SYNTHESIS AND COMPLEXATION OF BORONIC ACID DERIVATIVES WITH NITROGEN- AND PHOSPHOROUS- OXIDES

A thesis presented to the faculty of the Graduate School of Western Carolina University in partial fulfillment of the requirements for the degree of Master of Science in Comprehensive Chemistry.

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July 2021

ACKNOWLEDGEMENTS

I would like to thank my thesis research advisory committee for their guidance, patience, and advice throughout the process of completing my thesis. Specifically, I would like to thank Dr. William Kwochka for the encouragement and teachings that he has provided through my years of higher education. Additional thanks are due to Dr. Carmen Huffman for encouraging and gently pushing me towards the completion of the program. I would like to thank Western Carolina University for this opportunity to gain a degree that will prepare me for my future, with special thanks to the staff of the Chemistry and Physics Department. I would also like to largely thank my first lab-partner, Hannah Kline, who worked together with me on this project and without her encouragement I would not have been in this research group or able to complete my thesis. I would also like to thank additional peers who were instrumental in the completion of this thesis: Mary-Kate McQuade, Devan Woody, and Ashley Minot. I owe all of this to others who have supported me over the years: my family for instilling and nurturing the curiosity to understand the world and the way it works, my professors for proving the knowledge to understand it, and my friends for making it all worthwhile.

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ABSTRACT

SYNTHESIS AND COMPLEXATION OF BORONIC ACID DERIVATIVES WITH NITROGEN- AND PHOSPHOROUS- OXIDES

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The boron atom a boronic acid acts as a Lewis acid to form a dative bond with a variety of Lewis bases. In particular, the boron atom of both boronates and boroxines can easily form dative bond with either N- or P-oxides. Seven boronic acids were chosen for their varying degree of electron donating and electron withdrawing properties to be synthesized into boronates and boroxines. Initially a series of seven boronates and seven boroxines were complexed with 4-Picoline-*N*-oxide. Three of the seven boronates/boroxines were selected to be further complexed with two P-oxides, trioctylphosphine oxide and triphenylphosphine oxide. Through synthesis and characterization, I report the formation of a unique N- and P-oxide-boron dative bond structures via a two-step process with a variety of boronates and boroxines prepared in a single-step via microwave-assisted synthesis in a relatively high percent yield.

CHAPTER ONE: INTRODUCTION

1.1 Boronic Acid and Dative Bonding

Boron-containing compounds are plentiful in nature, with Borax (**Figure 1)** being perhaps the most well-known boron-containing compound.[1]

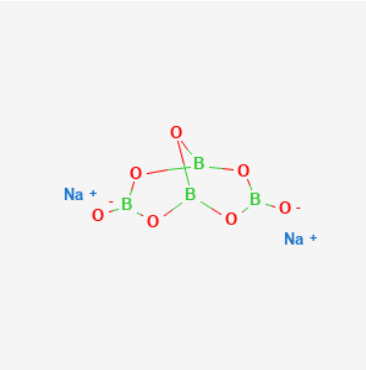


Figure 1. Basic Structure of Borax.

An important subset of the boron compounds is the boronic acids. A boronic acid is a boron atom that possesses two hydroxyl groups and one alkyl/aryl substituent.[2] Boronic acids, and their derivatives, play an important role in synthesis, materials, bio-organic, chemical biology, and medicinal chemistry.[3] Among the boronic acids derivatives, the phenyl boronic acid contains a six-membered ring bonded to the center boron; this structure is shown in **Figure 2.**

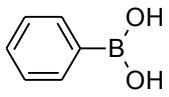


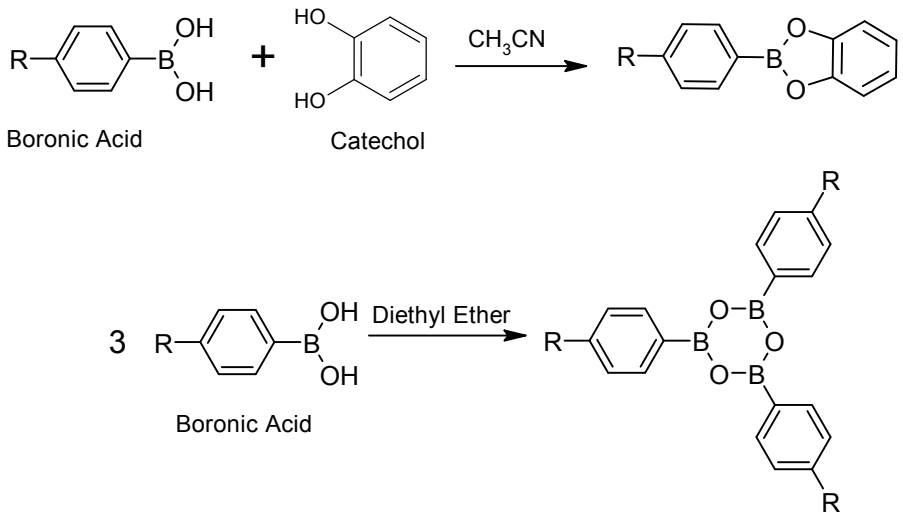
Figure 2. Basic Structure of Phenyl Boronic Acid.

The sp^2 hybridized boron only contains six valence electrons and is consequently deficient of two electrons, leaving a vacant p-orbital. This characteristic vacancy of the p-orbital allows for the boronic acid to act as a Lewis acid, which means that it acts as an electron pair

acceptor, where the strength of the boronic acid is influenced by both the electronegativity of the substituent on the aromatic ring and the substituent's proximity to the boron atom.[2]

The more electronegative the substituent is, the more acidic the boron becomes. This reactivity is due the planar nature of the boron atom and its empty p-orbital. In order to stabilize these synthetic boron-containing compounds, the boron atom can accept electrons from a heteroatom such as nitrogen or oxygen to both fill the vacant p-orbital and transform it from a planar, sp^2 hybridized geometry to a tetrahedral, sp^3 hybridized geometry. While boronic acids themselves are relatively unstable, they can easily be converted to the corresponding boronates and boroxines. Boronic acids are directly analogous in both physical and chemical properties to carboxylic acids; boronates are analogous to carboxylic acid esters, and boroxines are analogous to carboxylic acid anhydride.

The basic structures of a boronate and boroxine are shown in **Scheme 1**. In addition to its two boron-oxygen bonds which are covalently bound to a diol, in this case catechol, a boronate contains an 'R' group. Similarly, boroxines are composed of a six membered ring made of alternating boron and oxygen atoms, where the boron is bonded to existing 'R' groups. These 'R' groups on both the boronates and boroxines allow for a great deal of variety by exchanging the boronic acid used in their synthesis. Boroxines, reaction scheme shown in **Scheme 1** top panel**,** are prepared via self-condensation of three boronic acid molecules. Similarly, boronates, reaction scheme shown in **Scheme 1** bottom panel**,** are prepared in the condensation reaction between a boronic acid and a 1,2 with concurrent with a loss of water.



Scheme 1. Reaction Scheme of Boronate (top) and Boroxine (bottom).

Since the boron atom of these boronic acid derivatives can act as a Lewis acid, it is not surprising that the boron atom can react with a Lewis base to form a dative, or coordinate covalent, bond. Formation of that dative bond between a boron atom (Lewis acid) and an amine (Lewis base) is a highly selective process and is well understood. Dative bond complexes of boroxines and boronates, in particular, are well established in chemical literature.[4,5] An example of this, the well-explored pyridine B-N bond, is shown below in **Figure 3.**

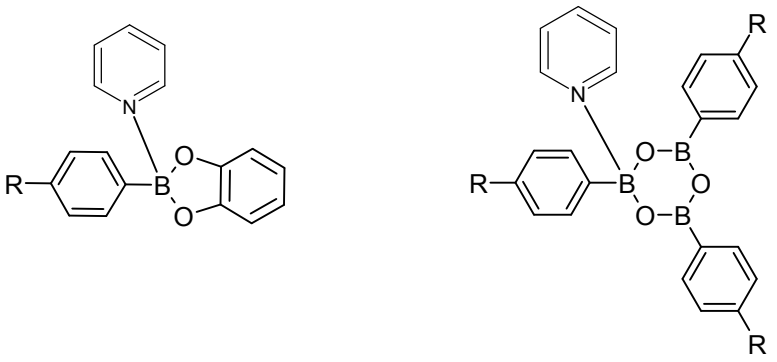


Figure 3. Pyridine complex with boronate (left) and boroxine (right).

This motif has brought great attention for the use in construction of a variety of supramolecular systems such as polymers, macrocycles, and rotaxanes, where the systems are

being held together via the weak interaction of the dative bond.[6,7,8,9] In February 2011, crystalline and soft molecular networks were constructed using dative Boron-Nitrogen bonds through a one-step, three component reaction.[10] In October 2015, the boron-nitrogen dative bond was used to provide a motif for reversible, strong, and directed interactions, leading to efficient self-assembly of organic building blocks of a supramolecular cage.[11] A recent increase in publications on boron- based dative bonds has been seen in an array of polymer science journals and journal themes. Of the recent publications, published in October 2020, there was a study of the polymeric interactions between Lewis bases and Lewis acids to be exploited in supramolecular polymeric systems.[12]

1.2 Nitrogen (N)- and Phosphorous (P)-Oxides

Non-metal oxides, such as the oxides of nitrogen and phosphorous, form covalent bonds between the non-metal and oxygen atoms. Thus, amines and phosphines form N-oxides and P-oxides, respectively. The most common N-oxide, dinitrogen oxide, is a colorless gas used for anesthetic purposes in minor medical procedures and is known colloquially as "laughing gas."

In contrast to the formation of elemental N-oxides, the organic N-oxides are typically prepared by the oxidation of tertiary amine using an oxidizing agent such as hydrogen peroxide.[13] The formation of N-oxides in the environment is frequently observed as the oxidative degradation reaction in pharmaceuticals and have been detected in wastewater, because nitrogen is the only non-metal that can obtain a positive charge at physiological pH.[13,14] The presence of these organic N-oxides treated wastewater presents significant health concerns.

P-oxides, on the other hand, are quite common in nature and exist in basically two common forms: tetraphosphorous decaoxide and tetraphosphorous hexoxide. Both naturally

occurring P-oxides are structurally based on the tetrahedral structure of elemental phosphorous. Organic P-oxides are not typically found in nature and are prepared by the oxidation of tertiary phosphines, primarily as byproducts of the Wittig reaction. Once these P-oxides are formed, they can react with acids or bases to form salts.[14]

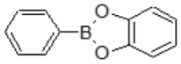
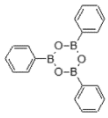
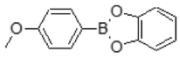
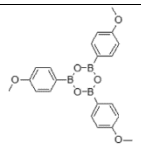
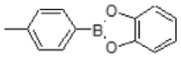
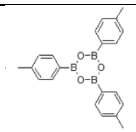
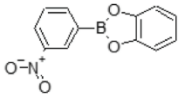
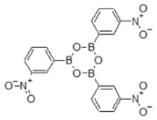
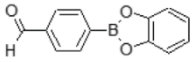
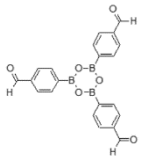
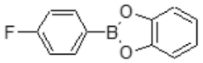
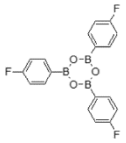
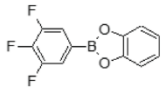
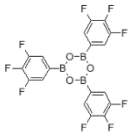
Although amine complexes of boronic acid derivatives have been heavily reported in the chemical literature, there is scarce study of the formation of N-oxide or P-oxide - Boron complexes. On both the N-oxides and the P-oxides, the bulk of the electron density resides on the oxygen atom. This abundance of electron density makes the oxygen atom a Lewis base, which can act similarly to the nitrogen atom of a pyridine molecule and form a dative bond with a boroxine or a boronate.

N- and P- oxides share similar compound structures of a phosphorous or nitrogen atom center bonded to three 'R' groups and a negatively charged oxygen atom. Nitrogen and phosphorous, though only one row apart on the periodic table, have differing properties that affect their impact as a Lewis base. Nitrogen has a lower electron affinity, smaller radius, and a higher electronegativity than phosphorous. During the formation of the dative bond, the electrons of the oxygen atom of the N- or P-oxide are donated to the sp^2 hybridized boron atom and, in the process, the boron atom transforms to a sp^3 hybridization.

1.3 Project Goals

Here, I report the formation of unique N-oxide – boron dative bonds and P-oxide – boron dative bonds via a two-step process with a variety of boronates and boroxines, listed in **Table 1**.

Table 1. Boronates and Boroxines.

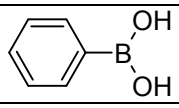
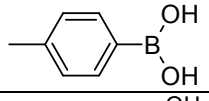
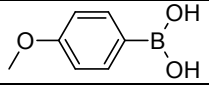
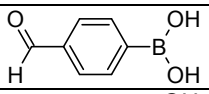
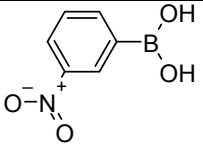
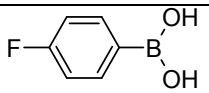
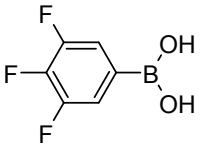
Boronic Acid	Boronate	Boroxine
Phenyl		
4-Methoxyphenyl		
Tolyphenyl		
3-Nitrophenyl		
4-Formylphenyl		
4-Fluorophenyl		
3,4,5-Trifluorophenyl		

In the first step, the boroxines and the boronates are prepared in a single-step via microwave-assisted synthesis, reaction scheme shown in **Scheme 1,** in a relatively high percent yield. Boronate being produced by a combination of boronic acid and catechol via a condensation reaction; Boroxine being produced by a combination of three equivalents of boronic acid via a condensation reaction. In the second step those boroxines and boronates are complexed with a variety of N-oxide and P-oxides to provide these unique dative bond complexes. For a boronate, reaction scheme shown in **Scheme 1** top panel, the hydrogens in the

hydroxide groups attached to the starting boronic acid and the catechol, and two oxygens will be lost through hydrolysis during the microwave synthesis. For a boroxine, the reaction scheme shown in **Scheme 1** bottom panel**,** the three oxygens and six hydrogens (three water molecules) are lost during a similar condensation procedure; a combination of three equivalents of the same boronic acid in a single reaction step eliminates contamination in the product and product spectra. This loss of hydrogen groups is evident in the ^{1}H NMR, which I primarily relied on using $CDCl_3$ as the solvent.

My approach to this study involved a selection seven different boronic acids differing in properties that are affected by the bonded 'R' group on the boron by the reaction scheme in **Scheme 1.** The boronic acids used in this study are phenyl boronic acids with a combination of electron donor groups and electron withdrawing groups, shown in **Table 2**.

Table 2. Electronic properties of boronic acids used.

Boronic Acid	Structure	Property
Phenyl		N/A
Tolyphenyl		Electron Donating
4-Methoxyphenyl		Electron Donating
4-Formylphenyl		Electron Withdrawing
3-Nitrophenyl		Electron Withdrawing
4-Fluorophenyl		Electron Withdrawing
3,4,5-Trifluorophenyl		Strong Electron Withdrawing

For an electron donor group, as the electrons are being pushed toward the boron, the boron atom will become less acidic. However, for electron withdrawing groups, the electrons will be drawn away from the centered boron, making the boron more acidic. The boron's strength as a Lewis acid will dictate the relationship between the dative bond and the properties of the oxides explored in this experimental series.

CHAPTER TWO: RESULTS AND DISCUSSION

2.1 Synthesis of Boronates and Boroxines

This thesis focuses on seven boronic acid derivatives synthesized into boronates and boroxines**.** The seven boronic acids have functional groups varying in electron withdrawing or donating abilities. The phenyl derivative is used as a reference guide for the remaining boronic acids. Of the seven, there are two electron donating groups, three electron withdrawing groups, and one very strong electron withdrawing groups. The boronate and boroxine synthesis are condensation reactions and are synthesized via microwave-assisted synthesis. The reaction scheme for step one in the reaction**,** combines the chosen boronic acid and catechol to produce a boronate and water. The difference between the synthesis of the boronate and boroxine is the lack of catechol and addition of two additional equivalents of the boronic acid to react with itself, still producing the boroxine and water. The produced water is caught in the Dean-Stark apparatus, specifically in the molecular sieves, used during the microwave synthesis.

