Electronic Supplementary Information

Cyclic Amino(Carboranyl) Silylene: Synthesis, Structure and Reactivity

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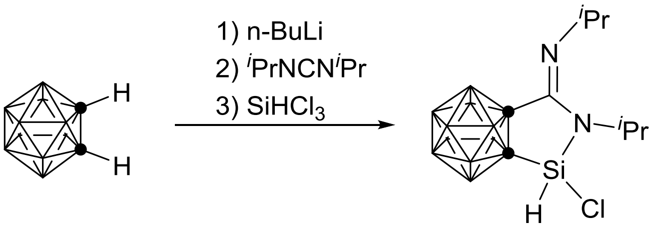
General Procedure. All operations were carried out under a dry argon or nitrogen atmosphere with standard Schlenk and glove box techniques. ^{1}H, ^{13}C, ^{11}B and ^{29}Si NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400, 100, 128 and 79 MHz, respectively. All chemical shifts were reported in δ unit with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, to external $BF_3\cdot OEt_2$ (0.00 ppm) and $SiMe_4$ (0.00 ppm) for boron and silicon chemical shifts. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, q = quartet, m = multiplet, br = broad signal. Elemental analyses were performed by MEDAC Ltd, U.K., or the Shanghai Institute of Organic Chemistry, CAS, China. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Compounds $KSiTMS_3$,[1] $LiCH_2TMS$,[2] and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene[3] were prepared according to literature procedures. All other chemicals were purchased from either Aldrich, J&K or Acros Chemical Co. and used as received unless otherwise specified.



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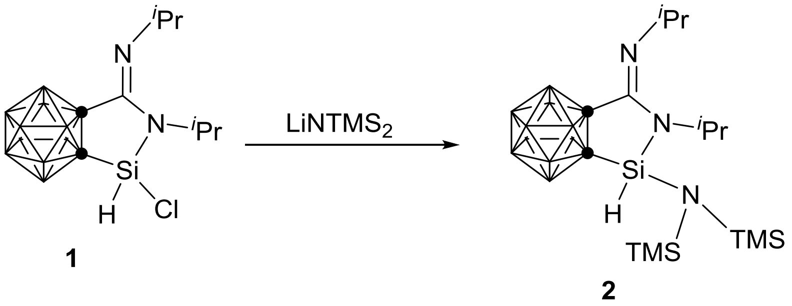
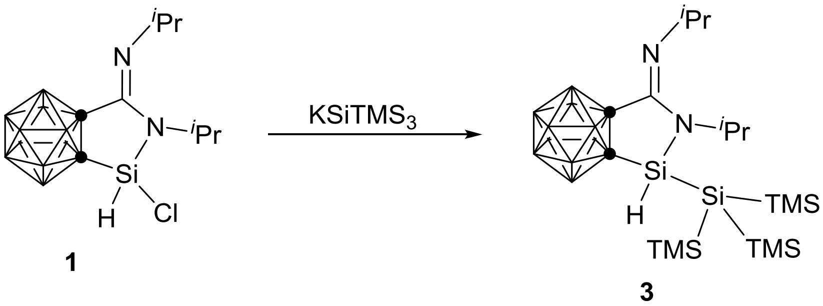
Preparation of 1,2-{C[N(^{i}Pr)]N(^{i}Pr)SiHCl}-1,2-$C_2B_{10}H_{10}$ (1). To an Et_2O solution (30 mL) of *o*-$C_2B_{10}H_{12}$ (1.152 g, 8.0 mmol) was slowly added via syringe n-BuLi (1.6 M in n-hexane, 10.0 mL, 16.0 mmol) at 0 °C under stirring. The reaction mixture was allowed to slowly warm to room temperature and stirred for 3 h, to which was slowly added via cannula an Et_2O solution (5 mL) of ^{i}PrNCN^{i}Pr (1.008 g, 8.0 mmol) at room temperature. The resulting mixture was allowed to stir overnight, to which was added via syringe $SiHCl_3$ (0.80 mL, 8.0 mmol) at -78 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. After removal of precipitate by filtration, the resultant clear solution was concentrated in vacuo to dryness. The residue was recrystallized from hexane to give compound **1** as colorless crystals (1.150 g, 43%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.08 (overlapped, 6H; CH*Me*$_2$), 1.19 (d, *J* = 6.4 Hz, 3H; CH*Me*$_2$), 1.30 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 4.16 (m, 1H; *CH*Me$_2$), 4.41 (m, 1H; *CH*Me$_2$), 5.59 (s, 1H; Si*H*). Noted that 10 BH signals were very broad and unresolved. $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2): δ 21.9, 22.0, 24.6, 24.8 (CH*Me*$_2$), 46.8, 48.1 (*C*HMe$_2$), 62.5, 74.3 (cage *C*), 141.0 (N*C*N). $^{11}B\{^{1}H\}$ NMR (128 MHz, CD_2Cl_2): δ -12.7 (2B), -10.2 (4B), -6.8 (2B), -2.2 (1B), -0.8 (1B). $^{29}Si\{^{1}H\}$

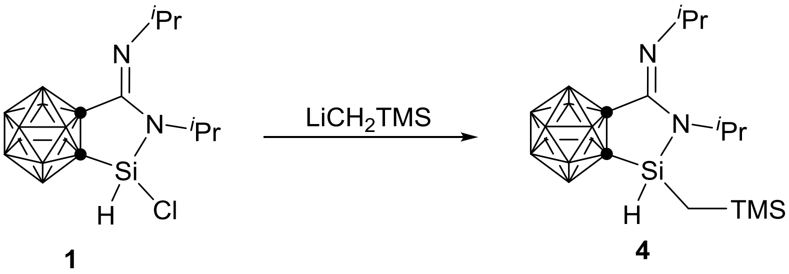
NMR (79 MHz, CD_2Cl_2): δ -17.5. Anal. Calcd for $C_9H_{25}B_{10}ClN_2Si$: C, 32.47; H, 7.57; N, 8.41. Found: C, 32.70; H, 7.29; N, 8.52.



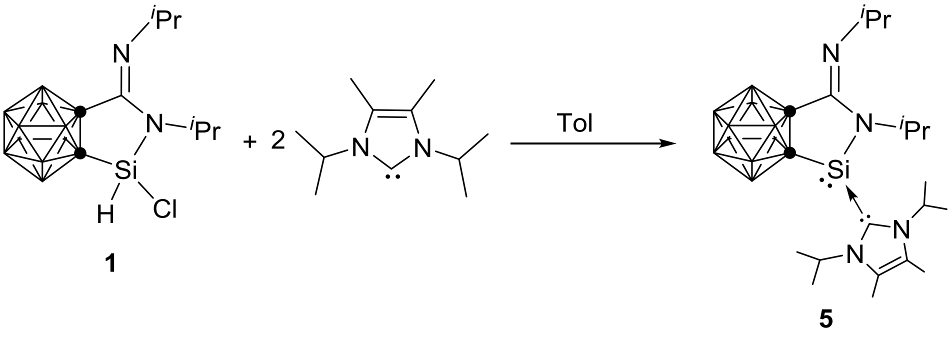
Preparation of 1,2-{C[N(^{i}Pr)]N(^{i}Pr)SiH[N(SiMe$_3$)$_2$]}-1,2-$C_2B_{10}H_{10}$ (2). Toluene (10 mL) was added to a mixture of **1** (333 mg, 1.0 mmol) and $LiNTMS_2$ (167 mg, 1.0 mmol) at room temperature under stirring. The resulting white suspension was allowed to stir overnight. After filtration, the colorless filtrate was concentrated to about 3 mL, from which compound **2** was isolated as colorless crystals after slow evaporation of the solvent (168 mg, 37%). ^1H NMR (400 MHz, CD_2Cl_2): δ 0.24 (s, 9H; Si*Me*$_3$), 0.30 (s, 9H; Si*Me*$_3$), 1.01 (d, *J* = 6.0 Hz, 3H; CH*Me*$_2$), 1.04 (d, *J* = 6.4 Hz, 3H; CH*Me*$_2$), 1.09 (d, *J* = 6.0 Hz, 3H; CH*Me*$_2$), 1.35 (d, *J* = 7.2 Hz, 3H; CH*Me*$_2$), 3.92 (m, 1H; *CH*Me$_2$), 4.43 (m, 1H; *CH*Me$_2$), 5.19 (s, 1H; Si*H*). Noted that 10 BH signals were very broad and unresolved. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 4.0, 4.4 (Si*Me*$_3$), 20.7, 21.7, 24.6, 25.0 (CH*Me*$_2$), 46.8, 48.0 (*C*HMe$_2$), 66.6, 75.2 (cage *C*), 142.1 (N*C*N). $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2): δ -13.4 (1B), -11.5 (2B), -10.6 (3B), -7.8 (1B), -6.9 (1B), -2.2 (1B), -1.4 (1B). $^{29}Si\{^1H\}$ NMR (79 MHz, CD_2Cl_2): δ 5.2 (*Si*Me$_3$), 8.4 (*Si*H). Anal. Calcd for $C_{15}H_{43}B_{10}N_3Si_3$: C, 39.35; H, 9.47; N, 9.18. Found: C, 39.51; H, 9.72; N, 9.13.



Preparation of 1,2-{C[N(^{i}Pr)]N(^{i}Pr)SiH[Si(SiMe$_3$)$_3$]}-1,2-$C_2B_{10}H_{10}$ (3). To a toluene solution (10 mL) of **1** (100 mg, 0.3 mmol) was added via cannula a toluene solution (5 mL) of $KSiTMS_3$ (86 mg, 0.3 mmol) at -40 °C under stirring. The reaction mixture was allowed to warm to room temperature and stirred overnight. After removal of the precipitate and solvent, the residue was recrystallized from hexane to give compound **3** as colorless crystals (98 mg, 60%). ^{1}H NMR (400 MHz, C_6D_6): δ 0.25 (s, 27H; Si*Me*$_3$), 1.09 (overlapped, 6H; CH*Me*$_2$), 1.43 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 1.61 (d, *J* = 6.4 Hz, 3H; CH*Me*$_2$), 3.41 (m, 1H; *CH*Me$_2$), 4.52 (m, 1H; *CH*Me$_2$), 5.39 (s, 1H; Si*H*). Noted that 10 BH signals were very broad and unresolved. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 3.1 (Si*Me*$_3$), 19.0, 21.0, 24.7, 24.8 (CH*Me*$_2$), 48.2, 49.4 (*C*HMe$_2$), 66.3, 75.5 (cage *C*), 142.0 (N*C*N). ^{11}B{^{1}H} NMR (128 MHz, C_6D_6): δ -11.9 (2B), -9.3 (3B), -7.0 (2B), -6.3 (1B), -1.8 (1B), -1.0 (1B). ^{29}Si{^{1}H} NMR (79 MHz, C_6D_6): δ -135.3 (*Si*(SiMe$_3$)$_3$), -9.1 ((Si(*Si*Me$_3$)$_3$)), 5.0 (*Si*H). Anal. Calcd for $C_{18}H_{52}B_{10}N_2Si_5$: C, 39.66; H, 9.61; N, 5.14. Found: C, 39.81; H, 9.38; N, 5.15.

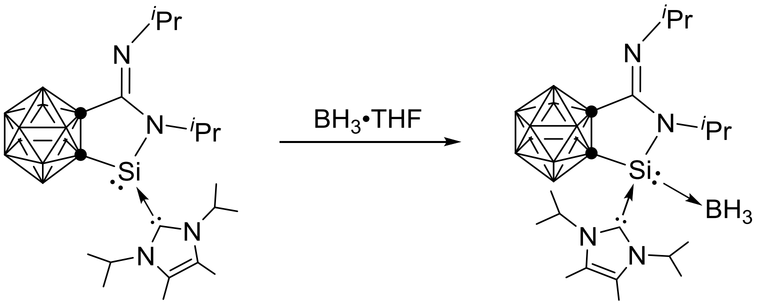


Preparation of 1,2-{C[N(^{i}Pr)]N(^{i}Pr)SiH[CH$_2$(SiMe$_3$)]}-1,2-$C_2B_{10}H_{10}$ (4). This compound was prepared as colorless crystals from **1** (167 mg, 0.5 mmol) and LiCH$_2$TMS (47 mg, 0.5 mmol) in toluene (10 mL) using the same procedure reported for **3**: yield 60% (116 mg). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.16 (s, 9H; Si*Me*$_3$), 0.36 (d, *J* = 5.2 Hz, 2H; C*H*$_2$), 1.05 (overlapped, 6H; CH*Me*$_2$), 1.14 (d, *J* = 6.4 Hz, 3H; CH*Me*$_2$), 1.23 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 4.12 (m, 1H; *CH*Me$_2$), 4.43 (m, 1H; *CH*Me$_2$), 4.88 (d, *J* = 4.4 Hz, 1H; Si*H*). Noted that 10 BH signals were very broad and unresolved. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 0.6 (Si*Me*$_3$), 2.7 (*C*H$_2$), 21.7, 22.4, 24.9, 25.0 (CH*Me*$_2$), 46.2, 47.6 (*C*HMe$_2$), 64.8, 75.4 (cage *C*), 142.8 (N*C*N). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2): δ -12.5 (2B), -9.8 (4B), -7.0 (2B), -2.5 (1B), -1.6 (1B). ^{29}Si{^{1}H} NMR (79 MHz, CD_2Cl_2): δ -6.2 (*Si*Me$_3$), 0.5 (*Si*H). Anal. Calcd for $C_{13}H_{36}B_{10}N_2Si_2$: C, 40.59; H, 9.43; N, 7.28. Found: C, 40.19; H, 9.19; N, 7.37.



Preparation of 1,2-{C[N(^{i}Pr)]N(^{i}Pr)Si(I^{i}Pr)}-1,2-$C_2B_{10}H_{10}$ (5). To a toluene solution (20 mL) of **1** (167 mg, 0.5 mmol) was added a toluene solution (20 mL) of

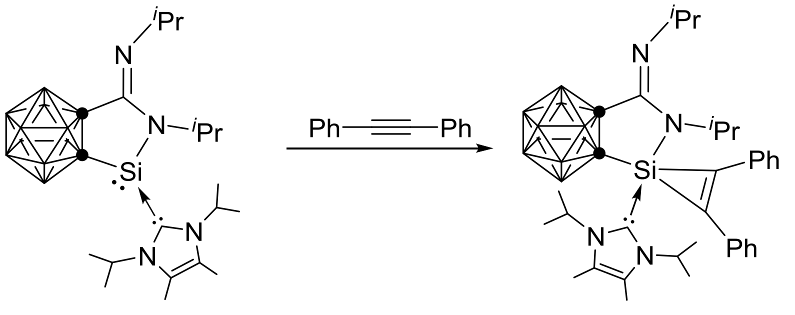
1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (I^{i}Pr; 180 mg, 1.0 mmol) via cannula at -40 ^{o}C under stirring. The reaction mixture was allowed to warm to room temperature and stirred overnight. After removal of the precipitate and solvent, compound **5** was obtained as a pale yellow solid. The product was washed with cold toluene (2 x 2 mL) and dried in vacuo (195 mg, 82%). X-ray quality crystals were obtained by recrystallization from a mixed solvent of THF/toluene at room temperature. ^{1}H NMR (400 MHz, THF-d_8): δ 1.05 (overlapped, 6H; CH*Me*$_2$), 1.10 (d, *J* = 5.6 Hz, 3H; CH*Me*$_2$), 1.36 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 1.47 (d, *J* = 5.2 Hz, 6H; CH*Me*$_2$), 1.53 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 1.64 (d, *J* = 7.2 Hz, 3H; CH*Me*$_2$), 2.30 (s, 3H; C*Me*), 2.31 (s, 3H; C*Me*), 4.05 (m, 1H; *CH*Me$_2$), 4.56 (m, 1H; *CH*Me$_2$), 4.90 (m, 1H; *CH*Me$_2$), 5.43 (m, 1H; *CH*Me$_2$). Noted that 10 BH signals were very broad and unresolved. ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 10.5, 10.6, 20.8, 21.0, 21.4, 22.5, 22.6, 23.9 (CH*Me*$_2$, C*Me*$_3$, *Me*), 47.4, 47.6, 49.4, 52.0 (*C*HMe$_2$), 78.7, 78.9 (cage *C*), 127.6 (N*CC*N), 149.4 (N*C*N), 163.7 (*C*Si). ^{11}B{^{1}H} NMR (128 MHz, THF-d_8): δ -15.2 (2B), -11.5 (2B), -10.5 (2B), -8.9 (2B), -5.8 (1B), -4.9 (1B). ^{29}Si{^{1}H} NMR (79 MHz, THF-d_8): δ -4.3. Anal. Calcd for $C_{20}H_{44}B_{10}N_4Si$: C, 50.38; H, 9.30; N, 11.75. Found: C, 50.35; H, 9.13; N, 11.87.



