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Supporting Information

Hidden Silylium-Type Reactivity of a Siloxane-Based Phosphonium–Hydroborate Ion Pair

*Nicolò Fontana, Noel Angel Espinosa-Jalapa, Michael Seidl, and Jonathan O. Bauer**

Institut für Anorganische Chemie, Fakultät für Chemie und Pharmazie, Universität Regensburg, Universitätsstraße 31, D-93053 Regensburg, Germany

Corresponding Author: jonathan.bauer@ur.de

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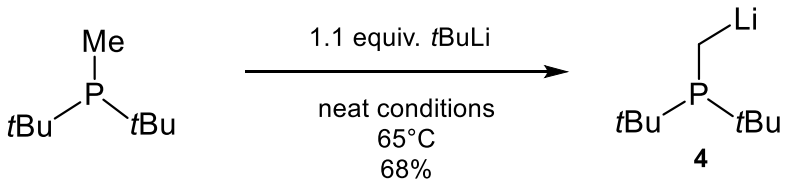
1. General Remarks

All experiments were performed in an inert atmosphere of purified nitrogen by using standard Schlenk techniques or an MBraun Unilab 1200/780 glovebox. Glassware was heated at 140°C prior to use. Diethyl ether (Et_2O), dichloromethane (DCM), hexane, pentane, tetrahydrofuran (THF), and toluene were dried and degassed with an MBraun SP800 solvent purification system. *n*-Butyllithium (2.5 M or 1.6 M solution in hexane, Merck KGaA), dichlorophenylsilane (97 %, Merck KGaA), di-*tert*-butyl(methyl)phosphine (97%, Merck KGaA), *tert*-butyllithium (1.9 M solution in pentane, Merck KGaA), sulphur (99%, Merck KGaA) and hydrogen chloride (2.0 M solution in diethyl ether, Merck KGaA) were used as received without any further purification. Tris(pentafluorophenyl)borane [BCF, $B(C_6F_5)_3$][1] and $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$[2] were synthesized following reported procedures. C_6D_6 and CD_2Cl_2 used for NMR spectroscopy were dried over Na/K amalgam and CaH_2, respectively. NMR spectra were either recorded using a Bruker Avance 400 (400.13 MHz) or a Bruker Avance III HD 400 (400.13 MHz) at 25 °C. Chemical shifts (δ) are reported in parts per million (ppm). ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to tetramethylsilane ($SiMe_4$, δ = 0.0 ppm) as external standard, with the deuterium signal of the solvent serving as internal lock and the residual solvent signal as an additional reference. $^{11}B\{^1H\}$, $^{19}F\{^1H\}$, $^{29}Si\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra are referenced to $BF_3{\cdot}OEt_2$, $CFCl_3$, $SiMe_4$, and H_3PO_4, respectively. For the assignment of the multiplicities, the following abbreviations are used: s = singlet, d = doublet, t = triplet m = multiplet. For simplicity, multiplets of order higher than one are described approximating them to the closest first-order type. High-resolution mass spectrometry was carried out on a Jeol AccuTOF GCX and an Agilent Q-TOF 6540 UHD spectrometer. Elemental analyses were performed on a Vario MICRO cube apparatus.

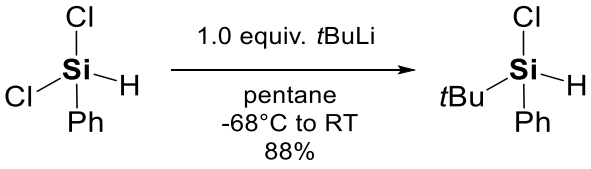
2. Synthetic Procedures

2.1. Synthesis of *t*Bu$_2$PCH$_2$Li (4)



Compound **4** was synthesized according to a procedure by Lerner *et al.*[3] In a glovebox, a Schlenk flask was loaded with pure di-*tert*-butylmethylphosphine (2.0 g, 12.5 mmol, 1.0 equiv.). After connecting the flask to a Schlenk line, *tert*-butyllithium (7.3 ml of a 1.9 M solution in pentane, 13.8 mmol, 1.1 equiv.) was added carefully. The resulting clear solution was stirred during 15 min at room temperature. Afterwards, a distillation bridge with a receiving Schlenk flask was connected and the Schlenk containing the mixture was gradually heated up to 65°C while gently stirring. The system was allowed to react under these conditions for 16 h during which the solvent was slowly distilled off and the oily residue turned into a pale-yellow solid. The distillation bridge with the receiving Schlenk flask was removed while flowing nitrogen from both ends to prevent possible flames. The solid was washed with dry pentane (3 x 5 ml) and carefully dried in vacuum giving pure compound **4** as a white solid (1.41 g, 8.5 mmol, 68%). Spectroscopic data were in accordance with those reported in the literature.[3]

2.2. Synthesis of *t*BuPhSi(H)Cl



A two-necked Schlenk flask featuring a dropping funnel was filled with pentane (80 mL) and PhHSiCl$_2$ (4.57 g, 25.8 mmol, 1.0 equiv.). The whole mixture was cooled down to -68°C. *tert*-butyllithium (15.2 mL of a 1.7 M solution in pentane, 25.8 mmol, 1.0 equiv.) was loaded in the dropping funnel and diluted with additional pentane (35 mL). The diluted *tert*-butyllithium solution was added dropwise to the solution of PhHSiCl$_2$ in pentane at -68°C over a period of 1h under vigorous stirring. The clear solution was then allowed to slowly warm up to room temperature and stirred overnight at room temperature. The obtained white suspension was transferred by means of PTFE tubing to a fritted column layered with Celite®, filtered and the remaining solids washed with more pentane (2 x 20 mL). The clear colorless filtrates were collected, and all volatiles removed under vacuum yielding pure *t*BuPhSi(H)Cl as a clear colourless oil (4.84 g, 24.3 mmol, 88%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ= 0.92 [s, 9H, C(C*H*$_3$)$_3$], 5.01 [s with ^{29}Si satellites, $^1J_{H\text{-}Si}$ = 223.6, 1H, Si*H*], 7.08–7.14 [m, 3H, *H*$_{Ph}$], 7.51–7.54 [m, 2H, *H*$_{Ph}$]. **^{13}C{^{1}H} NMR** (100.62 MHz, C_6D_6, 298 K): δ= 19.4 [s, *C*(CH$_3$)$_3$], 25.4 [s, C(*C*H$_3$)$_3$], 128.3 [s, *C*$_{Ph}$], 131.0 [s, *C*$_{Ph}$], 131.7 [s, *C*$_{Ph}$], 134.8 [s, *C*$_{Ph}$]. **^{29}Si{^{1}H} NMR** (79.49 MHz, C_6D_6, 298 K): δ 11.5. **HR-MS (EI+)**, calculated m/z for $C_{10}H_{15}SiCl$ [M]$^+$: 198.06261; found: 198.06276.

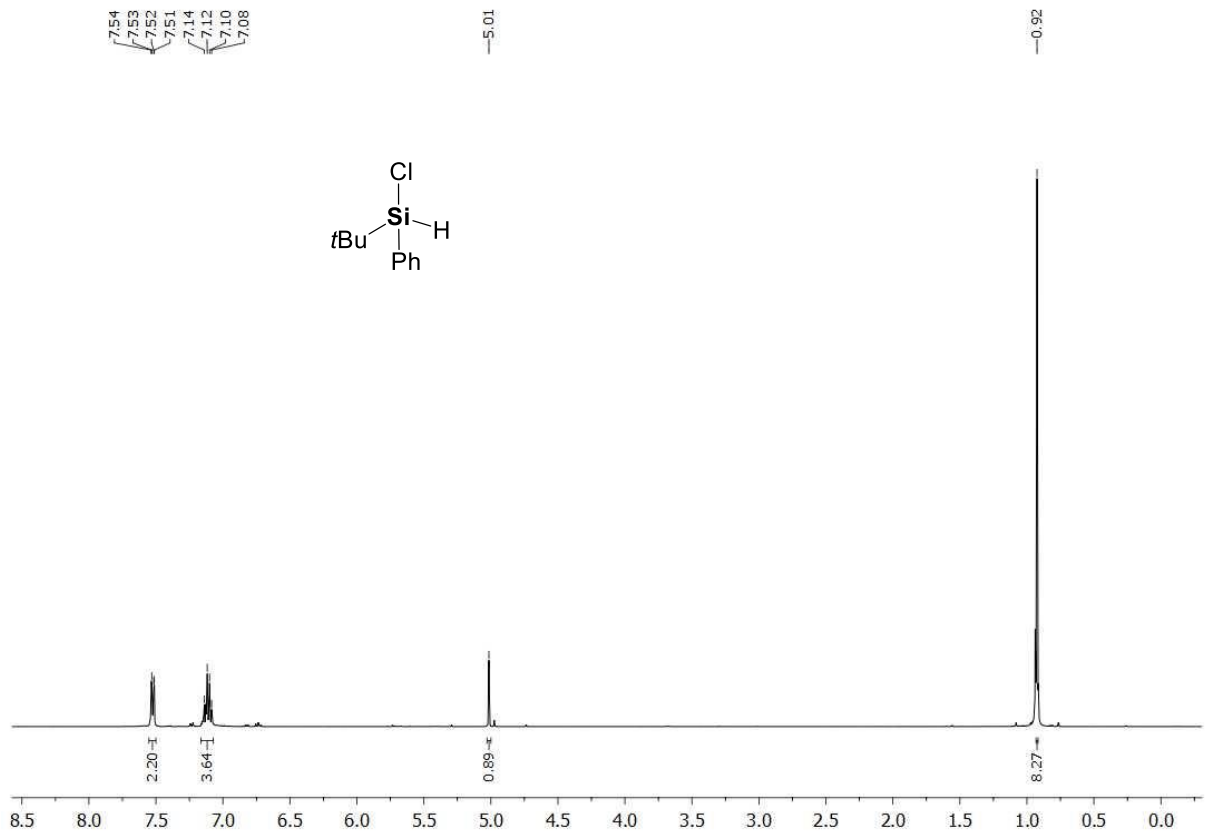


Figure S1. ^{1}H NMR spectrum (C_6D_6, 298 K) of *t*BuPhSi(H)Cl.

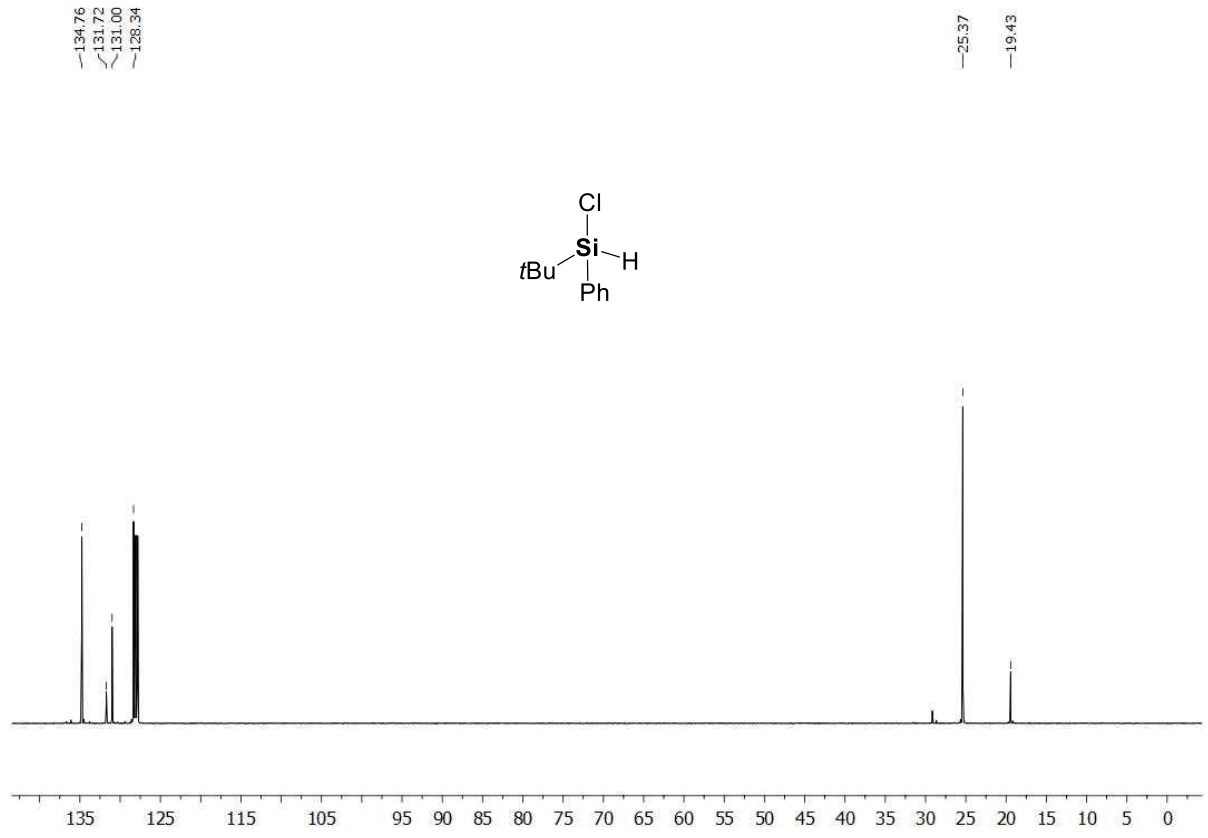


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of *t*BuPhSi(H)Cl.

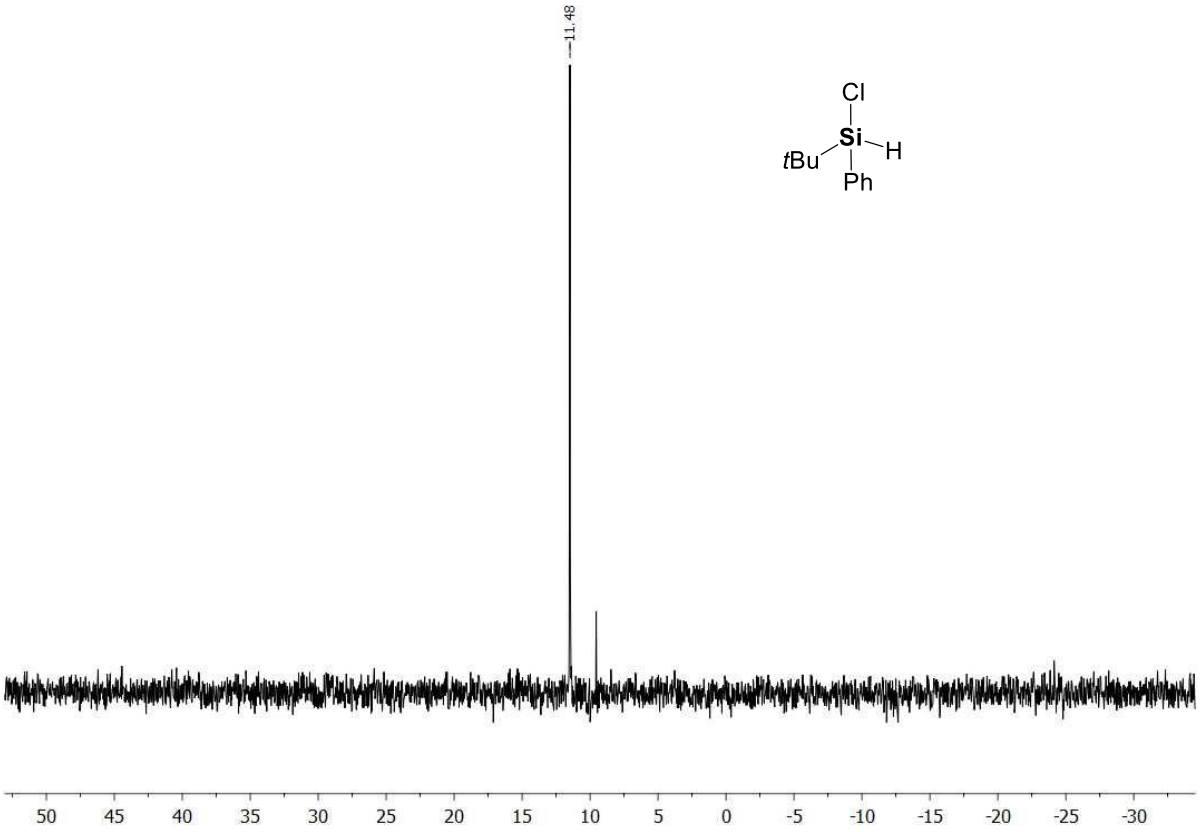
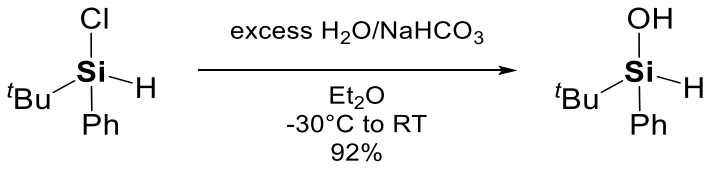


Figure S3. $^{29}Si\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of *t*BuPhSi(H)Cl.

