Phenyl Replacement Reactions: Solvent Effects on Reactions of Boroxines with Primary Amines

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Western Carolina University in partial fulfillment of the

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By

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ABSTRACT

Phenyl Replacement Reactions: Solvent Effects on Reactions of Boroxines with Primary Amines

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Western Carolina University (January 2015)

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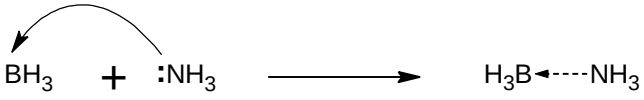
When primary amines are reacted with boroxines in solvents such as diethyl ether or THF, a dative bond forms between the lone pair of electrons on the nitrogen atom and a boron atom in a predictable manner. However, when the highly complexing solvent dioxane is used, evidence of a phenyl displacement reaction has been observed. In this work I examined the effects of a variety of electron donating and withdrawing groups on boroxines, specifically whether or not these groups have an effect on the proposed outcome of the hypothesized phenyl displacement reaction. The types of boroxines and amines were varied as well as their relative ratios. The resulting reaction mixtures were evaluated by ^{1}H-NMR, GC-MS and FT-IR. The nitrogen boron dative bond complex formed rather than the desired phenyl replacement product.

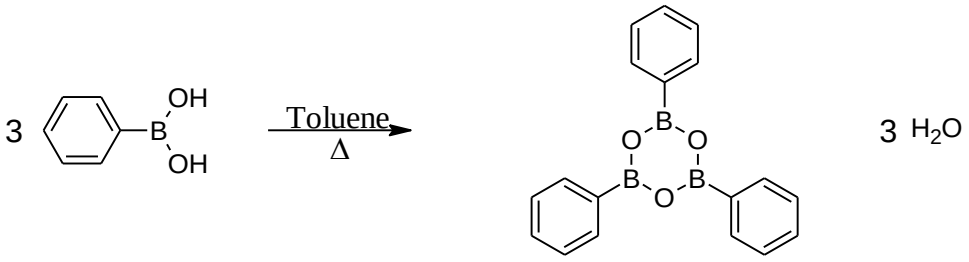
CHAPTER ONE: INTRODUCTION

1.1 Background

In freshman chemistry we are taught that there are two types of bonding that can occur between atoms in a molecule. When the electronegativity values of two atoms are quite different, the resulting bond is classified as being *ionic* and when the electronegativity values are similar, the bonding is classified as *covalent***,** depending upon the specific atoms involved. One subcategory of the covalent bond category is the *coordinate covalent bond* in which one of the atoms acts as the Lewis acid, or electron acceptor, while the other acts as a Lewis base, or electron donor. In a coordinate covalent, or *dative* bond the Lewis base contributes both electrons to form that bond. In a bond between boron and nitrogen atoms, the nitrogen acts as the Lewis base and donates both electrons to form a dative bond with boron (Scheme 1). The boron atom acts as the Lewis acid because it has an unoccupied p-orbital while nitrogen has an SP^3 p-orbital occupied by a lone pair of electrons.[1]



Scheme 1. The formation of a dative bond between borane and ammonia.

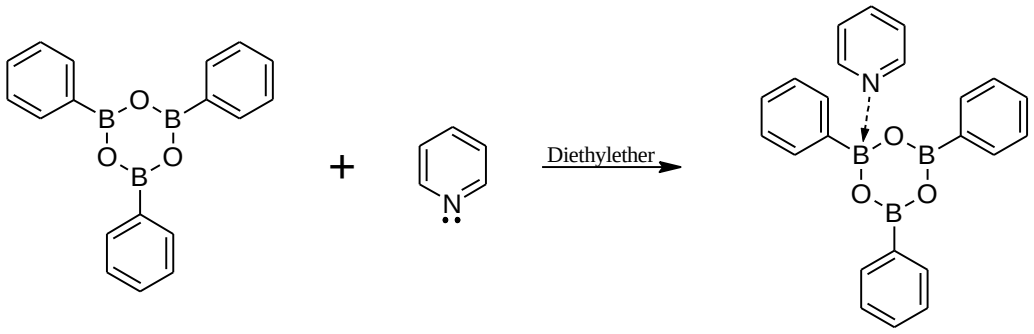


Scheme 2. Reaction of phenyl boronic acid to produce phenyl boroxine.

In a complexation reaction similar to that described in (Scheme 1), larger boron containing molecules called *boroxines* can complex with Lewis bases. The reaction for the formation of these boroxines can be seen in (Scheme 2). Boroxines are formed by the reflux of boronic acids with a Dean-Stark trap and condenser [2]. The Dean-Stark trap is used for the azeotropic removal of water resulting in high yields of product.

Figure 1. Picture of a Dean-Stark trap.

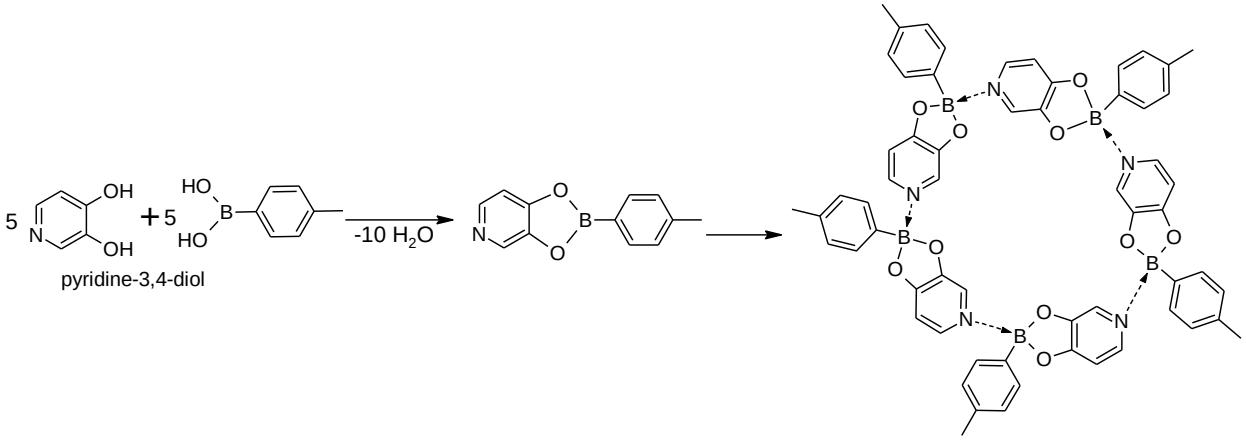
The boron atoms in the boroxine are good Lewis acids and can form a dative bond with a Lewis base such as pyridine (Scheme 3). The resulting bond is dynamic, so while in solution the nitrogen atom will associate and dissociate rapidly between all three boron atoms[6].



Scheme 3. Reaction between phenylboroxine and pyridine forming a complex via dative bond.

1.2 Complexes created by dative bonds

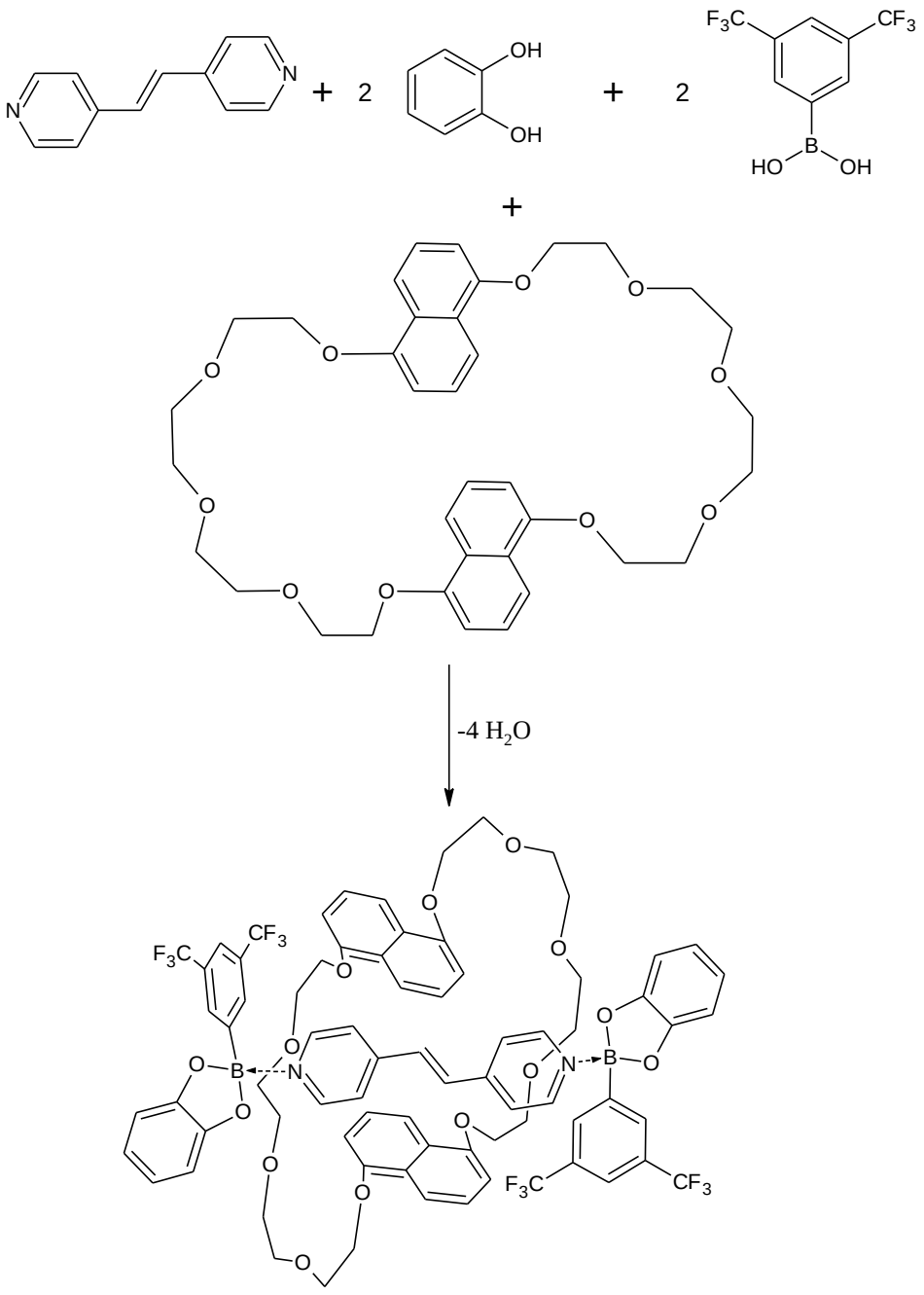
The dative bond complexes can be used to create larger and more intricate structures. An example of these structures is a macrocycle, or a large molecule in a cyclic conformation. These macrocycles are often created in what's commonly referred to as a "one pot" synthesis where all the reactants are added at one time though more than one reaction takes place[5]. In the example below (Scheme 4) the boronate is formed first via condensation reaction followed immediately by the dative bonds forming between the nitrogen and boron atoms to form the complex[4].



Scheme 4. A condensation reaction of 4-methylphenyl boronic acid and 3,4-dihydroxy pyridine to form a macrocycle.

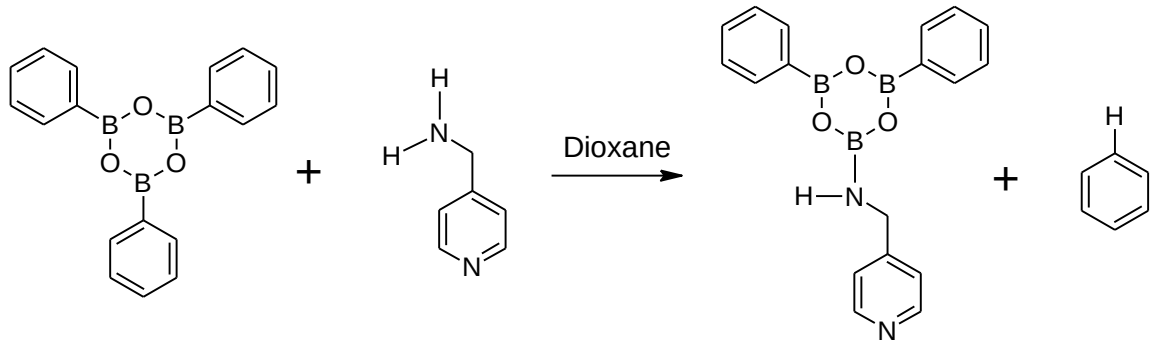
These self-assembling structures can be taken one step further to create a type of molecules known as rotaxanes. A rotaxane is a large macrocycle with another smaller molecule threaded

through the middle of it which is capped on both ends to prevent the macrocycle form slipping off[7]. (Scheme 5)



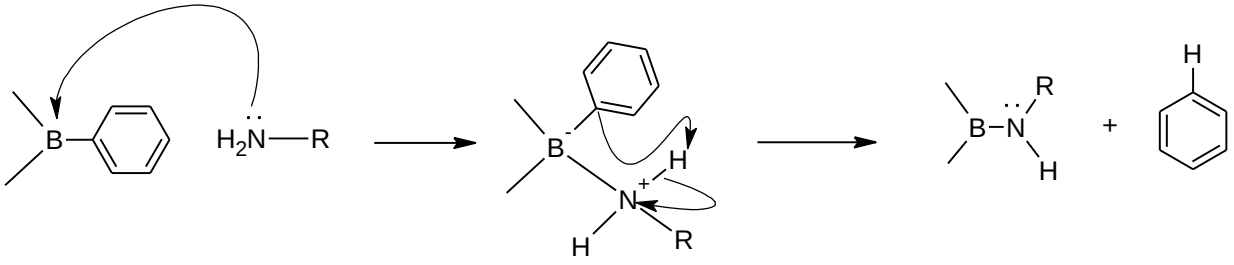
Scheme 5. Reaction to create a self-assembling rotaxane.

These amine-boroxine complexes are well known and have been studied extensively[3]. However, we have found evidence that when the reaction solvent was changed from diethyl ether to 1,4-dioxane, the dative bond complex no longer forms and a different type of reaction occurs. In his 1968 doctoral thesis John Ritchey[4] proposed that due to coordinating ability of dioxane, a primary amine does not form the complex with a boroxine, but instead a phenyl group on the boroxine is replaced by the amine. (Scheme 6).



Scheme 6. The reaction between phenylboroxine and 4-(aminomethyl) pyridine in 1,4-dioxane solvent.

In the case of phenylboroxine, benzene is produced as a byproduct. This benzene byproduct was what first led Ritchey to both propose and investigate that the replacement reaction was taking place. In his thesis Ritchey proposed a reaction mechanism for the phenyl replacement shown in (Scheme 7).



Scheme 7. Reaction mechanism proposed by Ritchey for phenyl replacement reaction.

The reaction proposed by Ritchey used only phenyl boroxine, in this work several boroxines were tested. The boroxines varied in the functional groups in the 4 position of the phenyl group, the structures of these compounds can be seen in Figure 2. The functional groups were varied to test the effect of electron donating and electron withdrawing groups. The electron withdrawing functional groups should favor the replacement reaction taking place.

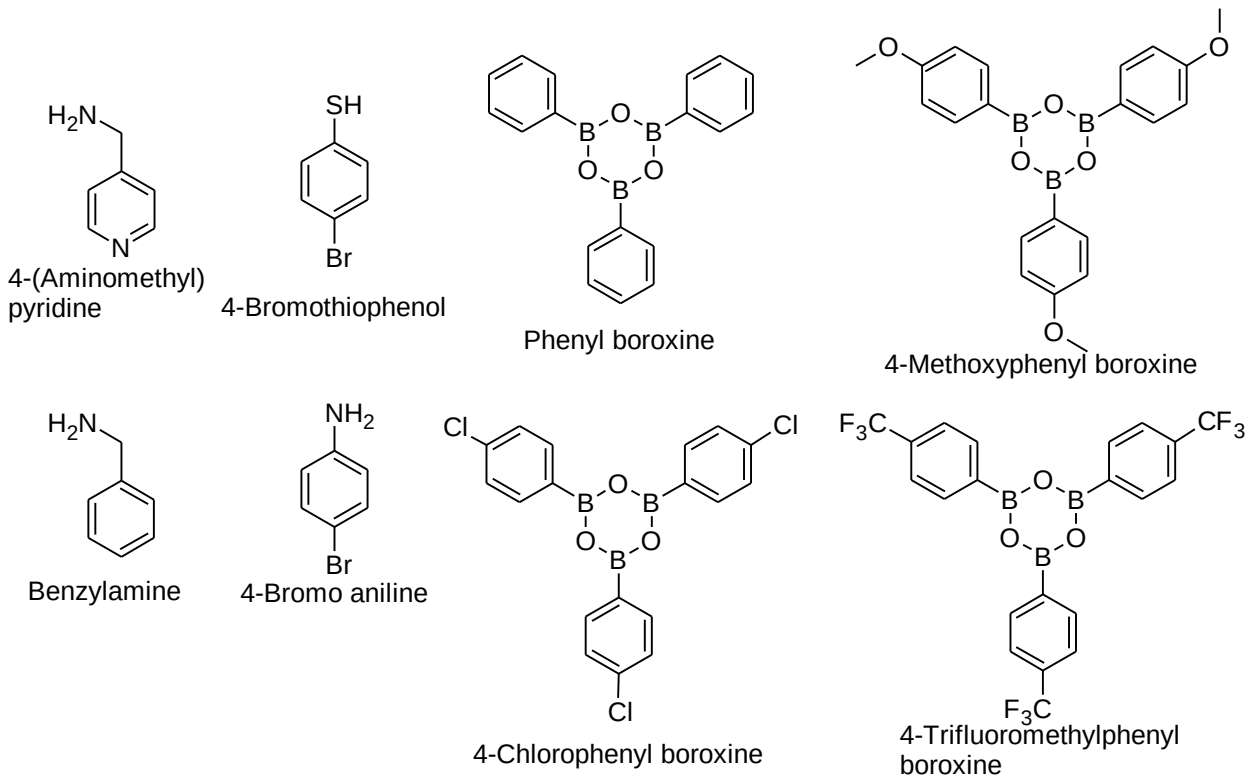
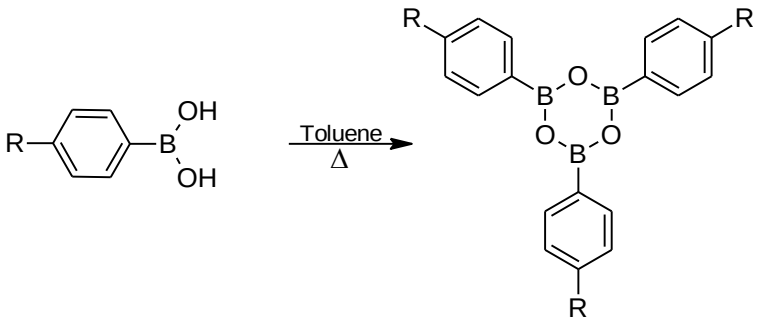


Figure 2. Structures of boroxines and amines used.

CHAPTER TWO: RESULTS AND DISCUSSION

2.1 Displacement and Complexation Reactions

This project focused on trying to replicate and better understand a displacement reaction proposed by Dr. John Ritchey in his 1968 doctoral thesis. The complexation reactions between boroxines and amines have been studied and well documented while the displacement reaction proposed by Ritchey has little documentation. The main goal of the project was to first see if the reaction worked as Ritchey proposed. The second goal was to optimize the reaction if it did indeed work as Ritchey described.



The first step for any of the reactions is the production of the boroxine from the boronic acid. The boroxines produced varied with R representing CH_3O, H, CF_3 or Cl. All of the boroxines were produced the same way with the boronic acid being placed in a round bottom flask with a toluene solvent and heated to reflux with a Dean stark trap. In every case the product produced a white powdery solid. The white solids were confirmed by ^{1}H NMR to be the boroxine with small amounts of the boronic acid still present (Figure 1).

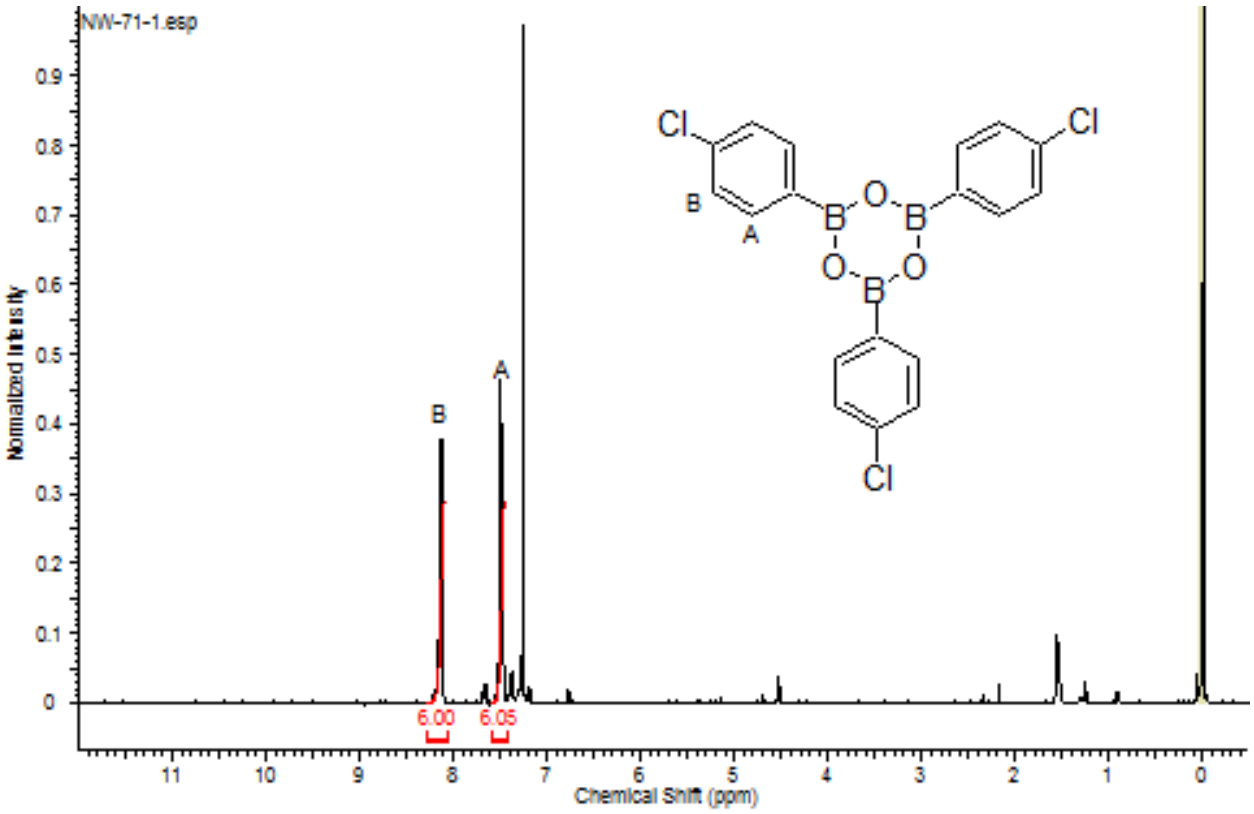
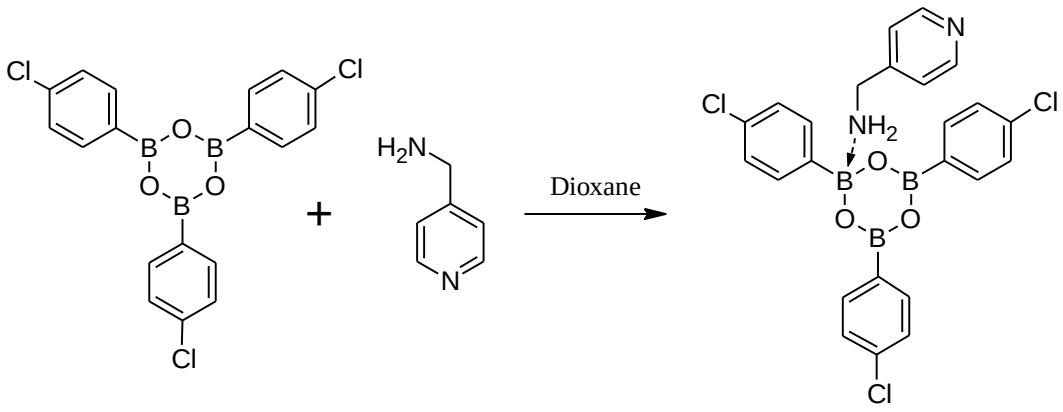


Figure 3. ^{1}H NMR spectrum of 4-chlorophenyl boroxine with trace amounts of 4-chlorophenyl boronic acid in $CDCl_3$.



The first reactions trying to replicate Ritchey's results were run in wet dioxane with results being very poor. Anhydrous dioxane was used for all reactions thereafter and the first reaction in the series was 4-chlorophenyl boroxine and 4-(aminomethyl) pyridine run in a 1:1 ratio at room temperature. The dioxane solvent proved difficult to fully remove in most if not all

cases which resulted in percent yields above 100% as well as dioxane being present in ^{1}H NMR spectra at 3.7 ppm. By looking at the integrations of the ^{1}H NMR it can be seen that the replacement reaction did not take place but a complexation reaction took place instead. It can also be seen that the amine is complexed to the boroxine by the amine nitrogen not the pyridine nitrogen by the disappearance of the peak at 1.49 ppm.

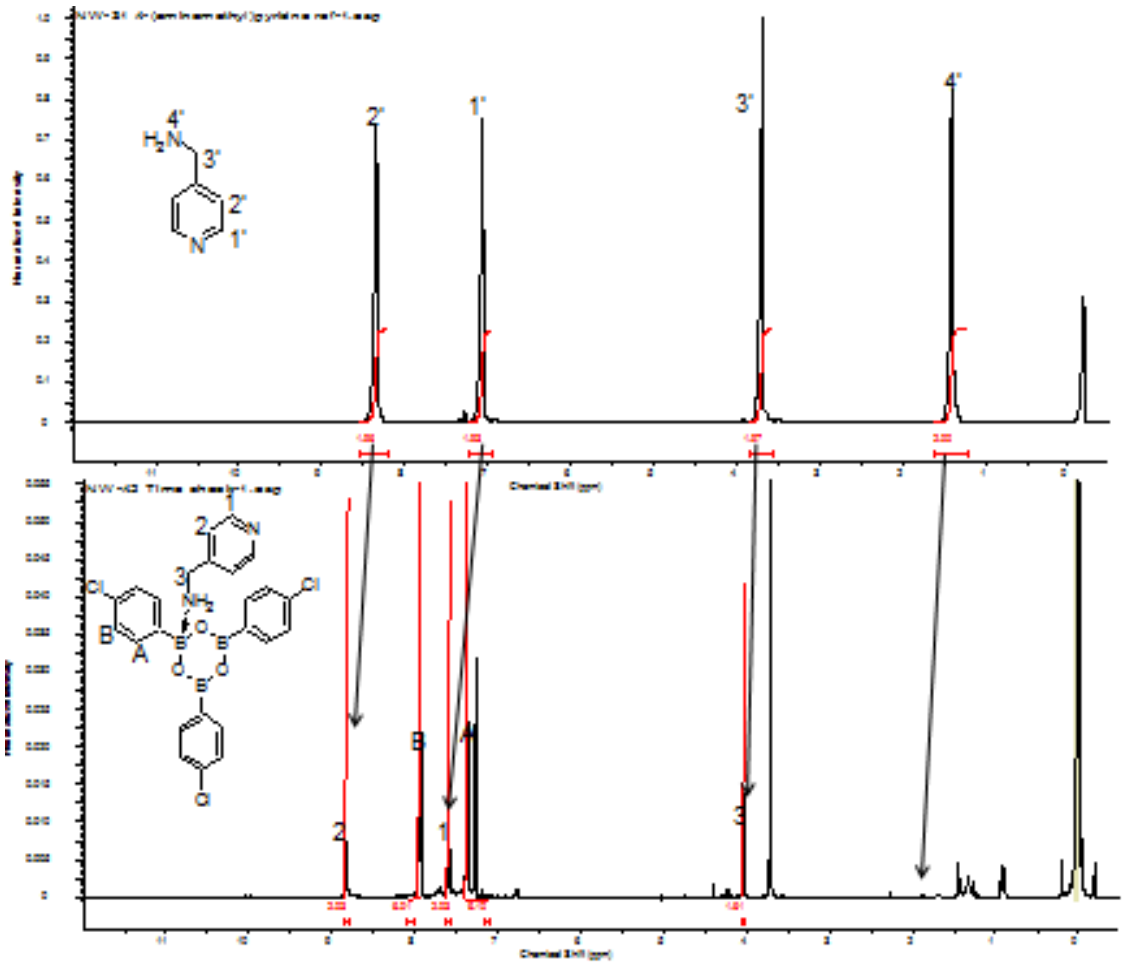
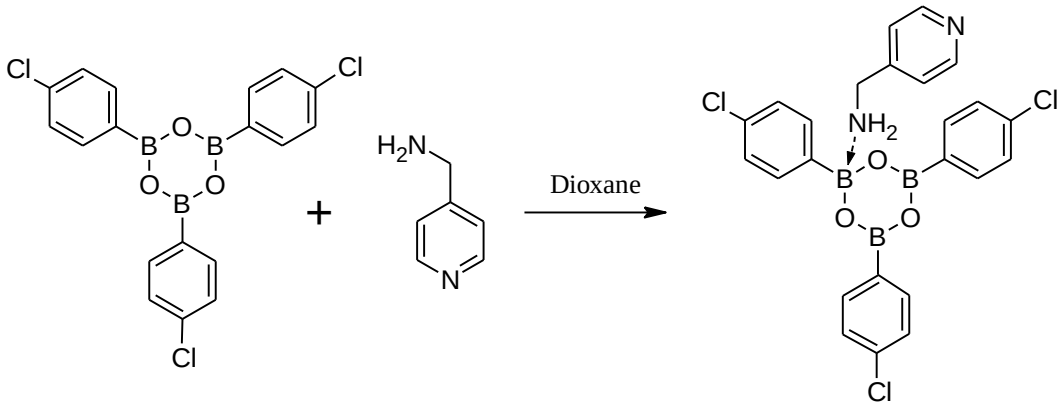


Figure 4. ^{1}H NMR spectra of complex with 4-cholorophenyl boroxine and 4-(aminomethyl) pyridine in $CDCl_3$.



The boroxine was then changed to 4-methoxyphenyl boroxine reacting with the 4-(aminomethyl) pyridine and the ratio was kept at 1:1 at room temperature. The ^{1}H NMR confirmed that the complex formed by the integrations of the boroxine peaks. If the displacement reaction had occurred then the doublets at 6.9 ppm and 8.0 ppm would only integrate to 4H instead of the 6H that they are. The shifts in the peaks at 4.0, 7.5, and 8.8 ppm as well as the disappearance of the peak at 1.49 ppm show that the complex forms through the amine nitrogen not the pyridine nitrogen.

