STUDIES ON DODECABORATE DIANION AND CARBORATE ANION AMINATION AND THEIR USE IN STABILIZATION OF ARYLDIAZONIUM CATIONS

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STUDIES ON DODECABORATE DIANION AND CARBORATE ANION AMINATION AND THEIR USE IN STABILIZATION OF ARYLDIAZONIUM CATIONS

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ABSTRACT

STUDIES ON DODECABORATE DIANION AND CARBORATE ANION AMINATION AND THEIR USE IN STABILIZATION OF ARYLDIAZONIUM CATIONS

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Boron is one of the most interesting elements in the periodic table. Boron chemistry is not ordinary due to the bonding. The bonding in boron related compounds is classified as non-classical bonds. Due to the bonding nature of boron, boron clusters have interesting properties, i.e. weakly coordinating ability. With this in mind, in this thesis, dodecaborate dianion and carborate anion were synthesized. The synthesized boron cages were derivatized and were subjected to amination reactions with two different synthetic routes. These cages were also used to capture aryldiazonium cations as salts and these cations were introduced to the clusters. Moreover, captured aryldiazonium cations were subjected to hetero Diels-Alder reactions.

Keywords: Dodecaborate, Carborate, Amination, Aryldiazonium cations

ÖZ

DODEKABORAT DİANYONUNUN VE KARBORAT ANYONUNUN AMİNLENMESİ VE ARİLDİAZONYUM KATYONLARININ STABİLİZASYONUNDA KULLANIMI ÜZERİNE ÇALIŞMALAR

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Bor, periyodik tablodaki en ilginç elementlerden biridir. Bor kimyası, bağ yapma bakımından alışılmışın dışındadır. Bor içeren bileşiklerdeki bağlar klasik olmayan bağlar olarak sınıflandırılmıştır. Borun bu bağ yapma doğası nedeniyle, bor kafesleri zayıf koordine olma gibi ilginç özelliklere sahiptir. Bunu akılda tutarak, bu tezde, dodekaborat dianyonu ve karborat anyonu sentezlenmiştir. Sentezlenen bor kafesleri türevlendirilmiş ve bu kafeslere amin fonksiyonel grubu takılmaya çalışılmıştır. Ayrıca bu kafesler arildiazonyum katyonlarının tuz olarak yakalanmasında kullanılmışlardır ve arildiazonyum katyonları bu kafeslere bağlanmıştır. Yakalanan arildiazonyum katyonları üzerinde hetero Diels-Alder tepkimeleri denenmiştir.

Anahtar Kelimeler: Dodekaborat, Karborat, Aminleme, Arildiazonyum katyonları

To my beloved family

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ABBREVIATIONS

NIS	*N*-iodosuccinimide
NBS	*N*-bromosuccinimide
NCS	*N*-chlorosuccinimide
THF	Tetrahydrofuran
MeCN	Acetonitrile
DCM	Dichloromethane
DMAP	4-(Dimethylamino)pyridine

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SCHEMES

CHAPTER 1

INTRODUCTION

1.1 Boron Atom

Boron is one of the most interesting elements in the periodic table which is the first member of group 13. It is different than the other members of group 13 by being a nonmetal, whereas all the other members of this group are classified as metals.

Besides being the only nonmetal in its group, boron has many interesting properties. Boron has three electrons with four atomic orbitals which makes boron electron deficient.[1] Detailed discussion about electron deficiency of boron atom is given later in the text. As a member of group 13, boron has $2s^2 2p^1$ electron configuration and can form three colvalent bonds by electron sharing which makes the boron atom not obeying the octet rule and its compounds to act as Lewis acids with one empty p orbital.[2]

Moreover, boron is an inert atom in its mineral forms, which makes it not available for an attack (exceptions are Fluorine and Nitric acid).[2] Also, being a semi-conductor and absorbing neutrons are the properties of boron atom.[3]

Boron is not found in nature in its elemental form. It is found in different minerals. Louis Joseph Gay-Lussac, Louis Jacques Thenard and Humphyry Davy were the ones who had first obtained elemental boron by heating boric acid with potassium in 1808 but resulting elemental boron was with low purity.[4]

Boron containing compounds have many application areas. The most common ones are glass, ceramic, agriculture and detergent industries and these four account for 80% of consumption of boron. Uncommon application areas are spacecrafts, aircrafts, nuclear applications, military vehicles, fuels, electricity sector,

communication sector, polymeric materials, nanotechnology, automotive industry, energy sector, metallurgy and construction sector.[3]

One of the most important properties of boron atom is its capacity of forming cluster compounds with hydrogen, carbon and metals.

1.2 Boron Minerals

As mentioned earlier, boron does not exist in elemental form in the nature. It is found as minerals which are natural compounds that consist of B_2O_3 in different proportions. Commercially important minerals are cholemanite, kernite, ulexite, pandermite, boracite, szaibelyite, hydroboracite and borax (Table 1).[3]

Table 1. Boron Minerals and Their Chemical Formulas

Name of the Mineral	**Formula of the Mineral**
Borax	$Na_2B_4O_7.10H_2O$
Cholemanite	$CaB_3O_4(OH)_3.H_2O$
Kernite	$Na_2B_4O_5(OH)_4.2H_2O$
Ulexite	$NaCaB_5O_9.8H_2O$
Pandermite	$Ca_4B_{10}O_{19}.7H_2O$
Boracite	$Mg_3B_7O_{13}Cl$
Szaibelyite	$(Mg,Mn)BO_3H$
Hydroboracite	$CaMgB_6O_8(OH)_6.3H_2O$

Total boron reserve of the world is 4.5 billion tons and can be listed in decreasing order as Turkey(73%), Russia(7%), USA(6%), China(4%), Chile(3%), Peru(2%), Serbia(2%), Bolivia(1%), Argentina(1%) and Kazakhstan(1%) (Figure 1).[3]

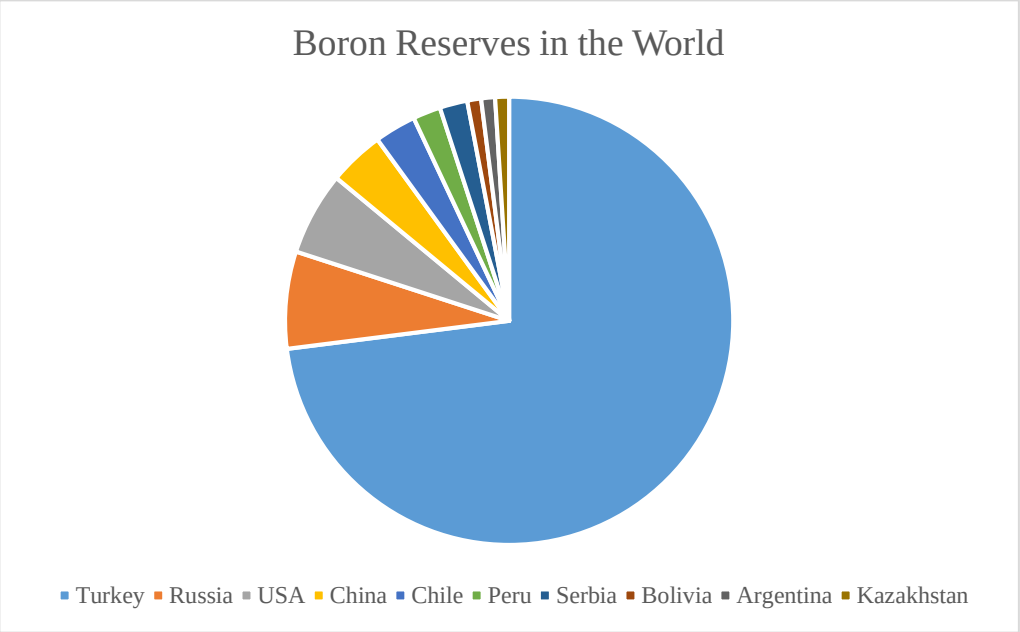
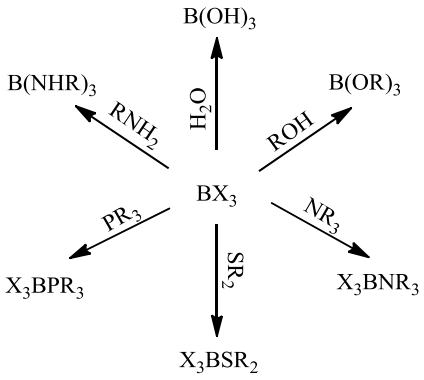


Figure 1. Boron Reserves in the World

1.3 Boron Trihalides, Boron-Oxygen Compounds & Boron Nitrogen Compounds

1.3.1 Boron Trihalides

Boron trihalides have incomplete octet and they act as Lewis acids. Lewis acidity order of boron trihalides is $BBr_3 > BCl_3 > BF_3$.[2] Boron trihalides have trigonal-planar geometry with the formula of BX_3. Boron has an exception here too which is its halides are monomeric in gas, liquid and solid phases. Trifluoride and trichloride compounds of boron are gases where tribromide is a liquid and triiodide is solid. Boron trihalide compounds undergo protolysis, complex formation and substitution reactions (Scheme 1).[2]



Scheme 1. Reactions of Boron Trihalides

1.3.2 Boron-Oxygen Compounds

Boric acid, $B(OH)_3$, is the simplest of boron oxygen compounds. In aqueous solutions, it acts as a Bronsted acid but it is too intricate to explain as a simple proton transfer reactions. In reality, it is a weak Lewis acid and the complex compounds forming from the reactions of boric acid with water can be regarded as source of protons (Scheme 2).[2]

$$B(OH)_3(aq) + 2H_2O(l) \rightleftharpoons H_3O^+(aq) + [B(OH)_4]^-(aq)$$

Scheme 2. Reaction of Boric Acid with Water

B_2O_3 is the most important oxide and can be prepared by dehydration of $B(OH)_3$ (scheme 3).[2]

$$2B(OH)_3(s) \xrightarrow{\text{heat}} B_2O_3(s) + 3H_2O(l)$$

Scheme 3. Formation Boron Oxide from Boric Acid

B_2O_3 crystals have boron atom conneted to oxygens which propagates. This is one of the main component of borosilicate glass which is used to produce laboratory glassware because of their high heat resistance.[2]

Sodium perborate, $Na_2[B_2(O_2)_2(OH)_4].6H_2O$, can be used in cleaning materials as a bleach over hydrogen peroxide by reason of being more stable and releasing oxygen only at high temperatures.[2]

1.3.3 Boron-Nitrogen Compounds

Boron-nitrogen containing compounds are very similar to carbon-carbon containing compounds with a relationship of being isoelectronic such as borazine, $B_3N_3H_6$, which is isoelectronic with benzene. In 1926, Alfred Stock had first synthesized borazine by reacting diborane with ammonia. In the borazine compound, N atoms carry a partially negative charge where B atoms carry a partially positive charge which makes the B atoms are available to electrophilic attack.[2]

The simplest B-N compound, BN (boron nitride), in its stable form consists of planar sheets as graphite and it is stable up to 1000 ^oC and can be obtained from the reaction of boron oxide with ammonia (Scheme 4).[2]

$$B_2O_3(l) + 2NH_3(g) \xrightarrow{1200^oC} 2BN(s) + 3H_2O(g)$$

Scheme 4. Formation of Boron Nitride from Boron Oxide

Although B-N containing compounds are isoelectronic with C-C containing compounds, properties are very different resulting from the electronegativity difference between boron and nitrogen atoms. As an example, NH_3BH_3 is solid where its isoelectronic molecule ethane is a gas at room temperature. In addition to their differences in states in room temperature, their polarities differ too (ammoniaborane is a polar molecule where ethane is a nonpolar molecule).[2]

1.4 Borohydrides

Borohydrides are compounds that are composed of boron and hydrogen atoms. The simplest compound of this group is called diborane (B_2H_6). From the structure of diborane (Figure 2), it could be easily understood that the bonds cannot be described as classical 2 center, 2 electron bonds. Resulting from its electron deficiency, these bonds should be described as 3 center, 2 electron bonds.

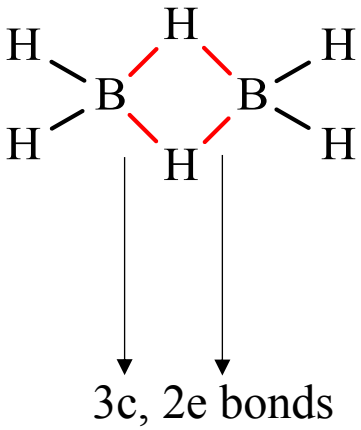


Figure 2. Structure of Diborane and types of its bonds

Diboranes react with Group 1 metal hydrides to form metal salts of tetrahydridoborate anions. Examples of these metal salts of tetrahydridoborates are $LiBH_4$, $NaBH_4$, KBH_4 and $RbBH_4$.[2]

Borohydrides, especially the smaller ones, react with air spontaneously (scheme 5), and are hydrolyzed by water (Scheme 6).[2]

$$B_2H_6(g) + 3O_2(g) \longrightarrow 2B(OH)_3(s)$$

Scheme 5. Reaction of Diborane with Air

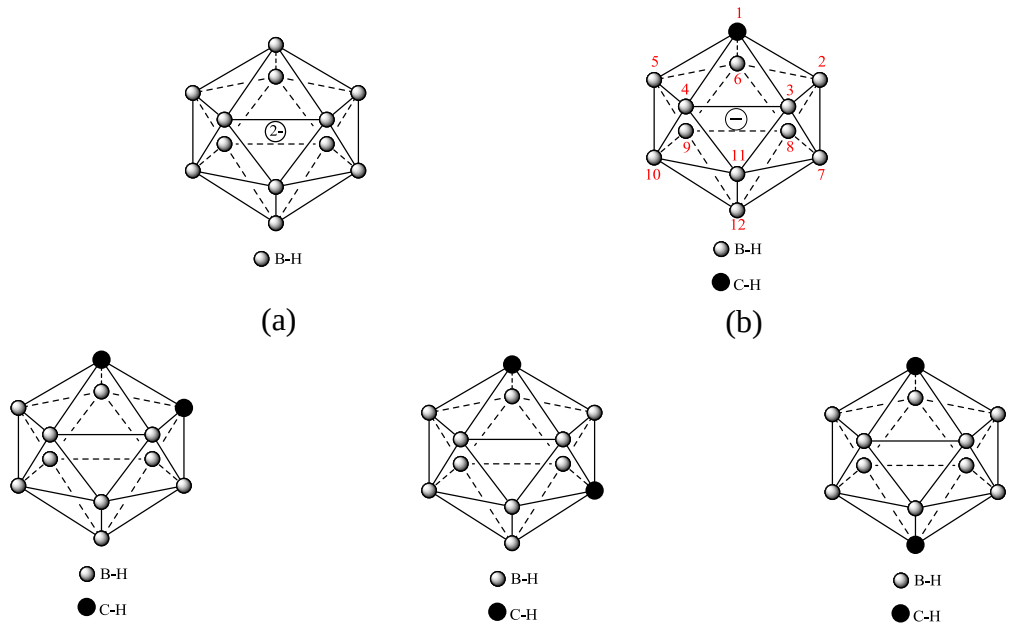
$$B_2H_6(g) + 6H_2O(l) \longrightarrow 2B(OH)_3(aq) + 6H_2(g)$$

Scheme 6. Hydrolysis of Diborane with Water

Vide supra, diborane is the smallest compound as a borohydride and it is the starting material for synthesizing higher boranes by pyrolysis. Higher boranes will be discussed exhaustively below.

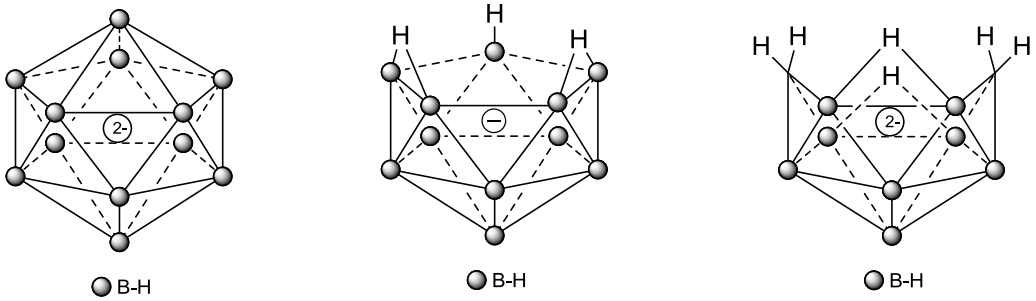
1.4.1 Higher Boron Clusters

At the present time, many compounds in borane chemistry such as borohydrides, carboranes, metallaboranes, metallacarboranes and others are known after Alfred Stock developed the techniques for synthesizing them.[5] Before 1940, structures of larger clusters were thought to be more open and described as resonating one-electron bonds by Pauling.[5] In 1940s, bridge structure of diborane were described by Stitt.[5] This BHB bridge was formulated by Longuet-Higgins afterwards.[5] $B_{10}H_{11}$ was the first higher borane to be structurally characterized. Then, B_5H_9 and B_4H_{10} were described.[5] Main structures of boron clusters can be divided into three main groups as closo, nido and arachno. Closo structures have the general formula of $B_nH_n^{2-}$ for boranes and $C_2B_{n-2}H_n$ for carboranes (Figure 3) where nido structures have the general formula of B_nH_{n+4} for boranes and $C_mB_{n-m}H_{n-m+4}$ for caboranes. Arachno structures have the general formula of B_nH_{n+6} for boranes and $C_2B_{n-2}H_{n+4}$ for carboranes. Closo form can be described as a closed polyhedra and removal of one vertex from closo structure results in nido structures where removal of 1 vertex from nido structures or two vertices from closo structures results in arachno structures (Figure 4).[6] With this in hand, one can simply say that closo boranes or carboranes have n vertices, nido boranes or carboranes have n-1 vertices and arachno ones have n-2 vertices.[7] In closo boranes and carboranes, there are n B-H units and all of them can be classified as exo-B-H bonds. Nido boranes and carboranes are composed of n B-H units as exo B-H bonds and remaining hydrogens occupy BHB bridges. Moreover, arachno boranes and carboranes have n exo B-H units too and remaining hydrogens may occupy BHB bridges or they may be in endo B-H positions.[8]



(a) (b) (c) (d) (e)

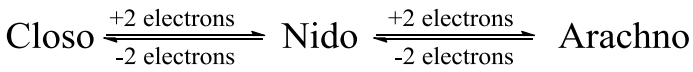
Figure 3. (a) dodecahydro-*closo*-dodecaborate, (b) mono-carba-*closo*-dodecaborate with numbering, (c) *o*-carborane, (d) *m*-carborane, (e) *p*-carborane



(a) (b) (c)

Figure 4. (a) closo structure, (b) nido structure, (c) arachno structure

These three species can be converted to each other by oxidation-reduction, addition of Lewis bases and removal of a substituent (Scheme 7).[8]



Scheme 7. Oxidation-Reduction Reactions of Boron Clusters

Vertex numbering for carba-*closo*-dodecaborate can be done for $CB_{11}H_{12}$ starting with the carbon atom as 1, pentagonal ring consists boron atoms closer to carbon atom should be numbered as 2-6, other pentagonal ring composed of boron atoms can be numbered as 7-11 and the boron atom on the bottom of the cluster should be numbered as 12.[9]

1.4.1.1 Electron Deficiency and Electron Delocalization in Boron Clusters

For three-dimensional boron clusters, it is not possible to talk about octet rule and 18-electron rule where electron deficiency and large electron delocalization occurs.[1] Electron deficiency in boron containing clusters can be described as there are less electrons than the required number of electrons for forming classical 2 center 2 electron bonds.[6] These structures have the characteristic property of having 3 center 2 electron bonds forming trigonal faces in hypercoordination which results in the low electron density in skeletal bonds.[7] For example, there are 50 electrons and 42 bonds in $(B_{12}H_{12})^{2-}$.[10] Using multicenter bonds to describe the bonding in electron deficient compounds became accustomed. For boranes, every boron atom that forms four bonds can be involved in 2 center BH bonds, 2 center BB bonds, three center BHB bonds and three center BBB bonds.[8] Another way of forming 3 center bonds was described by forming fractional bonds with the fractional use of orbitals which gives boron atom the potential to form 4 bonds and since fractional atomic orbitals are used, violation of the Pauli exclusion is unpronounceable (Figure 5).[5]

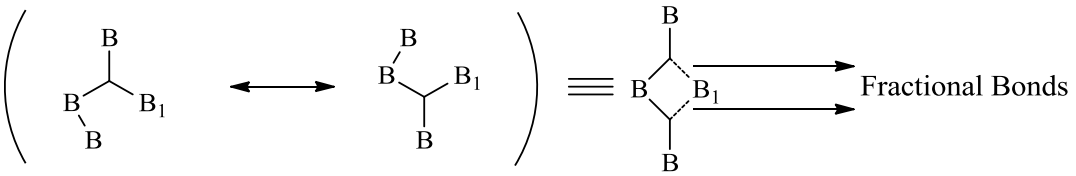


Figure 5. Fractional Bonds of Boron Atom

1.4.1.2 Aromaticity in Boron Clusters

Cyclic molecules having electron delocalization are considered as aromatic molecules and they cannot be shown with Lewis structures. The property of aromaticity cannot be measured experimentally due to the lack of specific quantum mechanical operator. On the other hand, aromatic molecules have characteristic properties such as being highly stable, having low reactivity, bond length equalization and having unusual magnetic and spectroscopic properties. Moreover, aromatic compounds have high symmetry and degenerate HOMO (highest occupied molecular orbitals) with fully occupied or same-spin half-filled which gives the aromatic compounds extra stabilization.[11]

Closo boranes and carboranes are considered as aromatic compounds since they prefer substitution reactions instead of addition reactions.[12] In addition to preference of substitution reactions over addition reactions, NICS (nucleus-independent chemical shift) values support the idea of being aromatic by having negative values. As an example, 5-membered ring part has -34.6 ppm and 3-membered ring part has -48.3 ppm NICS values in $B_{12}H_{12}^{2-}$.[13]

1.4.1.3 Wade's Rule

The structures of boron clusters cannot be explained by Hückel's 4n+2 π electron rule for aromaticity. There was a need for a method to describe their structures. In 1970s, Wade proposed a formula for understanding the structures of boron clusters where knowing the formula is enough to determine the structure.[2] While counting the electrons, Wade focused on the skeletal electrons which means he ignored the exo B-H or C-H bonds. For boranes and carboranes, a C-H unit provides 3 electrons and a B-H unit provides 2 electrons to the skeleton. For closo structures, there are n+1 skeletal electron pairs where nido structures have n+2 skeletal electron pairs and arachno structures have n+3 skeletal electron pairs.[14] Another approach to Wade's rules coming from the relation between number of vertices and the skeletal bond pair. The formula can be expressed as basically 2N+2 skeletal electrons rule where N is the number of vertices and very different from the *n* in Hückel's rule. In Hückel's rule, there is no relation between *n* and the structure but in Wade's rule, N is related with nothing but the structure.[13] For $B_{12}H_{12}^{2-}$, there are 26 skeletal electrons (24 coming from B-H units and 2 coming from the charge) with 12 vertices that forms the cluster and putting 12 in the formula, gives the number of skeletal electron as 26.[6]

Table 2. Skeletal Electron Pairs and Examples of Closo, Nido and Arachno Structures

Type	**Formula**	**Skeletal electron pairs**	**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, B_6H_{10}
Arachno	B_nH_{n+6}	n+3	B_4H_{10} , B_5H_{11}

1.5 $B_{12}H_{12}^{2-}$ Anion

Boranes were discovered in 1912 by Alfred Stock but they were thought to be used only in research areas as they are chemically very different.[15] In 1955, Longuet-Higgins and Roberts predicted that the icosahedral borane ($B_{12}H_{12}^{2-}$) should be in dianion form to be stable by calculations.[16] Hawthorne and Pitochelli proved this prediction experimentally in 1960 with very low yield since $B_{12}H_{12}^{2-}$ was the side product.[17] After some time, production of $B_{12}H_{12}^{2-}$ with high yields were succeeded and properties were examined. Group 1A salts of *closo*-dodecaborate anion are thermally stable. For example, Li and Na salts do not decompose below 600 ^{o}C where Cs salt is stable up to 810 ^{o}C .[18,19,20]

1.5.1 Synthesis of $B_{12}H_{12}^{2-}$

There are several synthetic pathways to obtain $B_{12}H_{12}^{2-}$ with high yields. One of them is the reaction between smaller boranes and borane complexes with Lewis bases such as triethylamine. For example, reactions of triethylamine-borane complex with diborane at 180 ^{o}C, pentaborane at 125 ^{o}C and pentaborane dimer at 100 ^{o}C gives $B_{12}H_{12}^{2-}$ as triethylammonium salt with yields 90%, 90% and 59%, respectively. Also, pyrolysis of triethylamine-borane with decaborane(14) at 190 ^{o}C gives $B_{12}H_{12}^{2-}$ as product with 92% yield.[21,22,23] Second method is based on the reaction of group 1A tetrahydroborates with boranes or triethylamine-borane complex as in the first method. As an example, $NaBH_4$ reacts with diborane to give the desired product with 80% yield at 180 ^{o}C.[7,8] In addition to that, $NaBH_4$ also reacts with decaborane at 160 ^{o}C to give the expected product with 91% yield.[17,24] Another way to obtain $B_{12}H_{12}^{2-}$ is the reaction of $NaBH_4$ or KBH_4 with borane complexes of triethylamine or trimethylamine at 200-250 ^{o}C gives $B_{12}H_{12}^{2-}$ as desired product with a yield of 95%.[17] The other synthetic pathway to obtain $B_{12}H_{12}^{2-}$ is pyrolysis of borohydrides. For example, pyrolysis of $(Et_4N)BH_4$ gives tetraethylammonium salts of $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{11}H_{14}^{-}$ and $B_{12}H_{12}^{2-}$. Major product of this pyrolysis at 185 ^{o}C is

$(Et_4N)_2[B_{10}H_{10}]$ and if this reactions proceeds with the presence of triethylamine-borane complex, $(Et_4N)_2[B_{12}H_{12}]$ is the major product.[25] In addition to pyrolysis of borohydrides, pyrolysis of octahydrotriborates (B_3H_8) also provides closo-dodecaborate anion. Pyrolysis of group 1A metal salts of octahydrotriborates gives the desired product as a mixture with other higher boranes at high temperatures. Also, pyrolysis of Mg, Sr and Ca salts of octahydrotriborates, gives *closo*-dodecaborate anion with reasonable yields and again pyrolysis of tetraalkyammonium salts of octahydrotriborates gives the desired product.[17]

Since diborane is toxic and decaborane is expensive, a new method was developed to synthesize *closo*-dodecaborate anion with cheap starting materials which are $NaBH_4$ and iodine. Iodine was dissolved in diglyme and added to the suspension of sodium borohydride in digylme in 6h dropwise at 100 ^oC. Solution is stirred overnight for the completion of disproportionation of octahydrotriborate to $[B_{12}H_{12}]^{2-}$ and BH_4^-. Solvent is evaporated and remaining solid is dissolved in water. Then, the solution is acidified with hydrochloric acid. Solution is stored at 6 ^oC overnight and filtration is applied to collect the precipitate formed which is boric acid. To the filtrate, $Et_3N.HCl$ is added and filtered to obtain $(Et_3NH)_2[B_{12}H_{12}]$ with 51% yield (Scheme 8).[26]

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

$$BH_4^- \longleftarrow B_3H_8^- \longrightarrow B_{12}H_{12}^{2-}$$

$$5Na[B_3H_8] \longrightarrow Na_2[B_{12}H_{12}] + 3Na[BH_4] + 8H_2\uparrow$$

$$Na[BH_4] + HCl + 3H_2O \longrightarrow H_3BO_3 + NaCl + 4H_2\uparrow$$

$$Na[B_{12}H_{12}] + 2Et_3N.HCl \longrightarrow (Et_3NH)_2[B_{12}H_{12}] + 2NaCl$$

Scheme 8. Synthesis of $B_{12}H_{12}^{2-}$ from $NaBH_4$

1.5.2 Derivatization of $B_{12}H_{12}^{2-}$

Synthesized triethylamine salt of $B_{12}H_{12}^{2-}$ can be easily converted to alkali metal salts such as sodium, potassium and cesium. Synthetic pathway for changing the cation is simply adding triethylamine salt to solution of NaOH, KOH or CsOH in water. Cs salt differs from the other ones since $Cs_2B_{12}H_{12}$ is less soluble in water and immediate precipitation of Cs salt occurs where sodium and potassium salts needs solvent evaporation step.[26] In addition to these salts, silver salt can be prepared too but this time sodium salt is used as a starting material. In this procedure, both $AgNO_3$ and $Na_2B_{12}H_{12}$ dissolves in deionized water. Then, the solution containing silver nitrate is added to the solution containing sodium salt slowly and rapid precipitation occurs as $Ag_2B_{12}H_{12}$.[27] Moreover, from the silver salt of dodecaborate anion, salts with nitrogen containing cations can be prepared with metathesis reactions.[27]

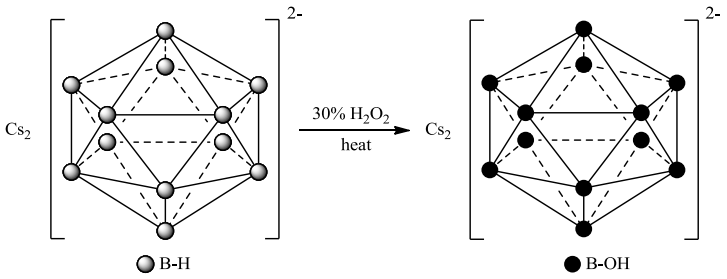
1.5.2.1 Halogenation

Halogenation reactions of $B_{12}H_{12}^{2-}$ results in monohalogenated to perhalogenated compounds according to reaction conditions. The simplest way to halogenate $B_{12}H_{12}^{2-}$ is to react it with hydrogen halides. In these reactions, hydrogen halide is bubbled into solution containing tetrabutylammonium salt of $B_{12}H_{12}^{2-}$ in dichloromethane. Although this reaction does not work in 5h at room temperature, monohalogenated compound is formed with little amount of starting material at 60 ^oC in 1 hour. At 80 ^oC, monohalogenation and some amount of dihalogenated compounds are formed. If the reaction proceeds 5h, no starting material will be left.[28] Hexafluoro compound can be obtained with again hydrogen halide (HF) but this time reaction temperature should be 200 ^oC and the required time is 5h. Hexachlorination can also be achieved with the reaction of $(H_3O)_2[B_{12}H_{12}].5H_2O$ with chlorine at 0 ^oC where hexabromination is performed with the reaction of $Na_2B_{12}H_{12}.2H_2O$ and bromine at 5 ^oC. Perbromination can also be achieved with same procedure but since the reaction rate is significantly decreased after some time, temperature should be

risen to 50 ºC and excess bromine is needed.[29] Achieving periodinated compound is a challenge and it can be managed with the reaction of cesium salt of $B_{12}H_{12}^{2-}$ with iodine in acetic acid at 230 ºC and 2.5 hours with microwave assistance.[30] Synthesizing perchloro derivative of *closo*-dodecaborate anion is succeeded with bubbling chlorine into solution containing $Na_2B_{12}H_{12}$ in water at room temperature for five hours and for completion of the reaction, another 24 hours at 100 ºC is needed.[26]

1.5.2.2 Hydroxylation

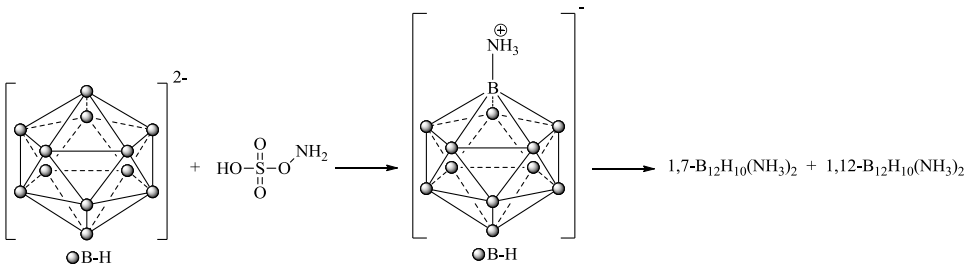
Monohydroxylation of $B_{12}H_{12}^{2-}$ can be achieved in different ways. One of them is heating the mixture of $B_{12}H_{12}^{2-}$ with 1-methylpyrrolidin-2-one at 180 ºC followed by hydrolysis.[31,32] Second method is to react *closo*-dodecaborate anion with sulfuric acid at 90 ºC.[33] Also, refluxing $B_{12}H_{12}^{2-}$ with acetic acid results in monohydroxylation.[17] Dihydroxylation can be achieved by heating the solution containing $B_{12}H_{12}^{2-}$ in acetone and hydrochloric acid to 80 ºC and expected product is obtained as 1,2-dihydroxy derivative or 1,7-dihydroxy derivative.[34] In perhydroxylation of *closo*-dodecaborate anion, there are many obstacles to overcome. One of them is the formation of boric acid results from the reaction of $Cs_2B_{12}H_{12}$ with hydrogen peroxide. Since boric acid is more stable than perhydroxylated derivative of *closo*-dodecaborate anion, formation of boric acid is favored. The other problem is to get rid of excess hydrogen peroxide when the expected product does not precipitate. With this information in hand, a method to synthesize perhydroxylated compounds is developed. The reaction procedure involves using hydrogen peroxide but only to dissolve the cesium salt and the reaction temperature is kept below 105 ºC. According to these regulations, synthesis of $Cs_2B_{12}(OH)_{12}$ is achieved (Scheme 9).[35]



Scheme 9. Synthesis of $B_{12}(OH)_{12}^{2-}$

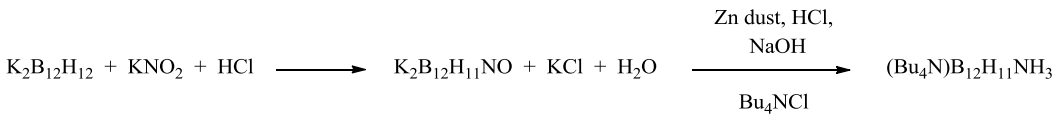
1.5.2.3 Amination

Amination of $B_{12}H_{12}^{2-}$ can be achieved with hydroxylamine-*O*-sulfonic acid which is used for the amination of aromatic molecules with the help of acid catalyst. In amination of $B_{12}H_{12}^{2-}$, there is no need for an acid catalyst and procedure can simply be applied in aqueous solution. This amination process may result in monosubstitution or disubstitution if equivalency of hydroxylamine-*O*-sulfonic acid is increased.[36] Since amine group is bonded as $-NH_3$, every NH_3 bonded to the cluster increase the charge of the cluster by 1. For example, if one NH_3 is bonded to the cluster, the total charge will be -1 and if two NH_3 are bonded to the cluster, the total charge will be zero (Scheme 10).



