SYNTHESIS OF DODECABORATE DIANIONS AND THEIR USE IN
STABILIZING ARYL DIAZO COMPOUNDS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMISTRY

JANUARY 2022

Approval of the thesis:

SYNTHESIS OF DODECABORATE DIANIONS AND THEIR USE IN STABILIZING ARYL DIAZO COMPOUNDS

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ABSTRACT

SYNTHESIS OF DODECABORATE DIANIONS AND THEIR USE IN STABILIZING ARYL DIAZO COMPOUNDS

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January 2022, 102 pages

Borane cages have been known to be weakly coordinating. Synthesis of these borane cages are known to be difficult. In this study, dodecahydro-*closo*-dodecaborate was synthesized starting from sodium borohydride. It was further modified to dodecachloro-*closo*-dodecaborate and dodecabromo-*closo*-dodecaborate. Using the weakly coordinating properties of these dianions, diazonium salts were captured. Characterization of these diazonium salts were done. It was further found that these diazonium salts are stable at least for four weeks. Electron withdrawing groups destabilized diazonium salts that the dry form explodes violently.

Keywords: *closo*-dodecaborate, borane, diazonium cation, perhalogenation

ÖZ

DODEKABORAT DİANYONLARIN SENTEZİ VE ARİL DİAZO BİLEŞİKLERİNİN STABİLİZE EDİLMESİ İÇİN KULLANIMI

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Boran kafeslerinin zayıf bir şekilde koordine olduğu bilinmektedir. Bu boran kafeslerinin sentezinin zor olduğu bilinmektedir. Bu çalışmada, sodyum borhidrürden başlanarak dodekahidro-kloso-dodekaborat sentezlendi. Ayrıca dodekakloro-kloso-dodekaborat ve dodekabromo-kloso-dodekaborat olarak modifiye edildi. Bu dianyonların zayıf koordinasyon özellikleri kullanılarak diazonyum tuzları yakalandı. Bu diazonyum tuzlarının karakterizasyonu yapıldı. Ayrıca bu diazonyum tuzlarının en az dört hafta boyunca stabil olduğu bulundu. Elektron çeken gruplar, kuru halde şiddetli bir şekilde patlayan diazonyum tuzlarını kararsızlaştırdı.

Anahtar Kelimeler: kloso-dodecaborat, boran, diazonyum katyon, perhalojenasyon

To my beloved Mother, Father and Brothers

ACKNOWLEDGMENTS

It was my goal to be a scientist in order to leave something to the world after me. I knew that it is hard and stressful. I would like to thank the people who have supported me even in these difficult and stressful times.

First and foremost, I would like to express my sincere gratitude to my supervisor Prof. Dr. Akın Akdağ, for his patience, encouragement and guidance. His knowledge, experience and point of view against science and life always inspired me. He taught me to fight for what I care about and never give up. I think it is the most significant lesson in my life.

Besides my advisor, I would like to express my sincere gratitude to my coadvisor Prof. Dr. Ceyhan Kayran İşçi for her support. She gave me an opportunity to use her laboratory.

I would like to thank the rest of the committee members: Prof. Dr. Gülsün Gökağaç Arslan, Prof. Dr. Özdemir Doğan and Prof. Dr. Atilla Cihaner for assisting me with their valuable comments, thoughts and criticisms in shaping the final draft of this study.

I would like to thank my group members: Gizem Çalışgan Ünay, Perihan Düzenli , Ece Ayça Erdoğan, Ege Hoşgör, Bengi Şentürk, Sevban Doğan Ekici, Doruk Baykal, Berçin Verda Asya, Bulem Çakmak, Nihat Aksoy, Sadia Tul Munna and Oğuzhan Albayrak. Their perspectives on science and humanity have always enlightened me.

I would like to thank Ozan Ünver for his friendship, colleague, support and inspiration. We motivated each other, shared experiences and overcome problems together. He is the one I always enjoy to discuss about the boron chemistry.

The last but the most, I would like to thank my family Vildan Aydemir, Mehmet Nuri Aydemir, Volkan Aydemir and İbrahim Aydemir for their endless love. Their love and support made me stronger woman than I thought. I love you so much.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

FIGURES

xviii

LIST OF SCHEMES

SCHEMES

LIST OF ABBREVIATIONS

ABBREVIATIONS

Diglyme	Diethylene glycol dimethyl ether
DCM	Dichloromethane
Et$_3$N	Triethylamine
DMSO	Dimethyl sulfoxide

CHAPTER 1

INTRODUCTION

1.1   Boron Mineral

Boron element is processed from its minerals since it is not found as a pure substance in nature.[1] The planet earth contains 4.5 billion tons of boron reserves, and 3.71 million tons of these minerals have been consumed. Turkey is rich in boron mineral, 73% of the world's reserves which is equal to 3.3 billion tons. According to reports of ETIMADEN, 230 different mineral sources of boron are found in nature and they are mostly different boron oxides; In <u>Table 1</u>, listed ones have commercial importance.[2]

Table 1. Name of the mineral and their molecular formulas those are commercially important

Name of The Mineral	Molecular Formula
Natural Boric Acid (Sassolite)	H_3BO_3
Kernite	$Na_2B_4O_7.4H_2O$
Tincalconite	$Na_2B_4O_7.5H_2O$
Tincal (Borax)	$Na_2B_4O_7.10H_2O$
Probertite	$NaCaB_5O_9.5H_2O$
Ulexite	$NaCaB_5O_9.10H_2O$

Colemanite	$Ca_2B_6O_{11}.5H_2O$
Meyerhofferite	$Ca_2B_6O_{11}.7H_2O$
Inyoite	$Ca_2B_6O_{11}.13H_2O$
Pandermite	$Ca_2B_{10}O_{19}.7H_2O$
Inderite	$Mg_2B_6O_{11}.15H_2O$
Hydroboracite	$MgCaB_6O_{11}.6H_2O$
Boracite	$Mg_2B_7O_{13}Cl$
Ascharite	$Mg_2B_2O_5.H_2O$
Datolite	$Ca_2B_2Si_2O_9.H_2O$

Boron minerals can be categorized in three broad groups concerning the origin and geological environment; 1) result of intrusive, skarn mineral with silicates and iron oxides 2) results of marine sediment, magnesium oxide and 3) results of volcanic activity and continental sediment, hydrated sodium and calcium borates.[3] Borax (Tincal), Colemanite, Kernite and Ulexite are third group mineral sources and they are mostly supplied from Turkey (Table 2).

Table 2. Supplied boron minerals from Turkey

Supplied Minerals	Molecular Formula
Borax (Tincal)	$Na_2B_4O_7.10H_2O$
Kernite	$Na_2B_4O_7.4H_2O$
Colemanite	$Ca_2B_6O_{11}.5H_2O$
Ulexite	$NaCaB_5O_9.10H_2O$

From an industrial point of view, borax ($Na_2B_4O_7.10H_2O$) is the most significant mineral since it dissolves in water easily and crushes readily. Turkey supplies most of the demand for borax due to its abundance. Kernite ($Na_2B_4O_7.4H_2O$) has less solubility than borax, and it has four water molecules. Colemanite ($Ca_2B_6O_{11}.5H_2O$) is calcium-containing borate mineral, most of the mines of colemanite are also found in Turkey. The solubility of colemanite is low in water but it easily dissolves in acidic solutions. Ulexite ($NaCaB_5O_9.8H_2O$) contains both sodium and calcium and is found near the surface in mines.

In the last decades, the demand for boron-containing materials has been increasing. In 2019, 3.71 million tones boron products were used in the world. More than half of demand was supplied by Turkey. Turkey exported 53% of boron compounds to Asia, 29% to Europe, 16% to America, and 1% to Africa. Export products of boron from Turkey are generally in the form of boron minerals. Refined boron compounds are more feasible than the minerals economically. With this in mind, Turkey has to enhance the number of refined boron compounds and its research and development potential. For instance, polyhedral cage-like compounds of boron have an important place in research since they have both scientific and industrial applications.

1.2   Boron Atom

In 1808, elemental boron firstly extracted from borax by heating it in the presence of potassium in two different countries independently. In France, Louis-Josef Gay-Lussac and Louis-Jacques Thénard and in England, Sir Humphry Davy worked on the subject. Boron was in hand but it was not pure.[4] In 1892, high purity boron element was obtained by Henri Moissan. Elemental boron is the only nonmetal member of Group 13 in periodic table. The electronic configuration of boron is $1s^22s^22p^1$. In its neutral compounds, boron acts like Lewis acid due to empty p-orbitals lacking octet. In classical sense, it forms three covalent bonds. In boron compounds, octet rule is not obeyed. Therefore, it has interesting and different chemical properties.[1] For instance, cubic boron nitride is used for certain high

temperature applications in which diamond can not be used because it forms carbides with the material being ground. Borosilicate has high heat resistibility, reactivity of boranes are very high due to non-classical B-H bonds and burning amorphous boron gives high heat.[4]

1.3   Boron Clusters

Besides classical molecular structure, boron can from clusters which deviate from classical bonding scheme *vide infra*. The clusters can be classified as polymeric and cage-like (Figure 1). This thesis will not include polymeric clusters rather it will deal with boron cages. To further understand boron cages, one needs to understand boron hydrides.
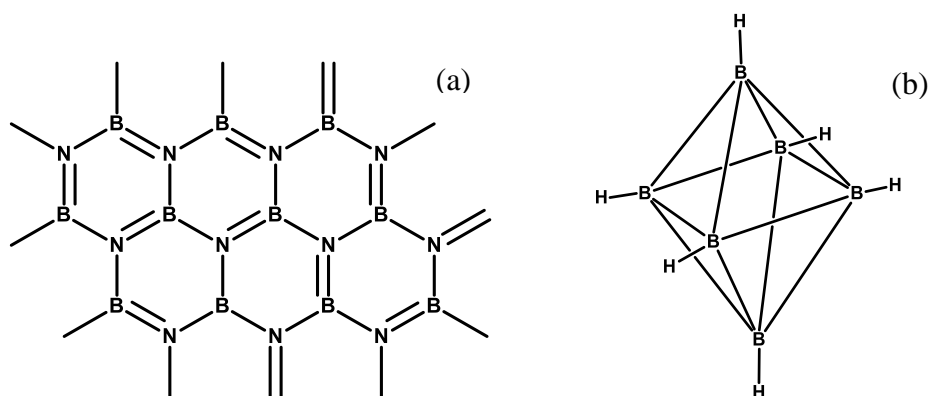
Figure 1. a) Polymeric Boron Nitride, b) Cage-like $B_6H_6^{2-}$

1.3.1   Borohydrides

Hydrogen binary compounds of boron are called borohydrides, in short boranes.[1] Diborane is the smallest member of boranes which contains two boron and six hydrogen atoms. It was first synthesized by Alfred Stock.[5] Stock synthesized B_4H_6, B_5H_9, B_5H_{11} and B_6H_{10}. These small borane compounds are volatile and toxic. These boranes readily react with air.[1] To overcome these difficulties, Stock created a special vacuum line system to synthesize lower borane molecules.

Before the 1940s, the structure of borane compounds was thought more like chains. Later, it was understood that the structures are not straightforward that and found boranes are electron deficient molecules. Longuet-Higgins stated that diborane has 3 center-2 electron (3c,2e) B-H-B hydrogen bridge bonds (Figure 2).[6] The cage-like structure of boranes was clarified by X-Ray diffraction studies at low temperatures and theoretical calculations.[5] The structure, bond type, and the number of electrons in the borane molecules were systematized by Wade's Rule.[7,8]
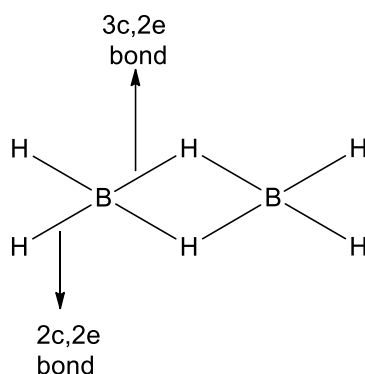
Figure 2. Structure and bonding of diborane [5]

1.3.2   Wade's Rule

When the boranes were first synthesized by Alfred Stock, their chemical structures were not understood completely. The structures were imagined like chains in 1940s. After discovering the B-H-B bond which has 3-center and 2-electrons, it was postulated that boranes have different structures than proposed before.[6] X-ray structural studies and theoretical calculations showed that boranes have a cage-like structure.[9]

The detailed structural pattern of boranes and carboranes was explained in the publication of Robert William and Kenneth Wade. Besides, this publication also clarified other mixed metal clusters and similarities between borane-carborane clusters and mixed metal clusters.[8]

Counting the total number of skeletal electron pairs (SEP) is the fundamental principle of Wade's rule.[1,7] According to the Wade's rule, out three valence electrons of boron, only two of them used as skeleton electron (in the construction boron clusters) third electron is used in the external B-H bond (exo bond) (Figure 3).
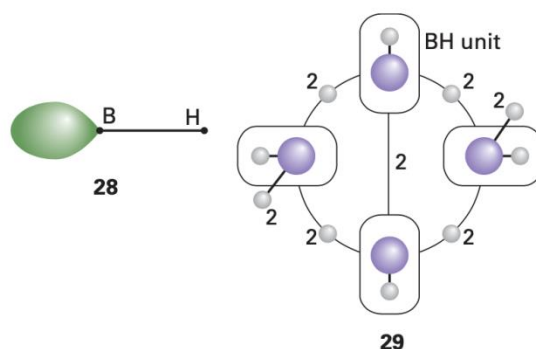
Figure 3. The skeleton electron in tetraborane B_4H_{10} [1]

There are main types of such clusters which are *closo-*, *nido-* and *arachno* for borohydride clusters (Table 3).

Table 3. Type and skeletal electron of borohydride clusters[1]

Type	Formula	Skeleton electron	Examples
closo-	$[B_nH_n]^{2-}$	n+1	$[B_5H_5]^{2-}$ to $[B_{12}H_{12}]^{2-}$
nido-	B_nH_{n+4}	n+2	B_2H_6, B_5H_9
arachno-	B_nH_{n+6}	n+3	B_4H_{10}, B_5H_{11}

Closo- type of borane clusters showed with empirical formula as $B_nH_n^{2-}$ (n=6 to 12) and $B_{n-2}C_2Hn$ (n=5 to 12) and they have 'n+1' paired skeletal electrons and 'n' skeletal atoms. Skeletal atoms which are B or C found at each corner of the closed

polyhedron and found as exo- BH or CH. *Closo-* clusters are either thermally stable or chemically unreactive. For example, pentaborane(5) is in *closo-* form shown in Figure 4.
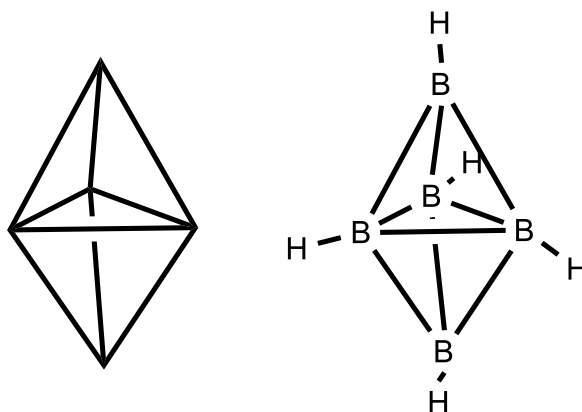
Figure 4. Structure of *closo*-pentaborane(5)

Nido- type of borane clusters showed with empirical formula as B_nH_{n+4}, $CB_{n-1}H_{n+3}$, $C_2B_{n-2}H_{n+2}$, $C_3B_{n-3}H_{n+1}$, and $C_4B_{n-4}H_n$ and have n+4 skeletal electrons. 'n' exo-BH located at each corner. Besides the exo-BH and exo-CH bonds, *nido-* clusters have extra hydrogen atoms, and these hydrogens are located between the two B atoms like the B-H-B bridge. Although *nido-* is more reactive than *closo-*, its reactivity is not as much as *arachno*. For example, pentaborane(9) is in *nido-* form shown in Figure 5.
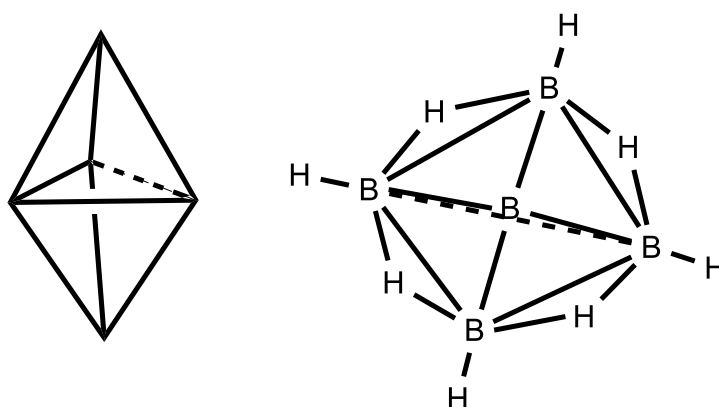
Figure 5. Structure of *nido*-pentaborane(9)

Arachno-type of borane clusters showed with empirical formula B_nH_{n+6} and $C_2B_{n-2}H_{n+4}$ and have n+6 skeletal electrons. *Arachno-* type contains exo-BH, B-H-B, and endo-BH bonds. The position of endo-BH is tangential according to the pseudo spherical surface of polyhedral. The *arachno-* form of pentaborane(11) is shown in Figure 6.
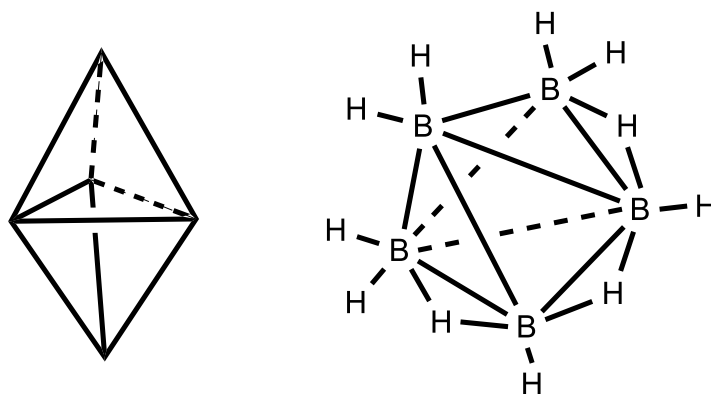
Figure 6. Structure of *arachno*-pentaborane(11)

In summary, *closo-* clusters are more stable than the opened ones (*nido-* and *arachno-*), so stability order for such clusters is *closo- > nido- > arachno-* cluster. On the contrary, open clusters are much more reactive than *closo-* ones, so reactivity order is opposite of the stability order. Structural correlation between *closo-* to *arachno-* is shown in Figure 7.
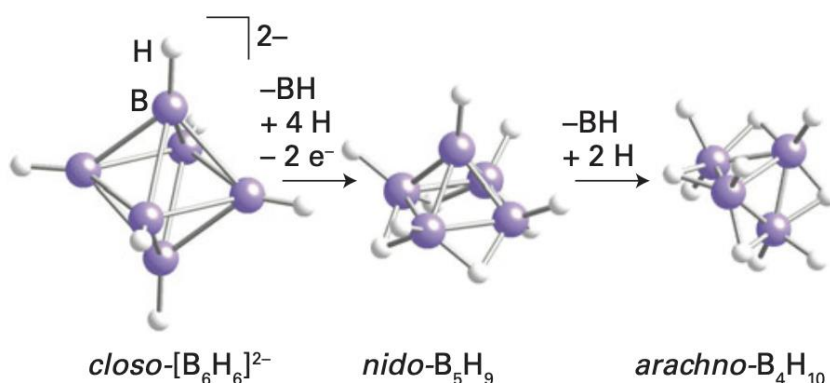
Figure 7. Structural correlation between *closo-* to *arachno-*[1]

1.3.3   Nomenclature and Numbering
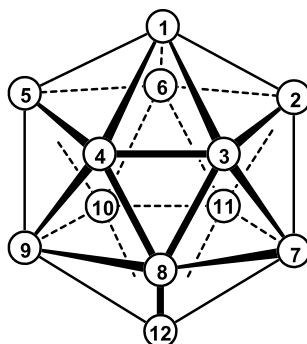
Figure 8. Numbering of boron clusters

Cage-like boron compounds have specific naming and numbering methods. According to IUPAC recommendation, clockwise-in-planes numbering systems are used for boron-containing cages.[10] This system depends on the highest order of symmetry axis of the cluster and for heteroatom containing clusters; the highest atomic number brings higher priority for numbering. The example for this is given for 12 membered cluster shown in Figure 8.

Boron compounds can be found as closed (*closo-*) or opened (*nido-, arachno-, hypho-, klado-*) forms. In the course of naming of boron clusters, the prefixes according to Wade's rule are used.[7] In the IUPAC recommendation, boranes are used for neutral boron hydrides and the number of hydrogen atoms is written in parenthesis, such as dodecaborane(12) for $B_{12}H_{12}$. Before the 2019 recommendation of IUPAC, anionic borates called hydroborates and in the literature, it is still used like this. However, in the 2019 recommendation, IUPAC changed this as hydridoborates. Moreover, for anionic borates both hydrogen and boron atoms are written with a prefix, and the 'ate' suffix is also added to the name. The charge of a molecule is needed to write in parenthesis. For instance, $[B_{12}H_{12}]^{2-}$ is named as dodecahydrido-*closo*-dodecaborate (2-) and numbering should be like in the Figure 8.[10]

1.3.4 The Localized Bond Approach

The idea that boron has different bond types than classical chemical bonds was first put forward by Stitt through his heat capacity experiment on diborane and examination of diborane in infrared and Raman Spectra.[11] A few years later, W.N. Lipscomb and his coworkers proved that boron clusters contain both 2c,2e classical, and 3c,2e non-classical bond types.[5] In classical chemical bonds, two nuclei form bonds through one electron pairs and they are called 2c,2e. B-H bonds in clusters are examples of 2c,2e bonds. However, in 3c,2e bond types, three nuclei bond with one electron pairs. B-H-B and B-B-B bonds in clusters are classified as 3c,2e bonds. The reason for 3c,2e bonds is that boron has three valence electrons in four valence orbitals. Explaining 3c,2e bonds also helps to understand the cluster or cage-like structures of the borohydrides.

1.3.5 Aromaticity

By using graph theory, resonance energy of $B_nH_n^{2-}$ type polyhedral boranes were calculated by Aihara and it was shown that $B_nH_n^{2-}$ types closed boron polyhedra (n $\geq$ 6) have positive resonance energies.[12] On this basis, it was thought that these types of compounds have aromatic character. However, this aromatic character is different than the 2-dimensional Hückel aromaticity due to polyhedral cage-like structures. Polyhedral surfaces of boron cages are formed with 3 triangularly bounded boron atoms. Localized orbital of these 3 centered B-B-B bonds interacts with each other and linear combinations of these interactions cause 3-Dimensional aromatic character.[12] It was also shown that not only the closed clusters but also the *nido-* and *arachno-* boranes have aromatic character. However, the aromaticity of closed clusters is much more than the opened ones due to the electron delocalization. The most aromatic borane is $B_{12}H_{12}^{2-}$ since it is also a very symmetric compound.

1.3.6   Electron Deficiency

In the early studies of boron clusters, these compounds were described as 'electron deficient' by Alfred Stock and other chemists because of their non-classical multicenter bonds.[5] This misunderstanding resulted from an incorrect interpretation of the reactivity of borohydrides. After comprehension of the cluster and bonding structure of borohydrides and carboranes, Grimes defended the opposite in the 3rd edition of his book 'carborane'.[13] He argued that the reactivity of small borohydrides consequence of the hydrogen-richness of compounds rather than lack of electrons. Moreover, many boron clusters are considerably stable in air and $B_nH_n^{2-}$ anions and their carborane derivatives are substantially unreactive toward water and oxygen. Among the examples of Grimes, the thermodynamic stability of $B_{12}H_{12}^{2-}$ and $C_2B_{10}H_{12}$ results from the correct number of electrons. These closed cage-like compounds are opened if any electrons are added to the cage. Energy level also increases to a higher level and open cage compounds are formed. Boron clusters are not only electrophilic compounds since they are both electron donors and acceptors under different conditions. According to Grimes, using the 'electron poor' term rather than 'electron deficient' is more convenient for an explanation of structures of boron cluster compounds.

1.3.7   Weakly Coordinating Ability

Long ago, $[PF_6]^-$, $[NO_3]^-$ and $[ClO_4]^-$ anions are labeled as non-coordinating anions. Because in aqueous solution, these anions and metal centers are not coordinated.[14] Nowadays, instead of non-coordinating, weakly coordinating term is used. Part of modern weakly coordinating anions is halogenated borates and carborates. Especially the *closo*-12-vertex borate and carborate anions have many application as weakly coordinating anions because they have high stability. The other reasons for using these *closo*-12-vertex anions are that preparation of these anions is easier and reactivity of them is lower than opened (*nido-* and *arachno-*) anions and smaller

closo- anions. Moreover, partial or perhalogenation enhance the chemical and electronic stability of the *closo*-12-vertex anions and also increase the weakly coordination ability.[15] There are some studies in the literature about the synthesis and application of halogenated carborate anions[16] and halogenated *closo*-dodecaborate anion.[15] In this thesis, perchlorination and perbromination of dodecaborates will be part of studies.

1.3.8   Dodecahydro-*closo*-dodecaborate Anion ($B_{12}H_{12}^{2-}$)

Theoretically, evidence of dodecahydro-*closo*-dodecaborate ($B_{12}H_{12}^{2-}$) could be synthesized and stability was shown in 1955 by Longuet-Higgins & Roberts.[6] After 5 years of this proposal, it was obtained experimentally as a side product of a reaction of triethylamine and 2-iododecaborane.[17] In the literature and in this thesis, it is named dodecahydro-*closo*-dodecaborate. However, in the updated IUPAC recommendation, it is changed as dodecahydrido-*closo*-dodecaborate.[10] It has an icosahedron structure (Figure 9) and a highly symmetric compound with I_h symmetry.[18] This simple compound also has high stability due to its 3-Dimensional aromatic character.[12] Moreover, $B_{12}H_{12}^{2-}$ anion has resistance to high acidic conditions and it is a chemically and thermally stable compound. It has weakly coordinating ability and this skill is important for the application area of this anion. [19,16]

○ B-H
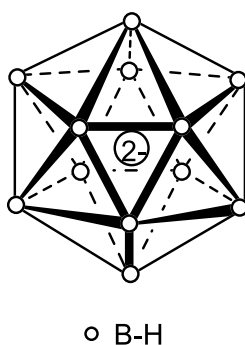
Figure 9. Structure of dodecahydro-*closo*-dodecaborate(2-) ($B_{12}H_{12}^{2-}$)

1.3.8.1   Synthesis of Dodecahydro-*closo*-dodecaborate ($B_{12}H_{12}^{2-}$) Anion

The existence of $B_{12}H_{12}$ was firstly discussed by Eberhardt, Crawford & Lipscomb in 1954 through molecular orbitals of structure.[5] With that, atomic orbital-based calculations were performed by Longuet-Higgins & Roberts.[6] These calculations showed that $B_{12}H_{12}^{2-}$ anion might exist and this anion is stable when compared with $B_{12}H_{12}$. In 1960, $B_{12}H_{12}^{2-}$ anion was firstly obtained as a side product of the reaction of triethylamine and 2-iododecaborane.[17] However, the yield of $B_{12}H_{12}^{2-}$ in this reaction was very low (4%).

For the synthesis of dodecahydro-*closo*-dodecaborate anion, some research groups enhanced different synthetic methods. These methods can be classified according to starting materials.

In the first approach, the synthesis depends on the reaction of H_3B.Lewis base (L) complexes or Lewis bases (generally triethylamine, Et_3N) with different boranes.

Triethyl amine-borane complex reacts with diborane and produces triethyl ammonium dodecahydro-*closo*-dodecaborate at 180 °C and the yield of the reaction is 90% as shown in Scheme 1. [20]

$$2\ (C_2H_5)_3N.BH_3 + 5\ B_2H_6 \longrightarrow ((C_2H_5)_3NH)_2B_{12}H_{12}\ +\ 11H_2$$
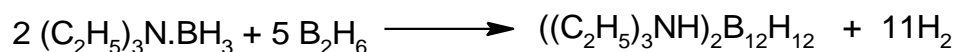
Scheme 1. Synthesis of triethylammonium dodecahydro-*closo*-dodecaborate starting with triethyl amine-borane and diborane at 180 °C

This reaction can be performed with different H_3B.L complexes. When L is trimethylamine, the yield of the reaction decreases 40-60% or when L is trimethyl phosphine, the yield of the reaction is very low. Also, some side products are formed like $B_{12}H_{11}N(CH_3)_3^-$ and $B_{12}H_{11}P(CH_3)_3^-$. The results showed that these reactions depend on the base-boron adduct. The hindered bases like triethylamine give higher yields than less hindered ones. Less hindered bases also cause the formation of $H_2B(base)_2^+$ type cations.

Triethylamine-borane complex reacts with pentaborane(9) at 125 ^oC and triethylammonium dodecahydro-*closo*-dodecaborate is formed in 90% yield.[21] Scheme 2 depicts this reaction.

$$2 \ (C_2H_5)_3N. \ BH_3 + 2B_5H_9 \xrightarrow[\text{10 hours}]{125 \ ^oC} ((C_2H_5)_3NH)_2B_{12}H_{12} + 5 \ H_2$$
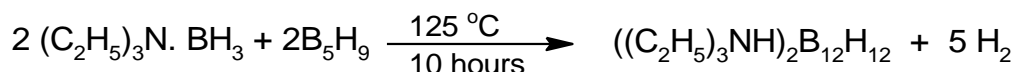
Scheme 2. Synthesis of triethylammonium dodecahydro-*closo*-dodecaborate starting with triethyl amine-borane and pentaborane at 125 ^oC

Triethylamine-borane complex reacts with decaborane(14) at 190 ^oC under pressure and triethylammonium dodecahydro-*closo*-dodecaborate is formed in 92% yield as shown in Scheme 3.[21]

$$2(C_2H_5)_3N.BH_3 + B_{10}H_{14} \xrightarrow[\text{ultrasene}]{190 \ ^oC} ((C_2H_5)_3NH)_2B_{12}H_{12} + 3 \ H_2$$
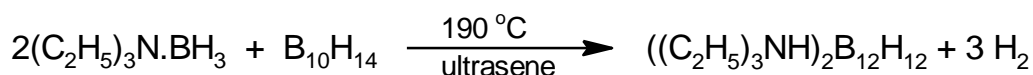
Scheme 3. Synthesis of triethylammonium dodecahydro-*closo*-dodecaborate starting with triethyl amine-borane and decaborane at 190 ^oC

Instead of the Lewis base-borane complex, the Lewis base can be used but the yield of the reactions decreases.