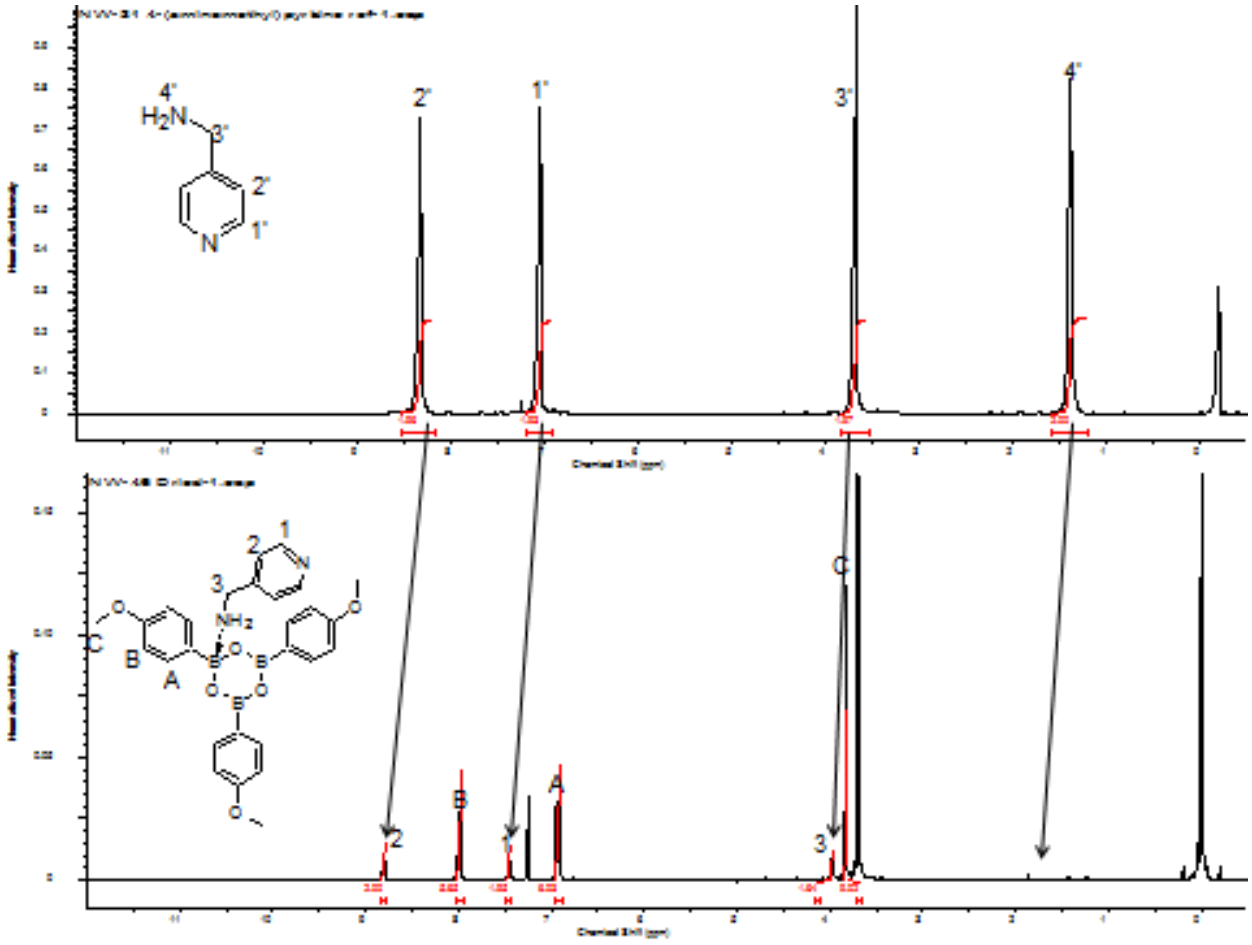
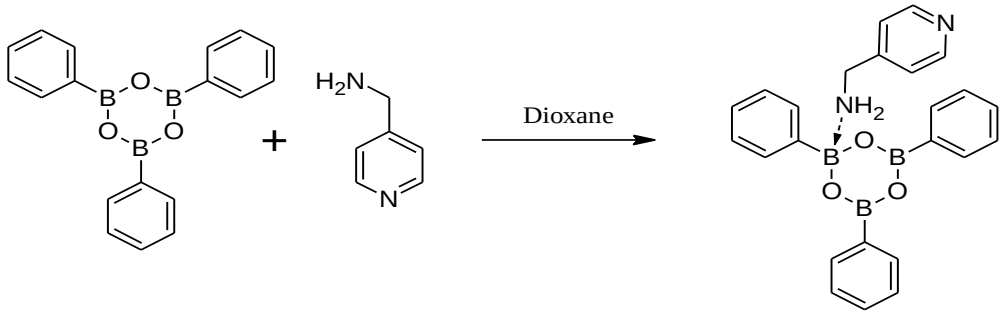


Figure 5. ^{1}H NMR spectra of complex formed between 4-chlorophenyl boroxine and 4-(aminomethyl) pyridine in $CDCl_3$.



The boroxine was again changed, this time to phenyl boroxine, and reacted once again in a 1:1 ratio with 4-(aminomethyl) pyridine. The reaction was run at room temperature with stirring just like the previous experiments. The displacement reaction did not occur, the ^{1}H NMR shows the integrations of the boroxine peaks totaling 6H and 9H instead of the desired 4H and

6H. The signals for the hydrogens on the 3, 4, and 5 phenyl carbons are overlapped thus showing up as 6:9H rather than 6:6:3H. The disappearance of the 1.49 ppm signal of the amine peaks also show that the complexation occurs between the amine nitrogen and not the pyridine nitrogen.

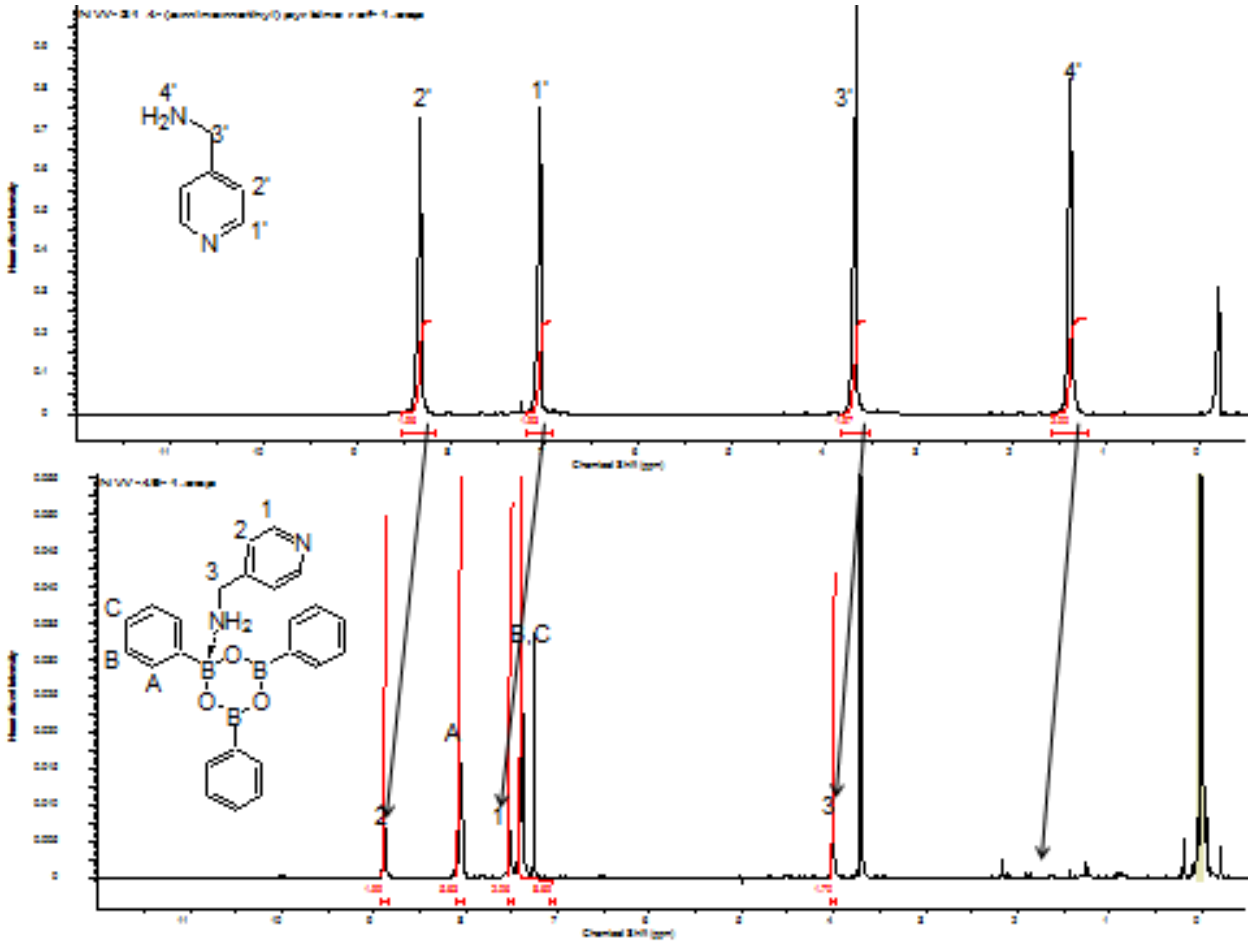
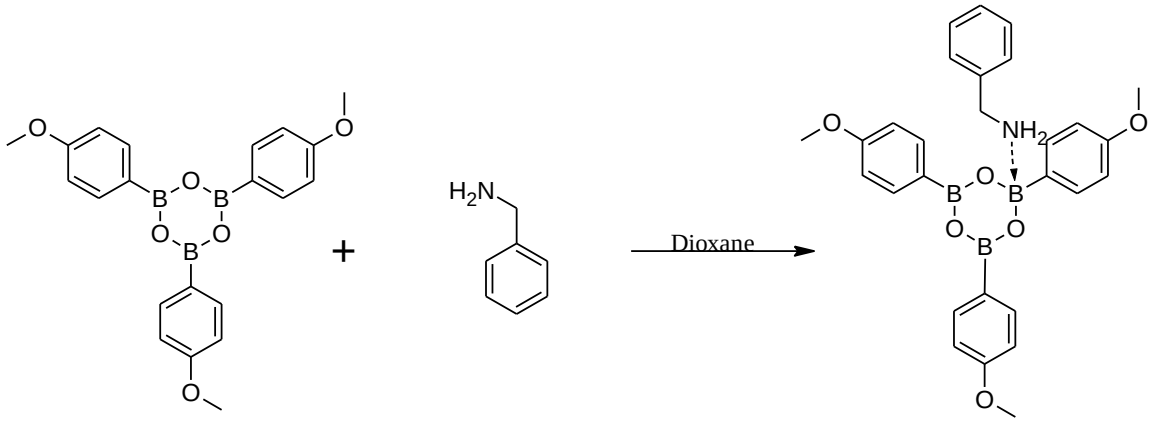


Figure 6. ^{1}H NMR spectra of complex formed between phenyl boroxine and 4-(aminomethyl) pyridine in $CDCl_3$.



After the reactions between several boroxines and 4-(aminomethyl) pyridine resulted in the complexation products forming instead of the desired displacement products the amine was changed. Benzyl amine was chosen in the hopes that it would help force the displacement reaction having no nitrogen in the aromatic ring portion of the molecule. The thought behind changing to an amine with only one nitrogen was to try to eliminate any competition with in the amine itself. Benzyl amine was now reacted with 4-methoxyphenyl boroxine in a 1:1 ratio at room temperature. The ^{1}H NMR shows that the displacement reaction once again did not take place. The integration of the boroxine peaks in the NMR confirms that all three methoxyphenyl rings are still intact. The disappearance of the amine nitrogen peak at 1.40 ppm confirms that the complex forms.

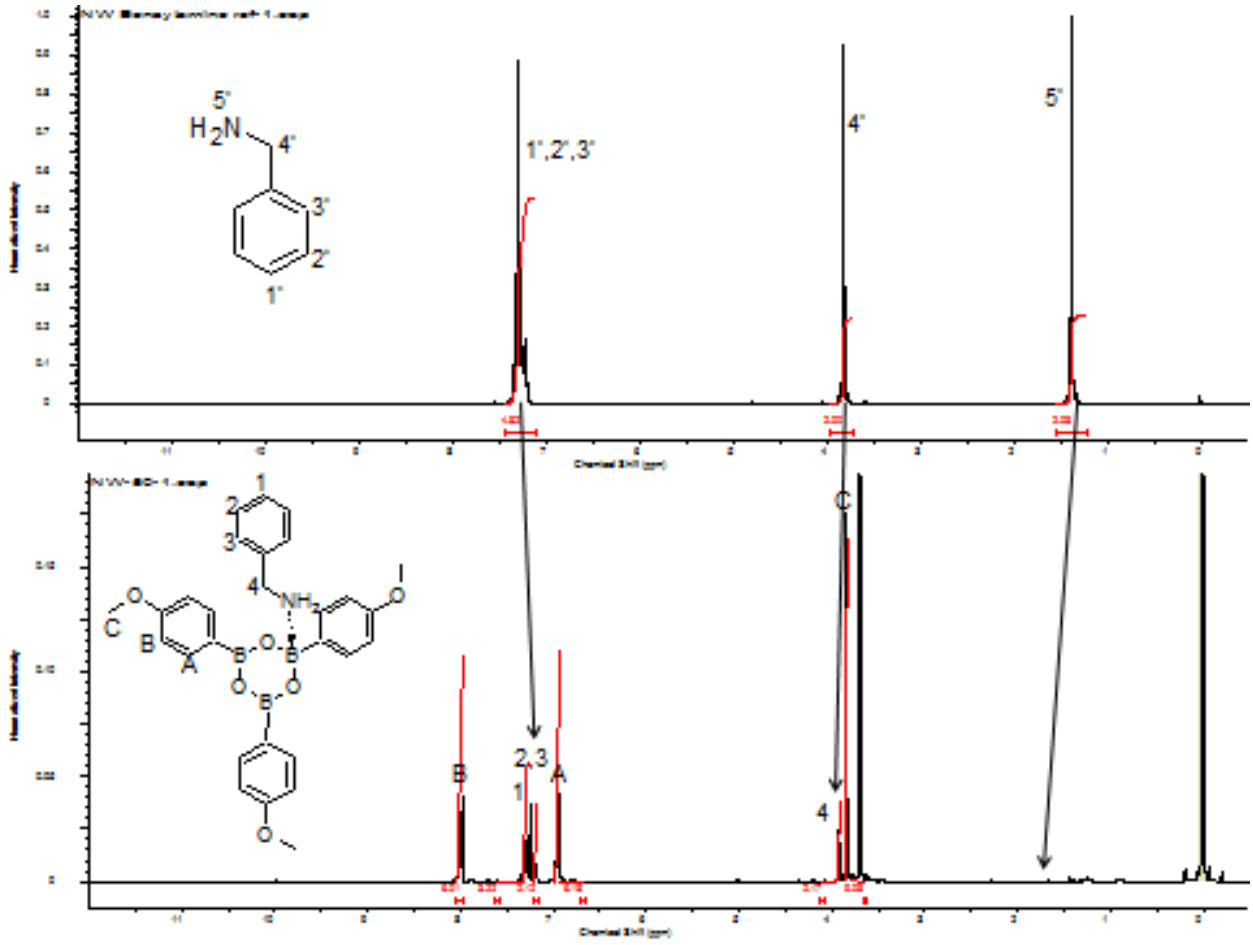
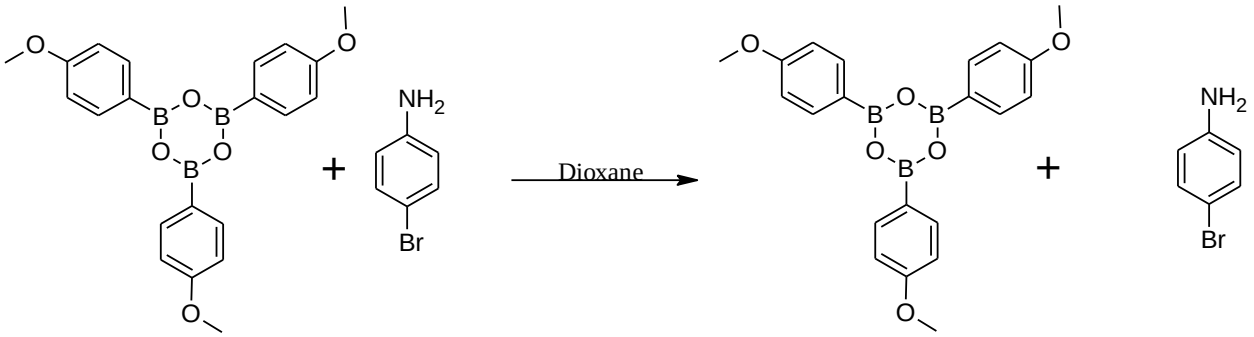


Figure 7. ^{1}H NMR spectra of complex formed between benzyl amine and 4-methoxyphenyl boroxine in $CDCl_3$.



The amine was changed after the benzyl amine formed a complex. This time p-bromoanilline was used as the amine. P-bromoaniline was chosen since it's a fairly ridged molecule with an electron withdrawing group on it. The electron withdrawing group on the amine

combined with the electron donating group on the boroxine would promote the replacement reaction. P-bromoaniline was reacted with 4-methoxyphenyl boroxine in a 1:1 ratio. The reaction between the boroxine and p-bromoanilline resulting in nothing other than starting materials being recovered indicating that neither the complex nor the replacement product formed. The ^{1}H NMR confirms this with no chemical shifts on the part of the boroxine or amine occurring, no changes in integration occurred either.

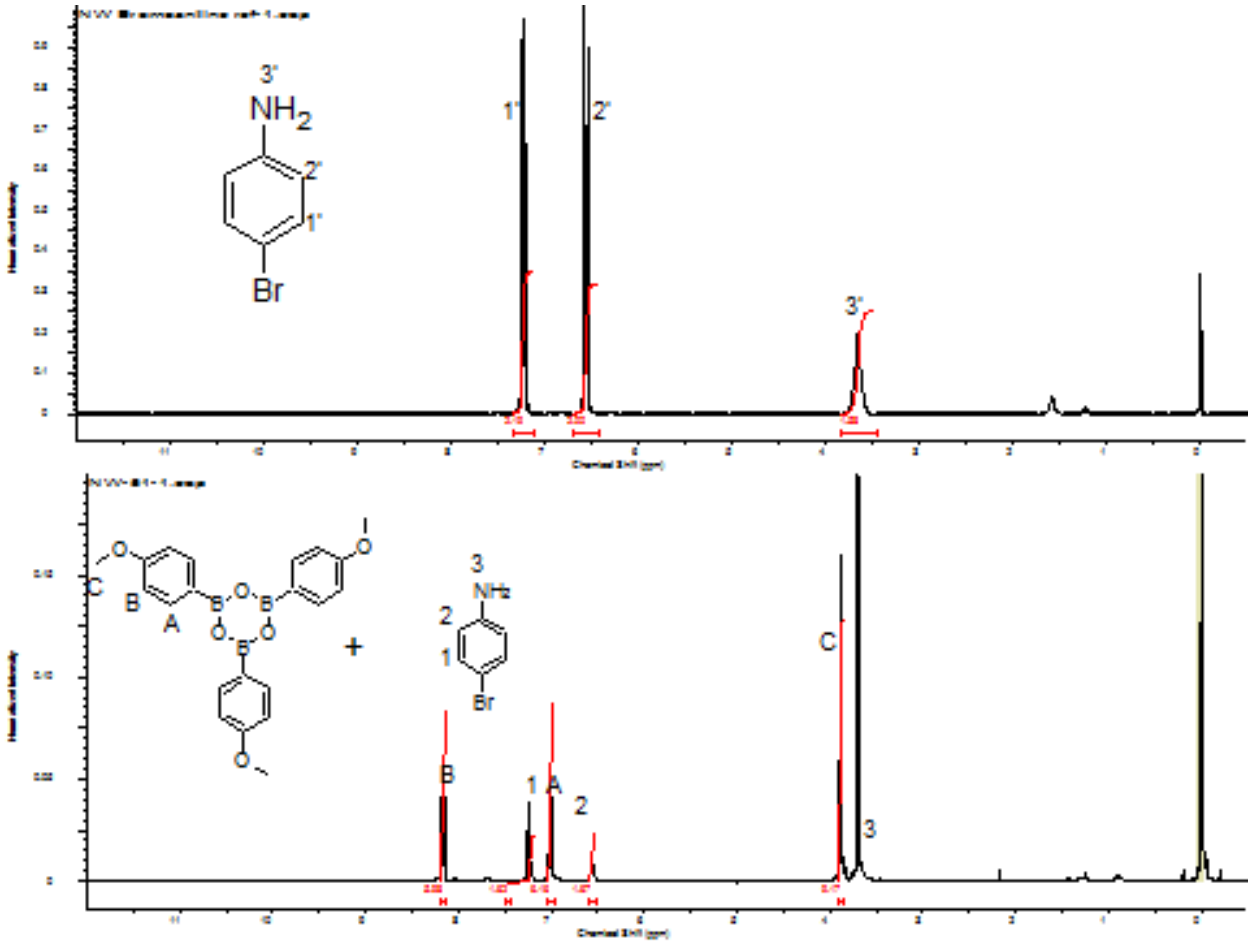
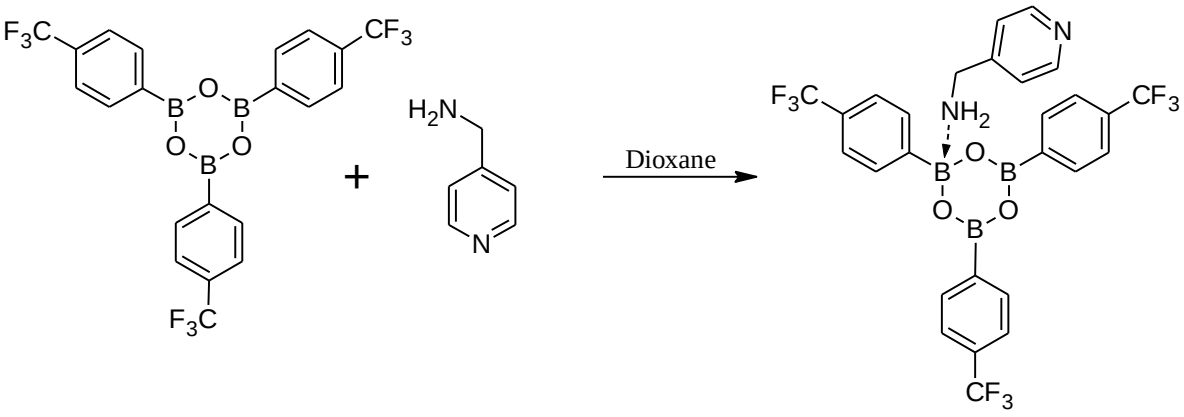


Figure 8. ^{1}H NMR spectra of p-bromoanilline and 4-methoxyphenyl boroxine after attempted reaction in $CDCl_3$.



4-Trifluoromethylphenyl boroxine was produced to be reacted with 4-(aminomethyl) pyridine. The reaction was done in a 1:1 ratio at room temperature like all other reactions up to this point. The ^{1}H NMR shows that the displacement reaction once again did not take place. The integrations for the peaks of the boroxine do not change but remain their 6H values. The disappearance of the peak at 1.49 ppm indicates that the complex forms between the amine nitrogen and not the pyridine nitrogen.

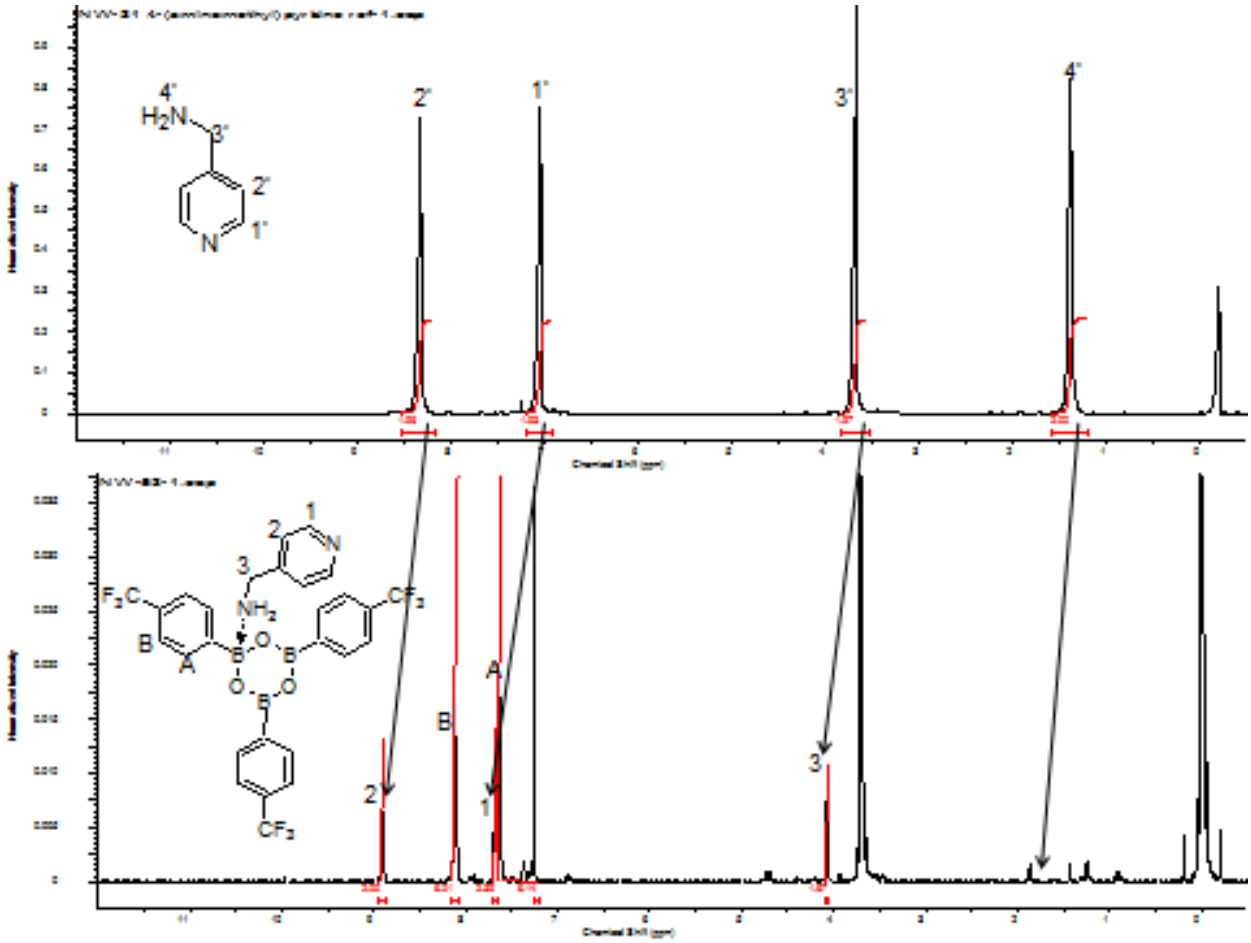


Figure 9. ^{1}H NMR spectra of complex formed between 4-trifluoromethylphenyl boroxine and 4-(aminomethyl) pyridine in $CDCl_3$.

None of the reactions Ritchey ran while working with the theorized displacement reactions were done above average room temperature, so it was thought that heating the reaction may help in promoting the displacement reaction rather than the complexation. 4-Trifluoromethylphenyl boroxine was once again reacted with 4-(aminomethyl)pyridine in a 1:1 ratio however this time the reaction was heated to reflux for 90 minutes. The reaction formed the complex yet again, this can be seen in the ^{1}H NMR. The integrations for the boroxine remain the same at 6H for each of its respective peaks. The disappearance of the peak at 1.49 ppm show that the complex if formed though the amine nitrogen not the pyridine nitrogen.

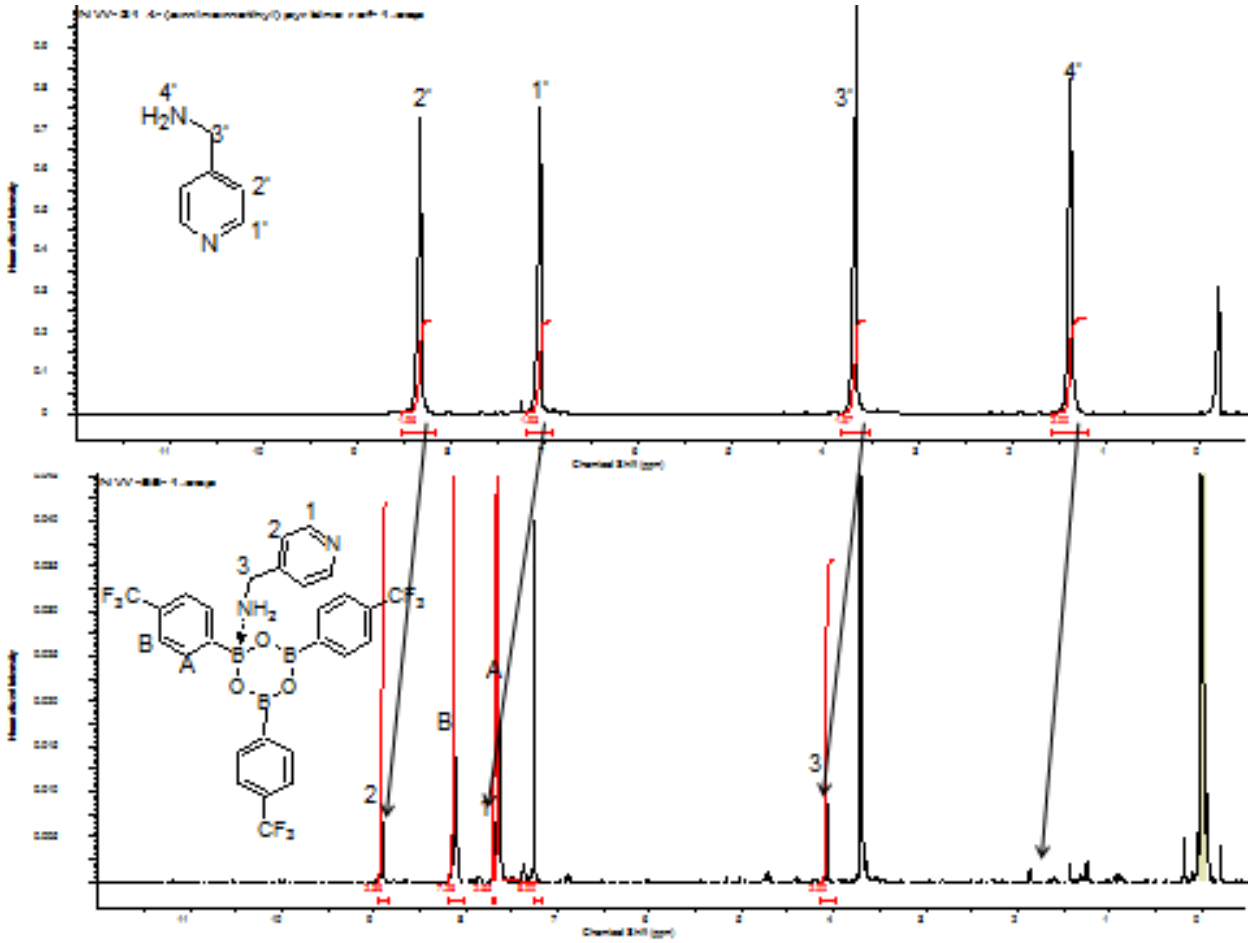


Figure 10. ^{1}H NMR spectra of the heated reaction forming the complex between 4-trifluoromethylphenyl boroxine and 4-(aminomethyl) pyridine in $CDCl_3$.

The reaction between 4-trifluoromethylphenyl boroxine and 4-(aminomethyl) pyridine was carried out once more but the ratio of amine to boroxine was changed and the amount of time the solution was heated increased. The amine to boroxine ratio was increased to 22:1. In this case the reaction was heated to reflux but this time for 6 hours. The ^{1}H NMR showed that the displacement reaction did not occur because the integrations for the boroxine remained constant at 6H. Although the amine was added in a large excess the integrations show that in the product only half the number of hydrogens are present as there should be. Additionally the signal 3.68 ppm is completely missing which could indicate that the amine bonded through the pyridine nitrogen rather than the amine nitrogen.

