Tutor/s

Dr. Jordi García Gómez
Departament de Química orgànica

Dr. Alexandr Shafir
IQAC-CSIC

Grau de Química

Treball Final de Grau

Synthesis of BN hexahydronaphthalene via triallylborane and dialylamine.

Síntesis del BN hexahidronaftalè mitjançant trialilborà i dialilamina.

Pol Roca Codina

March, 2022

Universitat de Barcelona

B:KC Barcelona Knowledge Campus
Campus d'Excel·lència Internacional

Odiar el treball dur pot arribar a ser una obsessió fins al punt de no deixar-lo acumular-se.

Herbert C. Brown

Agrair primer de tot a l'Alex Shafir, per la paciència i el temps dedicat en mi, i gràcies a ell haver tornat a tocar gairebé tots els camps d'aquesta carrera tan bonica que és la química. Per la oportunitat brindada al IQAC-CSIC, i el coneixement compartit amb mi.

A la meva família per el recolzament incondicional i el temps dedicat en mi, i haver confiat en el meu esforç tot i haver hagut temps durs.

REPORT

CONTENTS

1. SUMMARY

Polycyclic aromatic hydrocarbons (PAHs) have always been of great importance in the context of chemical and materials science research,[1] with a recent emphasis placed on the modulable photophysical properties of extended π-systems in certain sectors of organic conductors,[2] among others. The cause of its properties relies in the number of π-conjugations and the electronic delocalization.

However, new applications appear when applying the BN isosterism. That means including a boron-nitrogen bond to substitute a carbon-carbon bond. In doing so, the "normal" apolar C=C unit in such molecules is replaced with the more polar BN units, thus creating a dipoles and causing differences in reactivity and properties.[3][4][5] This has led to the potential of aromatic BN compounds for the isosteric substitution of phenyl and naphthyl groups in medicinal chemistry, thus creating new avenues in drug design through BN-isosterism.[6] The aromatic relocation of electrons provides stability to the molecule and allows its study.

Still limited by the lack of synthetic methodologies for the preparation of these compounds in sufficient quantities, aromatic BN compounds are of great interest. On the other hand, the effects of these substitutions are still poorly studied, and any progress is extremely important.

The aim of this project has been to improve the synthesis of a particular member of the BN aromatic family, specifically of one of the isomers of the so-called BN-naphthalene core. While this compound has gained much attention as building block in organic electronic design, its synthesis has remained highly challenging and low yielding. In this TFG project, we aim to provide a much-improved route towards these molecules. Specifically, with the reaction between triallylborane and dialylamine for the formation of the adduct, and subsequent release of propene to form a key tetra-allylic precursor. This species then undergoes efficient ring-closing olefin metathesis (RCOM) by treatment with Grubbs type I catalyst. The metathesis of enynes with these reagents has also been studied, following the same procedure but using di-propargylamine in the propenolysis step.

Keywords: BN aromatics, BN hexahydronaphthalene, BN naphthalene, metathesis of olefins, metathesis of enynes.

2. RESUM

Els hidrocarburs aromàtics policíclics (HAP) sempre han tingut una gran importància en el context de la investigació química i de la ciència dels materials,[1] amb un èmfasi recent posat en les propietats fotofísiques modulables dels sistemes π en determinats sectors de conductors orgànics,[2] entre altres. La causa de les seves propietats es basa en el nombre de conjugacions π i la deslocalització electrònica.

Tanmateix, apareixen noves aplicacions en quan s'usa l'isosterisme BN. Això vol dir incloure un enllaç bor-nitrogen per substituir un enllaç carboni-carboni. En fer-ho, la unitat C=C apolar "normal" d'aquestes molècules es substitueix per les unitats BN més polars, creant així dipols i provocant diferències en la reactivitat i les propietats. [3][4][5] Això ha donat lloc al potencial dels compostos BN aromàtics per a la substitució isostèrica de grups fenil i naftil en la química medicinal, creant així noves vies en el disseny de fàrmacs mitjançant l'isosterisme BN.[6] La reubicació aromàtica dels electrons proporciona estabilitat a la molècula i permet el seu estudi.

Encara limitats per la manca de metodologies sintètiques per a la preparació d'aquests compostos en quantitats suficients, els compostos BN aromàtics són de gran interès. D'altra banda, els efectes d'aquestes substitucions encara estan poc estudiats i qualsevol progrés és extremadament important.

L'objectiu d'aquest projecte ha estat millorar la síntesi d'un membre concret de la família BN aromàtica, concretament d'un dels isòmers de l'anomenat nucli BN-naftalè. Tot i que aquest compost ha guanyat molta atenció com a element bàsic en el disseny electrònic orgànic, la seva síntesi s'ha mantingut molt difícil i de baix rendiment. En aquest projecte de TFG, pretenem oferir una ruta molt millorada cap a aquestes molècules. Concretament, amb la reacció entre trialilborà i dialilamina per a la formació de l'adducte, i posterior alliberament de propè per formar un precursor tetraal·lílic clau. A continuació, aquesta espècie se sotmet a una metàtesi d'olefines de tancament d'anell (RCOM) eficient mitjançant tractament amb catalitzador Grubbs tipus I. També s'ha estudiat la metàtesi d'enins amb aquests reactius, seguint el mateix procediment però utilitzant di-propargilamina en l'etapa de propenòlisi.

Paraules clau: BN aromàtics, BN hexahidronaftalè, BN naftalè, metàtesis de olefines, metàtesis de enins.

3. INTRODUCTION

3.1. BACKGROUND IN PAHS

3.1.1. Definition and origin

Polycyclic fragrant hydrocarbons (PAHs) are aromatic hydrocarbons with two or more fused benzene rings. In the strictest definition, this compound family does not contain heteroatoms or further ring substituents. Nevertheless, in most cases PAHs serve as basis for a wider series of molecular structures, which may include other functional group and substituents. Polyarenes containing up to four rings are referred to as light PAHs, and those that contain more than four rings are heavy PAHs, an example is provided in Figure 1. Although the exact properties depend on each particular structure, in some cases the "heavy" derivatives may prove to be more stable in harsh conditions, but may also be more harmful than the light PAHs to nature and animal health.[3]

PAHs happen normally in coal, rough oil, and gasoline. They tend to be produced when coal, oil, gas, wood, rubbish, and tobacco are burned. They can then bind to themselves and other PAHs formed, or break down into smaller molecules, that spread through the air. Cigarette smoke contains a large number of these products that will later remain in the environment.[7]

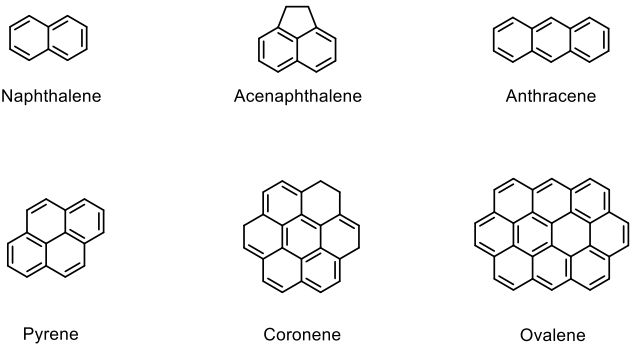


Figure 1. Some PAHs with different molecular weight. As an example, naphthalene would be considered a light PAH and ovalene a heavy PAH.

PAHs are abundant throughout the universe. They are linked to new stars and exoplanets and appear to have formed as early as a few billion years after the Big Bang. They are thought to contain more than 20% of the carbon in the cosmos and are a likely starting material for the first beginnings of life.[7]

3.1.2. Environment and health

From an environmental point of view, a variety of carbonaceous species, including PAH's have been proven to sediment and stay in the environment, given their typically low reactivity under a variety of conditions. There is a lot of PAHs release due to refineries, sewage treatment plants, river runoff, tanker oil transportation and shipping as the most important examples.[8]

However, a lot of PAHs constitute a major health problem, with some studies showing how specific PAHs can induce not only lung cancer, but also arrange of other pathologies. People living in the cities are at a high risk of getting this and other respiratory diseases since there is a much higher concentration than in rural areas, and thus more presence of the specific molecules that can derivate in lung failures.[9]

Benzo[*a*]pyrene (B[*a*]P) is the most known molecule and the one measured when estimating the carcinogenic levels of the air. In fact, recent studies also suggest that there are two PAHs molecules that can cause up to 10 times more risk of developing this cancer, namely the dibenzo[*a,h*]anthracene (DBA) and dibenzo[*a,l*]pyrene (DB[*a,l*]P),[7][9] shown in Figure 2

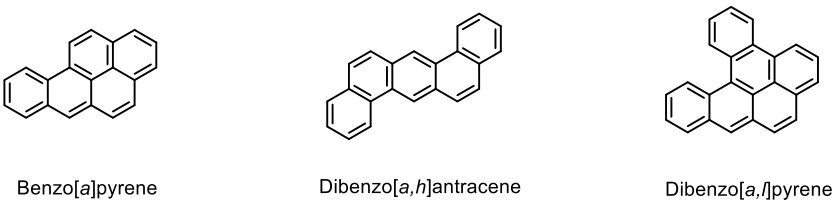


Figure 2. The three main most common PAHs in city air that contribute to lung cancer.

People living in cities tend to get up to an 8% more cancer than people living in rural areas, or far from zones affected by air pollution and areas with a low PAHs index. Although it is still not very well known how these biological mechanisms happen, everything seems to indicate that

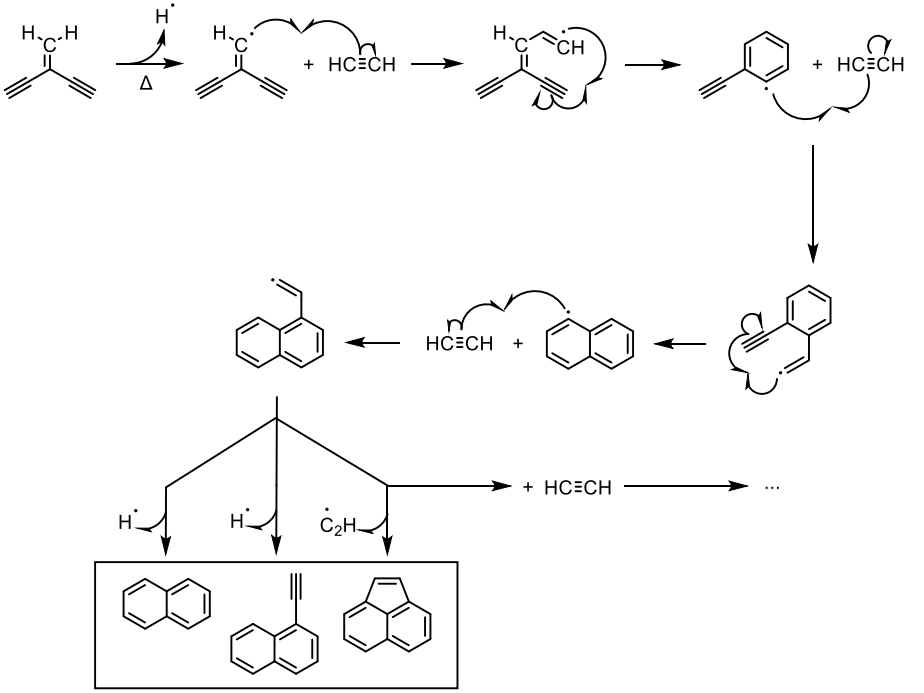
these PAHs form adducts with DNA, causing errors when cells start duplicating to create new ones. These new cells, now with a corrupted DNA, duplicate again until there is a moment that cancer cells are being created.[9][10]

Large amounts of carcinogenic PAHs might be emitted from incomplete combustion reactions in both coal tar factories and biomass fuels. To demonstrate this, a study done in 2014 recruited 100 coal plant workers and 25 biomass farmers in Qujing, China. The levels of 10 mono-hydroxylated PAHs (OH-PAHs) in their urine were measured. These results showed that coal plant workers dealing directly with these products had up to 30 times more PAHs dissolved in urine than the limit recommended by the Environmental Protection Agency (EPA). Citizens from rural areas nearby also showed up to 5 times higher PAHs levels than the recommended limits. The 8-hydroxy-20-deoxyguanosine (8-OHdG) levels in the urine were also determined in biomass farmers, since 8-OHdG is one of the predominant forms of free radical-induced oxidative lesions, and has therefore been widely used as a biomarker for oxidative stress and carcinogenesis. It would serve to evaluate the oxidative DNA damage induced by the PAHs in biomass farmers. The results showed that these levels were up to 6 times higher than the average.[9]

Another study, also done in China, focused on the dermal absorption of PAHs during normal cooking activities, such as a barbeque. This study showed that light PAHs are more likely to be absorbed through the skin, while the heavy PAHs were inhaled. The highest concentration of all types of PAHs was in the cooked food. Air, food, and cotton clothing samples were analyzed. This study showed the presence of up to16 new different PAHs were found in high concentrations.[11]

3.1.3. Synthesis

It should be noted that PAH's are well not products of pyrolysis of organic matter. Specifically, heating generates free radicals, which can then combine to form polycyclic and aromatic molecule.[12]

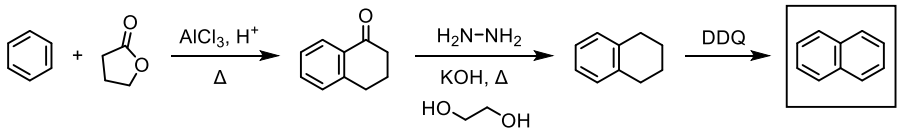


Scheme 1. Example of a detailed mechanism of the production of PAHs with heat. Molecules that keep reacting end up being heavy PAHs.[12]

In Scheme 1 there is a possible formation of some simple PAHs. Heating initiates the formation of a radical that can react with other molecules that have a π system and get bigger each time. It does not stop until there is a loss of another radical molecule. However, reactions via radical paths are very unpredictable, so other ways are applied in the laboratories to synthesize these products. The methods offer more control to obtain the desired products. The quickest and easiest way to obtain naphthalene -for example- it is via the dehydrogenation of tetralin using Pt and Al_2O_3.

But there are endless ways to do it in a more controlled way. To obtain this same naphthalene it is possible to use a Fidel-Krafts acylation between benzene and γ-butyrolactone in the presence of heat. With a later Wolff–Kishner reduction, the ketone group can be removed. A final treatment with an oxidant like 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or Pt / Al_2O_3 causes a

dehydrogenation reaction, resulting in the desired product.[13][14][15] Scheme 2 proposes a synthetic path.



Scheme 2. Possible path for the synthesis of naphthalene. γ-Butyrolactone and benzene are used as reagents, and undergo a Fidel-Krafts reaction. A posterior Wolff–Kishner reaction eliminates the ketone, and finally DDQ caused the dehydrogenation.[13][14][15]

3.1.4. Properties

As said in the beginning, PAHs are also good semi-conductors. The large number of π-systems helps delocalize electric charges, therefore being able to induce an electron flux. For the same reason they can absorb UV light and some heavy PAHs also absorb visible light. This offers them excellent optoelectronic qualities that have been studied for possible applications as organic electronic materials. For example, they are of great potential for the development of efficient devices (Organic Solar Cells (OSCs), Organic Light-Emitting Diodes (OLEDs), Organic Field-Effect Transistors (OFETs)) in the field of plastic electronics.[2] In Table 1 there are some potential data about certain PAHs.

Table 1. Some half-cell potentials of certain aromatic compounds against the saturated calomel electrode.[16] The heavier the molecule is, the lower potential it has. The more π-

Compound	Potential (V)
Benzene	-3.42
Naphthalene	-2.51
Anthracene	-1.96
Perylene	-1.67
Pentacene	-1.65

Another very important application they have is in asymmetric catalysis. Enantiomeric selection can be crucial since biological creatures have enzymes that specifically detect one certain order of atoms. For instance, racemic mixtures or the wrong enantiomeric form can develop into fatal effects on animal health. To solve this, scientists have been working in finding new pathways that provide only the desired form of the molecule.[17]

PAHs can help in certain reactions to assure the obtention of only one racemic form. For example, BINOL and BINAP, illustrated in Figure 3, are two synthetic molecules developed to exploit the axial dissymmetry induced by the restricted rotation about the biaryl bond.[1]

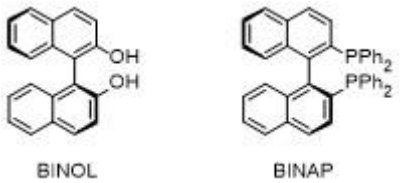


Figure 3. Molecular structure of BINOL and BINAP[1].

These two molecules work with processes such as Diels-Alder, Mukaiyama aldol, aldehyde allylation, hydrogenation, alkene isomerization, and Heck reaction.[1][17]

3.2. BORAZINES

3.2.1. Definition and origin

Borazine, shown in Figure 4, was discovered in 1926 by Alfred Stock and Erich Pohland when reacting diborane with ammonia.[18] Around 1940, Nils Wiberg proposed the alias of ‘‘inorganic benzol’’ for borazine since the B–N bond lengths are equivalent, which is the landmark of aromaticity for hydrocarbons, and because the number of π electrons is the same as in benzene. However, there is an electronegativity difference between boron and nitrogen, so the aromaticity may be expected to be lower in borazine than in benzene.[19]

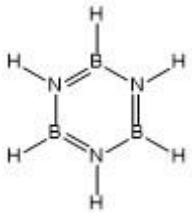
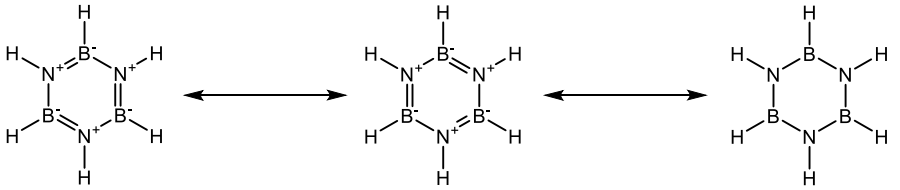


Figure 4. Molecular structure of borazine.

