STUDIES ON CLOSO-DODECABORATE DIANION DERIVATIVES USES IN CATALYTIC REACTIONS

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

BY

OĞUZHAN ALBAYRAK

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

AUGUST 2021

Approval of the thesis:

STUDIES ON CLOSO-DODECABORATE DIANION DERIVATIVES USES IN CATALYTIC REACTIONS

submitted by **OĞUZHAN ALBAYRAK** in partial fulfillment of the requirements for the degree of **Master of Science** i**n Chemistry, Middle East Technical University** by,

Prof. Dr. Halil Kalıpçılar
Dean, Graduate School of **Natural and Applied Sciences** _____

Prof. Dr. Özdemir Doğan
Head of the Department, **Chemistry** _____

Prof. Dr. Akın Akdağ
Supervisor, **Chemistry, METU** _____

Examining Committee Members:

Prof. Dr. Adnan Bulut
Chemistry Department, Kırıkkale University _____

Prof. Dr. Akın Akdağ
Chemistry Department, METU _____

Prof. Dr. Özdemir Doğan
Chemistry Department, METU _____

Prof. Dr. Gülay Ertaş
Chemistry Department, METU _____

Prof. Dr. Ali Çırpan
Chemistry Department, METU _____

Date: 20.08.2018

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Albayrak, Oğuzhan :

Signature :

ABSTRACT

STUDIES ON CLOSO-DODECABORATE DIANION DERIVATIVES USES IN CATALYTIC REACTIONS

Albayrak, Oğuzhan
Master of Science, Chemistry
Supervisor : Prof. Dr. Akın Akdağ

August 2021, 106 pages

Icosahedral boron clusters are versatile and unique types of boron compounds due to their high symmetry, stability, and low toxicity. These clusters have negative charges. Due to the delocalization of negative charge, these boron clusters are weakly coordinating anions. Moreover, the salts of these clusters could be dissolved in organic solvents. With these in mind, the salts could be used in organic synthesis by making the positively charged counter cation for catalytic activity. That is, in the metal salts of these clusters, metal cations are considered to be 'naked'. In this study, the synthesis of unsubstituted closo-dodecaborate dianion was synthesized from sodium borohydride. Amino and oxo derivatives are synthesized and characterized. Both periodinated and perchlorinated derivatives were also synthesized, isolated and the effects on the catalytic activity of copper cation were studied. It was found that a ligand for copper is necessary to carry out Cu-mediated Ullmann's coupling and Cu-mediated TEMPO alcohol oxidation reactions.

Keywords: Boranes, closo-dodecaboranes, copper catalysis, perhalogenated boranes, borane derivatives

ÖZ

KLOSO-DODEKABORAT DİANYON TÜREVLERİNİN KATALİTİK TEPKİMLERDEKİ KULLANIMLARI ÜZERİNE ÇALIŞMALAR

Albayrak, Oğuzhan
Yüksek Lisans, Kimya
Tez Yöneticisi: Prof. Dr. Akın Akdağ

Ağustos 2021, 106 sayfa

İkozahedral bor kümeleri, yüksek simetri, kararlılık ve düşük toksisitelerinden dolayı çok yönlü ve benzersiz bor bileşikleridir. Bu kümeler negatif yüklere sahiptir. Negatif yükün delokalizasyonu nedeniyle, bu bor kümeleri zayıf koordine edici anyonlardır. Ayrıca bu kümelerin tuzları organik çözücüler içinde çözülebilir. Bu bakış açısıyla, tuzlar katalitik aktivite için pozitif yüklü karşı katyon oluşturarak organik sentezlerde kullanılabilir. Bu kümelerin tuzlarındaki metal katyonları için bir diğer deyişle 'çıplak' olarak söz edilebilir. Bu çalışmada, sodyum borhidrürden sübstitüe edilmemiş kloso-dodekaborate dianyon sentezi yapılmıştır. Amino ve okso türevleri sentezlenip, karakterize edilmiştir. Hem periyotlu hem de perklorlu türevleri sentezlenip izole edilmiş ve bakır katyonunun katalitik aktivitesi üzerindeki etkileri incelenmiştir. Bakır aracılı Ullmann eşleşme tepkimelerini ve TEMPO alkol oksidasyon tepkimelerini gerçekleştirmek için bakır için bir ligandın gerekli olduğu bulunmuştur.

Anahtar Kelimeler: Boranlar, kloso-dodekaboranlar, bakır katalizör, halojenli boranlar, boran türevleri

To my beloved mother

ACKNOWLEDGMENTS

On this long and challenging *journey* where it is impossible to walk alone, I would like to mention the people who enlightened my path.

First and foremost, I would like to express my sincere gratitude to my supervisor Prof. Dr. Akın Akdağ for his guidance and patience through this *journey.* In these five years, I have learned a lot from him, and I am still learning.

Besides my advisor, I would like to thank the rest of the committee members: Prof. Dr. Özdemir Doğan, Prof. Dr. Ali Çırpan, Prof. Dr. Gülay Ertaş, and Prof. Dr. Adnan Bulut for their valuable comments, criticisms, and assistance in shaping the final draft of this study. I am thankful for their effort and time.

I would like to thank Prof. Dr. Ahmet M. Önal for DPV and CV measurements and his contributions to electrochemical studies.

I would like to thank Ulusal Bor Araştırma Enstitüsü (BOREN) for scholarship. (2018-30-06-30-004)

I would like to thank all my group members, Perihan Öztürk Düzenli, Ece Ayça Erdoğan, Bengi Şentürk, Ege Hoşgör, Doruk Baykal, Berçin Verda Asya, Bulem Çakmak, Nihat Aksoy, Sevban Doğan Ekici, Fatmanur Aydemir, Sadia Tul Munna and Ozan Ünver for sharing time and experiences, valuable and motivating discussions and friendship. Nothing would be easier without their support.

All these years in this journey and in my life, I have met extraordinary people who made me feel like the luckiest person in this universe. Thanks to their love, inspiration, support, and brotherhood, I have become who I am. My dearest friends, Taylan İçgen, Fatih Arıkan, Mert Kaptanoğlu, Faruk Osman Oruç, Fırat Acar, Atakan Arda Nalbant, Uğur Ekşi and Sadık Atalay. I am glad that I have you in my life. I am also deeply thankful to my sisters Gökçe Tidim and Beril Özdemir, who warm my heart and bring joy to my life, whatever the circumstance is.

I would like to thank my teacher, elder sister, and dear friend Gizem Ünay whose hard work and dedication to her job always inspired me. Thank you from the bottom of my heart for being my *Star of Eärendil* even I am in the darkest.

My most unique and deepest gratitude is devoted to my family, who support and love me endlessly. Dilek Topaloğlu, Mustafa Albayrak, and Aslıhan Albayrak. I love you so much.

TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

LIST OF SCHEMES

SCHEMES

LIST OF ABBREVIATIONS

ABBREVIATIONS

THF	Tetrahydrofuran
DMF	N,N-Dimethylformamide
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
NMP	N-Methyl-2-pyrrolidone
MeCN	Acetonitrile
EtOH	Ethanol
EtOAc	Ethyl acetate
acac	Acetylacetone
TEMPO	2,2,6,6-Tetramethylpiperidine 1-oxyl

CHAPTER 1

INTRODUCTION

1.1 Boron Atom

Boron was first discovered by two French chemists Gay-Lussac and Thénard, and by an English chemist Humphry Davy in 1808. Sir Humphry Davy realized when electrical current is applied to borate solutions, some brown precipitate forms. Then he used potassium to reduce borates, performed some experiments on this newly discovered material, and named this material *boracium*. Gay-Lussac and Thénard proved that boric acid is the oxidation of boron by first heating boric acid with iron to get boron and then to expose it to open air and oxidizing boron to boric acid.[1] Boron is the group 13 element with an atomic number of 5. Boron has two isotopes, ^{10}B (19.78%) and ^{11}B (80.22%), such that the average mass of boron is 10.81. Elemental boron is a metalloid and solid at room temperature. Although boron is a relatively inert metalloid, it is flammable and explosive when in contact with strong oxidizing agents.

1.1.1 Boron Minerals

Boron occurs in nature as boron oxides in boron minerals. The composition of boron oxide varies in different ores. For example, Kernite ($Na_2B_4O_7.4H_2O$), Ulexite ($NaCaB_5O_9.8H_2O$), Colemanite ($Ca_2B_6O_{11}.5H_2O$), Borax ($Na_2B_4O_7.10H_2O$) contains 51.0%, 43.0%, 50.8%, and 36.6% boron oxide respectively, and are commercially important minerals (Table 1).[2]

Table 1. Commercially important boron minerals

Mineral	Chemical Composition	B_2O_3 content weight percent
Boracite	$Mg_3B_7O_{13}Cl$	62.2
Colemanite	$Ca_2B_6O_{11}.5H_2O$	50.8
Datolite	$CaBSiO_4OH$	24.9
Hydroboracite	$CaMgB_6O_{11}.6H_2O$	50.5
Kernite	$Na_2B_4O_7.4H_2O$	51.0
Priceite	$Ca_4B_{10}O_{19}.7H_2O$	49.8
Probertite	$NaCaB_5O_9.5H_2O$	49.6
Sassolite	H_3BO_3	56.3
Szaibelyite	$MgBO_2OH$	41.4
Tincal	$Na_2B_4O_5(OH)_4.8H_2O$	36.5
Tincalconite	$Na_2B_4O_7.5H_2O$	47.8
Ulexite	$NaCaB_5O_9.8H_2O$	43.0

Tourmaline is a borosilicate compound containing various metals is the most abundant boron mineral on earth. However, it is not practical to use it as a boron source since it contains only 3.1% boron.[3] Turkey, the USA, Russia, Argentina, Peru, and China are located on boron mineral reserves. Turkey has the biggest of all reserves, 72% of all the boron deposits holding in 803 million tons. The next following boron reserve bearer is the USA, keeping in a total of 80 million tons.[2] Tincal, Colemanite, and Ulexite are the essential boron minerals for Turkey. Eskişehir-Kırga region has the largest tincal reserves. Colemanite is produced in different regions of Kütahya, Balıkesir and Bursa. Ulexite ore is also obtained from Balıkesir. Eti Holding, a state-owned company, is the only authorized company to process the boron minerals for all those productions.[2] Boron has large fields of applications such as fiberglass, heat-resistant glass, glazes, ceramics, cleaning materials and micronutrients. Annual consumptions of these are 41% for fiberglass

and heat-resistant glass, 13% is for glazes and ceramic additives, 12% is for cleaning materials and 6% is for fertilizers.[2]

1.2 Boranes

Boranes first discovered by Alfred Stock in 1912.[4] Stock discovered that the decomposition of magnesium boride with acid yielding liquid borane (B_4H_{10}) and upon heating, this liquid turns into a gaseous compound which will be later characterized then proved to be diborane (B_2H_6), the simplest member of boranes (Figure 1).[5]

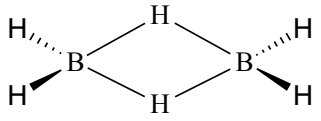


Figure 1. Molecular structure of diborane

For a long time, researches on these exotic compounds for military purposes and warfare technology have been founded. Many military related studies, as rocket fuels, were done on these compounds. Later on, the idea was abandoned but after all those years working on these compounds provided many routes of synthesis of various borane compounds.[6]

1.3 Polyhedral Boranes

After the discovery of diborane and other neutral borohydrides (B_2H_6, B_4H_{10}, B_5H_9 etc.) a great necessity emerged to explain their bonding model, because different from the traditional point of view of bonding model, number of valance electrons are not enough to form classical bonds ($2e^-$/bond) between atoms in molecule formula. In 1921, Dilthey first proposed the bridging hydrogens.[7] Later Bell and Longuet-Higgins using the vibrational spectrum of diborane deduced the structure of B_2H_6 contains B-H-B connectivity. Three-center two-electron (3c2e) concept is further

studied to explain the structure of boranes. After spectroscopic studies conforming the B-H-B bonds, It was stated that, Lipscomb and coworkers came up with a model that explained all the borane structures (Figure 2).[7]

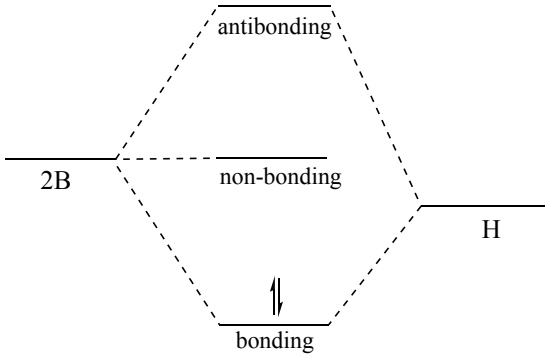
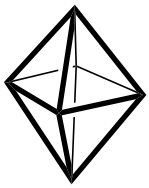
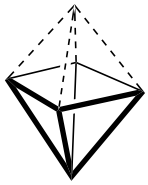
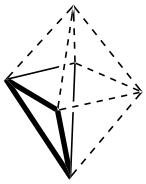


Figure 2. Localized Bonding Model of three-center-two-electron Bonding in a Single B-H-B Bridge.

A few decades later, for his contributions of revealing the borane structures and chemical bonding, Lipscomb awarded with Nobel Prize of Chemistry in 1976. In three-center two-electron concept, each atom provides one orbital to form one bonding and two antibonding orbitals such that two electrons reside in that one bonding orbital. For n number of atoms, n/3 number of bonding orbital exist and can be filled with 2n/3 electrons. This also explains that some structures depending on number n, shows more stability than the others.[7]

There are 3 main types of structures for the borane clusters which are called closo, nido, and arachno (Table 2).

Table 2. Polyhedral boron structures

			
Name of the polyhedral cluster	Closo	Nido	Arachno
Number of vertices	n	n-1	n-2
Types of bonding	B-H bonds	B-H bonds	B-H bonds
	B-B bonds	B-B bonds	B-B bonds
	-	B-H-B bons	B-H-B bonds
General Formula	$B_nH_n^{2-}$	B_nH_{n+4}	$B_nH_{n+5}^{-}$

Among all those structures there is no bridging hydrogen in the closo boranes. Nido and arachno structures, there are bridging hydrogens. The general formula for closo structure of boranes is $B_nH_n^{2-}$ and the most stable anions of these structures are in between n=6-12. In those anions, $B_7H_7^{2-}$ is the least stable one due to heptahydro-closo-heptaborate anion is the least symmetrical one which causes the deficiency of charge delocalization. The nido structure of boranes is the one vertex less form of closo boranes. The name nido comes from Latin word '*nidus*' meaning that nest. General formula for nido structure of borane clusters is B_nH_{n+4}. Diborane (B_2H_6) and decahydro-nido-decaborate ($B_{10}H_{14}$) are the famous examples of this type of boranes.

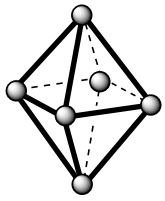
As anionic example for this class can be given as borohydride anion (BH_4^-) The arachno structure is the one less vertex of nido structure and it comes from Latin word '*arachne*' meaning that spider. The general formula for arachno structure of boranes is $B_nH_{n+5}^-$. As an example, arachno-triborane anion $B_3H_8^-$ which is used as

building block for the synthesis of higher order of boranes can be given. The stability of structures is decreased from closo to arachno.[8]

Determination of structures of polyhedral clusters of boranes and carbaboranes were hard. In 1976, Ken Wade developed a rule to predict the shape of those clusters by counting the total number of electrons and determining the electrons required to cluster formation. He stated that, a cluster with n, n-1, n-2, and n-3 vertices and n+1 skeletal electron pair have closo, nido, and arachno structures, respectively.[9] For instance, for the molecule $B_{12}H_{12}^{2-}$ number of total electrons of the cluster is 50, total electrons for B-H bonding are 24, then total number of skeletal electrons are 26. According to wade's rule for n+1 skeletal electron pairs (26/2) 13 in this case, n=12 meaning that $B_{12}H_{12}^{2-}$ has a closo structure.

1.4 Closo-boranes

In 1964, James L. Boone is first synthesized and isolated hexahydro-closo-hexaborate dianion, $B_6H_6^{2-}$, by refluxing diborane and sodium borohydride in diglyme (Figure 3).[10]



$B_6H_6^{2-}$

Figure 3. Hexahydro-closo-hexaborate dianion

In 1966, F. Klanberg and E. Muetterties have started a series to complete the other polyhedral borane anions. Decomposing the alkali metal salts of triborane anions, $B_3H_8^-$ under vacuum at 200-230 ^oC yielded different polyhedral compounds, but they were be able to isolate and characterize $B_9H_9^{2-}$, and $B_{11}H_{11}^{2-}$ anions (Figure 4).

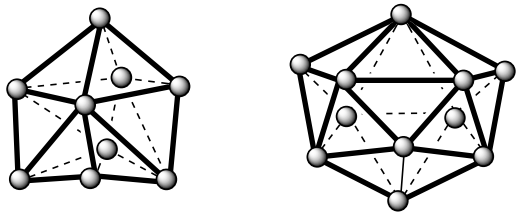


Figure 4. (a) Nonahydro-closo-nonaborate; (b) undecahydro-closo-undecaborate dianions

Even though the yield of $B_9H_9^{2-}$ anion was low,[11] one year later, in 1967, Muetterties and coworkers exposing the aqueous solution of $B_9H_9^{2-}$ into the air at above 25 °C, yielded the other small boranes, $B_7H_7^{2-}$ and $B_8H_8^{2-}$ (Figure 5).[12]

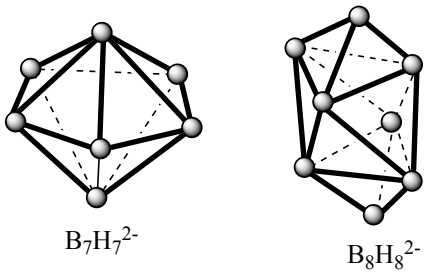


Figure 5. (a) Heptahydro-closo-heptaborate; (b) octahydro-closo-octaborate dianions

In 1960, Anthony Pitochelli and Frederick Hawthorne, by refluxing 2-iododecaborane and triethylamine in benzene yielded very little amount of triethylammonium dodecahydro-closo-dodecaborate salt, $(NHEt_3)_2B_{12}H_{12}$, and triethylammonium decahydro-closo-decaborate (Figure 6).[13]

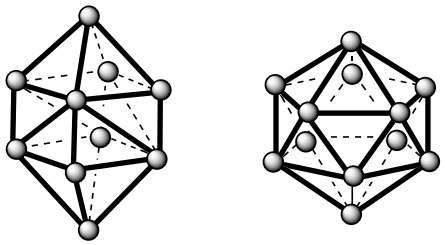


Figure 6. (a) Decahydro-closo-dodecaborate; (b) dodecahydro-closo-dodecaborate dianions

1.4.1 Carbaboranes

Carbaboranes, also known as carboranes, are one of the polyhedral cluster types of boranes. Different from polyhedral borane clusters, which have only BH units, they have at least one CH unit in the cluster. Carboranes, likewise other polyhedral boranes, are synthesized after theoretical considerations. In 1962, William Lipscomb and Roald Hoffman performed computational studies on polyhedral boranes as well as carboranes.[14] After Longuet-Higgins stated that dodecahydro-closo-dodecaborate can exist only with minus two charges ($B_{12}H_{12}^{2-}$), it seemed possible to obtain monocarboranes ($CB_{11}H_{12}^{1-}$) and dicarboranes ($C_2B_{10}H_{12}$). Since BH^- is isoelectronic with CH unit, if one BH^- is replaced with CH unit, one can get monocarborane anions (Figure 7).

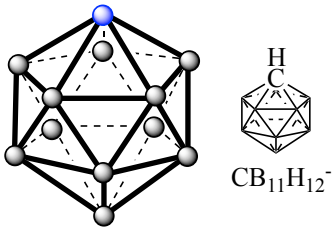
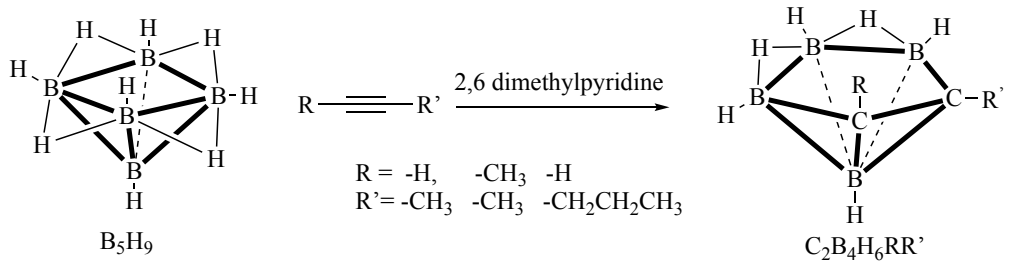


Figure 7. Monocarborane molecule

If two B-H^- units are replaced with two C-H units, one can get dicarboranes which are neutral icosahedral boron clusters. Likewise polyhedral boranes, carboranes were

also interested in military researches. After World War II, these borohydrides based exotic compounds were thought to replace hydrocarbon-based rocket fuels due to capacity of generating more energy.[15] As far as we know, these compounds were synthesized at first in 1950s but become available at common literature after early 1960s. One of the early publications on the synthesis of the carboranes is the study of Onak, Williams and Weiss. In 1961, Onak and coworkers synthesized nido-$C_2B_4H_6$ with hydrogen, methyl and propyl derivatives using pentaborane as borane source and corresponding alkynes in the presence of 2,6-dimethylpyridine (Scheme 1).[16]



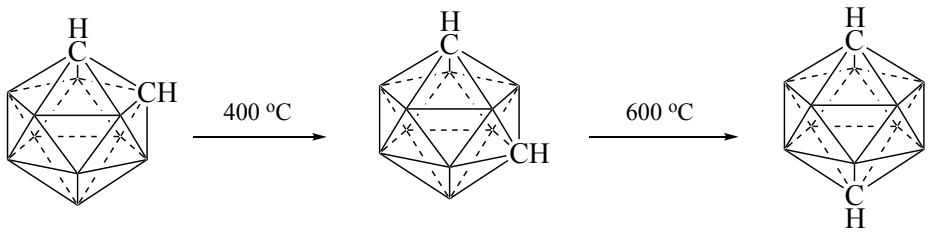
Scheme 1. Synthesis of dicarborane from pentaborane

Two isomers of closo-$C_2B_4H_6$ and closo-$C_2B_3H_5$ was synthesized by Shapiro and coworkers by the electrochemical reaction of pentaborane (B_5H_9) and acetylene.[17]

Two years later, in 1963, 1,2-$C_2B_{10}H_{12}$ was synthesized and characterized by Thiokol and Olin-Mathieson and reported as series of papers[18,19,20]. 1,7- and 1,12- isomers were also synthesized by thermal rearrangement and characterized.[21]

Replacing BH^- unit with CH unit changes the overall polarity of borane cluster, resulting highly polarized CH bond. Unlike the hydrogens bonded with boron, the hydrogen on carbon atom in carboranes becomes acidic which can be abstracted by the help of a base and easy derivatization of carboranes on carbon-side. Since carboranes are boron cluster with replaced some BH units with CH units, they also follow the same structural base as boranes. The numbering starts on the carbon of the polyhedral and follows the same rule of numbering borane cluster. For dicarboranes the position 1,2-,1,7-, and 1,12- are called ortho, meta, and para

respectively. For instance, 1,2-dicarborane is also called ortho-carborane (Scheme 2).



$C_2B_{10}H_{12}$ ortho- ***o-***

$C_2B_{10}H_{12}$ meta- ***m-***

$C_2B_{10}H_{12}$ para- ***p-***

Scheme 2. Thermal isomerization of dicarboranes

Electron counting and Wade's rule can predict the thermodynamically preferred structure but it cannot predict the stability relation of the structures. Especially carboranes since there is a hetero atom, carbon, in the formula. Unsubstituted dicarborane case, the stability increases from ortho isomer to para isomer.[22]

The synthetic route for carboranes may vary. The common way can be summarized by the reaction of polyhedral boranes and alkynes either in solution or in gas phase by the help of electrical discharge.[23] As a characteristic feature of carboranes they can rearrange the position of carbons more favorable isomer thermodynamically. This is called thermal cage isomerization. For example, thermal isomerization of unsubstituted dicarborane occurs as heating ortho-carborane up to 400 °C results in meta-carborane, and heating meta-carborane above 600 °C results in para-carborane (Scheme 2).[22] For the substituted carboranes case, as the substituents on carbon gets bigger at size in other words as the substituents gets bulkier, the energy to isomerize the carboranes is lowered.[24]

Same as $B_{12}H_{12}^{2-}$ anion, $CB_{11}H_{12}^{1-}$ and $C_2B_{10}H_{12}$ are hydrophobic. Since the derivatization on carbon for carboranes is readily available, carboranes are used in biomolecule synthesis. There are plenty of examples of derivatization of amino acids with carboranes such as alanine[25,26], and tyrosine[27], nucleic acids or peptides.[28,29]

1.4.2 Closo-dodecaboranes

Dodecahydro-closo-dodecaborate anion, $B_{12}H_{12}^{2-}$, is the member of the boranes has the highest symmetry with a point group I_h. 12 boron and 12 hydrogen atoms are arranged to form icosahedral structure, showing incredible thermal stability.

In 1955, Longuet-Higgins and Roberts first performed the MO-LCAO calculations, and they stated that, $B_{12}H_{12}$ cluster may only exist with 2- charges.[30] After the calculation and the prediction, in 1960, Hawthorne-Pitochelli first synthesized and isolated dodecahydro-closo-dodecaborate dianion by refluxing 2-iododecaborane and triethyl amine in benzene. However, the yield was too low, only 3.8% (Scheme 3).[13]

$$B_{10}H_{13}I + N(CH_2CH_3)_3 \xrightarrow[\text{reflux, 5h}]{\text{dry benzene}} [HN(CH_2CH_3)_3]_2B_{10}H_{10} + [HN(CH_2CH_3)_3]_2B_{12}H_{12}$$

3.8%

Scheme 3. First synthesis of triethylammonium dodecahydro-closo-dodecaborate

To increase the yield, different routes of synthesis were studied. In 1963, Ellis and coworkers proposed that, refluxing the freshly synthesized NaB_3H_8 solution is yielding dodecahydro-closo-dodecaborate (Scheme 4).[31]

$$NaBH_4 + B_2H_6 \xrightarrow{>50\ ^oC} NaB_3H_8 + H_2$$

> 90% yield

$$NaB_3H_8 \xrightarrow[120\ ^oC]{\text{dimethoxy ethane}} Na_2B_{12}H_{12}$$

50% yield

Scheme 4. Synthesis of closo-dodecaborane from triborane

In their study, they used different base-borane adduct and compared the yield of forming polyhedral borane compounds (Table 3).

Table 3. Base-borane adduct studies

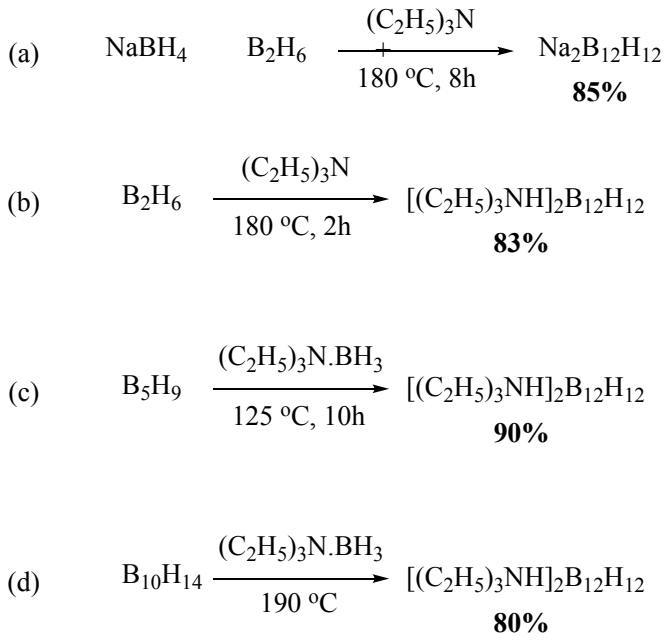
Base-borane adduct	Temperature (°C)	$B_{12}H_{12}^{2-}$ yield (%)
$(C_2H_5)_3NBH_3$	180	>90
$(CH_3)_3NBH_3$	175	40-60
$(CH_3)_3PBH_3$	175	low
$(CH_3)_3AsBH_3$	175	Not observed
$(CH_3)_2SBH_3$	70	Not observed
$(CH_3)_2SBH_3$	150	1

In 1964, Miller and Muetterties thought that to synthesize polyhedral boranes, at first the Lewis base-borane complex must be synthesized since borohydride and Lewis's base are strongly related. They prepared several alkylated amine borane complexes and reported the relative yields of borane compounds (Table 4).

Table 4. Amine studies

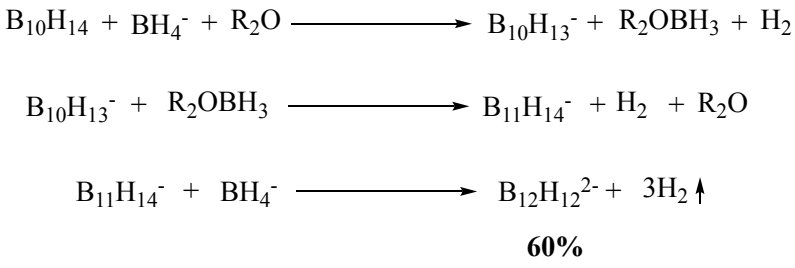
Amine	$B_{12}H_{11}NR_3^-$ yield (%)	$B_{12}H_{12}^{2-}$ yield (%)
$N(CH_3)_3$	27	64
$N(CH_3)_2C_2H_5$	11	80
$NCH_3(C_2H_5)_2$	8	80
$N(C_2H_5)_3$	0-5	80-100
$N(CH_2)_5CH_3$	13	55

Heating triethylamine borane with sodium borohydride at 180 °C yielded 85% , with diborane at 180 °C yielded 83%, with pentaborane (B_5H_8) at 125 °C yielded 90%, with decaborane ($B_{10}H_{14}$) at 190 °C yielded 80% triethylammonium dodecahydro-closo-dodecaborate (Scheme 5).[32]



Scheme 5. (a) closo-dodecaborane synthesis from diborane and sodium borohydride, (b) closo-dodecaborane synthesis from diborane, (c) closo-dodecaborane synthesis from pentaborane, (d) closo-dodecaborane synthesis from decaborane.

In same year, Adams and coworkers proposed heating at 90 °C decaborane ($B_{10}H_{14}$) with one equivalent sodium borohydride in diethylene glycol dimethyl ether, diglyme, forms undecaborane, $B_{11}H_{14}^-$, then after addition of second equivalent sodium borohydride and refluxing in diglyme yielded 60% dodecahydro-closo-dodecaborate (Scheme 6).[33]



Scheme 6. Synthesis of closo-dodecaborane from decaborane

1.4.2.1 Weakly Coordination

Weakly coordinating anions is the anion that shows low coordination affinity to its surrounding cations. To achieve this, the electrons on anion must be stabilized by delocalization on the overall molecule.[34] Weakly coordinating anion concept first thought for the ions like BF_4^-, $CF_3SO_3^-$, SbF_6^- etc. As the coordination and bonding characteristics of polyhedral boranes studied, they show also weakly coordinating anion phenomena due to their powerful electron delocalization ability, so that, the $B_{12}H_{12}^{2-}$ anions are weakly coordinating anions. Recent studies show that, perhalogenated closo-dodecaborate anions ($B_{12}Cl_{12}$, $B_{12}Br_{12}$, $B_{12}I_{12}$) are more promising weakly coordinating anions due to their higher electron delocalization ability compared to dodecahydro-closo-dodecaborate anion and larger size.[8]

Weakly coordinating ability of the polyhedral boron clusters resulting the counter cation to be 'naked'. Considering the extreme low basicity of anion makes the conjugate acid pair to be strongly acidic. The DFT studies of gas phase closo-dodecaborate derivatives performed by Koppel and coworkers. According to their scale of Gibbs Free energy of the Acid comparison, sulfuric acid has the value of 301.2 where the hydronium dodecahydro-closo-dodecaborane has the value of 268. Furthermore, in the same scale hexafluoro antimonic acid has the value 255.5 where hydronium dodecafluoro-closo-dodecaborane has the value 213.[35] As the electron withdrawing substituents are added to cluster, it results in increase in acidity of the molecule.

