Experimentally Calculated Stoichiometric Ratios of Boroxine-Picoline Systems for Future Application in Molecular Machines

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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ABSTRACT

To contribute to the body of knowledge of chemical systems related to molecular machines, the coordination ratios of various boronic acid derivatives and picoline were studied. Several different boroxines and boronates were synthesized using two methods with varying success. The boroxines were synthesized using both a heating mantle method and a microwave assisted method. The boronates were only synthesized using the microwave assisted method. The boroxine synthesis was more complete using the microwave method but there were other issues that caused many of the boroxines to be unsuitable for this study. The boronates were too impure to use as they were, and purification techniques were employed. Silica, paper, and alumina chromatography were all unable to separate the starting materials from the products. Boroxines were chosen as the molecule of choice for this study as the purity could be corrected for more easily. To determine the coordination ratio between any boroxine and picoline, a Job's plot method was used. Based on the Job's plot for 4-methoxytriphenylboroxine:Picoline, the coordination ratio for that system is 1:1. All other boroxines were too sensitive to water to be used with this method. Suggestions for future studies with these systems are discussed.

CHAPTER ONE: BACKGROUND AND INTRODUCTION

The concept of molecular machines is a recent idea that is characterized by their ability to process and transfer energy, electrons, or information[1]. In 2016, three chemists were awarded the Nobel prize in chemistry for their contributions to this area of research[2]. These molecular machines can then be manipulated by electrochemical, chemical, and photonic stimuli[3] to, at least in theory, do work.

Research in molecular machines got its start in a field of chemistry referred to as chemical topology which was pioneered in the early 1960's by Wasserman[4]. The field of molecular machines was later advanced by work on the syntheses of a **catenane**[1]. A catenane is a system of interlocked macrocycles held within one another by mechanical forces, creating a ring-in-ring system[5] as shown below in **figure 1**.

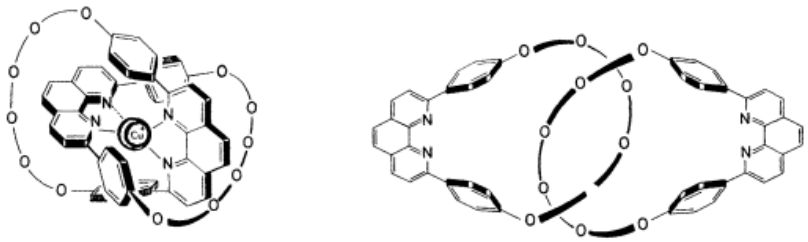


Figure 1. Example of Catenate and Catenand[5]

These systems can be built by a threading approach where a straight chain molecule impales the center of a ring and then reacts with itself, or by templated methods where transition metal complexation (Figure 1, Left) causes the system to be built up from a centralized point[1].

[5] Republished with permission of Royal Society of Chemistry, from Molecular structure of a catenand and its copper(I) catenate: complete rearrangement of the interlocked macrocyclic ligands by complexation, Cesario, M.; Dietrich-Buchecker, C. O.; Guilhem, J.; Pascard, C.; Sauvage, J. P., 5, 1985; permission conveyed through Copyright Clearance Center, Inc.

Since these breakthroughs research has been focused on creating more complex and more poly-catenated systems.

Another integral member to the family of molecular machines are the molecular systems known as **rotaxanes**[6] as shown below in **figure 2**.

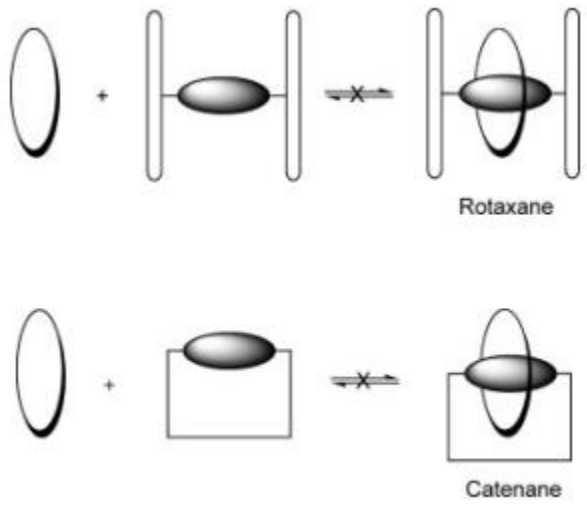


Figure 2. Example of Rotaxane and Catenane[6]

A rotaxane is a system where a ring is pierced by a stoppered rod. The ring is free to move from end to end of the rod but is unable to move past the stoppers which are bulky groups that are larger than the empty space of the ring will allow to pass through. These systems can be synthesized in many ways including capping, snapping, clipping, slipping, and using an active metal template[7]. All these methods involve combining the pieces together in a way that they become mechanically locked to one another. Synthesis of molecular machines have typically involved the use of pyridines and other nitrogen-containing compounds such as those reported by Harper[6] as shown below in **figure 3**.

[6] Reprinted from Elsevier Books, Jason B. Harper,Karin S. Schaffarczyk McHale, Comprehensive Heterocyclic Chemistry IV, 1-25, 2022, with permission from Elsevier.

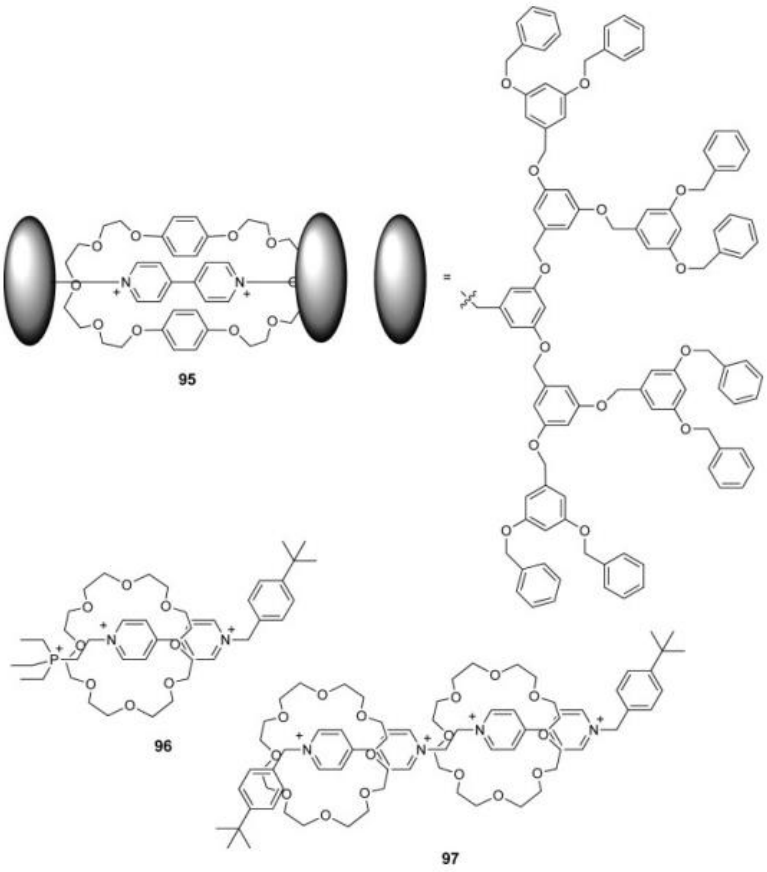


Figure 3. Example of pyridine containing rotaxanes[6]

The nitrogen atom acts as an electron donor which facilitates the organizational assembly of the molecules with an electron acceptor which can then form either a catenane or rotaxane. Once pre-assembled, the rings can be prepared via the synthesis of the molecules as with transition metal-based synthesis[8] or by using a weak molecular force to guide the components of the system together.

The weak force responsible for guiding this molecular assembly is known as a **coordinate-covalent** or **dative** bond. It differs from typical covalent bonds in that the two atoms

[6] Reprinted from Elsevier Books, Jason B. Harper,Karin S. Schaffarczyk McHale, Comprehensive Heterocyclic Chemistry IV, 1-25, 2022, with permission from Elsevier.

that are bonded (coordinated) do not share electrons with each other. One atom, which acts as a Lewis base, shares a lone pair with another atom, which acts as a Lewis Acid. This coordination is more easily broken than a covalent bond, but less transient than a hydrogen bond. An example of a dative bond is shown with orbital diagrams below in **figure 4** as well as a simplified chemical structure diagram in **figure 5**.

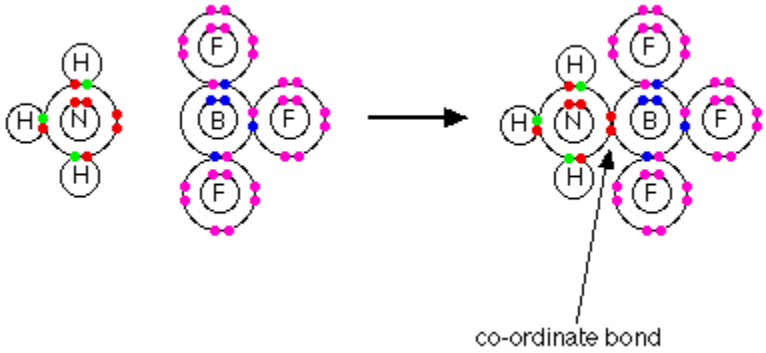


Figure 4. Example of Dative Bonding[9]

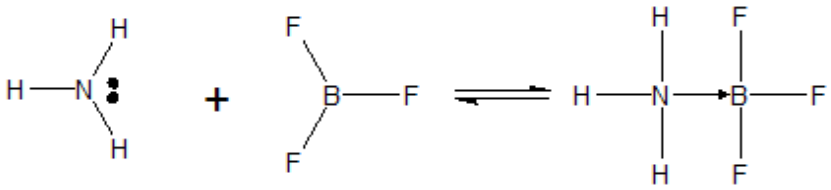


Figure 5. Chemical Structure Diagram of a Dative Bond

Knowing what systems have been successful in the past allow for new assembly strategies to be evaluated. For this reason, new research projects might take an existing system and change a small portion or even a single molecule and then study the changes that causes to the system. These changes could include, physical size of each molecule, changes in numbers of coordination sites, or their locations. Another variable that can be adjusted is the strength of each coordination site.

This evaluation of assembly strategies could be done in many ways, but with my work, which consists of examining the dative bond that exists between the Lewis base picoline and the Lewis acid of a boroxine/boronate, we can easily manipulate the acidity of the boron by changing the electron density around the boron atom with electron-withdrawing groups such as fluorine. These systematic changes to the electronic environment of the boron would change the acidity and therefore, potentially change the strength of the boron-picoline bond. With the change in acidity of that coordination site, the dative bond between the boronate and the picoline will either bond more strongly and have shorter bond distance, OR the coordination number of that molecule may increase where more than one picoline will chemically interact with the boronate at a time. To gain any useful knowledge from these changes in interactions, they must be quantified and compared to a control system or previously researched system.

A simple method to determine the coordination ratio of an acid-base equilibrium is called the method of continuous variation or **Job's plot** method. This method, popularized by Job[10] (Olson, 2011), is typically used to determine the ratio of the reaction coefficients that are in equilibrium in the

$$nA + mB \leftrightarrow A_nB_m \quad (1)$$

form of **Equation 1,** where **A** and **B** are the free species and A_nB_m is the complex of A and B coordinated in the ratio of n:m at equilibrium[10]. One use of this method is to plot an observable parameter such as change in chemical shift of a specific ^{1}H NMR peak ($\Delta\delta$) vs molar ratio of A:B before equilibrium. If this plot is parabolic or angular the maximum or minimum of the plot is used to calculate coordination number, or **n**. Once this max or min is known, the X value of this point is used to calculate the molar ratio of the system at equilibrium using

$$X = \frac{n}{n+m} \quad (2)$$

equation 2, where **X** is the x-value of the maximum or minimum and **n** and **m** are the stochiometric coefficients of the two system components. In general, a Job's plot can be created and used to find the n-value of an association when a *chemical property* changes as *mole fraction* changes. Recently, Job's method has been largely used in protein-binding site analysis where a property such as fluorescence is measured over the series of varying molar ratios of protein:binder-molecule[11]. The shapes of these plots can vary, but the most common is parabolic where the maximum or minimum of the parabola corresponds to the [X] value of significance. In some cases, the shape can be more closely related to exponential decay functions where the parameter ceases to change once it hits a saturation point which corresponds to n.

Historically, molecular machine structures have been based around either oxygen, nitrogen, or sulfur containing molecules. The interactions between these molecules are varied and widely useful such as in molecular transport which allows a molecule to "step" in either direction along a backbone using random movement of a functionalized chain in conjunction with changes in chemical environment[12], as shown below in **figure 6**.

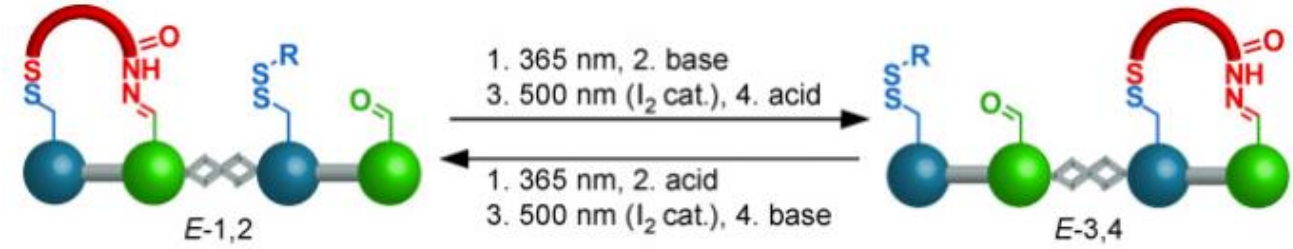


Figure 6. "Walking" Molecular Machine[12]

Molecular muscles, which are a datively guided, rotaxane-based, flection[13] shown below in **figure 7**.

[12]Reprinted From Angewandte Chemie International Edition, 50 David A. Leigh, Edzard M. Geertsema, Max von Delius, et al, Light-Driven Transport of a Molecular Walker in Either Direction along a Molecular Track, 6, 2010, with permission from John Wiley and Sons. Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

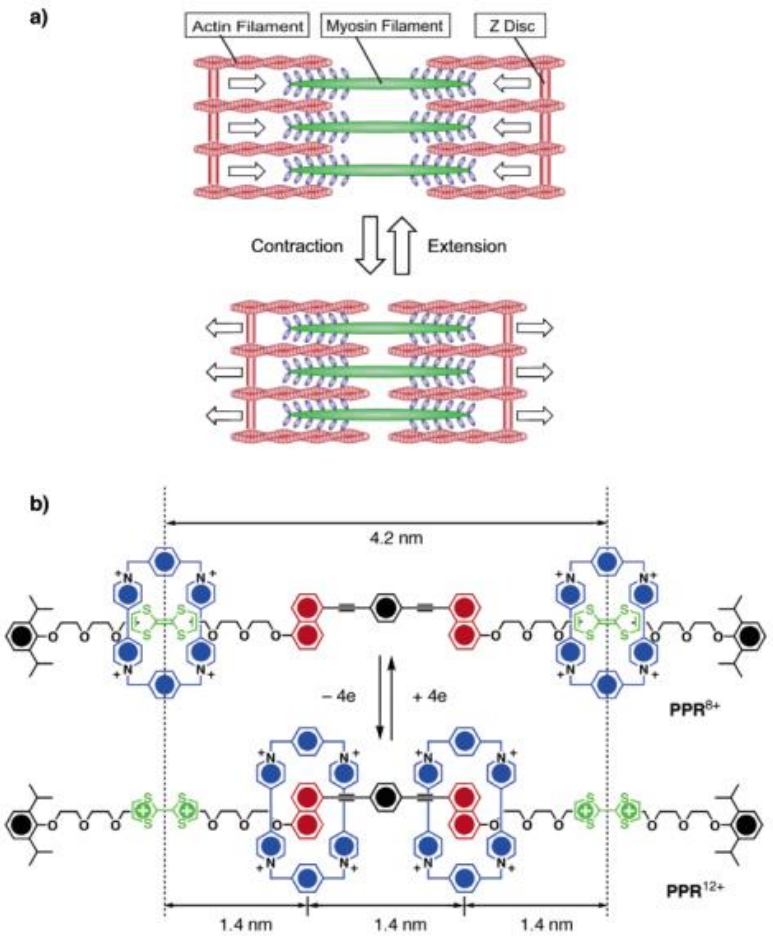


Figure 7. Biological Muscle vs Molecular Machine Muscle[13]

This system allows the rings of the rotaxane (blue) to be manipulated to different "stations" (green) along the rod of the rotaxane based on electrical changes to the system. These rotaxanes are held in place at a "station" by dative bond interactions. If a molecule is attached to one or both ends of the rings (blue), this movement can be used to cause a flexion of another component similar to biological muscle contractions.

The usefulness of these molecule systems, which are so integral to the field of molecular machines, begs the question: "What other molecular interactions could be useful for the proof-of-

[13] Republished under the Standard *ACS AuthorChoice/Editors' Choice* usage agreement. https://pubs.acs.org/doi/10.1021/ja051088p, This is an unofficial adaptation of an article that appeared in an ACS publication. ACS has not endorsed the content of this adaptation or the context of its use.

concept for molecular machine development?". To address this question, we have chosen to study the dative bonding interaction between a Lewis acid (a boronate or boroxine) and a Lewis base (picoline). More specifically, in this thesis, I have assessed the stochiometric interactions of several fluorinated aryl boronic esters (boronates) with various ratios of picoline and quantified those ratios using the Job's plot method. With these properties quantified, more of these nitrogen-boron dative bonds could become integrated into existing compounds or become integral to developing new systems.

CHAPTER 2: RESULTS AND DISCUSSION

For the purpose of reporting this research, I have divided this chapter into four parts: the **synthesis** of boroxines and boronates, the attempted **purification** of boroxines and boronates, the **complexation** of boroxines and boronates with picoline, and the calculated **Job's plots** for a select group of the complexes.

Synthesis of Boroxines and Boronates

The boroxines and boronates used in this research project were prepared using a heat source to accomplish the condensation reaction either by the conventional (heating mantle) method or by microwave-assisted synthesis. All boroxines and boronates were characterized by ^{1}H NMR.

Boroxines

4-Methoxytriphenylboroxine from conventional heating

^{1}H NMR

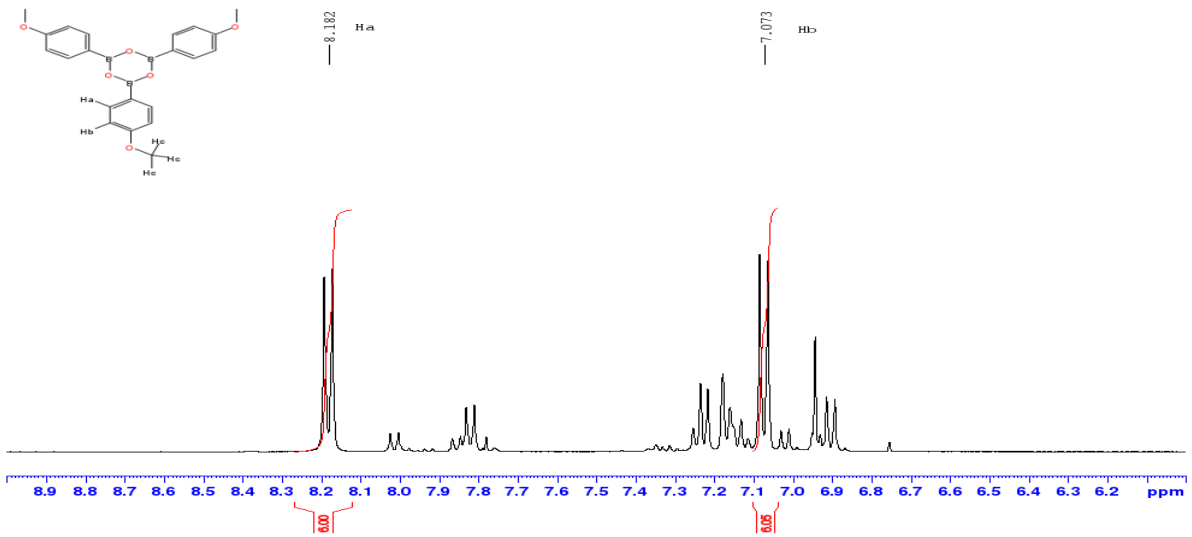


Figure 8. Aromatic Region ^{1}H NMR 4-methoxytriphenylboroxine

As expected, there are major aromatic peaks corresponding to Ha and Hb on the phenyl rings of 4-methoxy boroxine in **figure 8**. The peaks are both doublets with integrations of 6H each. Minor peaks are present which correspond to boronic acid but the boroxine signals are most significant. This all suggests the boroxine was created, but the equilibria of this reaction stopped short of pure product.

^{1}H NMR

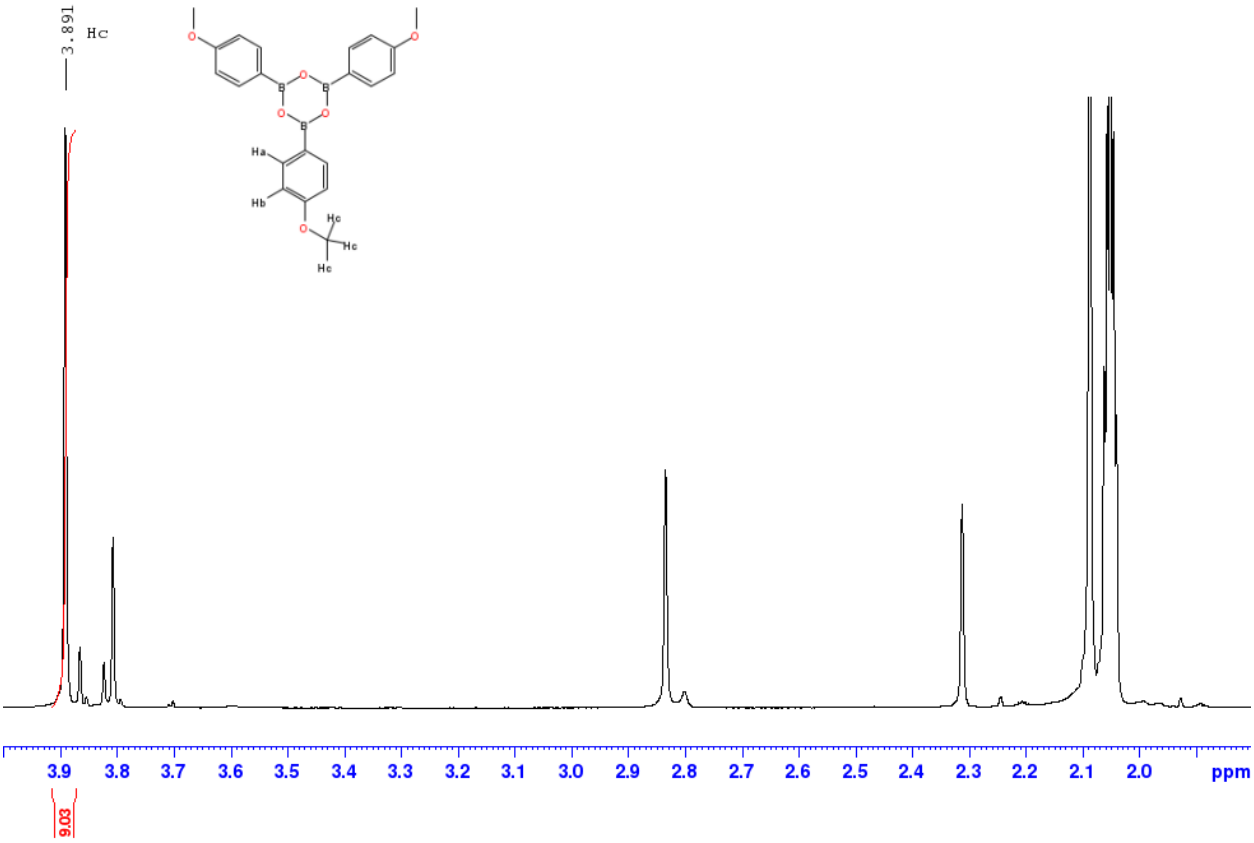


Figure 9. Non-aromatic Region ^{1}H NMR 4-methoxytriphenylboroxine

In the non-aromatic region of **figure 9**, there is a multiplet around 2.05 which is the solvent residual. This peak is used to calibrate the X axis and is set to δ 2.05. The labeled major peak is the Hc peak of the methyl group on the methoxy. It is a singlet with integration of 9H.

The methyl of the boronic acid is present around 3.8 as a singlet but is obviously in much smaller quantity.

Triphenylboroxine from conventional heating

^{1}H NMR

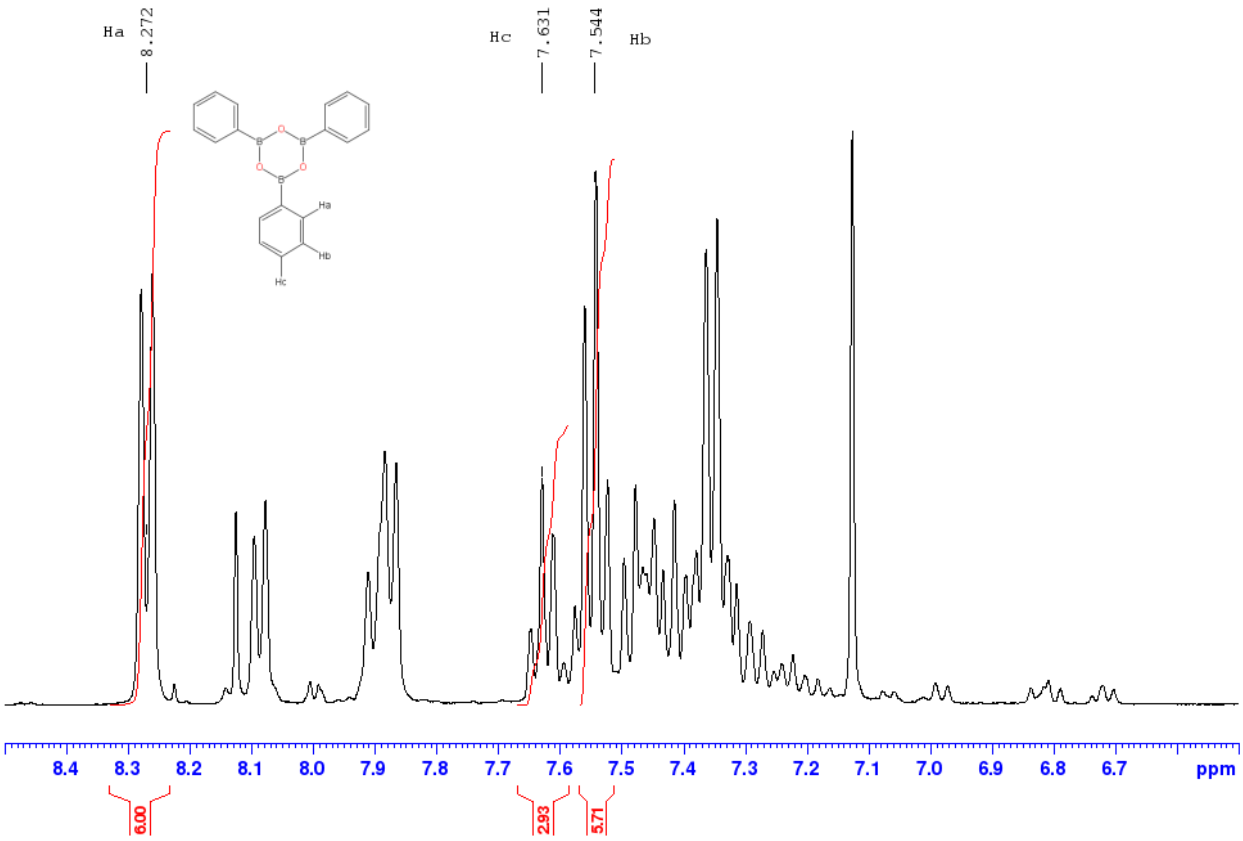


Figure 10. Aromatic Region ^{1}H NMR Triphenylboroxine Conventional heating Method

At first glance the **Figure 10** spectrum is much messier. Three signals of the boroxine were found around δ 8.30, 7.65, and 7.55 with integrations of 6, 3, and 6 respectively. Signals of the boronic acid were present around δ 8.10, 7.40 and 7.35 respectively. The ratio between the boroxine and boronic acid peaks are much more similar than with 4-methoxytriphenylboroxine. This suggests the reaction did not proceed to completion and shows the trend that the product becomes less pure using this method as the level of fluorination increases.

