SYNTHESIS OF CARBORANE DERIVATIVES FOR CHARACTERIZATION OF CARBOCATIONS

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SYNTHESIS OF CARBORANE DERIVATIVES FOR CHARACTERIZATION OF CARBOCATIONS

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ABSTRACT

SYNTHESIS OF CARBORANE DERIVATIVES FOR CHARACTERIZATION OF CARBOCATIONS

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Weakly coordinating anions are extremely versatile species for capturing and characterizing cationic intermediates. Among these anions, carboranes and some boranes are known to be the most weakly coordinating anions. In this thesis, the carboranes and boranes were synthesized in order to capture and characterize unusual carbocations. $B_{11}H_{14}^{-}$ was synthesized from $NaBH_4$. Undecaborate was converted to $B_{10}H_{14}$ by oxidation and extrusion of one boron vertex. The $B_{10}H_{14}$ was successfully converted to ortho-carborane. $B_{11}H_{14}^{-}$ was treated with I_2, and then $B_{12}H_{12}^{2-}$ was synthesized. Dodecaborane and $CB_{11}H_{12}^{-}$ were methylated on boron vertex to get $B_{12}Me_{12}^{2-}$ and $HCB_{11}Me_{11}^{-}$. The methylated boranes and carborane cages are more hydrophobic and weakly coordinating anions.

Keywords: Boron, Borane, Carborane, Decaborane, Dodecaborane

ÖZ

KARBORAN TÜREVLERİNİN KARBOKATYONLARIN TANIMLANMASI İÇİN SENTEZİ

Doğan, Sevban
Yüksek Lisans, Kimya
Tez Danışmanı: Doç. Dr. Akın Akdağ

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Az koordine olan anyonlar, katyonik ara ürünlerin yakalanması ve tanımlanması için çok önemlidirler. Bunların arasında karboranlar ve bazı boranlar bilinen en koordine olmayan anyonlardır. Bu tezde, karboranlar ve boranlar sentezlenmiş olup sıradışı karbokatyonların yakalanması ve karakterize edilmesi için kullanılacaktır. $B_{11}H_{14}^-$ $NaBH_4$ kullanılarak sentezlendi. Undekaborat, bir bor verteksinin oksidasyonu ve ekstrüzyonu ile $B_{10}H_{14}$'e dönüştürüldü. $B_{10}H_{14}$ başarıyla orto-karborana dönüştürüldü. $B_{11}H_{14}^-$ I_2 ile muamele edildi ve $B_{12}H_{12}^{2-}$ sentezlendi. Dodekaboran ve $CB_{11}H_{12}^-$, $B_{12}Me_{12}^{2-}$ ve $HCB_{11}Me_{11}^-$ elde etmek için bor verteksinden metillendi. Metillenmiş boran ve karboran kafesleri daha hidrofobik ve zayıf koordine edici anyonlardır.

Anahtar Kelimeler: Bor, Boran, Karboran, Dekaboran, Dodekaboran

To the longing memory of my grandfather, Cemal Hasan Kara Koşcan

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CHAPTER 1

INTRODUCTION

1.1. Boron Atom

Boron is an interesting element in chemistry that in its neutral compounds boron lacks on octet. Boron and boron containing materials are already in use in various areas in today's modern life. This crucial element is found in different kind of minerals in nature and 73 % of world's boron mineral reserves are in Turkey (*ETIMADEN 2016 ANNUAL REPORT*, 2016). Minerals are utilized both as is and as processed materials.

Turkey exports some amount of boron minerals to China and Europe cheaply. The minerals are usually processed usually in the exported countries; after that Turkey imports boron containing products with higher costs. Turkey use only 3 % of refined boron for synthesis of boron containing chemicals (*ETIMADEN 2016 ANNUAL REPORT*, 2016). One of the important boron containing chemicals is carborane. Although carboranes do not have immediate daily uses, they are constantly being researched to find use for them. In Turkey, recently such a quest has been embarked on. Nevertheless, until this study, carborane production has not been performed in Turkey to our best of knowledge. Although, carborane derivatives mostly are purchased from foreign vendors, the main producer company is KATCHEM which is located at Prague, Czech Republic. However, sales of carboranes have many limitations such as special export licenses, time consuming procedures, permissions from Ministry of Foreign Affairs of Turkey, Arms Control and Disarmament Department because of their usage in defense industry as a military goods ("KATCHEM spol, s. r. o.," 2017). Besides many limitations, their high cost is an another factor that limiting studies about them. Despite all of these difficulties, carboranes and their derivatives have a very important role in the development of wide array of new materials. To deeply understand carboranes, firstly one should understand boron atom and its clusters. This very big and adventurous area can lead to improvement of science besides industrial applications.

Boron belongs to group 13 first row element and has incomplete octet in its natural neutral compounds. Empty p-orbitals makes neutral boron compounds act as a Lewis acid (Atkins, Overton, Rourke, Weller, & Armstong, 2009). Compound of boron element has been known for thousands of years besides the fact that elemental structure known only since 1808 (Quadbeck-Seeger, 2007b). In that year by Sir Humphry Davy and by Joseph Louis Gay-Lussac and Louis Jacques Thenard, boron element was found in two different research groups located in different countries. Sir Humphry Davy's boron production is based on reduction of boronic acid with potassium (Quadbeck-Seeger, 2007b). Even boron has not been seen as an evolutionary element, it can be referred as a trace amount vital element for plants in their growing parts. Moreover, boron was observed in some plants like, apple, sultanas, red grapes, *etc.* (Quadbeck-Seeger, 2007a).

1.1.1. Boron Mineral

In nature boron is not found in its elemental form; boron compounds are usually in *ortho*-boric acid form and borates form in boron minerals and volcanic spring waters. Most boron is mined in Turkey in ton scales (Lide, 2005). Boron minerals are boron oxide containing compounds (Atkins et al., 2009). According to annual report of ETİMADEN in 2016, boron mineral reserves are 4.5 billion tons, production capacity in these reserves was 5.6 million tons with respect to the 3.8 million tons consumption around the world. 3.3 billion tons of boron reserves are found in Turkey which come up to 73 % of world's boron reserves. Despite the fact that more than 230 boron minerals are known, only few of them have commercial importance. Mainly the important ones are tincal, colemanite, kernite, ulexite, pandermite *etc.* Boron reserves in Turkey mainly consist of tincal (borax), colemanite and ulexite (the important boron minerals are tabulated in Table 1.1) (*ETIMADEN 2016 ANNUAL REPORT*, 2016).

Such minerals when used as additives have also a characteristic green flame and they are fire retardant.

Table 1.1. *Type of minerals, names and their formulas that found in Turkey's Boron Reserve.*

Type of Mineral	Name of Mineral	Formula
Hydrogen Borate	Sasolite	H_3BO_3
Sodium Borates	Tincal (Borax)	$Na_2B_4O_7.10H_2O$
	Tincalconite	$Na_2B_4O_7.5H_2O$
	Kernite (Rasorite)	$Na_2B_4O_7.4H_2O$
Sodium-Calcium Borates	Ulexite	$NaCaB_5O_9.8H_2O$
Calcium Borates	Colemanite	$Ca_2B_6O_{11}.5H_2O$
	Pandermite (Priceite)	$CaB_{10}O_{19}.7H_2O$
Calcium Borosilicate	Havlite	$Ca_4Si_2B_{10}O_{23}.5H_2O$
Magnesium Borate	Hydroboracite	$CaMgB_6O_{11}.11H_2O$
	Boracite	$Mg_3B_7O_{13}Cl$
Other Borates	Cahnite	$CaAsBO_6.2H_2O$

Borax is one of important boron containing minerals and has $Na_2B_4O_7.10H_2O$ empirical formula and its name was derived from Arabic word which is buraq (Quadbeck-Seeger, 2007b). Laundry, mild antiseptics and borosilicate glasses are some of borax's uses areas in Turkey (*ETIMADEN 2016 ANNUAL REPORT*, 2016). Borax and other minerals can be processed to produce special boron products. Some of products were listed in Table 1.4 that are produced in Turkey ("Boron Products," 2012). Table 1.2 shows concentrated borates (boron minerals) and Table 1.3 shows refined borates of Turkey.

Table 1.2. *Boron Minerals of Turkey, Concentrated Borates.*

Concentrated Borates	Formula
Ulexite	$NaCaB_5O_9.8H_2O$
Tincal (Borax pentahydrate)	$Na_2B_4O_7.5H_2O$
Colemanite	$Ca_2B_6O_{11}.5H_2O$

Table 1.3. *Refined Borates of Turkey.*

Refined Borates	Formula
Borax Decahydrate	$Na_2B_4O_7.10H_2O$
Borax Pentahydrate	$Na_2B_4O_7.5H_2O$
Anhydrous Borax	$Na_2B_4O_7$
Boric Acid	H_3BO_3 or $B(OH)_3$
Anhydrous Boric Acid	$B(OH)_3$
Sodium *Meta*-borate	$NaBO_2$
Sodium Perborate	$NaBO_3.nH_2O$
Sodium Pentaborate	$NaB_5O_{15}.nH_2O$

Table 1.4. *Special Boron Products of Turkey.*

Chemical Name	Formula	Chemical Name	Formula
Titanium Diboride	TiB_2	Boron Fiber	B
Magnesium Diboride	MgB_2	Ferroboron	FeB
Zinc Borate	$B_2O_6Zn_3$	Boron Carbide	B_4C
Potassium Borate	BK_3O_3	Boron Phosphate	BPO_4
Ammonium Borate	$BH_{12}N_3O_3$	Boron Nitride	BN
Barium Borate	BaB_2O_4 or $Ba(BO_2)_2$	Sodium Borohydride	$NaBH_4$
Trimethyl Borate	$B(OCH_3)_3$	Lithium Borohydride	$LiBH_4$
Copper *Meta*-borate	CuB_2O_4	Potassium Borohydride	KBH_4
Lithium Tetraborate	$B_4Li_2O_7$	Magnesium Borohydride	$Mg(BH_4)_2$
Fluoboric Acid	HBF_4	Phenyl Boronic Acid	$C_6H_7BO_2$
Fluoborate Salts	BF_4 salts	Boric Acid Esters	$B(C_2H_5O)_3$
Boron Trichloride	BCl_3	Boron Trifluoride	BF_3

Boron has 9.5 Mohs hardness which is the hardest material after diamond (Diamond: 10 Mohs) (Lide, 2005). Mohs hardness is used for the hardness for minerals and its range is from one to ten. Cubic boron nitride is known to be as hard as diamond.

Oxidation of boron hydrides is highly exothermic (Lide, 2005). Some of rocket fuel studies focused on boron hydrides and other type of boron clusters due to their high hydrogen storage capacity (Alexander & Schroeder, 1963; Fein, Grafstein, et al., 1963; Fein, Bobinski, Mayes, Schwartz, & Cohen, 1963; Grafstein, Bobinski, Dvorak, Paustian, et al., 1963; Grafstein, Bobinski, Dvorak, Smith, et al., 1963; Grafstein & Dvorak, 1963; Heying, Ager, Clark, Alexander, et al., 1963; Heying, Ager, Clark, Mangold, et al., 1963; Schroedbr & Vickers, 1963; H. Schroeder, Heying, & Reiner, 1963). High stability through covalent bonds of some boron molecular networks are comparable with carbon's covalent bond stabilities. Elemental boron and borax do not endanger human life but some boron hydrogen compounds have toxic properties hence, need caution during exposure (Lide, 2005).

1.2. Boron Clusters

Boron can form many kinds of clusters which are polymeric or cage-like (Atkins et al., 2009). This study is focused on cage-like structures.

1.2.1. Borohydrides

Borohydride molecules have boron and hydrogen atoms in their structures. The simplest structure of hydrogen containing boron molecules is diborane which has 2 boron and 6 hydrogen atoms in its structure. Diborane's bonds are not solely classical 2 centered, 2 electron (*2c,2e*) bonds on its structure. It has also nonclassical 3 centered, 2 electron (*3c,2e*) bonds on bridging B-H-B (Boron-Hydrogen-Boron) bonds (Atkins et al., 2009). 3D structure of diborane was reproduced in Avagadro program and reproduced in Figure 1.1 (Hanwell et al., 2012). Such phenomenon is observed throughout all boron hydride molecules and cages. To understand the number of electrons and bonds in these structures, Wade's rules were devised. Complete understanding in borane chemistry can lead to new molecules which can lead to novel materials with unexpected properties.

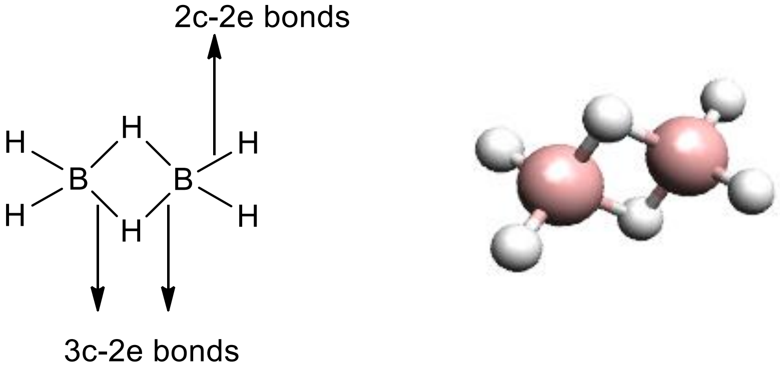


Figure 1.1. (Hanwell et al. 2012) (Left) Structure of diborane and its bond types. (Right) 3D structure of diborane (structure was reproduced in Avogadro program)

1.2.1.1. Wade's Rule

Boron hydride clusters and their derivatives have special bonding patterns and structures. In the first years they were discovered, the structures were not completely understood (Alfred Stock & Kuss, 1923). First boron clusters were thought as chains instead of cluster or cage. After development of chemical analysis techniques and sophisticated quantum chemical calculations, real structures were understood. Full structural pattern for borohydrides (boranes and carboranes) was firstly illustrated by Robert E. Williams (Williams, 1976) in the same publication with Ken Wade's article that explained properties of structure types (Wade, 1976).

Borohydride clusters have many types of structures, the well-known are *closo-*, *nido-* and *arachno-* types (Wade, 1976). *Closo-* type of clusters have $B_nH_n^{2-}$ (n= 6→12) and $C_2B_{n-2}H_n$ (n=5→12) emprical formulas in general and n+1 pairs of skeletal electrons (Atkins et al., 2009). "n" indicates number of skeletal atoms (boron or carbon) in another way "n" is a number of triangular faced cluster vertex. *Closo-* type clusters have *exo*-B-H and C-H bonds meaning bonding forms away from the cluster center (Wade, 1976). *Closo-* type borohydrides are thermally stable and chemically unreactive.

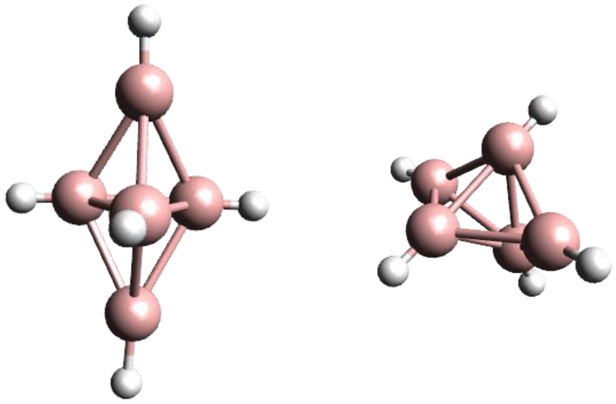


Figure 1.2. Structure of *closo*-pentaborane(5) from different positions. (3D structures were reproduced in Avogadro program) (Hanwell et al. 2012)

Nido- type of clusters have B_nH_{n+4}, $CB_{n-1}H_{n+3}$, $C_2B_{n-2}H_{n+2}$, $C_3B_{n-3}H_{n+1}$ and $C_4B_{n-4}H_n$ emprical formulas in general and n+2 pairs of skeletal electrons. Extra hydrogen atoms in *nido*- clusters are bridging between two boron atoms and other hydrogens are located as *exo*-B-H and C-H bonds like in *closo*- clusters (Wade, 1976). *Nido*- type cluster stability is between *closo*- and *arachno*- type stabilities.

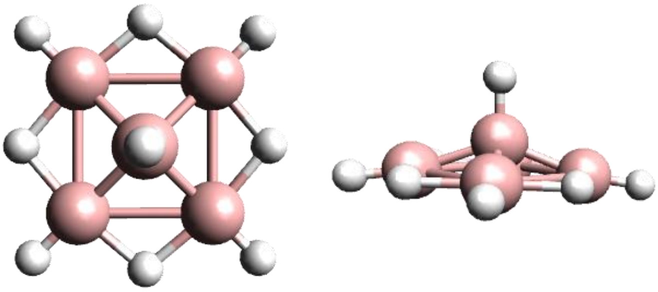


Figure 1.3. Nido-pentaborane(9) from different positions. (3D structures were reproduced in Avogadro program) (Hanwell et al., 2012)

Arachno- type of clusters have B_nH_{n+6} and $C_2B_{n-2}H_{n+4}$ emprical formulas in general and n+3 pairs of skeletal electrons. *Arachno*- types have n number *exo*-B-H bonds with B-H-B bonds and *endo*-B-H bonds. *Endo*-bonds are tangential to pseudo spherical surface of cluster (Wade, 1976). *Aracho*-type borohydrides are not stable at room temperature and they are highly reactive clusters (Atkins et al., 2009).

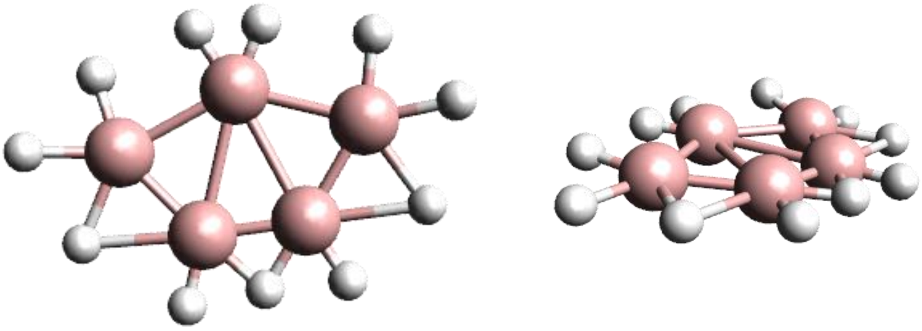


Figure 1.4. Structure of *arachno*-pentaborane(11) from different positions. (3D structures were reproduced in Avogadro) (Hanwell et al., 2012)

To sum up, *closo*- clusters are most stable ones and going from *closo*- to *arachno* cluster the stability decreases and reactivity increases. *Nido*- and *arachno*-clusters are incomplete polyhedral structures. *Closo*- clusters do not have B-H-B bridging bonds but *nido*- and *arachno*- have. From *closo*- to *arachno*- clusters, number of hydrogen atoms per boron atom increases, hence number of skeletal electron for per boron atom also increases. This increase also causes the clusters, with same number of boron and/or carbon atom but different number of hydrogen and charge, to become more open (*closo*-clusters → *arachno*-clusters).

Structure determination of these clusters can be done with Wade's Rules by counting total number of skeleton electron pairs (SEP) (Atkins et al., 2009; Wade, 1976). Boron has three valance electron and hydrogen has one. Hence, from one B-H unit totally four electrons can be used. Two electrons are used in B-H bonds which are *exo*-bonds. Rest two electrons are counted as skeleton electrons. Moreover, if boron atom in cluster has two hydrogen atoms, one B-H is treated as a unit and second one is counted as skeleton electrons. Wade's Rules can be also used for other types of clusters. For boranes and carboranes, all skeletal boron and carbon atoms have hydrogen or different substituent through *exo*-bonds. Other than *exo*-bond (B-H bonds which are not in the skeleton) electrons, remaining valence electrons are for the skeletal bonding (Wade, 1976).

1.2.2. Metalloboranes and Metallocarboranes

Metalloboranes and metallocarboranes are mostly known as a having one metal atom per cluster. However, having two or more metal atoms in a cluster show a close relationship between metal and boron cluster. Metal salts of boranes and carboranes are different from metalloboranes and metallocarboranes. Metal salts of them do not have metal in cluster structure, metal only stays as a cation. On the other hand, metalloborane and metallocarborane clusters have metal in cluster structure (Wade, 1976). (*Figure 1.5*)

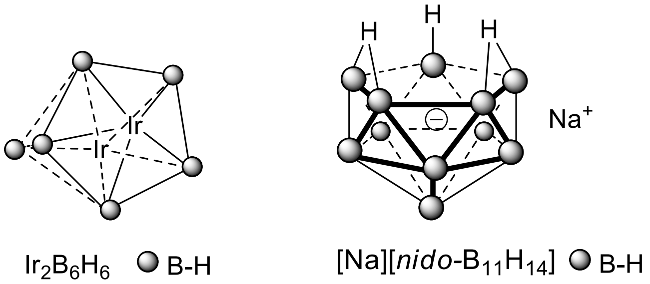


Figure 1.5. (Left) Metalloborane. (Right) Metal cation of borane (Wade 1976).

Some particular examples can show that metal atom can be shared by two *nido*-carborane or borane clusters. In these clusters, it can be assumed that metal contribute three atomic orbitals to the skeletal bonding of each cluster (Wilson, Warren, & Hawthorne, 1969), (Wing, 1968).

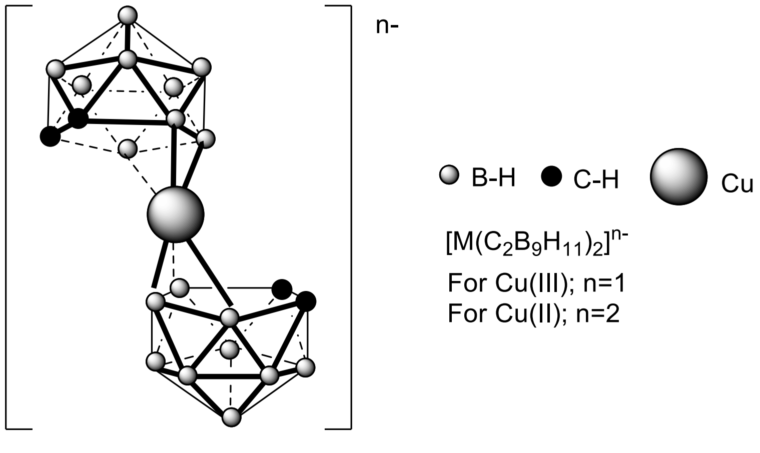


Figure 1.6. Metalloborane that metal contribute three atomic orbitals of each cluster (Wing, 1968).

Skeletal valance electrons of metallic elements change the type of metallic linkages in the formation of clusters. Metallic element skeletal valance electrons were summarized and given with formulas by Kiremire (Kiremire, 2017). Usually metals are associated with carbonyls, cyclopentadienyl and hydrides which are known as associate ligands. Type of associate ligands and metallic elements designate the skeletal linkages of the metallic fragment.

Formation of metalloboranes has complex synthetic routes. By the formation of borane anion and addition of metal ligand complex, metalloboranes can be synthesized and many other synthesis routes were summarized by Greenwood (B. N. N. Greenwood, Kennedy, Savory, Staves, & Trigwell, 1978).

Hawthorne and coworkers have achieved one of the leading methods to synthesis of metallocarboranes (Hawthorne, Young, & Wegner, 1965). This reaction was based on synthesis of $Fe(B_9C_2H_{11})_2^{2-}$ and $Fe(B_9C_2H_{11})_2^{-}$. By the abstraction of a proton in THF, $B_9C_2H_{12}^{-}$ was converted to $B_9C_2H_{11}^{2-}$, then with the addition of $FeCl_2$ desired product was obtained.

1.2.3. Carboranes

Formally named as carbaboranes, carboranes are polyhedral molecular clusters of boron and carbon atoms. Despite the classical bonds of carbons in organaboranes, in carborane skeletons carbon atom neighbors 3 to 6 other atoms to stabilize the skeleton structure. Their stability comes from delocalization of electrons through nonclassical (*3c,2e* bonds) covalent bonds. Since mid-1950s, carboranes have been studied because of their bonding types and structures by theoreticians and boron chemists. In last decades, industrially carboranes have been getting attention due to their capacity to form exceedingly heat-stable polymers (Grimes, 2016b).

Carborane structure was predicted before its synthesis report by William Lipscomb and Roald Hoffmann theoretically (Hoffmann & Lipscomb, 1962). The structure carboranes was predicted by pioneering of boron hydride chemist Alfred Stock (Grimes, 2016a); (Stock & Kuss, 1923). The first carborane synthesis was performed in the post-World War II era through U.S. government program (i.e ZIP, HEF) to prepare high energy generating compounds of boron hydrides different from hydrocarbons for rocket and aircraft fuels. All of these syntheses were performed in secret in 1950s. Preparations, synthetic methods, and even their existence had not been known until late 1963 when they were reported in literature (Alexander & Schroeder, 1963; Fein, Grafstein, et al., 1963; Fein, Bobinski, et al., 1963; Grafstein, Bobinski, Dvorak, Paustian, et al., 1963; Grafstein, Bobinski, Dvorak, Smith, et al., 1963; Grafstein & Dvorak, 1963; Heying, Ager, Clark, Alexander, et al., 1963; Heying, Ager, Clark, Mangold, et al., 1963; Papetti & Heying, 1963; Schroedbr & Vickers, 1963; H. Schroeder et al., 1963). Idea of reality of carborane came after the discovery and isolation of the $B_{12}H_{12}^{2-}$ dianion by Pitochelli and Hawthorne as a $C_2B_{10}H_{12}$ cluster (Pitochelli & Hawthorne, 1960). The number of carbons can vary in these structures. Widespread numbers are 1 or 2 for carbon atom but 3 and 4 even 5 and 6 carbon containing boron clusters have been observed (not isolated) (Grimes, 2016a).

1.2.3.1. Nomenclature and Numbering

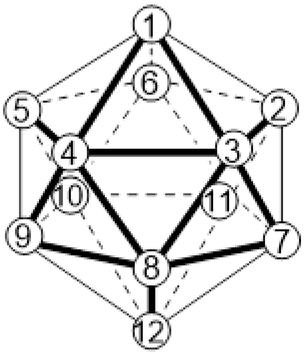


Figure 1.7. Numbering of boron and carborane cages.

Formally named as carbaboranes, carboranes are known as polyhedral carbon containing boranes. One or more boron atom of these polyhedral borane clusters exchanged with carbon, they become carboranes (Grimes, 2016b). They have special numbering and naming system. According to IUPAC rules, clusters naming goes on in a clockwise manner based on the highest order symmetry axis of the cluster which is B_n for carbon and other hetero atoms, highest priority come with highest atomic number. If we consider *closo*-dodecaborane(12), numbering of atoms in the structure should be according to *Figure 1.7*. Before numbering, they also get prefixes according to Wade's Rules. Closed cages named as a *closo*-, in the case of missing vertexes, *nido*-, *arachno*- and *hypho*- are used. Another rule while naming them is the hydrogen number which comes after name of clusters in parenthesis. For example; $C_2B_5H_7$ is called as a *closo*-dicarbapentaborane(7). Carbon position is also important to indicate different isomers with same empirical formula and can be shown by numbers. For example; $C_2B_{10}H_{12}$ is called as a *closo*-1,2-dicarbadecaborane(12), *closo*-1,7-dicarbadecaborane(12) and *closo*-1,12-dicarbadecaborane(12) to indicate clusters that *ortho*-, *meta*- and *para*- isomers of each other, respectively.

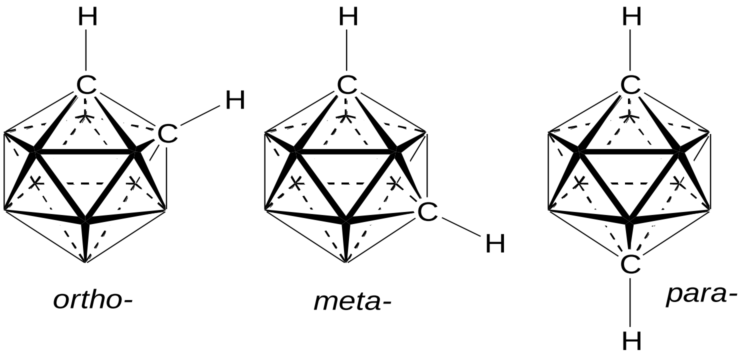


Figure 1.8. Structure of *ortho-*, *meta-* and *para-* carboranes. Other vertices are B-H.

1.2.3.2. Structure and Bonding of Carboranes

Carboranes are nonclassical molecules and their bonds cannot be thought as simple electron pair bonds (*2c,2e*) (Grimes, 2016b). They have 5 or 6 neighbors including hydrogen or substituent of carbon or boron atoms of clusters. Delocalization of electrons on skeletal framework enables the bonding system of cluster between carbon and boron atoms. Connecting lines in clusters do not indicate their bonding systems. Lines mainly represent polyhedral geometry of clusters. Development of computational tools and density functional theory (DFT) suggested structures and bonding properties for carboranes. Structure and bonding in carboranes became clear consequently.

Boranes and carboranes are mostly defined as cages but in 1966 F.A. Cotton defined them as clusters for the first time (Cotton, 1966). Two reasons were shown for definition difference;

1. Having more than one type nuclear like as binuclear or ternuclear, cause polyhedral relation, hence should not be named as cage.
2. Being packed very closely is not characteristic property or common behavior for cages rather than polyhedral clusters.

1.2.3.3. The Localized-bond Approach

Boron has the ability to form bonds by one electron pair with three or more atoms. Low electronegativity and having four valance orbital with three valance electrons, boron is capable of making nonclassical bonds. W.N. Lipscomb and his coworkers showed structures successfully and indicate 2 centered, 2 electrons (*2c,2e*) and 3 centered, 2 electrons (*3c,2e*) bond properties of boron clusters which come up with multicenter bonding (Lipscomb, 1963). *2c,2e* means one electron pair links two nuclei as in classical chemical bonds and Boron-Hydrogen bond in these clusters. *3c,2e* means one electron pair links three nuclei as in Boron-Hydrogen-Boron and Boron-Boron-Boron bonds in these clusters. Carbon can also make multicenter bonding in electron delocalized clusters such as agostic interactions of metal complexes and nonclassical carbocations and as well as in carboranes.

1.2.3.4. Carborane Aromaticity

Aromaticity of carboranes was proven by many theoretical and experimental results. First studies were done about boranes, especially on $B_{12}H_{12}^{2-}$ dianion (Schleyer & Najafian, 1998). All results show that electron delocalization of clusters and position of orbitals cause characteristic aromaticity. Orbitals form two different sets in clusters. First set of orbitals and polyhedral surface are tangential surfaces. Second set of orbitals is center directed. Hence, σ-bonded interactions form and cause aromaticity. Beyond closed-cage aromaticity *nido*- and *arachno*- carboranes also show aromaticity, but not as much as *closo*- ones because of the less electron delocalization.

