

Synthetic, Structural and Reactivity Studies of Boryl-Ethynyl Silylene

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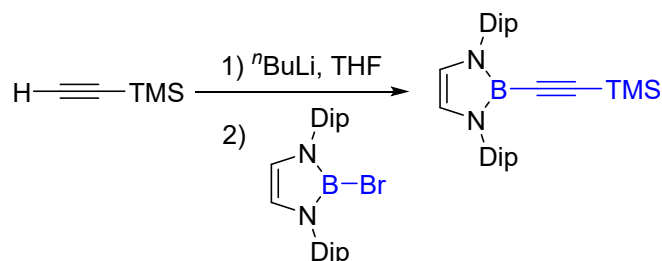
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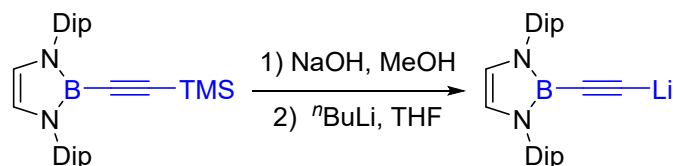
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1. Synthesis, physical and spectroscopic data

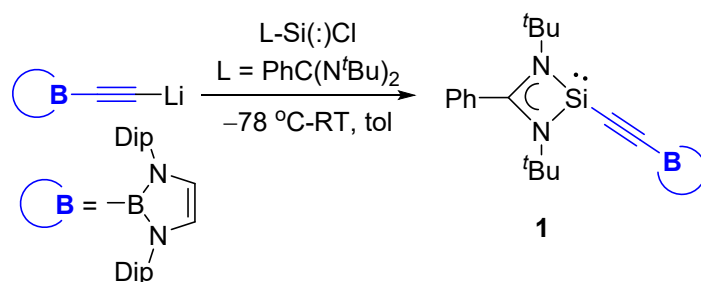
General considerations: All reactions were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH₂, and distilled under nitrogen. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. (HCDipN)₂B-Br (Dip = 2,6-*i*-Pr₂C₆H₃)^[S1], LGe(:)Cl [L = PhC(N^{*i*}Bu)₂]^[S2] and LSi(:)Cl^[S3] have been reported previously and were prepared according to modified literature procedures. ¹H, ¹³C, ¹¹B, ¹⁹F, and ²⁹Si NMR spectra were recorded on a Bruker Avance 500 MHz, spectrometers at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad. Compounds [(HCDipN)₂]B-CC-TMS, [(HCDipN)₂]B-CC-Li, **1**, **1'**, **2**, **3**, **4**, **5**, and **6** for HRMS were analyzed by positive mode electrospray ionization (ESI) using Agilent 6530 QTOF mass spectrometer. Coupling constants *J* are given in Hz. Melting points were measured with BUCHI Labortechnik AG.



Preparation of [(HCDipN)₂]B-CC-TMS: A solution of trimethylsilylacetylene (0.63 mL, 5.0 mmol) in THF (50 mL) was cooled to -78 °C and ⁿBuLi (2.0 mL, 2.5 M solution in hexane, 5.0 mmol) was then slowly added over a period of 5 min. Subsequently, the reaction mixture was warmed to room temperature and stirred for 1 h. Following this, a solution of (HCDipN)₂B-Br (2.37 g, 5.0 mmol) in THF (20 mL) was added to the Schlenk flask. After stirring the mixture overnight, the solvent was removed under vacuum, resulting in the formation of [(HCDipN)₂]B-CC-TMS (1.87 g, 80.2%). ¹H NMR (500 MHz, CDCl₃): δ = -0.11 (s, SiMe₃, 9H), 1.25 (d, CHMe₂, 12H, *J* = 4.5 Hz), 1.26 (d, CHMe₂, 12H, *J* = 5.0 Hz), 3.03 (sept, CHMe₂, 4H, *J* = 7.0 Hz), 6.26 (s, NCH, 2H), 7.24 (d, ArH, 4H, *J* = 8.0 Hz), 7.35 (t, ArH, 2H, *J* = 8.0 Hz); ¹³C NMR (125 MHz, CDCl₃): δ = 146.25, 138.44, 127.34, 123.22, 123.15, 119.19, 113.27, 28.44, 24.34, 24.07, -0.37 ppm; ¹¹B NMR (160 MHz, CDCl₃): δ = 18.41 ppm; HRMS (ESI): *m/z* calcd for C₃₁H₄₅BN₂Si: 484.3569 [(M+H)]⁺; found: 484.3562.

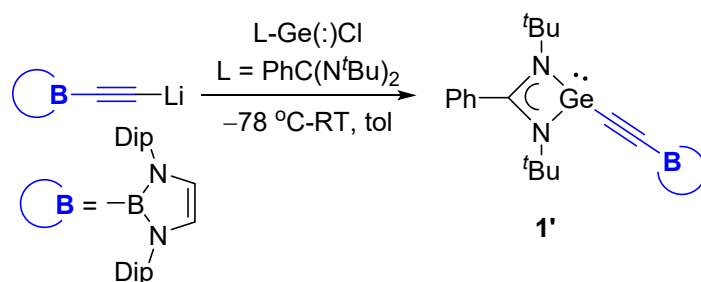


Preparation of [(HCDipN)₂]B-CC-Li: In a 500 mL round bottom flask equipped with a stir bar, [(HCDipN)₂]B-CC-TMS (3.54 g, 7.3 mmol), distilled THF (50 mL), 20% (w/v) NaOH solution (50 mL) and methanol (60 mL) were added. The solution was stirred vigorously for 2 h at room temperature, producing a clear solution. After stirring, water (80 mL) and chloroform (60 mL) were added to the flask producing a white precipitate. The precipitate was removed via filtration, and the filtrate was placed in a separatory funnel. The organic layer was collected and dried with sodium sulfate. After the solvent was removed under vacuum and THF (50 mL) was added, it was used directly for next step without further purification and ⁿBuLi (2.0 mL, 2.5 M solution in hexane, 5.0 mmol) was added dropwise at $-78\text{ }^{\circ}\text{C}$ via a syringe in 5 min. The reaction mixture was subsequently warmed to room temperature and stirred for 4 h. The solvent was evaporated to obtain a light yellow solid [(HCDipN)₂]B-CC-Li (1.44 g, 47%). ¹H NMR (500 MHz, C₆D₆): δ = 1.26 (d, CHMe₂, 12H, J = 6.5 Hz), 1.36-1.39 (m, CHMe₂, 12H; THF-CH₂, 8H), 3.33-3.37 (m, CHMe₂, 4H; THF-CH₂, 8H), 6.04 (s, NCH, 2H), 7.12-7.16 (m, ArH, 6H); ¹³C NMR (125 MHz, C₆D₆): δ = 146.46, 140.70, 127.96, 127.57, 126.45, 122.67, 118.05, 67.79, 28.25, 25.35, 24.29, 23.89 ppm; ¹¹B NMR (160 MHz, C₆D₆): δ = 19.13 ppm; HRMS (ESI): m/z calcd for C₂₈H₃₆BN₂Li: 417.3232 [(M+H)]⁺; found: 417.3220.

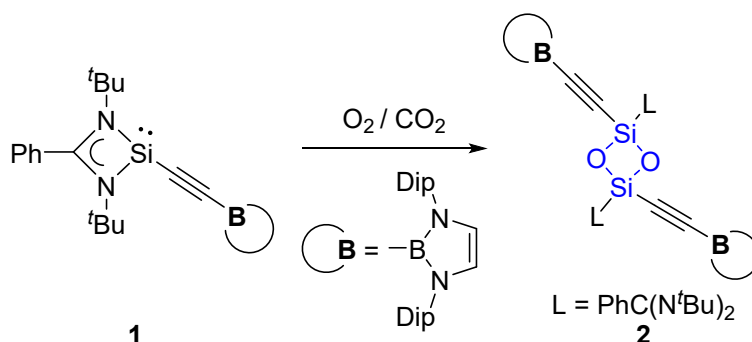


Preparation of 1: A mixture of [(HCDipN)₂]B-CC-Li (0.84 g, 2.0 mmol) and LSi(:)Cl (0.59 g, 2.0 mmol) was placed in a 100 mL Schlenk flask and toluene (50 mL) was added at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was then warmed to room temperature and stirred for 8 h to give an orange solution. The volatiles were removed under vacuum and the residue was extracted with hexane (30 mL). The filtrate was evaporated to obtain **1** (0.97 g, 72%) as a yellow powder. Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of **1** in hexane

at room temperature. ^1H NMR (500 MHz, C_6D_6): δ = 0.94 (s, ^tBuH , 18H), 1.29 (d, CHMe_2 , 12H, J = 7.0 Hz), 1.51 (d, CHMe_2 , 12H, J = 7.0 Hz), 3.34 (sept, CHMe_2 , 4H, J = 7.0 Hz), 6.15 (s, NCH , 2H), 6.84-7.03 (m, ArH , 5H), 7.19-7.24 (m, ArH , 6H); ^{13}C NMR (125 MHz, C_6D_6): δ = 160.66, 146.49, 139.38, 134.44, 129.70, 129.55, 128.60, 128.47, 128.35, 127.67, 123.43, 119.29, 53.12, 31.15, 28.84, 25.09, 24.22 ppm; ^{11}B NMR (160 MHz, C_6D_6): δ = 19.84 ppm; ^{29}Si NMR (99 MHz, C_6D_6): δ = 6.10 ppm; HRMS (ESI): m/z calcd for $\text{C}_{43}\text{H}_{59}\text{BN}_4\text{Si}$: 670.4711 [(M+H)]⁺; found: 670.4703.

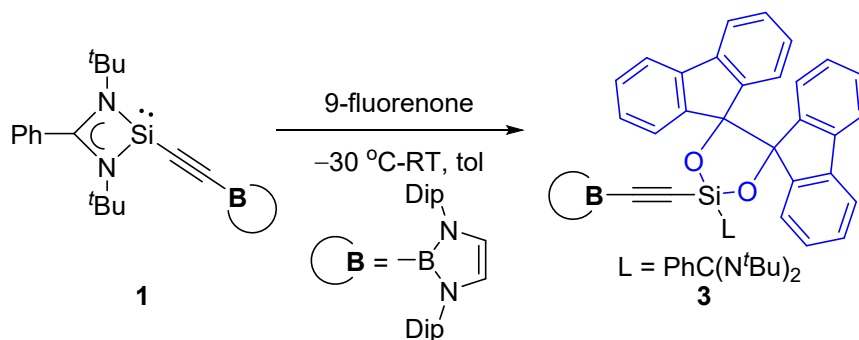


Preparation of 1': A mixture of [(HCDipN)₂]B-CC-Li (0.84 g, 2.0 mmol) and LGe(:)Cl (0.68 g, 2.0 mmol) was placed in a 100 mL Schlenk flask and toluene (50 mL) was added at -78 °C. The reaction mixture was then warmed to room temperature and stirred for 8 h to give an orange solution. The volatiles were removed under vacuum and the residue was extracted with hexane (30 mL). The filtrate was evaporated to obtain **1'** (0.95 g, 67%) as a yellow powder. Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of **1'** in hexane at room temperature. ^1H NMR (500 MHz, C_6D_6): δ = 0.80 (s, ^tBuH , 18H), 1.25 (d, CHMe_2 , 12H, J = 8.5 Hz), 1.48 (d, CHMe_2 , 12H, J = 8.5 Hz), 3.30 (sept, CHMe_2 , 4H, J = 8.5 Hz), 6.10 (s, NCH , 2H), 6.86-7.02 (m, ArH , 5H), 7.13-7.15 (m, ArH , 4H), 7.17-7.20 (m, ArH , 2H); ^{13}C NMR (125 MHz, C_6D_6): δ = 166.77, 146.47, 139.48, 136.34, 129.41, 129.23, 128.79, 127.74, 127.70, 127.67, 123.40, 119.22, 52.98, 31.41, 28.84, 25.17, 24.22 ppm; ^{11}B NMR (160 MHz, C_6D_6): δ = 18.73 ppm. HRMS (ESI): m/z calcd for $\text{C}_{43}\text{H}_{59}\text{BN}_4\text{Ge}$: 712.4184 [(M+H)]⁺; found: 712.4193.



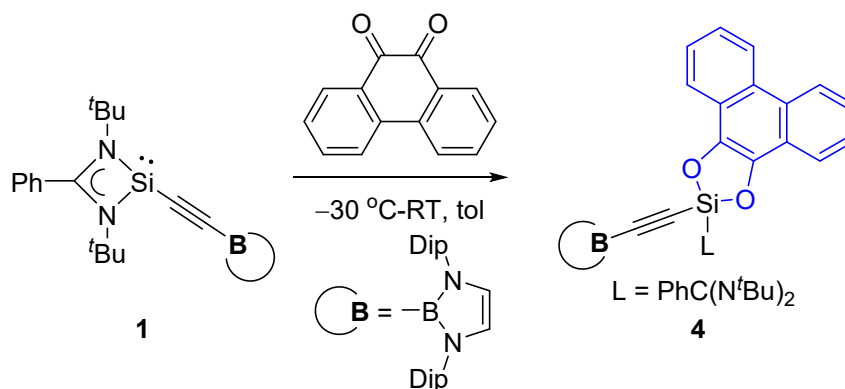
Preparation of 2: Method A: A solution of **1** (0.67 g, 1.0 mmol) in toluene (50 mL) was filled with dry O₂ at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. The volatiles were removed under vacuum to obtain **2** (0.38 g, 55%) as a colorless powder. Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of **2** in hexane at room temperature.

Method B: A solution of **1** (0.67 g, 1.0 mmol) in toluene (50 mL) was filled with dry CO₂ and stirred for 2 h. The volatiles were removed under vacuum to obtain **2** (0.30 g, 43%) as a colorless powder. ¹H NMR (500 MHz, C₆D₆): δ = 1.07 (s, ^tBuH, 36H), 1.29 (d, CHMe₂, 24H, *J* = 7.0 Hz), 1.51 (d, CHMe₂, 24H, *J* = 7.0 Hz), 3.31 (sept, CHMe₂, 8H, *J* = 7.0 Hz), 6.14 (s, NCH, 4H), 7.23-7.30 (m, ArH, 22H); ¹³C NMR (125 MHz, C₆D₆): δ = 170.49, 153.01, 146.56, 140.94, 139.50, 135.31, 128.47, 128.35, 128.01, 127.48, 123.27, 119.25, 53.78, 31.91, 28.85, 25.29, 24.43 ppm; ¹¹B NMR (160 MHz, C₆D₆): δ = 18.97 ppm; ²⁹Si NMR (99 MHz, C₆D₆): δ = -114.65 ppm; HRMS (ESI): *m/z* calcd for C₈₆H₁₁₈B₂N₈O₂Si₂: 1372.9322 [(M+H)]⁺; found: 1372.9315.

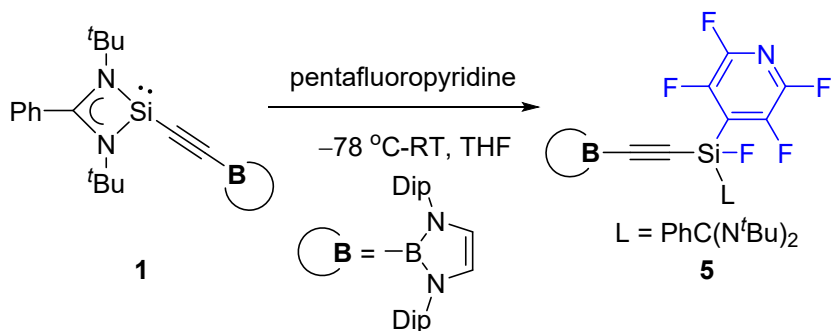


Preparation of 3: A mixture of **1** (0.67 g, 1.0 mmol) and 9-fluorenone (0.36 g, 2.0 mmol) was placed in a 100 mL Schlenk flask and toluene (50 mL) was added at -30 °C. The reaction mixture was warmed to room temperature and stirred for 8 h. The volatiles were removed in vacuo and the residue was washed with hexane (10 mL) to give a colorless powder **3** (0.36 g, 35%). Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of **3** in toluene at room temperature. ¹H NMR (500 MHz, C₆D₆): δ = 1.02 (s, ^tBuH, 18H), 1.31 (d, CHMe₂, 12H, *J* = 8.5 Hz), 1.54 (d, CHMe₂, 12H, *J* = 8.5 Hz), 3.42 (sept, CHMe₂, 4H, *J* = 8.5 Hz), 6.14 (s, NCH, 2H), 6.82 (t, ArH, 2H, *J* = 9.0 Hz), 6.94-7.10 (m, ArH, 13H), 7.24-7.31 (m, ArH, 7H), 7.44 (d, ArH, 1H, *J* = 8.5 Hz), 7.87 (d, ArH, 2H, *J* = 9.5 Hz), 8.08 (d, ArH, 2H, *J* = 9.5 Hz); ¹³C NMR (125 MHz, C₆D₆): δ = 173.16, 148.57, 146.49, 141.18, 140.35, 139.55, 134.23, 129.78, 129.38,

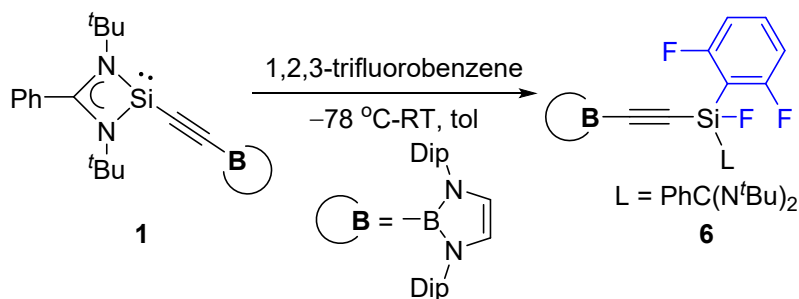
129.33, 128.62, 128.57, 127.46, 126.77, 126.48, 125.29, 123.73, 120.05, 119.67, 119.26, 91.30, 54.89, 31.89, 28.97, 25.32, 24.37 ppm; ^{11}B NMR (160 MHz, C_6D_6): $\delta = 18.59$ ppm; ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -102.65$ ppm; HRMS (ESI): m/z calcd for $\text{C}_{69}\text{H}_{75}\text{BN}_4\text{O}_2\text{Si}$: 1030.5869 $[(\text{M}+\text{H})]^+$; found: 1030.5865.



Preparation of 4: A mixture of **1** (0.67 g, 1.0 mmol) and 9,10-phenanthrenequinone (0.21 g, 1.0 mmol) was placed in a 100 mL Schlenk flask and toluene (50 mL) was added at -30 °C. The reaction mixture was then warmed to room temperature and stirred for 8 h. The volatiles were removed under vacuum and the residue was extracted with hexane (30 mL). The filtrate was evaporated to obtain **4** (0.74 g, 84%) as a colorless powder. Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of **4** in toluene at -20 °C. ^1H NMR (500 MHz, C_6D_6): $\delta = 1.15$ (s, ^tBuH , 18H), 1.19 (d, CHMe_2 , 12H, $J = 9.0$ Hz), 1.33 (d, CHMe_2 , 12H, $J = 9.0$ Hz), 3.17 (sept, CHMe_2 , 4H, $J = 8.5$ Hz), 6.07 (s, NCH , 2H), 6.75-6.82 (m, ArH , 2H), 6.90-6.92 (m, ArH , 2H), 6.99-7.11 (m, ArH , 7H), 7.38-7.43 (m, ArH , 2H), 7.55-7.59 (m, ArH , 2H), 8.35 (dd, ArH , 2H, $J = 10.0$ Hz), 8.60 (d, ArH , 2H, $J = 10.0$ Hz); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 173.54, 146.20, 139.15, 138.60, 133.17, 129.80, 128.40, 128.35, 128.16, 127.97, 127.78, 127.55, 126.63, 126.21, 125.69, 123.42, 123.32, 121.32, 119.40, 54.76, 31.79, 28.73, 24.70, 24.21$ ppm; ^{11}B NMR (160 MHz, C_6D_6): $\delta = 18.80$ ppm; ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -103.85$ ppm; HRMS (ESI): m/z calcd for $\text{C}_{57}\text{H}_{67}\text{BN}_4\text{O}_2\text{Si}$: 878.5235 $[(\text{M}+\text{H})]^+$; found: 878.5229.