In the second approach, the synthesis depends on the reaction of alkali metal tetrahydroborate with $H_3B.L$ complex or boranes.[21]

Sodium borohydrate reacts with diborane to produce sodium dodecahydro-*closo*-dodecaborate anion and the yield range of this reaction is from 75 to 85 % (Scheme 4).[20]

$$2 \ NaBH_4 + 5 \ B_2H_6 \xrightarrow[\text{100-180 }^oC]{Et_3N \ (\text{solvent})} Na_2B_{12}H_{12} + 13 \ H_2$$
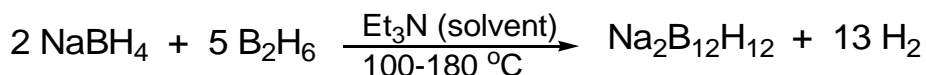
Scheme 4. Synthesis of sodium dodecahydro-*closo*-dodecaborate starting with sodiumborohydride and diborane at 100-180 ^oC

Sodium borohydride reacts with decaborane to produce sodium dodecahydro-*closo*-dodecaborate anion. In the 1960s the yield of this reaction was 60% [22] but in the 1970s it was increased to 91% [23] (Scheme 5).

$$2 \ NaBH_4 \ + \ B_{10}H_{14} \ \xrightarrow[\text{diglyme}]{160 \ ^{\circ}C} \ Na_2B_{12}H_{12} \ + \ 5 \ H_2$$
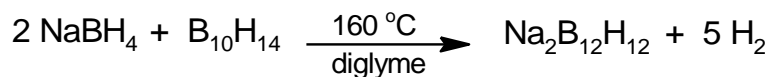
Scheme 5. Synthesis of sodium dodecahydro-*closo*-dodecaborate starting with sodiumborohydride and decaborane at 160 $^{\circ}C$

In the highest yield synthesis of dodecahydro-*closo*-dodecaborate (95%), sodium borohydride or potassium borohydride reacts with $Me_3N.BH_3$ complexes in alkanes that have a high boiling point like dodecane and hexadecane at 200 to 250 $^{\circ}C$.[18]

In the third approach, the synthesis depends on the pyrolytic transformation between borohydrides. Although pyrolysis of $(Et_4N)BH_4$ gives a mixture of $(Et_4N)_2B_{12}H_{12}$ and $(Et_4N)B_{10}H_{14}$, pyrolysis of $Et_3N.BH_4$ gives $(Et_3NH)_2B_{12}H_{12}$ as a main product. [24,25]

During pyrolysis reaction of octahydrotriborate anion, the major product is altering based on temperature, nature of cation, and solvent. These conditions also affect the yield of the reactions. In the 1960s, sodium octahydrotriborate ($Na[B_3H_8]$) was refluxed in diethylene glycol dimethyl ether (diglyme) and as a result of pyrolysis reaction $(Et_3NH)_2B_{12}H_{12}$ was obtained with 65% yield.[25] After that, the yield of the reaction was enhanced to 90%. The cation of the octahydrotriborate changes as potassium, products of pyrolysis are a mixture of $[B_{12}H_{12}]^{2-}$ and $[B_9H_9]^{2-}$ even if the temperature is above 200 $^{\circ}C$.[24] The cation changes as cesium or rubidium, products of pyrolysis are a mixture of $[B_{12}H_{12}]^{2-}$, $[B_{10}H_{10}]^{2-}$ and $[B_9H_9]^{2-}$ when the temperature of pyrolysis is above 200 $^{\circ}C$.[26] Pyrolysis reactions of calcium, magnesium, and strontium octahydrotriborate are also applied to obtain $[B_{12}H_{12}]^{2-}$ in acceptable yield.[27] Although pyrolysis of tetrapropylammonium salt of octahydrotriborate gives the $[B_{12}H_{12}]^{2-}$ as a major product, tetramethyl, tetraethyl, and tetrabutylammonium salts of octahydrotriborate give the mixture of $[B_{12}H_{12}]^{2-}$, $[B_{10}H_{10}]^{2-}$ and $[B_9H_9]^{2-}$.[28]

In other approaches for the synthesis of $[B_{12}H_{12}]^{2-}$, instead of starting with borohydride, NaH reacting with BCl_3-H_2 at 250–350 °C yields $NaBH_4$ and $Na_2[B_{12}H_{12}]$ but $(Na_2[B_{12}H_{12-n}Cl_n]$ ($n = 1$–6)) chlorinated derivatives also occur as a result of a reaction.[29] This method is usually ignored because of its production of mixtures.

In another approach, boric acid reacts with sodium borates and different reducing materials to obtain $[B_{12}H_{12}]^{2-}$.[30] Moreover, cage expansion reactions of $[B_{10}H_{10}]^{2-}$ and $[B_{11}H_{11}]^{2-}$ gave the $[B_{12}H_{12}]^{2-}$ anion.[31,32]

With all of the reaction reviewed, we decided that we would continue our synthesis by pyrolysis reaction method starting with $NaBH_4$. The reactions performed will need inert atmospheres. Along this line, Knapp and his coworkers' procedure looks promising as to applying in our laboratories.[33]

1.3.8.2   Cation Exchange of dodecahydro-*closo*-dodecaborate Anion

As stated before, dodecahydro-*closo*-dodecaborate anion and its derivatives are weakly coordinating anions. Solubility of the salts of dodecahydro-*closo*-dodecaborate changes from cation to another cation. With this in mind, cation exchange reactions were studied. According to the literature knowledge, Na^+ and K^+ salt of dodecahydro-*closo*-dodecaborate anion are more water soluble salt, Cs^+ salt of anion is less water soluble when it compared with Na^+ and K^+.[33] Cations like Ba^{2+} and Cu^{2+} are water soluble. However, strongly polarizable cation salts like Ag^+, Cu^+ and Hg^{2+} are water insoluble. Salts of dodecahydro-*closo*-dodecaborate with ammonium cation (R_3HN^+ and R_4N^+) such as Me_3NH^+, Et_3NH^+, Bu_3NH^+, Me_4N^+, Et_4N^+, Bu_4N^+, $hexyl_4N^+$ are also insoluble in water solubility but they are soluble in organic solvents.[34]

Table 4. Solubility of dodecahydro-*closo*-dodecaborate with different cations

Cation	Solubility in Water
K^+	Soluble
Na^+	Soluble
Ba^{2+}	Soluble
Cu^{2+}	Soluble
Cs^+	Low Soluble
Ag^+	Insoluble
Cu^+	Insoluble
Hg^{2+}	Insoluble
R_3NH^+	Insoluble
R'_4N^+	Insoluble

R= Me, Et, Bu,

R'= Me, Et, Bu, hexyl

1.3.8.3 Applications of Dodecahydro-*closo*-dodecaborate ($B_{12}H_{12}^{2-}$)

Dodecahydro-*closo*-dodecaborate anion and its derivatives have significant application areas for different purposes. High borohydrides are known as materials that have high energy density. This ability renders them for military purposes. Through the reports of USA Ballistic Research Laboratories, there were many studies to enhance the burning rates of propellants (very high burning rate; VHBR) and dodecahydro-*closo*-dodecaborate and decaborate were used as catalysts and oxidizer on these studies.[35] Salts of dodecahydro-*closo*-dodecaborate have kinetic stability to both oxidation and reduction and also have resistance thermal decomposition.[36] Per functionalization of $B_{12}H_{12}^{2-}$ such as $B_{12}Cl_{12}^{2-}$ makes these

potentials more reversible.[37] That's why; Li salts of $B_{12}H_{12}^{2-}$ and $B_{12}Cl_{12}^{2-}$ are used as non-aqueous electrolytes for rechargeable lithium batteries. [38,39] In the early 1970s, room-temperature stable liquid crystal compounds were used for electro-optic devices.[40] For a useful liquid crystal; spherical symmetry, thermally and chemically stability, solvolytic stability, and electronic polarizability are necessary. Due to these properties, dodecahydro-*closo*-dodecaborate clusters and some other boron clusters are very useful for liquid crystals and are used for optic materials.[40] Nowadays, medicine is a mostly used area for the application of dodecahydro-*closo*-dodecaborate due to low toxicity.[41] Boron Neutron Capture Therapy (BNCT) is the main area in medicinal usage.[42]

1.4   Aryl Diazonium Cations

Aromatic diazonium cations are essential intermediates for synthesis of organic azo dyes. Azo dyes recently received more attention due to its photochemical properties (cis-trans conversion).[43] These cations are known as high energy materials. Although these highly energetic cations have wide range application areas, the serious drawbacks of the diazonium cations are explosive nature and instability.[44] Due to the instability of diazonium cations, it is hard to isolate the diazonium intermediate. The successive reactions should be done in the same medium as soon as diazonium is formed at lower temperatures since they are very sensitive against heat and mechanical force when isolated.[44] Therefore, transferring diazonium cations to other reaction media require a safe way. Although isolating the diazonium cation is not safe, exchanging the counter anion could make it possible. For instance, BF_4^- and $TosO^-$ salts are reported to be stable. [44]

 Aryl diazonium hexafluorophosphate, tetrafluoroborates and diazonium o-benzenedisulfonimides have been isolated and the electrochemical properties were studied.[45] Furthermore, 4-substituted phenyldiazonium tetrafluorobarate was used in electrochemical reduction reactions.[45] Diazonium modified electrodes are also used in sensitive DNA sensor.[46] It is also used in new energy technology trend Microbial

Fuel Cell (MFC) application.[47] According to literature, in order to achieve electroactive biofilms, aryldiazonium reaction is a new alternative.[47]

Due to versatility of aryl diazonium salts, isolated diazonium salts are in high demand. As mentioned earlier, several counter anions were found to stabilize diazonium salts enough to isolate them. However, the substituent on the aryl group changes the stability of the aryl diazonium salts. Therefore, there is a need for new stabilizing counter anions for aryl diazonium salts.

CHAPTER 2

AIM OF THE STUDY

Aryl diazonium cations are highly reactive compounds. They are usually formed as Cl⁻ salts. When one wants to isolate the chloride salts, they violently explode. It is almost impossible to store these salts. However, BF_4^- and $TosO^-$ salts were found to be stable and isolable. Nevertheless, literature reports that not all the diazonium salts are stabilized by these counter anions. In this thesis, dodecahydro-*closo*-dodecaborate anion will be examined as a stabilizing counter anion. For this, dodecahydro-*closo*-dodecaborate, perchlorinated *closo*-dodecaborate, and perbrominated *closo*-dodecaborate will be synthesized starting from $NaBH_4$.

Y= Cl, OH, NO₂
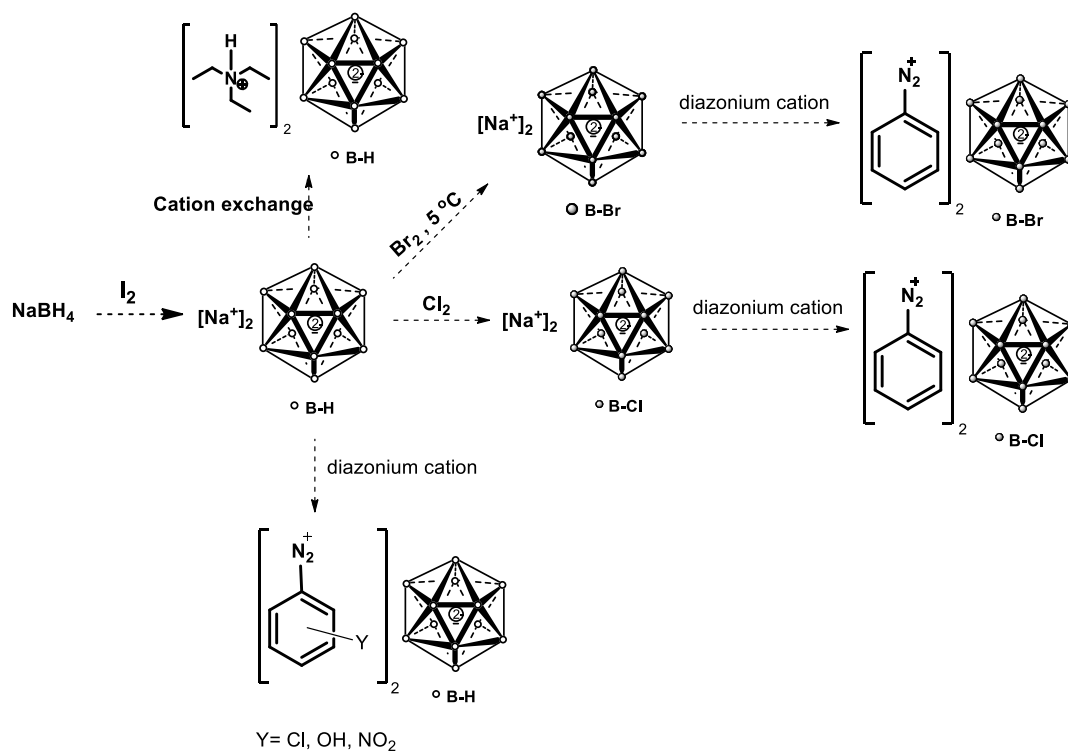
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Synthesis

3.1.1 Synthesis of dodecahydro-*closo*-dodecaborate

In the literature, several different methods have been used to synthesize dodecahydro-*closo*-dodecaborate. Several methods start with diborane which is difficult to handle under ordinary laboratory conditions. Another method starts with decaborane which is neurotoxic and expensive. One of the alternative syntheses has been developed which uses sodium borohydride and iodine. For this study, the latter synthesis was employed with modifications to get dodecahydro-*closo*-dodecaborate. This chosen method is simple and safe to run in our laboratories (*vide infra*).

For the synthesis of dodecahydro-*closo*-dodecaborate, experimental set up was found to be extremely important to have high yields. Both sodium borohydride and diglyme have moisture sensitivity. Furthermore, air sensitivity also occurs during the course of the reaction. Therefore, the reaction has been performed under inert Argon atmosphere. The experimental setup used in this study is shown in Figure 10. During the reaction, toxic and volatile small boron compounds and hydrogen gas are formed. To pacify these toxic volatile byproducts, the reaction was done in a well-ventilated hood and acetone trap was used.
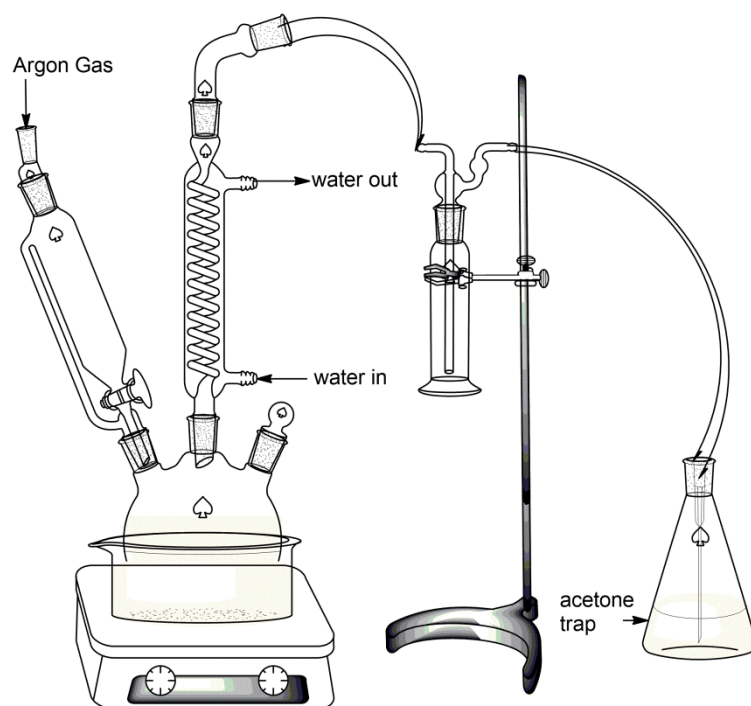
Figure 10. Experimental set up for the synthesis of dodecahydro-*closo*-dodecaborate

Synthesis of dodecahydro-*closo*-dodecaborate is a stepwise reaction. In the first step, sodium borohydride reacts with iodine in diglyme at 110 °C. In this step, sodium octahydrotriborate is formed *in situ* as shown in Scheme 6. Sodium borohydride has low solubility in diglyme at room temperature, so temperature of the oil bath was raised to 110 °C. Iodine solubility is good in diglyme yet slow. With high stirring rate, iodine was dissolved in diglyme in a few hours at room temperature. The other important point is addition rate of iodine to $NaBH_4$ solution in diglyme. When iodine solution addition is more than 10 ml/min, the yield of end product is lower than 10 %. When the addition rate is decreased to 4 ml/min, the yield is significantly increased up 60 %. Furthermore, literature reports that the ratio of $NaBH_4$: I_2 should be between 3 and 6. [33]

$$3\ NaBH_4 + I_2 \longrightarrow NaB_3H_8 + 2\ NaI + 2H_2$$

Scheme 6. Synthesis of sodium octahydrotriborate *in situ*

After the addition of iodine is completed, the second step in the synthesis begins. Second step of this reaction involves the thermal decomposition reactions. Octahydrotriborate decomposes to mainly dodecahydro-*closo*-dodecaborate at higher temperatures more than 180 °C. To get high yields of final product, reaction time should be more than 24 hours and temperature needs to be higher than 180 °C. Therefore, in this part, temperature of the oil bath was increased to 200 °C and the reaction was furthered more than overnight. To get rid of diglyme, distillation was set up and diglyme was collected. The overall reaction scheme is given in Scheme 7.

$$5 \ NaB_3H_8 \longrightarrow Na_2B_{12}H_{12} + 3 \ Na[BH_4] + 8 \ H_2$$
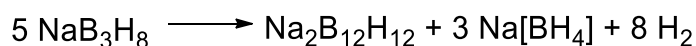
Scheme 7. Synthesis of sodium dodecahydro-*closo*-dodecaborate

For purification of dodecahydro-*closo*-dodecaborate, acidic work-up should be done to get rid of any lower boranes. Hydrochloric acid solution was added to convert lower boranes to boric acid (Scheme 8). Solution was kept at 4 °C overnight for filtration since boric acid was crystallized in cold water. On the other hand, sodium salt of dodecahydro-*closo*-dodecaborate dissolved in water well.

$$Na[BH_4] + HCl + 3 \ H_2O \longrightarrow B(OH)_3 + NaCl + 4H_2$$
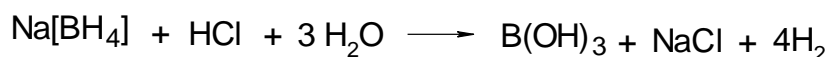
Scheme 8. Conversion of sodium borohydride to boric acid

After filtration, sodium salt was converted to triethylamonium salt since trialkylammonium salts precipitate in water and separated by filtration easily (Scheme 9). Trialkylammonium salts of dodecahydro-*closo*-dodecaborates dissolves in common organic solvents. Other byproducts (NaI and NaCl) stayed in water.
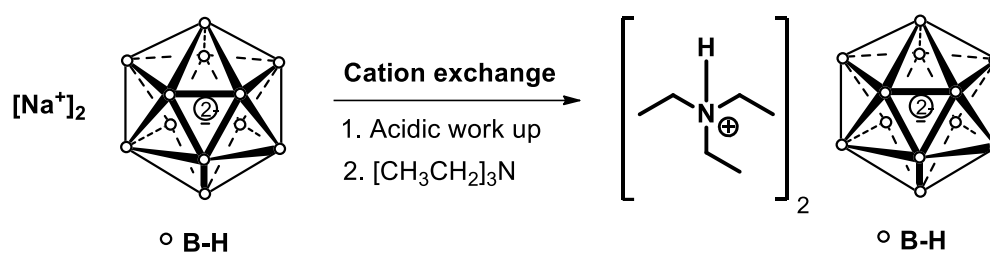
Scheme 9. Synthesis of triethylammonium dodecahydro-*closo*-dodecaborate

Characterization was done with IR (Figure 11). In the spectrum, there was a peak around 2476 cm^{-1} (B-H stretching), N-H stretching was monitored at 3125 cm^{-1} and data is in agreement with literature. [33]
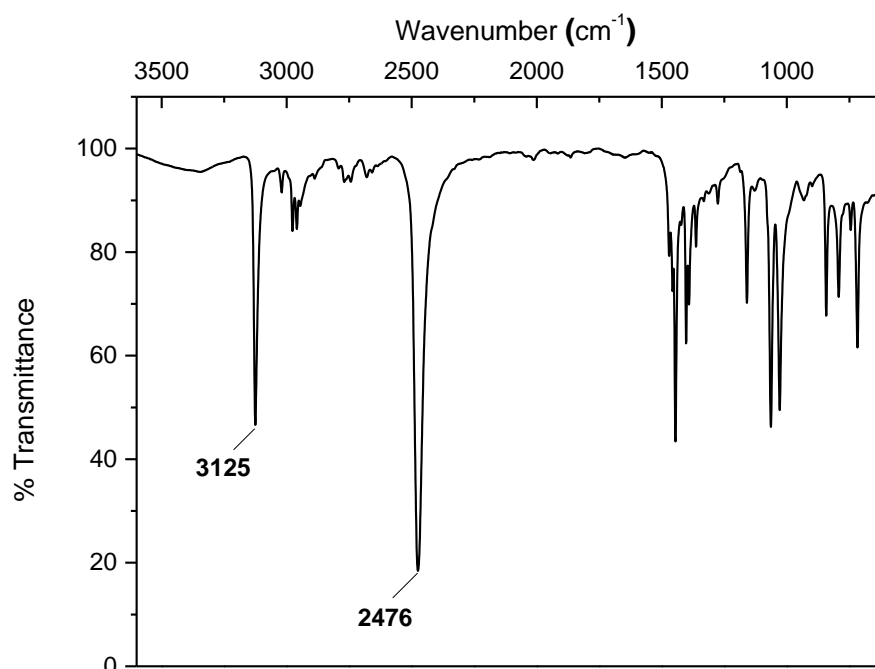
Figure 11. IR spectrum of compound triethylammonium dodecahydro-*closo*-dodecaborate

3.1.2   Synthesis of dodecachloro-*closo*-dodecaborate

Halogenation of dodecahydro-*closo*-dodecaborate anion increases the weakly coordinating ability of the borane cages. As distinct from classical anion, dodecahydro-*closo*-dodecaborate has different chemical properties. In order to

change the Coulomb repulsion, dianionic dodecahydro-*closo*-dodecaborate constrains the cations to dimerization and increases the lattice enthalpy.[15] However, these lead to decrease the solubility of dication-dianion. This in mind, to increase the weakly coordinating ability of dodecahydro-*closo*-dodecaborate, perchlorination was performed.

There are different synthesis methods in the literature for dodecachloro-*closo*-dodecaborate. In this study, two of these methods were used for the synthesis of the two different salts of dodecachloro-*closo*-dodecaborate. For the synthesis of triethylammonium salt of dodecachloro-*closo*-dodecaborate, important part is chlorine bubbling inside the reaction. Simple and effective set-up was used which is shown in the Figure 12.
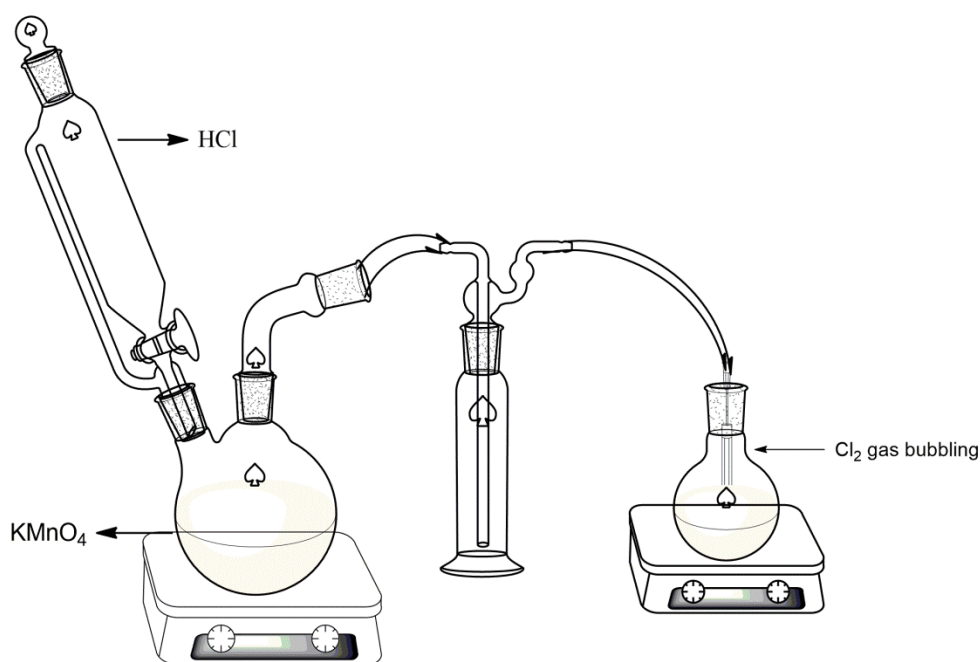
Figure 12. Experimental set up for the synthesis of triethylammonium dodecachloro-*closo*-dodecaborate

HCl was dropwise added into permanganate solution in water and chlorine gas was formed. This gas is bubbled through sodium salt of dodecahydro-*closo*-dodecaborate in water at room temperature for 5 hours and the reaction was refluxed at 100 °C for

a few hours. Firstly, partial halogenation was occurred (Scheme 10). It was understood by IR spectrum since there was a peak around in 2549 cm^{-1} (Figure13).

$$Na_2B_{12}H_{12} + 12\ Cl_2 \xrightarrow{Et_3N} [Et_3NH]_2B_{12}H_{(12-x)}Cl_x + x\ HCl + 2\ NaCl$$
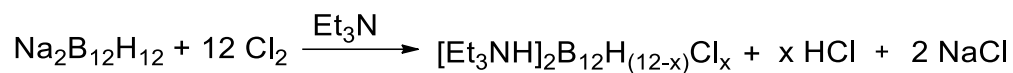
Scheme 10. Synthesis of partially chlorinated *closo*-dodecaborate
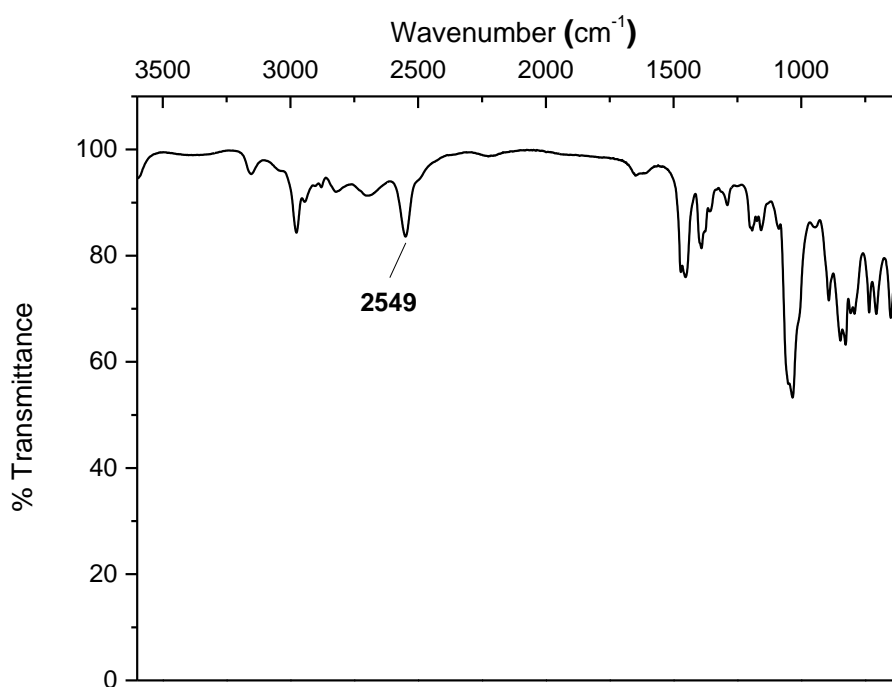
Figure 13. IR spectrum of partially chlorinated *closo*-dodecaborate

Reaction was monitored by IR spectroscopy until the B-H peak at around 2476 cm^{-1} disappeared. This means, after the 8 hours with chlorine bubbling at 100 °C, the full chlorination of *closo*-dodecaborate was accomplished with isolated yield of 54% (Scheme 11). B-H peak around 2549 cm^{-1} in the IR spectrum was disappeared shown in Figure 14.
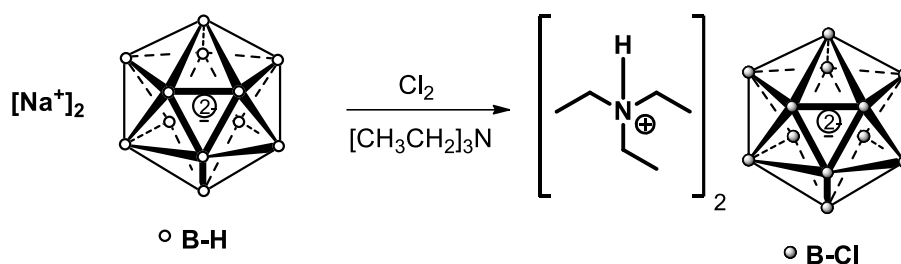
Scheme 11. Synthesis of triethylammonium dodecachloro-*closo*-dodecaborate
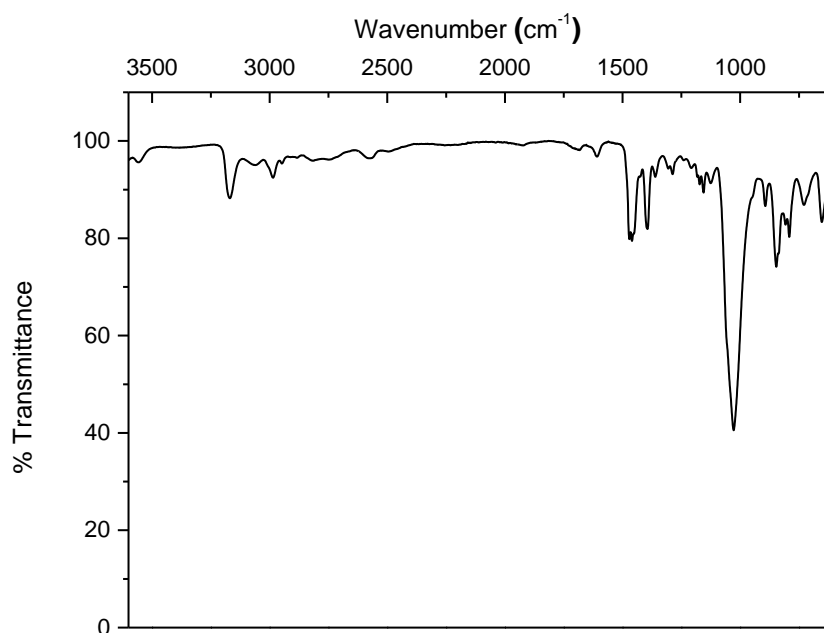
Figure 14. IR spectrum of triethylammonium dodecachloro-*closo*-dodecaborate

Although the synthesis method seems simple, care must be taken since chlorine gas is poisonous. Moreover, yield of the reaction was not high enough. Therefore, another method was needed.

