

Abstract

C—C bond activation has been an active area of research due to its extensive range of applications in industry and synthesis. Despite its significance, the cleavage of a C—C bond has been challenging due to the thermodynamic stability and steric hindrance of C—C σ -bonds.¹ Continuing with previous experimental results, this study focuses on using Density Functional Theory (DFT) calculations on the C—CN bond activation of *para*-substituted benzonitriles with [Ni(dmpe)] and [Ni(dippe)] fragments. These calculations were conducted on the UT-Austin Texas Advanced Computing Center, Stampede2 system. A comparison of the computational results and the previously reported experimental results confirm that there is a great correlation between the Hammett constants (σ_p) and the equilibrium constants (K_{eq}).

Introduction/Background

- In 2002, Garcia and Jones published experimental work on the cleavage of C—CN bonds in aromatic nitriles using a zerovalent nickel. A portion of their published experiment were studying the *para*-substituent effect of benzonitriles and their derivatives.²
- Hammett Plot is used to describe the linear free-energy relationship between equilibrium constants/reaction rates and the Hammett constants (σ_p).³
- It is important for us to use and compare computational methods with experimental results as a benchmark for future studies on the *ortho*- and *meta*- substitution effects.

Figure 1. Equilibrium Reaction of Benzonitriles and Derivatives

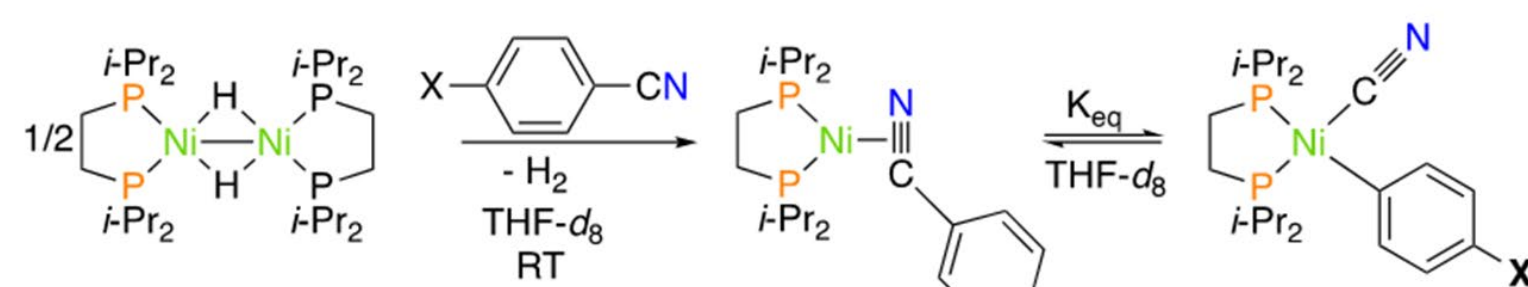
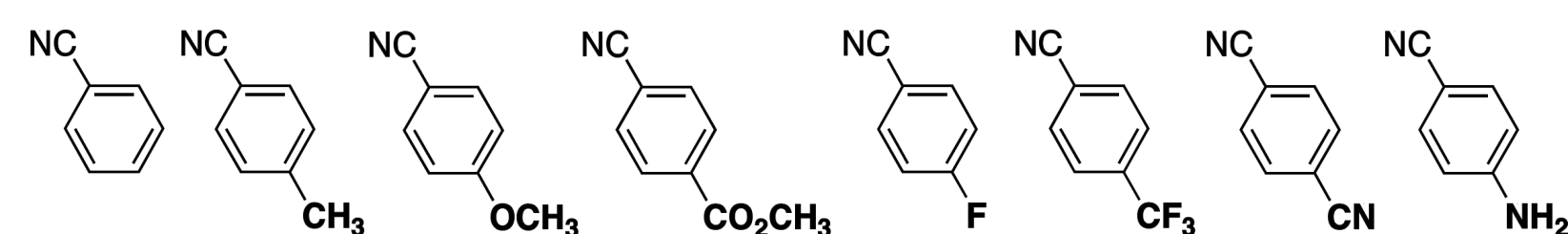
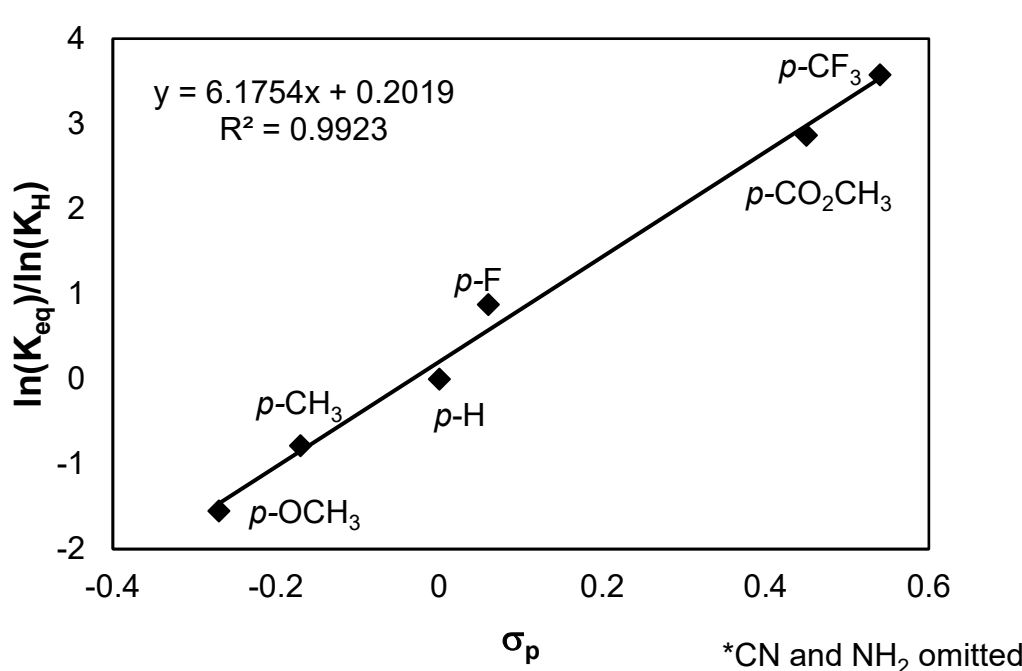