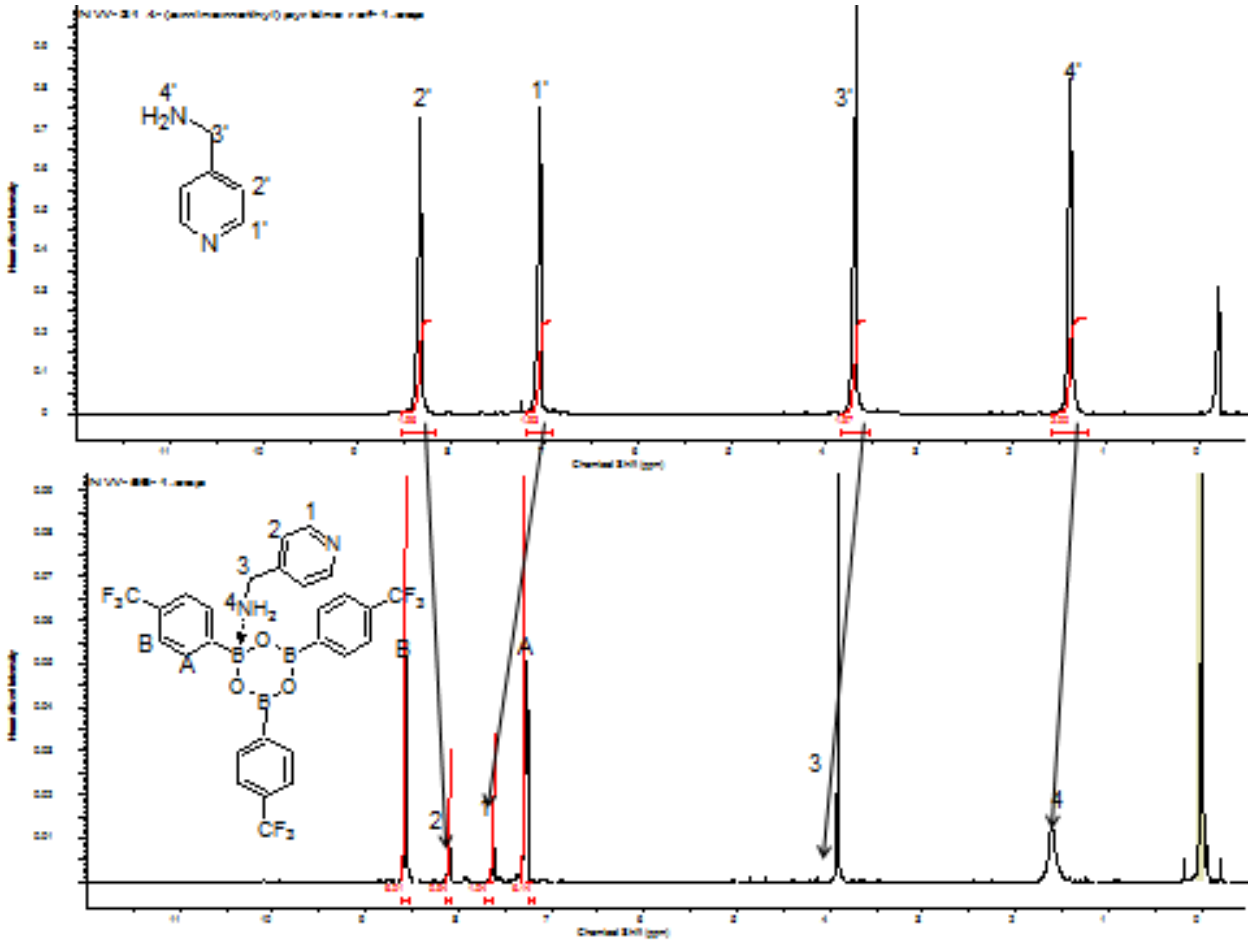
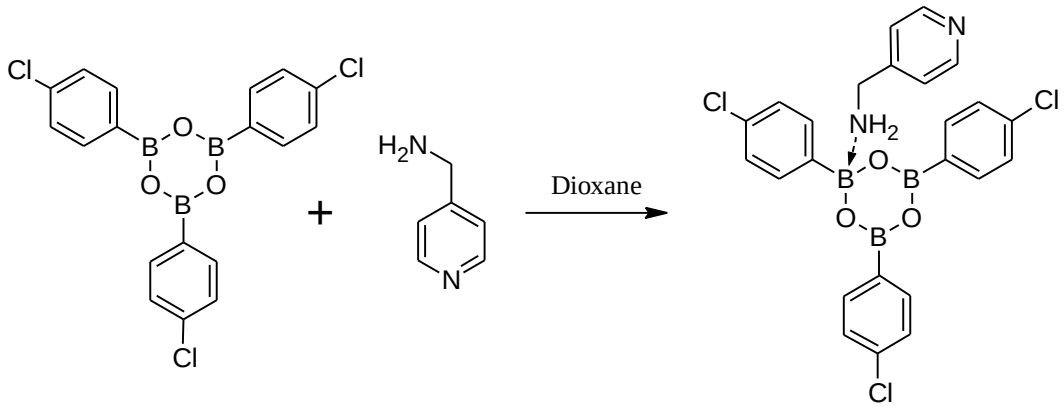


Figure 11. ^{1}H NMR spectra of the heated reaction between 4-trifluoromethylphenyl boroxine and excess 4-(aminiomethyl) pyridine in $CDCl_3$.



The reaction between 4-chlorophenyl boroxine and 4-(aminomethyl) pyridine was rerun. This time since heating seems to, at least some degree, affect the outcome the reaction would be heated to reflux. The reflux of this reaction differed slightly in that it used the reaction

microwave instead of a normal heating mantle. The microwave was chosen because it will heat reactions to reflux much quicker and is much steadier than heating with a heating mantle. The reaction was carried out in a 1:1 ratio like previous reactions. The ^{1}H NMR shows the complex occurring instead of the displacement. The integration for the boroxine peaks remaining at 6H and the disappearance of the signal at 1.49 ppm for the amine show that the complexation has occurred though the amine nitrogen and not the pyridine nitrogen.

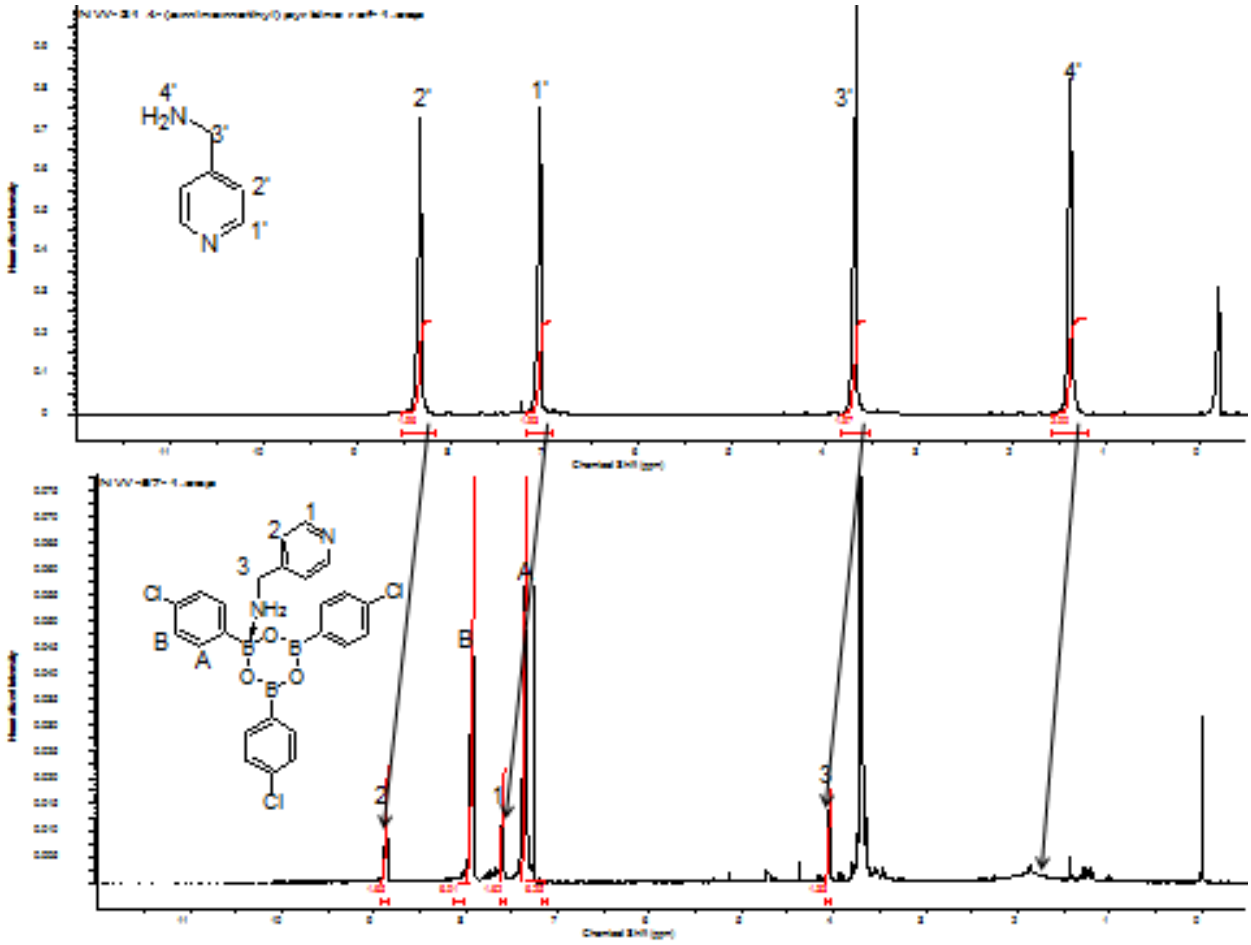


Figure 12. ^{1}H NMR spectra of the complex formed between 4-chlorophenyl boroxine and 4-(aminomethyl) pyridine in $CDCl_3$.

The next reaction was run with a highly saturated solution of 4-chlorophenyl boroxine in the dioxane solvent. The amount of amine used was the same 0.1205 mmol amount used in previous reactions. The reaction was also carried out at room temperature instead of at reflux.

The ^{1}H NMR shows that the complex formed yet again with the integrations for the boroxine being 6H. The hydrogens in the complex exhibit chemical shifts, namely the disappearance of the peak at 1.49 ppm, characteristic of being complexed though the amine nitrogen rather than the pyridine nitrogen. The integrations of the 4-(aminomethyl) pyridine are off by about 1 hydrogen each the reason for this is still unknown.

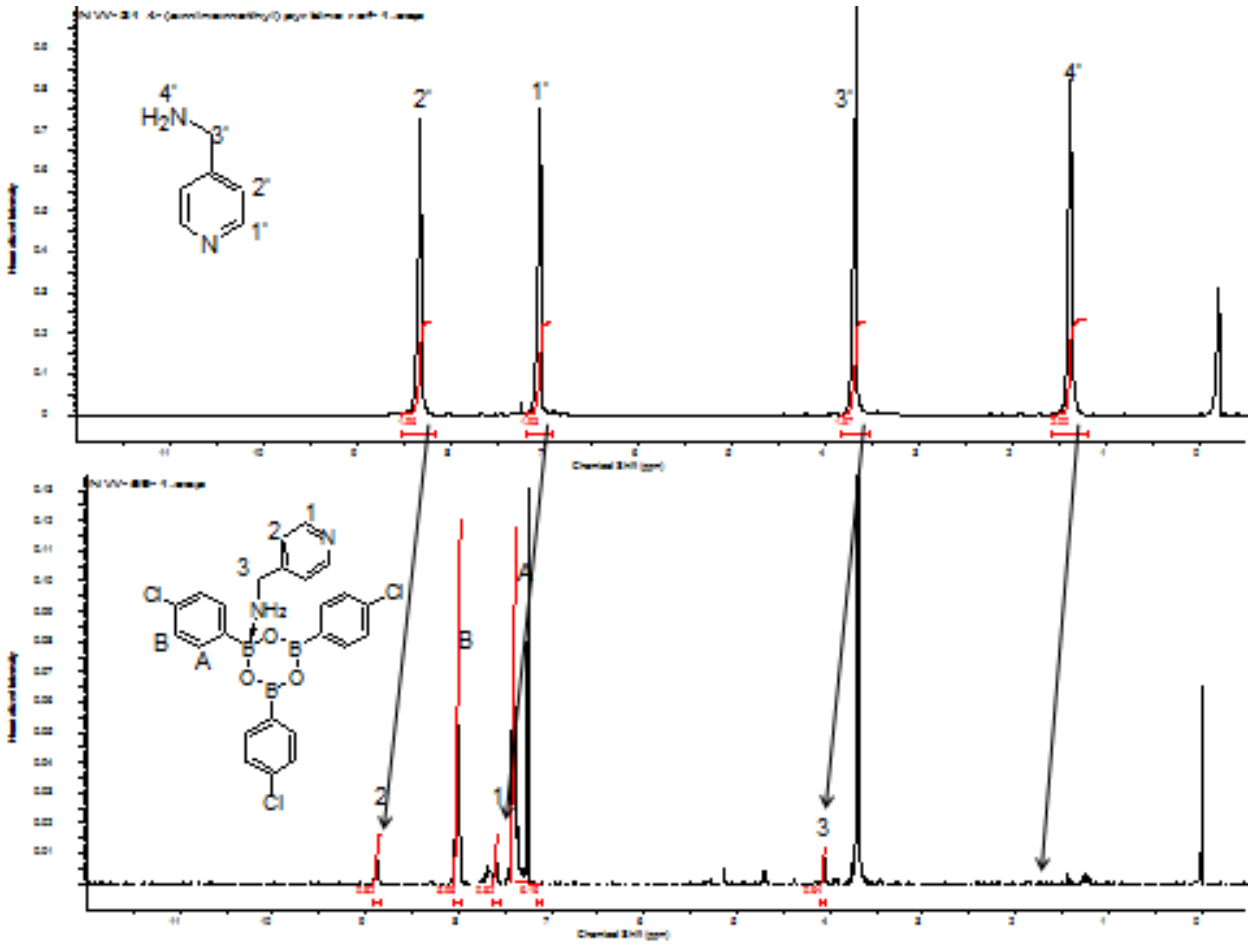
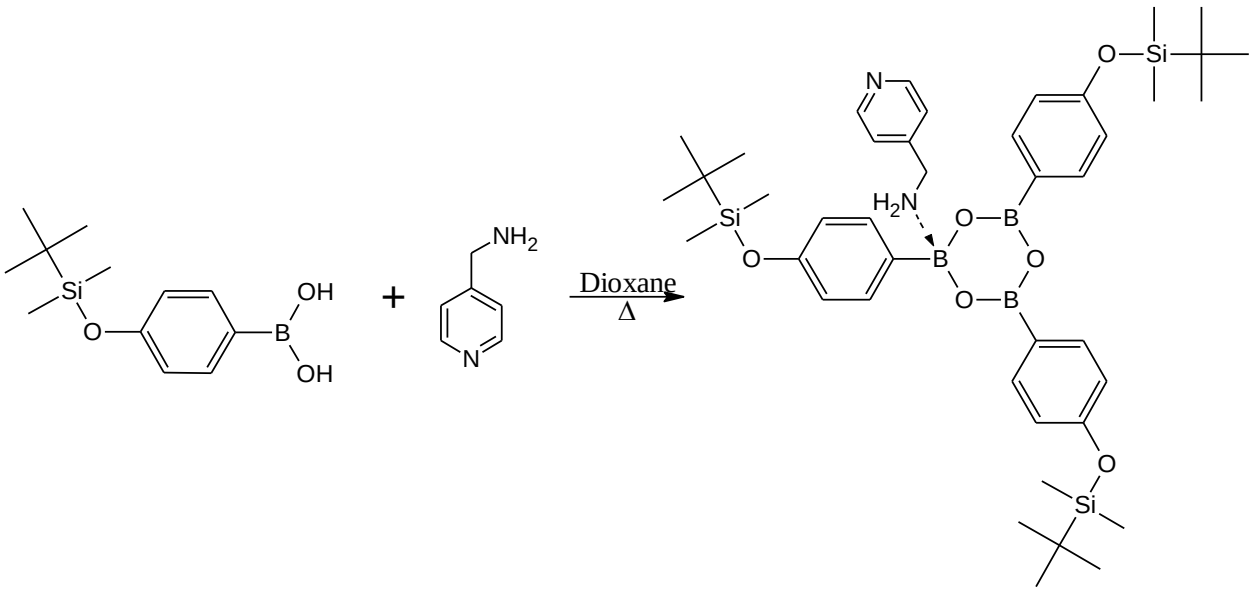


Figure 13. ^{1}H NMR spectra of the complex formed between excess 4-chlorophenyl boroxine and 4-(aminomethyl) pyridine in $CDCl_3$.



One common practice in the creation of boroxine-amine complexes is what's commonly referred to as a "one pot method" where the boronic acid is combined with the amine in the reaction flask rather than the boroxine. This method works quite well when forming complexes so it was decided to test if it could possibly work in the displacement reactions. To test this one pot method for the displacement reactions 4-(tert-butyldimethylsiloxy)phenyl boronic acid was used in a 3:1 ratio to 4-(aminomethyl) pyridine. This method did not work for creating the displacement product but did still produce the complex. ^{1}H NMR shows that the integrations for the boroxine remain at the 3:1 ratio. The chemical shifts for the amine show that the dative bond formed is through the amine nitrogen and not the pyridine nitrogen.

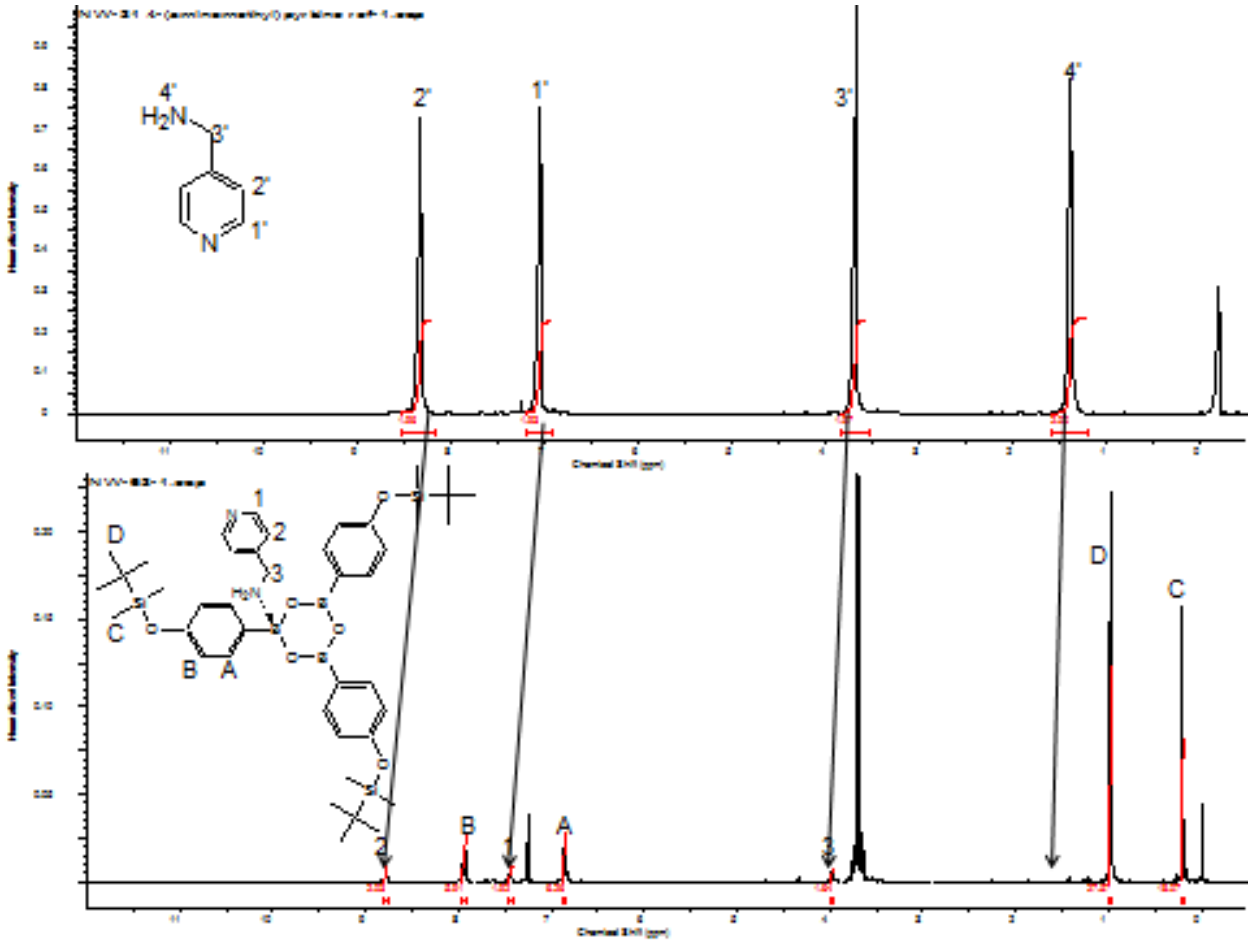
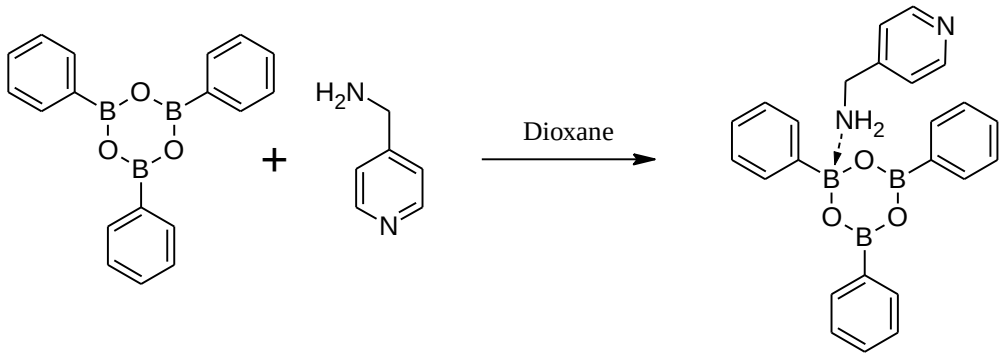


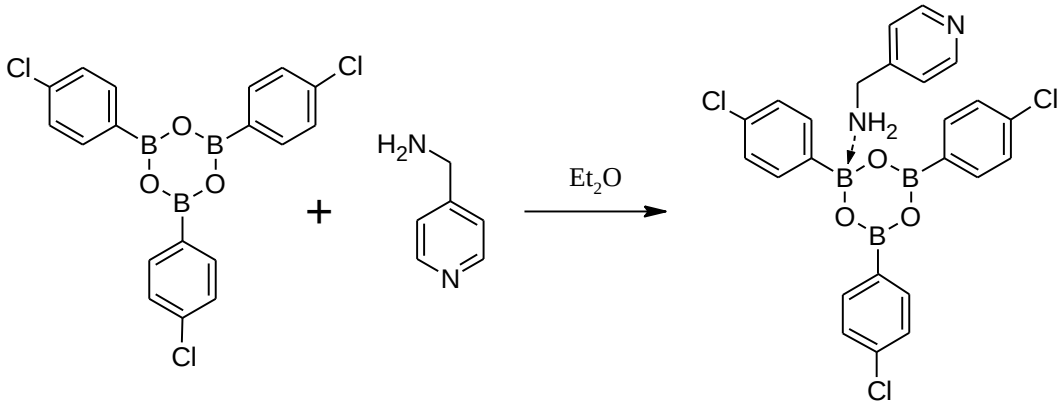
Figure 14. ^{1}H NMR spectra of the complex formed between 4-(tert-butyldimethylsiloxy)phenyl boronic acid and 4-(aminomethyl) pyridine $CDCl_3$.



The reaction between phenyl boroxine and 4-(aminomethyl) pyridine was carried out again in 1:1 ratio and heated to reflux for 5 hours. Samples from the condensate forming on the inside of the inside of the condenser were taken during the reflux. These samples would be

tested by GC-MS to test for the presence of benzene. The samples obtained during reflux were taken every hour in hopes that the presence of benzene would be detected. Since free benzene in the reaction mixture would indicate that there was a displacement reaction occurring. After the five samples were collected GC-MS spectra were obtained of each, none of which showed the presence of any benzene.

At this point we were relatively certain that Ritchey's proposed displacement reaction did not and will not take place. To confirm this several reactions were repeated using diethyl ether as the solvent instead of the dioxane. The reason for this is it is know that using an ether solvent will result in the complex forming so by repeating the reactions we would have spectra of a complex to compare directly with the products formed by the reactions done in dioxane.



The first reaction run for comparison was the 4-chlorophenyl boroxine reacted with the 4-(aminomethyl) pyridine. Since the reaction was carried out in diethyl ether the complex formed as predicted and was confirmed by ^{1}H NMR. When the NMR spectra of the complex is compared to the spectra of the reaction run in dioxane the chemical shifts match almost identically. However a slight variation was noticed in one of the chemical shifts for the 4-(aminomethyl) pyridine, but the shift only varies by less than 0.2 ppm so is with in an acceptable range.

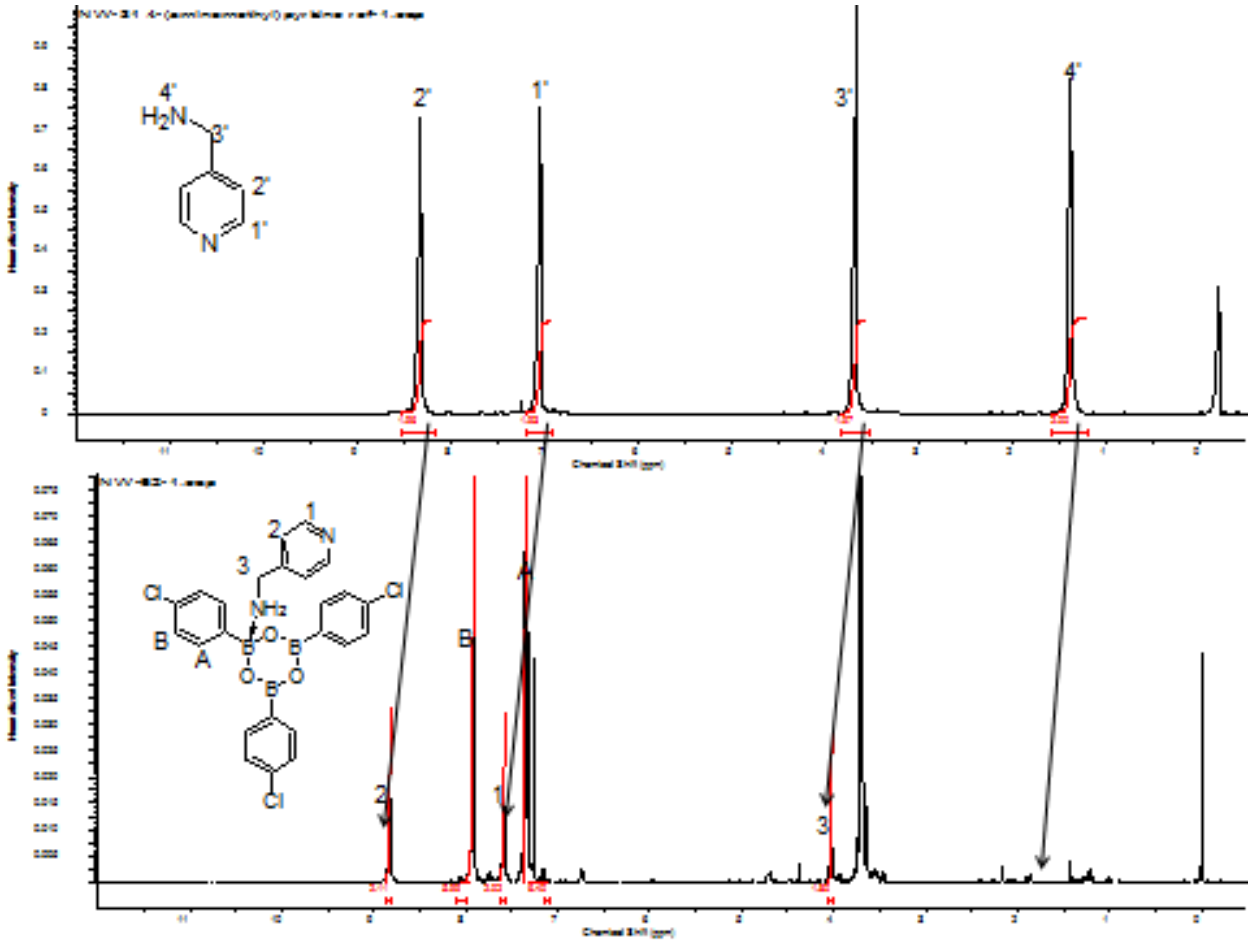
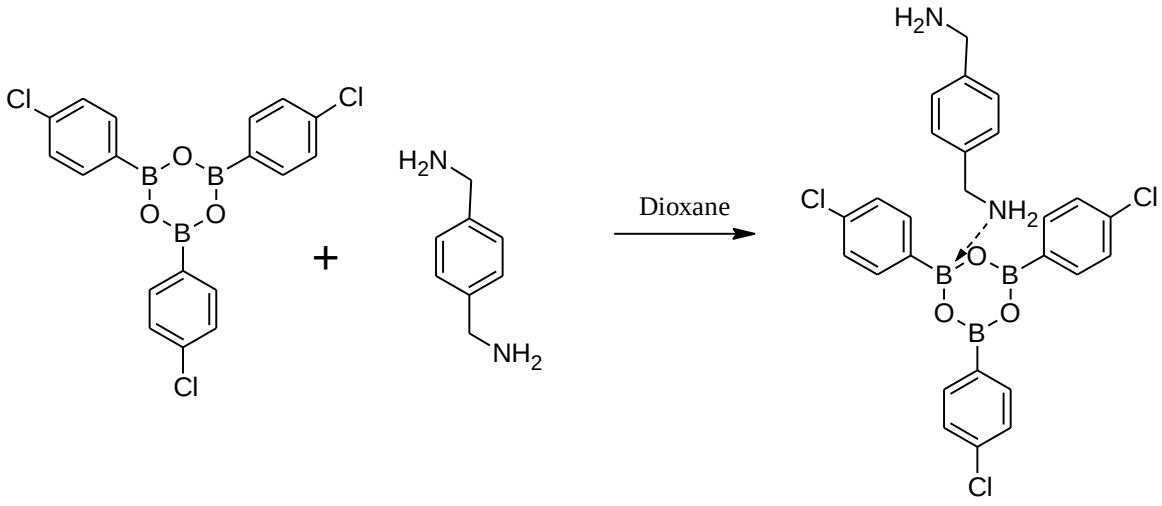


Figure 15. ^{1}H NMR spectra comparing both complexes formed from the reaction of 4-chlorophenyl boroxine and 4-(aminomethyl) pyridine in $CDCl_3$.



4-Chlorophenyl boroxine was reacted with xylene diamine in a 1:1 ratio in a dioxane solvent to test a potential alternative amine for the displacement reaction to occur. Since the

xylene diamine has two amine nitrogen atoms it would be possible for it to form a bond between two boroxines. As expected the displacement reaction did not occur. The complex between one of the boroxines and the xylene diamine did form. The ^{1}H NMR spectra shows that the integration for the boroxine is 6 hydrogens meaning that the complex formed between only one amine and one boroxine. The chemical shift of the xylene diamine also helps confirm the complexation forming.

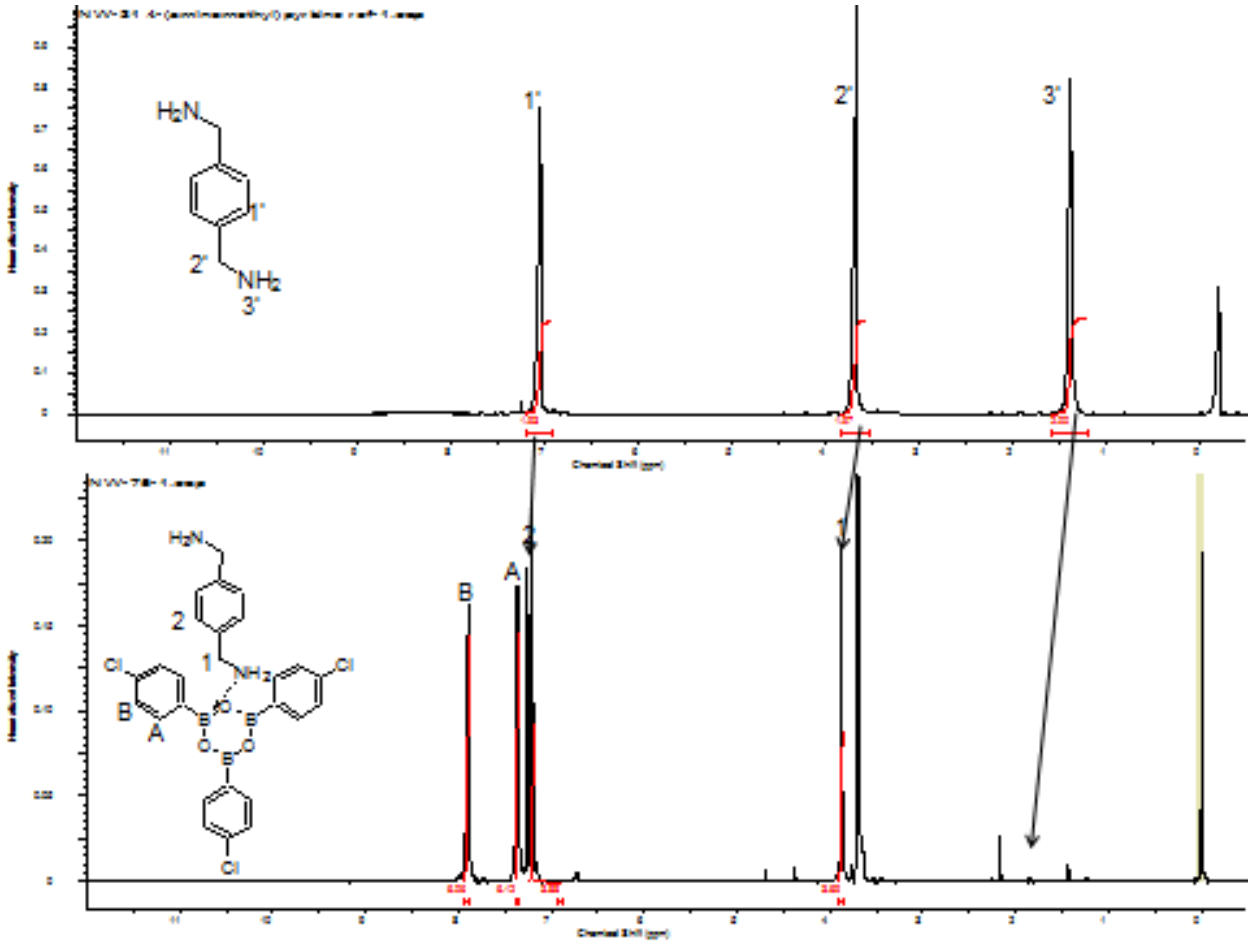


Figure 16. ^{1}H NMR spectra of the complex formed between 4-chlorophenyl boroxine and xylene diamine in dioxane solvent in $CDCl_3$.