4-Fluorotriphenylboroxine from conventional heating

^{1}H NMR

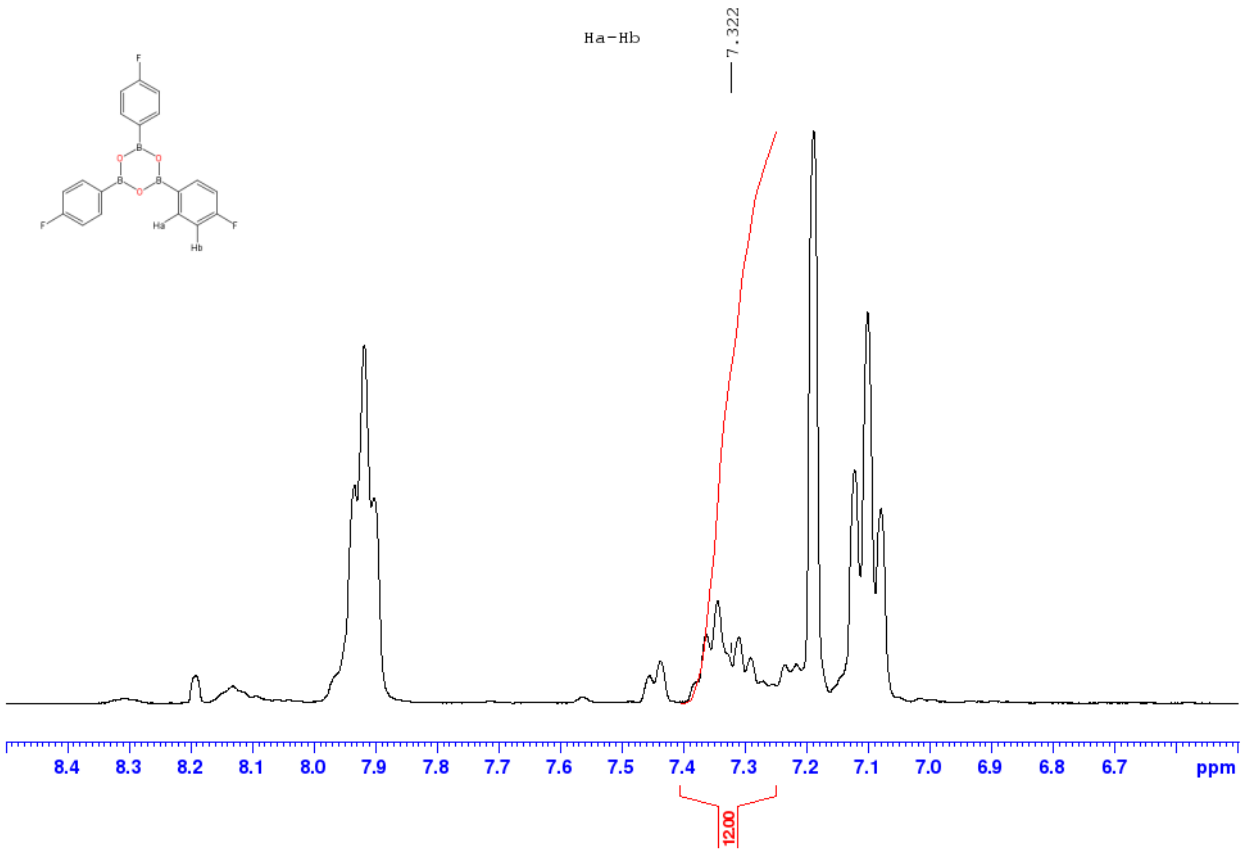


Figure 11. Aromatic Region ^{1}H NMR 4-fluorotriphenylboroxine Conventional heating Method

The boroxine signals in **Figure 11** were hard to resolve and were in much lower abundance compared to the boronic acid signals around 7.90 and 7.10. This conventional heating method is not compatible with 4-fluorotriphenylboroxine.

3,4,5-*Trifluorotriphenylboroxine from conventional heating*

^{1}H NMR

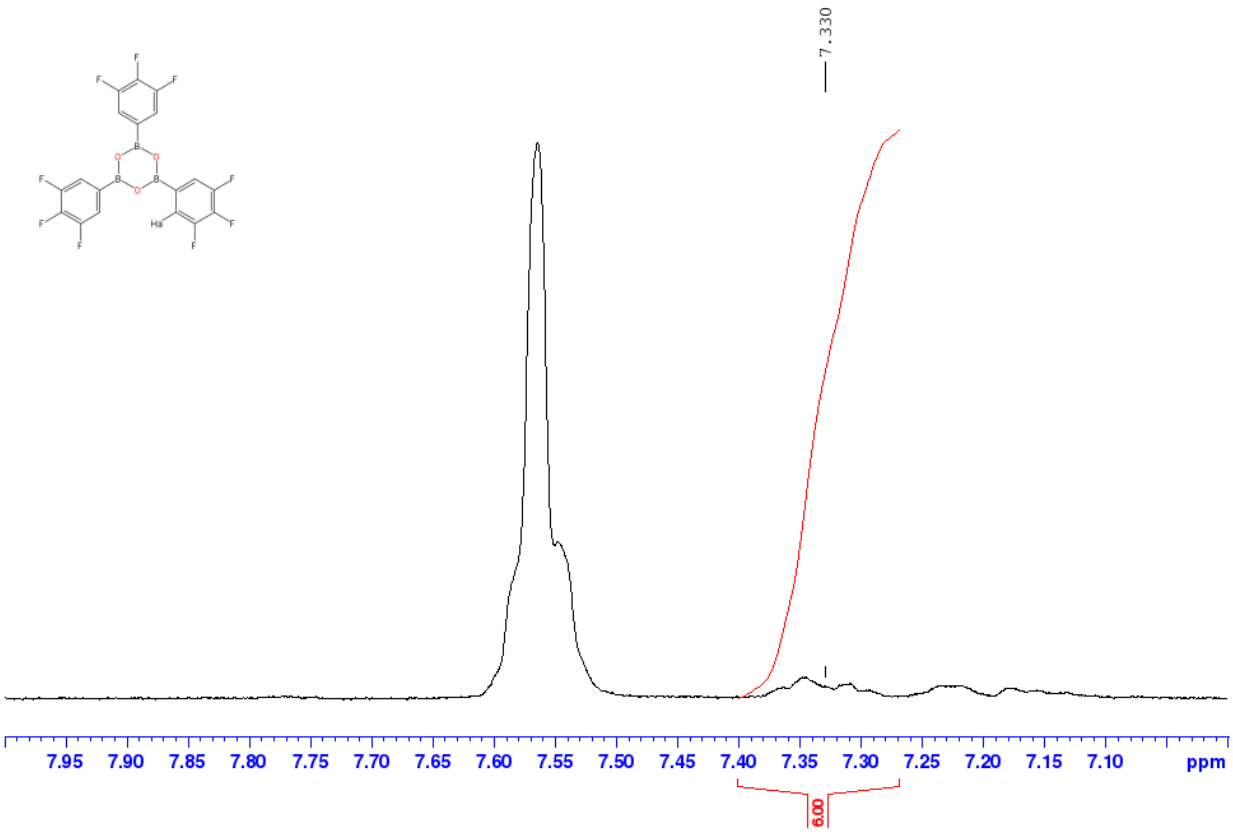


Figure 12. Aromatic Region ^{1}H NMR 3,4,5-trifluorotriphenylboroxine Conventional heating Method

Similar to the 4-fluorotriphenylboroxine spectrum, **Figure 12** shows almost no boroxine was created and the conventional heating method is not compatible with 3,4,5-trifluorotriphenylboroxine.

Triphenylboroxine from microwave heating

^{1}H NMR

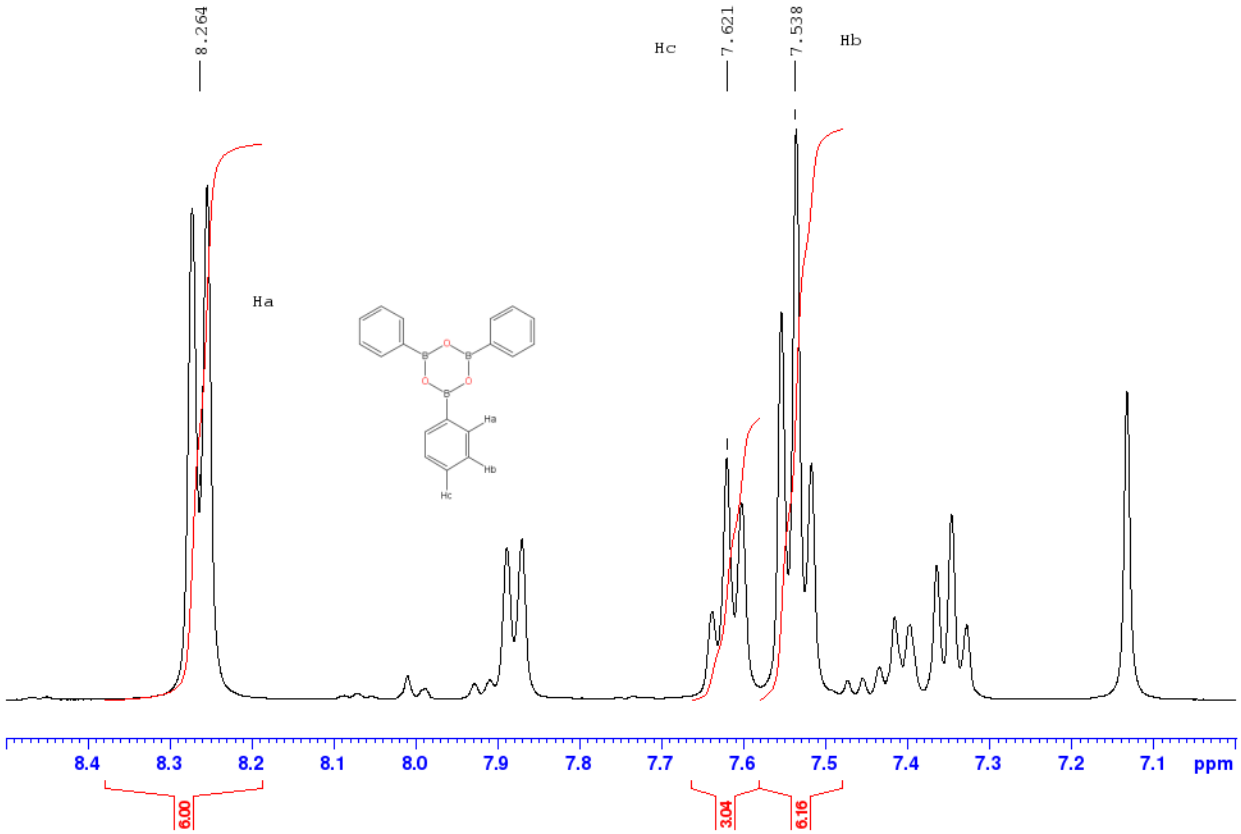


Figure 13. Aromatic Region ^{1}H NMR Triphenylboroxine Microwave Method

Figure 13 is dissimilar to the conventional heating method spectra. Boroxine peaks present around δ 8.25, 7.60, and 7.55 with multiplicity of doublet, triplet, triplet, with integrations of 6, 3, 6 respectively. Signals for boronic acid are present around δ 7.90, 7.40, and 7.35. Based on relative integrations boroxine is the major product and is relatively pure. This spectrum is evidence that the microwave method is vastly superior to convention heating as it produced a product that is more pure and has produced little to no side products as the spectrum is much cleaner.

4-Fluorotriphenylboroxine from microwave heating

^{1}H NMR

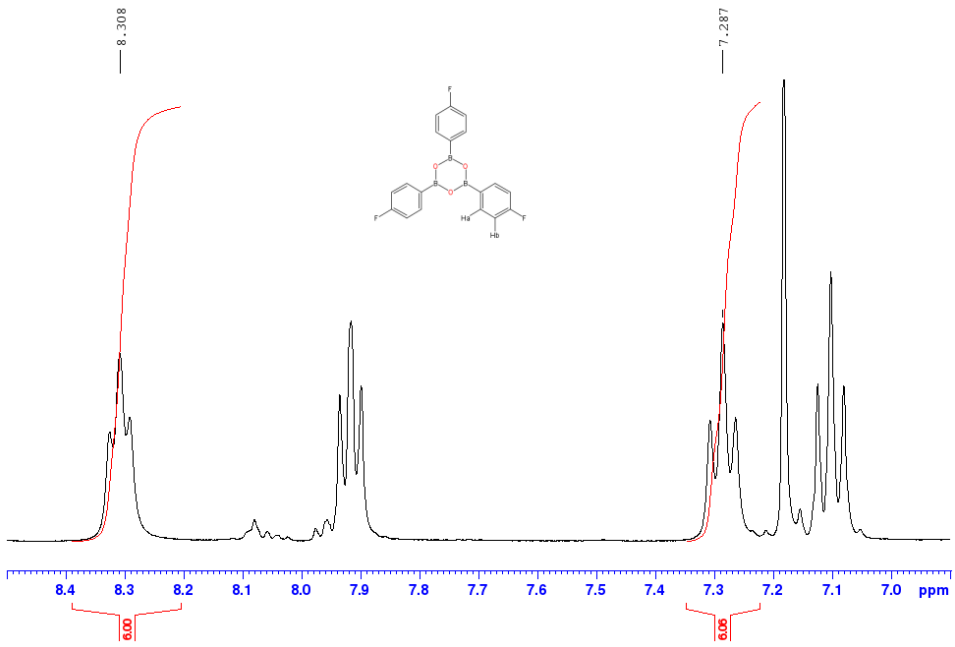


Figure 14. ^{1}H NMR 4-fluorotriphenylboroxine Microwave Method Crash Precipitate

Figure 14 shows the same problem arises as the level of fluorination increases. Both boroxine and boronic acid peaks are present; however, the integrations of each suggest the abundance of boroxine to boronic acid is approximately 1:1. This is outside the acceptable purity for use in a Job's plot without correcting for purity mathematically.

3,4,5-Trifluorotriphenylboroxine from microwave heating

^{1}H NMR

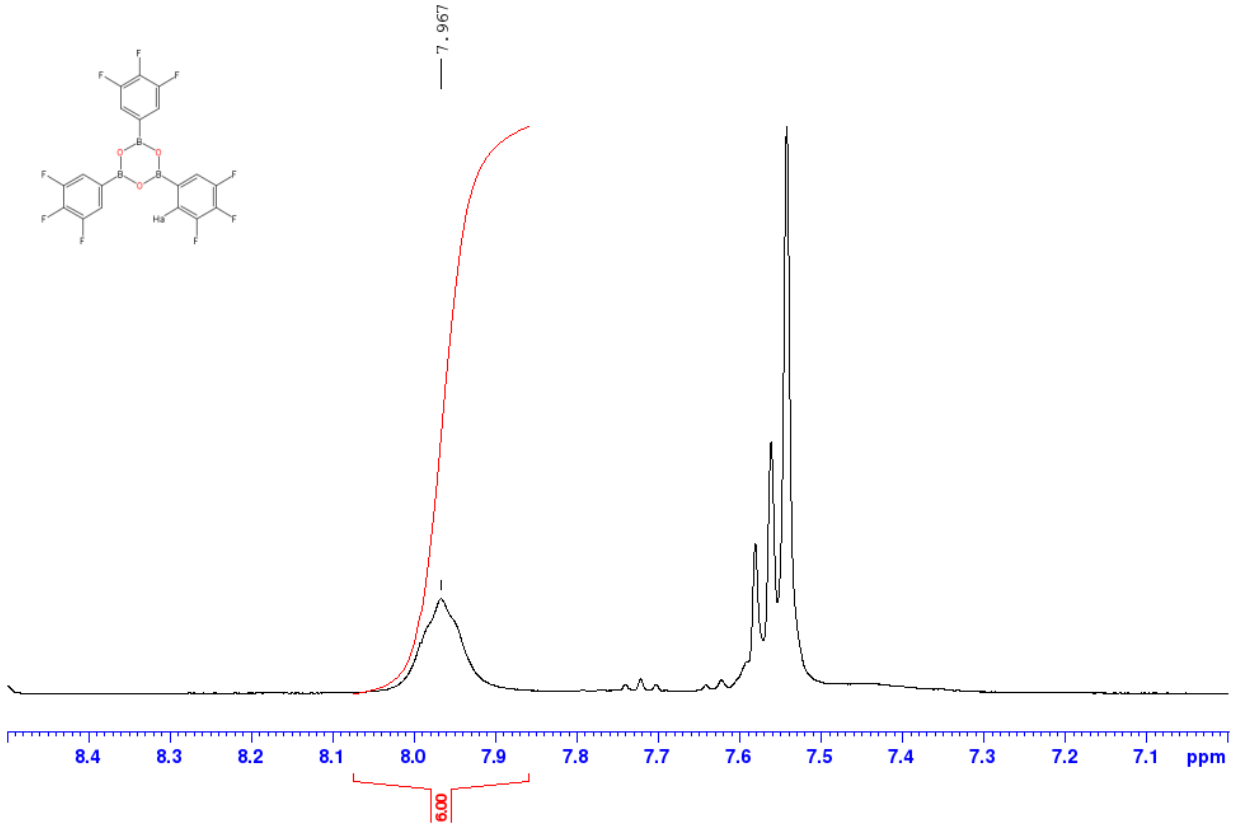


Figure 15. Aromatic Region 3,4,5-trifluorotriphenylboroxine Microwave Method

To continue the trend, **Figure 15** suggests 3,4,5-trifluorotriphenylboroxine was produced, but the relative abundance to boronic acid is even less than that of the 4-fluorotriphenylboroxine. Purification steps would need to be taken or mathematical corrections would need to be done for use in a Job's plot.

It becomes obvious from the NMR that for these reactions a large portion of starting material remains unreacted. This is problematic for creating samples for a Job's plot because it causes the mole fraction value to become highly uncertain. A trend was found in both the %yield of the crude product and of the purity of the crude product as shown below in **Table 1**. As the

level of fluorination increases the yield and purity of the reaction decreases. An explanation for this could be the weakened boron-oxygen bond and increased water sensitivity. Another possible explanation could be in acetone the equilibrium favors the reverse reaction. Suggestions for changes to the procedure are discussed in the Job's plot section.

Table 1. Yield, %Yield of Crude, and Relative Boroxine Abundance %-Boroxine-Conventional heating Method

Boroxine	**Yield (mg)**	**% Yield Crude**	**Relative Boroxine Abundance %**
4-methoxytriphenyl	604.8	98.37	78.56
triphenyl	357.8	85.87	59.24
4-fluorotriphenyl	237.0	57.90	16.63
3,4,5-fluorotriphenyl	82.2	16.67	7.09

Relative boroxine abundance was calculated using equation 3 below.

$$Relative\ Boroxine\ Abundance\ \% = \frac{\sum BXN_{Int}}{\sum BXN_{Int} + \sum BA_{Int}} \cdot 100\% \quad (3)$$

Where BXN_{Int} is the integration of all peaks associated with the boroxine, and BA_{Int} is the integration of all peaks associated with the boronic acid.

Boronates

All boronates were prepared by microwave-assisted heating and characterized by ^{1}H NMR

4-Methoxydiphenylboronate from microwave heating

^{1}H NMR

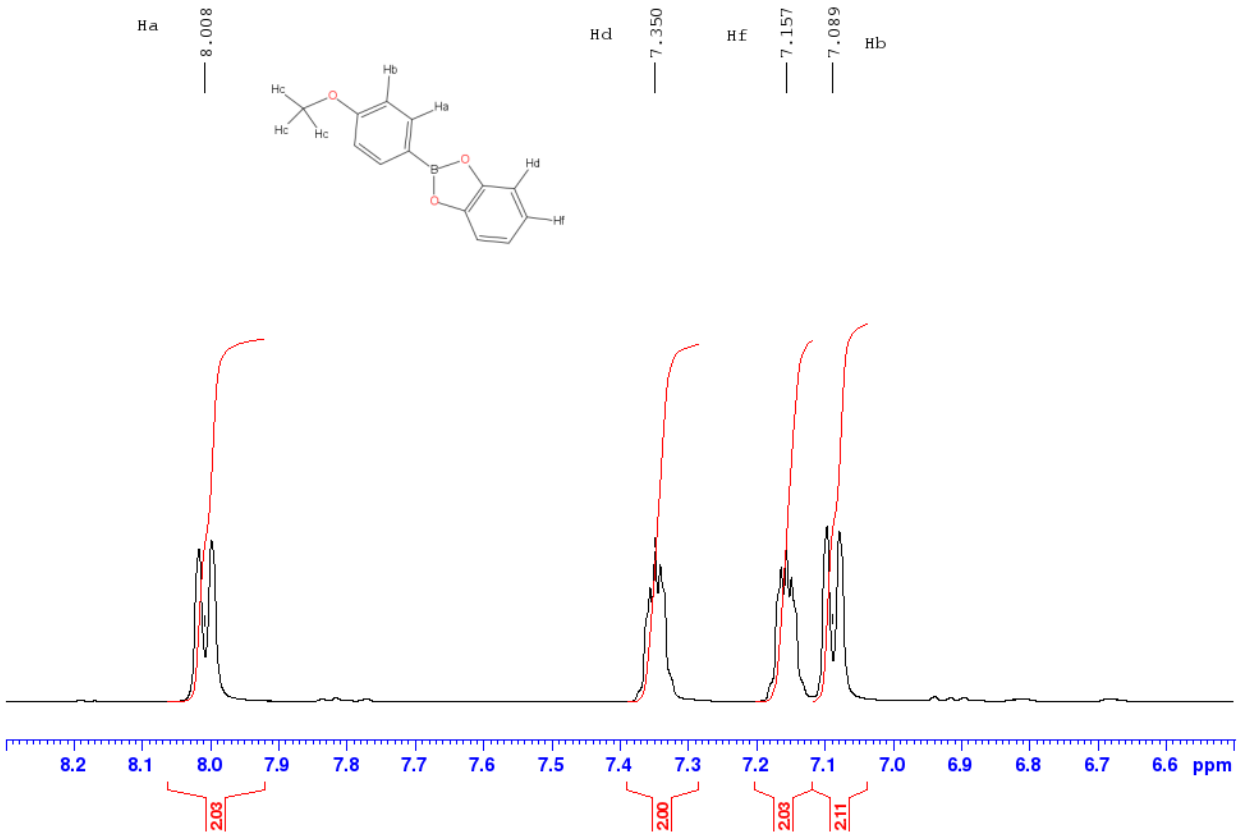


Figure 16. Aromatic Region of 4-methoxydiphenylboronate ^{1}H NMR

The spectrum for 4-methoxydiphenylboronate in **figure 16** is as expected. Peaks around δ 8.00, 7.35, 7.15, and 7.10 with multiplicity of doublet, triplet, triplet, and doublet with integrations of , 2H, 2H, 2H, and 2H respectively. Non-aromatic region is shown below in **figure 17** and shows a signal around δ 3.90, with a multiplicity of singlet and integration of 3H.

^{1}H NMR

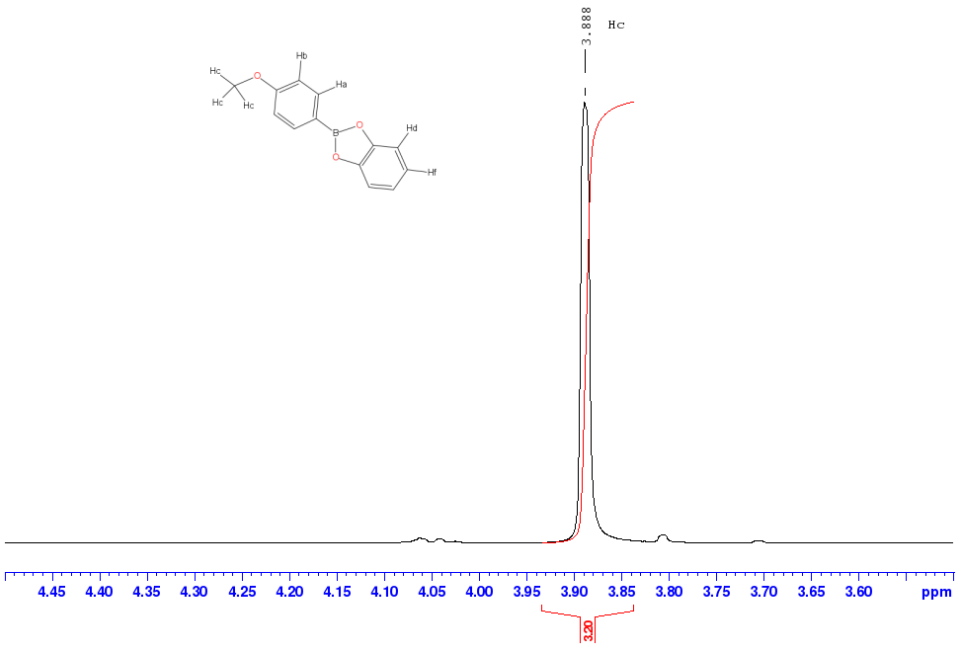


Figure 17. Non-Aromatic Region 4-methoxydiphenylboronate ^{1}H NMR

Diphenylboronate from microwave heating

^{1}H NMR

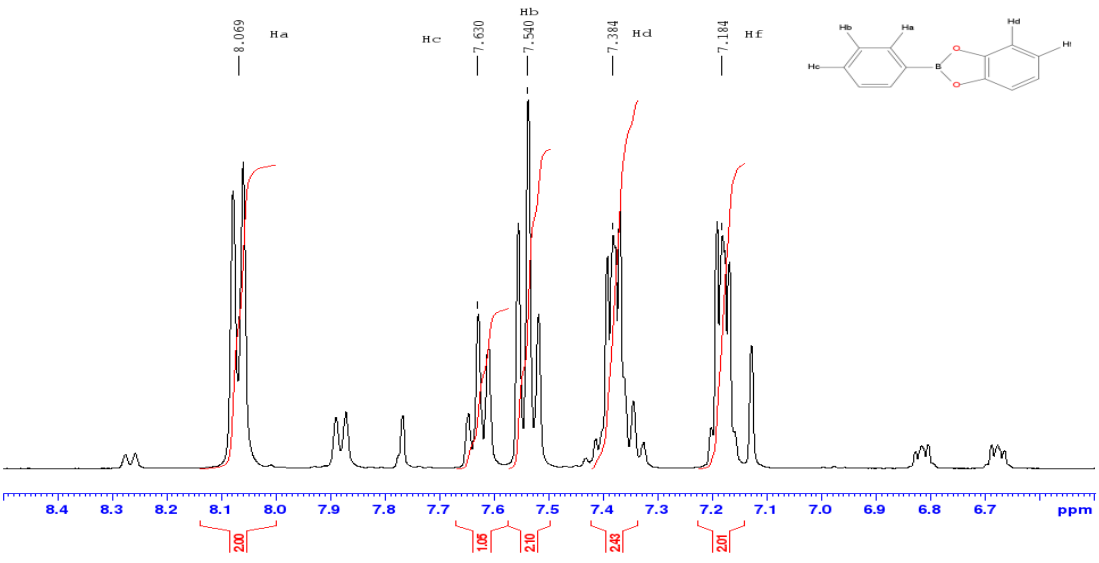


Figure 18. Aromatic Region Diphenylboronate ^{1}H NMR

The spectrum for diphenylboroxine in **Figure 18** is also as expected with major signals around δ 8.05, 7.60, 7.55, 7.40, and 7.20 with multiplicities of doublet, triplet, triplet, multiplet, and multiplet, with integrations of 2H, 1H,2H, 2H, 2H respectively. Minor peaks that correspond to boronic acid are present around δ 7.90, 6.80, and 6.65. The boronic acid peaks are present at such a small relative quantity they can mostly be ignored.

4-*Fluorodiphenylboronate from microwave heating*

^{1}H NMR

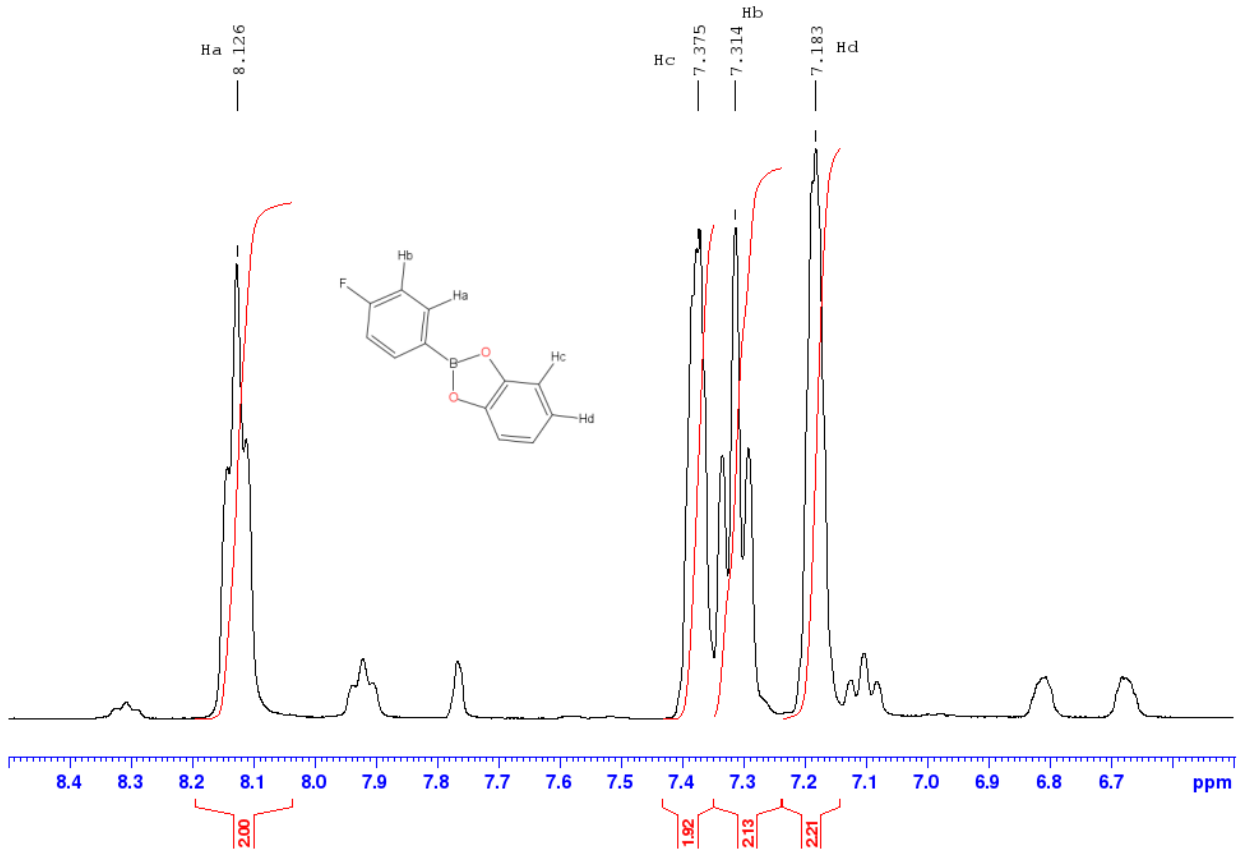


Figure 19. Aromatic Region 4-fluorodiphenylboronate ^{1}H NMR

This ^{1}H NMR spectra in **Figure 19** is also what is expected for the 4-fluorodiphenylboroxine. Peaks around δ 8.10, 7.40, 7.30, and 7.20 with multiplicities of triplet, singlet, triplet, and singlet with integrations of 2H, 2H, 2H, and 2H respectively. The ratio of

boronate to boronic acid is slightly higher than that of diphenylboroxine but it is still majorly boronate.

