# Structure and Reactivity of Bulky Boryl-Stabilized Group 13/14 Imides







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**Abstract**

This thesis reports on investigations into the synthesis, electronic structure and reactivity of Group 13 and 14 element compounds featuring multiple bonds to nitrogen, with emphasis on the design and stabilization of systems featuring unconventional bonding modes, supported by sterically encumbered boryl ligands.

Chapter 1 introduces the area of current research into group 13/14 imido compounds, including the synthesis, characterization and reactivity studies reported to date, with a particular focus on iminoboranes and silaimines. Chapters 2-5 take the form of papers. Chapters 2, 3 and 5 are published papers; chapter 4 is a manuscript which has been submitted for publication. In all cases, I am the first author, having contributed all of the synthesis and spectroscopic characterization, and more than half of the DFT analysis; I prepared the initial manuscript text and supporting information in each case. A declaration to this effect can be found at the end of each chapter, signed by myself and my supervisor Prof. Simon Aldridge.

Chapter 2 details the first example of an all-inorganic BNBNB heterocumulene, isoelectronic with organic [4]cumulenes. The BNBNB chain is synthesized from a boryl-functionalized boron diamide and stabilized by bulky diazaborolyl ligands. Treatment with $B(C_6F_5)_3$ converts the bent structure to a linear form via rearrangement of the terminal groups, enhancing $\pi$-conjugation across the chain. Orbital analysis for the latter system confirms the presence of two orthogonal $\pi$-systems spanning the BNBNB core.

Chapter 3 explores the metathesis reactivity of the BNBNB cumulenes with $CO_2$, $CS_2$, $(H_2CDippN)_2PPCO$, and benzaldehyde. These reactions proceed via [2+2] cyclo-addition/cyclo-reversion steps, enabling transfer of the (boryl)N fragment to give (boryl)N=C=X products. The reaction with benzaldehyde affords a borylimine product via a (crystallographically characterized) four-membered cyclic intermediate, thereby supporting a bora-Wittig-type mechanism. Both bent and linear BNBNB species show similar reactivity in this regard.

Chapter 4 describes the use of the BNBNB cumulene as a precursor for a dianionic bis(borylamido) ligand in the stabilization of low-valent Ge(II) complexes. The reaction with $GeCl_2$·dioxane yields a $GeN_2B$ four-membered ring featuring a boron-bound chloride substituent. While Cl-for-alkyl or -amide substitutions proved unsuccessful, onward reaction with $Me_3SiN_3$ enables clean conversion to an azido-derivatized germylene adduct. This work highlights the potential of cumulenes as analogues of carbodiimides in ligand design/synthesis.

Chapter 5 reports reversible redox cycling between Si(IV) and Si(II) in a boryl and amidinate supported silanimine of the type (amid)Si(Boryl)(=$NSiMe_3$). Heating induces boryl migration from Si to N, forming a silylene, (amid)Si{$N(SiMe_3)$(Boryl)} followed by silyl migration back to Si(IV), regenerating an imidosilane, (amid)Si($SiMe_3$)(=NBoryl), featuring a borylimido group. DFT calculations reveal small energy differences between these isomeric forms but high transition state barriers, consistent with experimental observations (i.e. the necessity for high temperatures to achieve equilibrium). Related tin and germanium systems do not undergo similar redox shuttling, underscoring the uniqueness of silicon in this respect.

**Acknowledgements**

I wish to express my deepest gratitude to Professor Simon Aldridge for providing me with the extraordinary opportunity to pursue my doctoral studies at the University of Oxford. His steadfast guidance and unwavering encouragement were indispensable in helping me navigate the challenges of this journey. I am particularly grateful for his patience and belief in my potential, which enabled me to overcome initial academic limitations and grow as a researcher.

My sincere thanks also go to Professor Yuwen Wang for her insightful mentorship and invaluable advice, which greatly shaped my development. I am equally indebted to my dear friend Chenyang Hu, whose constant support and encouragement sustained me throughout this process.

To the Aldridge group, I extend my warmest appreciation for their collaboration and camaraderie. I am especially grateful to Aggy for sharing his computational and crystallographic expertise, to Dr. Andrew for his guidance during my first year, and to Liam, Max, and others for fostering such a collegial and stimulating work environment at CRL S1. Also other friend Yifan Yan for being by my side and sharing my daily life during my third year.

Finally, my profoundest thanks go to my family. Their unconditional support, both emotional and financial, made this achievement possible. I owe them more than words can express.

**Abbreviations**

The following abbreviations will be employed throughout this thesis:

Ad = 1-adamantyl

Ar = general aryl group

BCF = $B(C_6F_5)_3$

[B]/boryl= $(HCNDipp)_2B$

CAAC= Cyclic-alkyl amino carbene

Cp* = permethylcyclopentadiene

d = doublet

DFT = Density Functional Theory

Dipp = 2,6-diisopropylphenyl

Dmp = 2,6-$Mes_2$-$C_6H_3$

Dur = 2,3,5,6-$Me_4C_6H$

HOMO = Highest Occupied Molecular Orbital

iPr = isopropyl

$IMe_4$ = $((CH_3)CN(CH_3))_2C$

$I^iPrMe$ = $(^iPrNC(CH_3)_2)_2C$

LUMO = Lowest Unoccupied Molecular Orbital

m = multiplet

m = meta

Me = methyl

Mes = 2,4,6-$Me_3$-$C_6H_2$

Nacnac = $[(NArCMe)_2CH]^-$

NBO = Natural Bonding Orbitals

NHC = N-heterocyclic carbenes

NMR = Nuclear Magnetic Resonance

o = ortho

p = para

Ph = phenyl

R = aliphatic group (unless otherwise stated)

s = singlet

sept = septet

t = triplet

tBu = tert-butyl

THF = tetrahydrofuran

Tmp = 2,2,6,6-tetramethylpiperidino

Trip = 2,4,6-$^iPr_3C_6H_2$

TMS = trimethylsilyl

UV-Vis = Ultraviolet-Visible spectroscopy

VT = Variable temperature

## Chapter 1. Introduction

Multiple bonds between heavy main group elements have attracted significant interest and the field has undergone rapid development, since the first stable Si=Si bonded disilene $Mes_2Si=SiMes_2$ featuring bulky Mes (2,4,6-trimethylphenyl) substituents on silicon was isolated in 1981.[1] Remarkably, the disilene defied the so-called double bond rule, which postulated that p-block elements with a principal quantum number greater than two (third-period elements and below) cannot form stable multiple bonds.[2–4] In the same year, a further landmark was achieved in the field of main group multiple research: the first diphosphene Mes*P=PMes* (Mes* = 2,4,6-tri-tert-butylphenyl) was reported by Yoshifuji and coworkers.[5] Since then, a steady flow of homonuclear doubly bonded compounds featuring main group elements has been isolated and characterized.[3,6,7] Due to the inherently weak $\pi$ bonding of heavier main group elements, multiply bond derivatives of this type are reactive and typically labile. Thus, the design of sterically bulky ligands has emerged as a key strategy to overcome the challenges of synthesizing main group multiple bonds. For instance, smaller ligands often give rise to oligomers ($Ph_8Si_4$,[8] $Ph_{12}Sn_6$, [9] $Cp_4*Al_4$[10]), while bulkier substituents may hinder aggregation leading to the formation of unsaturated compounds.

Extension of this field into heteronuclear multiple bonds presents further challenges arising from the differences in orbital parity and energy between the two bonding atoms. The first example of a heteronuclear main-group multiple bond $(Me_3Si)_2Si=C(OSiMe_3)Ad$ was reported by the Brook group.[11] Compared to their homonuclear counterparts, heteronuclear multiple bonds between elements from different groups offer interesting comparisons in terms of

bonding and reactivity. For instance, $E^{13}$–$E^{15}$ derivatives featuring a formally vacant *p* orbital at the group 13 centre and a lone pair at the group 15 centre, offer the potential for donor–acceptor π bonding, being valence isoelectronic with carbon-carbon multiple bonds. By contrast, $E^{14}$–$E^{15}$ multiple bonds (as in phosphaalkynes, RCP), are of interest due to the fact that they have two centres of reactivity, a $\pi$ bond and a lone pair of electrons on the $E^{15}$ center.[12] $E^{13/14}$–$E^{15}$ multiple bonds have garnered substantial interest in both academic and industrial contexts owing to their unique electronic structures and potential applications, for example, as precursors to semiconductor materials.

In this chapter, the synthesis, characterization and reactivity of $E^{13/14}$–N imido compounds as well as borylamine/borylimido derivatives stabilized by a bulky boryl ligand will be discussed in detail.

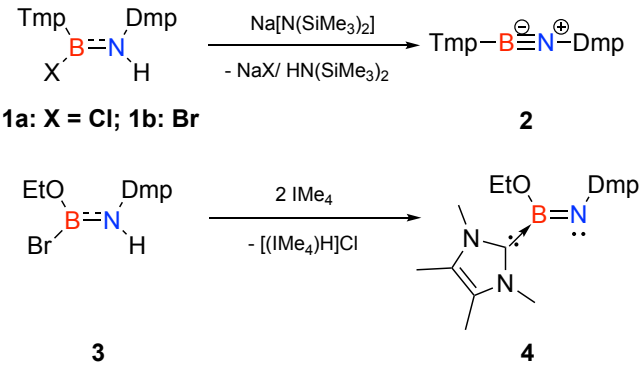
## Compounds featuring E13=N and related bonds

### *Iminoboranes*

Iminoboranes (RBNR') feature a B≡N unit, that is isoelectronic with an alkyne (RC≡CR'), but exhibit significantly different reactivity due to the strong polarity and the relative weakness of the B≡N triple bond.[13–16] As a consequence, a number of transient iminoboranes have been reported which readily undergo oligomerization or dimerization.[14,15] Nevertheless, a series of isolable monomeric species have been reported, stabilized through the use of bulky ligands, and which have enabled the understanding of iminoborane chemistry.[17]

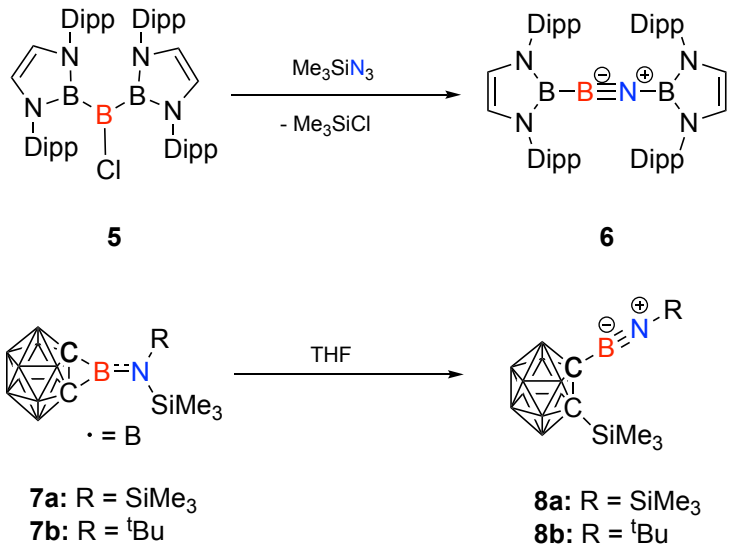
Elimination is the most versatile strategy for synthesizing iminoboranes, and involves the

removal of small molecules, such as trimethylhalosilanes, hydrogen halides, or dinitrogen, from appropriately functionalized precursors.[17,18] Base-promoted dehydrohalogenation remains the most widely employed approach for constructing classical diorgano-iminoboranes. This method typically utilizes bulky alkali-metal amides, such as lithium or sodium bis(trimethylsilyl)amide (MHMDS, M = Li or Na), or lithium tert-butyl(trimethylsilyl)amide, which facilitate the removal of hydrogen halides from functionalized aminoborane precursors. Power and co-workers demonstrated that treatment of the sterically enumbered aminoborane precursors TmpB(X)=N(H)Dmp (X = Cl, Br) **1** with NaHMDS produced the iminoborane Tmp-B≡N−Dmp, **2** (Scheme 1), which is characterized by a characteristic $^{11}$B NMR resonance at 10.6 ppm and a short B≡N bond length of 1.254(3) Å.[19] In addition to conventional dehydrohalogenation, elimination reactions can also be facilitated by N-heterocyclic-carbene (NHCs), which act as strong Brønsted bases. Cui and co-workers demonstrated this strategy in the synthesis of NHC-coordinated iminoborane **4**, through the deprotonation of aminoborane **3** with the NHC, $IMe_4$.[20]




**Scheme 1**. Elimination of hydrogen halides from aminoboranes for the syntheses of iminoboranes.

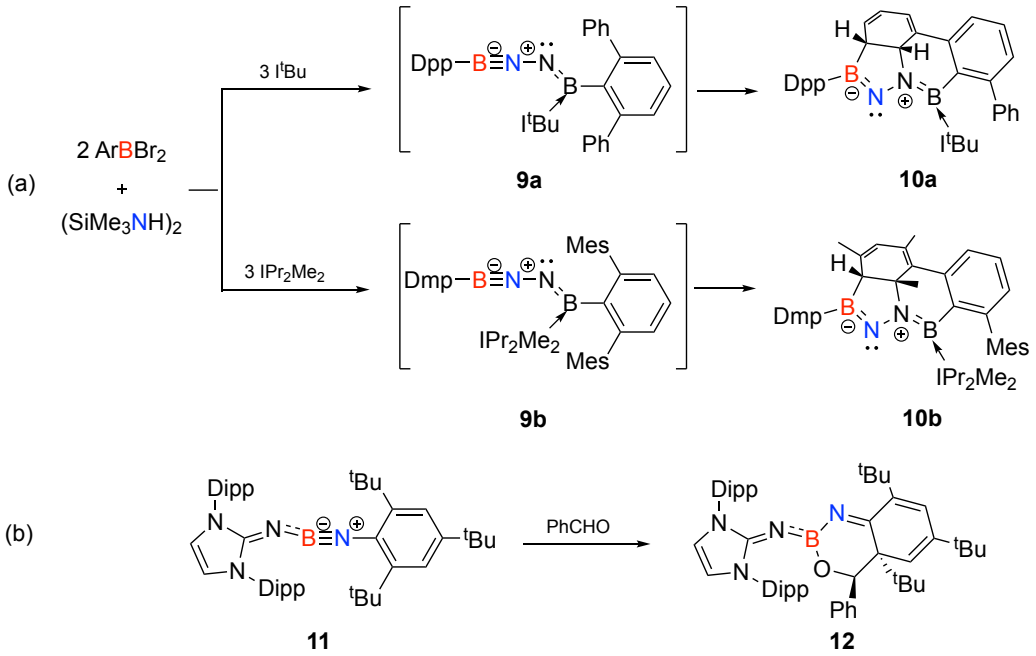
Another approach towards iminoborane synthesis utilizes diazo compounds via elimination of dinitrogen. This method typically involves the transfer of a nitrogen unit from a diazo precursor (e.g. $Me_3SiN_3$) to a boron center with the release of nitrogen gas. This approach can generate iminoboranes under mild conditions, offering a clean and efficient route to these highly reactive species. A recent example of a novel diboryl iminoborane was synthesized by Su and co-workers, who treated a diboryl-substituted chloroborane **5** with azidotrimethylsilane ($Me_3SiN_3$) at room temperature to produce diboryl iminoborane **6**, featuring a nearly linear B−B−N−B core (with bond angles of B−B−N = 176.7(8)° and B−N−B = 178.1(6)°), and a B≡N bond length of 1.240(7) Å.[21] In addition to diazo transfer, rearrangement reactions have also been shown to generate iminoboranes. For instance, the rearrangement of carborane-fused boriranes of type **7** has been shown to produce iminoboryl o-carboranes, such as (Me$_3$Si)Cb−B≡N−R (Cb = $B_{10}C_2H_{10}$, R = SiMe$_3$, $^t$Bu) **8**, featuring B≡N bond lengths of 1.238(3) Å and 1.220(2) Å, respectively.[22]




**Scheme 2.** Selected routes to different Iminoboranes species.

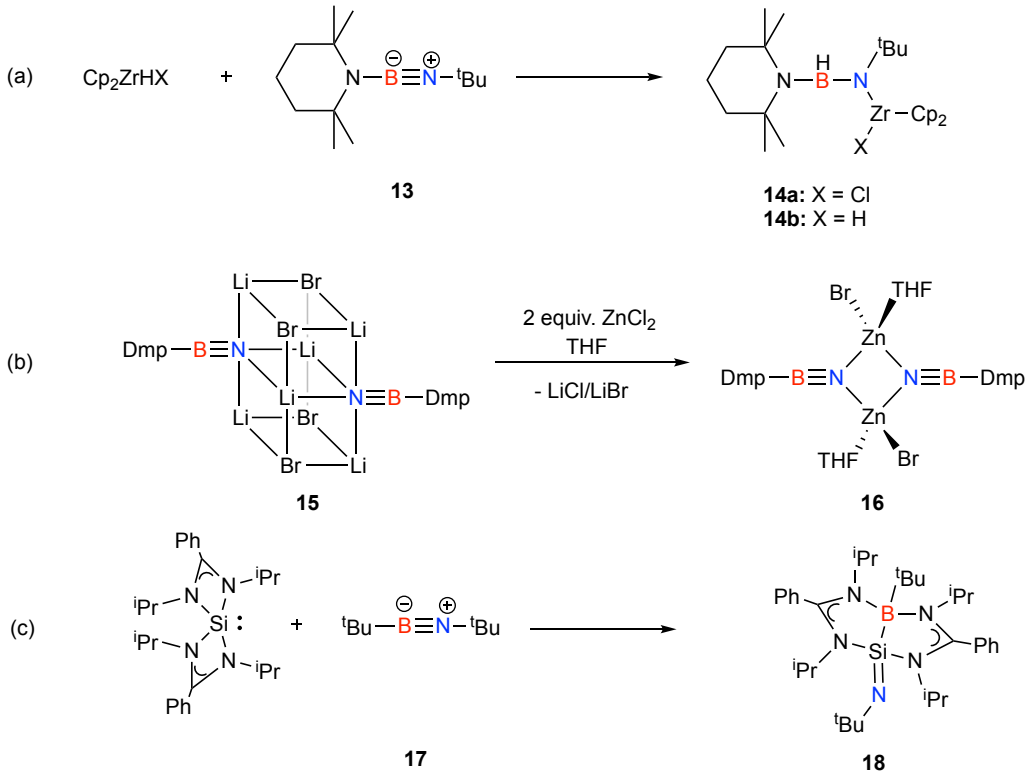
Owing to the polarity of the BN bond, iminoboranes and related derivatives have been shown to primarily undergo 1,2-addition and cycloaddition reactions. Various polar covalent bonds have been reported to be cleaved by monomeric iminoboranes via 1,2-addition or [2+2] cycloaddition reactions. [17,23]

The 1,2-addition reaction was widely demonstrated in early studies, which were summarized by the Nöth group in 1988.[23] In 2020, Kong and co-workers demonstrated intramolecular 1,3-dipolar cycloadditions of the BNN unit within compounds of type **9** with relatively inert arenes.[24] This study revealed that BN-constituted π-conjugated systems can serve as the 4e component for [4+2] cycloaddition reactions with alkenes. Kong and co-workers further reported unprecedented de-aromative hetero-Diels–Alder (HAD)-like reactions between aryliminoboranes **11** and various aldehydes in 2022.[25] This chemistry generates a variety of bicyclic products in which the ring contains three different second-period heteroatoms.




**Scheme 3.** Reactivity of iminoboranes: (a) [2+2] cycloaddition; (b) [4+2] cycloaddition.

Apart from addition reactions, the BN π-bonds in iminoboranes can also act as a $\eta^2$-ligand for coordination to transition metals, as shown in compound **14** reported by Noth and coworkers in 1985.[26] Furthermore, an example of a boraiminolithium species (**15**) has even been reported; this system demonstrated iminoborane-transfer reactions which may become powerful tools in the exploration of unprecedented N-functionalized iminoboranes for synthetic chemistry.[27] In addition, although the BN triple bonds of iminoboranes are difficult to cleave, due to bond dissociation energies (BDE) of ca. 170 kcal/mol,[28] the Braunschweig group described the insertion of main group reagents into the BN triple bonds, as shown in Scheme 4(c).[29]

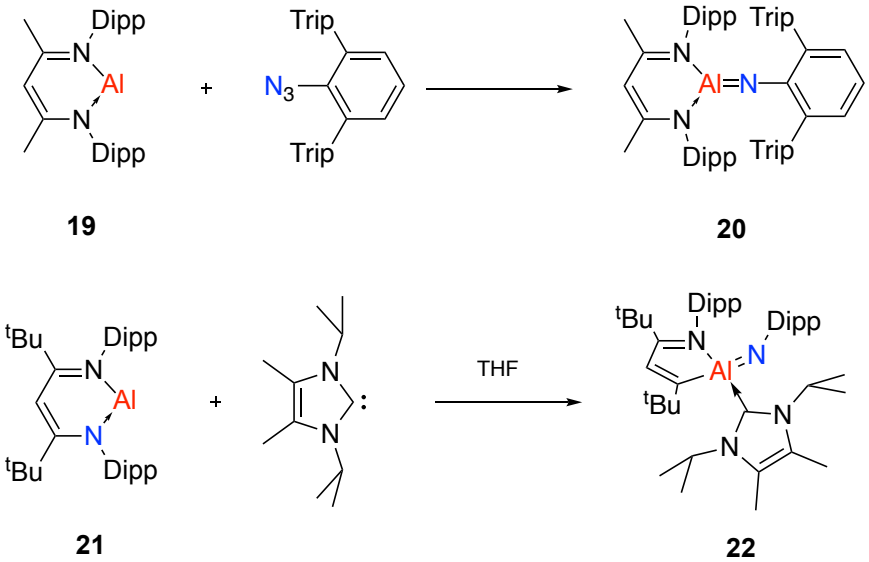



**Scheme 4.** Reactivity of Iminoboranes (a) Coordination reaction (b) Iminoborane-transfer reaction (c) Cleavage of BN triple bonds.

***Aluminium imides***

Although monomeric imides have been developed for the lightest group 13 element boron,[15] only a few examples of heavier group 13 imide compounds have been spectroscopically and structurally characterized.

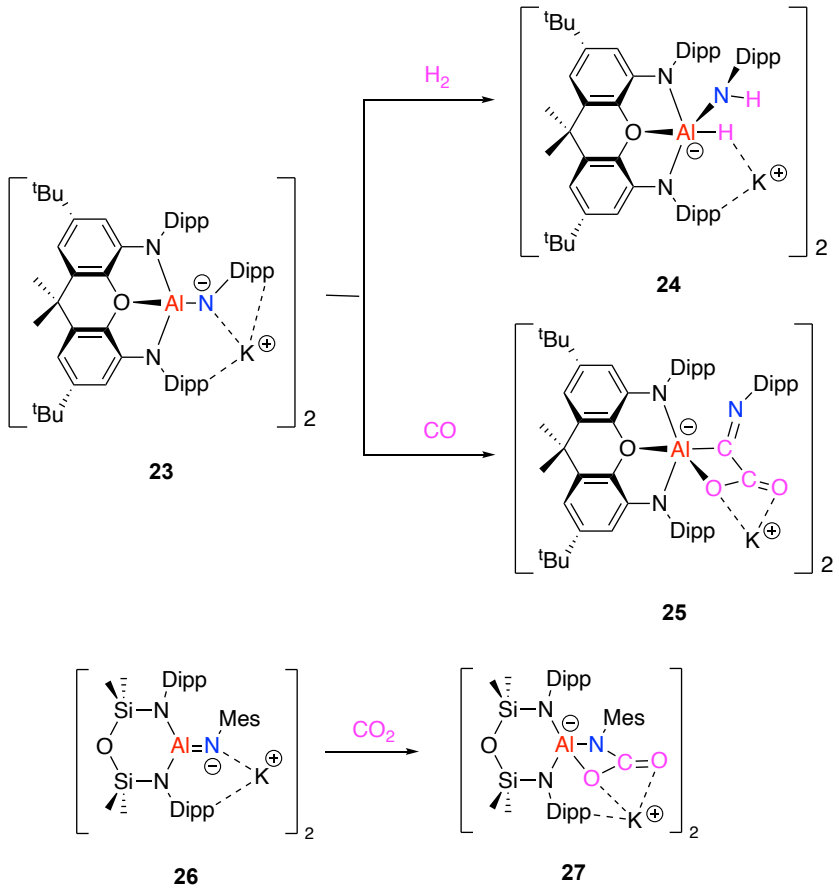
In 2001, Power and co-workers synthesized the first stable monomeric imide of the heavier group 13 elements (**20**) via the reaction of the monomeric aluminium(I) β-ketiminate {HC(MeCDippN)$_2$}Al **19** with the sterically encumbered azide $N_3C_6H_3Trip_2$-2,6.[30] Subsequently, an isolable monomeric base-stabilized iminoalane **22** was obtained by the Cui group through the cleavage of one of the C-N bonds of a β-ketiminate supporting ligand (Scheme 5).[31] **22** bears a terminal Al=N bond, made possible by utilizing a bulky chelating ligand, and is highly reactive towards PhCCH, $PhNH_2$, and CO.




**Scheme 5.** The first isolable monomeric (base)-stabilized iminoalanes.

Subsequently, the Aldridge group reported an anionic imide complex of aluminium, which was

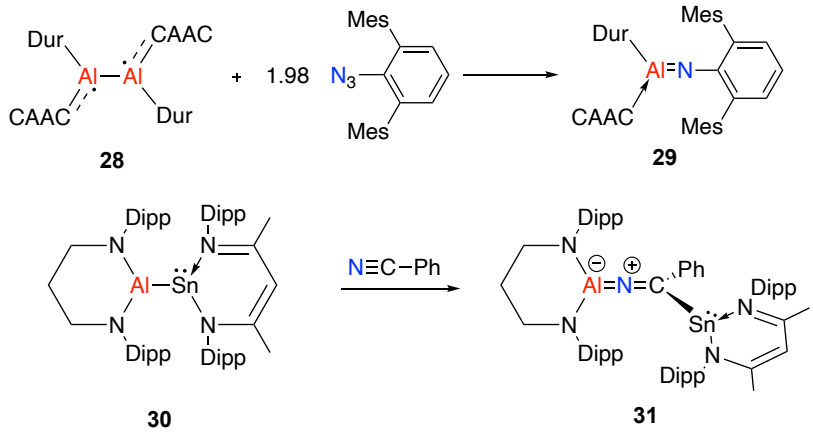
accessed from the reaction of the aluminyl anion $K_2[(NON)Al(NDipp)]_2$ **23** with $DippN_3$.[32] Due to the high reactivity of the Al-N unit, the anionic imide complex activates a number of strong chemical bonds (such as $H_2$ and CO). Anker and co-workers reported another terminal aluminum imide (**26**) synthesized via the reaction of a related aluminyl anion with $MesN_3$, which undergoes similar [2+2] cycloaddition with $CO_2$, further demonstrating the unique reactivity of low-coordinate aluminum imides toward small molecules.[33]




**Scheme 6.** Activation reactions of anionic aluminum imides towards $H_2$, CO and $CO_2$.

More recently, two novel synthetic routes to obtain aluminum imides have been reported. In 2024, Braunschweig *et al.,* demonstrated that the highly electron-rich CAAC-stabilized (1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene) DurAlAlDur diradical **28** reacts with

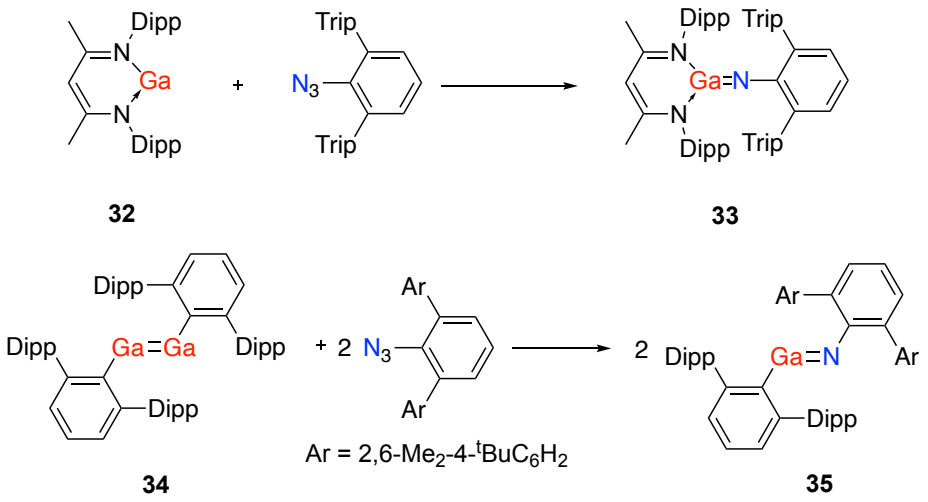
bulky organic azides (e.g. $^{Mes}TerN_3$) in a ca. 1:2 ratio, to form a new aluminum imide (**29**). When 4 equiv. of azide were added, a planar cyclic $Al_2N_2$ species and a linear triazene derivative were obtained.[34] In addition, the first example of an Al-containing allene (Al=N=C) **31** was obtained via a nitrile-insertion reaction using a heterobimetallic Al-Sn precursor (Scheme 7).[35]




**Scheme 7.** New routes to a range of aluminium imides.

***Gallium imides***

Among heavier Group 13 metal imide derivatives, strongly associated oligomers $(RMNR')_n$ ($n \geq 4$; R or R′ = alkyl, aryl, or H) featuring cage structures are dominant.[36] As such, sterically crowded substituents have been exploited to isolate monomeric gallium imides. The first $\beta$-diketiminate-stabilized gallium imide $\{HC(MeCDippN)_2\}GaNC_6H_3\text{-}Trip_2\text{-}2,6$ (**33**) possessing sufficiently large substituents to allow a monomeric structure was obtained in good yield by Power and co-workers via the reaction of the corresponding metal(I) species and a bulky terphenyl azide.[30]

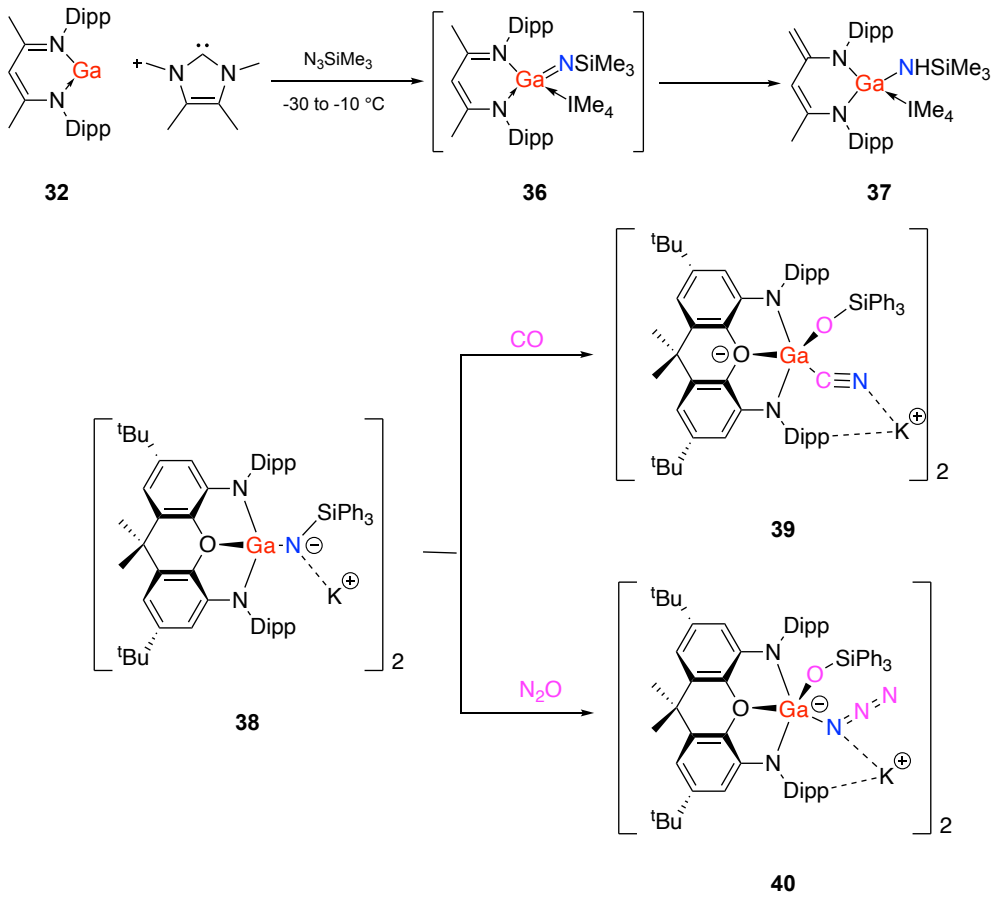



**Scheme 8.** (upper) The first isolable monomeric base-stabilized gallium imide; (lower) the first two-coordinate gallium imide.

Due to the weak Ga-Ga bond in the dimer Ar′GaGaAr′ (**34**; Ar′ = $C_6H_3$Dipp-2,6), dissociation into :GaAr' monomers is possible in hydrocarbon solution.[37,38] As such, dimeric **34** reacts with 2 equiv. of the azide $N_3$Ar'' (Ar″ = $C_6H_2Me_2$-2,6-$^t$Bu-4) at ca. 0 °C to generate the two-coordinate gallium imide **35**.[39] The Ga-N bond (1.701(2) Å) is markedly shorter than in previous imide species (e.g. **33**: 1.742(3) Å).[30]

In addition to isolable species, a transient gallium imide has been synthesized by Nikonov and coworkers. {HC(MeCDippN)$_2$}Ga=NSiMe$_3$ **36** generated from $Me_3SiN_3$ and {HC(MeCDippN)$_2$}Ga, has been reported to activate the C-H bonds of pyridine, cyclohexanone, ethyl acetate, DMSO and $OPEt_3$ to afford the corresponding amides.[40]

More recently, the Aldridge group reported gallium silylimide **38**, which reacts with CO leading to $CN^-$ formation, as shown in Scheme 9. Treatment with $N_2O$ on the other hand, leads to the generation of the azide ion $N_3^-$ via oxide/nitride exchange.[41]

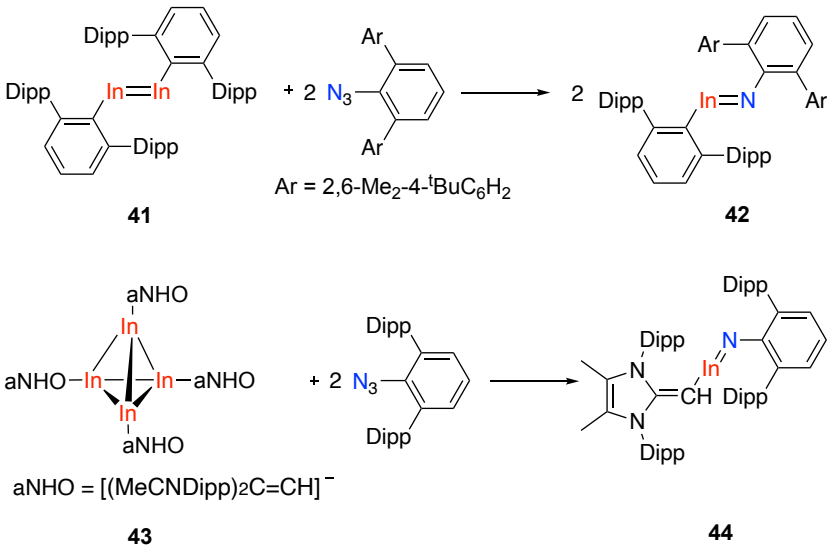



**Scheme 9.** (upper) C–H bond activation by a transient gallium imide; (lower) activation reactions of an anionic gallium imide with $H_2$ and CO.

### *Indium imides*

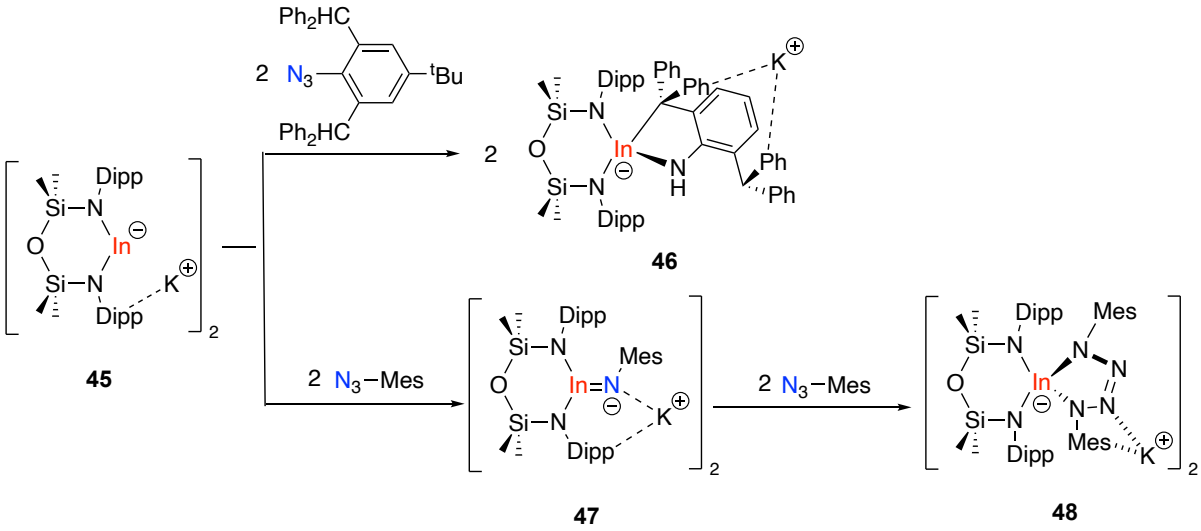
Due to synthetic challenges, there are few examples of indium imides and these are restricted to three structurally characterized examples. The first indium imide **42** was synthesized by the Power group in 2003 via the reaction of diindene **41** with two equivalents of a sterically bulky azide.[39] The product, **42**, shows a trans-bent geometry with a C-In-N angle of 142.2(1)° and an In-N bond length (1.928(3) Å) which is markedly shorter than In-N single bonds.[42] More recently, tetrameric indium species **43** has been shown to react with the bulky organoazide 2,6-$Dipp_2C_6H_3N_3$, leading to the formation of a new indium imide **44** in 31 % yield. By contrast

with **42**, a C-In-N bond angle of 170.39(12)° has been measured crystallographically, implying a close-to-linear geometry at the indium centre.[42,43]




**Scheme 10.** Indium imides synthesized from dimeric or tetrameric indium(I) precursors.

In 2019, Coles and coworkers demonstrated that the treatment of an indyl anion with different azides could be used to generate In-N bonds. When 4-$^{t}$Bu-2,6-$Ph_2C_6H_2N_3$ is used as the nitrogen source, an amine was obtained via intramolecular C-H bond activation by a transient indium imide. By contrast, an isolable In=N species (**47**) can be produced using $MesN_3$, which, nonetheless, reacts with excess azide through a [2+3] cycloaddition reaction to afford the indium tetrazenido compound **48**.[44]

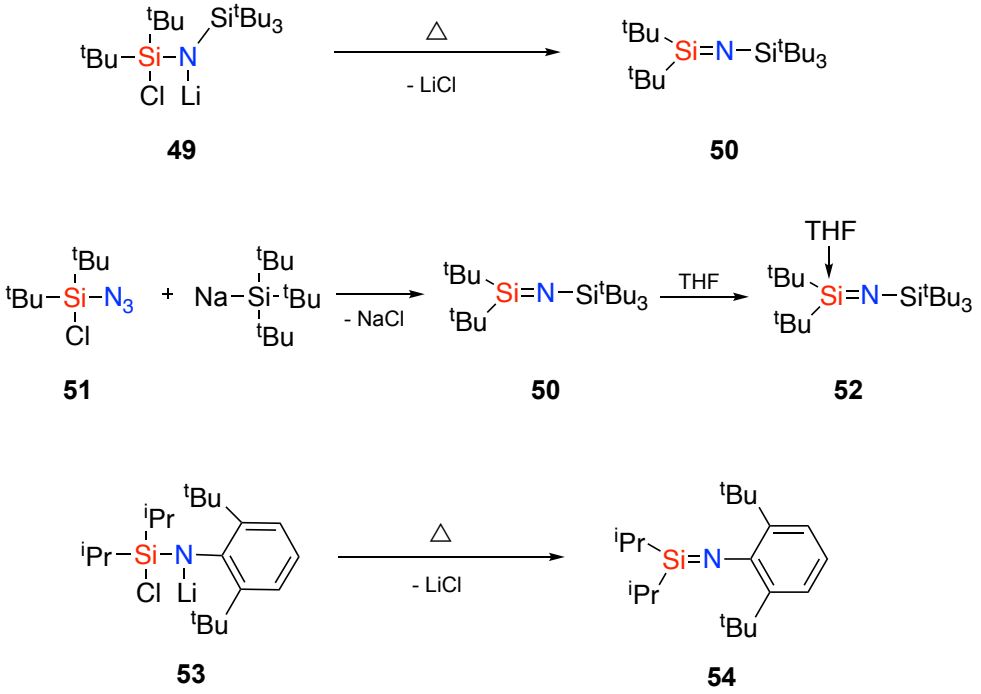



**Scheme 11.** Reduction of different organic azides by indyl-anions.

## Compounds featuring E14=N and related bonds

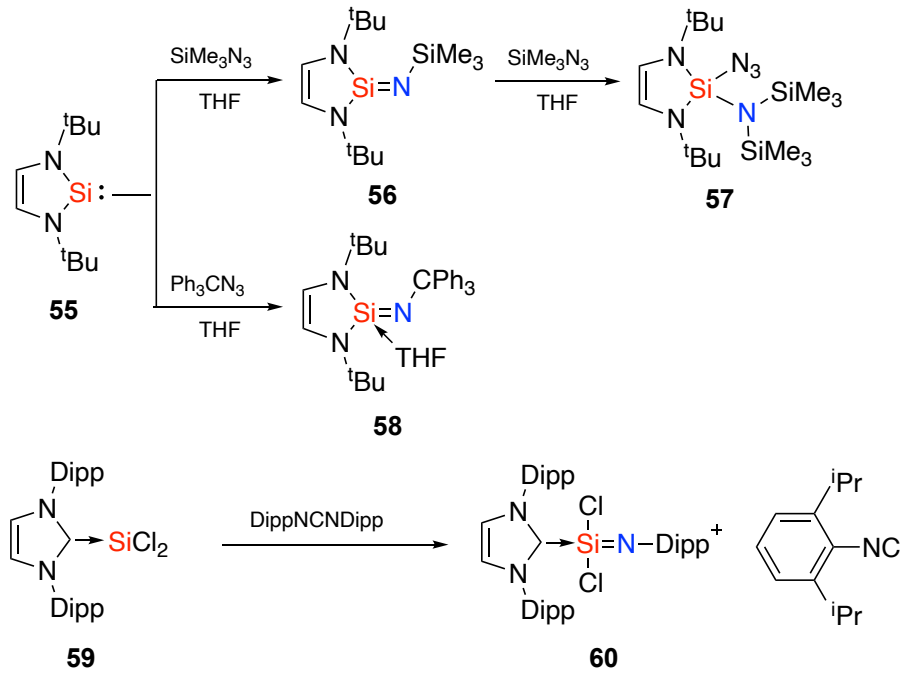
### *Silaimines*

Silaimines are fascinating compounds with the highly polarized $Si^{\delta+}$–$N^{\delta-}$ double bond, imparting high levels of reactivity.[45,46] The first stable silaimine $^{t}Bu_2Si{=}NSi^{t}Bu_3$ (**50**) was synthesized via the slow thermal elimination of LiCl from precursor **49**, and was reported by the group of Wiberg in 1985.[47] One year later, an alternative route to **50** was established via the reaction between the corresponding azido-chlorosilane and silyl sodium, a reaction which affords the THF-coordinated adduct **52** and THF-free **50** (Scheme 12).[48] In the same year, another base-free silaimine $^{i}Pr_2Si{=}N(C_6H_2{}^{i}Pr_3\text{-}2,4,6)$ (**54**) was successfully isolated by Klingebiel and coworkers.[49]




**Scheme 12.** The early syntheses of THF coordinated and free silanimines.

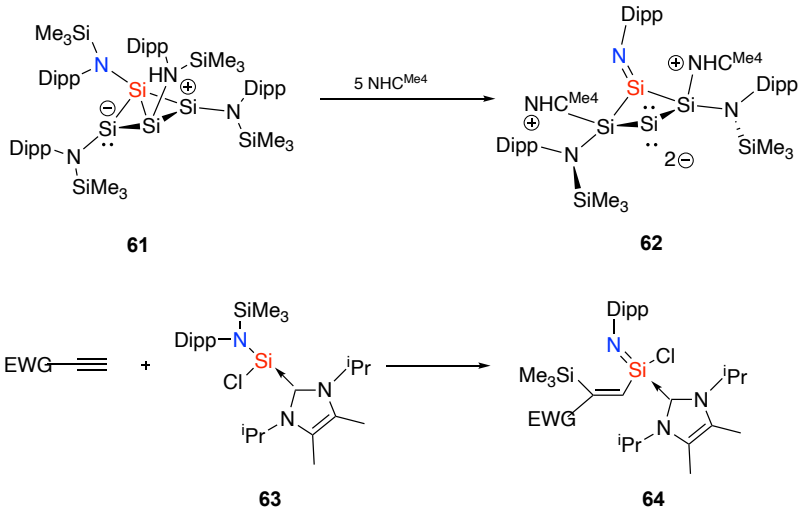
Subsequently, with the development of a series of stable base-free and base-stabilized silylenes,[50–52] a third route to silaimines - through the direct reaction of silyenes with organic azides - has been extensively explored. This method for silaimine synthesis was first reported by Denk and co-workers in 1994.[53] The reaction of a stable silylene **55** with trityl azide, $Ph_3CN_3$, leads to rapid evolution of nitrogen gas and formation of the base-stabilised silaimine **58**. By contrast, in the reaction with the less sterically encumbered substrate $Me_3SiN_3$, the initially formed (unstable) silaimine is trapped by the addition of a second equivalent of azide, yielding the corresponding azidosilane **57**.




**Scheme 13.** Reaction of the stable silylenes with covalent azides/cabodiimides.

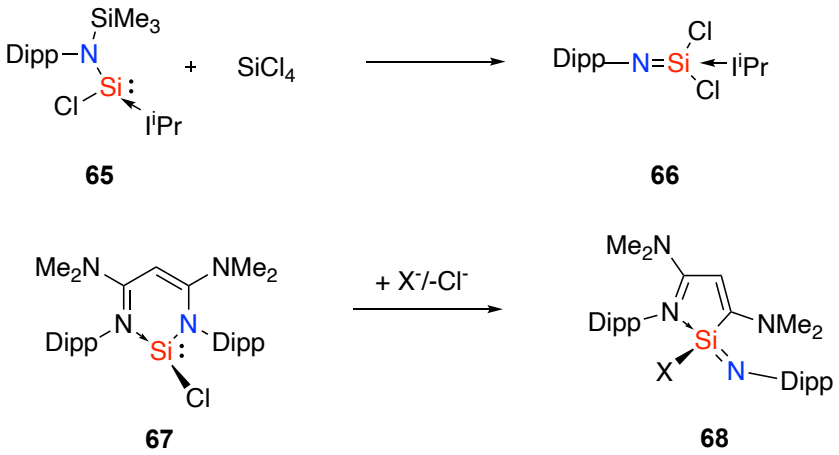
On the other hand, with silylenes now available, treatment with carbodiimides represents an alternative route to access silaimines. The Roesky group first reported the reaction of a bulky carbodiimide with silylene **59**, which unexpectedly afforded the carbene-stabilised dichlorosilaimine **60**.[54]

In the absence of organoazides or carbodiimides, compounds that feature Si=N double bonds can be generated by silyl shift reactions. For example, the cyclic carbene-stabilised silicon compound **62** featuring a Si=N double bond and a two-coordinate Si center, was isolated from the reaction of bicyclic silamide **61** with 5 equiv. of $NHC^{Me4}$.[55] On the other hand, Cui and coworkers demonstrated that the reactions of silylene **63** with electron-deficient alkynes provides a facile 1,4-silyl migration route to the corresponding alkenes, with accompanying formation of a Si=N bond.[56]




**Scheme 14** Examples of silyl shift reactions to synthesise silaimines.

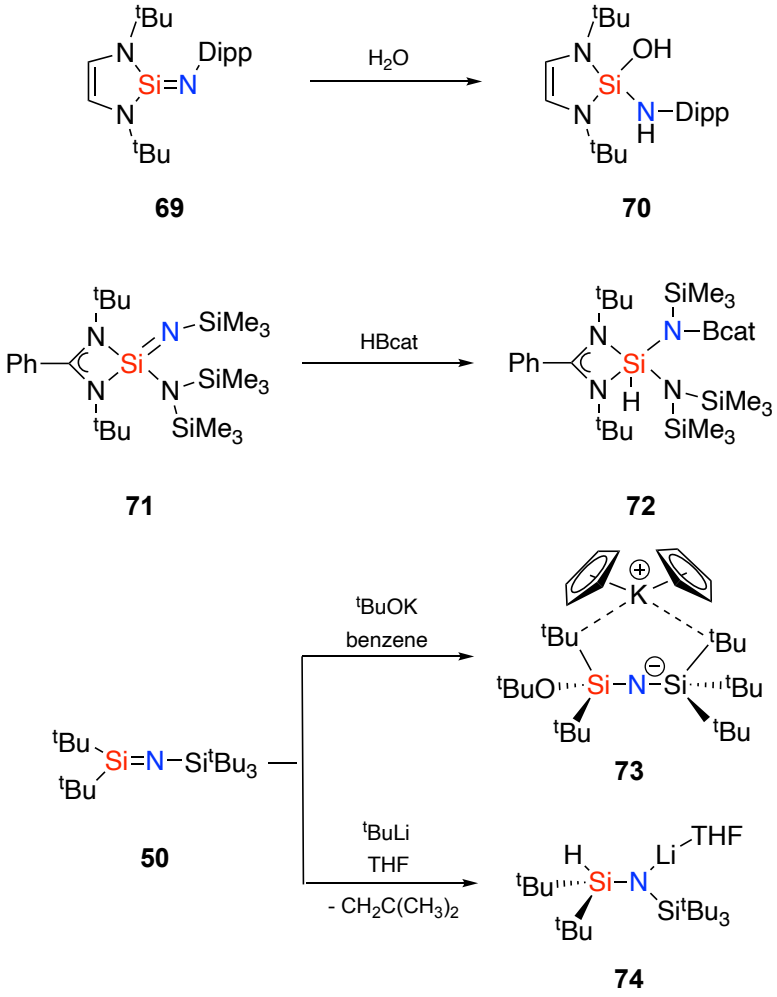
Subsequently, the same group also reported that NHC-supported silylene **65** reacts with $SiCl_4$ to give base-stabilized silaimine **66**, which decomposes completely in $C_6D_6$ at 70 °C.[46] More recently, the use of an amino-functionalised β-diketiminate ligand in silylene chemistry has been shown by the Aldridge group to give access to iminosilane systems; heterocyclic ring contraction of the 6-membered ring to a 5-membered ring accompanies Cl-substitution, yielding silaimines of type **68**.[57]




**Scheme 15** Other synthetic routes to silaimines.

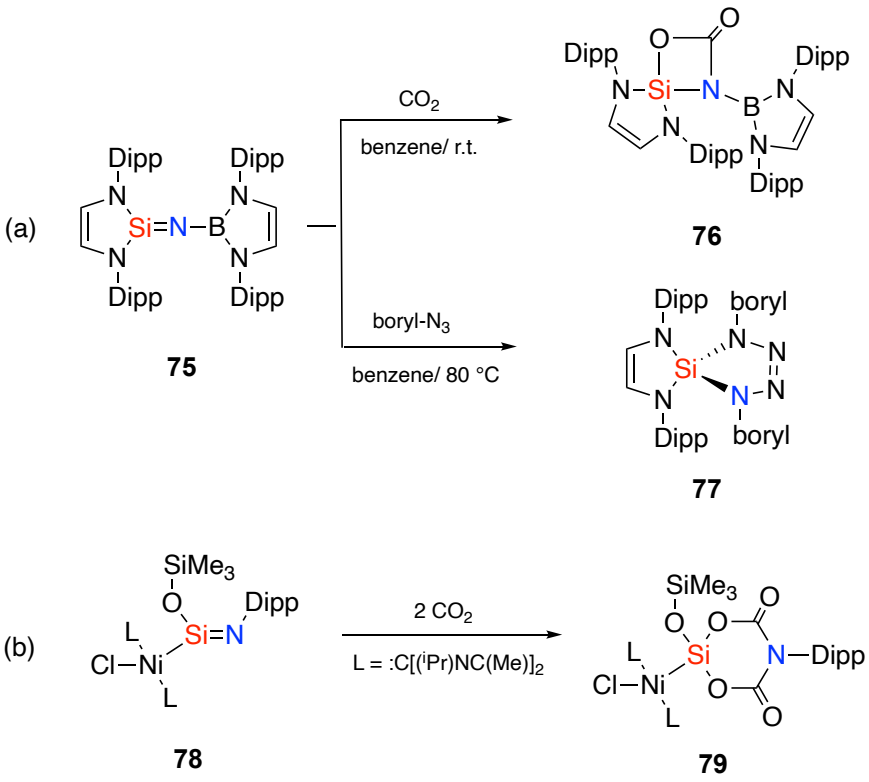
As a range of base-free and base-stabilized silaimines have now been reported their patterns of reactivity have started to emerge; Si=N doubly bonded systems are expected to be highly reactive due to the electronegativity difference between Si and N, and the relatively weak nature of the associated π-bond.[58] Many silaimine species exhibit the capacity for onward activation of the Si=N bonds via addition/cycloaddition reactions.

Cui and co-workers demonstrated a representative example of 1,2-addition to the Si=N bond. The reaction of a base-free N-heterocyclic silanimine **69** with water resulted in the amino-silanol **70**, which is characterized by two singlet peaks ($\delta_H$ = 3.96, 2.46 ppm) consistent with the formation of Si-OH and N-H bonds.[59] In another example, the reaction of silaimine **71** with the borane HBcat proceeds through cleavage of the B-H bond, as indicated by the appearance of a new $^{11}$B NMR signal at 26.9 ppm.[58] The Harder group further reported the addition of polar reagents to silaimine **50**, including metal alkoxides such as KO$^t$Bu and AdOK, driven by the thermodynamically favorable affinity of Si for O. By contrast, the treatment of **50** with $^t$BuLi in THF, resulted in 1,2 addition of LiH (rather than $^t$BuLi) to the Si=N bond, yielding the lithium amide complex $^t$Bu$_3$Si($^t$Bu$_2$HSi)NLi(THF), **74**.[60]




**Scheme 16** Examples of 1,2 additions to silaimines.

The Jones group demonstrated that silaimine **75** undergoes a [2+2] cycloaddition with $CO_2$ to form $(HCDippN)_2Si\{OC(=O)N[B(NDippCH)_2]\}$ under mild conditions, while the reaction with the bulky boron azide $(HCDippN)_2BN_3$, affords a borasilatetrazoline **77** via a [3+2] cycloaddition reaction.[61] In addition, Driess *et al.* have reported that metallo-iminosilane **78** reacts with $CO_2$, to form the siladicarboxylate **79**, via a net [2+2+2] cycloaddition pathway.[62]

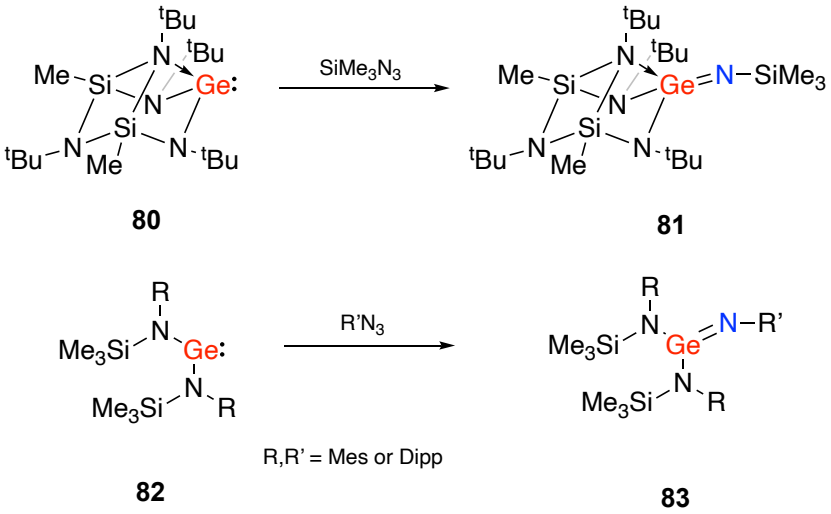



**Scheme 17.** Cycloaddition of silaimines (a) [2+2]/[2+3] cycloaddition (b) [2+2+2] cycloaddition.

***Germaimines***

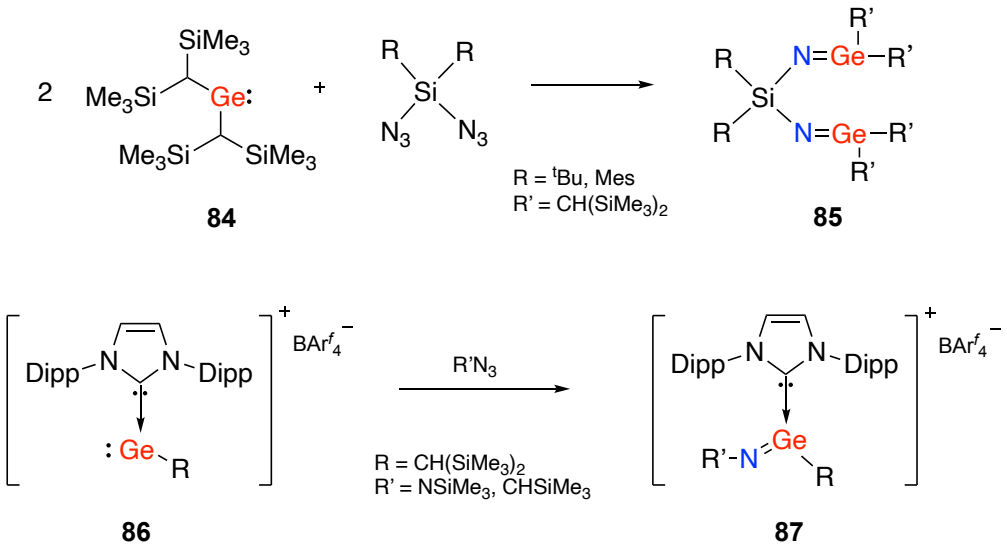
Compared to C=N and Si=N double bonds, the Ge=N double bond is more polarized and weaker due to poorer overlap between the germanium and nitrogen orbitals, resulting in these systems being more reactive and difficult to isolate.[63] The first evidence for a germaimine was as an intermediate in the reactions of germylenes with phenyl azide, leading to the formation of cyclic or linear germazanes featuring -[Ge-N]$_n$- linkages in the final product(s).[64] Subsequently, a Lewis base stabilized Ge=N-containing compound was obtained from the reaction of base-stabilised germylene **80** with trimethylsilylazide. The Ge=N double bond (1.688(9) Å) is significantly shorter than a typical single Ge-N bond (1.86 Å).[65,66] Subsequently,

Meller and coworkers reported the first isolable base free germanimines, **83**, from the reactions of $ArN_3$ with $[(Me_3Si)ArN]_2Ge$ (Ar = Mes or Dipp), with the structures being confirmed by X-ray diffraction,.[67] The Ge and N lengths were found to be between 1.691(2) and 1.703(2) Å, in good agreement with *ab initio* predictions based on the simpilified system $H_2Ge{=}NH$ (1.695 Å).[68]



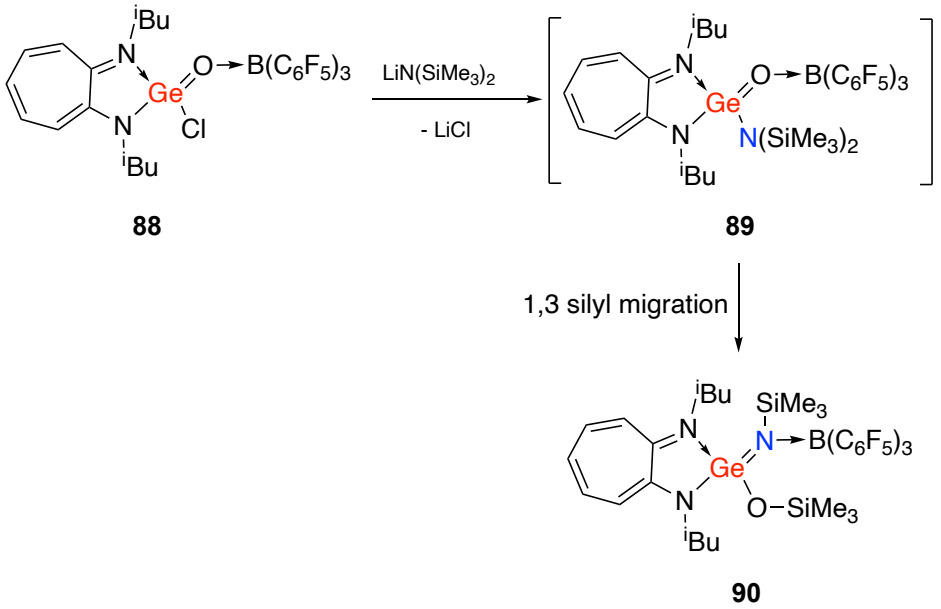

**Scheme 18.** The first syntheses of base-stablised and -free germaimines.

The first bis-germaimines (**85**) were synthesized by the Ando group through the reaction of bis[bis(trimethylsilyl)methyl]germylene with diazidosilanes in 1994.[69] More recently, a two-coordinate germanium cation was synthesized, which can be employed as a precursor to access the first example of a germanium cation featuring a Ge=N multiple bond (**87**). This work demonstrates that an electrostatic repulsion strategy can serve as an alternative to conventional steric protection to prevent oligomerization.[70]



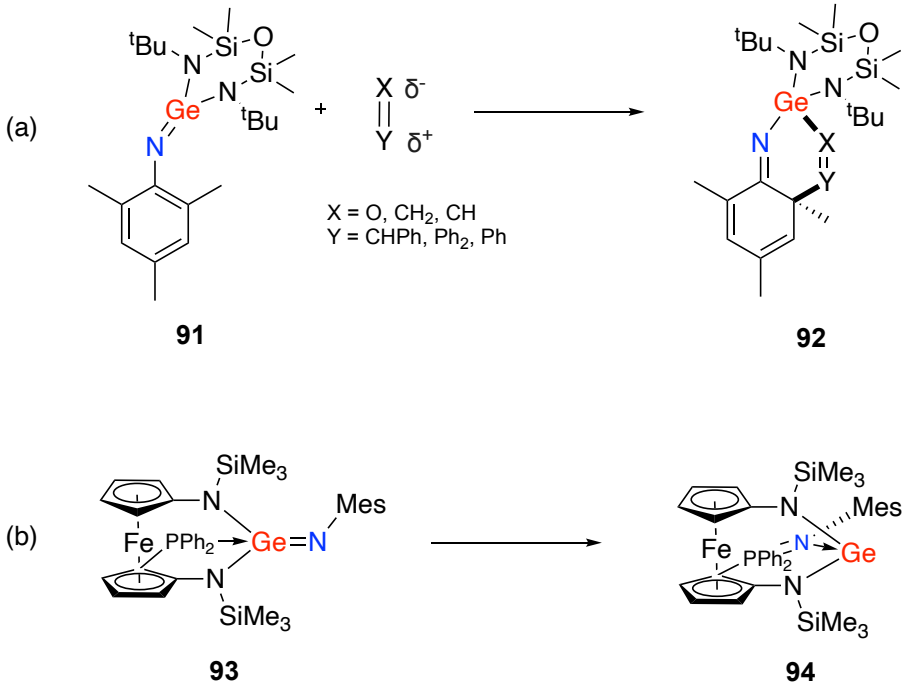

**Scheme 19.** The synthesis to different germaimines.

On the other hand, Nagendran *et al.* targeted the germaamide **89**, featuring a Ge=O bond, but this resulted in an unexpected (and stable) germaimine **90** via 1,3-silyl migration of a trimethylsilyl group from N to O.[71]




**Scheme 20.** The syntheses of germaimines by 1,3-silyl migration.

The polar Ge=N multiple bond bears some resemblance in terms of reactivity to transition metal imido compounds. As such, 1,2-addition/[2+2] cycloaddition reactions involving germaimines have been widely explored that resemble those of transition metal imido complexes.[72–75] Notably, the Fulton group demonstrated unusual [4+2] cycloaddition reactions, a metallo-Diels-Alder type reaction between (NON$^{tBu}$)Ge=NMes **91** and aldehydes, ketones, alkenes, and alkynes. Aryl stabllized germanimines were also shown to be subject to activation of intramolecular C-H bonds.[76] In 2022, the Siemeling group reported a donor functionalized germaimine **93** which slowly isomerizes to the corresponding iminophosphorane germylene **94**.[77]

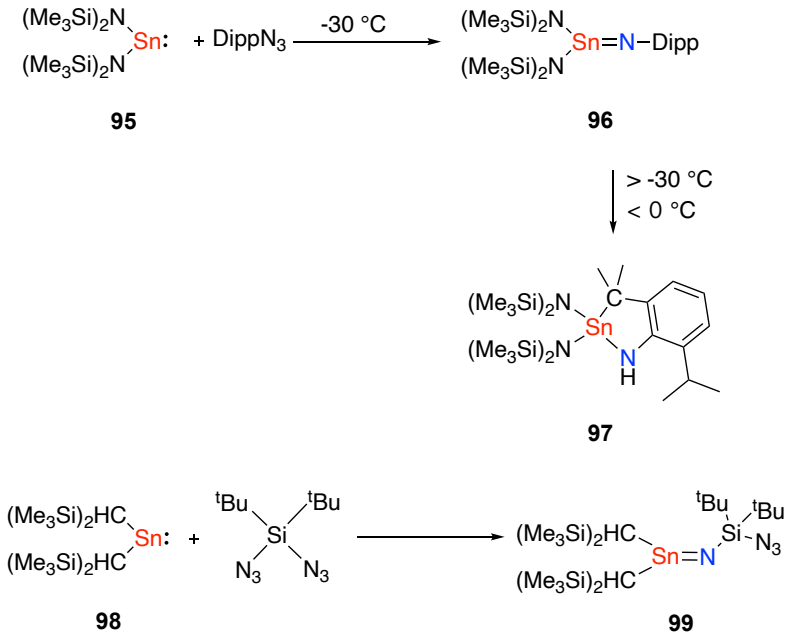



**Scheme 21.** (a) Metallo-Diels-Alder reaction of a germaimine; (b) $RN^{2-}$ group migration.

***Stannaimines***

Despite the rapid development of heavier group 14 imine derivatives, examples of isolable

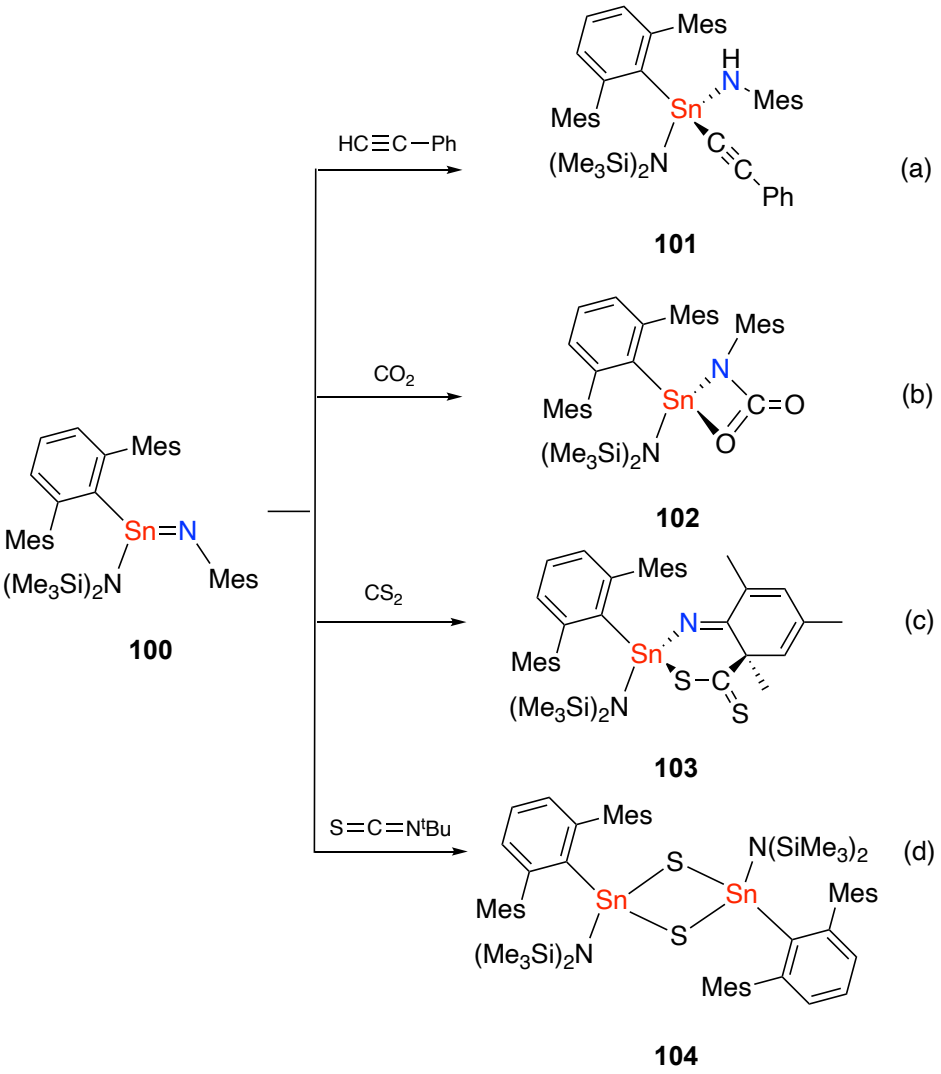
stannaimines are still rare, due to the fact that species containing the Sn=N unit are polar and poorly π stabilized, and therefore extremely reactive. In 1993, the first stannaimine **96** was isolated, which is stable at low temperatures (-30 °C); the Sn=N double bond activates the C-H bond of one of the Dipp groups intramolecularly above 0 °C.[78] Remarkably, the $^{119}$Sn spectrum of the stannanimine exhibited a high field signal at -3.5 ppm, in contrast to the downfield chemical shifts typically observed for Sn=P complexes.[79] One year later, the first room temperature stable N-(azidosilyl)stannanimine **99** was reported by Ando and co-workers. Treatment of the stannylene **98** with diazidosilane, resulted in the formation of stannaimine **99**, using a similar synthetic strategy to that employed for the preparation of the first germaimine (seen above).




**Scheme 22.** The first syntheses of stannaimines.

Three decades later the Aldridge group reported three new stannaimines which are stable under ambient conditions, including **100** – which is supported by sterically bulky σ- and π-

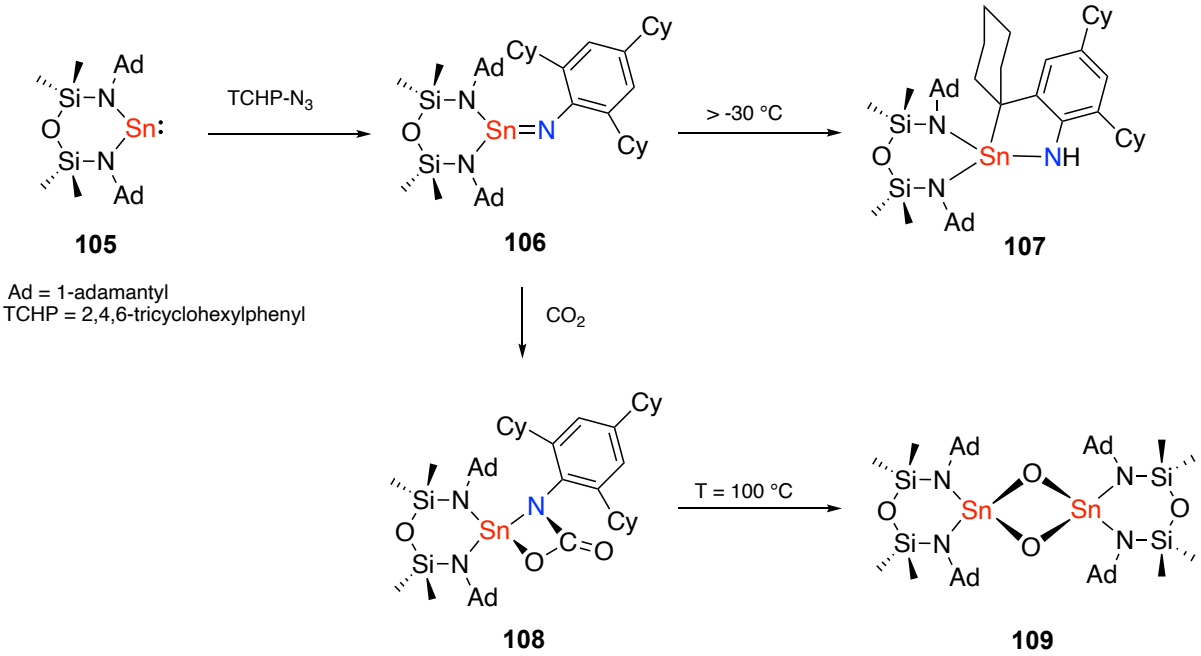
donor substituents. In terms of reactivity, 1,2-addition reactions, [2+2] and [4+2] cycloaddition reactions, and rare 14 group double bond metathesis chemistry have been demonstrated in detail.[80]




**Scheme 23.** Stannaimine reactivity: (a) 1,2-addition reactions; (b) [2+2] cycloaddition reactions; (c) [4+2] cycloaddition reactions; (d) metathesis chemistry.

More recently, stannaimine **106** was synthesized at – 30 °C from the corresponding stannylene; **106** is stable in the solid-state, but activates a C-H bond of one of the pendant Cy groups in solution. **106** was also shown to engage in metathesis chemistry with $CO_2$ at high

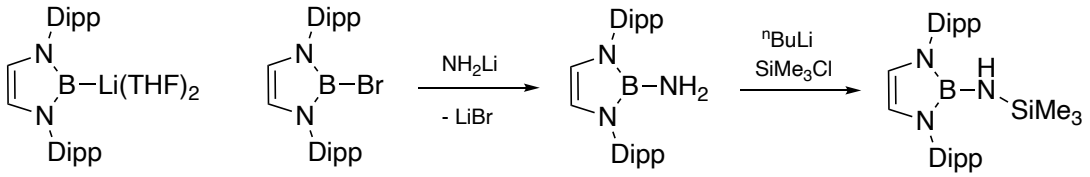
temperatures, via a mechanism involving an initial Sn=N/O=C cycloaddition reaction.[81]




**Scheme 24.** Synthesis of stannaimine **106** and its metathesis chemistry with $CO_2$.

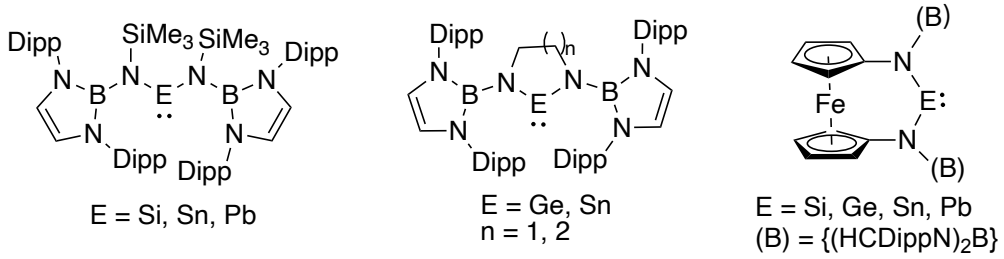
***Borylamine/Borylimido Compounds***

The steric bulk Dipp-substituted diazaborolyl group {$(HCDippN)_2B$} has been widely used to access electron-rich main group complexes, owing to its strongly donating properties.[82–94] To avoid the challenges associated with the synthesis of the lithium reagent {$(HCDippN)_2B$}$Li(THF)_2$,[82–84] the more accessible bromoborane reagent {$(HCDippN)_2$}BBr can be reacted with $NH_3$ to afford the bulky borylamine $(HCDippN)_2BNH_2$,[95] which in turn can be reacted with $Me_3SiCl$[95] or $Ph_3SiCl$[96] after deprotonation with $^nBuLi$. These protio-ligands, {$(HNDippN)_2$}$BN(SiR_3)H$ have the potential to be deprotonated and the resulting (boryl)(silyl)imides can act as weaker N π-donors (compared to more commonly used amide ligands) due to N→B π bonding. [95,97,98]




**Scheme 25.** Precursors to Dipp-substituted borylamide ligands

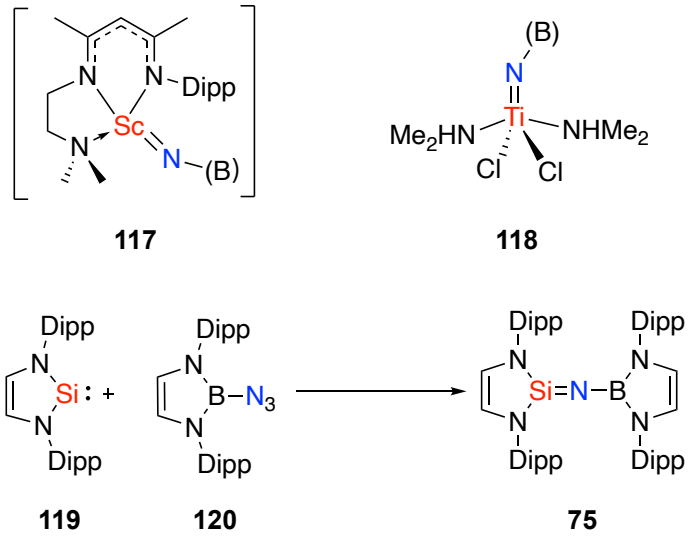
From these borylamines in hand, further deprotonation typically affords alkali metal amides which can be used as ligands to stabilize acyclic low oxidation state group 14 compounds (e.g. **114**).[95] Notably, the Jones group demonstrated the formation of germanium(I) and tin(I) dimers and clusters stabilized by (boryl)amido ligands.[98] Moreover, to access saturated N-heterocyclic germylene and stannylene compounds of type **115**, the Aldridge group showed that the readily available bromoborane $\{(HCDippN)_2\}BBr$, could be reacted with 1,2-diaminoethane or 1,3-diaminopropane in the presence of the triethylamine to generate bifunctional borylamines, from which the corresponding cyclic gerymylene and stannylene systems could then be accessed.[99] Similarly, Siemeling *et al.* utilized a similar method to synthesize the ferrocenediyl-backbone N-heterocyclic tetrylenes **116** (Si-Pb).[100]




**Scheme 26.** Examples of borylamide-supported tetrylene compounds.

In addition to boryamides, borylimido ligands have reported in association with group 3 and 4

transition metals (notably Sc[101] and Ti[102,103]). The only known example of a main group (borylimido) complex was reported by Jones and co-workers to be synthesized by the reaction of a cyclic silylene and the bulky boron azide $(HCDippN)_2BN_3$.[61] The reactivity of these silaimines with respect to cycloaddition has been discussed above (see Scheme 17a).




**Scheme 27.** (upper) Examples of group 3/4 borylimides; (lower) an example of a boryl substituted silaimine.

***Aims of the work***

Through a combination of synthetic, spectroscopic, crystallographic, and computational analysis, the work aims to highlight new ligand design supported by bulky boryl ligands, advancing the chemistry of E–N multiple bonds. The primary objective is to explore the chemistry of iminoboranes with a particular emphasis on the development of all-inorganic cumulenes. While cumulenes are well established in organic chemistry, their inorganic analogues remain rare. This study aims to synthesise a novel class of all-inorganic heterocumulene stabilised by bulky diazaborolyl substituents. After that, the metathesis

reactivity and the cumulene as a precursor for a dianionic bis(borylamido) ligand are further researched.

The secondary aims focus on Group 14 imido chemistry, particularly the stabilisation of heavier imines. The Si(II) species have been widely synthesised, but silicon-containing compounds, as well as spontaneous reductive processes from Si(IV) precursors to Si(II) species, are scarce. This thesis demonstrates that sterically demanding boryl and amidinate ligands can facilitate unusual reactivity in silaimine complexes, enabling reversible Si(IV)/Si(II) redox shuttling without the need for additional reagents.

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## Chapter 2. Syntheses and geometric modification of inorganic cumulenes

### Introduction

Iminoboranes (RB≡NR′) are isoelectronic with alkynes but exhibit distinct reactivity due to the polarized and relatively weak nature of the B≡N triple bond. The most common synthetic route involves base-promoted dehydrohalogenation of aminoboranes. Alternatively, nitrogen atom transfer from diazo compounds such as $Me_3SiN_3$ offers a mild and efficient synthetic pathway.

Although various stable iminoboranes have been isolated, few examples of all-sp-hybridized chains (above 3 atoms) of B and N atoms have yet been reported. In this chapter, a novel class of all-inorganic heterocumulene is disclosed, including a five-atom BNBNB chain, which is isoelectronic with carbon-based cumulenes. The BNBNB core is stabilized by terminal diazaborolyl groups, and its geometry can be modulated from bent to linear via modification of the end groups using $B(C_6F_5)_3$.

**Inorganic cumulenes: tuning the geometric and electronic structure of a five-atom BNBNB chain**

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**Abstract**

Molecular chains of two-coordinate carbon atoms (cumulenes) have long been targeted, due to interest in the electronic structure and applications of extended π systems, and their relationship to the carbon allotrope, carbyne. While formal (isoelectronic) B=N for C=C substitution has been employed in 2-D materials, unsaturated one-dimensional all-inorganic 'molecular wires' are unknown. Here, we report high-yielding synthetic approaches to hetero-cumulenes containing a five-atom BNBNB chain, the geometric structure of which can be modified by choice of end group. The diamido-capped system is bent at the 2-/4-positions, and natural resonance theory calculations reveal significant contributions from B=N(:)–B≡N–B resonance forms featuring a lone pair at N (consistent with observed N-centred nucleophilicity). Molecular modification to generate a linear system best described by a B=N=B=N=B resonance structure involves chemical transformation of the capping groups (using $B(C_5F_5)_3$) to enhance their π-acidity and conjugate the N-lone pairs.

**Introduction**

Cumulenes are a family of carbon-rich molecules featuring a contiguous chain of two-coordinate carbon atoms terminated at each end by a three-coordinate carbon centre. A chain of *n*+1 carbon atoms linked via *n* C=C double bonds in this way defines an [*n*]cumulene ($n \geq 3$), with examples featuring 'simple' aryl end groups typically adopting geometrically linear structures (e.g. **I**, Figure 1).[1–3] The rigid, conjugated frameworks of these systems have

attracted interest in the context of applications as semi-conductors,[4,5] and as single-molecule wires,[6–8] as well as models for the carbon allotrope carbyne.[9,10]

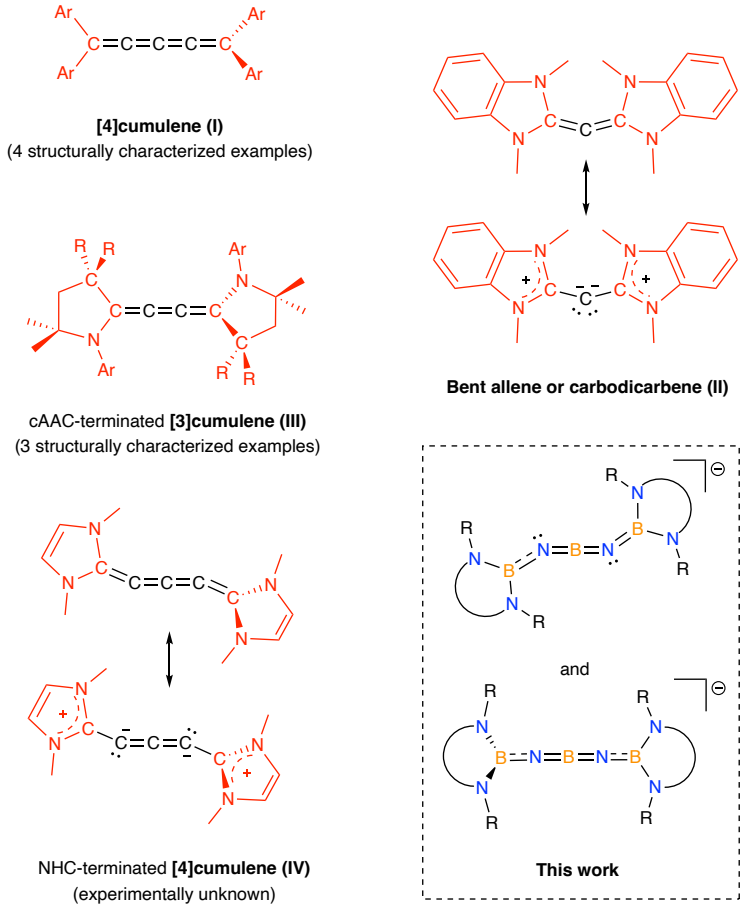



**Figure 1**: Cumulene and related systems of relevance to the current study.

More recently, [*n*]cumulenes featuring $CX_2$ end groups formally derived from *cyclic* carbenes have attracted significant interest due to their ability to stabilise alternative non-linear geometries within the *n*-1 two-coordinate carbons of the 'encapsulated' fragment. Although not strictly cumulenes (since $n < 3$), this scenario is exemplified by related bent allene systems (e.g. **II**),[11,12] which can also be described in terms of a contributing carbo-dicarbene resonance structure. Recent quantum chemical calculations suggest that the π-acceptor capabilities of the carbene fragment are crucial in determining the stability of a linear geometry relative to

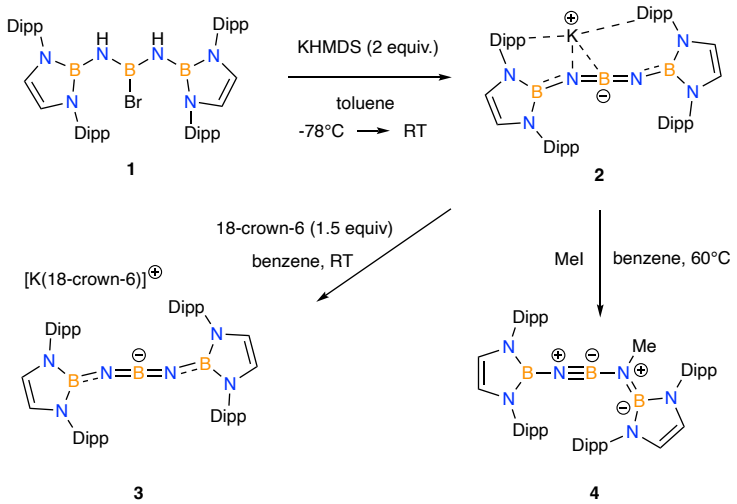
alternative bent structures featuring lone pair character at the 2-position. As such, the relative π-acceptor capabilities $CAr_2$ > cAAC > NHC (cAAC = cyclic amino alkyl carbene; NHC = N-heterocyclic carbene) suggests that non-linear structures are most likely to be encountered with NHC termini. Consistently, each of the (three) cAAC-terminated [3]cumulenes (**III**) reported to date is linear,[13–15] in similar fashion to systems featuring $CAr_2$ end units, while NHC-terminated [4]cumulenes (**IV**) are calculated to possess bent ground state geometries.[16] That said, no examples of NHC terminated cumulenes of *any* chain length (i.e. $n \geq 3$) have yet been structurally characterized to validate these claims.

