Supplementary Information (SI) for Chemical Science.

# Supplementary Information

## Redox Non-Innocent Bis-Silylene Aluminium Complexes with a Carborane Backbone

Artemis Saddington, Shenglai Yao, Christian Lorent and Matthias Driess*

### Contents

# 1 General Considerations

## General methods and characterization

All experiments were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or an MBraun inert atmosphere glove box under purified $N_2$ fitted with a gas purification and recirculation unit. Glassware was oven-dried at 120 °C for at least 16 h before use. Solvents were dried using standard methods and stored over 3 Å molecular sieves. THF, hexane and diethyl ether were obtained from an inert solvent purification system and then distilled from sodium/benzophenone. Toluene and dichloromethane were obtained from an inert solvent purification system and degassed with dry $N_2$. 1,2-difluorobenzene was dried over 3 Å molecular sieves. NMR spectra were recorded in benzene-$D_6$, THF-$D_8$, dichloromethane-$D_2$ or *o*-dichlorobenzene-$D_4$. THF-$D_8$ and benzene-$D_6$ were dried by distillation from sodium/benzophenone and stored over 3 Å molecular sieves. Dichloromethane-$D_2$ and *o*-dichlorobenzene-$D_4$ were dried and stored over 3 Å molecular sieves.

The solution $^1$H, $^{13}$C, $^{11}$B and $^{29}$Si NMR spectra were recorded on Bruker Spectrometers AV 400 or 500 with residual solvent signals as internal reference ($^1$H and $^{13}$C{$^1$H} NMR) or external standards ($^{11}$B and $^{11}$B{$^1$H} NMR: $BF_3.OEt_2$, 0.0 ppm; $^{29}$Si{$^1$H} NMR: $SiMe_4$, 0.0 ppm). $^{27}$Al NMR signals were too broad to be observed. Generally, $^{29}$Si NMR signals were also not observed, even with H,Si-HMQC experiments. High-resolution MS spectra were measured on a Thermo Scientific LTQ orbitrap XL. Elemental analyses were performed on a Flash EA 1112 CHNS Analyzer by the analytical service at the Institute of Chemistry, Technical University of Berlin, Germany. Satisfactory elemental analysis could not be achieved for compounds **3**, **4a**, **5a** and **5b**.

## Single crystal X-ray diffraction and structure determination

The crystals were mounted on a glass capillary in per-fluorinated oil and measured in a cold $N_2$ flow. The data of **2b**, **3**, **4a**, **4b** and **5b** were collected on an Oxford Diffraction Supernova, Single source at offset, Atlas at 150 K (Cu- Kα-radiation, $\lambda$ = 1.5418 Å). The structures were solved with the SHELXT[1] and refined with Olex2[2,3] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. In the molecular structure of compound **2b**, two of the iodine atoms are disordered over two orientations with an occupancy ratio of 0.55:0.45. One THF molecule can be found in the asymmetric unit, but it is severely disordered and has been removed with the solvent-mask procedure in Olex2. In the single crystal containing compound **4a**, one toluene molecule can be found in the asymmetric unit, but it is severely disordered and has been removed with the solvent-mask procedure in Olex2. In the single crystal containing compound **4b**, two toluene molecules can be found in the asymmetric unit, but they are severely disordered and have been removed using the squeeze routine of platon program. In the molecular structure of compound **5b**, two THF molecules can be found in the asymmetric unit, but they are severely disordered and have been removed with the solvent-mask procedure in Olex2. CCDC deposit numbers for the reported compounds are as follows: 2418300 (compound **2b**), 2418301 (compound **3**), 2418298 (compound **4a**), 2418297 (compound **4b**) and 2418302 (compound **5b**). The supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/.

## EPR Spectroscopy

The EPR spectra were accumulated on a Bruker EMXplus spectrometer equipped with an ER 4122 SHQE resonator. Experimental conditions: 1 mW microwave power, microwave frequency: 9.3 GHz, 2 G modulation amplitude, 100 kHz modulation frequency. The simulation of the spectrum was performed using the MATLAB toolbox EasySpin (version 5.2.25).[4] The power saturation data was fitted to an empirical equation as described by Hirsh et al.[5]

## Preparation of starting materials

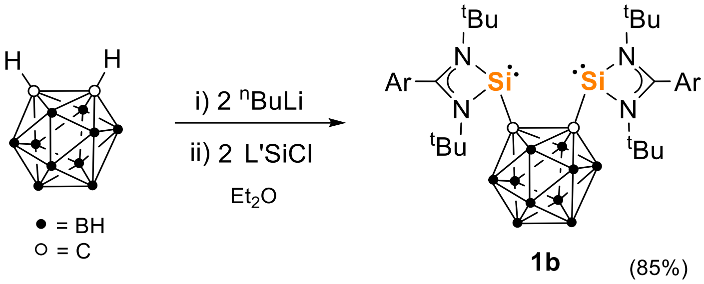
Bis-silylene **1a** was prepared from 1,2-$C_2B_{10}H_{12}$ and LSiCl according to literature procedures.[6,7] The modified chlorosilylene (*p*-($^t$Bu)$C_6H_4$)C(N$^t$Bu)$_2$SiCl was synthesized according to literature procedure from *p*-($^t$Bu)$C_6H_4$Br.[8] Potassium graphite ($KC_8$) was prepared by reacting potassium with previously dried graphite in a 1:8 molar ratio at 160 °C for 2 h. Potassium naphthalenide was prepared by reacting potassium with one molar equiv naphthalene crystals in THF and stirred 12 h. The solvent was removed *in vacuo* giving K($C_{10}H_8$) as a black powder to be stored in the glovebox. Crystalline [K($C_{10}H_8$)(THF)] was prepared according to literature procedure.[9] K/KI (5% w/w) was prepared according to literature procedure.[10] The $^{Me}$cAAC-5 carbene was prepared according to literature procedure.[11]

Aluminium iodide ($AlI_3$) was prepared by reacting iodine ($I_2$) crystals (1.5 equivs) with aluminium metal ribbon (1.1 equivs) in toluene at 60 °C for at least 3 h (until it turned colorless).[12] The hot solution was decanted and microcrystalline $AlI_3$ was crashed out with cooling then separated and dried *in vacuo*. Yield: 87% (4.6 g).

Gallium diiodide '$GaI_2$' was prepared from the reaction of Ga metal (1 equiv) with $I_2$ (1 equiv) in toluene at 60 °C for at least 3 h (until the solvent turned colorless).[13,14] The toluene was removed *in vacuo* and the '$GaI_2$' solid isolated as a pale-green powder. Yield: 90% (4.0g).

## A2 Synthesis and Characterization of compounds 1b – 5

### Compound **1b**



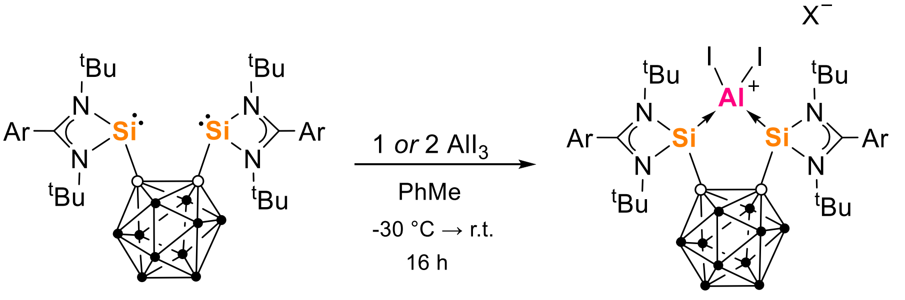
**1b** (85%)

Ar = $p$-$C_6H_4$($^t$Bu)

Compound **1b** was prepared in the same manner as the reported compound **1a** in 85% yield, using silylene ($p$-($^t$Bu)$C_6H_4$)C(N$^t$Bu)$_2$SiCl (L'SiCl) instead of PhC(NtBu)$_2$SiCl (LSiCl).

**$^1$H NMR** (500 MHz, $C_6D_6$, 298 K, ppm) $\delta$ = 7.37 – 7.33 (m, 2H, Ar*H*), 7.09 – 7.02 (m, 6H, Ar*H*), 3.89 – 2.60 (br., 10H, B*H*), 1.30 (s, 36H, NC(C*H*$_3$)$_3$), 1.12 (s, 18H, Ar-C(C*H*$_3$)$_3$). **$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$, 298 K, ppm) $\delta$ = 168.7 (N*C*N), 153.3, 131.8, 130.7, 128.6, 128.1, 125.2, 123.9, (Ar*C*), 85.6 (*C*Si), 54.1 (N*C*(CH$_3$)$_3$), 34.7 (Ar-*C*(CH$_3$)$_3$), 32.2 (NC(*C*H$_3$)$_3$), 31.2 (Ar-C(*C*H$_3$)$_3$). **$^{11}$B NMR** (161 MHz, $C_6D_6$, 298 K, ppm) $\delta$ = 0.8 (d, $J_{BH}$ = 88.9 Hz), -5.0 (d, $J_{BH}$ = 127.5 Hz), -9.4 (br.). **$^{29}$Si{$^1$H} NMR** (99 MHz, $C_6D_6$, 298 K, ppm) $\delta$ = 19.1. **HRMS** (APCI) *m/z* calcd for $C_{40}H_{72}B_{10}N_4Si_2$+3(OH): 823.6367 [*M*+3(OH)]; found: 823.6375.

### Compounds **2a**, **2b**, **2c**



**1**

**1a**: Ar = Ph

**1b**: Ar = $p$-$C_6H_4$($^t$Bu)

**2a,b,c** (76-85%)

**2a**: Ar = Ph, X = I

**2b**: Ar = Ph, X = $AlI_4$

**2c**: Ar = $p$-$C_6H_4$($^t$Bu), X = I

General procedure:

*o*-carboranyl-bis(silylene) **1a** or **1b** was mixed with $AlI_3$ in a Schlenk flask. The mixture was cooled to -30 °C and toluene was added with rapid stirring. The reaction flask was allowed to slowly warm to room temperature and stirred overnight (ca. 16 h). On warming, the golden color of the bis(silylene) disappeared and precipitate formed, giving a pale-yellow suspension. The precipitate was separated by cannula filtration, washed with $Et_2O$ and then dried under vacuum for 2 h at 50 °C.

**2a**: Ligand **1a** (1.10 g, 1.66 mmol) was reacted with $AlI_3$ (0.685 g, 1.68 mmol, 1.0 equiv) in toluene (30 mL) to give **2a** as a colorless powder (1.41 g, 79%).

**$^1$H NMR** (400 MHz, *o*-DCB-$d_4$, 298 K) $\delta$ =7.54 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, Ph*H*), 7.22 – 7.38 (m, 8 H, Ph*H*), 2.30 – 3.47 (br., 10H, B*H*), 1.36 (s, 36 H, C(C*H*$_3$)$_3$). **$^1$H,$^{13}$C-HSQC NMR** (400 MHz, *o*-DCB-$d_4$, 298 K) $\delta_C$ = 131.5, 128.2, 128.2, 128.1, 128.0 (*C*$_6$H$_5$), 31.3 (C(*C*H$_3$)$_3$). **$^1$H,$^{13}$C-HMBC NMR** (400 MHz, *o*-DCB-$d_4$, 298 K) $\delta_C$ = 129.1 (*i*-*C*$_6$H$_5$), 56.2 (*C*(CH$_3$)$_3$). Elemental analysis calculated for $C_{32}H_{56}B_{10}N_4Si_2AlI_3$: C 35.96, H 5.28, N 5.24; found: C 34.94, H 6.13, N 4.81.

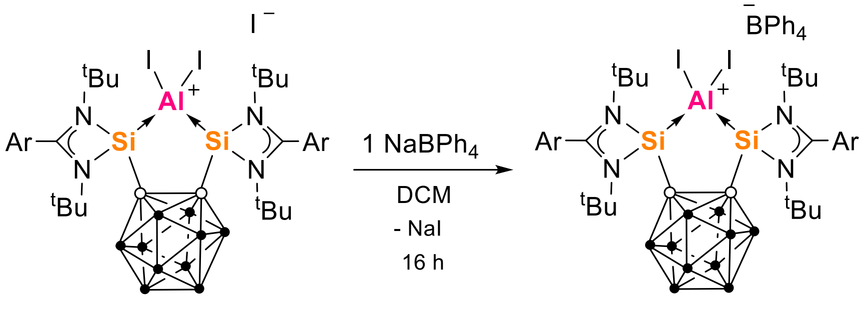
**2b**: Ligand **1a** (0.500 g, 0.76 mmol) was reacted with $AlI_3$ (0.616 g, 1.51 mmol, 2 equiv), giving **2b** as a colorless powder (0.960 g, 85%). Crystals suitable for scXRD analysis were grown from a saturated $Et_2O$ solution at -22 °C in 2 d.

Elemental analysis calculated for $C_{32}H_{56}B_{10}N_4Si_2Al_2I_6$: C 26.03, H 3.82, N 3.79; found: C 25.91, H 4.08, N 3.56.

**2c**: Ligand **1b** (1.52 g, 1.97 mmol) was reacted with $AlI_3$ (0.80 g, 1.96 mmol, 1 equiv), producing **2c** as a pale-yellow solid (1.77 g, 76%).

**$^1$H NMR** (500 MHz, $CD_2Cl_2$, 298 K, ppm) $\delta$ = 7.60 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ar*H*), 7.53 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, Ar*H*), 7.32 (d, $^3J_{HH}$ = 7.3 Hz, 2H, Ar*H*), 2.02 – 3.38 (br., 10H, B*H*), 1.38 (s, 36H, NC(C*H*$_3$)$_3$), 1.36 (s, 18H, Ar-C(C*H*$_3$)$_3$). **$^{13}$C{$^1$H} NMR** (126 MHz, $CD_2Cl_2$, 298 K, ppm) $\delta$ = 181.3 (N*C*N), 156.1, 129.6, 128.8, 127.4, 125.6, 125.6 (Ar*C*), 76.7 (*C*Si), 57.2 (N*C*(CH$_3$)$_3$), 35.6 (Ar-*C*(CH$_3$)$_3$), 32.3 (NC(*C*H$_3$)$_3$). 31.5 (Ar-C(*C*H$_3$)$_3$). **$^{11}$B{$^1$H} NMR** (126 MHz, $CD_2Cl_2$, 298 K, ppm) $\delta$ = 1.9, -3.5, -8.7, -13.2. Elemental analysis calculated for $C_{40}H_{72}B_{10}N_4Si_2AlI_3$: C 40.68, H 6.15, N 4.74; found: C 40.17, H 5.80, N 4.41.

## Compound **2d**



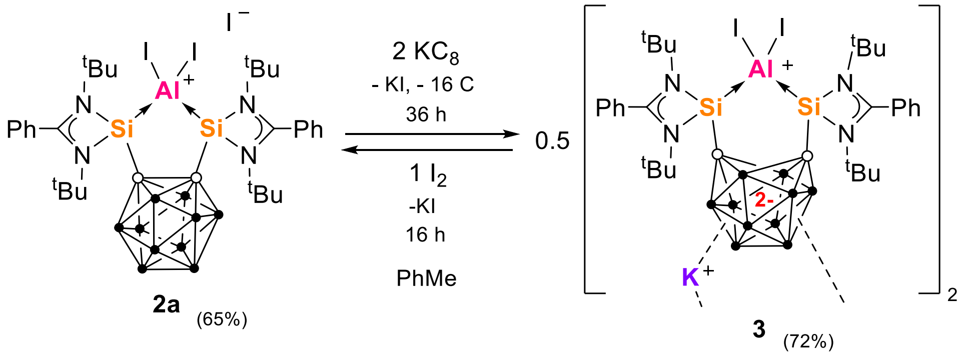
**2c** **2d** (91%)

Ar = *p*-$C_6H_4$($^{t}$Bu)

Compound **2c** (400mg, 0.34 mmol) was loaded in a Schlenk flask with $NaBPh_4$ (122 mg, 0.36 mmol, 1.05 equiv) and then dissolved in dichloromethane (20 mL). The mixture was stirred overnight (ca. 16 h) to ensure full dissolution of $NaBPh_4$, giving a colorless cloudy mixture. The solvent was removed *in vacuo*, washed with hexane and the resulting pale-yellow solid was dried for 1 h at 55 °C, giving **2d** (423 mg, 91%).

**$^{1}$H NMR** (500 MHz, $CD_2Cl_2$, 298 K) $\delta$ = 7.64 (td, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 1.4 Hz, 4H, Ar*H*), 7.47 (dd, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 1.9 Hz, 2H, Ar*H*), 7.35 (dd, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 1.9 Hz, 2H, Ar*H*), 7.33 – 7.28 (m, 8H, B-Ph*H*), 7.02 (t, $^{3}J_{HH}$ = 7.4 Hz, 8H, B-Ph*H*), 6.87 (t, $^{3}J_{HH}$ = 7.1 Hz, 4H, B-Ph*H*), 3.21 – 2.11 (br., 10H, B*H*), 1.39 (s, 18H, Ar-C(C*H*$_3$)$_3$), 1.35 (s, 36H, NC(C*H*$_3$)$_3$). **$^{13}$C{$^{1}$H} NMR** (126 MHz, $CD_2Cl_2$, 298 K) $\delta$ = 185.9 (N*C*N), 165.2, 164.8, 164.4, 164.0, 157.6, 136.4, 136.4, 130.0, 127.4, 126.4, 126.2, 126.2, 126.2, 126.2, 125.4, 122.3 (Ar*C*), 58.3 (N*C*(CH$_3$)$_3$), 35.8 (Ar-*C*(CH$_3$)$_3$, 32.3 (NC(*C*H$_3$)$_3$), 31.4 (Ar-C(*C*H$_3$)$_3$). **$^{11}$B NMR** (161 MHz, $CD_2Cl_2$, 298 K) $\delta$ = 3.5 (br., *B*H), -1.1 (br., *B*H), -6.6 (s, *B*Ph$_4$), -9.0 (br., *B*H), -13.1 (br., *B*H).

## Compound **3**



### Reduction of **2a**

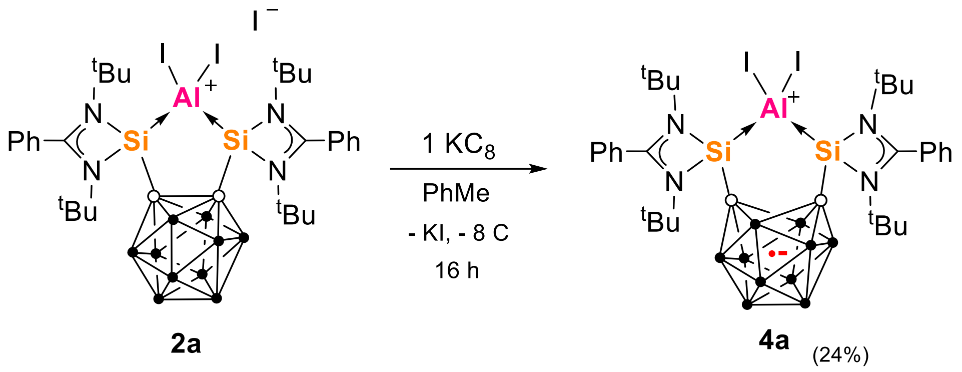
Compound **2a** (0.700 g, 0.65 mmol) was mixed with excess $KC_8$ (0.44 g, 3.25 mmol, 5 equiv) in a Schlenk flask and then suspended in toluene (50 mL). The suspension was stirred for 36 h to give a dark red-brown suspension. The suspension was allowed to settle then cannula filtered to give a bright red solution. The solution was concentrated by 50% and stored at -22 °C. After storage in the freezer for 2 d, red needle-like crystals formed. The crystals were confirmed by scXRD analysis to be [**3**($C_6H_5Me$)$_2$]. The crystals were separated from the supernatant by decanting and dried for 2 h at 45 °C to give **4** as a pink powder (458 mg, 72%). Crystals of [**3**($Et_2O$)$_4$] suitable for scXRD analysis were grown from a concentrated $Et_2O$ solution stored at -22 °C overnight.