2.3. Synthesis of *t*BuPhSi(H)OH



To a stirred solution of *t*BuPhSi(H)Cl (3.68 g, 18.55 mmol) in diethyl ether (60 ml) at -30°C, H_2O (2 ml, 111.11 mmol) was added followed by an excess of $NaHCO_3$. The resulting suspension was then allowed to slowly warm up to room temperature and reacted overnight under vigorous stirring. Afterwards, the reaction mixture was dried with $MgSO_4$, the white suspension filtered, and the remaining solids washed with diethyl ether (2 x 20 ml). The clear colorless filtrates were collected and all the volatiles were gently removed under vacuum, without an external source of heating, to yield pure *t*BuPhSi(H)OH as a clear colorless oil (3.08 g, 17.08 mmol, 92%). Batches of freshly prepared silanol, dissolved in hexane and stored at -30°C are stable over a period of months, otherwise the neat isolated silanol slowly converts to the respective siloxane at room temperature.

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ= 0.97 [s, 9H, C(C*H*$_3$)$_3$], 2.59 [s, 1H, O*H*], 5.05 [s with ^{29}Si satellites, $^{1}J_{HSi}$ = 204.6, 1H, Si*H*], 7.17–7.18 [m, 3H, H_{Ph}], 7.56–7.57 [m, 2H, H_{Ph}]. **^{13}C{^{1}H} NMR** (100.62 MHz, C_6D_6, 298 K): δ= 17.7 [s, *C*(CH$_3$)$_3$], 25.2 [s, C(*C*H$_3$)$_3$], 127.7 [s, C_{Ph}], 129.9 [s, C_{Ph}], 134.1 [s, C_{Ph}], 135.0 [s, C_{Ph}]. **^{29}Si{^{1}H} NMR** (79.49 MHz, C_6D_6, 298 K): δ= 0.9. **HR-MS (EI+)**, calculated. m/z for $C_{10}H_{16}OSi$ $[M]^+$: 180.09649; found: 180.09652. **CHN Analysis** $C_{10}H_{16}OSi$; calculated: C 66.61; H 8.94; found: C 65.34; H 8.31.

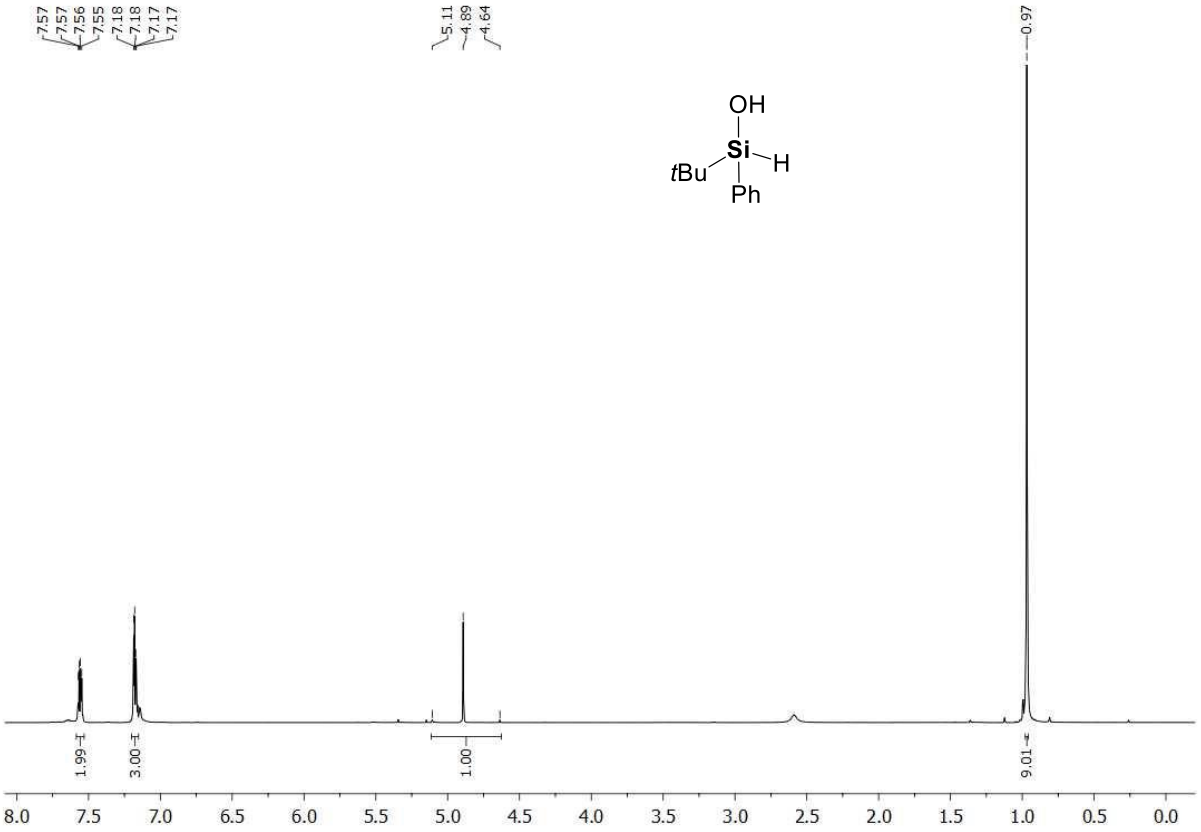


Figure S4. ^{1}H NMR spectrum (C_6D_6, 298 K) of *t*BuPhSi(H)OH.

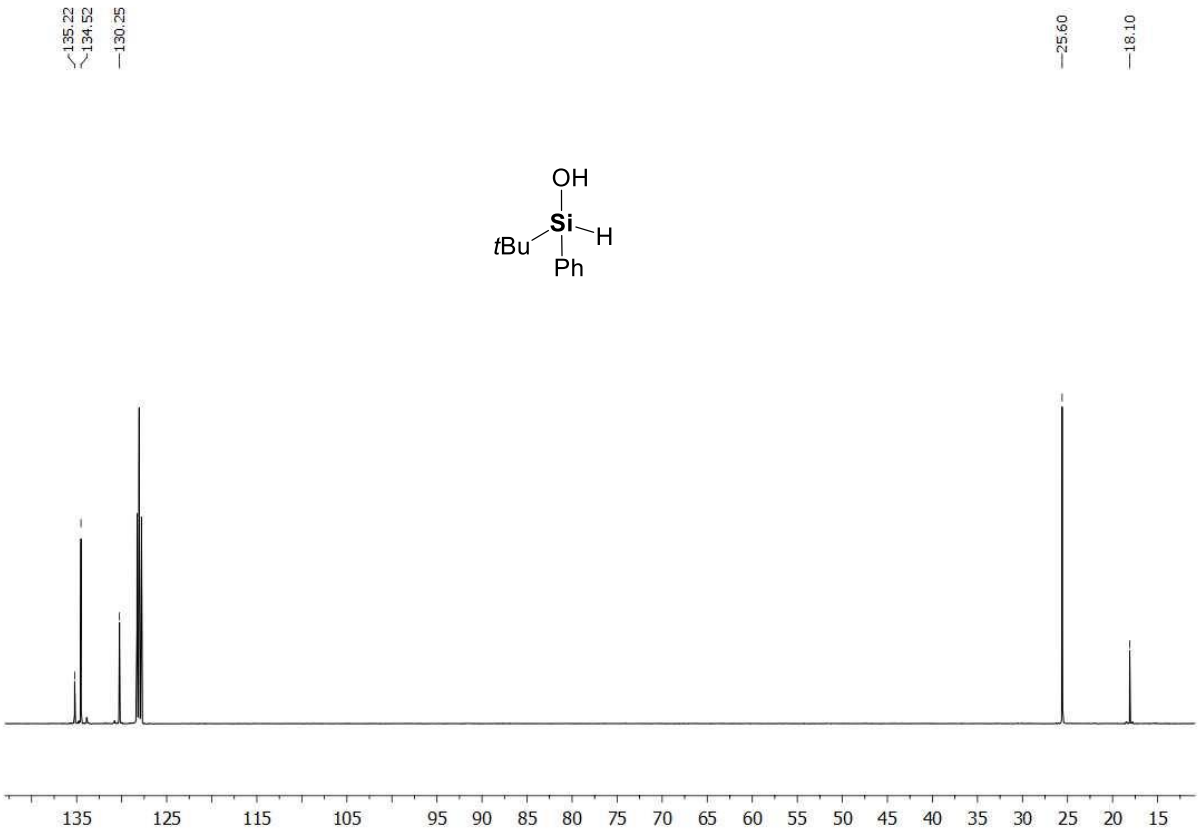


Figure S5. ^{13}C{^{1}H} NMR spectrum (C_6D_6, 298 K) of *t*BuPhSi(H)OH.

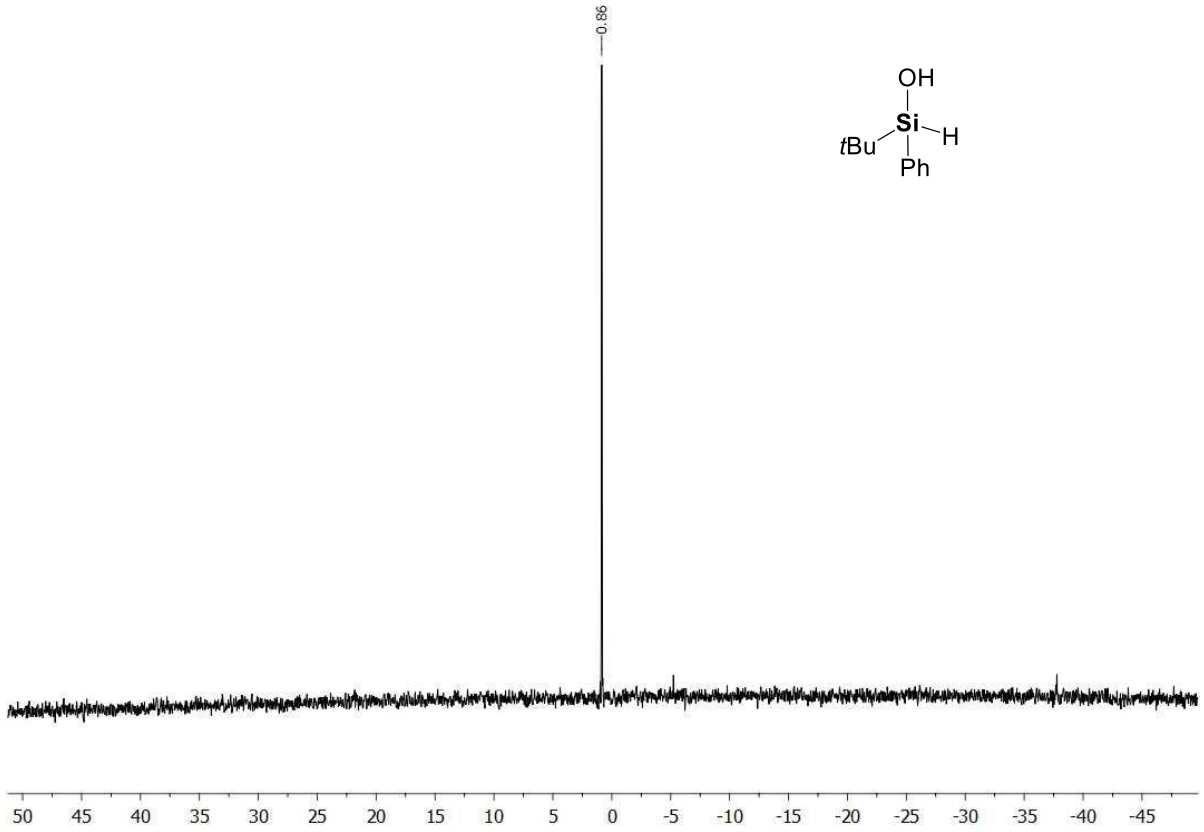
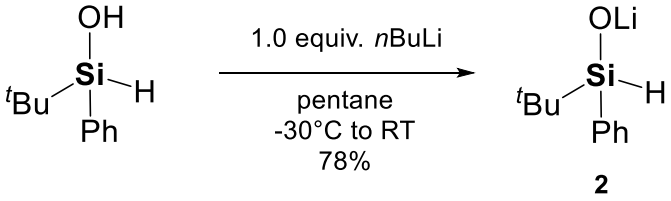


Figure S6. $^{29}Si\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of *t*BuPhSi(H)OH.

2.4. Synthesis of *t*BuPhSi(H)(OLi) (2)



2

n-Butyllithium (6.8 ml, 2.5 M in hexane, 17.08 mmol, 1.0 equiv.) was added dropwise to a solution of *t*BuPhSiH(OH) (3.08 g, 17.08 mmol, 1.0 equiv.) in pentane (40 ml) at -30°C. The resulting clear pale-yellow solution was then allowed to slowly warm up to room temperature under vigorous stirring. After additional 2 h of stirring at room temperature, the Schlenk flask containing the whole mixture was sealed and stored at -30°C leading to the precipitation of the lithiated silanolate **2** as a clear colorless crystalline solid over a period of three days. Afterwards, the cold mother-liquor (-30°C) was removed *via* suction filtration and the solid dried under vacuum affording pure silanolate **2** as a white solid (2.48 g, 13.32 mmol, 78%).

^{1}H NMR (400.13 MHz, THF-d_8, 298 K): δ= 0.82 [s, 9H, C(CH_3)$_3$], 4.83 [s with ^{29}Si satellites, $^{1}J_{HSi}$ = 180.4, 1H, Si*H*], 7.17 [m, 3H, H_{Ph}], 7.56 [m, 2H, H_{Ph}]. **^{13}C{^{1}H} NMR** (100.62 MHz, THF-d_8, 298 K): δ= 18.9 [s, *C*(CH$_3$)$_3$], 26.2 [s, C(*C*H$_3$)$_3$], 126.2 [s, C_{Ph}], 127.1 [s, C_{Ph}], 134.1 [s, C_{Ph}], 144.6 [s, C_{Ph}]. **^{29}Si{^{1}H} NMR** (79.49 MHz, THF-d_8, 298 K): δ= -14.8. **^{7}Li{^{1}H} NMR** (155.50 MHz, THF-d_8, 298 K): δ= 0.3. **HR-MS (ESI+)**, calculated. m/z for $C_{20}H_{30}O_2Si_2$ [2M + Li]$^{+}$: 379.2264; found: 379.2252. **CHN Analysis** $C_{10}H_{15}LiOSi$: calculated: C 64.49, H 8.12; found: C 64.36; H 8.08.