1.2.3.5. Electron Deficiency

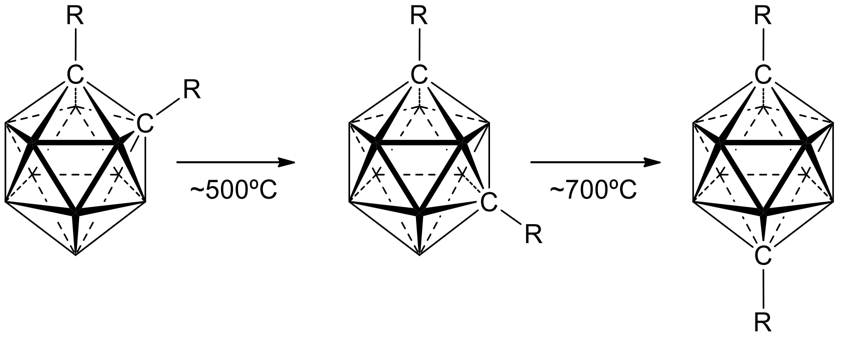
Electron-deficiency has been apparent for boron hydrides and carboranes since their first isolation by Alfred Stock and other scientists due to multicenter bonding (Alfred Stock & Kuss, 1923). Grimes argues the reverse, meaning these compounds are not electron deficient in his book “carboranes” (Grimes, 2016b). The examples given for this argument are $B_{12}H_{12}^{2-}$ for boron hydrides and $C_2B_{10}H_{12}$ for carboranes. Having right number of electrons make them very stable. In condition of addition any electron, cages should open, hence energy levels come to higher states to form other clusters. Properties of cage carbon atom are not same for all carborane clusters; carbon-bound groups experience electron withdrawing power and boron-bound toward groups bonded to carbon, electron withdrawing power is observed, but toward boron-bound groups experience electron donor power. Moreover, *m*-carboranyl (*meta*-isomers) derivatives are the most electron releasing units in carbon containing substituents class. As a consequence, Russell N. Grimes propose to use “electron-poor” to explain their condition not “electron-deficient” in order to avoid any confusion. In this thesis both definitions are used because we did not do any study to confirm reactions towards these definitions.

1.2.3.6. Synthesis and Reactivity

As mentioned in *section 1.2.3*, first synthesis of carboranes were done to obtain new energetic rocket and aircraft fuels while working with boranes (Grimes, 2016c). First carboranes were side products of the reaction between alkynes and boranes. Obtained carborane products were the first stable characterized *closo*-carboranes besides alkyl derivatives of them. Within years, synthesis methods were developed to generate specifically carborane products under safer conditions and less costly routes. Boranes were also used as starting materials.

Most known icosahedral carboranes are the isomers of $C_2B_{10}H_{12}$ cluster. Theoretically mechanisms of rearrangements were reported by Lipscomb and coworkers as a diamond-square-diamond (DSD) mechanism (Kaczmarczyk, Dobrott, & Lipscomb, 1962). In many years, new mechanisms were proposed with new products and more experimental data were serve to literature (Wu & Jones, 1989). First observed rearrangements were *ortho*- to *meta*- isomerization, occured at around 300 ºC and at 450 ºC *ortho*-cluster isomerizes to *meta*- cluster completely. These experiments were reported by Grafstein, Dvorak and their coworkers in 1963 (Grafstein, Bobinski, Dvorak, Smith, et al., 1963). Then higher temperature isomerization experiments were performed by Papetti and Heying, hence *meta*- to *para*- experiments were also reported (Papetti & Heying, 1964). Intermolecular rearrangements of $C_2B_{10}H_{12}$ cluster as well as $B_{12}H_{12}^{2-}$ were theoretically calculated by Christopher A. Brown and Michael L. McKee by using density functional theory methods (Brown & McKee, 2006).

Ortho-, *meta*- and *para*-$C_2B_{10}H_{12}$ clusters have many transition states. In these theoretical calculations, results were compared with the experimental data. Observations showed consistent results. The triangular-face rotation mechanism and *closo*- to *nido*- to *closo*- mechanism were assumed as lowest free energy pathways for *ortho*- to *meta*- and *meta*- to *para*- rearrangements, respectively (Brown & McKee, 2006).



Scheme 1.1. Isomerization of carborane. Other vertices are B-H.

1.3. $CB_{11}H_{12}^-$ Anion

$CB_{11}H_{12}^-$ anion is one of the *closo*-carboranes and has *2c,2e* (B-H and C-H bonds) and *3c,2e* bonds (skeleton bonds). *3c,2e* bonding clusters mostly defined as electron deficient structures (Alfred Stock & Kuss, 1923) but as explained in section "1.2.3.5 Electron Deficiency" in some cases this definition might cause to confusion. On the other hand, this cluster can be characterized by delocalized electron deficient bonding and skeletal bonds mostly known as low electron density bonds. $CB_{11}H_{12}^-$ has special stability; CH and BH^- units are isoelectronic of each other.

Bonds of cluster are formed by thirteen pairs of valance electrons and its skeleton consists of twenty triangular faces which form icosahedron. Thirteen pairs of valance electrons are not enough to form complete twenty triangular faces, seven of them stay empty, but because of the electron delocalization in cluster, bonding system forms delocalized cluster. 2-centered B-H and B-B bonds form localized bonds and 3-centered B-H-B and B-B-B bonds form delocalized bonds (Lipscomb, 1963). In 1963, Lipscomb (Lipscomb, 1963) assigned valance electrons to edges or faces of clusters and in 1991, Wade (Olah, Wade, & Williams, 1991) assigned them to the vertices of the polyhedron. $CB_{11}H_{12}^-$ cluster is mono anion and this explained as having six positive charges in carbon nucleus and five positive charges in boron nucleus by Douvris and Michl (Douvris & Michl, 2006). Negative charge of cluster oriented toward carbon atom.

1.3.1. Synthesis of $CB_{11}H_{12}^-$ Anion

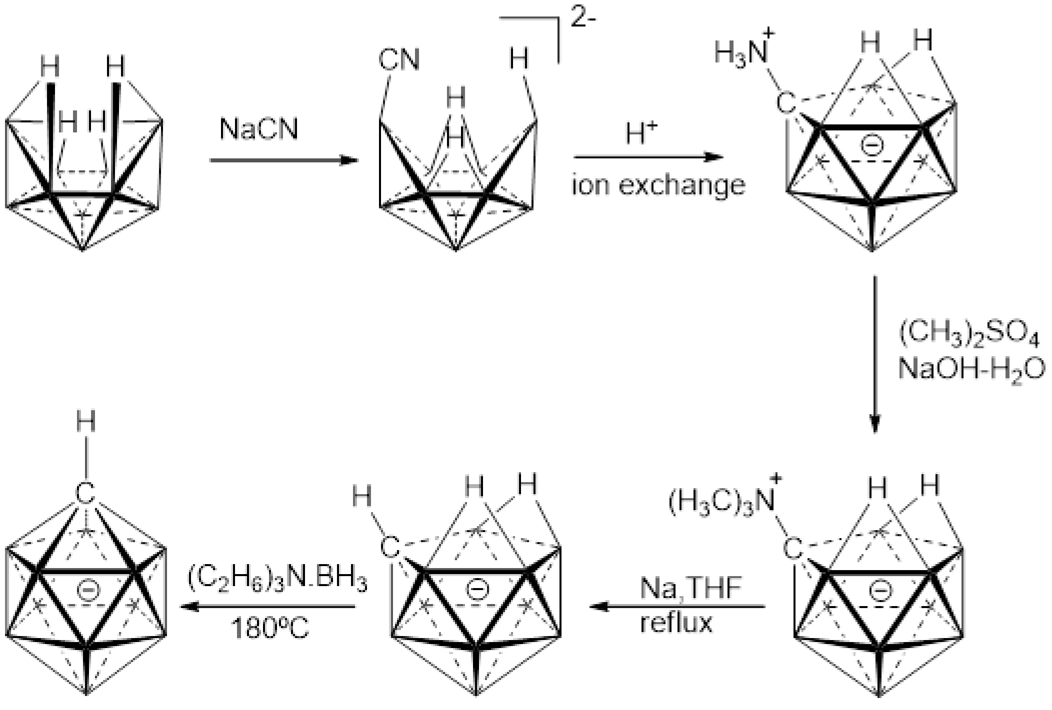
Unfortunately, there is no known way to synthesis $CB_{11}H_{12}^-$ directly from small molecules. Most groups preferred to synthesize $CB_{11}H_{12}^-$ from $B_{10}H_{14}$ which synthesis and structure was proven (Cyvin, Brunvoll, & Cyvin, 1984; Muetterties, 1963). In synthesis pathway after smaller boron or carbon containing clusters synthesizes, $CB_{11}H_{12}^-$ can be formed. $CB_{11}H_{12}^-$ can be synthesized in four different methods.

- Boron insertion
- Carbon insertion

- Boron extrusion
- Carbon extrusion

1.3.1.1. Boron Insertion

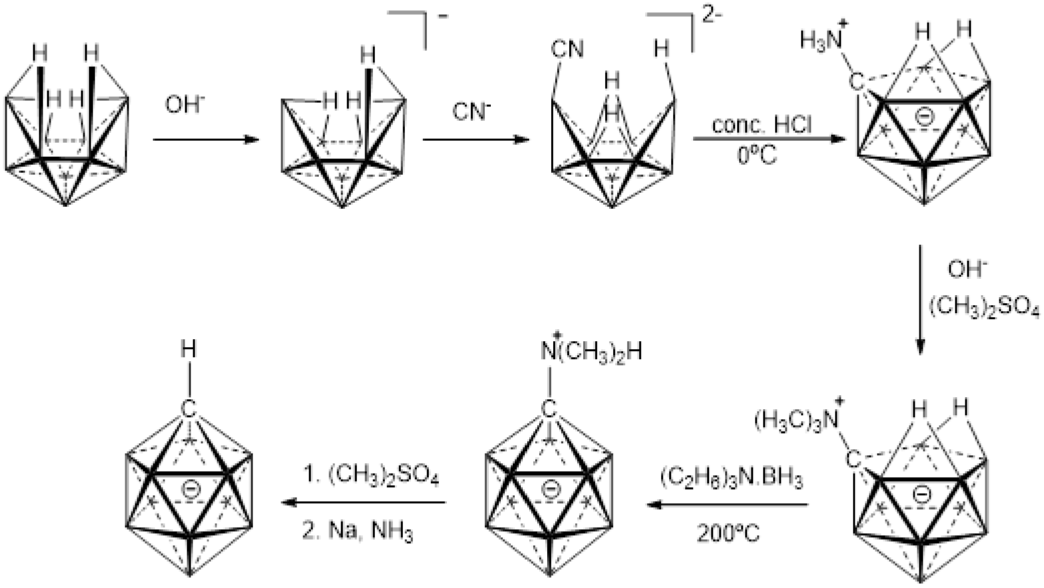
Knoth is first scientist who synthesized$CB_{11}H_{12}^-$ by boron insertion to $CB_{10}H_{13}^-$ (Knoth, 1967). Commercially available $B_{10}H_{14}$ was used as a starting material. Then -CN addition was done and with acid treatment carbon incorporated in cluster. Amino group was protonated and methylated, respectively, to easily remove trimethylamine substituent with sodium in THF.



Scheme 1.2. Knoth's synthesis. Other vertices are B-H.

At last step, by addition of triethylamine borohydride to the $CB_{10}H_{13}^-$, only gave $CB_{11}H_{12}^-$. When $CB_{10}H_{13}^-$ is heated to 300-320 ºC, a mixture of $CB_{11}H_{12}^-$ and CB_9H_{10} was observed. (*Scheme 1.2*)

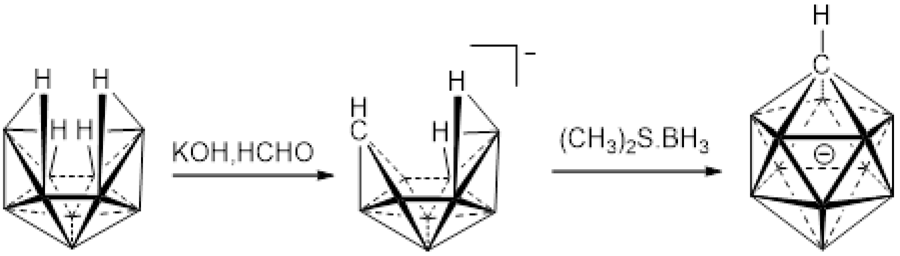
First development for Knoth's method was done by Heřmánek and his group (Plesek, Jelinek, Drdakova, & Hermanek, 1983). $B_{10}H_{14}$, decaborane, was again used as a starting material and deprotonated with sodium hydroxide. At the second step, *arachno*-$B_{10}H_{13}CN^{2-}$ was formed by treatment with cyanide, converted to $CB_{10}H_{12}NH_3$ and methylated. Instead of conversion of trimethylamine to hydrogen, like in Knoth's experiments, Heřmánek's group closed the cluster by addition of $(CH_3CH_2)_3NBH_3$ at 200 ºC. However, observations showed that one methyl group of amino was lost during this step, hence by the addition of dimethylsulfate, amino group trimethylated again and reduction was done in liquid ammonia by sodium to synthesize $CB_{11}H_{12}^-$. This method known as a basis method used by Katchem to produce $CB_{11}H_{12}^-$ for commercial porposes (Quintana & Sneddon, 1990).



Scheme 1.3. Heřmánek synthesis. Other vertices are B-H.

Other modifications came from groups of Fox and Hughes, to improve safer and efficient way (Batsanov et al., 2002). Instead of using cyanide, isocyanides such as tert-butyl isocyanide and cyclohexylisocyanide were used.

The most convenient method can be the group of Kennedy's method which basically has two steps and started from decaborane. By taking advance of Brellochs reaction *nido*-decaborane turned to *arachno*-$CB_9H_{14}^-$. Then *closo*- cluster was synthesized by addition of $(CH_3)_2SBH_3$ (Franken et al., 2004).



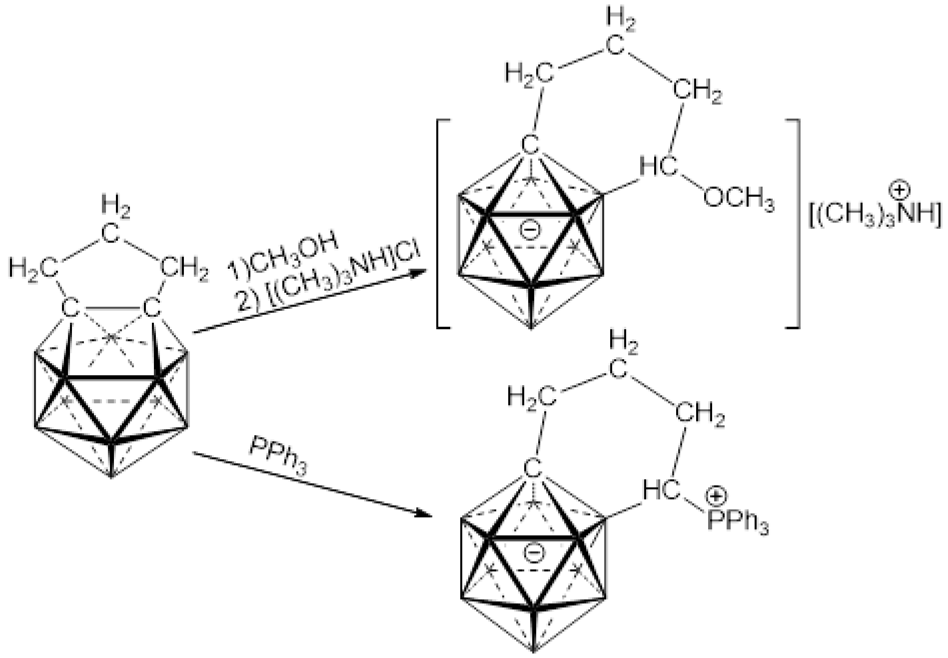
Scheme *1.4*. Kennedy synthesis. Other vertices are B-H.

1.3.1.2. Carbon Insertion

Boron insertion methods are multistep methods; hence carbon insertion can be seen as an easier method. Last added vertex to cluster is carbon in this insertions. Carborane can be synthesized from $B_{11}H_{14}^-$ by dichlorocarbene insertion (Franken et al., 2001). Carbenoid formation mechanism in the process is not proven yet. However, DFT calculations on reaction pathway was done and accepted by scientists (Rempala & Michl, 2003) (Carbon insertion mechanism is shown in *Figure 3.6*). Sodium hydride was used to deprotonate $B_{11}H_{14}^-$, and ethoxide was used to deprotonate chloroform for the last carbon vertex. Instead of using chloroform, bromoform and iodoform were also tried, however, main products were not $CB_{11}H_{12}^-$. Even in reaction with iodoform, iodoform took an oxidant role and lead to the formation of *closo*-$B_{11}H_{11}^{2-}$ (Douvris & Michl, 2006).

1.3.1.3. Carbon Extrusion and Boron Extrusion

Carbon extrusion reactions are based on loss of carbon vertex from supercarboranes. Having more than twelve vertices on carboranes named them as supercarboranes. 1,2-$(CH_2)_3$-1,2-$C_2B_{11}H_{11}$ is 13-vertex carborane which was transformed to a 12-vertex carborane also changed its position from *endo*- to *exo*- by treating with different kind of bases (Zhang, Chan, & Xie, 2008),(Jelinek, Plesek, Mares, Hermanek, & Stibr, 1987).



Scheme 1.5. Carbon extrusion reactions. Other vertices are B-H.

Even if carbon atom extrusions from carborane clusters seem rare reactions, they had been observed in different studies which were summarized by Maik Finze (Finze, 2007).

Boron extrusion reaction was observed with carbon atom extrusion while 2,3-$(CH_2)_3$-2,3-$C_2B_{12}H_{12}$ cluster converted from 14-vertex carborane to 12-vertex CB_{11} cluster (Zhang, Zheng, Chan, & Xie, 2009).

1.4. $B_{12}H_{12}^{2-}$ Anion

Academically studied boron clusters were considered interesting molecules for several years (A. Stock, 1933). $B_{12}H_{12}^{2-}$ anion named as dodecahydro-*closo*-dodecaborate anion and its icosahedron structure shows its simplicity and high symmetry (Sivaev, Bregadze, & Sjöberg, 2002). It is known as a weakly coordinating anion (Strauss, 1993), (Reed, 1998) and its high stability in acidic conditions as well as its thermal stability. It is stable in 3M HCl at 95 ºC. Stability of $B_{12}H_{12}^{2-}$ anion comes from its bonding in cage and aromatic character in three-dimension (Aihara, 1978), (R. B. King, 2001).

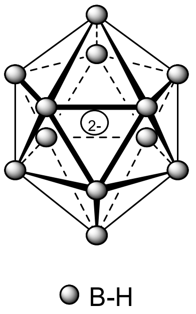


Figure 1.9. $B_{12}H_{12}^{2-}$ has icosahedral symmetry (I_h)

1.4.1. Synthesis of $B_{12}H_{12}^{2-}$ Anion

In 1955 Longuet-Higgins and Roberts predicted stable form of dodecaborane with calculations that it is only stable as a dianion (Longuet-Higgins & Roberts, 1955). Experimentally proof was done by Hawthorne and Pitochelli in 1960. $B_{12}H_{12}^{2-}$ anion was observed as a side product of 2-iododecaborane and triethylamine reaction (Pitochelli & Hawthorne, 1960). High yield synthesis methods were done by in years (Adams, Siedle, & Grant, 1964; Ellis, Gaines, & Schaeffer, 1963; N. N. Greenwood & Morris, 1963; Miller, Miller, & Muetterties, 1963, 1964). First type methods were based on Lewis base (generally triethylamine) and borane complexes with other boranes. (*Scheme 1.6*)

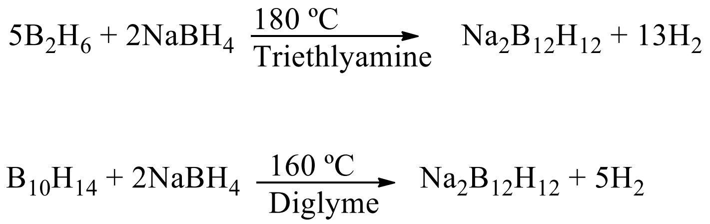
$$7B_2H_6 + 4(CH_3CH_2)_3N \xrightarrow{180\ ^{\circ}C,\ 2h} [(CH_3CH_2)_3NH]_2B_{12}H_{12} + 12H_2$$
$$+ 2(CH_3CH_2)_3NBH_3$$

$$12B_5H_9 + 10(CH_3CH_2)_3N \xrightarrow{125\ ^{\circ}C,\ 10h} 5[(CH_3CH_2)_3NH]_2B_{12}H_{12} + 24H_2$$

$$21/_{10}\ B_{10}H_{14} + 3(CH_3CH_2)_3NBH_3 \xrightarrow[\text{in ultrasene}]{190\ ^{\circ}C} [(CH_3CH_2)_3NH]_2B_{12}H_{12}$$
$$\text{(paraffinic mixture)} \qquad + (CH_3CH_2)_3NB_{12}H_{12}^{-} + 71/_{10}H_2$$

Scheme 1.6. Synthesis reactions of *closo*-dodecaborate from Lewis Base-borane complex and boranes.

Second type methods were based on reactions of alkali metal tetrahydroborates with boranes or Lewis base - borane complexes (Miller et al., 1964). (*Scheme 1.7*)



$$5B_2H_6 + 2NaBH_4 \xrightarrow[\text{Triethlyamine}]{180\ ^{o}\text{C}} Na_2B_{12}H_{12} + 13H_2$$

$$B_{10}H_{14} + 2NaBH_4 \xrightarrow[\text{Diglyme}]{160\ ^{o}\text{C}} Na_2B_{12}H_{12} + 5H_2$$

Scheme 1.7. Second type methods for the synthesis of *closo*-dodecaborate.

Decaborane ($B_{10}H_{14}$) which is highly toxic was used as a starting material for the second reaction which is shown in *Scheme 1.7*. To avoid from it as a starting material, using high boiling alkanes as a solvent (boiling point up to 200-250 ºC) and $NaBH_4$ or KBH_4 with $(CH_3CH_2)_3N.BH_3$ or $(CH_3)_3N.BH_3$ complexes were preferred by scientists as a convenient method for the synthesis of $B_{12}H_{12}^{2-}$ anion (Sivaev et al., 2002). Instead of using boron hydrides, NaH and BCl_3-H_2 mixture was also tried by Grüner and his coworkers (Bernard et al., 2002). Unfortunately, chloro derivatives were also observed as side products. $Na_2[B_4O_5(OH)_4].nH_2O$ and H_3BO_3 were also tried (Harzdorf, Niederprüm, & Odenbach, 1970). $B_{12}H_{12}^{2-}$ anion was synthesized by cage-expansion reactions (Volkov, Dirk, Englert, & Paetzold, 1999) and from other borate anions (Kabbani, 1996; Klanberg & Muetterties, 1966; Volkov et al., 1999).

As well as synthesis of $B_{12}H_{12}^{2-}$, forming their metal and ammonium cations were usually studied. Lithium (Kuznetsov & Klimchuk, 1971, 1972), sodium (Kuznetsov & Klimchuk, 1971, 1972; Muetterties, Balthis, Chia, Knoth, & Miller, 1964), potassium (Kuznetsov & Klimchuk, 1971, 1972; Muetterties et al., 1964), rubidium (Kuznetsov & Klimchuk, 1971, 1972), cesium (Benham, Lord, Butler, & F. R. Gilson, 1987; Kuznetsov & Klimchuk, 1971, 1972; Muetterties et al., 1964), aluminium (Muetterties et al., 1964) and copper (I) (Malinina, Goeva, Solntsev, & Kuznetsov, 1993; Malinina, Polyakova, Goeva, & Kuznetsov, 2002), silver (I) (Kuznetsov, Kulikova, & Kanaeva, 1976; Kuznetsov, Solntsev, & Klimchuk, 2013; Uspenskaya, Solntsev, & Kuznetsov, 1973), NH_4^+, $(CH_3)_2NH_2^+$ (Malinina et al., 1993), $(CH_3)_3NH^+$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $(CH_3CH_2)_3NH^+$, $(CH_3CH_2)_4N^+$ (Malinina et al., 1993, 2002) are some of them. Crystal structures of them gained attention during years. By the single-crystal X-ray diffraction method potassium, cesium, tetrahydrated of sodium salt (Malinina et al., 2002; Ponomarev, Lyubeznova, Solntsev, & Kuznetsov, 1991; Solntsev, Kuznetsov, & Ponoma, 1976), tetramethylamine, trimethylamine salts have been designated (Malinina et al., 1993).

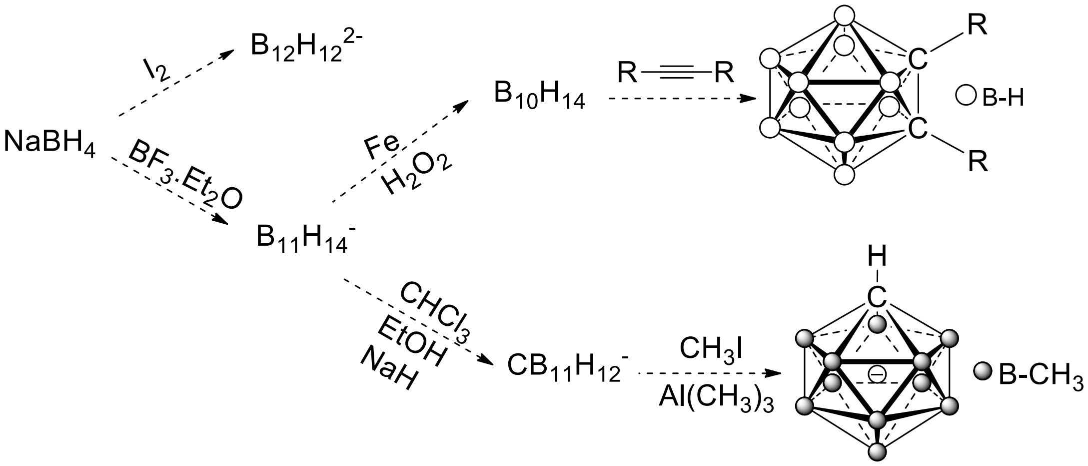
1.5. Applications of $B_{12}H_{12}^{2-}$ and $CB_{11}H_{12}^{-}$ Anion

$B_{12}H_{12}^{2-}$ anion is versatile cluster and has many application areas. As carborane clusters they also produced in ZIP, HEF projects during World War II (Grimes, 2016a). They are known as a high energy density materials and used as propellants for high burning composites (M. a. Schroeder, 1998; Sivaev, 2017). Lithium rechargeable batteries are another field that dodecaborane derivatives can be used (Johnson, 1980, 1981, 1982). Lithium salts of dodecahydrododecaborane and dodecachlorododecaborane are examples of them. As mentioned before, boron clusters are thermally stable and polymers of dodecaborane and dodecacarbaborane clusters, too (Hertler & Raasch, 1964). They can be also form non-linear optics materials (Kaszynski & Douglass, 1999) means liquid crystals at room temperature which can be used for electro-optics and ion selective electrode (Fibbioli, Berger, Schmidtchen, & Pretsch, 2000). Dodecaborane was also studied for nuclear waste purification (Bernard et al., 2002; Gruner, Bonnetot, & Mongeot, 1997) because of its weak hydrogen bonds which can be formed between cluster and metal mono anion and dianion. In organic chemistry, $B_{12}H_{12}^{2-}$ was used as a catalyst in synthesizes (Drake, 1999). Being used very much in organic chemistry, dodecaborane and dodecacarbaborane derivatives were also studied in medicinal chemistry. Boron Neutron Capture Therapy (BNCT) has led to this field (Hawthorne, 1993; Nedunchezhian, Aswath, Thıruppathy, & Thirugnanamurthy, 2016). Nuclear medicine (Tolmachev, Bruskin, Sivaev, Lundqvist, & Sjöberg, 2002), X-ray contrast agent (Dominique & Spielvogel, 1993; Grainger, Hon, & Hon, 1982; Wilbur, 1995) are other application areas that dodecaboranes have been used.

CHAPTER 2

AIM OF THE STUDY

Boron and carborane cages are interesting compounds due to their potential applications in numerous fields. Although, these boron cages are commercially available, they are almost impossible to import into Turkey due to the long bureaucratic processes and strategic importance. With this in mind, in this thesis we aimed to synthesize and modify such cages in our laboratories (This study will be the first to synthesize the compound in Turkey to our best knowledge). The feasibility of these syntheses in laboratories are going to be tried potentially for the purpose of the large scale synthesis. Our synthetic scheme starts with a simple, easy way to handle boron compounds, sodium borohydride ($NaBH_4$). Our reaction scheme that we are going to follow is summarized below.



Scheme 2.1. Reactions that are going to be followed in this thesis.

Silver salts are usually facilitated for carbocation formation from alkyl halides. Silver precipitates as silver halide leaving behind the carbocation and the anion of the silver salt. To study carbocations one needs to have them "naked". This is usually not possible with ordinary anions. However, silver salts of carborane and borane cages will be usefull for such a purpose since these cages are weakly coordinating.

CHAPTER 3

RESULTS AND DISCUSSION

Turkey has 73 % of world's boron mineral resources but not all of them are valuable minerals as they are mined. They should be processed or they are being sold to other countries in order to be converted to valuable form of boron products. Turkey exports boron speciality chemicals which are not produced in Turkey, despite the fact that they can be produced in Turkey with little investment and research. Only 3 % of processed reserve has been used in chemical synthesis. Accordingly, in this study borane and carborane cages were synthesized in order to use further reactions in future.

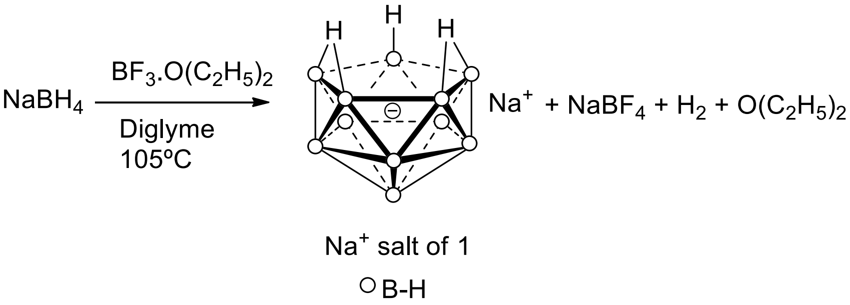
Boranes show different properties according to their structure type (*closo*-, *nido*-, *arachno*-) and to their counter cation if they are anionic. It is well known that, some boranes are not stable and explode in contact with air, nevertheless some of them are very stable in the form of salts. They are also fire retardant compounds and has characteristic green flame.

Figure 3.1. Filter paper was washed with trimethylamine salt of undecaborane solution and when burned show green flame. Photo was taken in our lab.

This study starts with converting $NaBH_4$ into *nido*-$B_{11}H_{14}^-$ anion, inturn, will be converted into *closo*-carboranes and decaborane (*nido*-$B_{10}H_{14}$).

3.1. Conversion of $NaBH_4$ into *nido*-$B_{11}H_{14}^-$

Our reaction of conversion of $NaBH_4$ into *nido*-$B_{11}H_{14}^-$ was summarized in *Scheme 3.1*. This reaction involves $NaBH_4$ treated with $BF_3.O(CH_2CH_3)_2$. This reaction produces numerous volatile boron cages which are toxic (as literature indicates) (Geis et al., 2009). Therefore, a special reaction setup should be used (*vide infra*).



Scheme 3.1. Synthesis of sodium salt of *nido*-undecaborate.