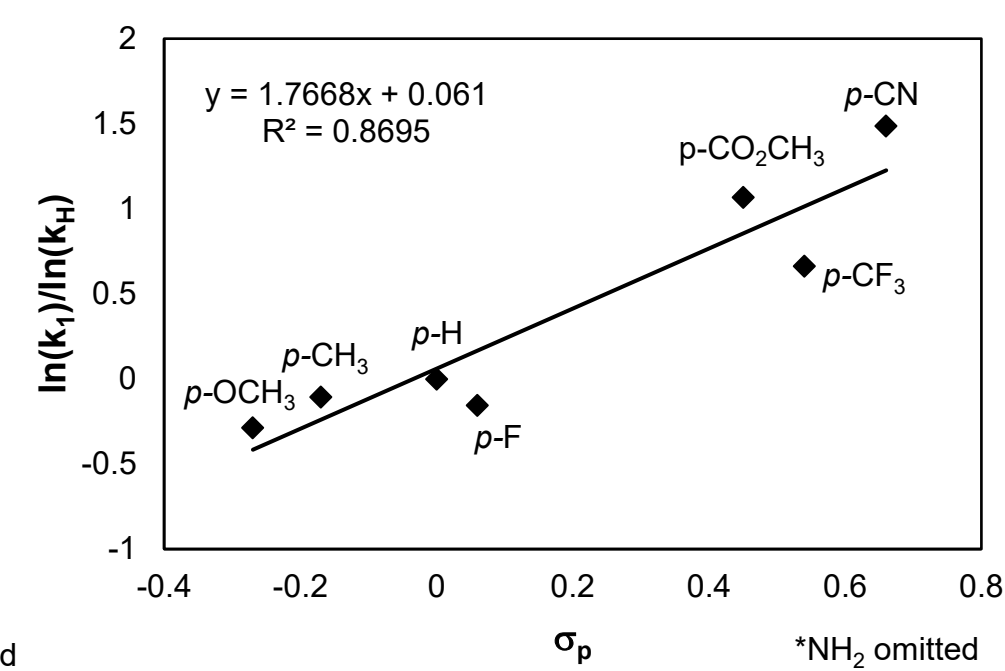
Figure 2. Benzonitriles Investigated with *para*-substituents