**$^1$H NMR** (500 MHz, THF-d$_8$, 298 K) $\delta$ = 7.59 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ph*H*), 7.56 – 7.45 (m, 8H, Ph*H*), 1.31 (s, 36 H, C(C*H*$_3$)$_3$). **$^{13}$C{$^1$H} NMR** (125 MHz, THF-d$_8$, 298 K) $\delta$ = 174.6 (NCN), 132.5, 131.5, 131.3, 130.5, 129.8, 129.1, 128.8, 128.7, 126.2 (Ph-*C*), 55.0 (*C*(CH$_3$)$_3$), 32.3 (C(*C*H$_3$)$_3$). **$^{11}$B{$^1$H} NMR** (161 MHz, THF-D$_8$, 298 K) $\delta$ = -3.2, -7.2, -16.6, -32.6.

### Oxidation of **3**

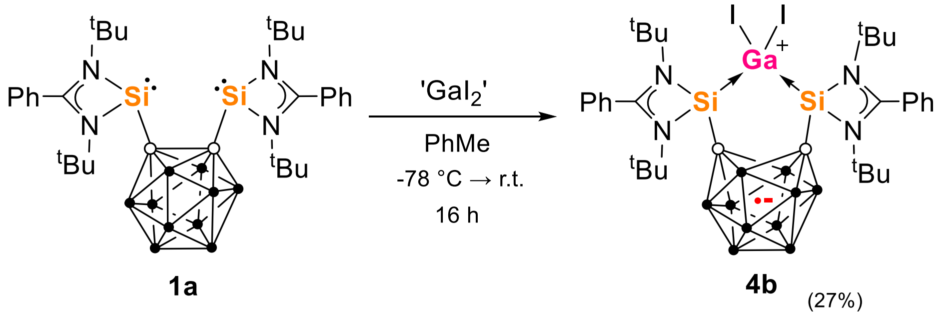
Dimer **3** (50 mg, 0.051 mmol) was added to a Schlenk flask with $I_2$ crystals (15 mg, 0.059 mmol, 1.16 equiv) and then dissolved in toluene (6 mL). The reaction was stirred overnight (ca. 16 h) and the red color of the solution faded to pale yellow and appeared cloudy. The toluene was removed *in vacuo* and the residue was extracted with 1,2-difluorobenzene (3 + 1 mL) and filtered *via* filter cannula. The solvent was removed *in vacuo*, leaving **2a** as a colorless solid (39.5 mg, 65%).

## Compound **4a**



Complex **2a** (0.36 g, 0.34 mmol) was mixed with $KC_8$ (0.115 g, 0.85 mmol, 2.5 equiv) in a Schlenk flask and then suspended in toluene. The suspension was stirred overnight (ca. 16 h) to give a dark brown suspension. The suspension was allowed to settle then cannula filtered to give a dark red solution. The solution was stored at -22 °C for 4 d giving dark brown crystals of **4a** (75 mg, 24%). These crystals were suitable for scXRD analysis. **4a** is NMR silent and was characterized by EPR.

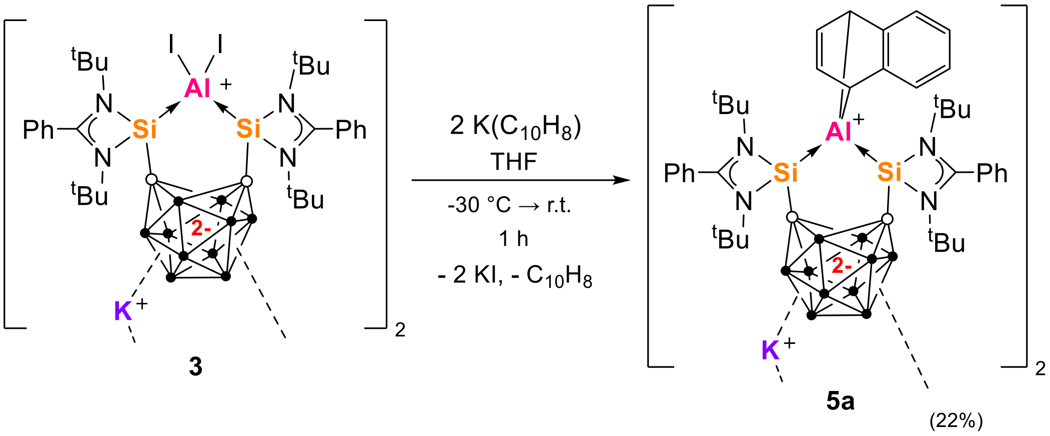
## Compound **4b**



Ligand **1a** (250 mg 0.38 mmol), was mixed with ‘$GaI_2$’ (170 mg, 0.53 mmol, 1.4 equiv) in a Schlenk flask. The mixture was cooled to -78 °C and toluene (ca. 50 mL) was added with rapid stirring. The reaction flask was allowed to slowly warm to room temperature and stirred overnight (ca. 16 h). On warming, the golden color of the bis(silylene) darkens with the reaction turning into a dark red suspension. The suspension was allowed to settle then cannula filtered to give a dark red-purple solution. The solution was stored at -22 °C overnight giving a mixture of dark red crystals and yellow crystals of **4b** in three crops (combined 102 mg, 27%). Both crystal types were measured by scXRD, with the yellow crystals giving better quality data. **4b** is NMR silent and was characterized by EPR.

**HRMS** (APCI) *m/z* calcd for $C_{32}H_{56}B_{10}N_4Si_2GaI_2$: 983.2386 [*M*]; found: 983.2381; 1056.2887 [*M*+4($H_2O$)]; found: 1056.2959. Elemental analysis calculated for $C_{32}H_{56}B_{10}N_4Si_2GaI_2$: C 39.04, H 5.73, N 5.69; found: C 38.22, H 6.06, N, 5.46.

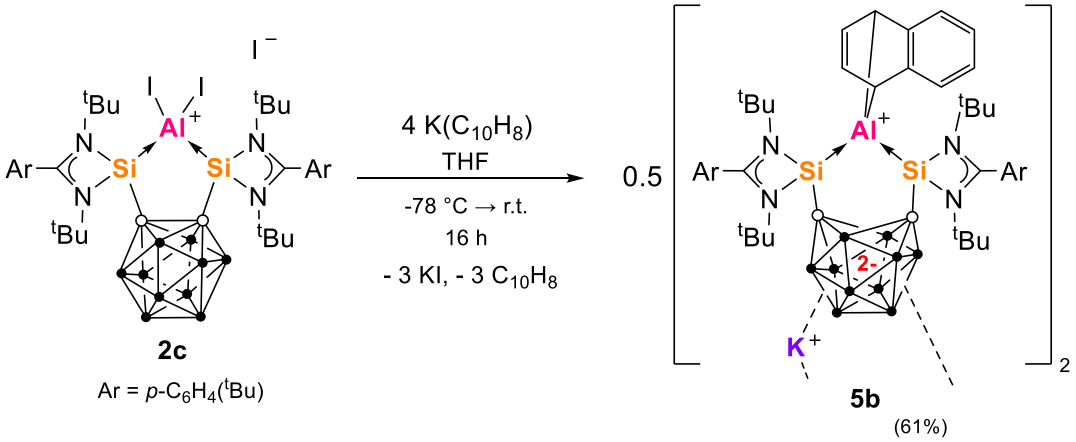
Compound **5a**



Dimer **3** (0.250 g, 0.127 mmol, 1 equiv) was mixed with K($C_{10}H_8$) (85 mg, 0.508 mmol, 4 equiv) in a Schlenk flask. The mixture was cooled to -30 °C and THF (7 mL) was added with rapid stirring and allowed to warm quickly to room temperature. The mixture was then stirred for 1 h then cannula filtered, and the solvent removed *in vacuo*. The brown residue was extracted with toluene (3 x 30 mL) and filtered via cannula into a new flask. The cloudy orange filtrate was stored at -22 °C for 7 d, yielding **5a** as orange crystals (47 mg, 22%). These crystals could not be measured by scXRD.

**$^1$H NMR** (500 MHz, THF-$d_8$, 298 K, ppm) $\delta$ = 7.56 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Ph*H*), 7.49 (m, 4H, Ph*H*), 7.42 (m, 2H, Ph*H*), 7.35 (td, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.1 Hz, 1H, Ph*H*), 7.26 (d, $^3J_{HH}$ = 7.6 Hz, 1H, Ph*H*), 7.10 (d, $^3J_{HH}$ = 7.4 Hz, 1fH, Ph*H*), 6.93 (dd, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 3.2 Hz, 2 H, Naph-*H*), 6.80 (dd, $^3J_{HH}$ = 5.3 Hz, $^4J_{HH}$ = 3.2 Hz, 2 H, Naph-*H*), 6.38 (dd, $^3J_{HH}$ = 4.5 Hz, $^4J_{HH}$ = 3.2 Hz, 2 H, C=C*H*), 3.04 (m, 2 H, AlC*H*), 1.28 (s, 18 H, C(C*H*$_3$)$_3$), 1.09 (s, 18 H, C(C*H*$_3$)$_3$). **$^{13}$C{$^1$H} NMR** (125 MHz, THF-$d_8$, 298 K, ppm) $\delta$ = 170.8 (N*C*N), 170.6 (N*C*N), 149.8 (Naph-*C*), 133.7, 133.5, 132.2, 131.2, 131.1, 130.8, 129.8, 129.4, 129.1, 128.8, 128.7, 128.1 (Ph-*C), 126.2 (H*C*=*C*H), 121.7 (Naph-*C*H), 121.4 (Naph-*C*H), 54.5 (*C*(CH$_3$)$_3$), 54.1 (*C*(CH$_3$)$_3$), 48.2 (AlCH), 32.4 (C(*C*H$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$). **$^{11}$B NMR** (161 MHz, THF-D$_8$, 298 K, ppm) $\delta$ = 10.9 (br.), -1.9 (d, $J_{BH}$ = 96.7 Hz), -15.1 (s), -21.2 (d, $J_{BH}$ = 107.7 Hz). **$^1$H,$^{29}$Si-HMQC NMR** (500 MHz, THF-D$_8$, 298 K, $J_{SiH}$ = 3z Hz, NUS 50%, ppm) $\delta_{Si}$ = 30.7, 40.4.

### Compound **5b**



**2c** (300 mg, 0.252 mmol, 1 equiv) was mixed with $K(C_{10}H_8)$ (170 mg, 1.02 mmol, 4 equiv) in a Schlenk flask in the glovebox. The mixture was cooled to -78 °C and THF (8 mL) was added with rapid stirring and allowed to warm quickly to room temperature, turning dark brown rapidly. The mixture was left to stir for 16 h then the solvent removed *in vacuo*. The brown residue was extracted with $Et_2O$ (x mL) and stirred for 5 min. The mixture was allowed to settle then filtered via cannula into a new flask. The brown filtrate was concentrated and then stored at -22 °C for 3 d, yielding red-orange crystals. The crystals were separated from the supernatant and washed with 2 x 1 mL $Et_2O$ before drying *in vacuo* to give **5b** as an orange solid (161 mg, 61%). Crystals of **5b** grown from $Et_2O$ solutions were suitable for scXRD analysis.

**$^1$H NMR** (500 MHz, $C_6D_6$, 298 K, ppm) $\delta$ = 7.48 (dd, $^3J_{HH}$ = 5.2 Hz, $^4J_{HH}$ = 3.2 Hz, 2H, Ar$H$), 7.39 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, Ar$H$), 7.33 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar$H$), 7.29 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.4 Hz, 1H, Ar$H$), 7.27 – 7.11 (m, 6H, Ar$H$), 7.07 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar$H$), 6.94 (t, $^3J_{HH}$ = 3.8 Hz, 2H, C=C$H$), 3.62 (t, $^3J_{HH}$ = 3.8 Hz, 2H, AlC$H$), 1.45 (s, 18H, $NC(CH_3)_3$), 1.35 (s, 18H, $NC(CH_3)_3$), 1.13 (s, 18H, Ar-$C(CH_3)_3$). **$^{13}$C{$^1$H} NMR** (125 MHz, $C_6D_6$, 298 K, ppm) $\delta$ = 171.7 (N$C$N), 171.6 (N$C$N), 153.8, 153.6, 149.1, 134.1, 131.0, 129.8, 129.5, 129.0, 128.9, 128.7, 128.6, 128.2, 128.0, 126.1, 125.1, 125.0, 124.9, 124.8, 124.5, 121.9, 121.6 (Ar$C$, $C$=$C$), 67.9 ($C$Si), 54.0 ($NC(CH_3)_3$), 53.7 ($NC(CH_3)_3$), 47.7 (Al$C$H), 34.8 (Ar-$C(CH_3)_3$, 34.8 (Ar-$C(CH_3)_3$, 32.2 ($NC(CH_3)_3$), 32.0t ($NC(CH_3)_3$), 31.2 (Ar-$C(CH_3)_3$). **$^{11}$B NMR** (161 MHz, $C_6D_6$, 298 K, ppm) $\delta$ = 0.3 (br.), -6.1 (br.), -15.4 (br.), -30.0 (br.). **$^{29}$Si NMR** (99 MHz, $C_6D_6$, 298 K, ppm) $\delta$ = 29.4, 39.1. **HRMS** (ESI) $m/z$ calcd for fragment $C_{31}H_{60}B_{10}N_2SiAlO_5$: 705.5241 [$M$–$K^+$–$(C_{19}H_{31}N_2Si)$+5$(H_2O)$]; found: 705.4322.

## Attempts to trap fleeting low valent Al species

a) Dropwise addition of crystalline [K($C_{10}H_8$)(THF)] (4 molar equivs) dissolved in THF to a suspension of 1 molar equiv **2c** and 1 equiv $^{Me}$cAAC-5 cooled to -78 °C gave a dark brown mixture. On warming it lightened to a golden orange color after stirring 1 h at r.t.. The solvent was removed in vacuo and the residue extracted with $Et_2O$, but no crystalline material grew after 3 weeks. $^1$H NMR aliquots showed naphthalene as the major product and a complicated mixture.

b) In an attempt to access a radical product directly, 1 equiv [K($C_{10}H_8$)(THF)] dissolved in THF was added dropwise to a solution of 0.5 molar equiv of dimer **3** with and 1 equiv $^{Me}$cAAC-5 in THF cooled to -78 °C. This resulted in a dark red filtrate. No products could be crystallized from THF alone or with layering of $Et_2O$.

c) Reduction of the $BPh_4$ salt **2d** with K/KI (approx. 5 equiv K, 5% w/w) in $Et_2O$ in the presence of one equiv $^{Me}$cAAC-5 led to the formation of very dark blue mixtures after a few hours of stirring. This was promising as unsaturated silylene- or cAAC-Al species (e.g. **III**, Figure 1) have been reported to give solutions with intense colors, such as dark-violet, -blue and -green.[15–17] Using toluene as the solvent instead, a dark blue mixture was only obtained in 48 hours of stirring. The blue color was not observed when using **2c** as a reactant (instead of **2d**) or without the addition of cAAC. While some small blue crystals could be grown from $Et_2O$/hexane solution, they decomposed during attempted measurement, deforming and changing color. All other attempts to isolate the dark blue compound from $Et_2O$, toluene, benzene/hexane and $iPr_2O$ as single-crystals suitable for scXRD failed.

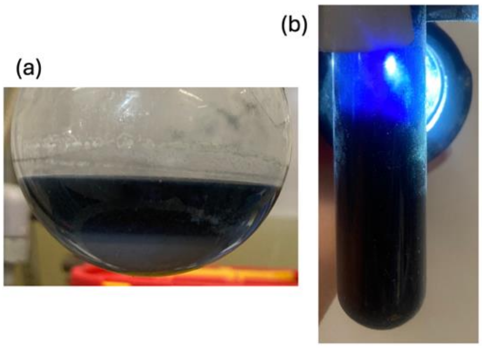


**Figure S1.** Color of the resulting mixture from the reaction of **2d** with K/KI and $^{Me}$cAAC-5. (a) reaction mixture allowed to settle (b) filtered reaction mixture held in front of a torch.

