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**A Regioselective Route to Negative Coefficient of Thermal Expansion
Materials for Tuning Epoxy Thermomechanics**

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**A Regioselective Route to Negative Coefficient of Thermal Expansion
Materials for Tuning Epoxy Thermomechanics**

by

Meghan Kiker

Thesis

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Dedication

Dedicated to my family, Sydnie & Harvey, and Lynn, Henry & Keldy. Thank you to my PI, Zachariah Page, for his guidance and for always being in my corner.

Abstract

A Regioselective Route to Negative Coefficient of Thermal Expansion Materials for Tuning Polymer Thermomechanics

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The University of Texas at Austin, 2021

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Thermoset polymers are widely used due to their low cost and versatile high-performance material properties. These materials have found primary applications as heterogenous mixtures (composites) in adhesives, encapsulants, and more. However, thermosets and composites are known to have large coefficients of thermal expansion (CTE), which differ from the CTE of the substrates they are often applied to. A large CTE mismatch results in localized stress and sometimes cracking of the substrate, precluding utility of such thermosets/composites in certain applications, such as optoelectronics where adhesives and encapsulants would be highly beneficial. Remedies for this problem include using fillers such as silica or inorganic metals to lower the CTE of the composites, but these solutions can increase the mass and materials cost and shorten device lifetime. The incorporation of negative coefficient of thermal expansion (NTE) materials into the polymer backbone as a tunable handle has emerged as a promising alternative. The following thesis will describe a six-step regiospecific synthesis to obtain a diepoxy-substituted dibenzocyclooctene (DBCO) derivative that is anticipated to exhibit improved NTE behavior relative to state-of-the-art materials.

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INTRODUCTION

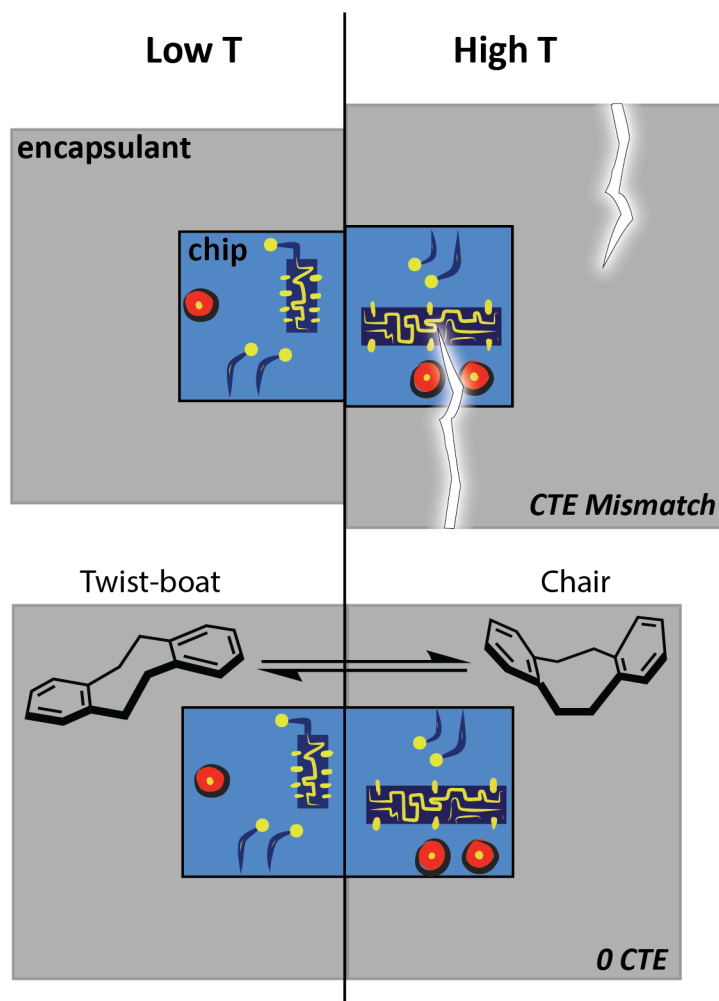
Thermoset polymers are widely used due to their low cost and wide range of chemical, mechanical, thermal, and optical properties (e.g. epoxy adhesives or optical elements, poly(urethane) coatings and foams, poly(acrylate) surface coatings, nanocomposites, and biocompatible hydrogels) that can be tuned to meet various requirements and applications.¹⁻⁶ The application of these materials spans a wide range from adhesives to encapsulation and can be used homogeneously or mixed with another material to form composites.⁷ For example, the dentistry field makes use of several different composites where material properties such as durability, toughness, optical properties (aesthetic), and adhesiveness of the composites are highly important.⁸⁻¹⁰ Thus, composites often require additional components in the monomer matrix to tune the physical properties and to further improve the material.

A problem that arises with these composite materials is a CTE mismatch where encapsulants and their substrates expand at different rates.^{11, 12} This can lead to performance and device lifetime issues (e.g. shortened device durability or sudden failure), and particularly for encapsulated or laminated materials, warping¹³, cracking, delamination, or harm to the substrate encapsulated (i.e., chip board). The use of negative thermal expansion (NTE) or low CTE fillers has been used to alleviate CTE mismatch with some success.¹⁴⁻²⁰ These materials are typically inorganic compounds, such as ZrW_2O_8 (CTE ~ -9 ppm/ $^{\circ}\text{C}$)²¹⁻²³, GaMn_3 (CTEs as low as -70 ppm/ $^{\circ}\text{C}$)²⁴, or ScF_3 (CTE ~ -14 ppm/ $^{\circ}\text{C}$)²⁵ and can change the overall composite CTE by over an order of

magnitude. However, to accomplish this a large amount of filler of up to potentially 90 wt % is required and thereby introduces processing limitations, such as reduced degree of polymerization and complex mixing procedures. Additionally, poor interfacing between the filler and composite material can further decrease material properties and performance by embrittling or reducing material toughness or thermal conductivity, interfere with optical properties by increasing scattering,¹⁰ increase final weight of the material, and add cost due to expensive fillers.⁷

An alternative approach to reduce CTE mismatch is accomplished by harnessing conformational structure change in the polymer backbone.^{26, 27} Previous work has shown incorporation of DBCO into polyarylamide materials, and more recently by Foster et al. the incorporation of this framework into epoxy/aniline thermosets by installing aniline substituents off the benzyl rings.²⁹ Thermal analysis and density functional calculations of this diamino-DBCO (DADBCO) show that the NTE behavior of this compound is comes from a reversible twist-boat to chair isomerization (Figure 1) and is further dependent on the cis- or trans-isomer produced.²⁸ The produced mixture of DADBCO presented a weak NTE and upon isolation of the isomers it was seen that the trans-DADBCO exhibited little to no NTE while the cis-DADBCO had a strong negative behavior.²⁸ The synthetic route to obtain DADBCO, while relatively short and high-yielding, results in a mixture of the cis- and trans- isomers that is difficult to separate and leads to a low yielding isolation of the cis-DADBCO. Herein we report a six-step synthesis to obtain a cis only diepoxy-substituted DBCO that can be used to make an epoxy/aniline thermoset with the desired NTE properties. Furthermore, only the

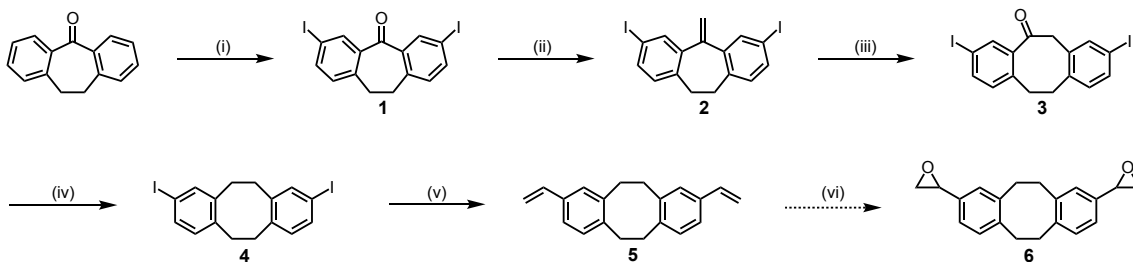
DADBCO has been introduced, leaving the co-epoxy monomer as a non-stimuli responsive component. This is an opportunity to reach greater degrees of NTE behavior and tunability within a composite material removing the need for additional filler or additives.



Scheme 1. Illustration showing one of the issues that arises from CTE mismatch in encapsulation (cracking) (top). By incorporating NTE compounds into the polymer backbone, a composite CTE of zero can be achieved (bottom).

RESULTS AND DISCUSSION

To synthesize the DEDBCO, we looked to develop an alternative synthesis that would guarantee the cis isomer that would exhibit the NTE rather than separate a mixture of cis and trans isomers as Foster et al. did. The proposed synthetic route to obtain compound **6** (DEDBCO) (Scheme 2) was adapted in part from a procedure reported by Kardelis et al. (steps 1-3) and extended to achieve the DBCO framework and install epoxy functional groups (steps 4-6). Furthermore, this route can be easily modified from compound **4** to attach other groups such as an aminoalcohol which is a future target of interest of this project.



