Supporting Information

A Self-Hydrosilylation of Phosphanylhydrosilylalkynes Promoted by $B(C_6F_5)_3$? An Experimental and Mechanistic Study

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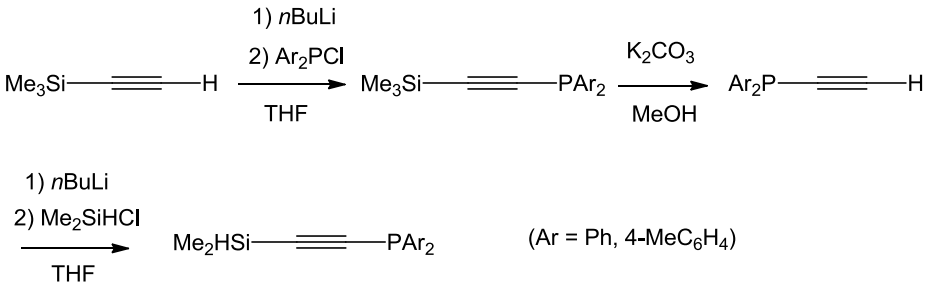
Content:

I. Experimental section

Materials and Methods All manipulations were carried out under dry argon or nitrogen atmosphere by using Schlenk line and glovebox techniques. Organic solvents as toluene, *n*-hexane and diethyl ether were dried by refluxing with sodium/potassium benzophenone under N_2 prior to use. NMR (^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P) spectra were recorded on Bruker Avance II 400 spectrometer. Melting point of compound was measured in a sealed glass tube using the Büchi-540 instrument. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercial reagents were purchased from Energy Chemical and J&K Chemical Co. and used as received. Compounds $(4\text{-}MeC_6H_4)_2PCl$,[S1] $Ph_2PC{\equiv}CH$,[S2] $(4\text{-}MeC_6H_4)_2PC{\equiv}CH$,[S3] and $B(C_6F_5)_3$[S4] were prepared by referencing to literatures.



Scheme S1 Preparation route for diarylphosphanylhydrosilylalkyne

Synthesis of $Ph_2PC{\equiv}CH$ At –78 ℃, *n*BuLi (25 mL of 2.4 M *n*-hexane solution, 60 mmol) was added dropwise to a stirring solution of $Me_3SiC{\equiv}CH$ (8.5 mL, 60.00 mmol) in Et_2O (100 mL). The mixture was left to warm to room temperature and then to keep stirring for an additional 1 h. This reaction mixture was cooled down to −78 ℃ again and to it Ph_2PCl (10.8 mL, 60 mmol) was added. The reaction solution was left to warm to room temperature. After additional stirring for 10 h, the suspension formed was filtrated to remove LiCl and the filtrate was evaporated to dryness. The residue was dissolved in MeOH (150 mL) and to it K_2CO_3 (16.6 g, 120 mmol) was added. The mixture was stirred at room temperature for 12 h. To it H_2O (50 mL) was added and separable organic and water solution phases were formed. The organic layer was collected together with the one extracted from the water phase by Et_2O (3 × 50 mL). All volatiles of the organic part were removed *in vacuo* and the crude product was purified by flash-chromatography (SiO_2 stuffing, V_{EtOAc} : V_{hexane} = 1:12). Finally, compound $Ph_2PC{\equiv}CH$ was obtained as an off-white powder after removal of the eluent solvents. Yield: 8.8 g (70%). The ^{1}H and ^{31}P NMR data of $Ph_2PC{\equiv}CH$ were measured for identification. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 3.25 (s, 1 H, ≡C*H*), 7.36 (m, 6 H), 7.62 (m, 4 H) (*Ph*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = –34.2.

Synthesis of $(4\text{-}MeC_6H_4)_2PC{\equiv}CH$ At –78 ℃, *n*BuLi (8.8 mL of 2.4 M *n*-hexane solution, 21.2 mmol) was added dropwise to a stirring solution of $Me_3SiC{\equiv}CH$ (1.2 mL, 21.2 mmol) in Et_2O (60 mL). The mixture was left to warm to room temperature and then to keep stirring for 1 h. This reaction mixture was cooled down to −78 °C again and to it a solution of $(4\text{-}MeC_6H_4)_2PCl$ (5.27 g, 21.2 mmol) in Et_2O (30 mL) was added. The reaction solution was left to warm to room temperature and then to keep stirring for another 10 h. The LiCl generated was filtered off and the filtrate was evaporated to dryness. The residue was

dissolved in MeOH (120 mL) and to it K_2CO_3 (5.86 g, 42.4 mmol) was added. After stirring at room temperature for 12 h, to it H_2O (50 mL) was added. The organic phase was collected together with the one extracted from the water phase by Et_2O (3 × 40 mL). All volatiles of the organic phase part were removed *in vacuo* and the crude product was purified by flash-chromatography (SiO_2 stuffing, V_{EtOAc} : V_{hexane} = 1:12). Finally, compound $(4\text{-}MeC_6H_4)_2PC{\equiv}CH$ was obtained as an off-white powder after removal of the eluent solvents. Yield: 2.83 g (56%). The ^1H and ^{31}P NMR data of $(4\text{-}MeC_6H_4)_2PC{\equiv}CH$ were measured for identification. ^1H NMR (400 MHz, C_6D_6, 298 K, ppm): δ = 1.99 (s, 6 H, *p-Me*), 2.73 (s, 1 H, ≡C*H*), 6.90 (m, 4 H), 7.63 (m, 4 H) (C_6H_4). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K, ppm): δ = –35.6.

Synthesis of $Me_2HSiC{\equiv}CPPh_2$ (1a) At –78 ℃, *n*BuLi (4.20 mL of 2.4 M *n*-hexane solution, 10.00 mmol) was added dropwise to a stirring solution of $Ph_2PC{\equiv}CH$ (2.10 g, 10.00 mmol) in Et_2O (60 mL). After the mixture was left to warm to room temperature and keep stirring for an additional 6 h, it was cooled again to –78 °C and to it a little excess of Me_2SiClH (1.14 mL, 10.80 mmol) was added. This mixture was left to warm to room temperature and keep stirring for an additional 12 h. The LiCl generated was filtered off and the filtrate was evaporated to dryness under reduced pressure, affording **1a** as colorless oil. Yield: 2.55 g (95%). ^1H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 0.46 (d, $^3J_{HH}$ = 3.8 Hz, 6 H, Si*Me*), 4.45 (ds, $^3J_{HH}$ = 3.8 Hz, J_{PH} = 1.2 Hz, 1 H, Si*H*), 7.46 (m, 6 H), 7.78 (m, 4 H) (*Ph*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = –3.0 (Si*Me*), 105.2 (d, J_{PC} = 14.9 Hz, P*C*≡), 113.5 (d, J_{PC} = 3.0 Hz, Si*C*≡), 128.7 (d, J_{PC} = 7.6 Hz), 129.1, 132.6 (d, J_{PC} = 21.1 Hz), 135.7 (d, J_{PC} = 6.1 Hz) (*Ph*). $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = –37.4. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = –32.5. IR (KBr plate, cm^{-1}): ν = 2010 (C≡C), 2142 (Si–H). Anal. calcd (%) for $C_{16}H_{17}PSi$ (M_r = 268.37): C, 71.61; H, 6.38. Found: C, 71.66; H, 6.40.

Synthesis of $Me_2HSiC{\equiv}CP(4\text{-}MeC_6H_4)_2$ (1b) At –78 ℃, *n*BuLi (3.30 mL of 2.4 M *n*-hexane solution, 8.0 mmol) was added dropwise to a stirring solution of $(4\text{-}MeC_6H_4)_2PC{\equiv}CH$ (1.91 g, 8.0 mmol) in Et_2O (50 mL). After the mixture was left to warm to room temperature and keep stirring for an additional 6 h, it was cooled again to –78 °C and to it Me_2SiClH (1.10 mL, 10.0 mmol) was added. This mixture was left to warm to room temperature and keep stirring for an additional 12 h. The LiCl generated was filtered off and the filtrate was evaporated to dryness under reduced pressure, affording **1b** as colorless oil. Yield: 2.18 g (92%). ^1H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 0.32 (d, $^3J_{HH}$ = 3.8 Hz, 6 H, Si*Me*), 2.35 (s, 6 H, *p-Me*), 4.26 (ds, 1 H, $^3J_{HH}$ = 3.8 Hz, J_{PH} = 1.2 Hz, Si*H*), 7.17 (m, 4 H), 7.50 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = –3.0 (Si*Me*), 21.3 (*p-Me*), 106.0 (d, J_{PC} =15.6 Hz, P*C*≡), 112.7 (d, J_{PC} =3.2 Hz, Si*C*≡), 129.5 (d, J_{PC} = 8.0 Hz), 132.5, 132.7, 139.0(C_6H_4). $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = –37.5. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = –34.4. IR (KBr plate, cm^{-1}): ν = 2099 (C≡C), 2141 (Si–H). Anal. calcd (%) for $C_{18}H_{21}PSi$ (M_r = 296.42): C, 72.94; H, 7.14. Found: C, 72.80; H, 7.09.

Synthesis of $[(E)\text{-}(C_6F_5)_3BCH{=}C(PPh_2)SiMe_2]_2$ (2a) and $(Z)\text{-}(C_6F_5)_2BCH{=}C(PPh_2)SiMe_2\text{-}(C_6F_5)$ (3a) At room temperature, a solution of **1a** (1.69 g, 6.30 mmol) in toluene (10 mL) was added dropwise to a solution of $B(C_6F_5)_3$ (3.22 g, 6.30 mmol) in toluene (40 mL). The mixture was stirred for 1.5 h, during which compound **2a** was precipitated. After collection of **2a** by filtration, the filtrate was concentrated (to ca. 4 mL) and to it *n*-hexane (6 mL) was added. The

solution was kept at –20 ℃ for 24 h, and colorless crystals of **3a** were formed. For compound **2a**, yield: 1.72 g (34% based on **1a**). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 0.0 (d, J_{PH} = 8.0 Hz, 6 H, Si*Me*), 7.32–7.37 (m, 4 H), 7.43–7.48 (m, 4 H) , 7.64–7.68 (m, 2 H) (*Ph*), 9.42 (d, J_{PH} = 46.7 Hz, 1 H, *H*C=). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –14.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –163.9 (m, 6 F, *m-F*), –158.1(m, 3 F, *p-F*), –128.4(m, 6 F, *o-F*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = 2.1. The ^{13}C and ^{29}Si NMR data were not obtained due to not good solublility of **2a**. Anal. calcd (%) for $C_{68}H_{34}B_2F_{30}P_2Si_2$ (M_r = 1560.69): C, 52.33; H, 2.20. Found: C, 52.12; H, 2.17. For compound **3a**, yield: 1.57 g (32% based on **1a**). Mp: 115 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 0.51 (s, 6 H, Si*Me*), 7.38–7.41 (m, 8 H), 7.50–7.53 (m, 2 H) (*Ph*), 9.07 (d, J_{PH} = 99.7 Hz , 1 H, *H*C=). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = –1.0 (Si*Me*), 125.3 (d, J_{PC} = 36.8 Hz, Si*C*=), 129.0 (d, J_{PC} =10.3 Hz), 132.1, 132.2 (d, J_{PC} =9.3 Hz), 141.1 (d, J_{PC} = 27.0 Hz)(*Ph*), 107.8 (m), 116.0 (br), 136.0 (br), 138.5 (br), 143.7 (br), 146.0 (br), 147.8 (br), 148.4 (br), 150.2 (br) (C_6F_5), 194.6 (br, B*C*=). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –4.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –163.4 (m, 4 F, *m*-F), –157.0 (m, 2 F, *p*-F), –130.2 (m, 4 F, *o*-F) (BC_6F_5), –160.5 (m, 2 F, *m*-F), –150.2 (m, 1 F, *p*-F), –125.7 (m, 2 F, *o*-F) (SiC_6F_5). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = –14.4. ^{31}P{^{1}H} NMR (162 MHz, CCl_3, 298 K, ppm): δ = 26.0. Anal. calcd (%) for $C_{34}H_{17}BF_{15}PSi$ (M_r = 780.35): C, 52.33; H, 2.20. Found: C, 52.37; H, 2.23. X-ray quality single-crystals of **2a** were obtained by mixing **1a** and $B(C_6F_5)_3$ in toluene undistubed at room temperature for10 h.

Synthesis of [(*E*)-$(C_6F_5)_3$BCH=C[P(4-Me$C_6H_4)_2$]SiMe$_2$ (2b) and (*Z*)-$(C_6F_5)_2$BCH=C-[P(4-Me$C_6H_4)_2$]SiMe$_2$(C_6F_5) (3b) At room temperature, a solution of **1b** (0.296 g, 1 mmol) in toluene (5 mL) was added dropwise to a solution of $B(C_6F_5)_3$ (0.512 g, 1 mmol) in toluene (8 mL). The mixture was stirred for 1.5 h, during which compound **2b** was precipitated. After collection of **2b** by filtration, the filtrate was concentrated (to ca. 2 mL) and to it *n*-hexane (4 mL) was added. The solution was kept at –20 ℃ for 24 h, and colorless crystals of **3b** were formed. For compound **2b**, yield: 0.26 g (32% based on **1b**). Mp: 199 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 0.0 (d, J_{PH} = 7.9 Hz, 6 H, Si*Me*), 2.45 (s, 6 H, *p-Me*), 7.23 (m, 4 H), 7.27 (m, 4 H)(C_6H_4), 9.32 (d, J_{PH} = 49.7 Hz, 1 H, *H*C=). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –14.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –164.2 (m, 6 F, *m-F*), –158.6(m, 3 F, *p-F*), –128.2(m, 6 F, *o-F*). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 298 K, ppm): δ = 1.5. The ^{13}C and ^{29}Si NMR data were not obtained due to not good solublility of **3a**. Anal. calcd (%) for $C_{72}H_{42}B_2F_{30}P_2Si_2$ (M_r = 1616.82): C, 53.49; H, 2.62. Found: C, 53.37; H, 2.53. For compound **3b**, yield: 0.24 g (30% based on **1b**). Mp: 132 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 0.49 (s, 6 H, Si*Me*), 2.38 (s, 6 H, *p-Me*), 7.16 (m, 4 H), 7.22 (m, 4 H) (C_6H_4), 9.00(d, J_{PH} = 98.7 Hz , 1 H, *H*C=). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = –0.9 (Si*Me*), 21.5 (*p-Me*), 121.9 (d, J_{PC} = 39.1 Hz, Si*C*=), 129.7 (d, J_{PC} =10.6 Hz), 132.1 (d, J_{PC} =9.7 Hz), 141.6 (d, J_{PC} =28.3 Hz), 142.8 (d, J_{PC} =2.8 Hz) (C_6H_4), 107.9 (m), 116.3 (br), 135.9 (br), 138.3 (br), 138.8 (br), 141.3 (br), 146.0 (br), 147.6 (br), 148.4 (br), 150.2 (br) (C_6F_5), 194.0 (br, B*C*=). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –4.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –163.6 (m, 4 F, *m*-F), –157.4 (m, 2 F, *p*-F), –130.2 (m, 4 F, *o*-F) (BC_6F_5), –160.9 (m, 2 F, *m*-F), –150.9 (m, 1 F, *p*-F), –125.7 (m, 2 F, *o*-F) (SiC_6F_5). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = –14.9. ^{31}P{^{1}H} NMR (162 MHz, CCl_3, 298 K, ppm): δ = 25.1. Anal. calcd (%) for $C_{36}H_{25}BF_{15}PSi$ (M_r = 808.41): C, 53.49; H,

2.62. Found: C, 53.13; H, 2.56. X-ray quality single-crystals of **2b** were obtained from the NMR tube in $CDCl_3$ undistubed at room temperature for 24 h.

Synthesis of [(*E*)-$(C_6F_5)_3$BCH=C(PHPh$_2$)Si(Me$_2$)]$_2$O (4) At room temperature, H_2O (0.002 g, 0.1 mmol) was added to a solution of **2a** (0.078 g, 0.05 mmol) in $CDCl_3$ (0.4 mL). The mixture was kept at room temperature. Two days later, colorless crystals of **4** were formed. Yield: 0.074 g (93%). Mp: 225 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = –0.32 (s, 6 H, Si*Me*), 7.43 (d, J_{PH} = 464.2 Hz, 1 H, P*H*), 7.43–7.48 (m, 4 H), 7.65–7.70 (m, 4 H), 7.80–7.84 (m, 2 H) (*Ph*), 8.71 (d, J_{PH} = 57.8 Hz , 1 H, *H*C=). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = 1.88 (Si*Me*), 117.0 (d, J_{PC} = 87.0 Hz), 130.7 (d, J_{PC} = 12.7 Hz), 133.9 (d, J_{PC} =10.1 Hz), 135.5 (*Ph*), 115.7 (m), 123.0 (br), 123.7 (br), 135.8 (br), 138.1 (br), 140.4 (br), 146.9 (br), 149.3 (br) (C_6F_5), 128.8 (d, J_{PC} = 81.8 Hz, Si*C*=), 209.5 (H*C*=). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –15.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –164.9 (m, 6 F, *m-F*), –159.6 (m, 3 F, *p-F*), –129.6 (m, 6 F, *o-F*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = 5.5. ^{31}P{^{1}H} NMR (162 MHz, CCl_3, 298 K, ppm): δ = 6.1. IR (KBr plate, cm^{-1}): ν = 1996 (P–H). Anal. calcd (%) for $C_{68}H_{34}B_2F_{30}OP_2Si_2$ (M_r = 1576.69): C, 51.80; H, 2.17. Found: C, 51.92; H, 2.16.

Synthesis of [$(C_6F_5)_3$BCH=CSi(Me$_2$)P(Ph$_2$)][C(Me)(Ph)O] (5) At room temperature, PhC(O)CH_3 (0.048 g, 0.4 mmol) was added to a solution of **2a** (0.318 g, 0.2 mmol) in pyridine (6 mL). After the mixture was kept stirring at room temperature for 5 h, the solvent was removed in vacuum and the residue was dissolved in toluene/*n*-hexane (2 mL/2 mL). The solution was kept at –20 ℃ for 24 h, and colorless crystals of **5** were formed. Yield: 0.30 g (82%). Mp: 229 ℃. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = –0.34 (s, 3 H), 0.38 (s, 3 H) (Si*Me*), 2.01 (d, J_{PH} = 14.6 Hz, 3 H, C*Me*), 6.80 (m, 2 H), 7.09 (m, 2 H), 7.31–7.42 (m, 5 H), 7.57–7.68 (m, 6 H), 7.80–7.84 (m, 1 H) (*Ph*), 8.96 (d, J_{PH} = 43.7 Hz, 1 H, *H*C=). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = –0.40, 1.35 (Si*Me*), 28.4 (d, J_{PH} = 10.1 Hz, C*Me*), 82.3 (d, J_{PC} = 55.5 Hz, *C*O), 118.1 (d, J_{PH} = 25.9 Hz, Si*C*=), 117.4 (d, J_{PC} = 34.6 Hz), 125.5, 128.4, 129.2 (d, J_{PC} = 3.2 Hz), 129.2 (d, J_{PC} = 7.9 Hz), 130.1 (d, J_{PC} = 11.8 Hz), 134.3 (d, J_{PC} = 2.5 Hz), 134.8 (d, J_{PC} = 8.4 Hz), 135.1 (d, J_{PC} = 3.2 Hz), 135.4 (d, J_{PC} = 8.8 Hz), 138.0, 139.7 (*Ph*), 118.3 (m), 118.6 (m), 138.4 (m), 140.4 (m), 147.2 (m), 149.5 (m) (br) (C_6F_5), 205.1 (H*C*=). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –15.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –164.9 (m, 6 F, *m-F*), –160.2 (m, 23 F, *p-F*), –130.6 (m, 6 F, *o-F*). ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = 19.4. ^{31}P{^{1}H} NMR (162 MHz, CCl_3, 298 K, ppm): δ = 32.3. Anal. calcd (%) for $C_{42}H_{25}BF_{15}OPSi$ (M_r = 900.51): C, 56.02; H, 2.80. Found: C, 56.11; H, 2.87.

Synthesis of {$(C_6F_5)_2$BCH=C[SiMe$_2$(C_6F_5)]P(Ph$_2$)}[C(Me)(Ph)O] (6) At room temperature, PhC(O)CH_3 (0.012 g, 0.1 mmol) was added to a solution of **3a** (0.078 g, 0.1 mmol) in $CDCl_3$ (0.4 mL). The mixture was kept at room temperature. Three days later, colorless crystals of **6** were formed. Yield: 0.085 g (94%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 0.23 (s, 3 H), 0.42 (s, 3 H) (Si*Me*), 1.97 (d, J_{PH} = 15.2 Hz, 3 H, C*Me*), 6.7 (m, 2 H), 7.14–7.26 (m, 6 H), 7.45–7.48 (m, 2 H), 7.56–7.72 (m, 5 H) (*Ph*), 9.46 (d, J_{PH} = 53.9 Hz, 1 H, *H*C=). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 298 K, ppm): δ = –0.35, 0.53 (Si*Me*), 26.1 (d, J_{PH} = 11.7 Hz, C*Me*), 79.9 (d, J_{PC} = 49.2 Hz, *C*O), 115.9 (d, J_{PH} = 41.3 Hz, Si*C*=), 116.5 (d, J_{PC} = 83.9 Hz), 122.3 (d, J_{PC} = 64.4 Hz), 126.8, 128.1 (d, J_{PC} = 12.0 Hz), 128.2 (d, J_{PC} = 3.7 Hz), 128.3 (d, J_{PC} = 2.4

Hz), 129.6 (d, J_{PC} = 10.6 Hz), 133.6 (d, J_{PC} = 8.4 Hz), 133.9 (d, J_{PC} = 2.9 Hz), 134.1 (d, J_{PC} = 3.0 Hz), 135.1 (d, J_{PC} = 8.2 Hz), 141.3 (*Ph*), 108.5 (m), 123.9 (br), 129.1 (m), 130.6 (m), 132.1 (m), 135.8 (br), 138.4 (br), 140.3 (br), 143.7 (br), 146.4 (br), 147.8 (br), 148.8 (br), 150.3 (br) (C_6F_5), 196.2 (H*C*=). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$, 298 K, ppm): δ = –3.5 (br). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 298 K, ppm): δ = –165.2 (m, 2 F, *m-F*), –164.4 (m, 2 F, *m-F*), –160.3 (m, 1 F, *p-F*), –159.3 (m, 1 F, *p-F*), –133.4 (m, 2 F, *o-F*), –132.2 (m, 2 F, *o-F*) (BC_6F_5), –160.7 (m, 2 F, *m-F*), –150.2 (m, 1 F, *p-F*), –125.2 (m, 2 F, *o-F*) (SiC_6F_5). $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$, 298 K, ppm): δ = –6.4. $^{31}P\{^1H\}$ NMR (162 MHz, CCl_3, 298 K, ppm): δ = –0.1. Anal. calcd (%) for $C_{42}H_{25}BF_{15}OPSi$ (M_r = 900.51): C, 56.02; H, 2.80. Found: C, 56.07; H, 2.88.

II. X-ray crystallographic details

X-ray Crystallographic Analysis Crystallographic data for compounds **2a**$_{0.5}$·toluene, **3a**, **4**·toluene and **6** were collected on an Oxford Gemini S Ultra system and for **2b**$_{0.5}$·1.25 $CHCl_3$, **3b** and **5** on a Rigaku Oxford Diffraction system. During measurements a graphite-monochromatic Cu-K_α radiation (λ = 1.54178 Å) was applied for **2a**$_{0.5}$·toluene, **2b**$_{0.5}$·1.25 $CHCl_3$, **3b**, **4**·toluene, **5** and **6** and the Mo-K_α radiation (λ = 0.71073 Å) was used for **3a**. Absorption corrections were all employed using the spherical harmonics program (multi-scan type). All the structures were solved by direct methods (SHELXS-97)[S5] and refined against F^2 using SHELXL-2014.[S6] In general, the non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using a riding mode with U_{iso} tied to the U_{iso} of the parent atoms unless otherwise specified. In **2b**$_{0.5}$·1.25 $CHCl_3$, one $CHCl_3$ was located in disorder and treated by the PART method, where final refinement gave two parts as C(38)H(38A)Cl(4)Cl(5)Cl(6) with occupation of 0.61941 and C(38A)H(38B)Cl(4A)Cl(5A)Cl(6A) with occupation of 0.39059. In **4**·toluene, one phenyl group in **4** was located in disorder and treated by the PART method, where final refinement gave two parts as C(5)C(6)C(7)C(8)C(9)C(10) with occupation of 0.74981 and C(5A)C(6A)C(7A)C(8A)C(9A)C(10A) with occupation of 0.25019. The toluene molecule was also located in disorder and treated by the PART method, where final refinement gave two parts by C(81)C(82)C(83)C(84)C(85)C(86)C(87) with occupation of 0.40813 and C(81A)C(82A)C(83A)C(84A)C(85A)C(86A)C(87A) with occupation of 0.59187. In addition, the PH hydrogen atom was added by Fourier synthesis and refined isotropically. A summary of cell parameters, data collection, and structure solution and refinements is given in Table S1.

Table S1 Crystal data and refinements

	2a$_{0.5}$ toluene	**2b**$_{0.5}$ ·1.25 $CHCl_3$	**3a**
CCDC	1865512	1865513	1865514
Empirical formula	$C_{41}H_{25}BF_{15}PSi$	$C_{37.25}H_{22.25}BCl_{3.75}F_{15}PSi$	$C_{34}H_{17}BF_{15}PSi$
formula weight	872.48	957.61	780.35
crystal system	Triclinic	Orthorhombic	Triclinic
space group	*P*–1	*Fdd*2	*P*–1
a/Å	11.2183(9)	35.6477(3)	9.9289(5)
b/Å	12.6268(11)	36.9030(3)	12.0268(6)
c/Å	15.4800(15)	12.09680(10)	14.7530(7)
α/deg	66.773(9)	90.00	76.372(4)
β/deg	70.324(8)	90.00	79.509(4)
γ/deg	71.966(7)	90.00	69.177(5)
V/Å^3	1857.4(3)	15913.4(2)	1590.87(14)
Z	2	16	2
ρ_{calcd}/g·cm^{-3}	1.560	1.599	1.629
μ/mm^{-1}	1.945	4.135	0.239
F(000)	880	7656	780
crystal size/mm^3	0.20 ×0.20 ×0.10	0.20 ×0.05 ×0.18	0.20 ×0.20 ×0.20
θ range/deg	3.20–62.09	3.45–73.93	3.05–26.50
index ranges	$-12 \le h \le 11$	$-42 \le h \le 44$	$-12 \le h \le 12$
	$-14 \le k \le 13$	$-43 \le k \le 44$	$-14 \le k \le 15$
	$-17 \le l \le 15$	$-10 \le l \le 14$	$-16 \le l \le 18$
collected data	10778	39637	12279
unique data	5758 (R_{int} = 0.0367)	5815 (R_{int} = 0.0349)	6587 (R_{int} = 0.0244)
completeness to *θ*	98.5	98.1	99.8
data/restraints/parameters	5758/0/535	5815/223/600	6587/0/471
GOF on F^2	1.035	1.047	1.040
final *R* indices [$I > 2$ (*I*)]	R_1 = 0.0410 wR_2 = 0.0930	R_1 = 0.0428 wR_2 = 0.1225	R_1 = 0.0391 wR_2 = 0.0823
R indices (all data)	R_1 = 0.0560 wR_2 = 0.1044	R_1 = 0.0435 wR_2 = 0.1235	R_1 = 0.0482 wR_2 = 0.0864
Largest diff peak/hole (e·Å^{-3})	0.288/–0.241	0.944/–0.296	0.280/–0.281

[a] $R_1 = \sum(||F_o|-|F_c||)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)]^{1/2}$, GOF = $[\sum w(F_o^2-F_c^2)^2/(N_o-N_p)]^{1/2}$.

(to be continued)

	3b	**4** toluene
CCDC	1865515	1865516
Empirical formula	$C_{36}H_{21}BF_{15}PSi$	$C_{75}H_{44}B_2F_{30}OP_2Si_2$
formula weight	808.40	1670.84
crystal system	Triclinic	Triclinic
space group	*P*–1	*P*–1
a/Å	11.5534(49)	11.0069(12)
b/Å	11.9238(5)	11.1895(10)
c/Å	13.8924(3)	29.9621(15)
α/deg	88.901(9)	80.938(6)
β/deg	73.743(8)	87.066(7)
γ/deg	69.443(7)	89.252(8)
V/Å^3	1717.94(10)	3639.3(5)
Z	2	2
ρ_{calcd}/g·cm^{-3}	1.563	1.525
μ/mm^{-1}	2.050	1.967
F(000)	812	1680
crystal size/mm^3	0.3×0.20×0.10	0.60×0.40×0.20
θ range/deg	3.96–70.00	2.99–62.65
index ranges	$-13 \le h \le 14$	$-8 \le h \le 11$
	$-13 \le k \le 14$	$-11 \le k \le 11$
	$-16 \le l \le 16$	$-29 \le l \le 31$
collected data	17258	21959
unique data	6299 (R_{int} = 0.0377)	11277 (R_{int} = 0.1020)
completeness to *θ*	96.7	96.8
data/restraints/parameters	6299/0/491	11277/990/1079
GOF on F^2	1.069	1.233
final *R* indices [$I > 2$ (*I*)]	R_1 = 0.0611 wR_2 = 0.1837	R_1 = 0.1258 wR_2 = 0.3366
R indices (all data)	R_1 = 0.0657 wR_2 = 0.1905	R_1 = 0.1695 wR_2 = 0.4107
Largest diff peak/hole (e·Å^{-3})	1.22/–0.671	0.867/–0.704

[a] $R_1 = \sum(||F_o|-|F_c||)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)]^{1/2}$, GOF = $[\sum w(F_o^2-F_c^2)^2/(N_o-N_p)]^{1/2}$.

(to be continued)

	5	**6**
CCDC	1883080	1865517
Empirical formula	$C_{49}H_{33}BF_{15}OPSi$	$C_{42}H_{25}BF_{15}OPSi$
formula weight	992.62	900.51
crystal system	monoclinic	monoclinic
space group	*P*2(1)/*c*	*C*2/*c*
a/Å	12.6405(1)	36.7083(8)
b/Å	14.6125(1)	11.2563(2)
c/Å	24.3671(2)	18.6415(4)
α/deg	90	90
β/deg	102.702(2)	98.690(2)
γ/deg	90	90
V/Å^3	4390.68(6)	7614.2(3)
Z	4	8
ρ_{calcd}/g·cm^{-3}	1.502	1.571
μ/mm^{-1}	1.739	1.939
F(000)	2016	3632
crystal size/mm^3	0.20×0.20×0.20	0.26×0.24×0.21
θ range/deg	3.55–68.99	4.11–62.15
index ranges	$-15 \le h \le 14$	$-38 \le h \le 41$
	$-13 \le k \le 17$	$-12 \le k \le 12$
	$-29 \le l \le 29$	$-18 \le l \le 21$
collected data	29362	11905
unique data	8013 (R_{int} = 0.0176)	5940 (R_{int} = 0.0202)
completeness to *θ*	98.0	98.9
data/restraints/parameters	8013/0/617	5940/0/553
GOF on F^2	1.026	1.026
final *R* indices [$I > 2$ (*I*)]	R_1 = 0.0288 wR_2 = 0.0729	R_1 = 0.0321 wR_2 = 0.0856
R indices (all data)	R_1 = 0.0311 wR_2 = 0.0740	R_1 = 0.0349 wR_2 = 0.0883
Largest diff peak/hole (e·Å^{-3})	0.326/–0.328	0.302/–0.303

[a] $R_1 = \sum(||F_o|-|F_c||)/\sum|F_o|$, $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)]^{1/2}$, GOF = $[\sum w(F_o^2-F_c^2)^2/(N_o-N_p)]^{1/2}$.

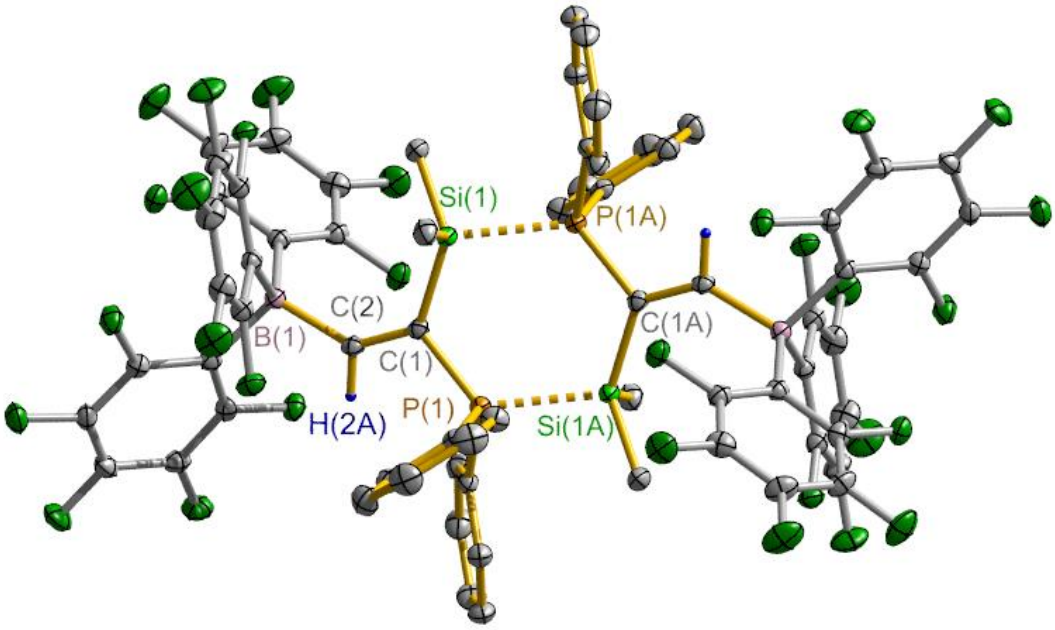


Figure S1 X-ray crystal structure of **2a** with thermal ellipsoids at 30% probability level. H atoms except for those of HC= are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.343(4), C(1)–Si(1) 1.882(2), C(1)–P(1) 1.821(2), C(2)–B(1) 1.653(4), Si(1)–P(1A) 2.323(1); Si(1)–C(1)–P(1) 114.91(13), Si(1)–C(1)–C(2) 127.48(19), C(2)–C(1)–P(1) 116.52(19), B(1)–C(2)–C(1) 133.7(2) (A: symmetry for -x, -y+1, -z+1).

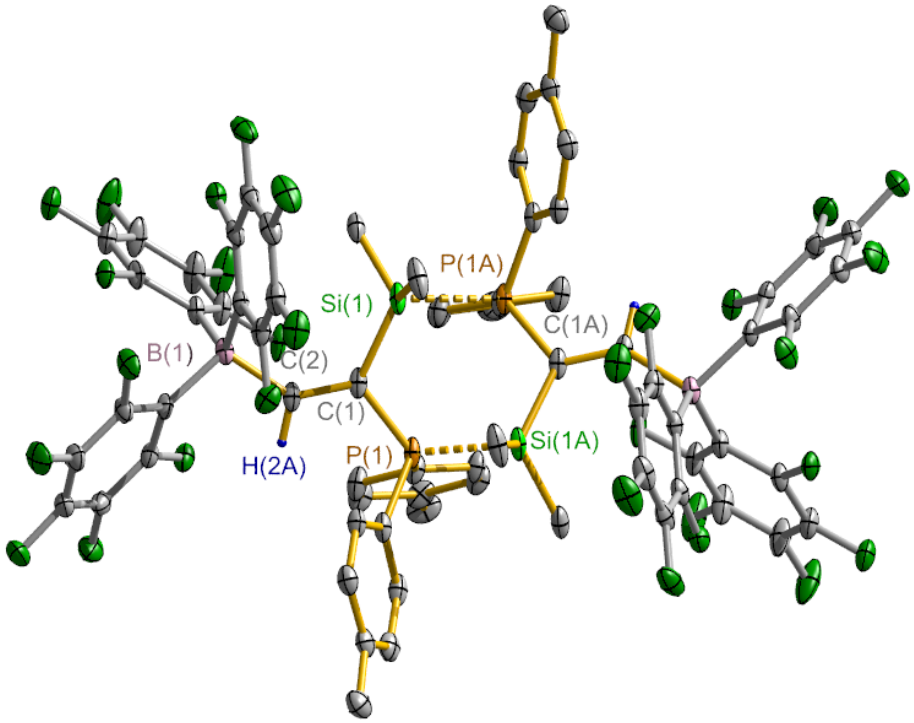


Figure S2 X-ray crystal structure of **2b** with thermal ellipsoids at 30% probability level. H atoms except for those of the HC= are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.361(4), C(2)–B(1) 1.655(4), C(1)–P(1) 1.806(3), C(1)–Si(1) 1.884(3), Si(1)–P(1A) 2.314(1); C(1)–C(2)–B(1) 133.9(3), C(2)–C(1)–P(1) 116.2(3)，C(2)–C(1)–Si(1) 126.1(2), Si(1)–C(1)–P(1) 117.70(15) (A: symmetry for -x, -y, z).

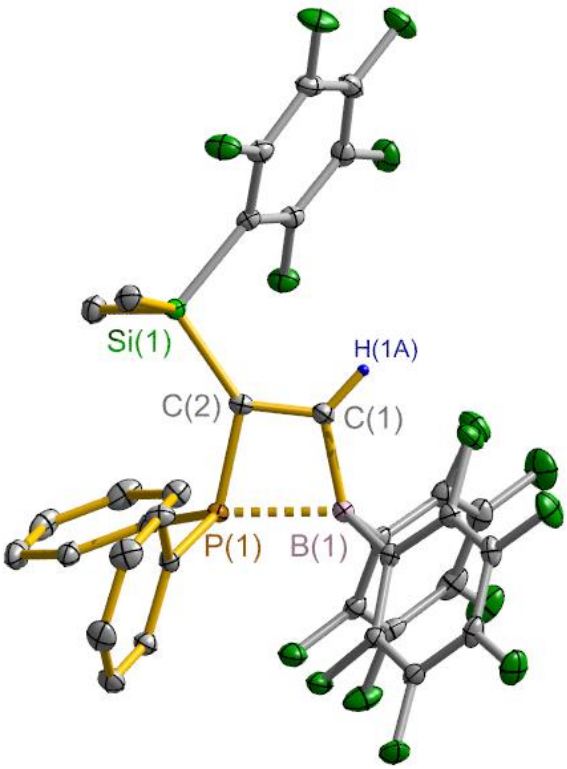


Figure S3 X-ray crystal structures of **3a** with thermal ellipsoids at 30% probability level. H atoms except for that of HC= are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.354(2), C(1)–B(1) 1.625(3), C(2)–Si(1) 1.8757(18), C(2)–P(1) 1.8030(17), P(1)–B(1) 2.038(2); B(1)–C(1)–C(2) 108.73(15), C(1)–C(2)–Si(1) 131.12(13), Si(1)–C(2)–P(1) 133.38(10), P(1)–C(2)–C(1) 94.62(12).