Preparation of 5: To a solution of **1** (0.67 g, 1.0 mmol) in THF (50 mL) was slowly added pentafluoropyridine (0.17 g, 1.0 mmol) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was warmed to room temperature and stirred for 16 h. The volatiles were removed under vacuum and the residue was washed with hexane (10 mL) to give **5** as a colorless powder (0.60 g, 69%). Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of **5** in benzene at room temperature. ^1H NMR (500 MHz, C_6D_6): δ = 0.78 (br, ^tBuH , 18H), 1.25 (d, CHMe_2 , 6H, J = 5.5 Hz), 1.26 (d, CHMe_2 , 6H, J = 5.0 Hz), 1.45 (d, CHMe_2 , 6H, J = 7.0 Hz), 1.52 (d, CHMe_2 , 6H, J = 7.0 Hz), 3.23-3.28 (m, CHMe_2 , 4H), 6.12 (s, NCH , 2H), 6.93-6.97 (m, ArH , 3H), 7.07-7.09 (m, ArH , 2H), 7.14-7.19 (m, ArH , 6H). ^{13}C NMR (125 MHz, C_6D_6): δ = 172.88, 146.29, 146.24, 138.74, 137.31, 133.21, 130.01, 129.33, 128.57, 128.48, 128.35, 128.01, 127.96, 125.70, 123.61, 123.51, 119.80, 54.88, 31.25, 28.91, 28.87, 24.82, 24.69, 24.41, 24.29 ppm; ^{11}B NMR (160 MHz, C_6D_6): δ = 19.87 ppm; ^{29}Si NMR (99 MHz, C_6D_6): δ = -112.48 ($^1J(^{29}\text{Si}-^{19}\text{F})$ = 313.83 Hz) ppm; ^{19}F NMR (471 MHz, C_6D_6): δ = -81.08 (s, Si-F), -93.38 (br, $o\text{-F}$), -129.73 (br, $m\text{-F}$), -136.45 (br, $m\text{-F}$) ppm; HRMS (ESI): m/z calcd for $\text{C}_{48}\text{H}_{59}\text{BF}_5\text{N}_5\text{O}_2\text{Si}$: 871.4560 [($\text{M}+\text{H}$) $^+$]; found: 871.4556.



Preparation of 6: To a solution of **1** (0.67 g, 1.0 mmol) in toluene (20 mL) was added 1,2,3-trifluorobenzene (0.1 mL, 1.0 mmol) at room temperature. The reaction mixture was heated at $70\text{ }^{\circ}\text{C}$ and stirred for 2 days to give a pale yellow solution. The volatiles were removed in vacuo and

the residue was washed with hexane (10 mL) to give a colorless powder **6** (0.28 g, 35%). Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of **6** in toluene at $-20\text{ }^{\circ}\text{C}$. ^1H NMR (500 MHz, C_6D_6): $\delta = 0.73$ (br, $t\text{-BuH}$, 9H), 1.09 (br, $t\text{-BuH}$, 9H), 1.29 (d, CHMe_2 , 6H, $J = 5.0$ Hz), 1.31 (d, CHMe_2 , 6H, $J = 5.0$ Hz), 1.55 (d, CHMe_2 , 6H, $J = 7.0$ Hz), 1.60 (d, CHMe_2 , 6H, $J = 7.0$ Hz), 3.35 (sept, CHMe_2 , 4H, $J = 7.0$ Hz), 6.17 (s, NCH , 2H), 6.51 (t, ArH , 2H, $J = 8.0$ Hz), 6.64-6.70 (m, ArH , 1H), 6.94-7.02 (m, ArH , 3H), 7.19-7.24 (m, ArH , 8H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 171.08, 146.40, 146.36, 139.08, 134.49, 130.41, 130.33, 130.25, 129.61, 128.89, 128.35, 128.15, 127.96, 127.69, 123.46, 119.60, 111.28, 54.48, 31.98, 30.98, 28.93, 28.90, 24.95, 24.81, 24.49, 24.38$ ppm; ^{11}B NMR (160 MHz, C_6D_6): $\delta = 18.42$ ppm; ^{29}Si NMR (99 MHz, C_6D_6): $\delta = -108.30$ ($^1J(^{29}\text{Si}-^{19}\text{F}) = 314.82$ Hz) ppm; ^{19}F NMR (471 MHz, C_6D_6): $\delta = -82.60$ (s, Si-F), -95.83 (br, $o\text{-F}$), -103.56 (br, $o\text{-F}$) ppm; HRMS (ESI): m/z calcd for $\text{C}_{49}\text{H}_{62}\text{BF}_3\text{N}_4\text{Si}$: 802.4898 [(M+H)] $^+$; found: 802.4904.

2. Crystal Structure Determination of Compounds **1**, **1'**, **2**, **3**, **4**, **5**, and **6**

X-ray data collection and structural refinement. Intensity data for compounds **1**, **1'**, **2**, **3**, **4**, **5**, and **6** were collected using a Bruker D8 Venture diffractometer, while the crystals were measured at 170 K. Using Olex2^[S4], the structure was solved with the SHELXT^[S5] structure solution program using Intrinsic Phasing and refined with the SHELXL^[S6] refinement package using Least Squares minimisation. All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC: 2334108-2334113 and 2350865 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via http://www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Summary of Data Collection and Structure Refinement of **1**, **1'**, and **2**.

	1	1'	2
Formula	C ₄₃ H ₅₉ BN ₄ Si	C ₄₃ H ₅₉ BGeN ₄	C ₈₆ H ₁₁₈ B ₂ N ₈ O ₂ Si ₂
Fw	670.84	715.34	1373.68
cryst system	triclinic	triclinic	monoclinic
space group	P-1	P-1	P2 ₁ /n
Size (mm ³)	0.4 × 0.35 × 0.26	0.47 × 0.34 × 0.26	0.16 × 0.08 × 0.06
T, K	170.00	170.00	170.00
<i>a</i> , Å	9.4740(4)	9.510(2)	13.5861(4)
<i>b</i> , Å	13.9943(5)	13.991(3)	20.8352(5)
<i>c</i> , Å	16.2737(6)	16.363(3)	14.9701(5)
α , deg	90.635(2)	90.448(8)	90
β , deg	90.829(2)	90.819(9)	100.0350(10)
γ , deg	106.097(2)	105.882(8)	90
V, Å ³	2072.53(14)	2093.6(8)	4172.7(2)
Z	2	2	2
ρ_{calc} g·cm ⁻³	1.075	1.135	1.093

μ , mm ⁻¹	0.089	0.764	0.092
Refl collected	43950	41024	48004
T_{min}/T_{max}	0.721/0.746	0.481/0.746	0.701/0.746
[R _{int}]	0.0332	0.0800	0.0612
R [I>2sigma(I)]	0.0456	0.0606	0.0453
R _w [I>2sigma(I)]	0.1159	0.1624	0.1024
GOF	1.021	1.051	1.030
Largest diff peak/hole[e·Å ⁻³]	0.27/-0.36	1.22/-1.18	0.20/-0.24

Table S2. Summary of Data Collection and Structure Refinement of **3** and **4**.

	3·(Tol)	4
Formula	C ₇₆ H ₈₃ BN ₄ O ₂ Si	C ₅₇ H ₆₇ BN ₄ O ₂ Si
Fw	1123.36	879.04
cryst system	monoclinic	monoclinic
space group	Cc	P2 ₁ /n
Size (mm ³)	0.36 × 0.25 × 0.18	0.16 × 0.06 × 0.04
T, K	170.00	170.00
<i>a</i> , Å	11.7650(3)	12.9587(3)
<i>b</i> , Å	23.8074(5)	24.1745(5)
<i>c</i> , Å	23.7692(6)	24.1745(5)
α , deg	90	90
β , deg	97.7210(10)	103.5590(10)
γ , deg	90	90
V, Å ³	6597.3(3)	5127.2(2)
Z	4	4
ρ_{calc} g·cm ⁻³	1.131	1.139
μ , mm ⁻¹	0.084	0.090

Refl collected	37753	49442
T_{min}/T_{max}	0.667/0.746	0.709/0.746
[R _{int}]	0.0446	0.0645
R [I>2sigma(I)]	0.0519	0.0468
R _w [I>2sigma(I)]	0.1261	0.0979
GOF	1.041	1.024
Largest diff peak/hole[e·Å ⁻³]	0.36/-0.45	0.18/-0.34

Table S3. Summary of Data Collection and Structure Refinement of **5** and **6**.

	5	6·(Hex)
Formula	C ₄₈ H ₅₉ BF ₅ N ₅ Si	C ₅₅ H ₇₆ BF ₃ N ₄ Si
Fw	839.90	889.09
cryst system	monoclinic	triclinic
space group	P2 ₁ /c	P-1
Size (mm ³)	0.35 × 0.08 × 0.03	0.12 × 0.06 × 0.03
T, K	170.00	170.00
a, Å	19.2831(16)	10.3023(9)
b, Å	10.4515(8)	12.3860(11)
c, Å	24.172(2)	21.4630(19)
α, deg	90	89.209(3)
β, deg	103.424(3)	85.161(3)
γ, deg	90	84.249(3)
V, Å ³	4738.4(7)	2715.2(4)
Z	4	2
ρ_{calc} g·cm ⁻³	1.177	1.087
μ, mm ⁻¹	0.106	0.091
Refl collected	66249	52245

T_{min}/T_{max}	0.682/0.746	0.652/0.746
[R _{int}]	0.1101	0.0921
R [I>2sigma(I)]	0.0897	0.1055
R _w [I>2sigma(I)]	0.2304	0.2739
GOF	1.026	1.024
Largest diff peak/hole[e·Å ⁻³]	1.91/-0.59	1.90/-0.64

3. UV-Vis spectrum of 1 and 1'

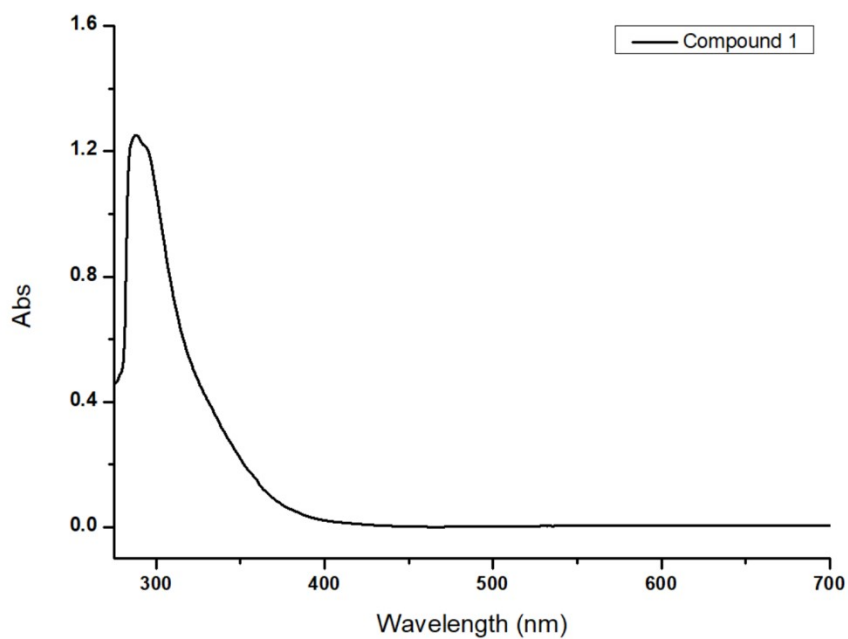


Figure S1. UV-Vis absorption spectrum of compound **1** (10^{-5} M) in toluene (Ultraviolet spectrum was recorded on a Perkin Elmer Lambda 750 UV/Vis spectrophotometer).

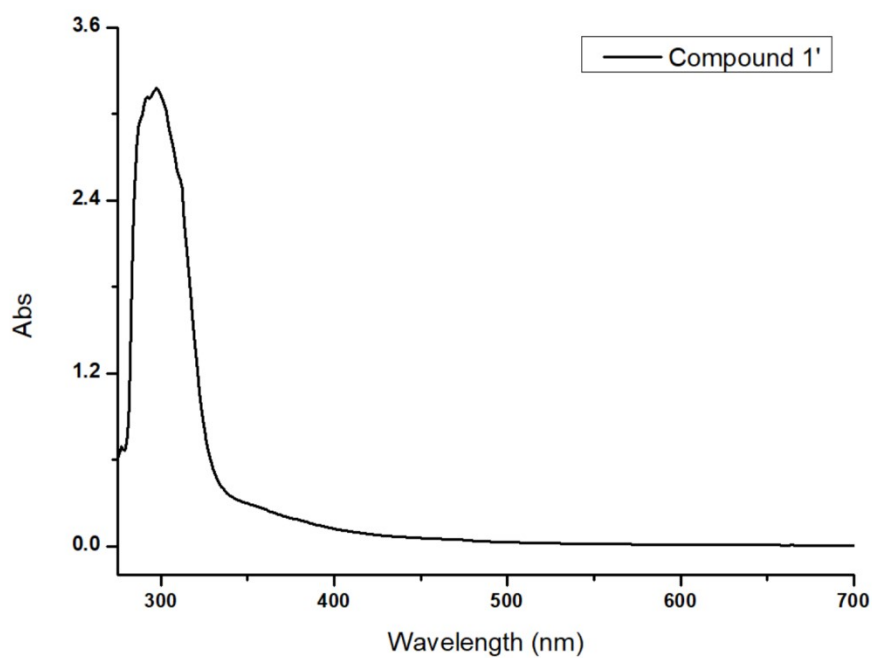


Figure S2. UV-Vis absorption spectrum of compound **1'** (10^{-5} M) in toluene (Ultraviolet spectrum was recorded on a Perkin Elmer Lambda 750 UV/Vis spectrophotometer).

4. Theoretical calculations

Gaussian 09 (Revision D.01) was used for all density functional theory (DFT) calculations.^[S7] Geometry optimization, frequency calculations, and Natural bond order (NBO) analysis on **1**, **1a**, and **1b** were performed at the M06-2X/6-31G(d,p) level of theory. Atomic charges of **1**, **1a**, and **1b** were determined according to the Hirshfeld charge analysis by Multiwfn 3.8 (dev) program.^[S8-S10]

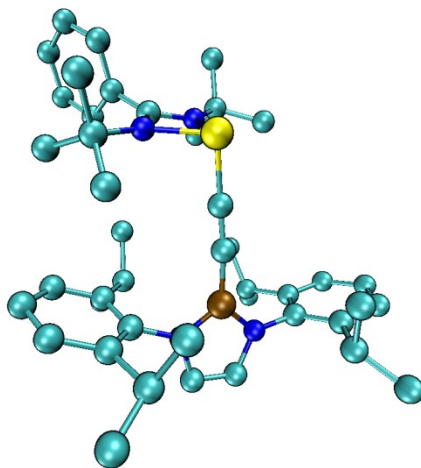


Figure S3. Calculated optimized structures for **1** at M06-2X/6-31G(d,p) level of theory.

Table S4. Optimized structures of **1** (atom, x-, y-, z- positions in Å)

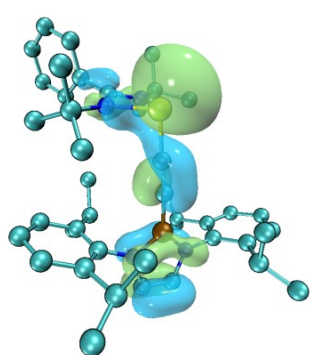
Si	1.46351312	0.79172086	-2.36026574
N	-2.15177579	-1.73805581	0.90597900
N	-3.40018597	0.12427053	0.53920856
N	2.42343381	1.82813297	-1.09925379
N	2.72977927	-0.25877195	-1.42632230
C	-0.00988146	0.38176956	-1.26896912
C	-1.00851003	0.03317279	-0.65351090
C	-3.33714900	-1.83195180	1.63640476
H	-3.55066323	-2.69305202	2.25379492
C	-4.08346731	-0.72460413	1.41338007
H	-5.05790154	-0.46148348	1.79959222
C	-1.07404595	-2.66184233	1.03845826

C	-1.10083034	-3.85938556	0.30080552
C	-0.04059745	-4.75241451	0.45485765
H	-0.03818275	-5.68473962	-0.10140252
C	1.02155655	-4.46050499	1.30545833
H	1.83967763	-5.16662152	1.41437784
C	1.04011697	-3.26293883	2.00751189
H	1.87759092	-3.03854675	2.66419853
C	-0.00304462	-2.33943430	1.88701435
C	-2.20829413	-4.10924807	-0.70801420
H	-3.11776632	-3.62534554	-0.33609880
C	-1.83264344	-3.44055139	-2.03951632
H	-1.62025731	-2.37441494	-1.90773620
H	-2.64277622	-3.54804236	-2.76902170
H	-0.93336181	-3.91285125	-2.45316734
C	-2.51904073	-5.59174445	-0.92151271
H	-1.69837454	-6.10622099	-1.43295133
H	-3.40750988	-5.69753068	-1.55137942
H	-2.70620416	-6.10630248	0.02614935
C	0.05501901	-1.03214342	2.65994753
H	-0.82461628	-0.43628048	2.39599077
C	1.29606333	-0.22244062	2.26652996
H	2.21170635	-0.75854782	2.54678427
H	1.30279138	0.74349163	2.78592784
H	1.31223346	-0.03697139	1.18495455
C	0.01087543	-1.27996558	4.17184233
H	-0.89077265	-1.83320852	4.45171338
H	0.01346255	-0.32864486	4.71468396
H	0.87979557	-1.85964029	4.50335095
C	-3.88180223	1.42131312	0.18685152

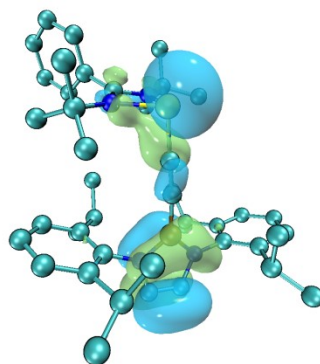
C	-4.65600665	1.57137382	-0.97437779
C	-5.08603444	2.85573067	-1.31302897
H	-5.67954797	3.00309003	-2.21047452
C	-4.76255309	3.94946819	-0.51917514
H	-5.10356837	4.94171784	-0.79925972
C	-4.00618929	3.77638100	0.63403224
H	-3.76291987	4.63853714	1.24810383
C	-3.55552456	2.51055251	1.01233303
C	-4.96431882	0.38064688	-1.86581908
H	-4.88096939	-0.52336755	-1.25282631
C	-3.92244888	0.28406720	-2.98928570
H	-3.97462874	1.17248856	-3.62931564
H	-4.10964305	-0.59717877	-3.61260247
H	-2.90639195	0.21798413	-2.58834733
C	-6.38040397	0.42155993	-2.44674162
H	-7.13258418	0.56058461	-1.66419254
H	-6.59547346	-0.51617613	-2.96855267
H	-6.49492719	1.23036896	-3.17623279
C	-2.69823788	2.32638342	2.25472692
H	-2.78085695	1.27891732	2.56603500
C	-1.22190822	2.60538129	1.93519211
H	-0.84991326	1.95000440	1.13952901
H	-0.60376165	2.45404855	2.82888366
H	-1.09422433	3.64425980	1.60638262
C	-3.16313783	3.19322715	3.42876060
H	-2.98392950	4.25734857	3.24177210
H	-2.60720452	2.92527192	4.33279110
H	-4.23050200	3.05864943	3.62814979
C	3.24899035	0.81374064	-0.83517948

C	2.49412368	3.25293911	-0.76673087
C	1.25128247	3.88741409	-1.39857962
H	1.27300975	3.78104130	-2.48848398
H	1.20754567	4.95369599	-1.15755665
H	0.34312508	3.40518382	-1.01925262
C	3.75730330	3.90440855	-1.34115006
H	4.66066072	3.50691182	-0.86934411
H	3.73255122	4.98596128	-1.17026937
H	3.81613758	3.72483246	-2.41969410
C	2.42919714	3.44287279	0.75360373
H	1.57105829	2.89774289	1.16123333
H	2.31540983	4.50551803	0.99309459
H	3.34114865	3.08485131	1.23864775
C	4.56811606	0.87987284	-0.14431838
C	5.73052324	0.92639545	-0.91825797
H	5.64926734	0.95564870	-2.00163749
C	6.97778359	0.94589894	-0.30135885
H	7.87845126	0.98545902	-0.90572627
C	7.06807256	0.91386774	1.08874487
H	8.04119946	0.92429926	1.56951370
C	5.90987321	0.87048886	1.86130472
H	5.97830419	0.84488701	2.94423310
C	4.66046574	0.85529604	1.24771744
H	3.75328880	0.81108215	1.84319450
B	-2.15351676	-0.49083691	0.19795164
C	3.13221139	-1.66722038	-1.48274708
C	4.07295527	-1.89209207	-2.67236870
H	3.60391658	-1.54568906	-3.59857570
H	4.30834962	-2.95681088	-2.77544113

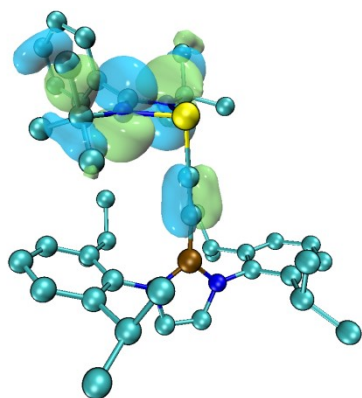
H	5.01129873	-1.34625695	-2.52989943
C	3.79882450	-2.13055701	-0.18363683
H	4.80126104	-1.71281447	-0.05828931
H	3.88410869	-3.22228521	-0.19996036
H	3.18393937	-1.85220289	0.67826558
C	1.83243086	-2.45603694	-1.68297902
H	1.15262391	-2.29742020	-0.83858858
H	2.04575232	-3.52648582	-1.76912612
H	1.32112153	-2.13255981	-2.59857660



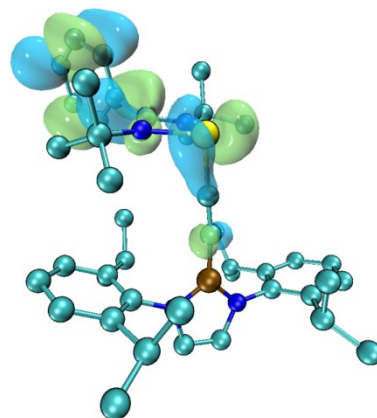
HOMO (-6.08 eV)



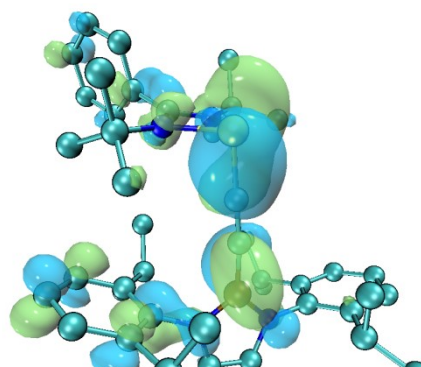
HOMO-1 (-6.66 eV)



HOMO-2 (-7.35 eV)



LUMO (0.14 eV)



LUMO+2 (0.76 eV)

Figure S4. Plots of the frontier orbitals of compound **1** (isovalue = 0.03).