Due to coulombs forces, it's challenging to abstract protons from dianions and instability of dianions in the gas phase, polyhedral boron clusters show surprising high acidity in the gas phase.[36] In condensed phase neutral diprotic superacids $H_2B_{12}Cl_{12}$ and $H_2B_{12}Br_{12}$ is synthesized and isolated by Reed and coworkers.[37] These acids are also capable of protonate benzene in a solution.

1.4.2.2 Aromaticity

The aromaticity which can be shortly defined as *unusual stability*. It was thought as its related with cyclic systems with conjugated p-orbitals and certain number of electrons which brings unusual stability to the compounds. The rule, known as Hückel's rule, emphasizes 4n+2 number of electrons are necessary.

Closo- type borohydrides which have $B_nH_n^{2-}$ general formula, are 3-dimensional molecules. From the Wade's rule these polyhedrons have 2n+2 vertices. In Wade's rule of electron counting of skeletal electrons, later refined by Mingos who took consideration of exo-electrons which corresponds the B-H bonds of the cluster. Finally Wade-Mingos rule become 4n+2 which resembles Hückel's aromaticity.

The aromaticity idea of dodecahydro-closo-dodecaborate anion comes from the tendency to retain 3-dimensional structure of molecule under extreme thermal conditions. That's why Lipscomb and coworkers thought that, $B_{12}H_{12}^{2-}$ dianion shows super-aromaticity in 1969. Nowadays, it is widely accepted that closo-polyhedral boranes are aromatic because of the supporting information from nucleus-independent chemical shifts (NICS), resonance energy and bond length calculations.[38]

The aromaticity of deltahedral boron clusters comes from the resemblance of Kekule structure of benzene. In Kekule structure there are exactly same number of carbon-carbon double and carbon-carbon single bonds where the bonds alter to resonance hybrid structures (Figure 8). In deltahedral boron clusters ($B_nH_n^{2-}$ $5 < n < 13$) the number of B_2 two-center-two-electron bonds and B_3 there-center-two-electron bonds are same. Thus, the two-center-two-electron bonds and three-center-two-electron bonds alter (Figure 8).

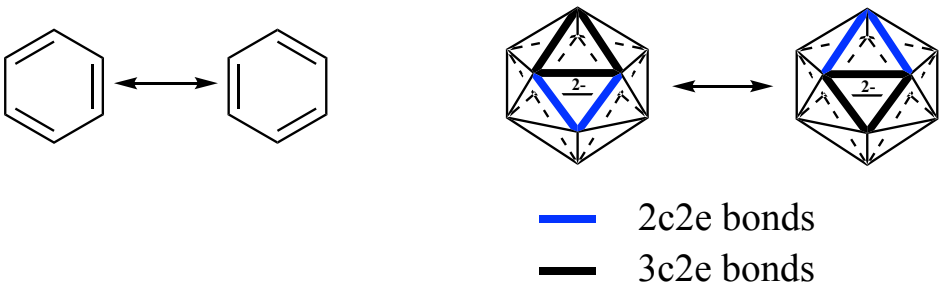


Figure 8. Hybrid resonance structures of C_6H_6 and $B_{12}H_{12}^{2-}$

1.5 Substitution on Boron Clusters

It is important to substitute the hydrogens on cluster with other hetero atoms. Beside the direct usage of $B_{12}H_{12}^{2-}$, substituting the hydrogen with halogens changes the coordination ability of the clusters due to increasing size and dispersion of negative charge. Substituting B-H bonds partially or completely with oxygen, nitrogen, sulfur etc. helps to insert such cluster to different organic compounds.[8]

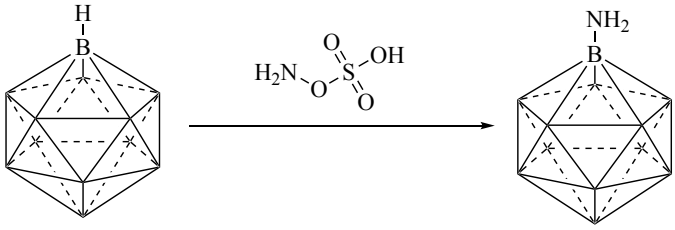
1.5.1 Monosubstitution

Introducing a hetero-atom into the dodecahydro-closo-dodecaborate anion can be performed through a nucleophilic attack from the heteroatom. Due to the hydridic nature of the cluster, initially formed oxonium or ammonium intermediates can be easily stabilized then in suitable conditions, and they are readily reactive for the other electrophilic centers.[39]

1.5.1.1 Amino Derivative

Amino derivative of boron clusters can be further derivatized to obtain new drugs for treatments of various diseases due to their high lipophilicity, low toxicity for biologic systems and unusual electronic structure. For mono amination of closo-dodecaborate most used method is by using hydroxylamine-*O*-sulfonic acid. Sodium

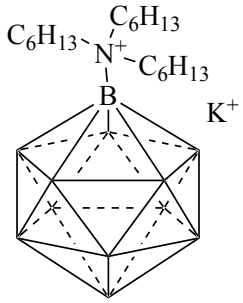
salt of closo-dodecaborate reacts with hydroxylamine-*O*-sulfonic acid in aqueous media to yield mono substituted derivative of closo-dodecaborate (Scheme 7).



Scheme 7. Monoamination of closo-dodecaborate anion

In literature,[40,6] it is also stated that, depending on the reaction time and temperature, poly-amine substituted derivatives are also formed.

The aminated dodecaborates are also used as ionic liquids. Ionic liquid is a term to define the salts in the liquid phase. Generally, it is defined for the salts having melting point below 100 °C. Ionic liquids have broad and important field of application since they can be used as electrolytes or solvents. For instance, table salt NaCl melts at 801 °C, and it is not practical to use that liquid as the named applications. For this purpose, some salts of dodecahydro-closo-dodecaborate salts are developed. For example, Gabel and coworkers found that potassium salt of N,N,N-trialkylated derivatives of dodecahydro-closo-dodecaborate have a melting point at 65 °C (Figure 9).[39]

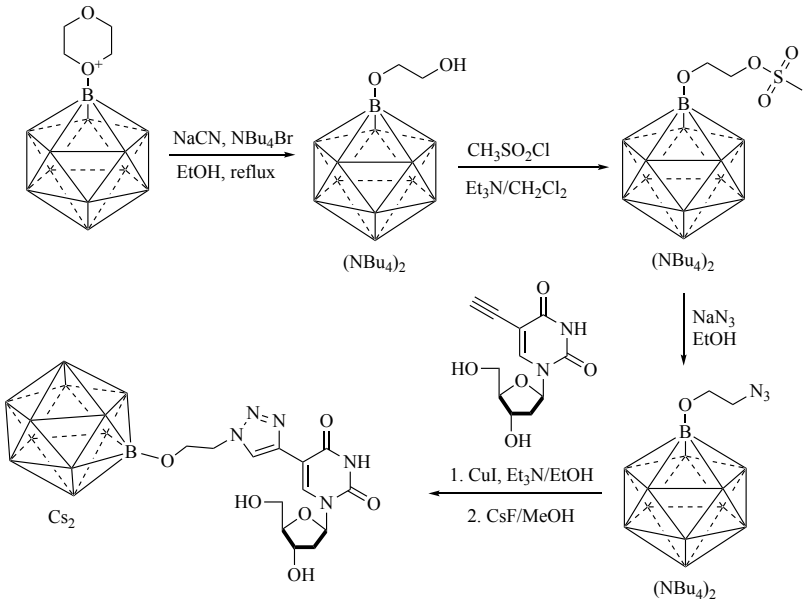


Melting point 65 °C

Figure 9. Potassium trialkylated-closo-dodecaborate as ionic liquid

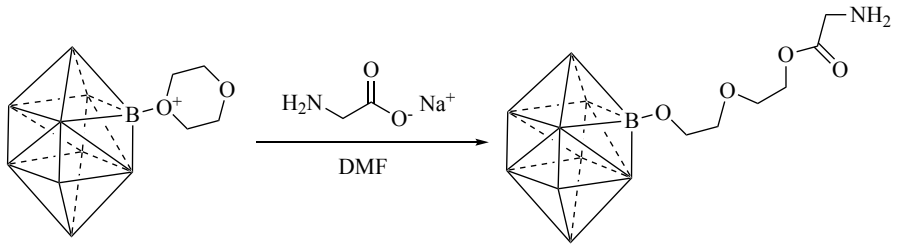
1.5.1.2 Oxonium Derivative

Derivatizing $B_{12}H_{12}^{2-}$ anion with cyclic oxonium derivatives are important synthons for further synthesis of bioactive molecules. After the insertion of cyclic oxonium to the cluster, the rest becomes organic synthesis and straight forward organic reactions. For instance, recently Loskova and coworkers reported a facile synthesis of deoxyadenosine derivative of $B_{12}H_{12}^{2-}$ anion (Scheme 8).[41]



Scheme 8. Deoxyadenosine derivative of closo-dodecaborane

Matveev and coworkers are synthesized amino acid derivative of decaborane starting from oxonium derivative closo-decaborane (Scheme 9)**.**[42]



Scheme 9. Glycine derivative of closo-dodecaborane

1.5.1.3 Mercapto Derivative

Boron Neuron Capture Therapy is a treatment method based on a nuclear reaction of ^{10}B isotope. When the boron compounds, in this case boron cluster rich with ^{10}B isotope, are bombarded with neutron gun and then consequent nuclear reaction occurs yielding $^{7}Li^{+}$ cations and highly energetic alpha particles (Figure 10). This phenomenon is used to kill tumor cells causing cancer.

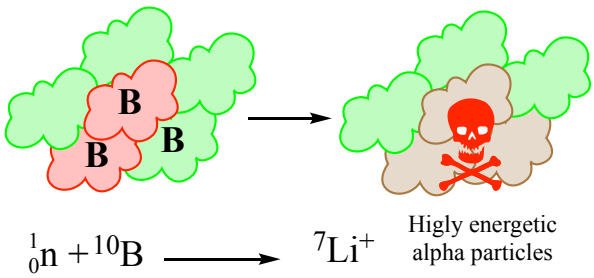
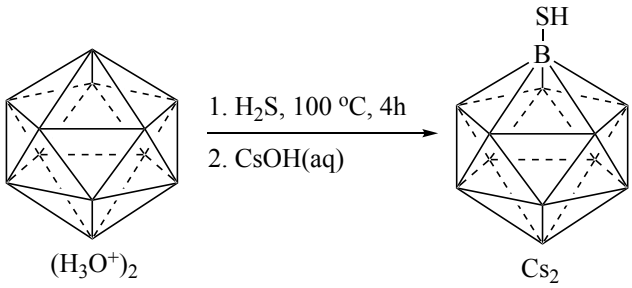


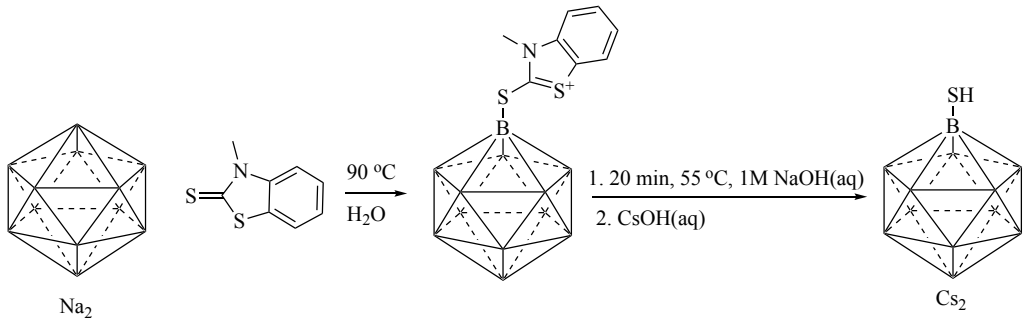
Figure 10. Boron Neutron Capture Therapy

Closo-dodecaborates are in interest for high boron content, high lipophilicity and low toxicity in biological systems.[43] There are several reports of forming mercapto derivative of closo-dodecaborate anion in the literature.[45] The first synthesis in solvent-free conditions, using hydrogen sulfide and hydronium salt of dodecaborate yields Mercapto-closo-dodecaborate (Scheme 10).[44]



Scheme 10. First synthesis of mercapto-closo-dodecaborate

In 1978 Eugene and coworkers synthesized mercapto derivative with different conditions. Starting from hydronium salt of closo-dodecaborate and N-methyl benzothiazole-2-thione then hydrolysis of the product yield Mercapto derivative efficiently (Scheme 11).[45]



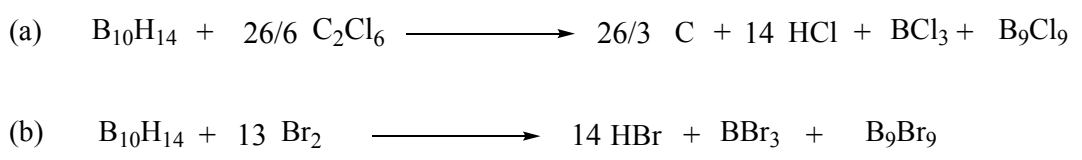
Scheme 11. Efficient mercapto-closo-dodecaborate synthesis

1.5.2 Persubstitution

Unique bonding character and 3D-aromaticty coming from the electron delocalization of these exotic molecules draws a lot of attention. Persubstitution is meaning that the complete substitution of radial hydrogens on the cluster with different heteroatoms or molecules. Polarization, electronic structure and electron delocalization is related with the radial substituents. Changing the substituents brings new insights about the weakly coordinating anion concept. Persubstituted -closo-dodecaborane anions have wide range of applications such as weakly-coordinating anions, radio imaging and boron-neutron capture therapy.[46] Since 3D aromaticity is mainly related with closo-structures of boron clusters, in this section, it is focused on persubstitution of closo-boranes.

1.5.2.1 Perhalogenation

First example of the smallest perhalogenated boron cluster is reported in 1953. Atoji and Lipscomb[47] reported that tetrachloro-closo-tetraborate (B_4Cl_4) which is obtained from the decomposing B_2Cl_4 is not halogenated after the synthesis B_4H_4. Instead, it is synthesized from B-Cl units. On the other hand, in the case of other boranes starting from hexahydro-closo-hexaborate, the synthesis path is started with unsubstituted boron cluster, then moves on with the replacement of hydrogens with halogens. Perhalogenation of B_6H_6 cluster is first reported by Preetz and Fritze in 1984. Starting from B_6H_6, under strong basic conditions, halogenation was performed with free halogens, B_6X_6 (X = Cl, Br, I).[48] Relatively larger boranes, B_nH_n for n=7,11 except n=10, somehow the studies on perhalogenation of those clusters are limited. Kurtz and Morrison reported perbrominated boron clusters B_nBr_n (n= 7,11) by decomposition of B_2Br_4 at elevated temperatures in 1997.[49] Hönle and coworkers reported the synthesis of B_9Cl_9 by degradation of $B_{10}H_{14}$ with C_2Cl_4 (and B_9Br_9 by degradation of $B_{10}H_{14}$ with elemental bromine (Scheme 12).[50]



Scheme 12. (a) perchlorination of closo-nonaborane, (b) perbromination of closo-nonaborane

In 1963, Muetterties and coworkers published the perhalogenation of $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$ anions. Perchlorinated, perbrominated, and periodinated derivatives of $B_{10}H_{10}$ and $B_{12}H_{12}$ anions are accomplished by using elemental halogens. The speed of halogenation of $B_{10}H_{10}$ and $B_{12}H_{12}$ differs due to relative stability of these clusters. As expected, the halogenation of decaborane is faster than the halogenation of dodecaborane. The reactivity of the halogens against boron clusters as expected decreases from chlorine to iodine. For both anions, partial halogenation happens very fast. According to Muetterties and coworkers $B_{10}H_9I$ cannot be obtained by just using

one equivalent of iodine since even one equivalent of halogen is used partial halogenation occurs with an appreciable rate.[51]

Using supercritical hydrogen fluoride at 550 °C, Solntsev and coworkers successfully synthesized first example of $B_{12}F_{12}^{2-}$ anion as cesium salt, with a yield of 38%.[52] Later Strauss and coworkers improved the synthesis of perfluorination of closo-dodecaborate with an appreciable yield, up to 74%.[53,54] When elemental fluorine and hydrogen fluoride are used for perfluorination in the presence of water, 1-hydroxy-undecafluoro-closo-dodecaborate ($B_{12}F_{11}OH$) is obtained.[51] Reaction with hydrogen fluoride and $B_{12}H_{12}^{2-}$ results in different degrees of fluorination, which can be separated. In the case of chlorination of $B_{12}H_{12}$ anion, Ozerov and coworkers reported that perchlorination of closo-dodecaborate can be achieved sulfuryl chloride SO_2Cl_2 as a chlorinating agent instead of elemental chlorine gas (Scheme 13).[55]

$$Na_2B_{12}H_{12} + SO_2Cl_2 \xrightarrow[CsCl]{MeCN} Cs_2B_{12}Cl_{12}$$

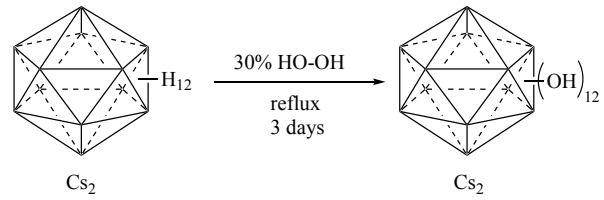
Scheme 13. Perchlorination of closo-dodecaborane without chlorine gas

For the characterization, the infrared absorption frequencies of perhalogenated dodecaboranes are similar. The characteristic signals for $B_{12}Cl_{12}^{2-}$, $B_{12}Br_{12}^{2-}$, $B_{12}I_{12}^{2-}$ are 1030 cm^{-1}, 1000 cm^{-1} and 940 cm^{-1} respectively.[51]

Perhalogenated clusters, like unsubstituted clusters, shows unexpected stability. For instance, $B_{12}I_{12}$ anion which has 93% iodine, shows no degradation under the treatment of chlorine, 20% sodium hydroxide at 85 °C, or sulfuric acid at 150 °C.[51] Thermal stability of the closo-dodecaborate clusters has already been known. In the case of perhalogenated derivatives, the thermal stability of clusters remains same. For example, when $Cs_2B_{10}Cl_{10}$ is heated up to 600 °C under vacuum only 4% of its mass lost. $Cs_2B_{12}Cl_{12}$ on the other hand, lost is only 3% when heated to 700 °C as expected. Further heating up to 900 °C, 50% of its mass is lost and degraded in to boron trichloride.[51]

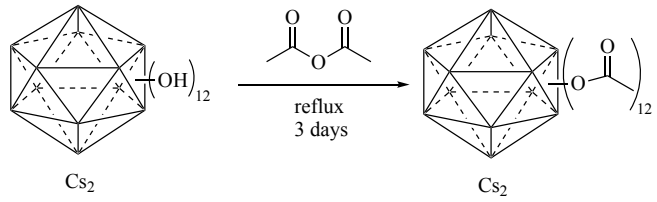
1.5.2.2 Perhydroxylation

Perhydroxylation of cesium salt of dodecaborate is first reported by Hawthorne and coworkers. Several days reacting cesium dodecahydro-closo-dodecaborate, $Cs_2B_{12}H_{12}$, with 30% hydrogen peroxide resulted in cesium dodecahydroxo-closo-dodecaborate, $Cs_2B_{12}(OH)_{12}$ (Scheme 14).[56]



Scheme 14. Perhydroxylation of closo-dodecaborane

By using cation exchange, different salts of perhydroxy-closo-dodecaborate salts are also isolated. Changing the cation from cesium to tetrabutylammonium, solubility of salt increases in organic solvent thus makes easy to further derivatization.[57,58] Esterification of hydroxy groups or perhydroxy-closo-dodecaborate first reported by Hawthorne and coworkers. They used acetic anhydride and benzoyl chloride in esterification reactions, and isolated both ester derivatives (Scheme 15).[59]



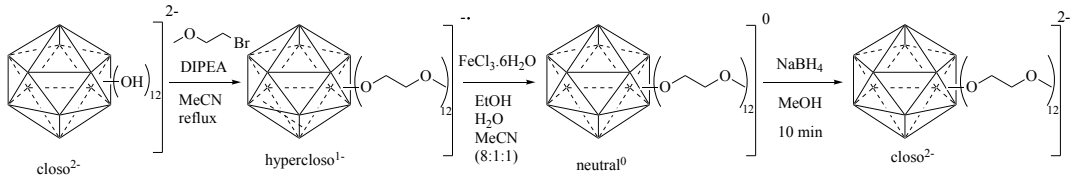
Scheme 15. Peresterification of closo-dodecaborate

Same as esterification, etherification is also possible for these clusters and Hawthorne and coworkers refluxing benzyl chloride and perhydroxy-closo-dodecaborate in acetonitrile for 6 days, obtained $B_{12}(OPh)_{12}$ as ammonium salt with 48% yield.[46] Since the reaction times for these reactions are very long, in 2016,

Spokoyny and coworkers reported that tetrabutylammonium salt of $B_{12}(OPh)_{12}$ is synthesized at 140 °C in microwave in 15 minutes with 63% yield.[60]

In 1955, Longuet-Higgins clearly stated[30] that dodecahydro-closo-dodecaborate can only exist with 2- charges $B_{12}H_{12}^{2-}$. This statement holds for unsubstituted closo-dodecaborate which has very high oxidation potentials. Applying those potentials results in degradation in boron cluster.[61] On the other hand, single oxidation of perhalogenated closo-dodecaborate can form stable hypercloso-$B_{12}X_{12}^{-}$ species.[62] In 1999, Hawthorne and coworkers reported the single oxidation and isolation of $B_{12}(CH_3)_{12}^{-}$ and $B_{12}(OH)_{12}^{-}$ anions.[63]

Recently, Goswami and coworkers published the peresterified derivative of closo-dodecaborate anion is single oxidized two times and obtained hyper closo-dodecaborate and neutral closo-dodecaborate anions (Scheme 16).[64]



Scheme 16. Single oxidation of closo-dodecaborane derivatives

Those are used as biothiol sensor probe where it discriminates the bio-thiols from amino acids.

1.6 Boron Metal Complexes

Metalloboranes are the coordination compounds of boranes and carboranes with metals. The coordination can be through B-H-M bridge, through B-M direct bonding or through B-H bonding.

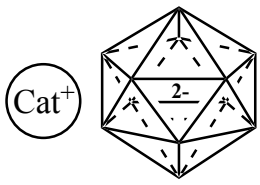
In classical bonding, two electrons are required to form a bond between two centers such as ethene (C_2H_6). However, in borohydride chemistry such as diborane, B_2H_6, there are not enough electrons to form bond between this much of centers.[65] Boron and its hydrides are electron deficient compounds since boron has not enough

valance electrons to use in bonding. To overcome this electron deficiency, boron compounds accept electron pairs and act as Lewis's base L • BH_3 where L = CO, $(CH_3)_2O$, $(CH_3)_3N$ etc. or forms polyhedral clusters with three-center-two-electron bonds.[66] After the three-center-two electron bonding model explained the connectivity of these compounds, it was also realized the similarity between polyhedral boron compounds and olefin-metal coordination compounds where three-center-two-electron bonding can be observed (Figure 11).[65]

B_3 (3c2e) olefin-metal (3c2e)

Figure 11. Three-center-two-electron bonding for B_3 and olefin-metal complexes

The negative two charge is also distributed evenly in the cluster. This distribution of charge in large space makes deltahedral borane clusters a perfect candidate for weakly coordinating anions.[65] The aromaticity of deltahedral boron clusters, a possible candidate of weakly coordinating anions, complexation tendency of boron compounds and electronic resemblance of organic ligands in organometallic chemistry makes them potential ligands for organometallic reactions. In the literature,[6] several metal salts of dodecahydro-closo-dodecaborate anion are synthesized and isolated (Figure 12).



Cat^+: Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Zn^{2+}, Al^{3+}, Sc^{3+}, Zr^{4+}, Cu^+, Ag^+, Th^+

Figure 12. Numerous salts of dodecahydro-closo-dodecaborate dianion

The complexation reaction of deltahedral boron clusters, in this case decahydro-closo-decaborane, $B_{10}H_{10}^{2-}$, is performed by reacting salts of polyhedral borane anions and metal salts in the presence of organic ligand. During the complex formation, metathesis or redox reactions may occur in metal atom if several stable oxidation states exist.[67] A. Malinina and co-workers reported zinc (II) and cadmium (II) the complexes of decahydro-closo-decaborane starting from triethylammonium salt of closo-decaborane (Scheme 17).[68]

$$M(NO_3)_2 + (Et_3NH)_2B_{10}H_{10} \xrightarrow[\text{Bipy}]{\text{DMF}} [M(DMF)_6][B_{10}H_{10}]$$

M = Zn(II), Cd(II),

Scheme 17. Synthesis of closo-decaborane complexes

V. Avdeeva and co-workers synthesized and isolated the complexation product of closo-decaborate with Fe (II) and Fe (III) ions, bipyridine as an auxiliary ligand.[67] In 2019, Malinina and coworkers starting with hydronium salt of closo-dodecaborate and copper (I) chloride, synthesized and isolated bipyridylamine and bipyridine complexes.[69]

1.6.1 Boron Cluster Metal Complexes in Catalytic Reactions

In the literature,[6] the complexations of closo-dodecaborate and closo-decaborate is widely studied. Ni, Co, Fe, Cr, Mn, Pt, Pd, Ru, Pb, Hg, Cd, Zn, rare earth metals, and U complexes are studied in terms of weakly coordinating ability.

Highly symmetrical deltahedral boron dianions ($B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$) shows kinetic and thermal stability through oxidative-reductive environments. Unlike many other borane anions, closo-dodecaborate have lower toxicity makes them suitable candidates for catalytic usage in reactions. In 2019, E. Larm[70] and co-workers reported a study where gold nanoparticles of closo-decaborane are used in reduction of 4-nitrophenol to 4-aminophenol (Figure 13). In that study, gold and silver nanoparticles are synthesized and it is also reported $Cs_2B_{12}H_{12}$ has an effect of both

reducing and stabilizing the gold nanoparticles during the synthesis. Another advantage of using polyhedral clusters in catalytic reactions is that clusters are ^{13}C-NMR silent which is perfect for ^{13}C monitoring the catalyzed reaction.[70]

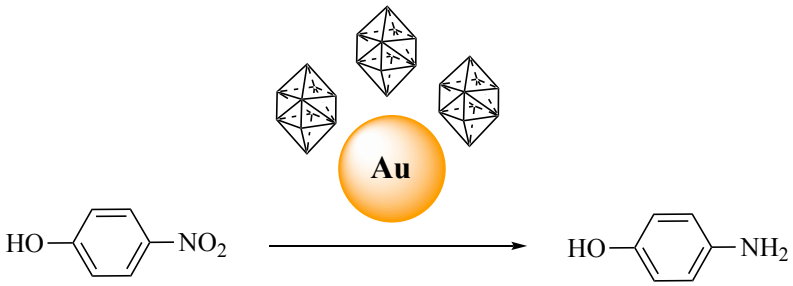


Figure 13. Nitrophenol reduction using closo-decaborane gold nanoparticles

1.7 Copper in Catalytic Reactions

Copper is a transition metal element in group 11. It is an earth abundant and low-cost metal. Copper has high boiling point which makes the copper a good candidate catalyst for wide range of chemical reactions. Copper has several available oxidation states Cu, Cu^{+}, Cu^{2+}, Cu^{3+} which is also necessary for the limit of the catalytic reactions. As a drawback, copper is susceptible of oxidizing easily to form various copper oxides. Fortunately, copper nanoparticles as well as copper oxide nanoparticles are modified and explored effective way of usages. Copper and copper-based nanoparticles have wide area of usages as catalyst such as photocatalysis, electrocatalysis, cross-coupling reactions and Ullmann reactions.[71]

The preparation of Cu-based nanomaterials can be done by two methods, bottom-up and top-down. The bottom-up method starts the atomic size level and builds up to nanoparticle size. On the other hand, the top-down method starts from larger sized materials and by treating to form nanosized material. It depends on the resources and the application area to decide which of the methods will be used. However, the bottom-up method is preferred since the size of nanoparticle is well controlled.[71]

Depending on the application or reaction conditions Cu-based nanoparticles can also be mounted on some supporters which increases the surface area and enhanced

features of the nanoparticles.[71] Various supporters are used such as activated carbon, carbon nanotubes, diamond, various polymers, silica, zeolite etc. Likewise copper complexes, copper-based nanoparticles are also widely used in catalytic reactions.

1.7.1 Copper Mediated Ullmann Reactions

Ullmann reactions are cross-coupling reactions where copper metal used in elevated temperatures. The classical Ullmann type reactions require high boiling point solvents and strong bases. To make the reaction conditions milder and easy to handle, several ligands and additives are in use. By enhancing the reactivity of copper, people overcome the drawbacks of copper mediated Ullmann reaction and improve the catalytic reactions.[72]

1.7.1.1 Copper-Mediated Ullmann Type C-N cross-coupling Reactions

Developing facile and low-cost C-N bond forming reactions are urgent and important. For this purpose, earth-abundant and cheap copper metal is a perfect candidate for the cross-coupling reactions. Improved ligand systems, temperature of the reaction and new bases are the studies performed recently for copper catalyzed C-N coupling reactions.[73] For copper-mediated cross-coupling reactions the reaction scheme can be simplified as reactants, copper source, base and ligand systems. The components of the scheme are studied and still under interest.

Unlike inorganic bases, the organic bases are handy in copper-catalyzed amination reactions since they can act as ligand and as base at the same time.[74] The amines are important for copper catalyzed reaction where they can act as both ligand and base. One of the first reports of these studies are from Liu and coworkers in 2009.[72] They studied Ullmann type C-N cross-coupling reactions using substituted bromo and iodobenzene as substrate, tetraalkyl ammonium and tetraalkyl phosphonium salts as organic ionic bases. They concluded, based on the outcomes of coupled product, being a good base not only related with its good solubility but also the ionization

ability where several electrical conductivities of organic ionic bases in an organic solvent is studied.[72]

Lo and coworkers studied copper catalyzed C-N coupling reactions using tetrabutyl phosphonium malonate as organic ionic base and several ligands. (DMEDA, 2,2'-bipyridine, N-methyl glycine, L/D-proline etc.) and concluded that the ligands having secondary amine functionality are increasing the reaction rate. For the ligands having alcohol or phenol functionalities having little or non-effecting the reaction rate.