The isolobal substitution of C=C for B=N dinuclear units represents a powerful design formalism that has been widely exploited in the synthesis of conjugated 2D materials derived from polycyclic aromatic hydrocarbons.[17–19] The application of this approach to cumulenic systems, however, has not been developed, despite the possibility for novel electronic properties stemming from the conjugation of *polar* unsaturated B=N units. Three-atom NBN[20–22] and BNB[23–25] chains have been reported, but the only longer example featuring alternating BN units, is a four-atom chain stabilised within the coordination sphere of a transition metal.[26] We have recently been interested in the synthesis of unsaturated compounds integrating BN units within an extended (conjugated) chain, and the modulation of electronic properties that result.[27] As part of these studies, we report here the first example of an inorganic analogue of a cumulene, a system with features a five-atom BNBNB chain and which, depending on the nature of the end groups, can possess either a bent or linear geometric structure.

## Results and Discussion

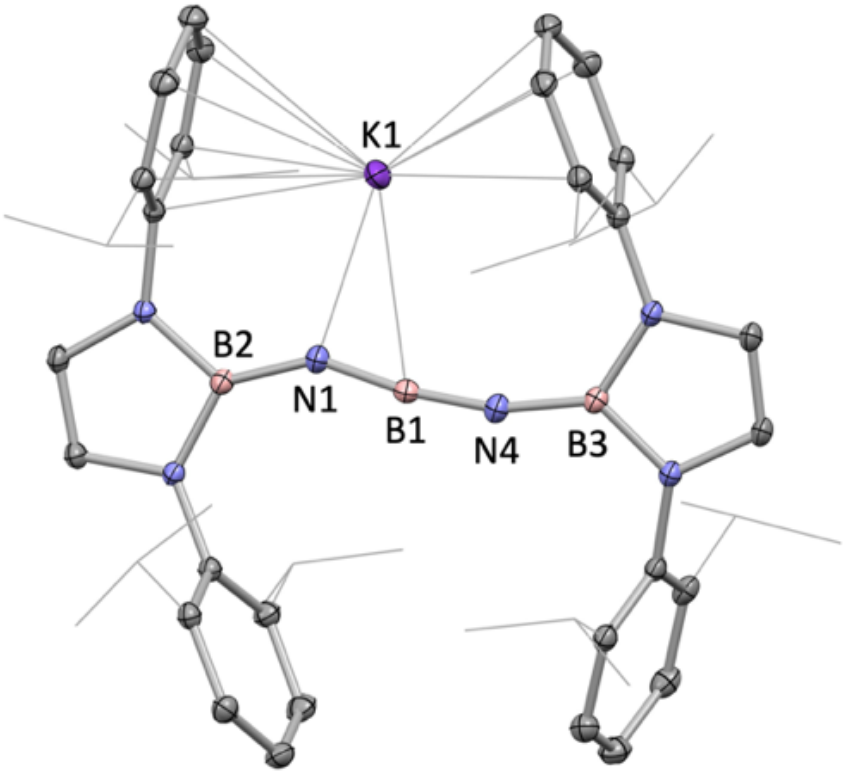
*Synthetic chemistry*

The reaction of {(HCDippN)$_2$}BNH$_2$ (borylNH$_2$) with BBr$_3$ in a 2:1 ratio in toluene in the presence of excess NEt$_3$ leads to the formation of ({(HCDippN)$_2$}BNH)$_2$BBr ((borylNH)$_2$BBr; **1**), which can be isolated as colourless crystalline material in 70% yield (Scheme S1). Subsequent double deprotonation of **1** can be achieved using two equivalents of K[N(SiMe$_3$)$_2$], to generate K[{(HCDippN)$_2$}BNBNB{(NDippCH)$_2$}] (**2**) in 66% yield (Scheme 1). **2** has been characterized by multinuclear NMR, elemental microanalysis and single crystal X-ray diffraction (Figure 2a). The $^{11}$B NMR signal for the diazaborolyl capping moieties is found at similar chemical shift to that for **1** ($\delta_B$ = 21.1 ppm, *cf.* 22.2 ppm), but the resonance associated with the central (two-coordinate) boron centre is too broad to be resolved from the baseline. The simple pattern of $^1$H NMR signals measured for **2** (e.g. one CH and two CH$_3$ signals for the Dipp substituents) implies rapid exchange of the K$^+$ counter-ion between equivalent sites on the NMR timescale.

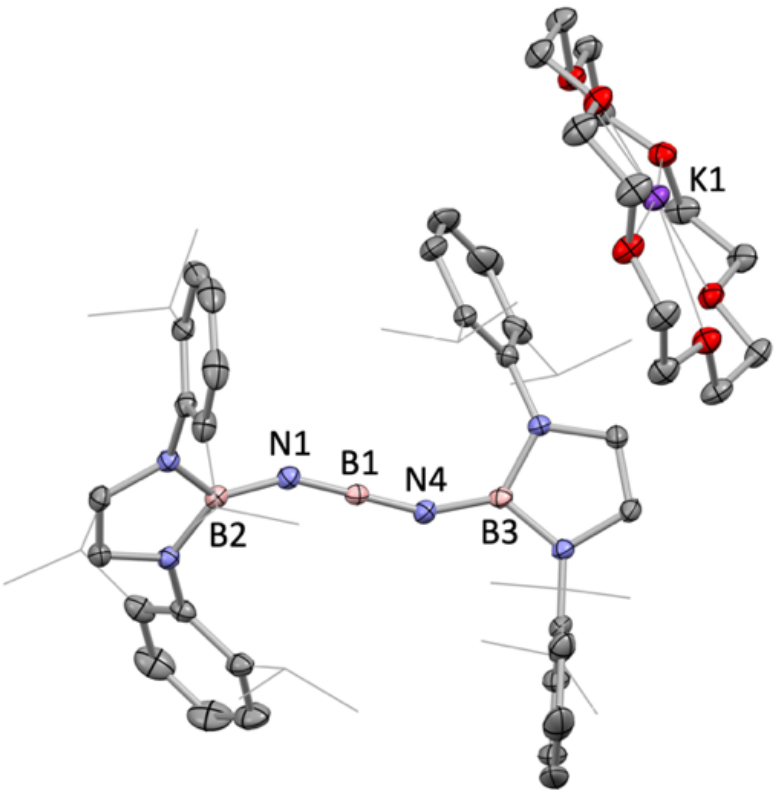



**Scheme 1**: Syntheses of compounds **2**–**4** from boryl-functionalized diamino(bromo)borane. **1**.

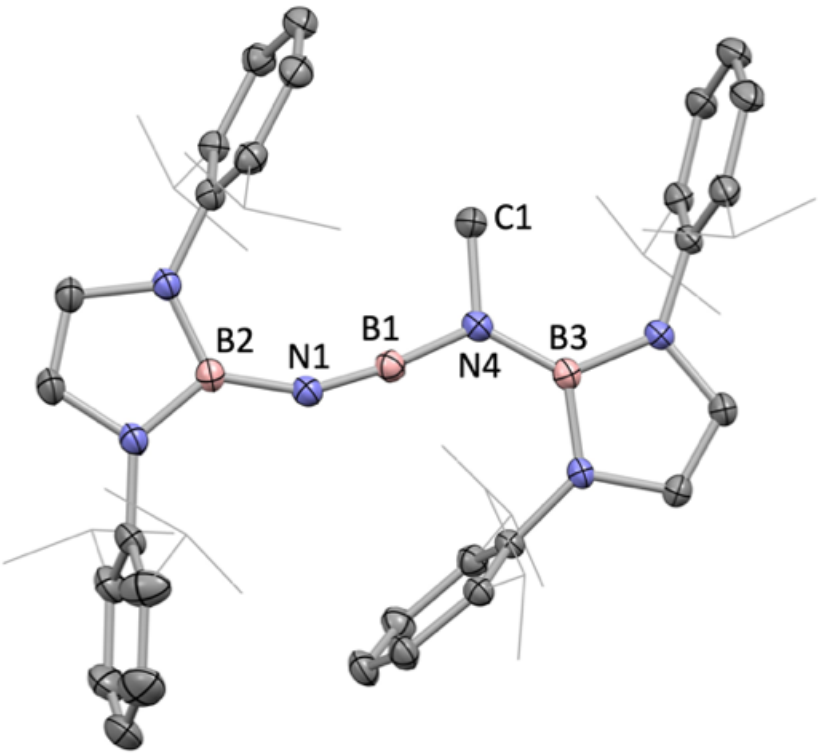
(a)




(b)



(c)




(d)

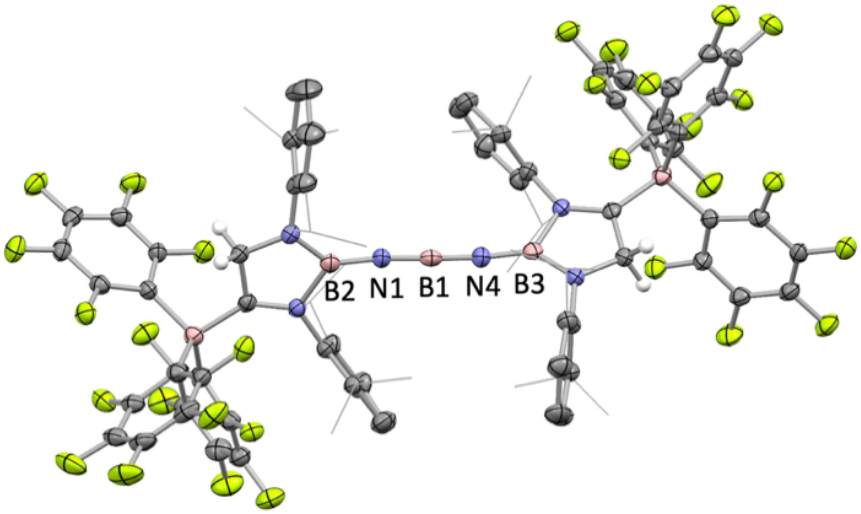



**Figure 2:** Molecular structures of (a) **2**, (b) **3**, (c) **4** and (d) the anionic component of **5** in the solid state as determined by X-ray crystallography. Benzene solvate molecule (for **2**), second disorder component (for **4**), counter-cation (for **5**) and all Hs omitted. $^{i}$Pr groups shown in wireframe format for clarity and thermal ellipsoids shown at the 35% probability level. Key bond lengths and angles listed in Table 1.

Sequestration of $K^+$ from **2** can readily be effected by the use of 18-crown-6 to yield [K(18-crown-6)][{(HCDippN)$_2$}BNBNB{(NDippCH)$_2$}] (**3**), which can be obtained as single crystals from benzene solution, and shown to consist (in the solid state) of well separated anionic and cationic components (Scheme 1 and Figure 2b). **3** has been characterized in similar fashion to **2**, and gives rise to analogous patterns of signals in the respective $^1$H and $^{13}$C NMR spectra; the $^{11}$B signal corresponding to the central boron atom is again too broad to be resolved.

Preliminary probes of the nucleophilic reactivity of the anionic component of **2**/**3** were carried out by exposure to MeI. The reaction proceeds via nucleophilic attack of one of the exocyclic nitrogen atoms at the electrophilic carbon, leading to the formation of {(HCDippN)$_2$}BNBN(Me)B{(NDippCH)$_2$} (i.e. (boryl)NBN(Me)(boryl), **4**). **4** has been characterized in the solid state by X-ray crystallography (Figure 2c), and in solution by multinuclear NMR methods, and can plausibly described as an iminoborane (XB≡NX') with boryl and amido X/X' substitutents, respectively. Desymmetrization is signalled by the pattern of resonances observed in the $^1$H NMR spectrum, e.g. two Dipp CH signals at 3.12 and 3.27 ppm, four Dipp $CH_3$ signals (at 1.15, 1.17, 1.23 and 1.27 ppm) and two boryl backbone resonances (5.84 and 5.96 ppm) for the methylated compound **4**.

*Geometric and electronic structure*

The structures of compounds **2**-**4** have been determined crystallographically. Each features a five-atom BNBNB framework capped at either end by two formally dianionic diazabutadiene

moieties. The structure of **3**, in particular, allows for discussion of geometric parameters of the BN-containing anion free from the perturbation of the associated counter-cation. The geometry around the central boron atom (B(1)) is linear (179.7(3)°), while the B–N–B angles around the exocyclic nitrogens (N(1) and N(4)) are narrower (151.3(2) and 152.0(2)°; Table 1). This bent geometry is consistent with that calculated for the (hypothetical) NHC-terminated [4]cumulene {(HCMeN)$_2$C}=C=C=C={C(NMeCH) which features an angle at C(2) of 136.7°(albeit with a relatively flat potential energy profile for bending in the region 120 - 180°).[16] Interestingly, the torsion angle between the two least-squares diazaborollyl planes (52.4°) falls close-to-midway between the idealised angles expected for even (90°) and odd cumulenes (0°).

The B–N distances associated with B(1) are short (1.307(4), 1.308(4) Å), with those involving B(2)/B(3) being somewhat longer (1.379(3), 1.383(4) Å), consistent with the increased coordination number at boron. In a broader context, the B(1)–N distances can be compared to compounds containing formal B≡N triple bonds, which are markedly shorter (e.g. 1.228(3) Å for Mes*BNNBMes*; Mes* = 2,4,6-$^t$Bu$_3$C$_6$H$_2$),[28–32] and to the BN distance between the two-coordinate boron and nitrogen centres in methylated derivative **4** (1.265(3) Å), which can also be described in terms of a resonance structure incorporating a B≡N triple bond. The B(1)–N distances are, however, noticeably shorter than typical B=N double bonds e.g. those found in the linear $BN_2^{3-}$ trianion (1.358(6) Å),[33,34] or in aminoboranes (e.g. 1.376(4) Å for $^i$Pr$_2$NB(C$_6$F$_5$)$_2$).[35] Consistently, the solid-state IR spectrum of **3** shows a band at 1890 cm$^{-1}$ (Figure S5), which is assigned to the antisymmetric BN stretching vibration of the central NBN unit, based on quantum chemical simulation. This can be compared to the antisymmetric BN

stretch measured for $BN_2^{3-}$ (1664 $cm^{-1}$),[36] and bands associated with the stretching of B≡N bonds, which fall between 1879 and 1982 $cm^{-1}$.[37–39]

In the case of **2**, which features a more closely bound $K^+$ counterion (e.g. K···N(1), K···B(1) and K···$C_{arene}$ contacts of 2.710(1), 3.019(1) and 3.167(1)-3.421(1) Å), the general structural features of **3** pertain, but there is a notable asymmetry in the B(1)–N distances (1.319(2), 1.286(2) Å), reflecting a shortening in the B(1)N unit remote from the $K^+$ counterion.

**Table 1.** Selected bond lengths (Å) and angles (°) associated with the central BNBNB unit of K[{(HCDippN)$_2$}BNBNB{(NDippCH)$_2$}] (**2**), [K(18-crown-6)][{(HCDippN)$_2$}BNBNB{(NDippCH)$_2$}] (**3**), {(HCDippN)$_2$}BNBN(Me)B{(NDippCH)$_2$} (**4**) and [{($H_2C(Ar_3B)C$(DippN)$_2$}BNBNB{(NDipp)$_2$C($BAr_3$)$CH_2$)}]$^-$ (the anionic component of **5**)

| | **2** | **3** | **4** | **5** |
|---|---|---|---|---|
| B(1)–N(1) | 1.319(2) | 1.308(4) | 1.265(3) | 1.278(7) |
| B(1)–N(4) | 1.286(2) | 1.307(4) | 1.398(3) | 1.295(7) |
| N(1)-B(1)-N(4) | 171.1(1) | 179.7(3) | 172.1(3) | 178.2(5) |
| B(2)–N(1) | 1.393(2) | 1.379(3) | 1.409(3) | 1.333(7) |
| B(3)–N(4) | 1.381(1) | 1.383(4) | 1.446(3) | 1.335(7) |
| B(2)-N(1)-B(1) | 147.0(1) | 152.0(2) | 153.8(2) | 174.1(4) |
| B(1)-N(4)-B(3) | 164.2(1) | 151.3(2) | 126.9(2) | 172.6(4) |

As in the case of **4**, this unsymmetrical structure can be rationalized in terms of an enhanced contribution from a resonance structure incorporating a B(1)≡N(4) triple bond (see below).

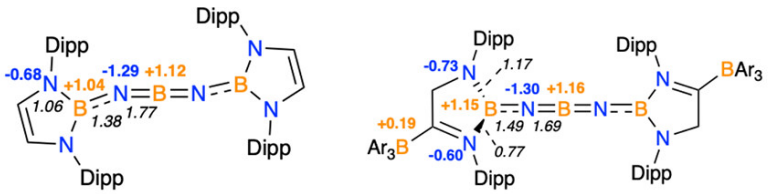
To better understand the electronic structure of **3**, density functional theory (DFT) calculations coupled with natural bond orbital (NBO) and natural resonance theory (NRT) analyses were carried out (Figure 3). The Mayer bond indices (MBIs) calculated for the two central bonds (B(1)−N(1) and B(1)−N(4)) are 1.77, while the corresponding values for B(2)−N(1) and B(3)−N(4) are lower (1.38), although still greater than those within the diazaborolyl heterocycles (1.06). NPA charge analysis determines (as expected) that the N atoms bear the negative charge (−1.29 au for N1/N4), while the central boron atom bears a positive charge (+1.12 au) and the three-coordinate borons charges of +1.04 au (Figure 3a). As such, the N-centered nucleophilic reactivity of these systems (i.e., reactions with electrophiles such as MeI) is readily understood.

Natural resonance theory (NRT) calculations were carried out to assess the relative contributions of different valence bond forms to the overall electronic structure of **3** (Figure 3b). This approach has proved to be highly informative in the case of novel compounds, particularly those comprised of elements from the second period of the Periodic Table. We exploited the simplified diminoborane model $[(H_2N)_2BNBNB(NH_2)_2]^-$, in order to avoid complications stemming from the large number of resonance structures associated with pendant aromatic rings and focus instead on the key BNBNB unit. In addition, we examined key resonance structures for both the (experimentally observed) bent geometry, and an alternative linear geometry. In contrast to the linear geometry, for which the dominant contributing structure (amounting to 31.9 %) features a contiguous chain of double bonds, B=N=B=N=B, the bent geometry is described best by four (essentially equivalent) B=N(:)–B≡N–B resonance forms, which involve a B≡N triple bond and a lone pair at the other N centre.[16] Taken together, these

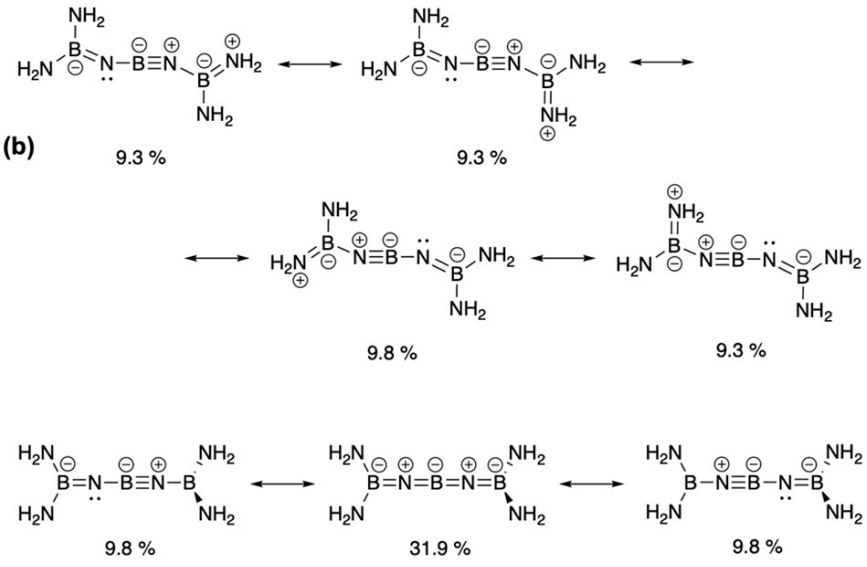
four resonance forms imply that there is BN π bonding across the central NBN unit in two orthogonal planes, while the BN units at the end of the chain are defined by π bonding in only one plane.

The molecular orbital picture of **3** reveals delocalized π systems along the central BNBNB fragment. The HOMO is, in effect, the out-of-phase combination of the nitrogen-based lone pairs (*E* = −2.97 eV, Figure 3c), while much lower-lying orbitals possess highly delocalized BN bonding character. As such, the HOMO−15 (*E* = −6.55 eV) is the in-phase combination of *p*π orbitals spanning the entire five-atom BNBNB chain, while the HOMO−14 (*E* = −6.23 eV) lies approximately orthogonal to it, and spans the central NBN core, lying closer to coplanar with the capping diazaborolyl heterocycles. In the case of compound **2**, the coordination of the $K^+$ counter-ion at one of the N atoms, presumably increases the B≡N character involving the remote (non-coordinating) nitrogen centre, and explains the observed shortening of the remote B(1)N(4) linkage in **2** compared to $K^+$-free **3**.

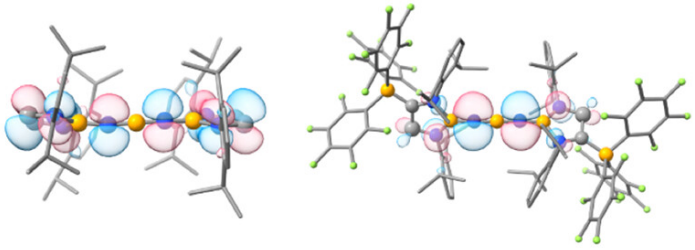
(a)




(b)

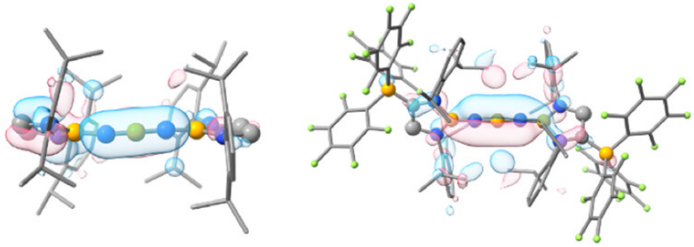



(c)



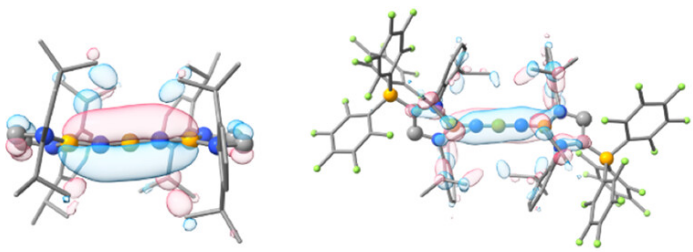
HOMO (**3**), -2.97 eV

HOMO (**5**), -5.66 eV



HOMO-14 (**3**), -6.23 eV

HOMO-24 (**5**), -8.10 eV



HOMO-15 (**3**), -6.55 eV

HOMO-25 (**5**), -8.19 eV

**Figure 3**. (a) Mayer bond indices (italics) and selected NPA charges of the anionic component of **3**; (b) Key resonance structures for a simplified model of the anionic component of **3** determined using NRT for both bent and linear isomers; (c) Key molecular orbitals for the anionic component of **3**: (upper left) HOMO (E = -2.97 eV, = -286.6 kJ $mol^{-1}$); (upper right) HOMO-1 (E = -3.54 eV, = -330.0 kJ $mol^{-1}$); (middle left) HOMO-2 (E = -4.21 eV, = -406.2 kJ $mol^{-1}$); (middle right) HOMO-3 (E = -4.97 eV, = -479.5 kJ $mol^{-1}$); (bottom left) HOMO-13 (E = -6.23 eV, = -601.1 kJ $mol^{-1}$); (bottom right) HOMO-15 (E = -6.55 eV, = -632.0 kJ $mol^{-1}$). Iso-surface value 0.03.

*Geometric and electronic modification*

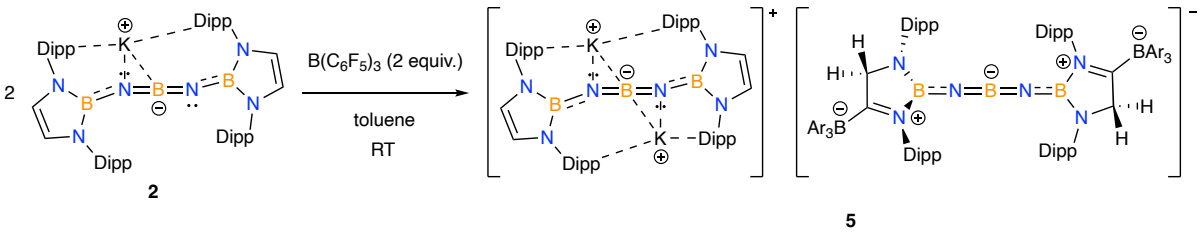
Attempts to probe the electrochemical oxidation of **2** or **3** reveal only features consistent with irreversible processes, and no clean reactivity is observed with a range of one- and two-electron chemical oxidants. On the other hand, the reaction of **2** with $B(C_6F_5)_3$ proceeds cleanly to give a more unsymmetrical product, as implied by $^1H$ NMR measurements; single crystals could be obtained from pentane solution and the structure of the ion pair **5** was confirmed by X-ray crystallography (Scheme 2 and Figure 2d).

While the cationic component is straightforwardly derived from **2** by uptake of the $K^+$ counterion from a second equivalent of the starting material, the anionic component has been transformed by the assimilation of a molecule of the borane at one of the backbone positions of each boryl heterocycle. Attack by the borane at the backbone carbon rather than at nitrogen

is presumably sterically driven (cf. the reaction with MeI), and finds precedent in boryl and carbene ligand chemistry.[40,41] This take-up of $B(C_6F_5)_3$, together with an accompanying 1,2-hydrogen shift leads to significant modification in the capping units at each end of the BNBNB chain. Most importantly, it leads to loss of the C=C bond within the heterocycle, with accompanying formation of a C=N bond involving one of the heterocyclic nitrogen atoms (*d*(C(3)N(2)) = 1.301(5) Å). This double bond effectively arises through sharing of the N-lone pair at N(2) with C(3), which in turn would be expected to render the boron atoms within the heterocycles (B2/3) significantly less π-stabilized.[40,41] As such, the capping heterocycles in the anionic component of **5** are significantly more π acidic than those in **2**/**3**, in a manner reminiscent of the difference between cAAC and NHC carbenes (single N-donor π-stabilized vs doubly-stabilized).[42] The most obvious structural consequence of this change is that the BNBNB moiety becomes linear, with the crystallographically determined angles at the nitrogen atoms being 173.8(4) and 172.8(4)° (cf. ca. 150° for **3**); the central boron atom remains linear (177.9(4)°, cf. 179.7(3)° for **3**).

With reference to quantum chemical calculations carried out on the isoelectronic all-carbon [4]cumulenes,[16] this geometric modification can be understood by consideration of the enhanced π-acceptor capabilities of the capping groups, which effectively lead to the lone pairs found at nitrogen in compounds **2**/**3** being conjugated into the BNBNB chain (Figure S6). This change is reflected in shorter chain-end BN distances for the anionic component of **5** (1.332(7)/1.340(7) Å vs. 1.379(3)/1.383(4) Å for **3**) and slightly higher MBIs (1.49 vs. 1.38). The molecular orbital picture for the anionic component of **5** is also consistent with the existence of a linear BNBNB chain featuring an approximately orthogonal alignment of the

capping heterocycles (torsion angle = 72.7°). As such, the near degenerate HOMO-24 and HOMO-25 orbitals (found at -8.10 and 8.19 eV, respectively) define orthogonal π-bonding orbitals spanning the two (overlapping) four-atom BNBN fragments (Figure 3c).




**Scheme 2**. Reaction of **2** with $BAr_3$ (Ar = $C_6F_5$) to generate a linear BNBNB chain.

## Conclusions

To summarize, we have developed all-inorganic heterocumulenes containing an unprecedented five-atom BNBNB core which are isoelectronic with their carbon analogues and have shown that by chemical modification of the capping end groups, the structure of this chain can be reconfigured from a bent geometry to a linear one.

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**Supporting information**

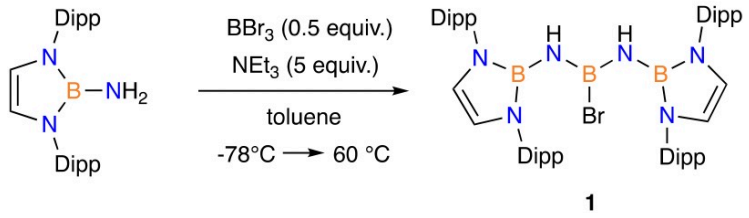
**General considerations**

All experiments were carried out under an atmosphere of dry argon or dinitrogen using standard Schlenk line or dry-box techniques. Solvents were degassed by sparging with argon and dried by passing through a column of appropriate drying agent using a commercially available Braun SPS and stored over potassium mirror under argon in a Teflon valve ampoule. NMR spectra were measured in $d_6$-benzene, with the solvent being dried over calcium hydride or molten potassium respectively, distilled, degassed by three freeze-pump-thaw-cycles and stored over 3 Å sieves. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. $^{1}$H and $^{13}$C{$^{1}$H} NMR spectra were measured on a Bruker Avance III HD Nanobay 400 MHz or Bruker Avance III 500 MHz spectrometer, and referenced internally to residual protio-solvent ($^{1}$H) or solvent ($^{13}$C) resonances; resonances are reported relative to tetramethylsilane (δ = 0 ppm). Assignments were confirmed using two-dimensional $^{1}$H-$^{1}$H, $^{13}$C-$^{1}$H, NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. The reported yields are the yields obtained after crystallisation and subsequent measurement of the material by single crystal-ray diffraction if not stated otherwise. Elemental analyses were carried out by London Metropolitan University or Elemental Microanalysis Ltd, Okehampton, Devon, UK.

**Preparation of starting materials**

The starting material $(HCDippN)_2BNH_2$ was prepared by the literature procedure.[S1]

**Synthetic procedures, characterising data and representative spectra of new compounds**




**Scheme S1.** Synthesis of {(HCDippN)$_2$BNH}$_2$BBr, **1**.

**{(HCDippN)$_2$BNH}$_2$BBr, 1.** (HCDippN)$_2$BNH$_2$ (515.7 mg, 1.28 mmol) and NEt$_3$ (0.26 mL, 1.86 mmol) were dissolved in toluene (15 mL) at -78 °C and BBr$_3$ added dropwise. The resulting solution was stirred for 15 min at -78 °C, warmed to room temperature, and then heated at 60 °C overnight with an accompanying colour change from yellow to light brown. Volatiles were then removed in vacuo, and the residue extracted with pentane (80 mL). The resulting solution was concentrated (to ca. 15 mL) and colourless crystals of **1** were obtained upon standing at -30 °C which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 5 mL).

Yield: 402.3 mg (70.3 %)

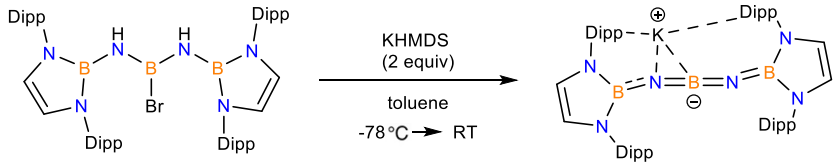
$^1$H NMR (500 MHz, C$_6$D$_6$, 298 K): $\delta_H$ 1.13 (d, $^3J_{H,H}$ = 7.0 Hz, 24H, CH$_3$ of Dipp), 1.16 (d, $^3J_{H,H}$ = 7.0 Hz, 24H, CH$_3$ of Dipp), 3.13 (br, 2H, NH), 3.17 (sept, 8H, C<u>H</u>(CH$_3$)$_2$ of Dipp), 5.98 (s, 4H, CH of boryl), 7.08 (m, 8H, m-ArH of Dipp), 7.19 (m, 4H, p-ArH of Dipp).

$^{11}$B{$^1$H} NMR (160 MHz, C$_6$D$_6$, 298 K): $\delta_B$ 22.2 (boryl), 28.3 (N-B-N)

$^{13}$C{$^1$H} NMR (126 MHz, C$_6$D$_6$, 298 K): $\delta_C$ 23.8, 24.9 (CH$_3$ of Dipp), 28.6 (<u>C</u>H(CH$_3$)$_2$ of Dipp),

117.9 (CH of boryl), 123.8 (m-Ar of Dipp), 127.7 (p-Ar of Dipp), 138.5 (CN of Dipp), 146. 6 (o-Ar of Dipp).

Elemental microanalysis: calc. for $C_{52}H_{74}B_3BrN_6$ (%): C 69.74 H 8.33 N 9.38; meas. C 69.59 H 8.35 N 8.94.




1 2

**Scheme S2**. Synthesis of [{(HCDippN)$_2$BN}$_2$B]K, **2**.

**[{(HCDippN)$_2$BN}$_2$B]K, 2.** To a solid mixture of **1** (490 mg, 0.54 mmol) and KHMDS (218 mg, 1.09 mmol) in a 100 mL Schlenk flask at -78 °C was added 40 mL toluene. The resulting solution was allowed to warm to room temperature and stirred for 12 h with formation of a brown precipitate and a colour change to light green. Volatiles were removed in vacuo and the residue extracted with pentane (120 mL). The resulting solution was concentrated to ca. 15 mL and colourless crystals of **2** were obtained which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 5 mL).

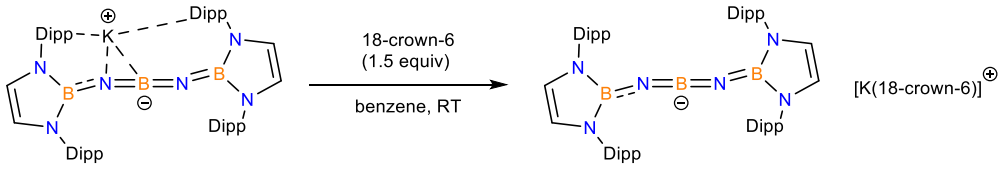
Yield: 301.8 mg (65.6 %)

$^1$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 1.15 (d, $^3J_{H,H}$ = 6.8 Hz, 24H, $CH_3$ of Dipp), 1.21 (d, $^3J_{H,H}$ = 6.8 Hz, 24H, $CH_3$ of Dipp), 3.40 (sept, $^3J_{H,H}$ = 6.9 Hz, 8H,C<u>H</u>$(CH_3)_2$ of Dipp), 6.00 (s, 4H, CH of boryl), 7.02 (m, 8H, m-ArH of Dipp), 7.05 (m, 4H, p-ArH of Dipp).

$^{11}B\{^{1}H\}$ NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 21.1 (boryl), not observed (N=B=N).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 24.0, 24.3 ($CH_3$ of Dipp), 28.5 ($\underline{C}H(CH_3)_2$ of Dipp), 115.8 (CH of boryl), 123.0 (m-Ar of Dipp), 126.1 (p-Ar of Dipp), 142.2 (CN of Dipp), 148.6 (o-Ar of Dipp).

Elemental microanalysis: calc. for $C_{52}H_{72}B_3KN_6$ (%): C 73.24 H 8.51 N 9.86; meas. C 72.76 H 8.85 N 9.54.




2 3

**Scheme S3**. Synthesis of [{(HCDippN)$_2$BN}$_2$B]K(18-crown-6), **3**.

**[{(HCDippN)$_2$BN}$_2$B]K(18-crown-6), 3. 2** (15 mg, 0.017 mmol) and 18-crown-6 (4.6 mg, 0.017) were dissolved in 2 mL benzene and stirred for 2 h at room temperature. The reaction mixture was concentrated (to ca. 0.4 mL) and colourless crystals of **3** were obtained upon standing at room temperature which were suitable for X-ray crystallography. These were isolated by filtration and washed twice with cold pentane (2 x 0.1 mL) and dried under vacuum.

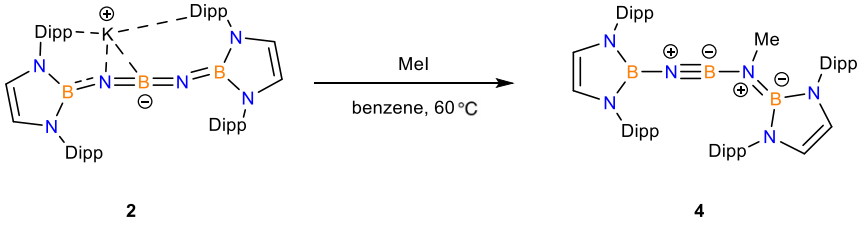
Yield: 17.6 mg (89.7 %)

$^{1}H$ NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 1.36 (d, $^{3}J_{H,H}$ = 6.8 Hz, 24H, $CH_3$ of Dipp), 1.42 (d, $^{3}J_{H,H}$ = 6.8 Hz, 24H, $CH_3$ of Dipp), 3.03 (s, 18-crown-6), 3.78 (sept, $^{3}J_{H,H}$ = 7.0 Hz, 8H,$C\underline{H}(CH_3)_2$ of Dipp), 6.10 (s, 4H, CH of boryl), 7.20 (m, 4H, p-ArH of Dipp), 7.21 (m, 8H, m-ArH of Dipp).

$^{11}B\{^{1}H\}$ NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 21.0 (boryl), not observed (N=B=N).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 24.4, 24.5 ($CH_3$ of Dipp), 28.7 ($\underline{C}H(CH_3)_2$ of Dipp), 70.2 (s, 18-crown-6), 116.4 (CH of boryl), 123.0 (m-Ar of Dipp), 125.0 (p-Ar of Dipp), 144.0 (CN of Dipp), 147.7 (o-Ar of Dipp).

Elemental microanalysis: calc. for $C_{64}H_{96}B_3KN_6O_6$ (%): C 68.82 H 8.66 N 7.52; meas. C 69.53 H 8.83 N 7.54.




2 4

**Scheme S4**. Synthesis of $[(HCDippN)_2BNBN(Me)B(NDippCH)_2]$, **4**.

**$[(HCDippN)_2BNBN(Me)B(NDippCH)_2]$, 4. 2** (20 mg 0.023 mmol) was dissolve in benzene (0.4 mL) and a drop of MeI (0.01 mL, excess) was added. The solution was heated at 60 °C overnight with the formation of a white precipitate. Volatiles were removed in vacuo and the residue extracted with pentane (4 mL). The resulting solution was concentrated to ca. 0.4 mL and colourless crystals of **4** were obtained upon standing at room temperature which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 0.1 mL).

Yield: 13.5 mg (69.4 %)

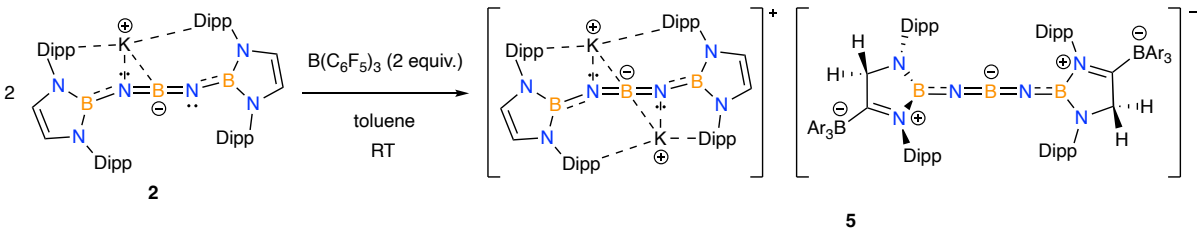
$^{1}H$ NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 1.15 (t, $^{3}J_{H,H}$ = 6.8 Hz, 12H, $CH_3$ of Dipp), 1.17 (t, $^{3}J_{H,H}$ =

6.8 Hz, 12H, $CH_3$ of Dipp), 1.23 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, $CH_3$ of Dipp), 1.27 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, $CH_3$ of Dipp), 1.85 (s, Me), 3.12 (sept, $^3J_{H,H}$ = 6.9 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 3.27 (sept, $^3J_{H,H}$ = 6.9 Hz, 2H,C<u>H</u>$(CH_3)_2$ of Dipp), 5.84 (s, 4H, CH of boryl), 5.96 (s, 2H, CH of boryl), 6.98 (m, 6H, ArH of Dipp), 7.11 (m, 6H, ArH of Dipp).

$^{11}B\{^1H\}$ NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 22.0 (boryl), 19.7 (N=B).

$^{13}C\{^1H\}$ NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 23.5, 24.4, 24.6, 24.8 ($CH_3$ of Dipp), 28.6, 28.8 (<u>C</u>H$(CH_3)_2$ of Dipp), 34.1 (Me), 117.2, 118.5 (CH of boryl), 123.4, 123.9, 126.9, 128.6, 137.8, 140.4, 146.1, 146.9 (Ar of Dipp).

Elemental microanalysis: calc. for $C_{53}H_{75}B_3N_6$ (%): C 76.82 H 9.12 N 10.14; meas. C 76.55 H 8.70 N 9.74.




**Scheme S5**. Synthesis of $[\{(C_6F_5)_3BCCH_2(DippN)_2BN\}_2B][\{(HCDippN)_2BN\}_2B]K_2$, **5**.

**$[\{(C_6F_5)_3BCCH_2(DippN)_2BN\}_2B][\{(HCDippN)_2BN\}_2B]K_2$, 5.** To a solid mixture of **2** (100mg, 0.12 mmol) and $B(C_6F_5)_3$ (60 mg, 0.12 mmol) in a 25 mL Schlenk flask at room temperature was added 4 mL toluene. The solution was stirred 30 min with a colour change to yellow. Volatiles were removed in vacuo, and the residue was extracted with pentane (20 mL). The resulting solution was concentrated to ca. 5 mL and colourless crystals of **5** were obtained

which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

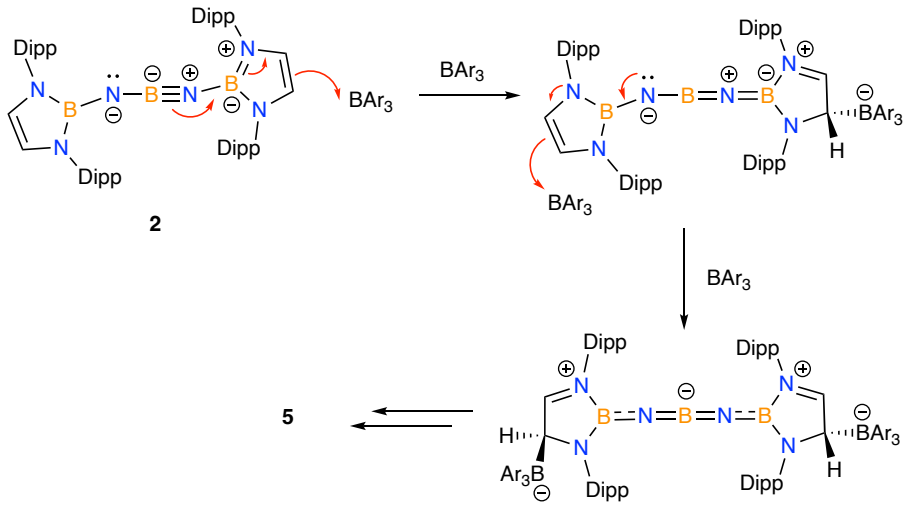
Yield: 76.2 mg (47.6 %)

$^{1}$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 0.94 (d and br, $^{3}J_{H,H}$ = 6.9 Hz, 48H, $CH_3$ of Dipp), 1.00 (br, 12H, $CH_3$ of Dipp), 1.12 (d, $^{3}J_{H,H}$ = 6.9 Hz, 24H, $CH_3$ of Dipp), 1.20 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H, $CH_3$ of Dipp), 3.08 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 8H,C<u>H</u>$(CH_3)_2$ of Dipp), 3.16 (sept, $^{3}J_{H,H}$ = 6.9 Hz, 8H,C<u>H</u>$(CH_3)_2$ of Dipp), 4.53 (br, 4H, $CH_2$ of boryl), 5.89 (s, 4H, CH of boryl), 6.56 (br, 3H, Ar-H), 6.77 (t, 2H, Ar-H), 6.92 (m, 12H, Ar-H), 700 (m, 7H, Ar-H)

$^{11}$B{$^{1}$H} NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ -15.1 ($B(C_6F_5)_3$), 20.2 (boryl), not observed (N=B=N).

$^{19}$F{$^{1}$H} NMR (470 MHz, $C_6D_6$, 298 K): $\delta_F$ -165.7, -163.8, -158.1, -157.6, -130.0, -126.8.

$^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 22.9, 24.0, 24.1, 24.5, 25.2, 26.0 ($CH_3$ of Dipp), 28.6, 28.7 (<u>C</u>H$(CH_3)_2$ of Dipp), 68.1 ($CH_2$ of boryl), 116.3 (CH of boryl), 123.4, 124.2, 126.8, 127.7, 128.7, 128.8, 137.1, 141.3, 148.1, 148.5 (Ar of Dipp).




**Scheme S6**. Proposed (partial) mechanism for the conversion of **2** to **5** (anionic components only included for clarity).

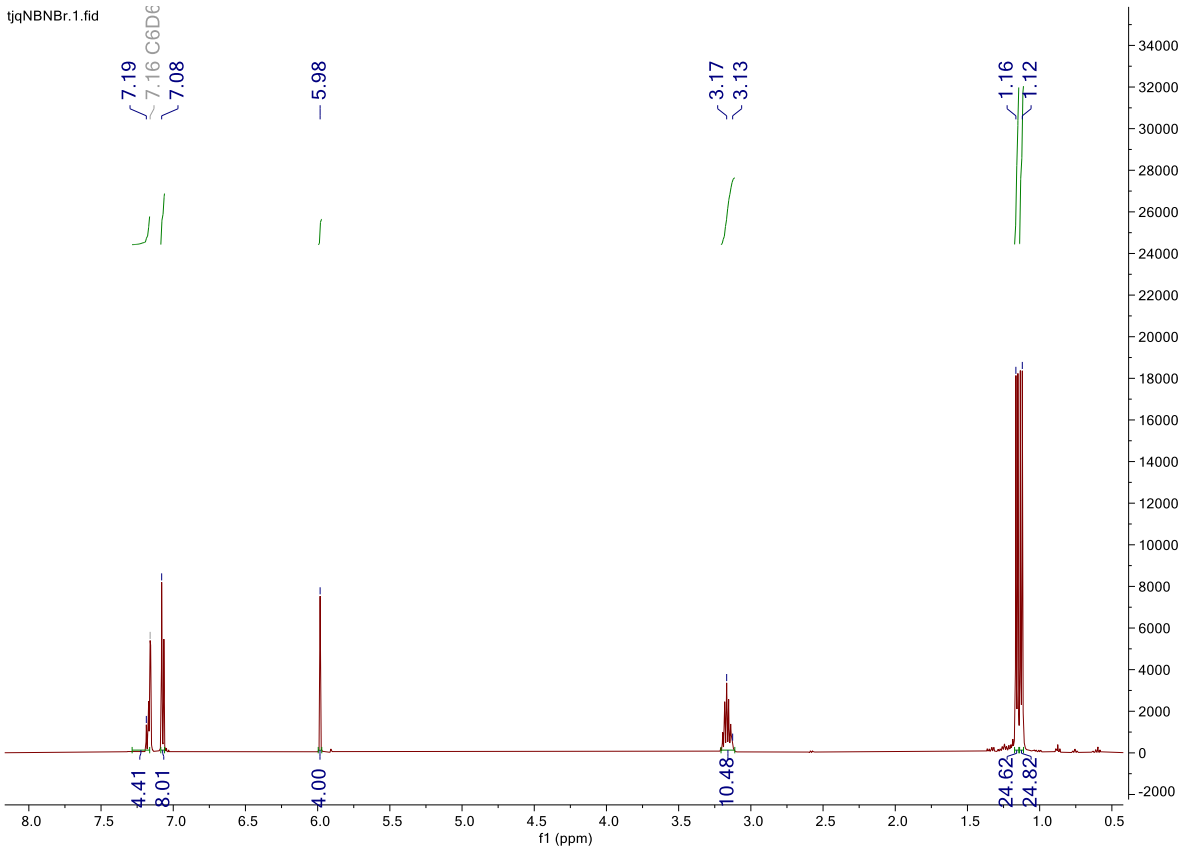



**Figure S1**. $^{1}$H NMR spectrum of **1** (500 MHz, $C_6D_6$, 298 K).

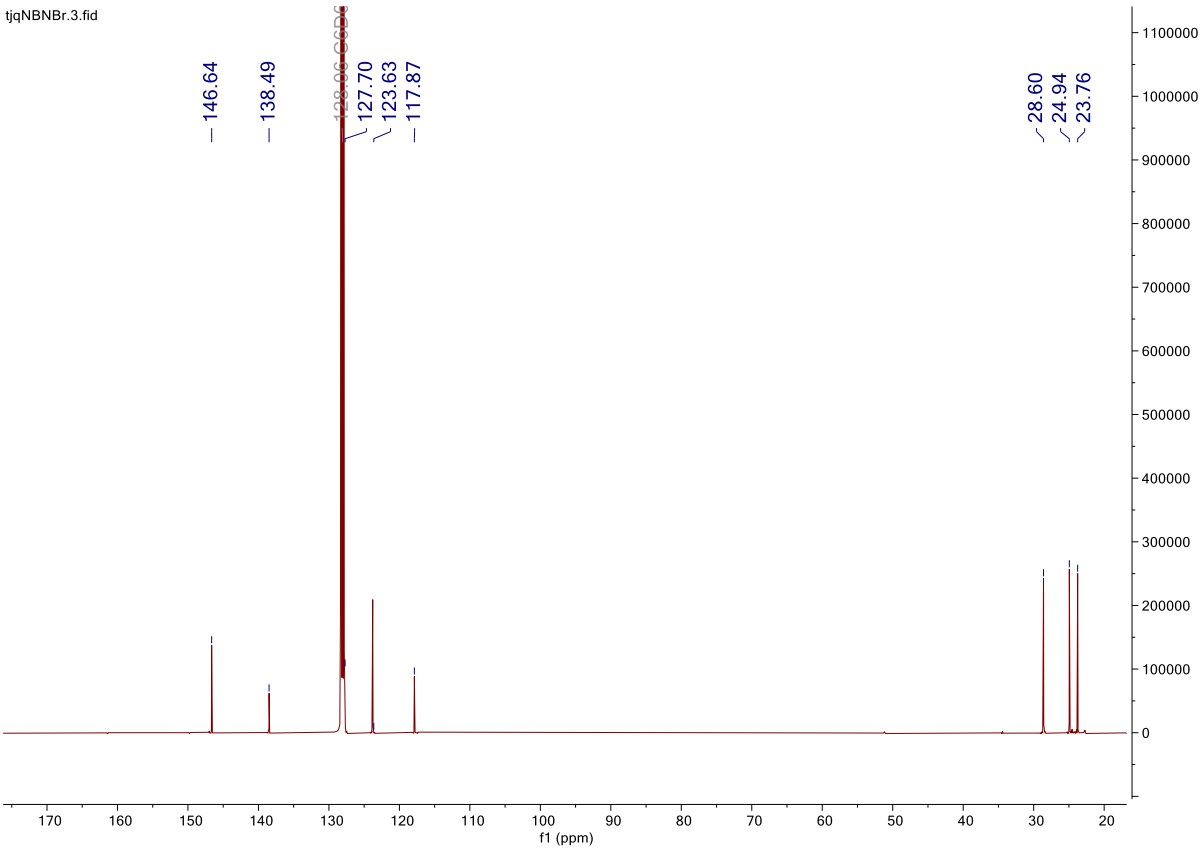



**Figure S2**. $^{13}$C NMR spectrum of **1** (126 MHz, $C_6D_6$, 298 K).

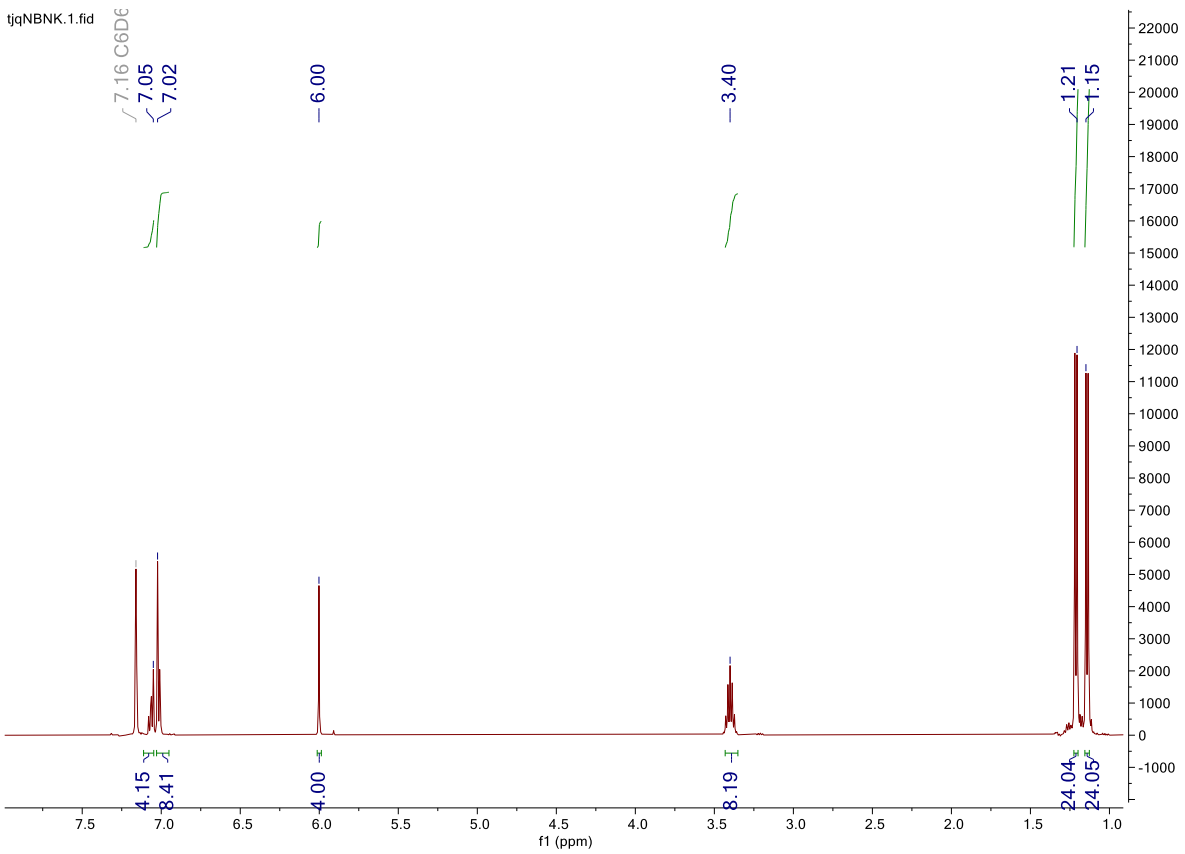



**Figure S3**. $^{1}$H NMR spectrum of **2** (500 MHz, $C_6D_6$, 298 K).

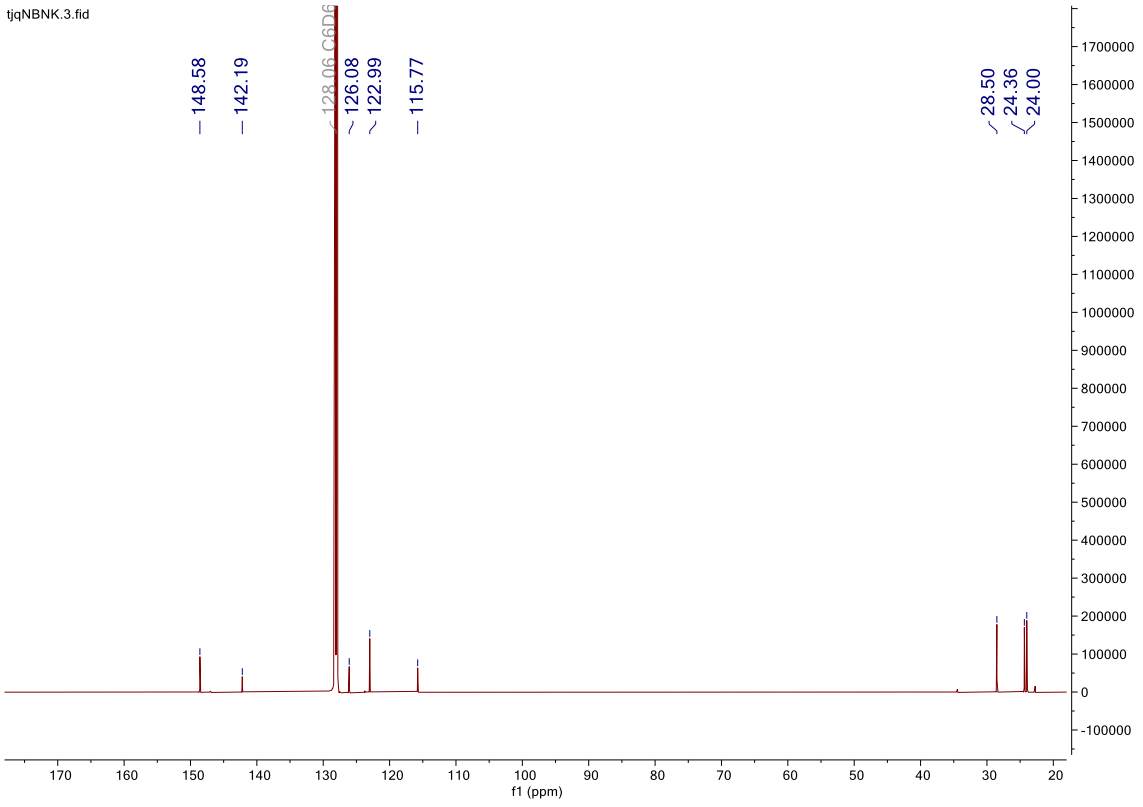



**Figure S4**. $^{13}$C{$^{1}$H} NMR spectrum of **2** (126 MHz, $C_6D_6$, 298 K).

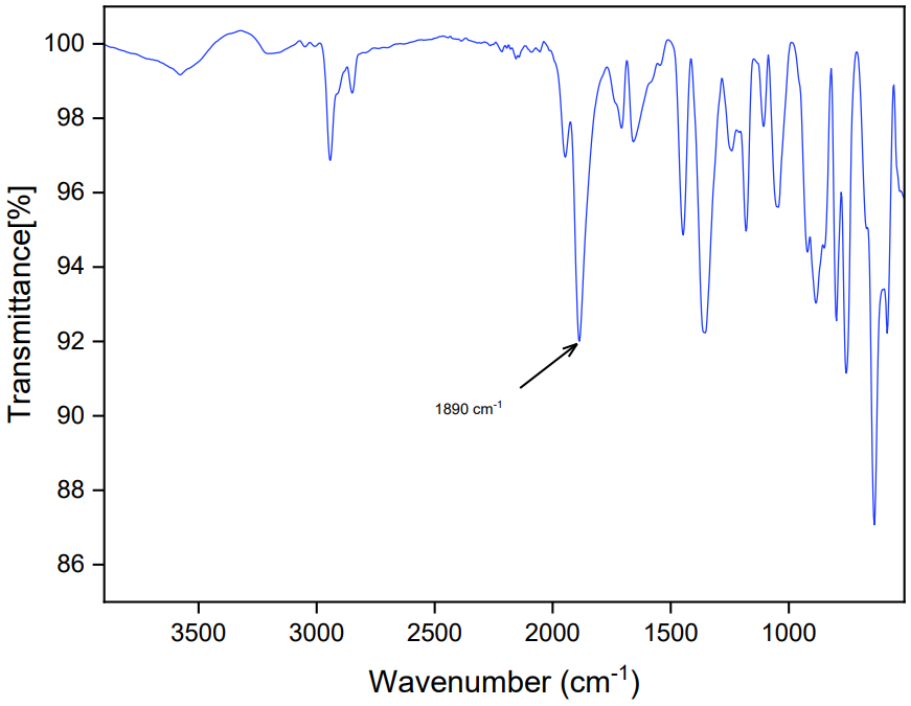



**Figure S5**. IR spectrum of **2**.

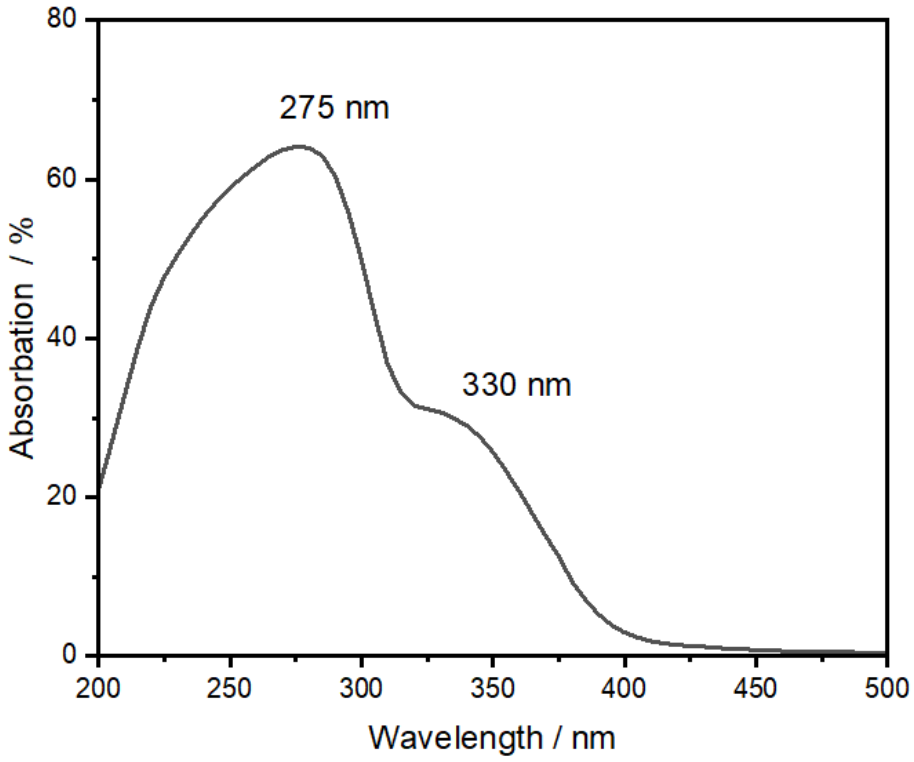



**Figure S6**. UV-vis spectrum of **2** in hexane.

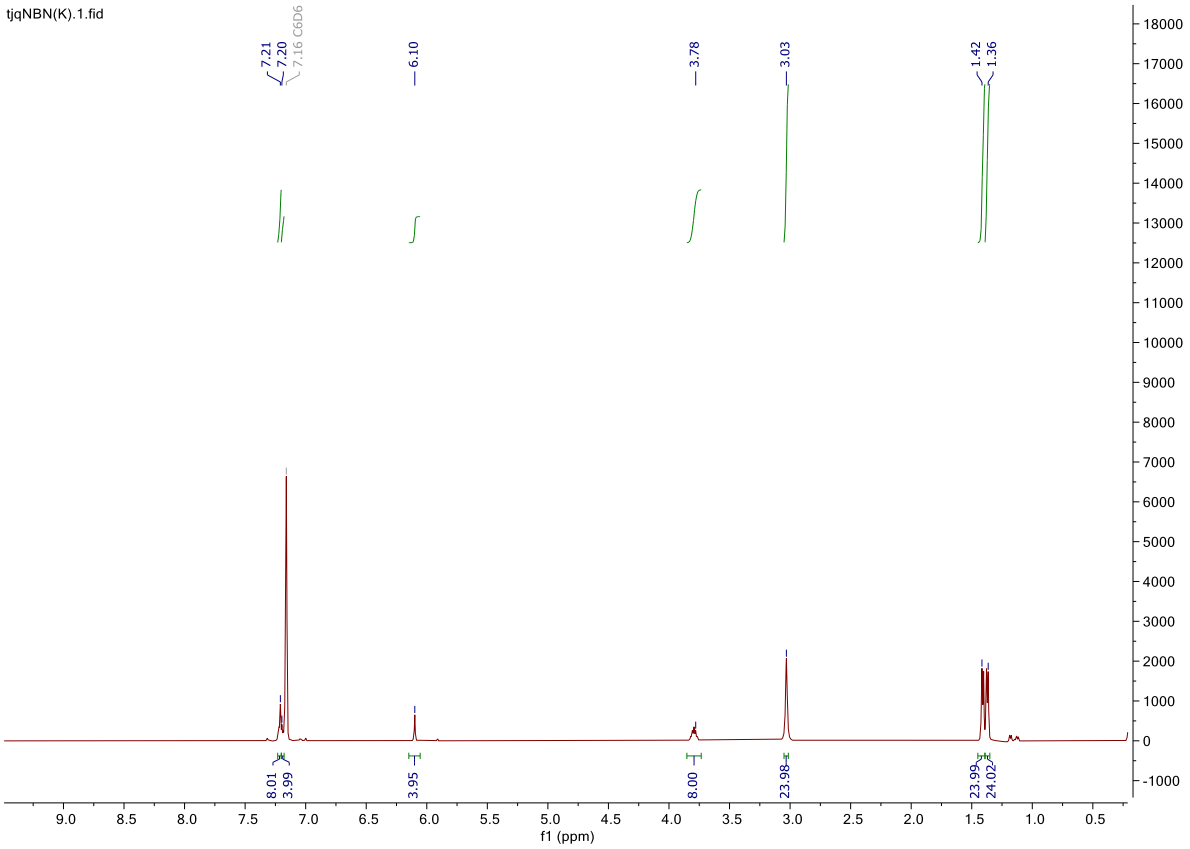



**Figure S7**. $^{1}$H NMR spectrum of **3** (500 MHz, $C_6D_6$, 298 K).

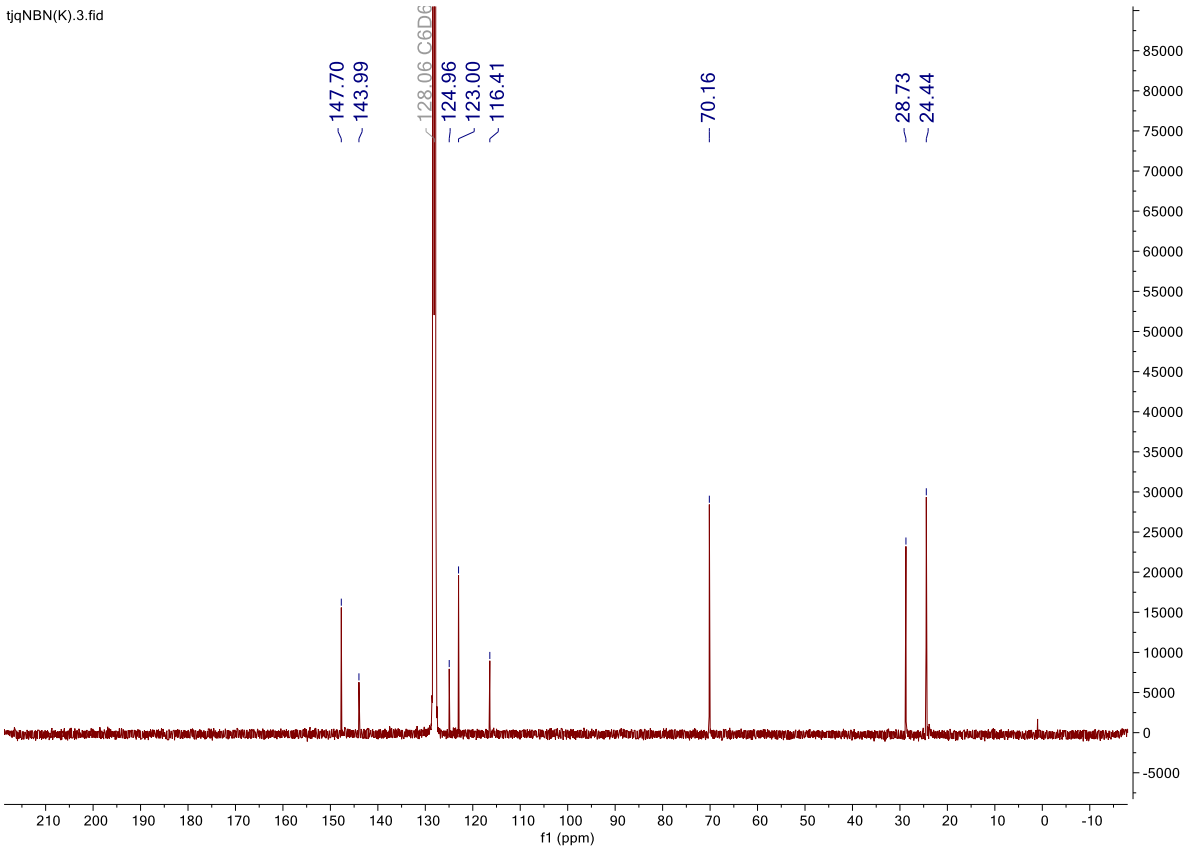



**Figure S8**. $^{13}$C{$^{1}$H} NMR spectrum of **3** (126 MHz, $C_6D_6$, 298 K).

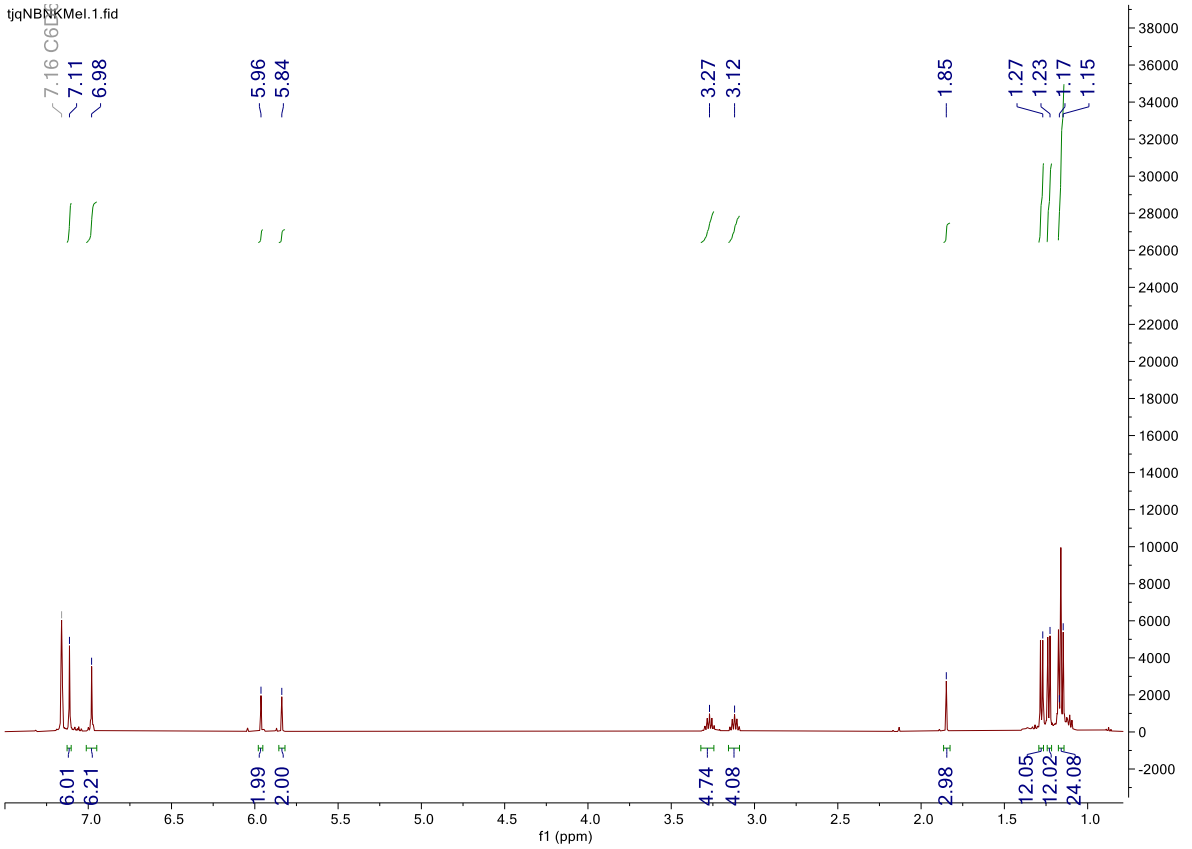



**Figure S9**. $^{1}$H NMR spectrum of **4** (500 MHz, $C_6D_6$, 298 K).

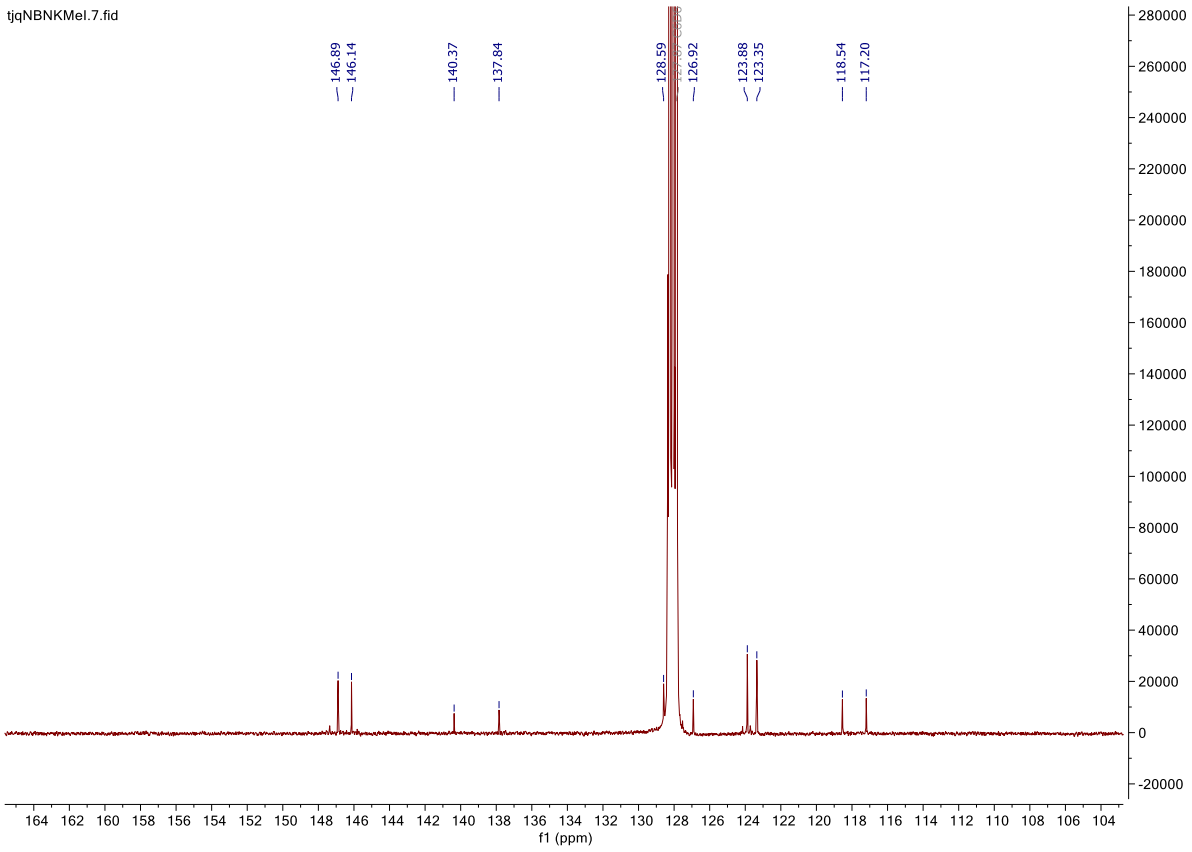



**Figure S10**. $^{13}$C{$^{1}$H} NMR spectrum of **4** (126 MHz, $C_6D_6$, 298 K).

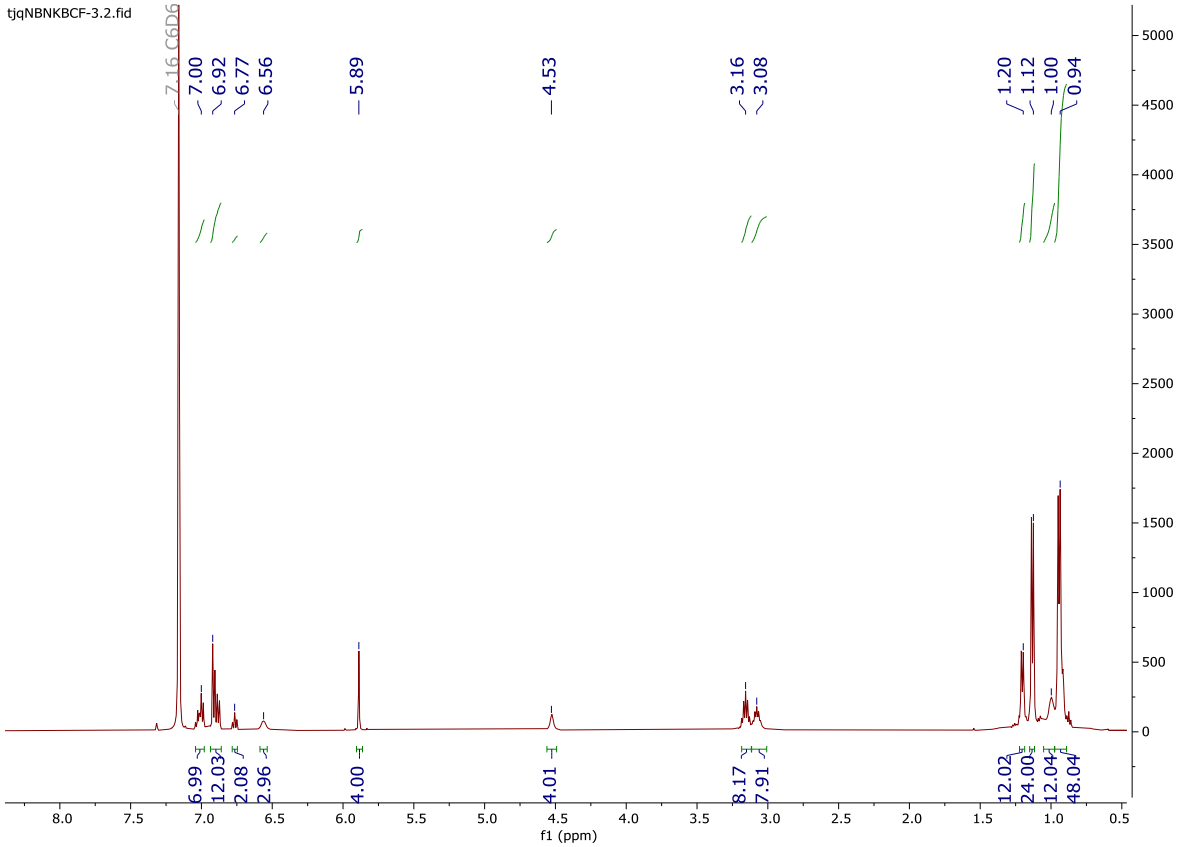



**Figure S11**. $^{1}H$ NMR spectrum of **5** (500 MHz, $C_6D_6$, 298 K).

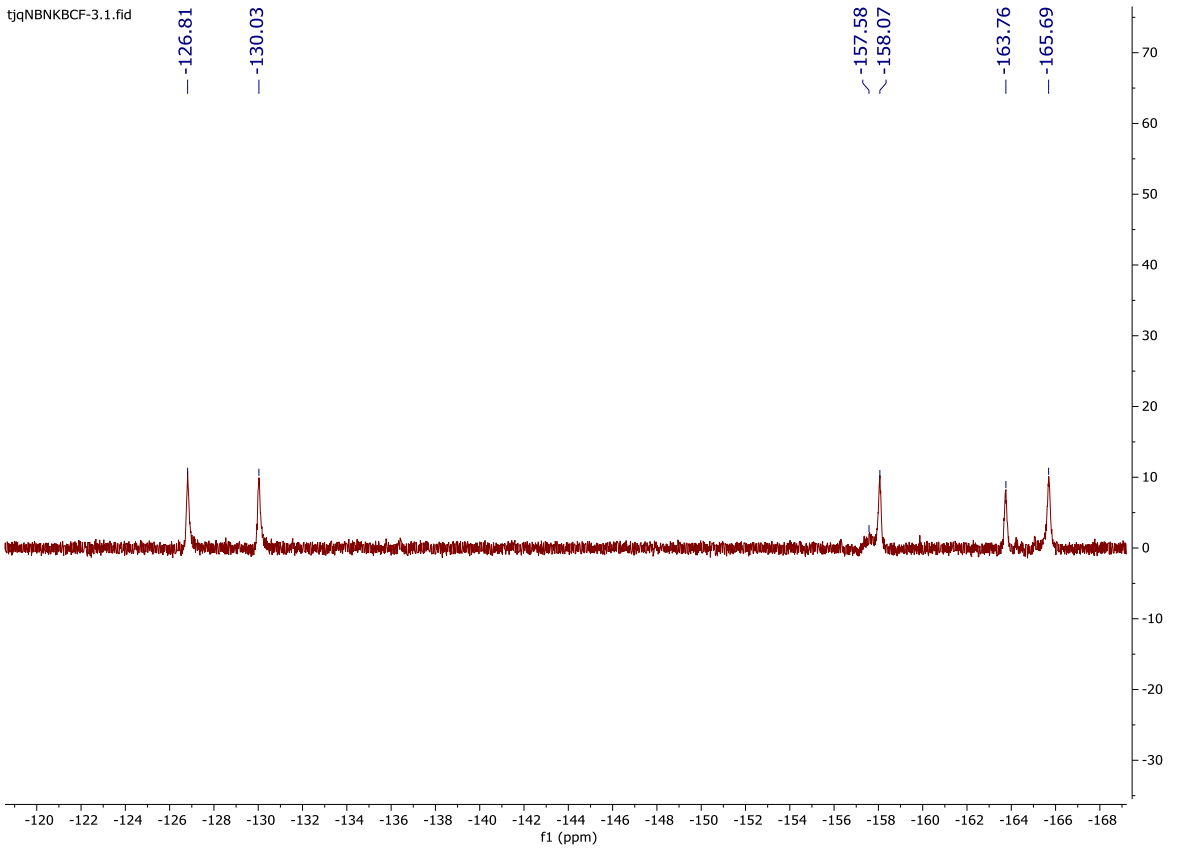



**Figure S12**. $^{19}F\{^{1}H\}$ NMR spectrum of **5** (470 MHz, $C_6D_6$, 298 K).

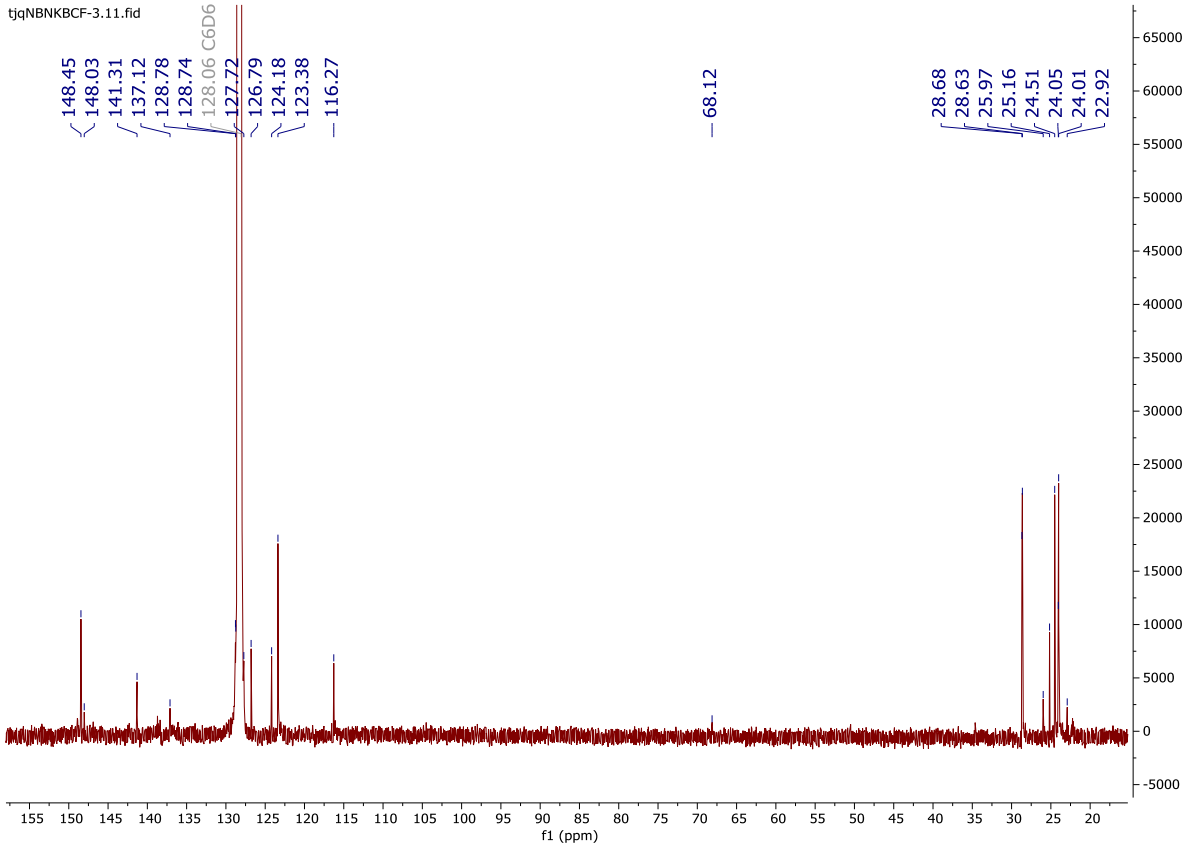



**Figure S13**. $^{13}C\{^{1}H\}$ NMR spectrum of **5** (126 MHz, $C_6D_6$, 298 K).

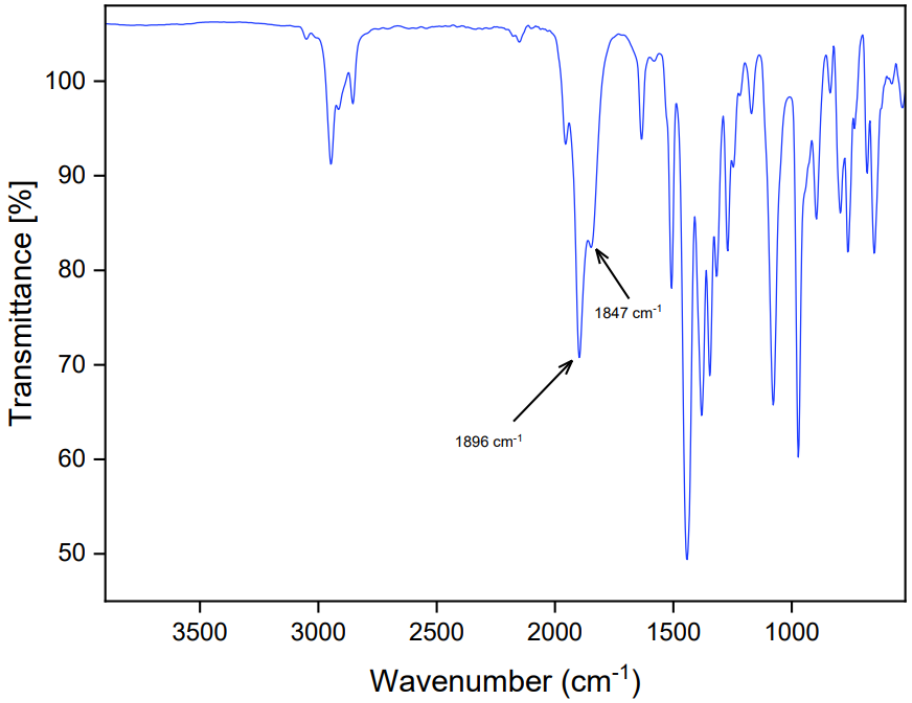



**Figure S14**. IR spectrum of **5**.

**Details of X-ray crystallography**

Single-crystal X-ray diffraction data for all compounds were collected on an Oxford Diffraction/Agilent SuperNova diffractometer equipped with a 135 mm Atlas CCD area detector or a Rigaku XtaLAB Synergy-DW VHF equipped with a PhotonJet-R dual wavelength rotating anode and HyPix-Arc 150° detector. Crystals were selected under Paratone-N oil, mounted on MiTeGen Micromount loops and quench-cooled using an Oxford Cryosystems open flow $N_2$ cooling device.[S2] Data were collected at 150 K using mirror monochromated Cu Kα radiation (λ = 1.5418 Å). Data collected were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[S3] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite.[S3] Structures were solved ab initio from the integrated intensities using SHELXT[S4] and refined on F2 using SHELXL[S5] with the graphical interface OLEX2[S6]. Selected crystallographic data are summarised in Table S1-S5, and full details are given in the supplementary deposited CIF files (2377734-37 and 2379472). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

**Table S1**. Selected crystallographic data and refinement parameters for compounds **1** and **2**.

| **Compound** | **1** | **2** |
|---|---|---|
| **Empirical formula** | $C_{104}H_{148}B_6Br_2N_{12}$ | $C_{55}H_{75}B_3KN_6$ |
| **Fw /g mol$^{-1}$** | 1791.02 | 891.74 |
| **T/K** | 150.15 | 100.00(10) |
| **Cell setting** | triclinic | monoclinic |
| **Space group** | P-1 | $P2_1/c$ |
| **a/Å** | 12.7280(5) | 10.91294(5) |
| **b/Å** | 19.2851(10) | 17.73369(8) |
| **c/Å** | 22.9944(10) | 27.28930(12) |
| **α/°** | 109.798(4) | 90 |
| **β/°** | 96.222(3) | 93.2201(4) |
| **γ/°** | 93.315(4) | 90 |
| **V/Å$^3$** | 5252.3(4) | 5272.87(4) |
| **Z** | 2 | 4 |
| **$\rho_{calc}$g/cm$^3$** | 1.132 | 1.123 |
| **μ/mm$^{-1}$** | 1.347 | 1.18 |
| **Radiation** | CuKα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| **Reflections collected** | 83631 | 216448 |
| **Independent reflections** | 21692 [$R_{int}$ = 0.1084] | 10932 [$R_{int}$ = 0.0681] |
| **parameters** | 1149 | 650 |
| **GooF** | 1.019 | 1.047 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0725, $wR_2$ = 0.1844 | $R_1$ = 0.0394, $wR_2$ = 0.1045 |
| **Final R indexes [all data]** | $R_1$ = 0.1344, $wR_2$ = 0.2279 | $R_1$ = 0.0404, $wR_2$ = 0.1053 |
| **CCDC ref** | 2377734 | 2377735 |

**Table S2**. Selected crystallographic data and refinement parameters for compounds **3** and **4**.

| **Compound** | **3** | **4** |
|---|---|---|
| **Empirical formula** | $C_{64}H_{96}B_3KN_6O_6$ | $C_{53}H_{75}B_3N_6$ |
| **Fw /g mol$^{-1}$** | 1116.99 | 828.62 |
| **T/K** | 150.15 | 100.00(10) |
| **Cell setting** | monoclinic | monoclinic |
| **Space group** | $P2_1$ | Pn |
| **a/Å** | 12.94630(10) | 10.68070(10) |
| **b/Å** | 19.3382(2) | 19.8291(2) |
| **c/Å** | 13.9330(2) | 11.88910(10) |
| **α/°** | 90 | 90 |
| **β/°** | 107.7870(10) | 94.6990(10) |
| **γ/°** | 90 | 90 |
| **V/Å$^3$** | 3321.50(7) | 2509.51(4) |
| **Z** | 2 | 2 |
| **$\rho_{calc}$g/cm$^3$** | 1.117 | 1.097 |
| **μ/mm$^{-1}$** | 1.096 | 0.476 |
| **Radiation** | CuKα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| **Reflections collected** | 41193 | 59412 |
| **Independent reflections** | 11552 [$R_{int}$ = 0.0388] | 8976 [$R_{int}$ = 0.0363, ] |
| **parameters** | 737 | 607 |
| **GooF** | 1.033 | 1.087 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0411, $wR_2$ = 0.1046 | $R_1$ = 0.0392, $wR_2$ = 0.1027 |
| **Final R indexes [all data]** | $R_1$ = 0.0458, $wR_2$ = 0.1092 | $R_1$ = 0.0431, $wR_2$ = 0.1049 |
| **CCDC ref** | 2377736 | 2377737 |

**Table S3**. Selected crystallographic data and refinement parameters for compound **5**.

| **Compound** | **5** |
|---|---|
| **Empirical formula** | $C_{140}H_{144}B_8F_{30}K_2N_{12}$ |
| **Fw /g mol$^{-1}$** | 2729.34 |
| **T/K** | 150(2) |
| **Cell setting** | triclinic |
| **Space group** | P-1 |
| **a/Å** | 12.0813(3) |
| **b/Å** | 24.6931(7) |
| **c/Å** | 27.2427(8) |
| **α/°** | 106.582(2) |
| **β/°** | 96.906(2) |
| **γ/°** | 98.386(2) |
| **V/Å$^3$** | 7592.8(4) |
| **Z** | 2 |
| **$\rho_{calc}$g/cm$^3$** | 1.194 |
| **μ/mm$^{-1}$** | 1.286 |
| **Radiation** | Cu Kα (λ = 1.54184) |
| **Reflections collected** | 108216 |
| **Independent reflections** | 29816 [$R_{int}$ = 0.0229] |
| **parameters** | 1865 |
| **GooF** | 0.933 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0614, $wR_2$ = 0.1368 |
| **Final R indexes [all data]** | $R_1$ = 0.1361, $wR_2$ = 0.1750 |
| **CCDC ref** | 2379472 |

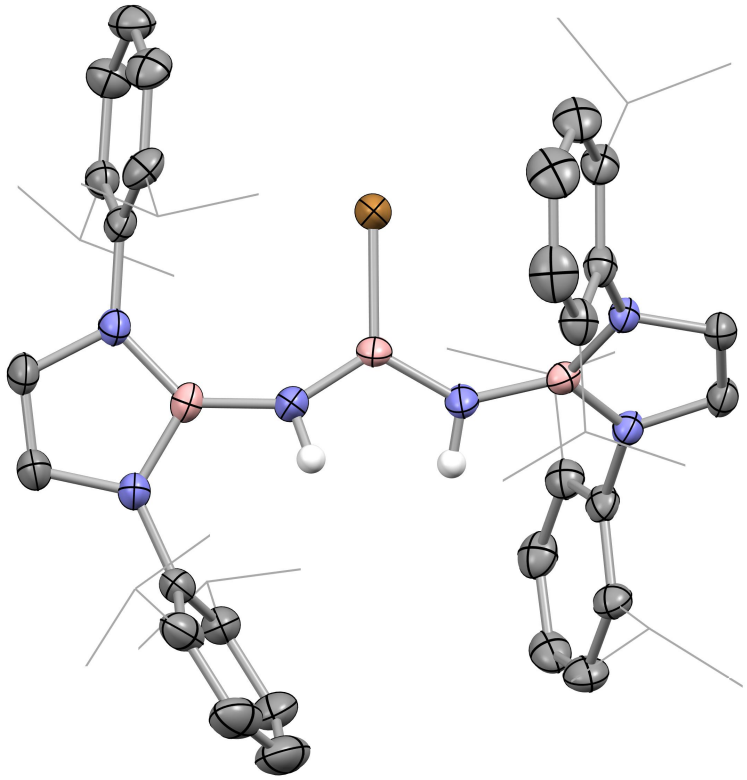


**Figure S15**. Molecular structure of one of the two independent molecules in the asymmetric unit of **1** in the solid state as determined by X-ray crystallography. Most Hs omitted and $^{i}$Pr groups shown in wireframe format for clarity; thermal ellipsoids shown at the 35% probability level.