Table S5. Selected data of WBI values of **1**.

Atom No	1	4	5	6
1. Si	0.0000	0.4472	0.4462	0.7394
4. N	0.4472	0.0000	0.1673	0.0184
5. N	0.4462	0.1673	0.0000	0.0178
6. C	0.7394	0.0184	0.0178	0.0000

Table S6. Selected data of Natural Bond Orbital Analysis of **1**.

(Occupancy) Bond orbital/ Coefficients/ Hybrids

```

-----
1. (1.63488) BD ( 1)Si  1 - N  4
      ( 5.31%)  0.2303*Si  1 s( 12.74%)p 6.63( 84.49%)d 0.22(  2.77%)
                                -0.0000  0.0018 -0.3535  0.0495 -0.0004
                                0.0024  0.4586  0.0318  0.0012  0.7071
                                -0.0158 -0.0026 -0.3646  0.0172 -0.1290
                                0.0863  0.0262  0.0028  0.0543
      ( 94.69%)  0.9731*N  4 s(  4.17%)p22.94( 95.79%)d 0.01(  0.04%)
                                0.0004 -0.2041 -0.0101 -0.0011  0.3438
                                0.0129  0.0369  0.0209  0.9152 -0.0004
                                0.0036 -0.0084  0.0153 -0.0070  0.0055

2. (1.61242) BD ( 1)Si  1 - N  5
      (  4.39%)  0.2094*Si  1 s( 12.66%)p 6.64( 84.03%)d 0.26(  3.31%)
  
```

-0.0000 0.0020 -0.3543 0.0335 -0.0004
0.0032 0.6438 0.0337 -0.0008 -0.6404
0.0382 -0.0029 -0.1107 0.0289 0.1403
0.0366 0.0303 -0.0813 0.0673

(95.61%) 0.9778* N 5 s(3.26%)p29.68(96.70%)d 0.01(0.04%)
0.0003 -0.1803 -0.0080 -0.0010 0.3712
0.0167 0.2875 -0.0118 0.8637

0.0077

-0.0082 -0.0012 -0.0123 -0.0003 0.0142

3. (1.96048) BD (1)Si 1 - C 6

(22.85%) 0.4780*Si 1 s(22.41%)p 3.42(76.55%)d 0.05(1.04%)
0.0000 -0.0001 0.4701 -0.0558 0.0004
-0.0002 0.5619 0.0273 0.0000 0.1973
0.0032 0.0004 0.6404 -0.0025 0.0254
0.0763 0.0230 0.0574 0.0084

(77.15%) 0.8783* C 6 s(50.96%)p 0.96(49.02%)d 0.00(0.02%)
-0.0005 0.7136 0.0214 -0.0009 -0.5460
0.0589 -0.1780 0.0148 -0.3943 0.0348
0.0034 0.0116 0.0026 0.0066 0.0010

14. (1.98517) BD (1) C 6 - C 7

(48.46%) 0.6962* C 6 s(48.44%)p 1.06(51.51%)d 0.00(0.05%)
0.0001 -0.6941 0.0514 -0.0011 -0.5847
-0.0404 -0.1958 -0.0120 -0.3644 -0.0200
-0.0089 -0.0154 -0.0050 -0.0113 0.0027

(51.54%) 0.7179* C 7 s(48.94%)p 1.04(51.02%)d 0.00(0.04%)
0.0002 -0.6979 0.0483 0.0004 0.5784
0.0294 0.2119 0.0125 0.3597 0.0185
-0.0078 -0.0139 -0.0046 -0.0096 0.0028

15. (1.94805) BD (2) C 6 - C 7

(49.39%) 0.7028* C 6 s(0.01%)p99.99(99.90%)d 5.82(0.08%)
20

0.0001 0.0114 0.0030 0.0007 -0.5029
 -0.0106 0.7825 0.0234 0.3647 0.0151
 0.0144 0.0036 0.0126 -0.0189 0.0091
 (50.61%) 0.7114* C 7 s(0.05%)p99.99(99.88%)d 1.37(0.07%)
 -0.0001 -0.0223 0.0011 0.0001 -0.5278
 -0.0028 0.7733 0.0109 0.3495 0.0036
 -0.0138 -0.0012 -0.0120 0.0167 -0.0082

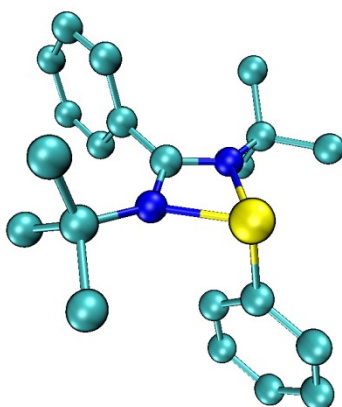


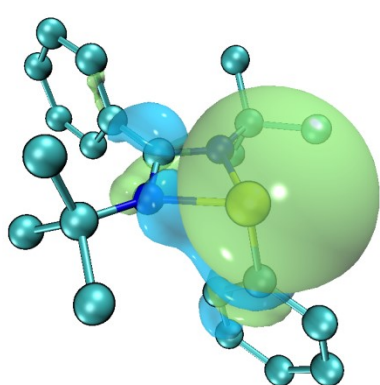
Figure S5. Calculated optimized structures for **1a** at M06-2X/6-31G(d,p) level of theory.

Table S7. Optimized structures of **1a** (atom, x-, y-, z- positions in Å)

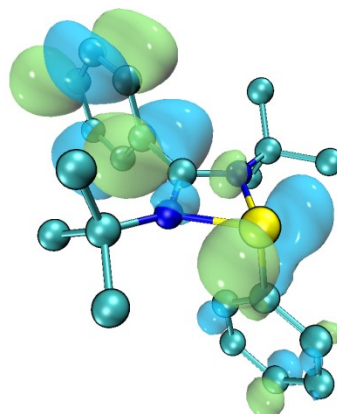
Si	1.26148569	0.25539732	-1.54422309
N	0.03532283	-0.97459450	-0.76924448
N	-0.08441079	1.14582351	-0.53850858
C	-0.74114754	0.00515518	-0.31699774
C	-0.06062095	-2.43021111	-0.63762240
C	1.10071319	-3.00082589	-1.45687978
H	0.99511331	-2.73520713	-2.51360079
H	1.12292153	-4.09125053	-1.37048965
H	2.05560949	-2.60548873	-1.09185349
C	-1.38525770	-2.97388437	-1.18638977
H	-2.23398122	-2.68056480	-0.56300197

H	-1.34920567	-4.06810448	-1.21380452
H	-1.55325713	-2.60767751	-2.20443677
C	0.11285620	-2.83044501	0.83300575
H	1.05267851	-2.42864962	1.22439607
H	0.12854136	-3.92145177	0.92867514
H	-0.71512901	-2.45009468	1.43941489
C	-2.11343843	-0.13544877	0.24897327
C	-3.22025586	-0.13665616	-0.60296212
H	-3.06862851	-0.05580745	-1.67599676
C	-4.50344681	-0.25490399	-0.07723977
H	-5.36108704	-0.25543305	-0.74243510
C	-4.68534631	-0.37588793	1.29882201
H	-5.68657020	-0.46858632	1.70755659
C	-3.58264764	-0.37935400	2.15006107
H	-3.72201048	-0.47320334	3.22229880
C	-2.29845173	-0.25818577	1.62725429
H	-1.43387465	-0.24645944	2.28580961
C	-0.51964836	2.54289671	-0.46196173
C	-1.44522625	2.88177473	-1.63676036
H	-0.95476973	2.63951903	-2.58479264
H	-1.69385195	3.94860801	-1.63248010
H	-2.37923869	2.31492697	-1.56881400
C	-1.21501231	2.85191615	0.86900223
H	-2.20342462	2.39067524	0.93445636
H	-1.34211835	3.93502491	0.96654339
H	-0.60531799	2.49987442	1.70808875
C	0.76432876	3.37351445	-0.55770931
H	1.43858489	3.13044679	0.26957670
H	0.53037921	4.44184498	-0.52427180

H	1.28619301	3.16701693	-1.49938431
C	2.60965397	0.16457466	-0.16598054
C	3.95362599	0.05786922	-0.54254757
C	2.32269899	0.17410324	1.20778945
C	4.97337901	-0.04279646	0.40576727
H	4.21039666	0.05342983	-1.60109493
C	3.32884581	0.07806585	2.16320966
H	1.28501462	0.26184311	1.53214840
C	4.66101140	-0.03212785	1.76065914
H	6.00846306	-0.12674033	0.08663155
H	3.08196932	0.08960270	3.22154408
H	5.44973571	-0.10711637	2.50375279



HOMO (-6.04 eV)



LUMO (0.15 eV)

Figure S6. Plots of the frontier orbitals of compound **1a** (isovalue = 0.03).

Table S8. Selected data of WBI values of **1a**.

Atom No	1	2	3	42
1. Si	0.0000	0.4357	0.4400	0.6802
2. N	0.4357	0.0000	0.1683	0.0128
3. N	0.4400	0.1683	0.0000	0.0122
42. C	0.6802	0.0128	0.0122	0.0000

Table S9. Selected data of Natural Bond Orbital Analysis of **1a**.

(Occupancy) Bond orbital/ Coefficients/ Hybrids

1. (1.60135) BD (1)Si	1 - N	2
(3.18%)	0.1782*Si	1 s(11.75%)p 7.12(83.69%)d 0.39(4.56%)
		-0.0000 0.0020 -0.3412 0.0329 -0.0007
		0.0031 0.5582 0.0172 0.0000 0.7202
		-0.0316 -0.0034 0.0622 0.0363 -0.1664
		-0.0063 -0.0911 -0.0358 0.0914
(96.82%)	0.9840* N	2 s(3.16%)p30.60(96.79%)d 0.01(0.04%)
		0.0000 -0.1778 -0.0028 0.0001 0.3657
		0.0119 -0.0891 0.0104 0.9088 0.0115
		0.0054 -0.0064 0.0122 -0.0047 0.0144
2. (1.62399) BD (1)Si	1 - N	3
(4.61%)	0.2147*Si	1 s(12.66%)p 6.66(84.28%)d 0.24(3.06%)
		-0.0000 0.0012 -0.3507 0.0595 0.0022
		0.0024 0.6382 0.0409 -0.0017 -0.6264
		0.0185 -0.0028 -0.2021 0.0193 0.1303
		0.0600 0.0224 -0.0620 0.0754
(95.39%)	0.9767* N	3 s(2.58%)p37.72(97.38%)d 0.02(0.04%)
		0.0005 -0.1603 -0.0109 -0.0015 0.2006
		0.0162 0.1201 -0.0145 0.9584 0.0013
		-0.0043 -0.0089 -0.0169 -0.0033 0.0045
3. (1.93236) BD (1)Si	1 - C	42
(22.59%)	0.4753*Si	1 s(25.92%)p 2.82(73.16%)d 0.04(0.92%)
		-0.0000 -0.0004 -0.5052 0.0627 -0.0008
		0.0001 -0.3912 -0.0338 -0.0001 0.1220
		-0.0079 -0.0010 -0.7500 -0.0024 -0.0128
		-0.0785 -0.0051 -0.0498 -0.0189

(77.41%) 0.8798* C 42 s(31.37%)p 2.19(68.62%)d 0.00(0.01%)
 -0.0001 -0.5594 -0.0275 0.0008 0.5994
 -0.0516 -0.0624 0.0016 0.5639 -0.0497
 -0.0001 -0.0077 0.0001 -0.0035 -0.0044

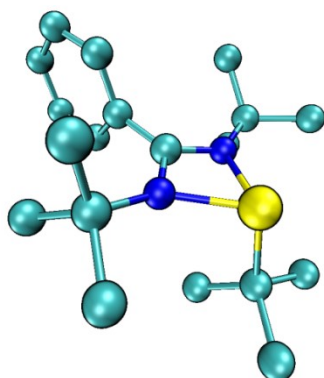


Figure S7. Calculated optimized structures for **1b** at M06-2X/6-31G(d,p) level of theory.

Table S10. Optimized structures of **1b** (atom, x-, y-, z- positions in Å).

Si	1.85027181	0.07296082	-1.00940316
N	0.41065366	-1.05751679	-0.43931629
N	0.36410315	1.08889882	-0.36798907
C	-0.37847016	-0.00634223	-0.21721827
C	0.08149474	-2.48885539	-0.48602965
C	1.19999339	-3.16931958	-1.28259731
H	1.20998895	-2.80459352	-2.31421182
H	1.04271940	-4.25226302	-1.29364327
H	2.18068958	-2.97056563	-0.84222209
C	-1.24697771	-2.77834182	-1.20140020
H	-2.11456652	-2.49327690	-0.60271567
H	-1.31720224	-3.85292497	-1.39966275
H	-1.28909931	-2.25052853	-2.16001351
C	0.02761407	-3.05807252	0.93737206
H	0.97367609	-2.89194328	1.46059515

H	-0.16946785	-4.13514499	0.90871156
H	-0.77386158	-2.58050321	1.51017705
C	-1.82955920	-0.03942894	0.12635082
C	-2.81315287	0.09793417	-0.85542037
H	-2.52199110	0.19225133	-1.89760054
C	-4.15807923	0.08698213	-0.49937074
H	-4.91964920	0.19067574	-1.26577138
C	-4.52621442	-0.06177136	0.83664759
H	-5.57599666	-0.06879071	1.11241101
C	-3.54731301	-0.20361634	1.81704727
H	-3.83101437	-0.31866118	2.85832778
C	-2.20082806	-0.19247121	1.46337694
H	-1.42858624	-0.28421221	2.22274295
C	-0.03186387	2.50064626	-0.42869993
C	-0.70175794	2.80780916	-1.77486160
H	-0.04961667	2.49977572	-2.59813560
H	-0.89917756	3.88144809	-1.86546301
H	-1.65576655	2.28132214	-1.86466652
C	-0.95556618	2.89728967	0.73051656
H	-1.96265731	2.48891824	0.61832052
H	-1.03791455	3.98864867	0.76604841
H	-0.54152783	2.55139749	1.68372585
C	1.26123479	3.31378776	-0.32390152
H	1.72438356	3.17921400	0.65813325
H	1.04884866	4.37820933	-0.46208081
H	1.97649542	3.00417179	-1.09499743
C	2.95213644	0.04608077	0.62125898
C	4.05605300	1.10267028	0.46773014
H	3.65712710	2.12083815	0.41663526

H	4.74491713	1.06402318	1.32434034
H	4.64663484	0.93272442	-0.44059865
C	2.18458347	0.28470163	1.92167979
H	1.78137375	1.30186788	1.97486885
H	1.34161006	-0.41238918	2.01964402
H	2.83836499	0.13965630	2.79490701
C	3.64394774	-1.32224113	0.70486994
H	2.93682615	-2.11742450	0.96419095
H	4.13455534	-1.59726397	-0.23822802
H	4.41913163	-1.31043017	1.48490986

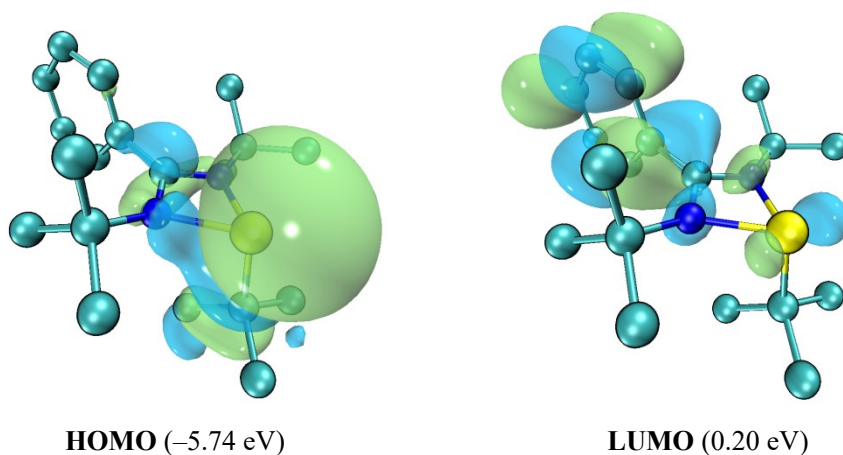


Figure S8. Plots of the frontier orbitals of compound **1b** (isovalue = 0.03).

Table S11. Selected data of WBI values of **1b**.

Atom No	1	2	3	42
1. Si	0.0000	0.4319	0.4304	0.6310
2. N	0.4319	0.0000	0.1671	0.0122
3. N	0.4304	0.1671	0.0000	0.0115
42. C	0.6310	0.0122	0.0115	0.0000

Table S12. Selected data of Natural Bond Orbital Analysis of **1b**.

(Occupancy) Bond orbital/ Coefficients/ Hybrids

1. (1.92336) BD (1)Si 1 - C 42

(22.51%) 0.4744*Si 1 s(19.13%)p 4.19(80.04%)d 0.04(0.84%)

-0.0000 -0.0013 -0.4359 0.0350 0.0004

-0.0004 -0.3632 -0.0329 -0.0000 0.0127

0.0016 -0.0009 -0.8167 -0.0166 -0.0004

-0.0620 0.0025 -0.0216 -0.0636

(77.49%) 0.8803* C 42 s(23.22%)p 3.31(76.76%)d 0.00(0.01%)

-0.0003 -0.4805 0.0363 0.0004 0.5375

-0.0296 -0.0224 -0.0007 0.6891 -0.0495

0.0001 -0.0094 -0.0002 -0.0025 -0.0074

5. References

- [S1] Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2008**, *130*, 16069–16079.
- [S2] S. Nagendran, S. S. Sen, H. W. Roesky, D. Koley, H. Grubmuller, A. Pal, R. Herbst-Irmer, *Organometallics* **2008**, *27*, 5459–5463.
- [S3] S. S. Sen, H. W. Roesky, D. Stern, J. Henn, D. Stalke, *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126.
- [S4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339–341.
- [S5] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3–8.
- [S6] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3–8.
- [S7] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.
- [S8] F. L. Hirshfeld, *Theoret. Chim. Acta (Berl)* **1977**, *44*, 129–138.
- [S9] R. F. W. Bader, *Acc. Chem. Res.* **1985**, *18*, 9–15.
- [S10] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.