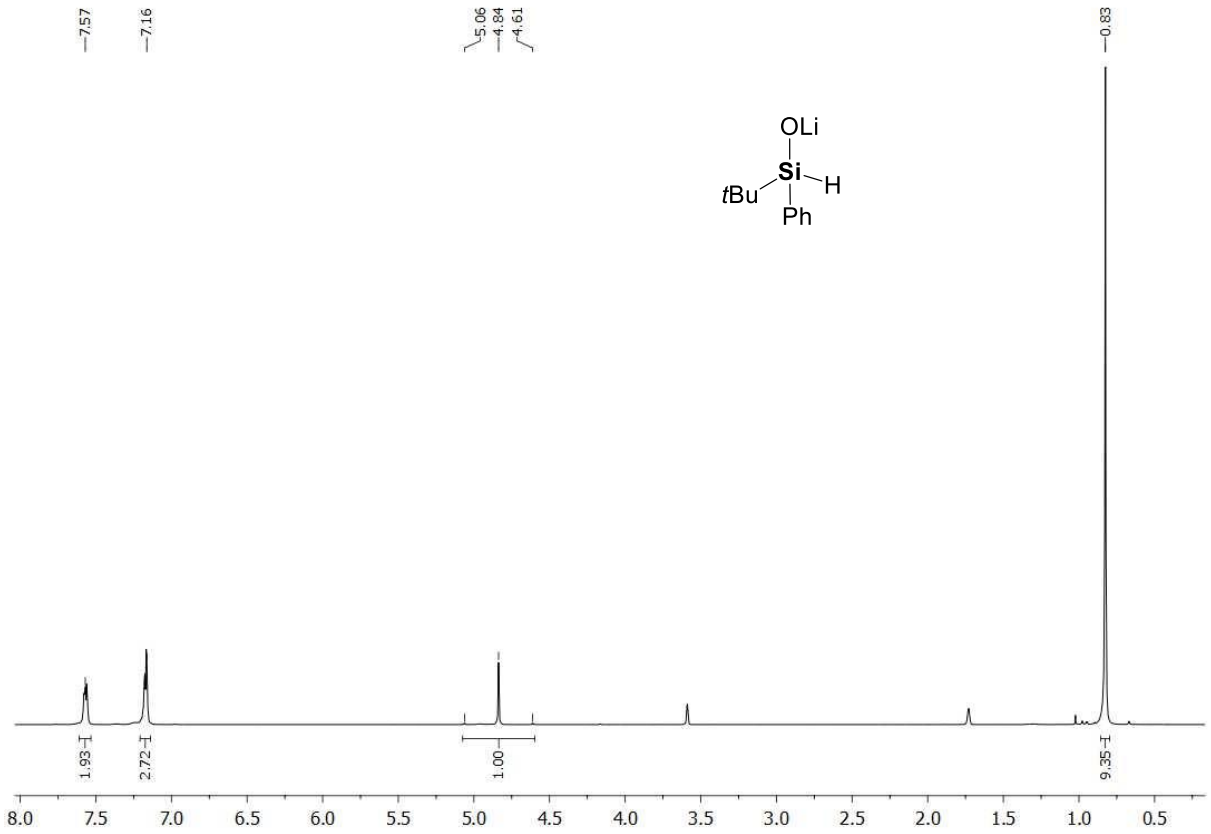


Figure S7. ^{1}H NMR spectrum (THF-d_8, 298 K) of *t*BuPhSi(H)(OLi) (**2**).

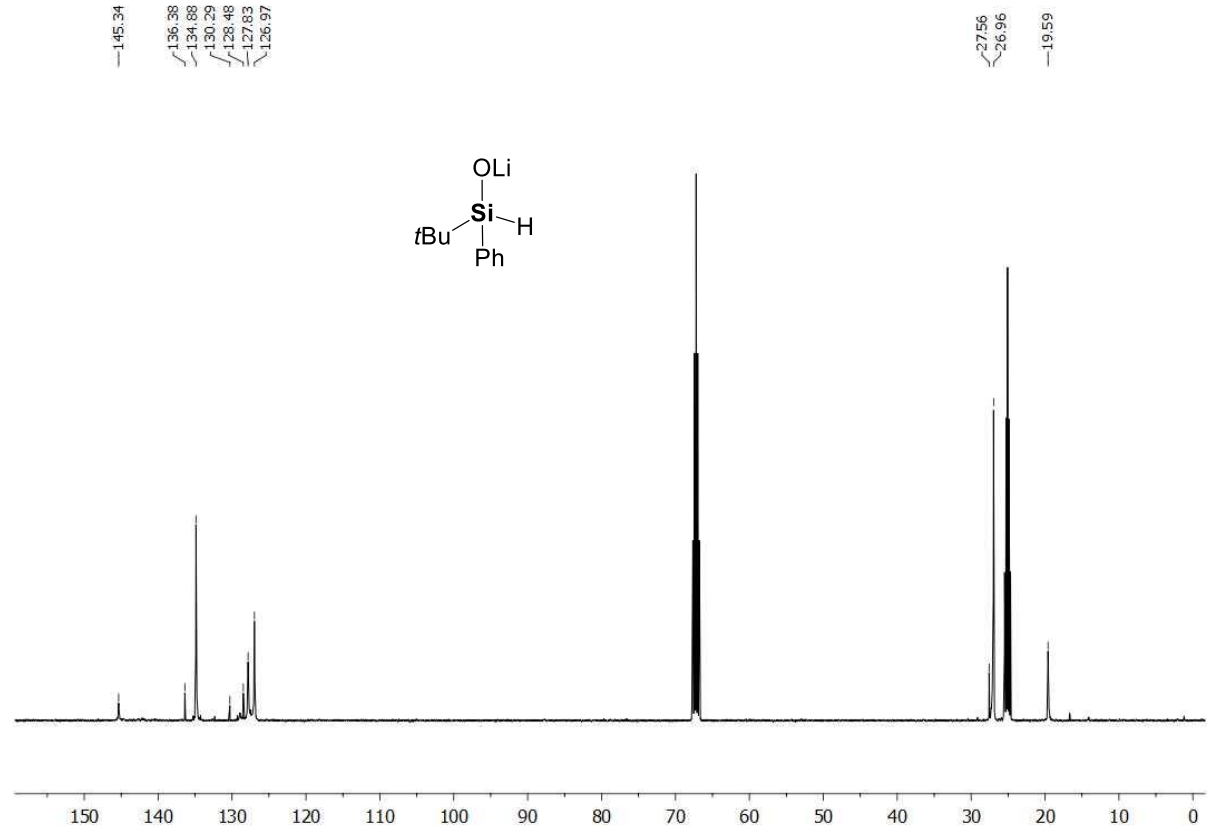


Figure S8. ^{13}C{^{1}H} NMR spectrum (THF-d_8, 298 K) of *t*BuPhSi(H)(OLi) (**2**).

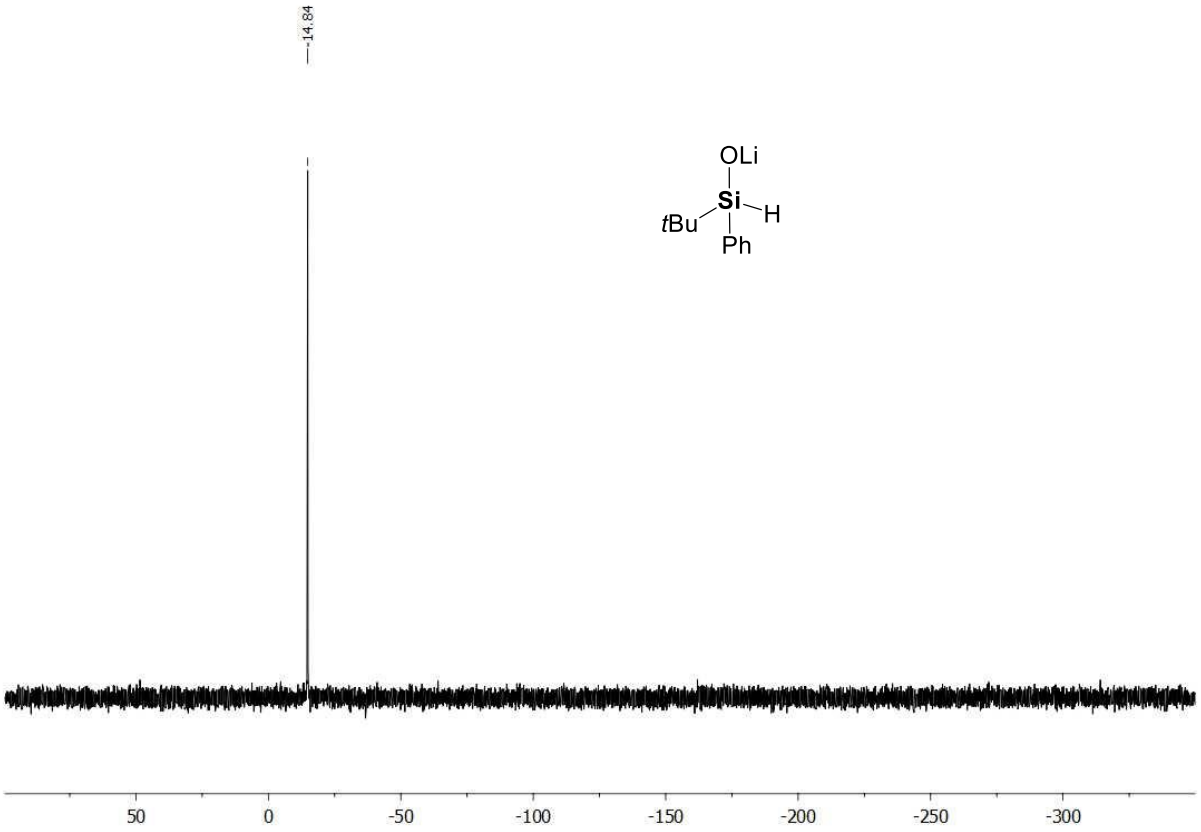


Figure S9. $^{29}Si\{^{1}H\}$ NMR spectrum (THF-d_8, 298 K) of *t*BuPhSi(H)(OLi) (**2**).

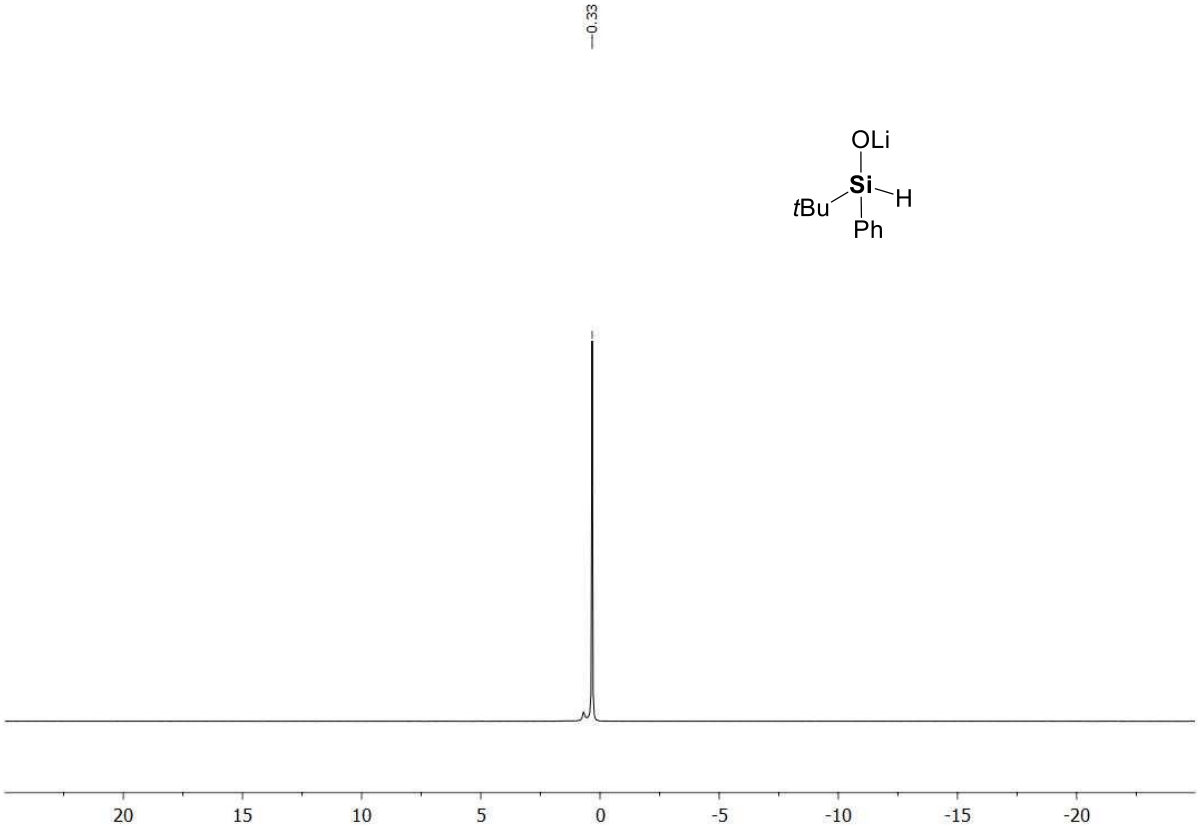
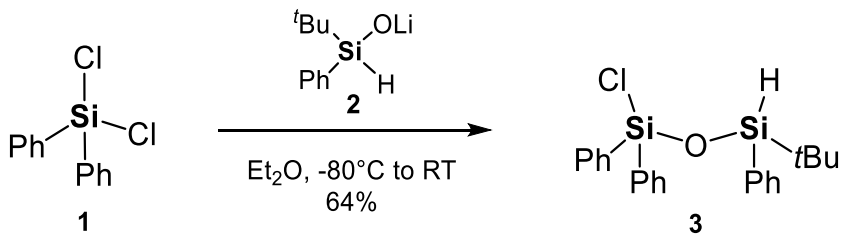


Figure S10. $^{7}Li\{^{1}H\}$ NMR spectrum (THF-d_8, 298 K) of *t*BuPhSi(H)(OLi) (**2**).

2.5. Synthesis of $Ph_2Si(Cl)OSiPh(H)tBu$ (3)



Lithium silanolate **2** (9.68 g, 52.0 mmol, 1.0 equiv.) was suspended in diethyl ether (100 ml) and the solution was cooled down to -80°C. Ph_2SiCl_2 **1** (13.2 g, 52.0 mmol, 1.0 equiv.) was added *via* syringe in one portion. The reaction mixture was stirred vigorously without further cooling for 15 h during which a white precipitate was formed. The solids were filtered off and rinsed three times with pentane (3 x 30 ml). All volatiles were removed under reduced pressure. The crude mixture was purified *via* Kugelrohr distillation (165 °C oven temperature, 1.0 x 10^{-3} mbar) affording pure product **3** as a colourless oil (13.2 g, 33.3 mmol, 64%).

^{1}H NMR (400.13 MHz, C_6D_6, 298 K): δ =1.00 [s, 9H, SiC(C*H*$_3$)$_3$], 5.18 [s, 1H, Si*H*], 7.08–7.14 [m, 9H, *H*$_{Ph}$], 7.60–7.62 [m, 2H, *H*$_{Ph}$], 7.74–7.76 [m, 4H, *H*$_{Ph}$]. **^{13}C{^{1}H} NMR** (100.61 MHz, C_6D_6, 298 K): δ = 18.5 [s, SiC*H*$_2$(CH$_3$)$_3$], 25.5 [s, SiCH$_2$(C*H*$_3$)$_3$], 128.2 [s, C$_{Ph}$], 128.4 [s, C$_{Ph}$], 130.5 [s, C$_{Ph}$], 131.2 [s, C$_{Ph}$], 134.0 [s, C$_{Ph}$], 134.1 [s, C$_{Ph}$], 134.6 [s, C$_{Ph}$]. **^{29}Si{^{1}H} NMR** (79.49 MHz, C_6D_6, 298 K): δ = -19.1 [s, ClSiO*Si*H], -3.3 [s, ClSi*O*SiH]. **CHN Analysis** $C_{22}H_{25}ClOSi_2$: calculated: C 66.55, H 6.35; found C 69.90, H 6.45. **HR-MS (ESI+)**, calculated. m/z for $C_{18}H_{16}ClOSi_2^+$ $[M-C_4H_9]^+$: 339.0428; found: 339.0426.