5 6

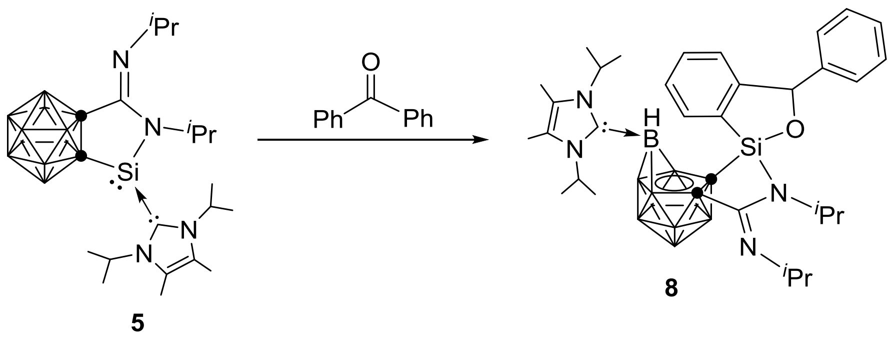
Preparation of 1,2-{C[N(^{i}Pr)]N(^{i}Pr)Si[(I^{i}Pr)(BH$_3$)]}-1,2-$C_2B_{10}H_{10}$ (6). To a THF solution (20 mL) of **5** (95 mg, 0.2 mmol) was added via syringe a THF solution of BH$_3$ ·THF (1.0 M, 0.2 mL, 0.2 mmol) at -78 ^{o}C under stirring. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. The color of the solution was changed from yellow to colorless. Volatiles were removed under vacuo. The residue was recrystallized from THF to give compound **6** as colorless crystals (36 mg, 37%). ^{1}H NMR (400 MHz, THF-d_8): δ 1.06 (d, *J* = 5.6 Hz, 3H; CH*Me*$_2$), 1.13 (overlapped, 6H; CH*Me*$_2$), 1.39 (d, *J* = 7.2 Hz, 3H; CH*Me*$_2$), 1.56 (overlapped, 6H; CH*Me*$_2$), 1.60 (d, *J* = 6.8 Hz, 6H; CH*Me*$_2$), 2.38 (s, 3H; C*Me*), 2.40 (s, 3H; C*Me*), 4.00 (m, 1H; *CH*Me$_2$), 4.54 (m, 1H; *CH*Me$_2$), 4.98 (m, 1H; *CH*Me$_2$), 5.53 (m, 1H; *CH*Me$_2$). Noted that 13 BH signals were very broad and unresolved. ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 10.8, 10.9, 20.4, 22.0, 22.4, 22.5, 22.6, 23.1 (CH*Me*$_2$, C*Me*$_3$, *Me*), 47.8, 48.0, 50.2, 53.4 (*C*HMe$_2$), 71.1, 76.0 (cage *C*), 130.2, 130.6

(N*C*N), 145.6 (N*C*N), 152.7 (*C*Si). ^{11}B NMR (128 MHz, THF-d$_8$): δ -40.3 (q, J_{BH} = 93 Hz; 1B), -13.6 (d, J_{BH} = 169 Hz; 1B), -10.8 (br, J_{BH} unresolved; 2B), -9.8 (br, J_{BH} unresolved; 2B), -8.2 (d, J_{BH} = 146 Hz; 2B), -7.0 (d, J_{BH} = 145 Hz; 1B), -2.4 (d, J_{BH} = 140 Hz; 2B). ^{29}Si{^{1}H} NMR (79 MHz, THF-d$_8$): δ 15.2 (br). Anal. Calcd for $C_{20}H_{47}B_{11}N_4Si$: C, 48.96; H, 9.66; N, 11.42. Found: C, 48.66; H, 9.86; N, 11.38.



5 **7**

Preparation of 1,2-{C[N(^{i}Pr)]N(^{i}Pr)Si[(I^{i}Pr)(PhCCPh)]}-1,2-$C_2B_{10}H_{10}$ (7). To a Schlenk flask containing a mixture of **5** (143 mg, 0.3 mmol) and PhCCPh (53 mg, 0.3 mmol) was added THF (20 mL) at room temperature under stirring. The reaction mixture was allowed to stir overnight, giving an orange-red solution. After removal of the solvent, the oil residue was crystallized from a mixed solvent of toluene/hexane at -30 ^{o}C to afford compound **7** as yellow crystals (150 mg, 71%). ^{1}H NMR (400 MHz, THF-d$_8$): δ 1.07 (overlapped, 9H; CH*Me*$_2$), 1.23 (d, *J* = 6.4 Hz, 3H; CH*Me*$_2$), 1.42 (d, *J* = 6.4 Hz, 3H; CH*Me*$_2$), 1.49 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 1.57 (d, *J* = 7.2 Hz, 3H; CH*Me*$_2$), 1.64 (d, *J* = 6.8 Hz, 3H; CH*Me*$_2$), 2.33 (s, 3H; C*Me*), 2.38 (s, 3H; C*Me*), 3.78 (m, 1H; *CH*Me$_2$), 4.50 (m, 1H; *CH*Me$_2$), 5.16 (m, 1H; *CH*Me$_2$), 5.35 (m, 1H; *CH*Me$_2$), 6.70 (d, *J* = 6.8 Hz, 2H; aromatic C*H*), 6.97 (t, *J* = 7.2 Hz, 1H; aromatic C*H*), 7.07 (d, *J* = 7.2 Hz, 1H; aromatic C*H*), 7.13 (m, 2H; aromatic C*H*), 7.17 (m, 2H; aromatic C*H*), 7.48 (d, *J* = 7.2 Hz, 2H; aromatic C*H*). Noted that 10 BH signals were very broad and unresolved. ^{13}C{^{1}H} NMR (100 MHz, THF-d$_8$): δ 10.5, 10.6, 20.6, 21.4, 21.5, 22.2, 22.3 (CH*Me*$_2$, C*Me*$_3$, *Me*), 48.1, 48.4, 52.0, 53.1 (*C*HMe$_2$), 74.6, 81.0 (cage *C*), 124.7, 125.2, 126.7, 126.9, 127.4, 128.4, 128.8, 129.0, 138.2, 142.8, 143.2 (aromatic *C*, N*CC*N), 152.8 (N*C*N), 157.6 (*C*Si), 198.6 (*C*Si*C*). ^{11}B{^{1}H} NMR (128 MHz, THF-d$_8$): δ -13.7 (3B), -12.1 (2B), -10.4 (2B), -9.3 (1B), -5.3 (2B). ^{29}Si{^{1}H} NMR (79 MHz, THF-d$_8$): δ -149.8. Anal. Calcd for $C_{37.5}H_{58}B_{10}N_4Si$ (**7** + 0.5C_7H_8): C, 64.24; H, 8.34; N, 7.99. Found: C, 64.07; H, 8.53; N, 7.62.



Preparation of 7,8-{C[N(^{i}Pr)]N(^{i}Pr)Si[OCH(Ph)C(CH)$_4$C]}-μ-9,10,11-(I^{i}Pr)BH-1,2-C$_2$B$_9$H$_9$ (8). THF (20 mL) was added to a mixture of **5** (143 mg, 0.3 mmol) and PhCOPh (55 mg, 0.3 mmol) at room temperature. After heating the mixture at 80 ^{o}C overnight, the solvent was removed. Compound **8** was obtained as colorless crystals, after crystallization from a mixed solvent of toluene/hexane (125 mg, 59%). ^{1}H NMR (400 MHz, THF-d$_8$): δ 0.86 (d, J = 6.4 Hz, 3H; CH*Me*$_2$), 1.00 (d, J = 6.0 Hz, 6H; CH*Me*$_2$), 1.07 (d, J = 7.2 Hz, 3H; CH*Me*$_2$), 1.36 (br m, 12H; CH*Me*$_2$), 2.24 (s, 6H; C*Me*), 4.27 (m, 1H; *CH*Me$_2$), 4.66 (m, 1H; *CH*Me$_2$), 5.40 (br s, 2H; *CH*Me$_2$), 6.08 (s, 1H; OC*H*), 6.90 (m, 1H; aromatic C*H*), 7.13 (m, 2H; aromatic C*H*), 7.30 (m, 5H; aromatic C*H*), 7.72 (m, 1H; aromatic C*H*). Noted that 10 BH signals were very broad and unresolved. ^{13}C{^{1}H} NMR (100 MHz, THF-d$_8$): δ 10.1, 20.7, 22.1, 22.4 (CH*Me*$_2$, C*Me*$_3$, *Me*), 44.8, 46.5, 51.1 (*C*HMe$_2$), 69.8 (cage *C*), 82.2 (O*C*H), 124.5, 128.1, 128.6, 129.1, 129.2, 129.4, 131.5, 133.3, 143.9 (aromatic *C*, N*CC*N), 151.5 (N*C*N), 155.3 (*C*B). ^{11}B{^{1}H} NMR (128 MHz, THF-d$_8$): δ -15.7 (3B), -13.5 (1B), -5.8 (2B), -4.1 (2B), 1.6 (1B), 29.3 (1B). ^{29}Si{^{1}H} NMR (79 MHz, THF-d$_8$): δ -2.1. Anal. Calcd for C$_{36.5}$H$_{58}$B$_{10}$N$_4$OSi (**8** + 0.5C$_7$H$_8$): C, 62.18; H, 8.29; N, 7.95. Found: C, 62.27; H, 8.46; N, 7.60.

X-ray Structure Determination. Single crystals were immersed in Paraton-N oil and sealed under argon in thin-walled glass capillaries. All data were collected at 296 K on a Bruker Kappa ApexII Duo Diffractometer using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[4] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares calculations on F^2 using the SHELXTL program package.[5] All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and refinement are given in Table S3. Details of the crystal structures were deposited in the Cambridge Crystallographic Data Centre with CCDC 1584293 for **2**, CCDC 1584294 for **3**, CCDC 1584295 for **5**, CCDC 1584296 for **6**, CCDC 1584297 for **7** C$_7$H$_8$, and CCDC 1584298 for **8**.

Computational Details. The geometry optimization of compound **5** was performed using the Gaussian09 program, Revision D.01,[6] at the B3LYP[7]-D3[8] theoretical level using 6-31g(d,p) basis set. Frequency calculations were made to determine the characteristics of all stationary points as energy minima. Orbital energies of compound **5** were calculated at the same level of theory. NBO analysis at the B3LYP/6-31g(d,p) level of theory was carried out using the NBO program implemented in the Gaussian 09 package. The graphics of the molecular orbitals were produced by using the visualizing software VMD.[9]

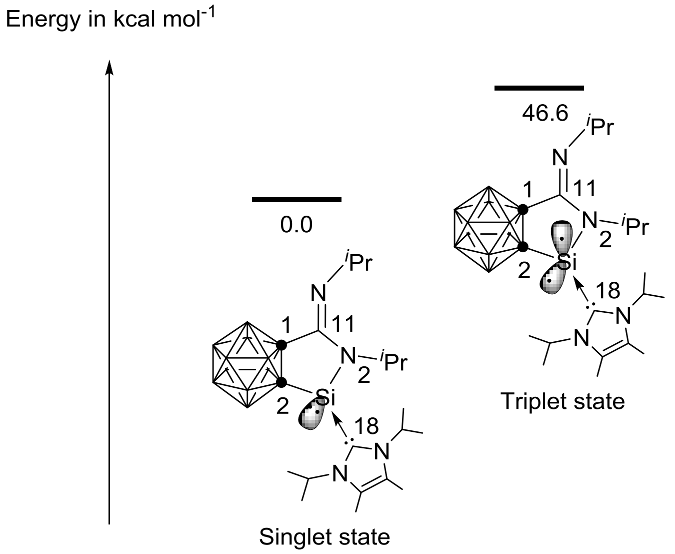
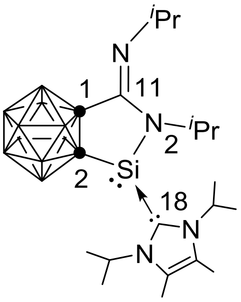


Fig. S1 Energy profiles (E in kcal mol^{-1}) calculated for **5** in singlet and triplet state at the B3LYP-D3/6-31G(d,p) level of theory.

Table S1. Selected experimental and calculated structural parameters of **5** (calculated at the B3LYP-D3/6-31G(d,p) level of theory)



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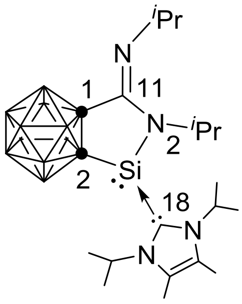
Bond length (Å)	Experimental	Calculated
C(1)-C(2)	1.654(2)	1.652
C(2)-Si	1.952(2)	1.974
Si-N(2)	1.806(2)	1.828
N(2)-C(11)	1.396(2)	1.398
C(11)-C(1)	1.521(2)	1.534
Si(1)-C(18)	2.018(2)	2.060

Bond angle (^{o})	Experimental	Calculated
C(1)-C(2)-Si	108.7(2)	108.5
C(2)-Si-N(2)	87.0(1)	87.1
Si-N(2)-C(11)	122.7(2)	122.0
N(2)-C(11)-C(1)	110.6(2)	111.2
C(11)-C(1)-C(2)	109.2(2)	109.7

Table S2. Results of the selected Wiberg bonding index



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Bond	Bonding Index
C(1)-C(2)	0.7151
C(2)-Si	0.5114
Si-N(2)	0.5542
Si-C(18)	0.6429
N(2)-C(11)	1.1292
C(11)-C1	0.9328

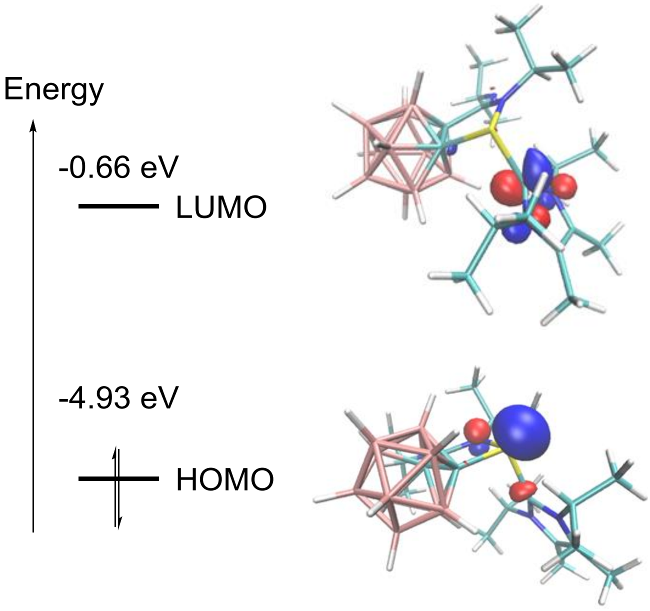

Fig. S2 Plots of the HOMO and LUMO orbitals of **5** calculated at the B3LYP-D3/6-31G(d,p) level of theory.