6. NMR spectrum

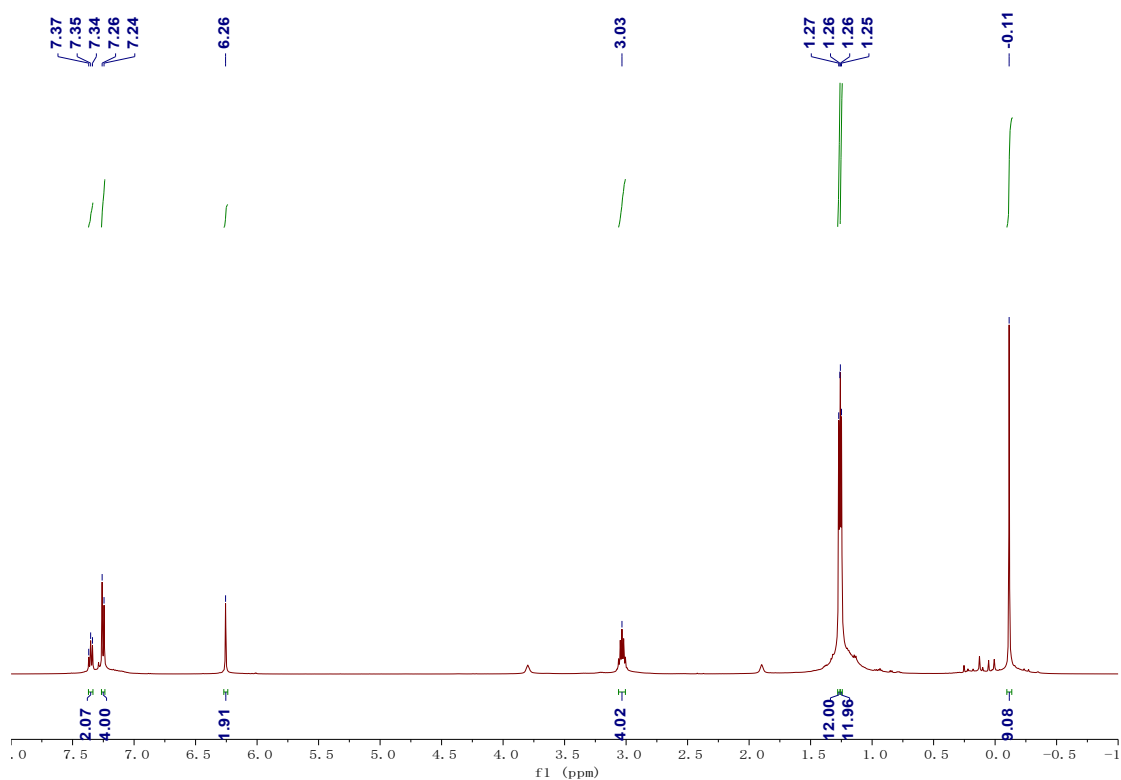


Figure S9. ^1H NMR (500 MHz) spectrum of $[(\text{HCDipN})_2]\text{B-CC-TMS}$ in CDCl_3 .

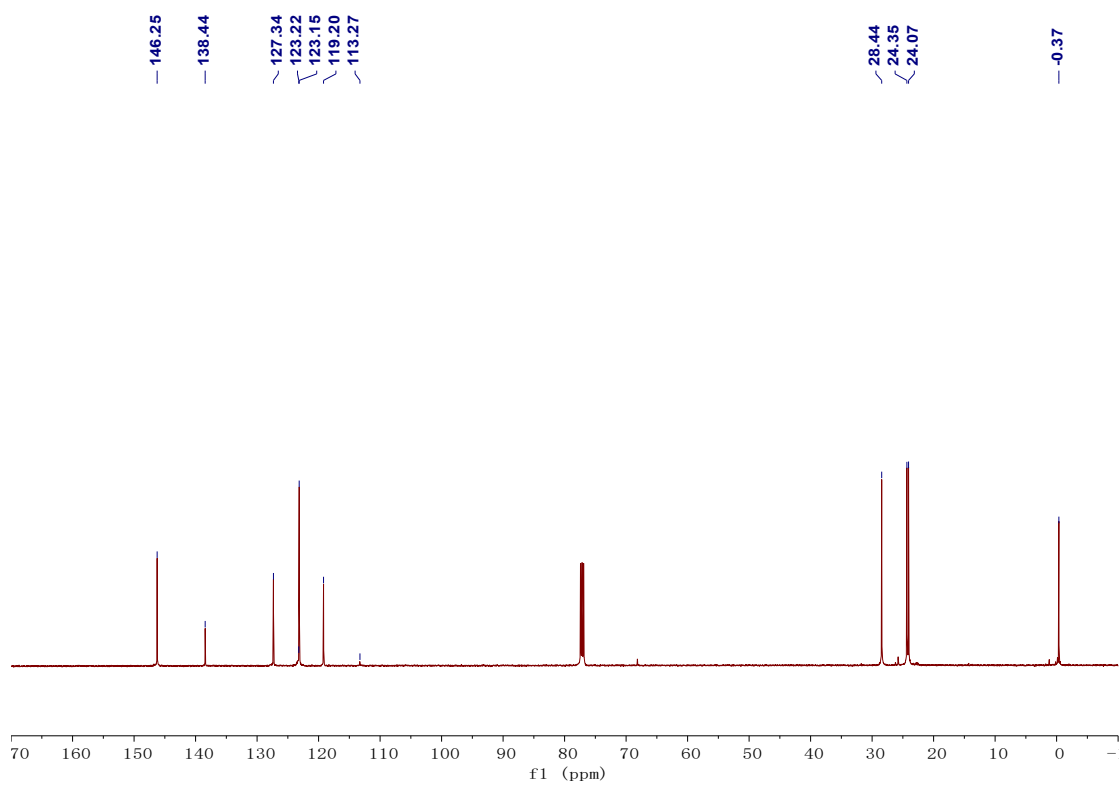


Figure S10. ^{13}C NMR (125 MHz) spectrum of $[(\text{HCDipN})_2]\text{B-CC-TMS}$ in CDCl_3 .

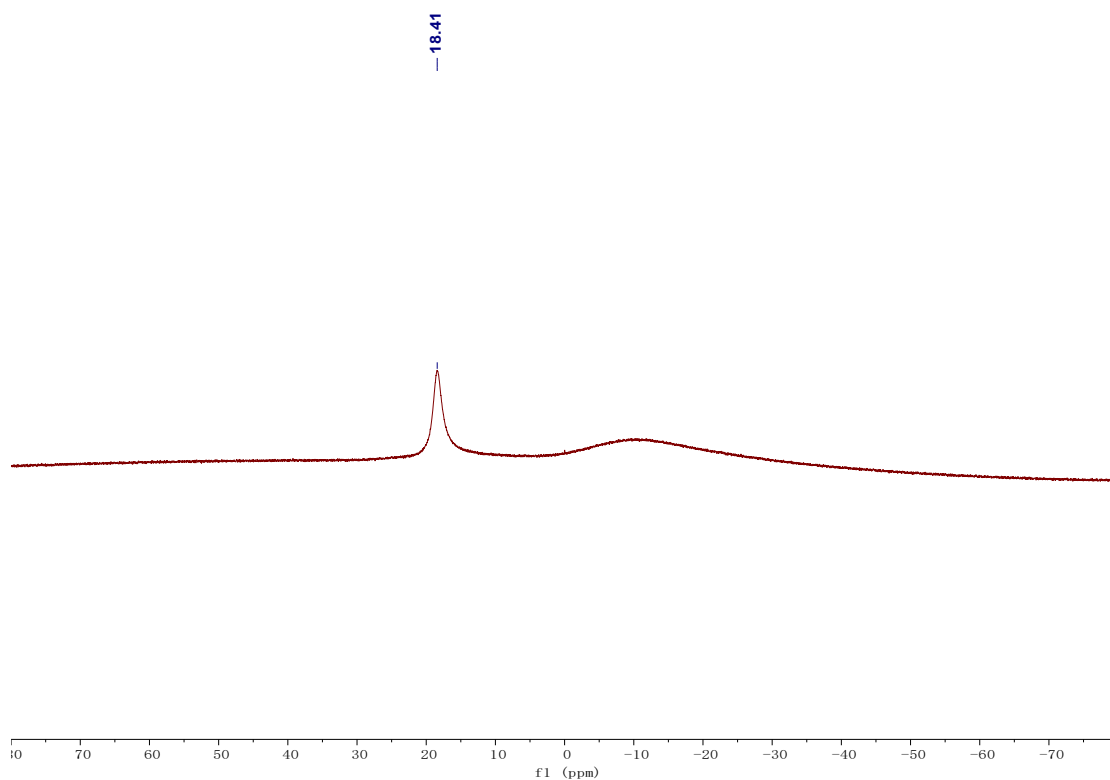


Figure S11. ^{11}B NMR (160 MHz) spectrum of $[(\text{HCDipN})_2]\text{B-CC-TMS}$ in CDCl_3 .

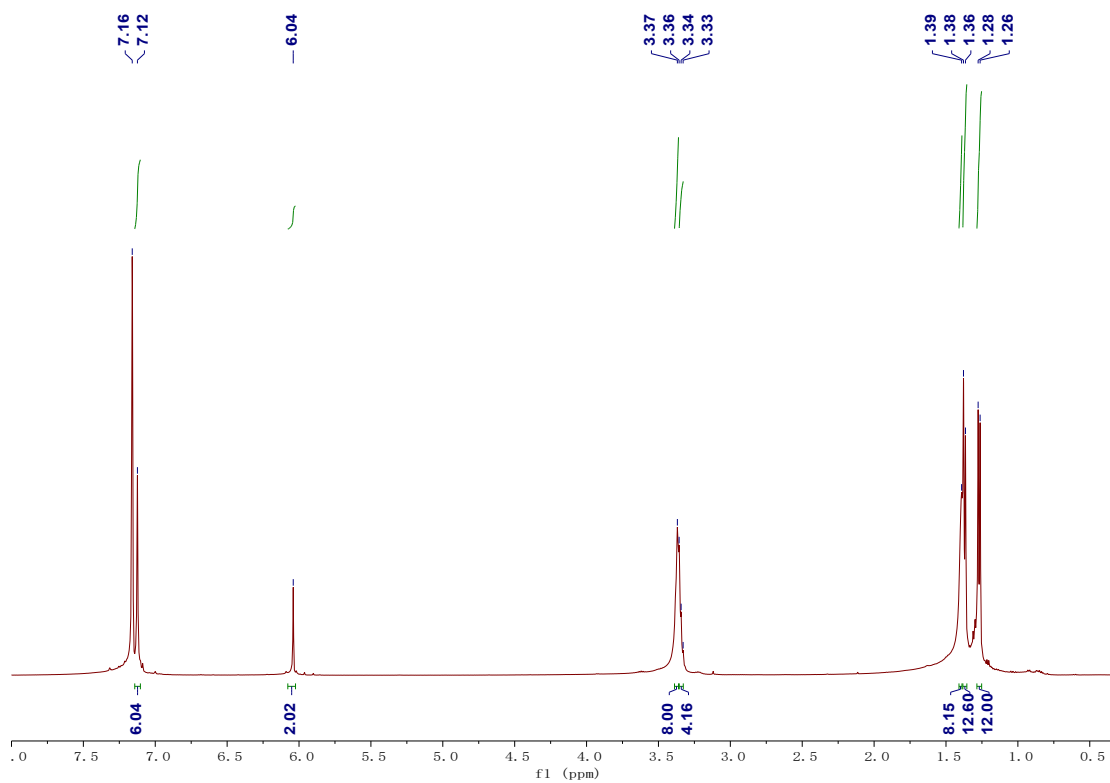


Figure S12. ^1H NMR (500 MHz) spectrum of $[(\text{HCDipN})_2]\text{B-CC-Li}$ in C_6D_6 .

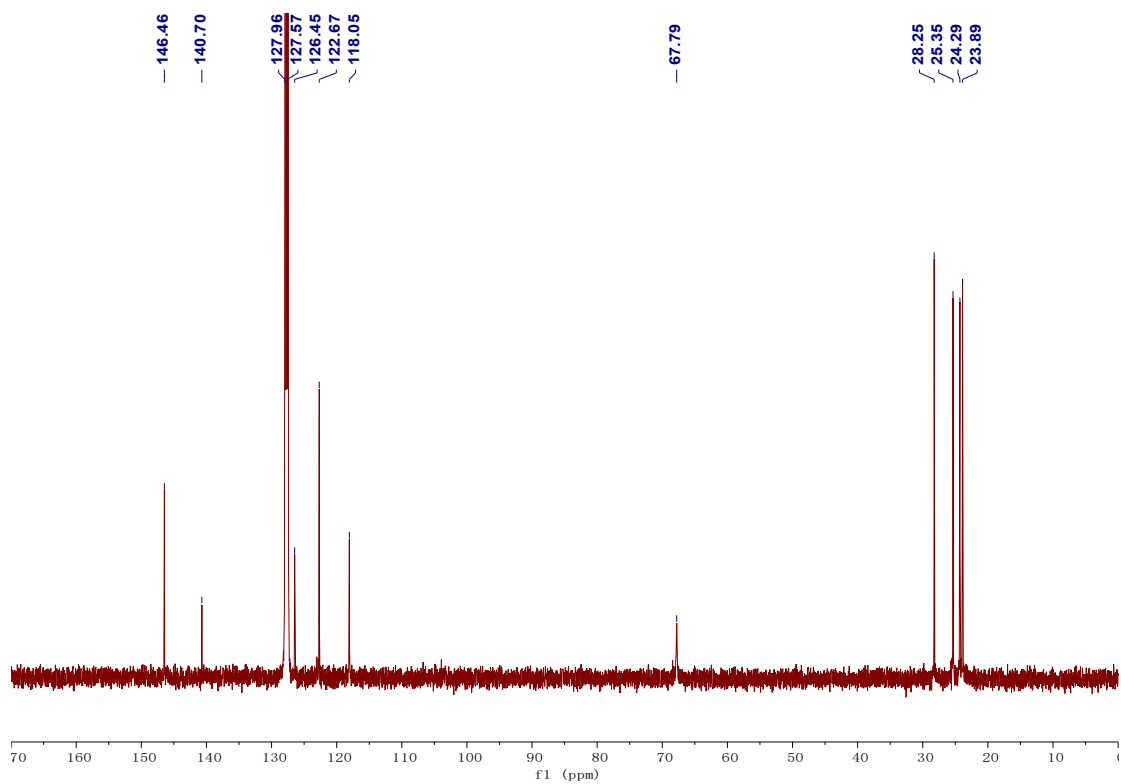


Figure S13. ^{13}C NMR (125 MHz) spectrum of $[(\text{HCDipN})_2]\text{B-CC-Li}$ in C_6D_6 .

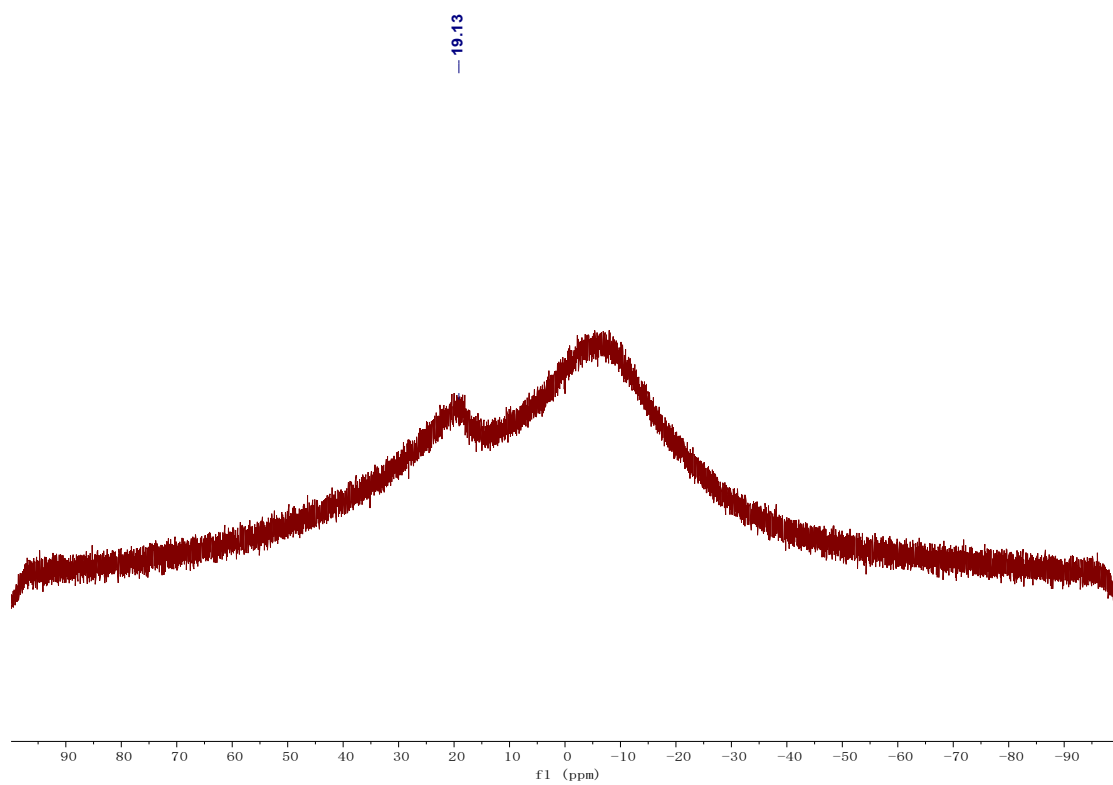


Figure S14. ^{11}B NMR (160 MHz) spectrum of $[(\text{HCDipN})_2]\text{B-CC-Li}$ in C_6D_6 .

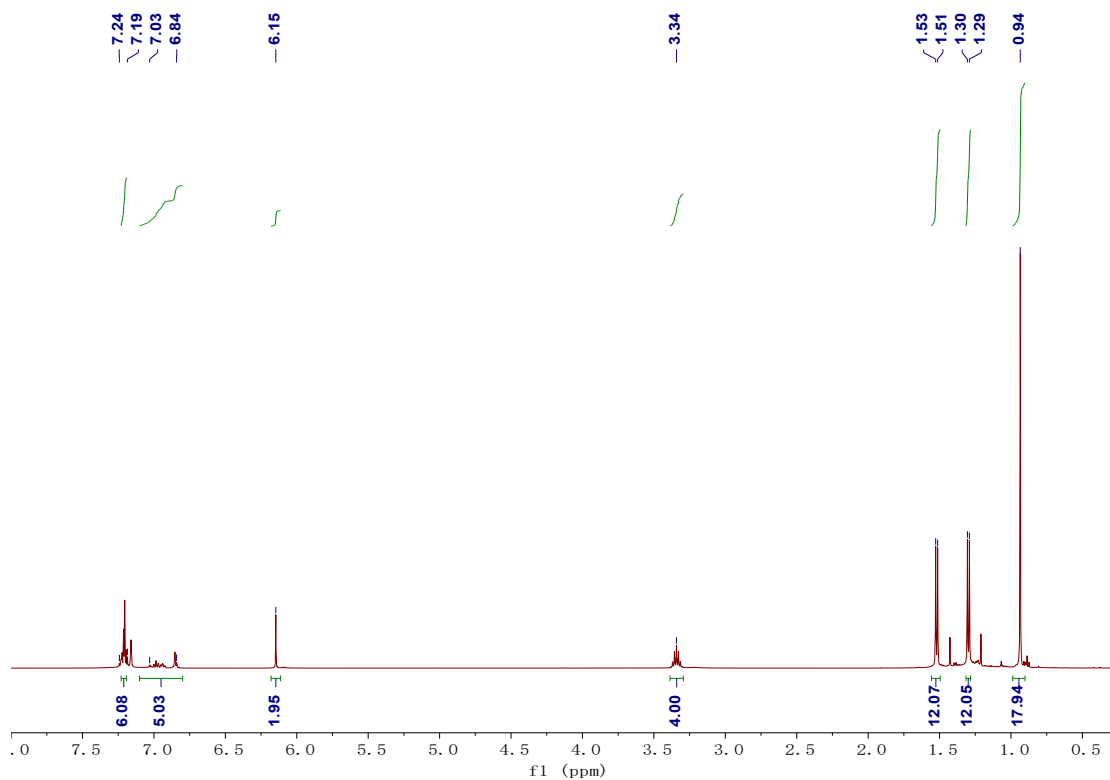


Figure S15. ^1H NMR (500 MHz) spectrum of **1** in C_6D_6 .