Scheme 2. Full six step proposed synthesis to achieve diepoxy-DBCO (**6**). Reagents and conditions: (i) I_2 , HNO_3 , H_2SO_4 , CH_3COOH , CCl_4 , reflux 5hr 28% yield; (ii) $MePPh_3^+I^-$, $KOtBu$, dry THF, $40^\circ C$, 4 hrs, 70% yield; (iii) $AgNO_3$, I_2 , 1:1 MeOH:dioxane, reflux 24 hr, 66% yield; (iv) 1:1 TFA: CH_2Cl_2 , Et_3SiH , ~6hrs, 80% yield; (v) $Pd(PPh_3)_4$, K_3PO_4 , THF, reflux, $CH_2=CHBF_3K$, 80% yield; (vi) mCPBA, CH_2Cl_2 , $0^\circ C$.

Steps 1-3 (**1**, **2**, **3**)

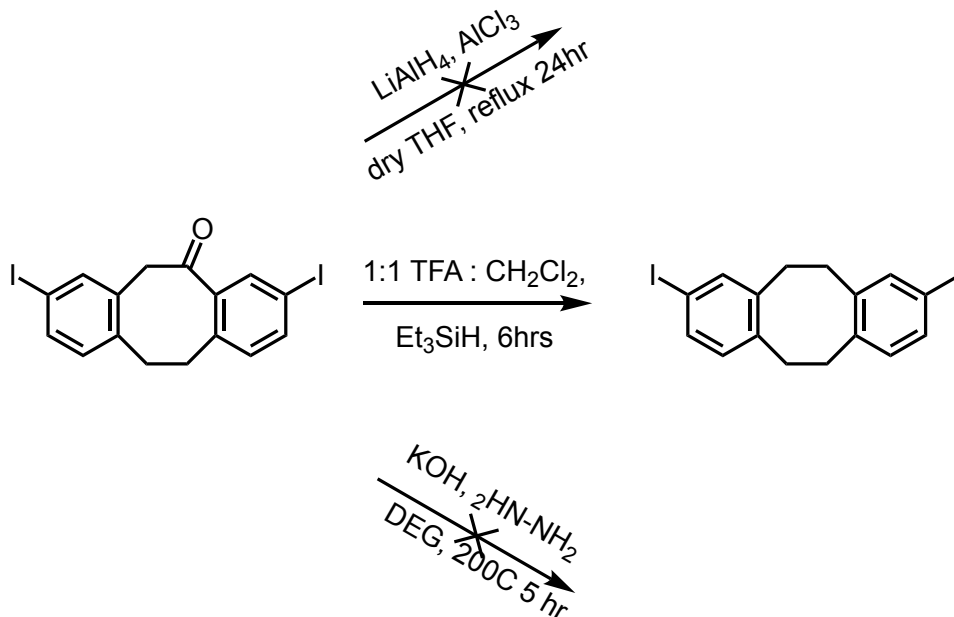
Previously reported methods to obtain the first three compounds (**1-3**) in this synthesis were followed in a similar fashion.³⁰ Some modifications to the work-up and purification for these steps were adopted to optimize reaction time and yield. The first step, iodination

of dibenzosuberone, proceeds through an electrophilic aromatic substitution resulting in 3,7-diiodo-10,11-dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-one (**1**). This initial reaction is low yielding at an average yield of 25-30% and attempts to improve yield have been unsuccessful, however the low cost of starting reagents allows for large scale up where approximately 40 grams of compound **1** can be made. The Wittig reaction to produce 3,7-diiodo-5-methylene-10,11-dihydro-5*H*-dibenzo[*a,d*][7]annulene (**2**) and subsequent ring expansion to produce 3,8-diiodo-11,12-dihydrodibenzo[*a,e*][8]annulen-5(6*H*)-one (**3**) proceed similarly as reported with a few modifications to the purification for both. The reaction time to completion for compound **2** was observed at ~4 hours over the reported 12 hours and purification through flash column chromatography found better separation using a solvent system of 4% dichloromethane in hexanes. Once filtered and concentrated by rotary evaporation compound **3** can be triturated in MeOH and filtered with no loss in yield rather than purification via flash column chromatography.

Ketone Reduction (3 to 4)

Three different reactions were attempted to reduce the ketone on compound **3**: a LiAlH₄ reduction, a Wolff Kishner reduction, and a reduction by trifluoroacetic acid and triethylsilane. The Wolff Kishner and LiAlH₄ reactions were unsuccessful and resulted in loss of starting material or no reaction at all, respectively. Only the trifluoroacetic acid/triethylsilane method resulted in a successful reduction of the ketone in high yield (80%) producing 2,9-diiodo-5,6,11,12-tetrahydrodibenzo[*a,e*][8]annulene (**4**) (Scheme 3). Furthermore, this reaction requires milder conditions, shorter reaction time, and relatively

less dangerous reagents than the LiAlH_4 or Wolff Kishner reductions. Compound **4** was confirmed by ^{13}C and ^1H NMR spectroscopy and mass spectrometry (exact mass calculated for $\text{C}_{16}\text{H}_{14}\text{I}_2$ 459.92, found 459.9182).



Scheme 3. Attempted synthetic routes to reduce ketone on compound 3.

Suzuki Coupling (4 to 5)

The Suzuki-Miyaura cross-coupling reaction is widely used to create new C-C bonds and was the obvious choice to install vinyl groups onto the DBCO framework. Conditions for this reaction utilized $\text{Pd}(\text{PPh}_3)_4$ and potassium vinyltrifluoroborate (in a biphasic solvent system of THF and aqueous potassium phosphate tribasic (2 M) with no need for a phase transfer catalyst. Optimization of reagent equivalents were examined to increase yield,

reduce reaction time, and reduce amount of catalyst required. An excess of vinyl trifluoroborate was used (2 equivalents per coupling site), and catalyst loading could be as low as 0.04 equivalents without affecting reaction time. This coupling step is high-yielding (80%) with a simple work-up and can be purified with a silica plug to produce 2,9-divinyl-5,6,11,12-tetrahydrodibenzo[a,e][8]annulene (**5**). Characterization by NMR spectroscopy showed successful addition of the vinyl groups with chemical shifts corresponding to the vinyl hydrogens appearing at 6.59, 5.64 and 5.13 ppm that integrate to a value of 2 each (Figure 1).

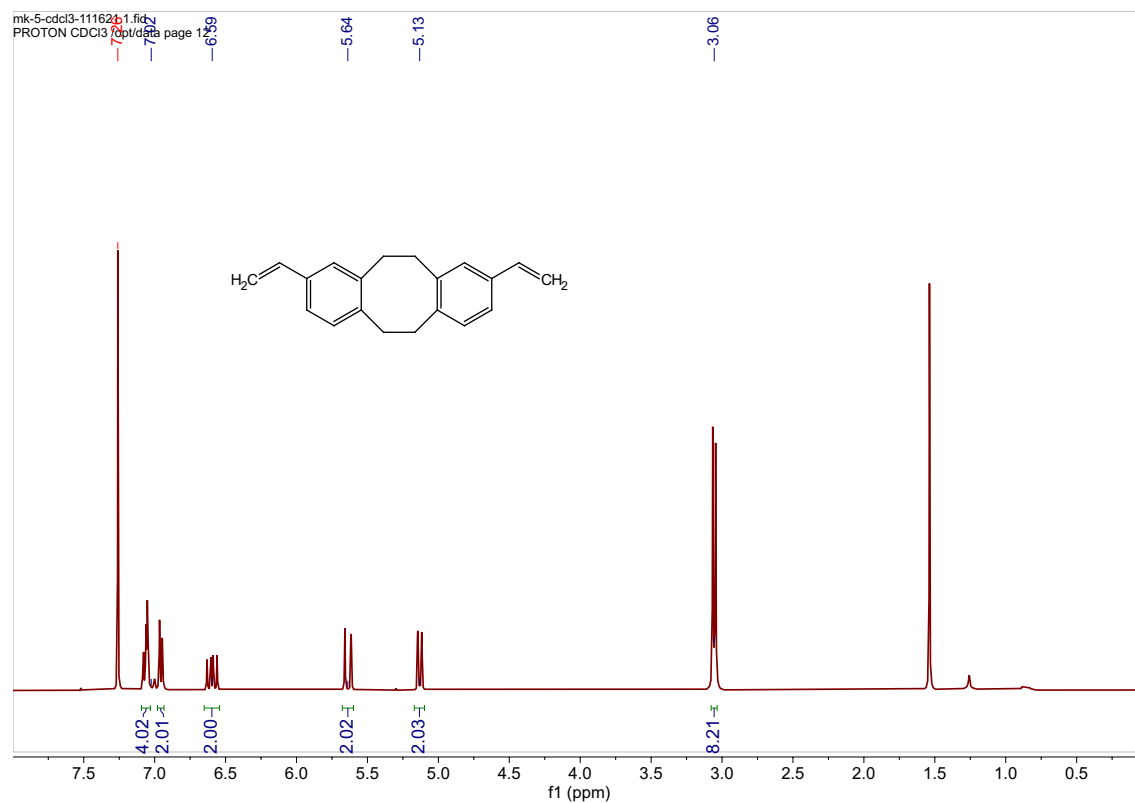


Figure 1. ¹H NMR spectrum of compound 5 in CDCl₃. Vinyl group proton shifts seen at 6.59, 5.64, 5.07 ppm with an integral value of 2 each.

