18-C17-H17 | 119.7 | C28-C27-H27A | 108.2 |
| C16-C17-H17 | 119.7 | C26-C27-H27A | 108.2 |
| O3-C18-C17 | 125.9(10) | C28-C27-H27B | 108.2 |
| O3-C18-C19 | 112.8(10) | C26-C27-H27B | 108.2 |
| C17-C18-C19 | 121.1(9) | H27A-C27-H27B | 107.4 |
| C20-C19-C18 | 124.5(9) | C27-C28-C29 | 114.4(10) |
| C20-C19-C24 | 118.5(10) | C27-C28-H28A | 108.7 |
| C18-C19-C24 | 116.9(10) | C29-C28-H28A | 108.7 |
| C21-C20-C19 | 123.2(9) | C27-C28-H28B | 108.7 |
| C21-C20-H20 | 118.4 | C29-C28-H28B | 108.7 |
| C19-C20-H20 | 118.4 | H28A-C28-H28B | 107.6 |
| C20-C21-C22 | 118.3(10) | C30-C29-C28 | 116.7(11) |
| C20-C21-H21 | 120.9 | C30-C29-H29A | 108.1 |
| C22-C21-H21 | 120.9 | C28-C29-H29A | 108.1 |
| C23-C22-C21 | 121.9(10) | C30-C29-H29B | 108.1 |
| C23-C22-H22 | 119.1 | C28-C29-H29B | 108.1 |
| C21-C22-H22 | 119.1 | H29A-C29-H29B | 107.3 |
| C22-C23-C24 | 121.0(9) | C29-C30-C31 | 115.2(12) |
| C22-C23-H23 | 119.5 | C29-C30-H30A | 108.5 |
| C24-C23-H23 | 119.5 | C31-C30-H30A | 108.5 |
| C23-C24-C15 | 123.0(9) | C29-C30-H30B | 108.5 |
| C23-C24-C19 | 117.0(10) | C31-C30-H30B | 108.5 |
| C15-C24-C19 | 120.0(9) | H30A-C30-H30B | 107.5 |
| N1-C25-C26 | 113.7(9) | C30-C31-C32 | 112.1(13) |
| N1-C25-H25A | 108.8 | C30-C31-H31A | 109.2 |
| C26-C25-H25A | 108.8 | C32-C31-H31A | 109.2 |
| N1-C25-H25B | 108.8 | C30-C31-H31B | 109.2 |
| C26-C25-H25B | 108.8 | C32-C31-H31B | 109.2 |
| H25A-C25-H25B | 107.7 | H31A-C31-H31B | 107.9 |


| C31-C32-H32A | 109.5 | H37A-C37-H37B | 107.8 |
| :---: | :---: | :---: | :---: |
| C31-C32-H32B | 109.5 | C39-C38-C37 | 115.6(15) |
| H32A-C32-H32B | 109.5 | C39-C38-H38A | 108.4 |
| C31-C32-H32C | 109.5 | C37-C38-H38A | 108.4 |
| H32A-C32-H32C | 109.5 | C39-C38-H38B | 108.4 |
| H32B-C32-H32C | 109.5 | C37-C38-H38B | 108.4 |
| O3-C33-C34 | 107.9(11) | H38A-C38-H38B | 107.4 |
| O3-C33-H33A | 110.1 | C38-C39-C40 | 121.4(18) |
| C34-C33-H33A | 110.1 | C38-C39-H39A | 107.0 |
| O3-C33-H33B | 110.1 | C40-C39-H39A | 107.0 |
| C34-C33-H33B | 110.1 | C38-C39-H39B | 107.0 |
| H33A-C33-H33B | 108.4 | C40-C39-H39B | 107.0 |
| C35-C34-C33 | 114.4(15) | H39A-C39-H39B | 106.7 |
| C35-C34-H34A | 108.7 | C39-C40-C41 | 123.5(18) |
| C33-C34-H34A | 108.7 | C39-C40-H40A | 106.4 |
| C35-C34-H34B | 108.7 | C41-C40-H40A | 106.4 |
| C33-C34-H34B | 108.7 | C39-C40-H40B | 106.5 |
| H34A-C34-H34B | 107.6 | C41-C40-H40B | 106.4 |
| C34-C35-C36 | 119.9(14) | H40A-C40-H40B | 106.5 |
| C34-C35-H35A | 107.3 | C42-C41-C40 | 127(2) |
| C36-C35-H35A | 107.3 | C42-C41-H41A | 105.6 |
| C34-C35-H35B | 107.3 | C40-C41-H41A | 105.6 |
| C36-C35-H35B | 107.3 | C42-C41-H41B | 105.6 |
| H35A-C35-H35B | 106.9 | C40-C41-H41B | 105.6 |
| C37-C36-C35 | 116.5(14) | H41A-C41-H41B | 106.1 |
| C37-C36-H36A | 108.2 | C41-C42-H42A | 109.5 |
| C35-C36-H36A | 108.2 | C41-C42-H42B | 109.5 |
| C37-C36-H36B | 108.2 | H42A-C42-H42B | 109.5 |
| C35-C36-H36B | 108.2 | C41-C42-H42C | 109.5 |
| H36A-C36-H36B | 107.3 | H42A-C42-H42C | 109.5 |
| C36-C37-C38 | 113.0(14) | H42B-C42-H42C | 109.5 |
| C36-C37-H37A | 109.0 | C11-N1-C1 | 127.9(8) |
| C38-C37-H37A | 109.0 | C11-N1-C25 | 115.6(8) |
| C36-C37-H37B | 109.0 | C1-N1-C25 | 116.5(8) |
| C38-C37-H37B | 109.0 | C18-O3-C33 | 116.4(9) |

Table M10N8.4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for M10N8. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C1 | 46(6) | 35(5) | 47(6) | 4(5) | 6(5) | -11(5) |
| C2 | 40(5) | 49(5) | 35(5) | -3(5) | 14(4) | -4(5) |
| C3 | 57(6) | 54(6) | 52(6) | -6(5) | 22(5) | -4(5) |
| C4 | 52(6) | 56(6) | 46(6) | 6(5) | 15(5) | -9(5) |
| C5 | 44(5) | 37(5) | 46(5) | -7(5) | 14(5) | 6(5) |
| C6 | 42(6) | 43(5) | 43(5) | 0(4) | 12(5) | -11(5) |
| C7 | 51(6) | 41(5) | 32(5) | -3(4) | 14(5) | $7(5)$ |
| C8 | 48(6) | 42(5) | 46(6) | 0 (4) | 17(5) | -3(5) |
| C9 | 41(5) | 43(5) | 46(5) | -1(5) | 20(5) | -7(5) |
| C10 | 39(5) | 29(4) | 35(5) | 1(4) | 21(4) | -5(4) |
| C11 | 48(6) | 40(5) | 43(6) | 14(5) | 19(5) | 1(5) |
| C12 | 39(6) | 40(5) | 41(5) | 0(4) | 21(5) | 7(4) |
| C13 | 56(6) | 55(6) | 55(6) | $-2(5)$ | 14(5) | 11(5) |
| C14 | 54(6) | 61(6) | 49(6) | 3(5) | 23(5) | 3(5) |
| C15 | 41(5) | 48(5) | 35(5) | -3(4) | 13(5) | -8(5) |
| C16 | 56(6) | 49(6) | 45(6) | -8(5) | 22(5) | $6(5)$ |
| C17 | 44(6) | 50(5) | 41(5) | -4(5) | 16(5) | -7(5) |
| C18 | 58(6) | 60(6) | 45(6) | 7(5) | 17(5) | 4(5) |
| C19 | 48(6) | 49(5) | 37(5) | -1(4) | 15(5) | 2(5) |
| C20 | 50(6) | 53(6) | 48(6) | -6(5) | 21(5) | 9(5) |
| C21 | 45(6) | 57(6) | 53(6) | -4(5) | 16(5) | -3(5) |
| C22 | 40(6) | 52(6) | 52(6) | 8(5) | 13(5) | 11(5) |
| C23 | 57(6) | 49(5) | 51(6) | 10(5) | 25(5) | $7(5)$ |
| C24 | 49(6) | 40(5) | 42(5) | 3(4) | 13(5) | 8(5) |
| C25 | 55(6) | 48(5) | 48(5) | -6(5) | 33(5) | 4(5) |
| C26 | 68(7) | 74(7) | 50(6) | 6(5) | 24(5) | -7(5) |
| C27 | 66(6) | 65(6) | 44(6) | -11(5) | 17(5) | -3(5) |
| C28 | 87(7) | 56(6) | 48(6) | -3(5) | 26(6) | -4(6) |
| C29 | 84(7) | 67(7) | 58(6) | -1(5) | 29(6) | 3(6) |
| C30 | 105(8) | 85(8) | 68(7) | 9(6) | 33(7) | -2(7) |
| C31 | 113(9) | 91(8) | 75(7) | 11(6) | 32(7) | 14(7) |


| C32 | $128(12)$ | $107(11)$ | $85(10)$ | $19(8)$ | $38(9)$ | $40(9)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| C33 | $71(7)$ | $74(7)$ | $58(6)$ | $2(5)$ | $42(6)$ | $-14(6)$ |
| C34 | $108(8)$ | $114(9)$ | $100(8)$ | $-5(7)$ | $51(7)$ | $-13(7)$ |
| C35 | $105(8)$ | $100(9)$ | $124(9)$ | $7(7)$ | $53(7)$ | $5(7)$ |
| C36 | $110(9)$ | $110(9)$ | $102(9)$ | $-4(7)$ | $53(7)$ | $1(7)$ |
| C37 | $107(9)$ | $117(9)$ | $116(9)$ | $-2(7)$ | $56(8)$ | $4(7)$ |
| C38 | $106(9)$ | $106(8)$ | $88(8)$ | $25(7)$ | $30(7)$ | $10(7)$ |
| C39 | $134(10)$ | $169(11)$ | $137(10)$ | $10(9)$ | $47(9)$ | $8(9)$ |
| C40 | $115(9)$ | $117(9)$ | $87(8)$ | $0(7)$ | $11(7)$ | $-3(8)$ |
| C41 | $146(11)$ | $173(12)$ | $135(11)$ | $16(9)$ | $28(9)$ | $0(9)$ |
| C42 | $138(13)$ | $197(16)$ | $81(10)$ | $-17(11)$ | $52(10)$ | $18(12)$ |
| N1 | $57(5)$ | $43(4)$ | $44(5)$ | $-2(4)$ | $22(4)$ | $0(4)$ |
| O1 | $70(5)$ | $61(5)$ | $48(5)$ | $-13(4)$ | $27(4)$ | $-19(4)$ |
| O2 | $60(5)$ | $61(5)$ | $53(4)$ | $4(4)$ | $34(4)$ | $0(4)$ |
| O3 | $69(5)$ | $86(5)$ | $48(4)$ | $-2(4)$ | $32(4)$ | $-22(4)$ |