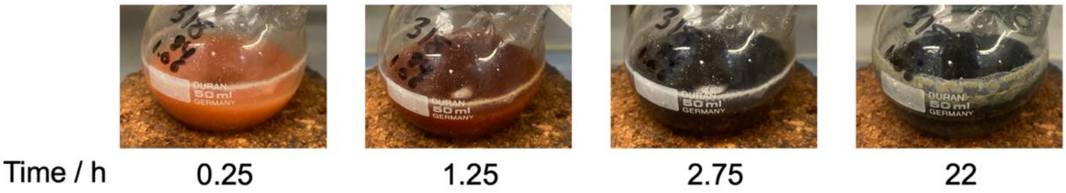


**Figure S2.** Color changes at the different time points for the reaction of **2d** with K/KI and $^{Me}$cAAC-5.

## A3 NMR Spectra

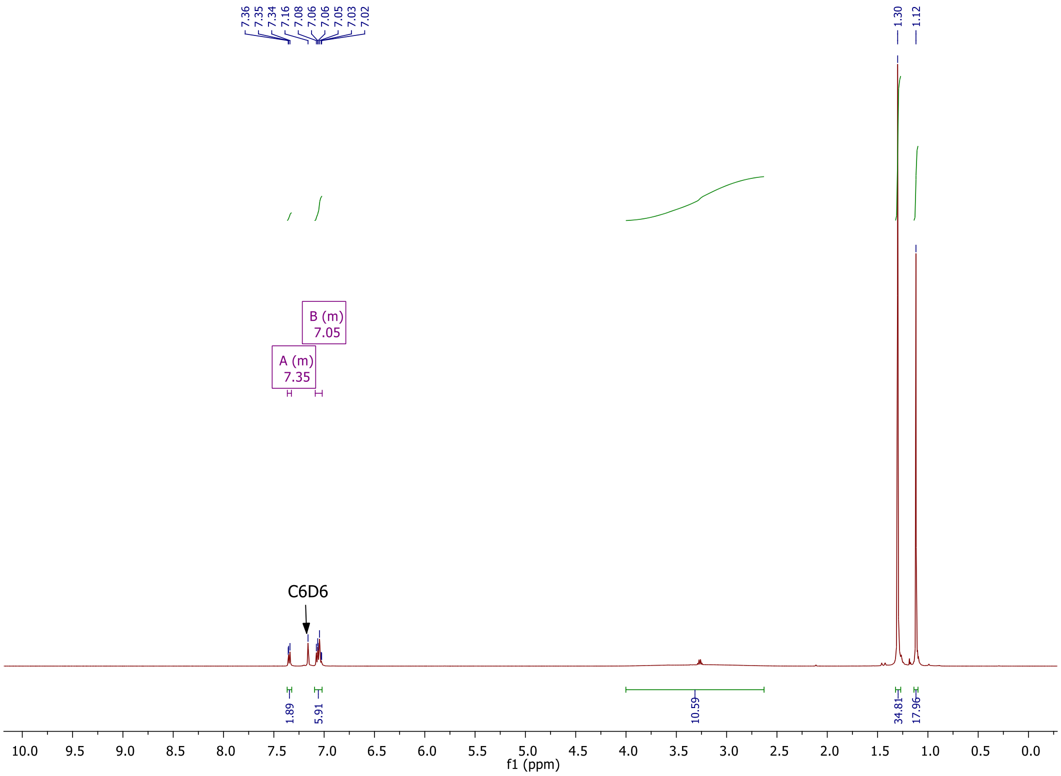


**Figure S3** $^{1}H$ NMR spectrum of **1b** in $C_6D_6$ under 1 bar $N_2$ at 298 K.

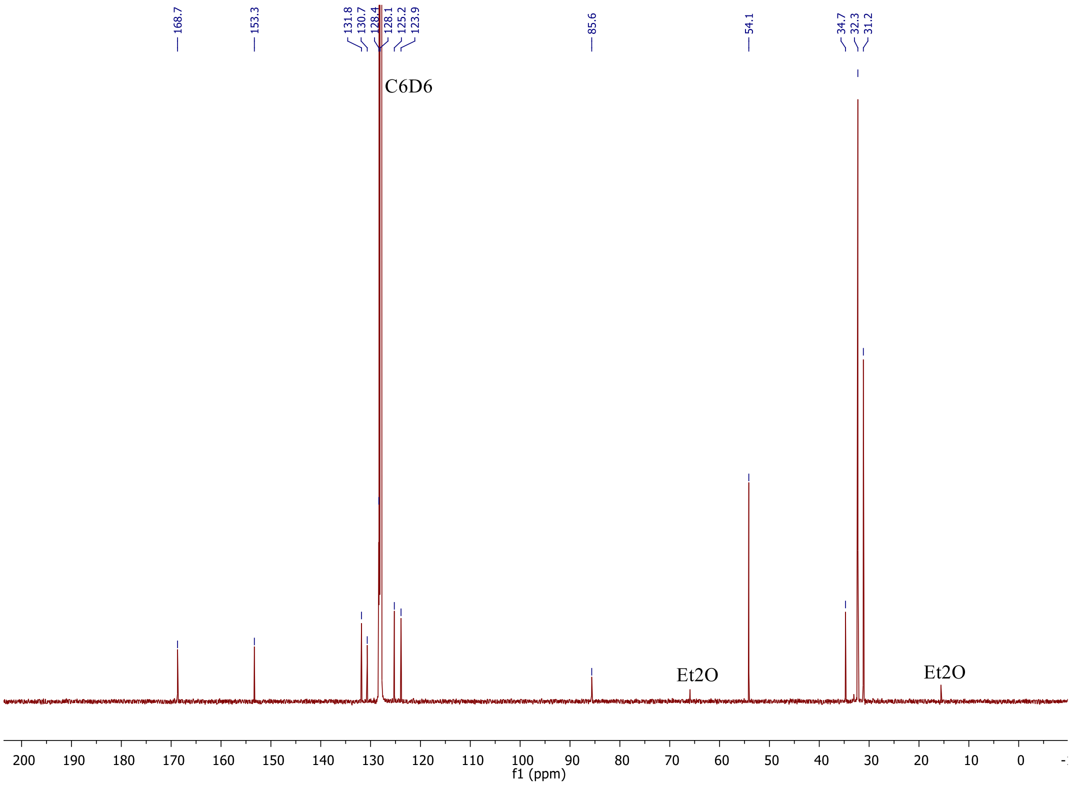


**Figure S4** $^{13}C\{^{1}H\}$ NMR spectrum of **1b** in $C_6D_6$ under 1 bar $N_2$ at 298 K.

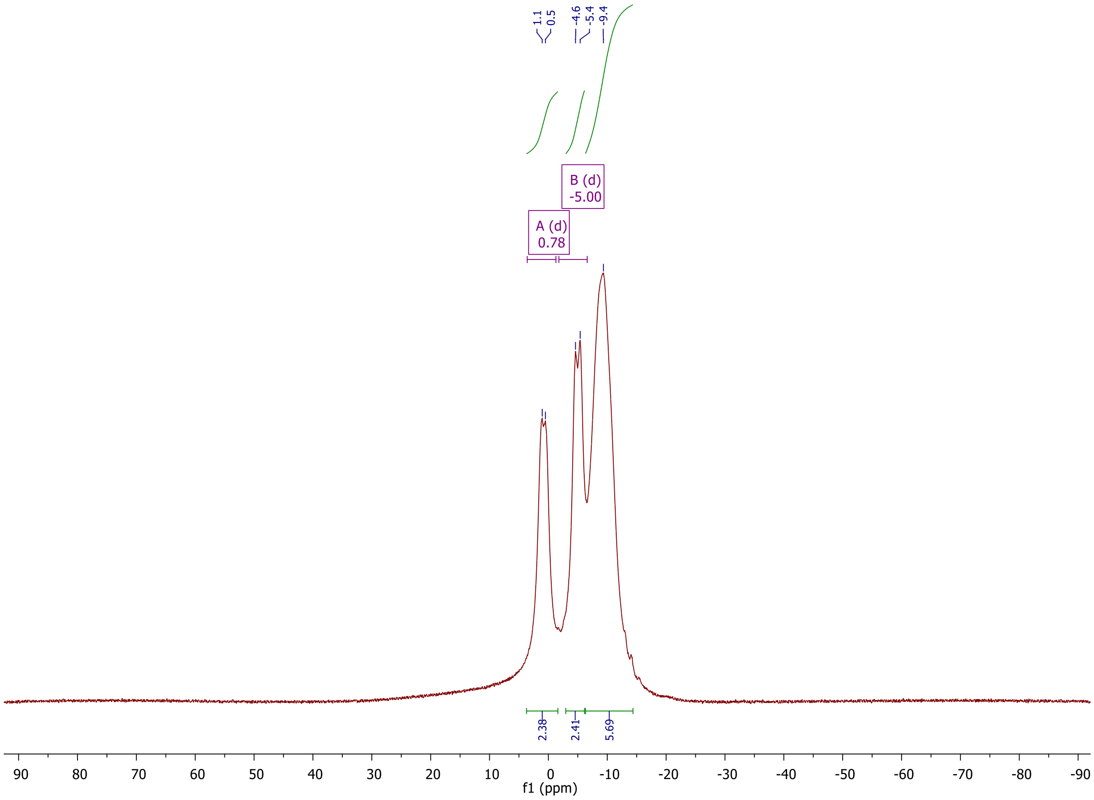


**Figure S5** $^{11}$B NMR spectrum of **1b** in $C_6D_6$ under 1 bar $N_2$ at 298 K.

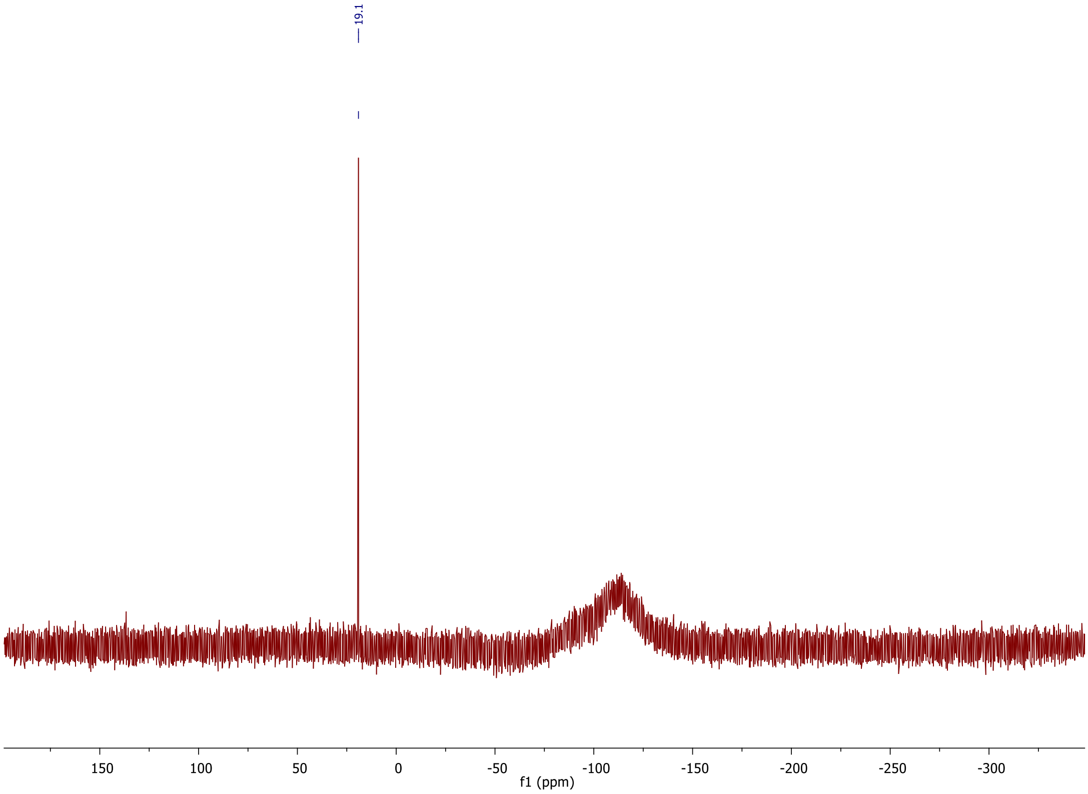


**Figure S6** $^{29}$Si{$^1$H} NMR spectrum of **1b** in $C_6D_6$ under 1 bar $N_2$ at 298 K.

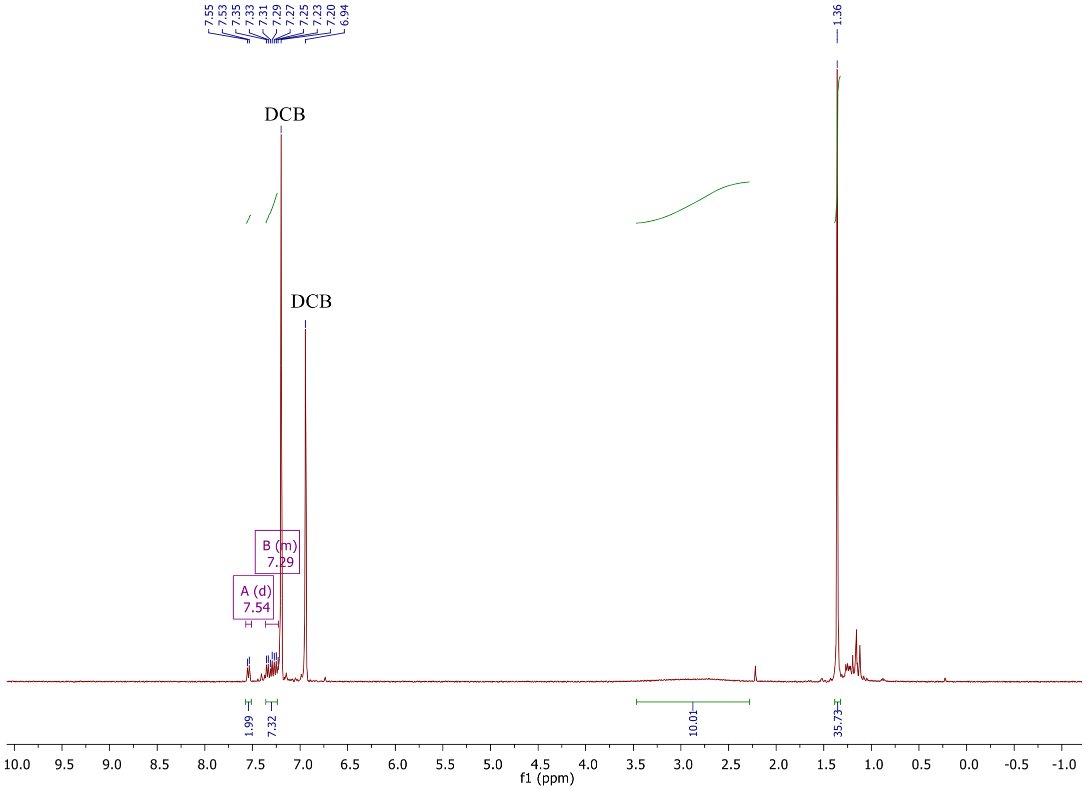


**Figure S7** $^{1}$H NMR spectrum of **2a** in *o*-$C_6D_4Cl_2$ under 1 bar $N_2$ at 298 K.

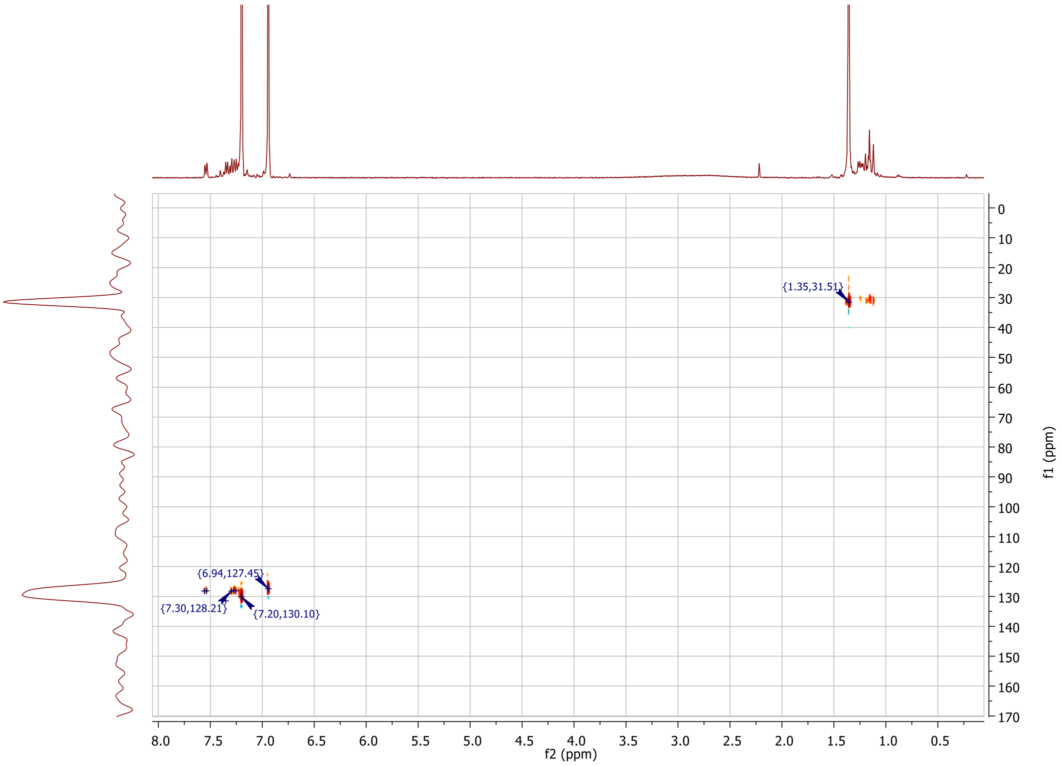


**Figure S8** $^{1}$H,$^{13}$C-HSQC NMR spectrum of **2a** in *o*-$C_6D_4Cl_2$ under 1 bar $N_2$ at 298 K.

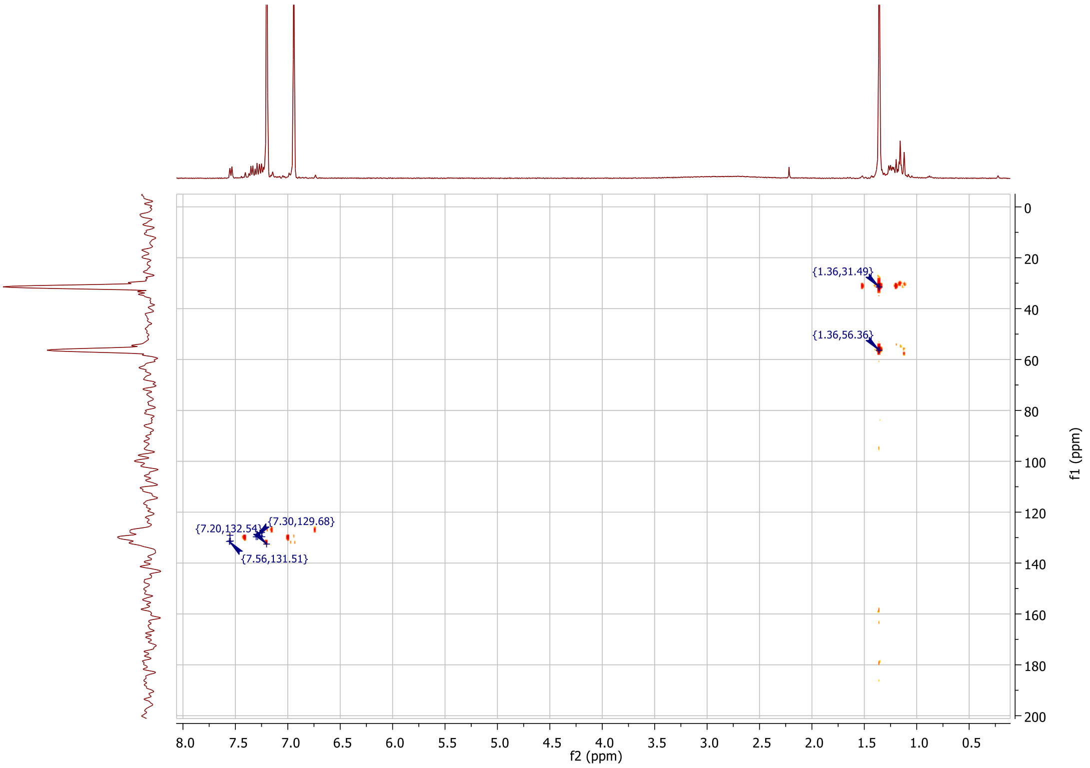