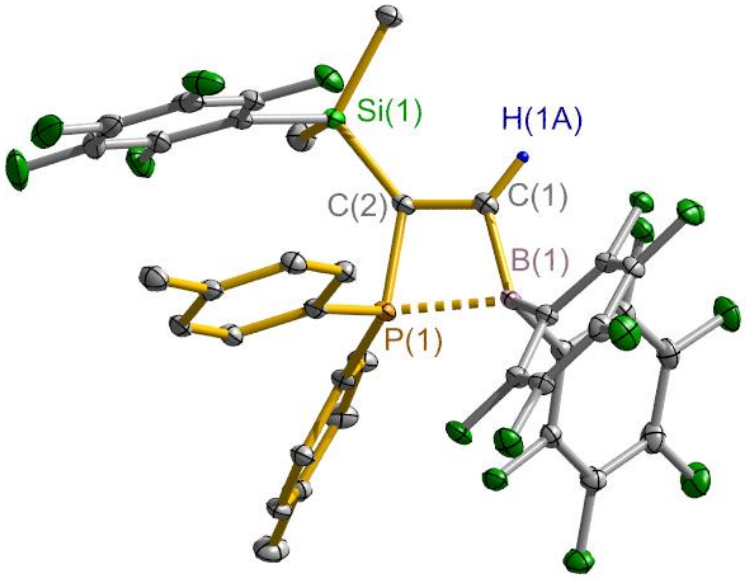


Figure S4 X-ray crystal structure of **3b** with thermal ellipsoids at 30% probability level. H atoms except for that of the HC= are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.356(4), C(1)–B(1) 1.631(4), C(2)–P(1) 1.805(2), P(1)–B(1) 2.030(3); C(1)–C(2)–P(1) 94.85(17), C(2)–P(1)–B(1) 77.86(11), P(1)–B(1)–C(1) 78.95(14), B(1)–C(1)–C(2) 107.6(2).

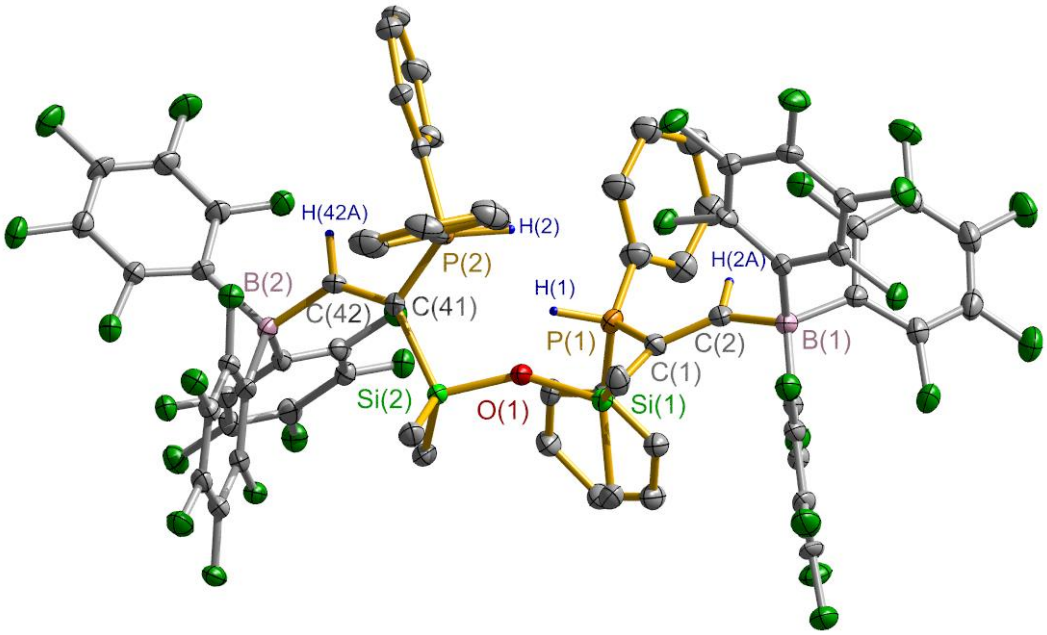


Figure S5 X-ray crystal structure of **4** with thermal ellipsoids at 20% probability level. H atoms except for those of =CH and PH are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.346(12), C(1)–B(1) 1.633(12), C(2)–Si(1) 1.896(8), C(2)–P(1) 1.802(8), Si(1)–O(1) 1.636(6), P(1)–H(2) 1.291(5); C(1)–C(2)–Si(1) 131.9(6), C(1)–C(2)–P(1) 114.4(6), B(1)–C(1)–C(2) 131.9(7), P(1)–C(2)–Si(1) 113.7(4), C(2)–Si(1)–O(1) 102.5(3), Si(1)–O(1) –Si(1A) 148.0(4).

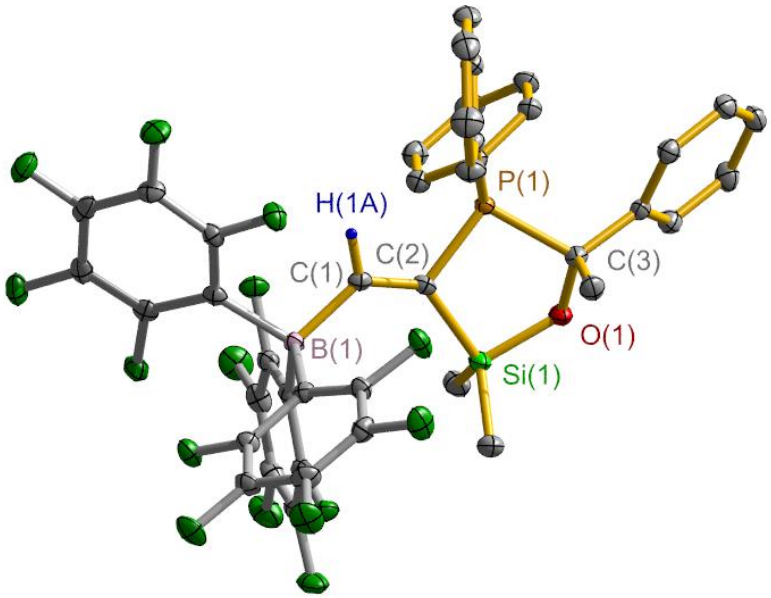


Figure S6 X-ray crystal structure of **5** with thermal ellipsoids at 50% probability level. H atoms except for that of the HC= are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.347(2), C(1)–B(1) 1.642(2), C(2)–Si(1) 1.891(1), C(2)–P(1) 1.798(1), P(1)–C(3) 1.883(1), O(1)–C(3) 1.424(2), O(1)–Si(1) 1.681(1); Si(1)–C(2)–P(1) 104.21(7), C(2)–P(1)–C(3) 98.13(3)，P(1)–C(3)–O(1) 100.33(8), C(3)–O(1)–Si(1) 119.63(8), O(1)–Si(1)–C(2) 97.19(5).

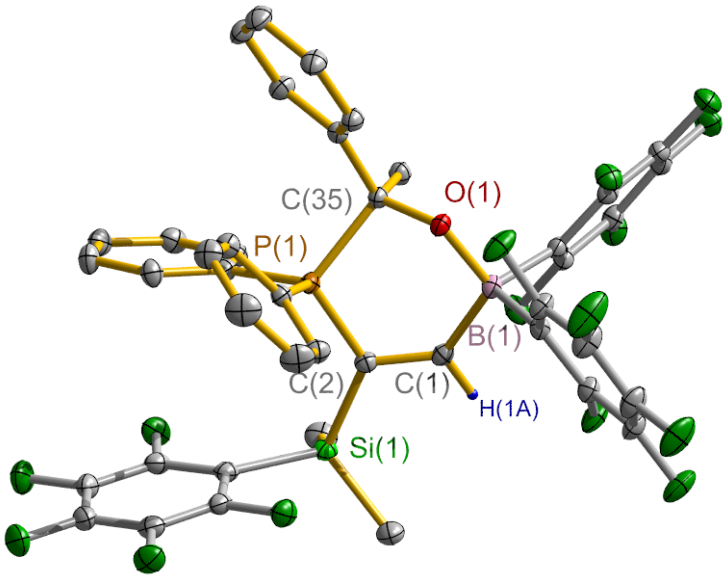


Figure S7 X-ray crystal structure of **6** with thermal ellipsoids at 30% probability level. H atoms except for that of the HC= are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.347(2), C(1)–B(1) 1.615(2), C(2)–Si(1) 1.880(2), C(2)–P(1) 1.787(2), P(1)–C(35) 1.891(2), O(1)–C(35) 1.408(2), O(1)–B(1) 1.493(2); C(1)–C(2)–P(1) 115.93(12), C(2)–P(1)–C(35) 105.23(7)，P(1)–C(35)–O(1) 101.93(10), C(35)–O(1)–B(1) 120.39(12), O(1)–B(1)–C(1) 111.82(13), B(1)–C(1)–C(2) 128.40(15).

III. Variable-temperature study on reaction of 1a and $B(C_6F_5)_3$.

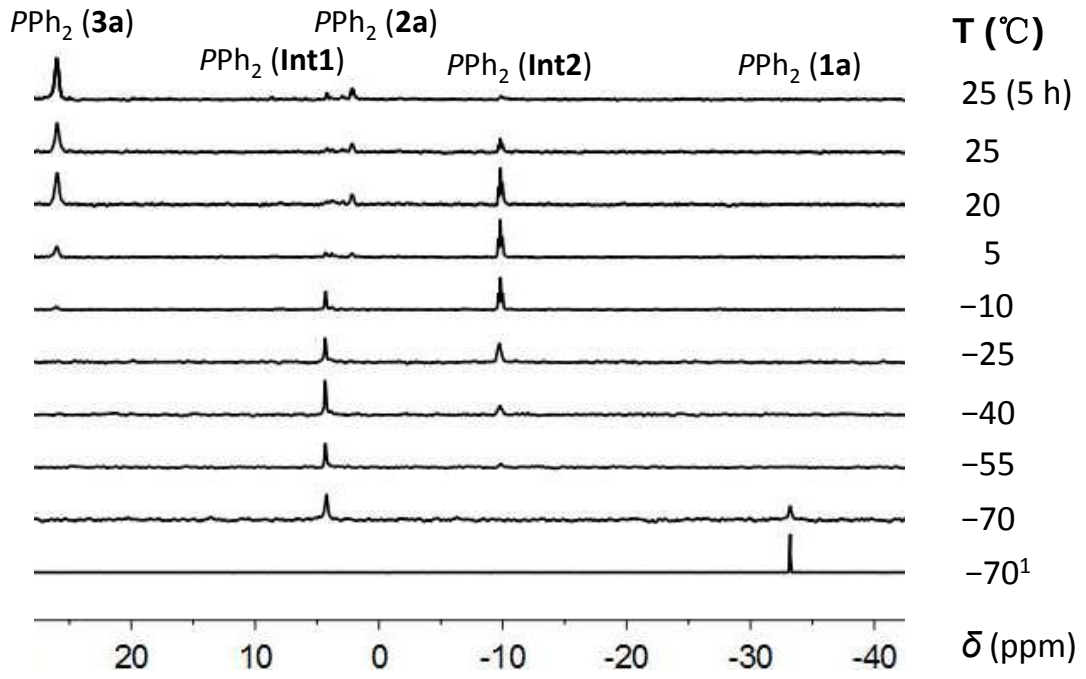


Figure S8 ^{31}P NMR spectra-recorded variable-temperature (from –70 to 25 ℃) reaction of **1a** and $B(C_6F_5)_3$ in $CDCl_3$. Exhibition of much lower integral intensity for the PPh_2 of **2a** than that of **3a** is due to precipitation of majority of the former from the reaction solution. [1]Data for **1a** at –70 ℃ before addition of $B(C_6F_5)_3$.

IV. Collected ^{1}H, ^{13}C, ^{11}B, ^{29}Si and ^{31}P NMR data for the enhanced functionalities.

Table S2. Summarized ^{1}H, ^{13}C, ^{11}B, ^{29}Si and ^{31}P NMR data for the functionalities contained in compounds **1a–6** (δ, ppm; J, Hz; in $CDCl_3$, at room temperature)

Comp.	^{11}B	^{29}Si	^{31}P	^{1}H			^{13}C	
				Si*H*	*H*C=	P*H*	P*C*≡, Si*C*≡	P*C*=, B*C*=
1a	-	–37.4	–32.5	4.45 (J_{HH} = 3.8, J_{PH} = 1.2)	-	-	105.2 (J_{PC} = 14.9), 113.5	-
1b	-	–37.5	–34.4	4.26 (J_{HH} = 3.8, J_{PH} = 1.2)	-	-	106.0 (J_{PC} = 15.6), 112.7 (J_{PC} = 3.2)	-
2a	–14.8	not obtained[1]	2.1	-	9.42 (J_{PH} = 46.7)	-	-	not obtained[1]
2b	–14.9	not obtained[1]	1.5	-	9.32 (J_{PH} = 49.7)	-	-	not obtained[1]
3a	–4.4	–14.4	26.0	-	9.07 (J_{PH} = 99.7)	-	-	125.33 (J_{PC} = 36.8), 194.6 (br)
3b	–4.3		25.1	-	9.00 (J_{PH} = 98.7)	-	-	121.9 (J_{PC} = 39.1), 194.0 (br)
4	–15.3	5.5	6.1	-	8.71 (J_{PH} = 57.8)	7.43 (J_{PH} = 464.2 Hz)	-	117.0 (J_{PC} = 84.3), 209.5 (br)
5	-15.2	19.4	32.3		8.96 (J_{PH} = 43.1)			118.1 (J_{PC} = 25.9), 205.1(br)
6	–3.5	–6.4	–0.1	-	9.46 (J_{PH} = 53.9)	-	-	115.9 (J_{PC} = 41.3), 196.2(br)

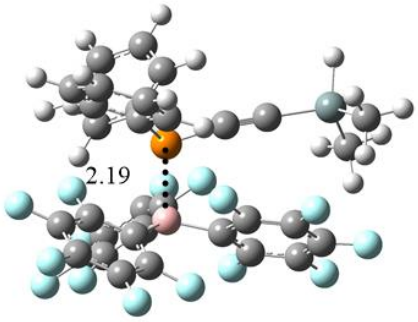
[1] Due to not good solubitlity of both **2a** and **2b**, the ^{13}C and ^{29}Si NMR data for them were not obtained.

Table S3. Summarized ^{19}F NMR data for the C_6F_5 group contained in compounds **2a–6** (δ, ppm in $CDCl_3$)

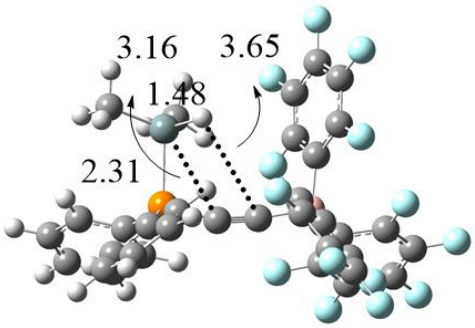
Comp.	^{19}F	
	BC_6F_5	SiC_6F_5
2a	–128.4 (*o*-*F*), –158.1 (*p*-*F*), –163.9 (*m*-*F*)	-
2b	−128.2(*o*-*F*), −158.6 (*p*-*F*), −164.2 (*m*-*F*)	-
3a	–130.0 (*o*-*F*), –157.0 (*p*-*F*), –163.4 (*m*-*F*)	–125.7 (*o*-*F*), –150.2 (*p*-*F*), –160.5 (*m*-*F*)
3b	−130.2 (*o*-*F*), −157.4(*p*-*F*), −163.6 (*m*-*F*)	−125.7 (*o*-*F*), −150.9 (*p*-*F*), −160.9 (*m*-*F*)
4	–129.6 (*o*-*F*), –159.6 (*p*-*F*), –164.9 (*m*-*F*)	-
5	–130.6 (*o*-*F*), –160.2 (*p*-*F*), –164.9 (*m*-*F*)	-
6	–132.2 (*o*-*F*), –133.4 (*o*-*F*), –159.3 (*p*-*F*), –160.3 (*o*-*F*), –164.4 (*m*-*F*), –165.2 (*o*-*F*)	–125.2 (*o*-*F*), –150.2 (*p*-*F*), –160.7 (*m*-*F*)

V. Theoretical calculations

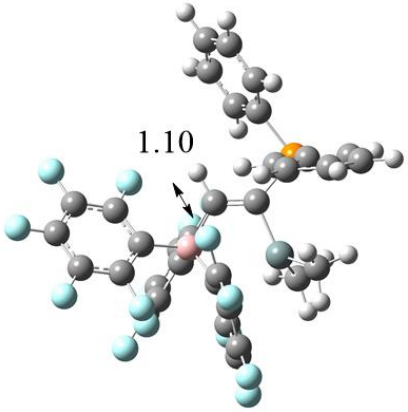
Methods: In this work, geometry optimizations were carried out without any symmetry restriction by means of density functional theory with the M06-2X functional. This functional used in this work is due to the fact that it has good performance for the fields concerning thermochemistry, kinetics, and non-covalent interactions (such as van der Waals interactions) in main group elements.[S7] The basis sets with split valence polarization (def2-SVP)[S8] from Ahlrichs and coworkers was applied for all atoms. The Berny analytical gradient optimization method using GEDIIS[S9] as implemented in the Gaussian09 program[S10] was employed in geometry optimization steps. Harmonic vibrational frequency calculations were performed on all structures to verify the nature of the stationary points located on the potential energy surface. That is, the local minimum (no imaginary frequencies) and the transition state (one imaginary frequency). The normal modes corresponding to the imaginary frequencies in the transition state structures are related to the vibrations of new forming bonds. In the free energy profile, we report ΔG (the Gibbs free energies) at 298.15 K and 1 atm. The solvation model (SMD) was performed to take solvation effects into account. All of these computations employed the triple zeta def2-TZVP basis set and use the optimized geometries obtained at M06-2X/def2-SVP level.



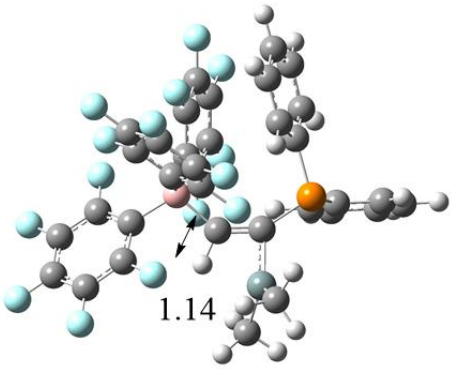
Int1



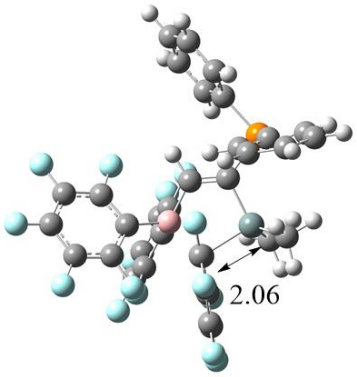
Int2



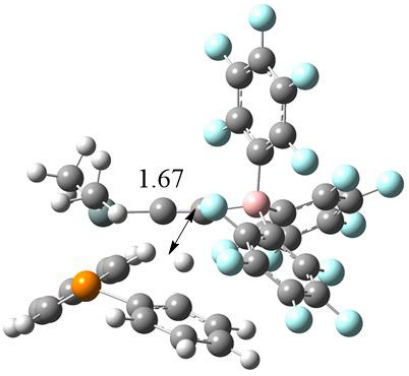
Int3



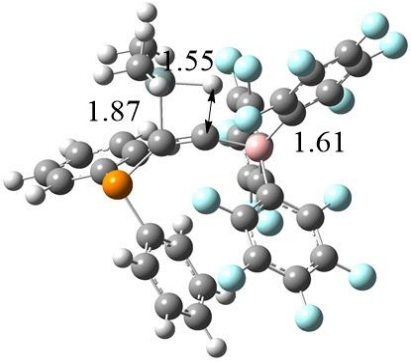
Int4



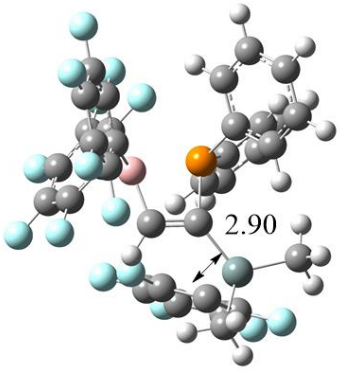
2a’



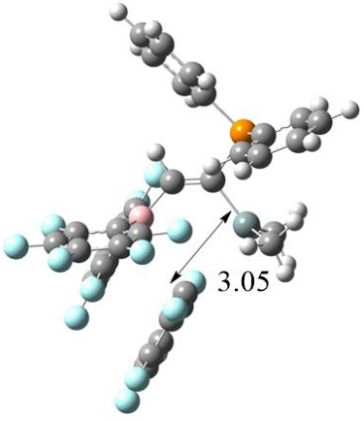
TS1



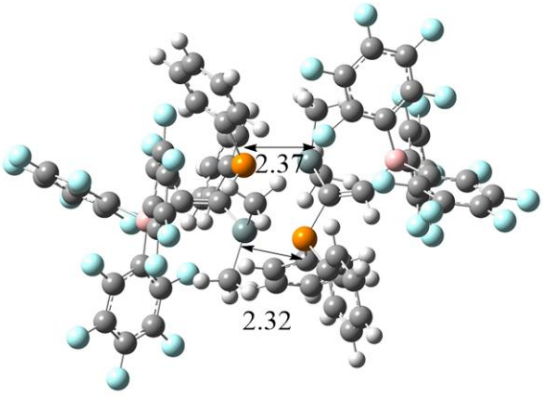
TS2



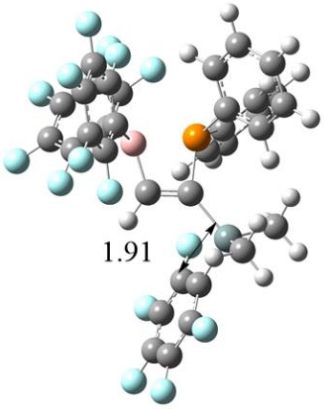
TS3



TS4



2a



3a

Figure S9 Optimized geometries for the intermediates, transition states, and products computed at the M06-2X/def2-SVP level of theory.

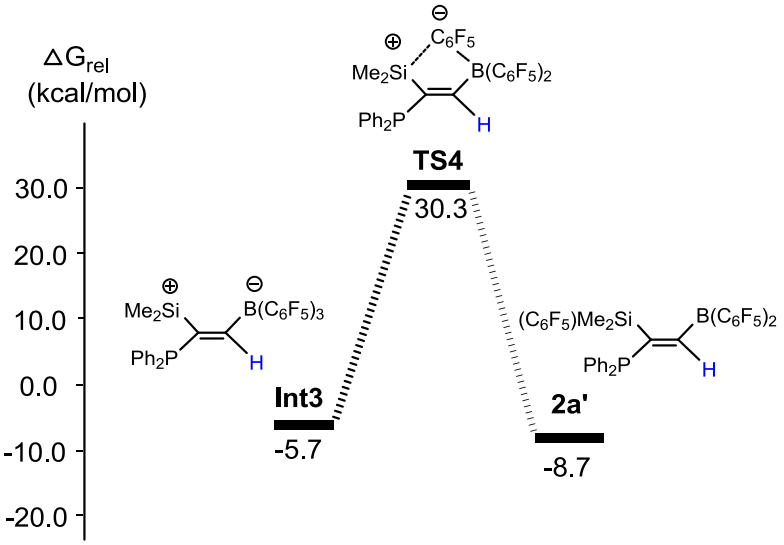


Figure S10 Computed free energy profile (kcal/mol) for probable formation of **2a'** from **Int3** through **TS4** computed at the M06-2X/def2-SVP level

Tables S4-S14 Geometrical coordinates of intermediates, transition states, and products computed at M06-2X/def2-SVP level of theory.

Table S4
M06-2X/def2-SVP
Int1

Atomic Number	Coordinates (Angstroms) X	Y	Z

6	1.557638	0.164235	-1.788110
6	2.771014	0.223537	-1.902980
15	-0.138636	-0.065813	-1.372966
6	-0.557657	-1.657762	-2.183336
6	0.266663	-2.142559	-3.205993
6	-1.685608	-2.395227	-1.797040
6	-0.031344	-3.349659	-3.832416
1	1.151540	-1.580953	-3.507528
6	-1.976579	-3.603320	-2.430016
1	-2.332689	-2.046355	-0.993059
6	-1.151252	-4.083386	-3.444794
1	0.621173	-3.719445	-4.624258
1	-2.852923	-4.173762	-2.118897
1	-1.378362	-5.032658	-3.932003
6	-1.052874	1.218029	-2.304721
6	-0.511905	2.500918	-2.449353
6	-2.325039	0.935992	-2.816513
6	-1.254653	3.498863	-3.076148
1	0.488017	2.721216	-2.077968
6	-3.064101	1.942540	-3.434113
1	-2.748086	-0.064959	-2.726915
6	-2.534027	3.226087	-3.557433
1	-0.827512	4.496435	-3.186813
1	-4.059094	1.718889	-3.820641
1	-3.115635	4.013026	-4.039771
14	4.636737	0.163477	-2.015872
1	4.921032	-0.380779	-3.370030
6	5.261234	-1.012733	-0.696805
1	4.643209	-1.921173	-0.655762
1	6.296553	-1.307658	-0.923559
1	5.254861	-0.544929	0.297355
6	5.336101	1.888179	-1.835511
1	6.423473	1.861184	-1.999364
1	4.894591	2.578395	-2.567670
1	5.152691	2.287814	-0.828973
5	-0.295848	0.034423	0.806585
9	-2.670565	-0.950543	2.393955
9	-3.315602	-3.496251	2.747678
9	-1.729400	-5.475137	1.782359
9	1.756239	-1.451901	2.517813
9	4.272213	-0.714810	2.826202
9	5.170284	1.633294	1.824993
9	3.448365	3.281046	0.498725
9	0.945808	2.496063	0.055410

9	-0.195035	2.589414	2.458010
9	-2.085822	4.429908	2.518333
9	-4.423314	4.073381	1.187029
9	-4.828014	1.769019	-0.225469
9	-2.937402	-0.110071	-0.270274
6	-0.702261	-1.489905	1.180894
6	-1.847930	-1.861692	1.882917
6	-2.208906	-3.194389	2.087391
6	-1.394940	-4.210417	1.600452
6	-0.224243	-3.887101	0.918372
6	0.089677	-2.548908	0.733192
6	1.207957	0.479925	1.239351
6	2.109006	-0.292185	1.975287
6	3.435984	0.085719	2.184087
6	3.898921	1.295230	1.683349
6	3.024148	2.126940	0.994950
6	1.723991	1.694123	0.787800
6	-1.444695	1.161508	1.028565
6	-1.300610	2.338232	1.763644
6	-2.285522	3.324829	1.818759
6	-3.485978	3.144760	1.141707
6	-3.691451	1.971475	0.421874
6	-2.683360	1.019123	0.407504
9	0.553323	-4.846236	0.444269
9	1.206393	-2.276496	0.051048

Table S5

M06-2X/def2-SVP

Int2

Atomic	Coordinates (Angstroms)		
Number	X	Y	Z
15	3.050441	-0.386282	-0.239546
14	3.043469	-0.911858	2.004922
5	-1.353461	0.083394	-0.144289
9	-2.423922	1.513801	2.339308
9	-2.506915	0.477489	4.784420
9	-1.650892	-2.060453	5.242780
9	-0.724283	-3.565540	3.169454
9	-0.695356	-2.563937	0.694984
9	0.272033	1.852693	1.436992
9	0.631599	4.464498	1.110734
9	-0.861667	5.839221	-0.717273

9	-2.673976	4.503708	-2.240071
9	-2.976576	1.885318	-2.003232
9	-4.152034	0.335772	0.141592
9	-6.072172	-1.006416	-1.193565
9	-5.379196	-2.769678	-3.143998
9	-2.760596	-3.178140	-3.731039
9	-0.856900	-1.866666	-2.411739
6	1.380594	-0.360397	-0.626227
6	0.167176	-0.246515	-0.514355
6	2.349387	-2.640418	2.046620
1	2.120110	-2.936798	3.081546
1	1.418543	-2.706334	1.464689
1	3.075569	-3.355539	1.632364
6	4.789191	-0.741757	2.655965
1	4.784541	-0.858411	3.750271
1	5.446413	-1.518020	2.239026
1	5.207058	0.248765	2.424097
6	-1.525080	-0.466092	1.399273
6	-2.006541	0.260255	2.484945
6	-2.055226	-0.258137	3.779954
6	-1.621593	-1.557530	4.018617
6	-1.152414	-2.326168	2.958048
6	-1.138021	-1.774075	1.681768
6	-1.367996	1.724446	-0.267454
6	-0.475662	2.467029	0.505745
6	-0.277411	3.833413	0.370445
6	-1.028429	4.535061	-0.568301
6	-1.952159	3.847586	-1.344588
6	-2.099408	2.466139	-1.190344
6	-2.431809	-0.703064	-1.072837
6	-3.787534	-0.529732	-0.803567
6	-4.794681	-1.203906	-1.483666
6	-4.441757	-2.109724	-2.481976
6	-3.101008	-2.316460	-2.781642
6	-2.124079	-1.614983	-2.074570
6	3.781806	1.241558	-0.575514
6	3.184489	2.345499	0.049750
6	4.862034	1.414538	-1.444568
6	3.674283	3.624192	-0.200013
1	2.323576	2.214640	0.710660
6	5.349889	2.699927	-1.680531
1	5.312357	0.558809	-1.950766
6	4.758720	3.799964	-1.061446
1	3.193280	4.480360	0.274503

1	6.188133	2.840378	-2.364001
1	5.139795	4.803276	-1.257362
6	3.884077	-1.678728	-1.190234
6	5.243421	-1.940511	-0.968755
6	3.147269	-2.451554	-2.093304
6	5.867689	-2.970098	-1.667155
1	5.817661	-1.337301	-0.260130
6	3.782876	-3.482636	-2.785112
1	2.083474	-2.249531	-2.245061
6	5.136667	-3.739351	-2.574885
1	6.926055	-3.174929	-1.501508
1	3.211802	-4.087672	-3.490167
1	5.627873	-4.547906	-3.118200
1	2.130998	0.127812	2.541123

Table S6
M06-2X/def2-SVP
Int3

Atomic Number	Coordinates (Angstroms) X	Y	Z
15	-3.293453	-1.196153	-1.349472
14	-1.265015	1.166194	-1.690299
5	0.732237	-0.100022	-0.034382
9	3.399476	0.917786	-0.286174
9	5.395398	-0.041328	-1.794033
9	4.964596	-2.175869	-3.423928
9	2.506310	-3.325758	-3.515509
9	0.518935	-2.394574	-2.033689
9	1.829851	1.986983	-2.083726
9	1.715696	4.592450	-1.699389
9	0.197450	5.607320	0.286270
9	-1.224495	3.976718	1.907808
9	-1.054143	1.353233	1.607060
9	1.966695	1.965605	1.902029
9	3.096401	1.397660	4.219137
9	3.300599	-1.177350	5.077033
9	2.315792	-3.185321	3.528249
9	1.165643	-2.645433	1.193319
6	-1.701914	-0.419396	-0.866354
6	-0.671857	-0.920910	-0.156973
1	-0.776662	-1.914820	0.292759
6	-2.449677	2.603203	-1.596787

1	-1.985739	3.551083	-1.909432
1	-3.266572	2.385511	-2.305609
1	-2.902698	2.715043	-0.602258
6	-0.513795	1.009131	-3.384052
1	-0.171143	1.970583	-3.791093
1	0.316897	0.291182	-3.389250
1	-1.309202	0.612854	-4.036600
6	-3.340169	-2.692650	-0.279636
6	-2.419643	-3.715494	-0.554107
1	-1.681841	-3.586228	-1.350542
6	-2.424728	-4.889790	0.194588
1	-1.691080	-5.668999	-0.017145
6	-3.367215	-5.070627	1.207602
1	-3.374684	-5.992832	1.790497
6	-4.300281	-4.070139	1.468929
1	-5.046111	-4.208181	2.253429
6	-4.286059	-2.883991	0.733835
1	-5.021271	-2.108016	0.951602
6	-4.440524	-0.024100	-0.495392
6	-5.603554	0.377290	-1.159042
1	-5.824014	-0.029445	-2.149070
6	-6.477173	1.294579	-0.570063
1	-7.382378	1.599114	-1.097809
6	-6.190754	1.818746	0.688150
1	-6.871728	2.536801	1.147956
6	-5.031858	1.422688	1.360925
1	-4.805205	1.829559	2.348035
6	-4.161671	0.507715	0.772530
1	-3.251427	0.202662	1.294000
6	1.862167	-0.678137	-1.084628
6	3.147982	-0.137268	-1.068849
6	4.201331	-0.610448	-1.840855
6	3.982212	-1.702709	-2.677071
6	2.722504	-2.286920	-2.722781
6	1.694457	-1.772046	-1.930451
6	0.357381	1.476197	-0.288580
6	1.094762	2.405827	-1.077009
6	1.041959	3.784030	-0.906693
6	0.259653	4.311528	0.118761
6	-0.481750	3.469047	0.945618
6	-0.394976	2.101429	0.750623
6	1.424592	-0.306525	1.453160
6	1.982045	0.674662	2.268922
6	2.601994	0.410126	3.488210

6	2.709815	-0.903268	3.926894
6	2.199134	-1.927042	3.135260
6	1.583580	-1.611287	1.926743

Table S7

M06-2X/def2-SVP

Int4

Atomic Number	Coordinates (Angstroms) X	Y	Z
15	2.461811	0.274156	1.515651
14	0.392120	-1.479553	3.001693
5	-1.368934	-0.266724	-0.023626
9	-2.612093	1.184905	-2.184835
9	-2.606436	3.844992	-2.565142
9	-1.471461	5.478834	-0.719033
9	-0.355899	4.412346	1.521395
9	-0.265323	1.783238	1.864694
9	-0.170510	0.582415	-2.732502
9	0.578062	-1.046354	-4.644827
9	0.285098	-3.742938	-4.385988
9	-0.788942	-4.754202	-2.092556
9	-1.540864	-3.126949	-0.129261
9	-3.721066	-1.321614	-1.610211
9	-6.143255	-1.821135	-0.648995
9	-6.694475	-1.459306	1.979781
9	-4.740175	-0.562697	3.656986
9	-2.308100	-0.015529	2.715769
6	1.013642	-0.800512	1.450232
6	-0.291687	-0.858485	1.084143
1	-0.871289	-1.709462	1.573771
6	0.185420	-0.393225	4.482193
1	0.836335	-0.728431	5.303176
1	0.427893	0.644740	4.219912
1	-0.859760	-0.443365	4.821260
6	0.050642	-3.289251	3.246864
1	0.885512	-3.739427	3.806411
1	-0.866721	-3.432636	3.835780
1	-0.053288	-3.807949	2.284327
6	-1.346504	1.351552	-0.204563
6	-1.993898	1.949155	-1.287531
6	-2.036653	3.324230	-1.488452
6	-1.471741	4.166067	-0.533802

6	-0.890795	3.619747	0.600432
6	-0.839535	2.235030	0.740172
6	-0.948658	-1.173595	-1.334524
6	-0.397059	-0.712598	-2.526125
6	0.012481	-1.555761	-3.559061
6	-0.114338	-2.931053	-3.422102
6	-0.662664	-3.444667	-2.249877
6	-1.047633	-2.564358	-1.246134
6	-2.884685	-0.644210	0.502535
6	-3.917278	-1.105121	-0.314195
6	-5.197845	-1.380509	0.165055
6	-5.486296	-1.195364	1.513271
6	-4.488784	-0.736460	2.366646
6	-3.230015	-0.466642	1.839902
6	2.349426	1.594464	0.232298
6	2.261587	2.926073	0.713963
6	2.298655	1.348822	-1.154846
6	2.046892	3.959423	-0.199049
6	2.044349	2.414635	-2.024318
6	1.886266	3.720168	-1.565952
1	1.952119	4.981250	0.177792
1	1.950060	2.205843	-3.092374
6	3.886561	-0.817123	1.039725
6	3.845484	-2.145465	0.552004
6	5.150039	-0.195019	1.219663
6	5.051824	-2.786320	0.237219
6	6.318057	-0.877579	0.881545
6	6.295123	-2.178347	0.381018
1	5.008407	-3.809119	-0.145004
1	7.278340	-0.374407	1.021989
6	5.288808	1.200252	1.774850
1	4.863395	1.954283	1.094883
1	4.768267	1.292324	2.739991
1	6.346459	1.445322	1.932123
6	2.597877	-2.974160	0.343967
1	2.178511	-3.316832	1.301609
1	1.799462	-2.441463	-0.186843
1	2.844343	-3.870625	-0.239057
6	7.569939	-2.885597	0.007560
1	8.023668	-2.425939	-0.883399
1	8.308033	-2.821599	0.819782
1	7.390025	-3.945627	-0.212461
6	2.369901	3.288939	2.177306
1	1.545828	2.857292	2.759479

1	3.310466	2.929613	2.615838
1	2.329581	4.378874	2.294524
6	2.536343	-0.014161	-1.744610
1	1.936415	-0.781796	-1.238936
1	2.277335	-0.023290	-2.811008
1	3.592726	-0.305151	-1.639340
6	1.518382	4.841523	-2.499553
1	0.454265	5.101197	-2.378735
1	2.100271	5.748123	-2.282133
1	1.680320	4.562246	-3.548400

Table S8

M06-2X/def2-SVP

2a’

Atomic Number	Coordinates (Angstroms) X	Y	Z
15	2.599873	0.267724	1.966008
14	0.549797	-1.788236	3.034503
5	-0.898158	-0.208440	-0.066733
9	-2.731389	1.317992	-1.593074
9	-3.969681	3.590203	-0.915583
9	-3.509173	4.724615	1.508919
9	-1.788579	3.524401	3.251419
9	-0.589281	1.262023	2.622860
9	-0.281680	2.273819	-1.818107
9	1.540089	2.357236	-3.715038
9	3.097105	0.214907	-4.260246
9	2.690249	-2.127221	-2.893254
9	0.758478	-2.292082	-1.083665
9	-1.797520	-1.347844	-2.756318
9	-3.851973	-2.987165	-3.116942
9	-5.365518	-3.797046	-1.017419
9	-4.772611	-2.921097	1.492261
9	-2.705863	-1.270081	1.887234
6	1.227363	-0.865892	1.644674
6	-0.004343	-0.972629	1.103044
1	-0.586219	-1.886950	1.441325
6	-0.001095	-0.931397	4.574891
1	0.415318	0.082559	4.623080
1	-1.099575	-0.850484	4.539810
1	0.275584	-1.505216	5.470477
6	0.369016	-3.632966	3.000641

1	-0.636418	-3.941803	3.320740
1	0.577459	-4.026744	1.997096
1	1.095524	-4.066277	3.705968
6	-1.585439	1.181507	0.459347
6	-2.490076	1.825476	-0.387304
6	-3.140538	3.009991	-0.063057
6	-2.907759	3.593815	1.180485
6	-2.033272	2.979474	2.066819
6	-1.410615	1.788700	1.695584
6	0.154489	-0.013189	-1.309712
6	0.389077	1.147188	-2.046070
6	1.341847	1.220623	-3.062548
6	2.142153	0.123960	-3.348291
6	1.940074	-1.060014	-2.647297
6	0.944841	-1.102169	-1.679634
6	-2.135075	-1.239999	-0.413196
6	-2.485417	-1.706787	-1.677836
6	-3.562913	-2.565656	-1.896594
6	-4.344646	-2.979819	-0.823440
6	-4.038870	-2.533389	0.458314
6	-2.956437	-1.676651	0.625489
6	2.591178	1.555054	0.656263
6	1.715321	2.631111	0.857837
6	3.451623	1.564689	-0.447450
6	1.664063	3.679573	-0.055723
1	1.076131	2.647330	1.743137
6	3.411725	2.629175	-1.348385
1	4.153560	0.743621	-0.608587
6	2.514087	3.679749	-1.161453
1	0.958430	4.497676	0.096775
1	4.067226	2.622547	-2.221664
1	2.472089	4.495482	-1.884049
6	3.975468	-0.836262	1.449079
6	3.828999	-1.803424	0.443585
6	5.227795	-0.655698	2.047930
6	4.921113	-2.569681	0.040684
1	2.858875	-1.954881	-0.035899
6	6.319733	-1.423072	1.642710
1	5.350048	0.093641	2.833699
6	6.167157	-2.379641	0.639729
1	4.794878	-3.310089	-0.750578
1	7.292706	-1.274015	2.113530
1	7.022277	-2.979189	0.323564