3,4,5-Trifluorodiphenylboronate from microwave heating

^{1}H NMR

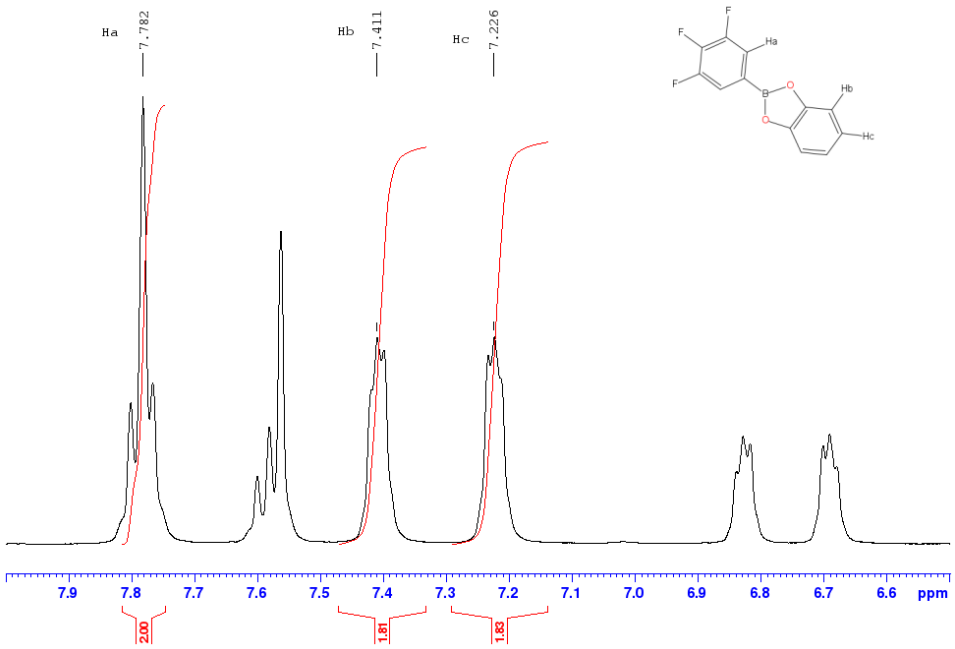


Figure 20. Aromatic Region 2,3,4-trifluorodiphenylboronate ^{1}H NMR

The ^{1}H NMR of 3,4,5-trifluorodiphenylboronate in **Figure 20** suggests that the limit of fluorination for a good synthesis has been reached. The relative ratio of boroxine to boronate is about 70:30 which is outside the acceptable purity for use in a Job's plot. It is possible to correct for purity mathematically; however, the use of relative ^{1}H NMR integrations for molar ratio is less accurate in a 3 component mixture. The large spread of chemical shift also makes the calculation less accurate.

2,3,4,5,6-Pentafluorodiphenylboronate from microwave heating

^{1}H NMR

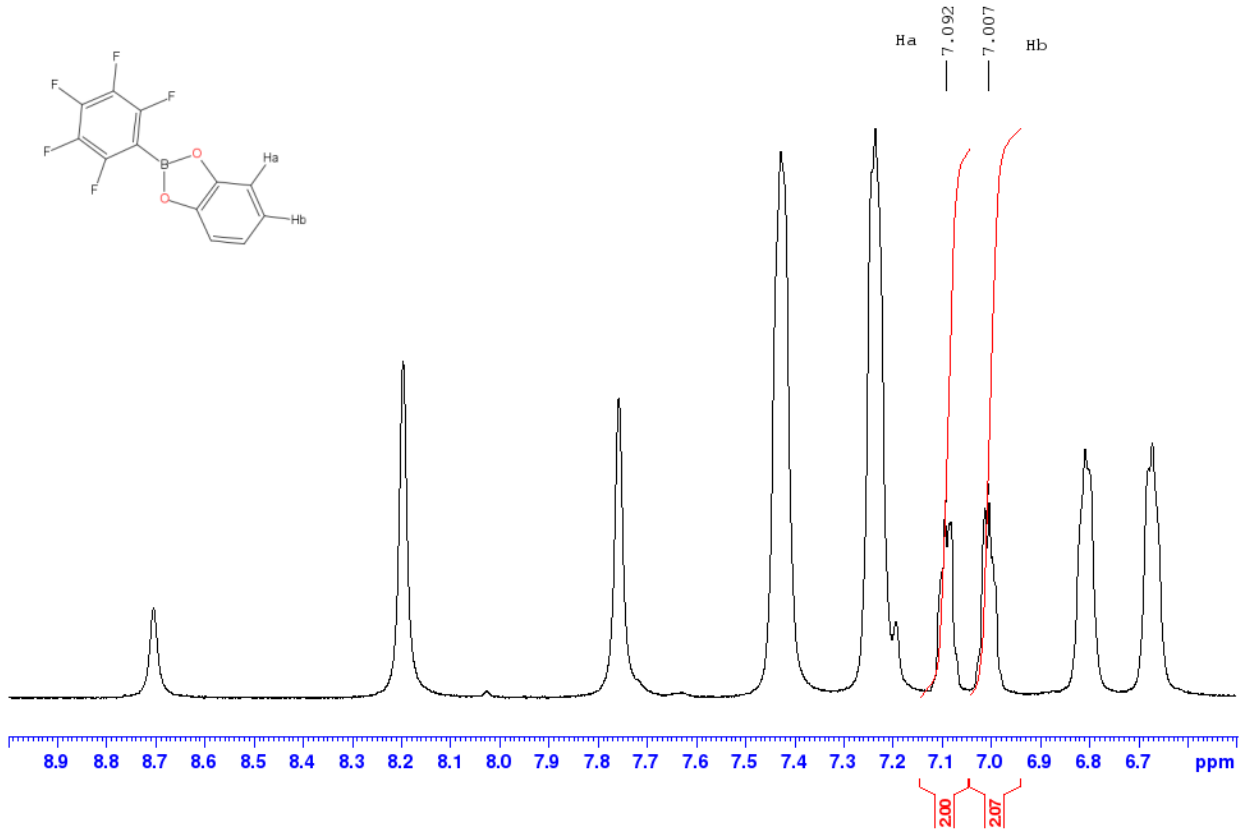


Figure 21. Aromatic Region 2,3,4,5,6-pentafluorodiphenylboronate ^{1}H NMR

Using ^{1}H NMR for characterization this molecule is possible due to the hydrogens on the catechol shown in **Figure 21**. If the product is created the chemical shifts of catechol will change or there will be two sets of catechol peaks corresponding to free catechol, and boronate catechol. There are several unexplainable signals in high relative abundance in the aromatic region.

It is obvious that little boronate was created. With all of the extra peaks that may be side products, correcting mathematically for purity would be difficult if not impossible.

Attempts at purifying boroxines and boronate

Silica Gel Chromatography

Silica gel was the first choice for separating the boronate. Silica TLC plates were spotted with boronic acid, catechol, and the product of boronate reactions. Several solvent systems were used including ethyl acetate:hexanes. Regardless of mixture ratios the product spot always had two spots corresponding to both starting material spots based on rf values. It is speculated that the silica is too acidic for use on boronates and breaks the boron-oxygen bond, converting all boronate back into boronic acid and catechol.

Cellulose Chromatography

To solve for the perceived acidity problem, cellulose chromatography, also known as paper chromatography, was investigated. Cellulose is a neutral stationary phase that should not break any boron-oxygen bonds. The other difference from silica is the polarity of cellulose is much lower and has less affinity for compounds. This creates less separation for polar compounds and was an issue for separating boronate. Even with a solvent system of pure cyclohexenes, the mobile phase was still too polar for proper separation. Once any fraction had material in it, all compounds were present. A likely reason is that the compounds are not soluble enough in non-polar solvents to all dissolve at once which creates a very wide band as it travels through the stationary phase. To solve this problem alumina chromatography was investigated.

Alumina Neutral Chromatography

Alumina neutral chromatography was investigated first because the alumina TLC plates arrived first. Several solvent systems in various ratios were used including 5% methanol:dicloromethane as the most polar. Even with the most polar solvent system, rf values were low at around 0.25 for the furthest travelled spot. This created moderate separation of catechol from the boronate but no separation of boronic acid from boronate. The product spot also had no distinct spot that did not correlate to a starting material. The pH of alumina neutral

can range between 6 and 8. This could have meant that again the boronate did not survive the interaction with the plate. Several columns were run which confirmed that there was not enough separation to use this method.

Alumina Basic Chromatography

This stationary phase was the least suitable of all. Even with the most polar solvent systems short of pure water nothing moved through the column at all. To confirm this a 3cm tall column was eluted with approximately 200mL of elutant and no compounds were present in the fractions.

For reasons of time and material waste, purification attempts were ceased. Attempts to create boroxine were started since the purity of boroxine can be corrected for using calculations.

Complexation of Boroxines and Boronates with Picoline

The general complexation of boronate with picoline is visualized in **figure 22** below.

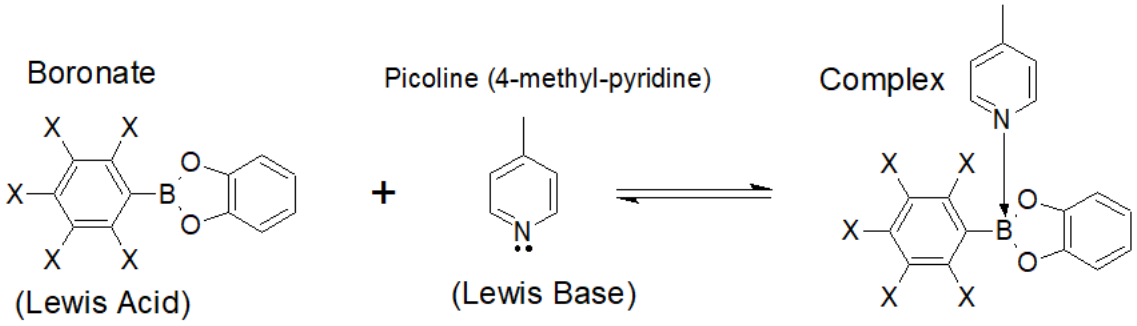


Figure 22. General Complexation of a boronate and picoline

The general complexation of boroxine with picoline is shown below in **figure 23**.

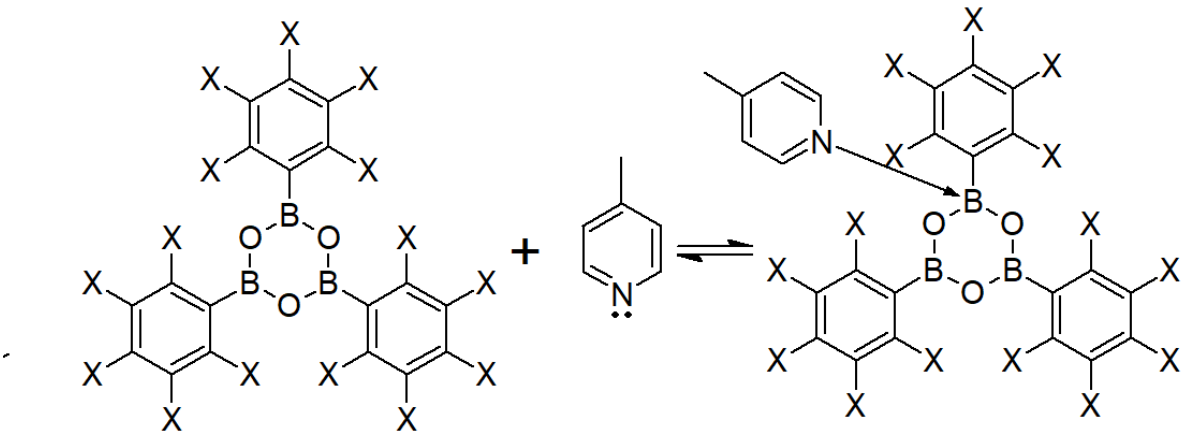


Figure 23. General Complexation of a boroxine and picoline

To achieve this complexation the two molecules simply need to be in solution together. The picoline acts as the Lewis base and the boronate acts as the Lewis acid. This reaction happens on a timescale much shorter than the time scale of the NMR. It would be classified as a fast or very fast reaction for dynamic NMR experiments. The electron donating effect of the picoline is what contributes to the change in chemical shift of the boronate peaks.

Job's Plots

By monitoring the dative bond coordination using ^{1}H NMR, the shape of the Job's plot will be most closely related to an exponential decay (decreasing form) function if the chemical shift of the peak moves up field over the series, or an exponential decay (increasing form) if the chemical shift moves downfield over the series. For these shapes of graphs, the significant point of the curve that corresponds to a [X] value is when the slope is insignificantly small. One way to choose a threshold for this point is to look at the range of points past a suspected [X] value. If the changes appear random and do not keep increasing or decreasing consistently then that range can be used as a threshold. The first point to enter that Y axis range is the point used to calculate [X]. From this [X] value it is rounded to the nearest chemically significant [X] value. The most common values are 0.33, 0.50, 0.66, for a 1:2, 1:1, and 2:1 ratio respectively. If a selected value

is evenly split between two significant values, it's preferred to round up since the purity of boroxine or boronate is not 100%.

Job's plots were done on the following complexes.

4-Methoxytriphenylboroxine:Picoline complex Job's Plot

For the creation of a Job's plot for 4-methoxytriphenylboroxine:Picoline, many ^{1}H NMR spectra were collected. When the series of ^{1}H NMR's are compared a shifting of a peak that corresponds to a proton on the boroxine is observed. **Figure 24** below shows the series of ^{1}H NMR's collected to produce the Job's plot. The series starts at the bottom at [X] ≈ 0.00 and proceeds upward to [X] = 0.33, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75 and 0.80, respectively.

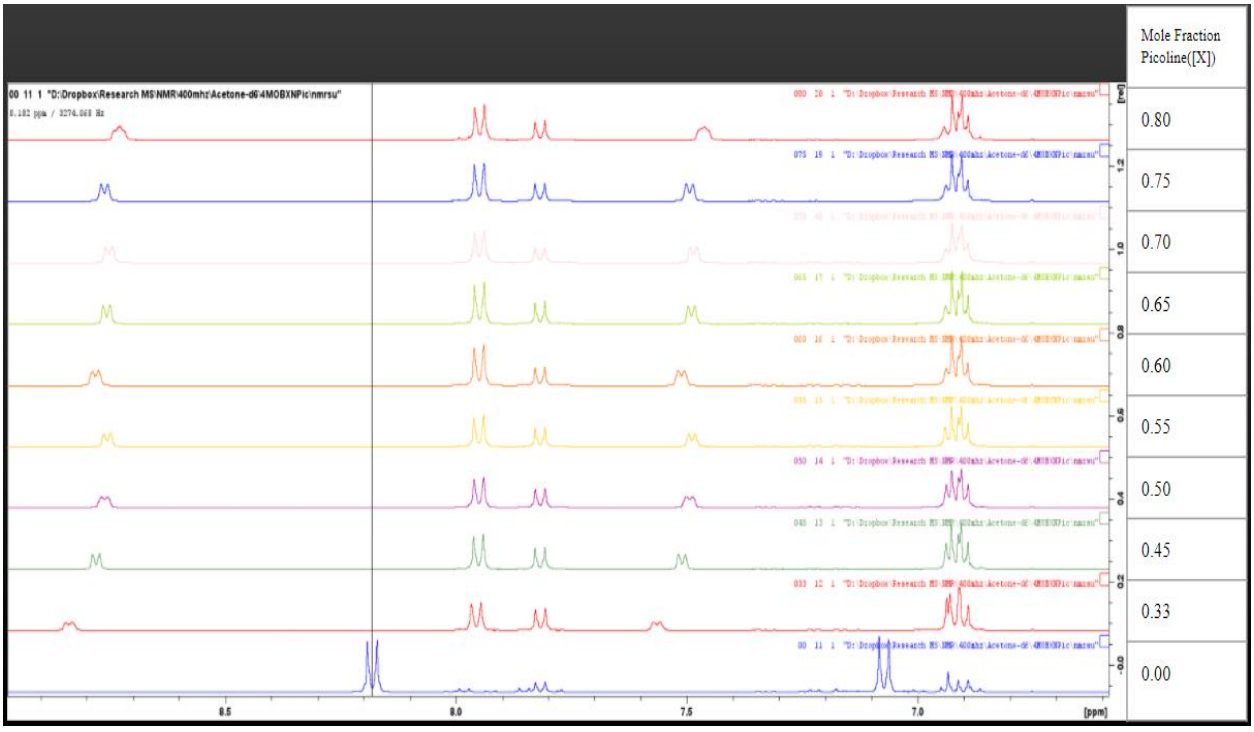


Figure 24. Aromatic Region of 4-methoxytriphenylboroxine:Pic ^{1}H NMR Series

For the data points used in the Job's plot the [X] value is corrected for using the relative integrations of a picoline peak vs a boroxine peak divided by the stochiometric ratio of the peaks.

The peak of interest is the doublet that starts at 8.1 ppm and shifts towards 7.9 ppm. This peak corresponds with Ha of the boroxine as shown in **Figure 25**.

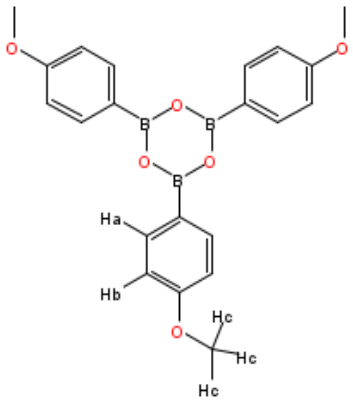


Figure 25. Structure of 4-methoxytriphenylboroxine with labeled protons

This peak was chosen because it did not overlap with any other peaks through the series. It is also important to select a peak that corresponds to a proton on the molecule that stays at a constant concentration. Concentration dependent chemical shifting can be seen in the picoline peaks which are the doublets that continue up field as their concentration increases. From plotting the mole fraction of each sample vs. the chemical shift of the peak of interest and Job's plot was created and is shown in **figure 26** below.

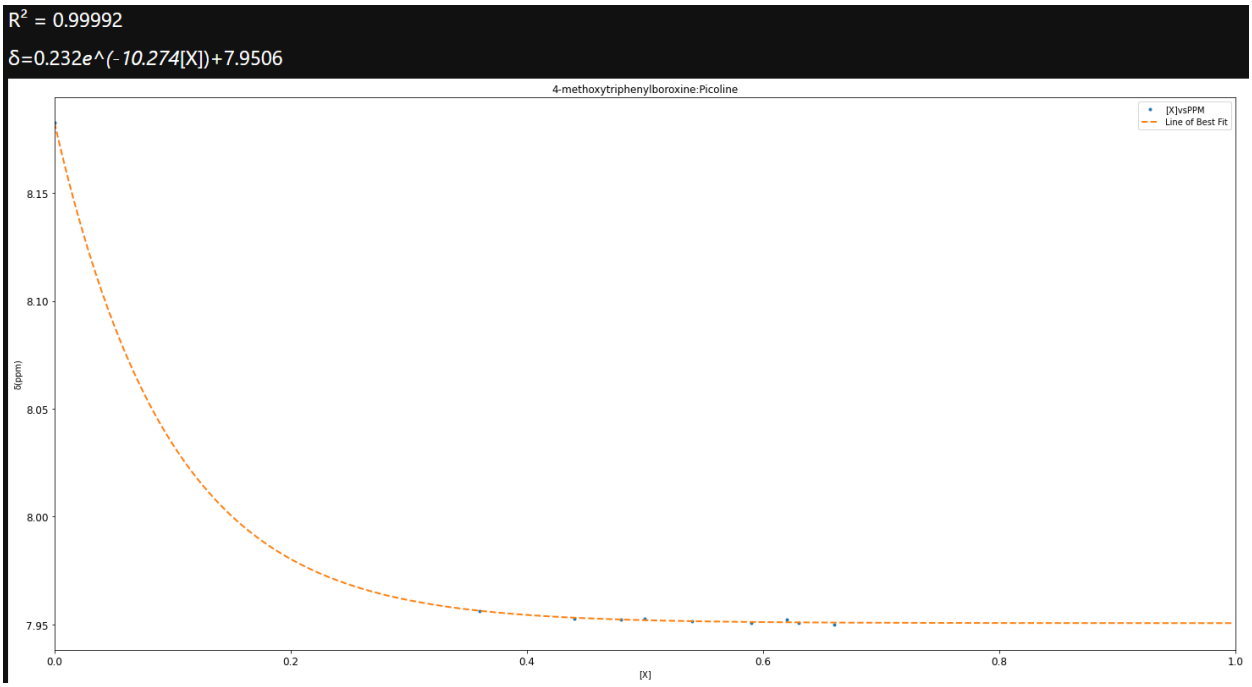


Figure 26. Job's Plot of 4-methoxytriphenylboroxine:Picoline

From the whole figure it is hard to determine visually where the chemical shift stops changing significantly. The Job's plot above is zoomed in below in **figure 27**.

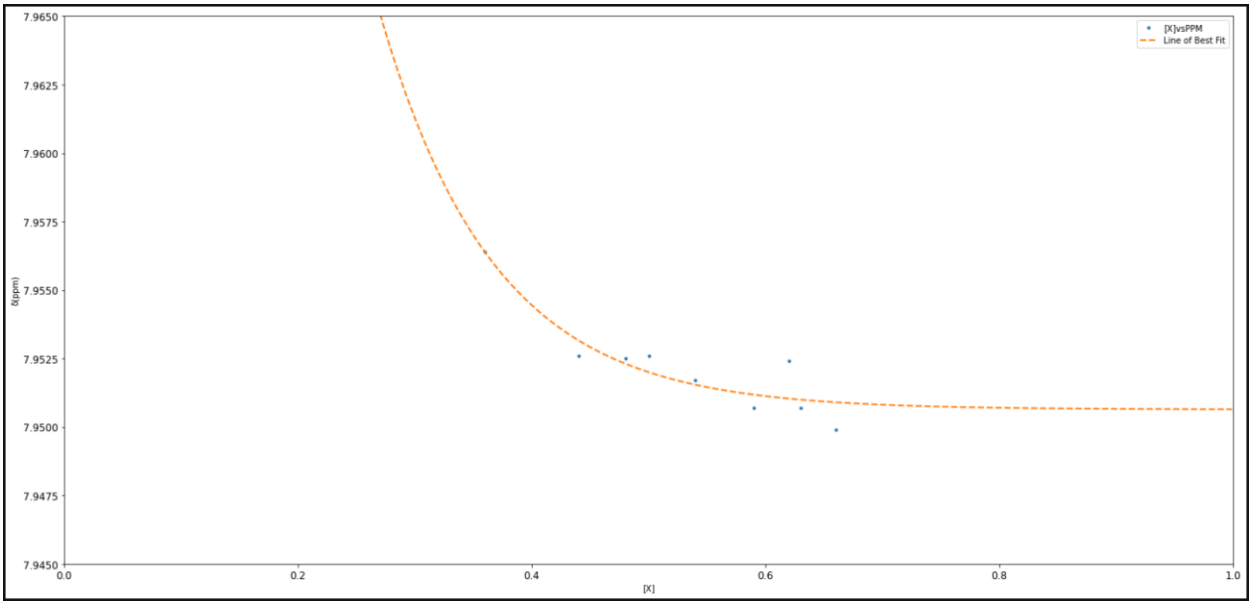


Figure 27. Zoomed Job's Plot of 4-methoxytriphenylboroxine:Picoline

As a Job's plot is a visual graphical method, there is not a standard mathematical method to calculate exact values for n in a non-parabolic function. When zoomed in the Y direction it becomes clear that the actual data points at some points are no longer changing chemical shifts based on changes in chemical environment but are fluctuating due to margins of error in the NMR and sample preparation. From the line of best fit it appears that the function enters the y domain of error at or around a mole fraction value of 0.45. That point is then rounded to the nearest significant mole fraction value which is 0.50 which corresponds to a 1:1 ratio of boroxine to picoline. The n value of 4-methoxytriphenylboroxine:picoline is 1.

Triphenylboroxine:Picoline Complex Job's Plot

The ^{1}H NMR series of triphenylboroxine:Picoline is shown below in **figure 28**. The peak used to generate the Job's plot is signified by a black line.

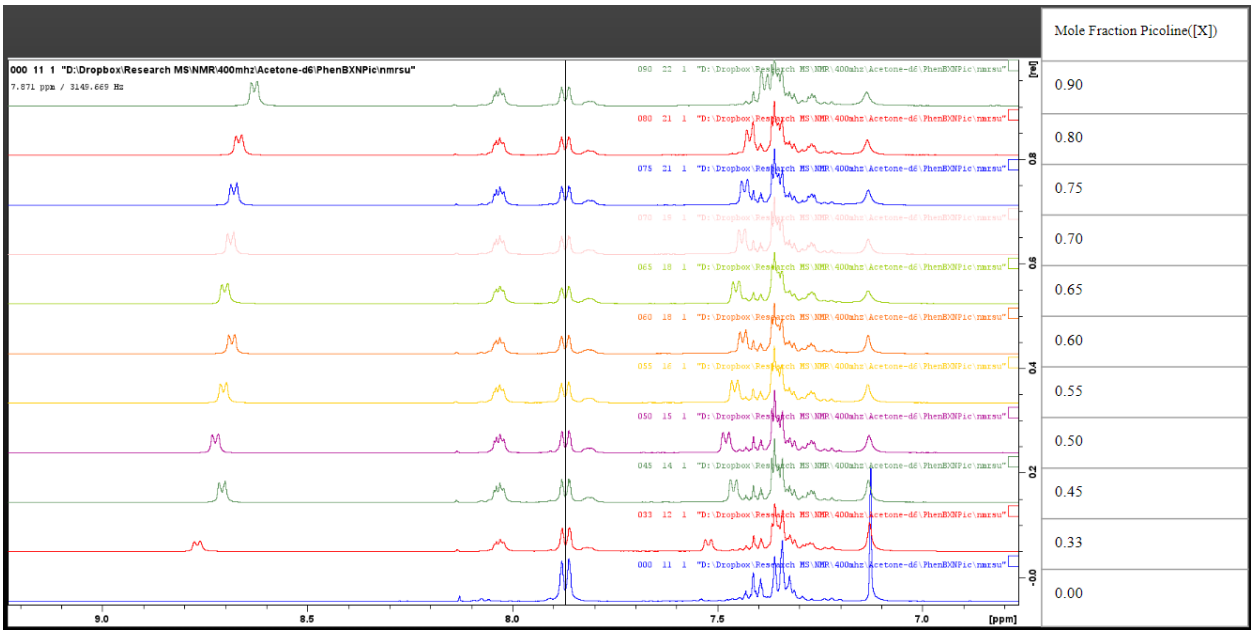


Figure 28. NMR series for triphenylboroxine

It is easy to tell that the peak did not shift over the course of the series. It was believed at the time that this peak was Ha of triphenylboroxine. Job's plot generated for triphenylboroxine is shown below in **figure 29**.