In second method, chlorine gas was not used. During the synthesis of cesium salt of dodecachloro-*closo*-dodecaborate, sulfuryl chloride was used as a chlorine source and the reaction was shown in Scheme 12. Reaction was started with dissolution of cesium salt of dodecahydro-*closo*-dodecaborate in acetonitrile as reported in the literature.[46] However, in our study, sodium salt of dodecahydro-*closo*-dodecaborate was used as a starting material instead of cesium salt, so it did not dissolve well. When the addition of sulfuryl chloride started, dissolution increased. To have better

yield, the addition of the sulfuryl chloride needs to be slow. At the end of the addition, the reaction was refluxed for 8 hours to complete the reaction. Although it was not obtained purely, the product was converted into cesium salt. Sodium salt of perchlorinated compound in water was added to cesium chloride and the cesium of dodecachloro-*closo*-dodecaborate was obtained as a white product.
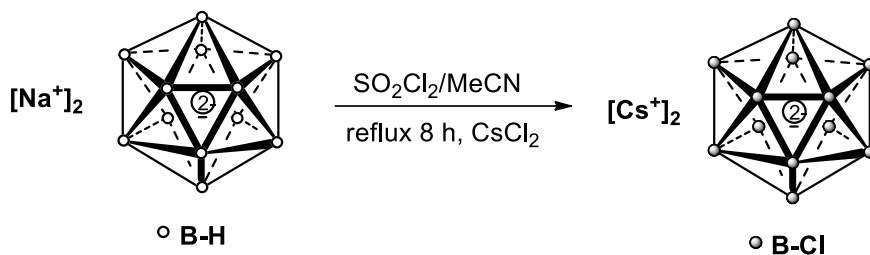
Scheme 12. Synthesis of cesium dodecachloro-*closo*-dodecaborate

B-H peak in the IR spectrum disappeared, there is no peak around 2480-2550 cm^{-1} indicating that there are no B-H peaks shown in Figure 15. The yield of the product was almost equal to the previous method. However, this method is much easier and safer to run in our laboratories.
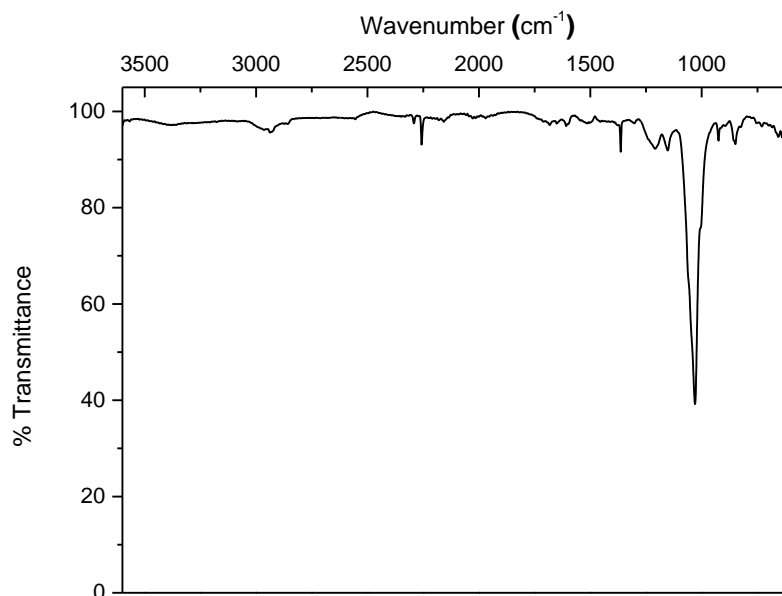
Figure 15. IR spectrum of cesium dodecachloro-*closo*-dodecaborate

3.1.3 Synthesis of dodecabromo-*closo*-dodecaborate

In order to make a comparison between the halogenated *closo*-dodecaborates, we also tried to synthesis of dodecabromo-*closo*-dodecaborate. This reaction started with the sodium salt of dodecahydro-*closo*-dodecaborate in water-methanol (1:1) solvent system. Bromine was added to the sodium salt of dodecahydro-*closo*-dodecaborate at 5 °C dropwise. Then, the chlorine gas was passed through the solution and the reaction temperature was raised to 50 °C. Chlorine was used to activate the bromine. The product was precipitated by the addition of triethylammonium chloride into the water solution (Scheme 13).
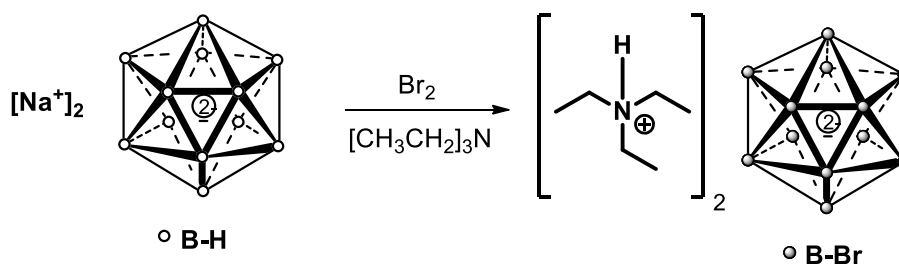
Scheme 13. Synthesis of triethylammonium dodecabromo-*closo*-dodecaborate

B-H peak around 2476 cm^{-1} in the IR disappeared and N-H peak around 3168 cm^{-1} appeared as shown in Figure 16. This shows the perbromination reaction is performed.
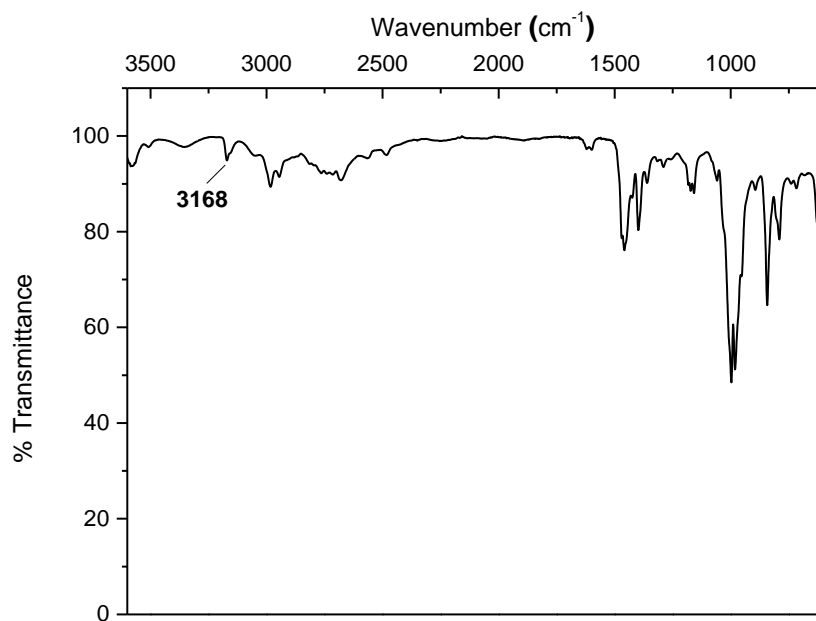
Figure 16. IR spectrum of compound triethylammonium dodecabromo-*closo*-dodecaborate

3.2   Cation Exchange of dodecahydro-*closo*-dodecaborate

There are many reports about cation exchange reactions of dodecahydro-*closo*-dodecaborate salts.[21,26,34]   Since the cation of the dodecahydro-*closo*-dodecaborate salts changes the solubility of the compound in solvents. As mentioned in the introduction part, trialkyl ammonium salts of dodecahydro-*closo*-dodecaborate are water insoluble but they are soluble in different organic solvents. On the other hand, sodium and potassium salts of dodecahydro-*closo*-dodecaborates are almost completely soluble in water. In our studies, to recover dodecahydro-*closo*-dodecaborate from water, trialkyl ammonium cation was used; when the reaction runs on the cage, the cation was exchanged with sodium cation. Different solubility behavior with different cations gave us an important question which is how it works with aryl diazonium cations and is it stable? The exchange is basically done with treatment of the trialkyl ammonium salts with NaOH followed by evaporation of volatiles.

32

3.2.1 Synthesis of benzenediazonium dodecahydro-*closo*-dodecaborate

Synthesis of diazonium cation reactions starts in classical way with aniline or its derivatives. After making aniline solution acidic in water, the reaction temperature decreased to 0 °C with ice bath. Sodium nitrite solution with water was added very slowly at 0 °C. Keeping the reaction temperature at 0 °C (as soon as possible) plays an important role in these reactions since diazonium cations are very reactive and explosive compounds. Then, sodium salt of dodecahydro-*closo*-dodecaborate solution with water was added dropwise and brown precipitates were obtained and isolated (Scheme 14).
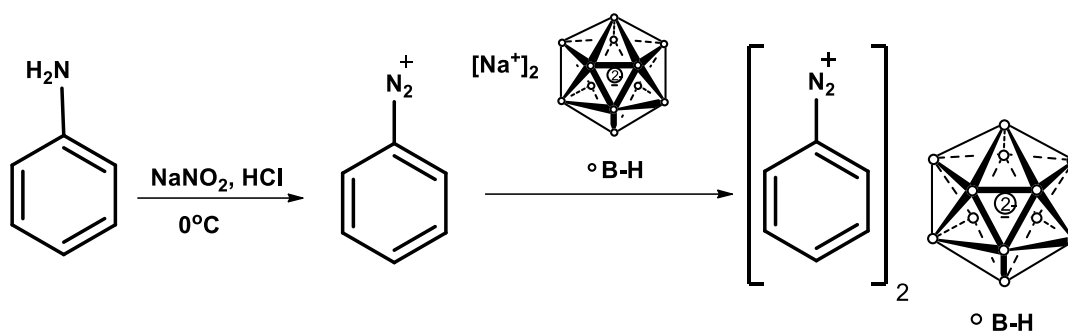
Scheme 14. Synthesis of benzenediazonium dodecahydro-*closo*-dodecaborate

The main characterization was done using IR spectroscopy. It is known that B-H stretching frequency appears at around 2476 cm^{-1} whereas N≡N absorption is around 2272 cm^{-1} (Figure 17). Benzenediazonium dodecahydro-*closo*-dodecaborate obtained in the reaction has the characteristic peaks of B-H and –N$_2^+$ units (Figure 17). Further characterization was done with HRMS to check if there is coupling between benzenediazonium and dodecahydro-*closo*-dodecaborate. However, HRMS result shows that coupling reaction did not occur (Appendix C for HRMS).
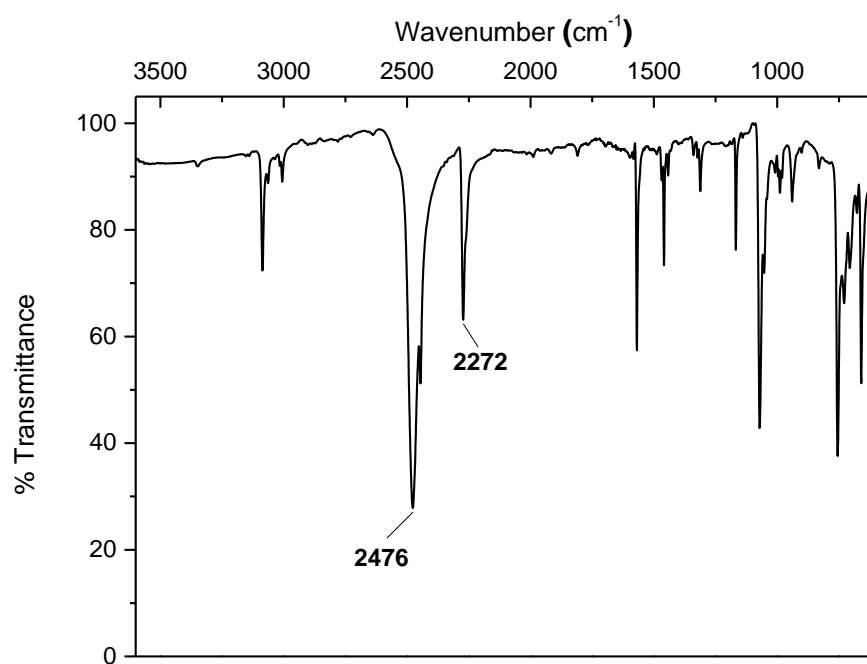
Figure 17. IR spectrum of compound benzenediazonium dodecahydro-*closo*-dodecaborate

As known, diazonium salts are not very stable compounds. Therefore, to control the stability of the final product, the compound was stored and checked by IR spectroscopy every week for four weeks (Figure 18). It has been observed that there was no change in the IR stretching frequency of the final product.
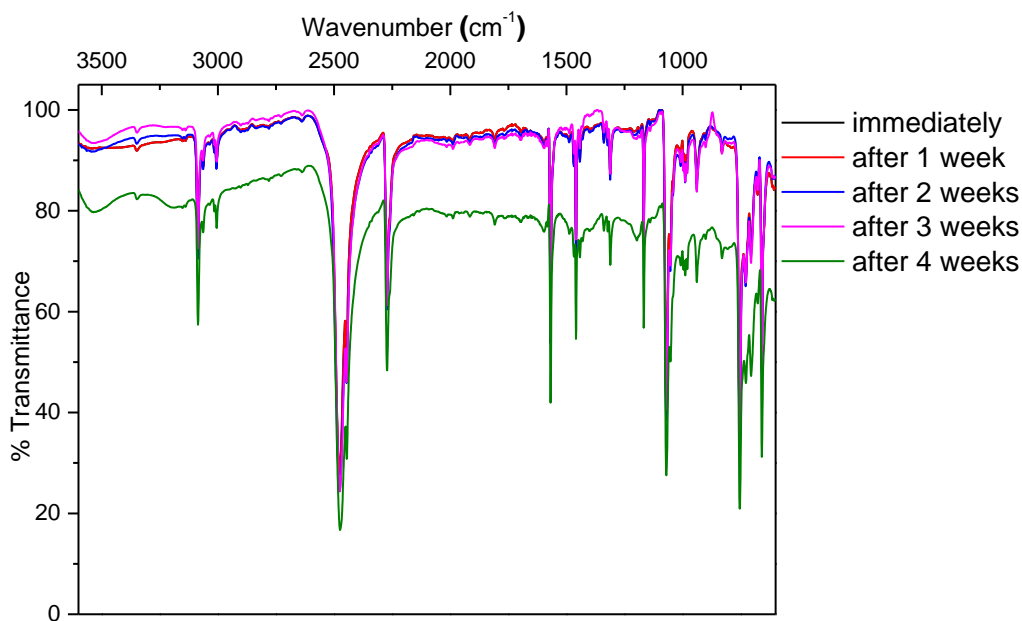
Figure 18. IR spectra of compound benzenediazonium dodecahydro-*closo*-dodecaborate for 4 weeks

Solubility of the benzenediazonium dodecahydro-*closo*-dodecaborate tested in various organic solvent and water. Even though it generally dissolves in organic solvents, it does not dissolve in water. Tested solvents are shown in table 5.

Table 5. Solubility of benzenediazonium dodecahydro-*closo*-dodecaborate in different solvents

Solvent	Solubility
Water	Insoluble
Chloroform	Insoluble
Methanol	Slightly soluble
Ethanol	Slightly soluble
Acetonitrile	Slightly soluble
Acetone	Soluble (not completely)
Dimethyl sulfoxide	Soluble

3.2.2 Synthesis of 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate

In order to monitor the effect of electron withdrawing group on diazonium cation and its reactions, 2-chloroaniline was used as a starting material. Acidic solution of 2-chloroaniline was cooled to 0 °C and turned to diazonium cation by adding sodium nitrite solution with water. When the sodium salt of dodecahydro-*closo*-dodecaborate solution with water was added into diazonium solution, orange precipitate occurred (Scheme 15).
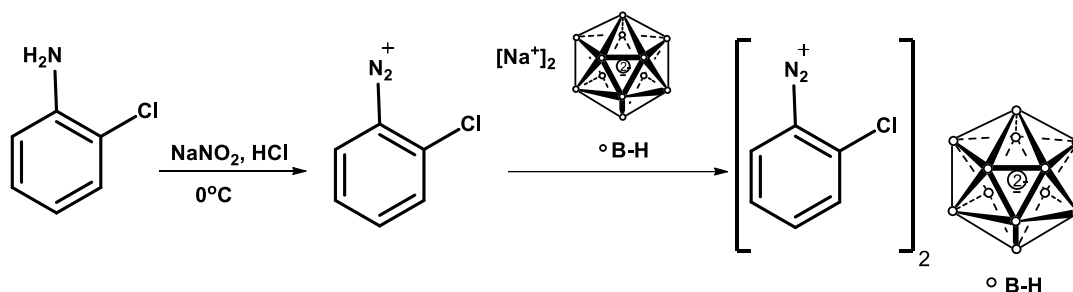
Scheme 15. Synthesis of 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate

This shows the electron withdrawing group does not cause azo coupling reaction. Diazonium cation is still stabilized with dodecahydro-*closo*-dodecaborate dianion. It is characterized by IR spectroscopy and B-H stretching of the compound was around 2453 cm^{-1} and N≡N peak was around 2266 cm^{-1} (Figure 19).
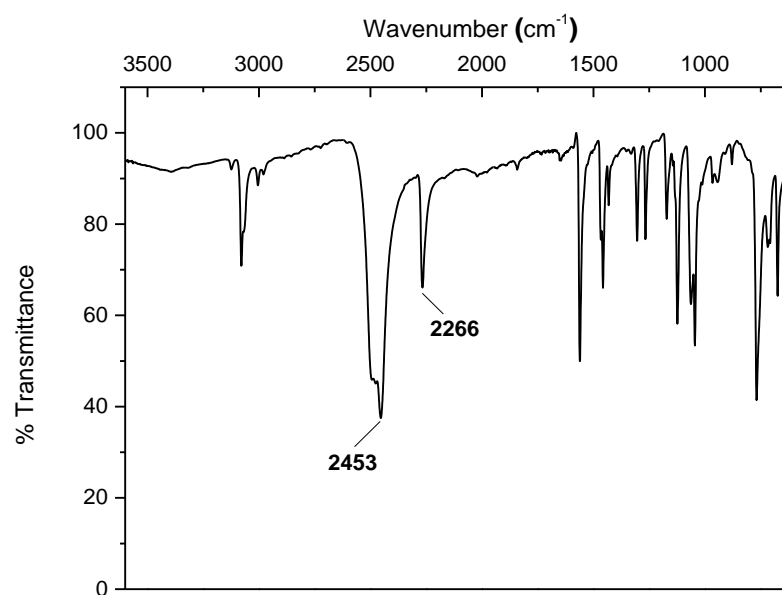
Figure 19. IR spectrum of 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate

The diazonium salt derived from *o*-chloroaniline was also tested for its stability by IR spectroscopy for 4 weeks. It was found that the compound was stable more than four weeks under ambient conditions (Figure 20).
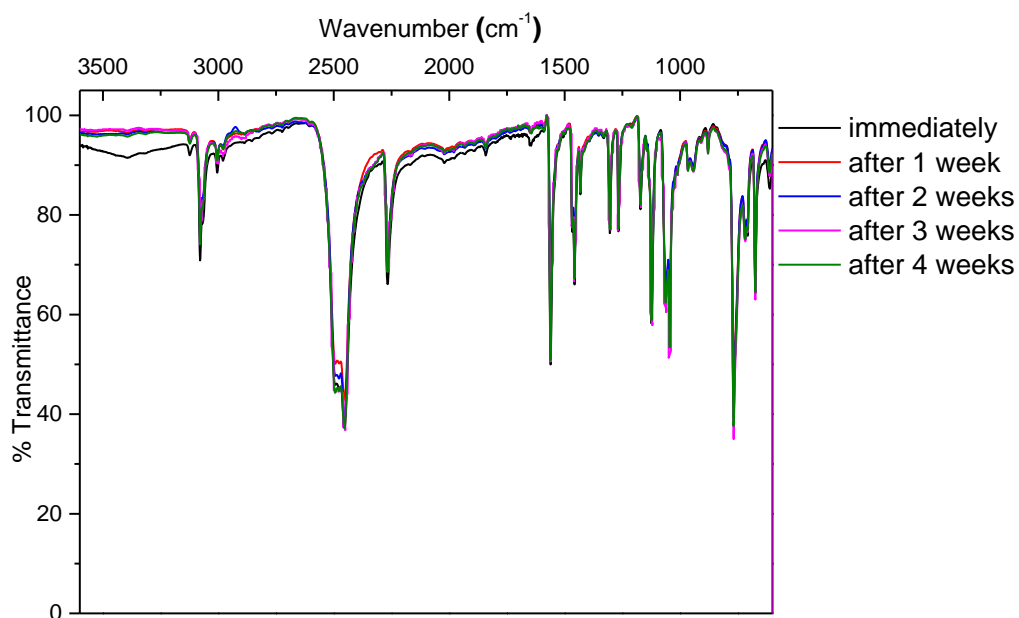
Figure 20. IR spectra of 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate for 4 weeks

^{1}H NMR was measured in DMSO in Figure 21. The signals between 7 and 8 ppm belong to the aromatic protons, and the signal between 0 and 2 ppm belongs to the proton from dodecahydro-*closo*-dodecaborate. The aromatic peaks shifting to low field (~8 ppm) indicates that an electron withdrawing group ($-N_2^+$) is attached to the benzene ring.
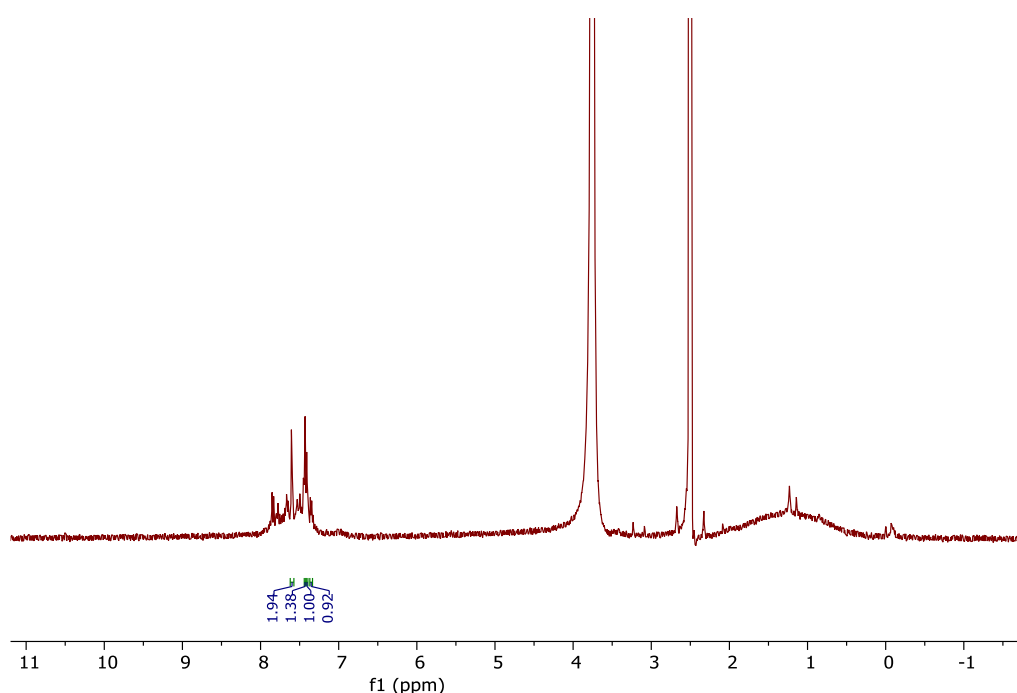
Figure 21. ^{1}H NMR spectrum of 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate in DMSO-d$_6$

3.2.3   Synthesis of 4-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate

To make a comparison between the stability of different diazonium salts of dodecahydro-*closo*-dodecaborate, 4-chloroaniline was also used as a starting compound. As in the previous preparation of diazonium salts, sodium nitrite solution was added into the acidic solution of 4-chloroaniline dropwise. Then, just after

adding the sodium salt of dodecahydro-*closo*-dodecaborate solution with water, dark orange precipitates were observed (Scheme 16).

Scheme 16. Synthesis of 4-chlorodiazonium salt of dodecahydro-*closo*-dodecaborate

During the characterization, it was monitored in the IR spectroscopy that the B-H peak of the dodecahydro-*closo*-dodecaborate shifted to 2469 cm^{-1} and N≡N stretching frequency appeared at around 2268 cm^{-1} (Figure 22). It is different than the B-H peak of 4-chlorodiazonium salt of dodecahydro-*closo*-dodecaborate.
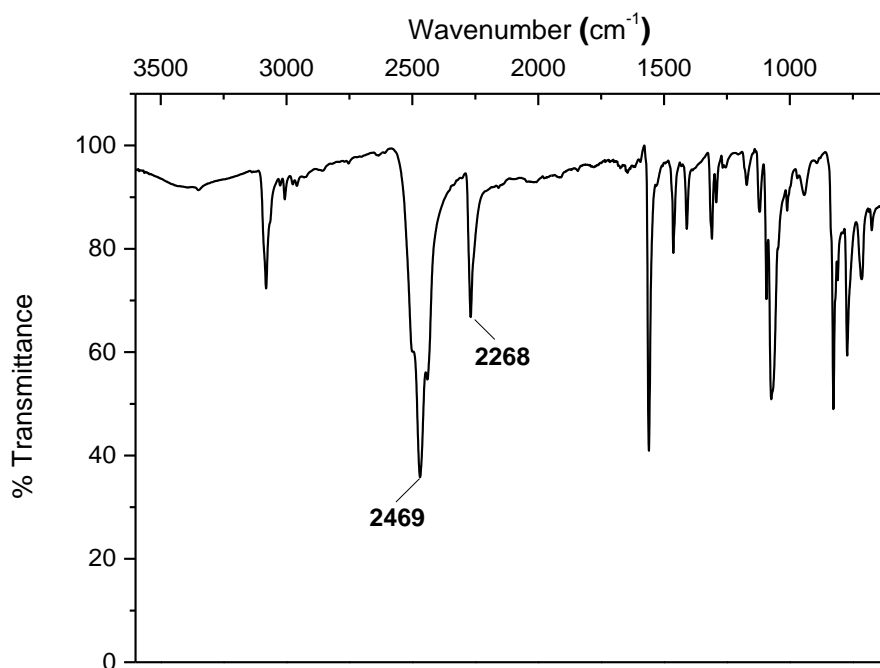
Figure 22. IR spectrum of 4-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate
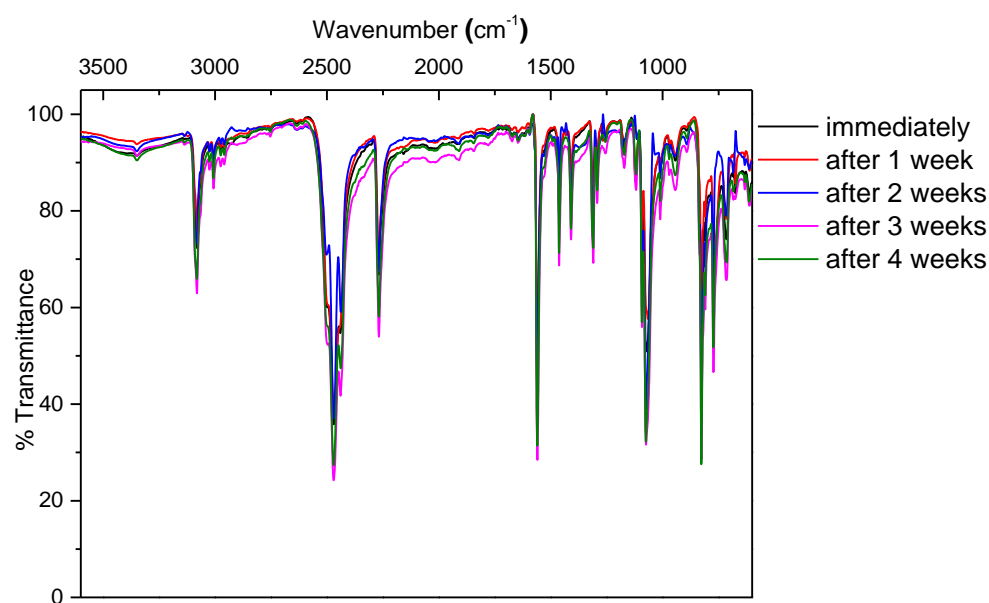
Figure 23. IR spectra of 4-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate for 4 weeks

Further characterization with HRMS confirmed the IR results (Appendix C). Moreover, stability of the compound was monitored with the IR for four weeks and shown in Figure 23. ^{1}H NMR was measured in DMSO in Figure 24. The signals between 8 and 9 ppm belong to the protons on the aromatic 4-chlorobenzenediazonium cation and the signal between 0 and 2 ppm belongs to the proton from dodecahydro-*closo*-dodecaborate.
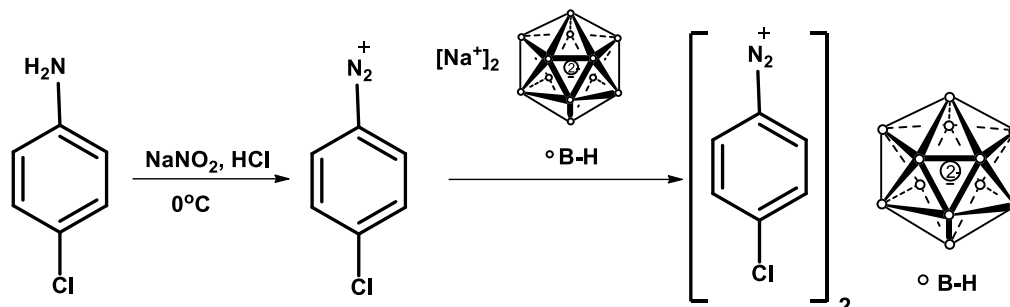

Figure 24. ^{1}H NMR spectrum of 4-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate in DMSO-d_6

### 3.2.4 Synthesis of 4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate

The reaction was started with 4-aminophenol acidic solution with water and turned it to a diazonium cation by using sodium nitrite solution as in classical diazonium preparation method.[45] When sodium salt of dodecahydro-*closo*-dodecaborate solution in water was added dropwise, the light brown precipitates occurred immediately (Scheme 17). Due to high solubility of the sodium salt of dodecahydro-*closo*-dodecaborate and its derivative in water, the coupling between the cage and the diazonium cation was not occurred, stating that the absorption peak appeared at 2469 cm^{-1} was due to B-H stretching and the peak at 2224 cm^{-1} belongs to N≡N stretching. As a result, we concluded the compound obtained was 4-hydroxydiazonium salt of dodecahydro-*closo*-dodecaborate (Figure 25). It was also supported with HRMS results (Appendix C).