Table S9

M06-2X/def2-SVP

TS1

Atomic Number	Coordinates (Angstroms) X	Y	Z
15	4.363980	1.178262	0.899414
14	2.824390	0.394746	2.401698
5	-1.088950	-0.193825	-0.033489
9	-3.595305	1.237163	0.903740
9	-4.998592	0.630236	3.069694
9	-4.295615	-1.478833	4.628438
9	-2.122463	-2.978183	3.971446
9	-0.688419	-2.381632	1.796215
9	-0.726993	2.242915	1.443456
9	-0.936593	4.746388	0.553816
9	-1.796640	5.228719	-1.982526
9	-2.341636	3.142912	-3.634231
9	-2.011620	0.650992	-2.822134
9	-3.550232	-1.189087	-1.089438
9	-3.899316	-3.287128	-2.719982
9	-1.746770	-4.607590	-3.720039
9	0.764369	-3.795529	-3.052860
9	1.128726	-1.716305	-1.446944
6	1.410468	-0.075438	1.308369
6	0.380782	-0.144780	0.626384
6	3.517722	-1.058193	3.350530
1	2.696274	-1.647321	3.784268
1	4.113541	-1.717310	2.706017
1	4.151898	-0.691762	4.170836
6	2.273810	1.799347	3.502245
1	1.568726	1.434306	4.263452
1	3.146749	2.233190	4.011324
1	1.768978	2.582071	2.919492
6	-2.052153	-0.530783	1.256053
6	-3.178847	0.200436	1.626789
6	-3.939092	-0.100309	2.755604
6	-3.584572	-1.181806	3.553434
6	-2.474691	-1.948573	3.214111
6	-1.743080	-1.613293	2.078777
6	-1.345771	1.312250	-0.638094
6	-1.106892	2.420362	0.175626
6	-1.244238	3.736172	-0.247973

6	-1.686752	3.985239	-1.543258
6	-1.963711	2.915549	-2.384684
6	-1.782722	1.609954	-1.925910
6	-1.205851	-1.397103	-1.131404
6	-2.471115	-1.835860	-1.522001
6	-2.677502	-2.909252	-2.380925
6	-1.575350	-3.587377	-2.897856
6	-0.295031	-3.171966	-2.555714
6	-0.141024	-2.086870	-1.694826
6	3.169934	1.824986	-0.314831
6	2.867951	3.196178	-0.263041
6	2.456558	1.014531	-1.236940
6	1.998846	3.762931	-1.188454
1	3.355436	3.826591	0.484309
6	1.614100	1.619993	-2.207074
1	2.777708	-0.013169	-1.419843
6	1.408212	2.985355	-2.197585
1	1.788459	4.833481	-1.141398
1	1.140797	0.984236	-2.959101
1	0.788349	3.456610	-2.960306
6	4.960791	-0.448438	0.248263
6	6.356651	-0.580498	0.196965
6	4.176783	-1.558013	-0.089649
6	6.952238	-1.783850	-0.182475
1	6.985365	0.272726	0.461765
6	4.768719	-2.758165	-0.478062
1	3.092009	-1.505317	-0.098207
6	6.157642	-2.877833	-0.519240
1	8.039843	-1.862397	-0.216245
1	4.132895	-3.600220	-0.755885
1	6.617484	-3.821067	-0.817887
1	1.616099	0.589463	-0.226902

Table S10

M06-2X/def2-SVP

TS2

Atomic Number	Coordinates (Angstroms) X	Y	Z
15	2.539868	0.793013	2.255093
14	0.493960	-1.876475	2.728932
5	-0.905783	-0.231660	-0.110029
9	-1.934768	0.912346	-2.469656

9	-2.495074	3.495131	-2.956390
9	-2.117474	5.354584	-1.008131
9	-1.210450	4.584878	1.432723
9	-0.634112	2.047720	1.924332
9	0.690596	1.032061	-2.444608
9	2.577586	-0.189407	-3.791807
9	3.090972	-2.839622	-3.400646
9	1.585281	-4.239016	-1.619420
9	-0.340400	-3.031336	-0.246122
9	-2.405402	-2.007352	-2.039844
9	-4.822256	-3.038203	-1.610904
9	-6.118237	-2.590046	0.728221
9	-4.943191	-1.074554	2.658829
9	-2.515405	-0.011233	2.236086
6	1.107445	-0.301957	1.935989
6	0.047381	-0.445434	1.210150
1	-0.683873	-1.782645	1.729957
6	-0.194470	-1.632004	4.439309
1	0.612539	-1.365908	5.136570
1	-0.927167	-0.814092	4.413086
1	-0.686996	-2.545761	4.798595
6	1.510110	-3.383672	2.329593
1	2.511730	-3.290922	2.773969
1	1.026629	-4.287981	2.724805
1	1.614643	-3.490168	1.241387
6	-1.185606	1.368043	-0.288179
6	-1.714103	1.802552	-1.503704
6	-2.021883	3.129982	-1.774955
6	-1.837035	4.082914	-0.775329
6	-1.367923	3.687168	0.469705
6	-1.055303	2.346584	0.694042
6	0.063507	-0.929337	-1.253055
6	0.833820	-0.268361	-2.206489
6	1.842829	-0.893003	-2.946010
6	2.101065	-2.242875	-2.756707
6	1.328382	-2.958680	-1.846419
6	0.335848	-2.294619	-1.138631
6	-2.349879	-0.961864	0.083543
6	-2.989545	-1.742475	-0.876216
6	-4.253423	-2.296584	-0.674540
6	-4.920999	-2.068897	0.524725
6	-4.318559	-1.294299	1.511943
6	-3.059285	-0.756957	1.265577
6	2.271924	2.186126	1.083401

6	1.965391	3.425972	1.659908
6	2.356230	2.078965	-0.307933
6	1.732471	4.539256	0.854631
1	1.894194	3.515128	2.746158
6	2.115849	3.190972	-1.113892
1	2.614999	1.125085	-0.772354
6	1.803683	4.419998	-0.533267
1	1.480007	5.496561	1.311798
1	2.165908	3.086932	-2.198045
1	1.612150	5.288668	-1.165739
6	3.803486	-0.245224	1.396969
6	3.515741	-1.105994	0.327679
6	5.126180	-0.138732	1.843905
6	4.529494	-1.840721	-0.285186
1	2.490871	-1.199916	-0.036756
6	6.141928	-0.869215	1.227084
1	5.362631	0.520279	2.682691
6	5.845082	-1.721496	0.164510
1	4.291140	-2.501233	-1.121892
1	7.168968	-0.775276	1.582771
1	6.639111	-2.295376	-0.315202

Table S11
M06-2X/def2-SVP
TS3

Atomic Number	Coordinates (Angstroms) X	Y	Z
15	-0.870666	-1.140366	0.490038
14	0.964616	-2.638198	-1.872999
5	-1.357427	0.587692	-0.494822
9	-0.752771	1.254927	2.365057
9	1.010769	3.093990	3.152537
9	2.300922	4.629801	1.327186
9	1.769145	4.327929	-1.318983
9	-0.035413	2.515912	-2.125746
9	-2.937637	0.057832	-2.916355
9	-5.574717	0.353465	-3.160647
9	-7.058194	1.230048	-1.063162
9	-5.852563	1.809592	1.299664
9	-3.204250	1.512690	1.564222
9	4.715837	-3.063122	-0.996169
9	6.762186	-1.553594	-0.080202

9	6.519220	1.139473	0.042511
9	4.212598	2.347788	-0.753226
9	2.181412	0.864769	-1.706605
6	-0.604734	-0.233326	-1.684721
1	-0.338842	0.107471	-2.692732
6	-0.238874	-1.441028	-1.172221
6	1.359832	-4.124464	-0.839076
1	0.690195	-4.966298	-1.075787
1	1.267651	-3.876979	0.228941
1	2.398126	-4.428006	-1.033032
6	0.991150	-2.796597	-3.716029
1	0.132061	-3.398355	-4.052181
1	1.920200	-3.283235	-4.040893
1	0.928062	-1.804459	-4.182703
6	0.498643	-1.270861	1.672537
6	0.446948	-2.067563	2.820393
1	-0.451920	-2.641976	3.054852
6	1.555400	-2.123355	3.665264
1	1.520545	-2.743884	4.561702
6	2.705154	-1.391561	3.367549
1	3.569096	-1.441589	4.031655
6	2.753932	-0.594633	2.222809
1	3.651940	-0.022070	1.981745
6	1.651246	-0.531548	1.376679
1	1.678980	0.090931	0.481152
6	-2.185937	-2.255180	1.027801
6	-3.093461	-1.767810	1.978283
1	-2.985121	-0.749966	2.364750
6	-4.136196	-2.581761	2.416065
1	-4.845418	-2.203041	3.153201
6	-4.277383	-3.872168	1.904002
1	-5.098700	-4.505058	2.243184
6	-3.377754	-4.354143	0.952979
1	-3.494291	-5.360876	0.549558
6	-2.330950	-3.546332	0.512659
1	-1.629751	-3.918868	-0.237766
6	-0.476095	1.812125	0.077367
6	-0.186869	2.014929	1.426830
6	0.743640	2.954288	1.863624
6	1.411535	3.739666	0.928101
6	1.136594	3.586181	-0.427663
6	0.193049	2.642519	-0.819483
6	-2.946159	0.787893	-0.664066
6	-3.611875	0.496652	-1.853819

6	-4.989251	0.639596	-2.008848
6	-5.751501	1.089503	-0.936235
6	-5.130608	1.388374	0.273778
6	-3.752412	1.234993	0.382038
6	3.405033	-1.139614	-1.416259
6	4.571768	-1.731058	-0.983229
6	5.640654	-0.977973	-0.493247
6	5.519213	0.410079	-0.428561
6	4.343142	1.030076	-0.850360
6	3.316593	0.233192	-1.351750

Table S12

M06-2X/def2-SVP

TS4

Atomic Number	Coordinates (Angstroms) X	Y	Z
15	-3.630264	-1.613430	-0.846672
14	-1.322713	-0.343845	-2.371365
5	0.242261	-0.285148	0.734538
9	3.075402	0.364266	0.950239
9	5.059044	-1.358500	0.696389
9	4.549049	-4.024820	0.503048
9	1.984025	-4.915081	0.509912
9	-0.028333	-3.195483	0.669645
9	2.104819	-1.764011	-2.058329
9	4.722328	-1.197556	-2.106181
9	5.568283	1.376265	-1.840417
9	3.765345	3.370084	-1.481937
9	1.137125	2.827056	-1.427685
9	-1.107380	2.068047	-0.286133
9	-0.928920	4.527870	0.720360
9	0.524775	4.978366	2.969081
9	1.825105	2.933375	4.179455
9	1.698701	0.466844	3.157402
6	-1.947313	-0.838851	-0.700230
6	-1.210255	-0.795224	0.420376
1	-1.681529	-1.188531	1.340634
6	-1.880508	1.217726	-3.187789
1	-1.266205	1.407185	-4.078544
1	-2.936547	1.111336	-3.489161
1	-1.796439	2.062783	-2.493360
6	-0.852035	-1.753060	-3.472510

1	-0.271427	-1.400376	-4.335092
1	-0.255200	-2.477465	-2.903460
1	-1.766947	-2.252488	-3.832885
6	-4.041740	-1.930029	0.915558
6	-3.497140	-3.087911	1.490676
1	-2.860732	-3.744026	0.890613
6	-3.749395	-3.398558	2.824762
1	-3.312517	-4.296405	3.264431
6	-4.567756	-2.567941	3.591678
1	-4.773754	-2.814049	4.634522
6	-5.125167	-1.425059	3.021197
1	-5.769847	-0.775991	3.616163
6	-4.860516	-1.101169	1.690013
1	-5.298742	-0.201409	1.254517
6	-4.598816	-0.100244	-1.266400
6	-5.704344	-0.244771	-2.114055
1	-5.979197	-1.238408	-2.476355
6	-6.448500	0.869397	-2.503689
1	-7.306844	0.746466	-3.165854
6	-6.088072	2.139263	-2.054989
1	-6.663945	3.011966	-2.367231
6	-4.987266	2.294273	-1.210678
1	-4.696728	3.287371	-0.863867
6	-4.246962	1.181124	-0.817002
1	-3.372020	1.308568	-0.175061
6	1.418262	-1.322157	0.834794
6	2.759833	-0.921476	0.881879
6	3.818692	-1.806217	0.744075
6	3.555964	-3.169463	0.620560
6	2.241053	-3.621871	0.616888
6	1.203805	-2.698497	0.712599
6	1.527589	0.507536	-1.720355
6	2.470659	-0.473637	-1.947626
6	3.838751	-0.215563	-1.967480
6	4.274858	1.099460	-1.816320
6	3.346114	2.119692	-1.624893
6	1.986259	1.804366	-1.604218
6	0.347932	1.167772	1.347534
6	-0.345184	2.243226	0.791258
6	-0.279675	3.534192	1.302914
6	0.466959	3.766620	2.453173
6	1.142726	2.715088	3.069555
6	1.068678	1.442629	2.514222

Table S13

M06-2X/def2-SVP

2a

Atomic Number	Coordinates (Angstroms) X	Y	Z
15	0.841860	-1.485216	1.099324
14	1.501807	-0.271219	-1.705963
5	4.628812	0.289932	-0.045071
9	6.775399	1.707283	-1.240554
9	6.873262	4.305138	-1.913245
9	4.720827	5.902025	-1.488498
9	2.453416	4.846428	-0.387024
9	2.349825	2.302877	0.297063
9	5.217859	0.699659	-3.093514
9	5.549635	-1.250233	-4.825687
9	5.521234	-3.855270	-4.031881
9	5.138312	-4.443150	-1.392568
9	4.840688	-2.489914	0.383376
9	7.459623	-0.914965	0.056702
9	9.023039	-0.930650	2.209954
9	8.193821	0.196013	4.532754
9	5.731429	1.360580	4.667055
9	4.164011	1.430873	2.500508
6	2.016348	-0.555406	0.084148
6	3.242813	-0.310739	0.596746
1	3.399955	-0.685669	1.613785
6	1.697029	-1.825159	-2.737233
1	1.620118	-1.582515	-3.806711
1	0.949641	-2.597416	-2.501183
1	2.697218	-2.243389	-2.544326
6	2.106419	1.226218	-2.640697
1	1.631419	1.209652	-3.634263
1	3.193307	1.191350	-2.784624
1	1.845091	2.172116	-2.152999
6	1.495518	-1.754752	2.772902
6	1.974961	-0.661898	3.512919
1	2.020948	0.335933	3.072495
6	2.447652	-0.856628	4.807605
1	2.855877	-0.009946	5.361409
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1	2.788798	-2.279537	6.393003
6	1.919949	-3.210753	4.652609

1	1.894477	-4.205799	5.098220
6	1.464463	-3.030106	3.346772
1	1.090904	-3.883330	2.777041
6	0.666811	-3.088877	0.270540
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1	-1.629988	-5.092398	-1.236784
6	0.504844	-5.440452	-1.209180
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6	1.750656	-4.979352	-0.771624
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6	5.772357	3.798117	-1.382735
6	4.670415	4.622535	-1.160984
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6	3.499224	2.734842	-0.251260
6	4.984948	-0.784726	-1.247671
6	5.198094	-0.541315	-2.601301
6	5.378805	-1.554147	-3.549170
6	5.364392	-2.883696	-3.149358
6	5.175645	-3.180291	-1.800594
6	5.006074	-2.138244	-0.899909
6	5.724427	0.240255	1.182316
6	6.991291	-0.334184	1.159240
6	7.830599	-0.359332	2.274163
6	7.409484	0.217813	3.467466
6	6.153562	0.813208	3.534248
6	5.358379	0.823914	2.394163
15	-0.836408	0.105945	-1.758096
14	-1.149519	-0.342500	1.402088
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9	-6.714755	-4.383421	3.203016
9	-4.626591	-4.744504	1.486506
9	-3.575087	-2.697746	0.194884
9	-4.392001	0.538771	3.497599
9	-3.610776	2.733255	4.729899
9	-2.889947	4.947047	3.323646
9	-2.976137	4.899383	0.605966

9	-3.748002	2.678550	-0.671199
9	-6.530231	2.542617	0.383184
9	-8.514459	2.829624	-1.363167
9	-8.902681	1.004307	-3.332496
9	-7.243189	-1.147293	-3.526296
9	-5.247691	-1.463312	-1.770213
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6	-3.212547	-0.019833	-0.572547
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6	-0.508628	1.289651	2.068384
1	-0.336124	1.221948	3.152236
1	0.431905	1.594550	1.582140
1	-1.258319	2.072689	1.882714
6	-2.014915	-1.406393	2.664163
1	-1.377595	-1.447684	3.561299
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6	-2.306989	-1.984944	-2.934238
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6	-2.702170	-2.772920	-4.015928
1	-3.390232	-3.602497	-3.848995
6	-2.238406	-2.491258	-5.298485
1	-2.553240	-3.108625	-6.140993
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1	-0.438171	4.890541	-0.772563
6	-1.784449	4.550987	-2.432698
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6	-5.040075	-1.126723	1.216868
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6	-6.701778	-2.068974	2.761339
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6	-5.128171	-3.532561	1.690078

6	-4.593850	-2.427666	1.031841
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6	-6.659438	1.607943	-0.555591
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6	-7.911781	0.849410	-2.469559
6	-7.061549	-0.247490	-2.569240
6	-6.031803	-0.380236	-1.644965

Table S14

M06-2X/def2-SVP

3a

Atomic Number	Coordinates (Angstroms) X	Y	Z
15	-0.735809	-0.415434	1.298794
14	2.354266	-1.783307	1.202383
5	-0.968519	0.198916	-0.619520
9	-2.508302	2.070598	1.154458
9	-2.721064	4.705146	0.770428
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9	-0.138020	4.373793	-3.145071
9	0.102414	1.723065	-2.759422
9	-0.406018	-2.032684	-2.485074
9	-2.228280	-3.508715	-3.743329
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9	-5.675637	-1.015805	-1.742538
9	-3.859038	0.477706	-0.466357
9	4.589057	-3.147445	-0.629810
9	6.557348	-1.996001	-2.013933
9	6.860480	0.694443	-1.985344
9	5.162533	2.241832	-0.536035
9	3.184100	1.101610	0.872468
6	0.559548	-0.361676	-0.654325
1	1.296571	-0.309872	-1.467834
6	0.813390	-0.945363	0.545075
6	2.597818	-1.314399	3.001490
1	1.723161	-1.605129	3.604669

1	2.724133	-0.226663	3.104218
1	3.483258	-1.815094	3.419964
6	2.250010	-3.636645	0.959504
1	1.388507	-4.046134	1.506196
1	3.159600	-4.139718	1.315698
1	2.120151	-3.873947	-0.105523
6	-0.368494	0.779996	2.620441
6	-0.959043	0.691304	3.884079
1	-1.651471	-0.121346	4.112579
6	-0.661327	1.646064	4.855698
1	-1.121713	1.573780	5.842021
6	0.217748	2.688395	4.567894
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6	0.805352	2.778602	3.304890
1	1.494305	3.593033	3.076978
6	0.514480	1.828603	2.329784
1	0.982966	1.894517	1.345155
6	-1.782808	-1.695305	2.035742
6	-3.172007	-1.523779	1.985329
1	-3.596728	-0.641559	1.499398
6	-4.007377	-2.480900	2.559771
1	-5.089255	-2.348184	2.519222
6	-3.461535	-3.605109	3.179088
1	-4.119020	-4.354333	3.622582
6	-2.077790	-3.776212	3.230326
1	-1.650804	-4.655896	3.713609
6	-1.237875	-2.821743	2.660133
1	-0.154687	-2.954742	2.701884
6	-1.171712	1.789584	-0.780701
6	-1.900530	2.596334	0.090544
6	-2.029761	3.971847	-0.087881
6	-1.428164	4.576077	-1.188212
6	-0.702884	3.804294	-2.091895
6	-0.591004	2.434821	-1.869406
6	-2.048558	-0.704409	-1.413201
6	-1.687966	-1.743855	-2.269523
6	-2.621149	-2.532731	-2.940338
6	-3.978094	-2.284695	-2.764191
6	-4.385711	-1.255244	-1.919851
6	-3.419686	-0.490506	-1.274825
6	3.796994	-1.068203	0.178664
6	4.690391	-1.823048	-0.578376
6	5.725214	-1.246181	-1.312984
6	5.884600	0.136344	-1.297721

6	5.012356	0.929204	-0.554683
6	3.995382	0.312033	0.165618

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VII. Collected ^{1}H, ^{31}P and/or ^{11}B, ^{13}C, ^{29}Si, ^{19}F NMR spectra of compounds 1a, 1b, 2a, 2b, 3a, 3b, 4, 5 and 6