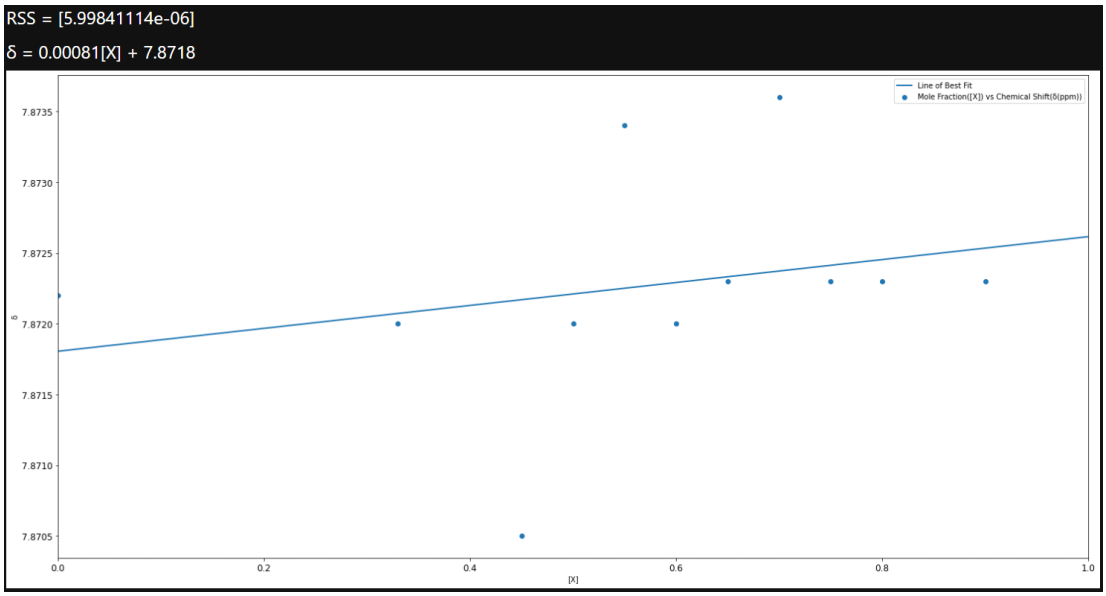


Figure 29. Job's plot for triphenylboroxine:Picoline

It is evident that this chemical system is different than that of 4-methoxytriphenylboroxine. There was no significant change in chemical shift over the range of mole fractions from 1:0 to 1:9. This confirms suspicions that the boroxine may not have been created in high enough purity from the conventional heating method. When compared to the ^{1}H NMR of the boronic acid that peak that was used was the same shift as Ha of the boronic acid. No peaks associated with the boroxine were present in the spectra. Another explanation for why the Job's plot failed is that there is trace amounts of water in the solvents. At the concentrations used to ensure all solids are dissolved without filtering, this trace amount of water is forcing the equilibrium back towards boronic acid.

Although this information is limited, it shows that the chemical shift of phenylboronic acid is not dependent on the concentration of picoline. This is evidence that picoline only binds

to boronic esters and not boronic acids. This development helps make calculations easier when correcting for the purity of boroxine.

Suggested Changes to Job's Plot method for Future Experiments

Several things could be changed in the Job's plot procedure to potentially negate any unwanted outcomes. If using a hygroscopic solvent like *acetone-d6*, the concentration of boroxine should be as high as possible while still fully dissolving. A switch to less hygroscopic solvents would be an good choice but in less polar solvents like chloroform, the excess boronic acid might not fully dissolve and filtering that solid out may remove some boroxine as well. This would probably make the mole fraction value even more uncertain than it already is.

Another idea that could be viable is incorporating a competition reaction where a weak base is added to the reaction mixture before synthesis. This weak base would stabilize the boroxine and help stop trace amounts of water from degrading the molecule. Then when it is added to the sample for a Job's plot, a stronger base which is being studied is added to displace the weak stabilizing base as shown in **Figure 30**.

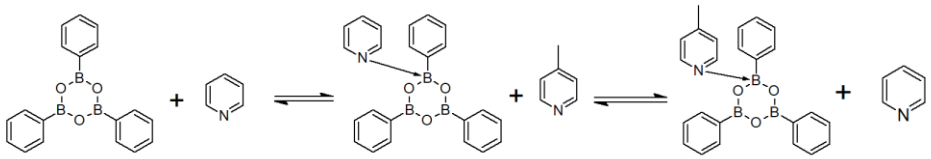


Figure 30. Displacement of Pyridine by Picoline

There are a couple of considerations for this. The stabilizing base would need to be significantly weaker than the coordinating base being studied. The equilibrium between the complexed weak base and complexed strong base would need to favor the strong base so heavily that the weak base could be ignored. The stabilizing base would need to be accounted for in the mass of boroxine used in the stock solutions. For a starting point a Job's plot for 4-methoxyboroxine:Picoline could be created using the modified method and compared to the one

generated in this experiment. If they have a similar shape and the same n value determination the new method would likely be viable on the other boronates.

Why Job's data for all boronates are absent

4-methoxydiphenylboronate, diphenylboronate, 4-fluorodiphenylboronate, 3,4,5-trifluorodiphenylboronate, and 2,3,4,5,6-pentafluorodiphenylboronate were all synthesized for this project. ^{1}H NMR's are included in **appendix A** below. It became apparent quickly that large portions of starting material had not reacted and the boronate would need to be purified before use in a quantitative study. It is not viable to correct for purity based on NMR integrations when there are many different molecules in the system over a wide range of chemical shifts. Several chromatographic purification methods (silica gel, paper, cellulose, alumina) were investigated for separating boronate from boronic acid and catechol.

CHAPTER 3: CONCLUSION

From the successful Job's plot of 4-methoxytriphenylboroxine:Picoline, it appears that the coordination ratio between 4-methoxytriphenylboroxine and picoline is 1:1 in acetone at room temperature.

For other boroxines which have boron atoms more electron deficient than 4-methoxytriphenylboroxine, the sample preparation for the Job's plot method used was incompatible and will need to be adjusted if retried. These modifications would mainly need to address the sensitivity of boroxines to water. Suggestions for these modifications are discussed in the results and discussion section. Many boronates and boroxines were synthesized, albeit at low purity. Purification methods to separate the boronic acids from the boroxines could be further explored.

CHAPTER 4: EXPERIMENTAL

General:

All reactions were performed in 100 mL round bottom flasks (RBF) using magnetic stirring at medium speeds, unless otherwise noted. All boronic acids were purchased from Oakwood Chemical. Catechol was purchased from Matheson Coleman & Bell. Acetone-d6(99.5 atom % D) was purchased from Acros Organic, Picoline was purchased from Tokyo Chemical Industry Company. Both acetone-*d6* and picoline were stored in a low-humidity desiccator. None of the reagents used needed further purification.

^{1}H NMR spectra were measured using a Bruker Ascend 400 Mhz spectrometer and are reported in ppm (multiplicity, integration and coupling constants in Hz), where acetone appears at 2.05 ppm.

Starting Materials:

This research included many starting materials to synthesize boronates, boroxines, and the complexes. Starting materials and target products are summarized in **Tables 2**, **3**, and **4** below.

Table 2. Boronic Acids

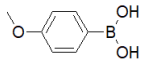
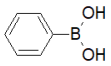
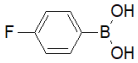
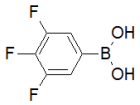
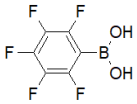
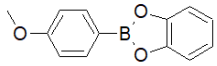
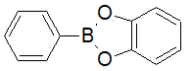
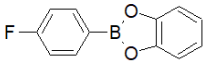
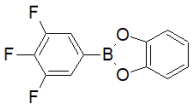
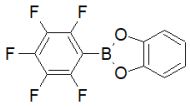
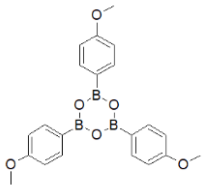
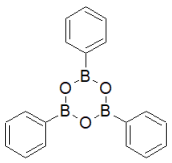
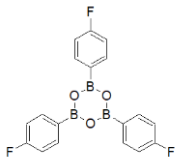
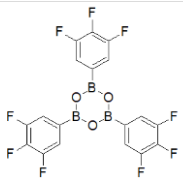
Phenylboronic Acid	Structure	Remarks
4-methoxyphenylboronic acid		Electron donating
phenylboronic Acid		N/A
4-fluorophenylboronic acid		Electron Withdrawing
3,4,5-trifluorophenylboronic acid		Very Electron Withdrawing
2,3,4,5,6-pentafluorophenylboronic acid		Most Electron Withdrawing, Requires F NMR

Table 3. Other Starting Materials

Starting Material	Structure	Remarks
Catechol		Diol
4-methylpyridine(picoline)		Lewis Base

Table 4. Target Products

Product	Structure
4-methoxydiphenylboronate	
diphenylboronate	
4-fluorodiphenylboronate	
3,4,5-trifluorophenylboronate	
2,3,4,5,6-pentafluorodiphenylboronate	
4-methoxytriphenylboroxine	
triphenylboroxine	
4-fluorotriphenylboroxine	
3,4,5-trifluorotriphenylboroxine	

Boroxine Synthesis-Conventional heating Method

Generalized reaction template is show below in **figure 31**.

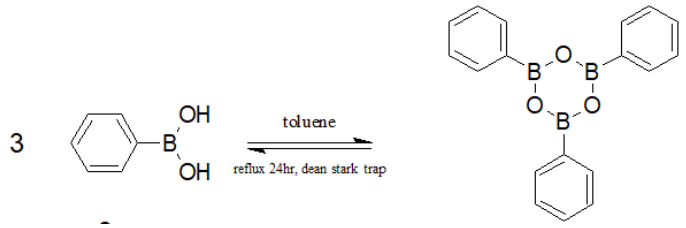
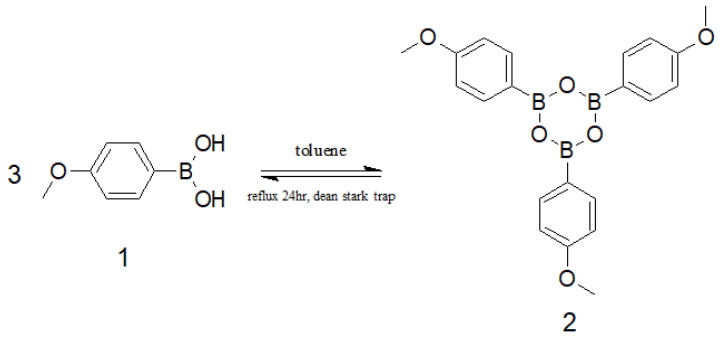


Figure 31. General Boroxine Reaction Template

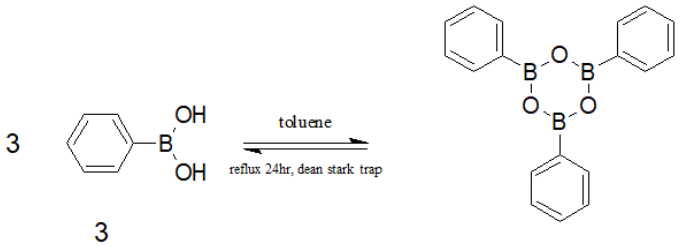
4-Methoxytriphenylboroxine



For the synthesis of 4-methoxytriphenylboroxine 697.5 mg (4.59 mmol) of 4-methoxyphenylboronic acid **1** was added to a 250 mL round bottom flask. Approximately 125 mL of toluene was added. Flask was placed onto a heating mantle and dean stark trap with 4Å molecular sieves and condenser were attached. Reaction mixture was refluxed for 24 hours. After cooling enough to be handled the flask was stoppered and placed into an ice bath for approximately 15 minutes. The mixture was filtered through a filter paper to remove any precipitate. The filtered solution was placed onto the roto-vap and all visible solvent was removed. It was then placed onto the high-vacuum system and was dried for 30 minutes at

approximately 1 torr. Product **2** is a white-yellow crystal, 0.604.8 g (98.37% crude yield).[1]H NMR (400 Mhz, acetone-*d6*) δ 8.182 (d,2H), 7.073(d, 2H), 3.891(s, 9H).

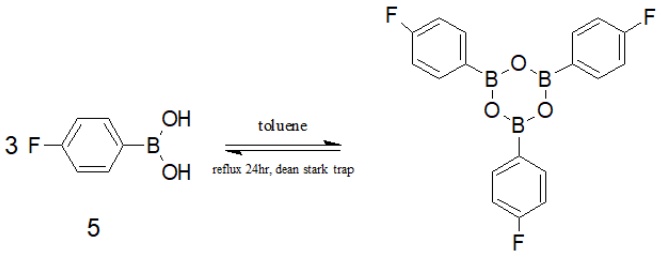
Triphenylboroxine



3 4

For the synthesis of triphenylboroxine, 489.0 mg (4.01 mmol) of phenylboronic acid **3** was added to a 250 mL round bottom flask. Remainder of procedure is identical to 4-methoxytriphenylboroxine. Product **4** was produced, 0.3578 g (85.87% crude yield) a white/yellow crystal. [1]H NMR (400 Mhz, acetone-d6) **δ** 8.272 (d, 6H), 7.631 (t, 3H), 7.544 (t, 6H)

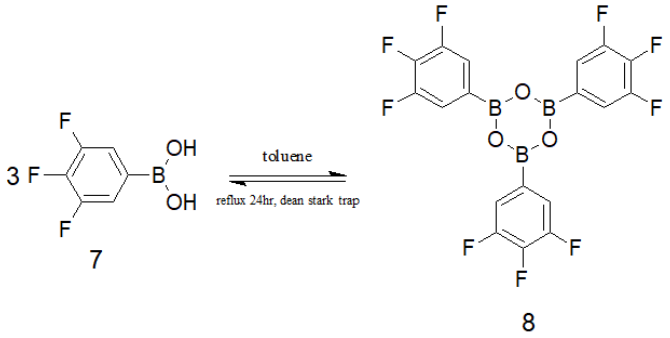
4-Fluorotriphenylborxine:



5 6

For the synthesis of 4-fluorotriphenylborxine, 469.8 mg (3.36 mmol) of 4-fluorophenylboronic acid **5** was added to a 250 mL round bottom flask. Remainder of procedure is identical to 4-methoxytriphenylboroxine. Product **6** is a yellow/brown crystal, 0.2370 g(57.90% crude yield). [1]H NMR (400 MhzMhz, acetone-d6) **δ** 7.322 (m,12H).

3,4,5-Trufluorotriphenylborxine



7 8

For the synthesis of 3,4,5-trufluorotriphenylborxine, 549.5 mg (3.12 mmol) of 3,4,5-fluorophenylboronic acid **7** was added to a 250 mL round bottom flask. Remainder of procedure is identical to 4-methoxytriphenylboroxine. Product **8** is a dark yellow crystal, 0.0822 g(16.67% crude yield). ^{1}H NMR (400 Mhz, acetone-d6) **δ** 7.330 (m, 6H).

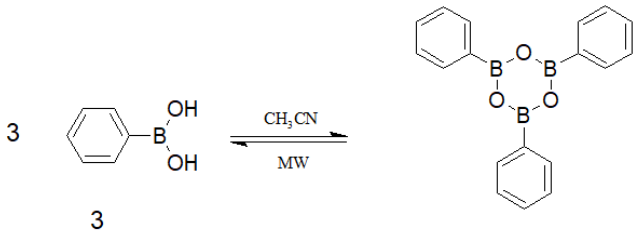
Boroxine Synthesis-Microwave-Assisted Method

General

Microwave assisted synthesis was adapted from Thomas, K. S.[14]

Phenylboronic acid was placed in a 100mL RBF. Approximately 60 mL of 3Å molecular sieve dried acetonitrile was added. Stir bar and boiling stones were added and flask was stoppered. Dean stark trap was filled with approximately 12mL of 1-2mm 3Å molecular sieves. Reaction was run using the Acetonitrile method in the microwave synthesizer. Parameters are as follows: Safety Temp:90C, Pressure: N/A, Power 65 W. Hold Time: 30 min. Flask contents were then filtered to remove any debris (molecular sieve dust, chips of boiling stone, etc.) and placed onto the roto-vap to remove all solvent. To further remove solvent the flask was placed onto the high-vacuum for 30 mins at approximately 1 torr.

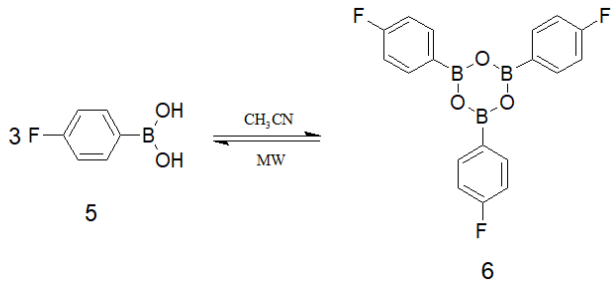
Triphenylboroxine



3 4

103.7 mg (0.85 mmol) of phenylboronic acid **3** was placed in a 100mL RBF. Approximately 60 mL of 3Å molecular sieve dried acetonitrile was added. Stir bar and boiling stones were added and flask was stoppered. Dean stark trap was filled with approximately 12mL of 1-2mm 3Å molecular sieves. Reaction was run using the Acetonitrile method in the microwave synthesizer. Parameters are as follows: Safety Temp:90^{o}C, Pressure: N/A, Power 65 W. Hold Time: 30 min. Flask contents were then filtered to remove any debris (molecular sieve dust, chips of boiling stone, etc.) and placed onto the roto-vap to remove all solvent. To further remove solvent the flask was placed onto the high-vacuum for approximately 30 mins at approximately 1 torr. Product **4** is a white crystal, 0.0874 g(98.87% crude yield). ^{1}H NMR (400 Mhz, acetone-d6) **δ** 8.264 (d, 6H), 7.621 (t, 3H), 7.538 (t, 6H).

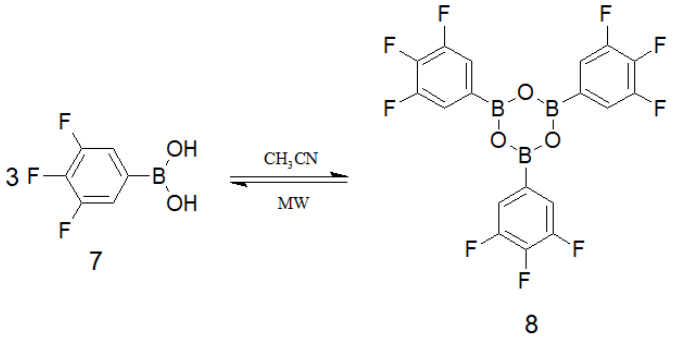
4-Fluorotriphenylboroxine



5 6

118.8 mg (0.85 mmol) of 4-fluorophenylboronic acid was placed in a 100mL RBF. Approximately 60 mL of 3Å molecular sieve dried acetonitrile was added. Stir bar was added and flask was stoppered. Remainder of procedure is identical to the triphenylboroxine method above. During the roto-vap portion of the procedure a large quantity of solid crashed out of solution. The roto-vap was paused and the solid was filtered out using gravity filtration. The remaining solution was placed back onto the roto-vap. Both portions of solids were placed onto the high-vacuum for 30 mins. Product **6** is a yellow crystal, 0.0153 g(14.78% crude yield). ^{1}H NMR (400 Mhz, acetone-d6) **δ** 8.308 (t, 6H), 7.287 (t, 6H).

3,4,5-Trifluorotriphenylboroxine



132.3 mg (0.75 mmol) of 3,4,5-trifluorophenylboronic acid was placed in a 100mL RBF. Approximately 60 mL of 3Å molecular sieve dried acetonitrile was added. Stir bar was added and flask was stoppered. Remainder of procedure is identical to the triphenylboroxine method above. Product **8** is a yellow crystal, 0.0509 g (42.85% crude yield). ^{1}H NMR (400 Mhz, acetone-d6) **δ** 7.967 (s, broad, 6H).

Characterization via ^{1}H NMR. Approximately 10.0 mg of product is added to small vial. 0.70 mL of acetone-d6 is added and all solid is allowed to dissolve. The solution is extracted via glass pipette and placed into an NMR tube. If all of the solid does not dissolve it is filtered through a kimwipe packed into a glass pipette. The sample is placed into the NMR and

allowed to equilibrate to a constant spin and temperature. NMR parameters are as follows: Frequency: 400 Mhz, Pulse Width: 7.59 µs, Acquisition Time: 3.9976959 s, Number of Points: 65536, Spectral Width 20.4850 ppm, Molecule Probed: Proton, Scans: 16. Additional experiment parameters are inherited from method H Proton.

General Boronate Synthesis

Generalized reaction template is displayed in **figure 31** below.

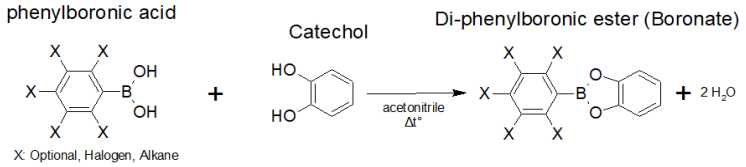


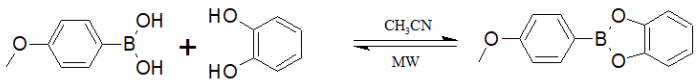
Figure 32. General Boronate Reaction Template

Reaction was adapted from Ritchey, J,M's synthesis of Phenyl-1,3,2-dioxyborolane[15] starting from commercially purchased catechol and boronic acids. The microwave-assisted synthesis of fluorinated boronates used is achieved by a Suzuki condensation reaction between a boronic acid with the desired fluorination, and catechol. Stoichiometric masses of boronic acid and catechol are added to a 100mL round bottom flask in a 1:1 ratio. Approximately 50mL of acetonitrile or ethyl acetate is added and the reaction mixture is placed into the microwave synthesizer. Dean stark trap is filled with 3Å molecular sieves and condenser is placed on top. Typical microwave procedure is as follows: Target temperature- Reflux, Prestirring-2:00 min, Ramp Time-15:00 min, Hold Time-15:00 min, Cooling Time≈20:00 min , Total Time≈55:00. After cooling until 50°C the flask is capped and left overnight. Contents are roto-vaped until visibly dry and placed onto the high-vacuum for 30 minutes to an hour for further drying. The product is a white crystalline solid which is characterized via ^{1}H NMR and melting point. Each boronate is synthesized from the respective boronic acid, all other steps are identical.

^{1}H NMR:

For qualitative characterization via ^{1}H NMR, approximately 10.0 mg is weighed and placed into a sample vial. A 0.70 mL volume of acetone-*d6* is added to the vial via glass syringe. Once all solid is dissolved, the solution is extracted by glass pipette and all the contents are placed into a standard ^{1}H NMR tube and capped. If all of the solid does not dissolve it is filtered through a kimwipe packed into a glass pipette. The sample is placed into the NMR and allowed to equilibrate to a constant spin and temperature. NMR parameters are as follows: Frequency: 400 Mhz, Pulse Width: 7.59 µs, Acquisition Time: 3.9976959 s, Number of Points: 65536, Spectral Width 20.4850 ppm, Molecule Probed: Proton, Scans: 16. Additional experiment parameters are inherited from method H Proton

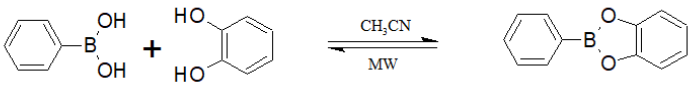
4-Methoxydiphenylboronate



1 9 10

256.6 mg (1.69 mmol) of 4-methoxyphenylboronic acid **1** and 137.7 mg (1.25 mmol) of catechol **9** were added to a 100 mL round bottom flask. Remainder of the procedure is identical to the general procedure listed above. Product is a white crystal, 0.2850 g(100.82% crude yield). ^{1}H NMR (400 Mhz, acetone-d6) **δ** 8.008 (d, 2H), 7.350 (t, 2H), 7.157 (t, 2H), 7.089 (d, 2H), 3.888 (s, 3H).

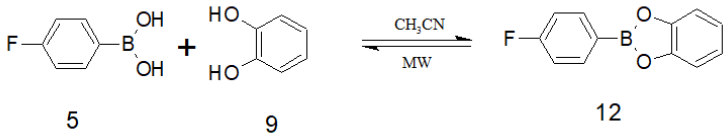
Diphenylboronate



3 9 11

331.4 mg (2.72 mmol) of phenylboronic acid**3** and 312.5 mg (2.84 mmol) of catechol **9** were added to a 100 mL round bottom flask. Remainder of the procedure is identical to the general procedure listed above. Product is white crystal, 0.572 g(107.54% crude yield). ^{1}H NMR (400 Mhz, acetone-d6) **δ** 8.069 (d, 2H), 7.630 (t, 1H), 7.540 (t, 2H), 7.384 (m, 2H), 7.184 (m, 2H).

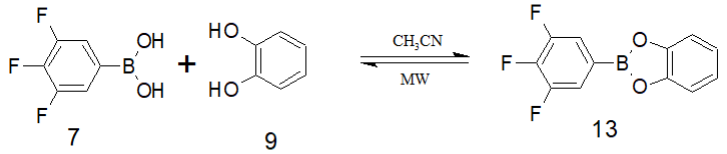
4-Fluorodiphenylboronate



5 9 12

4-fluorodiphenylboronate was synthesized by a slightly different method than above. 219.6 mg (1.57 mmol) of 4-fluorophenylboronic acid **5** and 183.3 mg (1.66 mmol) catechol **9** were added to 50mL round bottom flask. Approx. 25 mL of acetonitrile was added and the mixture was microwave synthesized, refluxed with dean stark trap with 3A molecular sieves, with a total reflux time of 55 mins. Product is a white/yellow crystal. ^{1}H NMR (400 Mhz, acetone-d6) **δ** 8.126(t, 2H), 7.375(m, 2H), 7.314(t, 2H),7.183(m, 2H).

3,4,5-Trifluorodiphenylboronate

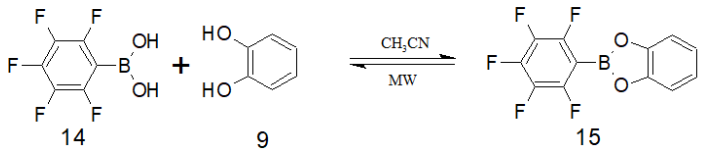


7 9 13

299.7 mg (1.70 mmol) of 3,4,5-trifluoroboronic acid **7** and 206.9 mg (1.25 mmol) of catechol **9** were added to a 100 mL round bottom flask. Approximately 60 mL of ethyl acetate was added to the flask. Remainder of the procedure is identical to the general procedure listed

above. Product is yellow crystal. ^{1}H NMR (400 Mhz, acetone-d6) **δ** 7.782 (t, 2H), 7.411 (t, 2H), 7.226 (t, 2H).

2,3,4,5,6-Pentafluorodiphenylboronate



For the synthesis of 2,3,4,5,6-pentafluoro-boronate, 256.6 mg (1.21 mmol) of 2,3,4,5,6-pentafluoro-boronic acid **14** and 137.7 mg (1.25 mmol) of catechol **9** were added to a 100 mL round bottom flask. Approximately 60 mL of ethyl acetate was added to the flask. Remainder of the procedure is identical to the general procedure listed above. Product is yellow/brown crystal, 0.3243 g(93.64% crude yield). ^{1}H NMR (400 Mhz, acetone-d6) **δ** 7.092 (m, 2H), 7.007 (m, 2H).

Sample Preparation For the Creation of a Job's Plot-Microwave Assisted Synthesis Products

Stock Solutions

For the creation of the stock solutions used in the Job's plot samples, a mass of boroxine was added to a volumetric flask. Distilled and dried acetone was added to the volumetric flask to half the total volume and the flask was swirled to dissolve all solids. The flask was filled to the mark after all solids had dissolved. These stock solutions were plugged with a rubber septum and wrapped in parafilm when not in use to prevent solvent evaporation. The masses of boroxine, volume of picoline and molarity of final solution are summarized in **Table 5** below. Molarity of solution assumes that the boroxine is 100% pure.

Table 5. Summary of Stock Solution Quantities

Stock Solution (Microwave Products)	**Mass Solute(mg)**	**Volume(mL)**	**Molarity Solution(M)**
triphenylboroxine	39.9	50.0	0.00256
4-fluorotriphenylboroxine	15.3	10.0	0.00418
3,4,5-trifluorotriphenylboroxine	N/A	N/A	N/A
Picoline	0.21 (mL)	100.0	0.023

Due to the problems associated with 4-fluorotriphenylboroxine and the low abundance of 3,4,5-fluorotriphenylboroxine, a stock solution for 3,4,5-fluorotriphenylboroxine was not created.

Sample Preparation

For each sample to be used in the Job's plot, a volume of each stock solution, boroxine and picoline respectively are combined in a 20 mL scintillation vial. This solution is briefly placed onto the roto-vap to remove the non-deuterated solvent. The sample material is then dissolved in 0.5 mL deuterated solvent, in this case that solvent is acetone-*d6*. The new solution is placed in an NMR tube, capped, and a ^{1}H NMR is taken of it.

Triphenylboroxine:Picoline

Sample preparation quantities for triphenylboroxine's Job's plot is summarized below in **Table 6**.

Table 6. Triphenylboroxine Sample Preparation Quantities of Stock Solutions

Desired Mole Fraction Picoline([X]	**Volume Triphenylboroxine Stock Solution (mL)**	**Volume Picoline Stock Solution (mL)**
0.00	0.85	0.00
0.33	0.85	0.05
0.40	0.85	0.07
0.45	0.85	0.09
0.50	0.85	0.11
0.55	0.85	0.13
0.60	0.85	0.16
0.65	0.85	0.20
0.70	0.85	0.25
0.75	0.85	0.32
0.80	0.85	0.43
0.90	0.85	0.96

These volumes assume that the product is 100% pure. If the boroxine stays at equilibrium the mole fraction values are accurate enough to give a proper n value. As will be discussed later this is not necessarily true for triphenylboroxine.