PHENYL BORONIC ACID. Phenyl boronic acid, the first of the seven established boronic acids explored, lacks a functional group on the aromatic ring and is therefore considered to be neither an electron withdrawing or electron donating. Both the phenyl boronate and boroxine were produced at high yields of 108% and 116%, respectively. The starting products for the phenyl boronate, shown in the reaction scheme in **Scheme 1** top panel**,** are equal parts phenyl boronic acid and catechol to form the phenyl boronate product. Phenyl boronic acid, the ^{1}H NMR shown in **Figure 4,** shows four peaks, three in the aromatic region corresponding to the five hydrogens displayed in the benzene ring, and one in the bonded hydroxyl region corresponding to the two hydrogens in the hydroxides. Catechol, in the ^{1}H NMR, shows three

peaks, two in the aromatic region corresponding to the five hydrogens displayed in the benzene ring, and one in the hydroxyl region corresponding to the two hydrogens attached to boron.

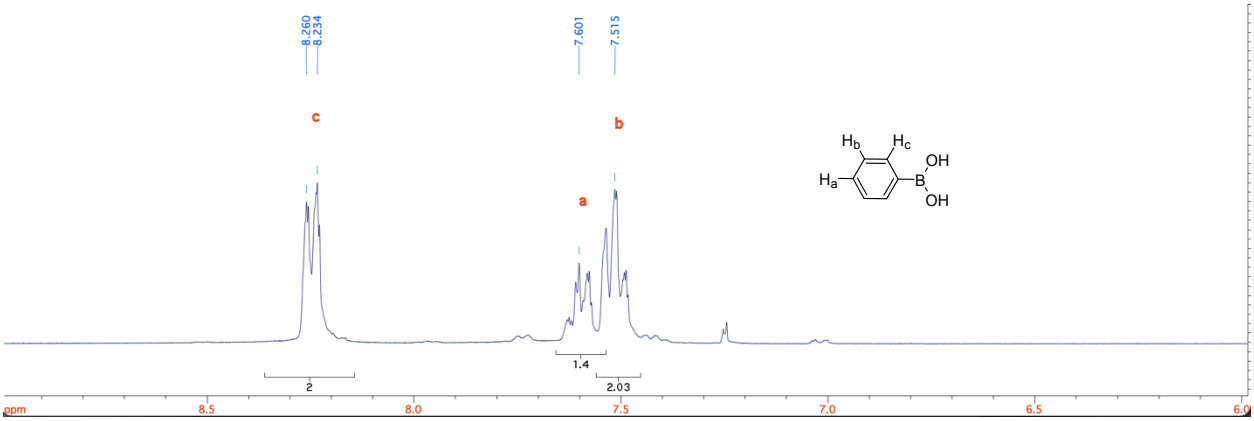


Figure 4. ^{1}H NMR of Phenyl Boronic Acid.

H_a corresponding to the hydrogen in the 4th position on the benzene ring, is found with integration 2H, a multiplet, and is in the aromatic region with peaks at 7.6 ppm. H_b observed near H_a, is a multiplet, with integration 2H, and peaks in the aromatic region at 7.5 ppm. H_c is observed as a multiplet, with integration 2H, and peaks in the aromatic region at 8.2 ppm.

Phenyl boronate**,** has five distinctive hydrogens in the ^{1}H NMR, shown in **Figure 5**. Small peaks shown slightly downfield from the product peaks are concluded as starting products remaining from the reaction. H_d and H_e, corresponding to the catechol benzene ring hydrogens, have an integration of 2H, are both doublets, are found in the aromatic region (7.3 and 7.1, respectively) and have a J constant of 9.2 Hz, further confirming their coupling. H_a has an integration of 2H, as expected, and is observed at 7.1 ppm. H_b and H_c, corresponding to the boronic acid benzene ring hydrogens, have an integration of 2H, are both doublets, are found in the aromatic region (7.5 and 8.0, respectively) and have a J constant of 6.6 Hz, further confirming their coupling.

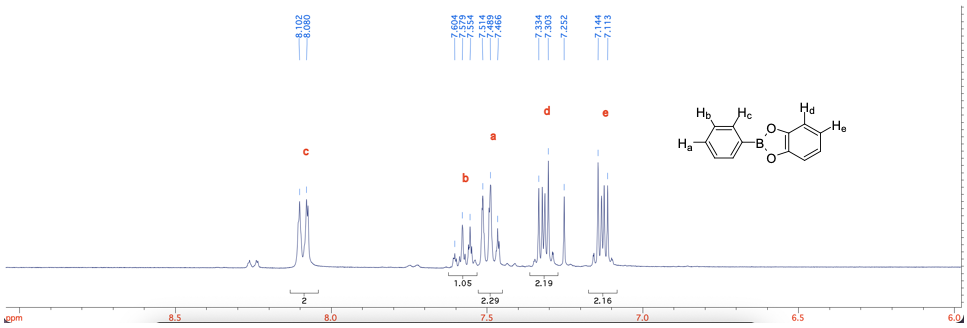


Figure 5. Phenyl Boronate ^{1}H NMR.

The phenyl boroxine produced has three hydrogens on the benzene ring, expected to be found in ^{1}H NMR spectrum in the aromatic region between 7.0 and 8.5 ppm. H_c is furthest downfield due to its proximity to the boron atom and is split into a doublet of doublets with an integration of 3H. Hydrogens H_a and H_b are coincident with one another and have a combined integration of 6H as shown in the ^{1}H NMR below in **Figure 6**.

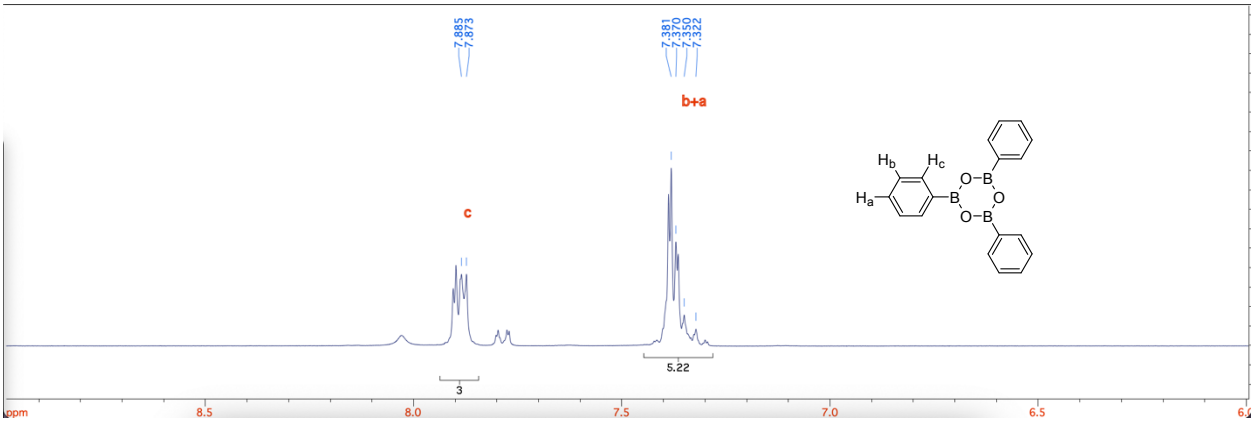


Figure 6. ^{1}H NMR of Phenyl Boroxine.

4-METHOXYPHENYL BORONIC ACID. Of the seven boronic acids chosen for this experimental series, the 4-Methoxyphenyl boronic acid is the only boronic acid containing a electron donor group since the oxygen atom has an electronegativity of 2.6. The 4-Methoxyphenyl boronic acid was used to produce both a boronate and a boroxine as shown in **Scheme 1**.

As shown in **Figure 7,** the ^{1}H NMR of the 4-methoxy boronic acid shows 3 of the 4 expected peaks. H_b and H_c, corresponding to the benzene ring hydrogens, have an integration of

2H, are both singlets, and are found in the aromatic region (8.1 and 6.9 respectively). The high electronegativity of oxygen has shifted the methyl group hydrogens downfield to 3.9 with an integration of 3H.

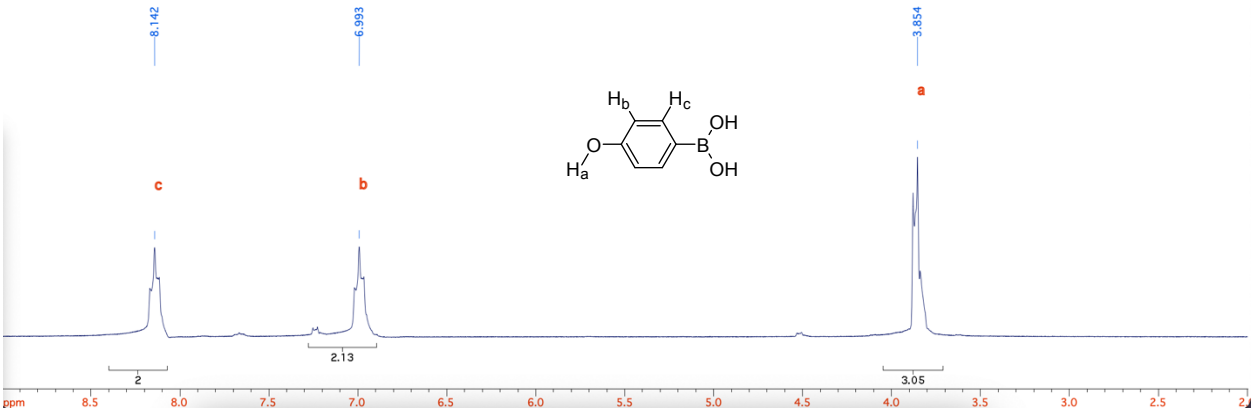


Figure 7. ^{1}H NMR of 4-Methoxyphenyl Boronic Acid with labeled Hydrogens.

Likewise, the 4-Methoxyphenyl boronate has five distinctive hydrogen groups in the ^{1}H NMR. For the ^{1}H NMR, shown in **Figure 8**, the two hydrogen groups on the –OH groups of the starting boronic acid should not be observed on the spectrum

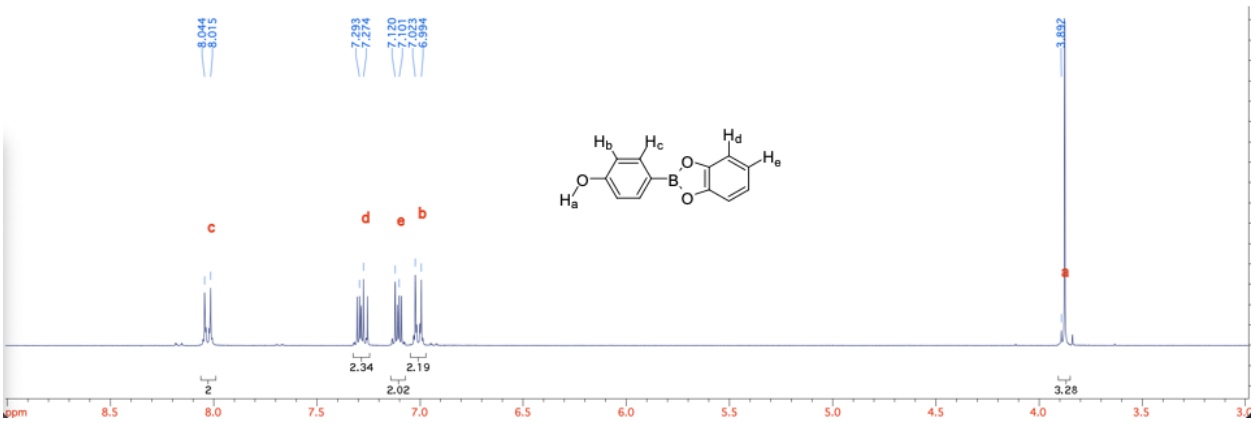


Figure 8. 4-Methoxyphenyl Boronate ^{1}H NMR.

The 4-Methoxy boronate ^{1}H NMR shows the 5 expected peaks. H_b and H_c, corresponding to the 4-methoxyphenyl boronic acid benzene ring hydrogens, have an integration of 2H, are

both doublets, are found in the aromatic region (7.0 and 8.0 respectively) and have a J constant of 8.7 Hz, further confirming their coupling. H_d and H_e, corresponding to the catechol benzene ring hydrogens, have an integration of 2H, are both doublets, are found in the aromatic region (7.3 and 7.1 respectively) and have a J constant of 5.8 Hz, further confirming their coupling. The singlet, H_e, corresponding to the methyl group attached to the oxygen, has an integration of 3H and is found at 3.81.

For the 4-methoxyphenyl boroxine, the three hydrogen groups should have integration equivalent to three times that of their original boronic acid state. The two hydrogens on the benzene, H_b and H_c, are expected to be found in the aromatic region between 7.0 and 8.5 ppm, be coupled together, doublets, and have an integration of 6H. H_a is expected to show a singlet with integration of 9H. The ^{1}H NMR, shown below in **Figure 9,** shows the experimental ^{1}H NMR.

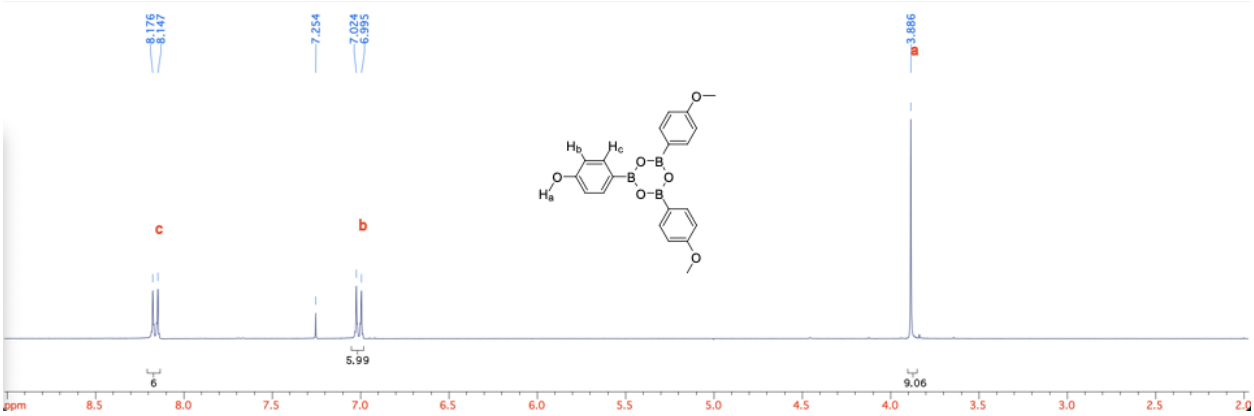


Figure 9. ^{1}H NMR of 4-Methoxyphenyl Boroxine.

As shown, H_b and H_c, have integration of 6H, has peaks in the aromatic region, 8.3 and 7.1 respectively, with a coupling constant of 8.72 Hz, confirming their coupling. H_a is designated at peak 4.0 as a singlet with integration 9H. Although a more complex molecule, being comprised of three parts boronic acid, a boroxine is shown to have a "simpler" ^{1}H NMR.

3,4,5-TRIFLUROPHENYL BORONIC ACID. Of the seven boronic acids chosen for this experimental series, the electron withdrawing 3,4,5-Trifluorophenyl boronic acid forming a boronate or boroxine, following the reaction scheme in **Scheme 1.** The 3,4,5-trifluorophenyl boronic acid, shown in **Figure 10,** has three highly electronegative fluorine atoms in the 3,4, and 5 positions of the benzene ring. This high electronegativity makes the boronic atom highly electron deficient.

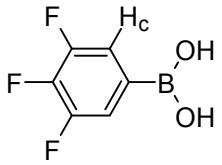


Figure 10. 3,4,5-Trifluorophenyl Boronic Acid.

In literature, it is expected to see two peaks distinctive to the boronic acid. 3,4,5-Trifluorophenyl boronic acid shows two peaks, one doublet in the aromatic region corresponding to the two hydrogens displayed in the benzene ring and a doublet in the bonded hydroxyl region corresponding to the two hydrogens in the hydroxides.

3,4,5-Trifluorophenyl boronate has three distinctive hydrogen groups expected to express peaks on an ^{1}H NMR; two less than the previously aforementioned 4-methoxyphenyl- due to the hindrance of the three fluorine's on the benzene ring. For the ^{1}H NMR of the boronate product, shown in **Figure 11**, we are expecting the lack of the two hydrogen groups on the –OH of the starting products and the appearance of the remaining labeled hydrogens close, but possibly slightly shifted, to their original peak position.