Scheme 10. Amination of $B_{12}H_{12}^{2-}$

In another synthetic pathway, amination can be achieved from the reduction of nitroso group bonded cluster. Nitrosation can be done by simply adding a solution of potassium nitrite in water to the solution of $K_2B_{12}H_{12}$ in 37% HCl slowly at 0 ^oC. Then, the solution should be stored at 0 ^oC for 1 hour. After that, the solution should be filtered to get rid of KCl precipitate and the filtrate is evaporated. To the obtained solid, ethanol is added and filtered again to eliminate additional KCl formed. Solvent is evaporated again. Solid is dissolved in acetonitrile and column chromatography is applied. Eluent is evaporated and obtained solid is dissolved in water. In order to form precipitate, Bu_4NCl is added to the solution to isolate nitroso derivative and precipitate is collected which is $(Bu_4N)_2B_{12}H_{11}NO$. Reduction should be applied before addition of Bu_4NCl since potassium salt is needed. Before the addition of Bu_4NCl, nitroso derivative was in the form of potassium salt which is soluble in water. To this solution, zinc dust and 20% HCl are added slowly. Then, 20% of NaOH is added to solution to eliminate zinc cations. After elimination of zinc cations, Bu_4NCl is added to the solution and precipitation of aminated derivative is formed (Scheme 11).[34]



Scheme 11. Nitrosation of $B_{12}H_{12}^{2-}$ and its reduction

1.6 Carboranes

While discussing carboranes, $CB_{11}H_{12}^-$ should be considered as the parent compound. In this part, $CB_{11}H_{12}^-$ anion and its derivatives (both from C vertex and B vertex) will be particularly discussed. ^{11}B NMR shifts of carborane clusters and the substituent effects are highly studied. Substituents on the furthest boron atom (position 12) do not affect the chemical shifts of other boron atoms on the cluster but results in downfield shift for the boron atom that they are on. Also, substituents on

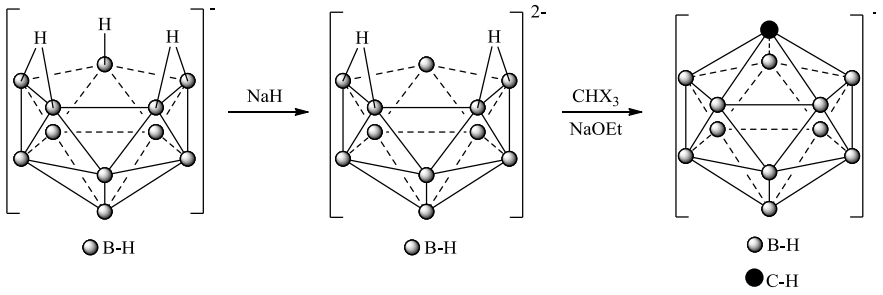
boron atoms can affect the shift of proton on the carbon atom. Substituents on B2-B6 affect the proton on carbon vertex most where substituents on B12 influences the proton on C vertex least.[6] $CB_{11}H_{12}^-$ anion and its derivatives should be considered as weakly coordinating anions and least basic anions in a way that their conjugate acids are the strongests.[6,37] Also, they have high thermal stability, high chemical stability and high positive redox potentials.[37] Parent carborane anion, $CB_{11}H_{12}^-$, cannot be oxidized by itself but its halogenated derivatives can be, as their anodic oxidation potentials are higher than the parent ion.[38] One of the derivatives of the parent ion is dodecamethylated form of CB_{11} cluster ($CB_{11}Me_{12}^-$) and it is also considered as weakly coordinating anion besides it is a very lipophilic compound. Using longer alkyl chains instead of methyl groups, increases the lipophilicity.[39] Another example for the derivatives of parent ion is C-hydroxycarboranes where derivatization occurs only at carbon vertex (vertices). C-hydroxycarboranes are highly acidic but unlike their organic analogues, phenols, they are more stable and silent in the near-UV region.[40] In addition to these derivatives, halogenation also affects the carborane clusters. As an example, halogenation on B2-B6 increases the acidity of the proton on C vertex.[6]

1.6.1 Synthesis of $(CB_{11}H_{12})^-$

First, it should be said that there is no way known to synthesize this anion from small molecules. In general, the parent ion is synthesized from smaller open cluster molecules or extrusion from larger clusters. There are four ways to synthesize $(CB_{11}H_{12})^-$ and they can be classified as; a) C-Insertion, b) B-Insertion, c) C-Extrusion and d) B-Extrusion.[6]

1.6.1.1 C-Insertion

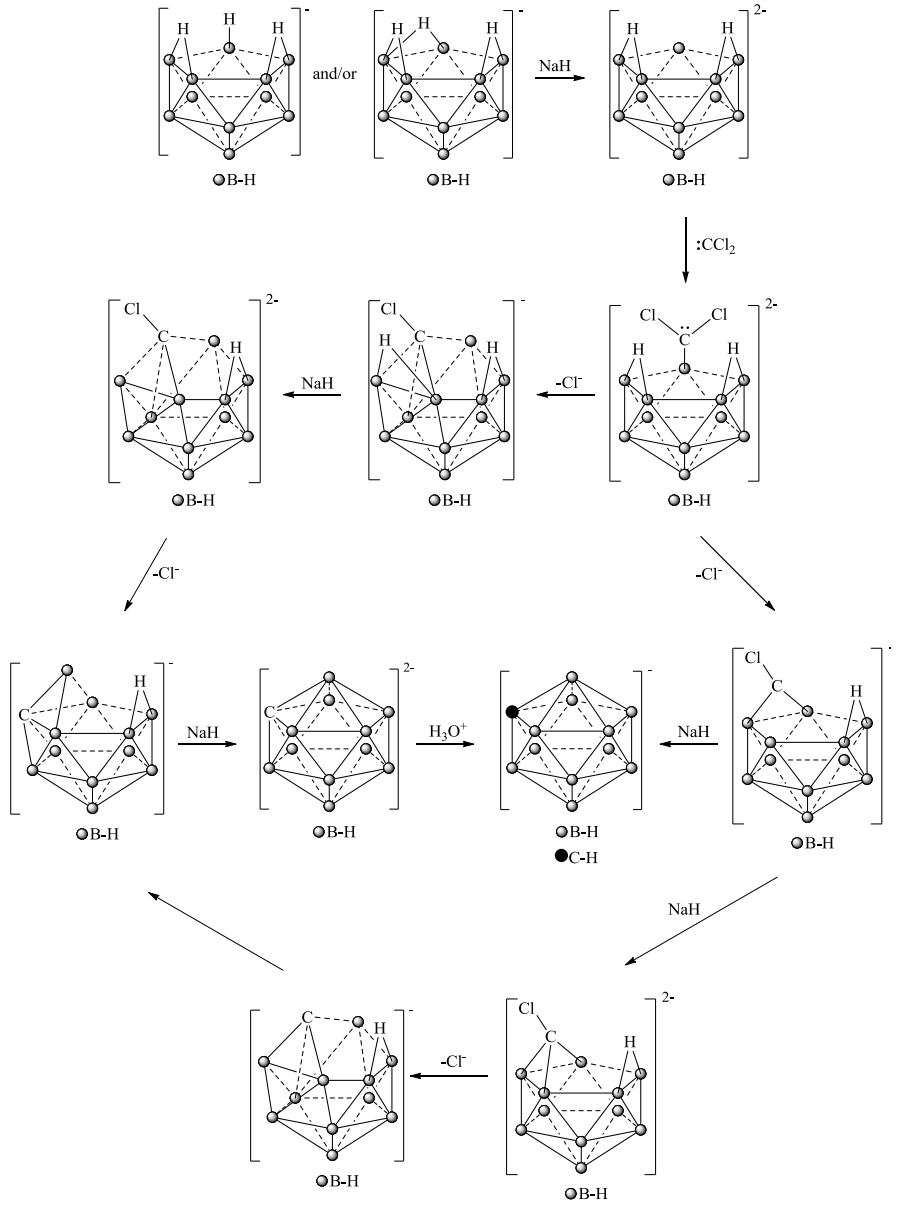
1.6.1.1.1 Michl's Method



Scheme 12. Michl's Method for Synthesizing $CB_{11}H_{12}^-$

In Michl's method, the starting material used is [*nido*-$B_{11}H_{14}$]$^-$ which can be obtained from the reaction between sodium borohydride and $BF_3.OEt_2$ and as a carbene source, both $CHCl_3$ and $CHBr_3$ were used but the yields were low (20-25%).[41] To increase the yield, dihalocarbenes were used but the attempts were unsuccessful because as temperature is increased to initiate carbene formation, cluster decomposition occurred. Another attempts were performed with using diethyl(dichloromethyl) phosphonate and tetraethyl(chloromethylene) bisphosphonate. These carbene sources increased the yield to 65% and 50% respectively. Trimethyl(trifluoromethyl) silane was used as a carbene source in another attempt with NBu_4Br as an initiator. This method was successful to increase the yield but the drawback was its reproducibility. In the last method, with the carbene source and the initiator, lithium halides are used as co-initiator with tetrabutylammonium bromide and the results were reproducible and the yields were high (94% is the highest) (Scheme 12).[37] Procedure of synthesizing $CB_{11}H_{12}^-$ anion in Michl's method can be summarized as; 1)Deprotonation of the starting material with NaH to obtain [*nido*-$B_{11}H_{13}$]$^-$, 2)Insertion of the carbene into [*nido*-$B_{11}H_{13}$]$^-$ to

obtain the desired product.[41] The more detailed reaction mechanism is given in Scheme 13.[41]

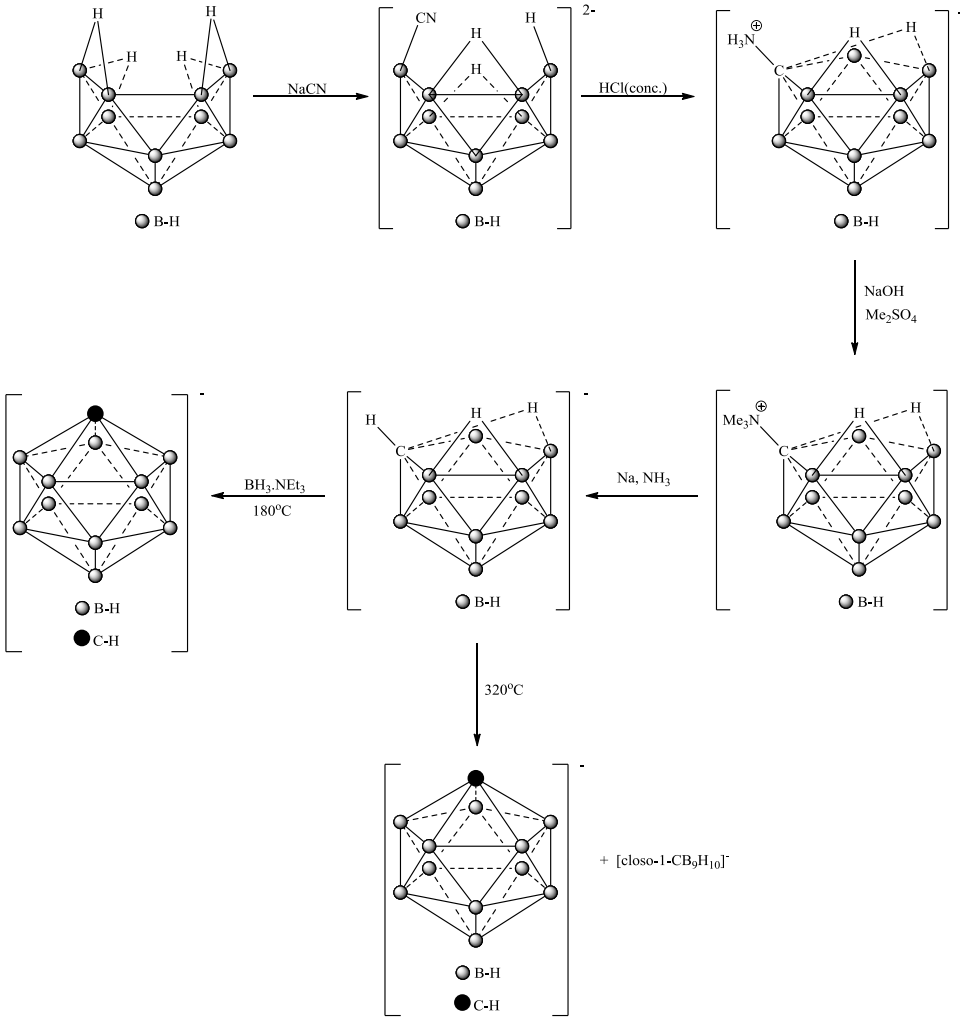


Scheme 13. Detailed Mechanism of Michl's Method

1.6.1.2 B-Insertion

1.6.1.2.1 Knoth's Method

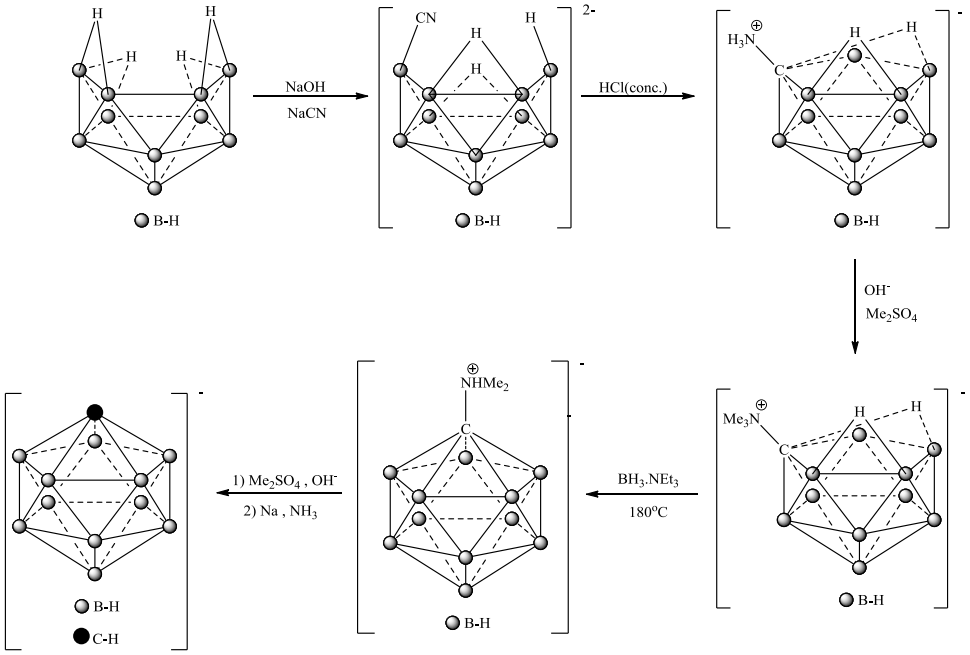
For synthesis of $CB_{11}H_{12}^-$ cluster, Knoth used decaborane as starting material. Reaction between decaborane and sodium cyanide gives [*arachno*-6-CN-$B_{10}H_{13}$]$^-$. Then, the arachno species is hydrolyzed with HCl to obtain [*nido*-7-H_3N-7-$CB_{10}H_{12}$]. Methylation of this nido species with Me_2SO_4 results in the formation of [*nido*-7-Me_3N-7-$CB_{10}H_{13}$]$^-$ and treating with sodium in liquid ammonia yielded [*nido*-7-$CB_{10}H_{13}$]$^-$. After obtaining [*nido*-7-$CB_{10}H_{13}$]$^-$, there are two possibilities to obtain $CB_{11}H_{12}^-$ cluster. One of them is reacting [*nido*-7-$CB_{10}H_{13}$]$^-$ with BH_3.NEt_3 and the other way is applying thermolysis on [*nido*-7-$CB_{10}H_{13}$]$^-$ but in this way, a side product is obtained which is [*closo*-1-CB_9H_{10}]$^-$ (Scheme 14).[42,43]



Scheme 14. Knoth's Method for Synthesizing $CB_{11}H_{12}^-$

1.6.1.2.2 Hermanek's Method

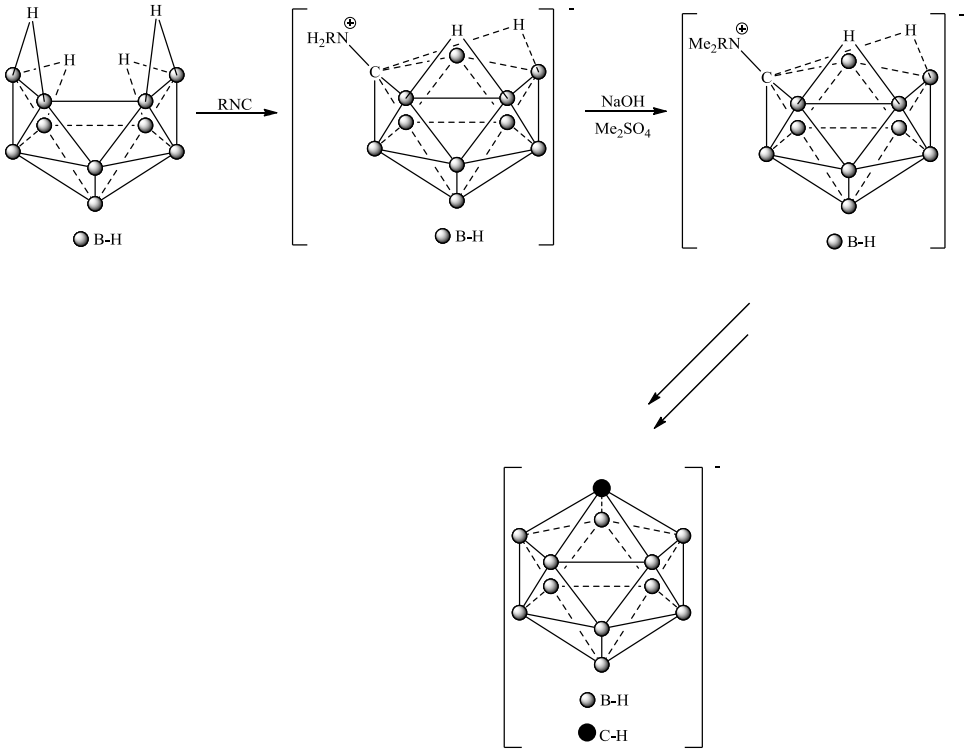
In Hermanek's method, the main difference from Knoth's method is using one equivalent of sodium cyanide. The other difference is applying boron insertion without deamination (Scheme 15).[44]



Scheme 15. Hermanek's Method for Synthesizing $CB_{11}H_{12}^-$

1.6.1.2.3 The method of Fox and Hughes

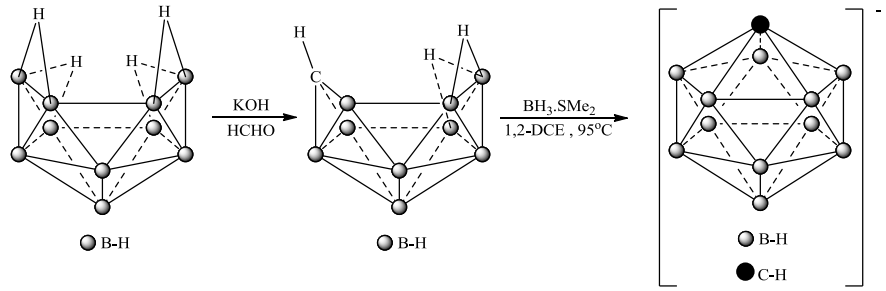
In the method of Fox and Hughes, isocyanide is used instead of cyanide and the rest is similar with both Knoth's and Hermanek's methods (Scheme 16).[45]



Scheme 16. Synthesis of $CB_{11}H1_2^-$ with the Method of Fox and Hughes

1.6.1.2.4 Kennedy's Method

In Kennedy's method, two boron vertex insertions exist and for this step, excess $BH_3.Me_2S$ is required and 3-4 days of heating is necessary (Scheme 17).[46]



Scheme 17. Synthesis of $CB_{11}H_{12}^-$ by Kennedy's Method

1.6.1.3 C-Extrusion

Carboranes having higher than 12 vertices are classified as supercarboranes and they can undergo both C-extrusion and B-extrusion.[6] As an example of a C-extrusion, 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ having 13 vertices carborane, reacts with methanol/sodium hydroxide mixture or triphenylphosphine and a carbon atom is extruded from the cluster to form a CB_{11} cage.[47]

1.6.1.4 B Extrusion

As mentioned in 'C-Extrusion', supercarboranes may undergo B-extrusion too. For example, 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$,14 vertex carborane cluster, reacts with MeOH and undergoes both B-extrusion and C-extrusion to form CB_{11} cluster.[48]

1.6.2 Derivatization of $CB_{11}H_{12}^-$ Anion and its Derivatives

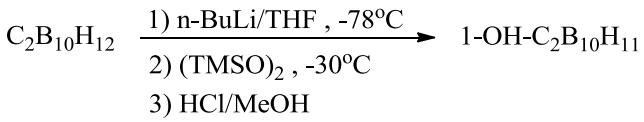
In $CB_{11}H_{12}^-$ anion, boron atoms at the positions 2-6, closest to C atom, are available to nucleophilic attack while the boron atom at the position 12, furthest to carbon atom, is available to electrophilic attack.[5] In this part, derivatization of $(CB_{11}H_{12})^-$ anion on carbon vertex, on boron vertex and with cage reduction-oxidation processes will be discussed.

1.6.2.1 On C vertex

1.6.2.1.1 Hydroxylation

As mentioned earlier in this work, C-hydroxycarboranes are cluster analogues of phenols and they are highly acidic, stable to oxidation and silent in near-UV region.[40] The types of $C_2B_{10}H_{12}$ molecules are *ortho*, *meta* and *para* where carbon atoms on the cluster located as 1,2 positions for *ortho*, 1,7 positions for *meta* and 1,12 positions

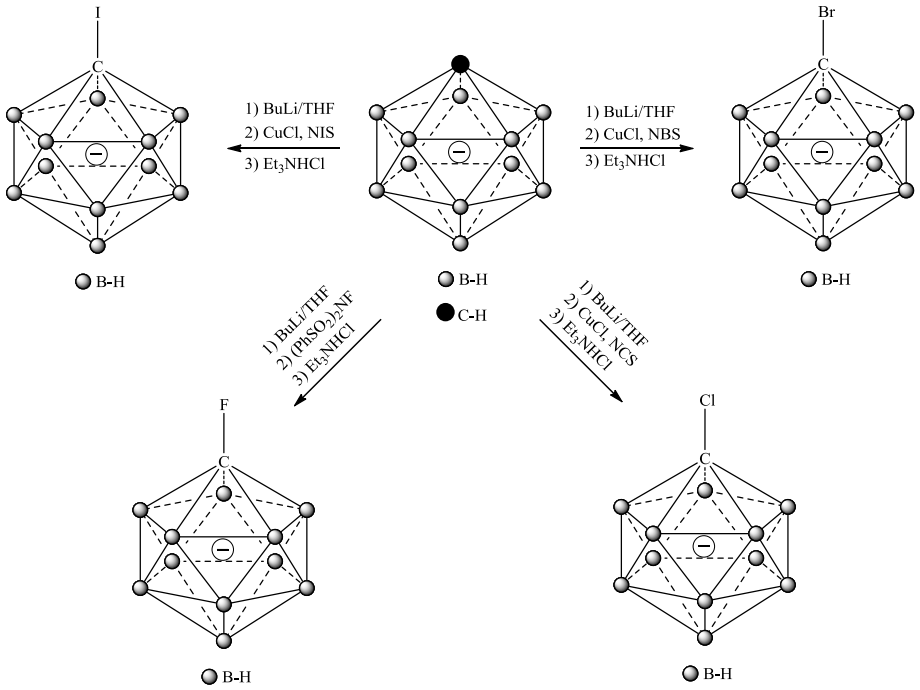
for *para*. These all clusters undergo mono hydroxylation reactions to form 1-Hydroxy-1,2-dicarba-*closo*-dodecaborane, 1-Hydroxy-1,7-dicarba-*closo*-dodecaborane and 1-Hydroxy-1,12-dicarba-*closo*-dodecaborane respectively (Scheme 18). Yields resulting from these reactions are 77%, 10% and 25% for ortho, meta and para carboranes respectively. The C-hydroxycarboranes resulted from these reactions, are very stable to acidic and basic solutions with low concentration, are soluble in most of the organic solvents and are strong acids with low pKa values where ortho is the most acidic and para is the least acidic. Also, they have characteristic IR spectrum where C-O bond gives peak at 1200 cm^{-1}, B-H bond gives peak at 2600 cm^{-1}, C-H bond gives peak at 2060 cm^{-1} and O-H strecthing gives rise at 3300 cm^{-1}.[40]



Scheme 18. Synthesis of 1-Hydroxy Dicarbaboranes

1.6.2.1.2 Halogenation

C-halogenated forms of $CB_{11}H_{12}^-$ anion are shown as 1-X-$CB_{11}H_{11}^-$ and they are considered as intermediates in procedures to obtain aryl substituted carboranes. Iodinated, brominated, chlorinated and fluorinated 1-X-$CB_{11}H_{11}^-$ anions as salts of trietylammonium are synthesized from cesium salt of $CB_{11}H_{12}^-$ anion in a similar synthetic pathway with yields of 59%, 40%, 43% and 85% respectively (Scheme 19).[49]



Scheme 19. C-Halogenation of $CB_{11}H_{12}^-$

1.6.2.1.3 Aromatic substitution

A carbenium ylide, $CB_{11}Me_{11}$, where C carries a positive charge and the whole cluster that carries a negative charge is available for an aromatic substitution reaction on its C vertex with all monosubstituted benzenes, *o*-xylene, naphthalene and biphenylene from their reactive sides (Scheme 20) (Figure 6).[50]

$$ArH + CB_{11}Me_{11} \longrightarrow Ar\text{-}C(BMe)_{11}^- + H^+$$

Scheme 20. Aromatic Substitution Reaction on $CB_{11}Me_{11}$ Carbenium Tlide

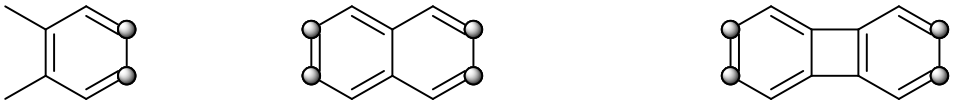
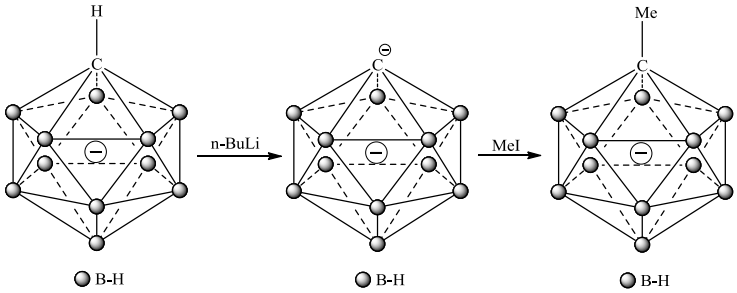


Figure 6. Reactive Sites (Shown with Circles) of *o*-xylene, naphthalene and biphenylene

1.6.2.1.4 Methylation on C vertex

In $CB_{11}H_{12}^-$ anion, the proton on C vertex is highly acidic and this carbon atom is readily converted to carbanion with the help of strong bases such as n-BuLi. When carbanion is formed, C atom becomes open to electrophilic attacks and methylation can be performed with MeI (Scheme 21).[51]

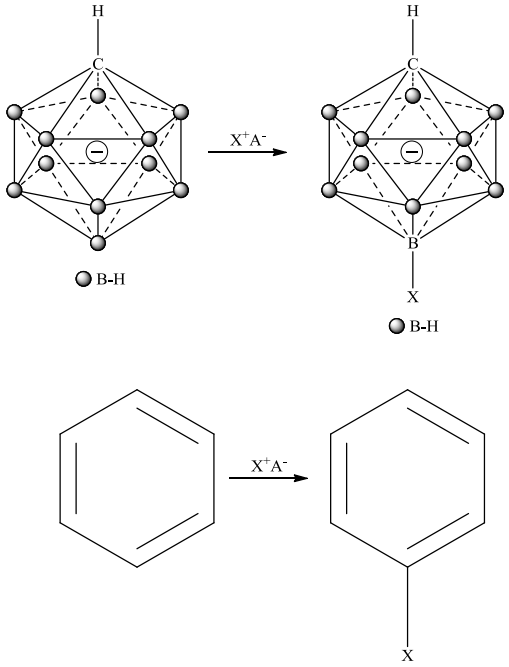


Scheme 21. Methylation of C vertex of $CB_{11}H_{12}^-$

1.6.2.2 On B vertex

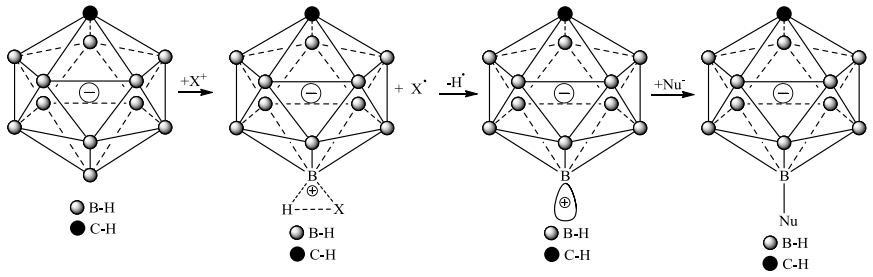
1.6.2.2.1 Electrophilic Substitution

B-H bonds on carboranes are open to electrophilic substitution as their organic analogues, arenes (Scheme 22).[12]

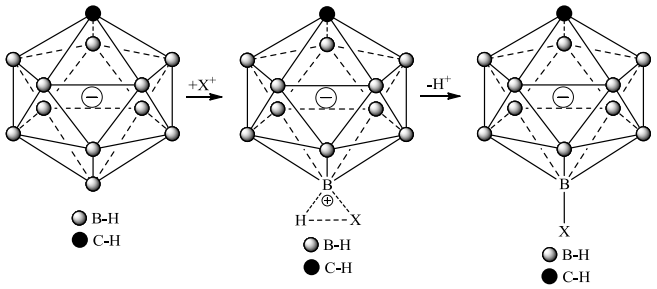


Scheme 22. Electrophilic Substitution Reactions of $CB_{11}H_{12}^-$ and Benzene

For this reactions, X can be halogens[52,53,54], alkyl groups[51,55] and metal cations[12]. There are two suggested mechanisms for electrophilic substitution on B vertex in carboranes. One of the mechanisms is called electron-transfer mechanism where the first step is taking an electron from cluster to form a radical one which is open to a nucleophilic attack (Scheme 23).[12] The second suggested mechanism is called sigma-bond insertion mechanism where an intermediate is formed as a three-membered ring that carries a positive charge which can readily lose one of three vertices to form a single bond. There are 3 possibilities in this step; i) losing B, ii) losing X and iii) losing H. In the third possibility, desired product is obtained (Scheme 24).[12]



Scheme 23. Electron Transfer Mechanism



Scheme 24. Sigma Bond Insertion Mechanism

1.7 Applications of Boron Containing Compounds

1.7.1 Applications of Carboranes

Carborane clusters are applicable to many fields because of their high stability, low nucleophilicity, lipophilicity, high redox potentials and being weakly coordinating anions.[56] Weakly coordinating anions are very important for the synthesis of highly reactive cations to stabilize them.[6] $CB_{11}H_{12}^-$ clusters can be used as superacids[57] and since they are weakly nucleophilic anions, they can stabilize protonated fullerene.[37,58] In addition to these properties, lithium salt of $CB_{11}Me_{11}^-$ anion is a useful reagent for pericyclic reactions as a catalyst.[39] Derivatives of $CB_{11}H_{12}^-$ anions are useful compounds in catalysis of organometallic reactions and radical polymerization reactions of alkenes.[59] For example, radicalic polymerization of isobutylene can be achieved if lithium salt of $CB_{11}Me_{12}^-$ is used as a catalyst.[60] Also,

lithium salt of $CB_{11}Me_{12}^-$ can be used as a supporting electrolyte for cyclic voltammetry.[61] As another example, derivatized form of $CB_{11}H_{12}^-$ from C vertex can be used as catalysts for dehalogenation reactions.[62,63] Halogenated forms of carboranes can be used to stabilize reactive cations.[9] Moreover, dicarba clusters of carboranes can be used in technology and medicine.[64] Furthermore, *para*-carborane derivatives can form ionic crystals, ionic liquids (liquid salts at room temperature or temperatures that are close to room temperature), rods, nanostructures, monolayers and they can be used in medical applications.[6,65,66] Apart from these properties of *para*-carboranes, they can be used in forming boron-carbide semiconductors and they are being the forerunner for neutron detectors and molecular scaffolds.[67]