Borazine has a preference for addition reactions. It seems that although borazine can be bestowed with a certain aromatic properties explained in Scheme 3, its reaction behavior does not lead towards reassembling the p-ring system.[19]



Scheme 3. Resonance of borazine. The number of π electrons in borazine obeys the 4n+2 rule and the BN bond lengths are equal, meaning it is aromatic.[20]

3.2.2. Properties

Borazines of polynuclear aromatic hydrocarbons, such as borazaphenanthrene and their substituted derivatives, are used to modify the fluorescence properties of biological substrates. Due to its characteristics, it can also be used for the preparation of electroluminescent devices[21][22] like borazaphenanthrene, shown in Figure 5.

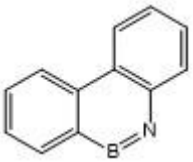
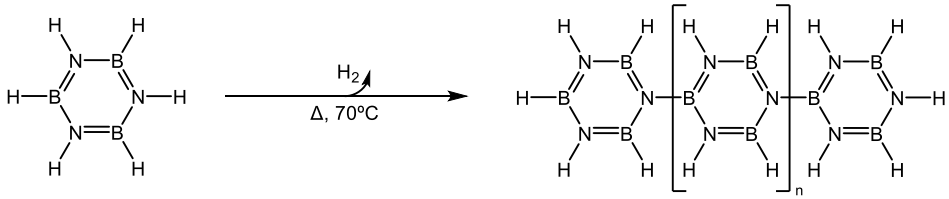


Figure 5. Molecular structure of borazaphenanthrene.

Borazine can also be used as a precursor to grow hexagonal boron nitride thin films and single layers on catalytic surfaces from many metals such as platinum via chemical vapor deposition. This plays an important role in nanotechnology.[23]

One derivate of borazine, polyborazylene, has been recently studied as a recycled hydrogen storage medium for hydrogen fuel cell vehicle applications, using a process in only one cell for digestion and reduction to recreate ammonia borane.[24] Its synthesis is simplified in Scheme 4.

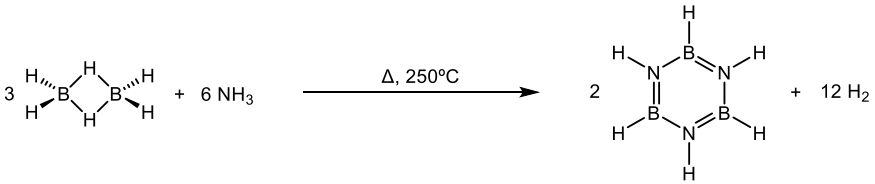


Scheme 4. Reaction of borazine with heat to release hydrogen and form polyborazylene.[25]

3.2.3. Synthesis

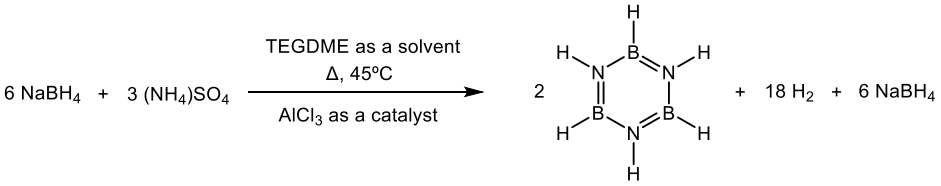
Borazine is very reactive to water, so the reactions must be done in a dry environment, with an inert atmosphere.

The first synthetic and easiest way, illustrated in Scheme 5, is still done in some laboratories via the reaction between diborane with ammonia.[18]



Scheme 5. Simplified reaction for the formation of borazine using diborane and ammonia as reagents.[18]

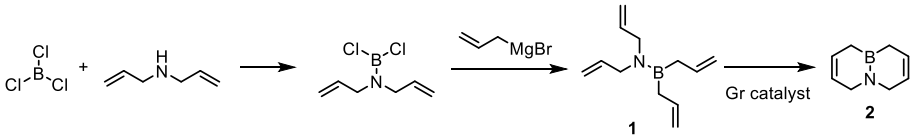
Although nowadays a more efficient reaction is used, using sodium borohydride and ammonium sulfate.[26][27] Scheme 6 shows it in a summed way.



Scheme 6. Simplified reaction for the formation of borazine using sodium borohydride and ammonium sulfate as reagents.[27]

3.3. PRECEDENTS IN THE FORMATION OF BN HEXAHYDRONAPHTHALENE AND BN NAPHTHALENE

The BN naphthalene was first prepared by Dewar et al. in 1964,[30] albeit in very yields. The target arene was obtained by dehydrogenating the saturated precursor BN hexahydronaphthalene over Pd/C at high temperatures. Thanks to newer advances and the recent metathesis of olefins, a new synthetic approach could be studied to obtain the same molecule with much higher yields.[29] In this case, the precursor BN hexahydronaphthalene was obtained by reacting boron trichloride and diallylamine, with a posterior Grignard reaction using allylbromide to obtain the BN tetraallyl, molecule **1**. Finally, using a Grubbs type I catalyst, the BN hexahydronaphthalene **2** is obtained via a metathesis of olefins. Scheme 7 summed the reaction.



Scheme 7. Simplified reaction for the formation of BN hexahydronaphthalene via the metathesis of olefins for the BN tetraallyl.

In a final dehydrogenation step, BN naphthalene, shown in Figure 6, can be obtained. The 4a,8a-azaboranaphthalene (BN naphthalene) has recently been used to build bigger aromatic systems, such as BN-doped perylenes, as well as a component in a light-emitting structure.[22]

While the olefin metathesis technique was a significant step forward, several issues remain unaddressed, the most significant of which is the inefficiency of the final aromatization process. Indeed, in cyclohexene, dehydrogenation of BN hexahydronaphthalene over Pd/C gives BN naphthalene in yields of less than 30%, and with a difficult-to-separate combination with BN-tetralin, the thermodynamically more stable isomer of BN naphthalene. The oxidative treatment of BN hexahydronaphthalene with DDQ is currently a widely utilized alternative to this method.[27]

The latter reaction, on the other hand, takes a whole week to complete and offers yields of a 17 percent of the desired 4a,8a-azaboranaphthalene.[28][29][31]

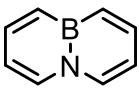


Figure 6. Molecular structure of BN naphthalene.

As it is clearly seen, these new methods still offer some problems, like the low yields to obtain BN naphthalene and the expensive cost of all the necessary reagents. Also, the reactions take quite some time and have to be prepared in different stages.

In order to overcome the problematic route to the tetra-allyl precursor **1**, we turned our attention to the chemistry of the rather simple but reactive organoborane, namely triallylboranes. Specifically, we wondered whether the reactivity of this species with amines, leading to the elimination of propene, could in fact be used to access species such as **1** in a more straightforward manner. Indeed, his reagent is easily produced and stored in large amounts, and its adducts with NH-containing amines can easily undergo a propenolysis upon heating. This would also mean that we do not need that many steps and time to get our desired product.

4. OBJECTIVES

When In this project there were two main objectives:

- To study a new synthetic way that can provide less steps in order to obtain the BN hexahydronaphthalene, and later purification to see its stability.
- To study the first synthetic way to produce a di-vinyl-BN-bicycle, reacting di-propargylamine and triallylborane, and a later metathesis of enynes with a Gr I catalyst.

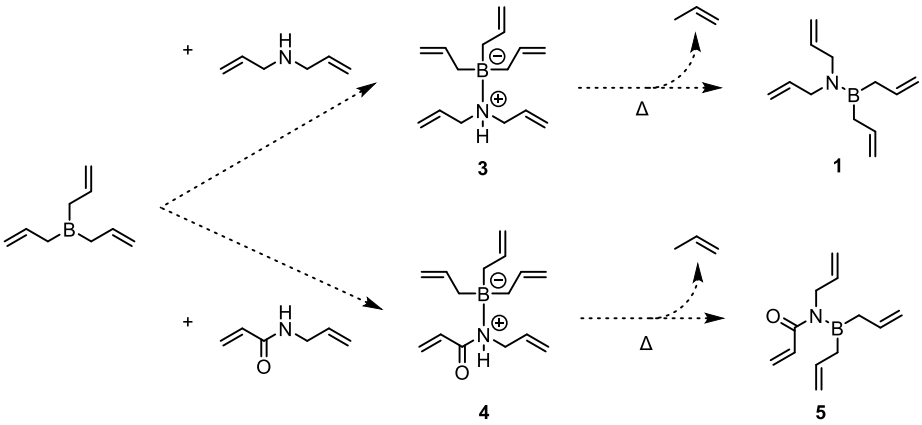
This last objective was not a planned from the beginning. It became a reality towards the end of the project, when observing that the reaction between the triallylborane and the dialylamine was a success.

The reaction shouldn't be taking place unless a compound containing two allylic groups was added, so the enyne metathesis could happen. However, every time we heated the adduct between the triallylborane and the dialylamine, some propene gas was released. So, a new question came, and that was if it could work without adding any diallylic compound.

5. RESULTS AND DISCUSSION

5.1. TRIALLYLBORANE

Following the outline of our objective, we envisage a synthetic process where the triallylborane reacts with an amine to produce the BN tetraallyl product. This reaction is initially expected to produce the B··N adduct **3** / **4**. After a heating process, this adduct could further evolve to the desired BN tetraallyl product **1** / **5** with loss of propene gas like in Scheme 8.



Scheme 8. Expected reaction of triallylborane with dialylamine and acrylamide, with a posterior heating process to conduct a propenolysis.

Following this outline, this work began with the synthesis of triallylborane. Based on the literature procedures,[35] this compound could be obtained via an in-situ Grignard reaction using allylbromide and magnesium in the presence of $BF_3 \cdot Et_2O$ under anhydrous and inert atmosphere conditions. After the reaction was complete, the remaining solvent (Et_2O) was distilled and the product was purified using vacuum distillation with rigorous exclusion of oxygen and moisture.

The first time we obtained the pure product, the reaction was done 50 mmol scale, obtaining approximately 5 mL of triallylborane. A ^{1}H NMR and a ^{11}B NMR were performed.

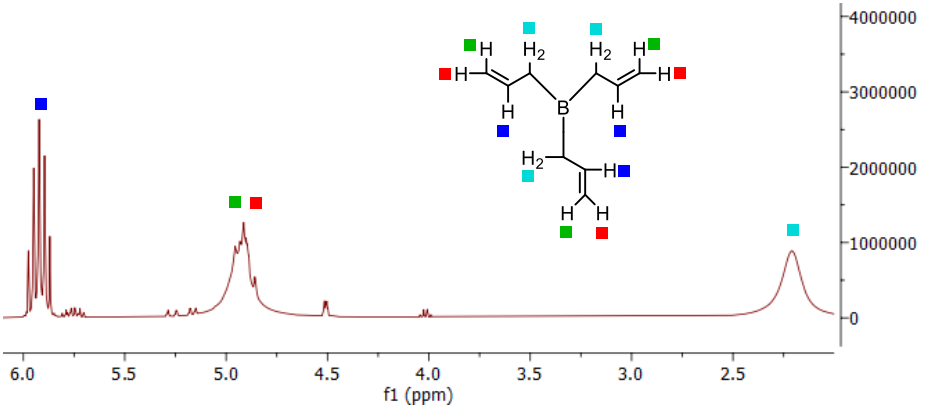


Figure 7. ^{1}H NMR obtained from the pure triallylborane. Some impurities were present as it is appreciable by the background noise.

The product was clearly appreciated, seen in Figure 7. The main multiplet peak at almost 6 ppms was the main indicator that triallylborane was formed. Also, the broad peak at around 5 ppms. These peaks indicate the olefins from our desired molecule. ^{11}B NMR was then studied.

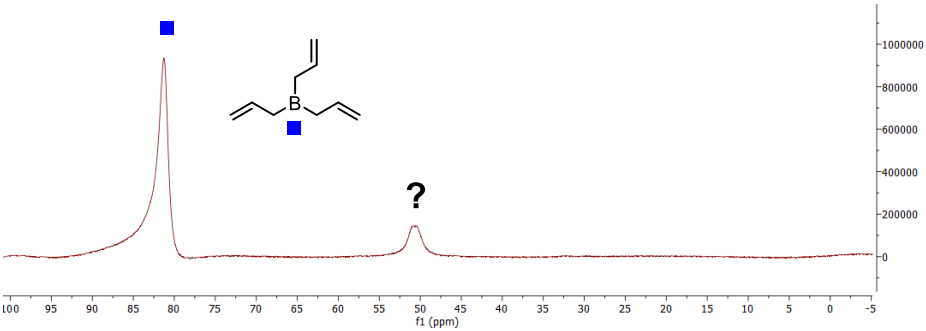


Figure 8. ^{11}B NMR obtained from the pure triallylborane. The blue dot indicates the peak corresponding to the boron from the triallylborane,[35] and the other peak was the main impurity.

Even though the reaction had been done with great care that no water or air got in contact with the reagents and products, some impurities appeared that were very clearly visible in the Figure 8. It was considered then that this impurity came from the NMR sample preparation. Most exactly, the water from our $CDCl_3$. A test adding water was performed to clear the doubts.

10 µL of water were added to the same NMR tube and a ^{1}H NMR and a ^{11}B NMR were performed and compared to the original ones.

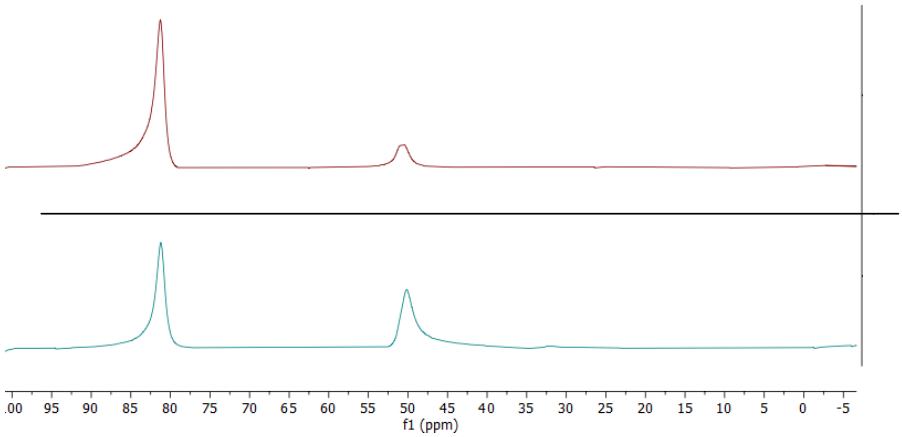


Figure 9. Comparative of the two ^{11}B NMRs. Above, the original triallylborane NMR after the distillation. Below, the NMR after the addition of water.

The test showed how the peak coming from triallylborane lost intensity, and the impurity peak grew, indicating the formation of a hydrolysis species. Since our product has three allyl groups, it can hydrolyze three times. We supposed a one-time hydrolyzation that, as mentioned before, came from our NMR preparation and not the product being impure. The increasing peak at 50 ppm should be the diallylboronic acid. A peak at around 30 ppm would indicate the allylboronic acid, from the loss of a second allyl group. A last peak at around 20 ppm would indicate the complete hydrolyzation of the molecule, and thus the formation of the boronic acid. Figure 10 shows all these compounds.

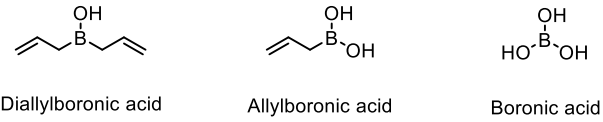
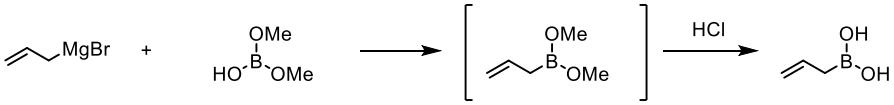


Figure 10. Molecular structures of the molecules that can be formed from the hydrolyzation of triallylborane.

The resulting solution was a colorless liquid. When trying to get rid of the excess solvent. After twelve minutes in it, the colorless solution turned yellow. After thirty minutes, there was almost no liquid present, only a few drops of a colorless oil and a white solid that had formed and stuck to the round bottom flask. ^{1}H and ^{11}B NMRs were performed on the oil drops but showed a mixture of different products, and allylboronic acid peaks were hard to identify. The most prominent peak was at M=238, being an unknown impurity. This appear to indicate that the allylboronic acid is more sensitive to moisture than expected.

The preparation of allylboronic acid was proposed following the method by Matthew N. Greyson.[33] It stated a Grignard reaction between allylmagnesium bromide and trimethyl borate, with a later treatment with hydrochloric acid as illustrated in Scheme 9.



Scheme 9. Simplified reaction between allylmagnesium bromide and trimethyl borate, with a final treatment with hydrochloric acid to obtain the allylboronic acid.

When most of the solvent was removed in the rotary evaporator, a yellow solution was obtained. It seemed that the product was very sensitive to the rotary evaporator, since getting rid of all the solvent ended up in the disappearance of the yellow color, and the obtention of a white solid and a colorless oil. A Gas Spectrometry coupled to Mass Spectrometry was performed. A peak at M=168 appeared, which corresponds to the allylboronic acid mass. ^{1}H and ^{11}B NMRs of the liquid and the white crystals was performed.

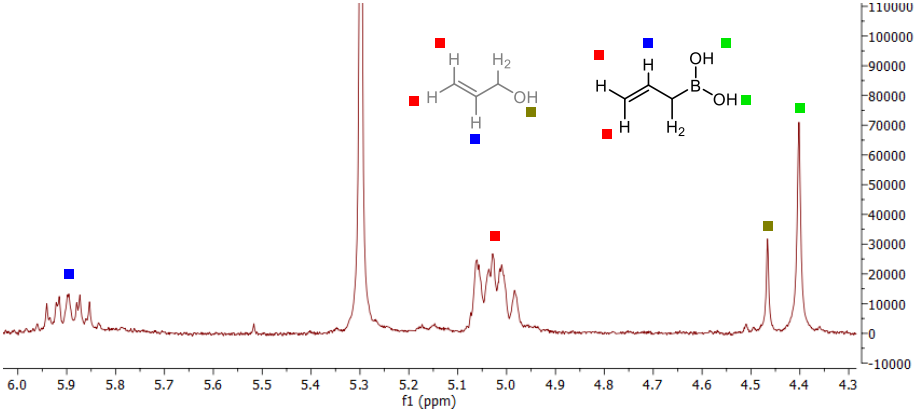


Figure 11. ^{1}H NMR of the allylboronic acid solution. The peak at 5.3 pm corresponds to dichloromethane solvent. The impurity allyl alcohol and allylboronic acid share very similar peaks and they overlap.