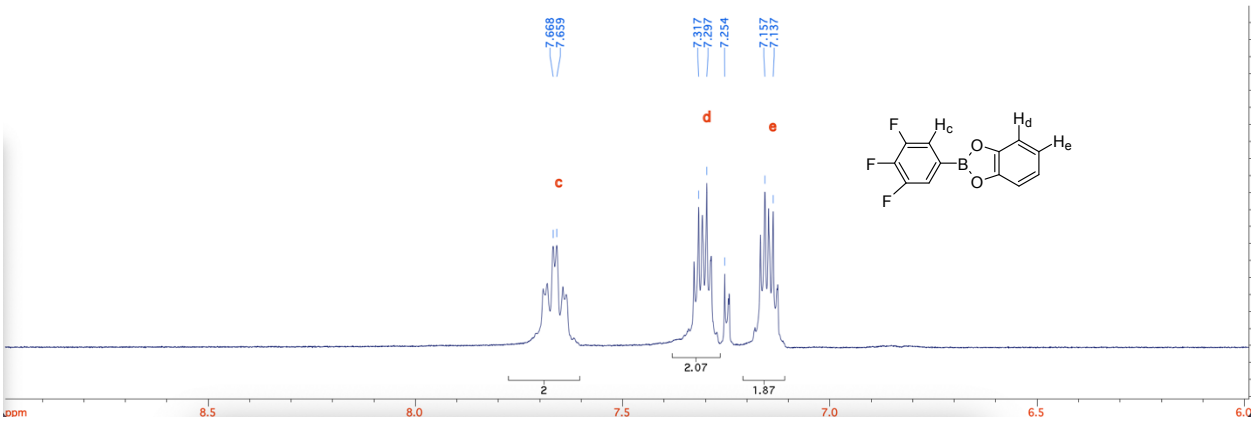


Figure 11. ^{1}H NMR of 3,4,5-Trifluorophenyl Boronate.

The 3,4,5-Triflurophenyl boronate ^{1}H NMR shows the 3 expected peaks. H_d and H_e, corresponding to the catechol benzene ring hydrogens, have an integration of 2H, are both multiplets, are found in the aromatic region (7.3 and 7.1 respectively). The multiplet, H_c, corresponding to the hydrogen on the benzene ring of the boronic acid has an integration of 2H and is found at 7.6 ppm. The ^{1}H NMR between the boronic acid and the boronate of the 3,4,5-Triflurophenyl shows an absence of the doublet at 3.9 ppm, corresponding to the hydrogens on the hydroxide groups on the boronic acid.

The ^{1}H NMR of the boroxine product should show the three hydrogen groups having an integration equivalent to three times that of their original boronic acid state. The one hydrogen on the benzene, H_c, is expected to be found in the aromatic region between 7.0 and 8.5 ppm, a doublet, and have an integration of 6H. The ^{1}H NMR, shown below in **Figure 12,** shows the experimental ^{1}H NMR.

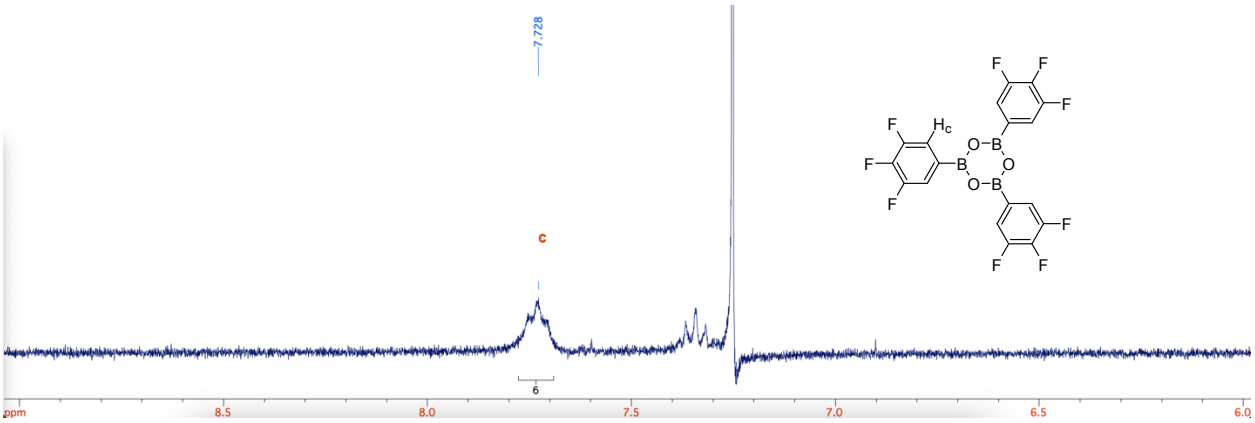


Figure 12. ^{1}H NMR of 3,4,5-Trifluorophenyl Boroxine.

As shown, H_c, has integration of 6H, is a singlet, and has a peak at 7.7 ppm. This ^{1}H NMR has an integration three times that of the boronate, as expected, and does not include the boronates' catechol hydrogen peaks. Additionally, the 3,4,5-Triflurophenyl boroxine only has two available hydrogens to be observed on the ^{1}H NMR; these hydrogens being coupled together and considered the "same" hydrogen.

2.2 N-oxide Complex

After the syntheses is complete and confirmed via characterization, each the 14 boronate and boroxines were complexed with 4-picoline N-oxide in a one-to-one reaction, such as in **Figure 13**.

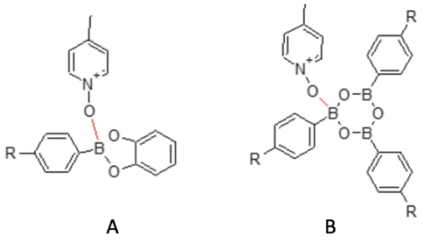


Figure 13. Basic Structure of the 4-Picoline N-oxide complex of a Boronate (A) and Boroxine (B).

The dative bond formed between the Lewis base, the boron in the boronate or boroxine, and the Lewis acid, the N- or P- oxide, will be shown through an observable shift in ^{1}H NMR spectrum with the addition of the protons from the oxide. The observable shifts are shifted up-field or down-field depending on the functional group attached to the boronic acid structure used in the synthesis of the boronate or boroxine. As electronegativity of the boronic acids' functional group increases, there is less shielding because of the decrease in electron density around the protons. This makes the boron deficient in electrons and a stronger Lewis acid.

4-Picoline N-oxide has three distinctive hydrogen groups that are expected to show three individual peaks. The two hydrogens on the benzene, H_f and H_g, are expected to be found in the aromatic region between 6.0 and 8.5 ppm, be coupled together, doublets, and have an integration of 2H. H_h is expected to show a singlet with integration of 3H. The ^{1}H NMR, shown below in **Figure 14**, shows the experimental ^{1}H NMR.

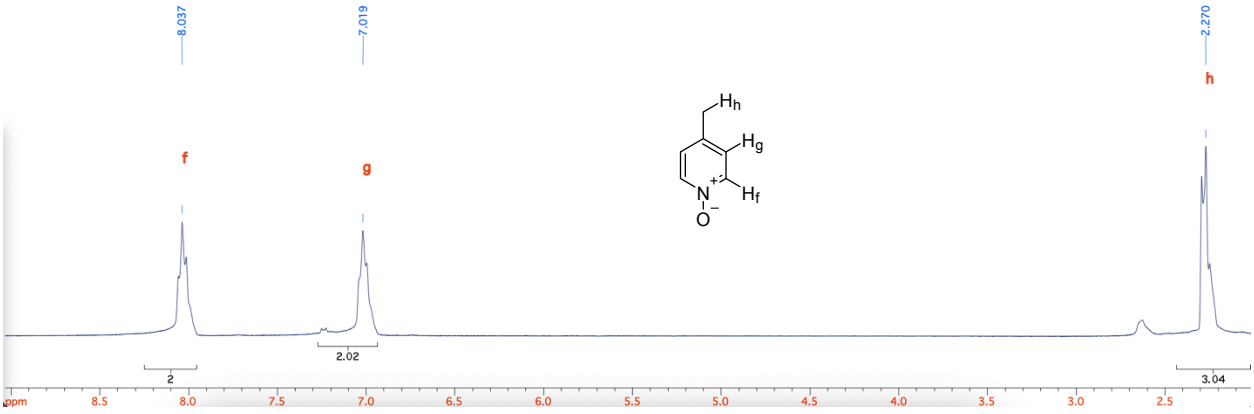


Figure 14. ^{1}H NMR of 4-Picoline N-oxide.

As shown, H_f and H_g, have integration of 2H, are doublets, and has peaks in region 7.0-8.0. The data shows coupling constants of H_f and H_g as 7.12, further confirming their coupling. H_h is designated at peak 2.2 as a singlet with integration expected of 3H.

The five hydrogen groups on the 4-Methoxyphenyl boronate are expected to show a shift versus their independent NMR when complexed with the N-oxide. 4-Methoxyphenyl boronate complexed with 4-Picoline N-oxide, shown in **Figure 15,** produces the ^{1}H NMR in **Figure 16**.

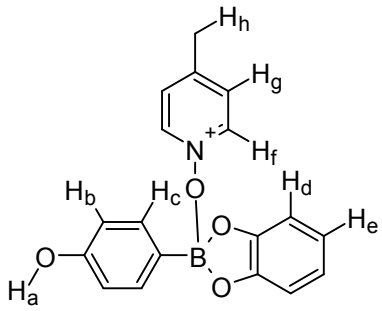


Figure 15. 4-Methoxyphenyl boronate complex with N-oxide.

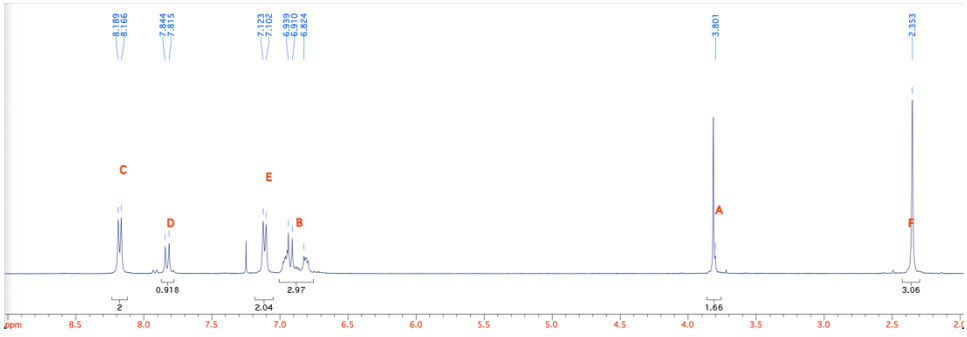


Figure 16. ^{1}H NMR of 4-Methoxyphenyl Boronate complex with N-oxide.

As shown, H_b and H_c, both have integration of 2H, has peaks in region 6.9 and 8.1 respectively, with a coupling constant of 6.60 Hz, confirming their coupling. H_d and H_e, both have integration of 2H, has peaks in region 7.8 and 7.1 respectively, with a coupling constant of 8.53 Hz, confirming their coupling. H_f is designated at peak 2.4 as a singlet with integration expected of 3H. H_a is a singlet at 3.8 with integration of 2H. This boronate-picoline complex shows a shift in the ^{1}H NMR spectra. The benzene ring hydrogens, H_b and H_c, shifted .3 ppm and .1 ppm downfield respectively; the catechol hydrogens, H_d and H_e, shifted .3 ppm and .2 ppm downfield respectively.

The three hydrogen groups on the boroxines are expected to show a shift versus their independent NMR. 4-Methoxyphenyl boroxine complexed with 4-Picoline N-oxide, shown in **Figure 17,** produces the ^{1}H NMR in **Figure 18**.

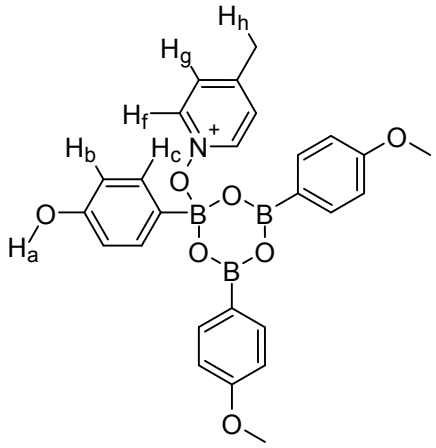


Figure 17. 4-Methoxyphenyl boroxine complex with N-oxide.

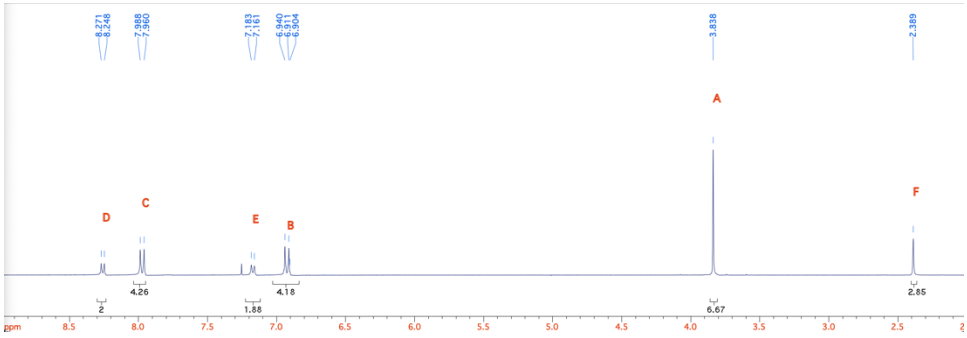


Figure 18. ^{1}HNMR of 4-Methoxyphenyl Boroxine complexed with N-oxide.

As shown, H_b and H_c, have integration of 4H, has peaks in region 6.9 and 7.9 respectively, with a coupling constant of 6.67 Hz, confirming their coupling. H_d and H_e, have integration of 2H, has peaks in region 8.2 and 7.1 respectively, with a coupling constant of 8.5 Hz, confirming their coupling. H_f is designated at peak 2.3 as a singlet with integration expected of 3H. H_a has integration 7H and is at 3.8. The benzene bonded to the functional group, has shifted upfield .6 and 1.5 ppm respectively, while the additional peaks are designated as the n-oxide benzene ring.

Observing the 4-Methoxyphenyl boronic acid products versus the 3,4,5-Trifluorophenyl boronic acid products allows for a unique comparison between an electron donating and electron withdrawing functional group, respectively. The 4-Methoxyphenyl boronic acid has an oxygen bonded to a methyl- group on the fourth carbon in the benzene ring. Oxygen, having a lower electronegativity, pushes the electrons more towards the boron in boronate/boroxine product. The three bonded fluorine's on the 3,4,5-Trifluoropenyl boronic acid are highly electronegative; as the substituent increases in electronegativity, the boron's valence becomes more deficient in in electrons. This deficiency makes the boron a stronger Lewis acid, hopefully making the dative bond stronger in the Lewis acid/base, complex, reaction. The three hydrogen groups on the 3,4,5-Triflurophenyl boronate are expected to show a shift versus their independent NMR when complexed with the N-oxide. 3,4,5-Triflurophenyl boronate complexed with 4-Picoline N-oxide, shown in **Figure 19,** produces the ^{1}HNMR in **Figure 20**.

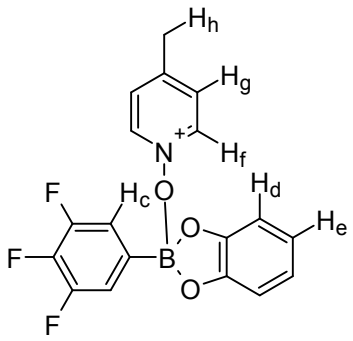


Figure 19. 3,4,5-Triflourophenyl boronate complex with N-oxide.

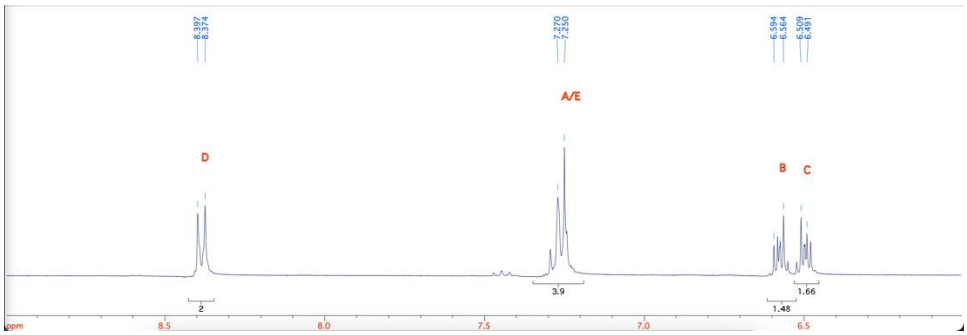


Figure 20. [1]HNMR of 3,4,5-Triflourophenyl boronate complexed with N-oxide.