Du F. and his coworkers recently published a study where Cu^{2+} mediated C-N coupling reactions performed and optimized. They have used a natural ligand called QCT (quebrachitol), which is an industrial by product of natural rubber production. In that study, several aliphatic and aromatic amines are used with aryl halides to form C-N bonds.[75]

Lo Q. and coworkers studied the C-N cross coupling reaction of benzylamine and iodobenzene. They used CuI as Cu^{+} source and the effect of ammonium and phosphonium bases are studied. They used salt forms of these bases and concluded that the counter cation of the base has little effect on the catalytic activity of copper. They obtained highest yields when both tetrabutyl ammonium and tetrabutyl phosphonium malonate is used. According to their study, it is important to note that when they used N-metylgycine end L-proline are used as base and ligand no product formation is observed. Although, these ligands are well known ligands that are used in C-N coupling reactions promoting high yields.[74]

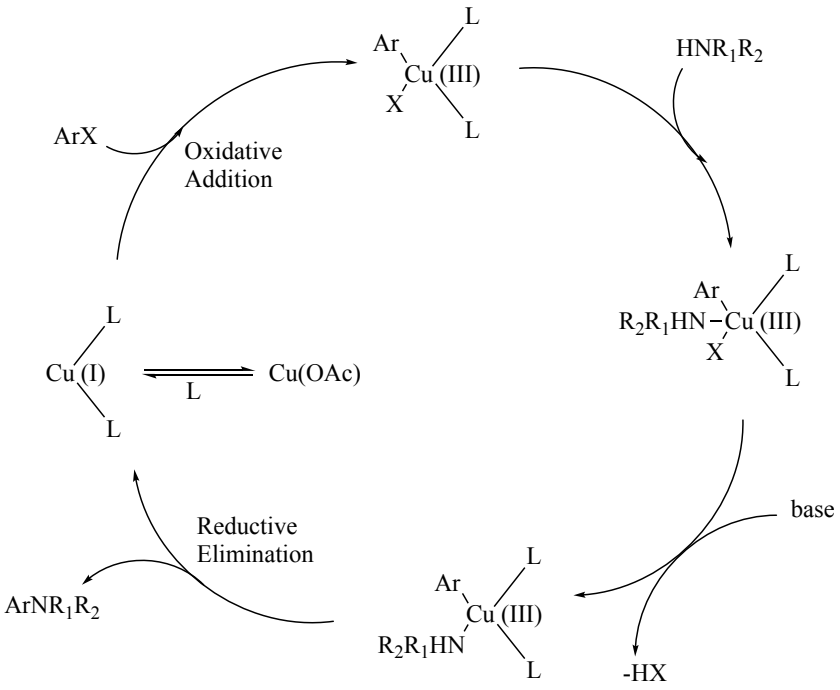


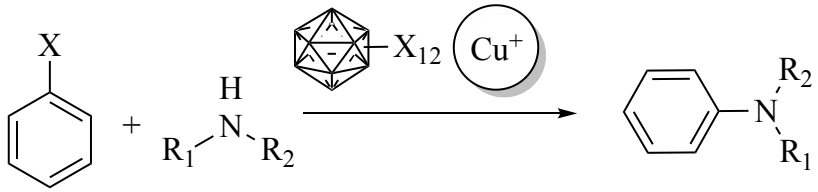
Figure 14. Proposed catalytic cycle for Cu(I) mediated coupling reactions

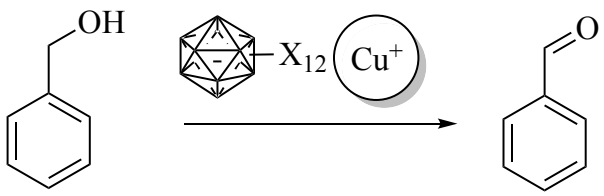
In the catalytic cycle of copper-catalyzed cross-coupling reactions, there are spectroscopic evidences of forming Cu (III) intermediate (Figure 14). However, the catalytic cycle is not deeply studied in terms of mechanistic and kinetically. Even though the Cu-mediated Ullmann type amination reactions are studied as substrate, as ligand/base system; the concept is still exotic since there is no superior reaction conditions for these types of reaction

CHAPTER 2

AIM OF THE STUDY

Polyhedral boron cages, due to their electron delocalization are known as weakly coordinating anions. Weakly coordinating ability of these molecules makes the counter cation ‘naked’, so the cation will be more active. Since the mechanism and kinetics of copper mediated C-N coupling reactions are not thoroughly studied in the literature and copper is a green and readily available metal, we decided to focus on copper metal. Our hypothesis is to use the weakly coordinating ability of closo-dodecaborate derivatives to make copper ‘naked’ in the reactions where we expect to increase catalytic efficiency of copper. The aim of this study is to synthesis and derivatization of dodecaborates and use them in the catalytic copper reactions which are copper mediated Ullmann reactions and copper catalyzed alcohol oxidation reactions.





CHAPTER 3

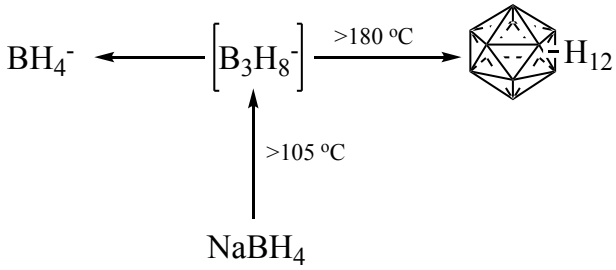
RESULTS AND DISCUSSION

3.1 Synthesis

3.1.1 Synthesis of triethylammonium dodecahydro-closo-dodecaborate

After the first synthesis of dodecahydro-closo-dodecaborate by Pitochelli and Hawthorn, different synthesis routes have been studied. From diborane to decaborane different starting materials and methods are currently in use.[6]

The synthesis of closo-dodecaborate is proceeding through *in situ* formation of triborane then disproportionation of triborane to borohydride and closo-dodecaborate dianion (Scheme 18). Since starting material, sodium borohydride, and intermediates are strong reducers and adding account in working at high temperatures, (180 ^{o}C) the reaction must be water and oxygen free. To sustain that, in the literature the reaction is carried out in glove box.[76] To adapt the procedure in our lab, a closed system with a constant argon flow is established (Figure 15). Since formation of possible intermediates (diboranes, triboranes etc.) are harmful, at the end of the system, an acetone trap is used.



Scheme 18. Disproportionation of triborane

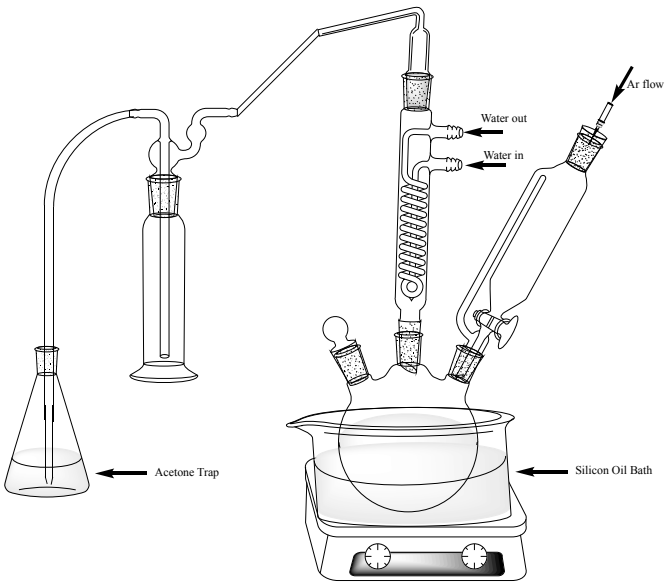


Figure 15. Reaction setup for the synthesis of triethylammonium dodecahydro-closo-dodecaborate

Before any chemical added into the system, setup is flushed with argon to make sure system is closed and air free. First iodine is dissolved in diglyme and charged in the pressure equalized dropping funnel. Sodium borohydride and diglyme are measured and added into three necked round-bottom-flask. Once the additions were completed and system was closed, argon flow was started. After obtaining the inert atmosphere in the system, stirring and heating were started. At this point, before the addition of iodine, temperature must be above 100 ºC where the sodium borohydride starts to dissolve in diglyme. This step is one of the important steps where the yield is directly affected, this was observed in our experiments. For example, the reaction was run at 110 ºC oil bath temperature, the reaction did not yield any product. There is usually at 10 ºC difference between oil bath and inside of the flask temperature. However, this is not always the case. When we measure the inside temperature, it was below 100 ºC. Therefore, if this reaction wanted to be run in an oil bath, the oil bath temperature must be around 120 ºC. After the right temperature is obtained, where sodium borohydride has started the dissolve in diglyme, iodine solution is added slowly, over six hours. It is also reported that, the slow addition of iodine increases the overall yield. As observed in this thesis and other studies in our lab.[77] After the

addition is completed, yellowish solution is obtained and the reaction let stir for overnight. At that time and temperature, triborane ($B_3H_8^-$) anion formation is established. Next day, the temperature is increased to reflux where the disproportionation is started. Disproportionation of triboranes result in formation of dodecahydro-closo-dodecaborate dianion and borohydride anions. After reflux, diglyme was evaporated. Due to safety concerns, the solvent mostly collected and thick slurry was obtained. However, in the literature[80], the mixture is distilled off to dryness because of any presence of the diglyme in the next steps decreases the precipitation of the desired product. Then distilled water was slowly added to solution to quench the reaction where the reactive intermediates such as triboranes and disproportionation product, borohydrides, are turn into boric acid. The water addition must be effectively slow since during the quenching hydrogen gas is evaluated. After the addition of distilled water, concentrated hydrochloric acid was added to complete precipitation of boric acid in the solution. Since the solubility of boric acid in water is low, and sodium salt of dodecahydro-closo-dodecaborate is efficiently soluble at low temperatures (less than 10 °C), the solution was left at 4 °C overnight to collect most of the boric acid. Then boric acid was filtrated and collected as colorless crystals. The IR spectrum of collected boric acid as follows (Figure 16).

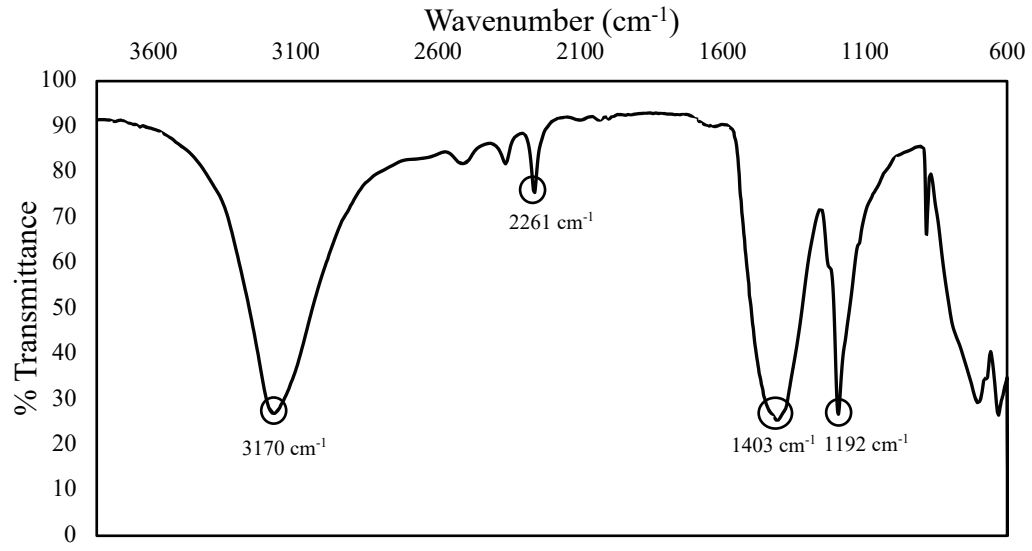


Figure 16. IR spectrum of boric acid

The characteristic signals are in accordance with the literature.[78] At that point, dissolved acidic solution of dodecahydro-closo-dodecaborate collected as numerous trialkyl ammonium counter cations. The triethylammonium salt is preferred in this study due to its availability and efficiency. That's why triethylamine was added into the acidic solution of dodecahydro-closo-dodecaborate and immediate white crystals of triethylammonium dodecahydro-closo-dodecaborate was precipitated. Leaving overnight in the 4 ºC completed the precipitation. For further purification, recrystallization over hot water or acetonitrile/water solvent system could be used. The IR spectrum of triethylammonium dodecahydro-closo-dodecaborate is as follows (Figure 17). Characteristic signals[79] are 2475 cm^{-1} for B-H stretching in closo-dodecaborate anion and 3125 cm^{-1} N-H stretching in triethylammonium cation.

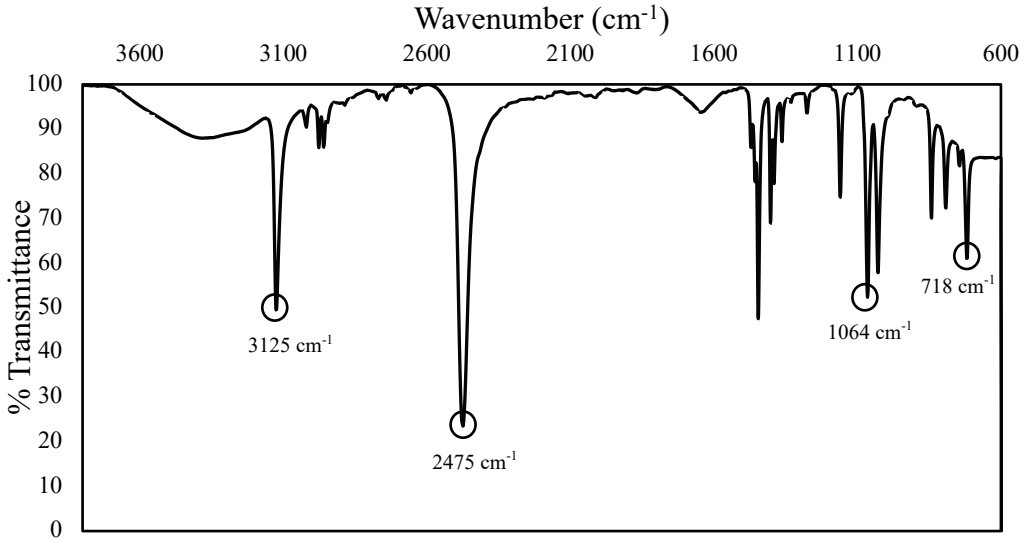
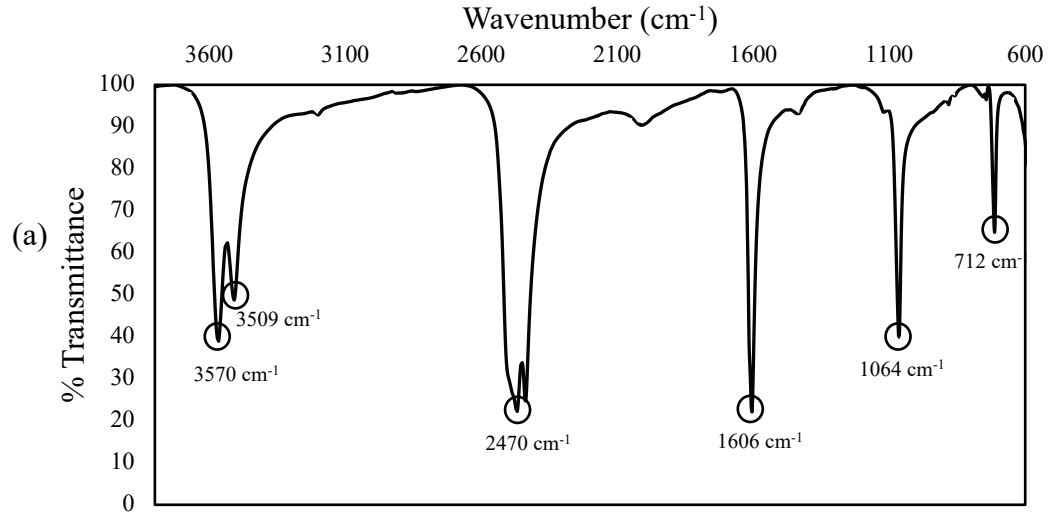


Figure 17. IR spectrum of triethylammonium dodecahydro-closo-dodecaborate

3.1.1.1 Cation Exchange Reactions of Dodecahydro-closo-dodecaborate Dianion

The cation exchange of triethylammonium salts can be performed by using the corresponding base of the desired cation, since, triethylammonium salts are acidic salts. To obtain sodium or potassium salts of dodecahydro-closo-dodecaborate dianion, sodium hydroxide or potassium hydroxide solutions were added into the suspension of triethylammonium dodecahydro-closo-dodecaborate in water. Hydroxide anion reacts with ammonium to yield free amine where after the evaporation of all volatiles, the sodium or potassium salt of dodecahydro-closo-dodecaborate was obtained. For alkali metal cations, sodium and potassium salts of dodecahydro-closo-dodecaborate is water soluble at room temperature. The salts are highly hygroscopic due to weak interaction between dodecahydro-closo-dodecaborate dianion with sodium and potassium. After removing the salts from vacuum system, white dry crystals of salt become wet immediately. IR spectra of sodium and potassium salts of dodecahydro-closo-dodecaborate is as in the Figure 18. The signals[80] at 1608 cm^{-1} and 3563 cm^{-1} indicates the water presence. The signals 2470 cm^{-1}, 1060 cm^{-1} and 710 cm^{-1} are the characteristic signals for dodecahydro-closo-dodecaborate dianion.



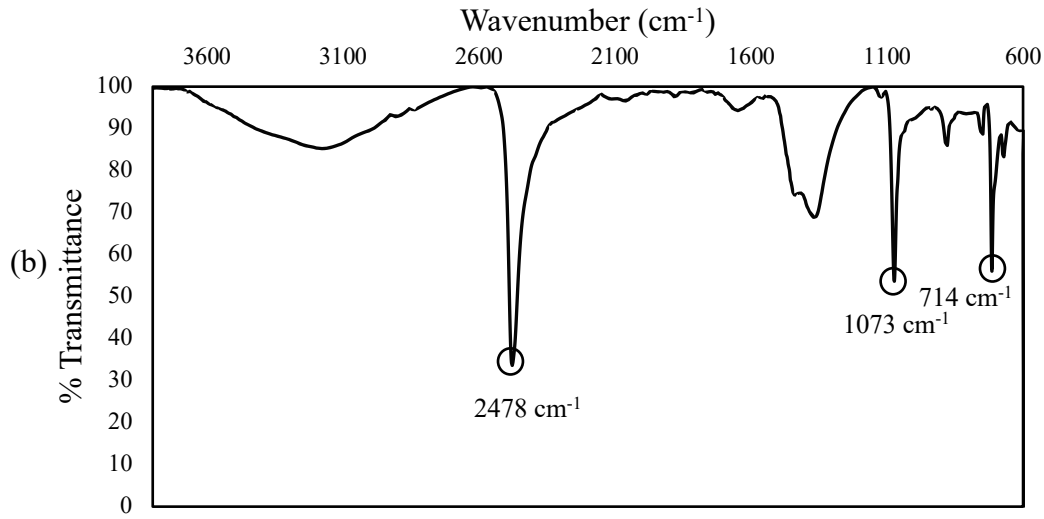


Figure 18. (a) IR spectrum of sodium dodecahydro-closo-dodecaborate; (b) IR spectrum of potassium dodecahydro-closo-dodecaborate

The cesium salt of closo-dodecaborate was synthesized from the sodium salt of closo-dodecaborate. Dissolving sodium dodecahydro-closo-dodecaborate in distilled water, cesium chloride was added. Immediate precipitation occurred. Filtrating the mixture yielded fine white cesium dodecahydro-closo-dodecaborate crystals (Figure 19). In IR spectra, it was observed that, sodium salt was found to be more hygroscopic than potassium salt which is more hygroscopic than cesium salt. This could be explained by the hardness of the cation. Hardness is coupled with *nakedness* of the cation gave the following order of hygroscopicity: $Na^+ > K^+ > Cs^+$

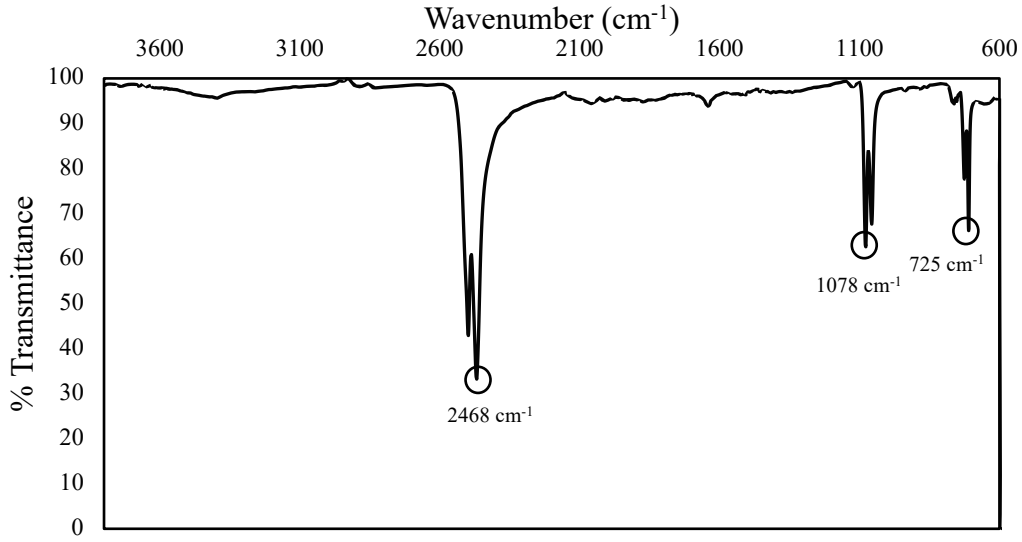


Figure 19. IR spectrum of cesium dodecahydro-closo-dodecaborate salt

Tetramethyl ammonium salt dodecahydro-closo-dodecaborate was obtained from sodium dodecahydro-closo-dodecaborate. Sodium dodecahydro-closo-dodecaborate was dissolved in water then tetramethyl ammonium chloride solution was added. White fine crystals of water-insoluble tetramethylammonium dodecahydro-closo-dodecaborate was immediately precipitated (Figure 20).

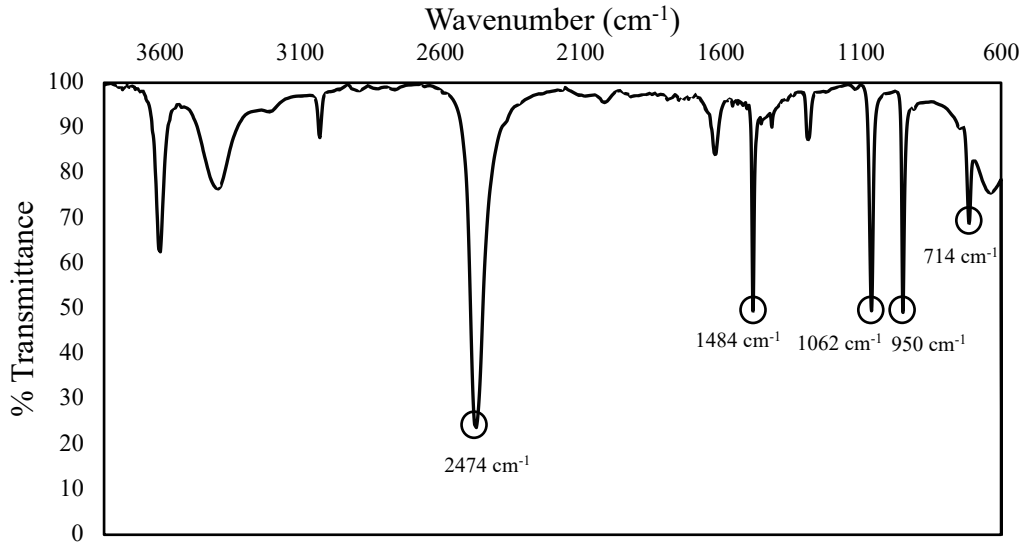


Figure 20. IR spectrum of tetramethylammonium-closo-dodecaborate

3.1.2 Synthesis of tetramethylammonium 1-amino-undecahydro-closo-dodecaborate

The amination reaction was carried out with hydroxylamine-*O*-sulfonic acid, a well-known aminating agent in the literature.[40] First, hydroxylamine-*O*-sulfonic acid was synthesized. Hydroxylamine hydrochloride was added into round-bottom-flask then slowly chlorosulfonic acid was added dropwise. Since chlorosulfonic acid is corrosive and water sensitive, the reaction must be carried out with care and water free environment. After mixing the reagents, white pasty mixture was obtained. Diethyl ether was added into the pasty mixture resulting in white precipitates which were collected by filtration, and washed with diethyl ether couple of times. IR spectrum of the product as follows (Figure 21). The spectrum is in accordance with the literature.[81]

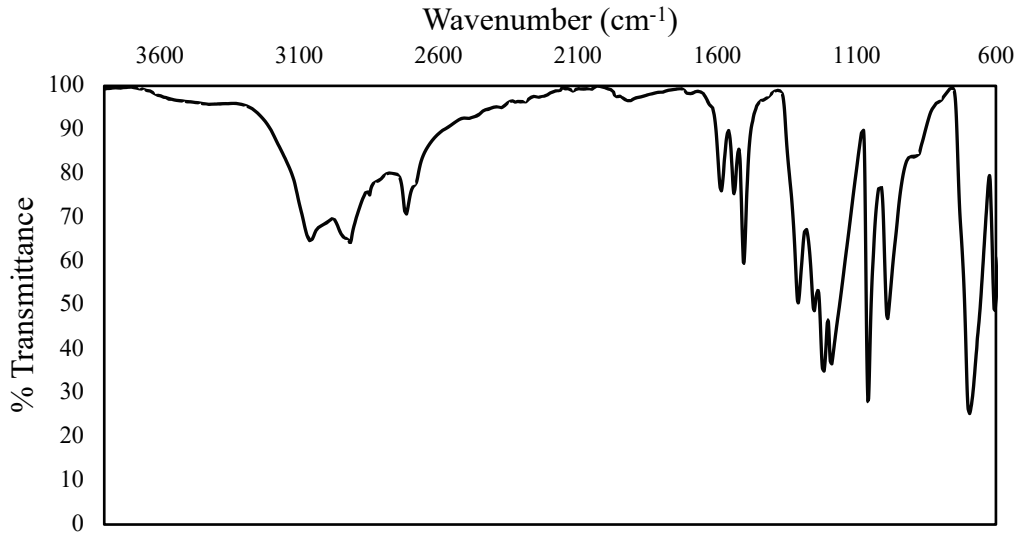


Figure 21. IR spectrum of hydroxylamine-*O*-sulfonic acid

Since the reaction media was water, the water-soluble sodium salt of dodecahydro-closo-dodecaborate was used for the amination reaction. Sodium dodecahydro-closo-dodecaborate was dissolved in water then hydroxylamine-*O*-sulfonic acid was added. The temperature increased to reflux. After the reaction was refluxed for three hours, it was cooled down to room temperature. In the literature, the reflux time and

hydroxylamine equivalency are crucial for the degree of amination in this procedure, refluxing it for a longer time with higher equivalents of hydroxylamine-*O*-sulfonic acid results in mixtures of diaminated products.[40,6] That is why, after three hours, the reaction was cooled down and work-up performed. The characterization of product was done by infrared spectroscopy which was readily available in our hands. For not to be confused or not to be masked with N-H stretching of triethylammonium counter cation, tetramethylammonium chloride was used as precipitating agent. In the IR spectrum of the collected product, the signals[40] at 3200-3250 cm^{-1} are N-H stretching of 1-amino-undecahydro-closo-dodecaborate (Figure 22).

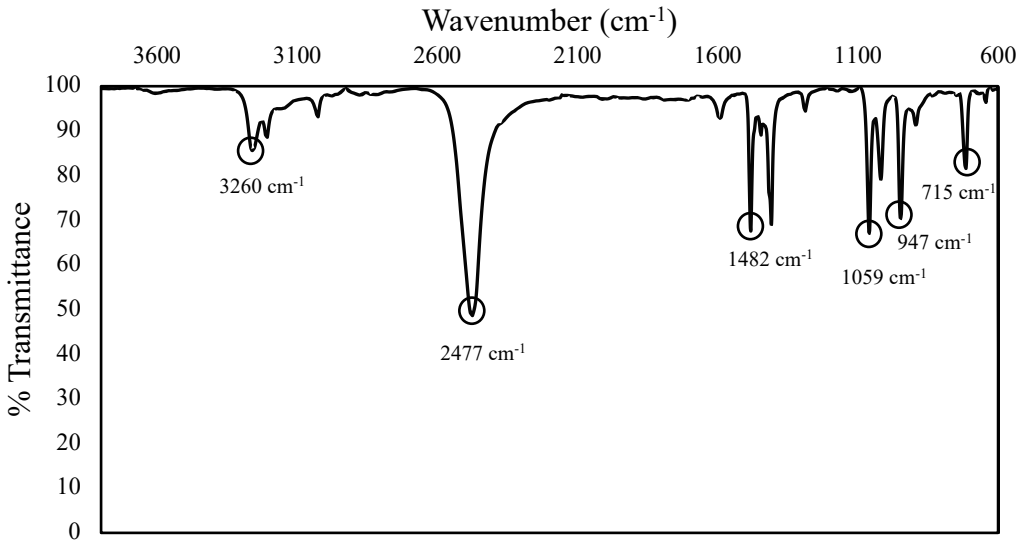


Figure 22. IR spectrum of tetramethylammonium 1-amino-undecahydro-closo-dodecaborate

To confirm the degree of amination of the cluster, high resolution mass spectrometry experiment was carried out, and confirmed that monoaminated product is obtained. Having a procedure working in our hands, the reaction was carried out with same conditions but this time triethylamine was used as precipitating agent in acidic conditions. However, it was observed that there was not expected N-H stretching in the IR spectrum. Then the reaction was carried out again and this time before adding any precipitating agent the reaction mixture divided into half, one half was acidified and triethylamine was added, and into the other half tetramethylammonium chloride

solution was added. From the IR spectra of these experiments (Figure 23), the one with tetramethylammonium added was precipitated out with amino-product where the other half precipitated out with the dodecaborane with no amine moiety.

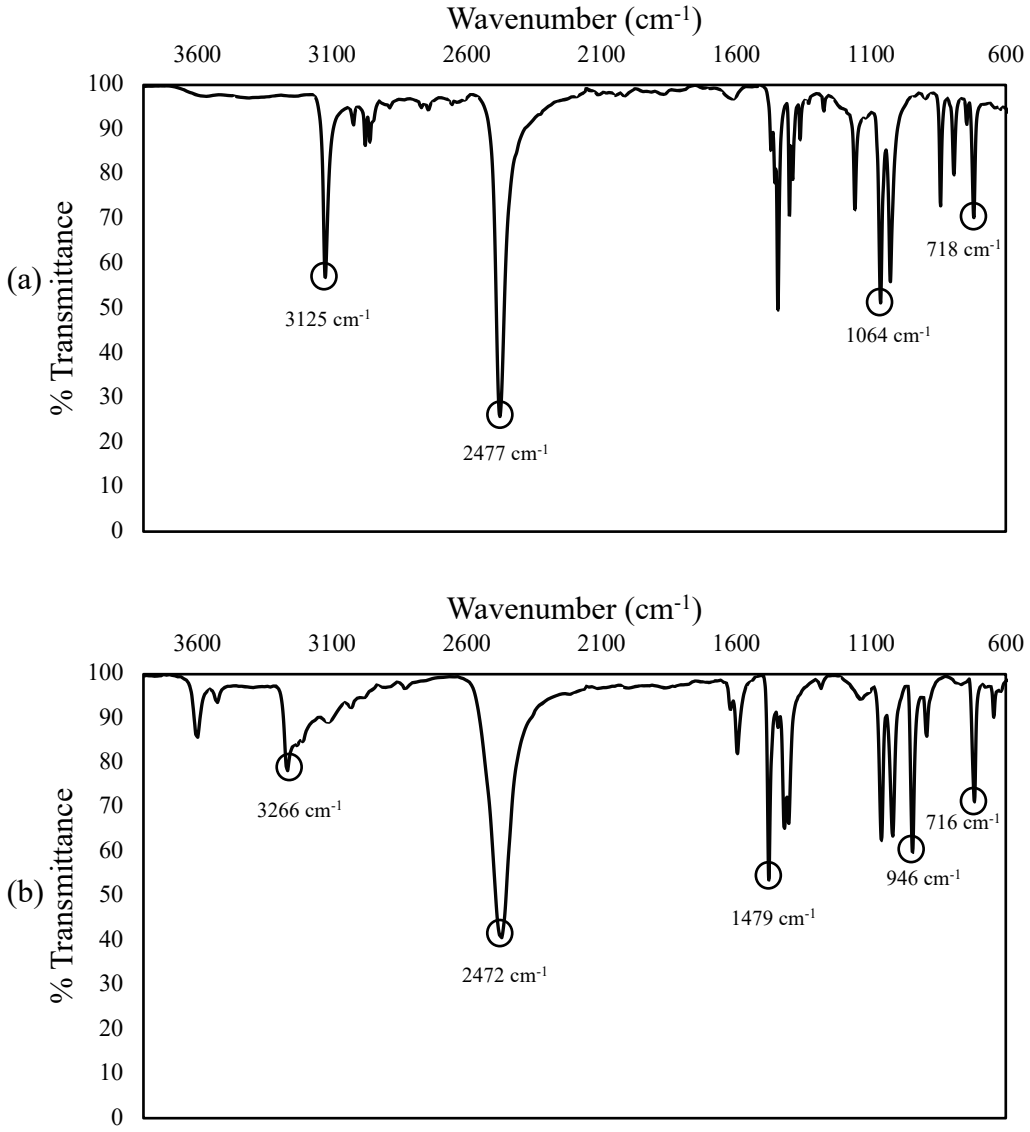


Figure 23. (a) The half precipitated with triethylamine; (b) the half precipitated with tetramethyl ammonium chloride

3.1.3 Synthesis of tetramethylammonium tetrahydrofuran-1-yl-undecahydro-closo-dodecaborate

The nature of B-H bonds of the dodecahydro-closo-dodecaborate are hydridic such that the Lewis acids can abstract the hydride on the cluster. For the synthesis of oxonium derivative, the hydride was abstracted by boron trifluoride diethyl etherate. Tetrahydrofuran, which was the solvent, attacked the electrophilic center and formed the oxonium moiety which was stabilized by the cluster. Since boron trifluoride is water sensitive, the THF must be freshly distilled and water-free. To eliminate competing reaction, the counter cation of dodecahydro-closo-dodecaborate dianion was chosen to be sodium. As a drawback, sodium dodecahydro-closo-dodecaborate is highly hygroscopic and brings water to the reaction. That's why boron trifluoride diethyl etherate was used very excess. Excess boron trifluoride diethyl etherate pacifies the water. First sodium dodecahydro-closo-dodecaborate was added into the freshly distilled dry THF and mixed for a while. The mixture was heterogeneous since the solubility of the sodium dodecahydro-closo-dodecaborate was low in the THF, then boron trifluoride diethyl ether was added to mixture and let stirred overnight at room temperature. Formed white crystals was dissolved in distilled water and after adding the tetramethylammonium chloride solution yielded the desired precipitate. The precipitate was left overnight at 4 ^{o}C to complete the precipitation. Then formed crystals were filtrated. From the IR spectrum (Figure 24), the signal at 2480 cm^{-1} represents the B-H bonding of the molecule.

