Syntheses and reactions of pyridinophanes and cyclophanes containing group 13 elements

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A dissertation submitted for the partial fulfillment of BS-MS dual degree in Science

Department of Chemical Sciences

Indian Institute of Science Education and Research Mohali

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Dedicated to my parents

Certificate of Examination

This is to certify that the dissertation titled **"Syntheses and reactions of pyridinophanes and cyclophanes containing group 13 elements"** submitted by **Mr. Salman Faris K** (Reg. No. MS16110) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

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Date:

Declaration

The work presented in this dissertation has been carried out by me under the supervision of **Dr. Sanjay Singh** at the Department of Chemical Sciences, Indian Institute of Science Education and Research Mohali.

This work has not been submitted to any other university or Institute for fulfillment of any degree, a diploma or a fellowship. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgment of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibiliography.

Salman Faris k

Date:

Place:

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Sanjay Singh

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Acknowledgment

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Abbreviations

δ	Chemical shift
Å	angstrom
Ar	Aryl
av	Average
bap	Bis(trimethylsilyl)-N,N'-2,6-diaminopyridine
C	Celcius
calcd	calculated
d	doublet
EI	Electron impact ionization
g	grams
HRMS	High resolution mass spectrometry
Hz	Hertz
h	Hours
IR	Infrared
m	Multiplet
m/z	Mass/charge
Me	Methyl group (CH_3)
min.	Minute
M.p.	Melting point
NMR	Nuclear magnetic resonance
ppm	parts per million
Py	pyridine
s	Singlet
$SiMe_3$	Trimethylsilyl
t	Triplet
THF	Tetrahydrofuran

Contents

Abstract

Fascinating chemistry of macrocycles has attracted a lot of attention among scientists due to their wide variety of applications in various fields in chemistry, biochemistry and life sciences. Plethora of research has already been done in the field of organic macrocycles, however synthesis and applications of macrocycles like pyridinophanes / cyclophanes containing B/Al in their backbone has been limited due to the difficulties in their synthesis and highly sensitive nature. Recently some macrocycles are reported in this field using 2,6-pyridinediamine moiety as the building block. Keeping these facts in mind we planned to develop macrocycles containing B/Al with bigger cavity size by using different building blocks like 1,3-benzenedimethanamine and 2,6-pyridinedimethanol with different boron and aluminum compounds. Later on, in this work we have tried to study the coordination of anions with the reported boron containing pyridinophanes.

1. Introduction

1.1. Importance of macrocycles and their applications in chemistry

Cyclic structures have always attracted chemists due to the conformational restriction provided by cyclization and a better insight into the three-dimensional molecular structure and the formation of wide variety of entities and configurations.[1] Macrocycles are cyclic framework of molecules which contains twelve or more atoms.[2]

The first macrocyclic polyether referred as crown ether was discovered by Charles Pedersen more than five decades ago which made a huge impact in the emergence of host-guest chemistry and supramolecular chemistry.[3,4] Later, Lehn and co-workers synthesized cryptands which showed complete encapsulation of alkali and alkaline earth metal cations.[5-10] Motivated from these works Donald J. Cram developed cavitands and spherands having cavities which can trap even smaller organic molecules.[11-14] Wide variety of macrocyclic compounds from different classes have been synthesized in the subsequent years.[15]

Artificial macrocyclic compounds like calixarenes, torands,[16] cucurbiturils and different cyclophanes,[17-20] were also synthesized later which had important implications in different aspects of macrocyclic chemistry like self-assembly processes and molecular recognition.[21]

Progresses in the anion complexation studies in the last few decades has helped in the synthesis of macrocyclic anion receptors,[22-24] containing groups like amides,[25] triazoles,[26] etc. which helps in the hydrogen bond donation.

Figure 1 represents a calixarene, crown ether, porphyrin, cavitand and cryptand which are some common examples of well-known organic macrocycles.[27]

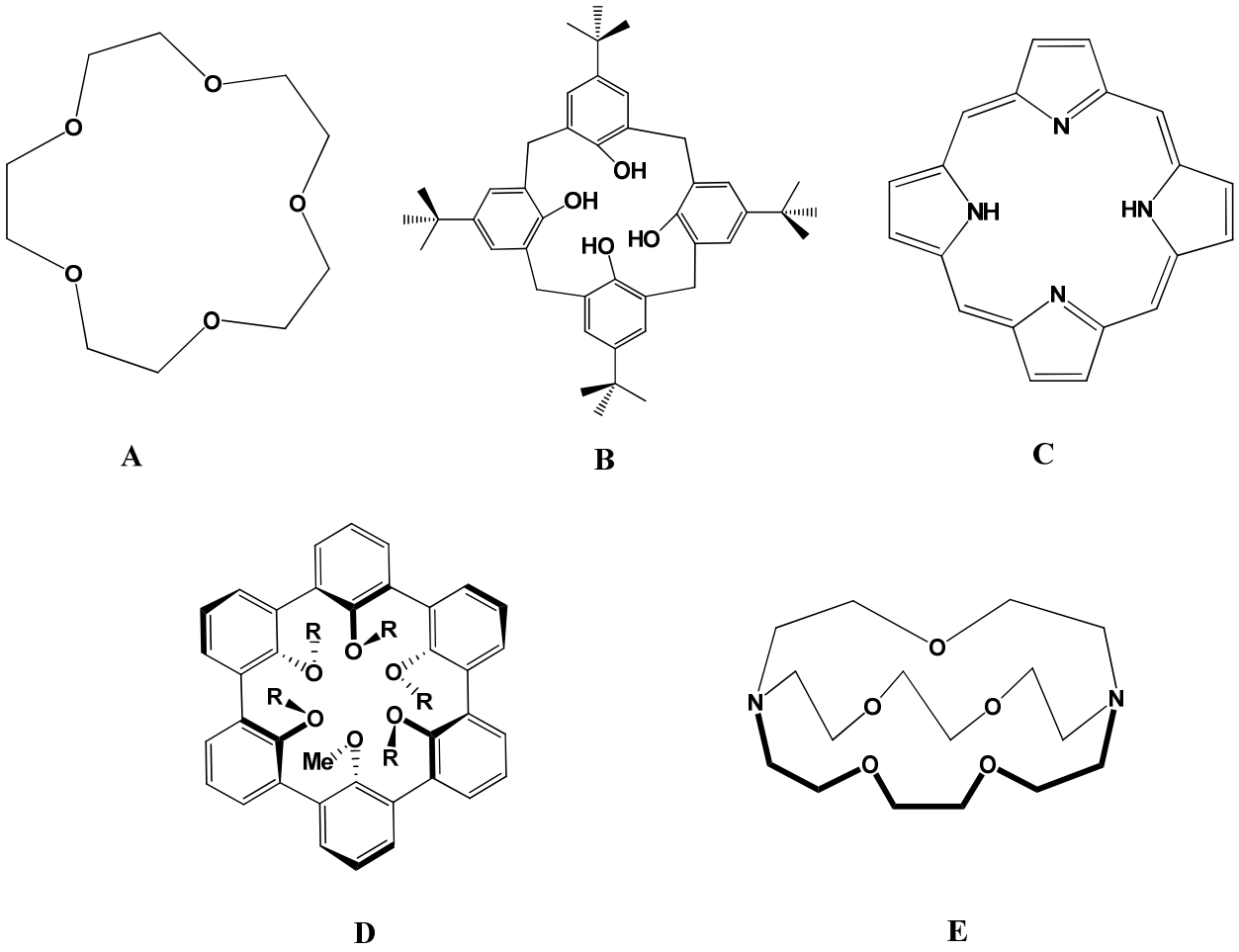


Figure 1. Some examples of common organic macrocycles: (**A**) a crown ether, (**B**) a calixarene, (**C**) a porphyrin, (**D**) a cavitand and (**E**) a cryptand.

1.2. Pyridinophanes and cyclophanes as building blocks in macrocyclic chemistry

Cyclophanes are types of macrocycles which consist of aromatic and aliphatic units.[28-31] In which the aromatic units are held in a face-to-face manner by the aliphatic bridges. Aromatic portion of the cyclophane unit can provide rigidity to the structure whereas the aliphatic part helps in the flexibility of the molecule.[32]

Pyridinophanes are analogous of cyclophanes in which one or both phenyl rings are replaced by pyridine units.[33] Presence of additional donor sites in pyridinophanes provides tunable

conformations compared to conventional cyclophanes.[34] These are well known for their applications like metal complexation and pyridoxal models.[35] Based on the substitution on pyridine ring there are mainly two types of pyridinophanes. 3,5-disubstituted pyridine moiety is used to assemble [n.n](3,5)pyridinophanes and 2,6-disubstituted pyridine units can form [n.n](2,6)pyridinophanes, where [n,n] represents there are 2 bridges with 'n' number of atoms in each (Figure 2).[36]

A **B**

Figure 2. Structures of syn-(2,6)pyridinophane **(A)** and anti-(3,5)pyridinophane **(B)** where (n = 1,2,3,..)

If we analyse the previous works on cyclophane and pyridinophane macrocyclic systems, plenty of research was already done on bridges containing donor atoms like -O-$SiMe_2$-O-, -CH_2-E-CH_2- (E = O, S, Se, NH), etc.[37] However, systems containing group 13 elements in the bridges have rarely been explored due to the lack of general synthetic strategy and the high sensitive nature of the suitable functional moiety of group 13 elements as compared to the synthesis of organic macrocycles. The presence of Lewis acidic centres or acceptor atoms in the bridges is important because of their potential to coordinate with donor guest molecules and also they can interact with the pyridine nitrogen which helps for the conformational rigidity of the macrocyclic system.[38,39]

In the previous attempts to assemble group 13 elements incorporated cyclophane or pyridinophane structures, Uhl and co-workers successfully synthesized cyclophanes containing aluminum in the bridges using hydroalumination reaction (Figure 3).[40]

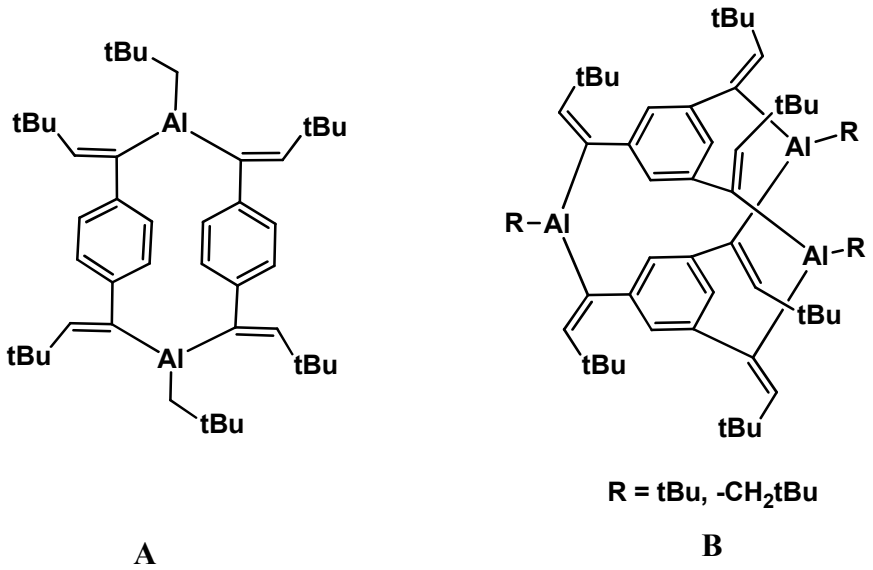


Figure 3. Structures of aluminum bridged (**A**) [3.3] and (**B**) [3.3.3] cyclophanes

In 2018, our group reported conformationally rigid novel tetraza-dibora[3.3](2,6)pyridinophanes and their aluminum analogues using bis(trimethylsilyl)-N,N′-2,6-diaminopyridine (bap) as precursor and it reacted with different alanes and chloro-boranes[38] (Figure 4).

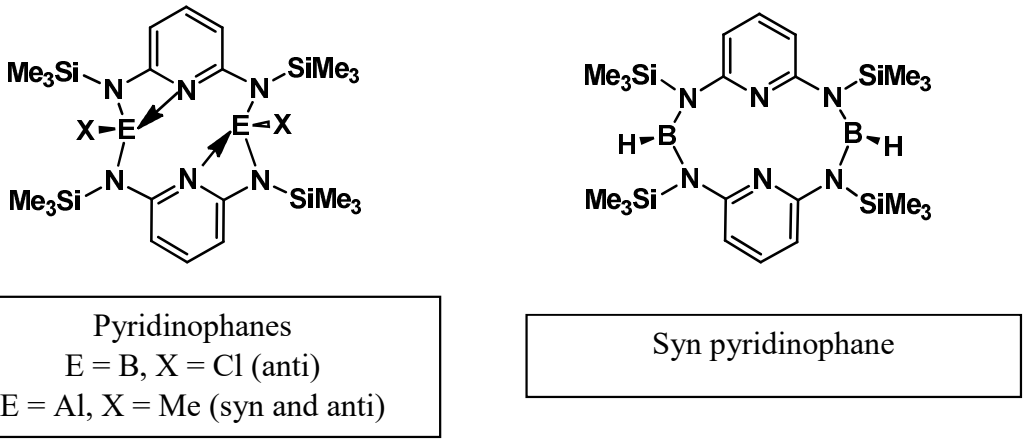


Figure 4. Tetraza-dibora[3.3](2,6)pyridinophane and its aluminum analogue.

In the recent work from our group, the first examples of organoaluminum bridged neutral and cationic bowl shaped pyridinophanes and an unprecedented bicyclic pyridinophane by varying the

relative stoichiometry of the building block bis(trimethylsilyl)-N,N′-2,6-diaminopyridine (bap) and AlH_3/$AlMe_3$ were reported[41] (see Figure 5 for the structures).

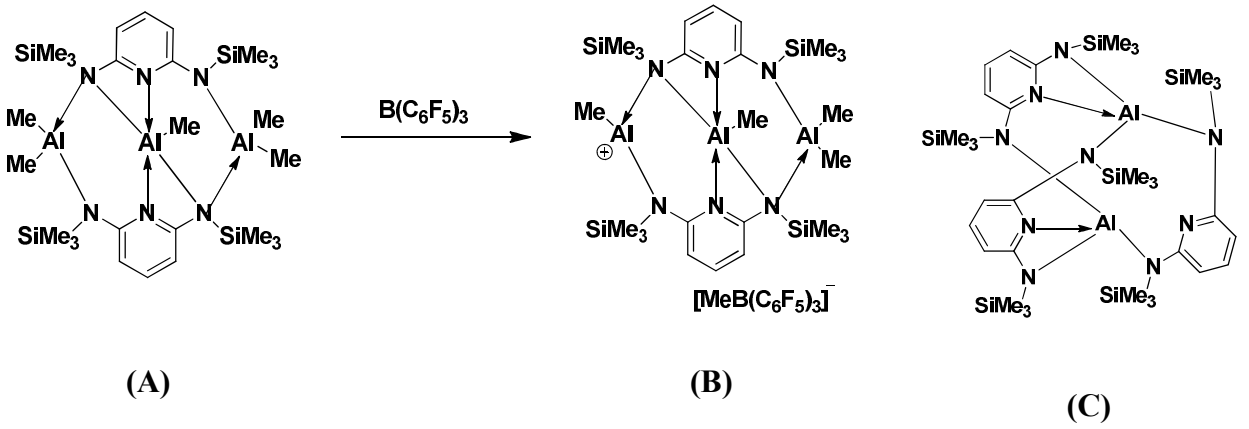
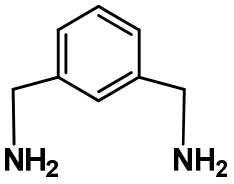
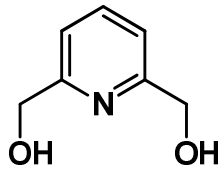


Figure 5. Organoaluminum bridged neutral (**A**) and cationic (**B**) bowl shaped pyridinophanes and aluminum containing bicyclic pyridinophane (**C**).