Table M10N8.5. Hydrogen coordinates ( $\mathrm{x} 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for M10N8.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| H3 | 5677 | -3328 | 1942 | 64 |
| H4 | 5211 | -2605 | 2277 | 61 |
| H5 | 5517 | 483 | 2560 | 50 |
| H8 | 6906 | 6955 | 2653 | 53 |
| H9 | 7352 | 6329 | 2318 | 50 |
| H16 | 5047 | 1904 | 3074 | 58 |
| H17 | 4608 | 2189 | 3409 | 53 |
| H20 | 5579 | 8739 | 3880 | 58 |
| H21 | 6279 | 11681 | 3839 | 61 |
| H22 | 6709 | 11404 | 3496 | 56 |
| H23 | 6411 | 8488 | 3193 | 61 |
| H25A | 7319 | -1915 | 1598 | 57 |
| H25B | 7747 | 367 | 1700 | 57 |
| H26A | 7283 | 3449 | 1430 | 75 |
| H26B | 6803 | 1347 | 1341 | 75 |
| H27A | 7923 | 335 | 1285 | 69 |
| H27B | 7398 | -1320 | 1163 | 69 |
| H28A | 7627 | 3948 | 1033 | 74 |
| H28B | 7112 | 2232 | 907 | 74 |
| H29A | 8224 | 695 | 892 | 81 |
| H29B | 7688 | -673 | 744 | 81 |
| H30A | 8162 | 1980 | 502 | 101 |
| H30B | 8043 | 4534 | 654 | 101 |
| H31A | 7086 | 4040 | 512 | 109 |
| H31B | 7213 | 1527 | 356 | 109 |
| H32A | 7643 | 6686 | 278 | 157 |
| H32B | 7076 | 5640 | 127 | 157 |
| H32C | 7642 | 4173 | 104 | 157 |
| H33A | 4403 | 2122 | 3770 | 77 |
| H33B | 4047 | 4633 | 3658 | 77 |


| H34A | 3850 | 3574 | 4039 | 124 |
| :--- | ---: | ---: | :--- | :--- |
| H34B | 4484 | 3958 | 4152 | 124 |
| H35A | 3815 | 7898 | 3931 | 127 |
| H35B | 4436 | 8231 | 4060 | 127 |
| H36A | 3866 | 10089 | 4313 | 124 |
| H36B | 3498 | 7467 | 4302 | 124 |
| H37A | 4606 | 7687 | 4543 | 131 |
| H37B | 4198 | 5218 | 4546 | 131 |
| H38A | 4051 | 10280 | 4757 | 118 |
| H38B | 3627 | 7875 | 4754 | 118 |
| H39A | 4704 | 7977 | 4998 | 172 |
| H39B | 4313 | 5451 | 4984 | 172 |
| H40A | 3761 | 7654 | 5202 | 129 |
| H40B | 4158 | 10153 | 5217 | 129 |
| H41A | 4461 | 5345 | 5435 | 181 |
| H41B | 4812 | 7991 | 5462 | 181 |
| H42A | 4196 | 9655 | 5680 | 203 |
| H42B | 4574 | 7234 | 5794 | 203 |
| H42C | 3944 | 6722 | 5677 | 203 |

Table M10N8.6. Torsion angles [ ${ }^{\circ}$ ] for M10N8.

| O1-C1-C2-C3 | 5.6(16) | C7-C6-C12-C10 | -0.4(14) |
| :---: | :---: | :---: | :---: |
| N1-C1-C2-C3 | -174.8(9) | C24-C15-C16-C17 | 1.7(16) |
| O1-C1-C2-C12 | -179.8(10) | C14-C15-C16-C17 | 179.2(10) |
| N1-C1-C2-C12 | -0.2(14) | C15-C16-C17-C18 | 0.5(17) |
| C12-C2-C3-C4 | 2.2(16) | C16-C17-C18-O3 | -177.8(10) |
| C1-C2-C3-C4 | 176.6(9) | C16-C17-C18-C19 | -2.7(17) |
| C2-C3-C4-C5 | -2.4(17) | O3-C18-C19-C20 | 0.7(16) |
| C3-C4-C5-C6 | 2.1(17) | C17-C18-C19-C20 | -175.1(11) |
| C4-C5-C6-C7 | 179.9(11) | O3-C18-C19-C24 | 178.3(9) |
| C4-C5-C6-C12 | -1.4(15) | C17-C18-C19-C24 | 2.6(16) |
| C5-C6-C7-C8 | -178.7(10) | C18-C19-C20-C21 | -177.0(10) |
| C12-C6-C7-C8 | 2.6(15) | C24-C19-C20-C21 | 5.4(16) |
| C5-C6-C7-C13 | -0.1(16) | C19-C20-C21-C22 | -3.6(17) |
| C12-C6-C7-C13 | -178.8(9) | C20-C21-C22-C23 | 1.4(16) |
| C6-C7-C8-C9 | -2.6(16) | C21-C22-C23-C24 | -1.2(16) |
| C13-C7-C8-C9 | 178.8(9) | C22-C23-C24-C15 | -179.4(10) |
| C7-C8-C9-C10 | $0.2(16)$ | C22-C23-C24-C19 | 2.9(15) |
| C8-C9-C10-C12 | $2.0(15)$ | C16-C15-C24-C23 | -179.3(10) |
| C8-C9-C10-C11 | -176.3(9) | C14-C15-C24-C23 | 3.2(16) |
| C9-C10-C11-O2 | -1.9(15) | C16-C15-C24-C19 | -1.7(16) |
| C12-C10-C11-O2 | 179.7(9) | C14-C15-C24-C19 | -179.1(10) |
| C9-C10-C11-N1 | 177.2(9) | C20-C19-C24-C23 | -4.8(15) |
| C12-C10-C11-N1 | -1.1(13) | C18-C19-C24-C23 | 177.4(9) |
| C3-C2-C12-C10 | 178.7(10) | C20-C19-C24-C15 | 177.4(10) |
| C1-C2-C12-C10 | 4.5(15) | C18-C19-C24-C15 | -0.4(15) |
| C3-C2-C12-C6 | -1.6(15) | N1-C25-C26-C27 | -173.5(9) |
| C1-C2-C12-C6 | -175.8(9) | C25-C26-C27-C28 | -169.1(11) |
| C9-C10-C12-C2 | 177.9(10) | C26-C27-C28-C29 | 178.4(11) |
| C11-C10-C12-C2 | -3.8(14) | C27-C28-C29-C30 | -172.2(12) |
| C9-C10-C12-C6 | -1.8(14) | C28-C29-C30-C31 | -65.3(17) |
| C11-C10-C12-C6 | 176.5(9) | C29-C30-C31-C32 | 178.5(12) |
| C5-C6-C12-C2 | 1.1(14) | O3-C33-C34-C35 | 60.3(19) |
| C7-C6-C12-C2 | 179.9(9) | C33-C34-C35-C36 | 176.2(14) |
| C5-C6-C12-C10 | -179.2(9) | C34-C35-C36-C37 | 53(2) |


| C35-C36-C37-C38 | $174.3(14)$ |
| :--- | :---: |
| C36-C37-C38-C39 | $177.9(18)$ |
| C37-C38-C39-C40 | $-175.6(19)$ |
| C38-C39-C40-C41 | $179(2)$ |
| C39-C40-C41-C42 | $-174(2)$ |
| O2-C11-N1-C1 | $-175.0(10)$ |
| C10-C11-N1-C1 | $5.9(15)$ |
| O2-C11-N1-C25 | $6.0(14)$ |
| C10-C11-N1-C25 | $-173.2(8)$ |
| O1-C1-N1-C11 | $174.4(10)$ |
| C2-C1-N1-C11 | $-5.2(15)$ |
| O1-C1-N1-C25 | $-6.6(15)$ |
| C2-C1-N1-C25 | $173.8(9)$ |
| C26-C25-N1-C11 | $-88.4(12)$ |
| C26-C25-N1-C1 | $92.4(11)$ |
| C17-C18-O3-C33 | $-11.5(17)$ |
| C19-C18-O3-C33 | $173.1(10)$ |
| C34-C33-O3-C18 | $179.0(12)$ |

[^3]
# Crystallographic Material for 2,6-difluoro-PDI 

## Crystallographic Material for 2,6-difluoro-PDI.

X-ray Experimental.
Table 1. Crystallographic Data for 2,6-difluoro-PDI.
Table 2. Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the nonhydrogen atoms of 2,6-difluoro-PDI.

Table 3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\circ}\right)$ for the non-hydrogen atoms of 2,6-difluoro-PDI.
Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of 2,6-difluoro-PDI.

Table 5. Fractional coordinates and isotropic thermal parameters $\left(\AA^{2}\right)$ for the hydrogen atoms of 2,6-difluoro-PDI.

Table 6. Torsion Angles $\left({ }^{0}\right)$ for the non-hydrogen atoms of 2,6-difluoro-PDI.

X-ray Experimental for $\mathrm{C}_{38} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{~F}_{4} \mathrm{O}_{4}$ (2,6-difluoro-PDI) Crystals grew as very long, thin red laths by sublimation. The data crystal was cut from a longer crystal and had approximate dimensions; $0.38 \times 0.030 \times 0.019 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{Cu} \mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA)$ with collimating mirror monochromators. A total of 1069 frames of data were collected using $\omega$ scans with a scan range of $1^{\circ}$ and a counting time of 12.5 seconds per frame for frames collected with a detector offset of $+/-41.3^{\circ}$ and 50 seconds per frame with frames collected with a detector offset of $112^{\circ}$. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.41.70a. ${ }^{1}$ The structure was solved by direct methods using

SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3. ${ }^{3}$ Structure analysis was aided by use of the programs PLATON ${ }^{4}$ and OLEX2. ${ }^{5}$ The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms).