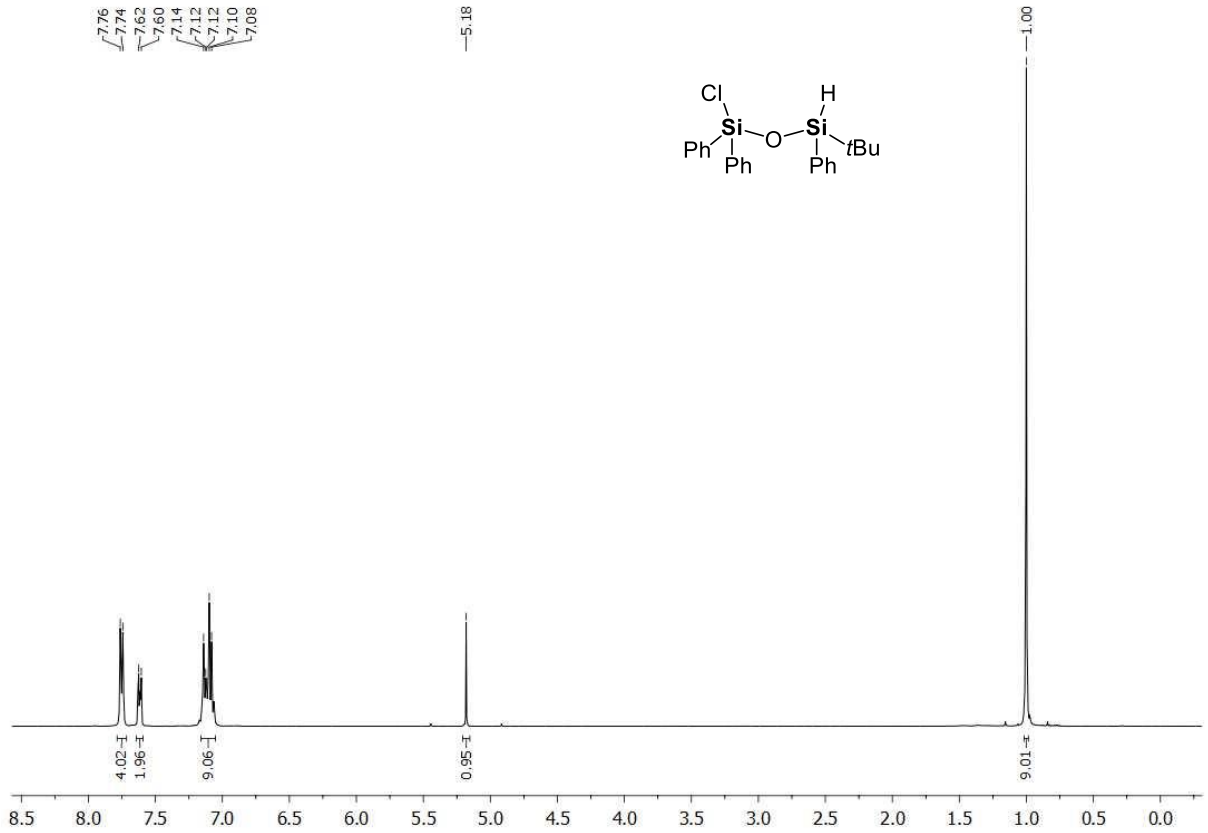


Figure S11. ^{1}H NMR spectrum (C_6D_6, 298 K) of compound **3**.

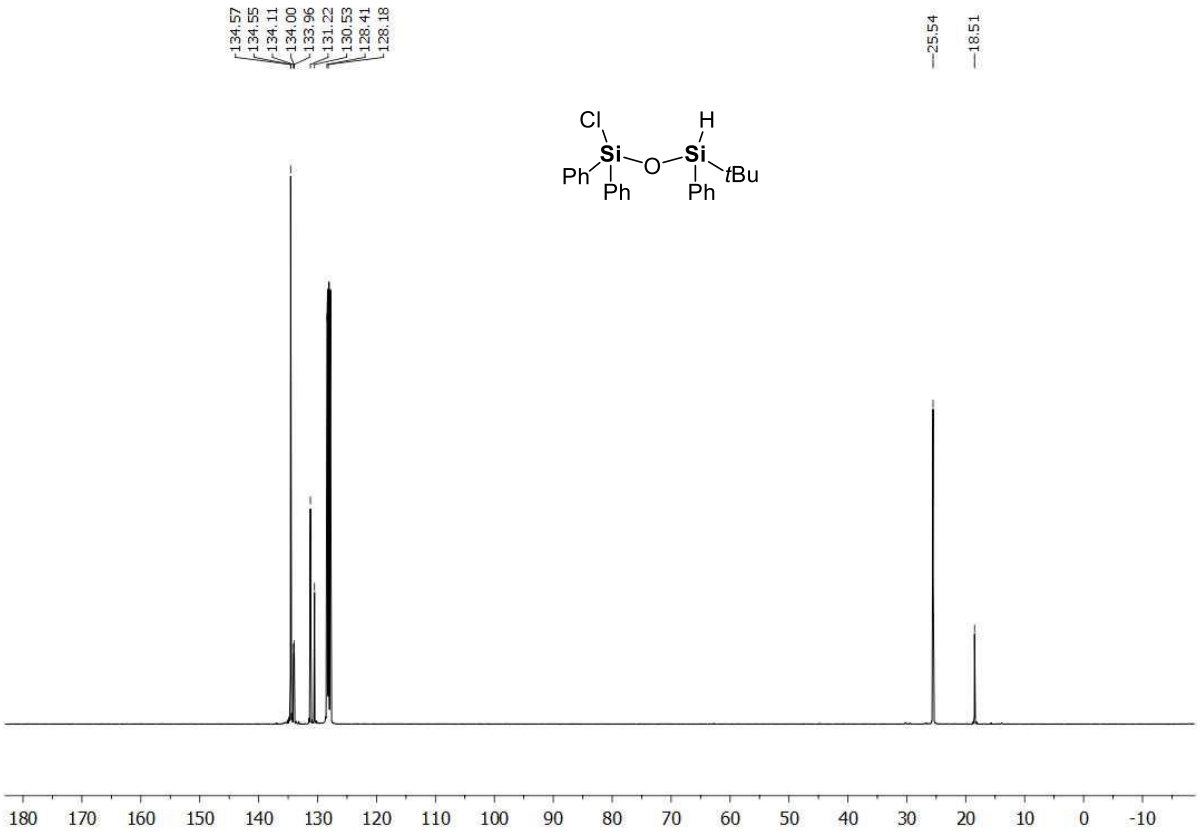


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of compound **3**.

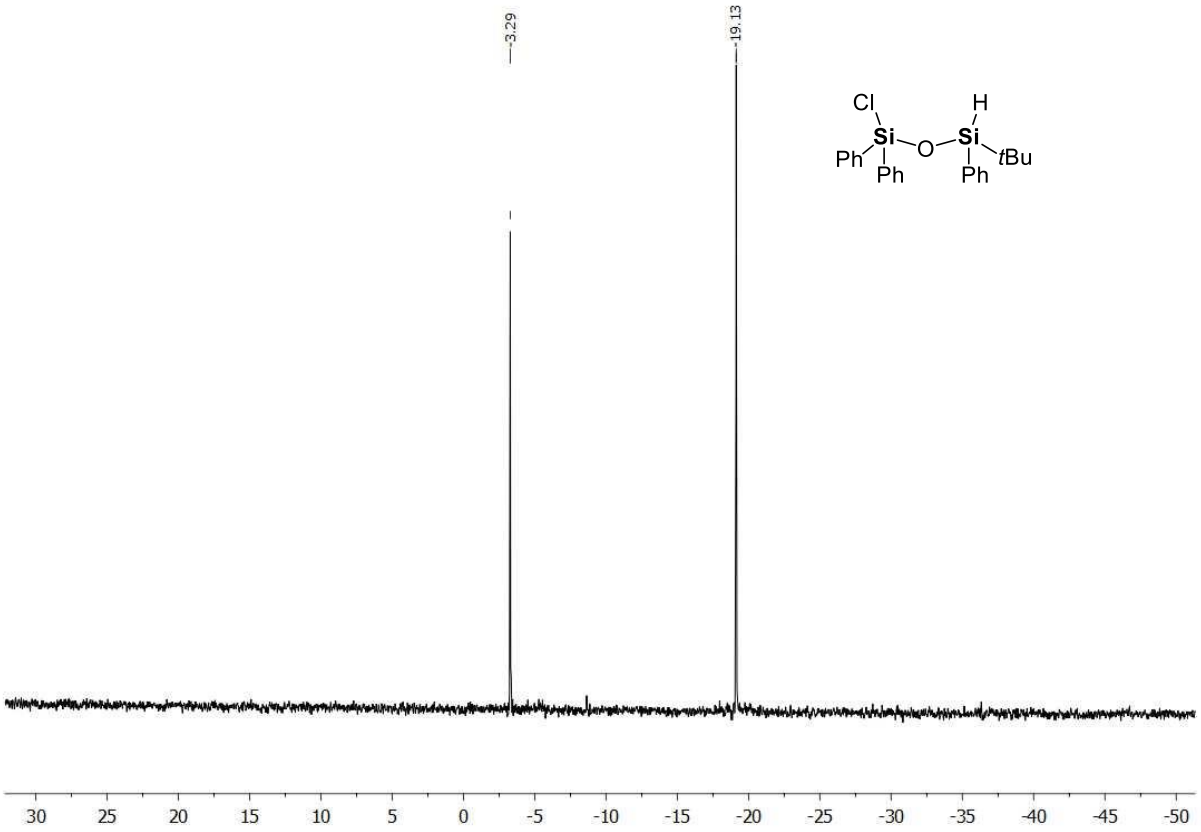
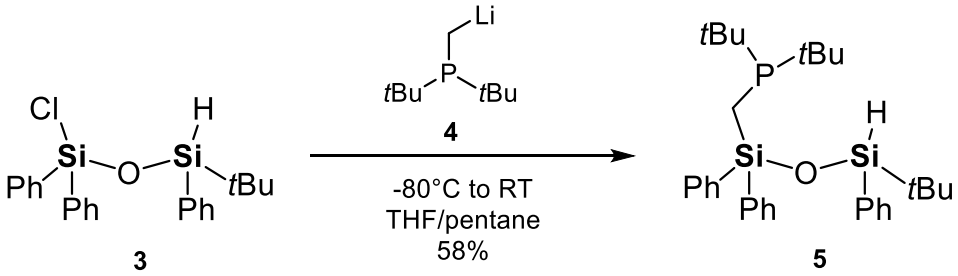


Figure S13. $^{29}Si\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of compound **3**.

2.6. Synthesis of (*t*Bu)$_2$PCH$_2$SiPh$_2$OSiPh(H)*t*Bu (5)



Siloxane **3** (3.85 g, 9.7 mmol, 1.0 equiv.) was dissolved in pentane (20 ml) and the solution was cooled down to -80 °C. Freshly prepared *t*Bu$_2$PCH$_2$Li (**4**) (1.61 g, 9.7 mmol, 1.0 equiv.) was added by the means of a PTFE cannula as a THF solution (10 ml). The reaction mixture was stirred for 15 h without further cooling. Afterwards, all volatiles were removed in vacuum yielding a colourless solid which was extracted with DCM (3 x 5 ml). The solids were filtered off by cannula filtration and the clear filtrates collected and dried under vacuum. The crude mixture was purified *via* Kugelrohr distillation (190°C oven temperature, 1.0 x 10^{-3} mbar) affording the desired compound **5** as a colourless oil (2.92 g, 5.6 mmol 58%).

^{1}H NMR (400.30 MHz, CD_2Cl_2, 298 K): δ =0.90 [s, 9H, SiC(C*H*$_3$)$_3$], 0.96 [d, $^3J_{P\text{-}H}$= 2.4 Hz, 9H, PC(C*H*$_3$)$_3$], 0.98 [d, $^3J_{P\text{-}H}$= 2.4 Hz, 9H, PC(C*H*$_3$)$_3$], 1.25 [b, 2H, SiC*H*$_2$P], 4.92 [s,1H, Si*H*], 7.28–7.39 [m, 9H, *H*$_{Ph}$], 7.60–7.63 [m, 2H, *H*$_{Ph}$], 7.66 [m, 2H, *H*$_{Ph}$], 7.68 [m, 2H, *H*$_{Ph}$]. **^{13}C{^{1}H} NMR** (100.66 MHz, C_6D_6, 298 K): δ = 6.8 [d, $^1J_{P\text{-}C}$= 44.5 Hz, Si*C*H$_2$P], 18.8 [s, Si*C*H$_2$(CH$_3$)$_3$], 25.9 [s, SiCH$_2$(*C*H$_3$)$_3$], 29.6 [d, $^2J_{P\text{-}C}$= 2.2 Hz, PC(*C*H$_3$)$_3$], 29.7 [d, $^2J_{P\text{-}C}$= 2.3 Hz, PC(*C*H$_3$)$_3$], 31.7 [d, $^1J_{P\text{-}C}$= 2.9 Hz, P*C*(CH$_3$)$_3$], 31.9 [d, $^1J_{P\text{-}C}$= 3.0 Hz, P*C*(CH$_3$)$_3$], 127.8 [s, C$_{Ph}$], 127.9 [s, C$_{Ph}$], 127.9 [s, C$_{Ph}$], 130.0 [s, C$_{Ph}$], 130.0 [s, C$_{Ph}$], 130.1 [s, C$_{Ph}$], 134.9 [s, C$_{Ph}$], 135.4 [m, C$_{Ph}$], 135.6 [s, C$_{Ph}$], 137.4 [dd, $J_{P\text{-}C}$= 1.8 Hz, $J_{P\text{-}C}$= 7.0 Hz, C$_{Ph}$]. **^{29}Si{^{1}H} NMR** (79.49 MHz, CD_2Cl_2, 298 K): δ = -12.6 [d, $^2J_{Si\text{-}P}$= 23.9 Hz, PCS*i*OSiH], -5.6 [s, PCSiO*Si*H]. **^{31}P{^{1}H} NMR** (162.04 MHz, CD_2Cl_2, 298 K): δ = 15.3 [s]. **CHN Analysis** $C_{31}H_{45}OPSi_2$: calculated: C 71.49, H 8.71; found C 71.96, H 8.81. **HR-MS (ESI+)**, calculated. m/z for $C_{31}H_{45}OPSi_2^+$ $[M+H]^+$: 521.2819; found: 521.2777.