The reaction between 4-cholrophenyl boroxine and xylene diamine was run again in a diethyl boroxine solvent. The reason this reaction was run was to confirm that only one bond would form between the xylene diamine and the boroxine not two. This also was used to

compare the results from the reaction in dioxane. When comparing the ^{1}H NMR spectra of the two reactions they are an exact match in both integration and chemical shift.

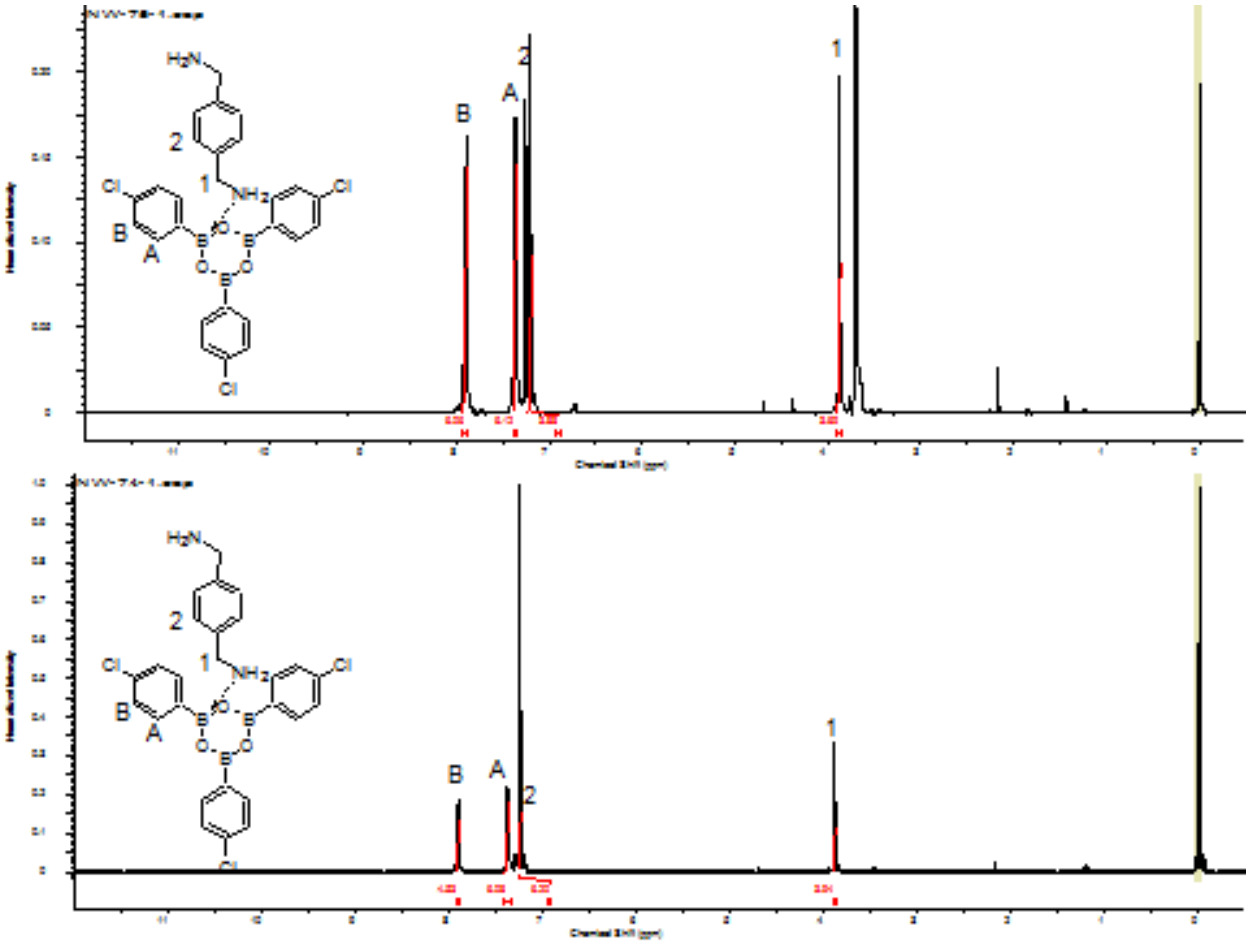


Figure 17. ^{1}H NMR spectra comparing the complexation reactions between 4-chlorophenyl boroxine and xylene diamine in both diethyl ether and dioxane solvents in $CDCl_3$.

CHAPTER THREE: CONCLUSION.

In our work with boroxines and amines in dioxane solvent systems we have shown that there is little to no sign that the replacement reaction proposed by Ritchey takes place. After reacting boroxines containing both electron withdrawing groups and electron donating groups with amines in 1:1 ratios at room temperature the replacement reaction never took place. Changing the amines did not cause the replacement reaction either nor did changing the relative ratios of the reactants. The amines formed the complexed through the amine nitrogen not the pyridine nitrogen in every case. Even when heating was added there was no sign of the replacement reaction taking place. The reaction proposed by Ritchey was tested under many different conditions all of which did not react the way he predicted.

CHAPTER FOUR: EXPERIMENTAL

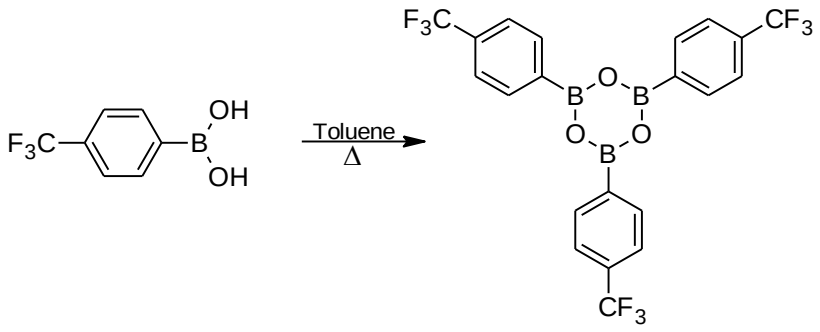
4.1: General.

All the reagents were purchased and used as is from commercial suppliers (Aldrich, Acros, or Fisher), unless otherwise stated. ^{1}H, COSY and ^{13}C NMR were recorded on a JEOL Eclipse+ 300 FT 300 MHz NMR Spectrometer.

4.2: Formation of boroxines from boronic acids.

Reaction of **4-trifluoromethylphenyl-boronic acid** in toluene to produce **4-trifuloromethyl phenylboroxine.**

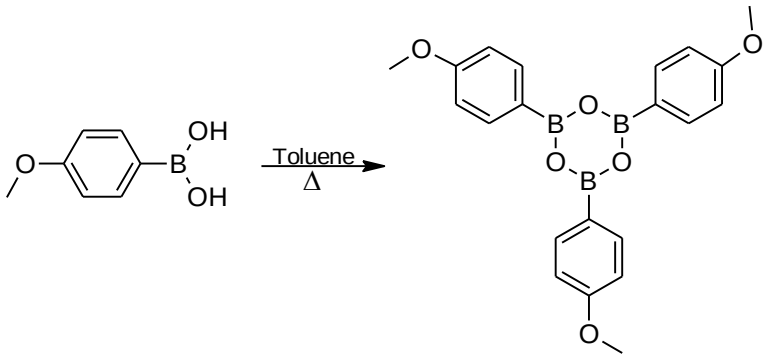
4-Trifluoromethylphenyl-boronic acid **1** (0.4981 g, 2.633 mmol) was placed in a 100 mL round bottom flask with a magnetic stir bar and toluene (40 mL). The flask was then fitted with a condenser and Dean-Stark trap. The solution was then heated to reflux for 1 hour in a reaction microwave. The solution was then cooled to room temperature and the solvent removed by rotary evaporation. The boroxine product **2** was then dried under vacuum. The product was obtained in a 98% yield. ^{1}H NMR ($CDCl_3$) 7.78 ppm (d, 6H), 8.35 ppm (d, 6H).



1 **2**

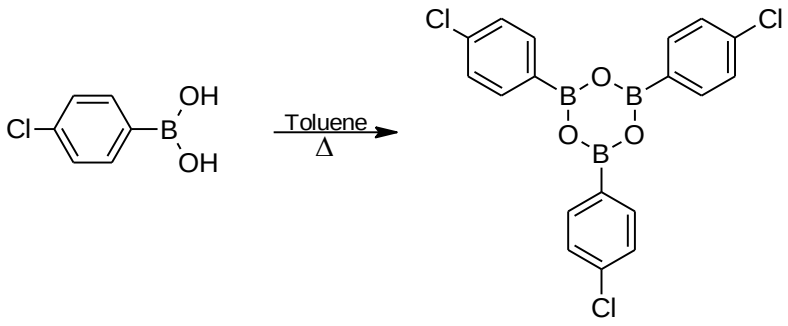
Reaction of **4-methoxyphenyl-boroinc acid** in toluene to produce **4-methoxyphenyl-boroxine**.

4-methoxyphenyl-boroinc acid **3** (0.5001 g, 3.2903 mmol) was placed in a 100 mL round bottom flask with a magnetic stir bar and toluene (40 mL). The flask was then fitted with a condenser and a Dean-Stark trap and heated to reflux for 2 hours. The solution was then cooled to room temperature and the solvent removed by rotary evaporation. The product was then dried under vacuum. The boroxine product **4** was obtained in a 96% yield. ^{1}H NMR ($CDCl_3$)3.88 ppm (s, 9H), 7.02 ppm (d, 6H), 8.16 ppm (d, 6H).



3 **4**

Reaction of **4-chlorophenyl-boronic acid** in toluene to produce **4-chloropheny boroxine**. 4-chlorophenyl boronic acid **5** (1.0008 g, 6.395 mmol) was placed in a 100 mL round bottom flask with a magnetic stir bar. Toluene (50 mL) was then added and the flask fitted with a Dean-Stark trap and a condenser. The reaction was heated to reflux for 35 minutes. The solution was then cooled to room temperature and the solvent removed by rotary evaporation. The product was then dried under vacuum. The boroxine product **6** was produced in a 96% yield. ^{1}H NMR ($CDCl_3$) 7.48 ppm (d, 6H), 8.13 ppm (d, 6H).

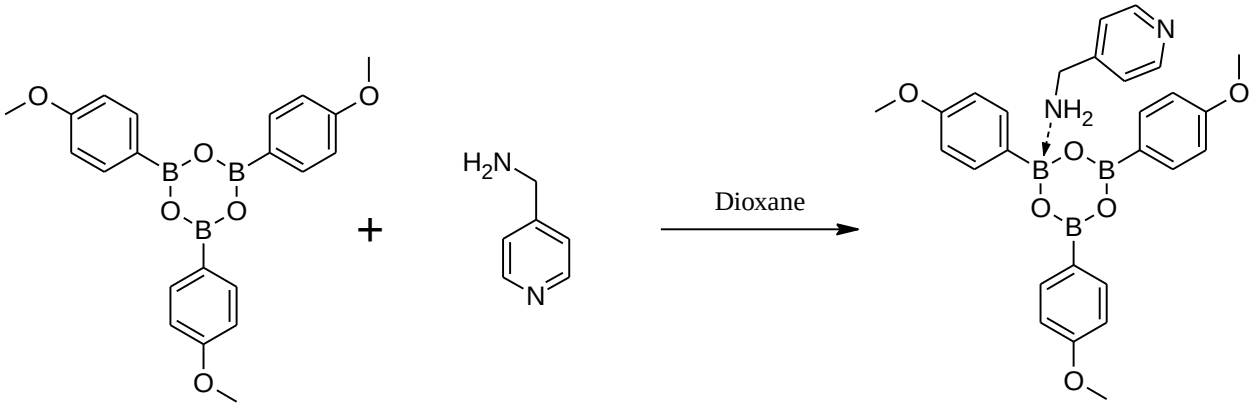


5 **6**

4.3: Reactions between boroxines and amines.

Reaction between **4-methoxyphenyl boroxine** and **4-(aminomethyl) pyridine** in dioxane solvent.

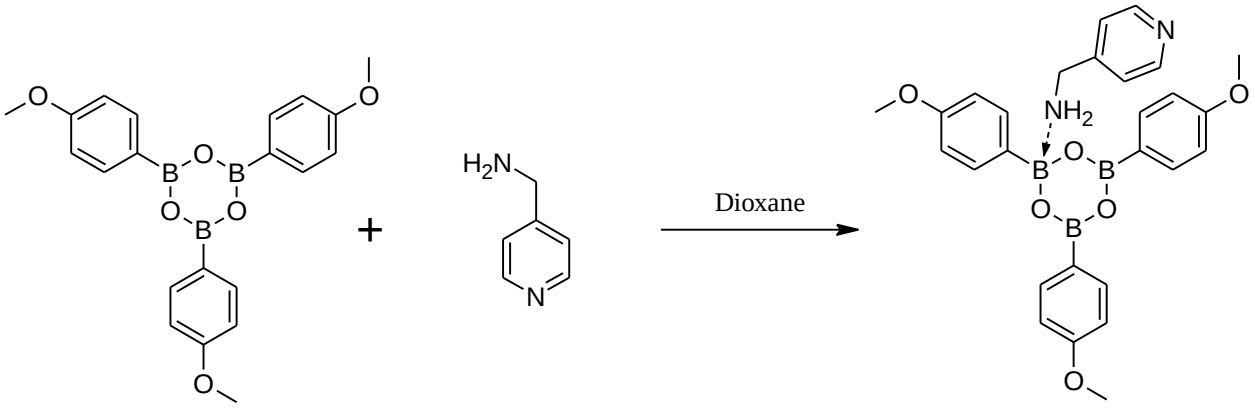
4-Methoxyphenyl boroxine **4** (0.0499 g, 0.1244 mmol) was combined in a 50 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.0126 mL, 0.1244 mmol). A magnetic stir bar was then added and the flask put under argon. Anhydrous 1,4-dioxane(10 mL) was then added to the flask and the solution stirred for approximately 72 Hours. The solvent was then removed by rotary evaporation and the product dried under vacuum pump. The resulting compound **8** was obtained in a 136% yield. ^{1}H NMR ($CDCl_3$) 3.83 ppm (s, 9H), 3.96 ppm (s, 2H), 6.92 ppm (d, 6H), 7.39 ppm (d, 2H), 8.0 ppm (d, 6H), 8.70ppm (d, 2H).



4 **7** **8**

Reaction between **4-methoxyphenyl boroxine** and **4-(aminomethyl) pyridine** in dioxane solvent.

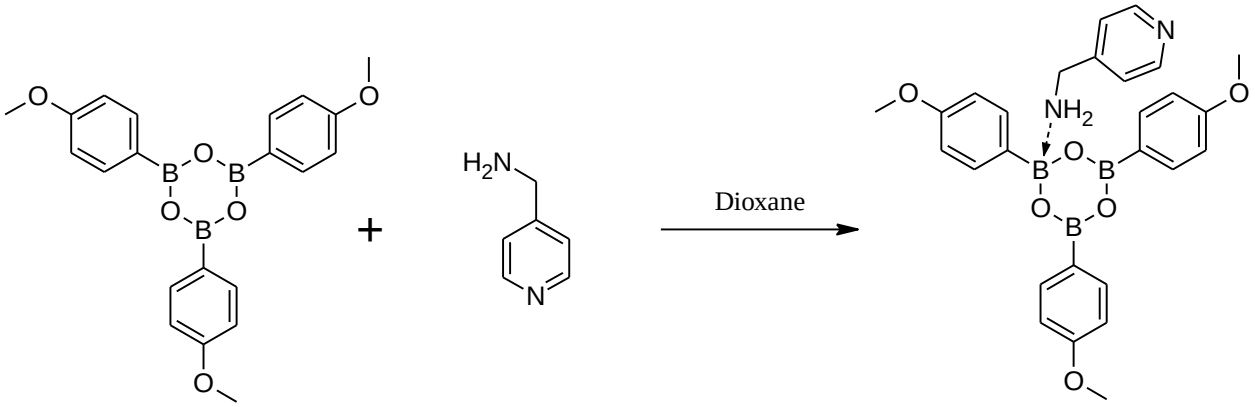
4-Methoxyphenyl boroxine **4** (0.0999 g, 0.2489 mmol) was combined in a 50 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.025 mL, 0.2489 mmol). A magnetic stir bar was then added and the flask put under argon. Anhydrous 1,4-dioxane(10 mL) was then added to the flask and the solution stirred for approximately 20 Hours. The 1,4-dioxane was removed by rotary evaporation. The product was then dissolved in chloroform and extracted with water. The extraction process lead a mix of product **8** and starting material but still resulted in a 70% yield. ^{1}H NMR ($CDCl_3$) 3.75 ppm (s, 2H), 3.84 ppm (s, 9H), 6.95 ppm (d, 6H), 7.33 ppm (d, 2H), 8.01 ppm (d, 6H).



4 **7** **8**

Reaction between **4-methoxyphenyl boroxine** and **4-(aminomethyl) pyridine** in dioxane solvent.

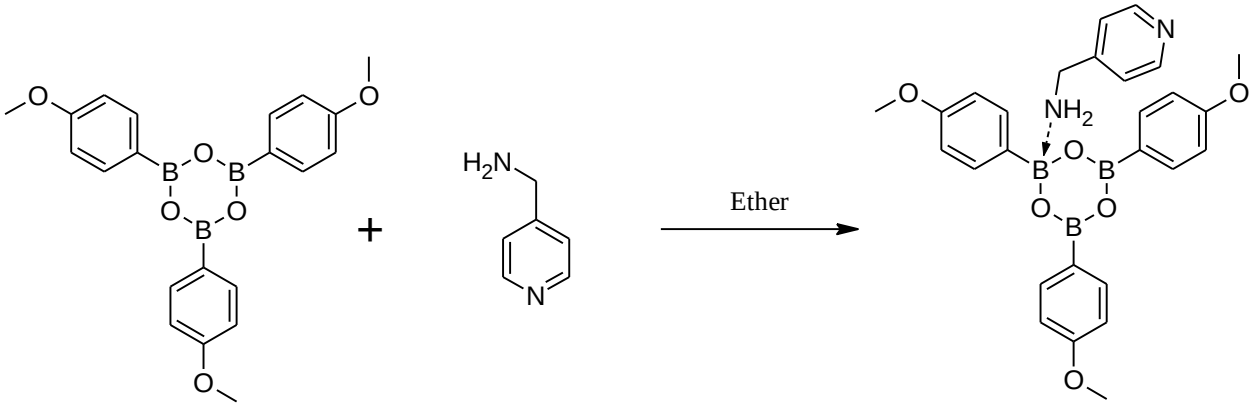
4-Methoxyphenyl boroxine **4** (0.1001 g, 0.2489 mmol) was combined in a 100 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.025 mL, 0.2489 mmol). A magnetic stir bar was then added and the flask put under argon. Anhydrous 1,4-dioxane(10 mL) was then added to the flask and the solution stirred for 18 Hours. The resulting product was split into two equal parts of 5 mL each. Both halves had the 1,4-dioxane was removed by rotary evaporation. The first half was simply dried on the vacuum pump and later tested by ^{1}H NMR ($CDCl_3$) 3.85 ppm (s, 9H), 4.0 ppm (s, 2H), 6.9 ppm (d, 6H), 7.45 ppm (d, 2H), 8.0 ppm (d, 6H), 8.8 ppm (d, 2H).The product was produced at a 79% yield. The second half of the product was then dissolved in chloroform and extracted three times with water. The extraction process lead to the product being a mix of product **8** and starting material and gave an 11.6% yield.



4 **7** **8**

Reaction between **4-methoxyphenyl boroxine** and **4-(aminomethyl) pyridine** in diethyl ether solvent.

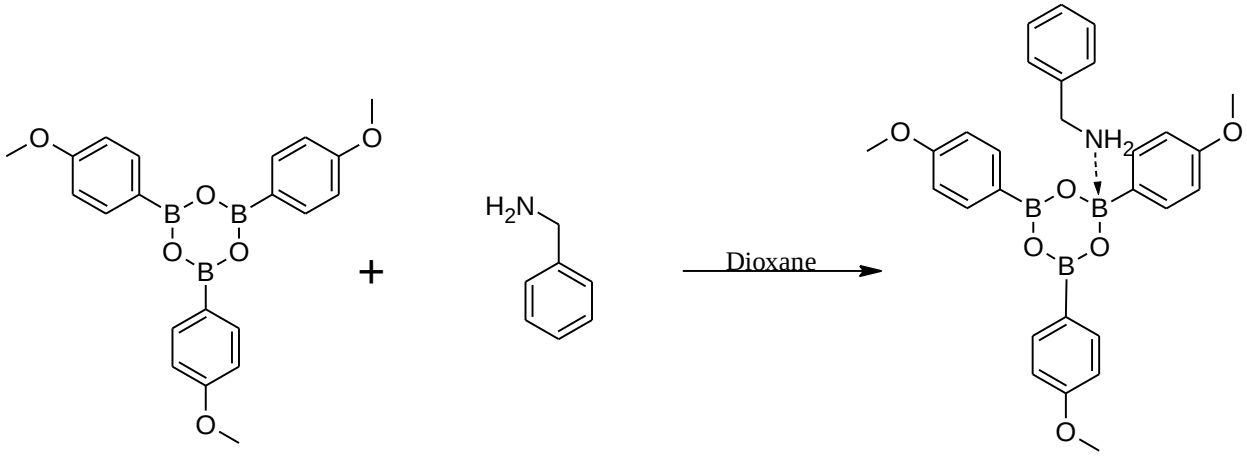
4-Methoxyphenyl boroxine **4** (0.0503 g, 0.1244 mmol) was added to a 50 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.0125 mL, 0.1244 mmol). Diethyl ether (20 mL) was then added to the flask with a magnetic stir bar. The reaction was stirred for 19 hours and the solvent removed by rotary evaporation. The product **8** was then dried for 1 hour under vacuum. The product was obtained in a 119% yield. ^{1}H NMR ($CDCl_3$) 3.83 ppm (s, 9H), 3.97 ppm (s, 2H), 6.92 ppm (d, 6H), 7.40 ppm (d, 2H), 8.10 ppm (d, 6H), 8.72 ppm (d, 2H).



4 **7** **8**

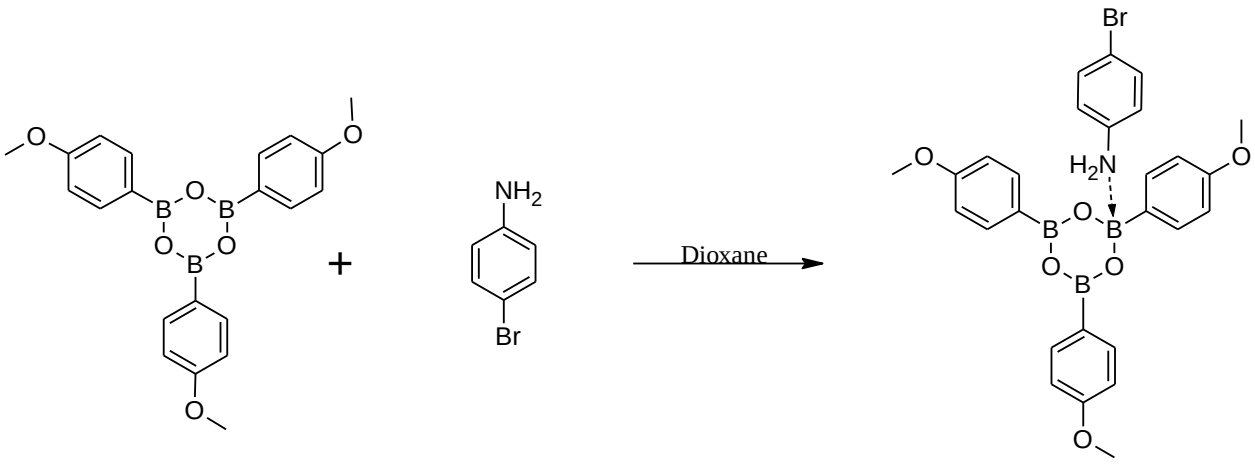
Reaction between **4-methoxyphenyl boroxine** and **benzyl amine** in dioxane solvent.

4-Methoxyphenyl boroxine **4** (0.1001 g, 0.2489 mmol) was added to a 100 mL round bottom flask with benzyl amine **9** (0.0270 mL, 0.2489 mmol). A magnetic stir bar was then added and the whole system put under argon. Anhydrous 1,4-dioxane (10 mL) was then added to the flask. The reaction was stirred for 20 hours. The solvent was then removed by rotary evaporation and the product dried under vacuum. The product **10** was obtained at a 141% yield. ^{1}H NMR ($CDCl_3$) 3.85 ppm (s, 2H), 3.95 ppm (s, 9H), 6.95 ppm (d, 6H), 7.2 ppm (d, 2H), 7.3 ppm (d, 2H), 8.0 ppm (d, 6H)



4 **9** **10**

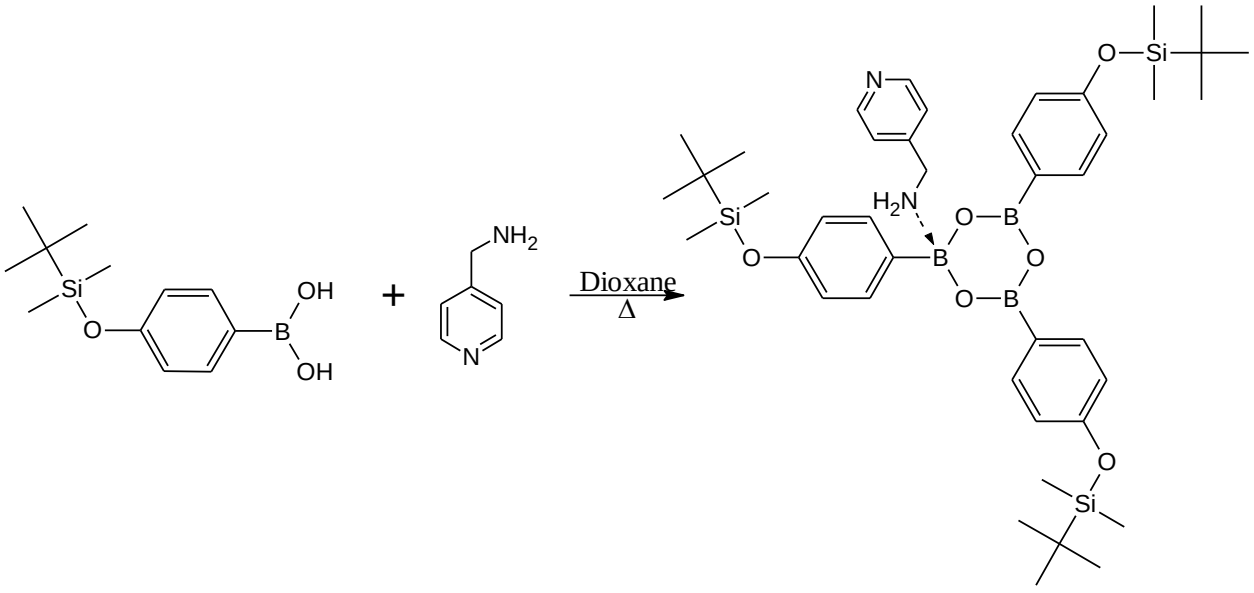
Reaction between **4-methoxyphenyl boroxine** and **p-bromoanilline** in dioxane solvent.4-Methoxyphenyl boroxine **4** (0.1004 g, 0.2489 mmol) was added to a 50 mL round bottom flask with p-bromoanilline **11** (0.0444 g, 0.2489 mmol). A magnetic stir bar was added to the flask and the system placed under argon atmosphere. Anhydrous 1,4-dioxane was then added to the flask and the reaction stirred for 19 hours. The solvent was then removed by rotary evaporation and the product dried under vacuum. The product **12** was obtained at a 158% yield. ^{1}H NMR ($CDCl_3$) 3.9 ppm (s, 9H), 6.55 ppm (d, 2H), 7.0 ppm (d, 6H), 7.2 ppm (d, 2H), 8.2 ppm (d, 6H)



4 **11** **12**

Reaction between **4-(tert-butyldimethylsiloxy) phenyl boronic acid** and **4-(aminomethyl) pyridine** in a dioxane solvent.

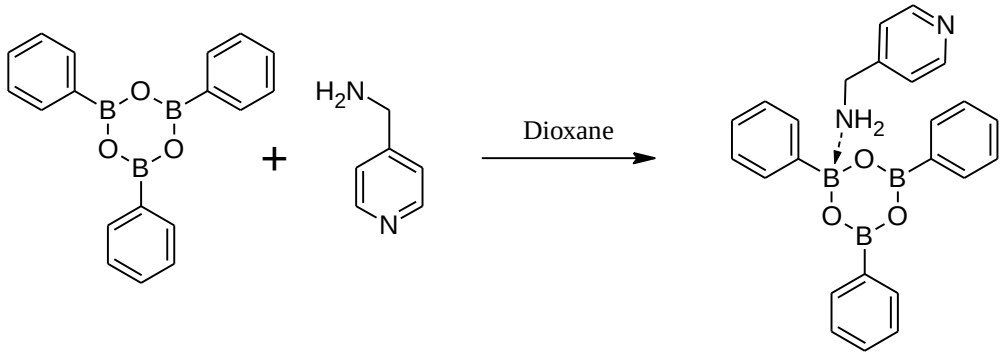
4-(Tert-butyldimethylsiloxy) phenyl boronic acid **13** (0.1011 g, 0.3969 mmol) was placed in a 100 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.0135 mL, 0.1322 mmol). A magnetic stir bar was added and the system placed under an argon atmosphere. Anhydrous 1,4-dioxane (10 mL) was then added. The system was then heated to reflux for 24 hours. The solvent was then removed by rotary evaporation and the product dried under vacuum. The product **14** was obtained at a 201% yield. ^{1}H NMR ($CDCl_3$) 0.3 ppm (s, 27H), 1.0 (s, 18H), 3.75 ppm (s, 2H), 6.9 ppm (d, 2H), 7.45 ppm (d, 6H), 7.95 ppm (d, 6H), 8.8 ppm (d, 2H)



13 **7** **14**

Reaction between **phenyl boroxine** and **4-(aminomethyl) pyridine** in a dioxane solvent.

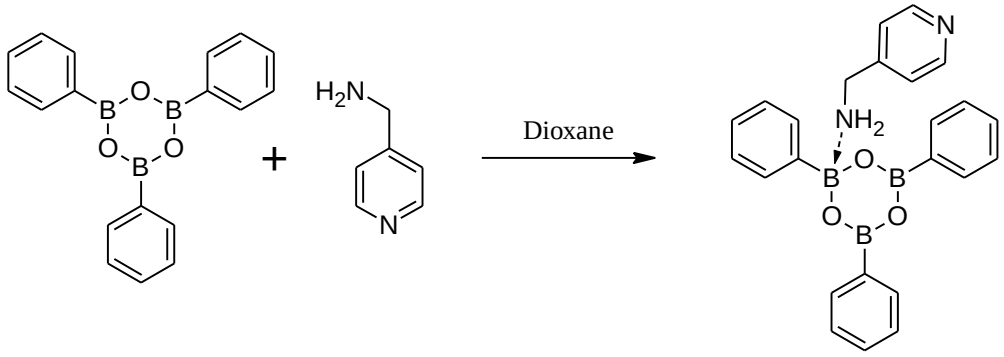
Phenyl boroxine **15** (0.1010 g, 0.3208 mmol) was placed in a 100 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.0325 mL, 0.3208 mmol). A magnetic stir bar was then added and the system put under an argon atmosphere. Anhydrous 1,4-dioxane (10 mL) was then added via syringe. The reaction was stirred for 24 hours. The solvent was removed by rotary evaporation and the product dried under vacuum. The product **16** was obtained at a 120% yield. ^{1}H NMR ($CDCl_3$) 4.0 ppm (s, 2H), 7.38ppm (t, 6H), 7.41 ppm (d, 2H), 7.5 ppm (d, 3H), 8.05 ppm (d, 6H), 8.9 ppm (d, 2H)



15 **7** **16**

Reaction between **phenyl boroxine** and **4-(aminomethyl)** pyridine in a dioxane solvent.