1.7.2 Applications of $B_{12}H_{12}^{2-}$

$B_{12}H_{12}^{2-}$ anion and its derivatives have many application areas such as medicine[68,69,70] and catalyst[71,72]. Also, in BNCT (Boron-Neutron Capture Therapy), some of the derivatives of dodecahydro-*closo*-dodecaborate anion can be used.[73,74,75] Lithium salts of $B_{12}H_{12}^{2-}$ and $B_{12}Cl_{12}^{2-}$ find an application area of rechargable lithium batteries.[76,77,78]

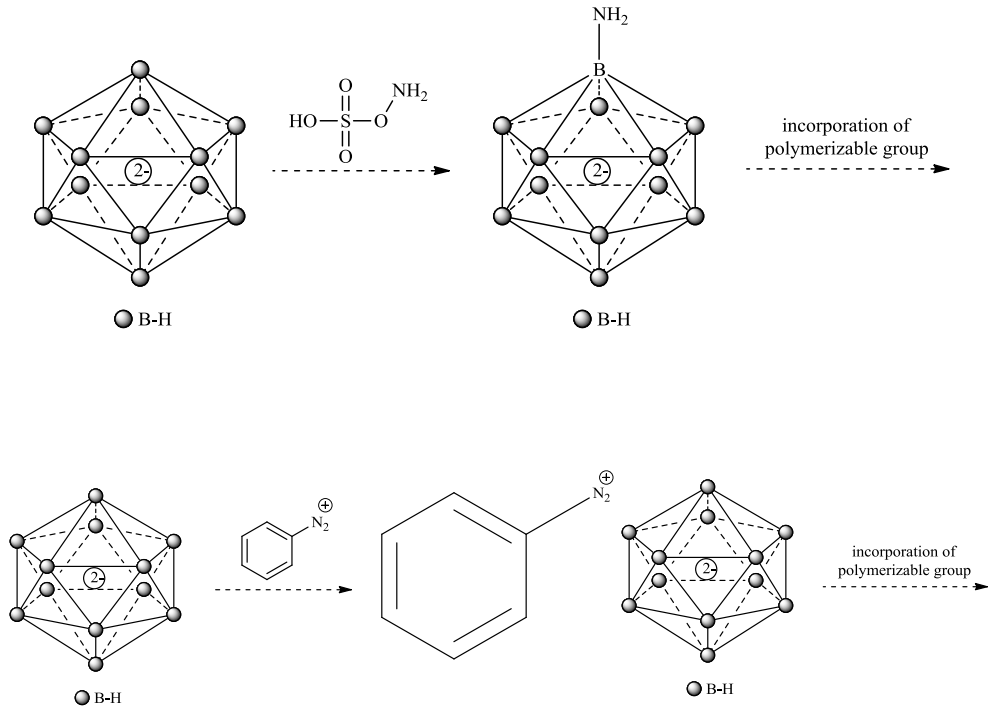
1.7.3 BNCT

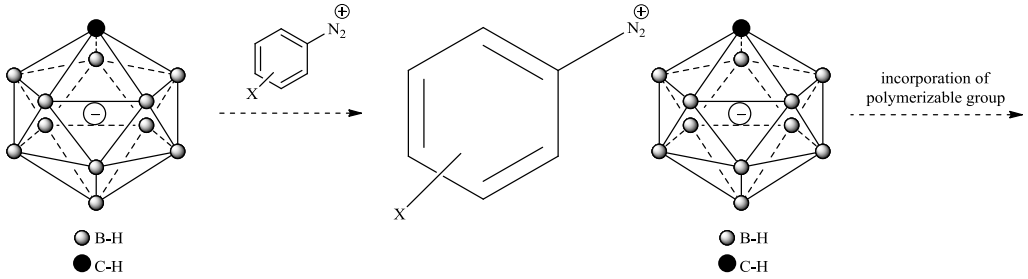
In 1936, Locher proposed that $B_{12}H_{12}^{2-}$ anion can be used in Boron-Neutron Capture Therapy (BNCT) to cure cancer. BNCT is based on placing ^{10}B isotope of boron atom in cancer cells and irradiating them with thermal neutron. After the irradiation, excited ^{10}B is formed and it decays to ^{4}He and ^{7}Li which creates high energy to destroy tumor cells where healthy cells are not damaged.[17,74]

CHAPTER 2

AIM OF THE STUDY

Carborane and boron clusters have been studied for their exploration of derivatizations and function. Apart from few studies, most of the studies are related to revealing properties of these clusters. The boron clusters are known for their stability and weakly coordinating abilities. Moreover, the salts of these clusters have solubilities in organic solvents. With these in mind, we aim at derivatization of dodecahydro-*closo*-dodecaborate and mono-carba-*closo*-dodecaborate anions. Specifically, this thesis aims to incorporate these clusters into a polymer via covalent bonding. First, we will explore amination of dodecaborate cages. Then, derivatization of dodecaborate cages will be explored with diazonium salts. Same reactions will be carried out for mono-carba-*closo*-dodecaborate. Our aim was summarized in the following Scheme.




B-H
C-H
X
incorporation of
polymerizable group
B-H
C-H

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Synthesis

3.1.1 Synthesis of dodecahydro-*closo*-dodecaborate

For the synthesis of dodecahydro-*closo*-dodecaborate dianion, many synthetic routes have been developed which have different starting materials. In our laboratory, a procedure was developed to carry out the procedure that uses sodium borohydride as starting material. This includes a constant Argon gas flow to make the atmosphere inert, an acetone trap connected to a condenser to capture the possible harmful intermediates such as lower boranes and a dropping funnel to control the addition of iodine into the reaction mixture.[26]

The procedure starts with ensuring the reaction setup is under inert atmosphere by flushing Argon gas. Sodium borohydride and diglyme are introduced in a 3-necked round bottom flask. Temperature of the oil bath should be around 120 ^{o}C (the reaction temperature was checked to be 105-110 ^{o}C) for the complete dissolution of sodium borohydride in diglyme. When the solid is completely dissolved, addition of iodine in diglyme is done in 6 hours dropwise. This step is one of the most important steps in this synthesis that affects the result. If the addition is done in a shorter time, the resulting compound will be obtained with a very low yield or will not be obtained at all. After the addition of iodine, the reaction is stirred overnight at 120 ^{o}C. During this stirring process, in the reaction vessel, the formation of $B_3H_8^-$ is achieved. Next, the temperature of the oil bath is raised to 185 ^{o}C to boil the solution under reflux condition. At that time, disproportionation of triborane to dodecahydro-*closo*-dodecaborate and BH_4^- is occurred. After 1 day of reflux, diglyme is removed from the mixture and distilled water is added to the residue slowly. For the

completion of precipitation of boric acid by reacting lower boranes with water, concentrated hydrochloric acid is added to the solution and kept in refrigerator. Since boric acid's solubility in water is low and solubility of sodium salt of dodecahydro-*closo*-dodecaborate is high, boric acid is collected with filtration as white crystals. Addition of triethylamine to the filtrate results in the formation of triethylammonium salt of dodecahydro-*closo*-dodecaborate but for this formation to complete, the solution was kept in refrigerator overnight. The expected compound is collected by filtering the solution. The IR spectrum of triethylammonium salt of dodecahydro-*closo*-dodecaborate (Figure 7) shows the characteristic peaks as 2475 cm^{-1} for B-H stretching and 3125 cm^{-1} for N-H stretching in the cation.[26]

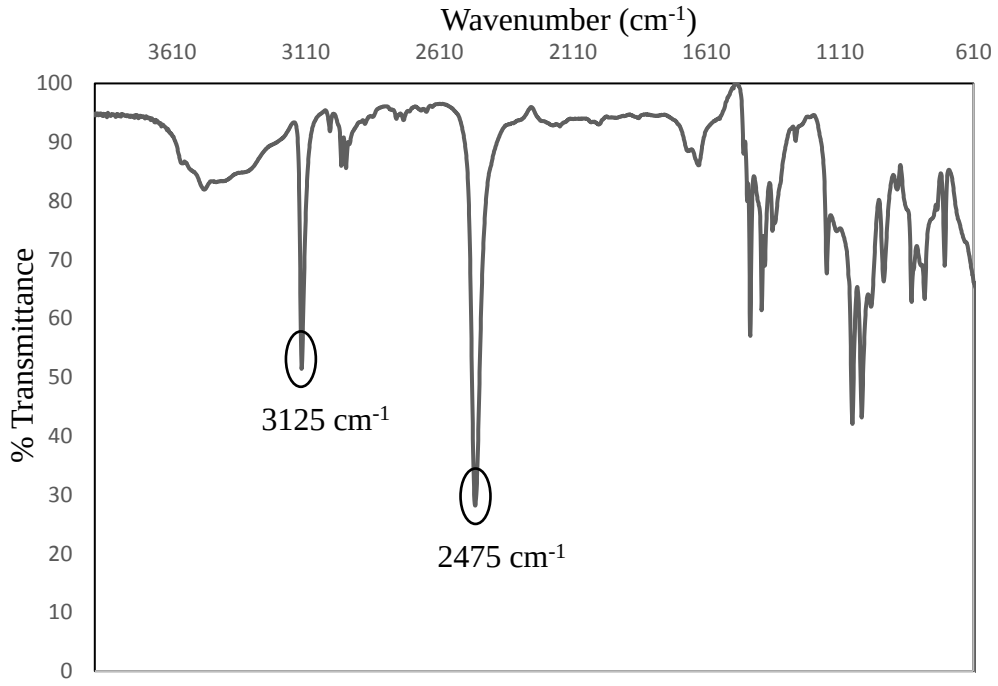


Figure 7. IR Spectrum of triethylammonium salt of dodecahydro-*closo*-dodecaborate

3.1.1.1 Amination of dodecahydro-*closo*-dodecaborate

For the amination of dodecahydro-*closo*-dodecaborate, two different synthetic routes are used. First, amination is achieved with hydroxylamine-*O*-sulfonic acid. In the second route, amination is accomplished with the reduction of nitroso group bonded to the cluster.

3.1.1.1.1 Amination of dodecahydro-*closo*-dodecaborate with synthesized hydroxylamine-*O*-sulfonic acid

In the first way to synthesize 1-amino-undecahydro-*closo*-dodecaborate, hydroxylamine-*O*-sulfonic acid is used. At first, the aminating agent, hydroxylamine-*O*-sulfonic acid, is synthesized with the reaction between hydroxylammonium sulfate and chlorosulfonic acid. For this synthesis, hydroxylammonium sulfate is added into a 3-necked round bottom flask and chlorosulfonic acid is added dropwise using a dropping funnel. After all the reactants are mixed, a white precipitate is obtained. Addition of diethyl ether to the solid resulted in the formation of white crystals which are collected with suction filtration.

For the second part of this synthesis, since the solvent of the amination reaction is water, we needed to convert our triethylammonium salt of dodecahydro-*closo*-dodecaborate (not soluble in water) into sodium salt of dodecahydro-*closo*-dodecaborate which is soluble in water. To achieve this, a NaOH solution is prepared and triethylammonium salt of dodecahydro-*closo*-dodecaborate is added into the solution. The solution is heated until it became a clear solution. Removal of the solvent resulted in the sodium salt of dodecahydro-*closo*-dodecaborate and since it is a very hygroscopic compound; characterization with IR spectroscopy is perfomed immediately after drying, even in this case water is observed in IR spectrum (see appendix).

The sodium salt of dodecahydro-*closo*-dodecaborate and hydroxylamine-*O*-sulfonic acid are mixed in water. After 3 hours of reflux, the solution is cooled to room

temperature and tetramethylammonium chloride is added into the solution to obtain the resulting compound as tetramethylammonium salt. Tetramethylammonium salt is used for practical purposes that no N-H peaks are present for the salt except that is arising from B-NH_2. The product is collected with filtration. The IR spectrum of the final product (Figure 8) has the peaks at 2471 cm^{-1} for B-H stretching and around 3200 cm^{-1} for N-H stretching. As can be inferred from the IR spectrum, the yield of the expected compound is low in the final product since the N-H stretching peak area ratio to B-H stretching is small.[36]

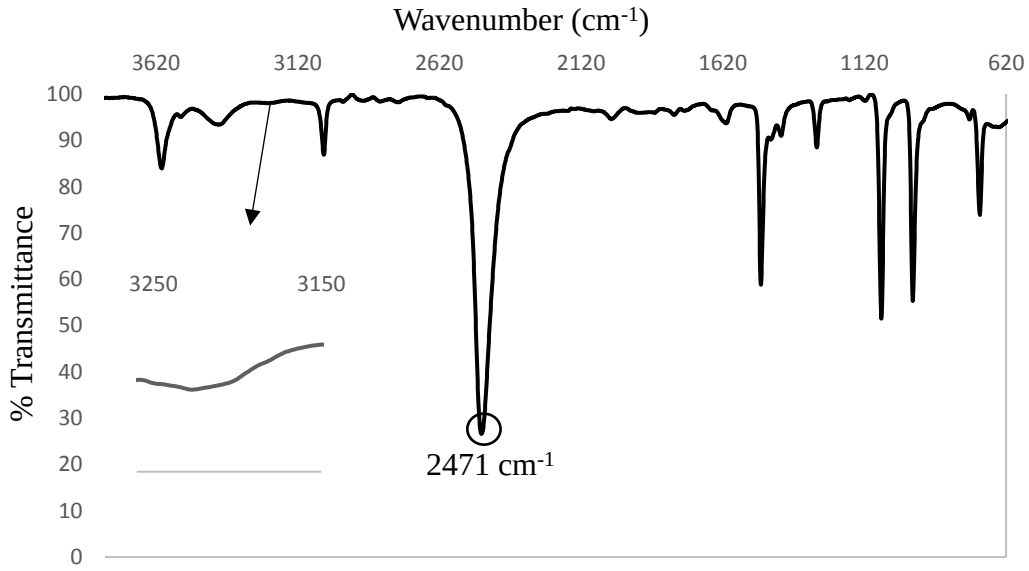


Figure 8. IR Spectrum of tetramethylammonium salt of 1-amino-undecahydro-*closo*-dodecaborate (with synthesized hydroxylamine-*O*-sulfonic acid)

3.1.1.1.2 Amination of dodecahydro-*closo*-dodecaborae with commercial hydroxylamine-*O*-sulfonic acid

From the previous result of the amination of dodecahydro-*closo*-dodecaborate, it was concluded that the synthesis of hydroxylamine-*O*-sulfonic acid was problematic. So, it was decided to use commercial hydroxylamine-*O*-sulfonic acid for the amination of dodecahydro-*closo*-dodecaborate. Same procedure was followed and the resulting compound was the expected one.[36] The IR Spectrum (Figure 9) has the characteristic

peaks at 2486 cm^{-1} for B-H stretching and 3223 cm^{-1} for N-H stretching.[36] This procedure yielded better than the previous reaction.

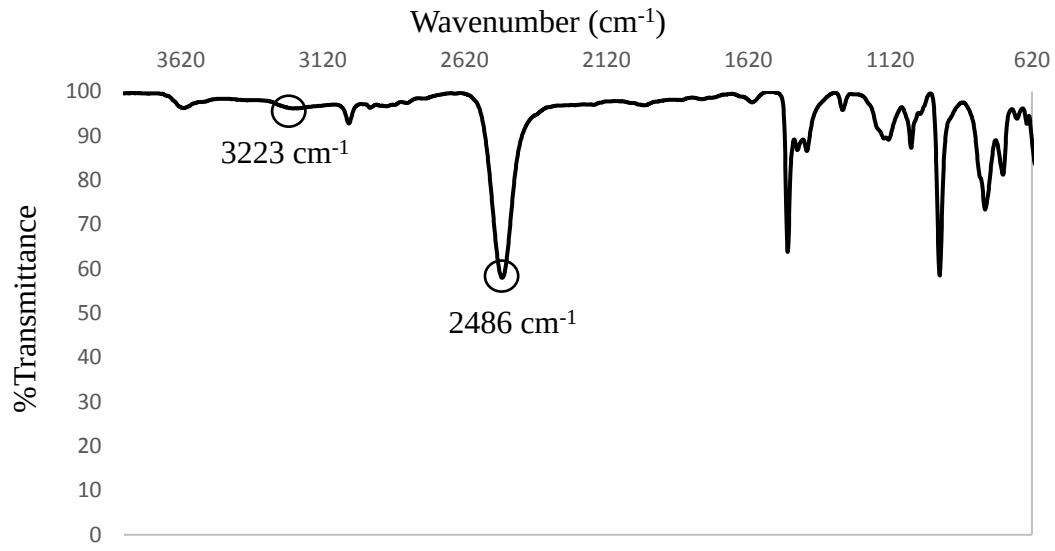


Figure 9. IR Spectrum of tetramethylammonium salt of 1-amino-undecahydro-*closo*-dodecaborate (with commercial hydroxylamine-*O*-sulfonic acid)

3.1.1.1.3 Amination of dodecahydro-*closo*-dodecaborate with the reduction of 1-nitroso-undecahydro-*closo*-dodecaborate

An alternative way was devised to synthesize 1-amino-undecahydro-closo-dodecaborate from 1-nitroso-undecahydro-*closo*-dodecaborate. To synthesize the nitroso compound, triethylammonium salt of dodecahydro-*closo*-dodecaborate was converted into potassium salt of dodecahydro-*closo*-dodecaborate in the same way with obtaining sodium salt of dodecahydro-*closo*-dodecaborate (*vide supra*). Concentrated HCl was added to the potassium salt and KNO_2 was added to the solution slowly in an ice bath. If the rate of the addition of KNO_2 is fast, there will be gas evolution and it should be avoided. After the addition, the solution became green and kept in ice bath for 1 hour. Then, distilled water and sulfuric acid are added to the solution. 1-nitroso-undecahydro-*closo*-dodecaborate is obtained with filtration after the addition of trimethylamine hydrochloride. The IR spectrum of the expected

compound (Figure 10) gives signals at 2493 cm^{-1} for B-H stretching and 1606 cm^{-1} for N-O stretching. This is consistent with the literature.[34]

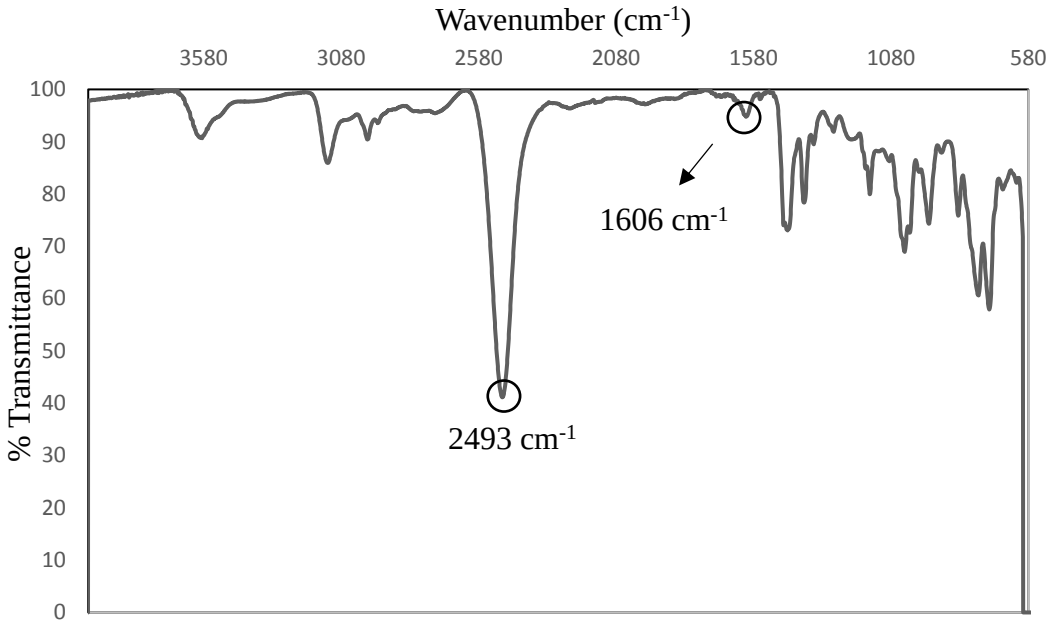


Figure 10. IR Spectrum of trimethylammonium salt of 1-nitroso-undecahydro-*closo*-dodecaborate

With the nitroso compound as trimethylammonium salt in hand, it was converted to potassium salt by treating the ammonium salt with KOH. To the potassium salt, Zn and HCl were added for reduction and filtered. The filtrate was first made alkaline to see whether precipitation will occur or not. Since no precipitation occurred, the filtrate was acidified again with HCl and an orange solution was obtained. After the addition of trimethylamine hydrochloride, the solution was filtered and the expected compound was collected. IR spectrum of the final compound (Figure 11) has characteristic peaks of B-H stretching at 2498 cm^{-1} and N-H stretching at 3132 cm^{-1}. Also, disappearance of the signal belonging to nitroso group indicates the product formation.[34]

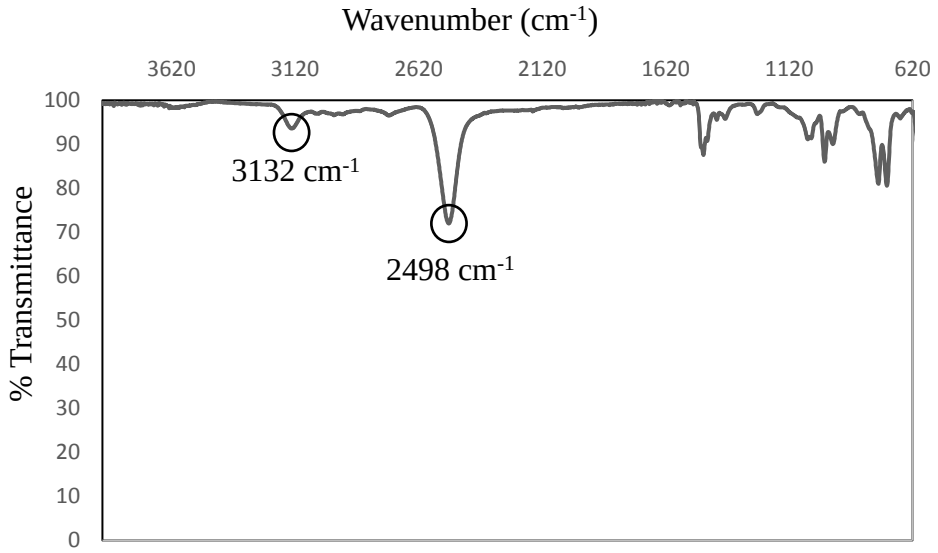


Figure 11. IR Spectrum of trimethylammonium salt of 1-amino-undecahydro-*closo*-dodecaborate (synthesized with the reduction of 1-nitroso-undecahydro-*closo*-dodecaborate)

3.1.1.1.4 Synthesis of Organic Compounds

After obtaining the 1-amino-undecahydro-*closo*-dodecaborate, we tried to introduce polymerizable organic moieties to the cluster from the amino group. With this, we can proceed to boron cage containing polymers for various applications.

3.1.1.1.4.1 Synthesis of 5-norbornene-2,3-dicarboxylic anhydride

Norbornene is known to react with Grubbs catalyst to get ring opening metahesis polymerization (ROMP) polymers. Therefore, we wanted to introduce norbornene units onto the dodecaborate. To do this, the amino borate was synthesized (*vide supra*). Cyclopentadiene was cracked and added onto maleic anhydride to get 5-norbornene-2,3-dicarboxylic anhydride (^{1}H NMR given in Figure 12).[79]

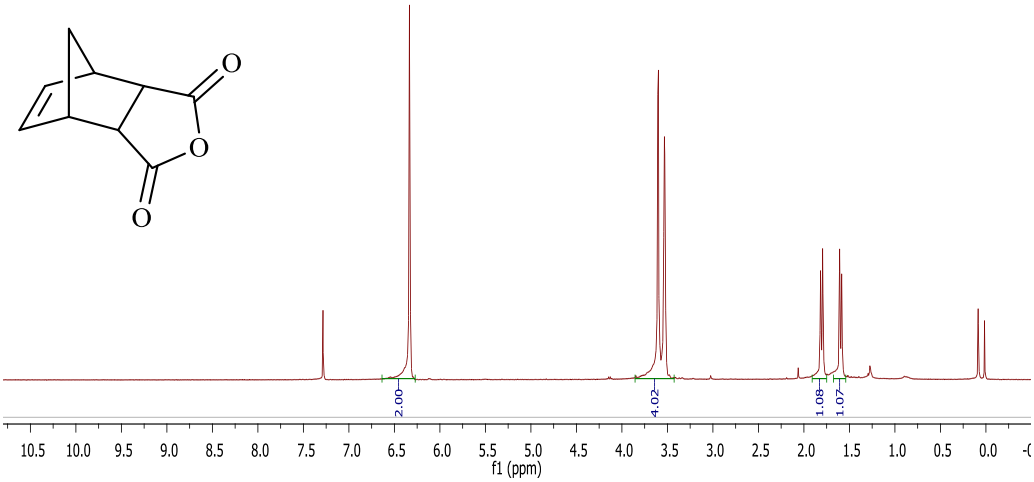
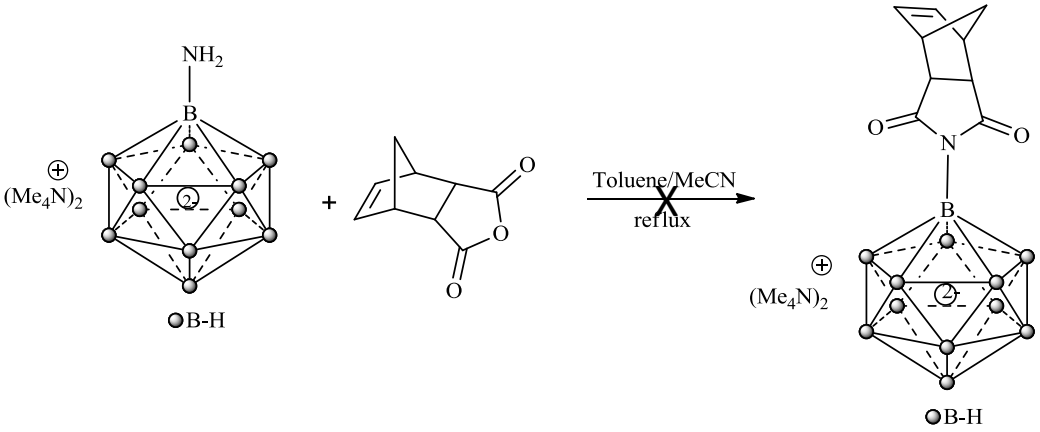


Figure 12. ^{1}H NMR Spectrum of 5-norbornene-2,3-dicarboxylic anhydride

3.1.1.1.4.2 Reaction between 5-norbornene-2,3-dicarboxylic anhydride with 1-amino-undecahydro-*closo*-dodecaborate

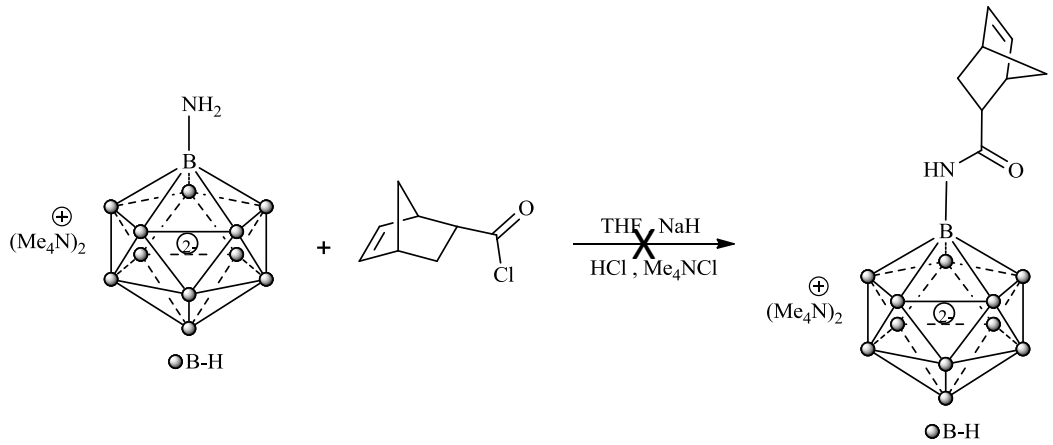
For this reaction, tetramethyl ammonium salt of 1-amino-undecahydro-*closo*-dodecaborate was treated with 5-norbornene-2,3-dicarboxylic anhydride in toluene-acetonitrile and refluxed overnight (Scheme 25). The expected compound could not be obtained from this reaction. The failure of this reaction was attributed to lower activity of amino group bonded to dodecaborate. Borane cages are known to be electron deficient which makes the lone pair on the amino group not to be that accessable for attacking as nucleophile.



Scheme 25. Reaction between 5-norbornene-2,3-dicarboxylic anhydride and 1-amino-undecahydro-*closo*-dodecaborate

3.1.1.1.4.3 Reaction between 5-norbornene-2-carbonyl chloride and 1-amino-undecahydro-*closo*-dodecaborate

After failing with 5-norbornene-2,3-dicarboxylic anhydride, 5-norbornene-2-carbonyl chloride was used (Scheme 26). This compound was tried due to the fact that acyl chlorides are more reactive than acid anhydrides. Tetramethylammonium salt of 1-amino-undecahydro-*closo*-dodecaborate was dissolved in freshly distilled THF and NaH was added to the solution. Then, 5-norbornene-2-carbonyl chloride in freshly distilled THF was introduced into the solution. After stirring the solution for 5 days, it was acidified with HCl solution and tetramethylammonium chloride was added to the solution. Precipitation was expected but it did not occur and the desired compound could not be obtained. The failure of this reaction further shows that the amino group is inert.



Scheme 26. Reaction between 5-norbornene-2-carbonyl chloride and 1-amino-undecahydro-*closo*-dodecaborate

3.1.1.2 Cation Exchange Reactions of dodecahydro-*closo*-dodecaborate

3.1.1.2.1 Synthesis of quinolin-1-ium salt of dodecahydro-*closo*-dodecaborate

With the start of SARS-Cov-2 (Covid 19), numerous drugs were proposed to treat the viral disease. One of the drugs was publically proposed to treat the disease was hydroxychloroquine. With that, we wondered if the quinoline, core part of hydroxyquinone, can act as a viral inhibitor. Quinoline was added to the acidic solution of dodecaborate and the quinolin-1-ium dodecaborate precipitated. ^{1}H NMR spectrum (Figure 13) of the solid proves that the expected compound was obtained. Viral inhibition was not observed for this compound (the compound was given to National Boron Institute for testing, the result was reported to us like that).

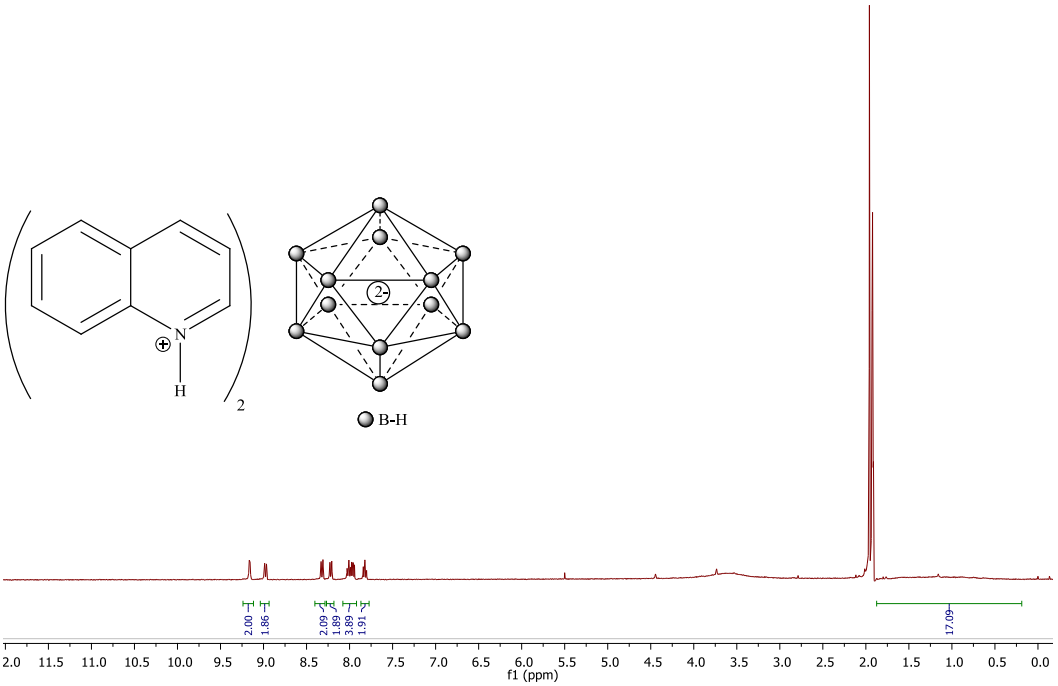


Figure 13. ^{1}H NMR Spectrum of quinolin-1-ium salt of dodecahydro-*closo*-dodecaborate

3.1.1.2.2 Synthesis of benzenediazonium salt of dodecahydro-*closo*-dodecaborate

With the cation exchange reaction with quinoline was achieved easily, it was wondered if diazonium salts could be stabilized with the dodecaborate. It was found that diazonium salts could be stabilized as salts of dodecaborates. As an example, benzenediazonium salt of dodecaborate was synthesized and its IR spectrum (Figure 14) shows the characteristic peaks for diazonium group at 2269 cm^{-1} and B-H stretching at 2472 cm^{-1}.