Motivated from these works and for continuation, we planned to synthesize macrocycles having bigger cavity size which will help in host encapsulation and may provide tunable conformation. In this work, I had used two building blocks, 1,3-benzinedimethanamine-N,N'-bis(trimethylsilyl) and 2,6-pyridinedimethanol to assemble aluminum or boron bridged macrocycles (Figure 6).



1, 3-benzinedimethanamine

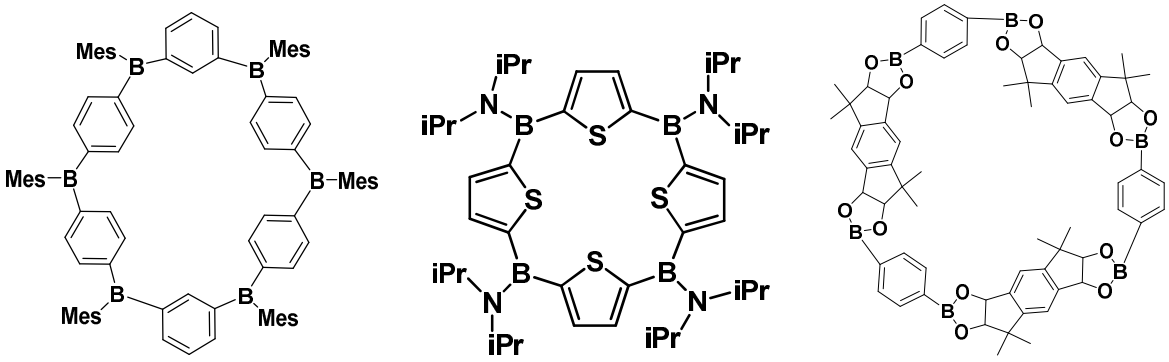


2,6-pyridinedimethanol

Figure 6: Building blocks used in this work to assemble new cyclophanes and pyridinophanes.

1.3. Boron containing macrocycles and anion coordination studies with tetraazadibora[3.3](2,6)pyridinophane

Organo boranes are highly sensitive to moisture and oxygen. The method of providing steric hindrance around tricoordinated boron can possibly help in the synthesis of air-stable boranes in which the empty p-orbital is sterically protected.[42,43] These organoboranes have vast applications in the fields like OLED, anion sensors, non-linear optics etc.[44] Figure 7 below shows some known examples of boron containing macrocyclic structures.[45,46]



Electron deficient hexabora-cyclophane

5,10,15,20-tetrabora-21,22,23,24-tetrathiaporphyrin

Boronic ester based macrocycle

Figure 7. Representative examples for some boron containing macrocyclic structures.

Due to the presence of an empty p_z orbital in sp^2 hybridized - trivalent B, dictating it strong Lewis acidity and high proclivity to co-ordinate with a Lewis base. Also nitrogen containing conjugated molecules are quintessential Lewis bases because of having a lone pair of electrons and highly dedicated towards trivalent boron. Molecules, that have B-N bond shows tunable optical properties and affluent redox properties because of strong electron deficient B-center, which produce intramolecular charge transfer (ICT) effect. Bazan et al. reported that electron deficient nature of N containing molecules can be amplified by coordinating it with boron containing Lewis acids which in turn causes the fractional transfer of charge from the Lewis base part to the Lewis acid.[47,48]

Generally, B-N bonds have high polarity and also help to fix the molecular conformation towards the coplanarity, due to this specificity, this bond is beneficial to the ordered molecular packing and charge transport. However, this B-N coordination bond is a chemical issue and effective to adjust the optoelectronic properties of nitrogen containing aromatic molecules.

Jakle and co-workers reported anion binding studies on electron deficient organo-boranes and it has shown that upon anion coordination the fluorescence activity of the organo-borane was quenched which indicate the potential in anion recognition and stimuli responsive optoelectronic materials[49] (see Figure 8 for the structure of the molecule).

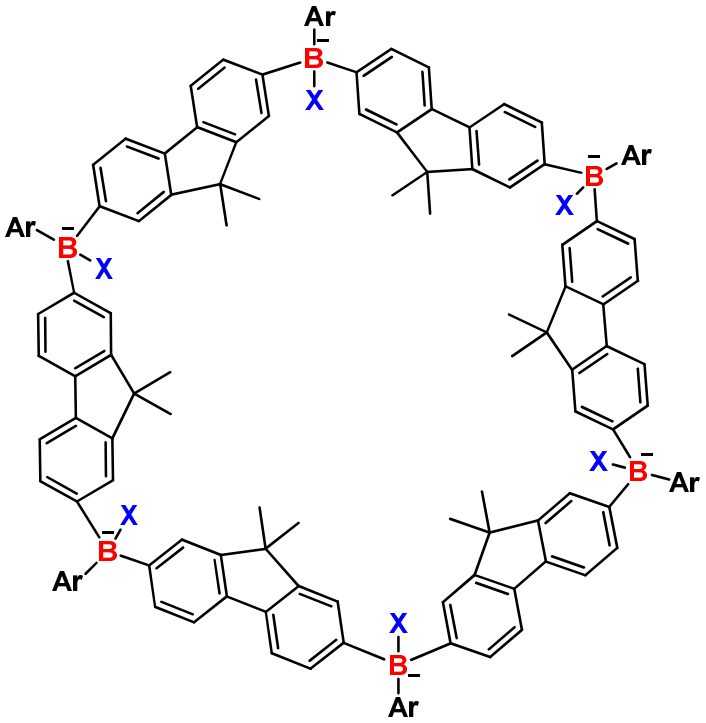


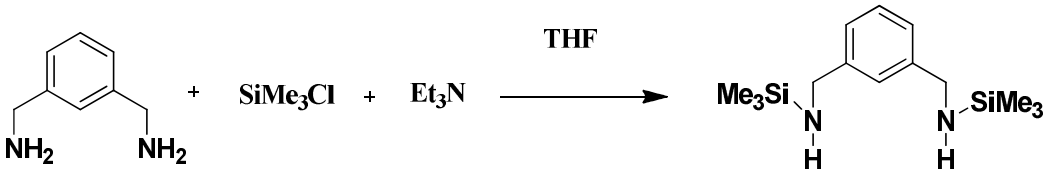
Figure 8. Boron Containing macrocycle for anion recognition

Diverse to this property, intramolecular B-N bond is very delicate and reversible, which can be easily defaced by nucleophile. So here we are trying to explore the chemistry and delicate nature of known pyridinophane molecules, containing B-N bond with nucleophile such as F^-, CN^- etc.

2. Results and discussion

2.1. Synthesis and characterization of 1,3-benzinedimethanamine-N,N'-bis(trimethylsilyl) (1)

The 1:2.2 reaction of *m*-xylylenediamine and Me_3SiCl was carried out at room temperature for 16 hours in the presence of triethylamine (5 equivalents) as a base to prepare the precursor 1,3-benzinedimethanamine-N,N'-bis(trimethylsilyl) **(1)** for further reactions (Scheme 1). Compound **1** was found to be a transparent liquid. Compound **1** was characterized using ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Four signals were found in the ^1H NMR spectrum of **1** at δ = 0.23 ppm (18H, s) for 2 trimethylsilyl groups, 0.87 ppm for –NH protons (2H), 4.06 ppm for protons of methylene groups attached to the benzene ring (4H) and at 7.4 ppm for phenyl protons (4H). In $^{13}C\{^1H\}$ NMR spectrum, the peak at δ = 0.20 ppm corresponds to the TMS group, 46.09 ppm represents N-CH_2, and the peaks at 125.17, 125.73, 128.30, 144.42 ppm correspond to the phenyl ring (Figure S1 and S2 in supporting information).

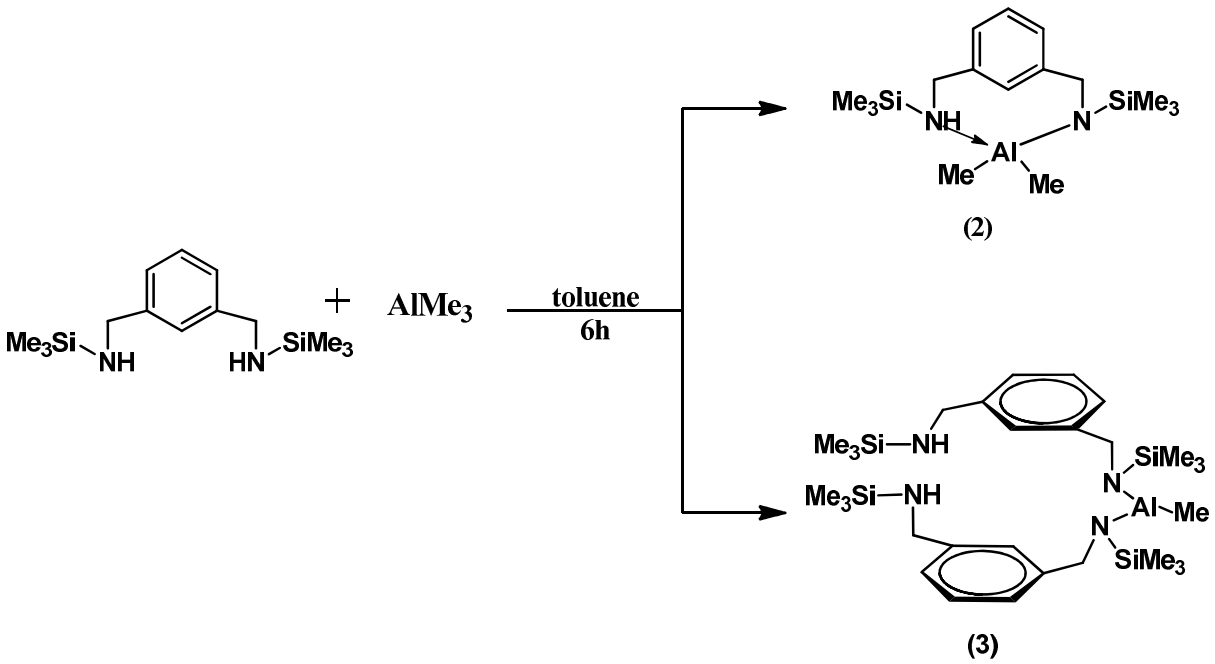


Scheme 1. Synthesis of 1,3-benzinedimethanamine-N,N'-bis(trimethylsilyl) **(1).**

2.2. Synthesis and characterization of [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$AlMe_2$ (2) and [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$_2AlMe$ (3)

The 1:1 reaction of 1,3-benzinedimethanamine-N,N'-bis(trimethylsilyl) **(1)** and $AlMe_3$ was carried out at room temperature and after 6 hours of reaction a light yellow colored viscous liquid product was obtained and after characterization by using HRMS and ^1H, $^{13}C\{^1H\}$ NMR spectroscopy we came to the conclusion of the presence of mononuclear complexes [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$AlMe_2$ **(2)** and [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$_2AlMe$ **(3)** in the mixture (Scheme 2). The HRMS spectrum showed a signal at *m/z* = 336.1982 (calcd. 336.1998 $[M+H]^+$) corresponding to **2**. Also, another signal in HRMS at *m/z* = 601.3586 (calcd. 601.3554 $[M+H]^+$) indicates the presence of another mononuclear complex **3** in the mixture (Figure S5 and Figure S6 in supporting information). In ^1H NMR spectrum, the signal at δ = 0.08 ppm represent TMS protons of **2** and the signal at 0.04 ppm represents TMS of **3**. Signal at -0.18 and -0.33 ppm

corresponding to the AlMe protons of **2** and **3**, respectively. Signals in 4.4-3.8 ppm chemical shift range are for methylene protons attached to the phenyl rings (Figure S3 in supporting information). In a similar 1:1 reaction of **1** and $AlMe_3$ which was extended for 24 h, we observed the same results as before.

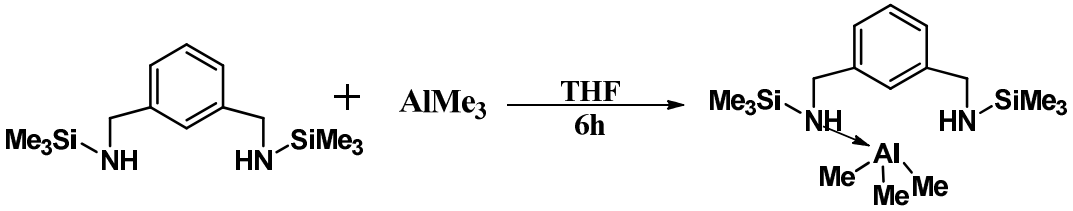


Scheme 2. Synthesis of [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$AlMe_2$ **(2)** and [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$_2$AlMe **(3)**

2.3. Synthesis and characterization of [1,3-($CH_2NHSiMe_3$)$_2C_6H_4$]$AlMe_3$ (4)

In anticipation to obtain the fully cyclized structure we have changed the relative proportions of **1** and $AlMe_3$ to 1:1.5 and we found that there is only a single peak for $AlMe_3$ as compared to two peaks in the 1:1 stoichiometric reaction (see the stacked ^{1}H NMR spectra Figure S8 in supporting information). Characterization using ^{1}H NMR spectroscopy revealed the formation of a mononuclear aluminum complex [1,3-($CH_2NHSiMe_3$)$_2C_6H_4$]$AlMe_3$ **(4)**. In ^{1}H NMR spectrum, the signal at δ = 0.06 ppm represent TMS protons and the signal at -0.45 ppm corresponds to the $AlMe_3$ protons. Signal at 3.35 and 1.02 ppm indicates the THF in reaction mixture and the signal

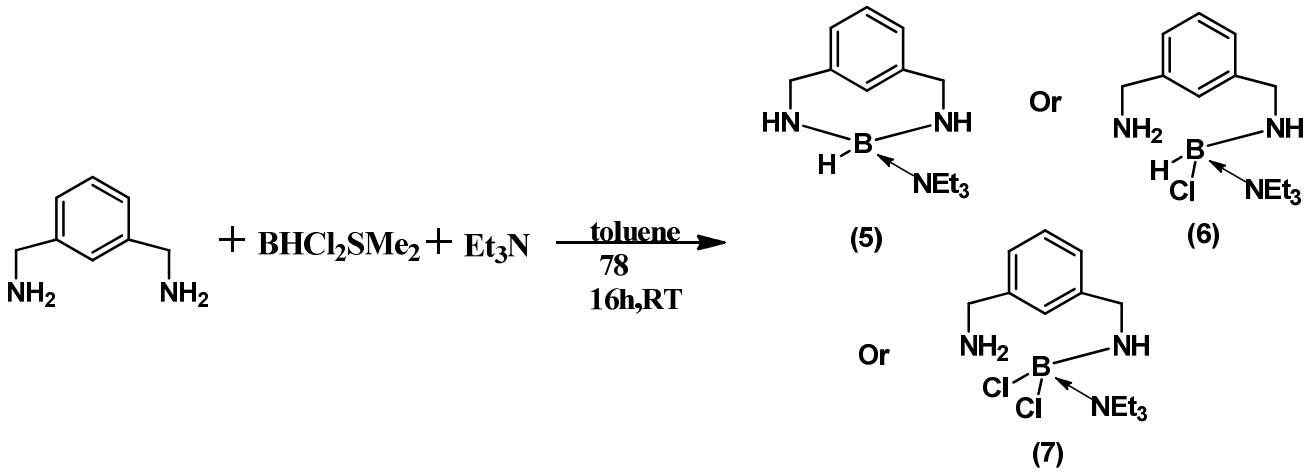
at 3.83 ppm is for the methyl protons attached to the phenyl ring (Figure S7 in supporting information).