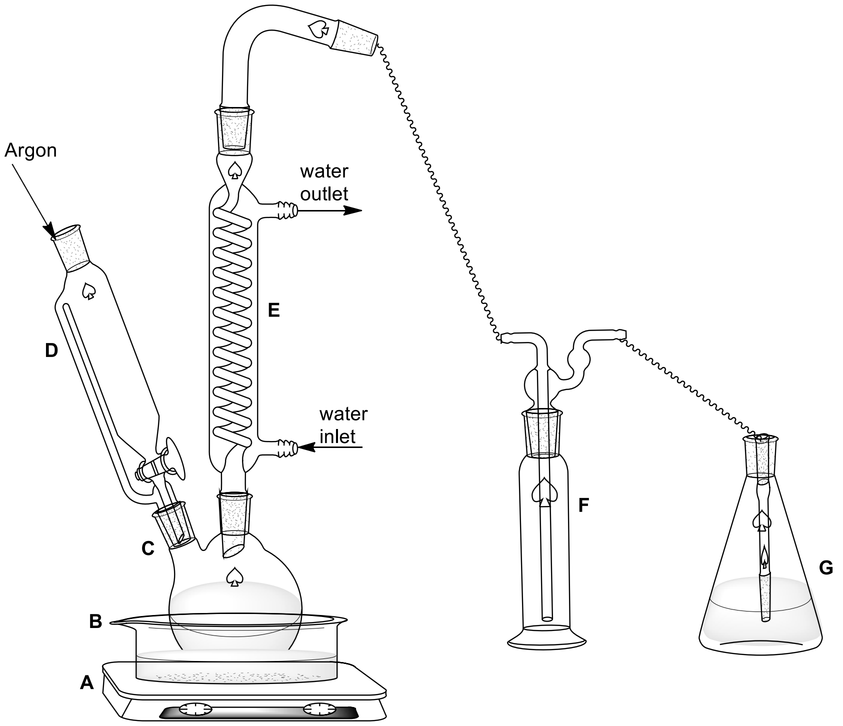


Figure 3.2. Reaction setup for the synthesis of compound 1

Figure 3.2 shows thermocouple magnetic stirrer (A), oil bath (B), two-necked round bottom flask, $NaBH_4$ in diglyme (C), dropper with as equalizer, $BF_3.O(CH_2CH_3)_2$ (D), reflux condenser (E), trap (F), acetone trap (G). This is our simpler reaction setup.

Na^+ salt of undecaborate (*nido*-$B_{11}H_{14}^-$) anion was synthesized according to Dunks' method (Dunks & Ordonez, 1978). Dunks and co-workers used mechanical stirrer, reservoir, pump, receiver and dry ice condenser which form very complicated setup for this synthesis. Firstly, setup was adapted to our laboratory conditions to reduce the expenses and to eliminate time-consuming steps within the safety rules. This setup was the simplest one to use for these reactions in our laboratory as shown in *Figure 3.2*. Lower boranes are volatile which can be pacified with acetone, so acetone trap (G) has to be used to prevent breathe of unpredictable borane gases in case of their toxicity and presence in air.

Stirring rate should be high enough during this reaction to prevent solidifying of precipitates. Using mechanical stirrer might work better however, using available lab equipments were preferred. Before starting to reaction $NaBH_4$ was added to the reaction medium with stirring bar and all set up was prepared on them. Reaction medium was flashed with argon and continued to addition of argon gas with balloon during all steps. Diglyme addition was done from sealed bottle of diglyme to septum closed reaction medium with syringe. $NaBH_4$ in diglyme was heated to 105 ºC, before the addition of $BF_3.O(C_2H_5)_2$ through dropping funnel. After reaching to 105 ºC, addition of $BF_3.O(C_2H_5)_2$ was started and done slowly to keep *ca.* 0.5 ml/min rate. During this reaction, it was shown in previous studies that there is also $B_3H_8^-$ anion formation (*Scheme 3.2*) (Dunks & Ordonez, 1978). Dunks and coworker were also synthesized $B_{11}H_{14}^-$from $B_3H_8^-$ anion.

$$5BH_4^- + 4BF_3.O(C_2H_5)_2 \longrightarrow 2B_3H_8^- + 3BF_4^- + 2H_2 + 4O(C_2H_5)_2$$

$$17B_3H_8^- + 16BF_3.O(C_2H_5)_2 \longrightarrow 5B_{11}H_{14}^- + 12BF_4^- + 16O(C_2H_5)_2 + 33H_2$$

Scheme 3.2. Formation of triborate during the synthesis of undecaborane.

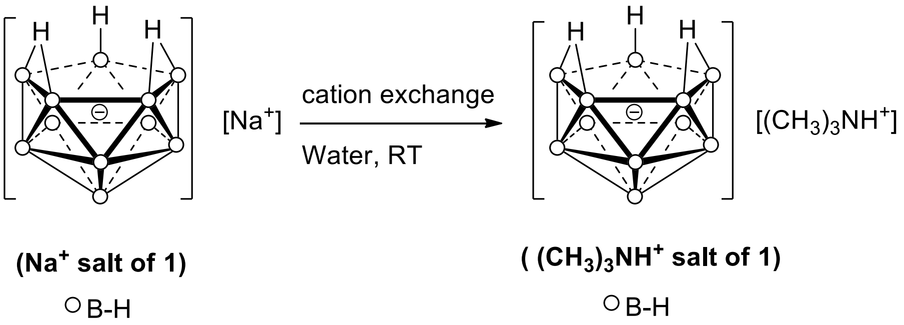
According to their studies, it was proposed an overall reaction for the synthesis of $B_{11}H_{14}^-$ from $NaBH_4$ (*Scheme 3.3*).

$$17NaBH_4 + 20BF_3.O(C_2H_5)_2 \longrightarrow 2NaB_{11}H_{14} + 15NaBF_4 + 20\ O(C_2H_5)_2 + 20H_2$$

Scheme 3.3. Synthesis of *nido*-undecaborate from $NaBH_4$

The yield of compound **1** was calculated according to this stoichiometry. However, this stoichiometry is for $[Na^+][B_{11}H_{14}^-]$, yield (41 %, assuming $NaBH_4$ is limiting reagent) was calculated for $[(CH_3)_3NH^+][B_{11}H_{14}^-]$ and assumed all synthesized sodium salts were converted to trimethylamine salt.

When the reaction was over, the reaction mixture was filtered to remove $NaBF_4$. The solution was evaporated careful enough not to dry it to dryness. As diglyme was lessened by evaporation, water was added to exchange diglyme with water. After all diglyme was evaporated with water, then water phase was taken out of rotary evaporator.



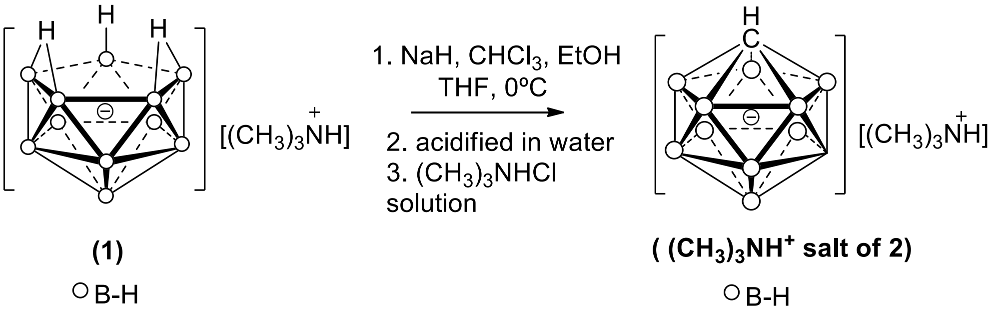
Scheme 3.4. Cation exchange reaction of **1**.

As shown in *Scheme 3.4*, cation exchange reaction was done for Na^+ salt of $B_{11}H_{14}^-$ to isolate this compound from water. Water was chosen as a solvent because $(CH_3)_3NH^+$ salt of *nido*-$B_{11}H_{14}^-$ has limited solubility in water. With the help of water-diglyme azeotrope, diglyme was removed from reaction medium. Na^+ salt of it can easily dissolve in water but trimethylammonium salt of it can be crystallized in water. $NaB_{11}H_{14}$ is pyrohoric. Hence, cation exchange reaction was done from Na^+ to $(CH_3)_3NH^+$, not only for isolation of compound but also to make the salt stable. ^1H

NMR of *nido*-$B_{11}H_{14}^-$ in d_6-acetone shows, B-H peaks ranging from 0.7-2.5 ppm due to boron coupling. This characteristic of *nido*-$B_{11}H_{14}^-$ ^1H NMR spectrum.

3.2. Synthesis of [$(CH_3)_3NH^+$][*closo*-$CB_{11}H_{12}^-$], (3)

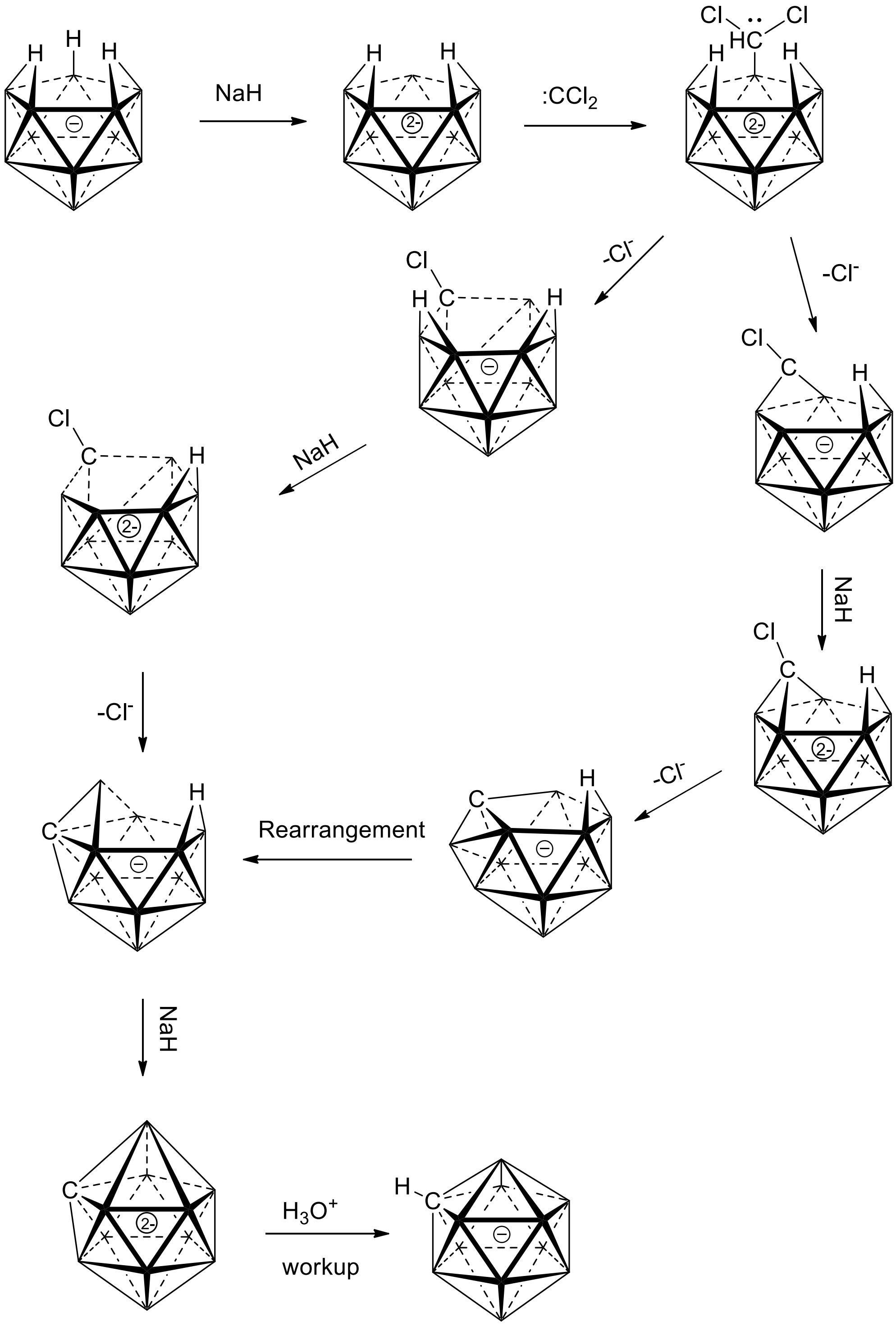
Before starting the synthesis of [$(CH_3)_3NH^+$][*closo*-$CB_{11}H_{12}^-$] (**3**), all required precautions should be taken.



Scheme 3.5. Reaction conditions for compound **2** according to Method 1.

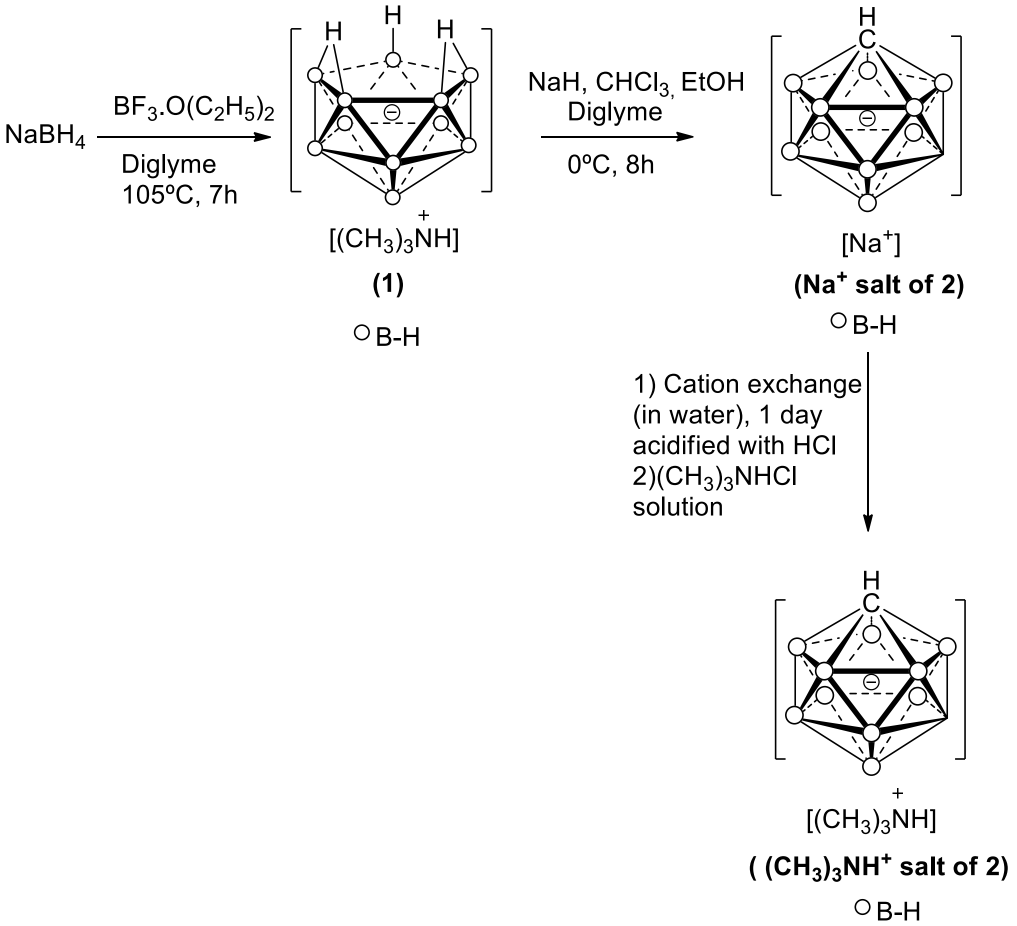
Synthesis of compound **2** is not easy in terms of safety. That in our laboratory, several minor incidents occurred during the synthesis. The minor accidents could turn into extremely large accidents in the hands of unexperienced researchers. As mentioned in the experimental part, two methods were performed for synthesize of compound **2**. First method is based on Michl's method (Franken et al., 2001). By dichlorocarbene insertion to compound **1**, compound **2** can be synthesized. As a starting material $B_{11}H_{14}^-$ was preferred because as it was explained above, it can be synthesized in our laboratories. For this synthesis, after three unsuccessful attempt that resulted with explosions, synthesis was successfully achieved. These explosions thought as that amount of NaH should be at same equivalent of $NaB_{11}H_{14}$. In the reference paper used NaH was 100 % on the other hand in these reactions 60% NaH in mineral oil was used and the amount was calculated according to 100 % NaH and with little excess amount which might lose during washing step. 60 % NaH was washed with hexane to remove mineral oil. Removel of mineral oil is important for the yield of reaction. The reaction was carried out in THF, first NaH was added to convert $(CH_3)_3NH^+$ into Na^+ salt and also convert *nido*-$B_{11}H_{14}^-$ into $B_{11}H_{13}^{2-}$. Then the solvent was removed to eliminate all the $(CH_3)_3N$. Dry salt was dissolved in dry THF which was put under argon atmosphere. Then two separate syringes, EtOH and $CHCl_3$ were added to this slurry slowly at 0 ºC. If temperature is ambient temperature, the reaction is so fast that it is difficult to control that the reaction explodes.

The formation mechanism of $CB_{11}H_{12}^-$ was studied by Josef Michl's group using computational methods (Rempala & Michl, 2003). Hydride abstracts one proton of cage and borane cage will become dianion. At this step *in situ* formed dichlorocarbene can be attached on boron atom whose proton was taken. At this step there is two different ways that both all them were plausible mechanisms. At the first one, the removal of chloride ion was continued by carbon insertion into the cage which still has one chloride on it. Then, it was assumed that mechanism goes on because of insoluble NaH. NaH continues to abstract protons from cage and with the acidic workup, cage was closed. At the second way, which is also possible that has lower activation energy during the removal of chloride ion and also hydronium ion by NaH. But has one more step than first one that cage reconstructs itself. (*Scheme 3.6*)



Scheme 3.6. Proposed mechanism for conversion of 1 to 2. B3LYP/6-31G (d,p) was used to calculate the reaction energies and activation barriers.(Rempala & Michl, 2003)

Method 2 was developed after explosions. Safety should be prior for scientists. *nido*-$B_{11}H_{14}^-$, (**1**), was not isolated in method 2 and reaction was continued in the same reaction flask to synthesis compound **2**.



Scheme 3.7. Reaction conditions for compound 2 according to Method 2.

Above mentioned reaction involves $B_{11}H_{14}^-$ as $(CH_3)_3NH^+$ salt. Then, to synthesize $CB_{11}H_{12}^-$ and separation, this compound was converted back Na^+ salt of it. This process was time consuming and involves risky steps in terms of safety. Therefore, we thought that after $[Na^+][B_{11}H_{14}^-]$ synthesis completed in diglyme and separation of $NaBF_4$ from the reaction mixture, we could treat $NaB_{11}H_{14}$ with NaH *in situ* then, treat them with EtOH and $CHCl_3$. This reaction also yields $[Na^+][CB_{11}H_{12}^-]$. However, the purification steps were lengthy and difficult. Synthesized $[Na^+][B_{11}H_{14}^-]$ was kept in diglyme which was reaction solvent at fridge until next step was achieved. It was assumed that formation yield of $[Na^+][B_{11}H_{14}^-]$ was 100 %. Hence, for the next step equivalents were calculated according to this assumption. Reaction solvent was homogeneous and taken portions assumed that have same amounts.

For the synthesis $CB_{11}H_{12}^-$, steps were followed which were explained in experimental part. To avoid any explosion, excess EtOH can be added to the reaction after all additions were completed to inactivate excess NaH. Solution was acidified with HCl to be sure from protonation of carborane cage. After finishing reaction, yellow oily matter was observed which needs purification. Purification steps took many times until obtaining crystals from reaction by recrystallization. All purification steps were done by methanol and water by changing their ratios. Changing ratio did not work so, separation was also done during these crystallizations. Product was as a trimethylamine salt which can precipitated in water and can be dissolved in MeOH. After many trials, all solvents were combined in order not to lose any product and then evaporated. After evaporation, 30 ml MeOH was added and oily matter was tried to be dissolved. Then filtration was done. 20 ml more MeOH was also added to wash undissolved oily substance. Dissolved part was yellow and residual matter was white. Collected MeOH phase was evaporated until approximately 5 ml solvent was left in the flask and 30 ml distilled water was added. Solution was kept at hood for two days to observe crystals. Formed crystals were filtered and same procedure was applied again. In that way, more purified products can be obtained.

3.3. Synthesis and Derivatization of *nido*-$B_{10}H_{14}$, (3)

For the synthesis of *nido*-$B_{10}H_{14}$, $NaB_{11}H_{14}$ is used as a starting material. Reaction setup is shown in *Figure 3.2*, $NaB_{11}H_{14}$ was used as synthesized without any purification. For the next step, water-diglyme azeotrope was also used to remove diglyme from reaction medium but with different way which was shown in *Figure 3.3* means by solvent exchange reaction. Dunks and coworkers were also synthesized decaborane(14) and their reaction conditions and setup were modified to our laboratory (Dunks, Palmer-Ordonez, & Hedaya, 1983). Highly complicated and high price glass equipment was not used in our laboratory. Setup was designed in a simplest way to do this reaction easily and in a safe manner.

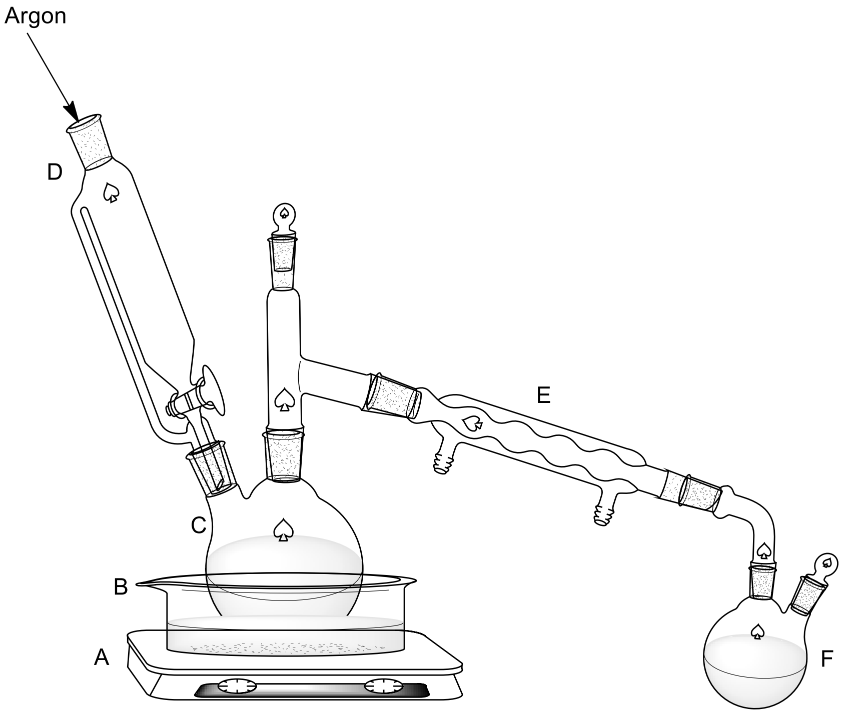


Figure 3.3. Simple distillation setup for the synthesis of *nido*-$B_{10}H_{14}^-$, **(4)**

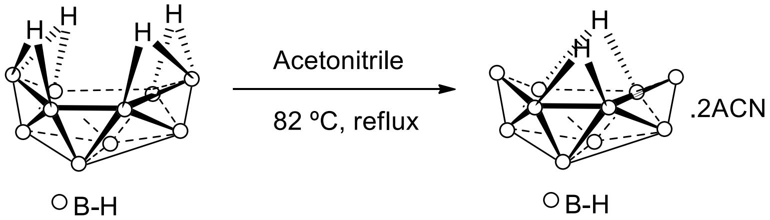
Figure 3.3 shows thermocouple magnetic stirrer (A), oil bath (B), two-necked round bottom flask, $NaBH_4$ in diglyme (C), dropper with gas equalizer, $BF_3.O(CH_2CH_3)_2$, H_2SO_4 aqueous solution and H_2O_2, respectively (D), condenser (E), round bottom flask to collect water (F).

While changing reaction setup from reflux to distillation setup, the reaction content was under argon gas. It is important to add water drop by drop in order to prevent bubbling and high pressure because of formation of H_2 and also to maintain same rate with the distillation. It is also necessary to give a vent to distillation apparatus in order not to pressurize the system. Solvent exchange step took three days until collecting 1 L of azeotrope solution. It might be better to use heating mantle in this step instead of oil bath to do faster distillation. After completed the addition of water to the diglyme solution of $NaB_{11}H_{14}$, $FeSO_4.5H_2O$ and cyclohexane were added to the solution slowly when reaction was in the ice bath. As $B_{10}H_{14}$ is hydrophobic material as it is formed, it is transferred into cyclohexane phase during the reaction. Aqueous solution of H_2SO_4 was cooled in the fridge not to add any hot solution to this exothermic reaction as described in the experimental section. Then 30 % H_2O_2 was added to the dropper and added slowly to the reaction mixture. During all these steps, reaction was in ice bath and ice was renewed all the time in order to maintain temperature at 25-30 ºC. Moreover, stirring should be always on and at high rate to maintain homogeneous solution. At this step, solution cannot be kept. It should be separated from water and precipitates. As mentioned before, decaborane is hydrophobic but when it stays in contact with water it starts to decompose to smaller borane cages. Hence, cyclohexane and water phases were separated immediately after filtration of reaction. During filtration more cyclohexane was used to wash precipitates and to collect all the product. Separation was done in extraction funnel and also cyclohexane phase was washed with water in order to remove other water soluble side products which were might still in the cyclohexane solution after filtration like $NaBF_4$, $B(OH)_3$ and Na_2SO_4. The presence of $B_{10}H_{14}$ was confirmed by addition of quinoline in a test tube in 1 ml cyclohexane decaborane solution. A red complex is formed. This red complex shows us the presence of $B_{10}H_{14}$ (Hill, Merrill, Russell, Hill, & Heacock, 1959). After observing red complex all decaborane product was converted to acetonitrile-decaborane complex to avoid from toxicity of decaborane and to easily undergo derivatization reaction. The decaborane acetonitrile complex was further characterized with IR spectroscopy. The peak at 2400 cm^{-1} shows the B-H stretching which is characteristic to borane cages. This is consistent with literature (Pérez, Sanz Miguel, & Macías, 2018). The reactions were summarized in *Scheme 3.8* and *Scheme 3.9*.

$$17NaBH_4 + 20BF_3.O(C_2H_5)_2 \longrightarrow 2NaB_{11}H_{14} + 15NaBF_4 + 20\ O(C_2H_5)_2 + 20H_2$$

$$2NaB_{11}H_{14} + 20H_2O + 8H_2O_2 + H_2SO_4 \longrightarrow B_{10}H_{14} + 12B(OH)_3 + 18H_2 + Na_2SO_4$$

Scheme 3.8. Overall reaction for the synthesis of *nido*-$B_{10}H_{14}$

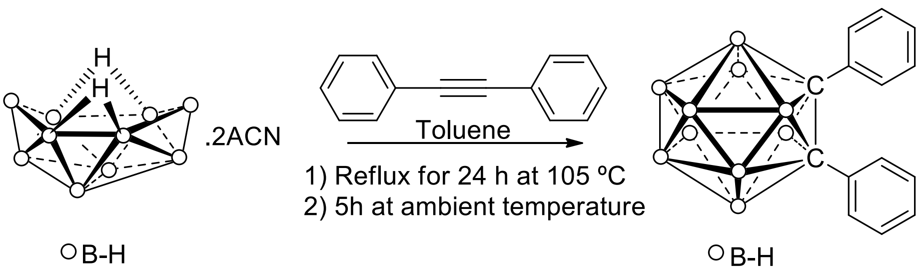


Scheme 3.9. Formation of acetonitrile-decaborane complex.

Decaborane(14) was kept in cyclohexane in order to prevent its contact with air. Hence, cyclohexane was taken with syringe from a closed round bottom flask and acetonitrile was added. Crystals were used as they are, that is, some cyclohexane stayed in reaction the medium. Cyclohexane does not have any effect to next step so, dodecaborane(14) was used as it is. Solution was taken to other closed round bottom flask with syringe for starting to this reaction. 60 ml of acetonitrile was added and condenser was set up upper side of the round bottom flask. Reaction was heated up to 82 ºC with thermocouple and refluxed during 2 hours then stirred at ambient temperature for a day. By decantation all solvent was removed.

3.4. Synthesis of *ortho*-carborane

Decaborane-acetonitrile complex is known to react with acetylenic compounds to form *ortho*-carborane derivatives. In order to prove this in our laboratories, we treated decaborane-acetonitrile complex with diphenyl acetylene under reflux conditions. The reaction yielded 1,2-Diphenyl dodecacarborane. The structure was confirmed by a ^{1}H NMR and ^{11}B NMR spectra. In ^{1}H NMR spectrum, the peaks around 7-7.5 ppm are for the protons on the phenyl rings. ^{11}B NMR of this compound shows the formation of Diphenyl *ortho*-carborane (Kahlert et al., 2015).



Scheme 3.10. Formation of 1,2-Diphenyl dodecacarborane(10)

Synthesized *ortho*-carborane was 1,2-Diphenyl dodecacarborane(10) which has two phenyl groups on carbon atom. Carbon atoms are in *ortho*-positions in borane cage. Reaction was performed by addition of diphenylacetylene to acetonitrile-dodecaborane cage and refluxing reaction at 105 ºC in toluene. By the evaporation of the solvent and purification by recrystallization in chloroform 1,2-Diphenyl dodecaborane(10) crystals were observed. ^{1}H NMR spectrum shows aromatic peaks.

3.5. Synthesis of *closo*-dodecaborate(12), $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$, (7)

Synthesis of dodecaborane **(7)** was also started from $NaBH_4$ which can be easily handed and found in laboratory conditions. Same setup was also used for this reaction (*Figure 3.2*). In this reaction, dropper with a pressure equalizing sidearm (D) was used to add I_2 in diglyme solution which was prepared one day before of the reaction. I_2 in diglyme solution was prepared one day before the reaction to prepare homogeneous I_2 solution because iodine solubility kinetics is slow in diglyme. However, with high rate stirring for many hours it can be dissolved completely. I_2 (62.66 g, 0.25 mmol) was added into 100 ml round bottom flask and closed with septum. Argon gas was provided with balloon and opening with one syringe to ensure gas cycling in the flask. Then diglyme was taken from stock solution which is sealed, by 50 ml syringe with portions until complete needed amount diglyme and argon gas was given to the stock solution with balloon by making pressure from inside then added to the round bottom flask which has I_2 inside. Addition was done slowly because bubbling. This solution was stirred for one day until starting to the reaction.

All setup was flushed with argon, $NaBH_4$ was added and stirring bar to a round bottom flask. Then, diglyme was added with syringe and stirring was started. Reaction was heated until 100 ºC and addition of I_2 in diglyme solution was started drop by drop (0.5 ml/min, approximately 2 hours and 30 minutes). 10 more ml diglyme was also used to wash out I_2 solids on dropping funnel. During the addition, insoluble $NaBH_4$ was slowly dissolved and yellow solution was observed. Dropping funnel was removed from setup and reaction was stirred overnight at 100 ºC and at 185 ºC for one day under argon atmosphere. During this heating $NaBH_4$ molecules formed $B_3H_8^-$ at 100 ºC and $B_3H_8^-$ molecules were disproportionate to $B_{12}H_{12}^{2-}$ and BH_4^- at 185 ºC and white solids were observed in solution (*Scheme 3.11*). During this reaction, hydrogen and some small boranes (like diborane) escape from reaction so, hood should be well ventilated. Moreover, escaped compounds were trapped in acetone to provide extra protection. Then, reaction was cooled to room temperature and diglyme was evaporated in rotary evaporator. White solids were remained after evaporation. The white solid was mainly composed of $NaB_{12}H_{12}$, $NaBH_4$ and NaI (*Scheme 3.11*).