Allyl alcohol appeared as an impurity due to allylic groups hydrolyzing. Since they share very similar peaks, they overlapped and were very difficult to separate. Another problem was that the hydrogen peaks from $-CH_2-$ coupled to the boron and alcohol group could not be identified. Since they were other impurities present and still a lot of diethyl ether and dichloromethane solvent, they overlapped with the other peaks, being unrecognizable.

^{1}H NMR of the white hairy crystals was also performed. It showed no signs of an organic molecule, but indicated that the solid was boric acid. It only dissolved in deuterated water.

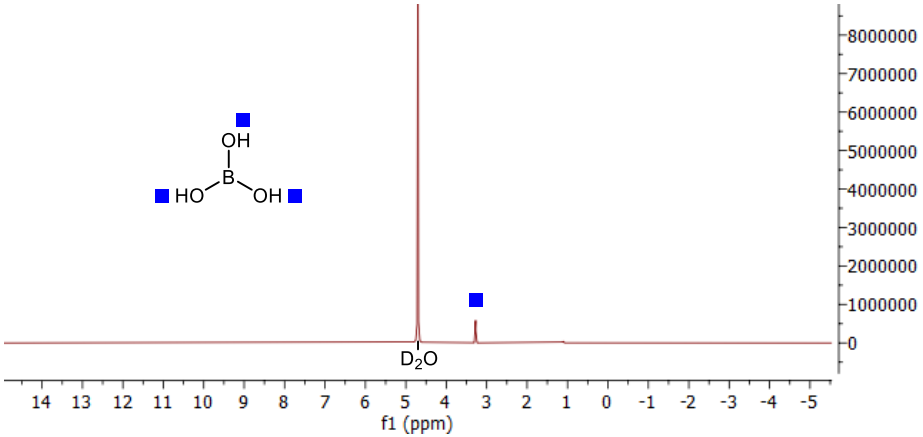


Figure 12. ^{1}H NMR of the white crystals. Peak at around 3.5 ppm indicated the presence of boronic acid.

The most important information came from the ^{11}B NMRs. Now knowing we have these two products, we have the ppm shifts from the boron in the allylboronic acid and the boronic acid. We can identify if the product of the hydrolyzation of triallylborane is allylboronic acid.

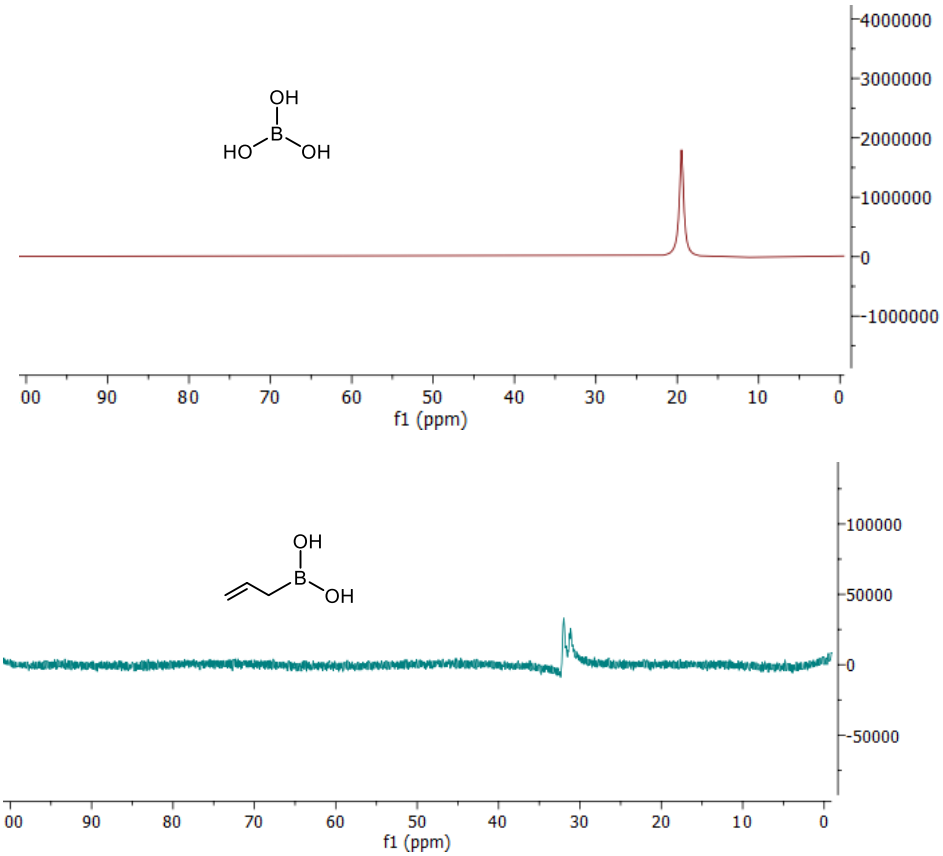
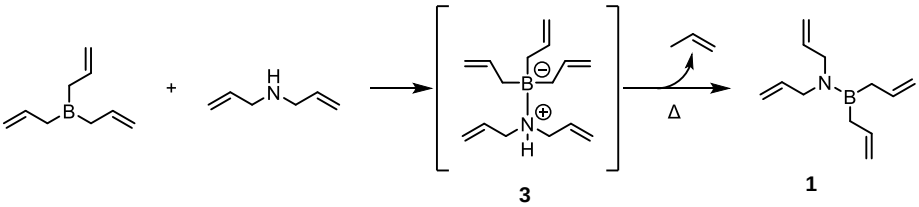


Figure 13. Comparative of the two ^{11}B NMRs. Above is the boric acid (obtained from the white solid) and below the allylboronic acid (obtained from the solution). They are in different intensities due to the quantity that formed.

Neither of these two products in Figure 13 match the peak in the ^{11}B spectra from the triallylborane at 50 ppm that grew when water was added. However, the growing peak is a direct result from the hydrolyzation of triallylborane. Knowing it can be hydrolyzed three times, and the ppms at which allylboronic acid and boric acid appear, it is safe to say that the impurity present in the triallylborane product is diallylboronic acid.

5.2. BN TETRAALLYL

With this question resolved, we could move on to the formation of BN tetraallyl. As stated earlier, the reaction between triallylborane and dialylamine was proposed as the synthetic way to form the adduct. A posterior heating process would be used to carry out the propenolysis (Scheme 10).



Scheme 10. Simplified reaction between triallylborane and diallylamine to produce the BN adduct, and later elimination of propene by heating at 40ºC.

Since we now knew that triallylborane was very sensitive to water, the reaction was carried out in a Schlenk flask, fresh out the oven, in an Ar atmosphere with three previous evacuate-refill cycles. As we did not quite know how the reaction would go, in the first test we reacted only 1 mmol of triallylborane with 1 mmol of dialylamine, each dissolved in 1 mL of anhydrous dichloromethane. The process was performed through a dropwise addition of the dialylamine in an ice bath. The adduct should form immediately but it was left stirring for an hour. After that time, a ^{1}H NMR was performed.

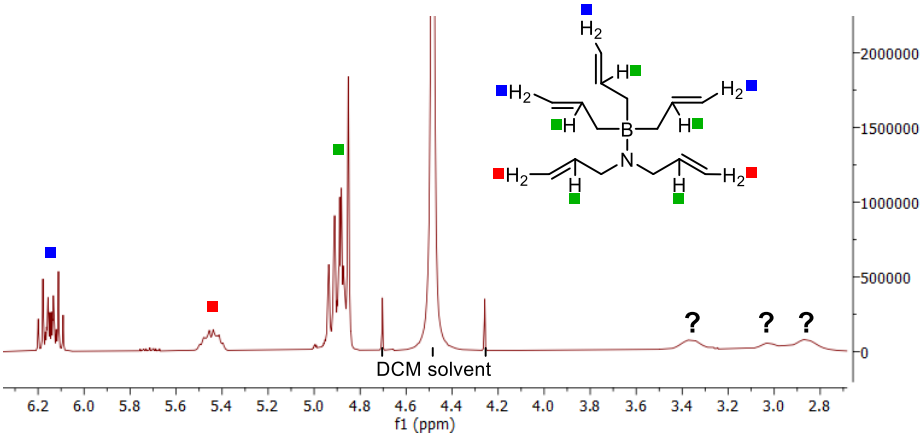


Figure 14. ^{1}H NMR of the adduct. Weak peaks marked at the right part of the spectra may be the BN tetraallyl forming.

This NMR showed signs of the reaction progressing towards another product, most likely the BN tetraallyl since with the adduct own heat when forming propenolysis could have started, so it would have been better to do an immediate NMR instead of waiting 1h.

Even though the results were not conclusive at all, the reaction was left stirring at 45ºC for two days. An NMR was performed 24 hours later but the peaks had not changed much. The Schlenk flask in which the reaction was taking place was sealed. Since we were working with such little quantiles, the propene formatting would not mean a problem in terms of pressure building up. For bigger quantities, it would be recommendable to open the Ar flux so gas can get out. Another NMR was performed 48h later.

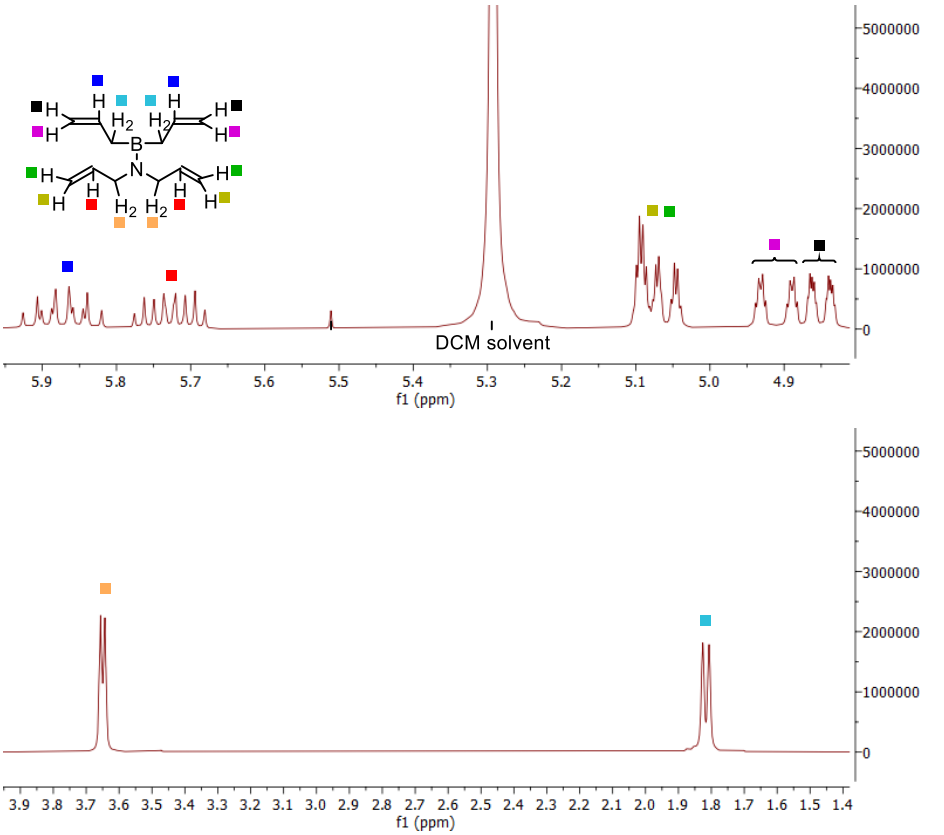


Figure 15. ^{1}H NMR of the BN tetraallyl. No impurities observed. dichloromethane was not evaporated at any moment.

As seen in Figure 15, the NMR shows a complete conversion to the target tetra-allyl product **1**. Since this experiment went so well, more were repeated but this time no dichloromethane was added and we worked with bigger quantities. 3 mmol of triallylborane were added directly to a bigger Schlenk flask, an ice bath was set, and 3 mmol of diallylamine were added dropwise. Conducting the experiment under solvent-free conditions allowed for the reaction time to be

shortened by raising the reaction temperature to 60ºC. When the temperature reached the desired 60ºC, ^{1}H NMR analyses were performed at 2, 4, 6, 8 and 24 hours.

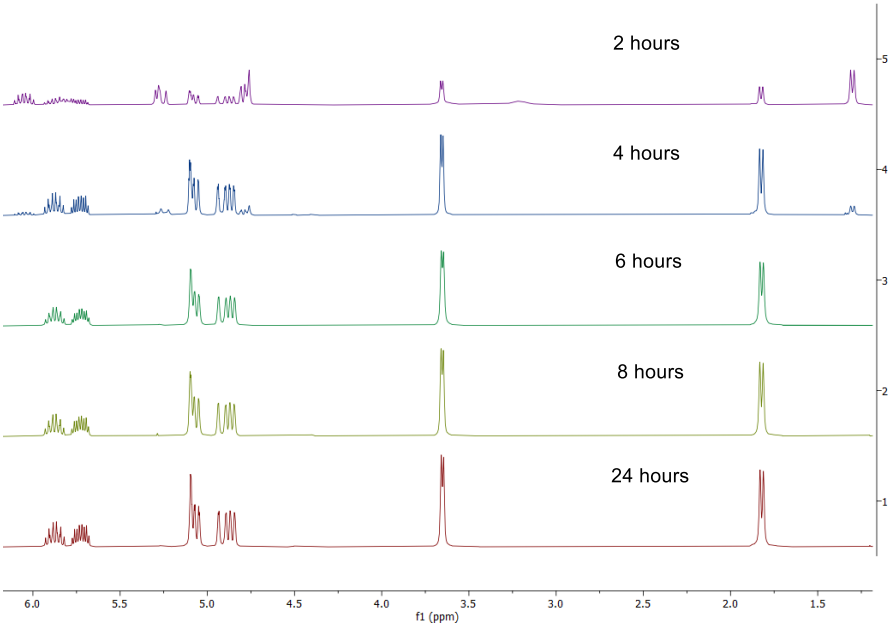


Figure 16. ^{1}H NMRs of the BN tetraallyl formation. From the top to the bottom: 2h, 4h, 6h, 8h, and 24h.

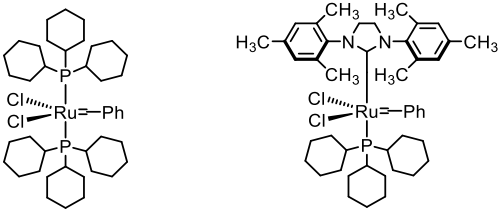
Indeed, while the 4h sample still contained small amounts of the B··N adduct, complete conversion was observed after 6h. At this stage, the 8h and 24h samples were measured so as to assess the thermal stability of the newly formed terra-allyl structure. There were no differences observed between the 6 and the 24 hours. Also, there were no impurities or remaining reagents. The reaction goes as good as the one with solvent. This type of reaction is better since in 6 hours we can get to our desired product instead of waiting two days. We also save solvent and the reaction gives a very high purity from what the NMR shows.

Figure 17. BN tetraallyl 24 hours later.

Figure 17 corresponds to a test performed in a scale of 8 mmol. It is the result obtained after 24 hours stirring at room temperature. The BN tetraallyl was obtained as a viscous clear liquid, with a colorless-to-light-yellow appearance.

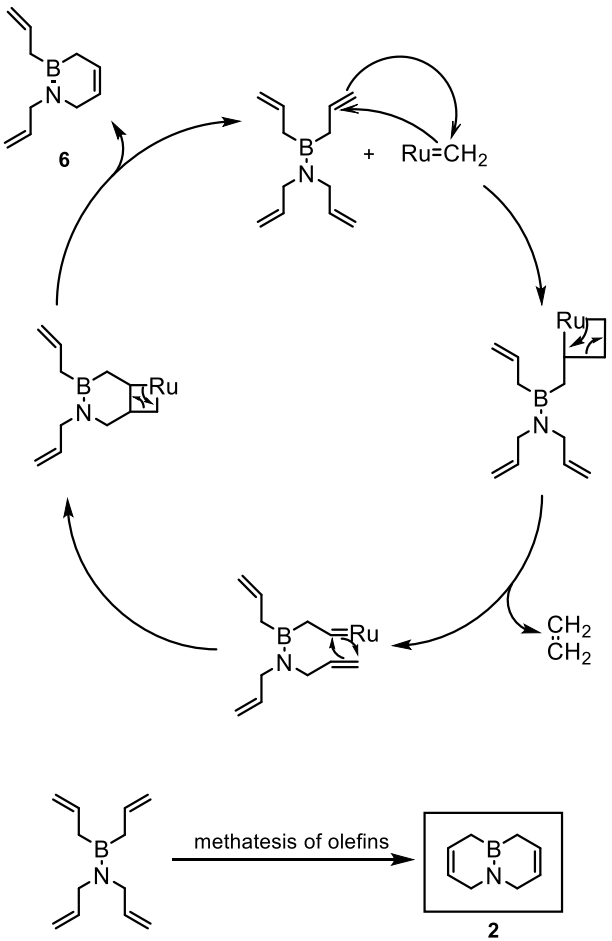
5.3. BN HEXAHYDRONAPHTHALENE

At this point the product was prepared to go through the metathesis of olefins. The reaction was proposed following Scheme 11. In this process, molecule **6** will be formed initially, next undergoing a second ring closure to give the desired bicyclic molecule **2**, BN hexahydronaphthalene. For this reaction we used the Grubbs type II catalyst, Due to the initial availability in the laboratory. Also, Grubbs I type catalyst would be used later. Figure 18 shows both catalysts.



Grubbs I Grubbs II

Figure 18. Molecular structure of Grubbs type II and I catalyst.



Scheme 11. Mechanism of the metathesis of olefins with our BN tetraallyl product. This reaction goes on until it reaches the most stable form, molecule **2**.

It should be noted that while the earlier reported synthesis of **1** required a prior distillation of the compound,[28][29] the propenolysis route appears to provide directly the desired molecule in pure form. Excitingly, this opens the door to using the liquid obtained after the propenolysis step in the following metathesis reaction. The initial test was performed using a 2 mol% loading of the Grubbs type II catalyst on a 2 mmol scale in 1 mL of anhydrous dichloromethane. The reaction

was left 24 hours at room temperature with constant stirring; an ^{1}H NMR analysis was performed after that time. To our delight, this analysis conformed a complete conversion of the open-chain tetra-allylic precursor to the target bicycle **2**.