Epoxidation of Vinyl Groups (5 to 6)

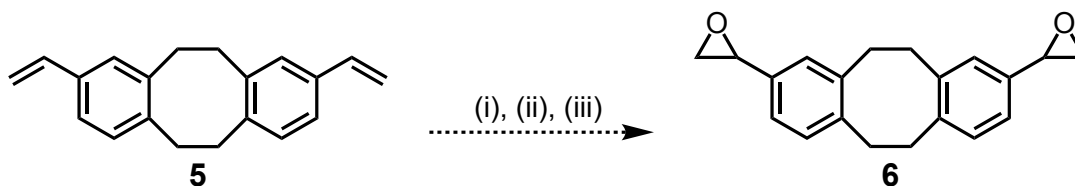
A general and widely used method of epoxidation by meta-chloroperoxybenzoic acid (mCPBA) was the initially proposed and attempted method to epoxidize the vinyl groups of **5** to obtain 2,9-di(oxiran-2-yl)-5,6,11,12-tetrahydrodibenzo[a,e][8]annulene (**6**). The procedure entails starting material and several equivalents per alkene of mCPBA dissolved in DCM at 0°C and stirred for approximately 1 hour. Upon completion, the product is washed with saturated solutions of sodium bisulfite and sodium bicarbonate to quench and remove excess mCPBA and 3-chlorobenzoic acid, washed with brine and dried with magnesium sulfate. Further purification by flash column chromatography has to date been unsuccessful. Ultimately, this method has been confirmed to produce the targeted DEDBCO by mass spectrometry, but purification and isolation requires further optimization. Furthermore, an insoluble solid has been isolated from the reaction mixture which is indicative of the product polymerizing with itself and crashing out. This was hypothesized to occur because of acidic reaction conditions and thus more neutral reactions were explored.

Hydrogen peroxide (H₂O₂), typically used as 30% in water, is a common alternative to mCPBA that is green and milder option for epoxidation due to its byproduct being water. Limnios et al. report a procedure compatible with a wide range of alkenes including aryl alkenes that uses H₂O₂ in tandem with acetonitrile, a buffer, and a catalytic amount of 2,2,2-trifluoroacetophenone that results in epoxides in high yields. This procedure was

adopted for our compounds and tried in two different solvents, tert-butyl alcohol and ethyl acetate, yet no change was seen in the starting material after 1 hour up to 24 hours later.

A second attempt at a more neutral synthesis follows a procedure for aryl alkenes that uses mCPBA but includes the addition of 0.3 M sodium bicarbonate (aq) to the reaction mixture.³² The reaction solution as reported is heterogeneous as the reagents used were all liquid or low melting solids, thus for the adapted synthesis a small amount of DCM was used to dissolve compound **5** and stirred vigorously with the aqueous sodium bicarbonate to ensure good mixing of the biphasic solution. By this method the disappearance of the vinyl groups of compound **5** could be seen by ¹H NMR spectroscopy as soon as 5 minutes after the addition of mCPBA. To further remove acidic conditions, washing with saturated sodium bisulfite (aq) was removed from the workup. Currently, the purification of this synthetic procedure is in progress, but shows promise as a successful route to compound **6**.

Another potential synthetic route to obtain the DEDBCO would follow a procedure reported by Yamada et al. that utilizes an alternative oxidizer, 2-hydroperoxy-4,6-diphenyl-1,3,5-triazine (Triazox). They show epoxidations at mild conditions and ambient temperature with high yields and non-acidic byproducts making it an attractive potential synthesis for our targeted molecule.



Scheme 4. Attempted syntheses for compound **6**. Reagents and conditions: (i) mCPBA, CH₂Cl₂, 0°C; (ii) 5 mol % 2,2,2-trifluoroacetophenone, t-BuOH or EtOAc, MeCN, buffer, H₂O₂, 1 h; (iii) mCPBA, 0.3 NaCO₃H (aq), CH₂Cl₂, 0°C.

CONCLUSIONS AND FUTURE WORK

Upon successful isolation of compound **6**, it will be polymerized with ethylenediamine (Scheme 5) and analyzed by differential scanning calorimetry (DSC) in which the sample polymer will be heated in tandem with a reference to measure the amount of energy required to heat it as a function of temperature, thermomechanical analysis (TMA) by using compression to measure the thermal expansion and contraction of the various polymer samples with changing temperature, thermogravimetric analysis (TGA) to measure the change in mass as a function of temperature, etc. to fully characterize the molecule's CTE. It is expected to be similar to the data reported by Foster et al. (Figure 1): A strong negative behavior at approximately 160°C seen for the *cis*-DADBCO.

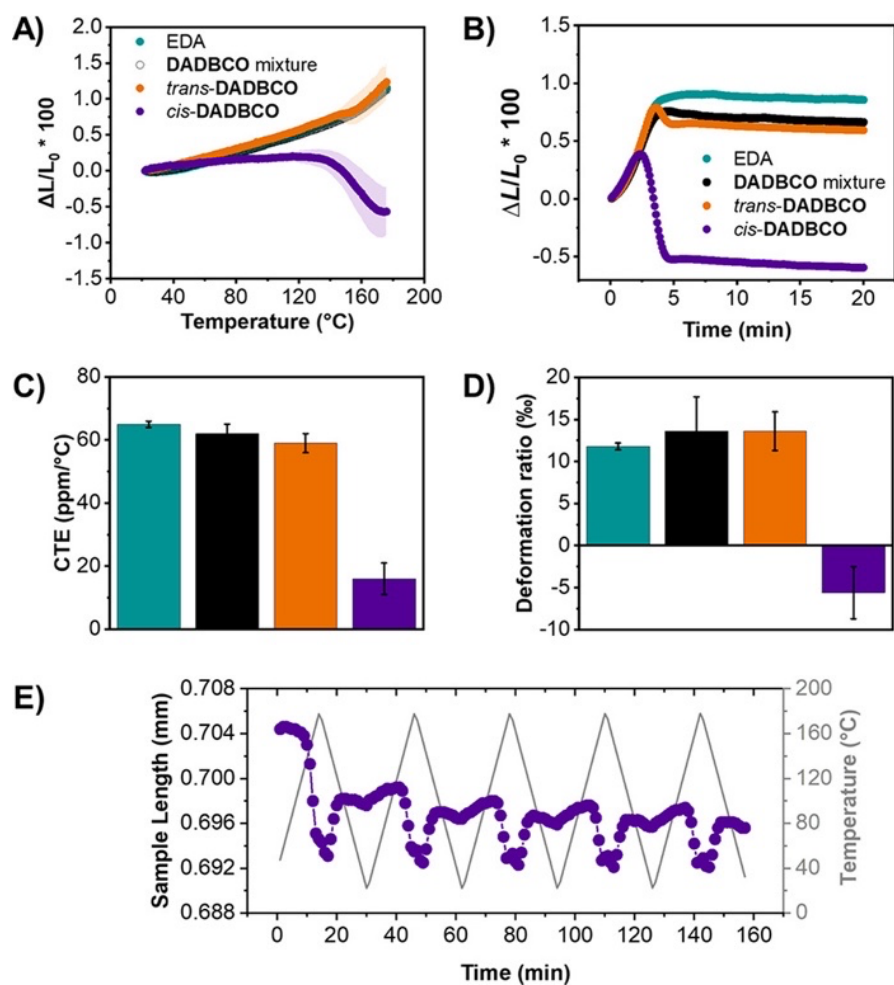
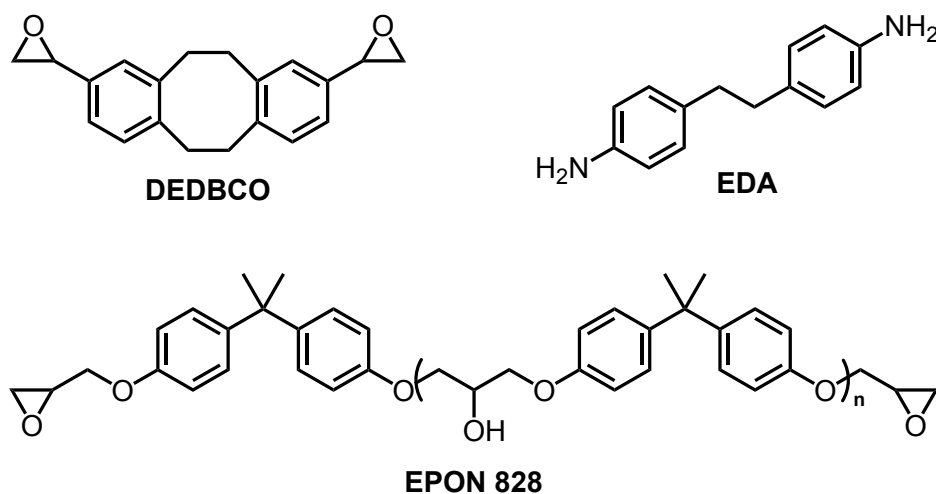