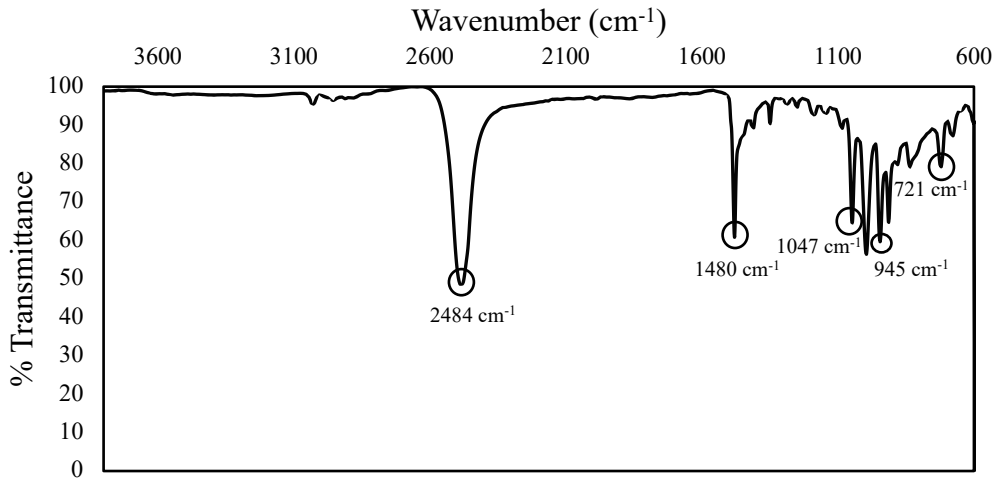


Figure 24. IR spectrum of tetramethylammonium tetrahydrofuran-1-yl-undecahydro-closo-dodecaborate

Crude ^{1}H NMR experiment was performed in DMSO (Figure 25). No further purification was performed. In the NMR spectrum, beside the chemical shifts and integral values, the integral of the protons on tetramethylammonium counter cation was comparable with the integral of the protons on the THF moiety. After inserting the oxonium moiety to the cluster, the overall charge of the cluster decreases by one, resulting with in total 1- charge. So that, only one tetramethylammonium is available as counter cation.

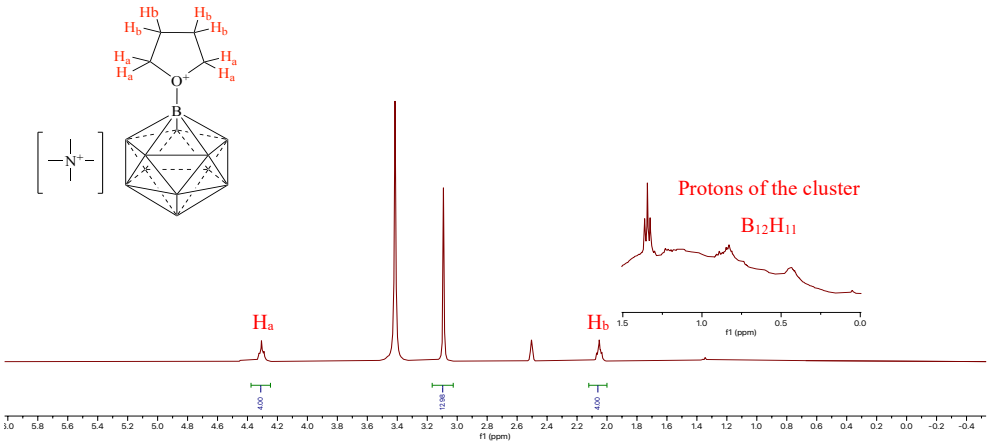


Figure 25. ^{1}H NMR spectrum of tetramethylammonium tetrahydrofuran-1-yl-undecahydro-closo-dodecaborate

3.1.4 Synthesis of tetramethylammonium 4-phthalimidobutoxy-undecahydro-closo-dodecaborate

Tetramethylammonium tetrahydrofuran-1-yl-undecahydro-closo-dodecaborate synthesized in previous step, was added into the DMF and dissolved. Stirred overnight at room temperature and formed white crystals were filtered. The filtrate was evaporated in *vacuo* and remaining white solids were dissolved in methanol. Tetramethylammonium chloride solution was added since in the previous experiment the overall charge of the cluster was 1-. After the nucleophilic attack from phthalimide to the bonded THF ring, the overall charge of the molecule become 2- again (Figure 26). The required tetramethylammonium cation become two equivalences. That's why, extra tetramethylammonium addition the mixture become necessary.

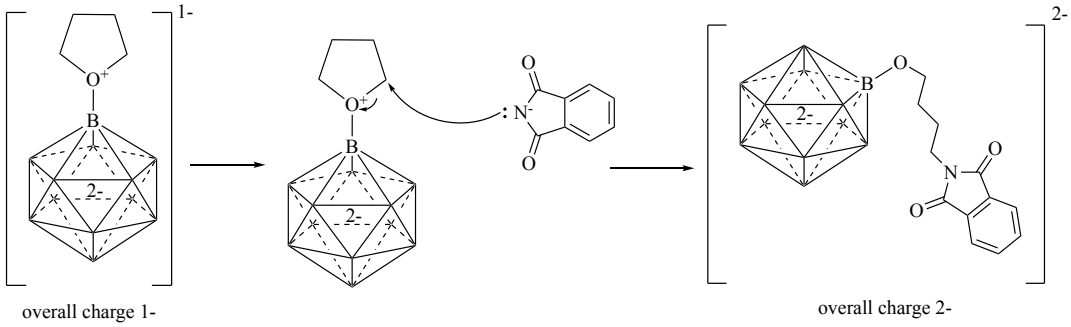


Figure 26. Overall charges of oxonium and oxy derivatives of closo-dodecaborate dianion

After the addition of extra tetramethylammonium, immediate precipitation observed and left overnight at 4 ^{o}C to complete the precipitation. Formed precipitates filtered and washed with DCM to remove soluble organic impurities and dried in air.

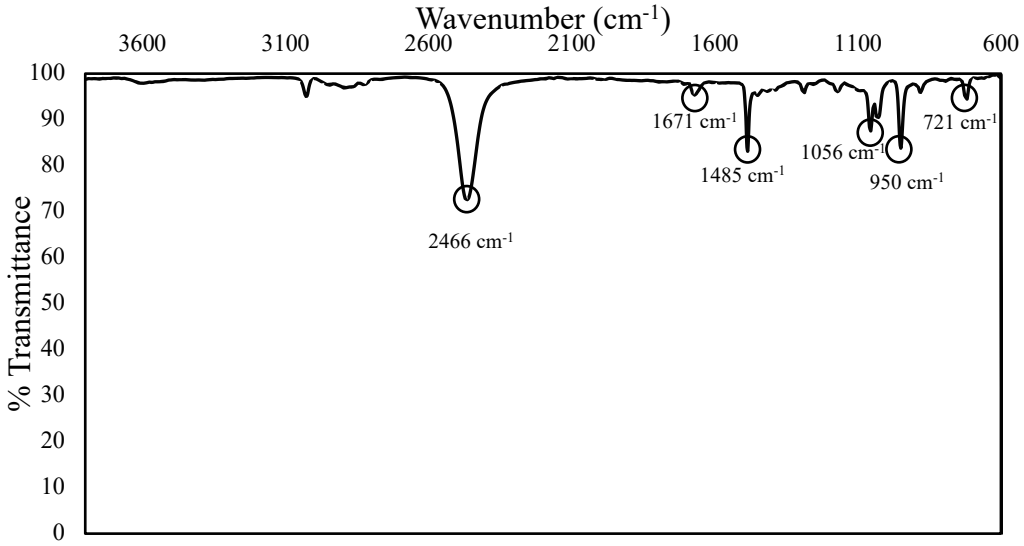


Figure 27. IR spectrum of tetramethylammonium 4-phthalimidobutoxy-undecahydro-closo-dodecaborate

Crude IR spectrum shows that (Figure 27), the signal at 2466 cm^{-1} represents B-H connectivity where the signal at 1671 cm^{-1} represents carbonyl units of phthalimide. Without any further purification NMR experiment was performed. In the NMR spectrum (Figure 28), besides from chemical shifts and integral values, the protons of tetramethylammonium counter cation are comparable and proves the THF ring bonded to cluster is opened, such that the overall charge of the cluster is 2-.

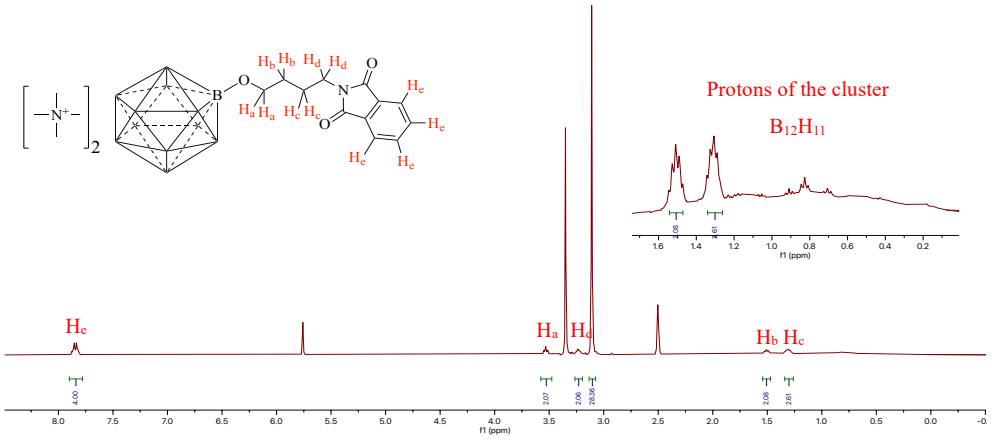


Figure 28. ^{1}H NMR spectrum of tetramethylammonium 4-phthalimidobutoxy-undecahydro-closo-dodecaborate

3.1.5 Synthesis of perhalogenated derivatives of closo-dodecaborate dianion

In the literature,[8] the weakly coordination ability of perhalogenated derivatives of closo-dodecaborate is stated. For complete halogenation of the cluster, the halogens with their larger sizes and their electronegativity, contributes the electron delocalization and dispersion of the cluster. The effect of these derivatives will be discussed in the catalytic studies section *vide infra*.

3.1.5.1 Synthesis of tetramethylammonium dodecaiodo-closo-dodecaborate

Since iodine is the biggest of all halogens, to increase the size of cluster and enhance the weakly coordinating ability of closo-dodecaborate dianion, we started from completely iodinated derivative of the cluster. In the literature,[51] the reaction is carried out with iodine monochloride as iodinating agent. So, we first prepared iodine monochloride by passing chlorine gas through elemental iodine. In the reaction setup, calcium chloride was connected in between chlorine generator and iodine monochloride since iodine monochloride is water sensitive. For generation of chlorine gas, we planned dropping hydrochloric acid into sodium hypochlorite solution. Due to low concentration of hypochlorite solution in our hands, there was no appreciable amount of chlorine gas formation. Then we moved on different method, by adding hydrochloric acid into potassium permanganate solution. Since the reaction is highly exothermic, ice bath was used to control the reaction. As the reaction proceeded, elemental iodine turned into thick liquid and covered the reaction vessel. The process performed three more times after bubbling stopped, and permanganate solution was renewed. Since in the reaction of periodination the iodine is used excess, the excess iodine in monochloride vessel was directly used without any attempt of purification or characterization. Since the aim was periodination of the cluster, if the desired product is obtained, indirect proof of iodine monochloride formation was found suitable.

Sodium dodecahydro-closo-dodecaborate and iodine is mixed and dissolved in 1,1,2,2-tetrachloro ethane. Then previously prepared iodine monochloride/iodine mixture was dissolved in tetrachloro ethane and added into the mixture. Temperature was increased to reflux, and the mixture was refluxed for two days. Then 10% sodium hydroxide solution was added to quench the reaction. The solution was filtered and tetramethylammonium chloride solution was added into the mixture, off-yellow crystals of tetramethylammonium dodecaiodo-closo-dodecaborate was precipitated. For further purification, the crude product was dissolved in acetonitrile and slowly distilled water was added until the recrystallization started. The mixture left overnight in room temperature and filtered. After recrystallization lighter colored crystals were obtained. From the IR spectrum (Figure 29), the signal of B-H stretching around 2480 cm^{-1} is disappeared. The signal[51] around 930 cm^{-1} is characteristic for B-I connectivity. The product was also characterized by HRMS, presented in *APPENDIX C*

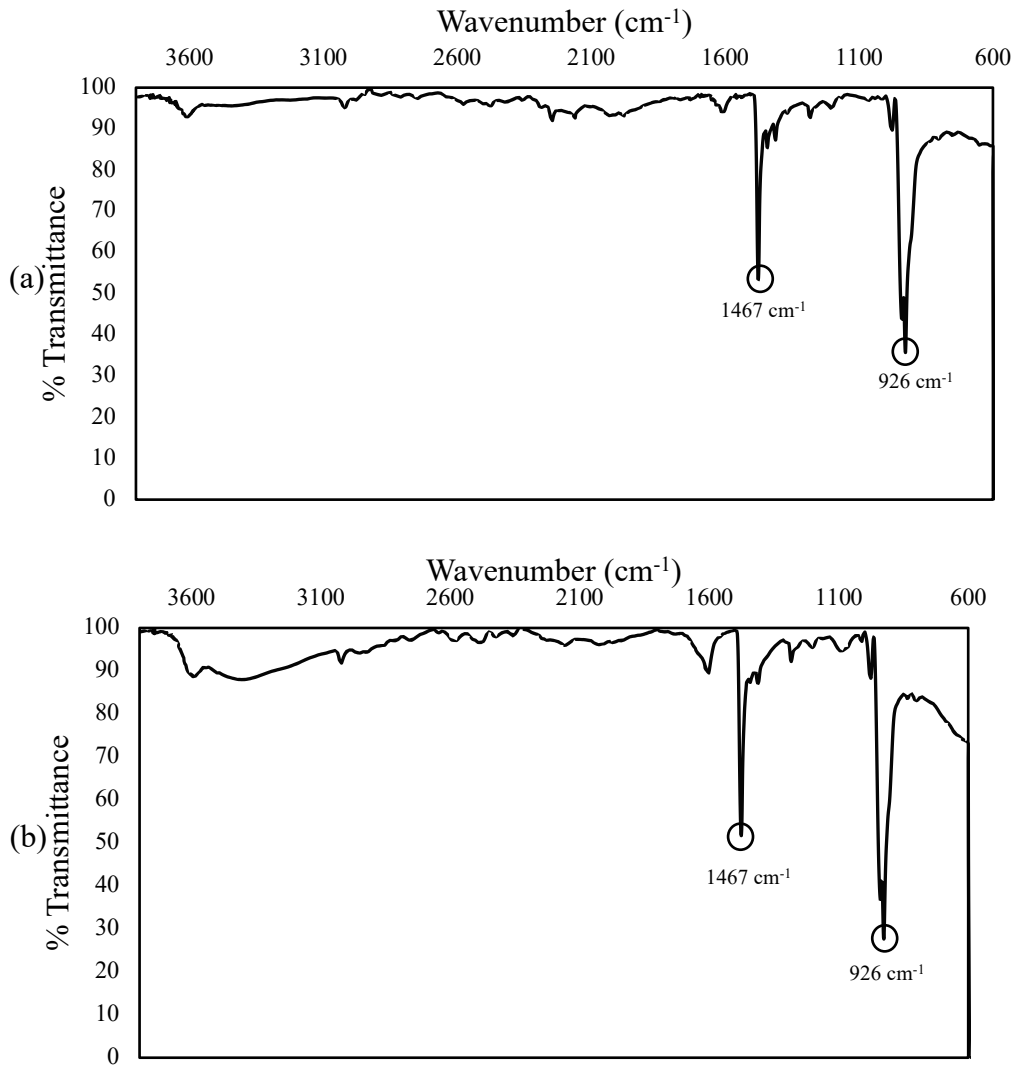


Figure 29. (a) IR spectrum of recrystallized; (b) crude tetramethylammonium dodecaiodo-closo-dodecaborate

3.1.5.2 Synthesis of dodecachloro-closo-dodecaborate

In the literature,[51] chlorination of dodecahydro-closo-dodecaborate is performed by with external chlorine gas bubbling through the solution. However, reaction time is long and sustaining reliable constant flow of chlorine gas is challenging. Therefore, we decided to look for a procedure to perform the chlorination with sulfuryl

dichloride which forms chlorine and sulfur dioxide gas *in situ*. Since sulfuryl dichloride is water sensitive, the reaction must be carried out in water free conditions and with care. That's why, closed system with sodium hydroxide trap was set for the reaction (Figure 30).

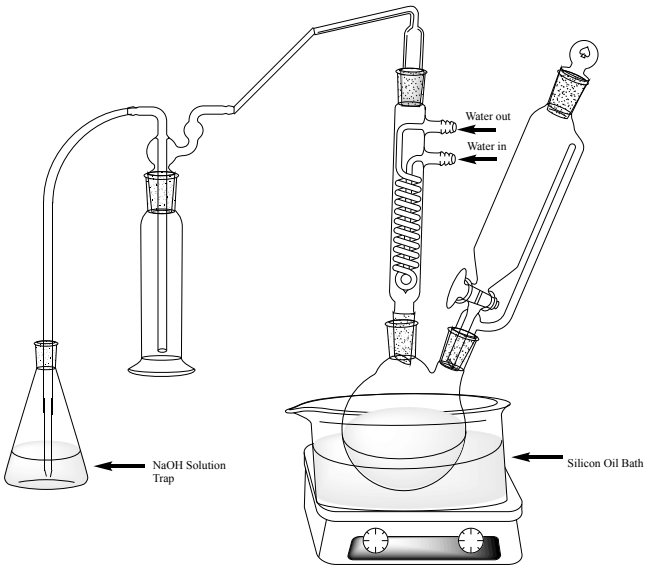


Figure 30. Reaction setup for perchlorination reaction.

Sodium salt of closo-dodecaborate was added into two necked round-bottom flask and acetonitrile was added. A cloudy solution was obtained because sodium dodecahydro-closo-dodecaborate is not completely soluble in acetonitrile. The pressure equalized dropper was charged with sulfuryl dichloride and connected to one neck and other neck charged with condenser. White stirring the mixture sulfuryl dichloride was added, and mixture let stir for about 20 minutes before applying any heat. Then mixture heated to reflux for 24 hours. Then all the volatiles were removed in *vacuo* and distilled water was added. Cesium chloride solution was prepared and after addition to the solution, immediate white cesium dodecachloro-closo-dodecaborate was precipitated. The collected solid was recrystallized with hot acetonitrile/water mixture yielding whiter crystals. From the IR spectra (Figure 31), the signal[51] at 1030 cm^{-1} is a characteristic signal for B-Cl bonds of the clusters. The disappearance of the signal at 2480 cm^{-1} shows there is not B-H bonding on the cluster.

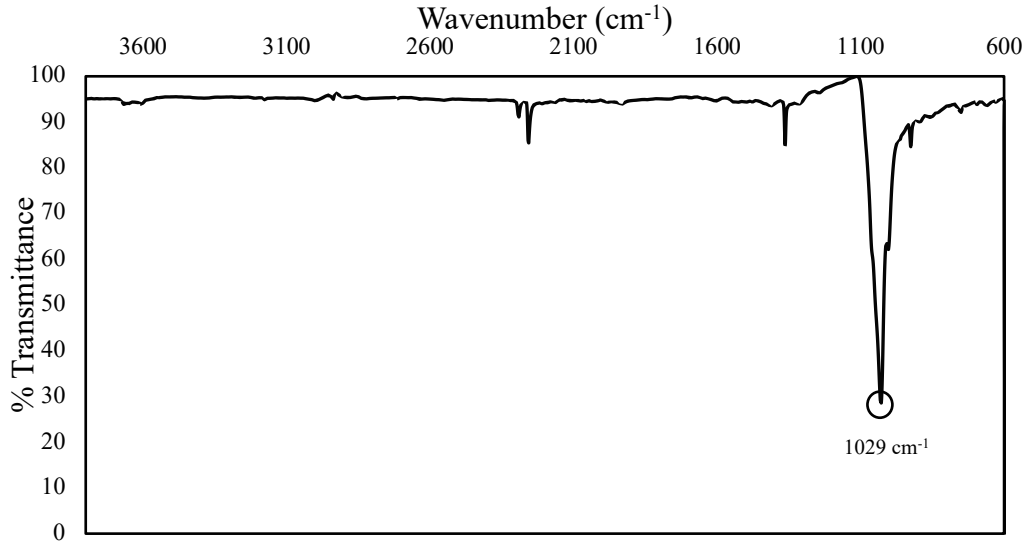


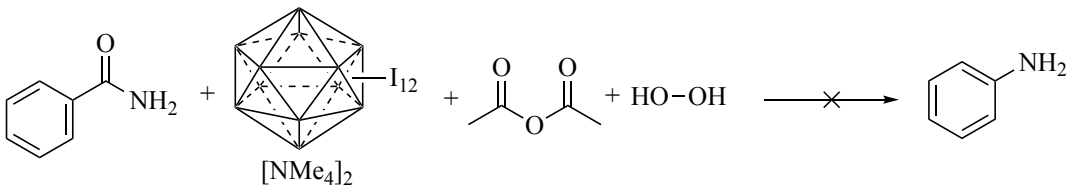
Figure 31. IR spectrum of cesium dodecachloro-closo-dodecaborate

3.2 Catalytic Studies

3.2.1 Hoffmann Degradation Reactions

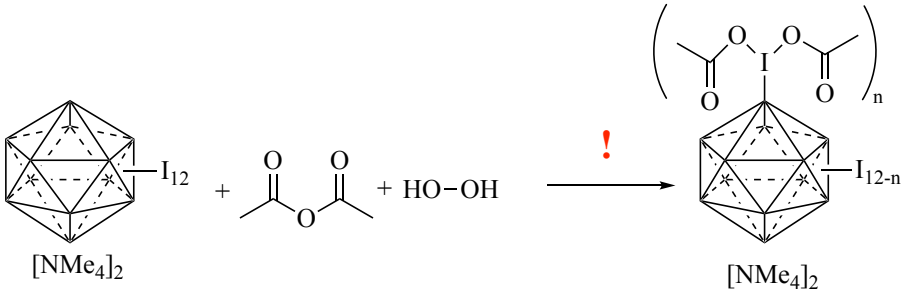
Hoffmann rearrangement reactions or Hoffmann degradation reactions are the reactions where the amides are rearranged to corresponding amines by losing carbonyl moiety. In the literature,[82] diacetoxy iodobenzene is used to perform the reaction. Having dodecaiodo-closo-dodecaborate dianion in our hands, we planned to study the same reaction with dodecaiodo-closo-dodecaborate dianion.

In the literature,[83] diacetylation of iodobenzene is performed by iodobenzene and acetic anhydride with hydrogen peroxide. First, we attempt to form diacetylated iodine *in situ* and directly react with benzamide to obtain aniline (Scheme 19).



Scheme 19. Hoffmann degradation reaction attempt by in situ diacetylated closo-dodecaborate

However, after the work-up and crude NMR experiment we observed no rearrangement product. Then we moved on to first isolate the diacetylated iodines on the cluster then carry on the reaction (Scheme 20).



Scheme 20. Reaction scheme of synthesis attempt of diacetylated iodo-closo-dodecaborate

Acetic anhydride and hydrogen peroxide were mixed and stirred for 4 hours at 40 ^{o}C, then tetramethylammonium dodecaiodo-closo-dodecaborate was added. From the previous attempt there was a distinct color change. Therefore, after the mixing for 5 minutes, approximately 2 ml of sample was taken for later examination. The mixture kept stirring and color change is observed after 15 minutes then another sample was taken for further examination and reaction let stir for overnight at room temperature. The stirring stopped and let yellow solids to settle down. The liquid part was decantated and removed in *vacuo.* **Off-white crystals observed and to collect the solids out of the round-bottom-flask, as the metal spatula make contact with the glass, the flask exploded violently**. The samples which were kept for further investigation needed to be safely disposed. Concentrated sodium thiosulfate solution was prepared and added into the sample taken after mixing 5 minutes, nothing happened and safely disposed. **However, when the thiosulfate solution was added**

into the sample taken after 15 minutes of mixing, was also exploded violently. This shows us the iodines on the cluster are readily reactive through the oxidants which may interfere with the future catalytic reactions that planned to conduct. That's why we stopped working of periodinated derivative and moved on to perchlorinated derivative of closo-dodecaborate.

3.2.2 Copper Mediated Ullmann type C-N coupling Reactions

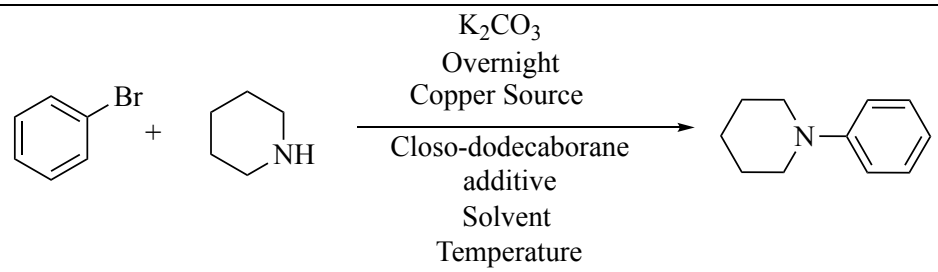
Copper catalyzed Ullmann coupling reactions are mainly performed for the aryl-aryl coupling reactions with an appropriate base at high temperatures. Either copper metal/alloys or copper (I) is used as catalytic purposes. In this study different copper (I) and dodecahydro-closo-dodecaborate salts, solvents, and temperatures were used (Table 5). The coupling reaction between bromobenzene and piperidine was studied.

Copper (I) oxide (Cu_2O), copper (I) chloride (CuCl) and copper (I) iodide (CuI) were used in separate experiments and compared the solubility and catalytic activity from the outcome of the reaction.

In the Cu-mediated Ullmann type reactions, high temperatures are required so that the high boiling point polar solvents were chosen. In the attempts 1-3 there was no auxiliary ligand were used. In the attempts 4 and 5 acetylacetone (acac) was used as an auxiliary ligand.

These were the preliminary studies to decide the reaction conditions such that various variables are changed at the same time. However, mixing the reactants and other additives followed by increasing the temperature to reflux temperature for overnight, yielded insignificant or none desired product formation.

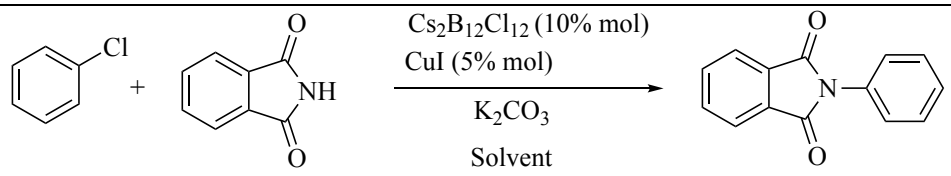
Table 5. Conditions for unsubstituted-closo-dodecaborate in catalytic studies



Copper Source		Closo-dodecaborane additive	Solvent	Temperature
1.	Cu_2O	$(NHEt_3)_2B_{12}H_{12}$	DMF	reflux
2.	CuI	$Na_2B_{12}H_{12}$	DMF	reflux
3.	CuI	$Na_2B_{12}H_{12}$	DMSO	150 °C
4.	CuCl	$Na_2B_{12}H_{12}$/acac	NMP	reflux
5.	CuCl	$(NHEt_3)_2B_{12}H_{12}$/acac	NMP	reflux

Since there was no product formation of any of these conditions, we focused on different reactants and dodecachloro-closo-dodecaborate dianion. Weakly coordinating ability of perhalogenated derivatives of closo-dodecaborate is higher than unsubstituted dodecahydro-closo-dodecaborate dianion. The coupling reaction of chlorobenzene and phthalimide were studied (Table 6). Copper (I) iodide was used as Cu^+ source (10 mol%) and potassium carbonate was used as base. Toluene, MeCN, and DMF were used as solvent separately. After dissolving chlorobenzene and phthalimide in the solvent, CuI, $Cs_2B_{12}H_{12}$, and K_2CO_3 are added and temperature increased to reflux temperature for 4 hours.

Table 6. Conditions for perchlorinated-closo-dodecaborate in catalytic studies



Copper Source		Closo-dodecaborane additive	Solvent	Temperature
1.	CuI	$Cs_2B_{12}Cl_{12}$	Toluene	reflux
2.	CuI	$Cs_2B_{12}Cl_{12}$	MeCN	reflux
3.	CuI	$Cs_2B_{12}Cl_{12}$	DMF	150 °C

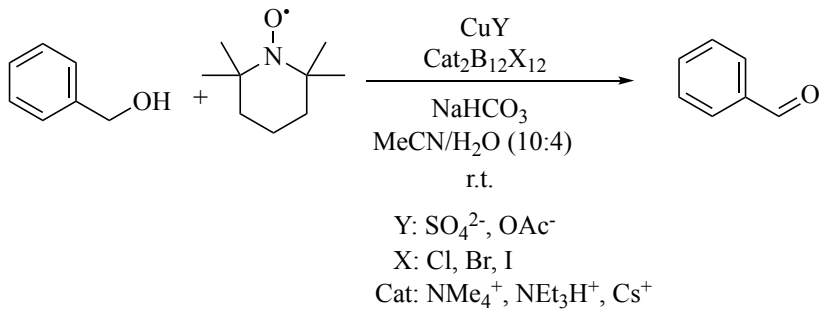
Then 10% sodium hydroxide was added to deprotonate the expected product. After washing the precipitate with distilled water, crude NMR experiment performed. From the spectrum, no coupling product formation observed.

3.2.3 Copper Mediated Alcohol Oxidation Reactions with TEMPO

In the literature,[84] Cu^{2+} cation is used in the oxidation reactions of alcohols with TEMPO. Bipyridine is used as ligand in the reaction where the catalytic activity is enhanced. It is also stated that, not use of bipyridine ligand the formation of oxidation product either trace or not observed. From this point, we planned a reaction where perchlorinated closo-dodecaborate may enhance the catalytic activity of Cu^{2+} ions without any auxiliary ligand.

We started with copper sulfate ($CuSO_4$) and copper acetate [$Cu(OAc)_2$] as Cu^{2+} source. Weakly coordinating anion was cesium dodecachloro-closo-dodecaborate salt. Sodium bicarbonate was used as base. The solvent system was acetonitrile/water mixture 10:4 ratio (Scheme 21). All the reactions performed at

room temperature. The reaction was monitored by TLC (1:2 EtOAc/Hexane) occasionally.



Scheme 21. Reaction scheme of copper catalyzed TEMPO oxidation of benzyl alcohol

From simultaneous reactions of $CuSO_4$ and $Cu(OAc)_2$ with same conditions, we decided to move on with $CuSO_4$ salt as Cu^{2+} source due to higher oxidation product from the crude NMR spectrum (Figure 32). The signal around 10 ppm belongs to aldehyde hydrogen of benzaldehyde, where the signal around 4.75 ppm belongs to the benzyl hydrogen of benzyl alcohol.