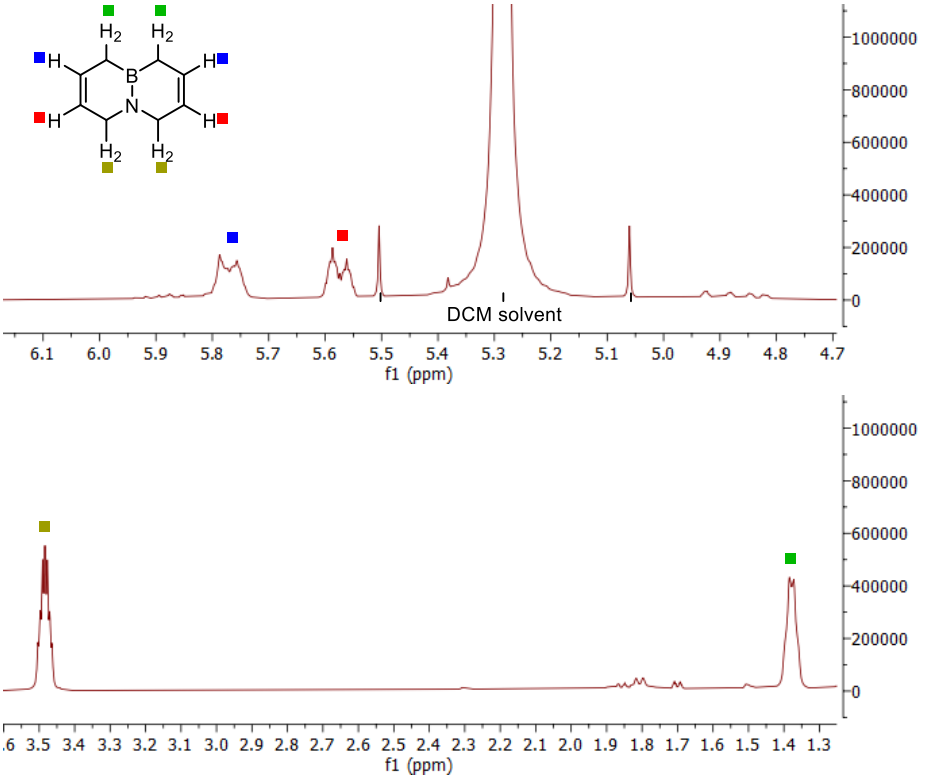
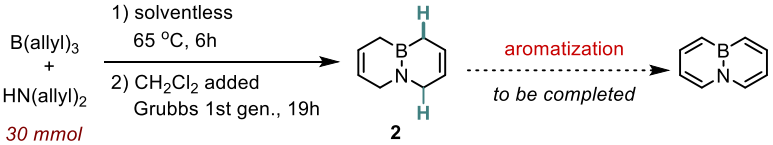


Figure 19. ^{1}H NMR of the BN hexahydronaphthalene after 24h stirring at room temperature with Grubbs type II catalyst.

Next, the experiment was repeated using Grubbs type I catalyst. This time, upon addition of the catalyst a subtle bubbling occurred, suggesting a faster metathesis reaction and a more intense ethylene gas evolution. After 24h an NMR was performed showing, once again, complete formation of the bicyclic target.

The overall study indicates that a) the formation of the bicyclic precursor can be telescoped thanks to the clean formation of the initial tetra-allyl BN precursor, and b) the Grubbs I catalyst provides faster reaction rates in the metathesis step. The overall process beginning with triallylborane can now be completed in a 30-hour span, including a 6h propenolysis step and 24h metathesis step.

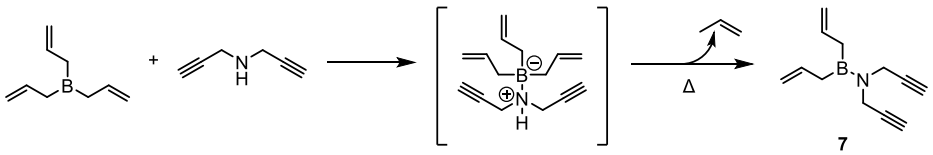
Due to lack of time the resulting desired product could not be purified via distillation. If we could have done so, a Kugelrohr would have been used since it distills via a short-path distillation small quantities of substances with high boiling points. At this stage, the only step left would be the final aromatization, which has already been developed in the lab during the TFM stage of Federica Rulli (IQS). This project is currently being continued by Guillem Sanz (TFM, UB), who will complete the integration of the entire process (Scheme 12).



Scheme 12. The overall new strategy leading to the BN-naphthalene target. The aromatization part would be the next step in the investigation

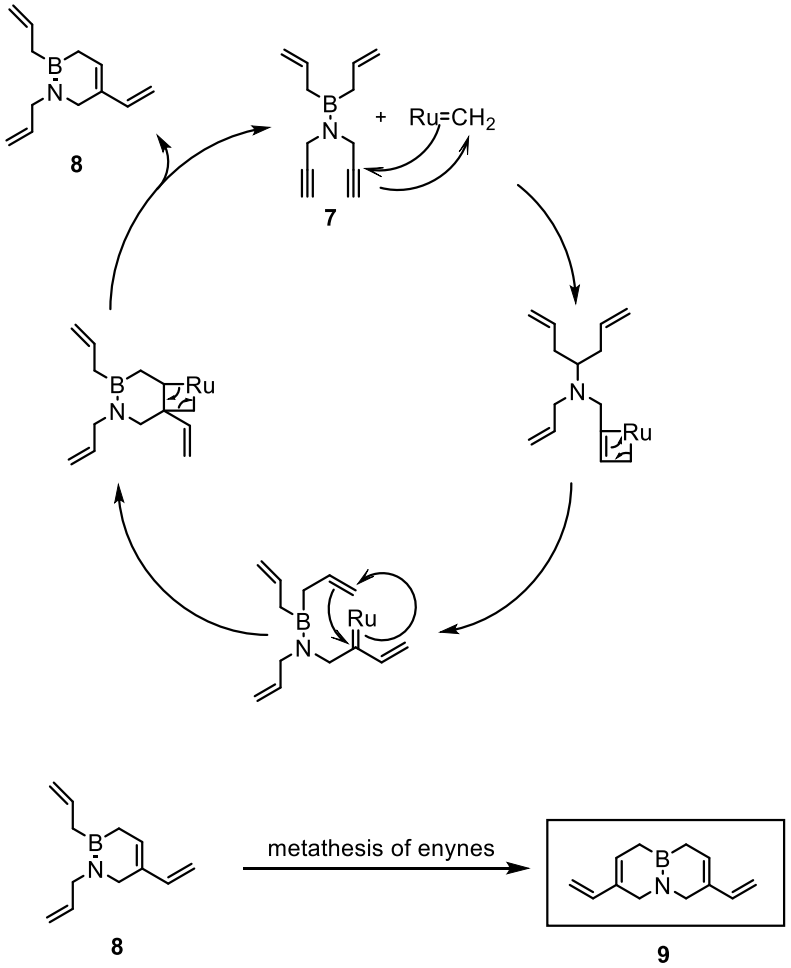
5.3. ACCESS TO THE BN-DOPED ARENE PRECURSORS VIA ENYNE METATHESIS

Another objective was the production of a di-vinyl-BN-bicycle following a procedure similar to the one used in the preparation of BN hexahydronaphthalene, but employing this time enyne metathesis approach. This time, Grubs type I catalyst would be used. First, we needed to make sure the reaction between triallylborane and di-propargylamine took place to form the BN diallyl-dipropargyl **7** (Scheme 13).



Scheme 13. Simplified reaction between triallylborane and di-propargylamine solvent-free, to produce the BN adduct, and later elimination of propene by heating at 60ºC.

After that, with a metathesis of enynes we could get to the desired product **9** (Scheme 14). The main challenge here is that is possible that the metathesis does not work without ethylene present. This happens due to the Ruthenium catalyst coupling first to the enyne group, and coupling again to another one. This deactivates the Grubbs catalyst and stops the reaction. The key benefit of ethylene lies in its capacity to suppress the uptake of a second enyne unit, and stopping catalyst deactivation, since the catalyst has a higher affinity for it.[32]



Scheme 14. Mechanism of the metathesis of enynes with our BN diallyl-dipropargyl product. This reaction is expected to give us our desired final di-vinyl-BN-bicycle, molecule **9**.

2 mmols of triallylborane and di-propargylamine were used for the test. As said in the beginning, same conditions and techniques used for the BN hexahydronaphthalene. A ^{1}H NMR was performed 24h later.

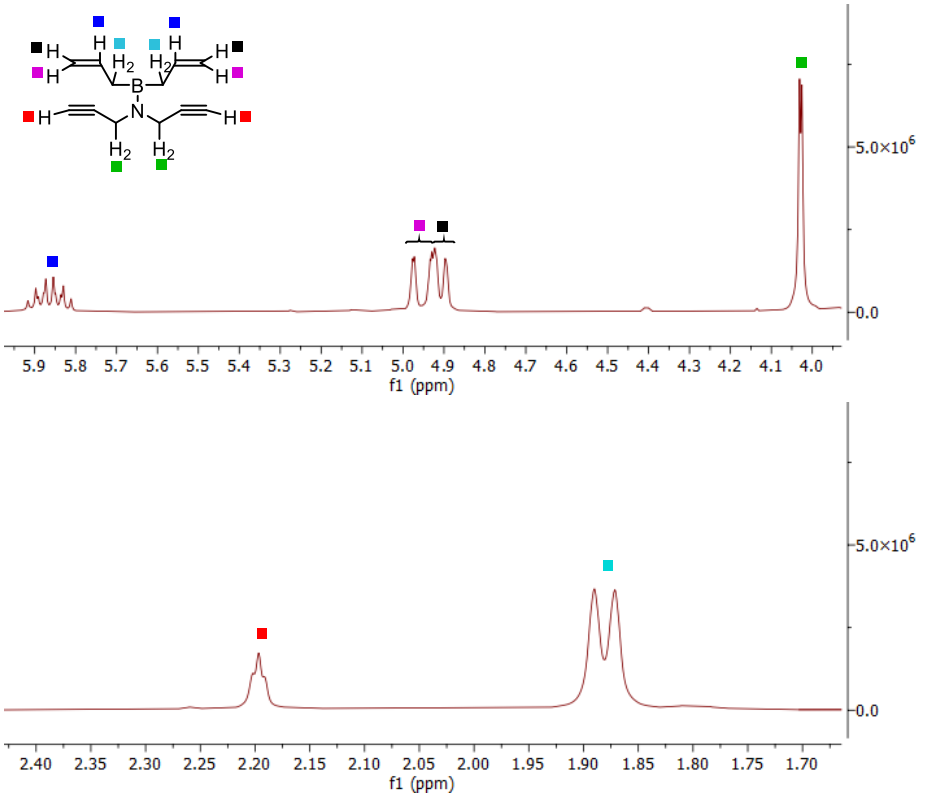


Figure 20. ^{1}H NMR of the BN diallyl-dipropargyl 24h after continuous stirring at room temperature.

The product came very clean, with no impurities whatsoever. Again, just like it was done with the BN tetraallyl, 2% mmol of Grubbs type I catalyst were added dissolved in 1 mL of anhydrous dichloromethane. The reaction was left stirring at room temperature for 4 days.

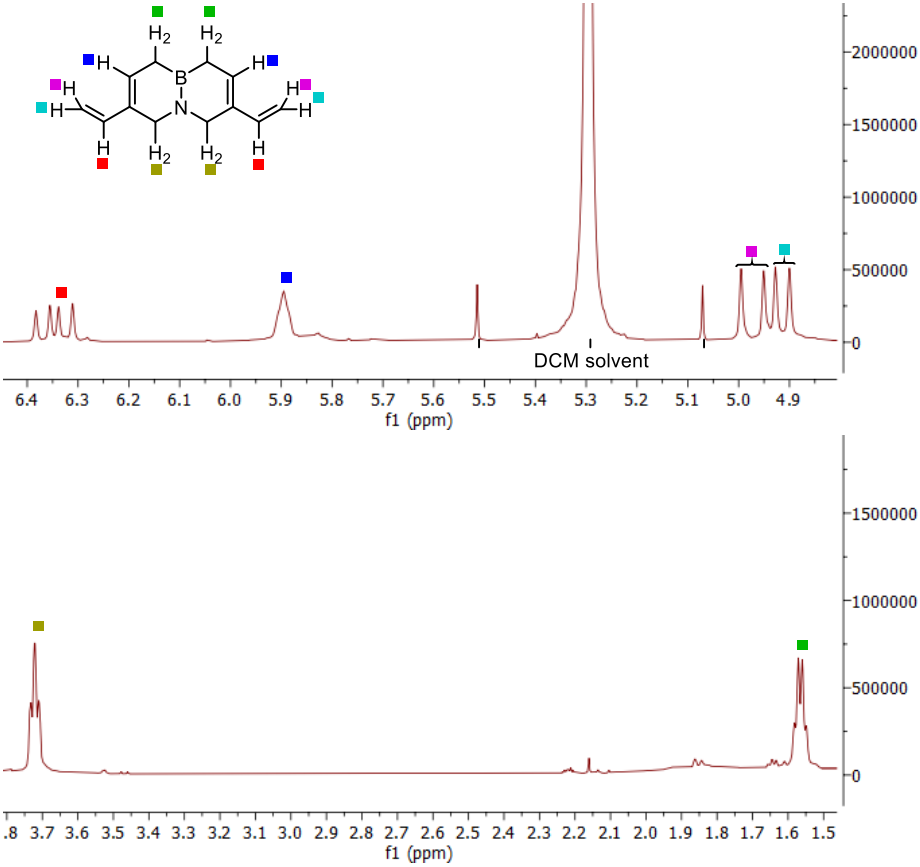


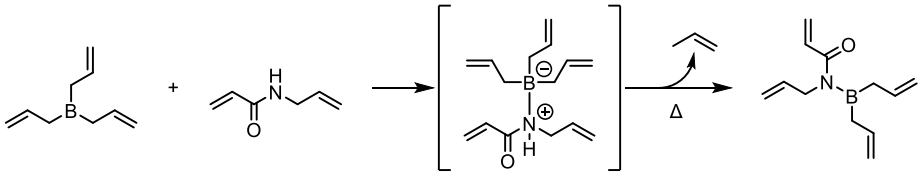
Figure 21. ^{1}H NMR of the di-vinyl-BN-bicycle after continuous stirring at room temperature for 96 hours.

To our delight, the NMR analysis of the resulting reaction mixture confirmed a rather clean formation of the desired bis-enyne BN system. Unfortunately, once again due to a lack of time it could not be purified to do further studies, or try other conditions like constant Ar flux instead of being sealed while reacting. Nevertheless, this result opened the door to a recent TFM project

(Guillem Sanz) who showed that the new divinyl species undergoes Diels-Alder reaction, thus opening the door to the formation of larger BN-doped heteroaromatics.

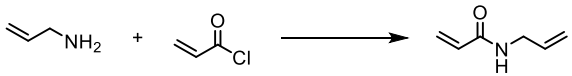
5.4. ALLYLACRYLAMIDE

This process was proposed in case the metathesis of olefins worked out. When we confirmed it was successful, we were very short of time. Nevertheless, we followed the literature[34] way to synthesize it and see if we could try at least one experiment between the allylacrylamide and the triallylborane, described in Scheme 15.



Scheme 15. Simplified reaction between triallylborane and allylacrylamide to first produce the BN adduct, and later elimination of propene by heating.

The reaction between allylamine and 2-propenoyl chloride should give allylacrylamide, like shown in Scheme 16.



Scheme 16. Simplified reaction between allylamine and 2-propenoyl chloride to obtain allylacrylamide.

It was treated with potassium carbonate to eliminate any hydrochloric acid that could have formed. Once dried, some tests were performed to see what solvent mixture was the best for extracting it in a column chromatography. Pure ethyl acetate gave the best (R_f = 0.06).

However, a fractionated column chromatography was selected as the extraction method. First a 4:1 hexane / ethyl acetate mixture was used. Then a 2:1, a 1:1 and finally pure ethyl acetate. Fractions 7 to 12 were selected and excess solvent was eliminated via rotary evaporator. It is

better to analyze allylacrylamide as soon as possible since it tends to polymerize. A ^{1}H NMR was performed right after the solvent was fully eliminated.

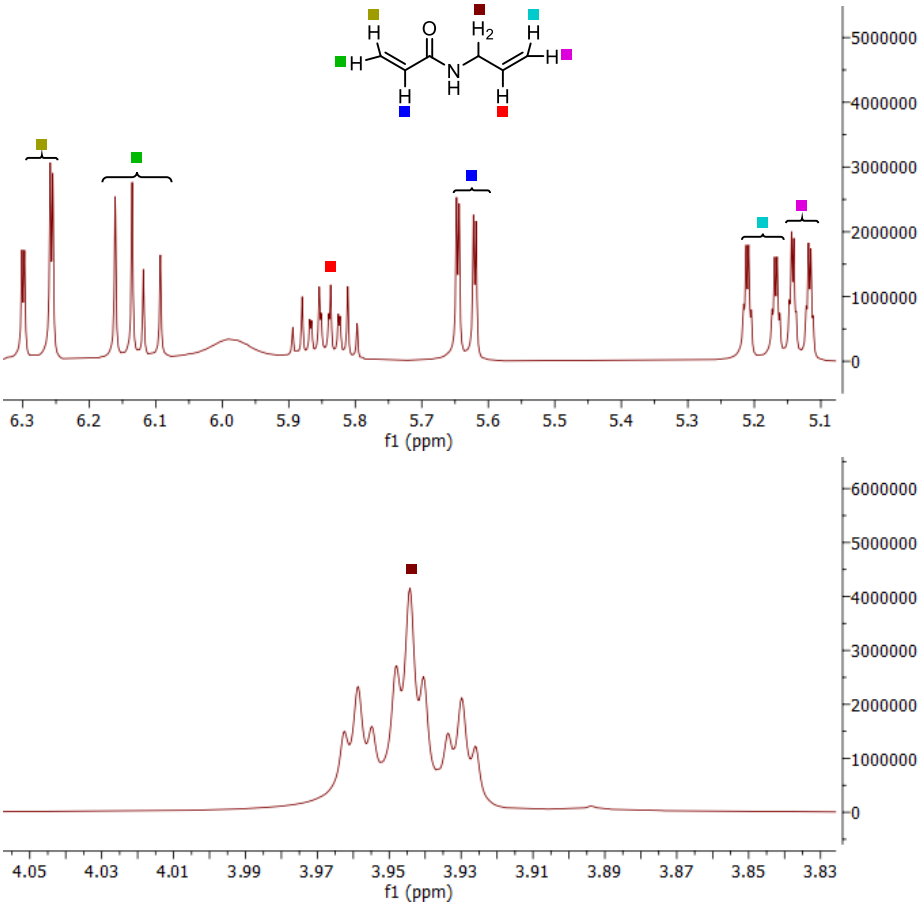


Figure 22. ^{1}H NMR of the purified allylacrylamide. Spectra came out with no impurities whatsoever. Weak but broad peak at approximately 6 ppm may be the hydrogen coupled to the nitrogen.