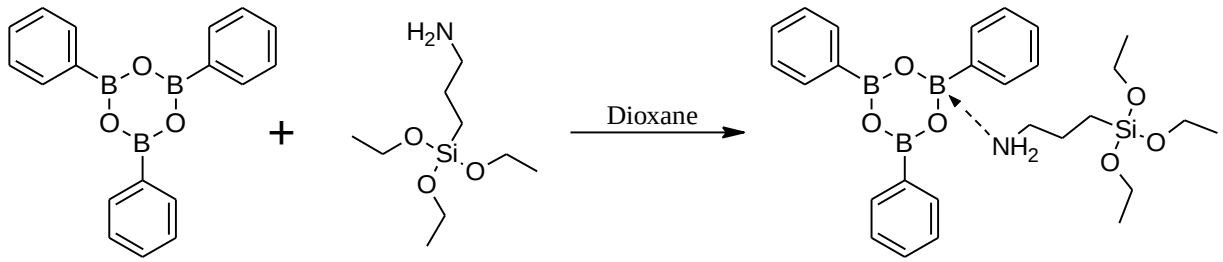
Phenyl boroxine **15** (0.0510 g, 0.1604 mmol) was placed in a reaction vial with 4-(aminomethyl) pyridine **7** (0.0165 mL, 0.1604 mmol). A magnetic stir bar was then added and the system put under an argon atmosphere. Anhydrous 1,4-dioxane (4 mL) was then added via syringe. The vial was fitted with a condenser and heated to 129-132^{o}C. Samples were taken every hour for 5 hours. The reaction mixture was transferred to a 35 mL round bottom flask and the vial rinsed 3 times with fresh dioxane (3 mL total). The solvent was removed by rotary evaporation and the product **16** dried under vacuum. The product was obtained in a 112% yield. ^{1}H NMR ($CDCl_3$) 4.02 ppm (s, 2H), 7.37 ppm (t, 6H), 7.40 ppm (d, 2H), 7.51 ppm (d, 3H), 8.05 ppm (d, 6H), 8.90 ppm (d, 2H)



15 **7** **16**

Reaction between **phenyl boroxine** and **3-(aminopropyl) triethoxy silane** in a dioxane solvent.

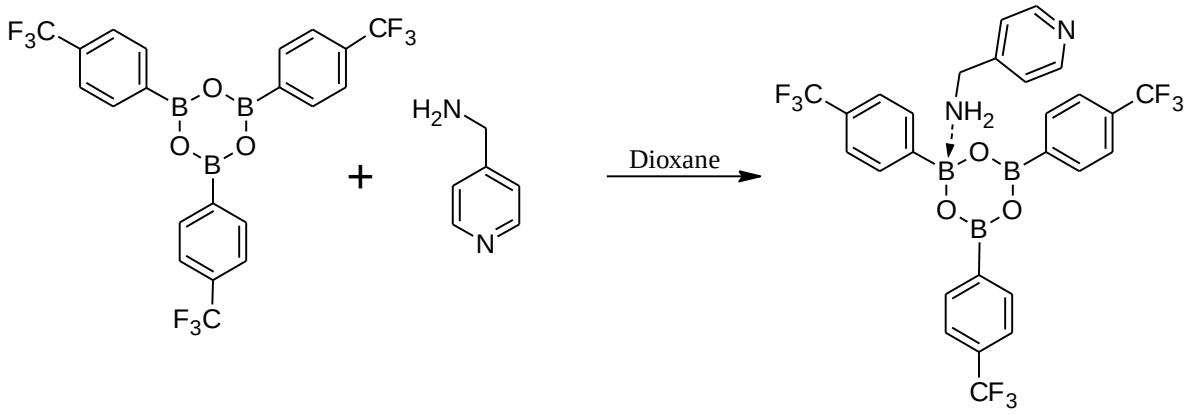
Phenyl boroxine **15** (0.1008 g, 0.3208 mmol) was placed in a 50 mL round bottom flask with 3-(aminopropyl) triethoxy silane **17** (0.0750 mL, 0.3208 mmol). A magnetic stir bar was then added and the system put under an argon atmosphere. Anhydrous 1,4-dioxane (10 mL) was added to the flask via syringe. The reaction was then heated to reflux for 6 hours and then stirred for an additional 18 hours. The solvent was removed by rotary evaporation and the product dried under vacuum for 24 hours. The product **18** was obtained at a 123% yield. ^{1}H NMR ($CDCl_3$) 1.3 ppm (m, 21H), 7.4 ppm (broad d, 12H), 8.1 ppm (broad d, 3H).



15 **17** **18**

Reaction between **4-trfluoromethylphenyl boroxine** and **4-(aminomethyl) pyridine** in a dioxane solvent.

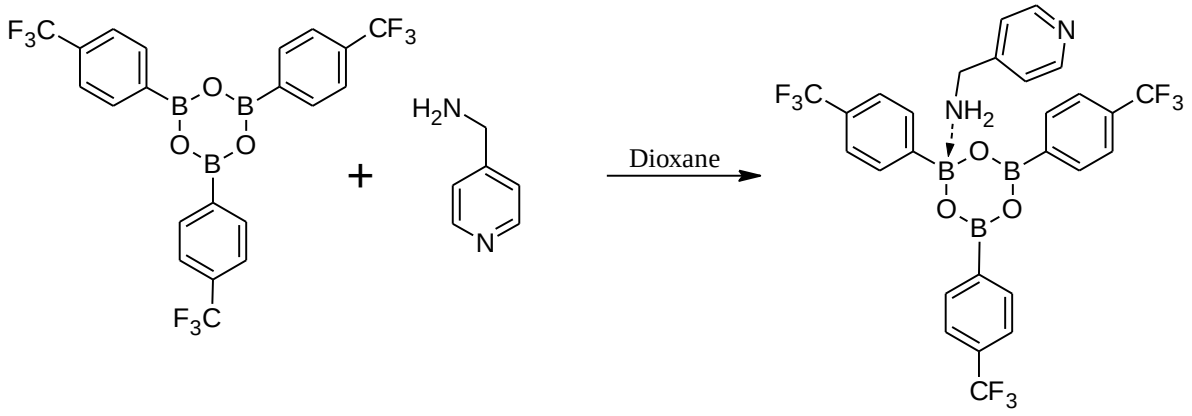
4-Trifluoromethylphenyl boroxine **2** (0.0997 g, 0.1939 mmol) was combined in a 50 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.0195 mL, 0.1939 mmol). A magnetic stir bar was then added and the system put under an argon atmosphere. Anhydrous 1,4-dioxane (10 mL) was added via syringe. The reaction was stirred for 48 hours. The solvent was removed by rotary evaporation and the product was dried under vacuum. The product **19** was obtained at a 154% yield. ^{1}H NMR ($CDCl_3$) 4.1 ppm (s, 2H), 7.65 ppm (d, 6H), 7.7 ppm (d, 2H), 8.1 ppm (d, 6H), 8.9 ppm (d, 2H).



2 **7** **19**

Reaction between **4-trfluoromethylphenyl boroxine** and **4-(aminomethyl) pyridine** in a dioxane solvent.

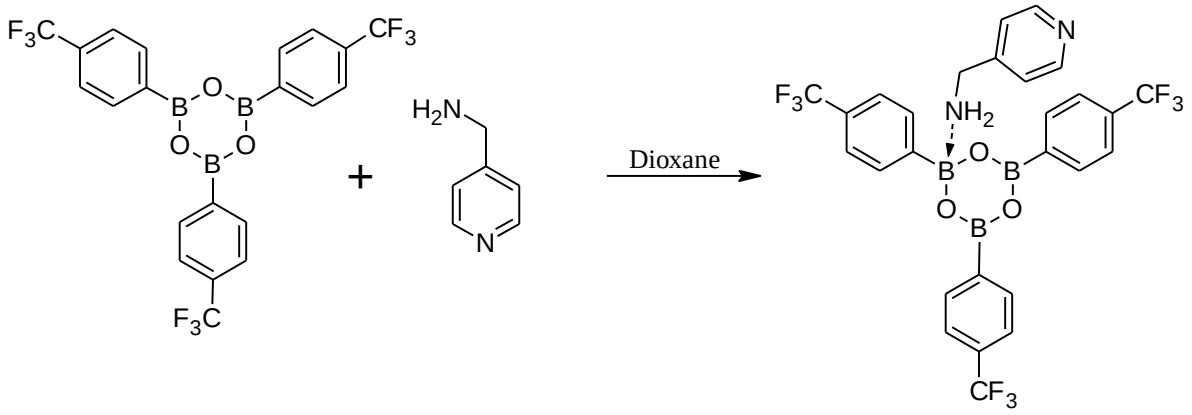
4-Trifluoromethylphenyl boroxine **2** (0.1005 g, 0.1939 mmol) was combined in a round bottom flask with 4-(aminomethyl) pyridine **7** (0.0195 mL, 0.1939 mmol). A magnetic stir bar was added and the system placed under an argon atmosphere. Anhydrous 1,4-dioxane (10 mL) was added via syringe. The solution was then heated to reflux for 1 hour. The solvent was removed by rotary evaporation and the product **19** dried under vacuum. ^{1}H NMR ($CDCl_3$) 4.1 ppm (s, 2H), 7.65 ppm (d, 6H), 7.7 ppm (d, 2H), 8.1 ppm (d, 6H), 8.9 ppm (d, 2H).



2 **7** **19**

Reaction between **4-trfluoromethylphenyl boroxine** and **4-(aminomethyl) pyridine** in a dioxane solvent.

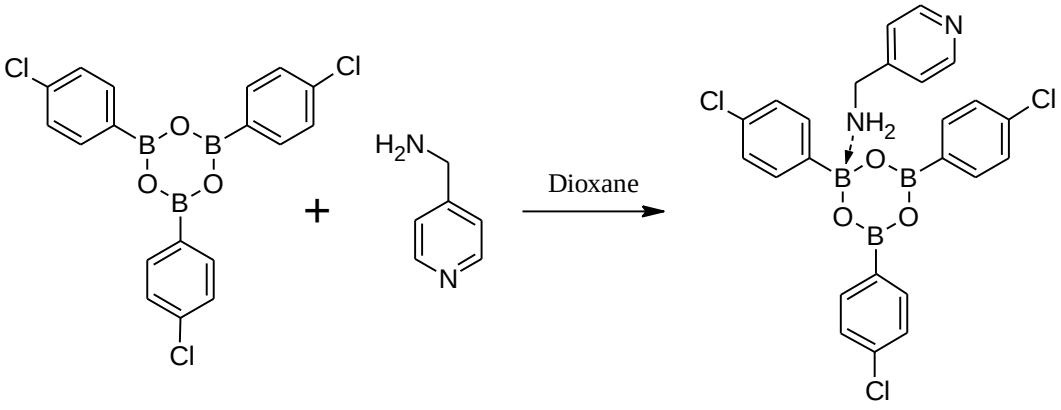
4-Trifluoromethylphenyl boroxine **2** (0.0688 g, 0.1334 mmol) was combined in a round bottom flask with 4-(aminomethyl) pyridine **7** (0.300 mL, 2.9545 mmol). A magnetic stir bar was added and the system was placed under an argon atmosphere. Anhydrous 1,4-dioxane (10 mL) was added via syringe. The solution was then heated to reflux for 6 hour. This reaction was run with an excess of the amine at approximately a 1:22 ratio. The solvent was removed by rotary evaporation and the product **19** dried under vacuum. ^{1}H NMR ($CDCl_3$) 1.6 ppm (broad s, 2H), 7.3 ppm (d, 6H), 7.6 ppm (d, 2H), 8.1 ppm (d, 2H), 8.6 ppm (d, 6H).



2 **7** **19**

Reaction between **4-chlorophenyl boroxine** and **4-(aminomethyl) pyridine** in dioxane solvent.

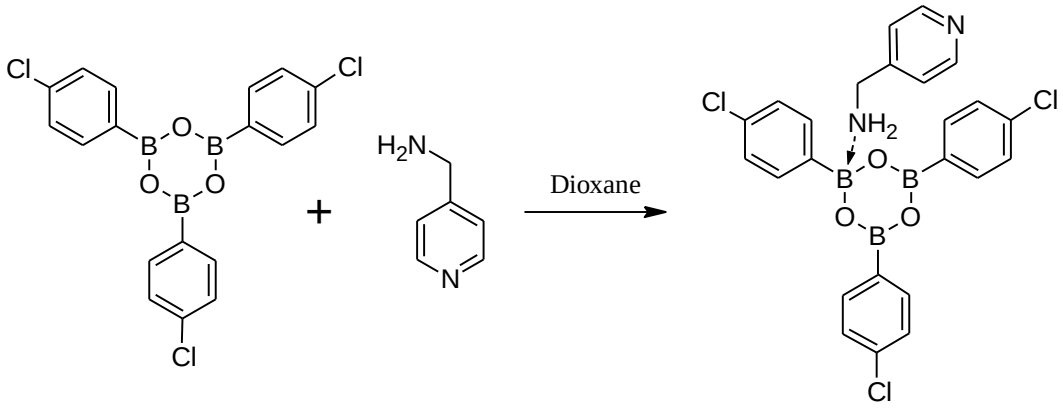
4-Chlorophenyl boroxine **6** (0.0481 g, 0.1205 mmol) was combined in a 50 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.0120 mL, 0.1205 mmol). A magnetic stir bar was then added and the flask put under argon. Anhydrous 1,4-dioxane(10 mL) was then added to the flask and the reaction stirred for 24 hours. The solvent was removed by rotary evaporation and dried under vacuum. The resulting product **20** had a 82.5% yield. ^{1}H NMR ($CDCl_3$) 4.1 ppm (s, 2H), 7.35 ppm (d, 6H), 7.6 ppm (d, 2H), 7.9 ppm (d, 6H), 8.8 ppm (d 2H).



6 **7** **20**

Microwave reaction of **4-chlorophenyl boroxine** and **4-(aminomethyl) pyridine** in a dioxane solvent.

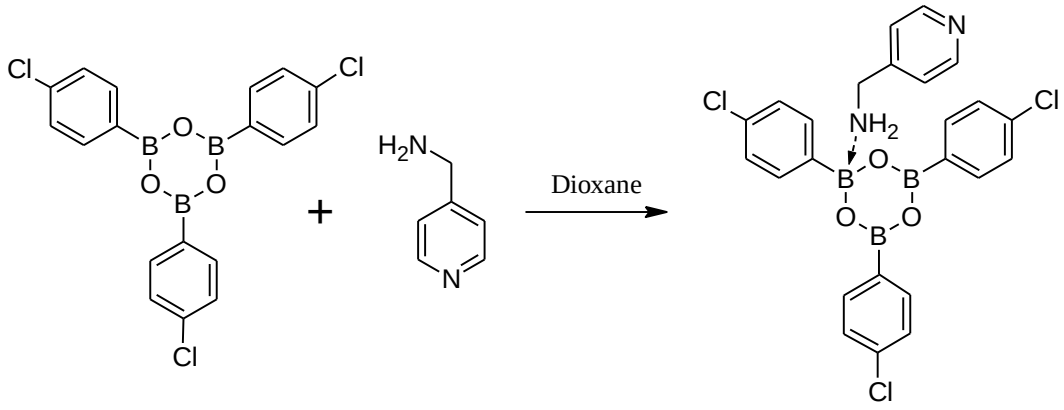
4-Chlorophenyl boroxine **6** (0.1004 g, 0.2409 mmol) was combined in a 100 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.0245 mL, 0.2409 mmol). A magnetic stir bar was added to the flask and the system put under an argon atmosphere. Anhydrous 1,4-dioxane (10 mL) was added to the flask via syringe. The solution was then heated to reflux for 30 minutes in the microwave. The solvent was removed by rotary evaporation and the product dried under vacuum. The product **20** was obtained in a 160% yield. ^{1}H NMR ($CDCl_3$) 4.1 ppm (s, 2H), 7.4 ppm (d, 6H), 7.6 ppm (d, 2H), 7.9 ppm (d, 6H), 8.9 ppm (d, 2H).



6 **7** **20**

Reaction of excess **4-chlorophenyl boroxine** and **4-(aminomethyl) pyridine** in a dioxane solvent.

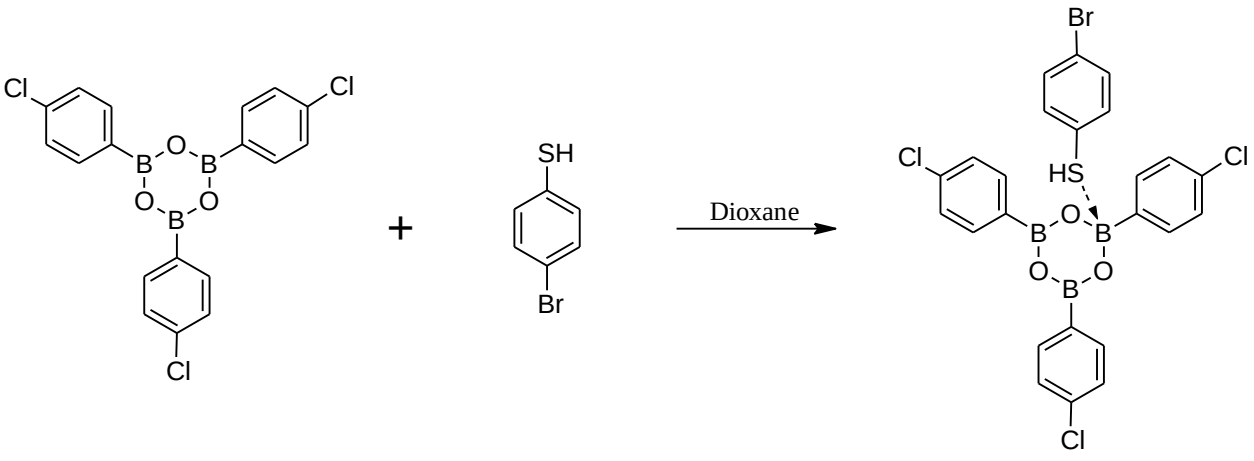
4-Chlorophenyl boroxine **6** (0.0519 g, 0.1205 mmol) was combined in a 10 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.0120 mL, 0.1205 mmol). A magnetic stir bar was added and the system was put under an argon atmosphere. Anhydrous 1,4-dioxane (3 mL). 4-chlorophenyl boroxine was then added until the solution was saturated. The solution was then vacuum filtered and approximately 1 mL of the solvent removed by rotary evaporation. The solution was then left for approximately 20 hours. A small amount of material formed a precipitate and was removed by filtration. The filtrate was then rotary evaporated and dried on the vacuum pump. The product **20** was obtained in 147% yield. ^{1}H NMR ($CDCl_3$) 4.1 ppm (s, 2H), 7.4 ppm (d, 6H), 8.0 ppm (d, 6H), 8.9 ppm (d, 2H).



6 **7** **20**

Reaction of **4-chlorophenyl boroxine** and **p-bromothiophenol** in a dioxane solvent.

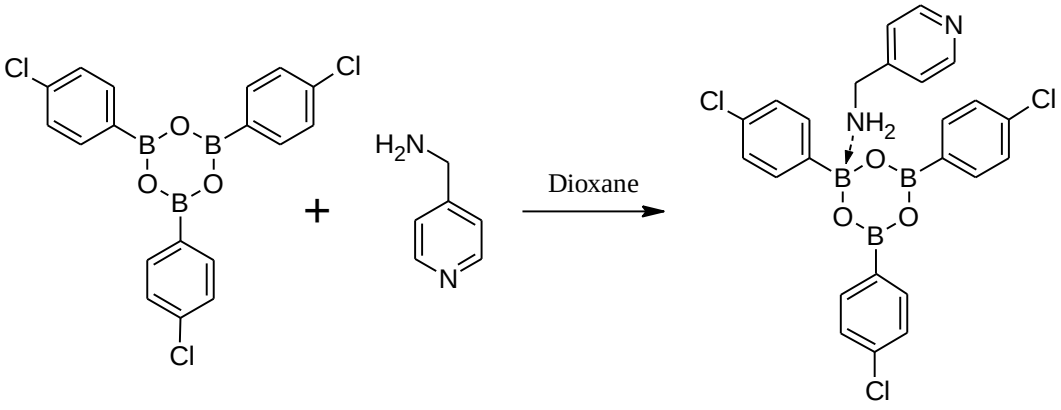
4-Chlorophenyl boroxine **6** (0.1050 g, 0.2409 mmol) was placed in a 100 mL round bottom flask with p-bromothiophenol **21** (0.0461 g, 0.2409 mmol). A magnetic stir bar was added and the entire system put under argon atmosphere. Anhydrous 1,4-dioxane (10 mL) was added via syringe. The reaction was stirred for 18 hours. The solvent was removed by rotary evaporation and the product dried under vacuum. The product **22** was obtained at a 122% yield. ^{1}H NMR ($CDCl_3$) 7.1 ppm (d, 2H), 7.5 ppm (d, 6H), 7.7 ppm (d, 2H), 8.1 ppm (d, 6H).



6 **21** **22**

Reaction of **4-chlorophenyl boroxine** and **4-(aminomethyl) pyridine** in dioxane solvent.

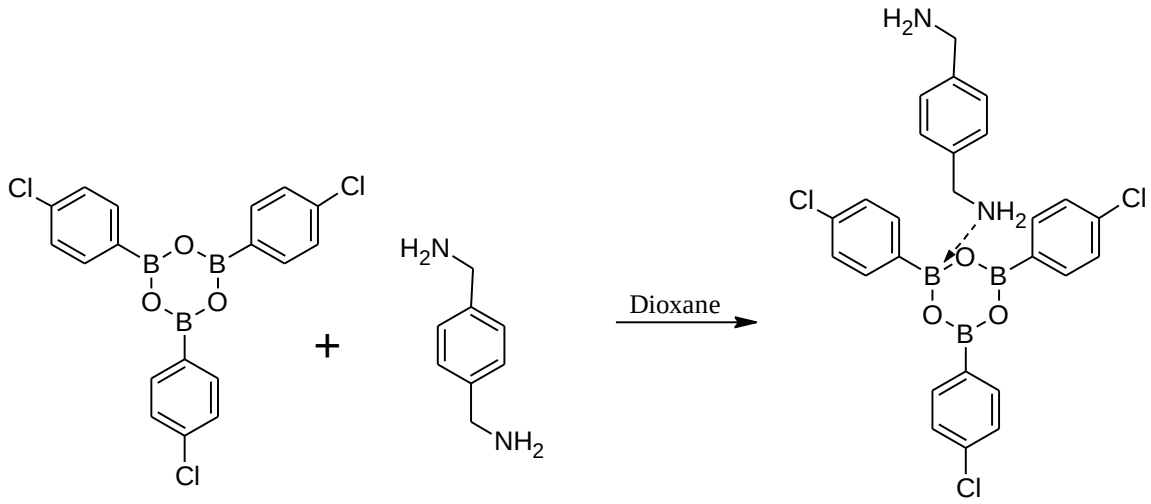
4-Chlorophenyl boroxine **6** (0.1000 g, 0.2409 mmol) was placed in a 100 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.0245 mL, 0.2409 mmol). A magnetic stir bar was added to the flask and the entire system was put under an argon atmosphere. Anhydrous 1,4-dioxane (10 mL) was then added via syringe. The reaction was stirred for 24 hours. The solvent was removed by rotary evaporation and the product dried under vacuum. The product **20** was obtained in a 162% yield. ^{1}H NMR ($CDCl_3$) 4.0 ppm (s, 2H), 7.35 ppm (d, 6H), 7.6 ppm (d, 2H), 7.9 ppm (d, 6H), 8.8 ppm (d, 2H).



6 **7** **20**

Reaction of **4-chlorophenyl boroxine** and **xylene diamine** in a dioxane solvent.

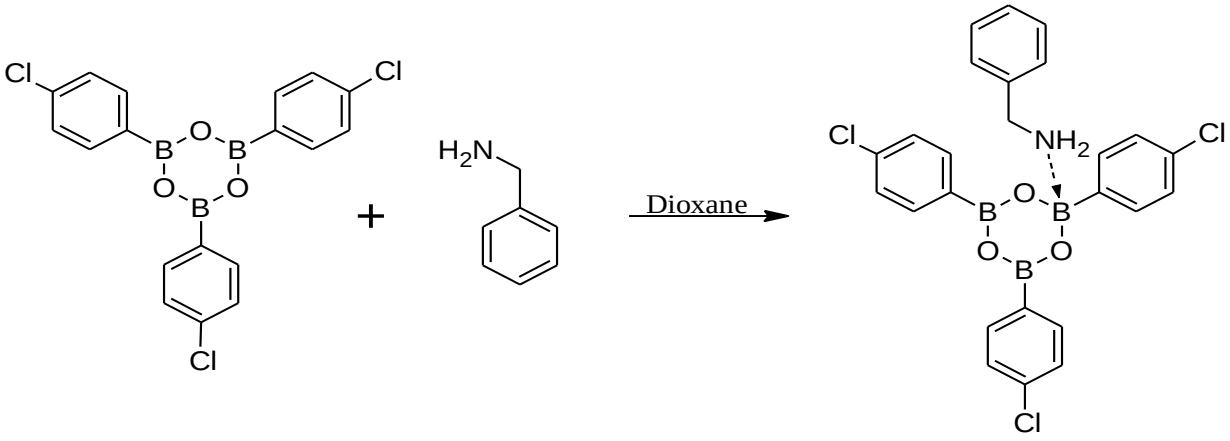
4-Chlorophenyl boroxine **6** (0.1010 g, 0.2409 mmol) was placed in a 50 mL round bottom flask with xylene diamine **23** (0.0332 g, 0.2409 mmol). A magnetic stir bar was added to the flask and the system put under an argon atmosphere. Anhydrous 1,4-dioxane was added to the flask via syringe. The reaction was stirred for 72 hours. The solvent was removed by rotary evaporation and the product dried under vacuum. The product **24** was obtained in a 127% yield. ^{1}H NMR ($CDCl_3$) 3.8 ppm (s, 4H), 7.2 ppm (d, 4H), 7.4 ppm (d, 6H), 7.9 ppm (d, 6H).



6 **23** **24**

Reaction of **4-chlorophenyl boroxine** and **benzyl amine** in a dioxane solvent.

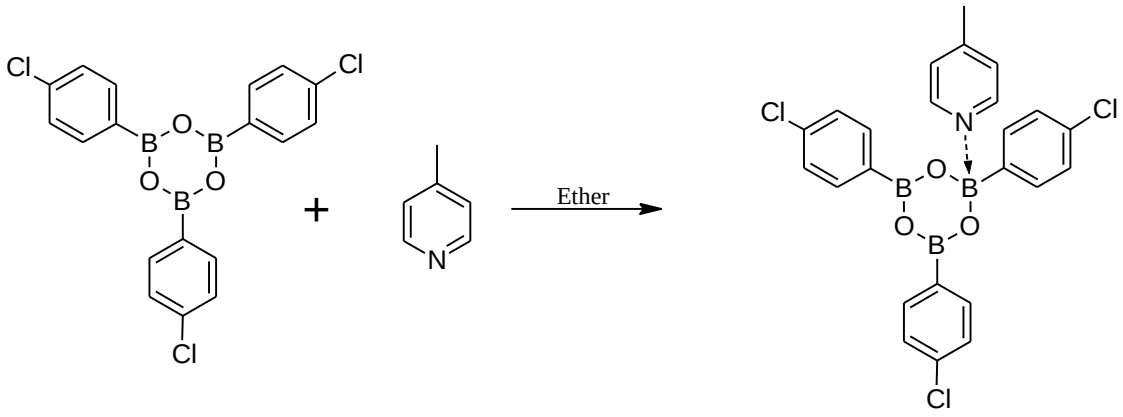
4-Chlorophenyl boroxine **6** (0.1016 g, 0.2409 mmol) was placed in a 50 mL round bottom flask with benzyl amine **9** (0.0265 mL, 0.2409 mmol). A magnetic stir bar was added to the flask and the entire system was put under an argon atmosphere. Anhydrous 1,4-dioxane was added to the flask via syringe. The reaction was stirred for 24 hours. The solvent was removed by rotary evaporation and the product **25** was dried under vacuum. The product was obtained in a 108% yield. ^{1}H NMR ($CDCl_3$) 3.93 ppm (s, 2H), 7.22 ppm (t, 1H), 7.36 ppm (d, 2H), 7.39 ppm (d, 6H) 7.92 ppm (d, 6H).



6 **9** **25**

Reaction of **4-chlorophenyl boroxine** and **picoline** in an ether solvent.

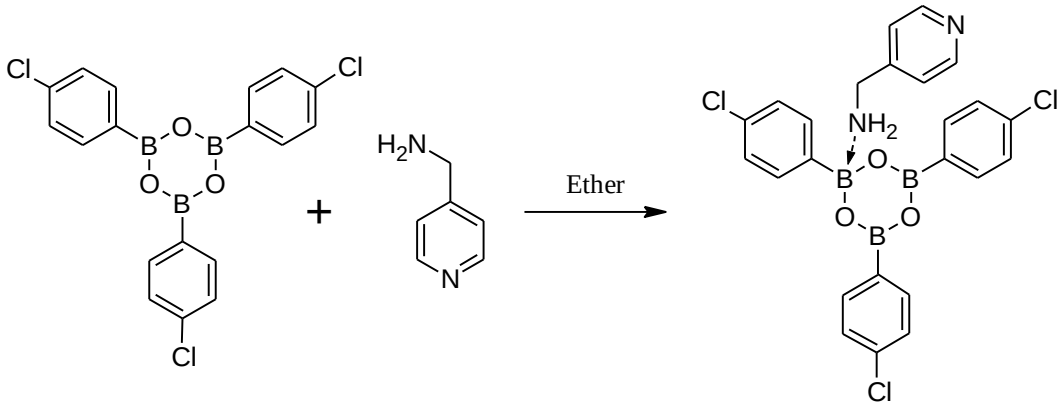
4-Cholorphenyl boroxine **6** (0.1004 g, 0.2409 mmol) was placed in a 50 mL round bottom flask with picoline **26** (0.0235 mL, 0.2409 mmol). A magnetic stir bar and diethyl ether (20 mL) were added to the flask. The reaction was heated to reflux and stirred for 4 hours. The solvent was removed by rotary evaporation and the product was dried under vacuum. The product **27** was obtained at a 68% yield. ^{1}H NMR ($CDCl_3$) 2.47 ppm (s, 3H), 7.37 ppm (d, 2H), 7.38 ppm (d, 6H), 7.98 ppm (d, 6H) 8.78 ppm (d, 2H).



6 **26** **27**

Reaction of **4-chlorophenyl boroxine** and **4-(aminomethyl) pyridine** in diethyl ether solvent.

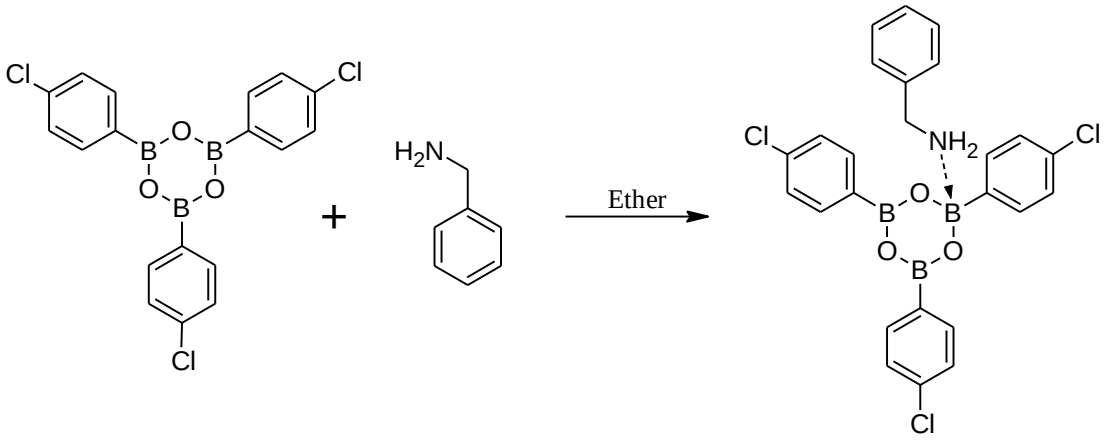
4-Chlorophenyl boroxine **6** (0.1004 g, 0.2409 mmol) was placed in a 50 mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.0245 mL, 0.2409 mmol). A magnetic stir bar and diethyl ether (20 mL) was added to the flask. The reaction was stirred for 18 hours. The solvent was removed by rotary evaporation and the product dried under vacuum. The product **20** was obtained in a 106% yield. ^{1}H NMR ($CDCl_3$) 2.36 ppm (broad, 2H), 3.94 ppm (s, 2H), 7.39 ppm (d, 6H), 7.49 ppm (d, 2H) 8.02 ppm (d, 6H), 8.79 ppm (d, 2H).