**Figure S9** $^1$H,$^{13}$C-HMBC NMR spectrum of **2a** in *o*-$C_6D_4Cl_2$ under 1 bar $N_2$ at 298 K.

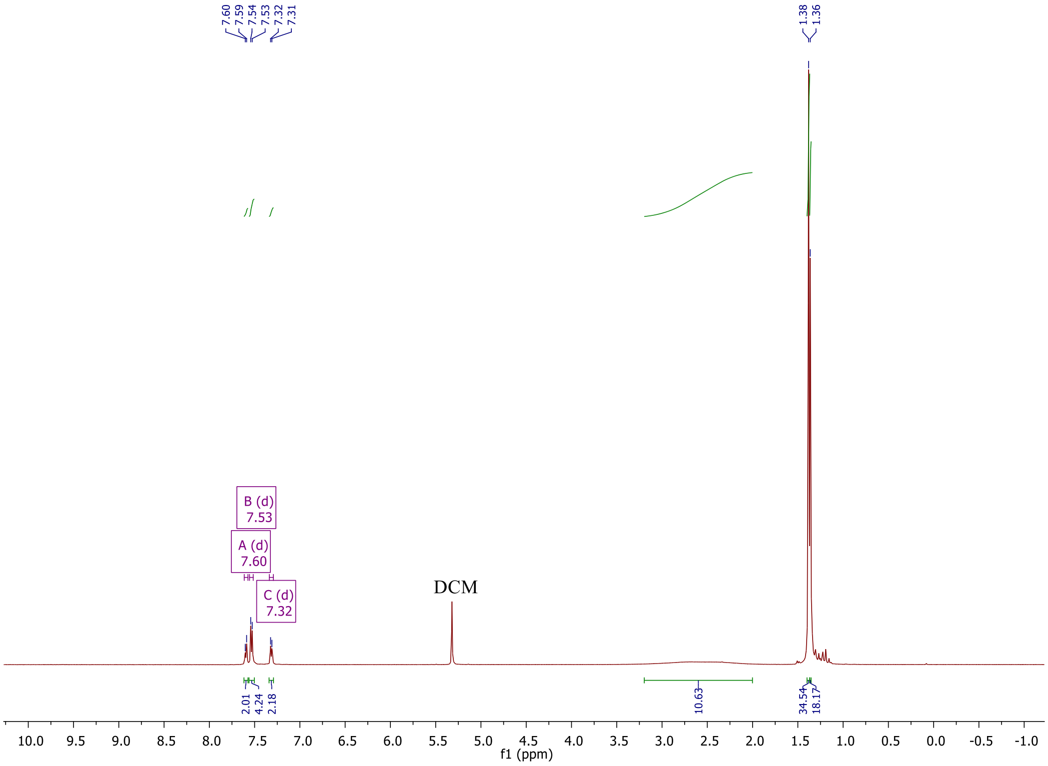


**Figure S10** $^1$H NMR spectrum of **2c** in $CD_2Cl_2$ under 1 bar $N_2$ at 298 K.

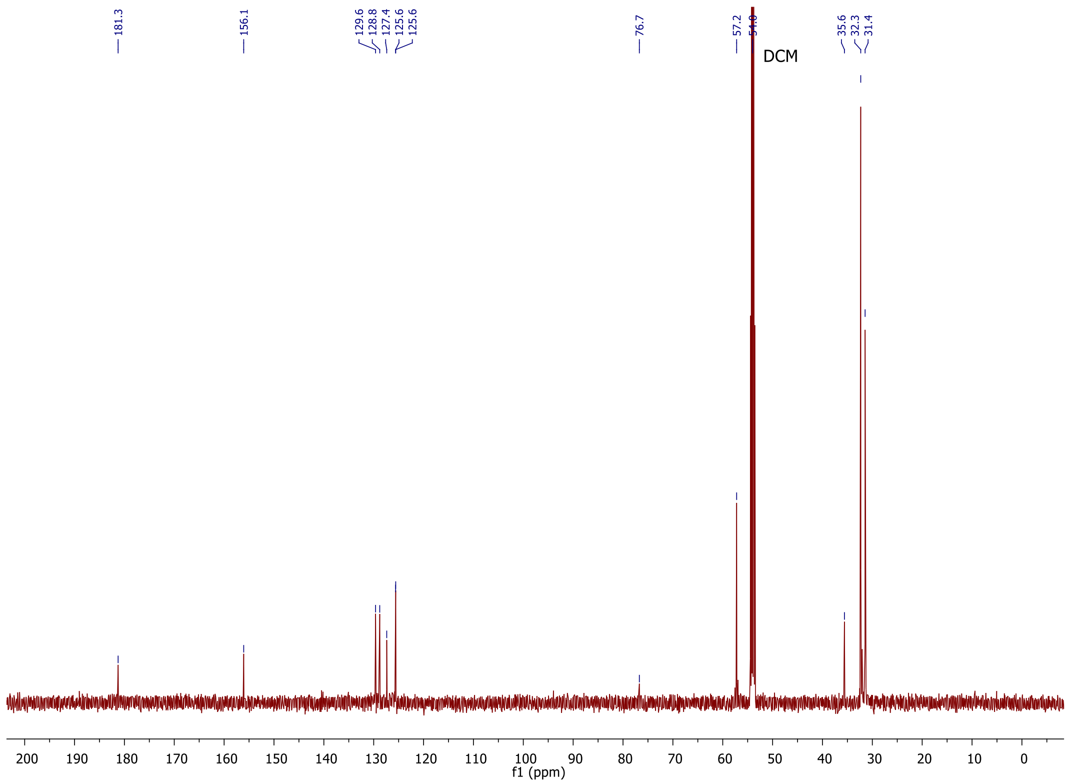


**Figure S11** $^{13}C\{^{1}H\}$ NMR spectrum of **2c** in $CD_2Cl_2$ under 1 bar $N_2$ at 298 K.

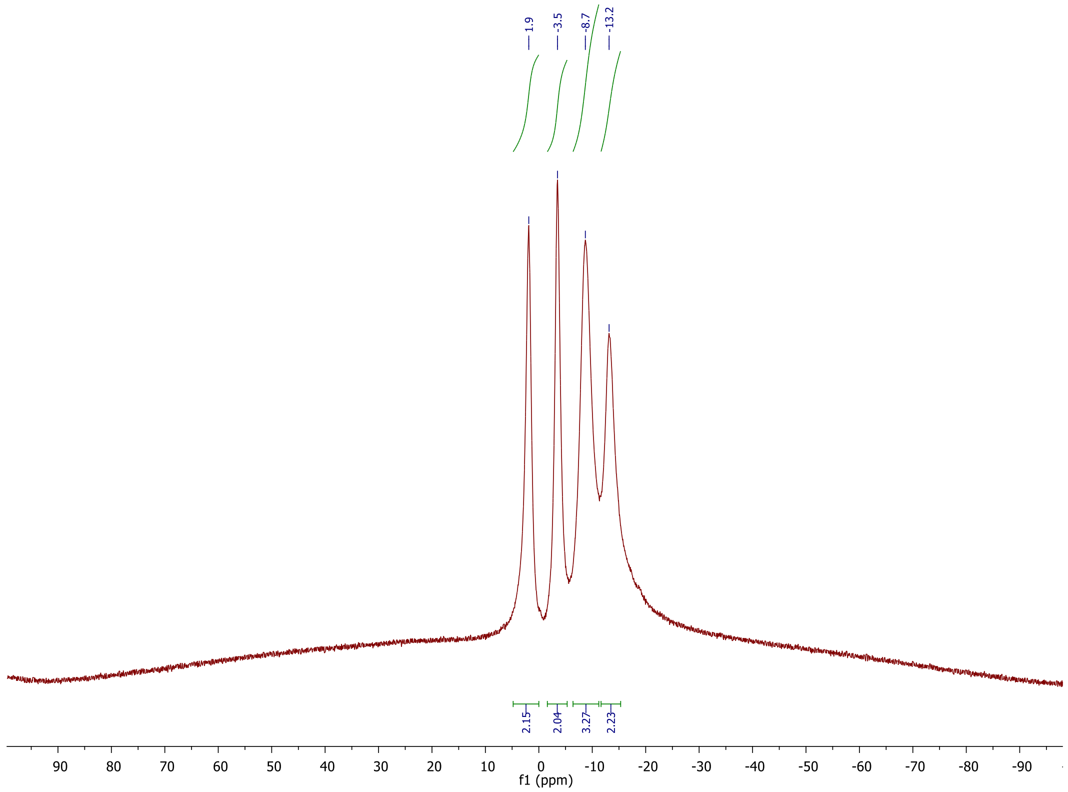


**Figure S12** $^{11}B\{^{1}H\}$ NMR spectrum of **2c** in $CD_2Cl_2$ under 1 bar $N_2$ at 298 K.

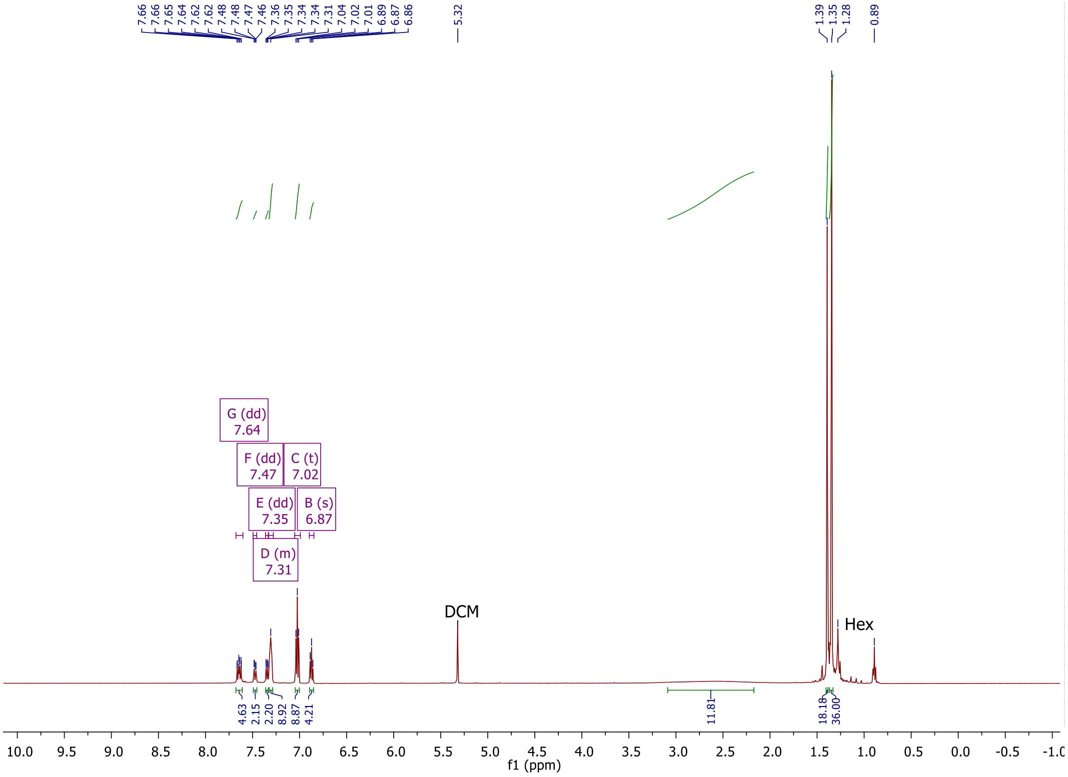


**Figure S13** $^1$H NMR spectrum of **2d** in $CD_2Cl_2$ under 1 bar $N_2$ at 298 K.

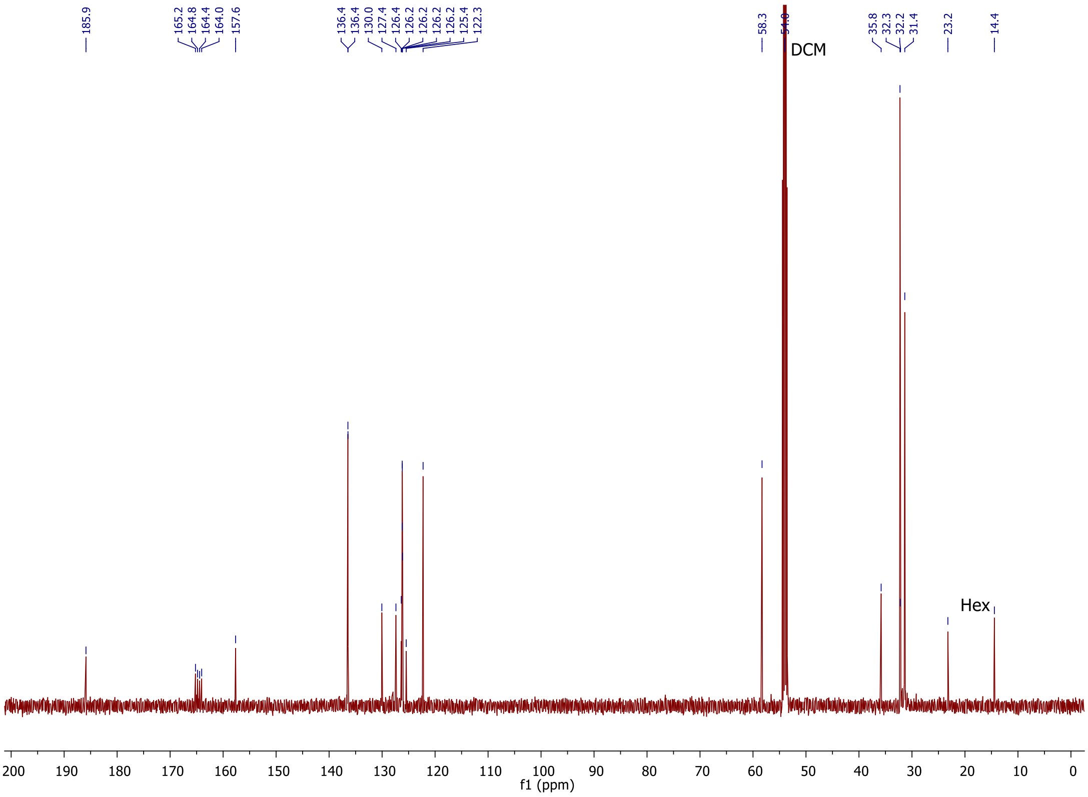


**Figure S14** $^{13}$C{$^1$H} NMR spectrum of **2d** in $CD_2Cl_2$ under 1 bar $N_2$ at 298 K.

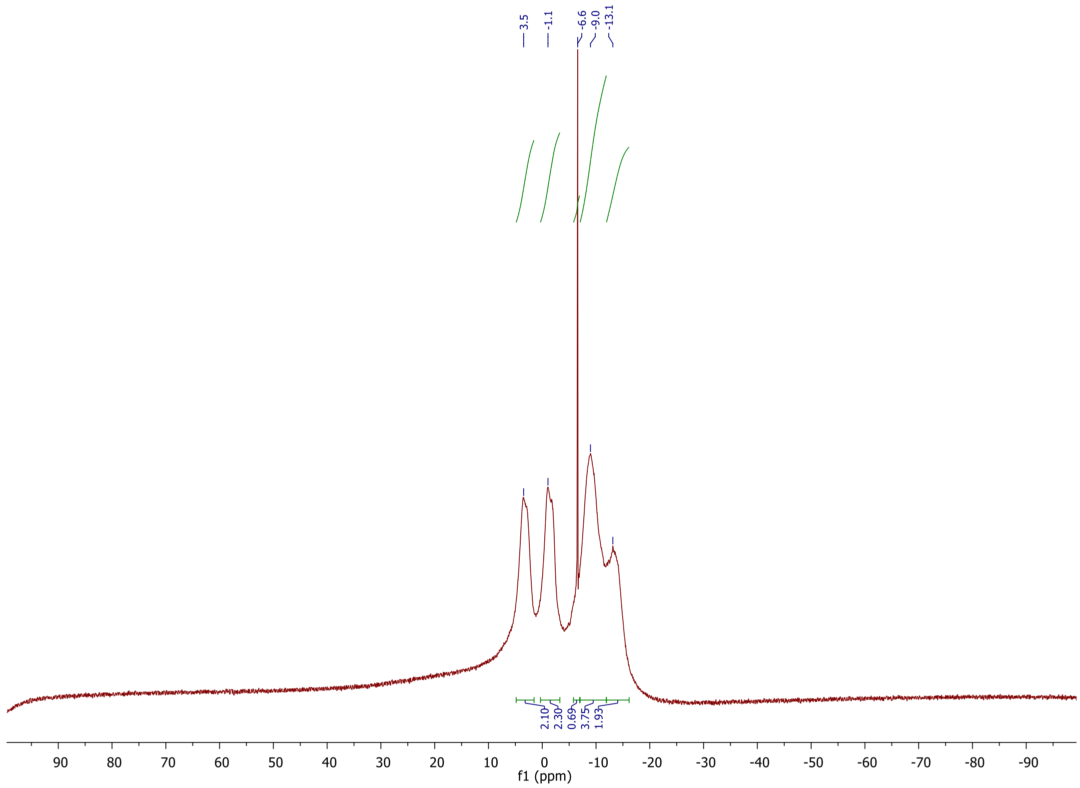


**Figure S15** $^{11}$B NMR spectrum of **2d** in $CD_2Cl_2$ under 1 bar $N_2$ at 298 K.

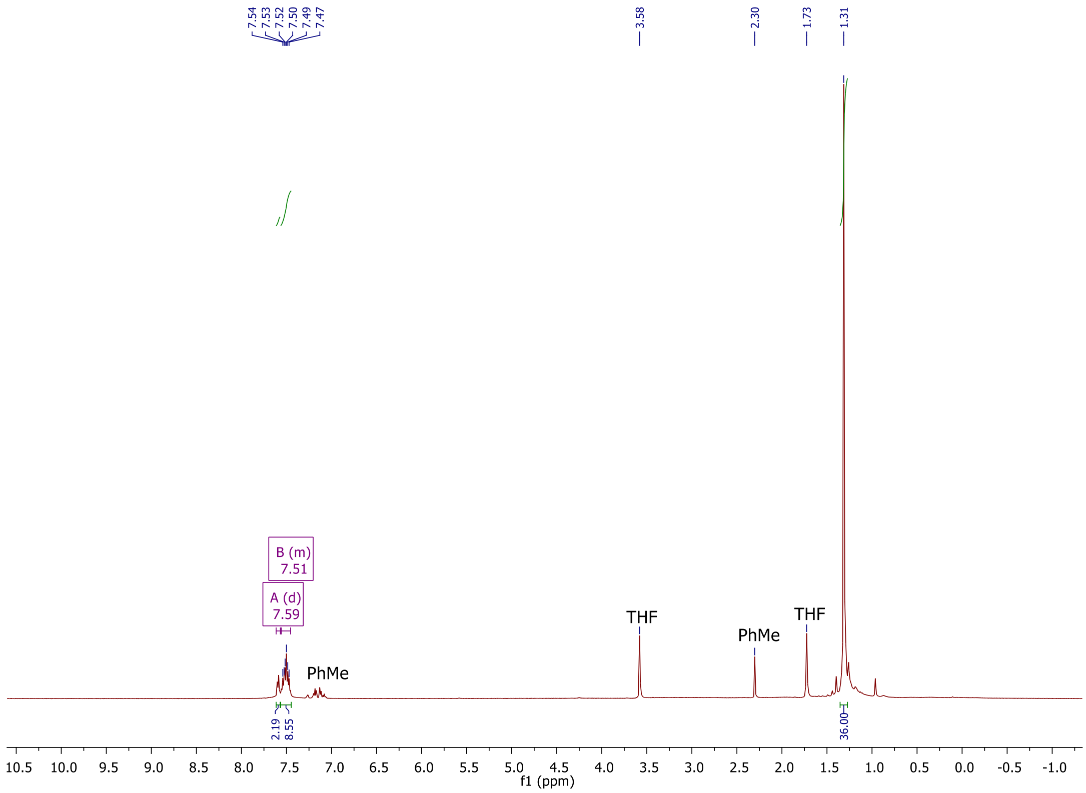