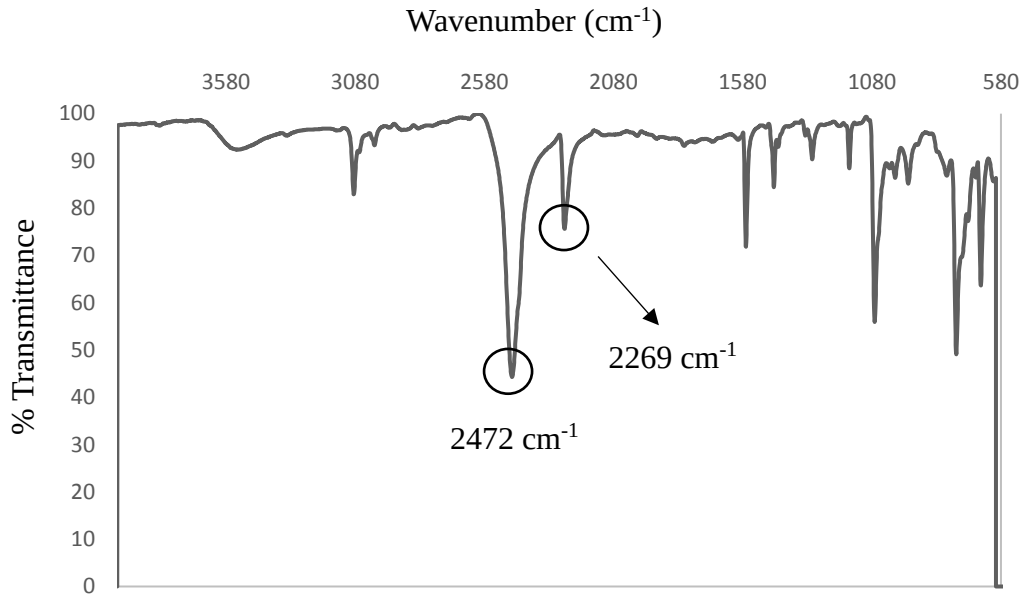
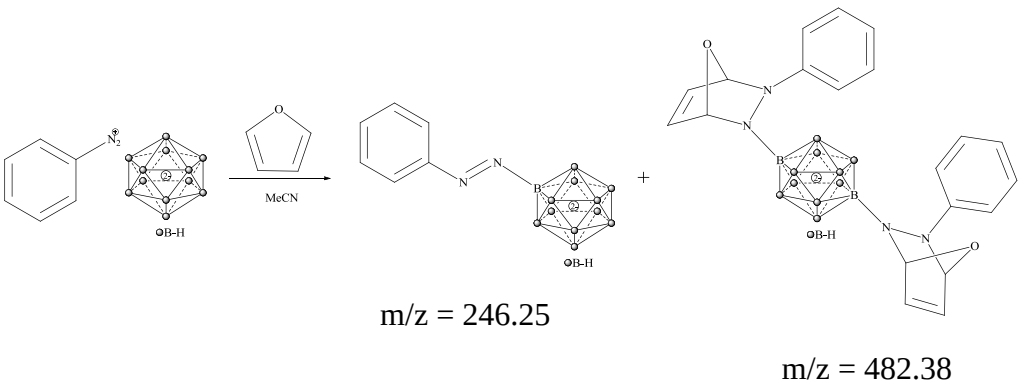


Figure 14. IR Spectrum of diazonium salt of dodecahydro-*closo*-dodecaborate

3.1.1.2.2.1 Diels-Alder Reaction on Diazonium Group



Scheme 27. Diels-Alder reaction between diazonium cation of dodecahydro-*closo*-dodecaborate and furan

With successfully obtained benzenediazonium salt of dodecaborate, it was decided to treat the diazonium salt with furan for a Diels-Alder reaction. Diazonium salt of dodecahydro-*closo*-dodecaborate was dissolved in MeCN, furan in MeCN was added to the solution. From the IR spectrum (Figure 15) of the obtained precipitate,

no results could be obtained since there were peaks around 2200 cm^{-1} and 1500-1600 cm^{-1} could be coming from both diazonium groups and diazo groups. For further characterization, high resolution mass spectroscopy experiment was carried out for the precipitate. From HRMS results (See Appendix), it was concluded that there were mono-substituted dodecahydro-*closo*-dodecaborate with benzenediazonium group and di-substituted dodecahydro-*closo*-dodecaborate with the product of the Diels-Alder reaction between benzenediazonium and furan (Scheme 27).

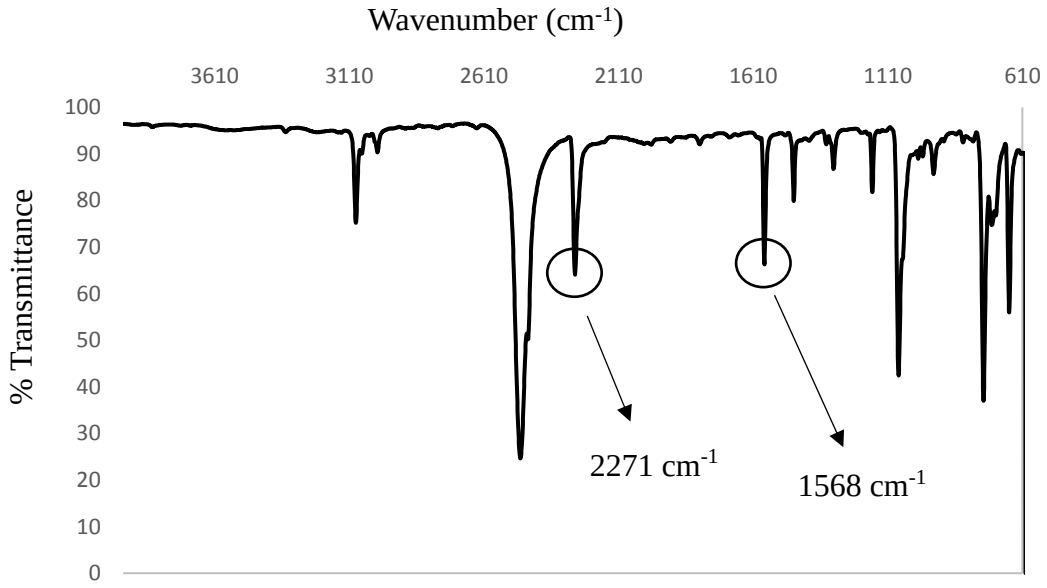


Figure 15. IR Spectrum of the obtained compound from Diels-Alder reaction on diazonium group

3.1.2 Synthesis of tetradecahydro-*nido*-undecaborate

After the synthesis and some derivatizations of dodecahydro-*closo*-dodecaborate, it was wondered how these reactions proceed with mono-carba-*closo*-dodecaborate which is more electron rich than the dodecahydro-*closo*-dodecaborate. Furthermore, functionalization of the mono-carba-*closo*-dodecaborate will furnish better control over the reactions due to its -1 charge. To do this, one has to start with the synthesis of undecaborate.

To get undecaborate, sodium borohydride was used as a starting material and diglyme was used as a solvent. Sodium borohydride and diglyme were mixed in a 3-necked round bottom flask equipped with a condenser connected to an acetone trap (to passify the escaped lower boranes) and a dropping funnel under inert atmosphere. For complete dissolution of sodium borohydride in diglyme, the temperature of the silicon oil bath was raised to 120 ^{o}C. Then, $BF_3.OEt_2$ was added to the solution dropwise over 5 hours. If this addition is too quick, the yield of the reaction is significantly lowered. After the addition, the solution was cooled to room temperature, the solids ($NaBF_4$) were removed by suction filtration. The filtrate containing undecaborate was subjected to solvent exchange by removing diglyme while adding water to the solution. After all diglyme was exchanged with water, trimethylammonium chloride was added to the solution to exchange sodium with trimethylammonium. Trimethylammonium salt of tetradecahydro-*nido*-undecaborate is insoluble in water, further, this salt is stable under ambient conditions. Sodium salt of undecaborate reacts violently with oxygen in the atmosphere. The trimethylammonium salt was filtered off, and it was recrystallized from acetone. Further recrystallization was done with MeOH/water mixture. The trimethylammonium salt of undecaborate was obtained with 42% yield. The characterization of the salt was done with IR Spectroscopy which shows characteristic B-H stretching at 2501 cm^{-1} (Figure 16).[80]

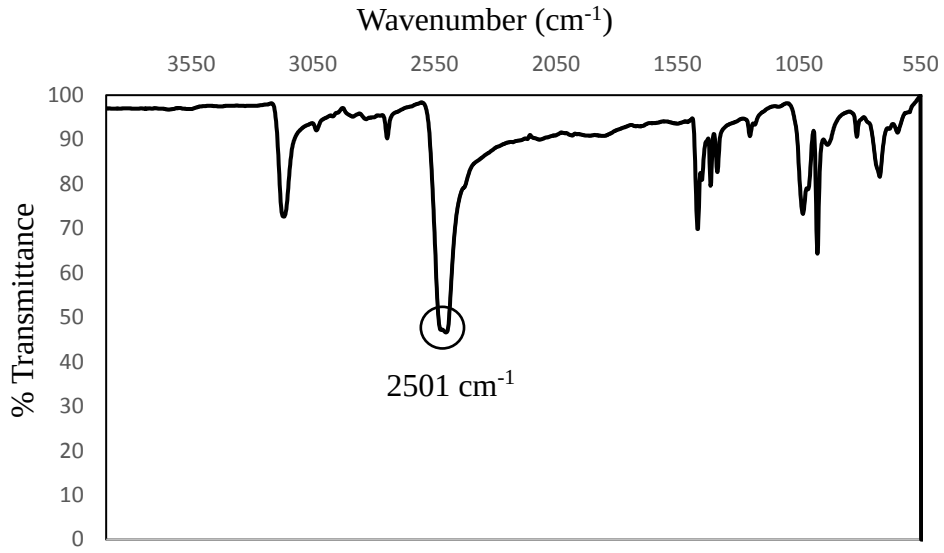


Figure 16. IR Spectrum of trimethylammonium salt of tetradecahydro-*nido*-undecaborate

3.1.3 Synthesis of mono-carba-*closo*-dodecaborate

Tetradecahydro-*nido*-undecaborate was dissolved in freshly distilled THF under Ar atmosphere and cooled to 0 ^{o}C, then, NaH was added to the solution slowly. Sodium hydride in mineral oil was washed with hexanes to get rid of mineral oil. There are two roles of sodium hydride addition to the solution; 1) to convert ammonium salt into sodium salt, 2) to convert $B_{11}H_{14}^-$ into $B_{11}H_{13}^{2-}$ which is the activated form of undecaborate. With these purposes in mind, excess NaH was added to the solution to convert ethanol into ethoxide in subsequent reaction. Then, the solvent was removed under reduced pressure. The remaining solid was added freshly distilled THF, the suspension was then flushed with Ar. To the suspension, chloroform and ethanol was added at 0 ^{o}C. The reaction was stirred overnight. In this reaction, dichlorocarbene was formed which was inserted reductively into the B_{11} cage. This reaction sequence yielded sodium salt of mono-carba-*closo*-dodecaborate. The mechanism of this was discussed in detail by Michl (this was discussed in the Introduction part, page 19).[41] The sodium salt of mono-carba-*closo*-dodecaborate dissolves in water while trialkylammonium salts are insoluble. Therefore, sodium

salt was made acidic then, trimethylammonium chloride was added to do cation exchange reaction. This furnished trimetylammonium salt of mono-carba-*closo*-dodecaborate off white solid collected by filtration. The characterization was done with IR Spectroscopy. The spectrum of the expected compound (Figure 17) shows signals at 3172 cm^{-1} for N-H stretching, 3037 cm^{-1} for C-H stretching and 2525 cm^{-1} for B-H stretching. For further purification of mono-carba-*closo*-dodecaborate, recrystallization with MeOH/water mixture was done.[41]

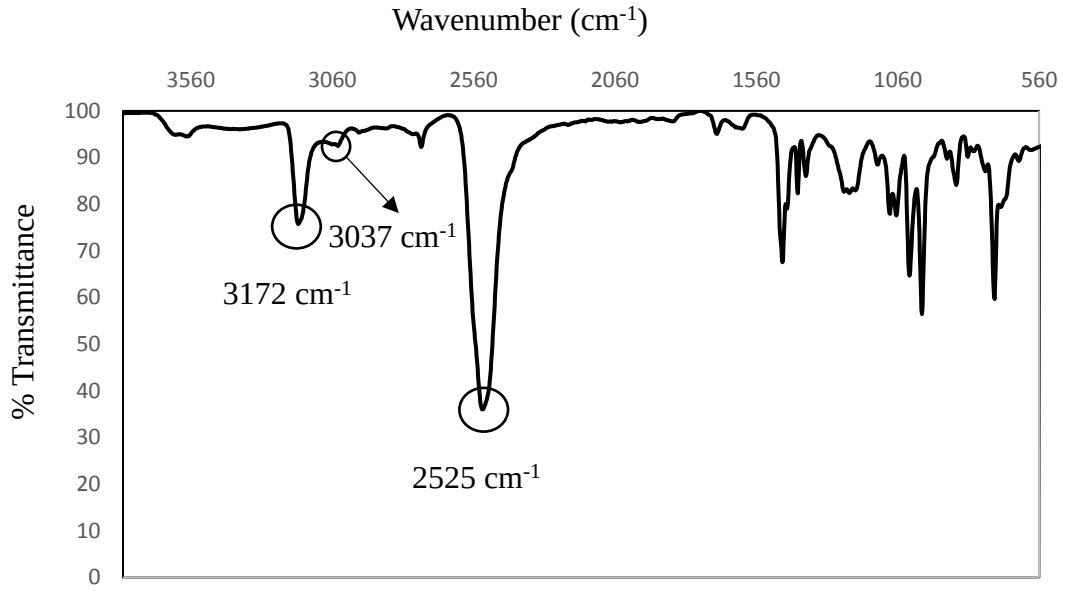
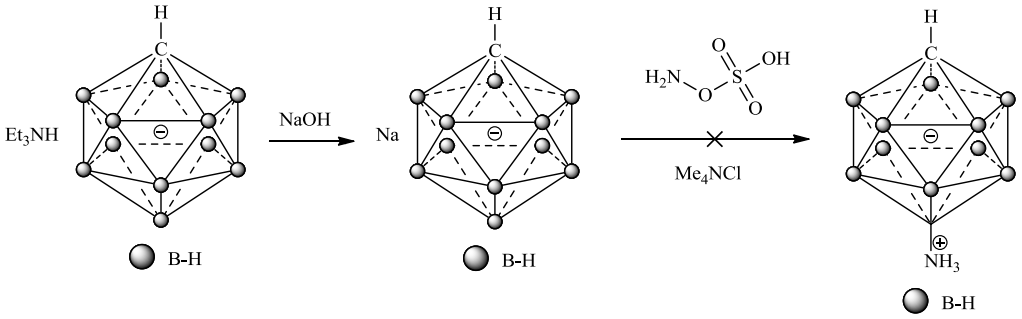


Figure 17. IR Spectrum of trimethylammonium salt of mono-carba-*closo*-dodecaborate

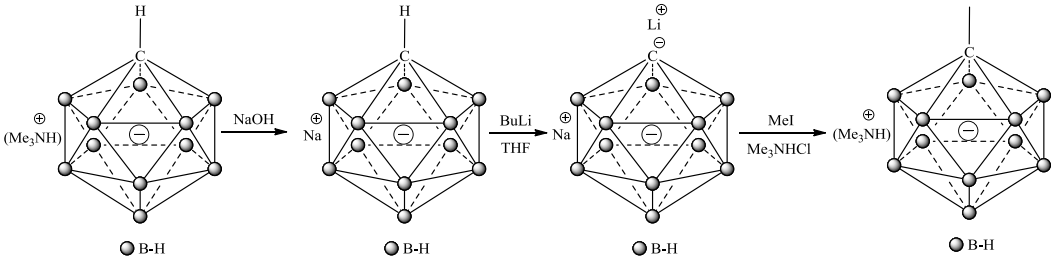
3.1.3.1 Reaction of mono-carba-*closo*-dodecaborate with hydroxylamine-*O*-sulfonic acid



Scheme 28. Amination of mono-carba-*closo*-dodecaborate

For the dodecahydro-*closo*-dodecaborate, we have shown that amination occured on the cage when treated with hydroxylamine-*O*-sulfonic acid. It is known that mono-*carba*-closo-dodecaborate is more electron rich than the dodecahydro-*closo*-dodecaborate cage. Therefore, it was expected that amination to occur at 12 position of mono-carba-*closo*-dodecaborate due to the electron density of the cluster.[6] For the amination of mono-carba-*closo*-dodecaborate, the same procedure was performed as in dodecahydro-*closo*-dodecaborate. The trimethylammonium salt of mono-carba-*closo*-dodecaborate was converted into sodium salt and dissolved in water. Then, the solution was treated with hydroxylamine-*O*-sulfonic acid and refluxed for 3 hours. After refluxing the solution, tetramethylammonium chloride was added to the solution for the formation of tetramethylammonium salt of 12-NH_2-$CB_{11}H_{12}$. Precipitation was occurred but obtained solid was the starting material as judged from IR spectrum.

3.1.3.2 Methylation of mono-carba-*closo*-dodecaborate on C vertex



Scheme 29. Methylation of mono-carba-*closo*-dodecaborate

Trimethylammonium salt of mono-carba-*closo*-dodecaborate was dissolved in freshly distilled THF. Then, at -78 ^{o}C, the solution was treated with BuLi in dry ice-acetone bath and stirred for 30 minutes. After the dry ice-acetone bath was removed, the solution was stirred at room temperature for additional 60 minutes. Subsequently, methyl iodide was added to the solution and stirred for 30 minutes. Reaction was quenched with distilled water, then the solvent was removed. The residue was acidified with HCl solution and the carborate was collected as solid after the addition of trimethylammonium chloride. The IR Spectrum (Figure 18) has the characteristic signals at 2522 cm^{-1} for B-H stretching and 1479 cm^{-1} for C-H stretching.[81] Also, NMR Spectrum (Figure 19) proves that the obtained product was the expected one.

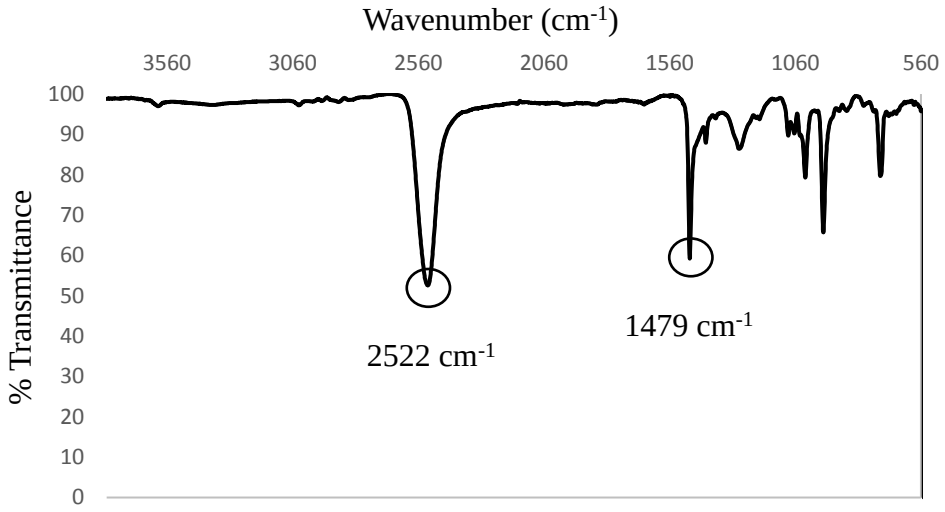


Figure 18. IR Spectrum of methylated mono-carba-*closo*-dodecaborate

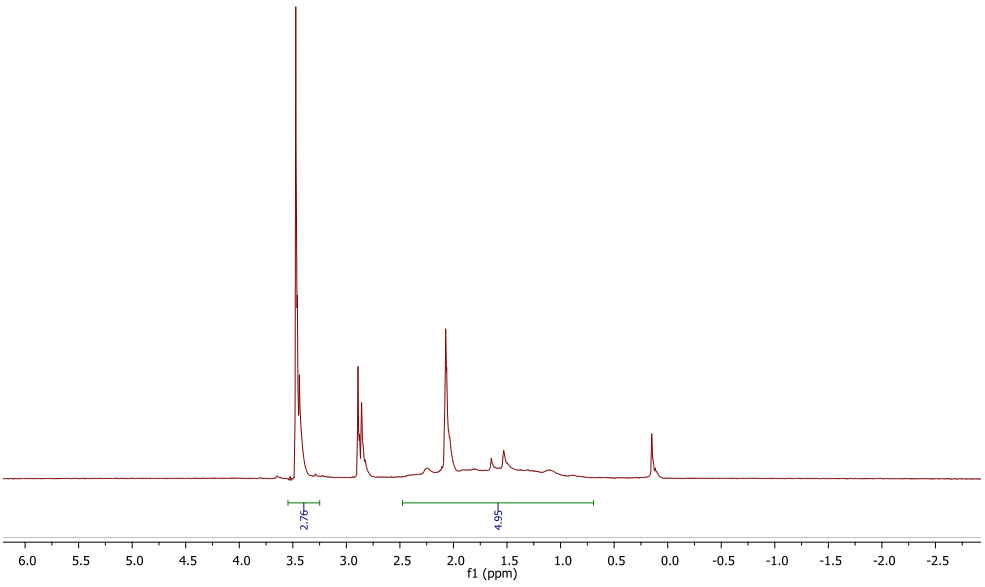


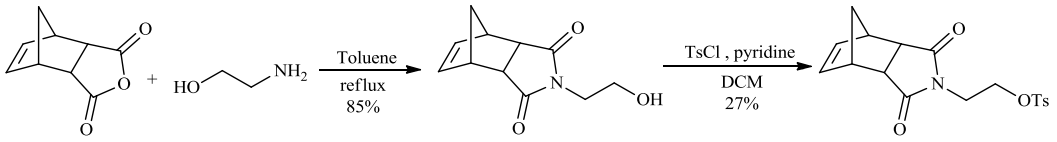
Figure 19. ^{1}H NMR Spectrum of methylated mono-carba-*closo*-dodecaborate (Due to the technical problems in NMR, the peaks are splitted. However, chemical shift values are consistent.)

3.1.3.2.1 Synthesis of Organic Compounds

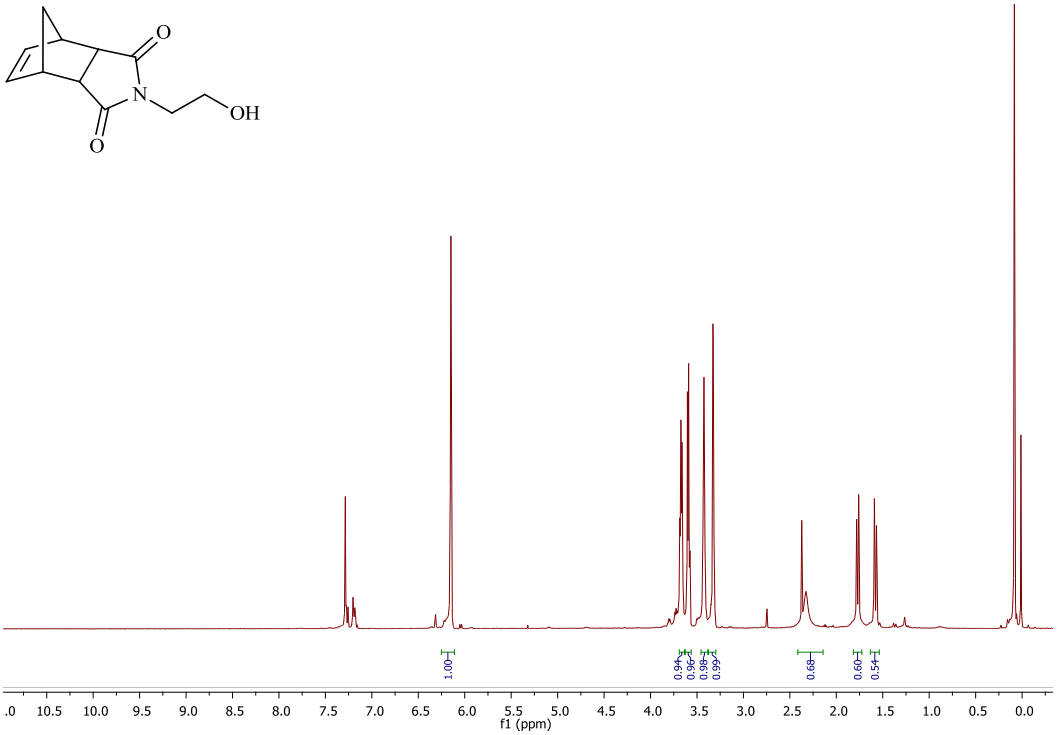
After successfully obtaining 1-CH_3-1-carba-*closo*-dodecaborate, it was wondered whether polymerizable organic units could be inserted on C vertex. For that, the following reactions were carried out.

3.1.3.2.1.1 Reaction between 5-norbornene-2,3-dicarboxylic anhydride and ethanolamine and tosylation

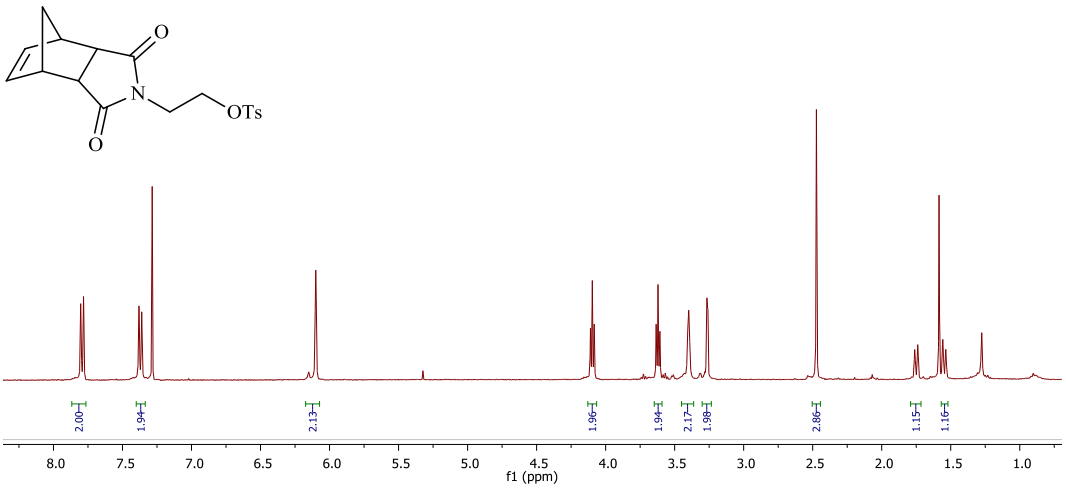
In the methylation reaction, methyl iodide was used as an electrophile in an S_N2 reaction. Toward this goal, we devised an electrophile based on the 5-norbornene-2,3-dicarboxylic anhydride (**ND**) which is treated with ethanolamine to get *N*-(hydroxyethyl)-5-norbornene-2,3-dicarboximide (**NDA**).[82] The alcohol moiety was tosylated by adding tosyl chloride onto the alcohol in the presence of pyridine.[83] The reactions furnished the desired tosylated compound, **NDAT** in 85% and 26.8% respectively. The reactions were summarized in Scheme 30. The compounds were characterized using ^{1}H NMR (Figure 20). In tosylation reaction, the excess tosyl chloride could not be removed with basic extraction. Therefore, filter paper was cut into the pieces and added to the DCM solution of the reaction mixture which contains excess tosyl choride. Excess tosyl chloride reacted with the –OH groups on filter paper.[84] After filtration, excess tosyl chloride is removed from the reaction mixture by yielding pure **NDAT.**



Scheme 30. Reaction between 5-norbornene-2,3-dicarboxylic anhydride and ethanolamine and tosylation



(a)

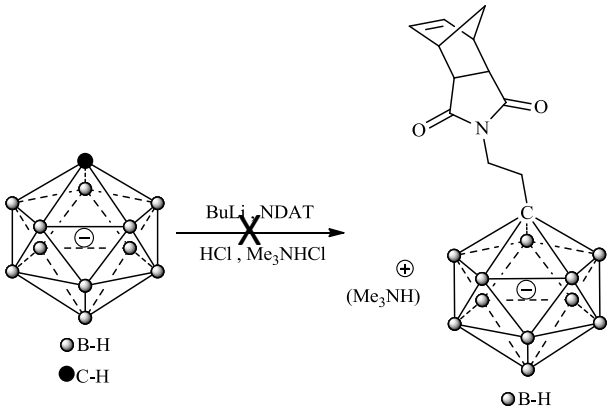


(b)

Figure 20. ^{1}H NMR Spectra of (a) **NDA** and (b) **NDAT**

3.1.3.2.1.2 Introducing tosylated N-(hydroxyethyl)-5-norbornene-2,3-dicarboximide to C vertex of mono-carba-*closo*-dodecaborate

With **NDAT** in hand, mono-carba-*closo*-dodecaborate was treated with BuLi as described in methylation reaction (3.1.3.2), then, treated with **NDAT** (Scheme 31). After stirring at room temperature 21 hours, the reaction was quenched and the work-up procedure described for methylation was applied. When the reaction mixture was characterized, it was concluded that the reaction did not give the desired compound. The steric crowdness around the electrophilic center is the reason for failure of this reaction.

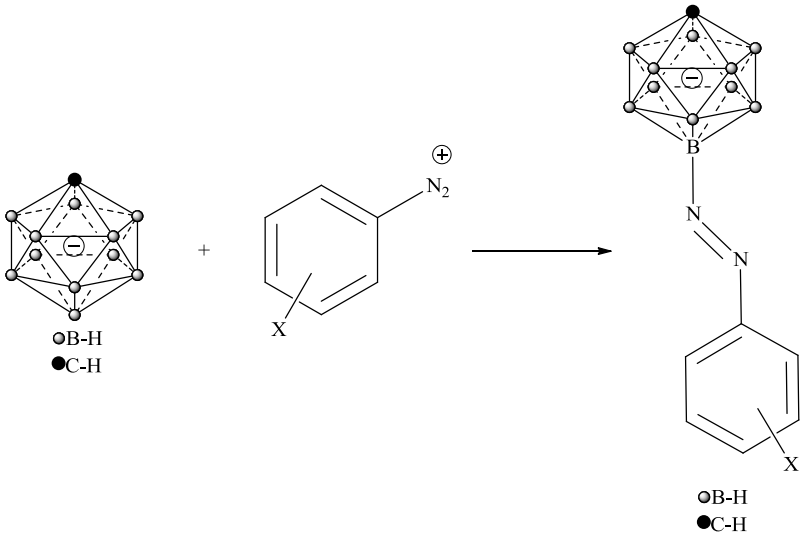


Scheme 31. Reaction between mono-carba-*closo*-dodecaborate and NDAT

3.1.3.3 Synthesis of different diazonium salts of mono-carba-*closo*-dodecaborate

With the failure of functionalizing mono-carba-*closo*-dodecaborate with polymerizable organic compounds, we decided to treat diazonium compounds with mono-carba-*closo*-dodecaborate. This reaction could possibly yield diazo dyes with one side being organic (this could be further functionalized by a polymerizable group) and other side being mono-carba-*closo*-dodecaborate. This idea is summarized in Scheme 32. This reaction was envisioned to occur smoothly despite

the fact that dodecahydro-*closo*-dodecaborate did not react this way in ordinary conditions.



Scheme 32. Summary of the reactions of diazonium cations and mono-carba-*closo*-dodecaborate

3.1.3.3.1 Synthesis of benzenediazonium salts of mono-carba-*closo*-dodecaborate

To test the above mentioned idea, aniline and its derivatives were converted to diazonium salt with $NaNO_2$ in acidic conditions at 0 ^oC. To the aqueous solutions of diazonium salts, the sodium salts of mono-carba-*closo*-dodecaborate were added. In each case, precipitate formation was observed and isolated with filtration. The precipitates were characterized with IR spectroscopy. From IR spectra, it was found that the salts isolated were diazonium salts of mono-carba-*closo*-dodecaborate with the characteristic peaks of B-H stretching *ca.* 2520 cm^{-1} and *ca.* 2200 cm^{-1} for diazonium group (Figure 21).