The Cartesian coordinate of compound **5** in singlet state

0 1

Si	-0.42342500	0.40871300	1.58539500
N	2.76976900	-1.44609500	0.04795800
N	0.98016400	-0.73821800	1.34849400
N	-1.90878400	-1.37809900	-0.56773800
N	-3.00597100	0.35693700	0.12983200
B	2.01954500	2.10536400	1.12874400
H	2.24043900	1.70814200	2.21889200
B	3.22227100	2.03775400	-0.17905800
H	4.30650800	1.64107700	0.08108500
B	2.39216900	1.53085400	-1.67493800
H	2.90263400	0.80188400	-2.45118700
B	0.68750400	1.26469300	-1.28302500
H	0.06648600	0.35960100	-1.70798400
B	0.80234500	3.31867400	0.72269800
H	0.18868800	3.81146100	1.60899500
B	2.52168700	3.59629500	0.33951400
H	3.17218000	4.39003300	0.93593100
B	2.74991800	3.24709500	-1.39794100
H	3.57002900	3.80344700	-2.05204300
B	1.16931000	2.75633100	-2.08070300
H	0.85122800	2.95322300	-3.20792500
B	-0.02140400	2.79392800	-0.75207000
H	-1.18863600	2.94530900	-0.88109500
B	1.24949200	4.04071300	-0.83834700
H	0.98790200	5.17119500	-1.09135300
C	1.91302900	0.93075700	-0.13564800
C	0.52747800	1.66077700	0.39198900
C	1.96630700	-0.51220800	0.38307500
C	3.89558900	-1.34796000	-0.86746500
H	4.15962900	-0.31628800	-1.11806100
C	5.11236200	-1.99059300	-0.18890700
H	5.98189200	-1.97567600	-0.85479700
H	5.37188800	-1.44976700	0.72643300
H	4.89234100	-3.02883400	0.08065900
C	3.53262800	-2.08079700	-2.16643900
H	4.38175600	-2.09208700	-2.85774000

H	3.24844000	-3.11586800	-1.94635100
H	2.69117400	-1.59055400	-2.66508700
C	1.17680200	-1.94200500	2.19759400
H	1.38080600	-2.78305400	1.52409100
C	2.39142500	-1.76211500	3.11976600
H	2.54937100	-2.66288400	3.72295300
H	3.29707300	-1.57785300	2.54045700
H	2.22473900	-0.91763400	3.79672500
C	-0.06443400	-2.27213500	3.03339900
H	0.07859200	-3.24533500	3.51481700
H	-0.23287400	-1.52892400	3.81757700
H	-0.97518200	-2.32839600	2.42965800
C	-1.78745200	-0.24994100	0.18887500
C	-0.77684200	-2.30458400	-0.84650900
H	0.06714600	-1.83837900	-0.34969600
C	-0.44900500	-2.39435900	-2.34102200
H	0.53893600	-2.84971200	-2.44803700
H	-1.16203000	-3.01407100	-2.88973100
H	-0.41412700	-1.40481000	-2.80127800
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H	-0.02747500	-4.22527100	-0.25277200
H	-1.28774900	-3.61369000	0.82490900
H	-1.71674700	-4.28985700	-0.75630900
C	-3.20294000	-1.48117200	-1.08644100
C	-3.68715600	-2.56532200	-1.99506400
H	-3.40094900	-3.55834600	-1.64494500
H	-4.77709400	-2.54080300	-2.05176500
H	-3.30460800	-2.44619900	-3.01373400
C	-3.89500900	-0.38945700	-0.64143300
C	-5.31137000	-0.00967100	-0.93282900
H	-5.84698700	0.30584800	-0.03470600
H	-5.37430700	0.80349400	-1.66280400
H	-5.84582800	-0.86593200	-1.34815400
C	-3.30753600	1.60764600	0.87682700
H	-2.32809200	1.97491400	1.18997300
C	-3.93879100	2.69207700	-0.00083400
H	-3.82964500	3.65453900	0.50651200
H	-3.43313600	2.76314500	-0.96633100

H	-5.00525600	2.52915200	-0.16816600
C	-4.10983100	1.29979600	2.14271100
H	-4.26451800	2.22268700	2.70924300
H	-5.09158600	0.87693800	1.91151400
H	-3.56033300	0.59764600	2.77481400

The Cartesian coordinate of compound **5** in triplet state

0 3

Si	-0.37692600	0.24743500	0.80717700
N	2.97226200	-1.81462800	0.37939000
N	0.76694200	-1.12224400	0.65468100
N	-2.42970600	-0.71720900	-1.08944800
N	-3.21541600	0.46301500	0.65168100
B	2.18951200	1.69125200	1.27553600
H	2.01771000	1.21958300	2.34631800
B	3.71884500	1.55844900	0.38647200
H	4.63323000	1.04851000	0.93516300
B	3.34090900	1.19616600	-1.32171400
H	3.99221500	0.43541800	-1.95035900
B	1.57815500	1.10250300	-1.48733500
H	1.06057700	0.26802300	-2.13466800
B	1.25682300	3.04378100	0.60906100
H	0.44519900	3.55344700	1.30628500
B	3.03004200	3.15501700	0.78164200
H	3.53251400	3.85193500	1.60016300
B	3.74592800	2.85505500	-0.83052200
H	4.77201300	3.34852300	-1.16595700
B	2.41229500	2.56451900	-1.98969700
H	2.47693300	2.84001400	-3.14237400
B	0.87699600	2.68094100	-1.08504600
H	-0.18552900	2.95656600	-1.53010600
B	2.22190300	3.78025300	-0.68964400
H	2.15500300	4.94214400	-0.92299800
C	2.36248800	0.59344900	-0.04417900
C	0.96207900	1.44786000	0.08441100
C	2.12011200	-0.87212300	0.32867000
C	4.39039600	-1.74838000	0.06309500
H	4.71095100	-0.76888100	-0.29931100

C	5.17606600	-2.06301600	1.34284700
H	6.25158500	-2.08093300	1.13826700
H	4.98443700	-1.30560700	2.10919000
H	4.87723800	-3.03798600	1.74125300
C	4.67526100	-2.77593700	-1.03986100
H	5.74326200	-2.79402400	-1.28065200
H	4.37033000	-3.77637300	-0.71626100
H	4.12118400	-2.52765900	-1.95045200
C	0.50511200	-2.47582800	1.22294700
H	1.16012300	-3.15173500	0.66792500
C	0.91884300	-2.51898600	2.70019100
H	0.80261900	-3.53177700	3.10032600
H	1.96364200	-2.22349200	2.81632900
H	0.29124000	-1.84261300	3.29171800
C	-0.93950900	-2.94139100	1.03761000
H	-1.00704000	-3.99173300	1.33978300
H	-1.64455000	-2.37171700	1.64985100
H	-1.26430400	-2.85986700	-0.00040200
C	-2.02090600	-0.01661900	0.07047000
C	-1.48172400	-0.96405400	-2.19036100
H	-0.50824300	-1.00316200	-1.69680800
C	-1.47308300	0.19809000	-3.19249300
H	-0.67764300	0.06231100	-3.93149700
H	-2.42503400	0.26194600	-3.72777600
H	-1.30270700	1.14604900	-2.67721500
C	-1.66732600	-2.32305400	-2.87809200
H	-0.76744900	-2.54794000	-3.45857500
H	-1.80978400	-3.12384100	-2.14782600
H	-2.51071300	-2.33243700	-3.57116200
C	-3.82571600	-0.61953500	-1.20662300
C	-4.60578000	-1.24327000	-2.31767000
H	-4.47874000	-2.33115900	-2.34195900
H	-5.66983000	-1.03596600	-2.19328100
H	-4.31554800	-0.85734200	-3.30034700
C	-4.30212100	0.06134200	-0.12600700
C	-5.72638700	0.35542300	0.22052500
H	-5.96598000	0.06708800	1.24862900
H	-5.96763500	1.41814200	0.11096500

H	-6.39495500	-0.20334000	-0.43611600
C	-3.22587500	1.09908600	1.97318700
H	-2.18349700	1.41832400	2.11777500
C	-4.08008300	2.37044700	2.03667700
H	-3.81494000	2.93203800	2.93745500
H	-3.89022500	3.00765400	1.16874200
H	-5.14949900	2.15746600	2.09021300
C	-3.55532900	0.09672300	3.08668900
H	-3.43793700	0.56666200	4.06850000
H	-4.58474800	-0.26564100	3.00601500
H	-2.88322500	-0.76428500	3.03466600

Table S3. Crystal Data and Summary of Data Collection and Refinement.

	2	**3**	**5**
formula	$C_{15}H_{43}B_{10}N_3Si_3$	$C_{18}H_{52}B_{10}N_2Si_5$	$C_{20}H_{44}B_{10}N_4Si$
mw	457.89	545.17	476.78
crystal size (mm^3)	0.50x0.40x0.30	0.50x0.50x0.40	0.35x0.26x0.19
crystal system	triclinic	monoclinic	monoclinic
space group	P-1	$P2_1/c$	$P2_1/n$
a, Å	10.688(1)	16.065(1)	11.579(1)
b, Å	11.029(1)	15.231(1)	18.035(2)
c, Å	13.764(1)	16.400(1)	13.655(1)
α, deg	92.86(1)	90	90
β,deg	95.80(1)	117.89(1)	98.23(1)
γ, deg	111.68(1)	90	90
V, Å^3	1493.3(2)	3546.8(4)	2822.2(5)
Z	2	4	4
D_{calcd}, Mg/m^3	1.018	1.021	1.122
Radiation (λ) (Å)	0.71073	0.71073	0.71073
2θ range, deg	2.98 to 50.48	3.88 to 50.50	3.77 to 61.51
μ, mm^{-1}	0.168	0.214	0.101
F(000)	492	1176	1024
no. of obsd reflns	5359	6426	8735
no. of params refnd	284	320	316
goodness of fit	1.052	1.075	1.024
R1	0.0850	0.0338	0.0572
wR2	0.2192	0.0893	0.1481

continued

	6	**7** C_7H_8	**8**
formula	$C_{20}H_{47}B_{11}N_4Si$	$C_{41}H_{62}B_{10}N_4Si$	$C_{33}H_{54}B_{10}N_4OSi$
mw	490.62	747.13	658.99
crystal size (mm^3)	0.50x0.40x0.30	0.50x0.40x0.30	0.50x0.40x0.30
crystal system	triclinic	orthorhombic	monoclinic
space group	*P*-1	*P*bca	$P2_1/n$
a, Å	9.664(1)	20.035(1)	13.195(1)
b, Å	12.614(1)	20.692(1)	18.898(1)
c, Å	14.622(1)	21.530(1)	16.106(1)
α, deg	108.68(1)	90	90
β,deg	97.91(1)	90	91.51(1)
γ, deg	110.43(1)	90	90
V, Å^3	1518.49(16)	8925.6(4)	4014.6(3)
Z	2	8	4
D_{calcd}, Mg/m^3	1.073	1.112	1.090
Radiation (λ) (Å)	0.71073	0.71073	0.71073
2θ range, deg	3.06 to 50.50	3.40 to 50.50	3.32 to 50.50
μ, mm^{-1}	0.095	0.086	0.090
F(000)	528	3200	1408
no. of obsd reflns	5433	8065	7274
no. of params refnd	337	505	446
goodness of fit	1.085	1.039	1.009
R1	0.0455	0.0638	0.0593
wR2	0.1267	0.1784	0.1294

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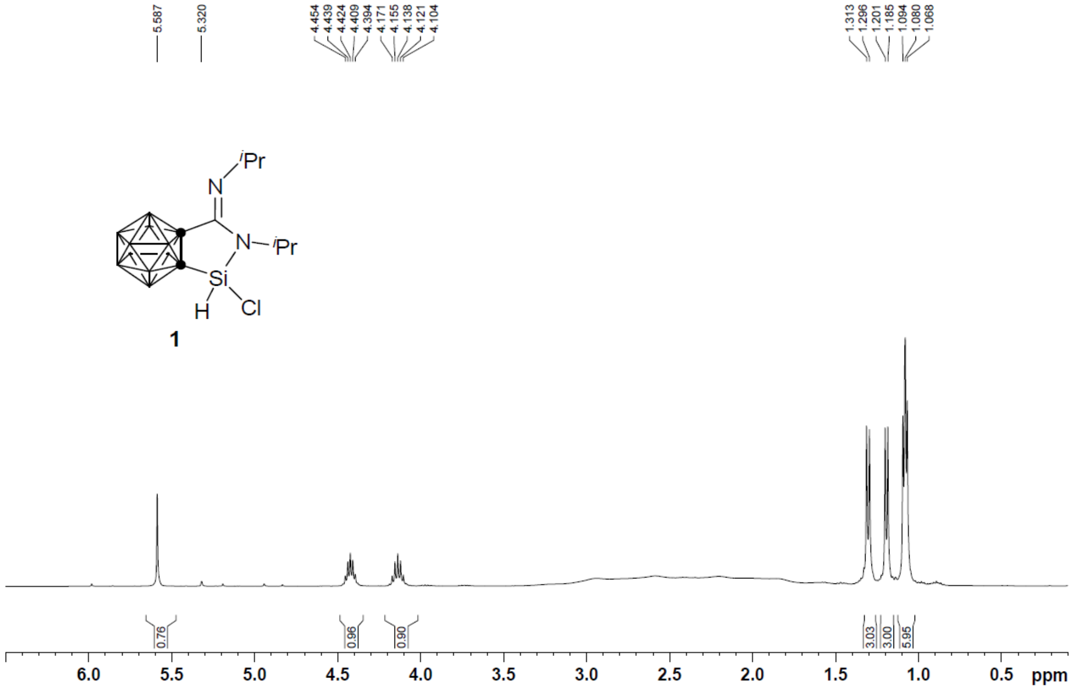

Fig. S2 ^{1}H NMR spectrum of compound **1** in CD_2Cl_2.