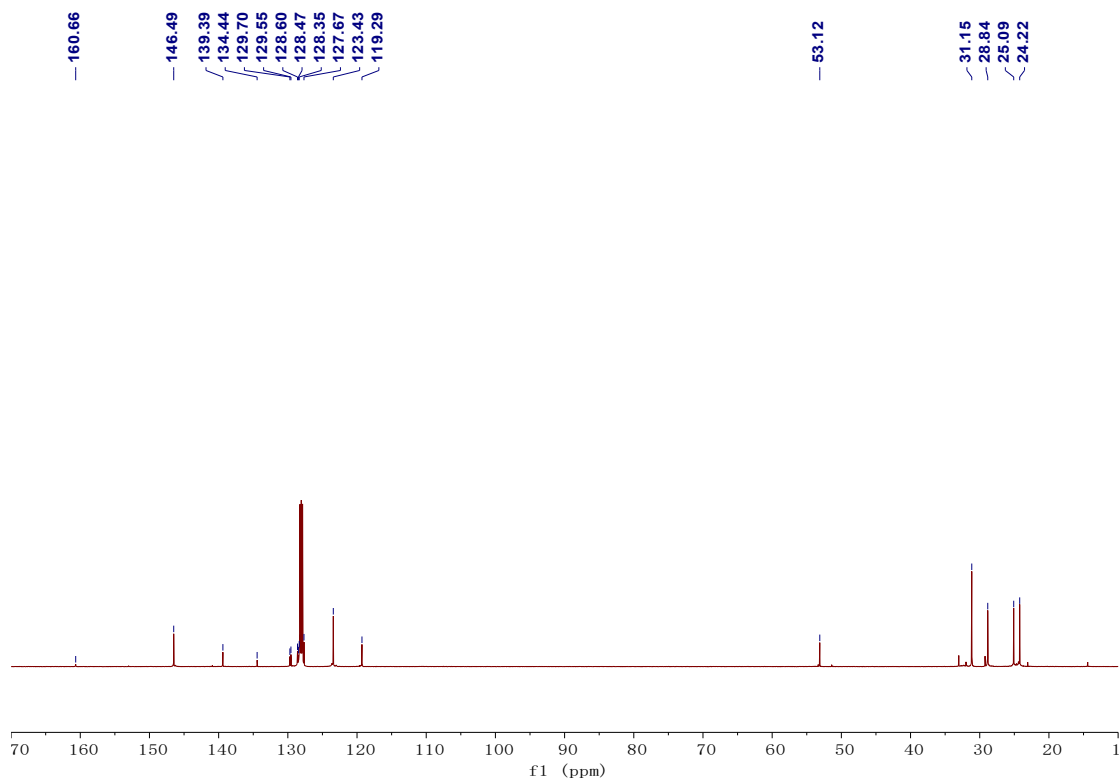


Figure S16. ^{13}C NMR (125 MHz) spectrum of **1** in C_6D_6 .

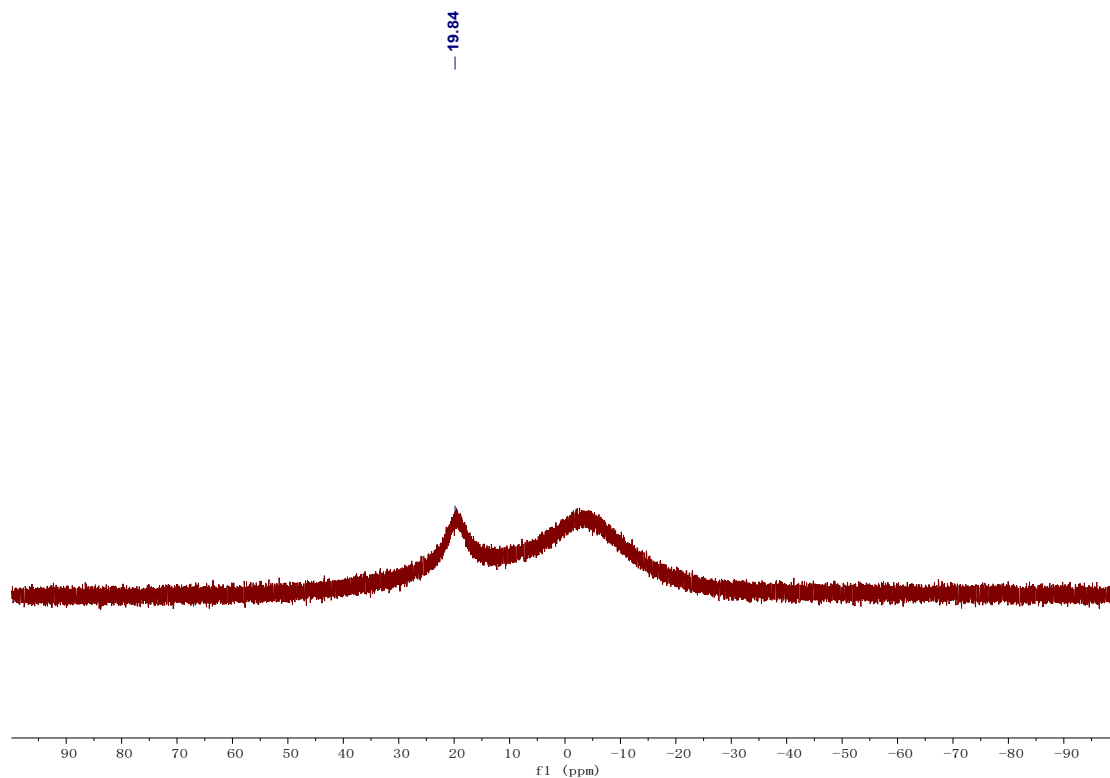


Figure S17. ^{11}B NMR (160 MHz) spectrum of **1** in C_6D_6 .

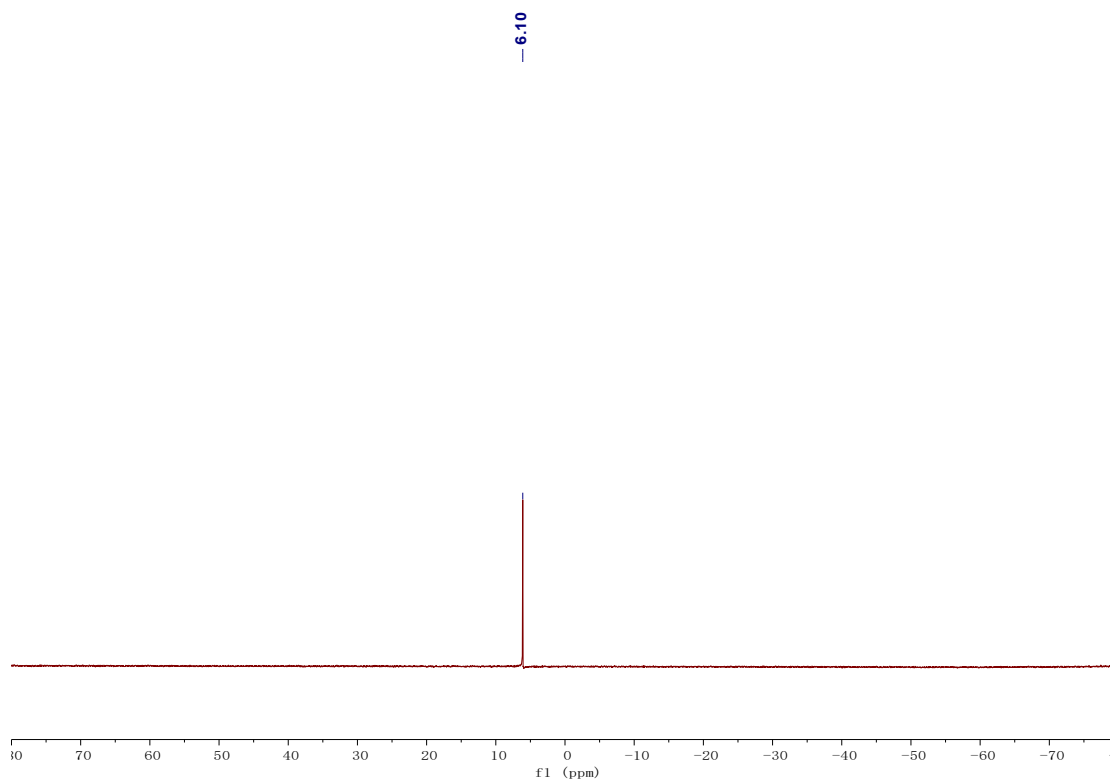


Figure S18. ^{29}Si NMR (99 MHz) spectrum of **1** in C_6D_6 .

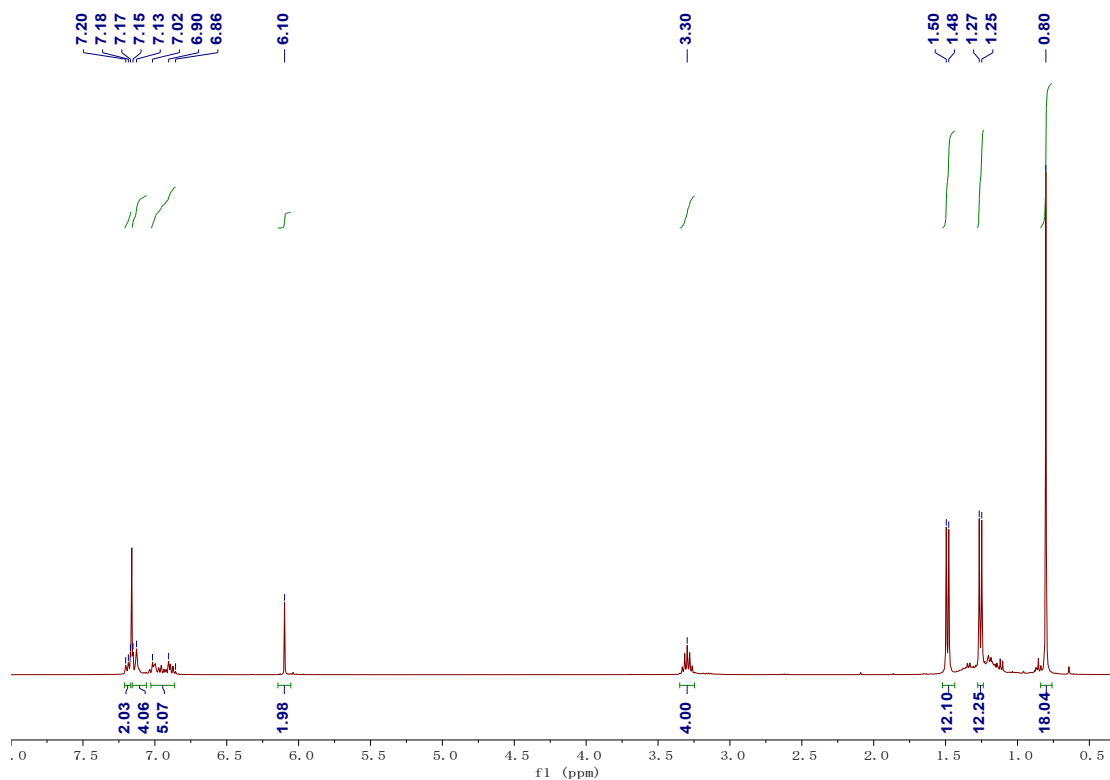


Figure S19. ^1H NMR (500 MHz) spectrum of **1'** in C_6D_6 .

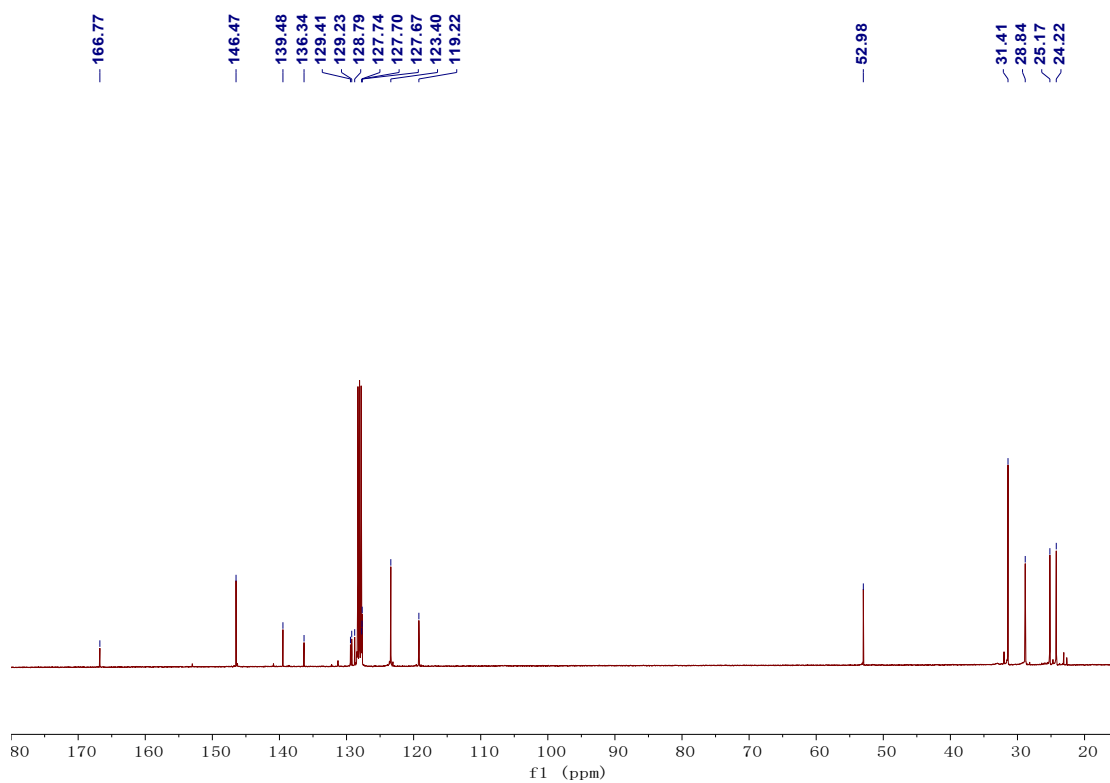


Figure S20. ^{13}C NMR (125 MHz) spectrum of **1'** in C_6D_6 .

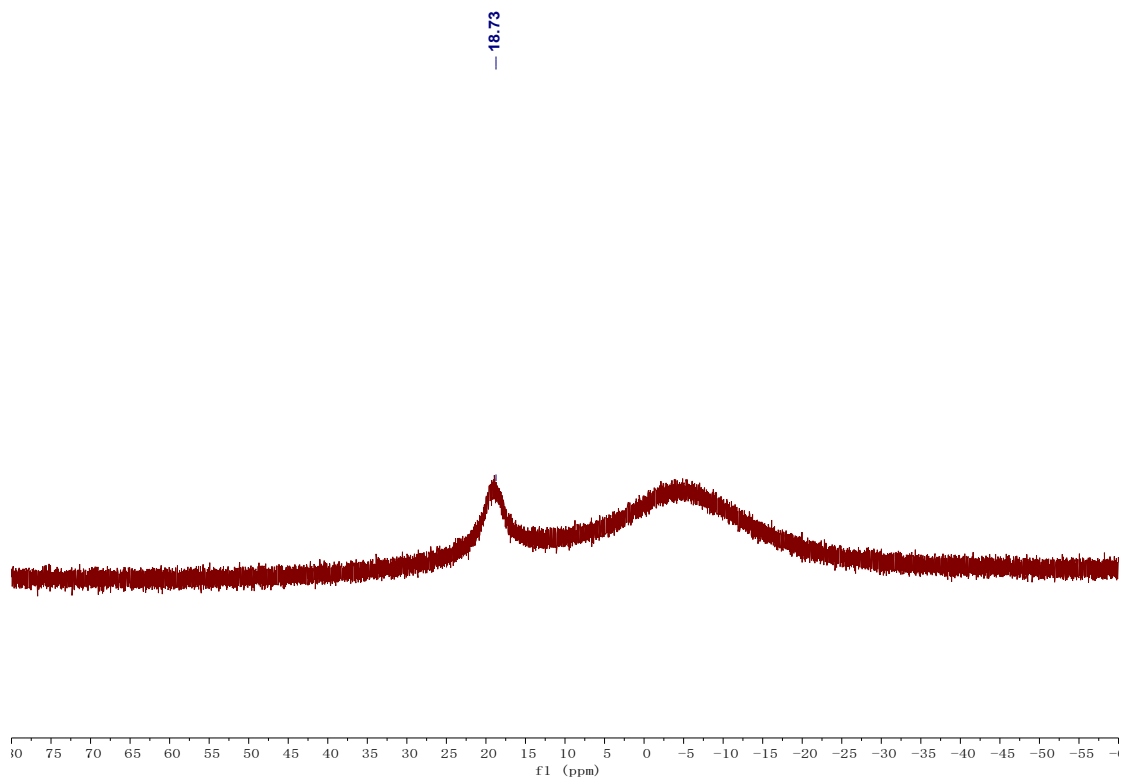


Figure S21. ^{11}B NMR (160 MHz) spectrum of **1'** in C_6D_6 .

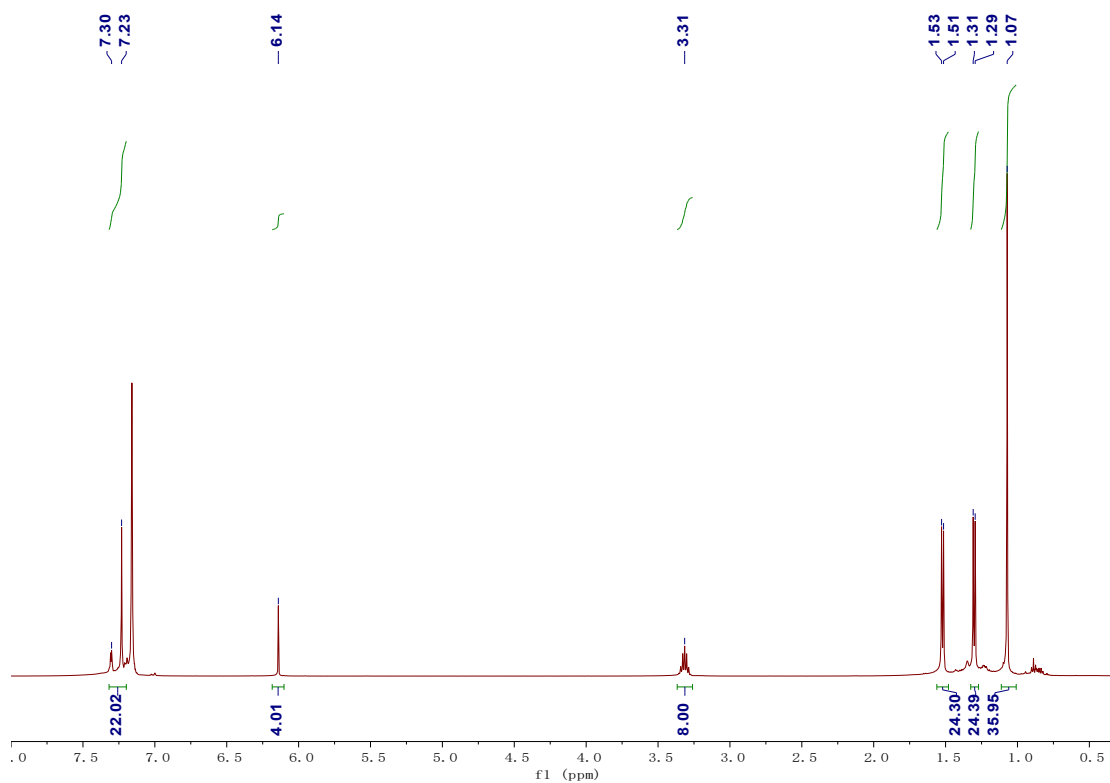


Figure S22. ^1H NMR (500 MHz) spectrum of **2** in C_6D_6 .