4-Ffluorotriphenylboroxine:Picoline

After the NMR data of triphenylboroxine was analyzed, significant uncertainties about boroxine concentration in sample solutions were brought to light. Only the first 0.00 mole fraction sample was made and tested. The quantities are summarized in **Table 7** below.

Table 7. First Sample Made for 4-Fluorotriphenylboroxine:Picoline

Mole Fraction Picoline	**Volume Boroxine Solution (mL)**	**Volume Picoline Solution (mL)**
0.00	0.77	0.00

It became clear that 4-fluorotriphenylboroxine was subject to the same problems that arose with triphenylboroxine. These problems will be discussed in greater detail in the results and discussion section.

Variable Concentration Dynamic NMR Series, For the Creation of a Job's Plot-Conventional heating Products

For the creation of a Job's plot, boroxine and picoline were combined in varying mole fractions and then dissolved in deuterated solvent.

Stock Solutions

To create each stock solution to be used for the Job's plot, a mass of solute was dissolved in a volume of solvent. **Table 8** below summarizes the masses and volumes of boroxine and picoline used to create the stock solutions of known concentration used in this dynamic NMR experiment.

Table 8. Summary of Quantities used to Create Stock Solutions

Stock Solution (Conventional heating Products)	**Mass Solute (mg)**	**Volume (mL)**	**Molarity Solution (M)**

4-methoxytriphenylboroxine	201.0	100.0	0.0050
triphenylboroxine	150.3	100.0	0.0048
3,4,5-trifluorotriphenylboroxine	47.3	50.0	0.0051
Picoline	0.1550 (mL)	100.0	0.0150

Sample Preparation

For the samples used in this dynamic NMR experiment the two stock solutions were mixed in the appropriate ratios to give the desired mole fractions of Picoline. These samples were then placed on the roto-vap until no visible solvent was left. The resulting solid was dissolved in 0.5 mL of acetone-*d6* and placed into an NMR tube and capped.

4-methoxytriphenylboroxine with Picoline:

Table 9 below summarizes the volumes of each stock solution used to create the samples for 4-Methoxytriphenylboroxine:Picoline.

Table 9. Sample Preparation Volumes for 4-methoxytriphenylboroxine: Picoline

Mole Fraction Picoline [X]	**Volume Boroxine Stock (mL)**	**Volume Picoline Stock (mL)**
0.00	1.00	0.00
0.33	1.00	0.16
0.45	1.00	0.27
0.50	1.00	0.33
0.55	1.00	0.41
0.60	1.00	0.50
0.65	1.00	0.62

0.70	1.00	0.78
0.80	1.00	1.00
0.90	1.00	3.00

The vials containing the volumes of stock solution were capped, swirled, and allowed to sit for 15 minutes. Each vial was then roto-vaped until no solvent was visible. The 0.00 mole fraction sample was white crystals while the complexed samples were transparent oils.

Triphenylboroxine-Conventional heating:Picoline

Table 10 below summarizes the volumes of each stock solution used to create the samples for triphenylboroxine:Picoline.

Table 10. Sample Preparation Volumes for 4-Methoxytriphenylboroxine: Picoline

Molar Ratio Picoline [X]	**Volume Boroxine Stock (mL)**	**Volume Picoline Stock (mL)**
0.00	1.04	0.00
0.33	1.04	0.16
0.45	1.04	0.27
0.50	1.04	0.33
0.55	1.04	0.41
0.60	1.04	0.50
0.65	1.04	0.62
0.70	1.04	0.78
0.75	1.04	1.00
0.8	1.04	1.34

0.9	1.04	3.00

The vials containing the volumes of stock solution were capped, swirled, and allowed to sit for 15 minutes. Each vial was then roto-vaped until no solvent was visible. The 0.00 mole fraction sample was white crystals while the complexed samples were transparent oils.

3,4,5-Trifluorotriphenylboroxine-Conventional heating:Picoline

Table 11 below summarizes the volumes of each stock solution used to create the samples for triphenylboroxine:Picoline.

Table 11. Sample Preparation Volumes for 3,4,5-trifluorotriphenylboroxine: Picoline

Molar Ratio Picoline [X]	**Volume Boroxine Stock (mL)**	**Volume Picoline Stock (mL)**
0.00	0.98	0.00
0.33	0.98	0.16
0.45	0.98	0.27
0.50	0.98	0.33
0.55	0.98	0.41
0.60	0.98	0.50
0.65	0.98	0.62
0.70	0.98	0.78
0.75	0.98	1.00
0.8	0.98	1.34
0.9	0.98	3.00

The vials containing the volumes of stock solution were capped, swirled, and allowed to sit for 15 minutes. Each vial was then roto-vaped until no solvent was visible. The 0.00 mole fraction sample was white crystals while the complexed samples were transparent oils.

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APPENDIX A: FIGURES

4-methoxyboronic acid and derivatives.