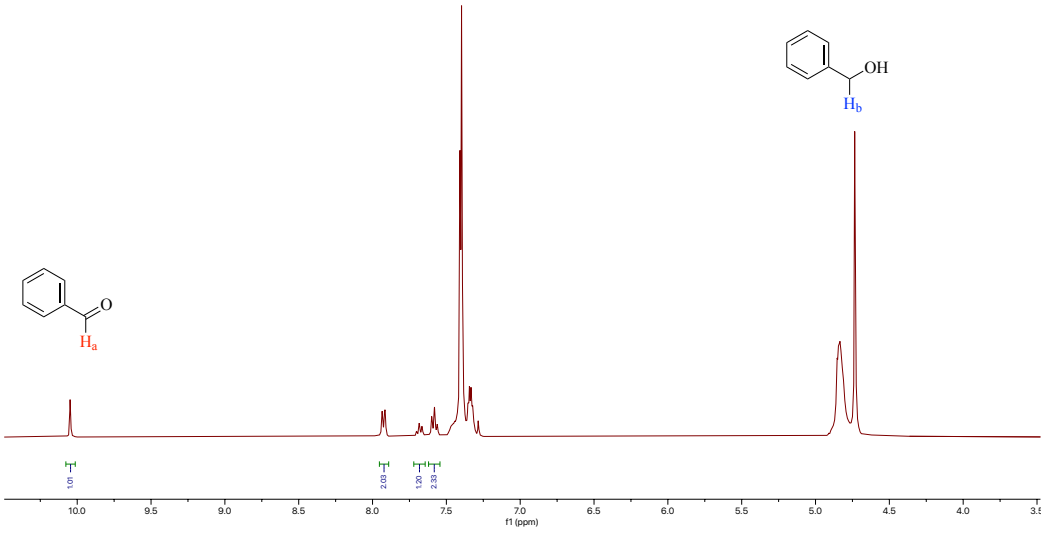


Figure 32. Crude ^1H NMR spectrum of copper sulfate utilized reaction.

To increase the yield of the oxidation product, same conditions were used and hydrogen peroxide was added to mixture (1 mL x 2 doses) however, after 2 days and

TLC monitoring hourly, there was still benzyl alcohol in the mixture. After 2 days reaction terminated and from the crude NMR experiment, the benzyl alcohol presence confirmed (Figure 33).

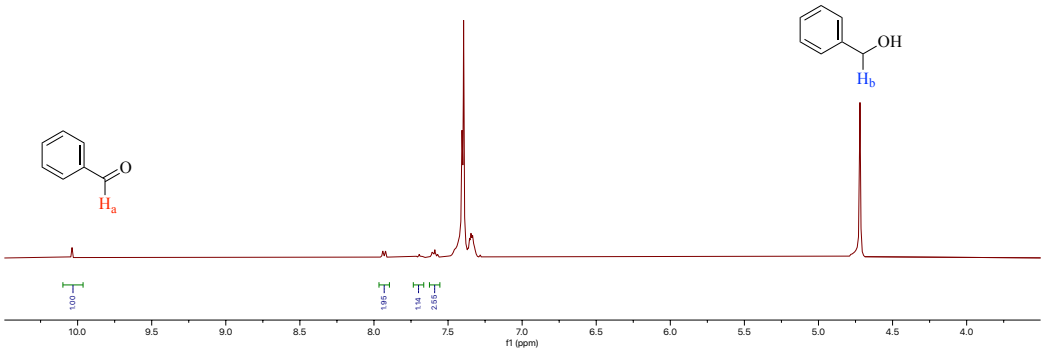


Figure 33. Crude ^{1}H NMR spectrum of hydrogen peroxide used reaction.

Then with the same conditions instead of hydrogen peroxide the oxygen is bubbled through the reaction medium for two hours. However, the oxidation product was too low. Without any closo-dodecaborate salt used, the control reactions were performed for a week, and it was observed that the oxidation of benzyl alcohol was occurred by observing the peak in ^{1}H NMR at around 10.1 ppm (Figure 34).

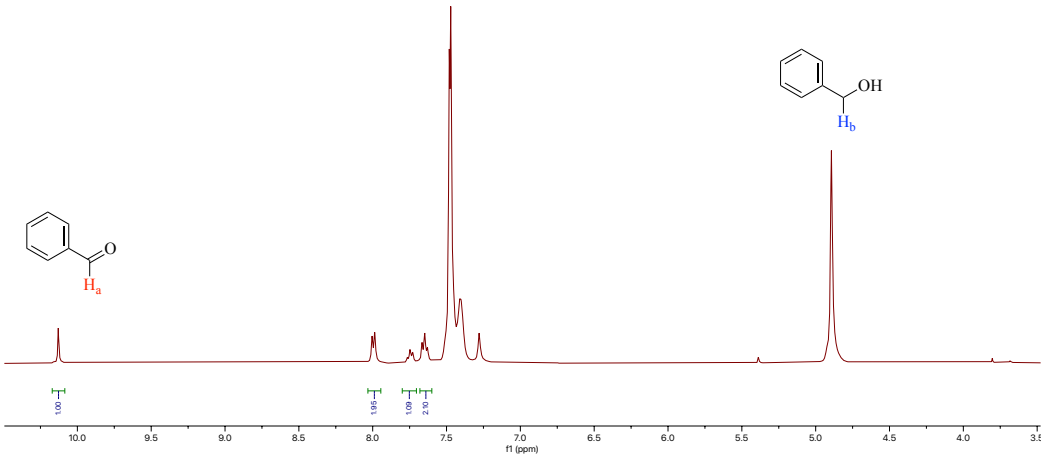


Figure 34. Crude ^{1}H NMR spectrum of test reaction.

3.3 Electrochemical Studies on Perhalogenated Boron Cages

Unsubstituted dodecahydro-closo-dodecaborate dianion can exist only with 2- charges so that electrochemical oxidation of these species results in dissociation of the cluster. However, persubstituted derivatives can be oxidized to hypo-closo radical or neutral -closo clusters. Having unsubstituted, perchlorinated, perbrominated and periodinated closo-dodecaborate in our hand, we performed Differential Pulse Voltammetry, DPV, experiments to explore oxidation potentials of the clusters.

As shown in the figure, dodecahydro-closo-dodecaborate shows two oxidation peaks (Figure 35). The cluster is oxidized at 1.51V and 1.80 V, respectively.

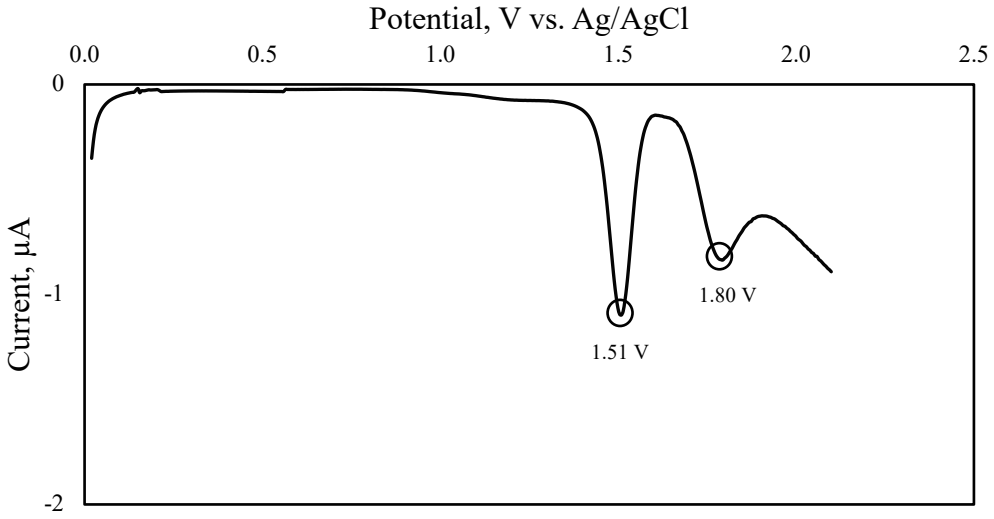


Figure 35. Differential Pulse Voltammetry voltammogram of tetramethyl ammonium dodecahydro-closo-dodecaborate

However, in the case of perhalogenated derivatives of the cluster. There are no possible oxidation peaks in between 2 V (Figure 36).

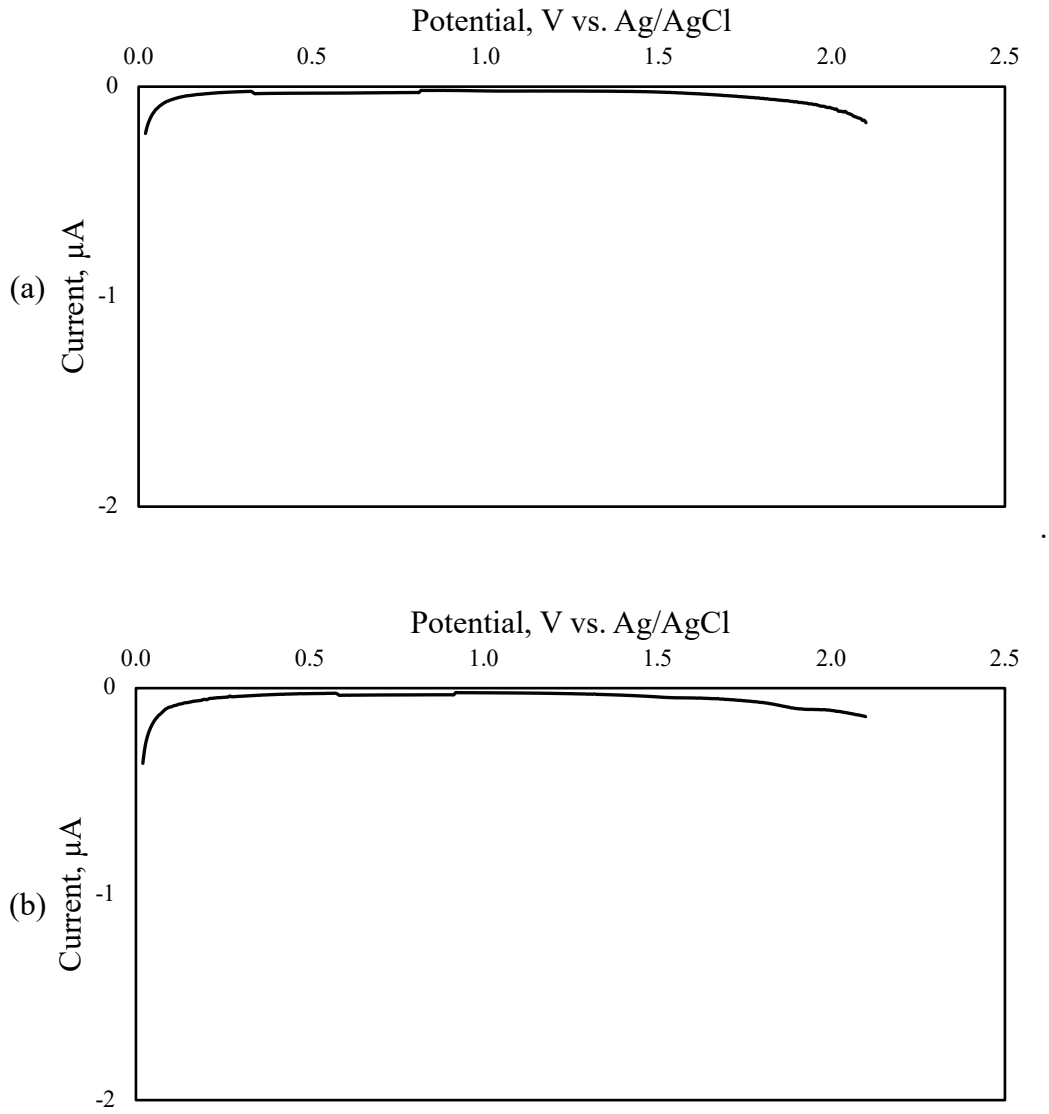


Figure 36. Differential Pulse Voltammetry voltammogram of (a) tetramethyl ammonium dodecachloro-closo-dodecaborate; (b) tetramethyl ammonium dodecabromo-closo-dodecaborate

In the periodinated-closo-dodecaborate case it can be seen from the DPV plot, there are oxidation peaks at 1.77 V and 1.99 V. These oxidation potentials possibly due to oxidation of iodines on the cluster (Figure 37).

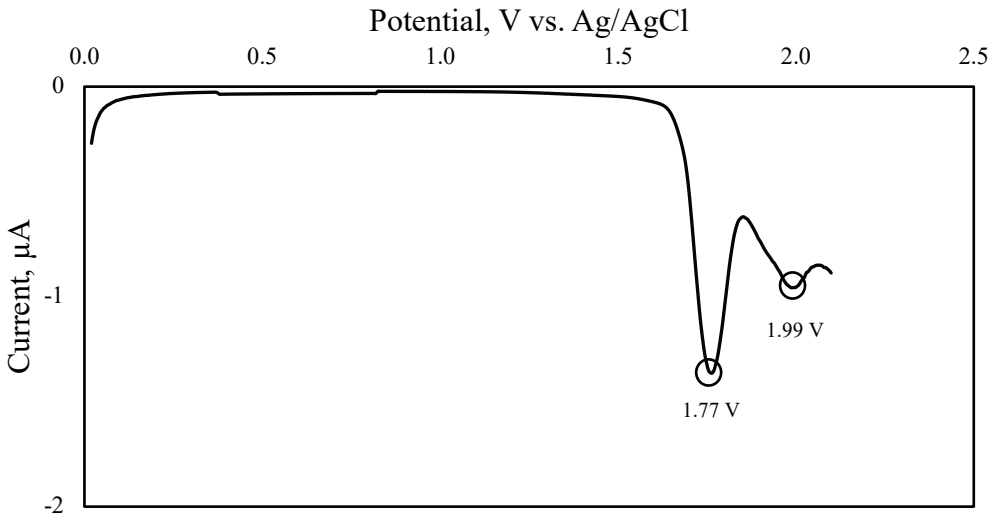


Figure 37. Differential Pulse Voltammetry voltammogram of tetramethyl ammonium dodecaiodo-closo-dodecaborate

When the $CuSO_4$ is added in to the unsubstituted closo-dodecaborate the oxidation signals changed to 1.53 and 1.82 V (Figure 38).

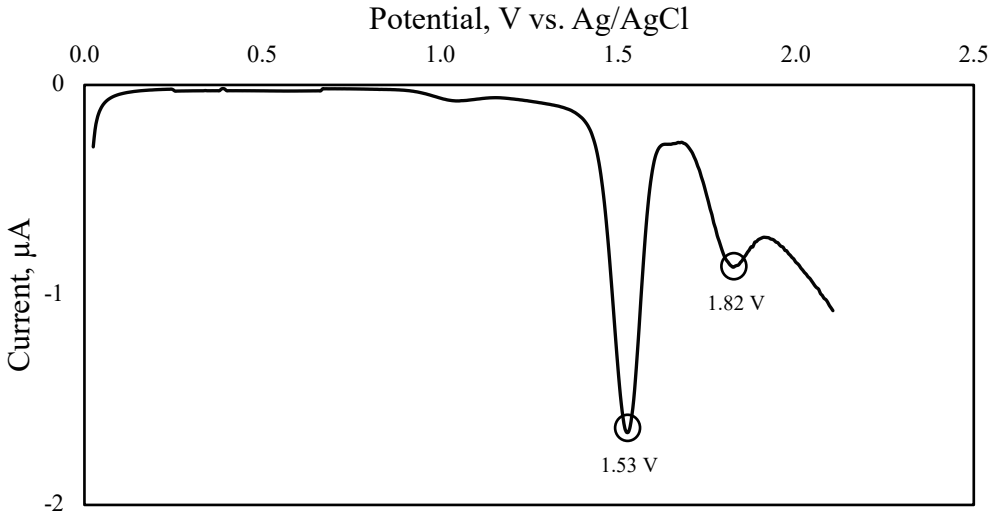


Figure 38. Differential Pulse Voltammetry voltammogram of tetramethyl ammonium dodecahydro-closo-dodecaborate with $CuSO_4$

The copper sulfate addition into the perhalogenated closo-dodecaboranes made no change in the oxidation potentials (Figure 39).

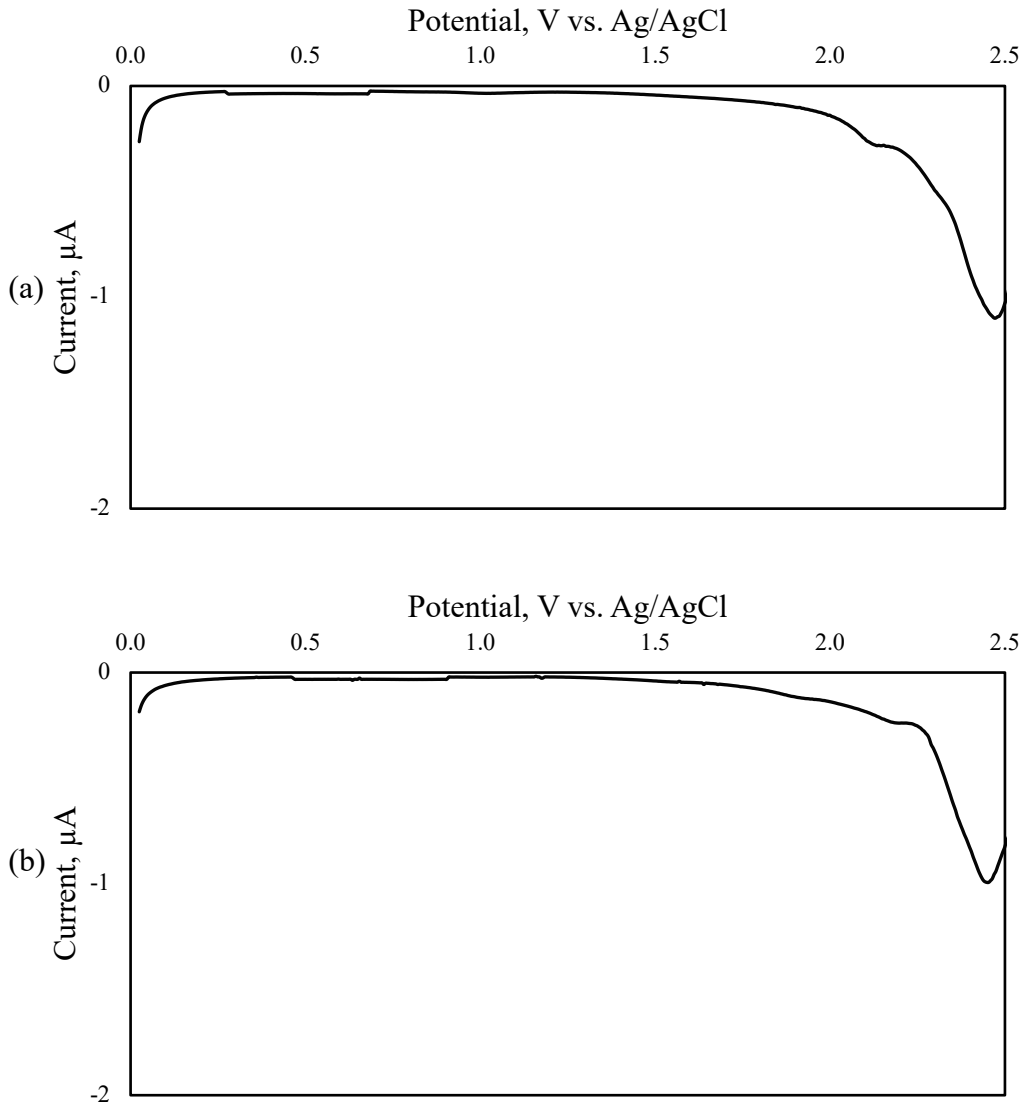


Figure 39. Differential Pulse Voltammetry voltammogram of (a) tetramethyl ammonium dodecachloro-closo-dodecaborate with $CuSO_4$, (b) tetramethyl ammonium dodecabromo-closo-dodecaborate with $CuSO_4$

The addition of copper sulfate into dodecaiodo-closo-dodecaborate changed the first oxidation from 1.77 to 1.67 and second potential signal become broader (Figure 40).

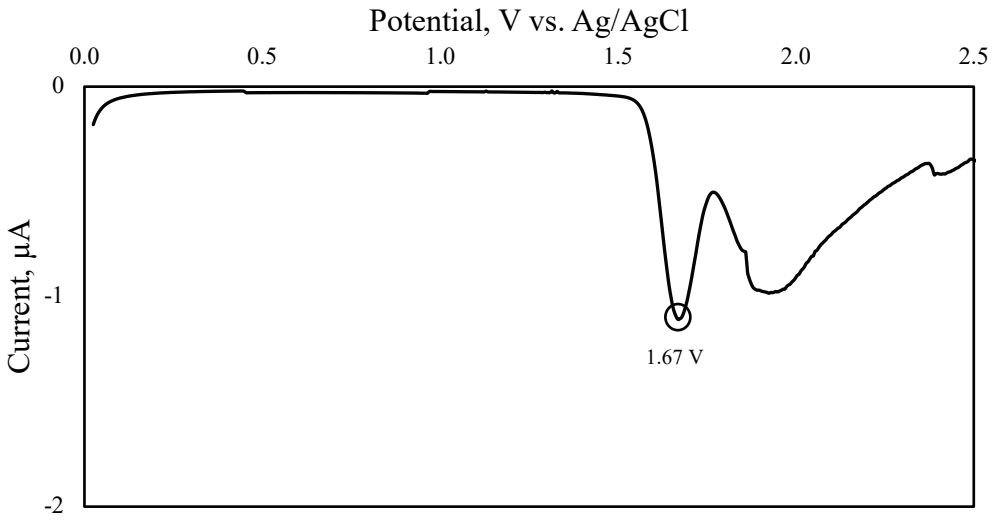


Figure 40. Differential Pulse Voltammetry voltammogram of tetramethyl ammonium dodecaiodo-closo-dodecaborate and $CuSO_4$

Differential pulse voltammetry studies showed that, copper added solutions without copper, the oxidation did not change. This is probably due to cation-anion interactions are not strong as expected. However, copper sulfate has low solubility in the acetonitrile solution.

CHAPTER 4

CONCLUSION

In this study, dodecahydro-closo-dodecaborate was synthesized from sodium borohydride as triethylammonium salt. By cation exchange reactions, sodium, potassium, cesium, and tetramethylammonium salts were synthesized and isolated. Tetramethylammonium tetrahydrofuran-1-yl-undecahydro-closo-dodecaborate, tetramethylammonium 4-phthalimidobutoxy-undecahydro-closo-dodecaborate and tetramethylammonium 1-amino undecahydro-closo-dodecaborate were synthesized, characterized and isolated. Perchlorinated and periodinated derivatives of closo-dodecaborate dianion was synthesized. Perchlorinated derivative was isolated as cesium salt and periodinated derivative was isolated as tetramethylammonium salt.

Weakly coordinating ability of the clusters through copper metal were studied. Copper catalyzed Ullmann type C-N coupling reactions and copper mediated TEMPO oxidation reactions were studied. For Cu-mediated Ullmann type reaction, without any auxiliary ligand use, it was observed that addition of closo-dodecaborate does not enhance the catalytic activity of copper and does not lead reaction to the completion in the conditions we have used. For the copper catalyzed alcohol oxidation reactions with TEMPO, usage of cesium dodecachloro-closo-dodecaborate increases the overall oxidation yield however, usage of hydrogen peroxide or oxygen gas did not lead reaction to completion. These results show that the ligand has a crucial role in catalytic reactions of Cu-mediated organic reactions.

CHAPTER 5

EXPERIMENTAL

For the representation of clusters, all the vertex of the polyhedra represent B-H unless otherwise is stated. For the heteroatom connectivity, that vertices were shown explicitly (Figure 41).

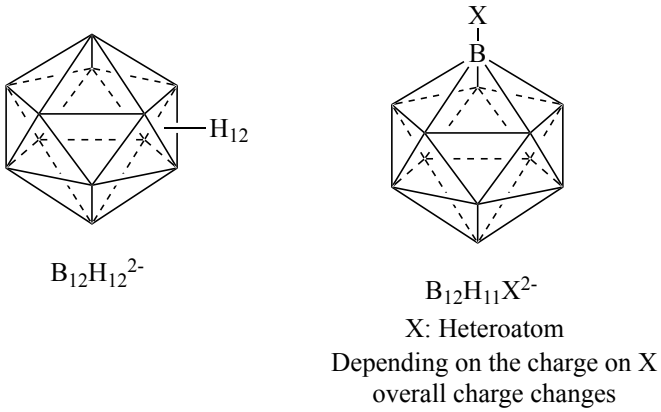


Figure 41. Representation of the clusters

5.1 Methods and Materials

All the starting materials used are purchased from Sigma Aldrich and used without any further purification. Thin layer chromatography (TLC) is used to monitor the reactions (Merck Silica Gel 60 F254) and visualized by powdered iodine and by UV light (254 nm)

Infrared (IR) spectra were recorded with Thermo Scientific Nicolet iS10 ATR-IR Spectrometer. The IR spectra of the compounds are processed with Microsoft Office Excel 2020 program.

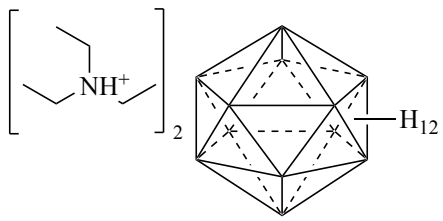
^{1}H nuclear magnetic resonance (^{1}H NMR) experiments performed in deuterated dimethyl sulfoxide (Merck), and deuterated chloroform (Merck) with Bruker Avance III Ultrashield 400 Hz NMR spectrometer. The chemical shifts were shown in parts per million (ppm) with trimethyl silane (TMS) as internal reference. The NMR spectra of synthesized compounds were processed with MestReNova Program.

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

Electrochemical measurements (DPV) were performed by using Gamry PCl4/300 potentiostat-galvanostat. Glassy carbon electrode as a working electrode, Ag/AgCl as a reference electrode and platinum wire as a counter electrode were used.

All the crude data were given in the *Appendix Section*.

5.2 Synthesis of triethylammonium dodecahydro-closo-dodecaborate [85]

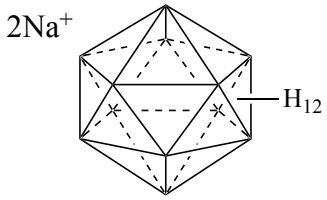


1

2.0 L three necked round bottom flask is charged with a 250 mL pressure equalized dropping funnel and condenser. Third neck was closed with stopper for additions. Condenser was connected with acetone trap. The reaction setup was purged with argon and kept under argon atmosphere. Sodium borohydride (100.0 g, 2.64 mol) and 350 mL diglyme were added into the flask and started heating up to 120 ^{o}C (silicon-oil bath temperature) Iodine (195.0 g, 0.77 mol) was dissolved in 250 mL diglyme and added into the 250 mL pressure equalized dropping funnel. Once the

sodium borohydride started to dissolve into diglyme, iodine started to added in a period of 6 hours. After the addition, the reaction let stir at the same temperature overnight. Then the temperature raised to 185 ºC (silicon-oil bath temperature) for 24 hours. After that, reflux condenser was replaced with distillation condenser and removed the solvent almost dryness. Reaction vessel let cool to room-temperature. 600 mL distilled water then 280 mL concentrated hydrochloric acid was slowly added. White boric acid crystals started to form. Mixture put at 4 ºC overnight to complete boric acid precipitation. Colorless boric acid crystals were filtered and 120 mL triethylamine was added to filtrate. Immediate white triethylammonium dodecahydro-closo-dodecaborate crystals formed. Recrystallization with acetonitrile/water mixture yielded 25.4 g (44 %) desired product. $[NHEt_3]_2[B_{12}H_{12}]$ IR: 2475 cm^{-1} (B-H str.), 3125 cm^{-1} (N-H str.)

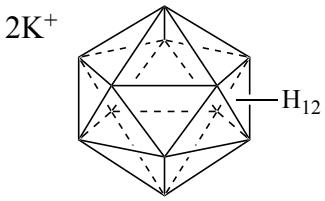
5.2.1 Synthesis of sodium dodecahydro-closo-dodecaborate



1a

Triethylammonium dodecahydro-closo-dodecaborate (1.60 g, 4.62 mmol) was put into a round-bottom-flask and suspension was obtained with some distilled water, typically 20 ml. Then previously prepared 10% sodium hydroxide solution (typically 10 g sodium hydroxide in 100 ml distilled water) was added dropwise (2 ml) until all the solids were disappeared and the solution was cleared. Then all the solvent was evaporated yielding white 0.90 g hygroscopic sodium dodecahydro-closo-dodecaborate crystals. *Since the sodium salt is very hygroscopic, yield calculation cannot be performed due to rapid water capture from the atmosphere during the weighing.* IR: 2470 cm^{-1} (B-H str.), 1064 cm^{-1}, 712 cm^{-1}.

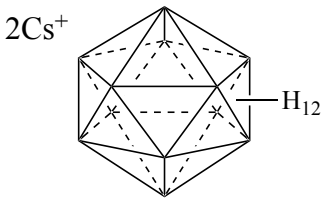
5.2.2 Synthesis of potassium dodecahydro-closo-dodecaborate



1b

Triethylammonium dodecahydro-closo-dodecaborate (0.60 g, 1.73 mmol) was put into a round-bottom-flask and suspension was obtained with some distilled water, typically 20 ml. Then previously prepared 10% potassium hydroxide solution was added dropwise (1 ml) until all the solids were disappeared and the solution was cleared. Then all the solvent was evaporated yielding 0.33 g (86.7%) white potassium dodecahydro-closo-dodecaborate crystals. IR: 2478 cm^{-1}(B-H str.) 1073 cm^{-1}, 714 cm^{-1}.

5.2.3 Synthesis of cesium dodecahydro-closo-dodecaborate

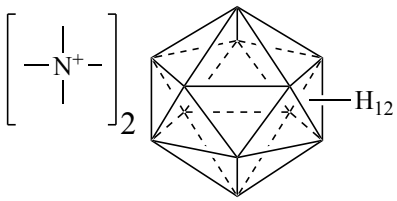


1c

Sodium dodecahydro-closo-dodecaborate (0.2 g, 1.06 mmol) was put into a beaker and dissolved in 10 mL distilled water. Then cesium chloride (2 g, 11.9 mmol) was added, immediate white cesium dodecahydro-closo-dodecaborate crystals precipitated. The mixture was filtrated and crystals were dried in open atmosphere

yielding 0.43 g (99.1%) white cesium dodecahydro-closo-dodecaborate crystals. IR: 2468 cm^{-1} (B-H str.) 1078 cm^{-1}, 710 cm^{-1}.

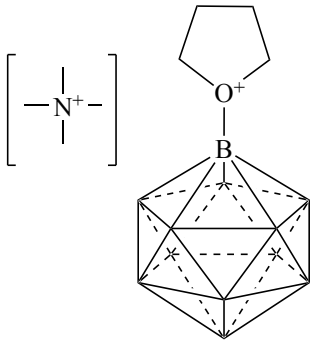
5.2.4 Synthesis of tetramethylammonium dodecahydro-closo-dodecaborate



1d

Sodium dodecahydro-closo-dodecaborate was dissolved in 10 ml distilled water. Then tetramethylammonium chloride solution was added. Immediate precipitation was observed. Precipitate was filtered and crystals were dried in air yielding tetramethylammonium dodecahydro-closo-dodecaborate. IR: 2474 cm^{-1} (B-H str.), 1062 cm^{-1}, 714.01 cm^{-1}, 1484 cm^{-1}, 950 cm^{-1}

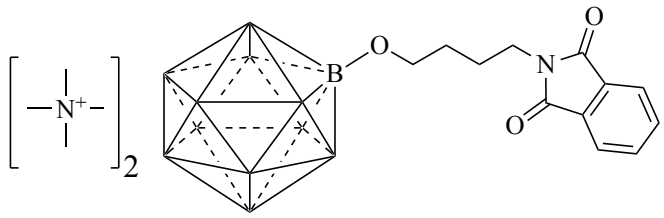
5.3 Synthesis of tetramethylammonium tetrahydrofuran-1-yl-undecahydro-closo-dodecaborate [86]



2

Sodium dodecahydro-closo-dodecaborate (2.3 g, 12.25 mmol) was added into 100 ml round-bottom-flask and 50 ml freshly distilled dry tetrahydrofuran was added. While heterogeneous mixture was stirred, 10 ml boron trifluoride diethyl etherate (11.5 g, 0.08 mol) was added. The mixture was stirred overnight at room temperature, then the reaction mixture was filtered and the solvent was distilled off in *vacuo*. Remaining residue was dissolved in 60 ml of distilled water then tetramethylammonium chloride (7.0 g, 0.06 mol) solution in 10 ml water was added. Immediate white tetramethylammonium tetrahydrofuran-1-yl-undecahydro-closo-dodecaborate crystals formed. The precipitate was filtrated and dried in air. No further purification was done, yielding 0.75g (21%) desired product. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 4.30 (m, 4H), δ 3.09 (s, 12H), δ 2.06 (m, 4H). IR: 2484 cm^{-1}(B-H str.), 1480 cm^{-1}, 1047 cm^{-1}, 721 cm^{-1}

5.4 Synthesis of tetramethylammonium 4-phthalimidobutoxy-undecahydro-closo-dodecaborate [86]

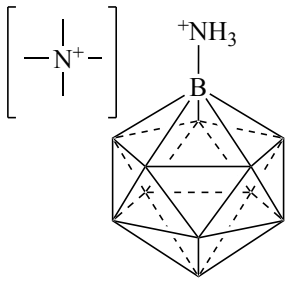


3

Tetramethylammonium tetrahydrofuran-1-yl-undecahydro-closo-dodecaborate (0.20 g, 0.62 mmol) was dissolved in 30 ml dimethylformamide and potassium phthalimide (0.15 g, 0.81 mmol) was added into the solution. The mixture was stirred overnight in room temperature. Then the solvent was distilled off in *vacuo* and the remaining residue was dissolved in 30 ml methanol. The undissolved white solids were filtered. Tetramethylammonium chloride (0.24 g, 2.2 mmol) was dissolved in 10 ml methanol, and added into the filtrate. Immediate white precipitate occurred and filtered. Washed with dichloromethane and dried in air, yielding expected

product. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.84 (m, 4H), δ 3.53 (t, 2H), δ 3.24 (t, 2H), δ 3.10 (s, 24H), δ 1.51 (m, 2H), δ 1.32 (m, 2H). IR: 2466 cm^{-1}(B-H str.), 1671 cm^{-1}(C=O), 1485 cm^{-1}, 1056 cm^{-1}, 950 cm^{-1}, 721 cm^{-1}.