**Details of quantum chemical calculations**

Geometry optimizations were carried out using the Gaussian 16 package with the M06-2X functional.[S7,S8] The def2-SVP basis set was used for all atoms.[S9,S10] Frequency calculations at same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum and one for transition states), and provide the thermal corrections of Gibbs free energy. Single-point energy calculations were performed at the M06-2X/def2-TZVP level of theory for the modelling of compounds in solution (benzene).[S11,S12] The gas-phase geometry was used for all the solution phase calculations. The SMD method was used with the corresponding solvent, while Bondi radii were chosen as the atomic radii to define the molecular cavity.[S13,S14] The corrections of Gibbs free energy from frequency calculations were added to the single-point energies to obtain the Gibbs free energy in solution. All energies reported in the paper correspond to the reference state of 1 mol/L, 298 K. Natural bond orbital (NBO) calculations were carried out using NBO 7.0 program at the M06-2X/def2-TZVP level of theory.[S15] The Mayer bond order calculation was performed using Multiwfn 3.8.[S16] Optimized structures and orbitals were visualized using ChimeraX.[S17] The bent isomer of $(NH_2)_2BNBNB(NH_2)_2$ was optimized by freezing the coordinates for all N and B atoms from the optimized geometry of **3**. The energy scans for the BNB bond angles in compounds **3** and **5** (Figure S16) were performed using the optimized geometry of **3**/**5** as a starting point, and performing constrained geometry optimizations at 5º intervals from 115º to 175º. Single-point energy calculations were performed at the M06-2X/def2-TZVP level of theory using these geometries in solution (benzene) to obtain E.

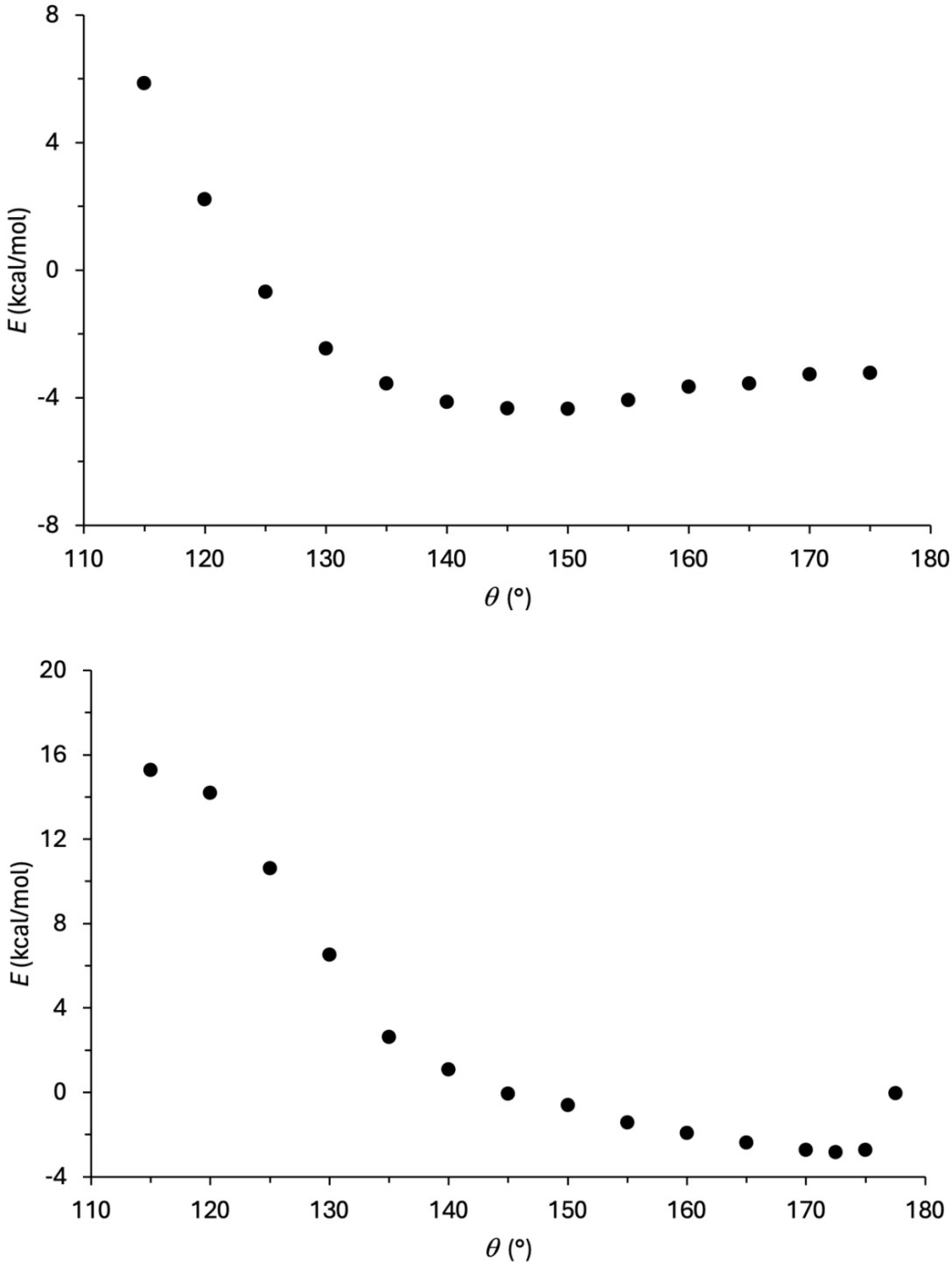



**Figure S16.** Energy scans for the BNB bond angles (θ) for the anionic components of compounds 3 (upper) and 5 (lower).

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**Declaration of author contribution**

**Statement of Authorship for joint/multi-authored papers for PGR thesis**

To appear at the end of each thesis chapter submitted as an article/paper

The statement shall describe the candidate's and co-authors' independent research contributions in the thesis publications. For each publication there should exist a complete statement that is to be filled out and signed by the candidate and supervisor **(only required where there isn't already a statement of contribution within the paper itself).**

| | |
|---|---|
| Title of Paper | Syntheses, Geometric and Electronic Structures of Inorganic Cumulenes |
| Publication Status | √ Published □ Accepted for Publication<br>□Submitted for Publication □Unpublished and unsubmitted work written<br>in a manuscript style |
| Publication Details | Tang, J., Hu, C., Crumpton, A. E., Dietz, M., Sarkar, D., Griffin, L. P. Griffin, Goicoechea. M. J. & Aldridge, S. (2024). Syntheses, Geometric and Electronic Structures of Inorganic Cumulenes. *Journal of the American Chemical Society*, *146*(45), 30778-30783. |

Student Confirmation

| | | | |
|---|---|---|---|
| Student Name: | Jianqin Tang | | |
| Contribution to the Paper | Performed all synthetic, spectroscopic work, as well as part of the quantum chemical calculations. Analysed and interpreted data. Wrote the draft manuscript and prepared the supporting information. | | |
| Signature | Jianqin Tang | Date | 20/06/2025 |

Supervisor Confirmation

By signing the Statement of Authorship, you are certifying that the candidate made a substantial contribution to the publication, and that the description described above is accurate.

| | | |
|---|---|---|
| Supervisor name and title: Professor Simon Aldridge | | |
| Supervisor comments<br>I can confirm that the information about this paper described by the candidate is accurate. | | |
| Signature S Aldridge | Date | 21 June 2025 |

## Chapter 3. Metathesis reactivity of inorganic cumulenes

### Introduction

Classical iminoboranes readily undergo 1,2-addition and [2+2] cycloaddition reactions with polar covalent bonds. More recently, BN $\pi$-conjugated systems have been shown to act as 4-electron components in [4+2] cycloadditions, exemplified by de-aromatizing hetero-Diels–Alder reactions between aryliminoboranes and aldehydes.

This chapter reveals that the five-atom BNBNB-chain in the inorganic cumulenes disclosed in chapter 2 exhibits unique metathesis reactivity with carbonyl-containing electrophiles (e.g., $CO_2$, $CS_2$, aldehydes), enabled by the intrinsic polarity of the chain. Through sequential [2+2] cycloaddition/cyclo-reversion steps, the BNBNB unit transfers a borylimide fragment to form (boryl)N=C=X species (X = O, S, P, or C), driven by thermodynamically favorable B–O bond formation. A key four-membered cyclic intermediate, K[(boryl)NB(O)OC(H)Ph], was isolated and offers support for a bora-Wittig-type mechanism proposed on the basis of DFT calculations.

**Metathesis chemistry of inorganic cumulenes driven by B–O bond formation**

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**Abstract**

The reaction chemistry of an unprecedented 'inorganic cumulene' - featuring a five-atom BNBNB chain - towards C=O (and related) multiple bonds is disclosed. In marked contrast to related all-carbon systems, the intrinsic polarity of the BNBNB chain (featuring electronic-rich nitrogen and electron-deficient boron centres) enables metathesis chemistry with electrophilic heteroallenes (such as $CO_2$) and with organic carbonyl compounds. Metathesis leads to {$(HCDippN)_2$}BN transfer chemistry via consecutive [2+2] cyclo-addition/cyclo-reversion steps. Transfer of the imide unit to [CO], [CS], [PP{$(NDippCH_2)_2$}] and [C(H)Ph] moieties generates (boryl)N=C=X systems (X = O, S, PP{$(NDippCH_2)_2$}, C(H)Ph), driven thermodynamically by B–O bond formation. An isolable complex of stoichiometry K[(boryl)NB(O)OC(H)Ph], formed via [2+2] cycloaddition to $[(boryl)N=B=O]^-$ can be shown to be an intermediate in the formation of (boryl)N=C(H)Ph, and provides corroborating evidence for a DFT-calculated mechanism proceeding via consecutive bora-Wittig steps.

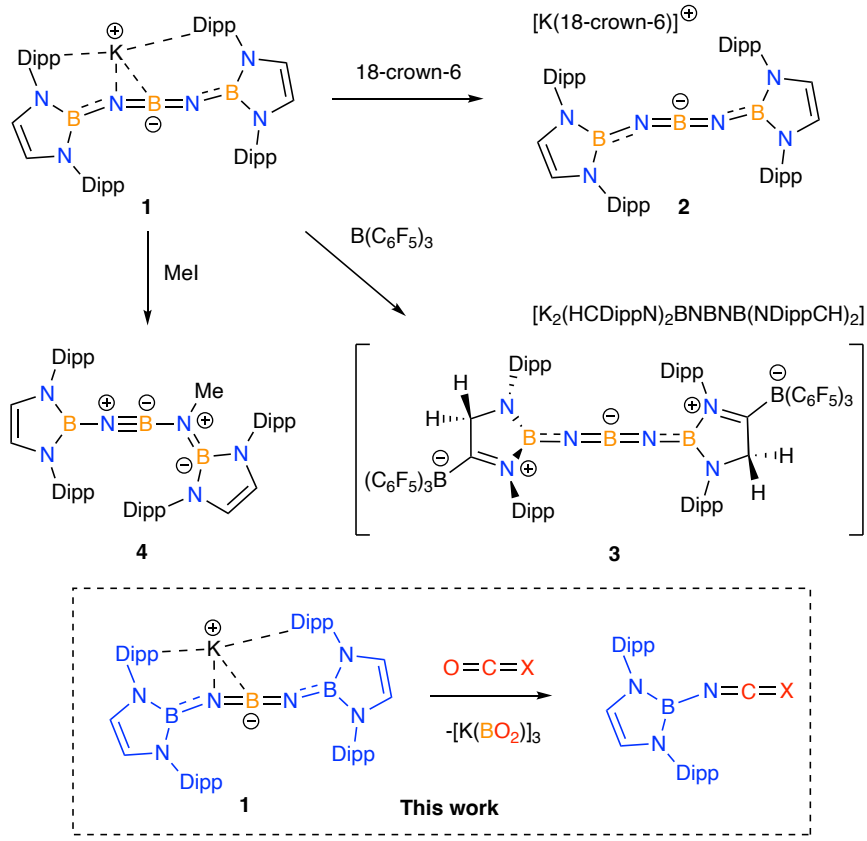
**Introduction**

Metathesis constitutes a powerful and widely used methodology in synthetic chemistry, with applications spanning organometallics, pharmaceuticals, fine chemicals and materials science.[1] While metathesis reactions utilising C=C bonds predominate, the possibility of exploiting C=O bonds in a similar fashion offers a strategy, for example, for the transformation of $CO_2$ into useful chemical products.[2] The use of oxophilic early transition metal complexes to accomplish C=O to C=NR transformations has been extensively reported,[3,4] and similar

chemistry using main group metal/metalloid derivatives has begun to be explored, driven for example by the formation of strong Al–O or Si–O bonds. [5,6] Given the similar thermodynamic driver associated with B–O bond formation (559 kJ $mol^{-1}$, cf. 595 kJ $mol^{-1}$ for Al–O), [7] we wondered whether boron-based non-metal systems could be employed to transform C=O into C=N bonds. [8,9]

We have recently developed high-yielding synthetic routes to 'inorganic cumulenes' (Scheme 1).[10,11] These five-atom BNBNB chains analogous to [4]cumulenes can possess either linear or bent structures (i.e. **2** or **3**) depending on the nature of the groups attached to the boron termini. Chemical modification of diamido-terminated **2** to generate a linear system best described by a B=N=B=N=B resonance structure involves assimilation of the strong Lewis acid $B(C_5F_5)_3$ to enhance the $\pi$ -acidity of the end groups and conjugate the N-lone pairs. In addition, preliminary studies of the reactivity of $K[(HCDippN)_2BNBNB(NDippCH)_2]$ (**1**) verify experimentally the intrinsic polarity within the BNBNB chain. The reaction of **1** with methyl iodide, for example, proceeds via nucleophilic attack by nitrogen to generate an iminoborane (**4**), featuring a formal BN triple bond.

The central NBN core of **1** can also be viewed as being a diimidoboryl anion isoelectronic with $CO_2$ itself, and we wanted to probe whether it might be capable of metathesis chemistry with O-containing heteroallenes, leading to exchange of borylimide/O atom fragments, driven thermodynamically by the formation of BO bond(s). We perceived that the previously demonstrated N-centred nucleophilicity of **1** might enable facile reactivity with substrates (such as $CO_2$ itself) which react primarily as electrophiles.[10]



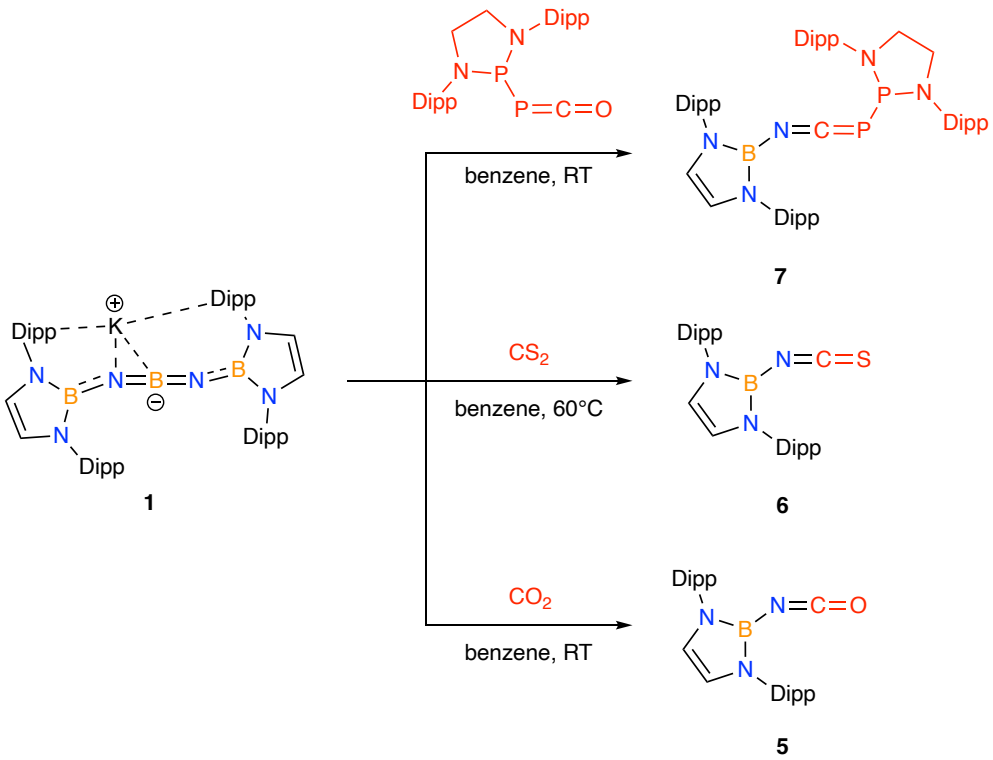

**Scheme 1.** Preliminary studies of 'inorganic cumulene' **1**. [10]

## Results and Discussion

The reactions of **1** with $CO_2$, $CS_2$ or the phosphaphosphinidene carbonyl $\{(H_2CDippN)_2\}PPCO$ proceed via O/N(boryl) metathesis, leading to the formation of the iminoboryl compounds (boryl)NCE (E = O (**5**), S (**6**) and $PP\{(NDippCH_2)_2\}$ (**7**); Scheme 2). **5** is a known compound, having recently been reported by Yuvaraj and Jones to be formed by N(boryl) transfer to $CO_2$ from a boryl-substituted silaimine at 80 °C (in ca. 40% yield).[5c] In the chemistry reported here, **5** is formed in excellent yield (*ca.* 90%), while the heavier C=E bonds in **6** (E = S) and **7** (E = P) are constructed in more modest yields (*ca.* 50% in each case). Both **6** and **7** are novel compounds, and each has been characterized by standard spectroscopic/analytical techniques and by X-ray crystallography (Figure 2). The $^{11}B$ NMR resonances determined for

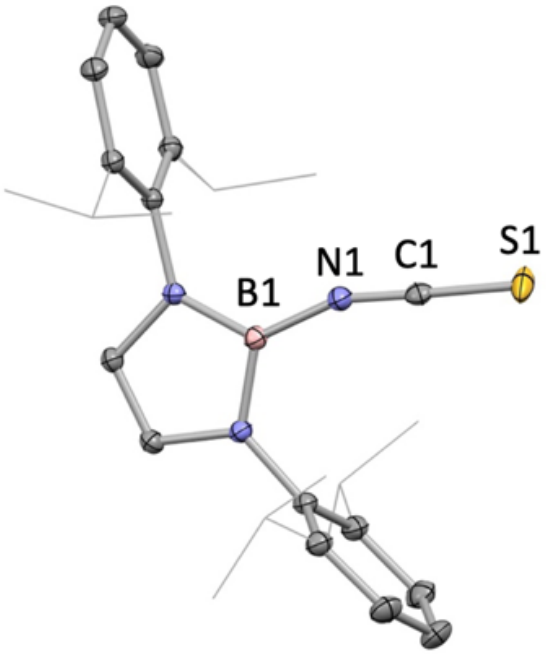
**6** and **7** ($\delta_B$ = 16.1 and 16.0 ppm) are similar to that measured for **5** ($\delta_B$ = 17.9 ppm), while the $^{31}$P signals measured for **7** ($\delta_P$ = -183.3 ppm, PP=C; 165.6 ppm, PP=C) are shifted from those reported for the precursor {($H_2$CDippN)$_2$}PPCO ($\delta_P$ = -245.6, 167.9 ppm) [12] to an extent that is markedly greater for the exocyclic phosphorus atom. Structurally, **5** - **7** are also similar, featuring comparable N=C distances (1.170(2), 1.179(7) and 1.184(3) Å), and a B–N–C angle which is marginally wider in the case of **7** (162.8(2)° vs. 159.4(1) and 156.8(4)° for **5** and **6**, respectively). [5c]

The identity of the co-product derived from the central boron atom is difficult to establish unequivocally, although the formation of a white precipitate suggests that (in the cases of **5** and **7** at least) it is possibly the well-known cyclic metaborate $K_3[B_3O_6]$ (i.e. the trimeric aggregate of $K[BO_2]$), consistent with its insolubility in organic solvents. [13]




**Scheme 2.** Metathesis reactions of compound **1** with $CO_2$, $CS_2$ and {($H_2$CDippN)$_2$}PPCO.

With a view to exploring further both the scope and mechanism of this metathesis chemistry, we investigated the reactivity of **1** with organic carbonyl compounds. Ketones featuring enolizable hydrogen atoms, however, react with **1** in a different manner, reflecting the basic nature of the N centres, leading to $\alpha$-deprotonation and assimilation of the corresponding enolate fragment at the central boron atom. Thus, the reaction of **1** with (excess) acetophenone leads to protonation of both nitrogen atoms, and the formation of a B-bound $OC(Ph)CH_2$ moiety (Scheme 3 and Figure 2).



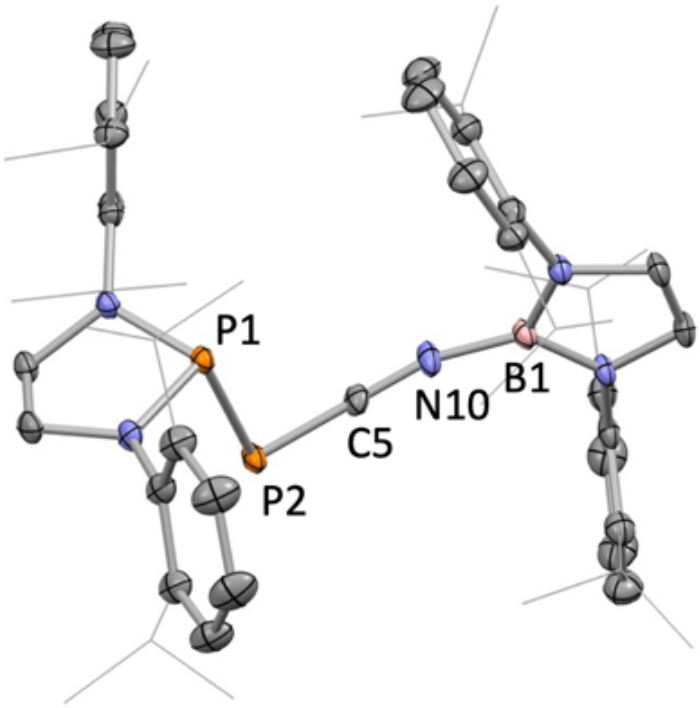



**Figure 1.** Molecular structures of **6** (upper) and one of the two independent molecules in the asymmetric unit of **7** (lower) in the solid state as determined by X-ray crystallography. Second disorder component and all Hs omitted, and $^{i}$Pr groups shown in wireframe format for clarity; thermal ellipsoids shown at the 35% probability level. Key bond lengths (Å) and angles (°): (for **6**) B1–N1 1.447(1), N1–C1 1.179(7), C1–S1 1.584(7), B1–N1–C1 156.8(4), N1–C1–S1 175.3(6); (for **7**) B1–N10 1.430(3), N10–C5 1.184(3), C5–P2 1.668(2), P2–P1 2.299(1), B1–N10–C5162.8(2), N10–C5–P2 178.7(2), C5–P2–P1 88.7(1).

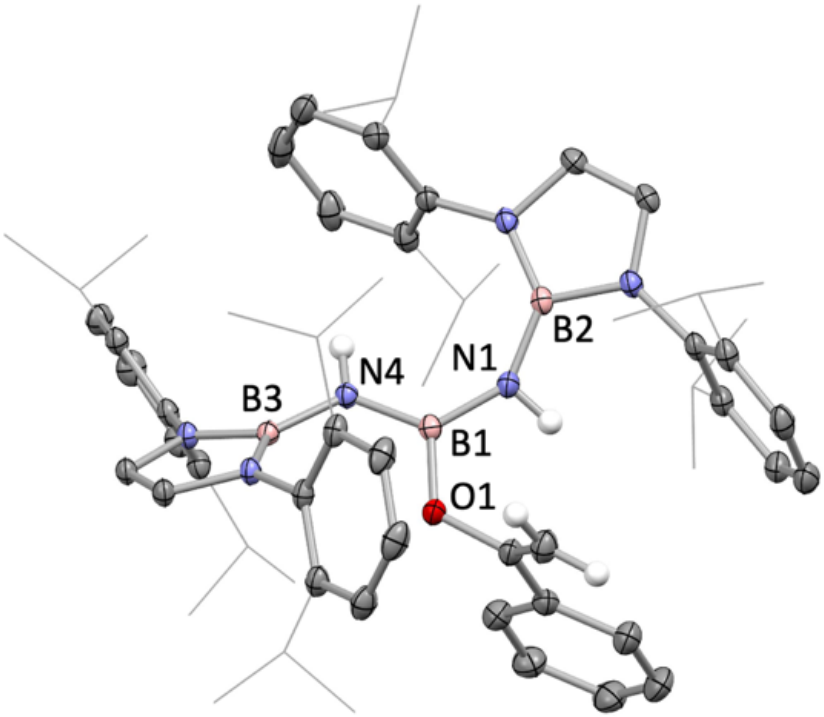
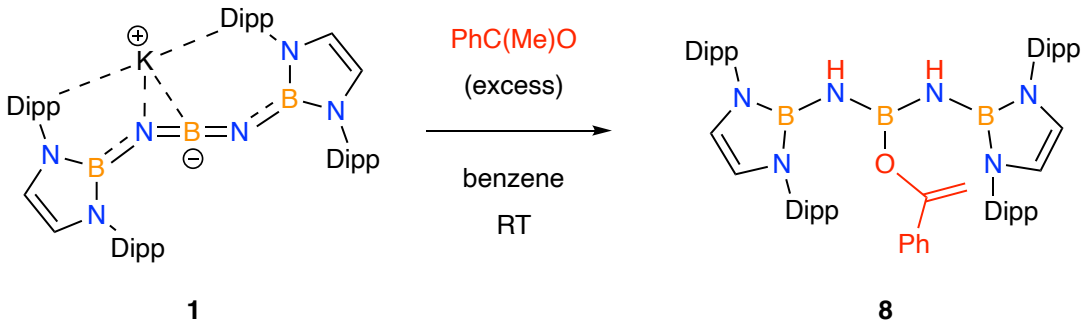



**Figure 2.** Molecular structure of **8** in the solid state as determined by X-ray crystallography. Most hydrogen atoms omitted and $^{i}$Pr groups shown in wireframe format for clarity; thermal ellipsoids shown at the 35% probability level. Key bond lengths (Å): B2–N1 1.438(2), N1–B1 1.426(2), B1–N4 1.420(1), N4–B3 1.451(1), B1–O1 1.398(1).

Non-enolizable carbonyls such as benzaldehyde, PhCHO, on the other hand, react via C=O bond cleavage in a manner similar to $CO_2$ and {$(H_2CDippN)_2$}PPCO, and (in addition) allow mechanistic detail to be uncovered. Addition of excess benzaldehyde to a solution of **1** in benzene, leads to the clean formation (over a period of ca. 12 h at room temperature) of the borylimine, *trans*-(boryl)NC(H)Ph (**10**), which has been characterized structurally by X-ray crystallography (Figure 3), and by standard spectroscopic/analytical methods. If the reaction is monitored *in situ* by $^{1}$H NMR spectroscopy in benzene-$d_6$ solution, an intermediate species

can be identified after 30 min (Figure S10), which is characterised by Dipp methine resonances at 3.61/3.89 ppm (each 2H), a boryl backbone signal (also 2H) at 6.05 ppm and a singlet (1H) at 5.28 ppm (*cf.* $\delta_H$ = 8.65 ppm for the imine proton of the final product **10**). If volatiles are removed in vacuo after 1 h, and the reaction mixture recrystallized from pentane, a mixture of crystals is obtained, which includes not only **10**, but also an intermediate K[(boryl)NB(O)OC(H)Ph], **9**, which precedes the formation of the final imine product via elimination of the K[$BO_2$] fragment (Scheme 4 and Figure 3).



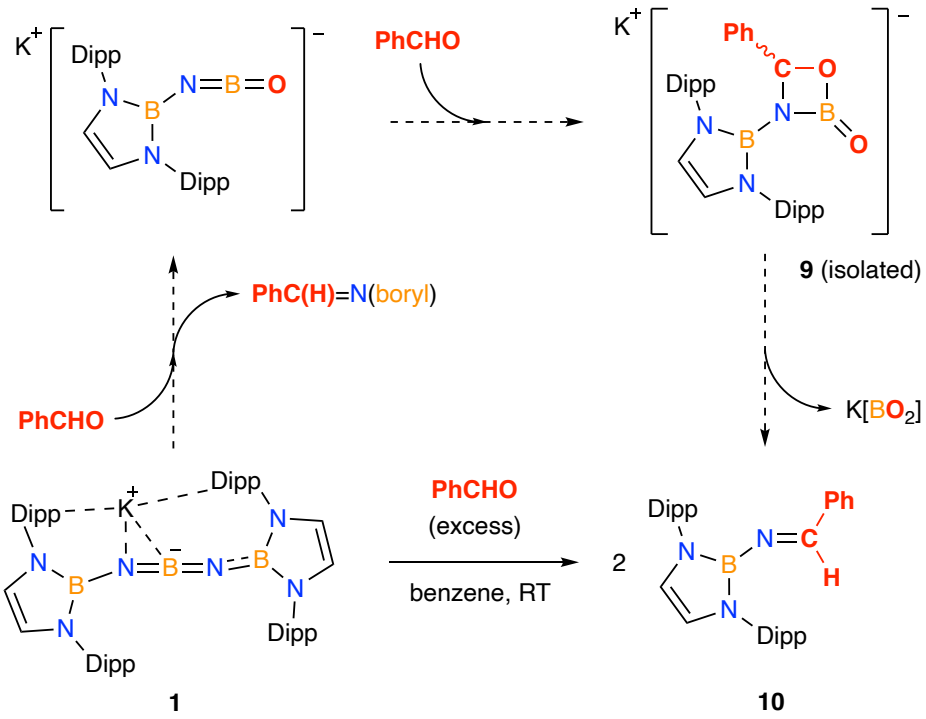

**1** **8**

**Scheme 3.** Reaction of **1** with acetophenone, leading to the formation of boron enolate **8**.

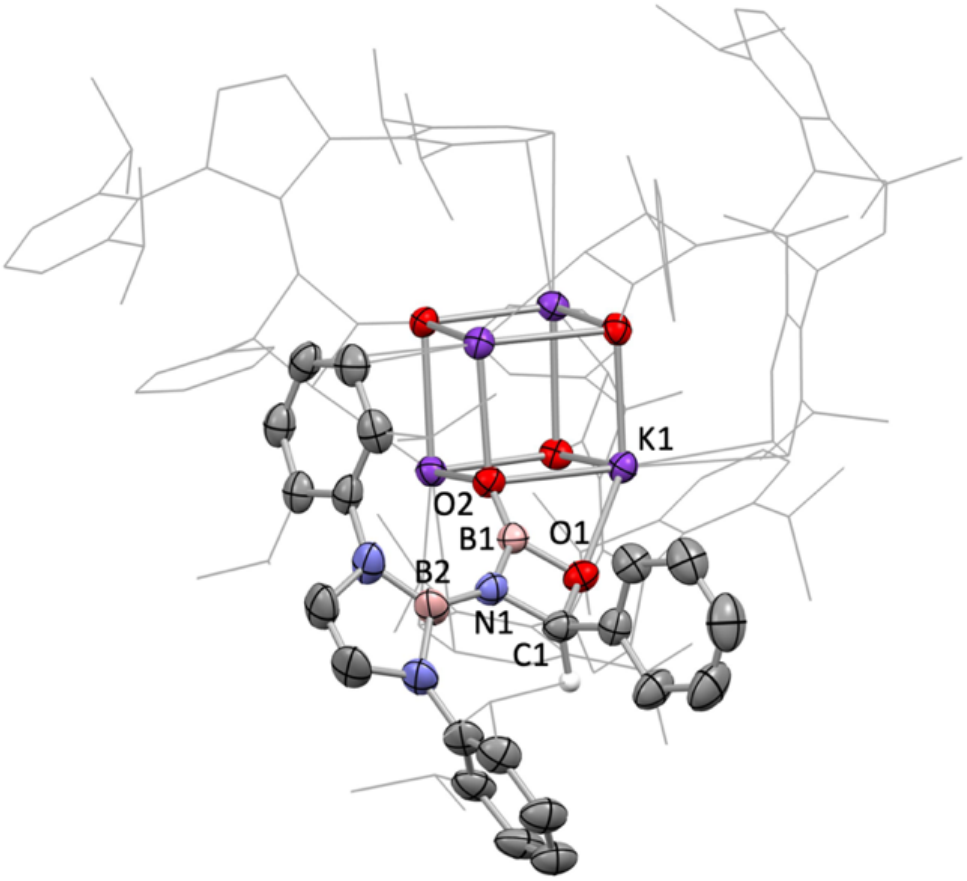
Analysis of crystalline **9** by X ray diffraction reveals that the solid material contains a tetrameric potassium salt (based on a cubic $K_4O_4$ core), and an organic fragment featuring a four-membered CBNO ring. [2+2]Cyclo-reversion via CO and BN bond cleavage presumably offers a route for the onward conversion of this species to borylimine **10**.

Structurally, the organic component of **9** can be viewed as being derived from cycloaddition of the C=O double bond of benzaldehyde across the N=B double bond of an intermediate species of the type [(boryl)N=B=O]$^-$. Geometrically, the bond length associated with the B–O

linkage within the four-membered ring (1.453(4) Å) is consistent with a single bond; the associated O atom participates in a weak contact with a single $K^+$ counterion, *d*(K···O) = 2.710(3) Å. By contrast, the exocyclic B–O bond is much shorter (1.283(4) Å), consistent with appreciable π-bonding character,[14] and the associated O atom bridges three $K^+$ cations (*d*(K···O) = 2.596(2), 2.604(2), 2.778(2) Å).




**Scheme 4.** Cycloaddition reactivity of **1** with benzaldehyde, PhCHO, leading to the formation of borylimine **1**


K1
O2
B1
O1
B2
N1
C1

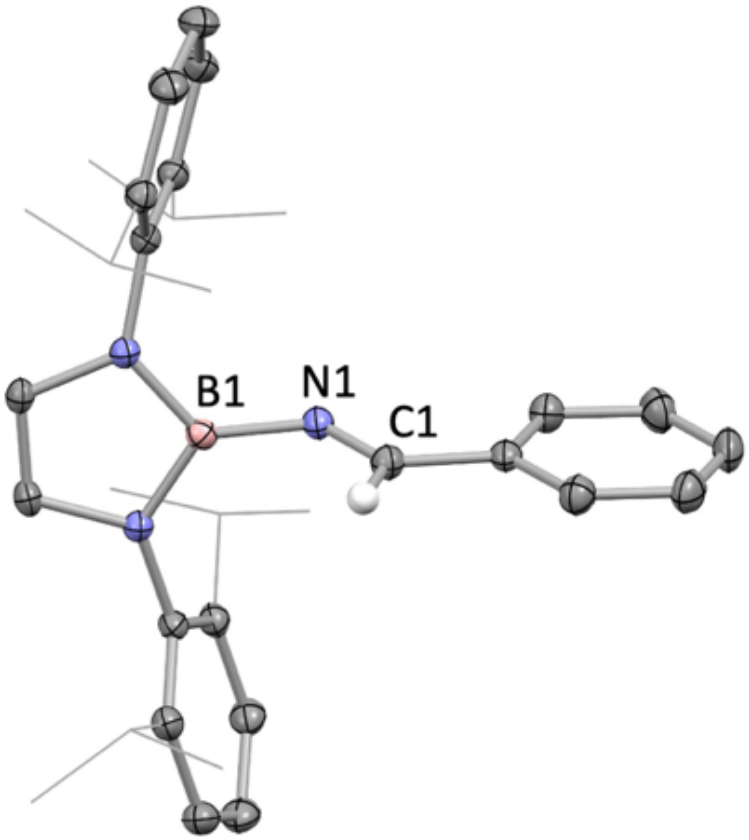

B1
N1
C1

**Figure 3.** Molecular structures of compounds **9** (upper) and **10** (lower) in the solid state as determined by X-ray crystallography. Thermal ellipsoids are drawn at 50% probability level. Most H atoms are omitted for clarity. Key bond lengths (Å) and angles (°): (for **6**) B2–N1 1.423(5), N1–C1 1.470(5), C1–O1 1.441(4), O1–B1 1.453(4), B1–N1 1.478(5), B1–O2 1.283(4); (for **7**) B1–N1 1.448(3), N1–C1 1.254(3), B1–N1–C1 126.1(2), N1–C1–C2 123.5(2).

These structural and reactivity data suggest that **1** acts as a transfer agent for the [(boryl)N] group via a Wittig-type reaction involving [2+2] cyclo-addition/cyclo-reversion steps. To further probe the mechanism of the reaction with benzaldehyde, we examined the potential energy surface by density function theory calculations (M06-2X/Def2-SVP//Def2-TZVP). The overall process involves two [2+2] cyclo-addition/reversion steps, each involving one of the B=N bonds associated with the central boron atom of **1** (Figure 4). The overall process is exergonic (by -20.5 kcal $mol^{-1}$), and successive steps occur via transition states which are *ca*. 25-30 kcal $mol^{-1}$ above the preceding intermediate. The first step in the reaction pathway is thought to be rate-determining and involves [2+2] cycloaddition of the C=O bond of PhCHO across one B=N unit of the anionic component of **1** to give **IN1**, which features an COBN four-membered ring bearing a pendant iminoboryl function. This step resembles the [2+2]cycloaddition reported by Jones in the room temperature reaction of $CO_2$ with the Si=N bond of a silaimine.[5c] In the case of **1** it is only slightly exergonic (-0.7 kcal $mol^{-1}$) and occurs via a barrier of +29.7 kcal $mol^{-1}$.

Subsequent cyclo-reversion to release a first equivalent of *trans*-(boryl)NC(H)Ph, and generate **IN2**, [(boryl)N=B=O]$^-$, involves traversing a slightly lower activation barrier of 25.1 kcal mol$^{-1}$, and provides an extra 8.4 kcal mol$^{-1}$ of thermodynamic stabilization. The uptake of a second equivalent of PhCHO occurs via a similar transition state to first generate a third intermediate **IN3**, akin to the structurally characterized system **9**. A similar [2+2] cyclo-reversion process then yields the observed second equivalent of *trans*-(boryl)NC(H)Ph. The last two steps incur activation barriers of 23.5 and 25.7 kcal mol$^{-1}$, respectively, and lead to a process which (overall) is exergonic to the tune of -20.5 kcal mol$^{-1}$. We postulate, given the relatively low transition state barriers calculated beyond **IN1**, that the crystallization of compound **9** from solution relates to the crystallinity/insolubility of the tetrameric potassium salt, rather than to the intrinsic reaction barrier associated with its onward conversion to the final product (which is relatively low).

Finally, we set out to probe whether the differing geometric and electronic structures of bent BNBNB anion **1**/**2** and their linear counterpart **3** might lead to differences in reactivity. Surprisingly, however, the reaction of **3** with MeI can be shown to generate the same iminoborane product (**4**) as is formed in the reactions of **1**/**2** under comparable conditions (Scheme 1). The accompanying release of $B(C_6F_5)_3$ can be confirmed by *in situ* $^{11}B$ and $^{19}F$ NMR measurements (Figures S13 and S14). These observations imply that the assimilation of the borane by the diazaborolyl heterocycle of **1**/**2** is chemically reversible – at least under these reactivity conditions.

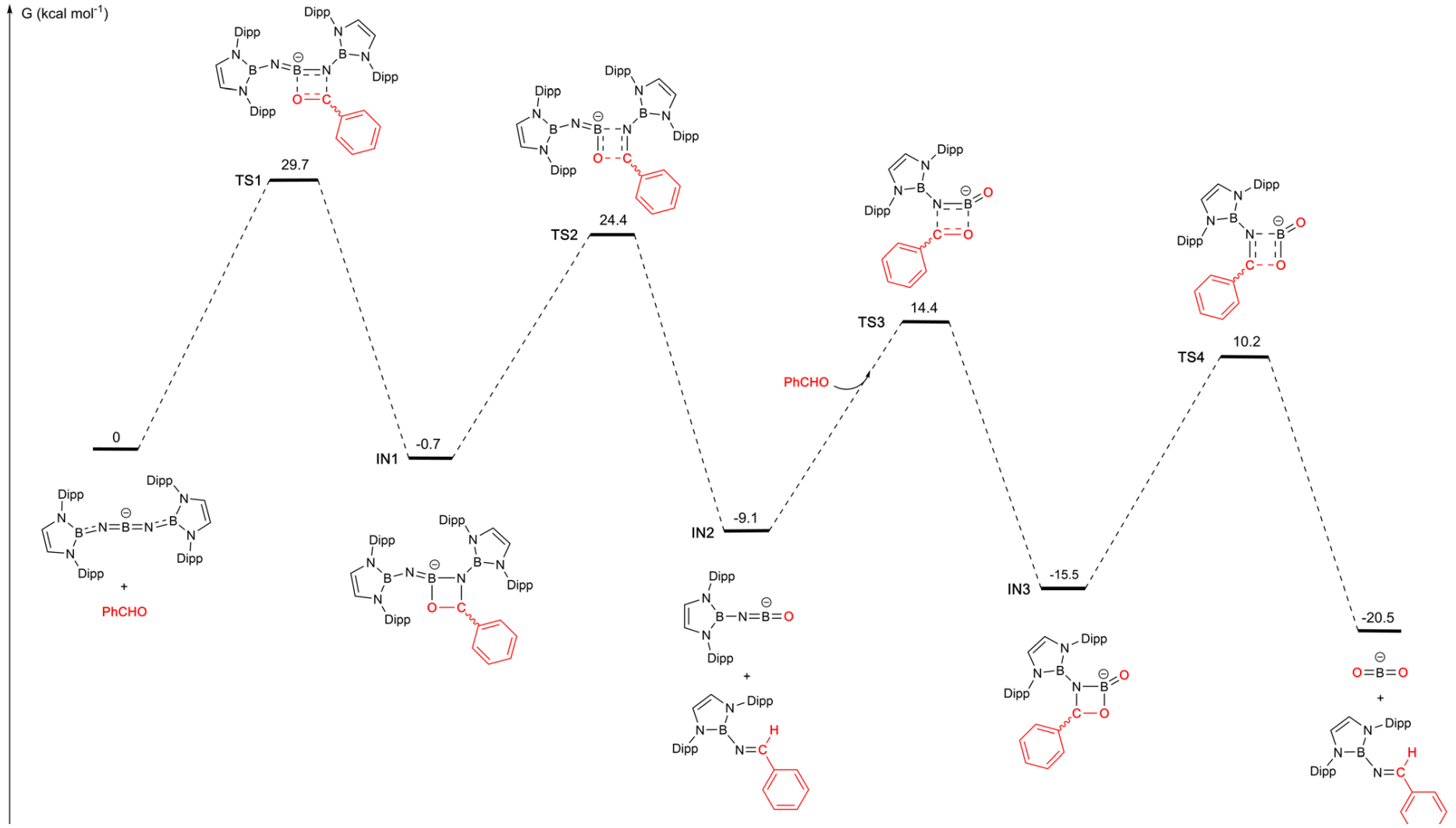



**Figure. 4** DFT calculated mechanism for the reaction of PhCHO with the anionic component of 1 (calculated at the M06-2X/Def2-SVP//Def2-TZVP level of theory with solvation modelled with smd, benzene; K+ counterions omitted for simplicity). [15]

## Conclusions

In conclusion, we report on the reaction chemistry of an unprecedented ‘inorganic cumulene’ - featuring a five-atom BNBNB chain - in particular with respect to species containing C=O (and related) multiple bonds. The intrinsic polarity of the BNBNB chain (featuring electronic-rich nitrogen centres) is demonstrated by metathesis chemistry with electrophilic heteroallenes such as $CO_2$, and with organic carbonyl compounds. Metathesis leads to {$(HCDippN)_2$}BN transfer chemistry via consecutive [2+2] cyclo-addition/cyclo-reversion steps. Transfer of the imide unit to [CO], [CS], [PP{$(NDippCH_2)_2$}] and [C(H)Ph] moieties generates the (boryl)N=C=X systems (X = O, S, PP{$(NDippCH_2)_2$}, C(H)Ph), via processes driven thermodynamically by B–O bond formation. An isolable complex of stoichiometry K[(boryl)NB(O)OC(H)Ph] (9), formed via [2+2] cycloaddition to $[(boryl)N=B=O]^-$ can be shown to be an intermediate in the formation of (boryl)N=C(H)Ph, and provides corroborating evidence for a DFT-calculated mechanism proceeding via consecutive bora-Wittig steps.

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[9] For metathesis involving B–O bond formation from a M=B unit see, for example: (a) D. L. Kays (née Coombs), J. K. Day, L.-l. Ooi and S. Aldridge, *Angew. Chem. Int. Ed*. **2005**, *44*, 7457 – 7460; (b) D. L. Kays (née Coombs), A. Rossin, J. K. Day, L.-l. Ooi and S. Aldridge, *Dalton Trans*. **2006**, 399 – 410; (c) H. Braunschweig, M. Burzler, K. Radacki and F. Seeler, *Angew. Chem. Int. Ed.* **2007**, *46*, 8071 – 8073; (d) G. A. Pierce, D. Vidovic, D. L. Kays, N. D. Coombs, A. L. Thompson, E. D. Jemmis, S. De and S. Aldridge, *Organometallics* **2009**, *28*, 2947 – 2960; (e) S. De, G. A. Pierce, D. Vidovic, D. L. Kays, N. D. Coombs, E. D. Jemmis and S. Aldridge, *Organometallics* **2009**, *28*, 2961 – 2975; (f) J. Bauer, H. Braunschweig, A. Damme, J. O. C. Jimenez-Halla, T. Kramer, K. Radacki, R. Shang, E. Siedler and Q. Ye, *J. Am. Chem. Soc.* **2013**, *135*, 8726 – 8734.

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[11] For a recent review of cumulene chemistry see, for example: D. Wendinger and R. R. Tykwinski, *Acc. Chem. Res.* **2017**, *50*, 1468-1479.

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[13] W. H. Zachariasen, *J. Chem. Phys.* **1937**, *5*, 919-922.

[14] Y. K. Loh, K. Porteous, M. A. Fuentes, D. C. H. Do, J. Hicks and S. Aldridge, *J. Am. Chem. Soc.* **2019**, *141*, 8073–8077.

[15] In the absence of $K^+$ counterions (for computational simplicity) the trimerization of $[BO_2]^-$ to $[B_3O_6]^{3-}$ makes little difference to the overall calculated free energy

change shown in Figure 4. This process is calculated to be close to thermo-neutral ($\Delta G$ = +0.5 kcal $mol^{-1}$)

**Supporting information**

**General considerations**

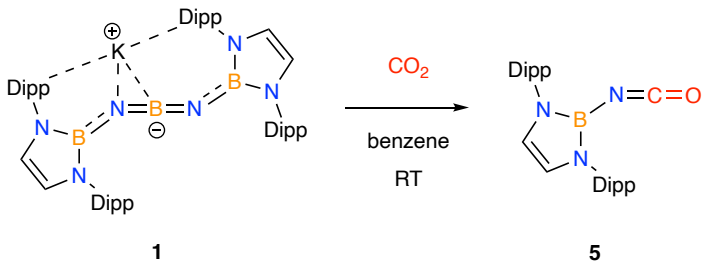
All experiments were carried out under an atmosphere of dry argon or dinitrogen using standard Schlenk line or dry-box techniques. Solvents were degassed by sparging with argon and dried by passing through a column of appropriate drying agent using a commercially available Braun SPS and stored over potassium mirror under argon in a Teflon valve ampoule. NMR spectra were measured in $d_6$-benzene, with the solvent being dried over calcium hydride or molten potassium respectively, distilled, degassed by three freeze-pump-thaw-cycles and stored over 3 Å sieves. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were measured on a Bruker Avance III HD Nanobay 400 MHz or Bruker Avance III 500 MHz spectrometer, and referenced internally to residual protio-solvent ($^{1}H$) or solvent ($^{13}C$) resonances; resonances are reported relative to tetramethylsilane (δ = 0 ppm). Assignments were confirmed using two-dimensional $^{1}H$-$^{1}H$, $^{13}C$-$^{1}H$, NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. The reported yields are the yields obtained after crystallisation and subsequent measurement of the material by single crystal-ray diffraction if not stated otherwise. Elemental analyses were carried out by London Metropolitan University or Elemental Microanalysis Ltd, Okehampton, Devon, UK.

**Preparation of starting materials**

$K[(HCDippN)_2BNBNB(NDippCH)_2]$, **1**, and $(H_2CDippN)_2PPCO$ were prepared by literature

procedures.[S1, S2]

**Synthetic procedures, characterising data and representative spectra of new compounds**




**Scheme S1.** Synthesis of $(HCDippN)_2BNCO$, **5**.

**$(HCDippN)_2BNCO$, 2.** A solution of **1** (100 mg 0.117 mmol) in benzene (5 mL) was degassed by three freeze-pump-thaw cycles, before $CO_2$ was admitted (at ca. 1 atm pressure), leading to a near colourless solution. After stirring for 12 h, volatiles were removed in vacuo and the resulting pale solid dissolved in 3 mL pentane. The solution was concentrated to ca. 1 mL and crystals of **5** were obtained upon standing at room temperature that were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

Yield: 89.6 mg (90.0 %)

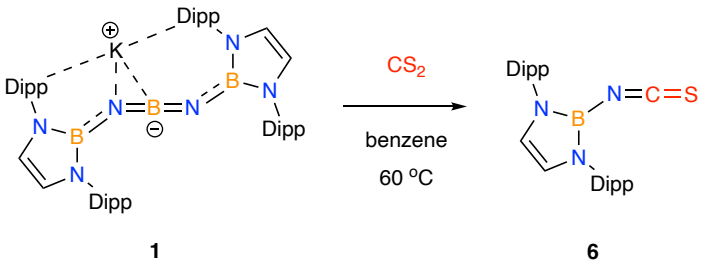
$^1H$ NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 1.18 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, $CH_3$ of Dipp), 1.25 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, $CH_3$ of Dipp), 3.14 (sept, $^3J_{H,H}$ = 6.8 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 5.95 (s, 2H, CH of boryl), 7.12 (m, 4H, m-ArH of Dipp), 7.21, (m, 2H, p-ArH of Dipp).

$^{11}B\{^1H\}$ NMR (128 MHz, $C_6D_6$, 298 K): $\delta_B$ 17.9 (boryl).

$^{13}C\{^1H\}$ NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 24.1, 24.3 ($CH_3$ of Dipp), 28.8 (<u>C</u>H$(CH_3)_2$ of Dipp), 118.2 (CH of boryl), 123.9 (m-Ar of Dipp), 128.4 (p-Ar of Dipp), 136.8 (CN of Dipp), 146.5 (o-

Ar of Dipp), not observed (N=C=O).

Elemental microanalysis: calc. for $C_{27}H_{36}BN_3O$ (%): C 75.52 H 8.45 N 9.79; meas. C 75.82 H 8.51 N 9.54.




**1** **6**

**Scheme S2.** Synthesis of $(HCDippN)_2BNCS$, **6**.

**$(HCDippN)_2BNCS$, 6. 1** (100 mg 0.117 mmol) was dissolved in benzene (10 mL) and a drop of $CS_2$ (ca. 0.02 mL, excess) added. The solution was heated at 60 °C overnight with a colour change from orange to red. Volatiles were removed in vacuo and the residue extracted with pentane (10 mL). The resulting solution was concentrated to ca. 2 mL and colourless crystals of **6** were obtained upon standing at room temperature which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

Yield: 51.3 mg (52.0 %)

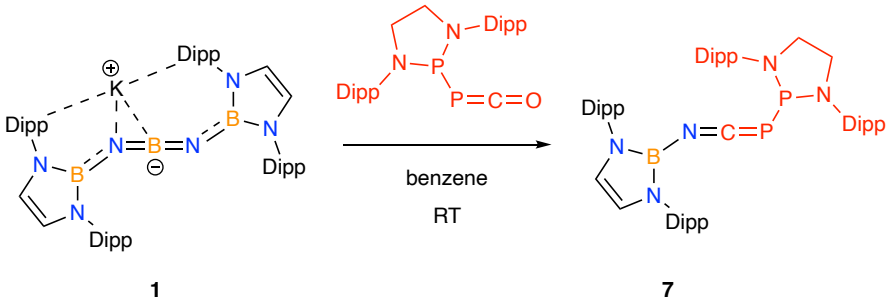
$^1$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 1.17 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, $CH_3$ of Dipp), 1.29 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, $CH_3$ of Dipp), 3.12 (sept, $^3J_{H,H}$ = 6.8 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 5.91 (s, 2H, CH of boryl), 7.13(m, 4H, m-ArH of Dipp), 7.20 (m, 2H, p-ArH of Dipp).

$^{11}$B{$^1$H} NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 16.1 (boryl).

$^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 24.0, 24.5 ($CH_3$ of Dipp), 28.9 (<u>C</u>H$(CH_3)_2$ of Dipp), 118.6 (CH of boryl), 123.9 (m-Ar of Dipp), 128.6 (p-Ar of Dipp), 136.4 (CN of Dipp), 146.3 (o-

Ar of Dipp), not observed (N=C=S).

Elemental microanalysis: calc. for $C_{27}H_{36}BN_3S$ (%): C 72.80 H 8.15 N 9.43; meas. C 72.76 H 8.26 N 9.17.




**1** **7**

**Scheme S3.** Synthesis of $(HCDippN)_2BNCPP(NDippCH_2)_2$, **7**.

**$(HCDippN)_2BNCPP(NDippCH_2)_2$, 7.** To a mixture of **1** (80 mg, 0.094 mmol) and $(CH_2DippN)_2PPCO$ (69.3 mg, 0.148 mmol) in a 25 mL Schlenk flask was added 5 mL benzene. The resulting solution was stirred for 12 h with a colour change to dark green. Volatiles were removed in vacuo and the residue extracted with pentane (3 mL). The resulting solution was concentrated to ca. 1 mL and colourless crystals of **7** were obtained upon standing at room temperature which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

Yield: 88.6 mg (55.2 %)

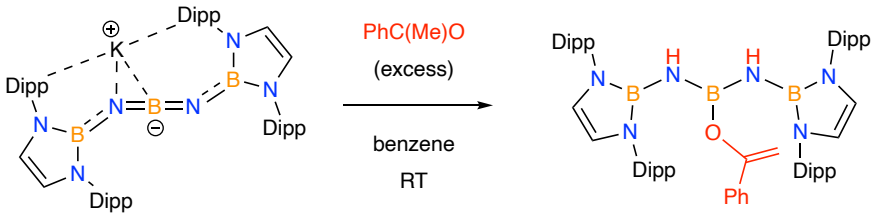
$^1$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 1.05 (d, $^3J_{H,H}$ = 7.0 Hz, 12H, $CH_3$ of (boryl)Dipp), 1.13 (d, $^3J_{H,H}$ = 7.0 Hz, 12H, $CH_3$ of (boryl)Dipp), 1.19, 1.25, (d, $^3J_{H,H}$ = 6.6 Hz, 12H, $CH_3$ of (phosphanyl)Dipp),1.31 (dd, $^3J_{H,H}$ = 6.6 Hz, 12H, $CH_3$ of (phosphanyl)Dipp), 3.03(sept, $^3J_{H,H}$ = 7.0 Hz, 4H,C<u>H</u>$(CH_3)_2$ of (boryl)Dipp), 3.11, 3.58 (m, 4H, $CH_2$ of phosphanyl), 3.48, 3.76 (m,

4H,C<u>H</u>(CH$_3$)$_2$ of (phosphanyl)Dipp), 5.86 (s, 2H, CH of boryl), 7.04 (m, 4H, m-ArH of (boryl)Dipp), 7.10(m, 6H, ArH of (phosphanyl)Dipp), 7.18(m, 2H, p-ArH of (boryl)Dipp).

$^{11}$B{$^{1}$H} NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 16.0 (boryl).

$^{31}$P NMR (162 MHz, $C_6D_6$, 298 K): $\delta_P$ -183.3 (d, P<u>P</u>=C),165.6 (d, <u>P</u>P=C).

$^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 23.9, 24.4 (CH$_3$ of Dipp), 24.7, 25.2, 25.9 (d, CH$_3$ of (phosphanyl)Dipp), 28.8 (<u>C</u>H(CH$_3$)$_2$ of (boryl)Dipp), 28.9, 29.5 (d, <u>C</u>H(CH$_3$)$_2$ of (phosphanyl)Dipp), 54.9 (d, CH$_2$ of phosphanyl), 118.5 (CH of boryl), 123.6 (m-Ar of (boryl)Dipp), 123.9 (m-Ar of (phosphanyl)Dipp), 124.9 (p-Ar of (phosphanyl)Dipp), 127.5 (o-Ar of (boryl)Dipp), 136.8 (CN of (boryl)Dipp), 137.8 (d, CN of (phosphanyl)Dipp), 146.2 (o-Ar of (boryl)Dipp), 148.7, 150.4 (o-Ar of (phosphanyl)Dipp), not observed (N=C=P).




**1** **8**

**Scheme S4.** Synthesis of [{(HCDippN)$_2$BN}$_2$B]OC(CH$_2$)Ph, **8**.

**[{(HCDippN)$_2$BN}$_2$B]OC(CH$_2$)Ph, 8. 1** (15 mg 0.018 mmol) was dissolved in benzene (4 mL) and a drop of acetophenone (0.01 mL, excess) added. The reaction mixture was stirred for 1 h with an accompanying colour change to light yellow. Volatiles were removed in vacuo and the residue extracted with pentane (3 mL). The resulting solution was concentrated to ca. 0.5 mL and yellow crystals of **8** were obtained upon standing at room temperature which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold

pentane (2 x 1 mL).

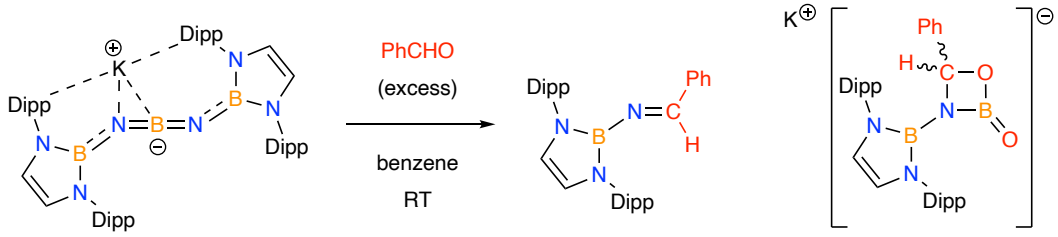
Yield: 7.8 mg (47.0 %)

$^{1}$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 1.16 (d, $^{3}J_{H,H}$ = 6.6 Hz, 24H, $CH_3$ of Dipp), 1.18 (d, $^{3}J_{H,H}$ = 6.6 Hz, 24H, $CH_3$ of Dipp), 2.56 (br, 2H, NH), 3.12, 4.43 (s, each 1H, C=$CH_2$), 3.28 (sept, $^{3}J_{H,H}$ = 6.8 Hz, 8H,C<u>H</u>$(CH_3)_2$ of Dipp), 5.97 (s, 2H, CH of boryl), 7.07 (m, 17H, ArH of Dipp).

$^{11}$B{$^{1}$H} NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 22.4 (boryl).

$^{13}$C{$^{1}$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 23.8, 25.5 ($CH_3$ of Dipp), 28.8 (<u>C</u>H$(CH_3)_2$ of Dipp), 97.7 (C=<u>C</u>$H_2$), 118.6 (CH of boryl), 124.2 (m-Ar of Dipp), 125.3, 128.8, 136.7 (Ph), 127.4 (p-Ar of Dipp), 139.6 (CN of Dipp), 146.3 (o-Ar of Dipp), 154.4 (<u>C</u>=$CH_2$).

Elemental microanalysis: calc. for $C_{60}H_{81}B_3N_6O$ (%): C 77.09 H 8.73 N 8.99; meas. C 76.89 H 8.51 N 9.12.




**1** **10** **9**

**Scheme S5.** Synthesis of (HCDippN)$_2$BN[$\kappa^2$-(C,B)-C(H)PhBO$_2$], **9** and (HCDippN)$_2$BNCHPh, **10**.

**(HCDippN)$_2$BN[$\kappa^2$-(C,B)-C(H)PhBO$_2$], 9**. **1**(100 mg 0.117 mmol) was dissolved in benzene (10 mL) and a drop of benzaldehyde (0.02 mL, excess) added. The resulting solution was stirred for 30 min, with an accompanying colour change to yellow. Volatiles were removed in

vacuo, and the residue extracted with pentane (5 mL). The resulting solution was concentrated to ca. 0.5 mL and a mix of colourless crystals of **9** (unstable in solvent and briefly visible in NMR) and **10** were obtained which were suitable for X-ray crystallography.

**(HCDippN)$_2$BNCHPh, 10**. **1** (100 mg 0.117 mmol) was dissolved in benzene (10 mL) and a drop of benzaldehyde (0.02 mL, excess) added. The resulting solution was stirred for 12 h with a colour change to light yellow. Volatiles were removed in vacuo and the residue extracted with pentane (5 mL). The resulting solution was concentrated to ca. 2 mL and colourless crystals of **10** were obtained which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

Yield: 16.6 mg (14.4 %)

$^1$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 1.27 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, $CH_3$ of Dipp), 1.29 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, $CH_3$ of Dipp), 3.43 (sept, $^3J_{H,H}$ = 6.9 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 6.19 (s, 2H, CH of boryl), 6.82 (m, m-ArH of Ph), 6.89 (m, p-ArH of Ph), 7.17 (m, m-ArH of Dipp), 7.22 (m, p-ArH of Dipp), 7.46 (m, o-ArH of Ph), 8.65 (s, PhC(H)=N).

$^{11}$B{$^1$H} NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 24.6 (boryl).

$^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 24.2, 24.4 ($CH_3$ of Dipp), 28.8 (<u>C</u>H$(CH_3)_2$ of Dipp), 119.0 (CH of boryl), 123.7 (m-Ar of Dipp), 128.6 (p-Ar of Dipp),128.6 (o-Ar of Ph), 128.7 (m-Ar of Ph), 131.2 (p-Ar of Ph), 138.8 (CN of Dipp), 146.6 (o-Ar of Dipp), 167.8 (C=N), overlap by solvent peak (Ph(<u>C</u>)-C=N).

**Reactions of 3 with electrophiles**

With MeI. **3** (15 mg, 0.011 mmol) was dissolved in $C_6D_6$ (0.4 mL) and a drop of MeI (0.01 mL, excess) added. The reaction mixture was heated at 60 °C overnight in a J-Young NMR tube with the formation of a white precipitate; monitoring by multinuclear NMR revealed essentially quantitative formation of **4** and $B(C_6F_5)_3$ (Figures S18 and S19).

With $CO_2$. A solution of **3** (15 mg, 0.011 mmol) in $C_6D_6$ (0.4 mL) was degassed by three freeze-pump-thaw cycles, before $CO_2$ was admitted (at ca. 1 atm pressure), leading to a near colourless solution; monitoring by multinuclear NMR revealed essentially quantitative formation of **5** (Figure S20).