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.1579 * \mathrm{P})^{2}+\right.$ $(0.1349 * \mathrm{P})]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.220 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0753 and a goodness of fit, $\mathrm{S},=1.03$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S, are given below. ${ }^{6}$ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. ${ }^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Rigaku Oxford Diffraction (2019). CrysAlicPro Software System, 1.171.41.70a.
2) SHELXT. (2015). G. M. Sheldrick. A program for crystal structure solution. Acta Cryst. A71, 3-8.
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4) Spek, A. L. (2009). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands. Acta Cryst. D65, 148-155.
5) OLEX2. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. and Puschmann, H. A Complete Structure Solution, Refinement and Analysis Program. J. Appl. Cryst. 42, 339-341.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection. $\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{o}}\right|-\left|\mathrm{F}_{\mathrm{C}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{o}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for 2,6-difluoro-PDI

| Formula weight | 642.54 |
| :---: | :---: |
| Temperature | 100.04(18) K |
| Wavelength | $1.54184 \AA$ |
| Crystal system | monoclinic |
| Space group | P $121 / \mathrm{n} 1$ |
| Unit cell dimensions | $\begin{array}{ll} \mathrm{a}=4.8899(3) \AA & \alpha=90^{\circ} . \\ \mathrm{b}=29.9472(14) \AA & \beta=105.044(6)^{\circ} . \\ \mathrm{c}=9.2362(6) \AA & \gamma=90^{\circ} . \end{array}$ |
| Volume | 1306.18(14) $\AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.634 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.069 \mathrm{~mm}^{-1}$ |
| F(000) | 656 |
| Crystal size | $0.38 \times 0.03 \times 0.019 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.951 to $68.245^{\circ}$. |
| Index ranges | $-5<=\mathrm{h}<=5,-33<=\mathrm{k}<=36,-9<=\mathrm{l}<=11$ |
| Reflections collected | 6974 |
| Independent reflections | $2352[\mathrm{R}(\mathrm{int})=0.0729]$ |
| Completeness to theta $=67.684^{\circ}$ | 98.6 \% |
| Absorption correction | Gaussian and multi-scan |
| Max. and min. transmission | 1.000 and 0.607 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 2352 / 0 / 217 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.033 |
| Final R indices [I $>2$ sigma(I)] | $\mathrm{R} 1=0.0753, \mathrm{wR} 2=0.2031$ |
| R indices (all data) | $\mathrm{R} 1=0.0858, \mathrm{wR} 2=0.2205$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.423 and -0.363 e. $\AA^{-3}$ |

Table 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 2,6-difluoro-PDI. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :---: | :---: | :---: | :---: | :---: |
| F1 | $4587(3)$ | $7085(1)$ | $6825(2)$ | $33(1)$ |
| F2 | 10772(3) | $6361(1)$ | $4462(2)$ | $32(1)$ |
| O1 | $7379(4)$ | $6627(1)$ | $9676(2)$ | $30(1)$ |
| $\mathrm{O} 2$ | $6669(4)$ | $5705(1)$ | $5691(2)$ | $29(1)$ |
| N1 | $6959(5)$ | 6170(1) | 7659(3) | $24(1)$ |
| C1 | 6387(6) | $6289(1)$ | $9009(3)$ | $24(1)$ |
| $\mathrm{C} 2$ | $4531(5)$ | 5983(1) | $9598(3)$ | $24(1)$ |
| C3 | $3855(6)$ | $6089(1)$ | 10913(3) | $26(1)$ |
| $\mathrm{C} 4$ | $2147(6)$ | $5803(1)$ | 11508(3) | 26(1) |
| C5 | $1095(5)$ | $5408(1)$ | 10780(3) | $22(1)$ |
| C6 | $1730(5)$ | 5295(1) | $9406(3)$ | 22(1) |
| C7 | $698(5)$ | 4897(1) | $8601(3)$ | $22(1)$ |
| C8 | 1388(5) | 4809(1) | $7266(3)$ | 24(1) |
| C9 | $3079(6)$ | 5098(1) | $6688(3)$ | 25(1) |
| $\mathrm{C} 10$ | 4134(5) | 5482(1) | $7451(3)$ | $22(1)$ |
| C11 | $5977(5)$ | 5783(1) | $6835(3)$ | $23(1)$ |
| C12 | 3484(5) | 5588(1) | $8817(3)$ | $23(1)$ |
| C13 | 8998(6) | 6447(1) | 7115(3) | 26(1) |
| C14 | 7734(5) | 6710(1) | $5716(3)$ | $24(1)$ |
| C15 | 5658(6) | 7035(1) | 5616(3) | $27(1)$ |
| C16 | $4681(6)$ | 7311(1) | 4404(4) | $31(1)$ |
| C17 | 5784(6) | 7258(1) | 3170(4) | $33(1)$ |
| C18 | $7866(6)$ | 6937(1) | $3192(3)$ | $31(1)$ |
| C19 | 8734(6) | 6673(1) | 4446(3) | 27(1) |

Table 3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for 2,6-difluoro-PDI.

| F1-C15 | 1.359(3) | C8-H8 | 0.95 |
| :---: | :---: | :---: | :---: |
| F2-C19 | 1.364(3) | C8-C9 | 1.397(4) |
| O1-C1 | 1.219(4) | C9-H9 | 0.95 |
| O2-C11 | 1.213(3) | C9-C10 | $1.376(4)$ |
| N1-C1 | 1.394(4) | C10-C11 | $1.488(3)$ |
| N1-C11 | 1.401(4) | C10-C12 | $1.415(4)$ |
| N1-C13 | 1.482(3) | C13-H13A | 0.99 |
| C1-C2 | 1.488(4) | C13-H13B | 0.99 |
| C2-C3 | $1.376(4)$ | C13-C14 | 1.503(4) |
| C2-C12 | 1.410(4) | C14-C15 | $1.392(4)$ |
| C3-H3 | 0.95 | C14-C19 | $1.388(4)$ |
| C3-C4 | 1.404(4) | C15-C16 | $1.372(4)$ |
| C4-H4 | 0.95 | C16-H16 | 0.95 |
| C4-C5 | 1.391(4) | C16-C17 | 1.391(4) |
| C5-C6 | 1.424(4) | C17-H17 | 0.95 |
| C5-C7\#1 | 1.480(4) | C17-C18 | $1.396(5)$ |
| C6-C7 | 1.424(4) | C18-H18 | 0.95 |
| C6-C12 | 1.431(4) | C18-C19 | 1.376(4) |
| C7-C8 | 1.386(4) |  |  |
| C1-N1-C11 | 125.3(2) | C5-C4-H4 | 119.6 |
| C1-N1-C13 | 118.0(2) | C4-C5-C6 | 119.6(2) |
| C11-N1-C13 | 116.4(2) | C4-C5-C7\#1 | 121.4(2) |
| O1-C1-N1 | 121.3(2) | C6-C5-C7\#1 | 119.0(3) |
| O1-C1-C2 | 121.9(2) | C5-C6-C7 | 122.3(2) |
| N1-C1-C2 | 116.9(2) | C5-C6-C12 | 118.9(3) |
| C3-C2-C1 | 119.4(3) | C7-C6-C12 | 118.8(2) |
| C3-C2-C12 | 120.3(2) | C6-C7-C5\#1 | 118.7(2) |
| C12-C2-C1 | 120.3(2) | C8-C7-C5\#1 | 122.0(2) |
| C2-C3-H3 | 119.7 | C8-C7-C6 | 119.3(2) |
| C2-C3-C4 | 120.6(3) | C7-C8-H8 | 119.1 |
| C4-C3-H3 | 119.7 | C7-C8-C9 | 121.7(2) |
| C3-C4-H4 | 119.6 | C9-C8-H8 | 119.1 |
| C5-C4-C3 | 120.8(3) | C8-C9-H9 | 119.9 |


| C10-C9-C8 | $120.2(2)$ | C19-C14-C13 | $121.8(2)$ |
| :--- | :--- | :--- | :--- |
| C10-C9-H9 | 119.9 | C19-C14-C15 | $114.3(3)$ |
| C9-C10-C11 | $119.6(2)$ | F1-C15-C14 | $116.8(2)$ |
| C9-C10-C12 | $120.2(2)$ | F1-C15-C16 | $118.5(2)$ |
| C12-C10-C11 | $120.2(2)$ | C16-C15-C14 | $124.6(3)$ |
| O2-C11-N1 | $120.0(2)$ | C15-C16-H16 | 120.9 |
| O2-C11-C10 | $123.3(2)$ | C15-C16-C17 | $118.2(3)$ |
| N1-C11-C10 | $116.7(2)$ | C17-C16-H16 | 120.9 |
| C2-C12-C6 | $119.7(2)$ | C16-C17-H17 | 119.9 |
| C2-C12-C10 | $120.6(2)$ | C16-C17-C18 | $120.2(3)$ |
| C10-C12-C6 | $119.7(2)$ | C17-C18-H18 | 119.9 |
| N1-C13-H13A | 108.5 | C19-C18-C17 | 120.9 |
| N1-C13-H13B | 108.5 | C19-C18-H18 | $118.2(3)$ |
| N1-C13-C14 | $115.0(2)$ | F2-C19-C14 | 120.9 |
| H13A-C13-H13B | 107.5 | F2-C19-C18 | $117.6(2)$ |
| C14-C13-H13A | 108.5 | C18-C19-C14 | $117.9(2)$ |
| C14-C13-H13B | 108.5 |  | $124.5(3)$ |
| C15-C14-C13 | $123.7(2)$ |  |  |