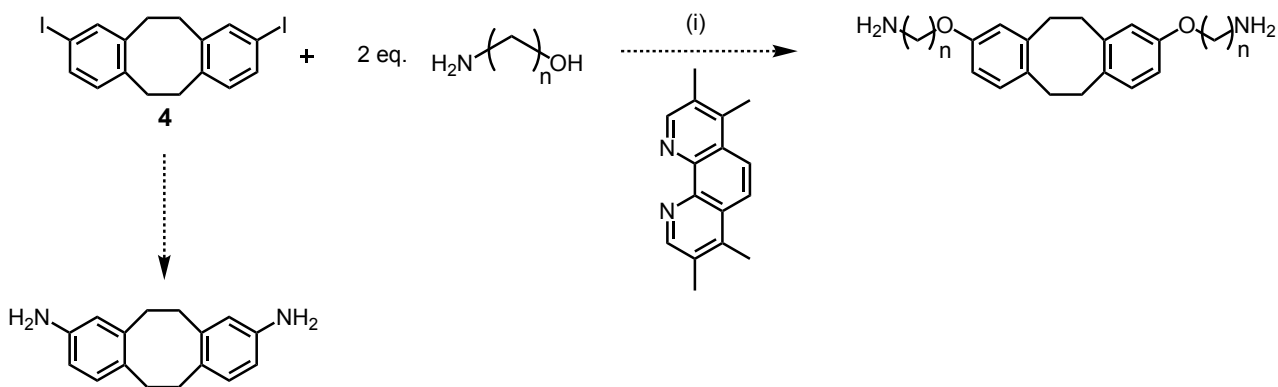
Figure 2. Thermal analysis data collected by Foster et al. showing CTE data of the various compounds they analyzed.



Scheme 5. Compounds that will be used for polymerization and thermal analysis.

Future work will concern installing other functional groups to explore other polymerizations such as an aliphatic amine chain to enable polyurethane polymerizations. We plan to target another diamino derivative of DBCO with alkyl spacers. The current proposed pathway to reach this molecule involves installing aliphatic aminoalcohol chains by an Ullmann type coupling starting from compound **4** based on work by Shafir et al (Scheme 6). Upon successful synthesis, this derivative's CTE properties will be examined in an analogous fashion to the DEDBCO, and its values compared to DADBCO, and the effect of the alkyl spacers evaluated. Additionally, DADBCO can be synthesized from compound **4** via an Ullmann type coupling and subsequent reduction, further enhancing the utility of this synthetic pathway. These two amine derivatives can be polymerized with the DEDBCO and the effect of two NTE monomers in the polymer backbone will be analyzed. Another derivative of interest is a diisocyanato-DBCO or

diol-DBCO to explore the NTE effect in polyurethanes, another highly used thermoset polymer used in encapsulation and related applications. All of these compounds are expected to display NTE behavior and will contribute to elimination of CTE mismatch without reducing material properties or requiring additional additives.



Scheme 6. Proposed synthesis to attach an aminoalcohol via an O-arylation Ullmann-type coupling from **4** and an additional pathway to obtain DADBCO via a similar coupling. Reagents and conditions: (i) 5% CuI, Cs_2CO_3 , toluene, 90°C .

SUPPORTING INFORMATION

Experimental Details

MATERIALS

Chemicals: 5-Dibenzosuberone ($\geq 99\%$) was purchased from Chem Impex. Nitric acid (Trace metal grade), Sulfuric acid (Trace metal grade), Acetic acid, glacial (Certified ACS), Iodine, resublimed crystals, ACS grade (99.8%), Potassium tert-butoxide 98%, Methyltriphenylphosphonium iodide (98.0%+), triethylsilane (TES), trifluoroacetic acid (TFA) $>99.9\%$, tetrakis(triphenylphosphine)palladium(0), 99% (99.9+%-Pd), silver nitrate (ACS, 99.9+% (metals basis)), Potassium phosphate tribasic (reagent grade, $\geq 98\%$) were purchased from Fisher Scientific. Potassium vinyltrifluoroborate was purchased from Chemscone. 3-chloroperoxybenzoic acid, 70-75%, balance 3-chlorobenzoic acid and water and Carbon tetrachloride were purchased from Acros Organics. Methanol (MeOH) (certified ACS), Dioxane (Certified ACS), Dichloromethane (DCM) (certified ACS), Chloroform (certified ACS), Hexanes (certified ACS), Acetonitrile (MeCN) (certified ACS), Tetrahydrofuran (THF) (certified ACS) were purchased from Fisher Chemical. All reagents/solvents were used as received without additional purification, unless otherwise noted. All reactions were done under a nitrogen atmosphere unless otherwise noted.

EQUIPMENT AND INSTRUMENTATION

Nuclear Magnetic Resonance (NMR)

NMR spectra were recorded on an Agilent MR 400 MHz spectrometer or a Varian VNMRs 400 MHz spectrometer using CDCl₃ as the solvent. ¹H NMR were carried out coupled and referenced to the CDCl₃ chemical shift at 7.26 ppm. ¹³C NMR were carried out decoupled and referenced to the CDCl₃ chemical shift at 77.16 ppm. NMR data was analyzed using MestReNova Software.

High Resolution Mass Spectrometry (HRMS)

HRMS was performed on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS using APCI or ESI and the data was subsequently analyzed using Agilent MassHunter Qualitative Analysis Software.

SYNTHESIS

3,7-diiodo-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-one (1) The synthesis was accomplished in an analogous fashion to that previously reported by Kardelis et al.. Solvent was removed by rotary evaporation to obtain a red-brown solid. The product was purified by dissolving in a minimal amount of 1:1 CHCl₃:Hx and filtered. The precipitate

was collected and recrystallized in EtOH to obtain an off white crystalline solid (28%).

HRMS (ESI): exact mass calculated for C₁₅H₁₀I₂O 459.88, found 459.8814.

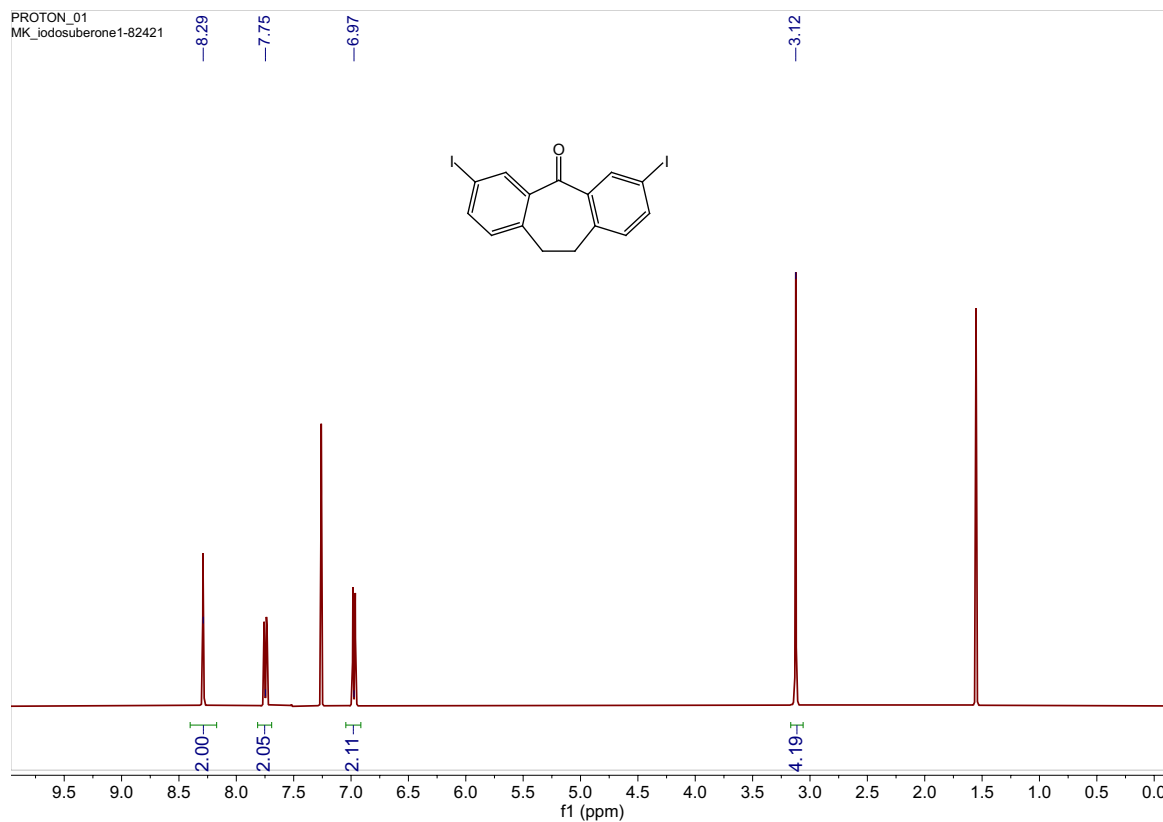


Figure S1. ¹H NMR of **1**.