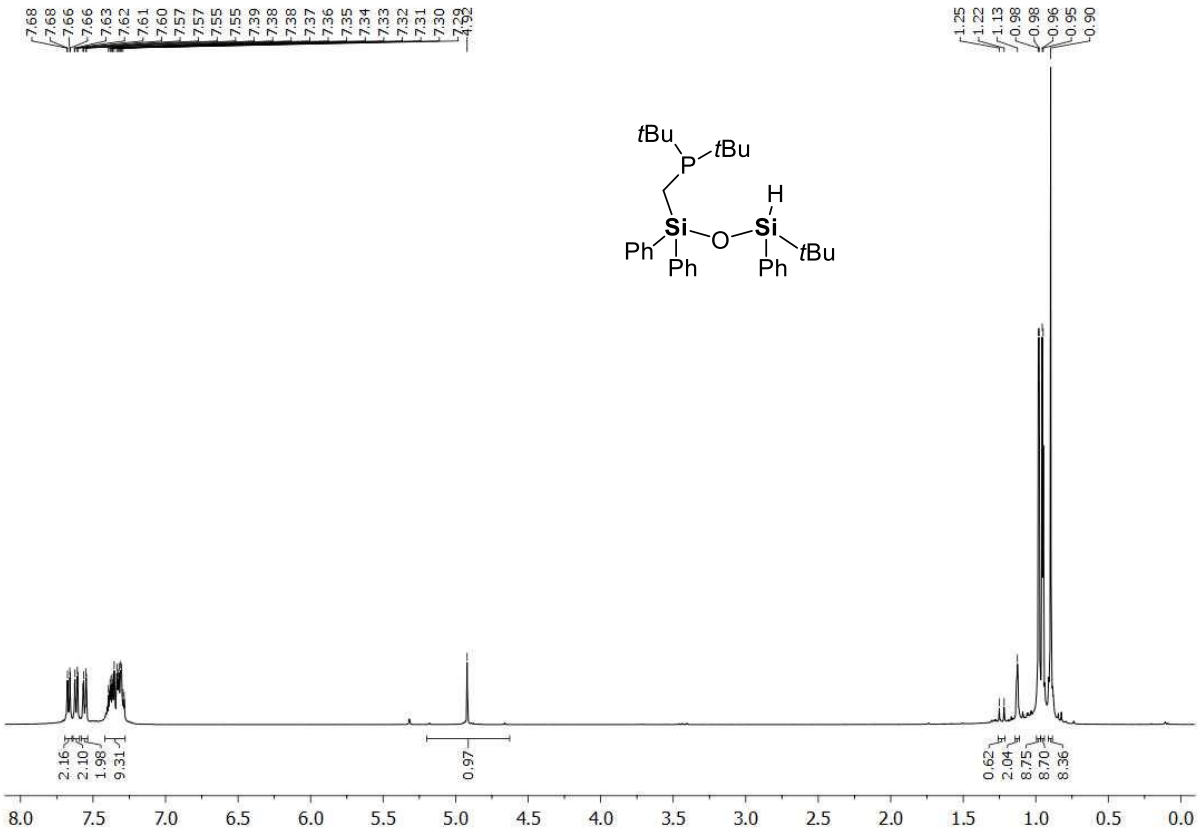


Figure S14. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of compound **5**.

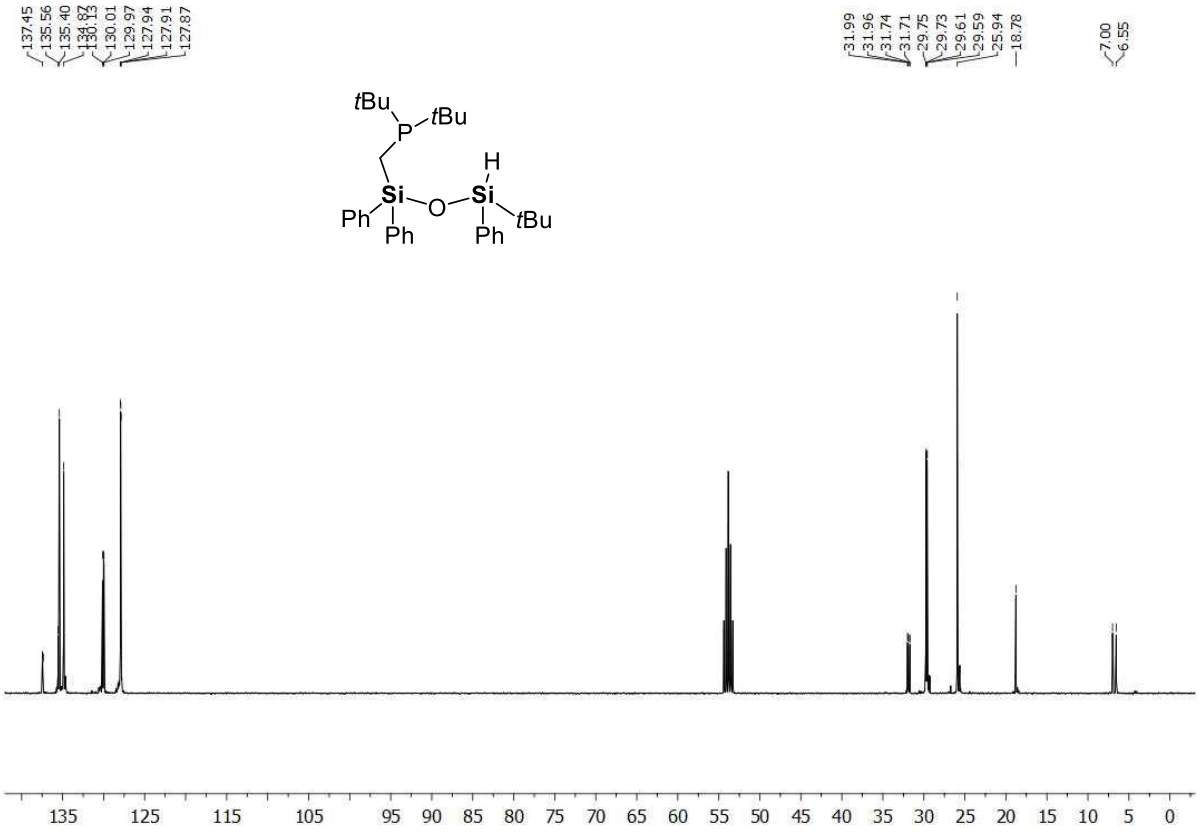


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of compound **5**.

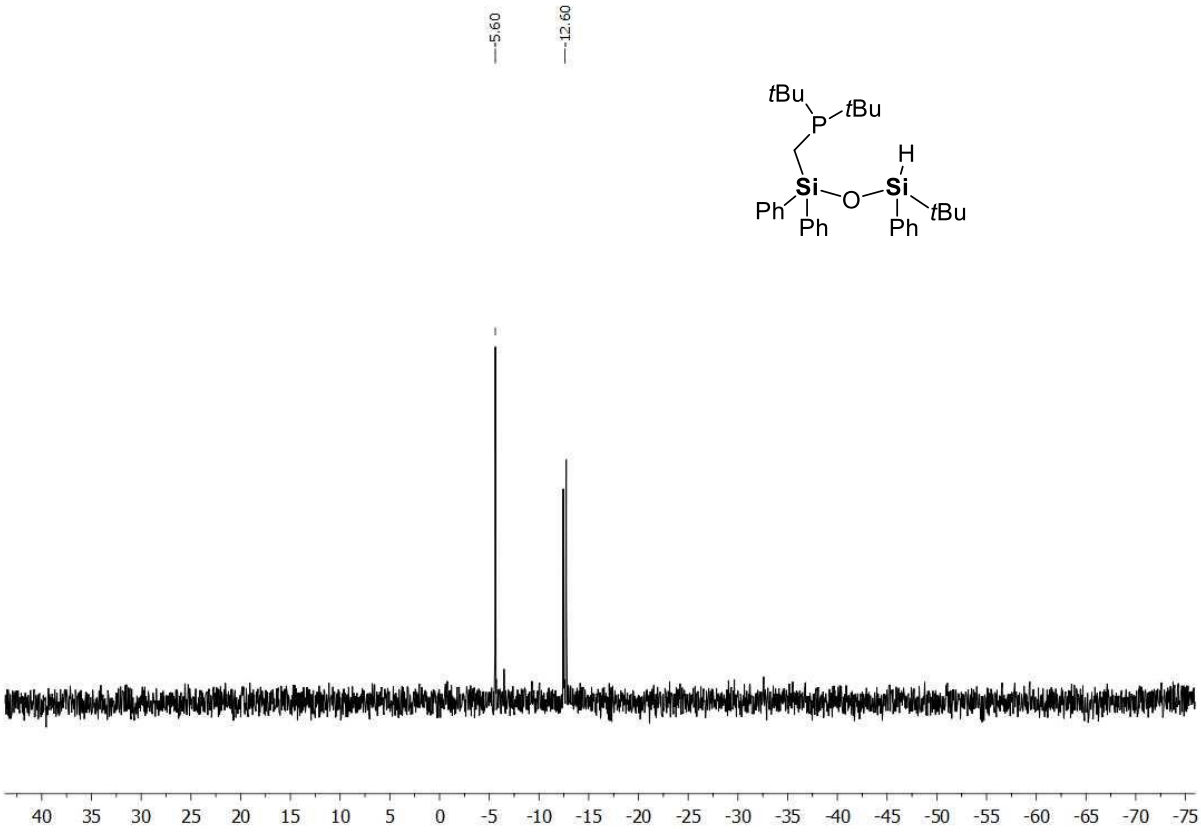


Figure S16. $^{29}Si\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of compound **5**.

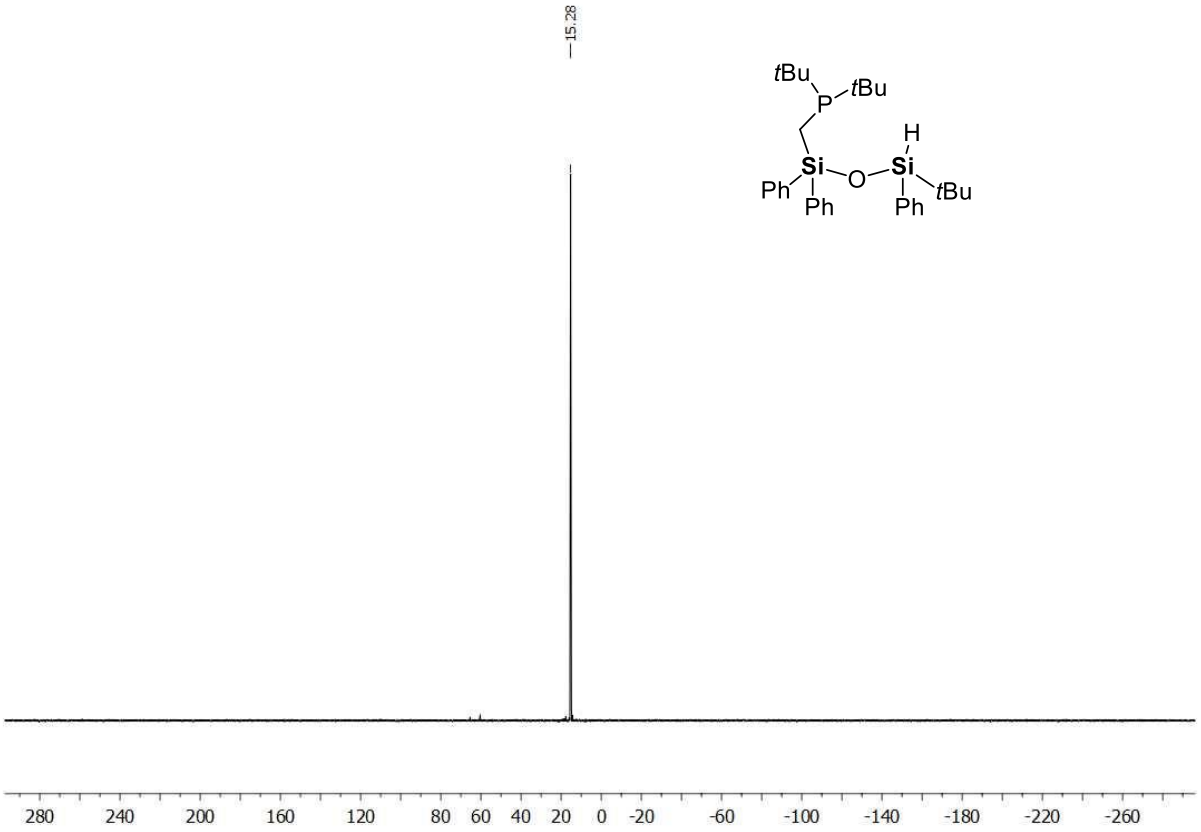
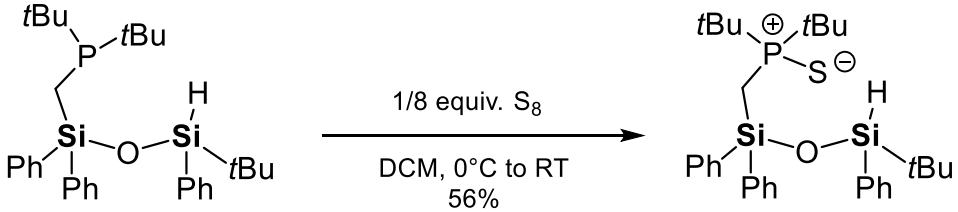


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **5**.

2.7. Synthesis of (*t*Bu)$_2$P(S)CH$_2$SiPh$_2$OSiPh(H)*t*Bu (6)



5 **6**

Siloxane **5** (3.27 g, 6.3 mmol, 1.0 equiv.) was dissolved in DCM (20 ml) and the solution was cooled down to 0°C. Pre-dried elemental sulphur (201 mg, 6.3 mmol, 1.0 equiv.) was added as a solid in one portion. The mixture was stirred without further cooling for 2 h during which the proceeding of the reaction could also be monitored by the disappearing of the solids. The solvent was removed in vacuum and the oily residue purified *via* Kugelrohr distillation (190°C oven temperature, 1.0 x 10^{-3} mbar). Compound **6** was obtained as a colourless oil (1.9 g, 3.5 mmol, 56 %). After two weeks, the oil spontaneously crystallized affording crystals suitable for single-crystal X-ray diffraction analysis.

^{1}H NMR (400.30 MHz, CD_2Cl_2, 298 K): δ =0.90 [s, 9H, SiC(CH_3)$_3$], 1.12 [d, $^3J_{P\text{-}H}$= 4.5 Hz, 9H, PC(CH_3)$_3$], 1.16 [d, $^3J_{P\text{-}H}$= 4.6 Hz, 9H, PC(CH_3)$_3$], 1.86 [d, 2H, $^1J_{P\text{-}H}$= 12.8 Hz, SiCH_2P], 4.96 [s, 1H, Si*H*], 7.29–7.40 [m, 10H, H_{Ph}], 7.55–7.57 [m, 2H, H_{Ph}], 7.75–7.76 [m, 3H, H_{Ph}]. **^{13}C{^{1}H} NMR** (100.66 MHz, CD_2Cl_2, 298 K): δ = 13.1 [d, $^1J_{C\text{-}P}$= 37.2 Hz Si*C*(CH$_3$)$_3$], 25.8 [s, SiC(*C*H$_3$)$_3$], 27.6 [dd, $^2J_{C\text{-}P}$= 1.8 Hz, $^2J_{C\text{-}P}$= 1.8 Hz PC(*C*H$_3$)$_3$], 38.6 [d, $^1J_{C\text{-}P}$= 42.1 Hz P*C*(CH$_3$)$_3$],18.7 [s, Si*C*H$_2$(CH$_3$)$_3$], 127.7 [d, $J_{C\text{-}P}$= 3.3 Hz, C_{Ph}], 128.0 [s, C_{Ph}], 130.2 [s, C_{Ph}], 134.6 [s, C_{Ph}], 134.9 [s, C_{Ph}], 135.9 [s, C_{Ph}], 135.9 [s, C_{Ph}], 136.0 [s, C_{Ph}], 136.3 [s, C_{Ph}], 136.4 [s, C_{Ph}]. **^{29}Si{^{1}H} NMR** (79.49 MHz, CD_2Cl_2, 298 K): δ = -15.2 [d, $^2J_{Si\text{-}P}$= 5.6 Hz PC*Si*OSiH], -4.2 [s, PCSiO*Si*H]. **^{31}P{^{1}H} NMR** (162.04 MHz, CD_2Cl_2, 298 K): δ = 73.9 [s]. **CHN Analysis** $C_{31}H_{45}OPSSi_2$: calculated: C 67.3, H 8.2; found C 67.73, H 7.33. **HR-MS (ESI+)**, calculated. m/z for $C_{31}H_{46}OPSSi_2^+$ $[M+H]^+$: 553.2540; found: 553.2541.