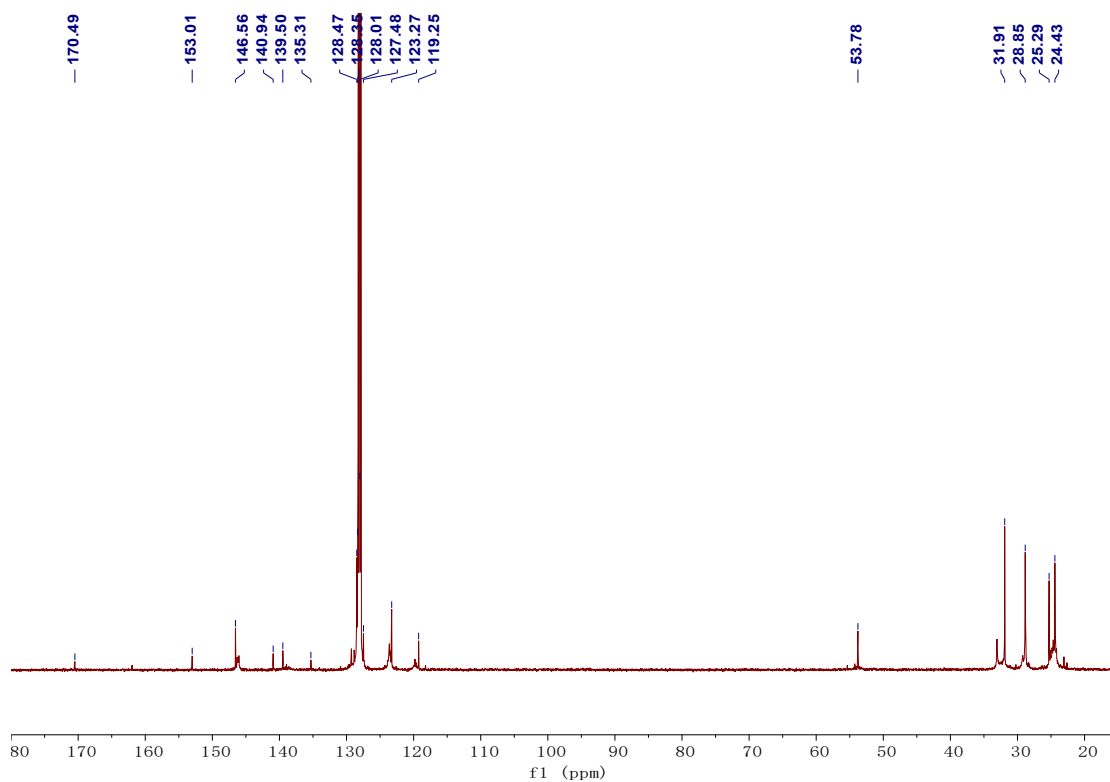


Figure S23. ^{13}C NMR (125 MHz) spectrum of 2 in C_6D_6 .

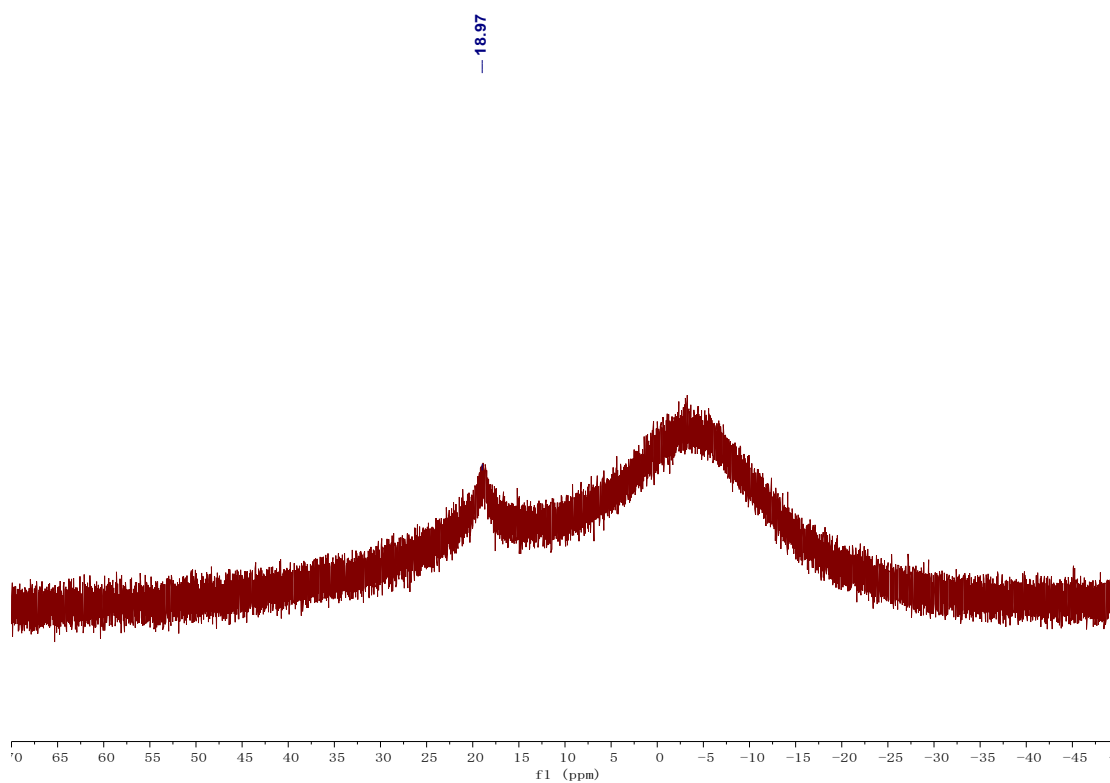


Figure S24. ^{11}B NMR (160 MHz) spectrum of 2 in C_6D_6 .

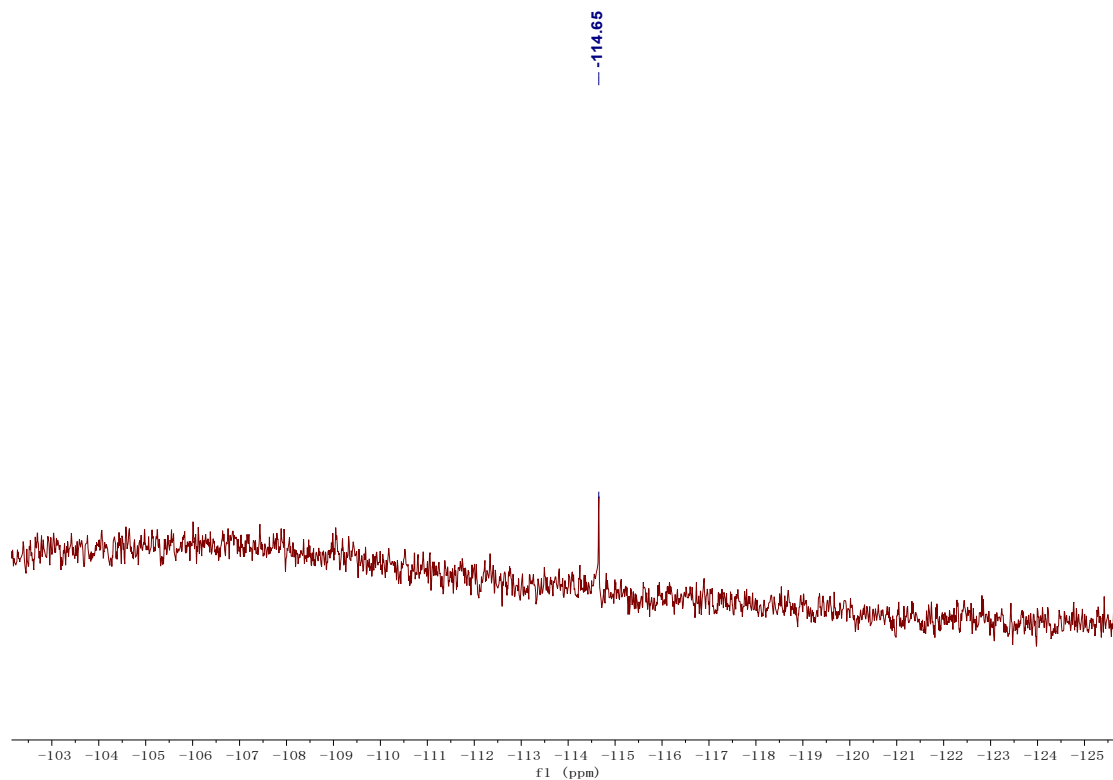


Figure S25. ^{29}Si NMR (99 MHz) spectrum of **2** in C_6D_6 .

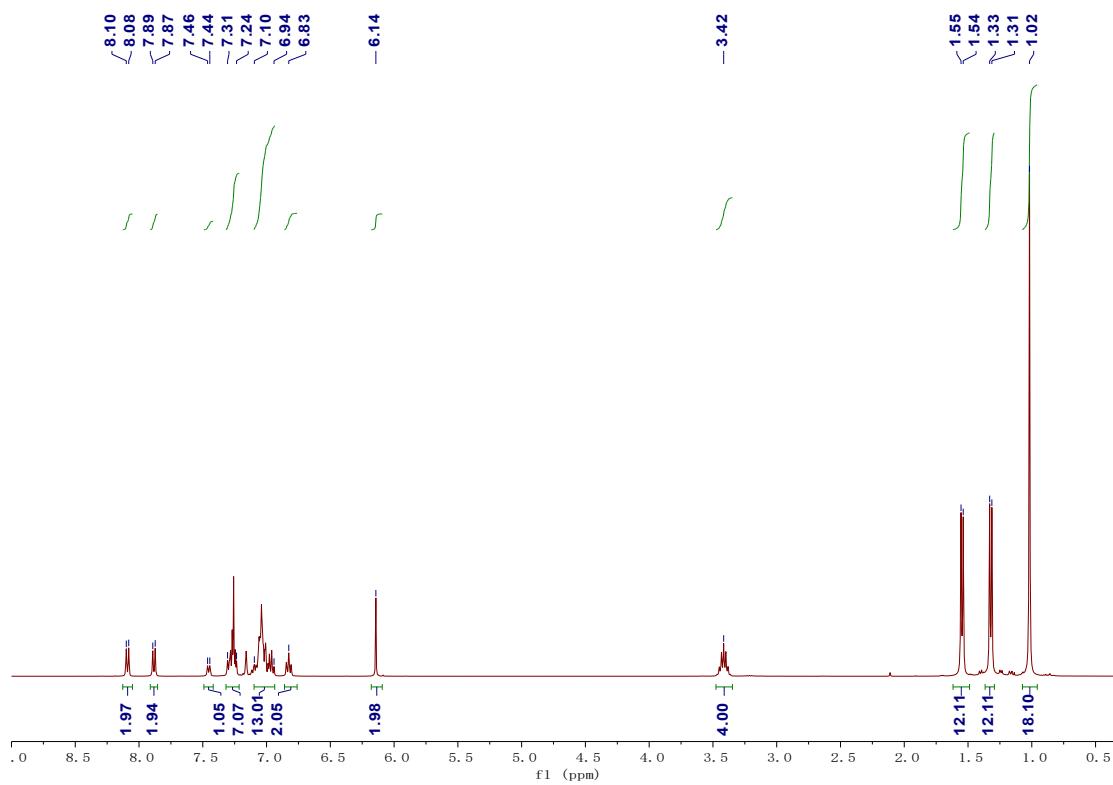


Figure S26. ^1H NMR (500 MHz) spectrum of **3** in C_6D_6 .

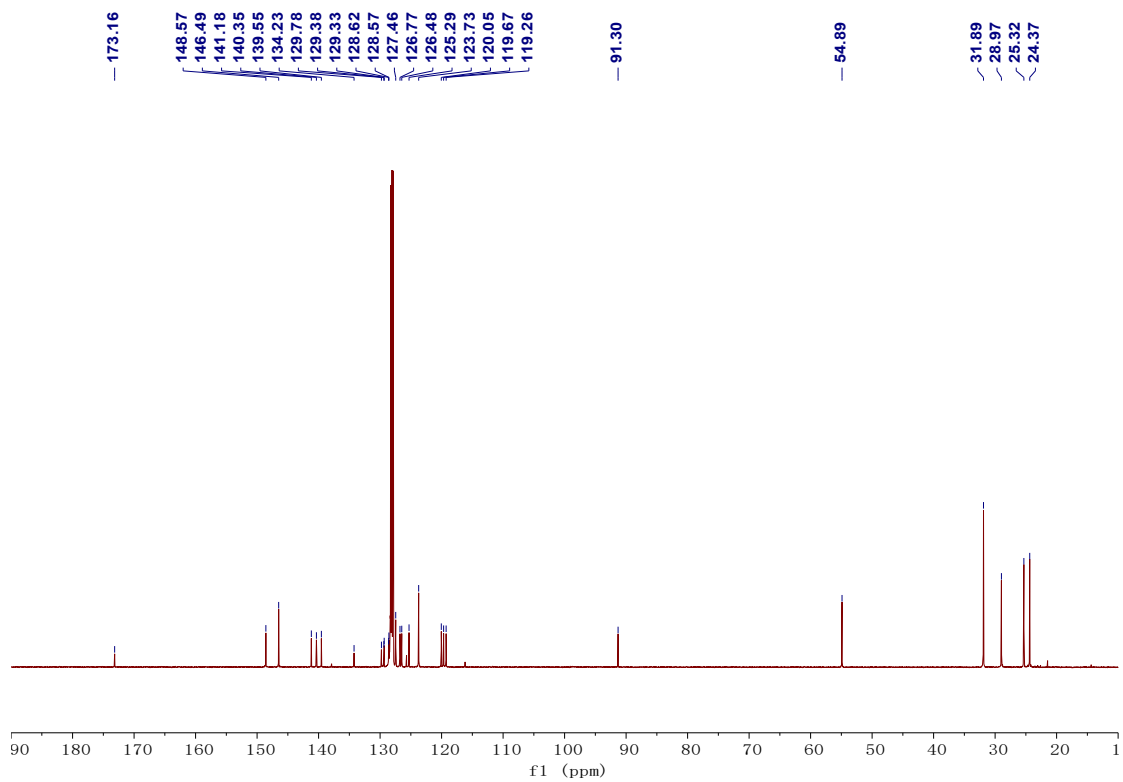


Figure S27. ^{13}C NMR (125 MHz) spectrum of **3** in C_6D_6 .

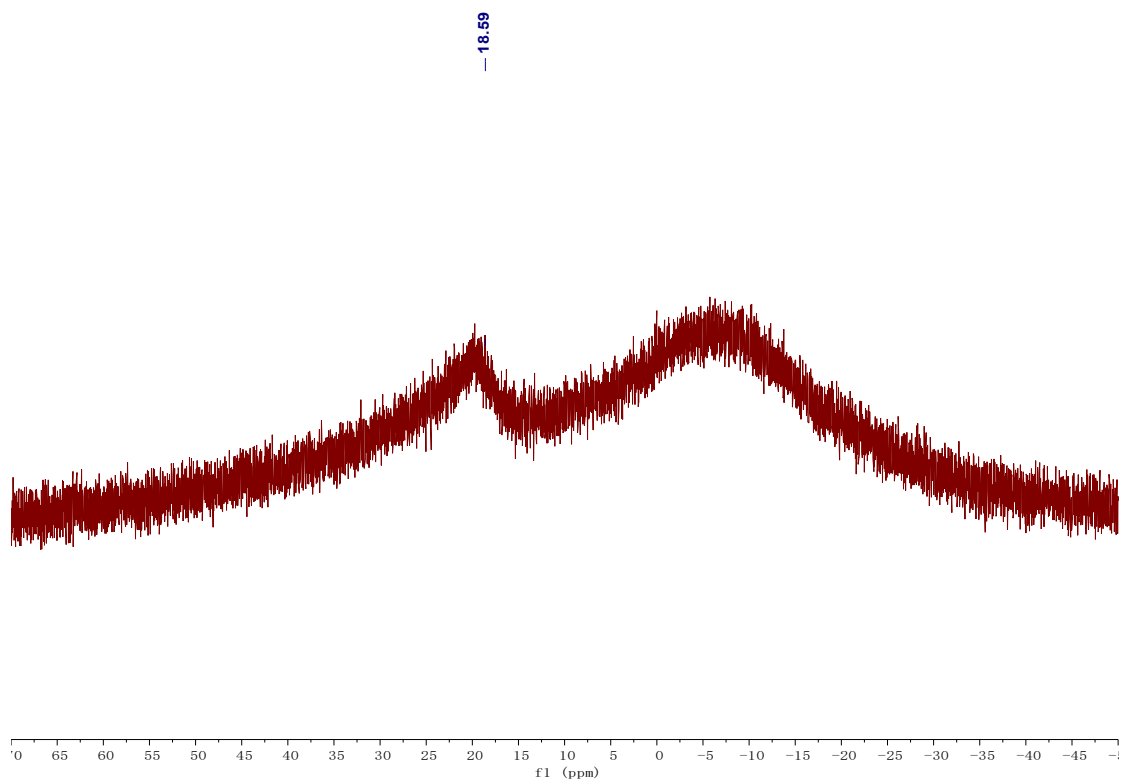


Figure S28. ^{11}B NMR (160 MHz) spectrum of **3** in C_6D_6 .

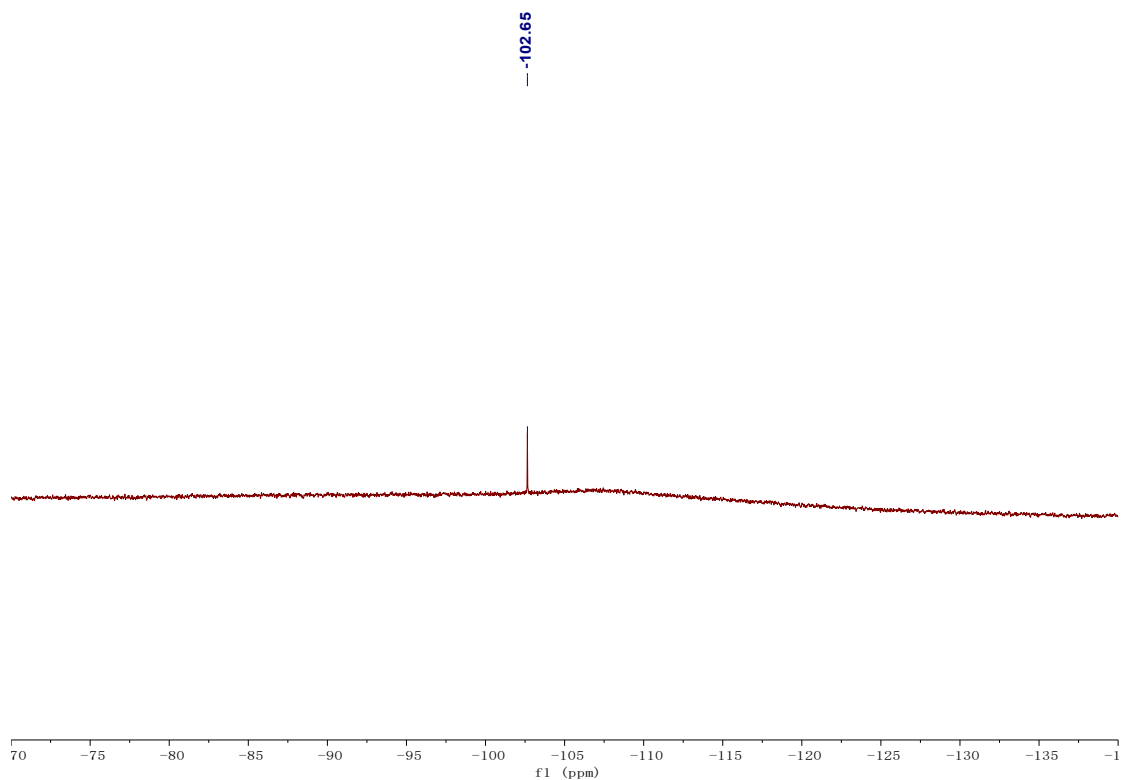


Figure S29. ^{29}Si NMR (99MHz) spectrum of **3** in C_6D_6 .