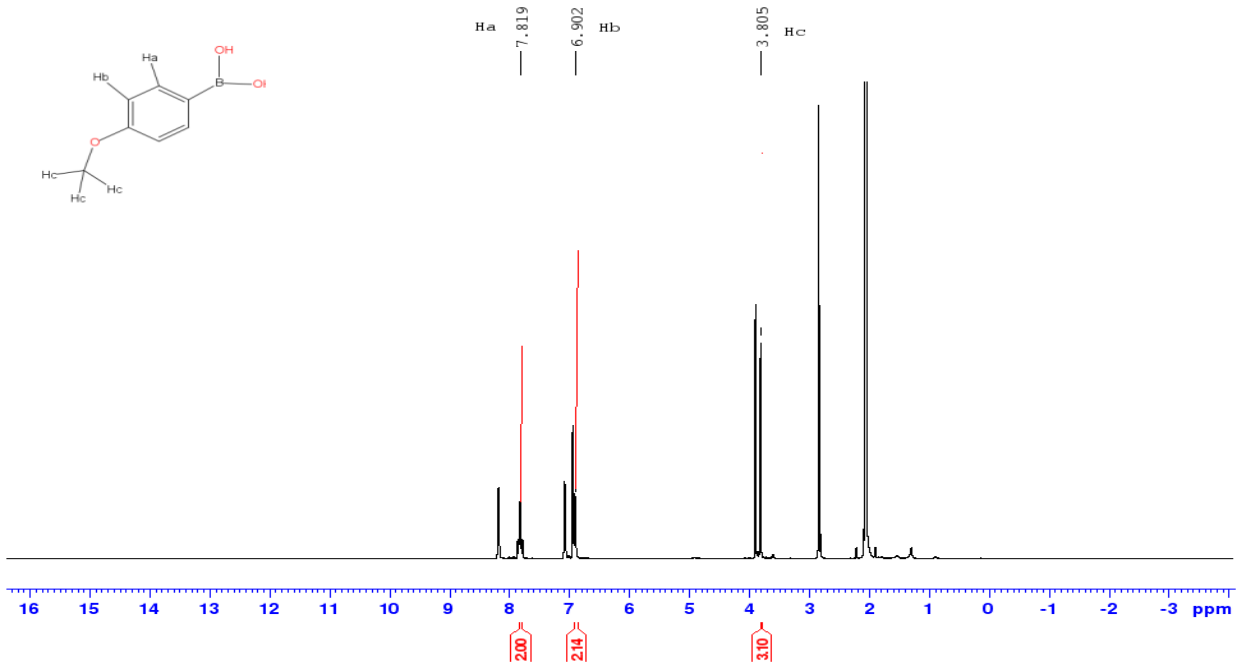

Figure A1. ^{1}H NMR of 4-methoxyboronic acid

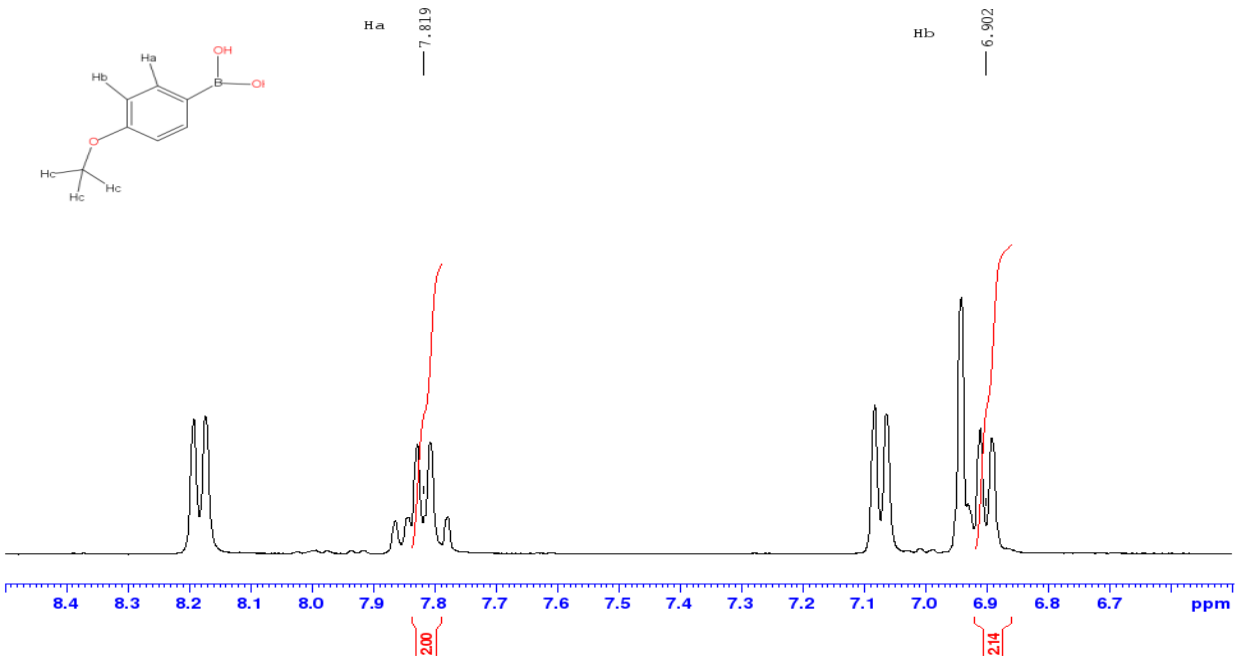

Figure A2. Aromatic Region ^{1}H NMR of 4-methoxyboronic acid

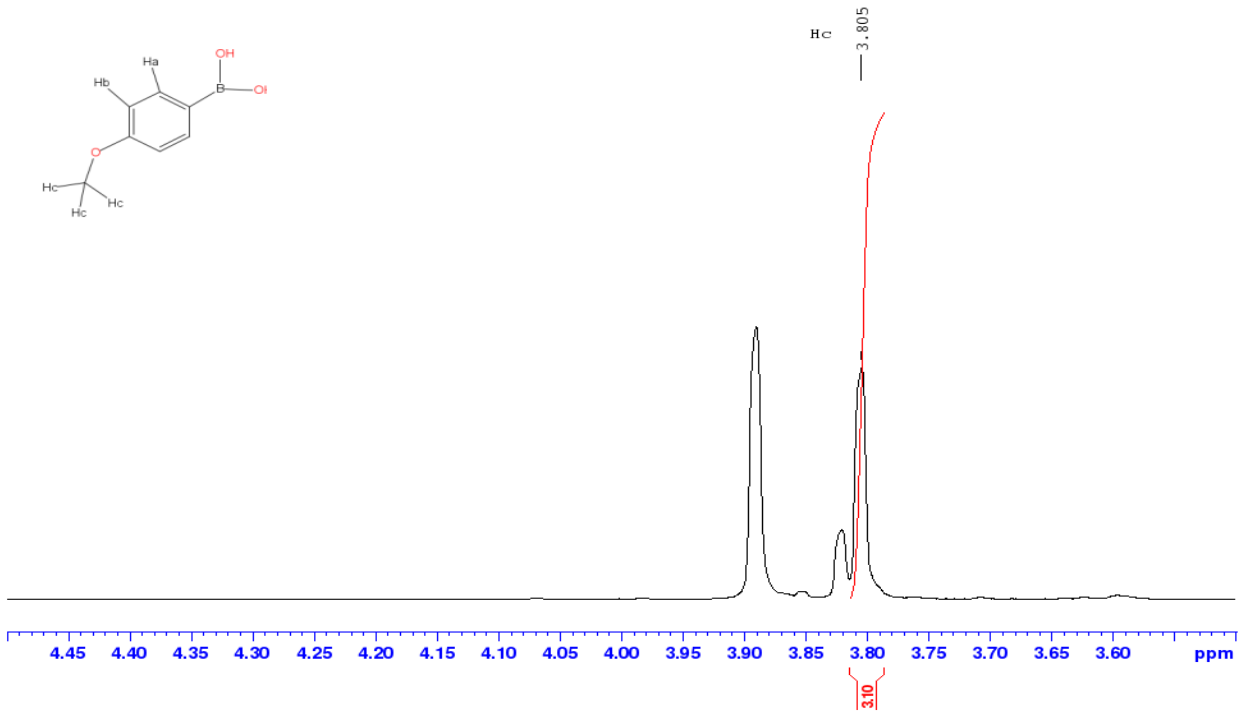

Figure A3. Non-aromatic Region ^{1}H NMR of 4-methoxyboronic acid

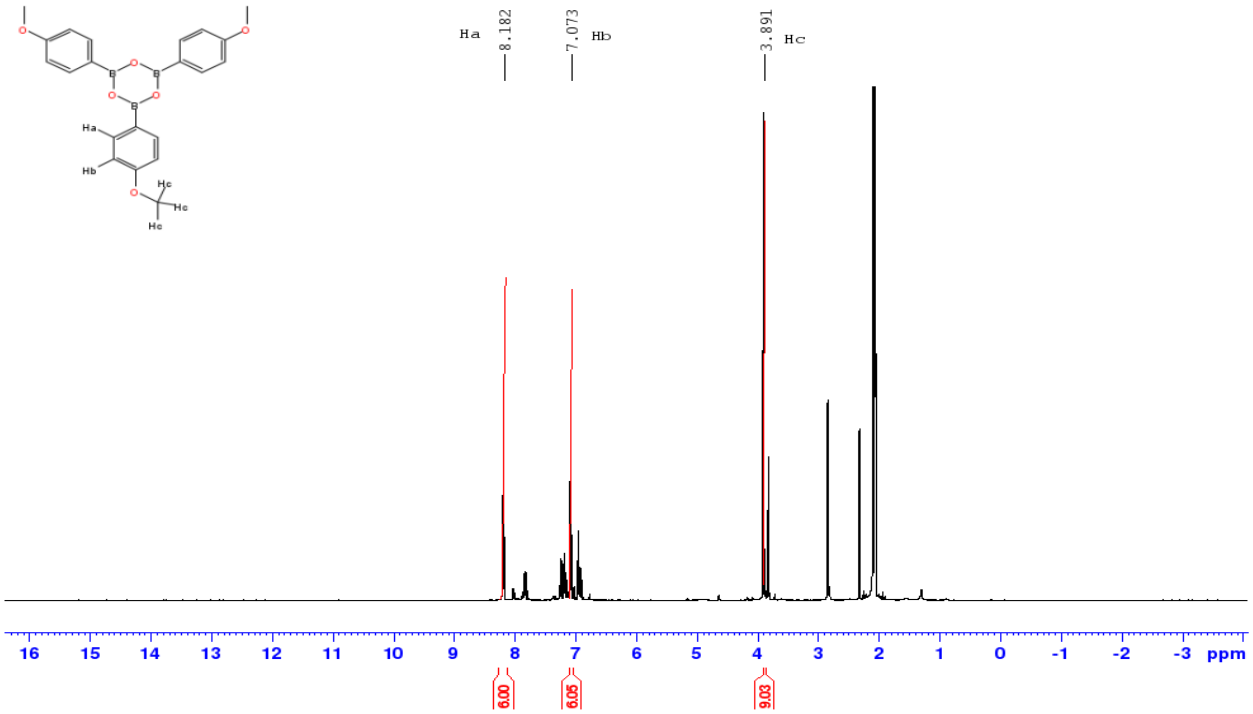

Figure A4. ^{1}H NMR 4-methoxytriphenylboroxine

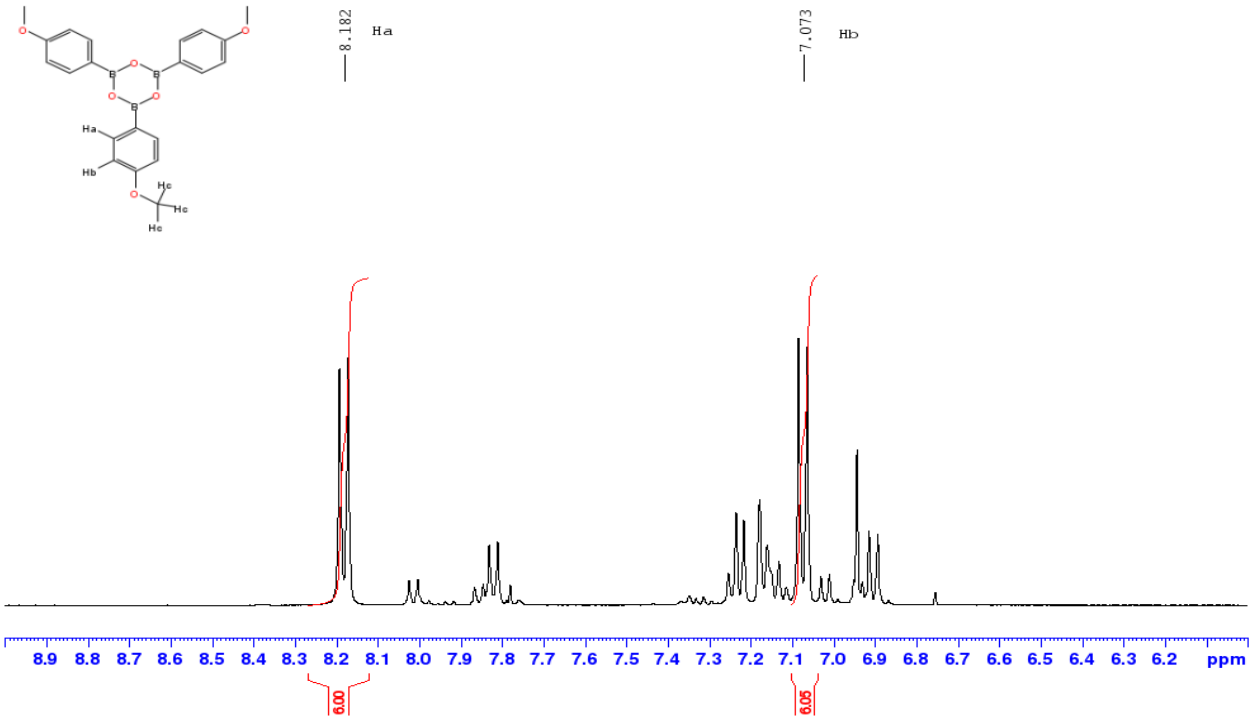

Figure A5. Aromatic Region ¹H NMR 4-methoxytriphenylboroxine

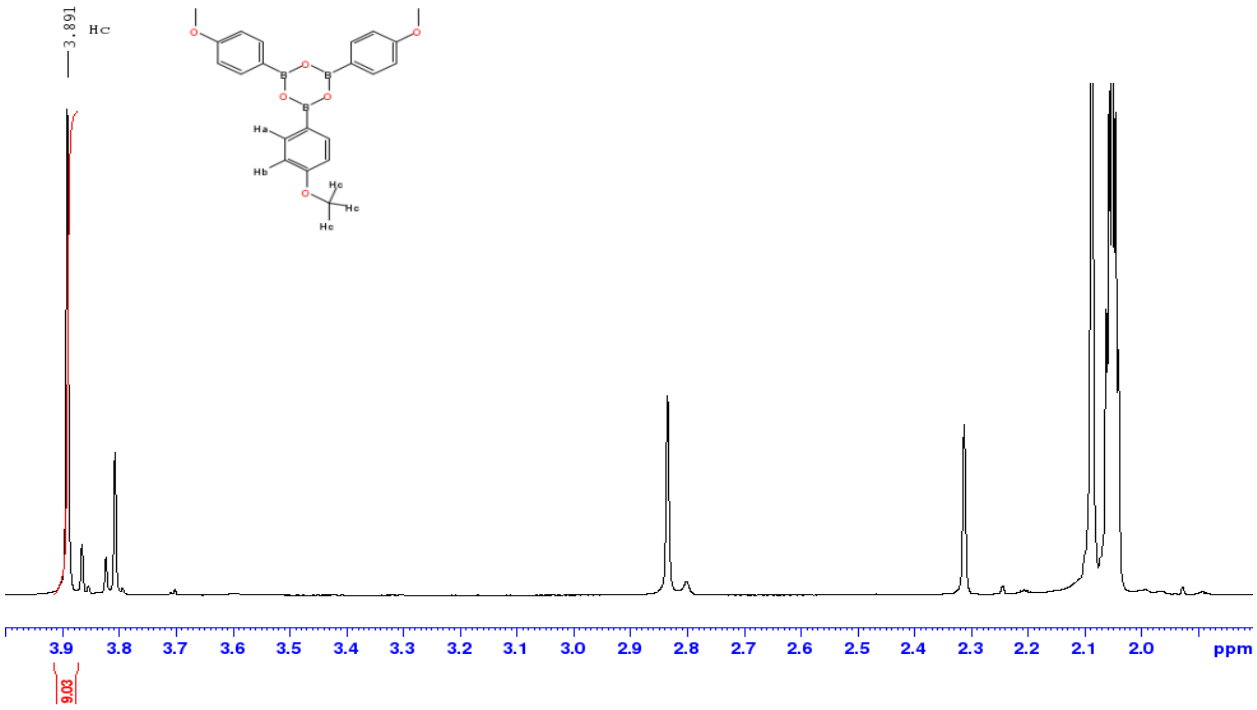

Figure A6. Non-aromatic Region ¹H NMR 4-methoxytriphenylboroxine

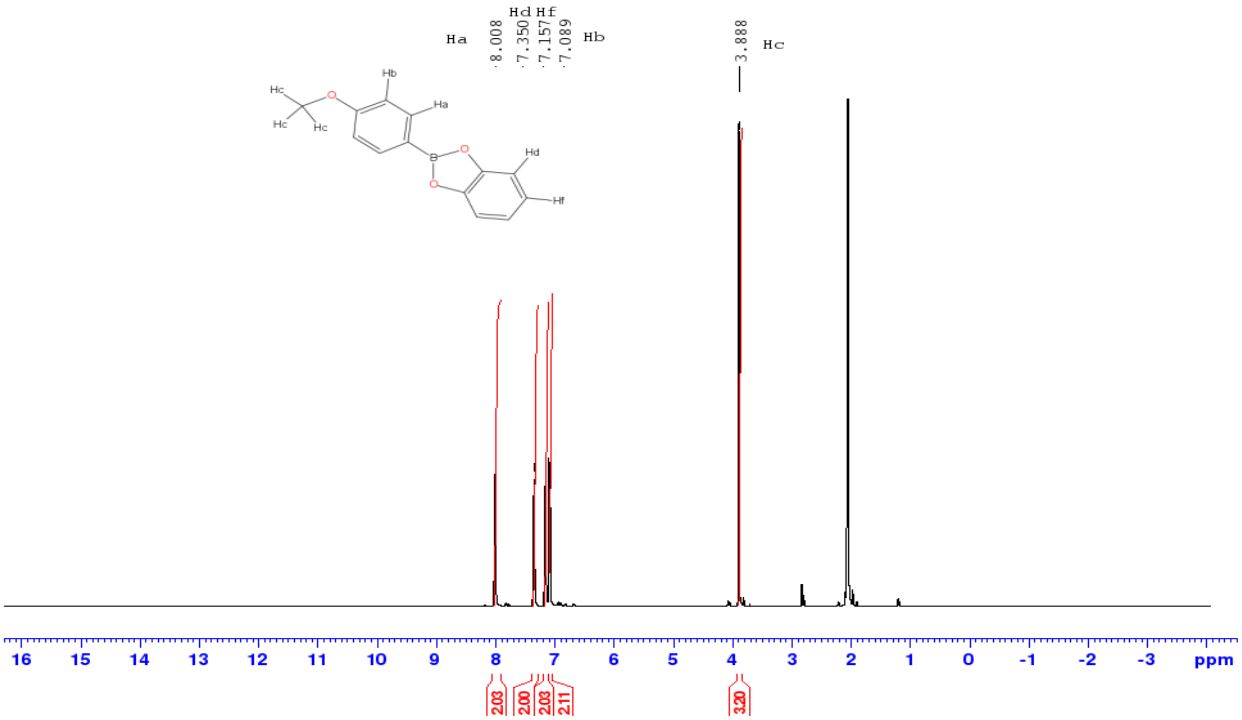

Figure A7. ^{1}H NMR 4-methoxydiphenylboronate

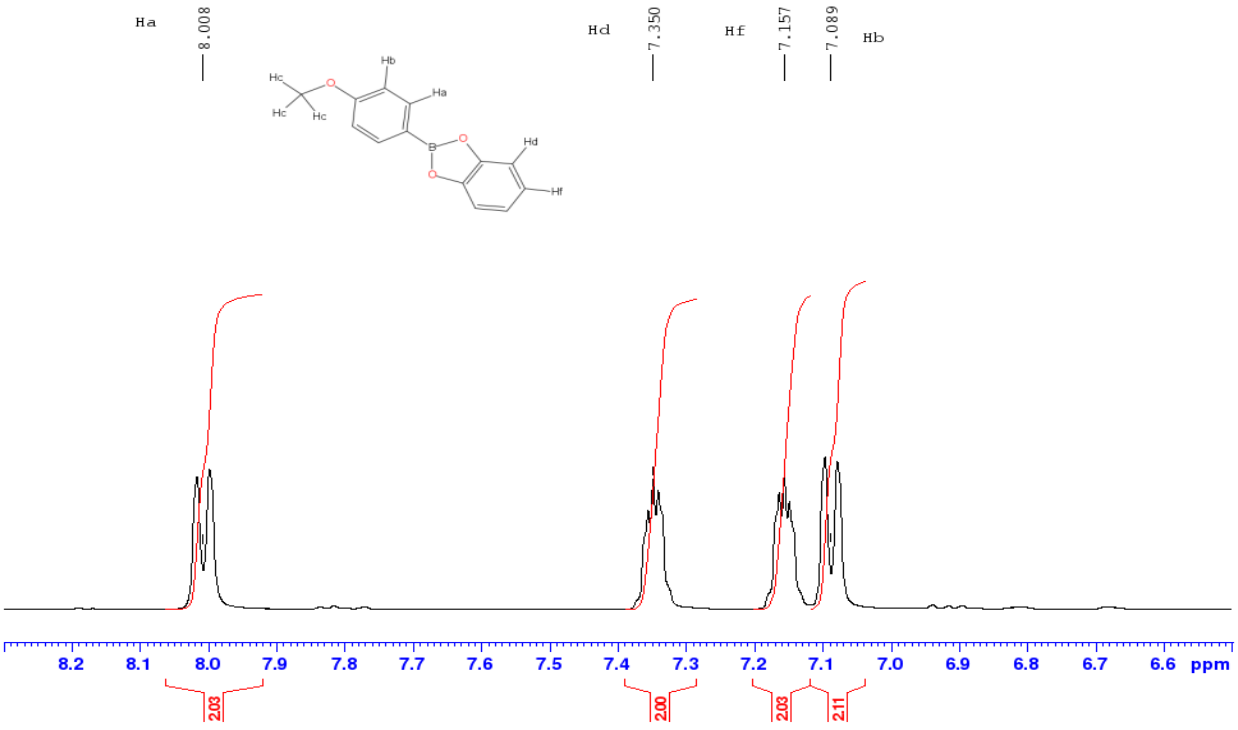

Figure A8. Aromatic Region ^{1}H NMR 4-methoxydiphenylboronate

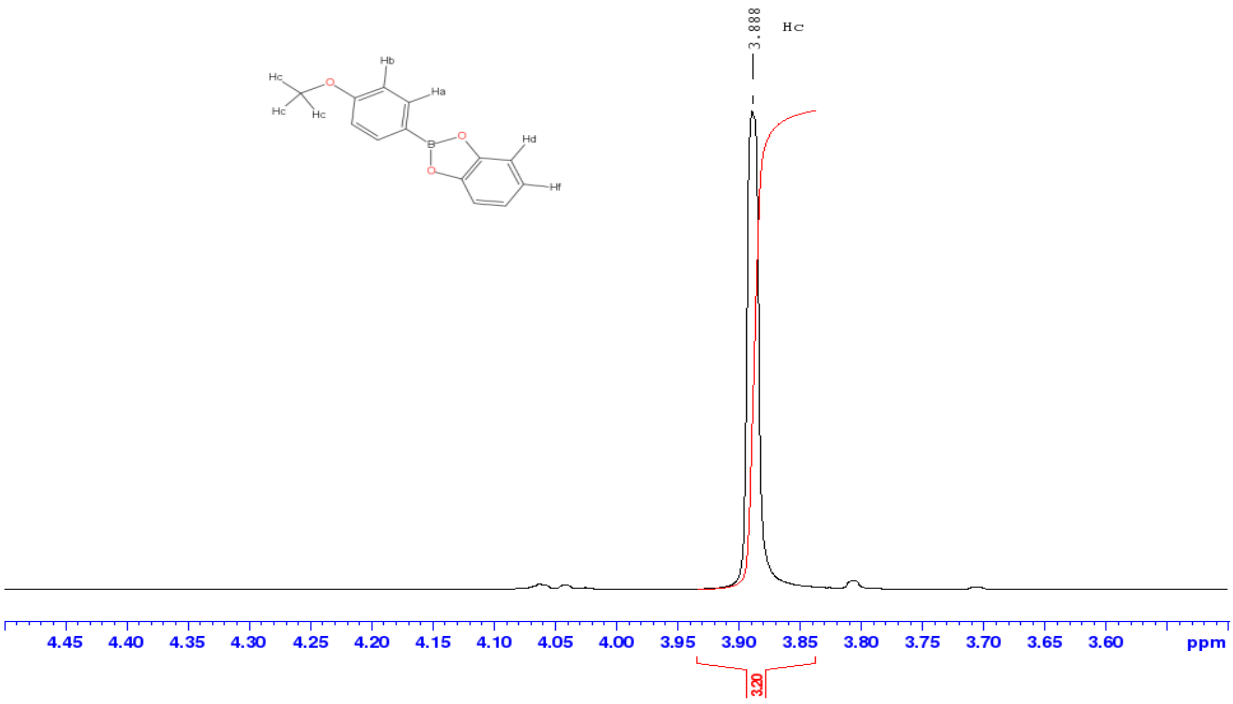

Figure A9. Non-aromatic region ^{1}H NMR 4-methoxydiphenylboronate

Phenylboronic acid and derivatives

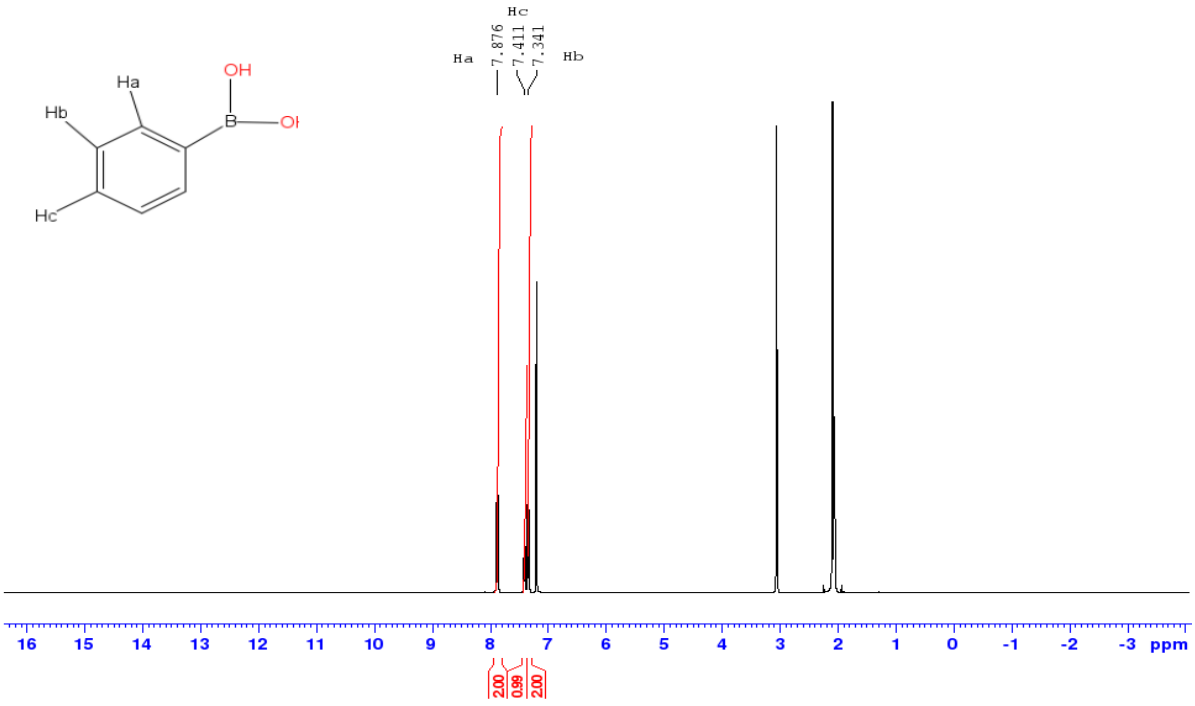

Figure A10. ^{1}H NMR Phenylboronic acid

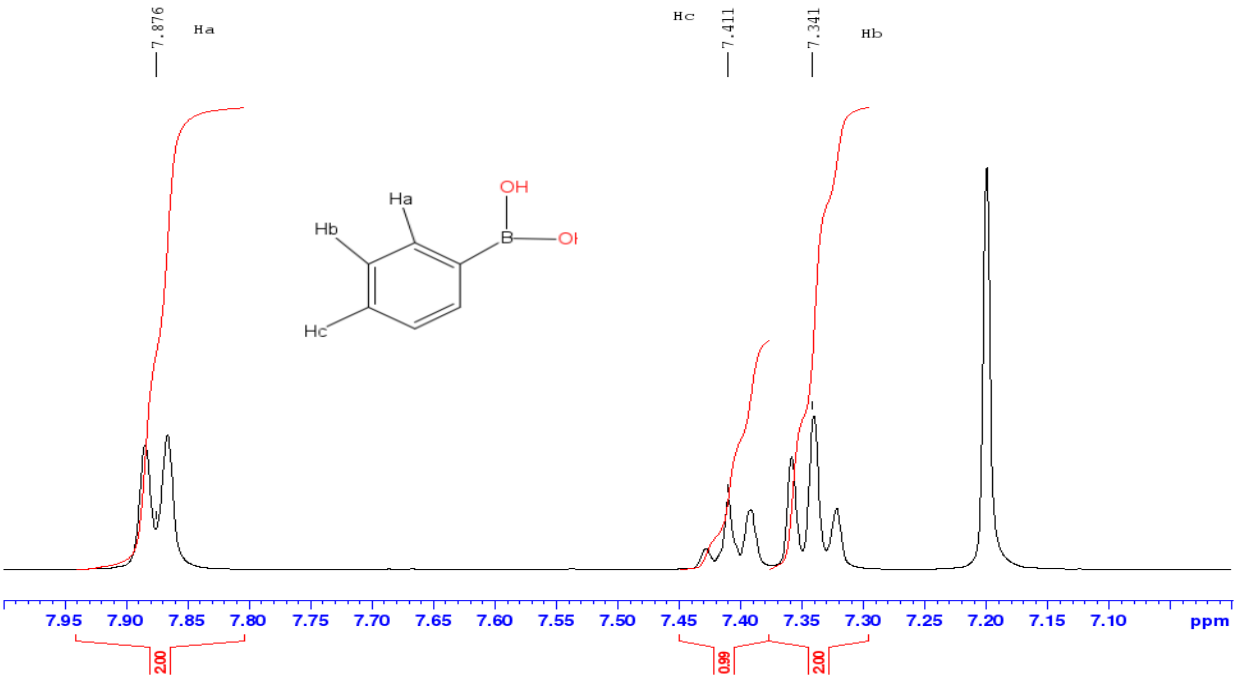

Figure A11. Aromatic Region Phenylboronic acid

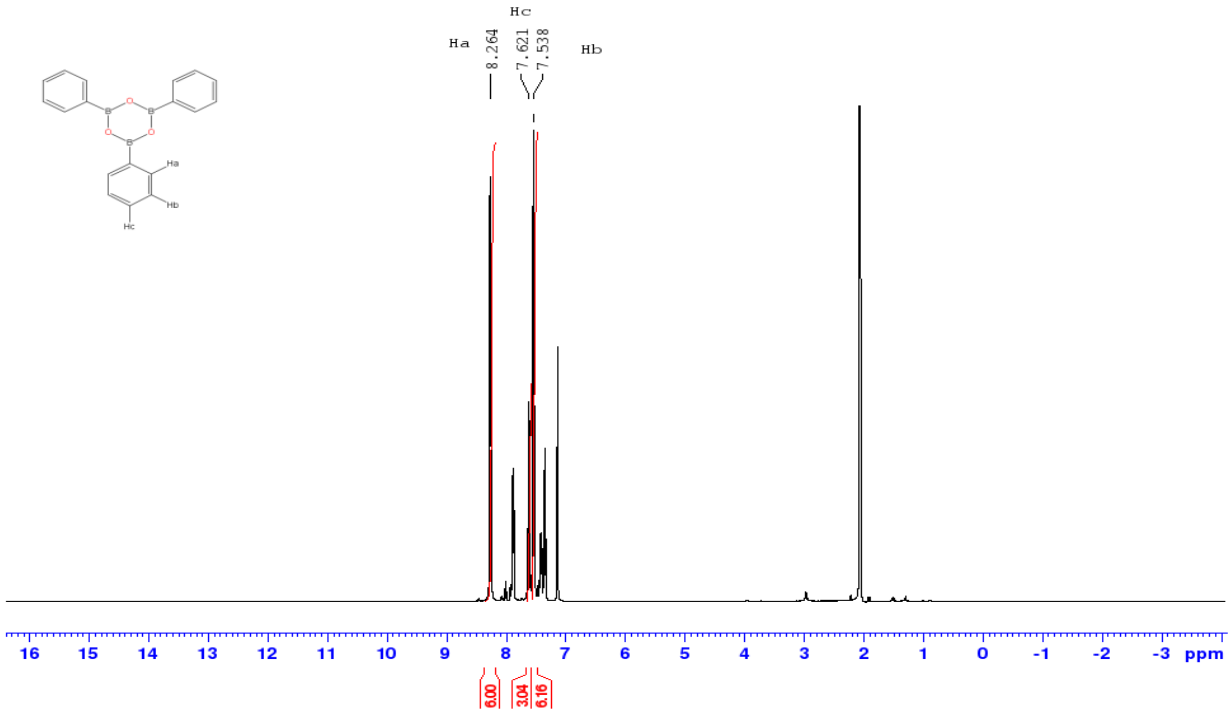

Figure A12. ^{1}H NMR Triphenylboroxine Microwave Method

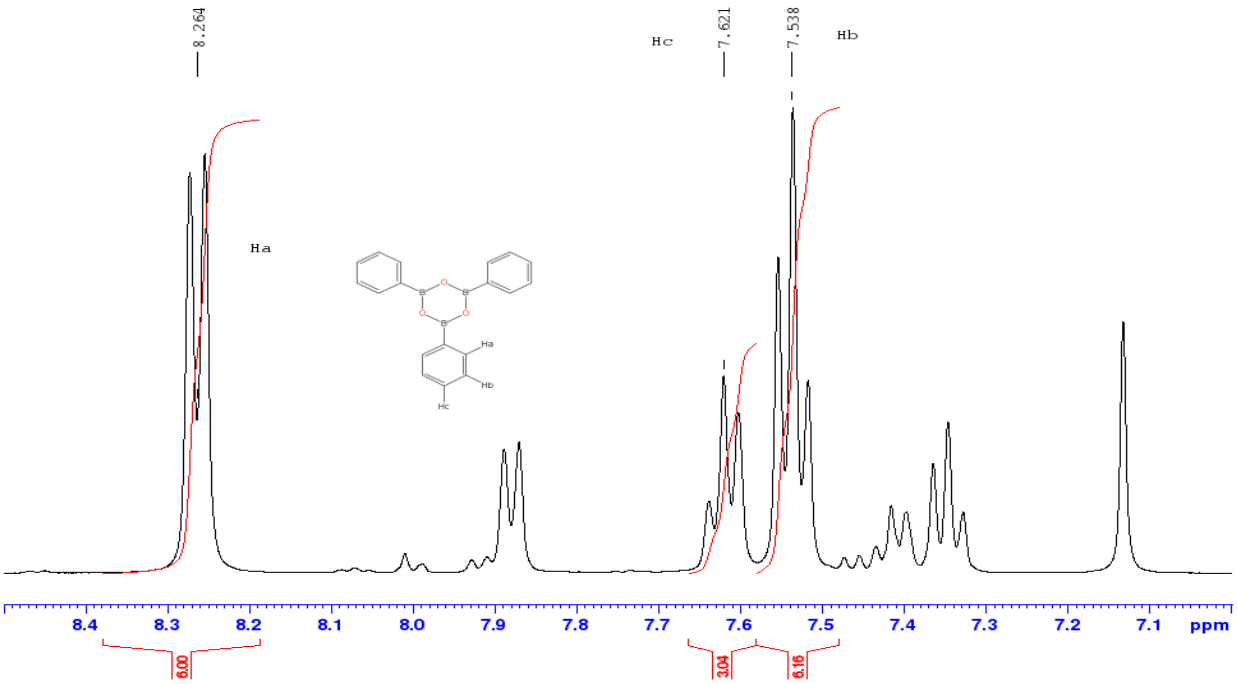

Figure A13. Aromatic Region ^{1}H NMR Triphenylboroxine Microwave Method

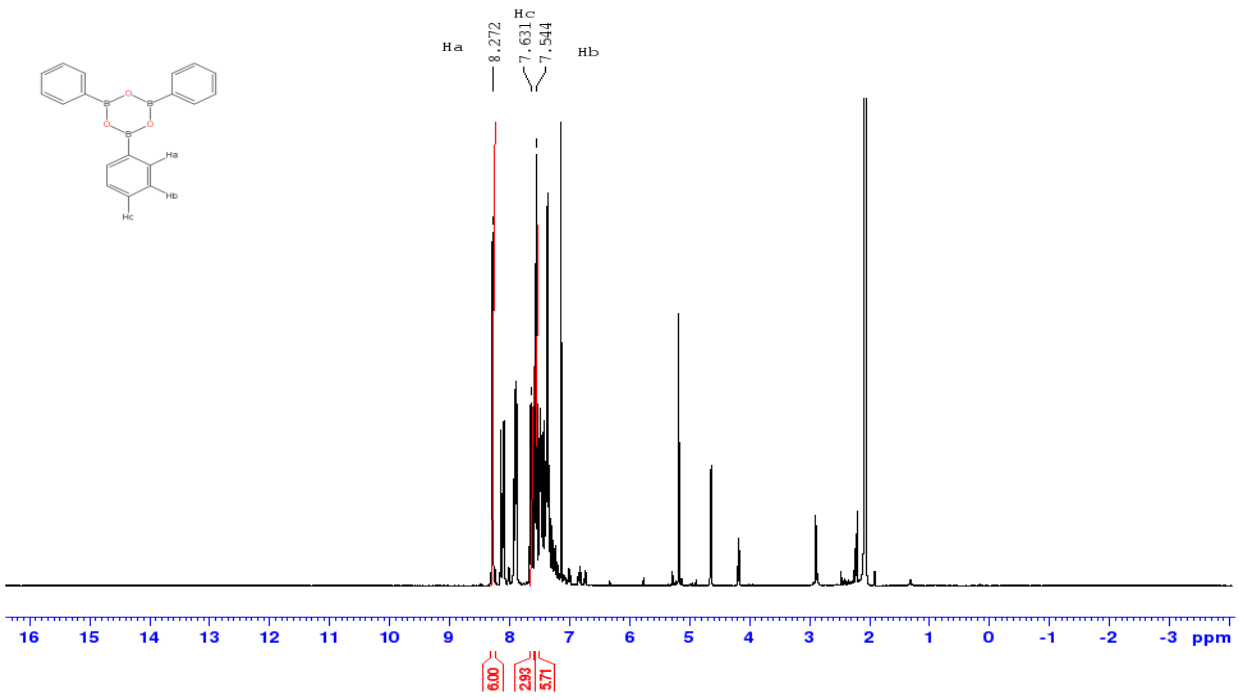

Figure A14. ^{1}H NMR Triphenylboroxine Conventional heating Method

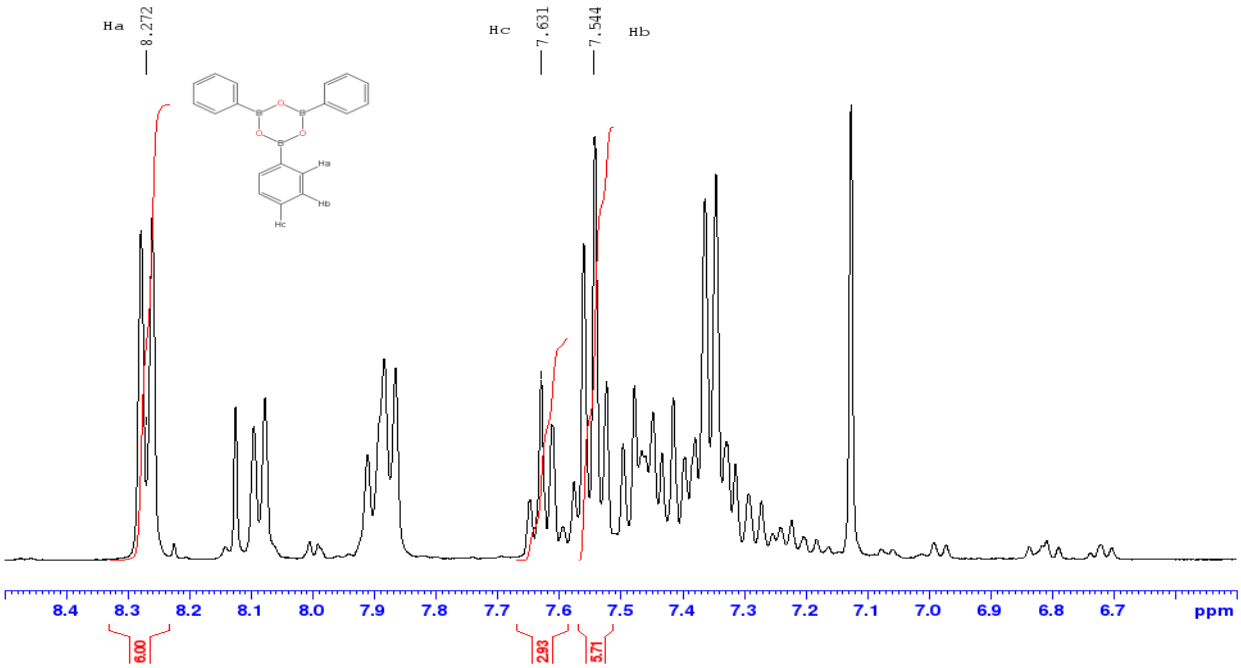

Figure A15. Aromatic Region ^{1}H NMR Triphenylboroxine Conventional heating Method