Symmetry transformations used to generate equivalent atoms:
\#1 -x,-y+1,-z+2

Table 4. Anisotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 2,6-difluoro-PDI. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| F1 | $35(1)$ | $34(1)$ | $35(1)$ | $1(1)$ | $17(1)$ | $7(1)$ |
| F2 | $32(1)$ | $32(1)$ | $38(1)$ | $-2(1)$ | $19(1)$ | $2(1)$ |
| O1 | $35(1)$ | $28(1)$ | $29(1)$ | $-1(1)$ | $13(1)$ | $-8(1)$ |
| O2 | $33(1)$ | $26(1)$ | $32(1)$ | $-2(1)$ | $18(1)$ | $-2(1)$ |
| N1 | $24(1)$ | $22(1)$ | $26(1)$ | $2(1)$ | $9(1)$ | $0(1)$ |
| C1 | $23(1)$ | $27(1)$ | $24(1)$ | $3(1)$ | $7(1)$ | $2(1)$ |
| C2 | $22(1)$ | $24(1)$ | $26(1)$ | $2(1)$ | $9(1)$ | $1(1)$ |
| C3 | $27(1)$ | $24(1)$ | $26(1)$ | $-3(1)$ | $7(1)$ | $-2(1)$ |
| C4 | $28(1)$ | $26(1)$ | $26(1)$ | $-2(1)$ | $12(1)$ | $-2(1)$ |
| C5 | $20(1)$ | $23(1)$ | $24(1)$ | $1(1)$ | $6(1)$ | $2(1)$ |
| C6 | $20(1)$ | $22(1)$ | $24(1)$ | $3(1)$ | $7(1)$ | $4(1)$ |
| C7 | $19(1)$ | $24(1)$ | $26(1)$ | $2(1)$ | $7(1)$ | $3(1)$ |
| C8 | $24(1)$ | $23(1)$ | $24(1)$ | $-2(1)$ | $7(1)$ | $1(1)$ |
| C9 | $28(1)$ | $27(1)$ | $24(1)$ | $0(1)$ | $12(1)$ | $4(1)$ |
| C10 | $21(1)$ | $24(1)$ | $24(1)$ | $3(1)$ | $8(1)$ | $3(1)$ |
| C11 | $23(1)$ | $23(1)$ | $25(1)$ | $2(1)$ | $10(1)$ | $5(1)$ |
| C12 | $19(1)$ | $24(1)$ | $25(1)$ | $2(1)$ | $6(1)$ | $4(1)$ |
| C13 | $24(1)$ | $26(1)$ | $29(2)$ | $1(1)$ | $11(1)$ | $-1(1)$ |
| C14 | $22(1)$ | $22(1)$ | $27(1)$ | $0(1)$ | $6(1)$ | $-4(1)$ |
| C15 | $24(1)$ | $26(1)$ | $31(2)$ | $-3(1)$ | $8(1)$ | $-3(1)$ |
| C16 | $25(1)$ | $25(1)$ | $43(2)$ | $2(1)$ | $6(1)$ | $-2(1)$ |
| C17 | $30(2)$ | $33(2)$ | $34(2)$ | $10(1)$ | $4(1)$ | $-8(1)$ |
| C18 | $30(2)$ | $36(2)$ | $28(2)$ | $0(1)$ | $10(1)$ | $-10(1)$ |
| C19 | $24(1)$ | $27(1)$ | $30(1)$ | $-3(1)$ | $9(1)$ | $-5(1)$ |
|  |  |  |  |  |  |  |

Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 2,6-difluoro-PDI.

|  | $x$ | $y$ | $z$ | U(eq) |
| :--- | ---: | ---: | ---: | :--- |
|  |  |  |  |  |
| H3 | 4551 | 6357 | 11423 | 31 |
| H4 | 1705 | 5880 | 12419 | 31 |
| H8 | 693 | 4544 | 6730 | 29 |
| H9 | 3501 | 5031 | 5765 | 30 |
| H13A | 10489 | 6249 | 6922 | 31 |
| H13B | 9924 | 6657 | 7920 | 31 |
| H16 | 3289 | 7532 | 4408 | 38 |
| H17 | 5119 | 7440 | 2310 | 39 |
| H18 | 8661 | 6902 | 2363 | 37 |

Table 6. Torsion angles [ ${ }^{\circ}$ ] for 2,6-difluoro-PDI. .

| F1-C15-C16-C17 | -179.9(2) | C8-C9-C10-C12 | -0.8(4) |
| :---: | :---: | :---: | :---: |
| O1-C1-C2-C3 | 1.6(4) | C9-C10-C11-O2 | -1.6(4) |
| O1-C1-C2-C12 | -178.2(2) | C9-C10-C11-N1 | 179.4(2) |
| N1-C1-C2-C3 | -178.8(2) | C9-C10-C12-C2 | -179.3(2) |
| N1-C1-C2-C12 | 1.4(4) | C9-C10-C12-C6 | 0.2(4) |
| N1-C13-C14-C15 | 61.2(4) | C11-N1-C1-O1 | 178.2(2) |
| N1-C13-C14-C19 | -124.3(3) | C11-N1-C1-C2 | -1.4(4) |
| C1-N1-C11-O2 | -177.9(2) | C11-N1-C13-C14 | 73.8(3) |
| C1-N1-C11-C10 | 1.1(4) | C11-C10-C12-C2 | 1.0(4) |
| C1-N1-C13-C14 | -112.2(3) | C11-C10-C12-C6 | -179.4(2) |
| C1-C2-C3-C4 | -178.9(2) | C12-C2-C3-C4 | 0.8(4) |
| C1-C2-C12-C6 | 179.2(2) | C12-C6-C7-C5\#1 | 179.5(2) |
| C1-C2-C12-C10 | -1.3(4) | C12-C6-C7-C8 | -0.7(4) |
| C2-C3-C4-C5 | -0.2(4) | C12-C10-C11-O2 | 178.1(2) |
| C3-C2-C12-C6 | -0.6(4) | C12-C10-C11-N1 | -0.9(4) |
| C3-C2-C12-C10 | 178.9(2) | C13-N1-C1-O1 | 4.8(4) |
| C3-C4-C5-C6 | -0.7(4) | C13-N1-C1-C2 | -174.8(2) |
| C3-C4-C5-C7\#1 | 179.7(2) | C13-N1-C11-O2 | -4.4(4) |
| C4-C5-C6-C7 | -179.5(2) | C13-N1-C11-C10 | 174.7(2) |
| C4-C5-C6-C12 | 1.0(4) | C13-C14-C15-F1 | -5.6(4) |
| C5-C6-C7-C5\#1 | -0.1(4) | C13-C14-C15-C16 | 173.1(3) |
| C5-C6-C7-C8 | 179.7(2) | C13-C14-C19-F2 | 5.1(4) |
| C5-C6-C12-C2 | -0.3(4) | C13-C14-C19-C18 | -173.0(3) |
| C5-C6-C12-C10 | -179.9(2) | C14-C15-C16-C17 | 1.5(4) |
| C5\#1-C7-C8-C9 | 179.9(2) | C15-C14-C19-F2 | -179.9(2) |
| C6-C7-C8-C9 | 0.1(4) | C15-C14-C19-C18 | 1.9(4) |
| C7\#1-C5-C6-C7 | 0.1(4) | C15-C16-C17-C18 | -1.2(4) |
| C7\#1-C5-C6-C12 | -179.5(2) | C16-C17-C18-C19 | 1.3(4) |
| C7-C6-C12-C2 | -179.9(2) | C17-C18-C19-F2 | -179.9(2) |
| C7-C6-C12-C10 | 0.6(4) | C17-C18-C19-C14 | -1.7(4) |
| C7-C8-C9-C10 | 0.6(4) | C19-C14-C15-F1 | 179.6(2) |
| C8-C9-C10-C11 | 178.8(2) | C19-C14-C15-C16 | -1.8(4) |

Symmetry transformations used to generate equivalent atoms:
\#1-x,-y+1,-z+2

End crystallographic info for 2,6-difluoro-PDI.

# Crystallographic Material for 3,4-difluoro-PDI 

## Crystallographic Material for 3,4-difluoro-PDI.

X-ray Experimental.
Table 1. 3,4-difluoro-PDI Crystallographic Data for 3,4-difluoro-PDI.
Table 2. Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the nonhydrogen atoms of 3,4-difluoro-PDI.

Table 3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\mathrm{O}}\right)$ for the non-hydrogen atoms of 3,4-difluoro-PDI.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of 3,4-difluoro-PDI.

Table 5. Fractional coordinates and isotropic thermal parameters $\left(\AA^{2}\right)$ for the hydrogen atoms of 3,4-difluoro-PDI.

Table 6. Torsion Angles $\left({ }^{\mathrm{O}}\right)$ for the non-hydrogen atoms of 3,4-difluoro-PDI.

X-ray Experimental for $\mathrm{C}_{38} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{~F}_{4} \mathrm{O}_{4}$ 3,4-difluoro-PDI: Crystals grew as very long, thin red laths by sublimation. The data crystal was cut from a longer crystal and had approximate dimensions; $0.34 \times 0.051 \times 0.027 \mathrm{~mm}$. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a $\mu$-focus $\mathrm{Cu} \mathrm{K} \alpha$ radiation source $(\lambda=1.5418 \AA$ ) with collimating mirror monochromators. A total of 835 frames of data were collected using $\omega$ scans with a scan range of $1^{\circ}$ and a counting time of 13.5 seconds per frame for frames collected with a detector offset of $+/-42.4^{\circ}$ and 49.5 seconds per frame with frames collected with a detector offset of $92.0^{\circ}$. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.41.70a. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement
parameters for the non-H atoms using SHELXL-2018/3. ${ }^{3}$ Structure analysis was aided by use of the programs PLATON ${ }^{4}$ and OLEX2. ${ }^{5}$ Most hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms). The hydrogen atoms on the methylene carbon atom bound to the disordered 3,4-difluorophenyl ring were observed in a $\Delta \mathrm{F}$ map and refined with isotropic displacement parameters.