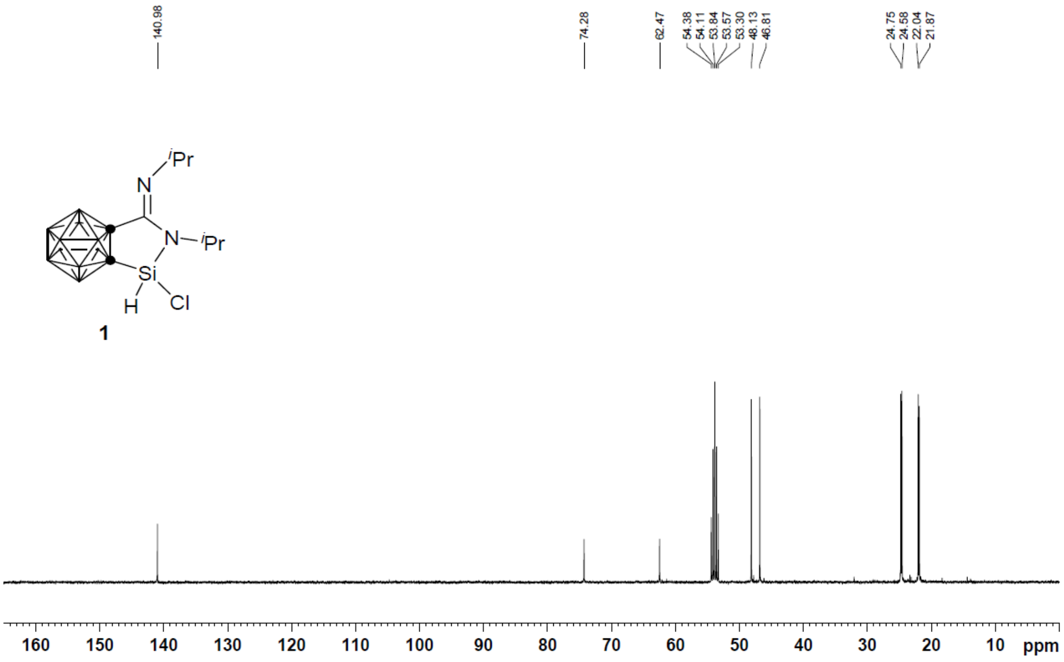

Fig.S3 ^{13}C NMR spectrum of compound **1** in CD_2Cl_2.

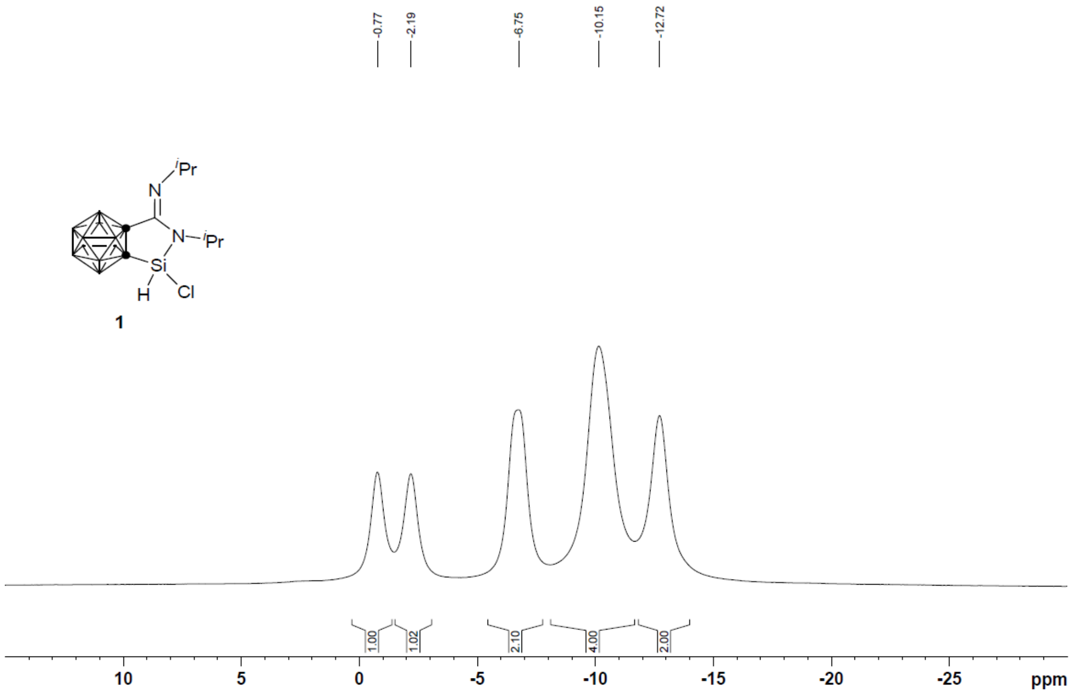

Fig. S4 $^{11}B\{^{1}H\}$ NMR spectrum of compound **1** in CD_2Cl_2.

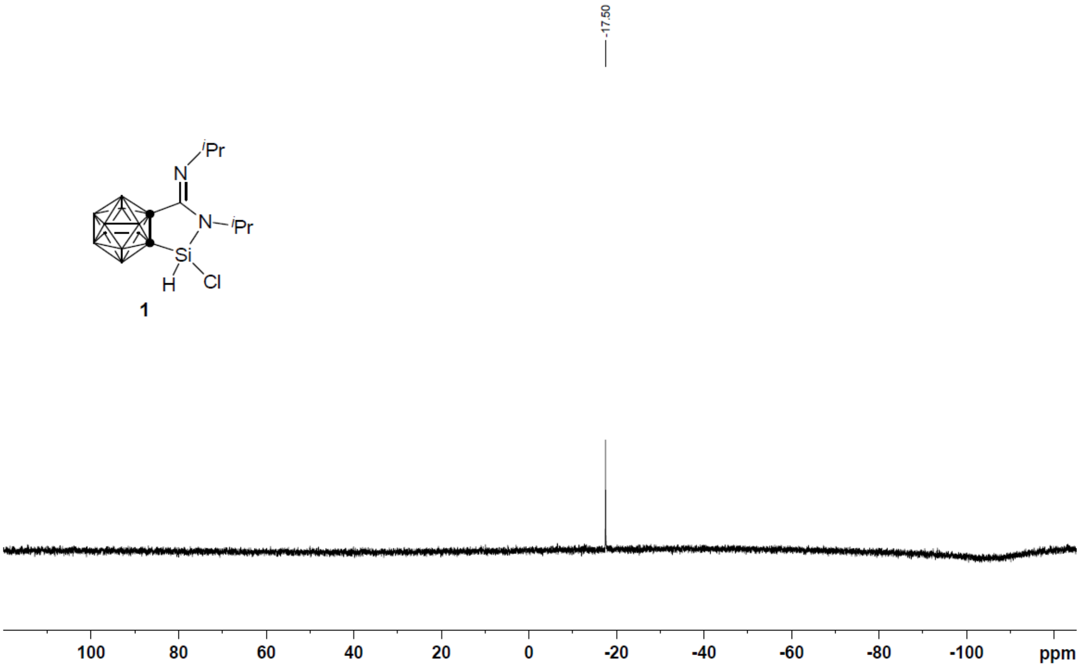

Fig. S5 ^{29}Si NMR spectrum of compound **1** in CD_2Cl_2.

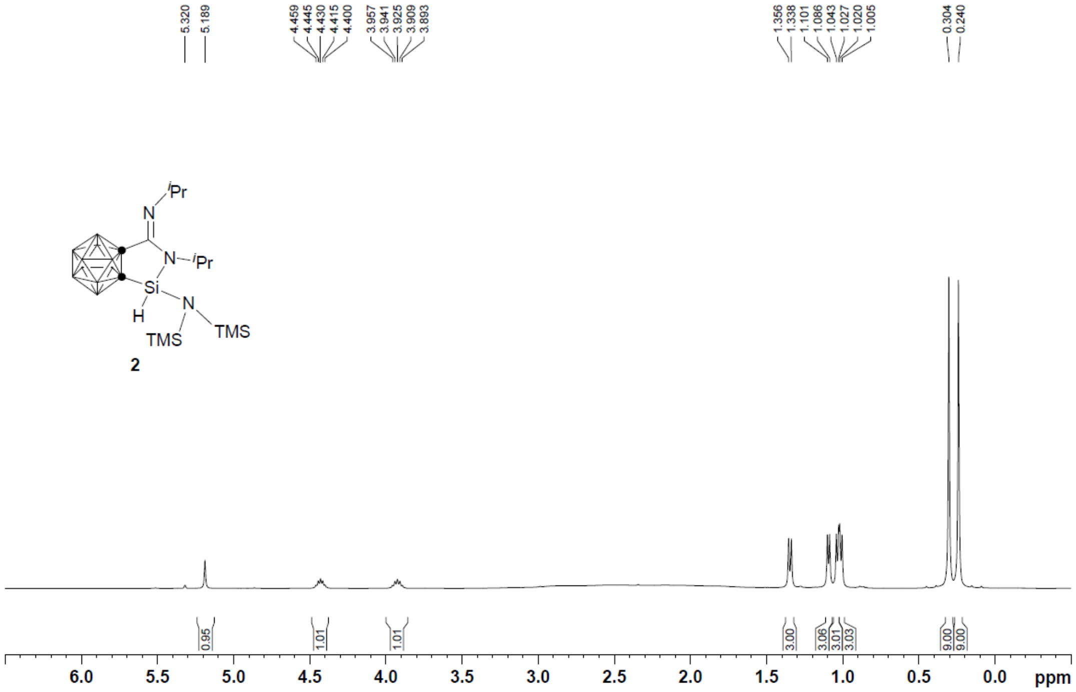

Fig. S6 ^{1}H NMR spectrum of compound **2** in CD_2Cl_2.

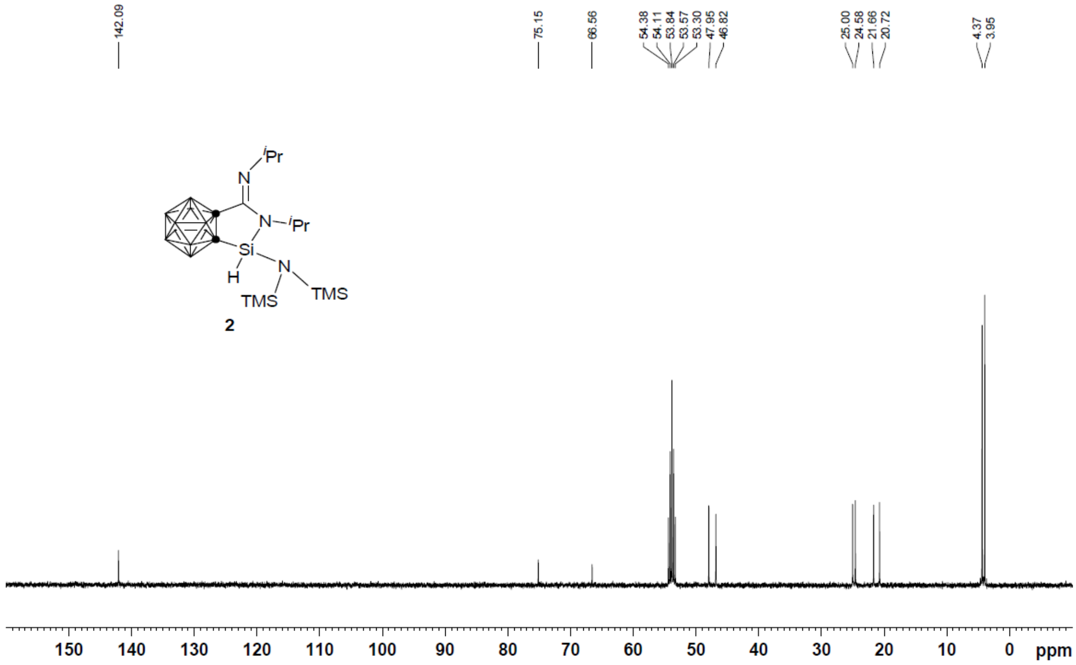

Fig. S7 ^{13}C NMR spectrum of compound **2** in CD_2Cl_2.

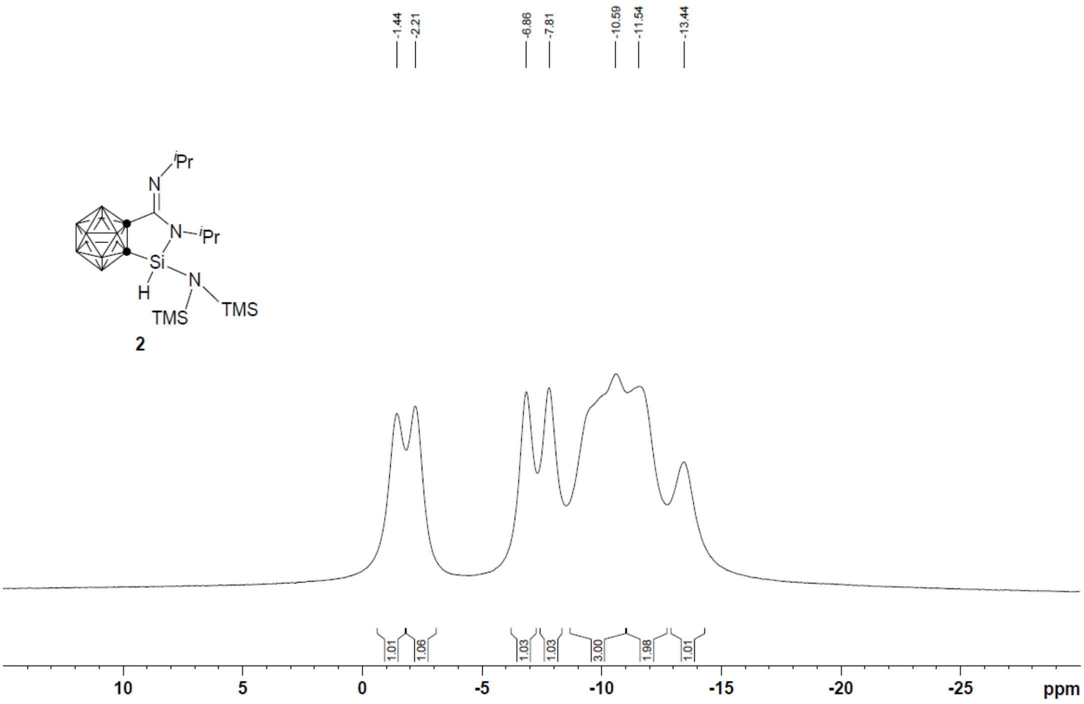

Fig. S8 $^{11}B\{^{1}H\}$ NMR spectrum of compound **2** in CD_2Cl_2.

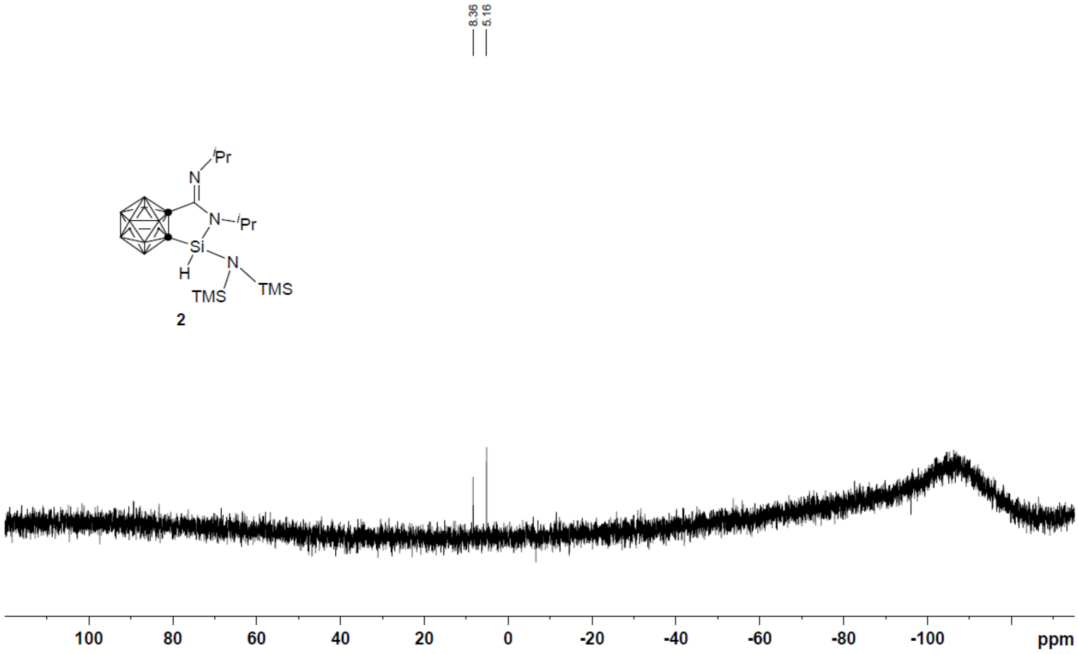

Fig. S9 ^{29}Si NMR spectrum of compound **2** in CD_2Cl_2.