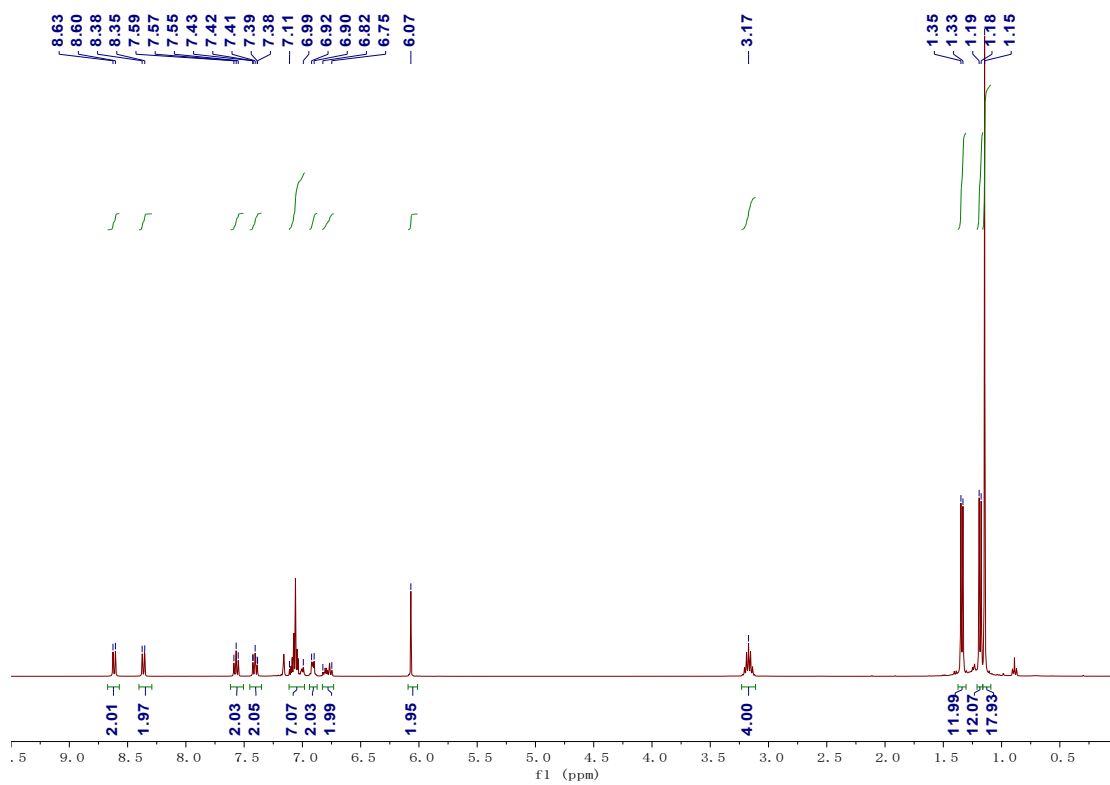


Figure S30. ^1H NMR (500 MHz) spectrum of **4** in C_6D_6 .

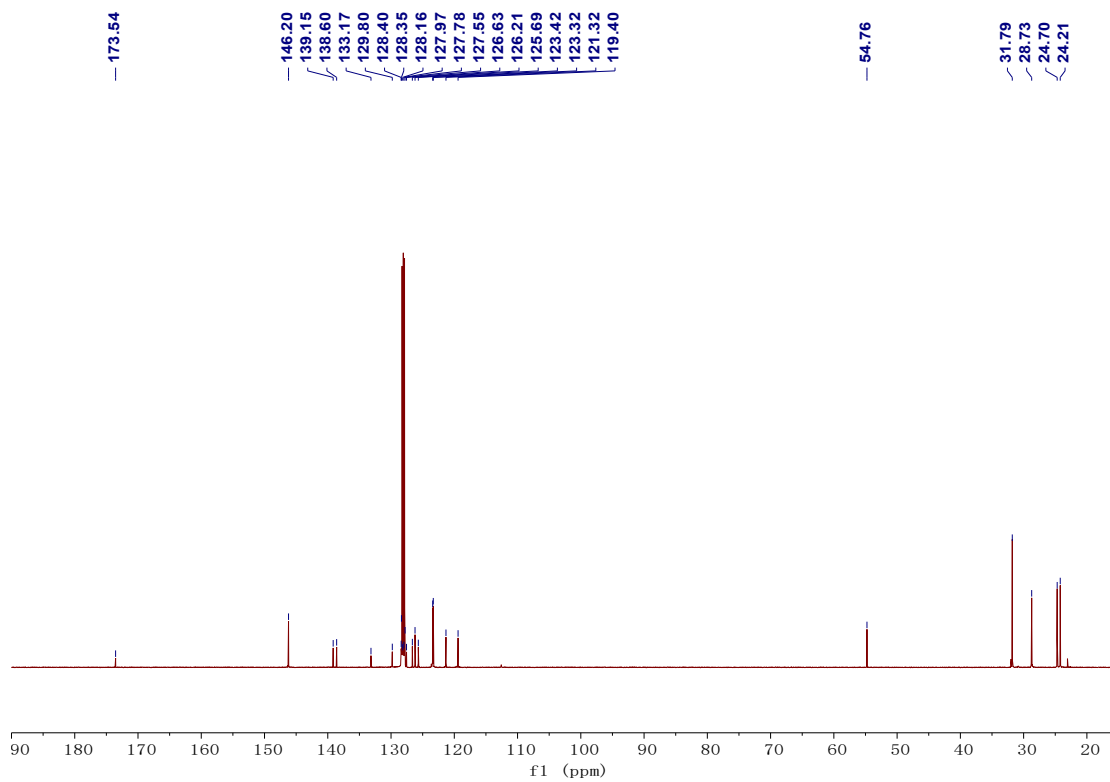


Figure S31. ^{13}C NMR (125 MHz) spectrum of **4** in C_6D_6 .

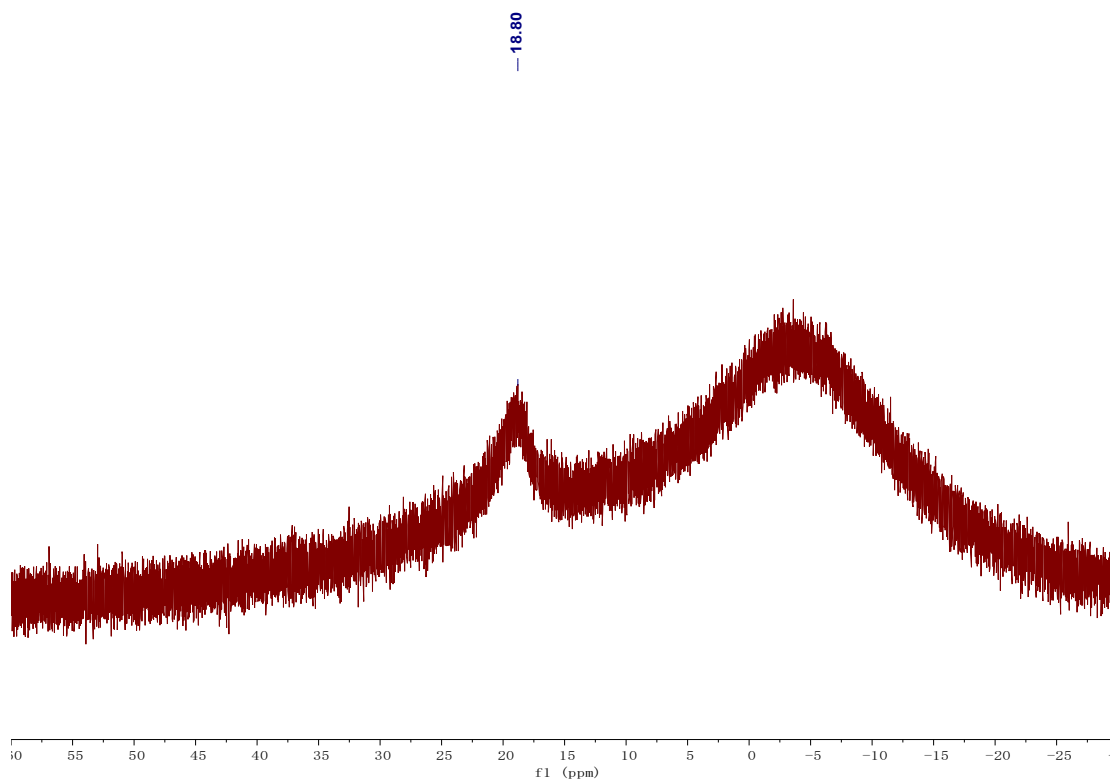


Figure S32. ^{11}B NMR (160 MHz) spectrum of **4** in C_6D_6 .

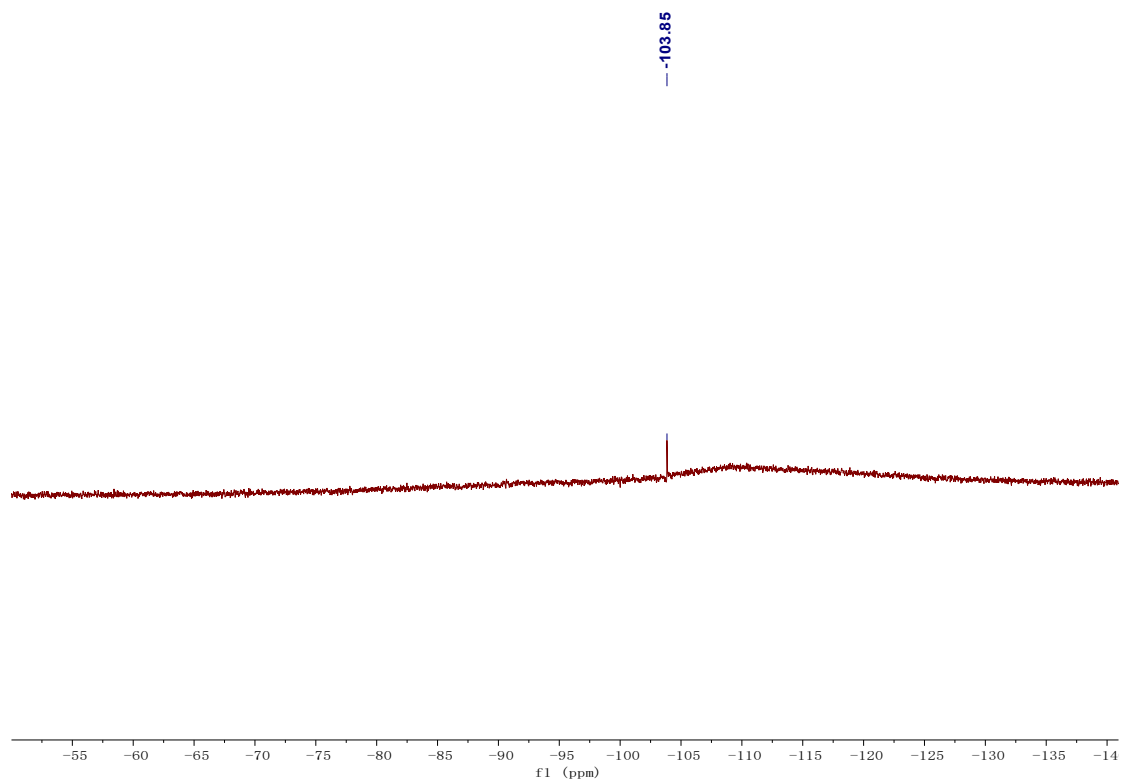


Figure S33. ^{29}Si NMR (99 MHz) spectrum of **4** in C_6D_6 .

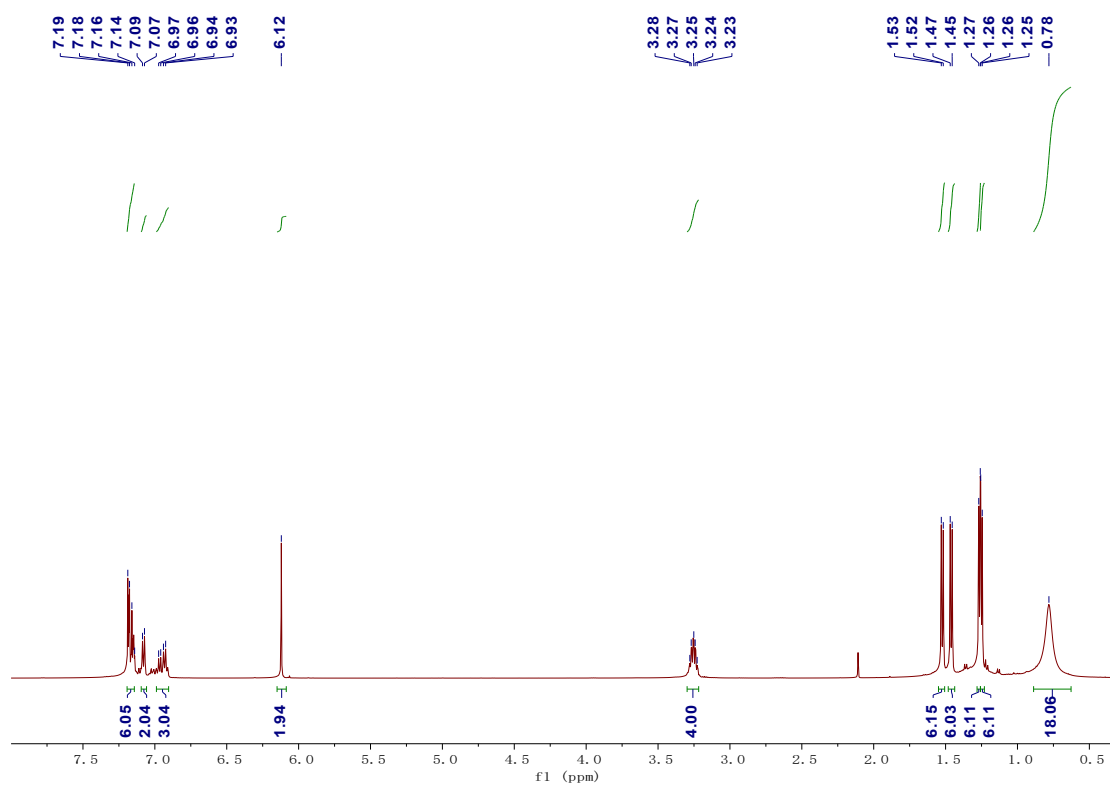


Figure S34. ^1H NMR (500 MHz) spectrum of **5** in C_6D_6 .

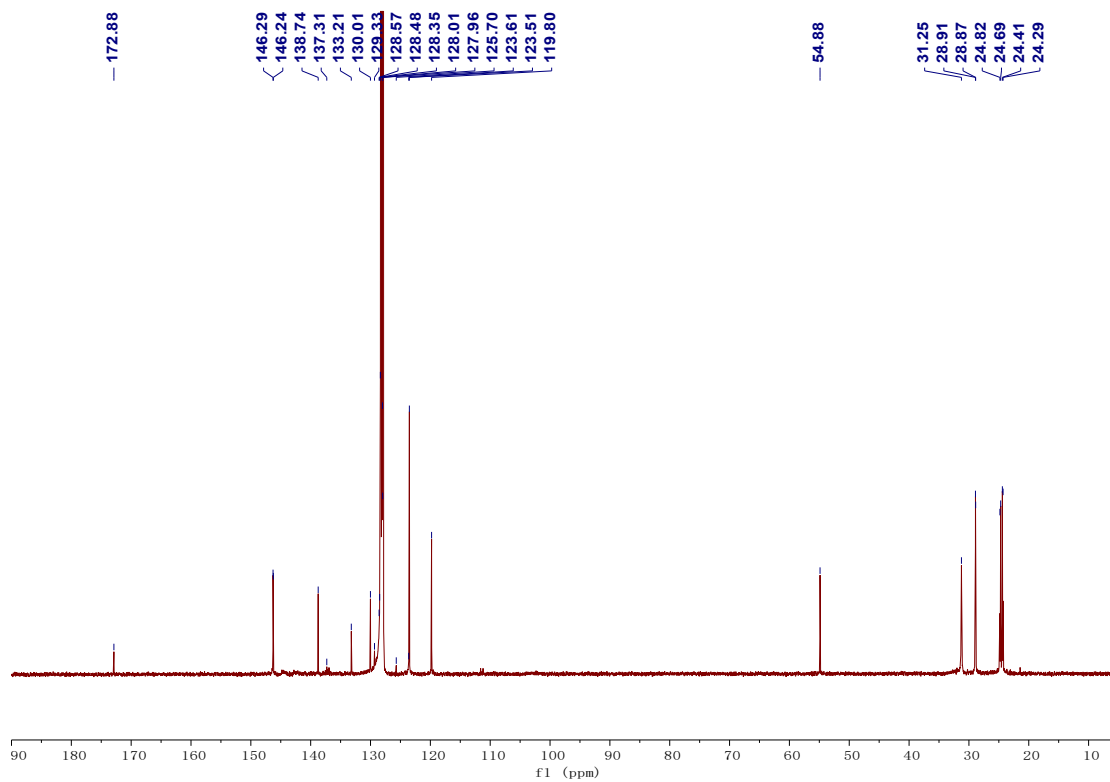


Figure S35. ^{13}C NMR (125 MHz) spectrum of **5** in C_6D_6 .

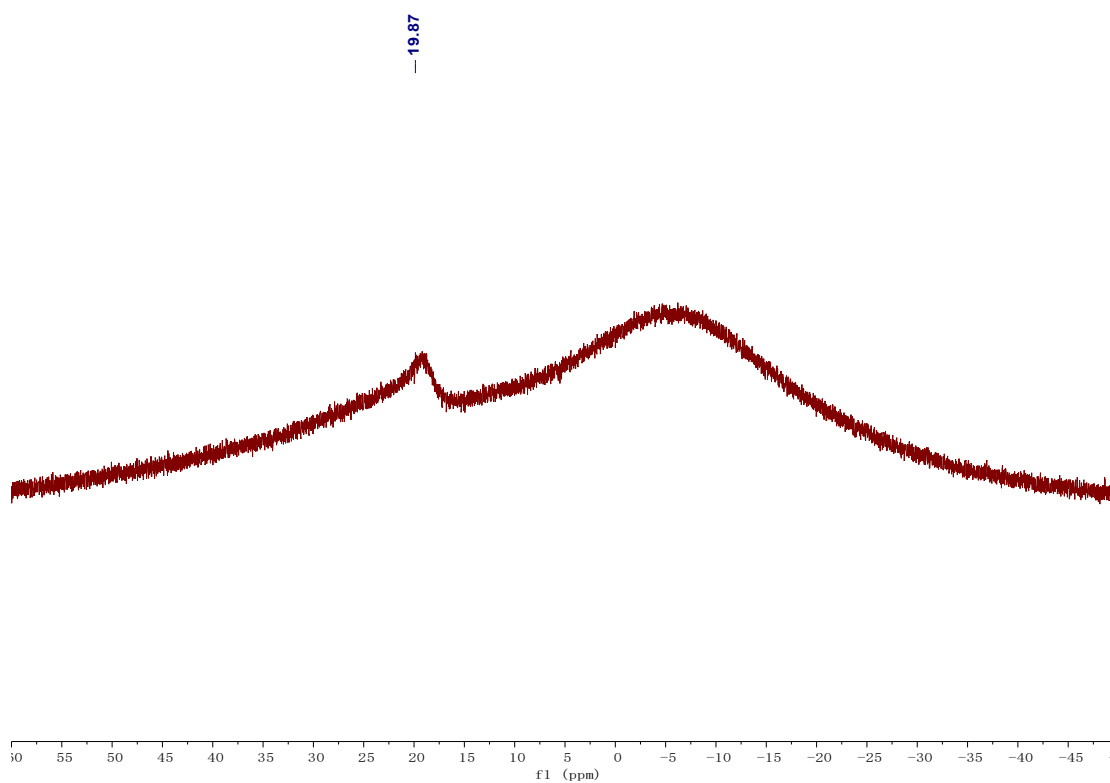


Figure S36. ^{11}B NMR (160 MHz) spectrum of **5** in C_6D_6 .