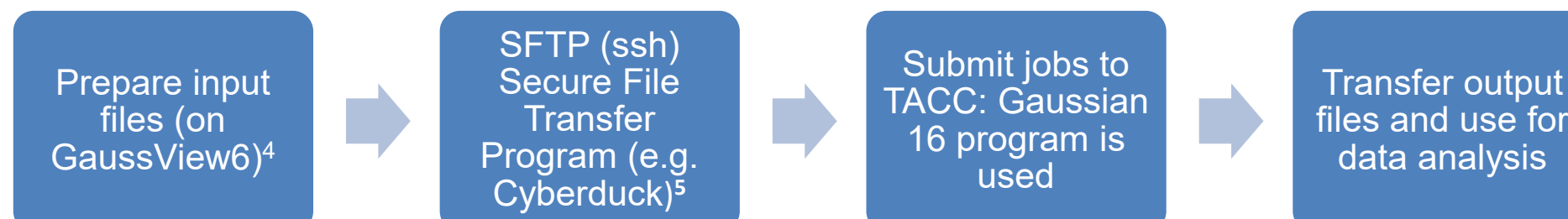
Graph 1. Experimental $\ln(K_{eq})$ vs. σ_p Hammett Plot'



Graph 2. Experimental $\ln(k_r)/\ln(k_f)$ vs. σ_p Hammett Plot



Computational Methods



- Gaussian16 was used for all calculations.⁶
- [Ni(dmpe)] and [Ni(dippe)] were both used and compared for a benchmark.
- Gas-phase structures were fully optimized in redundant internal coordinates⁷ with DFT and B3LYP⁸⁻⁹ functional.
- 6-31G(d,p)¹⁰ basis set for C, H, N, O and F.
- SDDALL basis sets
 - f polarization for Ni ($\alpha = 3.130$).¹¹
 - d polarization for P ($\alpha = 0.387$).¹²
- Solvent effects in THF were added using SMD.¹³
- Gibbs free energy calculated at 298.15 K and 1 atm
- Quasi-harmonic approximations were calculated to account for temperature effects on the geometry.

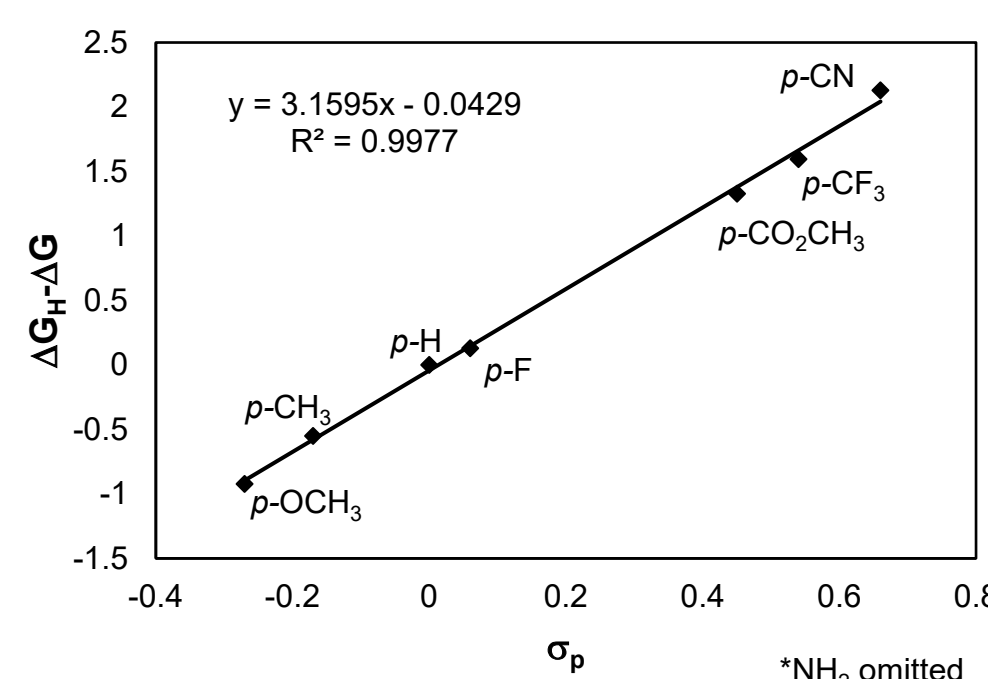
Figure 3. Stampede2 Supercomputer courtesy of TACC