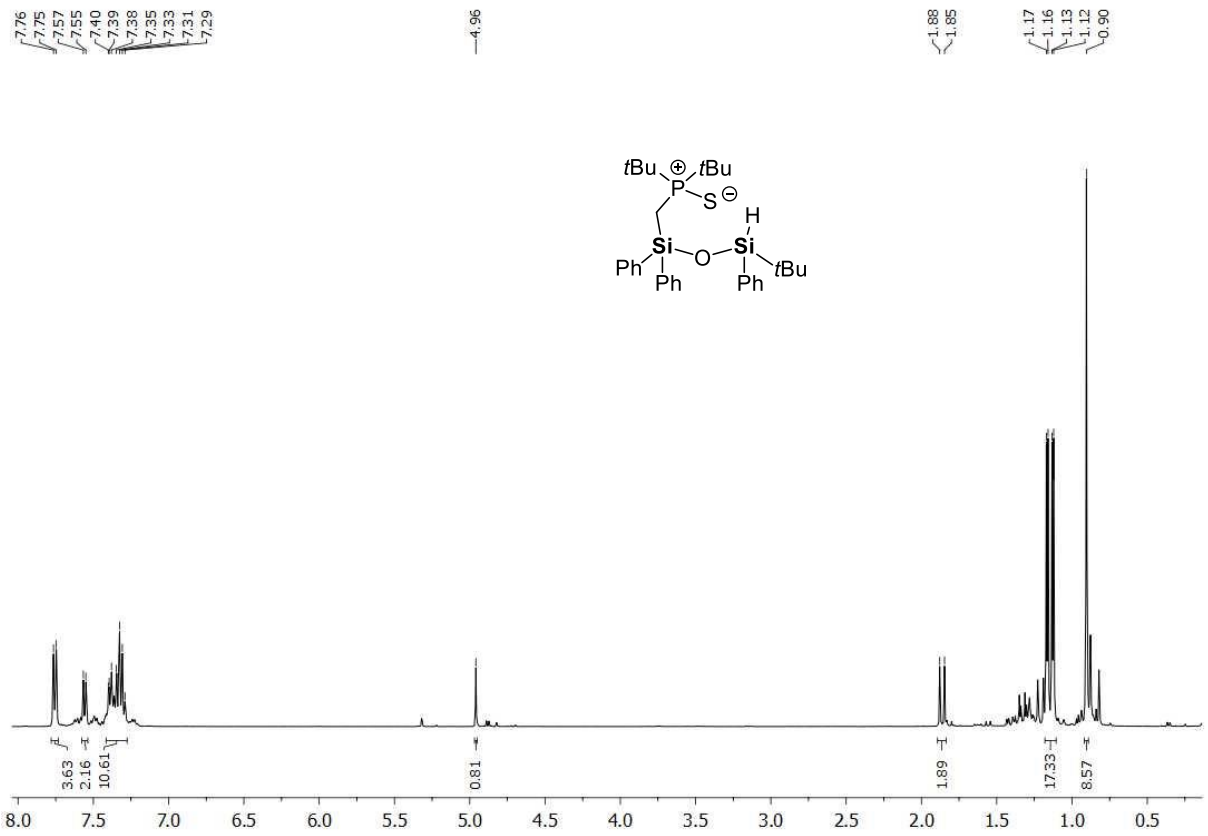


Figure S18. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of compound **6**.

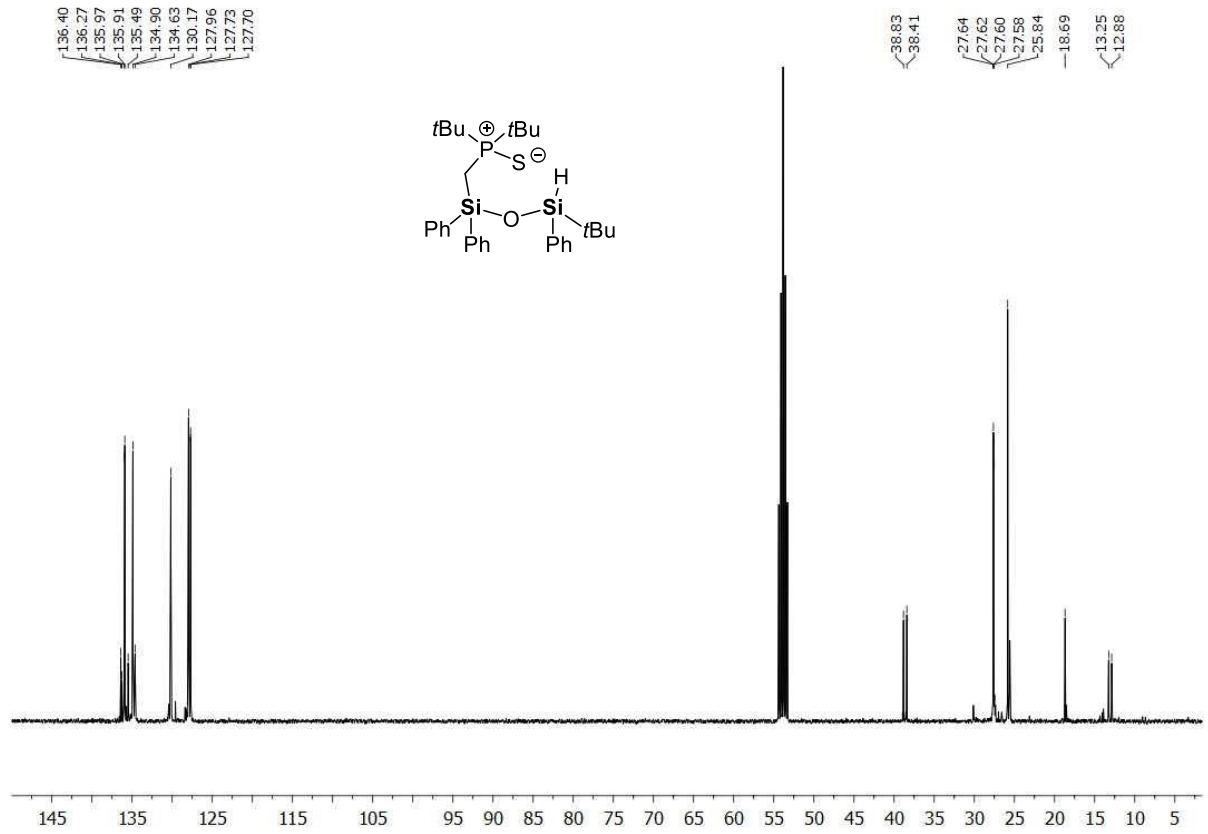


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of compound **6**.

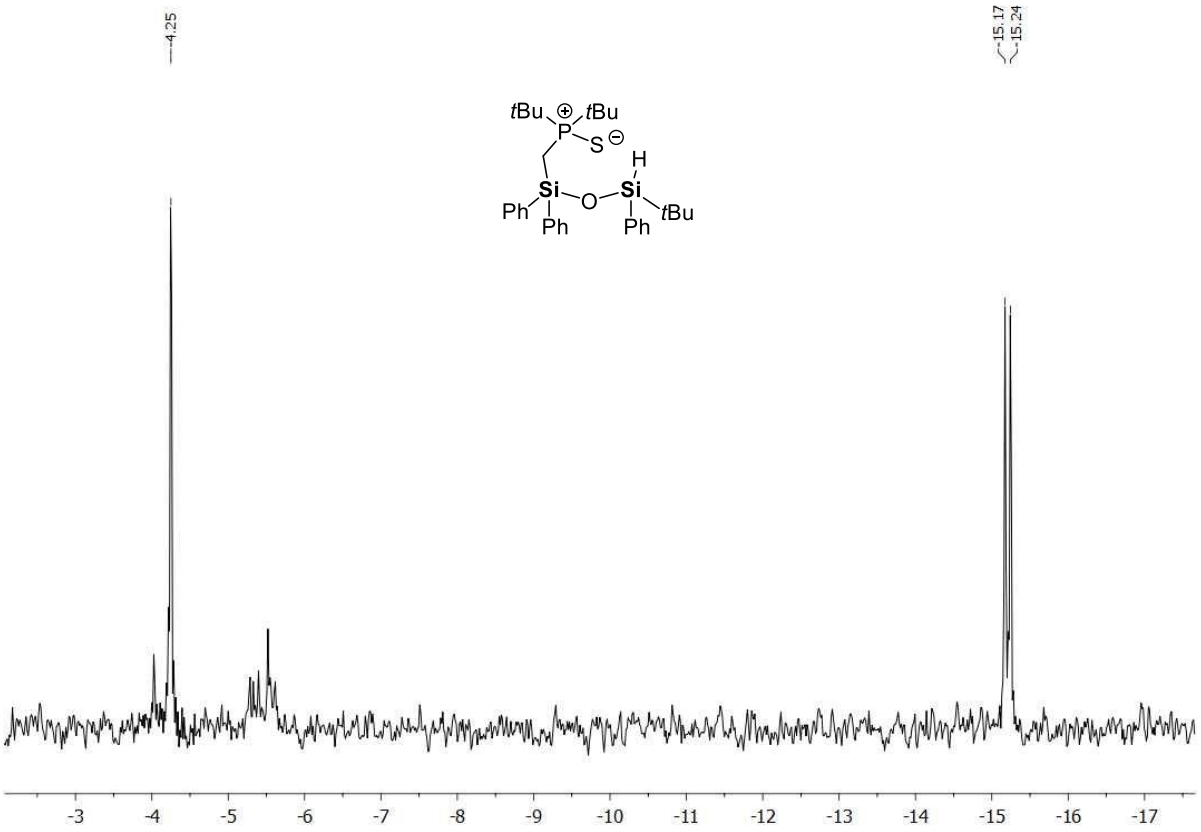


Figure S20. $^{29}Si\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of compound **6**.

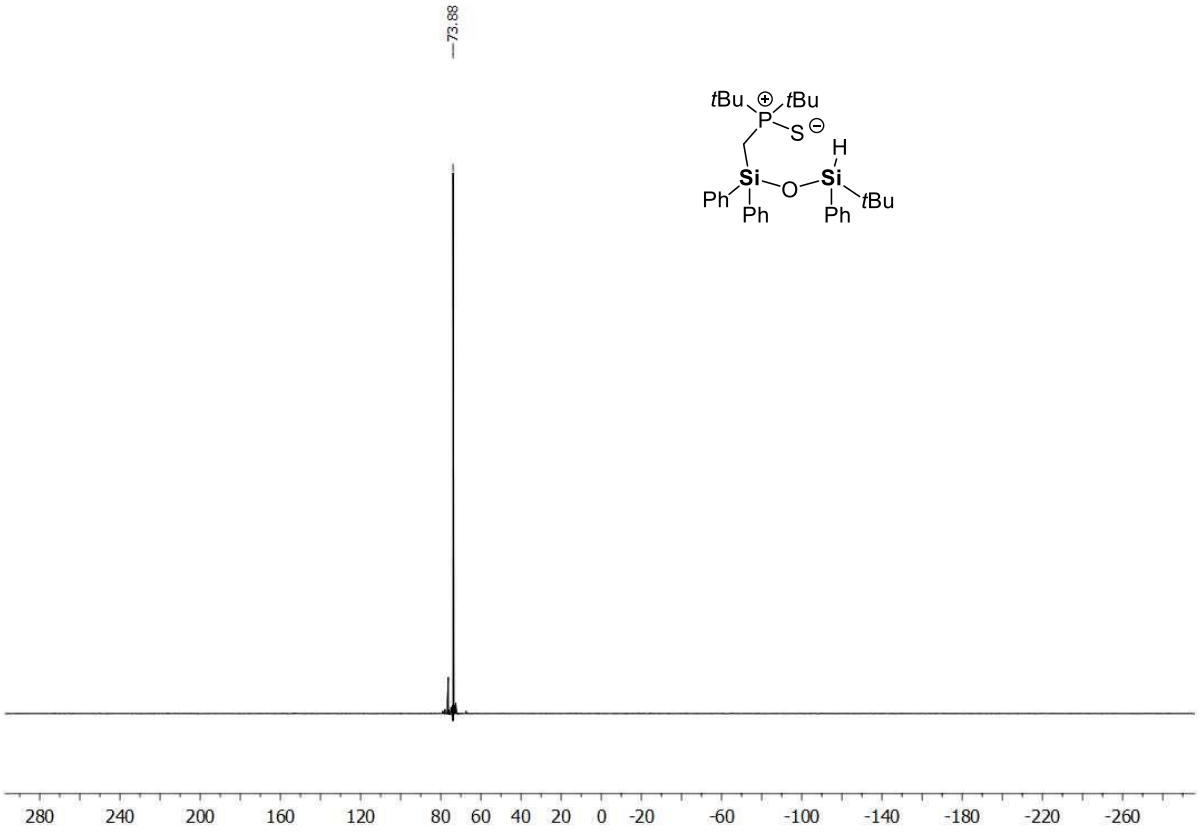
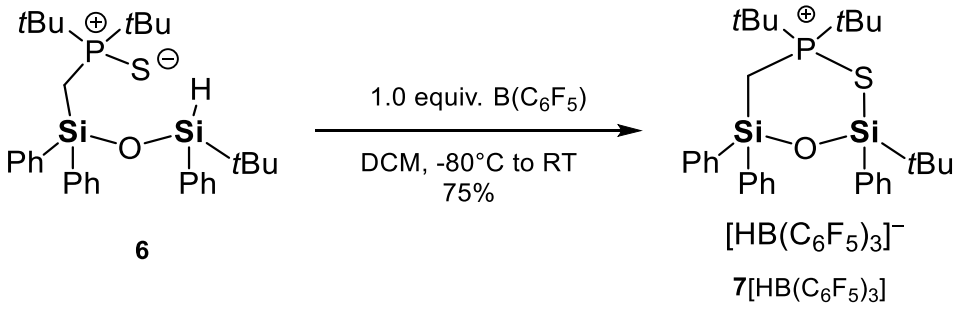


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **6**.

2.8. Synthesis of [(*t*Bu)$_2$P(S)CH$_2$SiPh$_2$OSiPhtBu][HB(C$_6$F$_5$)$_3$] {7[HB(C$_6$F$_5$)$_3$]}



6 **7**[HB(C$_6$F$_5$)$_3$]

Siloxane **6** (757 mg, 1.37 mmol, 1.0 equiv.) was dissolved in DCM (5 ml) and the solution was cooled down to -80°C. BCF (701 mg, 1.37 mmol, 1.0 equiv.) was added as a DCM solution (~5 ml). The mixture was stirred without further cooling for 12 h. The solvent was concentrated down to 1 ml and the compound was precipitated adding pentane (~10 ml). The upper liquid phase was removed using a PTFE cannula and the cloudy oil was further rinsed with pentane (2 ml). After removing all the volatiles in vacuum, the desired product **7**[HB(C$_6$F$_5$)$_3$] was obtained as a foamy solid (1.1 g, 1.0 mmol, 75%), which can be stored for several months at room temperature under an inert atmosphere without noticeable decomposition.