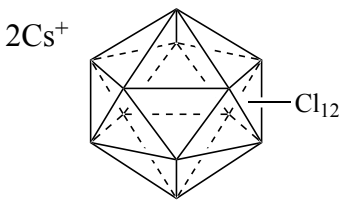
5.5 Synthesis of tetramethylammonium 1-amino-undecahydro-closo-dodecaborate [40]



4

Sodium dodecahydro-closo-dodecaborate (1.6 g, 8.66 mmol) is dissolved in 30 ml of distilled water and hydroxylamine-*O*-sulfonic acid (3.0 g, 17.33 mmol) is added. The solution was refluxed for 3 hours then cooled to room temperature. Tetramethylammonium chloride solution is added. Immediate white solid precipitation occurred. The resulting precipitate is filtered using vacuum filtration. No further purification done, yielding 1.3 g (64 %) of desired product. IR: 3260 cm^{-1} (N-H str.) 2477 cm^{-1} (B-H str.) 1591 cm^{-1} (N-H def.)

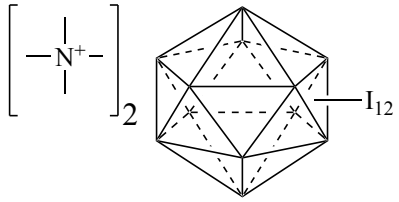
5.6 Synthesis of cesium dodecachloro-closo-dodecaborate [55]



5

250 ml two necked round bottom flask was charged with a 150 mL pressure equalized dropping funnel and condenser. Sodium dodecahydro-closo-dodecaborate (1.0 g, 5.33 mmol) was added into the round bottom flask and 30 ml of acetonitrile was added. Cloudy suspension was observed and slowly 30 ml of sulfuryl dichloride was added. Then mixture let stir 20 mins and heated to reflux for 24 hours. Then all the solvents were removed and 30 ml of water was added. Then 3 g of cesium chloride was dissolved in 10 ml water and added into the solution. Immediate precipitation observed. Precipitated white crystals were collected and recrystallized with acetonitrile water mixture, yielding 2.5 g, (57 %) of desired product. IR: 1029 cm^{-1} (B-Cl str.)

5.7 Synthesis of tetramethylammonium dodecaiodo-closo-dodecaborate [51]



6

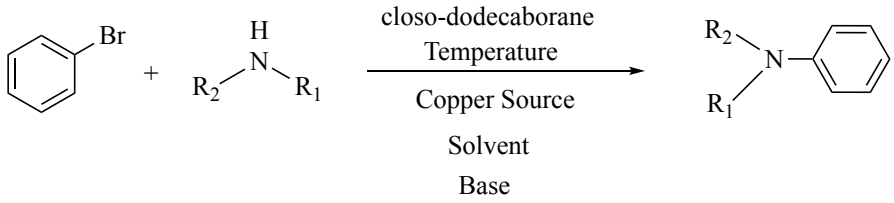
5.7.1 Preparation of ICl

Iodine (15 g) is taken in a round-bottom flask and chlorine gas passed through it by dropping approximately 100 ml of hydrochloric acid onto potassium permanganate (10g), and successfully generated the chlorine gas. The potassium permanganate is refreshed two more times with same amount. No characterization performed.

Sodium dodecahydro-closo-dodecaborate (1.0 g, 5.33 mmol) and iodine (3.0 g, 11.82 mmol) were added into a round-bottom flask and 20-25 ml 1,1,2,2-tetrachloro ethane were added. The mixture was let stir for 10 mins. Then previously prepared iodine monochloride was added using 20-25 ml 1,1,2,2-tetrachloro ethane into the reaction mixture and refluxed for 2 days. 100 ml of 10% sodium hydroxide solution

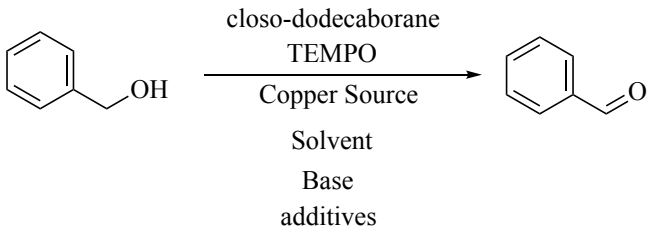
was prepared and added to reaction mixture, and stirred for 10 mins. Then mixture was filtered. Tetramethylammonium chloride (2.0 g, 18.24 mmol) was dissolved in 10 ml water and added to filtrate. Immediate precipitation occurred. The solids were collected and recrystallized using acetonitrile and water solvent system. Yielding 1.5 g (15%) of desired product. IR: 1476 cm^{-1}, 939 cm^{-1}, 926 cm^{-1} (B-I str.)

5.8 General Procedure for Ullmann Coupling Reactions.



Copper source (Cu^{+}), base and closo-dodecaborate salt was put in a round-bottom-flask and dissolved in the solvent. Then aryl halide and amine were added to the mixture and heated to typically reflux temperature. When high boiling point solvents were used, temperature kept between 130-140 ^{o}C typically. The reaction was monitored with TLC occasionally. Variables and specific conditions are discussed detailly in *CHAPTER 2*.

5.9 General Procedure for Alcohol Oxidation Reactions.



Copper source (Cu^{2+}), sodium bicarbonate, closo-dodecaborane source, TEMPO, and additives was first put in a 50 ml round-bottom-flask and 10:4 acetonitrile/water solvent mixture was added. Heterogeneous mixture was obtained and while stirring benzyl alcohol was added. Reaction typically left overnight at room temperature and monitored with TLC occasionally. Variables and specific conditions are discussed detailly in *CHAPTER 2*

REFERENCES

(1) Fryer, G. The Royal Society Is Collaborating with JSTOR to Digitize, Preserve, and Extend Access to Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences. *Society* **1985**, *308*, 379–430.

(2) Kar, Y.; Şen, N.; Demirbaş, A. Boron Minerals in Turkey, Their Application Areas and Importance for the Country's Economy. *Miner. Energy - Raw Mater. Rep.* **2006**, *20*, 2–10. https://doi.org/10.1080/14041040500504293.

(3) Shore, S. G. The Chemistry of Boron and Its Compounds (Muetterties, Earl L., Ed). *J. Chem. Educ.* **1968**, *45*, 211. https://doi.org/10.1021/ed045p211.1.

(4) Stock, A.; Kuss, E. Borwasserstoffe, VI.: Die Einfachsten Borhydride. *Berichte der Dtsch. Chem. Gesellschaft.* **1923**, *56*, 789–808. https://doi.org/10.1002/cber.19230560404.

(5) Wiberg, E. Bromide and Boron , Sulphide . The Numerous Publications on Improvements To. *pure appl. Chem.* **1977**, *49*, 691–700.

(6) Sivaev, I. B.; Bregadze, V. I.; Sjöberg, S. Chemistry of Closo-Dodecaborate Anion $[B_{12}H_{12}]^{2-}$: A Review. *Collect. Czechoslov. Chem. Commun.* **2002**, *67*, 679–727. https://doi.org/10.1135/cccc20020679.

(7) Alexandrova, A. N.; Boldyrev, A. I.; Zhai, H. J.; Wang, L. S. All-Boron Aromatic Clusters as Potential New Inorganic Ligands and Building Blocks in Chemistry. *Coord. Chem. Rev.* **2006**, *250*, 2811–2866. https://doi.org/10.1016/j.ccr.2006.03.032.

(8) Hansen, B. R. S.; Paskevicius, M.; Li, H. W.; Akiba, E.; Jensen, T. R. Metal Boranes: Progress and Applications. *Coord. Chem. Rev.* **2016**, *323*, 60–70. https://doi.org/10.1016/j.ccr.2015.12.003.

(9) Wade, K. Cluster Chemistry. *J. Chem. Educ.* **2002**, *79*, 16. https://doi.org/10.1016/s0277-5387(00)83104-6.

(10) Boone, J. L. Isolation of the Hexahydroclovohexaborate(2-) Anion, $B_6H_6^{2-}$. *J. Am. Chem. Soc.* **1964**, *86*, 5036–5036. https://doi.org/10.1021/ja01076a082.

(11) Klanberg, F.; Muetterties, E. L. New Polyhedral Borane Anions $B_9H_9^{2-}$ and $B_{11}H_{11}^{2-}$. *Inorg. Chem.,* **1966**, *5*, 1955–1960.

(12) Klanberg, F.; Eaton, D. R.; Guggenberger, L. J.; Muetterties, E. L. Chemistry of Boranes. XXVIII. New Polyhedral Borane Anions, $B_8H_8^{2-}$, $B_8H_8^-$, and $B_7H_7^{2-}$. *Inorg. Chem.* **1967**, *6*, 1271–1281. https://doi.org/10.1021/ic50053a001.

(13) Pitochelli, A. R.; Hawthorne, F. M. The Isolation of the Icosahedral $B_{12}H_{12}^{2-}$ Ion. *J. Am. Chem. Soc.* **1960**, *82*, 3228–3229. https://doi.org/10.1021/ja01497a069.

(14) Hoffmann, R.; Lipscomb, W. N. Theory of Polyhedral Molecules. I. Physical Factorizations of the Secular Equation. *J. Chem. Phys.* **1962**, *36*, 2179–2189. https://doi.org/10.1063/1.1732849.

(15) Grimes, R. N. Introduction and History. In *Carboranes*; Elsevier, 2016; pp 1–5. https://doi.org/10.1016/B978-0-12-801894-1.00001-9.

(16) Onak, T. P.; Williams, R. E.; Weiss, H. G. The Synthesis of $B_4C_nH_{2n+4}$ Compounds from Pentaborane-9 and Alkynes Catalyzed by 2,6-Dimethylpyridine. *J. Am. Chem. Soc.* **1962**, *84*, 2830–2831. https://doi.org/10.1021/ja00873a040.

(17) Shapiro, I.; Good, C. D.; Williams, R. E. The Carborane Series: $B_nC_2H_{n+2}$. I. $B_3C_2H_5$. *J. Am. Chem. Soc.* **1962**, *84*, 3837–3840. https://doi.org/10.1021/ja00879a010.

(18) Alexander, R. P.; Schroeder, H. Chemistry of Decaborane-Phosphorus Compounds. IV. Monomeric, Oligomeric, and Cyclic Phosphinocarboranes.

Inorg. Chem. **1963**, *2*, 1107–1110. https://doi.org/10.1021/ic50010a006.

(19) Schroeder, H.; Heying, T. L.; Reiner, J. R. A New Series of Organoboranes. II. The Chlorination of 1,2-Dicarbaclovododecaborane. *Inorg. Chem.* **1963**, *2*, 1092–1096. https://doi.org/10.1021/ic50010a003.

(20) Heying, T. L.; Ager, J. W.; Clark, S. L.; Alexander, R. P.; Papetti, S.; Reid, J. A.; Trotz, S. I. A New Series of Organoboranes. III. Some Reactions of 1,2-Dicarbaclovododecaborane(12) and Its Derivatives. *Inorg. Chem.* **1963**, *2*, 1097–1105. https://doi.org/10.1021/ic50010a004.

(21) Grafstein, D.; Dvorak, J. Neocarboranes, a New Family of Stable Organoboranes Isomeric with the Carboranes. *Inorg. Chem.* **1963**, *2*, 1128–1133. https://doi.org/10.1021/ic50010a011.

(22) Grimes, R. N. Structure and Bonding. In *Carboranes*; Elsevier, 2016; pp 7–18. https://doi.org/10.1016/B978-0-12-801894-1.00002-0.

(23) Grimes, R. N. Synthesis and Reactivity. In *Carboranes*; Elsevier, 2016; pp 19–22. https://doi.org/10.1016/B978-0-12-801894-1.00003-2.

(24) Grimes, R. N. Icosahedral Carboranes. In *Carboranes*; Elsevier, 2016; pp 503–615. https://doi.org/10.1016/B978-0-12-801894-1.00010-X.

(25) Karnbrock, W.; Musiol, H.-J.; Moroder, L. Enantioselective Synthesis of S-o-Carboranylalanine via Methylated Bislactim Ethers of 2,5-Diketopiperazines. *Tetrahedron* **1995**, *51*, 1187–1196. https://doi.org/10.1016/0040-4020(94)01014-Q.

(26) Radel, P. A.; Kahl, S. B. Enantioselective Synthesis of L- and D-Carboranylalanine. *J. Org. Chem.* **1996**, *61*, 4582–4588. https://doi.org/10.1021/jo952271b.

(27) Ujváry, I.; Nachman, R. J. Synthesis of 3-(12-Hydroxy-p-Carboranyl)Propionic Acid, a Hydrophobic, N-Terminal Tyrosine-Mimetic for Peptides. *Peptides* **2001**, *22*, 287–290. https://doi.org/10.1016/S0196-

9781(00)00381-8.

(28) Beletskaya, I. P.; Bregadze, V. I.; Osipov, S. N.; Petrovskii, P. V.; Starikova, Z. A.; Timofeev, S. V. New Nonnatural α-Amino Acid Derivatives with Carboranyl Fragments in α- and β-Positions. *Synlett* **2004**, 7, 1247–1248. https://doi.org/10.1055/s-2004-825594.

(29) Grimes, R. N. Carboranes in Medicine. In *Carboranes*; Elsevier, 2016; pp 945–984. https://doi.org/10.1016/B978-0-12-801894-1.00016-0.

(30) Roberts, M. D. V. The Electronic Structure of an Icosahedron of Boron Atoms. *Proc. R. Soc. London. Ser. A. Math. Phys. Sci.* **1955**, *230*, 110–119. https://doi.org/10.1098/rspa.1955.0115.

(31) Ellis, I. A.; Gaines, D. F.; Schaeffer, R. A Convenient Preparation of $B_{12}H_{12}^{2-}$ Salts. *J. Am. Chem. Soc.* **1963**, *85*, 3885–3885. https://doi.org/10.1021/ja00906a032.

(32) Miller, H. C.; Miller, N. E.; Muetterties, E. L. Chemistry of Boranes. XX. Syntheses of Polyhedral Boranes. *Inorg. Chem.* **1964**, *3*, 1456–1463. https://doi.org/10.1021/ic50020a026.

(33) Adams, R. M.; Siedle, A. R.; Grant, J. Convenient Preparation of the Dodecahydrododecaborate Ion. *Inorg. Chem.* **1964**, *3*, 461. https://doi.org/10.1021/ic50013a040.

(34) Mueller, L. O. Weakly Coordinating Anions and Lewis Superacidity, Albert-Ludwigs-Universität, **2008**.

(35) Lipping, L.; Leito, I.; Koppel, I.; Krossing, I.; Himmel, D.; Koppel, I. A. Superacidity of Closo-Dodecaborate-Based Brønsted Acids: A DFT Study. *J. Phys. Chem. A* **2015**, *119*, 735–743. https://doi.org/10.1021/jp506485x.

(36) Jenne, C.; Keßler, M.; Warneke, J. Protic Anions $[H(B_{12}X_{12})]^-$ (X=F, Cl, Br, I) That Act as Brønsted Acids in the Gas Phase. *Chem. - A Eur. J.* **2015**, *21* , 5887–5891. https://doi.org/10.1002/chem.201500034.

(37) Avelar, A.; Tham, F. S.; Reed, C. A. Superacidity of Boron Acids $H_2(B_{12}X_{12})$(X = Cl, Br). *Angew. Chemie - Int. Ed.* **2009**, *48*, 3491–3493. https://doi.org/10.1002/anie.200900214.

(38) Poater, J.; Solà, M.; Viñas, C.; Teixidor, F. π Aromaticity and Three-Dimensional Aromaticity: Two Sides of the Same Coin. *Angew. Chemie - Int. Ed.* **2014**, *53*, 12191–12195. https://doi.org/10.1002/anie.201407359.

(39) Justus, E.; Vöge, A.; Gabel, D. N-Alkylation of Ammonioundecahydro-Closo-Dodecaborate(1-) for the Preparation of Anions for Ionic Liquids. *Eur. J. Inorg. Chem.* **2008**, 33, 5245–5250. https://doi.org/10.1002/ejic.200800770.

(40) Hertler, W. R.; Raasch, M. S. Chemistry of Boranes. XIV. Amination of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ with Hydroxylamine-O-Sulfonic Acid. *J. Am. Chem. Soc.* **1964**, *86*, 3661–3668. https://doi.org/10.1021/ja01072a014.

(41) Laskova, J.; Kozlova, A.; Ananyev, I.; Bregadze, V.; Semioshkin, A. 2-Hydroxyethoxy-Closo-Undecahydrododecaborate(12)($[B_{12}H_{11}CH_2CH_2OH]^{2-}$) as a New Prospective Reagent for the Preparation of Closo-Dodecaborate Building Blocks and Thymidine and 2-Deoxyuridine Conjugates Linked via Short Spacer. *J. Organomet. Chem.* **2017**, *834*, 64–72. https://doi.org/10.1016/j.jorganchem.2017.02.009.

(42) Matveev, E. Y.; Akimov, S. S.; Kubasov, A. S.; Retivov, V. M.; Zhizhin, K. Y.; Kuznetsov, N. T. Synthesis and Study of Derivatives of the $[B_{10}H_{10}]^{2-}$ Anion with Amino Acids. *Russ. J. Inorg. Chem.* **2019**, *64*, 1513–1521. https://doi.org/10.1134/S003602361912009X.

(43) Ali, F.; S Hosmane, N.; Zhu, Y. Boron Chemistry for Medical Applications. *Molecules* **2020**, *25*, 1–24. https://doi.org/10.3390/molecules25040828.

(44) Wright, J.; Kaczmarczyk, A. Direct Synthesis of Dialkyl Sulfide Derivatives of Dodecahydrododecaborate(2-), $B_{12}H_{12}^{2-}$. *Inorg. Chem.* **1973**, *12*, 1453–

1454.

(45) Tolpin, E. I.; Wellum, G. R.; Berley, S. A. Synthesis and Chemistry of Mercaptoundecahydro-Closo-Dodecaborate(2-). *Inorg. Chem.* **1978**, *17*, 2867–2873. https://doi.org/10.1021/ic50188a037.

(46) Peymann, T.; Knobler, C. B.; Khan, S. I.; Hawthorne, M. F. Dodecahydroxy-Closo-Dodecaborate(2-). *J. Am. Chem. Soc.* **2001**, *123*, 2182–2185. https://doi.org/10.1021/ja0014887.

(47) Atoji, M.; Lipscomb, W. N. The Crystal and Molecular Structure of B_4Cl_4. *Acta Crystallogr.* **1953**, *6*, 547–550. https://doi.org/10.1107/s0365110x53001472.

(48) Preetz, W.; Peters, G. The Hexahydro-Closo-Hexaborate Dianion $[B_6H_6]^{2-}$ and Its Derivatives. *Eur. J. Inorg. Chem.* **1999**, *1999*, 1831–1846. https://doi.org/10.1002/(SICI)1099-0682(199911)1999:11<1831::AID-EJIC1831>3.0.CO;2-J.

(49) Kutz, N. A.; Morrison, J. A. 2N Framework Electron Clusters: Preparation and Relative Thermal Stabilities of the Polyhedral Boron Subbromides. *Inorg. Chem.* **1980**, *19*, 3295–3299. https://doi.org/10.1021/ic50213a019.

(50) Hönle, W.; Grin, Y.; Burkhardt, A.; Wedig, U.; Schultheiss, M.; Von Schnering, H. G.; Kellner, R.; Binder, H. Syntheses, Crystal Structures, and Electronic Structure of the Boron Halides B_9X_9(X=Cl, Br, I). *J. Solid State Chem.* **1997**, *133*, 59–67. https://doi.org/10.1006/jssc.1997.7309.

(51) Knoth, W. H.; Miller, H. C.; Sauer, J. C.; Balthis, J. H.; Chia, Y. T.; Muetterties, E. L. Chemistry of Boranes. IX. Halogenation of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. *Inorg. Chem.* **1964**, *3*, 159–167. https://doi.org/10.1021/ic50012a002.

(52) Axtell, J. C.; Saleh, L. M. A.; Qian, E. A.; Wixtrom, A. I.; Spokoyny, A. M. Synthesis and Applications of Perfunctionalized Boron Clusters. *Inorg. Chem.*

2018, *57*, 2333–2350. https://doi.org/10.1021/acs.inorgchem.7b02912.

(53) Ivanov, S. V.; Davis, J. A.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. Synthesis and Characterization of Ammonioundecafluoro-Closo-Dodecaborates(1-). New Superweak Anions. *Inorg. Chem.* **2003**, *42*, 4489–4491. https://doi.org/10.1021/ic0344160.

(54) Peryshkov, D. V.; Popov, A. A.; Strauss, S. H. Direct Perfluorination of $K_2B_{12}H_{12}$ in Acetonitrile Occurs at the Gas Bubble-Solution Interface and Is Inhibited by HF. Experimental and DFT Study of Inhibition by Protic Acids and Soft, Polarizable Anions. *J. Am. Chem. Soc.* **2009**, *131*, 18393–18403. https://doi.org/10.1021/ja9069437.

(55) Gu, W.; Ozerov, O. V. Exhaustive Chlorination of [B 12 H 12] 2− without Chlorine Gas and the Use of $[B_{12}Cl_{12}]^{2-}$ as a Supporting Anion in Catalytic Hydrodefluorination of Aliphatic C−F Bonds. *Inorg. Chem.* **2011**, *50*, 2726–2728. https://doi.org/10.1021/ic200024u.

(56) Peymann, T.; Herzog, A.; Knobler, C. B.; Hawthorne, M. F. Aromatic Polyhedral Hydroxyborates: Bridging Boron Oxides and Boron Hydrides. *Angew. Chemie Int. Ed.* **1999**, *38*, 1061–1064. https://doi.org/10.1002/(SICI)1521-3773(19990419)38:8<1061::AID-ANIE1061>3.0.CO;2-B.

(57) Peymann, T.; Knobler, C. B.; Khan, S. I.; Hawthorne, M. F. Dodecahydroxy-Closo-Dodecaborate(2-). *J. Am. Chem. Soc.* **2001**, *123*, 2182–2185. https://doi.org/10.1021/ja0014887.

(58) Farha, O. K.; Julius, R. L.; Lee, M. W.; Huertas, R. E.; Knobler, C. B.; Hawthorne, M. F. Synthesis of Stable Dodecaalkoxy Derivatives of Hypercloso-$B_{12}H_{12}$. *J. Am. Chem. Soc.* **2005**, *127*, 18243–18251. https://doi.org/10.1021/ja0556373.

(59) Maderna, A.; Knobler, C. B.; Hawthorne, M. F. Twelvefold Functionalization of an Icosahedral Surface by Total Esterification of $[B_{12}(OH)_{12}]^{2-}$: 12(12)-

Closomers. *Angew. Chemie Int. Ed.* **2001**, *40*, 1661–1664. https://doi.org/10.1002/1521-3773(20010504)40:9<1661::AID-ANIE16610>3.0.CO;2-U.

(60) Wixtrom, A. I.; Shao, Y.; Jung, D.; Machan, C. W.; Kevork, S. N.; Qian, E. A.; Axtell, J. C.; Khan, S. I.; Kubiak, C. P.; Spokoyny, A. M. Rapid Synthesis of Redox-Active Dodecaborane $B_{12}(OR)_{12}$ Clusters under Ambient Conditions. *Inorg. Chem. Front.* **2016**, *3*, 711–717. https://doi.org/10.1039/c5qi00263j.

(61) Wiersema, R. J.; Middaugh, R. L. Electrochemical Preparation and Halogenation of 1,1′-μ-Hydro-Bis(Undecahydro-Closo-Dodecaborate)(3-), $B_{24}H_{23}^{3-}$1. *Inorg. Chem.* **1969**, *8*, 2074–2079. https://doi.org/10.1021/ic50080a009.

(62) Rupich, M. W.; Foos, J. S.; Brummer, S. B. Characterization of Chloroclosoborane Acids as Electrolytes for Acid Fuel Cells. *J. Electrochem. Soc.* **1985**, *132*, 119–122. https://doi.org/10.1149/1.2113739.

(63) Peymann, T.; Knobler, C. B.; Hawthorne, M. F. An Unpaired Electron Incarcerated within an Icosahedral Borane Cage: Synthesis and Crystal Structure of the Blue, Air-Stable {[Closo-$B_{12}(CH_3)_{12}$]·}-Radical. *Chem. Commun.* **1999**, *12*, 2039–2040. https://doi.org/10.1039/a905406e.

(64) Goswami, L. N.; Everett, T. A.; Khan, A. A.; Hawthorne, M. F. Rational Design of a Stable Two One-Electron Redox-Active Closo-Dodecaalkoxyborane Ion as Biothiol Sensor. *Eur. J. Inorg. Chem.* **2020**, *2020*, 377–381. https://doi.org/10.1002/ejic.201901136.

(65) King, R. B. Analogies between the Chemical Bonding Topologies in Metal-Olefin Complexes and in Metallaboranes: The Role of Three-Center Two-Electron Bonding. *J. Organomet. Chem.* **2001**, *635*, 75–83. https://doi.org/10.1016/S0022-328X(01)00789-6.

(66) Greenwood, N. N. The Concept of Boranes as Ligands. *Coord. Chem. Rev.*

2002, *226*, 61–69. https://doi.org/10.1016/S0010-8545(01)00433-7.

(67) Avdeeva, V. V.; Malinina, E. A.; Kuznetsov, N. T. Coordination Chemistry of Iron Triad Metals with Organic N-Donor Ligands and Boron Cluster Anions $[B_{10}H_{10}]^{2-}$, $[B_{12}H_{12}]^{2-}$, and $[B_{10}Cl_{10}]^{2-}$: Complexation and Accompanying Processes. *Russ. J. Inorg. Chem.* **2017**, *62*, 1673–1702. https://doi.org/10.1134/S0036023617130022.

(68) Malinina, E. A.; Korolenko, S. E.; Goeva, L. V.; Buzanov, G. A.; Avdeeva, V. V.; Kuznetsov, N. T. Synthesis and Structure of $[M(DMF)_6][B_{10}H_{10}]$ (M = Zn(II), Cd(II)) as Precursors for Solid-Phase Synthesis of Trischelate Complexes $[M(L)_3][B_{10}H_{10}]$. *Russ. J. Inorg. Chem.* **2018**, *63*, 1552–1557. https://doi.org/10.1134/S0036023618120148.

(69) Malinina, E. A.; Kochneva, I. K.; Avdeeva, V. V. Synthesis and Structure of Mononuclear Copper (II) Complexes with Azaheterocyclic Ligands L (L = Bipy , BPA , and Phen). **2019**, *64*, 1210–1219. https://doi.org/10.1134/S0036023619100085.

(70) Larm, N. E.; Madugula, D.; Lee, M. W.; Baker, G. A. Polyhedral Borane-Capped Coinage Metal Nanoparticles as High-Performing Catalysts for 4-Nitrophenol Reduction. *Chem. Commun.* **2019**, *55*, 7990–7993. https://doi.org/10.1039/c9cc03428e.

(71) Gawande, M. B.; Goswami, A.; Felpin, F. X.; Asefa, T.; Huang, X.; Silva, R.; Zou, X.; Zboril, R.; Varma, R. S. Cu and Cu-Based Nanoparticles: Synthesis and Applications in Catalysis. *Chem. Rev.* **2016**, *116*, 3722–3811. https://doi.org/10.1021/acs.chemrev.5b00482.

(72) Yang, C. T.; Fu, Y.; Huang, Y. B.; Yi, J.; Guo, Q. X.; Liu, L. Room-Temperature Copper-Catalyzed Carbon-Nitrogen Coupling of Aryl Iodides and Bromides Promoted by Organic Ionic Bases. *Angew. Chemie - Int. Ed.* **2009**, *48*, 7398–7401. https://doi.org/10.1002/anie.200903158.

(73) Bhunia, S.; Pawar, G. G.; Kumar, S. V.; Jiang, Y.; Ma, D. Selected Copper-

Based Reactions for C−N, C−O, C−S, and C−C Bond Formation. *Angew. Chemie - Int. Ed.* **2017**, *56*, 16136–16179. https://doi.org/10.1002/anie.201701690.

(74) Lo, Q. A.; Sale, D.; Braddock, D. C.; Davies, R. P. Mechanistic and Performance Studies on the Ligand-Promoted Ullmann Amination Reaction. *ACS Catal.* **2018**, *8*, 101–109. https://doi.org/10.1021/acscatal.7b03664.

(75) Zhou, Q.; Du, F.; Chen, Y.; Fu, Y.; Sun, W.; Wu, Y. L-(−)-Quebrachitol as a Ligand for Selective Copper(0)-Catalyzed N-Arylation of Nitrogen-Containing Heterocycles. *J. Org. Chem.* **2019**, *84*, 8160–8167. https://doi.org/10.1021/acs.joc.9b00997.

(76) Geis, V.; Guttsche, K.; Knapp, C.; Scherer, H.; Uzun, R. Synthesis and Characterization of Synthetically Useful Salts of the Weakly-Coordinating Dianion $[B_{12}Cl_{12}]^{2-}$. *J. Chem. Soc. Dalt. Trans.* **2009**, 15, 2687–2694. https://doi.org/10.1039/b821030f.

(77) Doğan, S. Synhesis of Carborane Derivatives for Chracterization of Carbocations, Middle East Technical University, 2019.

(78) Medvedev, E. F.; Komarevskaya, A. S. IR Spectroscopic Study of the Phase Composition of Boric Acid as a Component of Glass Batch. *Glas. Ceram.* **2007**, *64*, 42–46. https://doi.org/10.1007/s10717-007-0010-y.

(79) Muetterties, E. L.; Merrifield, R. E.; Miller, H. C.; Knoth, W. H.; Downing, J. R. Chemistry of Boranes. III. The Infrared and Raman Spectra of $B_{12}H_{12}^{2-}$ and Related Anions. *J. Am. Chem. Soc.* **1962**, *84*, 2506–2508. https://doi.org/10.1021/ja00872a011.

(80) Max, J. J.; Chapados, C. IR Spectroscopy of Aqueous Alkali Halide Solutions: Pure Salt-Solvated Water Spectra and Hydration Numbers. *J. Chem. Phys.* **2001**, *115*, 2664–2675. https://doi.org/10.1063/1.1337047.

(81) Dutta, B.; Chowdhury, J. Existence of Dimeric Hydroxylamine-O-Sulfonic

Acid: Experimental Observations Aided by Ab Initio, DFT, Car-Parrinello and Born – Oppenheimer on the Fly Dynamics. *Chem. Phys. Lett.* **2019**, *732*, 136645. https://doi.org/10.1016/j.cplett.2019.136645.

(82) Zhang, B.; Li, X.; Guo, B.; Du, Y. Hypervalent Iodine Reagent-Mediated Reactions Involving Rearrangement Processes. *Chem. Commun.* **2020**, *56*, 14119–14136. https://doi.org/10.1039/D0CC05354F.