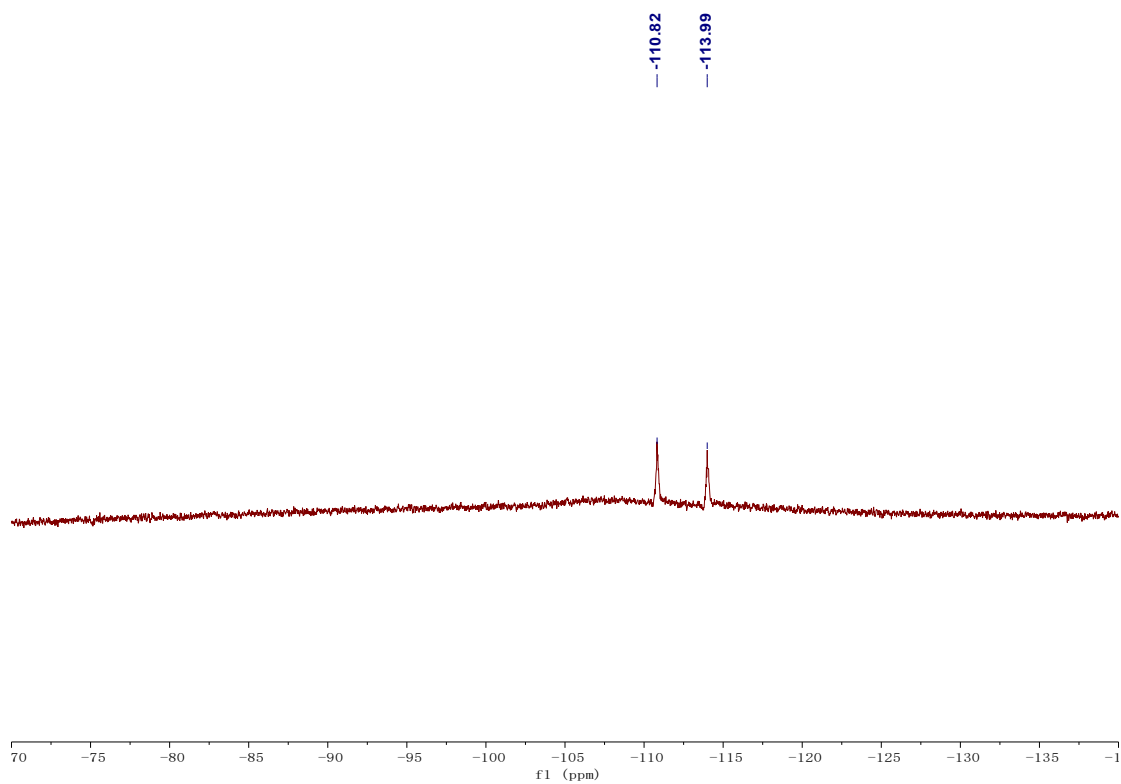


Figure S37. ^{29}Si NMR (99 MHz) spectrum of **5** in C_6D_6 .

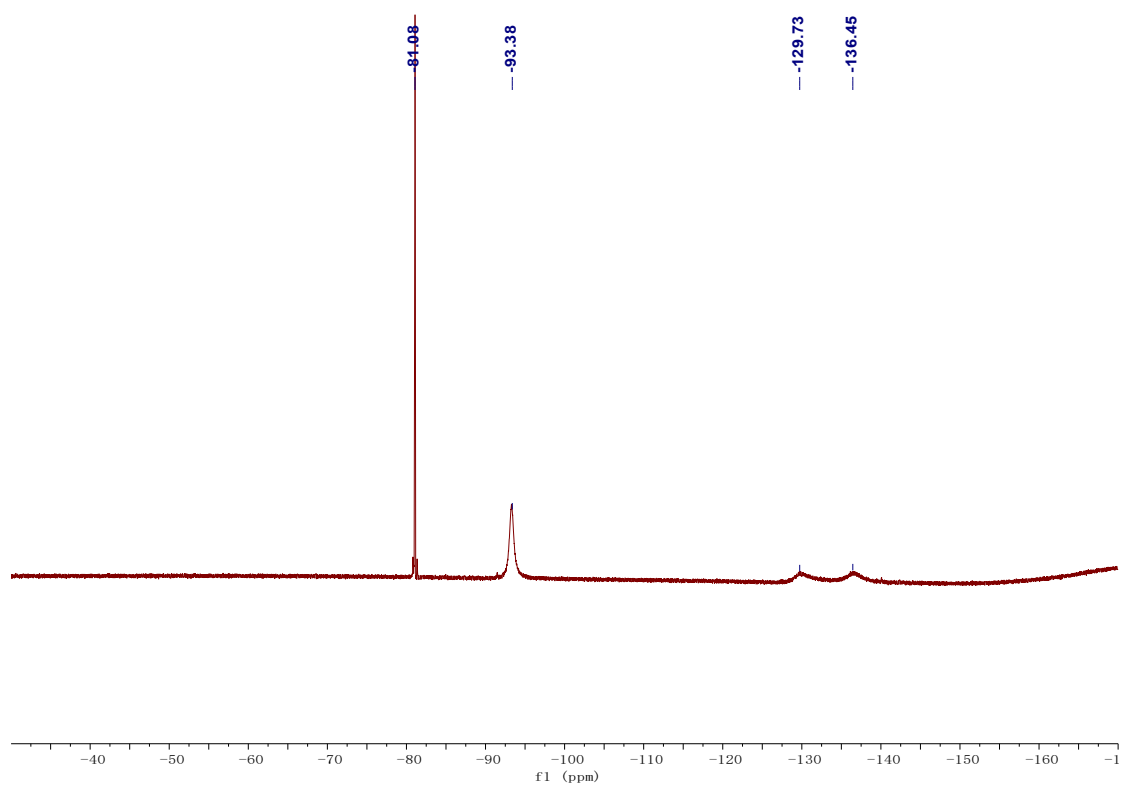


Figure S38. ^{19}F NMR (471 MHz) spectrum of **5** in C_6D_6 .

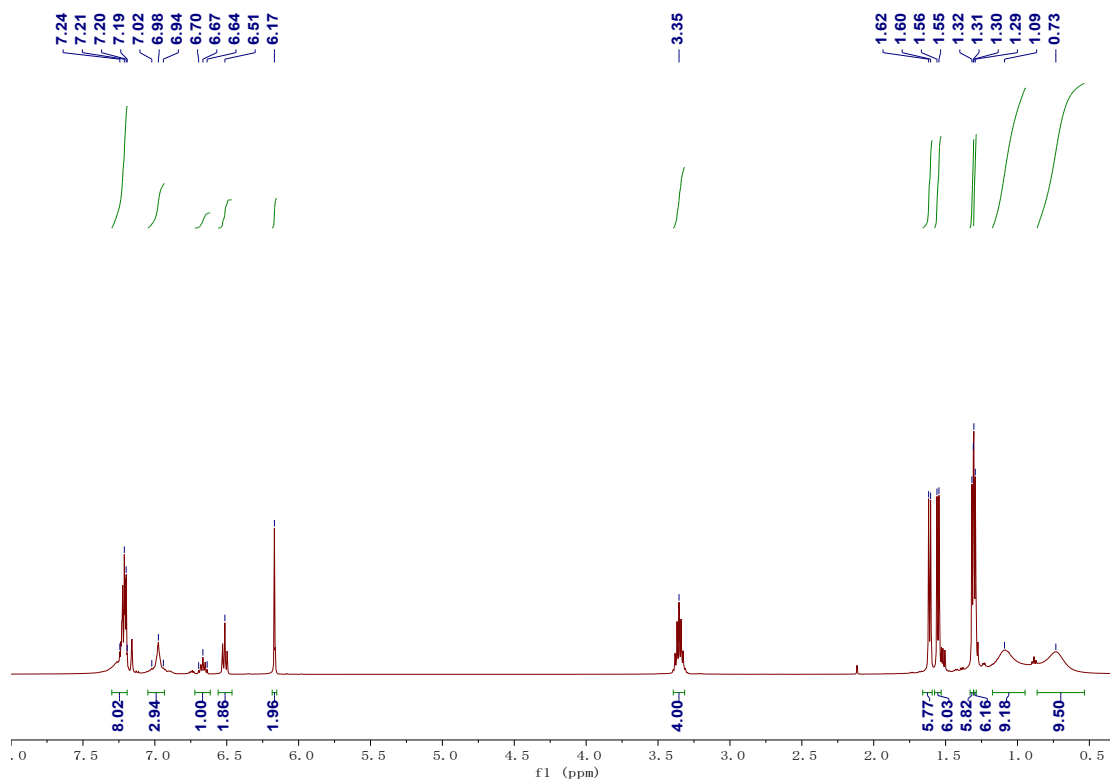


Figure S39. ^1H NMR (500 MHz) spectrum of **6** in C_6D_6 .

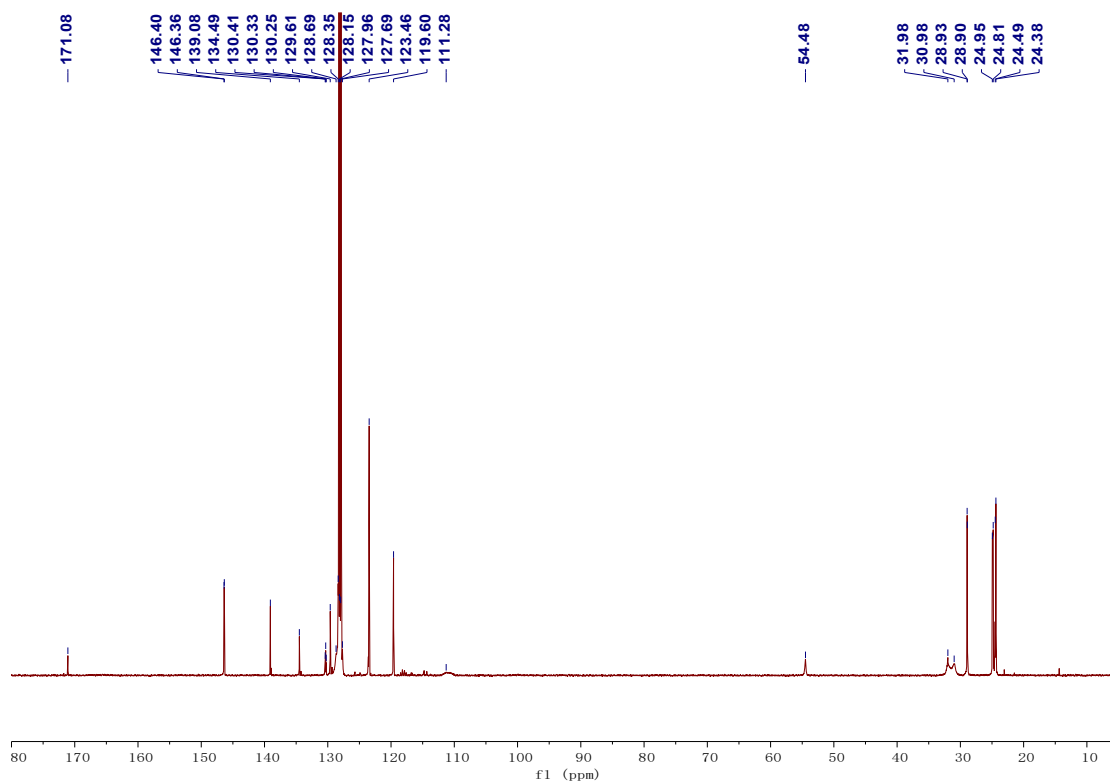


Figure S40. ^{13}C NMR (125 MHz) spectrum of **6** in C_6D_6 .

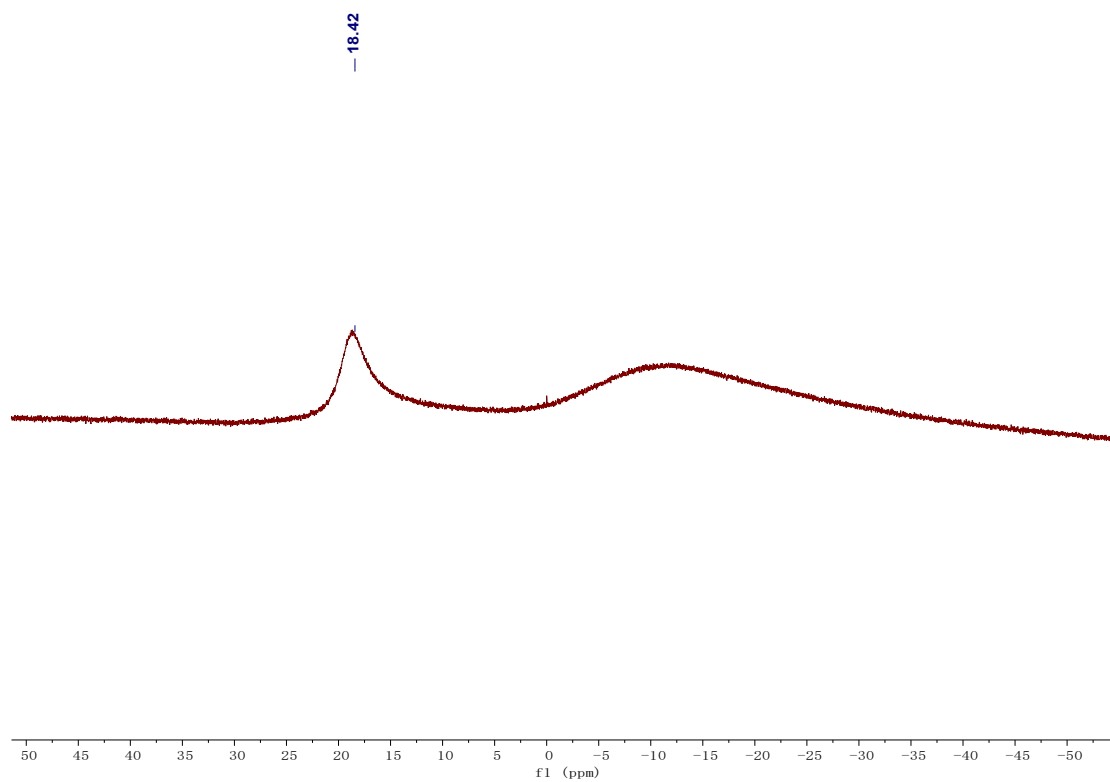


Figure S41. ^{11}B NMR (160 MHz) spectrum of **6** in C_6D_6 .

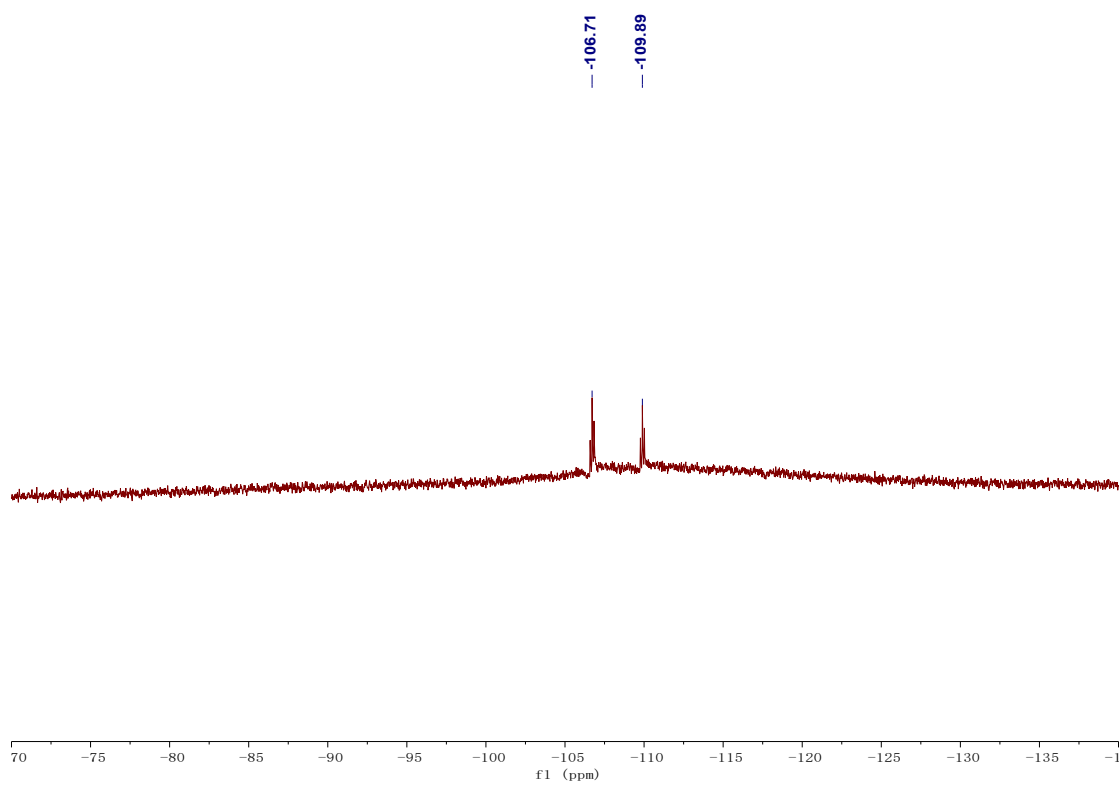


Figure S42. ^{29}Si NMR (99 MHz) spectrum of **6** in C_6D_6 .

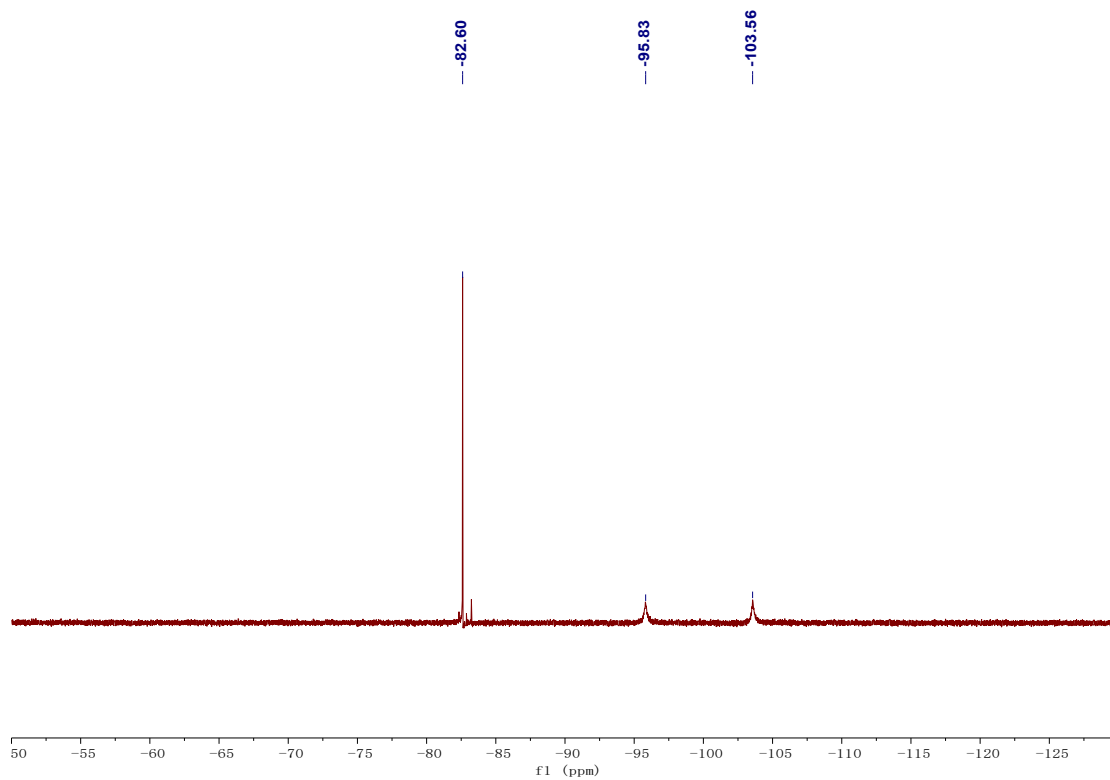


Figure S43. ^{19}F NMR (471 MHz) spectrum of **6** in C_6D_6 .