The product was obtained with a high purity, but there was still ethyl acetate present. Unfortunately, in the end it was not possible to try the BN formation since there was no more time available.

6. CONCLUSIONS

Seeing our results, we can conclude that we were able to accomplish our objectives partially. We could obtain our two products, but due to lack of time we could not practice more tests to them to study other proprieties.

For the BN hexahydronaphthalene, we can say that the proposed synthetic way between triallylborane and diallylamine works, but we cannot assure if the reaction is going to work only if the flask in which it is taking place is sealed. In our case, the reaction may have worked since there was enough space for all the propene and ethylene to be kicked out of the solution. But at the same time, we do not know what would happen if the Ar flux was constantly flushing. The reaction should work fine but it would be interesting to study it with and without being sealed, and see what differences in the products appear. Also, it would be a great study to use allylacrylamide instead of diallylamine.

For the di-vinyl-BN-bicycle, we can say that the reaction is successful, but very vague conclusions can be extracted. It is necessary to do more tests, see if all give the same results, and also repeat the sealing versus Ar flux experiments that should be done to the BN hexahydronaphthalene. Maybe using an ethylene source to study how the metathesis of enynes changes could also be interesting. Nevertheless, it is an important success .

7. EXPERIMENTAL SECTION

7.1. MATERIALS AND METHODS

Reagents: All commercially acquired reagents were used as received unless indicated otherwise.

Reaction conditions: All reactions requiring inert atmosphere were conducted under Ar using standard Schlenk line techniques, normally by applying 3 evacuate-refill cycles with argon. All glassware was previously dried in the oven overnight at 120ºC. When indicated, reactions were conducted in septum-sealed screw-top tubes so that the Ar atmosphere could be created by applying evacuate-refill cycles via a needle coupled to the Schlenk line. All other reactions were performed employing standard organic synthesis protocols.

Chromatography: TLC was performed using Merck aluminum-backed and plastic-backed plates of TLC Silica gel. The plates were revealed using UV light at 254 nm or by staining using potassium permanganate. Standard Flash Column chromatography was accomplished using silica gel (60 Å pore size, 230-400 μm mesh size).

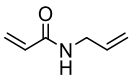
Gas Spectrometry coupled to Mass Spectrometry: Analyses were carried out at the IQAC Mass Spectrometry Facility, using a Thermo Scientific Trace 1310 Gas Chromatograph equipped with MS/MS Q Exactive GC Orbitrap.

Nuclear Magnetic Resonance: Spectroscopic experiments for the characterization of compounds were carried out at the *Servicio de Resonancia Magnética Nuclear* of the IQAC-CSIC on a Bruker Ascend 400 MHz (9.4 T field strength) with a room-temperature iProbe probe and SampleXPress 60-charger. The ^{1}H chemical shifts (δ) are quoted in parts per million (ppm) and referenced to the appropriate NMR solvent peak(s), which for ^{1}H measurements correspond to the residual protio component of the deuterated solvent. The ^{11}B chemical shifts are quoted with respect to $BF_3 \cdot OEt_2$ (0.00 ppm) and were not performed in quartz tubes, but in boron-glass tubes, meaning some background noise can be observed. Spin-spin coupling constants (J) are reported in Hertz (Hz).

7.2. SYNTHETIC PROCEDURES

7.2.1. Synthesis of 2-propenamide, N-2-propen-1-yl-, homopolymer[34]

Allylamine (1.7 mL, 21.7 mmol) was dissolved in anhydrous dichloromethane (5.0 mL) in a 25 mL round bottom flask. In another 25 mL flask, the 2-propenoyl chloride (3.7 mL, 45 mmol) was dissolved in anhydrous dichloromethane (10 mL), and the resulting solution was left in an ice bath for 10 min. The allylamine solution was then added dropwise, and the reaction was left stirring in the ice bath for 30 min, and then for additional 30 min at room temperature. Next, in a separatory funnel, the resulting solution was treated with 50 mL of a saturated potassium carbonate solution, and later with 50 mL brine solution. The organic layer was recovered and the excess solvent evaporated with a rotary evaporator. The resulting oily residue was analyzed by TLC on silica gel eluting with ethyl acetate (Rf = 0.6). The product was then purified via column chromatography employing the gradient 4:1 hexane/ethyl acetate → 2:1 hexane/ethyl acetate → ethyl acetate 99%. Fractions from seven to twelve were selected and the solvent was eliminated in the rotary evaporator. Pure allyl acrylamide was thus obtained as colorless oil (2.07 g, 86% yield)



Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.28 (dd, *J* = 17.0, 1.6 Hz, 1H), 6.13 (dd, , *J* = 17.0, 10.2 Hz, 1H), 5.85 (s, br, 1H, *N*H), 5.9-5.78 (m, 1H), 5.63 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.19 (app dq, *J* = 17.2, 1.6 Hz. 1H), 5.13 (app dq, *J* = 10.3, 1.4 Hz, 1H), 3.94 (app tt, , *J* = 5.8, 1.6 Hz, 2H).

7.2.2. Synthesis of tri-2-propen-1-ylborane[35]

Magnesium turnings (9.73 g, 400 mmol) were added to a 1 L three neck round bottom flask along with a stir bar. The flask was then equipped with a glass stopper, a septum and a reflux condenser connected to a Schlenk line. The following image (Figure 23) shows the initial setup.

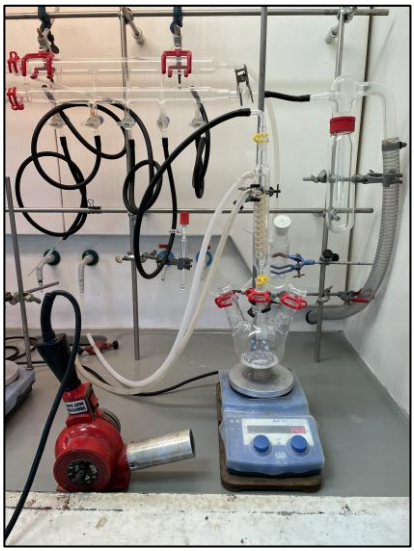


Figure 23. Initial setup for the triallylborane synthesis

The magnesium turnings were heated with a heat gun for 15 min to activate them and help dry the system, while it was connected to the vacuum. Once the system reached again room temperature, anhydrous diethyl ether (300 mL) was added, along with the boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$, 12.4 mL, 100 mmol). Once the addition was complete, the allylbromide (26 mL, 300 mmol) was added dropwise, making sure the Grignard reaction had initiated and kept going, while maintaining a gentle reflux. After 3h, the addition was complete and the reaction was left stirring at room temperature for 12h. The resulting solution was trespassed in ~100 mL portions to a clean 250 mL flask connected to a simple distillation system, previously dried and flushed with Ar using 3 evacuate-refill cycles. A water bath was set at 45ºC to distill off the ether with constant Ar flux. At the end of the distillation system, another dried 250 mL flask was connected to collect the solvent. When almost all the ether was distilled, another ~100 mL of the solution were added. When the flask containing the distilled ether was full, it was emptied in a residue container and connected again. This process was repeated until all the solvent was distilled. The remaining salts in the 1 L flask were washed with anhydrous diethyl ether (2 x 80 mL). Each washing was distilled adding one at a time to the system. The resulting solution was trespassed to a 100 mL flask dried and flushed with Ar using 3 evacuate-refill cycles. In the same

distillation system, now a 2-neck adaptor with a 25 mL flask and a 100 mL Schlenk flask was connected at the end. A vacuum / Ar purge was done 3 times. The 100 mL flask containing crude triallylborane was connected to the system, and a water bath was set at 50ºC. Aluminum foil was wrapped around to help maintain the temperature. An ice bath was set to the Schlenk flask to help condensation. The following Figure 24 shows the distillation setup.

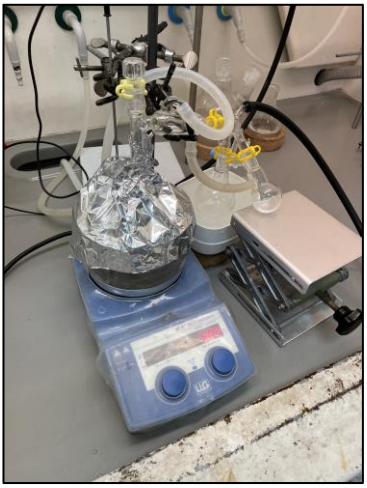
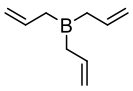


Figure 24. System setup to distill the triallylborane.

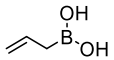
The pressure was brought down slowly to 7 mBar. Once it reached that temperature, the first two drops were collected in the 25 mL flask and discarded. Everything else was collected in the Schlenk flask. The temperature was brought up to 65ºC to help distill as much product as possible. After 20 min at that temperature, nothing more came off and the distillation was stopped. Pure triallylborane was thus obtained as a colorless liquid (7,72 g, 58% yield). Since the product is so sensitive to water, an NMR tube was left in the oven for an hour. Then, a needle connected to the Ar flow was introduced inside the tube. Triallylborane was measured with a 1 mL syringe, picking up a very little quantity, below the 0,1 mL mark. It was then added to the NMR tube. $CDCl_3$ (0.7 mL approximately) was added taking care that it dissolved all the triallylborane. The NMR cap was connected making sure no air got inside.



Colorless liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.98-5.86 (app dt, *J* = 21.3, 10.5 Hz, 3H), 5.13-4.65 (m, 6H), 2.21 (s, br, 6H). No ^{13}C spectrum could be collected due to the instability of the compound. ^{11}B NMR ($CDCl_3$, 400 MHz): δ 81.26 (s, br, 1B)

7.2.3. B-2-Propen-1-ylboronic acid[33]

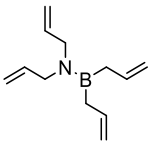
A 100 mL Schlenk flask dried in the oven was filled with Ar after three evacuate-refill cycles. It was then introduced in a Dewar with dry ice and acetone at -78ºC. Anhydrous diethyl ether (9 mL) were introduced and let to reach the temperature. Trimethylborane (1.5 mL, 13 mmol) were dissolved in 9 mL of anhydrous ether in an Ar filled flask. The solution was trespassed to the Schlenk flask and it was let to reach the temperature. Allylmagnesium bromide (11.5 mL, 11.6 mmol) were added dropwise and the solution was left stirring at -78ºC for 3h. After that time, an ice bath was set. A 2M solution of hydrochloric acid was set to 0ºC and it was added to the stirring reaction. Then, 1h at room temperature. The resulting solution was extracted 3x15 mL with a 5:1 diethyl ether / dichloromethane solution, and dried with magnesium sulfate. After filtering, the solution was set in the rotary evaporator without removal of all the solvent. The resulting solution had a strong yellow color that after a day in the fridge turned a light-yellow.



Light-yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.96-5.82 (m, 1H), 5.08-4.47 (m, 2H), 4.40 (s, 2H), 1.75 (app d, *J* = 22.9 Hz, 2H).

7.2.4. N,N,1,1-Tetra-2-propen-1-ylboranamine

A Schlenk flask, previously dried in the oven, was connected to an Ar flux after three evacuate-refill cycles. Triallylborane (0.37 mL, 2 mmol) was added to the flask, making sure the Ar flux was strong enough so no moisture got in. An ice bath was set and the triallylborane was let to cool down for 10 minutes. Diallylamine (0.25 mL, 2 mmol) were measured and added dropwise to the triallylborane with continuous strong stirring. The ice bath was changed after 5 min for an oil bath. The temperature was set to 60ºC and the solution was left stirring for 24h. BN tetraallyl came out as a light-yellow viscous liquid.



Light-yellow viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.96-5.82 (m, 2H), 5.80-5.68 (m, 2H), 5.14-5.04 (m, 4H), 4.93 (app dq, *J* = 17.0, 1.8 Hz, 2H), 4.87 (app dd, *J* = 10.0, 2.4 Hz, 2H), 3.67 (d, *J* = 5.3 Hz, 4H), 1.84 (d, *J* = 7.8 Hz, 4H).

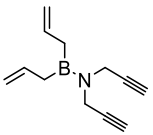
7.2.5. 1,4,6,9-Tetrahydro[1,2]azaborino[1,2-a][1,2]azaborine

Grubbs I type catalyst (33 mg, 2% mmol = 0.04 mmol) were added in a sealed septum sealed tub. Three evacuate-refill cycles were performed, and a constant Ar flux was set. Anhydrous dichloromethane (1 mL) was measured and added to the tube. The catalyst immediately dissolved, and was added to the same Schlenk flask containing the BN tetraallyl. It was left at room temperature 24 h, with constant stirring.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.85-5.74 (m, 2H), 5.80-5.68 (m, 2H), 5.63-5.55 (m, 2H),), 3.53-3.47 (m, 4H), 1.40 (app dd, *J* = 5.7 Hz, 4H).

7.2.6. BN diallyl-dipropargyl

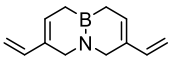
A Schlenk flask, previously dried in the oven, was connected to an Ar flux after three evacuate-refill cycles. Triallylborane (0.37 mL, 2 mmol) was added to the flask, making sure the Ar flux was strong enough so no moisture got in. An ice bath was set and the triallylborane was let to cool down for 10 minutes. Di-propargylamine (0.21 mL, 2 mmol) were measured and added dropwise to the triallylborane with continuous strong stirring. The ice bath was changed after 5 min for an oil bath. The temperature was set to 60ºC and the solution was left stirring for 24h. BN diallyl-dipropargyl came out as a garnet viscous liquid.



Garnet viscous liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.93-5.80 (m, 2H), 5.00-4.87 (m, 4H), 4.03 (d, *J* = 2.4 Hz, 4H), 2.19 (app t, *J* = 2.4 Hz, 2H), 1.88 (d, *J* = 7.6 Hz, 4H).

7.2.7. Di-vinyl-BN-bicycle

Grubbs I type catalyst (33 mg, 2% mmol = 0.04 mmol) were added in a sealed septum sealed tub. Three evacuate-refill cycles were performed, and a constant Ar flux was set. Anhydrous dichloromethane (1 mL) was measured and added to the tube. The catalyst immediately dissolved, and was added to the same Schlenk flask containing the BN diallyl-dipropargyl. It was left at room temperature 96 h, with constant stirring.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.35 (dd, *J* = 17.8, 11.0, 2H), 5.89 (app s, br, 2H), 4.97 (d, *J* = 17.8, 2H),), 4.91 (d, *J* = 11.0, 2H), 3.72 (app t, *J* = 4.8 Hz, 4H), 1.57 (app q, *J* = 4.7 Hz, 4H).