Scheme 3. Synthesis of $[1,3\text{-}(CH_2NHSiMe_3)_2C_6H_4]AlMe_3$ **(4)**

2.4. Synthesis and characterization of $[1,3\text{-}(CH_2NH)_2C_6H_4]BHNEt_3$ (5), $[1\text{-}(CH_2NH_2)\text{-}3\text{-}(CH_2NH)C_6H_4]BHClNEt_3$ (6) and $[1\text{-}(CH_2NH_2)\text{-}3\text{-}(CH_2NH)C_6H_4]BCl_2NEt_3$ (7)

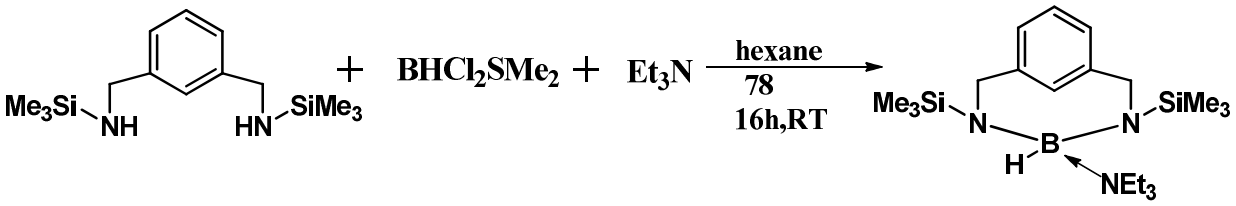
To see the coordination of boron with the linker 1,3-benzenedimethanamine we have carried out a stoichiometric reaction with $BHCl_2SMe_2$ in the presence of triethylamine (3 equivalent) for 16 hours. Characterization using ^1H, ^{11}B NMR spectroscopy and HRMS showed the formation of mixture of mononuclear boron complexes. ^1H NMR was not conclusive, but multiple doublet and singlet in the ^{11}B NMR indicated the formation of different complexes containing boron (Figure S9 in supporting information).



Scheme 4. Synthesis of $[1,3\text{-}(CH_2NH)_2C_6H_4]BHNEt_3$ **(5)**, $[1\text{-}(CH_2NH_2)\text{-}3\text{-}(CH_2NH)C_6H_4]BHClNEt_3$ **(6)** and $[1\text{-}(CH_2NH_2)\text{-}3\text{-}(CH_2NH)C_6H_4]BCl_2NEt_3$ **(7)**

2.5. Synthesis and characterization of [1,3-($CH_2SiMe_3N)_2C_6H_4$]$BHNEt_3$ (8)

In order to have a better control for the reaction discussed above for the synthesis of **5-7**, we made attempts to perform silylation of 1,3-benzenedimethanamine and its subsequent reaction with $BHCl_2SMe_2$. Therefore, we have tried a 1:1 reaction of disilylated 1,3-benzinedimethanamine **(1)** with $BHCl_2SMe_2$ at room temperature in the presence of triethylamine (3 equivalent) for 16 hours. The final sticky thick transparent liquid was characterized using ^1H, ^{11}B NMR spectroscopy and we concluded the formation of a mononuclear complex [1,3-($CH_2SiMe_3N)_2C_6H_4$]$BHNEt_3$ **(8)**.



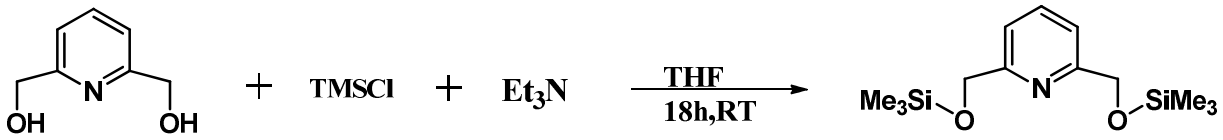
Scheme 5. Synthesis of [1,3-($CH_2SiMe_3N)_2C_6H_4$]$BHNEt_3$ **(8)**

^1H NMR spectrum of **8** showed one singlet at 0.16 ppm which represents the $SiMe_3$ protons, signal at 3.99 ppm represent the methylene protons attached to the phenyl rings. In ^{11}B NMR the doublet at δ = 3.65-4.83 ($^1J_{11B\text{-}1H}$ = 151 Hz) indicate the tetra-coordination of boron (Figure S10 and Figure S11 in supporting information).

2.6. Synthesis and characterization of [2,6-(CH_2-O-$SiMe_3)_2C_5H_3N$] (9)

The major difficulty faced during the reactions using 2,6-pyridinedimethanol was its partial solubility in most of the common solvents (THF, toluene, hexane) that we have used, even the products formed from the reaction between 2,6-pyridinedimethanol and some boron and aluminum compounds had low solubility in benzene and the presence of highly polar –OH moiety is accounted for the low solubility of 2,6-pyridinedimethanol.

We planned to silylate 2,6-pyridinedimethanol and use it for the further reaction. Silylation of 2,6-pyridine dimethanol was done by the 1:1 reaction of 2,6-pyridine dimethanol and trimethyl silyl chloride in the presence of excess of triethyl amine (5 equivalent) for 18 hours.

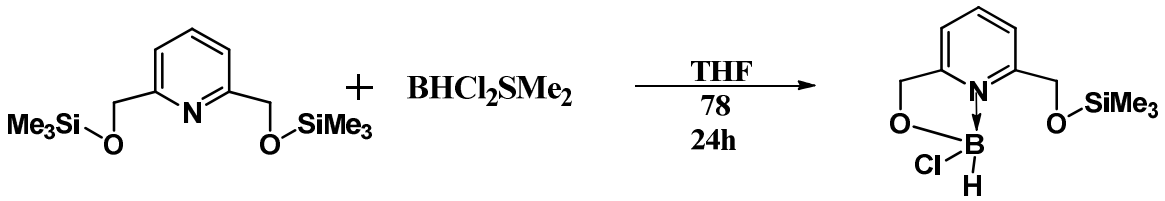


Scheme 6. Synthesis of [2,6-(CH_2-O-$SiMe_3$)$_2C_5H_3N$] **(9)**

^{1}H NMR spectrum of **9** showed one singlet at 0.16 ppm which represents the $SiMe_3$ protons, signal at 4.76 ppm represent the methylene protons attached to the phenyl rings and the signals at 7.35 and 7.69 represents the aromatic protons (Figure S12 in supporting information).

2.7. Synthesis and characterization of [2-(CH_2-O-BHCl)-6-(CH_2-O-$SiMe_3$)C_5H_3N] (10)

Stoichiometric reaction of di-silylated 2,6-pyridinedimethanol and dichloroborane dimethyl sulfide was carried out at room temperature for 24 hours to obtain white powdered product. Characterization using ^{1}H and ^{11}B NMR spectroscopy indicated minor amount of unreacted initial compound and the formation of mononuclear complex in major quantity.



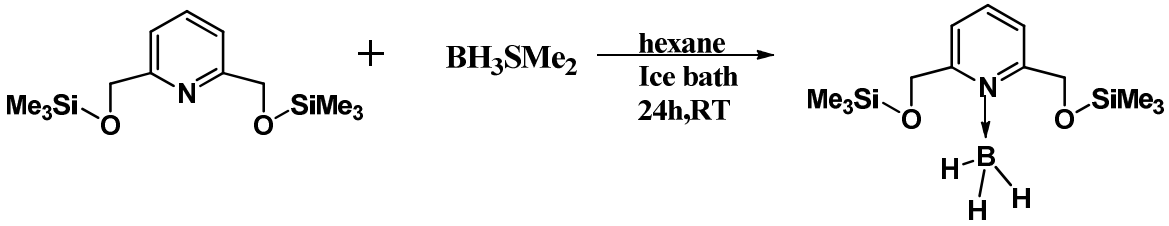
Scheme 7. Synthesis of [2-(CH_2-O-BHCl)-6-(CH_2-O-$SiMe_3$)C_5H_3N] **(10)**

^{1}H NMR spectrum of **10** showed one doublet at 0.19 ppm which represents the $SiMe_3$ protons, signal at 5.23 ppm and 5.09 ppm represent the methylene protons attached to the phenyl rings and the signals at 7.35 and 7.40 represents the aromatic protons. In ^{11}B NMR the singlet at δ = 8.43 ppm indicate the tetra-coordinated boron (Figure S13 and Figure S14 in supporting information).

2.8. Synthesis and characterization of [2,6-(CH_2O-$SiMe_3$)$_2C_5H_3N$]BH_3 (11)

The 1:2 reaction of di-silylated 2,6-pyridinedimethanol and borane dimethyl sulfide was carried out with an anticipation of BH_3 coordination with oxygen moiety and can be used for the further reaction to cyclize it. However the product characterization using ^{1}H NMR and ^{11}B NMR spectroscopy revealed the coordination of BH_3 with pyridine nitrogen.

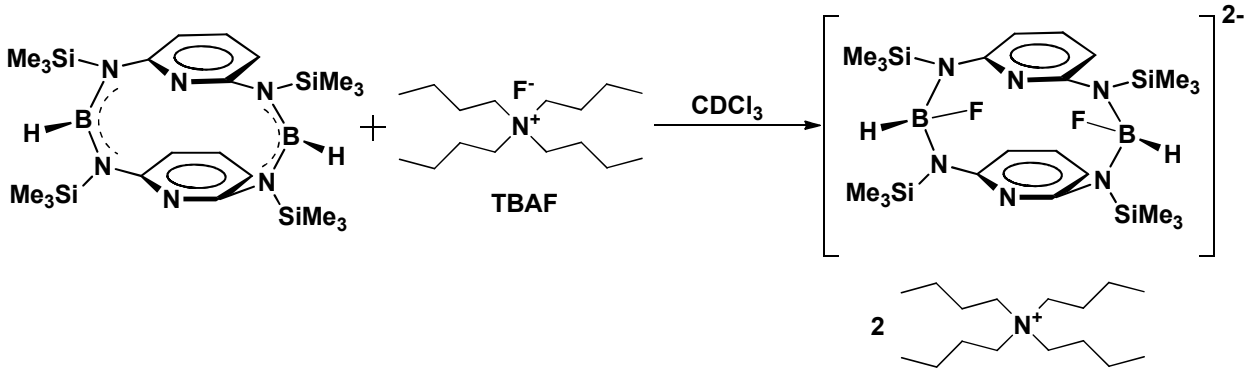
^{1}H NMR spectrum of **11** showed one sharp signal at δ = 0.07 ppm for TMS protons and the broad signal at 2.53 ppm corresponds to the B-H protons and the methylene protons attached to the phenyl ring resonates at 5.18 ppm. In ^{11}B NMR the singlet at δ = -19.83 ppm indicate the tetra-coordinated boron (Figure S15 and Figure S16 in supporting information).



Scheme 8. Synthesis of [2,6-(CH_2O-$SiMe_3$)$_2$$C_5H_3N$]$BH_3$ **(11)**

2.9. Synthesis and characterization of fluoride complex of tetraazadibora[3.3](2,6)pyridinophane (12)

Tetraazadibora[3.3](2,6)pyridinophane was synthesized using the reported procedure.[38] The 1:2 reaction of tetrazadibora[3.3](2,6)pyridinophane and tetrabutyl-ammonium fluoride (TBAF) was carried out at room temperature for 5-6 hours in $CDCl_3$ as the solvent.



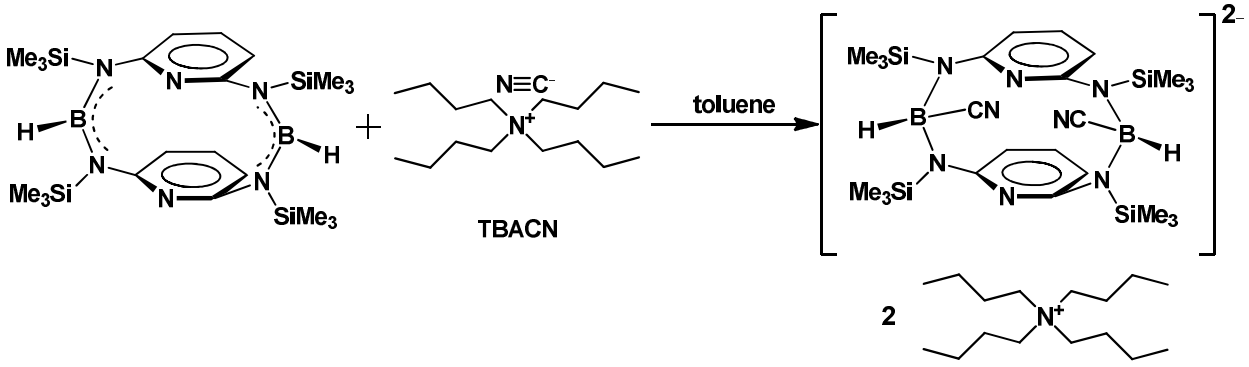
Scheme 9. Synthesis of [2,6-(Me_3SiN)$_2$$C_5H_3N$(BHF)]$_2^{2-}$ 2 $^{n}Bu_4N^{+}$**(12)**

^{1}H NMR spectrum of **12** showed one sharp signal at δ = 0.01 ppm for TMS protons and the aromatic signals at 7.07 and 5.80 ppm (Figure S17 in supporting information). ^{19}F NMR spectrum showed one equal intensity quartet signal from -144.56 to -144.69 ppm which represent the BF coupling ($^{1}J_{F\text{-}B}$ = 15 Hz) and a sharp signal at -128.69 ppm corresponding to the unreacted

TBAF (Figure S18 in supporting information). ^{11}B NMR spectrum showed one quartet signal from 0.46 to 0.86 ppm ($^{1}J_{B-F}$ = 16 Hz) (Figure S19 in supporting information). The characterization using NMR data was not conclusive and the ^{11}B and ^{19}F NMR spectra indicate the presence of BF_3 moiety. Crystals obtained from the reaction were not of quality suitable for single crystal X-ray characterization and further studies are required on the reaction to conclude the output of the reaction in an unambiguous manner.

2.10. Synthesis and characterization of cyano complex of tetraazadibora[3.3](2,6)pyridinophane (13)

Tetraazadibora[3.3](2,6)pyridinophane has been synthesized using the reported procedure.[38] The 1:2 reaction of tetrazadibora[3.3](2,6)pyridinophane and tetrabutyl-ammonium cyanide (TBACN) was carried out at room temperature for 5-6 hours in toluene as the solvent.