As shown, H_d is a doublet with an integration of 2H and peaks at 8.4 ppm. H_b and H_c, are multiplets, both have integration of ~2H, and has peaks in region 6.6 and 6.5 respectively, corresponding to the catechol hydrogens; having shifted upfield by .7 and .65 ppm respectively. H_a and H_e, the boronic acid benzene hydrogen and one of the N-oxide hydrogens, are observed in such close proximity that the two are indistinguishable, together having an integration of 4H (2H individually) and has peaks in the region 7.25.

The one hydrogen group on the boroxines are expected to show a shift versus their independent NMR. 3,4,5-Triflurophenyl boroxine complexed with 4-Picoline N-oxide, shown in **Figure 21,** produces the [1]HNMR in **Figure 22**.

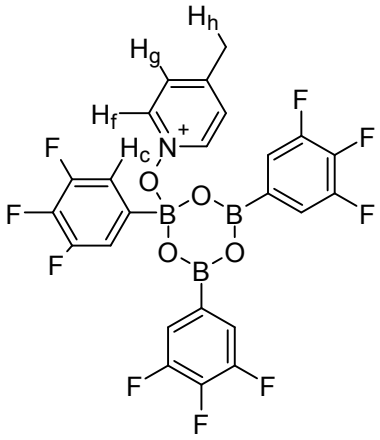


Figure 21. 3,4,5-Triflourophenyl boroxine complex with N-oxide.

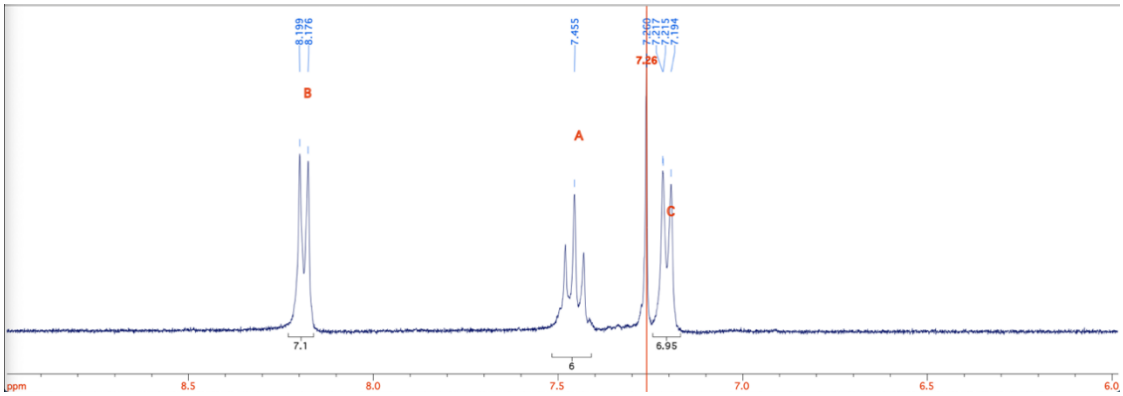


Figure 22. [1]HNMR of 3,4,5-Triflourophenyl boroxine complex with N-oxide.

As shown, H_a is a multiplet with an integration of 6H and peaks in region 7.4, having shifted a less significant .3 ppm upfield. H_b and H_c, are doublets, both have integration of ~7H, has peaks in region 8.1 and 7.2 respectively, and a coupling J constant of 6.7 Hz, further confirming their coupling. H_d is a singlet, has integration of 3H, and has a peak in region 2.8. H_b, H_c, and H_d, are all corresponding to the N-oxide hydrogens.

2.3 P-Oxide Complex

Three of the chosen boronates and boroxines - phenyl boronic acid, 4-methoxyphenyl boronic acid, and 3,4,5-trifluorophenyl boronic acid – were also complexed with triphenylphosphine oxide and trioctylphosphine oxide, such as in **Figure 23.**

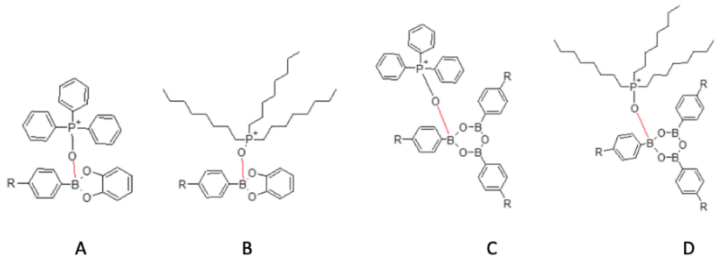


Figure 23. Basic Structure of the Triphenylphosphine Oxide complex of a Boronate (A) and Boroxine (C) and the Trioctylphosphine Oxide complex of a Boronate (B) and Boroxine (D).

P-oxides are limited to the insufficient amount of research done in the organics field. This hindrance is the main reason for the lack of starting products, where available health and safety information is a limited matter. That is, in part, the reason for the selection of the triphenylphosphine oxide and the trioctylphosphine oxide.

The percent yields for the phosphine-oxides were drastically lower than that of their N-oxide counterpart; almost all, excluding the 3,4,5-triflurophenyl, were below 75%. The exception, 3,4,5-Triflurophenyl, was the most difficult to obtain a clear spectrum. Even with a low percent yield, it was consistent through the complexation with the phosphine-oxides, that additional peaks could be observed through ^{1}H NMR. The dynamic properties of the dative bond make it plausible that the reaction may be time dependent and, thus, temperature dependent. Of the two phosphine-oxides, the trioctylphosphine oxide was problematic in producing solely oil-like products when complexed. This is most likely due to the nature of the procedure and the three long hydrocarbon chains attached to the phosphine-oxide. The more successful, 4-methoxyphenyl boronate complexes are observed below.

The 4-methoxyphenyl boronate complex with triphenylphosphine oxide complex, shown in **Figure 24,** produced an ^{1}H NMR, **Figure 25**, that shows distinctive peaks that can be paired to hydrogens in the product. However, as mentioned earlier, there are starting products observed through ^{1}H NMR.

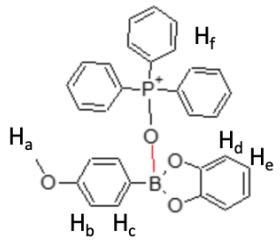


Figure 24. 4-Methoxyphenyl boronate complex with Triphenylphosphine-oxide.

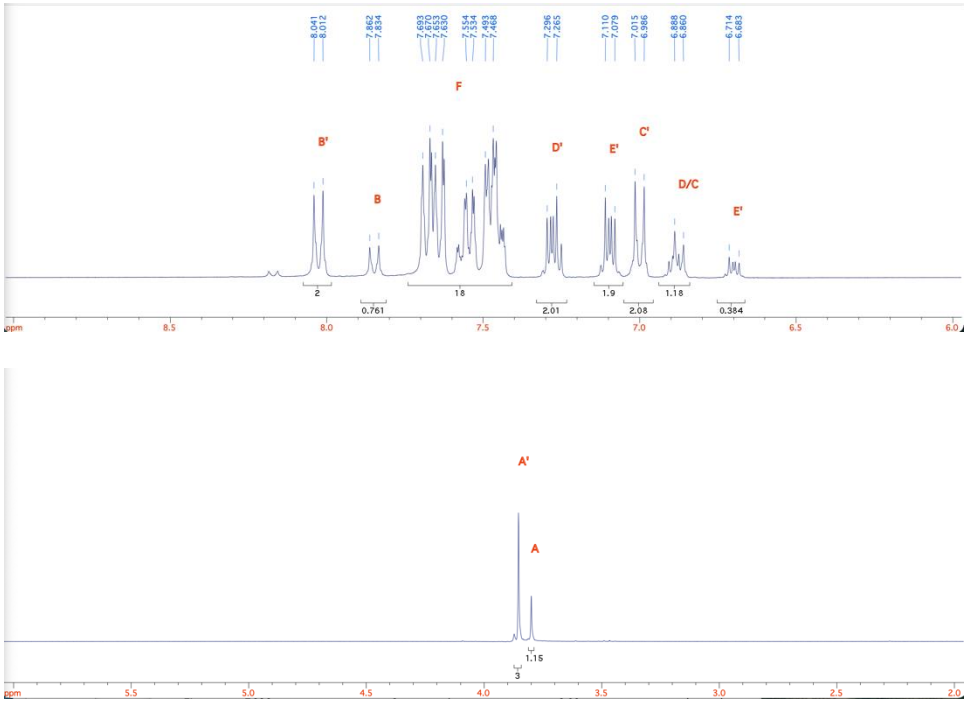


Figure 25. [1]HNMR of 4-Methoxyphenyl boronate complex with Triphenylphosphine-oxide (6.0-9.0 - top/ 2.0-6.0 - bottom).

It is observable that in the above spectrum, that both the complexed and uncomplexed form of boronate are within the same spectrum; the complexed peak is denoted as the derivative of the uncomplexed. This could either be starting products remaining in the reaction or because of the dynamic relationship of the produced system. The uncomplexed is a half of the complexed, shown in the "half" integrations. H_a and H_a', are the same hydrogen group in complexed and uncomplexed form, respectively; they appear as singlets with peaks at 3.8, with integration of 3H and 1H respectively. H_b'and H_c' are doublets that correspond to the complexed boronic acid benzene rings' hydrogen groups; the peaks are found at 8.0 and 7.0 ppm respectively, with integrations of 2H. Their uncomplexed counterparts, H_b and H_c, are found upfield at 7.8 and 6.87 ppm respectively; This is a shift by ~.2ppm. H_d'and H_e'are multiplets that correspond to the complexed catechol benzene rings' hydrogen groups; the peaks are found at

7.2 and 7.1 ppm respectively, with integrations of 2H. Their uncomplexed counterparts, H_d and H_e, are found upfield at 6.87 and 6.7 ppm respectively; This is a shift by .4ppm. The triphenyl-groups, H_f, are found as a multiplet between .7.4-7.7 ppm with integration of 18H.

It is the same for the 4-methoxyphenyl boronate complex with trioctylphosphine-oxide, **Figure 26,** that it is reasonable confer that there are complexed and uncomplexed products observed on the ^{1}H NMR spectrum, **Figure 27.**

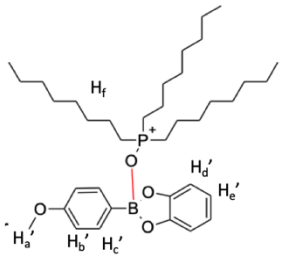


Figure 26. 4-Methoxyphenyl boronate complex with Trioctylphosphine-oxide.

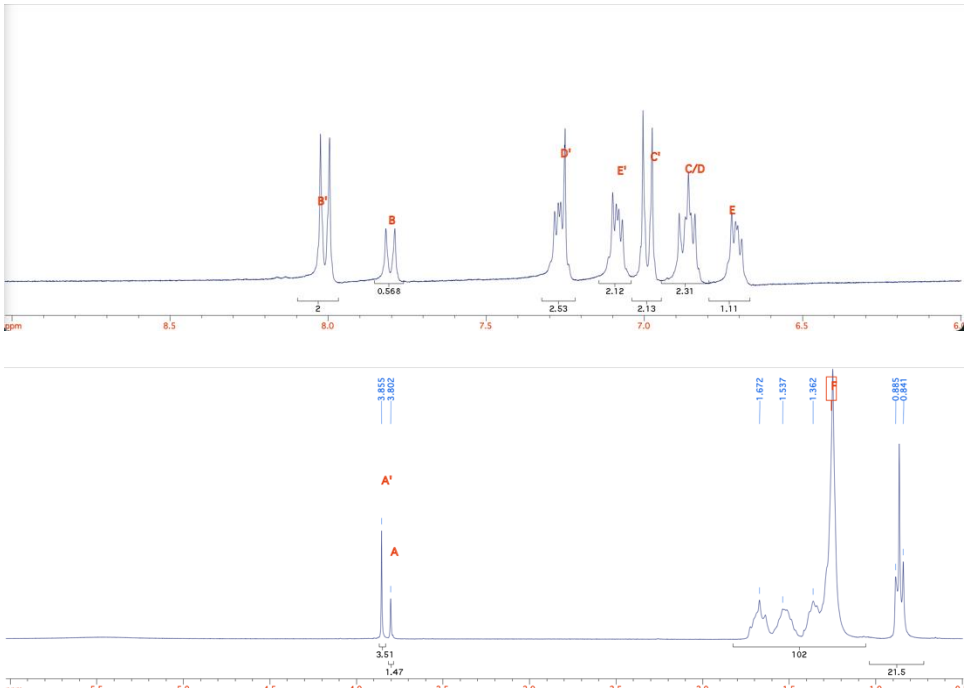


Figure 27. ^{1}H NMR of 4-Methoxyphenyl boronate complex with Trioctylphosphine-oxide (6.0-9.0ppm - top/ 0-6.0ppm - bottom).

It is observable that in the above spectrum, that both the complexed and uncomplexed form of boronate are within the same spectrum; the complexed peak is denoted as the derivative of the uncomplexed. This could either be starting products remaining in the reaction or because of the dynamic relationship of the produced system. The uncomplexed is a half of the complexed, shown in the "half" integrations. H_a and H_a', are the same hydrogen group in complexed and uncomplexed form, respectively; they appear as singlets with peaks at 3.8, with integration of 3H and 1.5H respectively. H_b'and H_c' are doublets that correspond to the complexed boronic acid benzene rings' hydrogen groups; the peaks are found at 8.1 and 7.0 ppm respectively, with integrations of 2H. Their uncomplexed counterparts, H_b and H_c, are found upfield at 7.8 and 6.85 ppm respectively; This is a shift by .2ppm. H_d'and H_e'are multiplets that correspond to the complexed catechol benzene rings' hydrogen groups; the peaks are found at 7.3 and 7.1 ppm respectively, with integrations of 2H. Their uncomplexed counterparts, H_d and H_e, are found upfield at 6.85 and 6.6 ppm respectively; This is a shift by .5ppm. The trioctyl-groups, H_f, are found as a multiplet between .8-1.8 ppm with integration of 102H and 21.5H.

Of the entire experimental series, the 3,4,5-Triflurophenyl boronate and boroxine complexes were the most difficult to produce and decipher characterization. For the 3,4,5-triflurophenyl boronate complexes, **Figure 28 and Figure 30,** are shown below. The trioctylphosphine oxide complex with 3,4,5-Triflurophenyl boronic acid derivative was the most difficult to obtain a clear spectrum. Below, **Figure 30,** shows the boronate complex with the trioctylphosohine oxide. The product consistently appeared oil-like in composition and, therefore, we were unable to obtain a readable NMR spectrum, the best of which is included in **Figure 31**. This is, in part, due to the nature of the eight hydrocarbon chains attached to the phosphine-oxide. This concluded that further instrumentation would need to be used to confirm

its' characterization and that ^{1}H NMR was not the most useful of the instrumentation available for analysis.

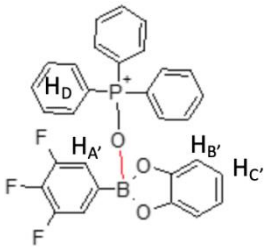


Figure 28. 3,4,5-Triflourophenyl boronate complex with Triphenylphosphine-oxide.

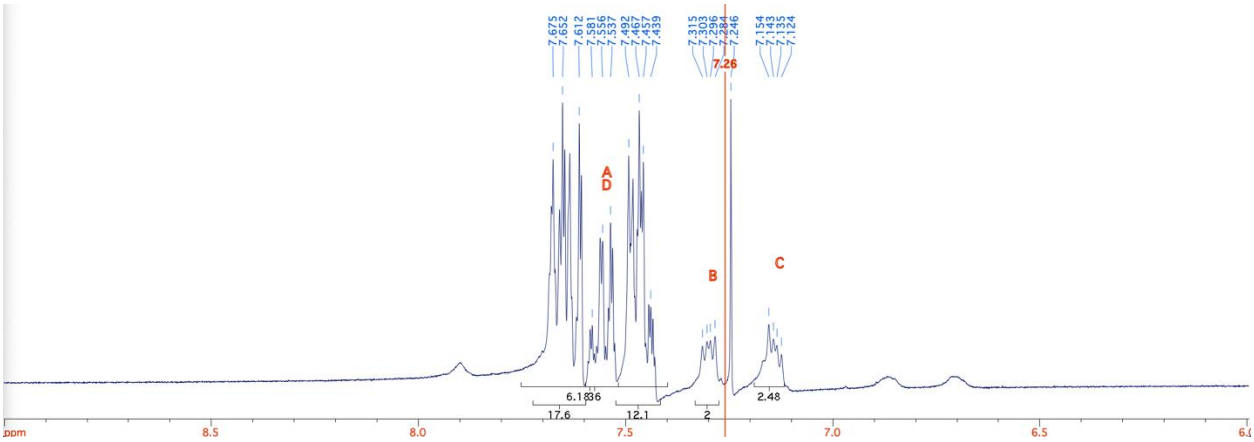


Figure 29. ^{1}HNMR of 3,4,5-Triflourophenyl boronate complex with Triphenylphosphine-oxide.