8. REFERENCES AND NOTES

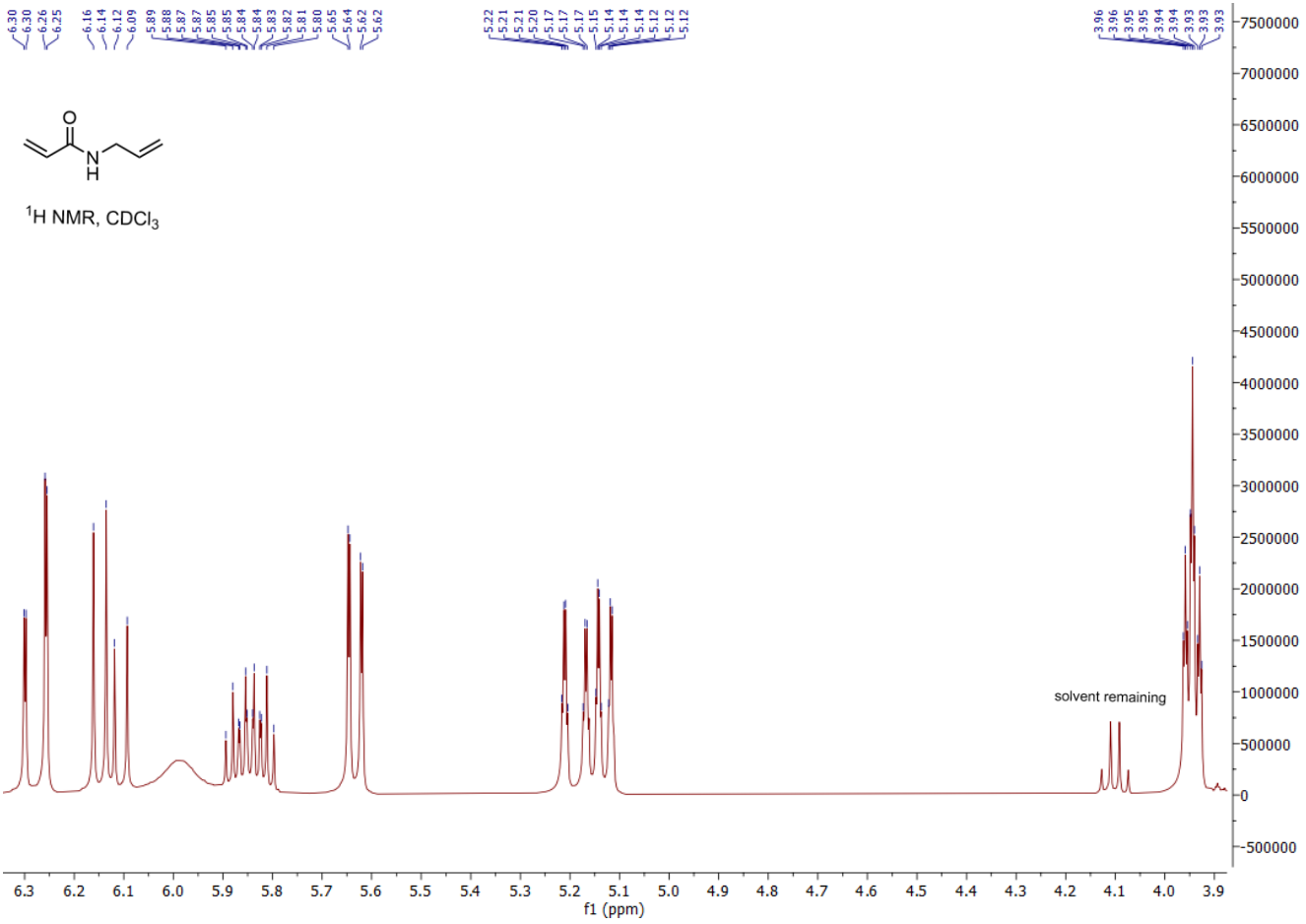
1. Yoon, T. P.; Jacobsen, E. N., *Science,* **2003,** *299,* 1691-1693.
2. Forrest, S. R.; Thompson, M. E., *Chem. Rev.,* **2007,** *107,* 923.
3. Luch, A., The Carcinogenic Effects of Polycyclic Aromatic Hydrocarbons; *Imperial College Press: London,* 2005.
4. Bosdet, M. J. D.; Piers, W. E., *Can. J. Chem.,* **2009,** *87,* 8.
5. Liu, Z.; Marder, T. B., *Angew. Chem*., **2008,** *47,* 242.
6. Kabalka, G. W., Use of organoboranes in modern medical imaging, *Pure and Applied Chemistry,* **1991,** *63(3),* 379-382.
7. Lawal, T. A., Polycyclic aromatic hydrocarbons. A review, *Cogent Environmental Science,* **2017,** *3(1).*
8. Tsapakis, M.; Apostolaki, M.; Eisenreich, S.; Stephanou, E. G., Environmental Science & Technology, **2006,** *40(16),* 4922-4927.
9. Okona-Mensah, K. B.; Battershill, J.; Boobis, A.; Fielder, R., An approach to investigating the importance of high potency polycyclic aromatic hydrocarbons (PAHs) in the induction of lung cancer by air pollution, *Food and Chemical Toxicology,* **2005,** *43(7),* 1103-1116.
10. Pope III, C. A.; Burnett, R. T.; Thun, M. J.; Calle, E. E.; Krewski, D.; Ito, K.; Thurston, G. D., Lung cancer, cardiopulmonary mortality and long-term exposure to fine particulate air pollution, *JAMA,* **2002,** *287(9),* 1132–1141.
11. Lao, J. Y.; Xie, S. Y.; Wu, C. C.; Bao, L. J.; Tao, S.; Zeng, E. Y., *Environmental Science & Technology,* **2018,** *52(15),* 8330-8338.
12. Richter, H.; Howard, J. B., Formation of polycyclic aromatic hydrocarbons and their growth to soot—a review of chemical reaction pathways, *Progress in Energy and Combustion Science,* **2000,** *26, Issues 4–6,* 565-608.
13. Garms, C.; Francke, W., Syntheses of ^{13}C-Labelled Polycyclic Aromatic Compounds, *Treatment of Contaminated Soil,* **2001,** 95-131.
14. King, A. O., Platinum on Alumina, *Encyclopedia of Reagents for Organic Synthesis,* **2001**.
15. Trost, B. M., Dehydrogenation Mechanisms. On the Mechanism of Dehydrogenation of Acenaphthene by Quinones, *Journal of the American Chemical Society,* **1967,** *89(8),* 1847–1851.
16. Ruoff, R. S.; Kadish, K. M.; Boulas, P.; Chen, E. C. M., Relationship between the electron affinities and half-wave reduction potentials of fullerenes, aromatic hydrocarbons, and metal complexes, *The Journal of Physical Chemistry,* **1995,** *99(21),* 8843–8850.
17. Skov, A. L.; Thrower, J. D.; Hornekær, L., Polycyclic aromatic hydrocarbons – catalysts for molecular hydrogen formation, *Faraday Discussions,* **2014,** *168,* 223-232.
18. Stock, A.; Pohland, E., Boric acid solution, VIII Regarding knowledge of B_2H_6 and B_5H_{11}, *Chemische Berichte,* **1926,** *59(9),* 2210–2215.
19. Islas, R.; Chamorro, E.; Robles, J.; Heine, T.; Santos, J. C.; Merino, G., Borazine: to be or not to be aromatic, *Structural Chemistry,* **2007,** *18(6),* 833–839.

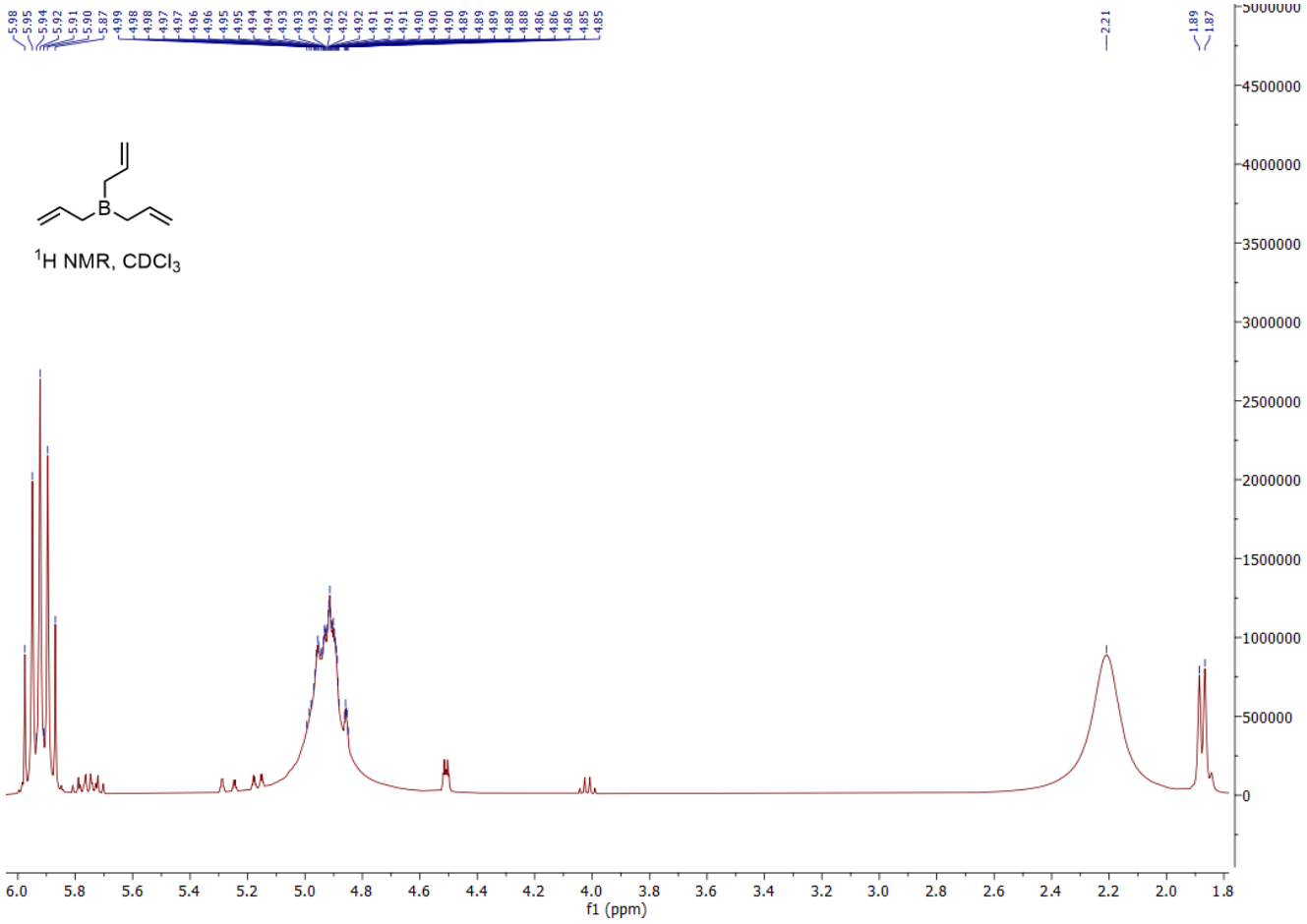
20. Harshbarger, W.; Lee, G. H.; Porter, R. F.; Bauer, S. H., Structure of borazine, *Inorganic Chemistry,* **1969,** *8(8),* 1683–1689.
21. Abengózar, A.; Sucunza, D.; García-García, P.; Vaquero, J. J., Remarkable effect of alkynyl substituents on the fluorescence properties of a BN-phenanthrene, *Beilstein Journal of Organic Chemistry,* **2019,** *15,* 1257–1261.
22. Kervyn, S.; Fenwick, O.; Di Stasio, F.; Shin, Y. S.; Wouters, J.; Accorsi, G.; Osella, S.; Beljonne, D.; Cacialli, F.; Bonifazi, D., Polymorphism, Fluorescence, and Optoelectronic Properties of a Borazine Derivative, *Chemistry - A European Journal,* **2013,** *19(24),* 7771–7779.
23. Kim, G.; Jang, A. R.; Jeong, H. Y.; Lee, Z.; Kang, D. J.; Shin, H. S., Growth of high-crystalline, single-layer hexagonal boron nitride on recyclable platinum foil, *Nano Letters*, **2013,** *13(4),* 1834–9.
24. Davis, B. L.; Dixon, D. A.; Garner, E. B.; Gordon, J. C.; Matus, M. H.; Scott, B., Stephens, F. H., Efficient regeneration of partially spent ammonia borane fuel, *Angewandte Chemie,* **2009,** *48(37),* 6812.
25. Wideman, T.; Sneddon, L. G., Convenient Procedures for the Laboratory Preparation of Borazine, *Inorganic Chemistry,* **1995,** *34(4),* 1002–1003.
26. Wideman, T.; Fazen, P. J.; Lynch, A. T.; Su, K.; Remsen, E. E.; Sneddon, L. G.; Chen, T.; & Paine, R. T., Borazine, Polyborazylene, β-Vinylborazine, and Poly(β-Vinylborazine), *Inorganic Syntheses,* **2007,** *32,* 232–242.
27. Li, J.; Zhang, C.; Li, B.; Cao, F.; Wang, S., An Improved Synthesis of Borazine with Aluminum Chloride as Catalyst, *European Journal of Inorganic Chemistry,* **2010,** *12,* 1763–1766.
28. Ashe, A. J. III; Fang, X. A, synthesis of aromatic five- and six-membered B-N heterocycles via ring closing metathesis, *Organic Letters,* **2000,** *2,* 2089-2091.
29. Fang, X.; Yang, H.; Kampf, J. W.; Holl, M. M. B.; Ashe, A. J., III. Syntheses of Ring-Fused B−N Heteroaromatic Compounds, *Organometallics,* **2006,** *25,* 513–518.
30. Dewar, M. J. S.; Gleicher, G. J.; Robinson, B. P., Synthesis and Nuclear Magnetic Resonance Spectrum of 10,9-Borazaronaphthalene, *Journal of the American Chemical Society,* **1964,** *86,* 5698-5699.
31. Sun, F.; Lv, L.; Huang, M.; Zhou, Z.; Fang, X., Palladium-Catalyzed Cross-Coupling Reactions of 4a,8a-Azaboranaphthalene, *Organic Letters,* **2014,** *16(19),* 5024-5027.
32. Grotevendt, A. G. D.; Lummiss, J. A. M.; Mastronardi, M. L.; & Fogg, D. E., Ethylene-Promoted versus Ethylene-Free Enyne Metathesis, *Journal of the American Chemical Society*, **2011,** *133(40).*
33. Grayson, M. N.; Pellegrinet, S. C.; Goodman, J. M., Mechanistic Insights into the BINOL-Derived Phosphoric Acid-Catalyzed Asymmetric Allylboration of Aldehydes, *Journal of the American Chemical Society,* **2012,** *134(5),* 2716–2722.
34. Blackwood, K. M.; Milne, P. E. Y.; Goodby, J. W.; Hall, A. W.; Kelly, S. M., Polymer production, **2000,** *WO2000006610A2,* WO 00/06610.
35. Thiedemann, B.; Gliese, P. J.; Hoffmann, J.; Lawrence, P. G.; Sönnichsen, F. D.; Staubitz, A., High molecular weight poly(N-methyl-B-vinylazaborine) - a semi-inorganic BN polystyrene analogue., *Chemical Communications,* **2017,** *53,* 7258-7261.

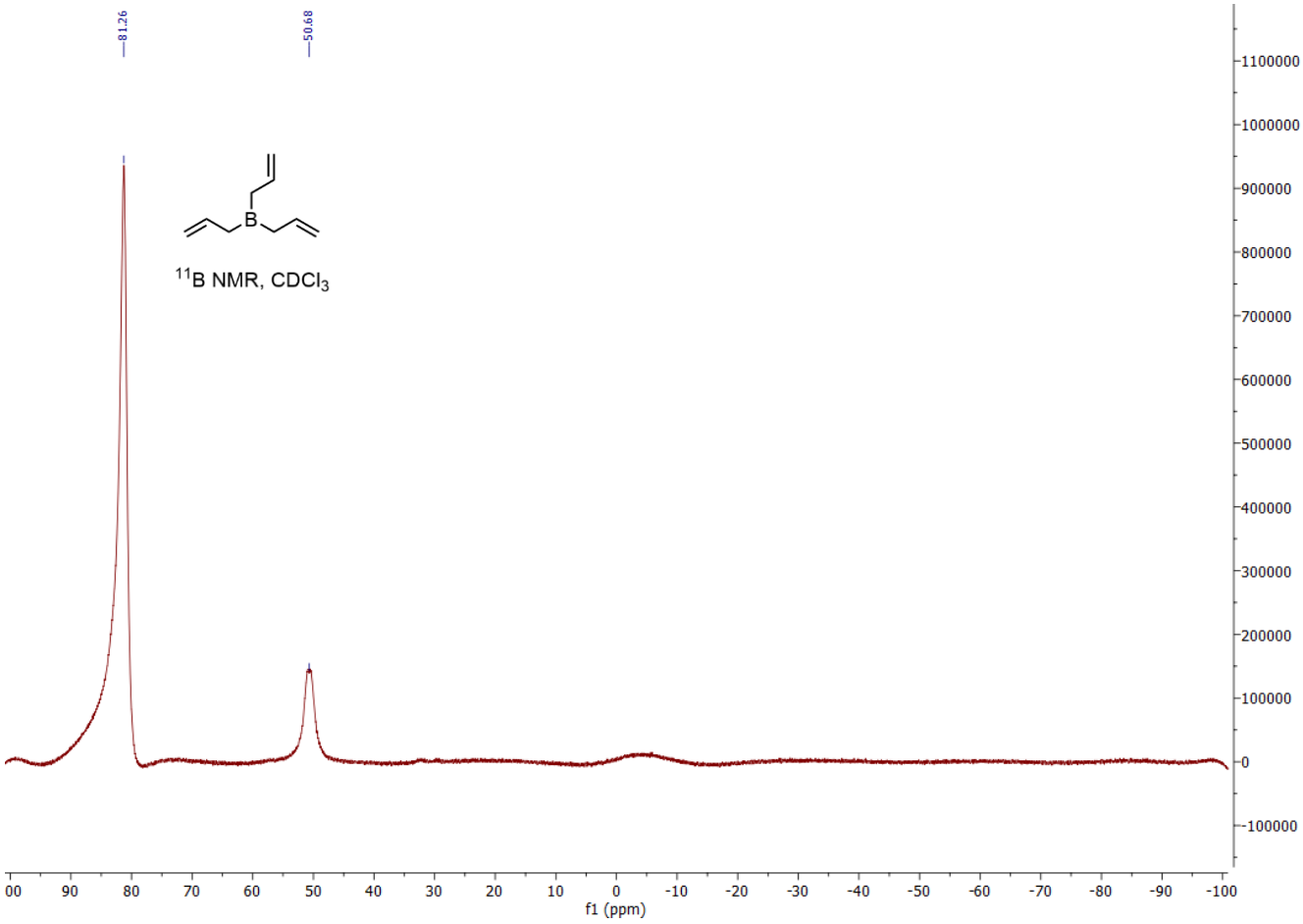
9. ACRONYMS

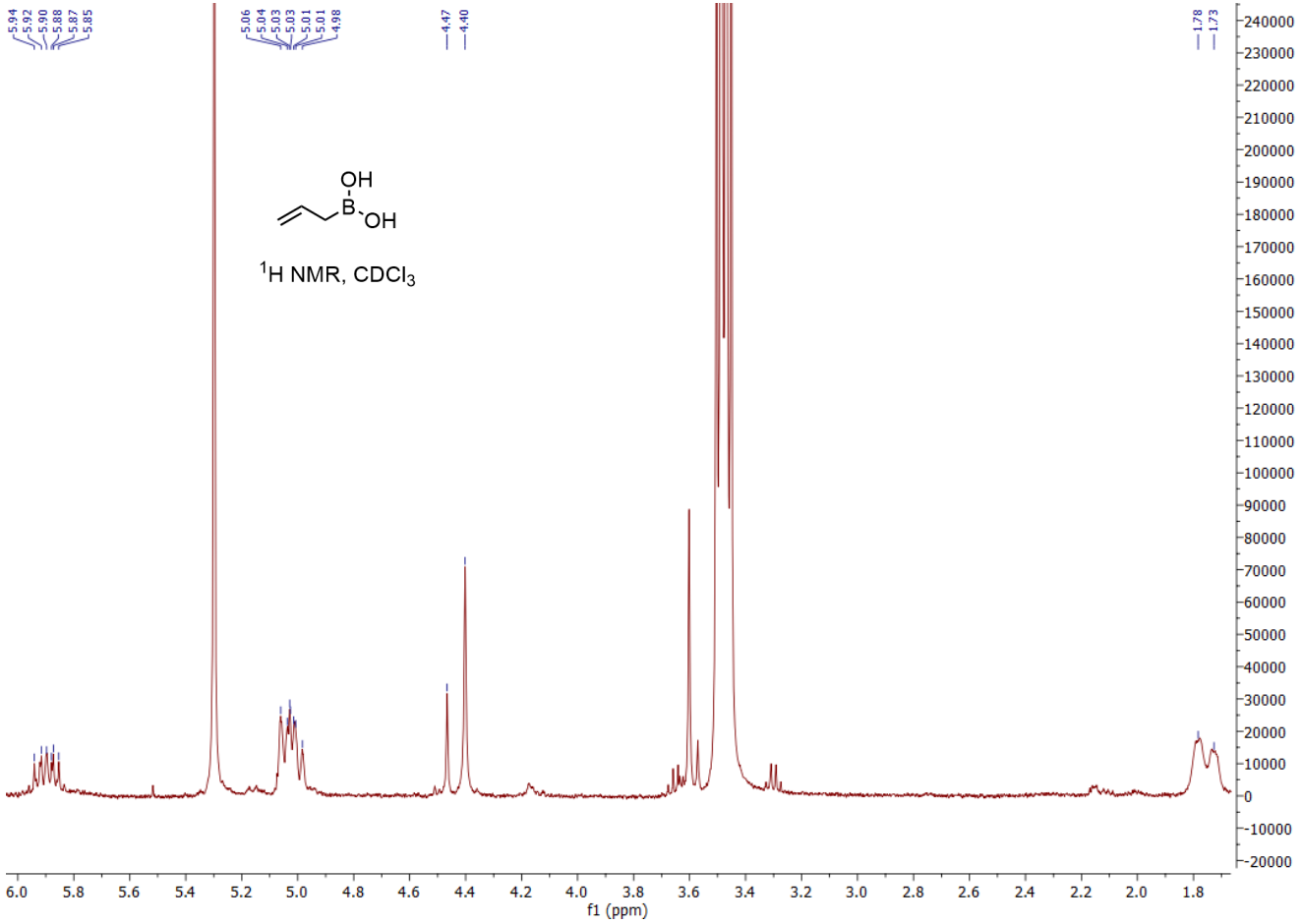
- Al_2O_3: Aluminum oxide.
- app: Apparent.
- Ar: Argon.
- $BF_3 \cdot OEt_2$: Boron trifluoride diethyl etherate.
- br: Broad.
- $CDCl_3$: Deuterated chloroform.
- g: Grams.
- Gr: Grubbs.
- h: Hours.
- L: Liters.
- mBar: Millibar.
- mg: Milligrams.
- min: Minutes.
- mL: Milliliters.
- mm: Millimeters.
- mM: Millimolar.
- mmol: Millimol.
- MW: Molecular weight.
- nm: Nanometers.
- NMR: Nuclear magnetic resonance.
- PAH: Polycyclic aromatic hydrocarbon.
- ppm: Parts per million.
- Pt: Platinum.
- TLC: Thin layer chromatography.
- UV: Ultraviolet.
- µL: Microliters.
- µm: Micrometers.