Stability of the compound was monitored for four weeks by using IR spectroscopy and shown in the Figure 26. ^{1}H NMR was performed in DMSO in Figure 27. The signals of doublet at 7 ppm and doublet at 8.4 ppm belong aromatic diazonium cation and the signal between 0 and 2 ppm belongs to the proton from dodecahydro-*closo*-dodecaborate. This compound has extra stability due to the existing on the strong electron donating group at the *para* position of the diazonium moiety. This is the reason why, we observed a clear NMR spectrum.

Scheme 17. Synthesis of 4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate
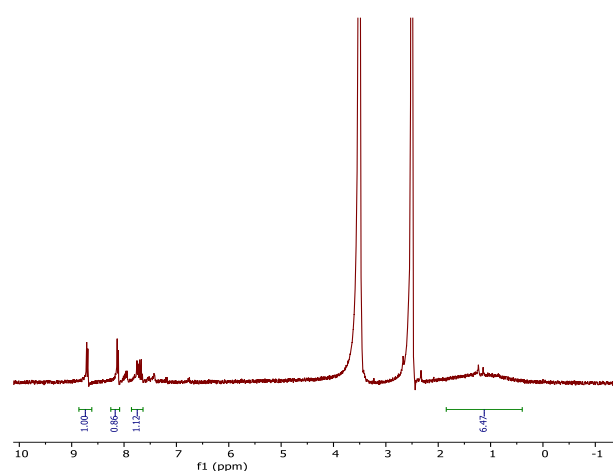
Figure 25. IR spectrum of 4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate
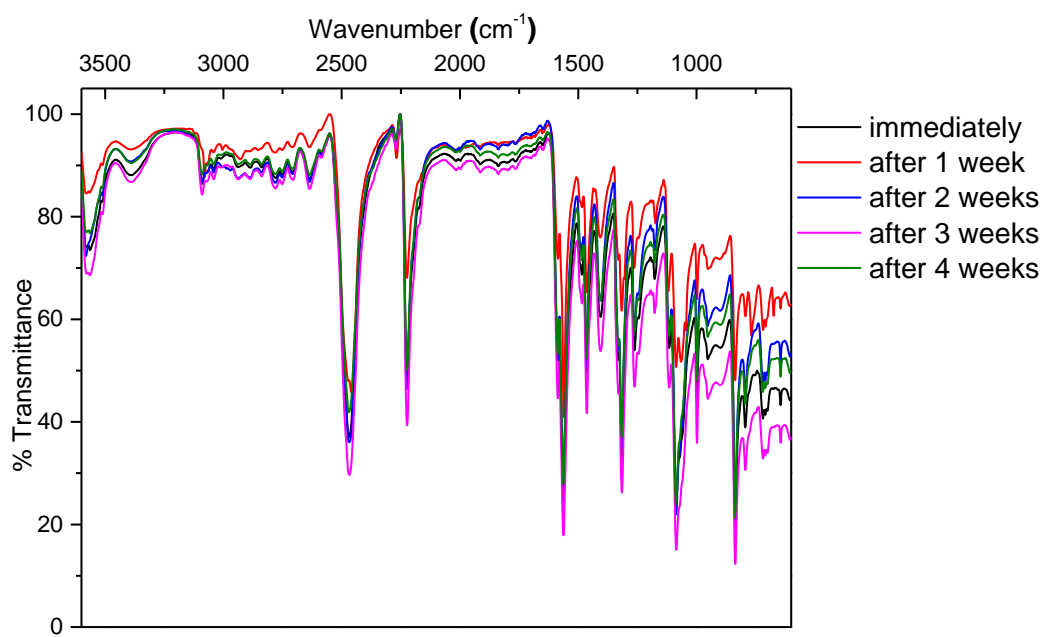
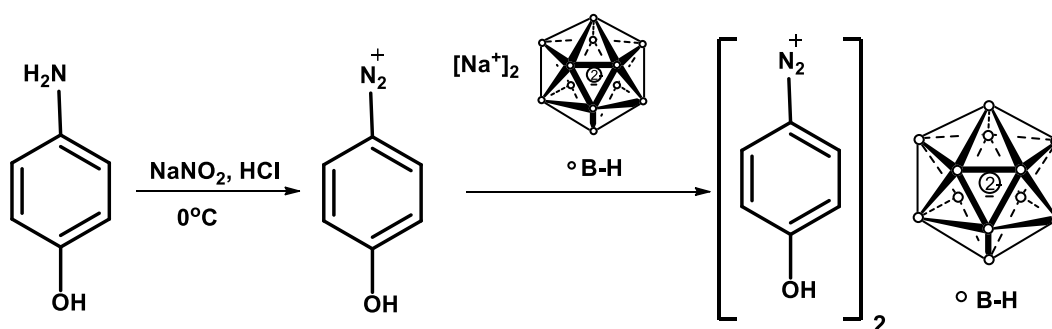**Figure 26.** IR spectra of 4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate for 4 weeks

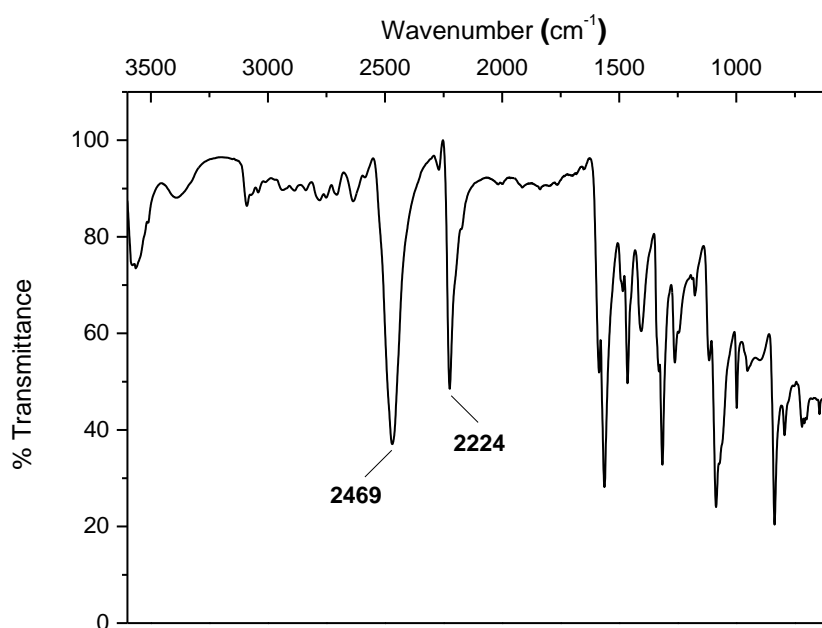**Figure 27.** ^{1}H NMR spectrum of 4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate in DMSO-d$_6$

3.2.5 Synthesis of 4-nitrobenzenediazonium dodecahydro-*closo*-dodecaborate

In order to monitor how electron withdrawing group affects the diazonium cation and its reactions, acidic solution of 4-nitroaniline was used as a starting material. Acidic solution of 4-nitroaniline was cooled to 0 °C and turned to diazonium cation with adding sodium nitrite solution with water. When the sodium salt of dodecahydro-*closo*-dodecaborate solution with water was added into diazonium solution, reddish precipitate was obtained (Scheme 18).

Scheme 18. Synthesis of 4-nitrobenzenediazonium dodecahydro-*closo*-dodecaborate

43

It is characterized by IR spectroscopy (Figure 28). B-H stretching of the compound was around 2466 cm^{-1} and N≡N stretching was at around 2283 cm^{-1}. However, 4-nitrobenzenediazonium dodecahydro-*closo*-dodecaborate was not a stable salt when it is completely dry. While transferring dry product into vial by using metal spatula, the product exploded violently. As a result of this experience, it was concluded that 4-nitrobenzenediazonium dodecahydro-*closo*-dodecaborate compound is not a stable salt. ^{1}H NMR was performed in DMSO in Figure 29. The signals between 7.5 and 9 ppm belongs aromatic diazonium cation and the signal between 0 to 2 ppm belongs to the proton from dodecahydro-*closo*-dodecaborate.
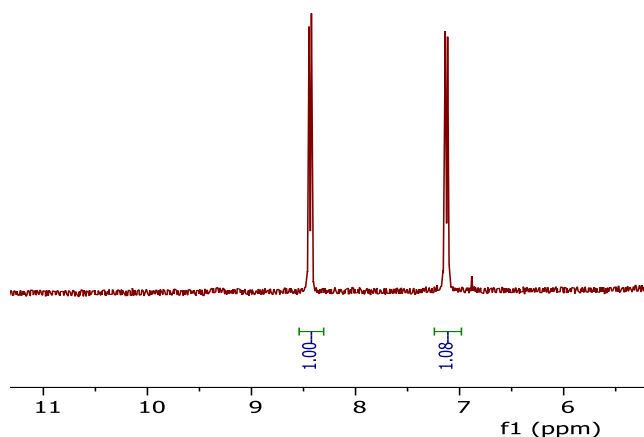

Figure 28. IR spectrum of 4-nitrobenzenediazonium dodecahydro-*closo*-dodecaborate

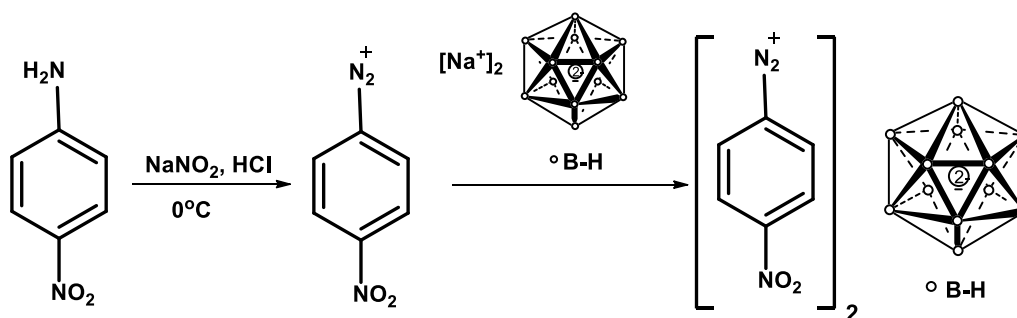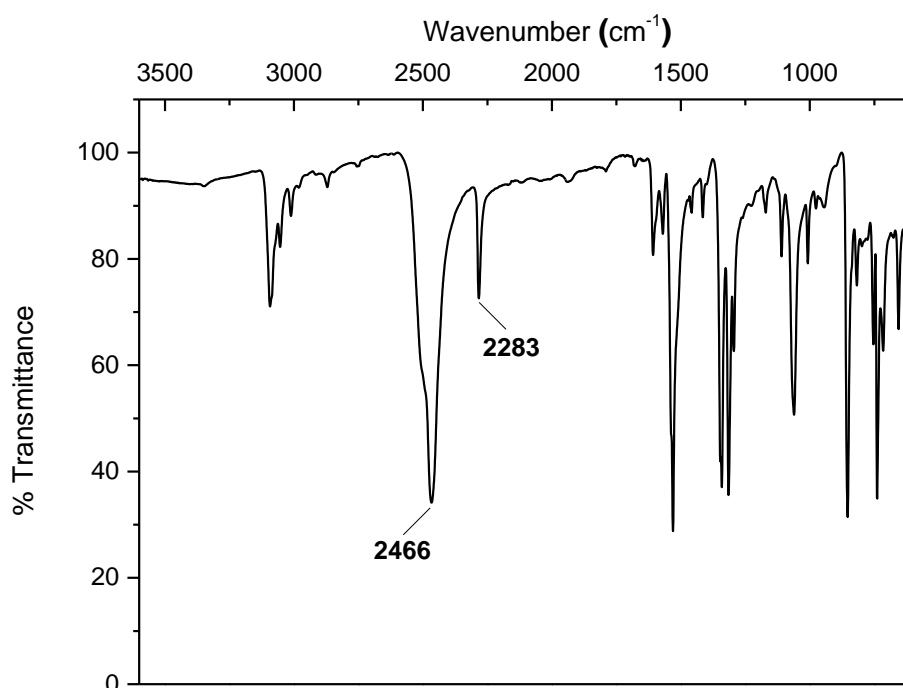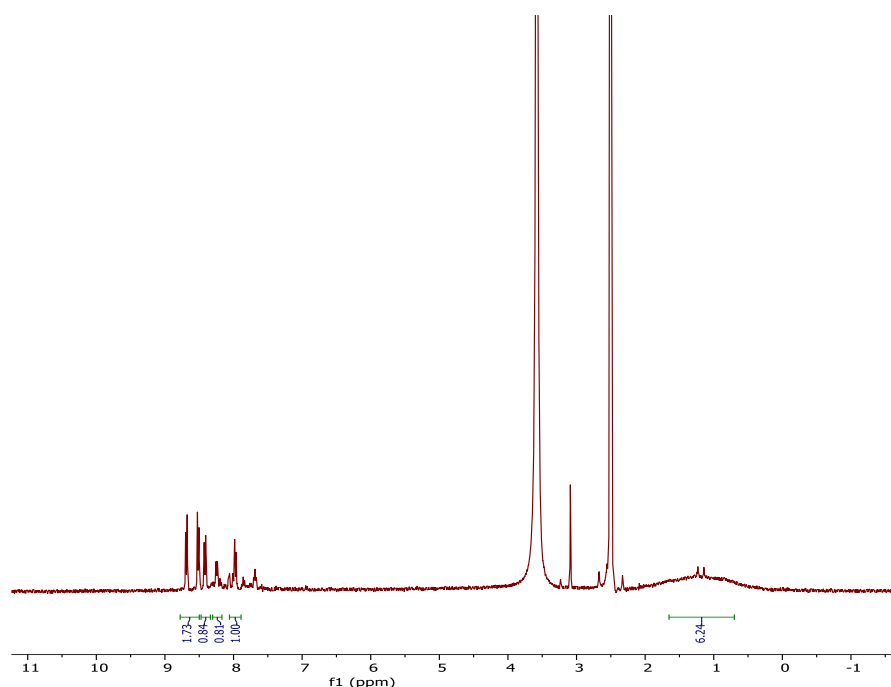**Figure 29.** ^{1}H NMR spectrum of 4-nitrobenzenediazonium dodecahydro-*closo*-dodecaborate in DMSO-d$_6$

3.2.6 Synthesis of benzenediazonium dodecachloro-*closo*-dodecaborate

As mentioned previously, partially or perchlorinated *closo*-dodecaborate dianion has weakly coordinating ability. We also tried to capture diazonium cation with chlorinated *closo*-dodecaborate. Diazonium cation was prepared by starting with acidic aniline solution at 0 °C and, sodium nitrite solution was added to turn aniline solution to make diazonium cation. When the sodium salt of chlorinated *closo*-dodecaborate was added, brownish precipitate formed immediately (Scheme 19). It was characterized by using IR spectrum. In IR spectrum, N≡N stretching was at around 2267 cm^{-1} (Figure 30).
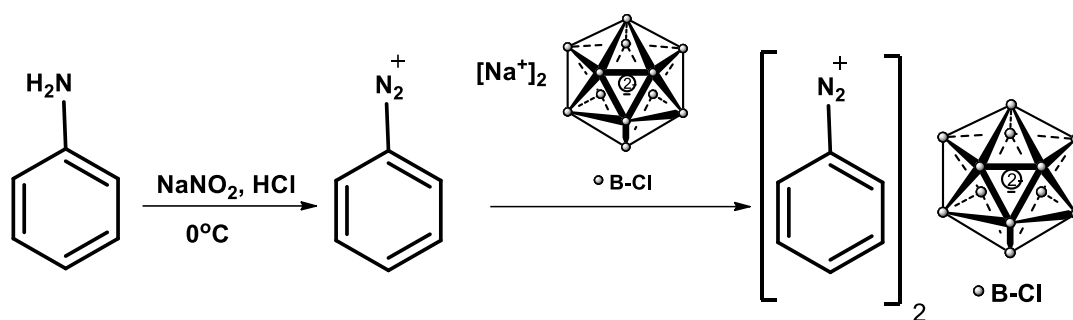
Scheme 19. Synthesis of benzenediazonium dodecachloro-*closo*-dodecaborate
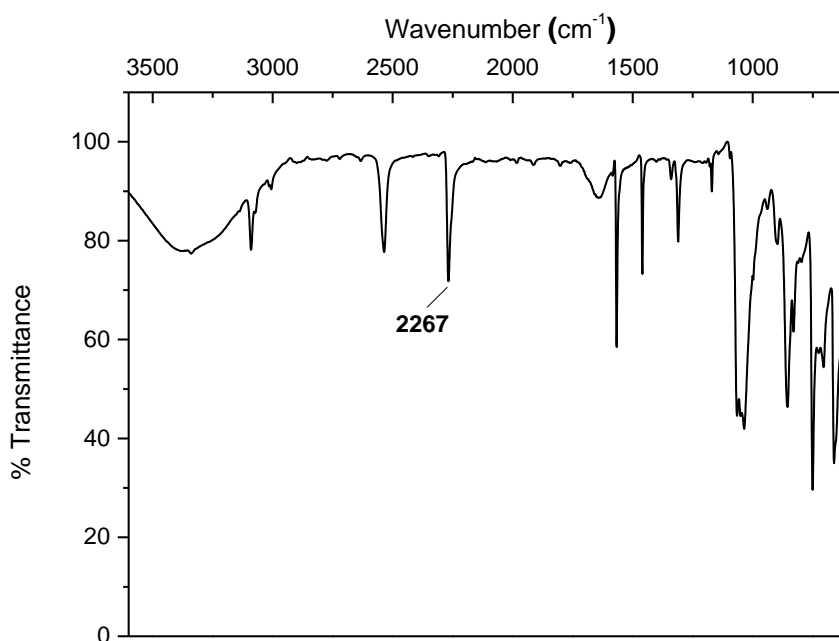
Figure 30. IR spectrum of benzenediazonium dodecachloro-*closo*-dodecaborate

3.2.7 Synthesis of benzenediazonium dodecabromo-*closo*-dodecaborate

In order to make a comparison between the halogenated *closo*-dodecaborates, we also tried to synthesize benzenediazonium salts of dodecabromo-*closo*-dodecaborate. By using a classical [47] method for the formation of diazonium cation, benzene diazonium cation was obtained as before. To gain benzene diazonium salt of dodecabromo-*closo*-dodecaborate, sodium salt of dodecabromo-*closo*-dodecaborate solution was added dropwise in benzene diazonium cation solution in

water. Precipitation immediately occurred and a reddish product was collected (Scheme 20) and characterized by using IR spectroscopy. In IR spectrum, N≡N stretching was at around 2264 cm^{-1} (Figure 31).

Scheme 20. Synthesis of benzenediazonium dodecabromo-*closo*-dodecaborate

Figure 31. IR spectrum of benzenediazonium dodecabromo-*closo*-dodecaborate

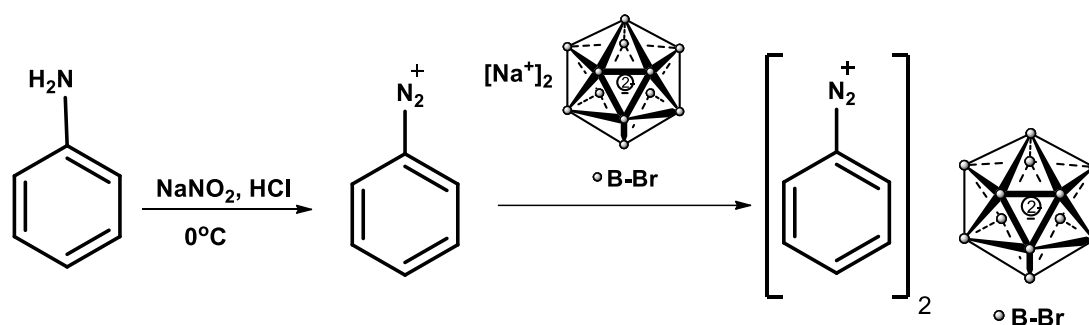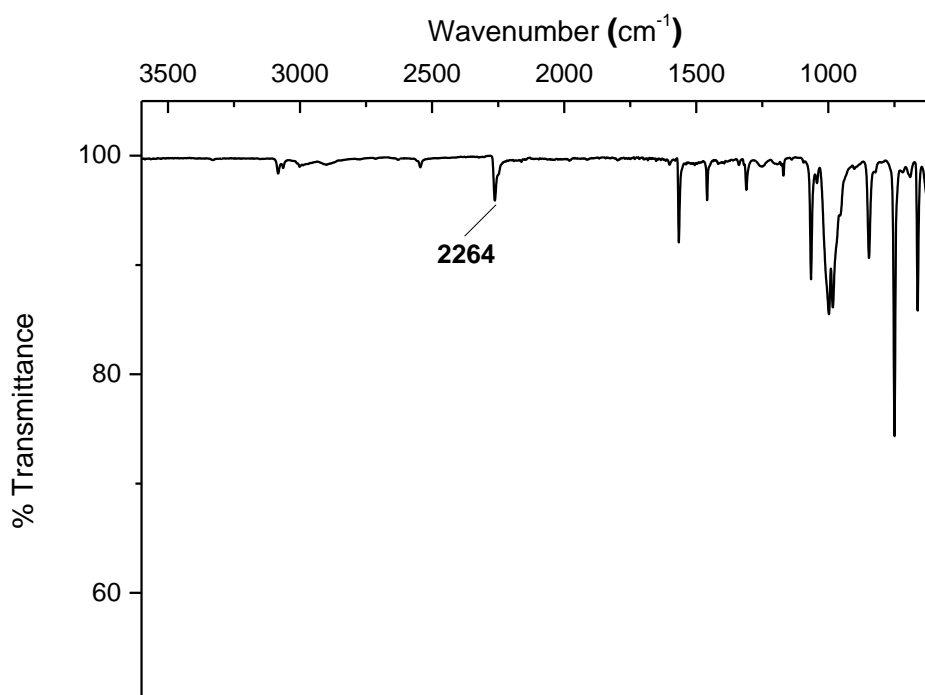**3.3 Azo Coupling from Diazonium Salt of dodecahydro-*closo*-dodecaborate and Derivatives**

In the literature reports, azocoupling reactions generally start with aniline and aryl diazonium cations are formed *in situ*.[45] However, in our studies, we isolated diazonium cations with dodecahydro-*closo*-dodecaborate dianion which is known as weakly coordinating dianion. According to 4 weeks further characterization with IR spectrum, except from 4-nitrobenzenediazonium dodecahydro-*closo*-dodecaborate, we decided that isolated diazonium cations are stable with *closo*-dodecaborate dianions. To ensure the reactivity of the diazonium cations, azocoupling reactions are designed as starting from aryl diazonium salts of dodecahydro-*closo*-dodecaborate and its halogenated derivatives.

3.3.1 Synthesis of 4-(dimethylamino)azobenzene from benzenediazonium dodecahydro-*closo*-dodecaborate and *N,N*-dimethylaniline

Stable benzenediazonium salt of dodecahydro-*closo*-dodecaborate solution with DCM was prepared and *N,N*-dimethyl aniline was added to the solution. Initially the color of the solution was grey. The activation of the benzene ring and the preparation of triethylammonium salt of dodecahydro-*closo*-dodecaborate were achieved by addition of Et_3N. The color of the solution turned grey to brownish. After evaporation of the solvents, products were obtained as brown solids (Scheme 21). Firstly, they were characterized by IR spectroscopy. The N≡N stretching around 2272 cm^{-1} in IR spectrum of benzene diazonium salt of dodecahydro-*closo*-dodecaborate was disappeared and N=N stretching around 1590 cm^{-1} was monitored. B-H stretching around 2476 cm^{-1} and N-H stretching around 3125 cm^{-1} were also observed (Figure 32).
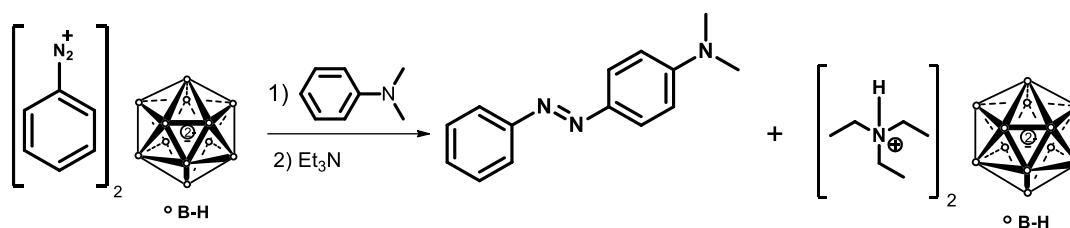
Scheme 21. Synthesis of 4-(dimethylamino)azobenzene from benzenediazonium dodecahydro-closo-dodecaborate and N,N-dimethylaniline
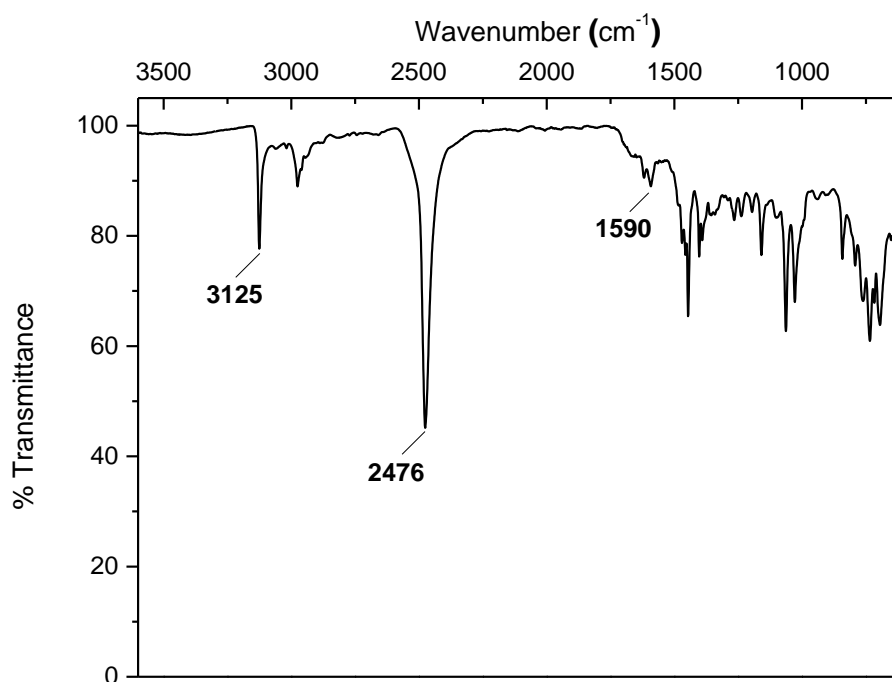
Figure 32. IR spectrum of 4-(dimethylamino)azobenzene and triethylammonium dodecahydro-*closo*-dodecaborate