6 **7** **20**

Reaction of **4-chlorophenyl boroxine** and **benzyl amine** in a diethyl ether solvent.

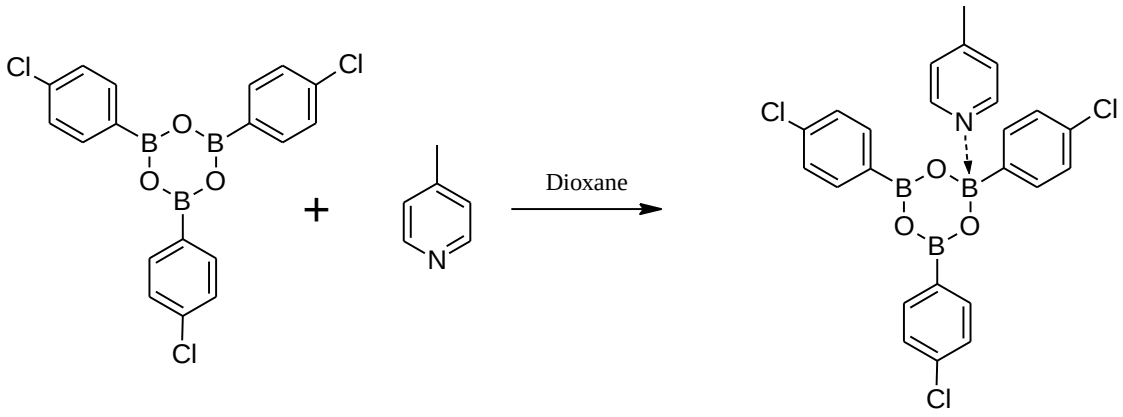
4-Chlorophenyl boroxine **6** (0.1001 g, 0.2409 mmol) was placed in a 50 mL round bottom flask with benzyl amine **9** (0.0260 mL, 0.2409 mmol). A magnetic stir bar and diethyl ether (20 mL) was added to the flask. The reaction was stirred for 36 hours. The solvent was removed by rotary evaporation and the product was dried under vacuum. The product **25** was obtained at a 108% yield. ^{1}H NMR ($CDCl_3$) 3.93 ppm (s, 2H), 7.22 ppm (t, 1H), 7.36 ppm (d, 2H), 7.39 ppm (d, 6H) 7.92 ppm (d, 6H).



6 **9** **25**

Reaction of **4-chlorophenyl boroxine** and **picoline** in a dioxane solvent.

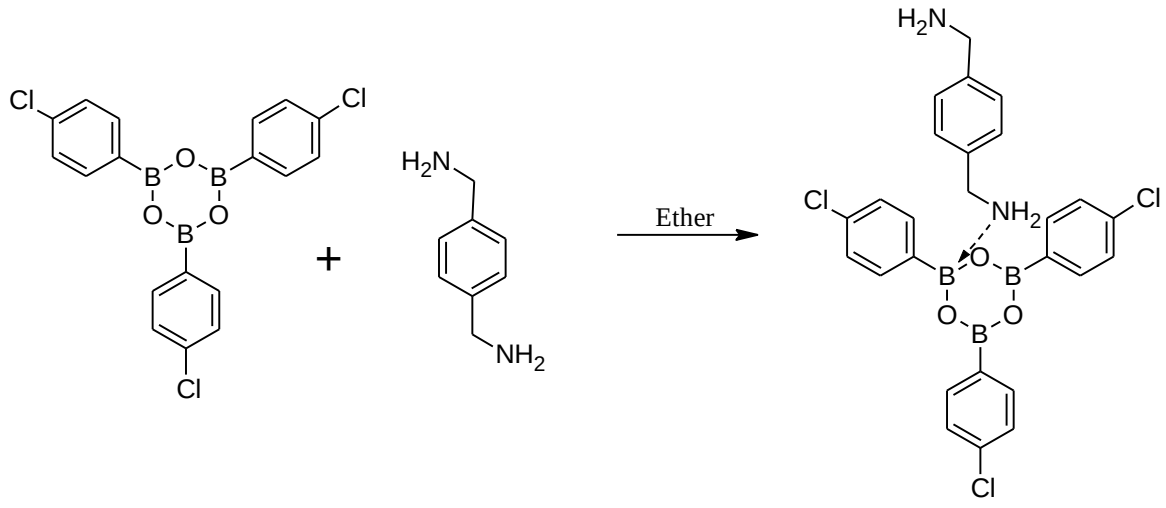
4-Chlorophenyl boroxine **6** (0.0994 g, 0.2409 mmol) was placed in a 50mL round bottom flask with picoline **26** (0.0235 mL, 0.2409 mmol). A magnetic stir bar was added to the flask and the entire system put under an argon atmosphere. Anhydrous dioxane (10 mL) was added to the flask via syringe. The reaction mixture was stirred for 48 hours and the solvent then removed by rotary evaporation and the product dried under vacuum. The product **27** was obtained in a 114% yield. ^{1}H NMR ($CDCl_3$) 2.49 ppm (s, 3H), 7.35 ppm (d, 6H), 7.41 ppm (d, 2H), 7.93 ppm (d, 6H) 8.78 ppm (d, 2H).



6 **26** **27**

Reaction of **4-chlorophenyl boroxine** and **xylene diamine** in a diethyl ether solvent.

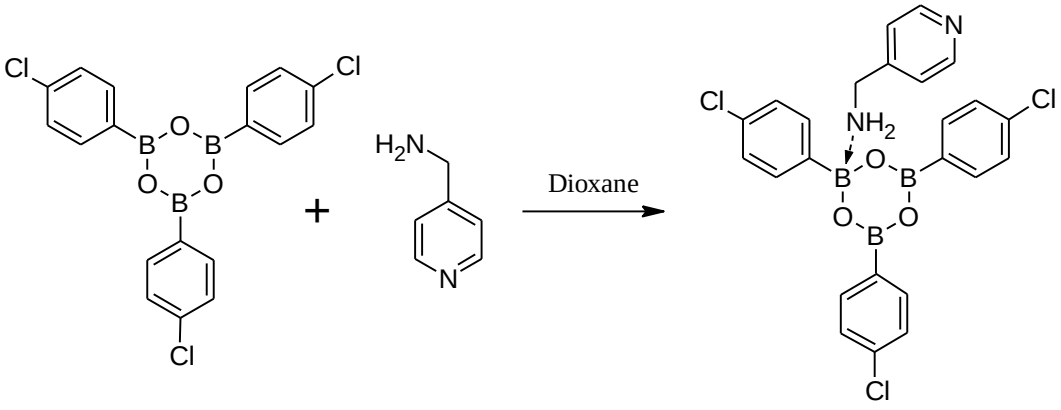
4-Chlorophenyl boroxine **6** (0.0996 g, 0.2409 mmol) was placed in a 100 mL round bottom flask with xylene diamine **23** (0.0335 g, 0.2409 mmol). A magnetic stir bar and diethyl ether (20 mL) was added to the flask. The reaction was stirred for 27 hours. The solvent was removed by rotary evaporation and the product dried under vacuum. The product **24** was obtained in a 68% yield. ^{1}H NMR ($CDCl_3$) 1.69 ppm (broad, 4H), 3.88 ppm (s, 4H), 7.23 ppm (s, 4H), 7.36 ppm (d, 6H) 7.92 ppm (d, 6H).



6 **23** **24**

Reaction of **4-chlorophenyl boroxine** and **4-(aminomethyl) pyridine** in dioxane solvent.

4-Chlororphenyl boroxine **6** (0.1006 g, 0.2409 mmol) was placed in a 100mL round bottom flask with 4-(aminomethyl) pyridine **7** (0.0245 mL, 0.2409 mmol). A magnetic stir bar was added to the flask with dioxane (10 mL). The flask was fitted with a condenser and heated to reflux for 2 hours. The solution was cooled to room temperature and the solvent removed by rotary evaporation. The product **20** was dried under vacuum for 12 hours and obtained in a 58% yield. ^{1}H NMR ($CDCl_3$) 1.78 ppm (broad, 2H), 3.99 ppm (s, 4H), 7.33 ppm (d, 4H), 7.48 ppm (d, 2H) 7.93 ppm (d, 4H), 8.73 ppm (d, 2H).



6 **7** **20**

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Appendix A: ^{1}H NMR Spectra of Products.

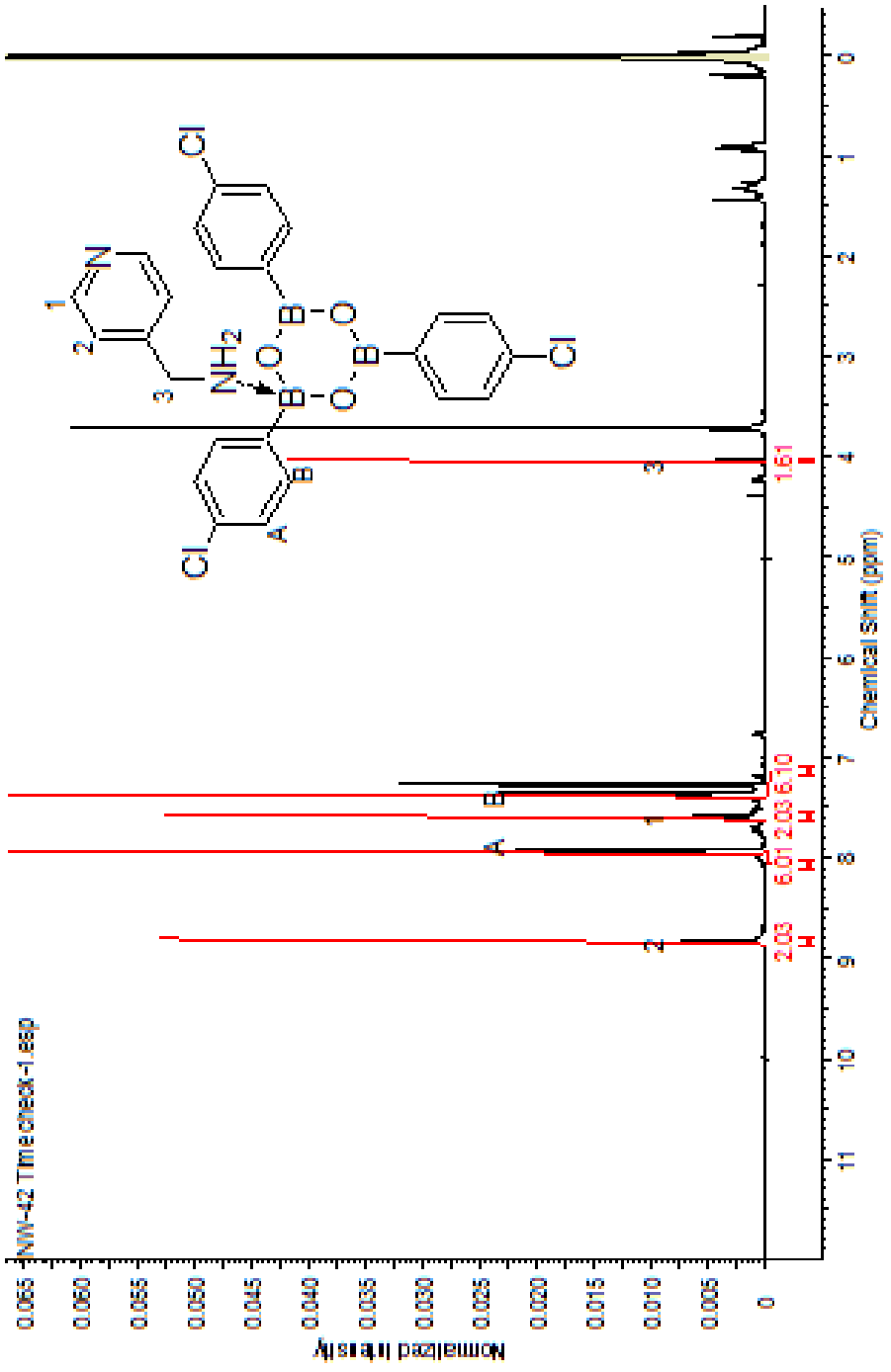

Figure A1. ^{1}H NMR spectrum of 4-chlorophenyl boroxine with trace amounts of 4-chlorophenyl boronic acid in $CDCl_3$.

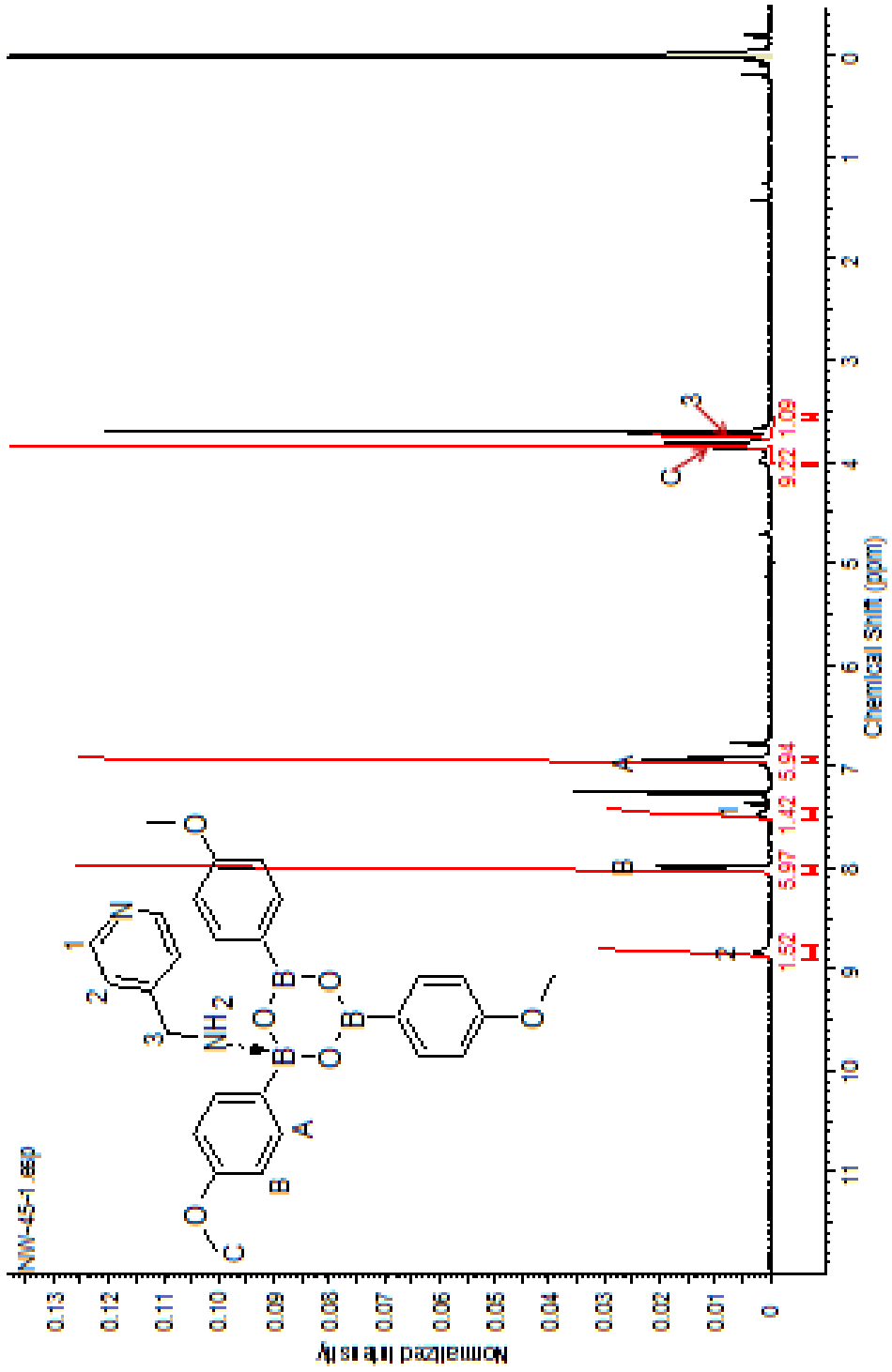

Figure A2. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and 4-methoxyphenyl boroxine in $CDCl_3$.

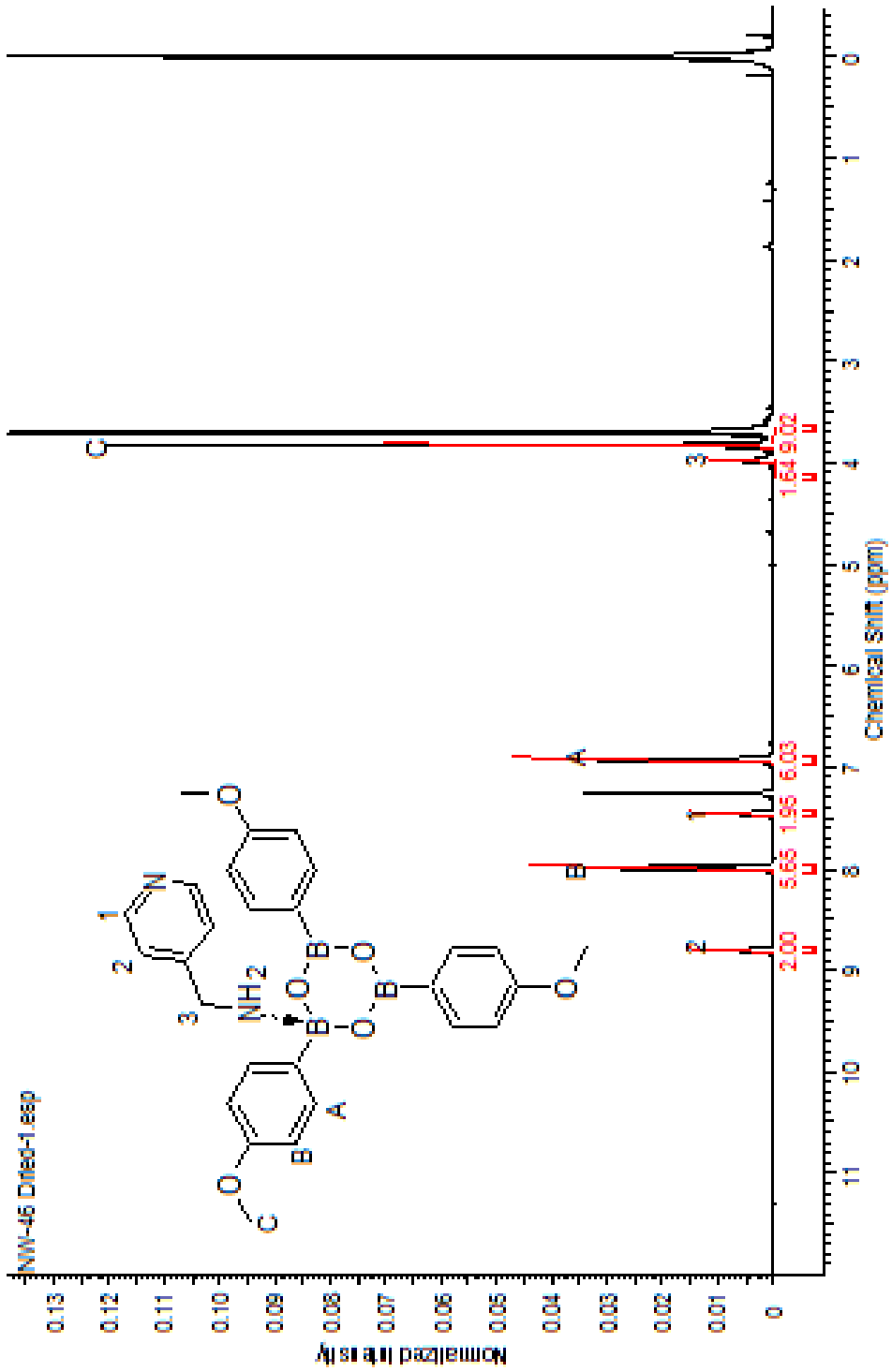

Figure A3. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and 4-methoxyphenyl boroxine in $CDCl_3$.

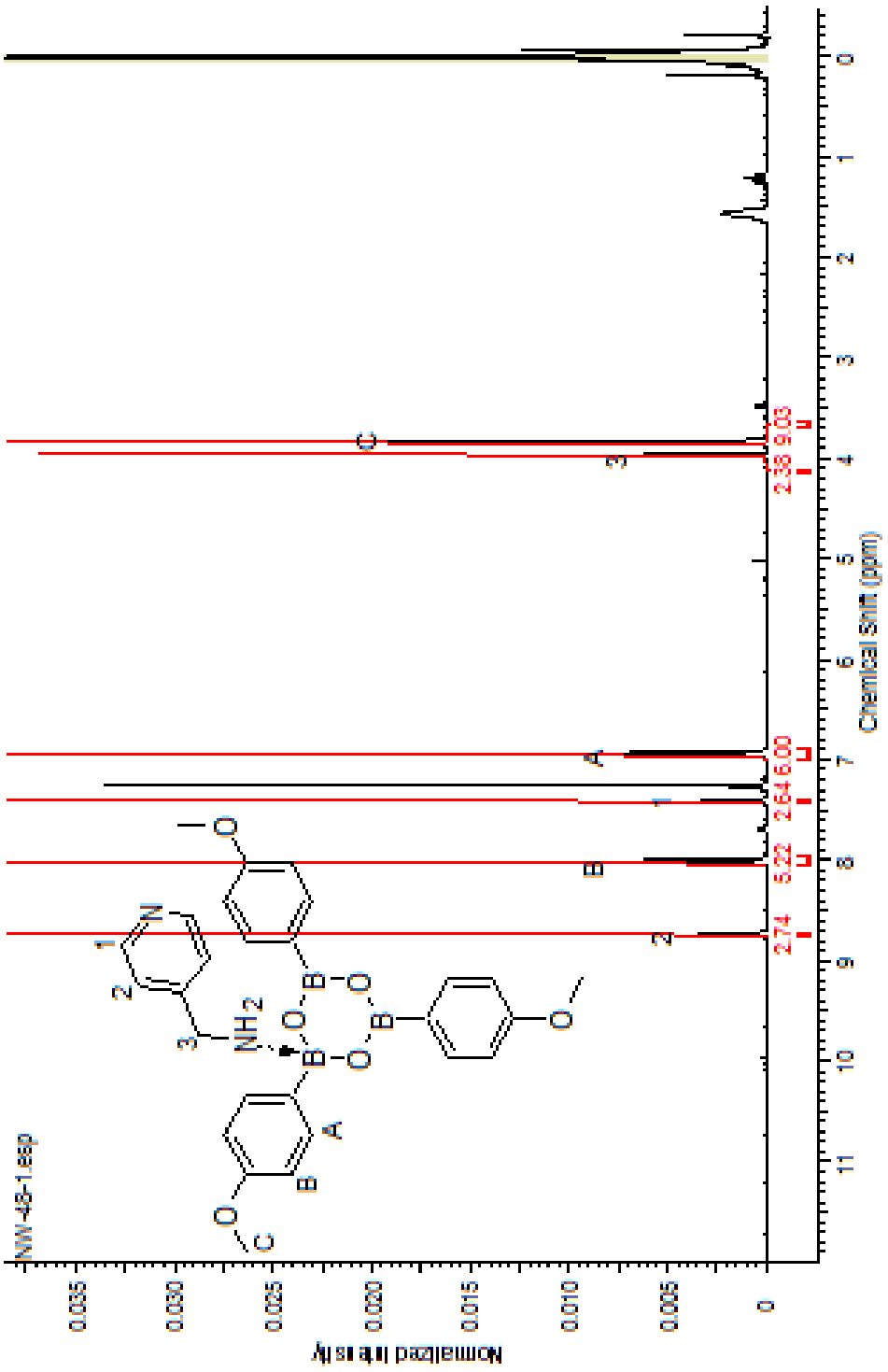

Figure A4. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and 4-methoxyphenyl boroxine in $CDCl_3$.

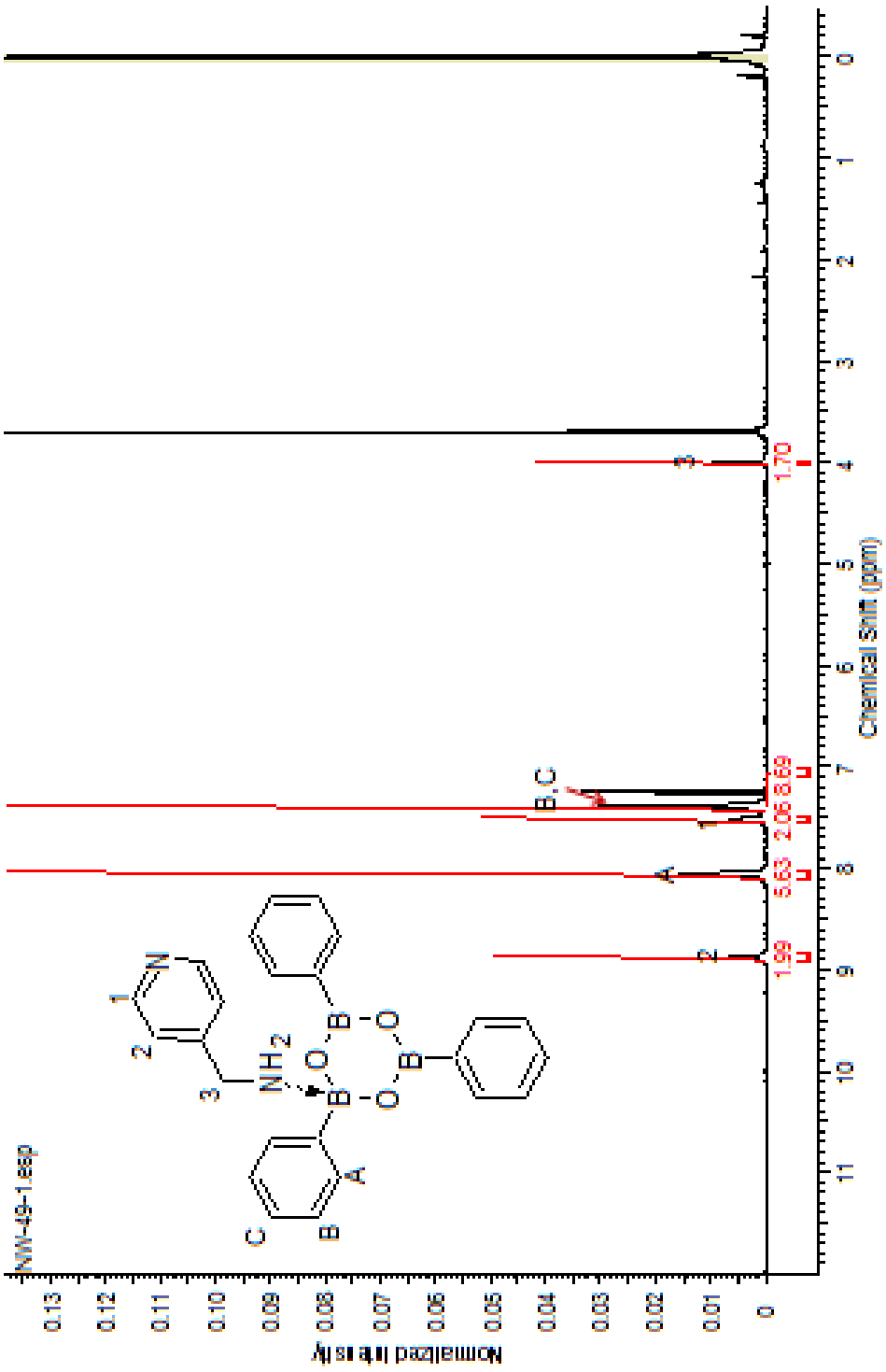

Figure A5. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and phenyl boroxine in $CDCl_3$

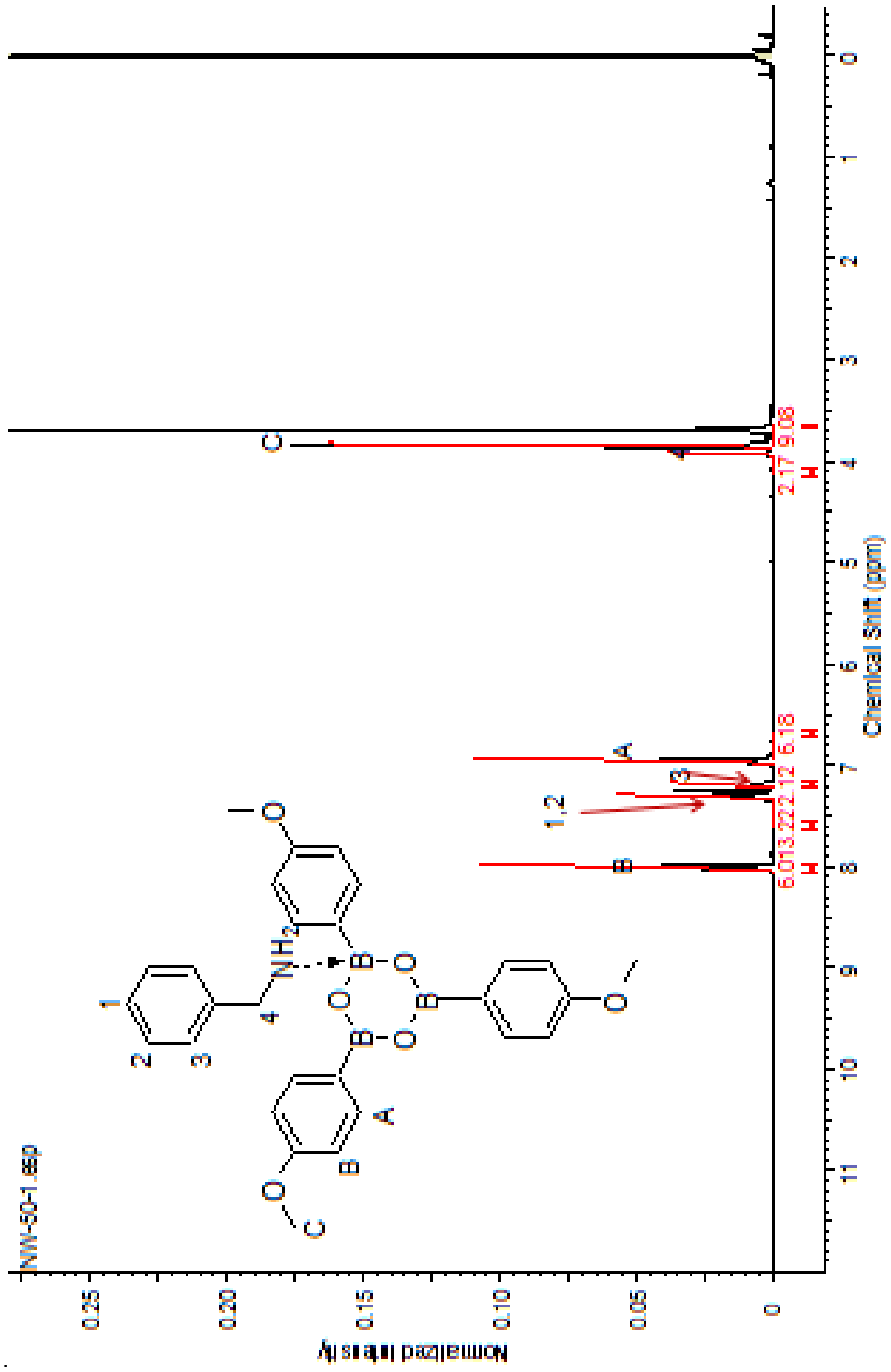

Figure A6. ^{1}H NMR spectrum of product of reaction of benzylamine and 4-methoxyphenyl boroxine in $CDCl_3$.