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{o}}\right)\right)^{2}+(0.1118 * \mathrm{P})^{2}+\right.$ $\left.\left(0.3107^{*} \mathrm{P}\right)\right]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3 . \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)$ refined to 0.222 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0882 and a goodness of fit, $\mathrm{S},=1.13$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S, are given below. 6 The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. ${ }^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Rigaku Oxford Diffraction (2019). CrysAlicPro Software System, 1.171.41.70a.
2) SHELXT. (2015). G. M. Sheldrick. A program for crystal structure solution. Acta Cryst. A71, 3-8.
3) Sheldrick, G. M. (2015). SHELXL-2016/6. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 3-8.
4) Spek, A. L. (2009). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands. Acta Cryst. D65, 148-155.
5) OLEX2. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. and Puschmann, H. A Complete Structure Solution, Refinement and Analysis Program. J. Appl. Cryst. 42, 339-341.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \Sigma \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection.
$\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{o}}\right|-\left|\mathrm{F}_{\mathrm{c}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{O}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

3,4-difluoro-PDI Table 1. Crystal data and structure refinement for 3,4-difluoro-PDI.

| Empirical formula | C38 H18 F4 N2 O4 |
| :---: | :---: |
| Formula weight | 642.54 |
| Temperature | 99.9(5) K |
| Wavelength | $1.54184 \AA$ |
| Crystal system | triclinic |
| Space group | P-1 |
| Unit cell dimensions | $\mathrm{a}=6.7264(12) \AA$ 这 $\quad \alpha=80.061(15)^{\circ}$. |
|  | $b=7.6893(12) \AA \quad \beta=85.935(16)^{\circ}$. |
|  | $\mathrm{c}=13.506(3) \AA \quad \gamma=73.353(15)^{\circ}$. |
| Volume | 659.0(2) $\AA^{3}$ |
| Z | 1 |
| Density (calculated) | $1.619 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $1.059 \mathrm{~mm}^{-1}$ |
| F(000) | 328 |
| Crystal size | $0.34 \times 0.051 \times 0.027 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 3.323 to $66.417^{\circ}$. |
| Index ranges | $-7<=\mathrm{h}<=7,-9<=\mathrm{k}<=6,-15<=1<=15$ |
| Reflections collected | 3383 |
| Independent reflections | $2170[\mathrm{R}(\mathrm{int})=0.0432]$ |
| Completeness to theta $=66.417^{\circ}$ | 94.1 \% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.23939 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 2170 / 399 / 298 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.206 |
| Final R indices [I $>2$ sigma(I)] | $\mathrm{R} 1=0.0882, \mathrm{wR} 2=0.2218$ |
| R indices (all data) | $\mathrm{R} 1=0.1146, \mathrm{wR} 2=0.2423$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.419 and -0.474 e. $\AA^{-3}$ |

3,4-difluoro-PDI Table 2. Atomic coordinates ( $\times 10^{4}$ ) and equivalent isotropic displacement parameters ( $\AA^{2} \mathrm{x}$ $10^{3}$ ) for $\mathbf{3 , 4}$-difluoro-PDI. U(eq) is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :--- | :---: | :---: | :---: | :---: |
| F1 |  |  |  |  |
| F2 | $2311(7)$ | $1607(8)$ | $6401(3)$ | $68(2)$ |
| O1 | $3105(7)$ | $-2030(9)$ | $6390(4)$ | $60(2)$ |
| O2 | $3396(5)$ | $961(4)$ | $1384(2)$ | $31(1)$ |
| N1 | $2692(5)$ | $5788(4)$ | $3028(2)$ | $38(1)$ |
| C1 | $3059(5)$ | $3364(4)$ | $2219(2)$ | $21(1)$ |
| C2 | $4046(6)$ | $2239(5)$ | $1514(3)$ | $23(1)$ |
| C3 | $5834(5)$ | $2687(5)$ | $935(3)$ | $18(1)$ |
| C4 | $6781(6)$ | $1688(5)$ | $192(3)$ | $23(1)$ |
| C5 | $8451(6)$ | $2107(5)$ | $-368(3)$ | $22(1)$ |
| C6 | $9246(6)$ | $3507(5)$ | $-195(3)$ | $18(1)$ |
| C7 | $8268(5)$ | $4580(4)$ | $564(3)$ | $18(1)$ |
| C8 | $8956(5)$ | $6070(5)$ | $770(3)$ | $18(1)$ |
| C9 | $7907(6)$ | $7088(5)$ | $1498(3)$ | $23(1)$ |
| C10 | $6209(6)$ | $6678(5)$ | $2032(3)$ | $26(1)$ |
| C11 | $5511(5)$ | $5235(5)$ | $1857(3)$ | $21(1)$ |
| C12 | $3683(6)$ | $4851(5)$ | $2420(3)$ | $26(1)$ |
| C13 | $6538(6)$ | $4162(4)$ | $1125(3)$ | $18(1)$ |
| C14 | $1248(6)$ | $2942(5)$ | $2796(3)$ | $24(1)$ |
| C15 | $1850(30)$ | $1627(15)$ | $3758(6)$ | $24(2)$ |
| C16 | $1927(12)$ | $2260(11)$ | $4650(6)$ | $28(2)$ |
| C17 | $2342(11)$ | $1030(13)$ | $5539(5)$ | $33(2)$ |
| C18 | $2743(11)$ | $-822(10)$ | $5503(5)$ | $31(2)$ |
| C19 | $2738(9)$ | $-1498(9)$ | $4618(5)$ | $29(1)$ |
| C14A | $2290(12)$ | $-261(9)$ | $3744(5)$ | $24(1)$ |
| C15A | $1830(80)$ | $1860(30)$ | $3846(13)$ | $26(3)$ |
| C16A | $2430(30)$ | $-50(20)$ | $4074(11)$ | $27(2)$ |
| C17A | $2740(20)$ | $-985(17)$ | $5061(12)$ | $25(2)$ |
| C18A | $2560(20)$ | $110(20)$ | $5789(9)$ | $27(3)$ |
| C19A | $1950(20)$ | $2020(20)$ | $5599(10)$ | $28(3)$ |
| F1A | $1560(30)$ | $2880(20)$ | $4632(12)$ | $27(3)$ |
|  | $-2739(11)$ | $5323(8)$ | $59(3)$ |  |

F2A 2834(15) -769(17) 6787(7) 55(3)

3,4-difluoro-PDI Table 3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for 3,4-difluoro-PDI.

| F1-C16 | $1.312(8)$ | C13-C14 | 1.504(8) |
| :---: | :---: | :---: | :---: |
| F2-C17 | $1.373(8)$ | C13-C14A | 1.530(13) |
| O1-C1 | $1.226(5)$ | C13-H13A | 0.97(5) |
| O2-C11 | $1.220(5)$ | C13-H13B | 1.02(5) |
| N1-C1 | 1.401(5) | C14-C15 | 1.384(12) |
| N1-C11 | $1.399(5)$ | C14-C19 | 1.400 (13) |
| N1-C13 | $1.483(5)$ | C15-H15 | 0.95 |
| C1-C2 | $1.479(5)$ | C15-C16 | 1.386(12) |
| C2-C3 | $1.377(5)$ | C16-C17 | 1.380(11) |
| C2-C12 | $1.415(5)$ | C17-C18 | 1.384(9) |
| C3-H3 | 0.95 | C18-H18 | 0.95 |
| C3-C4 | 1.393(6) | C18-C19 | 1.374(9) |
| C4-H4 | 0.95 | C19-H19 | 0.95 |
| C4-C5 | 1.391(5) | C14A-C15A | 1.40(2) |
| C5-C6 | $1.431(5)$ | C14A-C19A | 1.39(2) |
| C5-C7\#1 | $1.475(5)$ | C15A-H15A | 0.95 |
| C6-C7 | $1.427(5)$ | C15A-C16A | 1.400(17) |
| C6-C12 | $1.427(5)$ | C16A-C17A | 1.375(17) |
| C7-C8 | $1.389(5)$ | C16A-F1A | 1.285(14) |
| C8-H8 | 0.95 | C17A-C18A | 1.391(15) |
| C8-C9 | $1.392(6)$ | C17A-F2A | 1.398(14) |
| C9-H9 | 0.95 | C18A-H18A | 0.95 |
| C9-C10 | 1.383(5) | C18A-C19A | 1.366(16) |
| C10-C11 | 1.474(6) | C19A-H19A | 0.95 |
| C10-C12 | 1.412(5) |  |  |
| C1-N1-C13 | 117.9(3) | C12-C2-C1 | 120.3(3) |
| C11-N1-C1 | 124.1(3) | C2-C3-H3 | 119.8 |
| C11-N1-C13 | 117.9(3) | C2-C3-C4 | 120.3(3) |
| O1-C1-N1 | 119.9(4) | C4-C3-H3 | 119.8 |
| O1-C1-C2 | 122.6(4) | C3-C4-H4 | 119.0 |
| N1-C1-C2 | 117.4(3) | C5-C4-C3 | 122.1(4) |
| C3-C2-C1 | 119.6(3) | C5-C4-H4 | 119.0 |
| C3-C2-C12 | 120.1(3) | C4-C5-C6 | 118.5(4) |


| C4-C5-C7\#1 | $122.3(3)$ | C19-C14-C13 | $118.8(8)$ |
| :--- | :--- | :--- | :--- |
| C6-C5-C7\#1 | $119.1(3)$ | C14-C15-H15 | 120.0 |
| C7-C6-C5 | $122.0(4)$ | C14-C15-C16 | $120.0(7)$ |
| C7-C6-C12 | $118.9(3)$ | C16-C15-H15 | 120.0 |
| C12-C6-C5 | $119.1(3)$ | F1-C16-C15 | $121.0(8)$ |
| C6-C7-C5\#1 | $118.9(3)$ | F1-C16-C17 | $120.5(7)$ |
| C8-C7-C5\#1 | $121.9(3)$ | C17-C16-C15 | $118.5(7)$ |
| C8-C7-C6 | $119.2(3)$ | F2-C17-C16 | $118.2(7)$ |
| C7-C8-H8 | 119.3 | F2-C17-C18 | $119.0(6)$ |
| C7-C8-C9 | $121.4(3)$ | C16-C17-C18 | $122.8(6)$ |
| C9-C8-H8 | 119.3 | C17-C18-H18 | 120.9 |
| C8-C9-H9 | 119.5 | C19-C18-C17 | $118.2(6)$ |
| C10-C9-C8 | $121.0(4)$ | C19-C18-H18 | 120.9 |
| C10-C9-H9 | 1219.5 | C14-C19-H19 | 120.9 C19-C19A-C14A-H19A |