Scheme 10. Synthesis of $[2,6\text{-}(Me_3SiN)_2C_5H_3N(BHCN)]_2^{2-}$ 2 $^{n}Bu_4N^{+}$ **(13)**

^{1}H NMR spectrum of **13** showed one sharp signal at δ = 0.08 ppm for TMS protons and the aromatic signals at 7.13 and 6.05 ppm (Figure S20 in supporting information). In the ^{11}B NMR spectra one broad signal at -27 ppm represent the BCN coordination (Figure S22 in supporting information). In $^{13}C\{^{1}H\}$ NMR spectrum the sharp 'CN' signal which comes in the $^{13}C\{^{1}H\}$ NMR spectrum of TBACN at 162 ppm shifted to the range of 125-140 ppm (Figure S21 in supporting information). IR spectrum showed characteristic B-CN stretch at 2275 cm^{-1} (Figure

S23 in supporting information). All these spectroscopic data confirming the CN coordination with the electron deficient boron in the pyridinophane.

3. Conclusion

The present thesis contains work carried out with 2,6-pyridinedimethanol and 1,3-benzenedimethanamine moieties with aluminum and boron containing compounds in anticipation of obtaining macrocyclic compounds. Repeated attempts were done by varying the stoichiometry of the precursors, silylation of starting compounds and varying the reaction conditions to cyclize the moiety and the characterization using ^{1}H, ^{11}B, HRMS etc. indicated the formations of various types of mononuclear or dinuclear complexes. Unlike the similar previous reports, reactions with 1,3-benzenedimethanamine moiety under reflux conditions was not successful since the compound was getting decomposed. Further manipulations and change of reaction conditions are required for the successful completion of these reactions and to cyclize the moiety. The studies carried out with anions and pyridinophane indicated the coordination of anions with the electron deficient boron centers which suggest the potential for various applications in anion recognition and stimuli-responsive materials. However the characterization studies were not conclusive and further trials need to be done.

4. Experimental section

4.1. General procedure

All synthesis and handling of reagents were carried out under an inert atmosphere of nitrogen using standard Schlenk line techniques or a glove box where O_2 and H_2O levels were maintained below 1 ppm. All the glassware were dried at 150 °C for at least 12 h in an oven and assembled hot and cooled in vacuum prior to use. Solvents were purified by MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich Chemical and used without further purification.

4.2. Synthesis of 1,3-benzinedimethanamine-N,N'-bis(trimethylsilyl) (1)

A solution of *m*-xylylene diamine (1,3-benzenedimethanamine) (5.0 g, 36.7 mmol) in 30 mL of THF and Et_3N (25.6 mL, 183.5 mmol) was taken in a flask and TMSCl (10.3 mL, 80.7 mmol) was added dropwise into it under stirring. Mixture was stirred overnight at room temperature. Volatiles were removed under vacuum. White precipitate formed was filtered and a colorless liquid was obtained. Yield: 4.63 g (45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s, 18H, TMS), 0.79 (s, 2H, NH), 3.98 (s, 4H, -CH_2-) ppm. $^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ = 0.20, 46.09, 125.17, 125.73, 128.30, 144.42) ppm.

4.3. Synthesis of [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$AlMe_2$ (2) & [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$_2AlMe$ (3)

To a solution of **1** (1.5 g, 5.3 mmol), $AlMe_3$ (2.7 mL, 5.3 mmol, 2 M in toluene) was added at -78 °C and the mixture kept under stirring for 20 minutes at the same temperature and was subsequently allowed to warm to 0 °C and kept it in the ice bath for next 15 minutes. Mixture then warmed to room temperature and continued the reaction for 6 hours. Volatiles removed under vacuum and the product was washed with hexane. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.08 (s, 18 H, TMS of **2**), 0.04 (s, 36 H, TMS of **3**), 4.47-3.81 (12H, N-Me of **2** & **3**), 7.15 (12H, Ph). HRMS (ESI): *m/z* calculated for $C_{16}H_{32}AlN_2Si_2$:$[M+H]^+$ 336.1998; Found 336.1982. *m/z* calculated for $C_{29}H_{57}AlN_4Si_4$: $[M+H]^+$ 601.3554; found 601.3586.

4.4. Synthesis of [1,3-$(CH_2NHSiMe_3)_2C_6H_4$]$AlMe_3$ (4)

A solution of **1** (1.9 g, 7 mmol) was taken in THF and $AlMe_3$ (5.2 mL, 10.5 mmol, 2M in toluene) was added into it at -78 °C and the mixture kept under stirring for 20 minutes at the same temperature and was subsequently allowed to warm to 0 °C slowly and kept in ice bath for another 45 minutes and let it warm to RT. Reaction continued at RT for 6 hours and volatiles were removed to get a light yellow liquid product **4**. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.06 (s, 18 H, TMS), -0.45 (s, 9 H, AlMe), 3.83 (4H, N-Me), 3.35 (broad s, 2H, NH) 7.25-7.09 (4H, Ph).

4.5. Synthesis of [1,3-$(CH_2NH)_2C_6H_4$]$BHNEt_3$ (5), [1-(CH_2NH_2)-3-$(CH_2NH)C_6H_4$]$BHClNEt_3$ (6) and [1-(CH_2NH_2)-3-$(CH_2NH)C_6H_4$]BCl_2NEt_3 (7)

To a solution of 1,3-benzenedimethanamine (0.5 g, 1.8 mmol) in toluene and triethylamine (0.7 mL, 5.4 mmol), $BHCl_2SMe_2$ (0.2 mL, 1.8 mmol) was added dropwise at -78 °C under stirring. After 15-20 min let the mixture warm to RT and continued stirring at RT for 16h. Filtered the salts to get a colorless liquid product. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 1.51-2.74 (d), 3.65-4.83 (d), 7.41 (s) ppm.

4.6. Synthesis of [1,3-$(CH_2SiMe_3N)_2C_6H_4$]$BHNEt_3$ (8)

To a solution of **1** (1.1 g, 4 mmol) in hexane and triethylamine (1.7 mL, 12 mmol), $BHCl_2SMe_2$ (0.5 mL, 4 mmol) was added dropwise at -78 °C under stirring. After 15-20 min let the mixture warm to RT and continued stirring at RT for 16 h. Filtered the salts at the end of the reaction to get a sticky thick liquid product. And crystallized it in THF at -10 °C to afford colorless crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 18 H, TMS), 3.99-4.26 (4H, N-Me), 3.23 & 1.37 (-NEt_3), 7.27 (4H, Ph). ^{11}B NMR (128 MHz, $CDCl_3$): δ = 3.65-4.83 (d, $^1J_{11B\text{-}1H}$ = 151 Hz) ppm.

4.7. Synthesis of [2,6-(CH_2-O-$SiMe_3$)$_2$$C_5H_3N$] (9)

Pyridinedimethanol (1.0 g, 7.2 mmol) and Et_3N (5 mL, 36 mmol) in THF was taken in one flask. TMSCl (2.0 mL, 15.8 mmol) was added dropwise into the mixture at 0 °C under stirring. After 15 minutes the mixture was allowed to warm to room temperature and reaction continued for 18 h. Salt were filtered off and the filtrate dried under vacuum to obtain light yellow colored liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 18H, TMS), 4.76 (s, 4H, -CH_2-O), 7.35 (d, 2H, *m*Ar-H), 7.69 (t, 1H, *p*Ar-H) ppm.

4.8. Synthesis of [2-(CH_2-O-BHCl)-6-(CH_2-O-$SiMe_3$)C_5H_3N] (10)

The di-silylated pyridinedimethanol (0.2 g, 0.7 mmol) in THF was taken in one flask and $BHCl_2SMe_2$ (0.1 mL, 0.7 mmol) was added dropwise at -78 °C under stirring. Reaction continued at room temperature for 24 h and filtered the final mixture and dried under vacuum to obtain the white powdery material. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 9H, TMS), 5.23-5.09 (4H, -CH_2-O), 7.40 (d, 2H, *m*Ar-H), 7.91 (t, 1H, *p*Ar-H) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 8.43 (s) ppm.

4.9. Synthesis of [2,6-(CH_2O-$SiMe_3$)$_2$$C_5H_3N$]$BH_3$ (11)

The di-silylated pyridinedimethanol (2.6 g, 9.1 mmol) in hexane was taken in one flask and BH_3SMe_2 (1.72 mL, 18.2 mmol) was added dropwise at 0 °C under stirring. Continued the reaction for 20h. Filtered the mixture and dried it to obtain thick jelly liquid material. (Alternatively, the reaction was carried out in toluene under heating condition and the spectroscopic characterization of the product was identical in both the cases). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.07 (s, 18H, TMS), 2.53 (broad, 3H, -BH), 5.18 (s, 4H, -CH_2-O), 7.62 (d, 2H, *m*Ar-H), 7.36 (t, 1H, *p*Ar-H) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 19.83 (s) ppm.

4.10. Synthesis of $[2,6\text{-}(Me_3SiN)_2C_5H_3N(BHF)]_2^{2-}$ 2 $^nBu_4N^+$ (12)

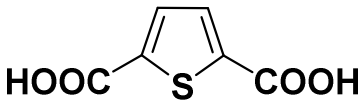
Crystals of tetraazadibora[3.3](2,6)pyridinophane (40.0 mg, 0.076 mmol) in $CDCl_3$ were taken in an NMR tube. Tetrabutyl-ammonium fluoride (39.7 mg, 0.152 mmol) was added into it from glow box and kept it at RT for 5-6 hour. ^1H NMR (400MHz, $CDCl_3$): δ = 0.01 (s, 36 H, TMS), 3.20, 1.57, 1.37, 0.93 (TBA protons), 7.07 (2H, Ph), 5.80 (4H, Ph) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -144.56—144.69 (q, $^1J_{F\text{-}B}$ = 15 Hz) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 0.46-0.86 (q, $^1J_{B\text{-}F}$ = 16 Hz) ppm.

4.11. Synthesis of $[2,6\text{-}(Me_3SiN)_2C_5H_3N(BHCN)]_2^{2-}$ 2 $^nBu_4N^+$ (13)

Crystals of tetraazadibora[3.3](2,6)pyridinophane (0.27 g, 0.5 mmol) in toluene was taken in one flask. Tetrabutyl-ammonium cyanide (0.27 mg, 1 mmol) was added into it from glow box and kept under stirring at RT for 5-6 h. Dried the solvent to obtain yellow sticky material. IR (KBr, ῡ cm^{-1}) 2923 and 2861 (nujol), 2275 (B-CN), 1455, 1375, 1265, 1035, 795. ^1H NMR (400MHz, $CDCl_3$): δ = 0.08 (s, 18 H, TMS), 3.16, 1.55, 1.34, 0.83 (TBA protons), 7.13 (1H, Ph), 6.05 (2H, Ph) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = -27.02 (broad) ppm.

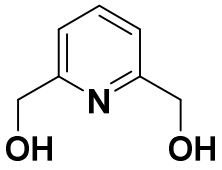
5. Future directions

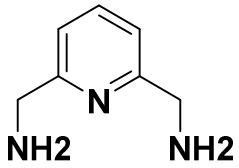
1. Apart from pyridine and benzene containing building blocks, I am planning to explore 2,5-disubstituted thiophenes for reaction with different alanes and boranes.



Reducing thiophene dicarboxylic acid into its diamine derivative and followed by silylation and treatment with alanes and boranes may help in the formation of unprecedented B/Al bridged macrocycles.

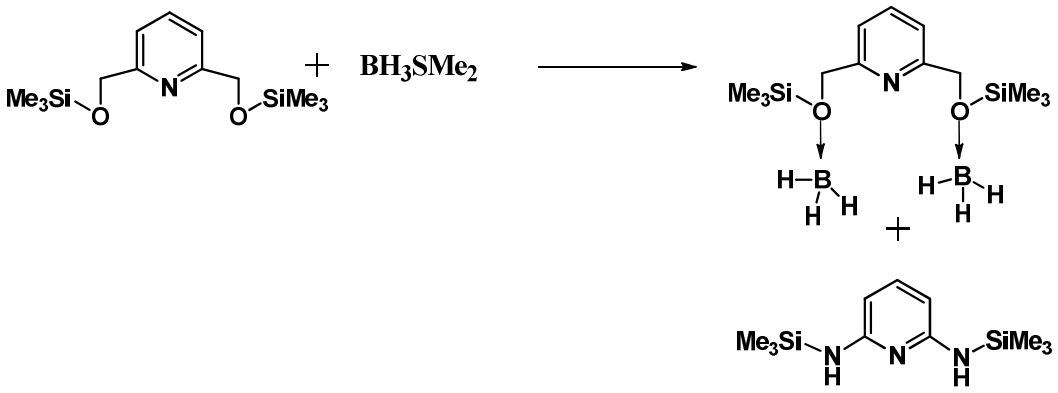
2. Since the solubility of 2,6-pyridinedimethanol is low, converting it into 2,6-pyridinedimethanamine followed by silylation would help to improve the solubility.





3. Silylated 2,6-pyridinedimethanol can be used for various cross reactions with 2,6-pyridine diamine or 1,3-benzenedimethanamine in presence of different boranes.

   If we are able to coordinate BH_3 with the oxygen moiety of silylated pyridine dimethanol by varying the reaction conditions, then its further reactions with silylated diamino pyridine may help in cyclisation.



4. Other than boron compounds we can try reactions of **9** (see Section 2.6) with different aluminum compounds. Also, we can extend the anion coordination studies to Al containing pyridinophanes as well.