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

$$5NaB_3H_8 \longrightarrow Na_2B_{12}H_{12} + 3NaBH_4 + 8H_2$$

Scheme 3.11. Formation equation for dodecaborane.

White solids were dissolved in 180 ml distilled water and addition of water was also slow because of hydrogen evaluation. Then 84 ml HCl (37%) in 100 ml water was added drop by drop again the same reason. At the reference study, concentrated HCl was used but in our study used concentrated HCl caused to dark brown particles in reaction medium immediately and lower the yield. Hence, used HCl was diluted in our study and added drop by drop. During this addition, color change was also observed from white to green, blue, pink and yellow, respectively. HCl addition was done to remove formed $NaBH_4$ from reaction medium as boric acid (Scheme *3.12*). Acidified solution was kept at -4 ºC in fridge for a night to give time crystallization of boric acids. Formed colorless boric acid crystals were removed from solution by vacuum filtration. Residue was checked by IR and found to be boric acid (3177.12 cm^{-1}, 1403.08 cm^{-1}, 1193.22 cm^{-1}). Filtrate was taken in round bottom flask and 150 ml $(CH_3CH_2)_3N$ was slowly added to the solution. During this addition color change was observed. Color change was observed from yellow, to red, to pink, to blue, to grey, to green and finally to white, respectively. Reaction was stirred overnight to complete precipitation of $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$.

$$NaBH_4 + HCl + 3H_2O \longrightarrow B(OH)_3 + NaCl + 4H_2$$

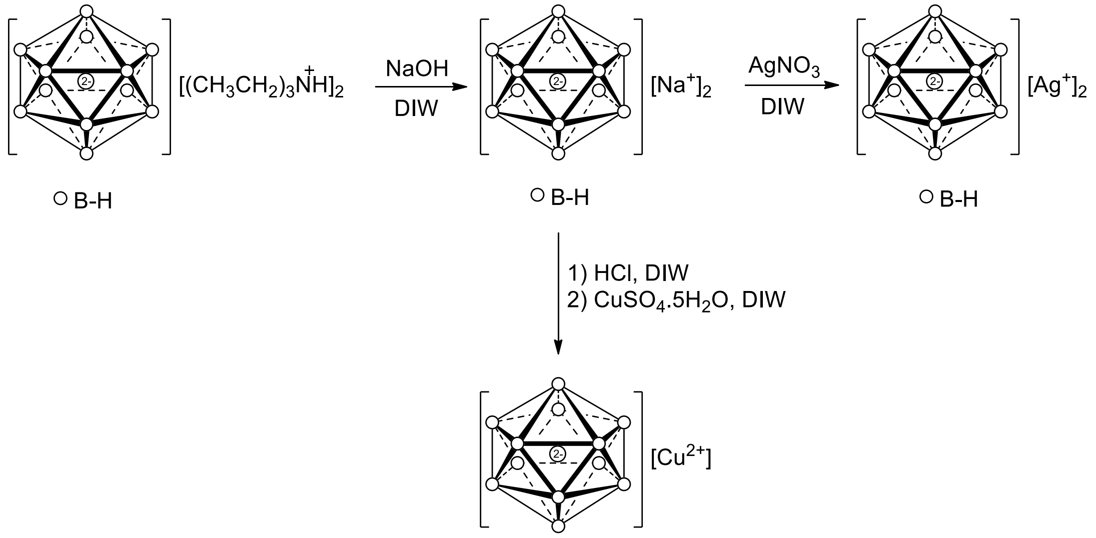
Scheme 3.12. Removal of sodium borohydride from reaction medium.

For further purification of $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$, recrystallization was done in hot water, alternatively, cold water was added to crystals and stirred for 6 hours then filtered to get purified $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ crystals. Boric acid is more soluble than $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ in water. This crystallization step was repeated three times until boric acid peaks disappeared from the IR spectrum.

$B_{12}H_{12}^{2-}$ was characterized by IR and ^{11}B NMR. IR spectrum shows a peak at 2476 cm^{-1} which is consistent with the literature (Geis et al., 2009). Furthermore, proton coupled ^{11}B NMR shows a doublet around -15 ppm.

3.6. Derivatization of dodecaborane, $B_{12}H_{12}^{2-}$

$[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$, (**6**) crystals were converted into $[Ag^+]_2$, (**7**) and $[Cu^{2+}]$, (**8**) salts and methylation reaction was done (Compound **9**). Then completely methylated dodecaborane anion was converted to $[Ag^+]_2$, (**10**) (*Scheme 3.13*).



Scheme 3.13. Cation exchange reaction of $B_{12}H_{12}^{2-}$

3.6.1. Formation of silver salt of $B_{12}H_{12}^{2-}$

For synthesis of $[Ag^+]_2[B_{12}H_{12}^{2-}]$, **(7)**, $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ was suspended in deionized water and experimental procedure was performed. NaOH was used to convert triethyl ammonium salt to sodium salt and $AgNO_3$ was added to form Ag^+ salt of $B_{12}H_{12}^{2-}$. When addition was finished, a solid compound precipitated. The solid is $Ag_2B_{11}H_{12}$ which is light sensitive. All lights at laboratory and light of hood was turned off and the reaction was filtered. Residue was washed with deionized water in order to remove water soluble impurities. Residue was dried to obtained compound **7** as a grey color powder. Product did not dissolve in any solvent so allowing only IR analysis, IR spectrum of $Ag_2B_{11}H_{12}$ was recorded and shown in *Figure 6.28.*

Carbocation formation could occur from organohalides. To abstract halogen atom from molecule, silver is facilitated. Silver halides precipitates and carbocation and anion remains in solution. If anion is a weakly coordinating anion like $B_{12}H_{12}^{2-}$or $CB_{11}H_{12}^-$, then carbocation will be naked and characterized in solution. That is why turning all boranes and carboranes into silver salt is a curial step for the characterization of carbocations.

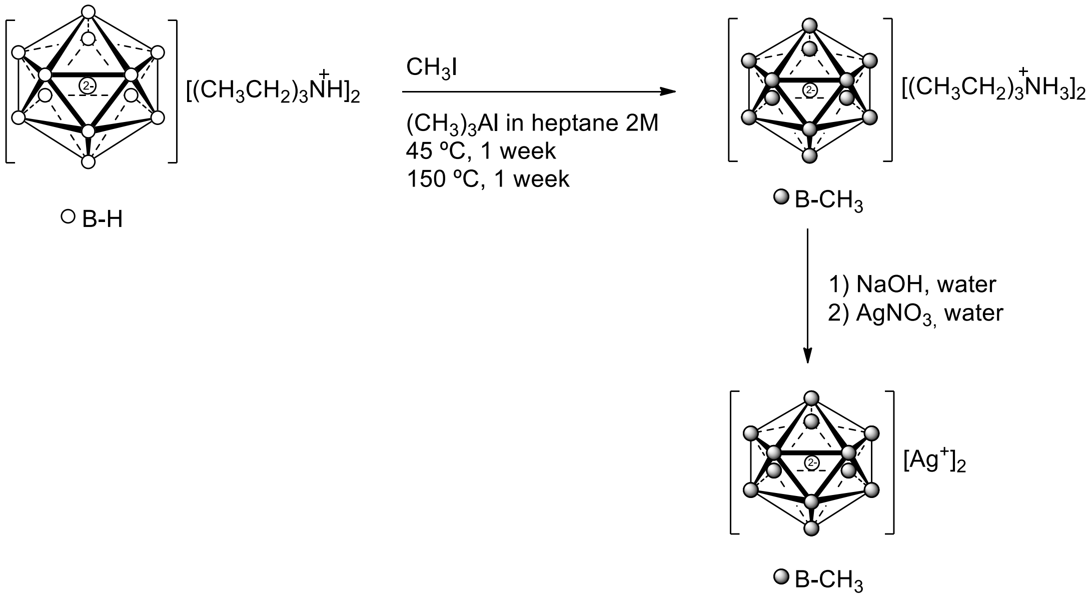
3.6.2. Formation of copper salt of $B_{12}H_{12}^{2-}$

In the synthesis of $[Cu^{2+}][B_{12}H_{12}^{2-}]$, (**8**), same procedure with the formation of silver salt until the evaporation of $(CH_3CH_2)_3N$ was applied. Then HCl (37 v %, 1 ml) was added drop by drop. $CuSO_4.5H_2O$ was added to the reaction medium and solvent was evaporated under reduced pressure to the dryness. 25 ml MeOH was added on blue solids and solution became green color with precipitated white Na_2SO_4. Na_2SO_4 was separated from solution by filtration and filtrate was evaporated. After evaporation solution was turned to brown solids on the glass of reaction flask.

Figure 3.4. Compound 8 in MeOH solution with white sodium sulphate precipitates at the bottom.

3.6.3. Methylation of $B_{12}H_{12}^{2-}$

Another derivatization reaction of $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ is methylation reaction (*Figure 3.14*). All boron atoms on the cluster will be methylated after this reaction. 100 ml one necked round bottom flask was taken, $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ (0.50 g, 1.45 mmol) was added. Magnetic stirring bar was also added and flask was closed with septum. Argon gas was given with balloon and opening was given by syringe head. Gas outlet with syringe head was given to reaction to prevent overpressure medium during additions. Then $(CH_3)_3Al$ (2 M in Heptane, 40.00 ml) was added slowly and reaction was stirred for 20 minutes until gas evaluation and white cloudiness disappeared from the reaction medium. Then CH_3I (3.00 ml, 48.00 mmol) was added slowly. Reaction was always under argon atmosphere and opening was still there until all cloudiness was disappeared from the reaction medium. After finishing additions, round bottom flask was taken into oil bath. Temperature was settled to 45 ºC and stirred for one week.



Scheme 3.14. Methylation of compound 6 and further reactions.

After one week, reaction was taken into sand-bath and settled with condenser. Before settled with condenser do not forget to grease sockets in order to prevent grip of glasses. Reaction temperature was raised to 150 ºC and stirred for one more week. After the heating process was completed, reaction was cooled to room temperature and solvent was evaporated. Formed solid part was stirred in n-pentane (50.00 ml) for 20 minutes and decantation was done. N-pentane addition can be also performed by two portions to remove all excess $(CH_3)_3Al$. Stayed n-pentane was taken with glass pipette and ethanol (50.00 ml) was added drop by drop because of bubbling. Then reaction was stirred for 1 hour at room temperature. Filtration was done with sintered frit glass funnel by vacuum filtration. Filter paper does not work on this step because of formed jelly like solids. Solids on sintered frit glass funnel was washed with distilled water and then solids were dissolved in acetonitrile (100.00 ml) and filtered. For further purification recrystallization can be done with EtOH:Acetonitrile (10:1) by hot filtration (50 ºC).

3.6.4. Formation of silver salt of $B_{12}(CH_3)_{12}^{2-}$

For the synthesis of $[(CH_3CH_2)NH^+]_2[B_{12}(CH_3)_{12}^{2-}]$, (**10**) (0.75 g, 1.45 mmol) was taken into 50 ml round bottom flask and 25.00 ml distilled water was added. Reaction was stirred for 5 - 10 minutes at ambient temperature to obtain homogeneous solution. However, compound **9** was not dissolved properly until the addition of NaOH (0.12 g, 2.90 mmol) for cation exchange reaction. Cation of the salt was converted from $(CH_3CH_2)_3NH^+$ to Na^+. NaOH was dissolved in distilled water, the alkaline solution was added to the triethyl ammonium salt. After addition and stirring for 30 minutes at ambient temperature, the reaction solution was evaporated at 90 ºC (Boiling point of $(CH_3CH_2)_3N$ is 89 ºC, for complete evaporation temperature was at 90 ºC). $AgNO_3$ (0.49 g, 2.90 mmol) was added into 25 ml round bottom flask which was covered with alumina foil and 10 ml deionized water was added. $AgNO_3$ solution was stirred for 15 minutes at ambient temperature and homogeneous solution was obtained. Before addition of $AgNO_3$ solution, the reaction flask was covered up with aluminum foil and the product was protected from light. $AgNO_3$ solution was added to reaction medium drop by drop. During the addition large quantity of dark brown solid compound precipitated, the reaction was stirred for 30 minutes at ambient temperature. Then all lights at laboratory and light of hood was closed and the reaction was extracted with Et_2O and water. Organic phase was dried on $MgSO_4$ and filtered. Organic solvent was evaporated to get the silver salt of permethylated dodecaborate.

3.7. Derivatization of dodeca-*closo*-carbaborane, $CB_{11}H_{12}^-$

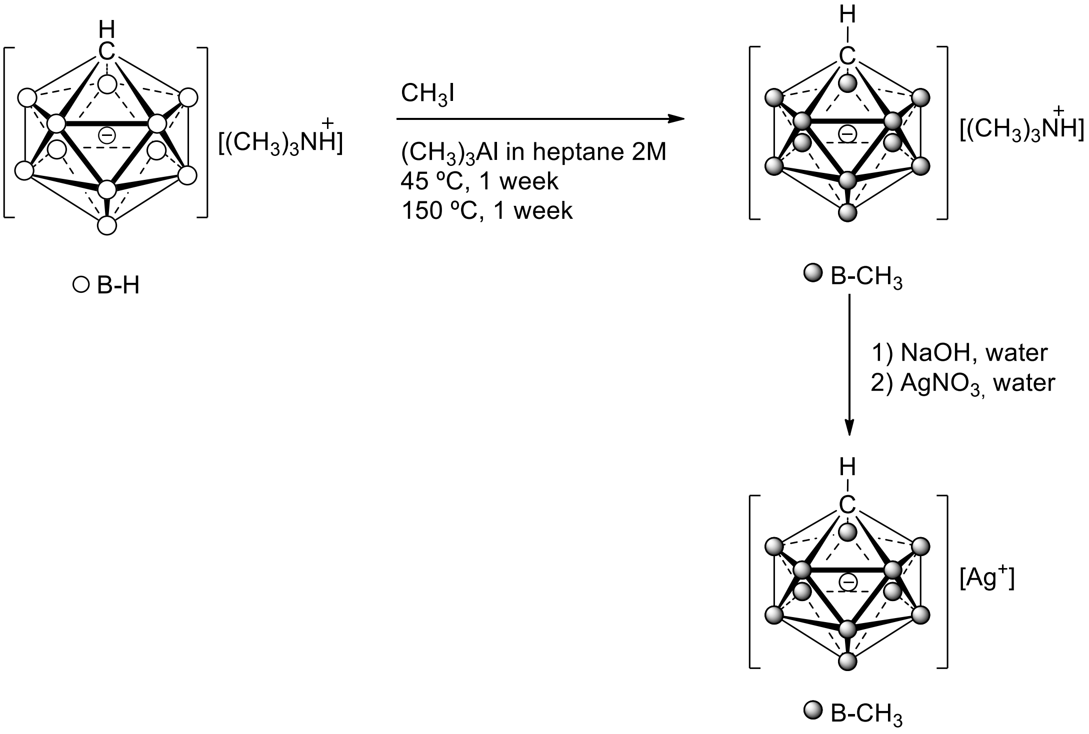
$[(CH_3)_3NH^+][CB_{11}H_{12}^{2-}]$, (**2**) crystals were methylated with above mentioned reaction. The same reaction conditions were applied to methylation of $CB_{11}H_{12}$ anion. Previously, such a reaction was accomplished with MeOTf (B. T. King, 2000). MeOTf is extremely reactive and toxic. Therefore elimination of this chemical from a reaction is desired.

For the methylation reaction, $[(CH_3)_3NH^+]$[*closo*-$CB_{11}H_{12}^-$] (0.09 g, 0.44 mmol) was added to the 50 ml round bottom flask which was flashed with argon and closed with septum. Argon was given with balloon and opening was given by syringe head. Gas outlet with syringe had was given to the reaction to prevent overpressure medium during additions until gas evaluation and white cloudiness were disappeared from the reaction medium. $(CH_3)_3Al$ (2 M in Heptane, 10.00 ml) was added with syringe. Then CH_3I (0.91 ml, 14.56 mmol) was added slowly, then, round bottom flask was taken into oil bath. Until addition of CH_3I, dissolvation of reactant could not be observed. Temperature was settled to 45 ºC and stirred for one week. After one week, the reaction was taken into sand bath and settled with condenser. The reaction was stirred at 150 ºC for one more week. Before settled with condenser do not forget to grease sockets in order to prevent grip of glasses. After one week stirring at 150 ºC, the reaction was cooled to room temperature and the solvent was evaporated. Stayed solid part was stirred in n-pentane (20.00 ml) for 20 minutes and decantation was done. N-pentane addition can also be done by two portions to remove all excess $(CH_3)_3Al$. Stayed n-pentane was taken with glass pipette. Ethanol (20.00 ml) was added and stirred for 1 hour at room temperature. Filtration was done with sintered frit glass funnel by vacuum filtration. Solids on sintered frit glass funnel was dissolved with water, collected in round bottom flask and $(CH_3)_3N.HCl$ (0.10 g, 1.00 mmol) was added to convert all product to $(CH_3)_3NH^+$ salt. Then, the reaction solution was stirred for 20 minutes at ambient temperature. 1 ml CH_3OH was added for crystallization and kept in hood. CH_3OH can dissolve product completely and in water $(CH_3)_3NH^+$ salts can be precipitated so, they were chosen as a crystallization solvent with water. Formed crystals were filtered and dried on filter paper. Then, dissolved with acetone (10.00 ml) and solvent was evaporated. Acetone was used to purify product. While waiting for crystallization, little excess amount $(CH_3)_3N.HCl$ can also be precipitated. Hence, acetone was used that only dissolve product not $(CH_3)_3N.HCl$.

3.7.1. Formation of Silver salt of $HCB_{11}(CH_3)_{11}^-$

Reaction was done in 50 ml round bottom flask and $[(CH_3)_3NH^+]$[*closo*-$HCB_{11}(CH_3)_{11}^-$] (0.10 g, 0.29 mmol) was added into 20 ml deionized water. Then, NaOH (0.04 g, 1.05 mmol) was added and stirred at room temperature for 20 minutes.

Reactant cannot be dissolved in deionized water until the addition of NaOH for cation exchange reaction. Cation of the reactant was change to Na^+ from $(CH_3)_3NH^+$ after this step. Volatiles were removed under reduced pressure until half of the solvent was evaporated. Round bottom flask was covered with aluminia foil to protect product from light. $AgNO_3$ solution (0.05 g, 0.30 mmol) was prepared in 10.00 ml deionized water in the 25 ml round bottom flask which was also covered with aluminia foil and was added drop by drop to the reaction medium. Color of the solution turned to dark brown from yellow during addition of $AgNO_3$ solution. Reaction was stirred at room temperature for 1 hour. Then all lights at laboratory were closed and extraction was done with Et_2O. Organic phase was dried over $MgSO_4$ and filtered then evaporated. Extraction was done to remove water soluble side products like $NaNO_3$.



Scheme 3.15. Methylation of $CB_{11}H_{12}^-$ and further reactions.

CHAPTER 4

CONCLUSIONS

In this study, feasibility of synthesis of boron cages and carboranes were examined in our laboratories. The synthesis of such cages were successfully synthesized in our laboratories. Eleven and twelve vertex boron cages are relatively stable and were synthesized from $NaBH_4$. Synthesis of such compounds are relatively hard and long in terms of safety. This study proved that such synthesis could be done as experience gained with many failed experiments with minor accidents.

This study also proved that all of the carborane cages could be synthesized from $NaBH_4$, a relatively cheap and easy to handle compound. The hydride was converted to undecaborate cage with action of a Lewis acid, BF_3. Undecaborate was either converted to decaborane through an oxidation reaction or used as it is for the synthesis of $CB_{11}H_{12}^-$. Although these borate sodium salts are soluble in water, their $(CH_3)_3NH^+$ salts are insoluble. This makes isolation of these compounds affordable. The $(CH_3)_3NH^+$ salts are soluble in ethanol and methanol. With $CB_{11}H_{12}$ anion in hand, this compound could be converted to $CB_{11}(CH_3)_{11}H$ anion to increase the solubility of the salts in nonpolar solvents. Such a process previously done with MeOTf and CaH_2 in sulfolane. In this study, we discovered that CH_3I and $Al(CH_3)_3$ could do the methylation on $CB_{11}H_{12}$ anion where hydrides exchange with methyl group. It was also shown that the methylated carborane anion's cation could easily be exhnaged with other cations (With this many nacked cations could be prepared in our laboratories.). Such compounds could be used to capture carbocations and characterize them.

Decaborane(14) was also successfully synthesized from $B_{11}H_{14}^-$. The decaborane was proven to converted to o-carborane derivatives with acetylenic substances.

$B_{12}H_{12}^{2-}$ was also synthesized in the course of this study. The boron cage was synthesized from $NaBH_4$ with action of I_2. The dianion was converted to $B_{12}Me_{12}^{2-}$ with MeI in the presence of $AlMe_3$. This permethylated dianion could also be used in many cations counter anions. These, in turn, could be used in catalysis reactions or capturing different reactive dications.

In short, this thesis proved that the strategically important boron and carborane cages could be synthesized in our laboratories. These compounds could also be further derivatized for many potential applications. Such synthesis need to be done by experienced persons. This experience was also gained through this study.

CHAPTER 5

EXPERIMENTAL

5.1. Methods and Materials

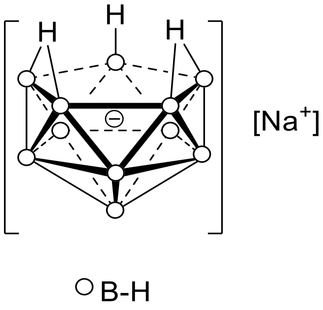
Caution ! During these reactions all required precautions should be taken! Gas mask, gloves, lab clothes and goggles should be used. All experiments should be done under good ventilated hood.

Structural determinations of compounds were done with the instruments as written below. ^{1}H and ^{13}C nuclear resonance spectra of compounds were recorded in $CDCl_3$, d_6-DMSO, d_6-Acetone and D_2O with Bruker Avance III Ultrashield 400 Hz NMR spectrometer. Chemical shifts were given in parts per million (ppm) with TMS as internal reference or with the chemical shift of the solvent which is also referenced to TMS. ^{11}B NMR spectra of compounds were recorded in 5 ml d_6-Acetone and D_2O with Magritek Spinsolve benchtop 60 MHz NMR spectrometer. ^{1}H, ^{13}C and ^{11}B NMR spectra of products were given in Appendix A. NMR spectra were processed with MestReNova processor.

Infrared spectra were recorded with Thermo Scientific Nicolet iS10 ATR-IR spectrometer. Peak positions were reported in reciprocal centimeter (cm^{-1}). IR spectra of products were given in Appendix B. IR spectra were further processed with OriginPro 2016 program.

All starting materials and solvents were purchased from Sigma Aldrich and were used without further purifications.

5.2. Synthesis of $[Na^+][\textit{nido}\text{-}B_{11}H_{14}^-]$, (1) (Dunks & Ordonez, 1978)

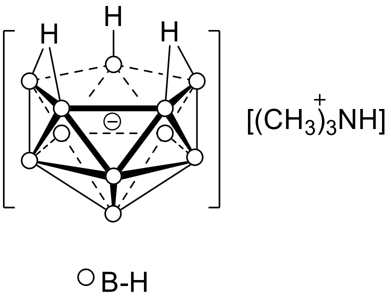


$NaBH_4$ (30.00 g, 0.79 mol) was added into three necked round bottom flask and a big stirring bar was used to stir reaction. One neck of the round bottom flask was used for dropper, second one closed with septum and used for solvent addition. Argon gas was purged through all the setup (*Figure 3.2*) and diglyme (230.00 ml) was taken with syringe from sealed diglyme glass bottle and was added to the round bottom flask. Reaction was stirred and heated until 105 ºC. Dropping funnel was filled with $BF_3.O(C_2H_5)_2$ (195.70ml, 1.60mol) and when reaction temperature rich to 105 ºC, $BF_3.O(C_2H_5)_2$ addition was started drop by drop from dropping funnel. Precipitates were formed during addition. After completion of addition reaction was stirred one more hour at 105 ºC, then cooled to room temperature. Reaction color was yellow. Reaction solution was filtered from medium frit with pump. Until all precipitates were formed to white color, they were washed with diglyme. Our product was in diglyme solution and without isolation it was used for further reaction.

Caution !

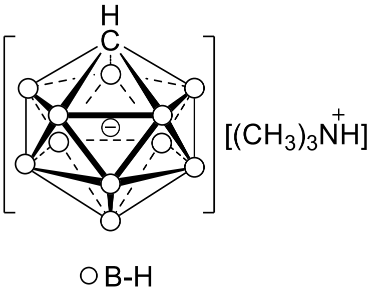
During this reaction because of hydrogen evolution and other small boron cages, acetone trap should be used and all required precautions should be taken before starting to this experiment.

5.3. Cation exchange of Compound 1 from Na$^+$ to (CH$_3$)$_3$NH$^+$



Diglyme solution of sodium salt of compound **1** was evaporated until half of it evaporated with rotary vacuum evaporator and drop by drop distilled water (as 50 ml portions totally 300 ml) was added and continued to evaporation of azeotrope solution (diglyme and water). This step was repeated six times until all diglyme was evaporated. $(CH_3)_3N.HCl$ (40.00 g, 0.40 mol) was added in to the homogeneous solution of compound **1** (sodium salt) and water. Immediately white crystals were formed and collected with filtration by using medium frit pump filtration. For further purification acetone recrystallization or washing with diethyl ether to remove yellow impurities can be done. Yield; 6.00 g, 0.031 mol, 41 %.

5.4. Synthesis of [(CH$_3$)$_3$NH$^+$][*closo*-CB$_{11}$H$_{12}^-$], (2) (Franken et al., 2001)



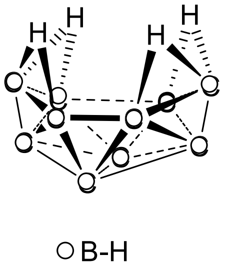
Method 1

Trimethylamine salt of compound **1** (6 g, 31.06 mmol) was dissolved in fresh distilled THF (120.00 ml) in the one necked round bottom flask. Argon gas was given to reaction and reaction medium was cooled to 0 ºC in an ice bath. NaH (60 w%, 20.00 g, 0.53 mol) was firstly washed with hexane (50 ml) to remove mineral oil and added to reaction slowly at 0 ºC. Remaining NaH solution was washed with ethanol. After 30 min stirring at room temperature THF was evaporated to dryness under reduced pressure. After evaporation 100 ml THF and 5 ml $CHCl_3$ were added slowly and respectively to reaction. Reaction mixture was stirred for 2 hours at room temperature and ethanol (10 ml) was added drop by drop at 0 ºC and continued to stir reaction solution for 4 hours at ambient temperature. All reactions were performed under argon atmosphere. Distilled water (150 ml) was added drop by drop and THF was evaporated under reduced pressure. The reaction solution was acidified by addition of HCl (37 v%, 25.00 ml in 40.00 ml distilled water). Acidification was monitored with blue litmus paper. Residual THF and ethanol were also evaporated. $Me_3N.HCl$ (7.00 g, 73.24 mmol) was added to aqueous reaction mixture and white precipitates were formed. Solution was filtered and precipitates was collected. For further purification, methanol/hot water (1:9) recrystallization was done to yield 1.5 g of compound **2** (7.38 mmol, 23.82 %).

Method 2

Diglyme solution of compound **1** (50 ml solution; 2.00 g, 13.00 mmol $NaB_{11}H_{14}$) was taken with syringe and added into the 250 ml round bottom flask which is closed with septum and filled with argon gas. Reaction was stirred at 0ºC in an ice-bath. NaH (4.40 g, 0.18 mol) was taken in a small beaker and washed with 20 ml distilled hexane. By decantation hexane and NaH was separated and nearly dry NaH was slowly added to the round bottom flask with spatula. After addition was completed, flask closed with septum and argon gas was given in a medium. Then, ethanol (10.00 ml) and $CHCl_3$ (5.00 ml) was taken in a same syringe and two reagents were mixed and added drop by drop to the round bottom flask at 0 ºC. Reaction was stirred at room temperature for overnight, then solvent was evaporated under reduced pressure. Water (40.00 ml) was added for solvent exchange and continued to evaporation to complete removal diglyme evaporation. After evaporation yellow precipitate was acidified with 37 v% 8.00 ml HCl in 60.00 ml water. Me_3NHCl (12.00 g, 0.13 mol) was added to water solution of the reaction and white precipitates were formed. Solution was filtered and precipitates were collected. For further purification, methanol/hot water (1:9) recrystallization was done to yield 1.02 g (4.90 mmol 5.25 %) in overall reaction.

5.5. Synthesis of *nido*-$B_{10}H_{14}$, (3)

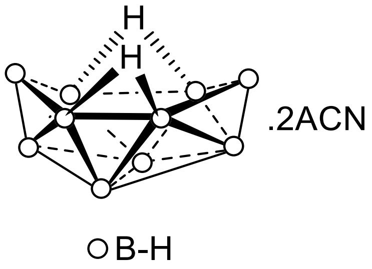


Caution!

nido-$B_{10}H_{14}$(decaborane) is neurotoxic matter. All lab safety equipments should be used. Most importantly proper gas mask has to be used.

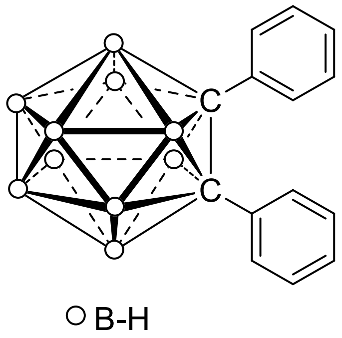
$NaBH_4$ (30.00 g, 0.79 mol) was introduced in 500 ml 2 necked round bottom flask as shown in *Figure 3.2*, then argon gas was given to the reaction medium and diglyme (250.00 ml) was added by syringe. Reaction was heated to 105 ºC. Dropping funnel was filled with $BF_3.O(C_2H_5)_2$ (195.74 ml, 1.59 mol) and when reaction temperature reach to 105 ºC, $BF_3.O(C_2H_5)_2$ addition was started drop by drop from dropping funnel over 8 hours. Precipitates were formed during addition. Reaction was stirred for 1 more hour at 105 ºC and cooled to room temperature. Condenser was changed with simple distillation apparatus (*Figure 3.3*) and distilled water (totally 785 ml) was added drop by drop while the reaction was heated until 125 ºC. After collecting 1 L diglyme-water azeotrope solvent reaction was cooled down to room temperature and taken into the ice bath. $FeSO_4.7H_2O$ (2.5 g, 8.99 mmol) and 125 ml cyclohexane were added. 18 ml H_2SO_4 in 18ml distilled water was cooled in fridge, then filled to the dropper and added drop by drop in an ice bath. After finishing this addition, H_2O_2 (40.00 ml, 30 v %) was added to the dropper and added very slowly to the reaction in an ice bath. Reaction was stirred 20 more minutes in an ice bath and filtered using filter paper. Filter cake was washed with 100 ml cyclohexane and cyclohexane phase washed with water, then evaporated at room temperature until crystal formation was observed and kept in fridge until crystallization was completed. Yield of this reaction was not determined because of neurotoxic property of decaborane. It is kept in cyclohexane and never dried or exposed to air. It was treated with acetonitrile for the next steps.