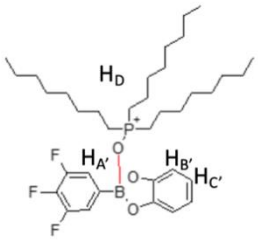


Figure 30. 3,4,5-Triflourophenyl boronate complex with Trioctylphosphine-oxide.

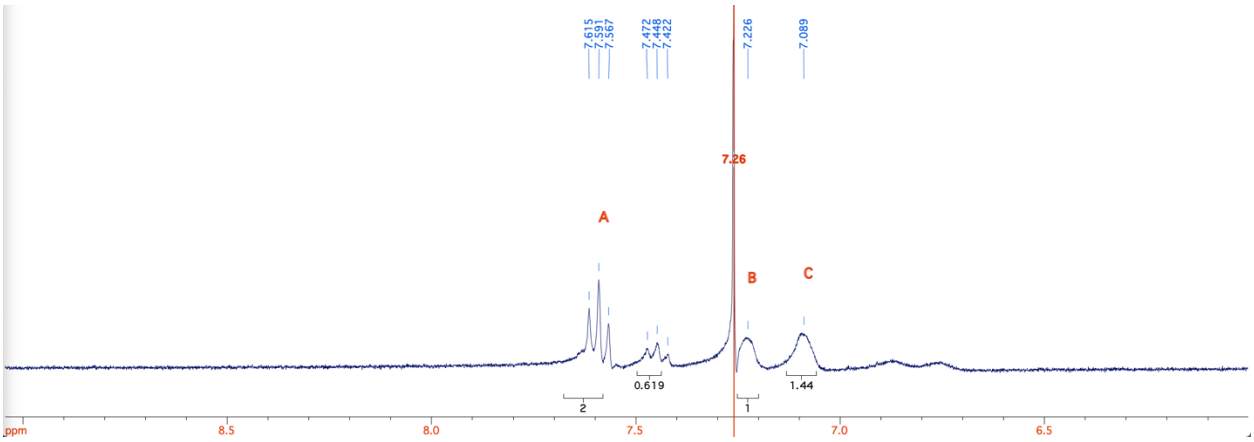


Figure 31. [1]HNMR of 3,4,5-Triflourophenyl boronate complex with Trioctylphosphine-oxide.

2.4 Percent Yields

My research project focused on the synthesis of boronates and boroxines (from boronic acids) to gain a better understanding of the relationship between the aforementioned complexation with n-oxides and p-oxides. This process is a two-step reaction, the first primarily focusing on the synthesis of the boronate or boroxine and the second focusing on the complex of those boronates or boroxines. Seven different boronic acids were used to prepare seven boroxines and seven boronates (**Table 1**) for a total of fourteen unique boron-containing compounds, from which a total of twenty-six complexes were synthesized: fourteen n-oxides and twelve p-oxides were prepared. The first complex of the experimental series included

synthesizing a n-oxide complex of each boronate and boroxine with picoline n-oxide shown in **Table 3**. The confirmation of a successful synthesis relies on key elements of ^{1}H NMR.

Table 3. Boronate and boroxine yields, and corresponding N-oxide complex yields.

Boronic Acid	**Structure**	**Boronate,** ***% Yield***	**Boronate Picoline N-Oxide Complex,** ***% Yield***	**Boroxine,** ***% Yield***	**Boroxine Picoline N-Oxide Complex,** ***% Yield***
Phenyl		108.3	75.99	116.8	106.4
4-Methoxyphenyl		91.9	77.8	100.6	106.4
Tolyphenyl		87.7	89.5	107.5	49.8
3-Nitrophenyl		94.5	94.4	103.8	80.7
4-Formylphenyl		95.0	94.3	99.0	87.5
4-Fluorophenyl		99.7	85.9	99.7	93.7
3,4,5-Trifluorophenyl		107.5	131.7	88.9	97.4

There is a plausible explanation for the higher than 100% yield found for some of the reactions. In several instances, boronic acid starting material are still present in small quantities (as determined by small quantities by ^{1}H NMR) especially in the case of the boroxine syntheses which contributed to the higher than quantitative yield. This boronic acid "impurity" could not be removed from the product. Due to the polarity and nucleophilicity of acetonitrile used as the solvent in the reaction, it tended to complex to the boron compounds and could not be removed, even under high vacuum conditions thereby producing greater than 100% yields. Throughout this research, there was good evidence that the products desired were formed, albeit with the complexed acetonitrile. However, upon complexation with the n-oxides and p-oxides the acetonitrile appears to have been completely displaced by the more powerful nucleophile.

Three of the boronic acid derivatives were also complexed with two different p-oxides to observe any significant shifts against their uncomplexed counterpart; the percent yields are shown in **Table 4.** It quickly became apparent that the percent yield of the complexation of the p-oxides to the boroxines and boronates were lower than the complexation boronates and boroxines with the N-oxide. Since the electronegativity for nitrogen atom (~3.0) is greater than that of the phosphorous atom (~2.1), it is logical that the n-oxides are stronger nucleophiles than the p-oxides and form the complexes in greater yields. The boroxine complexes with the trioctylphosphine-oxide produced an oil-like product. This is, in-part, due to the nature of trioctylphosphine-oxide as having three long carbon chains attached to the central phosphorous atom.

Table 4. Boronate and boroxine p-oxide complexes.

Boronic Acid	**Structure**	**Boronate Triphenyl-phosphine Oxide Complex, *% Yield***	**Boronate Trioctyl-phopshine Oxide Complex, *% Yield***	**Boroxine Triphenyl-phosphine Oxide Complex, *% Yield***	**Boroxine Trioctyl-phosphine Oxide Complex, *% Yield***
Phenyl		63.8	71.2	70.6	32.6
4-Methoxyphenyl		54.2	74.5	71.4	34.1
3,4,5-Trifluorophenyl		101.9	106.7	51.6	22.8

CHAPTER THREE: CONCLUSIONS

Throughout the wet chemistry aspect of this experimental series, there were fourteen boronic acid derivatives and twenty-six complexes produced. With each boronic acid, a boronate and boroxine were successfully produced and, most, with high yields. A dative bond between a boronic acid derivative, either boronate or boroxine, and a nitrogen- or phosphorous- oxide resulted in a B-O complex, which was observed through instrumental confirmation, i.e., melting point, ^{13}C NMR, and ^{1}H NMR. This dative bond allowed for a shift on the ^{1}H NMR spectra between the uncomplexed and complexed boronates and boroxines. Further, this shift can show significance depending on the functional groups' electron donating or electron withdrawing properties and whether the complex was synthesized with a nitrogen- or phosphorous- oxide.

A confirmed synthesis of the boronate shows no hydroxide hydrogens from the boronic acid and catechol, where the benzene hydrogen groups from both are still observed on the ^{1}H NMR. For a boroxine, a product formed by reacting with itself at three times equivalence, it was observed that the integration would be three-fold and a lack of hydrogens from the –OH groups on the boronic acid. Depending on the oxide complexed, there is an observable shift that ranges from anywhere between .1-1.5 ppm up or down field versus the uncomplexed ^{1}H NMR spectra. Shifts in the ^{1}H NMR, outlined in chapter two, can be seen from the phosphorous-oxide complex and can be analyzed as a continuation of this project. In this instance, there was a lower percent yield and the ^{1}H NMR showed both the complexed (shifted) and uncomplexed products on the same ^{1}H NMR. The 3,4,5-Trifluorophenyl boronates/boroxines complexed with the trioctylphosphine oxide had no obtainable ^{1}H NMR observed. The ^{1}H NMR of the 4-methoxyphenyl boronates complexed with the phosphorous-oxides showed both the complexed

and uncomplexed peaks of the hydrogens on the same spectrum, allowing for an easy comparison.

At the beginning of the research plan, it was in the procedure to use a variety of instrumentation to get the most valuable information from the produced compounds as possible in an academic setting. This led to the characterization of both the first step and second step products using ^{1}H NMR, ^{13}C NMR, Melting Point, GC-MS, and FT-IR. NMR and melting point were the only techniques used due to time constraints and further analysis was outside the scope of this work.

Specifically, this thesis focused on the synthesis and analysis of the complexed products and the dative bond in that complex. This dative bond is weak in nature and is observed to be fragile during analysis. To study the dynamic structure of the dative bond, further NMR spectra can be obtained, such as a temperature dependent study – starting at a low temperature and increasing at small increments. ^{19}F NMR could be utilized for further analysis of the complexes that did not product a clear spectrum, such as the 3,4,5-Trifluorophenyl boronate complexed with the trioctylphosphine oxide. Dative bond can be further studied through isothermal calorimetry to measure the bond strength. Any combination of these techniques could allow for a closer study in the understanding of the dative bond and the effect of the boronate/boroxine functional groups.

The nature of the dative bond – specifically the weak interaction between the boron and the oxygen in the oxide complex– allows for a reasonable expectation of dissociation due to the high temperatures of certain instrumentation, such as GC-MS. During the early stages of this thesis, the product was observed through GC-MS and spectra showed both the boronate and the n-oxide, but not a structure corresponding to the bonding of both. It was concluded that the

dative bond did not survive the high temperature of the column; therefore, GC-MS was not further pursued as an analytical tool. This is important to note in the instance that this project is continued. Other techniques, such as LC-MS, can be used to further analyze and understand these products.

IR spectroscopy could be used to confirm the presence or absnece of boronic acid and/or catechol because of the characteristic peaks associated with the alcohol groups. This technique, although useful, was not used to characterize all the products since NMR was typically suffiecient to confirm structures. It was, however, used in instances where there was a lack of confidence in the characterization ("messy" NMR, unusual physical appearance, etc.) and in further confirming in the early days of analysis.

Through this array of instrumentation, it was observable that the synthesis of the boronates, boroxines, and most complexes were successful. The condensation reaction in the production of the boronates and boroxines were successful in bonding at the anticipated site, which was confirmed through a magnitude of instrumentation. The dative bond, more fragile, caused initial complications, but was later resolved as the instrumentation was lessened and resources were utilized.

This thesis work allows for the continuation of research in the realm of boronic acid derivatives and their complexes. Along with the information that can be used to work towards any sub-set of boronic acid research (ie. molecular machines), this thesis topic can be further pursued in any number of ways. Directly, the two-step reaction shows promises towards being accommodating to a one-step reaction with varying parameters. Other boronic acids may be tested through the same procedure to extend the list of available boronates and boroxines to complex with oxides. Complexed nitrogen- oxides can be branched out to test for differences in

dative bond integrity. With this start, phosphorous- oxides can be further researched, allowing for more available knowledge in the scientific research community on the uses of these unique oxides.

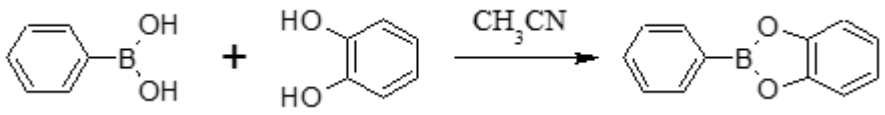
CHAPTER FOUR: EXPERIMENTAL

4.1 General Conditions

The boronic acids were obtained from Optima Chemical, Aldrich Chemical, and Oakwood Chemical and used directly from the bottle without further purification. Solvents, acetonitrile and diethyl ether, were obtained from Fisher Scientific and used directly from the bottle without further purification. The N-oxides and P-oxides were obtained from Sigma-Aldrich and used directly from the bottle without further purification. Catechol was recrystallized from benzene. Reactions were performed in oven-dried glassware equipped with a Teflon stirring bar. Microwave reactions were run in a CEM Discover Microwave Synthesizer which was open to the atmosphere. ^{1}H NMR and ^{13}C NMR spectra ($CDCl_3$) were collected using a JEOL Eclipse 300+ NMR spectrometer and GC/MS data were collected on an Agilent 7890A Gas Chromatograph with 150 position auto-sampler coupled to an Agilent 5975C Mass Spectrometer.

4.2 Synthesis of Phenyl Boronates

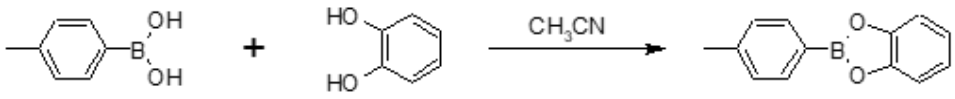
Phenyl boronate



1 **2** **3**

Phenyl boronic acid **1** (0.1 g, 0.44 mmol, 1 equ.) and catechol **2** (0.91 g, 0.44 mmol, 1 equ.) were combined in a 100 mL round bottom flask (RBF) equipped with a magnetic stir bar. Acetonitrile (50 mL) was added to the flask and fitted with a Dean-Stark trap containing 3Å molecular sieves in the collection portion of the trap. The mixture was refluxed in the microwave synthesizer at 85ºC for 15 minutes. The solvent was removed by rotary evaporation and vacuum pump (~1 torr) resulting in **3** (white powder, 0.20 g, 108.3% yield). Melting point 108.3-108.6 ℃. ^{1}H NMR (300 MHz, Chloroform) **δ** 8.10 (d, 2H), 7.55 (m, 3H), 7.32 (m, 2H), 7.12 (m, 2H). ^{13}C NMR (75 MHz, Chloroform) 148.6, 135.1, 132.5, 128.4, 122.9, 112.7

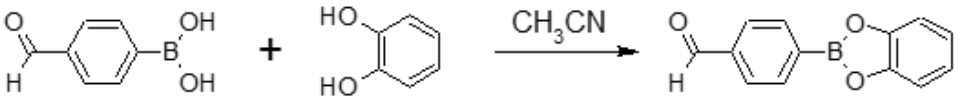
Tolyphenyl boronate



4 **2** **5**

Tolyphenyl boronate **5** was prepared in the same manner as phenyl boronate **3** to provide **5** as a light grey powder, 0.18 g, 91.9% yield. Melting point 138.6-139.0 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 7.99 (d, J = 7.71 Hz, 2H), 7.30 (d, J = 9.08Hz, 2H), 7.13 (d, J = 9.36Hz, 2H), 2.38 (s, 3H) . ^{13}C NMR (75 MHz, Chloroform): 148.6518, 142.9186, 135.1548, 129.2003, 122.7953, 22.0182.

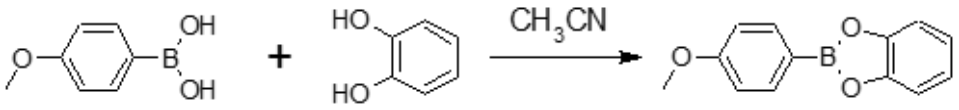
4-Formylphenyl boronate



6 **2** **7**

4-Formylphenyl boronate **7** was prepared in the same manner as phenyl boronate **3** to provide **7** as a white powder, 0.18 g, 94.5% yield. Melting point 177.2-177.6 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 10.1(s, 1H), 8.23 (d, J = 9.8Hz, 2H), 7.99 (d, J = 9.8Hz, 2H), 7.33 (m, 2H), 7.15 (m, 2H). ^{13}C NMR (75 MHz, Chloroform): 192.4, 148.3, 138.8, 135.5, 129.2, 123.2, 112.8.

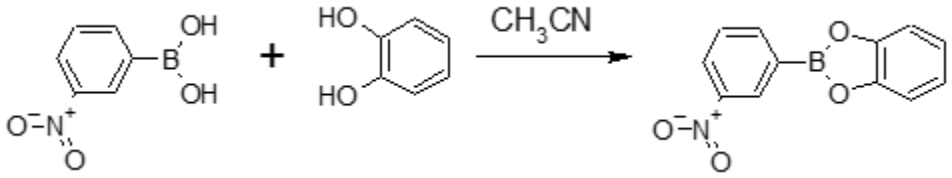
4-Methoxyphenyl boronate



8 **2** **9**

4-Methoxyphenyl boronate **9** was prepared in the same manner as phenyl boronate **3** to provide **9** as a white powder, 0.16 g, 87.7% yield. Melting point 124.0-125.2 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.04 (d, J = 8.81 Hz, 2H), 7.28 (m, 2H), 7.11 (m, 2H), 7.03 (d, J = 8.81 Hz, 2H), 3.8 (s, 3H). ^{13}C NMR (75 MHz, Chloroform): 164.53, 151.04, 139.62, 125.03, 116.334, 115.93, 115.07, 114.85, 57.59.