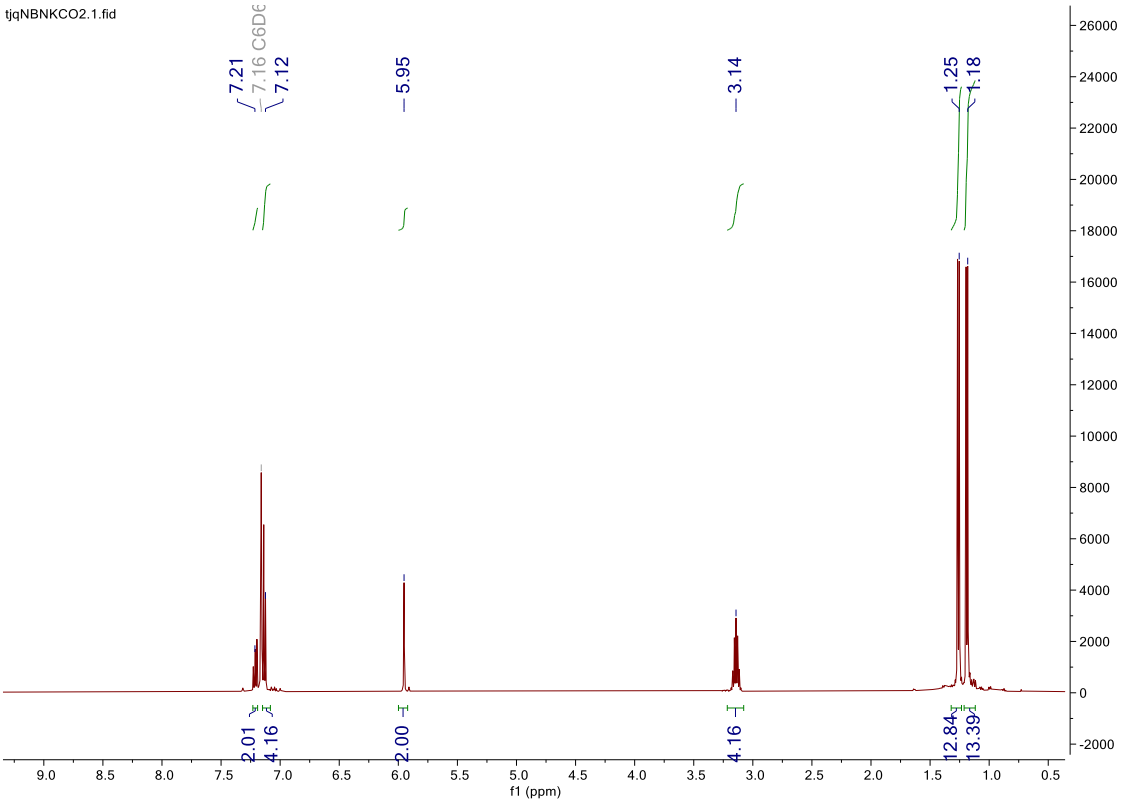



**Figure S1**: $^{1}$H NMR spectrum of **5** (500 MHz, $C_6D_6$, 298 K).

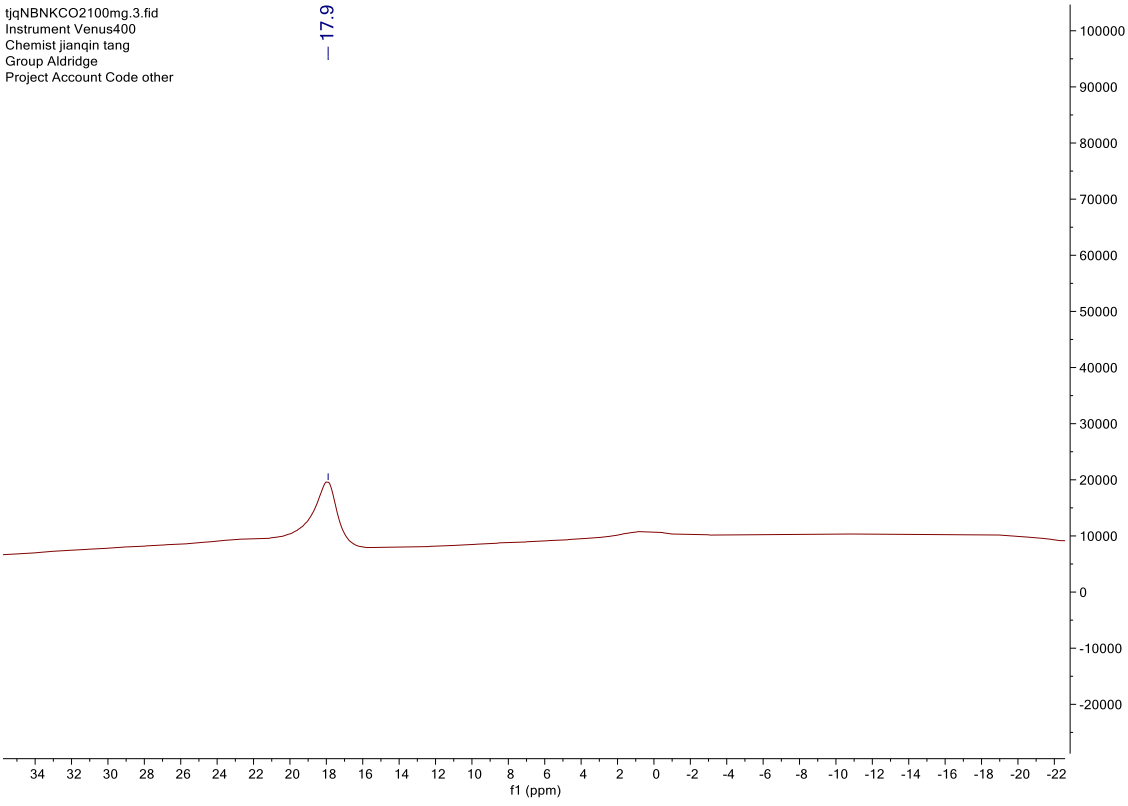



**Figure S2**: $^{11}$B{$^{1}$H} NMR spectrum of **5** (128 MHz, $C_6D_6$, 298 K).

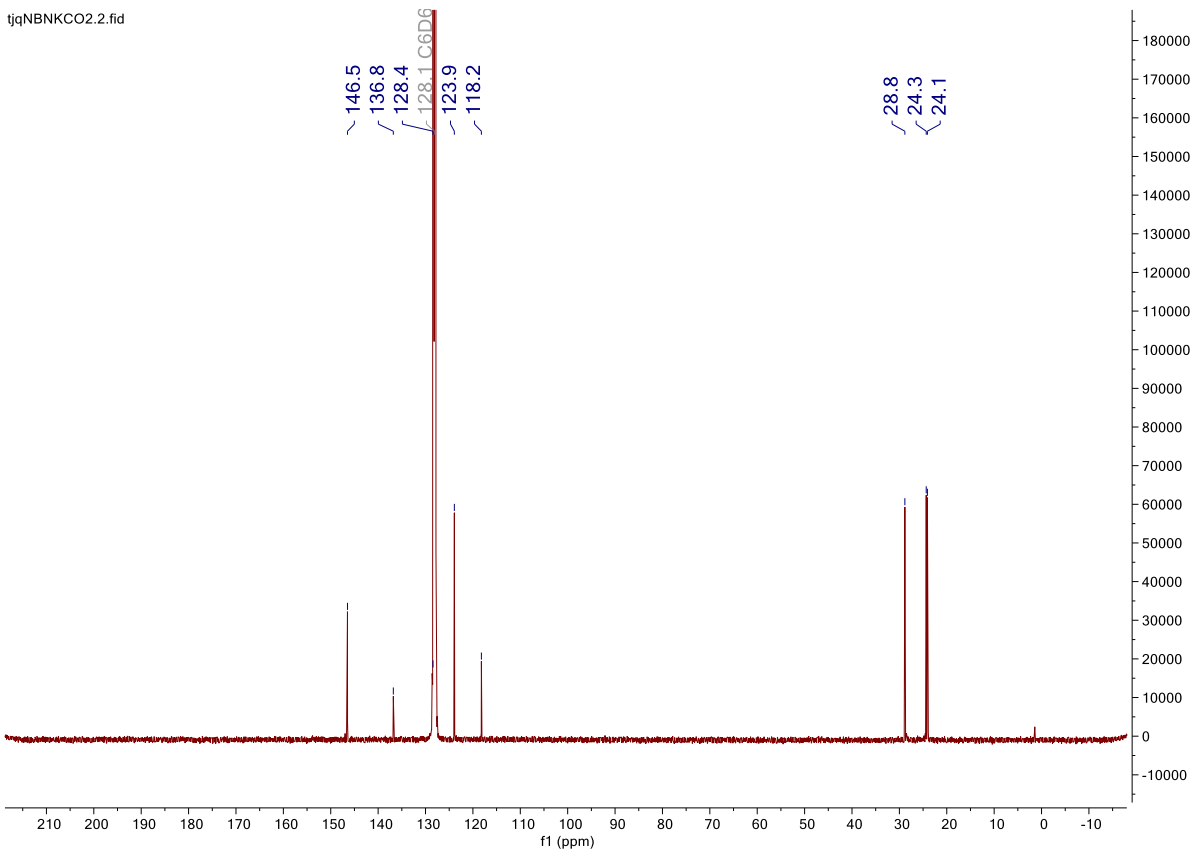



**Figure S3**: $^{13}C\{^{1}H\}$ NMR spectrum of **5** (126 MHz, $C_6D_6$, 298 K).

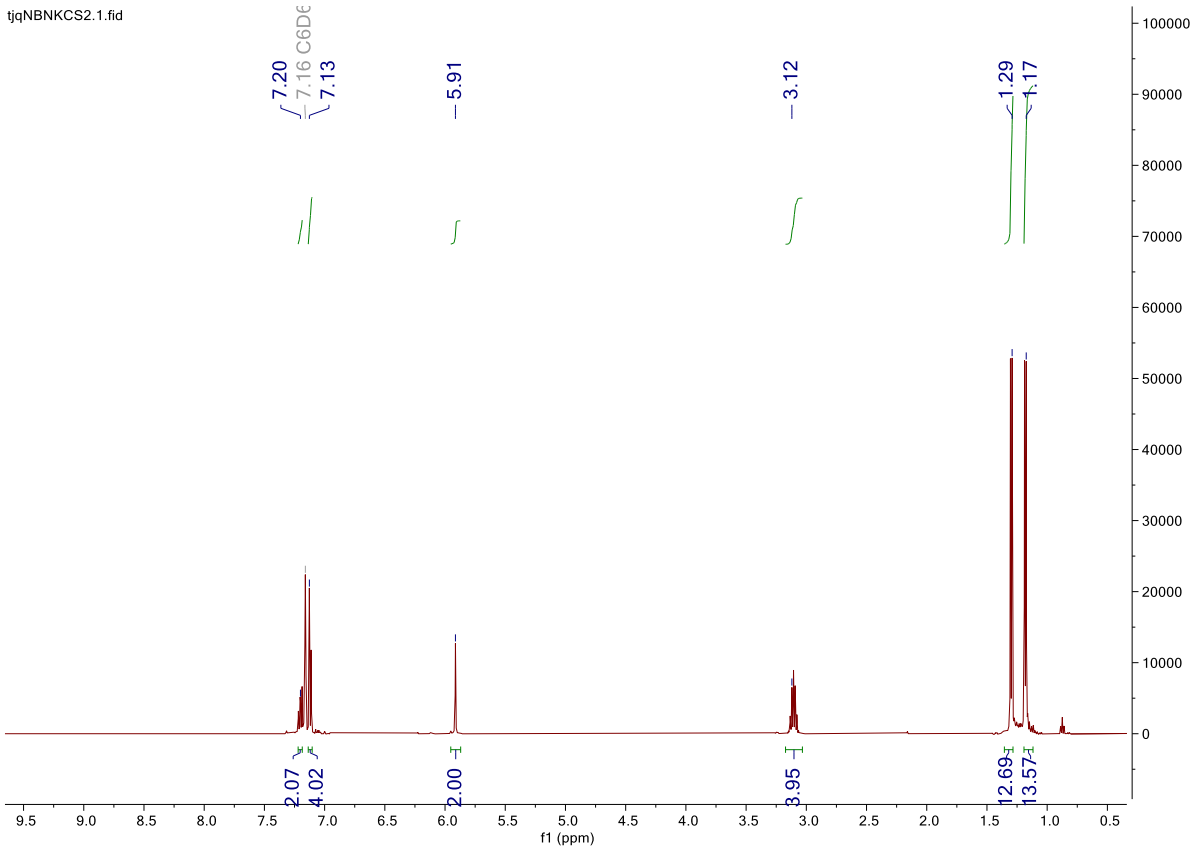



**Figure S4**: $^{1}H$ NMR spectrum of **6** (500 MHz, $C_6D_6$, 298 K).

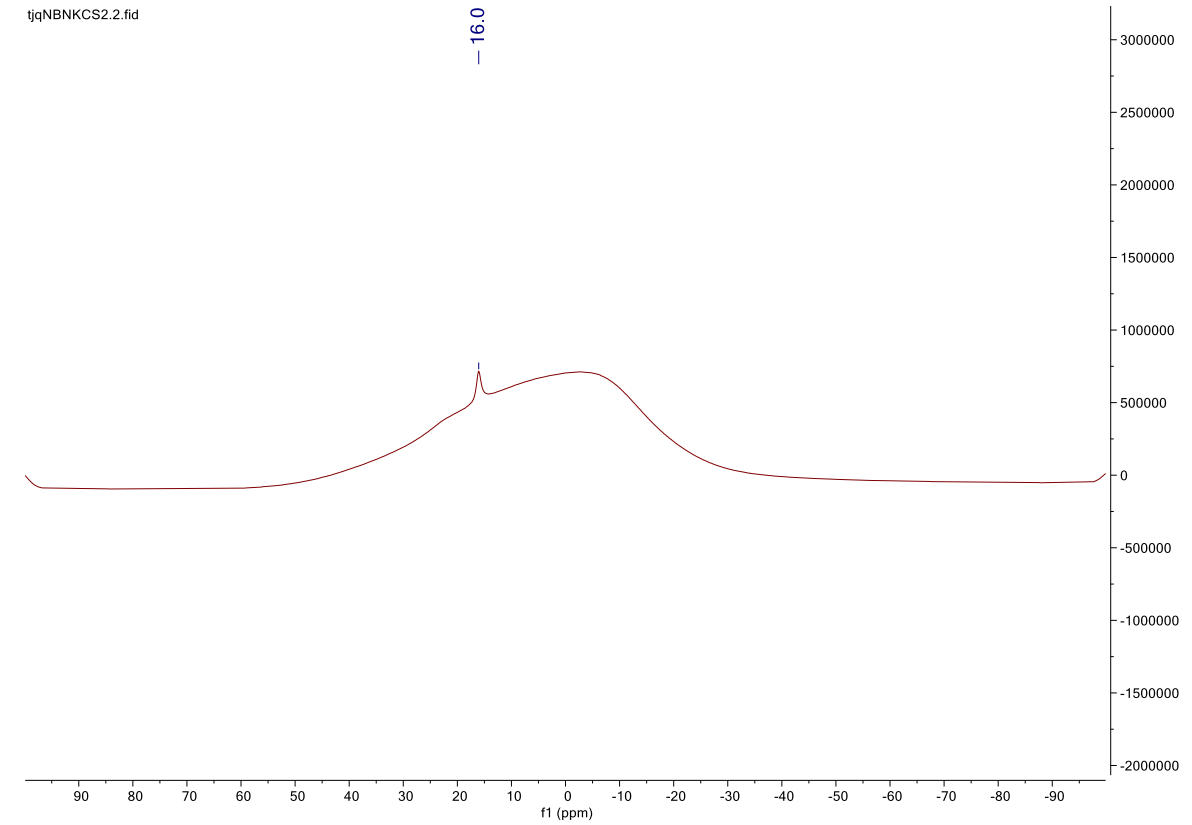



**Figure S5**: $^{11}B\{^{1}H\}$ NMR spectrum of **6** (160 MHz, $C_6D_6$, 298 K).

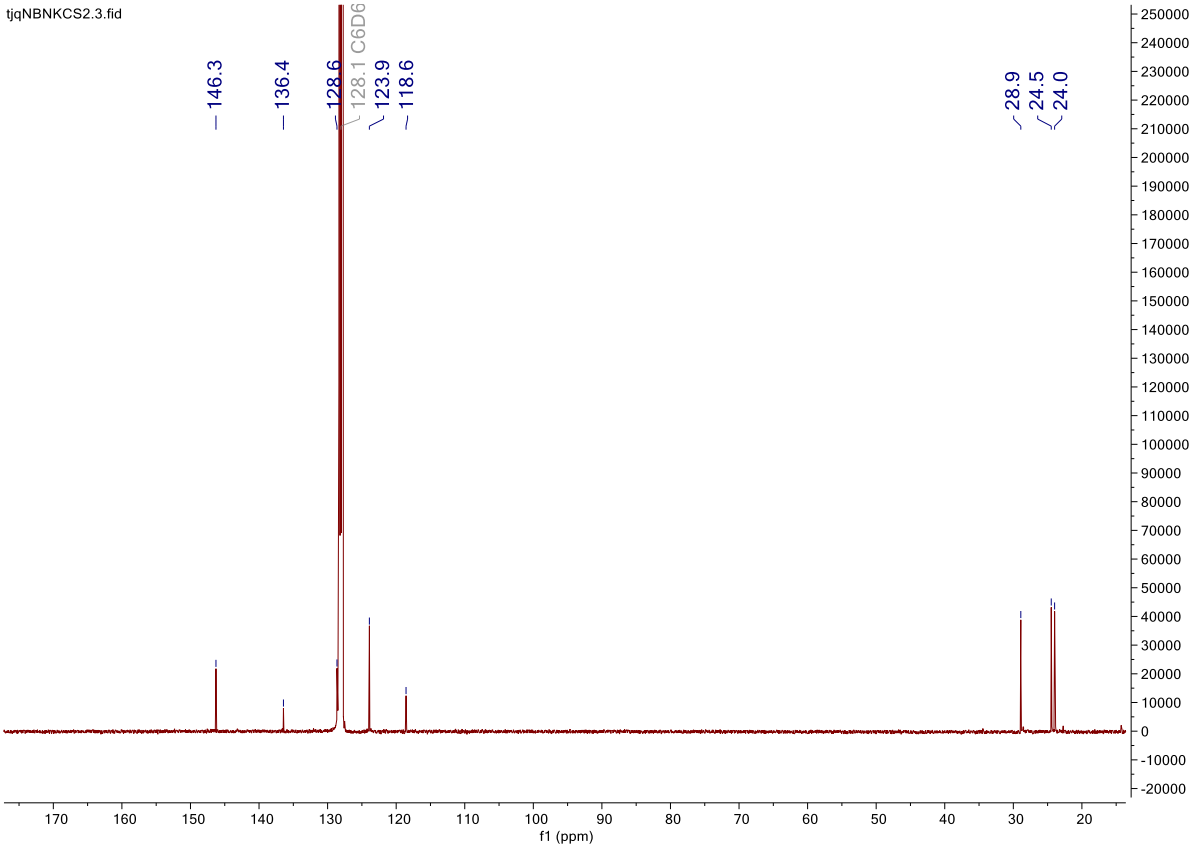



**Figure S6**: $^{13}C\{^{1}H\}$ NMR spectrum of **6** (126 MHz, $C_6D_6$, 298 K).

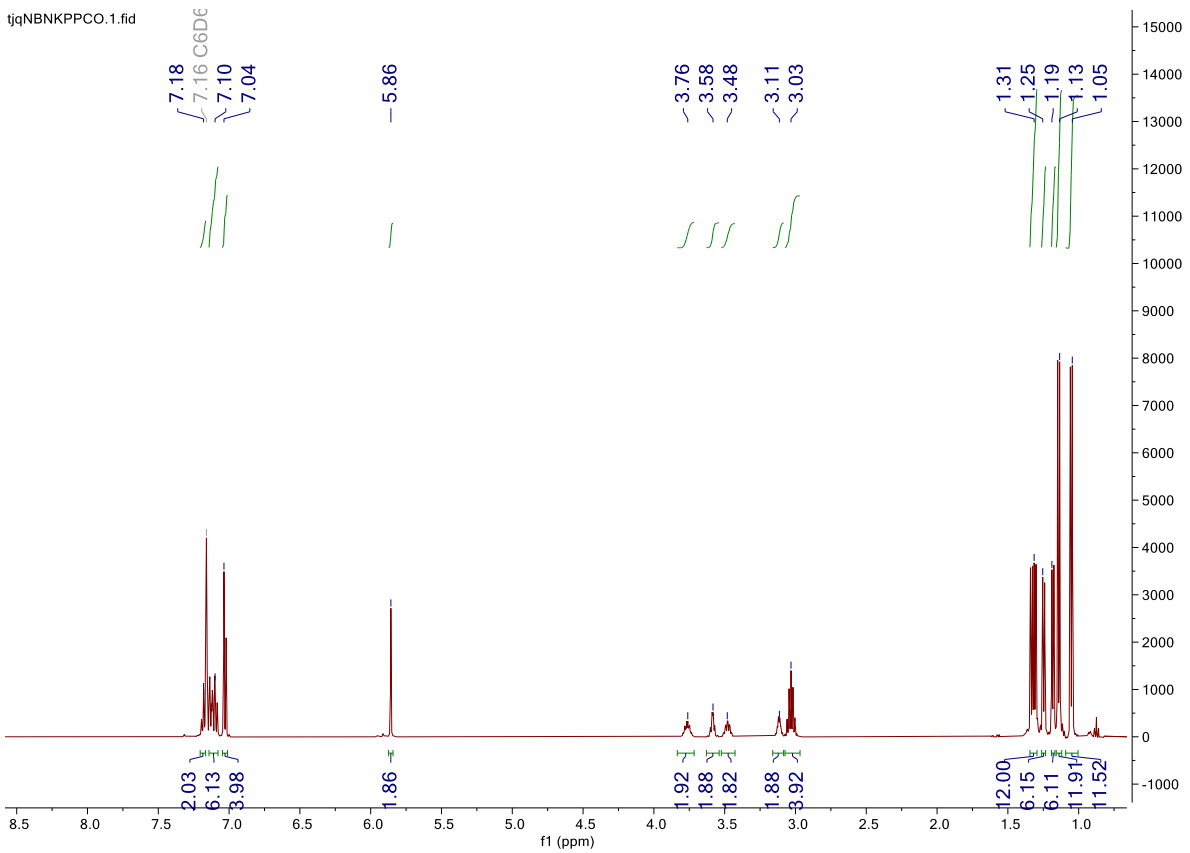



**Figure S7**: $^{1}H$ NMR spectrum of **7** (500 MHz, $C_6D_6$, 298 K).

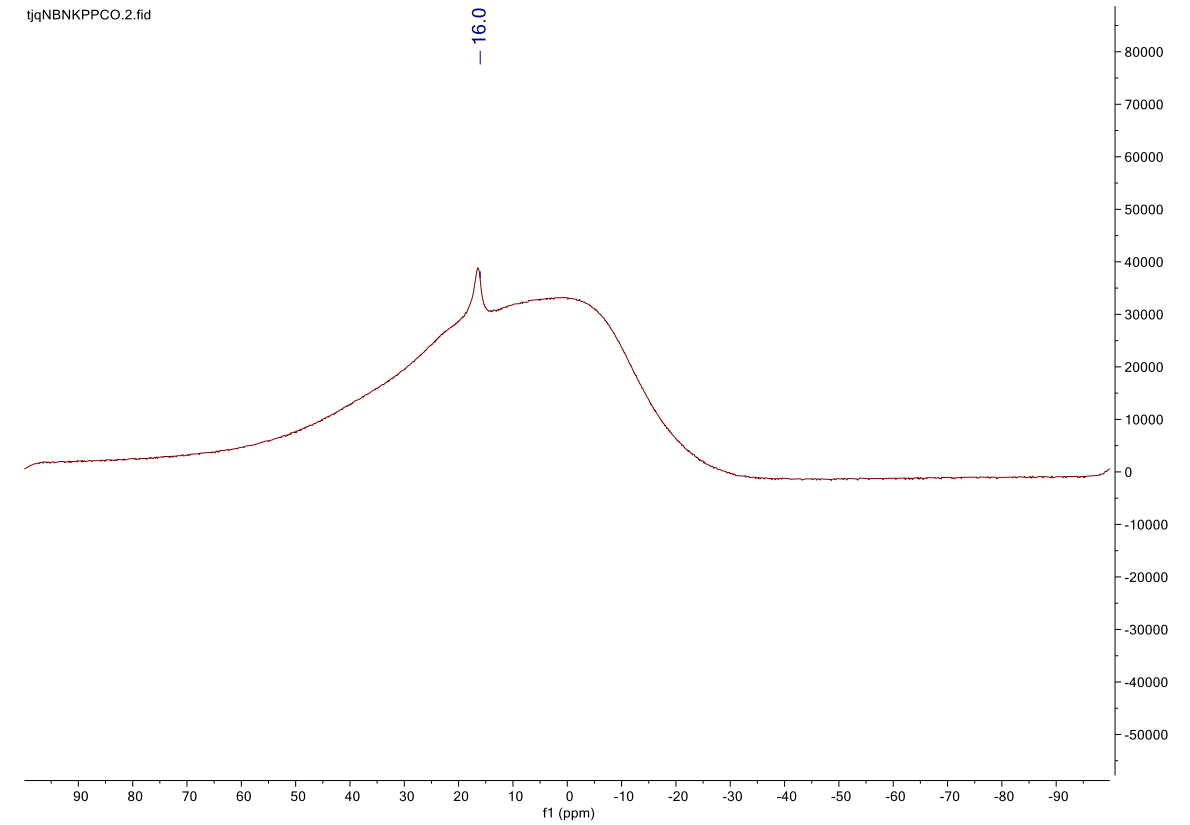



**Figure S8**: $^{11}B\{^{1}H\}$ NMR spectrum of **7** (160 MHz, $C_6D_6$, 298 K).

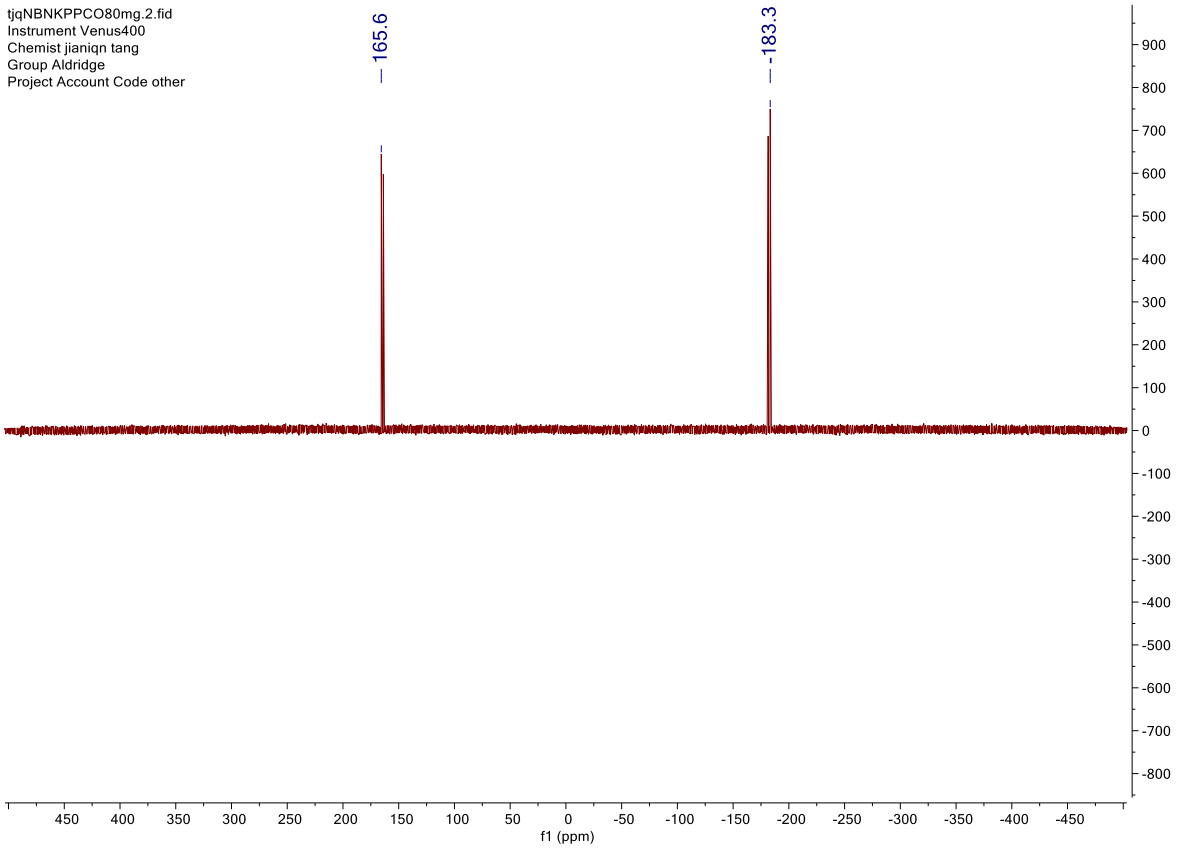



**Figure S9**: $^{31}P$ NMR spectrum of **7** (162 MHz, $C_6D_6$, 298 K).

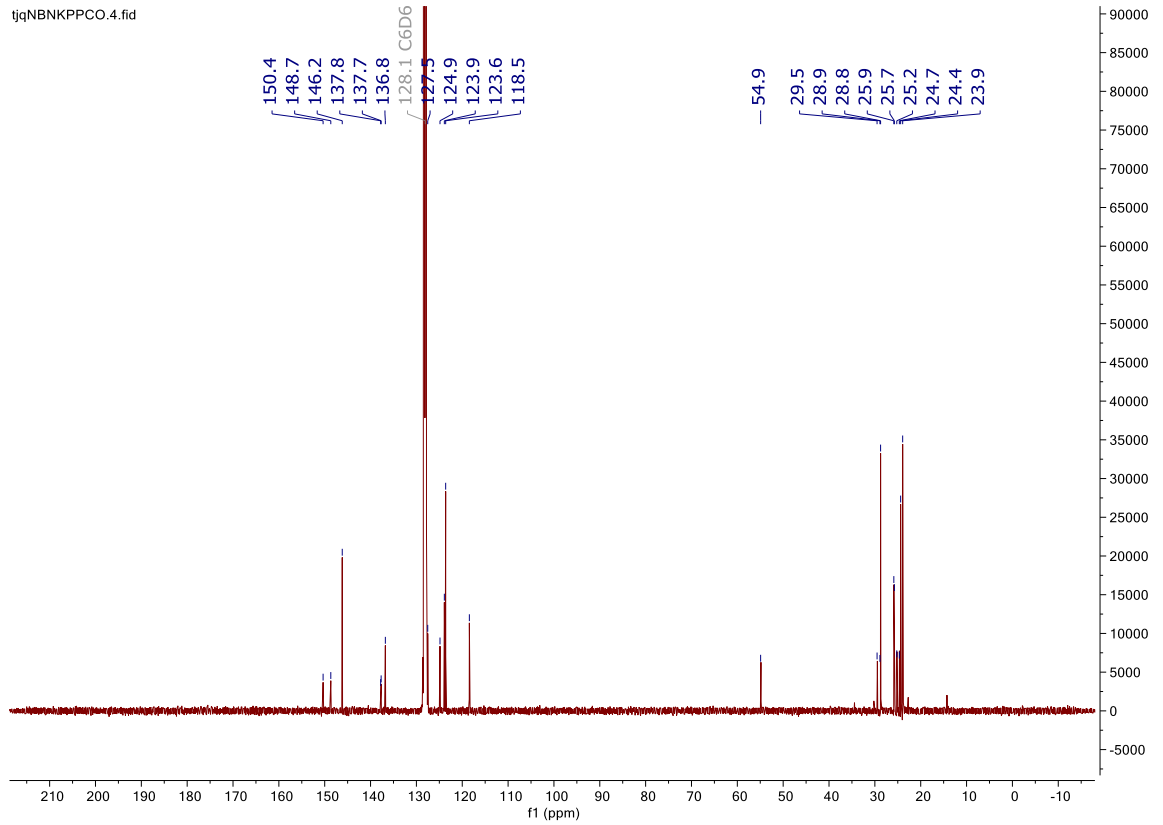



**Figure S10**: $^{13}C\{^1H\}$ NMR spectrum of **7** (126 MHz, $C_6D_6$, 298 K).

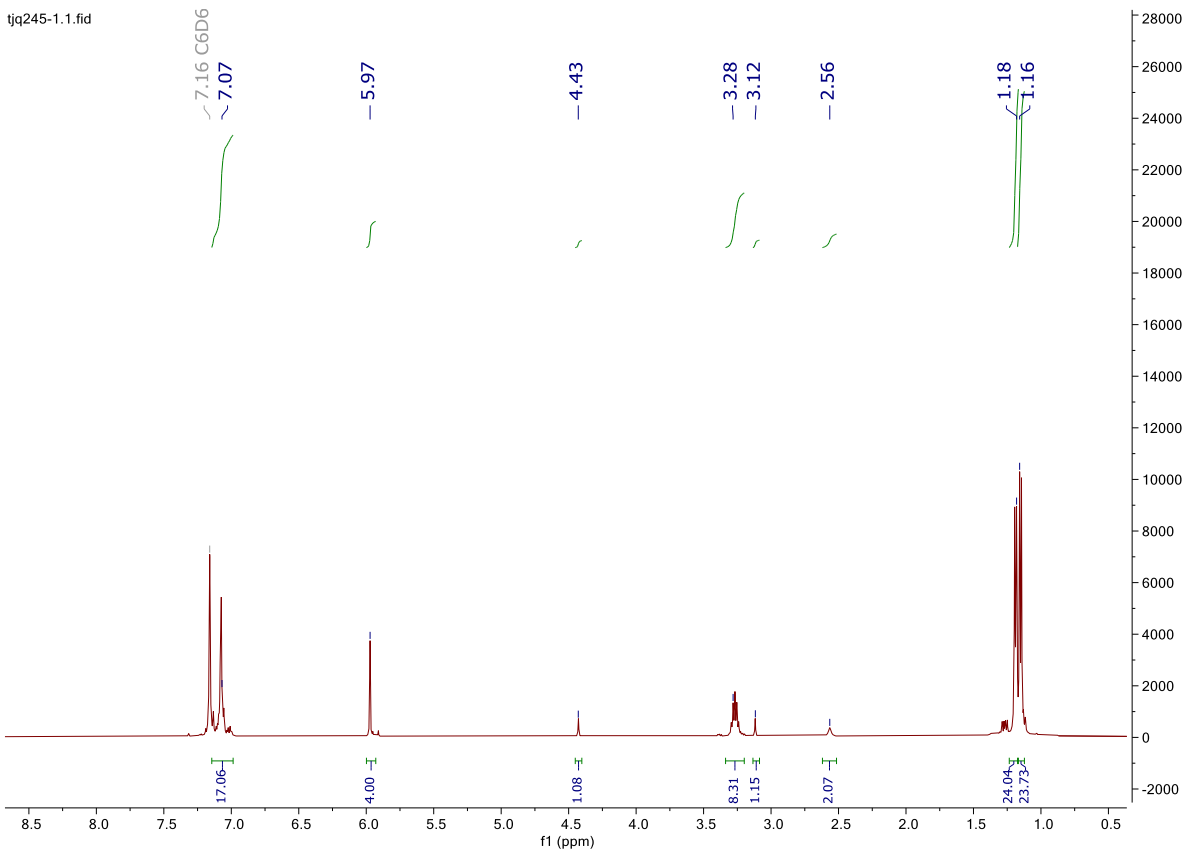



**Figure S11**: $^{1}$H NMR spectrum of **8** (500 MHz, $C_6D_6$, 298 K).

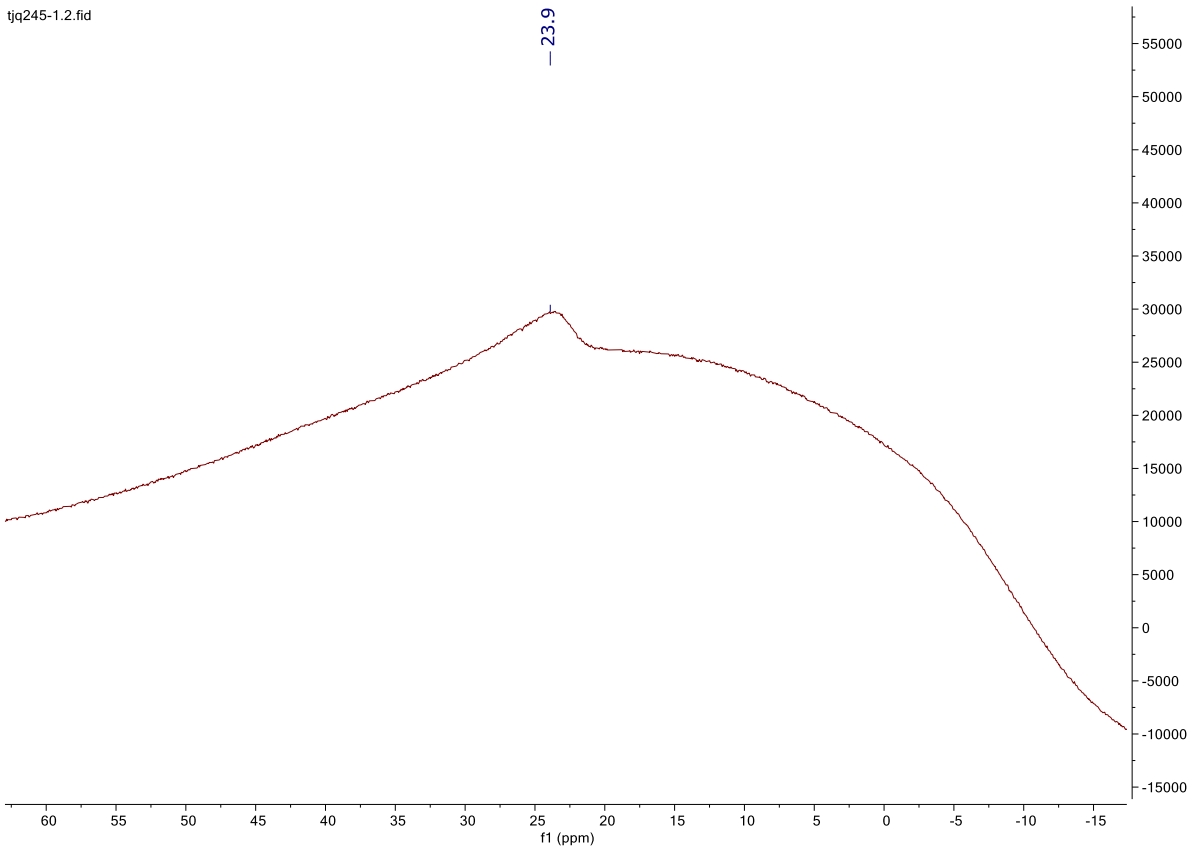



**Figure S12**: $^{11}$B{$^{1}$H} NMR spectrum of **8** (160 MHz, $C_6D_6$, 298 K).

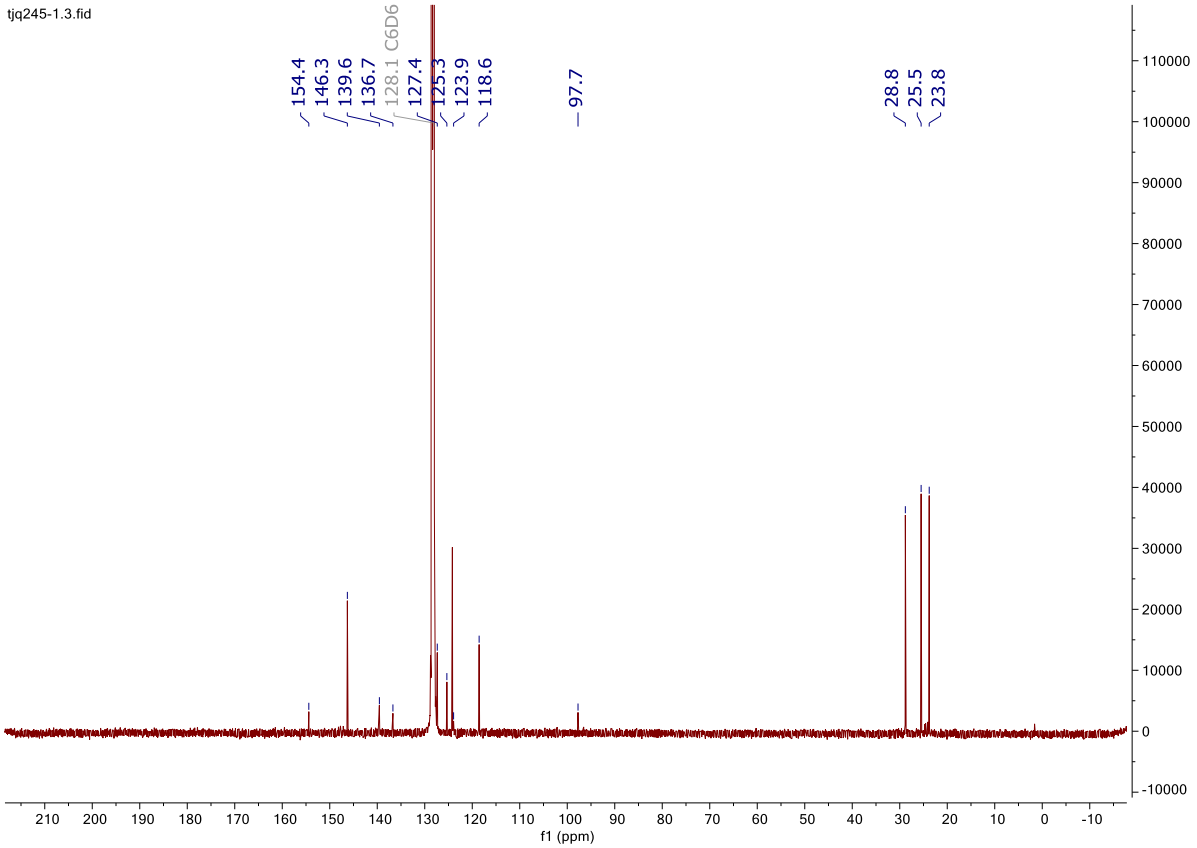



**Figure S13.** $^{13}C\{^{1}H\}$ NMR spectrum of **8** (126 MHz, $C_6D_6$, 298 K).

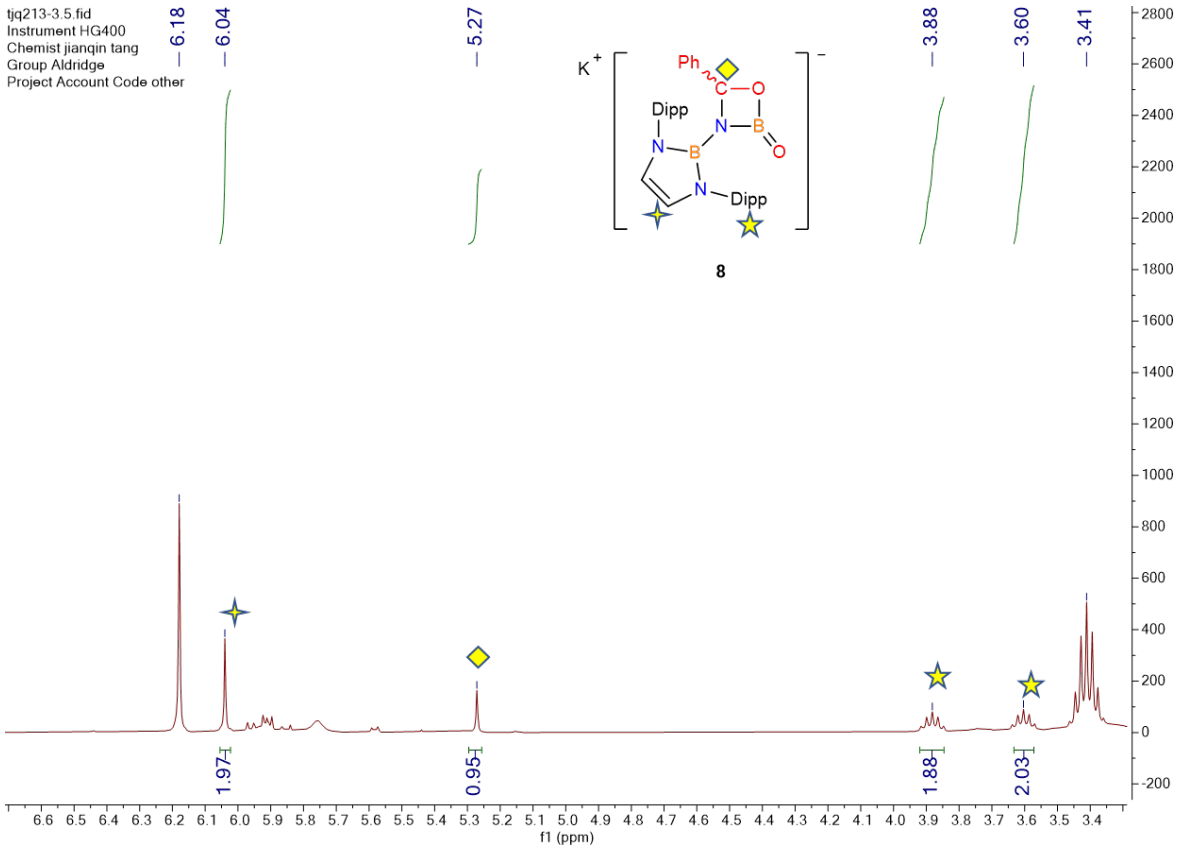



**Figure S14**: $^{1}H$ NMR spectrum(part) of **9** (400 MHz, $C_6D_6$, 298 K).

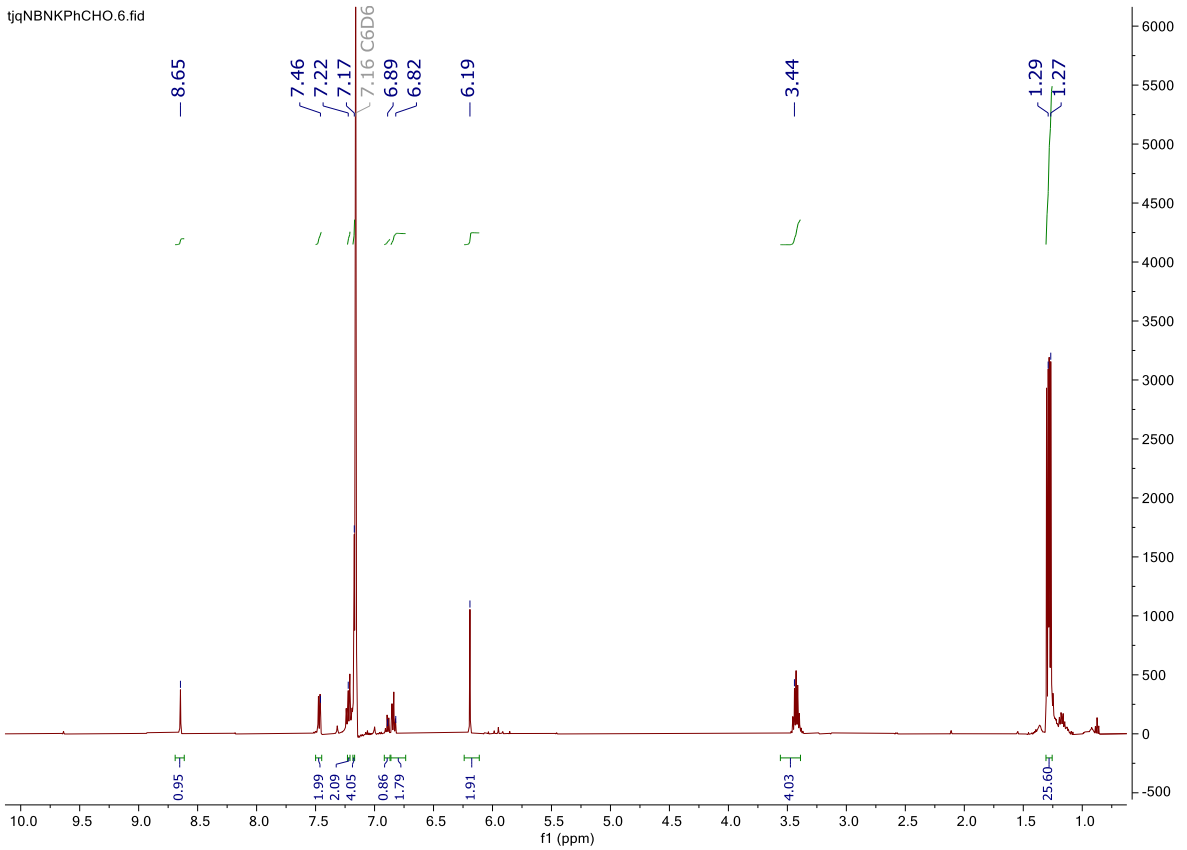



**Figure S15**: $^{1}$H NMR spectrum of **10** (500 MHz, $C_6D_6$, 298 K).

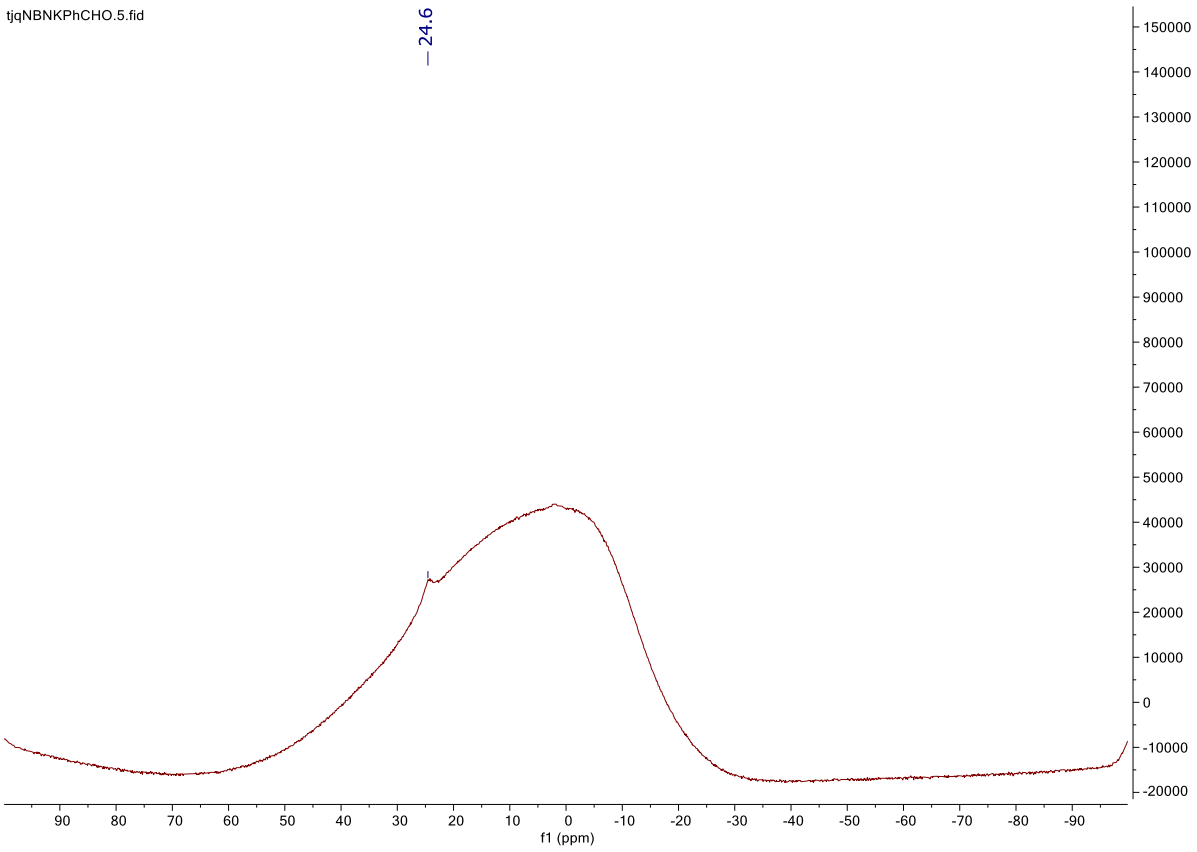



**Figure S16**: $^{11}$B{$^{1}$H} NMR spectrum of **10** (160 MHz, $C_6D_6$, 298 K).

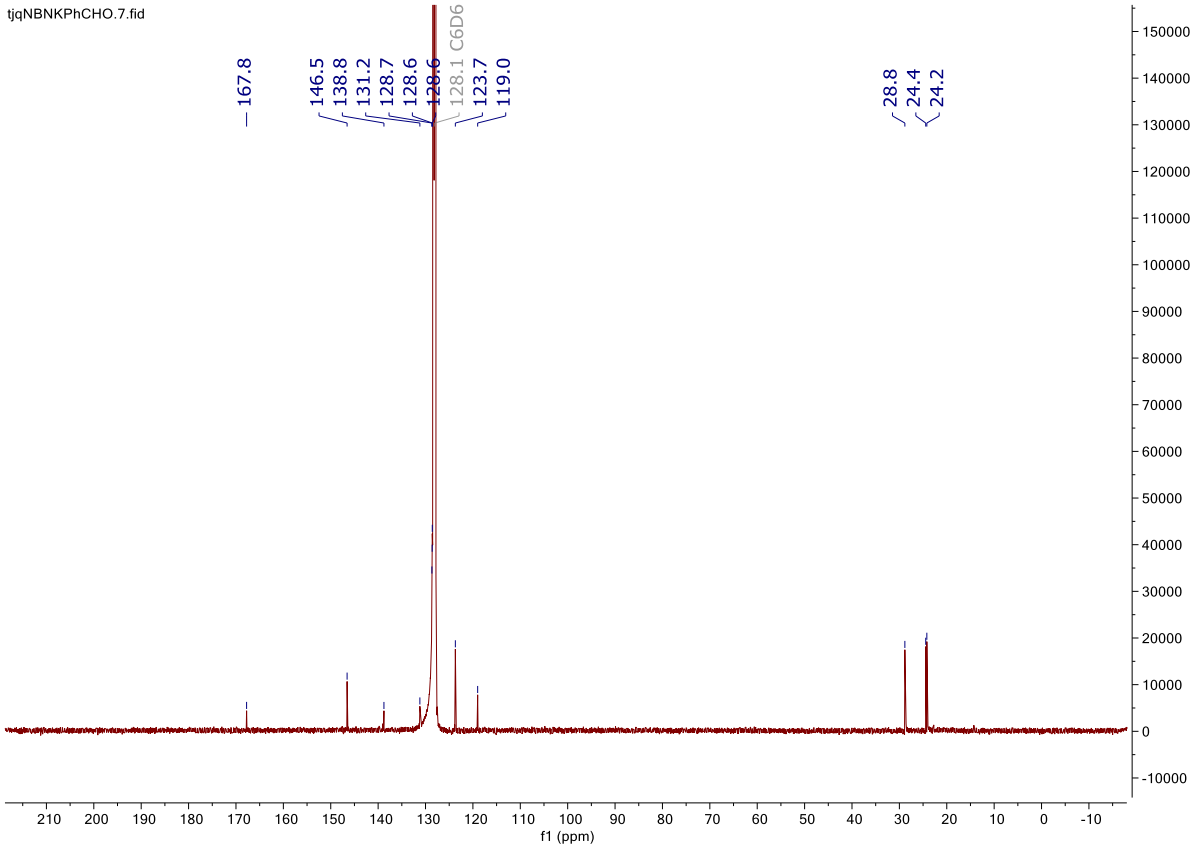



**Figure S17**: $^{13}C\{^{1}H\}$ NMR spectrum of **10** (126 MHz, $C_6D_6$, 298 K).

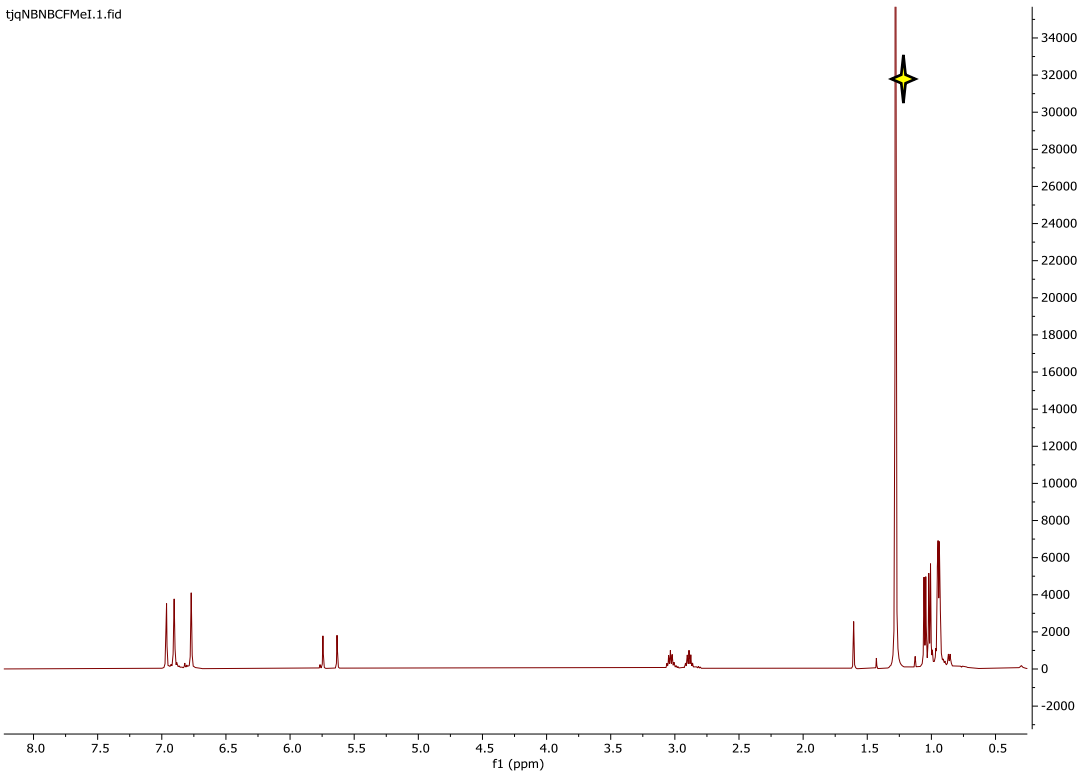



**Figure S18.** $^{1}H$ NMR monitoring of the reaction of **3** with MeI, showing the formation of **4** (500 MHz, $C_6D_6$, 298 K) (yellow star: excess MeI).

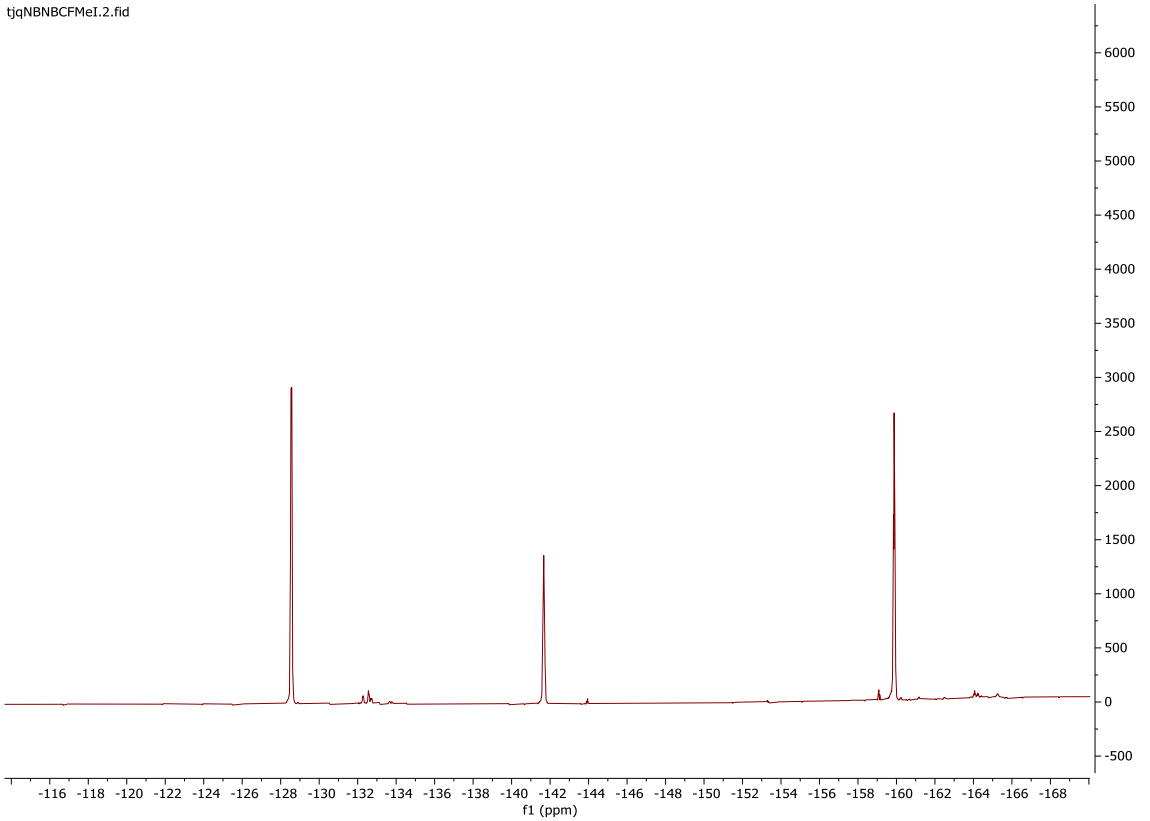



**Figure S19.** $^{19}F$ NMR monitoring of the reaction of **3** with MeI, showing the formation of $B(C_6F_5)_3$ (470 MHz, $C_6D_6$, 298 K).

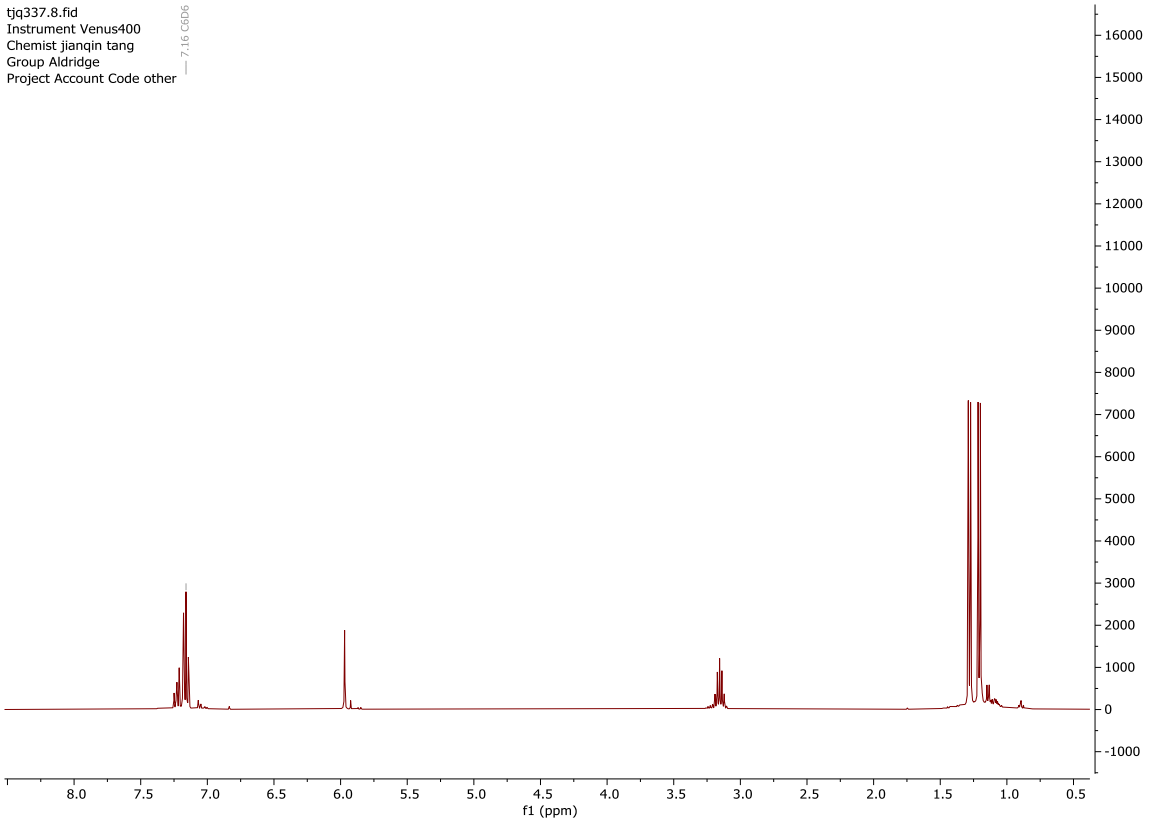



**Figure S20.** $^{1}H$ NMR monitoring of the reaction of **3** with $CO_2$, showing the formation of **5** (400 MHz, $C_6D_6$, 298 K).

**Details of X-ray crystallography**

Single-crystal X-ray diffraction data for all compounds were collected on an Oxford Diffraction/Agilent SuperNova diffractometer equipped with a 135 mm Atlas CCD area detector or a Rigaku XtaLAB Synergy-DW VHF equipped with a PhotonJet-R dual wavelength rotating anode and HyPix-Arc 150° detector. Crystals were selected under Paratone-N oil, mounted on MiTeGen Micromount loops and quench-cooled using an Oxford Cryosystems open flow $N_2$ cooling device.[S3] Data were collected at 150 K using mirror monochromated Cu Kα radiation (λ = 1.5418 Å). Data collected were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[S4] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite.[S4] Structures were solved ab initio from the integrated intensities using SHELXT[S5] and refined on $F^2$ using SHELXL[S6] with the graphical interface OLEX2[S7]. Selected crystallographic data are summarised in Tables S1-S3, and full details are given in the supplementary deposited CIF files (2377740-45). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

**Table S1**. Selected crystallographic data and refinement parameters for compounds **5** and **6**.

| **compound** | **5** | **6** |
|---|---|---|
| **Empirical formula** | $C_{27}H_{36}BN_3O$ | $C_{27}H_{36}BN_3S$ |
| **Fw /g mol$^{-1}$** | 429.4 | 445.46 |
| **T/K** | 100.00(10) | 100.00(10) |
| **Cell setting** | monoclinic | monoclinic |
| **Space group** | $P2_1/c$ | I2/a |
| **a/Å** | 12.67284(7) | 16.90996(6) |
| **b/Å** | 9.17962(5) | 9.55705(3) |
| **c/Å** | 22.43254(13) | 33.35081(10) |
| **α/°** | 90 | 90 |
| **β/°** | 96.7556(5) | 94.9584(3) |
| **γ/°** | 90 | 90 |
| **V/Å$^3$** | 2591.50(3) | 5369.63(3) |
| **Z** | 4 | 8 |
| **$\rho_{calc}$g/cm$^3$** | 1.101 | 1.102 |
| **μ/mm$^{-1}$** | 0.512 | 1.189 |
| **Radiation** | Cu Kα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| **Reflections collected** | 56620 | 109063 |
| **Independent reflections** | 5317 [$R_{int}$ = 0.0229] | 5534 [$R_{int}$ = 0.0239] |
| **parameters** | 297 | 311 |
| **GooF** | 1.026 | 1.027 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0399, $wR_2$ = 0.1008 | $R_1$ = 0.0353, $wR_2$ = 0.0895 |
| **Final R indexes [all data]** | $R_1$ = 0.0417, $wR_2$ = 0.1021 | $R_1$ = 0.0359, $wR_2$ = 0.0900 |
| **CCDC ref** | 2377740 | 2377741 |

**Table S2**. Selected crystallographic data and refinement parameters for compounds **7** and **8**.

| **compound** | **7** | **8** |
|---|---|---|
| **Empirical formula** | $C_{53}H_{74}BN_5P_2$ | $C_{60}H_{81}B_3N_6O$ |
| **Fw /g mol$^{-1}$** | 853.92 | 934.73 |
| **T/K** | 100.00(10) | 100.00(10) |
| **Cell setting** | monoclinic | monoclinic |
| **Space group** | $P2_1/c$ | C2/c |
| **a/Å** | 12.89680(10) | 22.24980(10) |
| **b/Å** | 19.8442(2) | 13.50310(10) |
| **c/Å** | 40.8371(5) | 37.4373(2) |
| **α/°** | 90 | 90 |
| **β/°** | 96.9990(10) | 99.0810(10) |
| **γ/°** | 90 | 90 |
| **V/Å$^3$** | 10373.42(18) | 11106.73(12) |
| **Z** | 8 | 8 |
| **$\rho_{calc}$g/cm$^3$** | 1.094 | 1.118 |
| **μ/mm$^{-1}$** | 1.04 | 0.498 |
| **Radiation** | Cu Kα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| **Reflections collected** | 167460 | 67625 |
| **Independent reflections** | 21356 [$R_{int}$ = 0.0625] | 11344 [$R_{int}$ = 0.0205] |
| **parameters** | 1691 | 698 |
| **GooF** | 1.084 | 1.029 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0581, $wR_2$ = 0.1446 | $R_1$ = 0.0406, $wR_2$ = 0.1037 |
| **Final R indexes [all data]** | $R_1$ = 0.0767, $wR_2$ = 0.1516 | $R_1$ = 0.0460, $wR_2$ = 0.1074 |
| **CCDC ref** | 2377742 | 2377745 |

**Table S3**. Selected crystallographic data and refinement parameters for compounds **9** and **10**.

| **compound** | **9** | **10** |
|---|---|---|
| **Empirical formula** | $C_{45}H_{52.4}B_2KN_3O_2$ | $C_{33}H_{42}BN_3$ |
| **Fw /g mol$^{-1}$** | 728.01 | 491.5 |
| **T/K** | 100.00(10) | 100.00(10) |
| **Cell setting** | tetragonal | monoclinic |
| **Space group** | I-4 | $P2_1/n$ |
| **a/Å** | 22.7178(7) | 9.70980(10) |
| **b/Å** | 22.7178(7) | 16.9985(2) |
| **c/Å** | 15.9414(8) | 17.7195(2) |
| **α/°** | 90 | 90 |
| **β/°** | 90 | 93.8430(10) |
| **γ/°** | 90 | 90 |
| **V/Å$^3$** | 8227.3(7) | 2918.06(6) |
| **Z** | 8 | 4 |
| **$\rho_{calc}$g/cm$^3$** | 1.175 | 1.119 |
| **μ/mm$^{-1}$** | 1.428 | 0.487 |
| **Radiation** | Cu Kα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| **Reflections collected** | 30711 | 24546 |
| **Independent reflections** | 8001 [$R_{int}$ = 0.0416] | 24546 |
| **parameters** | 527 | 345 |
| **GooF** | 1.016 | 1.055 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0551, $wR_2$ = 0.1556 | $R_1$ = 0.0501, $wR_2$ = 0.1745 |
| **Final R indexes [all data]** | $R_1$ = 0.0595, $wR_2$ = 0.1600 | $R_1$ = 0.0541, $wR_2$ = 0.1774 |
| **CCDC ref** | 2377743 | 2377744 |

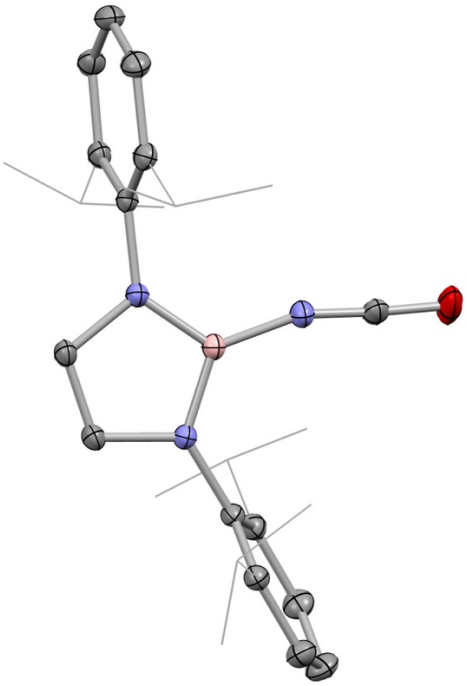


**Figure S21**. Molecular structure of **5** in the solid state as determined by X-ray crystallography. All Hs omitted and $^{i}$Pr groups shown in wireframe format for clarity; thermal ellipsoids shown at the 35% probability level.

**Details of quantum chemical calculations**

Geometry optimizations were carried out using the Gaussian 16 package with the M06-2X functional.[S8,S9] The def2-SVP basis set was used for all atoms.[S10,S11] Frequency calculations at same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum and one for transition states), and provide the thermal corrections of Gibbs free energy. Single-point energy calculations were performed at the M06-2X/def2-TZVP level of theory for the modelling of compounds in solution (benzene).[S12,S13] The gas-phase geometry was used for all the solution phase calculations. The SMD method was used with the corresponding solvent, while Bondi radii were chosen as the atomic radii to define the molecular cavity.[S14,S15] The corrections of Gibbs free energy from frequency calculations were added to the single-point energies to obtain the Gibbs free energy in solution. All energies reported in the paper correspond to the reference state of 1 mol/L, 298 K.

**Table S4.** Calculated energies of intermediates and transition states.

| Species | Thermal Corrections of Gibbs Free Energies (Hartree) | Solvation Energies (Hartree) |
|---|---|---|
| **1** (anionic component) | 1.061871 | -2428.25269 |
| PhCHO | 0.080626 | -345.564694 |
| (boryl)N=C(H)Ph | 0.615977 | -1471.941512 |
| IN3 | 0.632052 | -1647.489932 |
| IN2 | 0.522271 | -1301.886084 |
| BO2 | -0.008553 | -175.532068 |
| IN1 | 1.173277 | -2773.848201 |
| TS1 | 1.169813 | -2773.797297 |
| TS2 | 1.169729 | -2773.805785 |
| TS3 | 0.629418 | -1647.439945 |
| TS4 | 0.626958 | -1647.444168 |

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**Declaration of author contribution**

**Statement of Authorship for joint/multi-authored papers for PGR thesis**

To appear at the end of each thesis chapter submitted as an article/paper

The statement shall describe the candidate's and co-authors' independent research contributions in the thesis publications. For each publication there should exist a complete statement that is to be filled out and signed by the candidate and supervisor **(only required where there isn't already a statement of contribution within the paper itself).**

| | |
|---|---|
| Title of Paper | Metathesis chemistry of inorganic cumulenes driven by B–O bond formation |
| Publication Status | √ Published □ Accepted for Publication<br>□Submitted for Publication □Unpublished and unsubmitted work written<br>in a manuscript style |
| Publication Details | Tang, J., Hu, C., Crumpton, A. E., Griffin, L. P., Goicoechea, J. M., & Aldridge, S. (2025). Metathesis chemistry of inorganic cumulenes driven by B–O bond formation. *Chemical Science*. |

Student Confirmation

| | | | |
|---|---|---|---|
| Student Name: | Jianqin Tang | | |
| Contribution to the Paper | Performed all synthetic, spectroscopic work, as well as almost quantum chemical calculations. Analysed and interpreted data. Wrote the draft manuscript and prepared the supporting information. | | |
| Signature | Jianqin Tang | Date | 20/06/2025 |

Supervisor Confirmation

| | | |
|---|---|---|
| Supervisor name and title: Professor Simon Aldridge | | |
| Supervisor comments<br>I can confirm that the information about this paper described by the candidate is accurate. | | |
| Signature S Aldridge | Date | 21 June 2025 |

By signing the Statement of Authorship, you are certifying that the candidate made a substantial contribution to the publication, and that the description described above is accurate.

## Chapter 4. An inorganic cumulene as precursor to a dianionic bis(borylamido) ligand chelate

### Introduction

Amidinate and guanidinate ligands are classically synthesized via the reactions of carbodiimides with alkali metal alkyl or amide reagents, and have found widespread application in stabilizing metal complexes from across the Periodic Table. Sterically bulky amidinate and guanidinate ligands have been found to be particularly effective in stabilizing low valent main group complexes.

This chapter further demonstrates the reactivity of the boron-based inorganic cumulene, K[(HCDippN)$_2$BNBNB(NDippCH)$_2$], in this case as a carbodiimide analogue to access novel germylene(II) complexes featuring a chelating borylamido ligand. X-ray crystallography confirms the formation of four-membered GeN$_2$B rings in a series of compounds initially derived from GeCl$_2$·dioxane. DFT and NBO analyses support the germylene description, showing weak Ge–N bonding and a LUMO primarily centred on Ge. The work highlights the utility of boryl-based cumulenes as ligand platforms for stabilizing low-valent main group species.

**Synthesis of a diamido-germylene from an inorganic cumulene**

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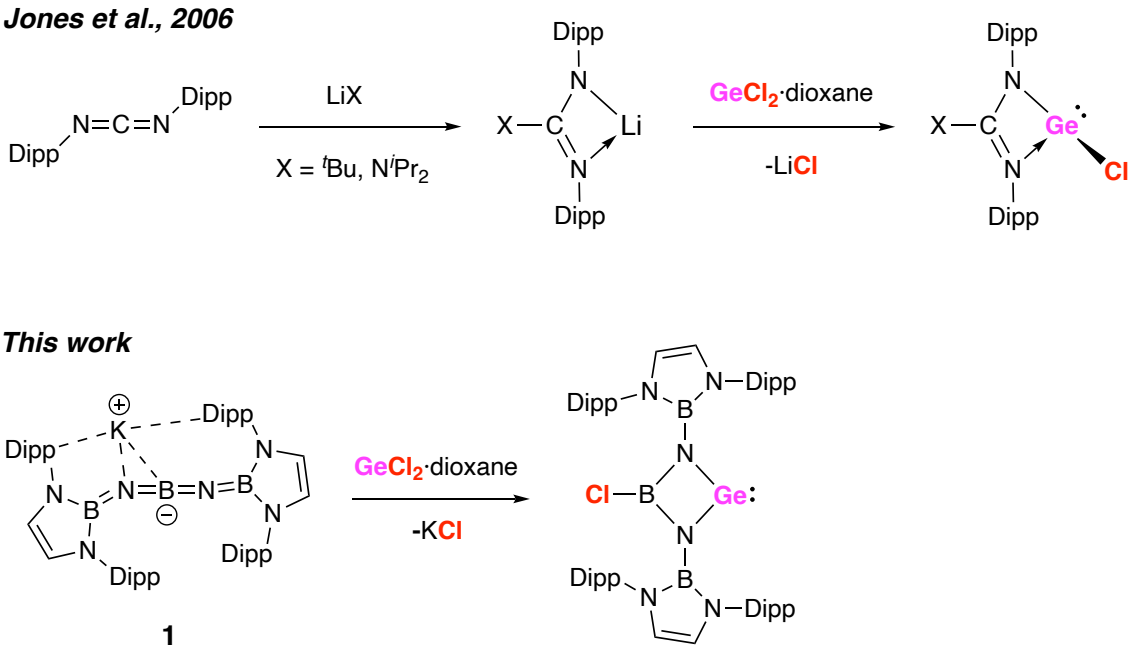
**Abstract**

The advent of boron-containing cumulenes as carbodiimide analogues allows for the one-pot synthesis of low-valent main-group species stabilized by a dianionic bis(borylamido) ligand chelate. We report here the synthesis and characterization of germylene complexes accessed via the reaction of $GeCl_2$·dioxane with K[(HCDippN)$_2$BNBNB(NDippCH)$_2$] (K[(boryl)NBN(boryl)], **1**). The four-membered N-heterocyclic germylene [ClB{(boryl)N}$_2$]Ge (**2-Cl**) so generated reacts further with 1,3,4,5-tetramethylimidazol-2-ylidene ($IMe_4$) to yield the structurally characterized Ge-bound adduct [ClB{(boryl)N}$_2$]Ge·$IMe_4$ (**3-Cl**). Reaction with trimethylsilyl azide ($Me_3SiN_3$) then affords the related azido-functionalized system [($N_3$)B{(boryl)N}$_2$]Ge·$IMe_4$ (**3-N$_3$**). DFT and NBO analyses of **2-Cl** reveal a greater partial positive charge at Ge vs. B (+1.37 *vs.* +0.90 e); taken together with the relative unimportance of Ge–N $\pi$ bonding (WBIs: Ge–N 0.44/0.46; B–N: 0.93, 0.94) these data rationalize the uptake of $IMe_4$ at germanium, rather than boron in a molecule offering two Lewis acidic centres (i.e. **3-Cl**/**3-N$_3$**).

**Introduction**

The reactions of carbodiimides (RN=C=NR) with alkali metal alkyl/aryl or amide reagents have been widely used to synthesize amidinate or guanidinate salts, which in turn have been employed as sources of chelating ligands for numerous metal complexes, {XC(RN)$_2$}ML$_n$, across the Periodic Table.[1] Within this sphere, Jones *et al.* reported in 2006 the use of the bulky amidinate and guanidinate ligands [Piso]$^-$ and [Giso]$^-$ (Piso = [$^t$BuC(DippN)$_2$]$^-$; Giso =

[$^{i}Pr_2NC(DippN)_2]^-$, where Dipp = $C_6H_3Pr^{i}_2$-2,6) to stabilize germanium(II) complexes (Scheme 1).[2,3] These divalent complexes can be further reduced by treatment with potassium metal to access the neutral Ge–Ge bonded germanium(I) dimers, $[Ge(Piso)]_2$ and $[Ge(Giso)]_2$.[2,4] Steric bulk is clearly critical to this chemistry: when smaller substituents were employed at the nitrogen and/or central carbon atoms (e.g. R = Dipp, X = H; R = $^{i}$Pr, X = Me), coordination of a second amidinate ligand has been shown to occur, leading to the formation of a tetracoordinate Ge centre.[3,5]




**Scheme 1.** (upper) Amidinato and guanidinato complexes of germanium derived from carbodiimide precursors; [3,5] (lower) this work.

Recently, we developed high-yielding synthetic routes to 'inorganic cumulenes' including the diazabutadiene-capped system K[(HCDippN)$_2$BNBNB(NDippCH)$_2$] (K[(boryl)NBN(boryl)], **1**).[6] The central $[N=B=N]^-$ core of this cumulene can also be viewed as a diimidoboryl unit isoelectronic with the [N=C=N] motif of a carbodiimide, and its nucleophilic reactivity has been

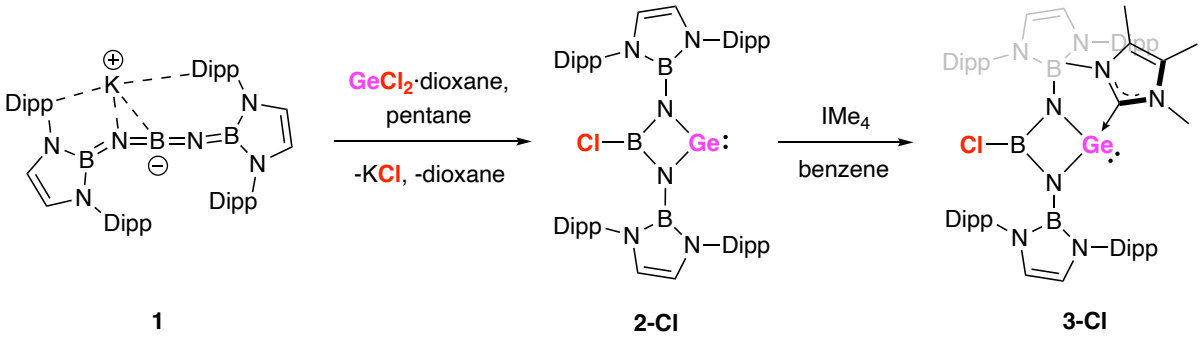
demonstrated *via* N-centred reactivity with electrophiles.[6,7] The presence of this anionic NBN core also prompted us to probe if it might be capable of being acting as a precursor to a sterically encumbered dianionic bis(borylamido) ligand of the type $[XB\{(boryl)N\}_2]^{2-}$. Related 'bora-guanidinate' ligands of the type $[R_2NB(ArN)_2]^{2-}$ have previously been synthesized exclusively by salt metathesis reactions of $R_2NBCl_2$ with anilide salts.[8-14]

Herein, we demonstrate the viability of this hypothesis, through the synthesis of the germylene complex, $[ClB\{(boryl)N\}_2]Ge$ from cumulenic precursor **1** and $GeCl_2$·dioxane. While this compound proved problematic in respect of structural characterization by X-ray crystallography, a related N-heterocyclic carbene (NHC) adduct could be accessed featuring the 1,3,4,5-tetramethylimidazol-2-ylidene ligand ($IMe_4$) bound at germanium. Crystallographic studies on this species, $[ClB\{(boryl)N\}_2]Ge{\cdot}IMe_4$, confirm the formation of a $GeN_2B$ four-membered ring and a boron-bound chloride substituent. Subsequent synthetic efforts focused on substitution of the halide substituent, with this being successfully accomplished in the case of the azido ($N_3^-$) group.

**Results and Discussion**

The reaction of K[(boryl)NBN(boryl)] (**1**)[6] with one equivalent of $GeCl_2$·dioxane in pentane afforded $[ClB\{(boryl)N\}_2]Ge$ (**2-Cl**; Scheme 2) as an orange pentane-soluble crystalline solid in ca. 60% yield. **2-Cl** was characterized by $^1H$, $^{11}B$ and $^{13}C$ NMR spectroscopy. Although crystals could be obtained from a cold pentane solution, issues related to crystal twining mean that the molecular structure determined by single-crystal X-ray diffraction analysis is not of

adequate quality to provide anything other than a connectivity map (see Supporting Information, Figure S11). Therefore, in an attempt to obtain definitive structural validation of **2-Cl**, the synthesis of a related Lewis base adduct was attempted. Treatment of **2-Cl** with one equivalent of the N-heterocyclic carbene 1,3,4,5-tetramethylimidazol-2-ylidene ($IMe_4$) in benzene led to a colour change of the solution from orange to light yellow over the period of 2 h. Recrystallization from pentane and storage overnight at room temperature resulted in yellow single crystals of [ClB{(boryl)N}$_2$]Ge·$IMe_4$ (**3-Cl**) suitable for X-ray crystallography (Scheme 2).




**Scheme 2.** Syntheses [ClB{(boryl)N}$_2$]Ge (**2-Cl**) and [ClB{(boryl)N}$_2$]Ge·$IMe_4$ (**3-Cl**) from the 'inorganic cumulene' **1**.

The $^1$H NMR spectrum of **2-Cl** is consistent with a $C_{2v}$ symmetric structure, featuring a single septet at 3.21 ppm and two doublets at 1.17 and 1.19 ppm for the boryl $^i$Pr groups. By contrast, the corresponding spectrum of **3-Cl** shows two septets (at $\delta_H$ = 3.49 and 3.35 ppm) and four doublets (at $\delta_H$ = 0.99, 1.21, 1.24, 1.27 ppm), consistent with the loss of one plane of symmetry within the molecule on binding the $IMe_4$ donor. The $^{11}$B NMR spectrum of **2-Cl** features broad signals at $\delta_B$ = 36.0 and 22.6 ppm assigned to the central B–Cl unit and boryl substituents, respectively; the former is absent in **3-Cl**, presumably due to broadening in the lower symmetry environment.

The molecular structure of **3-Cl** determined crystallographically is shown in Figure 1 (left) and confirms the expected connectivity.[8–14] The two Ge–N bonds (1.983(1) and 1.973(1) Å) are shorter than the Ge–N bonds of germanium(II) chlorides stabilized by amidinato ligands (2.003(4)-2.072(2) Å),[2,4] while the corresponding bonds found in [{$^{i}$Pr$_2$NB(XylN)$_2$}Ge]$_2$, a germylene stabilized by a related 'bora-guanidinate' ligand, are more disparate (1.9418(18) and 2.0880(18) Å) due to the N-bridged dimeric structure adopted in the solid state.[8] More directly comparable is the structure of the related base-stabilized monomer, {$^{i}$Pr$_2$NB(XylN)$_2$}Ge·DMAP (DMAP = 4-(*N*,*N*-dimethylamino)-pyridine which features slightly shorter Ge–N bond lengths of 1.9227(16) and 1.9186(16) Å, but a very similar bite angle at germanium (73.29(7) vs. 72.66(5) for **3-Cl**).[14] In a broader sense, the Ge(II) centre in **3-Cl** exhibits a distorted a trigonal pyramidal geometry with the sum of the bond angles at the metal centre being 264°, consistent with the low degree of *s*/*p* mixing expected for a heavier p-block element.

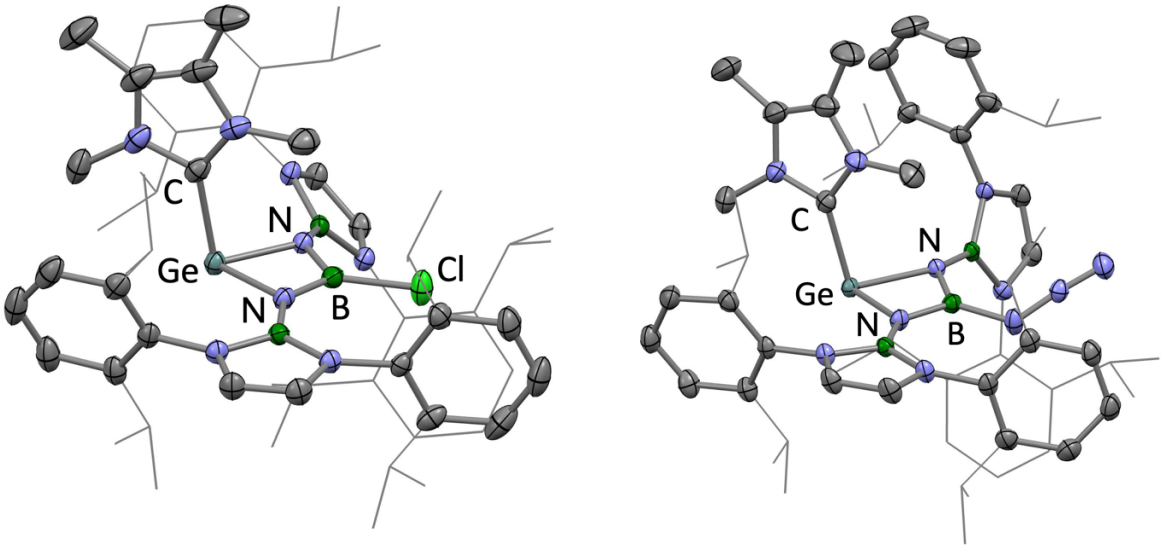
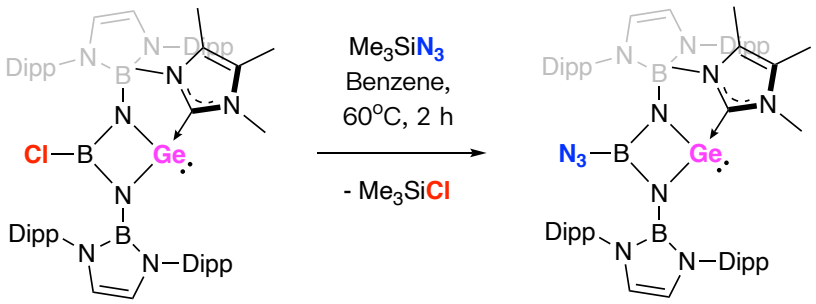



**Figure 1:** Molecular structures of [ClB{(boryl)N}$_2$]Ge·IMe$_4$, **3-Cl** (left) and

$[N_3B\{(boryl)N\}_2]Ge{\cdot}IMe_4$, **3-N$_3$** (right) in the solid state as determined by X-ray crystallography. Hydrogen atoms omitted and selected groups shown in wireframe format for clarity. Thermal ellipsoids set at the 30 % probability level. Key bond lengths (Å) and angles (°): (for **3-Cl**) Ge–N 1.983(1), 1.973(1), $B_{Cl}$–N 1.423(2), 1.410(2), N–Ge–N 72.66(5), N–B–N 111.6(1), C–Ge···B 102.1(1); (for **3-N$_3$**) Ge–N 1.977(1) 1.998(1), $B_{N3}$–N 1.413(2), 1.429(2), N–Ge–N 72.57(6), N–B–N 111.3(2), C–Ge···B 104.6(1).

Due to the labile nature of B–Cl bonds, we attempted to functionalize the boron centre of the ligand backbone in **2-Cl**/**3-Cl** by substituting the chloride with amide or alkyl groups. No reaction occurred with $K[N(SiMe_3)_2]$ even after prolonged heating presumably due to the sterically encumbered nature of the boryl substituents, while decomposition was observed with both MeLi and $^t$BuLi potentially due to the strong basicity of these reagents. Attempts to reduce **3-Cl** with $KC_8$ in THF (targeting B–B or Ge–Ge bond formation), proceeded instead to (cleanly) regenerate the starting material K[(boryl)NBN(boryl)], as shown by *in situ* NMR measurements. However, treatment of **3-Cl** with the softer reagent $Me_3SiN_3$ at 60 °C in benzene leads to clean Cl-for-azide substitution over a period of ca. 2 h, and the product $[N_3B\{(boryl)N\}_2]Ge{\cdot}IMe_4$, **3-N$_3$**, could be isolated in 50-60% yield (Scheme 3).




**3-Cl** **3-N$_3$**

**Scheme 3:** Reaction of [ClB{(boryl)N}$_2$]Ge·IMe$_4$ **3-Cl** with trimethylsilylazide to yield [N$_3$B{(boryl)N}$_2$]Ge·IMe$_4$ **3-N$_3$**.

As with **3-Cl**, the $^1$H NMR data for **3-N$_3$** are consistent with local $C_{2v}$ symmetry (two Dipp methine signals at $\delta_H$ = 3.36 and 3.44 ppm and four Dipp methyl signals at $\delta_H$ = 1.03, 1.20, 1.22 and 1.23 ppm); its IR spectrum shows a strong band at 2125 cm$^{-1}$, consistent with the antisymmetric stretching mode typically observed for the azide ligand (e.g. 2127 cm$^{-1}$ for gallium azide).[15] Colourless single crystals could be obtained from pentane solution and the formation of **3-N$_3$** from **3-Cl** by Cl-for-N$_3$ substitution at boron could therefore be confirmed by X-ray crystallography (Figure 1). Structurally, **3-N$_3$** and **3-Cl** are very similar, with comparable Ge–N (1.977(1)/1.998(1) Å vs 1.983(1)/1.973(1) Å, respectively) and B–N distances (1.413(2)/1.429(2) Å vs. 1.423(2)/1.410(2) Å), and N–Ge–N (72.57(6) vs. 72.66(5)°) and N–B–N angles (111.3(2) vs. 111.6(1)°) defining the four-membered chelate ring. The angle describing the orientation of the Ge–C$_{carbene}$ bond with respect to the chelate ring is also very similar in each case (∠C–Ge···B = 104.6(1) and 102.1(1)°), presumably reflecting the minor (and remote) degree of steric perturbation on substitution at boron.

To better understand the structures of **2-Cl**, **3-Cl** and **3-N$_3$**, Density Functional Theory (DFT) calculations coupled with natural bond orbital (NBO) analyses were carried out at the M06-2x/def2svp/def2-TZVP level of theory.[16–18] The optimized structure of **2-Cl** reproduces well that implied crystallographically (Figure S11); orbital analysis shows that the Ge-centred lone pair is primarily described by the HOMO-6 with the LUMO showing contributions from Ge- and (to a lesser extent) B-centred $p_z$ orbitals (Figure 3). Relatively low Wiberg Bond Orders (WBIs)

are determined for the Ge–N bonds (*ca*. 0.45; Table 1), with those for the B–N linkages being roughly twice as large, consistent with the expected differences in E–N π bonding. NPA charge analysis of **2-Cl** reveals that the N atoms bear substantial negative charges as expected (-1.46/-1.47 e), while the boron atom (and to a greater extent the Ge centre) bear positive charges (+0.90 and +1.37 e, respectively). The greater partial positive charge at Ge together with the spatial composition of the LUMO (Figure 3), and the relative unimportance of Ge–N π bonding, presumably underpin the uptake of $IMe_4$ at germanium (rather than boron) in a molecule offering two Lewis acidic centres. Consistently, there is little diminution in the WBIs associated with the Ge–N bonds on going from **2-Cl** to **3-Cl**, with the primary effect of carbene coordination being a reduction in the positive charge at Ge (+1.08 vs +1.37 e).

**Table 1**: Wiberg bond indices (WBI) and Natural population analysis (NPA) atomic charges (q) of the relevant bonds/atoms for **2-Cl**, **3-Cl** and **3-$N_3$**.

| ***WBI*** | **N-Ge** | **N-Ge** | **B-N** | **B-N** | **B-$N_{azide}$** |
|---|---|---|---|---|---|
| ***2-Cl*** | 0.44 | 0.46 | 0.94 | 0.93 | — |
| ***3-Cl*** | 0.42 | 0.43 | 0.97 | 0.96 | — |
| ***3-$N_3$*** | 0.44 | 0.46 | 1.04 | 0.97 | 0.84 |
| ***NPA*** | **Ge** | **N** | **N** | **B** | **$N_{azide}$** |
| ***2-Cl*** | +1.37 | -1.46 | -1.47 | +0.90 | — |
| ***3-Cl*** | +1.08 | -1.39 | -1.41 | +0.89 | — |
| ***3-$N_3$*** | +1.04 | -1.33 | -1.34 | +0.97 | -0.53 |

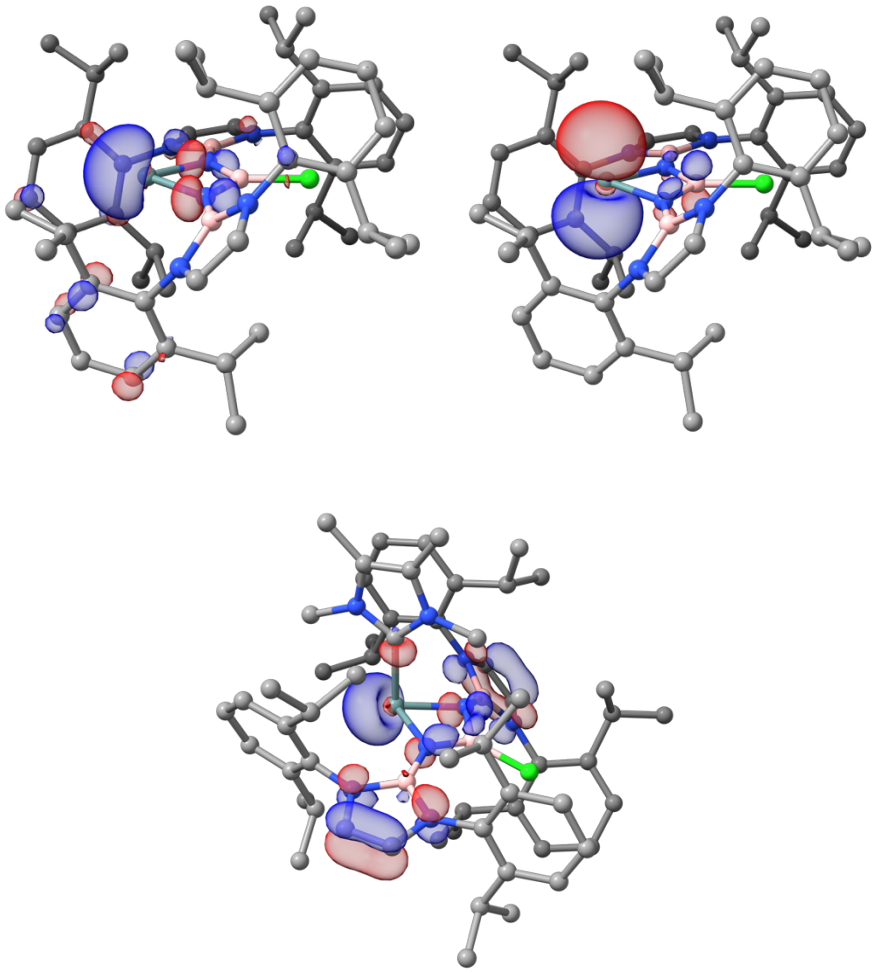


**Figure. 2**: Key molecular orbitals of **2-Cl** and **3-Cl**: (upper left) HOMO-6 of **2-Cl**; (upper right) LUMO of **2-Cl;** (lower) HOMO-1 of **3-Cl**.