5.6. Synthesis of bis-(acetonitrile)-decaborane$(CH_3CN)_2B_{10}H_{12}$, (4)



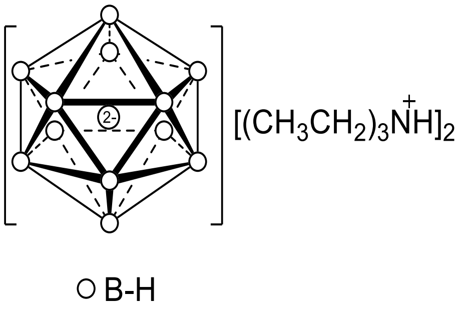
Compound **3** was kept in cyclohexane in closed round bottom flask. To remove cyclohexane from reaction medium syringe was used and stayed crystals were dissolved in acetonitrile (60.00 ml) and were taken into closed round bottom flask with syringe. Reaction was heated up until 82 ºC and refluxed for 2 hours and stirring was continued for one day at ambient temperature. By decantation solvent was removed from solids. Resultant product was 3.98 g (19.67mmol, 42.17 %)

5.7. Synthesis of 1,2-diphenyl dodecacarborane(10), (5)



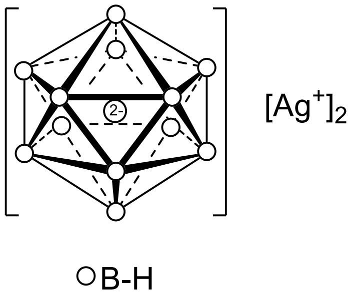
2.50g (12.58 mol) of bis-(asetonitrile)-decaborane (**4**) was taken into 100 ml round bottom flask and diphenylacetylene (2.24 g, 12.58 mol) was added with toluene (100.00 ml). Reflux was set at 105 ºC for 24 hours and stirred for 5 hours at ambient temperature. Solvent was evaporated under reduced pressure and recrystallization was done in chloroform and crystals were filtered. Mass of product was 2.57 g (8.67 mmol, 68.96 %).

5.8. Synthesis of *closo*-dodecaborate(12), $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$, (6)



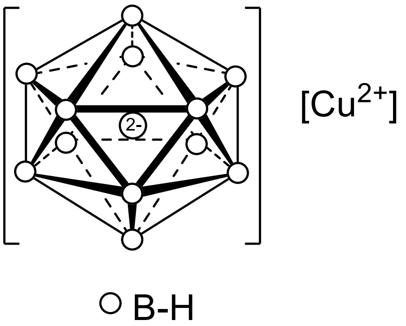
$NaBH_4$ (30.00 g, 0.79 mol) was introduced in 500 ml 3 necked round bottom flask. One of the neck of the round bottom flask was used for dropper, second one closed with septum and used for solvent addition and third one was used for condenser. Argon gas was given to all the setup and diglyme (200.00 ml) was taken with syringe from sealed diglyme glass bottle and was added to the round bottom flask. Reaction was stirred and heated until 100 ºC. Dropping funnel was filled with I_2-diglyme solution (62.66 g, 0.25 mmol of I_2 in 70.00 ml diglyme) and when reaction temperature rich to 100 ºC, I_2 addition was started drop by drop from dropping funnel. Precipitates were formed during addition. After completion of addition, the reaction was stirred overnight at 100 ºC, then temperature of the oil bath was increased to 185 ºC and stirred for one day . Reaction was cooled to room temperature and diglyme was evaporated. Distilled water (180.00 ml) was added very slowly and 84 ml HCl (37 %) in 100 ml distilled water was added drop by drop. Reaction was kept at fridge for a night to precipitation of boric acid. Precipitated colorless crystals were filtered by vacuum filtration and filtrate was taken in a new round bottom flask. 150 ml $(CH_3CH_2)_3N$ was added and stirred for overnight to complete precipitation. Colorless crystals were observed and filtered. For further purification recrystallization can be done with hot distilled water or $[(CH_3CH_2)NH^+]_2[B_{12}H_{12}^{2-}]$ crystals can be stirred in distilled water for 5 or 6 hours to remove more soluble boric acid from product. Product was 3.68 g (10.64 mmol, 20 %).

5.9. Synthesis of Silver salt of *closo*-dodecaborate(12), $[Ag^+]_2[B_{12}H_{12}^{2-}]$, (7)



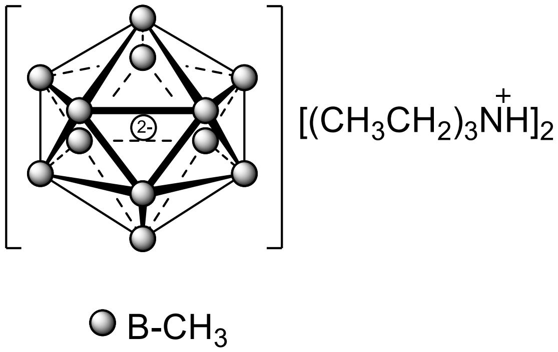
$[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ (0.10 g, 0.29 mmol) was dissolved in deionized water (25 ml) and stirred for 5 minutes. Then NaOH (0.02 g, 1.20mmol, 4 Eq) was added into this solution (in 100 ml round bottom flask). $AgNO_3$ (98.5 mg, 0.58 mmol, 2 Eq) was dissolved in 10 ml deionized water in 50 ml round bottom flask. $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ solution was evaporated to half. Silver nitrate solution was added drop by drop into $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ solution. Since the product and reaction are light sensitive, during this addition $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ round bottom flask was covered with aluminum foil and the product was protected from light. During addition large quantity of solid compound precipitated. After addition was completed, the reaction was stirred for 45 minutes at room temperature. Then, reaction mixture was filtered and the residue was washed with deionized water, dried to obtained the silver salt of *closo*-dodecaborate(12). Product was dark grey solid powder (0.09 g, 0.25 mmol, 86.21 %).

5.10. Synthesis of Copper salt of *closo*-dodecaborate(12), $[Cu^{2+}][B_{12}H_{12}^{2-}]$, (8)



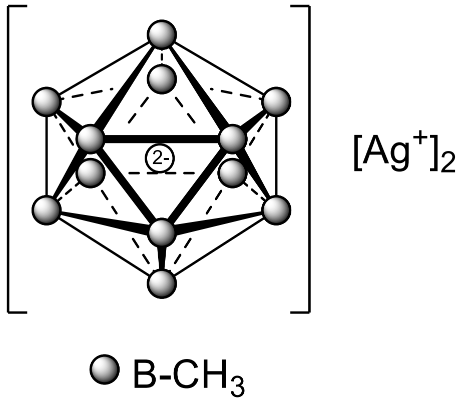
$[(CH_3CH_2)_3NH]_2[B_{12}H_{12}^{2-}]$ (0.06 g, 0.17 mmol) was dissolved in distilled water and NaOH (0.10 g, 2.50 mmol) was added and stirred for 10 minutes at room temperature. Half of solution was evaporated and 1 ml HCl (37 v %) was added drop by drop and stirred. $CuSO_4.5H_2O$ (0.43 g, 1.72 mmol) was added and reaction solution was evaporated to dryness. MeOH (25.00 ml) was added and formed precipitate (Na_2SO_4) was filtered. Filtrate was evaporated. Product was 32.76 mg (0.16 mmol, 93.83 %)

5.11. Synthesis of undecamethyl-*closo*-dodecaborate, $[(CH_3CH_2)NH^+]_2[B_{12}(CH_3)_{12}^{2-}]$, (9)



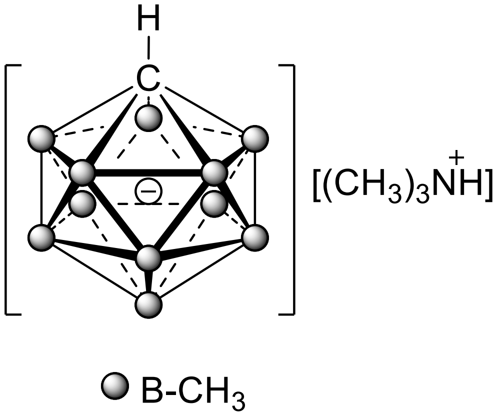
Suspension of $[(CH_3CH_2)_3NH^+]_2[B_{12}H_{12}^{2-}]$ (0.50 g, 1.45 mmol) in $(CH_3)_3Al$ (2M in heptane, 40.00 ml) was prepared in 100 ml round bottom flask which was flashed with argon gas and closed with septum. Gas outlet was also given to reaction to prevent overpressure medium. Then CH_3I (3.00 ml, 48.00 mmol) was added slowly and round bottom flask was taken into oil bath. Temperature was settled to 45 ºC and stirred for one week. After one-week reaction was taken into sand-bath and settled with condenser. Reaction was stirred at 150 ºC for one more week. After this procedure reaction was cooled to room temperature and solvent was evaporated. Solid part was stirred in n-pentane (50.00 ml) for 20 minutes and decantation was done. Ethanol (50.00 ml) was added and stirred for 1 hour at room temperature. Filtration was done with sintered frit glass funnel by vacuum filtration. Solids on sintered frit glass funnel was washed with distilled water and then solids were dissolved in acetonitrile (100.00 ml) and filtered. Organic solvent was evaporated. For further purification recrystallization can be done with EtOH:Acetonitrile (10:1) by hot filtration (50 ºC). Product was 0.74 g (1.45 mmol, 100 %)

5.12. Synthesis of silver salt of dodecamethyl-*closo*-dodecaborate, $[Ag^+]_2[B_{12}(CH_3)_{12}^{2-}]$, (10)



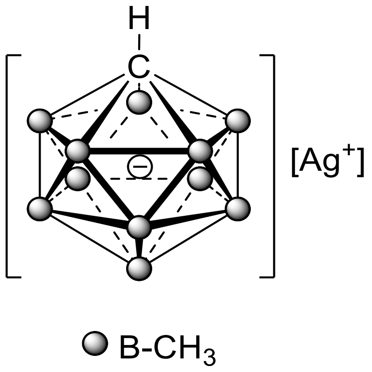
$[(CH_3CH_2)NH^+]_2[B_{12}(CH_3)_{12}^{2-}]$ (0.75 g, 1.45 mmol) was taken into 50 ml round bottom flask and 25.00 ml distilled water with 0.12 g NaOH (2.90 mmol) was added. Volatiles were evaporated under reduced pressure. $AgNO_3$ (0.49 g, 2.90 mmol) was added and brown precipitates were observed. Extraction was done with Et_2O and water. Organic phase was dried on $MgSO_4$ and filtered. Organic solvent was evaporated.

5.13. Synthesis of undecamethyl-*closo*-dodecacarbaborate, $[(CH_3)_3NH^+]$[*closo*-$HCB_{11}(CH_3)_{11}^-$], (11)



Suspension of $[(CH_3)_3NH^+]$[*closo*-$HCB_{11}H_{11}^-$] (0.09 g, 0.44 mmol) in $(CH_3)_3Al$ was prepared in the 50 ml round bottom flask which was flashed with argon and closed with septum. $(CH_3)_3Al$ (2 M in Heptane, 10.00 ml) was added with syringe. Gas outlet was also given to reaction to prevent overpressure medium. Then CH_3I (0.91 ml, 14.56 mmol) was added slowly and round bottom flask was taken into oil bath. Temperature was settled to 45 ºC and stirred for one week. After one week reaction was taken into sand-bath and settled with condenser. Reaction was stirred at 150 ºC for one more week. After this procedure reaction was cooled to room temperature and solvent was evaporated. Solid part was stirred in n-pentane (20.00 ml) for 20 minutes and decantation was done. Ethanol (20.00 ml) was added and stirred for 1 hour at room temperature. Filtration was done with sintered frit glass funnel by vacuum filtration. Solids on sintered frit glass funnel was dissolved with water and $(CH_3)_3N.HCl$ (0.10 g, 1.00 mmol) was added and the reaction solution was stirred. 1 ml CH_3OH was added and kept in hood for crystallization. Formed crystals were filtered and dried on filter paper then, dissolved with acetone (10.00 ml) and the solvent was evaporated. Product was 0.10 g (0.29 mmol, 65.62 %)

5.14. Synthesis of silver salt of undecamethyl-*closo*-dodecacarbaborate, $[Ag^+][closo\text{-}HCB_{11}(CH_3)_{11}^-]$, (12)



$[(CH_3)_3NH^+][closo\text{-}HCB_{11}(CH_3)_{11}^-]$ (0.10 g, 0.29 mmol) was added into 20 ml deionized water containing NaOH (0.04 g, 1.05 mmol) and stirred at room temperature for 20 minutes. Volatiles were removed under reduced pressure. Round bottom flask was covered with aluminia foil and $AgNO_3$ solution (0.05 g, 0.30 mmol in 10.00 ml deionized water) was added drop by drop. Color of the solution turned to dark brown from yellow during addition of $AgNO_3$ solution. Reaction was stirred at room temperature for 1 hour then, extraction was done with Et_2O and deionized water. Organic phase was dried over $MgSO_4$ and filtered then evaporated.

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APPENDICES

A. NMR Spectra

^{1}H and ^{13}C NMR spectra was recorded at Bruker Avance III Ultrashield 400 MHz using $CDCl_3$, d_6-DMSO, d_6-Acetone and D_2O as solvents. $_{11}$B nuclear magnetic resonance spectra of compounds were recorded in 5 ml d_6-Acetone and D_2O with Magritek Spinsolve benchtop 60 MHz NMR spectrometer.

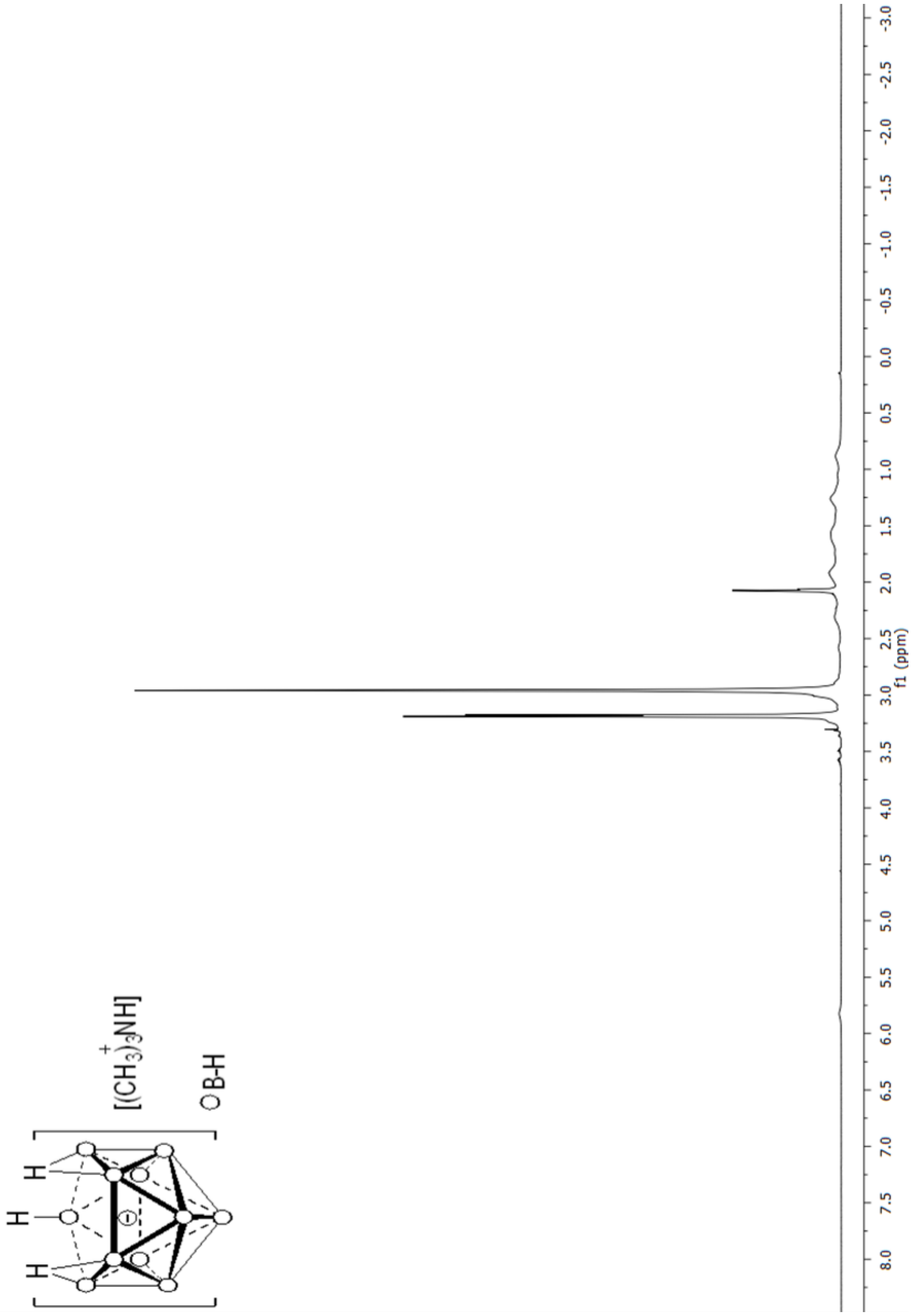

Figure 6.1. ^{1}H NMR Spectrum of **1** in d_6-acetone.

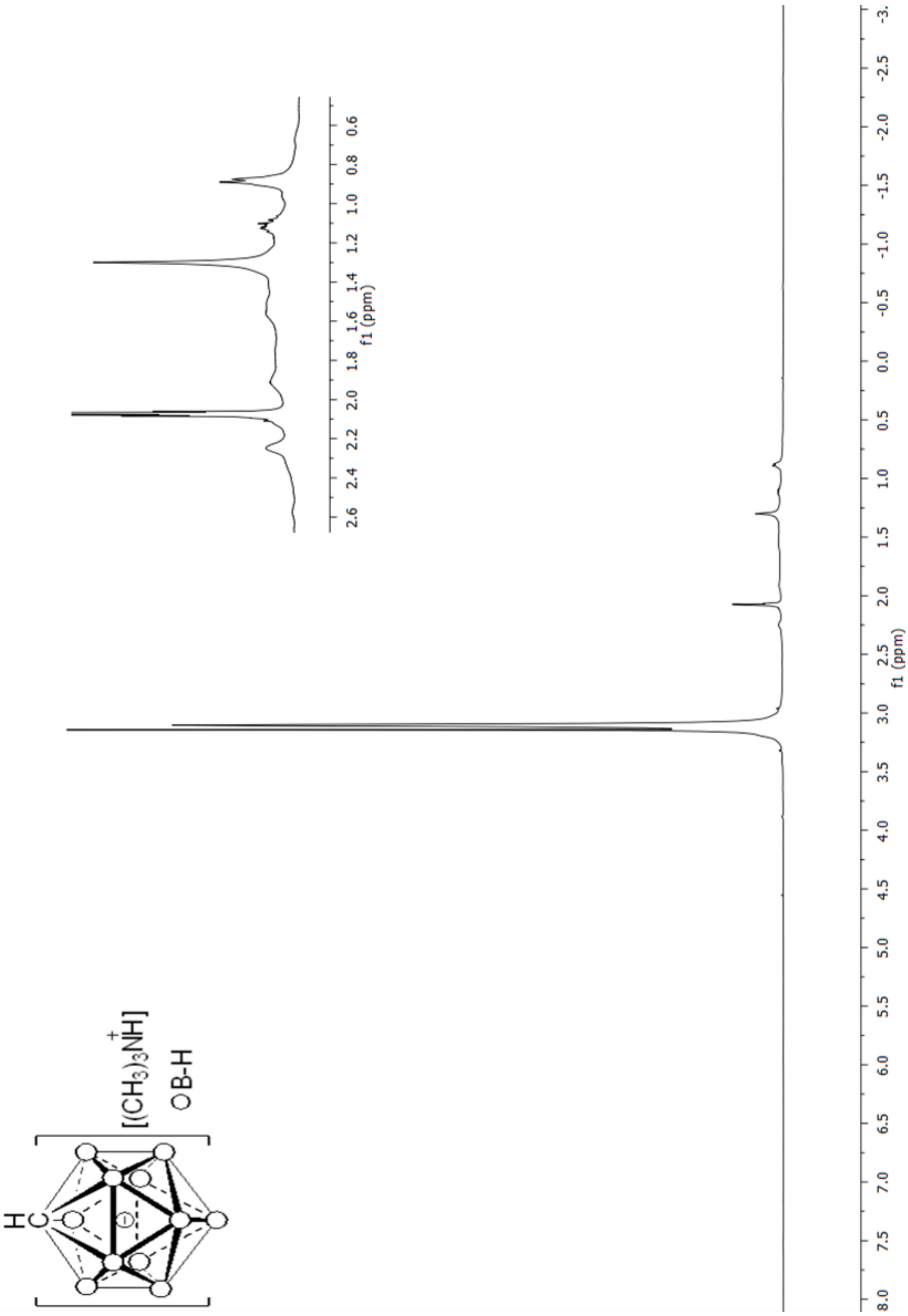

Figure 6.2. ^{1}H NMR Spectrum of **2** in d_6-acetone, method 1.

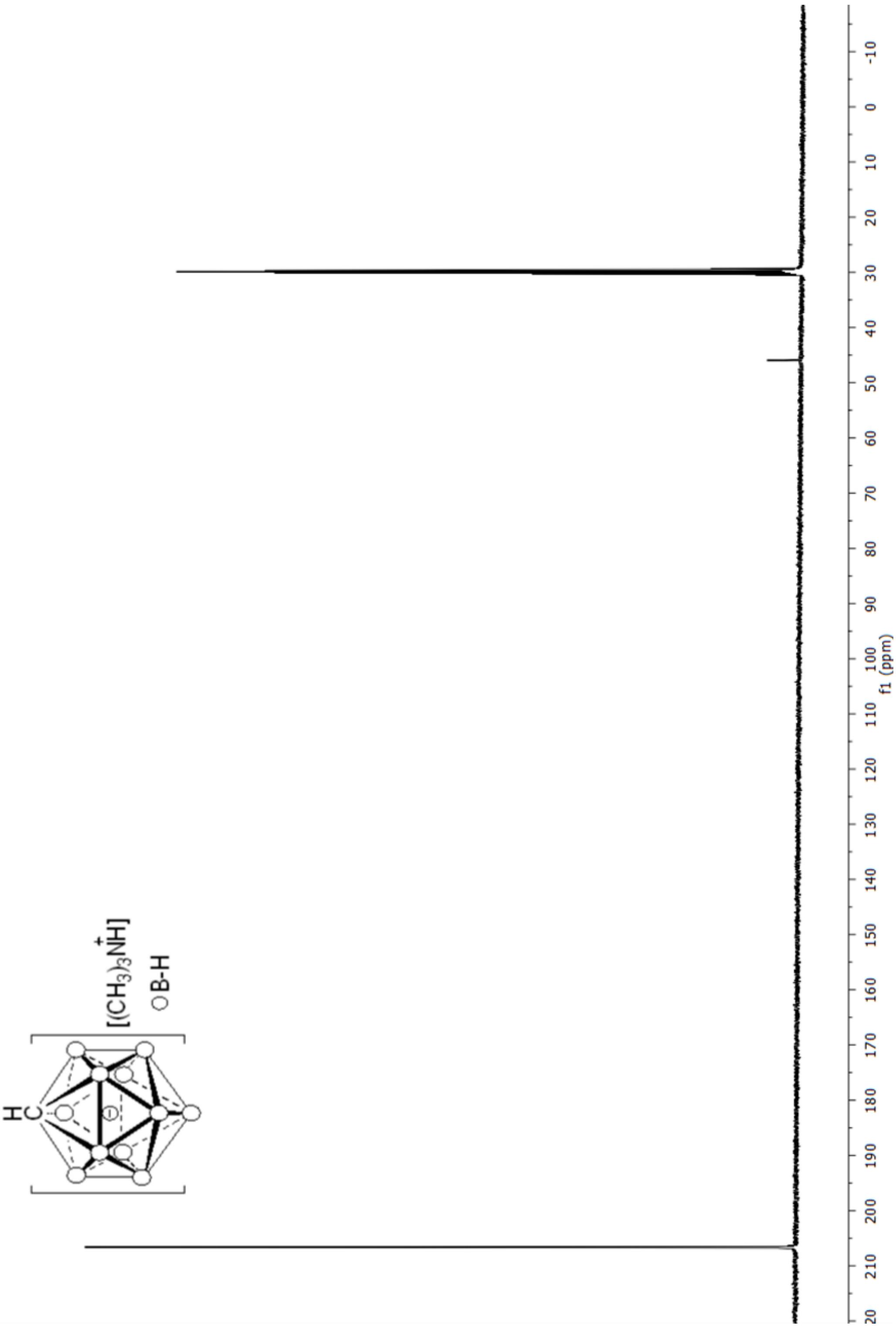

Figure 6.3. ^{13}C NMR Spectrum of **2** in d$_6$-acetone, Method 1.