3-Nitrophenyl boronate

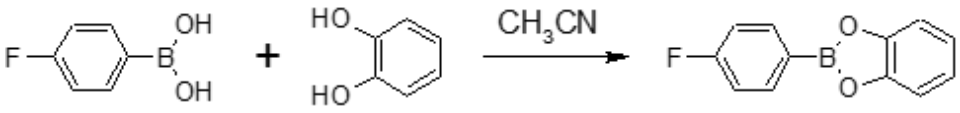


10 **2** **11**

3-Nitrophenyl boronate **11** was prepared in the same manner as phenyl boronate **3** to provide **11** as a white powder, 0.19 g, 95.0% yield. Melting point 178.3-179.9 ℃. ^{1}H NMR (300

MHz, Chloroform): **δ** 8.91 (s, 1H), 8.38 (t, 2H), 7.68 (t, 1H), 7.35 (m, 2H), 7.16 (m, 2H). ^{13}C NMR (75 MHz, Chloroform): 148.27, 140.72, 129.63, 126.97, 123.39, 112.93.

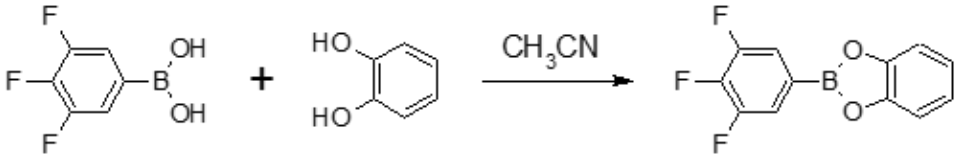
4-Fluorophenyl boronate



12 **2** **13**

4-Fluorophenyl boronate **13** was prepared in the same manner as phenyl boronate **3** to provide **13** as a white powder, 0.19 g, 99.7% yield. Melting point 101.6-102.1 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.21 (m, 1H), 8.08 (m, 2H), 7.30 (m, 2H), 7.16 (m, 5H). ^{13}C NMR (75 MHz, Chloroform): 167.5, 164.1, 148.5, 137.3, 122.9, 115.5, 112.6.

3,4,5-Trifluorophenyl boronate

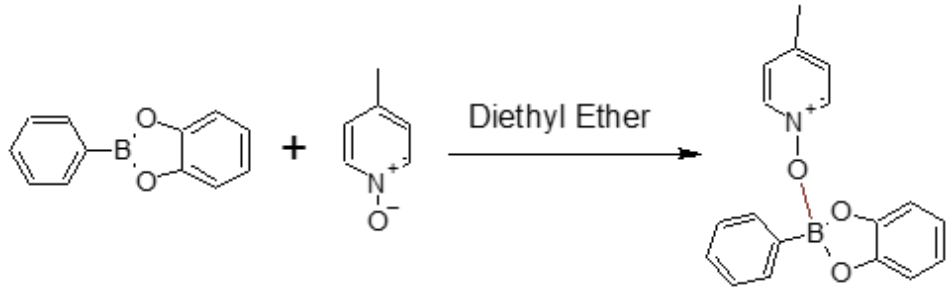


14 **2** **15**

3,4,5-Trifluorophenyl boronate **15** was prepared in the same manner as phenyl boronate **3** to provide **15** as a white powder, 0.20g, 107.5% yield. Melting point 190.1-194.3 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 7.15 (m, 2H), 7.32 (m, 2H), 7.68 (m, 2H). ^{13}C NMR (75 MHz, Chloroform): 167.5, 164.2, 148.5, 137.5, 137.4, 122.9, 115.8, 115.5, 115.2, 112.7, 77.5, 77.1, 76.7.

4.3 Complexation of Phenyl Boronates

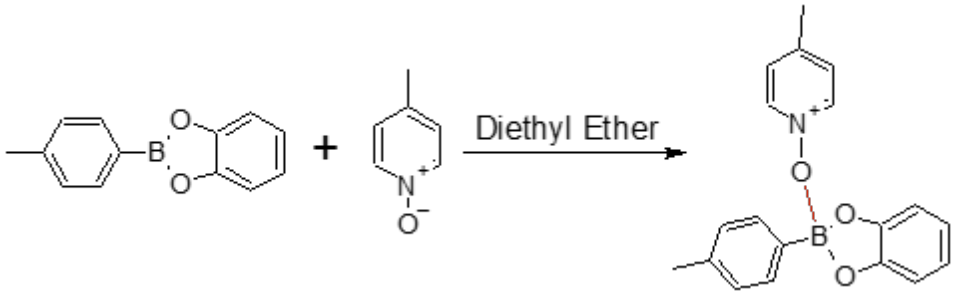
Phenyl boronate – picoline N-oxide complex



3 **16** **17**

Previously synthesized phenyl boronate **3** (0.1 g, 0.46 mmol) and picoline oxide **16** (0.95 g, 0.46 mmol) were combined in a 100mL RBF. Diethyl ether (50 mL) was added to the flask and stirred at room temperature for 30 minutes. The solvent was removed by rotary evaporation and vacuum pump (~1 torr) resulting in the **17** (yellow powder, 0.15 g, 75.99% yield). Melting point 152.8-153.8 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.29 (d, J = 6.60 Hz, 2H), 7.89 (m, 4H), 7.16 (d, J = 6.60 Hz, 2H), 6.97 (m, 2H), 6.81 (m, 2H). ^{13}C NMR (75 MHz, Chloroform): 151.0, 141.2, 132.6, 127.7, 127.5, 119.6, 110.0, 21.1.

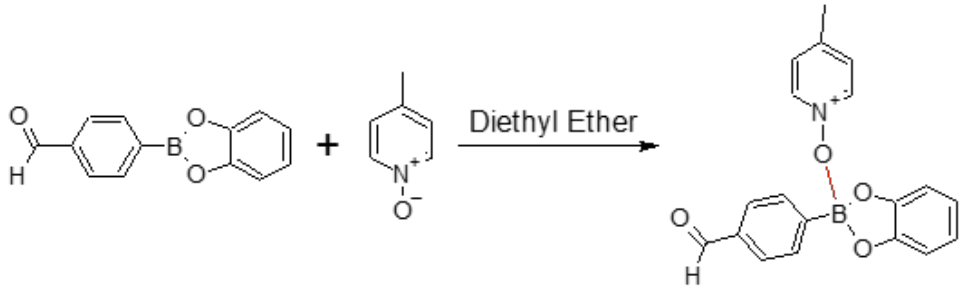
Tolyphenyl boronate – picoline oxide complex



5 **16** **18**

Tolyphenyl boronate N-oxide complex **18** was prepared in the same manner as the phenyl boronate N-oxide complex **17** to provide **18** as red flakes, 0.15 g, 77.8% yield. Melting point 164.7-165.0 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.19 (d, J = 6.88 Hz, 2H), 7.83 (d, J = 7.98 Hz,), 7.73 (d, J = 7.71 Hz, 2H), 7.24 (t, 2H), 7.17 (t, 2H), 7.04 (m, 2H), 6.92 (m, 2H), 5.29 (m, 3H), 3.41 (m, 3H), 2.37 (m, 1H). ^{13}C NMR (75 MHz, Chloroform): 150.28, 145.65, 140.42, 139.10, 133.12, 128.68, 126.93, 120.20, 110.49, 21.69, 20.94.

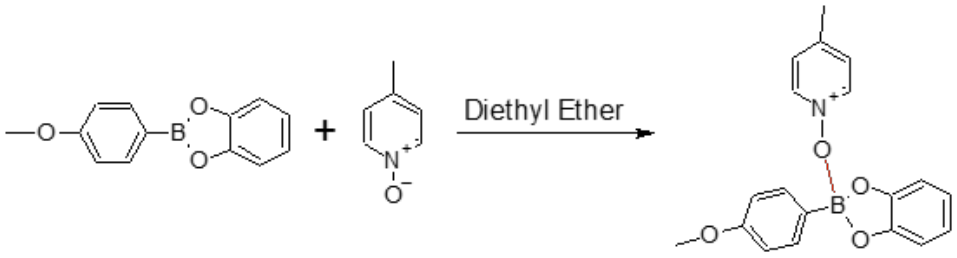
4-Formylphenyl boronate – picoline oxide complex



7 **16** **19**

4-Formylphenyl boronate N-oxide complex **19** was prepared in the same manner as the phenyl boronate N-oxide complex **17** to provide **19** as red powder, 0.18 g, 94.5% yield. Melting point 125.6-126.8 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 10.0 (s, 1H), 8.40 (d, J = 6.60 Hz, 2H), 7.93 (d, J = 7.98 Hz, 2H), 7.82 (d, J = 7.98 Hz, 2H), 6.71 (m, 2H), 6.59 (m, 2H). ^{13}C NMR (75 MHz, Chloroform): 193.3, 141.1, 132.6, 129.0, 127.1, 119.2, 109.5, 21.2.

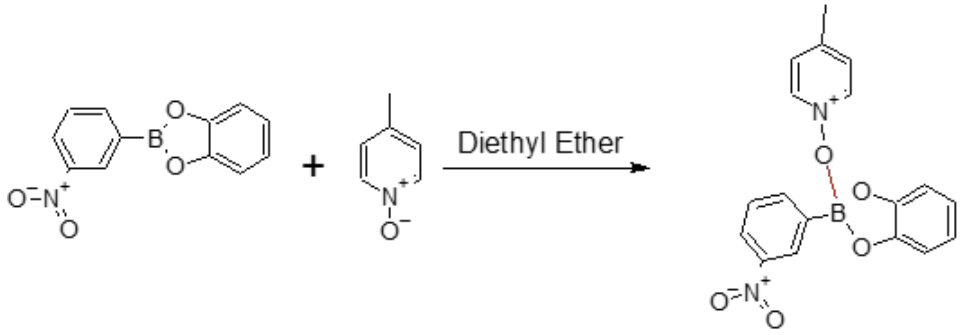
4-Methoxyphenyl boronate - picoline oxide complex



9 **16** **20**

4-Methoxyphenyl boronate N-oxide complex **20** was prepared in the same manner as the phenyl boronate N-oxide complex **17** to provide **20** as a pale-yellow powder, 0.17 g, 89.5% yield. Melting point 147.6-149.5 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.19 (d, J = 6.88 Hz, 2H), 7.95 (d, J = 8.81 Hz, 2H), 7.14 (d, J = 7.15 Hz, 2H), 6.98 (d, J = 8.81 Hz, 2H), 3.82 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, Chloroform): 161.11, 150.26, 140.35, 135.59, 126.94, 120.59, 113.25, 110.79, 77.20, 55.21, 20.92.

3-Nitrophenyl boronate - picoline oxide complex

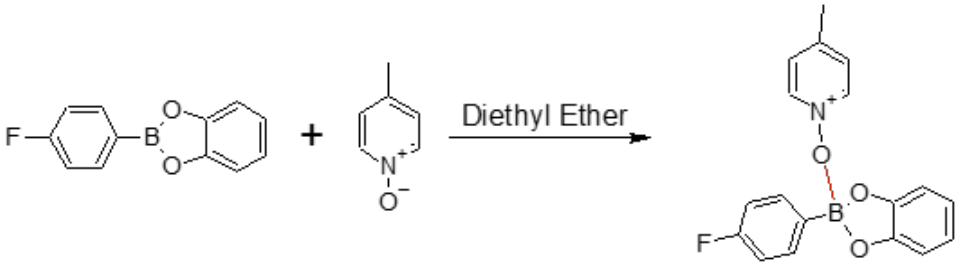


11 **16** **21**

3-Nitrophenyl boronate N-oxide complex **21** was prepared in the same manner as the phenyl boronate N-oxide complex **17** to provide **21** as a light-yellow powder, 0.19 g, 94.4% yield. Melting point 188.6-193.1 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.86 (s, 1H), 8.42 (t,

2H), 8.23 (m, 2H), 8.01 (m, 2H), 7.52 (t, 1H), 7.21 (m, 2H), 7.16 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, Chloroform): 148.26, 143.65, 140.78, 129.66, 129.58, 127.00, 123.42, 121.29, 115.56, 112.96, 77.56, 77.14, 76.72.

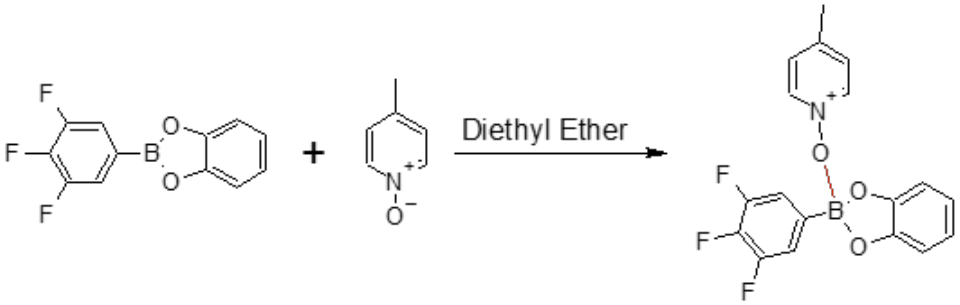
4-Fluorophenyl boronate - picoline oxide complex



13 **16** **22**

4-Flurophenyl boronate N-oxide complex **22** was prepared in the same manner as the phenyl boronate N-oxide complex **17** to provide **22** as a yellow powder, 0.18 g, 85.9% yield. Melting point 145.8-149.3 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.30 (d, J = 5.50 Hz, 2H), 7.83 (t, 2H), 7.20 (d, J = 6.33 Hz, 2H), 7.04 (m, 2H), 6.86 (m, 2H), 6.73 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, Chloroform): 150.87, 141.16, 134.50, 126.93, 119.74, 114.78, 114.62, 110.04, 77.25, 21.19.

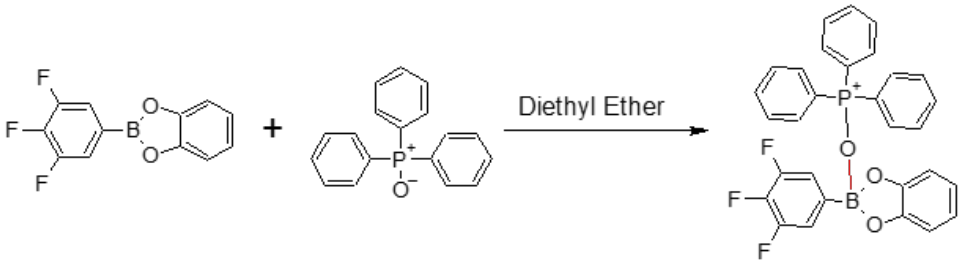
3,4,5-Trifluorophenyl boronate - picoline oxide complex



15 **16** **23**

3,4,5-Trifluorophenyl boronate N-oxide complex **23** was prepared in the same manner as the phenyl boronate N-oxide complex **17** to provide **23** as white powder, 0.24 g, 131.7% yield. Melting point 192.0-193.5 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 2.435 (s, 3H), 6.51 (m, 2H), 6.59 (m, 2H), 7.28 (m, 4H), 8.397 (d, 2H). ^{13}C NMR (75 MHz, Chloroform): 150.8, 141,2, 134.6, 134,5, 126.9, 119.7, 114.7, 114.5, 110.0, 77.6, 77.1, 76.7, 21.2.

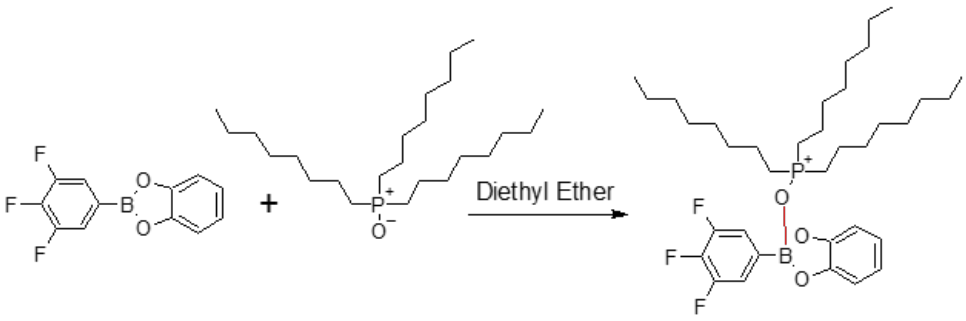
3,4,5-Trifluorophenyl boronate - triphenylphosphine oxide complex



15 **24** **25**

3,4,5-trifluorophenyl boronate triphenylphosphine oxide complex **25** was prepared in the same manner as the phenyl boronate N-oxide complex **17** to provide **25** as light brown, 0.21 g, 101.9% yield. Melting point Beyond Instrument Limit. ^{1}H NMR (300 MHz, Chloroform): **δ** 7.55 (t, 6H), 7.29 (dd, 2H), 7.14 (dd, 2H), 7.55 (m, 36H). ^{13}C NMR (75 MHz, Chloroform): 154.89, 142.16, 133.61, 127.92, 121.68, 115.89, 115.70, 112.63, 78.85, 77.91.