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Supporting Information

Heteronuclear NMR spectra (^{1}H, $^{13}C\{^{1}H\}$, ^{11}B, ^{19}F) and HRMS spectra of compounds reported in this project work

Contents

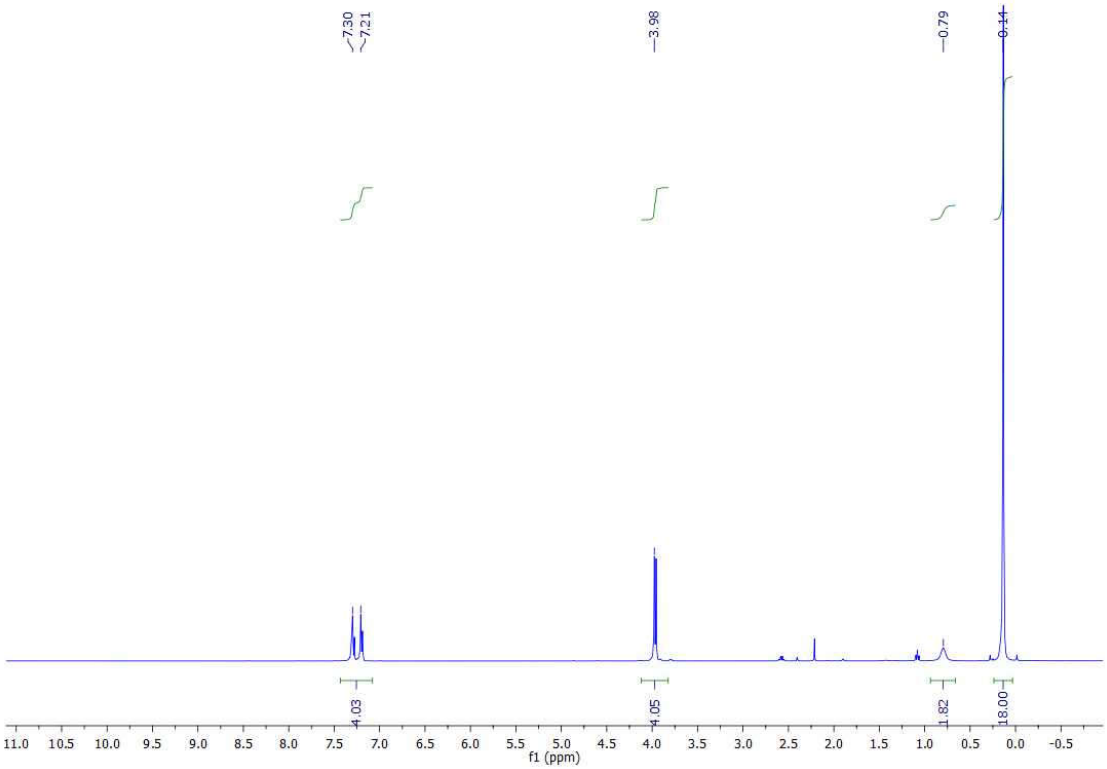

Figure S1. ^{1}H NMR spectrum (400MHz, $CDCl_3$) of benzinedimethanamine,N,N'-bis(trimethylsilyl) **(1)**

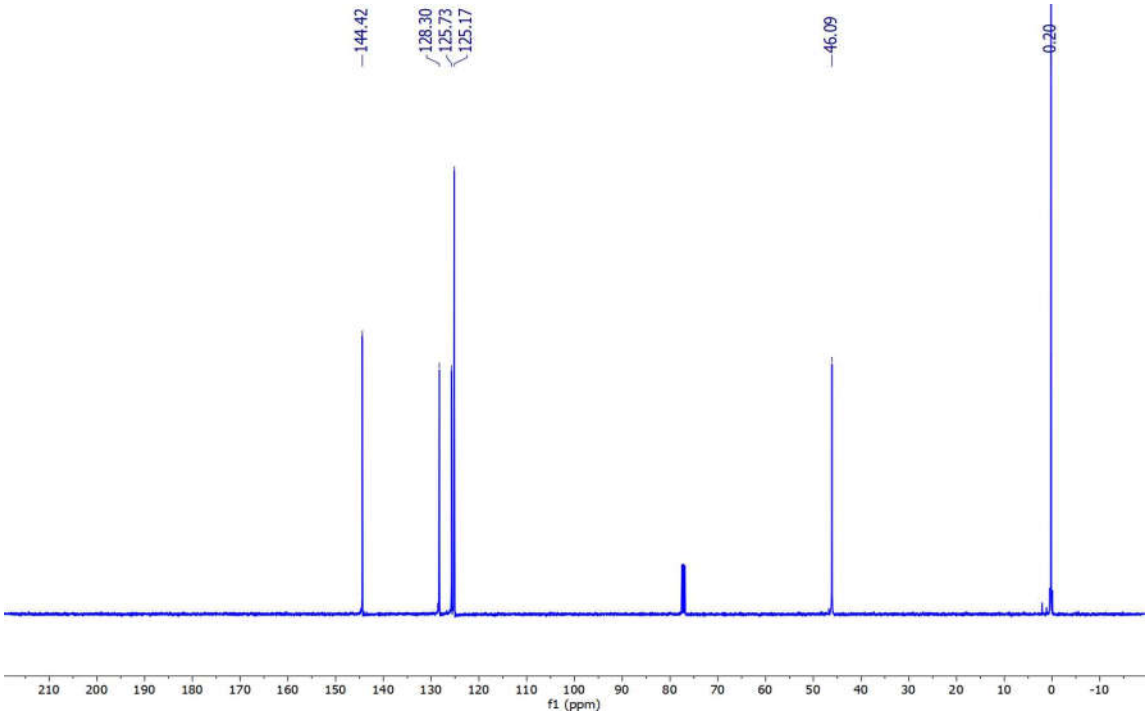

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of benzinedimethanamine,N,N'-bis(trimethylsilyl) **(1)**

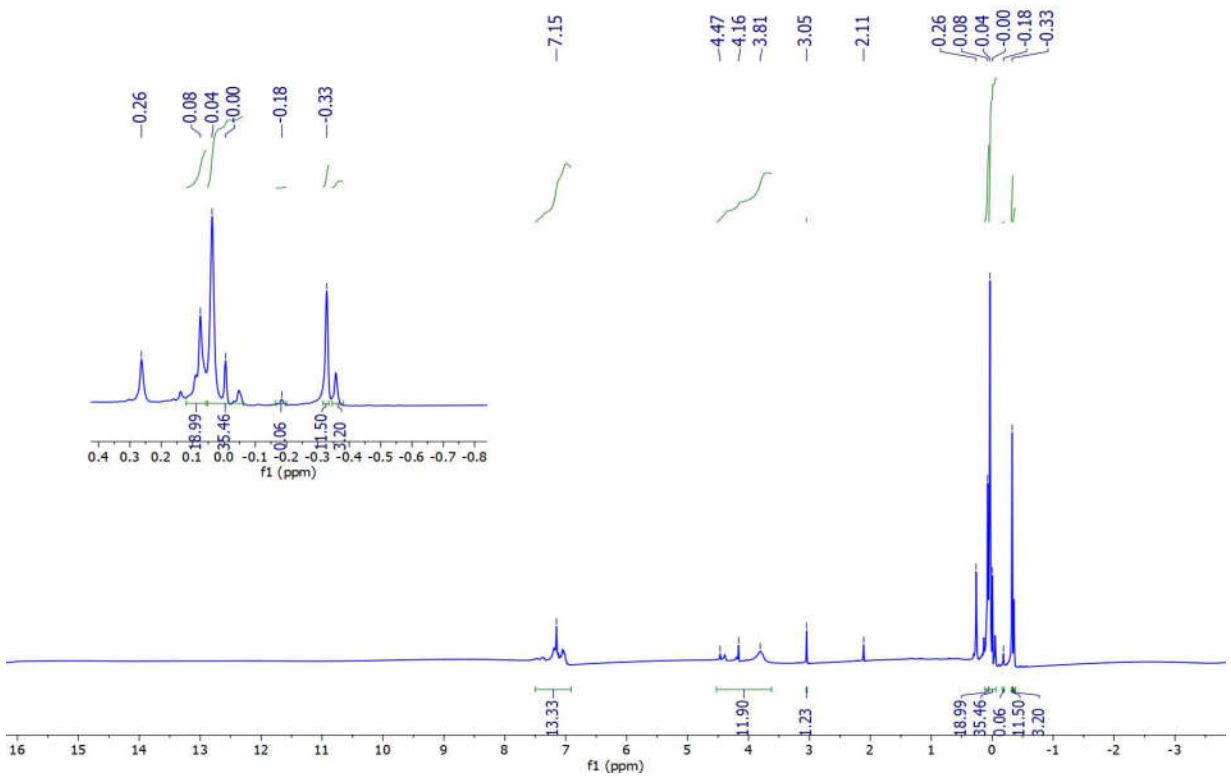

Figure S3. ^{1}H NMR spectrum (400MHz, C_6D_6) of [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$AlMe_2$ **(2)**& [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$_2$AlMe **(3)**

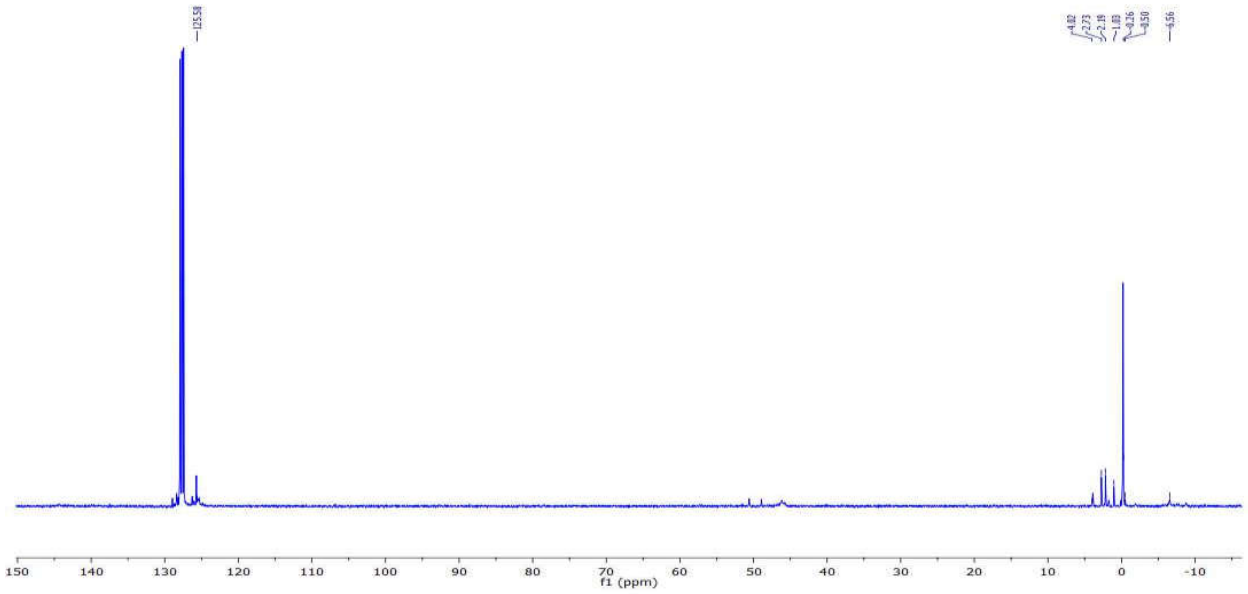

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, C_6D_6) of [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$AlMe_2$ **(2)**& [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$_2$AlMe **(3)**

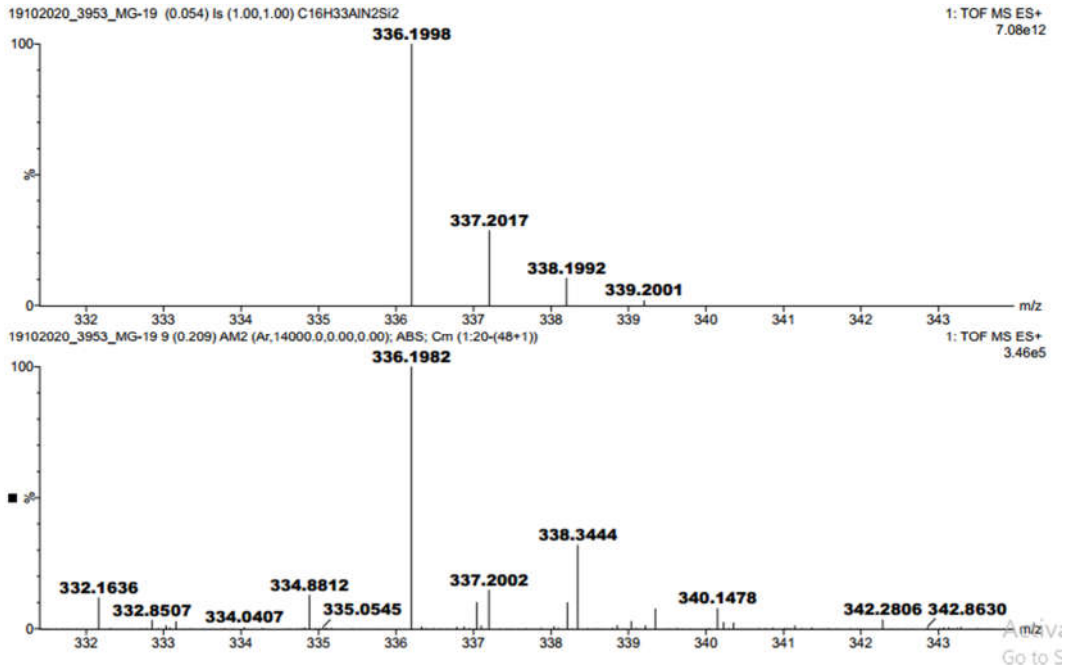

Figure S5. HRMS spectrum [calculated (top) and observed (bottom)] of [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$AlMe_2$ **(2)**

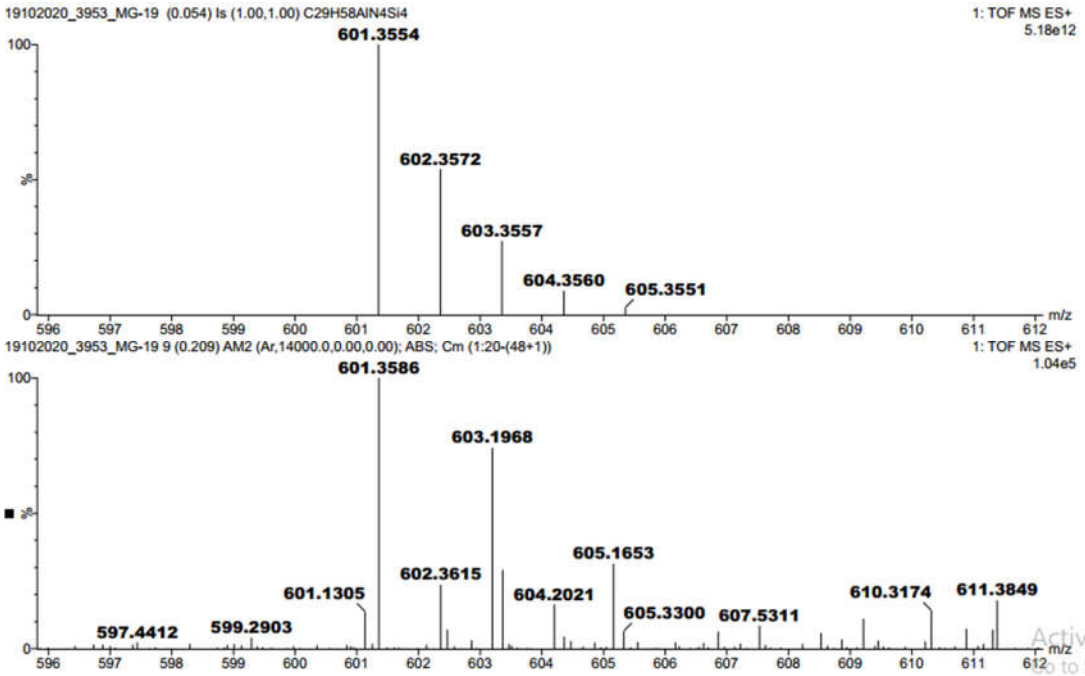

Figure S6. HRMS spectrum [calculated (top) and observed (bottom)] of [1-(CH_2NSiMe_3)-5-($CH_2NHSiMe_3$)-C_6H_4]$_2AlMe$ **(3)**