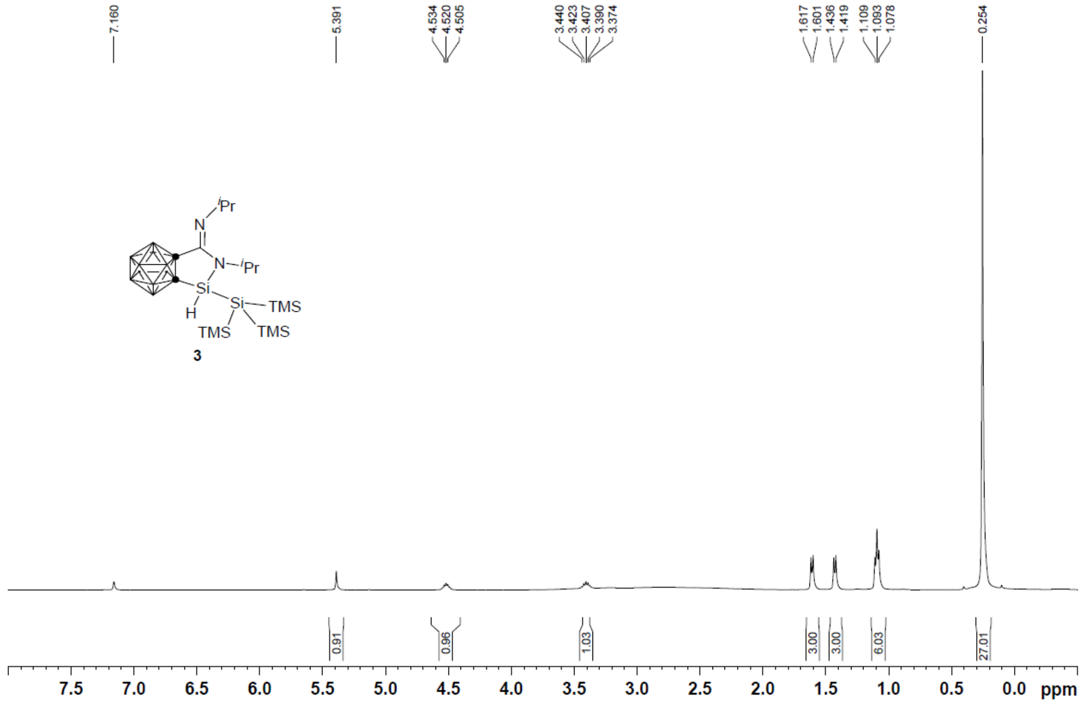

Fig. S10 ^{1}H NMR spectrum of compound **3** in C_6D_6.

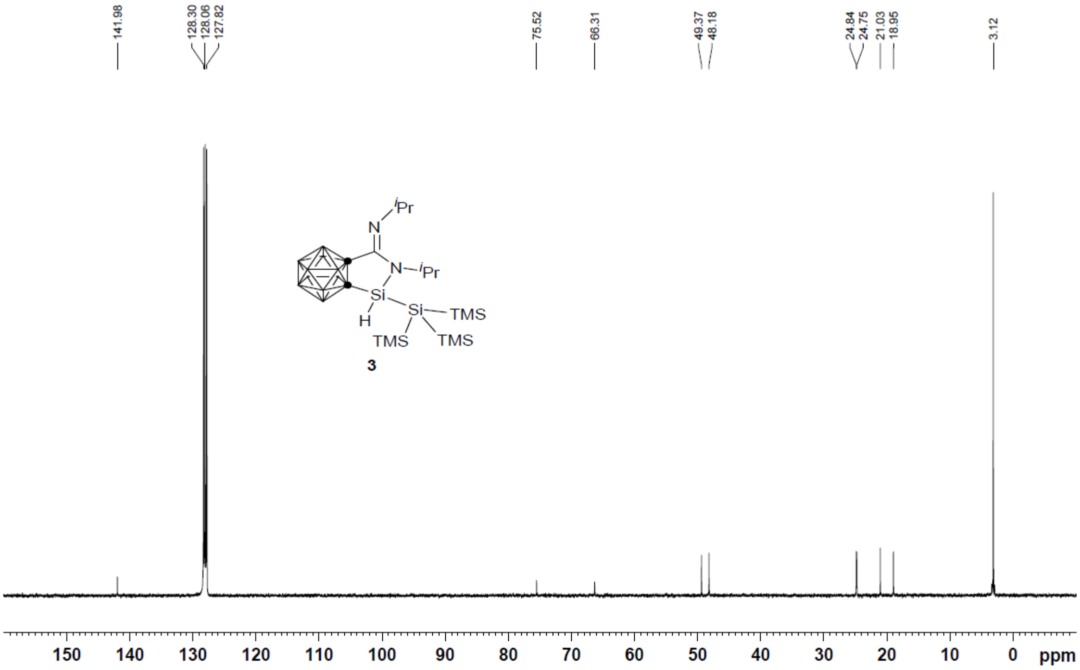

Fig. S11 ^{13}C NMR spectrum of compound **3** in C_6D_6.

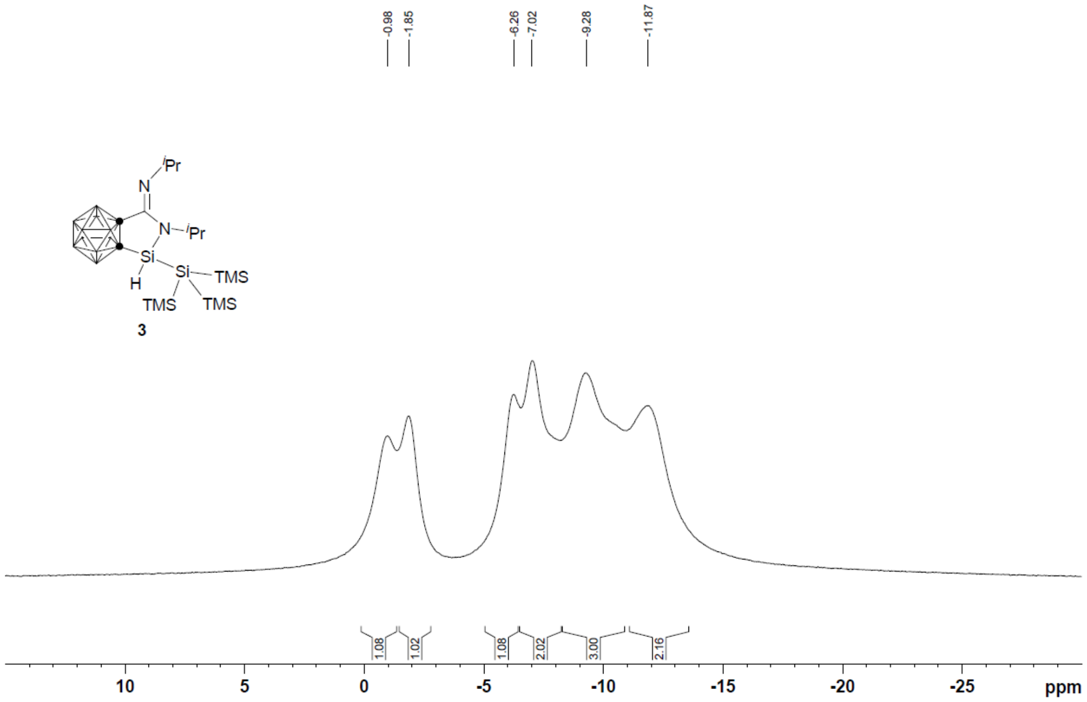

Fig. S12 ^{11}B{^{1}H} NMR spectrum of compound **3** in C_6D_6.

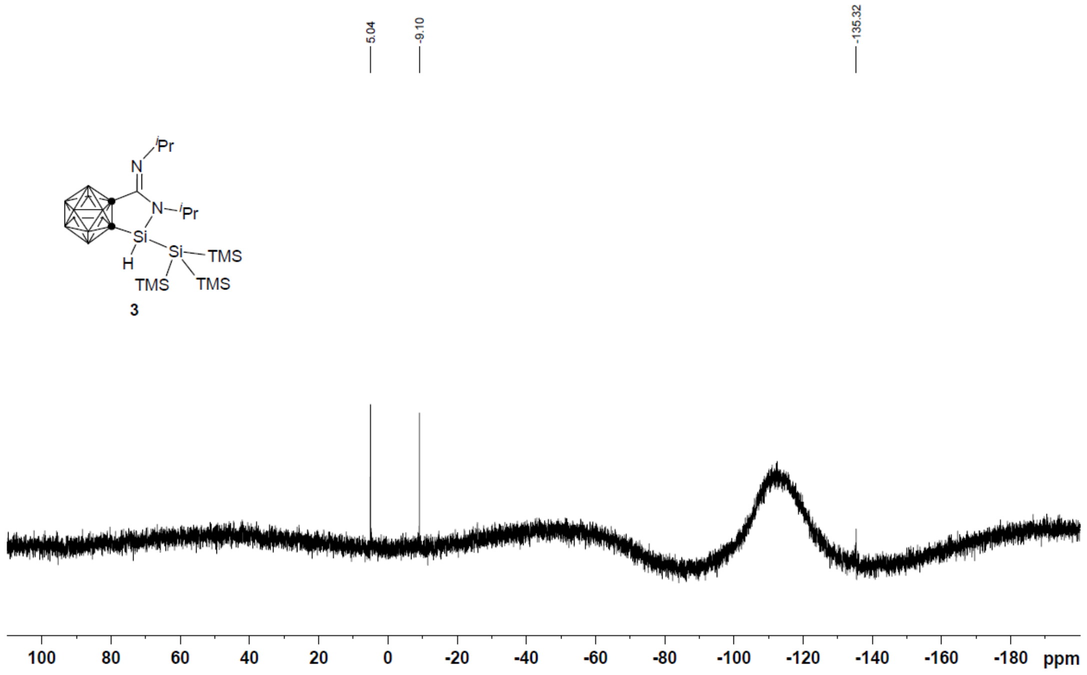

Fig. S13 ^{29}Si NMR spectrum of compound **3** in C_6D_6.

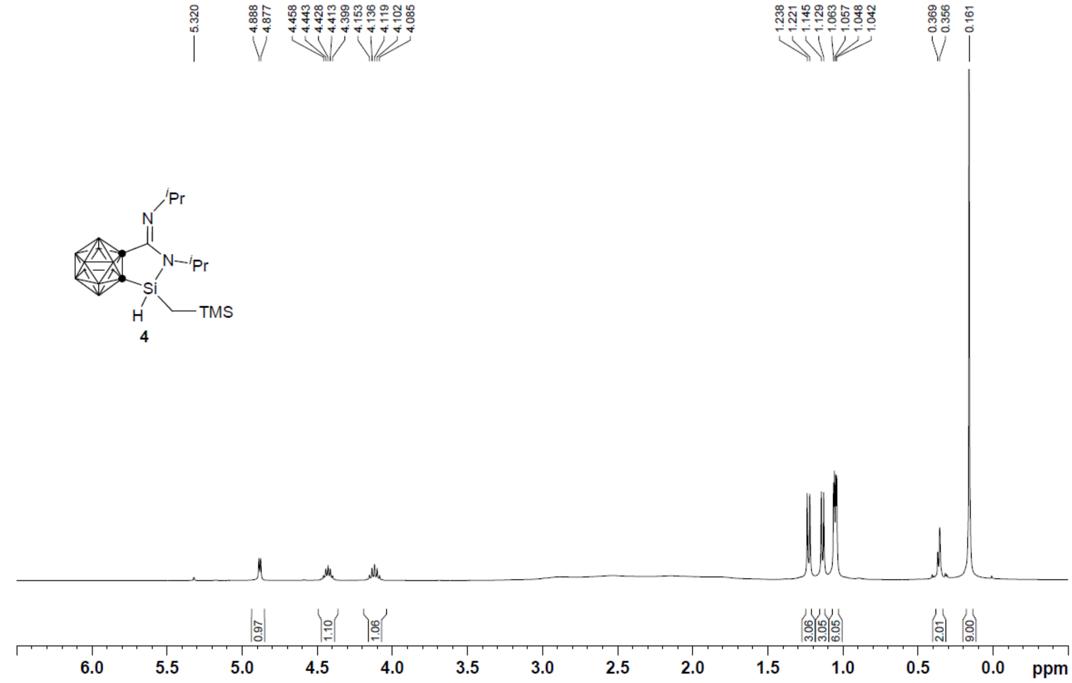

Fig. S14 ^{1}H NMR spectrum of compound **4** in CD_2Cl_2.

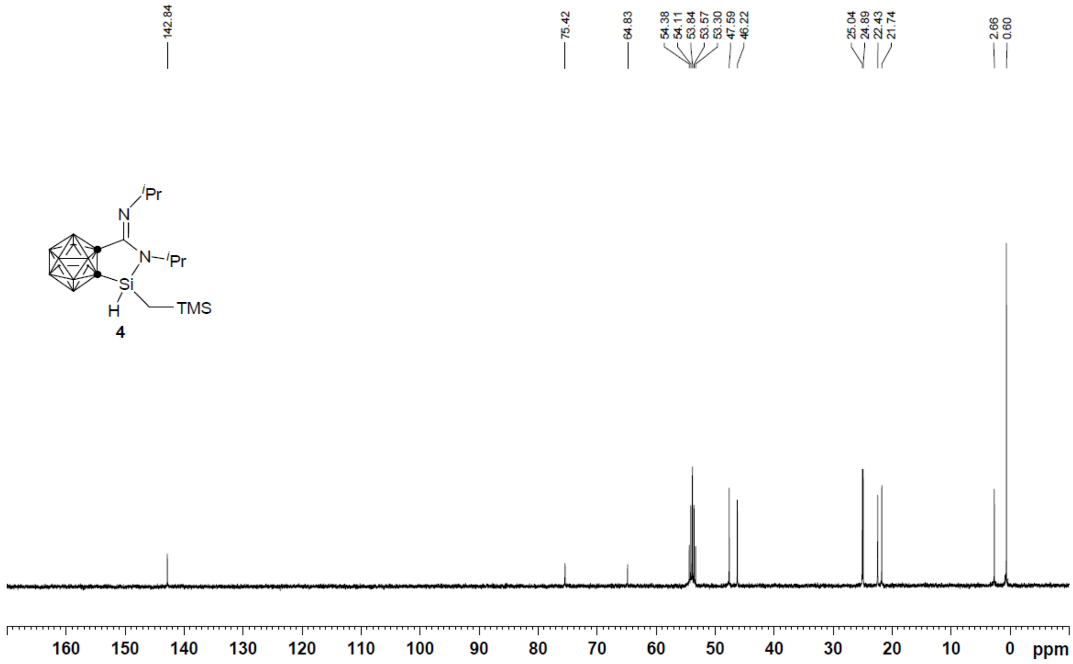

Fig. S15 ^{13}C NMR spectrum of compound **4** in CD_2Cl_2.