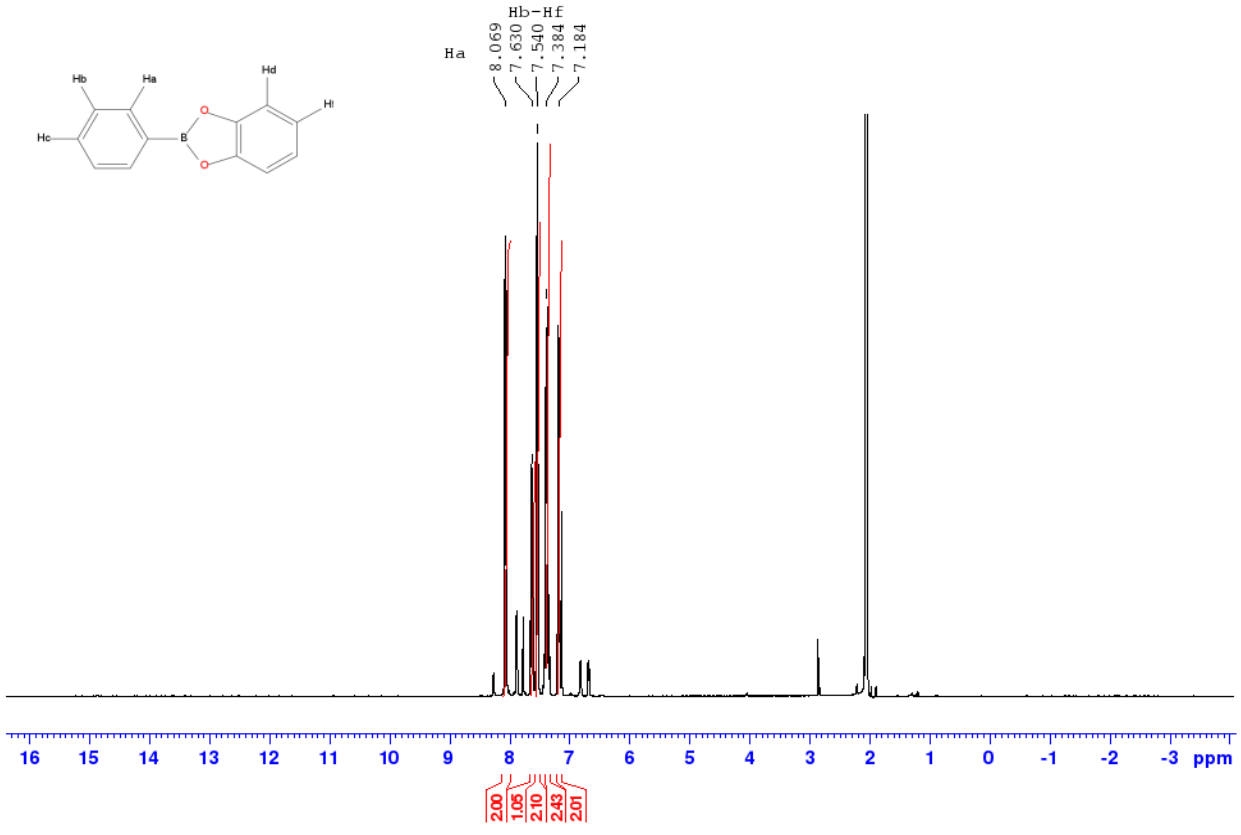

Figure A16. ^{1}H NMR Diphenylboronate

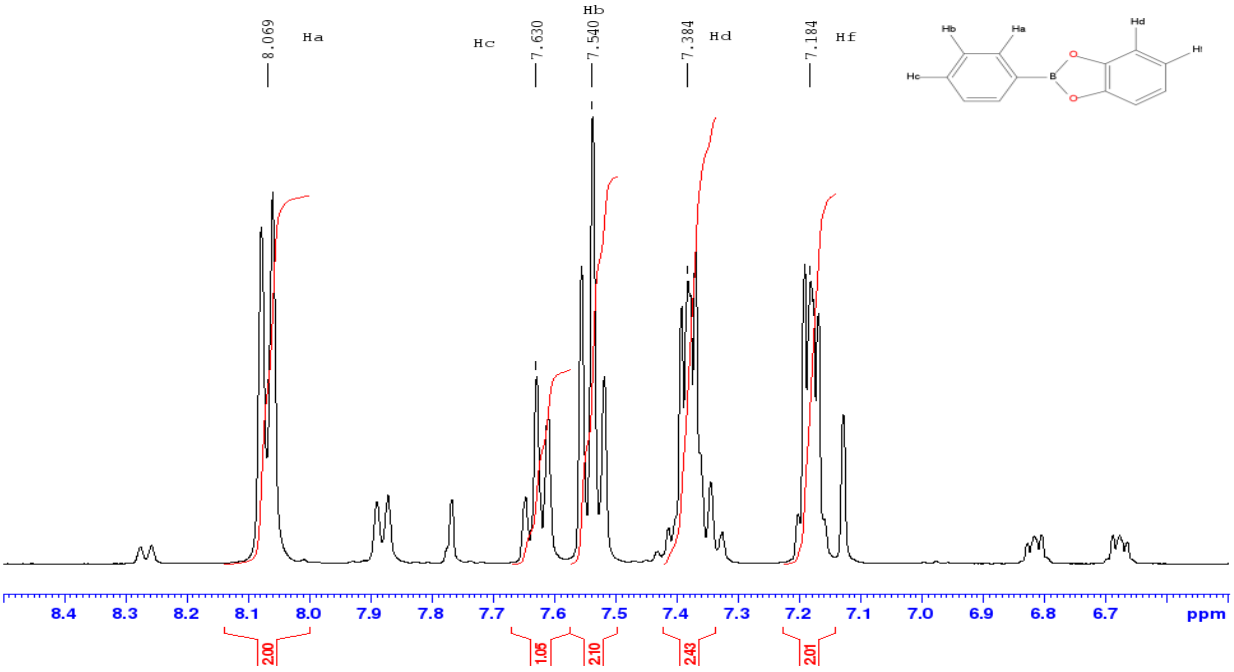

Figure A17. Aromatic Region ¹H NMR Diphenylboronate

4-fluorophenylboronic acid and Derivatives

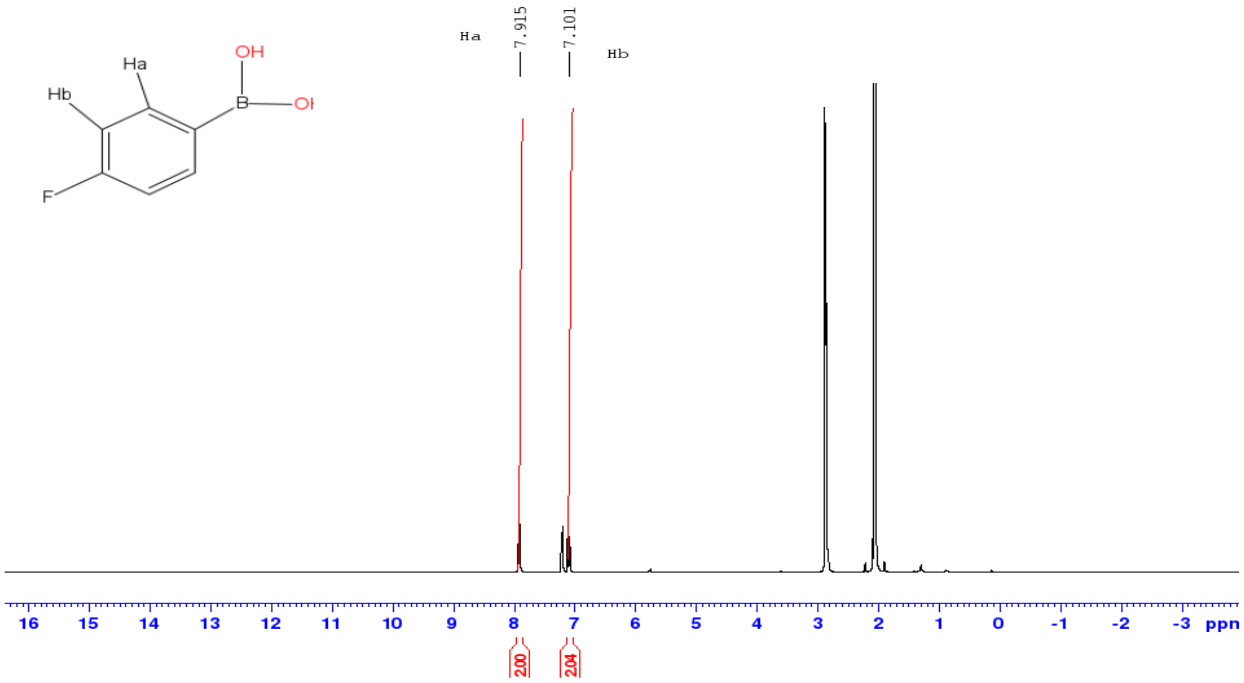

Figure A18. ¹H NMR 4-fluoroboronic acid

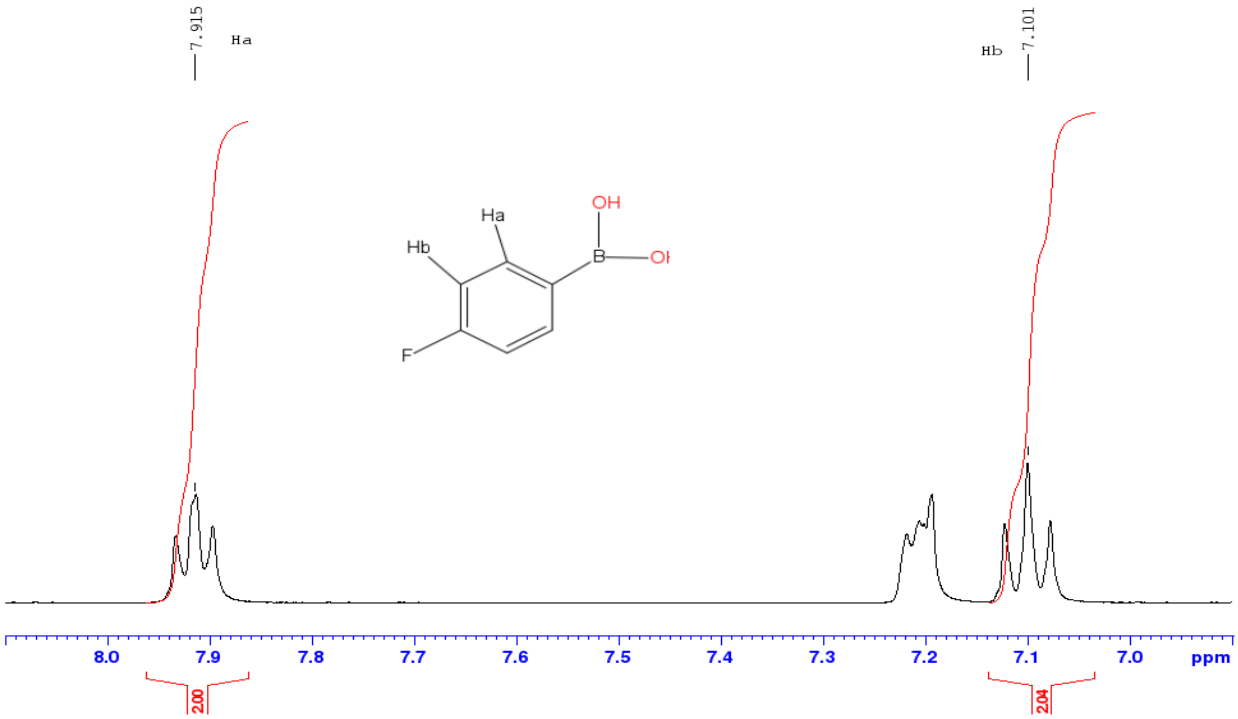

Figure A19. Aromatic Region 4-fluorophenylboronic acid

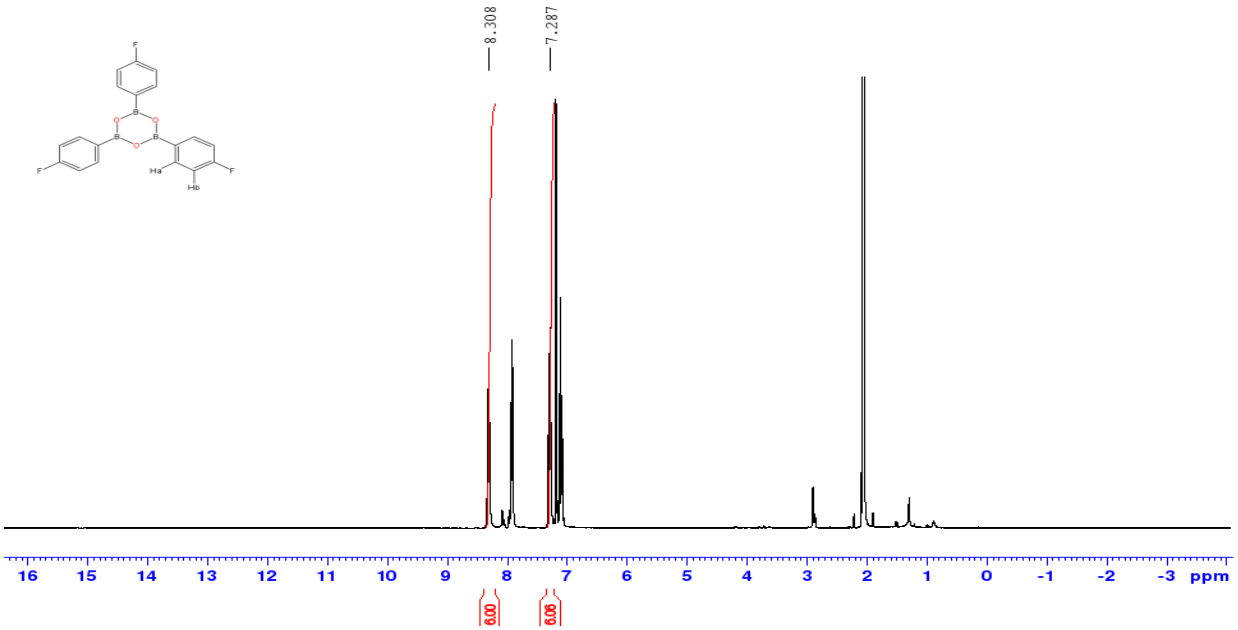

Figure A20. ^{1}H NMR 4-fluorotriphenylboroxine Microwave Method Crash

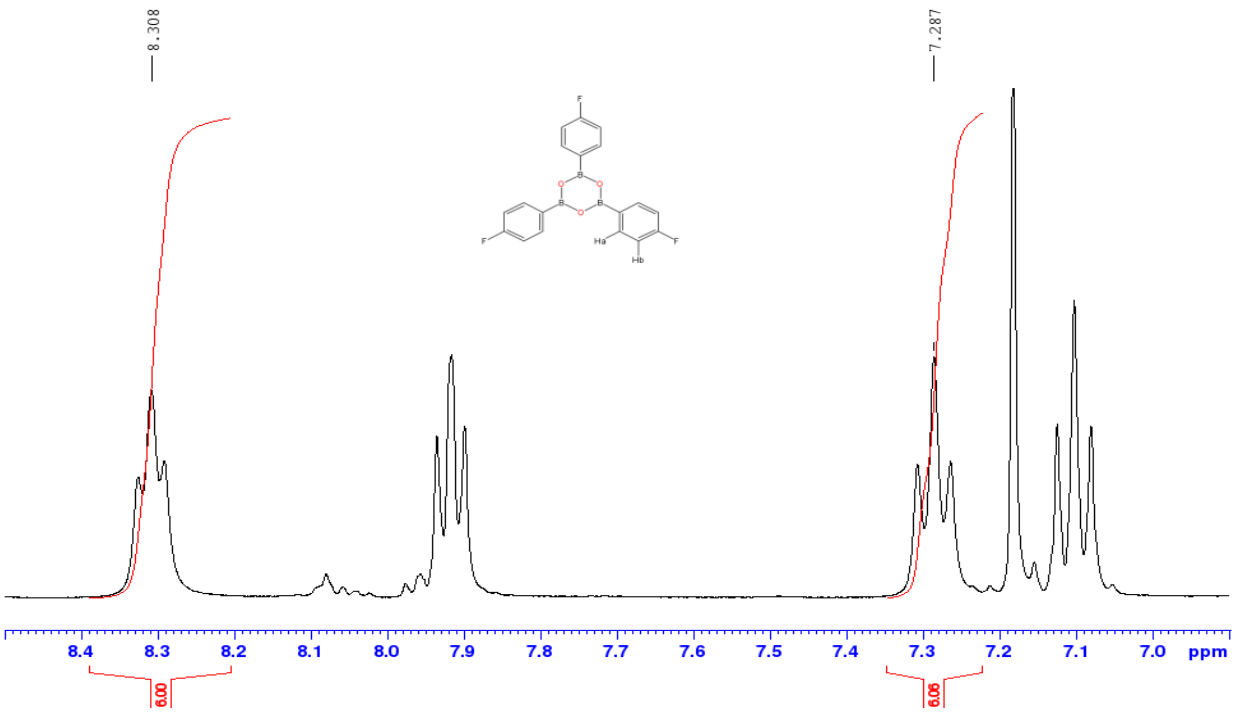

Figure A21. Aromatic Region ¹H NMR 4-fluorotriphenylboroxine Microwave Method Crash

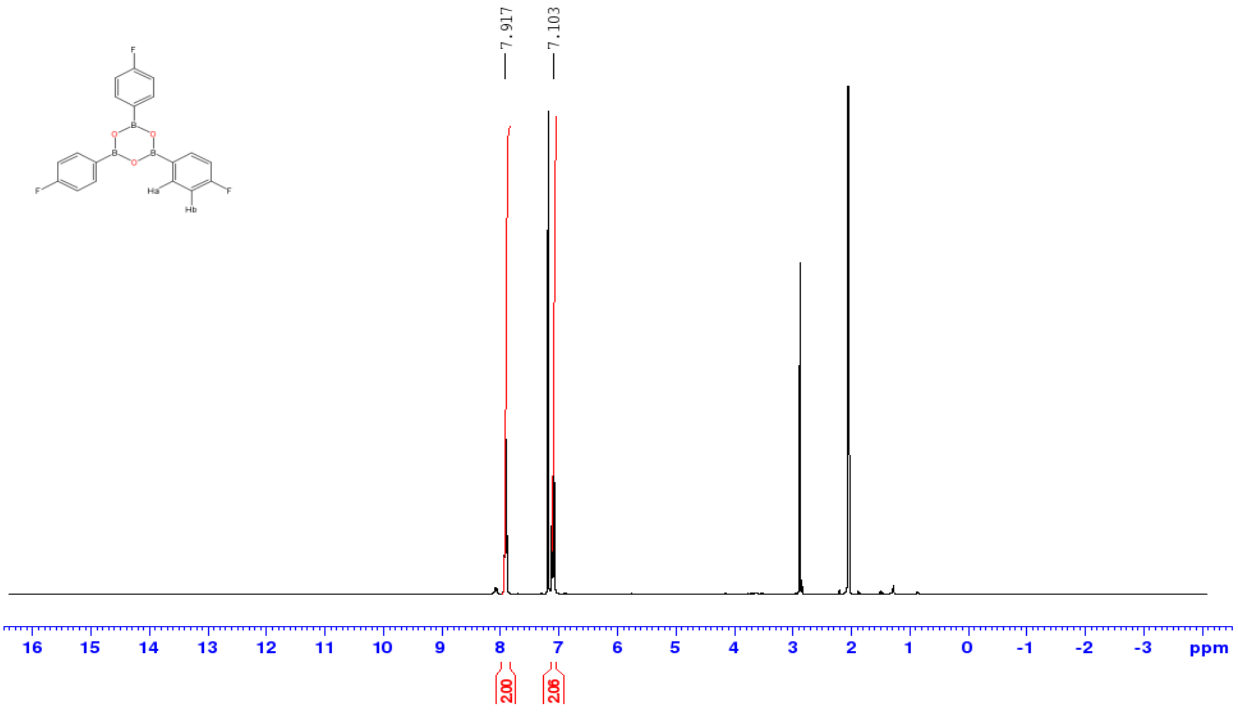

Figure A22. ¹H NMR 4-fluorotriphenylboroxine Microwave Method Remainder

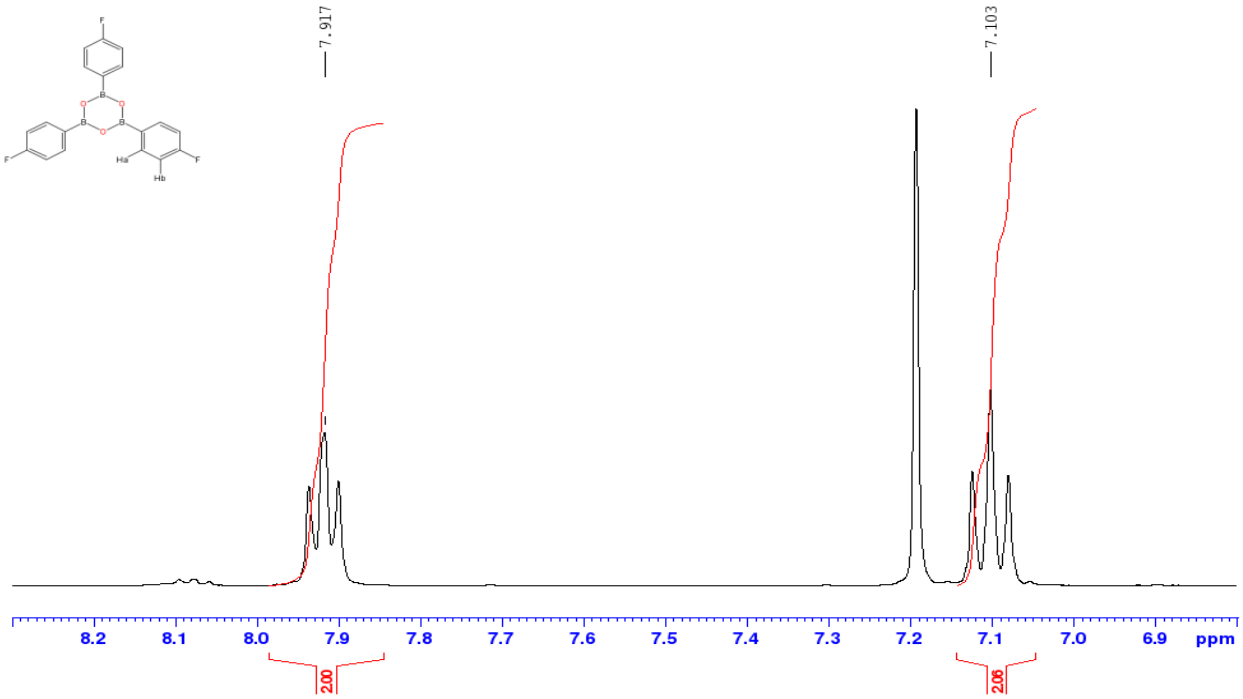

Figure A23. Aromatic Region ¹H NMR 4-fluorotriphenylboroxine Microwave Method

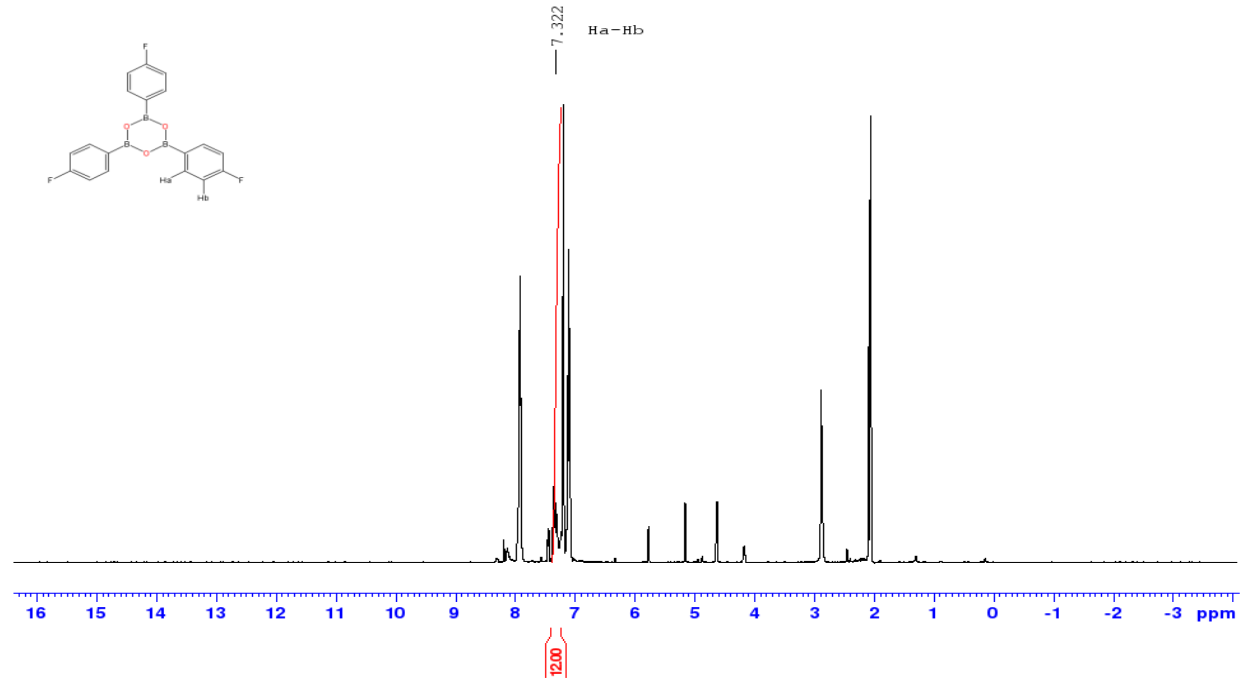

Figure A24. ¹H NMR 4-fluorotriphenylboroxine Conventional heating Method

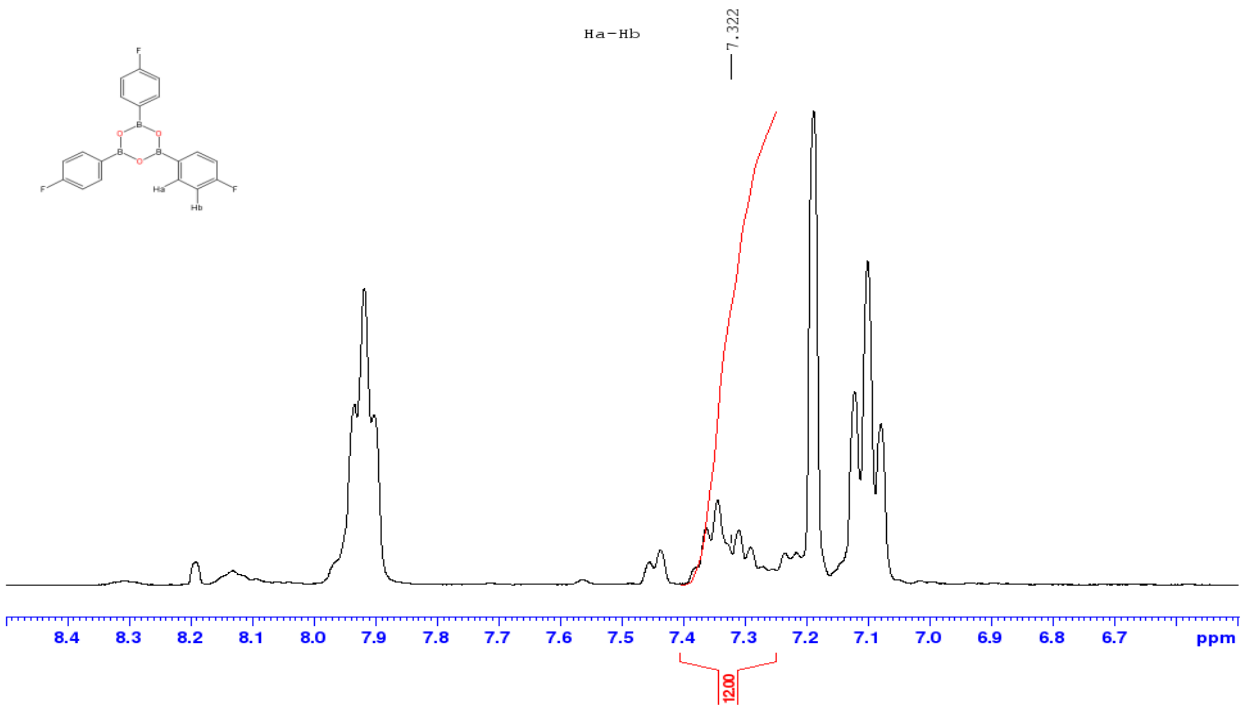

Figure A25. Aromatic Region ¹H NMR 4-fluorotriphenylboroxine Conventional heating Method