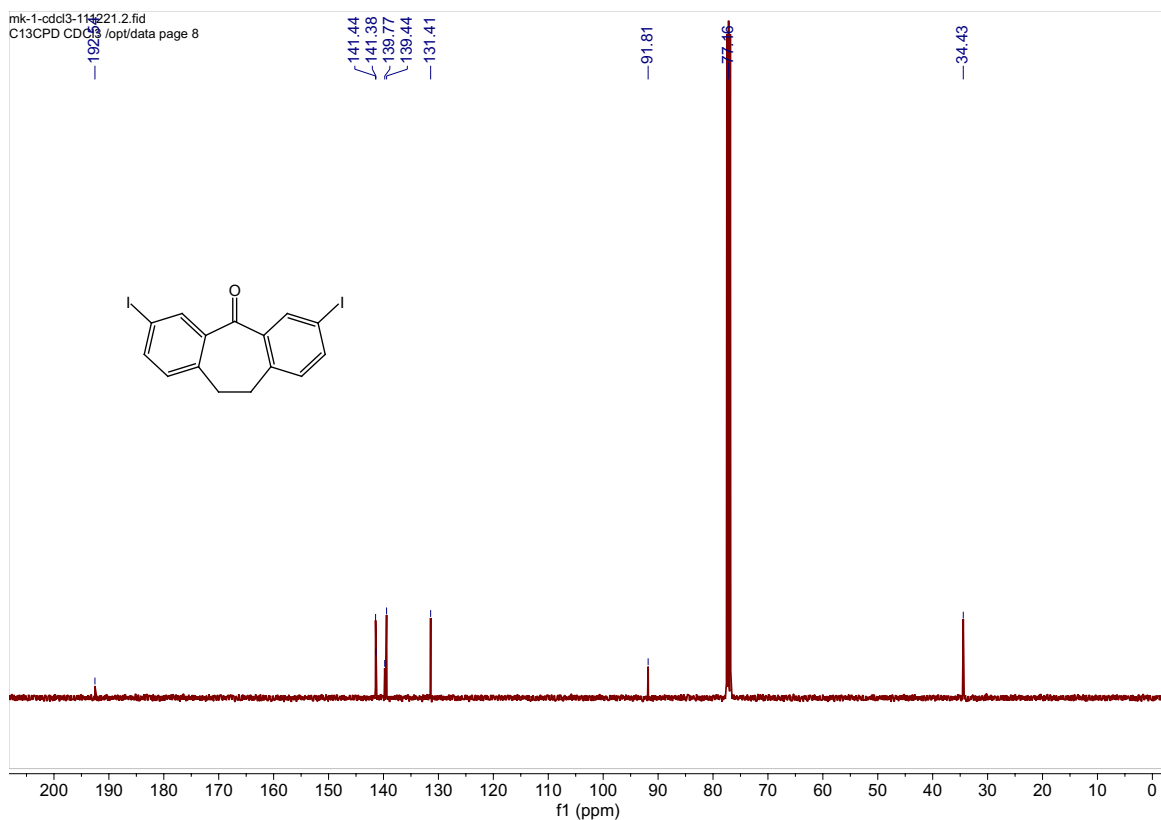


Figure S2. ^{13}C NMR of **1** in CDCl_3 .

Elemental Composition Report

Page 1

Multiple Mass Analysis: 2 mass(es) processed - displaying only valid results

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

3 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

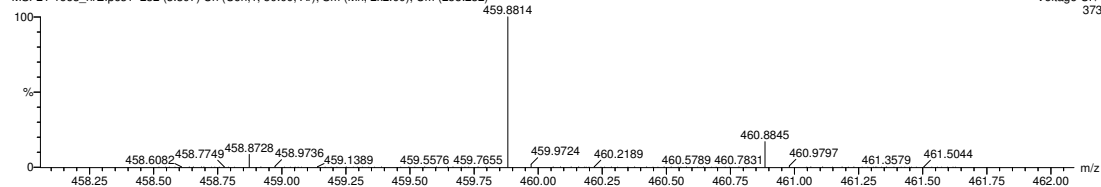
Elements Used:

C: 0-100 H: 0-100 O: 1-1 I: 2-2

1 NCTE

MSF21-1663_hrElpos1 282 (3.307) Cn (Cen,1, 50.00, Ar); Sm (Mn, 2x2.00); Cm (258.282)

Voltage Cl+
373



Minimum:	20.00				-1.5			
Maximum:	100.00		5.0	10.0	50.0			
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula	
459.8814	100.00	459.8821	-0.7	-1.5	10.0	2773022.8	C15 H10 O I2	

Figure S3. HRMS of **1**.

3,7-diiodo-5-methylene-10,11-dihydro-5H-dibenzo[a,d][7]annulene 2 The synthesis was accomplished in an analogous fashion to that previously reported by Kardelis et al.. The product was purified by flash chromatography (4% DCM in Hx) to obtain a white powder (70%). HRMS (ESI): exact mass calculated for C₁₆H₁₂I₂ 457.90, found 457.9031.

Figure S4. ¹H NMR of **2** in CDCl₃.

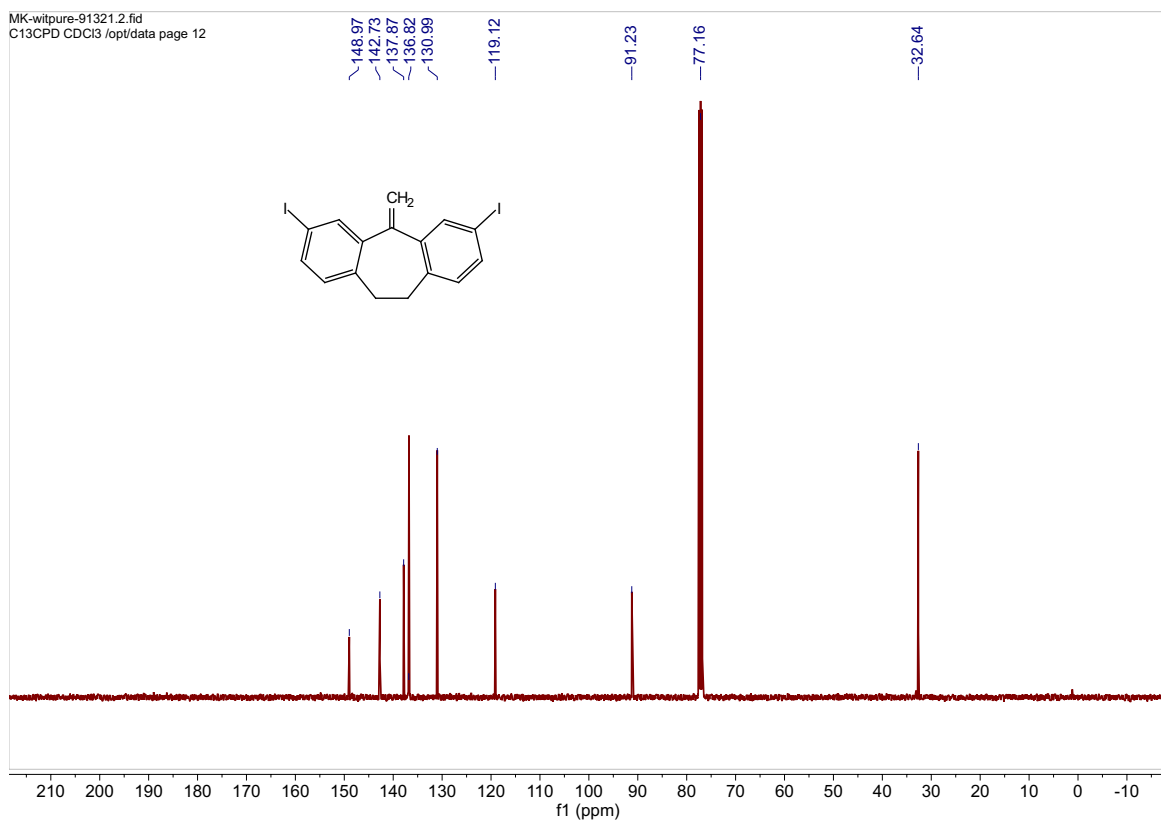


Figure S5. ¹³C NMR of **2** in CDCl₃.