We tried to separate organic phase and inorganic phase by using DCM extraction. The compounds were not separated well (Figures 33 and 34). Even after further purification of the final product, ^{1}H NMR spectrum clearly showed that azobenzene and dodecahydro-closo-dodecaborate were not separated properly.
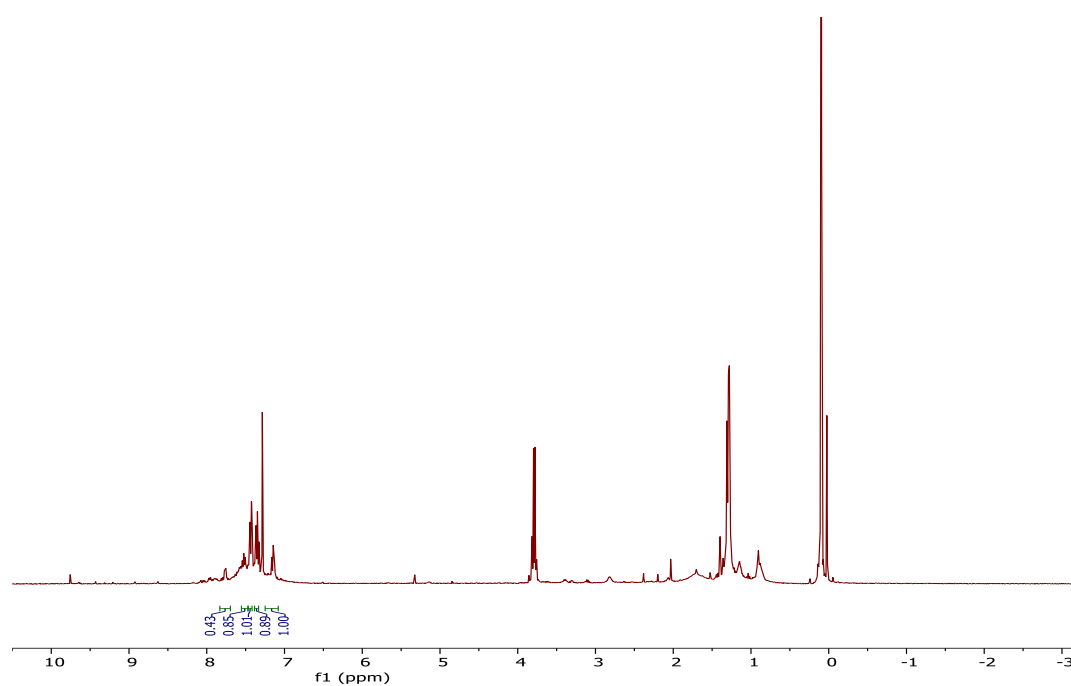
Figure 33. ^{1}H NMR spectrum of 4-(dimethylamino)azobenzene and triethylammonium dodecahydro-*closo*-dodecaborate in chloroform-d
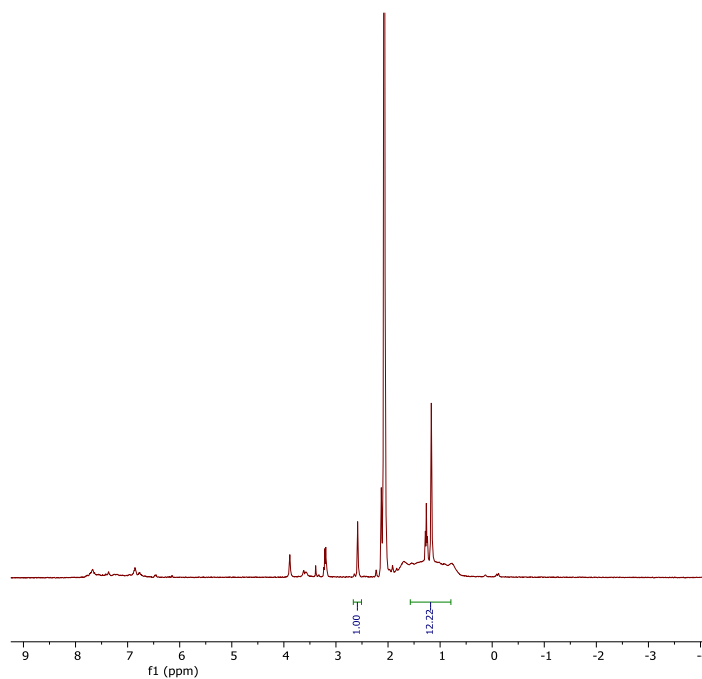
Figure 34. ^{1}H NMR spectrum of 4-(dimethylamino)azobenzene and triethylammonium dodecahydro-*closo*-dodecaborate in acetone-d$_6$

3.3.2 Synthesis of 2-chloro-4'-(dimethylamino)azobenzene from 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate

In the previous part, we decided that the electron withdrawing group on benzene ring did not cause the azocoupling reaction between 2-chloro-benzenediazonium cation and dodecahydro-*closo*-dodecaborate dianion and they form a stable salt. Moreover, we tried to make azo coupling between 2-chlorobenzenediazonium which is stabilized by dodecahydro-*closo*-dodecaborate and *N,N*-dimethylaniline. Since the salt is insoluble in water, DCM was used to dissolve the salt and triethylamine was used for both activate the ring and precipitation of dodecahydro-*closo*-dodecaborate anion as a Triethylammonium salt (Scheme 22). For characterization with IR spectrum, it was monitored that N≡N stretching in around 2266 cm^{-1} was disappeared and N=N stretching in around 1592 cm^{-1} formed shown as in Figure 35. B-H stretching around 2475 cm^{-1} and N-H stretching around 3125 cm^{-1} were also observed.
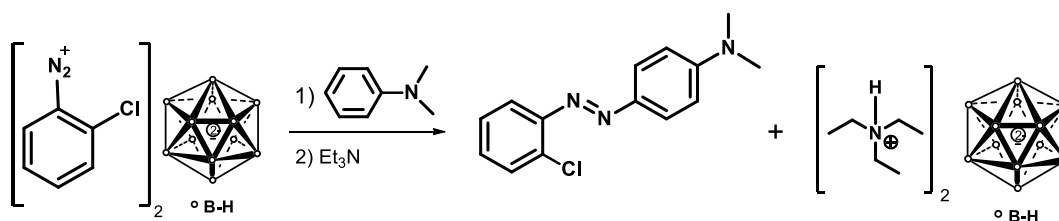
Scheme 22. Synthesis of 2-chloro-4'-(dimethylamino)azobenzene from 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate
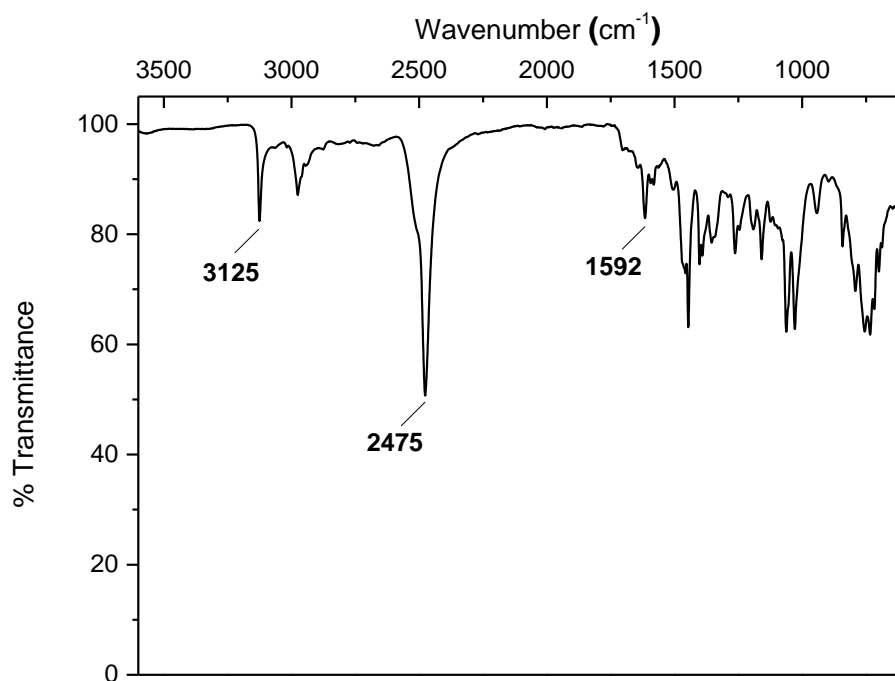
Figure 35. IR spectrum of 2-chloro-4'-(dimethylamino)azobenzene and triethylammonium dodecahydro-*closo*-dodecaborate mixture

3.3.3 Synthesis of 4-hydroxyazobenzene from benzenediazonium dodecachloro-*closo*-dodecaborate and phenol

In this reaction, azocoupling reaction was tried between the benzenediazonium salt of dodecachloro-*closo*-dodecaborate and phenol. Different from the other azo coupling methods in this thesis study, the reaction was applied at 0 °C. After azocoupling reaction, the solution was treated with triethylamine and triethylammonium salt of dodecachloro-*closo*-dodecaborate was formed (Scheme 23). When it was characterized by IR spectrum, N≡N stretching at around 2267 cm^{-1} was disappeared and N=N stretching at around 1579 is observed as shown in Figure 36. Further characterization was done by ^{1}H NMR spectrum, shown in Figure 37.
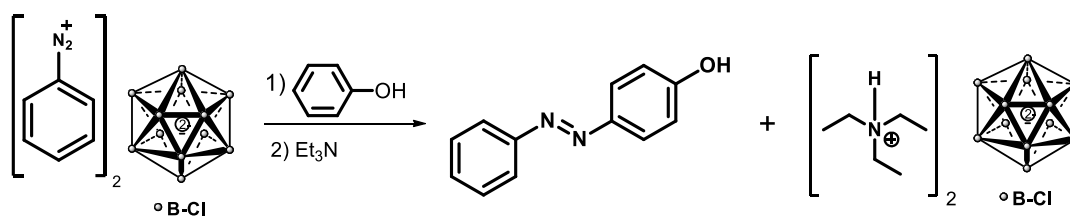
Scheme 23. Synthesis of 4-hydroxyazobenzene from benzenediazonium dodecachloro-*closo*-dodecaborate and phenol
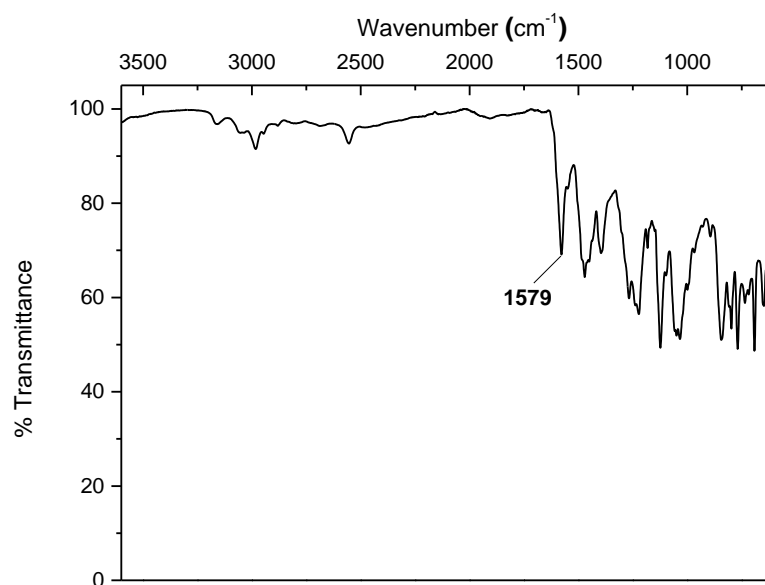
Figure 36. IR spectrum of 4-hydroxyazobenzene and triethylammonium dodecachloro-*closo*-dodecaborate
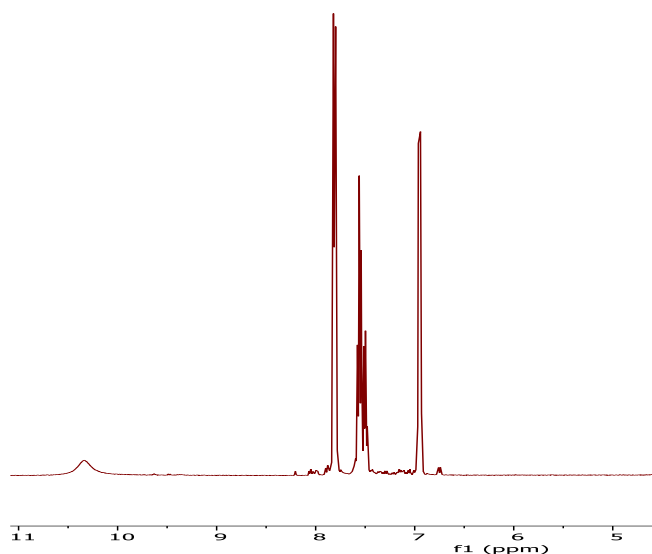
Figure 37. ^{1}H NMR spectrum of 4-hydroxyazobenzene in DMSO-d$_6$

3.3.4   Synthesis of 4-(dimethylamino)azobenzene from benzenediazonium dodecabromo-*closo*-dodecaborate

Previously, we described the halogenated *closo*-dodecaborate more weakly coordinating dianion than dodecahydro-*closo*-dodecaborate. Therefore, we created a reaction between the diazonium cation and dodecabromo-*closo*-dodecaborate. After that, to understand the activity of this salt, azo coupling reaction was performed between this salt and *N,N*-dimethylaniline. Since diazonium salt of dodecahydro-*closo*-dodecaborate and derivatives are insoluble in water, DCM was chosen as a solvent. Dodecabromo-*closo*-dodecaborate was treated with Et$_3$N and turned to triethylammonium dodecahydro-*closo*-dodecaborate. Reaction is shown in Scheme 24.
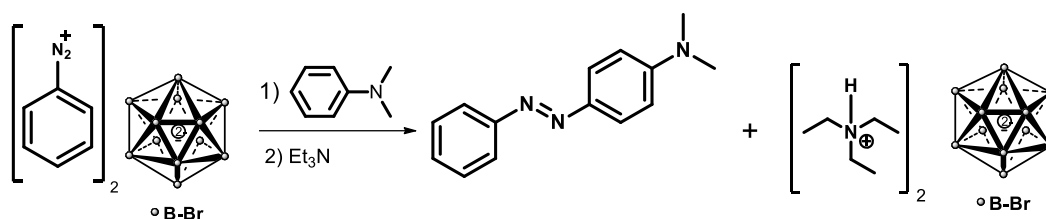
Scheme 24. Synthesis of 4-(dimethylamino)azobenzene from benzenediazonium dodecabromo-*closo*-dodecaborate

The reaction was followed by IR spectroscopy. It was observed that the stretching band at 2262 cm^{-1} due to N≡N bond disappeared and a new absorption band appeared at 1591 cm^{-1} corresponding to the formation of N=N bond (Figure 38). However, it was certainly to characterize B-Br stretching in the IR spectrum. UV-Vis absorption spectrum of 4-dimethylamino-azobenzene was measured in DCM contain an absorption band at 408 nm corresponding to the presence of 408-410 nm in the literature (Figure 39). [47]
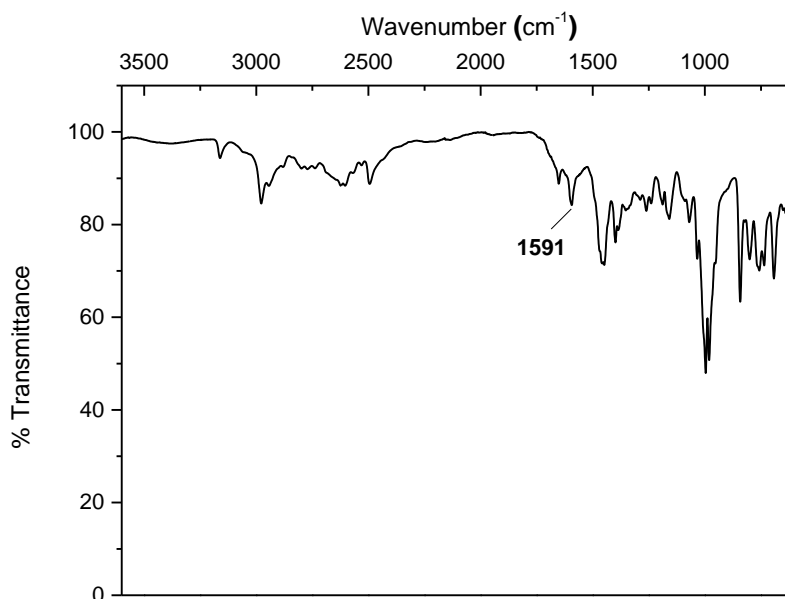
Figure 38. IR spectrum of 4-(dimethylamino)azobenzene and triethylammonium dodecabromo-*closo*-dodecaborate mixture
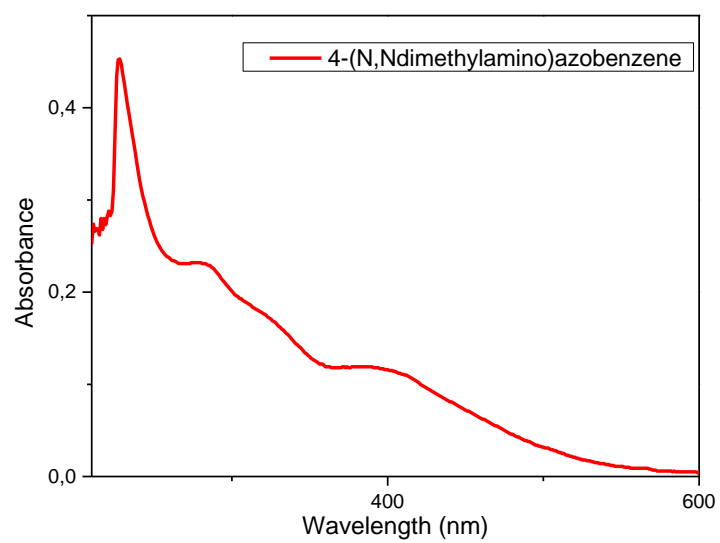
Figure 39. UV-Vis absorption spectroscopy of 4-(dimethylamino)azobenzene in DCM

CHAPTER 4

CONCLUSION

In this study, triethylammonium salt of dodecahydro-*closo*-dodecaborate dianion was synthesized starting from sodium borohydride. The sodium salt of this anion was synthesized and isolated by using cation exchange reaction. Benzenediazonium dodecahydro-*closo*-dodecaborate, 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate, 4-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate, 4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate and 4-nitrobenzenediazonium dodecahydro-*closo*-dodecaborate were synthesized, isolated and charecterized by means of IR and NMR spectroscopy. The stability of prepared diazonium salts were followed by means of IR spectrum (in Table 6). Perchlorinated and perbrominated derivatives of *closo*-dodecaborate were synthesized. Perchlorinated *closo*-dodecaborate was isolated as triethylammonium and cesium salts, perbrominated *closo*-dodecaborate was isolated as triethylammonium salt.

The weakly coordinating ability of both dodecahydro-*closo*-dodecaborate and perhalogenated derivatives (perchlorinated and perbrominated) were used to capture diazonium cations. The diazonium cations were characterized by IR spectroscopy mainly. Further chemical characterization was done by reacting diazonium salt with N,N dimethylaniline and phenol. It was found that diazonium cations could be captured and stored at ambient conditions for at least four weeks. This is the first of its kind to our best of knowledge.

Table 6. Stability of the diazonium cations with dodecahydro-*closo*-dodecaborate dianion for four weeks

Compounds	Stability for four weeks
Benzenediazonium dodecahydro-*closo*-dodecaborate	Stable
2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate	Stable
4-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate	Stable
4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate	Stable
4-nitrobenzenediazonium dodecahydro-*closo*-dodecaborate	Not stable

CHAPTER 5

EXPERIMENTAL

All solvents and starting materials used are purchased from Sigma Aldric and used without any further purification.

Infrared (IR) spectra were recorded with Thermo Scientific Nicolet iS10 ATR-IR Spectrometer. The IR spectra of the synthesized compounds are processed with Origin Pro-2015 and are given in Appendix A.

[1]H nuclear magnetic resonance spectra of the compounds were recorded in deuterated acetone and deuterated DMSO with Bruker Avance III Ultrashield 400 Hz NMR spectrometer. The chemical shifts were specified in parts per million (ppm) with tetramethylsilane (TMS) as an internal reference. ^{1}H NMR spectra of compounds were given in Appendix B. NMR spectra of compounds were processed with MestReNova program.

UV-Vis measurements were performed with Shimadzu UV-2450 spectrophotometer. Spectroscopic measurements were applied in dichlorometane (DCM) of gradient grade. UV absorption spectra were performed with OriginPro 2015 program.

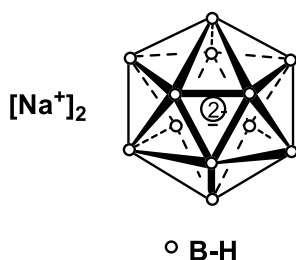## 5.1 Synthesis of dodecahydro-*closo*-dodecaborate and Cation Exchange

5.1.1 Synthesis of triethylammonium dodecahydro-*closo*-dodecaborate
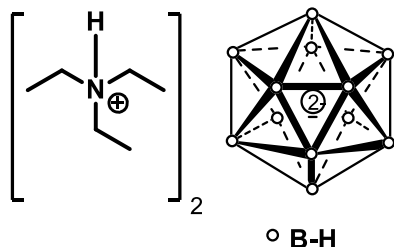
NaBH$_4$ (60.0g, 1.58 mol) was added into a 1 L 3-necked round bottom flask. These necks were equipped with dropping funnel which was used for solution addition, condenser and septum which was used for gas addition. Also, magnetic stirring bar was put into the flask. Diglyme (300 mL) (diethylene glycol dimethyl ether) was added on NaBH$_4$ and argon gas was given to the reaction. During the reaction, argon atmosphere was conserved. Temperature of the reaction was increased to 110 °C in oil bath and dissolution of NaBH$_4$ was observed. On the other hand, iodine (I$_2$) (125 g, 0.49 mol) was dissolved in diglyme (260 mL). Iodine solution was prepared and put into the dropping funnel by using syringe under Argon atmosphere. When temperature of the reaction was 110 °C, iodine solution was added dropwise. During the addition, gas evolution was observed and this gas was passed through the acetone trap. Also, precipitation in the solution was observed. Iodine addition was completed in 8 hours. Then, the reaction mixture was stirred at same temperature for overnight. Next day, oil bath temperature was increased to 200 °C and reaction mixture was stirred for one day. Reaction mixture was then cooled to room temperature and acidified with HCl (168 mL 37% HCl and 268 mL distilled water). Acidification was done very slowly since the reaction was bubbled. Acidified solution was stored into fridge at +4 °C for overnight and colorless boric acid crystals were obtained. Boric acid was filtered while the solution was still cold. The filtrate solution was kept in a beaker and stirred with (CH$_3$CH$_2$)$_3$N (210 mL) for one night and precipitate

formation completed. Obtained white solids were filtered and product was obtained [(CH$_3$CH$_2$)$_3$NH$^+$]$_2$[B$_{12}$H$_{12}$$^{2-}$] (27.0314 g, 59.05%). IR: 2475 cm^{-1} (B-H stretching)

5.1.2   Synthesis of sodium dodecahydro-*closo*-dodecaborate

[(CH$_3$CH$_2$)$_3$NH$^+$]$_2$[B$_{12}$H$_{12}$$^{2-}$] (3.0 g, 8.68 mmol) was added into round bottom flask and 15 mL NaOH solution (NaOH (0.76g, 19.00 mmol) with 15 mL distilled water) was added. Solution was heated until it became clear and evaporated to dryness. Also, white solids were dried under vacuum pump. Amount of the white product was 2.4611 g (13.16 mmol).

5.1.3   Diazonium Cations

5.1.3.1   Synthesis of benzenediazonium dodecahydro-*closo*-dodecaborate
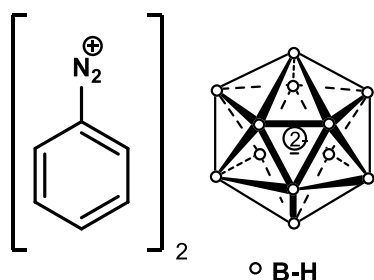
Aniline (0.73g, 8.00 mmol) was dissolved in 3M acidic HCl solution which is prepared from dilution of 5 mL 37% v/v HCl to 20 mL with distilled water. Solution was cooled to 0 °C. Sodium nitrite (0.69 g, 10.00 mmol) was dissolved in 20 mL distilled water in a beaker and added dropwise into the acidified aniline solution.
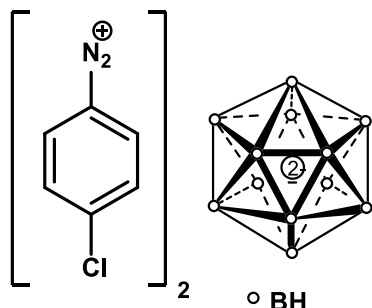
Solution was stirred for 3 hours. Sodium dodecahydro-*closo*-dodecaborate (2,89 mmol) was dissolved in 5 mL distilled water and added into diazonium solution dropwise at 0 °C and precipitation occurred. Obtained precipitates were filtered and washed with ethanol and ether (0.4381 g).IR: 2476 cm^{-1} (B-H stretching), 2272 cm^{-1} (N≡N stretching)

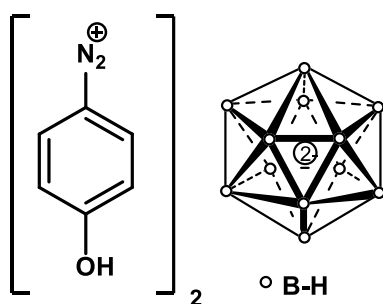### 5.1.3.2 Synthesis of 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate
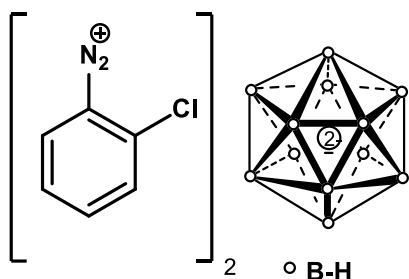
2-chloroaniline (1.02g, 8.00 mmol) was dissolved in 20 mL 3M acidic HCl solution and cooled to 0 °C. Sodium nitrite (0.69g, 10.00 mmol) was dissolved in 20 mL distilled water in a beaker and added dropwise into the acidified o-chloroaniline solution. Solution was stirred for 30 minutes. Sodium dodecahydro-*closo*-dodecaborate (2,89 mmol) was dissolved in 5 mL distilled water and added into diazonium solution dropwise at 0 °C. Orange precipitation obtained (0.6247 g,). IR: 2453 cm^{-1} (B-H stretching), 2266 cm^{-1} (N≡N stretching)

5.1.3.3 Synthesis of 4-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate

4-chloroaniline (1.02g, 8.00 mmol) was dissolved in 20 mL 3M acidic HCl solution and cooled to 0 °C. Sodium nitrite (0.69g, 10.00 mmol) was dissolved in 20 mL distilled water in a beaker and added dropwise into the acidified p-chloroaniline solution. After 30 minutes stirring, sodium dodecahydro-*closo*-dodecaborate (2,89 mmol) was dissolved in 5 mL distilled water and added into diazonium solution dropwise at 0 °C. Dark orange precipitation obtained (0.7361 g). IR: 2469 cm^{-1} (B-H stretching), 2268 cm^{-1} (N≡N stretching)
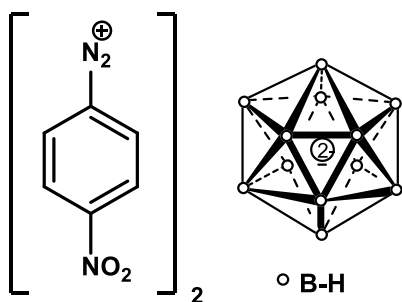
5.1.3.4 Synthesis of 4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate

4-aminophenol (0.87g, 8.00 mmol) was dissolved in 3M acidic HCl solution and cooled to 0 °C. Sodium nitrite (0.69g, 10.00 mmol) was dissolved in 20 mL distilled water in a beaker and added dropwise into the acidified diazonium solution. Solution was stirred for 30 minutes. Sodium dodecahydro-*closo*-dodecaborate (2,89 mmol)

was dissolved in 5 mL distilled water and added into diazonium solution dropwise at 0 °C. Light brown precipitation was obtained (0.7361 g). IR: 2469 cm^{-1} (B-H stretching), 2224 cm^{-1} (N≡N stretching).

5.1.3.5 Synthesis of 4-nitrobenzenediazonium dodecahydro-*closo*-dodecaborate

4-nitroaniline (1.105 g, 8.00 mmol) was dissolved in 3M acidic HCl solution and cooled to 0 °C. Sodium nitrite (0.69g, 10.00 mmol) was dissolved in 20 mL distilled water in a beaker and added dropwise into the acidified p-chloroaniline solution. After 30 minutes stirring, sodium dodecahydro-*closo*-dodecaborate (2,89 mmol) was dissolved in 5 mL distilled water and added into diazonium solution dropwise at 0 °C. Reddish-brown precipitates were filtered. When the residue was collected to vial with metal spatula, the product exploded. IR: 2466 cm^{-1} (B-H stretching), 2283 cm^{-1} (N≡N stretching)

5.2 Synthesis and Cation Exchange of dodecachloro-*closo*-dodecaborate

5.2.1 Synthesis of triethylammonium dodecachloro-*closo*-dodecaborate
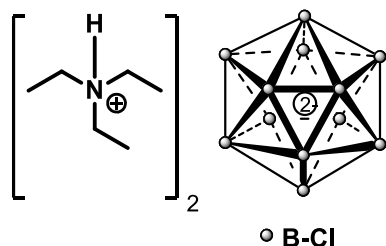
$[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ (1.0 g, 2.89 mmol) was taken into 50 mL round bottom flask. NaOH (0.25 g, 6.36 mmol) was dissolved in 10 mL distilled water. 10 mL NaOH solution was added into $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$. Solution was heated until became clear and evaporated until dryness. Solid was dissolved in 10 mL distilled water. On the other hand, HCl (80 mL, 37 %) was added dropwise into $KMnO_4$ and Cl_2 gas was came out. This gas was bubbled into the solution for 5 hours at room temperature and 8 hours at 100 °C. Solution was cooled to room temperature and acidified with HCl (37 %). Acidic solution was treated with triethylamine and precipitation occurred. Reaction was filtered (1.19 g, 54%).

5.2.2 Synthesis of cesium dodecachloro-*closo*-dodecaborate
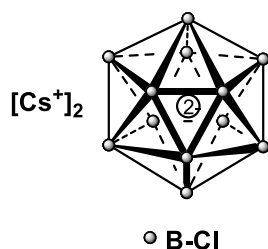
$[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ (1.0 g, 2.89 mmol) was taken into 50 mL round bottom flask. NaOH (0.25 g, 6.36 mmol) was dissolved in 10 mL distilled water. NaOH solution (10 mL) was added into $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$. Solution was heated until became clear and evaporated until dryness. Also, solid was dried under vacuum.