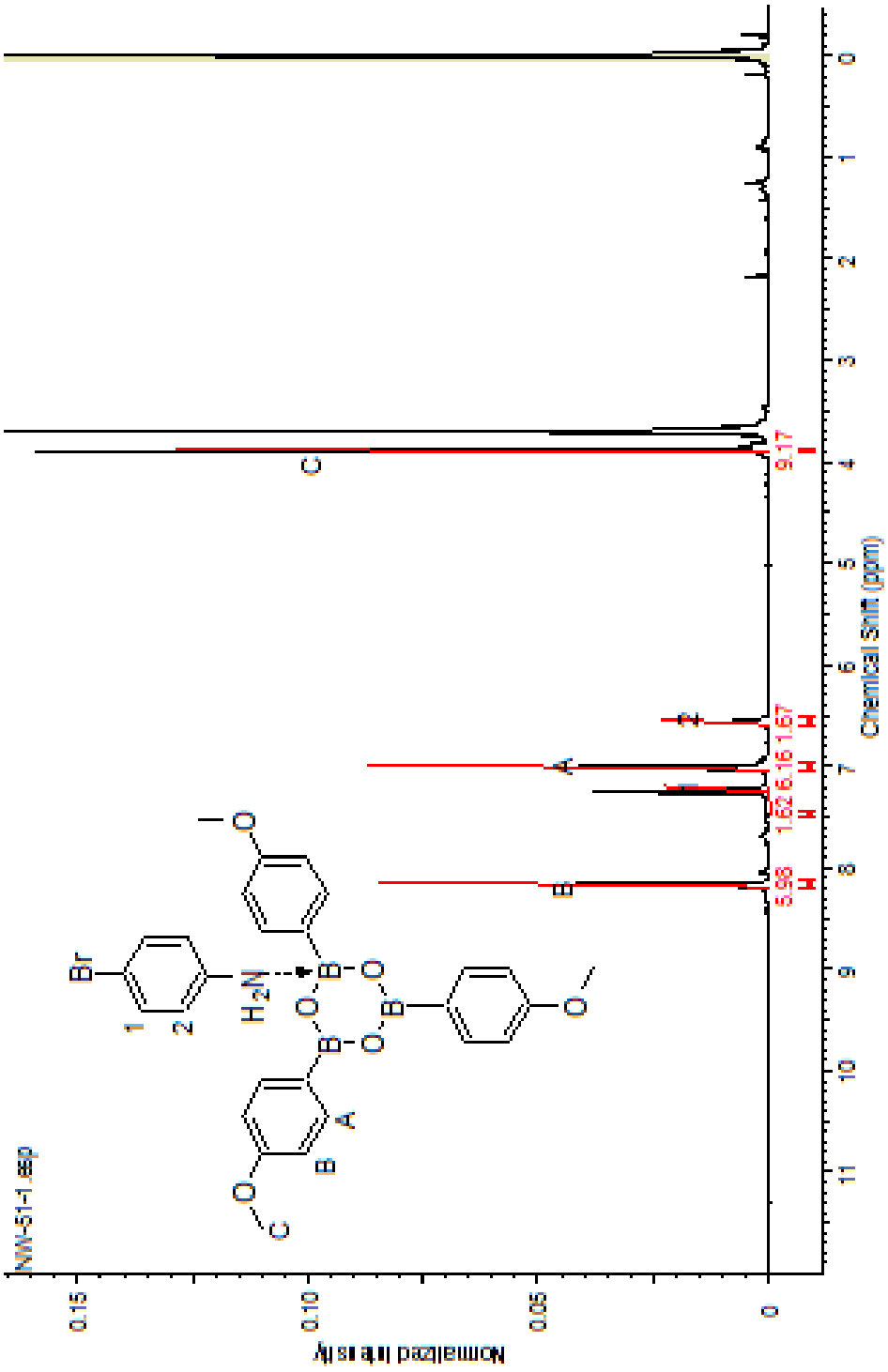

Figure A7. ^{1}H NMR spectrum of product of reaction of 4-bromoaniline and 4-methoxyphenyl boroxine in $CDCl_3$.

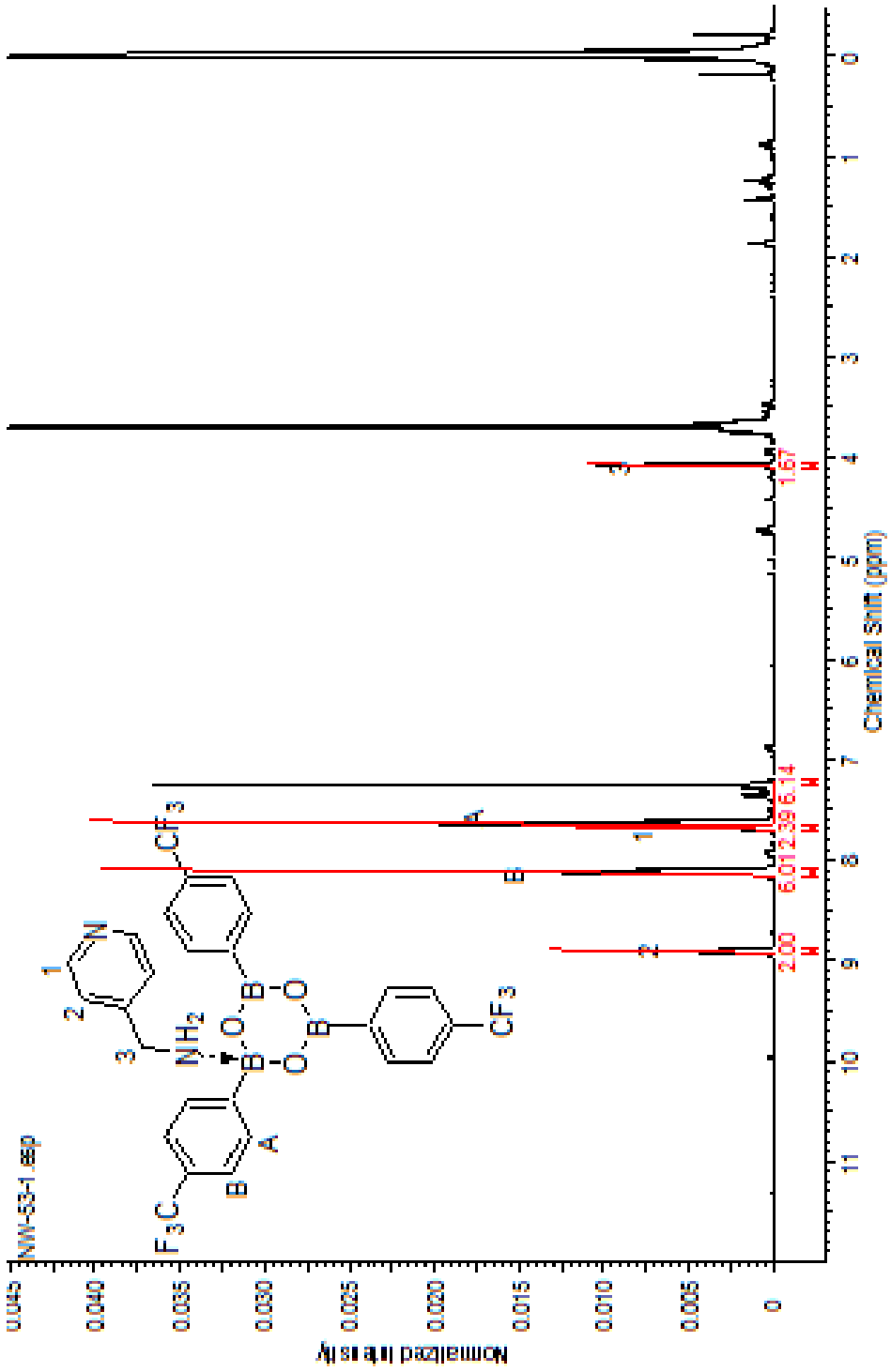

Figure A8. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and 4-triflouromethylphenyl boroxine in $CDCl_3$.

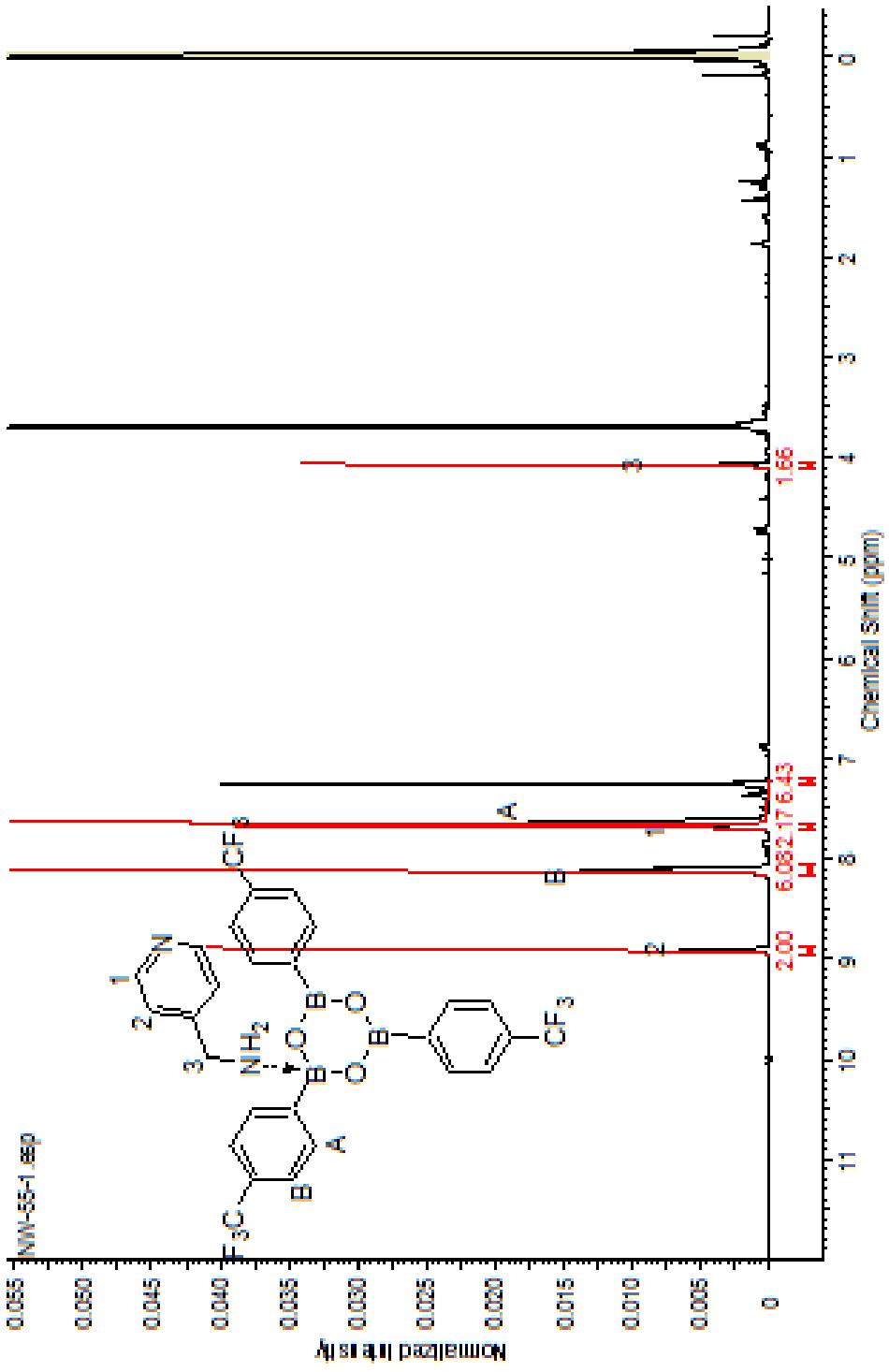

Figure A9. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and 4-triflouromethylphenyl boroxine in $CDCl_3$.

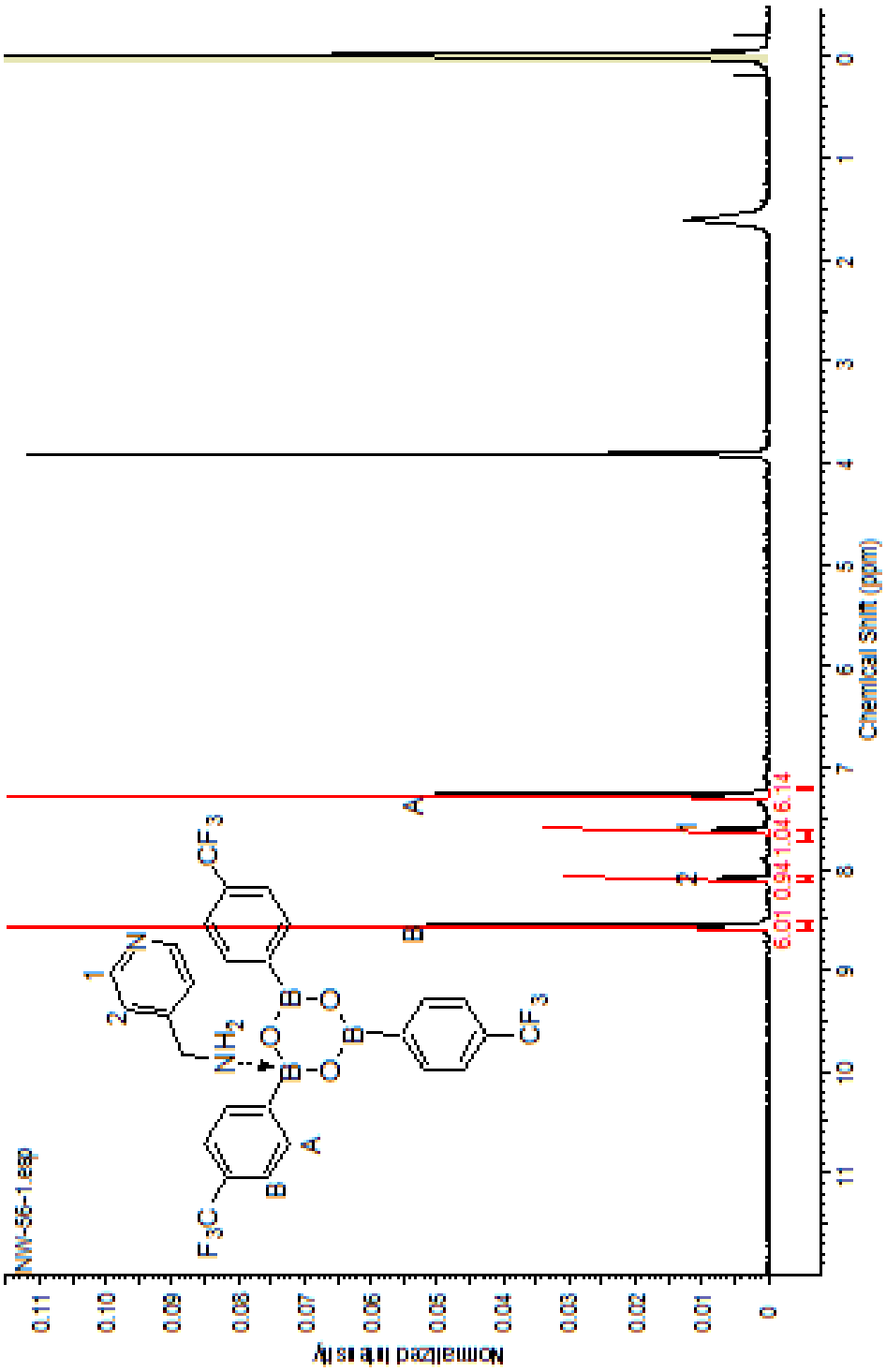

Figure A10. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and 4-triflouromethylphenyl boroxine in $CDCl_3$.

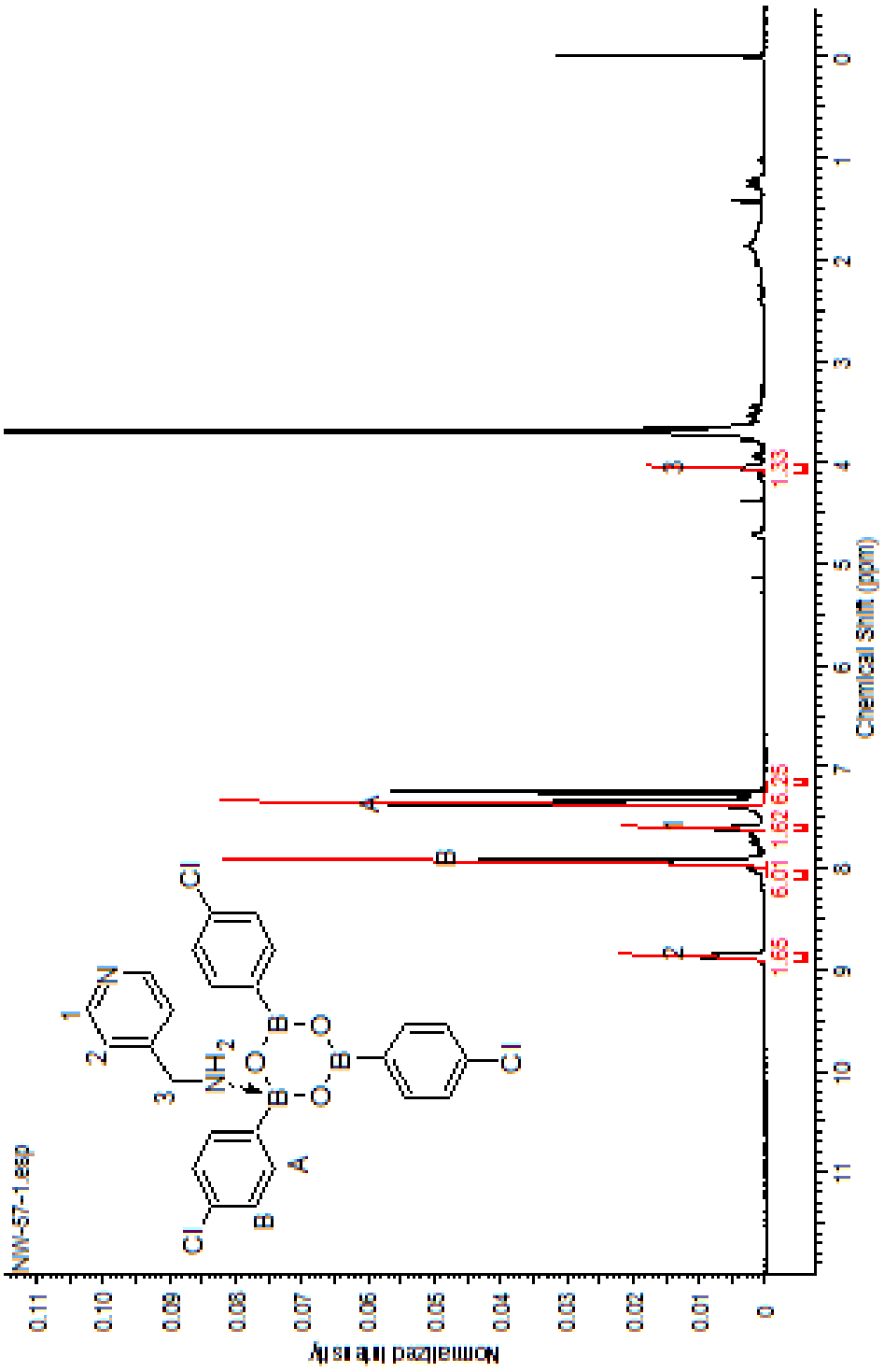

Figure A11. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and 4-chlorophenyl boroxine in $CDCl_3$.

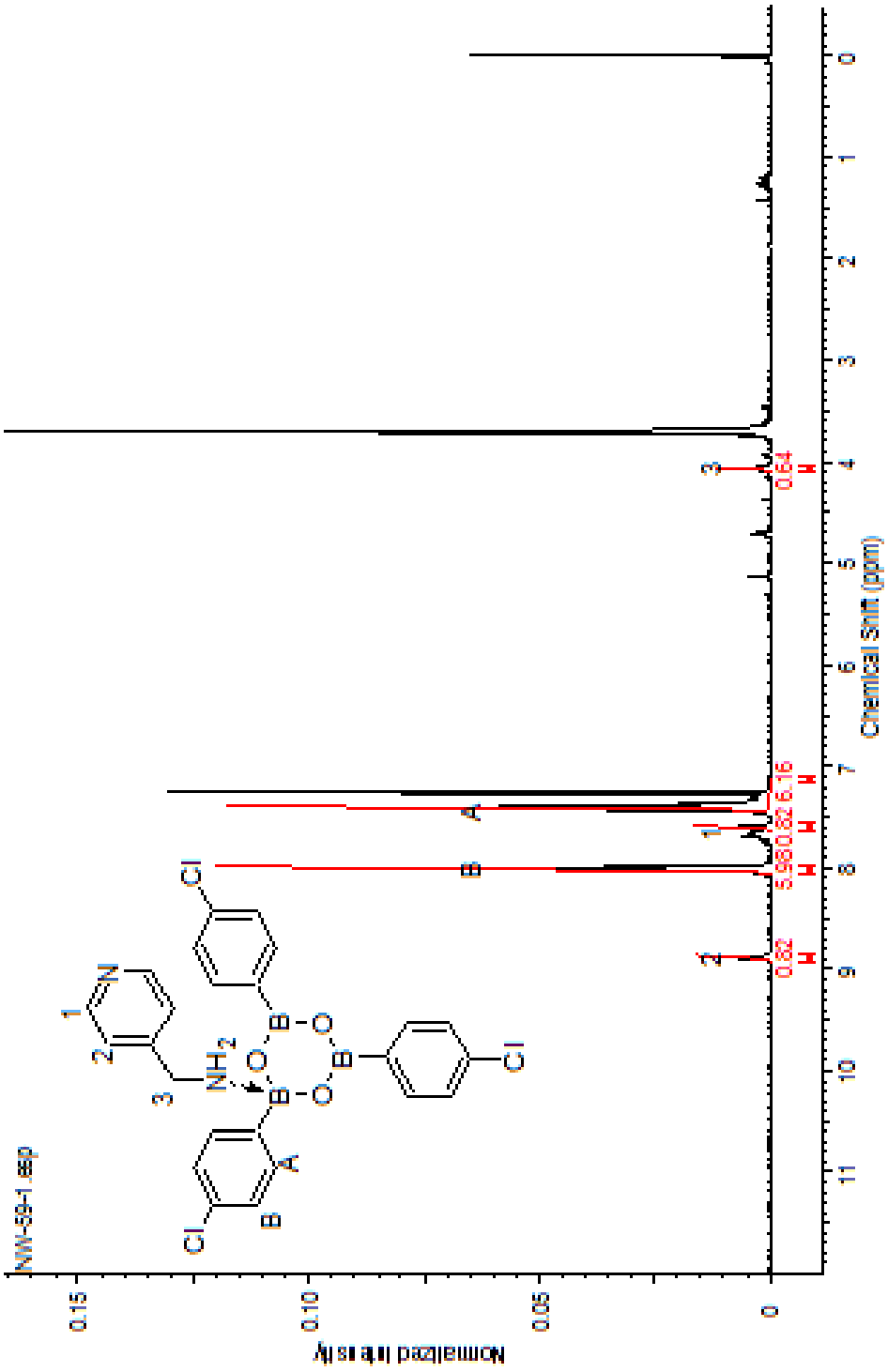

Figure A12. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and 4-chlorophenyl boroxine in $CDCl_3$.

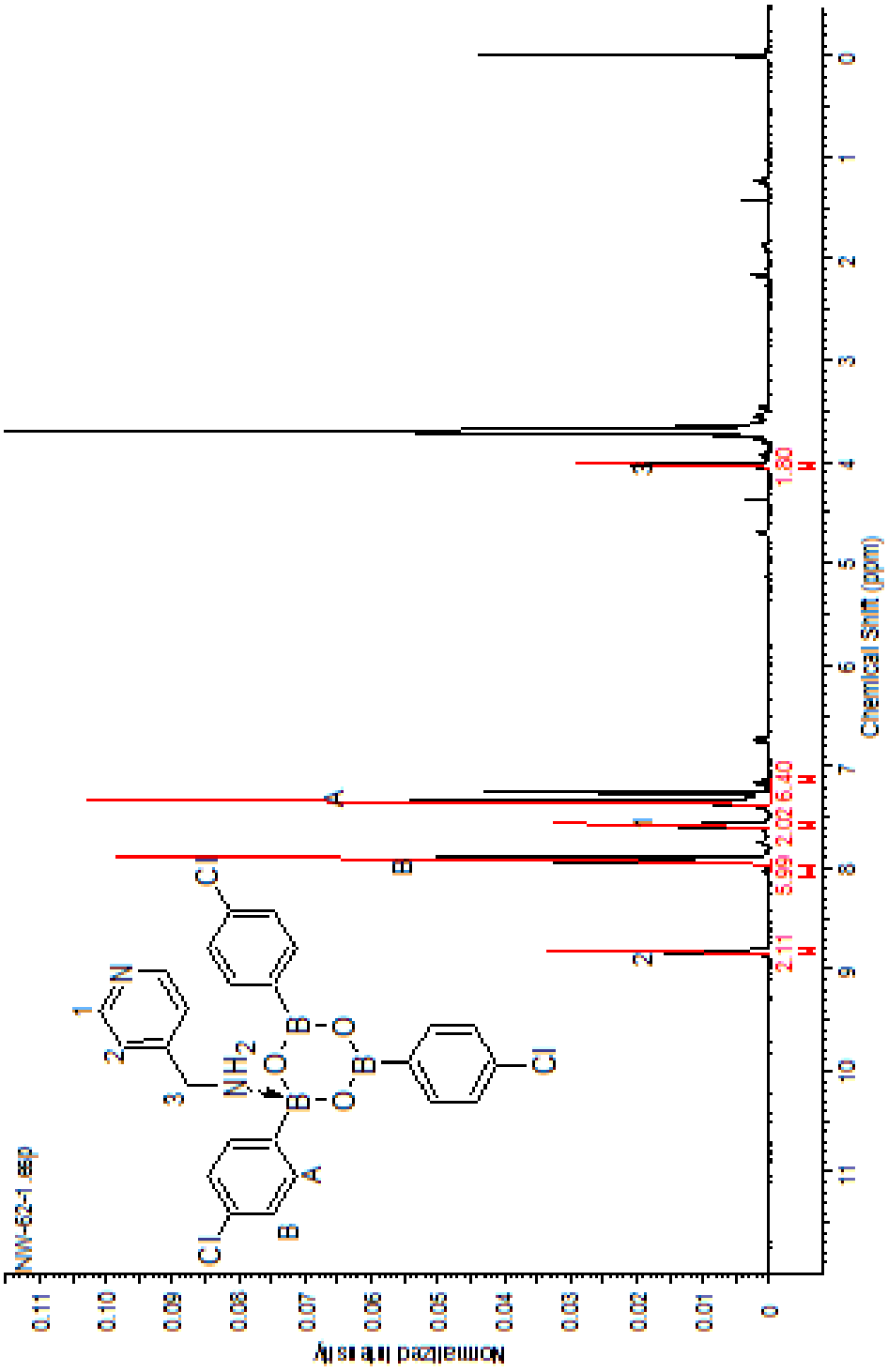

Figure A13. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and 4-chlorophenyl boroxine in $CDCl_3$.

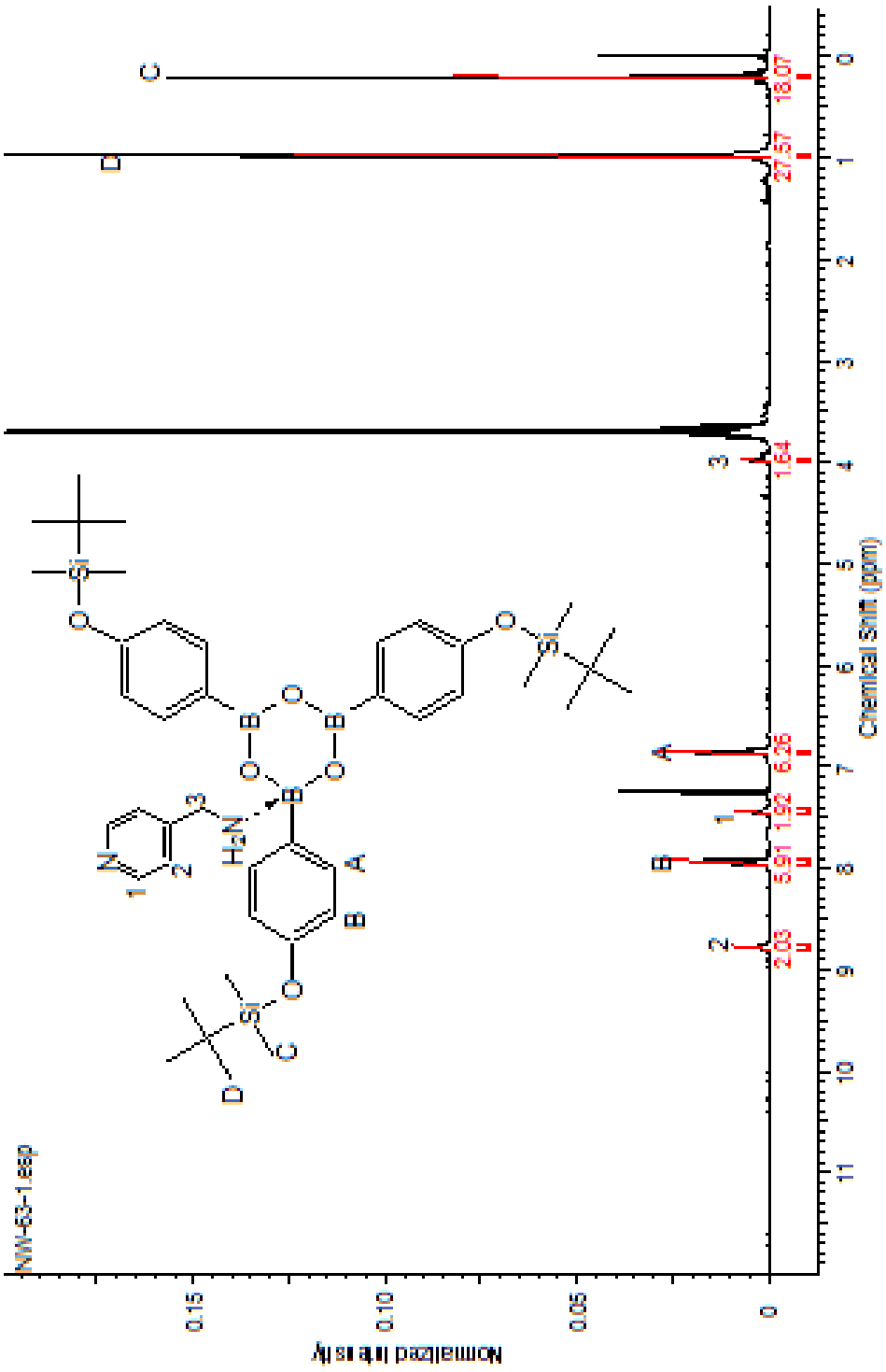

Figure A14. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and 4-(Tert-butyldimethylsiloxy) phenyl boronic acid in $CDCl_3$.

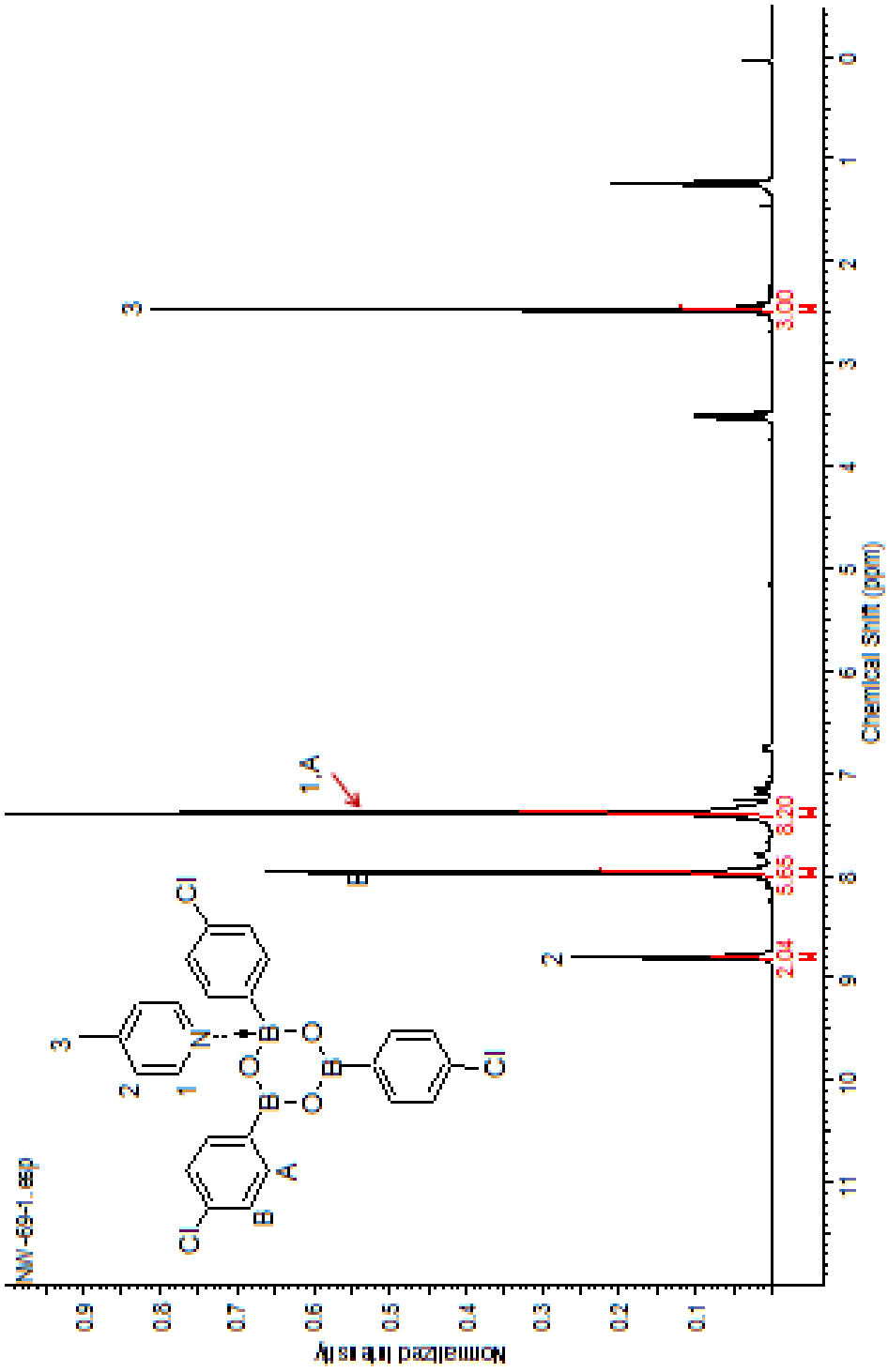

Figure A15. ^{1}H NMR spectrum of product of reaction of picoline and 4-chlorophenyl boroxine in $CDCl_3$.