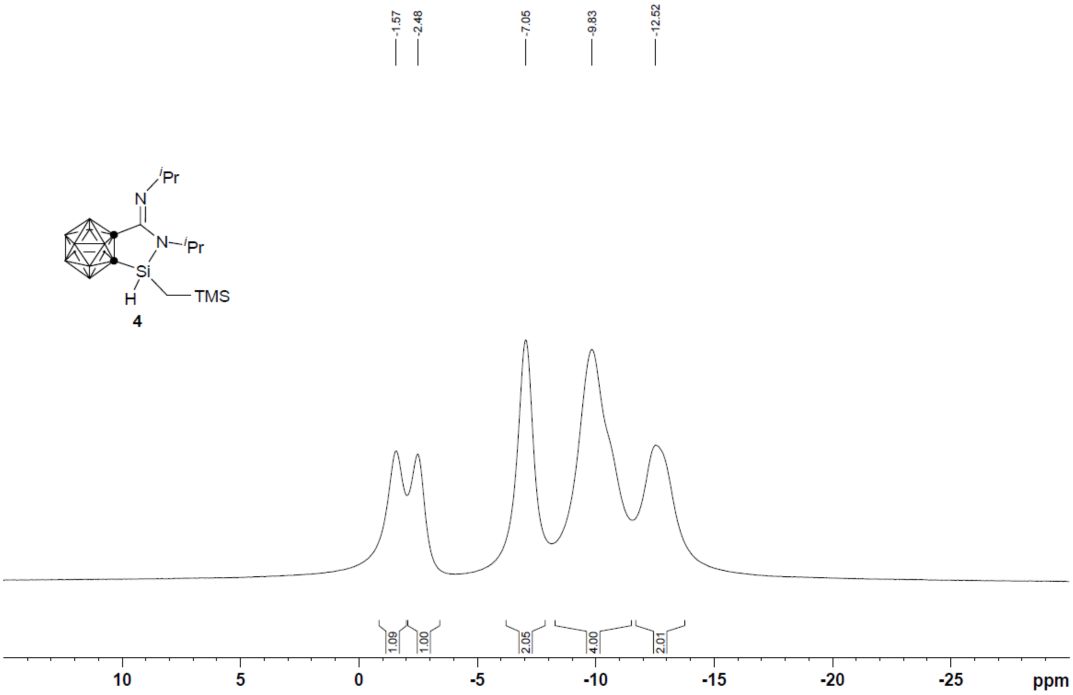

Fig. S16 $^{11}B\{^1H\}$ NMR spectrum of compound **4** in CD_2Cl_2.

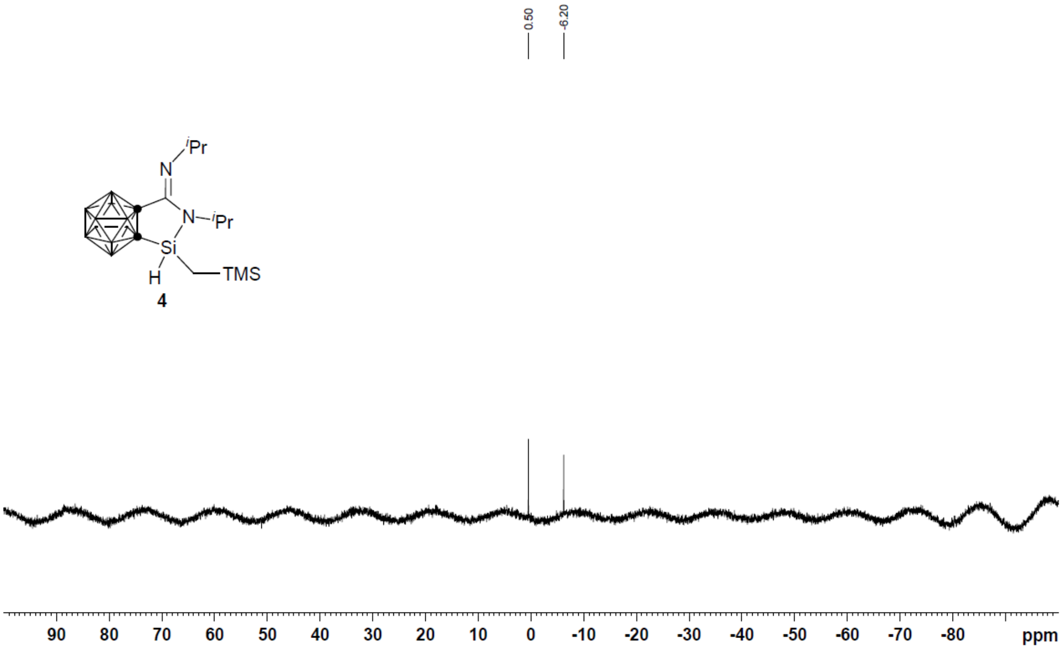

Fig. S17 ^{29}Si NMR spectrum of compound **4** in CD_2Cl_2.

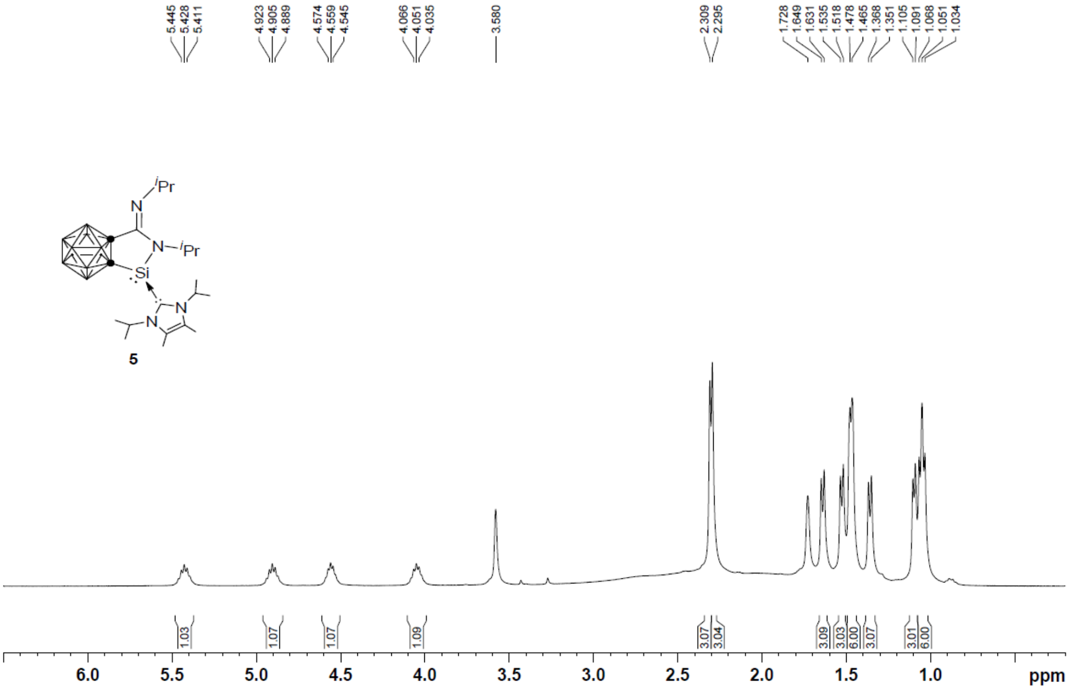

Fig. S18 ^{1}H NMR spectrum of compound **5** in THF-d_8.

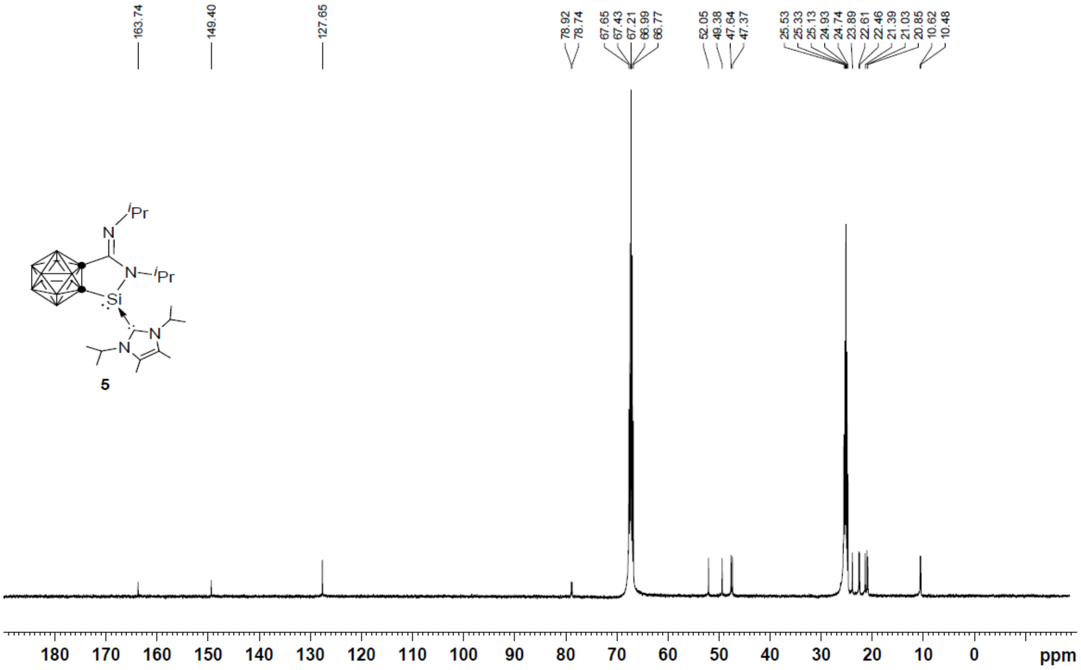

Fig. S19 ^{13}C NMR spectrum of compound **5** in THF-d_8.

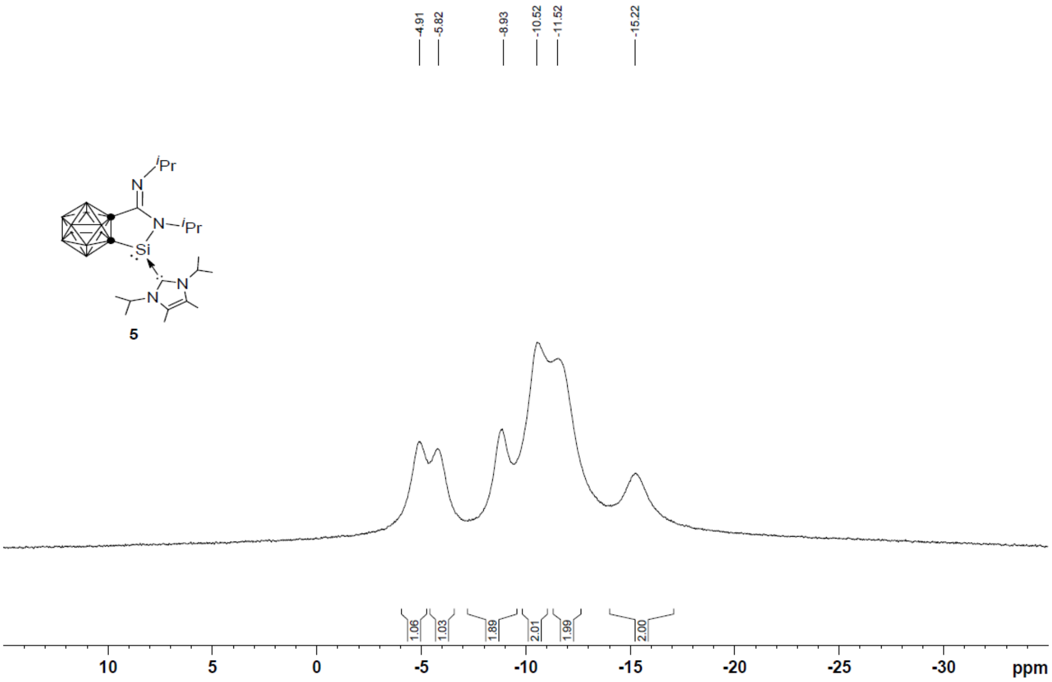

Fig. S20 $^{11}B\{^{1}H\}$ NMR spectrum of compound **5** in THF-d_8.

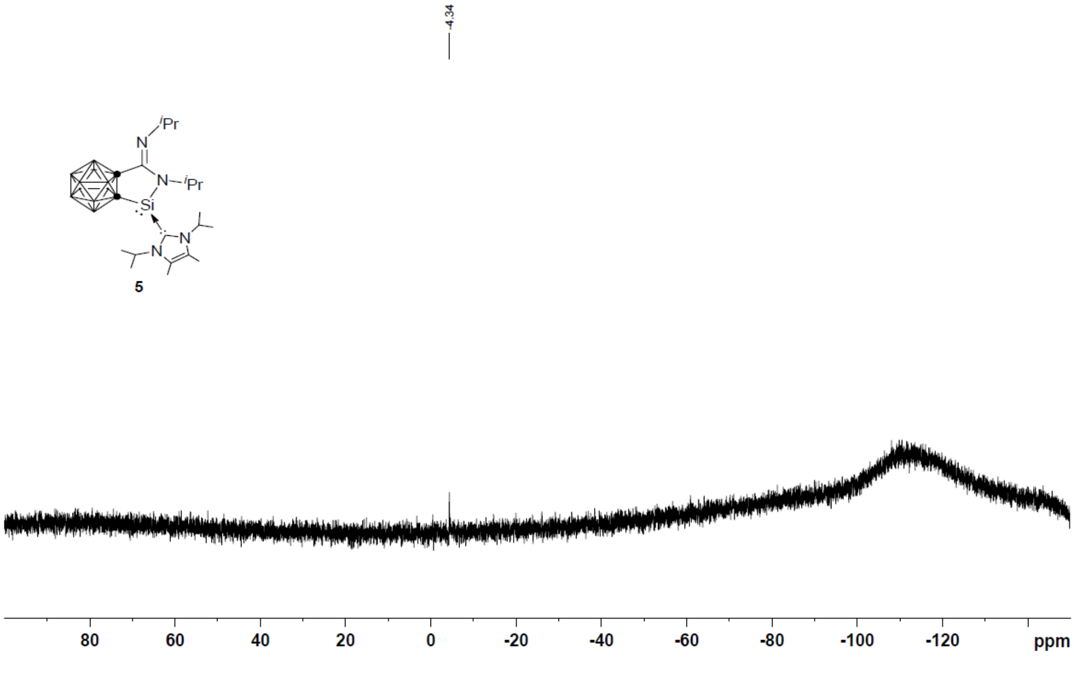

Fig. S21 ^{29}Si NMR spectrum of compound **5** in THF-d_8.