65

30 mL CH_3CN was added into solid and stirred for 20 minutes. SO_2Cl_2 (30 mL) was added dropwise into the solution. After finishing the addition, solution was refluxed for 8 hours and stirred overnight at room temperature. Solvent was evaporated and solid was dissolved in 15 mL distilled water. When $CsCl_2$ was added into the solution, white precipitates occurred. Precipitates were filtered and white solids were collected.

### 5.2.3   Synthesis of benzenediazonium dodecachloro-*closo*-dodecaborate
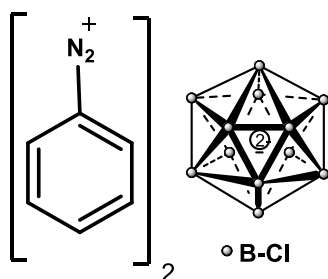
$[(CH_3CH_2)_3NH^+]_2[B_{12}Cl_{12}^{2-}]$ (0.5 g, 0.659 mmol) was taken into 25 mL round bottom flask. NaOH (0.057 g, 1.45 mmol) was dissolved in 10 mL distilled water and added into $[(CH_3CH_2)_3NH^+]_2[B_{12}Cl_{12}^{2-}]$. Solution was heated until became clear and evaporated until dryness. Then, solid was dissolved in 2.5 mL distilled water.

Aniline (0.061 g, 0.659 mmol) was dissolved in 3M acidic HCl solution. Solution was cooled to 0 °C. Sodium nitrite (0.058 g, 0.82 mmol) was dissolved in 2 mL distilled water in a beaker and added dropwise into the acidified aniline solution. Solution was stirred for 30 minutes and 2.5 mL $Na_2B_{12}Cl_{12}$ solution was added slowly. Precipitation occurred immediately and precipitates were filtered (0.18 g,). IR: 2267 cm^{-1} (N≡N stretching)

5.3 Synthesis and Cation Exchange of dodecabromo-*closo*-dodecaborate

5.3.1 Synthesis of triethylammonium dodecabromo-*closo*-dodecaborate
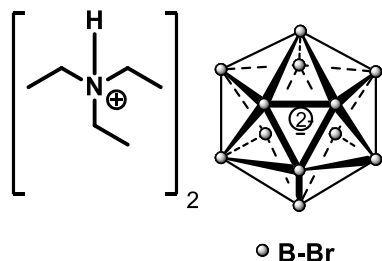
$[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ (1.0 g, 2.89 mmol) was taken into 50 mL round bottom flask. NaOH (0.25 g, 6.36 mmol) was dissolved in 10 mL distilled water. 10 mL NaOH solution was added into $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$. Solution was heated until became clear and evaporated until dryness. Solid was dissolved 10 mL 50% aqueous methanol solution and cooled to 5-10 °C by using ice bath. Bromine (1.92 mL, 37.57 mmol) was added dropwise with syringe. Half of the bromine was added dropwise and the remained bromine was added in one portion without any cooling. Solution was stirred 20 minutes and chlorine gas was passed into the solution in order to capturing excess bromine. The temperature of the solution was raised to 50 °C and cooled to room temperature. Acidified with H_2SO_4 (2 mL) and treated with Et_3N. Precipitated white solid was collected with filtration. The amount of the product was 1.65 g.

### 5.3.2 Synthesis of benzenediazonium dodecabromo-*closo*-dodecaborate
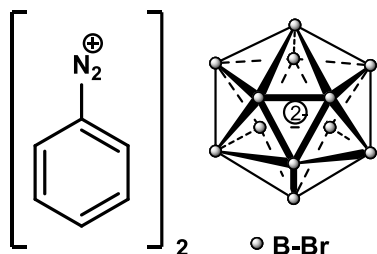
$[(CH_3CH_2)_3NH^+]_2[B_{12}Br_{12}^{2-}]$ (0.3 g, 0.23 mmol) was taken into 25 mL round bottom flask. NaOH (0.024 g, 0.51 mmol) was dissolved in 10 mL distilled water and added into $[(CH_3CH_2)_3NH^+]_2[B_{12}Br_{12}^{2-}]$. Solution was heated until became clear and evaporated until dryness. Then, solid was dissolved in 2.5 mL distilled water.

Aniline (0.021g, 0.23 mmol) was dissolved in 3M acidic HCl solution. Solution was cooled to 0 °C. Sodium nitrite (0.020g, 0.28 mmol) was dissolved in 2 mL distilled water in a beaker and added dropwise into the acidified aniline solution. Solution was stirred for 30 minutes and 2.5 mL $Na_2B_{12}Br_{12}$ solution was added slowly. Obtained orange precipitates were filtered (0.2240 g,). IR: 2262 cm^{-1} (N≡N stretching)
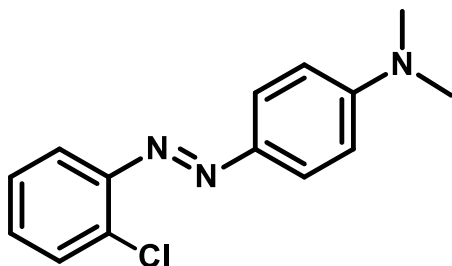
5.4   Azo Coupling from Diazonium Salt of dodecahydro-*closo*-dodecaborate

5.4.1   Synthesis of 4-(dimethylamino)azobenzene from Benzenediazonium dodecahydro-*closo*-dodecaborate and *N,N*-dimethylaniline
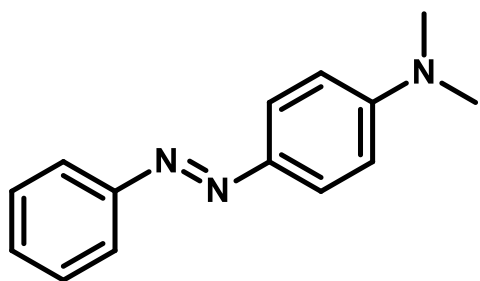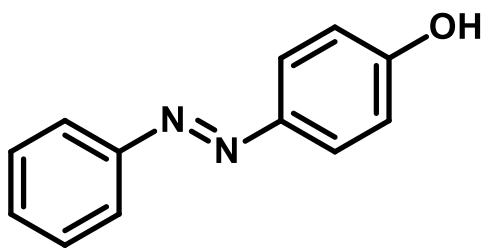

Benzenediazonium dodecahydro-*closo*-dodecaborate (0.0605g, 0.172 mmol) and *N,N*-dimethylaniline (44 µL, 0.345 mmol) were added into flask and 2.5 mL DCM was added. During the addition of Et$_3$N (96 µL), color of the solution turned gray to brownish. Stirred 1 hour and evaporated *in vacuo*. Further purification was applied by DCM extraction but compounds did not separate well. IR: 1592 cm^{-1} (N=N stretching)

5.4.2 **Synthesis of 2-chloro-4'-(dimethylamino)azobenzene from 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate and *N,N*-dimethylaniline**

2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate (0.072g, 0.172 mmol) and N,N-dimethylaniline (44 µL, 0.345 mmol) were added into flask and 2.5 mL DCM was added. To solution medium, Et$_3$N (96 µL) was added. Stirred 1 hour and evaporated by *vacuo.* IR: 1615 cm^{-1} (N=N stretching)

5.4.3 **Synthesis of 4-hydroxyazobenzene from benzenediazonium dodecachloro-*closo*-dodecaborate and phenol**

Benzenediazonium dodecachloro-*closo*-dodecaborate (0.018g, 0.24 mmol) was dissolved in DCM and cooled to 0 °C. Phenol (0.045g, 0.48 mmol) was added into solution and stirred 30 minutes. To solution medium, Et$_3$N (1 mL) was added. Stirred

1 hour at 0 °C and 1 hour at room temperature. Precipitation was occurred and filtered. IR: 1579 cm^{-1} (N=N stretching).

5.4.4 **Synthesis of 4-(dimethylamino)azobenzene from benzene diazonium dodecabromo-*closo*-dodecaborate and *N,N*-dimethylaniline**
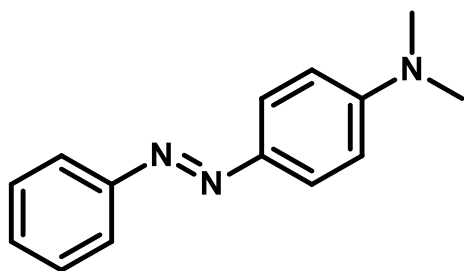
Benzenediazonium dodecabromo-*closo*-dodecaborate (0.22g, 0.172 mmol) and *N,N*-dimethylaniline (44 µL, 0.345 mmol) were added into flask and 2.5 mL DCM was added. During the addition of Et$_3$N (96 µL). Stirred overnight and evaporated *in vacuo.* IR: 1579 cm^{-1} (N=N stretching)

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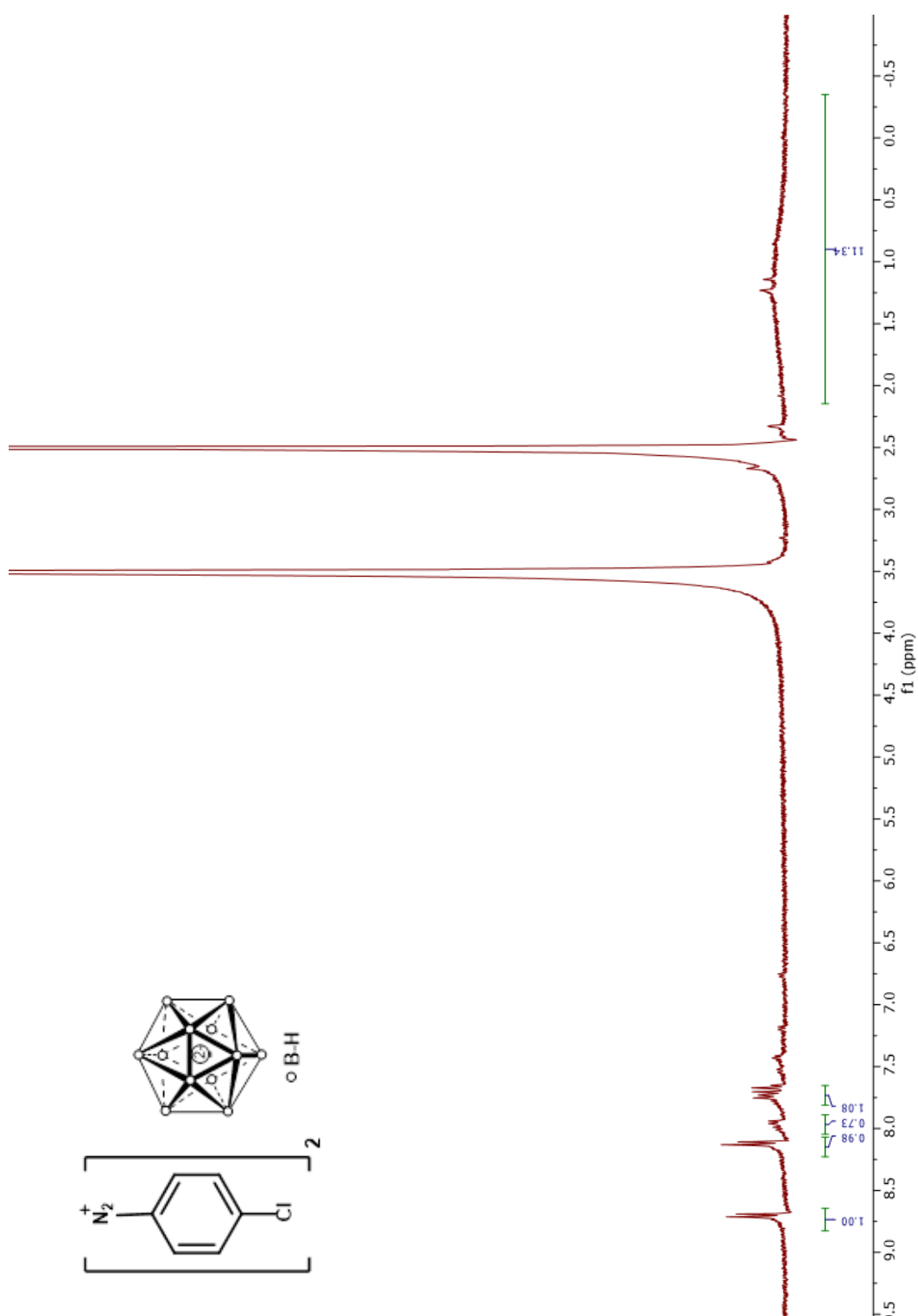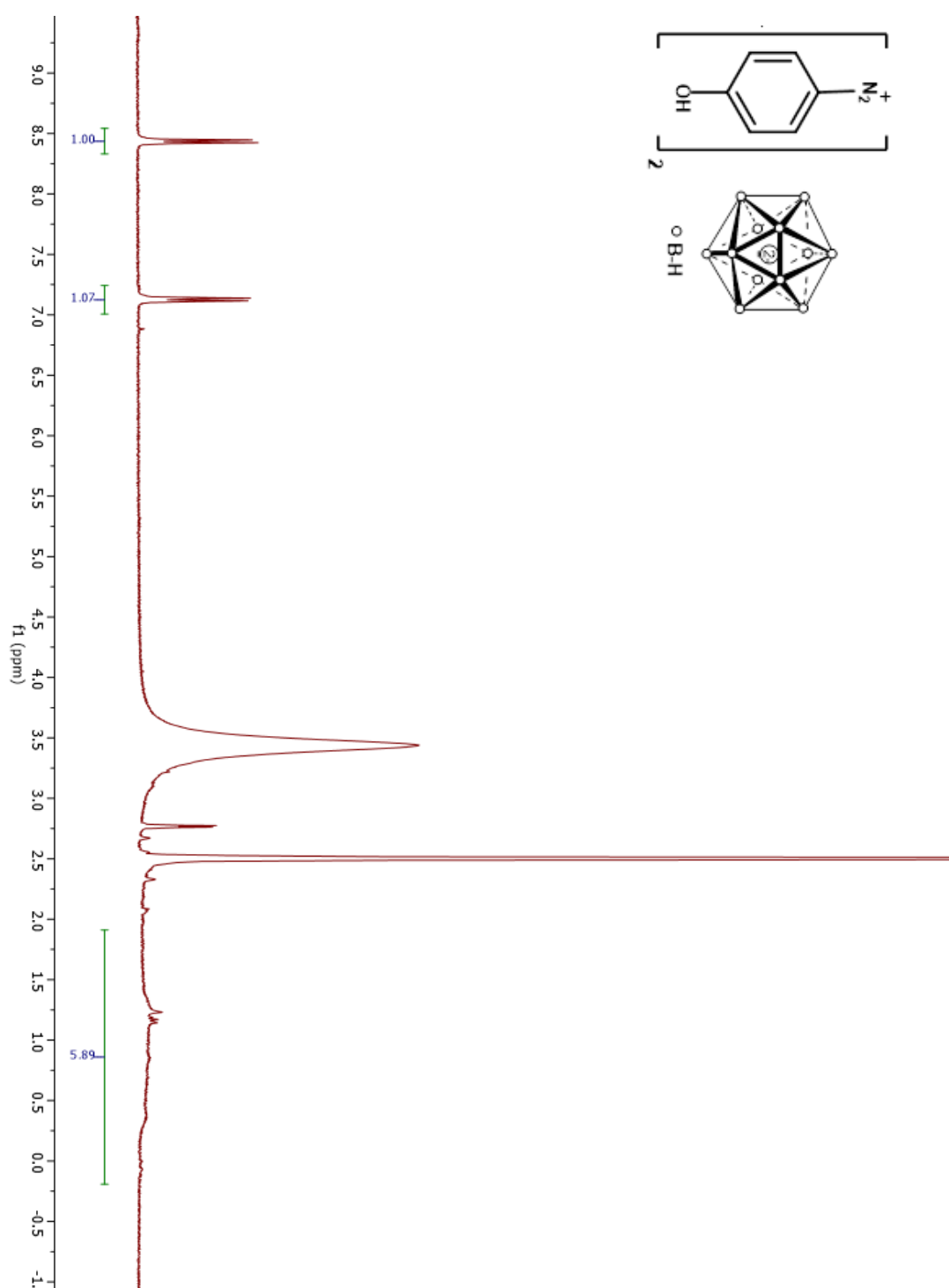
APPENDICES

A. NMR Spectra

NMR spectra were recorded at Bruket Avance III Ultrashield 400 Hz. DMSO was used as solvent in all records.
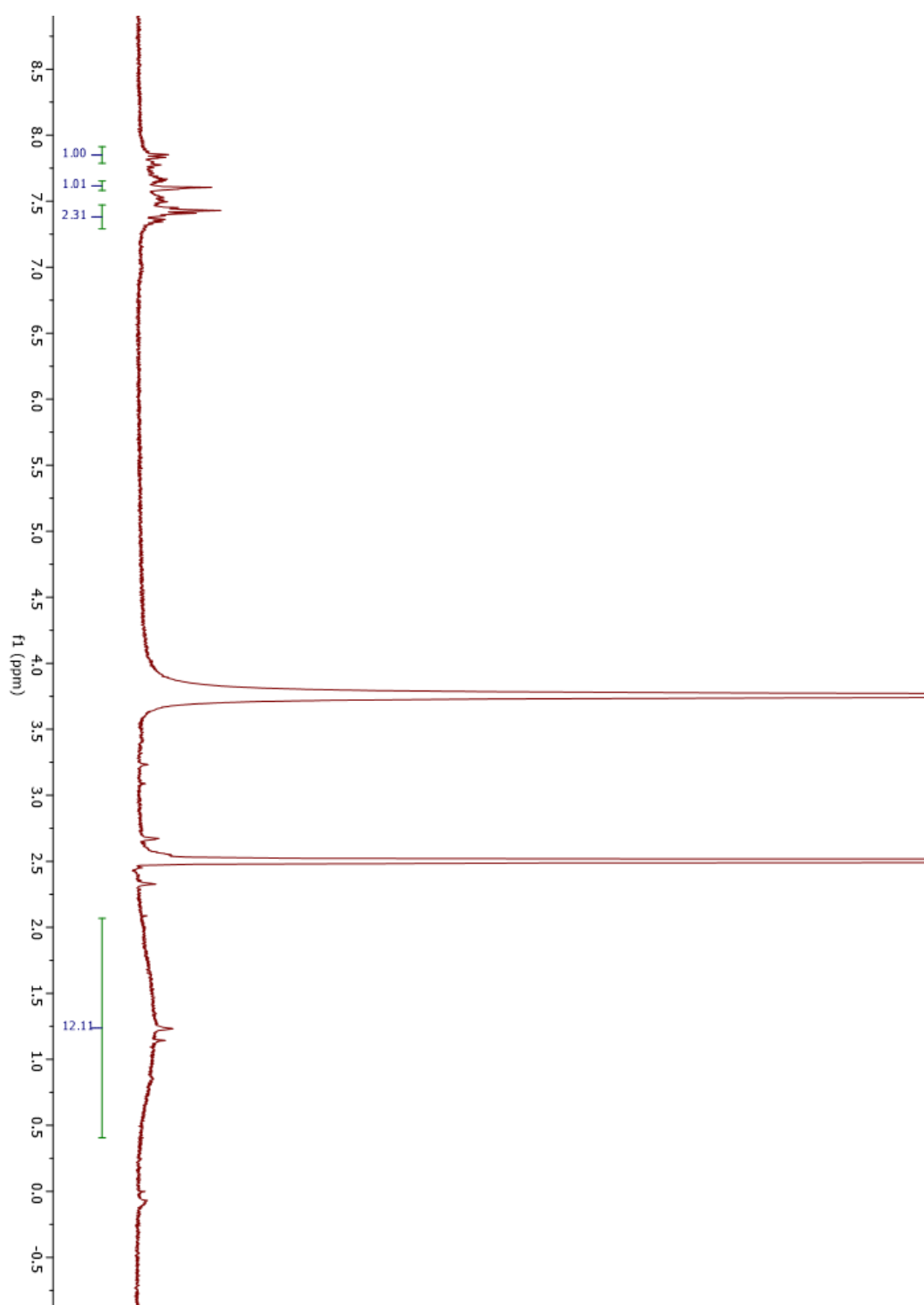
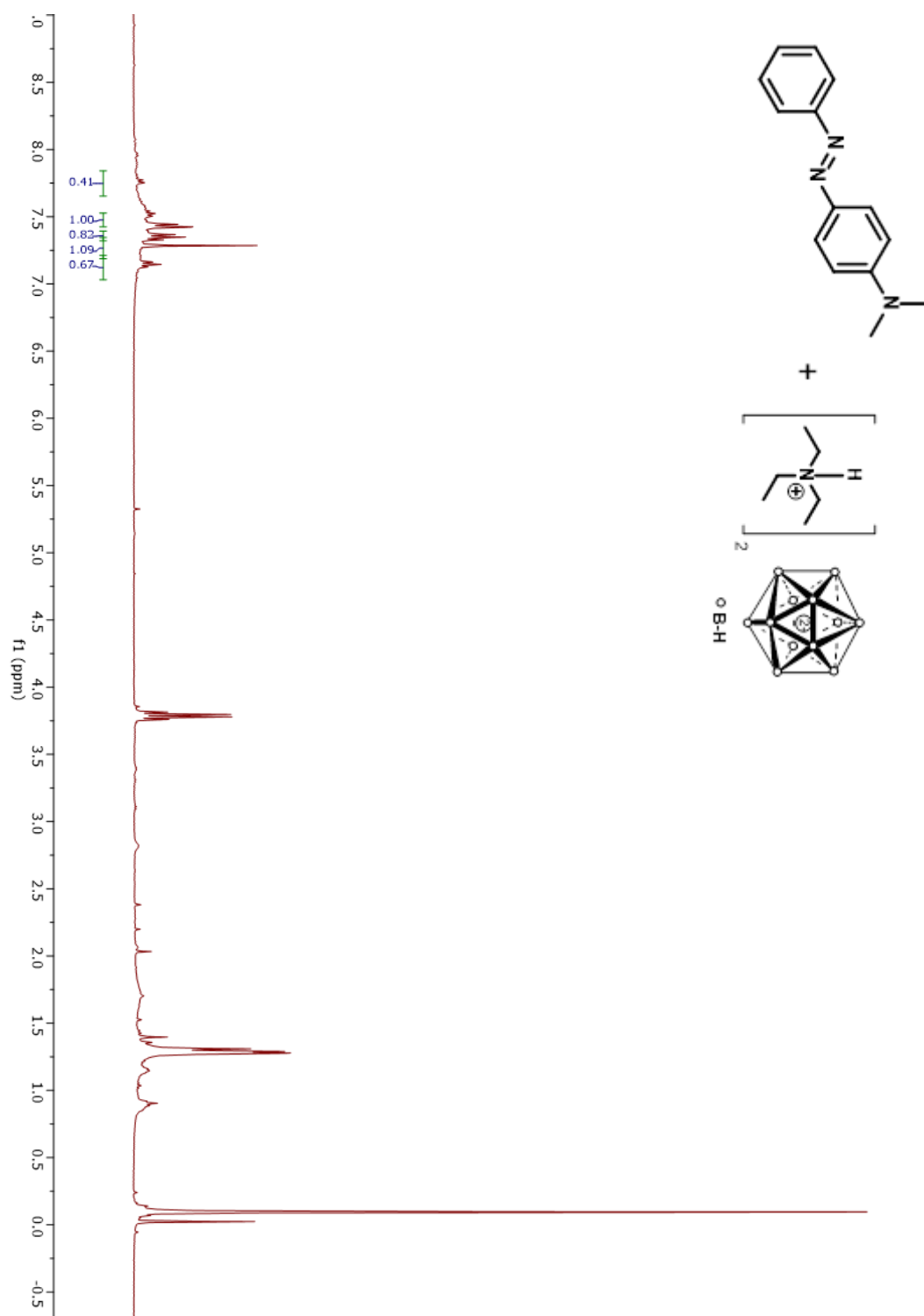**Figure 40.** ^{1}H NMR spectrum of 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate

Figure 41. ^{1}H NMR spectrum of 4-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate

Figure 42. ^{1}H NMR spectrum of 4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate

Figure 43. ^{1}H NMR spectrum of 4-nitrobenzenediazonium dodecahydro-*closo*-dodecaborate
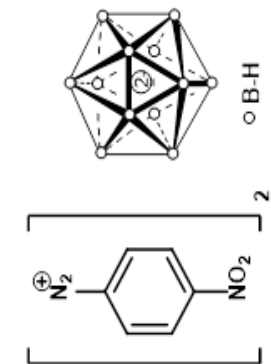
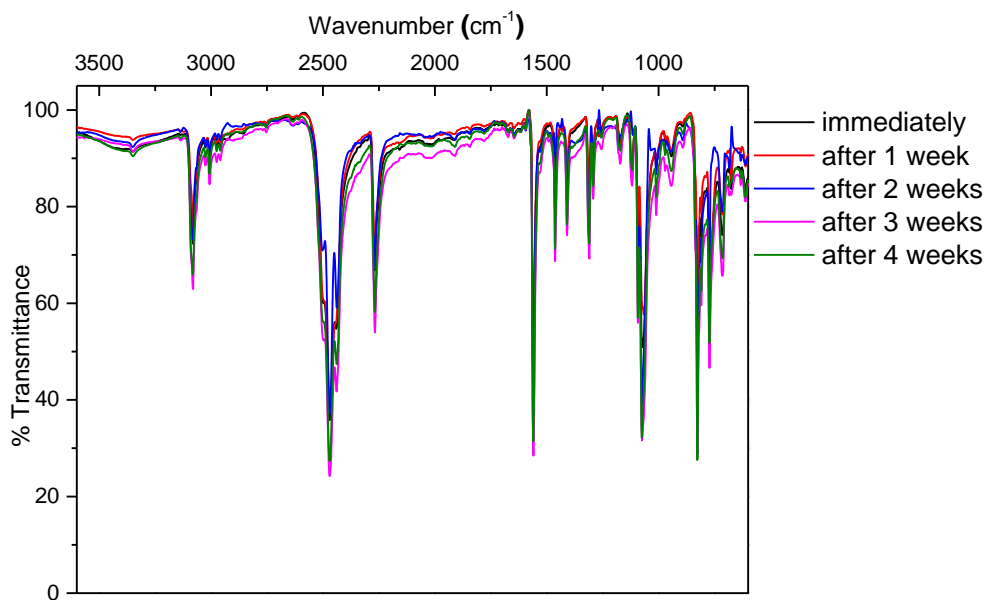**Figure 44.** ^{1}H NMR spectrum of 4-(dimethylamino)azobenzene and triethylammonium dodecahydro-*closo*-dodecaborate in chloroform-d (organic phase)
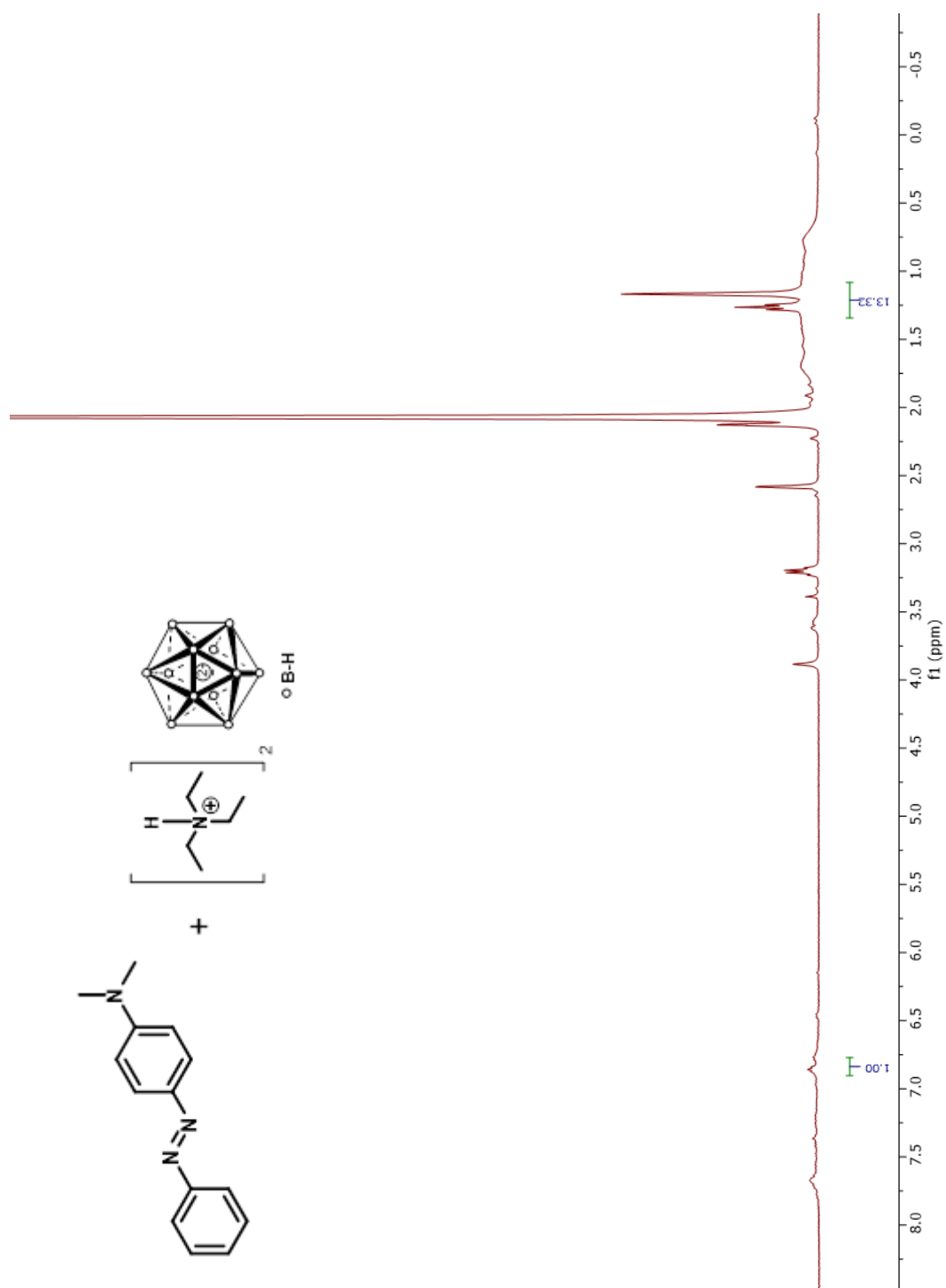
Figure 45. ¹H NMR spectrum of 4-(dimethylamino)azobenzene and triethylammonium dodecahydro-*closo*-dodecaborate in acetone-d₆ (aqueous phase)
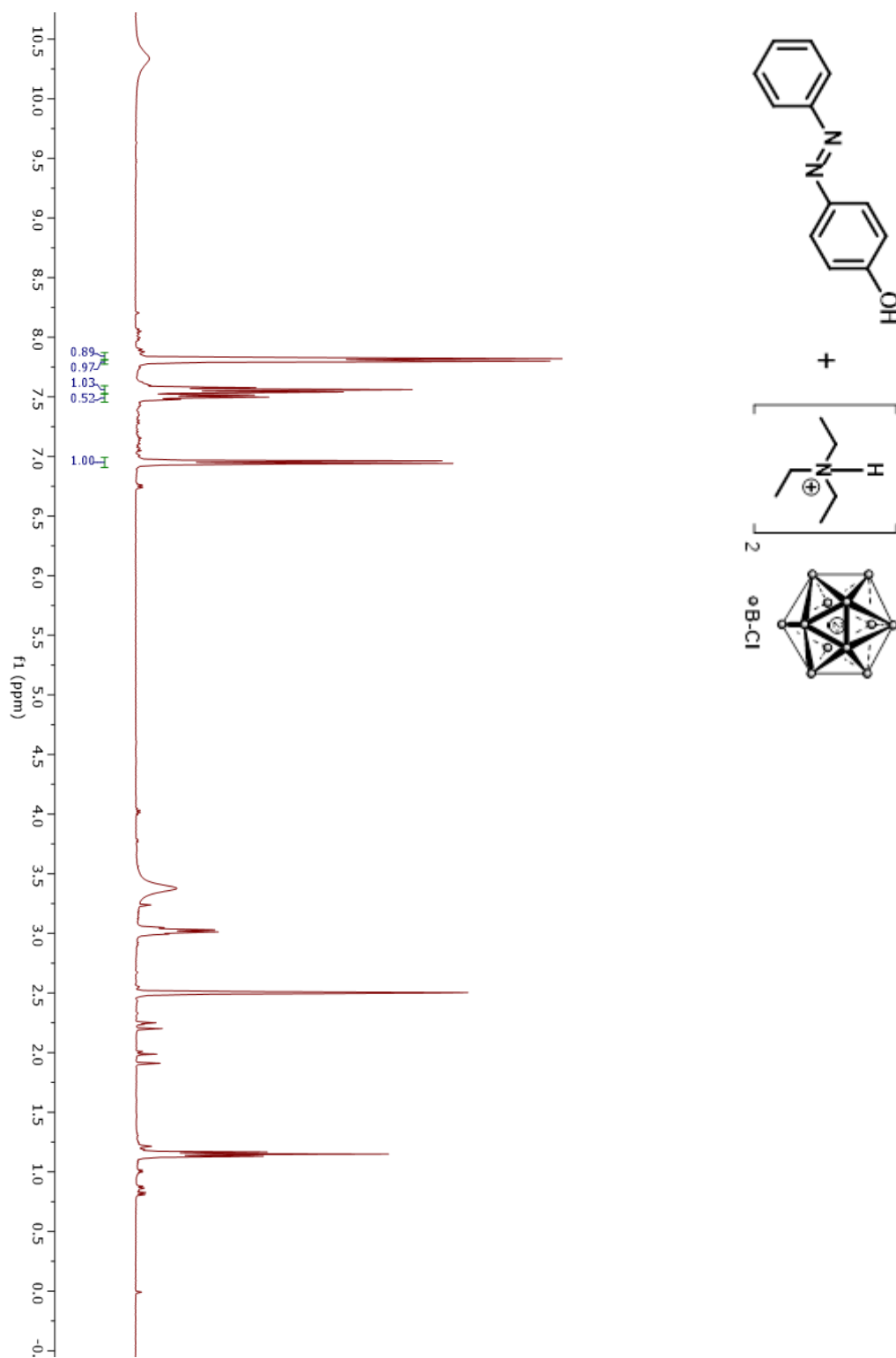
Figure 46. ^{1}H NMR spectrum of 4-hydroxyazobenzene and triethylammonium salt of dodecachloro-*closo*-dodecaborate in DMSO-d$_6$