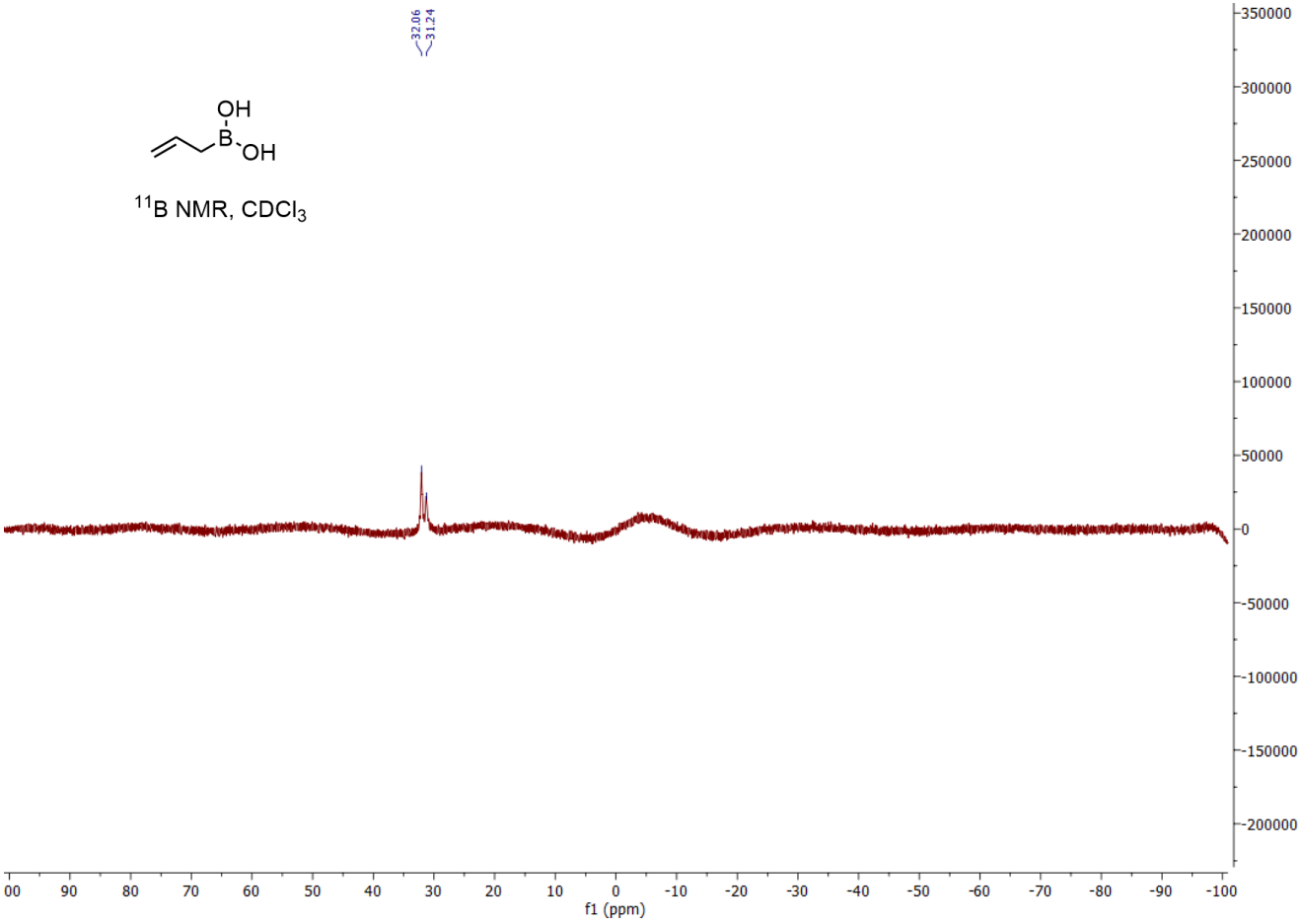
APPENDICES: NMR SPECTRA

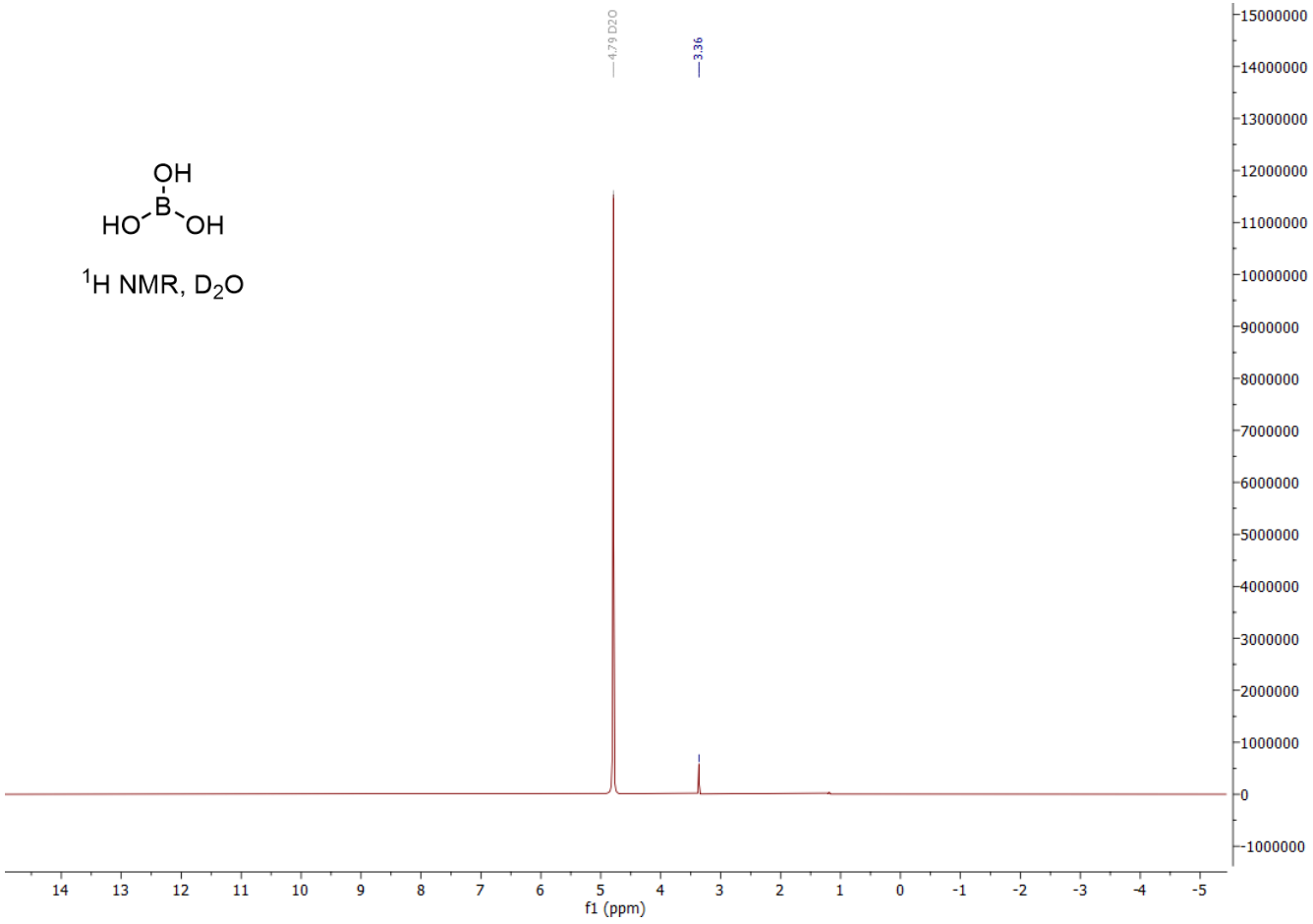

6.30
6.30
6.26
6.25
6.16
6.14
6.12
6.09
5.89
5.88
5.87
5.87
5.85
5.85
5.84
5.84
5.83
5.82
5.81
5.80
5.65
5.64
5.62
5.62
5.22
5.21
5.21
5.20
5.17
5.17
5.15
5.14
5.14
5.14
5.12
5.12
5.12
3.96
3.96
3.95
3.95
3.94
3.94
3.93
3.93
3.93
O
N
H
1H NMR, CDCl3
solvent remaining
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
f1 (ppm)

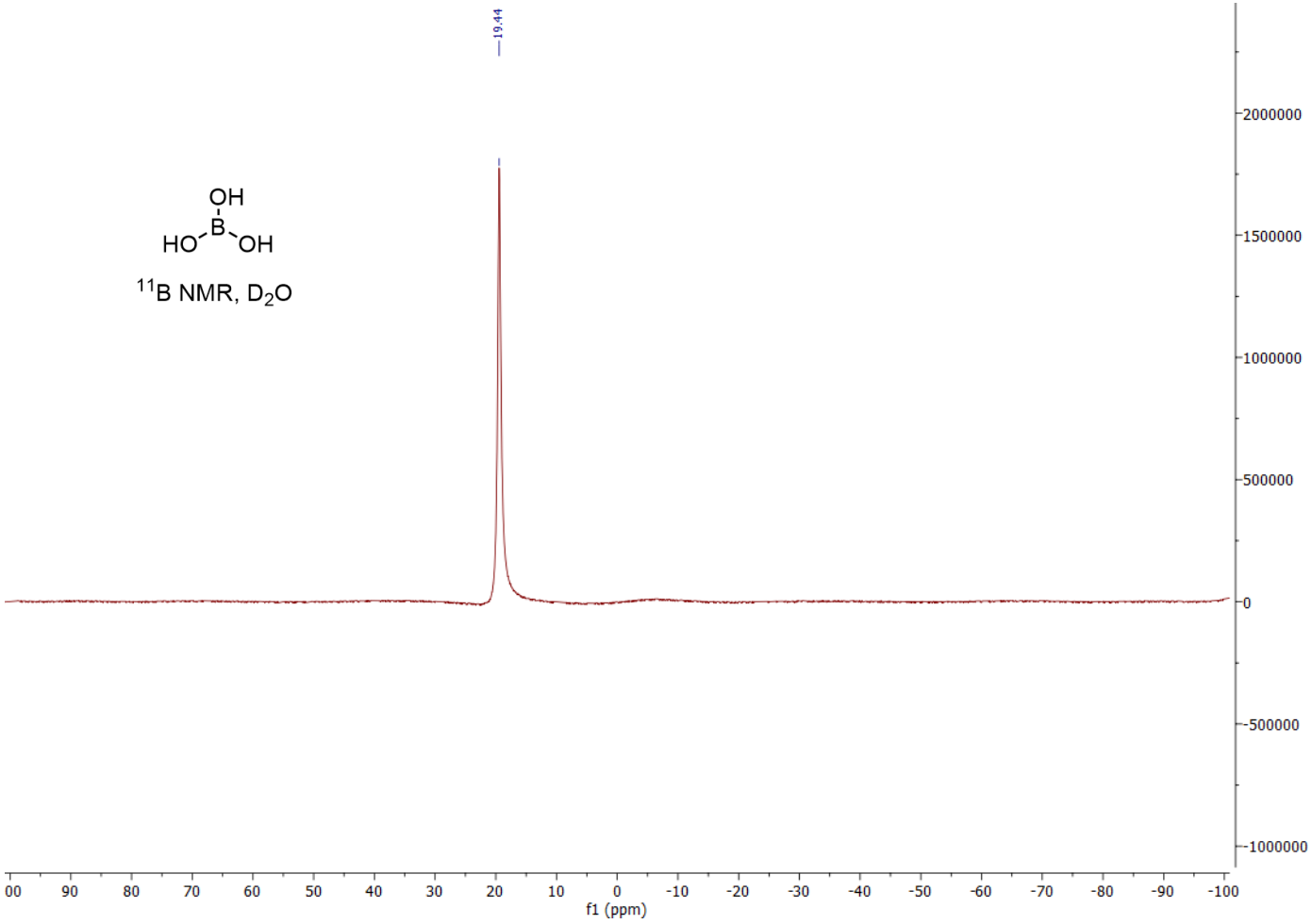

5.98
5.95
5.94
5.92
5.91
5.90
5.87
4.99
4.98
4.98
4.97
4.97
4.96
4.96
4.95
4.95
4.94
4.94
4.93
4.93
4.93
4.92
4.92
4.92
4.91
4.91
4.91
4.90
4.90
4.90
4.89
4.89
4.89
4.88
4.88
4.86
4.86
4.86
4.85
4.85
2.21
1.89
1.87
B
1H NMR, CDCl3
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f1 (ppm)

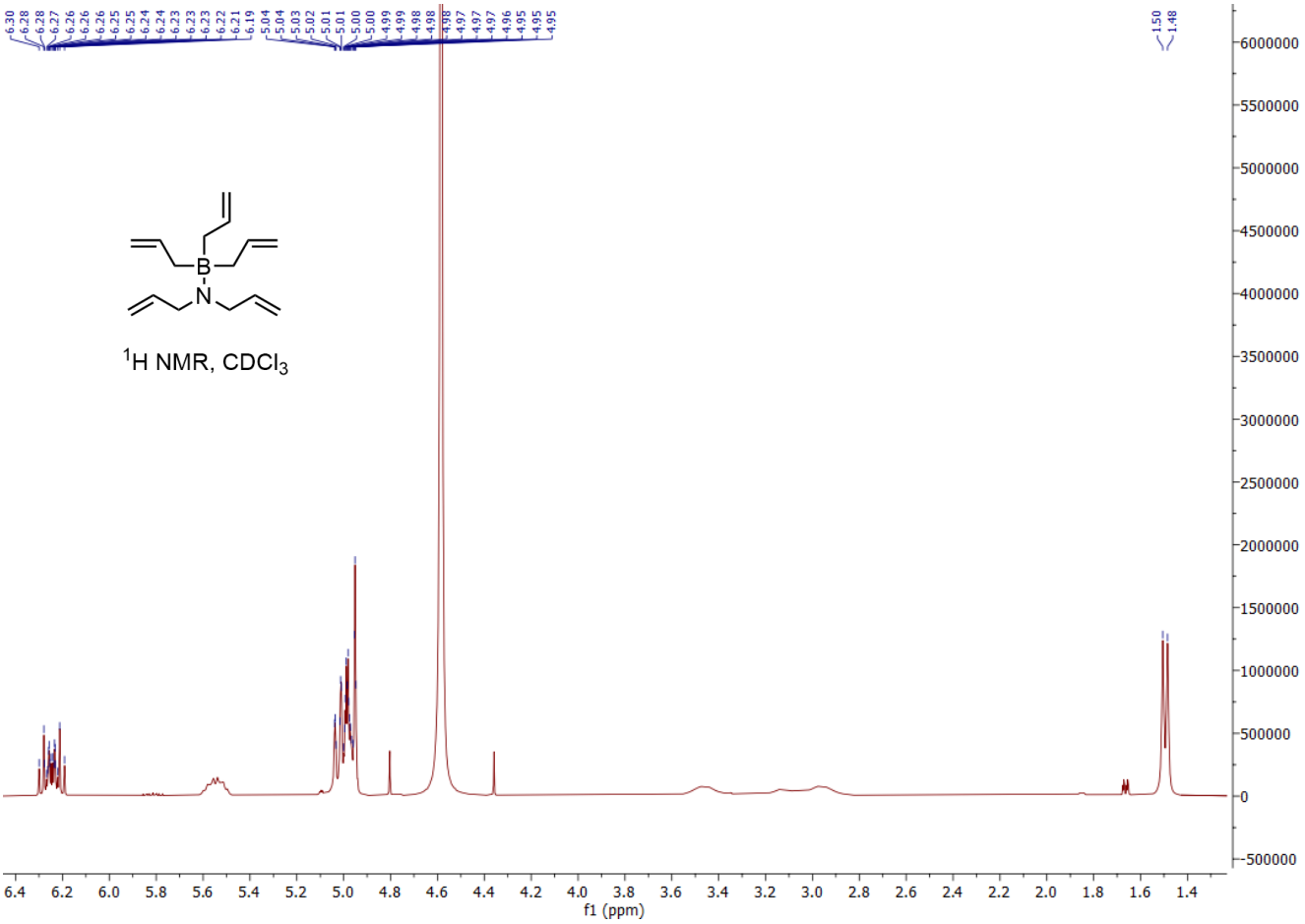

81.26
50.68
B
^{11}B NMR, $CDCl_3$
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