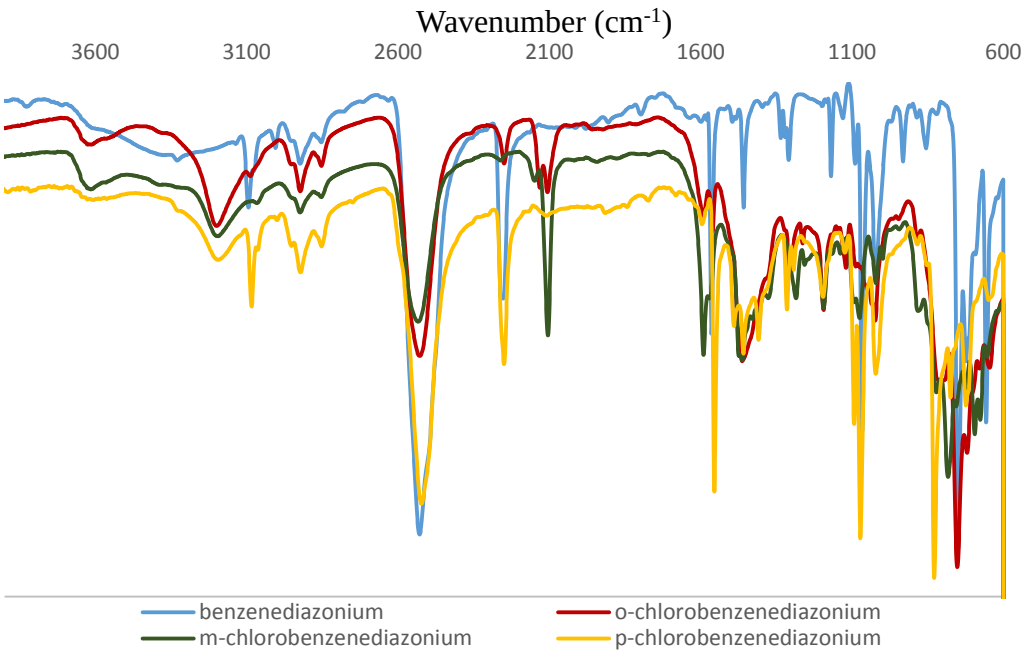
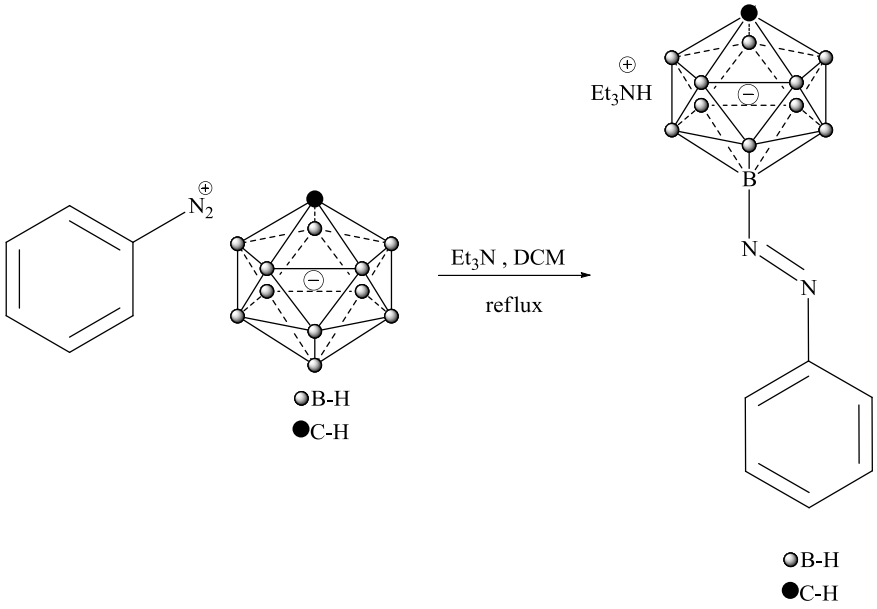


Figure 21. IR Specra of aryldiazonium salts of mono-carba-*closo*-dodecaborate

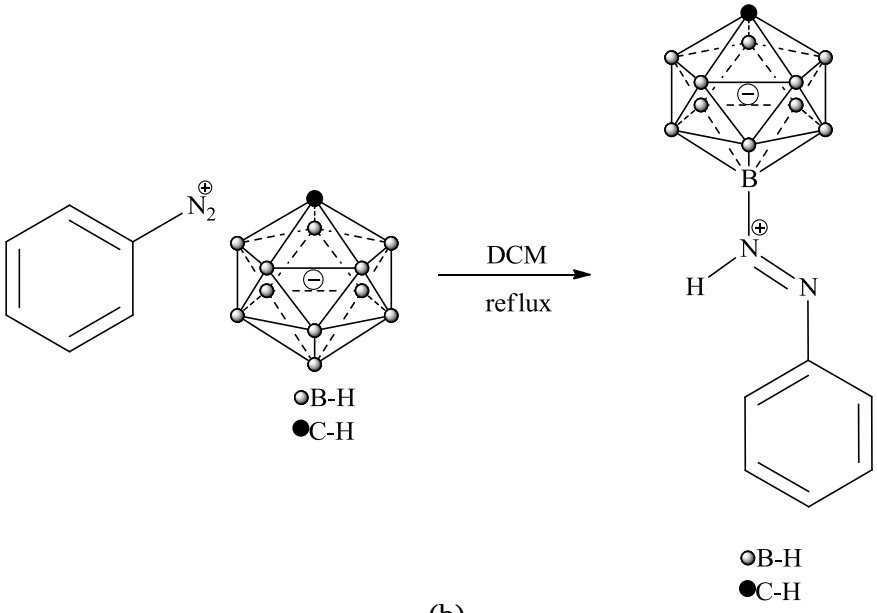
3.1.3.3.1.1 Converting diazonium salts into diazo compounds

With diazonium salts of mono-carba-*closo*-dodecaborate in hand, it was concluded that room temperature does not provide enough energy for the mono-carba-*closo*-dodecaborate to attach the diazonium cations to form diazo dyes for electron rich diazonium cations. For electron deficient diazonium cations, a mixture of diazonium salts and diazo compounds was observed. To convert diazonium cations into diazo compounds, the salt was dissolved in DCM and refluxed for 5 hours in the presence of triethylamine as a base (Scheme 33). The resulting solutions were evaporated and the residues were characterized with IR spectroscopy. IR spectra show the disappearance of peak *ca.* 2200 cm^{-1} and the appearance of peak *ca.* 1590 cm^{-1} which is characteristic for -N=N- stretching. The results are summarized in Figure 21. With this result in mind, it was decided to check the effect of the base. For that, the salt solution in DCM was refluxed without a base (Scheme 33). In this case, we observed the disappearance of diazonium peak and appearance of azo peaks as well. Based on

these observations, the mechanism of this reaction was proposed to be proceeding through nitrogen insertion to B-H bond as summarized in Scheme 34.

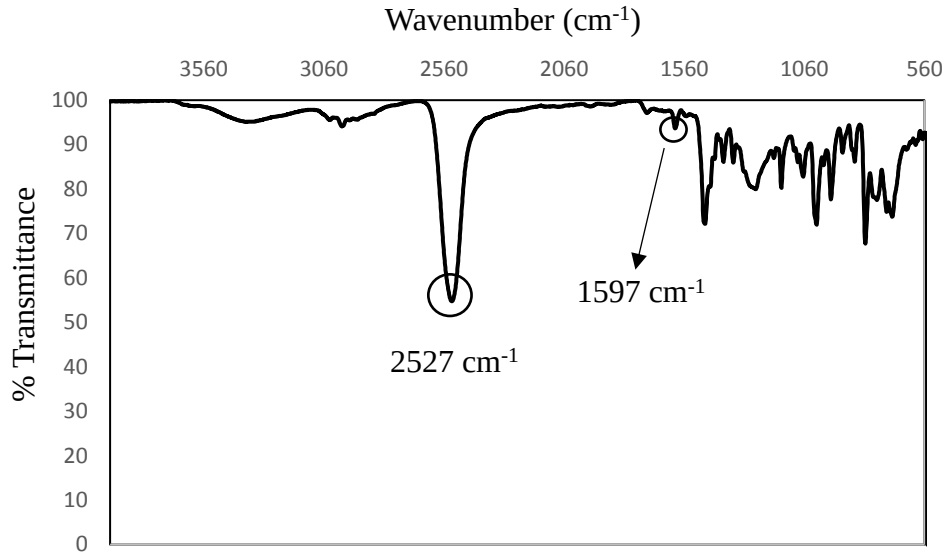


(a)

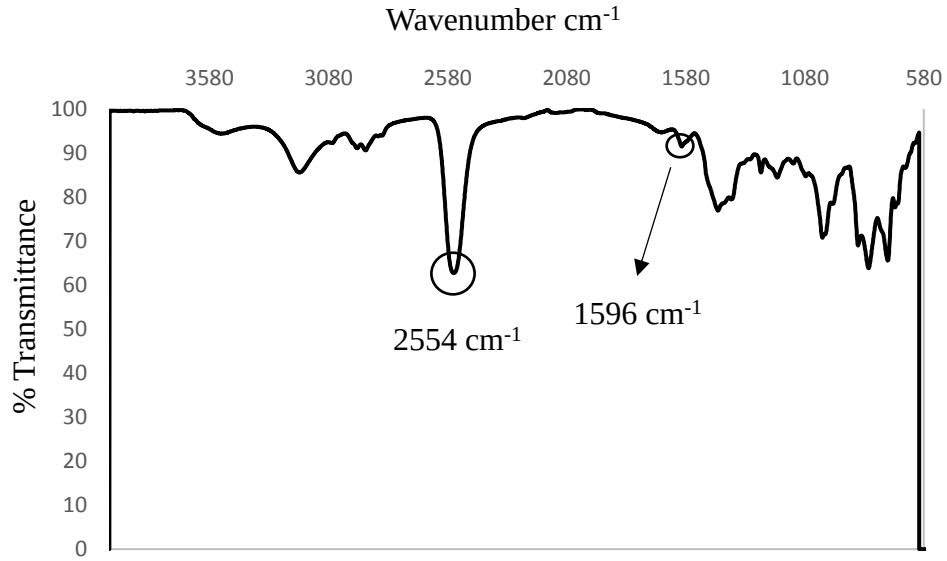


(b)

Scheme 33. Introducing the benzenediazonium cation to mono-carba-*closo*-dodecaborate (a) with a base, (b) without a base

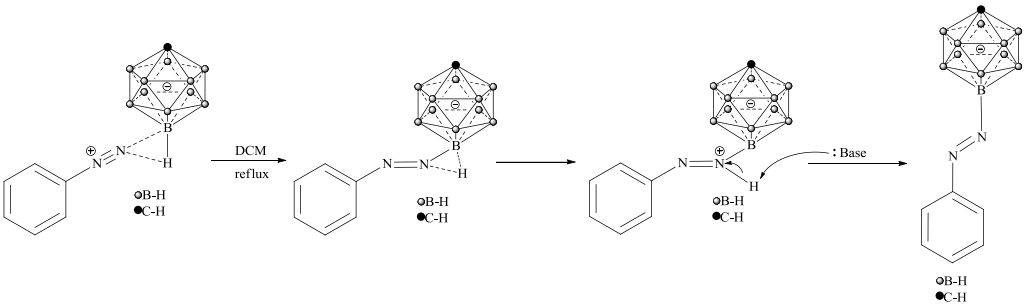


(a)



(b)

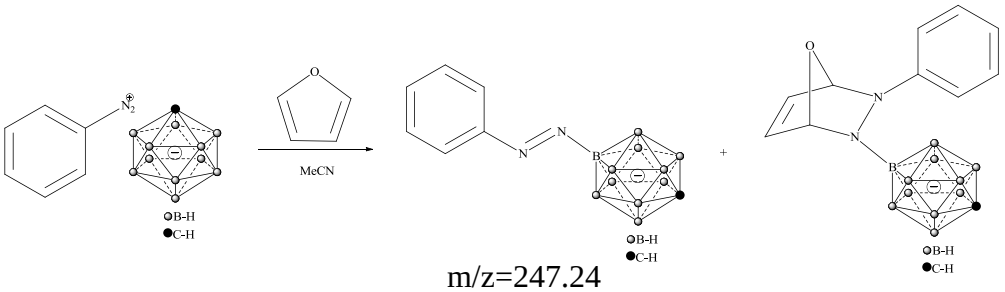
Figure 22. IR spectra of products after reflux (a) with a base ,(b) without a base



Scheme 34. Proposed mechanism of introducing benzenediazonium cation to mono-carba-*closo*-dodecaborate

3.1.3.3.1.2 Diels-Alder Reaction on Diazonium Cation of benzenediazonium salt of mono-carba-*closo*-dodecaborate

To explore the reactions of diazonium salts further, we decided to use them in hetero Diels-Alder reactions in which diazonium will be dienophile and furan will act as diene (Scheme 35). To do this reaction, diazonium salt was dissolved in MeCN. To this, furan solution in MeCN was added. The resulting mixture was stirred at room temperature for 1 hour and the solvent was evaporated. The residue was characterized with IR spectroscopy and HRMS. IR spectrum of the residue showed the presence of diazo compound. Further characterization was done with HRMS showing m/z peaks at 247.24 and 315.2904 which corresponds to Compound 14 and Compound 14a respectively.



m/z=247.24

14

m/z=315.27

14a

Scheme 35. Diels-Alder reaction between diazonium cation of mono-carba-*closo*-dodecaborate and furan

CHAPTER 4

CONCLUSION

In this study, dodecahydro-*closo*-dodecaborate and mono-carba-*closo*-dodecaborate were synthesized successfully. The published procedures were improved for convenient synthesis in our laboratory. Dodecahydro-*closo*-dodecaborate was functionalized with amine group with treatment of the borate with hydroxylamine-*O*-sulfonic acid. Another amination procedure was employed by introducing nitroso group on dodecahydro-*closo*-dodecaborate followed by reduction. The further reactions on the 1-amino-undecahydro-*closo*-dodecaborate failed in our hands. With this in mind, benzenediazonium salt of dodecahydro-*closo*-dodecaborate was reacted with furan. To run a hetero Diels-Alder reaction, the expected product formation was observed. However, the product was not obtained with high yield and high purity to further proceed to polymerization.

Similarly, mono-carba-*closo*-dodecaborate anion was treated with hydroxylamine-*O*-sulfonic acid, the reaction did not proceed as expected. Therefore, the carborate was functionalized by reactions with substituted benzenediazonium cations. These reactions found to be efficient for derivatization of mono-carba-*closo*-dodecaborate and this could be used to synthesize carborate containing polymers.

CHAPTER 5

EXPERIMENTAL

5.1 Methods and Materials

All starting materials and solvents were purchased from Sigma Aldrich and were used without further purifications. The reactions were monitored by thin layer chromatography (TLC) (Merck Silica Gel 60 F254) and visualized by UV light at 254 nm.

Structural evaluation of the synthesized compounds was accomplished with the instruments stated below.

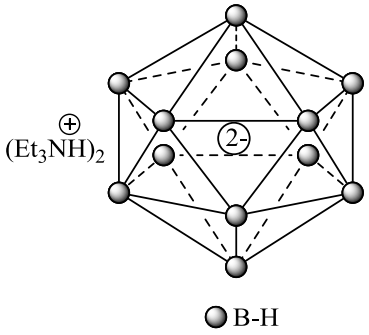
^{1}H nuclear magnetic resonance spectra of the compounds were recorded in deuterated solvents with Bruker Avance III Ultrashield 400 Hz NMR spectrometer. The chemical shifts were stated in parts per million (ppm) with tetramethylsilane (TMS) as internal reference.

^{1}H NMR spectra of compounds were given in Appendix A. NMR spectra were processed with MestReNova program.

Infrared (IR) Spectra were recorded with Thermo Scientific Nicolet iS10 ATR-IR spectrometer. Signal locations were reported in reciprocal centimeter (cm^{-1}). The IR spectra of the compounds synthesized are given in Appendix B. IR spectra were processed with Microsoft Office Excel program.

High Resolution Mass Spectra (HRMS) were processed in negative mode on (ES-) using Time of Flight mass analyzer. The high resolution mass spectra of compounds synhesized are given in Appendix C.

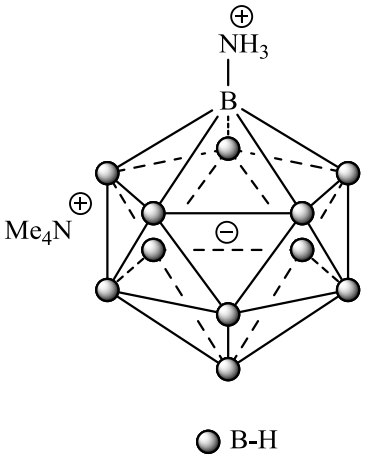
5.2 Synthesis of triethylammonium salt of dodecahydro-*closo*-dodecaborate



1

A 3-necked round bottom flask equipped with a condenser (connected to an acetone trap), a dropping funnel and a stopper is charged with 30 g (0.793 mol) $NaBH_4$ and 150 mL of diglyme under Ar atmosphere. The silicon oil bath is heated to 120 ^oC to dissolve the sodium borohydride in the reaction mixture. 62.5 g (0.246 mol) I_2 is dissolved in 200 mL of diglyme and added to the dropping funnel. The solution of iodine in diglyme is added to the solution containing sodium borohydride dropwise in 6 hours. After the addition, the solution is stirred overnight at 120 ^oC. Temperature of the oil bath is increased to 185 ^oC and the solution is stirred for 1 day. The solvent is removed with distillation. 143 mL of distilled water is added to the residue and 84 mL 37% HCl is added to the reaction mixture slowly. The reaction vessel is stored in refrigerator overnight for completion of the formation of boric acid. The reaction mixture is filtered and boric acid is collected. To the filtrate, 150 mL Et_3N is added and white crystals of triethylammonium salt of dodecahydro-*closo*-dodecaborate are started to form immediately. The expected product is collected by filtering the reaction mixture. (15.728 g, 0.046 mol, 68.9%) IR: 2473 cm^{-1} (B-H str.), 3125 cm^{-1} (N-H str.)

5.2.1 Synthesis of 1-amino-undecahydro-*closo*-dodecaborate with synthesized hydroxylamine-*O*-sulfonic acid



2

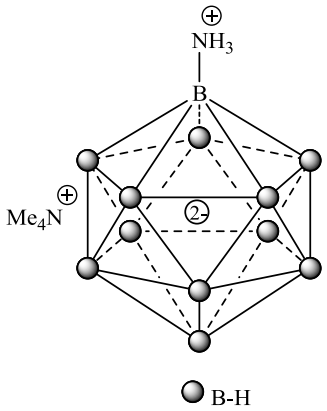
5.2.1.1 Preparation of hydroxylamine-*O*-sulfonic acid

5 g (30.5 mmol) hydroxylammonium sulfate is charged into a 3-necked round bottom flask equipped with a NaOH trap, a drying agent and a dropper containing 11.8 mL (177 mmol) chlorosulfonic acid. The acid is added to the solid slowly with the help of a dropper and resulting solution is stirred for 30 minutes. The reaction vessel is put into an oil bath at 100 ^{o}C for 7 minutes and cooled to room temperature. The flask contaning the solution is placed in an ice bath and 40 mL diethyl ether is added dropwise. After the addition, white powder is observed and collected with suction filtration. Hydroxylamine-*O*-sulfonic acid is washed with 60 mL THF and 49 mL diethyl ether. Obtained product is used without further characterization.

0.25 g (6.358 mmol) NaOH is dissolved in water and 1 g (2.89 mmol) $(Et_3NH)_2B_{12}H_{12}$ is added to the solution. Solvent is removed and the residue is dissolved with 15 mL of distilled water. Then, 0.65 g (5.78 mmol) of prepared hydroxylamine-*O*-sulfonic acid is added to the solution and refluxed for 3 hours. The solution is cooled to room temperature and Me_4NCl is added. The product is

collected by filtering the solution with very low yield. IR: 2471 cm^{1} (B-H str.), around 3200 cm^{-1} (N-H str.)

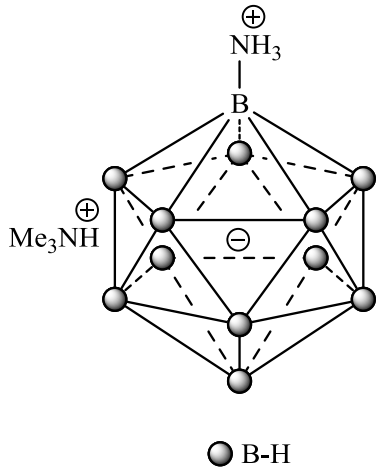
5.2.2 Synthesis of 1-amino-undecahydro-*closo*-dodecaborate with commercial hydroxylamine-*O*-sulfonic acid



3

0.47 g (11.726 mmol) NaOH is dissolved in water and 1.84 g (5.33 mmol) $(Et_3NH)_2B_{12}H_{12}$ is added to the solution. Solvent is removed and the residue is dissolved with 7 mL of distilled water. Then, 1.2 g (10.66 mmol) of commercial hydroxylamine-*O*-sulfonic acid is added to the solution and refluxed for 3 hours. The solution is cooled to room temperature and Me_4NCl is added. The product is collected by filtering the solution with 25.78% yield. IR: 2486 cm^{1} (B-H str.), 3223 cm^{-1} (N-H str.)

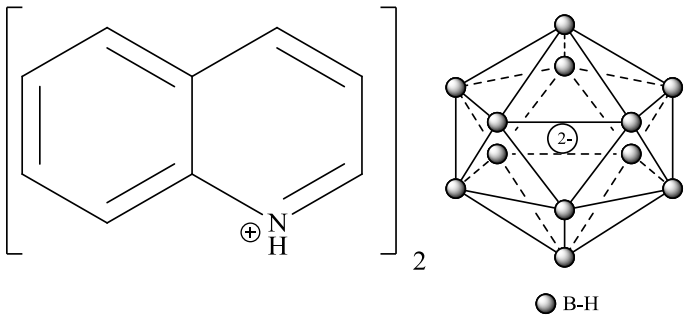
5.2.3 Synthesis of 1-amino-undecahydro-*closo*-dodecaborate with the reduction of 1-nitroso-undecahydro-*closo*-dodecaborate



4

0.18 g (3.15 mmol) KOH is dissolved in distilled water and 0.5 g (1.43 mmol) $(Et_3NH)_2B_{12}H_{12}$ is added to the KOH solution. The solvent is removed and to the residue, 5 mL 37% HCl is added. The reaction flask is placed in a NaCl-ice bath. 0.3 g (3.43 mmol) KNO_2 is dissolved in distilled water and added to the solution dropwise. The solution is kept at 0 ^oC for 1 hour. 2 mL H_2SO_4 in 20 mL distilled water is added to the solution. After the addition of Me_3NHCl, the solution is filtered and the solid ($(Me_3NH)_2B_{12}H_{11}NO$) is collected. IR: 2511 cm^{-1} (B-H str.), 1635 cm^{-1} (N-O str.). 0.18 g (3.15 mmol) KOH is dissolved in distilled water and the collected nitroso derivative of dodecahydro-*closo*-dodecaborate is added to the solution. The solvent is removed and to the residue, 0.9 g (13.7 mmol) Zn and 8 mL 20% HCl are added. The solution is filtered and to the filtrate, 15 mL 20% NaOH is added. The solution is acidified with 30 mL 37% HCl in distilled water and Me_3NHCl is added to the solution. The desired compound is obtained after filtration. IR: 2498 cm^{-1} (B-H str.), 3132 cm^{-1} (N-H str.)

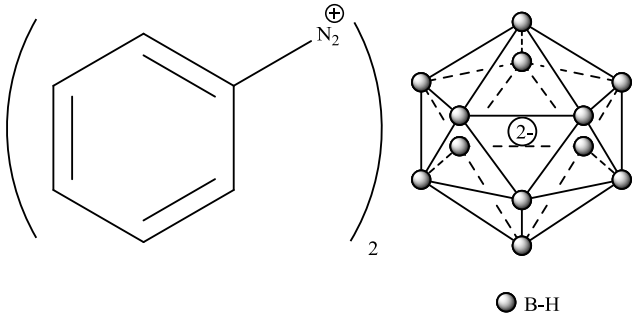
5.2.4 Synthesis of quinolin-1-ium salt of dodecahydro-*closo*-dodecaborate



5

0.13 g (3.18 mmol) NaOH is dissolved in 10 mL of distilled water. 0.5 g (1.445 mmol) $(Et_3NH)_2B_{12}H_{12}$ is added to the NaOH solution and heated until the solution becomes clear. Solvent is removed until dryness and HCl solution is added to the residue. 0.4 mL (3.18 mmol) quinoline is charged into the acidic solution and white solid is started to form. The desired compound is collected with filtration with 95% yield. NMR is taken in d-Acetone.

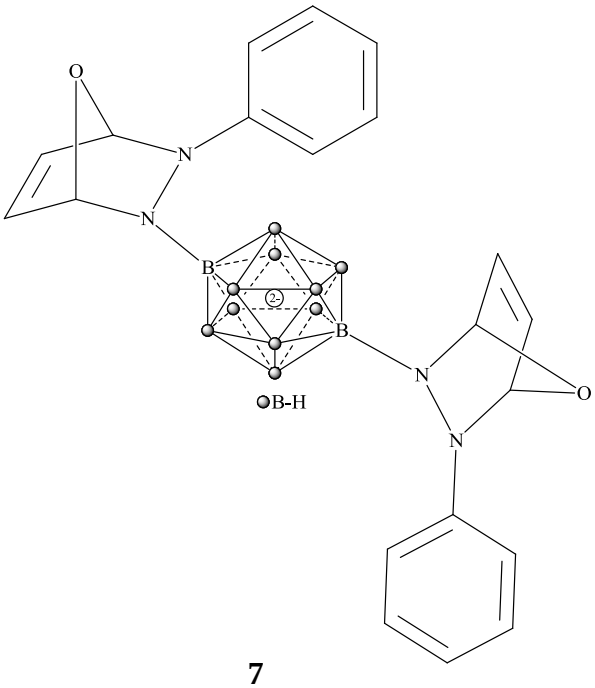
5.2.5 Synthesis of benzenediazonium salt of dodecahydro-*closo*-dodecaborate



6

0.235 g (5.863 mmol) NaOH is dissolved in distilled water and 0.925 g (2.665 mmol) $(Et_3NH)_2B_{12}H_{12}$ is added to the solution. The solution is heated until it becomes clear and then, solvent is removed resulted in sodium salt of dodecahydro-*closo*-dodecaborate. 0.49 mL (5.33 mmol) aniline is mixed with 7.6 mL 37% HCl in 38.6 mL distilled water. 0.465 g (6.65 mmol) $NaNO_2$ is dissolved in distilled water and added to the solution slowly at 0 ^oC. The solution is stirred for 1 hour and obtained sodium salt of dodecahydro-*closo*-dodecaborate in distilled water is introduced to the solution slowly at 0 ^oC. The solution is stirred for additional 2 hours and expected product is collected with filtration with 30% yield. IR: 2269 cm^{-1} for diazonium group and 2472 cm^{-1} for B-H stretching.

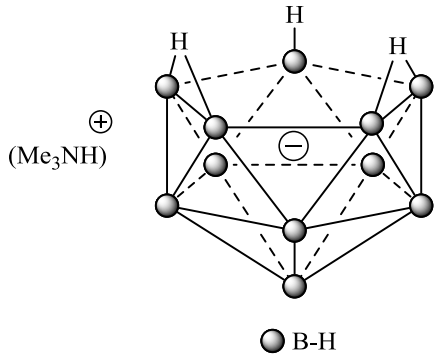
5.2.6 Diels-Alder reaction between the cation of benzenediazonium salt of dodecahydro-*closo*-dodecaborate and furan



7

0.2826 g (0.8 mmol, 1 eqv.) benzenediazonium salt of dodecahydro-*closo*-dodecaborate is dissolved in acetonitrile. 0.23 mL (3.2 mmol, 4 eqv.) furan is mixed with acetonitrile and added to the solution slowly at room temperature. After stirring for 1 hour, the solution is cooled to 0 ^{o}C and filtered. Obtained solid contained the expected product and detailed explanation of the characterization was given in Chapter 3.

5.3 Synthesis of trimethylammonium salt of tetradecahydro-*nido*-undecaborate

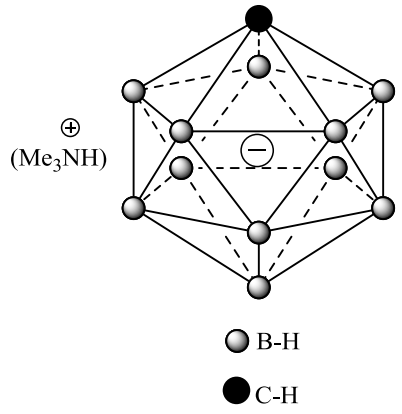


8

30 g (0.793 mol) $NaBH_4$ and 150 mL of diglyme are charged into a 3-necked round bottom flask equipped with a dropping funnel, a condenser (connected to an acetone trap) and a stopper under Ar atmosphere. Temperature of the silicon oil bath is raised to 120 ^{o}C for complete dissolution of sodium borohydride. 125 mL (0.995 mol) $BF_3.OEt_2$ is added to the solution dropwise with dropping funnel in 5 hours. Then, the reaction mixture is cooled to room temperature and suction filtration is applied. During the filtration process, both the reaction flask and the solid are washed with diglyme until the solid becomes white. To the filtrate, solvent exchange procedure is applied with portions of 150 mL distilled water (total 1050 mL) and the evaporated liquid is nearly 1060 mL. Resulting solution is cooled to room temperature and 6.5

g (0.068 mol) trimethylammonium chloride is added to the solution. The solution is stored in refrigerator overnight and filtered. Obtained solid is dissolved in acetone and heated to reflux. Distilled water is added to the solution until cloudiness is observed. The solution is cooled to room temperature and stored in refrigerator overnight. The solution is filtered and the collected solid is dried yielding 5.8 g (0.03 mol, 41.7%) $(CH_3)_3NHB_{11}H_{14}$. IR: 2501 cm^{-1} (B-H str.), 3169 cm^{-1} (N-H str.)

5.4 Synthesis of trimethylammonium salt of mono-carba-*closo*-dodecaborate

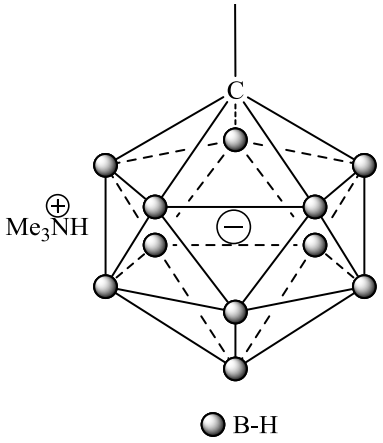


9

5.0 g (0.026 mol) trimethylammonium salt of tetradecahydro-*nido*-undecaborate is dissolved in freshly disttiled THF under Ar atmosphere and cooled to 0 ^oC in an ice bath. 17.5 g (0.648 mol) NaH is washed with hexane and added to the solution slowly. The solution is stirred for 1 hour at room temperature and solvent is removed. After evaporation, freshly distilled THF is added to the flask to dissolve the solid. Then, 12.5 mL (0.156 mol) $CHCl_3$ is added slowly at 0 ^oC. The solution is stirred for 1 hour at room temperature and EtOH is added to the solution dropwise at 0 ^oC and allowed to stir overnight. Next day, the solvent is removed and distilled water is added to the residue. The solution is acidified with 40 mL 37% HCl + 80 mL distilled water. After the acidification process, trimethylammonium chloride is added to the solution and filtered. Obtained solid is dissolved with minimum amount of MeOH

with heating and after all the solid is dissolved, distilled water is added to the solution and filtered. To the filtrate, trimethylammonium chloride is added and some precipitation occurred. The desired product is collected with filtration yielding 0.18 g (0.9 mmol, 3.41%). IR: 3172 cm^{-1} (N-H str.), 3037 cm^{-1} (C-H str.), 2525 cm^{-1} (B-H str.)

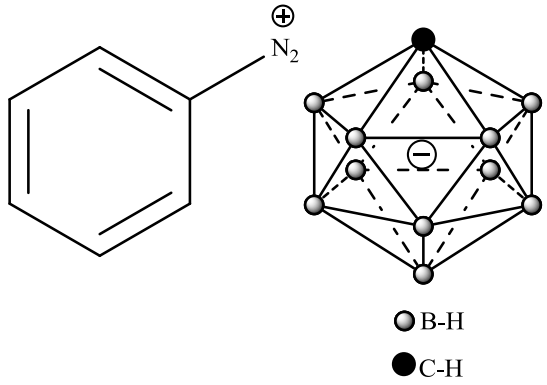
5.4.1 Synthesis of 1-methyl-mono-carba-*closo*-dodecaborate



10

1 g (4.93 mmol) $(Me_3NH)(CB_{11}H_{12})$ is dissolved 50 mL freshly distilled THF. 13 mL (19.72 mmol) BuLi is added to the solution at -78 ºC. The solution is stirred for 30 minutes in dry ice-acetone bath and additional 60 minutes at room temperature. 0.6 mL (9.86 mmol) MeI is added to the solution and stirred for 30 minutes. 10 mL distilled water is added to the solution and the solvent is evaporated until dryness. To the residue, HCl solution is added for acidification and Me_3NHCl is added to the acidified solution. After filtering the solution, the desired compound is obtained. IR: 2522 cm^{-1} (B-H str.), 1479 cm^{-1} (C-H str.)