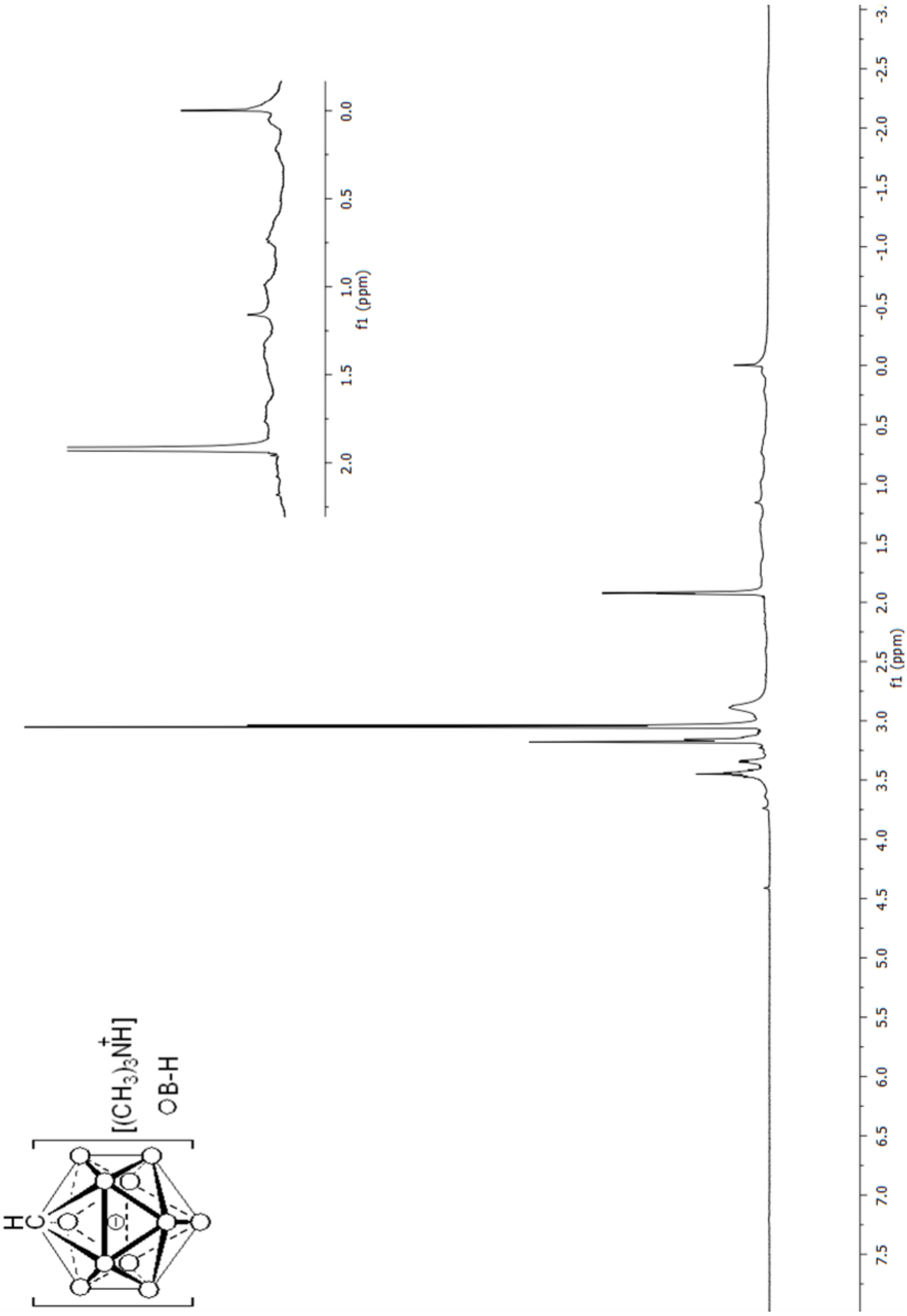

Figure 6.4. ^{1}H NMR Spectrum of **2** in d_6-acetone, Method 2

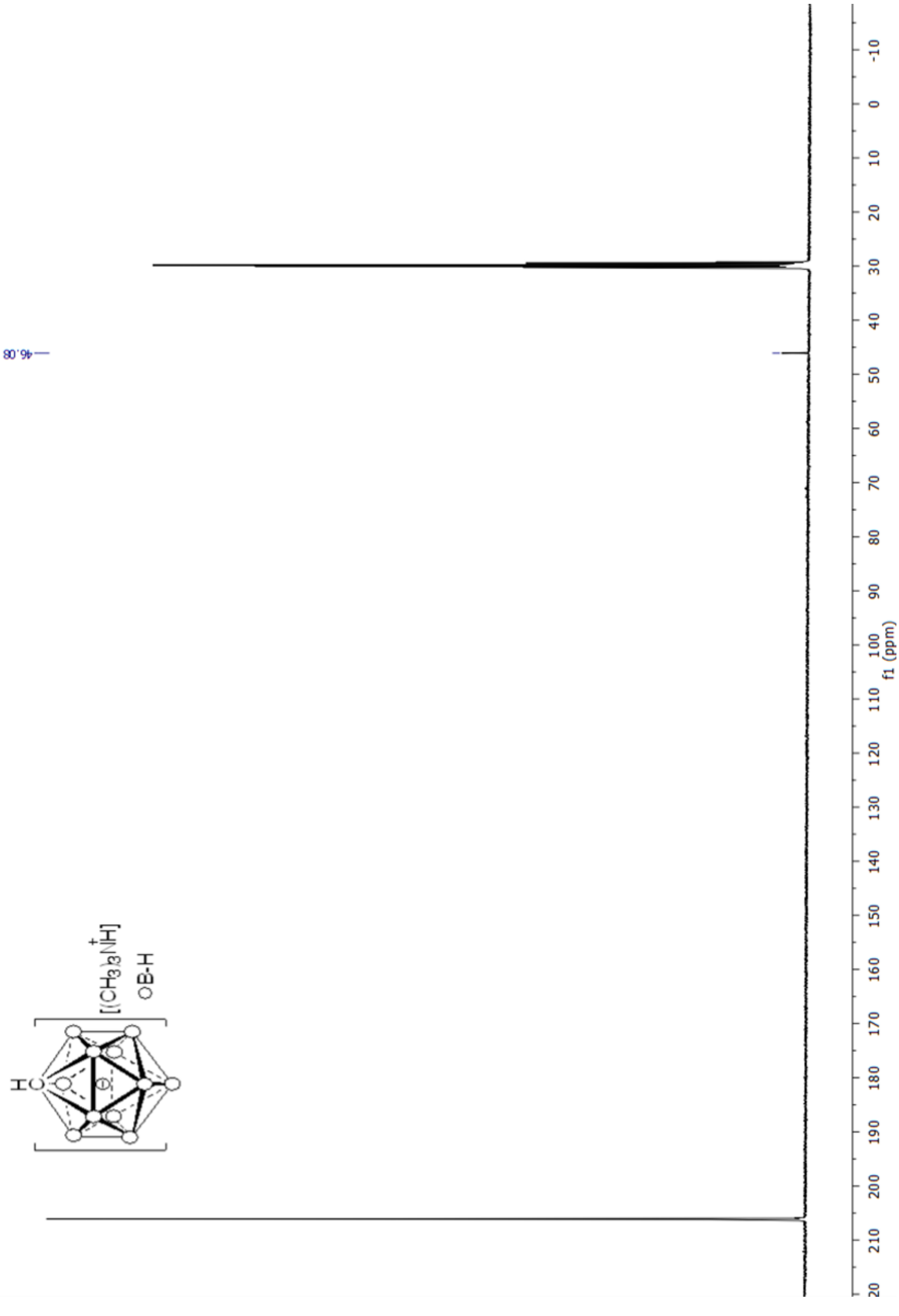

Figure 6.5. ^{13}C NMR Spectrum of **2** in d$_6$-acetone, Method 2

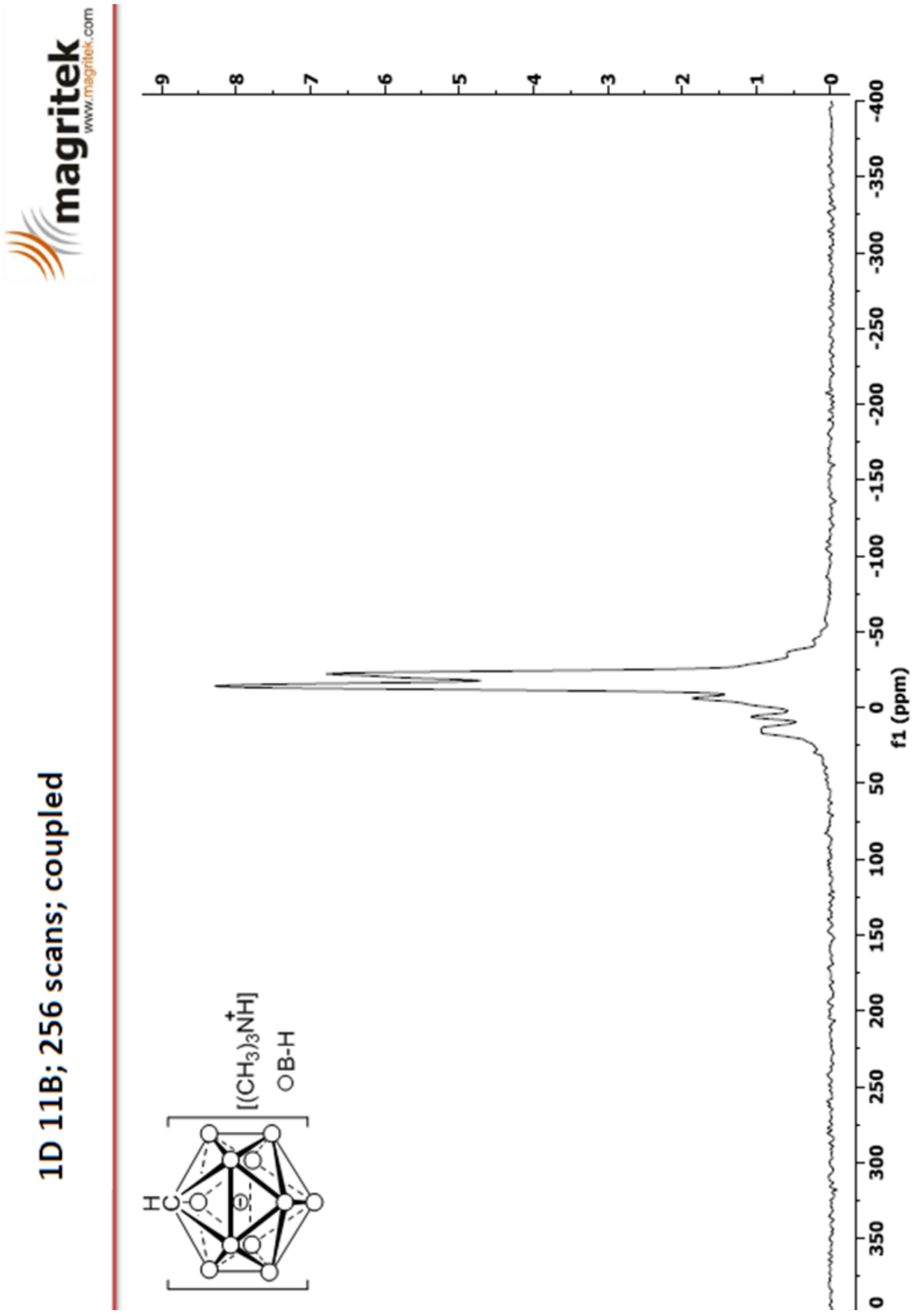

Figure 6.6. Coupled ^{11}B NMR Spectrum of **2** in d_6-acetone.

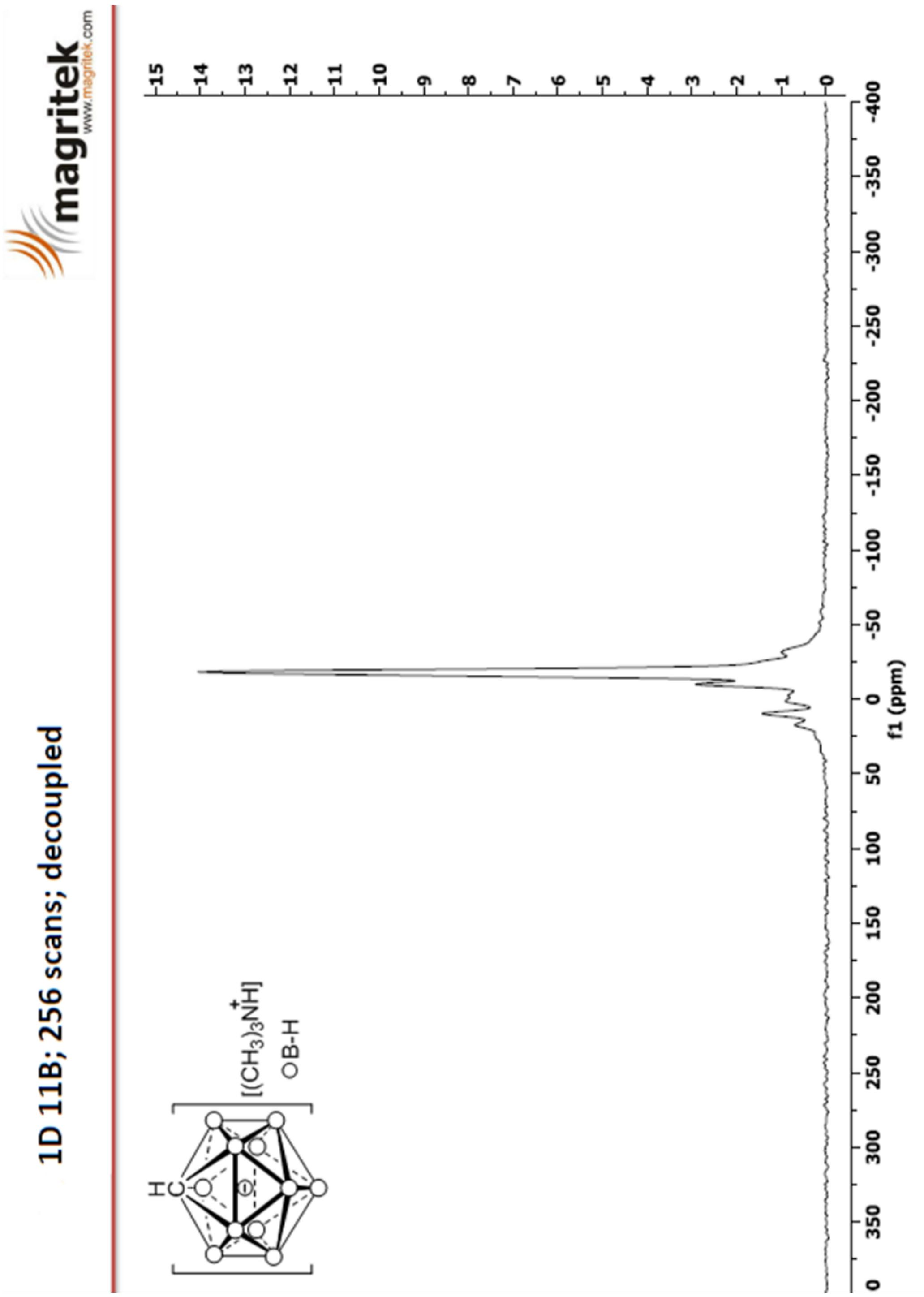

Figure 6.7. Decoupled ^{11}B NMR Spectrum of **2** in d$_6$-acetone.

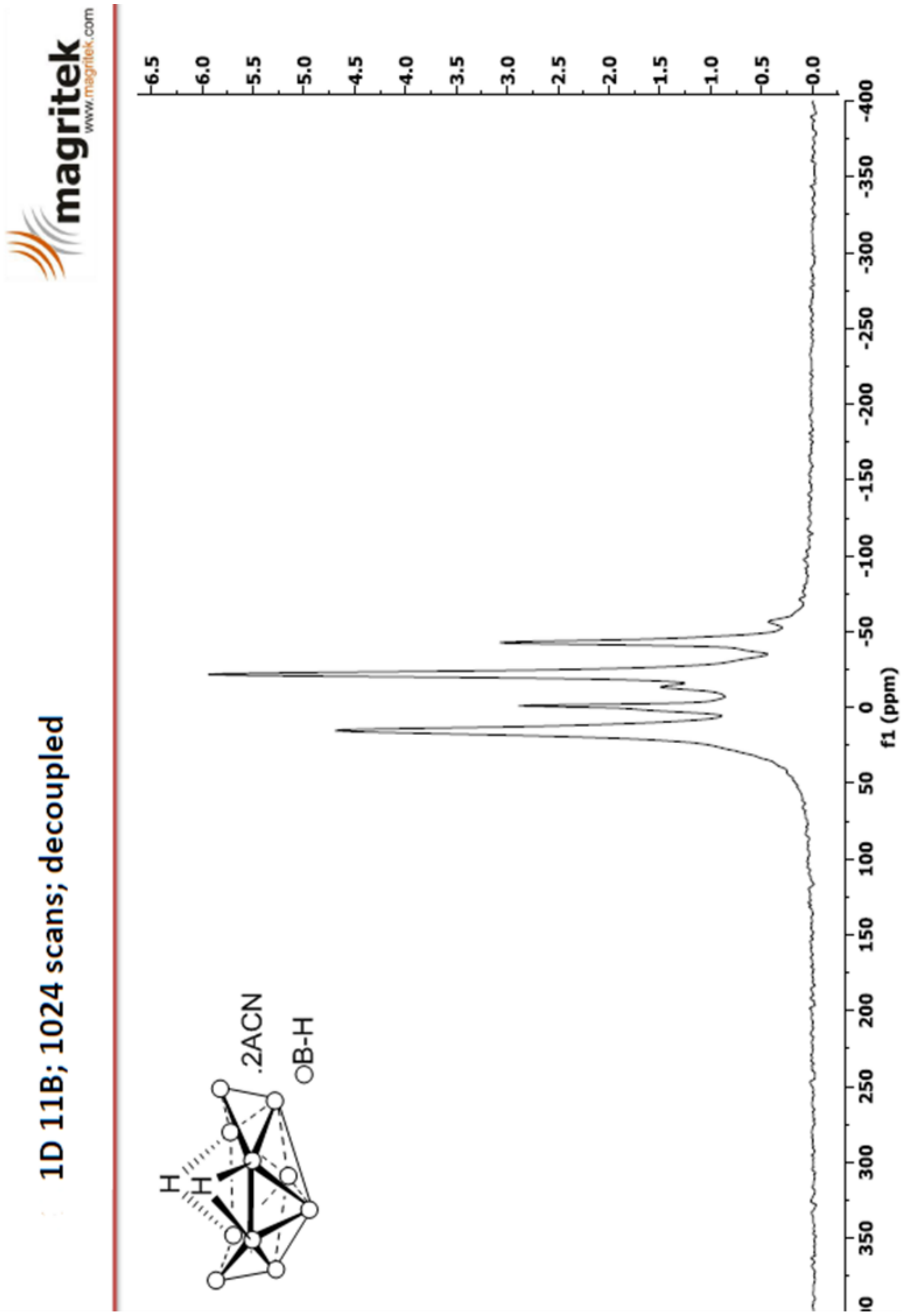

Figure 6.8. Decoupled ^{11}B NMR Spectrum of **4** in d_6-acetone.

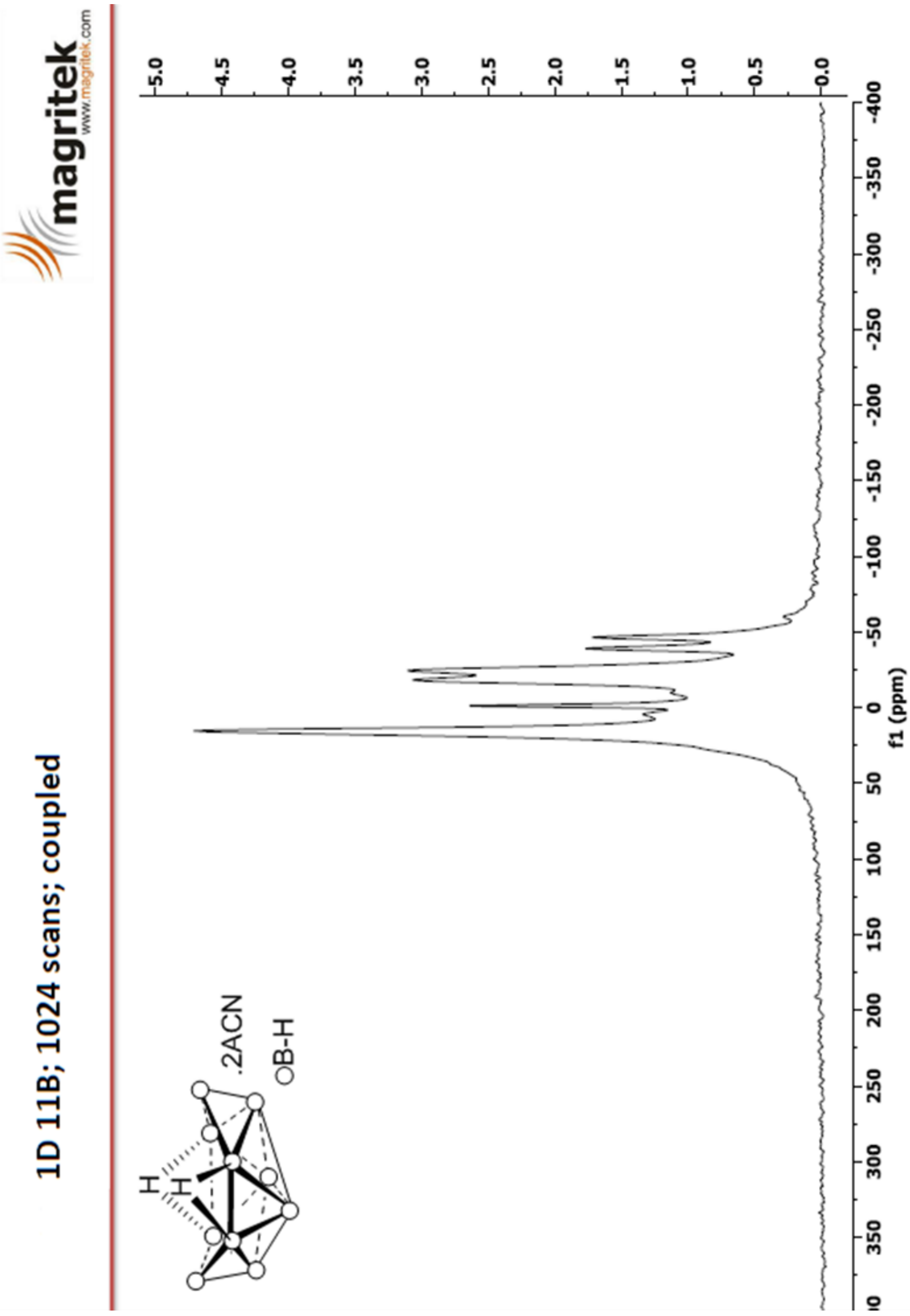

Figure 6.9. Coupled ^{11}B NMR Spectrum of **4** in d$_6$-acetone.

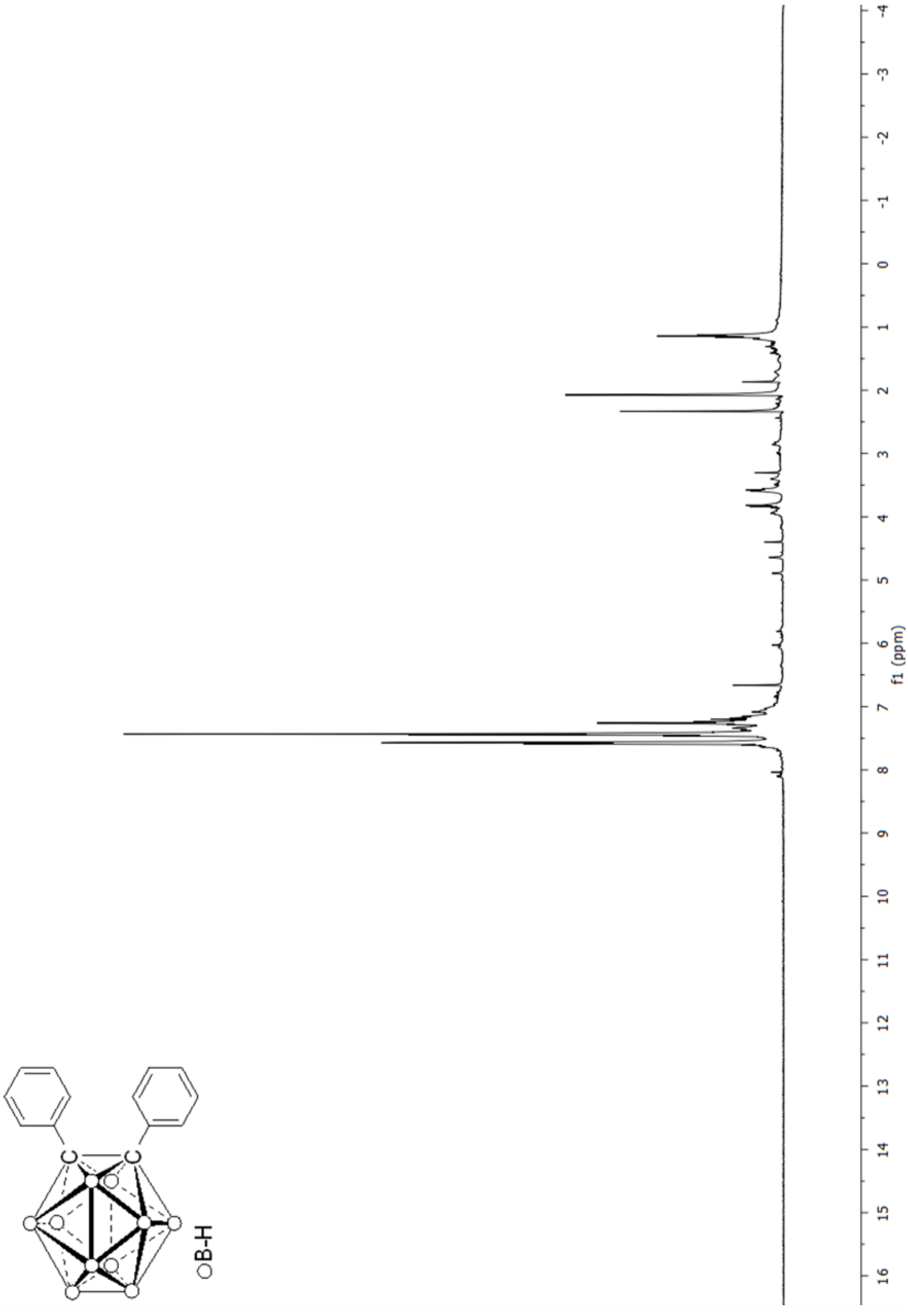

Figure 6.10. ^{1}H NMR Spectrum of **5** in d_6-acetone.

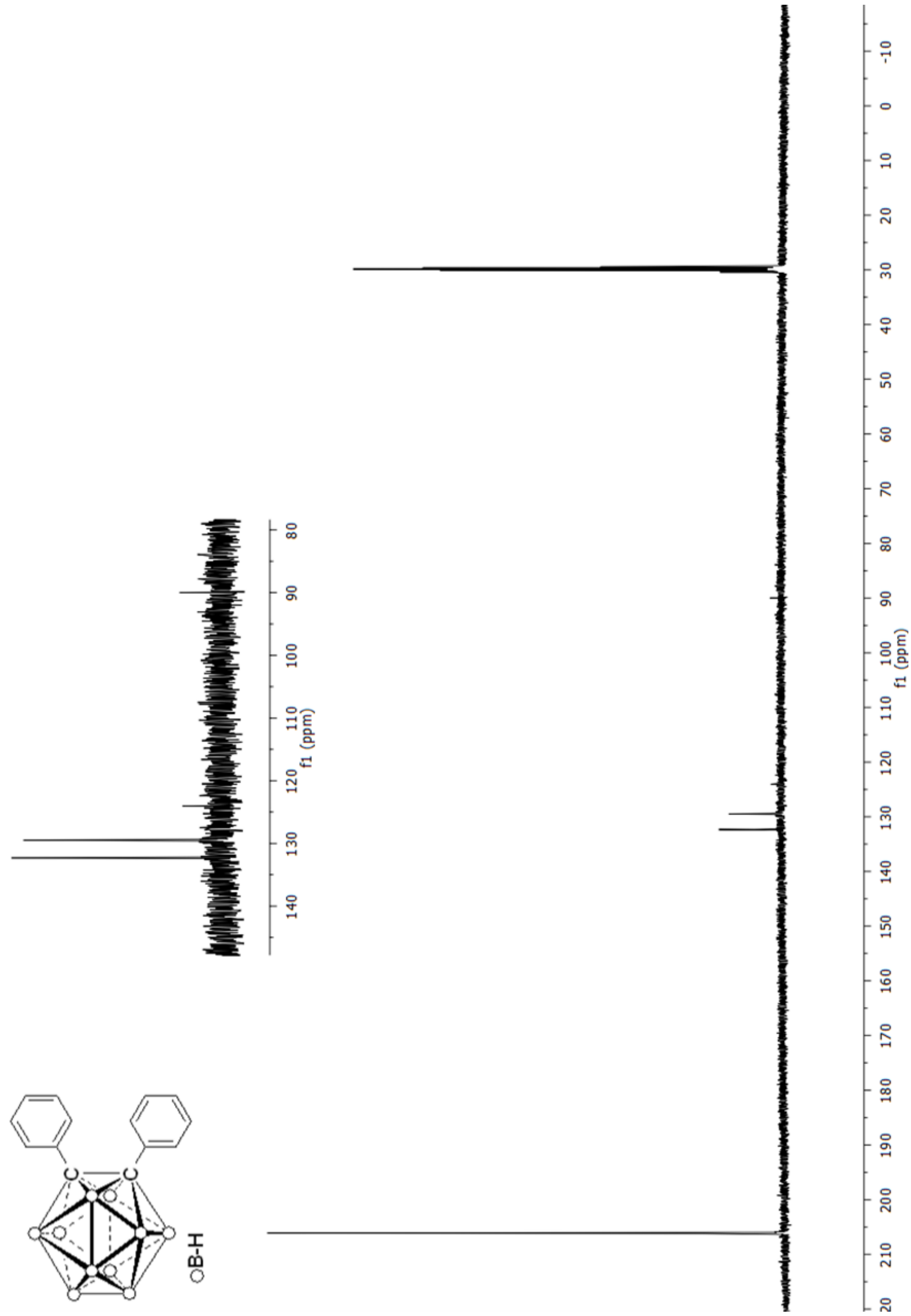

Figure 6.11. ^{13}C NMR Spectrum of **5** in d_6-acetone.

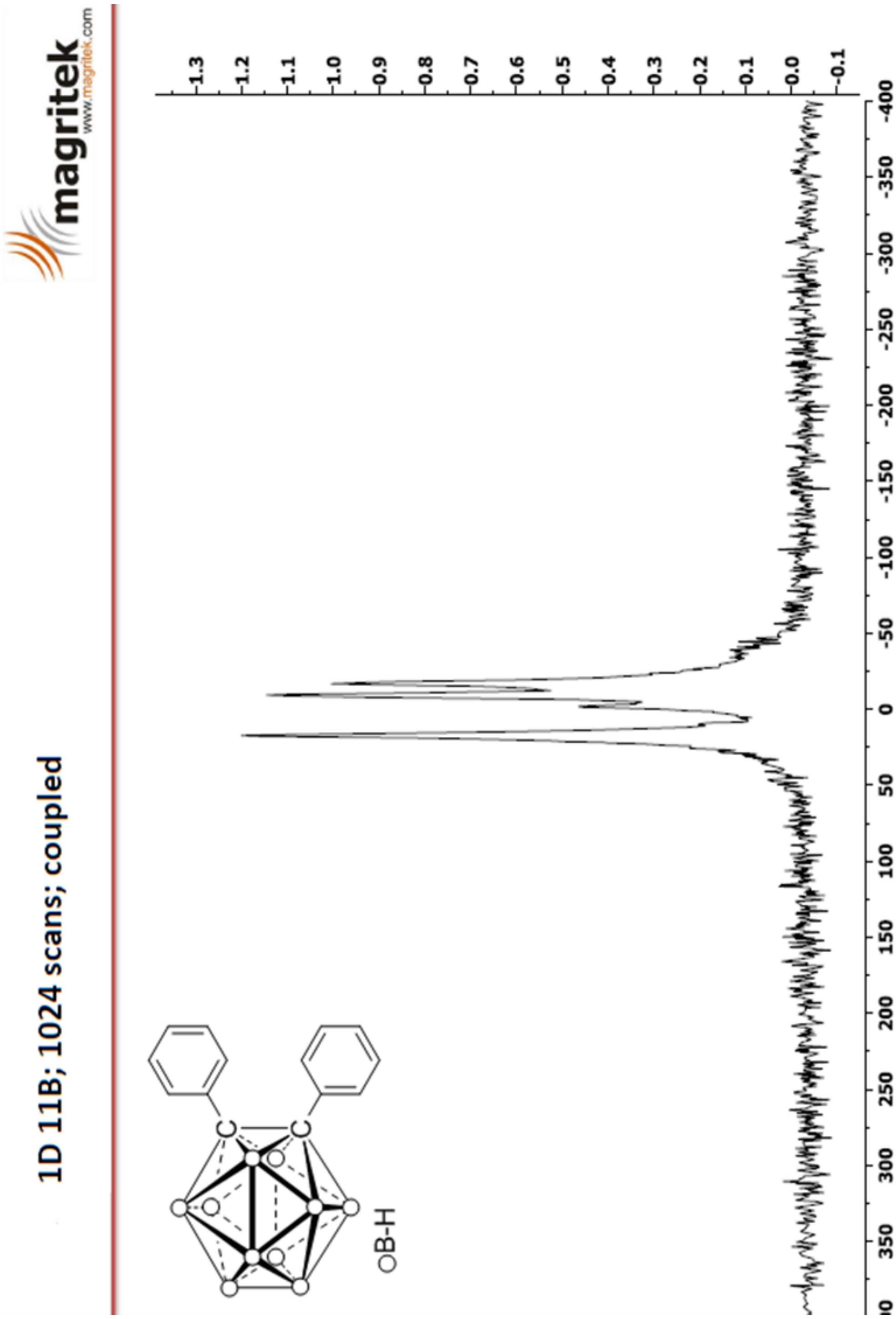

Figure 6.12. Coupled ^{11}B NMR Spectrum of **5** in d$_6$-acetone.

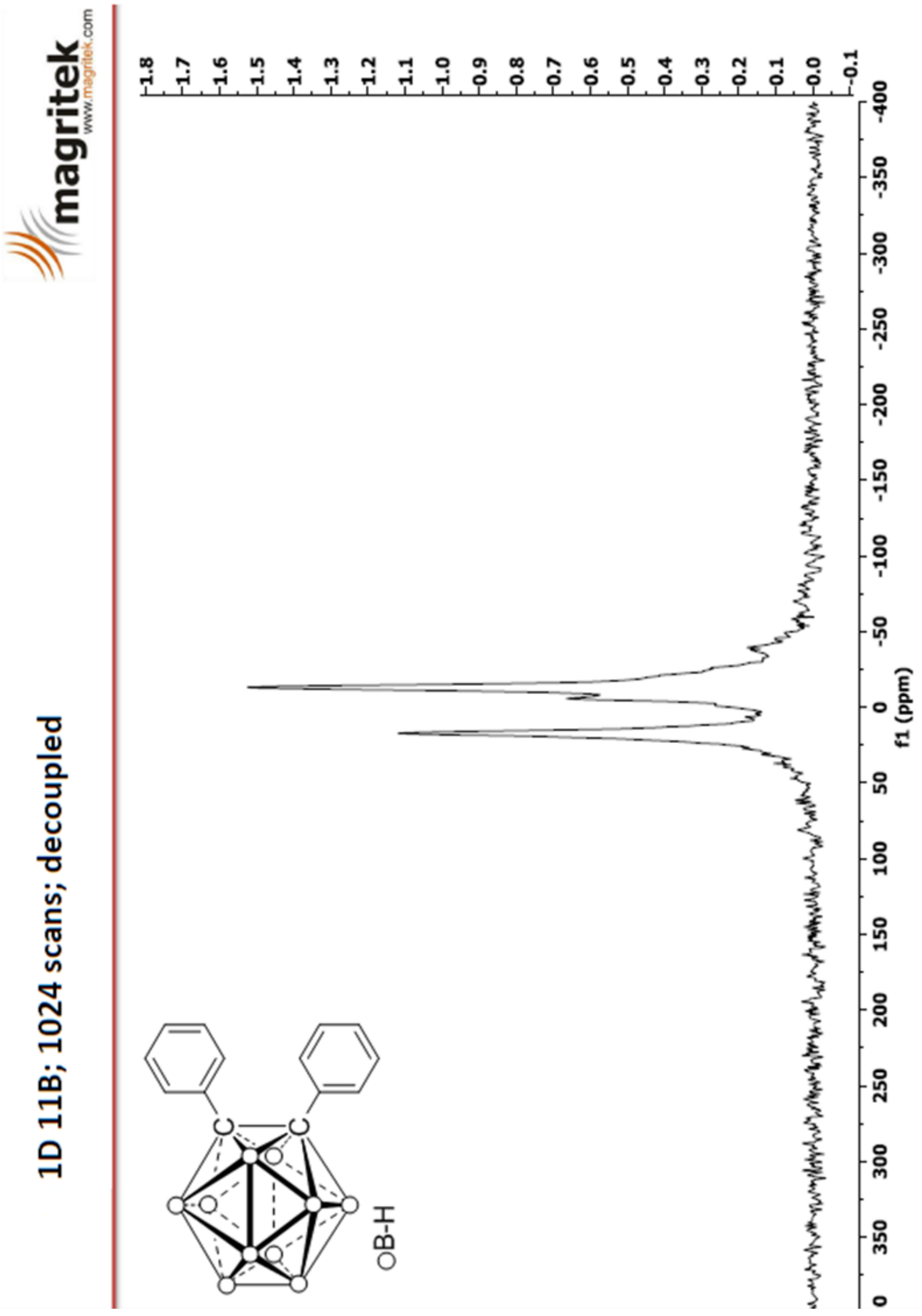

Figure 6.13. Decoupled ^{11}B NMR Spectrum of **5** in d$_6$-acetone.