**Figure S16** $^{1}$H NMR spectrum of **3** in THF-$D_8$ under 1 bar $N_2$ at 298 K.

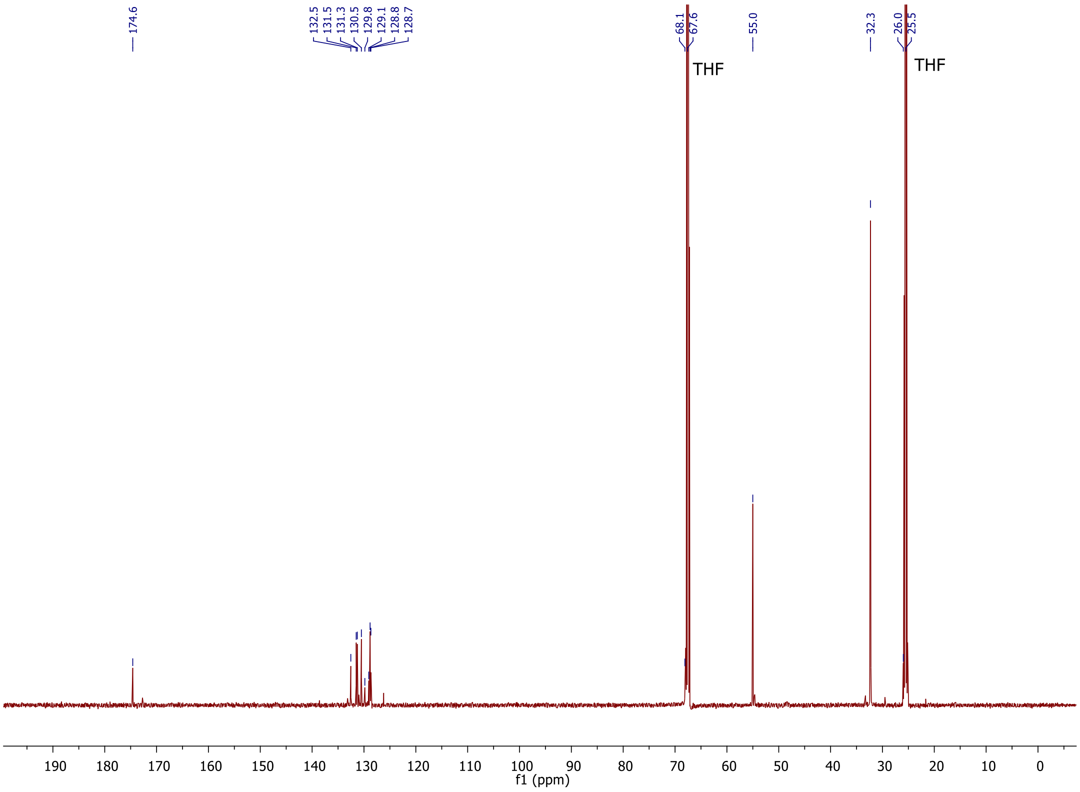


**Figure S17** $^{13}C\{^{1}H\}$ NMR spectrum of **3** in THF-$D_8$ under 1 bar $N_2$ at 298 K.

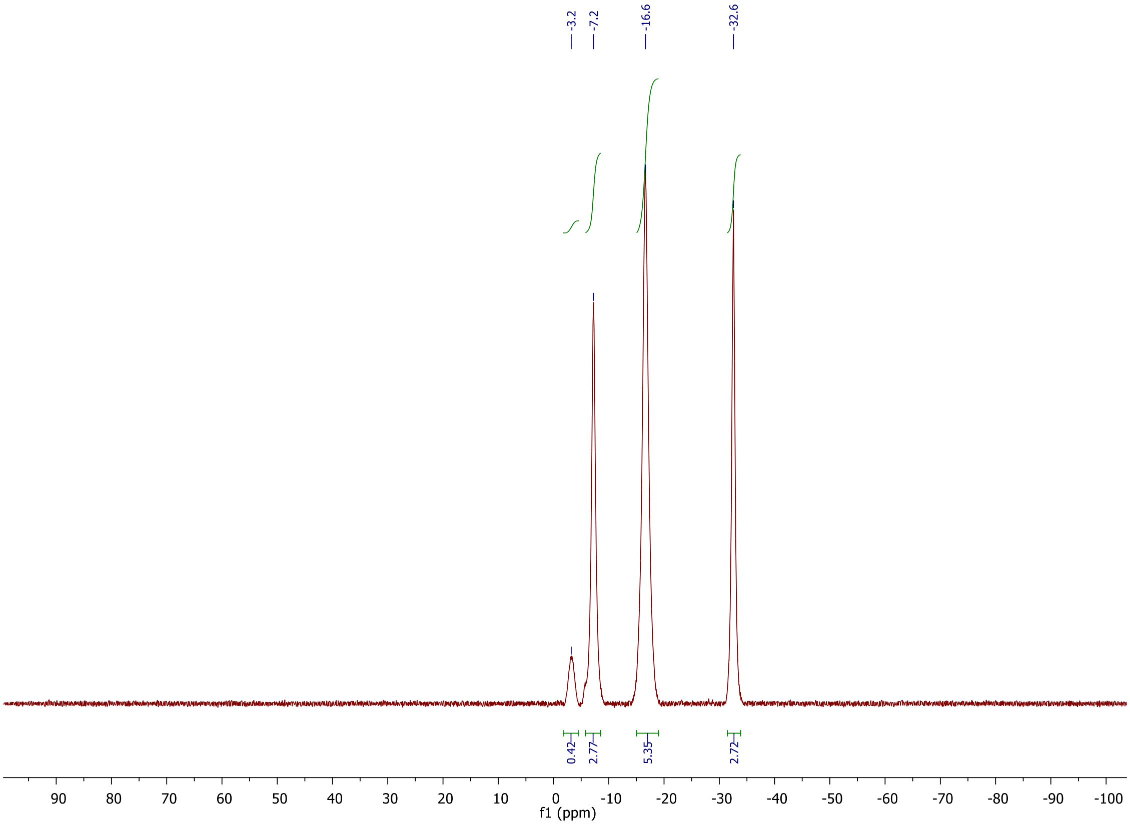


**Figure S18** $^{11}B\{^{1}H\}$ NMR spectrum of **3** in THF-$D_8$ under 1 bar $N_2$ at 298 K.

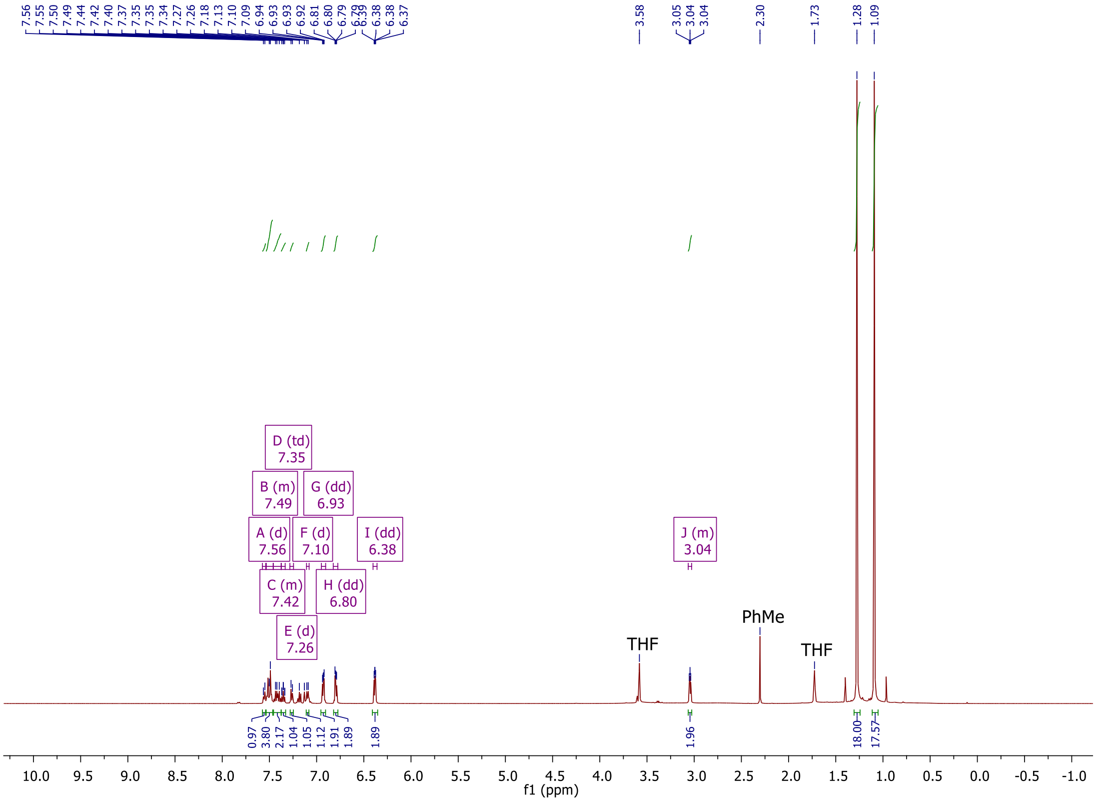


**Figure S19** $^1$H NMR spectrum of **5a** in THF-D$_8$ under 1 bar N$_2$ at 298 K.

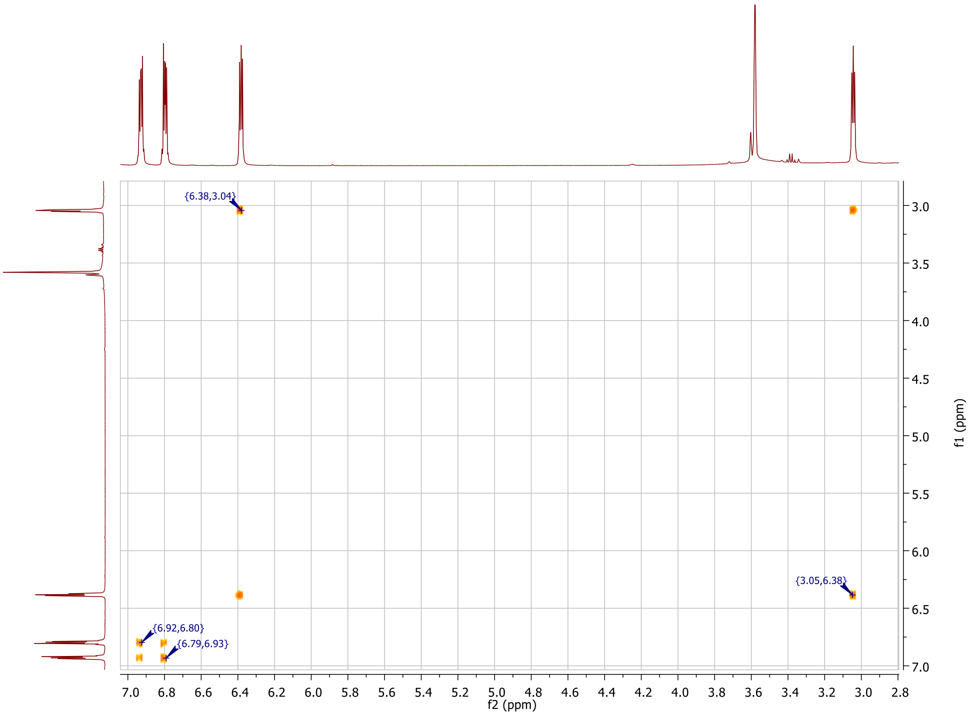


**Figure S20** $^1$H,$^1$H-COSY NMR spectrum of **5a** in THF-D$_8$ under 1 bar N$_2$ at 298 K.

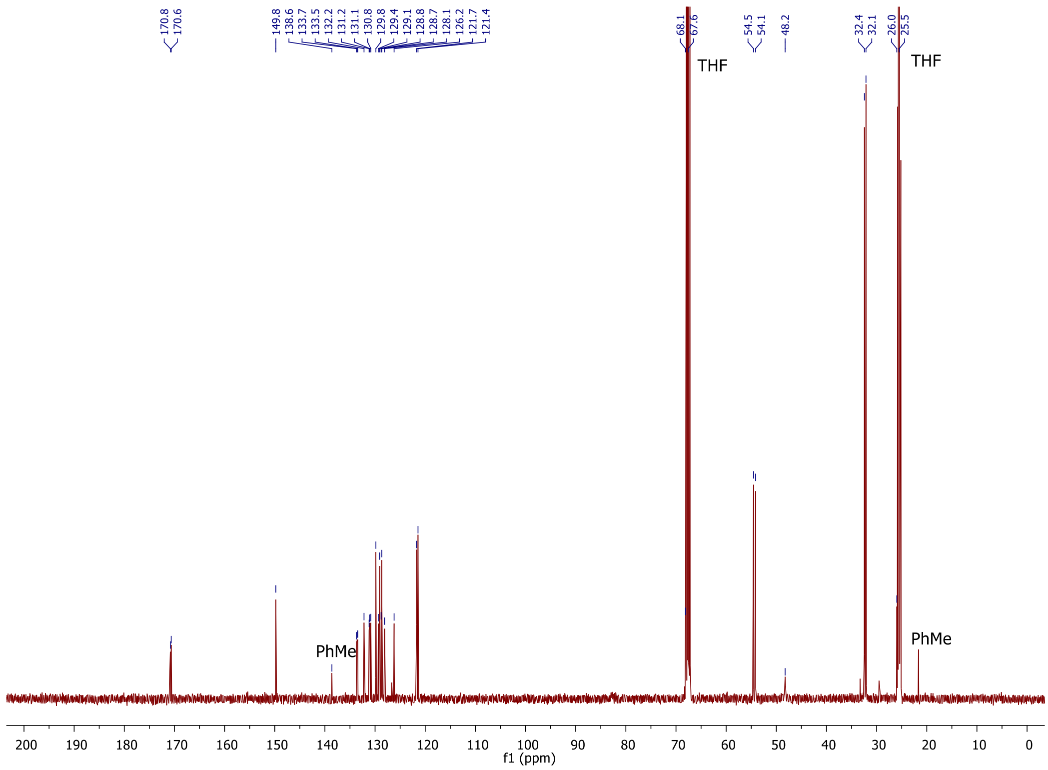


**Figure S21** $^{13}C\{^1H\}$ NMR spectrum of **5a** in THF-$D_8$ under 1 bar $N_2$ at 298 K.

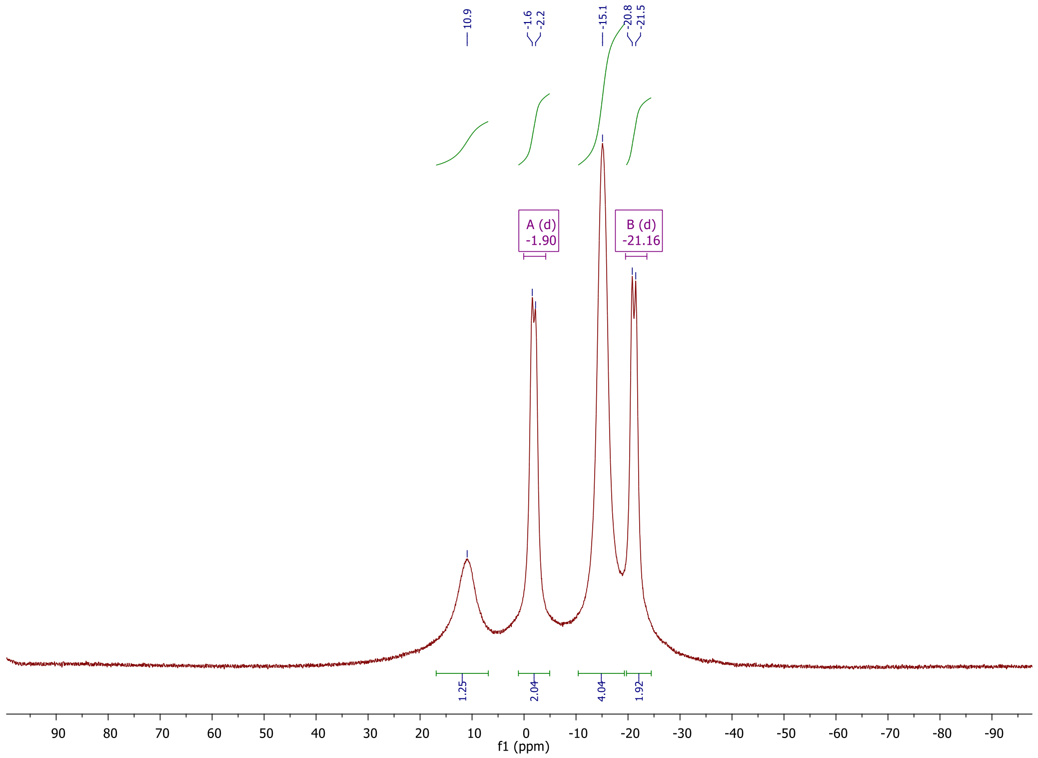


**Figure S22** $^{11}B$ NMR spectrum of **5a** in THF-$D_8$ under 1 bar $N_2$ at 298 K.

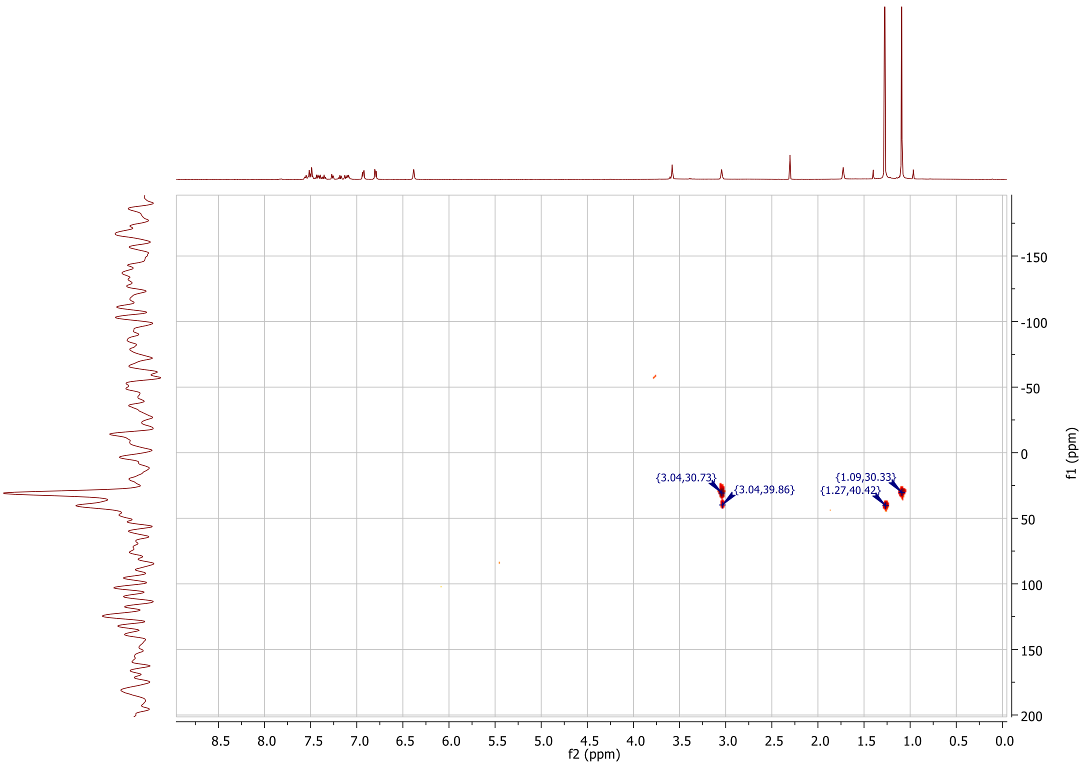


**Figure S23** $^{1}H,^{29}Si$-HMQC NMR spectrum of **5a** in THF-$D_8$ under 1 bar $N_2$ at 298 K (NUS 50%, $J_{HSi}$ = 3 Hz).