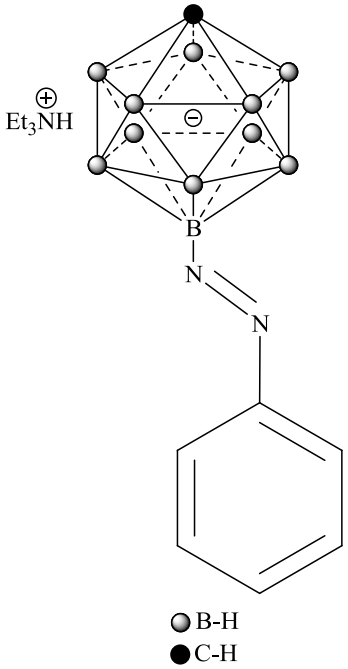
5.4.2 Synthesis of benzenediazonium salt of mono-carba-*closo*-dodecaborate



11

0.165 mL (1.81mmol, 1 eqv.) aniline is mixed with 15.75 mL 2M HCl solution. 0.16 g (2.26 mmol, 1.25 eqv.) $NaNO_2$ is dissolved in distilled water and added to the solution slowly at 0 ^oC. Solution is stirred for 1h. 0.3 g (1.81 mmol, 1 eqv.) $NaCB_{11}H_{12}$ is dissolved in water and added to the solution slowly at 0 ^oC. Solution is stirred for 2h. Solution is filtered and the obtained solid is the expected product. IR: 2528 cm^{-1} (B-H str.), 2259 cm^{-1} (diazonium group).

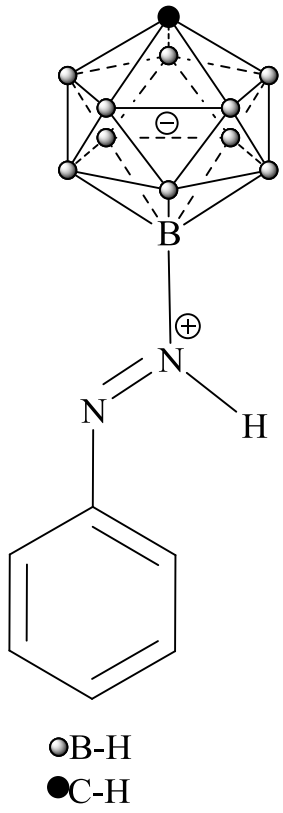
5.4.2.1 Introduction of benzenediazonium to the cluster with a base



12

Benzenediazonium salt of mono-carba-*closo*-dodecaborate is dissolved in DCM and Et_3N is added into the solution. The solution is refluxed for 5h and solvent is removed. The residue is the expected compound. IR: 2527 cm^{-1} (B-H str.), 1597 cm^{-1} (diazo group).

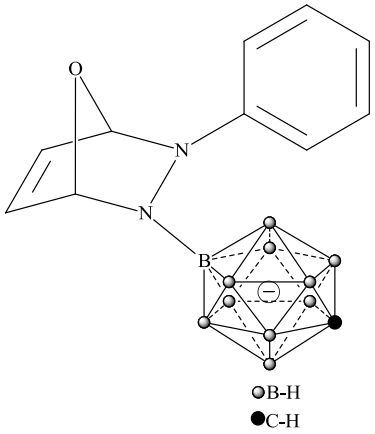
5.4.2.2 Introduction of benzenediazonium to the cluster without a base



13

Benzenediazonium salt of mono-carba-*closo*-dodecaborate is dissolved in DCM and the solution is refluxed for 5h. Then, the solvent is removed. The residue is the expected compound. IR: 2554 cm^{-1} (B-H str.), 1596 cm^{-1} (diazo group).

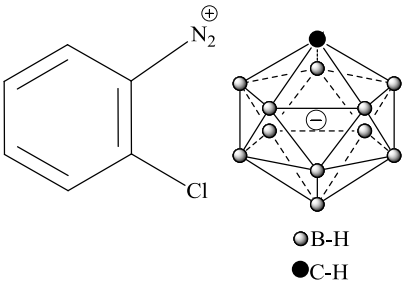
5.4.2.3 Diels-Alder reaction between the cation of benzenediazonium salt of mono-carba-*closo*-dodecaborate and furan



14

0.1450 g (0.585 mmol, 1 eqv.) benzenediazonium salt of mono-carba-*closo*-dodecaborate is dissolved in acetonitrile. 0.1 mL (1.170 mmol, 2 eqv.) furan is mixed with acetonitrile and added to the solution slowly at room temperature. After stirring for 1 hour, the solution is cooled to 0 ^{o}C and solvent is removed. The residue contained the expected product and detailed explanation of the result was given in Chapter 3.

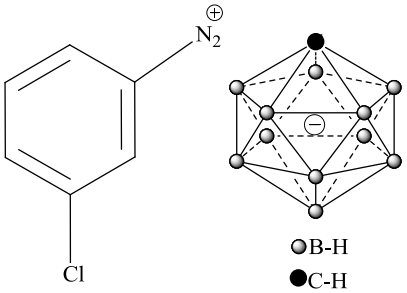
5.4.3 Synthesis of *o*-chlorobenzenediazonium salt of mono-carba-*closo*-dodecaborate



15

0.19 mL (1.81 mmol, 1 eqv.) *o*-chloroaniline is mixed with 15.75 mL 2M HCl solution. 0.16 g $NaNO_2$ (2.26 mmol, 1.25 eqv.) is dissolved in 15 mL water and added to the solution slowly at 0 ºC and stirred for 1h. 0.3 g $NaCB_{11}H_{12}$ (1.81 mmol, 1 eqv.) is dissolved in water and added to the solution slowly at 0 ºC. Solution is stirred for 2h and filtered. Obtained solid on filter paper is black and sticky and is the desired compound. IR: 2528 cm^{-1} (B-H str.), 2249 cm^{-1} (diazonium group).

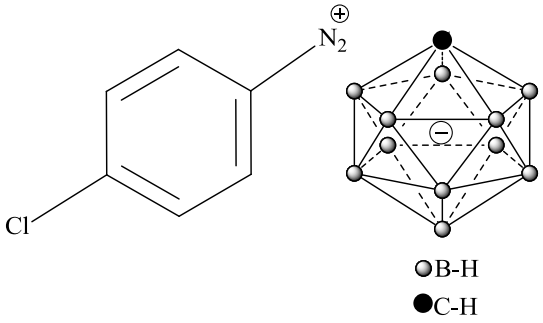
5.4.4 Synthesis of *m*-chlorobenzenediazonium salt of mono-carba-*closo*-dodecaborate



16

0.19 mL (1.81 mmol, 1 eqv.) *m*-chloroaniline is mixed with 15.75 mL 2M HCl solution. 0.16 g $NaNO_2$ (2.26 mmol, 1.25 eqv.) is dissolved in 15 mL water and added to the solution slowly at 0 ºC and stirred for 1h. 0.3 g $NaCB_{11}H_{12}$ (1.81 mmol, 1 eqv.) is dissolved in water and added to the solution slowly at 0 ºC. Solution is stirred for 2h and filtered. Obtained solid on filter paper is black and sticky and is the desired compound. IR: 2533 cm^{-1} (B-H str.), 2261 cm^{-1} (diazonium group).

5.4.5 Synthesis of *p*-chlorobenzenediazonium salt of mono-carba-*closo*-dodecaborate



17

0.231 g (1.81 mmol, 1 eqv.) *p*-chloroaniline is mixed with 15.75 mL 2M HCl solution. 0.16 g $NaNO_2$ (2.26 mmol, 1.25 eqv.) is dissolved in 15 mL water and added to the solution slowly at 0 ^oC and stirred for 1h. 0.3 g $NaCB_{11}H_{12}$ (1.81 mmol, 1 eqv.) is dissolved in water and added to the solution slowly at 0 ^oC. Solution is stirred for 2h and filtered. Obtained solid is the expected compound. IR: 2522 cm^{-1} (B-H str.), 2249 cm^{-1} (diazonium group).

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APPENDICES

A. NMR Spectra

Nuclear Magnetic Resonance (NMR) spectra were recorded at Bruker Avance III Ultrashield 400 Hz. $CDCl_3$ and Acetone-D6 were used as solvent in all the records.

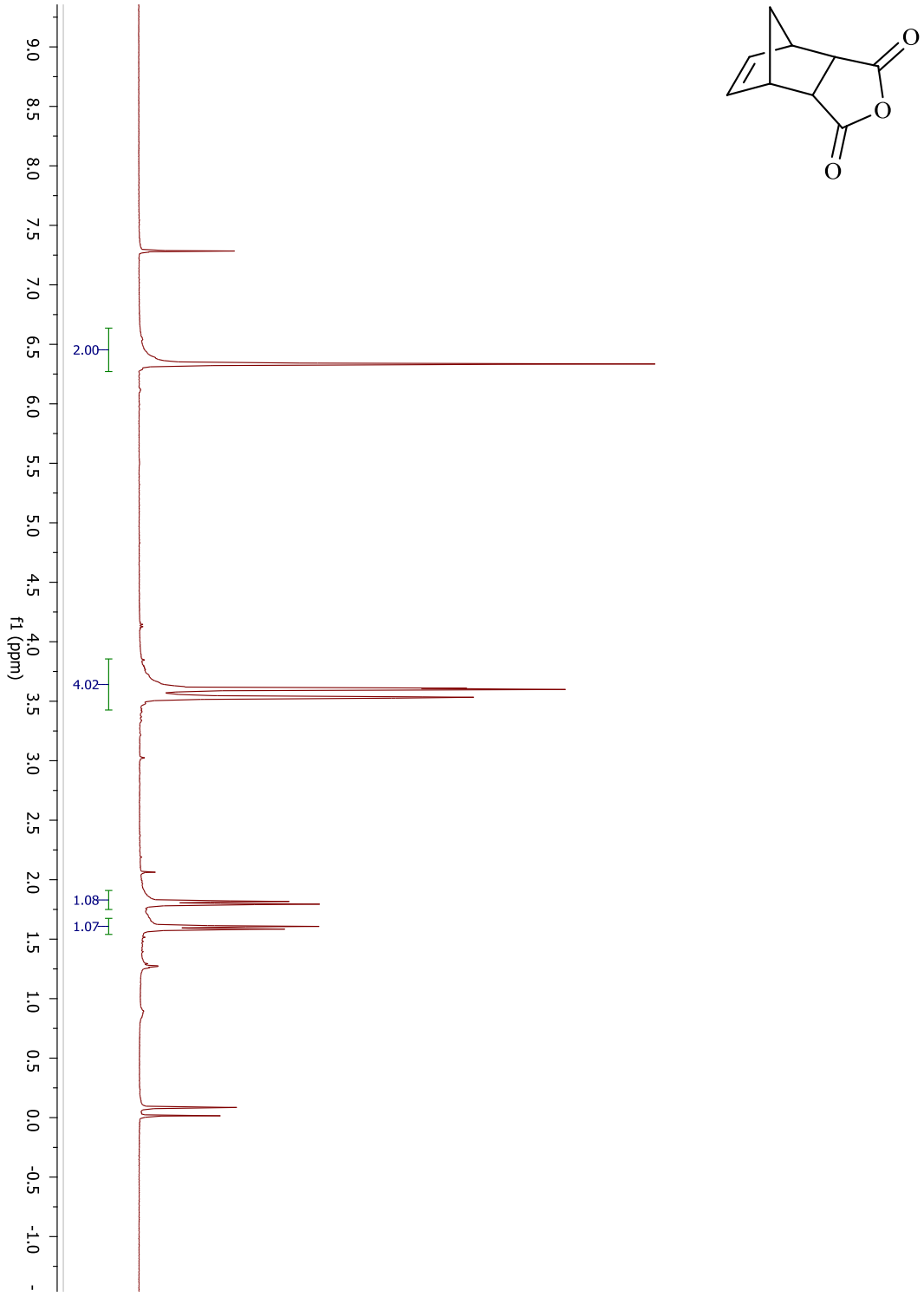

Figure 23. ^{1}H NMR Spectrum of 5-norbornene-2,3-dicarboxylic anhydride in $CDCl_3$

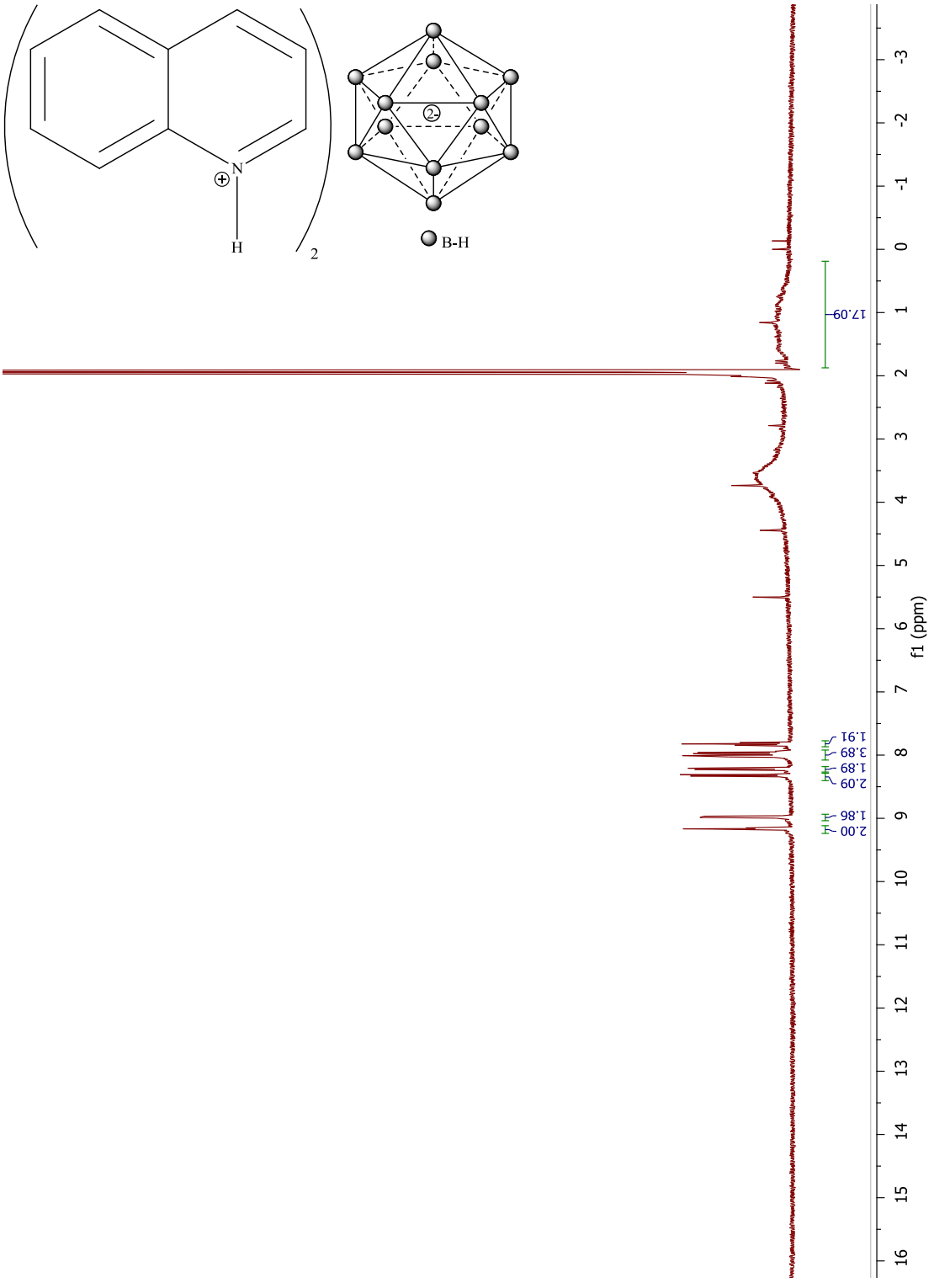

Figure 24. ^{1}H NMR Spectrum of Compound **5** in d-Acetone

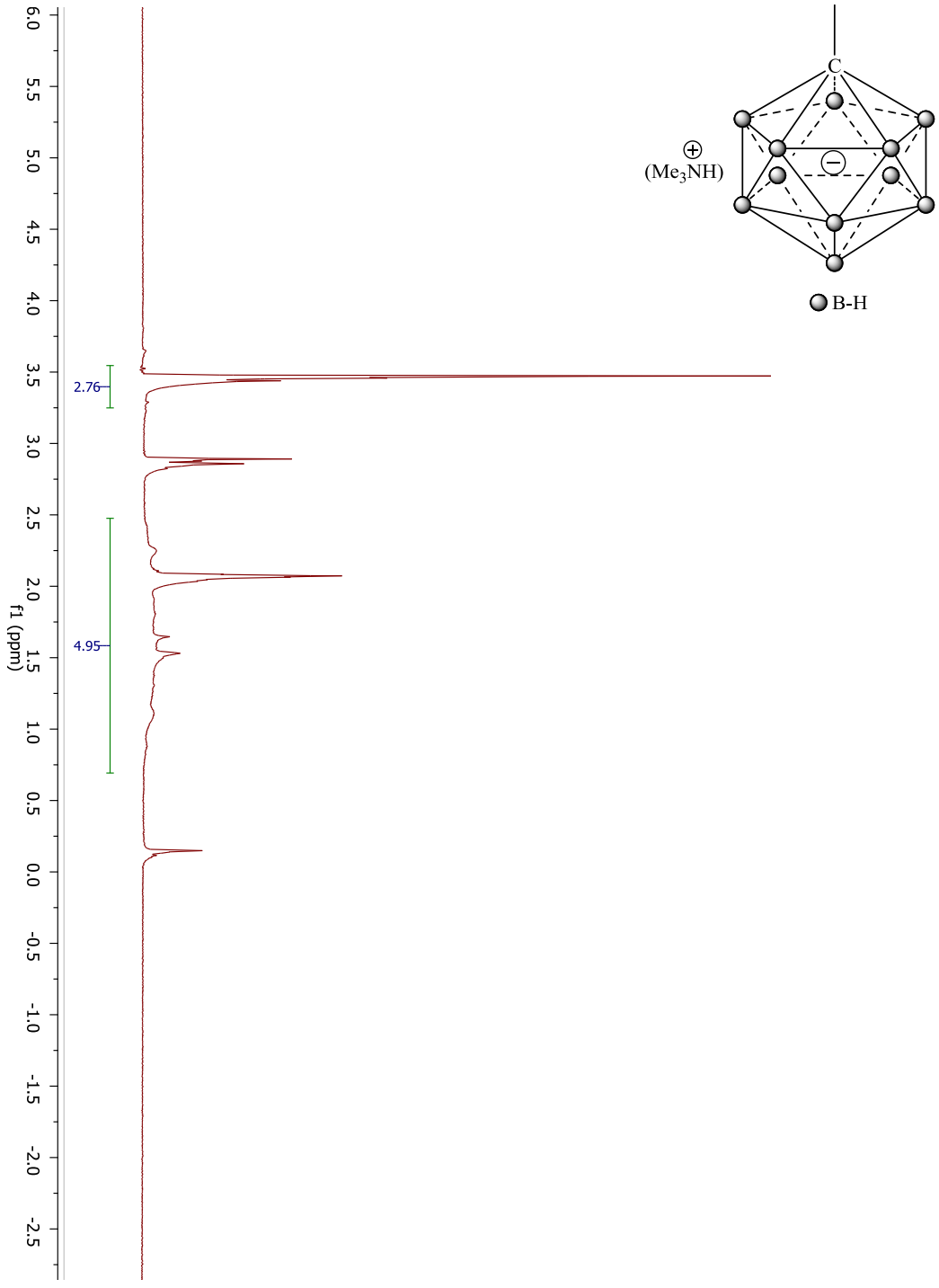

Figure 25. ^{1}H NMR Spectrum of Compound **10** in d-Acetone

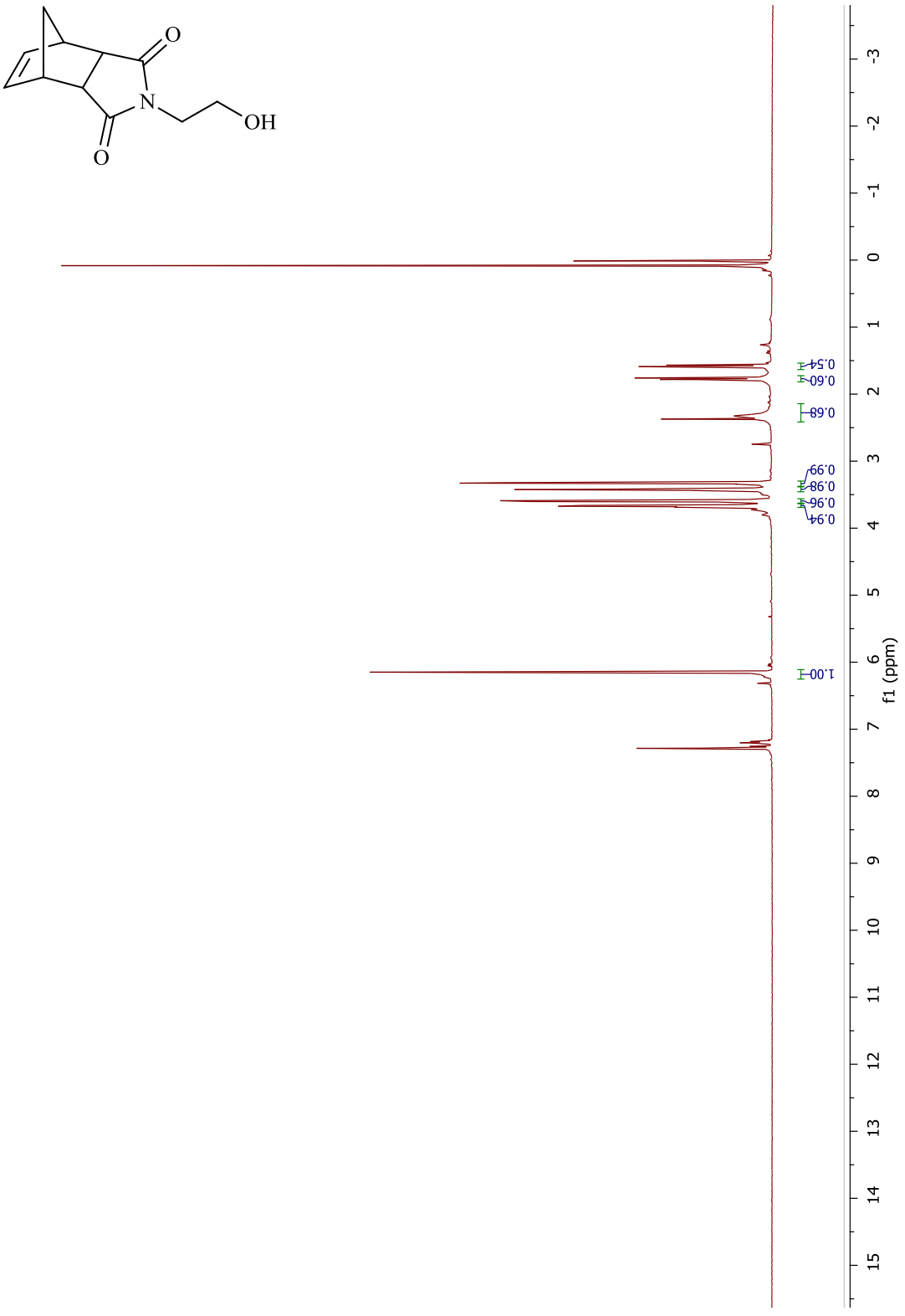

Figure 26. ^{1}H NMR Spectrum of N-(hydroxyethyl)-5-norbornene-2,3-dicarboximide in $CDCl_3$

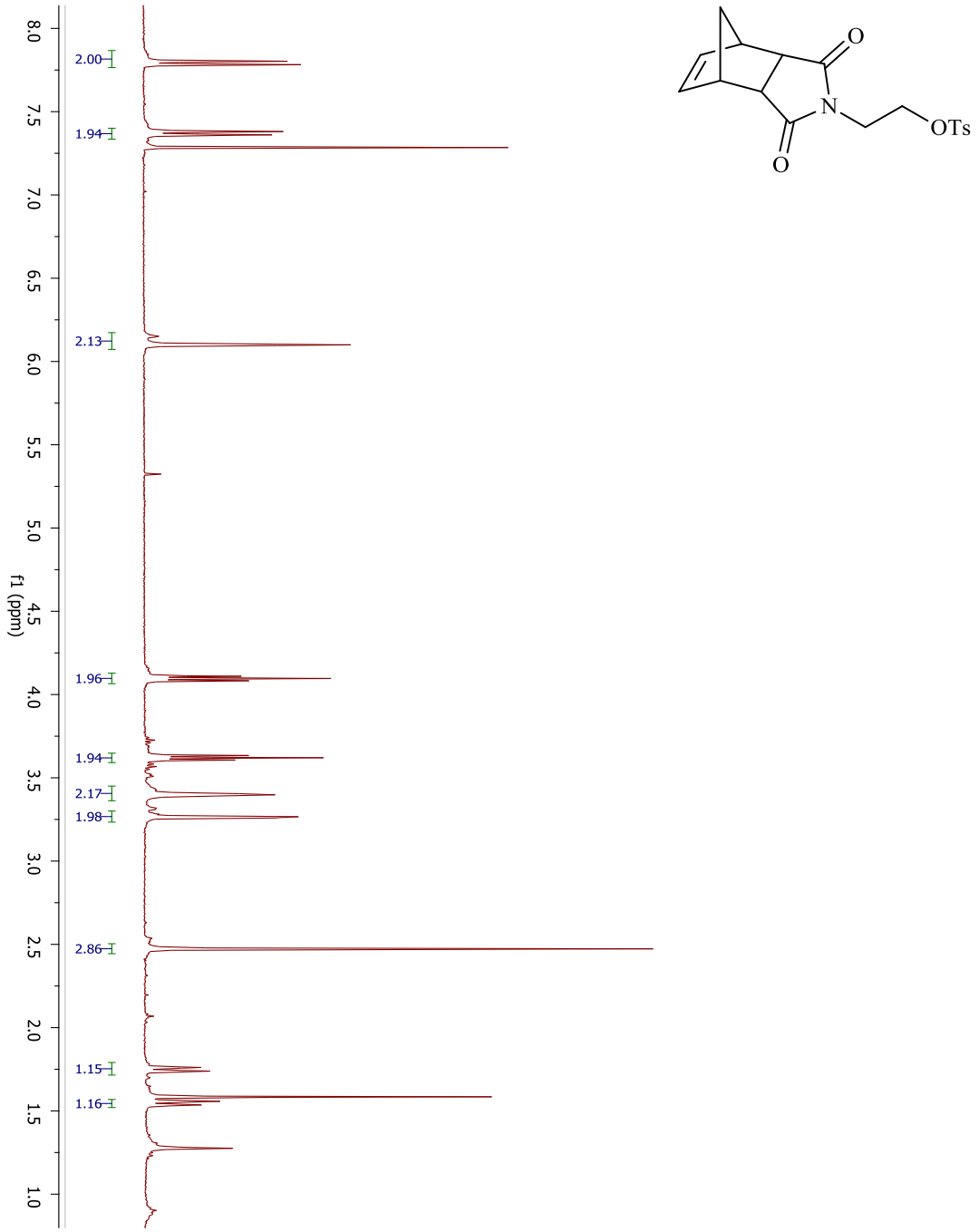

Figure 27. ^{1}H NMR Spectrum of tosylated N-(hydroxyethyl)-5-norbornene-2,3-dicarboximide in $CDCl_3$

B. Infrared Spectra

IR spectra were recorded at Thermo Scientific Nicolet iS10 ATR-IR spectrometer.