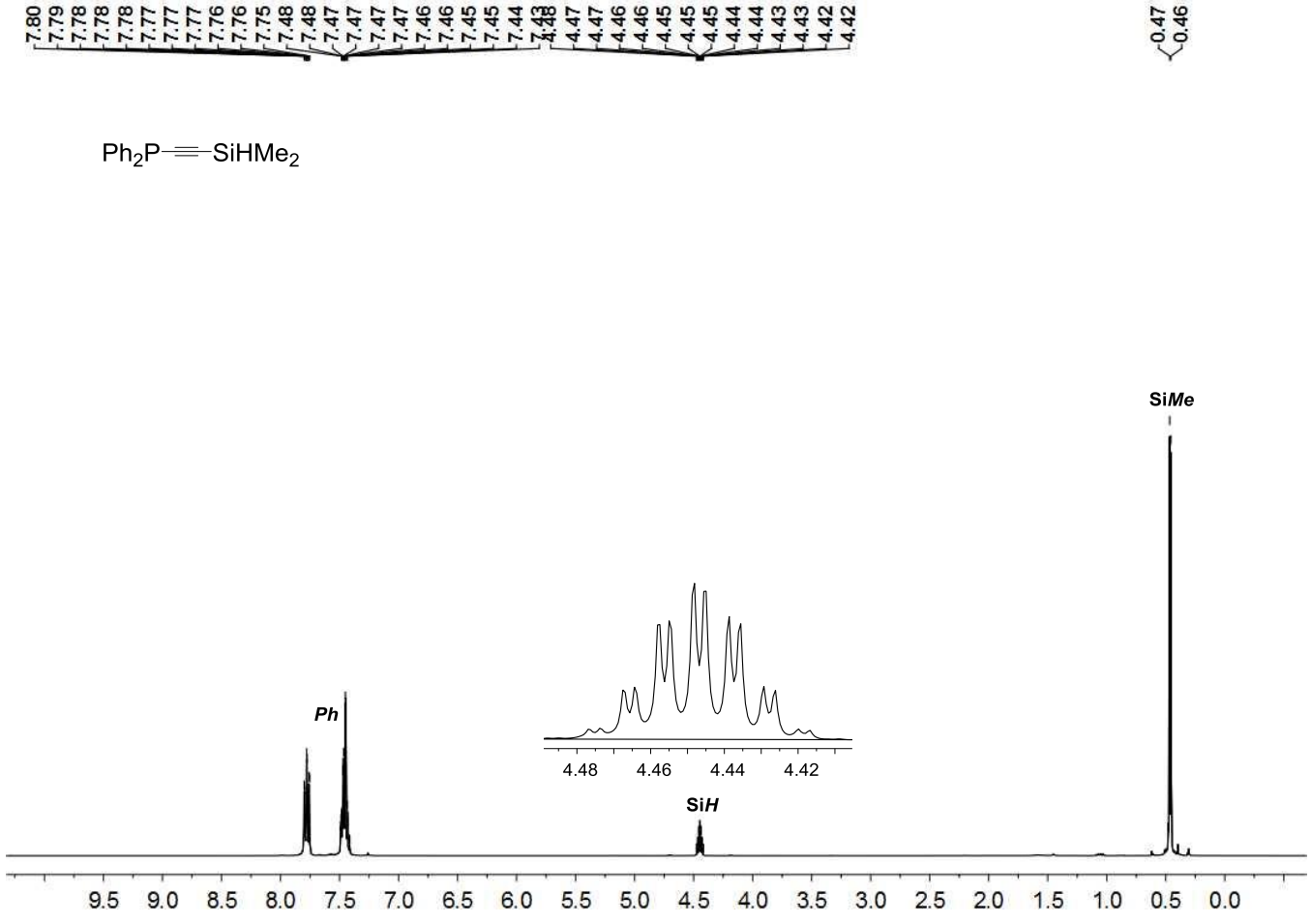

Figure S1-1. ^{1}H NMR spectrum of **1a** in $CDCl_3$

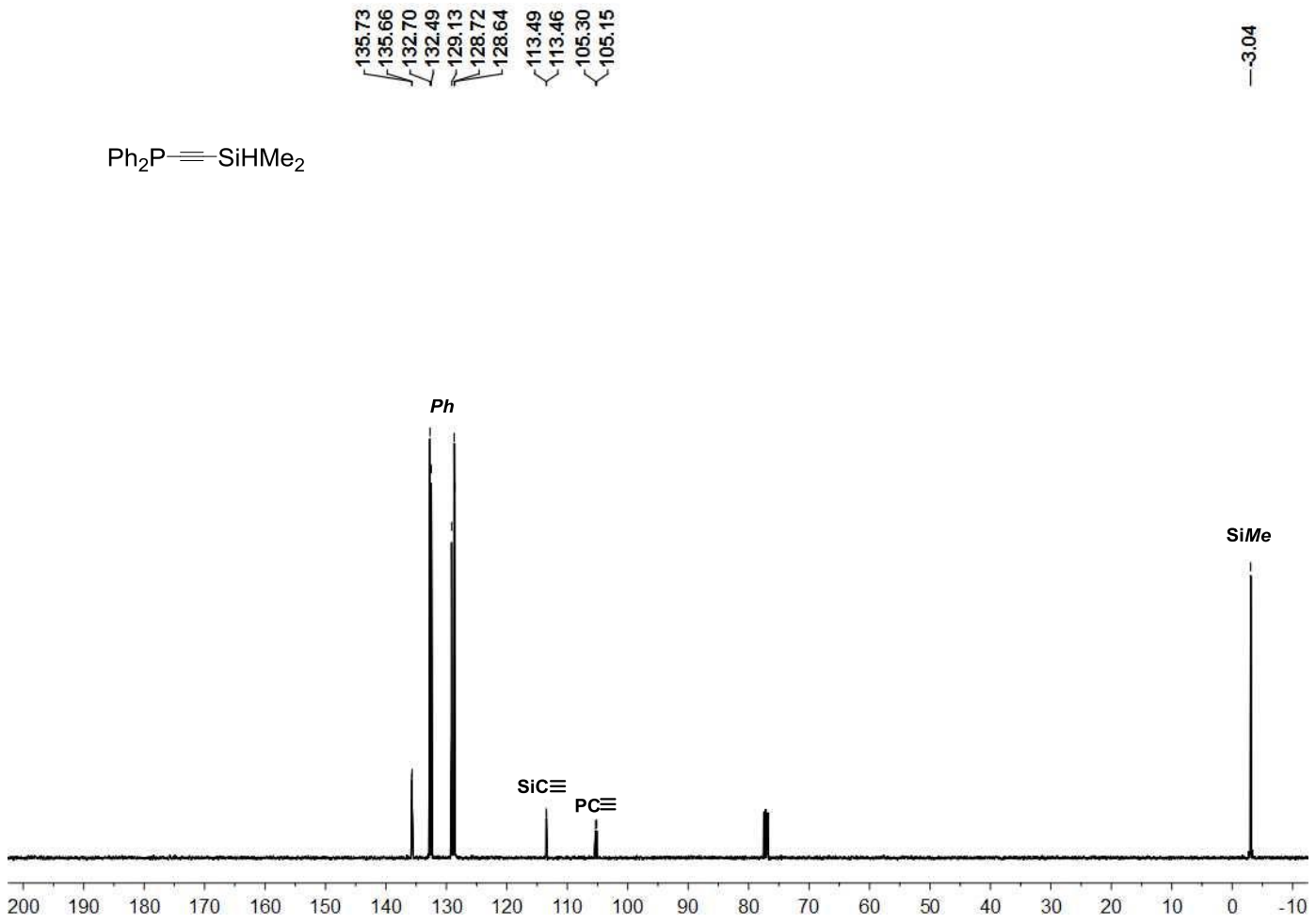

Figure S1-2. $^{13}C\{^{1}H\}$ NMR spectrum of **1a** in $CDCl_3$

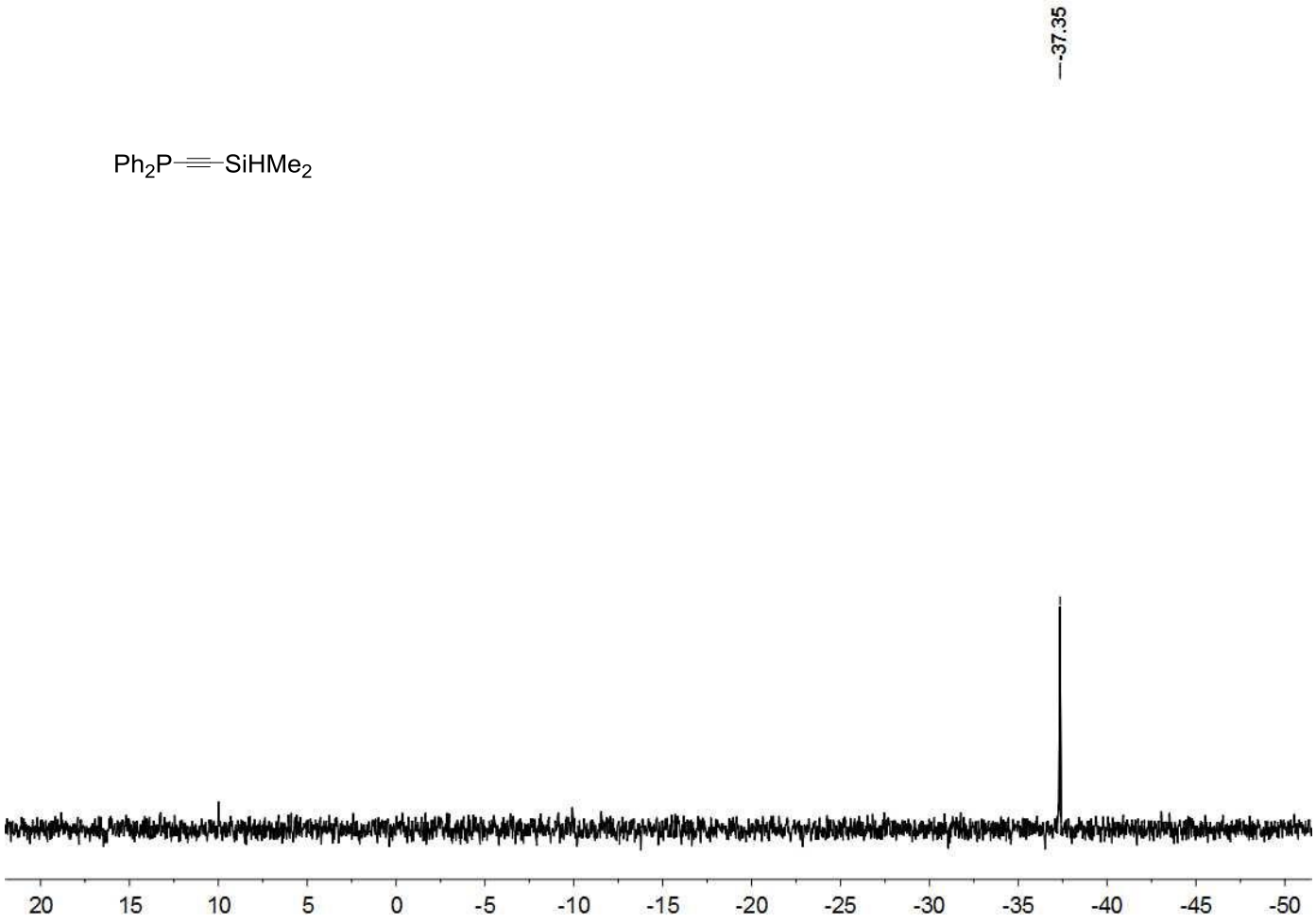

Figure S1-3. ^{29}Si NMR spectrum of **1a** in $CDCl_3$

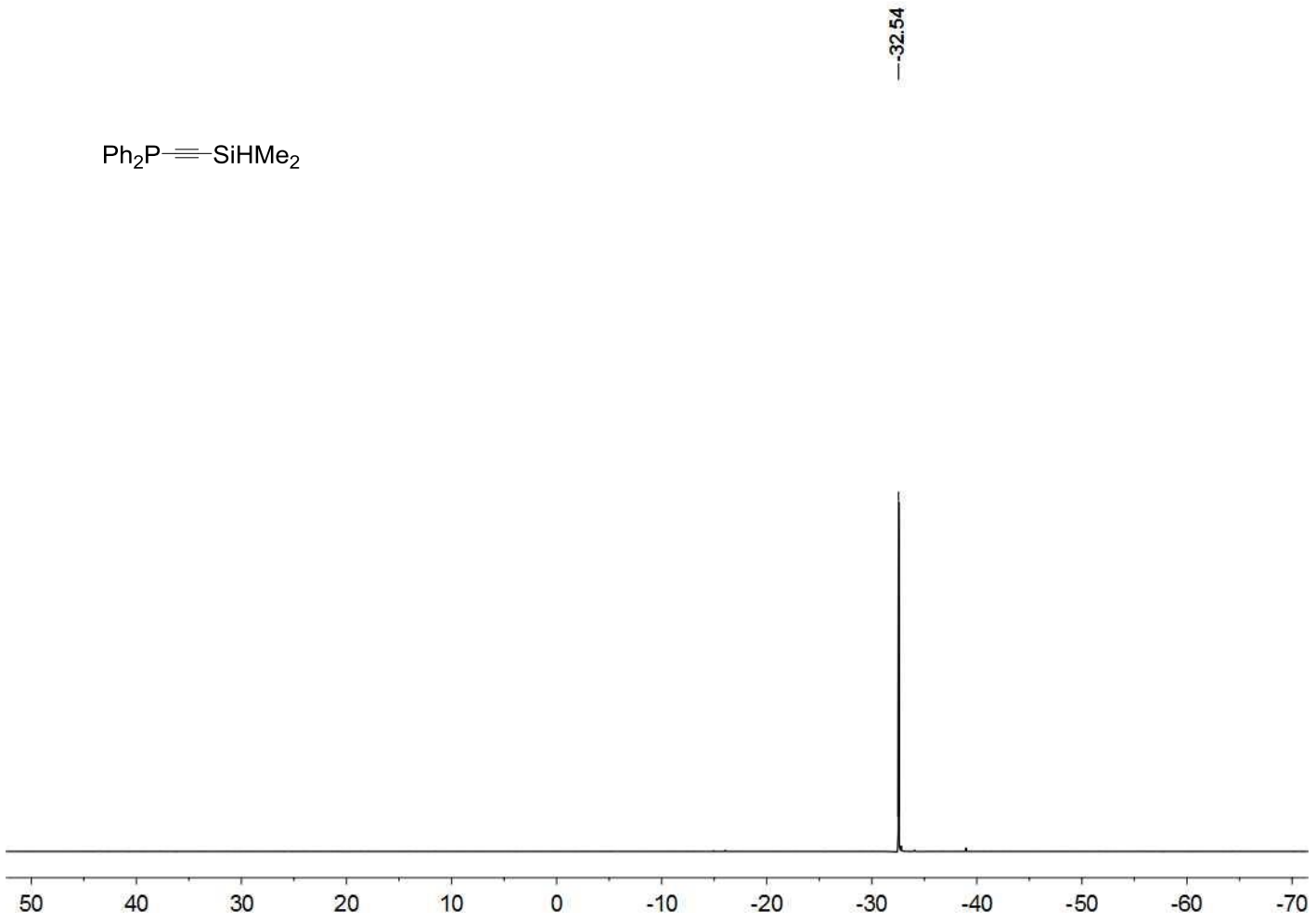

Figure S1-4. ^{31}P NMR spectrum of **1a** in $CDCl_3$

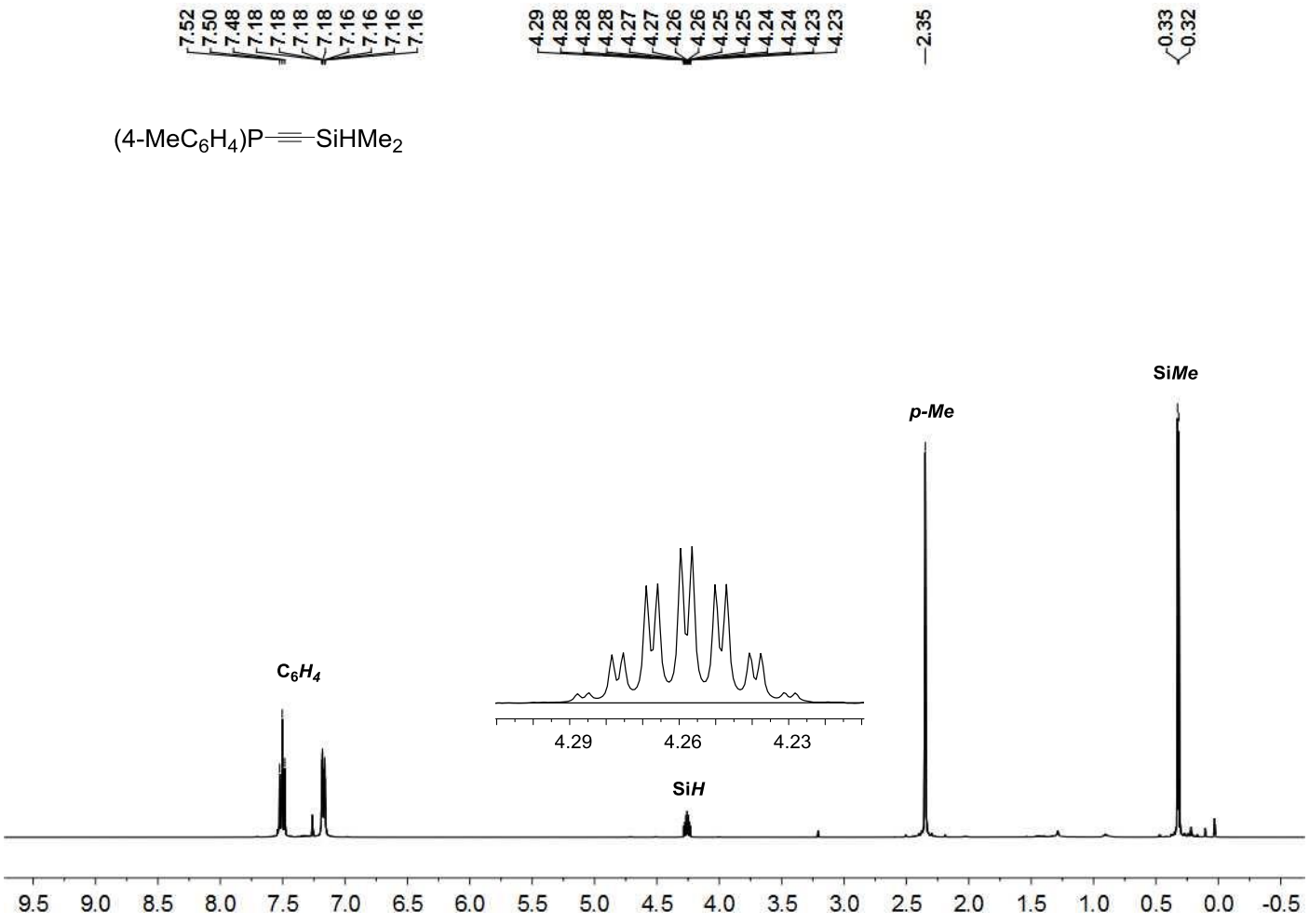

Figure S2-1. ^{1}H NMR spectrum of **1b** in $CDCl_3$

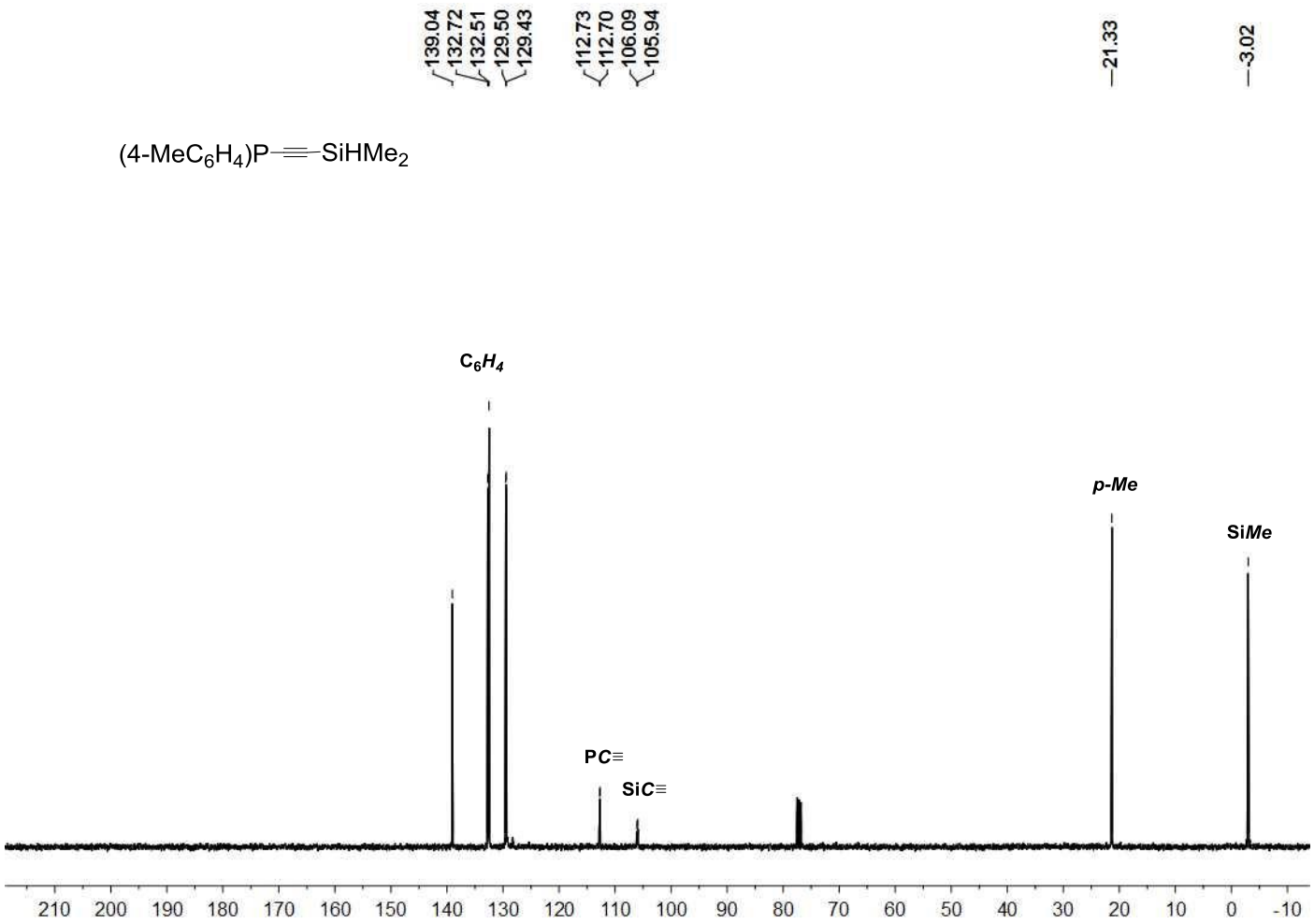

Figure S2-2. $^{13}C\{^{1}H\}$ NMR spectrum of **1b** in $CDCl_3$

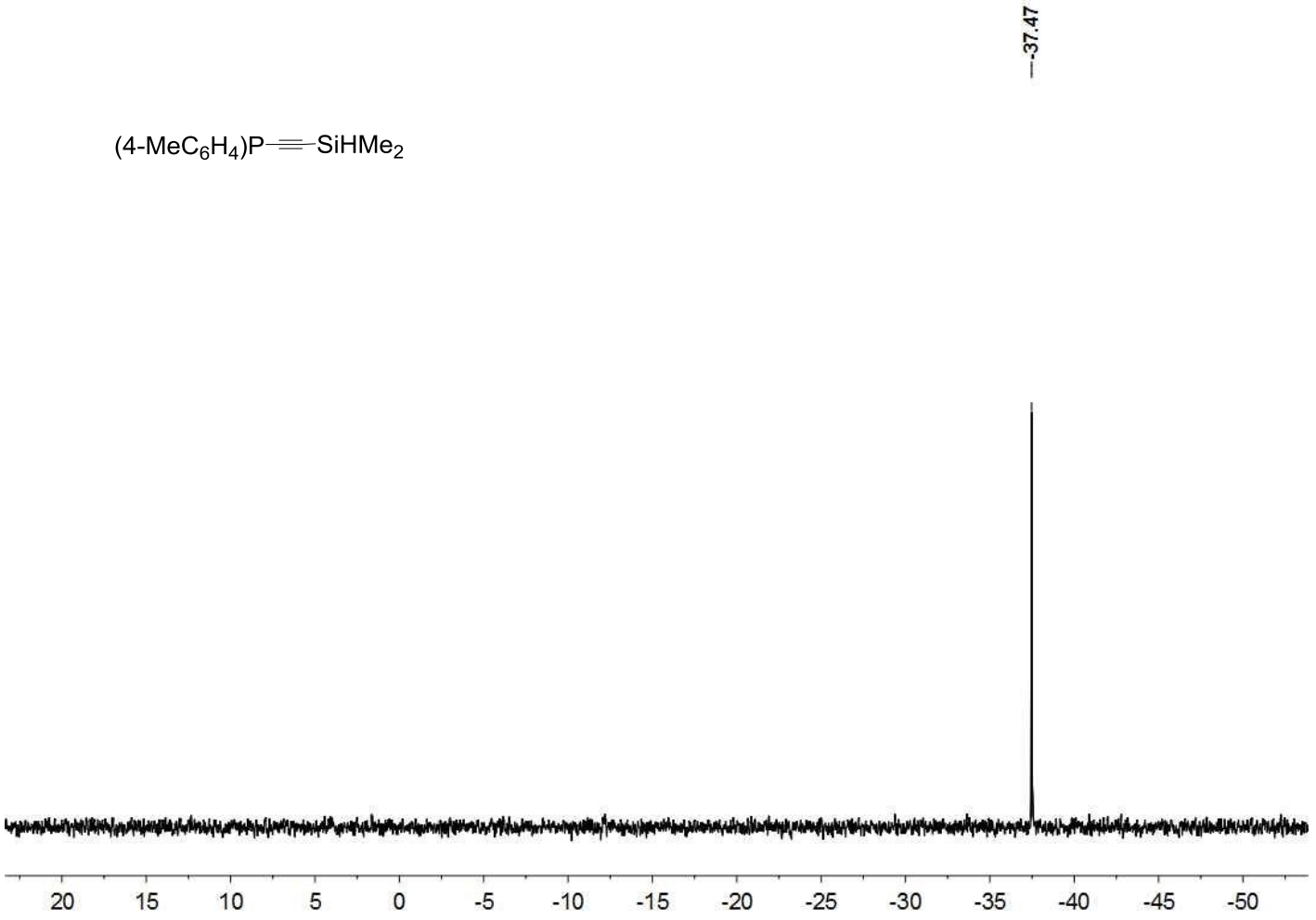

Figure S2-3. ^{29}Si NMR spectrum of **1b** in $CDCl_3$

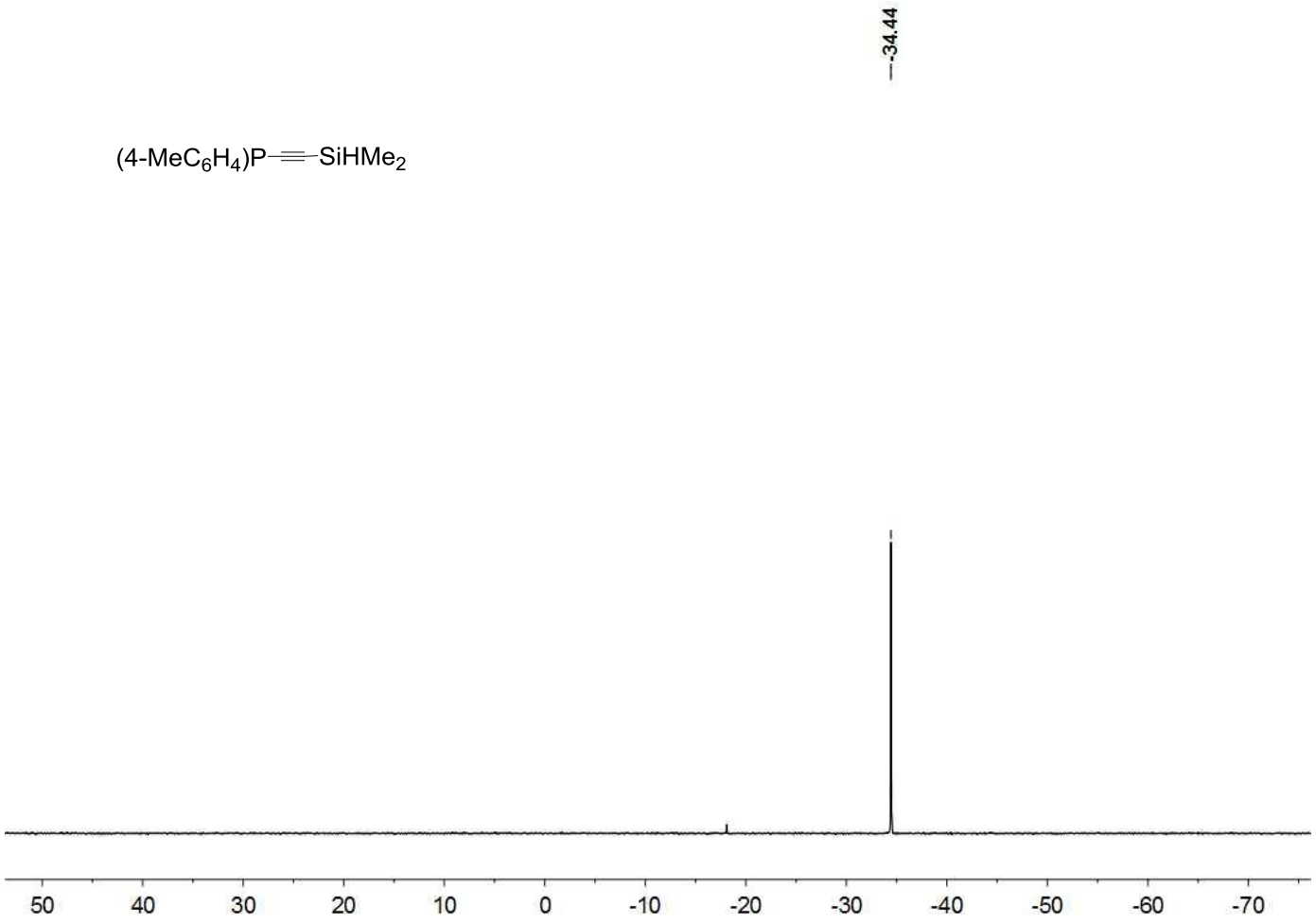

Figure S2-4. ^{31}P NMR spectrum of **1b** in $CDCl_3$

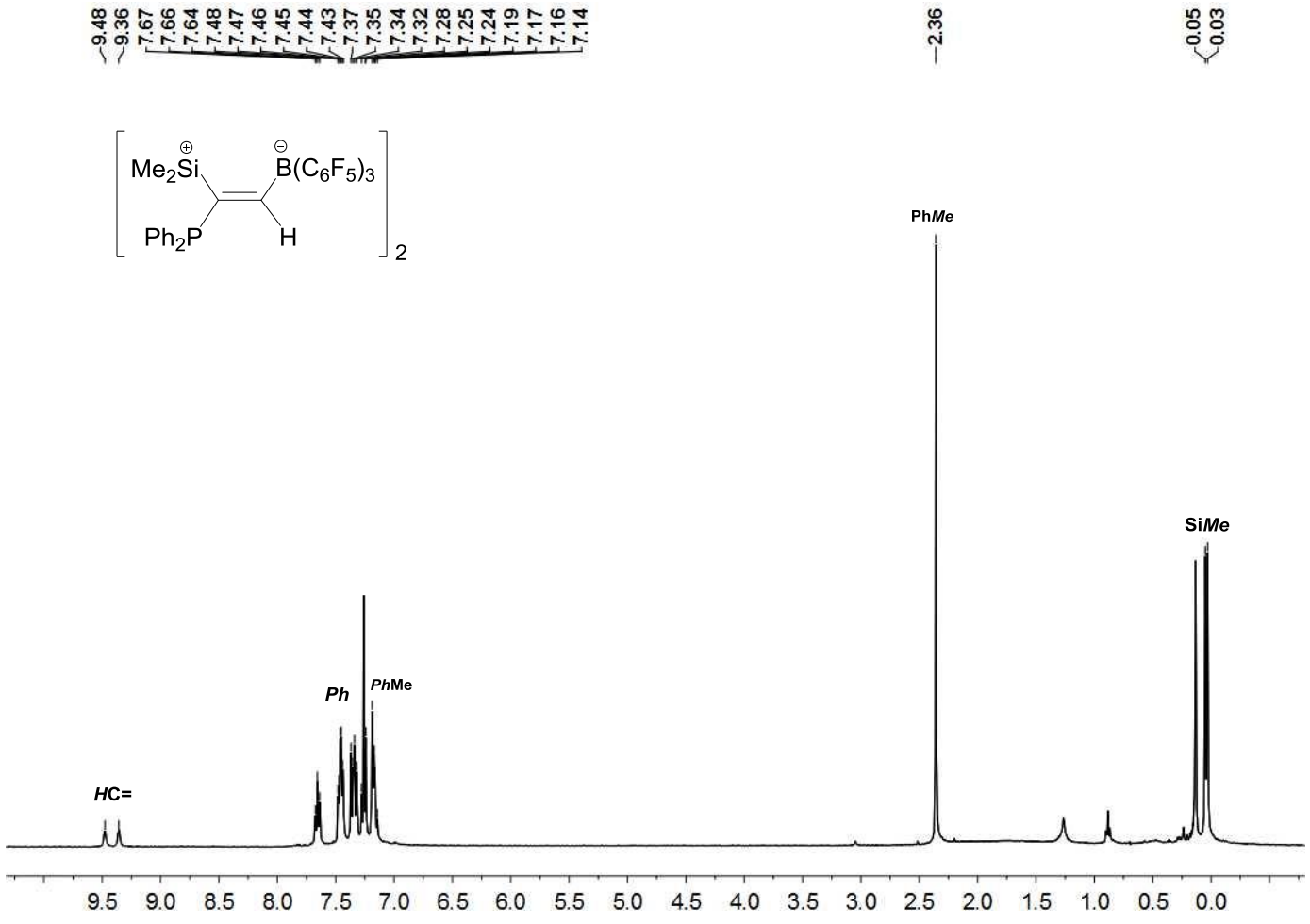

Figure S3-1. ^{1}H NMR spectrum of **2a** in $CDCl_3$ (toluene)

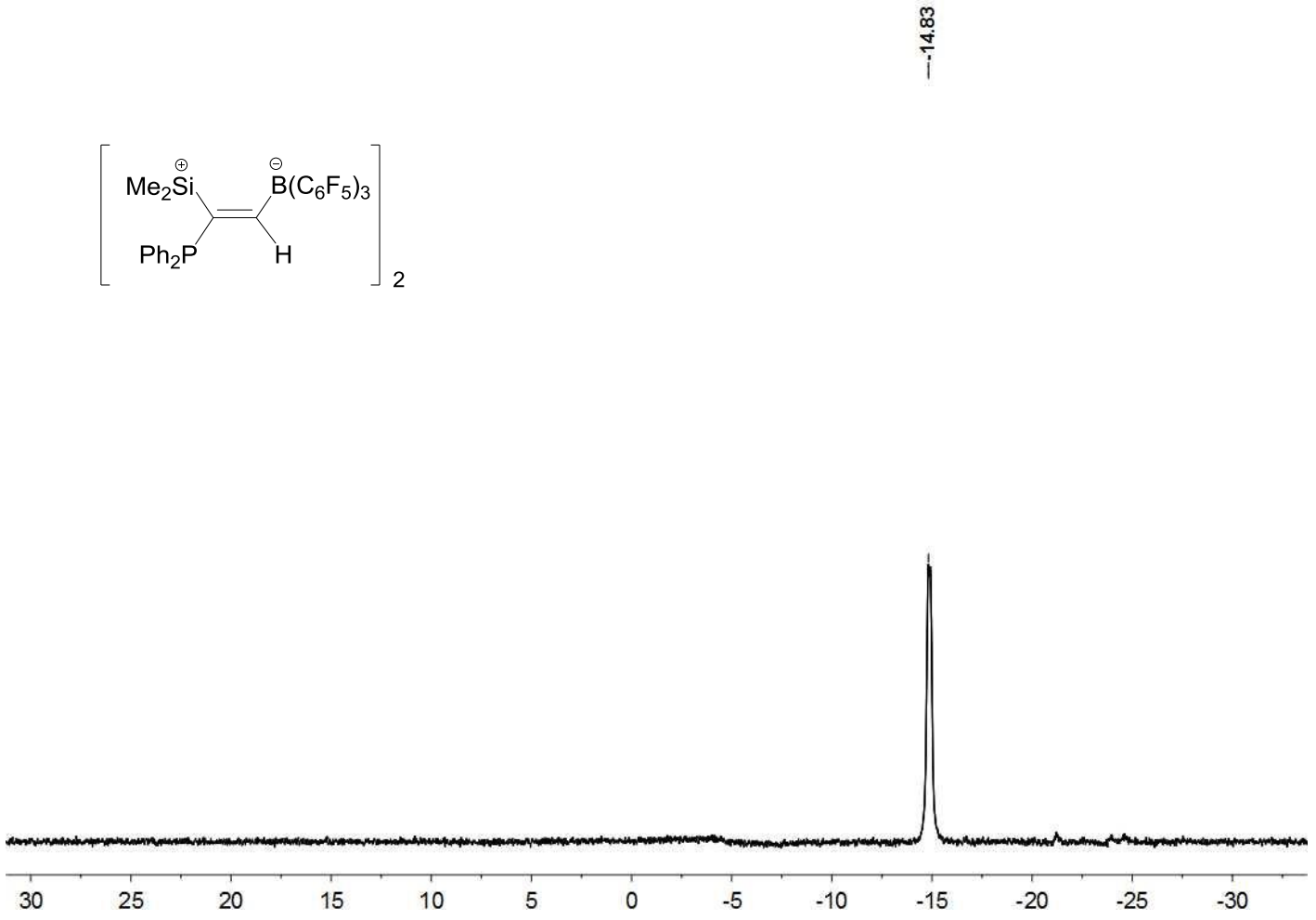

Figure S3-2. ^{11}B NMR spectrum of **2a** in $CDCl_3$(toluene)