## Conclusions

The use of a boron-containing hetero-cumulene, $K[(HCDippN)_2BNBNB(NDippCH)_2]$, as an anionic carbodiimide surrogate allows for synthesis of germylene species stabilized by a dianionic chelating bis(borylamido) ligand. The reaction with $GeCl_2$·dioxane generates the four-membered N-heterocyclic germylene $[ClB\{(boryl)N\}_2]Ge$ (**2-Cl**) in one step (together with

KCl), which in turn takes up one equivalent of $IMe_4$ (at germanium) to yield the structurally characterized adduct [ClB{(boryl)N}$_2$]Ge·$IMe_4$ (**3-Cl**). The borylamido ligand can be modified at the backbone boron position by Cl-for-azide substitution using $Me_3SiN_3$ to afford the related adduct [($N_3$)B{(boryl)N}$_2$]Ge·$IMe_4$ (**3-$N_3$**).

## Experimental

Included here are synthetic and characterizing data for compounds **2-Cl** and **3-Cl**. Complete data for all novel compounds, representative spectra, and details of crystallographic and quantum chemical studies are included in the Supporting Information.[19]

**2-Cl**: **1** (150 mg, 0.17 mmol) and $GeCl_2$·dioxane (40 mg, 0.17 mmol) were dissolved in pentane (30 mL) leading to a colour change from colourless to orange. After stirring for 12 h, the solution was concentrated to a third of its original volume, and orange crystals of **2-Cl** obtained on standing at – 30 °C, which were isolated by filtration and washed with cold pentane (2 x 5 mL). Yield: 95.4 mg (0.10 mmol, 59 %). $^1$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 1.17 (d, $^3J_{H,H}$ = 7.1 Hz, 24H, $CH_3$ of Dipp), 1.19 (d, $^3J_{H,H}$ = 7.1 Hz, 24H, $CH_3$ of Dipp), 3.21 (sept, $^3J_{H,H}$ = 7.1 Hz, 8H,C<u>H</u>($CH_3$)$_2$ of Dipp), 6.00 (s, 4H, CH of boryl), 7.05 (m, 8H, m-ArH of Dipp), 7.10 (m, 4H, p-ArH of Dipp). $^{11}$B{$^1$H} NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 22.6 (boryl), 36.0 (B-Cl). $^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 24.0, 25.1 ($CH_3$ of Dipp), 28.8 (CH of boryl), 117.9 (CH of boryl), 124.3 (m-Ar of Dipp), 127.9 (p-Ar of Dipp), 139.9 (CN of Dipp), 146.8 (o-Ar of Dipp).

**3-Cl**: **2-Cl** (50 mg, 0.05 mmol) and $IMe_4$ (6.7 mg, 0.05 mmol) were dissolved in benzene (10 mL) leading to a colour change from orange to yellow. After stirring for 2 h, volatiles were

removed in vacuo and the resulting pale solid dissolved in pentane (20 mL). The resulting solution was concentrated to ca. 3 mL and crystals of **3-Cl** were obtained upon standing at room temperature that were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL). Yield: 33.7 mg (0.03 mmol, 60 %). $^{1}$H NMR (400 MHz, $C_6D_6$, 298 K): $\delta_H$ 0.99 (d, $^{3}J_{H,H}$ = 6.9 Hz, 24H, $CH_3$ of Dipp), 1.21 (d, $^{3}J_{H,H}$ = 6.9 Hz, 24H, $CH_3$ of Dipp), 1.24 (d, $^{3}J_{H,H}$ = 6.9 Hz, 24H, $CH_3$ of Dipp), 1.27 (d, $^{3}J_{H,H}$ = 6.9 Hz, 24H, $CH_3$ of Dipp), 1.34 (s, 6H, $CH_3C$=C), 3.07 (br, 6H, $CH_3N$), 3.35 (sept, $^{3}J_{H,H}$ = 6.7 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 3.50 (sept, $^{3}J_{H,H}$ = 6.7 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 5.94 (s, 4H, CH of boryl), 6.99 (m, 4H, p-ArH of Dipp), 7.09 (m, 8H, m-ArH of Dipp). $^{11}$B{$^{1}$H} NMR (128 MHz, $C_6D_6$, 298 K): $\delta_B$ 21.9 (boryl), B-Cl not observed. $^{13}$C{$^{1}$H} NMR (101 MHz, $C_6D_6$, 298 K): $\delta_C$ 7.4 (<u>C</u>$H_3$C=C), 22.7, 22.8, 25.3, 25.7 ($CH_3$ of Dipp), 28.3, 28.5 (CH of boryl), 118.2 (CH of boryl), 122.6 (m-Ar of Dipp), 122.8 ($CH_3$<u>C</u>=C), 126.1 (p-Ar of Dipp), 141.4 (CN of Dipp), 146.6, 147.0 (o-Ar of Dipp).

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**Supporting information**

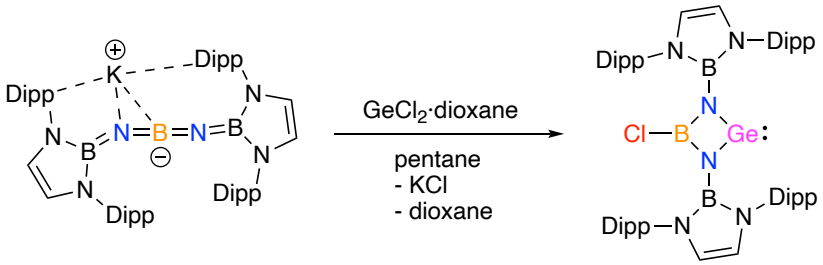
## 1. General considerations

All experiments were carried out under an atmosphere of dry argon or dinitrogen using standard Schlenk line and dry-box techniques. Solvents were degassed by sparging with argon and dried by passing through a column of appropriate drying agent using a commercially available Braun SPS and stored over potassium mirror under argon in a Teflon valve ampoule. NMR spectra were measured in benzene-$d_6$, with the solvent being dried over potassium, distilled, degassed by three freeze-pump-thaw-cycles and stored over 3 Å sieves. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. $^{1}$H and $^{13}$C{$^{1}$H} NMR spectra were measured on Bruker Avance III HD nanobay 400 MHz, or Bruker Avance III 500 MHz, and referenced internally to residual protio-solvent ($^{1}$H) or solvent ($^{13}$C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). Assignments were confirmed using two- dimensional $^{1}$H-$^{1}$H, $^{13}$C-$^{1}$H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. The reported yields are the yields obtained after crystallisation and subsequent measurement of the material by single crystal X-ray diffraction if not stated otherwise.

## 2. Preparation of starting materials

K[(HCDippN)$_2$BNBNB(NDippCH)$_2$][S1] and 1,3,4,5-tetramethylimidazol-2-ylidene (IMe$_4$)[S2] were prepared according to methods reported in the primary literature.

## 3. Synthetic procedures and characterizing data for new compounds




**1** **2-Cl**

**Scheme S1.** Synthesis of [ClB{(boryl)N}$_2$]Ge**, 2-Cl**.

**ClB{(HCDippN)$_2$BN}$_2$Ge**, **[ClB{(boryl)N}$_2$]Ge, 2-Cl**

K[(HCDippN)$_2$B-N=B=N-B(HCDippN)$_2$] (150 mg, 0.17 mmol) and $GeCl_2$·dioxane (40 mg, 0.17 mmol) were dissolved in pentane (30 mL) leading to a colour change from colourless to orange. After stirring for 12 h, the solution was concentrated to a third of its original volume, and orange crystals of **2-Cl** obtained on standing at – 30 °C, which were isolated by filtration and washed with cold pentane (2 x 5 mL).

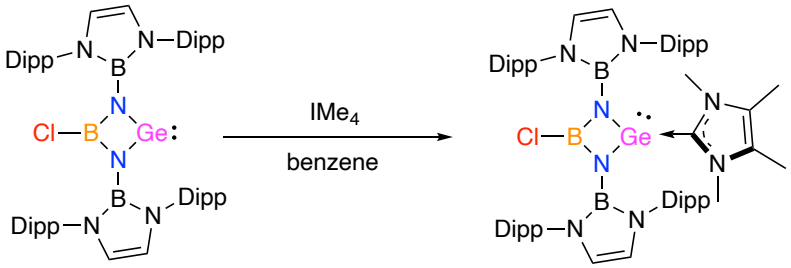
Yield: 95.4 mg (0.10 mmol, 59 %)

$^1$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 1.17 (d, $^3J_{H,H}$ = 7.1 Hz, 24H, $CH_3$ of Dipp), 1.19 (d, $^3J_{H,H}$ = 7.1 Hz, 24H, $CH_3$ of Dipp), 3.21 (sept, $^3J_{H,H}$ = 7.1 Hz, 8H,C<u>H</u>$(CH_3)_2$ of Dipp), 6.00 (s, 4H, CH of boryl), 7.05 (m, 8H, m-ArH of Dipp), 7.10 (m, 4H, p-ArH of Dipp).

$^{11}$B{$^1$H} NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 22.6 (boryl), 36.0 (B-Cl).

$^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 24.0, 25.1 ($CH_3$ of Dipp), 28.8 (CH of boryl), 117.9 (CH of boryl), 124.3 (m-Ar of Dipp), 127.9 (p-Ar of Dipp), 139.9 (CN of Dipp), 146.8 (o-Ar of

Dipp).




**2-Cl** **3-Cl**

**Scheme S2.** Synthesis of [ClB{(boryl)N}$_2$]Ge·IMe$_4$, **3-Cl**.

**ClB{(HCDippN)$_2$BN}$_2$Ge·IMe$_4$, [ClB{(boryl)N}$_2$]Ge·IMe$_4$, 3-Cl**

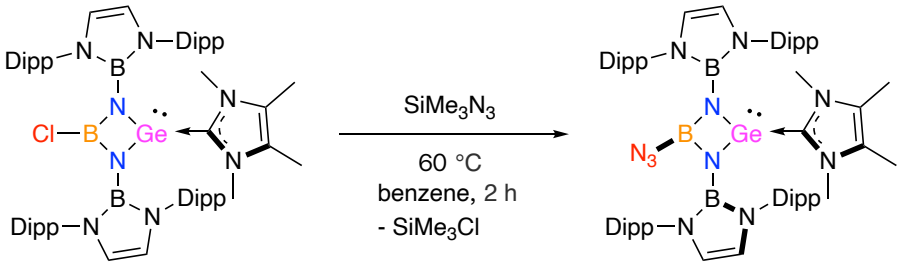
**2-Cl** (50 mg, 0.05 mmol) and IMe$_4$ (6.7 mg, 0.05 mmol) were dissolved in benzene (10 mL) leading to a colour change from orange to yellow. After stirring for 2 h, volatiles were removed in vacuo and the resulting pale solid dissolved in pentane (20 mL). The resulting solution was concentrated to ca. 3 mL and crystals of **3-Cl** were obtained upon standing at room temperature that were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

Yield: 33.7 mg (0.03 mmol, 60 %)

$^1$H NMR (400 MHz, $C_6D_6$, 298 K): $\delta_H$ 0.99 (d, $^3J_{H,H}$ = 6.9 Hz, 24H, $CH_3$ of Dipp), 1.21 (d, $^3J_{H,H}$ = 6.9 Hz, 24H, $CH_3$ of Dipp), 1.24 (d, $^3J_{H,H}$ = 6.9 Hz, 24H, $CH_3$ of Dipp), 1.27 (d, $^3J_{H,H}$ = 6.9 Hz, 24H, $CH_3$ of Dipp), 1.34 (s, 6H, $CH_3C$=C), 3.07 (br, 6H, $CH_3N$), 3.35 (sept, $^3J_{H,H}$ = 6.7 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 3.50 (sept, $^3J_{H,H}$ = 6.7 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 5.94 (s, 4H, CH of boryl), 6.99 (m, 4H, p-ArH of Dipp), 7.09 (m, 8H, m-ArH of Dipp).

$^{11}$B{$^1$H} NMR (128 MHz, $C_6D_6$, 298 K): $\delta_B$ 21.9 (boryl), B-Cl not observed.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $C_6D_6$, 298 K): $\delta_C$ 7.4 ($\underline{C}H_3C=C$), 22.7, 22.8, 25.3, 25.7 ($CH_3$ of Dipp), 28.3, 28.5 (CH of boryl), 118.2 (CH of boryl), 122.6 (m-Ar of Dipp), 122.8 ($CH_3\underline{C}=C$), 126.1 (p-Ar of Dipp), 141.4 (CN of Dipp), 146.6, 147.0 (o-Ar of Dipp).




**3-Cl** **3-$N_3$**

**Scheme S3.** Synthesis of $[(N_3)B\{(boryl)N\}_2]Ge{\cdot}IMe_4$, **3-$N_3$**.

**$N_3B\{(HCDippN)_2BN\}_2Ge{\cdot}IMe_4$, $[(N_3)B\{(boryl)N\}_2]Ge{\cdot}IMe_4$, 3-$N_3$**

**3-Cl** (60 mg, 0.06 mmol) was dissolved in benzene (10 mL) and a drop of $Me_3SiN_3$ (ca. 0.01 mL, excess) added. The solution was heated at 60 °C for 2 h with a colour change from yellow to light yellow. Volatiles were removed in vacuo and the residue extracted with pentane (20 mL). The resulting solution was concentrated to ca. 2 mL and colourless crystals of **3-$N_3$** were obtained upon standing at room temperature which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

Yield: 34.1 mg (0.03 mmol, 57 %)

$^{1}H$ NMR (400 MHz, $C_6D_6$, 298 K): $\delta_H$ 1.03 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H, $CH_3$ of Dipp), 1.20 (d, $^{3}J_{H,H}$ = 6.4 Hz, 12H, $CH_3$ of Dipp), 1.22 (d, $^{3}J_{H,H}$ = 6.8 Hz, 12H, $CH_3$ of Dipp), 1.23 (d, $^{3}J_{H,H}$ = 6.4 Hz, 12H, $CH_3$ of Dipp), 1.32 (s, 6H, $CH_3C=C$), 2.87 (br, 6H, $CH_3N$), 3.36 (sept, $^{3}J_{H,H}$ = 6.7 Hz,

4H,C<u>H</u>$(CH_3)_2$ of Dipp), 3.44 (sept, $^3J_{H,H}$ = 6.7 Hz, 4H,C<u>H</u>$(CH_3)_2$ of Dipp), 5.98 (s, 4H, CH of boryl), 7.05 (m, 8H, m-ArH of Dipp), 7.12 (m, 4H, p-ArH of Dipp).

$^{11}B\{^1H\}$ NMR (128 MHz, $C_6D_6$, 298 K): $\delta_B$ 25.6 (boryl), B-$N_3$ not observed.

$^{13}C\{^1H\}$ NMR (126MHz, $C_6D_6$, 298 K): $\delta_C$ 7.7 (<u>C</u>$H_3$C=C), 22.95, 23.04, 25.8, 26.2 ($CH_3$ of Dipp), 28.71, 28.74 (CH of boryl), 118.4 (CH of boryl), 123.0 (m-Ar of Dipp), 123.1 ($CH_3$<u>C</u>=C), 126.6 (p-Ar of Dipp), 141.4 (CN of Dipp), 147.1, 147.5 (o-Ar of Dipp).

IR ($\nu$/$cm^{-1}$): 2125, $\nu_{as}$(NN).

## 4. Representative spectra of new compounds

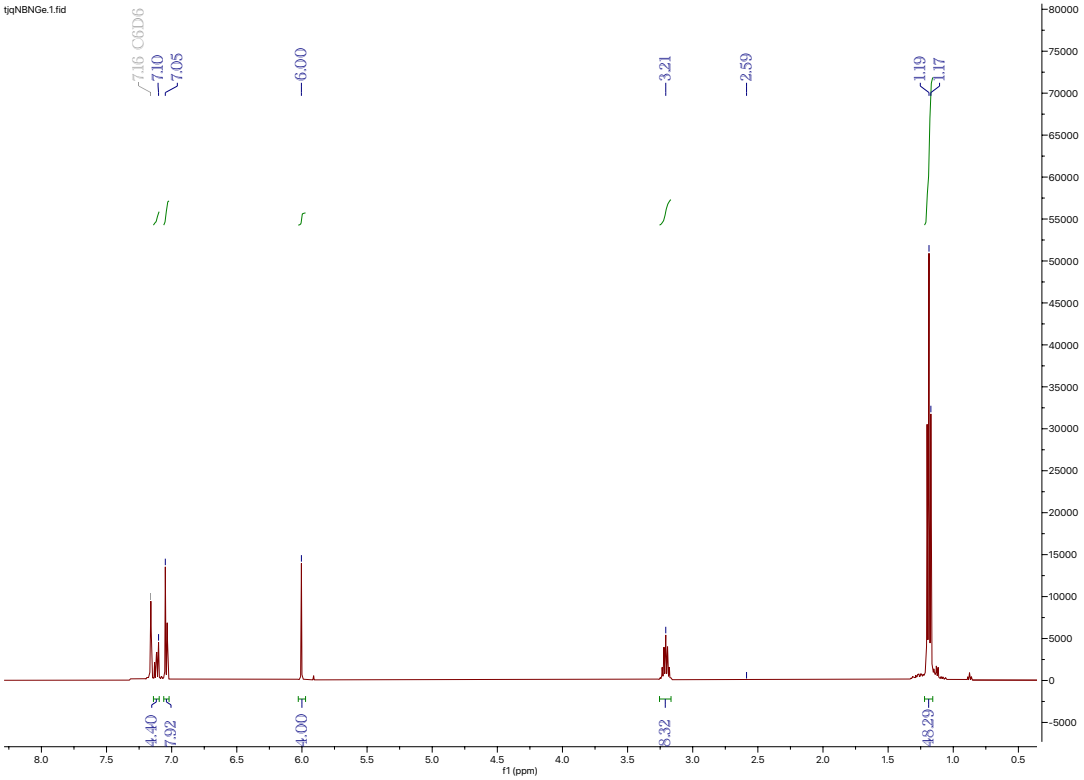



**Figure S1**: $^{1}H$ NMR spectrum of **2-Cl** in $C_6D_6$ at room temperature.

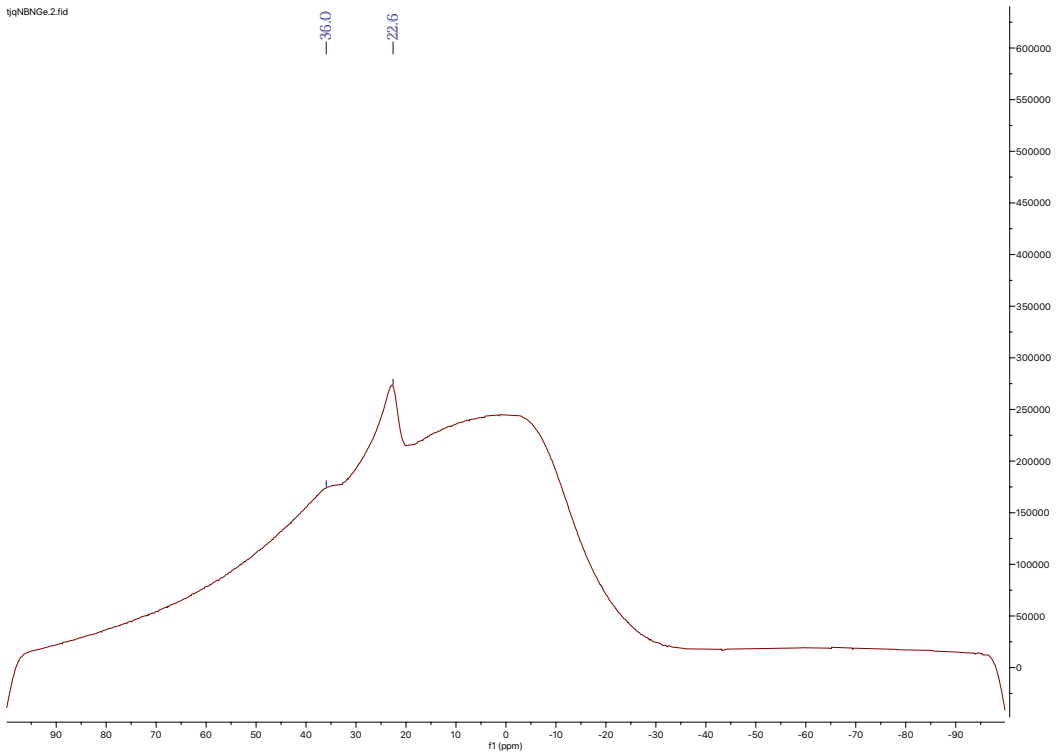



**Figure S2**: $^{11}B\{^{1}H\}$ NMR spectrum of **2-Cl** in $C_6D_6$ at room temperature.

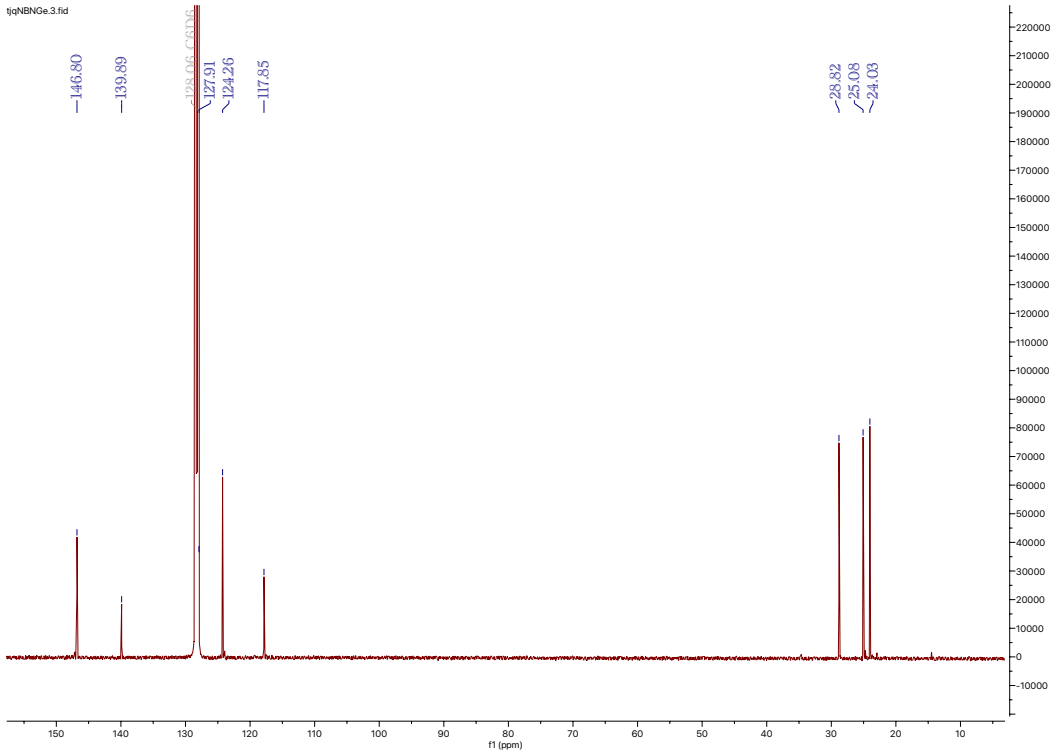



**Figure S3**: $^{13}C\{^{1}H\}$ NMR spectrum of **2-Cl** in $C_6D_6$ at room temperature.

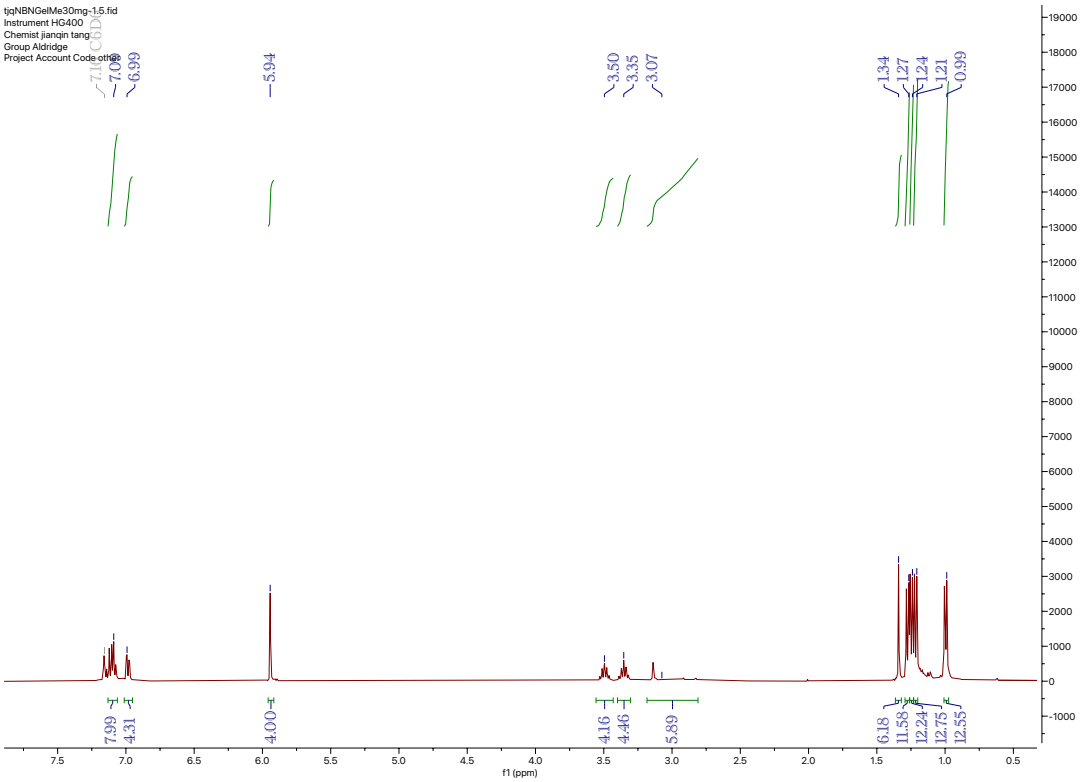



**Figure S4**: $^{1}H$ NMR spectrum of **3-Cl** in $C_6D_6$ at room temperature.

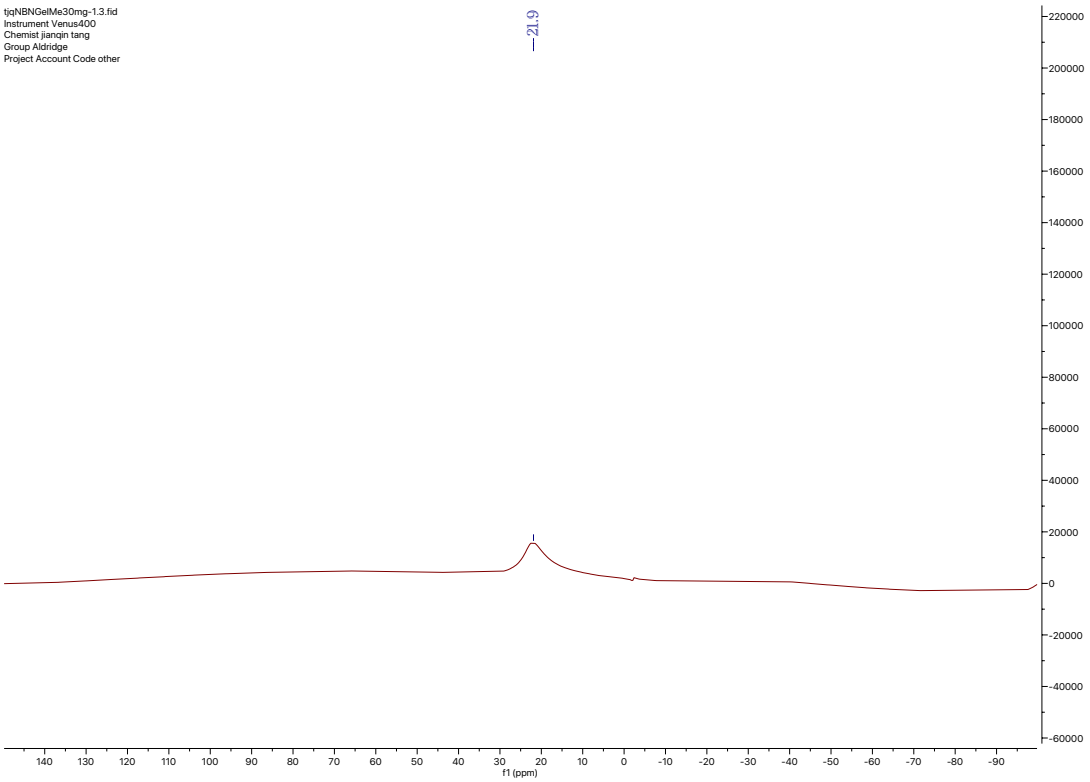



**Figure S5**: $^{11}B\{^{1}H\}$ NMR spectrum of **3-Cl** in $C_6D_6$ at room temperature.

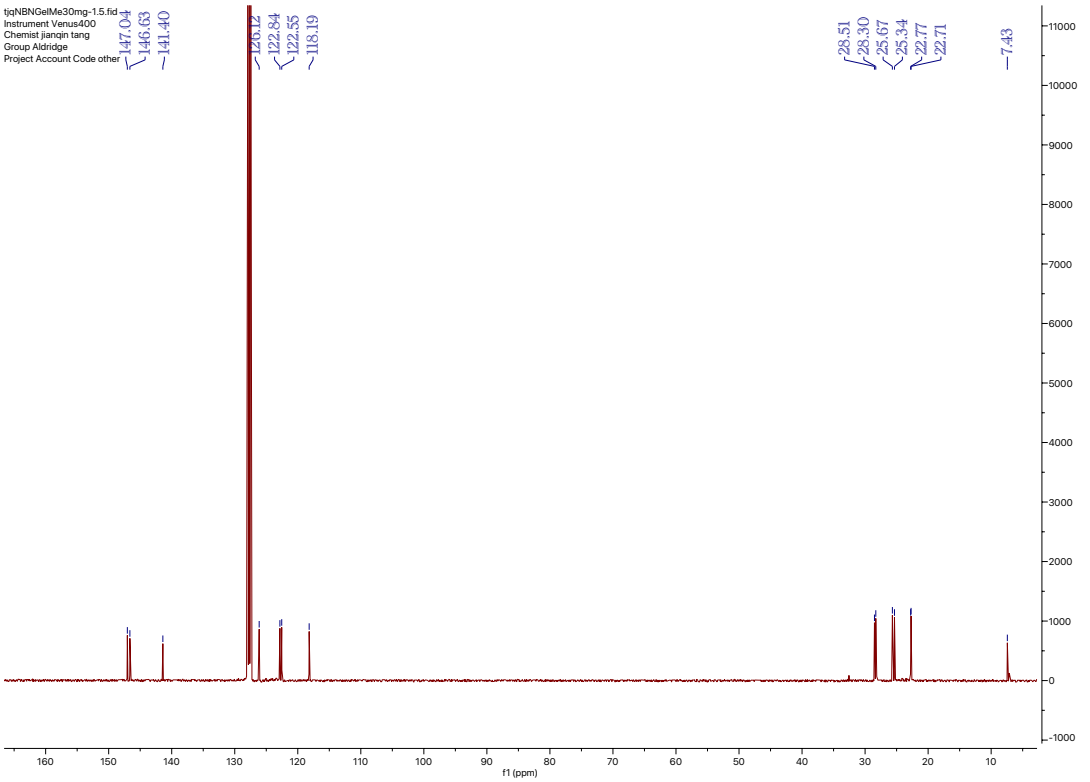



**Figure S6**: $^{13}C\{^{1}H\}$ NMR spectrum of **3-Cl** in $C_6D_6$ at room temperature.

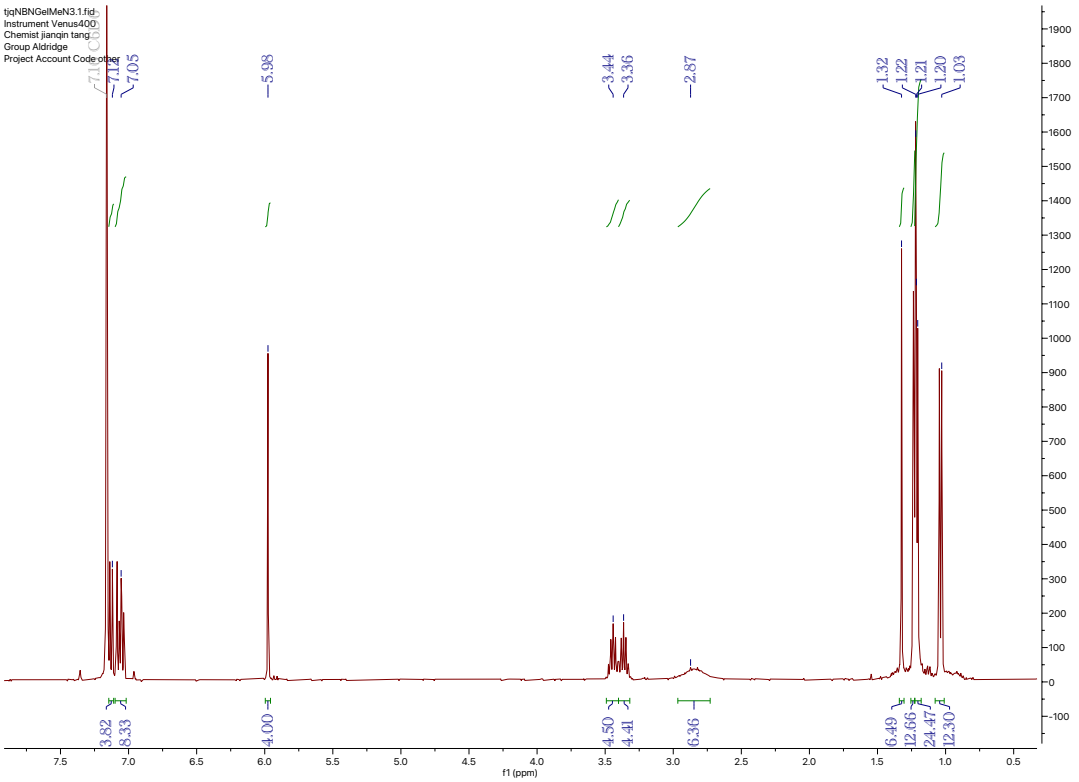



**Figure S7**: $^{1}$H NMR spectrum of **3-N$_3$** in $C_6D_6$ at room temperature.

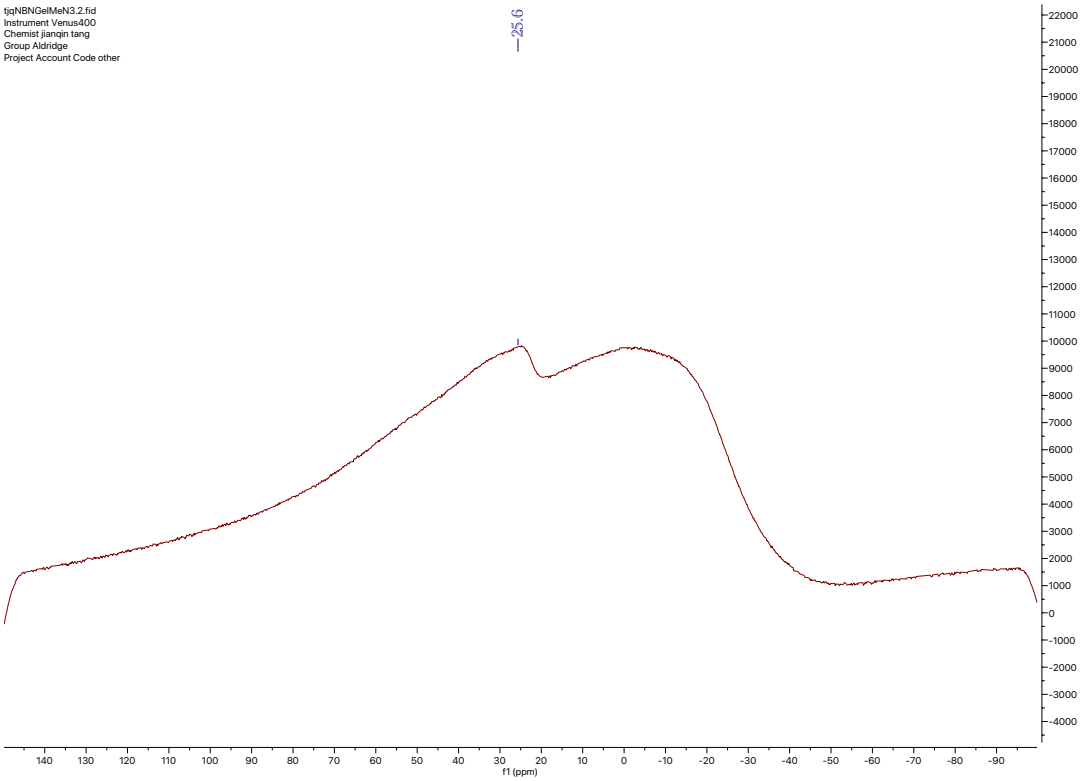



**Figure S8**: $^{11}$B{$^{1}$H} NMR spectrum of **3-N$_3$** in $C_6D_6$ at room temperature.

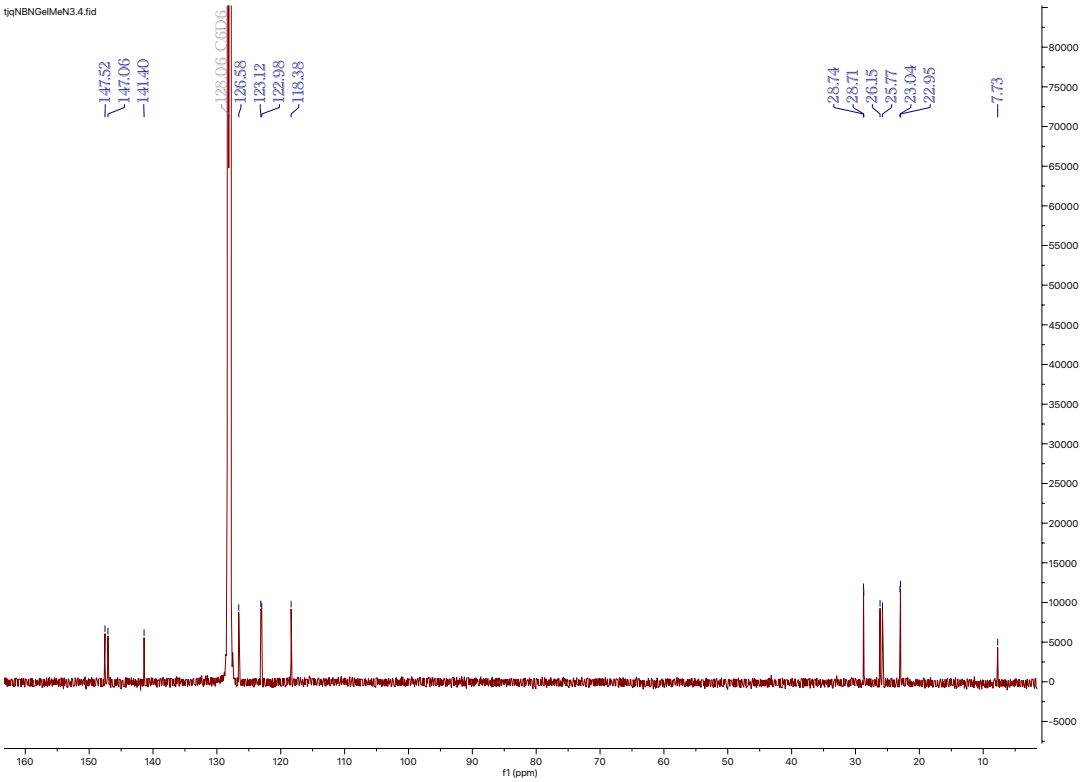



**Figure S9**: $^{13}C\{^{1}H\}$ NMR spectrum of **3-$N_3$** in $C_6D_6$ at room temperature.

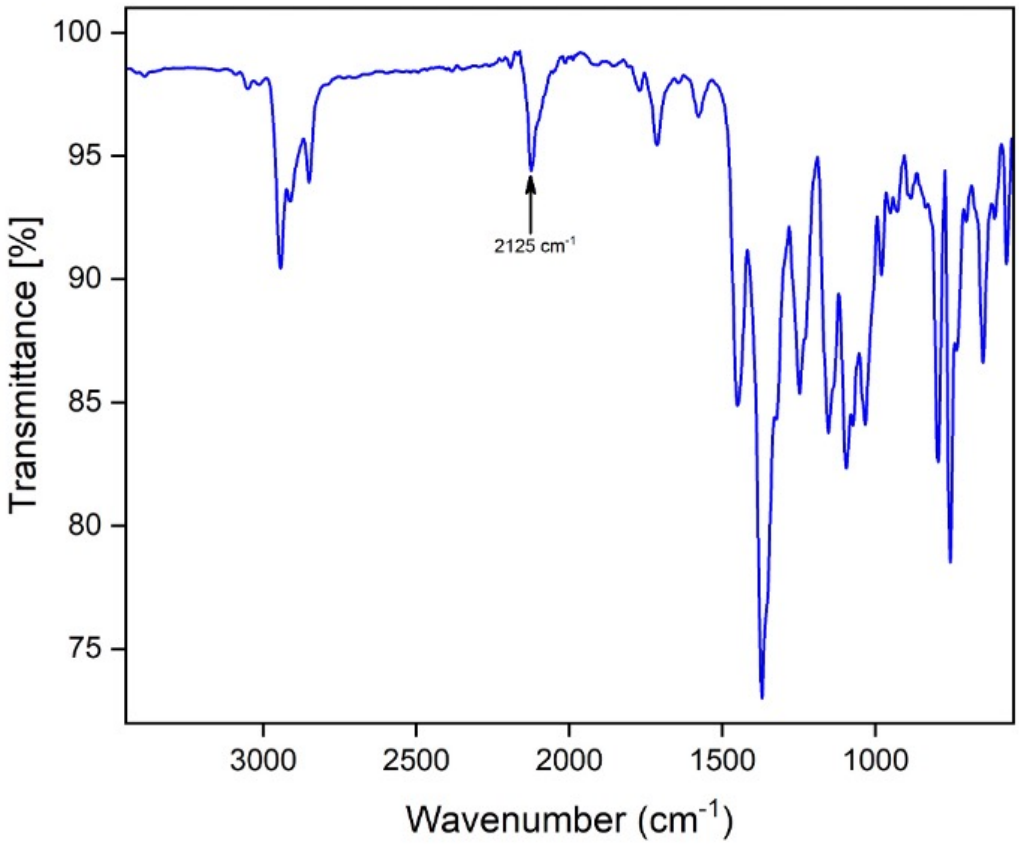



**Figure S10:** IR spectrum of **3-$N_3$**.

## 5. Details of X-ray crystallography

Single-crystal X-ray diffraction data for all compounds were collected on an Oxford Diffraction/Agilent SuperNova diffractometer equipped with a 135 mm Atlas CCD area detector or a Rigaku XtaLAB Synergy-DW VHF equipped with a PhotonJet-R dual wavelength rotating anode and HyPix-Arc 150° detector. Crystals were selected under Paratone-N oil, mounted on MiTeGen Micromount loops and quench-cooled using an Oxford Cryosystems open flow $N_2$ cooling device.[S3] Data were collected at 150 K using mirror monochromated Cu Kα radiation (λ = 1.5418 Å). Data collected were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[S4] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite.[S4] Structures were solved ab initio from the integrated intensities using SHELXT[S5] and refined on $F^2$ using SHELXL[S6] with the graphical interface OLEX2[S7]. Selected crystallographic data are summarised in Tables S1, and full details are given in the supplementary deposited CIF files (2466260, 2466261, 2467509). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

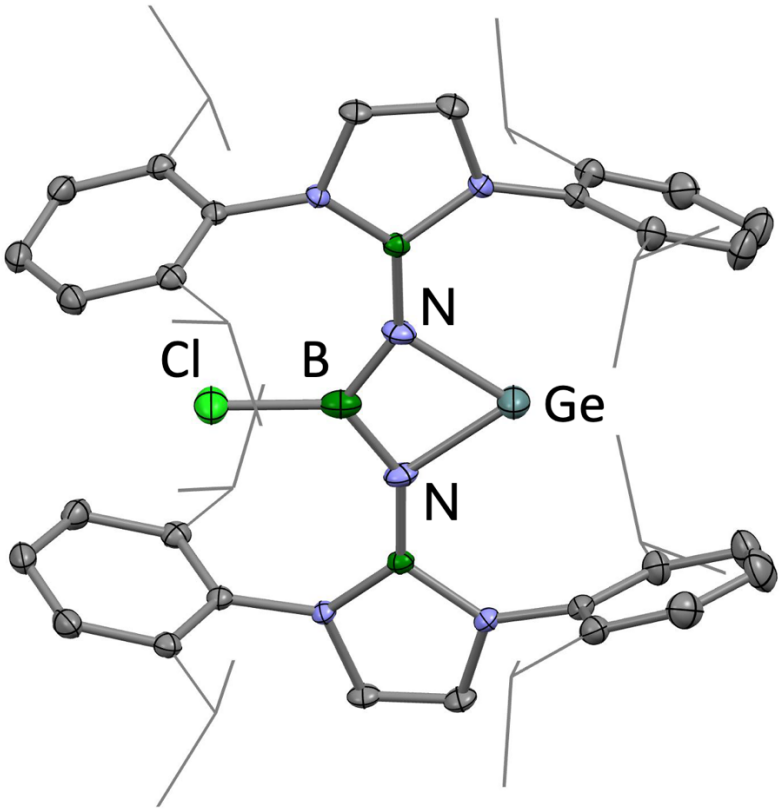



**Figure S11:** Outline molecular structure of one of the molecules in the unit cell of **2-Cl** in the solid state as determined by X-ray crystallography. Hydrogen atoms and other disorder components omitted, and selected groups shown in wireframe format for clarity. Thermal ellipsoids set at the 30 % probability level.

**Table S1**: Selected crystallographic data

| Identification code | **2-Cl** | **3-Cl** |
|---|---|---|
| Empirical formula | $C_{52}H_{72}B_3ClGeN_6$ | $C_{59}H_{84}B_3ClGeN_8$ |
| Formula weight | 922.50 | 1045.83 |
| Temperature/K | 100 K | 100 K |
| Crystal system | monoclinic | monoclinic |
| Space group | C2/c | P $2_1$/c |
| a/Å | 23.06090(10) | 13.1422(1) |
| b/Å | 25.13140(10) | 18.5136(1) |
| c/Å | 28.4867(2) | 25.2135(2) |
| α, β, γ/° | 90, 109.1370(10), 90 | 90, 104.988(1), 90 |
| Volume/Å$^3$ | 15597.18(17) | 5925.98(8) |
| Z | 12 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.160 | 1.172 |
| μ/mm$^{-1}$ | 1.424 | 1.438 |
| F(000) | 5806.0 | 2232.0 |
| Radiation | Cu Kα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 4.81 to 149.666 | 5.996 to 151.5 |
| Index ranges | -28 ≤ h ≤ 28, -31 ≤ k ≤ 31, -35 ≤ l ≤ 33 | -16 ≤ h ≤ 14, -23 ≤ k ≤ 23, -31 ≤ l ≤ 31 |
| Reflections collected | 196284 | 143263 |
| Independent reflections | 15879 [$R_{int}$ = 0.0303, $R_{sigma}$ = 0.0144] | 12153 [$R_{int}$ = 0.0361, $R_{sigma}$ = 0.0140] |
| Data/restraints/parameters | 15879/0/877 | 12153/561/669 |
| Goodness-of-fit on $F^2$ | 1.056 | 1.020 |
| Final *R* indexes [I>=2σ (I)] | $R_1$ = 0.0840, w$R_2$ = 0.2363 | $R_1$ = 0.0363, w$R_2$ = 0.0974 |
| Final *R* indexes [all data] | $R_1$ = 0.0881, w$R_2$ = 0.2397 | $R_1$ = 0.0382, w$R_2$ = 0.0986 |
| Largest diff. peak/hole / eÅ$^{-3}$ | 3.49/-2.34 | 0.51/-0.50 |
| CCDC ref | 2467509 | 2466261 |

| Identification code | **3-$N_3$** |
|---|---|
| Empirical formula | $C_{59}H_{84}B_3GeN_{11}$ |
| Formula weight | 1052.39 |
| Temperature/K | 100 K |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 12.83290(10) |
| b/Å | 21.76440(10) |
| c/Å | 21.72200(10) |
| $\alpha$, $\beta$, $\gamma$/° | 90, 95.33(4), 90 |
| Volume/Å$^3$ | 6040.73(6) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.157 |
| μ/mm$^{-1}$ | 1.031 |
| F(000) | 2248 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 5.76 to 144.26 |
| Index ranges | -15 ≤ h ≤ 15, -25 ≤ k ≤ 27, -27 ≤ l ≤ 26 |
| Reflections collected | 57600 |
| Independent reflections | 11880 [$R_{int}$ = 0.0275, $R_{sigma}$ = 0.0206] |
| Data/restraints/parameters | 11880 / 687 / 0 |
| Goodness-of-fit on $F^2$ | 1.047 |
| Final *R* indexes [I>=2σ (I)] | $R_1$ = 0.0383, w$R_2$ = 0.1031 |
| Final *R* indexes [all data] | $R_1$ = 0.0419, w$R_2$ = 0.1051 |
| Largest diff. peak/hole / eÅ$^{-3}$ | 1.299 / –0.499 |
| CCDC ref | 2466260 |

## 6. Details of quantum chemical calculations

Geometry optimizations were carried out using the Gaussian 16 package with the M06-2X functional.[S8,S9] The def2-SVP basis set was used for all atoms.[S10,S11] Frequency calculations at same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum and one for transition states), and provide the thermal corrections of Gibbs free energy. Single-point energy calculations were performed at the M06-2X/def2-TZVP level of theory for the modelling of compounds.[S12,S13] Natural bond orbital (NBO) calculations were carried out using NBO 7.0 program at the M06-2X/def2-TZVP level of theory.[S14]

## 7. References for supporting information


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**Declaration of author contribution**

**Statement of Authorship for joint/multi-authored papers for PGR thesis**

To appear at the end of each thesis chapter submitted as an article/paper

The statement shall describe the candidate's and co-authors' independent research contributions in the thesis publications. For each publication there should exist a complete statement that is to be filled out and signed by the candidate and supervisor **(only required where there isn't already a statement of contribution within the paper itself).**

| | |
|---|---|
| Title of Paper | Synthesis of a diamido-germylene from an inorganic cumulene |
| Publication Status | □ Published □ Accepted for Publication<br>√Submitted for Publication □ Unpublished and unsubmitted work written<br>in a manuscript style |
| Publication Details | Jianqin Tang, Agamemnon E. Crumpton, Maximilian Dietz and Simon Aldridge* |

Student Confirmation

| | | | |
|---|---|---|---|
| Student Name: | Jianqin Tang | | |
| Contribution to the Paper | Performed all synthetic, spectroscopic work, as well as all quantum chemical calculations. Analysed and interpreted data. Wrote the draft manuscript and prepared the supporting information. | | |
| Signature | Jianqin Tang | Date | 20/06/2025 |

Supervisor Confirmation

By signing the Statement of Authorship, you are certifying that the candidate made a substantial contribution to the publication, and that the description described above is accurate.

| | | |
|---|---|---|
| Supervisor name and title: Professor Simon Aldridge | | |
| Supervisor comments<br>I can confirm that the information concerning this paper described by the candidate is accurate. | | |
| Signature | Date | 21June 2025 |

## Chapter 5. Synthesis, characterization and reactivity of Silaimines/Stannaimines

### Introduction

Reversible shuttling between redox states represents a significant challenge in Main Group chemistry, especially with respect to potential applications in redox catalysis. This challenge is particularly apparent for lighter p-block elements such as silicon, for which the Si(II) state is typically highly reducing.

With the development of stable silylenes (Si(II)), direct reactions with organic azides or carbodiimides represent common methods to generate silaimines in the Si(IV) redox state. These species, characterized by highly polarized Si=NR bonds, are highly reactive. On the other hand, the Dipp-substituted diazaborolyl group {$(HCDippN)_2B$} is a very strong $\sigma$-donor ligand, and has been widely used in Main Group chemistry; we hypothesized that these electron-releasing properties might allow for the isolation of more stable silaimine species. This study reports the synthesis of a silaimine from such a silylene and trimethylsilyl azide, and highlights its reversible redox cycling between Si(IV) and Si(II) oxidation states, driven by redox-based ligand migration.

**Isomerization and insertion chemistry of imidosilanes enabled by reversible Si(IV)/Si(II) redox shuttling**

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**Abstract**

Spontaneous redox shuttling at silicon is very rare, primarily reflecting the thermodynamic challenges associated with reduction processes for lighter *p*-block elements. Here we show that the reactions of boryl-substituted silylene {PhC($^t$BuN)$_2$}Si{B(NDippCH)$_2$} with an organo-azide proceed through a Si(IV)-Si(II)-Si(IV) series of redox processes involving both oxidative and reductive ligand migration steps. Each of the isomeric compounds related through this reaction manifold is isolable (and can be structurally characterized by X-ray crystallography), with the overall free energy profile being close to thermo-neutral. Broader studies within group 14 imply that this redox shuttling is unique to silicon, and that reductive ligand migration also plays a role in O-atom insertion chemistry.

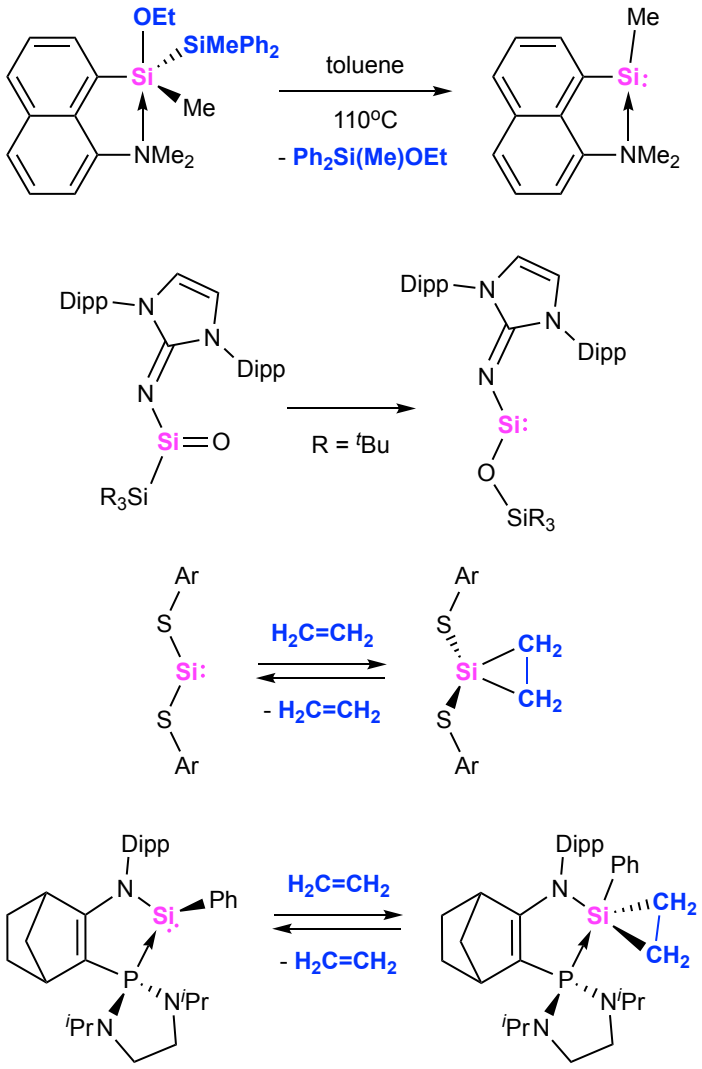
## Introduction

The activation of small molecules by Main Group compounds has become a highly topical challenge, driven both by fundamental discovery and by environmental imperatives centred around the avoidance of toxic, scarce and increasingly expensive Noble Metals. Such drivers have led to the development of *p*-block systems with frontier orbital symmetries and energies appropriate to interact in synergistic manner with molecules (such as $H_2$, CO and alkenes), which are both s donors and p acceptors).[1,2] Much of the derived small molecule activation chemistry reported to date has been stoichiometric, and the involvement of Main Group compounds in redox catalysis is rare.[3] This in turn reflects the fact that for lighter *p*-block elements the group oxidation state (*n*) is significantly favoured thermodynamically (and reductive elimination is not favourable); on the other hand, for heavier p-block elements the *n*-2 ('Inert Pair') oxidation state is often favoured, and oxidative addition is less easily effected. Examples of thermodynamically reversible processes are therefore relatively scarce.

Within Group 14 chemistry, Bielawski and co-workers reported the use of an *N,N*′-diamidocarbene to achieve the reversible activation of ammonia,[4] and heavier analogues of germanium and tin have been implicated in reversible bond activation processes.[5–9] In the case of silicon-containing compounds, spontaneous reductive processes leading to the formation of Si(II) species from Si(IV) precursors are rare. The formation of IDipp·$SiCl_2$ by the dehydrohalogenation of $HSiCl_3$, for example, relies on the accompanying formation of [(IDipp)H]Cl, in a formal oxidative process at divalent carbon which helps drive the reduction at silicon.[10,11] 'Acceptor-less' processes occurring in the absence of strongly reducing co-reagents can be enthalpically driven by the formation of a strong bond (e.g. Si–O), and/or entropically driven through evolution of a volatile co-product (Scheme 1).[12-15] Similar strategies have also been exploited in examples of *reversible* processes, e.g. the activation of alkenes or E–H bonds by silylene compounds under ambient conditions (Scheme 1).[16–19]

We have recently been interested in developing the chemistry of silylene (and related heavier

metallylene) systems stabilized by a combination of p-donating amidinate/guanidinate and strongly s-donating boryl ligands,[20] In this study, we report the synthesis of a (imido)silane derived from such a silylene and trimethylsilylazide. Most interestingly, we describe both its isomerization and chemical transformation through reversible cycling between Si(IV) and Si(II) states, enabled by redox-active ligand migration steps.

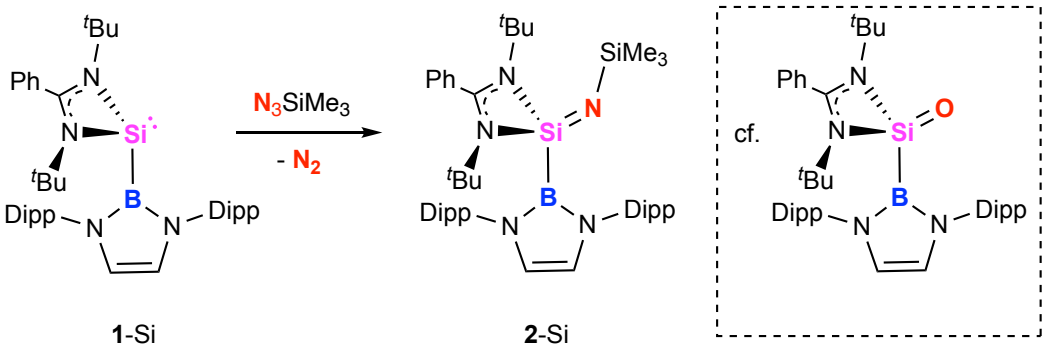



**Scheme 1** Spontaneous and/or reversible redox processes at silicon of relevance to the current study (Ar = -$C_6H_3Dipp_2$-2,6; Dipp = 2,6-$C_6H_3{}^iPr_2$).

## Results and Discussion

The reaction of silylene {PhC($^t$BuN)$_2$}Si(boryl), (**1**-Si; boryl = –B(NDippCH)$_2$) with trimethylsilyl azide at room temperature proceeds smoothly to generate (silylimido)silane {PhC($^t$BuN)$_2$}Si(boryl)(NSiMe$_3$) (**2**-Si; Scheme 2), which can be isolated as a colourless crystalline solid in 65% yield after recrystallization from pentane. We recently reported a similar synthetic approach to the silanone {PhC($^t$BuN)$_2$}Si(boryl)(O) by exposing **1**-Si to $N_2O$.[20] The identity of the (imido)silane product **2**-Si has been unambiguously determined by multinuclear NMR spectroscopy, elemental microanalysis and X-ray crystallography. The $^{29}$Si NMR signal ($\delta_{Si}$ = -49.3 ppm) is shifted noticeably upfield compared to precursor **1**-Si ($\delta_{Si}$ = 57.2 ppm), consistent with formal oxidation from Si(II) to Si(IV) (cf. $\delta_{Si}$ = -33.9 ppm for {PhC($^t$BuN)$_2$}Si(boryl)(O)).[20] The $^{11}$B NMR resonances for **2**-Si and its silanone analogue ($\delta_B$ = 23.7 and 24.1 ppm, respectively), are both shifted to high field compared to **1**-Si ($\delta_B$ = 29.1 ppm).[20]

Single crystals of **2**-Si could be grown from pentane solution and the solid-state structure determined by X-ray crystallography (Figure 1, left). The Si–B bond length (2.015(1) Å) is statistically identical to that reported for the silanone (2.016(2) Å), and markedly shorter than that of **1**-Si (2.066(1) Å), consistent with the smaller covalent radius of Si(IV) over Si(II).[20] The Si=N bond (1.597(1) Å) is somewhat longer than the Si=O bond measured for {PhC($^t$BuN)$_2$}Si(boryl)(O) (1.5406(9) Å) – as expected due to the larger covalent radius of nitrogen (0.71 vs. 0.66 A).[21]




**1**-Si **2**-Si

**Scheme 2**: Oxidation of silylene **1**-Si with trimethylsilylazide to yield (imido)silane **2**-Si.

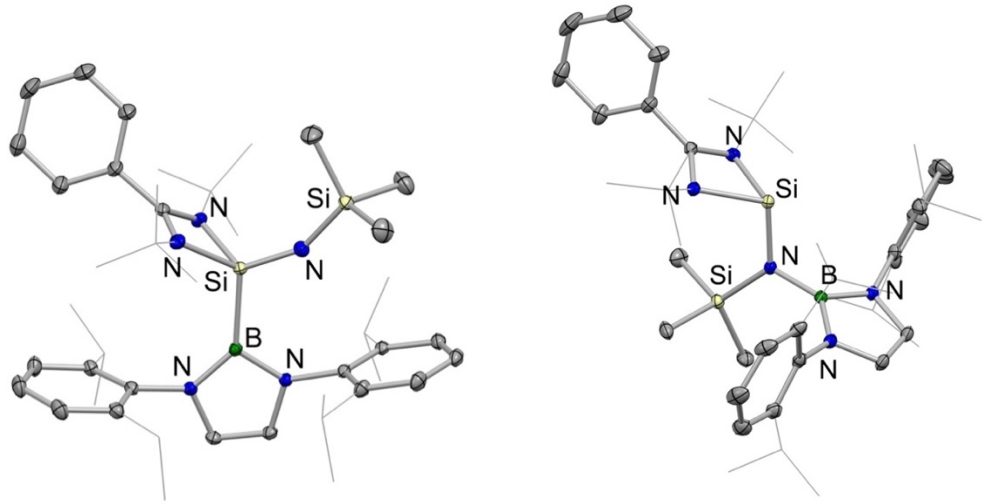
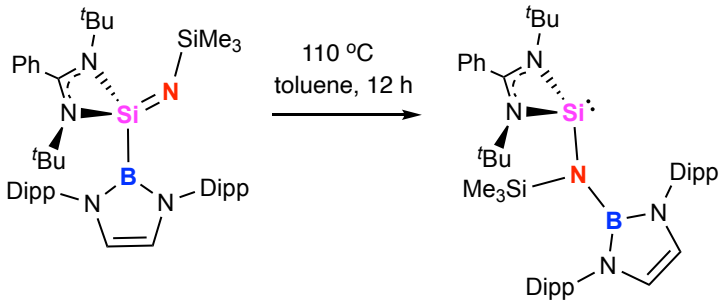



**Figure 1**: Molecular structures of **2**-Si (left) and **3**-Si (right) in the solid state as determined by X-ray crystallography. Hydrogen atoms omitted and selected groups shown in wireframe format for clarity. Thermal ellipsoids set at the 30 % probability level. Key bond lengths (A) and angles (°): (for **2**-Si) Si–$N_{imide}$ 1.597(1), Si–$N_{amidinate}$ 1.872(1), 1.851(1), Si–B 2.015(1), Si–N–Si 152.7(1); (for **3**-Si) Si–$N_{amide}$ 1.772(1), Si–$N_{amidinate}$ 1.918(1), 1.902(1).

In contrast to {PhC($^t$BuN)$_2$}Si(boryl)(O), heating **2**-Si at 110 °C in toluene over a period of 12 h leads to 90% conversion to a single new species, which is characterized by a $^{29}$Si NMR signal ($\delta_{Si}$ = -11.4 ppm) that is shifted downfield compared to the (imido)silane precursor (**2**-Si: $\delta_{Si}$ = -49.3 ppm), and which is similar to the signals reported for amidinate-supported silylenes, (e.g. {PhC($^t$BuN)$_2$}Si(NMe$_2$): $\delta_{Si}$ = -2.6 ppm; {PhC($^t$BuN)$_2$}Si{N(SiMe$_3$)$_2$}: $\delta_{Si}$ = -8.1 ppm).[22,23] The product of this thermal rearrangement (**3**-Si) could be isolated as a pale green crystalline solid in 50 % yield by recrystallization from pentane, and its identity as a silylene confirmed by X-ray crystallography (Figure 1, right). 1,2-Migration of the Si-bound boryl group to nitrogen leads to the formation of the sterically encumbered amido ligand –N(boryl)(SiMe$_3$), which is bound to Si(1) through a relatively long Si–N bond (1.772(1) Å). This distance can be put into context by Si–N separations of 1.724(2) Å measured for the less crowded dimethylamido derivative {PhC($^t$BuN)$_2$}Si(NMe$_2$) and 1.769(7) Å for the more closely comparable bis(trimethylsilyl)amido-silylene {PhC($^t$BuN)$_2$}Si{N(SiMe$_3$)$_2$}.[22,23] Consistently, the

methyl and methine $^{1}$H NMR signals for the 2,6-diisopropylphenyl (Dipp) groups of **3**-Si are broad, due to restricted boryl group rotation on the NMR timescale; these signals sharpen on raising the temperature to 45 °C.



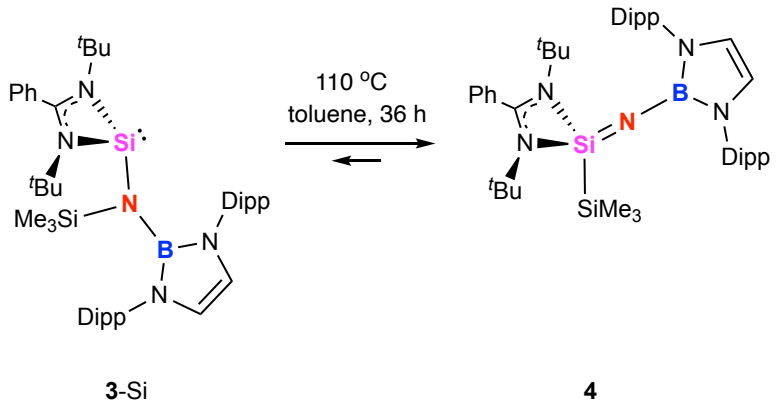

**2**-Si **3**-Si

**Scheme 3**: Thermal rearrangement of sila-imine **2**-Si to (borylamido) silylene 3-Si.

The transformation of **2**-Si into **3**-Si represents a rare example of spontaneous conversion of Si(IV) to Si(II) under thermal conditions without the addition of a reducing agent or the evolution of a volatile co-product.[11-14] Most closely related in the current context is the silyl-silanone to oxy-silylene conversion reported by Rieger and Inoue in 2017, driven by thermodynamically favourable Si–O (single) bond formation.[15] The feasibility of the conversion of **2**-Si to **3**-Si is supported by DFT calculations which suggest that boryl migration is exergonic by 5.0 kcal mol$^{-1}$ and incurs an activation barrier of ca. 30 kcal mol$^{-1}$ (consistent with a reaction that needs heating at 110 °C for 12 h; see below).

Interestingly, more extended heating of **2**-Si (or heating of **3**-Si over a period of 36 h) heads to further onward conversion to a species characterized by a $^{29}$Si signal in the region expected for an imidosilane derivative ($\delta_{Si}$ = -57.6 ppm cf. -49.3 ppm for **2**-Si). This new compound is also characterized by a markedly upfield shifted signal associated with the $SiMe_3$ group ($\delta_{Si}$ = -24.6 ppm, cf. -0.1 ppm for **3**-Si). Single crystals of the product (**4**) suitable for single crystal X-ray diffraction could be isolated from the reaction mixture, and confirm the formation of a

(borylimido)silane via 1,2-transfer of the trimethylsilyl group from N to Si (Scheme 4 and Figure 2). The conversion of **3**-Si to **4** proves impossible to drive to completion in our hands; the fact that it reaches equilibrium at ca. 70% conversion is consistent with DFT calculations which imply that the free energy difference between **3**-Si and **4** is very small (see below).




**3**-Si **4**

**Scheme 4**: Regeneration of Si(IV) through N-to-Si migration of the silyl substituent under forcing conditions.

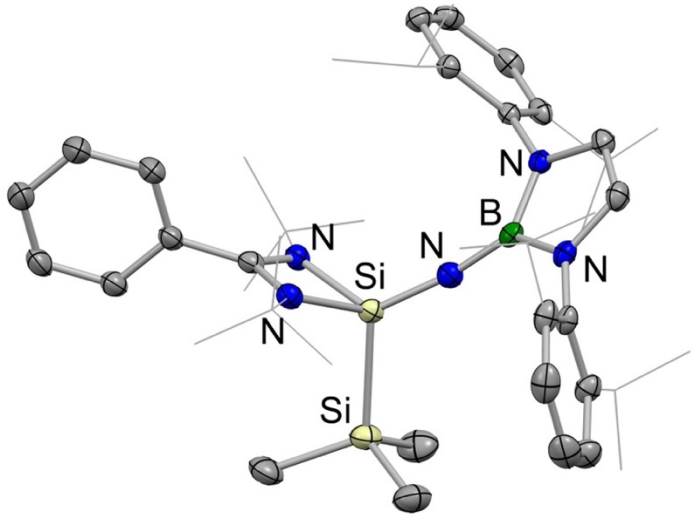



**Figure 2**: Molecular structure of **4** in the solid state as determined by X-ray crystallography. Hydrogen atoms omitted and selected groups shown in wireframe format for clarity. Thermal ellipsoids set at the 30 % probability level. Key bond lengths (A) and angles (°): Si–$N_{imide}$ 1.581(4), B–$N_{imide}$ 1.383(5), Si–$N_{amidinate}$ 1.863(3), 1.837(4), Si–Si 2.356(1), Si–N–B 169.3(3).

In order to gain insight into the mechanism of the redox shuttling at silicon linking compounds **2**-Si, **3**-Si and **4**, DFT calculations were performed at the R2-SCAN/Def2-TZVPPm level of theory (Figure 3). The first step in the reaction pathway is the migration of boryl group in **2**-Si from silicon to nitrogen, which occurs with an activation barrier of 29.4 kcal $mol^{-1}$ and is modestly exergonic ($\Delta G$ = -5.0 kcal $mol^{-1}$). That the resulting (amido)silylene **3**-Si is more stable than the isomeric (imido)silane is presumably – at least in part – due to the formation of a strong B–N bond. **3**-Si is highly sterically congested (as reflected in the broad signals for the boryl Dipp substituents seen in its $^{1}H$ NMR spectrum) and attempts to model an onward isomerization process which involves rotation about the Si–N bond (prior to N-to-Si migration of the $SiMe_3$ substituent) incur a prohibitively high activation barrier (> 45 kcal $mol^{-1}$). The lowest energy pathway which we have identified for this second step involves silyl ligand migration occurring concurrently with inversion at silicon through 'flipping' of the amidinate ligand. This results in the formation of (borylimido)silane **4**, via a process which is only slightly exergonic ($\Delta G$ = –1.7 kcal $mol^{-1}$) and occurs via a high activation barrier of +37.1 kcal $mol^{-1}$. While this barrier is high, it speaks to the reaction conditions required (110 °C, over 36 h) for the establishment of the equilibrium implied by the near thermo-neutrality of the transformation.

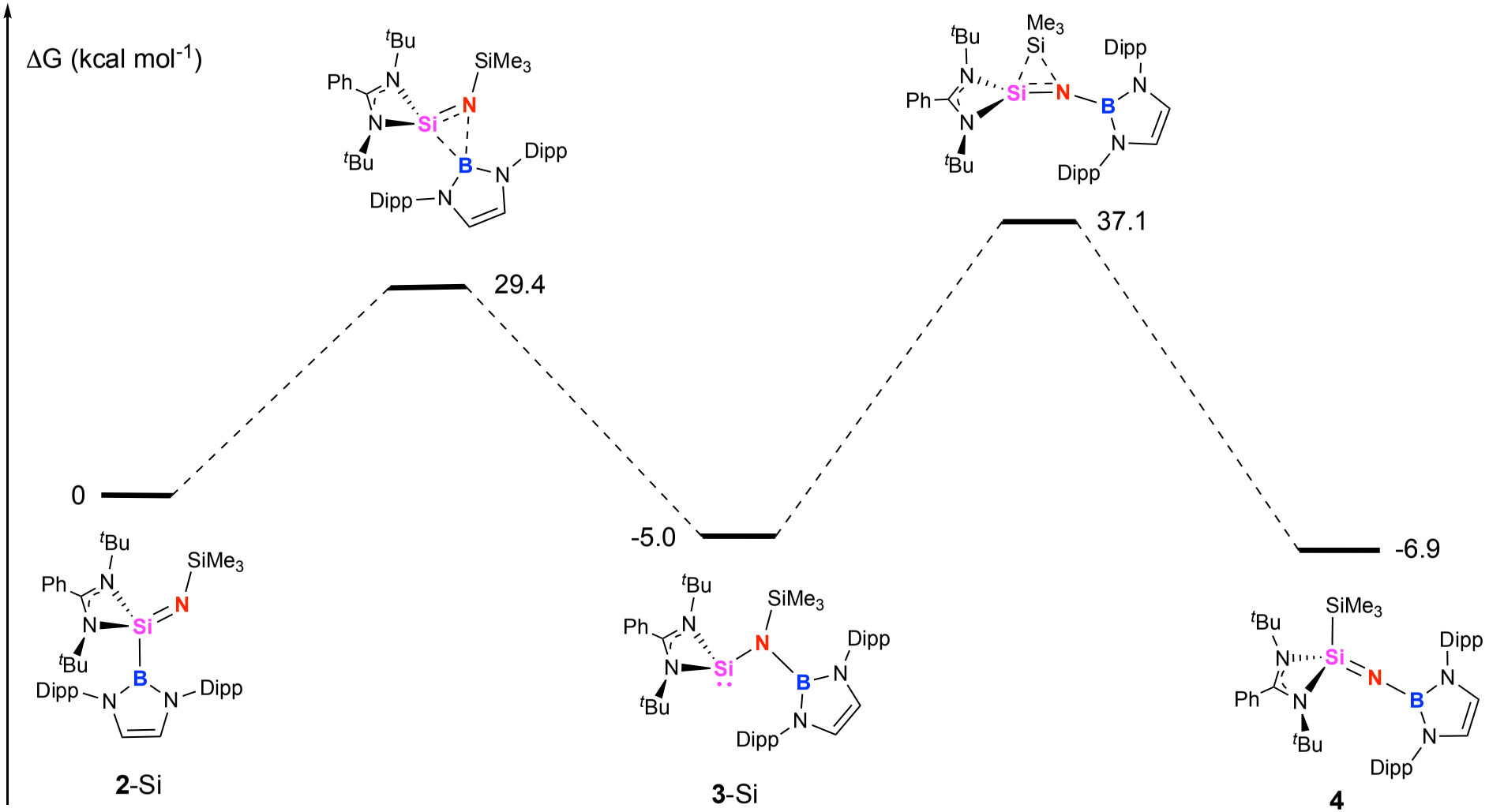
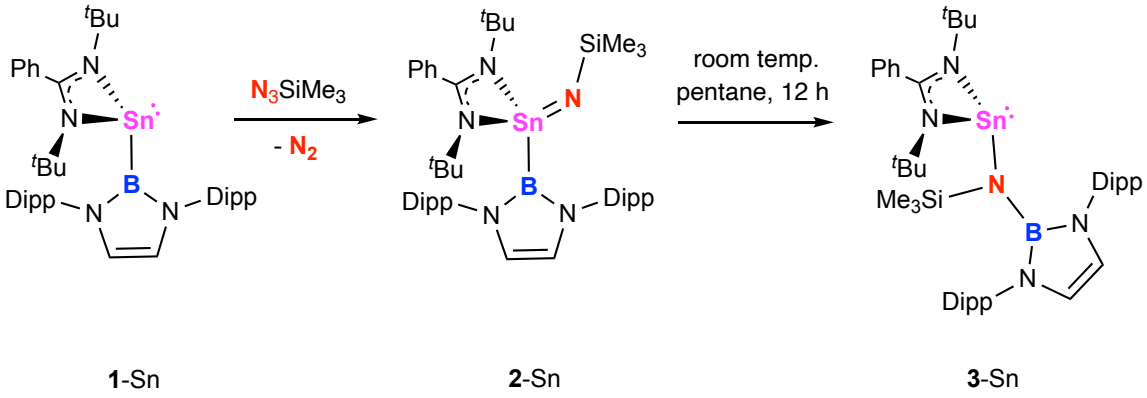



**Figure 3**˙ DFT calculated mechanism for the isomerization of (imido)silanes 2-Si and 4 via silylene 3-Si (calculated at the R2-SCAN-3c method level of theory with solvation modelled with C-PCM, toluene). Inset: alternative reaction pathways accessed via a transition state involving rotation about the Si–N bond in 3-Si incur much higher activation barriers, presumably on steric grounds.

In order to probe the wider relevance of this redox shuttling, the corresponding chemistry of stannylene **1**-Sn was also investigated (Scheme 5). These results are consistent with the greater thermodynamic stability of the +2 oxidation state for tin over silicon. Accordingly, (silylimido)stannane **2**-Sn can be accessed using $Me_3SiN_3$, via a similar synthetic approach to **2**-Si, and crystallized from minimal pentane over a period of several minutes. However, in contrast to its silicon congener, **2**-Sn is transformed in facile manner (12 h at room temperature) into tin(II) amide **3**-Sn, via a Sn-to-N boryl substituent migration analogous to that seen for **2**-Si/**3**-Si.




**1**-Sn **2**-Sn **3**-Sn

**Scheme 5**: (Silylimido)stannane formation from **1**-Sn and $Me_3SiN_3$ and subsequent reductive Sn-to N boryl substituent migration to yield (amido)stannylene **3**-Sn.

The molecular structures of **2**-Sn and **3**-Sn obtained crystallographically confirm the migration of the boryl substituent from tin to nitrogen (Figure 4). Structural features for these two compounds largely resemble their silicon counterparts, although the Sn–N–Si angle for **2**-Sn (131.2(1)º) is significantly narrower than the Si–N–Si angle for **2**-Si (152.7(1)º), presumably reflecting the smaller size of Si (over Sn) and the greater angular separation therefore required to minimize repulsive steric interactions with the silylimido substituent.

No evidence for onward conversion of **3**-Sn to a Sn(IV) borylimide species analogous to **4** was obtained experimentally, consistent with the enhanced stability of the E(II) oxidation state

lower down group 14. Moreover, this observation is supported by DFT calculations which imply that the free energy of a Sn(IV) species analogous to **4** would be much higher than **3**-Sn (ca. +46.1 kcal/mol$^{-1}$; Figure S25). Similar observations pertain for related (hypothetical) germanium systems (Figure S25) and the idea of shuttling between E(II) and E(IV) states in this ligand system is therefore unique to silicon.

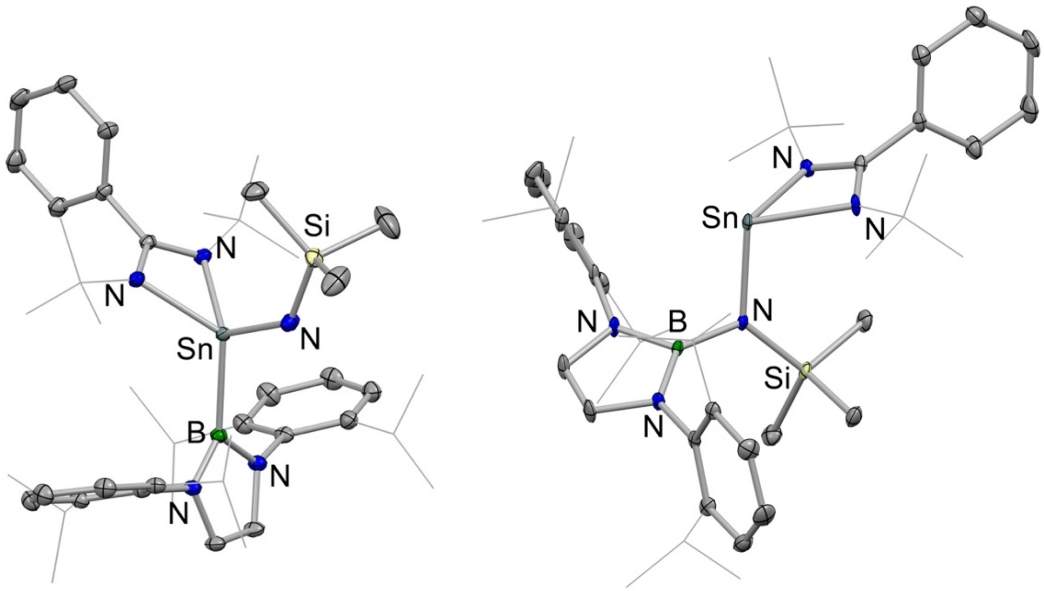
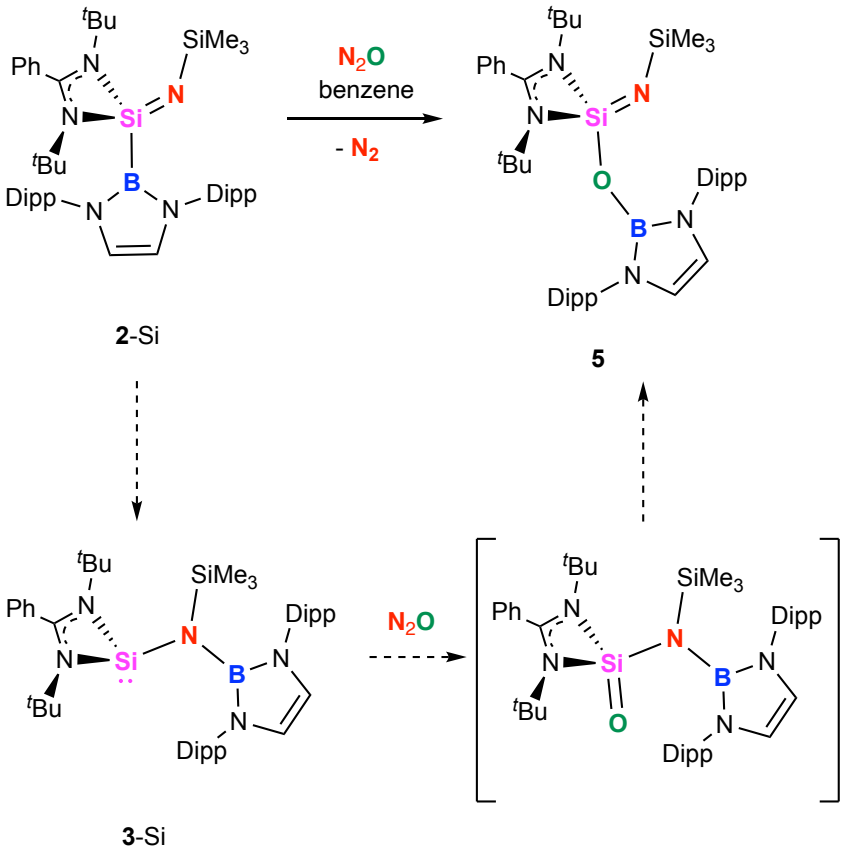



**Figure 4**: Molecular structures of **2**-Sn (left) and **3**-Sn (right) in the solid state as determined by X-ray crystallography. Hydrogen atoms omitted and selected groups shown in wireframe format for clarity. Thermal ellipsoids set at the 30 % probability level. Key bond lengths (A) and angles (°): (for **2**-Sn) Sn–$N_{imide}$ 1.914(1), Sn–$N_{amidinate}$ 2.176(1), 2.185(1), Sn–B 2.250(2), Sn–N–Si 131.2(1); (for **3**-Sn) Sn–$N_{amide}$ 2.118(1), Sn–$N_{amidinate}$ 2.230(1), 2.230(1).