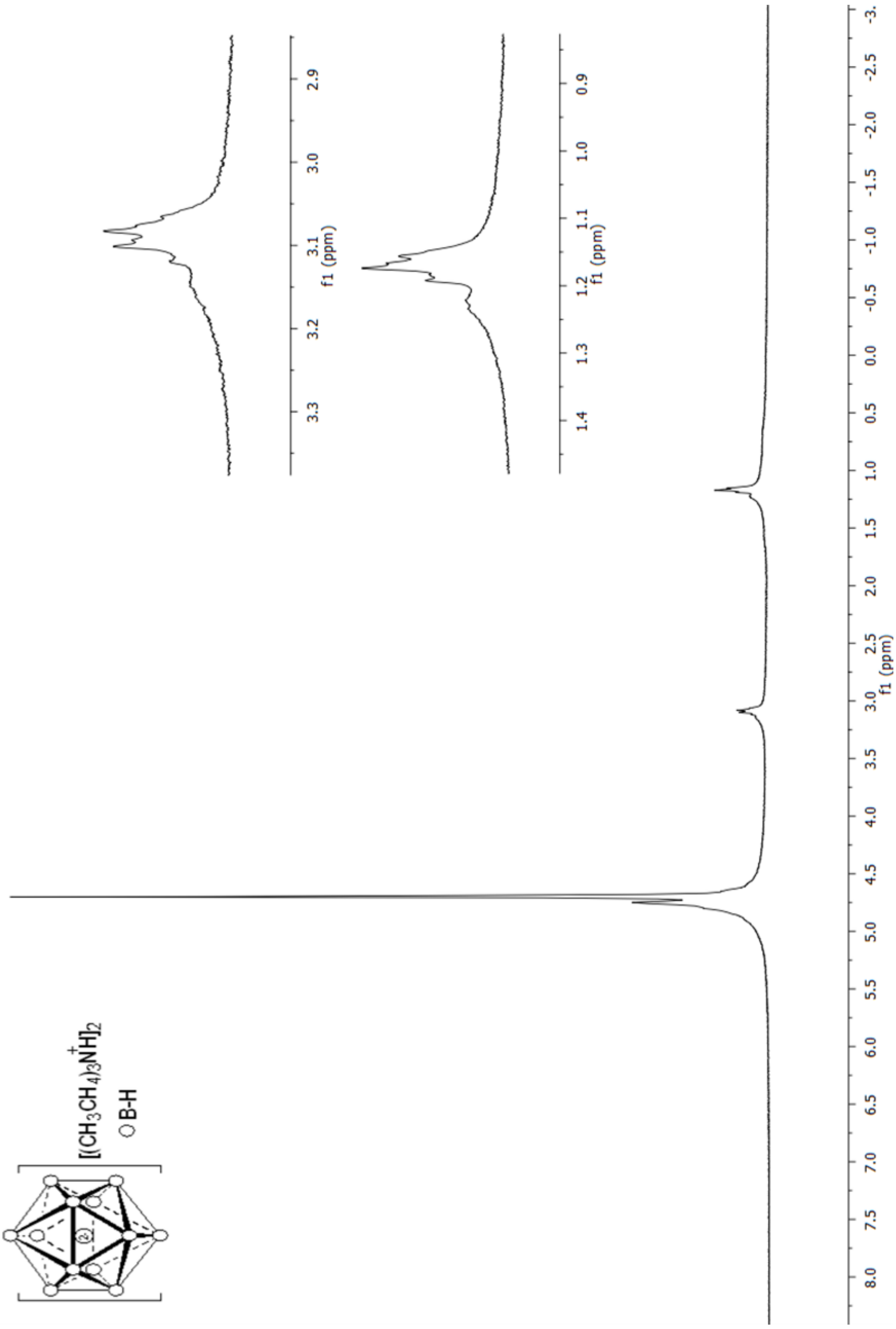

Figure 6.14. ^{1}H NMR Spectrum of **6** in D_2O.

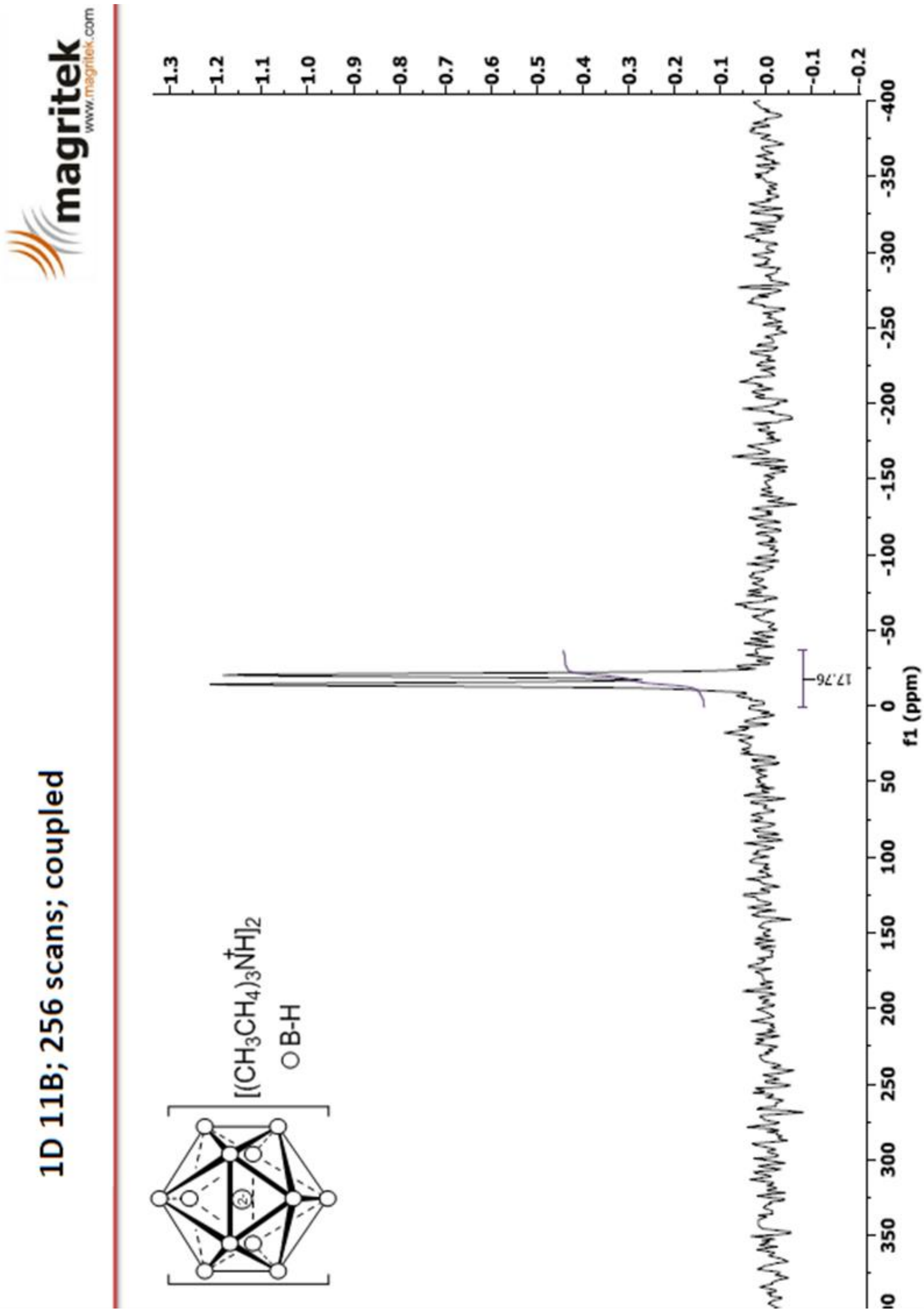

Figure 6.15. Coupled ^{11}B NMR Spectrum of **6** in D_2O.

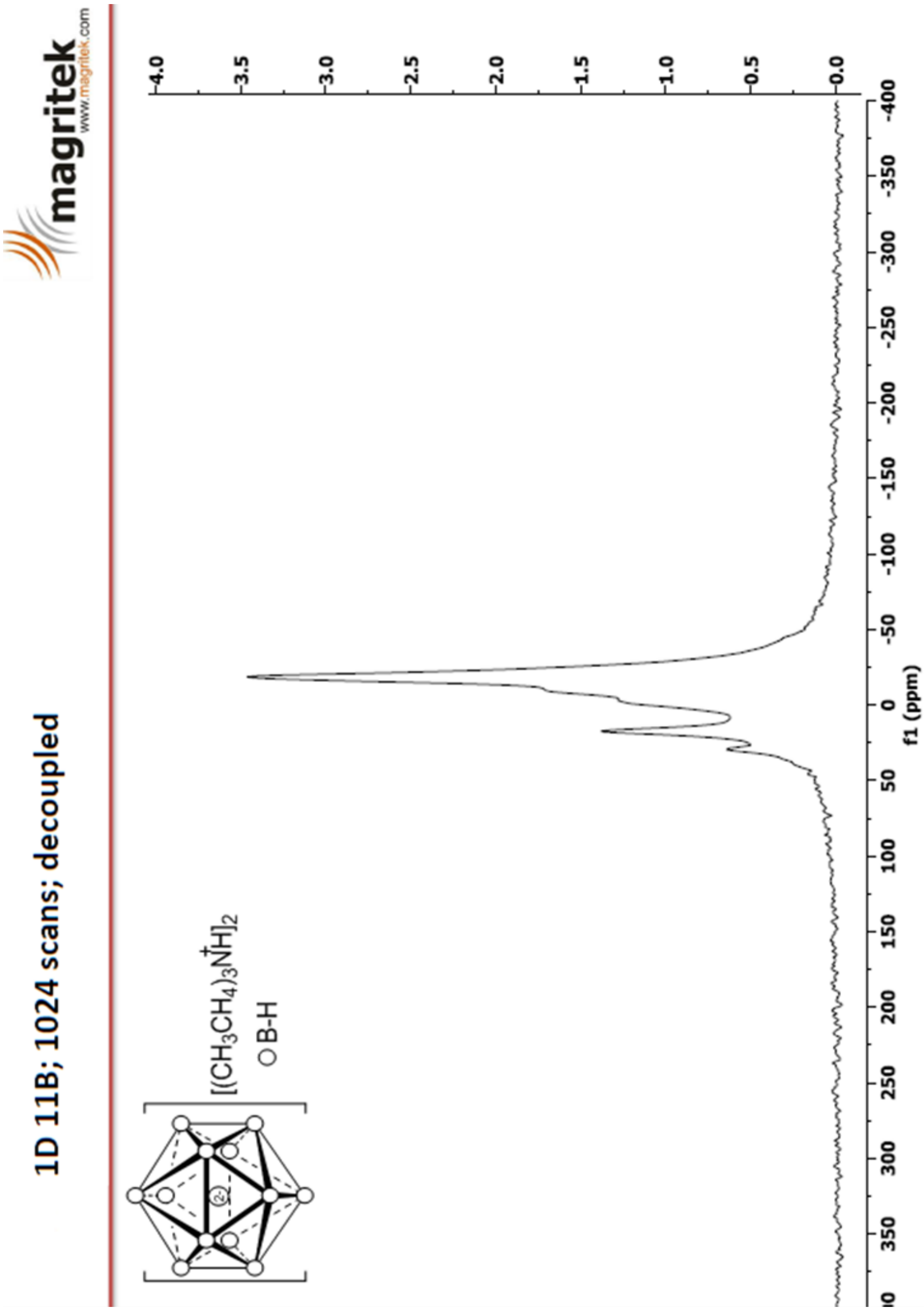

Figure 6.16. Decoupled ^{11}B NMR Spectrum of **6** in D_20.

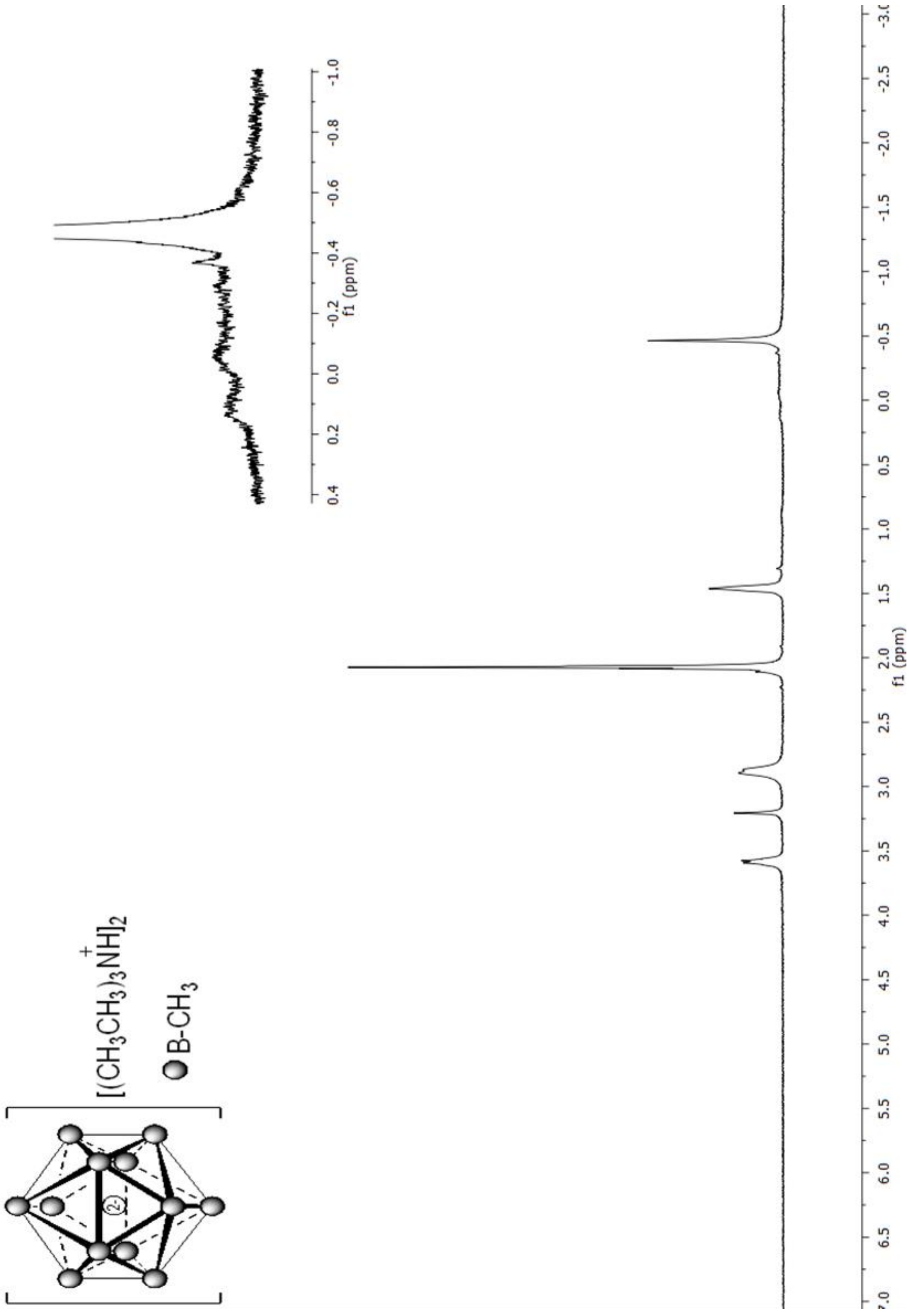

Figure 6.17. ^{1}H NMR Spectrum of **9** in d_6-acetone.

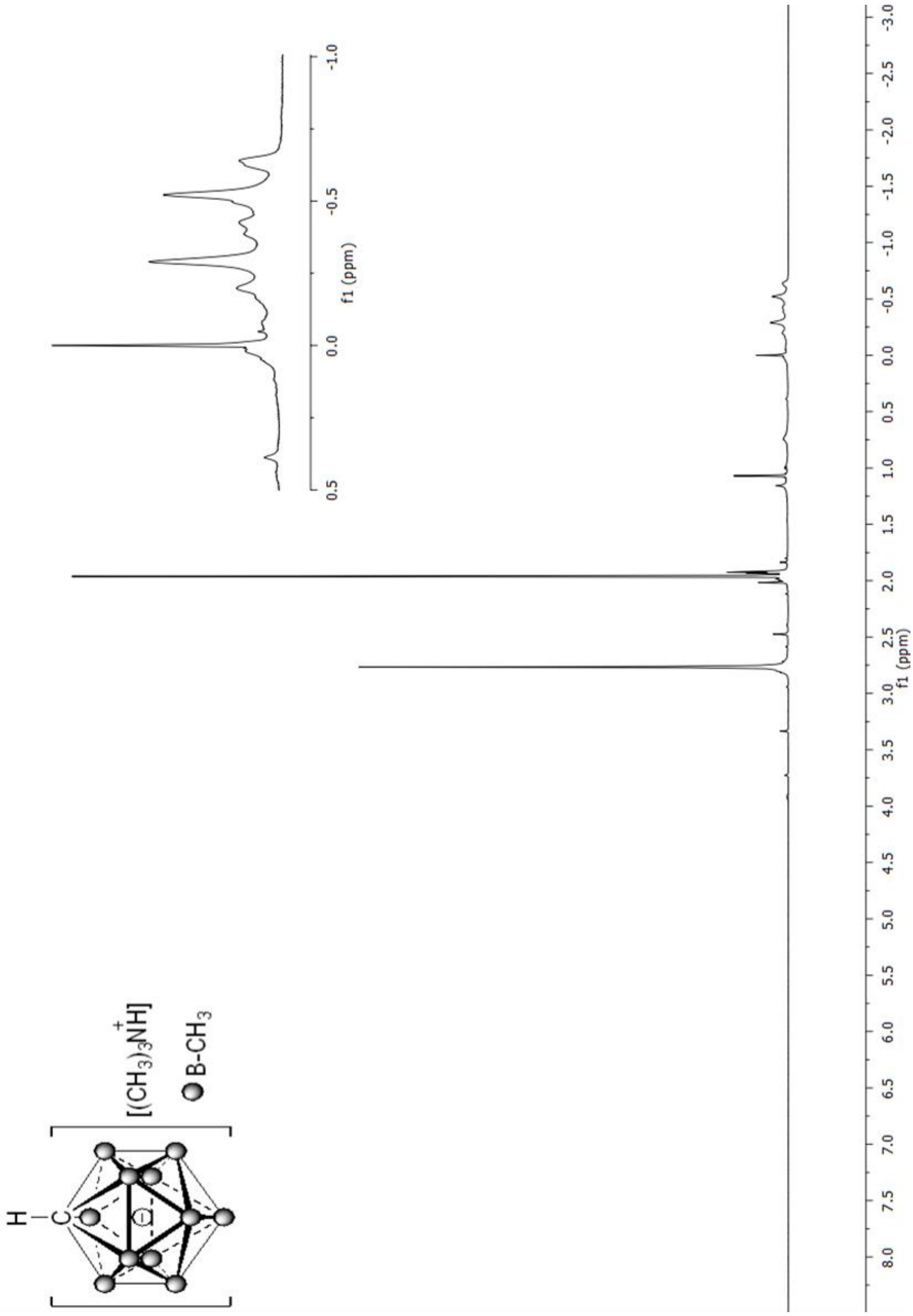

Figure 6.18. ^{1}H NMR Spectrum of **11** in d_6-acetone.

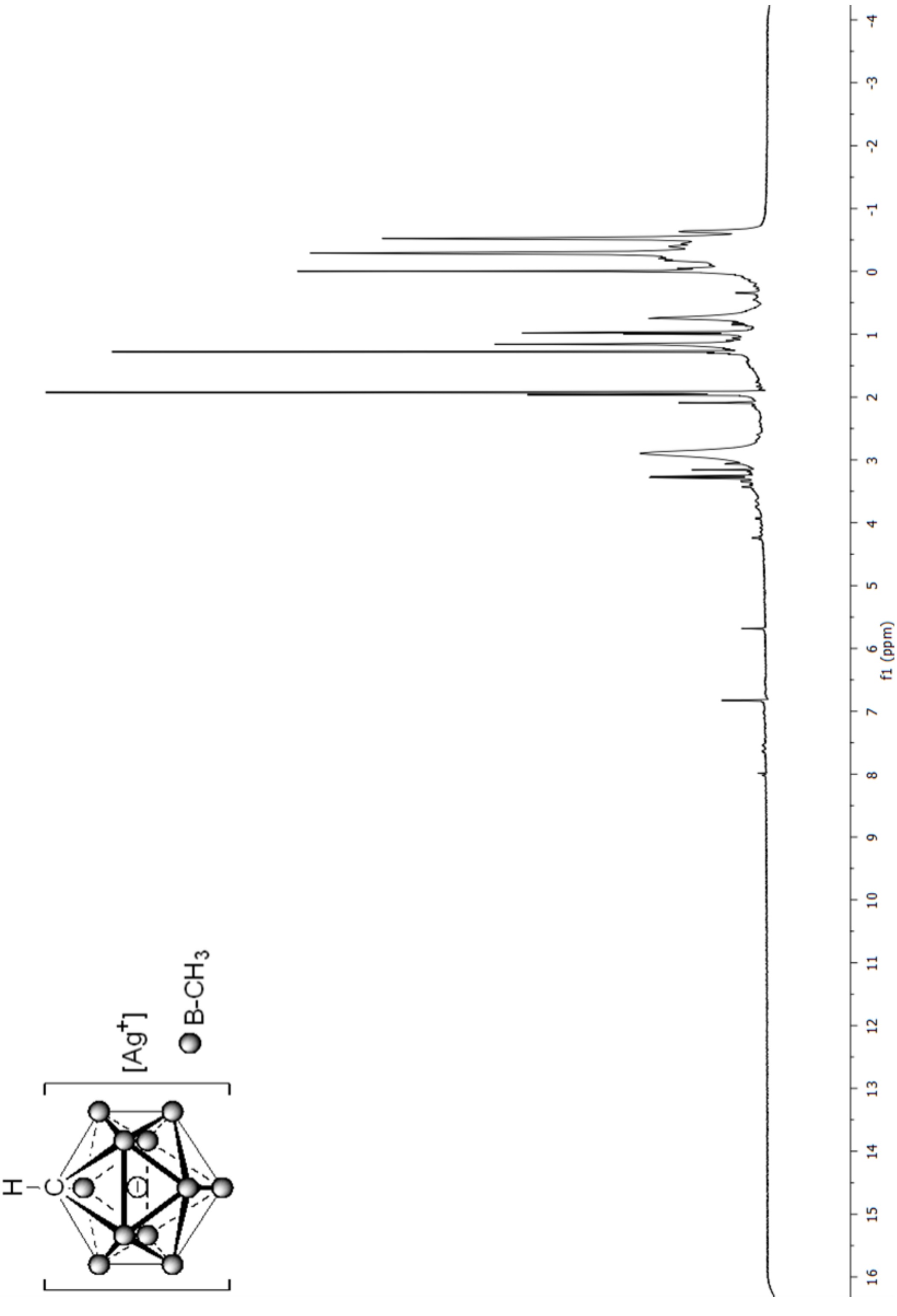

Figure 6.19. ^{1}H NMR Spectrum of **12** in d_6-acetone.

B. IR Spectra

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

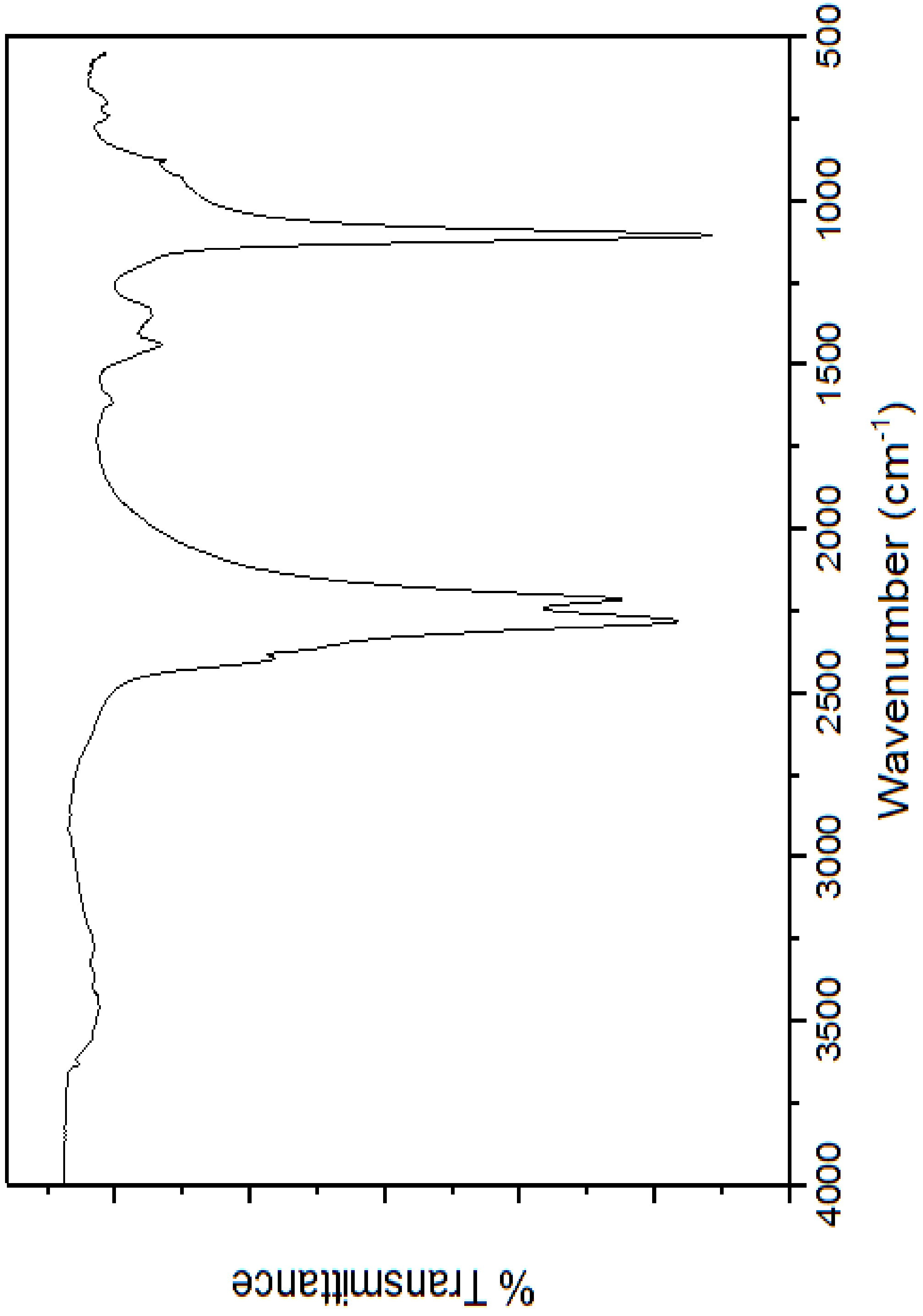

Figure 6.20. IR Spectrum of $NaBH_4$.

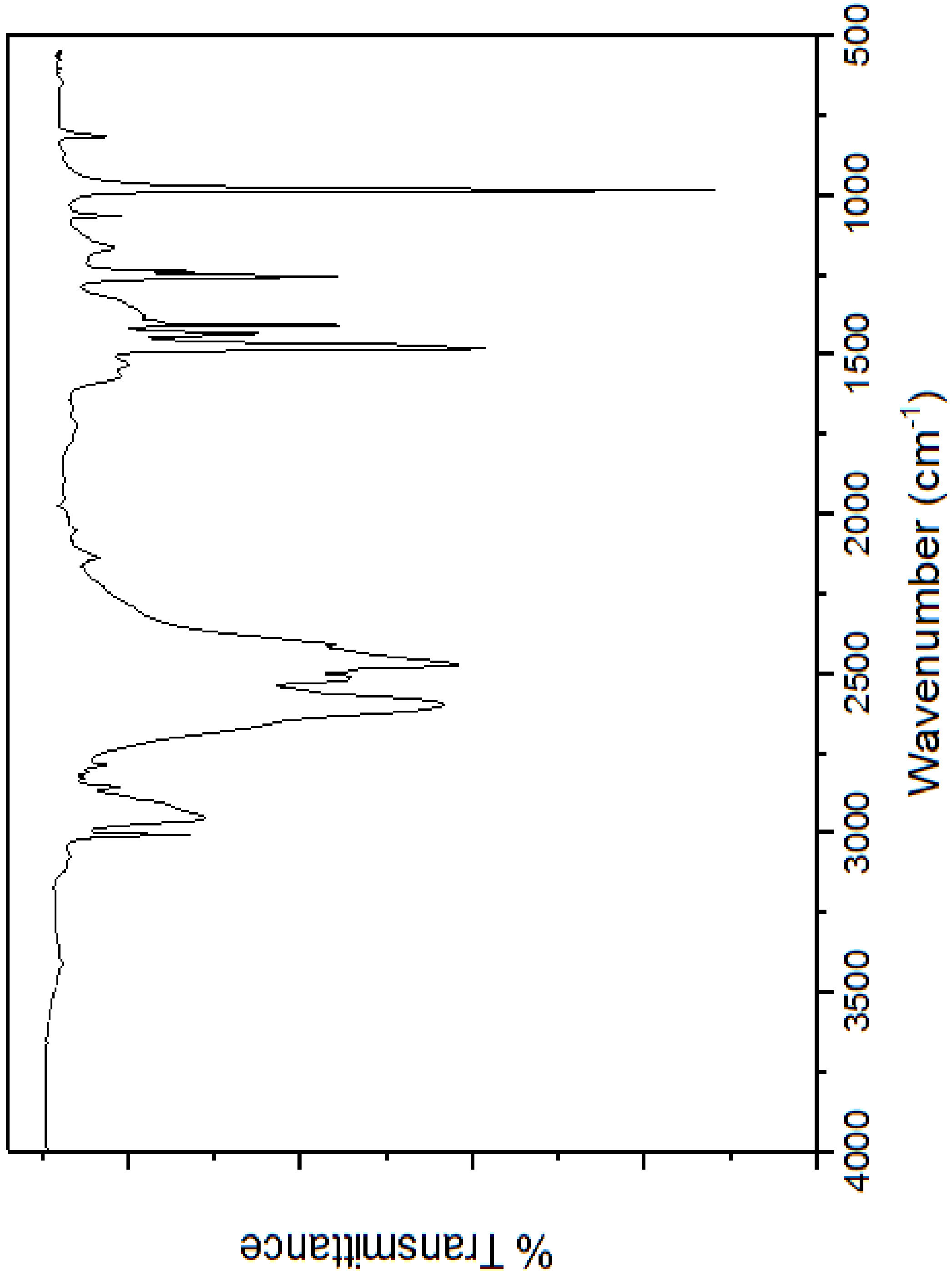

Figure 6.21. IR Spectrum of $(CH_3)_3N.HCl$.