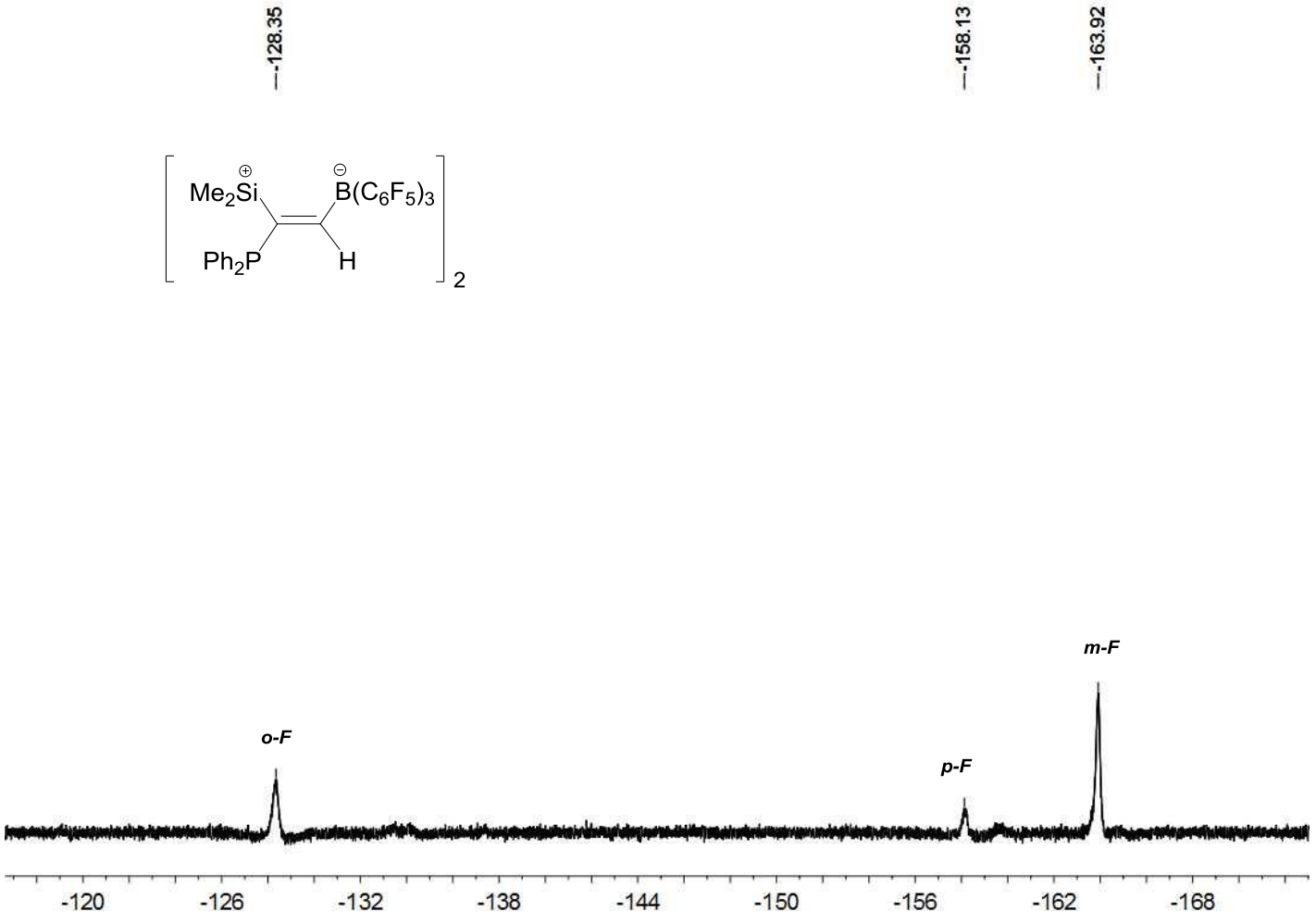

Figure S3-3. ^{19}F NMR spectrum of **2a** in $CDCl_3$

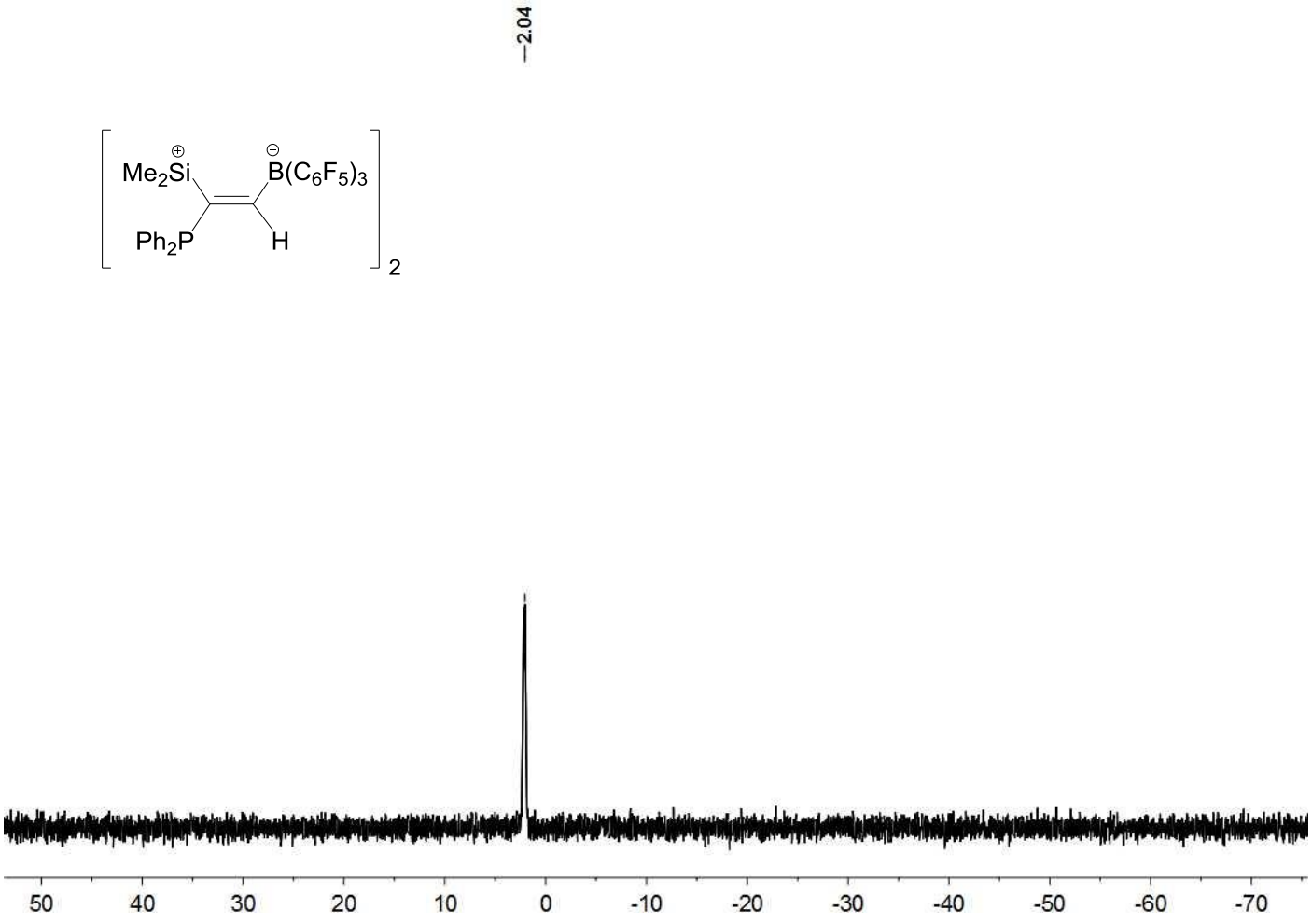

Figure S3-4. ^{31}P NMR spectrum of **2a** in $CDCl_3$

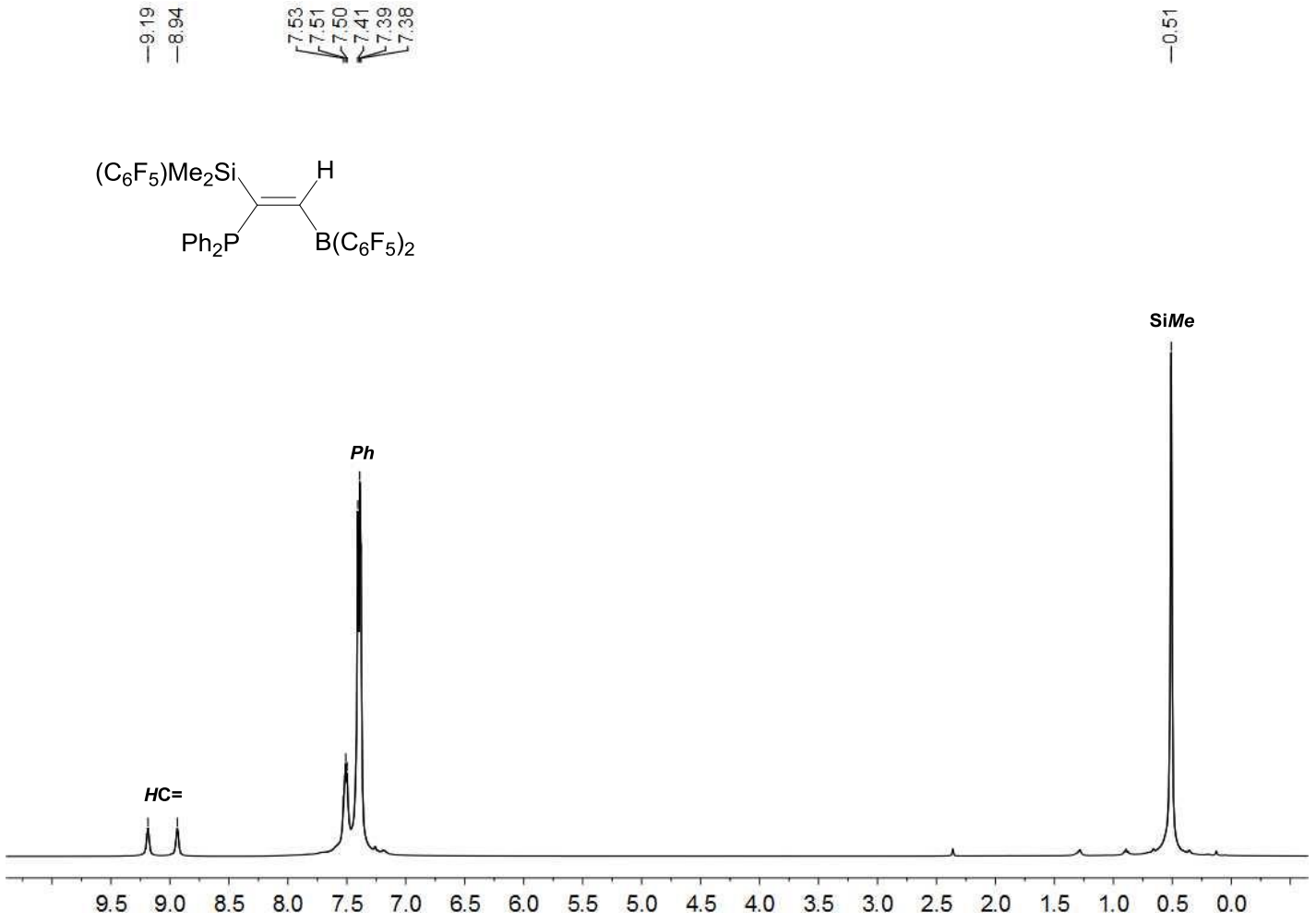

Figure S4-1. ^{1}H NMR spectrum of **3a** in $CDCl_3$

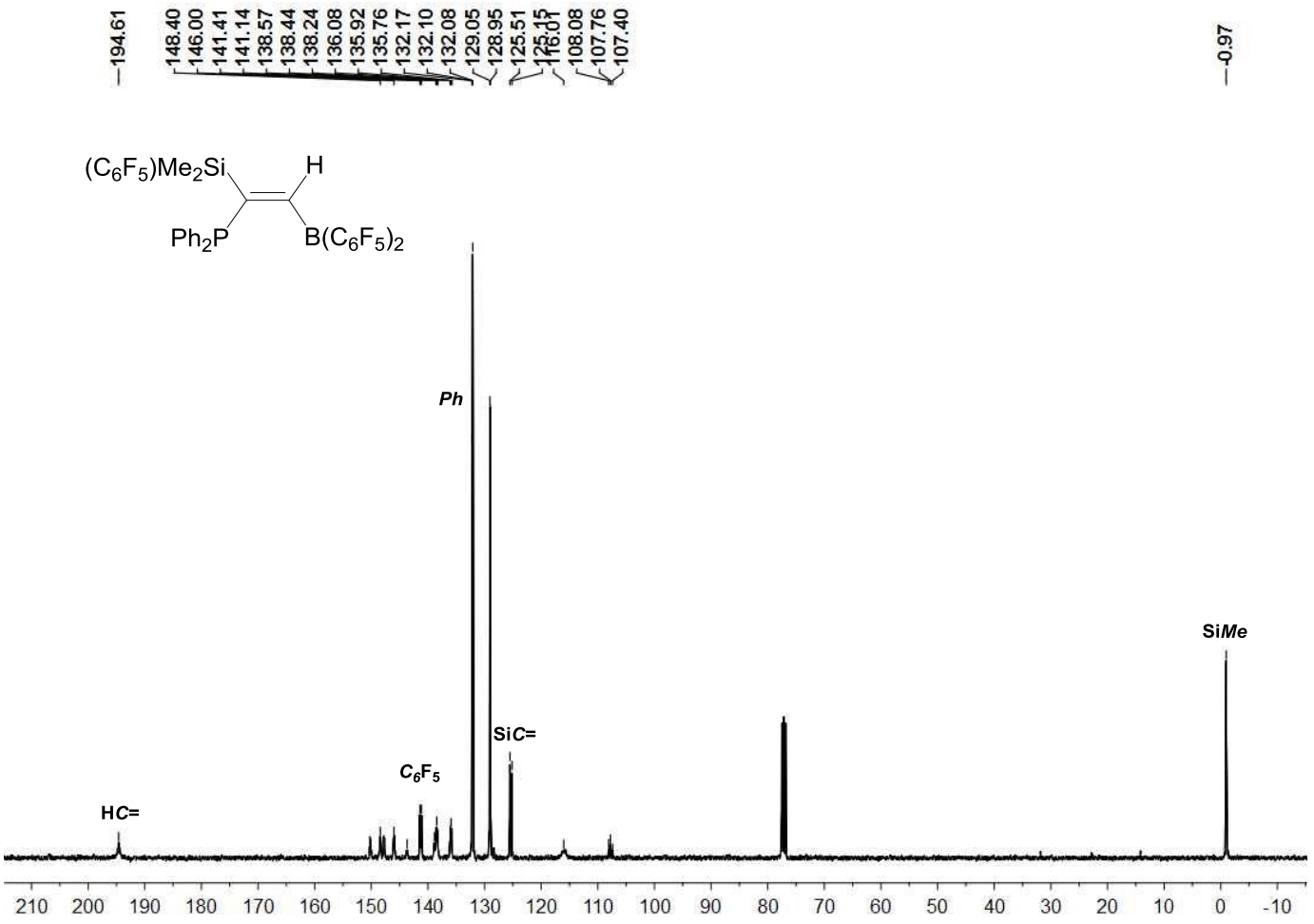

Figure S4-2. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$

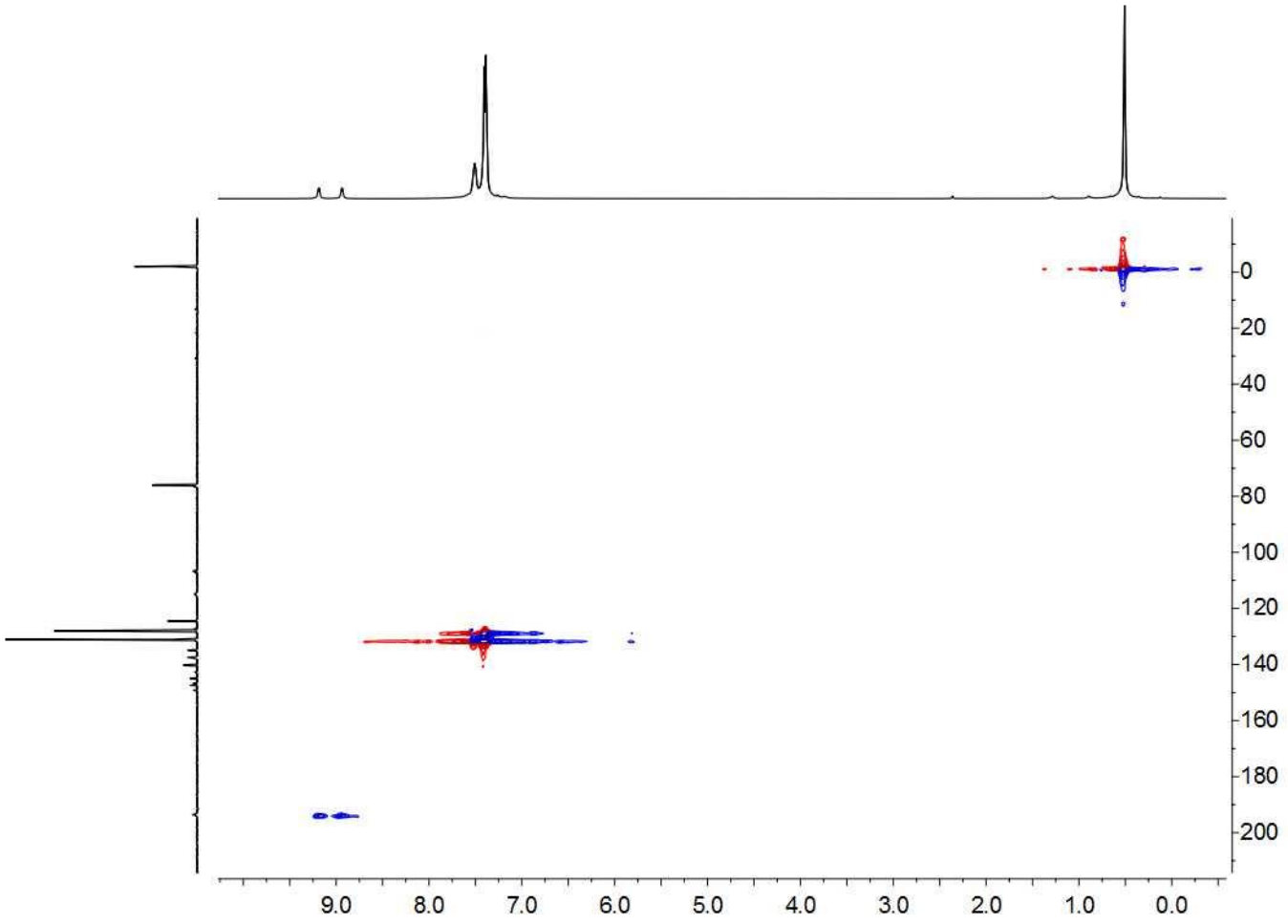

Figure S4-3. $^{1}H,^{13}C$-HSQC spectrum of **3a** in $CDCl_3$

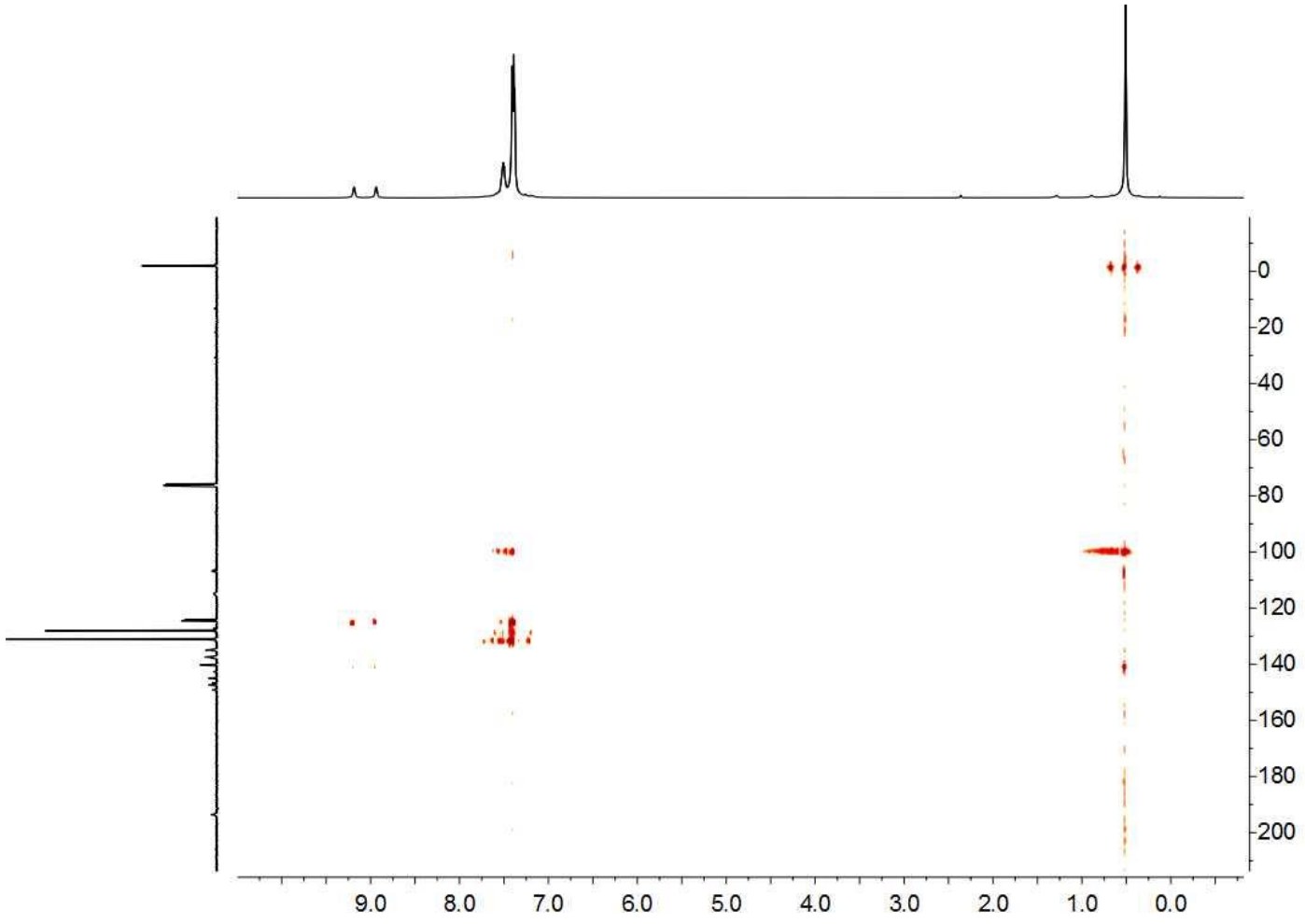

Figure S4-4. $^{1}H,^{13}C$-HMBC spectrum of **3a** in $CDCl_3$

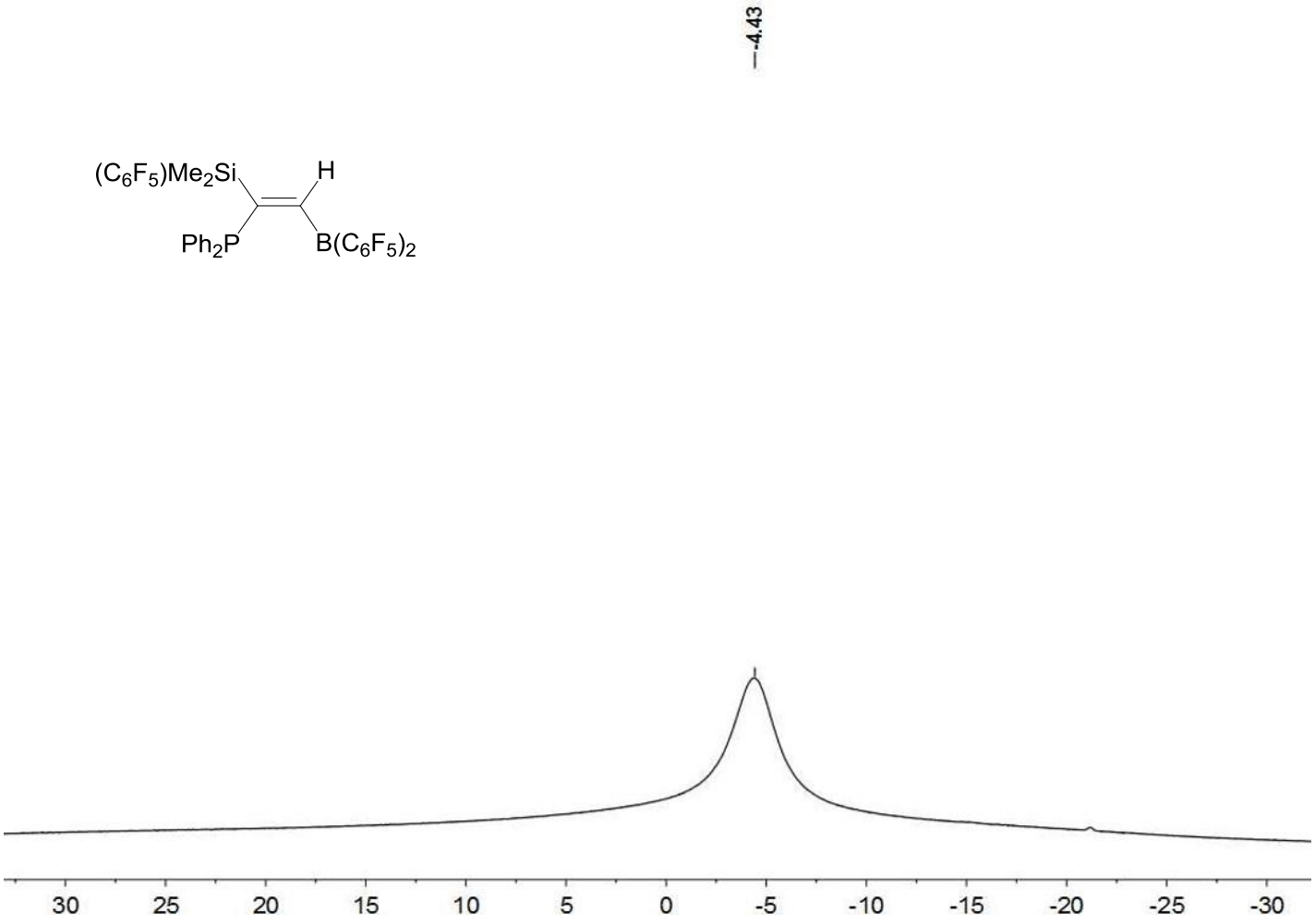

Figure S4-5. ^{11}B NMR spectrum of **3a** in $CDCl_3$

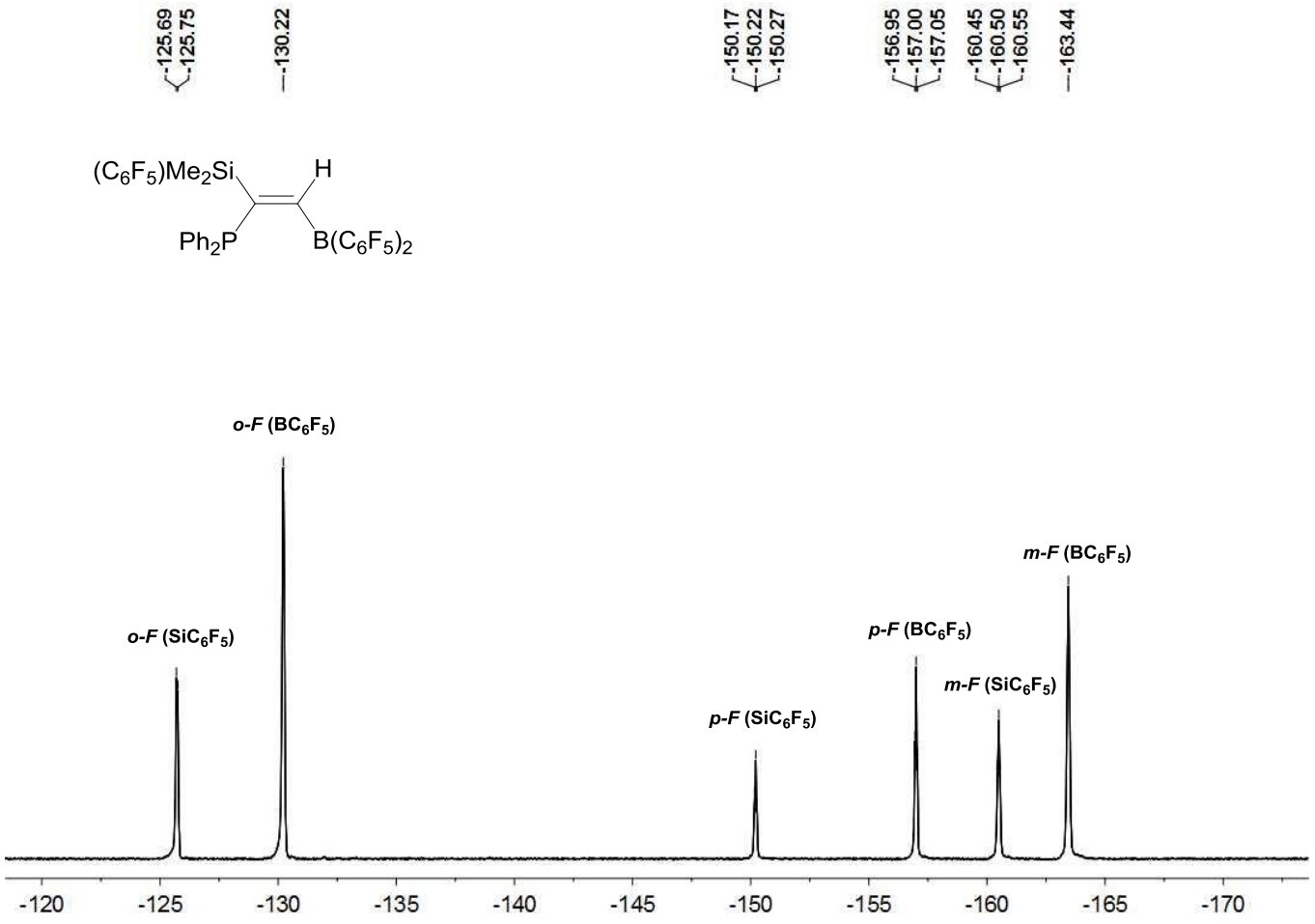

Figure S4-6. ^{19}F NMR spectrum of **3a** in $CDCl_3$

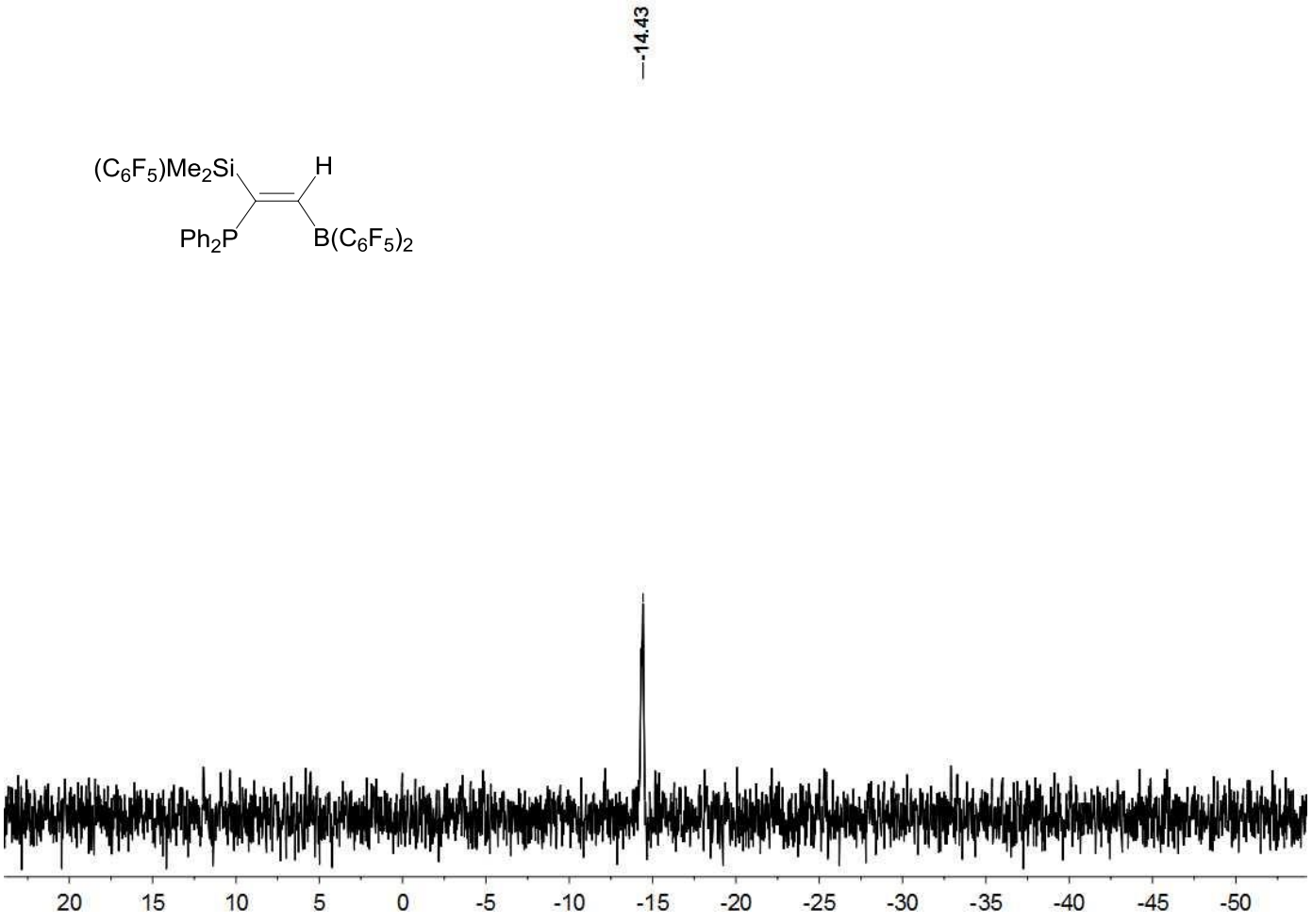

Figure S4-7. ^{29}Si NMR spectrum of **3a** in $CDCl_3$

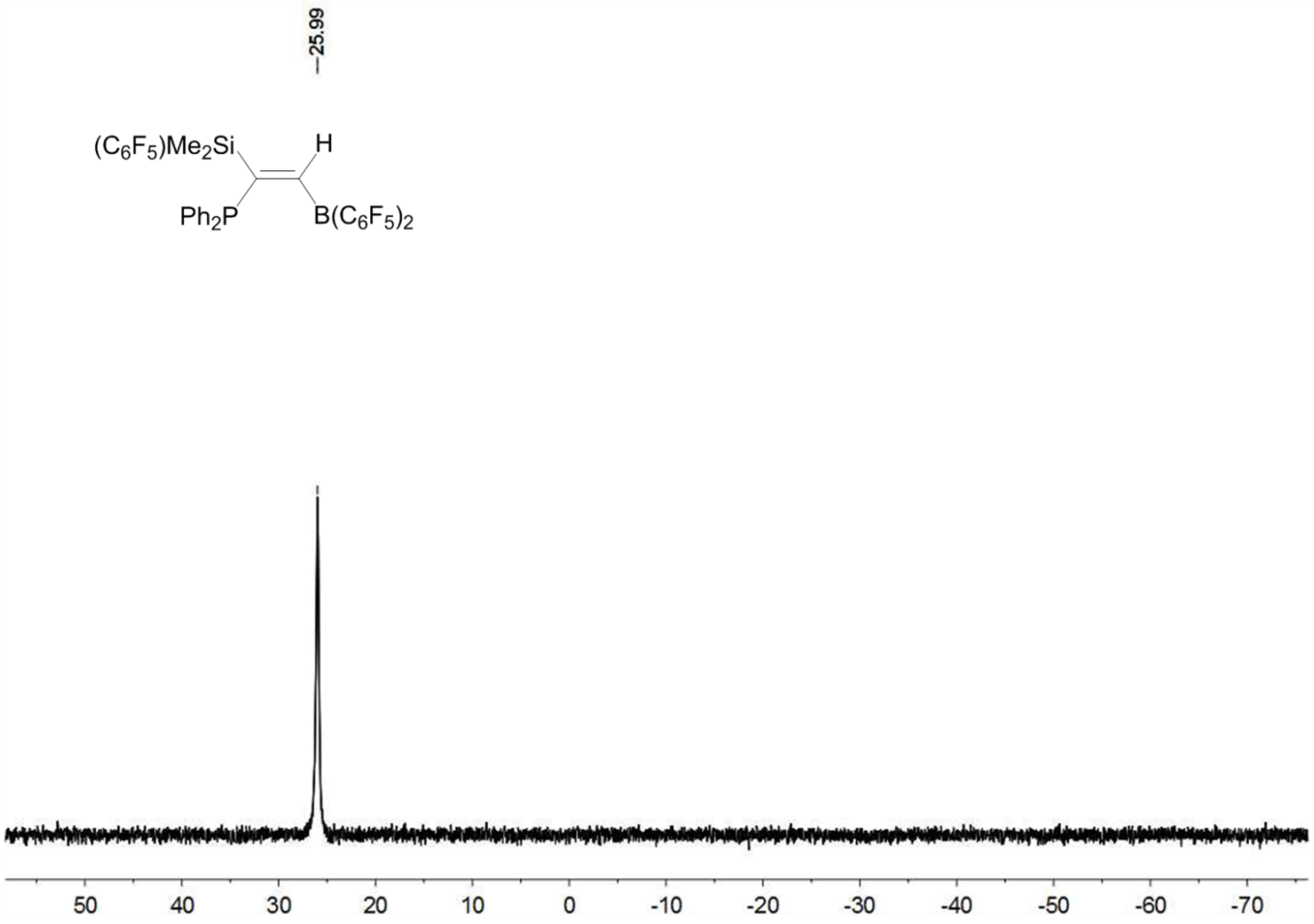

Figure S4-8. ^{31}P NMR spectrum of **3a** in $CDCl_3$

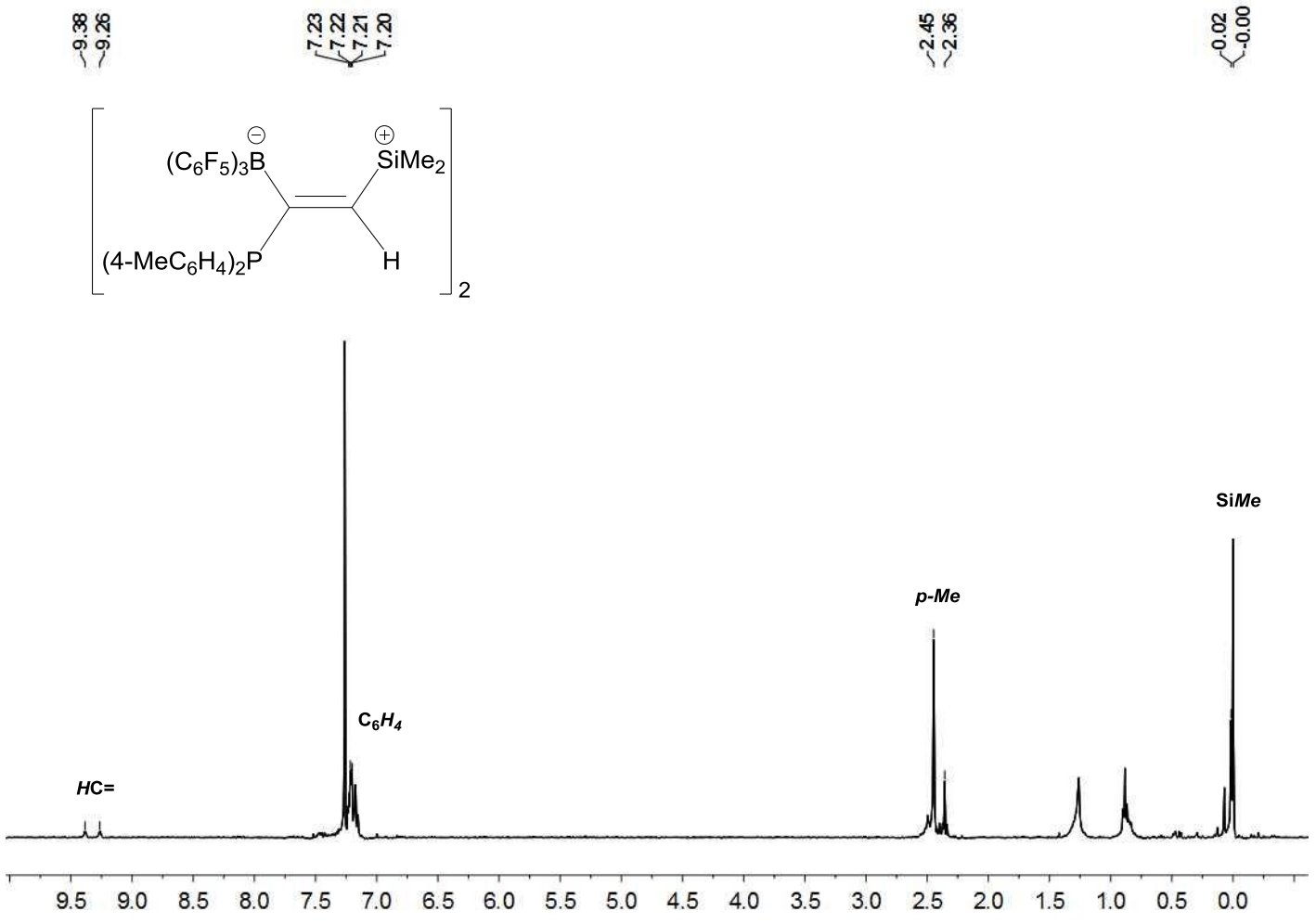

Figure S5-1. ^{1}H NMR spectrum of **2b** in $CDCl_3$

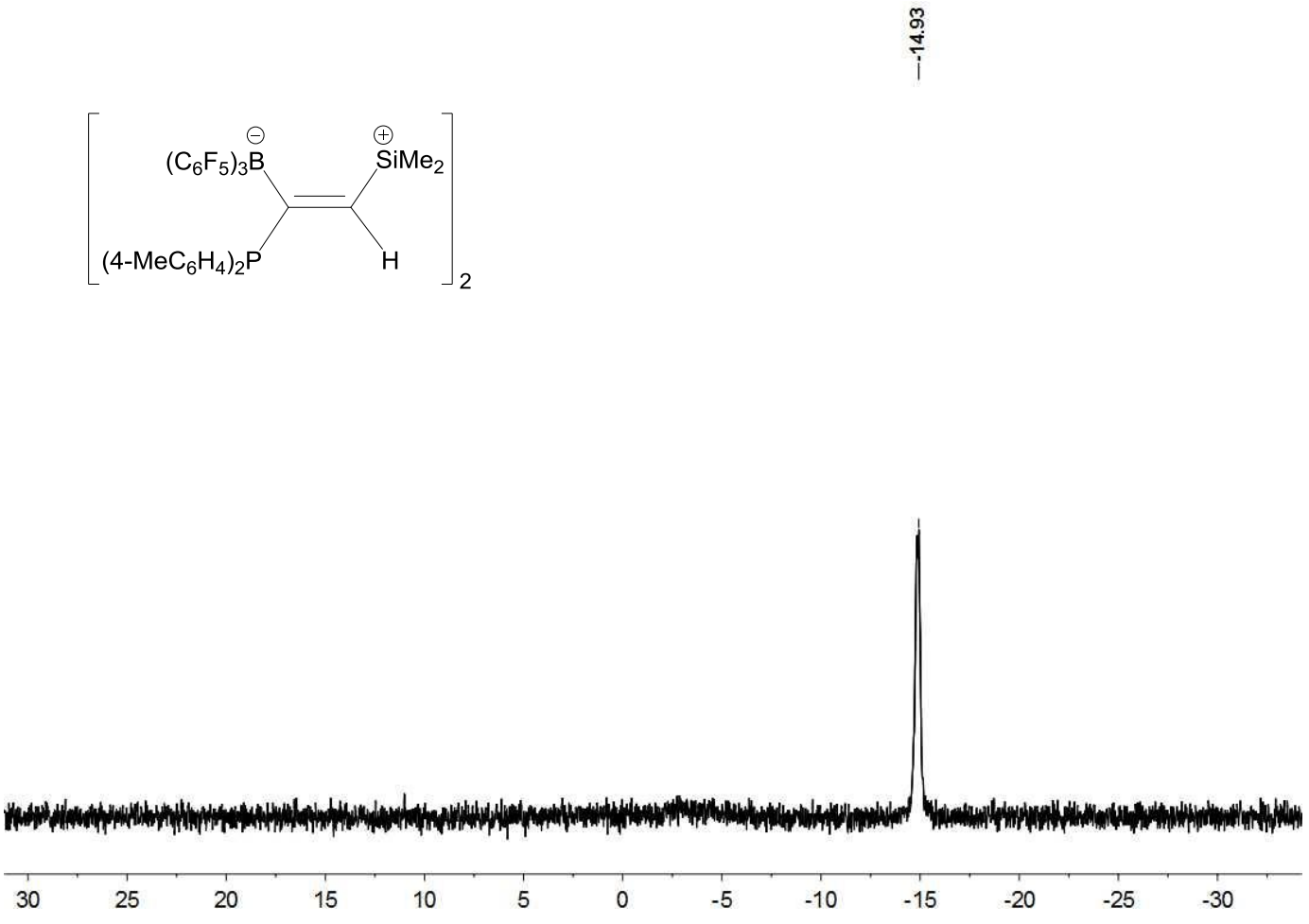