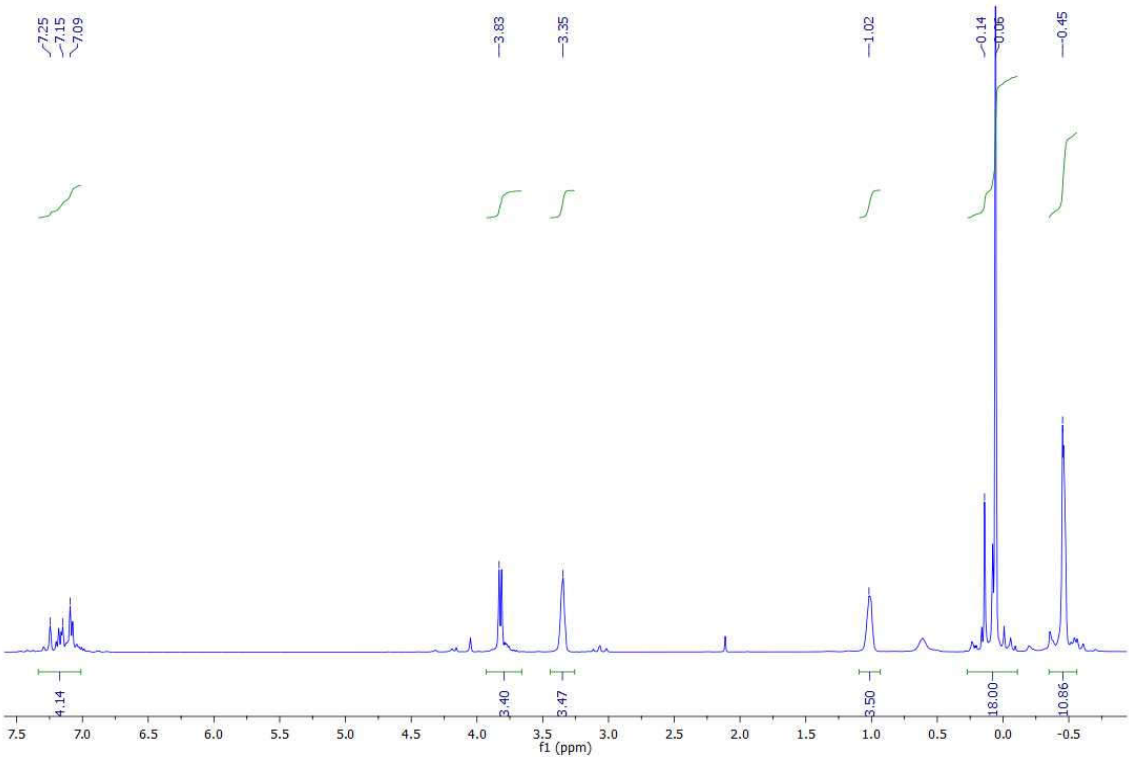

Figure S7. ^{1}H NMR spectrum (400MH, C_6D_6) of [1,3-$(CH_2NHSiMe_3)_2C_6H_4$]$AlMe_3$ **(4)**

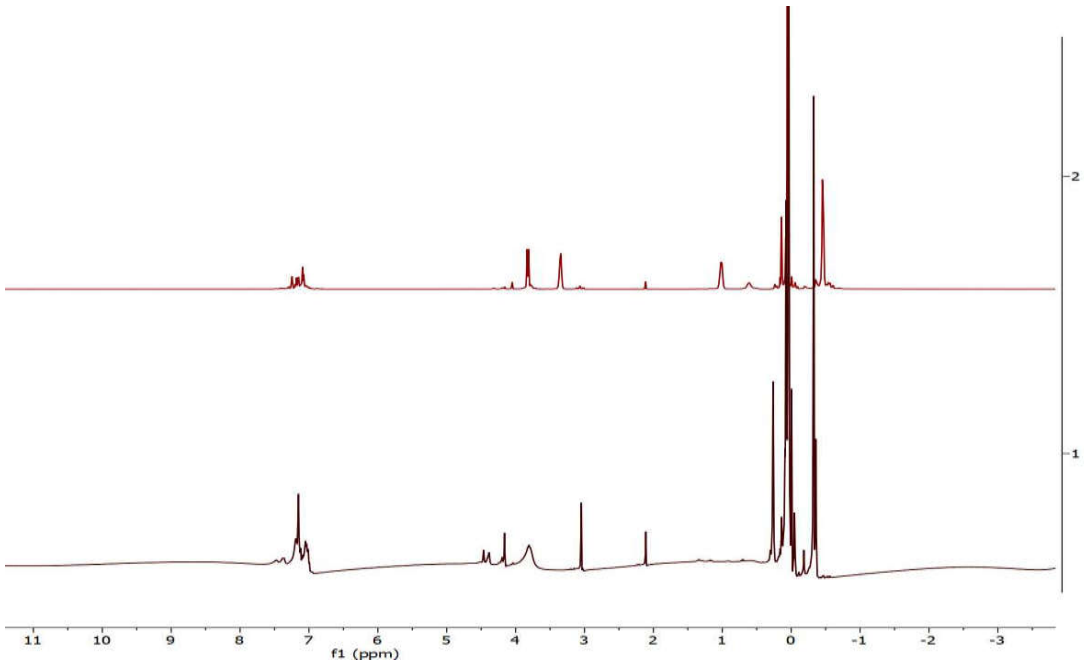

Figure S8. Stacked ^{1}H NMR spectrum (400MH, C_6D_6) of stoichiometric reactions of **(1)** and $AlMe_3$: 1:1.5 (top) and 1:1 (bottom)

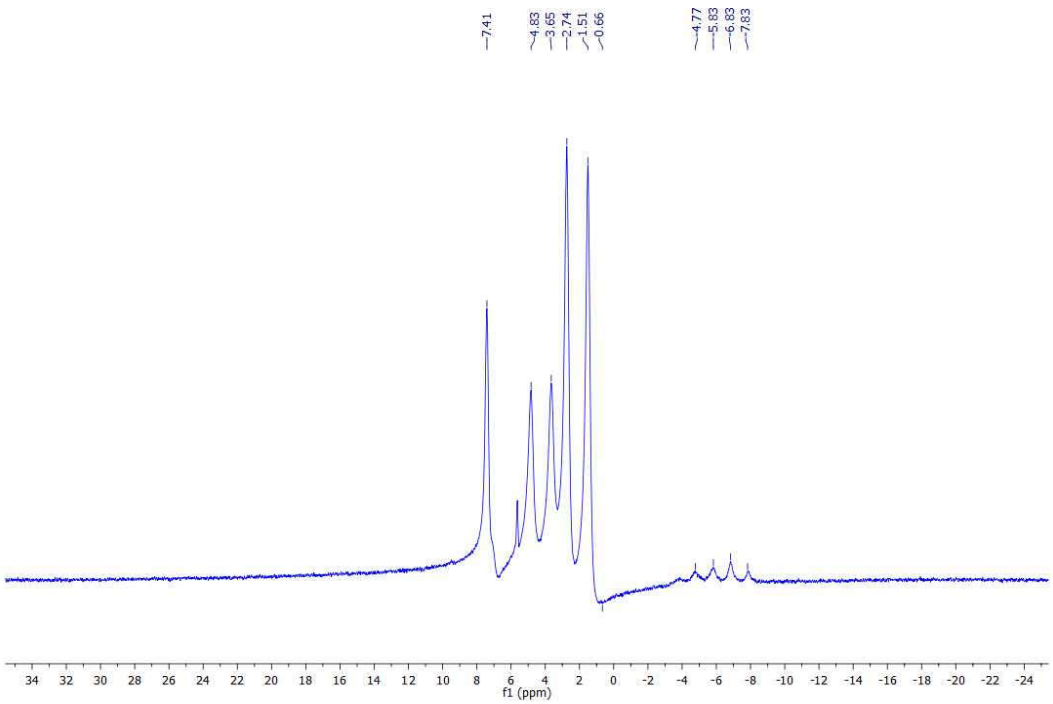

Figure S9. ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of $[1,3\text{-}(CH_2NH)_2C_6H_4]BHNEt_3$ **(5)**, $[1\text{-}(CH_2NH_2)\text{-}3\text{-}(CH_2NH)C_6H_4]BHClNEt_3$ **(6)** and $[1\text{-}(CH_2NH_2)\text{-}3\text{-}(CH_2NH)C_6H_4]BCl_2NEt_3$ **(7)**

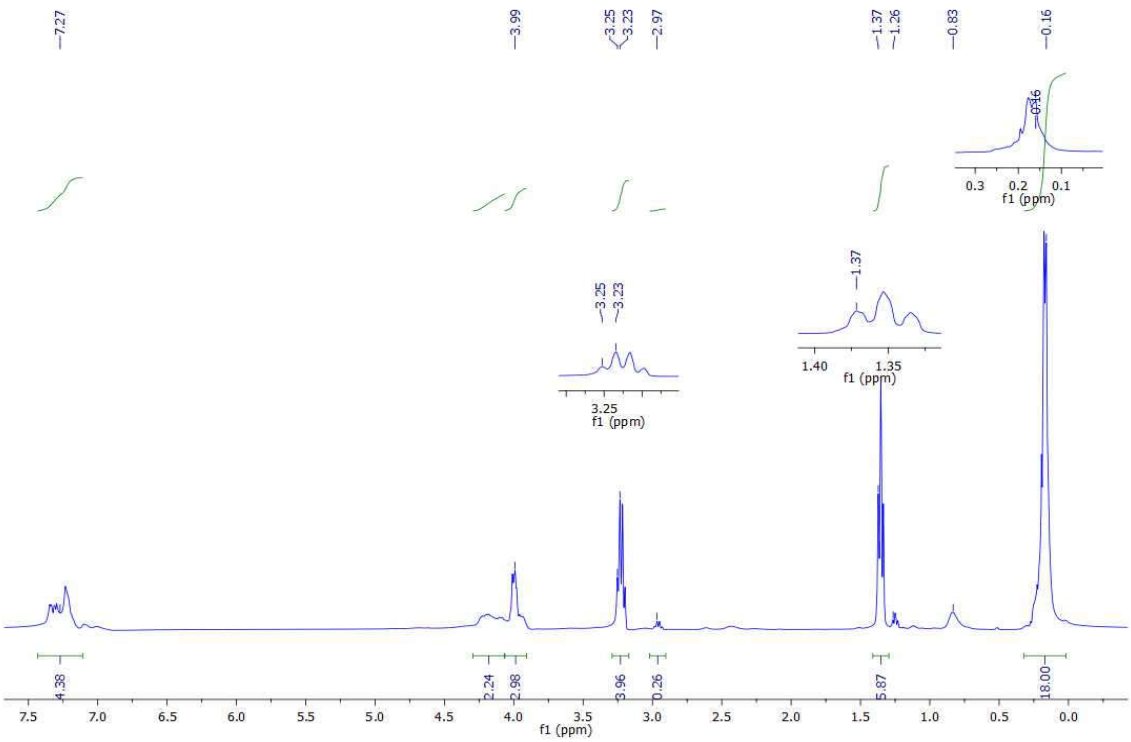

Figure S10. ^1H NMR (400MHz, $CDCl_3$) of $[1,3\text{-}(CH_2SiMe_3N)_2C_6H_4]BHNEt_3$ **(8)**

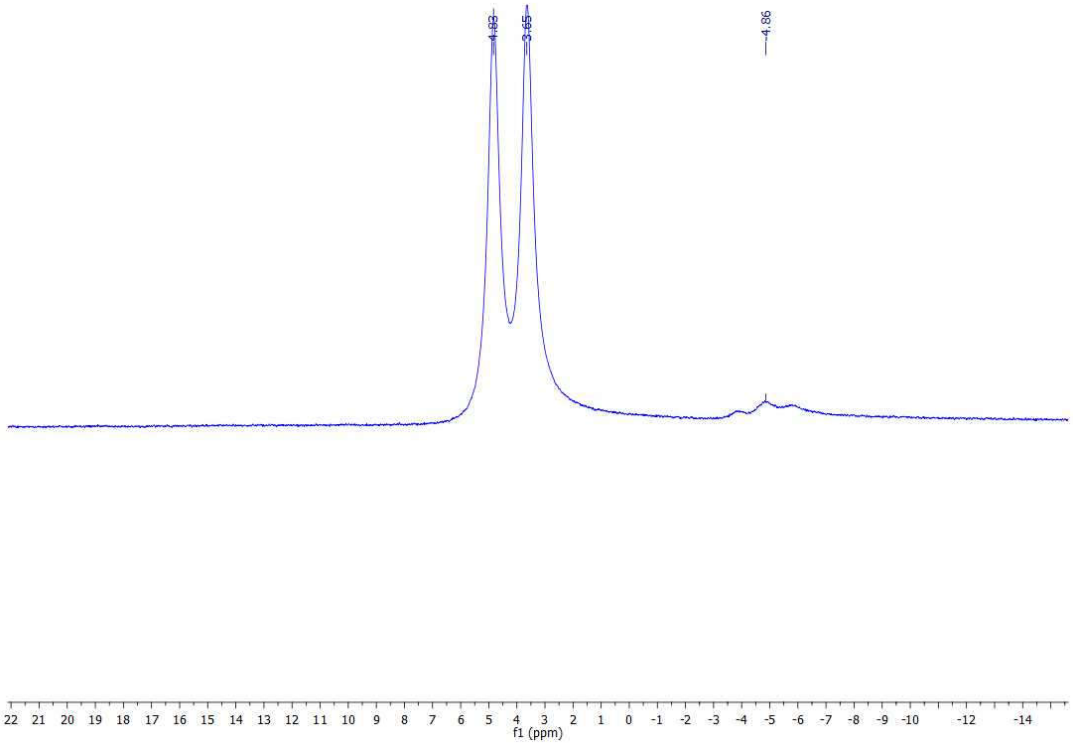

Figure S11. ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of $[1,3\text{-}(CH_2SiMe_3N)_2C_6H_4]BHNEt_3$ **(8)**

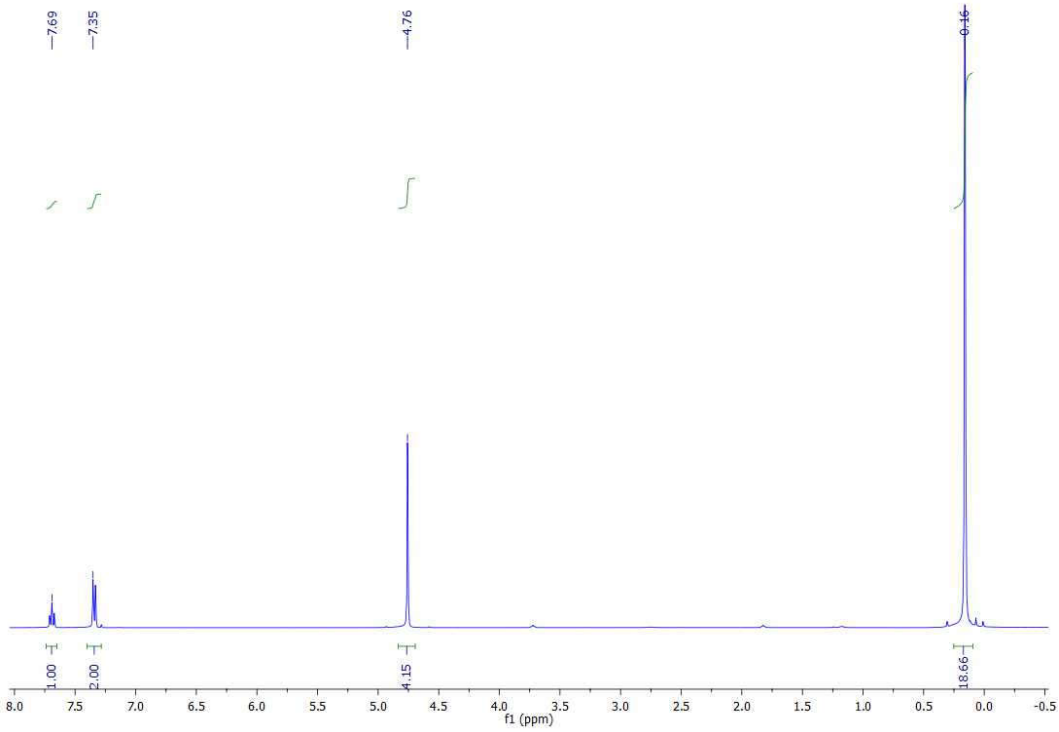

Figure S12. ^{1}H NMR spectrum (400MHz, $CDCl_3$) of $[2,6\text{-}(CH_2\text{-}O\text{-}SiMe_3)_2C_5H_3N]$ **(9)**