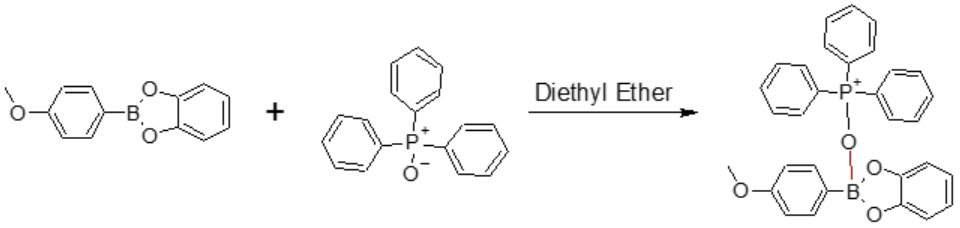
3,4,5-Trifluorophenyl boronate - trioctylphosphine oxide complex



15 **26** **27**

3,4,5-Trifluorophenyl boronate trioctylphosphine oxide complex **27** was prepared in the same manner as the phenyl boronate N-oxide complex **17** to provide **27** as dark brown oil. Melting point Beyond Instrument Limits. ^{1}H NMR (300 MHz, Chloroform): **δ** 7.59 (t, 2H), 7.23 (s, 1H), 7.09 (s, 1H), 1.55 (m, 55H). ^{13}C NMR (75 MHz, Chloroform): 151.88, 142.36, 137.59, 136,85, 127.95, 119.73, 112.76, 110.0, 22.66, 22.45, 21.28, 20.90.

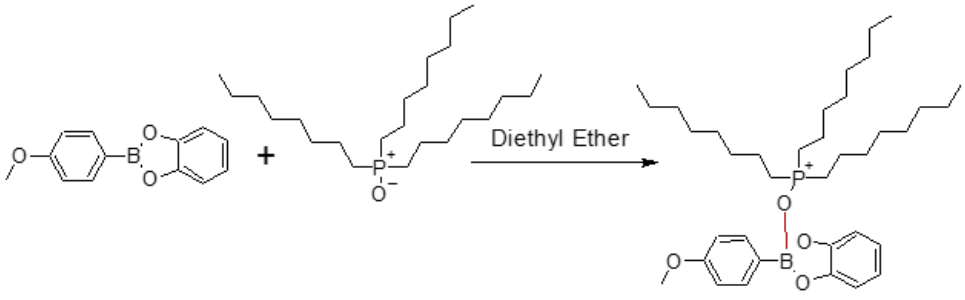
4-Methoxyphenyl boronate - triphenylphosphine oxide complex



9 **24** **28**

4-Methoxyphenyl boronate triphenylphosphine oxide complex **28** was prepared in the same manner as the phenyl boronate N-oxide complex **17** to provide **28** as dark brown, 0.15g, 74.5% yield. Melting point: Beyond Instrument Limit. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.02 (m, 2H), 7.66 (m, 7H), 7.54 (dd, 4), 7.48 (m, 7H), 7.28 (d, J=9.20Hz, 2H), 7.09 (d, J=9.20Hz, 2H), 7.00 (d, J=8.71Hz, d), 6.88 (d, J=8.50Hz, 1H), 3.85 (s, 3H), 3.79 (s, 1H). ^{13}C NMR (75 MHz, Chloroform): 167.61, 152.93, 142.36, 137.60, 134.94, 121.34, 113.74, 110.29, 20.92.

4-Methoxyphenyl boronate - trioctylphosphine oxide complex

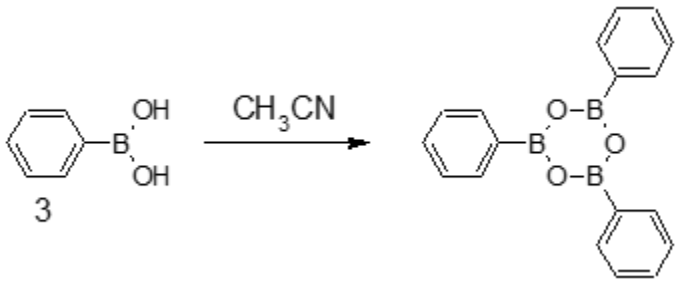


9 **26** **29**

4-Methoxyphenyl boronate trioctylphosphine oxide complex **29** was prepared in the same manner as the phenyl boronate N-oxide complex **17** to provide **29** as dark brown. Melting point: Beyond Instrument Limit. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.01 (d, J=8.69Hz, 2H), 7.26 (d, J=9.93Hz, 2H), 7.08 (d, J=9.14Hz, 2H), 6.99 (d, J=8.72Hz, 2H), 6.87 (d, 2H), 6.71 (d, 1H), 3.86 (s, 3H), 3.80 (s, 1H), 1.52 (m, 78H), 0.862 (d, 17H). ^{13}C NMR (75 MHz, Chloroform): 148.94, 140.67, 126.32, 120.49, 78.23, 76.83, 22.42, 20.64, 20.38.

4.4 Synthesis of Phenyl Boroxines

Phenyl boroxine



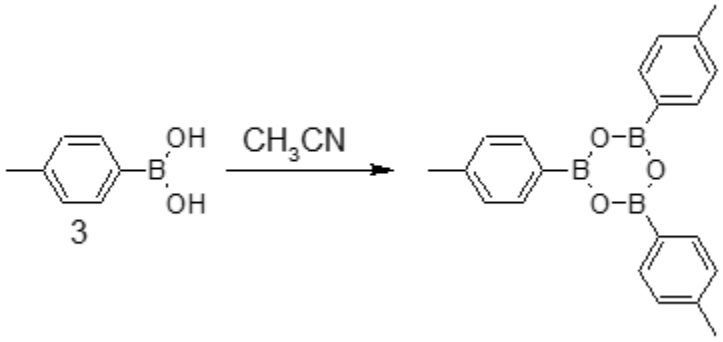
3

1 **30**

Phenyl boronic acid **1** (0.1 g, 1 mmol, 3 equ.) was combined in a 100 mL round bottom flask (RBF) equipped with a magnetic stir bar. Acetonitrile (50 mL) was added to the flask and

fitted with a Dean-Stark trap containing 3Å molecular sieves in the collection portion of the trap. The mixture was refluxed in the microwave synthesizer at 85ºC for 15 minutes. The solvent was removed by rotary evaporation and vacuum pump (~1 torr) resulting in **30** (white crystalline, 0.11 g, 116.8% yield). Melting point: 211.6 - 212.2 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 7.89 (m, 4H), 7.36 (m, 6H). ^{13}C NMR (75 MHz, Chloroform): 134.0, 130.0, 127.9.

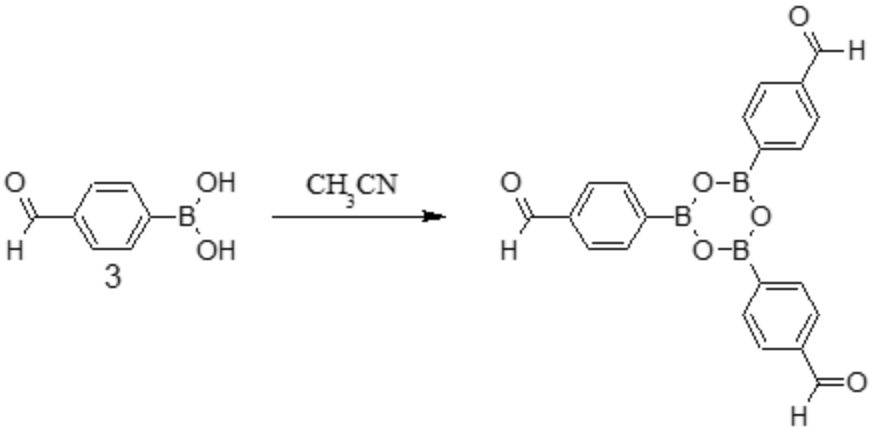
Tolyphenyl boroxine



3 **31**

Tolyphenyl boroxine **31** was prepared in the same manner as phenyl boroxine **30** to provide **31** as a white crystalline, 0.1 g, 100.6% yield. Melting point: 255.6-257.4 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.13 (d, J= 8.0 Hz, 6H), 7.25 (d, J = 7.5 Hz 6H), 2.43 (s, 9H). ^{13}C NMR (75 MHz, Chloroform):139.18, 135.68, 134.78, 134.11, 128.66, 21.79.

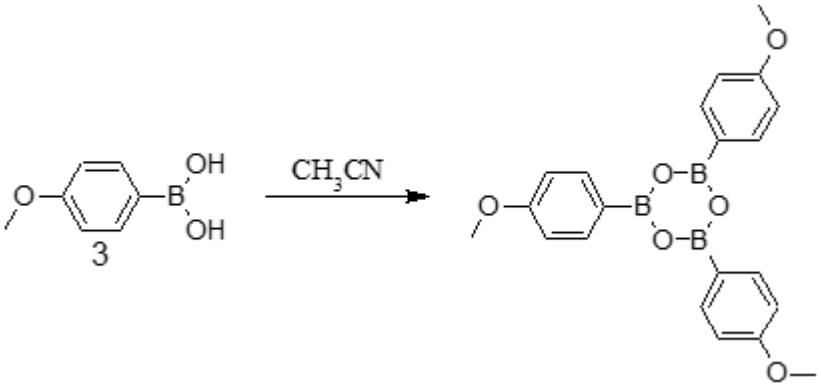
4-Formylphenyl boroxine



6 **32**

4-Formylphenyl boroxine **32** was prepared in the same manner as phenyl boroxine **30** to provide **32** as a yellow powder, 0.1 g, 103.8% yield. Melting point: 125.7-126.7 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 10.0 (s, 3H), 8.09 (d, J = 7.71Hz, 6H), 7.93 (m, J = 43.75 Hz, 6H). ^{13}C NMR (75 MHz, Chloroform): 194.0, 134.5, 128.8.

4-Methoxyphenyl boroxine

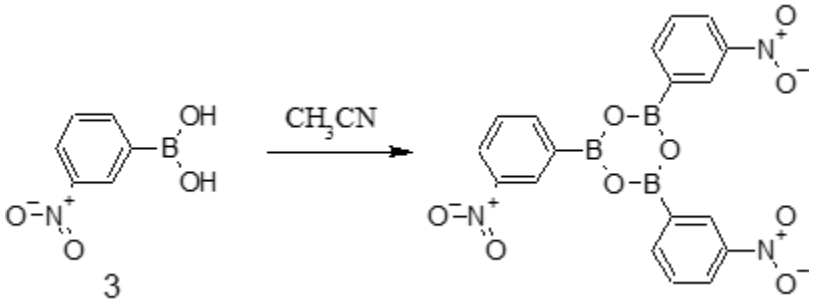


8 **33**

4-Methoxyphenyl boroxine **33** was prepared in the same manner as phenyl boroxine **30** to provide **33** as a white powder, 0.11 g, 107.5% yield. Melting point: 147.7-149.2 ℃. ^{1}H NMR

(300 MHz, Chloroform): **δ** 8.17 (d, J=8.79Hz, 2H), 7.02 (d, J=8.79Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (75 MHz, Chloroform): 163.24, 137.59, 113.59, 77.56, 77.14, 76.72, 55.25.

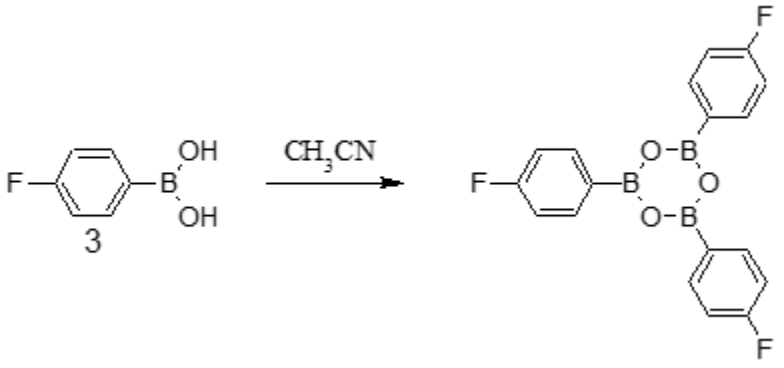
3-Nitrophenyl boroxine



10 **34**

3-Nitrophenyl boroxine **34** was prepared in the same manner as phenyl boroxine **30** to provide **34** as yellow crystalline, 0.1 g, 103.8% yield. Melting point 187.6-188.7 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.77 (m, 6H), 8.69 (m, 6H), 7.92 (m, 3H), 7.88 (d, 2H). ^{13}C NMR (75 MHz, Chloroform): 188.39, 176.64, 146.71, 130. 82, 123.94, 80.50, 77.68.

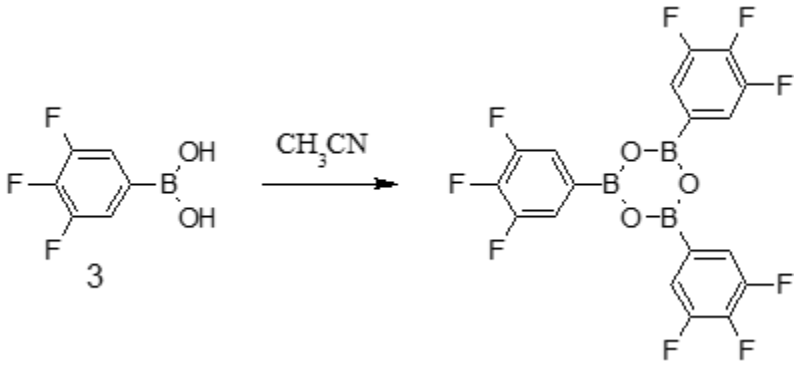
4-Fluorophenyl boroxine



12 **35**

4-Flourophenyl boroxine **35** was prepared in the same manner as phenyl boroxine **30** to provide **35** as white crystalline, 0.5 g, 99.7% yield. Melting point 175.8-182.3 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.76 (d, J=9.34Hz, 6H), 8.58 (d, J=9.35Hz, 6H). ^{13}C NMR (75 MHz, Chloroform): 138.1, 138.0, 115.5, 115.3, 77.5, 77.1, 76.7, 0.1.

3,4,5-Trifluorophenyl boroxine

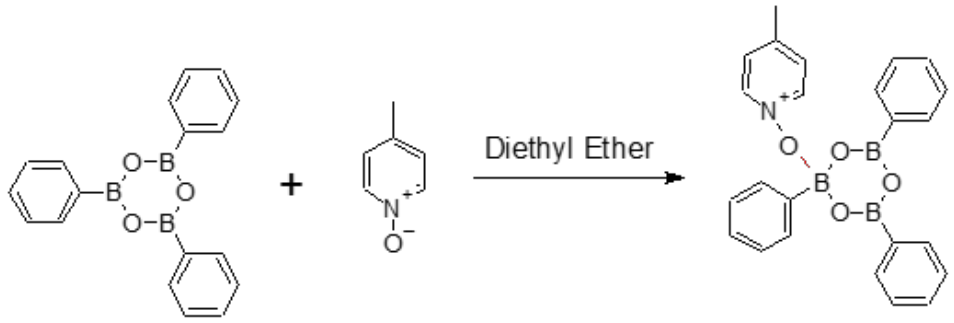


14 **36**

3,4,5-Trifluorophenyl boroxine **36** was prepared in the same manner as phenyl boroxine **30** to provide **36** as yellow crystalline, 0.48 g, 88.9% yield. Melting point 198.7-199.5 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 7.1 (s, 6H). ^{13}C NMR (75 MHz, Chloroform): 149.22, 145.72, 140.39, 139.10, 123.45, 80.94, 79.33, 68.81.