^{1}H NMR (400.30 MHz, CD_2Cl_2, 298 K): δ =1.06 [s, 9H, SiC(C*H*$_3$)$_3$], 1.22 [d, $^3J_{P\text{-}H}$= 17.6 Hz, 9H, PC(C*H*$_3$)$_3$], 1.5 [d, $^3J_{P\text{-}H}$= 17.7 Hz, 9H, PC(C*H*$_3$)$_3$], 2.08 [ddd(ABX), J_1= 13.2 Hz, J_2= 14.8 Hz, J_3= 57,1 Hz, 2H, SiC*H*$_2$P], 3.66 [bq, $^1J_{B\text{-}H}$= 80.3 Hz 1H, B*H*], 7.41–7.60 [m, 11H, *H$_{Ph}$*], 7.69–7.70 [m, 4H, *H$_{Ph}$*]. **^{11}B{^{1}H} NMR** (128.43 MHz, CD_2Cl_2, 298 K): δ = 25.56 [s, *B*H]. **^{13}C{^{1}H} NMR** (100.66 MHz, CD_2Cl_2, 298 K): δ = 0.9 [d, $^1J_{C\text{-}P}$= 24.5 Hz, Si*C*H$_2$P], 23.2 [s, Si*C*(CH$_3$)$_3$], 24.9 [s, SiC(*C*H$_3$)$_3$], 26.7 [s], 26.8 [s], 27.9 [s], 27.1 [s], 41.2 [dd, $^1J_{C\text{-}P}$= 30.6 Hz, $^1J_{C\text{-}P}$= 30.6 Hz, P*C*(CH$_3$)$_3$], 129.1 [s, C$_{Ph}$], 129.2 [s, C$_{Ph}$], 129.4 [s, C$_{Ph}$], 129.6 [s, C$_{Ph}$], 129.8 [s, C$_{Ph}$], 132.5 [t, *J*= 9.5 Hz C$_{Ph}$], 134.3 [s, C$_{Ph}$], 134.4 [s,C$_{Ph}$], 134.8 [s, C$_{Ph}$], 137.1 [bd, $^1J_{C\text{-}F}$= 250.0 Hz, C$_{Ar\text{-}borate}$], 140.0 [bd, $^1J_{C\text{-}F}$= 243.0 Hz, C$_{Ar\text{-}borate}$], 148.1 [bd, $^1J_{C\text{-}F}$= 247.1 Hz, C$_{Ar\text{-}borate}$]. **^{19}F{^{1}H} NMR** (376.66 MHz, CD_2Cl_2, 298 K): δ = -167.6 [t, $^3J_{F\text{-}F}$= 20.2 Hz, 6F], -164.9 [t, $^3J_{F\text{-}F}$= 20.3 Hz, 3F], -133.5 [bd, 6F]. **^{29}Si{^{1}H} NMR** (79.49 MHz, CD_2Cl_2, 298 K): δ = -16.6 [d, $^2J_{Si\text{-}P}$= 8.8 Hz, PC*Si*OSiS], -2.7 [d, $^2J_{Si\text{-}P}$= 5.6 Hz, PCSiO*Si*S]. **^{31}P{^{1}H} NMR** (162.04 MHz, CD_2Cl_2, 298 K): δ = 87.2 [s]. **CHN Analysis** $C_{49}H_{45}BF_{15}OPSSi_2$: calculated: C, 55.27; H, 4.26; found C 54.51, H 4.26. **HR-MS (LIFDI+)**, calculated. m/z for $C_{31}H_{44}OPSSi_2^+$ $[M]^+$: 551.2384; found: 551.2405.

According to a method introduced by Müller,[4] the Lewis acidity of **7**[HB(C$_6$F$_5$)$_3$] was experimentally investigated using *para*-fluorobenzonitrile (FBN) as a probe. Compound **7**[HB(C$_6$F$_5$)$_3$] (70 mg, 0.066 mmol, 1.0 equiv.) and FBN (8.0 mg, 0.066 mmol, 1.0 equiv.) were dissolved in CD_2Cl_2 (0.5 ml), loaded into a Young-type NMR tube, and subjected to NMR measurement. The diagnostic spectroscopic parameters show no interaction between cation **7** of hydroborate **7**[HB(C$_6$F$_5$)$_3$] and FBN:

^{13}C{^{1}H} NMR (100.66 MHz, CD_2Cl_2, 298 K): δ = 165.5 [d, $^1J_{C\text{-}F}$ = 257.9 Hz].

^{19}F{^{1}H} NMR (376.66 MHz, CD_2Cl_2, 298 K): δ = -103.38 [s].

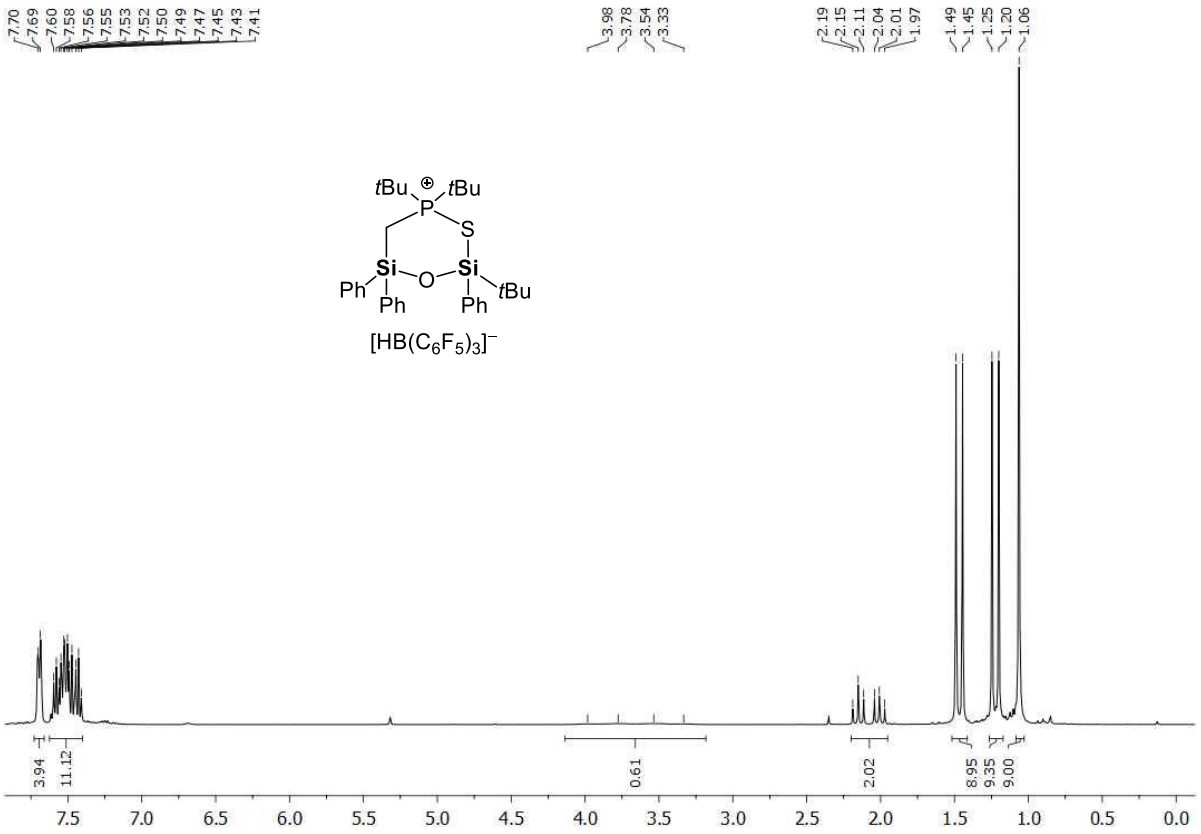


Figure S22. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of compound **7**[$HB(C_6F_5)_3$].

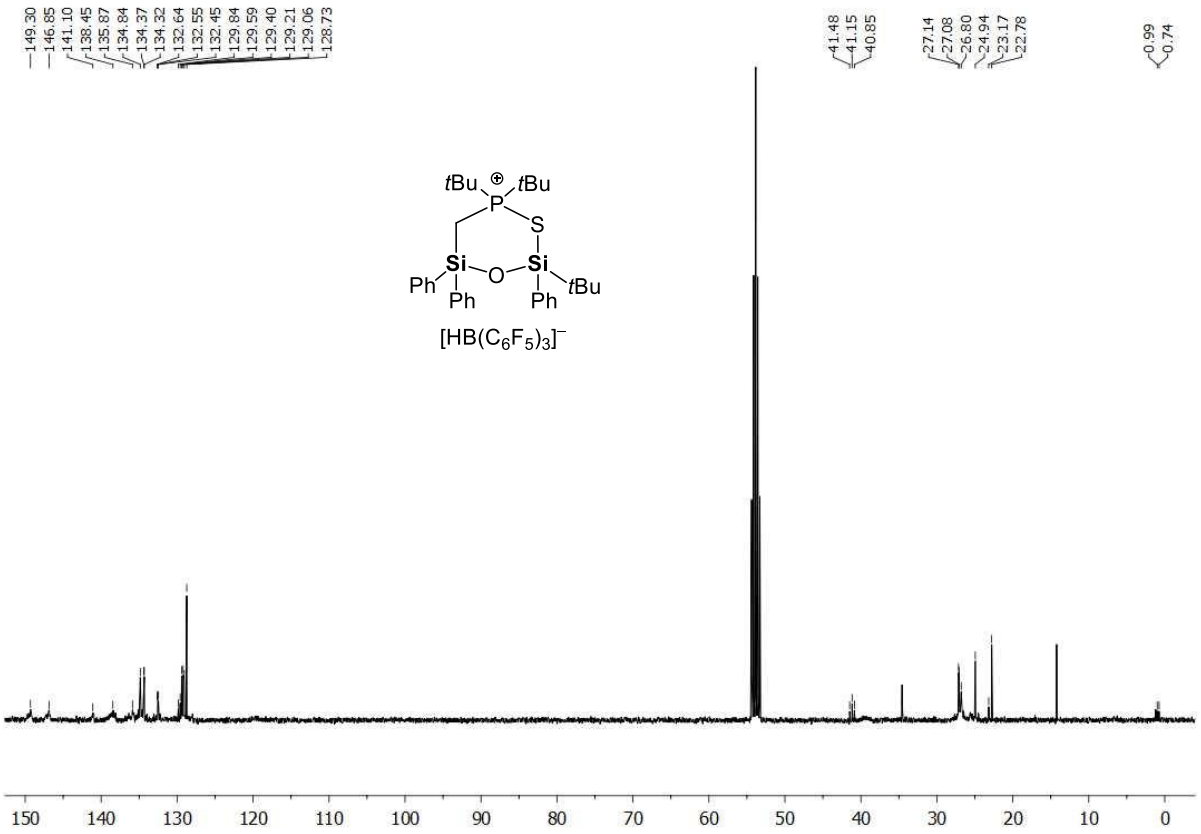


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **7**[$HB(C_6F_5)_3$].

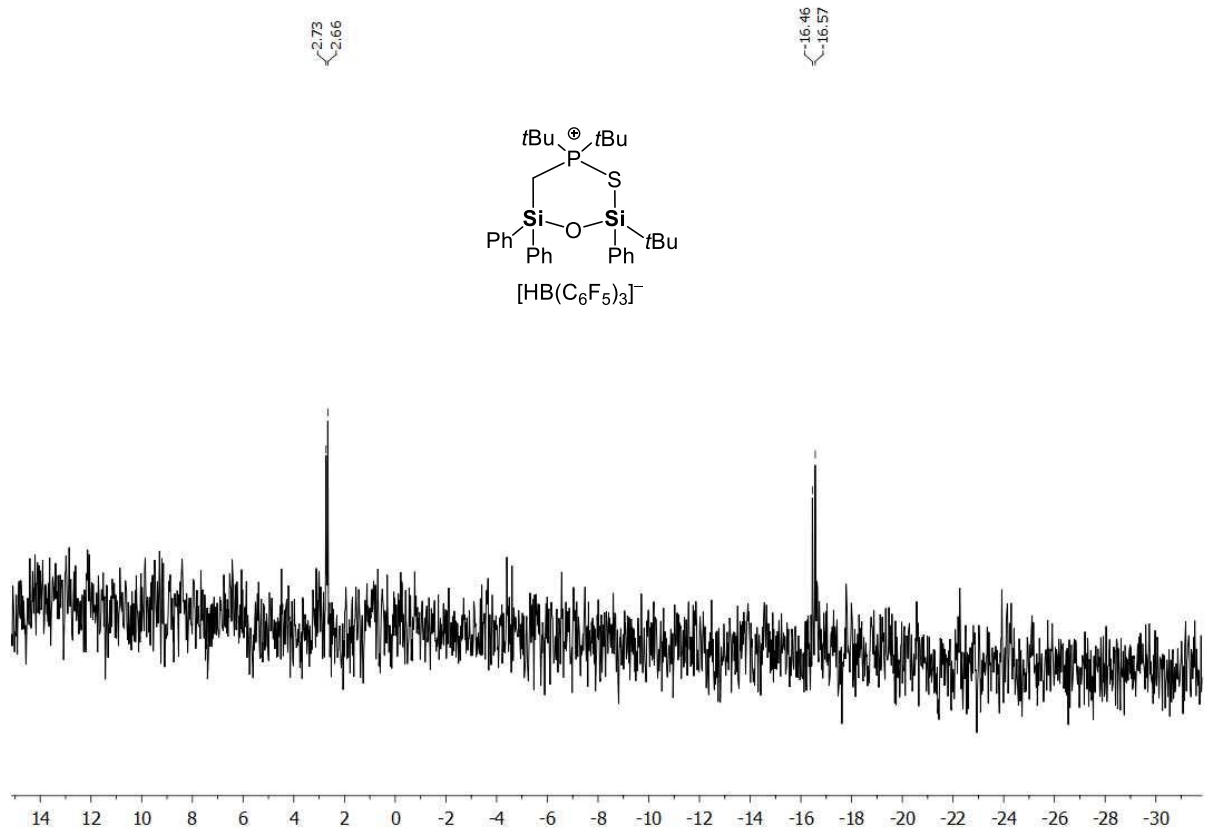


Figure S24. $^{29}Si\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **7**[$HB(C_6F_5)_3$].

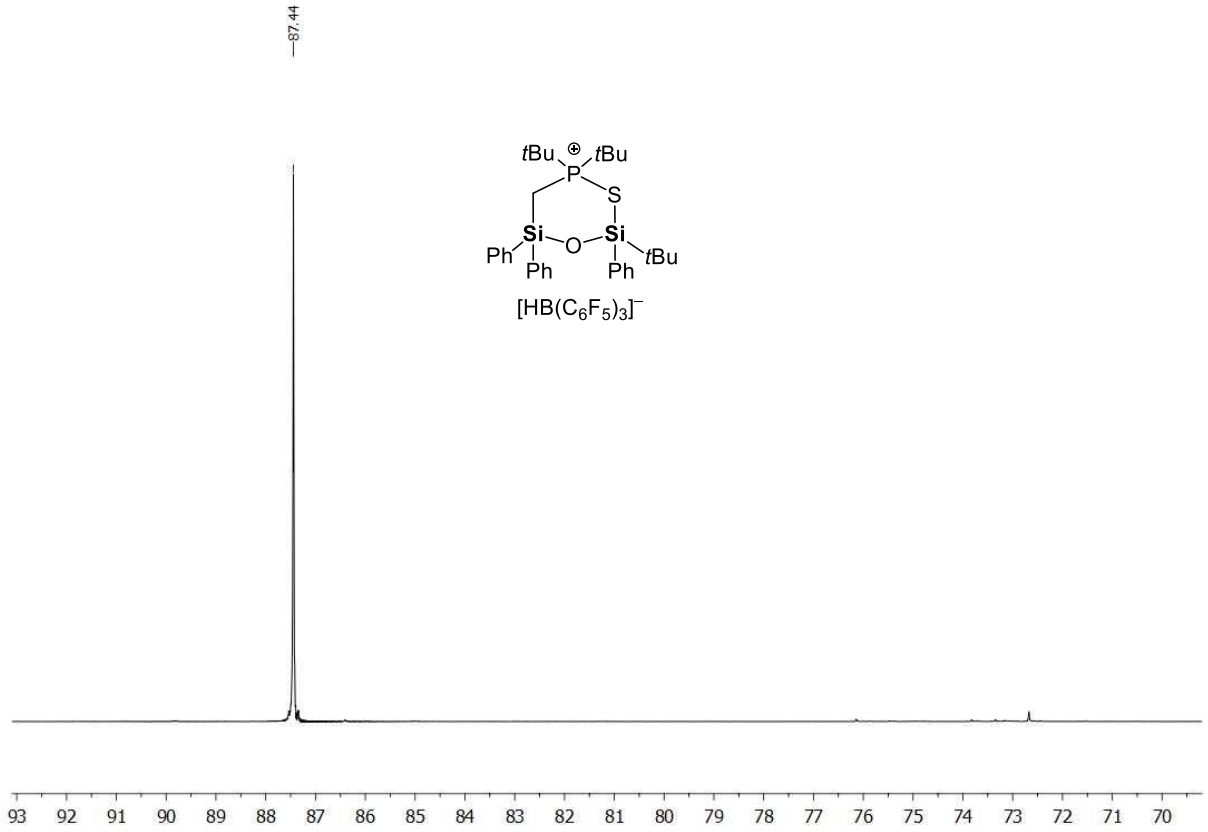


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **7**[$HB(C_6F_5)_3$].