The implications of ligand migration and redox reversibility in the context of *chemical reactivity* are illustrated by the reaction of **2**-Si with $N_2O$. This reaction results in formal O-atom insertion into the Si–B bond to give boryloxy compound **5** (Scheme 6 and Figure 5).[24] The reaction of **3**-Si with $N_2O$ gives the same product, implying that mechanistically this process proceeds via reductive ligand migration to generate silylene **3**-Si, followed by O-atom transfer from $N_2O$,

and finally N-to-O migration of the boryl group driven thermodynamically by B–O bond formation (and kinetically facilitated by the highly polar Si=O bond). Similar N-to-O migration has precedent in the reaction of (boryl){(Me$_3$Si)DippN}Si with $N_2O$.[25]




**Scheme 6**: Formal O-atom insertion into the Si-B bond of **2**-Si, facilitated by reductive ligand migration to give silylene intermediate **3**-Si.

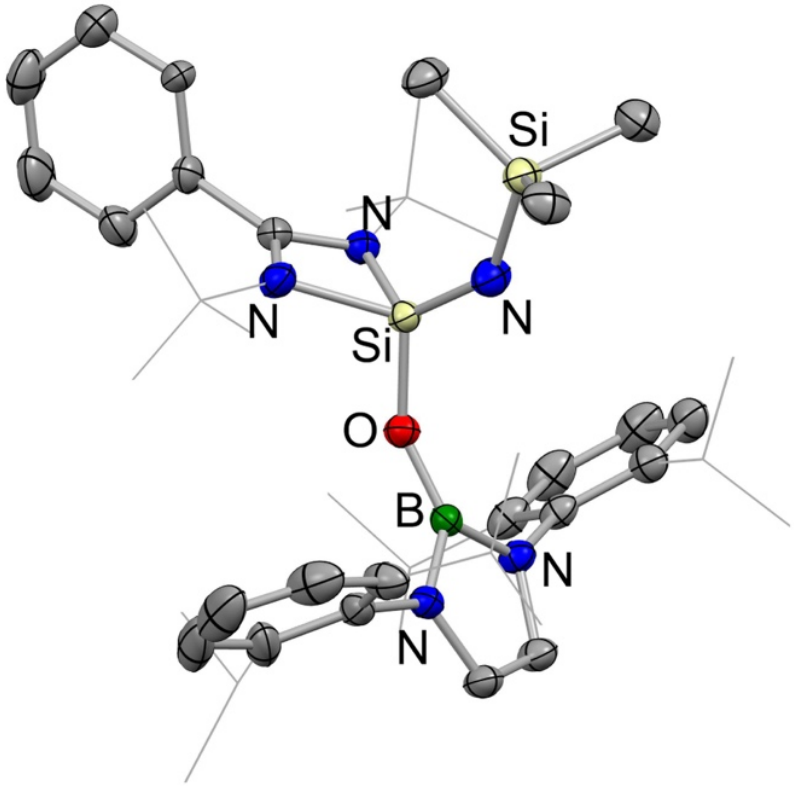



**Figure 5**: Molecular structure of **5** in the solid state as determined by X-ray crystallography. Hydrogen atoms omitted and selected groups shown in wireframe format for clarity. Thermal ellipsoids set at the 30 % probability level. Key bond lengths (A) and angles (°): Si–$N_{imide}$ 1.590(2), Si–$N_{amidinate}$ 1.827(2), 1.829(2), Si–O 1.616(1), B–O 1.363(2), Si–N–Si 139.5(1), Si–O–B 149.1(1).

## Conclusions

To conclude, in this work we have shown that the reaction of boryl-substituted silylene {PhC($^t$BuN)$_2$}Si(boryl) (**1**-Si) with trimethylsilylazide accesses a reaction manifold connected by a series of Si(IV)-Si(II)-Si(IV) steps, involving formal oxidative and reductive ligand migration processes. Quantum chemical calculations indicate that the Si(IV) species (i.e. imidosilanes **2**-Si and **4**) and the Si(II) species (amidosilylene **3**-Si) are very similar in energetic terms (within 5 kcal mol$^{-1}$). The stability of the Si(IV) species can be related to the strong σ-donor properties of the silyl and boryl ligands, while the stabilization of **3**-Si is related to the π-donor capabilities of the amidinate scaffold and to the relief of steric crowding at silicon due to migration of the highly encumbered boryl group. Wider studies within group 14 imply that these redox shuttling capabilities are unique to silicon, with the related germanium and tin systems weighted thermodynamically towards the E(II) state. In a broader context, these findings highlight the potential for rational ligand design to enable reversible redox processes centred on main-group element compounds.

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**Supporting information**

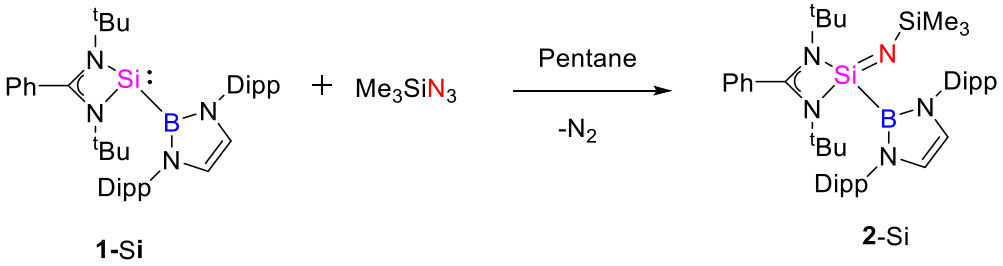
**General considerations**

All experiments were carried out under an atmosphere of dry argon or dinitrogen using standard Schlenk line and dry-box techniques. Solvents were degassed by sparging with argon and dried by passing through a column of appropriate drying agent using a commercially available Braun SPS and stored over potassium mirror under argon in a Teflon valve ampoule. NMR spectra were recorded in $d_6$-benzene or $d_8$-toluene, with the solvent being dried over calcium hydride or potassium respectively, distilled, degassed by three freeze-pump-thaw-cycles and stored over 3 Å sieves. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. NMR spectra were measured on Bruker Avance III HD nanobay 400 MHz, or Bruker Avance III 500 MHz, $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra referenced internally to residual protio-solvent ($^{1}H$) or solvent ($^{13}C$) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). $^{11}B$, $^{29}Si$ and $^{119}Sn$ spectra were referenced to external $BF_3{\cdot}Et_2O$, $SiMe_4$ and $SnMe_4$, respectively. Assignments were confirmed using two-dimensional $^{1}H$-$^{1}H$, $^{13}C$-$^{1}H$, $^{1}H$-$^{29}Si$ NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. The reported yields are the yields obtained after crystallisation and subsequent measurement of the material by single crystal-ray diffraction if not stated otherwise. Elemental analyses were carried out by London Metropolitan University or Elemental Microanalysis Ltd, Okehampton, Devon, UK.

**Preparation of starting materials**

**1**-Si and **1**-Sn were prepared according to methods reported in the primary literature.[S1]

**Synthetic procedures and characterising data for new compounds**




**1**-Si **2**-Si

**Scheme S1.** Synthesis of {PhC($^t$BuN)$_2$}{(HCDippN)$_2$B}SiN(SiMe$_3$), **2**-Si.

**{PhC($^t$BuN)$_2$}{(HCDippN)$_2$B}SiN(SiMe$_3$)**, **2**-Si

**1**-Si (200 mg, 0.31 mmol) was dissolved in pentane (30 mL) and $Me_3SiN_3$ (178.3 mg, 1.55 mmol) was added dropwise, leading to bubbling and a colour change from yellow to colourless. After 1 h the solution was concentrated to a third of its original volume, and colourless crystals of **2**-Si obtained on standing at -30 °C which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 × 5 mL).

Yield: 140 mg (0.19 mmol, 64.5 %).

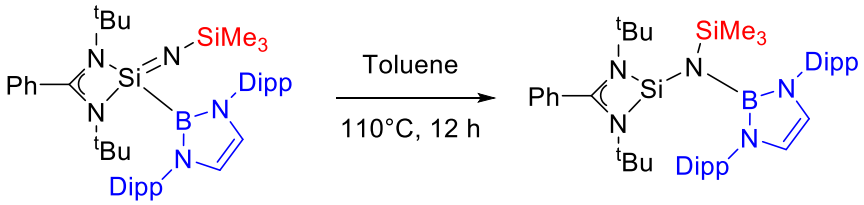
Elemental microanalysis: calc. for $C_{44}H_{68}BN_5Si_2$ (%): C 72.00 H 9.34 N 9.54; meas. C 72.37 H 9.07 N 8.97.

$^1$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 0.26 (s, 9H, SiMe$_3$), 1.04 (s, 18H, $^t$Bu), 1.23 (d, $^3J_{H,H}$ = 6.7 Hz, 12H, CH$_3$ of Dipp), 1.48 (d, $^3J_{H,H}$ = 6.9 Hz, 12H, CH$_3$ of Dipp), 3.34 (sept, $^3J_{H,H}$ = 6.8 Hz, 4H, C<u>H</u>(CH$_3$)$_2$ of Dipp), 6.28 (s, 2H, CH of boryl), 6.83, 6.92, 7.20 (m, 5H, ArH of Ph), 7.27-7.34 (m, 6H, ArH of Dipp).

$^{11}$B{$^1$H} NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 24.5.

$^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 6.5 (SiMe$_3$), 23.7, 26.7 (CH$_3$ of Dipp), 28.8 (<u>C</u>H(CH$_3$)$_2$ of Dipp), 31.8 (CH$_3$ of $^t$Bu), 53.8 (<u>C</u>CH$_3$ of $^t$Bu), 123.4 (CH of boryl), 123.6 (m-Ar of Dipp), 127.4 (p-Ar of Dipp), 127.5, 128.0, 128.4, 128.7, 130.0, 132.3 (Ph), 142.4 (CN of Dipp), 145.9 (o-Ar of Dipp), 174.8 (NCN of backbone).

$^{29}$Si{$^1$H} NMR (99 MHz, $C_6D_6$, 298 K): $\delta_{Si}$ -23.3 (s, SiMe$_3$), -49.3 (br, Si=N).




**2**-Si **3**-Si

**Scheme S2.** Synthesis of {PhC($^t$BuN)$_2$}SiN{B(NDippCH)$_2$}(SiMe$_3$), **3**-Si.

**{PhC($^t$BuN)$_2$}SiN{B(NDippCH)$_2$}(SiMe$_3$)**, **3**-Si

**2**-Si (200 mg, 0.27 mmol) was dissolved in toluene (10 mL) and stirred for 12 h at 110 °C. The reaction mixture was concentrated (to ca. 1 mL) and yellow crystals of **3**-Si obtained on standing at room temperature which were suitable for X-ray crystallography. These were isolated by filtration, washed twice with cold pentane (2 x 0.5 mL) and dried under vacuum.

Yield: 100 mg (0.14 mmol, 50.0 %).

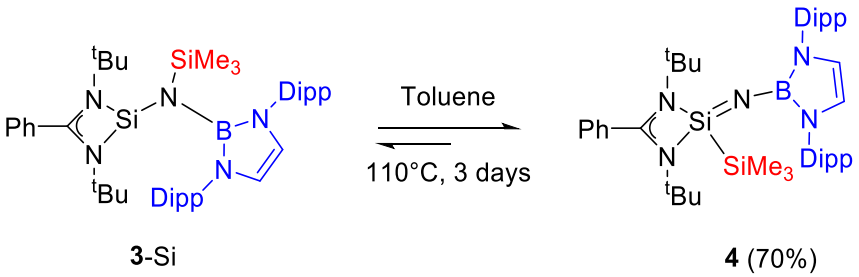
Elemental microanalysis: calc. for $C_{44}H_{68}BN_5Si_2$ (%): C 72.00 H 9.34 N 9.54; meas. C 71.15 H 9.08 N 9.54.

$^1$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 0.33 (s, 9H, SiMe$_3$), 0.88 (s, 18H, $^t$Bu), 1.33-1.74 (br, 24H, CH$_3$ of Dipp), 3.89 (br, 4H, C<u>H</u>(CH$_3$)$_2$ of Dipp), 6.16 (s, 2H, CH of boryl), 6.87, 7.13 (m, 5H, ArH of Ph), 7.26 (br, 6H, ArH of Dipp).

$^{11}$B{$^1$H} NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 26.1.

$^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 6.2 (SiMe$_3$), 23.1, 27.1 (CH$_3$ of Dipp), 28.4, 29.6 (<u>C</u>H(CH$_3$)$_2$ of Dipp), 32.2 (CH$_3$ of $^t$Bu), 53.7 (<u>C</u>CH$_3$ of $^t$Bu), 119.9 (CH of boryl), 123.9 (m-Ar of Dipp), 127.4 (p-Ar of Dipp), 127.6, 128.0, 128.4, 129.1, 130.7, 135.2 (Ph), 141.5 (CN of Dipp), 147.0, 148.7 (o-Ar of Dipp), 159.9 (NCN of backbone).

$^{29}$Si{$^1$H} NMR (99 MHz, $C_6D_6$, 298 K): $\delta_{Si}$ -0.1 (s, SiMe$_3$), -11.4 (s, silylene).




**3**-Si **4** (70%)

**Scheme S3.** Synthesis of {PhC($^t$BuN)$_2$}(Me$_3$Si)SiN{B(NDippCH)$_2$}, **4**.

**{PhC($^t$BuN)$_2$}(Me$_3$Si)SiN{B(NDippCH)$_2$}**, **4**

**3**-Si (100 mg, 0.14 mmol) was dissolved in toluene (5 mL) and stirred for 3 d at 110 °C. Volatiles were removed under vacuum, and the residue was extracted with pentane (10 mL). The resulting solution was concentrated to half of its original volume and stored at –30 °C, leading to the formation of light green crystals of **4,** suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 1 mL).

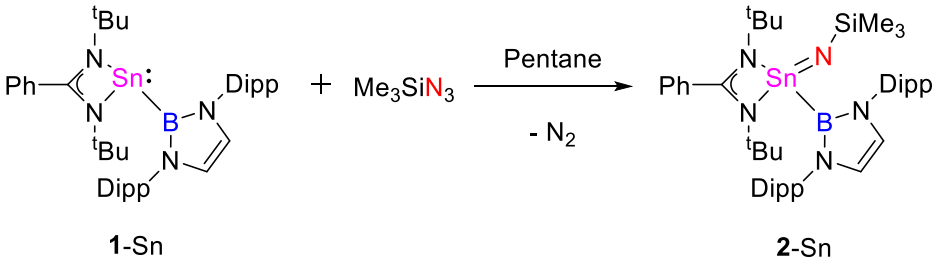
Yield: 24 mg (0.03 mmol, 24.0 %).

$^1$H NMR (400 MHz, $C_6D_6$, 298 K): $\delta_H$ 0.22 (s, 9H, SiMe$_3$), 0.78 (s, 18H, $^t$Bu), 1.45 (d, $^3J_{H,H}$ = 6.7 Hz, 12H, CH$_3$ of Dipp), 1.53 (d, $^3J_{H,H}$ = 6.7 Hz, 12H, CH$_3$ of Dipp), 3.86 (sept, $^3J_{H,H}$ = 6.7 Hz, 4H, C<u>H</u>(CH$_3$)$_2$ of Dipp), 6.21 (s, 2H, CH of boryl), 6.79, 6.90, 7.20 (m, 5H, ArH of Ph), 7.27 (m, 6H, ArH of Dipp).

$^{11}$B{$^1$H} NMR (128 MHz, $C_6D_6$, 298 K): $\delta_B$ 22.0.

$^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 0.1 (TMS), 24.5, 25.1 (CH$_3$ of Dipp), 28.7 (<u>C</u>H(CH$_3$)$_2$ of Dipp), 31.6 (CH$_3$ of $^t$Bu), 53.4 (<u>C</u>CH$_3$ of $^t$Bu), 117.2 (CH of boryl), 123.2 (m-Ar of Dipp), 125.8 (p-Ar of Dipp), 128.0, 128.4, 128.5, 128.6, 130.1, 131.6 (Ph), 143.9 (CN of Dipp), 147.5 (o-Ar of Dipp), 171.5 (NCN of backbone).

$^{29}$Si{$^1$H} NMR (99 MHz, $C_6D_6$, 298 K): $\delta_{Si}$ -24.6 (s, TMS), -57.6 (s, Si=N).




**Scheme S4.** Synthesis of {PhC($^t$BuN)$_2$}{(HCDippN)$_2$B}SnN(SiMe$_3$), **2**-Sn.

**{PhC($^t$BuN)$_2$}{(HCDippN)$_2$B}SnN(SiMe$_3$)**, **2**-Sn

**1**-Sn (200 mg, 0.24 mmol) was dissolved in pentane (10 mL) and $Me_3SiN_3$ (138.1 mg, 1.20 mmol) was added dropwise, leading to bubbling and a colour change from orange to colourless. Colourless crystals of **2**-Sn suitable for X-ray crystallography were obtained on standing at room temperature. These were filtered and washed with cold pentane (2 x 5 mL).

The solubility of **2**-Sn is low in toluene at –30 °C and it is not stable in THF at room temperature.

Yield: 100 mg (0.12 mmol, 50.0 %).

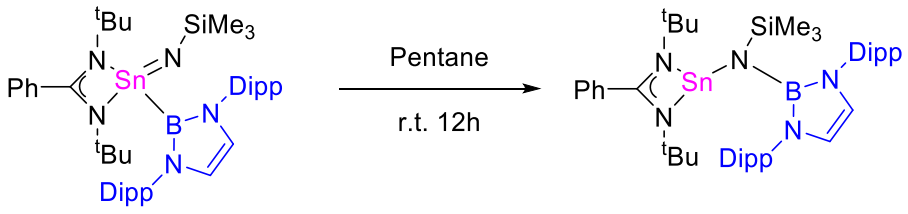
Elemental microanalysis: calc. for $C_{44}H_{68}BN_5SiSn$ (%): C 64.08 H 8.31 N 8.49; meas. C 64.08 H 8.28 N 7.89.

$^1$H NMR (400 MHz, $C_6D_6$, 298 K): $\delta_H$ 0.63 (s, 9H, SiMe$_3$), 0.69 (s, 18H, $^t$Bu), 1.21 (d, $^3J_{H,H}$ = 6.7 Hz, 12H, CH$_3$ of Dipp), 1.51 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, CH$_3$ of Dipp), 3.46 (sept, $^3J_{H,H}$ = 6.7 Hz, 4H, C<u>H</u>(CH$_3$)$_2$ of Dipp), 6.34 (s, 2H, CH of boryl), 6.88, 6.92, 6.96, 7.07, 7.22, 7.36 (m, 11H, ArH).

$^{11}$B{$^1$H} NMR (128 MHz, $C_6D_6$, 298 K): $\delta_B$ 30.8.

$^{13}$C{$^1$H} NMR (126 MHz, d$_8$-toluene, 223 K): $\delta_C$ 8.1 (SiMe$_3$), 24.8, 26.2 (CH$_3$ of Dipp), 29.2 (<u>C</u>H(CH$_3$)$_2$ of Dipp), 32.7 (CH$_3$ of $^t$Bu), 53.4 (<u>C</u>CH$_3$ of $^t$Bu), 124.5 (CH of boryl), 146.8 (o-Ar of Dipp). * Other Ar peaks obscured by d$_8$-toluene signals; N<u>C</u>N signal of backbone not observed because of low solubility

$^{119}$Sn{$^1$H} NMR: not observed.




**2**-Sn **3**-Sn

**Scheme S5.** Synthesis of {PhC($^t$BuN)$_2$}SnN{B(NDippCH)$_2$}(SiMe$_3$), **3**-Sn.

**{PhC($^t$BuN)$_2$}SnN{B(NDippCH)$_2$}(SiMe$_3$)**, **3**-Sn.

A solution of **2**-Sn (100 mg, 0.12 mmol) in pentane (20 mL) was stirred for 12 h at room temperature. The reaction mixture was slowly concentrated (to ca. 0.5 mL) and colourless crystals of **3**-Sn were obtained on standing at room temperature which were suitable for X-ray crystallography. These were isolated by filtration and washed with cold pentane (2 x 0.5 mL).

Yield: 43 mg (0.05 mmol, 43.0 %).

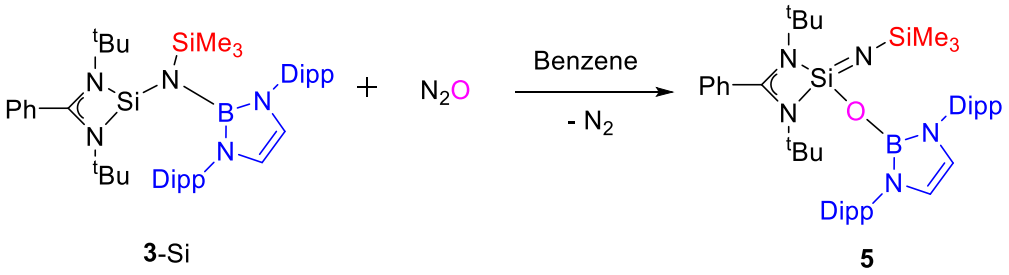
Elemental microanalysis: calc. for $C_{44}H_{68}BN_5SiSn$ (%): C 64.08 H 8.31 N 8.49; meas. C 64.09 H 8.09 N 8.15.

$^1$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 0.28 (s, 9H, SiMe$_3$), 0.84 (s, 18H, $^t$Bu), 1.31 (d, $^3J_{H,H}$ = 6.5 Hz, 12H, CH$_3$ of Dipp), 1.50 (br, 12H, CH$_3$ of Dipp), 3.77 (br, 4H, C<u>H</u>(CH$_3$)$_2$ of Dipp), 6.16 (s, 2H, CH of boryl), 6.89, 6.95, 7.19 (m, 5H, ArH of Ph), 7.24 (m, 6H, ArH of Dipp).* $\delta_H$ 0.30 (silicone grease).

$^{11}$B{$^1$H} NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 25.4.

$^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 5.2 (SiMe$_3$), 23.4, 26.4 (CH$_3$ of Dipp), 28.7 (br, <u>C</u>H(CH$_3$)$_2$ of Dipp), 33.0 (CH$_3$ of $^t$Bu), 52.6 (<u>C</u>CH$_3$ of $^t$Bu), 119.6 (CH of boryl), 123.8 (br, m-Ar of Dipp), 127.4 (p-Ar of Dipp), 126.8, 127.3, 128.4, 128.9, 129.5, 138.6 (Ph), 141.5 (CN of Dipp), 147.1 (o-Ar of Dipp), 168.3 (NCN of backbone).

$^{119}$Sn{$^1$H} NMR (187 MHz, $C_6D_6$, 298 K): $\delta_{Sn}$ -50.0 (br).




**Scheme S6.** Synthesis of {PhC($^t$BuN)$_2$}SnN{B(NDippCH)$_2$}(SiMe$_3$), **5**.

**{PhC($^t$BuN)$_2$}{(HCDippN)$_2$BO}SiN(SiMe$_3$)**, **5**. A solution of **3**-Si (20 mg, 0.03 mmol) in benzene was degassed by the freeze-pump-thaw before $N_2O$ was admitted (at ca. 1 atm pressure), leading to a colour change from yellow to colourless. Volatiles were removed under vacuum, and pentane (0.5 mL) was added. Crystals of **5** were obtained on standing at room temperature which were suitable for X-ray crystallography.

Yield: 5 mg (0.007 mmol, 24.5 %).

Elemental microanalysis: calc. for $C_{44}H_{68}BN_5OSi_2$ (%): C 70.46 H 9.14 N 9.34; meas. C 70.52 H 9.18 N 9.17.

$^1$H NMR (500 MHz, $C_6D_6$, 298 K): $\delta_H$ 0.54 (s, 9H, SiMe$_3$), 0.71 (s, 18H, $^t$Bu), 1.31 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, CH$_3$ of Dipp), 1.57 (d, $^3J_{H,H}$ = 6.8 Hz, 12H, CH$_3$ of Dipp), 3.61 (sept, $^3J_{H,H}$ = 6.8 Hz, 4H, C<u>H</u>(CH$_3$)$_2$ of Dipp), 6.04 (s, 2H, CH of boryl), 6.78, 6.84, 6.93 (m, 5H, ArH of Ph), 7.19 (m, 6H, ArH of Dipp).

$^{11}$B{$^1$H} NMR (160 MHz, $C_6D_6$, 298 K): $\delta_B$ 21.2.

$^{13}$C{$^1$H} NMR (126 MHz, $C_6D_6$, 298 K): $\delta_C$ 6.3 (SiMe$_3$), 24.6, 25.2 (CH$_3$ of Dipp), 28.8 (<u>C</u>H(CH$_3$)$_2$ of Dipp), 30.8 (CH$_3$ of $^t$Bu), 53.7 (<u>C</u>CH$_3$ of $^t$Bu), 117.6 (CH of boryl), 123.8 (m-Ar of Dipp), 127.5 (p-Ar of Dipp), 128.0, 128.2, 128.4, 130.2, 130.7(Ph), 139.6 (CN of Dipp), 147.5 (o-Ar of Dipp), 175.9 (NCN of backbone).

$^{29}$Si{$^1$H} NMR (99 MHz, $C_6D_6$, 298 K): $\delta_{Si}$ -21.7 (s, SiMe$_3$), -82.7 (s, Si=N).

## Representative NMR spectra for new compounds

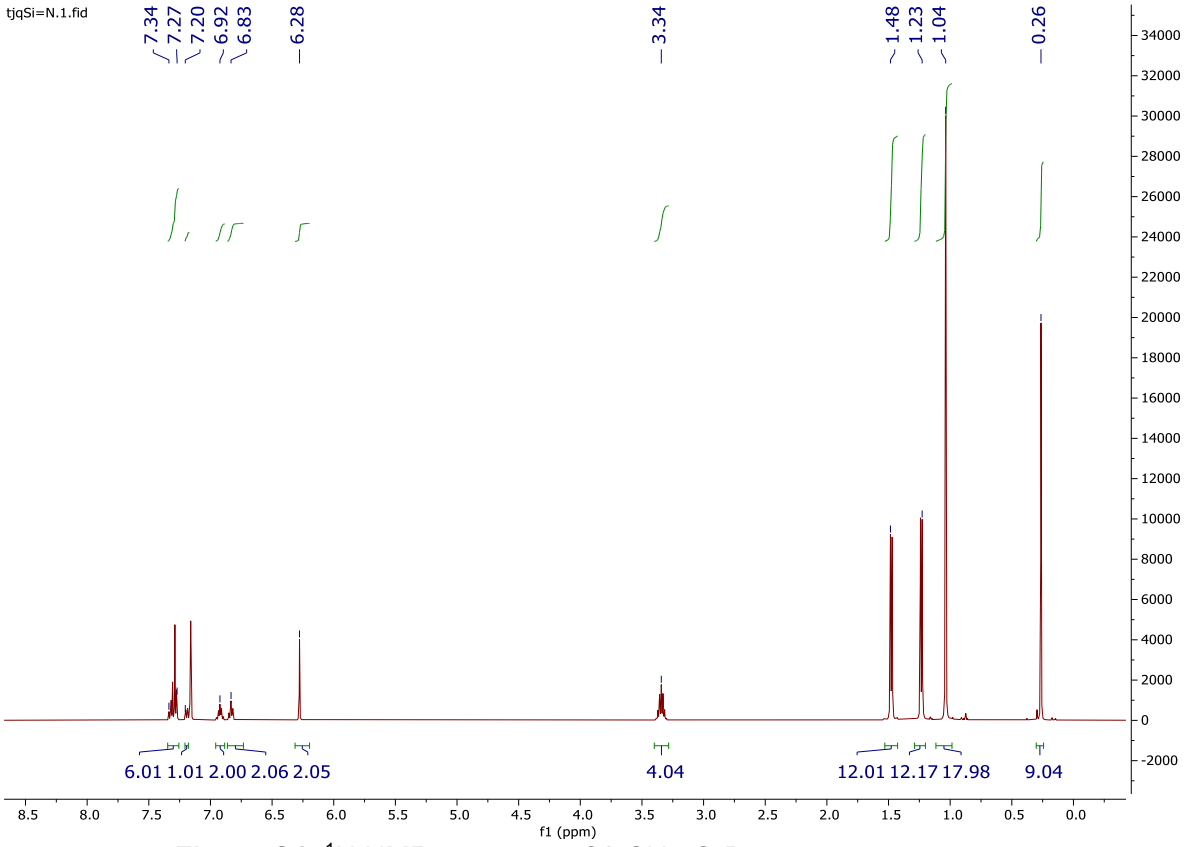



**Figure S1**: $^{1}H$ NMR spectrum of **2**-Si in $C_6D_6$ at room temperature.

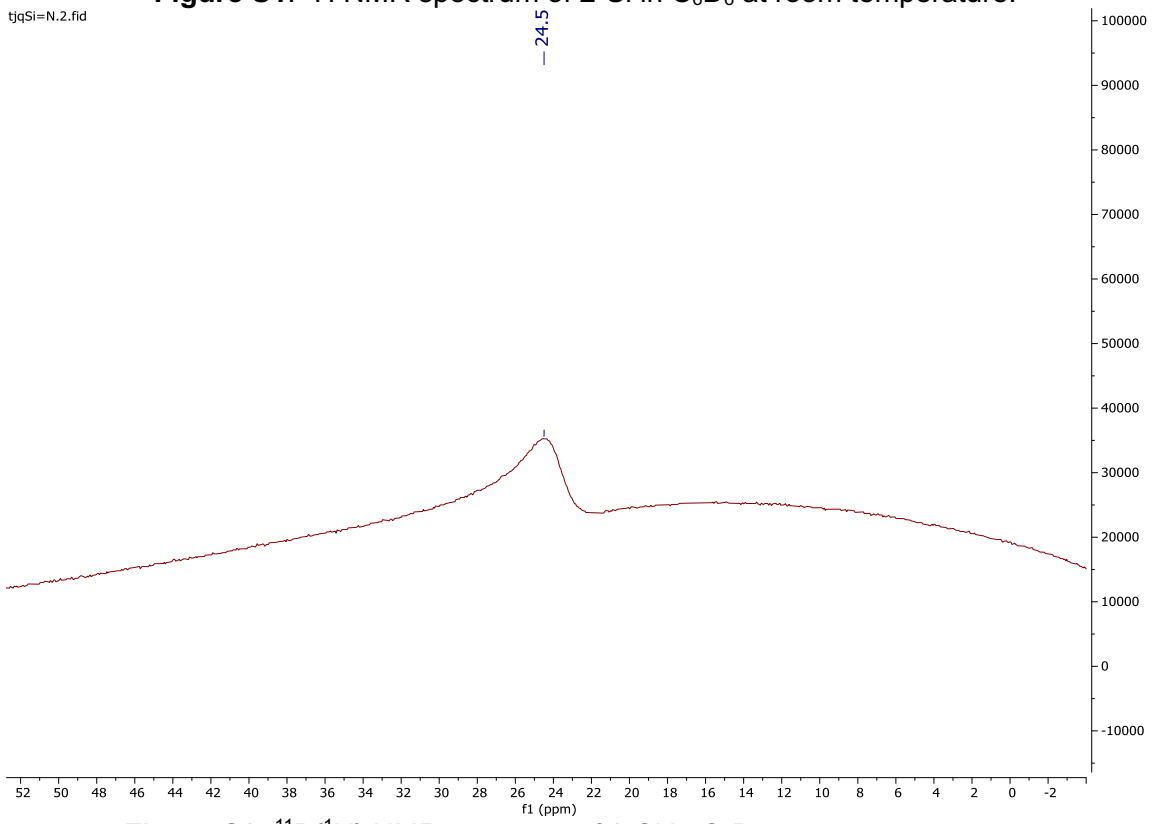



**Figure S2**: $^{11}B\{^{1}H\}$ NMR spectrum of **2**-Si in $C_6D_6$ at room temperature.

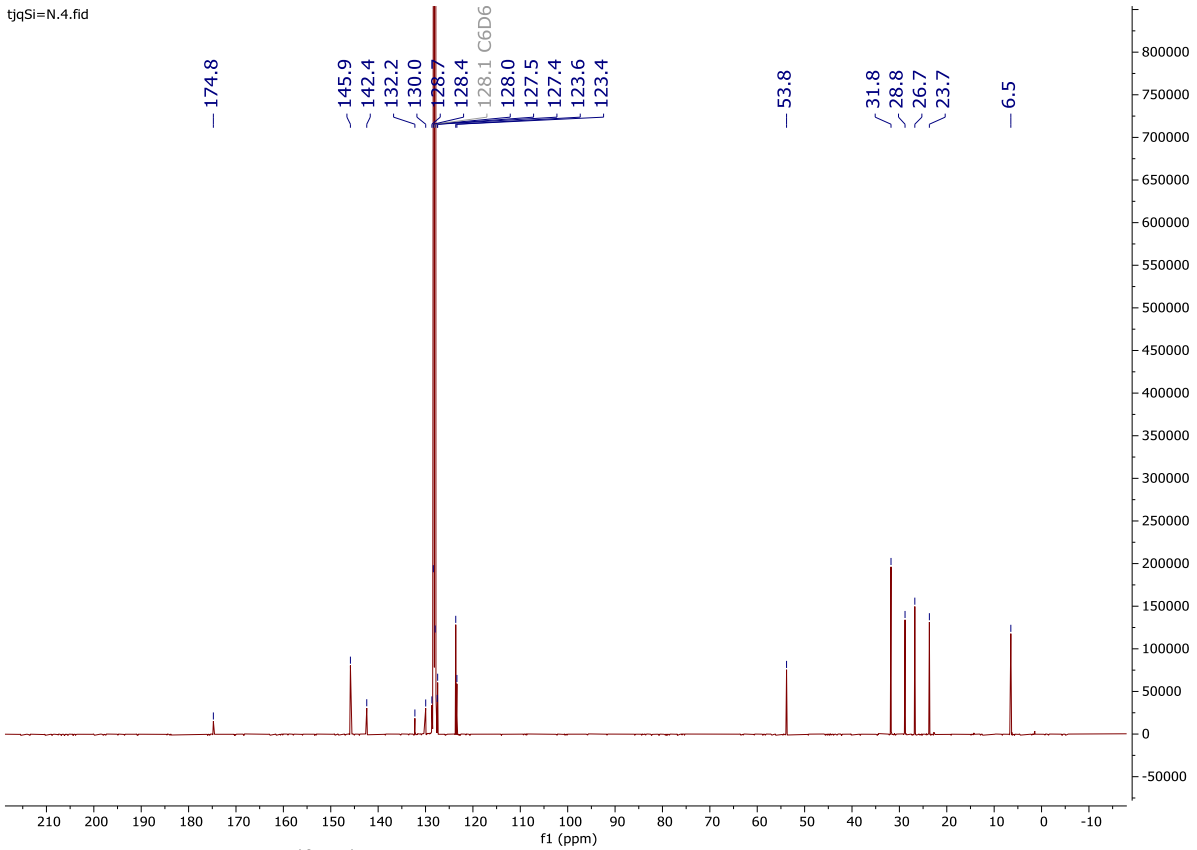



**Figure S3**: $^{13}C\{^{1}H\}$ NMR spectrum of **2**-Si in $C_6D_6$ at room temperature.

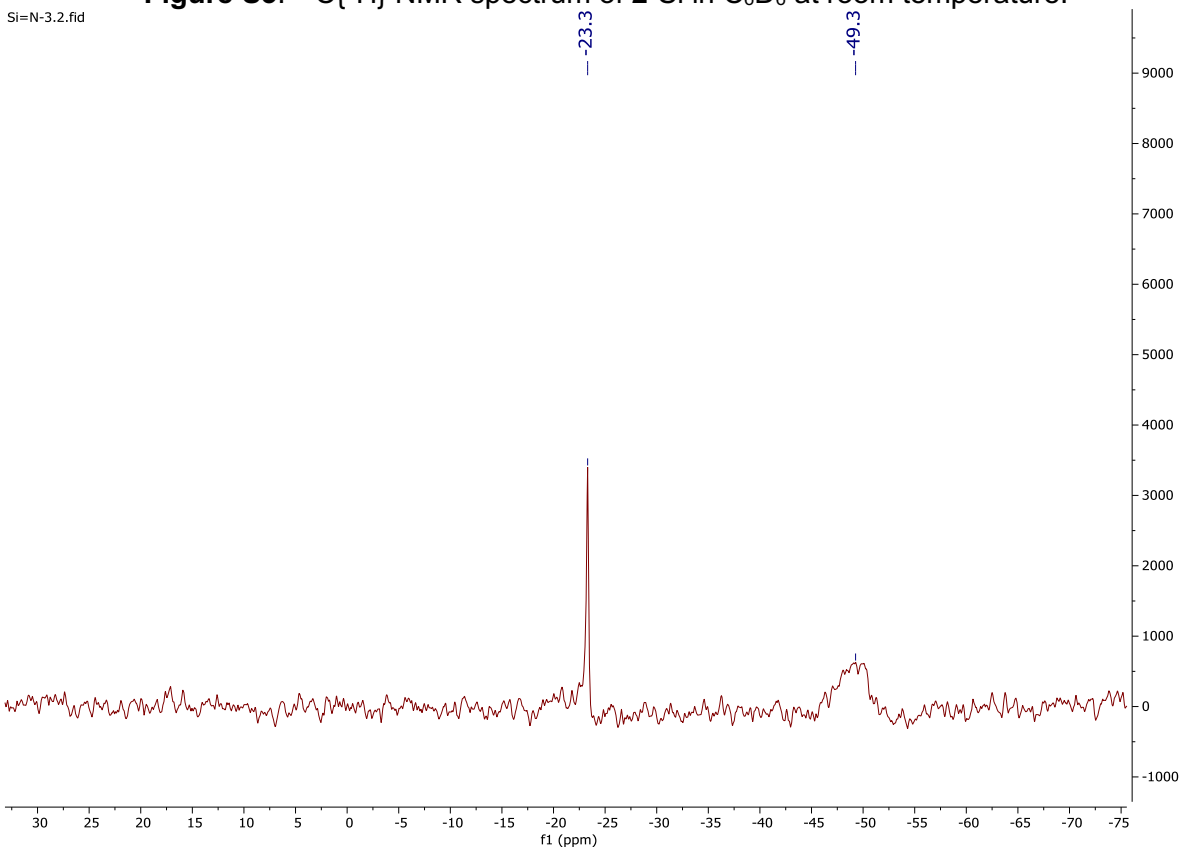



**Figure S4**: $^{29}Si\{^{1}H\}$ NMR spectrum of **2**-Si in $C_6D_6$ at room temperature.

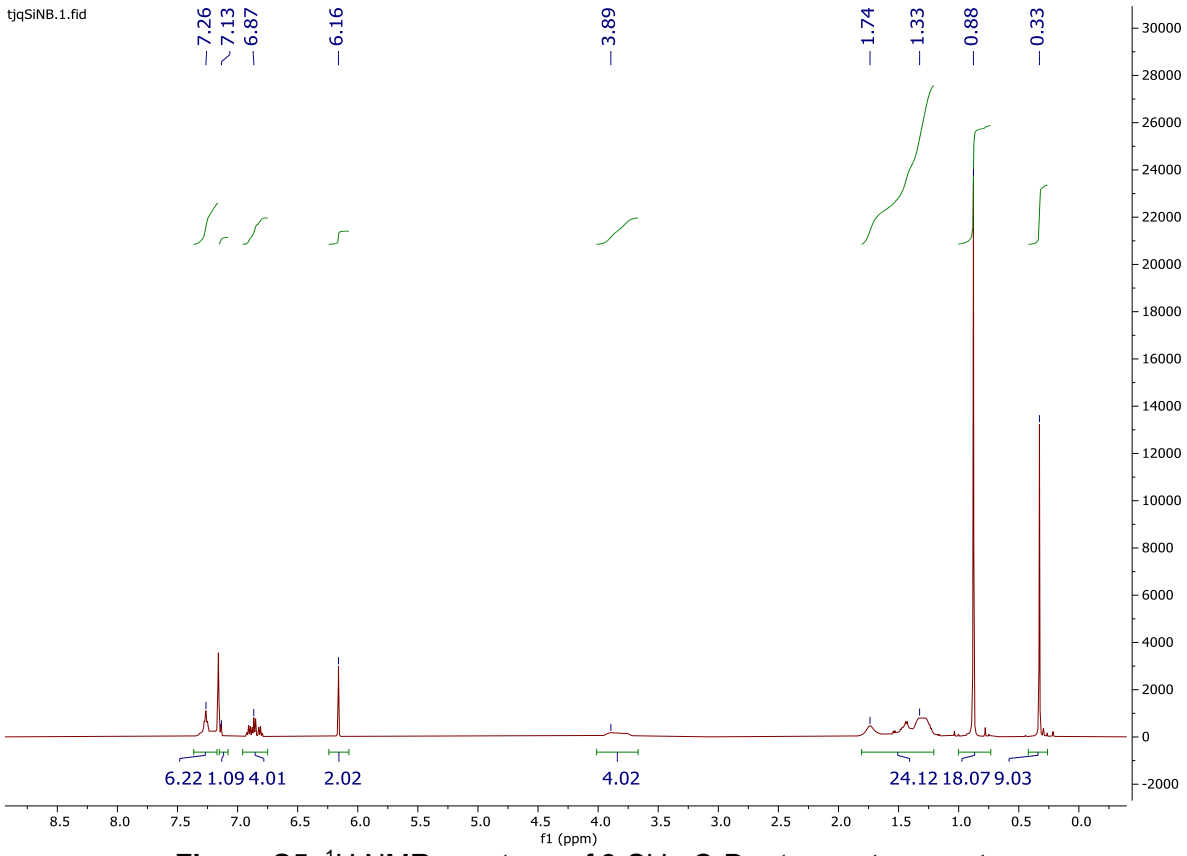



**Figure S5**: $^{1}$H NMR spectrum of **3**-Si in $C_6D_6$ at room temperature.

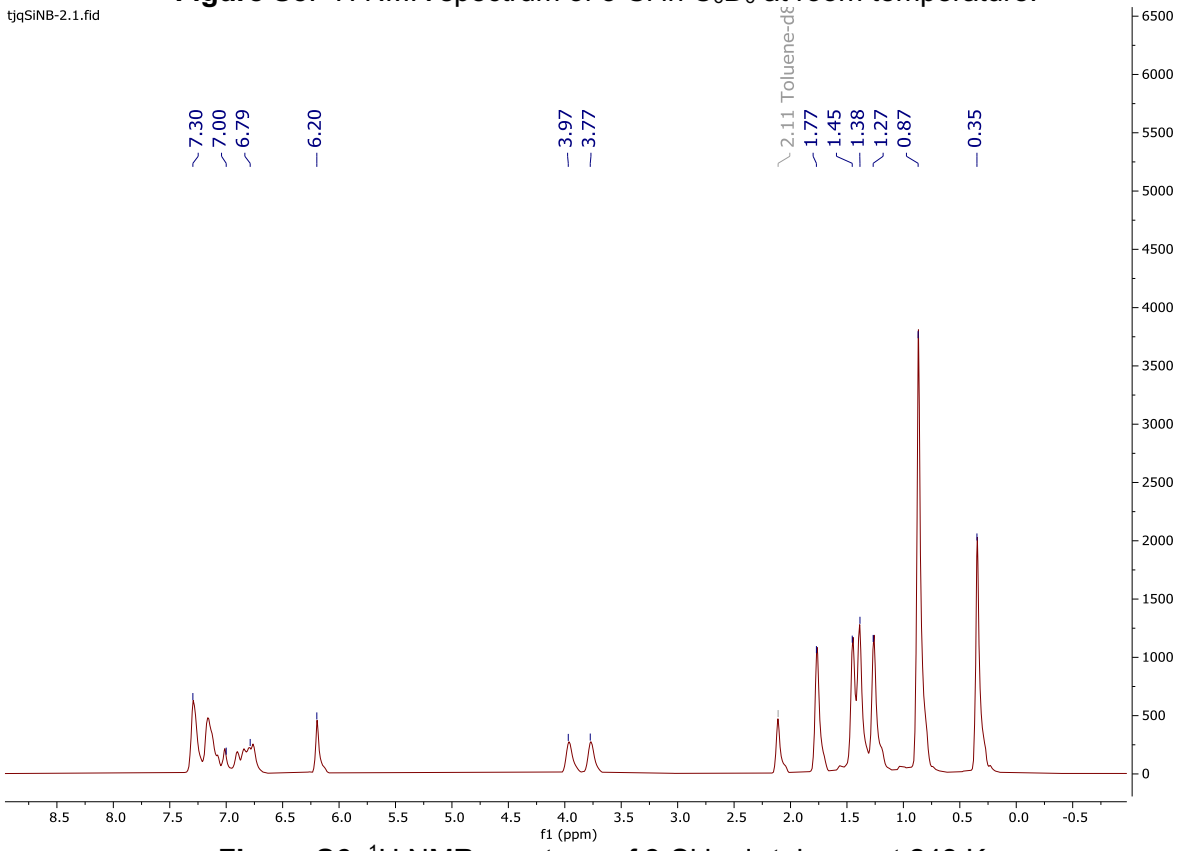



**Figure S6**: $^{1}$H NMR spectrum of **3**-Si in $d_8$-toluene at 243 K.

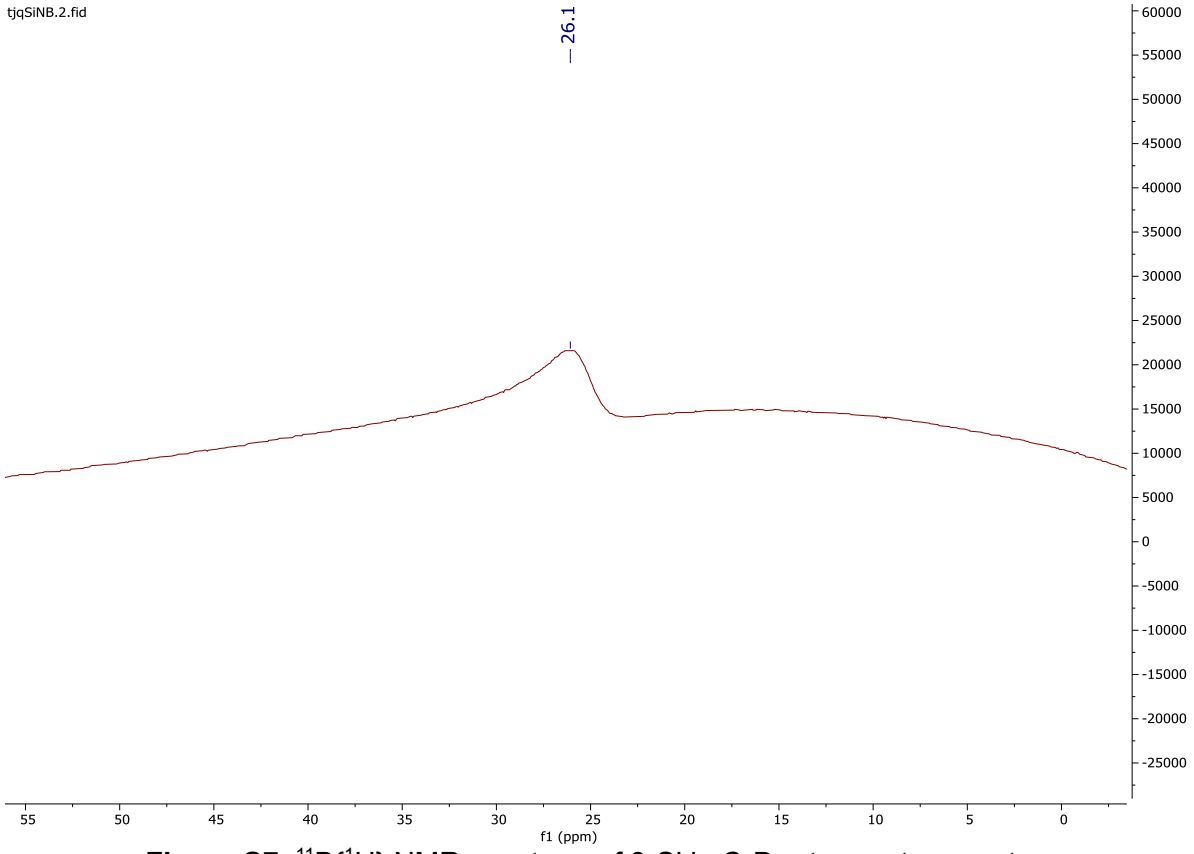



**Figure S7**: $^{11}B\{^{1}H\}$ NMR spectrum of **3**-Si in $C_6D_6$ at room temperature.

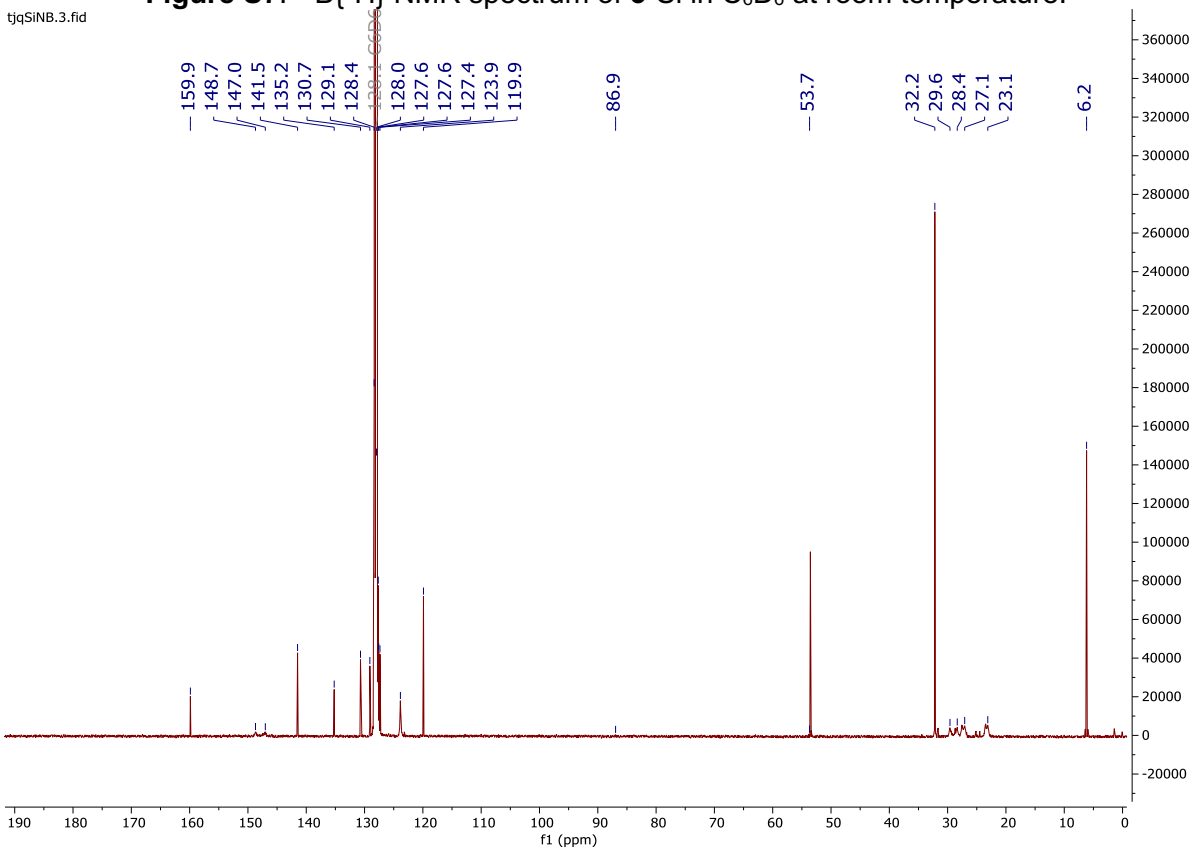



**Figure S8**: $^{13}C\{^{1}H\}$ NMR spectrum of **3**-Si in $C_6D_6$ at room temperature.

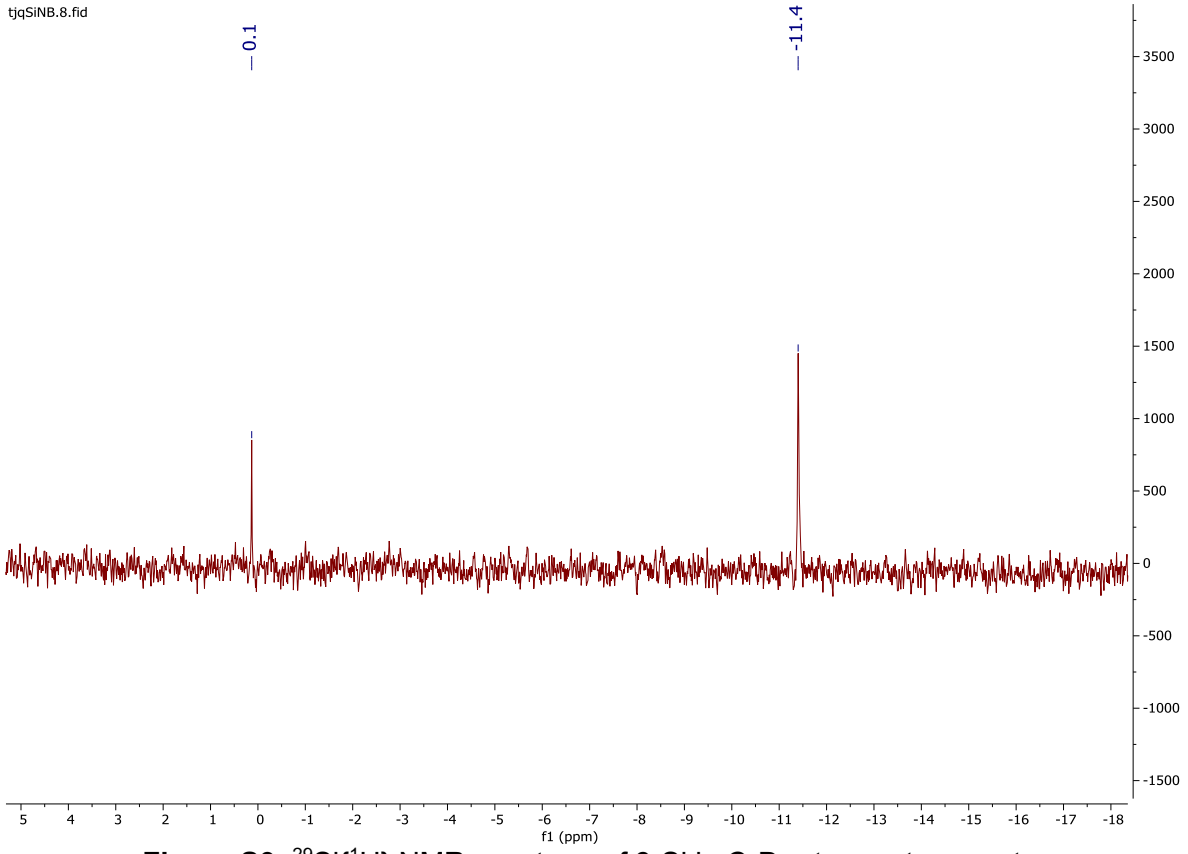



**Figure S9**: $^{29}Si\{^{1}H\}$ NMR spectrum of **3**-Si in $C_6D_6$ at room temperature.

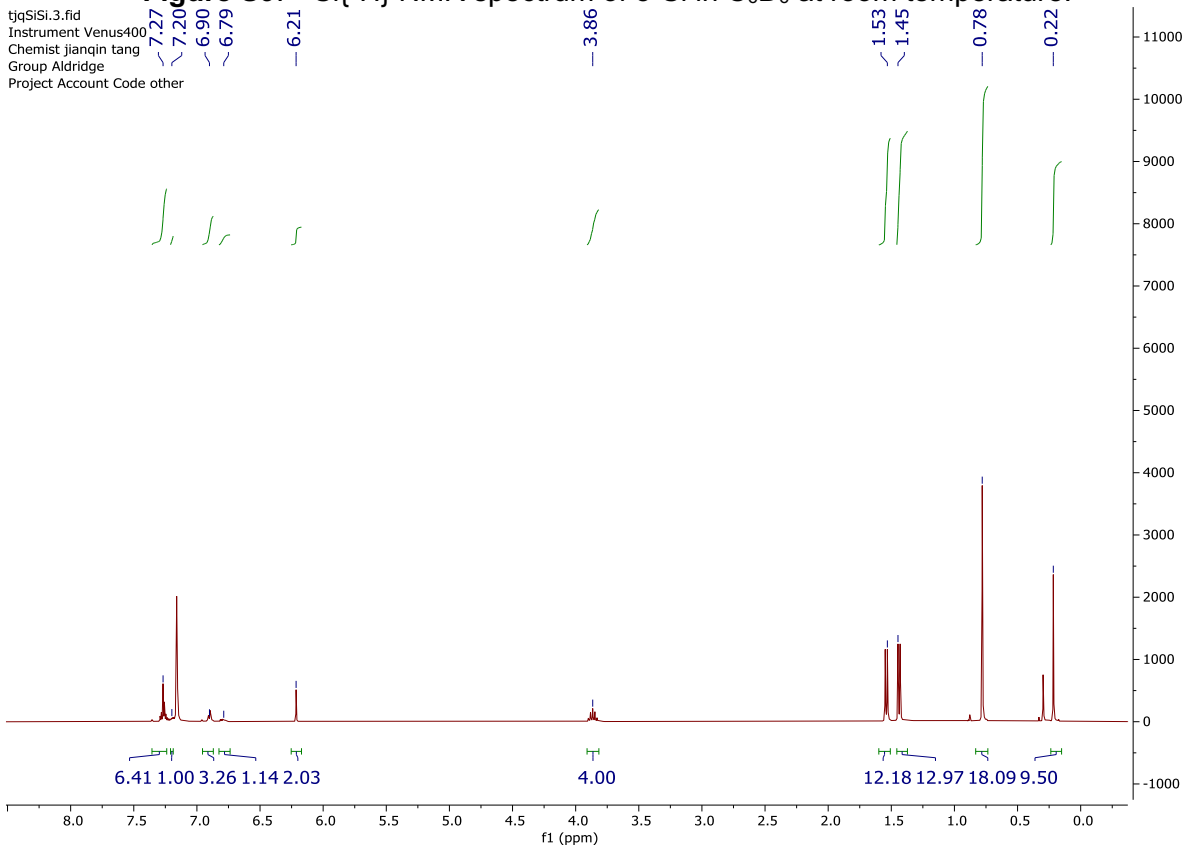



**Figure S10**: $^{1}H$ NMR spectrum of **4** in $C_6D_6$ at room temperature.

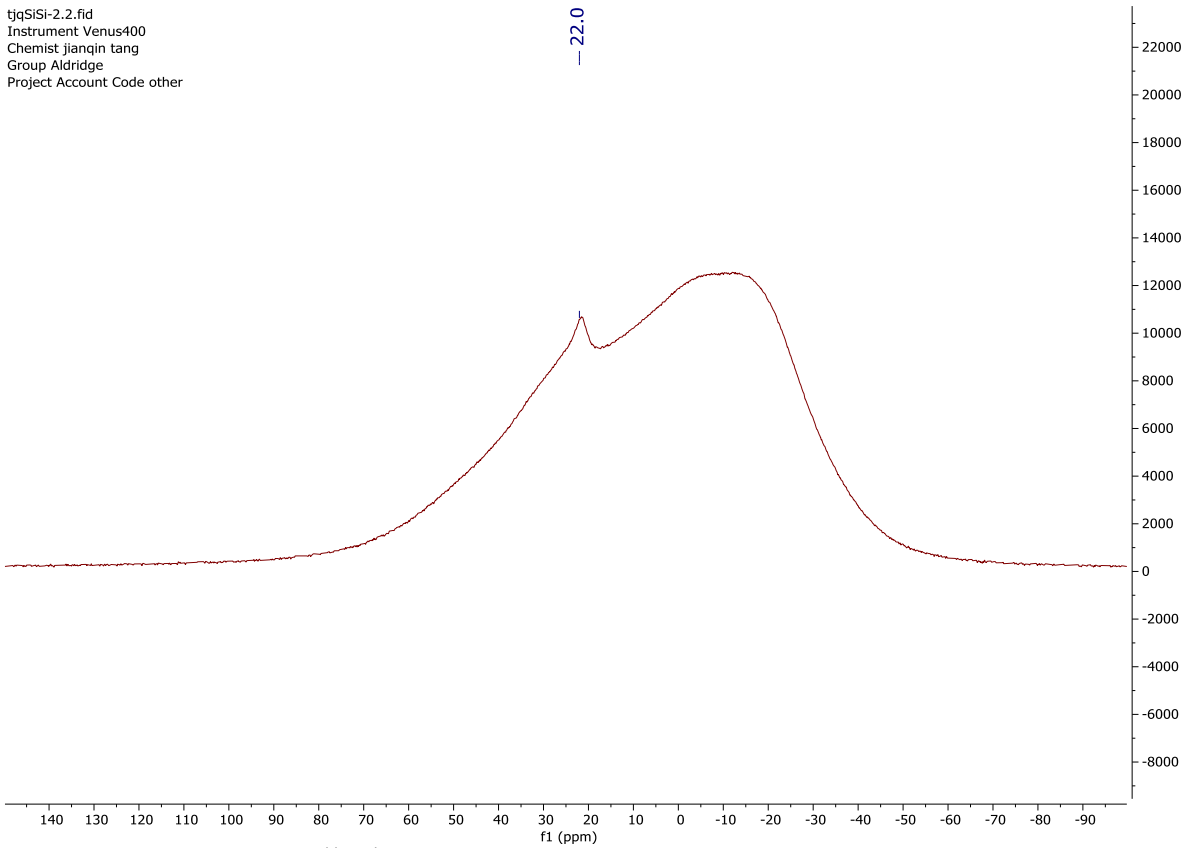



**Figure S11**: $^{11}B\{^{1}H\}$ NMR spectrum of **4** in $C_6D_6$ at room temperature.

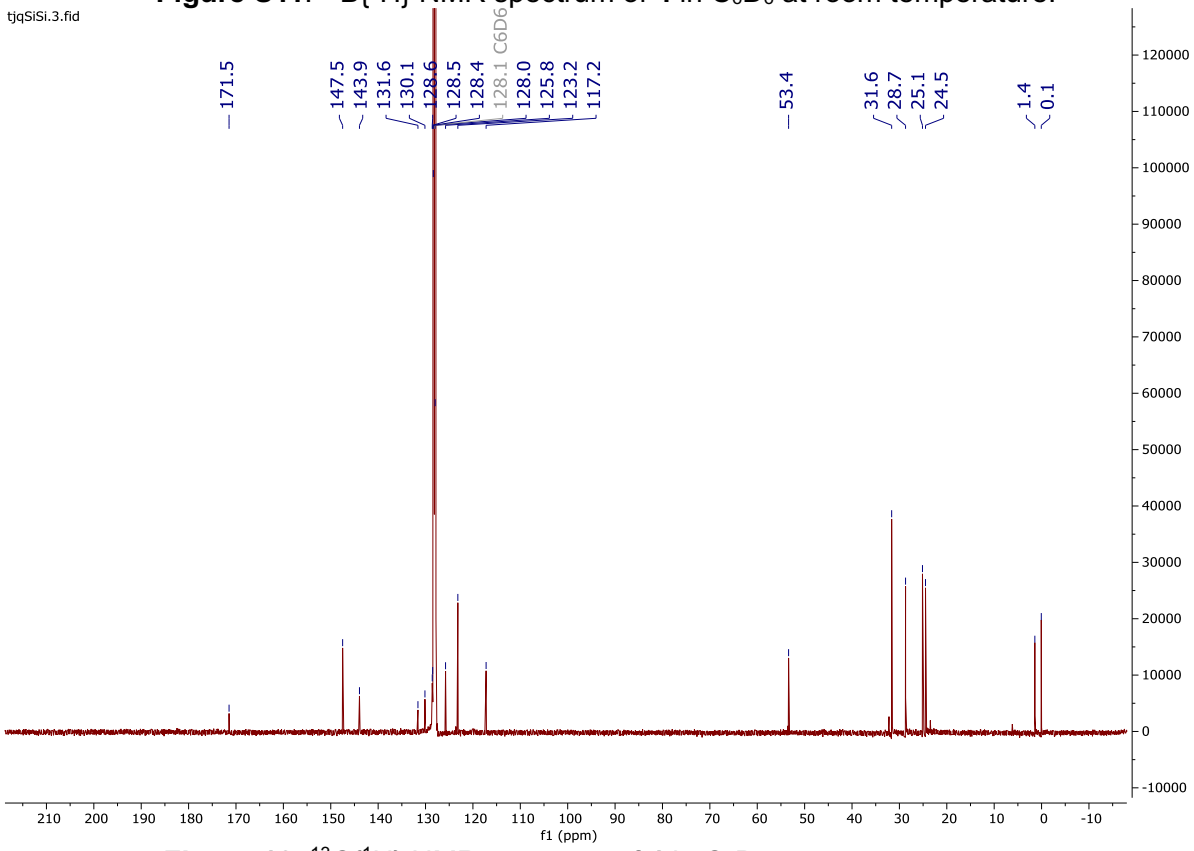



**Figure 12**: $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $C_6D_6$ at room temperature.

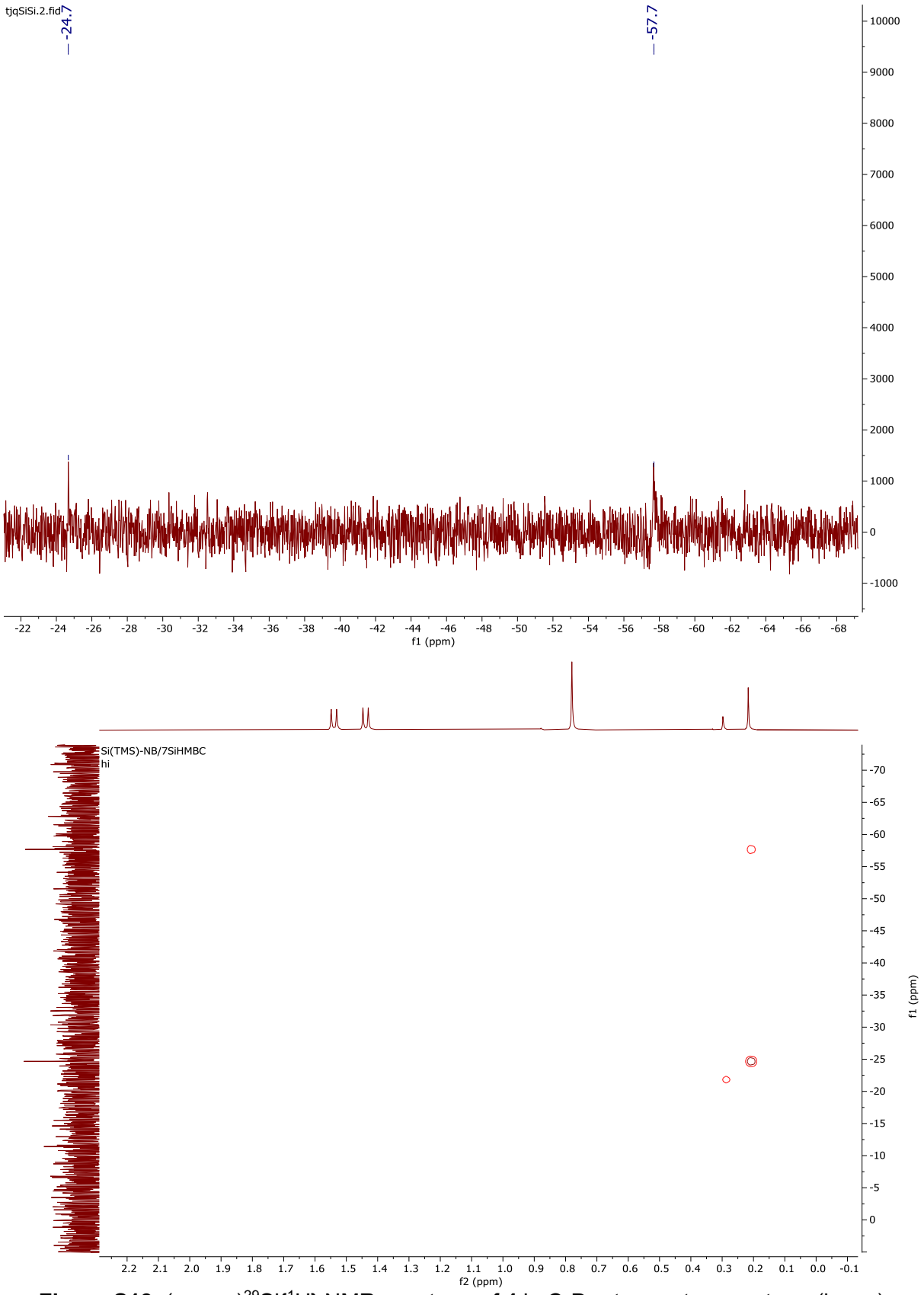



**Figure S13**: (upper )$^{29}$Si{$^{1}$H} NMR spectrum of **4** in $C_6D_6$ at room temperature; (lower) $^{1}$H/$^{29}$Si HMBC NMR spectrum of **4** in $C_6D_6$ at room temperature.

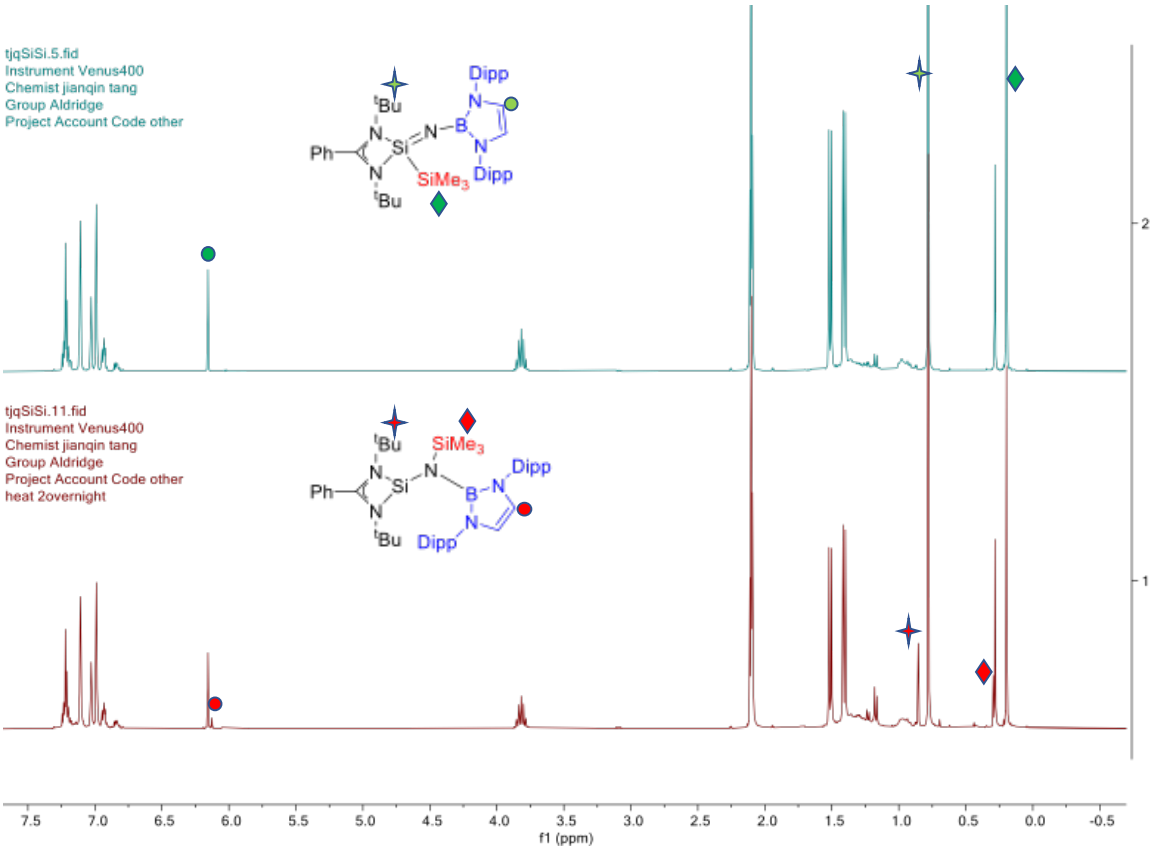



**Figure S14**:[1]H NMR spectra showing the re-equilibration of **4** (upper) into a mixture containing **4** and **3**-Si on heating in $C_7D_8$ (12 h, 110 °C).