Figure S5-2. ^{11}B NMR spectrum of **2b** in $CDCl_3$

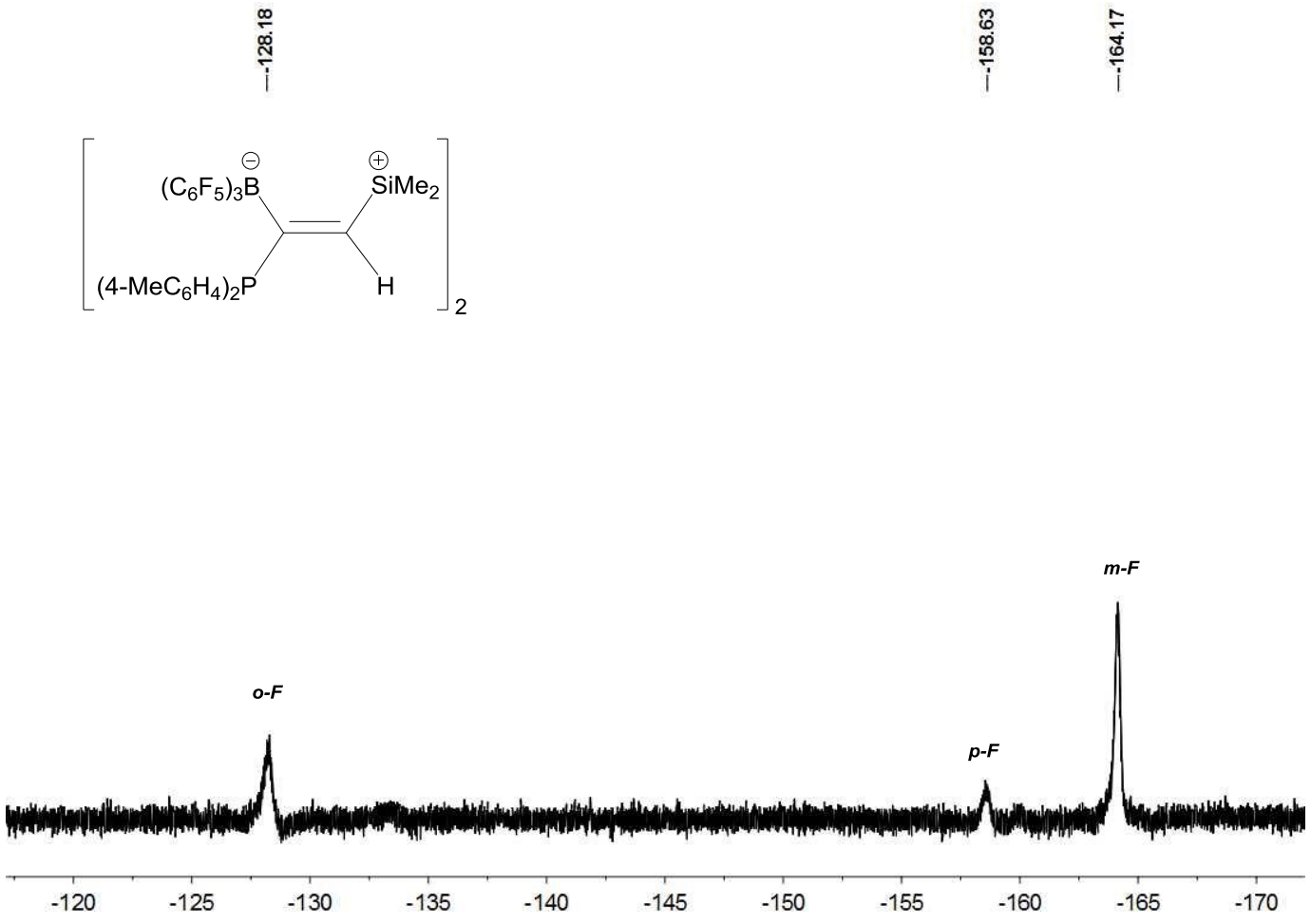

Figure S5-3. ^{19}F NMR spectrum of **2b** in $CDCl_3$

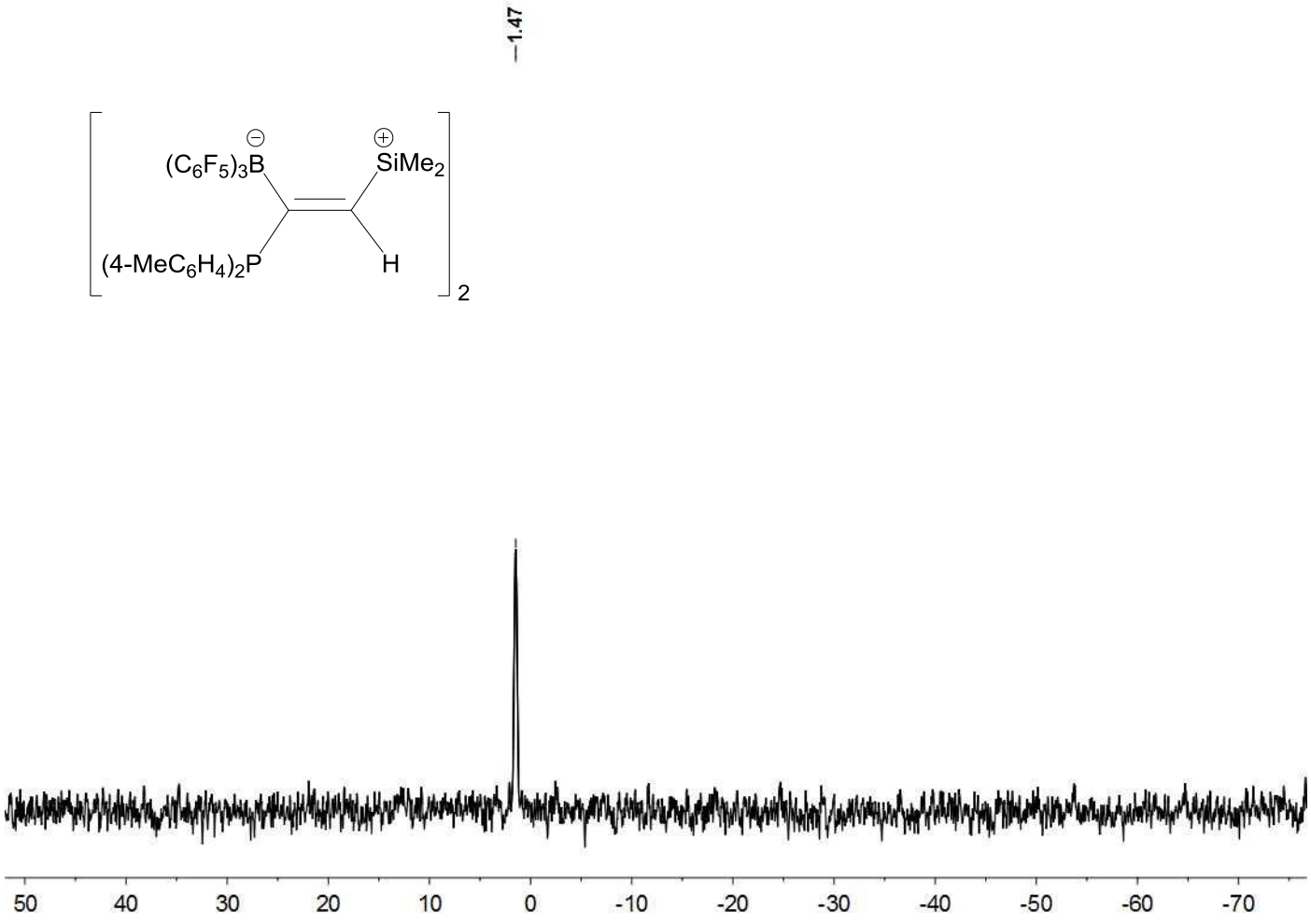

Figure S5-4. ^{31}P NMR spectrum of **2b** in $CDCl_3$

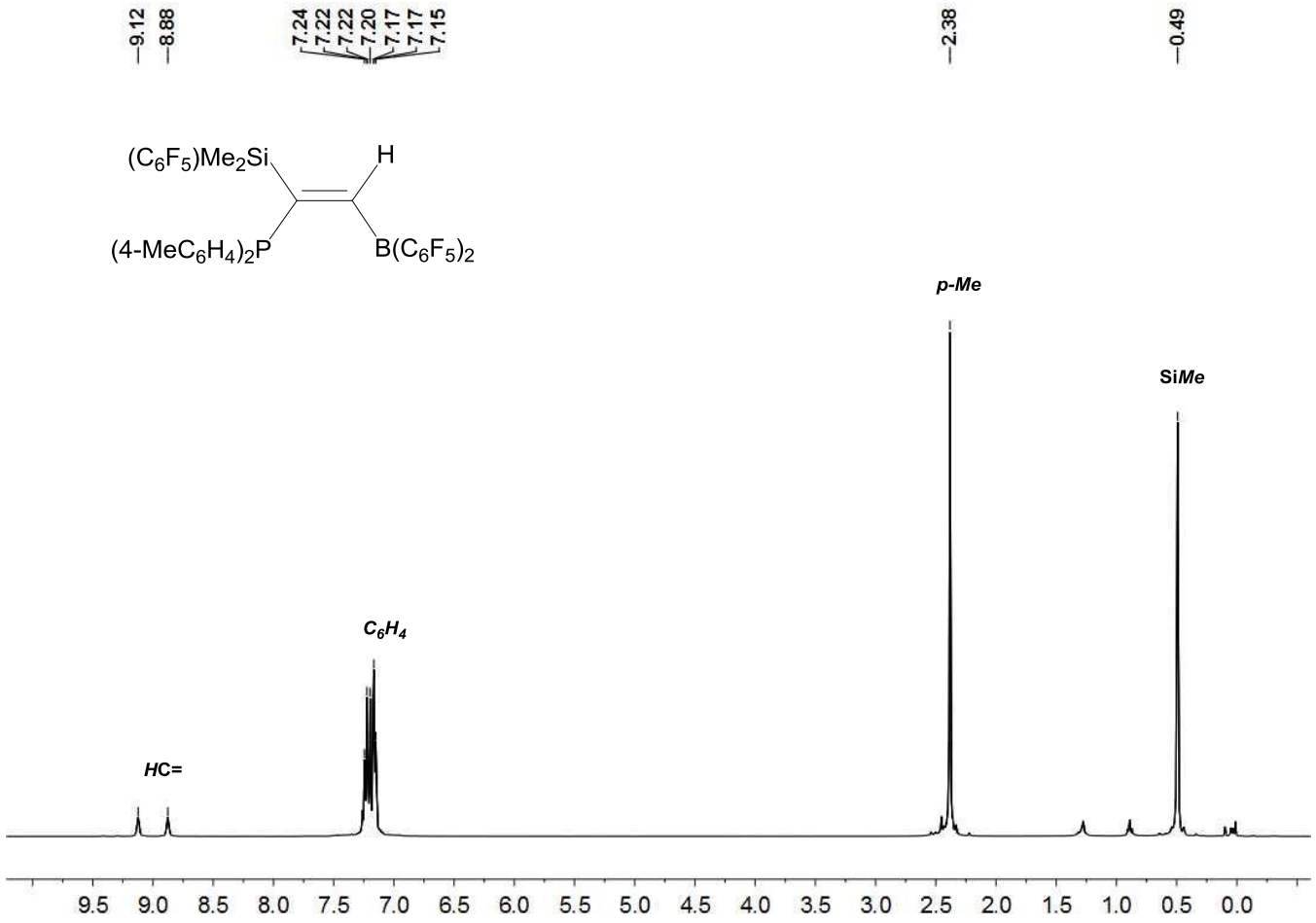

Figure S6-1. ^{1}H NMR spectrum of **3b** in $CDCl_3$

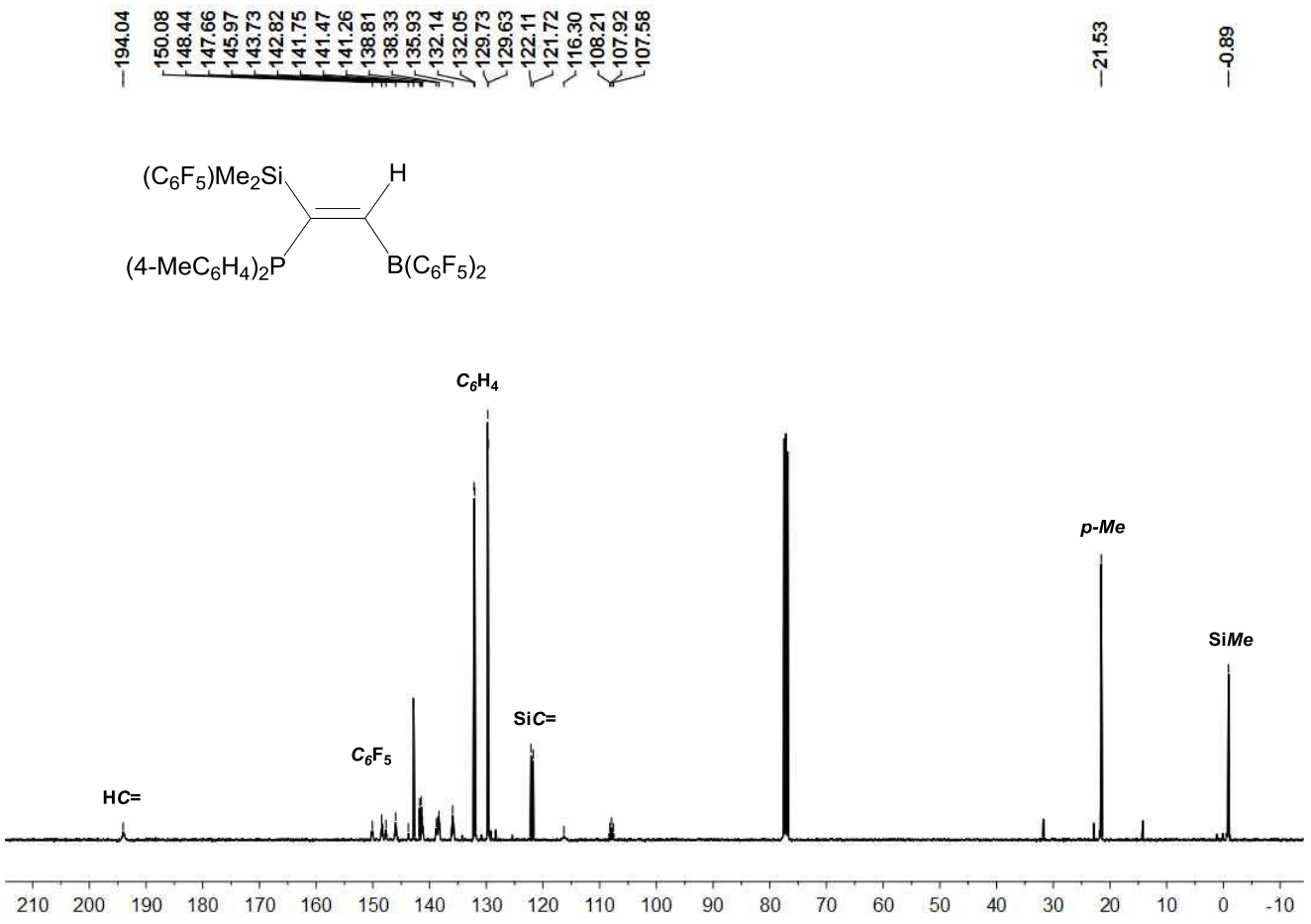

Figure S6-2. $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in $CDCl_3$

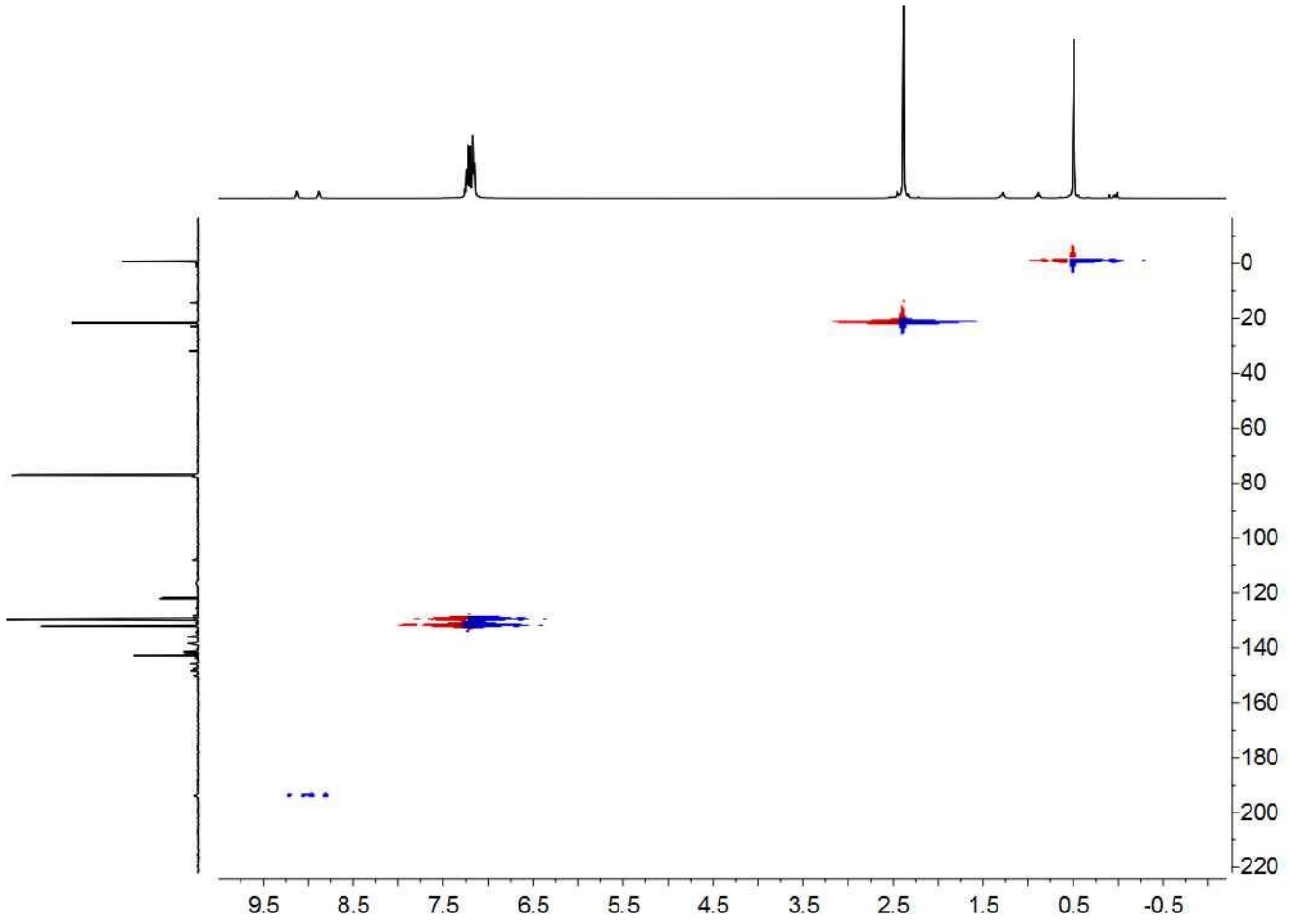

Figure S6-3. $^{1}H,^{13}C$-HSQC spectrum of **3b** in $CDCl_3$

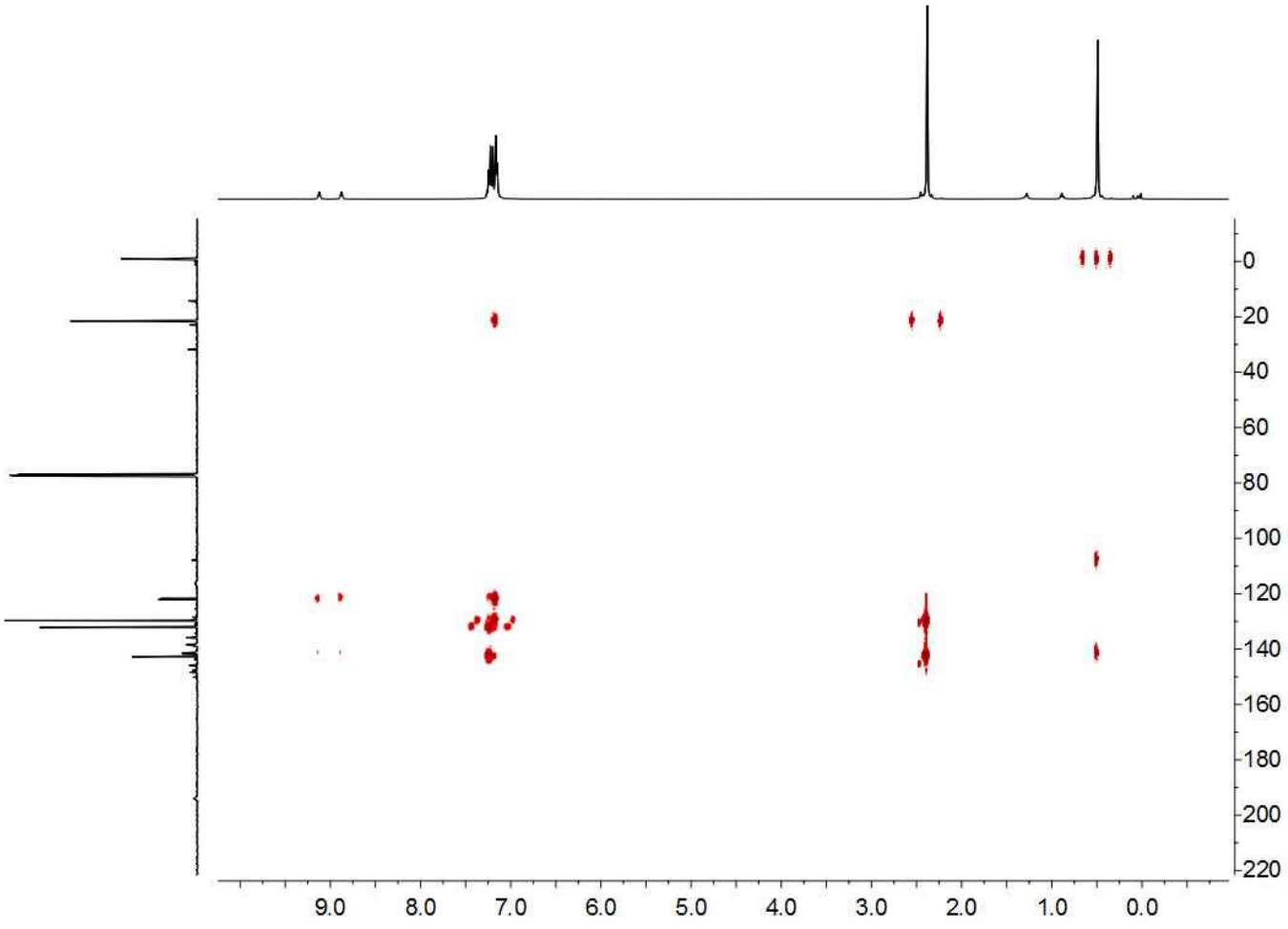

Figure S6-4. $^{1}H,^{13}C$-HMBC spectrum of **3b** in $CDCl_3$

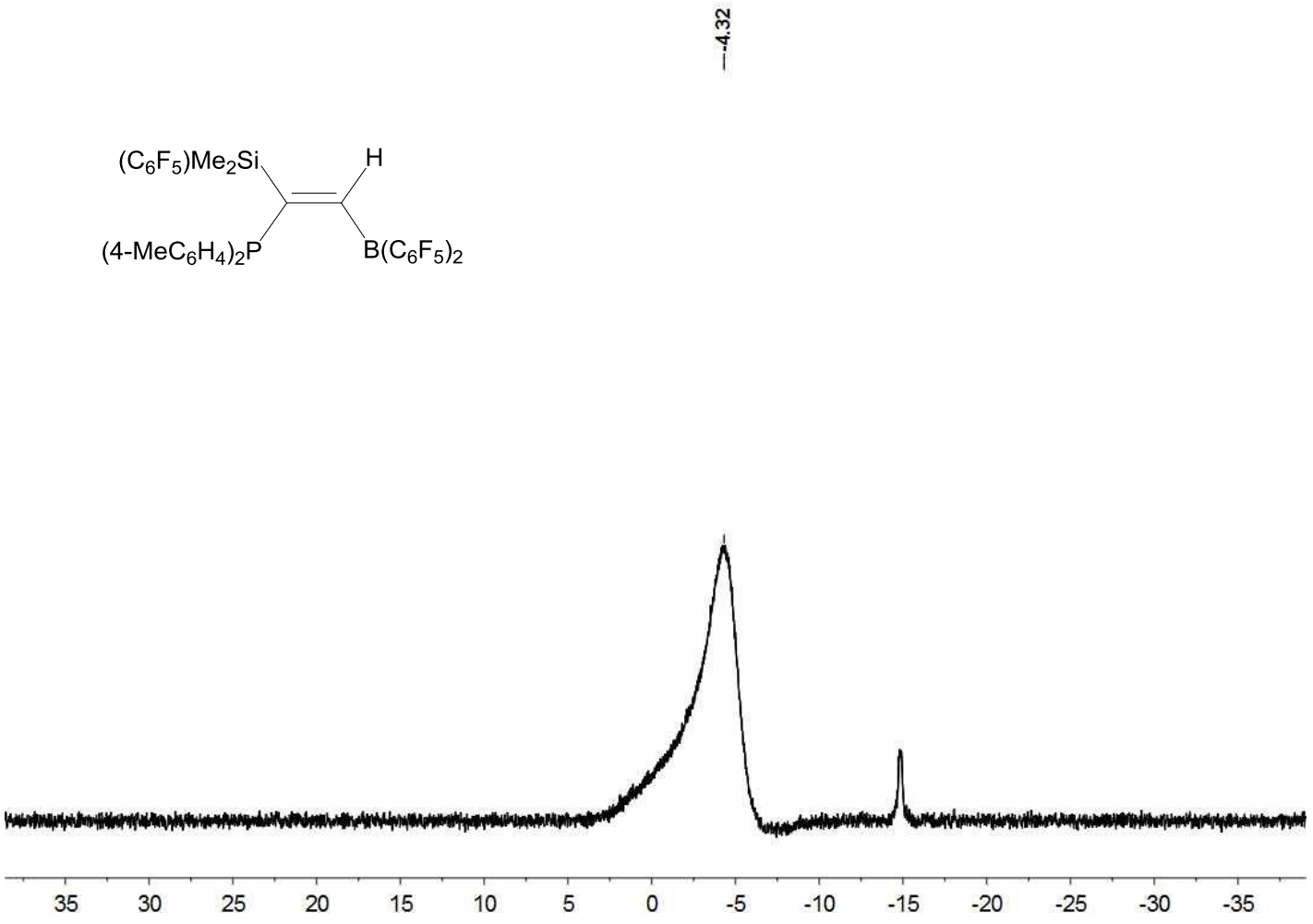

Figure S6-5. ^{11}B NMR spectrum of **3b** in $CDCl_3$

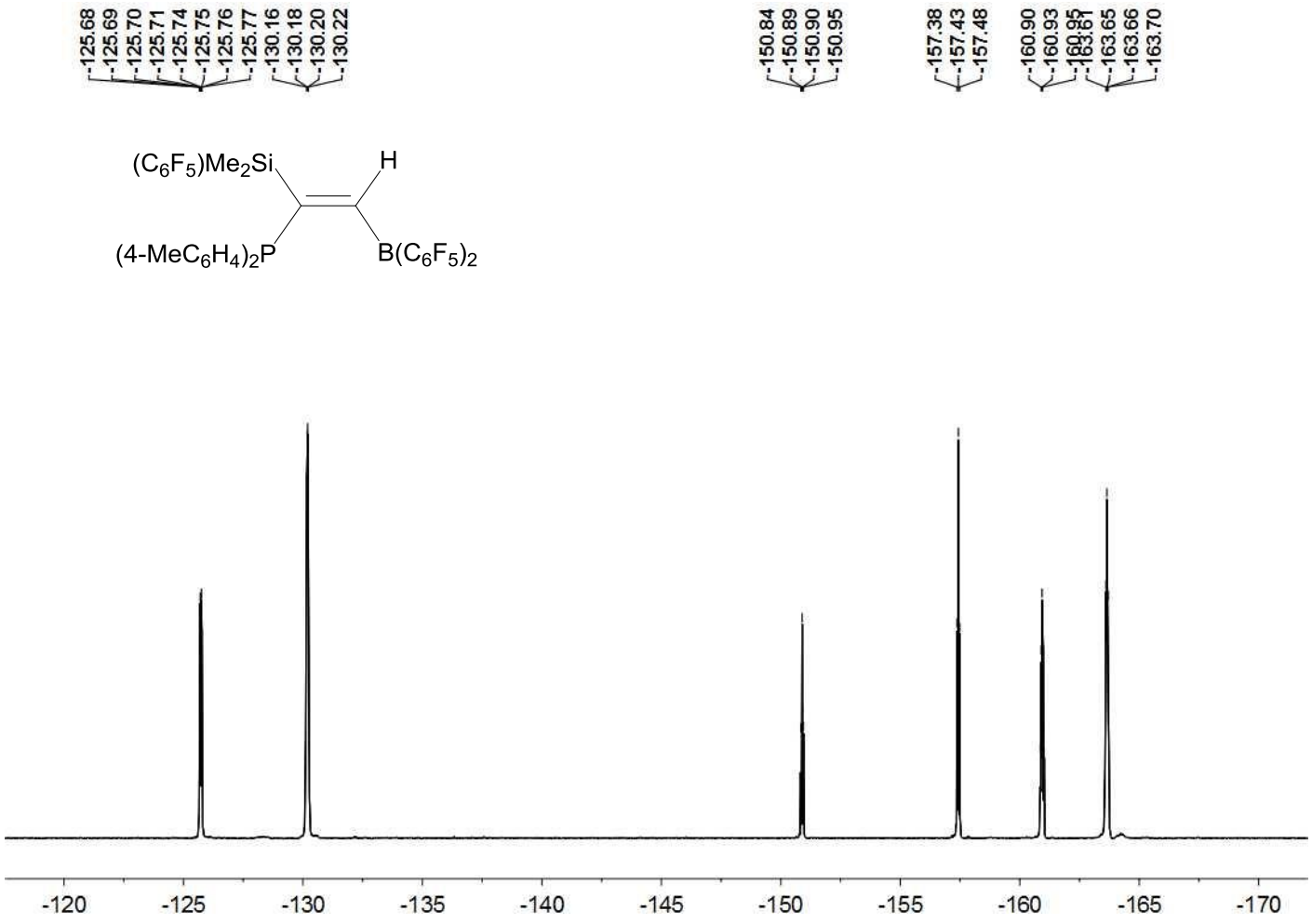

Figure S6-6. ^{19}F NMR spectrum of **3b** in $CDCl_3$

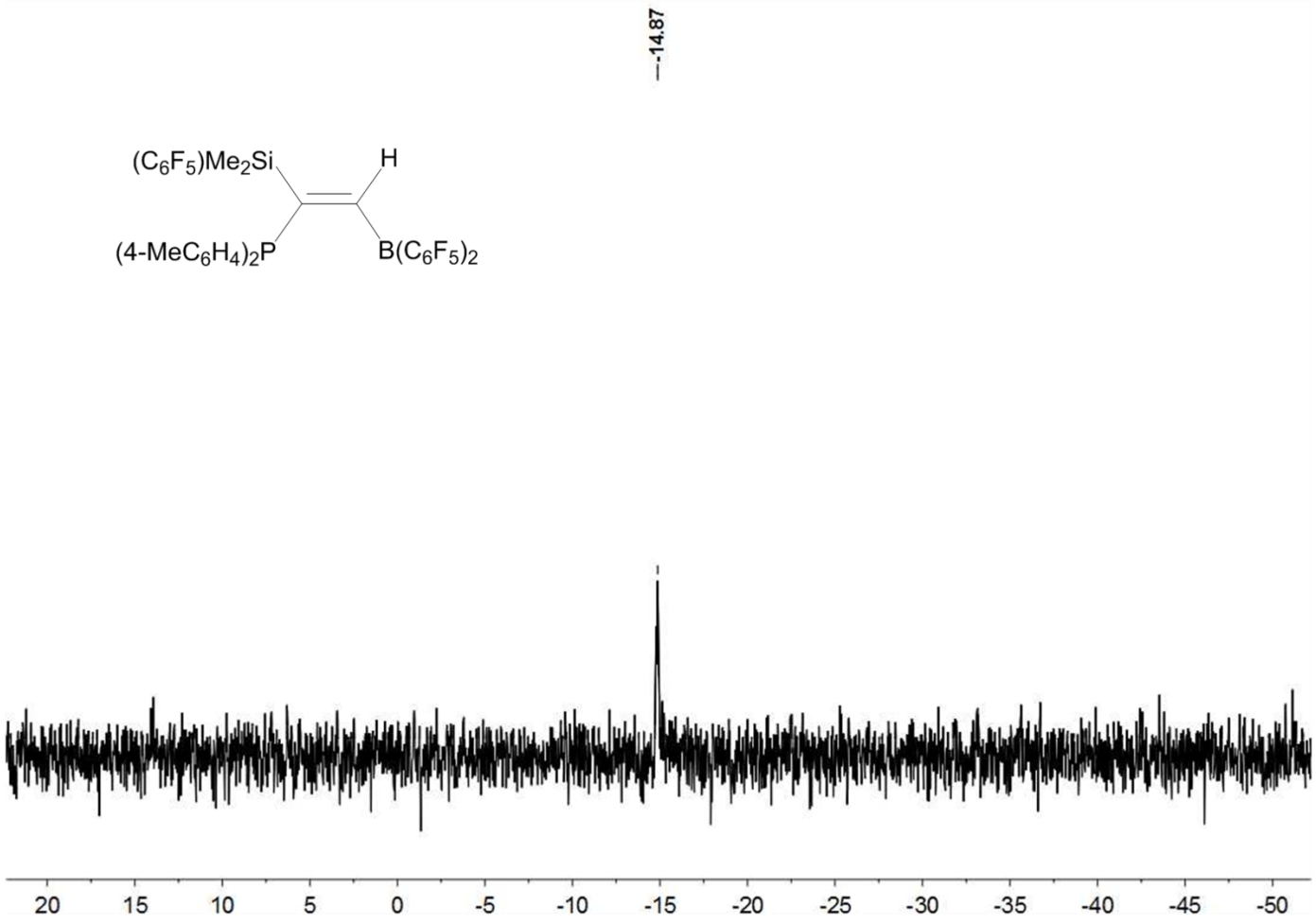

Figure S6-7. ^{29}Si NMR spectrum of **3b** in $CDCl_3$

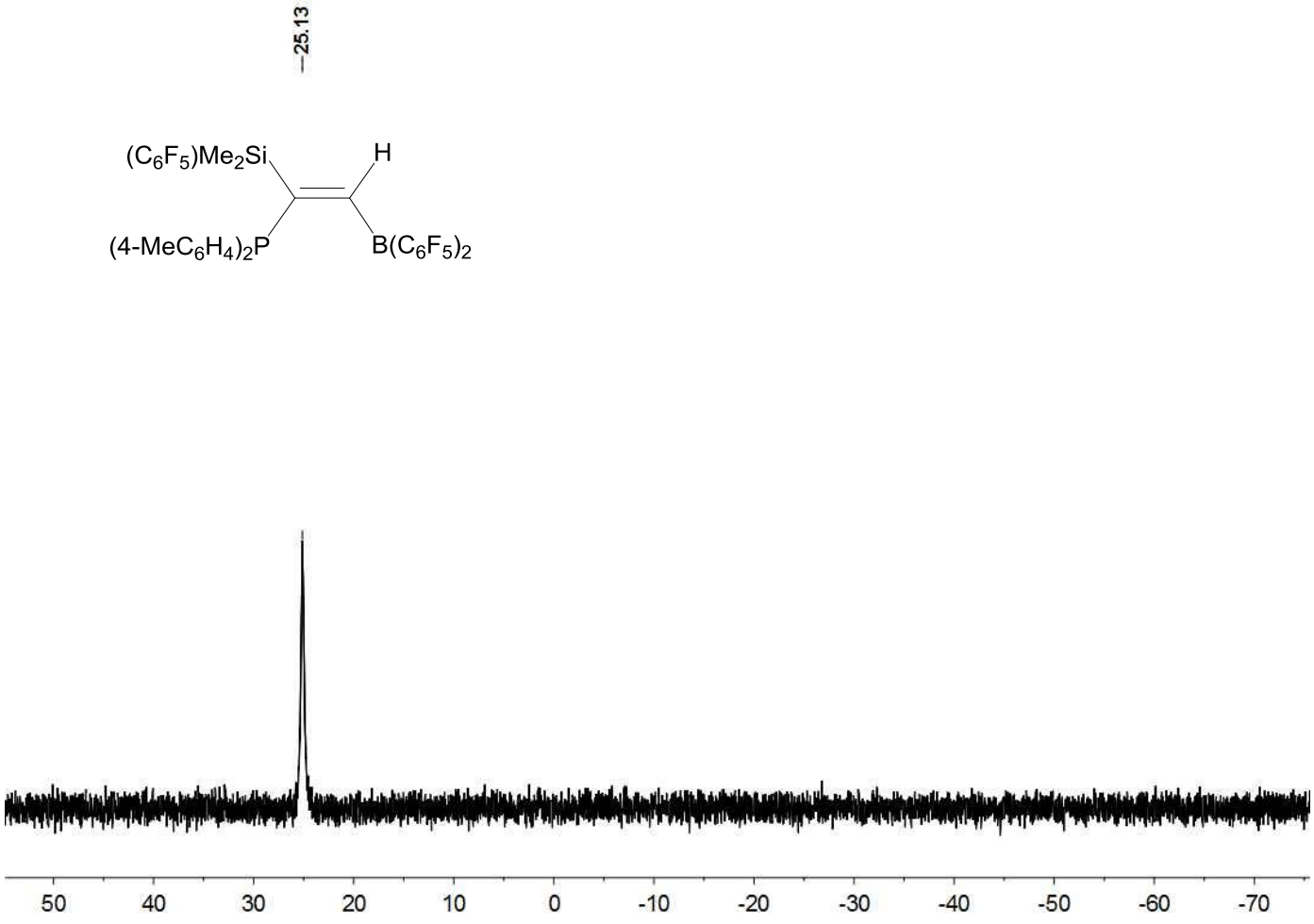

Figure S6-8. ^{31}P NMR spectrum of **3b** in $CDCl_3$

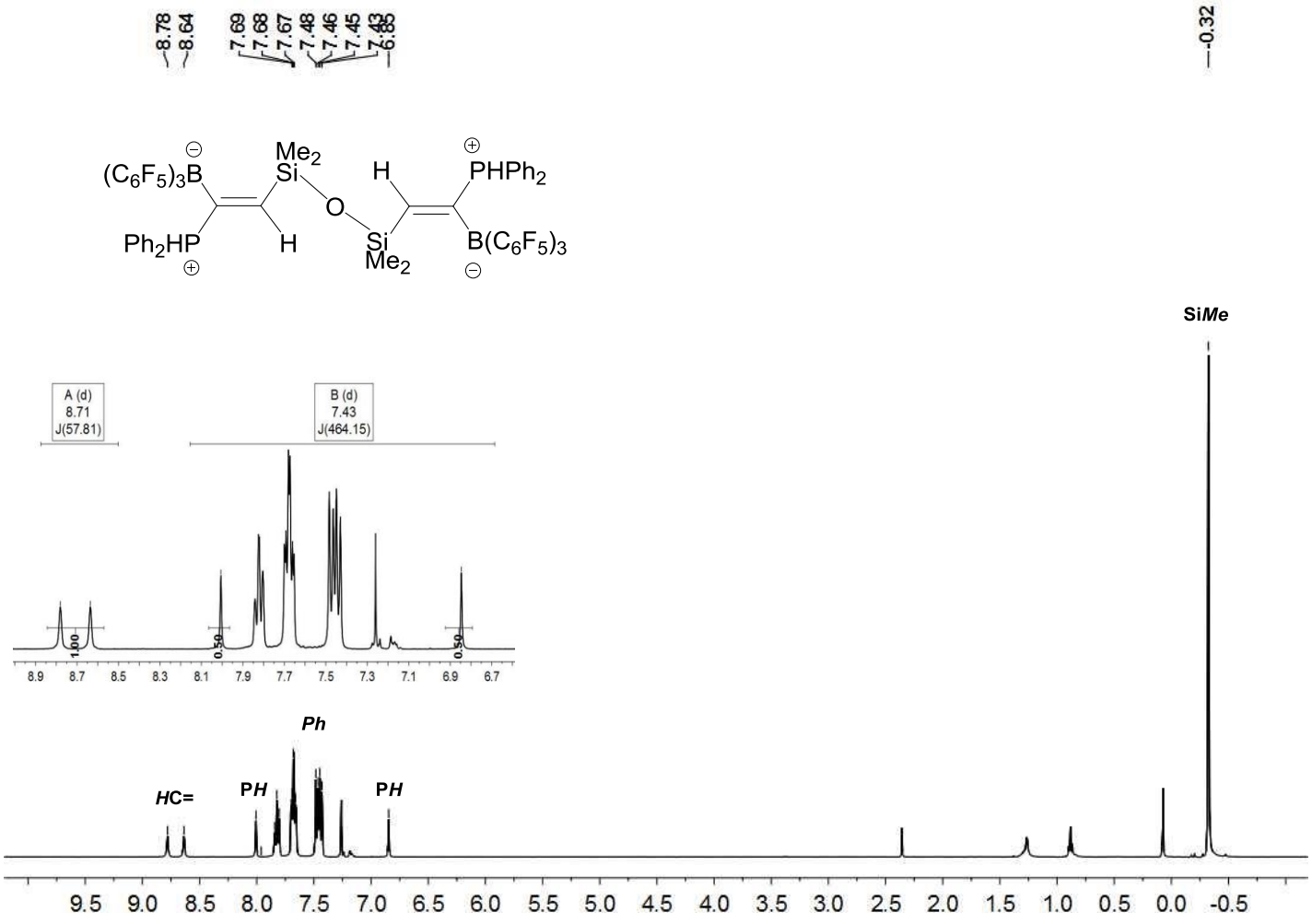

Figure S7-1. ^{1}H NMR spectrum of **4** in $CDCl_3$