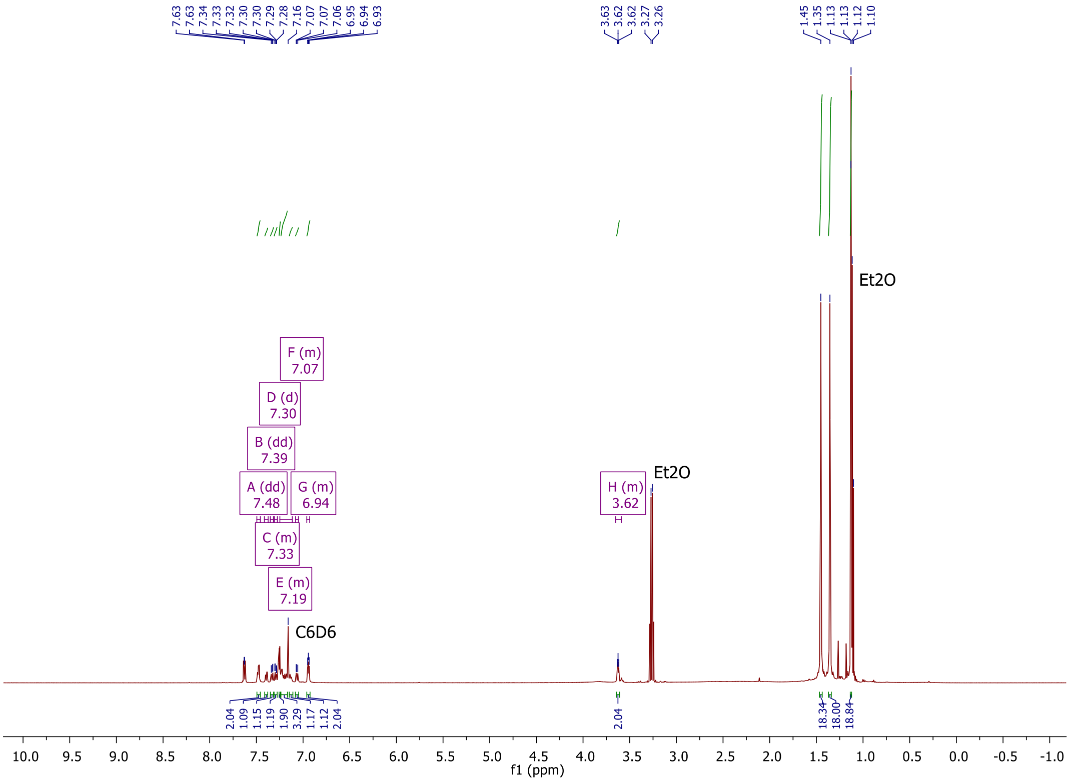


**Figure S24** $^{1}H$ NMR spectrum of **5b** in $C_6D_6$ under 1 bar $N_2$ at 298 K.

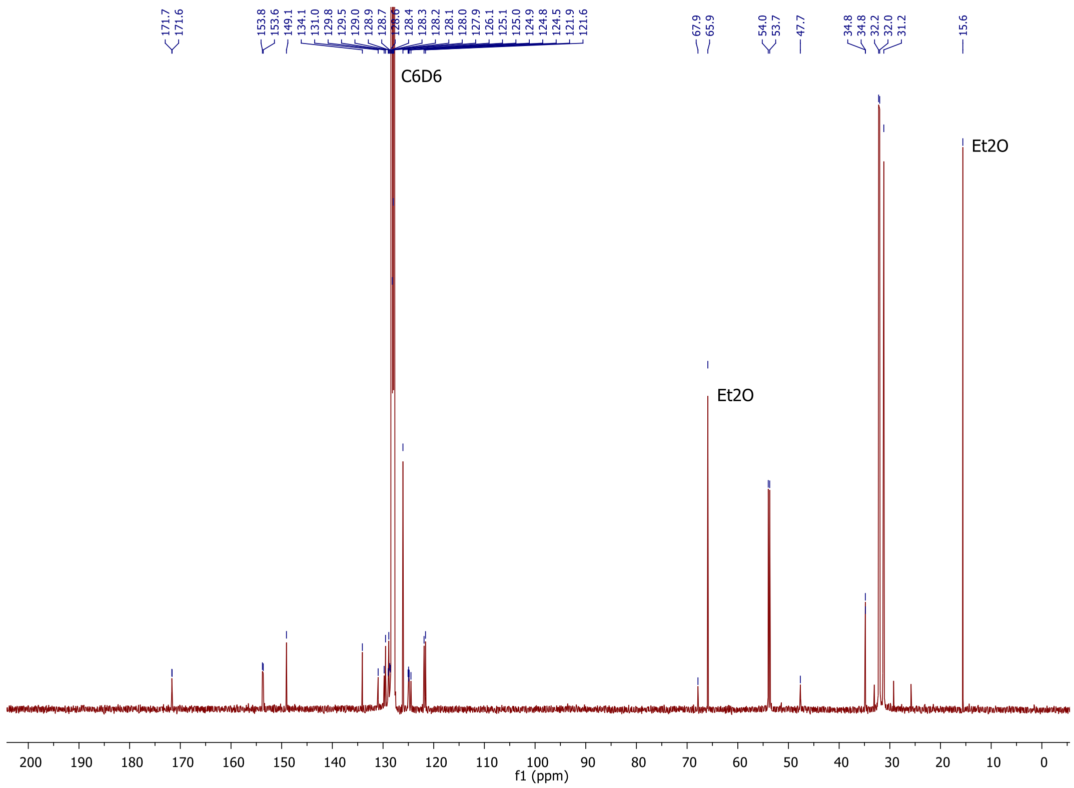


**Figure S25** $^{13}C\{^{1}H\}$ NMR spectrum of **5b** in $C_6D_6$ under 1 bar $N_2$ at 298 K.

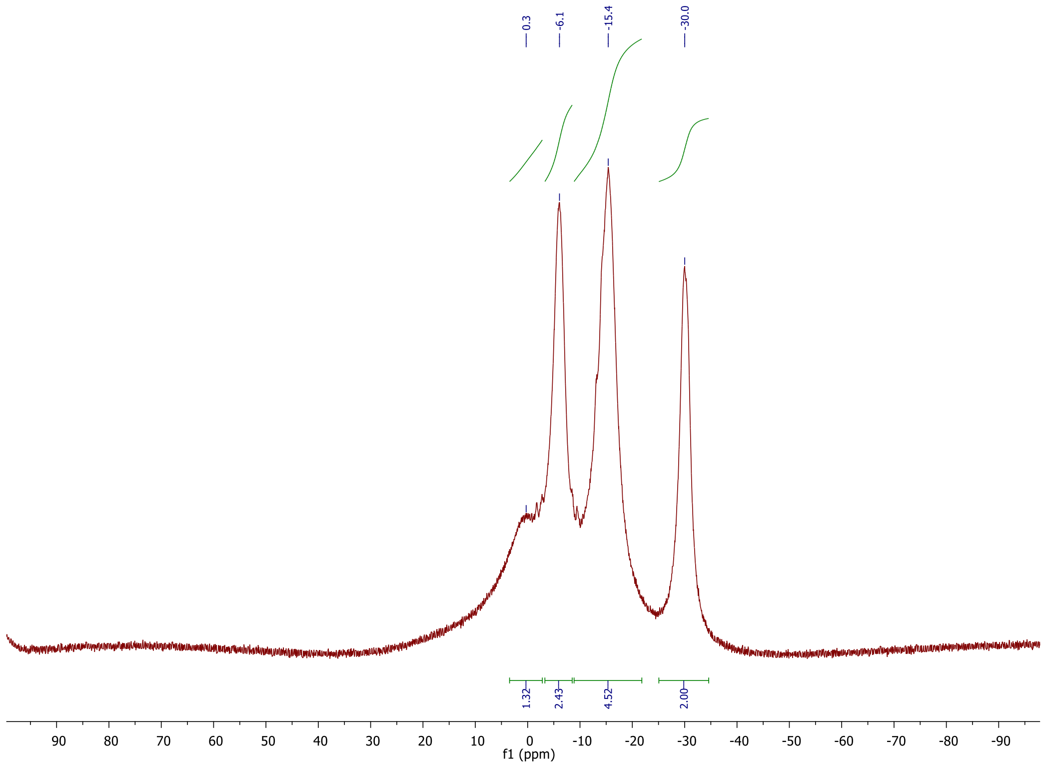


**Figure S26** $^{11}B$ NMR spectrum of **5b** in $C_6D_6$ under 1 bar $N_2$ at 298 K.

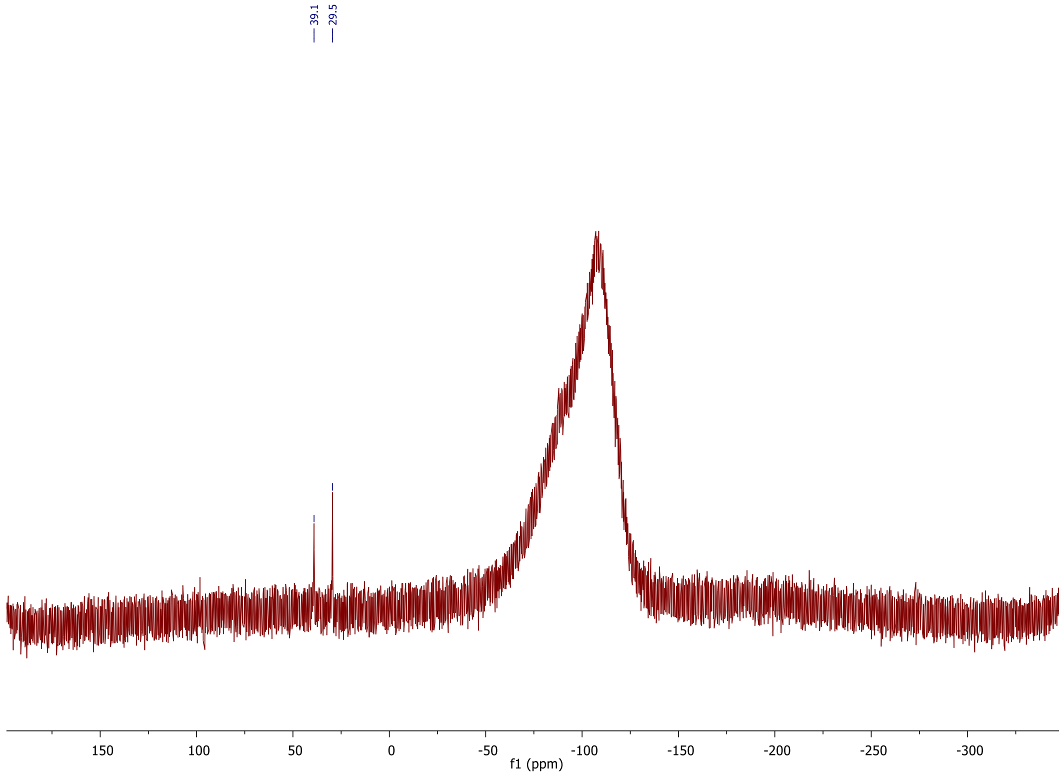


**Figure S27** $^{29}Si\{^1H\}$ NMR spectrum of **5b** in $C_6D_6$ under 1 bar $N_2$ at 298 K.

## A4 High Resolution Mass Spectrometry

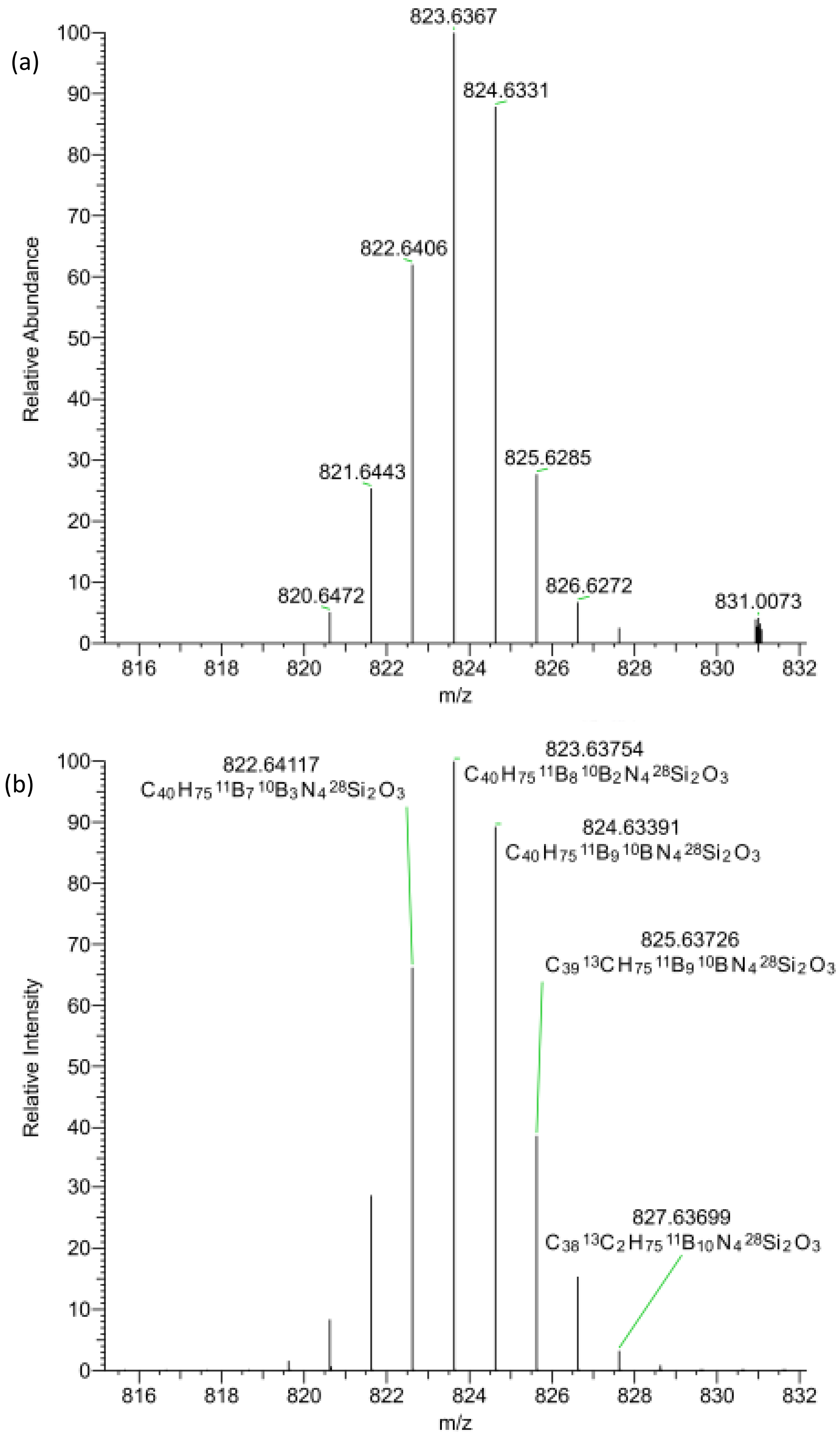


**Figure S28** (a) Experimental MS Spectrum of **1b** (b) Predicted MS Spectrum of **1b**-derived fragment

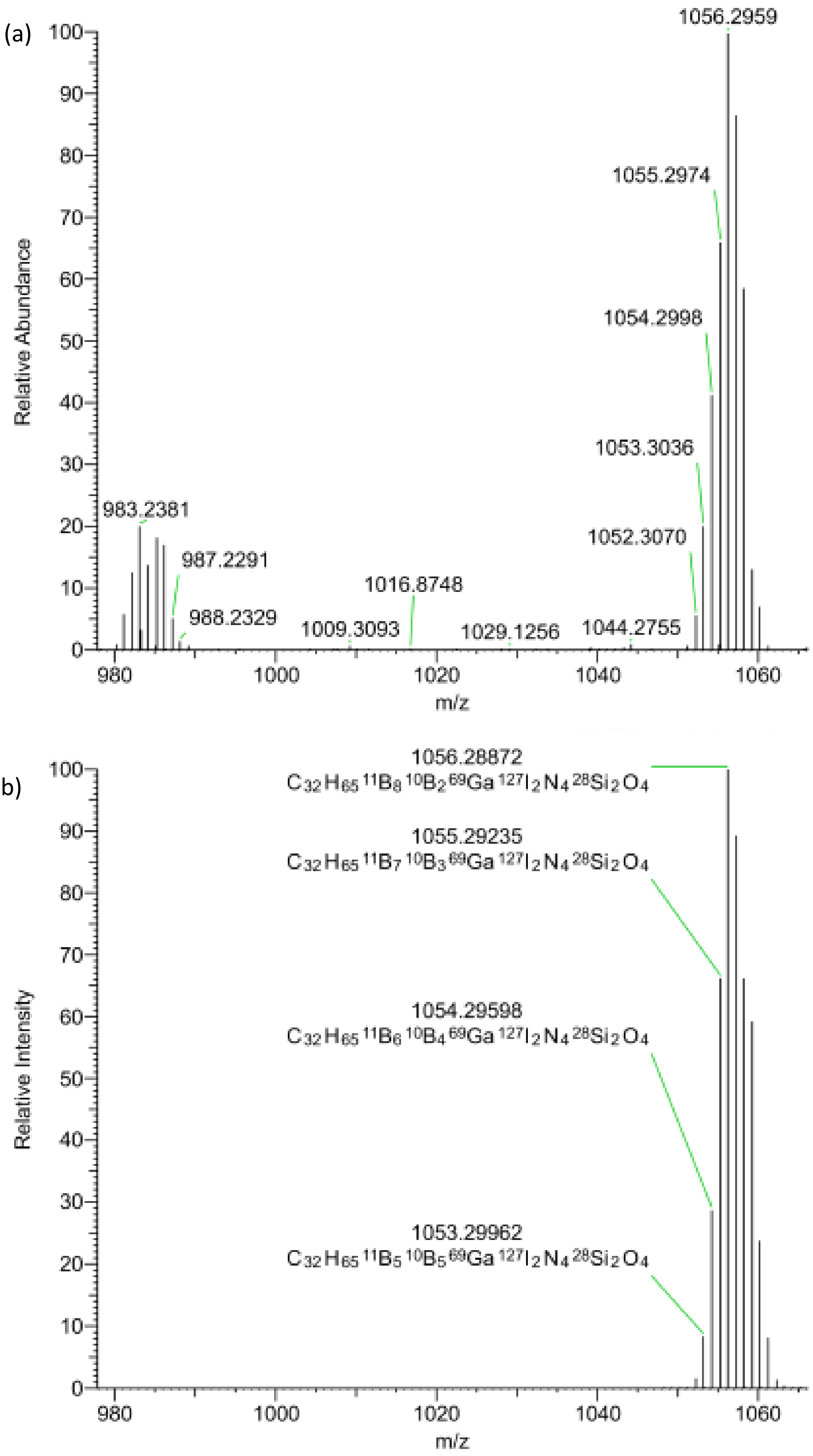


**Figure S29** (a) Experimental MS Spectrum of **4b** (b) Predicted MS Spectrum of **4b**-derived fragment

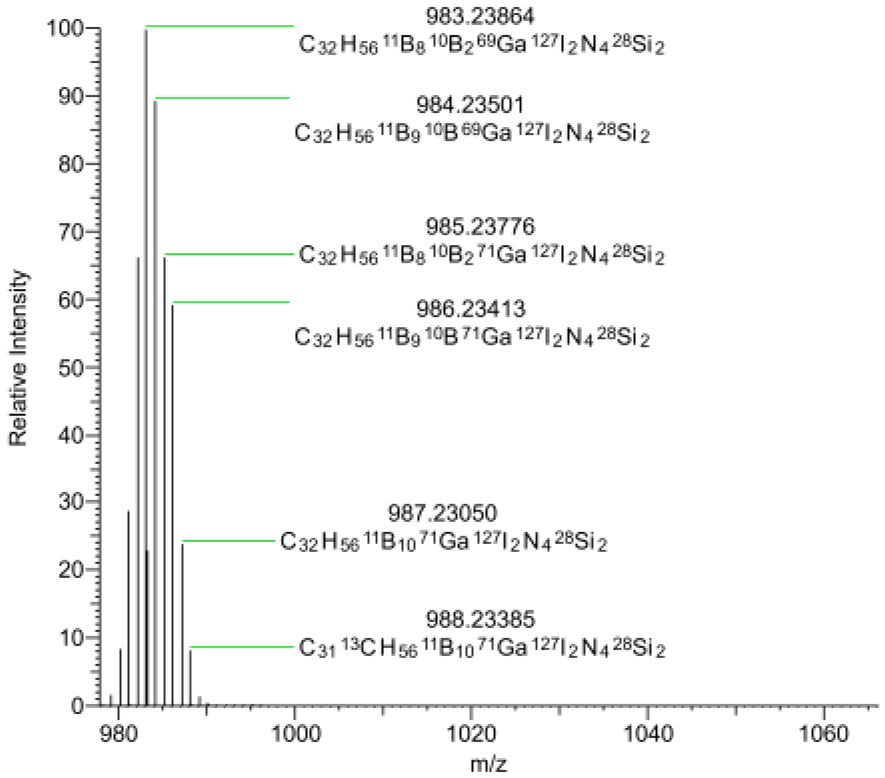


**Figure S30** Predicted MS Spectrum of **4b**

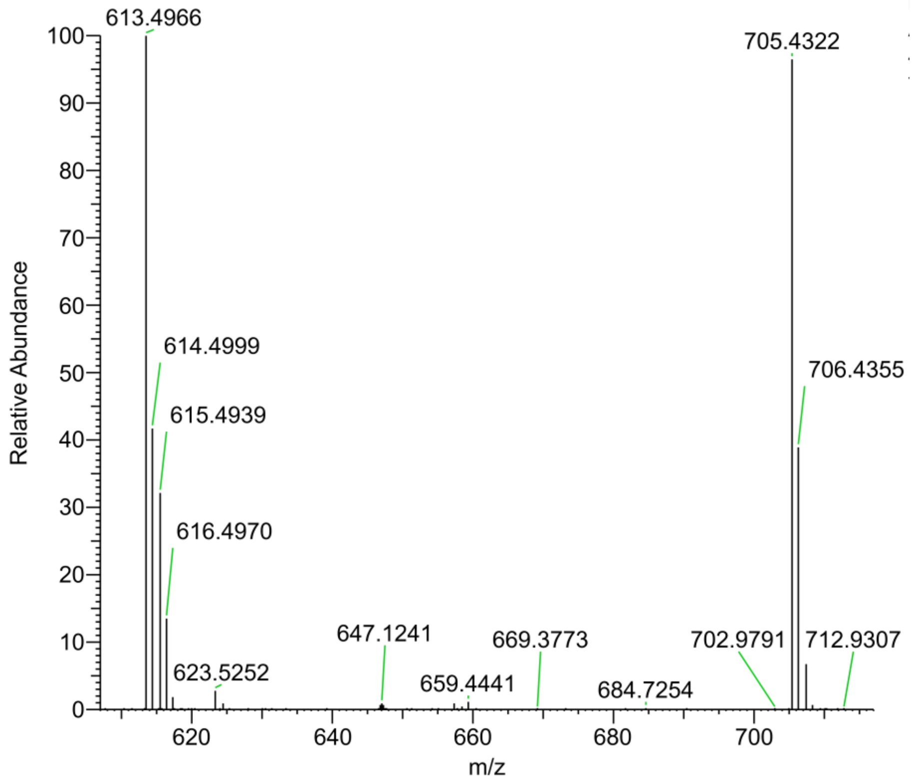


**Figure S31** Experimental MS Spectrum of **5b**

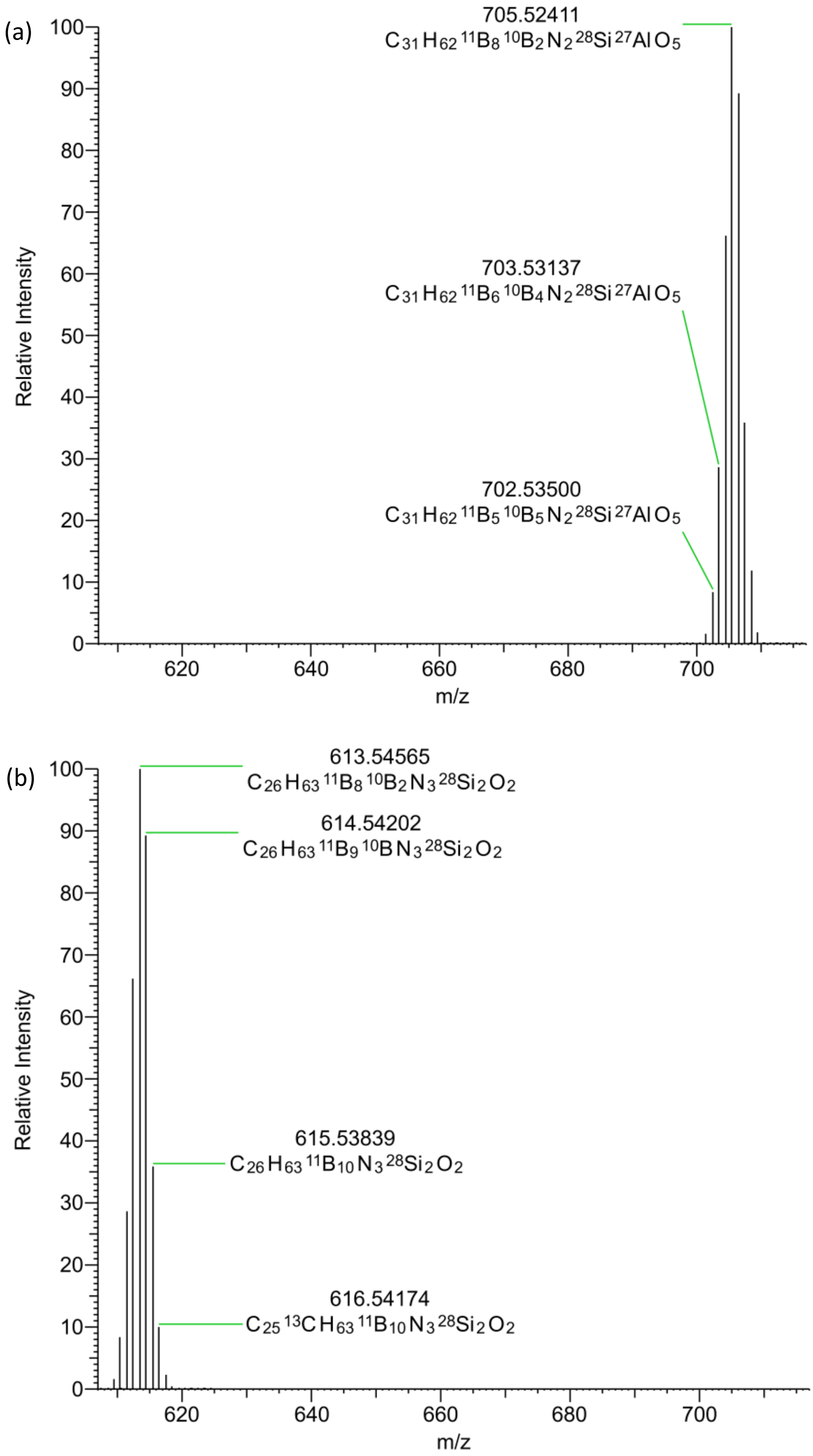


**Figure S32** (a) and (b) Predicted MS Spectra of **5b**-derived fragments

## A5 Single Crystal X-Ray Diffraction Data

**Table S1** Crystallographic Data and Structure Refinement for **2b**

| | | |
|---|---|---|
| Empirical formula | C32 H56 Al2 B10 I6 N4 Si2 | |
| CCDC number | 2418300 | |
| Crystal description | Colorless prism | |
| Formula weight | 1476.44 | |
| Temperature (K) | 150.0 | |
| Wavelength (Å) | 1.54184 | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/n$ | |
| Unit cell dimensions (Å or °) | a = 14.4094(4)<br>b = 17.2943(4)<br>c = 23.7145(6) | $\alpha$ = 90<br>$\beta$ = 92.257(3)<br>$\gamma$ = 90 |
| Volume (Å$^3$) | 5905.1(3) | |
| Z | 4 | |
| Density $\rho$ (calculated, g cm$^{-3}$) | 1.661 | |
| Absorption coefficient $\mu$ (mm$^{-1}$) | 25.646 | |
| F(000) | 2792 | |
| Crystal size (mm$^3$) | 0.21 x 0.11 x 0.07 | |
| Theta range for data collection (°) | 3.164 to 73.095 | |
| Index ranges | $-16 \leq h \leq 17$<br>$-20 \leq k \leq 21$<br>$-28 \leq l \leq 29$ | |
| Reflections collected | 42439 | |
| Independent reflections | 11605 [R(int) = 0.0656] | |
| Completeness to theta = 67.684° | 1.000 | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000<br>0.11885 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 11605 / 24 / 576 | |
| Goodness-of-fit on F$^2$ | 1.020 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0489, wR2 = 0.1138 | |
| R indices (all data) | R1 = 0.0787, wR2 = 0.1288 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole (e.Å$^{-3}$) | 1.043<br>-0.966 | |

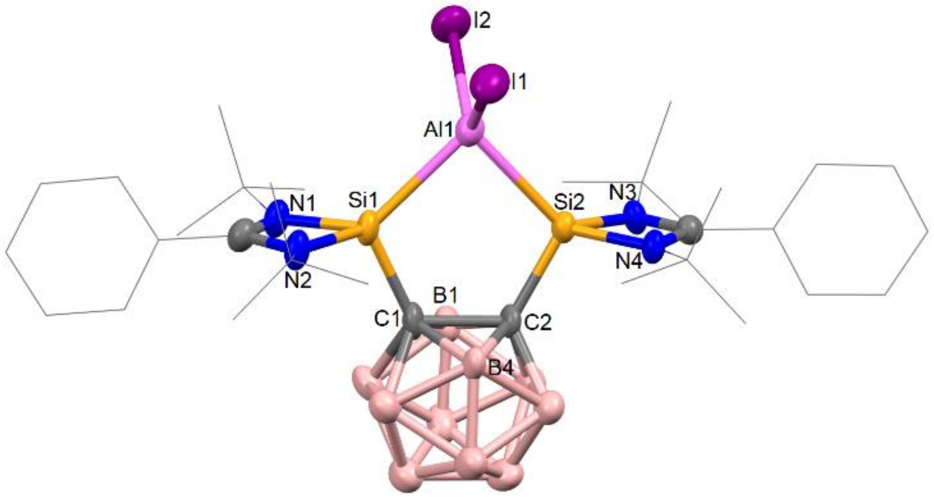


**Figure S33** Molecular Structure of **2b**-cation. Thermal ellipsoids are drawn at the 50% level. [AlI$_4$] counterion, H atoms and solvent molecules omitted for clarity.

**Table S2** Selected interatomic distances and angles of **2b**.

| Interatomic distances (Å) | | Angles (°) | |
|---|---|---|---|
| Al(1)-I(1) | 2.497(2) | I(1)-Al(1)-I(2) | 113.37(7) |
| Al(1)-I(2) | 2.510(2) | Si(1)-Al(1)-Si(2) | 89.07(8) |
| Al(1)-Si(1) | 2.496(3) | Si(1)-Al(1)-I(1) | 112.26(9) |
| Al(1)-Si(2) | 2.490(2) | Si(2)-Al(1)-I(1) | 113.63(8) |
| Si(1)-N(1) | 1.808(5) | C(1)-Si(1)-Al(1) | 108.12(19) |
| Si(1)-N(2) | 1.808(5) | C(2)-Si(2)-Al(1) | 107.94(19) |
| Si(2)-N(3) | 1.795(5) | Al(1)-Si(1)-N(1) | 127.23(19) |
| Si(2)-N(4) | 1.801(5) | Al(1)-Si(1)-N(2) | 127.24(18) |
| Si(1)-C(1) | 1.914(6) | Al(1)-Si(2)-N(3) | 127.09(18) |
| Si(2)-C(2) | 1.923(6) | Al(1)-Si(2)-N(4) | 125.89(17) |
| C(1)-C(2) | 1.729(8) | N(1)-Si(1)-N(2) | 73.5(2) |
| C(1)-B(1) | 1.700(9) | N(3)-Si(2)-N(4) | 73.4(2) |
| C(1)-B(4) | 1.713(9) | Si(1)-C(1)-C(2) | 117.4(4) |
| C(2)-B(1) | 1.710(10) | Si(2)-C(2)-C(1) | 117.5(4) |
| C(2)-B(4) | 1.705(9) | | |

**Table S3** Crystallographic Data and Structure Refinement for [**3**(OEt$_2$)$_4$]

| | | |
|---|---|---|
| Empirical formula | C48 H96 Al B10 I2 K N4 O4 Si2 | |
| CCDC number | 2418301 | |
| Crystal description | Red block | |
| Formula weight | 1277.44 | |