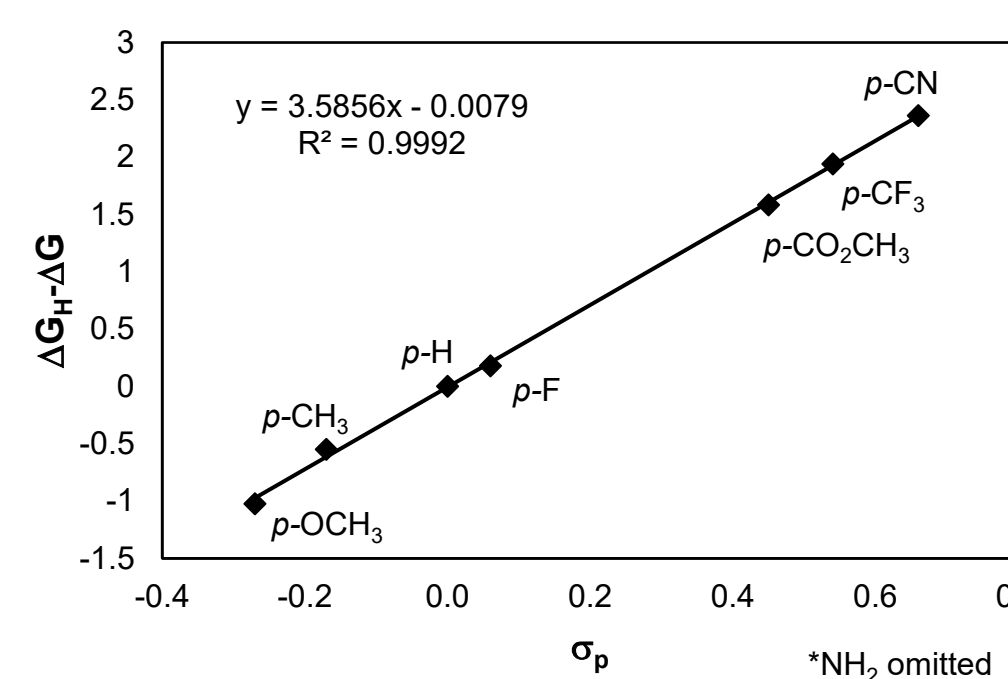
Results

Comparison of dmpe fragment and dippe fragment in DFT calculations

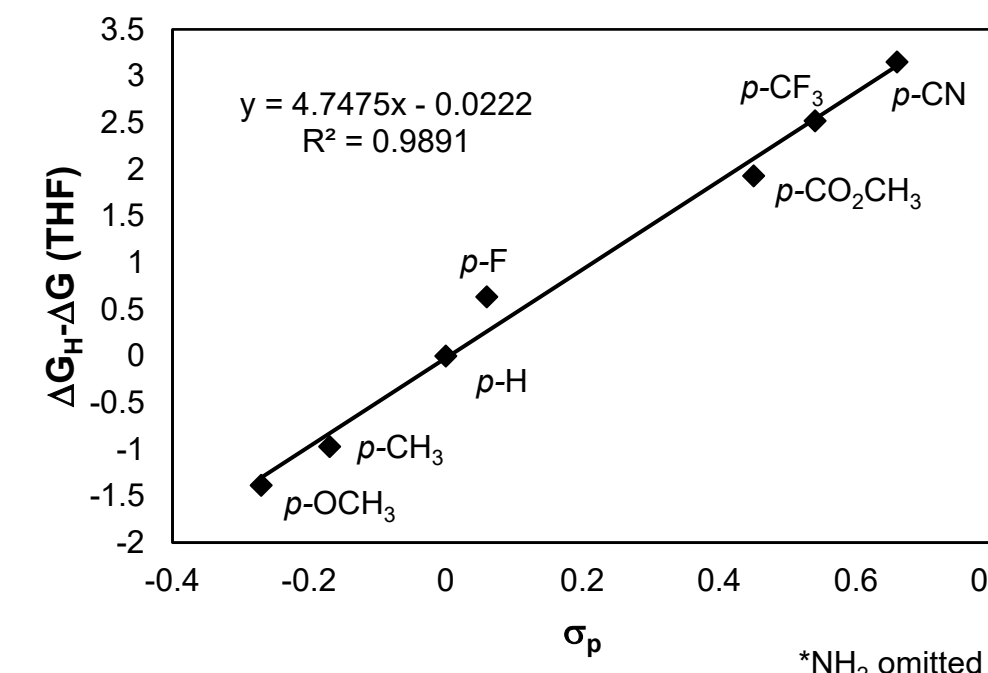
Graph 3. Hammett Plot of ΔG vs. σ_p with dmpe fragment'