(83) Varvoglis, A. Preparative Methods for Hypervalent Iodine Reagents. *Hypervalent Iodine Org. Synth.* **1997**, 9–18. https://doi.org/10.1016/b978-012714975-2/50004-1.

(84) Gamez, P.; Arends, I. W. C. E.; Reedijk, J.; Sheldon, R. A. Copper(Ii)-Catalysed Aerobic Oxidation of Primary Alcohols to Aldehydes. *Chem. Commun.* **2003**, *3*, 2414–2415. https://doi.org/10.1039/b308668b.

(85) Geis, V.; Guttsche, K.; Knapp, C.; Scherer, H.; Uzun, R. Synthesis and Characterization of Synthetically Useful Salts of the Weakly-Coordinating Dianion $[B_{12}Cl_{12}]^{2-}$. *Dalt. Trans.* **2009**, 15, 2687–2694. https://doi.org/10.1039/b821030f.

(86) Sivaev, I. B.; Semioshkin, A. A.; Brellochs, B.; Sjöberg, S.; Bregadze, V. I. Synthesis of Oxonium Derivatives of the Dodecahydro-Closo-Dodecaborate Anion $[B_{12}H_{12}]^{2-}$. Tetramethylene Oxonium Derivative of $[B_{12}H_{12}]^{2-}$ as a Convenient Precursor for the Synthesis of Functional Compounds for Boron Neutron Capture Therapy. *Polyhedron* **2000**, *19*, 627–632. https://doi.org/10.1016/S0277-5387(00)00293-X.