Multiple Mass Analysis: 2 mass(es) processed - displaying only valid results

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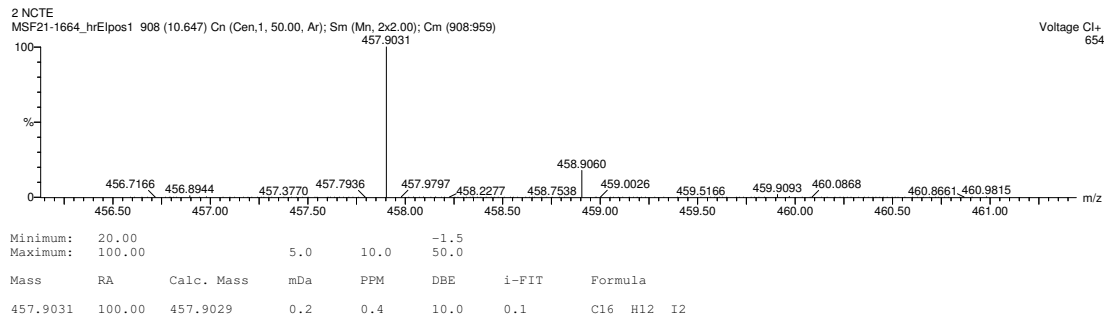
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

4 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 I: 2-2

Figure S6. HRMS of **2**.

3,8-diiodo-11,12-dihydrodibenzo[a,e][8]annulen-5(6H)-one **3** The synthesis was accomplished in an analogous fashion to that previously reported by Kardelis et al.. The product was purified by trituration in MeOH, the precipitate was filtered and washed with MeOH to obtain a white powder (60%). HRMS (ESI): exact mass calculated for C₁₆H₁₂I₂O 473.90, found 473.8986.

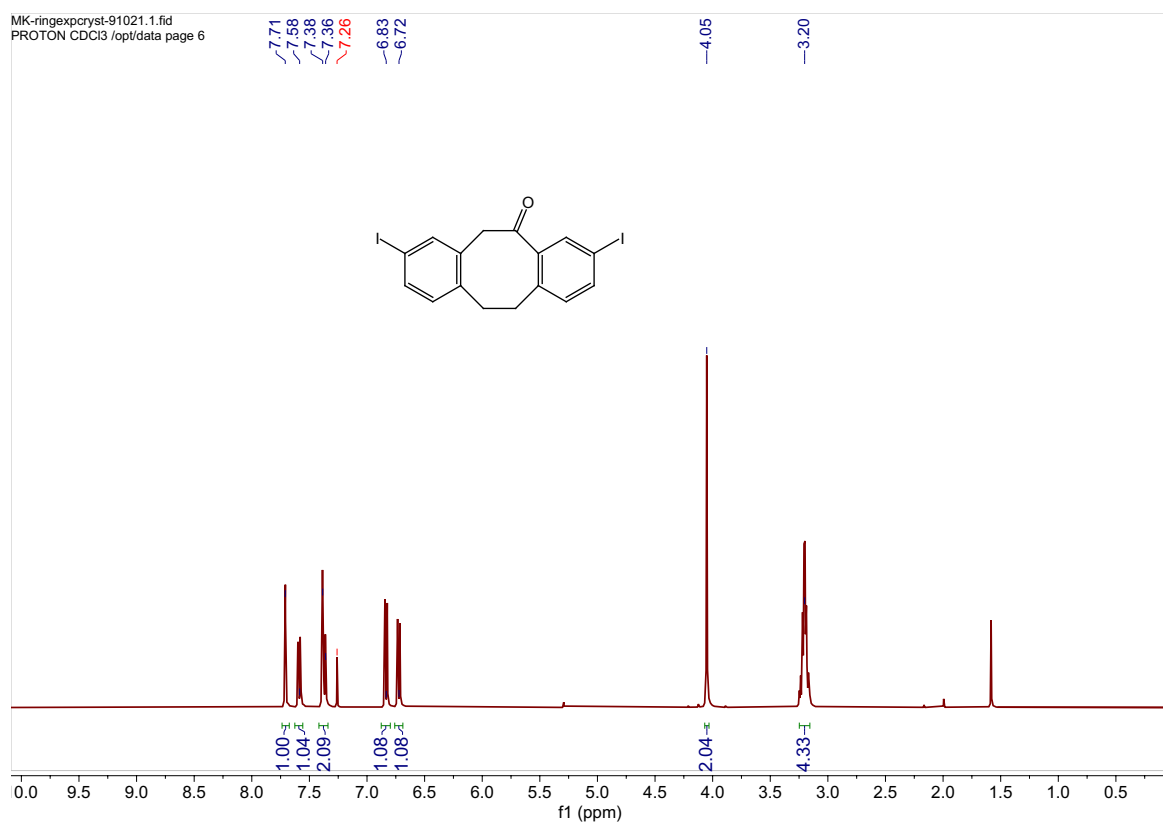


Figure S7. ^1H NMR of **3** in CDCl_3 .

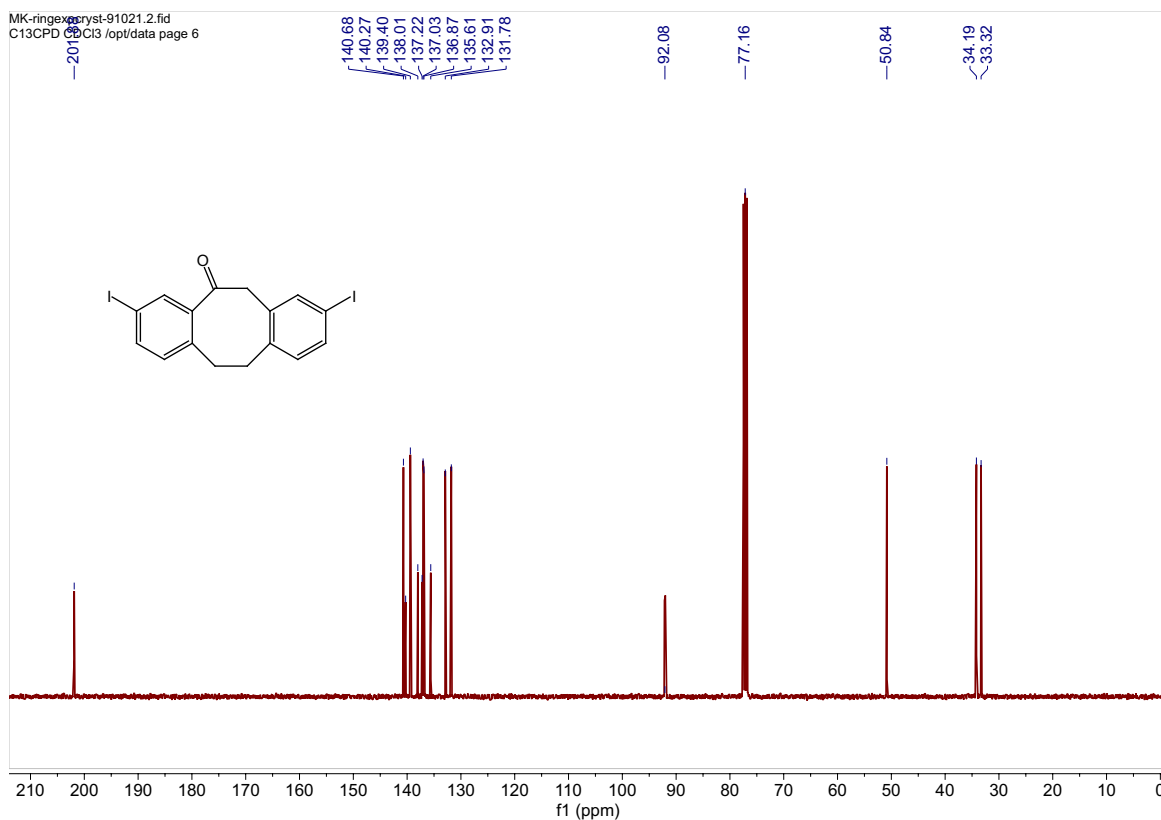


Figure S8. ^{13}C NMR of **3** in CDCl_3 .

Elemental Composition Report

Page 1

Multiple Mass Analysis: 2 mass(es) processed - displaying only valid results

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

15 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 O: 0-1 I: 2-2

3 NCTE

MSF21-1665hrElpos1 43 (0.504) Cn (Cen,1, 50.00, Ar); Sm (Mn, 2x2.00); Cm (21:76)

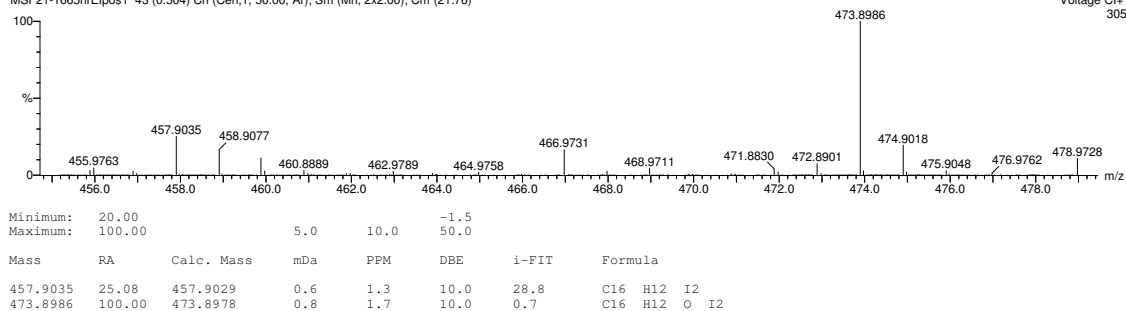


Figure S9. HRMS of **3**.