Symmetry transformations used to generate equivalent atoms:
\#1-x+2,-y+1,-z

3,4-difluoro-PDI Table 4. Anisotropic displacement parameters ( $\AA^{2} \times 10^{3}$ ) for 3,4-difluoro-PDI. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| F1 | 53(3) | 140(5) | 30(2) | -33(3) | -1(2) | -45(3) |
| F2 | 32(2) | 93(4) | 42(3) | 29(3) | -7(2) | -20(2) |
| O1 | 34(2) | 34(2) | 33(2) | -11(1) | 2(1) | -21(1) |
| O2 | 36(2) | 27(2) | 53(2) | -18(1) | 21(2) | -12(1) |
| N1 | 13(2) | 19(2) | 29(2) | -2(1) | -2(1) | -3(1) |
| C1 | 16(2) | 22(2) | 27(2) | -2(2) | -5(2) | -3(2) |
| C2 | 13(2) | 18(2) | 25(2) | -1(1) | -7(1) | -4(1) |
| C3 | 24(2) | 20(2) | 27(2) | -4(2) | -4(2) | -7(2) |
| C4 | 21(2) | 18(2) | 25(2) | -6(1) | -5(2) | -2(2) |
| C5 | 15(2) | 16(2) | 22(2) | -2(1) | -7(1) | -2(1) |
| C6 | 12(2) | 14(2) | 26(2) | -3(1) | -5(1) | 1(1) |
| C7 | 13(2) | 17(2) | 23(2) | -2(1) | -6(1) | -1(1) |
| C8 | 21(2) | 17(2) | 31(2) | -8(2) | -1(2) | -4(2) |
| C9 | 26(2) | 17(2) | 32(2) | -8(2) | 1(2) | -2(2) |
| C10 | 11(2) | 17(2) | 30(2) | -2(2) | -2(2) | 3(1) |
| C11 | 19(2) | 18(2) | 35(2) | -4(2) | 3(2) | $0(2)$ |
| C12 | 16(2) | 13(2) | 24(2) | -2(1) | -6(1) | $0(1)$ |
| C13 | 14(2) | 28(2) | 30(2) | -2(2) | $0(2)$ | -6(2) |
| C14 | 11(3) | 26(3) | 33(3) | -3(2) | -1(3) | -4(3) |
| C15 | 16(3) | 33(3) | 36(3) | -10(3) | 1(2) | -4(3) |
| C16 | 21(3) | 41(4) | 38(3) | -11(3) | -1(2) | -8(3) |
| C17 | 17(3) | 42(3) | 32(3) | -1(3) | -5(3) | -5(2) |
| C18 | 17(3) | 32(3) | 35(3) | -1(3) | -1(2) | -5(2) |
| C19 | 15(3) | 25(3) | 33(3) | -6(2) | 2(3) | -8(2) |
| C14A | 15(4) | 27(5) | 34(4) | -1(4) | $0(4)$ | -5(4) |
| C15A | 16(4) | 29(4) | 34(4) | -5(4) | $0(4)$ | -5(3) |
| C16A | 16(4) | 29(4) | 33(4) | -10(4) | -3(4) | -8(3) |
| C17A | 16(4) | 30(5) | 33(5) | -3(4) | -6(4) | -5(4) |
| C18A | 13(4) | 34(5) | 34(4) | -2(4) | -6(4) | -3(4) |
| C19A | 17(4) | 29(5) | 33(4) | -1(4) | -2(4) | -5(4) |
| F1A | 42(6) | 40(5) | 81(7) | 22(5) | -7(5) | -4(4) |


| F 2 A | $40(5)$ | $77(7)$ | $38(5)$ | $23(5)$ | $-10(4)$ |
| :--- | :--- | :--- | :--- | :--- | :--- |

3,4-difluoro-PDI Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters ( $\AA^{2} \times 10^{3}$ ) for 3,4-difluoro-PDI.

|  | $x$ | $y$ | $z$ | U(eq) |
| :--- | :---: | :---: | :---: | :---: |
|  |  |  |  |  |
| H3 | 6293 | 708 | 61 | 28 |
| H4 | 9067 | 1414 | -884 | 26 |
| H8 | 8359 | 8084 | 1634 | 27 |
| H9 | 5518 | 7401 | 2525 | 31 |
| H15 | 1692 | 3538 | 4652 | 34 |
| H18 | 3037 | -2781 | 4615 | 35 |
| H19 | 2276 | -690 | 3126 | 29 |
| H15A | 2636 | -748 | 3540 | 32 |
| H18A | 1814 | 2709 | 6131 | 34 |
| H19A | 1091 | 4182 | 4493 | 32 |
| H13A | $640(70)$ | $2440(60)$ | $2320(30)$ | $29(11)$ |
| H13B | $250(70)$ | $4180(60)$ | $2900(30)$ | $31(11)$ |

3,4-difluoro-PDI Table 6. Torsion angles [ ${ }^{\circ}$ ] for 3,4-difluoro-PDI.

| F1-C16-C17-F2 | 0.1(10) | C7-C6-C12-C10 | 1.2(5) |
| :---: | :---: | :---: | :---: |
| F1-C16-C17-C18 | 178.2(6) | C7-C8-C9-C10 | 0.2(6) |
| F2-C17-C18-C19 | 177.4(6) | C8-C9-C10-C11 | -178.8(3) |
| O1-C1-C2-C3 | 2.4(6) | C8-C9-C10-C12 | 0.0(6) |
| O1-C1-C2-C12 | -179.2(3) | C9-C10-C11-O2 | 2.0(6) |
| N1-C1-C2-C3 | -176.3(3) | C9-C10-C11-N1 | -179.4(3) |
| N1-C1-C2-C12 | 2.1(5) | C9-C10-C12-C2 | -179.7(3) |
| N1-C13-C14-C15 | 91.2(16) | C9-C10-C12-C6 | -0.7(5) |
| N1-C13-C14-C19 | -90.6(16) | C11-N1-C1-O1 | -179.9(3) |
| N1-C13-C14A-C15A | -92(4) | C11-N1-C1-C2 | -1.2(5) |
| N1-C13-C14A-C19A | 94(4) | C11-N1-C13-C14 | -89.6(6) |
| $\mathrm{C} 1-\mathrm{N} 1-\mathrm{C} 11-\mathrm{O} 2$ | 177.9(3) | C11-N1-C13-C14A | -80.2(11) |
| C1-N1-C11-C10 | -0.7(5) | C11-C10-C12-C2 | -0.9(5) |
| C1-N1-C13-C14 | 90.0(6) | C11-C10-C12-C6 | 178.1(3) |
| C1-N1-C13-C14A | $99.3(11)$ | C12-C2-C3-C4 | 0.8(5) |
| C1-C2-C3-C4 | 179.2(3) | C12-C6-C7-C5\#1 | 179.5(3) |
| C1-C2-C12-C6 | 179.9(3) | C12-C6-C7-C8 | -0.9(5) |
| C1-C2-C12-C10 | -1.1(5) | C12-C10-C11-O2 | -176.8(4) |
| C2-C3-C4-C5 | 1.0(6) | C12-C10-C11-N1 | 1.8(5) |
| C3-C2-C12-C6 | -1.7(5) | C13-N1-C1-O1 | 0.5(5) |
| C3-C2-C12-C10 | 177.3(3) | C13-N1-C1-C2 | 179.3(3) |
| C3-C4-C5-C6 | -1.9(5) | C13-N1-C11-O2 | -2.5(5) |
| C3-C4-C5-C7\#1 | 178.6(3) | C13-N1-C11-C10 | 178.8(3) |
| C4-C5-C6-C7 | -178.4(3) | C13-C14-C15-C16 | 175.3(12) |
| C4-C5-C6-C12 | 0.9(5) | C13-C14-C19-C18 | -176.4(11) |
| C5-C6-C7-C5\#1 | -1.1(5) | C13-C14A-C15A-C16A | -173(3) |
| C5-C6-C7-C8 | 178.4(3) | C13-C14A-C19A-C18A | 177(3) |
| C5-C6-C12-C2 | 0.9(5) | C14-C15-C16-F1 | -176.4(12) |
| C5-C6-C12-C10 | -178.2(3) | C14-C15-C16-C17 | 2.1(15) |
| C5\#1-C7-C8-C9 | 179.8(3) | C15-C14-C19-C18 | 2(2) |
| C6-C7-C8-C9 | 0.3(5) | C15-C16-C17-F2 | -178.5(6) |
| C7\#1-C5-C6-C7 | 1.2(6) | C15-C16-C17-C18 | -0.3(11) |
| C7\#1-C5-C6-C12 | -179.5(3) | C16-C17-C18-C19 | -0.8(10) |
| C7-C6-C12-C2 | -179.8(3) | C17-C18-C19-C14 | 0.0(14) |


| C19-C14-C15-C16 | $-3(2)$ | C16A-C17A-C18A-C19A | $-2(2)$ |
| :--- | :---: | :--- | :---: |
| C14A-C15A-C16A-C17A | $-5(4)$ | C17A-C18A-C19A-C14A | $-2(3)$ |
| C14A-C15A-C16A-F1A | $-179(3)$ | C19A-C14A-C15A-C16A | $1(5)$ |
| C15A-C14A-C19A-C18A | $3(5)$ | F1A-C16A-C17A-C18A | $-179.7(13)$ |
| C15A-C16A-C17A-C18A | $5(2)$ | F1A-C16A-C17A-F2A | $-5(2)$ |
| C15A-C16A-C17A-F2A | $179.3(14)$ | F2A-C17A-C18A-C19A | $-176.0(14)$ |

Symmetry transformations used to generate equivalent atoms:
\#1-x+2,-y+1,-z

End crystallographic info for 3,4-difluoro-PDI

## Crystallographic Material for 3,5-difluoro-PDI

## Crystallographic Material for3,5-difluoro-PDI.

X-ray Experimental.
Table 1. Crystallographic Data for 3,5-difluoro-PDI .
Table 2. Fractional coordinates and equivalent isotropic thermal parameters $\left(\AA^{2}\right)$ for the nonhydrogen atoms of $\mathbf{3 , 5}$-difluoro-PDI.

Table 3. Bond Lengths $(\AA)$ and Angles $\left({ }^{\mathrm{O}}\right)$ for the non-hydrogen atoms of 3,5-difluoro-PDI.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of 3,5-difluoro-PDI.

Table 5. Fractional coordinates and isotropic thermal parameters ( $\AA^{2}$ ) for the hydrogen atoms of 3,5-difluoro-PDI.

Table 6. Torsion Angles $\left({ }^{( }\right)$for the non-hydrogen atoms of 3,5-difluoro-PDI.

X-ray Experimental for $\mathrm{C}_{38} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{~F}_{4}$ (3,5-difluoro-PDI): Crystals grew as long, thin red needles by sublimation. The data crystal was cut from a larger crystal and had approximate dimensions of $0.3 \times 0.02 \times 0.02 \mathrm{~mm}$. The data were collected on Beamline 5.0.1 at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The synchrotron beamline produced a wavelength $=0.97741 \AA$. A total of 180 frames of data were collected using $\phi$-scans with a scan range of $1^{\circ}$ and a counting time of 1 seconds per frame for frames collected with a detector offset of $0.0^{\circ}$. The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection was performed using the Beamline Operating Software, BOS/B3. The unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.40.37a. ${ }^{1}$ The structure was solved by direct methods using SHELXT ${ }^{2}$ and refined by full-matrix least-squares on $\mathrm{F}^{2}$ with anisotropic displacement
parameters for the non-H atoms using SHELXL-2018/3. ${ }^{3}$ Structure analysis was aided by use of the programs PLATON ${ }^{4}$ and OLEX2 ${ }^{5}$. The hydrogen atoms on the carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 xUeq of the attached atom ( 1.5 xUeq for methyl hydrogen atoms). The molecule resides around a crystallographic inversion center at $1 / 2,1 / 2,1 / 2$.