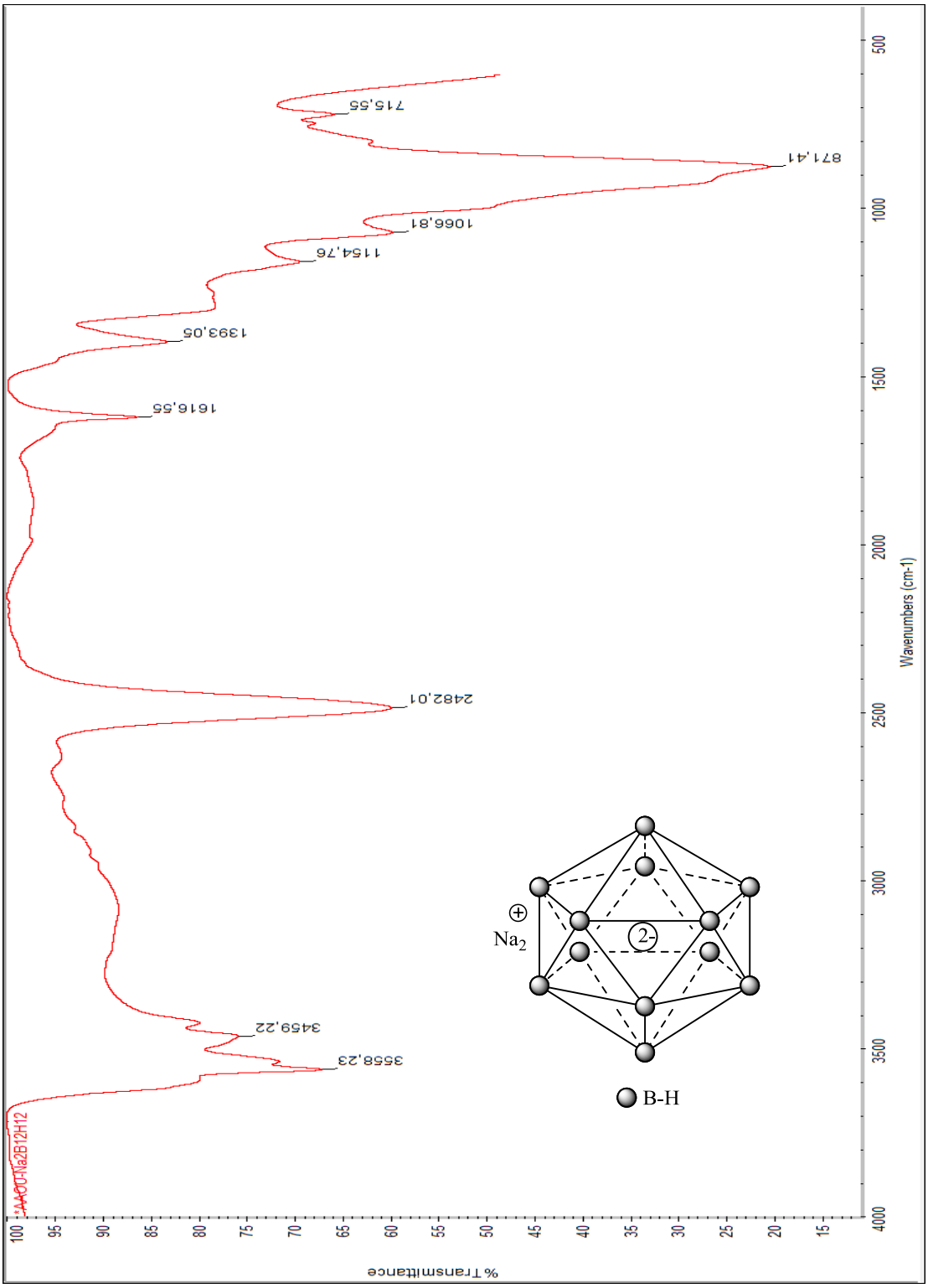

Figure 28. IR Spectrum of Na salt of dodecahydro-*closo*-dodecaborate

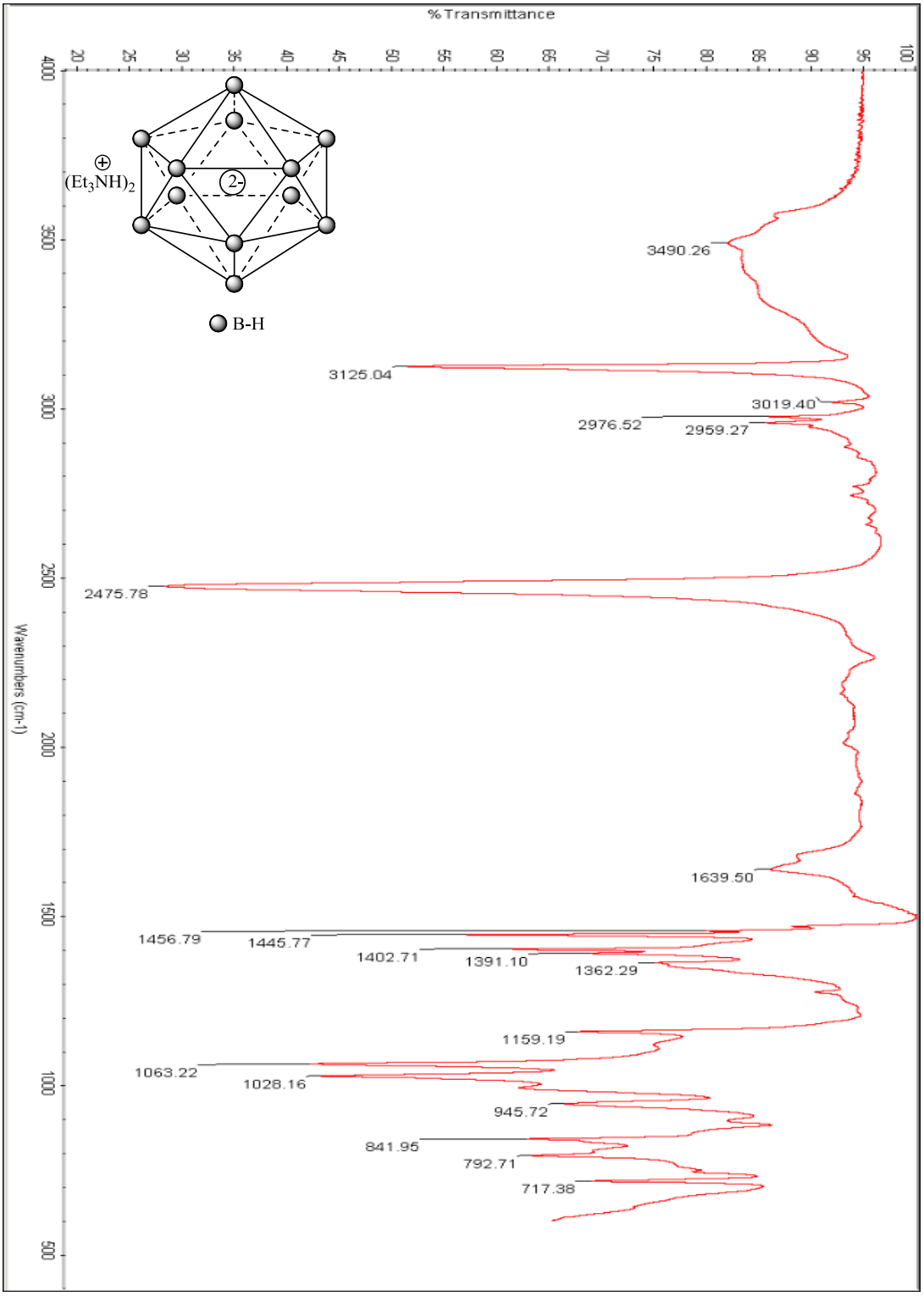

Figure 29. IR Spectrum of Compound **1**

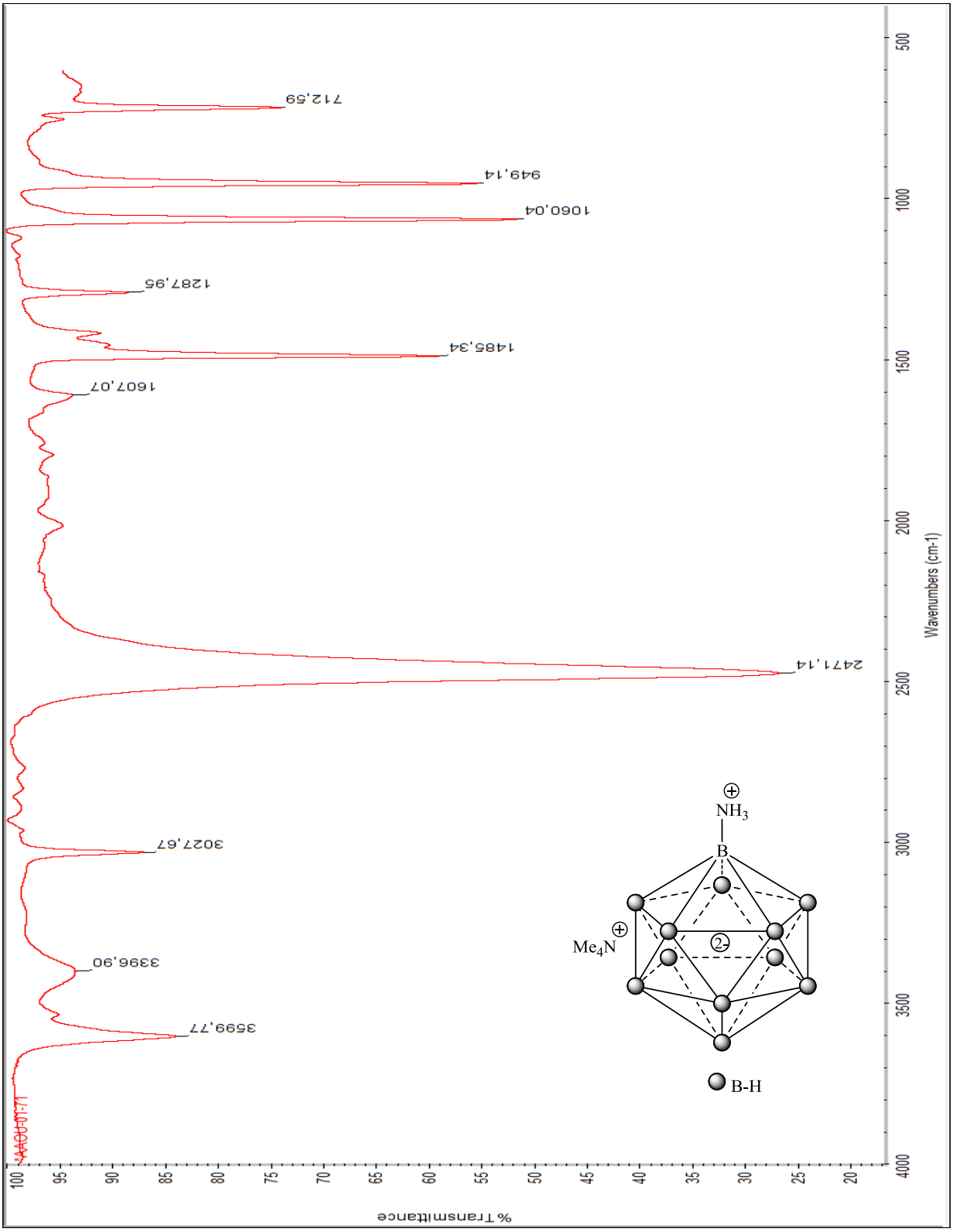

Figure 30. IR Spectrum of Compound **2**

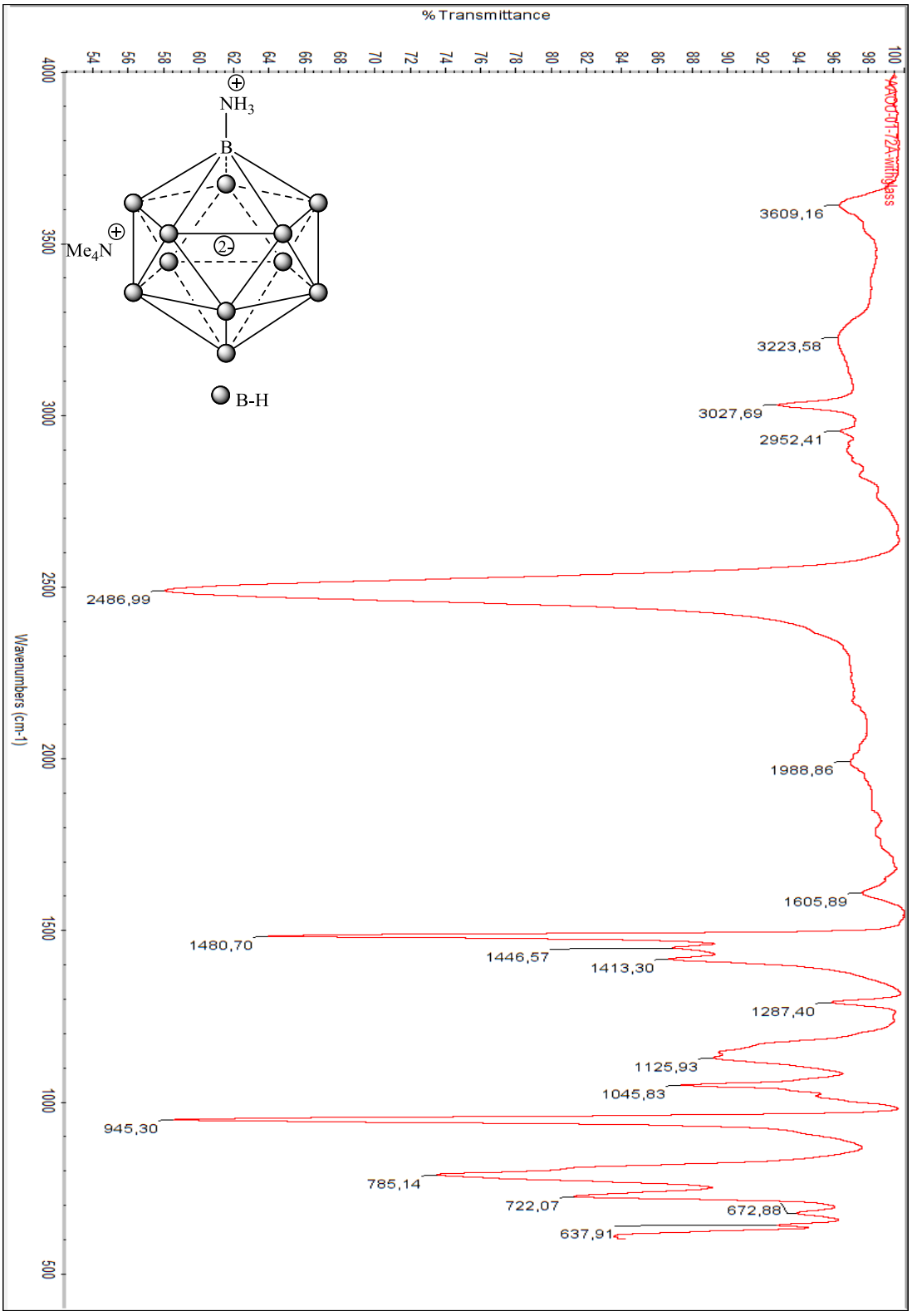

Figure 31. IR Spectrum of Compound **3**

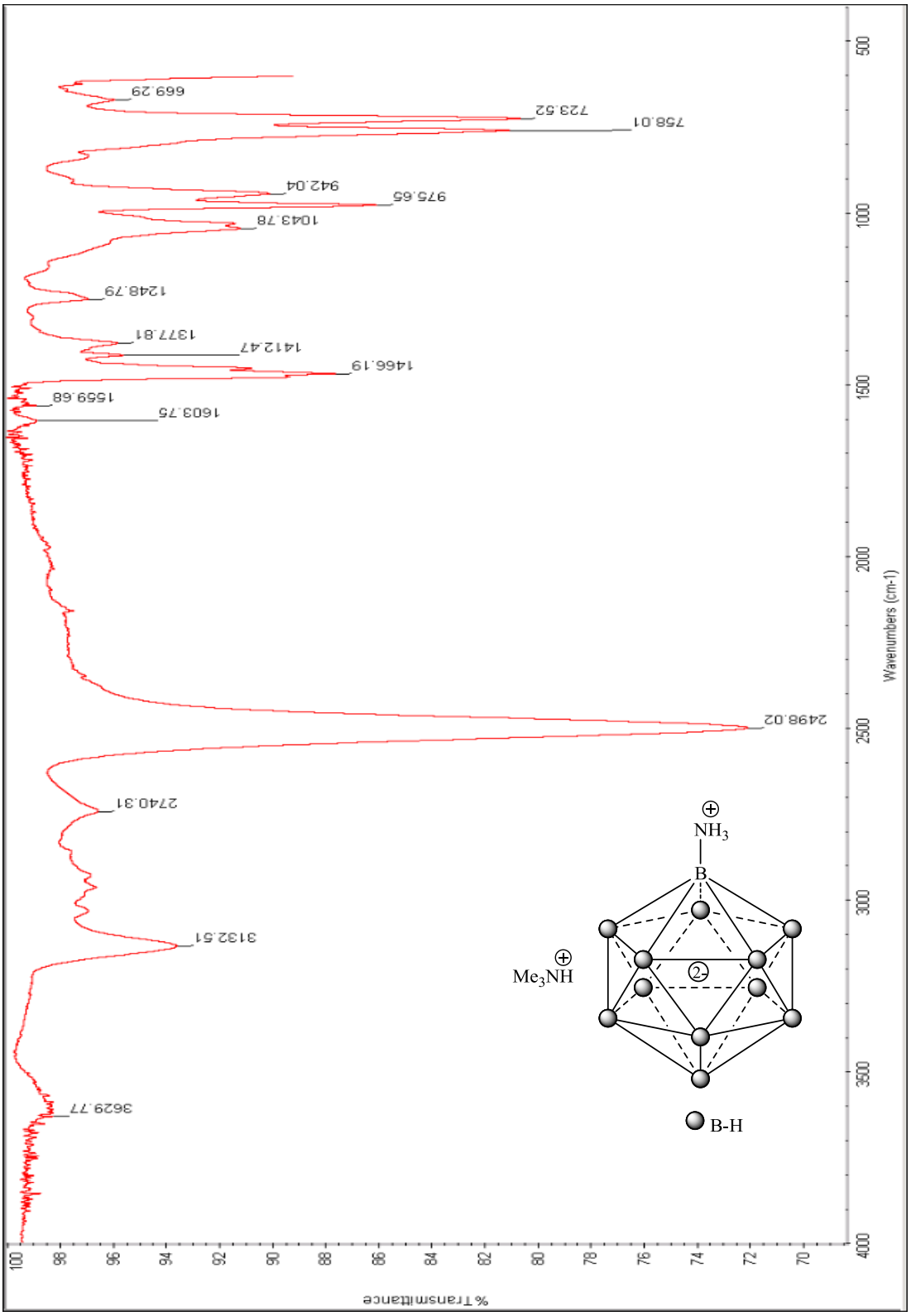

Figure 32. IR Spectrum of Compound **4**

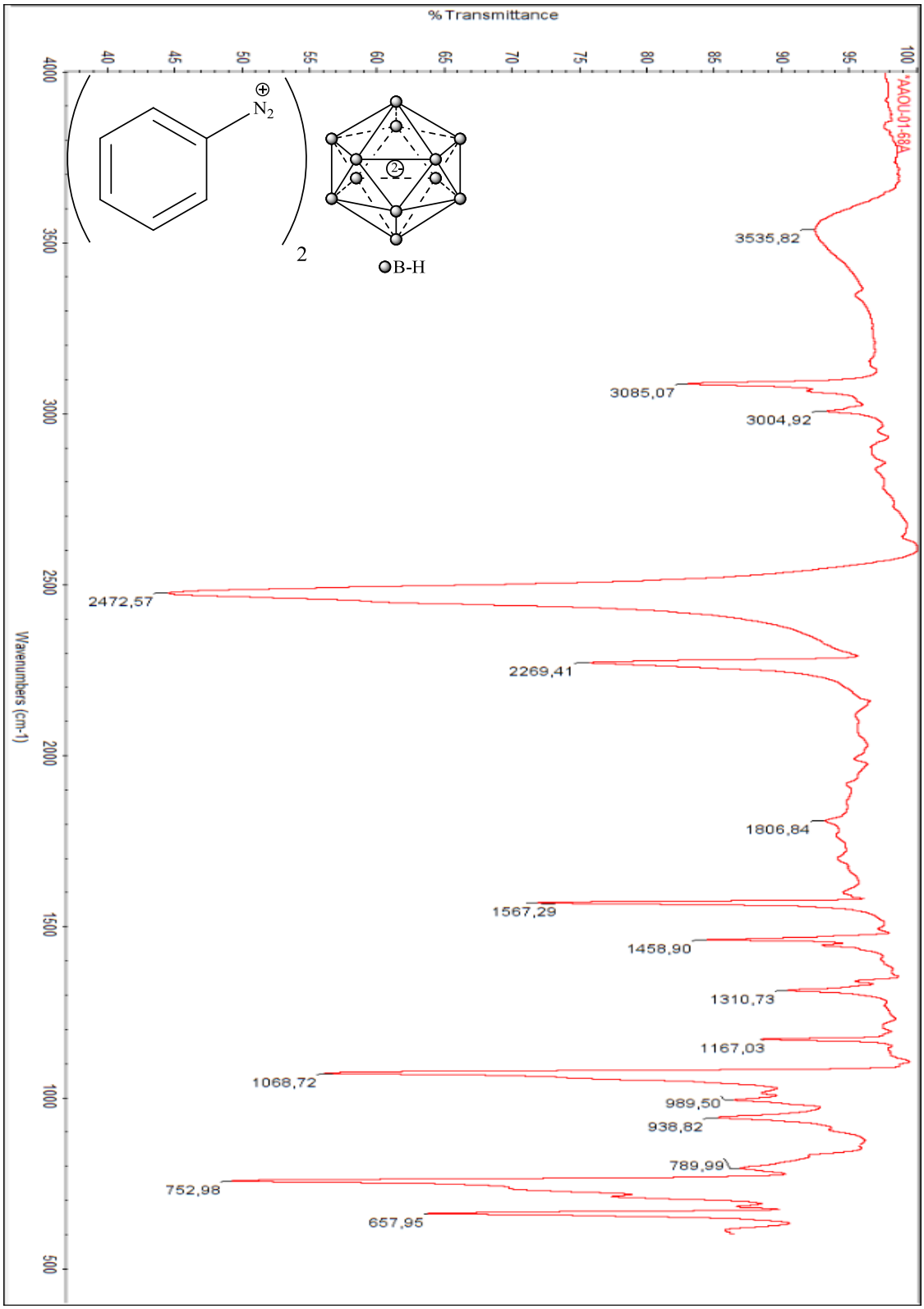

Figure 33. IR Spectrum of Compound **6**

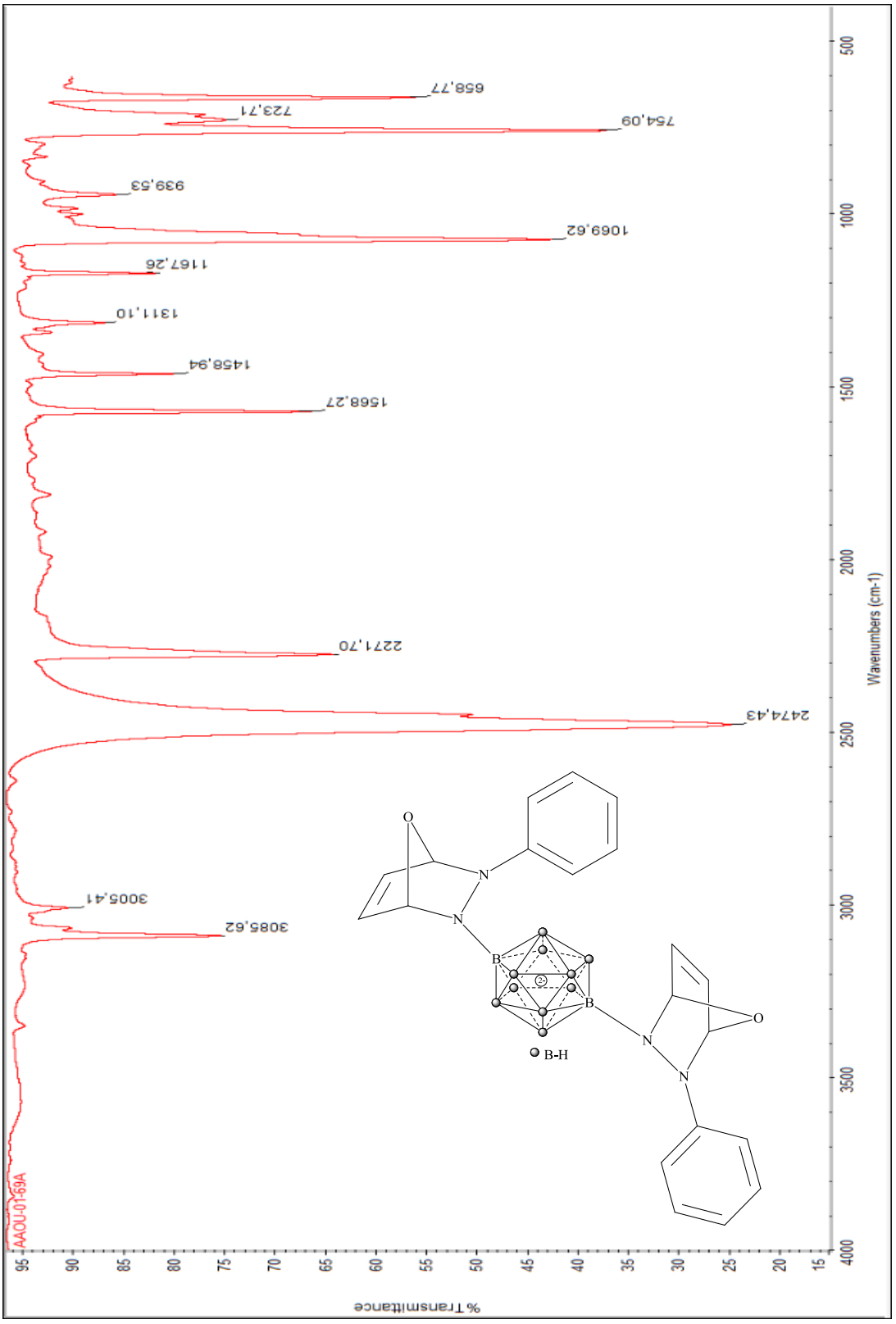

Figure 34. IR Spectrum of Compound **7**

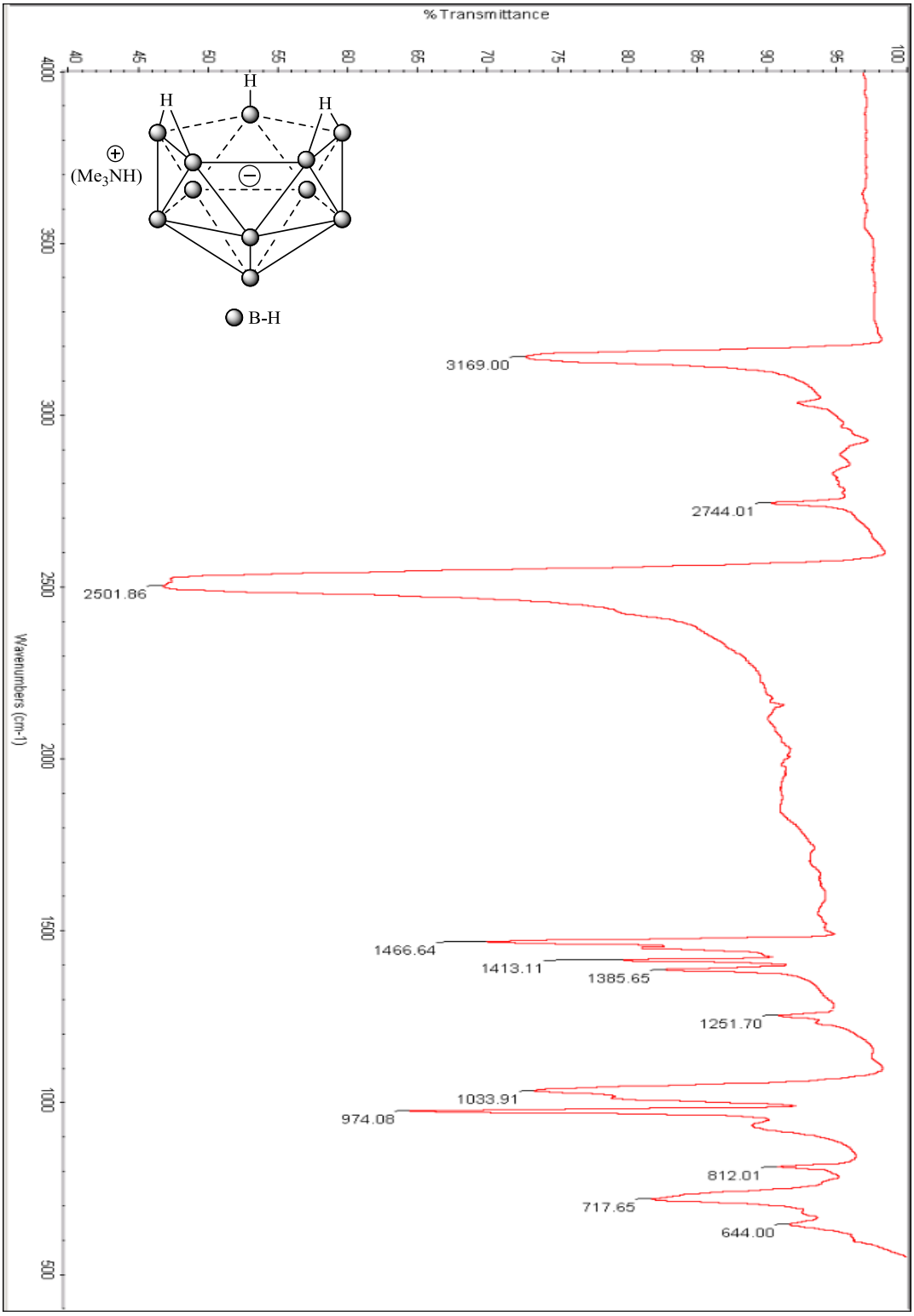

Figure 35. IR Spectrum of Compound **8**

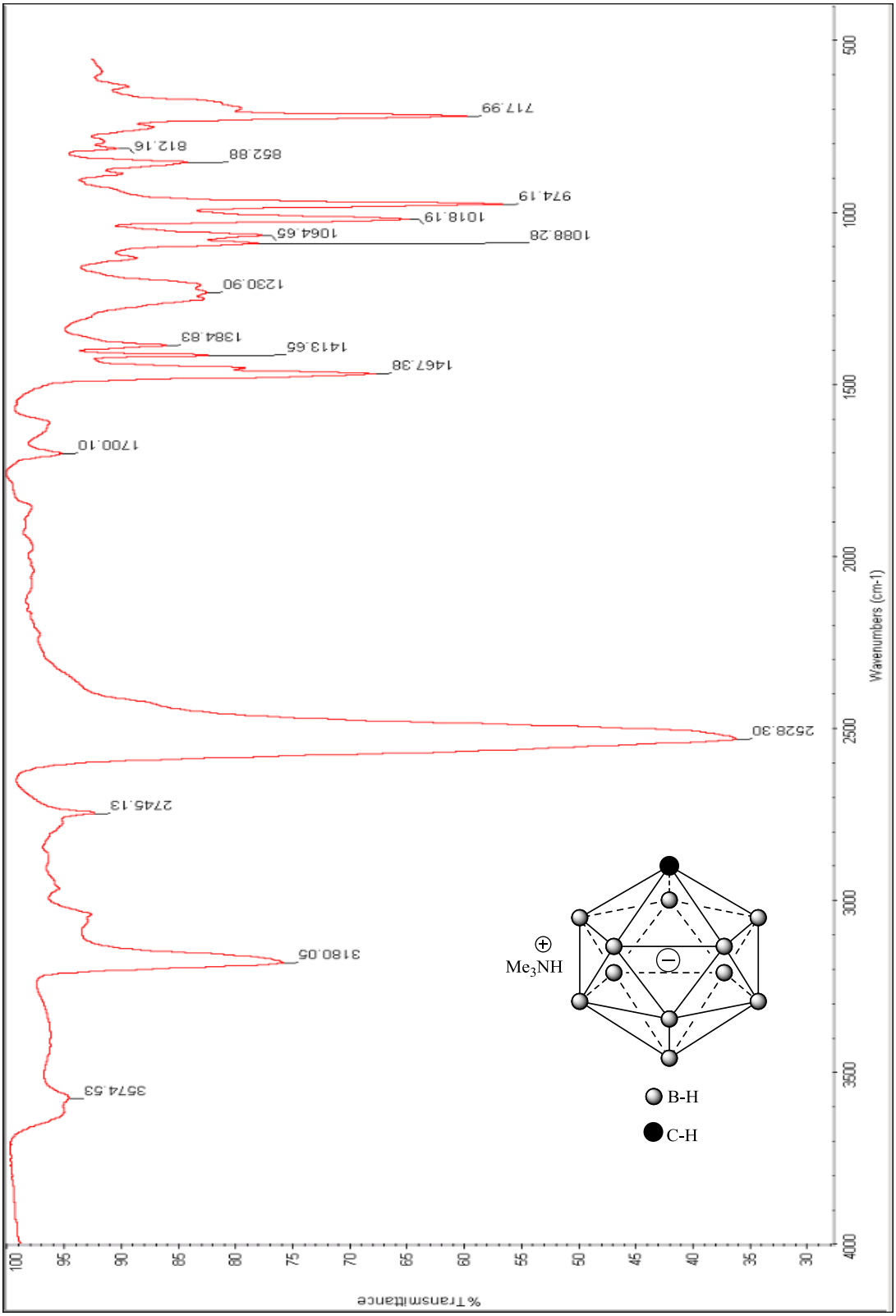

Figure 36. IR Spectrum of Compound **9**

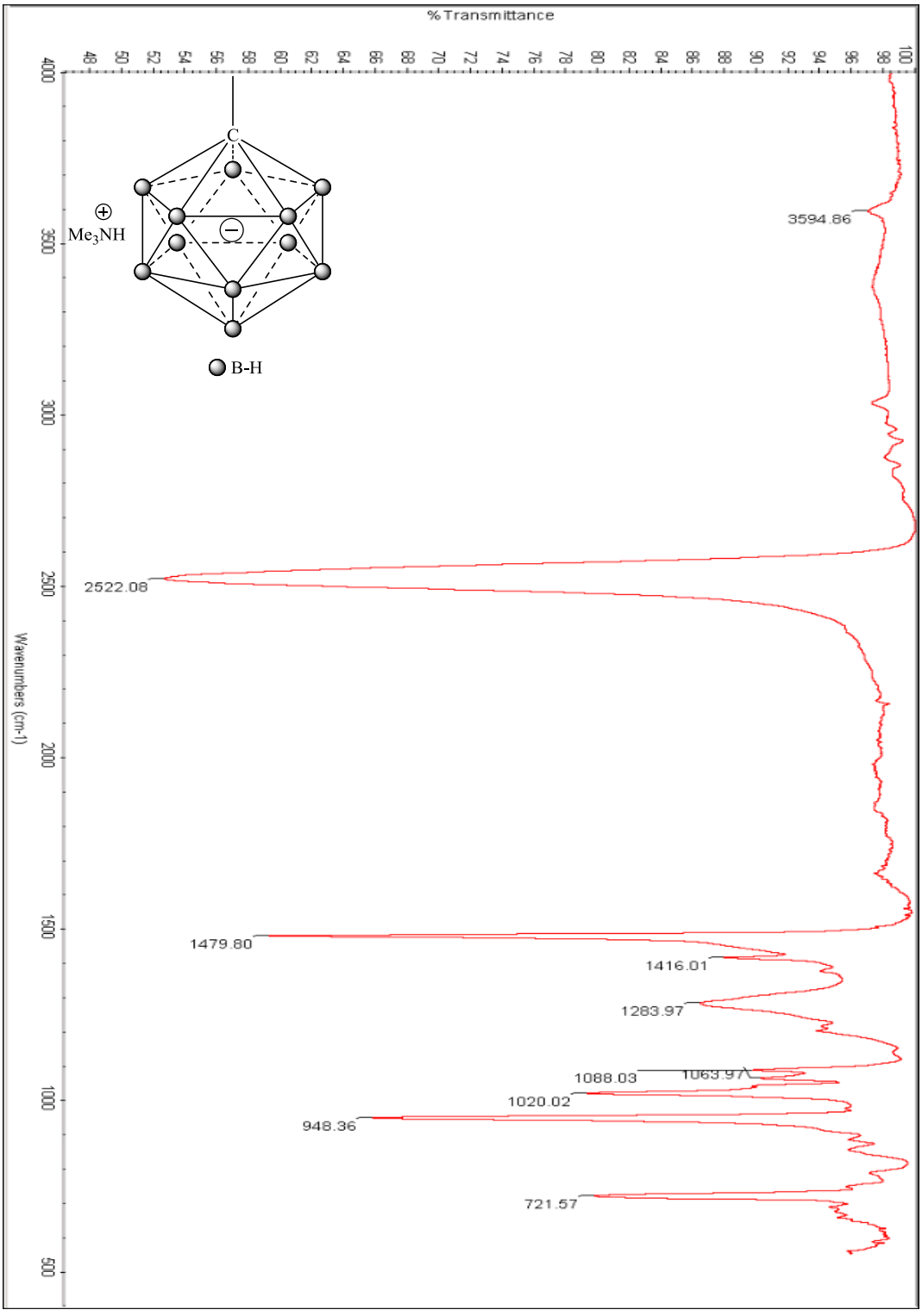

Figure 37. IR Spectrum of Compound **10**