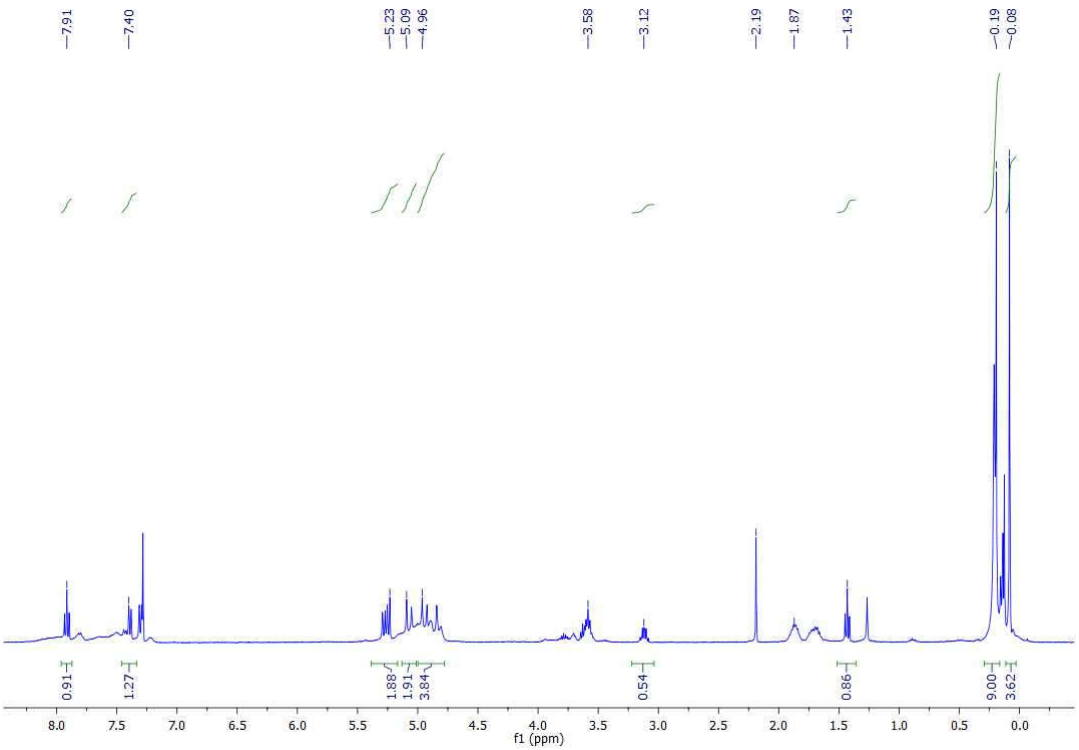

Figure S13. ^{1}H NMR spectrum (400MHz, $CDCl_3$) of [2-(CH_2-O-BHCl)-6-(CH_2-O-$SiMe_3$)C_5H_3N] **(10)**

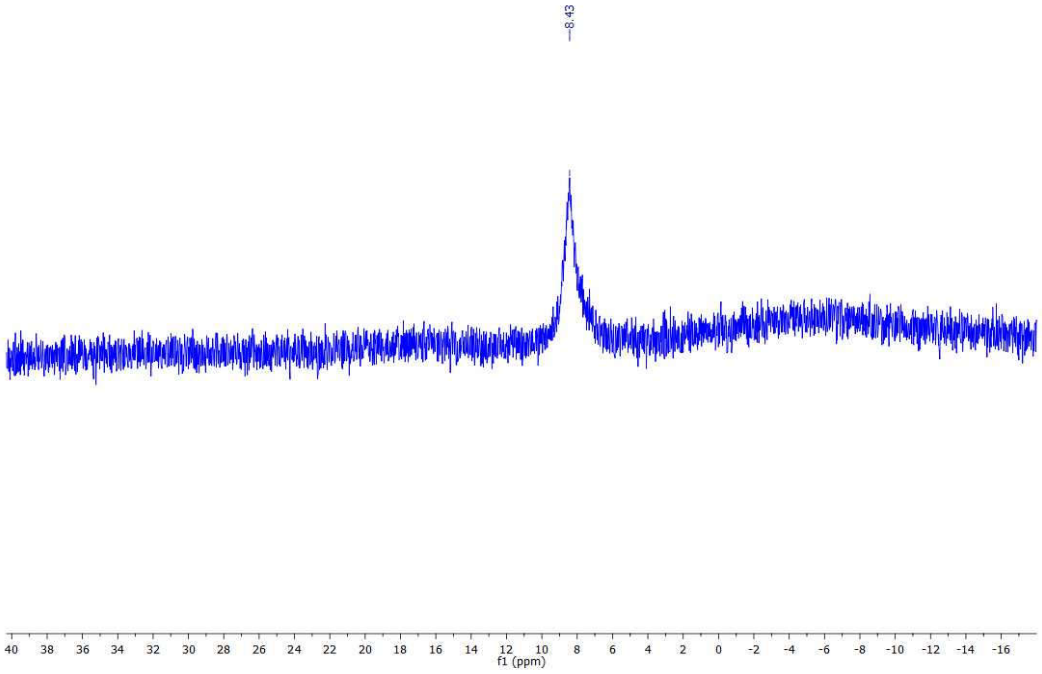

Figure S14. ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of [2-(CH_2-O-BHCl)-6-(CH_2-O-$SiMe_3$)C_5H_3N] **(10)**

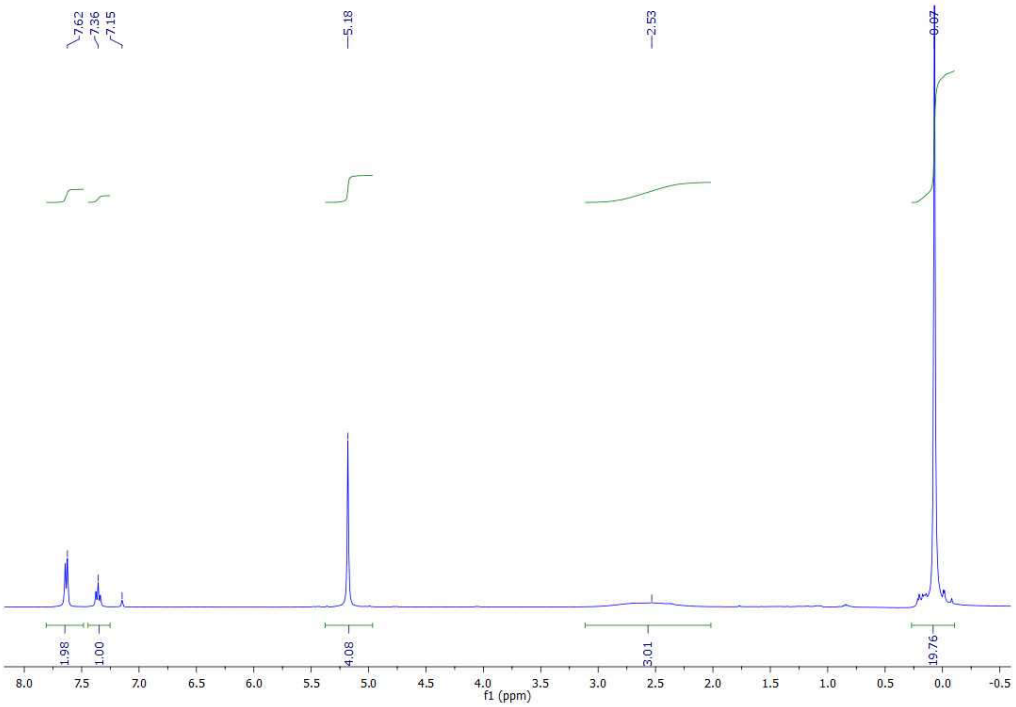

Figure S15. ^{1}H NMR spectrum (400MHz, C_6D_6) of $[2,6\text{-}(CH_2O\text{-}SiMe_3)_2C_5H_3N]BH_3$ **(11)**

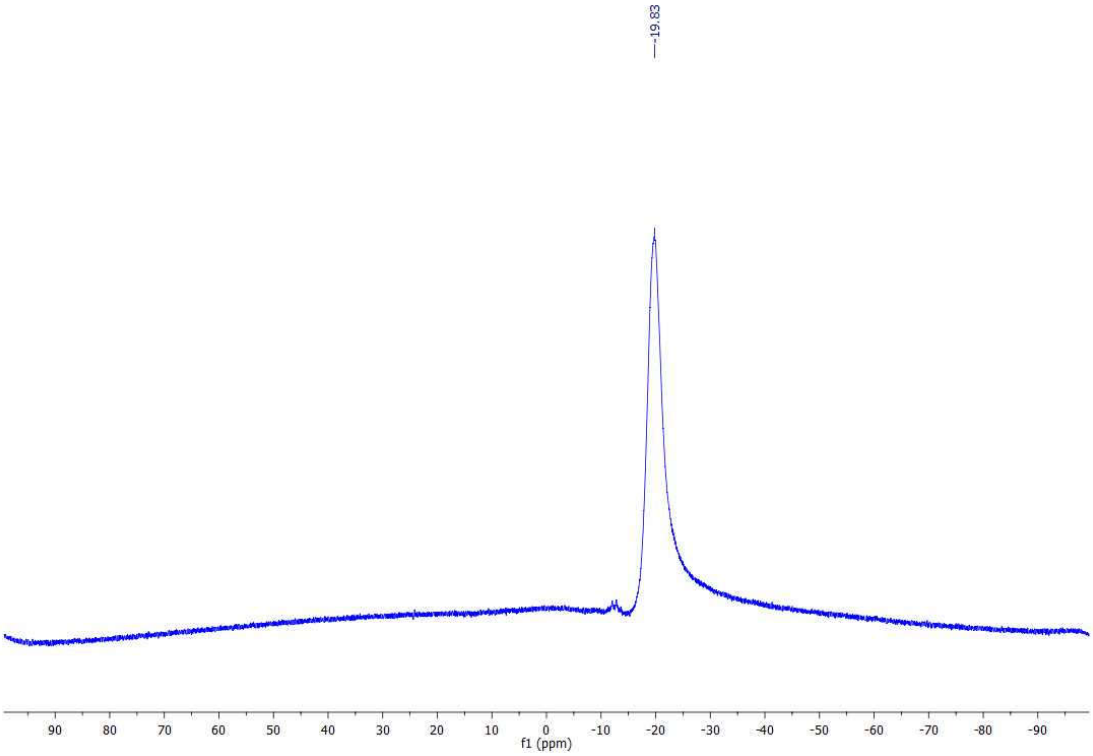

Figure S16. ^{11}B NMR spectrum (128 MHz, C_6D_6) of $[2,6\text{-}(CH_2O\text{-}SiMe_3)_2C_5H_3N]BH_3$ **(11)**

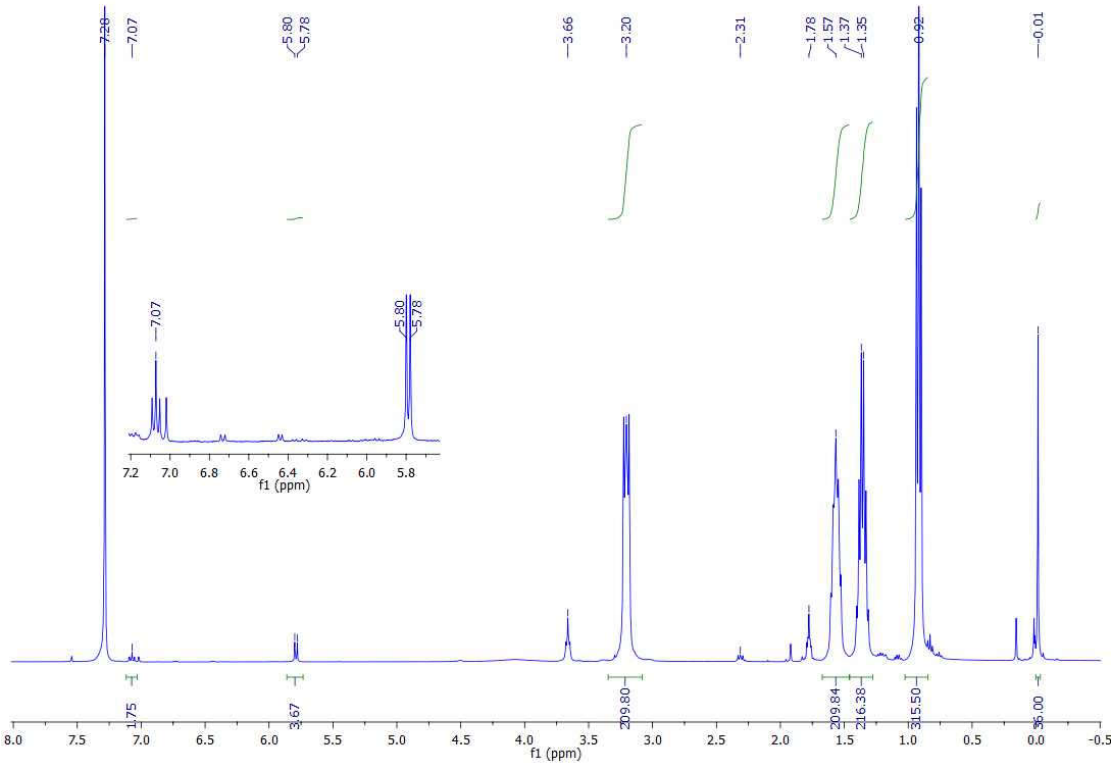

Figure S17. ^{1}H NMR (400MHz, $CDCl_3$) of $[2,6\text{-}(Me_3SiN)_2C_5H_3N(BHF)]_2^{2-}$ 2 $^{n}Bu_4N^+$ **(12)**