B. IR Spectra

IR spectra were recorded at Thermo Scientific Nicolet iS10 ATR-IR spectrometer.
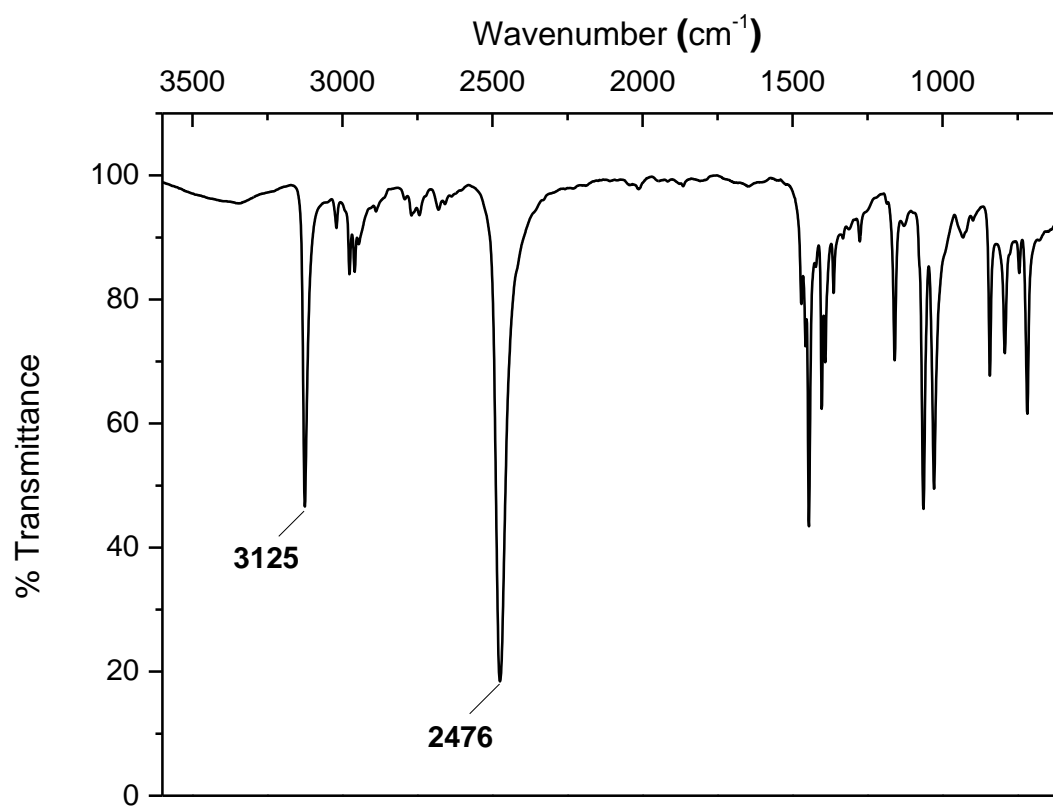
Figure 47. IR spectrum of compound triethylammonium dodecahydro-*closo*-dodecaborate
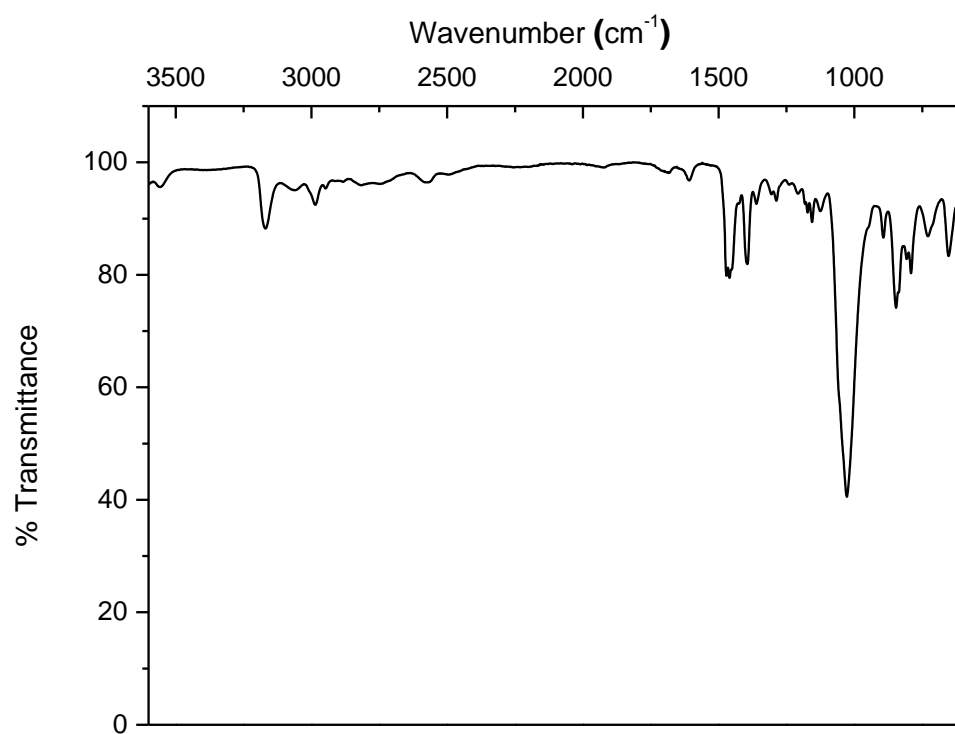
Figure 48. IR spectrum of compound triethylammonium dodecachloro-*closo*-dodecaborate
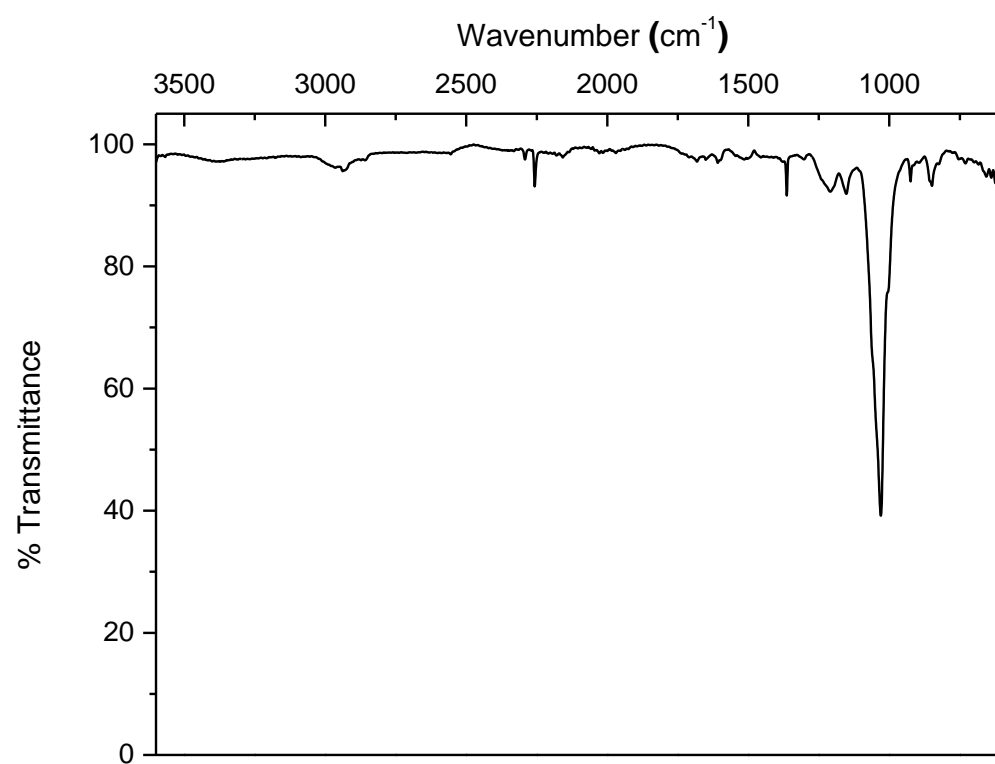
Figure 49. IR spectrum of compound cesium dodecachloro-*closo*-dodecaborate
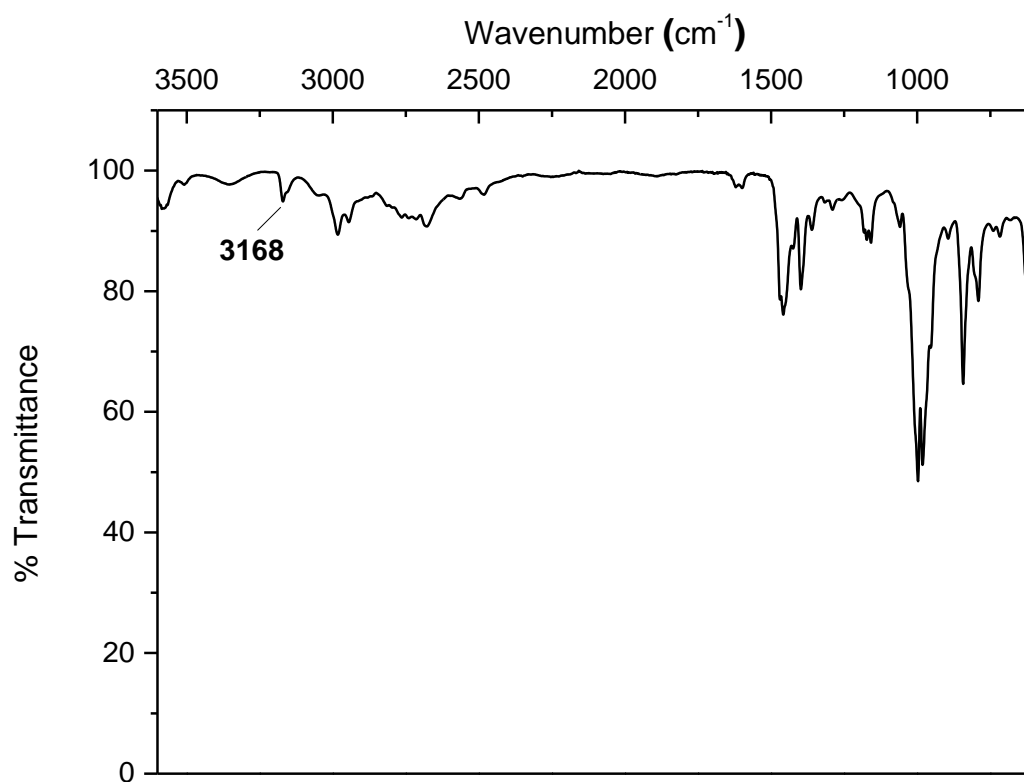
Figure 50. IR spectrum of compound triethylammonium dodecabromo-*closo*-dodecaborate
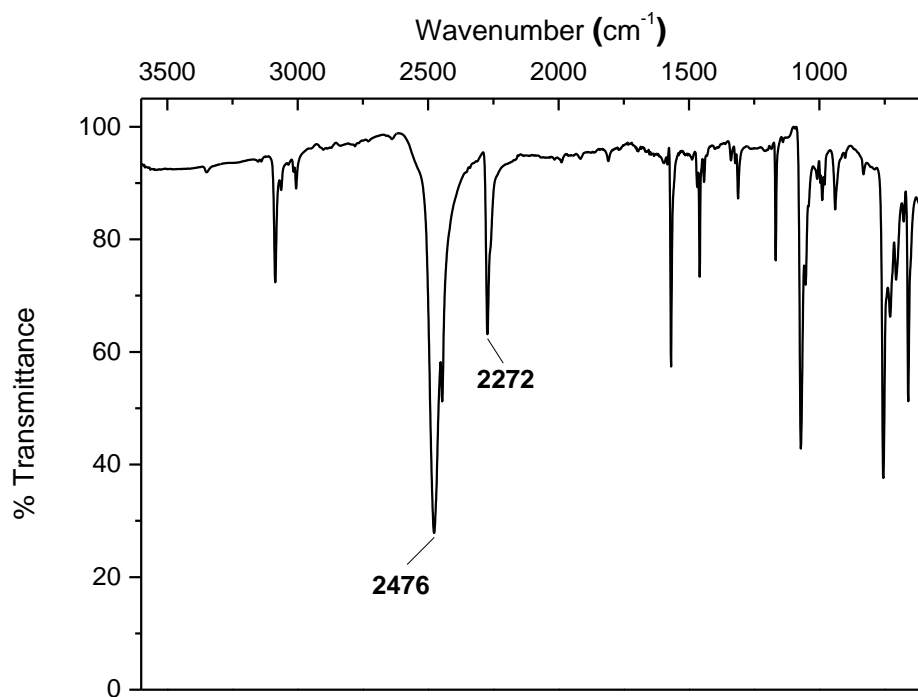
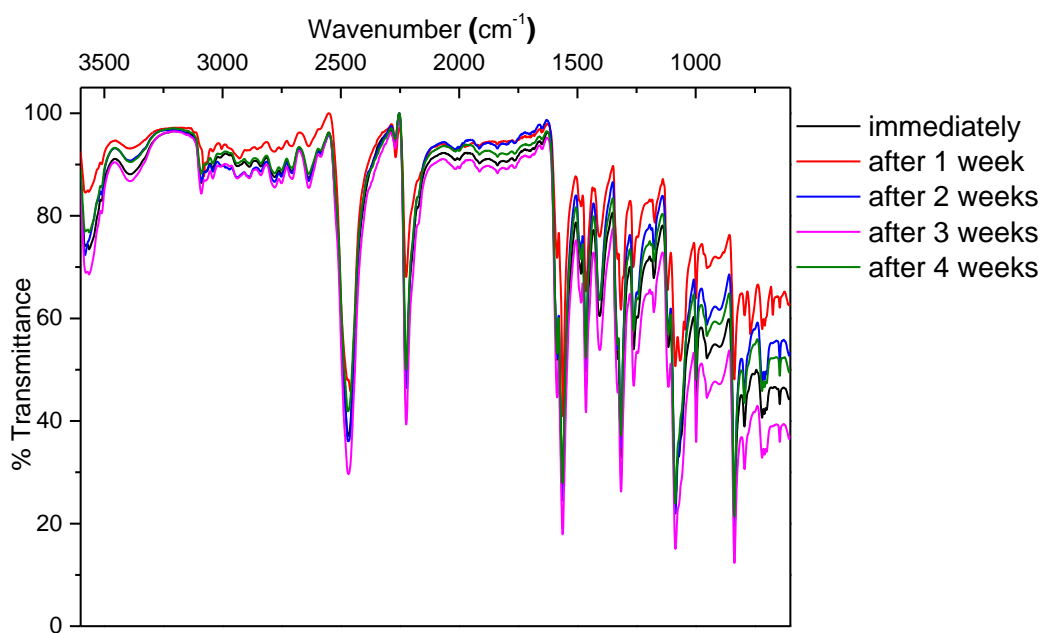**Figure 51.** IR spectrum of compound benzenediazonium dodecahydro-*closo*-dodecaborate (2-)
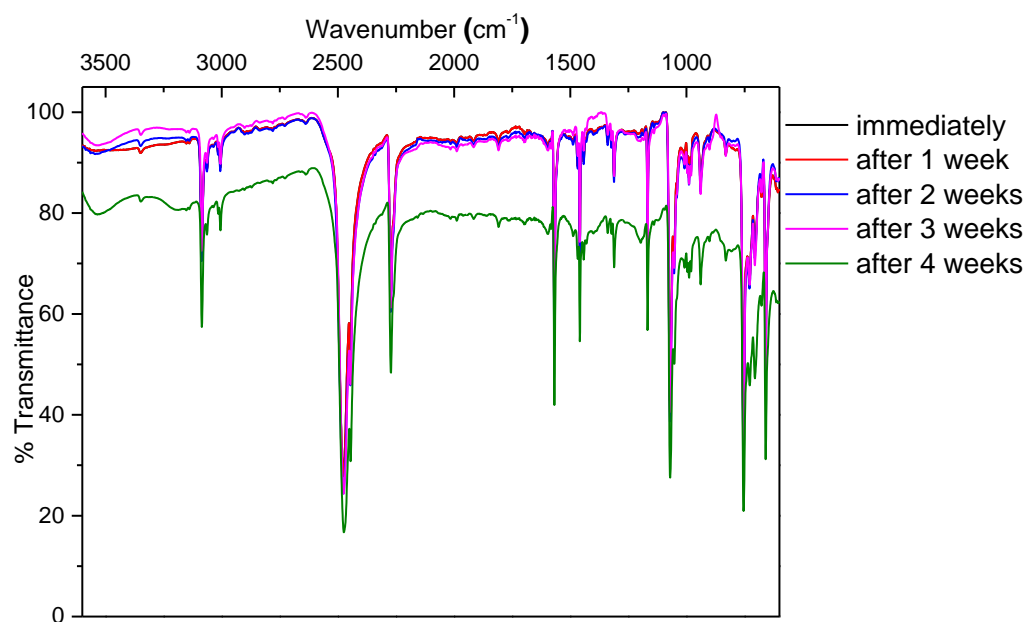
Figure 52. IR spectrum of compound benzenediazonium dodecahydro-*closo*-dodecaborate for 4 weeks
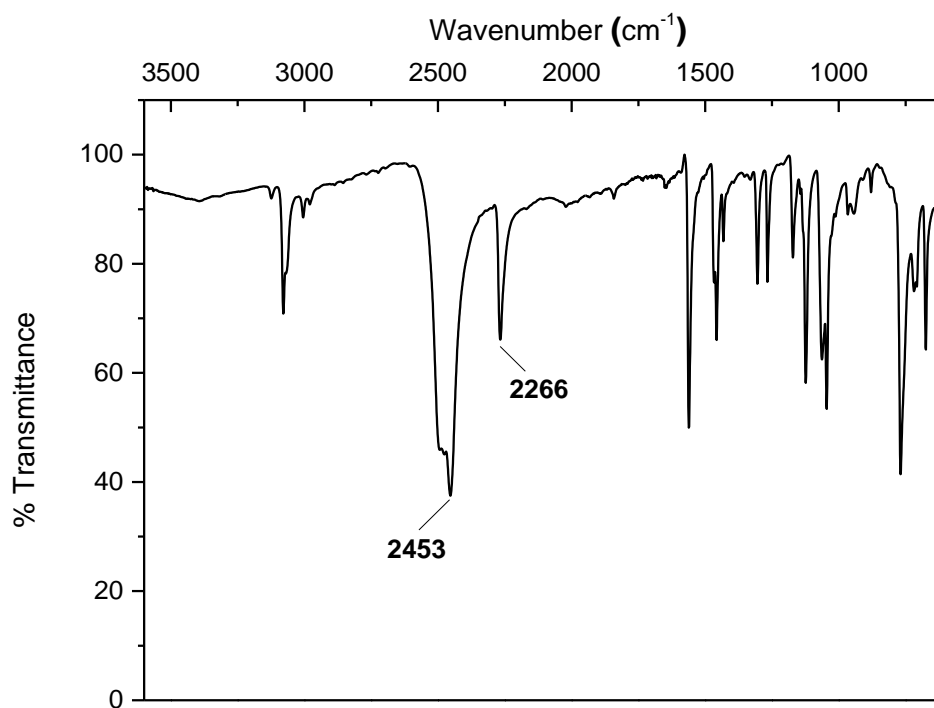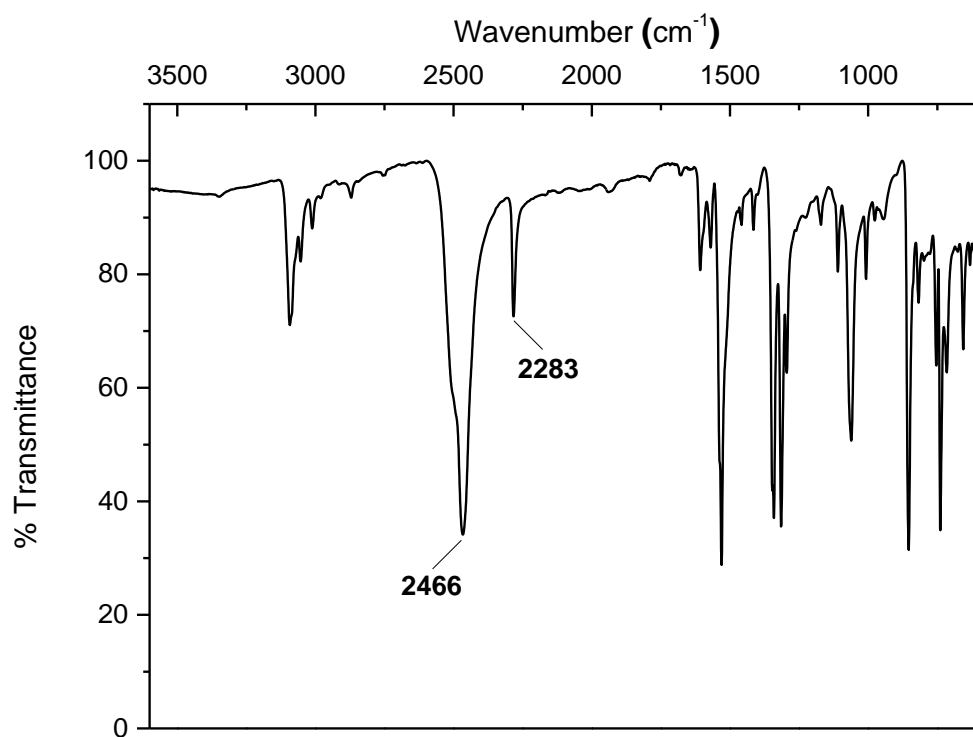
Figure 53. IR spectrum of compound 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate
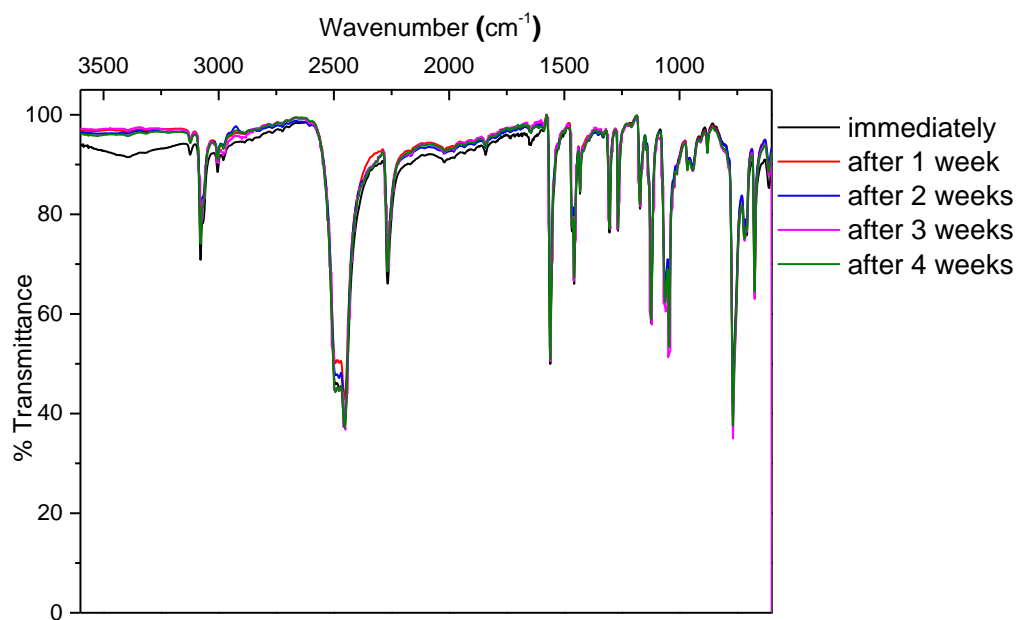
Figure 54. IR spectrum of 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate for 4 weeks
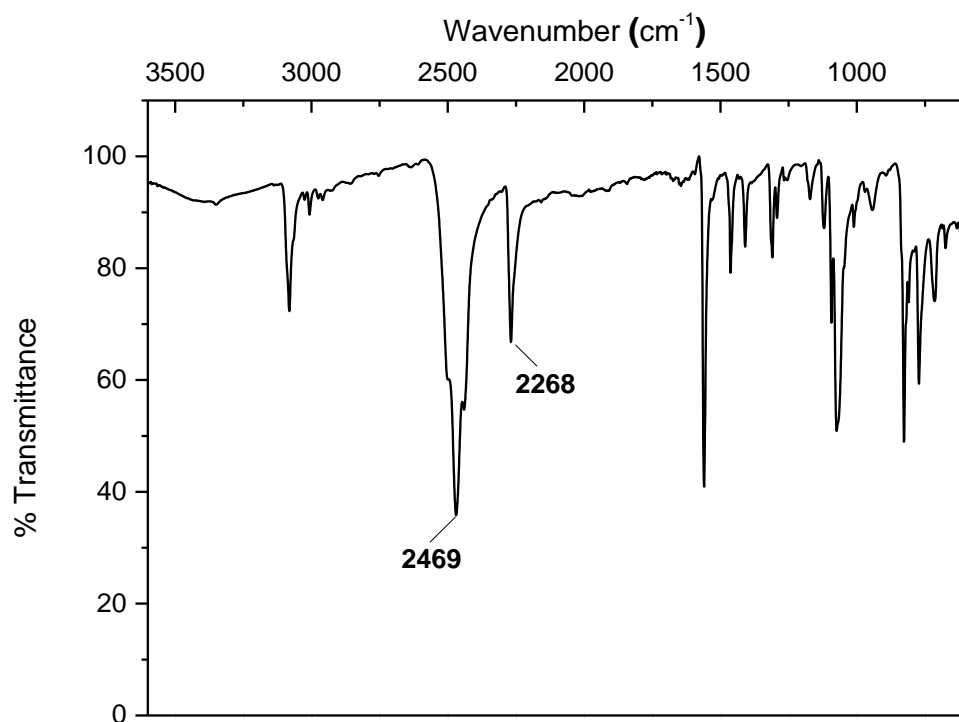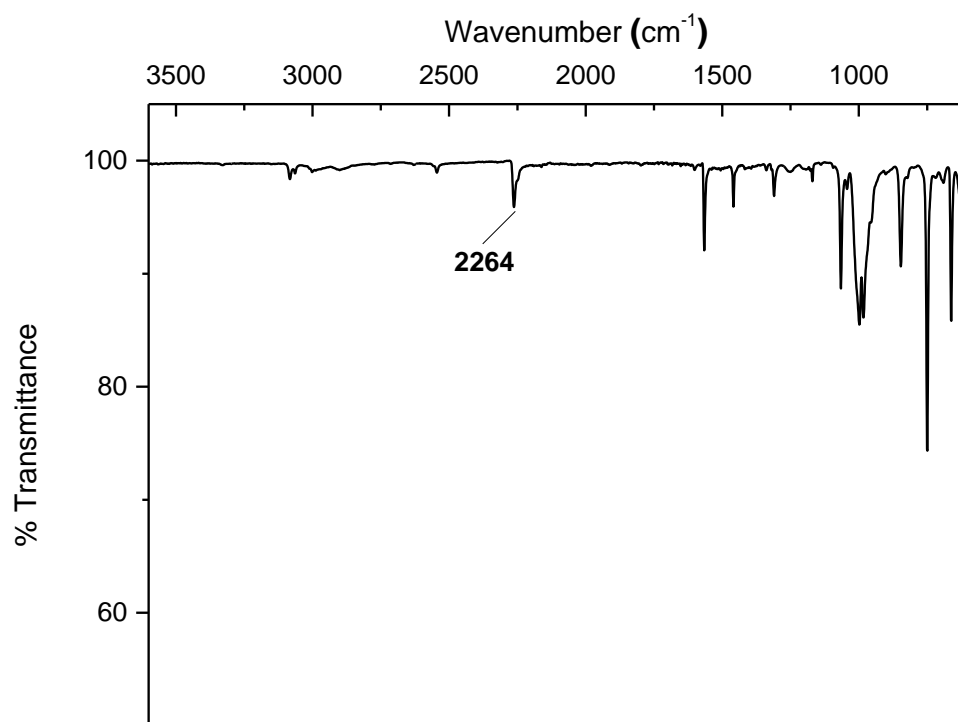
Figure 55. IR spectrum of compound 4-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate