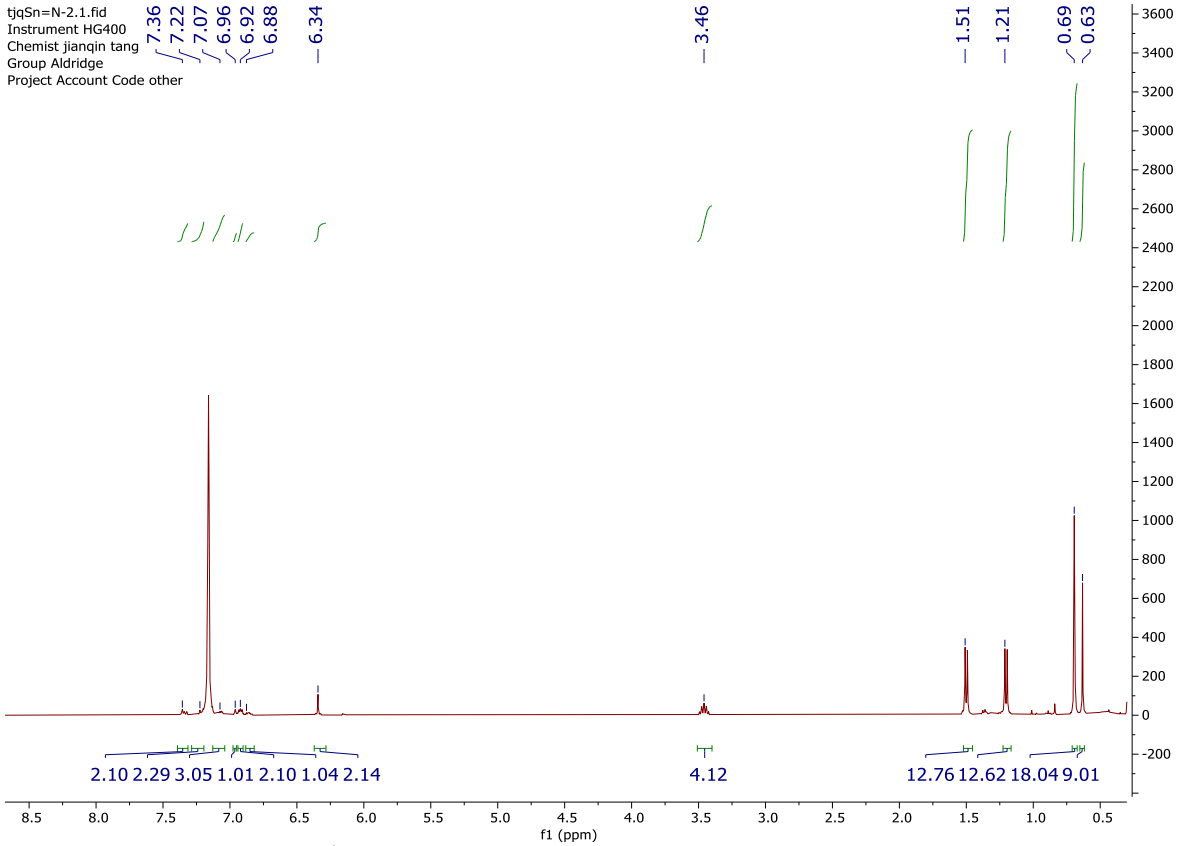



**Figure S15**: $^{1}$H NMR spectrum of **2**-Sn in $C_6D_6$ at room temperature.

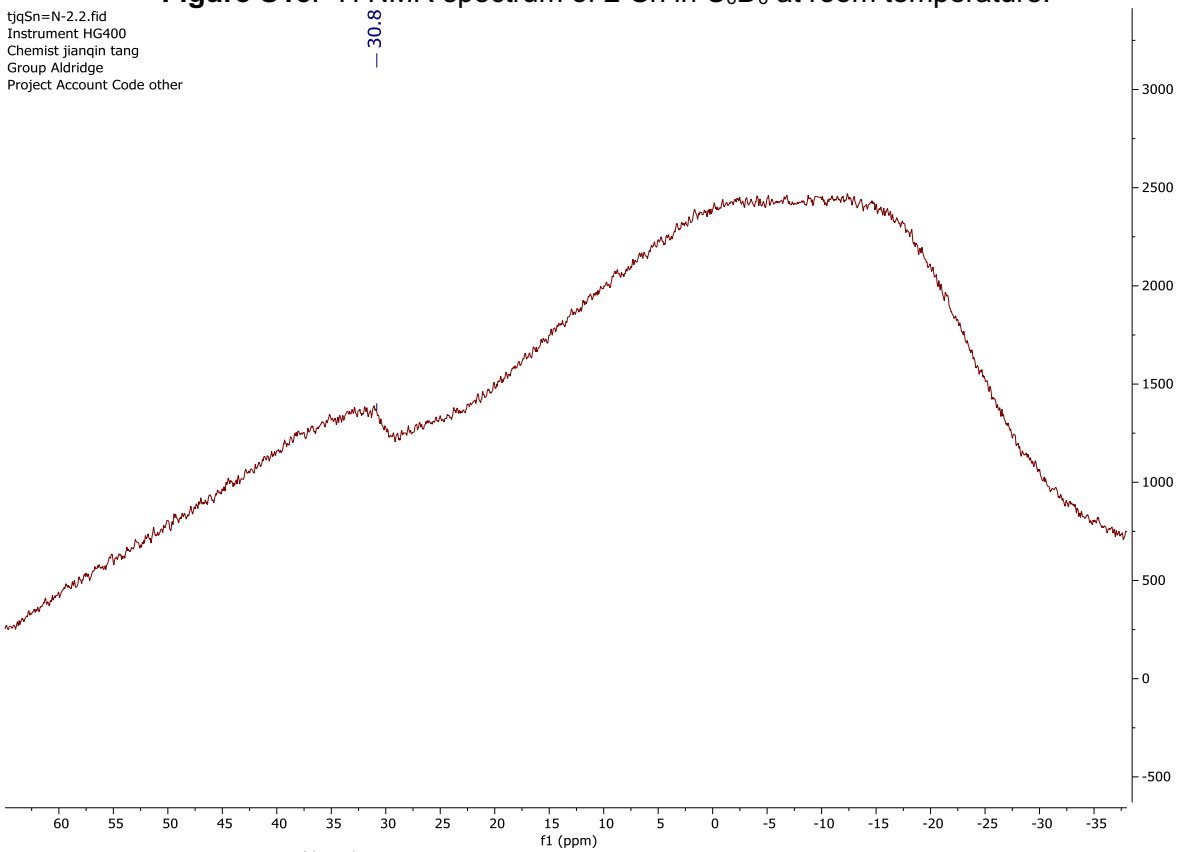



**Figure S16**: $^{11}$B{$^{1}$H} NMR spectrum of **2**-Sn in $C_6D_6$ at room temperature.

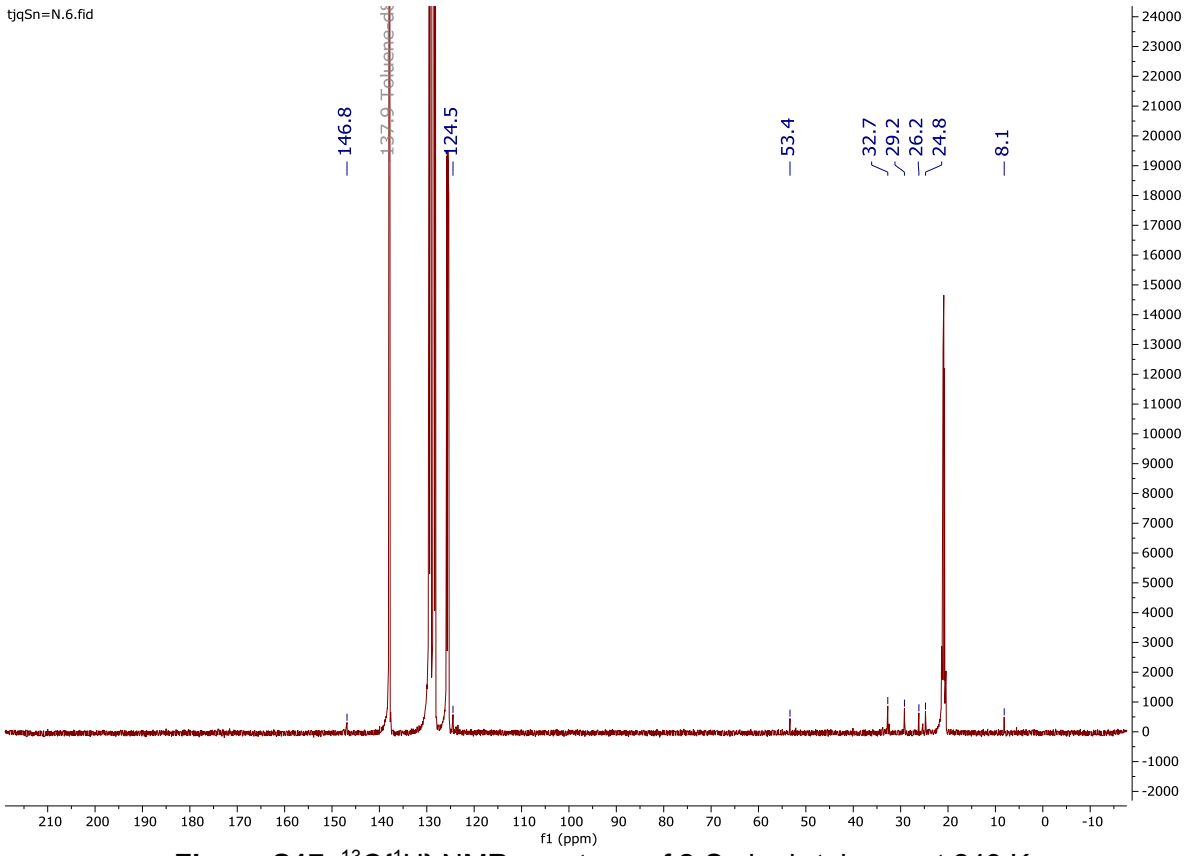



**Figure S17**: $^{13}C\{^{1}H\}$ NMR spectrum of **2**-Sn in $d_8$-toluene at 243 K.

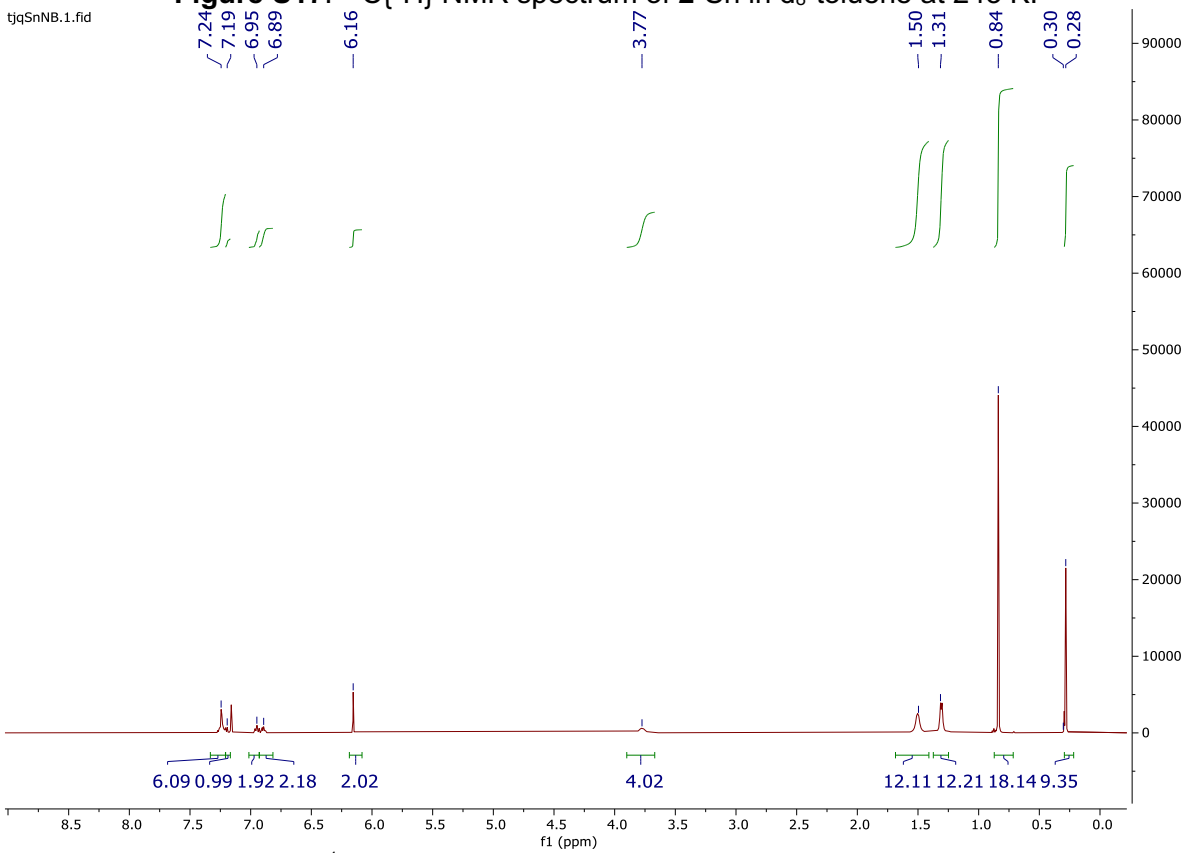



**Figure S18**: $^{1}H$ NMR spectrum of **3**-Sn in $C_6D_6$ at room temperature.

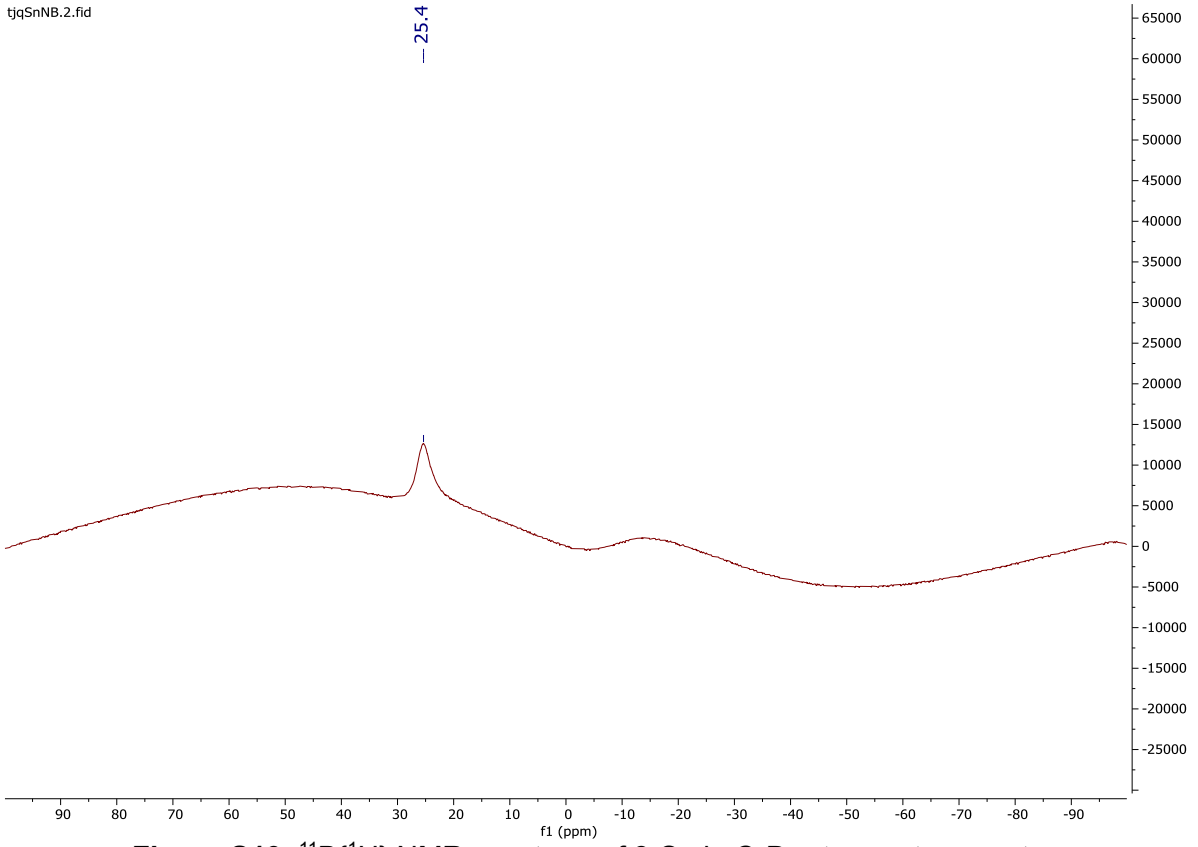



**Figure S19**: $^{11}B\{^{1}H\}$ NMR spectrum of **3**-Sn in $C_6D_6$ at room temperature.

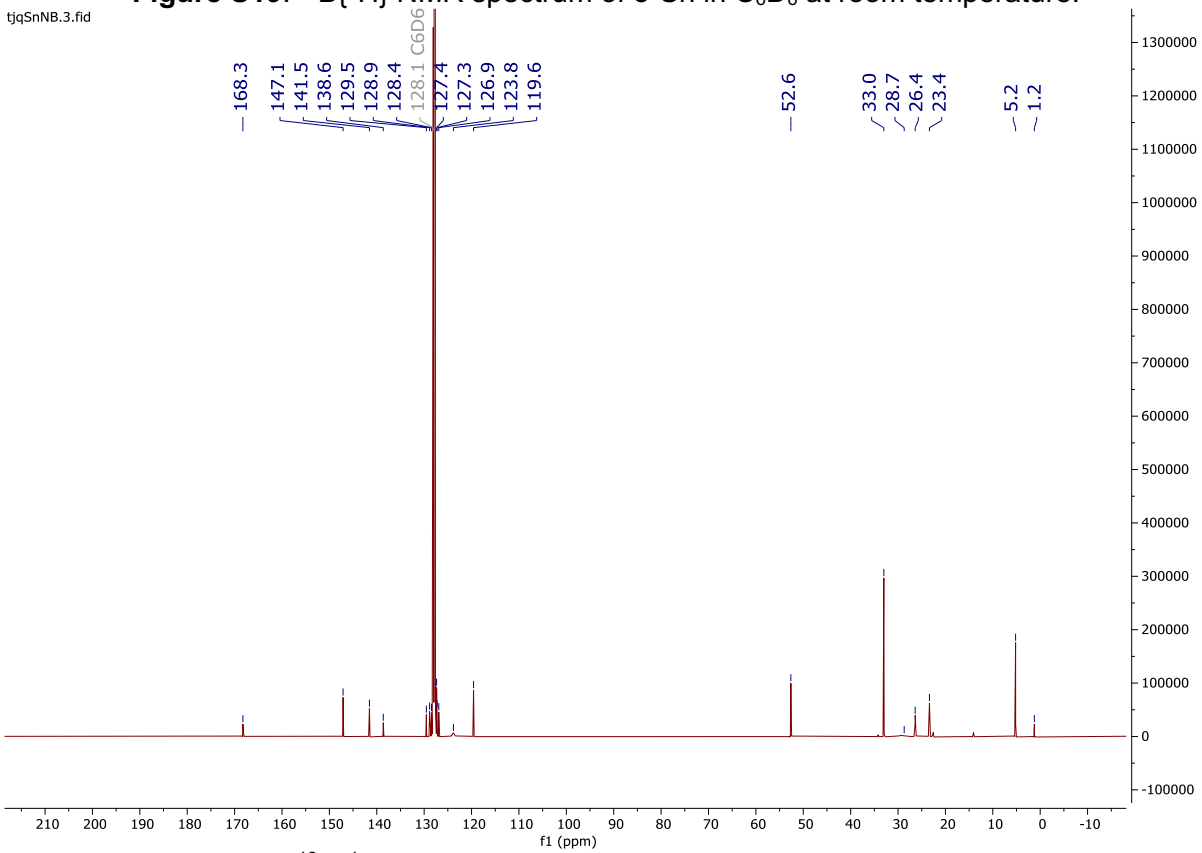



**Figure S20**: $^{13}C\{^{1}H\}$ NMR spectrum of **3**-Sn in $C_6D_6$ at room temperature.

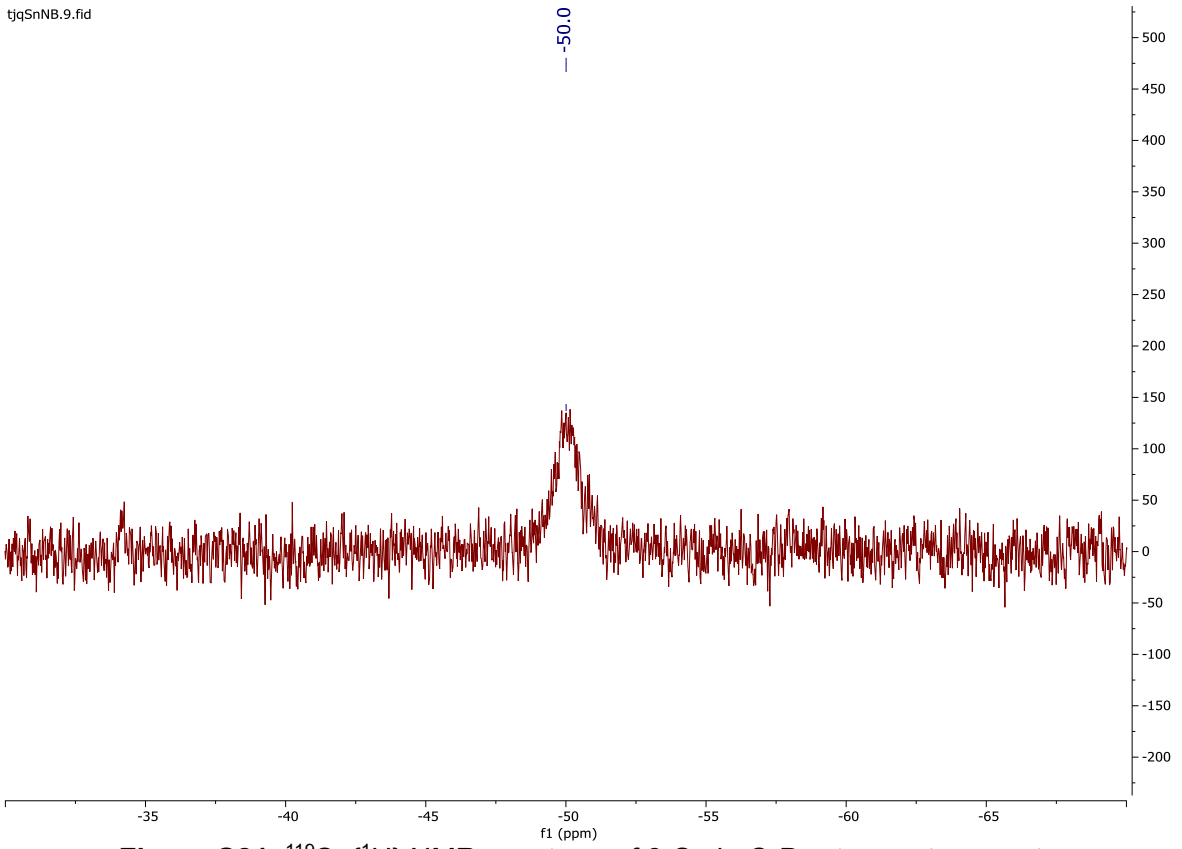



**Figure S21**: $^{119}Sn\{^{1}H\}$ NMR spectrum of **3**-Sn in $C_6D_6$ at room temperature.

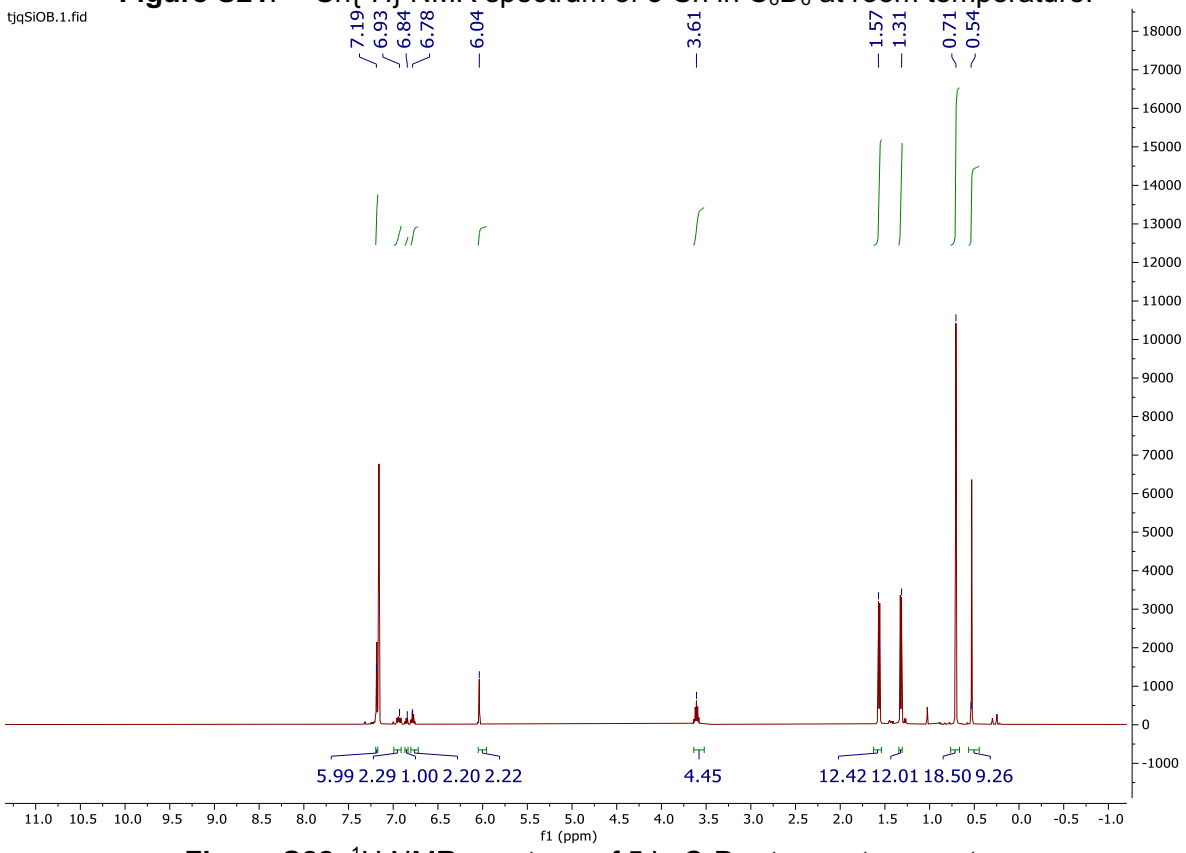



**Figure S22**: $^{1}H$ NMR spectrum of **5** in $C_6D_6$ at room temperature.




**Figure S23**: $^{11}B\{^{1}H\}$ NMR spectrum of **5** in $C_6D_6$ at room temperature.

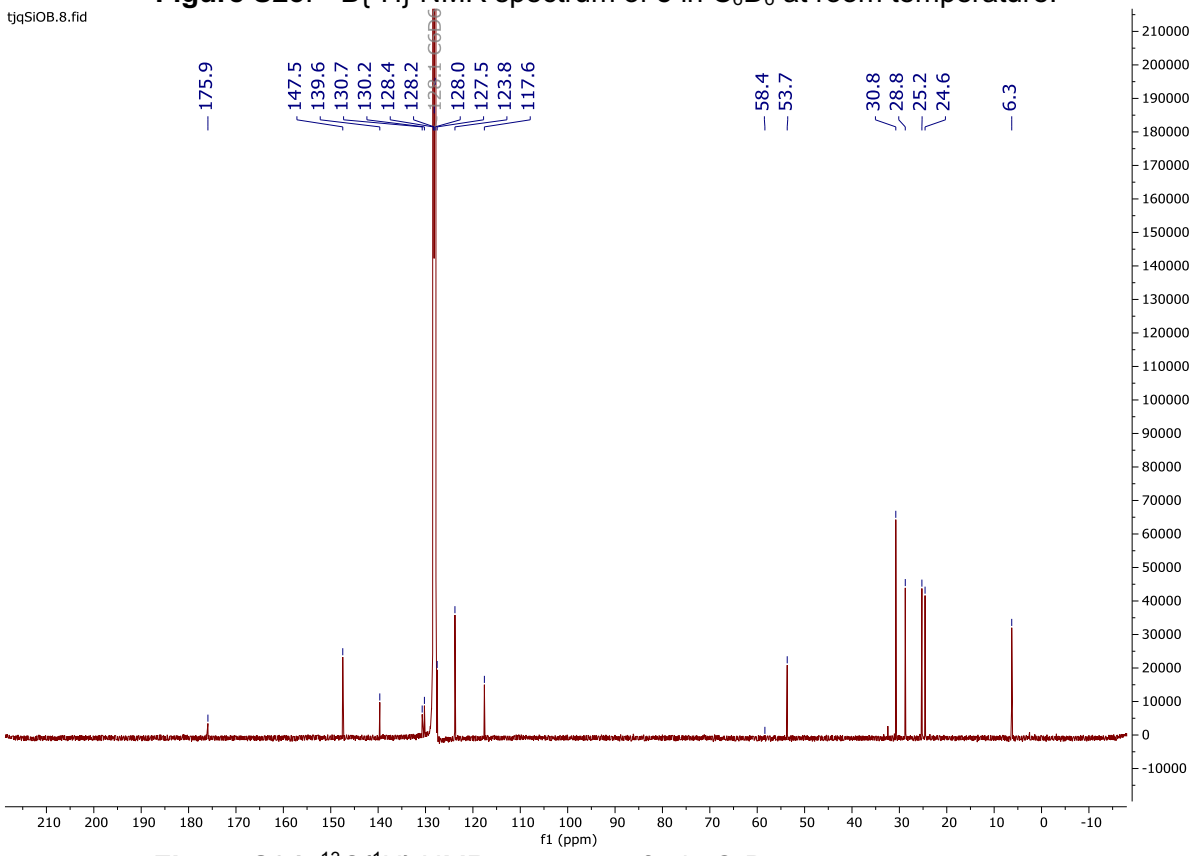



**Figure S24**: $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $C_6D_6$ at room temperature.

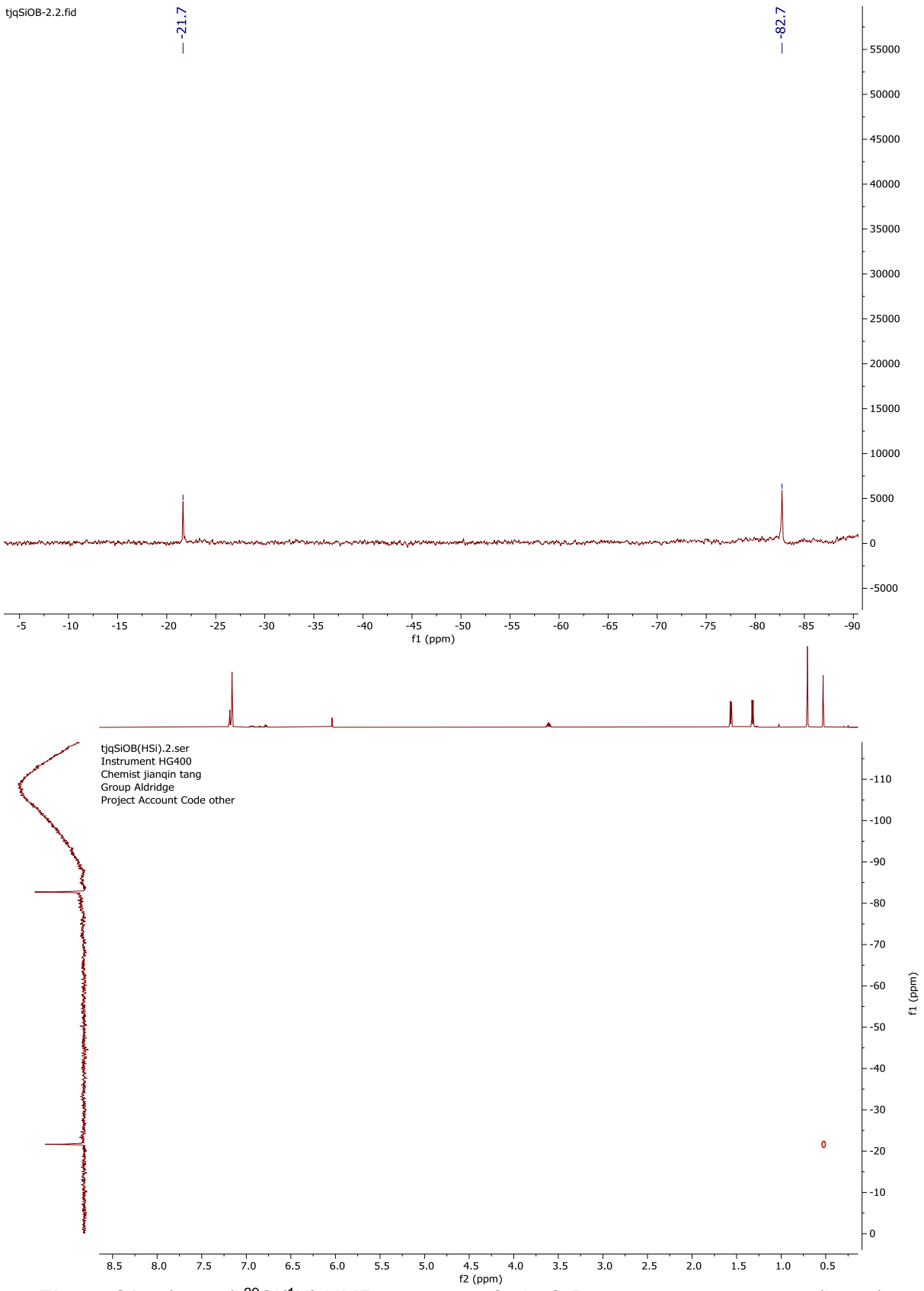



**Figure S25**: (upper) $^{29}Si\{^{1}H\}$ NMR spectrum of **5** in $C_6D_6$ at room temperature; (lower) $^{1}H/^{29}Si$ HMBC NMR spectrum of **5** in $C_6D_6$ at room temperature.

**Details of X-ray crystallography**

**Table S1**: Selected crystallographic data

| Identification code | **2**-Si | **3**-Si |
|---|---|---|
| Empirical formula | $C_{44}H_{68}BN_5Si_2$ | $C_{44}H_{68}BN_5Si_2$ |
| Formula weight | 734.02 | 734.02 |
| Temperature/K | 150.01(11) | 150.00(10) |
| Crystal system | monoclinic | triclinic |
| Space group | $P2_1/c$ | P-1 |
| a/Å | 14.19530(10) | 12.6777(2) |
| b/Å | 18.78600(10) | 13.2202(3) |
| c/Å | 17.02960(10) | 16.6109(3) |
| α/° | 90 | 90.047(2) |
| β/° | 98.2980(10) | 110.485(2) |
| γ/° | 90 | 117.338(2) |
| Volume/Å$^3$ | 4493.79(5) | 2272.62(9) |
| Z | 4 | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.085 | 1.073 |
| μ/mm$^{-1}$ | 0.965 | 0.955 |
| F(000) | 1600 | 800 |
| Crystal size/mm$^3$ | 0.25 × 0.2 × 0.2 | 0.27 × 0.21 × 0.18 |
| Radiation | CuKα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.292 to 152.314 | 7.674 to 153.936 |
| Index ranges | -17 ≤ h ≤ 17, -23 ≤ k ≤ 21, -21 ≤ l ≤ 21 | -15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -20 ≤ l ≤ 17 |
| Reflections collected | 46619 | 55072 |
| Independent reflections | 9334 [$R_{int}$ = 0.0335, $R_{sigma}$ = 0.0232] | 9449 [$R_{int}$ = 0.0414, $R_{sigma}$ = 0.0220] |
| Data/restraints/parameters | 9334/0/486 | 9449/0/486 |
| Goodness-of-fit on $F^2$ | 1.035 | 1.032 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0363, $wR_2$ = 0.0950 | $R_1$ = 0.0377, $wR_2$ = 0.1009 |
| Final R indexes [all data] | $R_1$ = 0.0421, $wR_2$ = 0.0999 | $R_1$ = 0.0438, $wR_2$ = 0.1072 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.27/-0.29 | 0.41/-0.27 |
| CCDC ref | 2429639 | 2429643 |

| Identification code | **4** | **5** |
|---|---|---|
| Empirical formula | $C_{44}H_{68}BN_5Si_2$ | $C_{44}H_{68}BN_5OSi_2$ |
| Formula weight | 734.02 | 750.02 |
| Temperature/K | 150.00(10) | 150.01(11) |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| a/Å | 10.6428(4) | 17.9575(2) |
| b/Å | 39.9620(9) | 10.98470(10) |
| c/Å | 11.8396(5) | 23.0147(3) |
| α/° | 90 | 90 |
| β/° | 115.634(5) | 91.2430(10) |
| γ/° | 90 | 90 |
| Volume/Å$^3$ | 4539.9(3) | 4538.76(9) |
| Z | 4 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.074 | 1.098 |
| μ/mm$^{-1}$ | 0.956 | 0.983 |
| F(000) | 1600 | 1632 |
| Crystal size/mm$^3$ | 0.4 × 0.4 × 0.4 | 0.1 × 0.1 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.574 to 153.402 | 7.684 to 152.958 |
| Index ranges | -13 ≤ h ≤ 13, -47 ≤ k ≤ 50, -14 ≤ l ≤ 14 | -22 ≤ h ≤ 22, -13 ≤ k ≤ 13, -28 ≤ l ≤ 28 |
| Reflections collected | 22532 | 14696 |
| Independent reflections | 22532 [$R_{int}$ = ?, $R_{sigma}$ = 0.0384] | 14696 [$R_{int}$ = ?, $R_{sigma}$ = 0.0110] |
| Data/restraints/parameters | 22532/1/487 | 14696/17/572 |
| Goodness-of-fit on $F^2$ | 1.049 | 1.058 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0687, $wR_2$ = 0.2049 | $R_1$ = 0.0529, $wR_2$ = 0.1575 |
| Final R indexes [all data] | $R_1$ = 0.0918, $wR_2$ = 0.2148 | $R_1$ = 0.0585, $wR_2$ = 0.1620 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.70/-0.50 | 0.36/-0.25 |
| CCDC ref | 2429641 | 2429640 |

| Identification code | **2**-Sn | **3**-Sn |
|---|---|---|
| Empirical formula | $C_{44}H_{68}BN_5SiSn$ | $C_{44}H_{68}BN_5SiSn$ |
| Formula weight | 824.62 | 824.62 |
| Temperature/K | 150.0(2) | 150.01(10) |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| a/Å | 11.93521(6) | 10.15370(10) |
| b/Å | 18.56922(7) | 20.1864(2) |
| c/Å | 21.25962(8) | 21.9443(3) |
| α/° | 90 | 90 |
| β/° | 97.6432(4) | 93.3950(10) |
| γ/° | 90 | 90 |
| Volume/Å$^3$ | 4669.86(3) | 4489.96(9) |
| Z | 4 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.173 | 1.22 |
| μ/mm$^{-1}$ | 4.838 | 5.031 |
| F(000) | 1744 | 1744 |
| Crystal size/mm$^3$ | 0.415 × 0.13 × 0.113 | 0.4 × 0.4 × 0.4 |
| Radiation | Cu Kα (λ = 1.54184) | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.344 to 152.658 | 8.072 to 152.76 |
| Index ranges | -15 ≤ h ≤ 15, -23 ≤ k ≤ 23, -26 ≤ l ≤ 26 | -10 ≤ h ≤ 12, -22 ≤ k ≤ 25, -27 ≤ l ≤ 27 |
| Reflections collected | 126615 | 50920 |
| Independent reflections | 9729 [$R_{int}$ = 0.0420, $R_{sigma}$ = 0.0144] | 9354 [$R_{int}$ = 0.0374, $R_{sigma}$ = 0.0222] |
| Data/restraints/parameters | 9729/342/508 | 9354/0/487 |
| Goodness-of-fit on $F^2$ | 1.054 | 1.049 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0218, $wR_2$ = 0.0560 | $R_1$ = 0.0299, $wR_2$ = 0.0777 |
| Final R indexes [all data] | $R_1$ = 0.0238, $wR_2$ = 0.0578 | $R_1$ = 0.0307, $wR_2$ = 0.0786 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.50/-0.65 | 1.20/-1.28 |
| CCDC ref | 2429642 | 2429644 |

**Details of quantum chemical calculations**

All computational work reported here was performed using ORCA (Revision 5.0.4).[S2] The meta-generalized-gradient approximation (mGGA) functional R2-SCAN[S3] was employed in conjunction with the Def2-TZVPPm[S4] basis set with the D4 dispersion correction,[S5] and employing the geometrical counterpoise correction gCPs5 (together known as the R2SCAN-3c method),[S4] and solvent of toluene with the conductor-like polarizable continuum model (C-PCM).[S6] The nature of the stationary points (minima) was confirmed by full frequency calculations, and are characterized by zero imaginary frequencies.

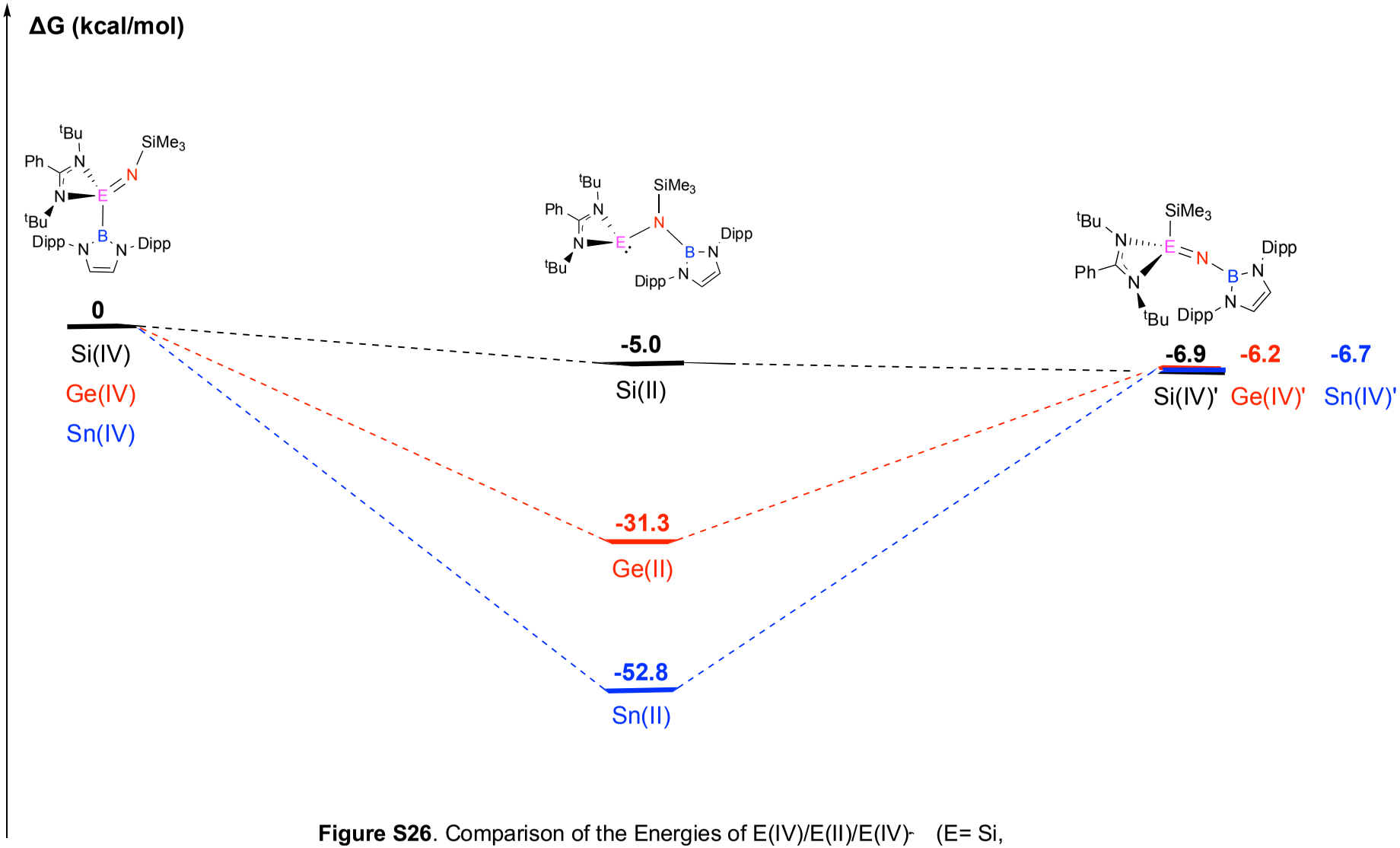



**Figure S26**. Comparison of the Energies of E(IV)/E(II)/E(IV)- (E= Si, Ge, Sn)

**References for supporting information**


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**Declaration of author contribution**

**Statement of Authorship for joint/multi-authored papers for PGR thesis**

To appear at the end of each thesis chapter submitted as an article/paper

The statement shall describe the candidate's and co-authors' independent research contributions in the thesis publications. For each publication there should exist a complete statement that is to be filled out and signed by the candidate and supervisor **(only required where there isn't already a statement of contribution within the paper itself).**

| | |
|---|---|
| Title of Paper | Isomerization and insertion chemistry of imidosilanes enabled by reversible Si(IV)/Si(II) redox shuttling |
| Publication Status | √Published □ Accepted for Publication<br>□Submitted for Publication □Unpublished and unsubmitted work written<br>in a manuscript style |
| Publication Details | Tang, J., Wang, Y., Crumpton, A., McManus, C., & Aldridge, S. (2025). Isomerization and insertion chemistry of imidosilanes enabled by reversible Si (IV)/Si (II) redox shuttling. *Angew. Chem. Int. Ed.*, e202505872. |

Student Confirmation

| | | | |
|---|---|---|---|
| Student Name: | Jianqin Tang | | |
| Contribution to the Paper | Performed all synthetic, spectroscopic work, as well as part quantum chemical calculations. Analysed and interpreted data. Wrote the draft manuscript and prepared the supporting information. | | |
| Signature | Jianqin Tang | Date | 20/06/2025 |

Supervisor Confirmation

By signing the Statement of Authorship, you are certifying that the candidate made a substantial contribution to the publication, and that the description described above is accurate.

| | | |
|---|---|---|
| Supervisor name and title: Professor Simon Aldridge | | |
| Supervisor comments<br>I can confirm that the information concerning this paper described by the candidate is accurate. | | |
| Signature | Date | 21 June 2025 |

## Chapter 6. Conclusions

This thesis describes group 13 and group 14 imido complexes stabilized by a highly sterically encumbered Dipp-substituted diazaborolyl group. Novel inorganic cumulenes (iminoboranes) have been obtained and their geometries shown to be tunable based on the nature of the end groups. The reactivity of these cumulenes was employed in metathesis processes and as precursors to a dianionic bis(borylamido) ligand comparable to monoanionic amidinate and guanidinate systems. New sila- and stannaimines have been synthesized, stabilized by an ancillary boryl group, and shown to undergo migration of the B-based ligand from Si/Sn to N.

Chapter 2 describes the first example of an all-inorganic heterocumulene featuring a five-atom BNBNB chain, which is isoelectronic with organic [4]cumulenes. The target compound, synthesized by deprotonation of a boryl-functionalized boron diamide precursor, crystallizes as a bent BNBNB chain capped by sterically demanding diazaborolyl groups. Structural reconfiguration from bent to linear occurs on reaction of K[{(HCDippN)$_2$}BNBNB{(NDippCH)$_2$}] with the strong Lewis acid B($C_6F_5$)$_3$, to form a linear BNBNB chain. The diazaborolyl terminii undergo electrophilic attack and rearrange to form more $\pi$-acidic, amine/imine N-donor heterocycles. This modification diminishes lone pair character at the chain N atoms and promotes their $\pi$-conjugation within the BNBNB chain, resulting in an overall linear geometry. This is further corroborated by orbital analysis, from Density Functional Theory, which reveals two nearly degenerate orthogonal $\pi$-bonding orbitals spanning the BNBN core.

Chapter 3 details the reactivity of K[{(HCDippN)$_2$}BNBNB{(NDippCH)$_2$}] in a range of metathesis processes with electrophilic heteroallenes ($CO_2$, $CS_2$, and {($H_2$CDippN)$_2$}PPCO)

and organic carbonyl compounds, resulting in the transfer of a (boryl)N unit and formation of (boryl)N=C=E (E = O, S, P) products. These transformations proceed via consecutive [2+2] cyclo-addition/cyclo-reversion steps (bora-Wittig-type) and are thermodynamically driven by strong B–O bond formation. Notably, the reaction with benzaldehyde yields a borylimine product, and enables the isolation and crystallographic characterization of a key intermediate, K[(boryl)NB(O)OC(H)Ph]. Both bent and linear BNBNB species show comparable reactivity, highlighting the chemical reversibility of borane coordination uncovered in chapter 3, and expanding the utility of main-group elements in small molecule metathesis and imine transfer chemistry.

Chapter 4 describes the synthesis of low-valent germylene complexes from the inorganic cumulene precursor, K[(HCDippN)$_2$BNBNB(NDippCH)$_2$] which features a central [N=B=N]$^-$ core isoelectronic with carbodiimides. Reaction of K[(HCDippN)$_2$BNBNB(NDippCH)$_2$] with GeCl$_2$·dioxane yields a four-membered N-heterocyclic germylene complex, [ClB{(boryl)N}$_2$]Ge, stabilized by a dianionic chelating bis(borylamido) ligand. Attempts to further modify the B–Cl moiety with amide or alkyl groups were unsuccessful due to steric hindrance or decomposition, but successful Cl-to-N$_3$ substitution using Me$_3$SiN$_3$ afforded (after carbene coordination) [(N$_3$)B{(boryl)N}$_2$]Ge·IMe$_4$ (**3-N$_3$**), This work highlights the utility of boron-based cumulenes as synthetic equivalents to carbodiimides for constructing low-valent main group element complexes with novel ligand frameworks.

Chapter 5 presents a rare example of reversible redox shuttling at a silicon centre, enabled by ligand migration. Upon heating, the (silylimido)silane (amid)Si(boryl){N(SiMe$_3$)} undergoes a

1,2-boryl migration from silicon to nitrogen, resulting in the formation of a sterically hindered (amido)silylene (amid)Si{N($SiMe_3$)(boryl)}. Further thermal treatment drives a second migration step involving the transfer of the trimethylsilyl group back to silicon, yielding the (borylimido)silane (amid)Si($SiMe_3$){N(boryl)}. DFT calculations indicate that these three isomeric species are close in free energy ($\Delta G \approx \pm 5$ kcal $mol^{-1}$), with the rearrangements occurring via high activation barriers consistent with the harsh conditions employed. Boryl migration is mildly exergonic ($\Delta G = -5.0$ kcal $mol^{-1}$), while the silyl migration step proceeds via a higher barrier (≈37 kcal $mol^{-1}$). Comparative studies with stannylene and germylene analogues demonstrate that such redox shuttling is thermodynamically disfavored for the heavier congeners. These results highlight a new design principle for achieving reversible redox transformations at main group centers through controlled ligand migration and therefore has broad implications for expanding the redox reactivity of p-block elements.

A wide range of future work is possible in the field of main-group element–nitrogen multiple bonding. For Group 13 systems, extending the chemistry of cumulenes beyond the BNBNB framework represents an important challenge. Longer chains, such as BNBBNB or BNBNBNB, may be accessible from amine–borane and haloborane precursors, followed by reduction. However, success will require careful design of the terminal substituents to stabilise the highly polar NBBN core. Another promising avenue is the use of inorganic cumulenes as ligands for transition-metal and low-valent main-group complexes, offering opportunities to activate small molecules and potentially catalytic behaviour.

For Group 14 chemistry, future studies can focus on exploring strategies to extend the

reversible redox shuttling of heavier group 14 elements beyond silicon. Additionally, these systems could be examined for the possibility of small molecule activation. If this reactivity can be applied to the Si(IV)/Si(II) redox cycle, it may form the basis of catalytic processes that parallel transition-metal redox chemistry.

The long-term vision of this research is to expand the synthetic scope, reactivity, and coordination chemistry. Future work has the potential to unlock new strategies in bonding and catalysis, while opening up opportunities for functional applications in materials and small-molecule transformations.

## Chapter 7. Appendix

### Chapter 2 Xyz coordinates for optimized structures

$(NH_2)_2BNBNB(NH_2)_2$ bent isomer

| | | | |
|---|---|---|---|
| N | -3.67276900 | 0.90021500 | 0.51136400 |
| N | 3.65015500 | -0.91838000 | 0.51210400 |
| N | -3.23409600 | -1.19620100 | -0.30669100 |
| N | -1.24439700 | 0.44051300 | -0.18592700 |
| N | 1.24170000 | -0.41711200 | -0.19899700 |
| N | 3.26079300 | 1.18892100 | -0.30018400 |
| B | -0.00235000 | 0.00849400 | -0.23036800 |
| B | 2.56836600 | -0.07826600 | -0.01893200 |
| B | -2.57043300 | 0.08599100 | -0.02165200 |
| H | 3.46972500 | -1.91368700 | 0.59161900 |
| H | 4.56116100 | -0.75549100 | 0.10156600 |
| H | 3.99527300 | 1.41949300 | 0.35824300 |
| H | 2.67992300 | 2.00269400 | -0.47481900 |
| H | -3.51467500 | 1.89897300 | 0.59679300 |
| H | -4.57674000 | 0.72100800 | 0.09189300 |
| H | -3.96795900 | -1.44314300 | 0.34639700 |
| H | -2.63432400 | -1.99664500 | -0.47861800 |

$(NH_2)_2BNBNB(NH_2)_2$ linear isomer

| | | | |
|---|---|---|---|
| N | -1.31090100 | -0.00090900 | -0.00094700 |
| N | 1.31087900 | -0.00044600 | -0.00057000 |
| B | -0.00000700 | -0.00063300 | -0.00070200 |
| B | -2.69570100 | -0.00015300 | -0.00009400 |
| B | 2.69570800 | 0.00009400 | 0.00009500 |
| N | -3.49086100 | 0.92169200 | -0.82344700 |
| H | -2.97343700 | 1.35460300 | -1.57897400 |
| H | -4.40007200 | 0.60326200 | -1.14015200 |
| N | -3.49095700 | -0.92108700 | 0.82411700 |
| H | -2.97338700 | -1.35473800 | 1.57910500 |
| H | -4.39965000 | -0.60176800 | 1.14137900 |
| N | 3.49018500 | 0.82497600 | 0.92115800 |
| H | 4.39924400 | 1.14183800 | 0.60246100 |
| H | 2.97226500 | 1.58052300 | 1.35341300 |
| N | 3.49162000 | -0.82418200 | -0.92028600 |
| H | 4.40062500 | -1.14046700 | -0.60084700 |
| H | 2.97465000 | -1.58009400 | -1.35306300 |

**3**

| | | | |
|---|---|---|---|
| N | 1.06648819 | 1.77638780 | 7.63183244 |

| | | | |
|---|---|---|---|
| N | 1.80602684 | 2.95921557 | 5.82060763 |
| N | 3.80788998 | 6.89247842 | 11.23329685 |
| N | 3.98700787 | 5.28874774 | 12.84726275 |
| N | 2.47824259 | 3.90634247 | 8.09399320 |
| N | 3.24241892 | 4.45760629 | 10.54901876 |
| C | 0.63934030 | 1.34842656 | 8.91559988 |
| C | -0.69885130 | 1.56216752 | 9.30311643 |
| C | 3.91622310 | 4.08457896 | 13.59064666 |
| C | 2.37931669 | 3.92120345 | 4.95157028 |
| C | 3.55787912 | 7.62722082 | 10.04663508 |
| C | 0.60841270 | 1.16800459 | 6.45476052 |
| H | 0.00701366 | 0.26834601 | 6.47477559 |
| C | 4.48761107 | 7.58361989 | 8.99295316 |
| C | 1.05267217 | 1.86569987 | 5.38056319 |
| H | 0.90120724 | 1.65828969 | 4.32938244 |
| C | -1.12114288 | 1.06991227 | 10.53981652 |
| H | -2.14962548 | 1.21743428 | 10.85679359 |
| C | 4.20659503 | 7.48716215 | 12.43652844 |
| H | 4.39591975 | 8.54981971 | 12.51488689 |
| C | 5.09437415 | 3.35219731 | 13.83466320 |
| C | 3.61375167 | 3.64343049 | 4.33111385 |
| C | 1.56185019 | 0.74038304 | 9.78929427 |
| C | 1.73259635 | 5.15601047 | 4.76855514 |
| C | -1.61468723 | 2.42214598 | 8.45048668 |
| H | -1.32177960 | 2.29715391 | 7.40190868 |
| C | -0.23357206 | 0.41888699 | 11.38726362 |
| H | -0.57481409 | 0.04781590 | 12.35038606 |
| C | 4.31158852 | 6.53409144 | 13.39704574 |
| H | 4.60274955 | 6.64651197 | 14.43309954 |
| C | 2.12605196 | 9.07382896 | 8.75343277 |
| H | 1.20535250 | 9.63840129 | 8.63691726 |
| C | 2.66175351 | 3.61065784 | 14.01284851 |
| C | 2.35543841 | 8.35509481 | 9.92666191 |
| C | 1.10011715 | 0.27955394 | 11.02420823 |
| H | 1.79210801 | -0.18964760 | 11.71685447 |
| C | 4.21088525 | 8.30746383 | 7.82919391 |
| H | 4.91677086 | 8.28074816 | 7.00272562 |
| C | 0.40592268 | 5.46544169 | 5.43506639 |
| H | 0.07822453 | 4.55879404 | 5.95531716 |
| C | 3.56335130 | 5.85612082 | 3.34204518 |
| H | 4.02990730 | 6.61422618 | 2.71801322 |
| C | 4.18845753 | 4.62607947 | 3.52412717 |
| H | 5.14307784 | 4.43809389 | 3.04111606 |
| C | 3.04857878 | 9.05516101 | 7.71236120 |

| | | | |
|---|---|---|---|
| H | 2.84871612 | 9.61098832 | 6.79980245 |
| C | 1.38860381 | 4.39603518 | 13.76202479 |
| H | 1.66284833 | 5.31261366 | 13.22875007 |
| C | 2.34804032 | 6.11622032 | 3.96004391 |
| H | 1.86927003 | 7.08206702 | 3.81677377 |
| C | 4.33198913 | 2.33649422 | 4.61449812 |
| H | 3.56810239 | 1.57806020 | 4.82277192 |
| C | 4.99416967 | 2.13548140 | 14.51076286 |
| H | 5.88802983 | 1.54851304 | 14.70238583 |
| C | 5.77657823 | 6.79163285 | 9.09593793 |
| H | 5.75285278 | 6.24290753 | 10.04320310 |
| C | 2.60469058 | 2.38292368 | 14.67886131 |
| H | 1.64228955 | 1.99529344 | 15.00497748 |
| C | 6.42190374 | 3.84207066 | 13.28675684 |
| H | 6.36520050 | 4.93424387 | 13.21375033 |
| C | 3.75792768 | 1.65108204 | 14.92739972 |
| H | 3.69563093 | 0.69669169 | 15.44422180 |
| C | 1.29438578 | 8.26441214 | 11.00904857 |
| H | 1.80216322 | 8.09192073 | 11.96505416 |
| C | 3.01165296 | 0.56597563 | 9.37491769 |
| H | 3.28846381 | 1.45358877 | 8.79391250 |
| C | -3.09611498 | 2.05387628 | 8.56302506 |
| H | -3.50008885 | 2.28783188 | 9.55453532 |
| H | -3.26053945 | 0.98793657 | 8.36972794 |
| H | -3.67624856 | 2.62837967 | 7.83247830 |
| C | 6.99301353 | 7.72816344 | 9.12617962 |
| H | 7.07600201 | 8.29553120 | 8.19128228 |
| H | 7.91617520 | 7.15063484 | 9.25416992 |
| H | 6.91827618 | 8.44489518 | 9.95165930 |
| C | 3.16278605 | -0.65832895 | 8.45799904 |
| H | 4.20231613 | -0.75984128 | 8.12391547 |
| H | 2.52536053 | -0.56513473 | 7.57295962 |
| H | 2.88231153 | -1.57446486 | 8.99274466 |
| C | 0.72230876 | 4.80593858 | 15.08297672 |
| H | 0.39206529 | 3.92728821 | 15.64997215 |
| H | -0.15798773 | 5.42925533 | 14.88649316 |
| H | 1.41407633 | 5.37594723 | 15.71303982 |
| C | 0.41524509 | 3.61354968 | 12.87254419 |
| H | 0.89530036 | 3.32037931 | 11.93378682 |
| H | -0.46226266 | 4.22664306 | 12.63434601 |
| H | 0.06476254 | 2.70326859 | 13.37234718 |
| C | 0.56357183 | 6.57430452 | 6.48343118 |
| H | 0.88002080 | 7.51527983 | 6.01777219 |
| H | 1.31179252 | 6.29372722 | 7.23090627 |

| | | | |
|---|---|---|---|
| H | -0.38923561 | 6.75306736 | 6.99654907 |
| C | -0.67273294 | 5.82763589 | 4.40513854 |
| H | -1.63854145 | 5.96735086 | 4.90473563 |
| H | -0.78535334 | 5.03711385 | 3.65487192 |
| H | -0.43088296 | 6.76005377 | 3.88142651 |
| B | 2.83188620 | 4.19119901 | 9.32939395 |
| C | 3.97773241 | 0.48163508 | 10.55882753 |
| H | 3.85819963 | -0.45270916 | 11.12062951 |
| H | 3.83870627 | 1.32262343 | 11.24743425 |
| H | 5.00920075 | 0.51331190 | 10.19096161 |
| C | 0.45286984 | 9.53528660 | 11.15455999 |
| H | 1.08355499 | 10.42244718 | 11.28060578 |
| H | -0.19771101 | 9.44923122 | 12.03185384 |
| H | -0.19436078 | 9.69744519 | 10.28519749 |
| B | 3.63598021 | 5.44811838 | 11.43390414 |
| C | 5.89943980 | 5.75985570 | 7.96708887 |
| H | 5.02135842 | 5.10710374 | 7.93933776 |
| H | 6.78981682 | 5.13829044 | 8.12029913 |
| H | 5.99382888 | 6.24382592 | 6.98718004 |
| B | 1.84813480 | 2.97382722 | 7.28599928 |
| C | 0.39289664 | 7.04665014 | 10.73928015 |
| H | -0.13594478 | 7.16976704 | 9.78575942 |
| H | -0.35276241 | 6.93536083 | 11.53627506 |
| H | 0.98011026 | 6.12398695 | 10.68283059 |
| C | 7.61768351 | 3.49521191 | 14.17783237 |
| H | 7.81672596 | 2.41766993 | 14.19212429 |
| H | 7.45859753 | 3.82623618 | 15.21018702 |
| H | 8.51911330 | 3.98637646 | 13.79495708 |
| C | 6.62753525 | 3.29535659 | 11.86382705 |
| H | 7.54902758 | 3.69808628 | 11.42587541 |
| H | 5.78558636 | 3.55901035 | 11.21469611 |
| H | 6.70688204 | 2.20138533 | 11.88771432 |
| C | 5.17923591 | 1.83533200 | 3.44173776 |
| H | 5.55772375 | 0.83118044 | 3.66249255 |
| H | 4.59615159 | 1.78653580 | 2.51528411 |
| H | 6.04906985 | 2.47799750 | 3.26459642 |
| C | 5.19207637 | 2.47968892 | 5.88148248 |
| H | 4.58680415 | 2.80764282 | 6.73260614 |
| H | 5.66497236 | 1.52291986 | 6.13454938 |
| H | 5.98308975 | 3.22328309 | 5.72177176 |
| C | -1.39418360 | 3.90080850 | 8.81827836 |
| H | -0.34042977 | 4.18253856 | 8.71509658 |
| H | -1.99294548 | 4.55282080 | 8.17016440 |
| H | -1.69268381 | 4.07979548 | 9.85903761 |

**5**

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|---|---|---|---|
| N | -2.26579009 | 10.25479785 | 19.02857172 |
| B | -2.02056040 | 11.18447062 | 18.15096062 |
| N | -1.78230581 | 12.08718028 | 17.24339375 |
| B | -2.64823592 | 9.18344877 | 19.76274440 |
| N | -3.94128388 | 9.08883531 | 20.61981707 |
| C | -3.96888035 | 7.99842723 | 21.34942581 |
| C | -2.69774346 | 7.23081139 | 21.07551409 |
| H | -2.08712432 | 7.19074103 | 21.99076244 |
| H | -2.93882873 | 6.18274902 | 20.83666989 |
| N | -2.01349226 | 7.93759836 | 20.02059316 |
| B | -5.04148628 | 7.30681897 | 22.41041493 |
| C | -4.91878631 | 10.14876470 | 20.47929569 |
| C | -5.00155485 | 11.15164930 | 21.46023182 |
| C | -5.91898924 | 12.18397204 | 21.25788365 |
| H | -6.01889828 | 12.96255359 | 22.00726373 |
| C | -6.69742046 | 12.23870680 | 20.11024304 |
| H | -7.40938511 | 13.04835545 | 19.97499263 |
| C | -6.54196067 | 11.27722931 | 19.12435169 |
| H | -7.12785805 | 11.34622947 | 18.21216330 |
| C | -5.63720887 | 10.22527224 | 19.27291688 |
| C | -4.07015211 | 11.17665060 | 22.65488328 |
| H | -3.84372127 | 10.14363337 | 22.92030329 |
| C | -4.67579686 | 11.84109434 | 23.89374823 |
| H | -4.73732488 | 12.92922188 | 23.77963433 |
| H | -4.04307489 | 11.63896371 | 24.76470180 |
| H | -5.67956802 | 11.46148898 | 24.10432908 |
| C | -2.74986844 | 11.87337272 | 22.28237086 |
| H | -2.27480804 | 11.41801326 | 21.40831689 |
| H | -2.04915093 | 11.83174108 | 23.12468668 |
| H | -2.93680548 | 12.92747528 | 22.04329398 |
| C | -5.49277068 | 9.22902760 | 18.13354212 |
| H | -4.69526627 | 8.52275070 | 18.38099916 |
| C | -5.09549745 | 9.93322932 | 16.82670254 |
| H | -4.89852868 | 9.19013095 | 16.04555310 |
| H | -4.19408799 | 10.53863011 | 16.95619761 |
| H | -5.89353280 | 10.59105660 | 16.46502598 |
| C | -6.78352501 | 8.42288728 | 17.92008127 |
| H | -7.59995787 | 9.08001070 | 17.59910728 |
| H | -7.10431945 | 7.91433493 | 18.83223727 |
| H | -6.62955157 | 7.66871329 | 17.13996315 |
| C | -0.68022746 | 7.58345479 | 19.66437961 |
| C | -0.47296128 | 6.76971068 | 18.53446913 |

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|---|---|---|---|
| C | 0.83817395 | 6.44668125 | 18.18296362 |
| H | 1.02596944 | 5.82871843 | 17.30990757 |
| C | 1.91282505 | 6.91240290 | 18.93240973 |
| H | 2.92776205 | 6.65111639 | 18.64427828 |
| C | 1.69257747 | 7.72145469 | 20.03823090 |
| H | 2.54023766 | 8.09236233 | 20.60917421 |
| C | 0.39675373 | 8.07777635 | 20.42158320 |
| C | -1.64661965 | 6.32816380 | 17.68108139 |
| H | -2.52836958 | 6.28208019 | 18.33030027 |
| C | -1.45894654 | 4.94528337 | 17.05113006 |
| H | -2.38937266 | 4.63217749 | 16.56530459 |
| H | -1.19473985 | 4.19382321 | 17.80315459 |
| H | -0.67691432 | 4.95079625 | 16.28381209 |
| C | -1.92718131 | 7.38369239 | 16.59780968 |
| H | -1.07156005 | 7.46231374 | 15.91578318 |
| H | -2.09626206 | 8.37098981 | 17.03953700 |
| H | -2.81081276 | 7.10904077 | 16.00957635 |
| C | 0.19479174 | 9.00146794 | 21.60864297 |
| H | -0.88034281 | 9.16785069 | 21.73922042 |
| C | 0.83197387 | 10.37336334 | 21.34754554 |
| H | 1.91973199 | 10.29195985 | 21.24016712 |
| H | 0.62484315 | 11.05373675 | 22.18157122 |
| H | 0.43422313 | 10.82188207 | 20.43132234 |
| C | 0.72792193 | 8.37969065 | 22.90652511 |
| H | 0.26653322 | 7.40409027 | 23.09882336 |
| H | 0.50922464 | 9.03258139 | 23.75891482 |
| H | 1.81343972 | 8.23506931 | 22.85978415 |
| B | -1.39815077 | 13.01154932 | 16.33295895 |
| N | -0.14076822 | 13.90882628 | 16.43745511 |
| C | -0.07233586 | 14.78492478 | 15.46419152 |
| C | -1.29611767 | 14.60183739 | 14.59741262 |
| H | -1.92191809 | 15.50616601 | 14.66474440 |
| H | -1.00298772 | 14.52426435 | 13.53852498 |
| N | -1.98507667 | 13.44226325 | 15.11051326 |
| B | 0.99667777 | 15.96618932 | 15.00799898 |
| C | 0.77316235 | 13.68402470 | 17.53614693 |
| C | 0.64112413 | 14.45620554 | 18.70127823 |
| C | 1.55500083 | 14.23122879 | 19.73301078 |
| H | 1.49241828 | 14.82849904 | 20.63810501 |
| C | 2.51920677 | 13.23841052 | 19.63160311 |
| H | 3.22871018 | 13.08486550 | 20.44026369 |
| C | 2.53808078 | 12.40373173 | 18.52326825 |
| H | 3.24787734 | 11.58205503 | 18.48366044 |
| C | 1.64821537 | 12.58579373 | 17.46405394 |

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|---|---|---|---|
| C | 1.62738338 | 11.56648246 | 16.33479811 |
| H | 0.85290612 | 11.85222008 | 15.61648148 |
| C | 1.25393830 | 10.18006670 | 16.88809922 |
| H | 1.12674350 | 9.47162420 | 16.06147679 |
| H | 0.32219121 | 10.21004993 | 17.45932924 |
| H | 2.04020947 | 9.79027754 | 17.54433050 |
| C | 2.95743415 | 11.47033011 | 15.57390859 |
| H | 2.88003801 | 10.70253541 | 14.79591717 |
| H | 3.77329639 | 11.18430996 | 16.24745502 |
| H | 3.23055316 | 12.41258084 | 15.09575064 |
| C | -0.52917359 | 15.39445310 | 18.93116463 |
| H | -1.04656471 | 15.54647974 | 17.98184684 |
| C | -0.11909715 | 16.76872700 | 19.46805517 |
| H | -0.99646175 | 17.42180348 | 19.52673532 |
| H | 0.30569058 | 16.69589887 | 20.47535719 |
| H | 0.61885842 | 17.24695268 | 18.81919967 |
| C | -1.52758148 | 14.72348789 | 19.89272002 |
| H | -2.40529026 | 15.36574798 | 20.03190284 |
| H | -1.86294670 | 13.75739359 | 19.50299817 |
| H | -1.06723746 | 14.55565202 | 20.87358101 |
| C | -3.28921233 | 13.10405284 | 14.65065812 |
| C | -3.42648577 | 12.09704975 | 13.67716185 |
| C | -4.71274780 | 11.74854145 | 13.26276442 |
| H | -4.84732403 | 10.96850270 | 12.51919503 |
| C | -5.82989495 | 12.38222364 | 13.79634273 |
| H | -6.82460123 | 12.09808726 | 13.46284962 |
| C | -5.67787090 | 13.36685374 | 14.76275480 |
| H | -6.55854853 | 13.84512139 | 15.18443212 |
| C | -4.40902307 | 13.74138270 | 15.21293604 |
| C | -2.20500632 | 11.36313885 | 13.15699321 |
| H | -1.35103404 | 12.04400227 | 13.24729953 |
| C | -2.31809146 | 10.94995800 | 11.68726177 |
| H | -2.58931543 | 11.79972463 | 11.05140180 |
| H | -3.06399522 | 10.16073204 | 11.54082043 |
| H | -1.35606587 | 10.55654064 | 11.34137882 |
| C | -1.91019464 | 10.14199414 | 14.04450892 |
| H | -2.73977799 | 9.42554408 | 13.99655313 |
| H | -1.77783855 | 10.43384349 | 15.09148378 |
| H | -0.99906056 | 9.63422777 | 13.70636333 |
| C | -4.27722707 | 14.78952132 | 16.30227995 |
| H | -3.21270874 | 14.92179986 | 16.52568779 |
| C | -4.95056278 | 14.32054825 | 17.59904230 |
| H | -4.81107779 | 15.06365636 | 18.39270519 |
| H | -6.02788926 | 14.17585309 | 17.45874487 |

| | | | |
|---|---|---|---|
| H | -4.52527184 | 13.37052004 | 17.93913441 |
| C | -4.82634589 | 16.14869171 | 15.84629940 |
| H | -4.65301224 | 16.90747335 | 16.61741183 |
| H | -4.33877066 | 16.48164749 | 14.92264777 |
| H | -5.90481565 | 16.09689287 | 15.65756077 |
| C | 0.00904527 | 17.14889174 | 14.38100522 |
| C | -0.97066689 | 17.71131582 | 15.20064505 |
| C | -1.88328247 | 18.67225524 | 14.80385837 |
| C | -1.86524714 | 19.11258030 | 13.48758172 |
| C | -0.93618214 | 18.57309087 | 12.61662323 |
| C | -0.03655255 | 17.60801021 | 13.06655645 |
| F | -1.06788555 | 17.29740661 | 16.48299166 |
| F | -2.78231379 | 19.17181428 | 15.66379543 |
| F | -2.73690064 | 20.03522851 | 13.06732206 |
| F | -0.91663023 | 18.97469639 | 11.33717710 |
| F | 0.78570723 | 17.12710726 | 12.11203049 |
| C | 2.00502804 | 15.38107777 | 13.83758093 |
| C | 1.98920283 | 14.11235854 | 13.27536111 |
| C | 2.91790649 | 13.66440841 | 12.34237251 |
| C | 3.93129108 | 14.51196203 | 11.92935941 |
| C | 3.99005522 | 15.79637507 | 12.45333627 |
| C | 3.03993551 | 16.19669353 | 13.37858481 |
| F | 1.04651031 | 13.20716170 | 13.62898159 |
| F | 2.84698448 | 12.41823457 | 11.85149759 |
| F | 4.83611568 | 14.10279165 | 11.03264395 |
| F | 4.95531794 | 16.63432783 | 12.04823638 |
| F | 3.12773026 | 17.47247956 | 13.80873569 |
| C | 1.99173373 | 16.52273853 | 16.21051104 |
| C | 2.01822124 | 17.80489431 | 16.76104080 |
| C | 2.92652875 | 18.21508240 | 17.73147700 |
| C | 3.89824469 | 17.34010698 | 18.18430265 |
| C | 3.95890685 | 16.07187089 | 17.63161395 |
| C | 3.03107281 | 15.70868167 | 16.66707194 |
| F | 1.16524766 | 18.77100057 | 16.36235131 |
| F | 2.86920270 | 19.45919743 | 18.23131444 |
| F | 4.77400518 | 17.71971312 | 19.12157028 |
| F | 4.92109847 | 15.22231703 | 18.01781735 |
| F | 3.20870493 | 14.48632191 | 16.13144561 |
| C | -6.06807588 | 8.36208286 | 23.17273576 |
| C | -7.11828984 | 8.93479446 | 22.45119571 |
| C | -8.10611247 | 9.74178448 | 22.99628235 |
| C | -8.09922671 | 9.99661396 | 24.35727067 |
| C | -7.10445270 | 9.42780716 | 25.13367101 |
| C | -6.12716292 | 8.63612217 | 24.54050597 |

| | | | |
|---|---|---|---|
| F | -7.24930746 | 8.68109170 | 21.13512247 |
| F | -9.06625029 | 10.26797119 | 22.22307295 |
| F | -9.03344168 | 10.77791586 | 24.91046839 |
| F | -7.08249396 | 9.65910926 | 26.45523801 |
| F | -5.24070401 | 8.11027037 | 25.41052427 |
| C | -4.07214440 | 6.47179378 | 23.47739925 |
| C | -3.08618707 | 7.15668001 | 24.19095757 |
| C | -2.20529340 | 6.57873219 | 25.08750199 |
| C | -2.26675928 | 5.20950435 | 25.30388326 |
| C | -3.20671296 | 4.46854933 | 24.61152298 |
| C | -4.07057228 | 5.09841550 | 23.71691842 |
| F | -2.94145853 | 8.48914419 | 24.00804909 |
| F | -1.29434821 | 7.31659102 | 25.73751327 |
| F | -1.43003473 | 4.62050358 | 26.16359906 |
| F | -3.26834582 | 3.14129854 | 24.79250091 |
| F | -4.91371258 | 4.25905105 | 23.08225466 |
| C | -6.02122534 | 6.24905456 | 21.59795359 |
| C | -7.09328859 | 5.66508111 | 22.27491946 |
| C | -8.00845561 | 4.80820606 | 21.68602758 |
| C | -7.86967623 | 4.47949531 | 20.34433380 |
| C | -6.81208428 | 5.01426354 | 19.63015391 |
| C | -5.92354176 | 5.87556067 | 20.26507326 |
| F | -7.25655078 | 5.88776805 | 23.59580985 |
| F | -9.00982487 | 4.27270739 | 22.39910096 |
| F | -8.73788327 | 3.64799700 | 19.75738346 |
| F | -6.66278713 | 4.71505463 | 18.33142117 |
| F | -4.92477067 | 6.34746311 | 19.48316265 |

**Chapter 3 Xyz coordinates for optimized structures**

**PhCHO**

| | | | |
|---|---|---|---|
| C | 3.43481100 | 1.01852900 | 0.00937100 |
| C | 4.82327200 | 1.02236600 | -0.14245000 |
| C | 5.51885600 | 2.22997400 | -0.15353600 |
| C | 4.82160500 | 3.42964200 | -0.01229200 |
| C | 3.43166300 | 3.42750800 | 0.14005300 |
| C | 2.73709000 | 2.22344900 | 0.15091800 |
| H | 5.35663000 | 0.07452100 | -0.25152700 |
| H | 6.60307600 | 2.23792600 | -0.27216800 |
| H | 5.36456300 | 4.37618600 | -0.02104400 |
| H | 2.89460200 | 4.37063000 | 0.25021700 |
| H | 1.65259700 | 2.18442400 | 0.26754100 |
| C | 2.69222400 | -0.26919900 | 0.02065100 |
| O | 1.50054700 | -0.36040800 | 0.14595600 |
| H | 3.33093100 | -1.17893200 | -0.09929800 |

**1** (anionic component only)

| | | | |
|---|---|---|---|
| N | 3.76389000 | 0.76964700 | 0.20547100 |
| N | -3.61635700 | -0.76975400 | 0.51321800 |
| N | 2.42913000 | 2.44059900 | -0.62093100 |
| N | 1.35455300 | 0.10758500 | -0.38722900 |
| N | -1.25591700 | -0.19916600 | -0.29940400 |
| N | -2.37801300 | -2.52448100 | -0.28650300 |
| C | 4.15619600 | -0.31657700 | 1.02686800 |
| C | 4.47803400 | 1.97194400 | 0.17631700 |
| H | 5.50816000 | 2.03144500 | 0.52131400 |
| C | 0.25363600 | 3.50211800 | -0.29852100 |
| C | -4.03469200 | 0.47671900 | 1.03434200 |
| C | 3.69485900 | 2.95378600 | -0.33094900 |
| H | 3.94446800 | 3.99734100 | -0.51460200 |
| C | -4.34455000 | 1.52965900 | 0.14699200 |
| C | -4.36051400 | -1.94877000 | 0.60495300 |
| H | -5.37058400 | -1.95795900 | 1.00993500 |
| C | -1.61950900 | -3.77209200 | -2.24228200 |
| C | 4.85660700 | -1.40413800 | 0.46731000 |
| C | -1.40075400 | -3.32964600 | -0.92011800 |
| C | -4.24034700 | 1.30923100 | -1.35409400 |
| H | -3.29004400 | 0.77817600 | -1.51771300 |
| C | -0.19938600 | -3.62641700 | -0.24255400 |
| C | -3.63274300 | -2.98304100 | 0.11825400 |
| H | -3.91413500 | -4.03090300 | 0.03165200 |
| C | -4.07099100 | 0.66672800 | 2.43157600 |
| C | 0.02287600 | -3.14034100 | 1.18127000 |
| H | -0.37771100 | -2.11734400 | 1.23654900 |
| C | -2.82221500 | -3.26074400 | -3.01971000 |
| H | -3.67294500 | -3.19304500 | -2.32618700 |
| C | 1.38159300 | 3.62635800 | -2.47841800 |
| C | 1.35560100 | 3.20987000 | -1.13103500 |
| C | 0.24309600 | 3.05053200 | 1.15386500 |
| H | 0.66068400 | 2.03376300 | 1.17387200 |
| C | -0.65010900 | -4.57497300 | -2.84990800 |
| H | -0.80471500 | -4.93503700 | -3.86823600 |
| B | 0.04750900 | -0.04373200 | -0.38128600 |
| C | -4.82109000 | 2.94357000 | 2.06498000 |
| H | -5.13201300 | 3.90991200 | 2.46712000 |
| C | -3.53493800 | -0.41902100 | 3.35119300 |
| H | -3.79189200 | -1.39211300 | 2.90924700 |
| C | -4.73585100 | 2.75877400 | 0.68743400 |
| H | -4.97288400 | 3.58995800 | 0.02230500 |

| | | | |
|---|---|---|---|
| C | 3.81135400 | -0.30033400 | 2.39303900 |
| C | -0.80355100 | 4.24459500 | -0.83473100 |
| H | -1.67405700 | 4.46357800 | -0.21439800 |
| C | -4.48523900 | 1.90601000 | 2.92924800 |
| H | -4.52391400 | 2.07133000 | 4.00719200 |
| B | -2.29611400 | -1.07401100 | -0.05462100 |
| C | 5.22476000 | -2.46357200 | 1.30100700 |
| H | 5.76458800 | -3.31608200 | 0.88510200 |
| C | 0.52898200 | -4.89452500 | -2.18313500 |
| H | 1.28536600 | -5.50936700 | -2.67508300 |
| C | 2.49133300 | 3.13395700 | -3.39347900 |
| H | 3.42696400 | 3.12895900 | -2.81527400 |
| C | 0.31841100 | 4.39259300 | -2.96460800 |
| H | 0.32411800 | 4.73323400 | -4.00111400 |
| C | -1.15608300 | 2.96651600 | 1.75811100 |
| H | -1.62772500 | 3.95782000 | 1.85744500 |
| H | -1.09618900 | 2.53517300 | 2.76878700 |
| H | -1.81026800 | 2.31782500 | 1.15499200 |
| C | -0.76617000 | 4.70185600 | -2.14892300 |
| H | -1.59880800 | 5.28626000 | -2.54629400 |
| C | -2.52424300 | -1.83992200 | -3.52058800 |
| H | -1.70069500 | -1.86549900 | -4.25176900 |
| H | -2.21388200 | -1.18254900 | -2.69479900 |
| H | -3.40919200 | -1.40366200 | -4.00983100 |
| C | 1.49448300 | -3.06599100 | 1.58034800 |
| H | 1.58419700 | -2.61710400 | 2.58035600 |
| H | 2.06426900 | -2.43284100 | 0.88141100 |
| H | 1.96390800 | -4.06221200 | 1.63033800 |
| C | 0.75605700 | -4.40897200 | -0.89910800 |
| H | 1.69606000 | -4.64031700 | -0.39751700 |
| C | -5.38811600 | 0.42769100 | -1.86171200 |
| H | -5.39332500 | -0.55283500 | -1.36600400 |
| H | -5.29263100 | 0.26196900 | -2.94597100 |
| H | -6.35760200 | 0.91832000 | -1.67582000 |
| C | 2.96489000 | 0.81979100 | 2.97671400 |
| H | 2.91178100 | 1.62512200 | 2.22958000 |
| B | 2.39935800 | 1.00736800 | -0.28825000 |
| C | 4.20040100 | -1.37897100 | 3.19425100 |
| H | 3.92972000 | -1.38653000 | 4.25304800 |
| C | -0.77295400 | -4.00788900 | 2.16446400 |
| H | -0.42689500 | -5.05343600 | 2.12009100 |
| H | -1.84815500 | -3.98772800 | 1.93353800 |
| H | -0.63513400 | -3.64593200 | 3.19528200 |
| C | 4.90489200 | -2.45092900 | 2.65694200 |

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|---|---|---|---|
| H | 5.19636600 | -3.28837300 | 3.29405500 |
| C | -4.17518600 | 2.60646700 | -2.15646900 |
| H | -5.12538300 | 3.16364100 | -2.11269200 |
| H | -3.97559600 | 2.37725700 | -3.21348200 |
| H | -3.36621400 | 3.25850500 | -1.79765100 |
| C | 5.10895200 | -1.44184200 | -1.02871600 |
| H | 5.23238800 | -0.39899700 | -1.35725600 |
| C | 1.15356500 | 3.95003500 | 1.99969400 |
| H | 2.18207700 | 3.96305900 | 1.61024300 |
| H | 1.18670100 | 3.59061100 | 3.04108800 |
| H | 0.77145200 | 4.98386800 | 2.00763900 |
| C | -3.24014400 | -4.16489600 | -4.17811900 |
| H | -4.18113700 | -3.80163400 | -4.61730600 |
| H | -3.39104000 | -5.20416300 | -3.84949100 |
| H | -2.48720500 | -4.16736200 | -4.98145200 |
| C | 2.71083100 | 4.01090500 | -4.62482500 |
| H | 1.85729600 | 3.95424700 | -5.31806400 |
| H | 3.59930200 | 3.66906600 | -5.17624600 |
| H | 2.85869400 | 5.06673000 | -4.35232300 |
| C | -2.00223000 | -0.32776600 | 3.39652700 |
| H | -1.57361500 | -0.27141600 | 2.38357300 |
| H | -1.57049700 | -1.19751400 | 3.91628900 |
| H | -1.69671800 | 0.58167700 | 3.93876200 |
| C | 3.87149700 | -2.00735500 | -1.73916700 |
| H | 3.99908900 | -1.97291300 | -2.83272600 |
| H | 2.96319400 | -1.44660100 | -1.46958500 |
| H | 3.71727700 | -3.05860600 | -1.44517000 |
| C | 6.36643800 | -2.21819600 | -1.41746800 |
| H | 6.25001000 | -3.29686000 | -1.22881200 |
| H | 7.25018500 | -1.86838700 | -0.86282800 |
| H | 6.56400000 | -2.09909600 | -2.49318600 |
| C | 3.57649600 | 1.41409500 | 4.24685500 |
| H | 2.97190900 | 2.26431200 | 4.59770200 |
| H | 4.60028400 | 1.77227200 | 4.06357400 |
| H | 3.61396300 | 0.67606000 | 5.06359500 |
| C | -4.12206700 | -0.38094300 | 4.76101100 |
| H | -3.79527100 | 0.51451100 | 5.31205200 |
| H | -3.77976300 | -1.25556100 | 5.33375000 |
| H | -5.22233400 | -0.38833500 | 4.74402600 |
| C | 1.53320700 | 0.32641000 | 3.21950000 |
| H | 1.51408800 | -0.46195500 | 3.99080800 |
| H | 1.10644300 | -0.08243300 | 2.29052300 |
| H | 0.89037800 | 1.15338800 | 3.56193900 |
| C | 2.19855800 | 1.68362800 | -3.80473800 |

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|---|---|---|---|
| H | 2.03131000 | 1.04450000 | -2.92563000 |
| H | 3.03319400 | 1.26760900 | -4.39058900 |
| H | 1.28792500 | 1.64619500 | -4.42339800 |

**TS1**

| | | | |
|---|---|---|---|
| N | 0.69781500 | 1.96236200 | 7.85609900 |
| N | 1.96108300 | 3.12576500 | 6.34144500 |
| N | 3.98918600 | 7.25041900 | 11.28599500 |
| N | 4.33317500 | 5.40005900 | 12.59312400 |
| N | 2.01081500 | 3.97511600 | 8.77182500 |
| N | 4.12117000 | 4.93832100 | 10.06357700 |
| C | 0.31027500 | 1.30296200 | 9.05104400 |
| C | -1.02617400 | 1.39551700 | 9.48796400 |
| C | 4.18246500 | 4.09525300 | 13.14712100 |
| C | 3.07245000 | 3.82814500 | 5.81233400 |
| C | 3.44885300 | 8.17931700 | 10.34871600 |
| C | 0.55292000 | 1.39159600 | 6.58567700 |
| H | -0.09683200 | 0.53517200 | 6.41694600 |
| C | 4.27334600 | 8.79225500 | 9.38717700 |
| C | 1.29944300 | 2.08218700 | 5.69212100 |
| H | 1.39170800 | 1.92612800 | 4.61993000 |
| C | -1.39610600 | 0.72998000 | 10.65997100 |
| H | -2.42678300 | 0.78454200 | 11.01415600 |
| C | 4.14759600 | 7.63729600 | 12.62095700 |
| H | 4.10480800 | 8.68473700 | 12.91043600 |
| C | 5.28945800 | 3.42980500 | 13.70613800 |
| C | 4.25856200 | 3.13031400 | 5.48991500 |
| C | 1.28095200 | 0.59603500 | 9.79364100 |
| C | 3.00193900 | 5.23043800 | 5.68738700 |
| C | -1.99690300 | 2.28090600 | 8.72389200 |
| H | -1.75941900 | 2.17641200 | 7.65471200 |
| C | -0.45715400 | 0.00402200 | 11.38934700 |
| H | -0.75813400 | -0.50942200 | 12.30516500 |
| C | 4.35661400 | 6.54591500 | 13.39226100 |
| H | 4.52473900 | 6.48759700 | 14.46569400 |
| C | 1.56489700 | 9.48810700 | 9.58828600 |
| H | 0.50368300 | 9.74215800 | 9.64435400 |
| C | 2.90262900 | 3.49140800 | 13.13052400 |
| C | 2.07770700 | 8.50357000 | 10.43723500 |
| C | 0.86641600 | -0.05233900 | 10.96361900 |
| H | 1.60107700 | -0.59965300 | 11.55661200 |
| C | 3.71781300 | 9.77139000 | 8.55693000 |
| H | 4.34900900 | 10.24842000 | 7.80374700 |
| C | 1.73099400 | 5.99164700 | 6.02545400 |

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|---|---|---|---|
| H | 1.09666000 | 5.32681600 | 6.62331400 |
| C | 5.27392600 | 5.23888300 | 4.82937700 |
| H | 6.13577900 | 5.79093200 | 4.44917400 |
| C | 5.33747600 | 3.85700300 | 4.97772700 |
| H | 6.25812400 | 3.32970200 | 4.71626900 |
| C | 2.37949700 | 10.13162300 | 8.66235400 |
| H | 1.96346900 | 10.89692100 | 8.00423800 |
| C | 1.67277900 | 4.25075900 | 12.65423800 |
| H | 1.97328400 | 4.89841600 | 11.81826500 |
| C | 4.11399100 | 5.91609700 | 5.19025300 |
| H | 4.06936800 | 7.00243200 | 5.08721400 |
| C | 4.38461000 | 1.62380000 | 5.67135500 |
| H | 3.53894600 | 1.29437500 | 6.29101600 |
| C | 5.10747200 | 2.14392300 | 14.22720000 |
| H | 5.96270500 | 1.61560700 | 14.65554800 |
| C | 5.70191900 | 8.34277800 | 9.17278700 |
| H | 5.97749700 | 7.70248500 | 10.02019700 |
| C | 2.77211100 | 2.19965200 | 13.64744500 |
| H | 1.79997300 | 1.70590500 | 13.61272700 |
| C | 6.66627100 | 4.06916700 | 13.76243100 |
| H | 6.59659800 | 5.04405300 | 13.26183400 |
| C | 3.86382900 | 1.52678700 | 14.19044600 |
| H | 3.74198800 | 0.51460600 | 14.58054600 |
| C | 1.13937800 | 7.76153600 | 11.37456500 |
| H | 1.74906200 | 7.12595900 | 12.02999300 |
| C | 2.72889600 | 0.52420200 | 9.33455300 |
| H | 2.98594900 | 1.46820000 | 8.83317800 |
| C | -3.46298800 | 1.89981300 | 8.91916200 |
| H | -3.79731200 | 2.09786600 | 9.94942600 |
| H | -3.63896400 | 0.83550400 | 8.70287200 |
| H | -4.10002500 | 2.49808800 | 8.25091400 |
| C | 6.69984500 | 9.50005900 | 9.11632900 |
| H | 6.53166100 | 10.14067800 | 8.23611900 |
| H | 7.72275500 | 9.10043400 | 9.04175600 |
| H | 6.63754300 | 10.13222000 | 10.01476800 |
| C | 2.91347100 | -0.61906800 | 8.32902600 |
| H | 3.95414100 | -0.63875600 | 7.97179500 |
| H | 2.25328700 | -0.49818700 | 7.45694200 |
| H | 2.68944100 | -1.59075700 | 8.80017800 |
| C | 1.15099000 | 5.14739700 | 13.78597900 |
| H | 0.85243800 | 4.52973100 | 14.64811000 |
| H | 0.26842800 | 5.71380500 | 13.44898700 |
| H | 1.91226800 | 5.86633400 | 14.12147900 |
| C | 0.55805800 | 3.35449800 | 12.12535900 |

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|---|---|---|---|
| H | 0.92716200 | 2.67792100 | 11.34300000 |
| H | -0.22939100 | 3.97672700 | 11.67669100 |
| H | 0.09123200 | 2.75507700 | 12.92315100 |
| C | 1.99833600 | 7.23591300 | 6.87011300 |
| H | 2.58450000 | 7.99296000 | 6.32457300 |
| H | 2.54838800 | 6.98140500 | 7.79017800 |
| H | 1.04952700 | 7.70981100 | 7.16563900 |
| C | 0.97060900 | 6.33919000 | 4.74080700 |
| H | 0.02877400 | 6.86080100 | 4.97233700 |
| H | 0.73196400 | 5.43008400 | 4.16915400 |
| H | 1.57651400 | 6.99586700 | 4.09572900 |
| B | 3.05778100 | 4.44728200 | 9.35460000 |
| C | 3.73077200 | 0.41322500 | 10.48171700 |
| H | 3.68977900 | -0.56683000 | 10.98774200 |
| H | 3.55975300 | 1.20410400 | 11.22752800 |
| H | 4.74053500 | 0.57075800 | 10.07971500 |
| C | 0.34689600 | 8.71076300 | 12.27577400 |
| H | 1.01971600 | 9.35973600 | 12.85573700 |
| H | -0.27172000 | 8.13755600 | 12.98302800 |
| H | -0.32835200 | 9.35524200 | 11.69150900 |
| B | 4.12734100 | 5.80353600 | 11.20466500 |
| C | 5.76878600 | 7.48831300 | 7.90318200 |
| H | 5.09804100 | 6.61893300 | 7.97692100 |
| H | 6.78976500 | 7.11426000 | 7.74008400 |
| H | 5.46757900 | 8.08263300 | 7.02367300 |
| B | 1.59210500 | 3.10809200 | 7.75583900 |
| C | 0.21212100 | 6.84171900 | 10.57104800 |
| H | -0.42293900 | 7.42575100 | 9.88502500 |
| H | -0.45037300 | 6.27649400 | 11.24597400 |
| H | 0.78293200 | 6.11659200 | 9.96907900 |
| C | 7.09296000 | 4.32494500 | 15.21212200 |
| H | 7.18021900 | 3.37834600 | 15.76845700 |
| H | 6.36178900 | 4.95569900 | 15.73880400 |
| H | 8.07164400 | 4.82763400 | 15.24524400 |
| C | 7.71518200 | 3.23374600 | 13.02263200 |
| H | 8.68012900 | 3.76290000 | 12.99846000 |
| H | 7.40933400 | 3.03950500 | 11.98512100 |
| H | 7.87253500 | 2.26444500 | 13.52158300 |
| C | 4.29847700 | 0.90700500 | 4.31834600 |
| H | 4.31691900 | -0.18524100 | 4.45735900 |
| H | 3.38100300 | 1.16943700 | 3.77240000 |
| H | 5.15549600 | 1.18386100 | 3.68269700 |
| C | 5.65901200 | 1.22001800 | 6.41739800 |
| H | 5.65989600 | 1.66470000 | 7.42422800 |

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|---|---|---|---|
| H | 5.70235800 | 0.12261100 | 6.50687700 |
| H | 6.56667400 | 1.53349000 | 5.87577100 |
| C | -1.76209800 | 3.74995500 | 9.10212900 |
| H | -0.70167900 | 4.02405500 | 8.99498700 |
| H | -2.36659200 | 4.41851600 | 8.46938200 |
| H | -2.05180900 | 3.91706700 | 10.15223700 |
| O | 4.93287300 | 2.87014900 | 9.01980600 |
| C | 5.34086700 | 3.74868200 | 9.84684200 |
| C | 6.59010200 | 4.53997300 | 9.43508200 |
| C | 7.13821200 | 4.29829200 | 8.17343300 |
| C | 7.24854400 | 5.42000800 | 10.29840700 |
| C | 8.32845300 | 4.91242100 | 7.78595500 |
| H | 6.60000100 | 3.61179000 | 7.51883500 |
| C | 8.43670000 | 6.04361100 | 9.91379300 |
| H | 6.82341700 | 5.62017400 | 11.28688400 |
| C | 8.98501700 | 5.78536400 | 8.65589500 |
| H | 8.74561500 | 4.71178700 | 6.79620000 |
| H | 8.93839600 | 6.73018900 | 10.59975700 |
| H | 9.91917700 | 6.26506600 | 8.35586400 |
| H | 5.45309400 | 3.44771400 | 10.92135500 |

**IN1**

| | | | |
|---|---|---|---|
| N | 0.59398700 | 2.04417900 | 7.84671200 |
| N | 2.06410300 | 3.05240300 | 6.39990800 |
| N | 3.79144700 | 7.29941000 | 11.36469900 |
| N | 4.32341100 | 5.47021000 | 12.62823400 |
| N | 2.02964000 | 3.96186000 | 8.83652200 |
| N | 4.11983100 | 5.03271600 | 10.10034700 |
| C | 0.17969500 | 1.34788500 | 9.00718100 |
| C | -1.12750300 | 1.53640700 | 9.50222700 |
| C | 4.28565100 | 4.14017600 | 13.13273900 |
| C | 3.18720200 | 3.70527200 | 5.85229400 |
| C | 3.28378300 | 8.23818200 | 10.42223300 |
| C | 0.52238900 | 1.42892000 | 6.59077200 |
| H | -0.17657000 | 0.61795100 | 6.39326100 |
| C | 4.14635000 | 8.86852300 | 9.50896300 |
| C | 1.37862100 | 2.03341500 | 5.73728200 |
| H | 1.53026000 | 1.84111600 | 4.67649500 |
| C | -1.52785800 | 0.82174600 | 10.63336900 |
| H | -2.53543500 | 0.95416500 | 11.03122400 |
| C | 3.95181500 | 7.67921700 | 12.70110100 |
| H | 3.82734200 | 8.71527400 | 13.00728800 |
| C | 5.44776300 | 3.54868500 | 13.66123000 |
| C | 4.32152800 | 2.95980300 | 5.45349000 |