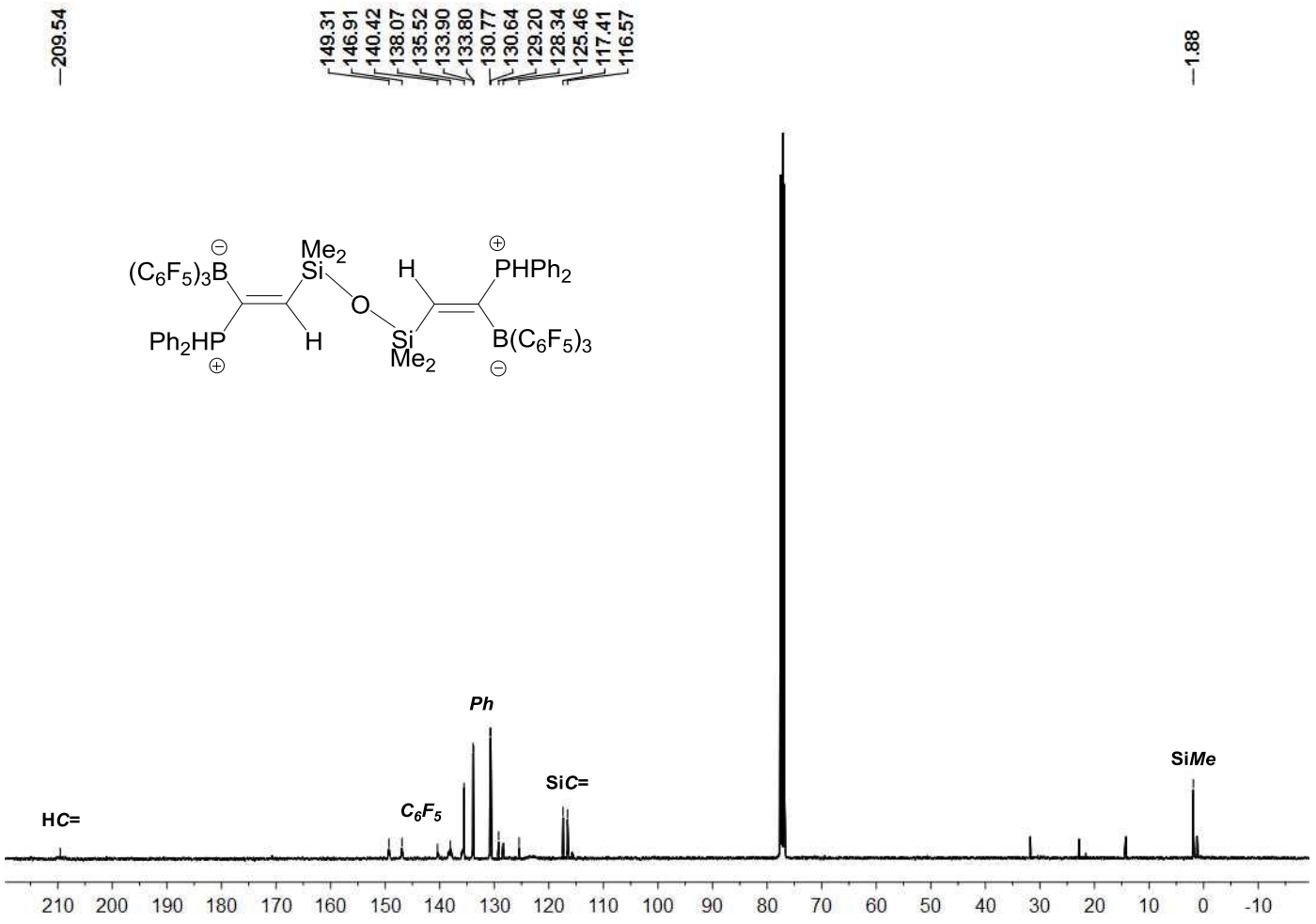

Figure S7-2. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in $CDCl_3$

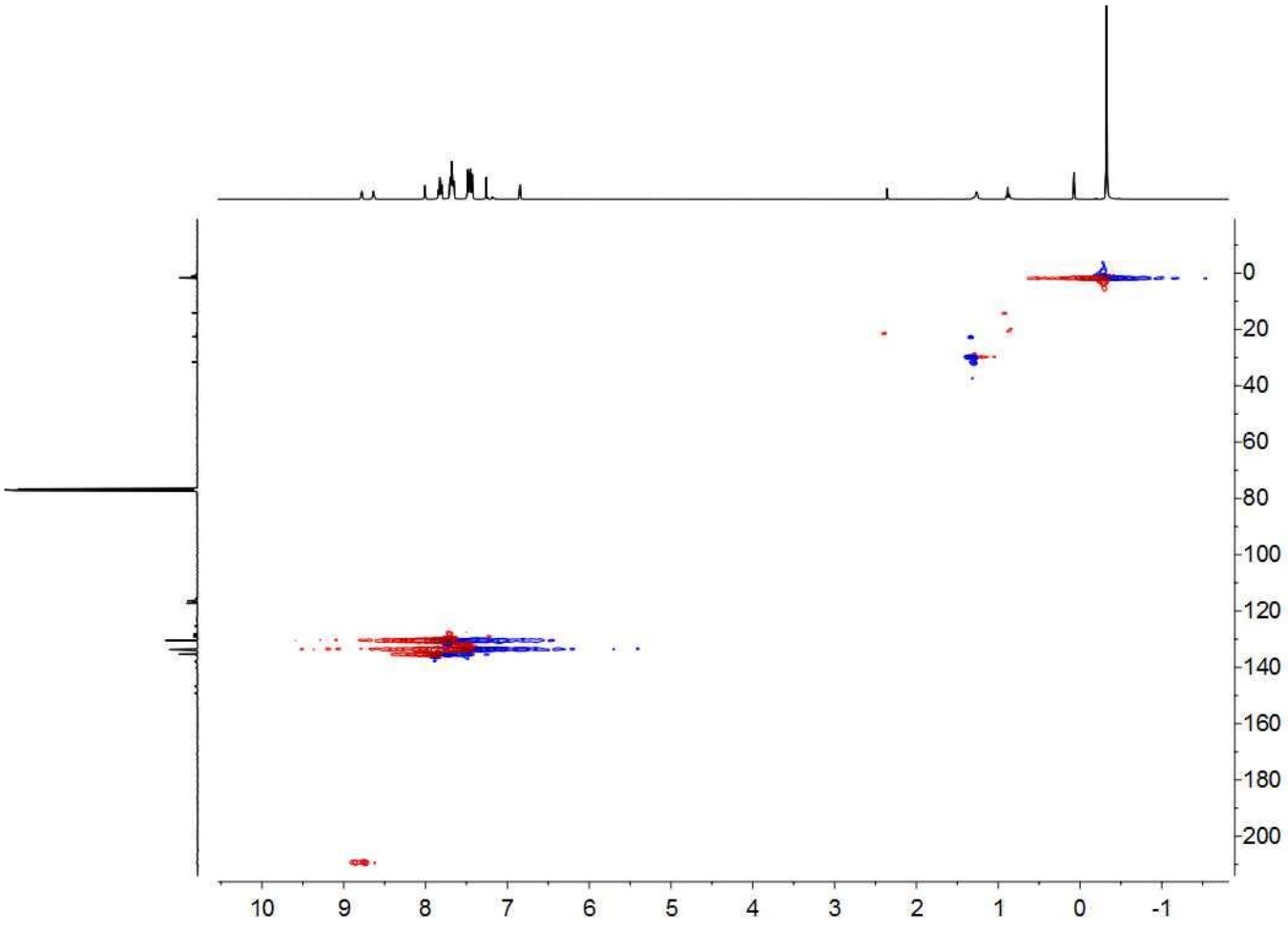

Figure S7-3. $^{1}H,^{13}C$-HSQC spectrum of **4** in $CDCl_3$

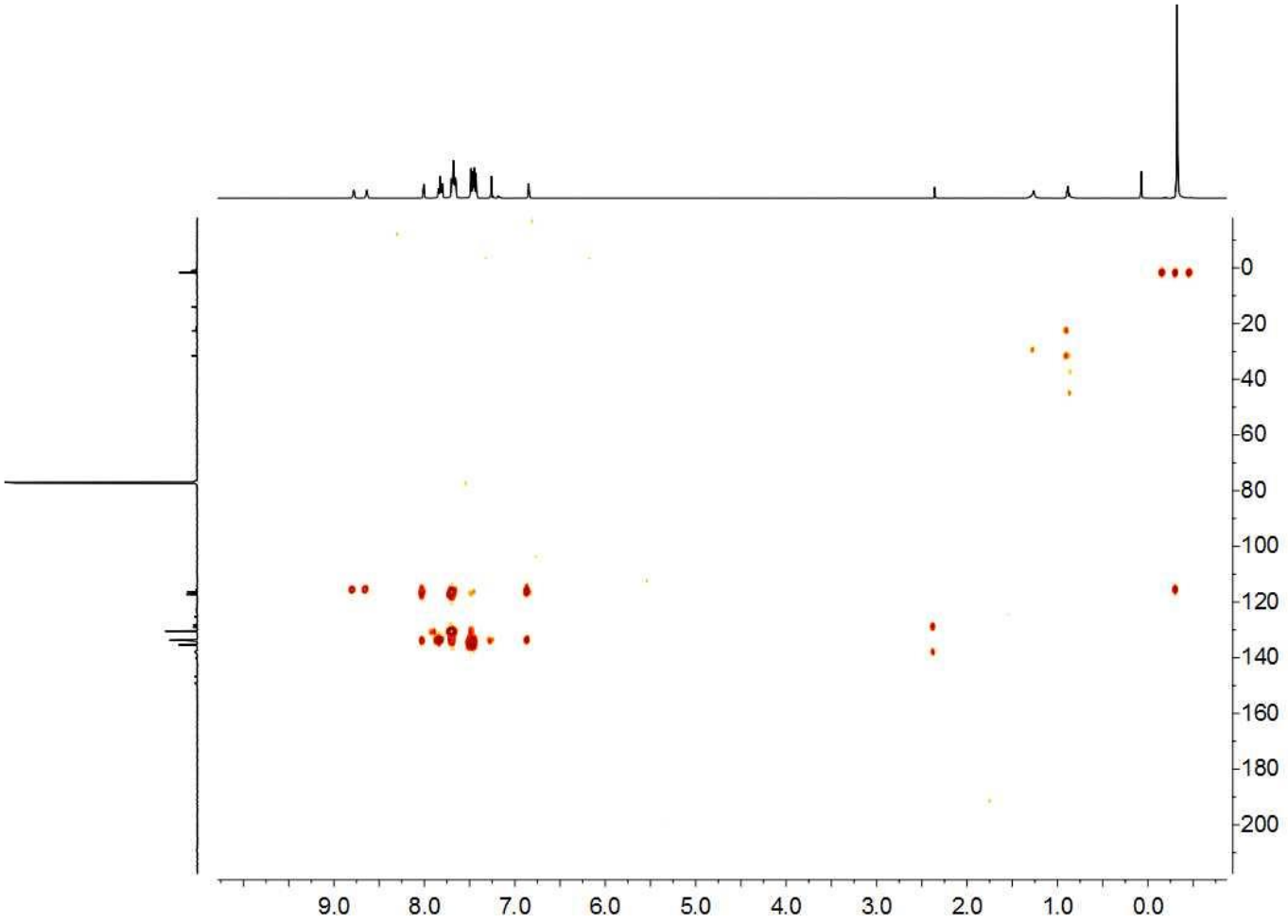

Figure S7-4. $^{1}H,^{13}C$-HMBC spectrum of **4** in $CDCl_3$

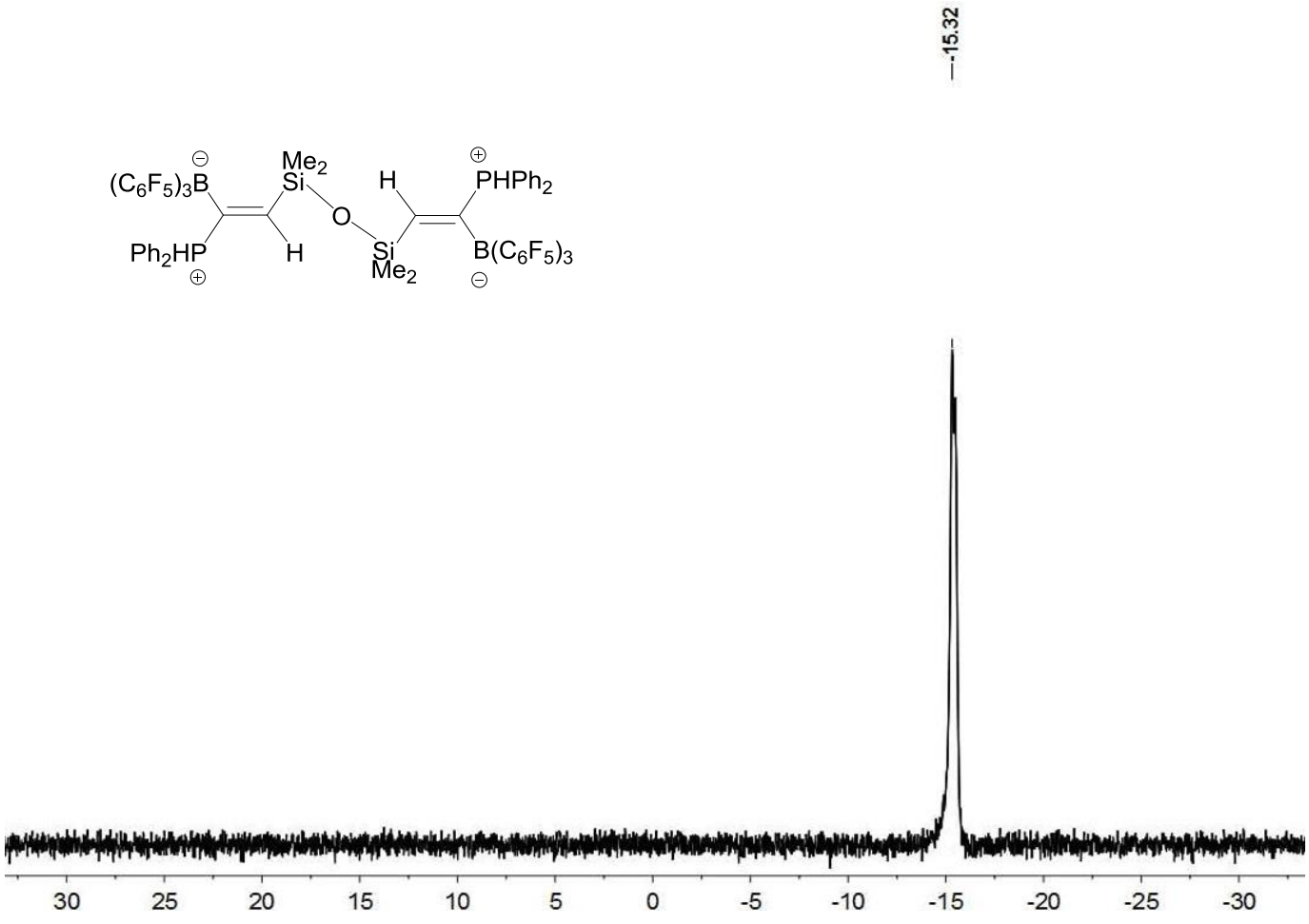

Figure S7-5. ^{11}B NMR spectrum of **4** in $CDCl_3$

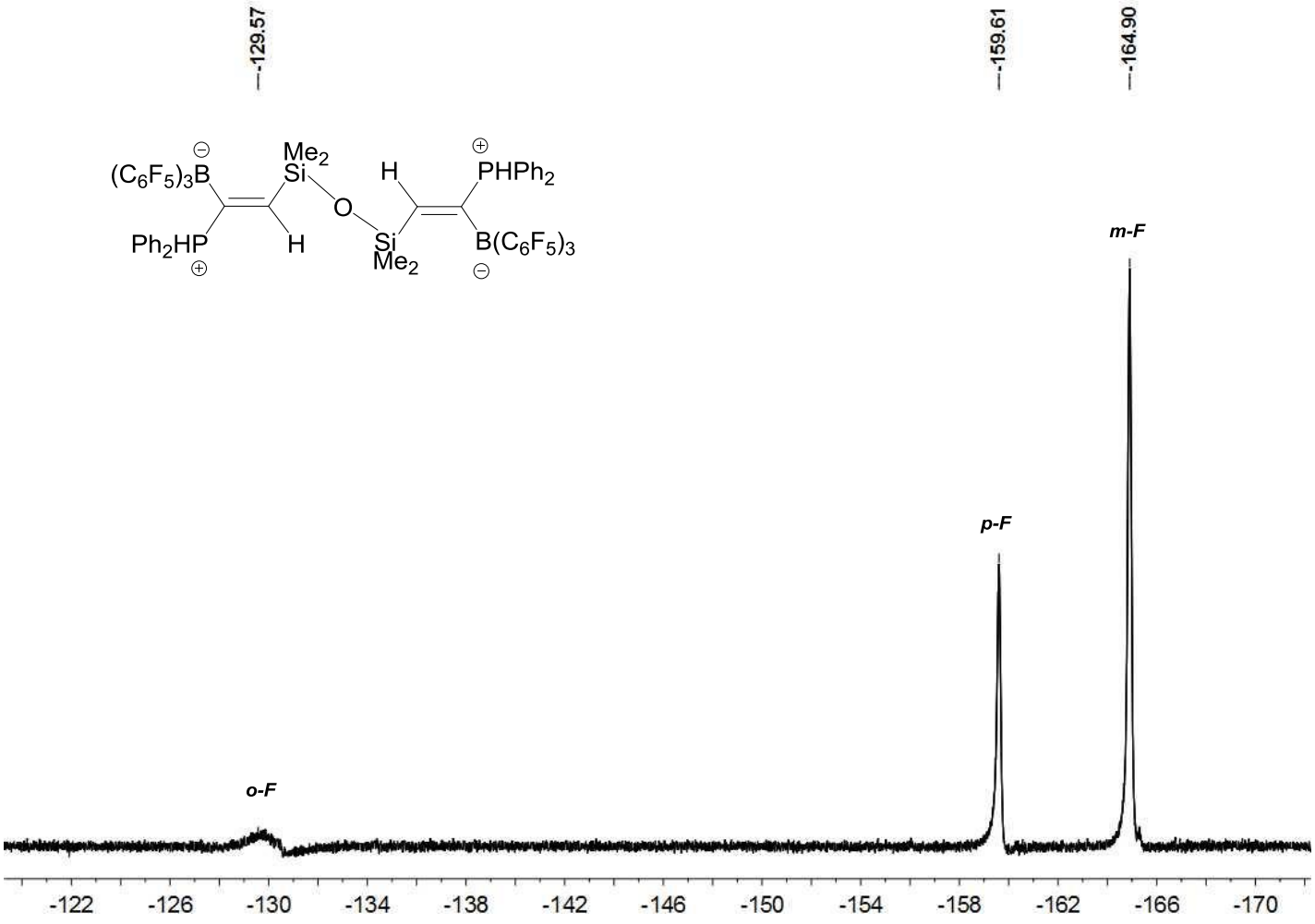

Figure S7-6. ^{19}F NMR spectrum of **4** in $CDCl_3$

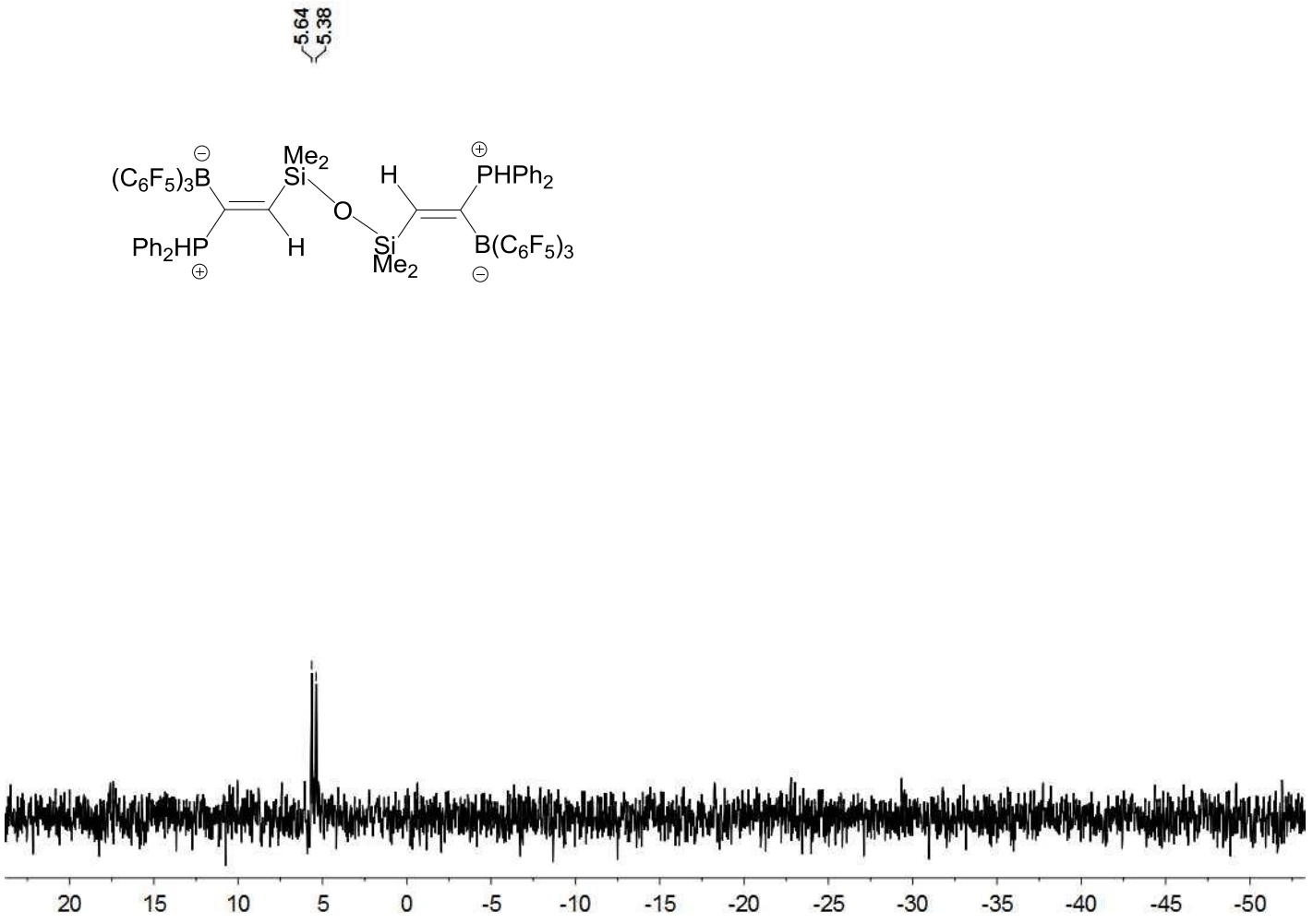

Figure S7-7. ^{29}Si NMR spectrum of **4** in $CDCl_3$

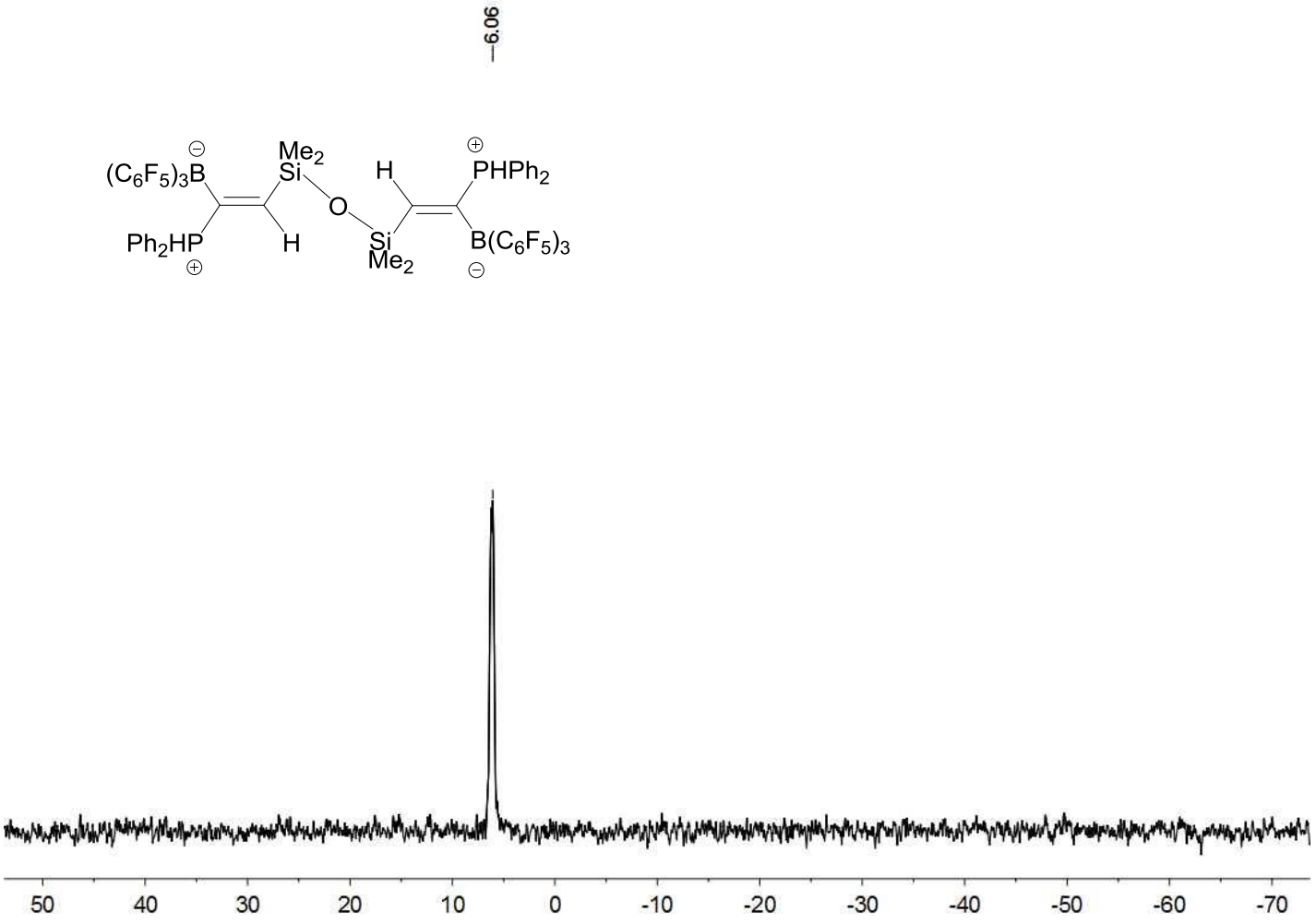

Figure S7-8. ^{31}P NMR spectrum of **4** in $CDCl_3$

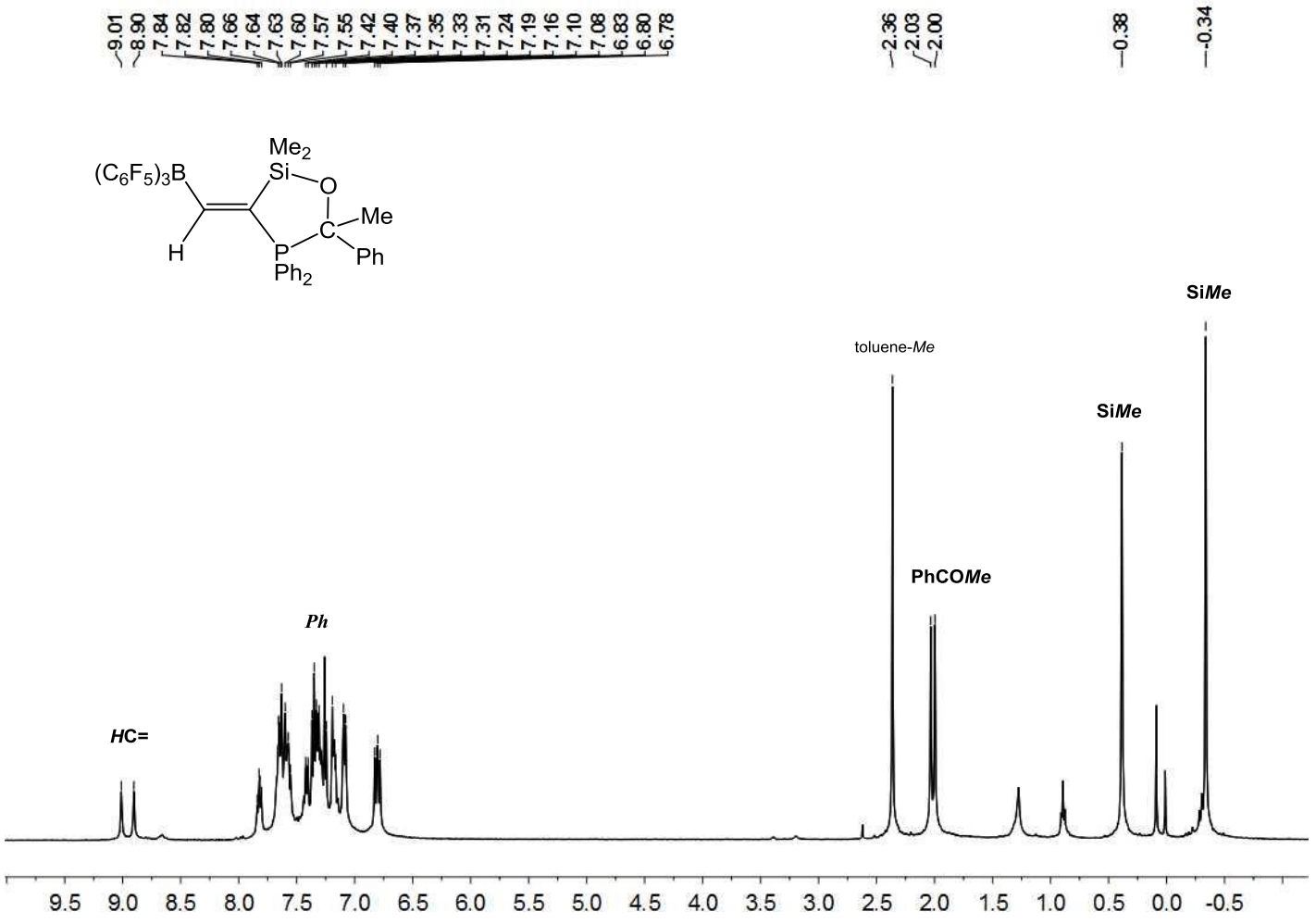

Figure S8-1. ^{1}H NMR spectrum of **5** in $CDCl_3$

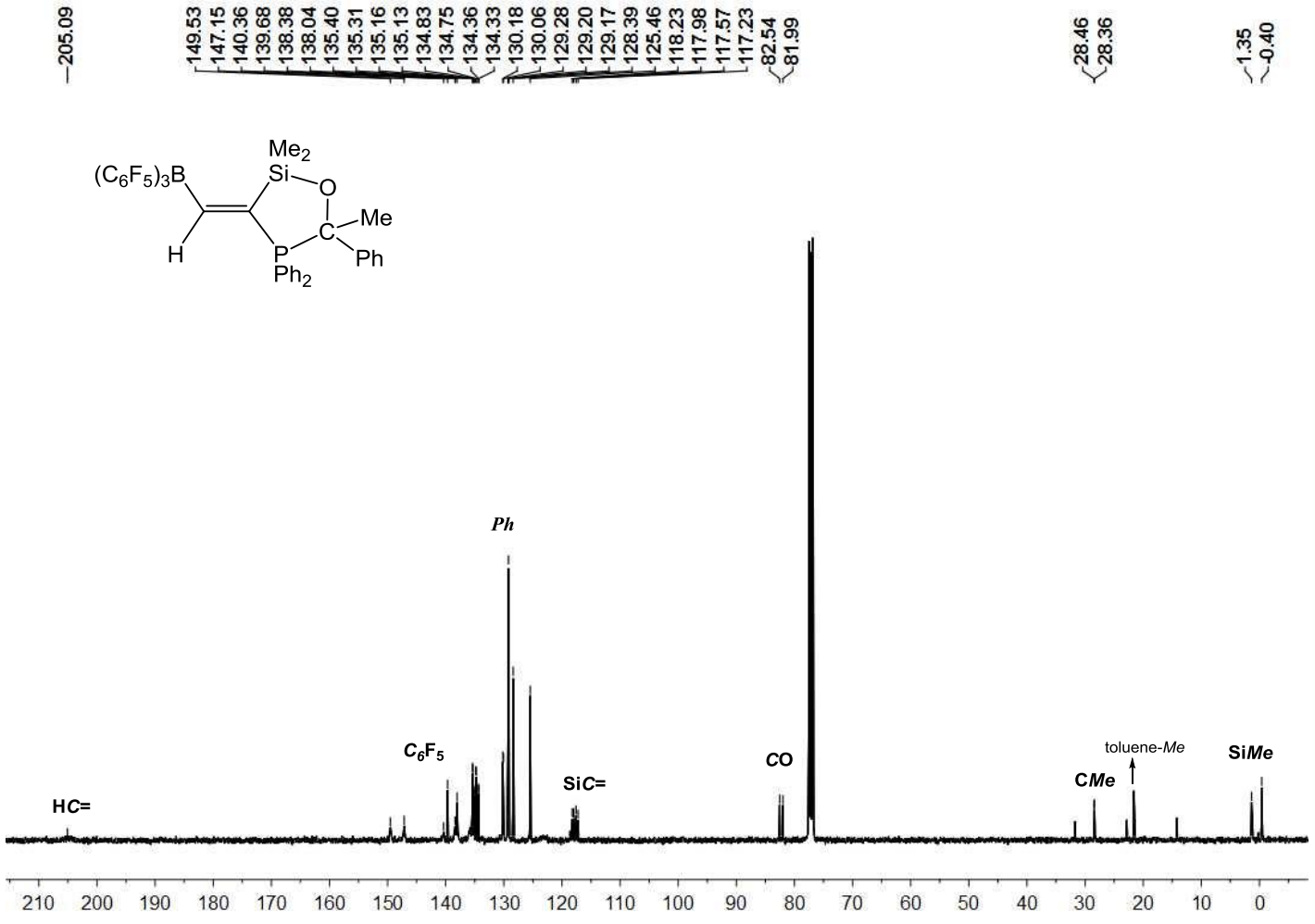

Figure S8-2. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in $CDCl_3$

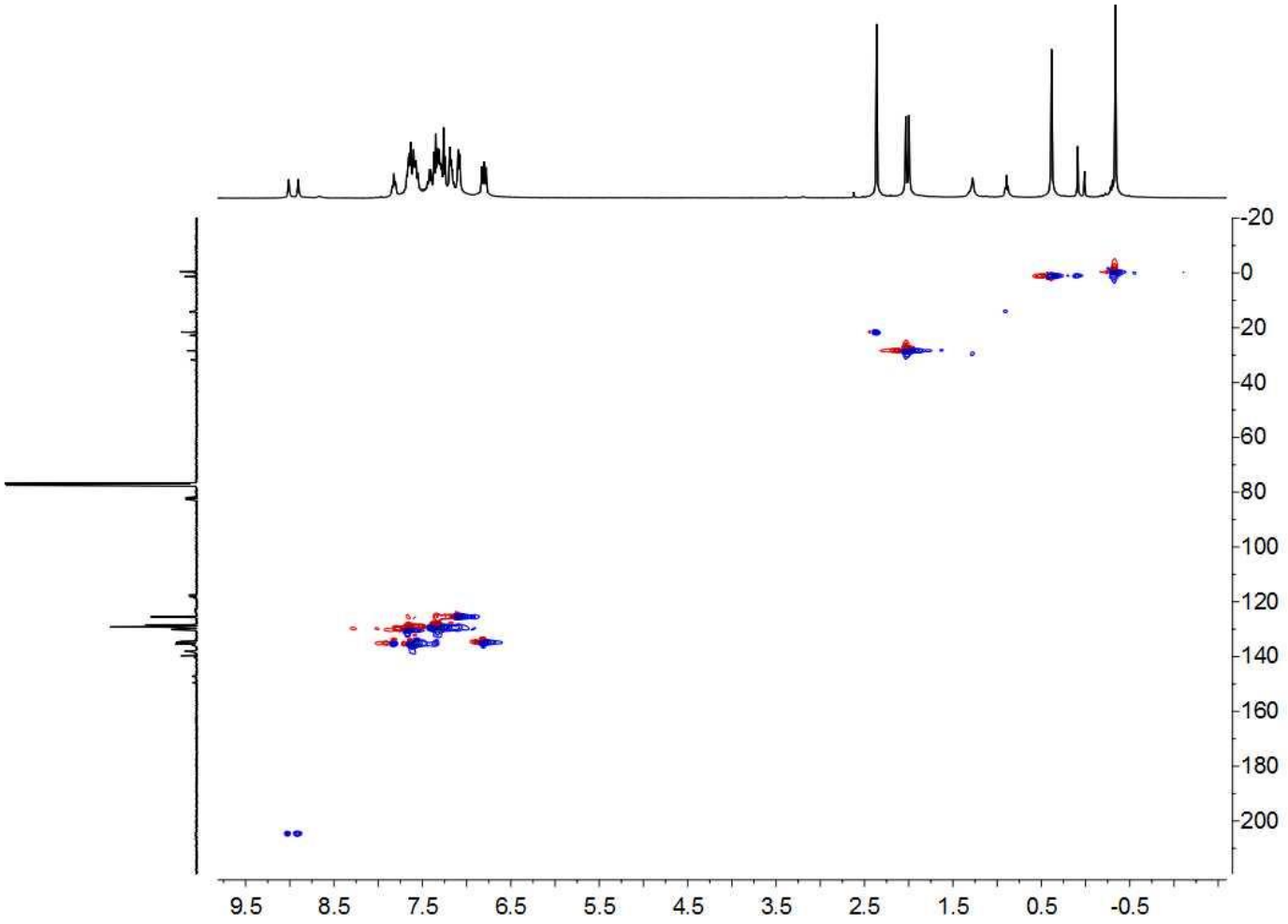

Figure S8-3. $^{1}H,^{13}C$-HSQC spectrum of **5** in $CDCl_3$

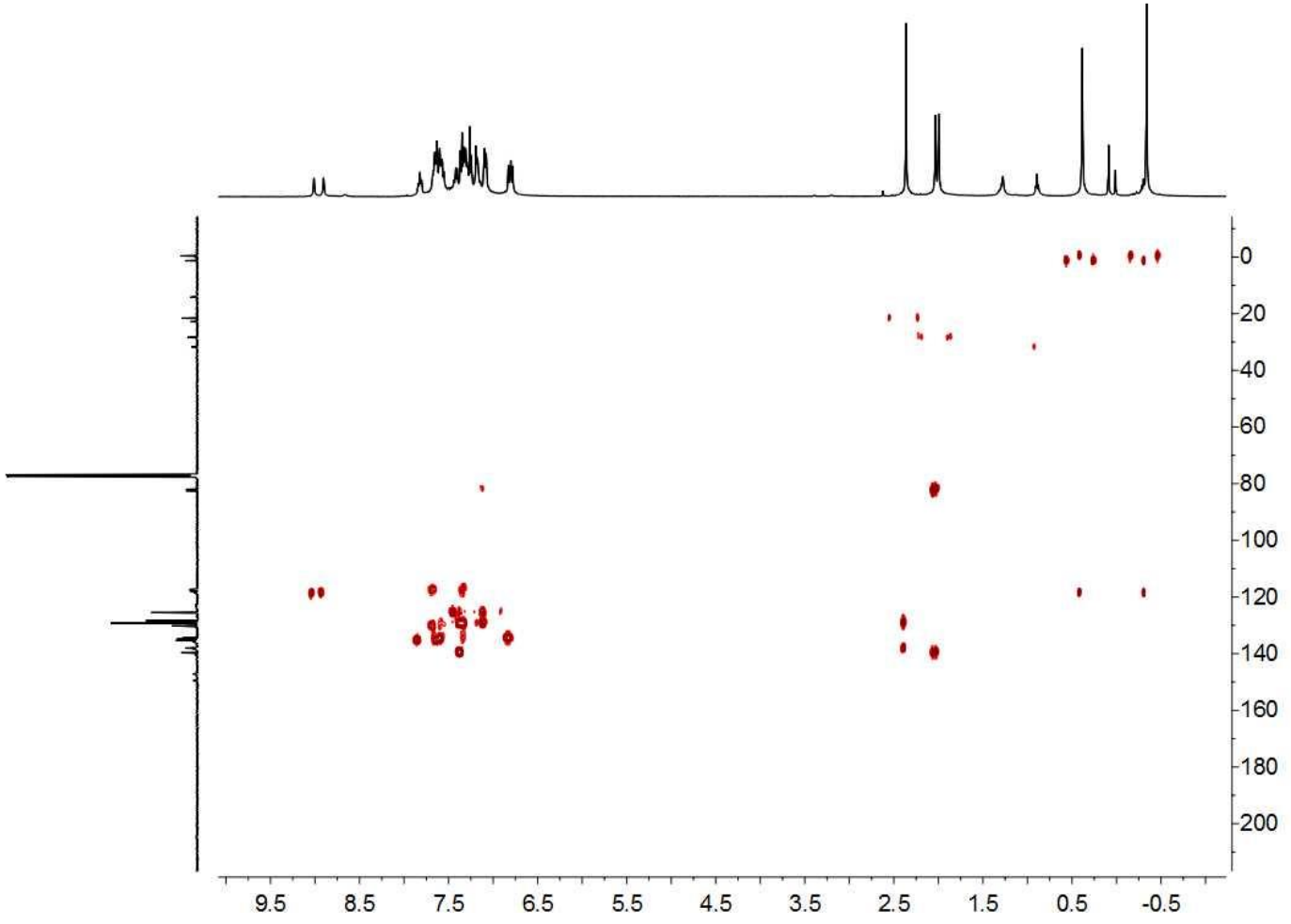

Figure S8-4. $^{1}H,^{13}C$-HMBC spectrum of **5** in $CDCl_3$

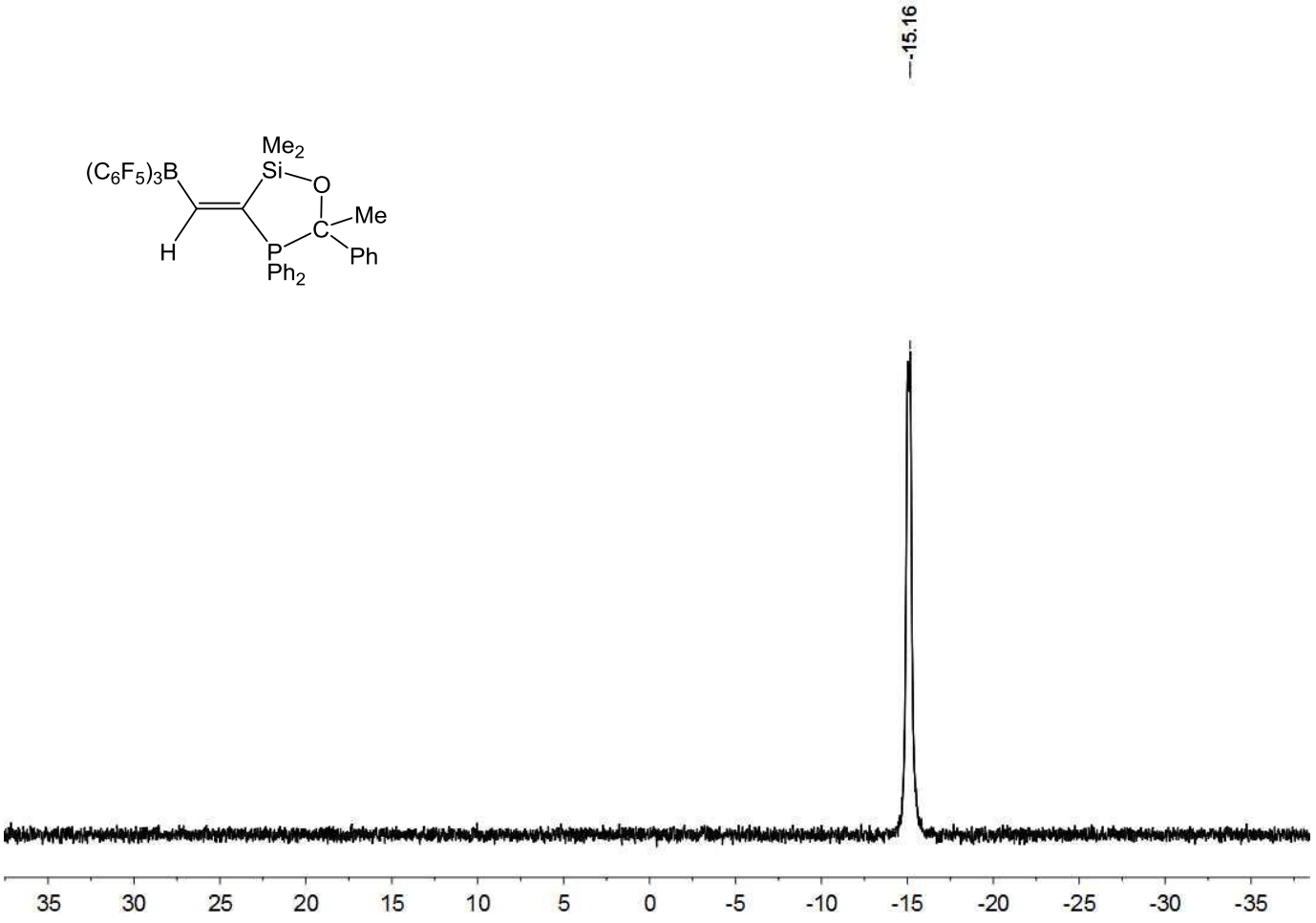