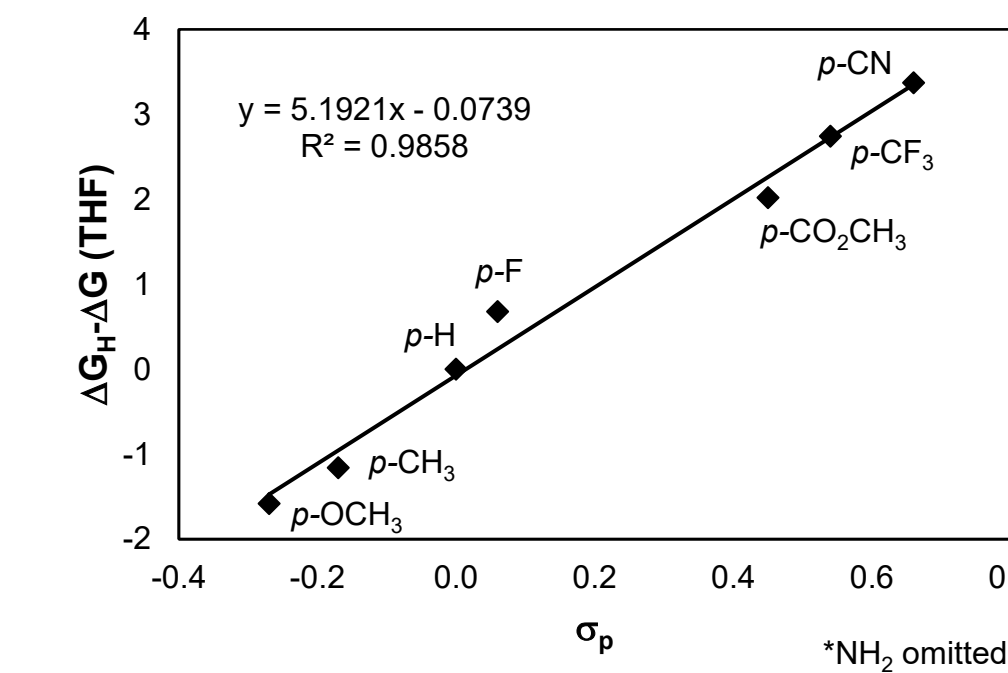
Graph 4. Hammett Plot of ΔG vs. σ_p with dippe fragment'



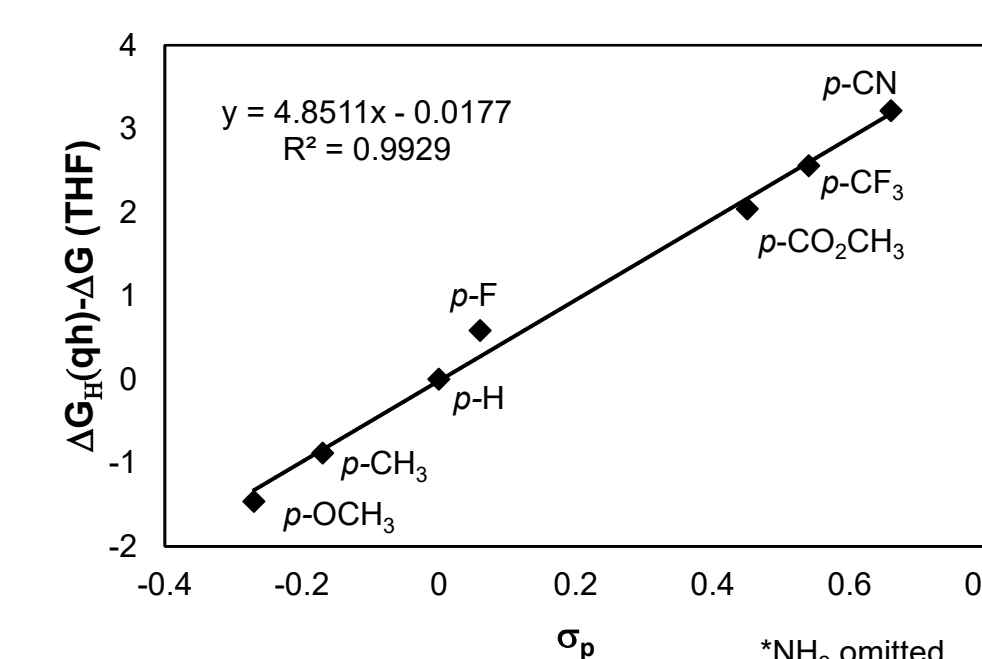
Graph 5. Hammett Plot of ΔG (THF) vs. σ_p with dmpe fragment'