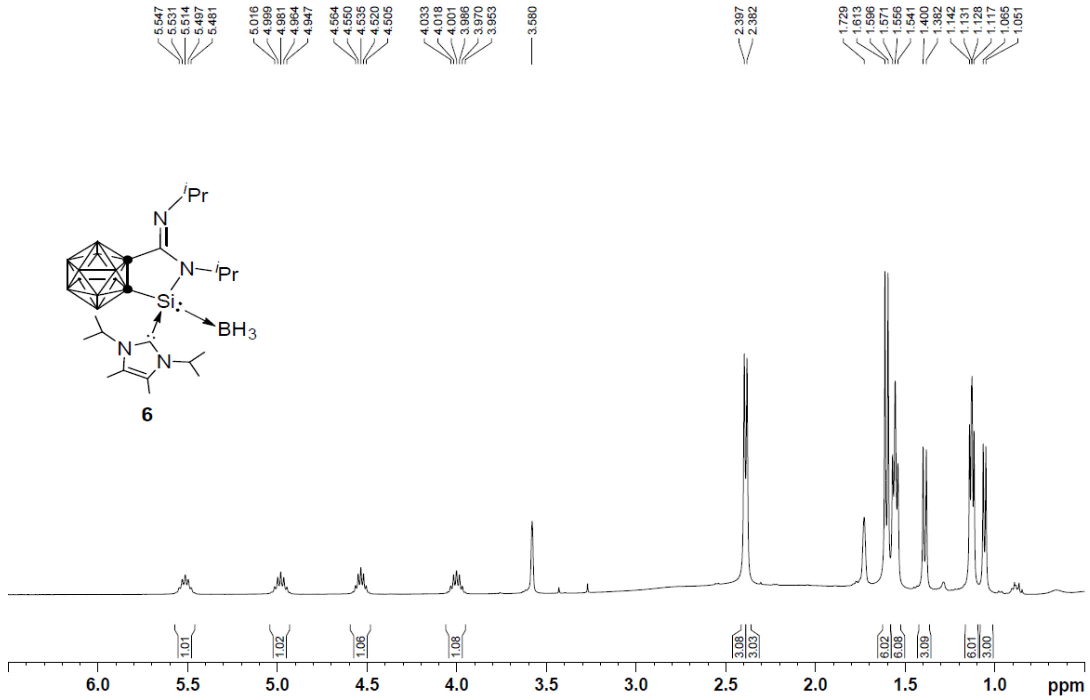

Fig. S22 ^{1}H NMR spectrum of compound **6** in THF-d_8.

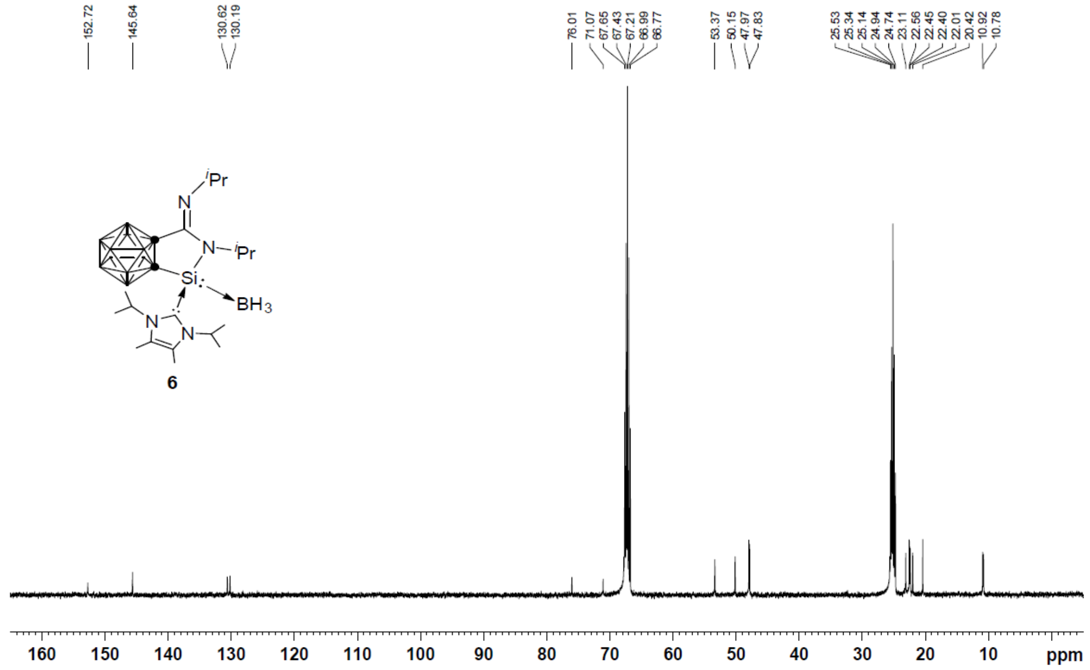

Fig. S23 ^{13}C NMR spectrum of compound **6** in THF-d_8.

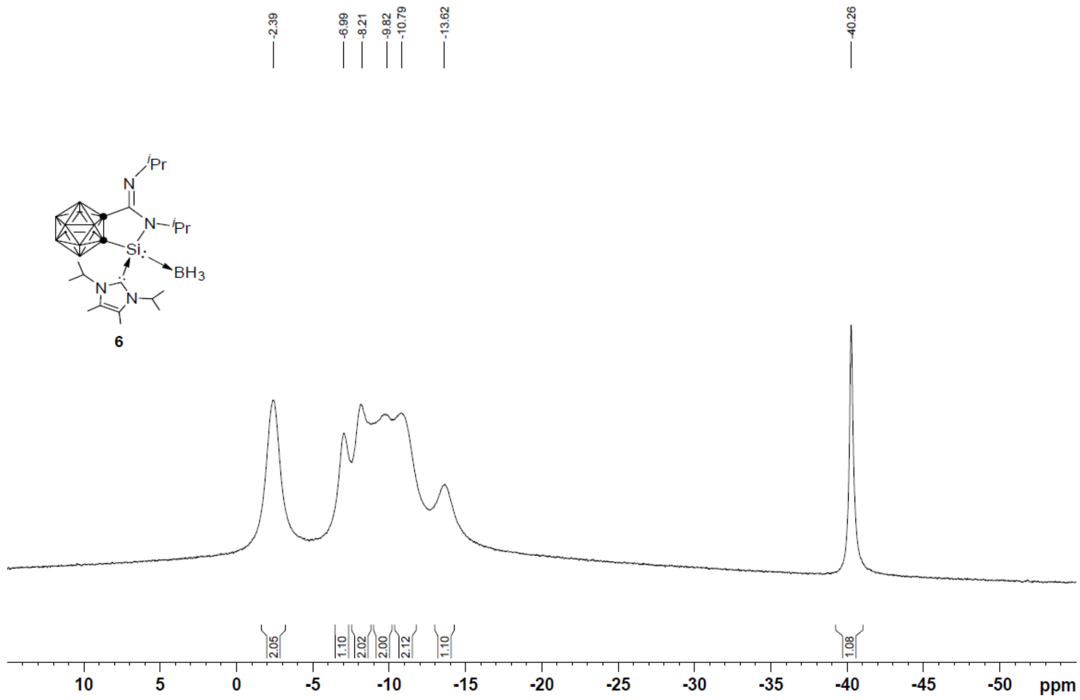

Fig. S24 $^{11}B\{^{1}H\}$ NMR spectrum of compound **6** in THF-d_8.

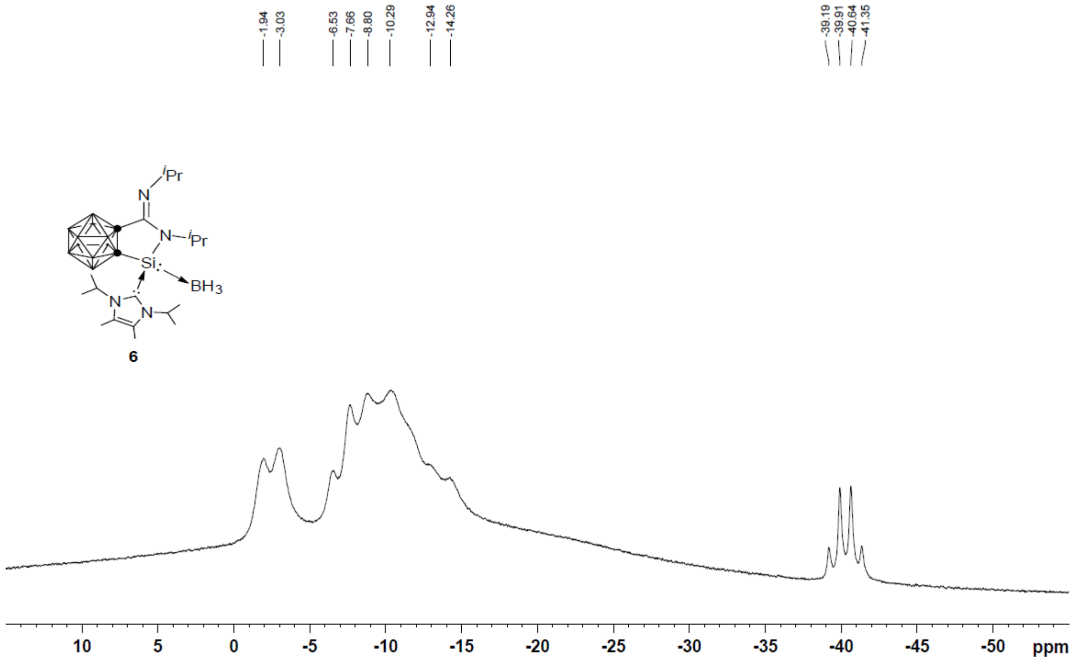

Fig. S25 ^{11}B NMR spectrum of compound **6** in THF-d_8.

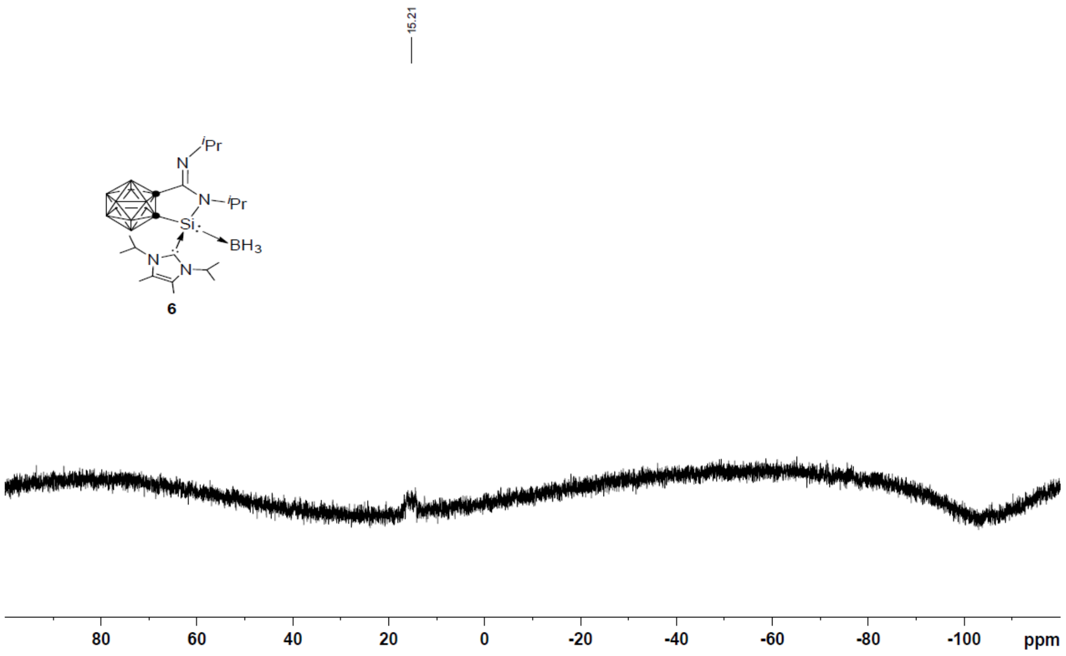

Fig. S26 ^{29}Si NMR spectrum of compound **6** in THF-d$_8$.

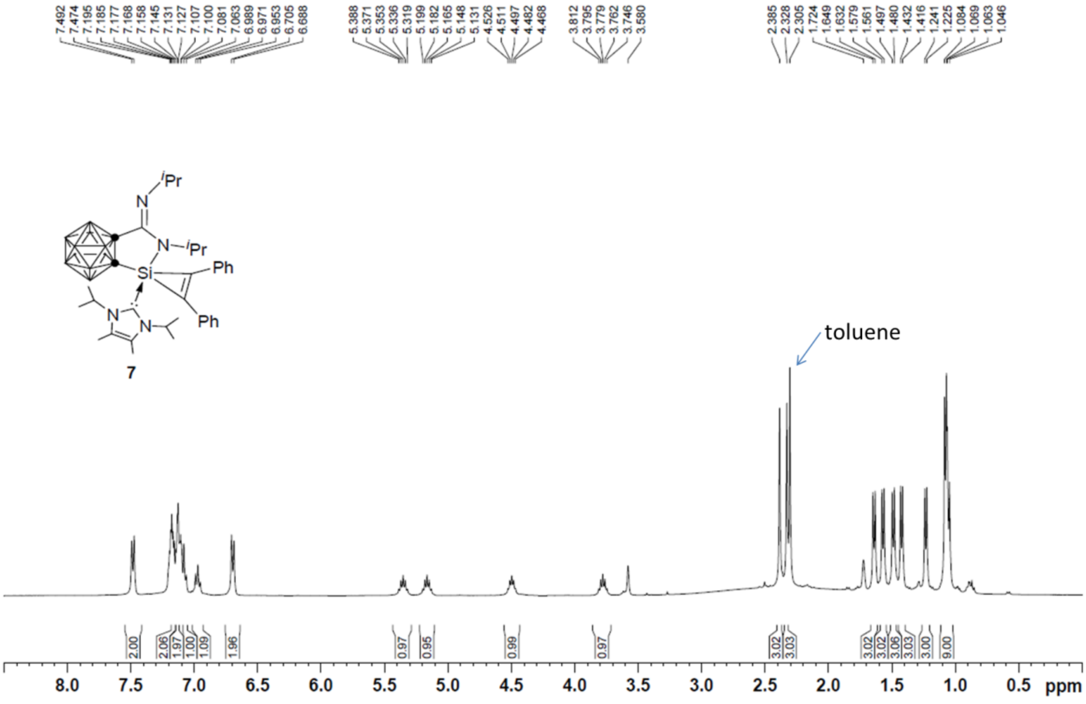

Fig. S27 ^{1}H NMR spectrum of compound **7** in THF-d$_8$.

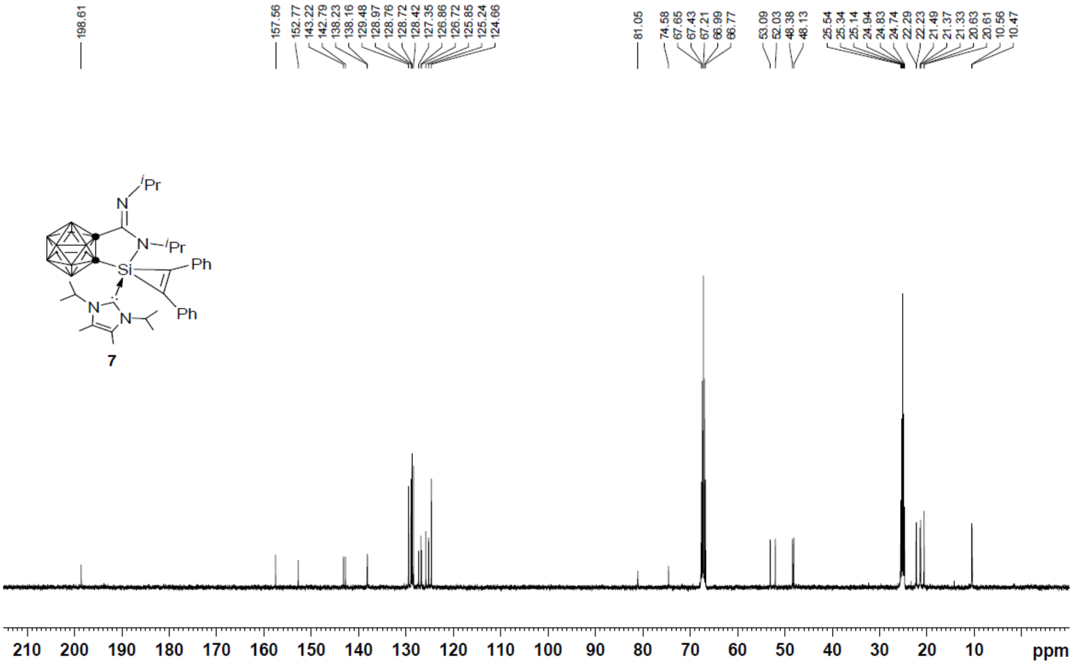

Fig. S28 ^{13}C NMR spectrum of compound **7** in THF-d$_8$.