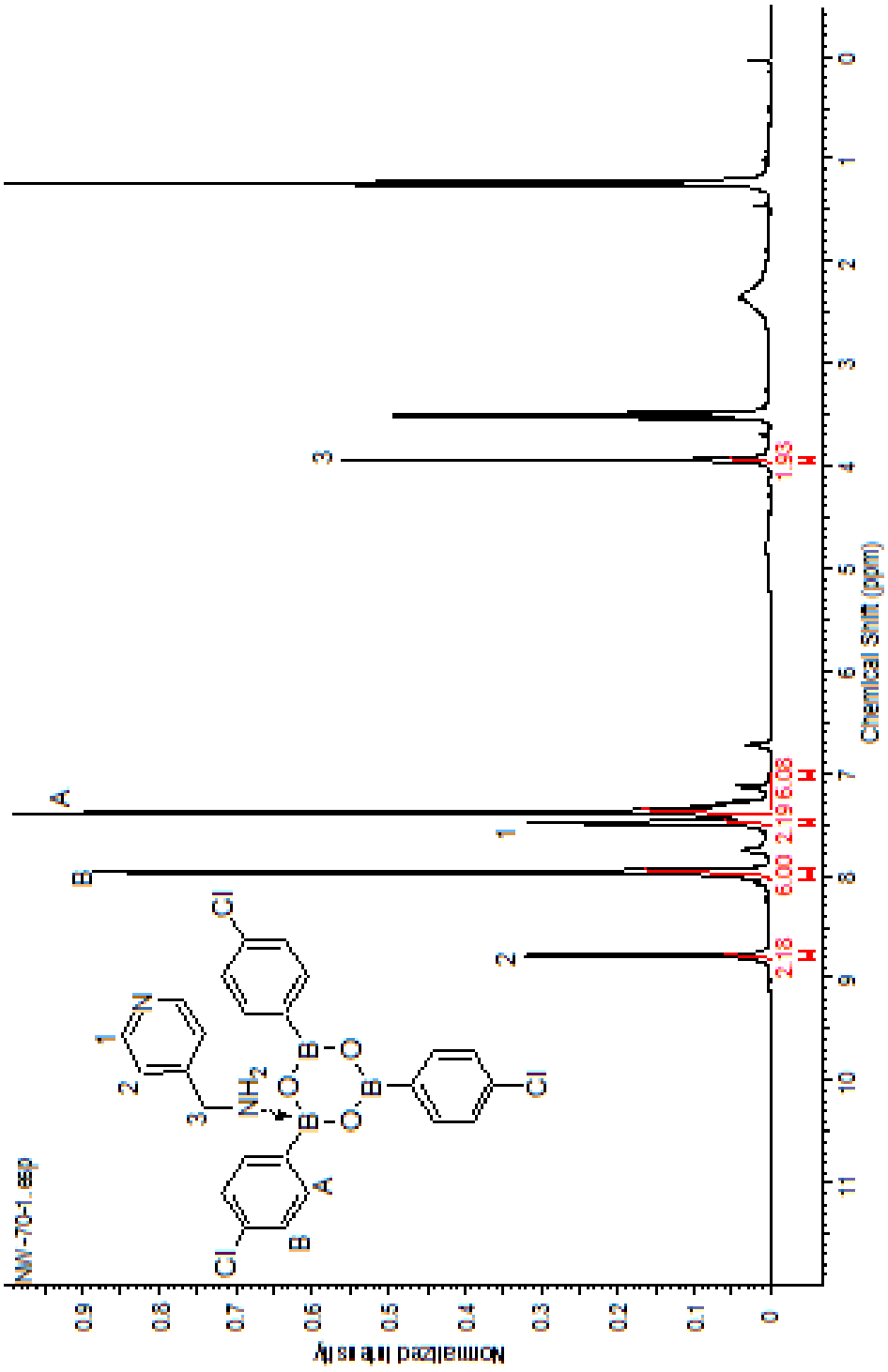

Figure A16. ^{1}H NMR spectrum of product of reaction of 4-(aminomethyl) pyridine and 4-chlorophenyl boroxine in $CDCl_3$.

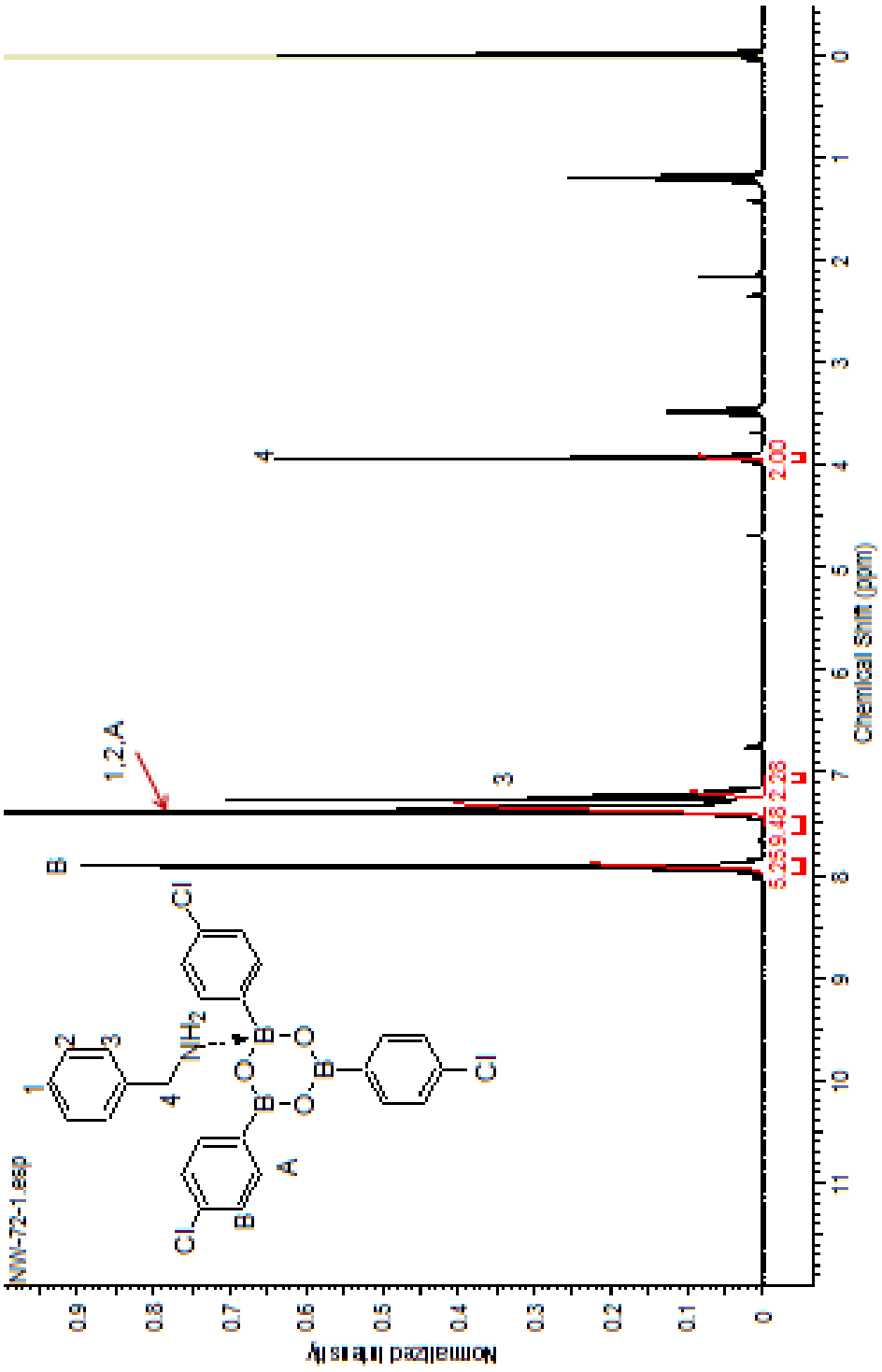

Figure A17. ^{1}H NMR spectrum of product of reaction of benzylamine and 4-chlorophenyl boroxine in $CDCl_3$.

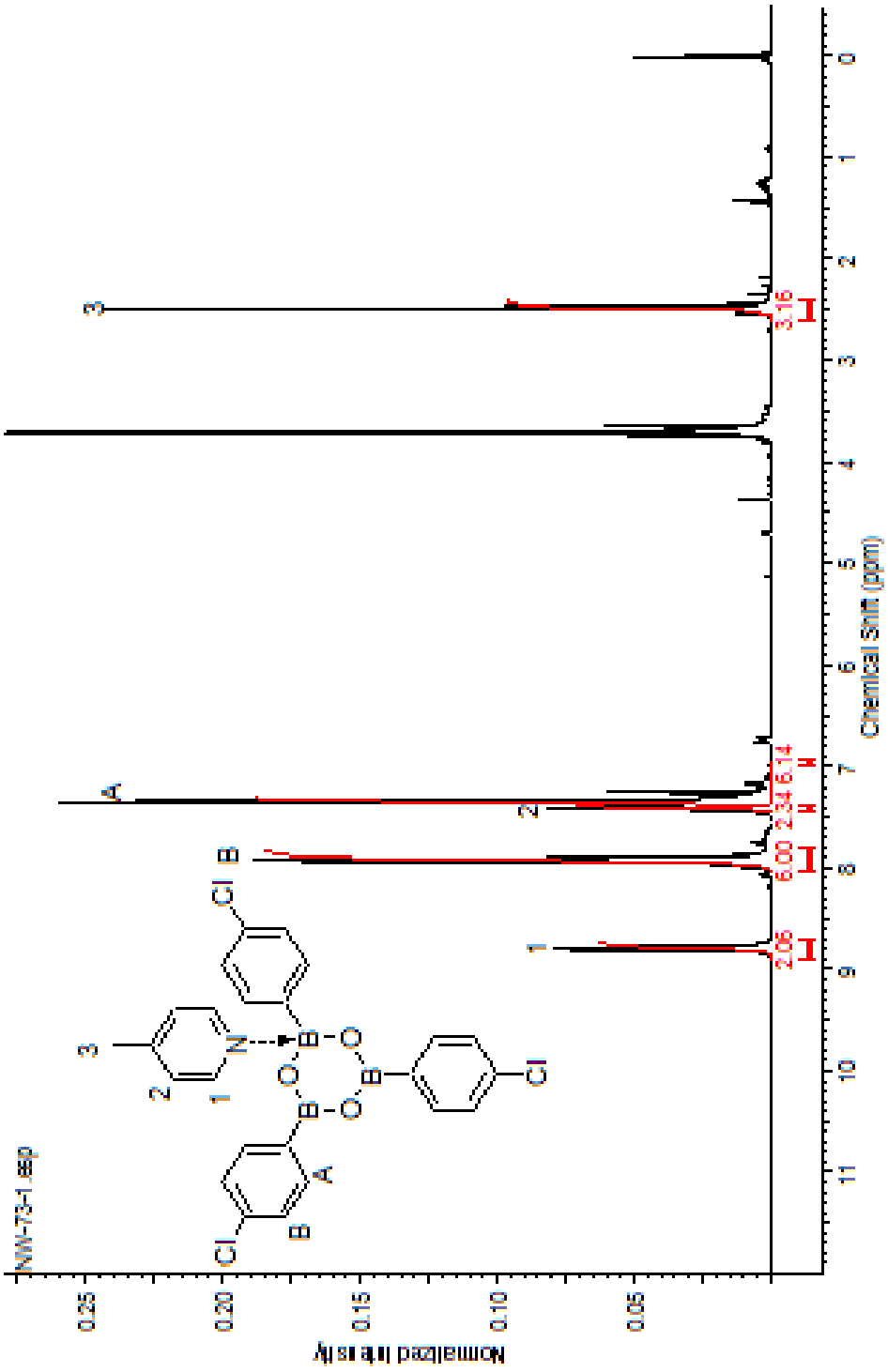

Figure A18. ^{1}H NMR spectrum of product of reaction of picoline and 4-chlorophenyl boroxine in $CDCl_3$.

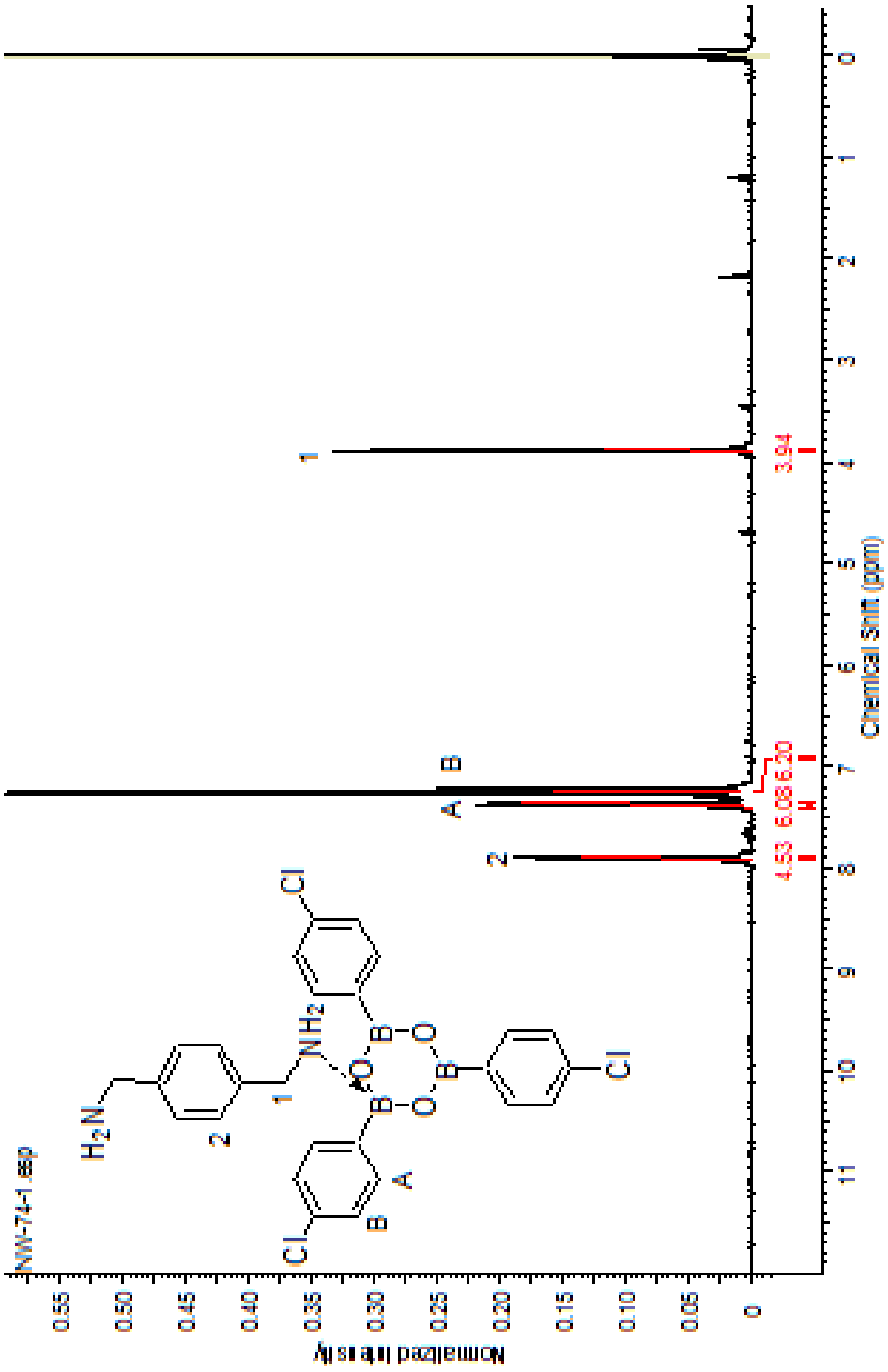

Figure A19. ^{1}H NMR spectrum of product of reaction of xylene diamine and 4-chlorophenyl boroxine in $CDCl_3$.

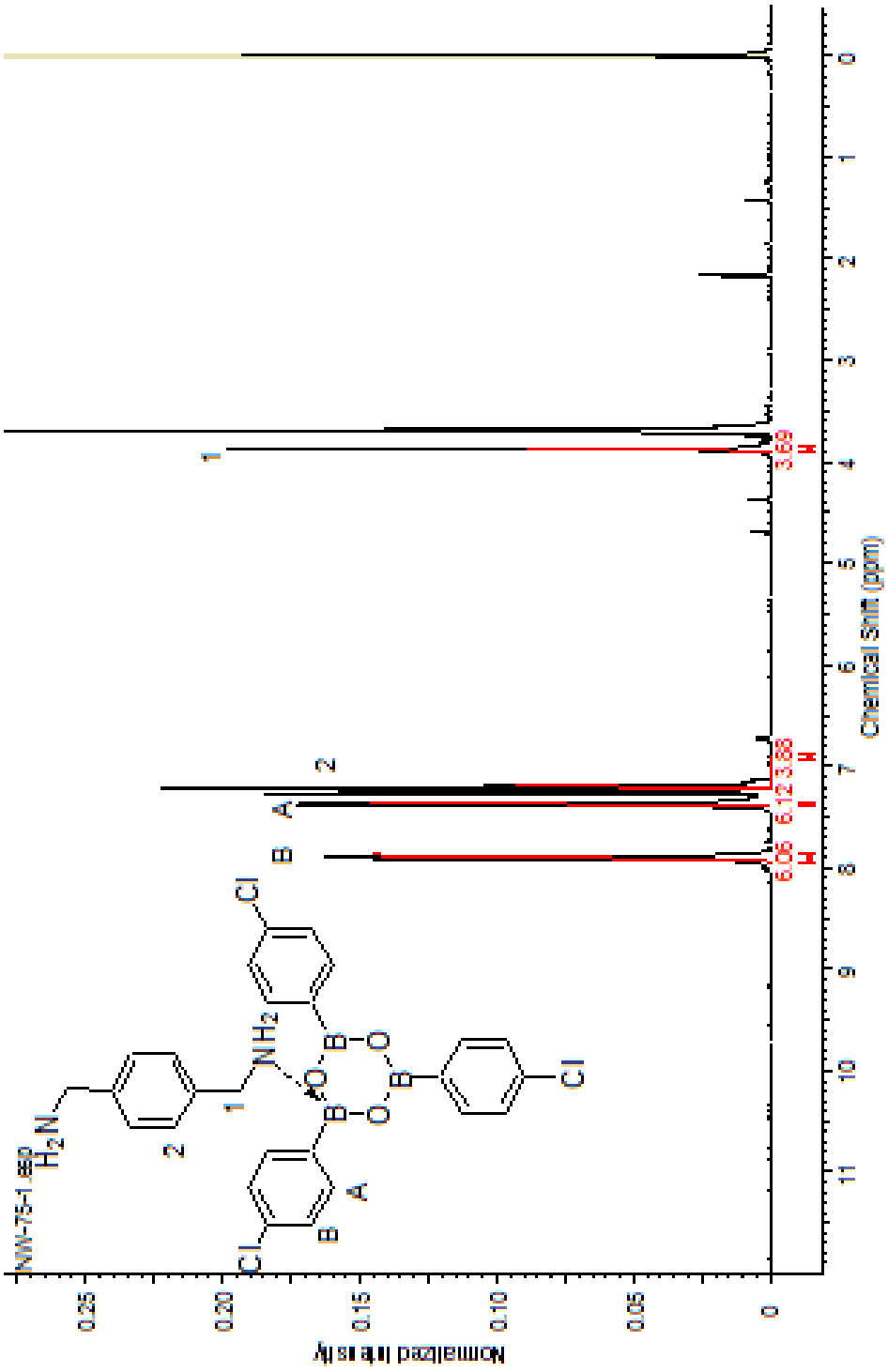

Figure A20. ^{1}H NMR spectrum of product of reaction of xylene diamine and 4-chlorophenyl boroxine in $CDCl_3$.

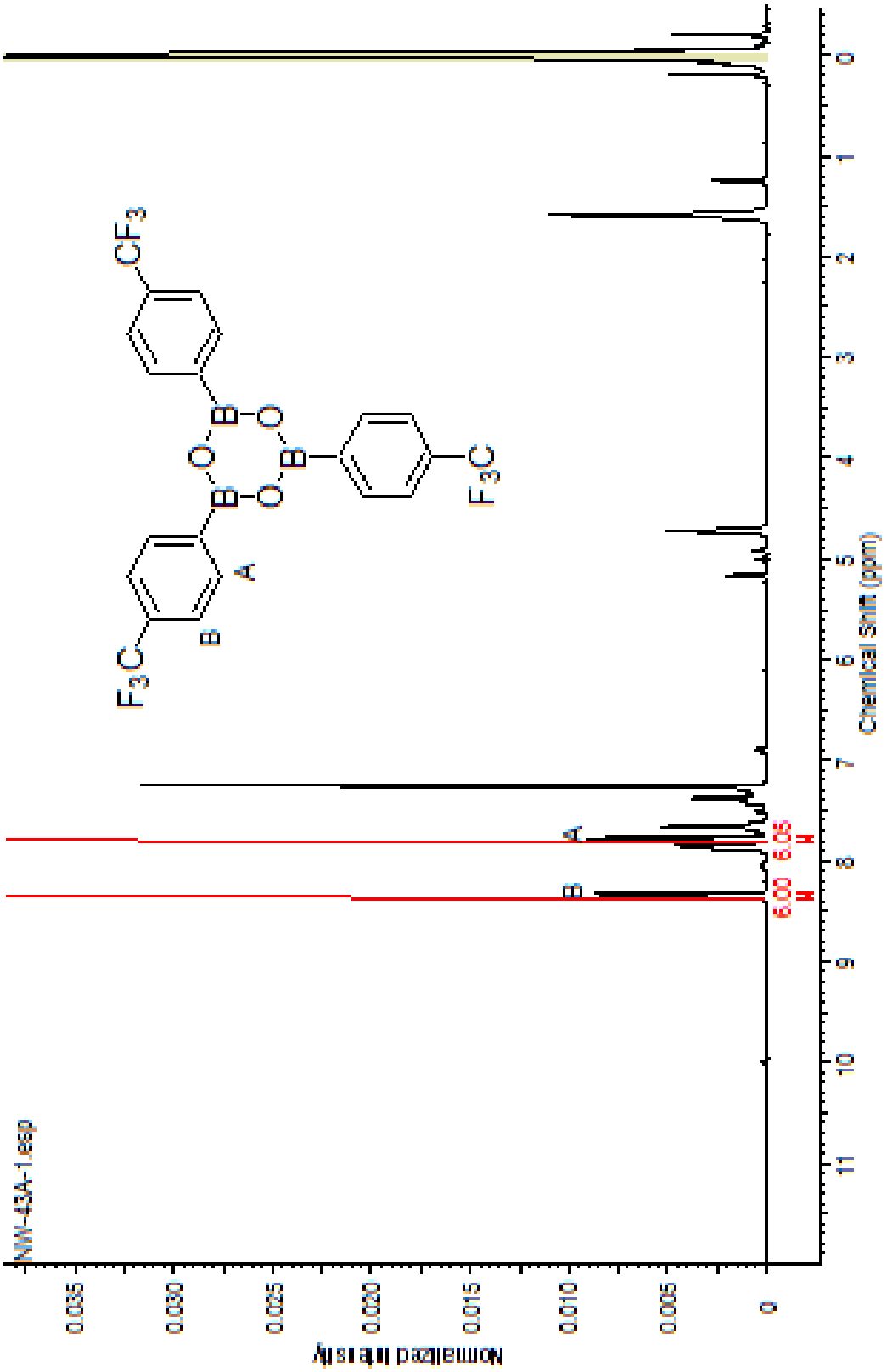

Figure A21. ^{1}H NMR spectrum of 4-triflouromethylphenyl boroxine in $CDCl_3$.

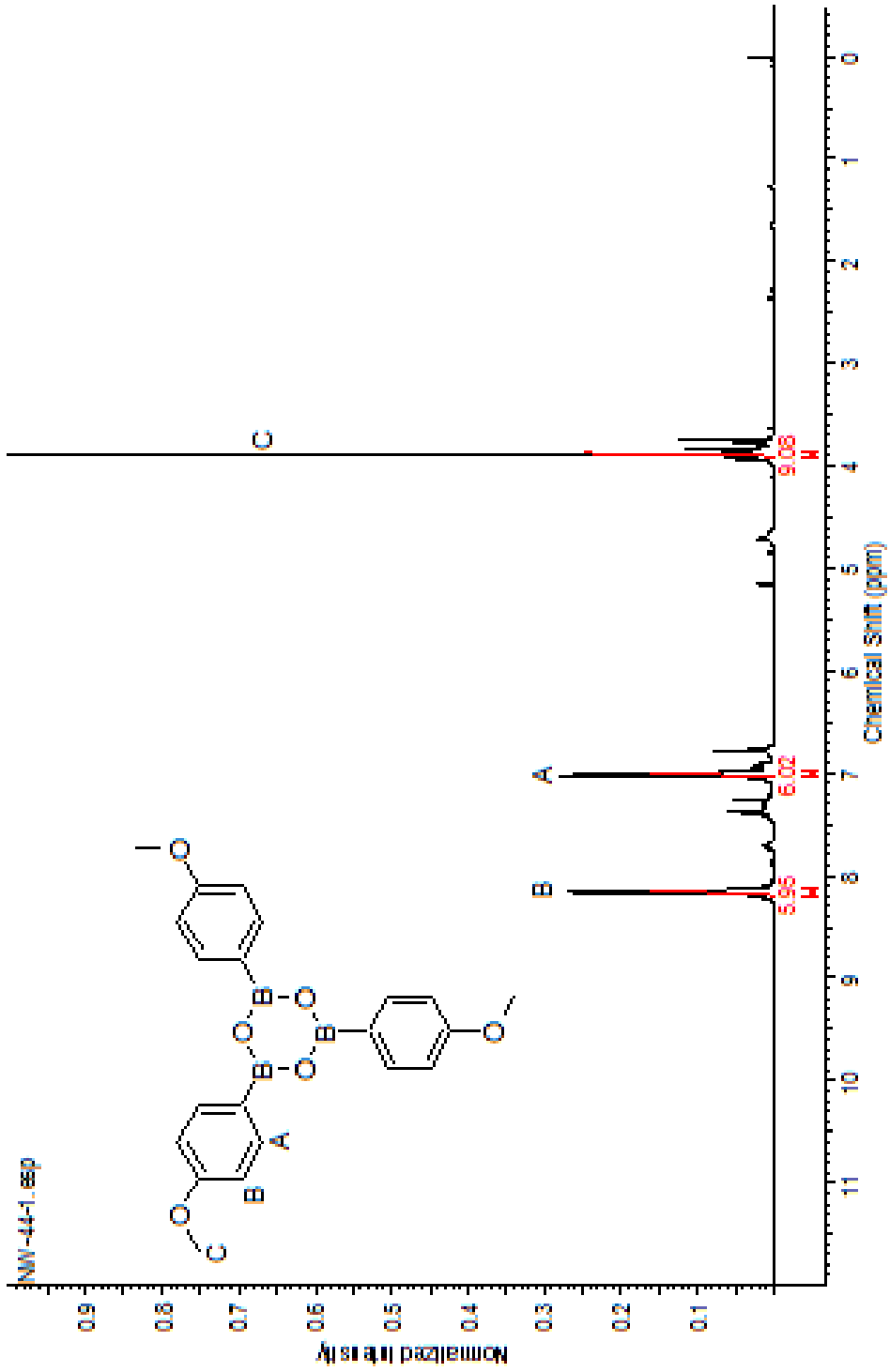

Figure A22. ^{1}H NMR spectrum of 4-methoxyphenyl boroxine in $CDCl_3$.

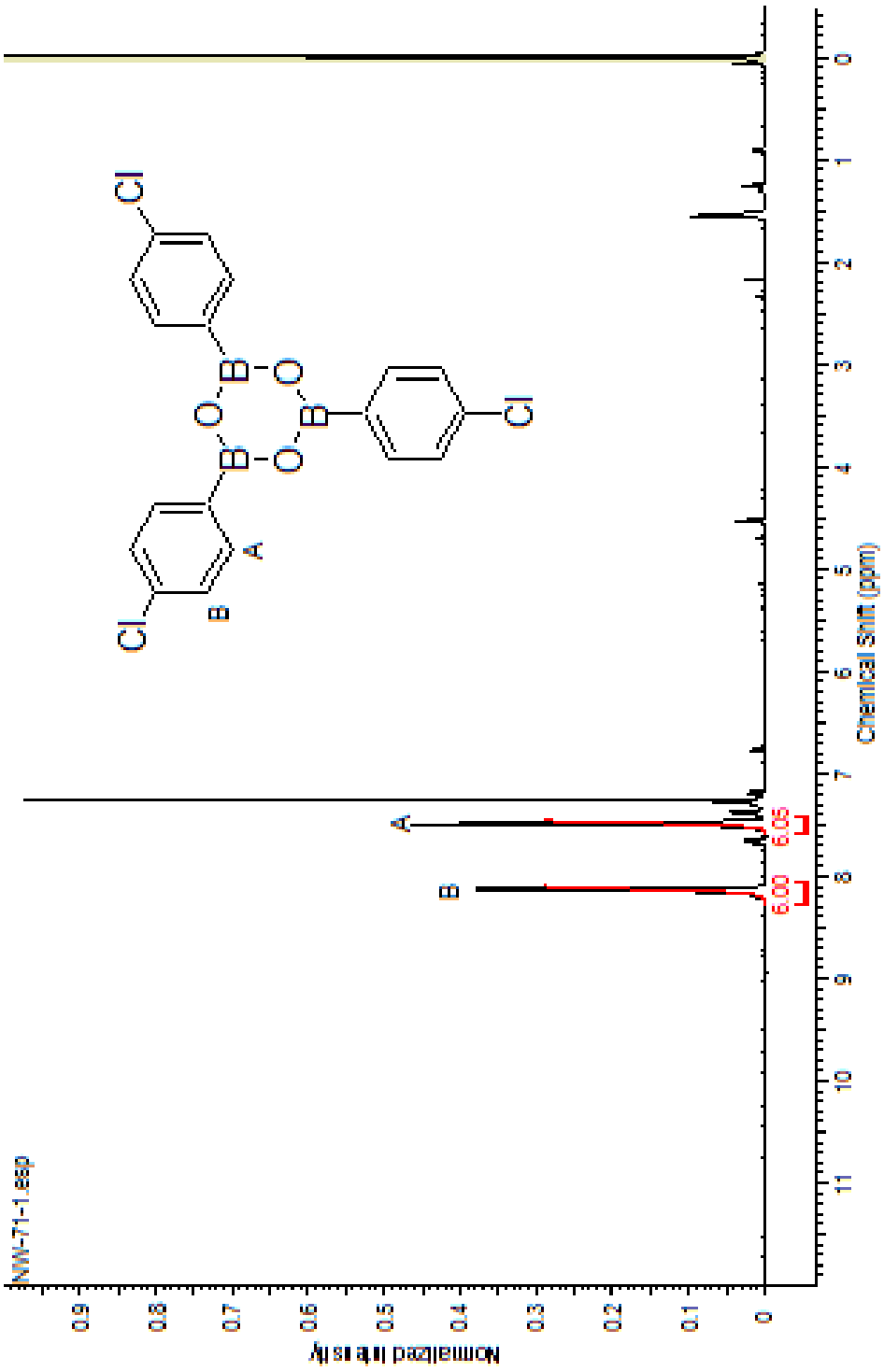

Figure A23. ^{1}H NMR spectrum of 4-chlorophenyl boroxine in $CDCl_3$.