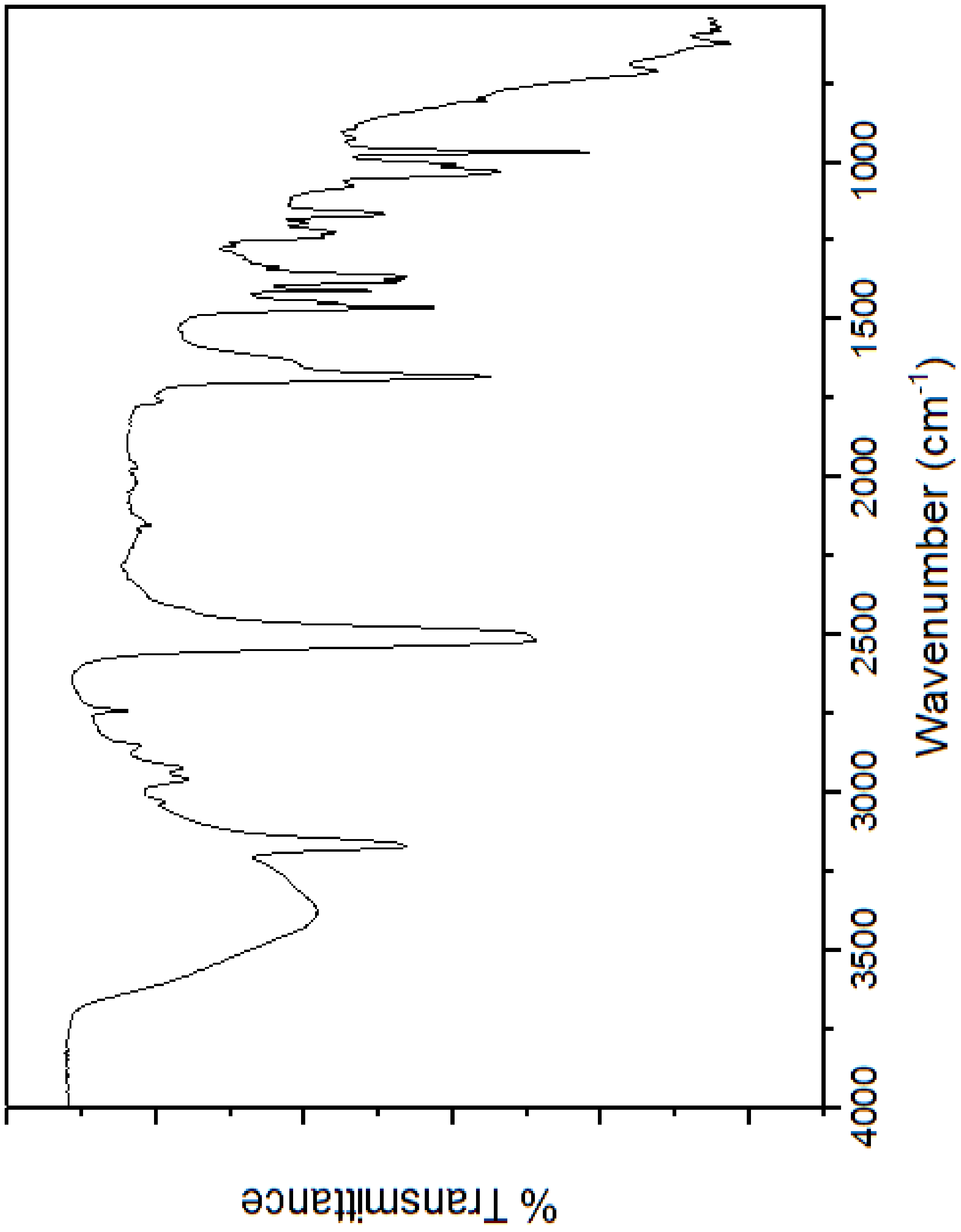

Figure 6.22. IR Spectrum of $(CH_3)_3NH^+$ salt of **1** ($B_{12}H_{12}^{2-}$).

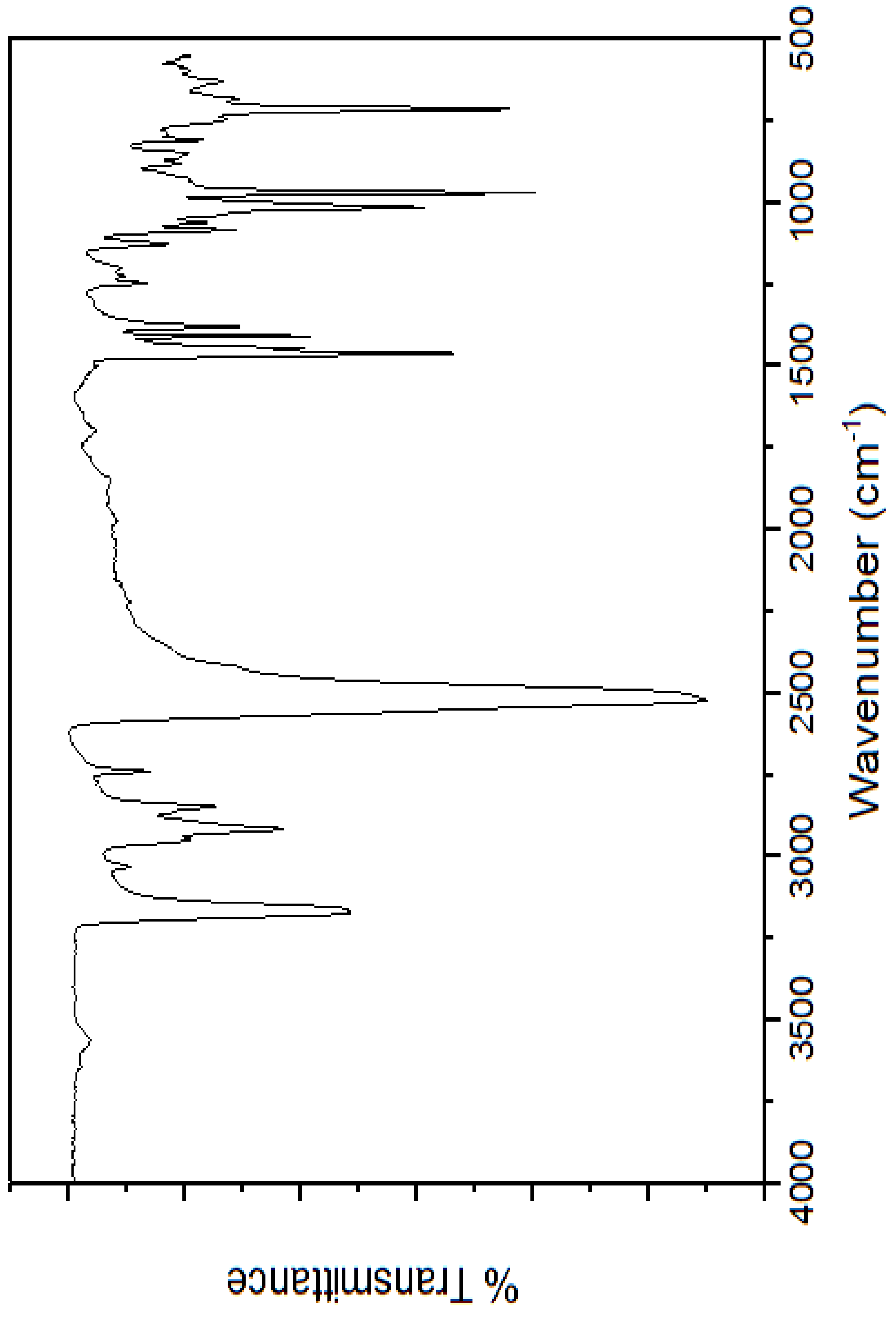

Figure 6.23. IR Spectrum of **2**, ($CB_{11}H_{12}^-$), Method 1.

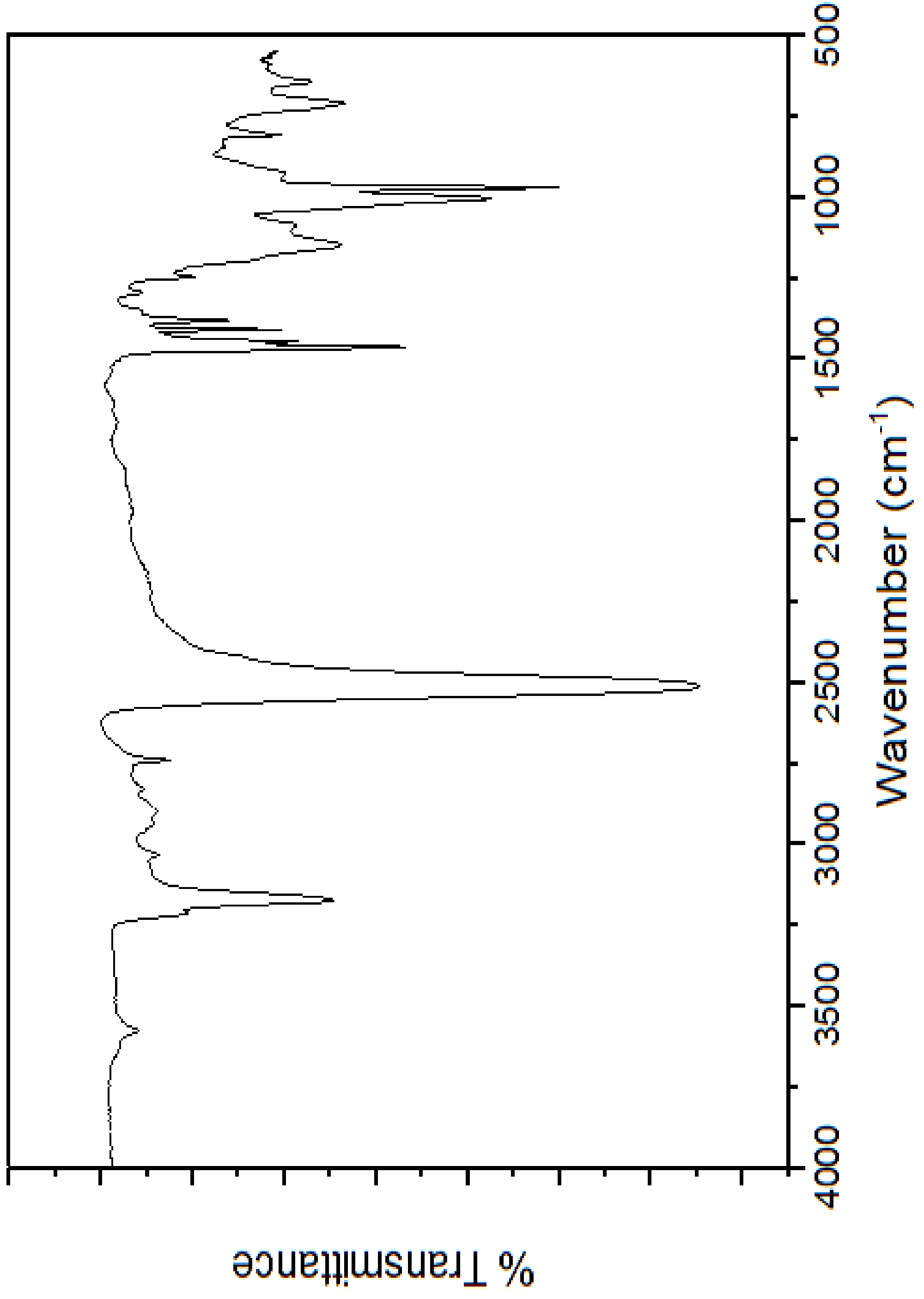

Figure 6.24. IR Spectrum of **2**, ($CB_{11}H_{12}^-$), Method 2.

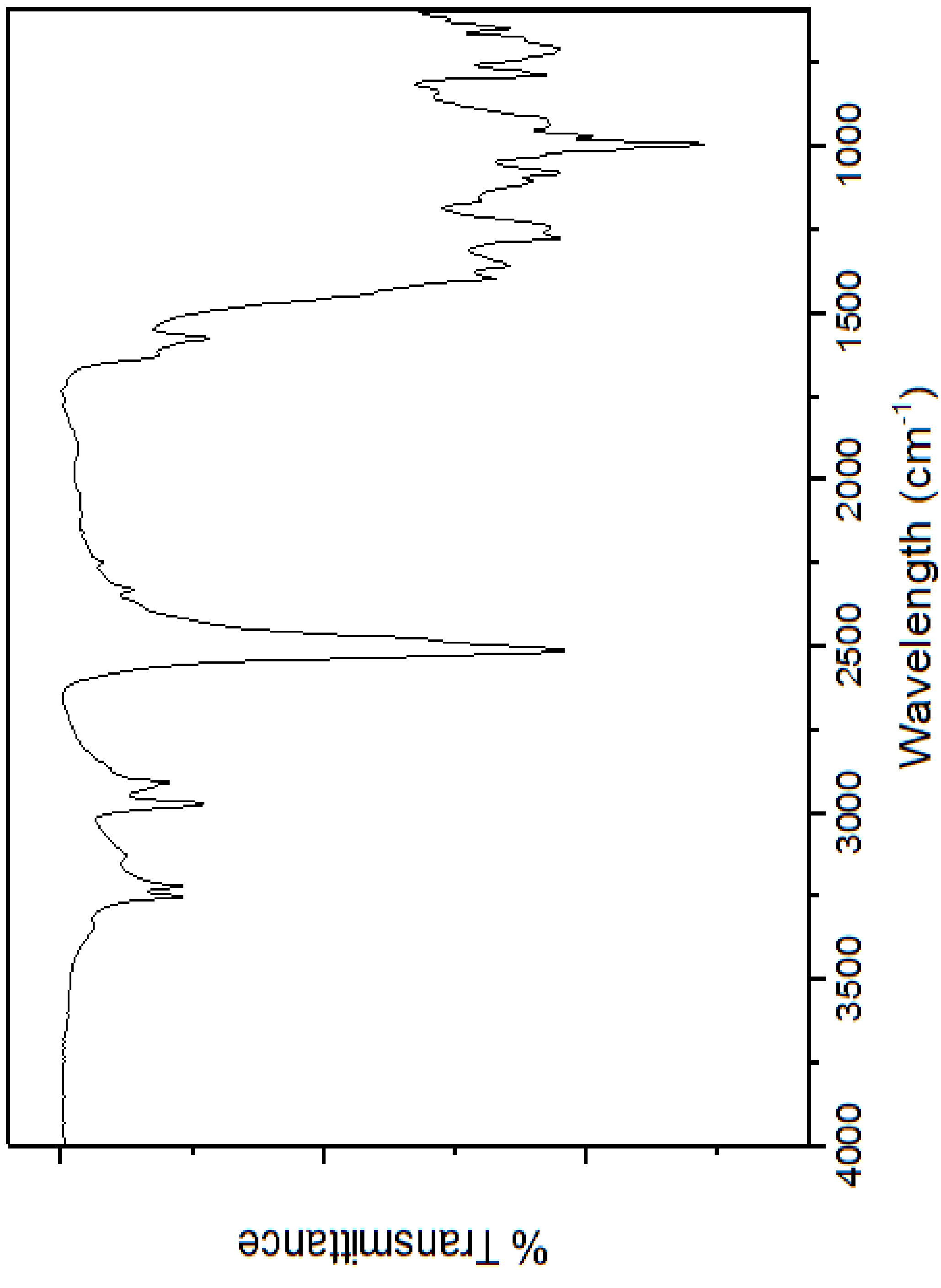

Figure 6.25. IR Spectrum of **4**, (Decaborane-acetonitrile complex).

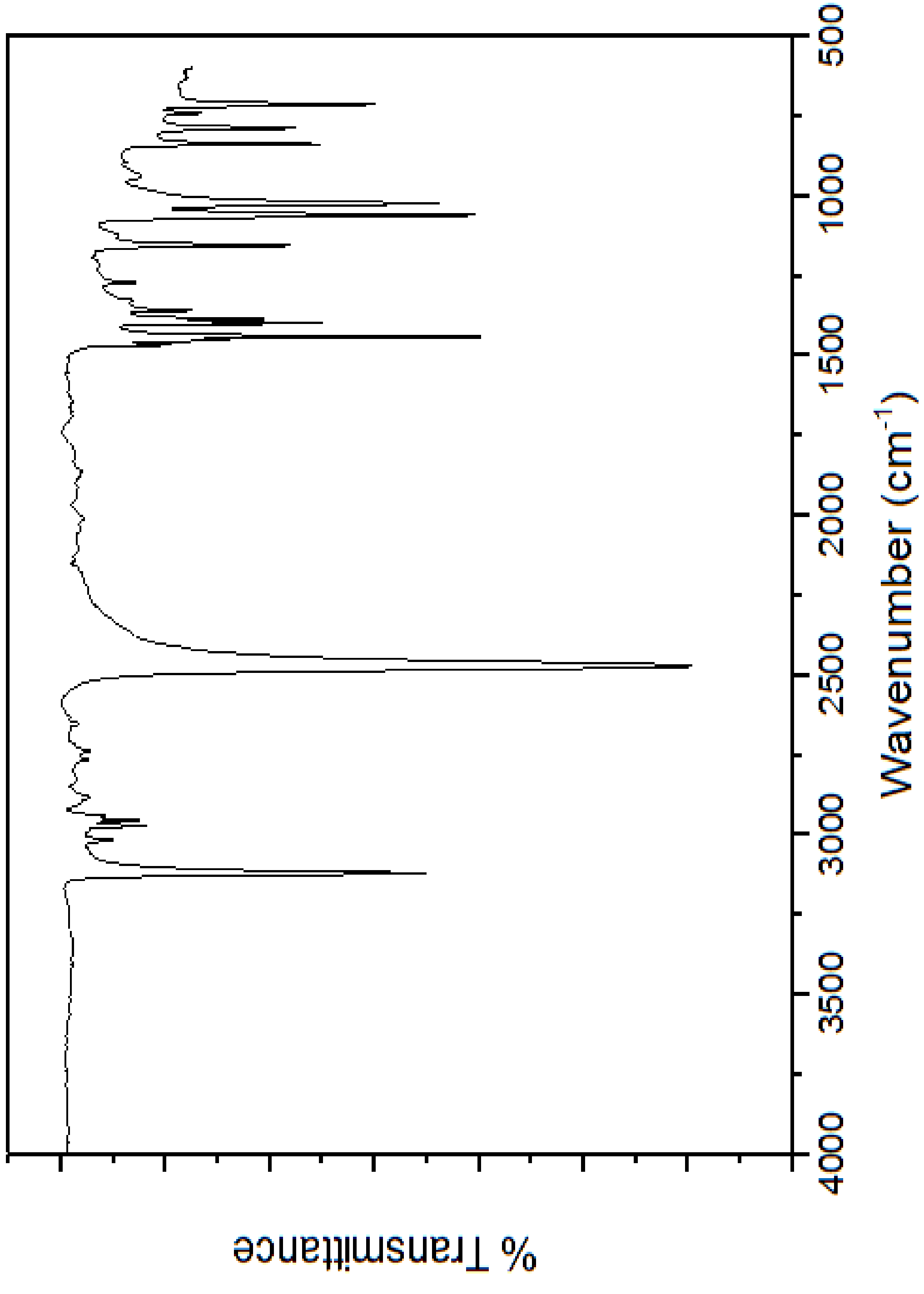

Figure 6.26. IR Spectrum of **6**, $[(CH_3CH_2)_3NH]_2B_{12}H_{12}$.

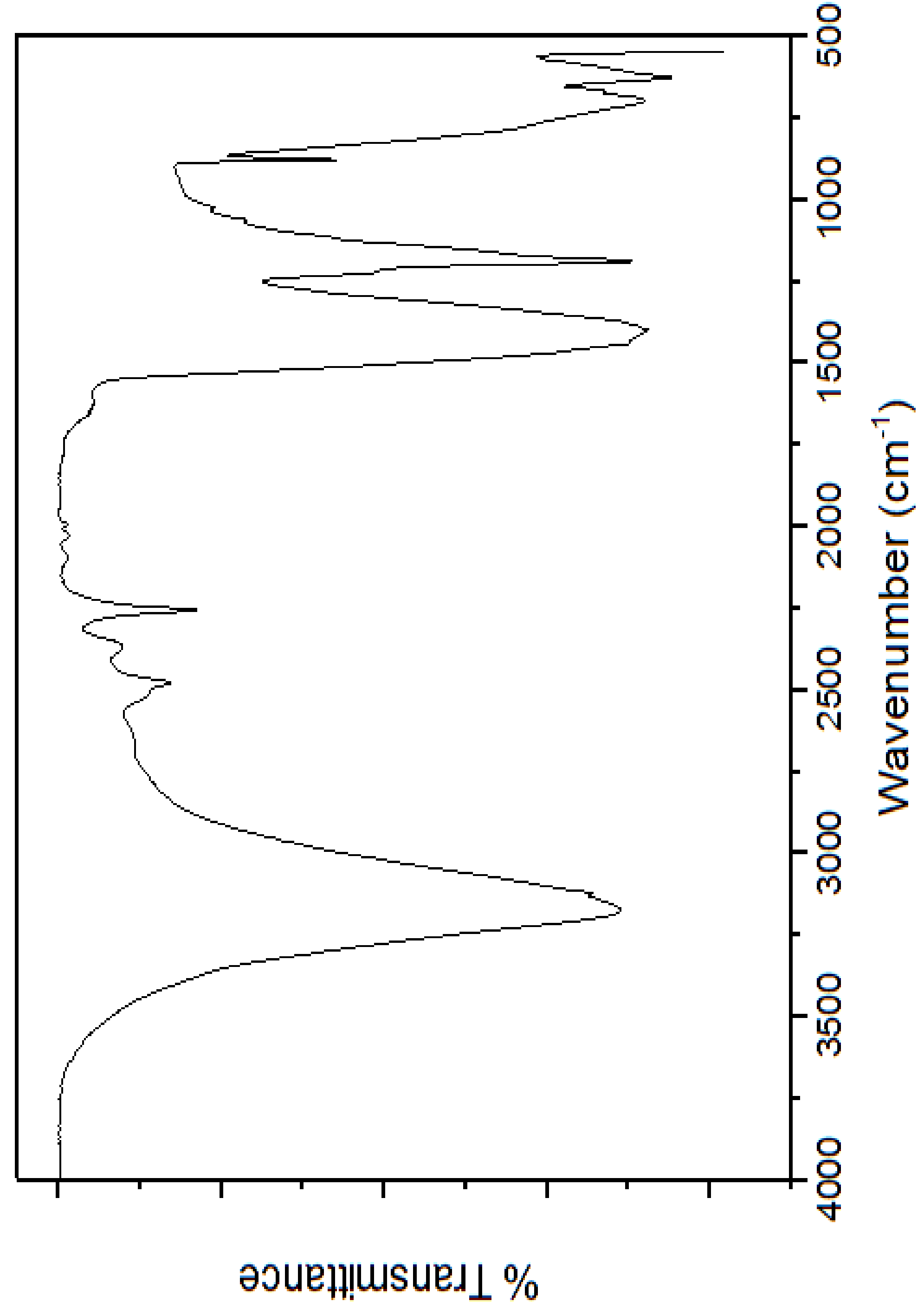

Figure 6.27. IR Spectrum of $B(OH)_3$ from the synthesis of **6.**

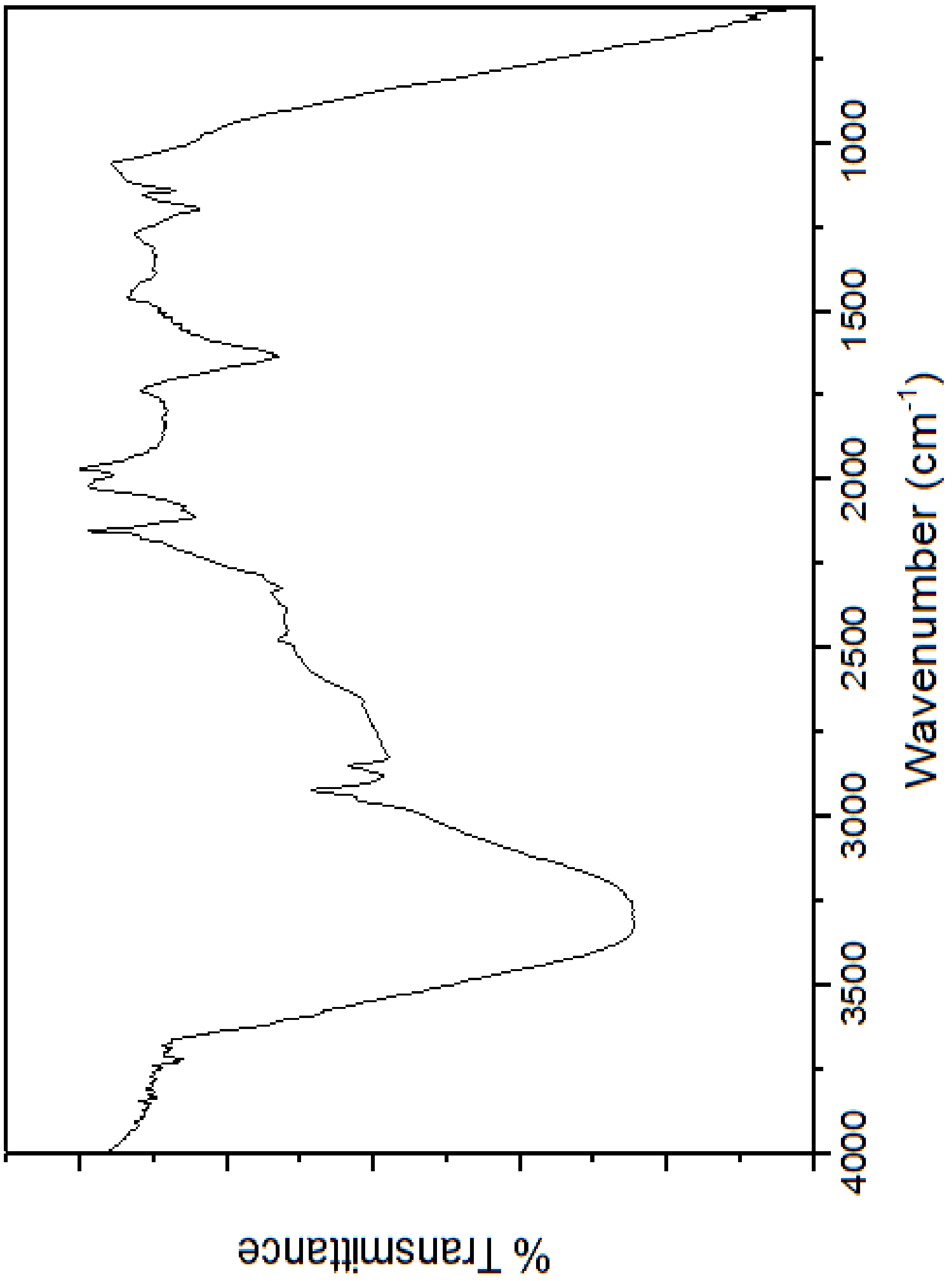

Figure 6.28. IR Spectrum of **7**, $[Ag]_2B_{12}H_{12}$.

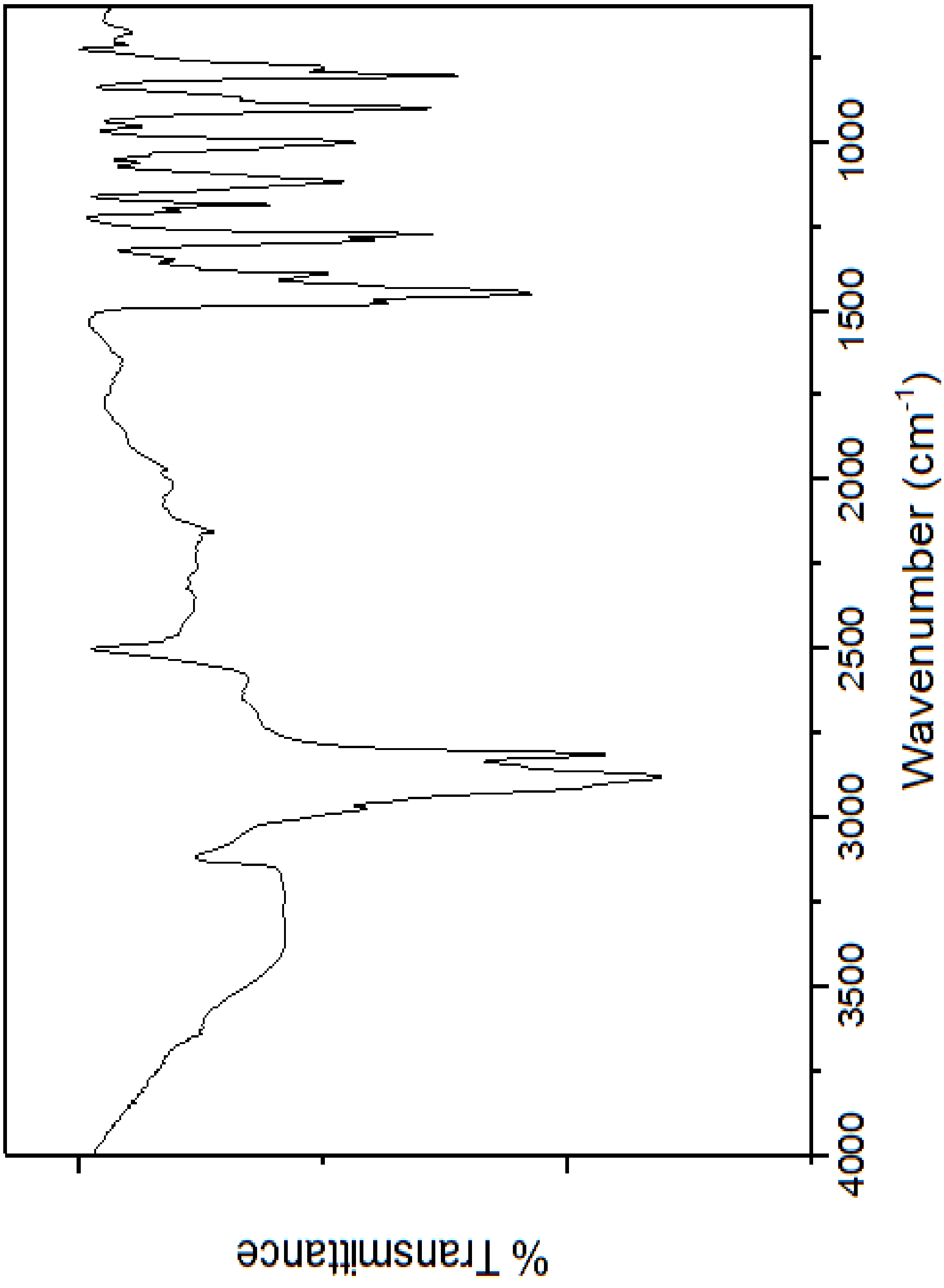

Figure 6.29. IR Spectrum of **9**, $[(CH_3CH_2)_3NH]_2B_{12}(CH_3)_{12}$.