2,9-diiodo-5,6,11,12-tetrahydrodibenzo[*a,e*][8]annulene (4) To a round bottom flask was added **3** (6.32 g, 13.3 mmol), DCM (47 mL), and TFA (47 mL). Triethylsilane (TES) (21.3mL, 10 eq, 133 mmol) was slowly added to the solution and let stir at room temperature for 5 hours. Reaction was monitored by TLC (R_f of 0.8 in 1:4 DCM:HX). Upon completion, the reaction was cooled in a salt-ice bath for 30 minutes before using 4 M NaOH to neutralize the TFA (monitored by pH paper). The reaction was then extracted with DCM (3 x 50 mL). The organic phase was washed with water (3 x 50 mL) and brine (1 x 50 mL) and dried over MgSO₄. The solution was dried by rotary evaporation and purified by recrystallization in acetonitrile to yield a white powder (**4**) (4.9 g, 80%) ¹H NMR (400 MHz, CDCl₃) ¹³C NMR (100 MHz, CDCl₃) HRMS (ESI): exact mass calculated for C₂₀H₂₀ 459.92, found 459.9182.

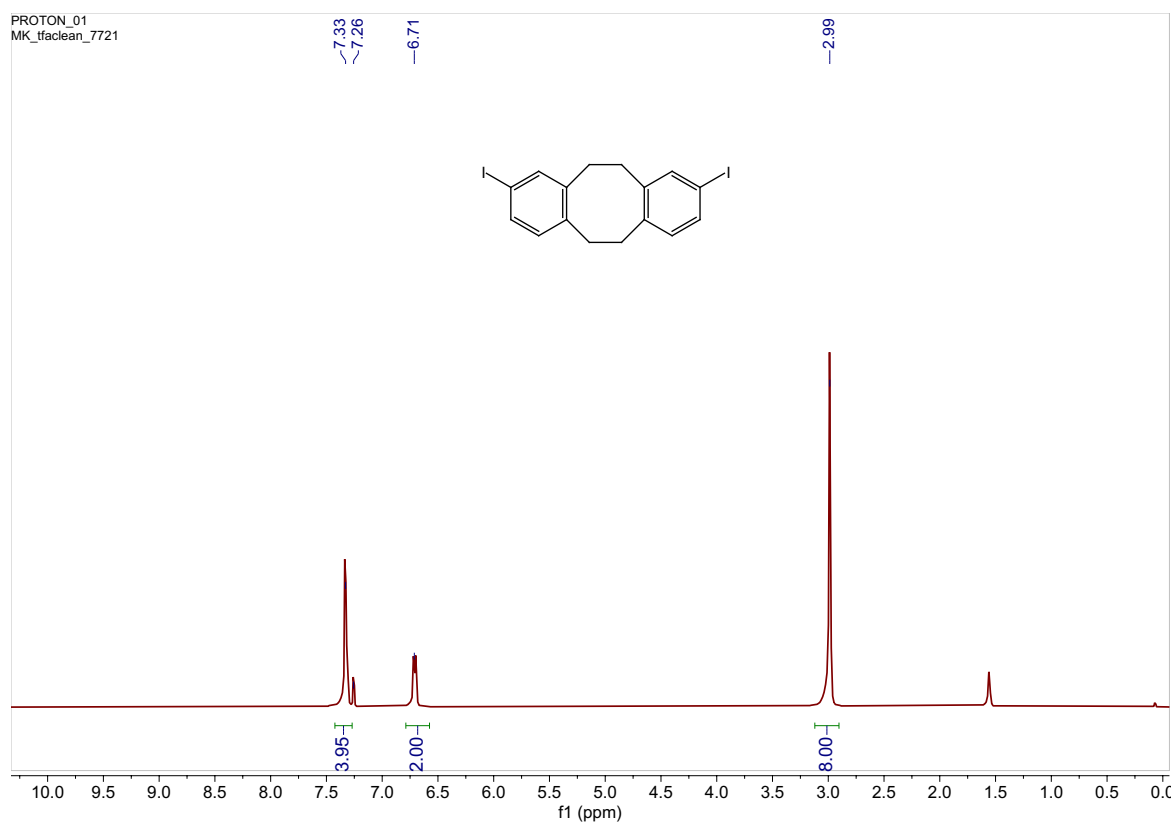


Figure S10. ^1H NMR of **4** in CDCl_3 .

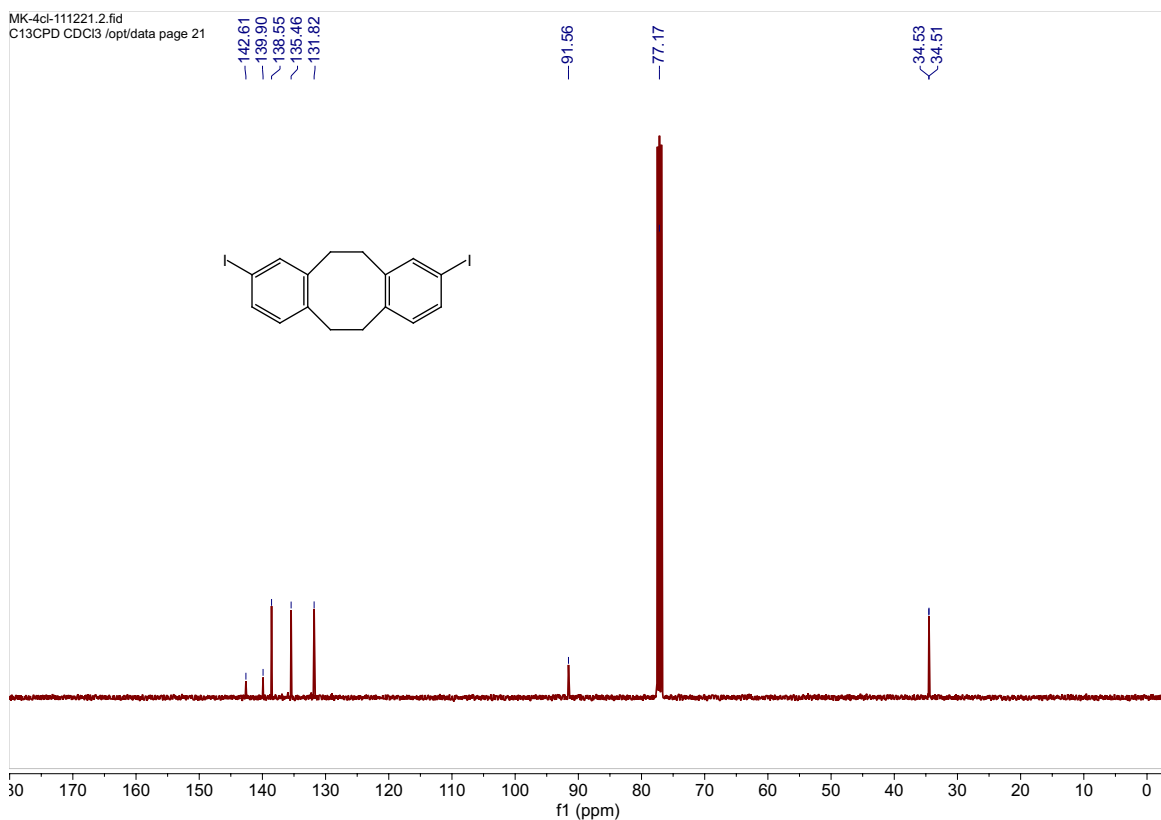


Figure S11. ^{13}C NMR of **4** in CDCl_3 .

Elemental Composition Report

Page 1

Multiple Mass Analysis: 3 mass(es) processed - displaying only valid results

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

16 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 2-1000 I: 0-2

Iodinated DBCOD

MSF21-0961_hrClpos1 767 (8.993) Cn (Cen,1, 30.00, Ht); Sm (Mn, 3x3.00); Cm (715:768)

Voltage Cl+
2.10e4

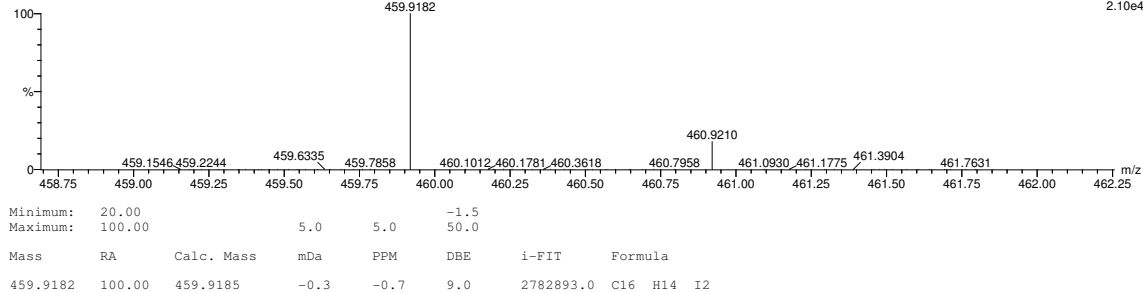


Figure S12. HRMS of **4**.