| Temperature (K) | 150(2) | |
| Wavelength (Å) | 1.54184 | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/n$ | |
| Unit cell dimensions (Å or °) | a = 14.7194(3) | $\alpha$ = 90 |
| | b = 30.6034(7) | $\beta$ = 94.863(2) |
| | c = 15.2868(3) | $\gamma$ = 90 |
| Volume (Å$^3$) | 6861.4(3) | |
| Z | 4 | |
| Density $\rho$ (calculated, g cm$^{-3}$) | 1.237 | |
| Absorption coefficient $\mu$ (mm$^{-1}$) | 8.492 | |
| F(000) | 2640 | |
| Crystal size (mm$^3$) | 0.23 x 0.17 x 0.09 | |
| Theta range for data collection (°) | 2.888 to 67.495 | |
| Index ranges | $-17 \leq h \leq 17$<br>$-25 \leq k \leq 36$<br>$-18 \leq l \leq 16$ | |
| Reflections collected | 26143 | |
| Independent reflections | 12351 [R(int) = 0.0381] | |
| Completeness to theta = 67.684° | 0.999 | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000<br>0.69472 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 12351 / 148 / 669 | |
| Goodness-of-fit on F$^2$ | 1.010 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0491, wR2 = 0.1228 | |
| R indices (all data) | R1 = 0.0664, wR2 = 0.1372 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole (e.Å$^{-3}$) | 1.238<br>-0.904 | |

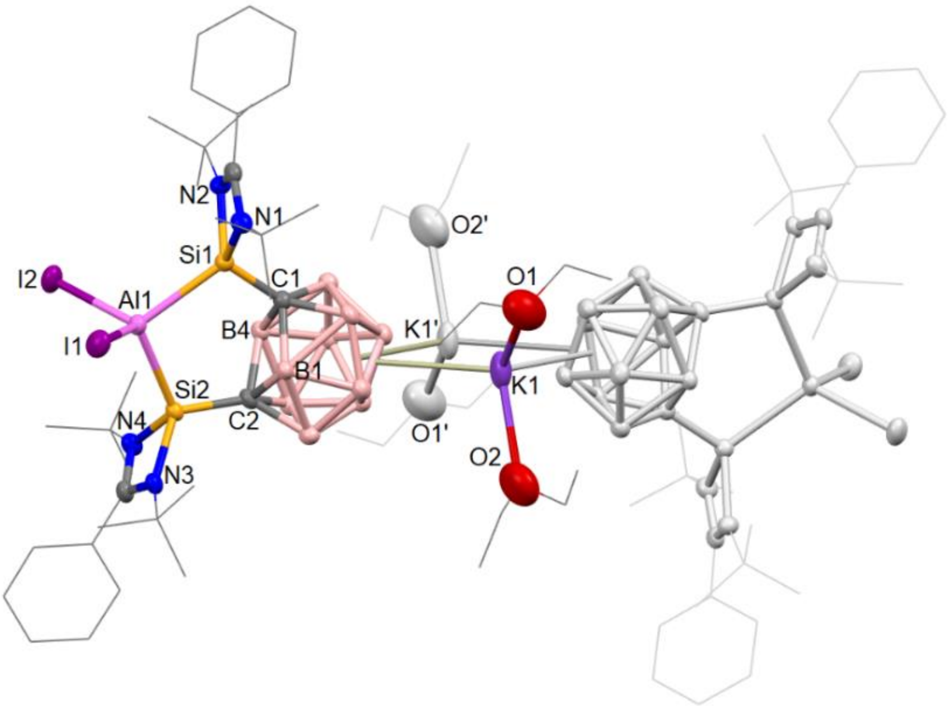


**Figure S34** Molecular Structure of [**3**($OEt_2$)$_4$]. Thermal ellipsoids are drawn at the 50% level. H atoms and solvent molecules omitted for clarity.

**Table S4** Selected interatomic distances and angles of [**3**($OEt_2$)$_4$].

| Interatomic distances (Å) | | Angles (°) | |
|---|---|---|---|
| Al(1)-I(1) | 2.5688(13) | I(1)-Al(1)-I(2) | 103.62(4) |
| Al(1)-I(2) | 2.5786(13) | Si(1)-Al(1)-Si(2) | 101.99(6) |
| Al(1)-Si(1) | 2.4950(17) | Si(1)-Al(1)-I(1) | 110.60(6) |
| Al(1)-Si(2) | 2.5060(17) | Si(2)-Al(1)-I(1) | 115.49(6) |
| Si(1)-N(1) | 1.830(4) | C(1)-Si(1)-Al(1) | 107.89(15) |
| Si(1)-N(2) | 1.836(4) | C(2)-Si(2)-Al(1) | 107.63(15) |
| Si(2)-N(3) | 1.833(4) | Al(1)-Si(1)-N(1) | 120.35(13) |
| Si(2)-N(4) | 1.834(4) | Al(1)-Si(1)-N(2) | 121.45(13) |
| Si(1)-C(1) | 1.794(4) | Al(1)-Si(2)-N(3) | 120.36(13) |
| Si(2)-C(2) | 1.795(4) | Al(1)-Si(2)-N(4) | 120.25(14) |
| C(1)-B(1) | 1.684(6) | N(1)-Si(1)-N(2) | 71.96(17) |
| C(1)-B(4) | 1.698(7) | N(3)-Si(2)-N(4) | 71.59(17) |
| C(2)-B(1) | 1.698(7) | C(1)-B(1)-C(2) | 99.8(3) |
| C(2)-B(4) | 1.691(6) | C(1)-B(4)-C(2) | 99.5(3) |
| C(1)···C(2) | 2.587 | Si(1)-C(1)···C(2) | 111.15 |
| K(1)···cage | 3.188 | Si(2)-C(2)···C(1) | 111.31 |
| K(1’)···cage | 3.166 | cage···K(1)···cage | 111.17 |

**Table S5** Crystallographic Data and Structure Refinement for **4a**

| | | |
|---|---|---|
| Empirical formula | C46 H72 Al B10 I2 N4 Si2 | |
| CCDC number | 2418298 | |
| Crystal description | Red prism | |
| Formula weight | 1126.13 | |
| Temperature (K) | 150.15 | |
| Wavelength (Å) | 1.54184 | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions (Å or °) | a = 14.6482(7) | $\alpha$ = 105.669(4) |
| | b = 14.8290(7) | $\beta$ = 106.625(5) |
| | c = 18.4781(10) | $\gamma$ = 100.731(4) |
| Volume ($\text{Å}^3$) | 3548.9(3) | |
| Z | 2 | |
| Density $\rho$ (calculated, g cm$^{-3}$) | 1.054 | |
| Absorption coefficient $\mu$ (mm$^{-1}$) | 7.600 | |
| F(000) | 1146 | |
| Crystal size (mm$^3$) | 0.19 x 0.14 x 0.11 | |
| Theta range for data collection (°) | 3.230 to 72.972 | |
| Index ranges | $-17 \leq h \leq 18$<br>$-18 \leq k \leq 15$<br>$-21 \leq l \leq 22$ | |
| Reflections collected | 26771 | |
| Independent reflections | 13734 [R(int) = 0.0611] | |
| Completeness to theta = 67.684° | 0.998 | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000<br>0.30943 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 13734 / 0 / 588 | |
| Goodness-of-fit on F$^2$ | 0.975 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0534, wR2 = 0.1353 | |
| R indices (all data) | R1 = 0.0753, wR2 = 0.1537 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole (e.$\text{Å}^{-3}$) | 1.290<br>-1.384 | |

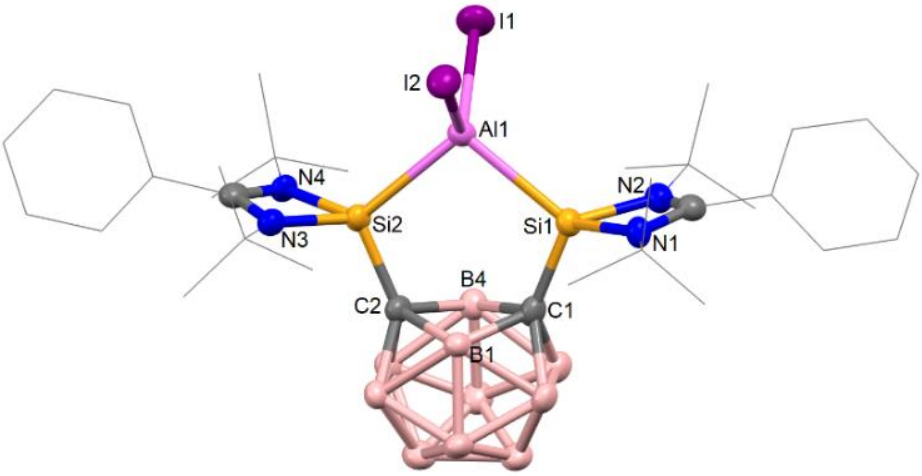


**Figure S35** Molecular Structure of **4a**. Thermal ellipsoids are drawn at the 50% level. H atoms and solvent molecules omitted for clarity.