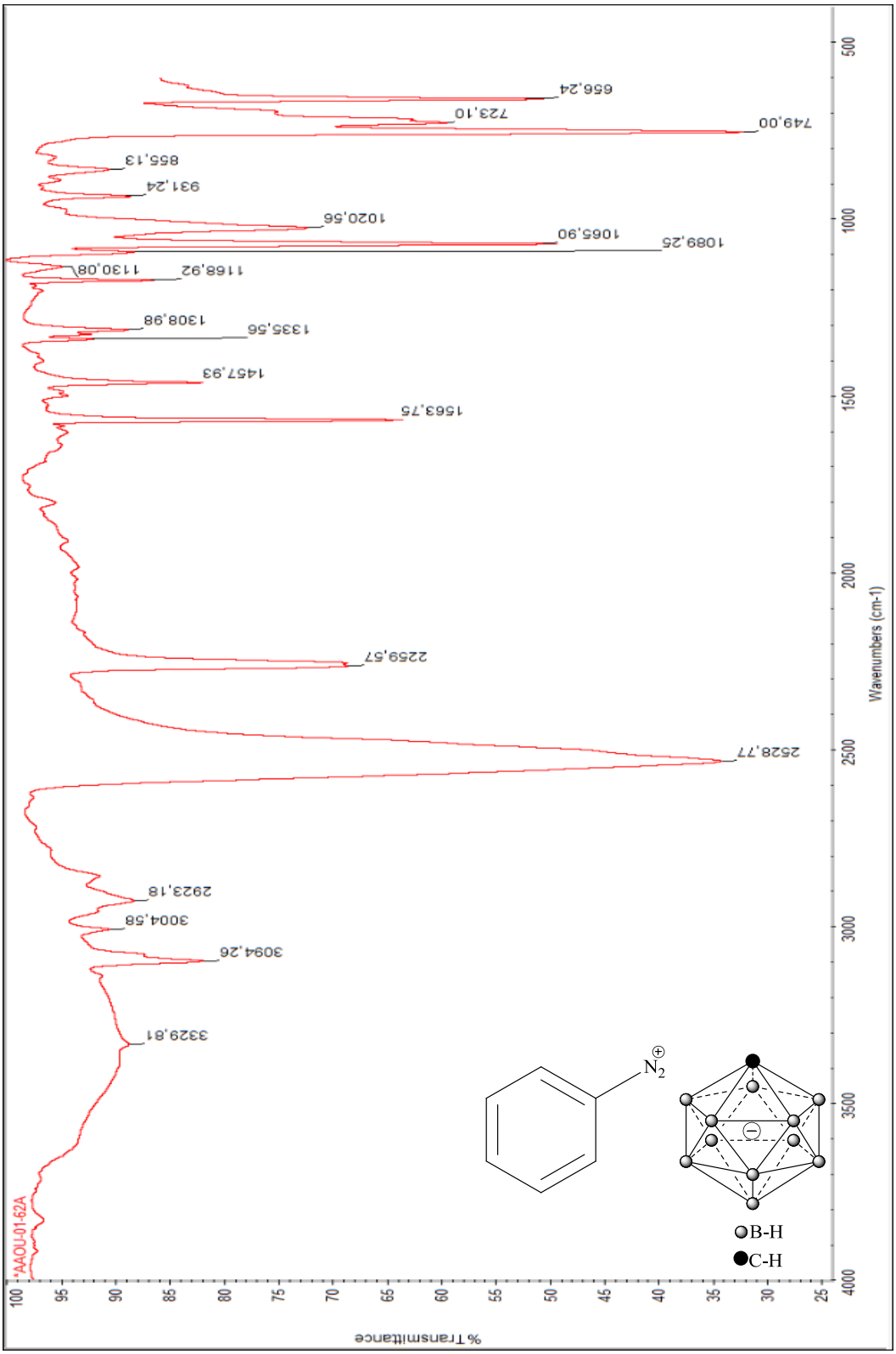

Figure 38. IR Spectrum of Compound **11**

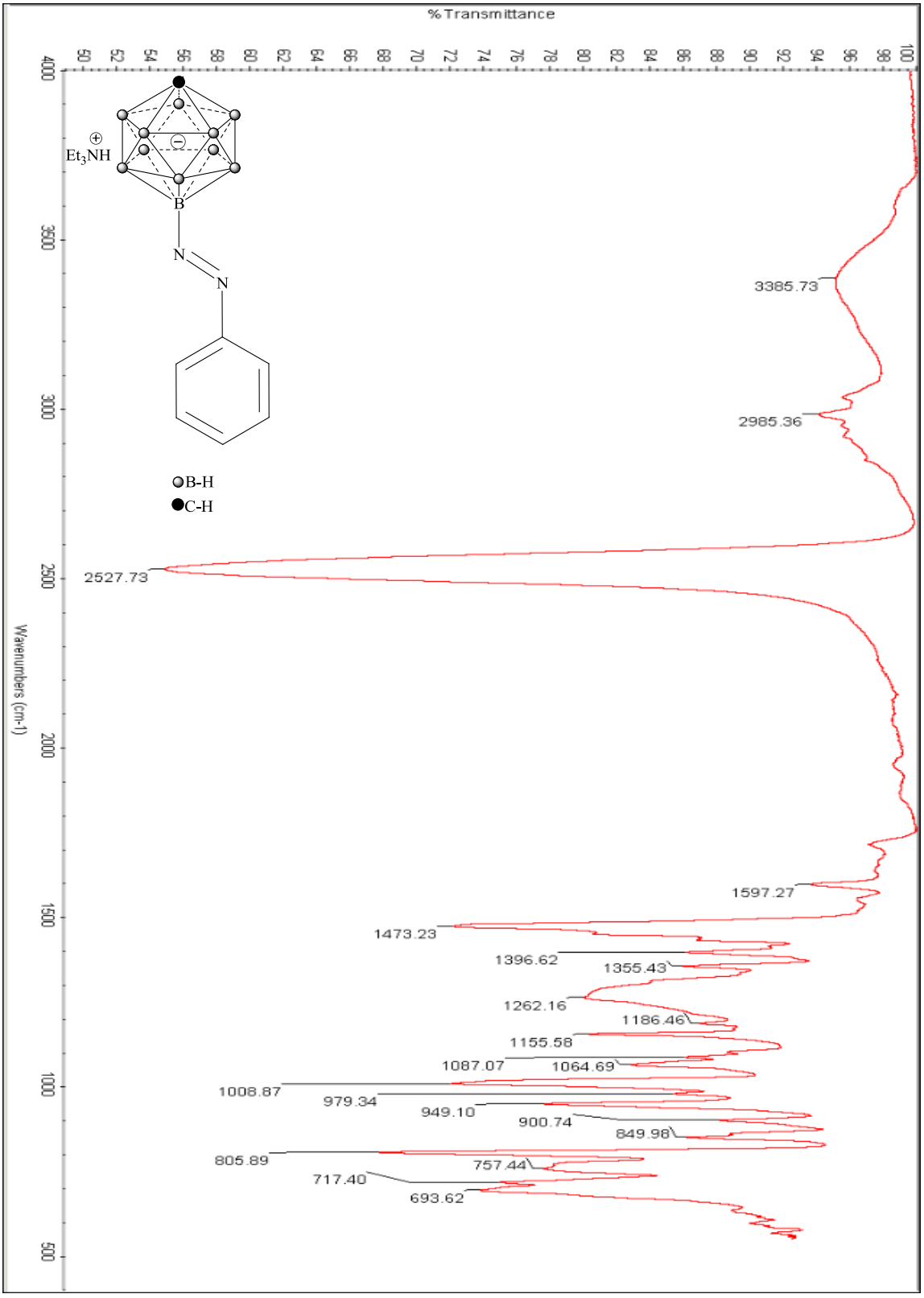

Figure 39. IR Spectrum of Compound **12**

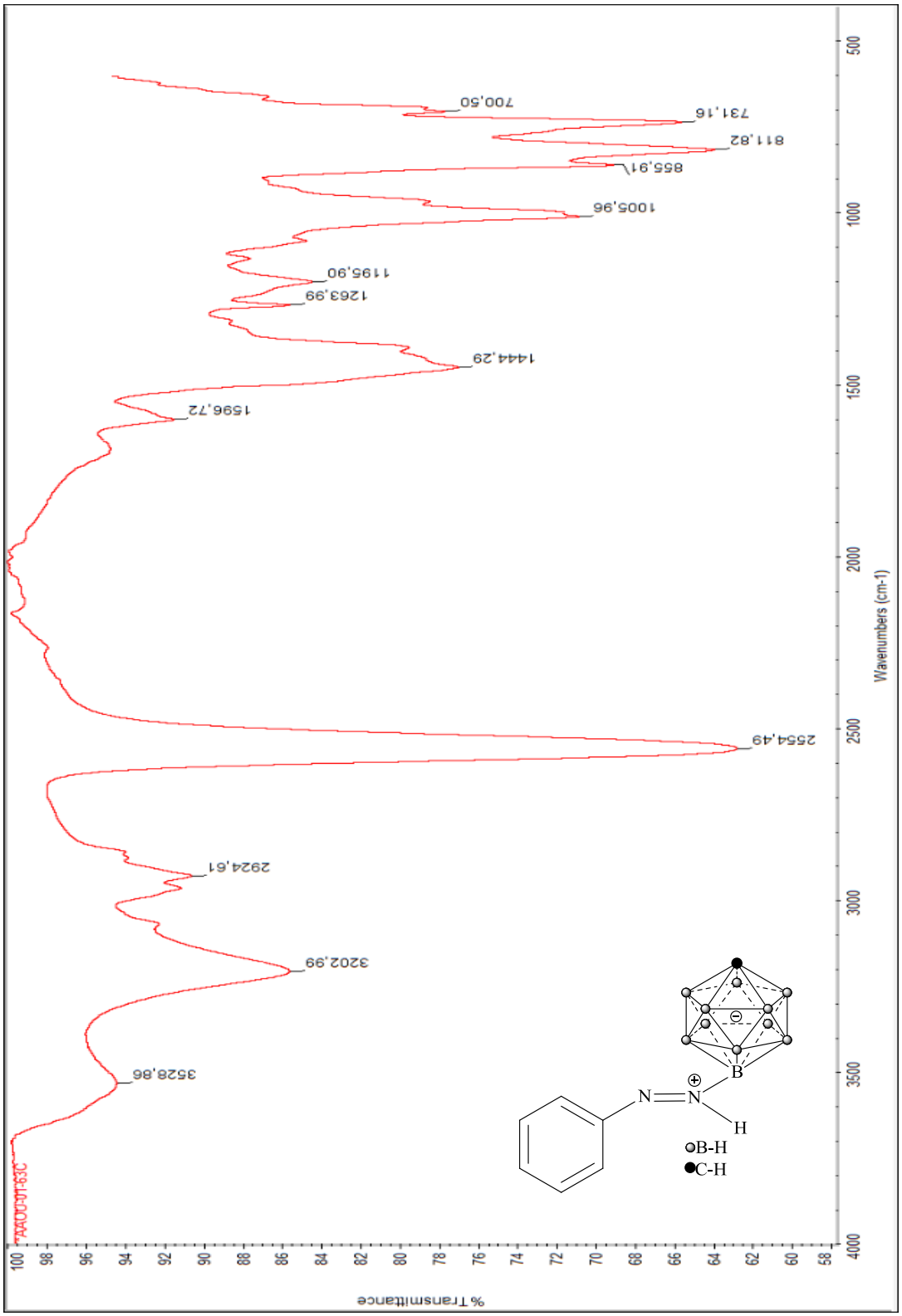

Figure 40. IR Spectrum of Compound **13**

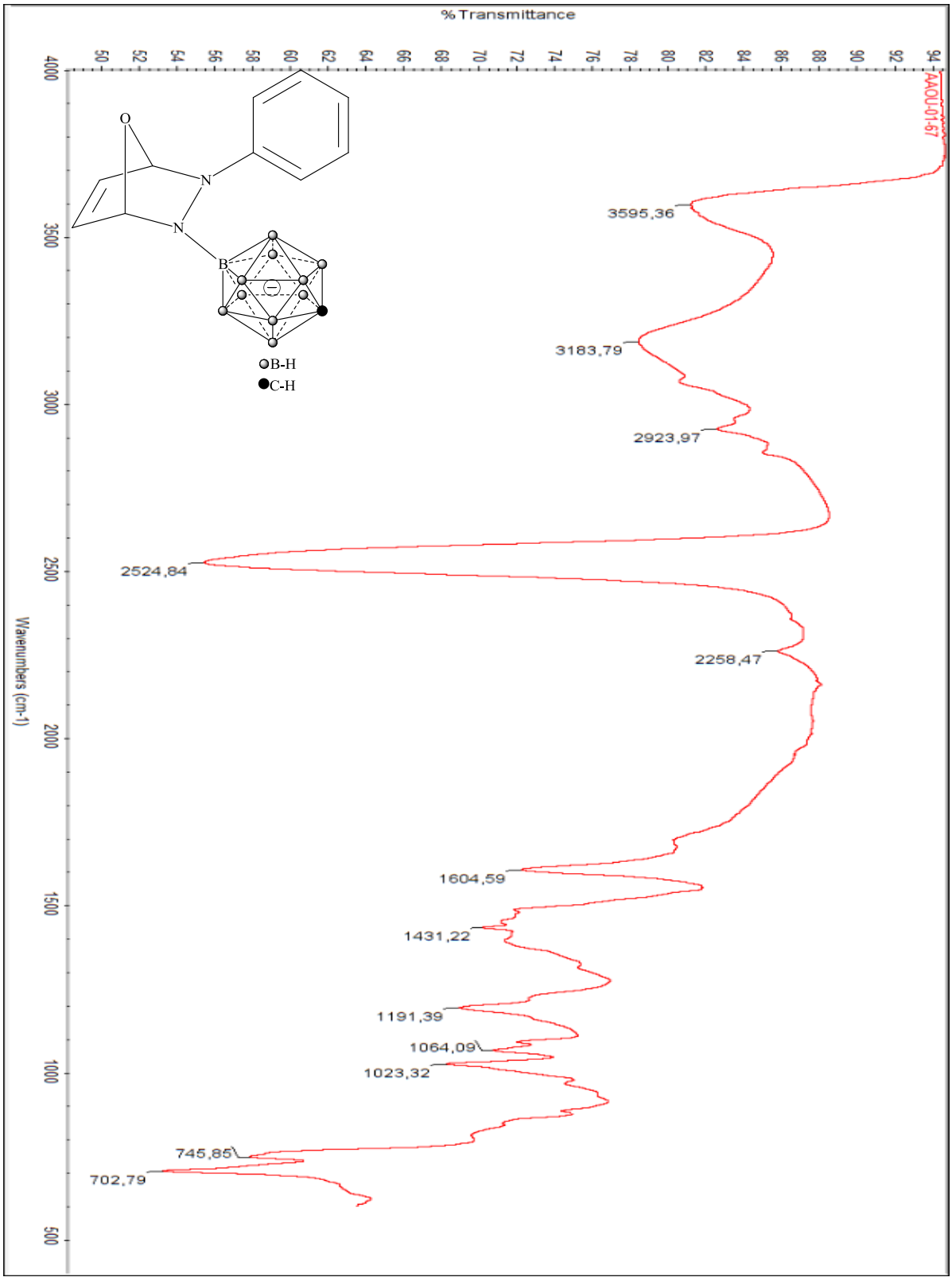

Figure 41. IR Spectrum of Compound **14**

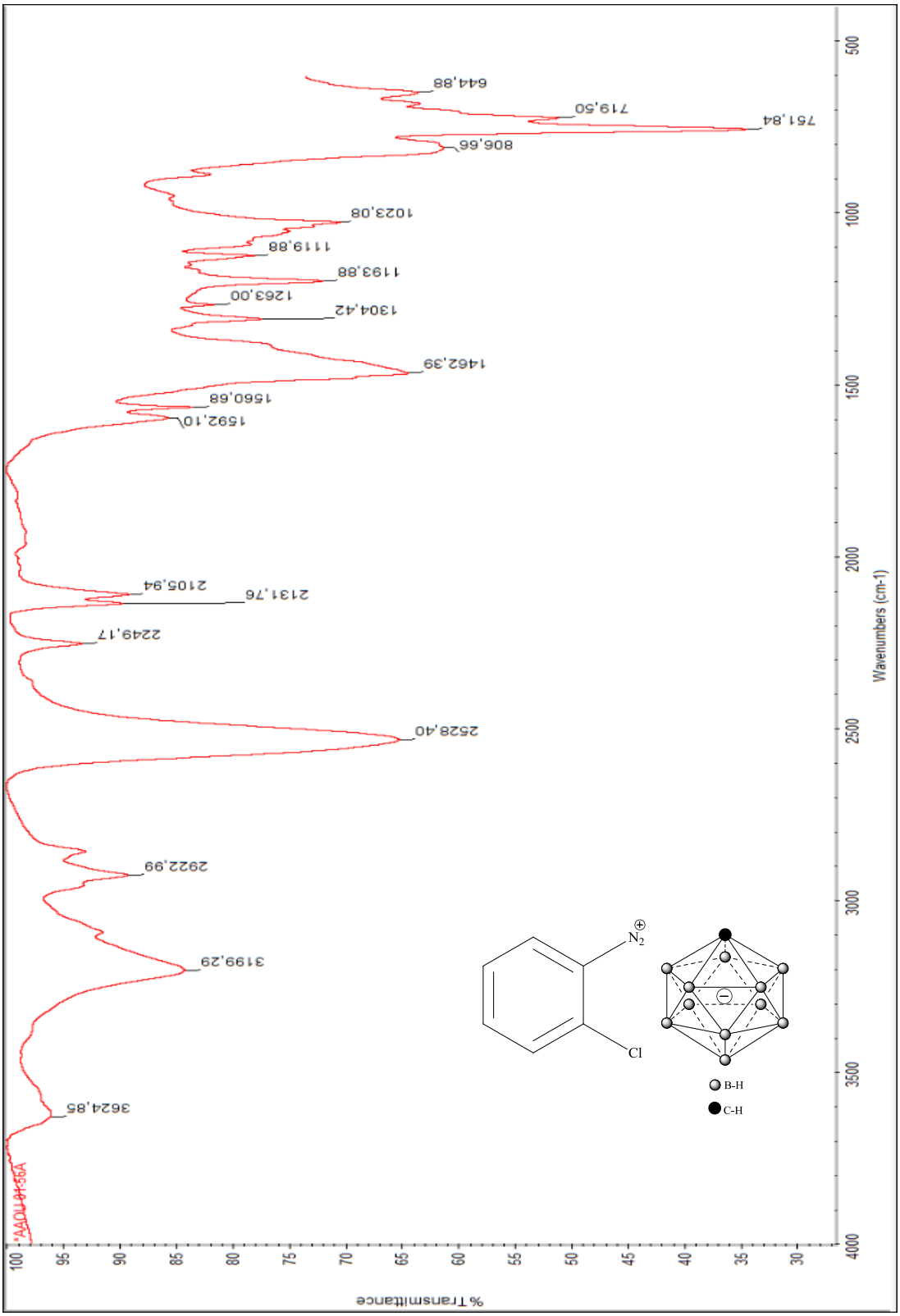

Figure 42. IR Spectrum of Compound **15**

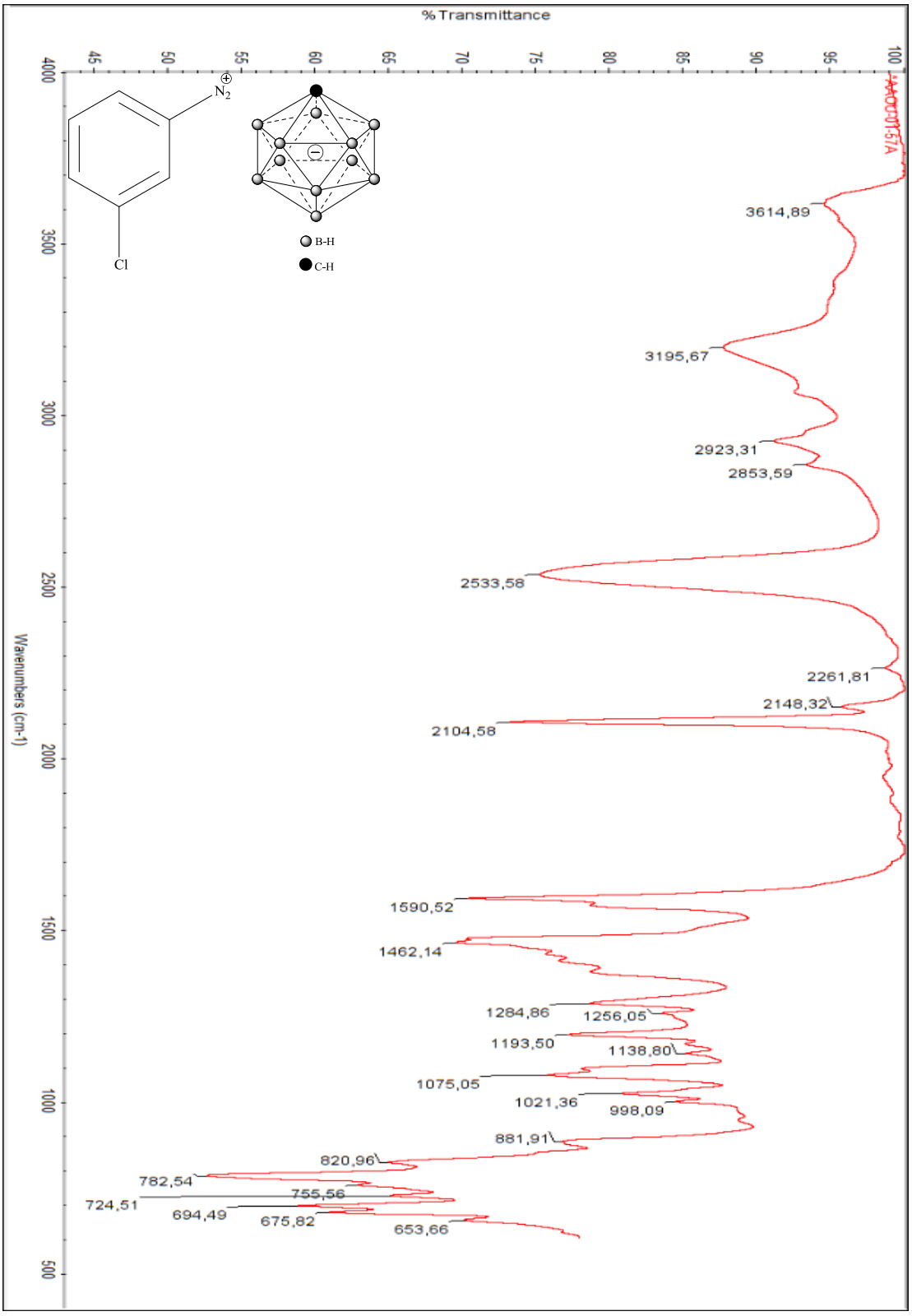

Figure 43. IR Spectrum of Compound **16**

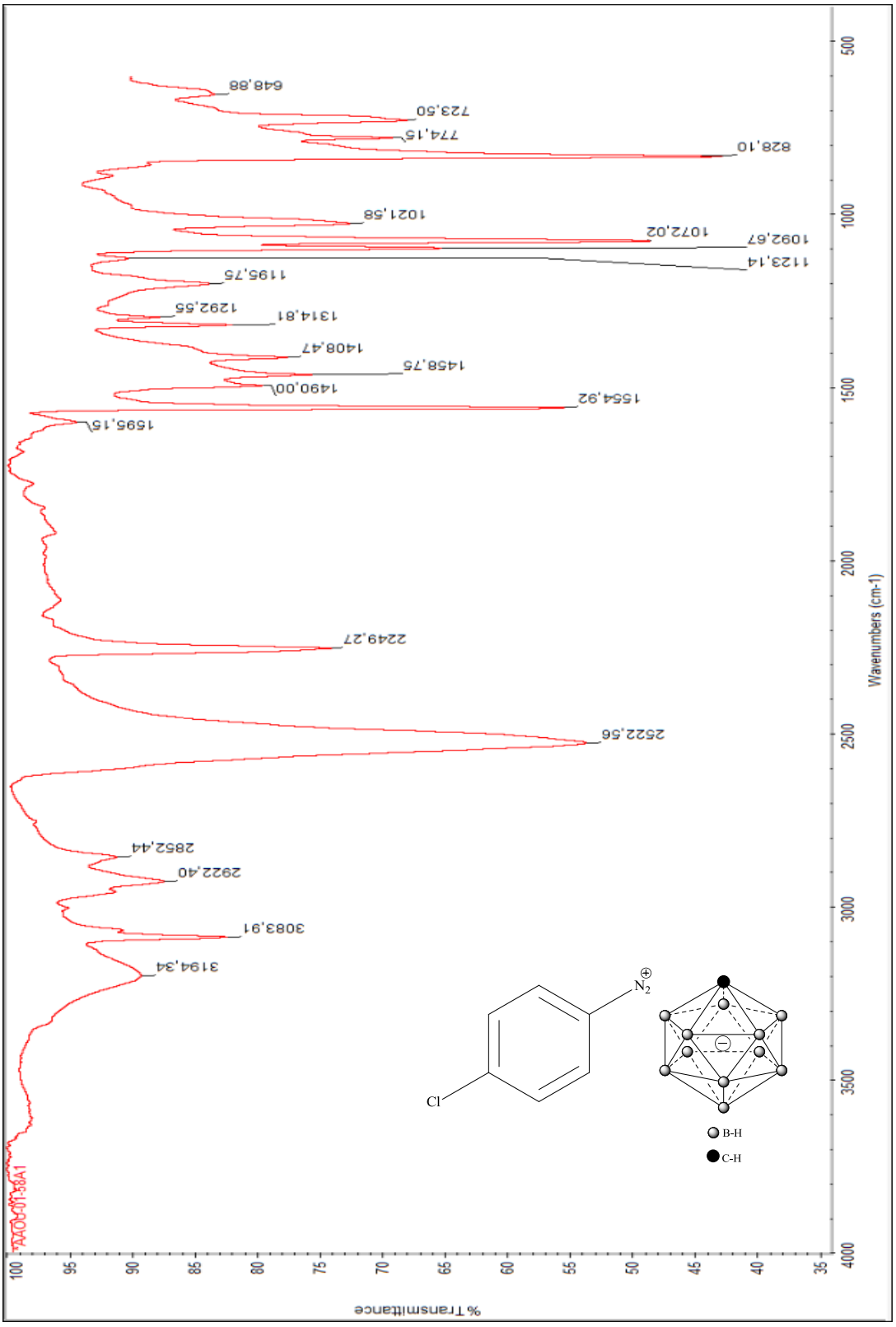

Figure 44. IR Spectrum of Compound **17**

C. HRMS Spectra

High Resolution Mass Spectra (HRMS) spectra were processed in negative mode on (ES-) using Time of Flight mass analyzer.

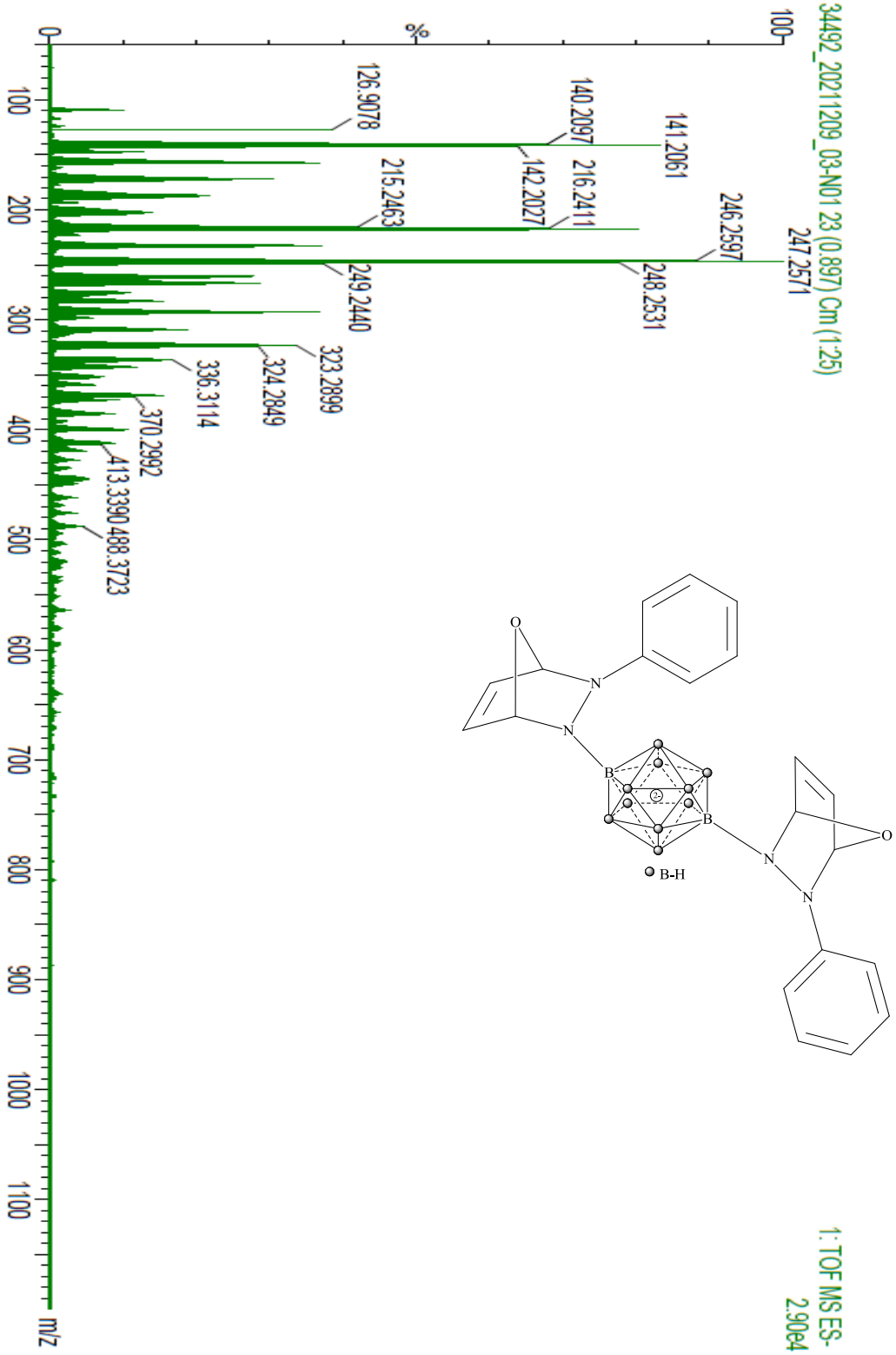

Figure 45. HRMS Spectrum of Compound **7**

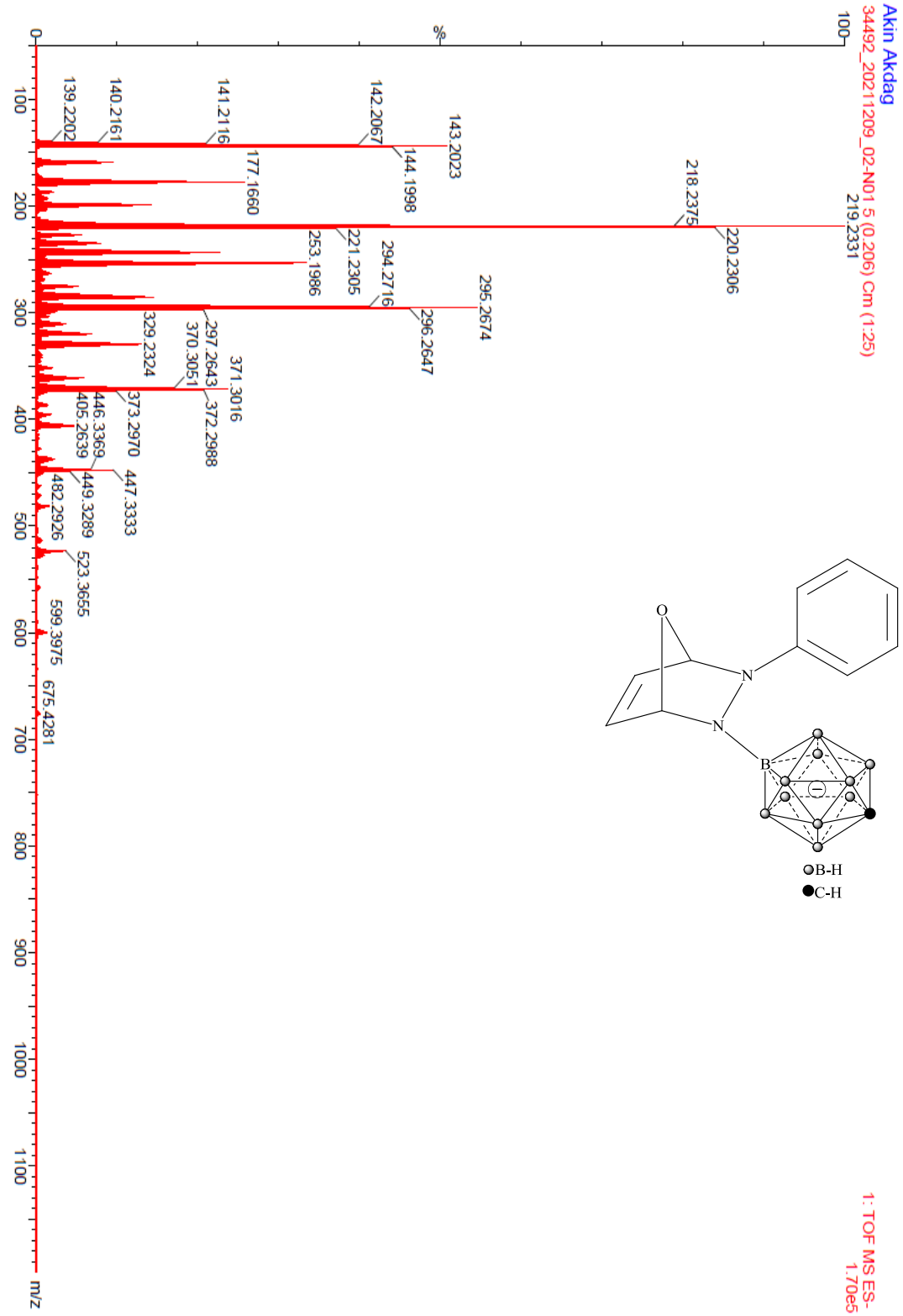

Figure 46. HRMS Spectrum of Compound **14**