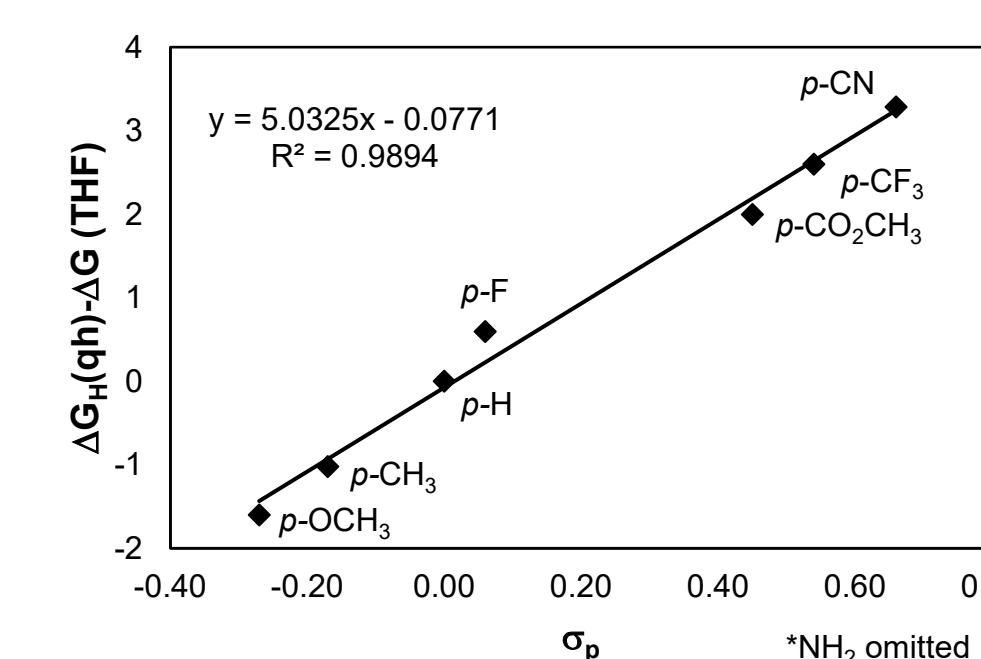
Graph 6. Hammett Plot of ΔG (THF) vs. σ_p with dippe fragment'



Graph 7. Hammett Plot of ΔG (THF) with quasi-harmonic approximations vs. σ_p with dmpe fragment



Graph 8. Hammett Plot of ΔG (THF) with quasi-harmonic approximations vs. σ_p with dippe fragment