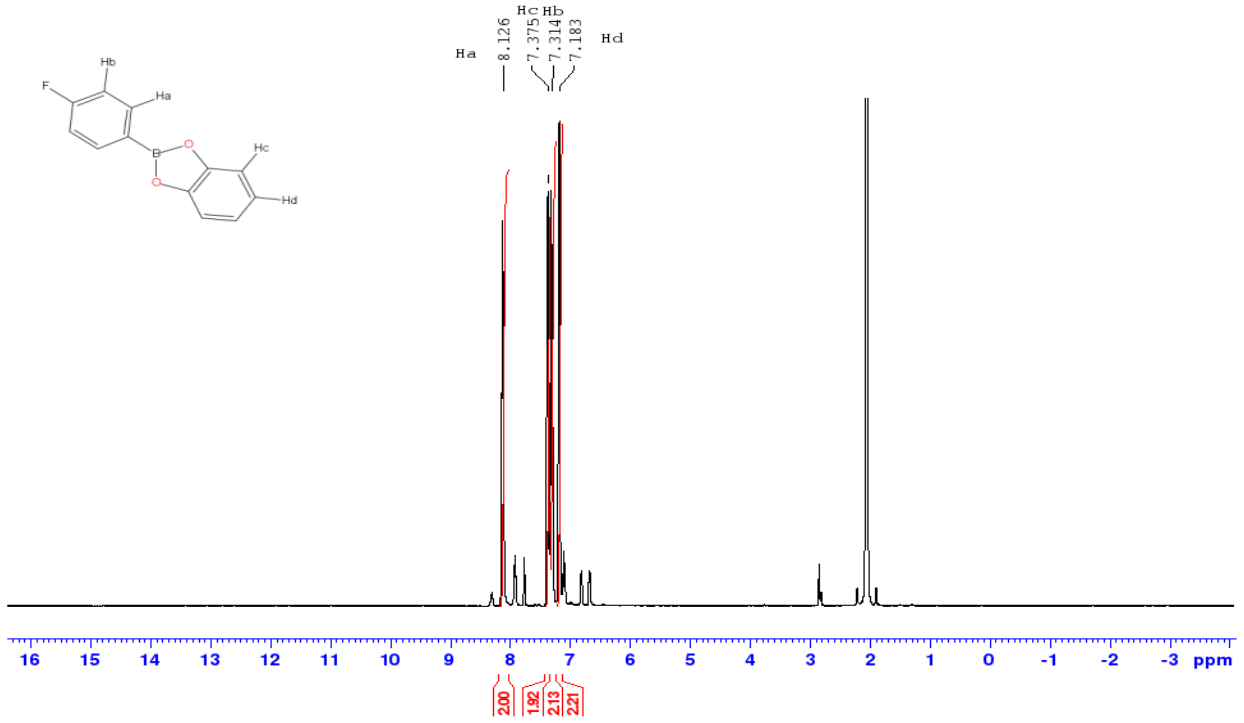

Figure A26. ¹H NMR 4-fluorodiphenylboronate

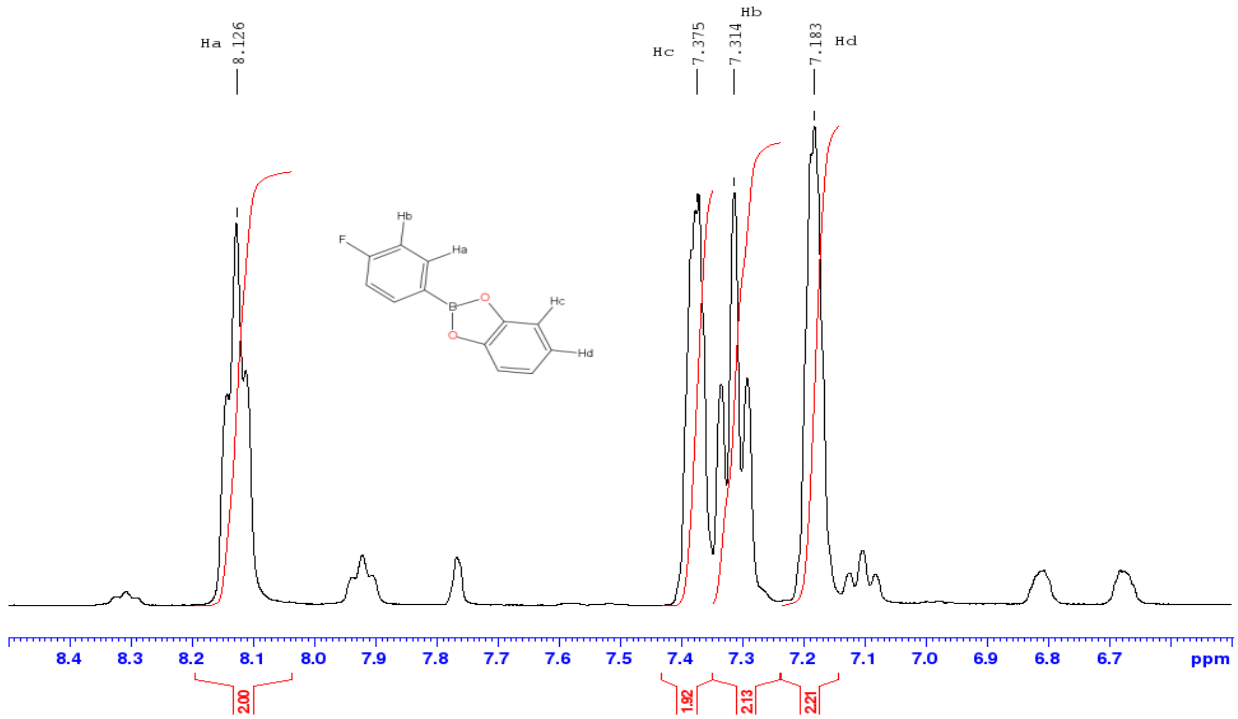

Figure A27. Aromatic Region ¹H NMR 4-fluorodiphenylboronate

3,4,5-trifluorophenylboronic acid and Derivatives

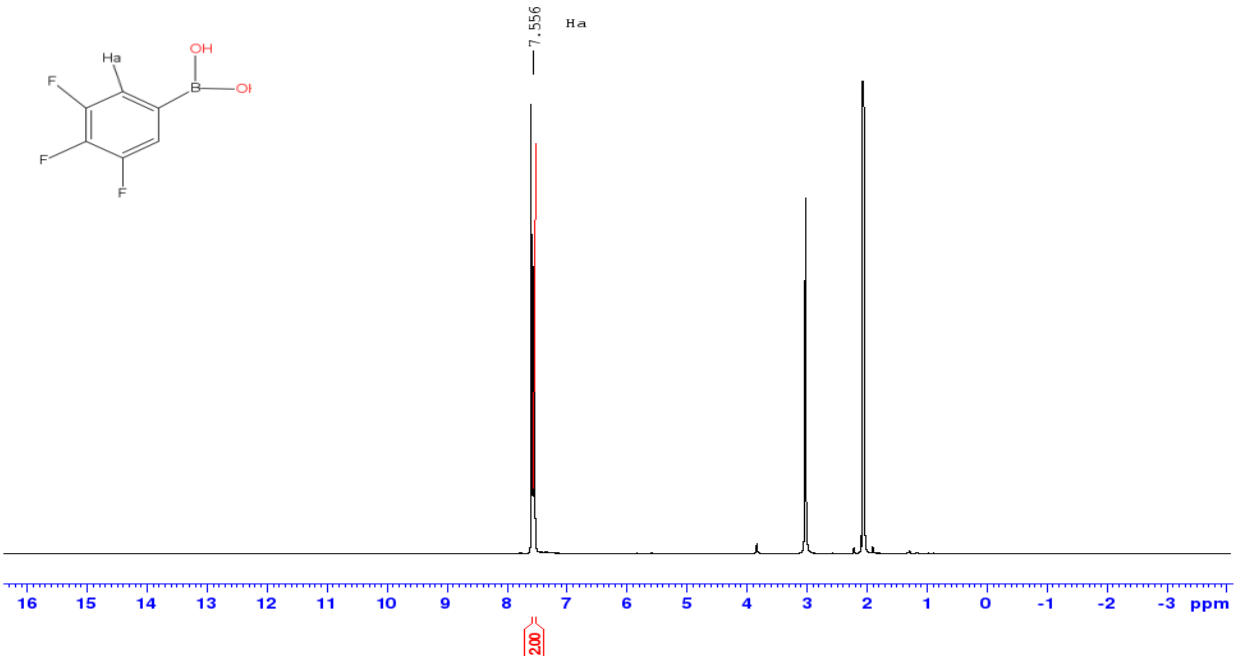

Figure A28. ¹H NMR 3,4,5-trifluorophenylboronic acid

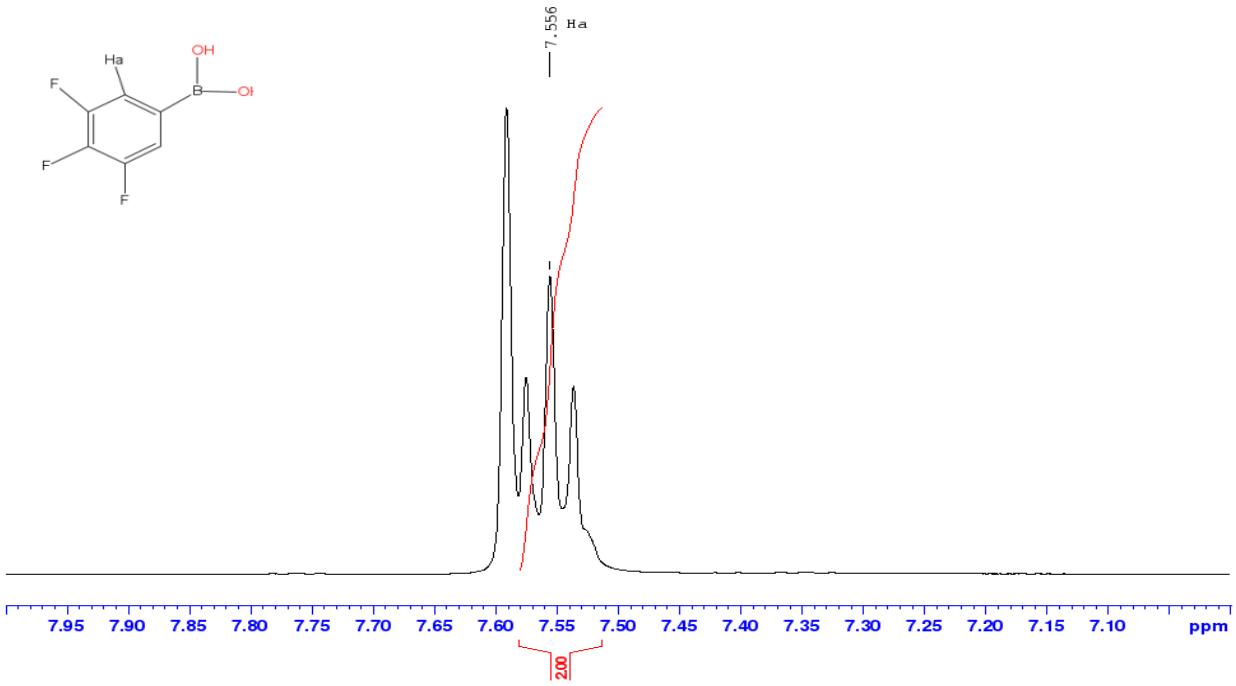

Figure A29. Aromatic Region ¹H NMR 3,4,5-trifluorophenylboronic acid

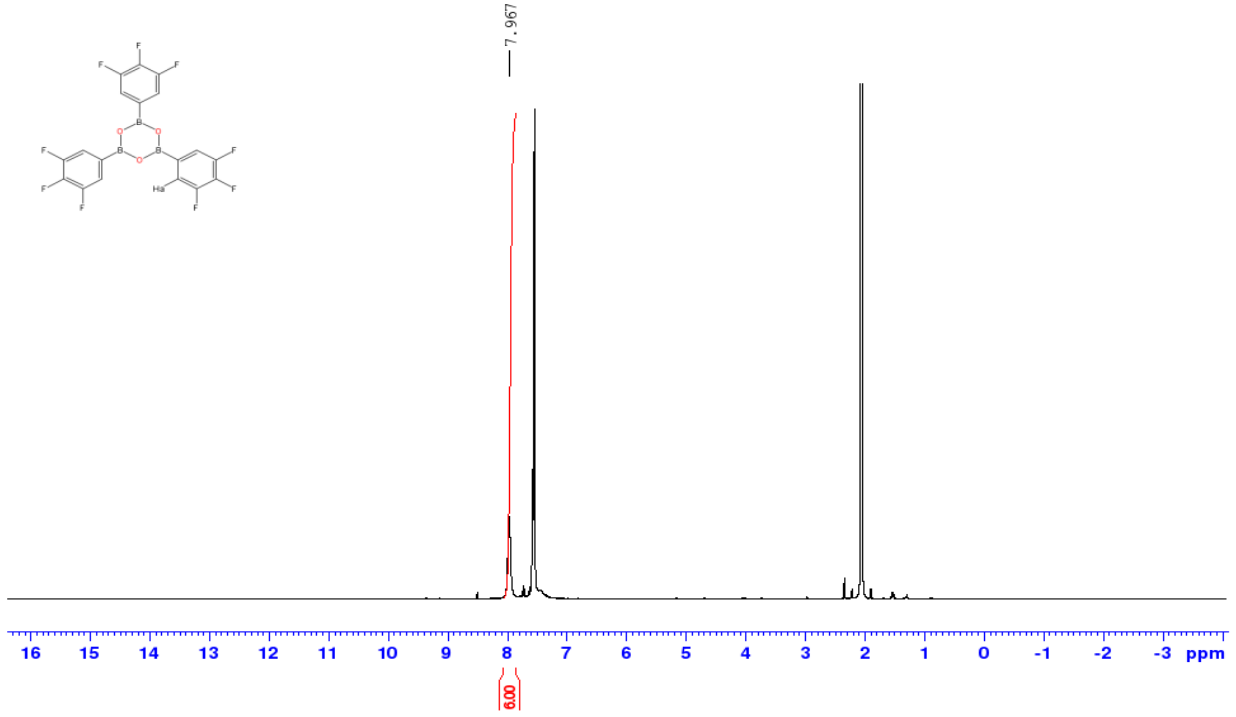

Figure A30. ¹H NMR 3,4,5-trifluorotriphenylboroxine Microwave Method

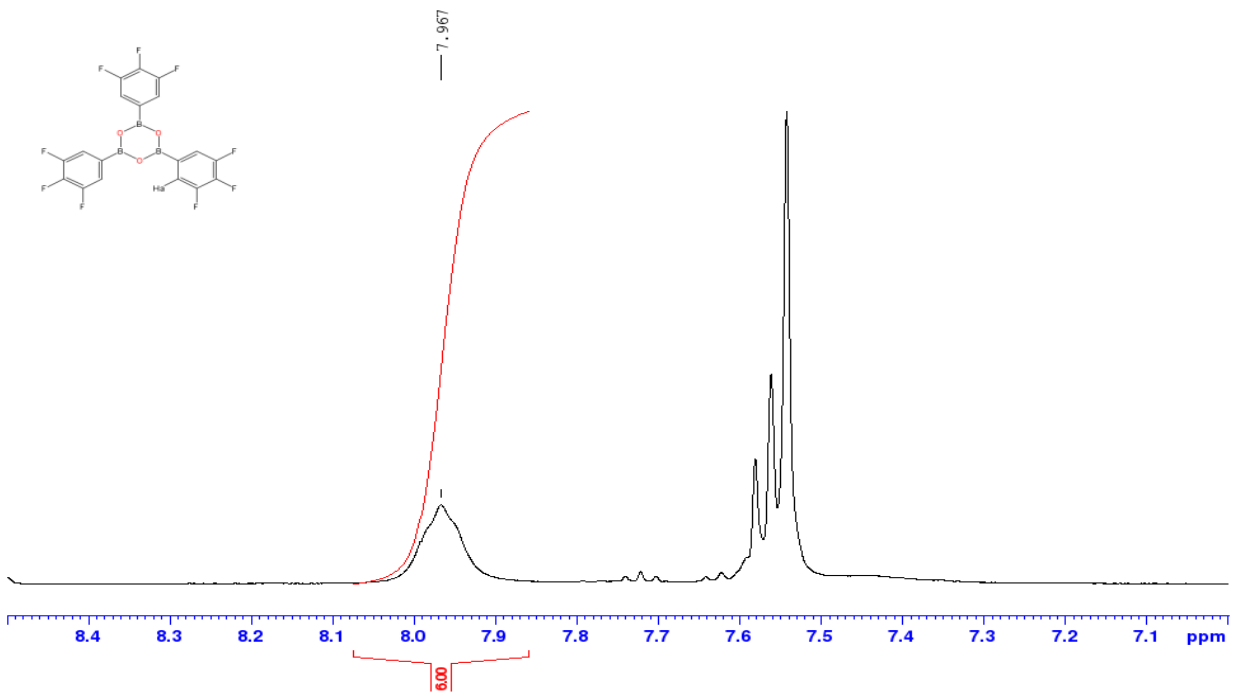

Figure A31. Aromatic Region 3,4,5-trifluorotriphenylboroxine Microwave Method

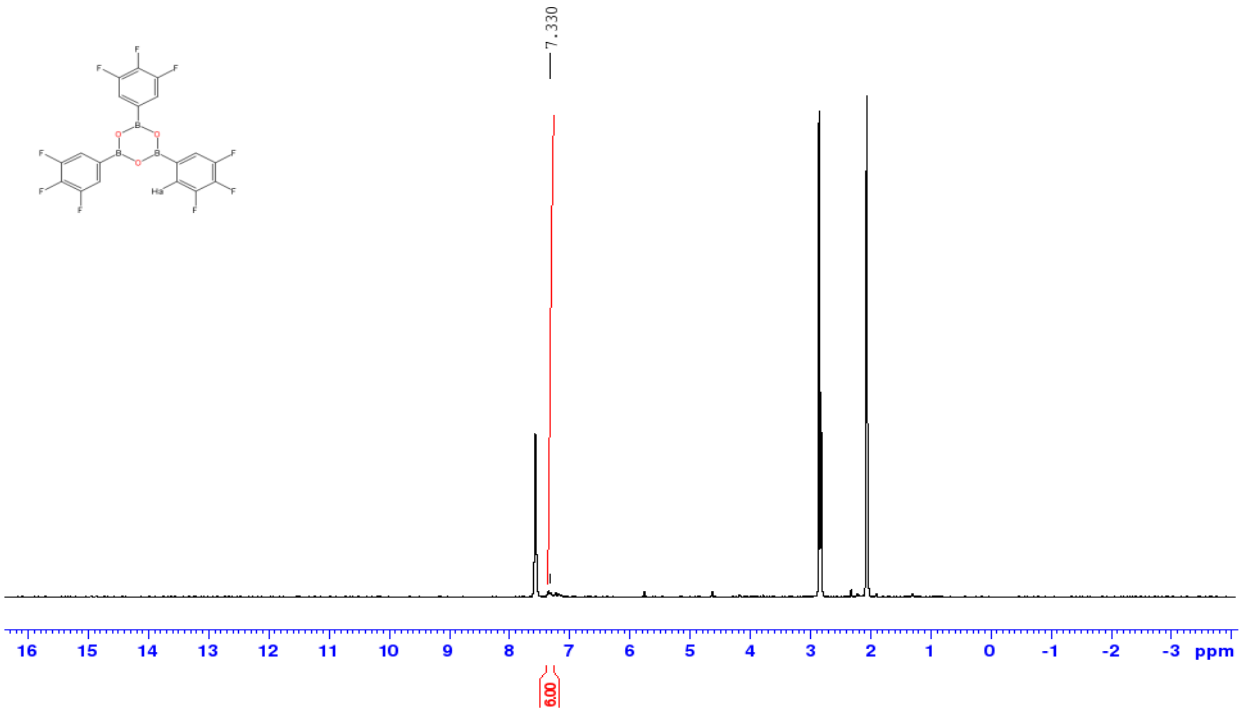

Figure A32. ^{1}H NMR 3,4,5-trifluorotriphenylboroxine Conventional heating Method

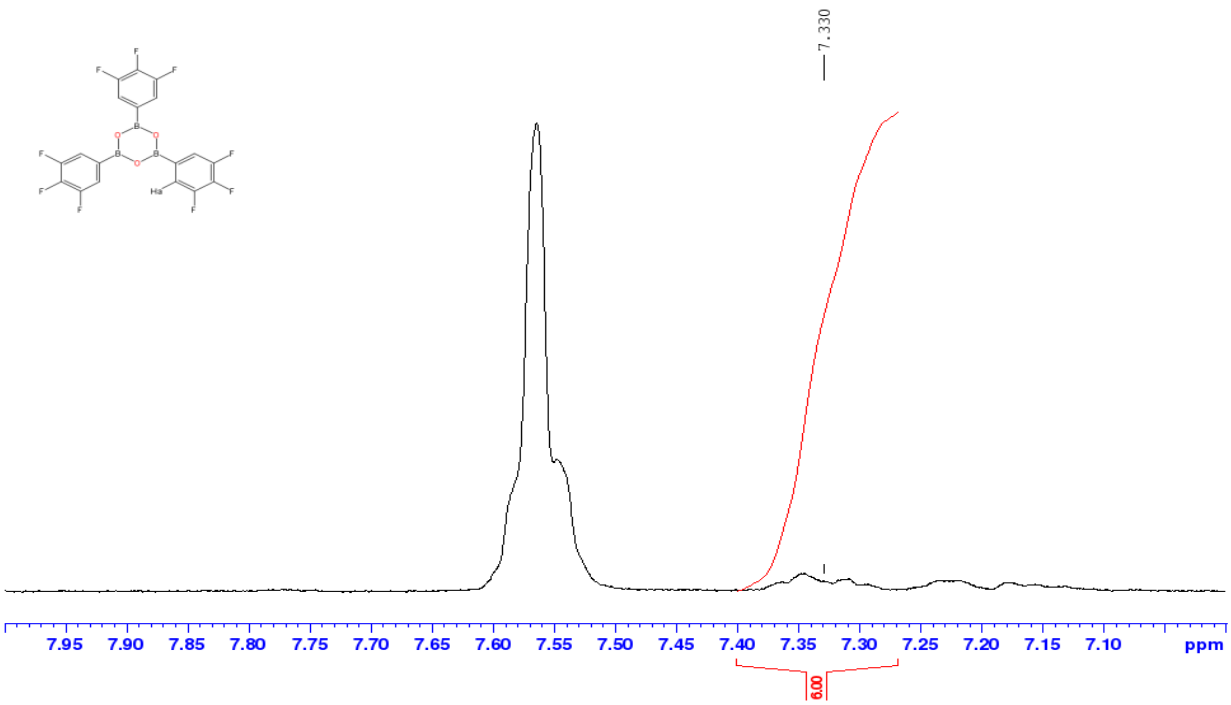

Figure A33. Aromatic Region ¹H NMR 3,4,5-trifluorotriphenylboroxine Conventional heating Method

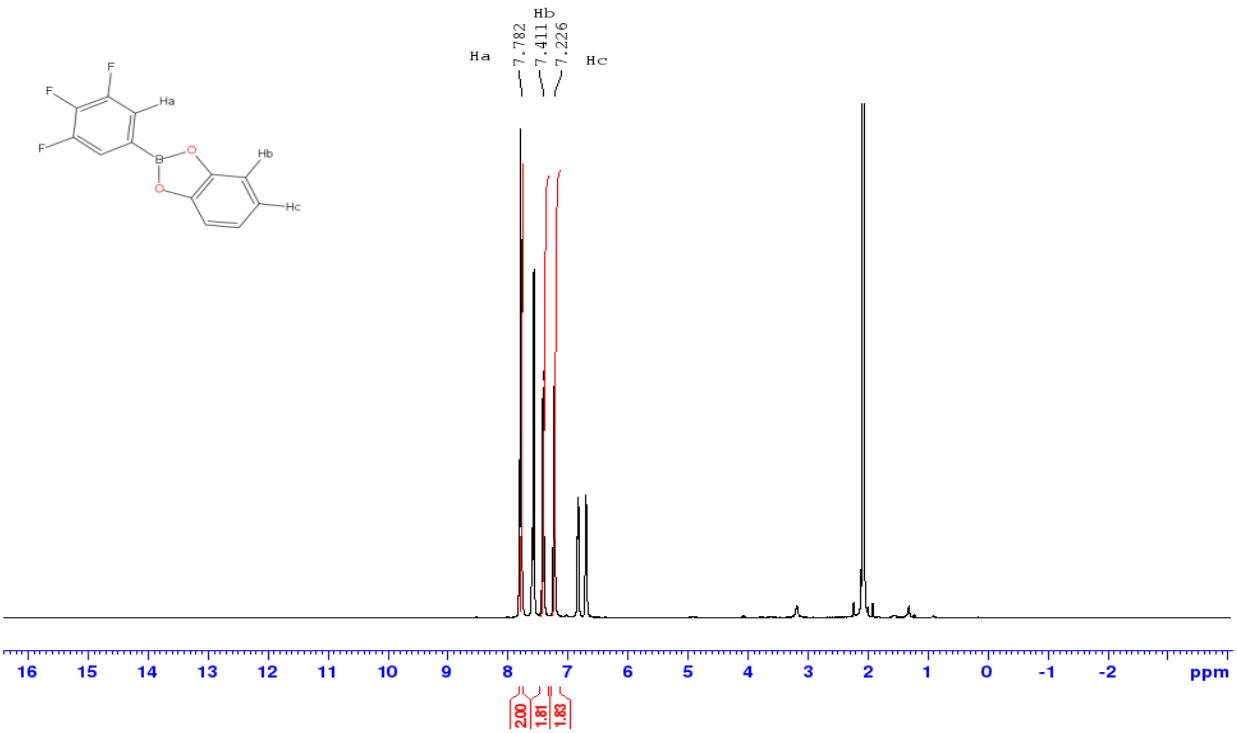

Figure A34. ¹H NMR 3,4,5-trifluorodiphenylboronate

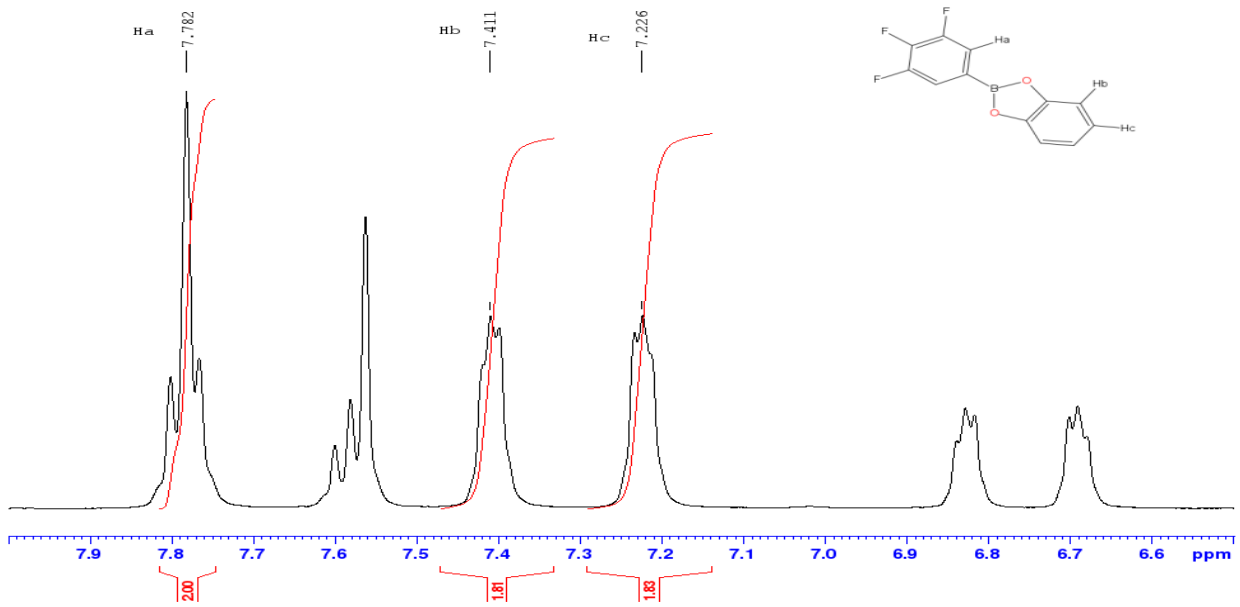

Figure A35. Aromatic Region ¹H NMR 3,4,5-trifluorodiphenylboronate

2,3,4,5,6-pentafluorophenylboronic acid and Derivatives

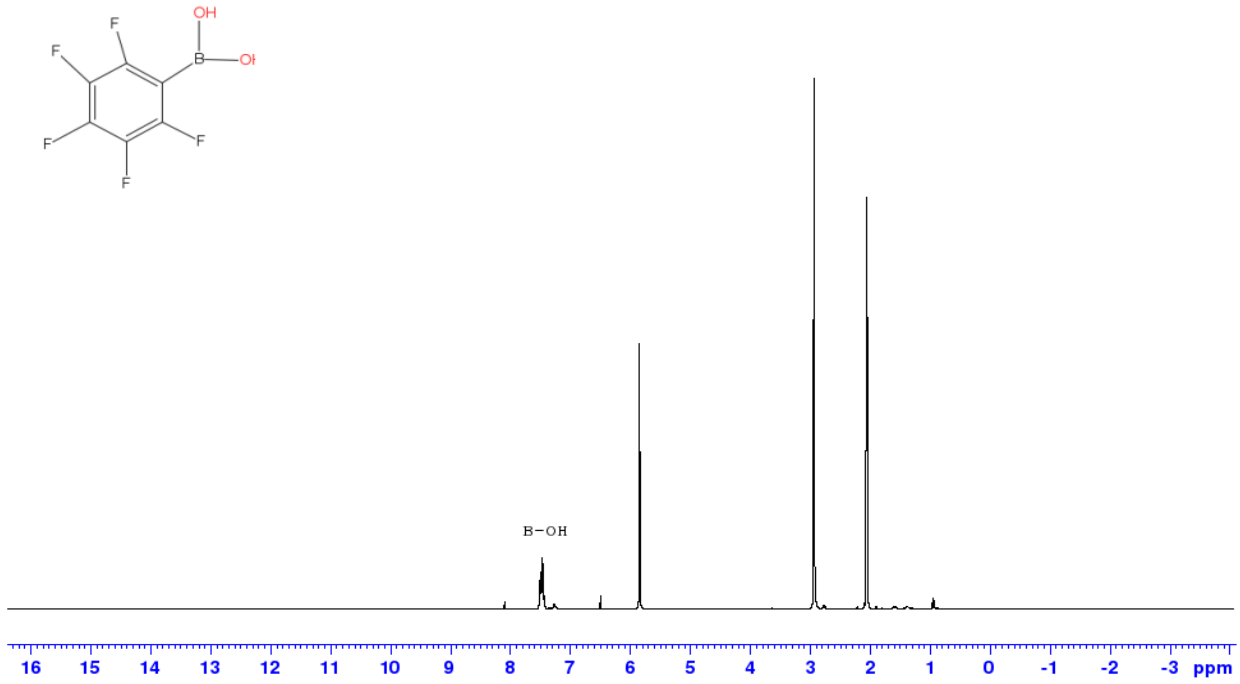

Figure A36. ¹H NMR 2,3,4,5,6-pentafluorophenylboronix acid

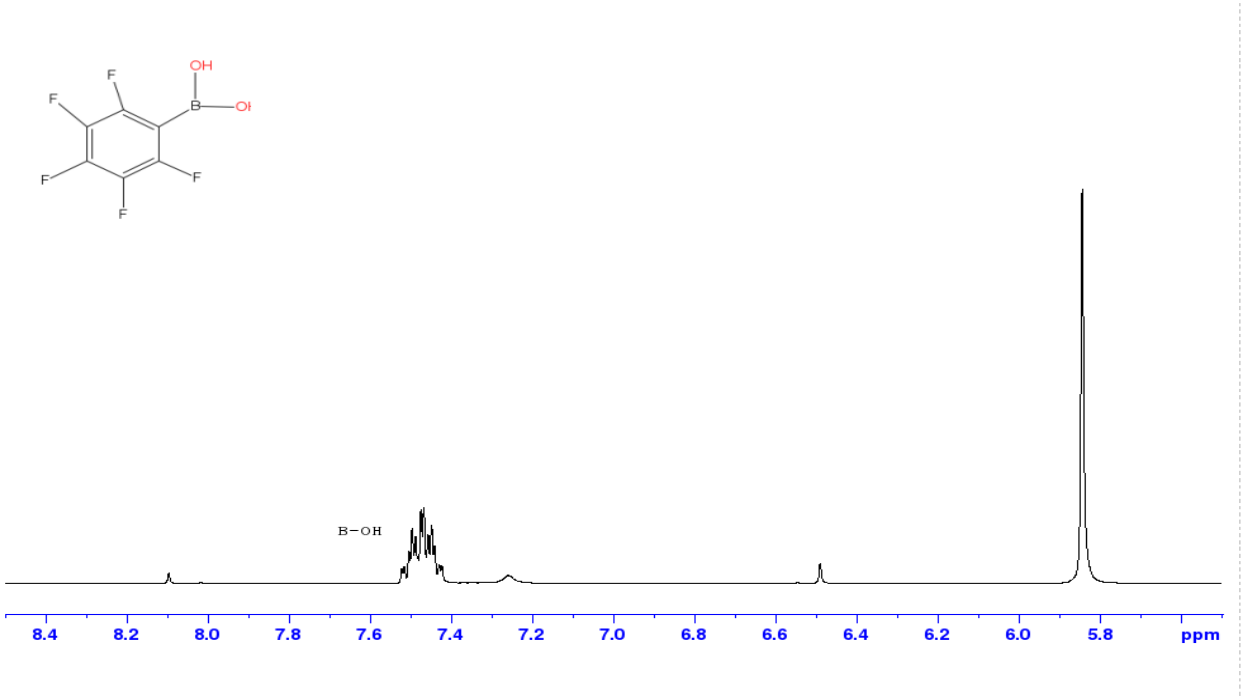

Figure A37. Aromatic Region 2,3,4,5,6-pentafluorophenylboronix acid

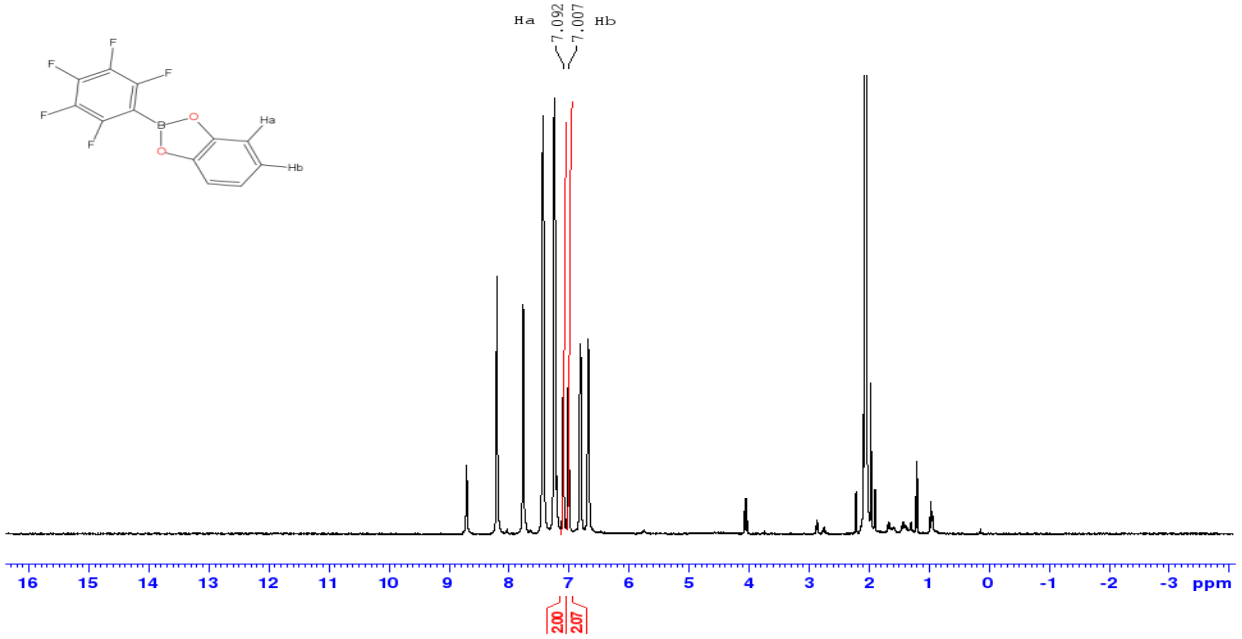

Figure A38. ^{1}H NMR 2,3,4,5,6-pentafluorodiphenylboronate

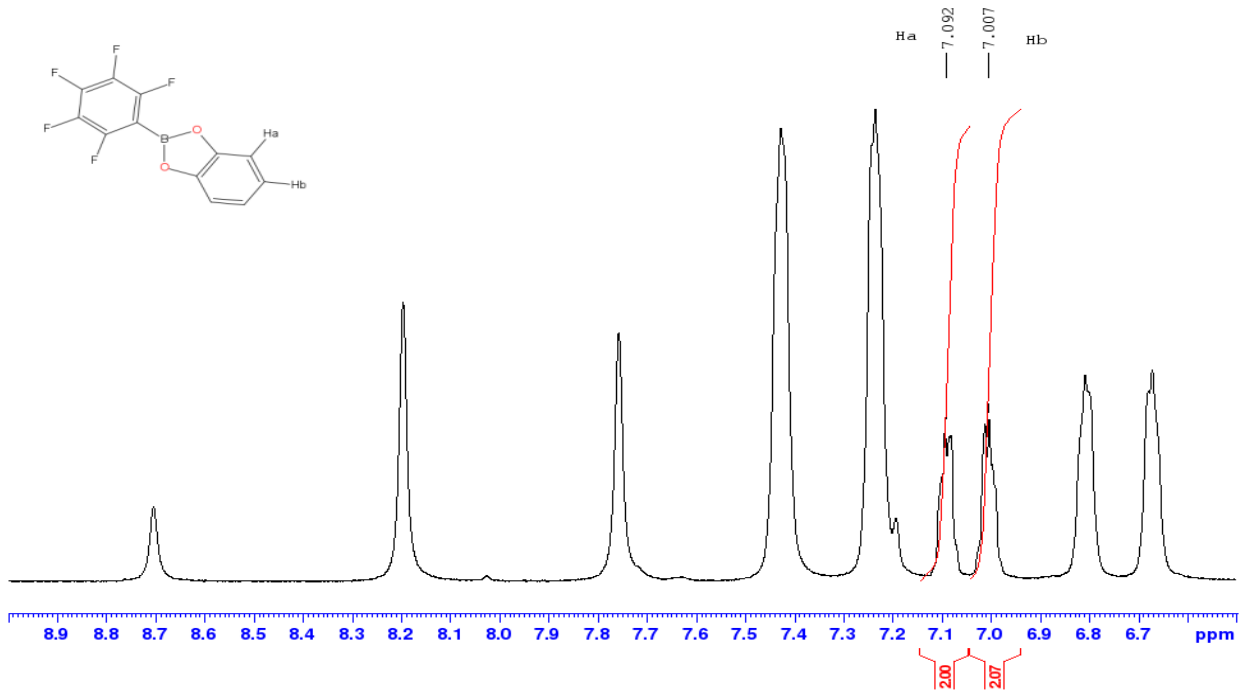

Figure A39. Aromatic Region ^{1}H NMR 2,3,4,5,6-pentafluorodiphenylboronate