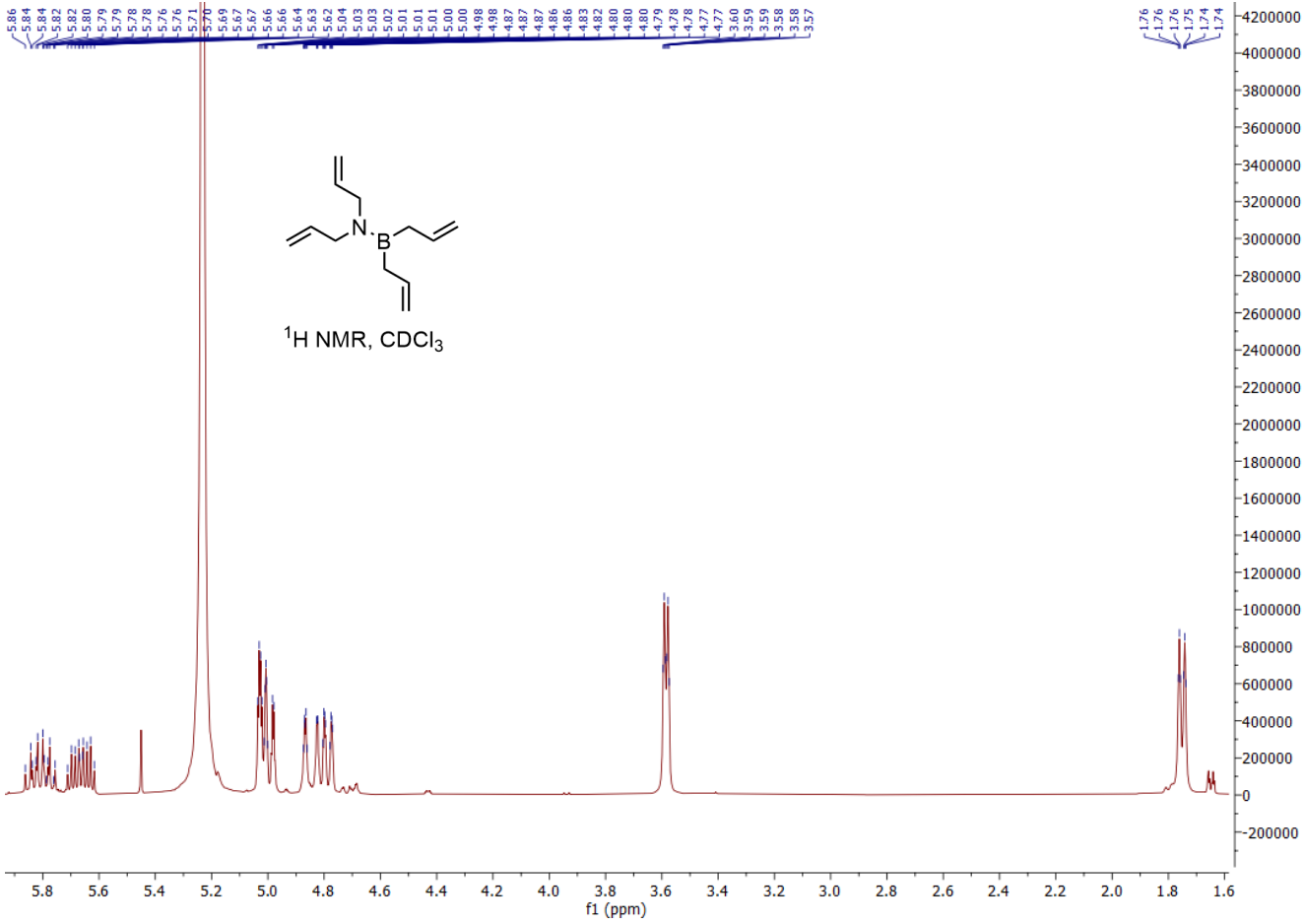

5.94
5.92
5.90
5.88
5.87
5.85
5.06
5.04
5.03
5.03
5.01
5.01
4.98
4.47
4.40
1.78
1.73
OH
B
OH
1H NMR, CDCl3
240000
230000
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f1 (ppm)

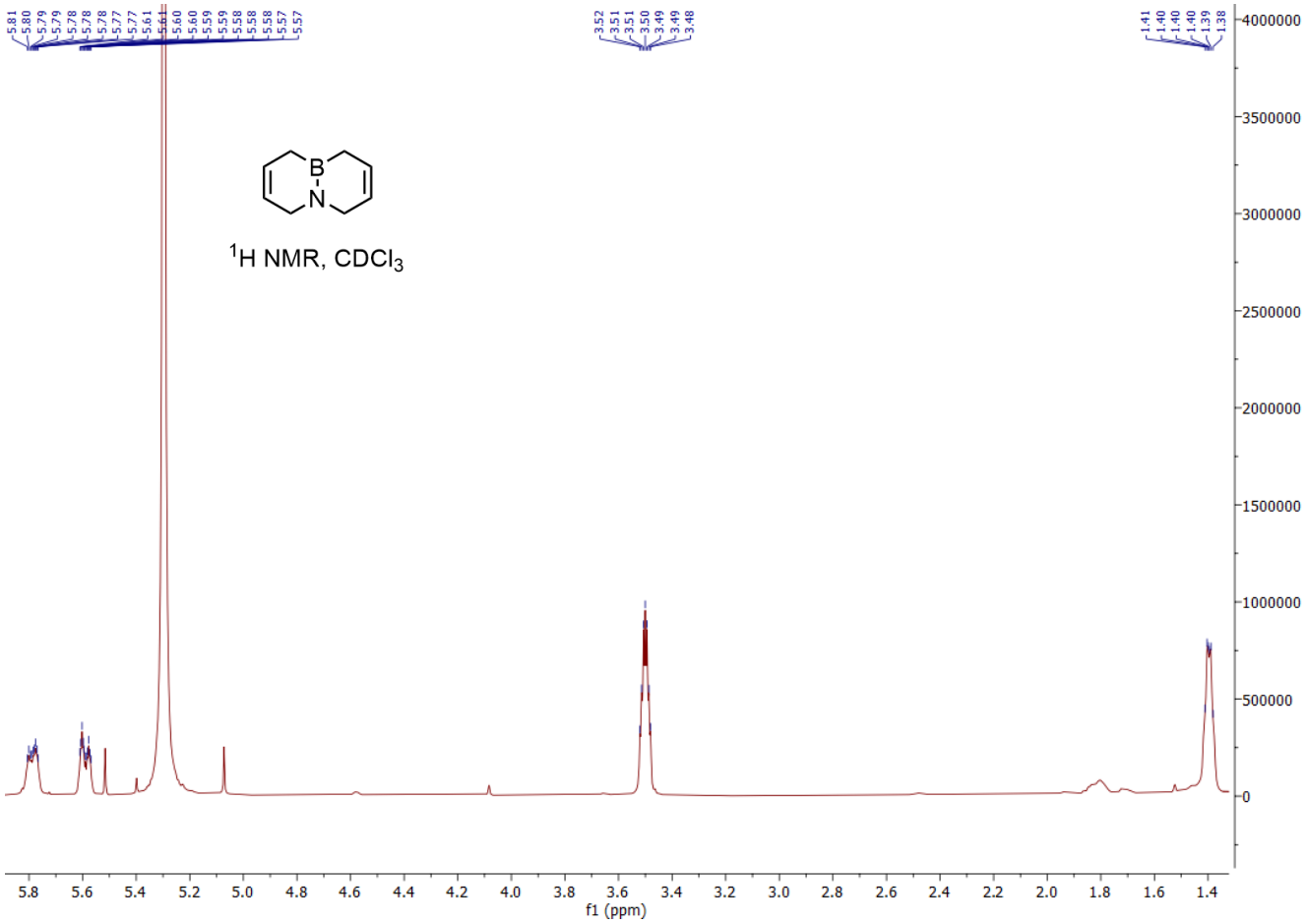

32.06
31.24
OH
B
OH
11B NMR, CDCl3
350000
300000
250000
200000
150000
100000
50000
0
-50000
-100000
-150000
-200000
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

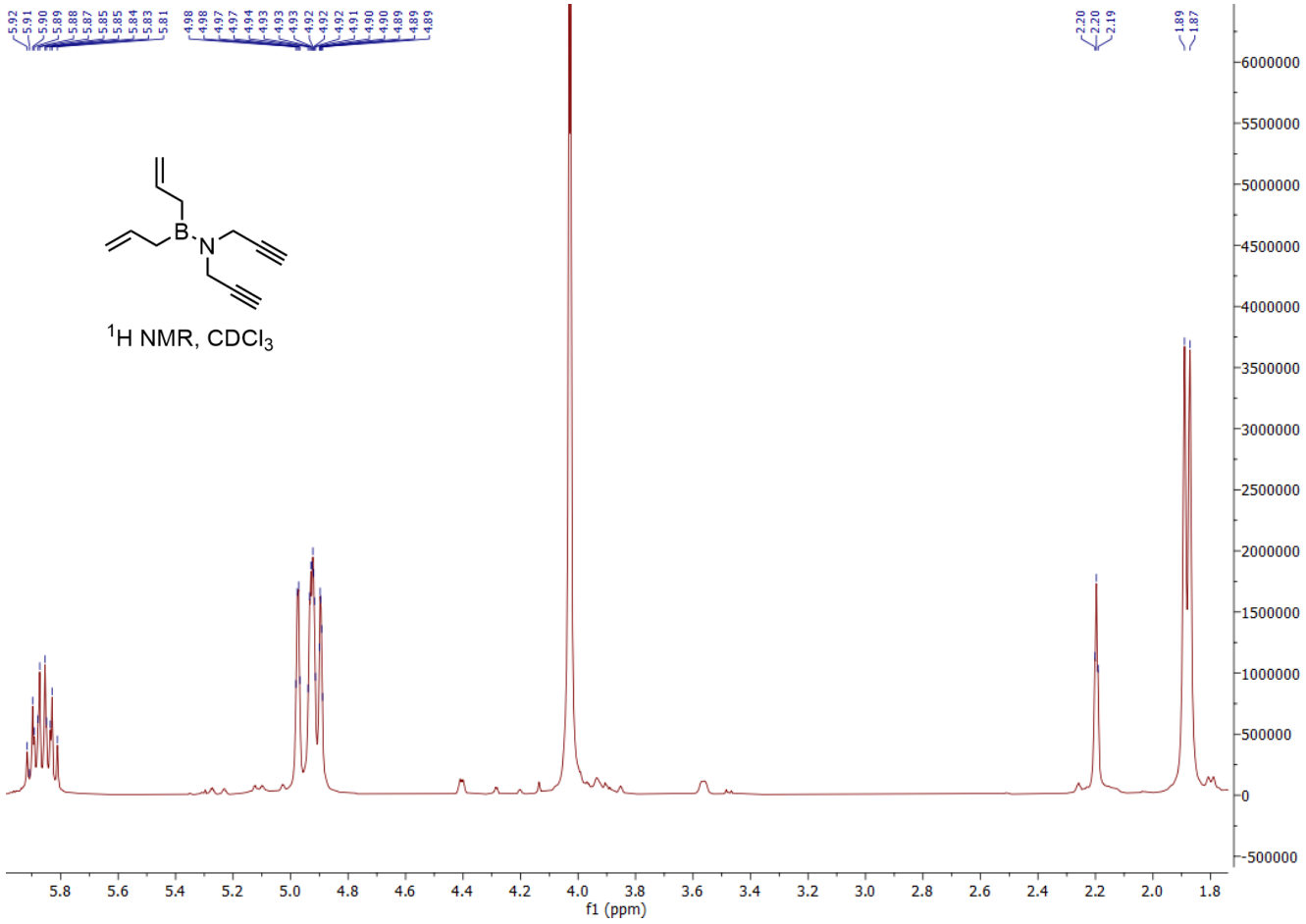

4.79 D2O
3.36
OH
HO
B
OH
^{1}H NMR, D_2O
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f1 (ppm)

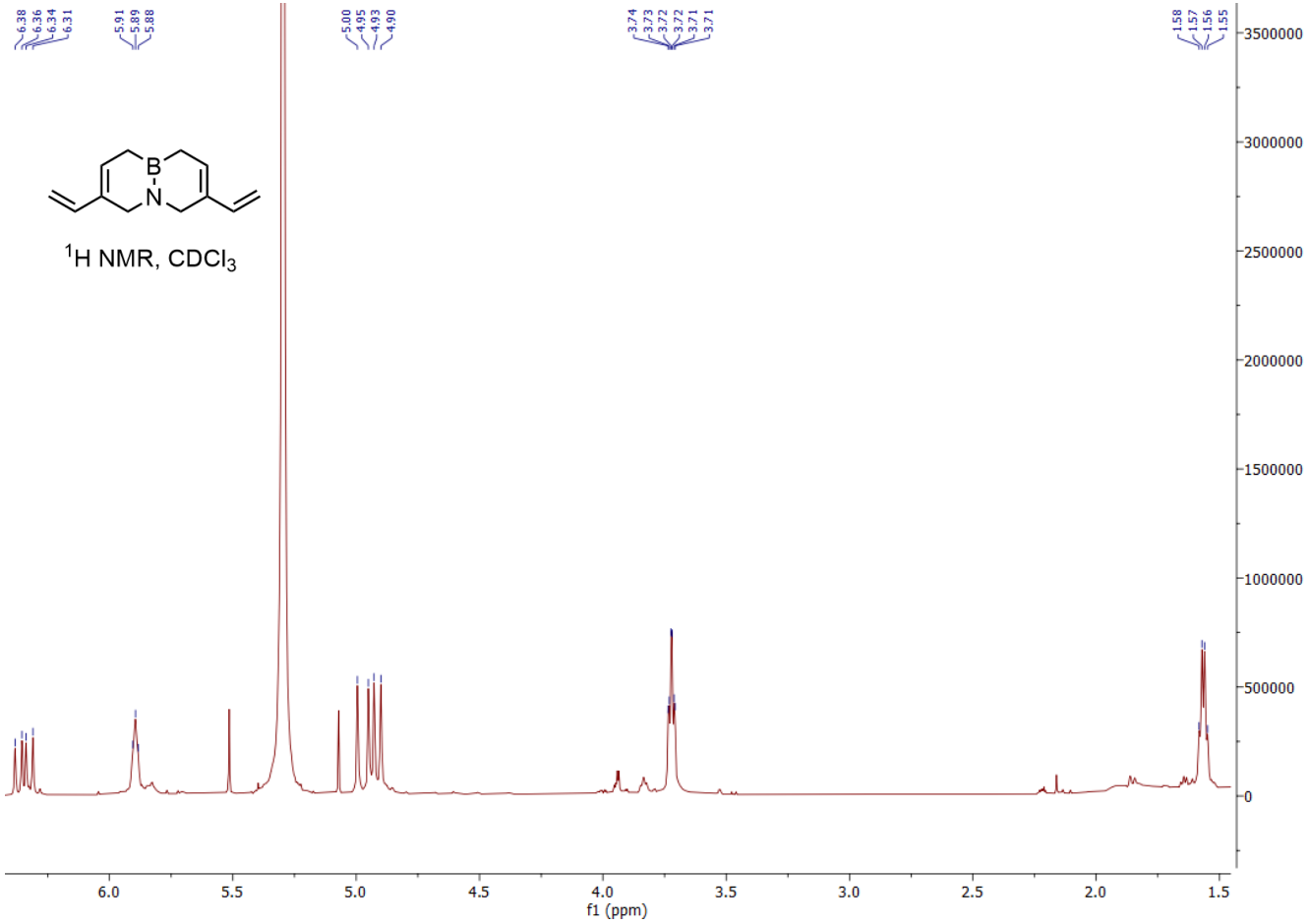

19.44
OH
HO
B
OH
^{11}B NMR, D_2O
2000000
1500000
1000000
500000
0
-500000
-1000000
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)


6.30 6.28 6.28 6.27 6.26 6.26 6.26 6.25 6.25 6.24 6.24 6.23 6.23 6.23 6.22 6.21 6.19
5.04 5.04 5.03 5.02 5.01 5.01 5.00 5.00 4.99 4.99 4.98 4.98 4.98 4.97 4.97 4.97 4.96 4.95 4.95 4.95
1.50 1.48
B
N
^{1}H NMR, $CDCl_3$
6000000 5500000 5000000 4500000 4000000 3500000 3000000 2500000 2000000 1500000 1000000 500000 0 -500000
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
f1 (ppm)


^{1}H NMR, $CDCl_3$
f1 (ppm)


5.81
5.80
5.79
5.79
5.78
5.78
5.78
5.77
5.77
5.61
5.61
5.60
5.60
5.59
5.59
5.58
5.58
5.58
5.57
5.57
3.52
3.51
3.51
3.50
3.49
3.49
3.48
1.41
1.40
1.40
1.40
1.39
1.38
B
N
1H NMR, CDCl3
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f1 (ppm)


5.92
5.91
5.90
5.89
5.88
5.87
5.85
5.85
5.84
5.83
5.81
4.98
4.98
4.97
4.97
4.94
4.93
4.93
4.93
4.92
4.92
4.92
4.91
4.90
4.90
4.89
4.89
4.89
2.20
2.20
2.19
1.89
1.87
B
N
^{1}H NMR, CDCl$_3$
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f1 (ppm)


6.38
6.36
6.34
6.31
5.91
5.89
5.88
5.00
4.95
4.93
4.90
3.74
3.73
3.72
3.72
3.71
3.71
1.58
1.57
1.56
1.55
B
N
^{1}H NMR, CDCl$_3$
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)