APPENDICES

A. NMR Spectra

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

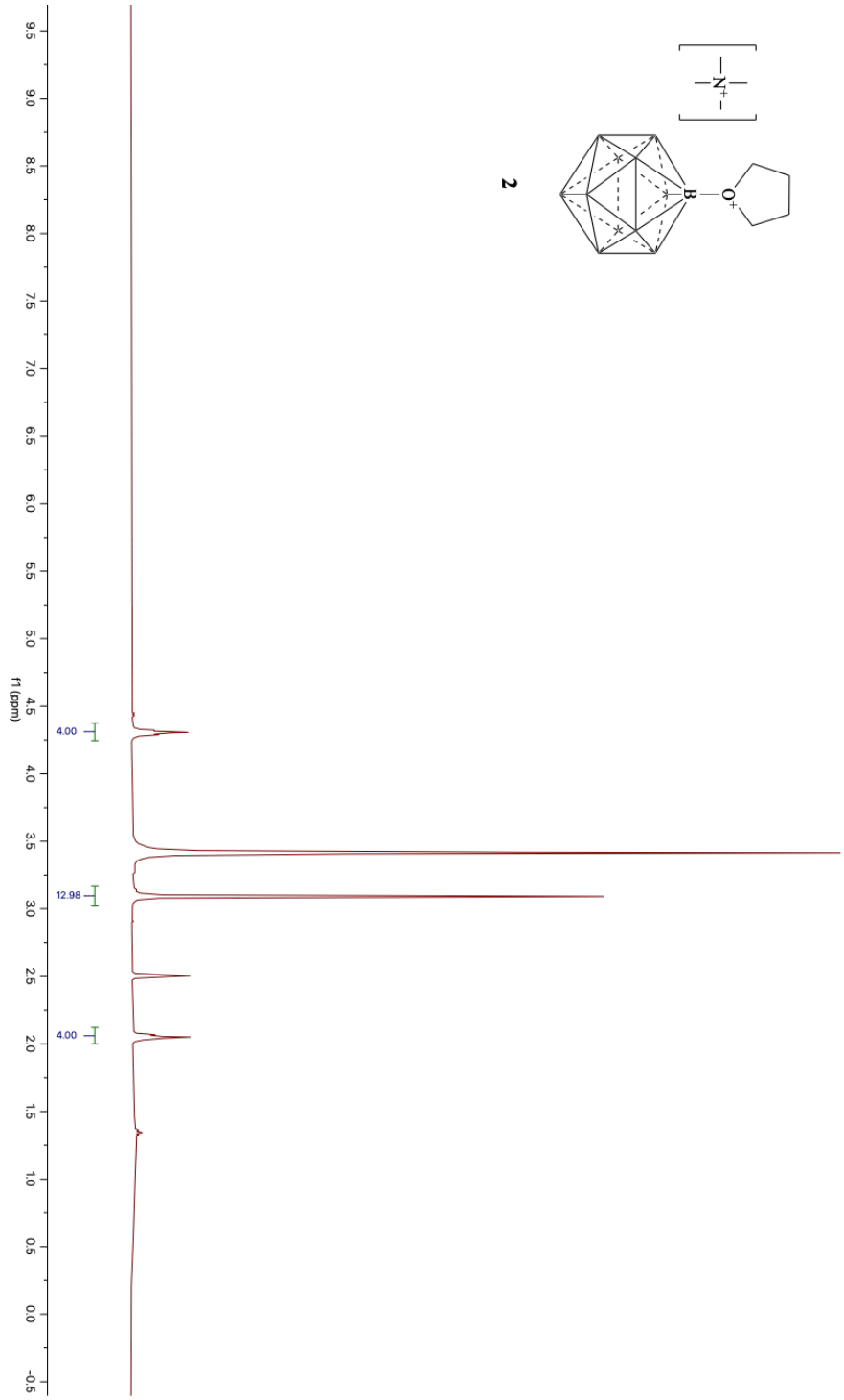


Figure 42. ^{1}H NMR Spectrum of Compound **2**

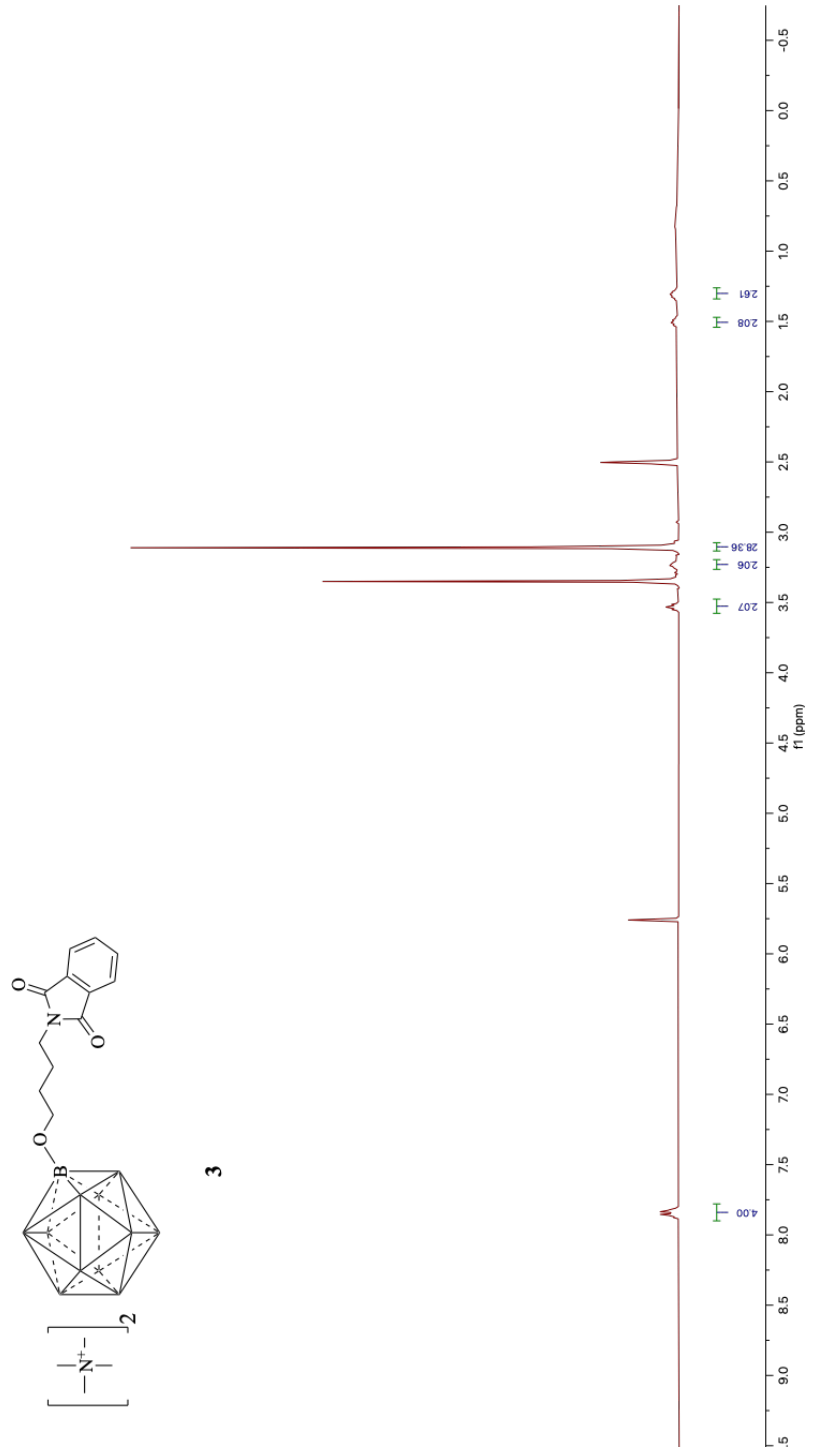


Figure 43. ^{1}H NMR Spectrum of Compound **3**

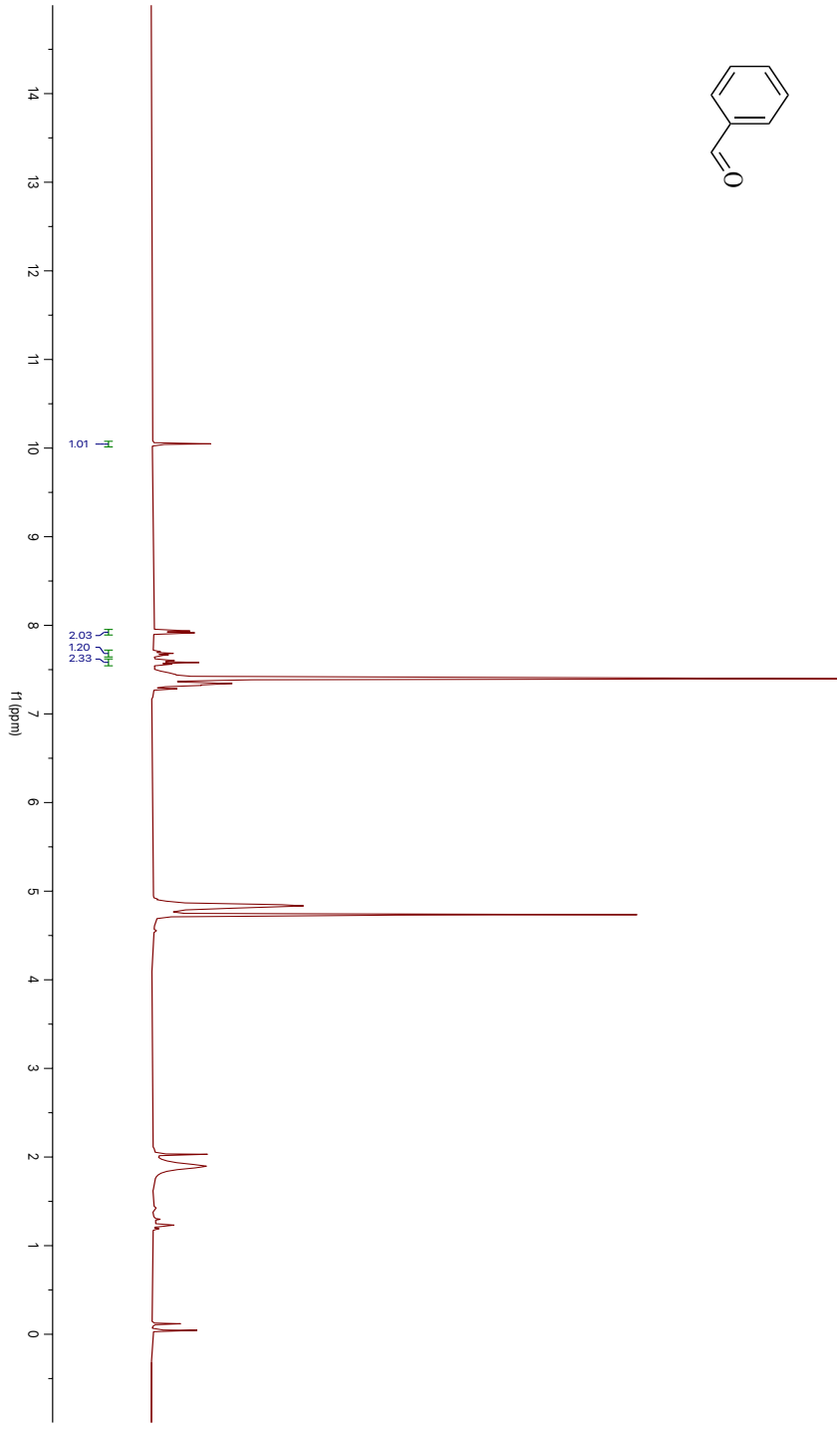


Figure 44. ^{1}H NMR Spectrum of copper sulfate utilized reaction

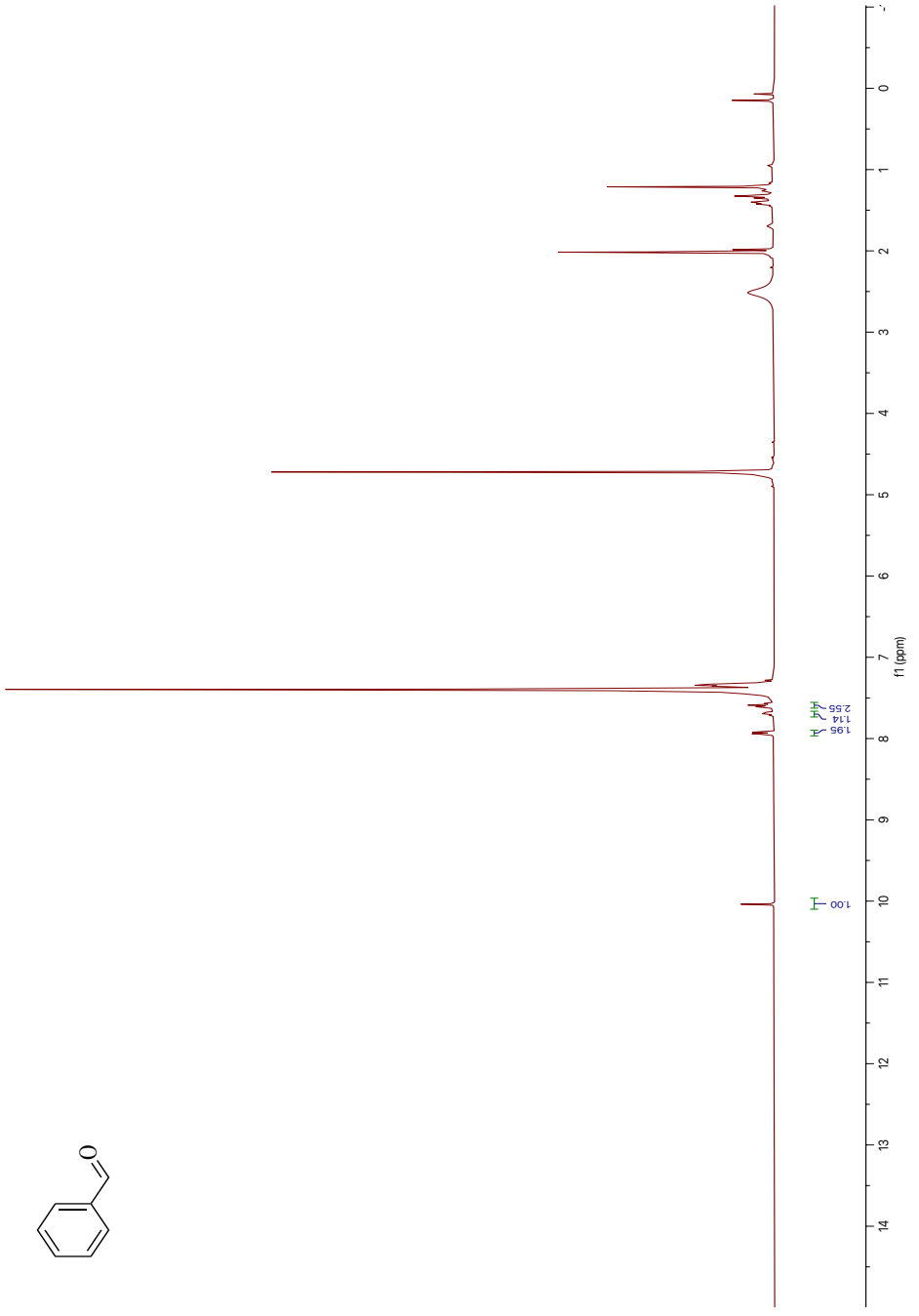


Figure 45. ^{1}H NMR Spectrum of hydrogen peroxide used reaction

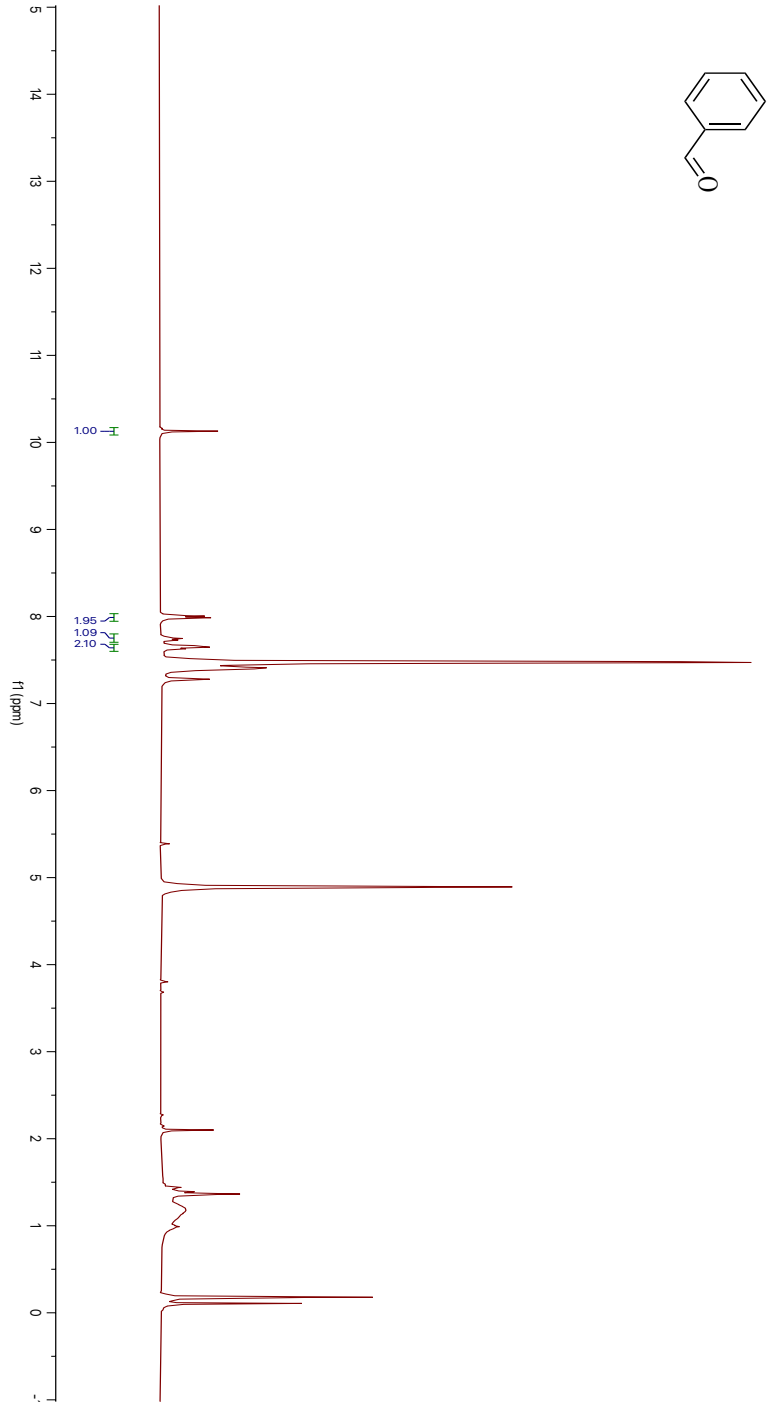


Figure 46. ^{1}H NMR Spectrum of test reaction

B. Infrared Spectra

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

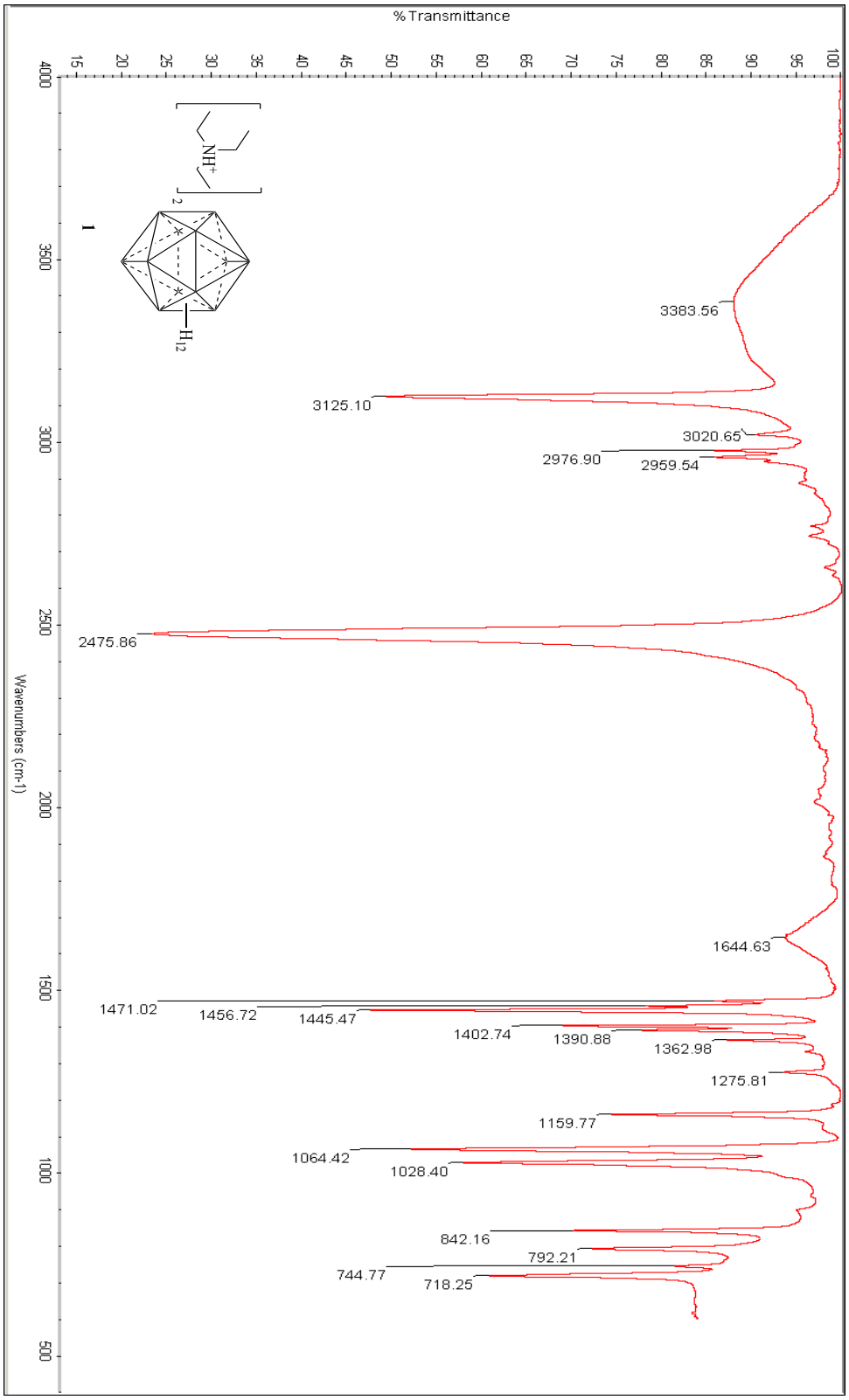


Figure 47. IR Spectrum of Compound **1**

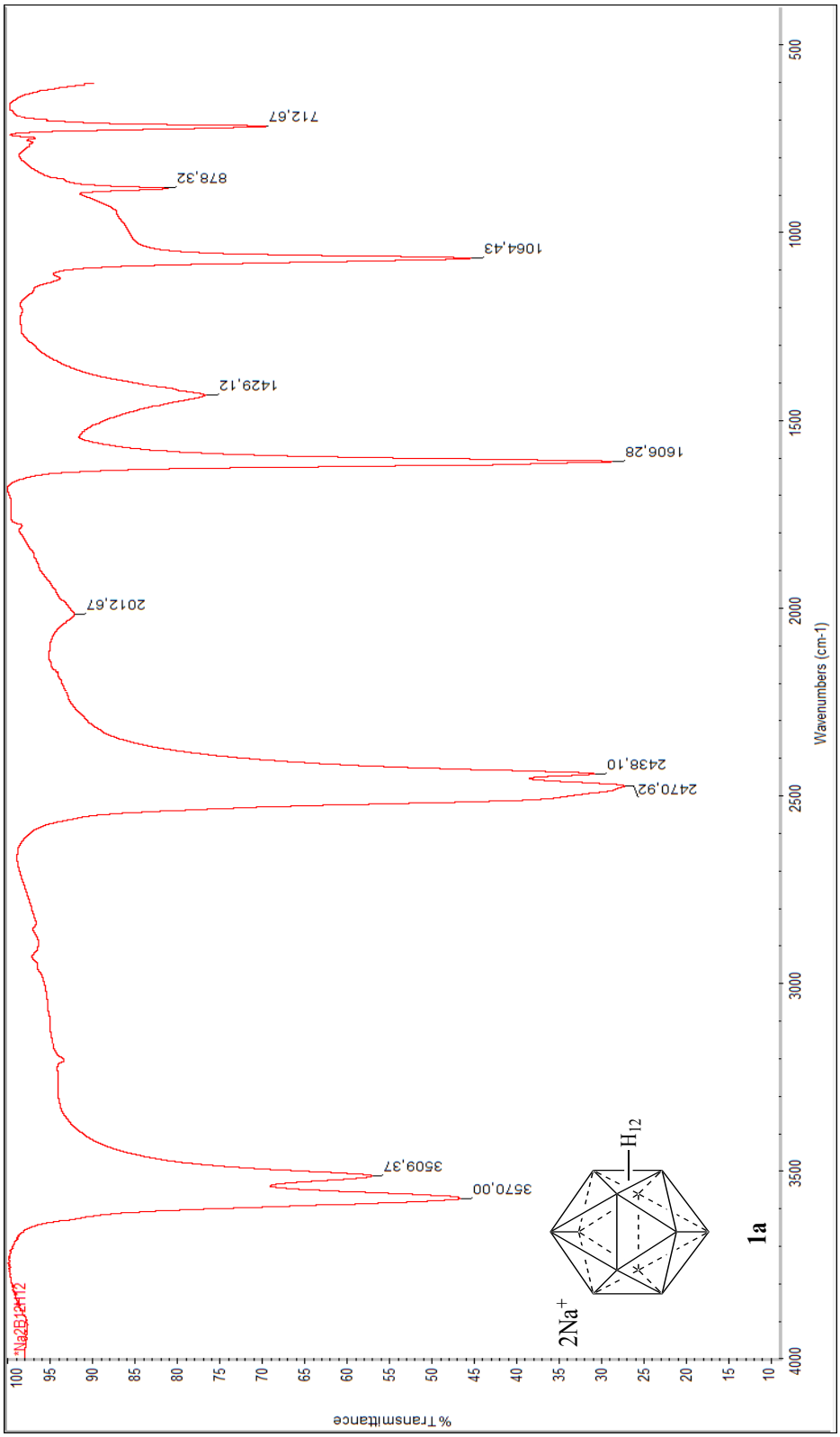


Figure 48. IR Spectrum of Compound **1a**

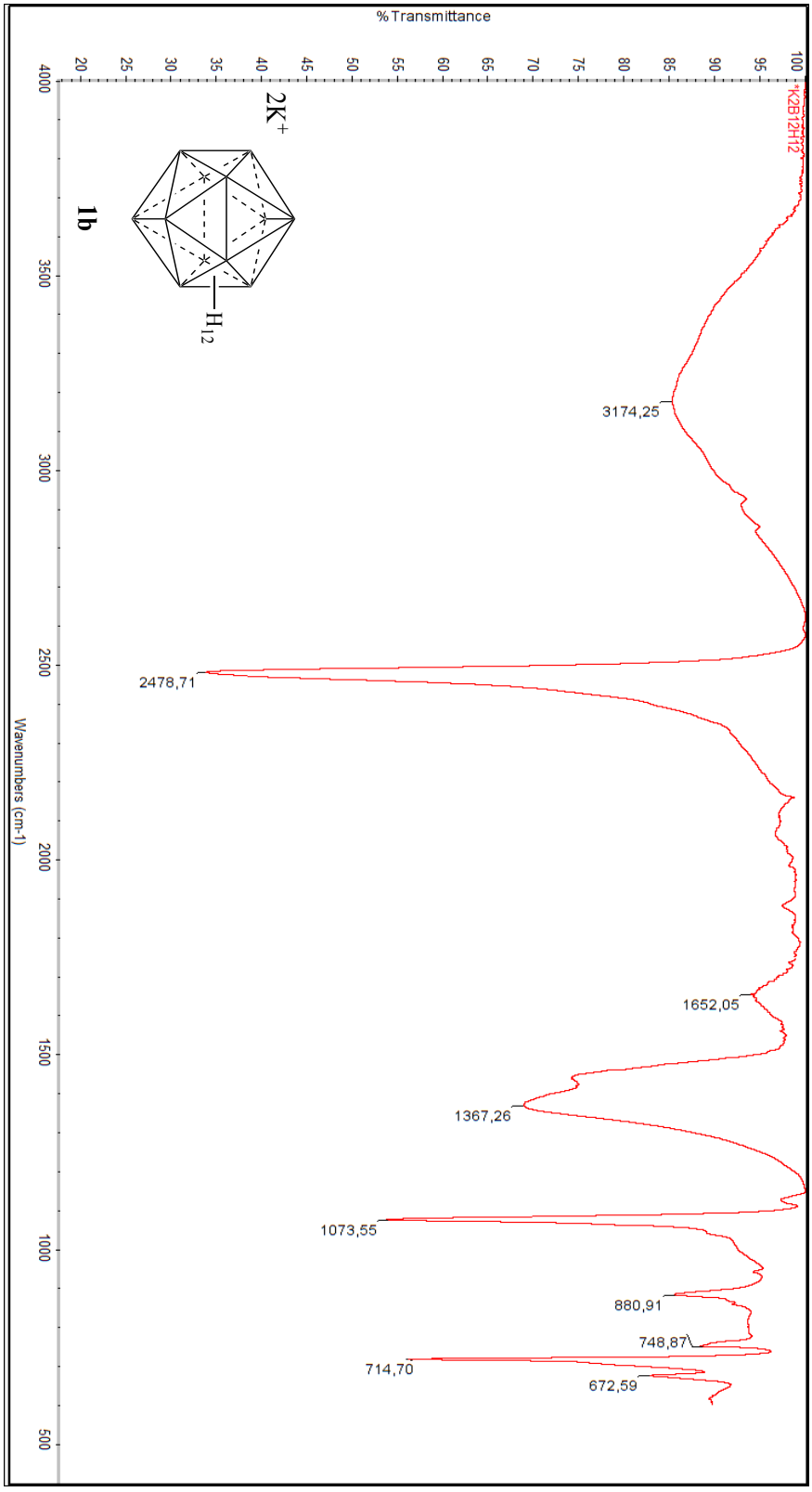


Figure 49. IR Spectrum of Compound **1b**

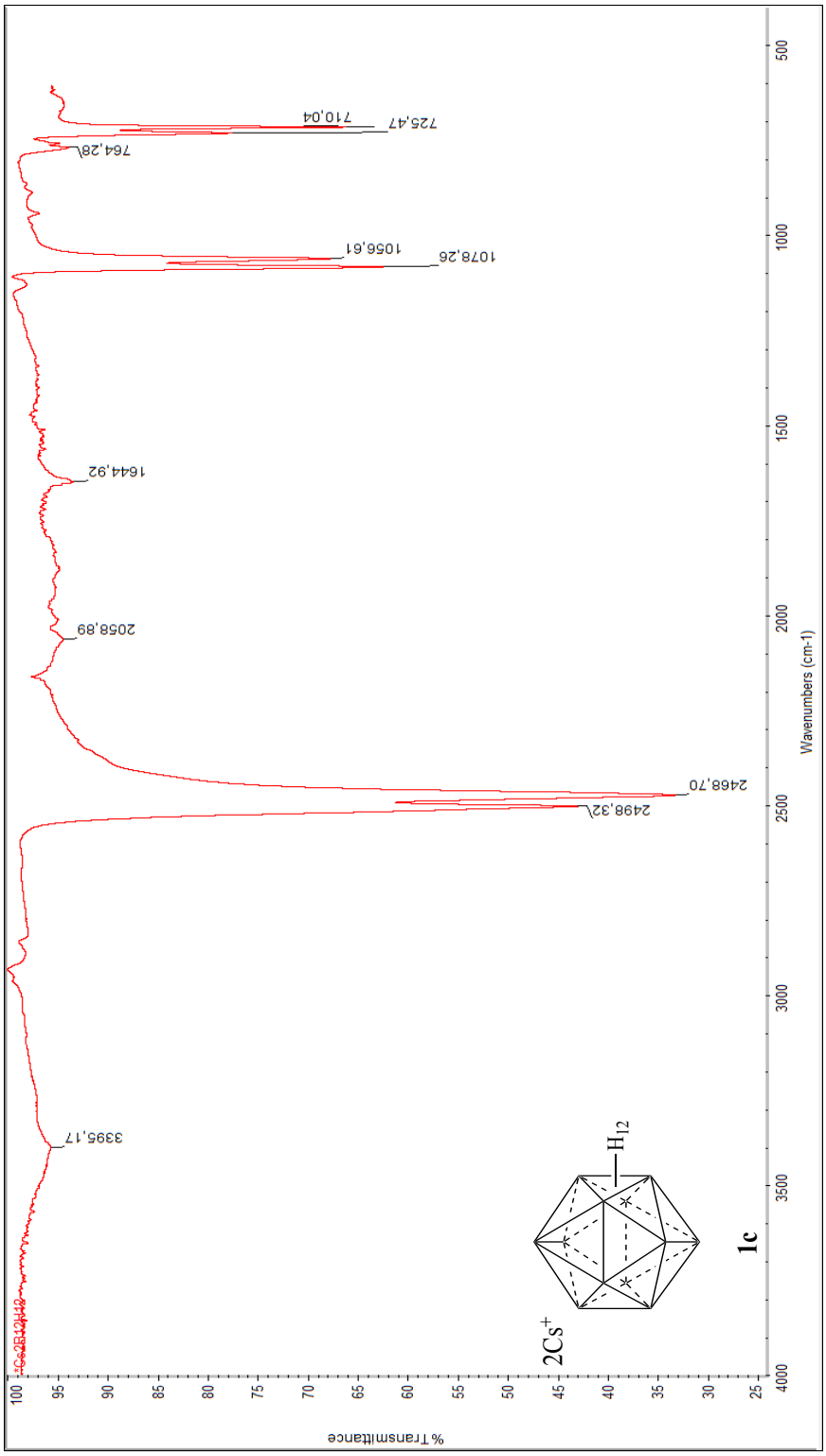


Figure 50. IR Spectrum of Compound **1c**

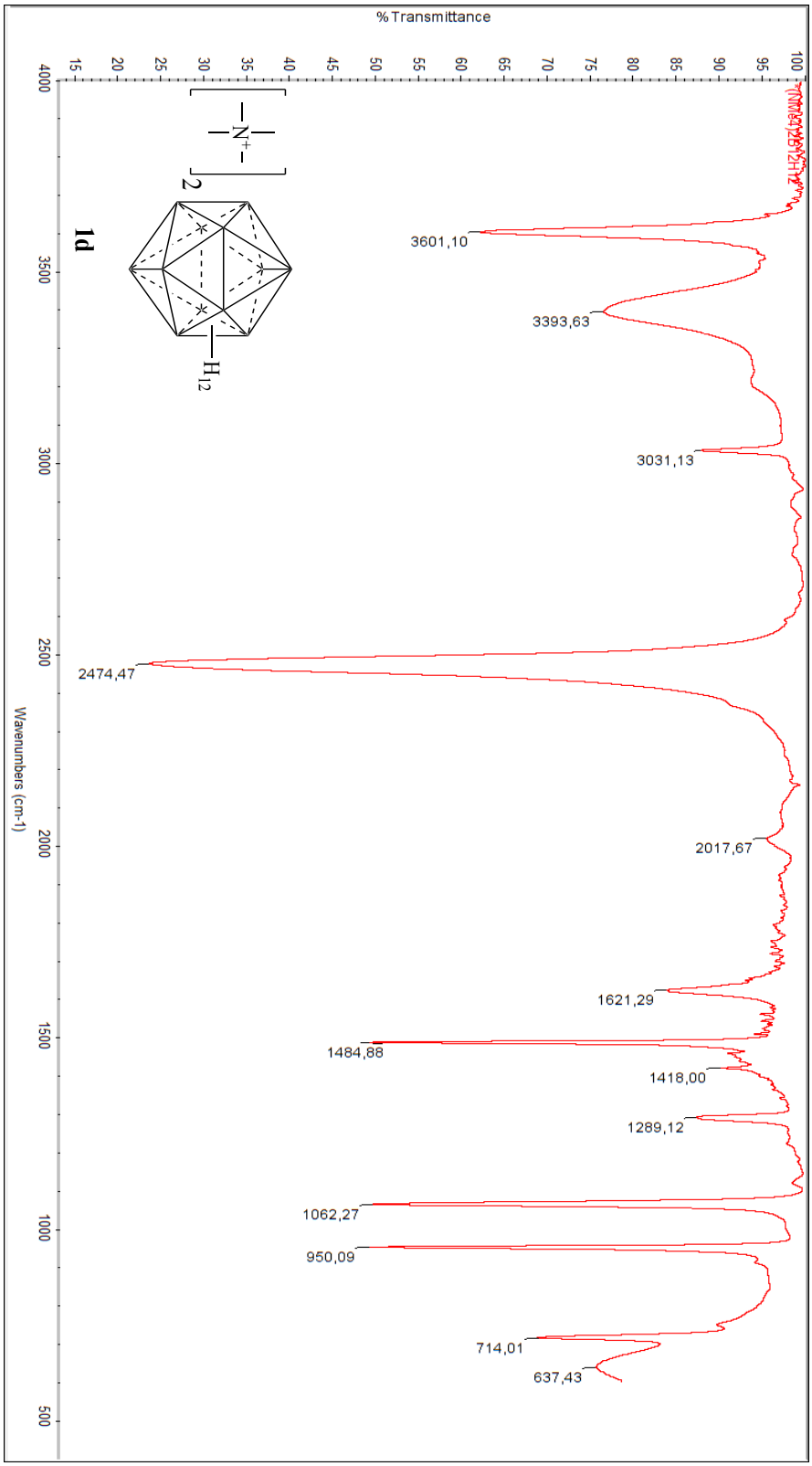


Figure 51. IR Spectrum of Compound **1d**

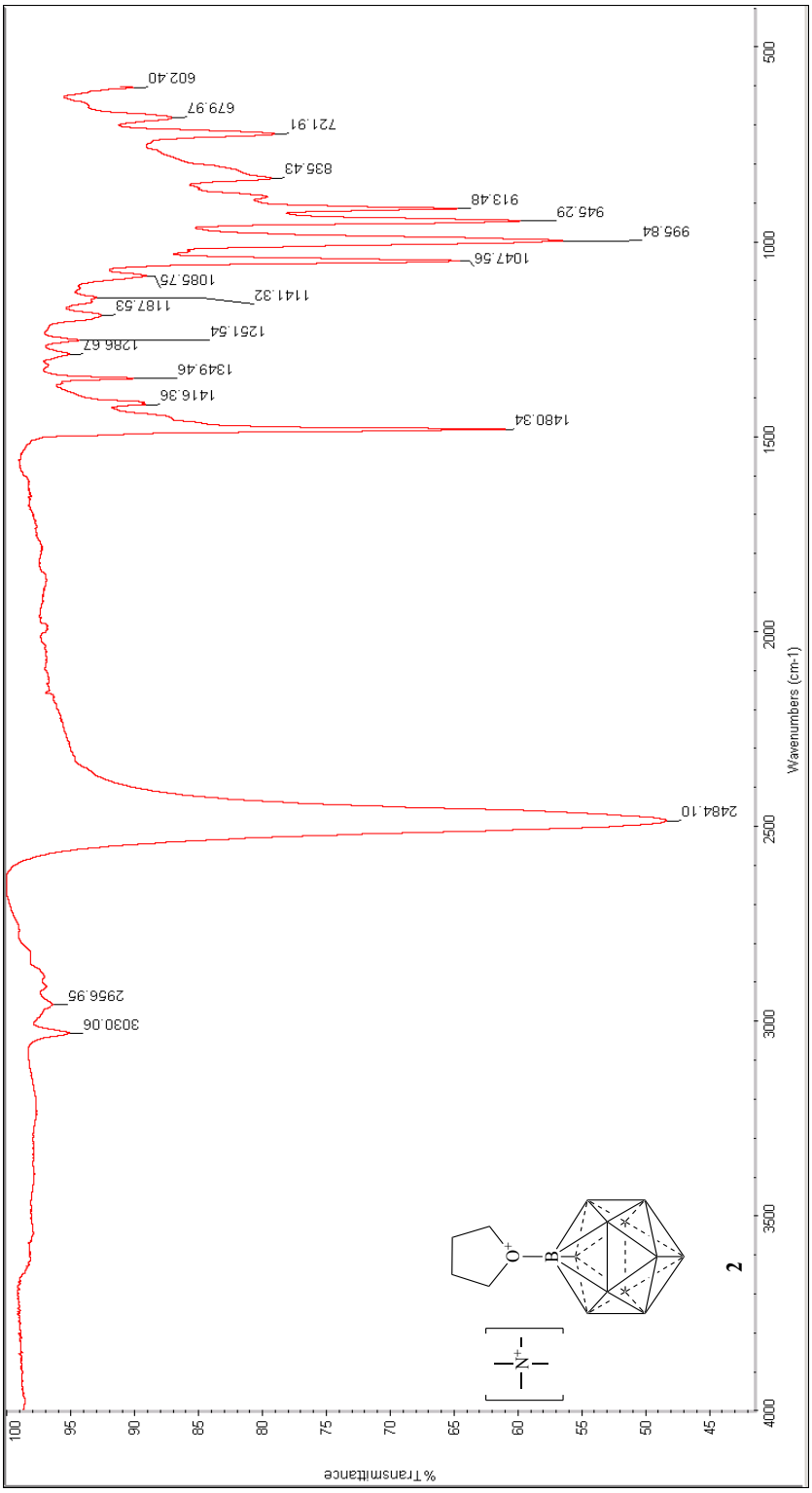


Figure 52. IR Spectrum of Compound **2**

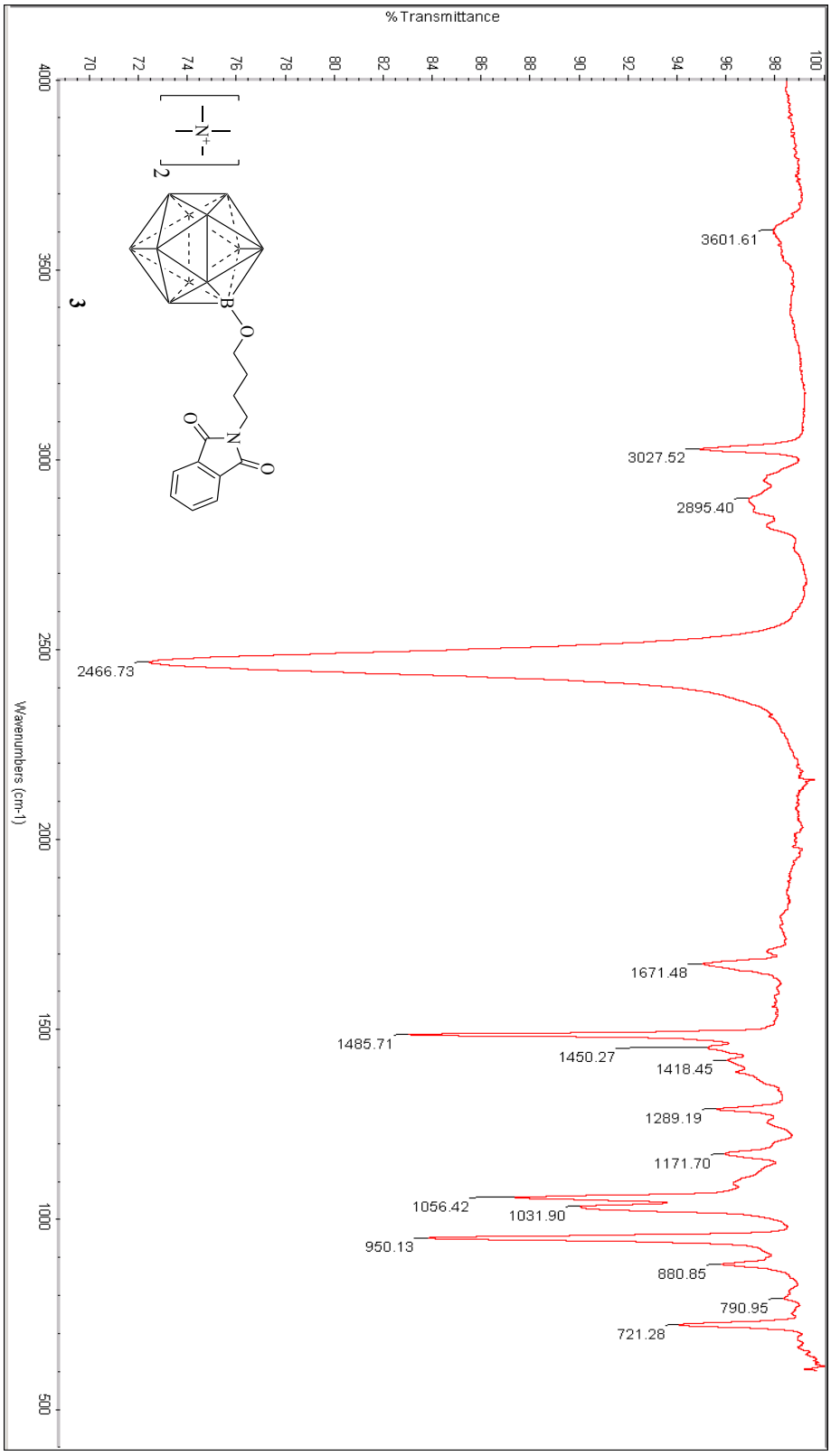


Figure 53. IR Spectrum of Compound **3**

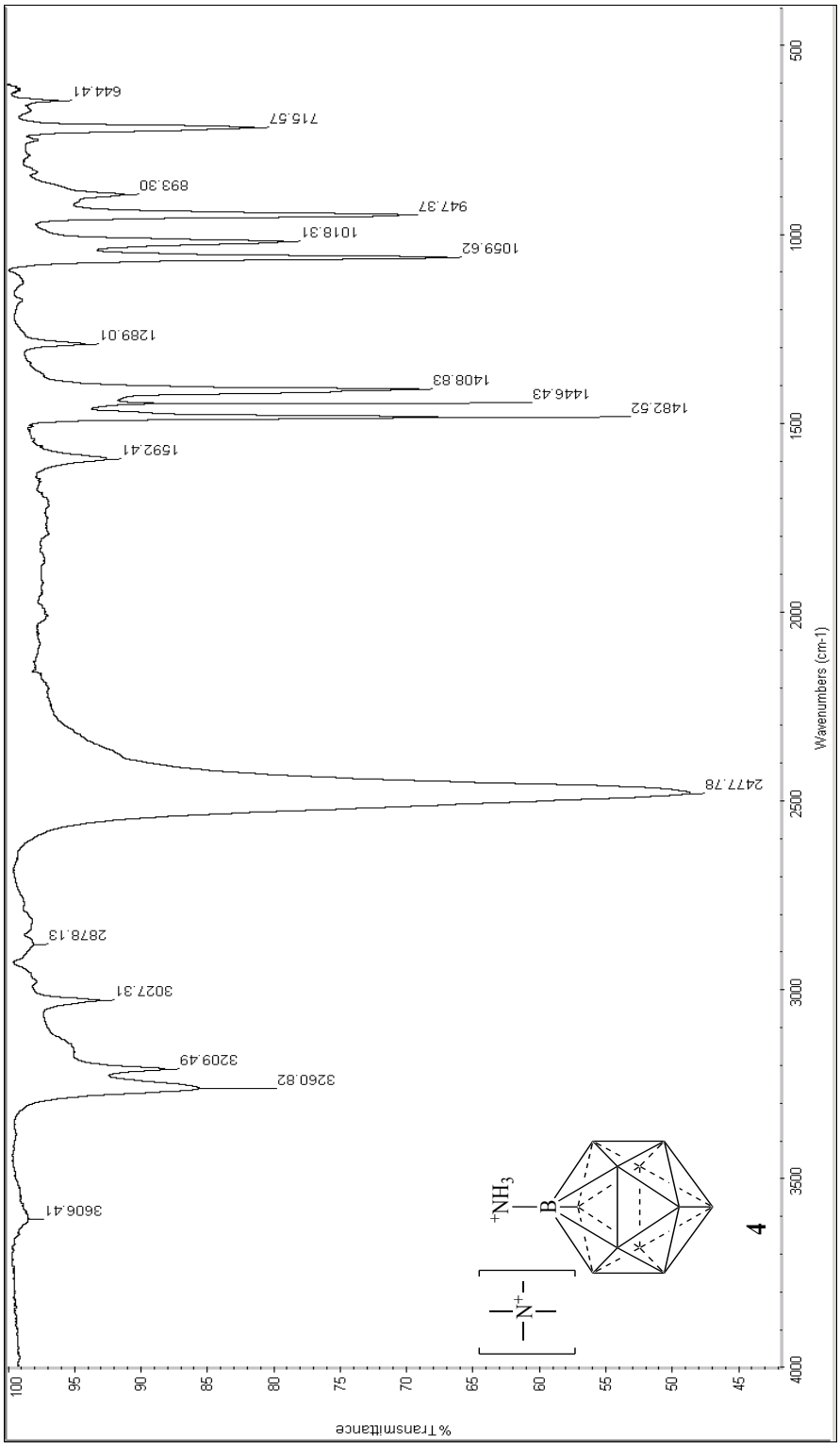


Figure 54. IR Spectrum of Compound **4**

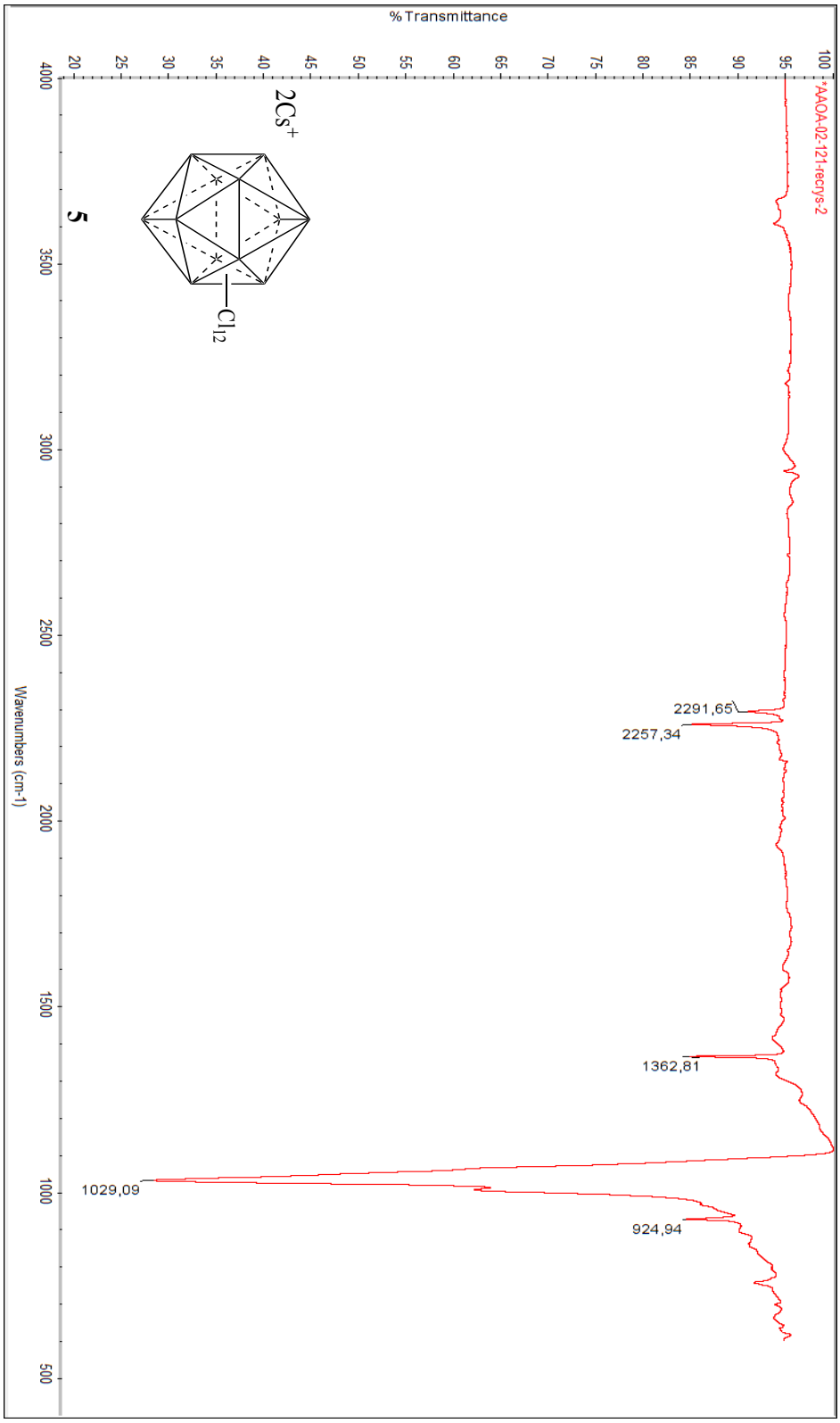


Figure 55. IR Spectrum of Compound **5**

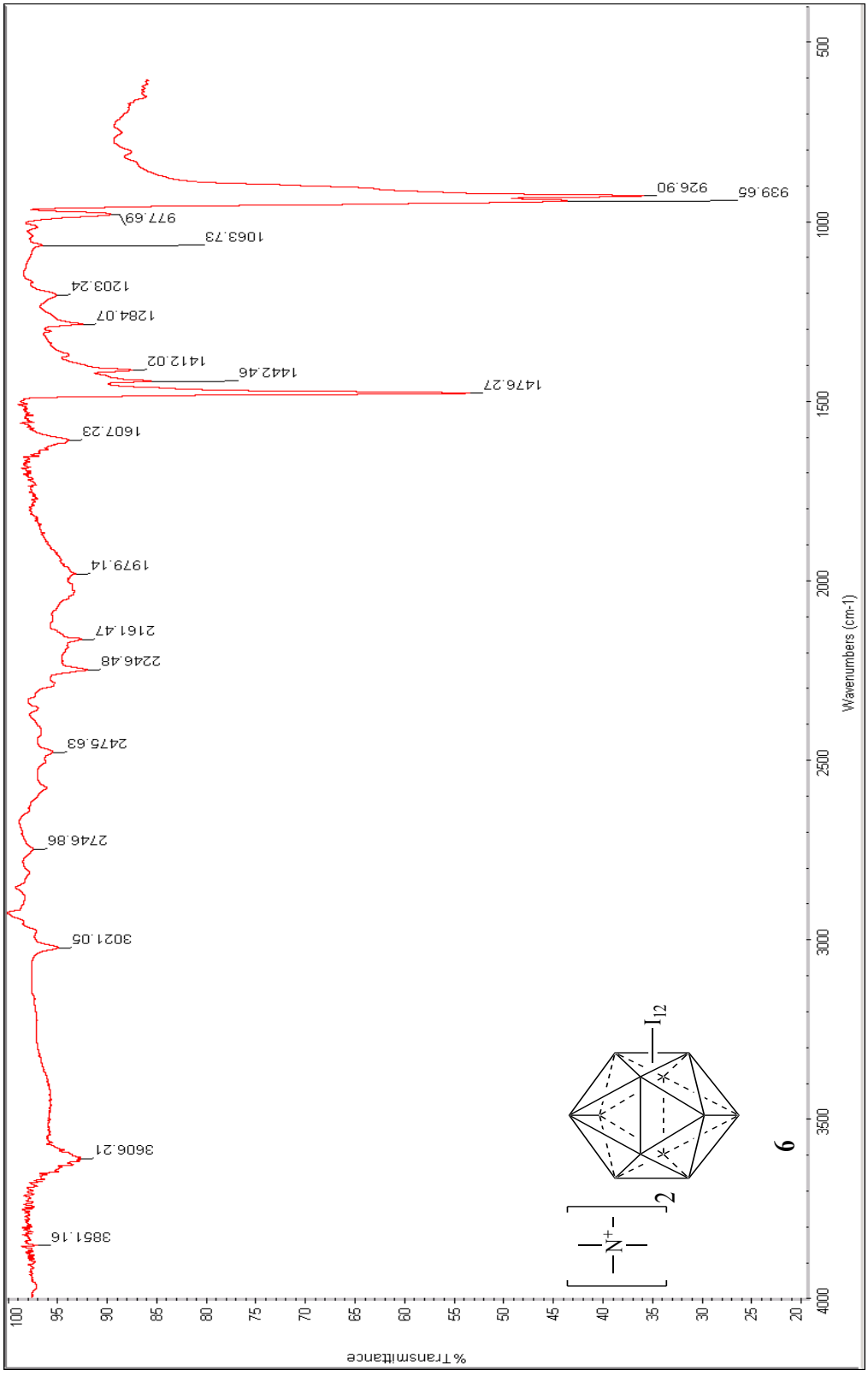


Figure 56. IR Spectrum of Compound **6**

C. HRMS Spectra

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

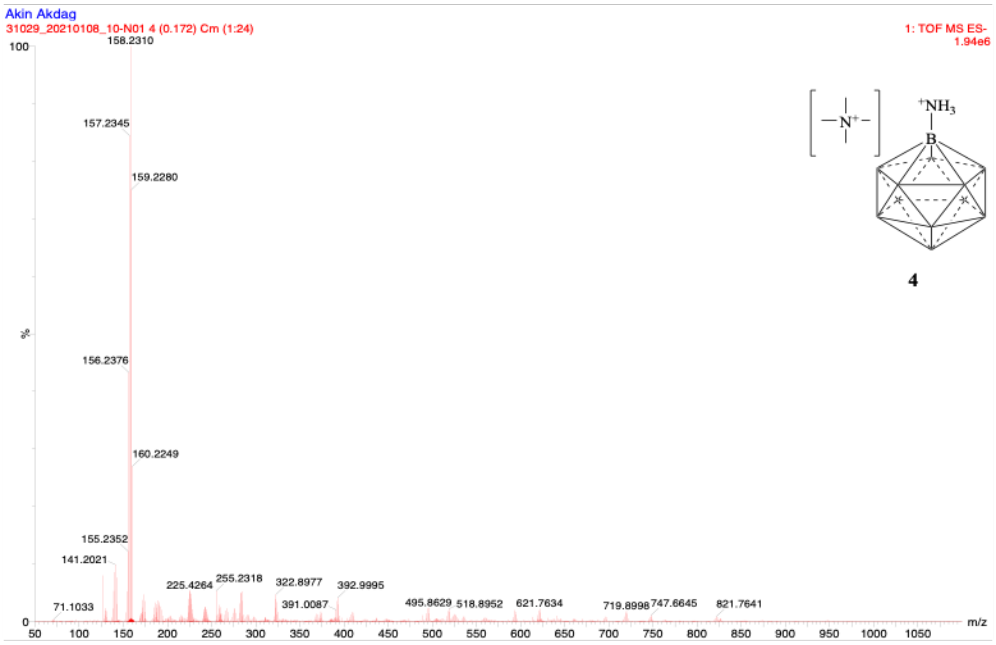


Figure 57. HRMS Spectrum of Compound **4**

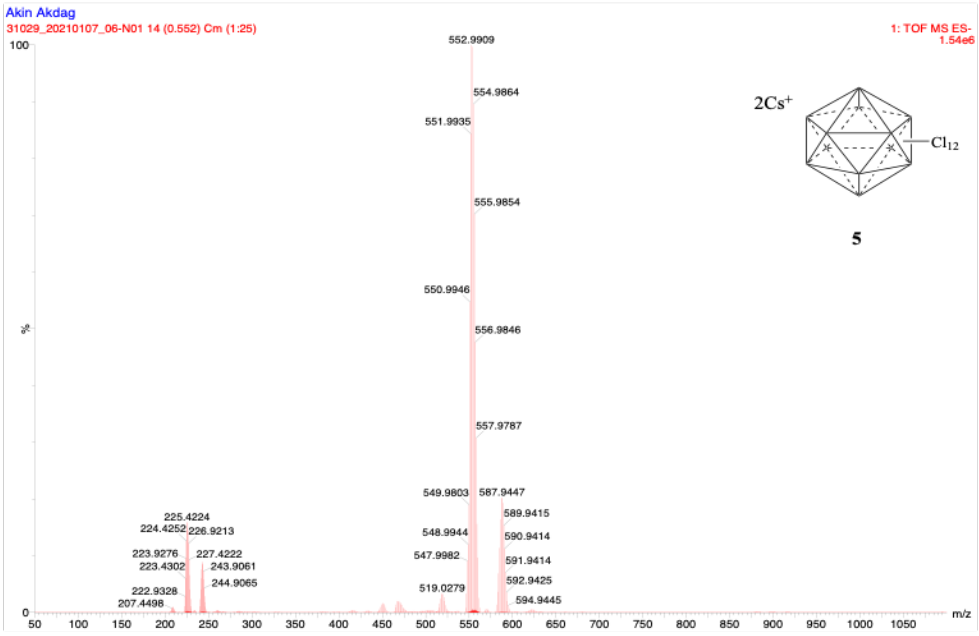


Figure 58. HRMS Spectrum of Compound **5**

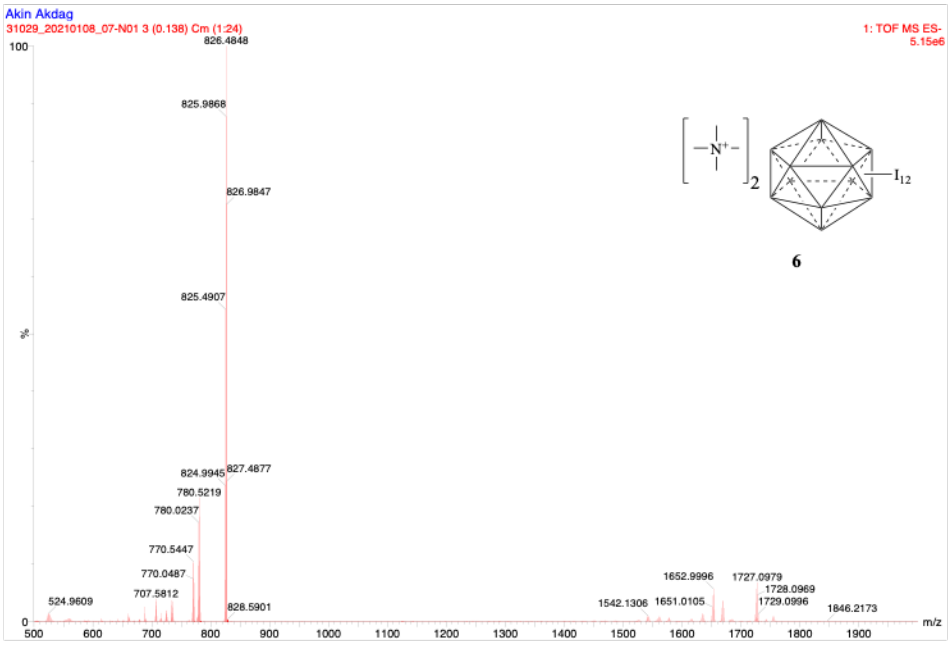


Figure 59. HRMS Spectrum of Compound **6**