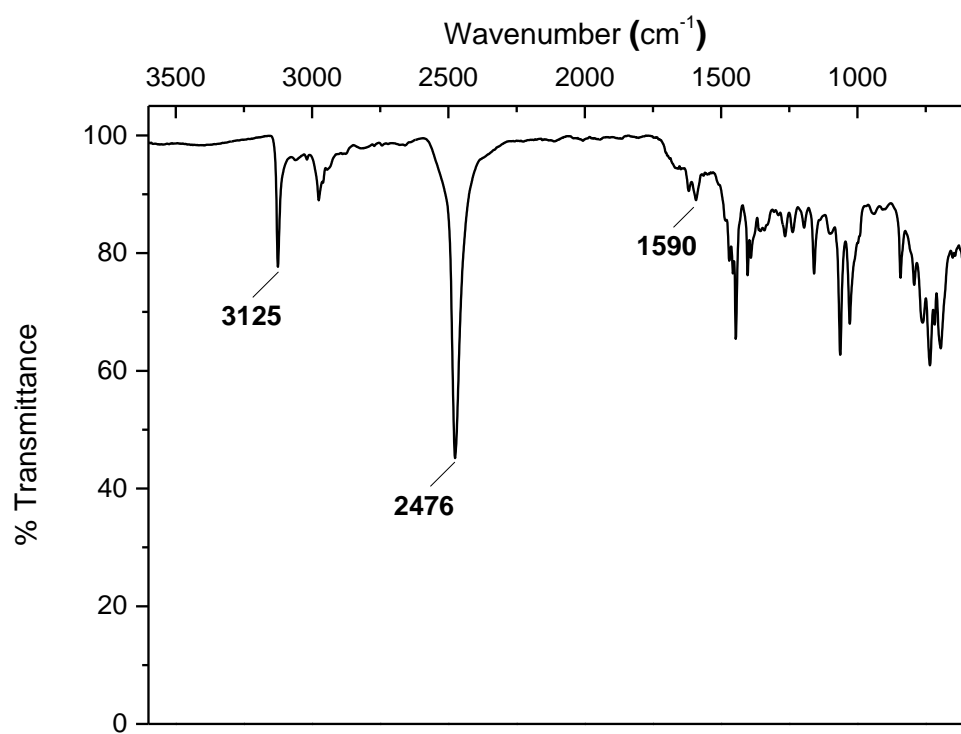**Figure 56.** IR spectrum of 4-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate for 4 weeks
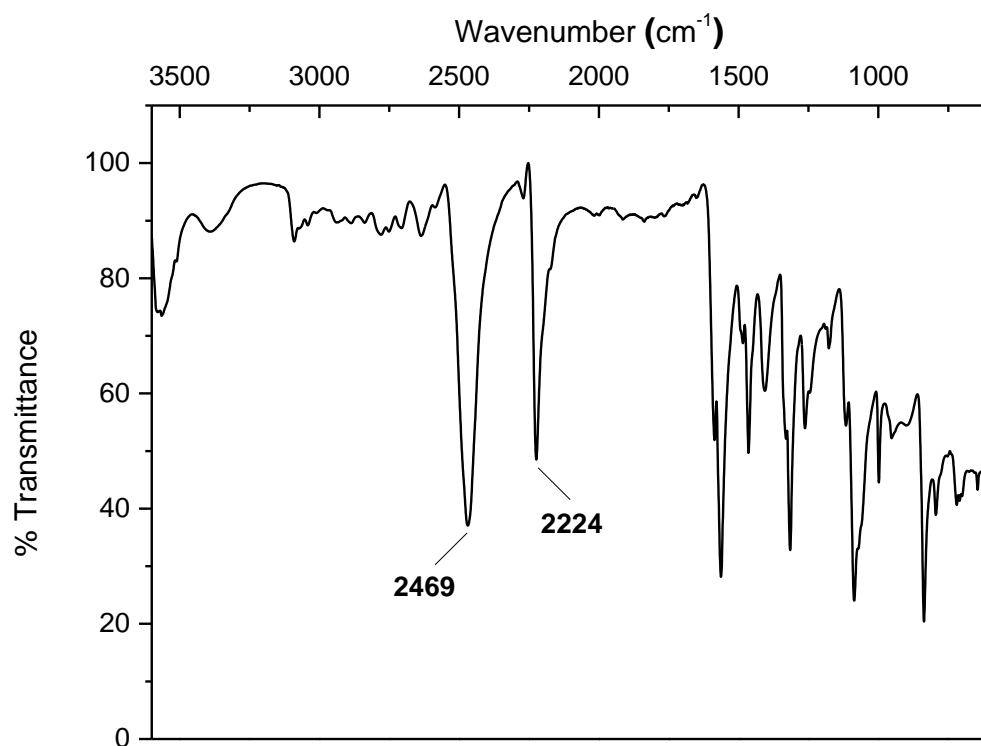
Figure 57. IR spectrum of compound 4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate (2-)

Figure 58. IR spectrum of 4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate for 4 weeks
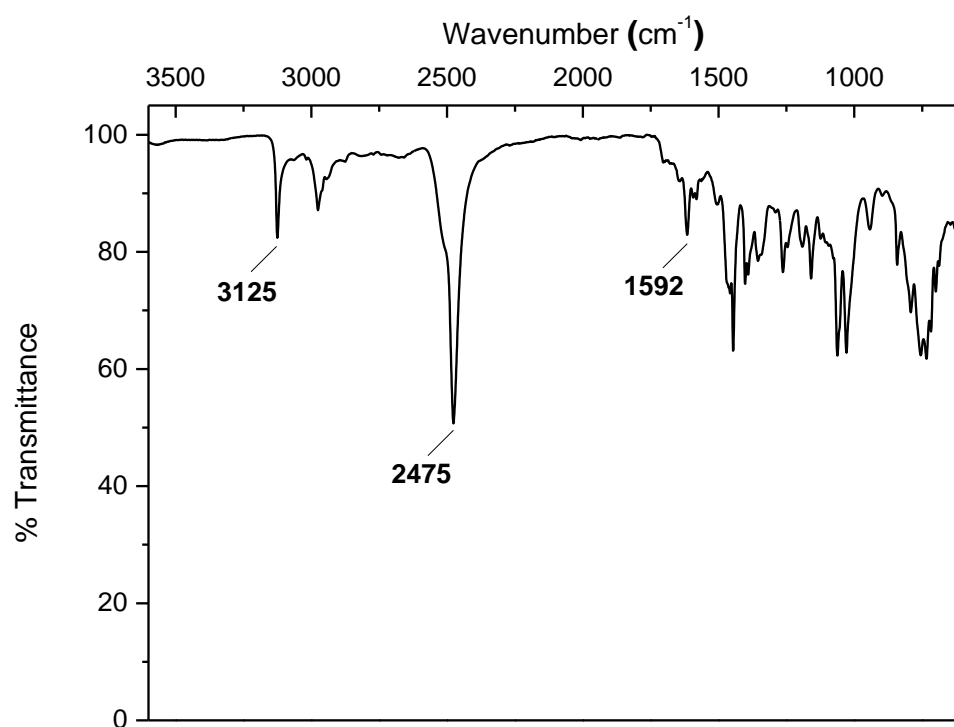
Figure 59. IR Spectrum of compound 4-nitrobenzenediazonium dodecahydro-
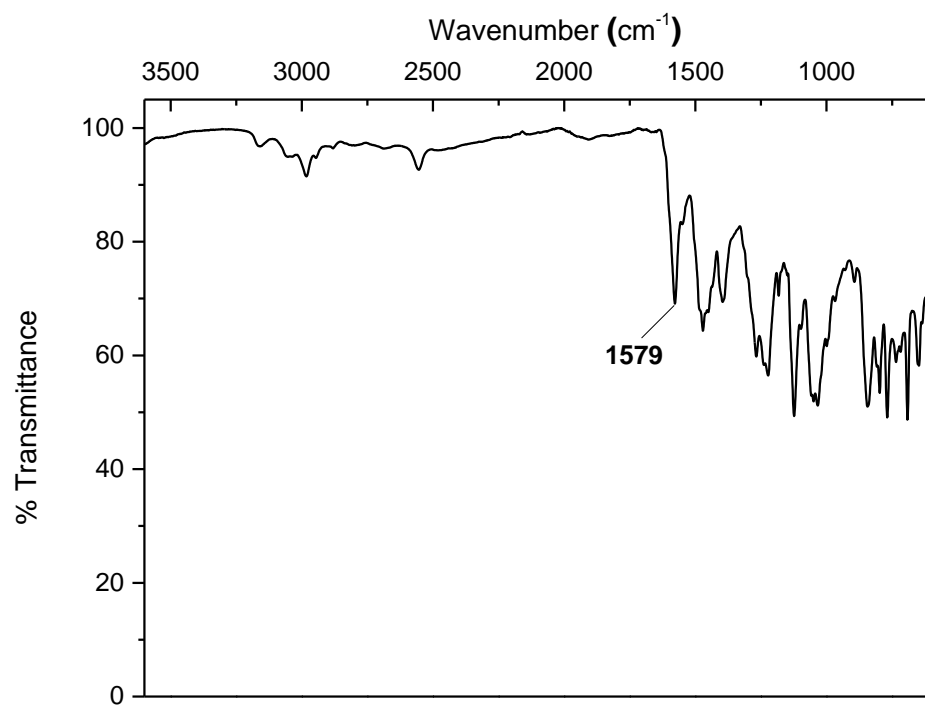*closo*-dodecaborate (2-)

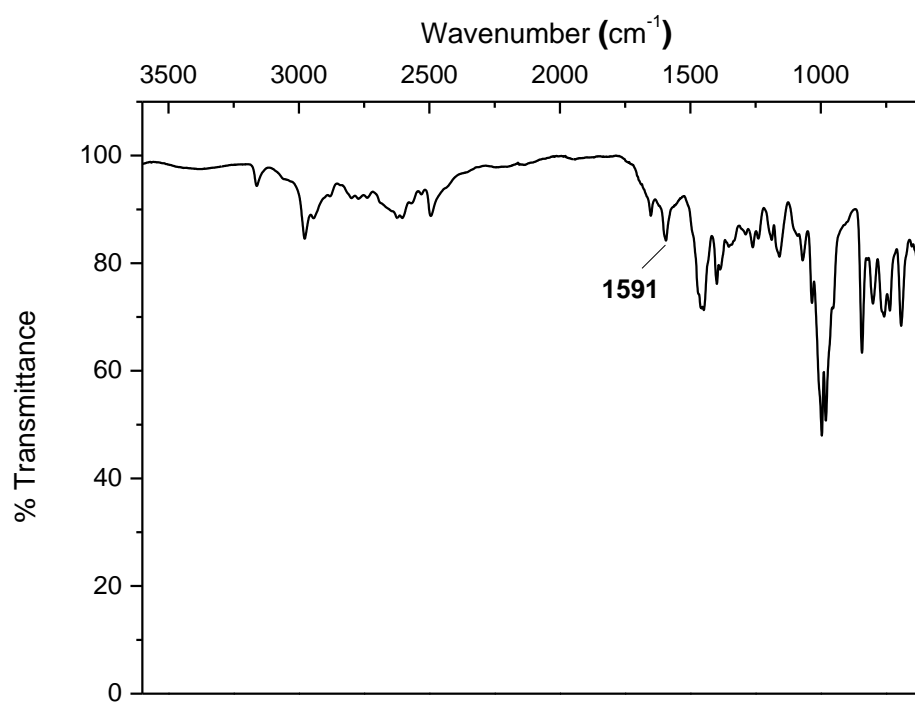**Figure 60.** IR Spectrum of compound benzenediazonium dodecabromo-*closo*-dodecaborate (2-)

Figure 61. IR spectrum of 4-(dimethylamino)azobenzene and triethylammonium dodecahydro-*closo*-dodecaborate

Figure 62. IR spectrum of 2-chloro-4'-(dimethylamino)azobenzene and triethylammonium dodecahydro-*closo*-dodecaborate mixture

Figure 63. IR spectrum of 4-hydroxyazobenzene and triethylammonium dodecachloro-*closo*-dodecaborate mixture
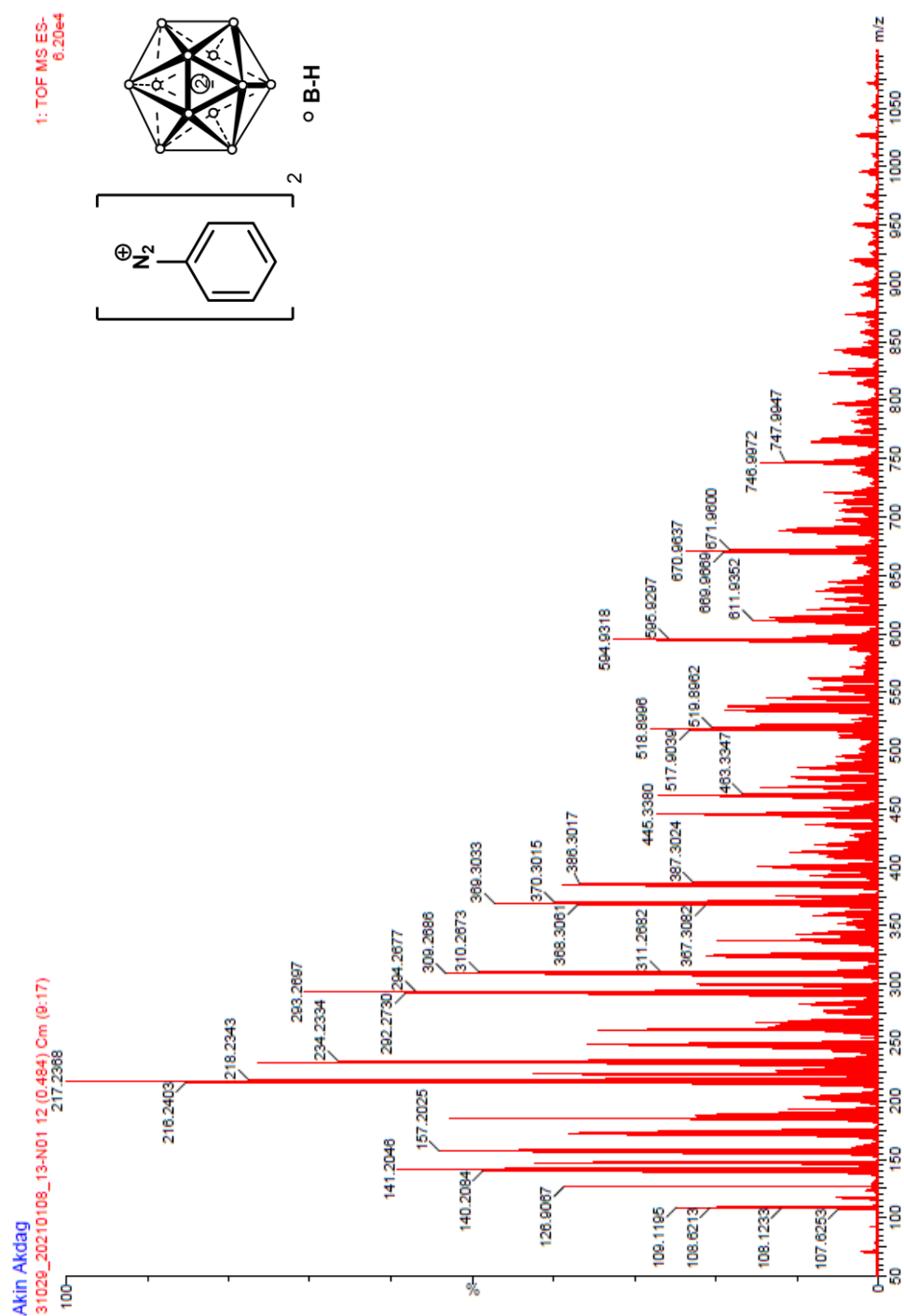
Figure 64. IR spectrum of 4-(dimethylamino)azobenzene and triethylammonium dodecabromo-*closo*-dodecaborate mixture
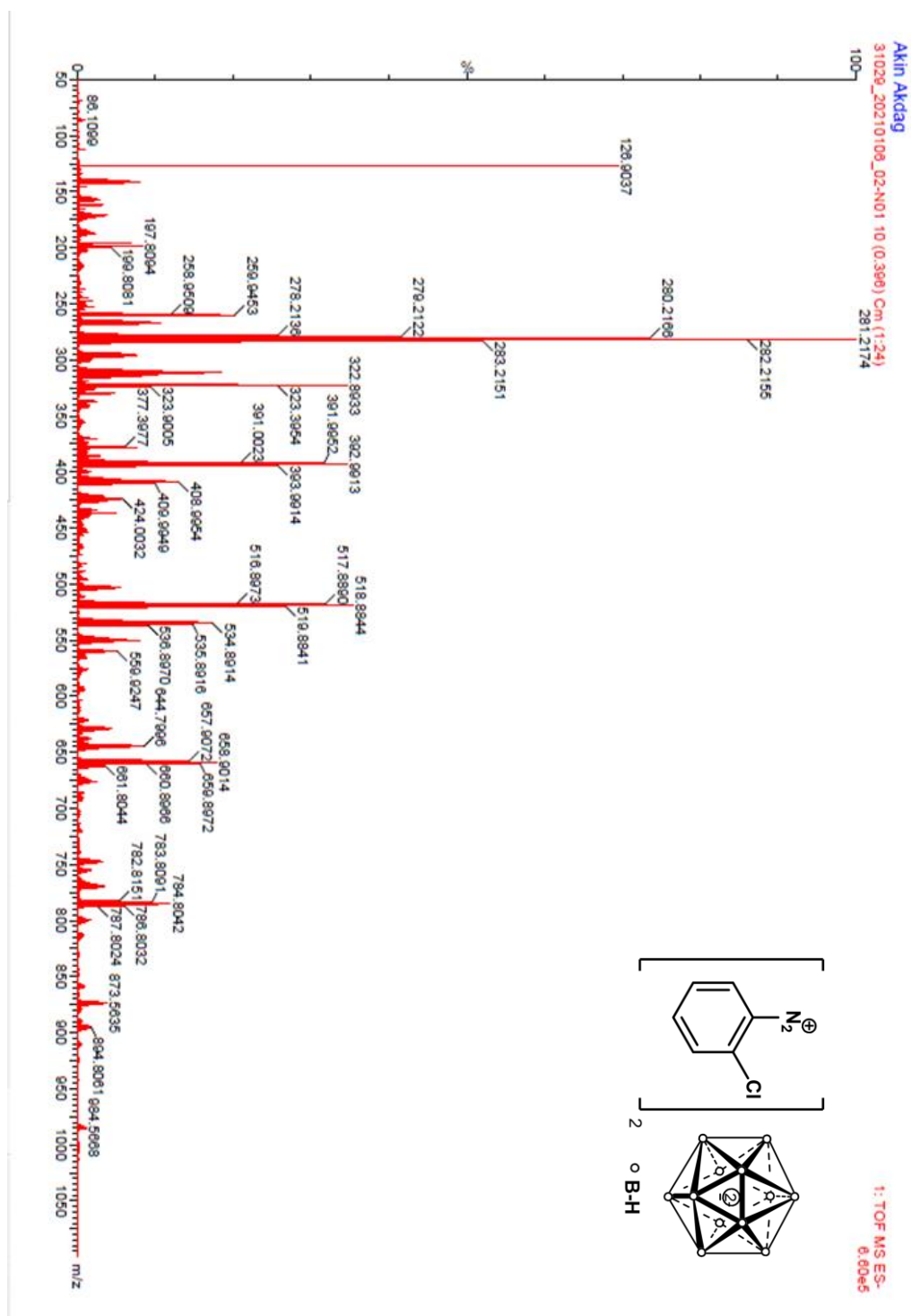
C. HRMS Spectra

High Resolution Mass Spectra (HRMS) Spectra were processed in negative mode on (ES-) using Time of Flight mass analyzer.
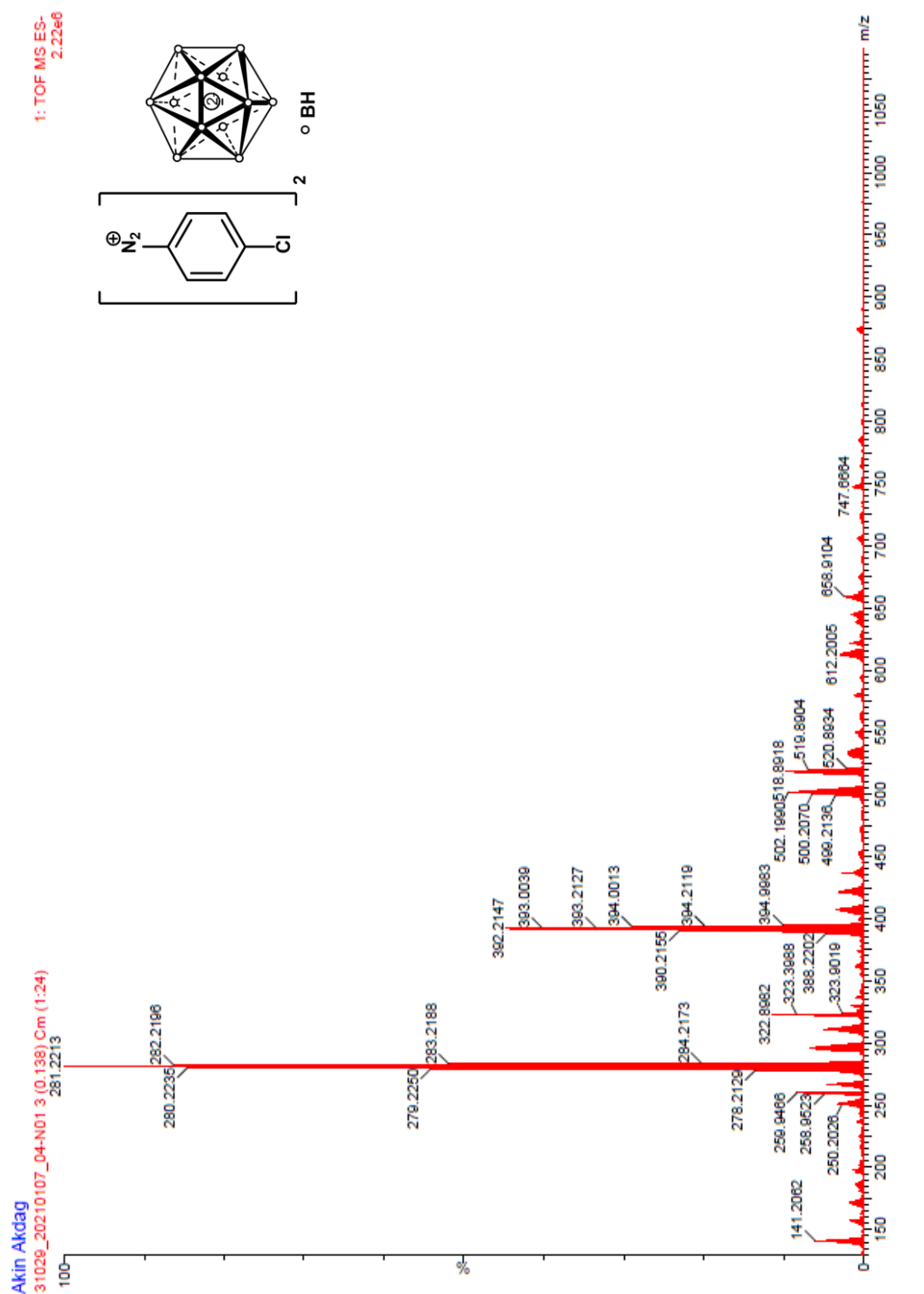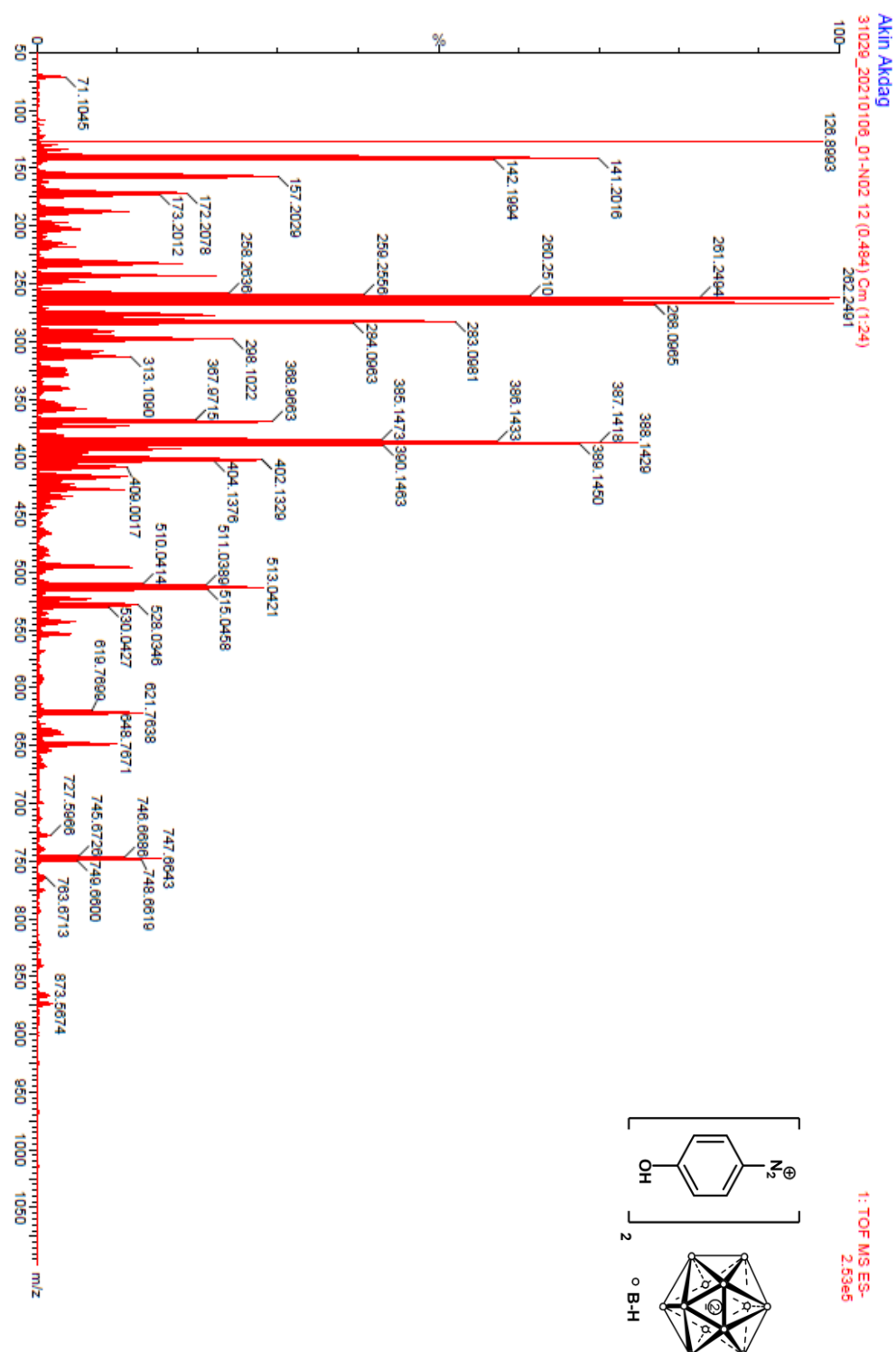
Figure 65. HRMS spectrum of benzenediazonium dodecahydro-*closo*-dodecaborate

Figure 66. HRMS spectrum of 2-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate

Figure 67. HRMS spectrum of 4-chlorobenzenediazonium dodecahydro-*closo*-dodecaborate

Figure 68. HRMS spectrum of 4-hydroxybenzenediazonium dodecahydro-*closo*-dodecaborate