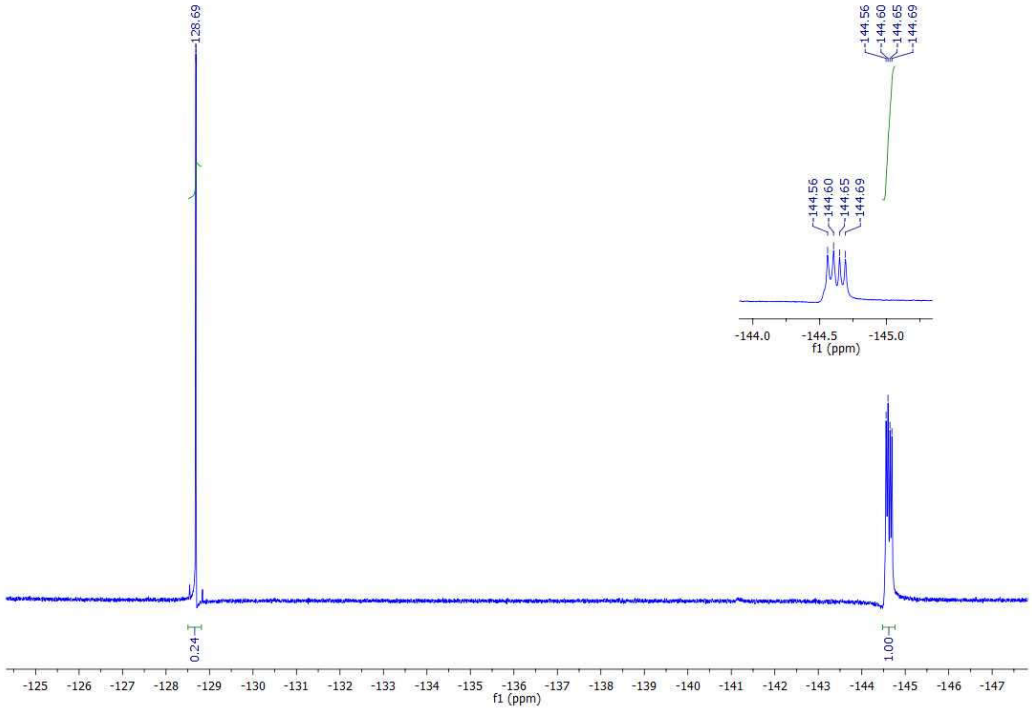

Figure S18. ^{19}F NMR (376 MHz, $CDCl_3$) of $[2,6\text{-}(Me_3SiN)_2C_5H_3N(BHF)]_2^{2-}$ 2 $^{n}Bu_4N^+$ **(12)**

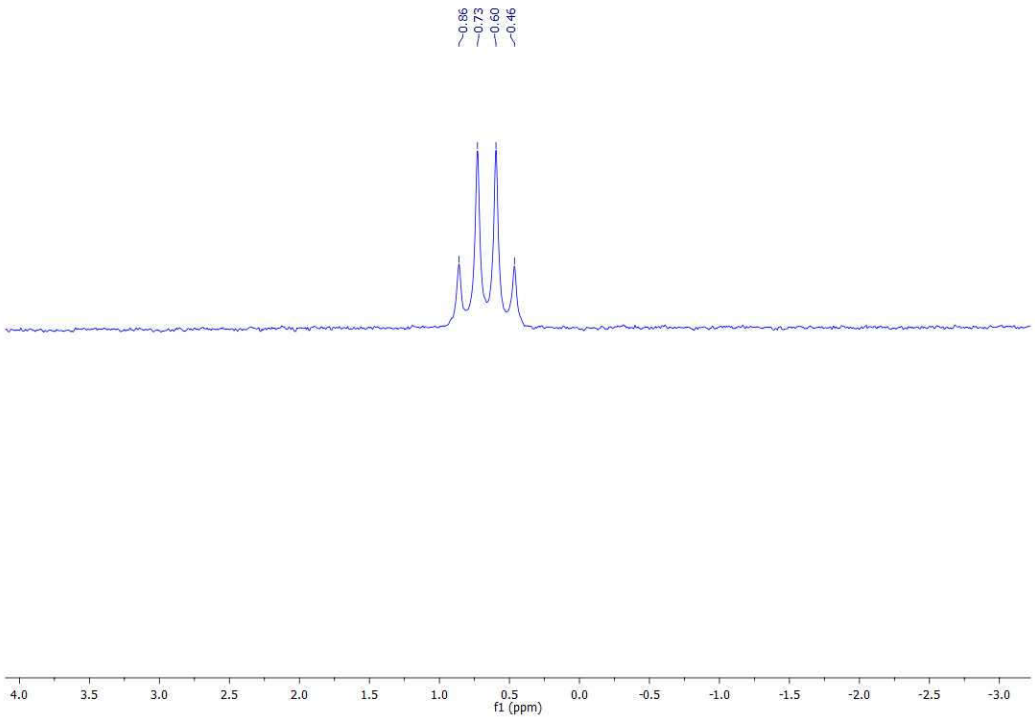

Figure S19. ^{11}B NMR spectrum of $[2,6\text{-}(Me_3SiN)_2C_5H_3N(BHF)]_2^{2-}$ 2 $^{n}Bu_4N^+$ **(13)**

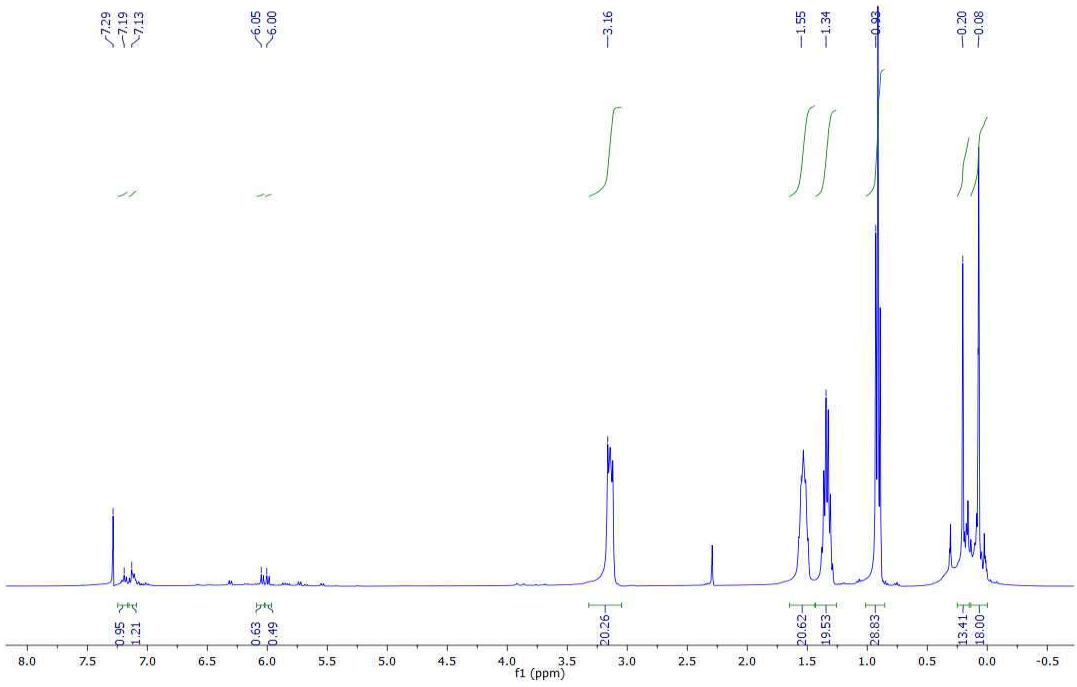

Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) of $[2,6\text{-}(Me_3SiN)_2C_5H_3N(BHCN)]_2^{2-}$ 2 $^{n}Bu_4N^+$ **(13)**

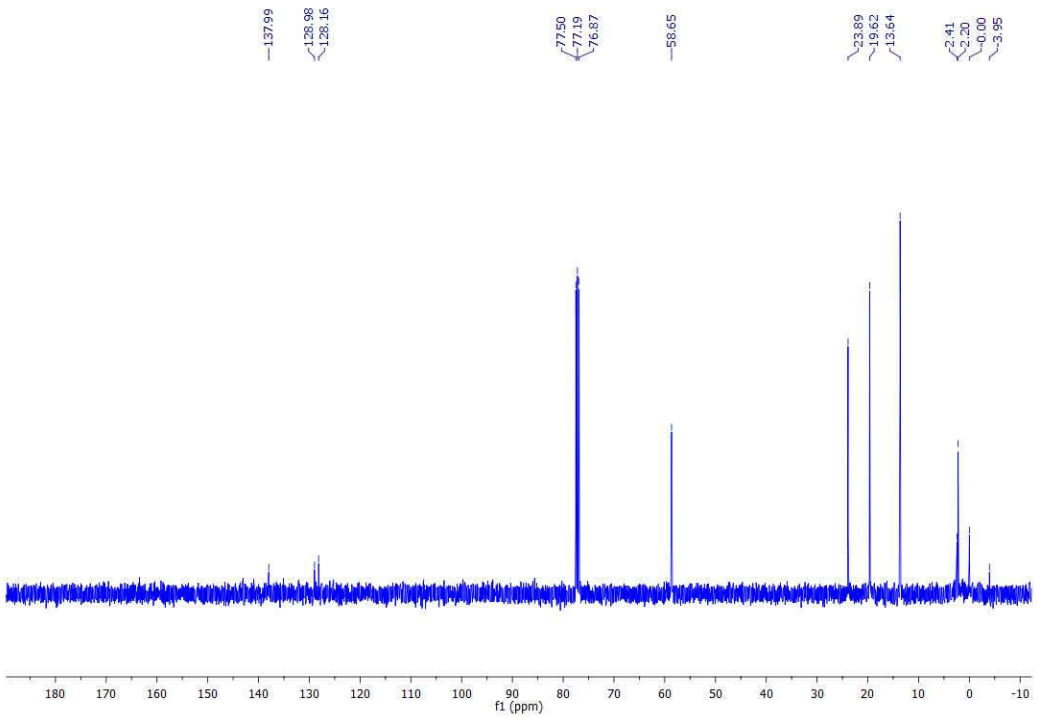

Figure S21. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) of $[2,6\text{-}(Me_3SiN)_2C_5H_3N(BHCN)]_2^{2-}$ 2 $^{n}Bu_4N^+$ **(13)**

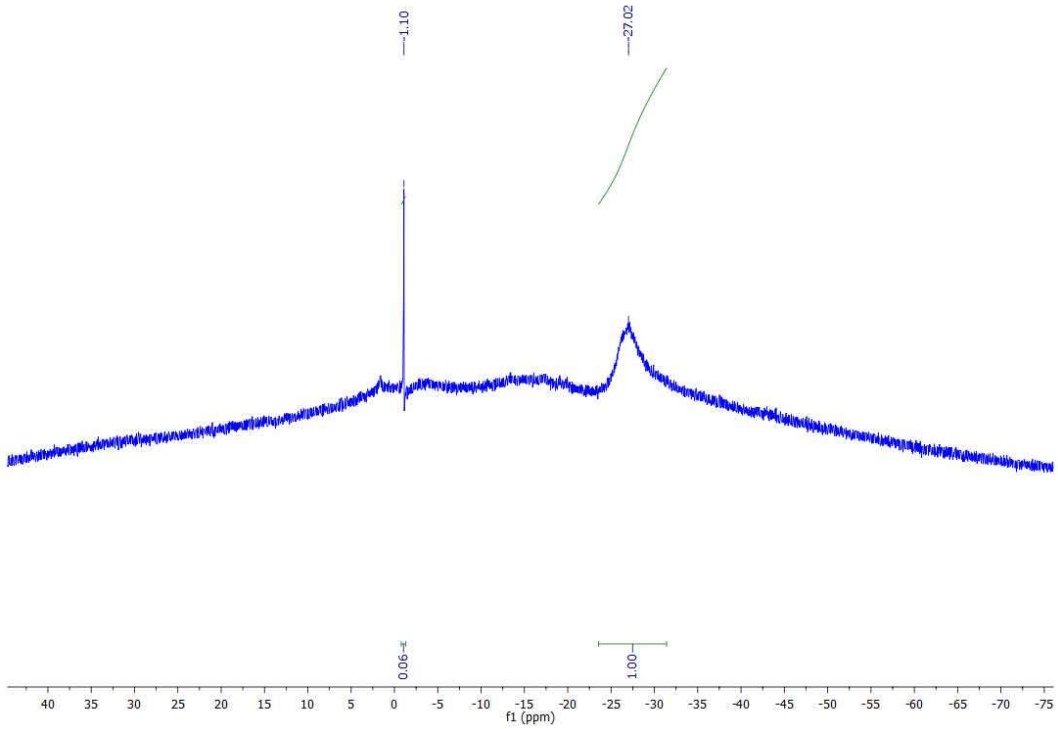

Figure S22. ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of $[2,6\text{-}(Me_3SiN)_2C_5H_3N(BHCN)]_2^{2-}$ 2 $^{n}Bu_4N^+$ **(13)**

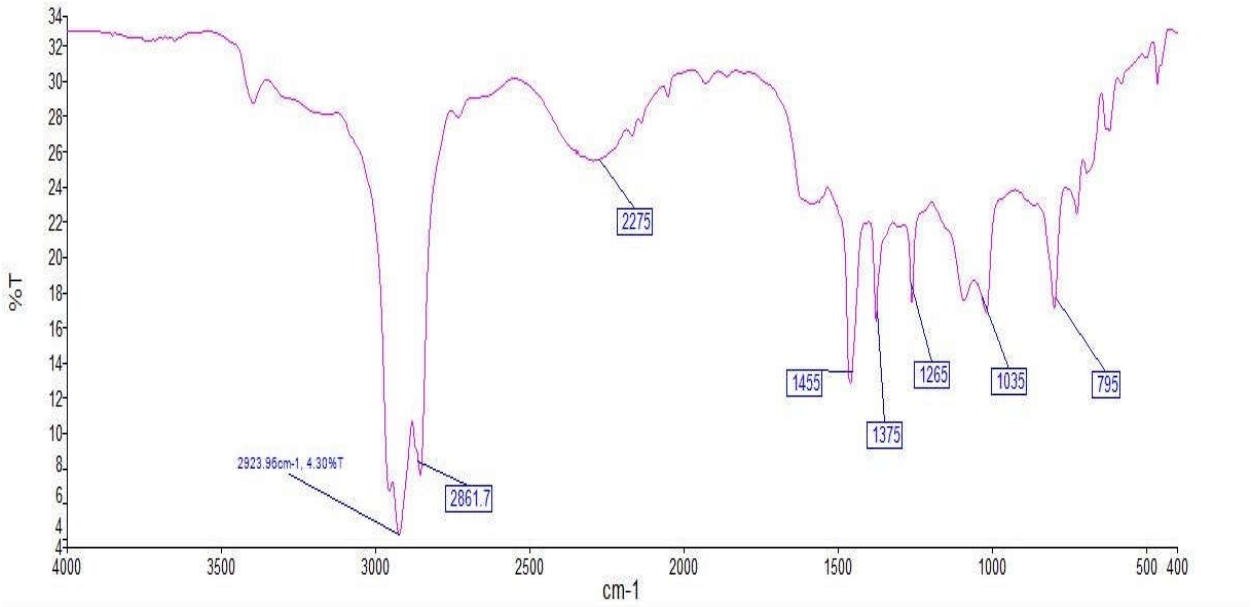

Figure S23. IR spectrum (Nujol) of $[2,6\text{-}(Me_3SiN)_2C_5H_3N(BHCN)]_2^{2-}$ 2 $^nBu_4N^+$ **(13)**