2,9-divinyl-5,6,11,12-tetrahydrodibenzo[*a,e*][8]annulene (5) To a two-neck round bottom flask was added THF (12.00 mL) and 2 M tripotassium phosphate (12.00 mL, aqueous). The reaction was degassed with argon for 5 minutes before adding compound **4** (1.07 g, 2.33 mmol), Potassium vinyltrifluoroborate (1.25 g, 9.30 mmol), and Pd(PPh₃)₄ (134 mg, 116 μmmol). The reaction was then degassed with argon for another 5 minutes, then heated to reflux for 12 h with vigorous stirring. Upon completion, the reaction was concentrated by rotary evaporation to remove THF, then extracted with DCM (3 x 50 mL), washed with H₂O (3 x 50 mL), brine (1 x 50mL), dried over MgSO₄, and filtered. The product was purified via silica plug using 1% DCM in Hx to load and rinsed with Hx. Solvent was removed by rotary evaporation to obtain a white powder (80%). ¹H NMR (400 MHz, CDCl₃) ¹³C NMR (100 MHz, CDCl₃) HRMS (ESI): exact mass calculated for C₂₀H₂₀ 260.16, found 260.1559.

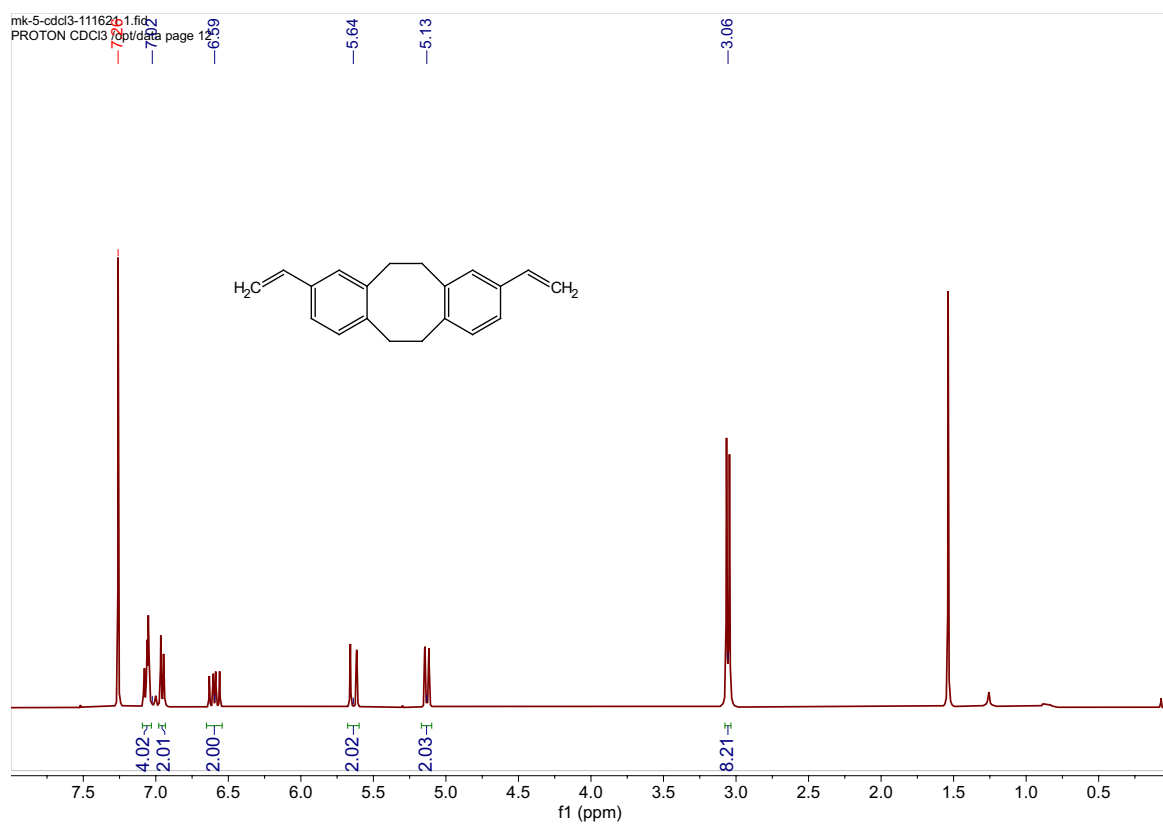


Figure S13. ^1H NMR of **5** in CDCl_3 .

mk-5-cdd3-111621.2.fid
C13CPD CDCl3 /opt/data page 12

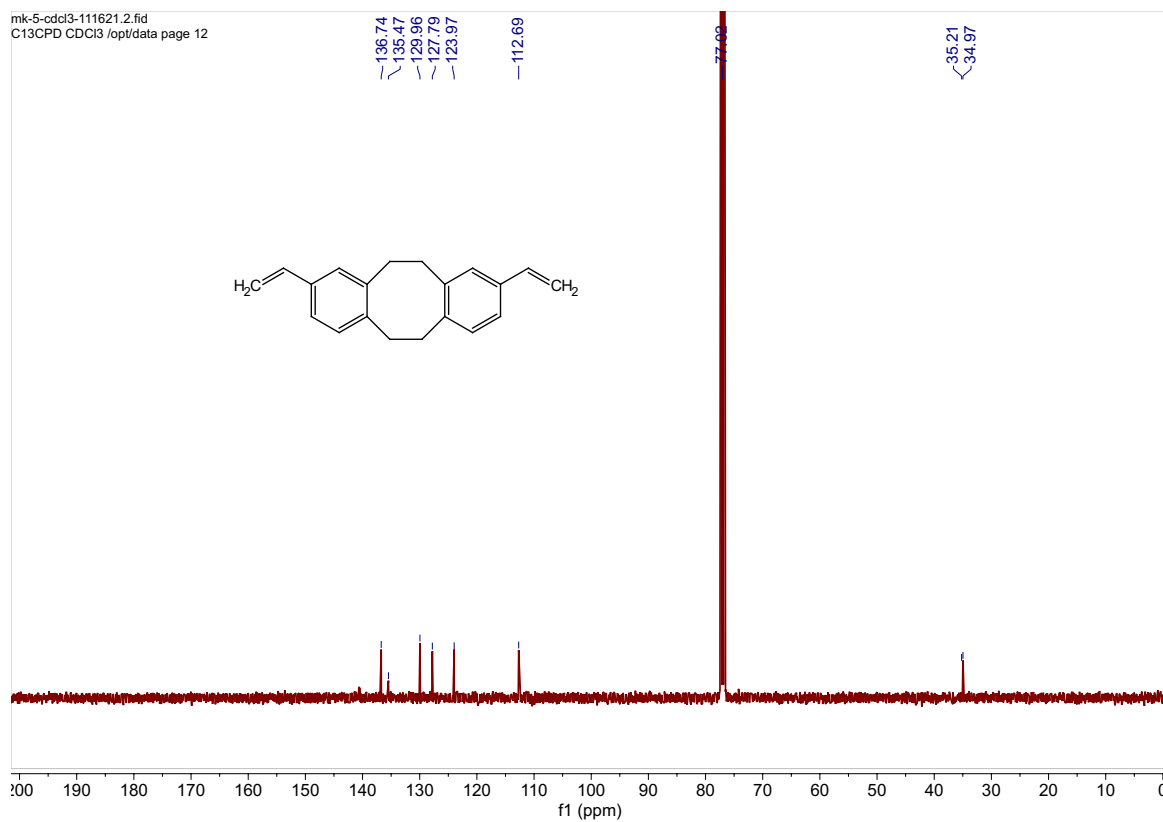


Figure S14. ¹³C NMR of **5** in CDCl₃.

Multiple Mass Analysis: 2 mass(es) processed - displaying only valid results

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

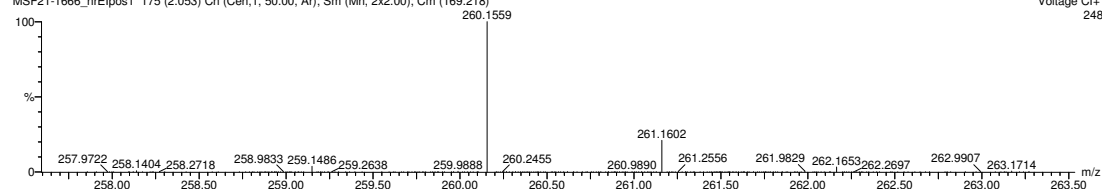
8 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100

5 NCTE

MSF21-1666_hrElpos1 175 (2.053) Cn (Cen,1, 50.00, Ar); Sm (Mn, 2x2.00); Cm (169.218)

Voltage Cl+
248

Minimum:	20.00				-1.5			
Maximum:	100.00		5.0	10.0	50.0			
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula	
260.1559	100.00	260.1565	-0.6	-2.3	11.0	0.4	C20	H20

Figure S15. HRMS of **5**.

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