The function, $\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2}$, was minimized, where $\mathrm{w}=1 /\left[\left(\sigma\left(\mathrm{F}_{\mathrm{O}}\right)\right)^{2}+(0.1547 * \mathrm{P})^{2}\right]$ and $\mathrm{P}=\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}+2\left|\mathrm{~F}_{\mathrm{c}}\right|^{2}\right) / 3$. $\mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ refined to 0.152 , with $\mathrm{R}(\mathrm{F})$ equal to 0.0571 and a goodness of fit, $\mathrm{S},=0.866$. Definitions used for calculating $\mathrm{R}(\mathrm{F}), \mathrm{R}_{\mathrm{w}}\left(\mathrm{F}^{2}\right)$ and the goodness of fit, S , are given below. 6 The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992). ${ }^{7}$ All figures were generated using SHELXTL/PC. ${ }^{8}$ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

## References

1) CrysAlisPro. Rigaku Oxford Diffraction, The Woodlands, TX, USA. CrysAlisPro Software System, 1.171.40.37a.
2) SHELXT. (2015). G. M. Sheldrick. A program for crystal structure solution. Acta Cryst. A71, 3-8.
3) Sheldrick, G. M. (2015). SHELXL-2018/3. Program for the Refinement of Crystal Structures. Acta Cryst., C71, 3-8.
4) Spek, A. L. (2009). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands. Acta Cryst. D65, 148-155.
5) OLEX2. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. and Puschmann, H. A Complete Structure Solution, Refinement and Analysis Program. J. Appl. Cryst. 42, 339-341.
6) $\quad \mathrm{R}_{\mathrm{W}}\left(\mathrm{F}^{2}\right)=\left\{\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{O}}\right|^{2}-\left|\mathrm{F}_{\mathrm{C}}\right|^{2}\right)^{2 / \sum \mathrm{w}}\left(\left|\mathrm{F}_{\mathrm{O}}\right|\right)^{4}\right\}^{1 / 2}$ where w is the weight given each reflection. $\left.\mathrm{R}(\mathrm{F})=\Sigma\left(\left|\mathrm{F}_{\mathrm{o}}\right|-\left|\mathrm{F}_{\mathrm{C}}\right|\right) / \Sigma\left|\mathrm{F}_{\mathrm{o}}\right|\right\}$ for reflections with $\mathrm{F}_{\mathrm{O}}>4\left(\sigma\left(\mathrm{~F}_{\mathrm{O}}\right)\right)$.
$\mathrm{S}=\left[\Sigma \mathrm{w}\left(\left|\mathrm{F}_{\mathrm{o}}\right|^{2}-\left|\mathrm{F}_{\mathrm{c}}\right|^{2}\right)^{2 /(n-p)}\right]^{1 / 2}$, where n is the number of reflections and p is the number of refined parameters.
7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.
8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical Xray Instruments, Inc., Madison, Wisconsin, USA.

## 3,5-difluoro-PDI Table 1. Crystal data and structure refinement for 3,5-difluoro-PDI.

| Empirical formula | C38 H18 F4 N2 O4 |
| :---: | :---: |
| Formula weight | 642.54 |
| Temperature | 100.15 K |
| Wavelength | 0.97741 Å |
| Crystal system | monoclinic |
| Space group | C $12 / \mathrm{c} 1$ |
| Unit cell dimensions | $\begin{array}{ll} \mathrm{a}=28.576(2) \AA & \alpha=90^{\circ} . \\ \mathrm{b}=4.3750(2) \AA & \beta=103.684(8)^{\circ} . \\ \mathrm{c}=22.0997(14) \AA & \gamma=90^{\circ} . \end{array}$ |
| Volume | 2684.5(3) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.590 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.270 \mathrm{~mm}^{-1}$ |
| F(000) | 1312 |
| Crystal size | $0.3 \times 0.02 \times 0.02 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.609 to $26.291^{\circ}$. |
| Index ranges | $-24<=\mathrm{h}<=22,-3<=\mathrm{k}<=3,-15<=\mathrm{l}<=19$ |
| Reflections collected | 1545 |
| Independent reflections | $704[\mathrm{R}(\mathrm{int})=0.0154]$ |
| Completeness to theta $=26.291^{\circ}$ | 68.5 \% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.64368 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 704 / 345 / 217 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.068 |
| Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ] | $\mathrm{R} 1=0.0571, \mathrm{wR} 2=0.1493$ |
| R indices (all data) | $\mathrm{R} 1=0.0586, \mathrm{wR} 2=0.1522$ |
| Extinction coefficient | $\mathrm{n} / \mathrm{a}$ |
| Largest diff. peak and hole | 0.194 and -0.209 e. $\AA^{-3}$ |

3,5-difluoro-PDI Table 2. Atomic coordinates ( $\mathrm{x} 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for 3,5-difluoro-PDI. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized $\mathrm{U}^{\mathrm{ij}}$ tensor.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :--- | :---: | :---: | :---: | :---: |
|  |  |  |  |  |
| C1 | $6510(2)$ | $6961(11)$ | $6788(2)$ | $47(2)$ |
| C2 | $6153(2)$ | $5967(10)$ | $6230(2)$ | $44(2)$ |
| C3 | $6289(2)$ | $3957(10)$ | $5823(2)$ | $52(2)$ |
| C4 | $5968(2)$ | $2937(9)$ | $5285(2)$ | $55(2)$ |
| C5 | $5495(2)$ | $3919(10)$ | $5142(2)$ | $46(2)$ |
| C6 | $5332(2)$ | $6001(10)$ | $5543(2)$ | $44(2)$ |
| C7 | $4845(2)$ | $7040(10)$ | $5426(3)$ | $48(2)$ |
| C8 | $4721(2)$ | $8965(10)$ | $5861(2)$ | $52(2)$ |
| C9 | $5051(2)$ | $9948(9)$ | $6398(2)$ | $52(2)$ |
| C10 | $5524(2)$ | $9004(10)$ | $6514(2)$ | $46(2)$ |
| C11 | $5869(2)$ | $10119(12)$ | $7075(3)$ | $52(2)$ |
| C12 | $5669(2)$ | $6960(10)$ | $6093(2)$ | $45(2)$ |
| C13 | $6704(2)$ | $10218(9)$ | $7710(2)$ | $53(2)$ |
| C14 | $6789(2)$ | $8061(9)$ | $8253(2)$ | $51(2)$ |
| C15 | $7252(2)$ | $7224(9)$ | $8543(2)$ | $60(2)$ |
| C16 | $7320(2)$ | $5313(11)$ | $9054(2)$ | $66(2)$ |
| C17 | $6952(2)$ | $4121(10)$ | $9277(2)$ | $62(2)$ |
| C18 | $6504(2)$ | $4951(11)$ | $8975(2)$ | $56(2)$ |
| C19 | $6404(2)$ | $6910(10)$ | $8472(2)$ | $56(2)$ |
| F1 | $7779(1)$ | $4465(6)$ | $9334(1)$ | $87(1)$ |
| F2 | $6124(1)$ | $3754(5)$ | $9162(1)$ | $72(1)$ |
| N1 | $6346(1)$ | $9095(8)$ | $7165(2)$ | $52(1)$ |
| O1 | $6923(1)$ | $6117(6)$ | $6922(1)$ | $57(1)$ |
| O2 | $5761(1)$ | $11921(7)$ | $7439(2)$ | $66(1)$ |

3,5-difluoro-PDI Table 3. Bond lengths $[\AA]$ and angles [ ${ }^{\circ}$ ] for 3,5-difluoro-PDI

| C1-C2 | 1.468(7) | C10-C12 | 1.422(7) |
| :---: | :---: | :---: | :---: |
| C1-N1 | $1.405(6)$ | C11-N1 | 1.402(6) |
| C1-O1 | $1.203(5)$ | C11-O2 | $1.218(5)$ |
| C2-C3 | 1.377(6) | C13-H13A | 0.99 |
| C2-C12 | 1.414(6) | C13-H13B | 0.99 |
| C3-H3 | 0.95 | C13-C14 | 1.500(6) |
| C3-C4 | 1.392(6) | C13-N1 | $1.468(5)$ |
| C4-H4 | 0.95 | C14-C15 | $1.377(6)$ |
| C4-C5 | 1.382(6) | C14-C19 | 1.396(6) |
| C5-C6 | $1.423(8)$ | C15-H15 | 0.95 |
| C5-C7\#1 | 1.454(7) | C15-C16 | 1.381(6) |
| C6-C7 | 1.429(6) | C16-C17 | $1.365(6)$ |
| C6-C12 | $1.422(6)$ | C16-F1 | 1.364(6) |
| C7-C8 | 1.387(6) | C17-H17 | 0.95 |
| C8-H8 | 0.95 | C17-C18 | 1.345(7) |
| C8-C9 | 1.397(6) | C18-C19 | 1.379 (6) |
| C9-H9 | 0.95 | C18-F2 | $1.356(5)$ |
| C9-C10 | 1.378(7) | C19-H19 | 0.95 |
| C10-C11 | 1.472(7) |  |  |
| N1-C1-C2 | 115.6(5) | C6-C5-C7\#1 | 118.2(5) |
| O1-C1-C2 | 124.2(6) | C5-C6-C7 | 122.5(5) |
| O1-C1-N1 | 120.2(5) | C5-C6-C12 | 117.8(5) |
| C3-C2-C1 | 119.4(5) | C12-C6-C7 | 119.6(6) |
| C3-C2-C12 | 117.9(5) | C6-C7-C5\#1 | 119.2(6) |
| C12-C2-C1 | 122.7(6) | C8-C7-C5\#1 | 123.1(5) |
| C2-C3-H3 | 118.9 | C8-C7-C6 | 117.7(6) |
| C2-C3-C4 | 122.2(4) | C7-C8-H8 | 118.5 |
| C4-C3-H3 | 118.9 | C7-C8-C9 | 122.9(4) |
| C3-C4-H4 | 119.8 | C9-C8-H8 | 118.5 |
| C5-C4-C3 | 120.5(5) | C8-C9-H9 | 119.9 |
| C5-C4-H4 | 119.8 | C10-C9-C8 | 120.2(5) |
| C4-C5-C6 | 120.1(6) | C10-C9-H9 | 119.9 |
| C4-C5-C7\#1 | 121.7(6) | C9-C10-C11 | 119.4(6) |