Figure S8-5. ^{11}B NMR spectrum of **5** in $CDCl_3$

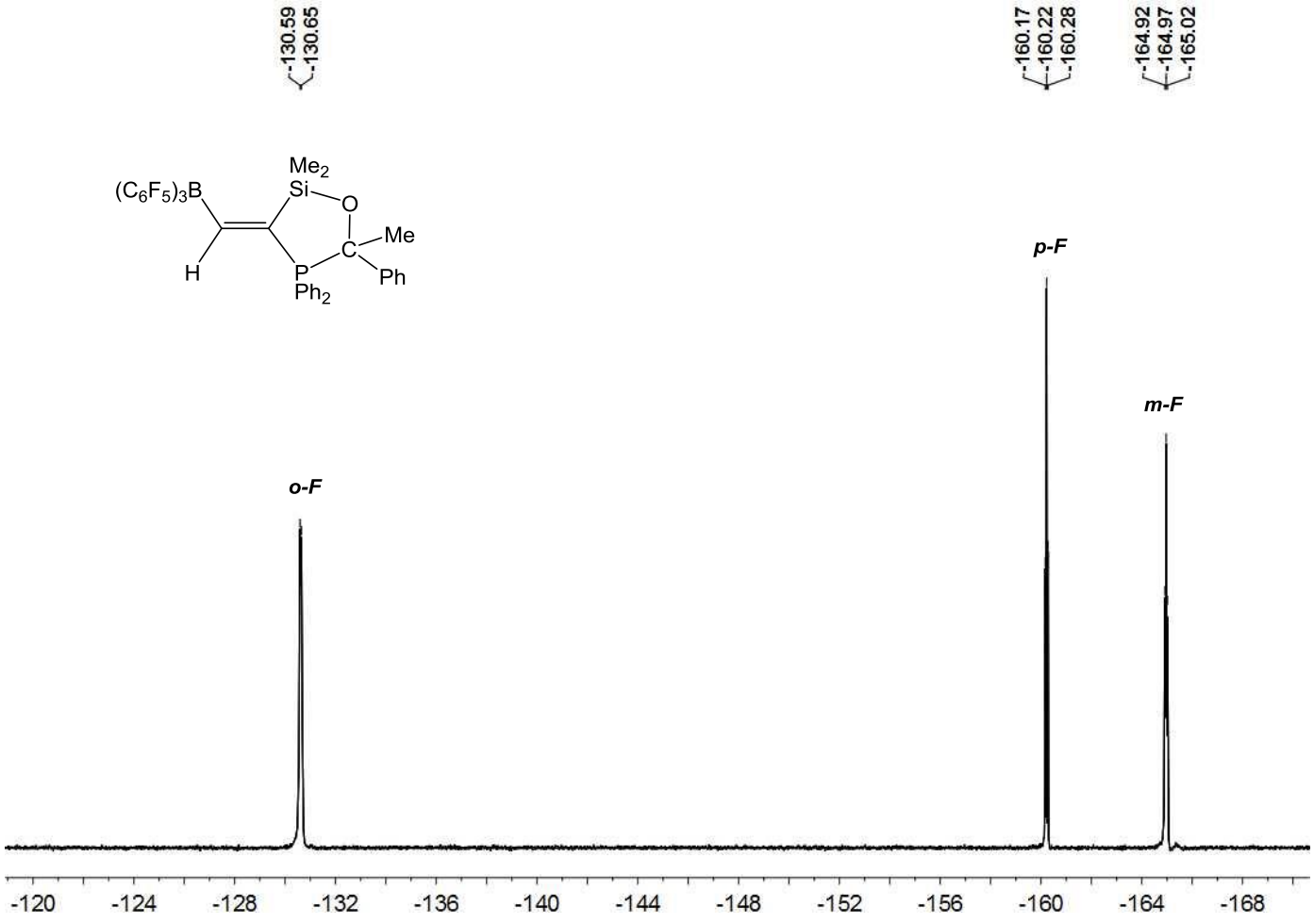

Figure S8-6. ^{19}F NMR spectrum of **5** in $CDCl_3$

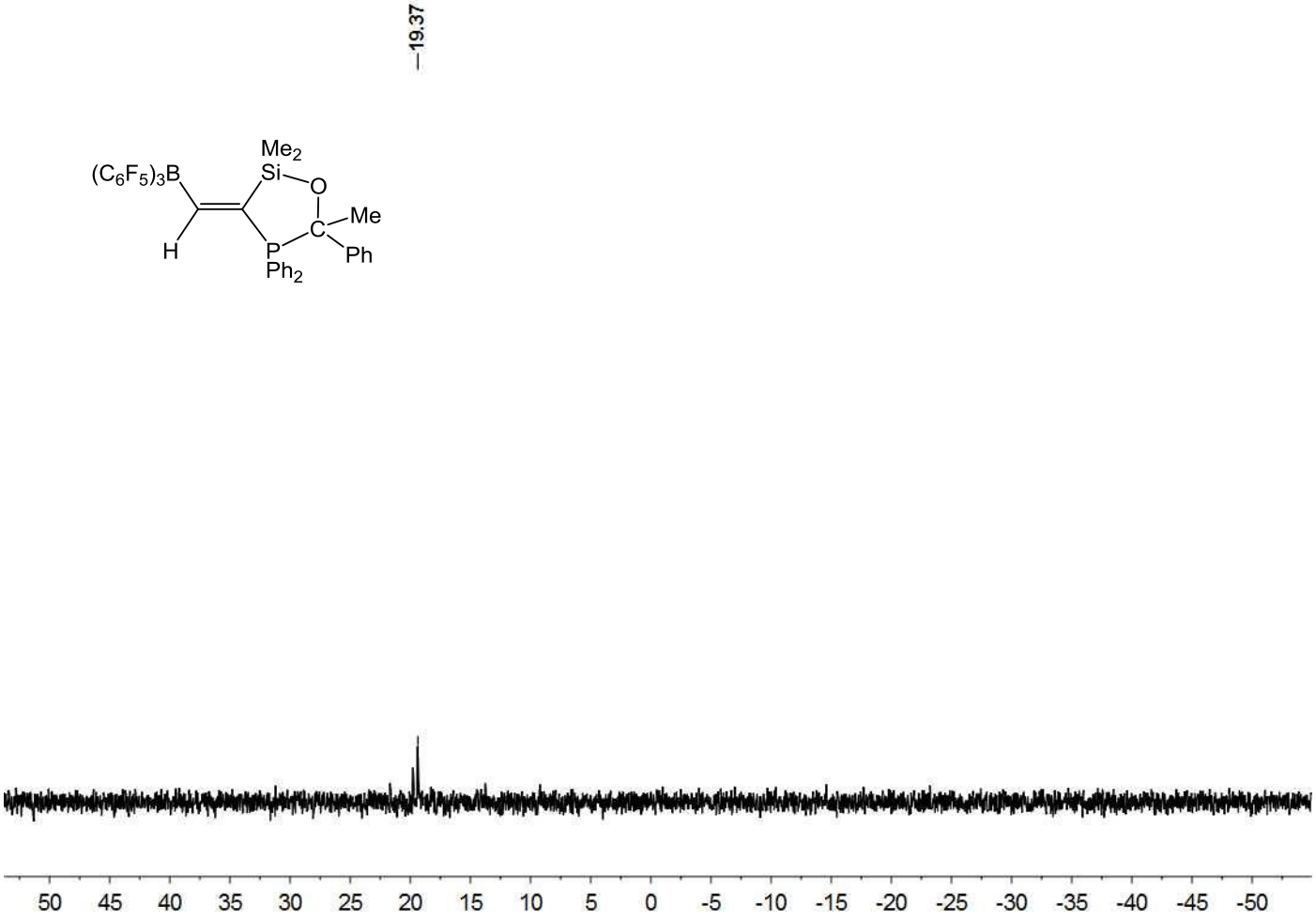

Figure S8-7. ^{29}Si NMR spectrum of **5** in $CDCl_3$

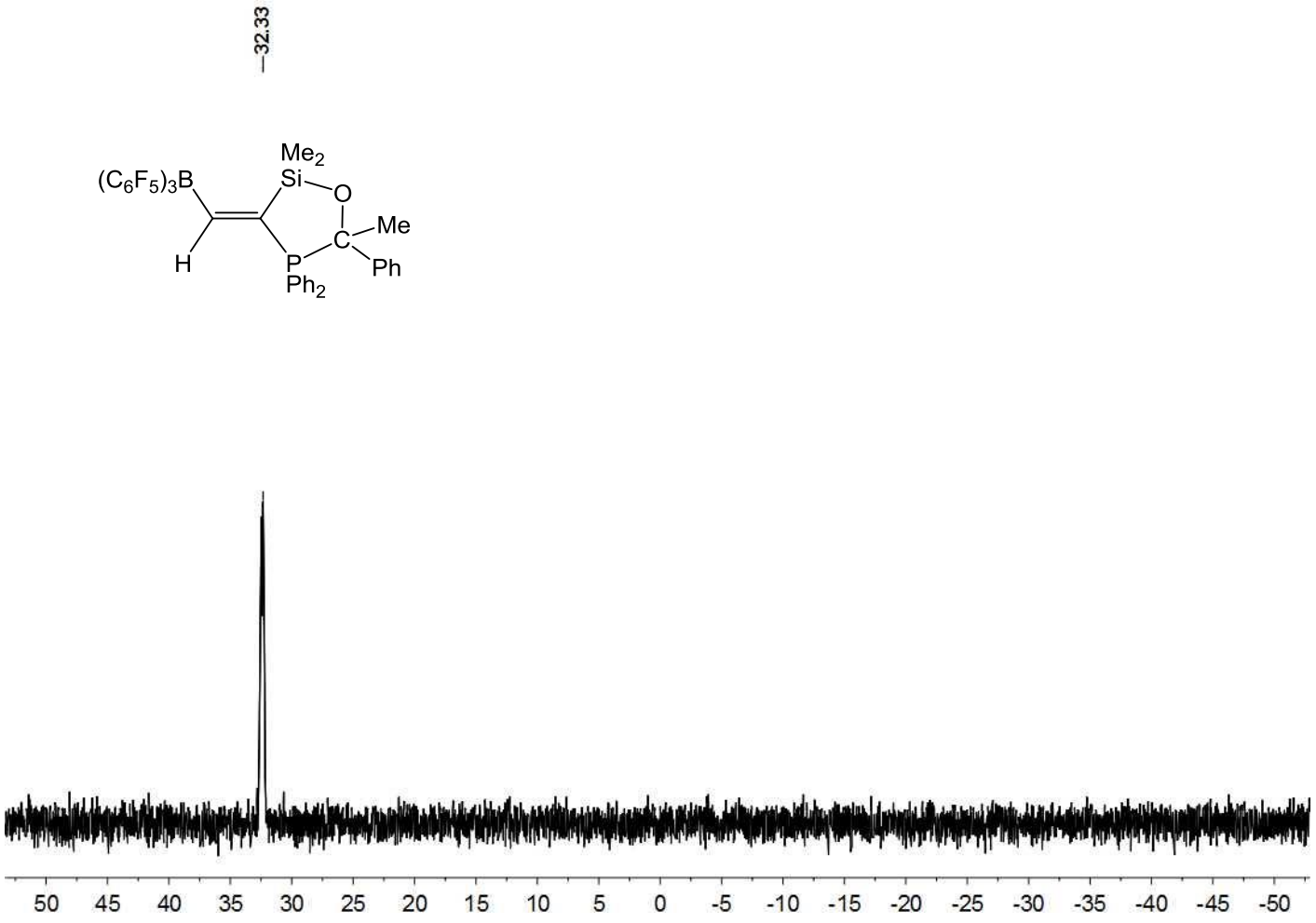

Figure S8-8. ^{31}P NMR spectrum of **5** in $CDCl_3$

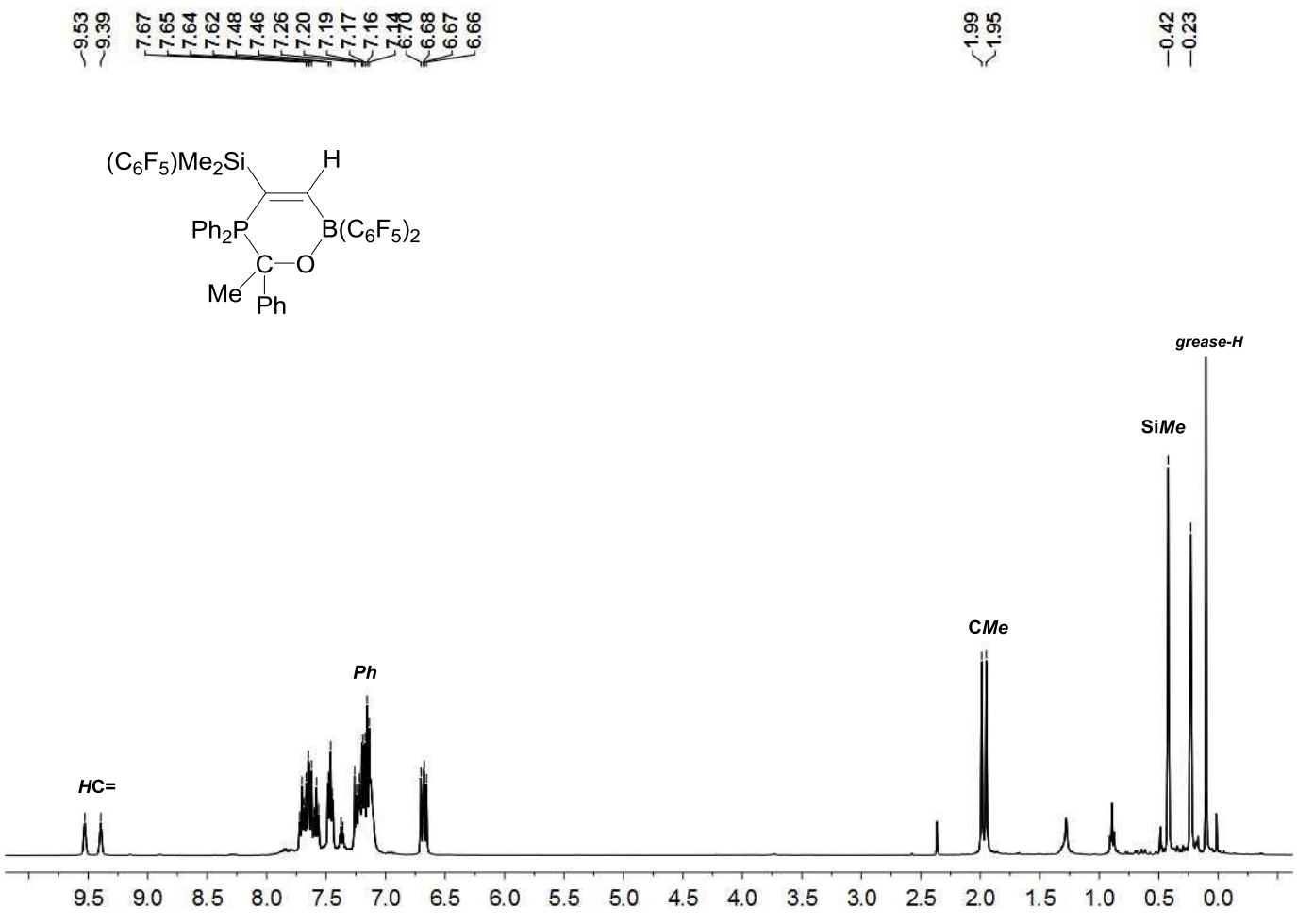

Figure S9-1. ^{1}H NMR spectrum of **6** in $CDCl_3$

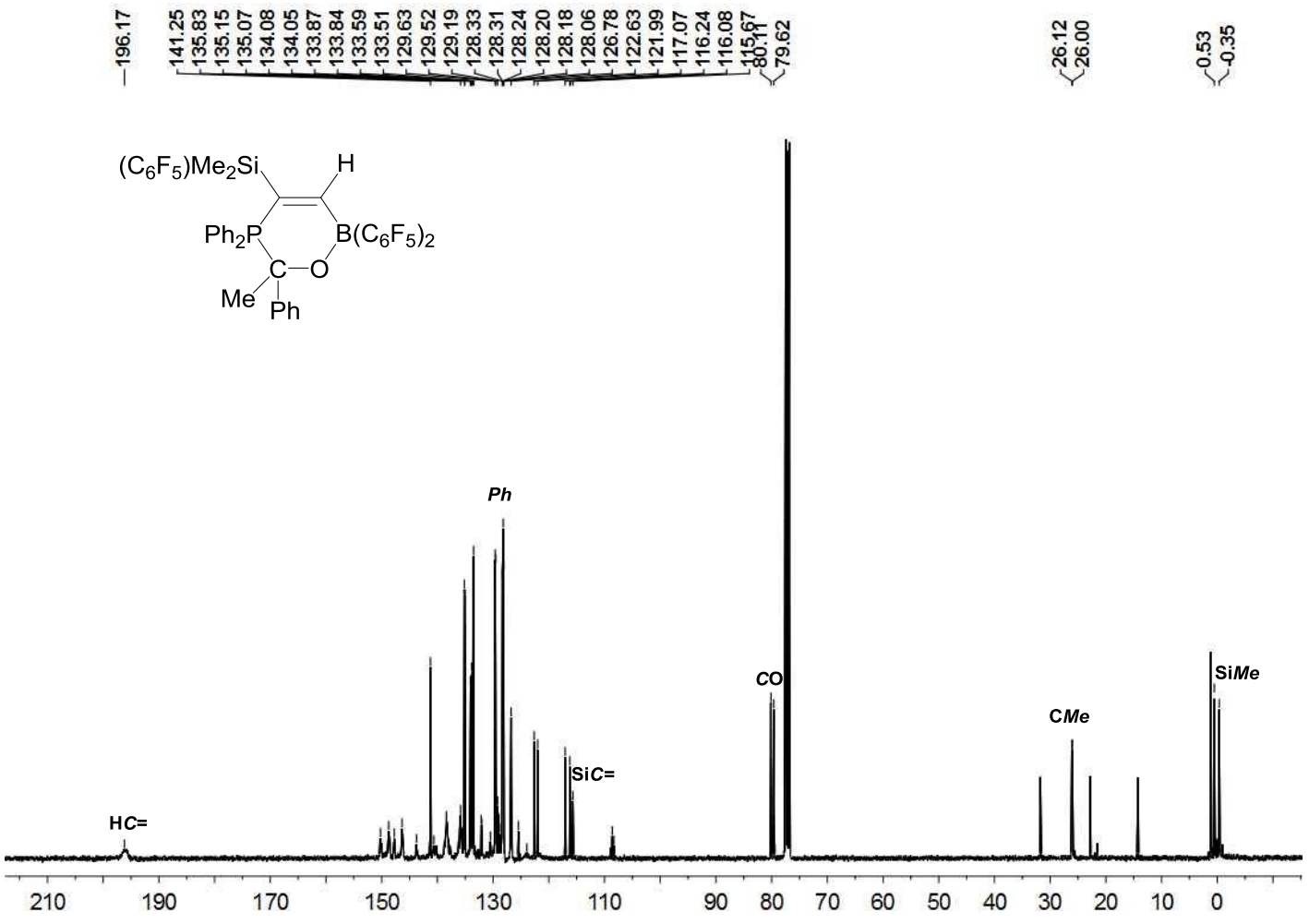

Figure S9-2. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in $CDCl_3$

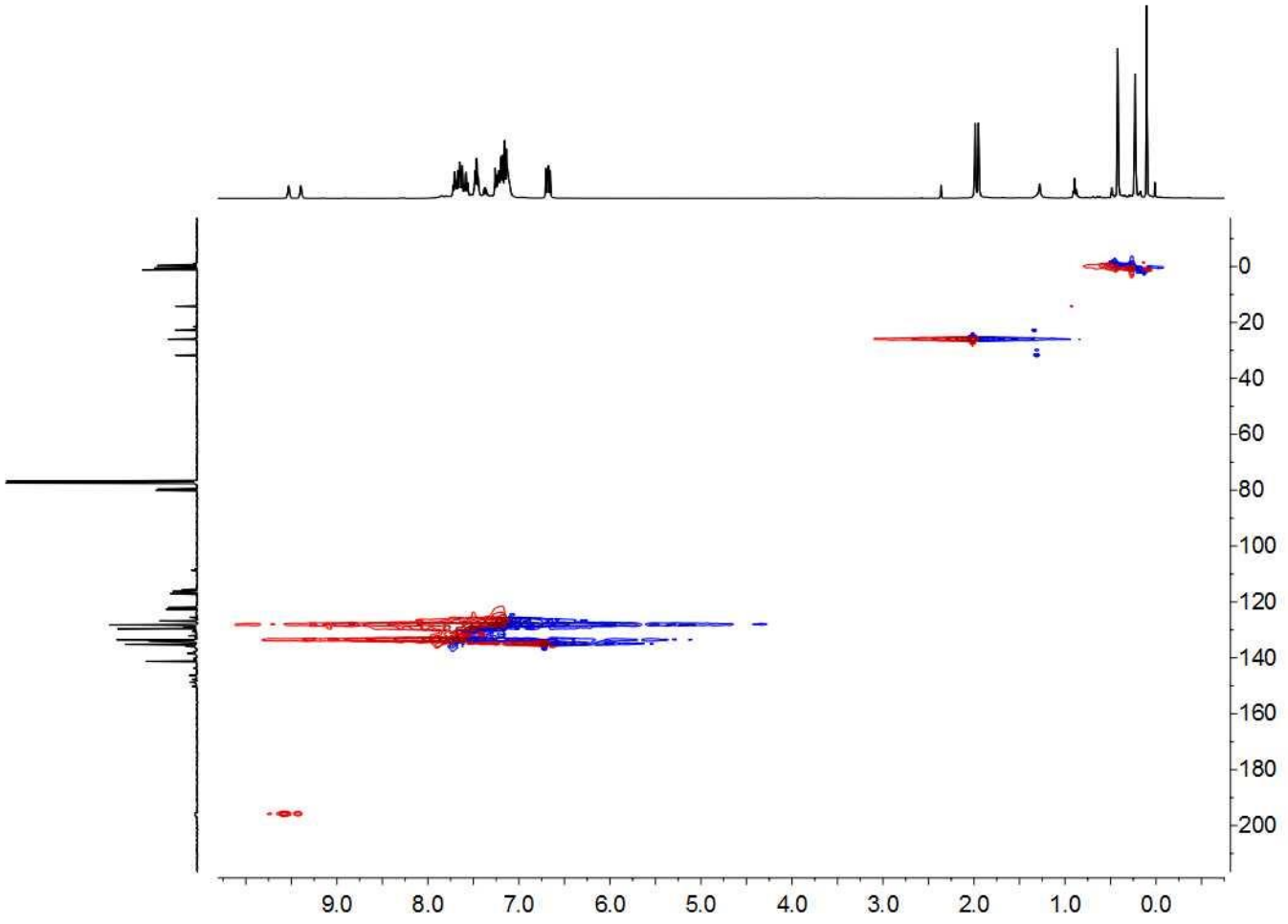

Figure S9-3. $^{1}H,^{13}C$-HSQC spectrum of **6** in $CDCl_3$

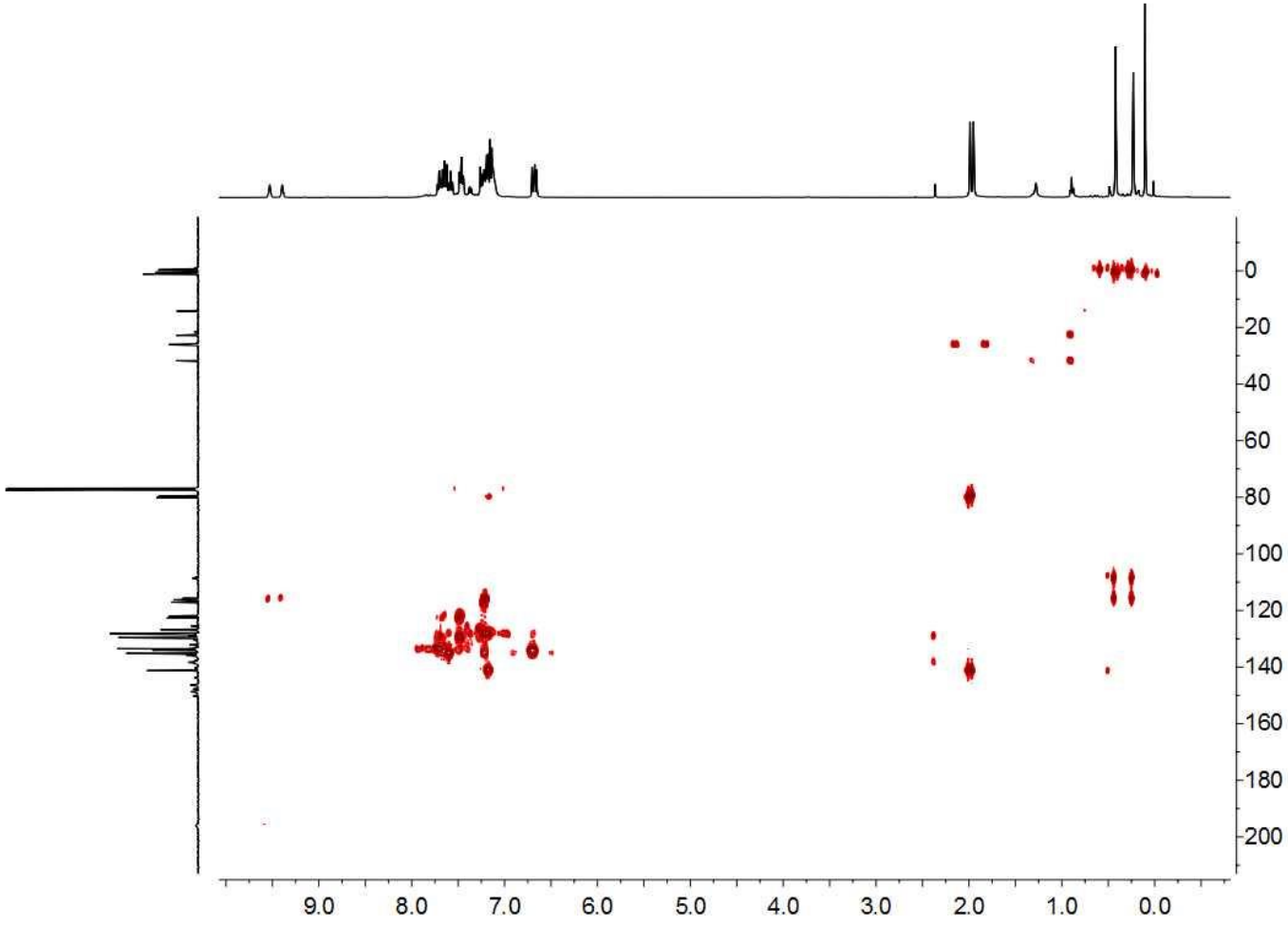

Figure S9-4. $^{1}H,^{13}C$-HMBC spectrum of **6** in $CDCl_3$

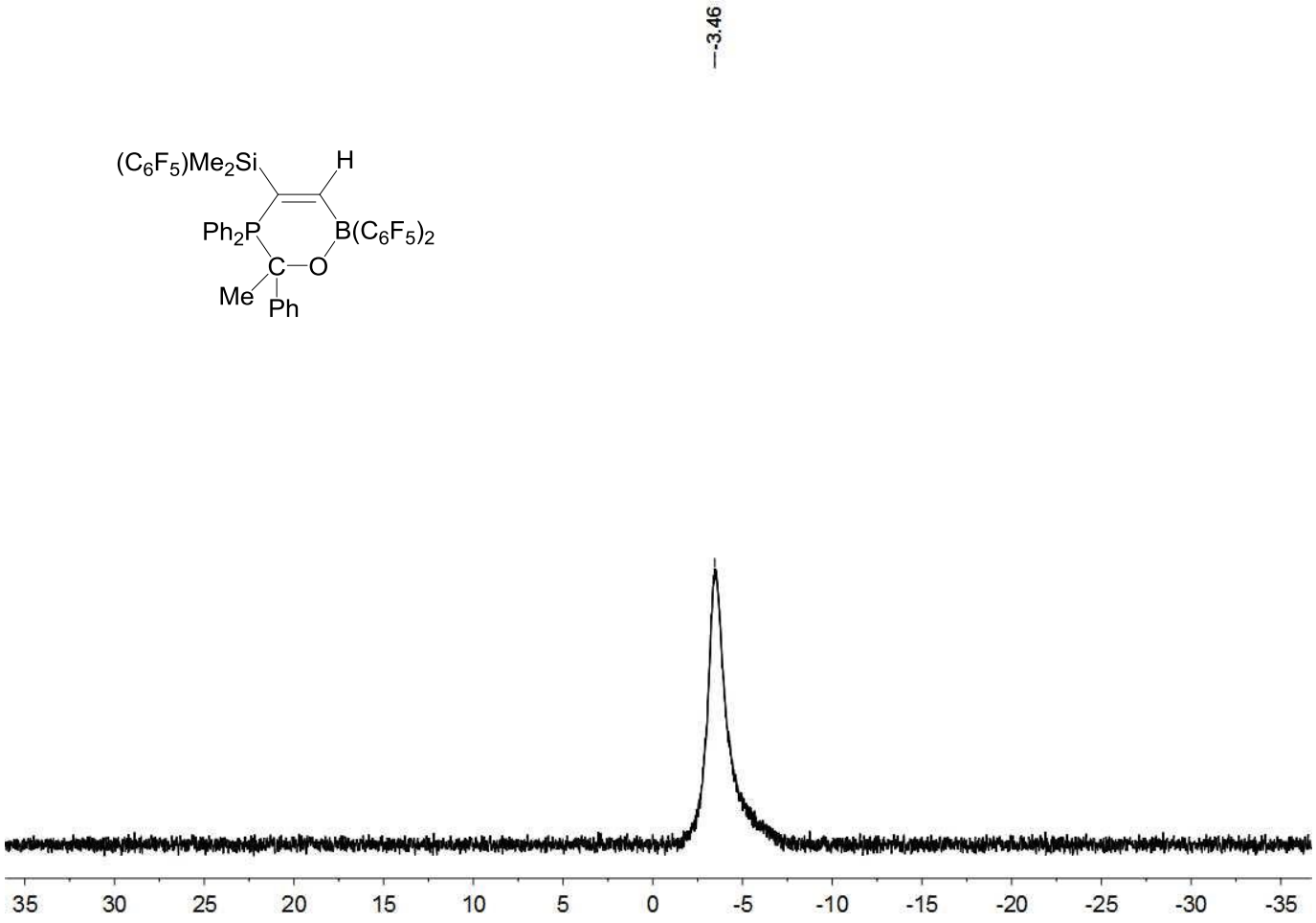

Figure S9-5. ^{11}B NMR spectrum of **6** in $CDCl_3$

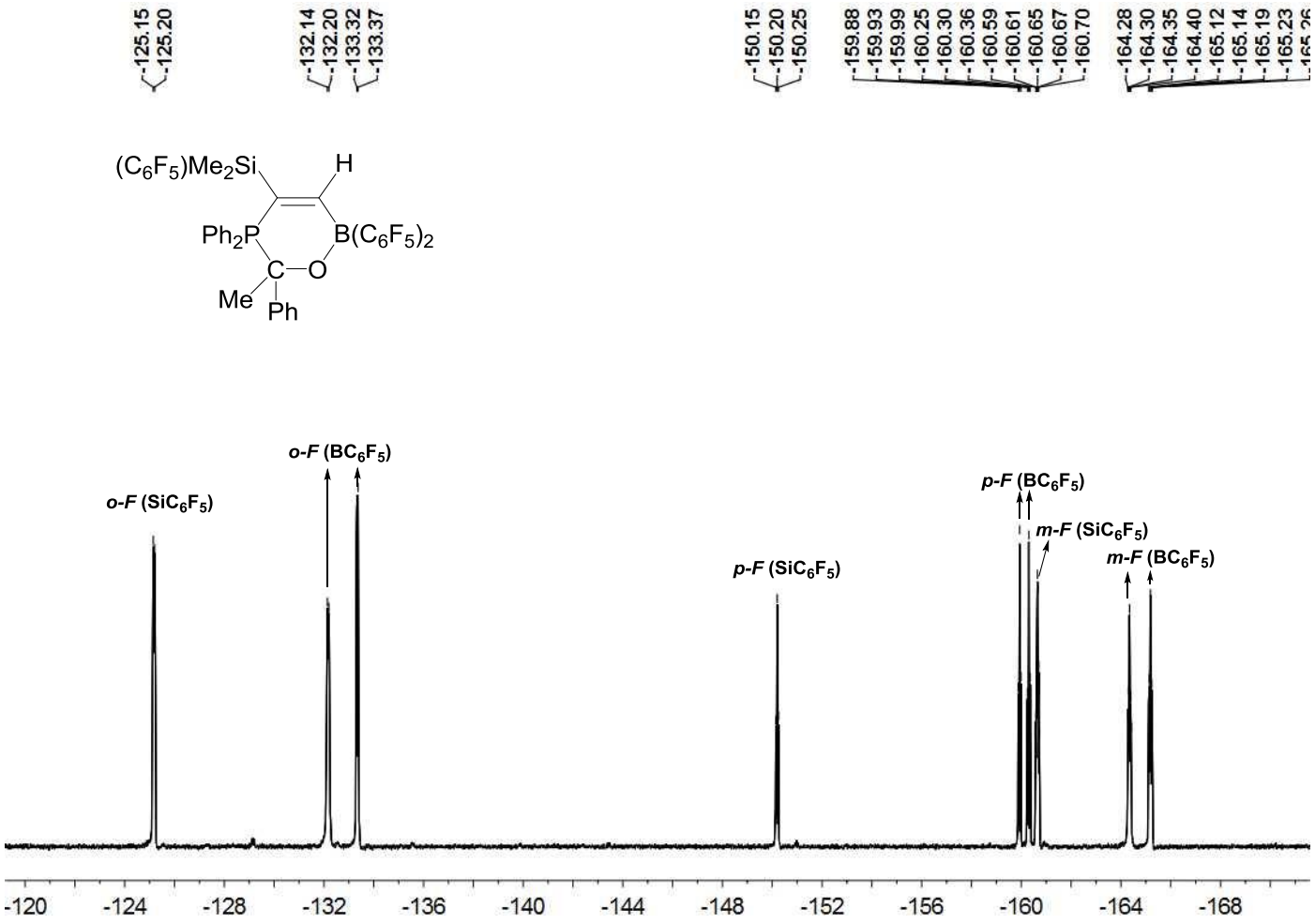

Figure S9-6. ^{19}F NMR spectrum of **6** in $CDCl_3$

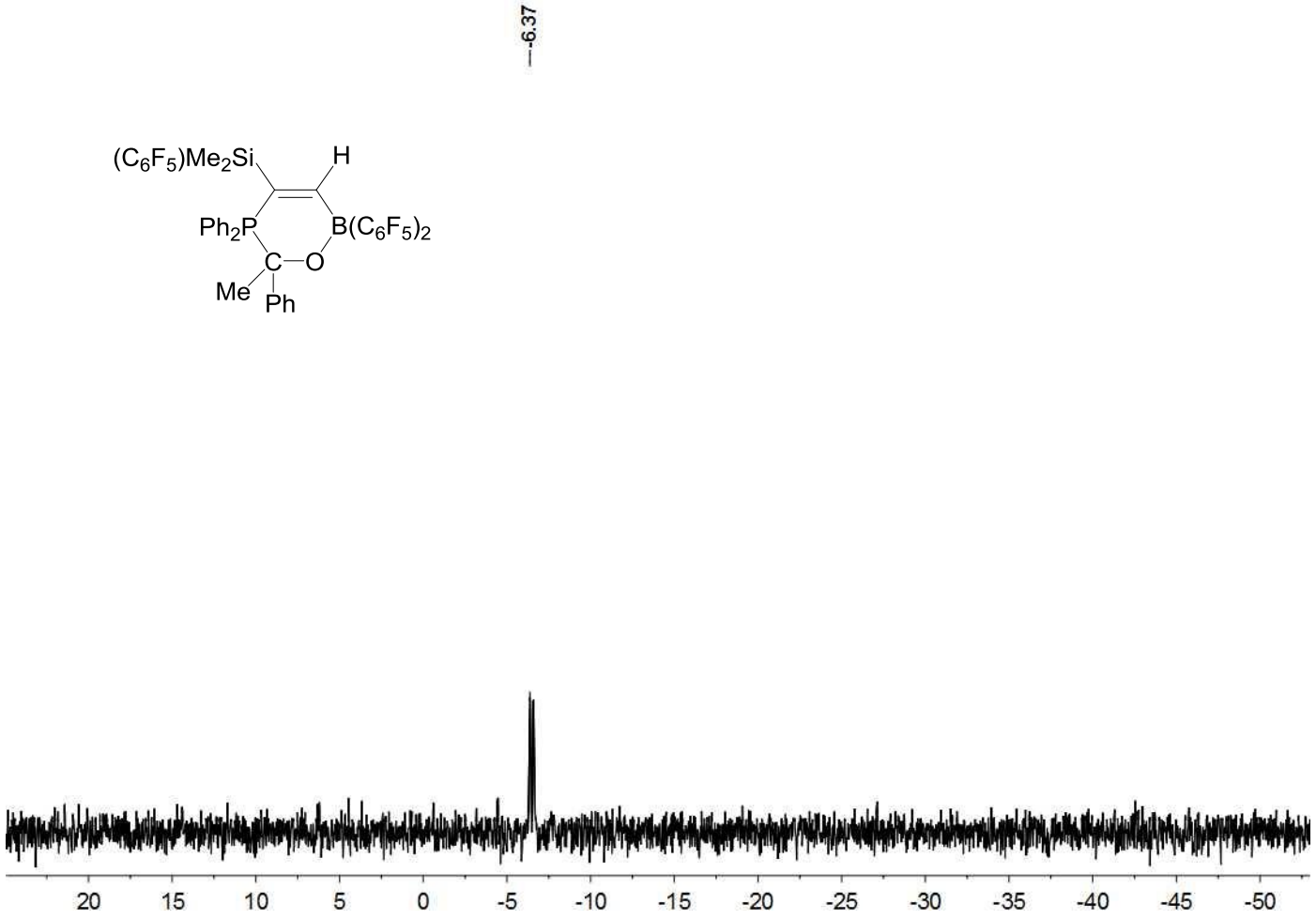

Figure S9-7. ^{29}Si NMR spectrum of **6** in $CDCl_3$

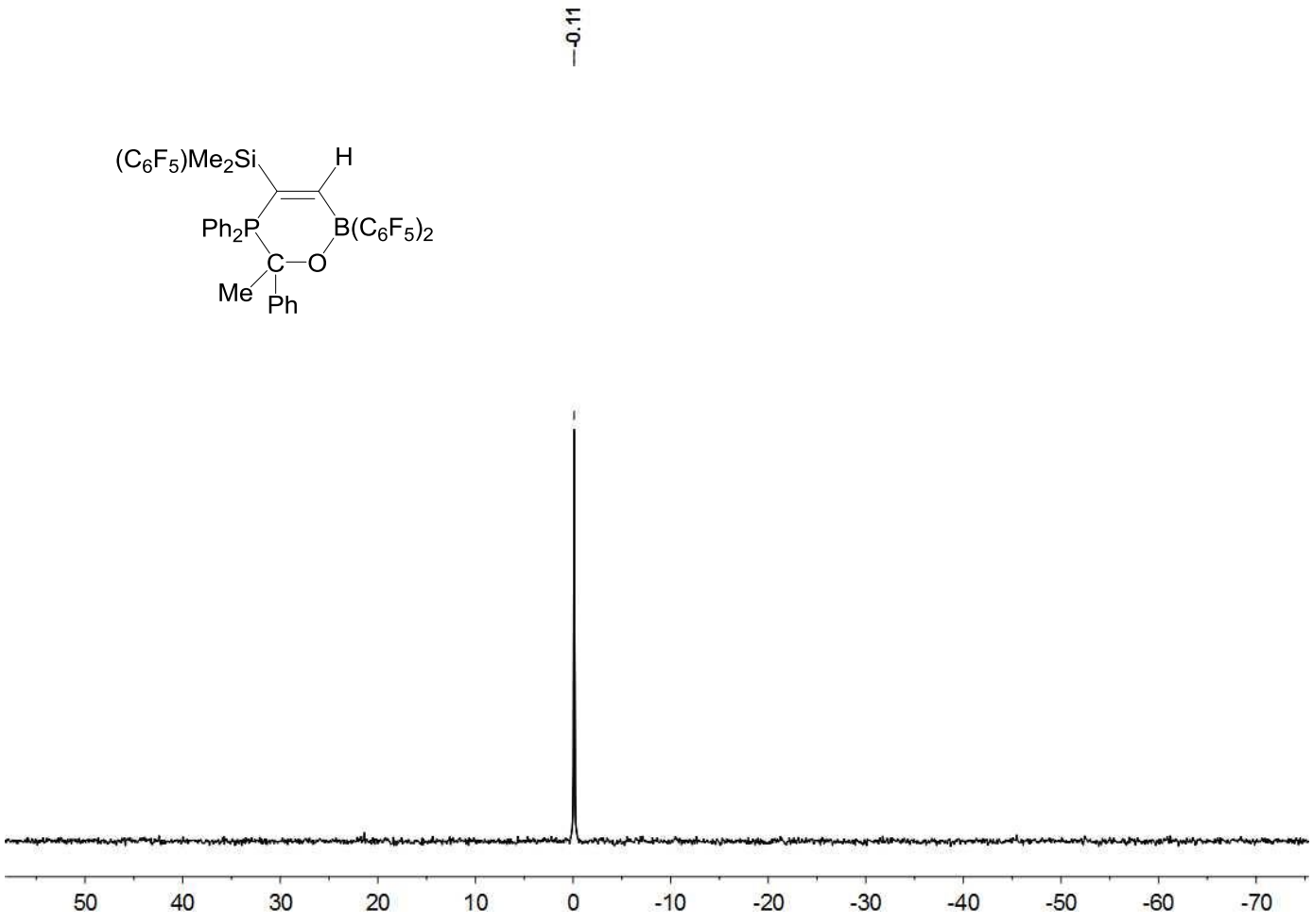

Figure S9-8. ^{31}P NMR spectrum of **6** in $CDCl_3$