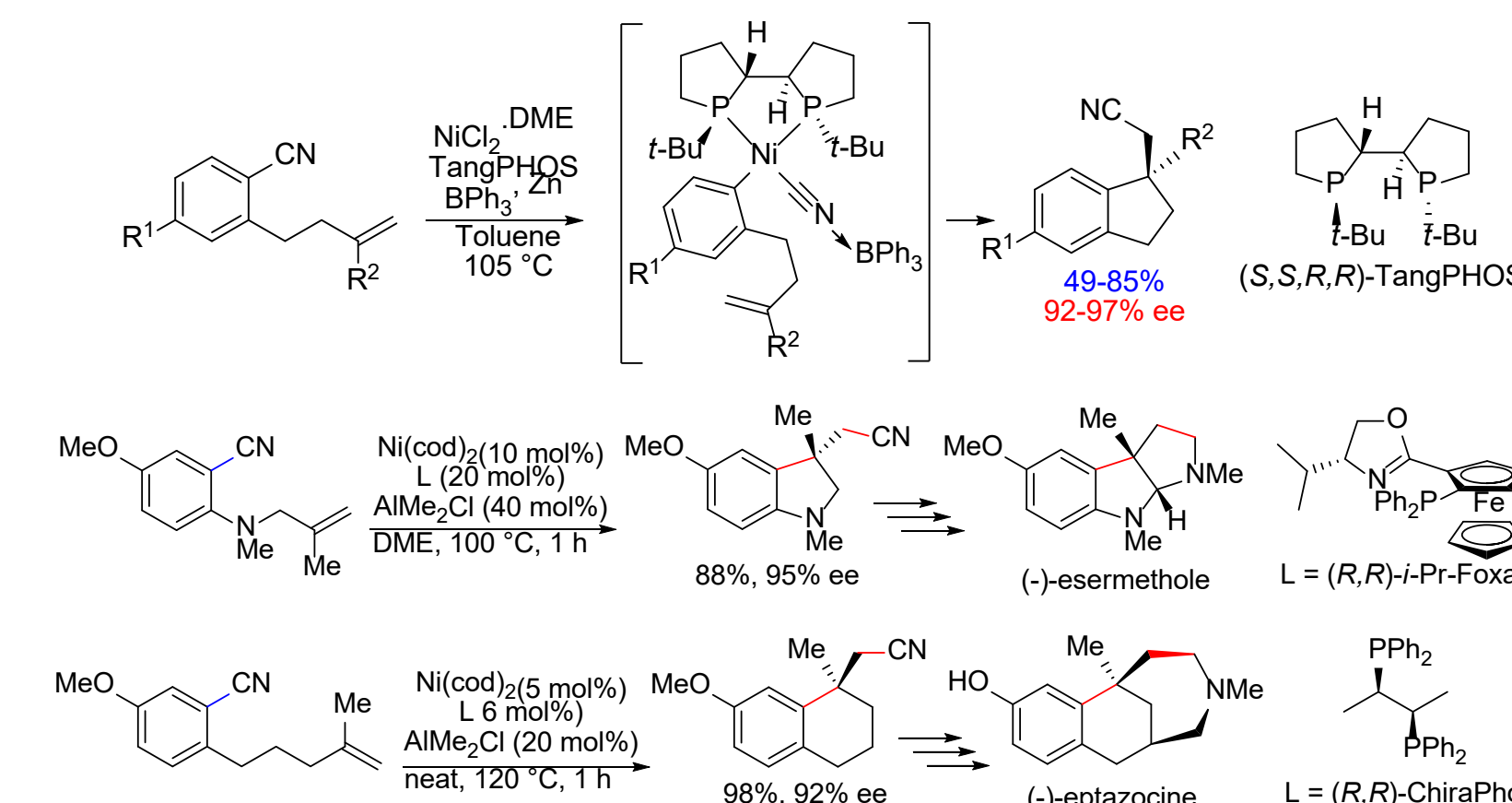


Discussion

- Comparison of the dmpe Hammett Plot slopes and the dippe Hammett Plot slopes show that using a simplified ligand (dmpe) to replace the bulkier ligand (dippe) had very minimal differences.
 - A simplified ligand is useful in our research computational calculations since it would simplify the calculations and run much faster than the dippe ligand.
- The amino group (-NH₂) substituent was removed from the Hammett Plots since there might have been H-bonding interaction with the THF solvent.
 - The most commonly used solvent model is the implicit solvent method (example: SMD), instead of the explicit solvent method. The use of the implicit solvent method might lead to an error with the calculations, possibly including H-bonding interaction with THF solvent.¹³
- Comparison of the dmpe Hammett Plot slopes and the K_{eq} experimental Hammett Plot slopes indicate that there is a good correlation between them.
 - DFT calculations overestimates the experimental results by 15-17% for ΔG in gas phase and THF and also with quasi-harmonic approximation in THF solvent calculations. This DFT overestimation was seen in C—H bond activation studies.¹⁴

Big Picture

Figure 4. Applications of C—CN Bond Activation in Natural Product Synthesis^{15,16}



Acknowledgements



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