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|---|---|---|---|
| C | 1.07977700 | 0.47250700 | 9.64712300 |
| C | 3.18015500 | 5.11258200 | 5.73009200 |
| C | -2.02911600 | 2.55005000 | 8.81910300 |
| H | -1.82839900 | 2.47195200 | 7.73998500 |
| C | -0.65364600 | -0.06397400 | 11.26275900 |
| H | -0.98147400 | -0.61898500 | 12.14432300 |
| C | 4.27110300 | 6.59870100 | 13.44975900 |
| H | 4.45793700 | 6.53698500 | 14.51979600 |
| C | 1.42768800 | 9.55593000 | 9.62058700 |
| H | 0.36588900 | 9.80965600 | 9.63849900 |
| C | 3.06402400 | 3.42610700 | 13.07035500 |
| C | 1.90796700 | 8.55144100 | 10.46376600 |
| C | 0.63669300 | -0.23270000 | 10.77311400 |
| H | 1.32182100 | -0.91855200 | 11.27788200 |
| C | 3.62141400 | 9.86654100 | 8.67976200 |
| H | 4.28002700 | 10.36336400 | 7.96317000 |
| C | 1.96117700 | 5.93949100 | 6.10327600 |
| H | 1.23398600 | 5.26574100 | 6.57059500 |
| C | 5.40444300 | 5.02068400 | 4.75001900 |
| H | 6.26705900 | 5.53454600 | 4.32095800 |
| C | 5.40210100 | 3.63473000 | 4.87622700 |
| H | 6.27725400 | 3.06184200 | 4.55624700 |
| C | 2.27966700 | 10.22204500 | 8.74305100 |
| H | 1.88881500 | 11.00418900 | 8.08931900 |
| C | 1.77829700 | 4.09710600 | 12.60553500 |
| H | 2.01503500 | 4.72843900 | 11.73706800 |
| C | 4.30391000 | 5.74813400 | 5.19246900 |
| H | 4.30596000 | 6.83768700 | 5.10487400 |
| C | 4.43009100 | 1.45788200 | 5.68527500 |
| H | 3.50751600 | 1.12167200 | 6.17578900 |
| C | 5.38095300 | 2.22754800 | 14.11907000 |
| H | 6.27738900 | 1.75664400 | 14.52973200 |
| C | 5.59357800 | 8.44472300 | 9.35587000 |
| H | 5.80902700 | 7.71121400 | 10.14441400 |
| C | 3.05246000 | 2.10177600 | 13.51589100 |
| H | 2.13166400 | 1.52182300 | 13.44221300 |
| C | 6.76272500 | 4.30447000 | 13.74245300 |
| H | 6.61983800 | 5.26450400 | 13.22636600 |
| C | 4.19839600 | 1.50428200 | 14.03691400 |
| H | 4.16597500 | 0.46693400 | 14.37528100 |
| C | 0.95210100 | 7.74391400 | 11.32519400 |
| H | 1.54061700 | 7.25348700 | 12.11274700 |
| C | 2.50488500 | 0.29018000 | 9.14920200 |
| H | 2.69623500 | 1.05692600 | 8.38513400 |

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|---|---|---|---|
| C | -3.51844000 | 2.30008300 | 9.04631400 |
| H | -3.80019900 | 2.47361700 | 10.09679100 |
| H | -3.80485200 | 1.27079200 | 8.78257700 |
| H | -4.11420600 | 2.99228100 | 8.43280000 |
| C | 6.56968700 | 9.61093800 | 9.52276100 |
| H | 6.43782900 | 10.36406800 | 8.72966600 |
| H | 7.60584200 | 9.24376500 | 9.46301100 |
| H | 6.43365400 | 10.11212400 | 10.49269600 |
| C | 2.68071700 | -1.07923800 | 8.48495800 |
| H | 3.70578000 | -1.18888100 | 8.09807900 |
| H | 1.98059700 | -1.19843000 | 7.64467900 |
| H | 2.49798400 | -1.89485800 | 9.20402600 |
| C | 1.22033100 | 4.98920700 | 13.72391400 |
| H | 0.96215600 | 4.37521100 | 14.60194100 |
| H | 0.30426400 | 5.49603300 | 13.38122500 |
| H | 1.93916800 | 5.75854200 | 14.03841300 |
| C | 0.71000300 | 3.11991900 | 12.13147400 |
| H | 1.09871300 | 2.44983100 | 11.35363100 |
| H | -0.12113900 | 3.68113900 | 11.68206100 |
| H | 0.29878300 | 2.51705200 | 12.95762600 |
| C | 2.29555800 | 7.02265800 | 7.12638400 |
| H | 3.01045700 | 7.75906400 | 6.72450300 |
| H | 2.72767800 | 6.57195500 | 8.03252400 |
| H | 1.38695300 | 7.57088900 | 7.42055100 |
| C | 1.31784200 | 6.53488100 | 4.84572800 |
| H | 0.40652300 | 7.09494500 | 5.10689400 |
| H | 1.04589800 | 5.74575600 | 4.12888300 |
| H | 2.00758400 | 7.22923200 | 4.33915200 |
| B | 3.32080500 | 4.11585400 | 9.21857200 |
| C | 3.52895900 | 0.51486700 | 10.26351300 |
| H | 3.44648600 | -0.24701100 | 11.05651900 |
| H | 3.39729700 | 1.50841600 | 10.71668700 |
| H | 4.54847400 | 0.47495000 | 9.85213400 |
| C | -0.10850800 | 8.60091100 | 12.01722300 |
| H | 0.34689700 | 9.42147600 | 12.59181400 |
| H | -0.69792200 | 7.98071400 | 12.70938500 |
| H | -0.81399000 | 9.03942400 | 11.29450700 |
| B | 4.04618200 | 5.87540900 | 11.25320900 |
| C | 5.78653500 | 7.74088900 | 8.00958600 |
| H | 5.11827600 | 6.87142600 | 7.92628600 |
| H | 6.82210400 | 7.38560700 | 7.90311900 |
| H | 5.56646700 | 8.42772500 | 7.17444100 |
| B | 1.60904300 | 3.12154100 | 7.81447100 |
| C | 0.30781800 | 6.63944800 | 10.47722800 |

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|---|---|---|---|
| H | -0.31661800 | 7.08047500 | 9.68195500 |
| H | -0.34159600 | 6.00517300 | 11.10235500 |
| H | 1.05001600 | 5.98322800 | 9.99104500 |
| C | 7.13062400 | 4.61258200 | 15.19800800 |
| H | 7.27325300 | 3.68146700 | 15.76897300 |
| H | 6.33909700 | 5.19134300 | 15.69560200 |
| H | 8.06648200 | 5.18986400 | 15.25020300 |
| C | 7.89801400 | 3.55167200 | 13.04198900 |
| H | 8.80826100 | 4.17017000 | 13.00892000 |
| H | 7.62787900 | 3.29203300 | 12.00846500 |
| H | 8.14514800 | 2.61999800 | 13.57446300 |
| C | 4.55964400 | 0.69060300 | 4.36630700 |
| H | 4.59483800 | -0.39423800 | 4.55120200 |
| H | 3.71077700 | 0.89870200 | 3.69812000 |
| H | 5.48218200 | 0.97098400 | 3.83295800 |
| C | 5.58299600 | 1.12813500 | 6.63946800 |
| H | 5.42880200 | 1.63590400 | 7.60261500 |
| H | 5.63589800 | 0.04106800 | 6.81197000 |
| H | 6.55383600 | 1.44772300 | 6.22579500 |
| C | -1.64077700 | 3.97019300 | 9.25130800 |
| H | -0.55792900 | 4.14233100 | 9.14275100 |
| H | -2.18198900 | 4.72130800 | 8.65425500 |
| H | -1.90831100 | 4.12341400 | 10.31000900 |
| O | 4.48721000 | 3.28048400 | 8.97249900 |
| C | 5.20440000 | 4.06823400 | 9.88832500 |
| C | 6.48559000 | 4.64340600 | 9.32026200 |
| C | 6.83975200 | 4.40601200 | 7.99187800 |
| C | 7.33190100 | 5.41316800 | 10.12564000 |
| C | 8.03829500 | 4.90741900 | 7.48243200 |
| H | 6.15627200 | 3.83046800 | 7.36718200 |
| C | 8.52694800 | 5.92025100 | 9.61712600 |
| H | 7.04683900 | 5.61476100 | 11.16255000 |
| C | 8.88893900 | 5.65860300 | 8.29329500 |
| H | 8.30044000 | 4.71312200 | 6.43992400 |
| H | 9.17952600 | 6.51912200 | 10.25602100 |
| H | 9.82767100 | 6.04891500 | 7.89515100 |
| H | 5.45136900 | 3.48991300 | 10.80522200 |

**TS2**

| | | | |
|---|---|---|---|
| N | 0.45559600 | 1.81853700 | 7.55503600 |
| N | 1.68129700 | 3.22460500 | 6.22390100 |
| N | 3.46708900 | 7.32044500 | 11.31034800 |
| N | 4.03782900 | 5.67246400 | 12.81358600 |
| N | 2.28433700 | 3.16303200 | 8.72341100 |

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|---|---|---|---|
| N | 4.38458100 | 5.15085400 | 10.27386600 |
| C | -0.02730300 | 1.02878400 | 8.62992800 |
| C | -1.28629900 | 1.32421300 | 9.19004600 |
| C | 4.39390500 | 4.47014000 | 13.46820200 |
| C | 2.82131300 | 3.87180500 | 5.67195400 |
| C | 3.10499500 | 8.11574500 | 10.19767900 |
| C | 0.02301100 | 1.70243100 | 6.22966200 |
| H | -0.79224300 | 1.03760100 | 5.95146500 |
| C | 4.09445700 | 8.54486500 | 9.28452400 |
| C | 0.76002200 | 2.52249500 | 5.44165200 |
| H | 0.69533200 | 2.67431300 | 4.36636300 |
| C | -1.75229800 | 0.53796400 | 10.24801700 |
| H | -2.72655800 | 0.74831600 | 10.69157700 |
| C | 3.28178900 | 7.77915600 | 12.61830200 |
| H | 2.93508700 | 8.79045200 | 12.82074300 |
| C | 5.60464700 | 4.40631400 | 14.19308600 |
| C | 3.98695800 | 3.11739500 | 5.43853000 |
| C | 0.78088100 | -0.00369700 | 9.15358900 |
| C | 2.77581400 | 5.25154300 | 5.38710900 |
| C | -2.04346300 | 2.55544400 | 8.72351300 |
| H | -1.87990900 | 2.65986900 | 7.64094200 |
| C | -0.97575200 | -0.49691500 | 10.75944700 |
| H | -1.34624500 | -1.09700900 | 11.59275800 |
| C | 3.62543700 | 6.81654200 | 13.50212500 |
| H | 3.59593700 | 6.85011600 | 14.58968200 |
| C | 1.42237900 | 9.35884500 | 8.98127900 |
| H | 0.38708700 | 9.67233400 | 8.84227700 |
| C | 3.55675100 | 3.33848500 | 13.34362500 |
| C | 1.75186100 | 8.49532500 | 10.03062000 |
| C | 0.28277400 | -0.75391000 | 10.22383000 |
| H | 0.89154000 | -1.55043200 | 10.65256800 |
| C | 3.70994700 | 9.37982400 | 8.22959200 |
| H | 4.45900900 | 9.71765300 | 7.51231400 |
| C | 1.53666600 | 6.05063400 | 5.74161700 |
| H | 0.66763000 | 5.40979200 | 5.52257900 |
| C | 5.06400900 | 5.11847800 | 4.58872100 |
| H | 5.94224000 | 5.60881100 | 4.16285300 |
| C | 5.10131800 | 3.76287400 | 4.89158900 |
| H | 6.01829600 | 3.19360600 | 4.71979600 |
| C | 2.39120700 | 9.80146900 | 8.08635600 |
| H | 2.11451100 | 10.46501800 | 7.26442000 |
| C | 2.23506400 | 3.43244700 | 12.59518500 |
| H | 2.40949700 | 4.05715700 | 11.70677700 |
| C | 3.91052100 | 5.85794500 | 4.84245200 |

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|---|---|---|---|
| H | 3.89647000 | 6.92493900 | 4.61648400 |
| C | 4.06710100 | 1.63739800 | 5.77439700 |
| H | 3.08707100 | 1.32726300 | 6.16479400 |
| C | 5.95240500 | 3.20052200 | 14.80900800 |
| H | 6.88116000 | 3.12822900 | 15.37657500 |
| C | 5.54580200 | 8.13865400 | 9.48280700 |
| H | 5.52984900 | 7.07025100 | 9.74626800 |
| C | 3.95789000 | 2.14733500 | 13.95614200 |
| H | 3.33467200 | 1.25783400 | 13.85818400 |
| C | 6.54938400 | 5.60095300 | 14.20217800 |
| H | 5.94132900 | 6.50947800 | 14.32435500 |
| C | 5.13898000 | 2.07707800 | 14.68832400 |
| H | 5.43180000 | 1.13842500 | 15.16297200 |
| C | 0.67474600 | 7.89363000 | 10.92472400 |
| H | 1.02974600 | 7.93542600 | 11.96366900 |
| C | 2.15051600 | -0.29435900 | 8.55727500 |
| H | 2.62145500 | 0.67871400 | 8.35669900 |
| C | -3.55015800 | 2.48322700 | 8.96401500 |
| H | -3.78994700 | 2.51469400 | 10.03801700 |
| H | -3.98660600 | 1.56494300 | 8.54336000 |
| H | -4.04614300 | 3.34663300 | 8.49680700 |
| C | 6.17351600 | 8.91503500 | 10.64728300 |
| H | 6.18122800 | 9.99644500 | 10.43194700 |
| H | 7.21356100 | 8.58985700 | 10.80636000 |
| H | 5.61801700 | 8.75090200 | 11.58194200 |
| C | 2.02293300 | -1.04414100 | 7.22556500 |
| H | 3.01934300 | -1.21214100 | 6.78647700 |
| H | 1.42317200 | -0.47815700 | 6.49871200 |
| H | 1.54621500 | -2.02535800 | 7.38204500 |
| C | 1.18910600 | 4.14815400 | 13.45929700 |
| H | 1.02622900 | 3.59573700 | 14.39902300 |
| H | 0.22866600 | 4.20511600 | 12.92442700 |
| H | 1.50815800 | 5.17177500 | 13.70600800 |
| C | 1.70169200 | 2.08704700 | 12.10470100 |
| H | 2.47132100 | 1.54044300 | 11.53954000 |
| H | 0.84559900 | 2.24358100 | 11.42980800 |
| H | 1.35845300 | 1.45116300 | 12.93739900 |
| C | 1.53080000 | 6.35283900 | 7.24433500 |
| H | 2.39324800 | 6.98351900 | 7.51362000 |
| H | 1.59746100 | 5.43727300 | 7.84808800 |
| H | 0.61613500 | 6.90138300 | 7.51770500 |
| C | 1.39270700 | 7.34525600 | 4.94341400 |
| H | 0.41395900 | 7.80307600 | 5.14979000 |
| H | 1.47482500 | 7.17489100 | 3.85903300 |

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|---|---|---|---|
| H | 2.15796900 | 8.07927500 | 5.24036700 |
| B | 3.32192000 | 3.20677000 | 9.47207800 |
| C | 3.08297900 | -1.04673100 | 9.50455500 |
| H | 2.74941600 | -2.08358600 | 9.67146900 |
| H | 3.15867200 | -0.54241300 | 10.47851500 |
| H | 4.09224500 | -1.08963600 | 9.07037100 |
| C | -0.65794400 | 8.63842300 | 10.87211200 |
| H | -0.53825000 | 9.71142200 | 11.08521100 |
| H | -1.35018700 | 8.21492300 | 11.61464900 |
| H | -1.13696800 | 8.53699600 | 9.88566600 |
| B | 3.99730300 | 5.93577100 | 11.35437400 |
| C | 6.39780200 | 8.28331500 | 8.22329500 |
| H | 5.93161600 | 7.78000100 | 7.36213600 |
| H | 7.38244700 | 7.82120400 | 8.38823600 |
| H | 6.56517600 | 9.34010200 | 7.95607800 |
| B | 1.53510600 | 2.79517800 | 7.60886400 |
| C | 0.46367300 | 6.41294700 | 10.58063000 |
| H | 0.00403200 | 6.31739600 | 9.58697100 |
| H | -0.20732900 | 5.93943200 | 11.31363300 |
| H | 1.41178600 | 5.85394000 | 10.56004700 |
| C | 7.56293500 | 5.56732600 | 15.34530900 |
| H | 8.30035200 | 4.76139500 | 15.20655800 |
| H | 7.07437900 | 5.41804100 | 16.31977900 |
| H | 8.12001500 | 6.51507700 | 15.37997500 |
| C | 7.27376500 | 5.72300100 | 12.85368800 |
| H | 7.96322500 | 6.58136200 | 12.86447200 |
| H | 6.56597700 | 5.86735300 | 12.02439500 |
| H | 7.85991200 | 4.81282500 | 12.64809900 |
| C | 4.34119700 | 0.79883100 | 4.52222500 |
| H | 4.34317600 | -0.27384000 | 4.77025400 |
| H | 3.57277200 | 0.97355200 | 3.75467700 |
| H | 5.32212400 | 1.04374800 | 4.08513300 |
| C | 5.10957400 | 1.36969600 | 6.86517800 |
| H | 4.88079000 | 1.92116000 | 7.78868000 |
| H | 5.14048400 | 0.29487900 | 7.10745400 |
| H | 6.11895900 | 1.67565500 | 6.54387100 |
| C | -1.44193100 | 3.79354100 | 9.40220100 |
| H | -0.35556100 | 3.85570000 | 9.23767600 |
| H | -1.90636500 | 4.71665900 | 9.02205500 |
| H | -1.61221200 | 3.74582100 | 10.49020000 |
| O | 4.37285100 | 2.82790000 | 10.18747400 |
| C | 5.20368800 | 4.03570500 | 10.42860400 |
| C | 6.34711600 | 3.94634300 | 9.42007100 |
| C | 6.31452300 | 4.68571300 | 8.23599800 |

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|---|---|---|---|
| C | 7.42112000 | 3.08321400 | 9.65795500 |
| C | 7.35514700 | 4.57532000 | 7.31248600 |
| H | 5.45854400 | 5.34516900 | 8.06814300 |
| C | 8.45741200 | 2.96586000 | 8.73315000 |
| H | 7.43478700 | 2.49774400 | 10.58166100 |
| C | 8.42837900 | 3.71785100 | 7.55712100 |
| H | 7.32271200 | 5.16377100 | 6.39359400 |
| H | 9.29303400 | 2.29101500 | 8.93087600 |
| H | 9.24311900 | 3.63682900 | 6.83435900 |
| H | 5.63218600 | 3.84893800 | 11.43191200 |

**IN2**

| | | | |
|---|---|---|---|
| O | 12.03478100 | 10.01509200 | 10.30164100 |
| N | 12.48609000 | 7.55076300 | 10.91495300 |
| N | 10.35774800 | 6.35934600 | 11.80642400 |
| N | 12.36467900 | 5.30031000 | 12.14887400 |
| C | 8.05718400 | 9.24609100 | 11.46522600 |
| H | 7.89633700 | 10.23305400 | 11.90076300 |
| C | 9.30886900 | 7.18675400 | 11.34447800 |
| C | 7.21160600 | 8.79657500 | 10.45677400 |
| H | 6.38671000 | 9.42509600 | 10.11480100 |
| C | 13.72196200 | 4.93835500 | 12.29210800 |
| C | 8.49621000 | 6.74765600 | 10.27620800 |
| C | 9.11343700 | 8.45475100 | 11.92791900 |
| C | 7.43583500 | 7.55765000 | 9.86185800 |
| H | 6.78939200 | 7.22995300 | 9.04601800 |
| C | 15.65200100 | 4.57733700 | 13.70377600 |
| H | 16.13366800 | 4.61154200 | 14.68233100 |
| B | 11.80720300 | 6.53262100 | 11.54333600 |
| B | 12.22455200 | 8.82349300 | 10.58357300 |
| C | 14.32946000 | 5.00859300 | 13.56465900 |
| C | 10.14439400 | 5.16160300 | 12.48861500 |
| H | 9.14593000 | 4.83735100 | 12.77722300 |
| C | 16.37390600 | 4.12881700 | 12.60149700 |
| H | 17.40809200 | 3.79960700 | 12.72236900 |
| C | 8.87344700 | 5.48599600 | 9.51650900 |
| H | 9.24289800 | 4.74731400 | 10.24294100 |
| C | 11.32898600 | 4.54243400 | 12.70314600 |
| H | 11.52116600 | 3.59742100 | 13.20793800 |
| C | 14.45810400 | 4.52873200 | 11.16050800 |
| C | 10.00696300 | 8.91793700 | 13.06635800 |
| C | 10.18853400 | 10.43357100 | 13.11262400 |
| H | 9.25321700 | 10.95688600 | 13.37103800 |
| H | 10.56650400 | 10.79097300 | 12.14331200 |

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|---|---|---|---|
| H | 10.92938200 | 10.69074900 | 13.88512300 |
| C | 15.78578500 | 4.12685400 | 11.33970500 |
| H | 16.37304300 | 3.80519400 | 10.47864700 |
| C | 12.79904400 | 3.36802000 | 9.66329100 |
| H | 12.32596600 | 3.37803800 | 8.66905200 |
| H | 12.00528500 | 3.43488400 | 10.42055400 |
| H | 13.31765400 | 2.40250600 | 9.78428000 |
| C | 13.79511200 | 4.52715000 | 9.79214200 |
| H | 13.24237900 | 5.47754500 | 9.72358400 |
| C | 14.79258900 | 4.49560000 | 8.63612800 |
| H | 15.32406700 | 3.53135700 | 8.57888300 |
| H | 15.53955000 | 5.29725600 | 8.72782400 |
| H | 14.26011600 | 4.63444700 | 7.68378600 |
| C | 13.62344600 | 7.19747600 | 14.50906800 |
| H | 14.65612200 | 7.56274800 | 14.62931500 |
| H | 12.98806900 | 7.70606800 | 15.25124300 |
| H | 13.28646000 | 7.47849000 | 13.49975000 |
| C | 13.58314800 | 5.67469700 | 14.70961500 |
| C | 14.10581400 | 5.29697900 | 16.09411900 |
| H | 14.13780400 | 4.20588100 | 16.23499400 |
| H | 13.45480200 | 5.72560600 | 16.87047800 |
| H | 15.11911300 | 5.69279200 | 16.26572300 |
| C | 10.03180200 | 5.81225100 | 8.56225900 |
| H | 10.38568800 | 4.90243000 | 8.05232400 |
| H | 10.87513500 | 6.27127700 | 9.10035400 |
| H | 9.69469900 | 6.53003400 | 7.79743000 |
| C | 7.71100700 | 4.84921700 | 8.75688400 |
| H | 6.84490400 | 4.67108400 | 9.41209600 |
| H | 8.02468500 | 3.88500500 | 8.32975200 |
| H | 7.37980900 | 5.48278800 | 7.91929300 |
| C | 9.49087700 | 8.35761300 | 14.39645800 |
| H | 10.15264700 | 8.65348900 | 15.22567200 |
| H | 9.44689400 | 7.25845100 | 14.36645100 |
| H | 8.47887300 | 8.73897200 | 14.61069500 |
| H | 12.52958200 | 5.36461700 | 14.65428700 |
| H | 11.00063300 | 8.48606600 | 12.88647700 |

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|---|---|---|---|
| N | 3.16497200 | 6.04311000 | 5.63085300 |
| N | 3.40439400 | 6.16717000 | 3.36415700 |
| N | 4.28436600 | 8.18723000 | 4.77463000 |
| C | 2.93538600 | 6.38827800 | 6.99478700 |
| C | 2.61125100 | 4.90528100 | 5.04497400 |
| H | 2.14680200 | 4.12663500 | 5.64513900 |

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|---|---|---|---|
| C | 2.75571300 | 4.97619200 | 3.69868700 |
| H | 2.44025800 | 4.26881700 | 2.93519600 |
| C | 3.62855500 | 6.57899300 | 2.02031800 |
| C | 5.13295900 | 8.68630500 | 3.97210600 |
| H | 5.52961800 | 8.12932200 | 3.09830900 |
| C | 1.81649700 | 7.18249900 | 7.30551000 |
| C | 2.88295900 | 7.66530700 | 1.50565500 |
| C | 5.04427400 | 5.11661800 | 7.60393200 |
| H | 4.77390600 | 4.51506200 | 6.72269100 |
| C | 3.81723500 | 5.92539400 | 7.98931600 |
| C | 4.60360600 | 5.92332000 | 1.24779400 |
| C | 1.81470200 | 8.34980800 | 2.34809600 |
| H | 2.20950900 | 8.45123600 | 3.36983000 |
| C | 5.66744400 | 10.05665700 | 4.11467700 |
| C | 6.50840500 | 10.57677000 | 3.12521700 |
| H | 6.76370700 | 9.95861900 | 2.26073200 |
| C | 5.45169400 | 4.79328100 | 1.80883000 |
| H | 5.18979700 | 4.66899900 | 2.86858500 |
| C | 3.13678800 | 8.06912700 | 0.19322900 |
| H | 2.58403700 | 8.90829400 | -0.22892600 |
| C | 1.60515700 | 7.52579900 | 8.64526000 |
| H | 0.74954900 | 8.15000900 | 8.91125000 |
| C | 4.80565100 | 6.35117800 | -0.07003900 |
| H | 5.55270600 | 5.84792900 | -0.68802800 |
| C | 0.87338200 | 7.69042500 | 6.22594800 |
| H | 1.09808600 | 7.14313500 | 5.29802100 |
| C | 5.33265700 | 10.84349900 | 5.22528500 |
| H | 4.68086500 | 10.41170400 | 5.98689000 |
| C | 3.56141500 | 6.28315700 | 9.31529400 |
| H | 4.22678100 | 5.93672200 | 10.10700900 |
| C | 5.83467900 | 12.13470600 | 5.33799700 |
| H | 5.57712100 | 12.74615600 | 6.20415900 |
| C | 4.08274500 | 7.41436000 | -0.59413500 |
| H | 4.25738400 | 7.74227000 | -1.62003000 |
| C | 6.67138100 | 12.65153200 | 4.34395000 |
| H | 7.06311400 | 13.66595200 | 4.43542300 |
| C | 7.00792200 | 11.87315000 | 3.23730600 |
| H | 7.66044400 | 12.27686900 | 2.46189100 |
| C | 2.46674100 | 7.08056000 | 9.64153200 |
| H | 2.28420300 | 7.35386200 | 10.68209900 |
| C | 0.54915100 | 7.48589700 | 2.42627000 |
| H | 0.10734500 | 7.36285000 | 1.42524400 |
| H | -0.20077000 | 7.96391600 | 3.07585100 |
| H | 0.76436600 | 6.48768400 | 2.83304000 |

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|---|---|---|---|
| C | 1.11705700 | 9.17992200 | 5.95538700 |
| H | 0.88893700 | 9.77883500 | 6.85142200 |
| H | 0.46939400 | 9.53411800 | 5.13763700 |
| H | 2.16595300 | 9.35871000 | 5.67711900 |
| C | -0.59448900 | 7.42199100 | 6.56614200 |
| H | -0.76767400 | 6.35638400 | 6.77382700 |
| H | -1.23882600 | 7.71808000 | 5.72488100 |
| H | -0.91851900 | 7.99760600 | 7.44643700 |
| C | 5.51161200 | 4.15916300 | 8.69911200 |
| H | 5.92455100 | 4.70271600 | 9.56232600 |
| H | 6.31073300 | 3.50951200 | 8.31417100 |
| H | 4.69115400 | 3.52099700 | 9.05779600 |
| C | 6.94435000 | 5.13203700 | 1.74154300 |
| H | 7.28557800 | 5.23712900 | 0.70045200 |
| H | 7.54002000 | 4.33439400 | 2.20931000 |
| H | 7.16256300 | 6.07378600 | 2.26565400 |
| C | 6.17954400 | 6.06166300 | 7.18941700 |
| H | 5.86241800 | 6.73662100 | 6.38216500 |
| H | 7.05665800 | 5.49159100 | 6.84771500 |
| H | 6.48452800 | 6.68345000 | 8.04531300 |
| C | 1.47257600 | 9.75913300 | 1.86900500 |
| H | 2.37379100 | 10.38099100 | 1.76619200 |
| H | 0.80491900 | 10.24495700 | 2.59482100 |
| H | 0.94791500 | 9.74556000 | 0.90134600 |
| B | 3.69186100 | 6.87857300 | 4.58692100 |
| C | 5.15674100 | 3.47137600 | 1.09315600 |
| H | 4.09271300 | 3.20503600 | 1.16801900 |
| H | 5.74819800 | 2.65343700 | 1.53027200 |
| H | 5.41053500 | 3.53778600 | 0.02383000 |

**TS3**

| | | | |
|---|---|---|---|
| O | 11.34381400 | 9.49350400 | 9.61756700 |
| O | 14.29141900 | 9.30411400 | 10.64231400 |
| N | 12.58194000 | 7.60594700 | 10.92222700 |
| N | 10.49384100 | 6.08345800 | 11.00272600 |
| C | 14.11699000 | 8.29250300 | 11.37457800 |
| N | 12.38879100 | 5.21301200 | 11.95619800 |
| C | 13.96088200 | 8.57016000 | 12.87288700 |
| C | 7.93867200 | 8.64907700 | 10.19342900 |
| H | 7.49638500 | 9.54583500 | 10.62892200 |
| C | 9.50443000 | 6.82355200 | 10.29922200 |
| C | 13.05680900 | 9.55018300 | 13.30234900 |
| H | 12.42428500 | 10.03590800 | 12.55323800 |
| C | 7.50579500 | 8.20830600 | 8.94848600 |

| | | | |
|---|---|---|---|
| H | 6.71815800 | 8.75010400 | 8.42115200 |
| C | 13.63017800 | 4.97906500 | 12.59761100 |
| C | 9.11695700 | 6.39760300 | 9.01161100 |
| C | 8.94255600 | 7.97048000 | 10.88914800 |
| C | 8.09884800 | 7.09605100 | 8.35794100 |
| H | 7.77617400 | 6.78166500 | 7.36450300 |
| C | 14.93521700 | 4.61293500 | 14.58830400 |
| H | 15.02103400 | 4.52471200 | 15.67045200 |
| C | 12.98940000 | 9.91073500 | 14.64459300 |
| H | 12.27555900 | 10.67134900 | 14.96999100 |
| B | 11.89792600 | 6.41063100 | 11.26451900 |
| B | 12.00620600 | 8.64812900 | 10.19985800 |
| C | 13.68550700 | 4.85711900 | 14.00621900 |
| C | 10.22400300 | 4.80695800 | 11.50080900 |
| H | 9.24014000 | 4.35529400 | 11.39324000 |
| C | 16.08744800 | 4.50337900 | 13.81613000 |
| H | 17.05071700 | 4.32668900 | 14.29861700 |
| C | 14.80896700 | 7.97915200 | 13.80675700 |
| H | 15.51971400 | 7.21809300 | 13.47168800 |
| C | 9.88417400 | 5.28374900 | 8.31543100 |
| H | 10.12579100 | 4.51436800 | 9.06373100 |
| C | 11.33806200 | 4.29546900 | 12.06630500 |
| H | 11.48443700 | 3.32116100 | 12.52567500 |
| C | 14.78822100 | 4.85489300 | 11.79980100 |
| C | 13.84535300 | 9.31273900 | 15.57850900 |
| H | 13.79775200 | 9.60201300 | 16.63059500 |
| C | 9.41130500 | 8.44960200 | 12.25256900 |
| C | 9.35102700 | 9.96877100 | 12.40154200 |
| H | 8.31470800 | 10.34102100 | 12.44600900 |
| H | 9.87106900 | 10.44458200 | 11.55689200 |
| H | 9.84689300 | 10.26718100 | 13.33786500 |
| C | 16.01337700 | 4.62644600 | 12.43276200 |
| H | 16.92248200 | 4.54210700 | 11.83688100 |
| C | 14.75740100 | 8.34875900 | 15.15504500 |
| H | 15.43163900 | 7.87575200 | 15.87363800 |
| C | 14.08149900 | 3.60924300 | 9.74129700 |
| H | 13.97753800 | 3.66050200 | 8.64651300 |
| H | 13.08768800 | 3.41781000 | 10.17041300 |
| H | 14.73619100 | 2.75680900 | 9.98480700 |
| C | 14.68020600 | 4.91421200 | 10.28230000 |
| H | 13.98893200 | 5.73270300 | 10.03449800 |
| C | 16.00416800 | 5.22479900 | 9.58806300 |
| H | 16.72551800 | 4.39818800 | 9.69193200 |
| H | 16.45948600 | 6.14215100 | 9.98880200 |

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|---|---|---|---|
| H | 15.83007200 | 5.37737900 | 8.51329200 |
| C | 11.71809100 | 6.34636400 | 14.72290700 |
| H | 12.39771200 | 7.17936300 | 14.94940700 |
| H | 10.87158100 | 6.38925400 | 15.42562300 |
| H | 11.31525900 | 6.49650900 | 13.71397200 |
| C | 12.43298600 | 4.99522200 | 14.87541600 |
| C | 12.70548500 | 4.74183600 | 16.35860900 |
| H | 13.17090100 | 3.76166500 | 16.53822900 |
| H | 11.75863700 | 4.77518200 | 16.91632300 |
| H | 13.36349200 | 5.52079300 | 16.77508300 |
| C | 11.21202500 | 5.84083500 | 7.78285300 |
| H | 11.80581900 | 5.04436100 | 7.30762400 |
| H | 11.81117100 | 6.28968200 | 8.58800300 |
| H | 11.01999000 | 6.62830900 | 7.03802200 |
| C | 9.10064400 | 4.60487700 | 7.19304500 |
| H | 8.11337200 | 4.26037100 | 7.53565000 |
| H | 9.65956400 | 3.73436700 | 6.81897100 |
| H | 8.94806400 | 5.28398600 | 6.34009100 |
| C | 8.63609200 | 7.73556300 | 13.36473200 |
| H | 9.00190200 | 8.05112900 | 14.35414400 |
| H | 8.75462300 | 6.64391200 | 13.28826800 |
| H | 7.56162600 | 7.97232400 | 13.29786700 |
| H | 14.77451100 | 7.39277700 | 11.24588500 |
| H | 10.46992100 | 8.17107700 | 12.35374400 |
| H | 11.72304100 | 4.22033200 | 14.54487300 |

**IN3**

| | | | |
|---|---|---|---|
| O | 11.28738700 | 9.51740000 | 9.80386600 |
| O | 13.64116200 | 9.45523000 | 10.69655200 |
| N | 12.57552700 | 7.69287300 | 11.14509000 |
| N | 10.56510500 | 6.11827300 | 11.05743200 |
| C | 13.85841700 | 8.29631200 | 11.46176400 |
| N | 12.42844300 | 5.28111600 | 12.11208400 |
| C | 14.06119500 | 8.64213600 | 12.92874300 |
| C | 7.97432000 | 8.58017100 | 10.06367100 |
| H | 7.47487500 | 9.46550200 | 10.45852200 |
| C | 9.60335600 | 6.82592600 | 10.28226900 |
| C | 13.21440400 | 9.58776200 | 13.52183700 |
| H | 12.42990500 | 10.04221800 | 12.91095100 |
| C | 7.62520800 | 8.10261600 | 8.80565800 |
| H | 6.84117200 | 8.60022600 | 8.23101200 |
| C | 13.69453200 | 5.05728400 | 12.69909600 |
| C | 9.31752100 | 6.37744000 | 8.97788900 |
| C | 8.97021800 | 7.95885500 | 10.82000600 |

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|---|---|---|---|
| C | 8.30513400 | 7.01832300 | 8.25908300 |
| H | 8.05946900 | 6.68365900 | 7.25004600 |
| C | 15.07612900 | 4.70089300 | 14.64446600 |
| H | 15.19383300 | 4.60476200 | 15.72393700 |
| C | 13.39066000 | 9.95403100 | 14.85207000 |
| H | 12.72760300 | 10.69469300 | 15.30404800 |
| B | 11.93472100 | 6.47400900 | 11.41753100 |
| B | 12.28361900 | 9.00481800 | 10.37983800 |
| C | 13.80764600 | 4.93123000 | 14.10250600 |
| C | 10.30590900 | 4.82894900 | 11.52524400 |
| H | 9.33949300 | 4.35683200 | 11.36050100 |
| C | 16.20206000 | 4.60995800 | 13.83091000 |
| H | 17.18404400 | 4.43852600 | 14.27627000 |
| C | 15.08143000 | 8.07400800 | 13.68818000 |
| H | 15.73971800 | 7.33120700 | 13.23014200 |
| C | 10.21009900 | 5.33237900 | 8.32712700 |
| H | 10.47179700 | 4.57872000 | 9.08499200 |
| C | 11.39472700 | 4.33345700 | 12.15370100 |
| H | 11.53612600 | 3.35673900 | 12.61042100 |
| C | 14.82763900 | 4.96018600 | 11.86060500 |
| C | 14.41993500 | 9.38322000 | 15.60949600 |
| H | 14.55967300 | 9.67474200 | 16.65261700 |
| C | 9.36812200 | 8.48252700 | 12.18790000 |
| C | 9.20368000 | 9.99549000 | 12.30897900 |
| H | 8.14452000 | 10.30180900 | 12.30909000 |
| H | 9.73306100 | 10.47396500 | 11.47151300 |
| H | 9.64084200 | 10.34188000 | 13.25895800 |
| C | 16.07692900 | 4.74247100 | 12.45142700 |
| H | 16.96640900 | 4.67076600 | 11.82467600 |
| C | 15.26200100 | 8.44012700 | 15.02558600 |
| H | 16.06430800 | 7.98134600 | 15.60791700 |
| C | 14.04855000 | 3.73159600 | 9.81543000 |
| H | 13.92561400 | 3.78647200 | 8.72301400 |
| H | 13.06070800 | 3.54790400 | 10.26080800 |
| H | 14.70134200 | 2.87402800 | 10.04579400 |
| C | 14.66886600 | 5.03012000 | 10.34805800 |
| H | 13.96731300 | 5.84824000 | 10.12769400 |
| C | 15.97020200 | 5.33742200 | 9.60999800 |
| H | 16.68304100 | 4.49957300 | 9.67391600 |
| H | 16.45978300 | 6.23852700 | 10.00822100 |
| H | 15.75852300 | 5.51024200 | 8.54508000 |
| C | 12.06437400 | 6.53718700 | 14.99149900 |
| H | 12.82640300 | 7.22040700 | 15.39435400 |
| H | 11.16080100 | 6.61372800 | 15.61588100 |

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|---|---|---|---|
| H | 11.80762000 | 6.88010000 | 13.98008000 |
| C | 12.58173300 | 5.09246400 | 14.99469000 |
| C | 12.81490100 | 4.63073700 | 16.43236200 |
| H | 13.20573100 | 3.60319100 | 16.47972900 |
| H | 11.86778800 | 4.66414100 | 16.99009300 |
| H | 13.52435700 | 5.29366200 | 16.95206300 |
| C | 11.51181200 | 6.01561800 | 7.88253600 |
| H | 12.22091100 | 5.28061700 | 7.46864100 |
| H | 11.98762200 | 6.54609200 | 8.72030100 |
| H | 11.29439700 | 6.76940000 | 7.11031400 |
| C | 9.55777300 | 4.60000800 | 7.15596100 |
| H | 8.58728400 | 4.16445000 | 7.43799900 |
| H | 10.21308200 | 3.78749900 | 6.80773200 |
| H | 9.39312100 | 5.27395200 | 6.30112600 |
| C | 8.62466700 | 7.72810600 | 13.29515400 |
| H | 8.94506900 | 8.08109800 | 14.28828400 |
| H | 8.82223900 | 6.64667600 | 13.23622900 |
| H | 7.53685000 | 7.88468700 | 13.20788100 |
| H | 14.73731400 | 7.71370700 | 11.11176200 |
| H | 10.44190900 | 8.28122200 | 12.30031300 |
| H | 11.78334300 | 4.46310900 | 14.57378000 |

**TS4**

| | | | |
|---|---|---|---|
| O | 11.23153600 | 10.52323500 | 10.53472800 |
| O | 13.60183800 | 9.68715400 | 10.48560600 |
| N | 12.75685500 | 7.27301600 | 11.17952900 |
| N | 10.61701900 | 5.85407300 | 11.11491000 |
| C | 13.77659500 | 8.02004900 | 11.41062800 |
| N | 12.44250200 | 4.95297200 | 12.19413700 |
| C | 14.00202400 | 8.56567500 | 12.79825400 |
| C | 8.26998800 | 8.58593900 | 10.23223500 |
| H | 7.86248000 | 9.50072500 | 10.66137600 |
| C | 9.70456400 | 6.65669700 | 10.38404100 |
| C | 13.07955400 | 9.41736300 | 13.41907900 |
| H | 12.20664100 | 9.76659300 | 12.86004800 |
| C | 7.91000000 | 8.21761000 | 8.94049900 |
| H | 7.20844900 | 8.83385500 | 8.37459600 |
| C | 13.68595400 | 4.76894700 | 12.83675700 |
| C | 9.38853200 | 6.30133800 | 9.05581600 |
| C | 9.15873400 | 7.81065400 | 10.98277200 |
| C | 8.46668400 | 7.08372700 | 8.35562800 |
| H | 8.19971800 | 6.82278800 | 7.33029600 |
| C | 15.00643300 | 4.58046500 | 14.85262300 |
| H | 15.08070000 | 4.55073400 | 15.94022800 |

| | | | |
|---|---|---|---|
| C | 13.28556300 | 9.83031200 | 14.73229500 |
| H | 12.56814400 | 10.50586400 | 15.20276300 |
| B | 12.00254600 | 6.16798500 | 11.47600600 |
| B | 12.39571700 | 10.10938600 | 10.47488700 |
| C | 13.75449500 | 4.72836900 | 14.24765800 |
| C | 10.31324900 | 4.57091300 | 11.57713800 |
| H | 9.33318000 | 4.12758300 | 11.41169600 |
| C | 16.16721500 | 4.49638800 | 14.09014300 |
| H | 17.13708900 | 4.39220100 | 14.58073200 |
| C | 15.11400200 | 8.12271600 | 13.51598700 |
| H | 15.82074600 | 7.43734500 | 13.03933400 |
| C | 10.14585200 | 5.16978500 | 8.37818600 |
| H | 10.29754800 | 4.36973500 | 9.11772000 |
| C | 11.37838300 | 4.04426800 | 12.22546800 |
| H | 11.47275600 | 3.06581000 | 12.69202100 |
| C | 14.85916200 | 4.68269500 | 12.05125500 |
| C | 14.40215400 | 9.38687600 | 15.44800000 |
| H | 14.55674300 | 9.71054700 | 16.47937400 |
| C | 9.52136900 | 8.17629800 | 12.41402700 |
| C | 9.19016600 | 9.62136500 | 12.77944600 |
| H | 8.10053000 | 9.78817000 | 12.82156100 |
| H | 9.64844400 | 10.31036500 | 12.05606400 |
| H | 9.59088700 | 9.84228400 | 13.78161800 |
| C | 16.09080600 | 4.55244600 | 12.70177400 |
| H | 17.00773000 | 4.49054000 | 12.11467900 |
| C | 15.31143800 | 8.52463900 | 14.83933700 |
| H | 16.17879300 | 8.15770900 | 15.39227700 |
| C | 14.17516600 | 3.36421700 | 10.02549900 |
| H | 14.08767400 | 3.37957500 | 8.92812300 |
| H | 13.17514700 | 3.18576500 | 10.44442500 |
| H | 14.82838100 | 2.52196500 | 10.30640100 |
| C | 14.76386300 | 4.68710500 | 10.53246600 |
| H | 14.06700600 | 5.49292200 | 10.25820200 |
| C | 16.09207700 | 4.97509700 | 9.83546600 |
| H | 16.81155800 | 4.15094900 | 9.96898400 |
| H | 16.55465000 | 5.90022400 | 10.21002100 |
| H | 15.92447900 | 5.09458600 | 8.75529600 |
| C | 12.10533200 | 6.42906100 | 15.05072900 |
| H | 12.92006000 | 7.05226000 | 15.45106200 |
| H | 11.20138500 | 6.59987500 | 15.65574000 |
| H | 11.90138500 | 6.76887900 | 14.02531000 |
| C | 12.50140200 | 4.94766400 | 15.08296900 |
| C | 12.63745600 | 4.46748300 | 16.52726400 |
| H | 12.98868800 | 3.42598700 | 16.58352100 |

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|---|---|---|---|
| H | 11.66307800 | 4.53067400 | 17.03340000 |
| H | 13.33978400 | 5.09742500 | 17.09498900 |
| C | 11.53365100 | 5.67610000 | 7.95884000 |
| H | 12.14174400 | 4.85512000 | 7.54651800 |
| H | 12.06800100 | 6.12539700 | 8.80906500 |
| H | 11.43007900 | 6.45372400 | 7.18563500 |
| C | 9.41120600 | 4.56191900 | 7.18456700 |
| H | 8.38934100 | 4.25195900 | 7.45033200 |
| H | 9.95565400 | 3.67907800 | 6.81736900 |
| H | 9.34403300 | 5.27361500 | 6.34718000 |
| C | 8.86248100 | 7.21089500 | 13.40807000 |
| H | 9.12805300 | 7.48972300 | 14.43968800 |
| H | 9.17823200 | 6.17078400 | 13.24505900 |
| H | 7.76511400 | 7.26130700 | 13.31388400 |
| H | 14.71903000 | 7.87051000 | 10.85124400 |
| H | 10.61463100 | 8.06456800 | 12.49086600 |
| H | 11.68139400 | 4.37871400 | 14.62116500 |

**$BO_2^-$**

| | | | |
|---|---|---|---|
| B | -2.05658400 | 1.17410800 | -0.41303100 |
| O | -1.14070900 | 0.31678300 | -0.47463400 |
| O | -2.97205700 | 2.03194900 | -0.35258700 |

## Chapter 4 Xyz coordinates for optimized structures

**2-Cl**

| | | | |
|---|---|---|---|
| Ge | 9.11537700 | 9.47941500 | 8.49549500 |
| Cl | 12.71886200 | 11.46888000 | 8.95052000 |
| N | 9.69229500 | 13.70726500 | 9.10448300 |
| N | 8.33057500 | 12.53119700 | 10.51256800 |
| N | 13.18837500 | 7.79931700 | 7.87928700 |
| N | 11.19683700 | 6.69530500 | 8.02765900 |
| N | 11.01924100 | 9.20424300 | 8.36341200 |
| N | 9.89948500 | 11.11519400 | 9.07113000 |
| C | 10.66714600 | 14.10299300 | 8.14877000 |
| C | 11.80244300 | 14.82547500 | 8.57227900 |
| C | 7.78582400 | 11.50143300 | 11.32894300 |
| C | 14.26243100 | 8.73506300 | 7.88457500 |
| C | 13.39574600 | 6.42333100 | 7.71734700 |
| H | 14.39022000 | 6.02525400 | 7.52911600 |
| C | 8.87912400 | 14.59417200 | 9.81609300 |
| H | 8.92568400 | 15.66691300 | 9.64855900 |
| C | 8.07570500 | 13.89953800 | 10.65728500 |
| H | 7.32909300 | 14.27273800 | 11.35421500 |
| C | 10.51221300 | 13.71492400 | 6.80229100 |

| | | | |
|---|---|---|---|
| C | 8.34580900 | 11.27220700 | 12.60271200 |
| C | 14.41350400 | 9.61388700 | 6.79565500 |
| C | 6.74156900 | 10.69639400 | 10.82569200 |
| C | 9.84637100 | 6.39683900 | 8.34028900 |
| C | 9.52133200 | 12.10375300 | 13.09281900 |
| H | 9.44017300 | 13.09750900 | 12.62850600 |
| C | 12.21677500 | 5.76464000 | 7.81113700 |
| H | 12.01570800 | 4.69916500 | 7.73173400 |
| C | 6.09032100 | 11.01830200 | 9.48850200 |
| H | 6.88919700 | 11.34224400 | 8.79991400 |
| C | 6.27928000 | 9.64086300 | 11.62054500 |
| H | 5.48277900 | 8.99465400 | 11.25050900 |
| C | 11.50164600 | 14.08453600 | 5.88559900 |
| H | 11.39579600 | 13.79207700 | 4.83814700 |
| C | 15.11329800 | 8.78926400 | 9.00474600 |
| C | 7.83147800 | 10.22498400 | 13.37336100 |
| H | 8.24309000 | 10.03214400 | 14.36505400 |
| C | 9.30237400 | 12.93931000 | 6.30515500 |
| H | 8.69905500 | 12.65527500 | 7.17704900 |
| C | 12.75541200 | 15.18617500 | 7.61680800 |
| H | 13.63772700 | 15.74897500 | 7.92842800 |
| C | 6.81224200 | 9.41220900 | 12.88581400 |
| H | 6.43061800 | 8.59198400 | 13.49674200 |
| C | 8.92745700 | 6.17172800 | 7.29372900 |
| C | 9.42789600 | 6.45907000 | 9.68556000 |
| C | 12.02494400 | 15.19577900 | 10.03070000 |
| H | 11.28794400 | 14.64354500 | 10.63153600 |
| C | 12.61263600 | 14.82021000 | 6.28234900 |
| H | 13.37270500 | 15.10199100 | 5.55192800 |
| C | 13.42157100 | 9.58580200 | 5.64297200 |
| H | 12.42418100 | 9.44204400 | 6.08882700 |
| C | 10.84398400 | 11.48262600 | 12.62339200 |
| H | 11.69567300 | 12.11617300 | 12.91361200 |
| H | 10.86877000 | 11.35873000 | 11.53122200 |
| H | 10.98212500 | 10.49019300 | 13.08067500 |
| C | 14.81782900 | 7.94931300 | 10.23858400 |
| H | 14.43782300 | 6.97330700 | 9.90190900 |
| C | 16.16388700 | 9.71076900 | 8.99055800 |
| H | 16.84215200 | 9.77288500 | 9.84210500 |
| C | 7.57668800 | 6.02085500 | 7.61805300 |
| H | 6.84632000 | 5.84784800 | 6.82683900 |
| C | 10.41065600 | 6.66334300 | 10.82746700 |
| H | 11.41059300 | 6.80776600 | 10.39354800 |
| C | 5.12425800 | 12.20076900 | 9.64302300 |

| | | | |
|---|---|---|---|
| H | 4.32404300 | 11.94483900 | 10.35428000 |
| H | 4.66010400 | 12.44704200 | 8.67643700 |
| H | 5.64156000 | 13.09639300 | 10.01110300 |
| C | 15.47250900 | 10.52463500 | 6.82764700 |
| H | 15.60946700 | 11.22569500 | 6.00444900 |
| B | 9.37250600 | 12.36824500 | 9.52916800 |
| C | 8.06152600 | 6.32053700 | 9.96247500 |
| H | 7.71439600 | 6.38332200 | 10.99655400 |
| C | 16.34722500 | 10.56595400 | 7.90866600 |
| H | 17.16935100 | 11.28348600 | 7.91574200 |
| C | 13.41477900 | 14.78283500 | 10.52512400 |
| H | 14.20979900 | 15.35245100 | 10.02052900 |
| H | 13.59381100 | 13.71351700 | 10.35106700 |
| H | 13.50413600 | 14.98052300 | 11.60386600 |
| C | 7.14389600 | 6.10590500 | 8.94019800 |
| H | 6.08264100 | 6.00196600 | 9.17264800 |
| C | 9.40267100 | 6.18033900 | 5.84898000 |
| H | 10.41783200 | 5.75615100 | 5.83653800 |
| C | 11.80081500 | 16.69552200 | 10.25611100 |
| H | 11.92529400 | 16.95255000 | 11.31864400 |
| H | 10.79569800 | 17.00974900 | 9.94149500 |
| H | 12.52900400 | 17.28442800 | 9.67670100 |
| C | 5.37202800 | 9.82825800 | 8.85410500 |
| H | 6.02026700 | 8.94110800 | 8.79810900 |
| H | 5.05514400 | 10.08600000 | 7.83325700 |
| H | 4.46505000 | 9.56292800 | 9.41881200 |
| C | 9.52938500 | 12.30114600 | 14.60885400 |
| H | 9.75110300 | 11.36301400 | 15.13974400 |
| H | 8.56430200 | 12.68127300 | 14.97378400 |
| H | 10.31130700 | 13.02176500 | 14.88796100 |
| B | 11.77990600 | 8.01803500 | 8.09656500 |
| C | 13.37096800 | 10.89586900 | 4.85987900 |
| H | 13.19931100 | 11.75343000 | 5.52839400 |
| H | 12.55066300 | 10.85914800 | 4.12763100 |
| H | 14.30122000 | 11.07063000 | 4.29741000 |
| C | 13.69066900 | 8.39914100 | 4.71031600 |
| H | 14.68895800 | 8.49211900 | 4.25514100 |
| H | 12.94659300 | 8.36786600 | 3.89971600 |
| H | 13.64740300 | 7.44391000 | 5.25254300 |
| C | 9.71023700 | 11.65147600 | 5.58033800 |
| H | 8.82717400 | 11.02421400 | 5.37732400 |
| H | 10.43160200 | 11.06314200 | 6.17013300 |
| H | 10.18484900 | 11.86991200 | 4.61108800 |
| C | 13.70664700 | 8.61509300 | 11.06375300 |

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|---|---|---|---|
| H | 14.03509700 | 9.60428500 | 11.41867200 |
| H | 13.45100800 | 7.99649900 | 11.93862000 |
| H | 12.79449000 | 8.76553900 | 10.46707700 |
| C | 16.04484300 | 7.68942500 | 11.11119600 |
| H | 16.87988800 | 7.27888500 | 10.52524000 |
| H | 15.79530200 | 6.97077300 | 11.90498800 |
| H | 16.39259900 | 8.60963900 | 11.60446100 |
| C | 8.42297900 | 13.81796700 | 5.40933500 |
| H | 8.97716500 | 14.14707800 | 4.51685700 |
| H | 8.08712900 | 14.71503800 | 5.94849000 |
| H | 7.53438500 | 13.26333000 | 5.07188800 |
| C | 10.46826100 | 5.41017600 | 11.70864700 |
| H | 9.49819500 | 5.22293400 | 12.19469400 |
| H | 11.22465900 | 5.53064100 | 12.49826600 |
| H | 10.72728900 | 4.52217900 | 11.11472500 |
| B | 11.19086500 | 10.56735000 | 8.78444300 |
| C | 10.07701200 | 7.90267200 | 11.66340000 |
| H | 10.14744100 | 8.83360400 | 11.07643400 |
| H | 10.78587400 | 8.00030500 | 12.49951000 |
| H | 9.06296500 | 7.85041200 | 12.08797100 |
| C | 9.50443200 | 7.62153100 | 5.33023900 |
| H | 9.86666000 | 7.63641200 | 4.29137200 |
| H | 10.20139900 | 8.21860000 | 5.93781700 |
| H | 8.51535500 | 8.10670600 | 5.35702600 |
| C | 8.52873700 | 5.33874000 | 4.92002500 |
| H | 7.53829200 | 5.79508800 | 4.77176400 |
| H | 8.38194600 | 4.32212400 | 5.31218000 |
| H | 9.00066300 | 5.26101700 | 3.93035400 |

**3-Cl**

| | | | |
|---|---|---|---|
| Ge | 8.13207800 | 12.84181400 | 9.66506300 |
| Cl | 4.12913200 | 13.54170100 | 8.59720400 |
| N | 7.50128000 | 9.98435400 | 7.55016800 |
| N | 6.70481800 | 12.27766800 | 8.39343800 |
| N | 6.61808800 | 14.07802700 | 9.89876300 |
| N | 5.29599700 | 15.01034900 | 11.95659000 |
| N | 7.50630300 | 15.55620300 | 11.78680600 |
| N | 5.41708600 | 10.59432800 | 6.82363800 |
| N | 10.58066600 | 14.03324100 | 8.22580200 |
| N | 8.84663200 | 14.87514800 | 7.29432500 |
| C | 8.83134400 | 15.81364200 | 11.35172900 |
| C | 8.85823900 | 9.91672100 | 7.96962800 |
| C | 5.69020500 | 15.71756300 | 13.09516600 |
| H | 4.98563300 | 15.93902500 | 13.89347100 |

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|---|---|---|---|
| C | 9.03898200 | 16.75880200 | 10.31761200 |
| C | 6.96501000 | 8.96192500 | 6.75851300 |
| H | 7.52000800 | 8.04711000 | 6.56368700 |
| C | 3.97565300 | 14.50529300 | 11.80678300 |
| C | 9.23437100 | 14.03860300 | 8.27818100 |
| C | 6.99980100 | 16.03962800 | 12.99999900 |
| H | 7.61428100 | 16.61547200 | 13.68710200 |
| C | 9.91507100 | 15.14203300 | 11.95406400 |
| C | 10.34929800 | 17.02057900 | 9.90921200 |
| H | 10.53656900 | 17.74388500 | 9.11482300 |
| C | 7.85935600 | 17.50942400 | 9.71496200 |
| H | 7.06601100 | 16.76823300 | 9.53027400 |
| C | 4.24099800 | 12.18634900 | 5.38900500 |
| C | 9.16690900 | 9.57321100 | 9.30201100 |
| C | 8.05381800 | 9.29714700 | 10.29960000 |
| H | 7.25222900 | 10.02271400 | 10.08939200 |
| C | 4.20108800 | 11.20460900 | 6.40015400 |
| C | 9.87429900 | 10.14227800 | 7.01407200 |
| C | 9.51548900 | 10.59634500 | 5.60608000 |
| H | 8.58962600 | 10.07936700 | 5.31383000 |
| C | 2.95289700 | 15.38743900 | 11.40054500 |
| C | 5.73428000 | 9.32028000 | 6.33911800 |
| H | 5.03619400 | 8.77050400 | 5.71240100 |
| C | 1.38528400 | 13.54055800 | 11.52932100 |
| H | 0.36767200 | 13.16122600 | 11.42142500 |
| C | 3.72156300 | 13.14693300 | 12.05585500 |
| C | 5.56533500 | 12.59754300 | 4.76775300 |
| H | 6.32012900 | 12.55072300 | 5.56739900 |
| C | 11.43079300 | 16.38728900 | 10.52051600 |
| H | 12.45020700 | 16.62931100 | 10.21095900 |
| C | 9.70789000 | 14.13448400 | 13.07421100 |
| H | 8.64138600 | 13.86392100 | 13.07727500 |
| C | 1.65930800 | 14.88166100 | 11.26668800 |
| H | 0.84923700 | 15.53989400 | 10.95094500 |
| C | 1.80017600 | 11.37028900 | 6.49555800 |
| H | 0.84520400 | 11.06356100 | 6.92704200 |
| C | 11.21217500 | 15.45992000 | 11.53172900 |
| H | 12.06426500 | 14.96839200 | 12.00680100 |
| C | 7.47298900 | 7.89260200 | 10.09207300 |
| H | 8.24402200 | 7.12764200 | 10.27393300 |
| H | 7.08667800 | 7.76185200 | 9.07237400 |
| H | 6.64413400 | 7.71736400 | 10.79478400 |
| B | 6.44201500 | 14.84612300 | 11.08835900 |
| C | 2.98379300 | 10.79534500 | 6.97000300 |

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|---|---|---|---|
| C | 8.18725200 | 18.19150600 | 8.38876300 |
| H | 8.84110900 | 19.06484700 | 8.53870700 |
| H | 7.26274500 | 18.55020100 | 7.91306700 |
| H | 8.69524500 | 17.50784900 | 7.69572100 |
| C | 2.40722800 | 12.68556000 | 11.92140500 |
| H | 2.18457600 | 11.63440600 | 12.11851000 |
| C | 7.45989200 | 15.14838500 | 6.94694200 |
| H | 6.99203800 | 14.24451200 | 6.53725900 |
| H | 7.42719000 | 15.95265300 | 6.20504900 |
| H | 6.91043200 | 15.44893500 | 7.84587400 |
| B | 6.52522100 | 11.06827900 | 7.64848400 |
| C | 3.28545800 | 16.82978900 | 11.04713400 |
| H | 4.05428500 | 17.17515900 | 11.75538400 |
| C | 9.93977800 | 15.38289400 | 6.61048100 |
| C | 1.82257800 | 12.33903200 | 5.50074000 |
| H | 0.89059300 | 12.78493400 | 5.14959800 |
| C | 11.04580700 | 14.85460600 | 7.21508600 |
| C | 2.92922800 | 9.78029100 | 8.09836200 |
| H | 3.95997900 | 9.61900800 | 8.44817000 |
| C | 3.89291000 | 16.90404000 | 9.63964700 |
| H | 4.77770800 | 16.25680700 | 9.55203900 |
| H | 4.18124800 | 17.93903800 | 9.39741700 |
| H | 3.16468300 | 16.55733200 | 8.89057200 |
| C | 4.82268800 | 12.18271900 | 12.46295900 |
| H | 5.78440600 | 12.70550100 | 12.36029200 |
| C | 10.51472800 | 9.45295300 | 9.65938000 |
| H | 10.77976400 | 9.19440800 | 10.68474600 |
| C | 11.52454800 | 9.63767200 | 8.72024300 |
| H | 12.56900100 | 9.51464600 | 9.01355100 |
| C | 7.29934300 | 18.54958100 | 10.69545000 |
| H | 6.92909500 | 18.08666400 | 11.61892500 |
| H | 6.46463500 | 19.09563100 | 10.23070800 |
| H | 8.08044200 | 19.28002000 | 10.95846100 |
| C | 11.46403200 | 13.21218400 | 9.03758700 |
| H | 12.25771700 | 13.83778700 | 9.46285400 |
| H | 11.89536000 | 12.41051100 | 8.42290200 |
| H | 10.88675000 | 12.76024200 | 9.85137800 |
| C | 3.03809700 | 12.74794900 | 4.95793900 |
| H | 3.04449200 | 13.51705400 | 4.18467900 |
| C | 11.20642000 | 9.98161600 | 7.40866700 |
| H | 12.00798400 | 10.12321700 | 6.68205900 |
| B | 5.87396700 | 13.28223800 | 8.98013400 |
| C | 8.48617700 | 9.48760400 | 11.75147900 |
| H | 7.61866200 | 9.38212000 | 12.41930600 |

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|---|---|---|---|
| H | 8.92076400 | 10.48540400 | 11.90853200 |
| H | 9.22022000 | 8.72721400 | 12.06010500 |
| C | 5.55558300 | 14.02173700 | 4.21367600 |
| H | 6.57816800 | 14.32759500 | 3.94199000 |
| H | 5.15835400 | 14.73680200 | 4.94962300 |
| H | 4.94357700 | 14.09674300 | 3.30203300 |
| C | 10.04984100 | 14.76124100 | 14.43182400 |
| H | 9.85819200 | 14.04710300 | 15.24621200 |
| H | 9.45587700 | 15.66499000 | 14.62283500 |
| H | 11.11380400 | 15.04372200 | 14.46913800 |
| C | 10.58052500 | 10.26771700 | 4.56190500 |
| H | 11.49343800 | 10.86542000 | 4.70999900 |
| H | 10.20119100 | 10.49894000 | 3.55613500 |
| H | 10.86033800 | 9.20469900 | 4.58675500 |
| C | 2.09173000 | 17.77647900 | 11.16128400 |
| H | 1.34075600 | 17.57409500 | 10.38256900 |
| H | 2.42334300 | 18.81662500 | 11.02980200 |
| H | 1.59914500 | 17.69321800 | 12.14093600 |
| C | 10.51240000 | 12.84858800 | 12.86791300 |
| H | 11.59725200 | 13.03493000 | 12.89513400 |
| H | 10.25480900 | 12.37388000 | 11.90983800 |
| H | 10.28456100 | 12.13130900 | 13.67039800 |
| C | 9.82747100 | 16.26599800 | 5.41454800 |
| H | 9.26659000 | 15.76910900 | 4.60863800 |
| H | 10.82793500 | 16.50058300 | 5.03238500 |
| H | 9.32343600 | 17.21660900 | 5.64260200 |
| C | 12.49802600 | 15.03361300 | 6.94028800 |
| H | 13.00874100 | 15.49406800 | 7.79979300 |
| H | 12.64378700 | 15.68533700 | 6.07102700 |
| H | 12.98935600 | 14.07163300 | 6.73183800 |
| C | 9.21454900 | 12.10000900 | 5.61242400 |
| H | 8.43078300 | 12.33923600 | 6.34563500 |
| H | 8.88030700 | 12.44009400 | 4.61918600 |
| H | 10.12148300 | 12.66674100 | 5.88284200 |
| C | 2.11566100 | 10.31271000 | 9.28051100 |
| H | 2.49226600 | 11.29418700 | 9.60213800 |
| H | 2.17535600 | 9.61455100 | 10.13000200 |
| H | 1.05123000 | 10.42250200 | 9.02074900 |
| C | 4.67370600 | 11.77265200 | 13.93153900 |
| H | 4.69445000 | 12.65315200 | 14.58977900 |
| H | 5.48946200 | 11.09714400 | 14.23117900 |
| H | 3.71935400 | 11.24835100 | 14.09657100 |
| C | 5.98973600 | 11.60174000 | 3.68083200 |
| H | 5.23585900 | 11.57228200 | 2.87867000 |

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|---|---|---|---|
| H | 6.09726200 | 10.58718500 | 4.08921300 |
| H | 6.95215200 | 11.89664100 | 3.23341500 |
| C | 2.37622100 | 8.43658000 | 7.61202000 |
| H | 1.34819600 | 8.55446500 | 7.23470700 |
| H | 2.35460100 | 7.70551500 | 8.43413300 |
| H | 2.98759300 | 8.01942100 | 6.79945800 |
| C | 4.86358900 | 10.95569000 | 11.54752400 |
| H | 3.95269500 | 10.34637300 | 11.65070500 |
| H | 5.72069300 | 10.31682800 | 11.80593200 |
| H | 4.95501000 | 11.24422600 | 10.48806300 |

**3-N3**

| | | | |
|---|---|---|---|
| N | 7.85568100 | 14.18029900 | 6.36492000 |
| B | 6.65445600 | 14.12415200 | 5.58059400 |
| Ge | 6.81326500 | 13.54415000 | 7.89264500 |
| N | 5.52505800 | 13.93282100 | 6.43093200 |
| N | 6.64485300 | 14.21156300 | 4.10713700 |
| N | 5.68568600 | 14.40845200 | 3.39599500 |
| N | 4.87078600 | 14.60856400 | 2.63956900 |
| B | 9.21545900 | 14.55698900 | 6.19789600 |
| N | 9.92624300 | 14.99372900 | 5.00879600 |
| C | 11.25088900 | 15.27494700 | 5.35434800 |
| H | 11.97232300 | 15.60061600 | 4.60864100 |
| C | 11.42919000 | 15.06599300 | 6.67835300 |
| H | 12.33144100 | 15.18117700 | 7.27358700 |
| N | 10.22780700 | 14.62092000 | 7.24507900 |
| C | 9.52479600 | 14.80988100 | 3.65691000 |
| C | 9.64413800 | 13.52434200 | 3.09386100 |
| C | 9.17525600 | 13.32449700 | 1.79305300 |
| H | 9.23861500 | 12.32966700 | 1.34530400 |
| C | 8.61009000 | 14.36896800 | 1.06659800 |
| H | 8.24069100 | 14.19360300 | 0.05471700 |
| C | 8.51346900 | 15.63592800 | 1.63353700 |
| H | 8.06457800 | 16.45005500 | 1.05919100 |
| C | 8.96387000 | 15.87690400 | 2.93483600 |
| C | 10.19846900 | 12.35387000 | 3.89135000 |
| H | 10.61559800 | 12.75032000 | 4.82866500 |
| C | 11.33613600 | 11.64459000 | 3.15298100 |
| H | 10.98315500 | 11.18084200 | 2.21904200 |
| H | 11.75890800 | 10.84520400 | 3.78016000 |
| H | 12.14343300 | 12.34675700 | 2.89968200 |
| C | 9.07922600 | 11.37260100 | 4.25858300 |
| H | 8.65401800 | 10.90613700 | 3.35559600 |
| H | 8.25906400 | 11.87986000 | 4.79068400 |

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|---|---|---|---|
| H | 9.46229700 | 10.56553900 | 4.90400000 |
| C | 8.78667100 | 17.25134800 | 3.55563500 |
| H | 9.17240200 | 17.19728800 | 4.58394800 |
| C | 7.30468400 | 17.63591100 | 3.62856000 |
| H | 6.86493000 | 17.71840300 | 2.62215800 |
| H | 7.17731900 | 18.60934000 | 4.12829900 |
| H | 6.72687900 | 16.88001800 | 4.18263200 |
| C | 9.59412300 | 18.31310600 | 2.80328500 |
| H | 9.24736800 | 18.40910300 | 1.76269600 |
| H | 10.66185300 | 18.05240200 | 2.77891900 |
| H | 9.48936100 | 19.29701800 | 3.28495100 |
| C | 10.11330200 | 14.23748300 | 8.60583000 |
| C | 10.13595600 | 15.21931300 | 9.61815400 |
| C | 10.04948100 | 14.80660900 | 10.95293700 |
| H | 10.08717800 | 15.55399800 | 11.74905900 |
| C | 9.92105500 | 13.46101000 | 11.27854400 |
| H | 9.85509200 | 13.15440000 | 12.32434000 |
| C | 9.87415600 | 12.50212900 | 10.26911200 |
| H | 9.76388100 | 11.45088400 | 10.53592100 |
| C | 9.97756700 | 12.86440200 | 8.92273200 |
| C | 10.28771800 | 16.69591800 | 9.29140300 |
| H | 10.11516200 | 16.81189200 | 8.21139700 |
| C | 11.70817300 | 17.18126100 | 9.60410900 |
| H | 12.46354600 | 16.60272400 | 9.05576800 |
| H | 11.92203500 | 17.07768600 | 10.67950000 |
| H | 11.82517600 | 18.24124600 | 9.33348700 |
| C | 9.26066100 | 17.56174200 | 10.02550000 |
| H | 9.33142700 | 18.60644200 | 9.68644500 |
| H | 9.43234100 | 17.56063000 | 11.11329700 |
| H | 8.23748600 | 17.20811100 | 9.84219300 |
| C | 10.00078000 | 11.81039200 | 7.82394400 |
| H | 9.41278800 | 12.20124500 | 6.98005400 |
| C | 9.36023800 | 10.48647000 | 8.23319600 |
| H | 9.27246000 | 9.83096100 | 7.35427400 |
| H | 8.34868100 | 10.64502100 | 8.63421900 |
| H | 9.96248400 | 9.95344400 | 8.98565600 |
| C | 11.43493000 | 11.58250300 | 7.32744600 |
| H | 11.43970400 | 10.85026000 | 6.50486800 |
| H | 12.06352400 | 11.18721800 | 8.14074900 |
| H | 11.88996100 | 12.51205400 | 6.95764500 |
| B | 4.21596900 | 13.45387400 | 6.10120500 |
| N | 3.85572100 | 12.13229900 | 5.62291600 |
| C | 2.48052300 | 12.09515100 | 5.39415900 |
| H | 1.98645000 | 11.20794900 | 5.00486900 |

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|---|---|---|---|
| C | 1.93735400 | 13.29064200 | 5.72565000 |
| H | 0.89789000 | 13.60693600 | 5.67827400 |
| N | 2.94717400 | 14.15722800 | 6.16202900 |
| C | 4.72133700 | 11.00269800 | 5.56504200 |
| C | 5.22562300 | 10.56505700 | 4.32699700 |
| C | 6.12382100 | 9.49086200 | 4.31632300 |
| H | 6.52266700 | 9.13659400 | 3.36348700 |
| C | 6.52556300 | 8.88281600 | 5.49811000 |
| H | 7.24171600 | 8.05939800 | 5.47390400 |
| C | 6.00839400 | 9.31825800 | 6.71724000 |
| H | 6.32592200 | 8.82475000 | 7.63618100 |
| C | 5.08931800 | 10.36836900 | 6.77664300 |
| C | 4.78001300 | 11.19399600 | 3.01873500 |
| H | 4.27002200 | 12.13718700 | 3.25987100 |
| C | 3.76407000 | 10.28758900 | 2.31282500 |
| H | 3.40851600 | 10.75640700 | 1.38330000 |
| H | 2.89280300 | 10.08511400 | 2.95206600 |
| H | 4.22276300 | 9.31985700 | 2.05549500 |
| C | 5.95170900 | 11.51854000 | 2.08852800 |
| H | 6.43385800 | 10.60189400 | 1.71209200 |
| H | 6.71766400 | 12.11916500 | 2.60095100 |
| H | 5.59473100 | 12.08572600 | 1.21575300 |
| C | 4.44348900 | 10.76857600 | 8.09732700 |
| H | 4.36350600 | 11.86692100 | 8.10470100 |
| C | 5.24970300 | 10.36069100 | 9.32848000 |
| H | 5.25861600 | 9.26786000 | 9.46215000 |
| H | 4.79214700 | 10.79380500 | 10.23091500 |
| H | 6.28515600 | 10.72242600 | 9.26747200 |
| C | 3.02047400 | 10.20146600 | 8.20109600 |
| H | 2.38421600 | 10.53746600 | 7.37237700 |
| H | 2.54911700 | 10.52370900 | 9.14357000 |
| H | 3.04779000 | 9.10070800 | 8.19295800 |
| C | 2.65136700 | 15.36249600 | 6.85667300 |
| C | 2.22862800 | 15.27969400 | 8.19745300 |
| C | 1.92623600 | 16.46420700 | 8.88044100 |
| H | 1.60046700 | 16.41644200 | 9.92194500 |
| C | 2.02929000 | 17.69677800 | 8.24805600 |
| H | 1.77677100 | 18.61196800 | 8.78736200 |
| C | 2.46156900 | 17.76578600 | 6.92404400 |
| H | 2.54646100 | 18.73984700 | 6.43992000 |
| C | 2.78568200 | 16.60977900 | 6.20871300 |
| C | 2.14895200 | 13.94577400 | 8.92344400 |
| H | 2.22658600 | 13.14254400 | 8.17700300 |
| C | 0.82243600 | 13.75543000 | 9.66148300 |

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| H | 0.70523300 | 14.47595400 | 10.48538500 |
| H | 0.77237100 | 12.74616000 | 10.09613100 |
| C | 3.34073000 | 13.79985000 | 9.87302000 |
| H | 4.28779300 | 13.87021200 | 9.31607100 |
| H | 3.31622900 | 12.82695900 | 10.38857400 |
| H | 3.33430500 | 14.59984200 | 10.63352100 |
| C | 3.26570100 | 16.67173800 | 4.76836900 |
| H | 4.09313300 | 15.94845900 | 4.69181900 |
| C | 3.79600700 | 18.04255100 | 4.35221100 |
| H | 4.26503800 | 17.96861900 | 3.36077800 |
| H | 4.54832500 | 18.43187400 | 5.05492400 |
| H | 2.98341500 | 18.78201300 | 4.27874100 |
| C | 2.17115000 | 16.22337900 | 3.79227000 |
| H | 2.55234000 | 16.24804800 | 2.76157000 |
| H | 1.30320900 | 16.89756100 | 3.86369200 |
| H | 1.83837200 | 15.19885100 | 4.00061400 |
| C | 6.49004800 | 15.42568500 | 8.88313900 |
| N | 6.14638100 | 16.63385000 | 8.39706100 |
| C | 5.64897300 | 17.45616100 | 9.39279000 |
| C | 5.70155400 | 16.72825600 | 10.54928500 |
| N | 6.23210800 | 15.49672000 | 10.20656700 |
| C | 6.29516300 | 17.02999500 | 7.00562600 |
| H | 7.13854600 | 16.47860400 | 6.57681300 |
| H | 6.49709000 | 18.10679700 | 6.95730000 |
| H | 5.38215400 | 16.78938600 | 6.44610500 |
| C | 5.24140400 | 18.86746100 | 9.14793100 |
| H | 6.11587400 | 19.50460800 | 8.94207600 |
| H | 4.72938800 | 19.26944200 | 10.03059100 |
| H | 4.55131500 | 18.93507100 | 8.29592800 |
| C | 5.33399800 | 17.07983600 | 11.94871100 |
| H | 4.89331900 | 18.08307200 | 11.98192300 |
| H | 6.21407100 | 17.07410000 | 12.60971300 |
| H | 4.59882000 | 16.37215000 | 12.36036300 |
| C | 6.48421300 | 14.43968400 | 11.17107200 |
| H | 6.97156200 | 13.60044100 | 10.66102200 |
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## Chapter 5 Xyz coordinates for optimized structures

### 2-Si

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| Si | 9.83501621704433 | 7.12726556504995 | 4.74790829251278 |
| Si | 10.43217363252974 | 4.03161984343987 | 4.90570745396059 |
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| N | 8.35484548449214 | 7.46151791853296 | 5.87342381908173 |
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| C | 12.19877241318533 | 10.72984554512525 | 4.36162403909347 |
| H | 12.32700820250180 | 11.78871554024092 | 4.18828934482097 |
| C | 13.12056226993338 | 9.80591404735129 | 4.71284463925158 |
| H | 14.18330225748648 | 9.92799226696506 | 4.87101434264510 |
| C | 9.87439039073017 | 10.89824332360343 | 3.70722456262667 |
| C | 13.33002499781560 | 7.40708863601330 | 4.99085457461926 |
| C | 13.19565334425471 | 7.62165296054540 | 7.52805133037900 |
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| C | 7.51871511874639 | 7.41991801173403 | 4.82959163275458 |
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| C | 14.54942345550083 | 5.84763315802731 | 6.34921907171168 |
| H | 14.83903291039032 | 5.46741013189761 | 7.32473216654097 |
| C | 9.93414670640093 | 11.21545284005982 | 2.33505271738242 |
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| C | 8.92529094033470 | 12.01798862848621 | 1.79445001419040 |
| H | 8.95443507354901 | 12.27299574835303 | 0.73881133395224 |
| C | 14.68415448402088 | 5.71566603296743 | 3.95223541675840 |
| H | 5.07823544558615 | 5.23410811509309 | 3.06106322056431 |
| C | 8.09937206562864 | 7.30223489856353 | 7.31933592293757 |
| C | 14.27738024309145 | 8.55440915568684 | 8.09662542309528 |
| H | 15.17021891555880 | 7.98067699948114 | 8.37231196588544 |
| H | 13.90969526842774 | 9.06697512569094 | 8.99311470213373 |
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| C | 6.04172972023650 | 7.55077018539474 | 4.87533111754322 |
| C | 7.89220173417037 | 7.20532503879776 | 2.30980727146925 |
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| H | 12.68861376547661 | 8.07784471749127 | 2.54739719705092 |
| C | 11.05876088100230 | 10.74388328254542 | 1.42784141765120 |
| H | 11.64208467477715 | 9.99103940373179 | 1.96825564999875 |

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| H | 7.10116152929557 | 13.09562230315489 | 2.14400449611654 |
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| H | 9.82593356665253 | 9.29872976216928 | 0.33837456096133 |
| H | 11.38392898920079 | 9.66768141291081 | -0.42254102573414 |
| H | 10.05860419589857 | 10.83127025630928 | -0.51768900917053 |
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| H | 6.08350433321949 | 9.68232859351974 | 4.59274050644153 |
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| H | 9.98307708365320 | 7.52611086905987 | 1.78595239768844 |
| H | 9.00284141801608 | 6.80615839461109 | 0.49050604684766 |
| H | 9.51157208569285 | 5.82056204439808 | 1.88428845666321 |
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| C | 7.92161070266849 | 5.81292452905285 | 7.64900481660304 |
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| H | 7.80013847380032 | 5.68281533071202 | 8.73005368654905 |
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| H | 12.16176227533622 | 3.62706853158414 | 6.64456074996096 |
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| H | 10.56140309325849 | 3.67432919045867 | 7.39792989008079 |
| C | 9.35454523850496 | 7.81909233884190 | 8.03017960156105 |
| H | 10.23971781944508 | 7.29416359696110 | 7.65963093571824 |
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| H | 6.87175850295934 | 8.08003784582231 | 8.90066643219799 |
| H | 5.93891485927054 | 7.64822664080839 | 7.46142196682437 |
| C | 6.81437906058762 | 6.15055675702118 | 2.02510106156496 |
| H | 7.10828947747890 | 5.17521101410064 | 2.42468367469321 |
| H | 6.68521242636789 | 6.05665400756617 | 0.94155249649945 |
| H | 5.84960733824693 | 6.43006677253457 | 2.45564326821244 |
| C | 3.86317506211912 | 6.55564115578756 | 5.14008717297407 |
| H | 3.24401983019143 | 5.67534245715342 | 5.28570725384663 |
| C | 11.99778354048136 | 11.90926993391708 | 1.07359220405523 |
| H | 11.46174282514990 | 12.66865362935640 | 0.49227496909579 |
| H | 12.83622434482091 | 11.54707827603946 | 0.46801844852292 |
| H | 12.40429684776851 | 12.39259912029650 | 1.96611634296610 |
| C | 4.07231275723179 | 8.93911372232488 | 4.83012491790277 |
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| C | 12.92164943422815 | 6.21869717082773 | 1.53228488672027 |
| H | 12.58824766750234 | 6.64566267417797 | 0.57902192006217 |
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| C | 3.27570567376553 | 7.81401021953943 | 5.02938101336645 |
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**TS1**

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| Si | -1.39653145740663 | 7.84260837529335 | 1.72696770668656 |
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| N | -0.26160093028883 | 4.11679665048347 | 3.35931708214660 |
| N | -0.23218367863164 | 8.37184022219764 | 5.84658184042633 |
| N | -0.87806998799576 | 7.19886997574348 | 3.24109997571284 |
| C | 2.88418318958122 | 5.78704712981385 | 2.93149868901823 |
| C | 1.06392620902866 | 4.02991630497720 | 3.19101130697515 |
| C | -2.23938773849126 | 8.25575953238182 | 6.86264234960227 |
| H | -3.10255544317445 | 8.43113543039928 | 7.49100923882171 |
| C | 1.85621746778823 | 2.78795525693590 | 2.99929661770623 |
| C | -3.21148834528618 | 6.18980486366772 | 6.07625207890447 |

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| C | 1.14203630028940 | 8.74892933324820 | 5.86198341695286 |
| C | 1.57763010814816 | 9.83125681573584 | 5.06963805961633 |
| C | 2.03545908946286 | 8.08014445934093 | 6.72119974802094 |
| C | -1.07275016883688 | 8.92543028088046 | 6.82727463867250 |
| H | -0.76235817869566 | 9.77539428585545 | 7.41989746970455 |
| C | -2.40684258287263 | 9.41761610829687 | 1.95829318091000 |
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| H | -3.26724029990150 | 9.26758745064557 | 2.61741345562731 |
| H | -2.78261564249392 | 9.76628164785696 | 0.98850612786074 |
| C | -4.34419108039282 | 6.15274042135904 | 5.23671865020964 |
| C | -1.28275935636521 | 3.04318849808257 | 3.36921650088790 |
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| C | 2.83777210386819 | 7.29814634454797 | 3.14436996590995 |
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| H | 3.76174536747867 | 7.75043695479108 | 2.77171971887386 |
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| H | -1.63007597370281 | 3.24035092953331 | 1.22969604007371 |
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| C | 3.08171303965040 | 5.49181664724297 | 1.43742730005722 |
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| H | 2.21657396806785 | 5.83189101347982 | 0.85996955292755 |
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| H | -3.93059714949950 | 3.53729119168400 | 8.08274872070184 |
| C | -0.96285662207933 | 1.93494693287652 | 4.37995515031976 |
| H | -1.82296041061472 | 1.26092548806919 | 4.45262120874711 |
| H | -0.77715682796234 | 2.35945705422366 | 5.37142015753446 |
| H | -0.09419445380309 | 1.34293133318911 | 4.08050710733784 |
| C | -0.95762953007594 | 4.10609823330075 | 7.86775310472975 |
| H | -1.49433060560381 | 3.15742732256444 | 7.98860773270886 |
| H | -0.13847207372835 | 4.12587913706351 | 8.59556678840578 |
| H | -0.52212294582004 | 4.13054912232307 | 6.86240386392546 |
| C | -5.29729569812814 | 5.15493480682989 | 5.44162944501343 |
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| H | -3.03091971682970 | 6.23010214184586 | 9.69446547311118 |
| H | -1.48719744857327 | 5.51604908139288 | 10.20294194401616 |
| H | -2.87351217073114 | 4.47108136899215 | 9.85759832801912 |
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**3-Si**

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**TS2**

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| C | 3.98544181534629 | 8.81668462209179 | 4.93577382257625 |
| H | 3.50572468450260 | 9.79076947335072 | 4.90751667552494 |
| C | 14.93385361495351 | 7.77626051552179 | 1.70762697349568 |
| H | 15.61340449306707 | 6.92889412840051 | 1.56269430402652 |
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| H | 14.68171923307895 | 8.17729781673708 | 0.71918314179979 |
| C | 12.89009297911879 | 6.28251277020499 | 1.64881337181183 |
| H | 12.59317894020063 | 6.68103739432550 | 0.67125931103449 |
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| H | 13.50420619877182 | 5.39048371608063 | 1.47985661349793 |
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| H | 8.57599464070606 | 2.38095407296553 | 4.56646032211225 |
| H | 8.40010265560816 | 3.79120414627119 | 3.51101821437459 |
| C | 3.21676930530153 | 7.66076566149824 | 5.05161508545795 |
| H | 2.13489126011911 | 7.73142692924033 | 5.11758271557428 |

**Ge(II)**

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| C | 1.54837826088799 | 2.80734990294946 | 0.53929615790645 |
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| H | 0.23632422086556 | 9.37939132840132 | 7.44591023965810 |
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| H | 3.86185210200442 | 8.45427221536441 | 7.39176773464682 |
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| H | 2.99535212619487 | 6.91614965710472 | 7.36963901249447 |
| C | 2.10293186442165 | 0.54032394477410 | 2.05771734990274 |
| H | 2.32138719930147 | -0.34150185429811 | 2.65318955841496 |
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**Ge(IV)'**

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| C | 7.76819319584452 | 23.63885871614444 | 1.89313966815806 |
| C | 3.80862096181261 | 22.79714317881632 | 6.23835638945532 |
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| H | 5.44421675042420 | 27.32926607319369 | 8.43577551862702 |
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| H | 4.39570456152874 | 19.44420388606412 | 6.08187064008325 |
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| H | 6.99447690731558 | 20.82558255477253 | 3.53280421290210 |
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| C | 9.96827382239184 | 25.76838664365189 | 1.17014438813602 |
| H | 9.51420310685165 | 25.80188176572153 | 0.17409424273682 |
| H | 10.53803389572627 | 24.84127467737644 | 1.26337108838917 |
| H | 10.66809324679233 | 26.60629541051371 | 1.25752469068829 |
| C | 1.55666464149782 | 23.43816220452813 | 7.18787386149344 |
| H | 0.78816956159557 | 24.21928898773413 | 7.18501339887535 |
| H | 1.96561686444444 | 23.36307429472768 | 8.20115733154818 |
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| H | 8.77840797897472 | 25.82956630958347 | 4.43428475740758 |
| C | 2.94788277001366 | 25.13469049038066 | 0.63717049181706 |
| H | 2.42470867672406 | 25.28350422341515 | 1.58874476314158 |
| H | 2.97560921055652 | 24.05973655027573 | 0.42922824422875 |
| H | 2.36091285958913 | 25.61873475371515 | -0.15305004692379 |
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**Sn(IV)**

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**Sn(II)**

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