| C9-C10-C12 | $119.4(5)$ | C14-C15-C16 | $118.4(5)$ |
| :--- | :--- | :--- | :--- |
| C12-C10-C11 | $121.2(4)$ | C16-C15-H15 | 120.8 |
| N1-C11-C10 | $116.7(6)$ | C17-C16-C15 | $123.7(5)$ |
| O2-C11-C10 | $123.1(5)$ | F1-C16-C15 | $118.1(5)$ |
| O2-C11-N1 | $120.2(5)$ | F1-C16-C17 | $118.2(5)$ |
| C2-C12-C6 | $121.5(6)$ | C16-C17-H17 | 121.9 |
| C2-C12-C10 | $118.3(5)$ | C18-C17-C16 | $116.2(5)$ |
| C10-C12-C6 | $120.2(5)$ | C18-C17-H17 | 121.9 |
| H13A-C13-H13B | 107.7 | C17-C18-C19 | $124.1(5)$ |
| C14-C13-H13A | 108.9 | C17-C18-F2 | $118.7(4)$ |
| C14-C13-H13B | 108.9 | C14-C19-H19 | $117.2(5)$ |
| N1-C13-H13A | 108.9 | C18-C19-C14 | 120.9 |
| N1-C13-H13B | 108.9 | C18-C19-H19 | $118.2(5)$ |
| N1-C13-C14 | $113.3(3)$ | C1-N1-C13 | 120.9 |
| C15-C14-C13 | $119.7(4)$ | C11-N1-C1 | $116.3(4)$ |
| C15-C14-C19 | $119.5(4)$ | C11-N1-C13 | $125.3(5)$ |
| C19-C14-C13 | $120.8(4)$ | $118.4(5)$ |  |
| C14-C15-H15 | 120.8 |  |  |

Symmetry transformations used to generate equivalent atoms:
\#1 -x+1,-y+1,-z+1

3,5-difluoro-PDI Table 4. Anisotropic displacement parameters ( $\AA^{2} \times 10^{3}$ ) for 3,5-difluoro-PDI. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |
| C 1 | $45(4)$ | $51(3)$ | $45(3)$ | $6(2)$ | $13(4)$ | $-9(3)$ |
| C 2 | $33(4)$ | $52(3)$ | $45(3)$ | $9(2)$ | $9(3)$ | $-1(2)$ |
| C 3 | $50(4)$ | $56(3)$ | $53(3)$ | $-1(2)$ | $18(3)$ | $2(2)$ |
| C 4 | $52(4)$ | $58(3)$ | $59(3)$ | $1(3)$ | $22(3)$ | $6(2)$ |
| C 5 | $51(4)$ | $45(3)$ | $46(4)$ | $-4(2)$ | $19(4)$ | $-2(3)$ |
| C 6 | $37(4)$ | $48(3)$ | $47(3)$ | $1(2)$ | $10(4)$ | $-2(2)$ |
| C 7 | $44(5)$ | $47(3)$ | $58(4)$ | $2(3)$ | $22(4)$ | $1(2)$ |
| C 8 | $40(4)$ | $55(3)$ | $61(3)$ | $-1(2)$ | $13(3)$ | $3(2)$ |
| C 9 | $47(4)$ | $54(3)$ | $56(3)$ | $-3(2)$ | $16(3)$ | $3(2)$ |
| C 10 | $36(4)$ | $50(3)$ | $51(3)$ | $3(2)$ | $8(3)$ | $0(2)$ |
| C 11 | $51(4)$ | $50(3)$ | $58(3)$ | $2(3)$ | $18(4)$ | $2(2)$ |
| C 12 | $36(4)$ | $48(3)$ | $48(3)$ | $5(2)$ | $7(3)$ | $3(2)$ |
| C 13 | $54(4)$ | $54(3)$ | $52(3)$ | $-5(2)$ | $14(3)$ | $-3(2)$ |
| C 14 | $55(4)$ | $51(3)$ | $50(3)$ | $-6(2)$ | $21(3)$ | $3(2)$ |
| C 15 | $60(4)$ | $64(3)$ | $59(3)$ | $6(2)$ | $21(3)$ | $-3(2)$ |
| C 16 | $52(4)$ | $75(3)$ | $71(4)$ | $7(3)$ | $13(3)$ | $-4(3)$ |
| C17 | $64(4)$ | $65(3)$ | $63(4)$ | $5(2)$ | $25(3)$ | $-10(3)$ |
| C18 | $58(4)$ | $61(3)$ | $59(3)$ | $-7(3)$ | $35(3)$ | $-9(3)$ |
| C19 | $57(4)$ | $59(3)$ | $60(3)$ | $-7(2)$ | $27(3)$ | $2(2)$ |
| F1 | $62(2)$ | $107(2)$ | $91(2)$ | $36(2)$ | $17(2)$ | $-3(2)$ |
| F2 | $70(2)$ | $79(2)$ | $80(2)$ | $-1(1)$ | $46(2)$ | $-11(1)$ |
| N1 | $52(3)$ | $52(3)$ | $56(3)$ | $-2(2)$ | $21(3)$ | $-1(2)$ |
| O1 | $42(3)$ | $66(2)$ | $65(2)$ | $-1(2)$ | $14(2)$ | $4(2)$ |
| O2 | $67(3)$ | $64(2)$ | $68(2)$ | $-15(2)$ | $18(2)$ | $4(2)$ |
|  |  |  |  |  |  |  |

3,5-difluoro-PDI Table 5. Hydrogen coordinates ( $\mathrm{x} 10^{4}$ ) and isotropic displacement parameters ( $\AA^{2} \times 10^{3}$ ) for 3,5-difluoro-PDI.

|  | $x$ | $y$ | $z$ | U(eq) |
| :--- | :---: | :---: | :---: | :---: |
|  |  |  |  |  |
| H3 | 6612 | 3243 | 5913 | 63 |
| H4 | 6075 | 1555 | 5015 | 66 |
| H8 | 4397 | 9644 | 5792 | 62 |
| H9 | 4949 | 11270 | 6683 | 62 |
| H13A | 6594 | 12206 | 7840 | 64 |
| H13B | 7012 | 10566 | 7591 | 64 |
| H15 | 7518 | 7942 | 8395 | 72 |
| H17 | 7009 | 2782 | 9625 | 75 |
| H19 | 6081 | 7461 | 8279 | 67 |

3,5-difluoro-PDI Table 6. Torsion angles [ ${ }^{\circ}$ ] for 3,5-difluoro-PDI.

| C1-C2-C3-C4 | -179.8(3) | C11-C10-C12-C2 | 1.2(6) |
| :---: | :---: | :---: | :---: |
| C1-C2-C12-C6 | 178.9(3) | C11-C10-C12-C6 | -177.8(3) |
| C1-C2-C12-C10 | 0.0(6) | C12-C2-C3-C4 | 1.0(6) |
| C2-C1-N1-C11 | 5.3(5) | C12-C6-C7-C5\#1 | 179.1(3) |
| $\mathrm{C} 2-\mathrm{C} 1-\mathrm{N} 1-\mathrm{C} 13$ | -177.4(3) | C12-C6-C7-C8 | -0.1(6) |
| C2-C3-C4-C5 | -0.2(6) | C12-C10-C11-N1 | 0.8(6) |
| C3-C2-C12-C6 | -1.9(6) | C12-C10-C11-O2 | 178.3(3) |
| C3-C2-C12-C10 | 179.2(3) | C13-C14-C15-C16 | 177.9(3) |
| C3-C4-C5-C6 | 0.3(6) | C13-C14-C19-C18 | -179.6(4) |
| C3-C4-C5-C7\#1 | 178.2(3) | C14-C13-N1-C1 | -80.8(4) |
| C4-C5-C6-C7 | -178.5(4) | C14-C13-N1-C11 | 96.8(4) |
| C4-C5-C6-C12 | -1.2(6) | C14-C15-C16-C17 | 2.2(6) |
| C5-C6-C7-C5\#1 | -3.5(6) | C14-C15-C16-F1 | 179.3(3) |
| C5-C6-C7-C8 | 177.2(3) | C15-C14-C19-C18 | -0.2(6) |
| C5-C6-C12-C2 | 2.0(6) | C15-C16-C17-C18 | -1.1(7) |
| C5-C6-C12-C10 | -179.1(3) | C16-C17-C18-C19 | -0.7(7) |
| C5\#1-C7-C8-C9 | -178.2(3) | C16-C17-C18-F2 | 177.8(3) |
| C6-C7-C8-C9 | 1.0(6) | C17-C18-C19-C14 | $1.3(6)$ |
| C7\#1-C5-C6-C7 | $3.5(6)$ | C19-C14-C15-C16 | -1.5(6) |
| C7\#1-C5-C6-C12 | -179.1(3) | F1-C16-C17-C18 | -178.2(4) |
| C7-C6-C12-C2 | 179.4(3) | F2-C18-C19-C14 | -177.2(3) |
| C7-C6-C12-C10 | -1.6(6) | N1-C1-C2-C3 | 177.8(3) |
| C7-C8-C9-C10 | -0.1(6) | N1-C1-C2-C12 | -3.0(5) |
| C8-C9-C10-C11 | 178.6(3) | N1-C13-C14-C15 | 129.1(4) |
| C8-C9-C10-C12 | -1.7(6) | N1-C13-C14-C19 | -51.4(5) |
| C9-C10-C11-N1 | -179.6(3) | O1-C1-C2-C3 | -0.4(6) |
| C9-C10-C11-O2 | -2.0(6) | O1-C1-C2-C12 | 178.7(3) |
| C9-C10-C12-C2 | -178.5(3) | O1-C1-N1-C11 | -176.4(4) |
| C9-C10-C12-C6 | 2.5(6) | O1-C1-N1-C13 | 1.0(5) |
| C10-C11-N1-C1 | -4.2(6) | O2-C11-N1-C1 | 178.1(3) |
| C10-C11-N1-C13 | 178.4(3) | $\mathrm{O} 2-\mathrm{C} 11-\mathrm{N} 1-\mathrm{C} 13$ | 0.8(6) |

Symmetry transformations used to generate equivalent atoms:
\#1-x+1,-y+1,-z+1

End 3,5-difluoro-PDI crystal information

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[^3]:    End crystallographic info for M10N8.