4.5 Complexation of Phenyl Boroxines

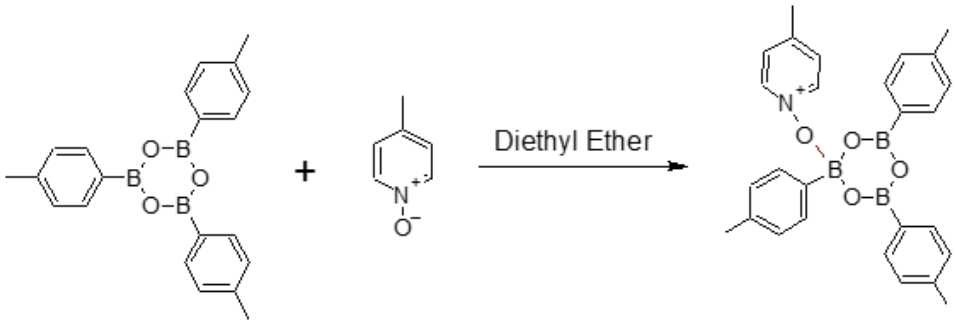
Phenyl boroxine – picoline N-oxide complex



30 **16** **37**

Previously synthesized phenyl boroxine **30** (0.5g, 0.4 mmol) and picoline oxide **17** (0.4 g, 0.4 mmol) were combined in a 100mL RBF. Diethyl ether (50 mL) was added to the flask and stirred at room temperature for 30 minutes. The solvent was removed by rotary evaporation and vacuum pump (~1 torr) resulting in **37** (yellow powder, 0.51 g, 106.4% yield). Melting point: 212.1-212.9 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.35 (d, J = 5.50 Hz, 2H), 7.92 (d, J = 6.60 H, 6H), 7.19 (d, J = 7.98 H, 7H), 2.31 (s, 13H). ^{13}C NMR (75 MHz, Chloroform): 141.5, 139.9, 134.4, 128.4, 126.8, 21.7.

Tolyphenyl boroxine – picoline N-oxide complex

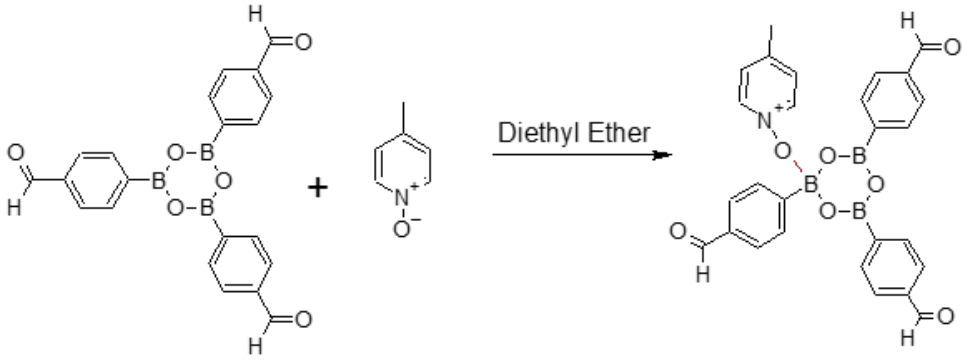


31 **16** **38**

Tolyphenyl boroxine N-oxide complex **38** was prepared in the same manner as phenyl boroxine N-oxide complex **37** to provide **38** as a white powder, 0.51 g, 106.4% yield. Melting

point: 170.9-171.6 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.31 (d, J = 8.8Hz, 2H), 7.94 (d, J = 8.8Hz, 6H), 7.19 (m, 8H), 2.4 (d, J = 7.8Hz, 12H). ^{13}C NMR (75 MHz, Chloroform): 141.6, 139.5, 134.2, 128.3, 126.8, 21.7.

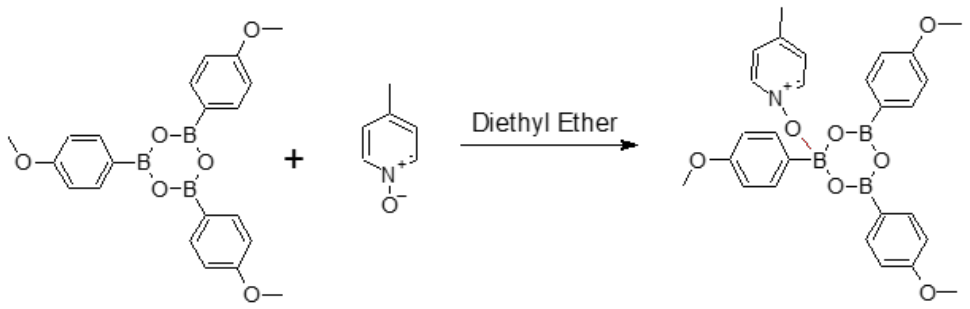
4-Formylphenyl boroxine – picoline N-oxide complex



32 **16** **39**

4-Formylphenyl boroxine N-oxide complex **39** was prepared in the same manner as phenyl boroxine N-oxide complex **37** to provide **39** as a white powder, 0.48 g, 87.5% yield. Melting point 145.3-147.2 ℃. ^{13}C NMR (75 MHz, Chloroform): 193.79, 137.89, 129.86, 77.62, 77.17, 76.54 .

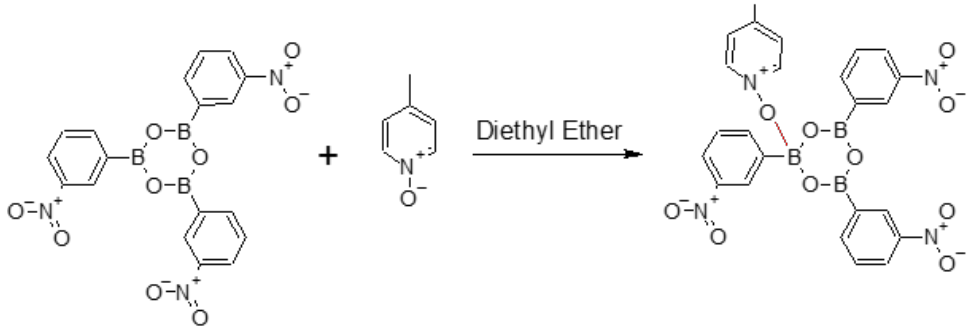
4-Methoxyphenyl boroxine – picoline N-oxide complex



33 **16** **40**

4-Methoxyphenyl boroxine N-oxide complex **40** was prepared in the same manner as phenyl boroxine N-oxide complex **37** to provide **40** as a white powder, 0.25 g, 49.8% yield. Melting point: 115.3-118.2 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.24 (d, J=6.87Hz, 2H), 7.95 (d, J=8.22Hz, 2H), 7.15 (d, J=6.60Hz, 2H), 6.91 (d, J=8.25Hz, 2H), 3.8 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, Chloroform): 139.74, 135.24, 126.99, 120.97, 113.67, 111.14, 77.58, 77.15, 76.73, 55.22, 20.77

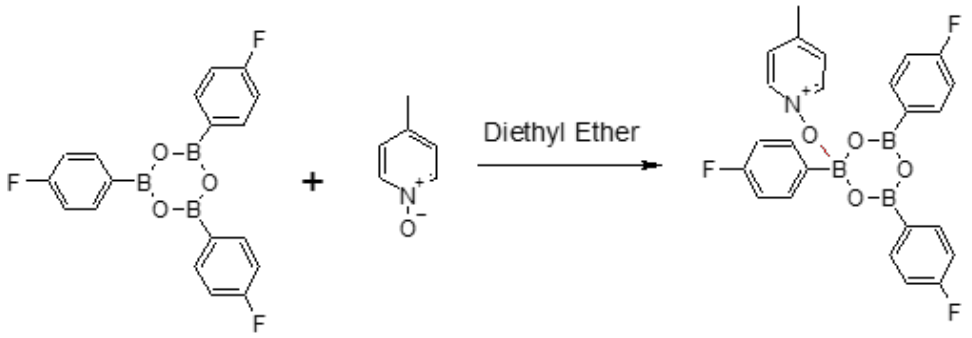
3-Nitrophenyl boroxine – picoline N-oxide complex



34 **16** **41**

3-Nitrophenyl boroxine N-oxide complex **41** was prepared in the same manner as phenyl boroxine N-oxide complex **37** to provide **41** as a yellow crystalline, 0.47 g, 80.74% yield. Melting point: 187.6-192.1 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.74 (d, 2H), 8.49 (d, 2H), 8.26 (m, 4H), 7.57 (t, 2H), 7.47 (d, 2H), 7.25 (s, 1H). ^{13}C NMR (75 MHz, Chloroform): 161.6, 155.71, 154.6, 148.27, 140.72, 129.63, 126.97, 120.9, 77.6, 77.2, 76.7.

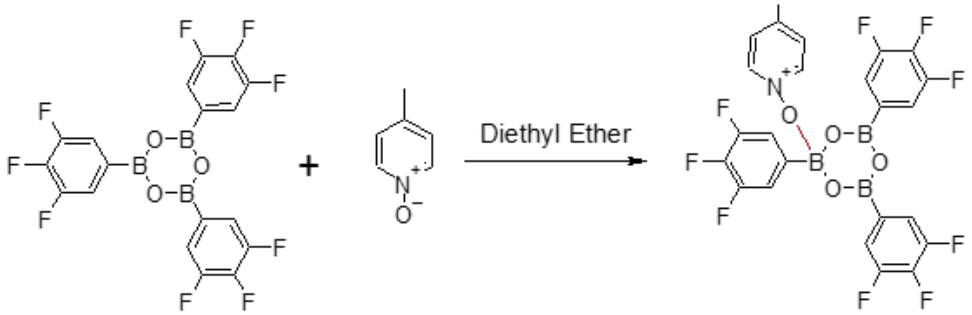
4-Flurophenyl boroxine – picoline N-oxide complex



35 **16** **42**

4-Flurophenyl boroxine N-oxide complex **42** was prepared in the same manner as phenyl boroxine N-oxide complex **37** to provide **42** as a white powder, 0.49 g, 93.7% yield. Melting point 156.7-161.3 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.78 (d, J=8.66, 6H), 8.40 (d, J=8.66, 6H), 7.81 (m, 2H), 7.68 (m, 2H), 2.99 (s, 3H)

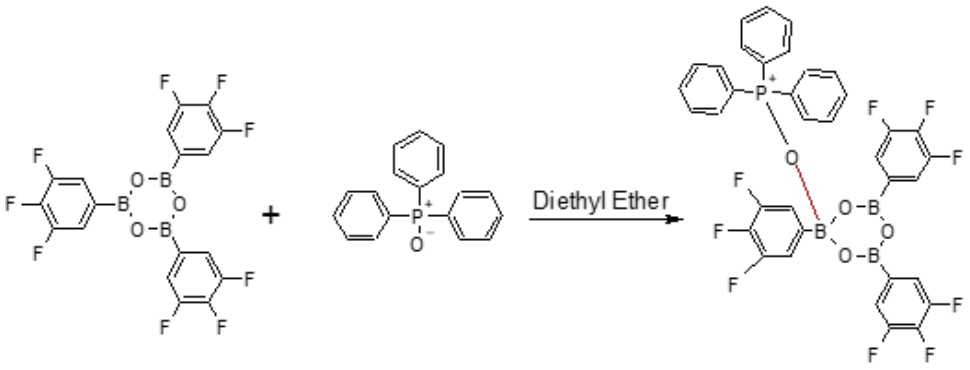
3,4,5-Trifluorophenyl boroxine -picoline N-oxide complex



36 **16** **43**

3,4,5-Trifluorophenyl boroxine N-oxide complex **43** was prepared in the same manner as phenyl boroxine N-oxide complex **37** to provide **43** as a pale yellow, 0.5 g, 97.4% yield. Melting point 188.9-189.9 ℃. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.56 (m, 6H), 7.60 (d, J=6.78Hz, 2H), 7.49 (d, J=6.78Hz, 2H), 3.14 (s, 3H). ^{13}C NMR (75 MHz, Chloroform): 135.84, 130.92, 130.21, 77.89, 77. 60, 76.93, 21.34.

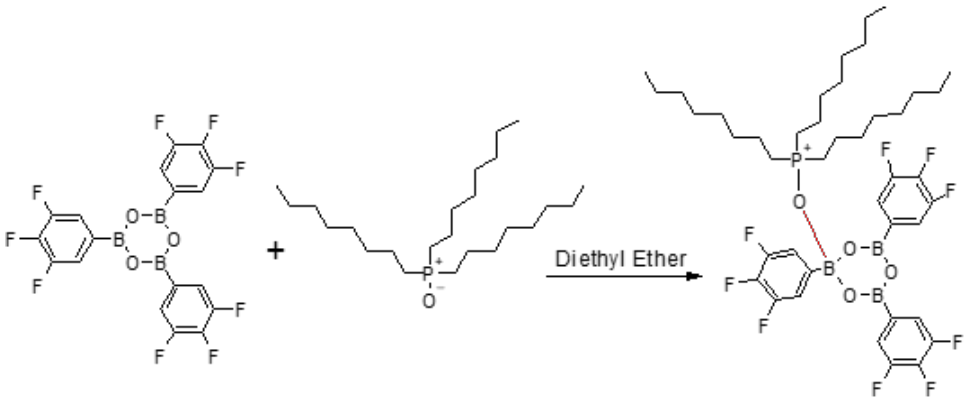
3,4,5-Trifluorophenyl boroxine - triphenylphosphine N-oxide complex



36 **24** **44**

3,4,5-Trifluorophenyl boroxine triphenylphosphine oxide complex **44** was prepared in the same manner as phenyl boroxine N-oxide complex **37** to provide **44** as dark brown, 0.26 g, 51.6% yield. Melting point: Beyond Instrument Limit. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.46 (m, 6H), 8.15 (d, J=6.55Hz, 6H), 7.89 (d, J=J=6.50Hz, 6H), 4.59 (s, 3H). ^{13}C NMR (75 MHz, Chloroform): 167.94, 158.34, 155.87, 154.39, 154.71, 148.96, 145.77, 120.28, 77/8, 76.9, 68.76.

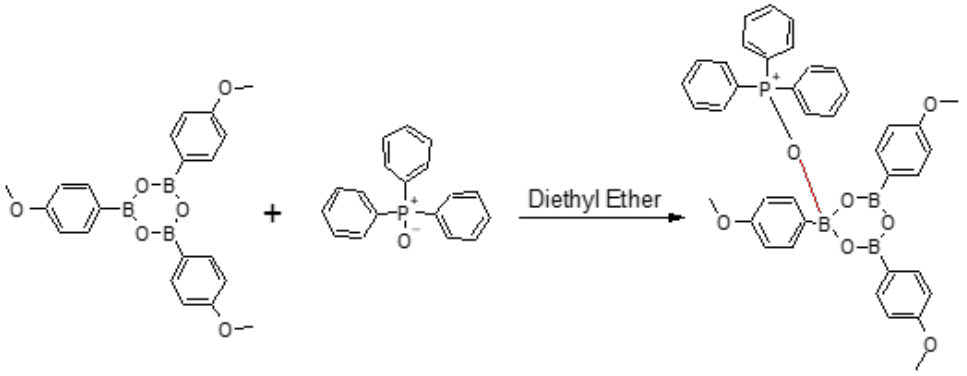
3,4,5-Trifluorophenyl boroxine - trioctylphosphine oxide complex



36 **26** **45**

3,4,5-Trifluorophenyl boroxine trioctylphosphine oxide complex **45** was prepared in the same manner as phenyl boroxine N-oxide complex **37** to provide **45** as dark brown oil. Melting point: Beyond Instrument Limit. ^{1}H NMR (300 MHz, Chloroform): **δ** -1.55 (m, 55H), 7.089 (m, 1H), 7.23 (m, 1H), 7.59 (m, 2H). ^{13}C NMR (75 MHz, Chloroform): 175.13, 168.78, 166.54, 166.24, 157.90, 154.68, 129.87, 79.67, 77.62, 75.89.

4-Methoxyphenyl boroxine – triphenylphosphine oxide complex



33 **24** **46**

4-Methoxyphenyl boroxine triphenylphosphine oxide complex **46** was prepared in the same manner as phenyl boroxine N-oxide complex **37** to provide **46** as dark brown, 0.45 g, 71.4% yield. Melting point: Beyond Instrument Limit. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.79 (d, J=7.68Hz, 6H), 8.63 (d, J=7.68Hz, 6H), 7.88 (m, 7H), 7.67 (m, 6H), 7.49 (m, 5H), 3.19 (s, 9H).^{13}C NMR (75 MHz, Chloroform): 134.1, 133.6, 130.1, 129.5, 77.6, 77.4, 76.2, 0.08

4-Methoxyphenyl boroxine – trioctylphosphine oxide complex

33 **26** **47**

4-Methoxyphenyl boroxine trioctylphosphine oxide complex **47** was prepared in the same manner as phenyl boroxine N-oxide complex **37** to provide **47** as dark brown oil. Melting point: Beyond Instrument Limit. ^{1}H NMR (300 MHz, Chloroform): **δ** 8.83 (d, J=8.20Hz, 6H), 8.76 (d, J=8.20Hz, 6H), 3.21 (s, 9H), 1.27 (m, 47H). ^{13}C NMR (75 MHz, Chloroform): 161.76, 159.28, 157.92, 157.64, 154.82, 152.68, 150.88, 141.23, 134.69, 134.50, 126.96. 55.28, 21.94

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