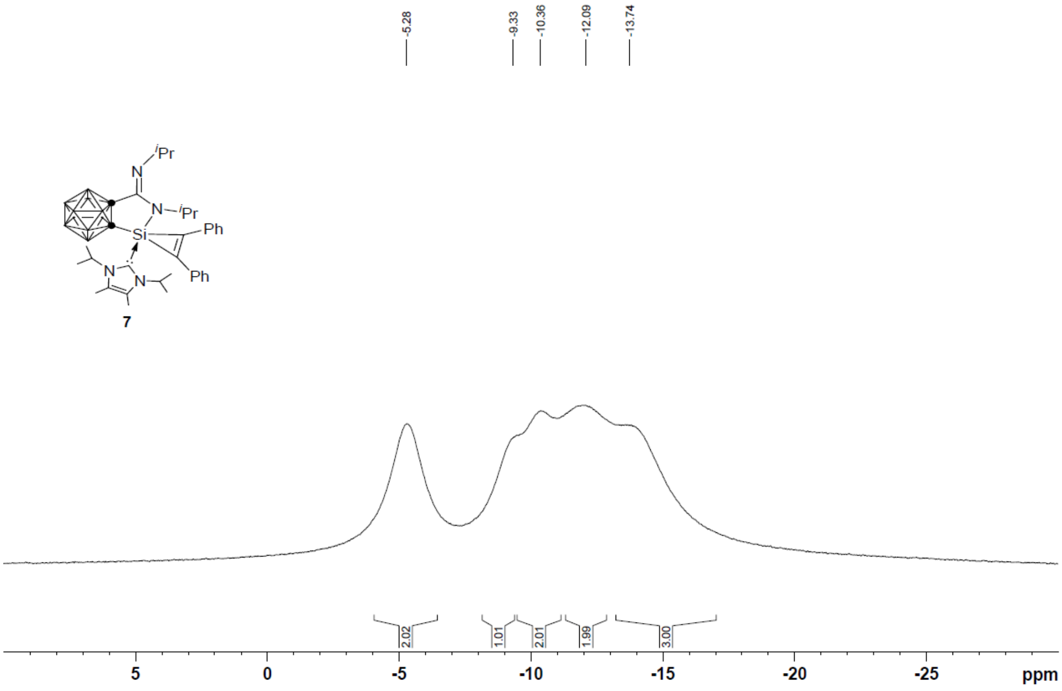

Fig. S29 ^{11}B{^{1}H} NMR spectrum of compound **7** in THF-d$_8$.

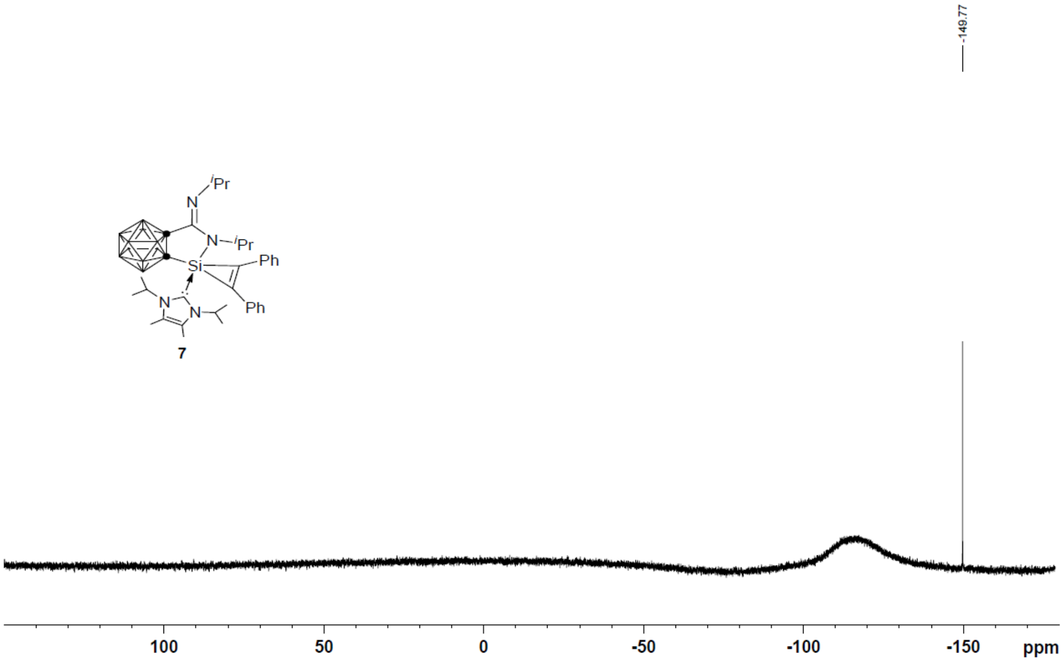

Fig. S30 ^{29}Si NMR spectrum of compound **7** in THF-d_8.

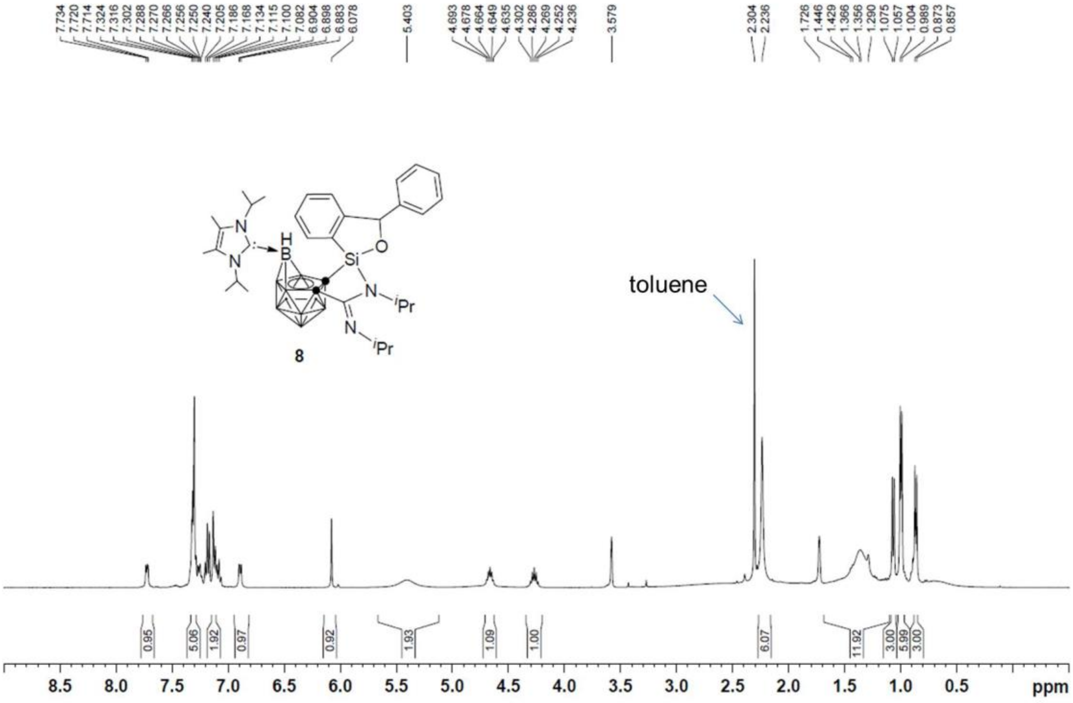

Fig. S31 ^{1}H NMR spectrum of compound **8** in THF-d_8.

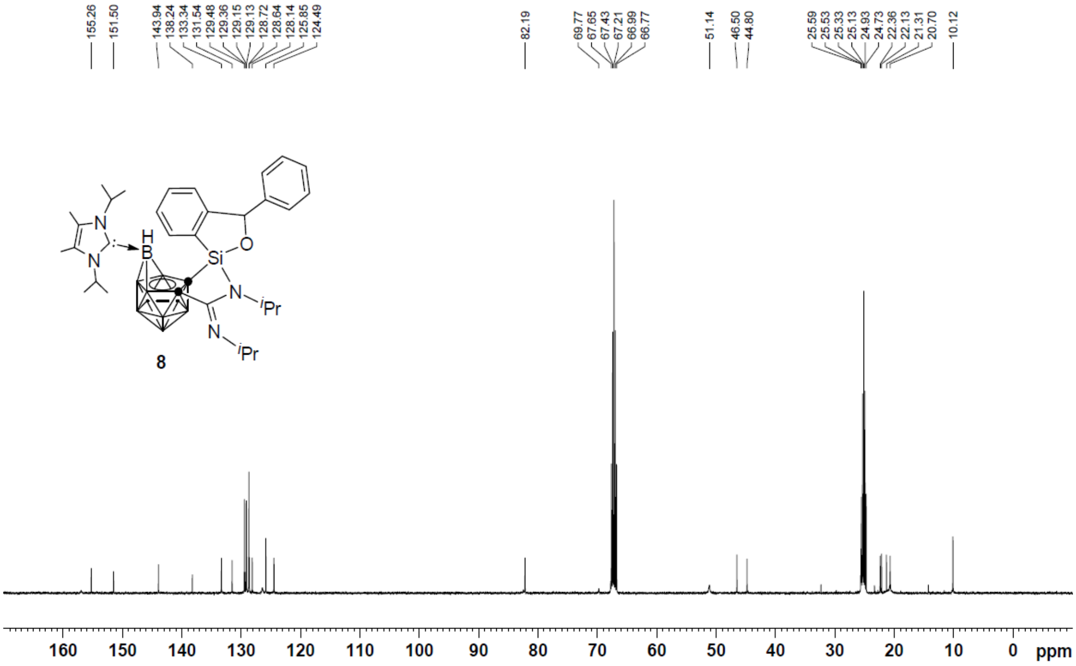

Fig. S32 ^{13}C NMR spectrum of compound **8** in THF-d$_8$.

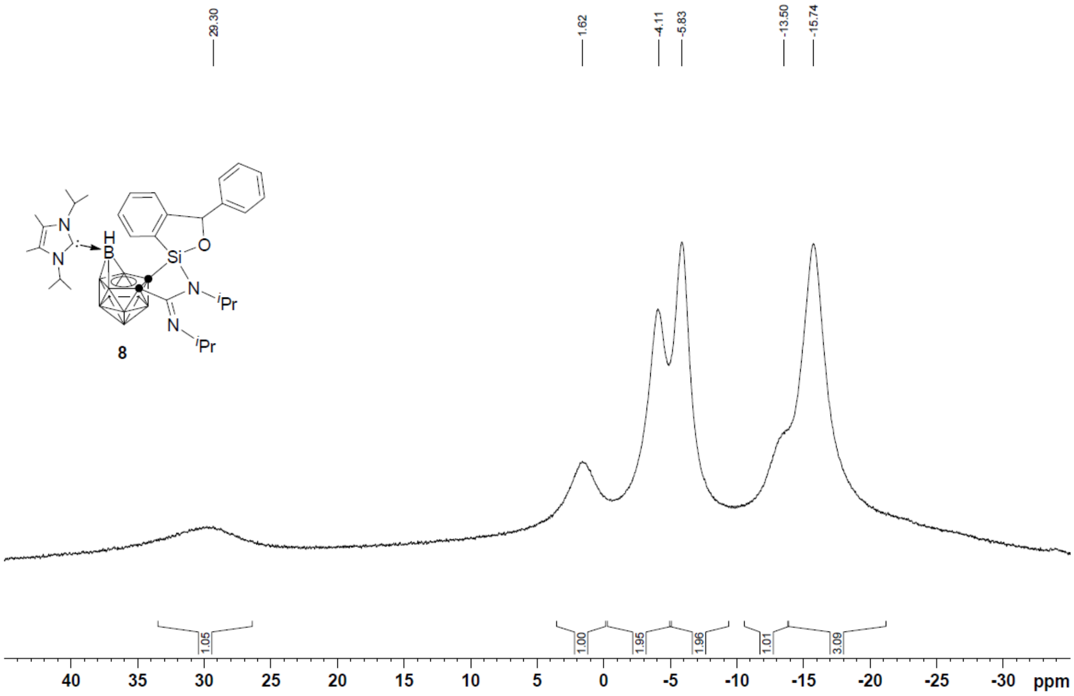

Fig. S33 ^{11}B{^{1}H} NMR spectrum of compound **8** in THF-d$_8$.

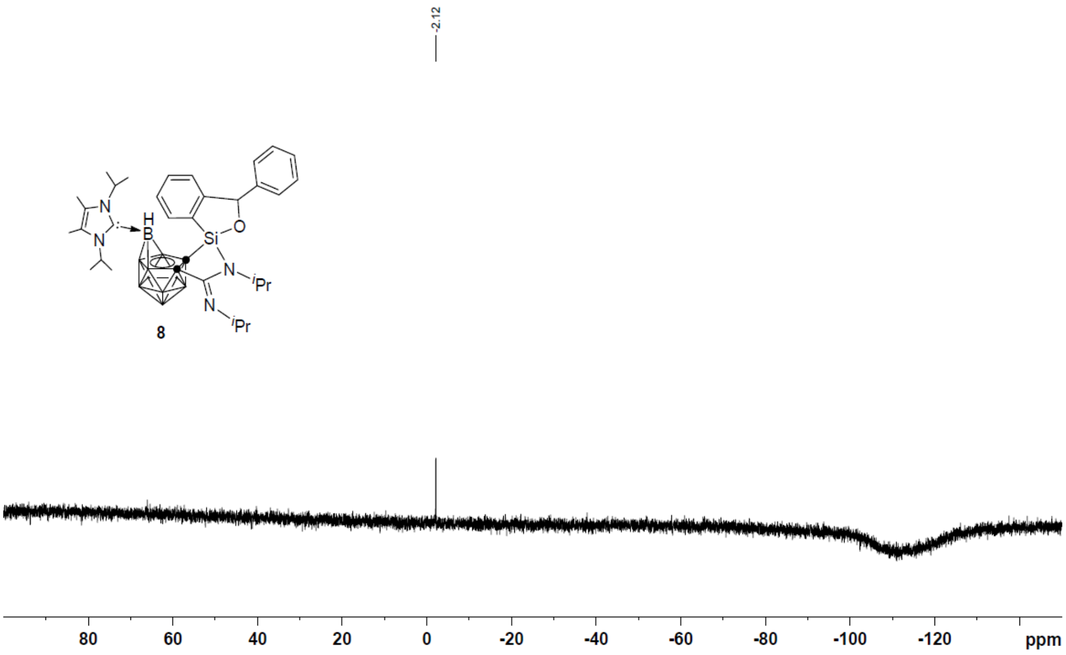

Fig. S34 ^{29}Si NMR spectrum of compound **8** in THF-d_8.