**Table S6** Selected interatomic distances and angles of **4a**

| Interatomic distances (Å) | | Angles (°) | |
|---|---|---|---|
| Al(1)-I(1) | 2.5466(13) | I(1)-Al(1)-I(2) | 106.37(5) |
| Al(1)-I(2) | 2.5448(14) | Si(1)-Al(1)-Si(2) | 99.84(6) |
| Al(1)-Si(1) | 2.5046(17) | Si(1)-Al(1)-I(1) | 113.15(6) |
| Al(1)-Si(2) | 2.4901(17) | Si(2)-Al(1)-I(1) | 112.99(5) |
| Si(1)-N(1) | 1.823(3) | C(1)-Si(1)-Al(1) | 107.45(14) |
| Si(1)-N(2) | 1.818(4) | C(2)-Si(2)-Al(1) | 107.84(14) |
| Si(2)-N(3) | 1.815(4) | Al(1)-Si(1)-N(1) | 123.03(13) |
| Si(2)-N(4) | 1.818(3) | Al(1)-Si(1)-N(2) | 123.58(13) |
| Si(1)-C(1) | 1.823(5) | Al(1)-Si(2)-N(3) | 122.08(13) |
| Si(2)-C(2) | 1.831(4) | Al(1)-Si(2)-N(4) | 122.48(13) |
| C(1)-B(1) | 1.733(7) | N(1)-Si(1)-N(2) | 72.31(16) |
| C(1)-B(4) | 1.742(6) | N(3)-Si(2)-N(4) | 72.56(17) |
| C(2)-B(1) | 1.739(6) | C(1)-B(1)-C(2) | 88.8(3) |
| C(2)-B(4) | 1.714(7) | C(1)-B(4)-C(2) | 89.4(3) |
| C(1)···C(2) | 2.431-- | Si(1)-C(1)···C(2) | 112.58 |
| | | Si(2)-C(2)···C(1) | 112.16 |

**Table S7** Crystallographic Data and Structure Refinement for **4b**

| | | |
|---|---|---|
| Empirical formula | C32 H56 Ga B10 I2 N4 Si2 | |
| CCDC number | 2418297 | |
| Crystal description | Orange block | |
| Formula weight | 984.60 | |
| Temperature (K) | 150(2) | |
| Wavelength (Å) | 0.71073 | |
| Crystal system | Orthorhombic | |
| Space group | Cmcm | |
| Unit cell dimensions (Å or °) | a = 23.2436(3)<br>b = 18.9817(3)<br>c = 13.9956(2) | $\alpha$ = 90<br>$\beta$ = 90<br>$\gamma$ = 90 |
| Volume ($\text{Å}^3$) | 6174.90(15) | |
| Z | 4 | |
| Density $\rho$ (calculated, g $\text{cm}^{-3}$) | 1.059 | |
| Absorption coefficient $\mu$ ($\text{mm}^{-1}$) | 1.505 | |
| F(000) | 1964 | |
| Crystal size ($\text{mm}^3$) | 0.21 x 0.14 x 0.09 | |
| Theta range for data collection (°) | 1.752 to 26.109 | |
| Index ranges | $-26 \le h \le 28$<br>$-22 \le k \le 23$<br>$-10 \le l \le 17$ | |
| Reflections collected | 12678 | |
| Independent reflections | 3236 [R(int) = 0.0321] | |
| Completeness to theta = 67.684° | 0.996 | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.00000<br>0.29306 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3236 / 13 / 140 | |
| Goodness-of-fit on $F^2$ | 1.065 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0380, wR2 = 0.1049 | |
| R indices (all data) | R1 = 0.0418, wR2 = 0.1084 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole ($\text{e.Å}^{-3}$) | 0.469<br>-1.359 | |

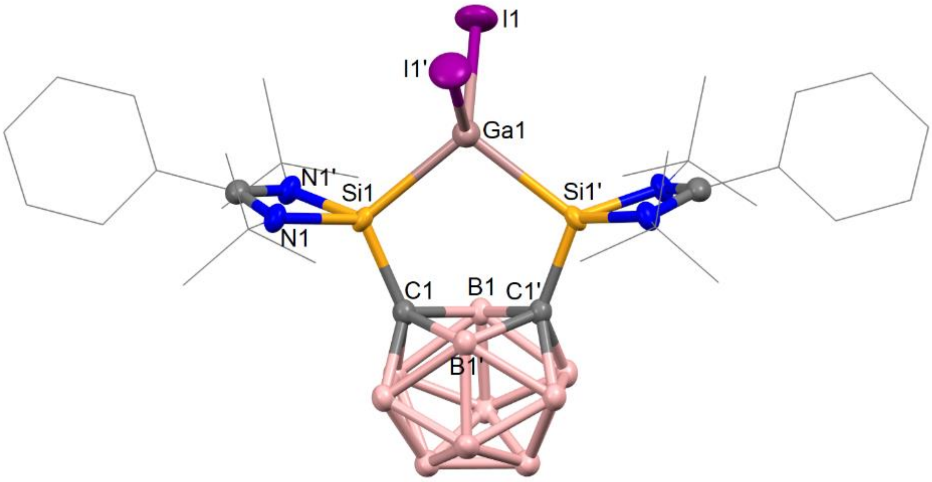


**Figure S36** Molecular Structure of **4b**. Thermal ellipsoids are drawn at the 50% level. H atoms and solvent molecules omitted for clarity.

**Table S8** Selected interatomic distances and angles of **4b**.

| Interatomic distances (Å) | | Angles (°) | |
|---|---|---|---|
| Ga(1)-I(1) | 2.5638(5) | I(1)-Ga(1)-I(1’) | 102.21(3) |
| Ga(1)-Si(1) | 2.4331(11) | Si(1)-Ga(1)-Si(1’) | 101.55(5) |
| Si(1)-N(1) | 1.806(2) | Si(1)-Ga(1)-I(1) | 113.395(12) |
| Si(1)-C(1) | 1.821(4) | C(1)-Si(1)-Ga(1) | 107.38(12) |
| C(1)-B(1) | 1.726(4) | Ga(1)-Si(1)-N(1) | 120.82(8) |
| C(1)···C(1’) | 2.415 | N(1)-Si(1)-N(1’) | 72.94(15) |
| | | C(1)-B(1)-C(1’) | 88.8(2) |
| | | Si(1)-C(1)···C(1’) | 111.84 |

**Table S9** Crystallographic Data and Structure Refinement for [**5b**($OEt_2$)$_4$]

<table>
<tr><td>Empirical formula</td><td colspan="2">C58 H100 Al B10 K N4 O2 Si2</td></tr>
<tr><td>CCDC number</td><td colspan="2">2418302</td></tr>
<tr><td>Crystal description</td><td colspan="2">Orange prism</td></tr>
<tr><td>Formula weight</td><td colspan="2">1115.17</td></tr>
<tr><td>Temperature (K)</td><td colspan="2">150.15</td></tr>
<tr><td>Wavelength (Å)</td><td colspan="2">1.54184</td></tr>
<tr><td>Crystal system</td><td colspan="2">Monoclinic</td></tr>
<tr><td>Space group</td><td colspan="2">$P2_1/c$</td></tr>
<tr><td>Unit cell dimensions (Å or °)</td><td>a = 21.7751(10)<br>b = 15.1015(3)<br>c = 24.8744(9)</td><td>$\alpha$ = 90<br>$\beta$ = 109.723(4)<br>$\gamma$ = 90</td></tr>
<tr><td>Volume (Å$^3$)</td><td colspan="2">7699.8(5)</td></tr>
<tr><td>Z</td><td colspan="2">4</td></tr>
<tr><td>Density $\rho$ (calculated, g cm$^{-3}$)</td><td colspan="2">0.963</td></tr>
<tr><td>Absorption coefficient $\mu$ (mm$^{-1}$)</td><td colspan="2">1.276</td></tr>
<tr><td>F(000)</td><td colspan="2">2408</td></tr>
<tr><td>Crystal size (mm$^3$)</td><td colspan="2">0.16 x 0.10 x 0.08</td></tr>
<tr><td>Theta range for data collection (°)</td><td colspan="2">3.483 to 67.500</td></tr>
<tr><td>Index ranges</td><td colspan="2">$-26 \le h \le 26$<br>$-17 \le k \le 18$<br>$-23 \le l \le 29$</td></tr>
<tr><td>Reflections collected</td><td colspan="2">54462</td></tr>
<tr><td>Independent reflections</td><td colspan="2">13867 [R(int) = 0.0847]</td></tr>
<tr><td>Completeness to theta = 67.684°</td><td colspan="2">0.999</td></tr>
<tr><td>Absorption correction</td><td colspan="2">Semi-empirical from equivalents</td></tr>
<tr><td>Max. and min. transmission</td><td colspan="2">1.00000<br>0.38121</td></tr>
<tr><td>Refinement method</td><td colspan="2">Full-matrix least-squares on $F^2$</td></tr>
<tr><td>Data / restraints / parameters</td><td colspan="2">13867 / 132 / 812</td></tr>
<tr><td>Goodness-of-fit on $F^2$</td><td colspan="2">1.021</td></tr>
<tr><td>Final R indices [I>2sigma(I)]</td><td colspan="2">R1 = 0.0845, wR2 = 0.2126</td></tr>
<tr><td>R indices (all data)</td><td colspan="2">R1 = 0.1177, wR2 = 0.2445</td></tr>
<tr><td>Extinction coefficient</td><td colspan="2">n/a</td></tr>
<tr><td>Largest diff. peak and hole (e.Å$^{-3}$)</td><td colspan="2">0.894<br>-0.457</td></tr>
</table>

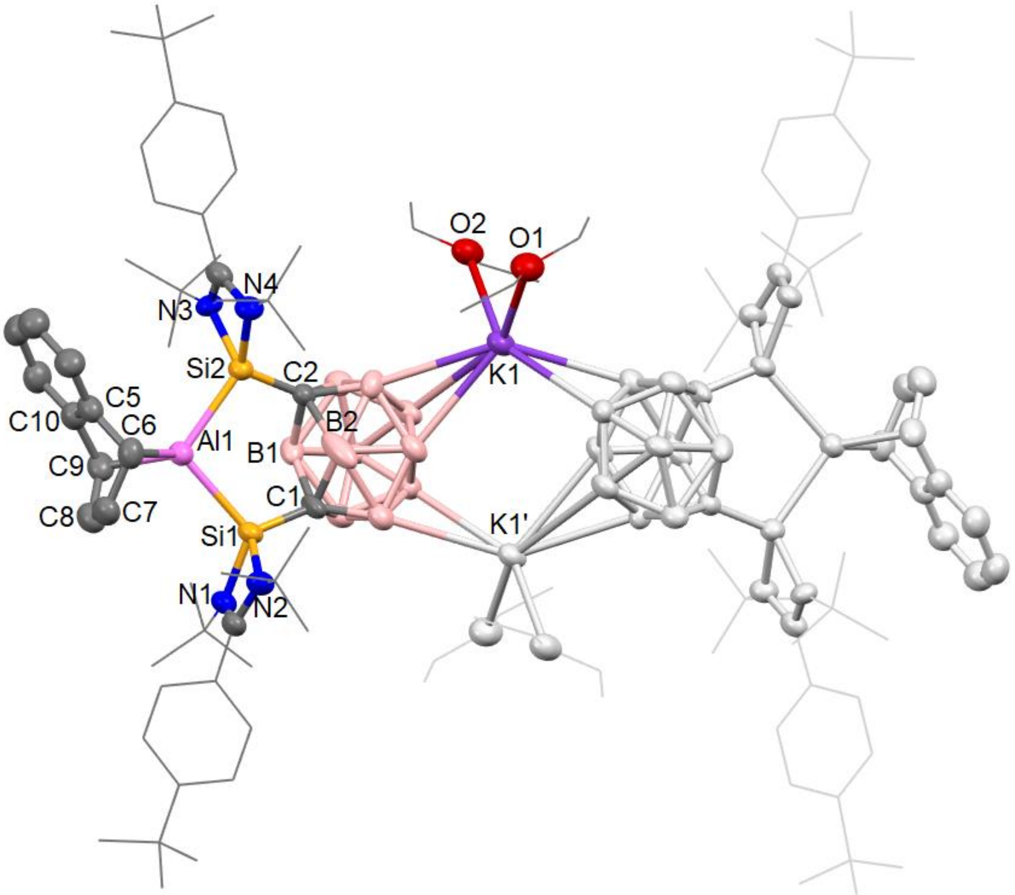


**Figure S37** Molecular Structure of [**5b**(OEt$_2$)$_4$]. Thermal ellipsoids are drawn at the 50% level. H atoms and solvent molecules omitted for clarity.

**Table S10** Selected interatomic distances and angles of [**5b**(OEt$_2$)$_4$].

| Interatomic distances (Å) | | Angles (°) | |
|---|---|---|---|
| Al(1)-C(6) | 2.056(4) | C(6)-Al(1)-C(9) | 77.49(17) |
| Al(1)-C(9) | 2.066(4) | Si(1)-Al(1)-Si(2) | 100.95(5) |
| Al(1)-Si(1) | 2.5010(15) | Si(1)-Al(1)-C(6) | 119.30(12) |
| Al(1)-Si(2) | 2.5253(15) | Si(2)-Al(1)-C(6) | 121.48(12) |
| C(6)-C(5) | 1.480(6) | C(5)-C(6)-C(7) | 109.6(3) |
| C(6)-C(7) | 1.527(6) | C(8)-C(9)-C(10) | 109.5(4) |
| C(7)-C(8) | 1.339(7) | C(6)-C(7)-C(8) | 113.2(4) |
| C(5)-C(10) | 1.414(6) | C(7)-C(8)-C(9) | 115.2(4) |
| C(9)-C(10) | 1.493(6) | C(1)-Si(1)-Al(1) | 108.4(3) |
| C(9)-C(8) | 1.503(6) | C(2)-Si(2)-Al(1) | 107.87(12) |
| Si(1)-N(1) | 1.838(3) | Al(1)-Si(1)-N(1) | 118.86(12) |
| Si(1)-N(2) | 1.834(4) | Al(1)-Si(1)-N(2) | 117.41(13) |
| Si(2)-N(3) | 1.843(3) | Al(1)-Si(2)-N(3) | 121.10(12) |
| Si(2)-N(4) | 1.848(3) | Al(1)-Si(2)-N(4) | 120.60(12) |

| | | | |
|---|---|---|---|
| Si(1)-C(1) | 1.847(9) | N(1)-Si(1)-N(2) | 71.30(15) |
| Si(2)-C(2) | 1.799(4) | N(3)-Si(2)-N(4) | 70.92(14) |
| C(1)-B(1) | 1.774(14) | C(1)-B(1)-C(2) | 99.1(5) |
| C(1)-B(2) | 1.678(10) | C(1)-B(2)-C(2) | 99.6(5) |
| C(2)-B(1) | 1.643(6) | Si(1)-C(1)···C(2) | 109.30 |
| C(2)-B(2) | 1.727(12) | Si(2)-C(2)···C(1) | 111.66 |
| C(1)···C(2) | 2.602 | | |

## References

[1] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.

[2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

[3] L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Acta Crystallogr. Sect. Found. Adv.* **2015**, *71*, 59–75.

[4] S. Stoll, A. Schweiger, *J. Magn. Reson.* **2006**, *178*, 42–55.

[5] D. J. Hirsh, G. W. Brudvig, *Nat. Protoc.* **2007**, *2*, 1770–1781.

[6] Y.-P. Zhou, S. Raoufmoghaddam, T. Szilvási, M. Driess, *Angew. Chem. Int. Ed.* **2016**, *55*, 12868–12872.

[7] S. S. Sen, H. W. Roesky, D. Stern, J. Henn, D. Stalke, *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126.

[8] C. Shan, S. Dong, S. Yao, J. Zhu, M. Driess, *J. Am. Chem. Soc.* **2023**, *145*, 7084–7089.

[9] T. A. Scott, B. A. Ooro, D. J. Collins, M. Shatruk, A. Yakovenko, K. R. Dunbar, H.-C. Zhou, *Chem Commun* **2009**, 65–67.

[10] J. Hicks, M. Juckel, A. Paparo, D. Dange, C. Jones, *Organometallics* **2018**, *37*, 4810–4813.

[11] V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709.

[12] F. J. M. Gil, M. A. Salgado, J. M. Gil, *Synth. React. Inorg. Met.-Org. Chem.* **1986**, *16*, 663–666.

[13] J. C. Beamish, M. Wilkinson, I. J. Worrall, *Inorg. Chem.* **1978**, *17*, 2026–2027.

[14] J. C. Beamish, A. Boardman, I. J. Worrall, *Polyhedron* **1991**, *10*, 95–99.

[15] S. K. Mellerup, Y. Cui, F. Fantuzzi, P. Schmid, J. T. Goettel, G. Bélanger-Chabot, M. Arrowsmith, I. Krummenacher, Q. Ye, V. Engel, B. Engels, H. Braunschweig, *J. Am. Chem. Soc.* **2019**, *141*, 16954–16960.

[16] D. Dhara, L. Endres, I. Krummenacher, M. Arrowsmith, R. D. Dewhurst, B. Engels, R. Bertermann, M. Finze, S. Demeshko, F. Meyer, F. Fantuzzi, H. Braunschweig, *Angew. Chem. Int. Ed.* **2024**, *63*, e202401052.

[17] X. Chen, D. Yang, F. Cao, Z. Mo, *J. Am. Chem. Soc.* **2024**, *146*, 29278–29284.