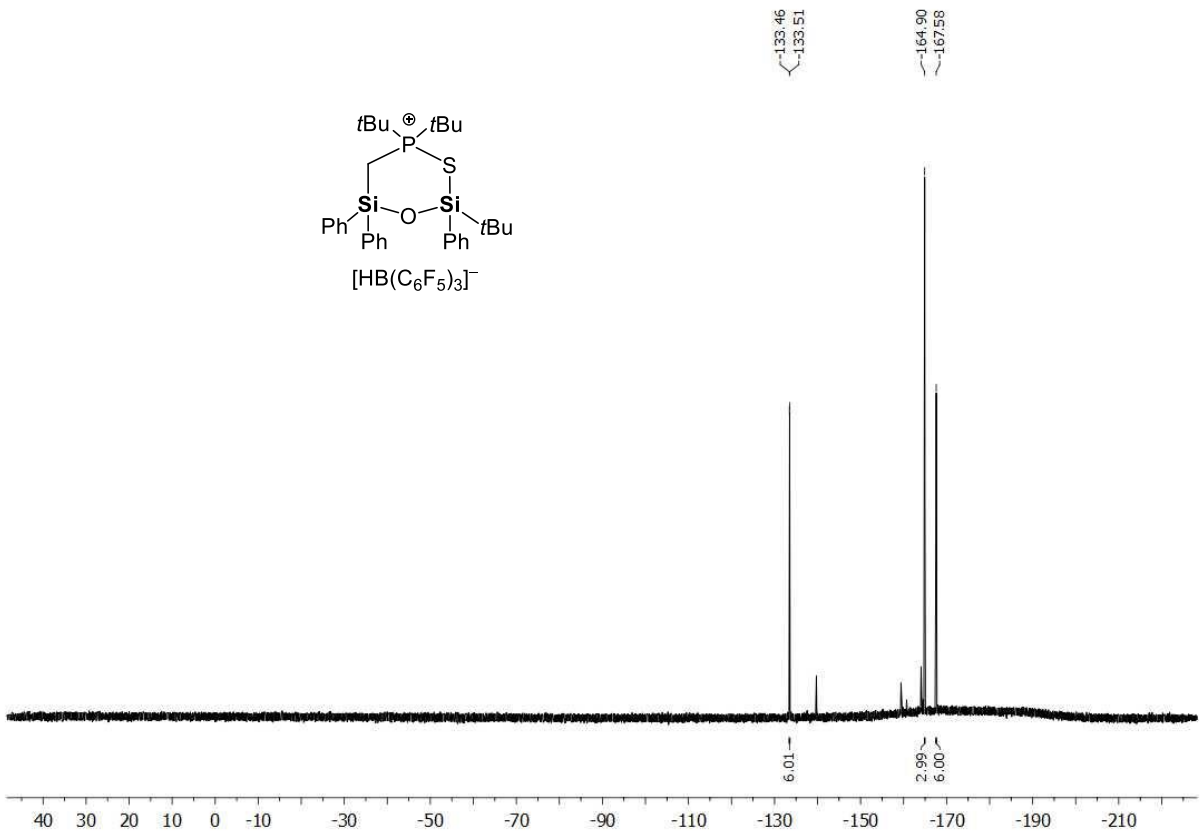


Figure S26. $^{19}F\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **7**[$HB(C_6F_5)_3$].

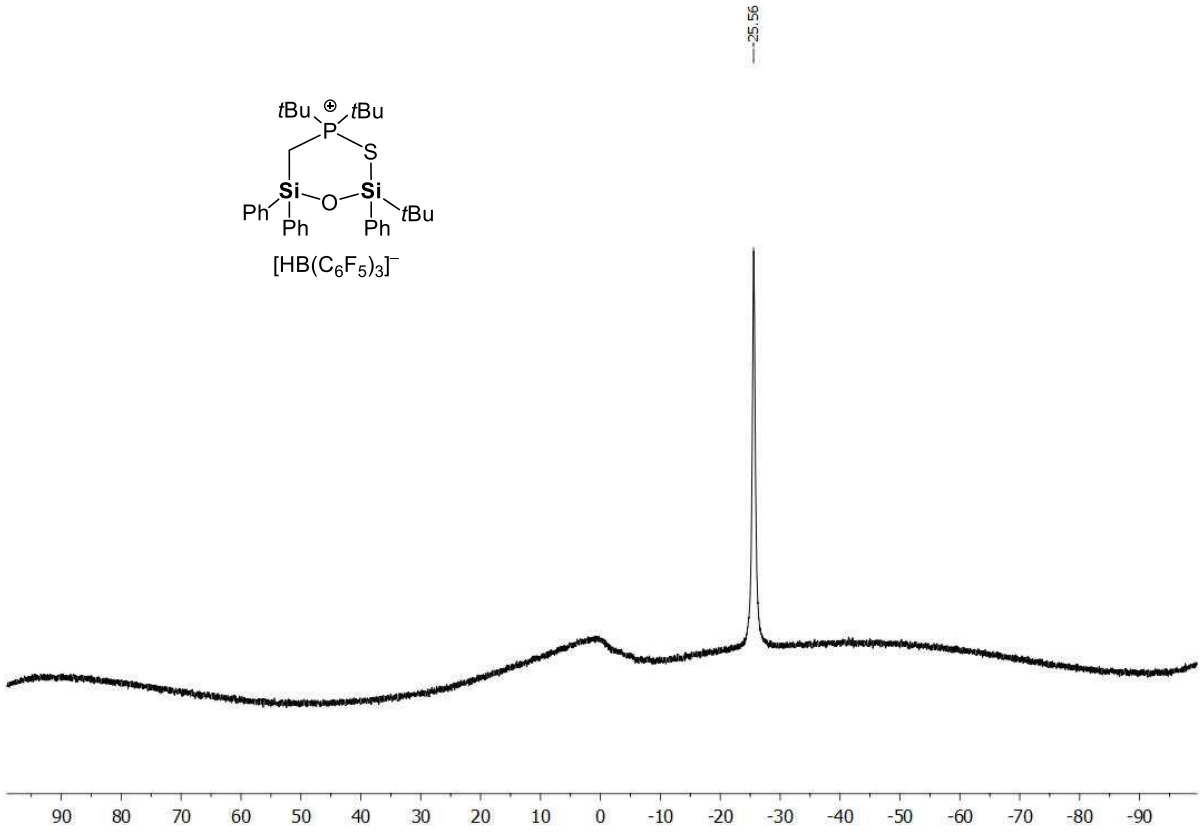
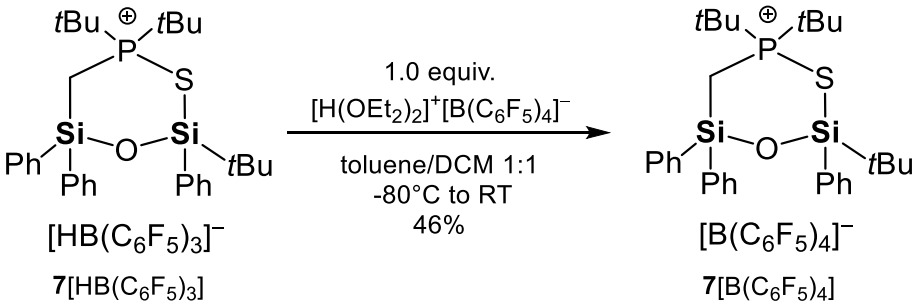


Figure S27. $^{11}B\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **7**[$HB(C_6F_5)_3$].

2.9. Synthesis of [(*t*Bu)$_2$P(S)CH$_2$SiPh$_2$OSiPh*t*Bu][B(C$_6$F$_5$)$_4$] {**7**[B(C$_6$F$_5$)$_4$]}



Compound **7**[HB(C$_6$F$_5$)$_3$] (100 mg, 0.094 mmol, 1.0 equiv.) was dissolved in toluene (5 ml) and the solution was cooled down to -80°C. [H(OEt$_2$)$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^–$ (77.8 mg, 0.094 mmol, 1.0 equiv.) was added dropwise as a DCM solution (~5 ml). The solution was stirred without further cooling for 3 h during which gas evolution was observed. An aliquot was dried directly in a Young-type NMR tube and the foamy solid was dissolved in CD_2Cl_2. Multinuclear NMR showed full conversion and complete selectivity towards the desired product. The solvent was concentrated down to ~1 ml and the compound was precipitated adding pentane (~10 ml). The upper liquid phase was removed using a PTFE cannula and the cloudy oil was further rinsed with pentane (2 ml). After removing all the volatiles in vacuum, the desired product **7**[B(C$_6$F$_5$)$_4$] was obtained as a foamy solid (52 mg, 0.043 mmol, 46%). Crystals suitable for X-ray diffraction analysis were obtained by vapour diffusion of pentane into a toluene solution of compound **7**[B(C$_6$F$_5$)$_4$].

^{1}H NMR (400.30 MHz, CD_2Cl_2, 298 K): δ =1.05 [s, 9H, SiC(C*H*$_3$)$_3$], 1.20 [d, $^3J_{P\text{-}H}$= 18.3 Hz, 9H, PC(C*H*$_3$)$_3$], 1.45 [d, $^3J_{P\text{-}H}$= 17.8 Hz, 9H, PC(C*H*$_3$)$_3$], 2.02 [ddd(ABX), J_1= 12.9 Hz, J_2= 14.8 Hz, J_3= 58,9 Hz, 2H, SiC*H*$_2$P], 7.41–7.49 [m, 6H, *H*$_{Ph}$], 7.51–7.62 [m, 5H, *H*$_{Ph}$], 7.64–7.68 [m, 4H, *H*$_{Ph}$]. **^{11}B{^{1}H} NMR** (128.43 MHz, CD_2Cl_2, 298 K): δ = -16.9 [s]. **^{13}C{^{1}H} NMR** (100.66 MHz, CD_2Cl_2, 298 K): δ = 0.8 [d, $^1J_{C\text{-}P}$= 24.5 Hz, Si*C*H$_2$P], 23.1 [s, Si*C*(CH$_3$)$_3$], 24.9 [s, SiC(*C*H$_3$)$_3$], 27.1 [dd, $^2J_{C\text{-}P}$= 0.8 Hz, $^2J_{C\text{-}P}$= 5.5 Hz, PC(*C*H$_3$)$_3$], 41.1 [dd, $^1J_{C\text{-}P}$= 30.3 Hz, $^1J_{C\text{-}P}$= 32.2 Hz, P*C*(CH$_3$)$_3$], 128.6 [s, C$_{Ph}$], 129.0 [s, C$_{Ph}$], 129.2 [s, C$_{Ph}$], 129.4 [s, C$_{Ph}$], 132.2 [s, C$_{Ph}$], 132.5 [t, *J*= 9.8 Hz C$_{Ph}$], 134.3 [d, $J_{C\text{-}P}$= 4.8 Hz, C$_{Ph}$], 134.8 [s, C$_{Ph}$], 135.5 [bs, C$_{Ar\text{-}borate}$], 137.4 [bs, C$_{Ar\text{-}borate}$], 137.9 [bs, C$_{Ar\text{-}borate}$], 147.4 [bs, C$_{Ar\text{-}borate}$], 149.8 [bs, C$_{Ar\text{-}borate}$]. **^{19}F{^{1}H} NMR** (376.66 MHz, CD_2Cl_2, 298 K): δ = -167.4 [t, $^3J_{F\text{-}F}$= 17.9 Hz, 8F], -163.6 [t, $^3J_{F\text{-}F}$= 19.4 Hz, 4F], -133.0 [bs, 8F]. **^{29}Si{^{1}H} NMR** (79.49 MHz, CD_2Cl_2, 298 K): δ = -16.5 [d, $^2J_{Si\text{-}P}$= 8.8 Hz PC*Si*OSiS], -2.7 [d, $^2J_{Si\text{-}P}$= 6.4 Hz PCSiO*Si*S]. **^{31}P{^{1}H} NMR** (162.04 MHz, CD_2Cl_2, 298 K): δ = 87.2 [s]. **HR-MS (FD+)**, calculated. m/z for $C_{31}H_{44}OPSSi_2^+$ [M]$^+$: 551.2384; found: 551.2407.

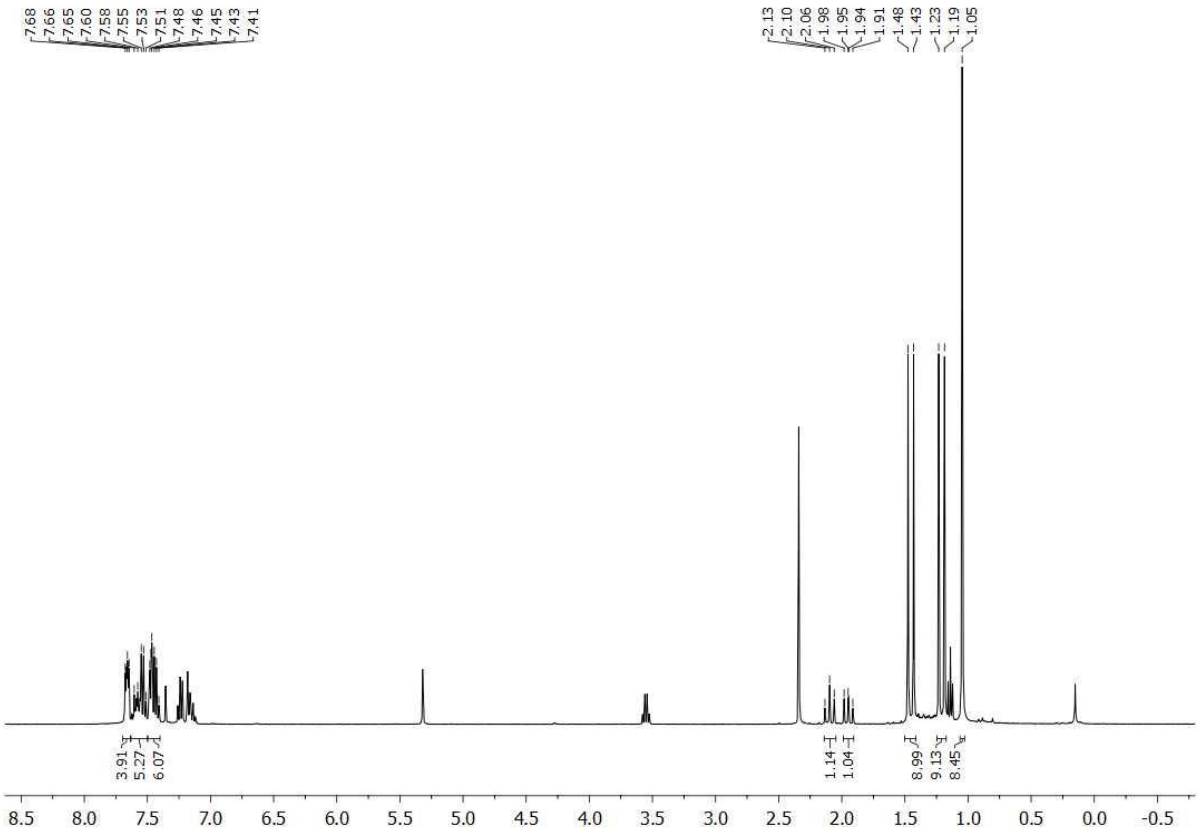


Figure S28. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of the crude reaction mixture.

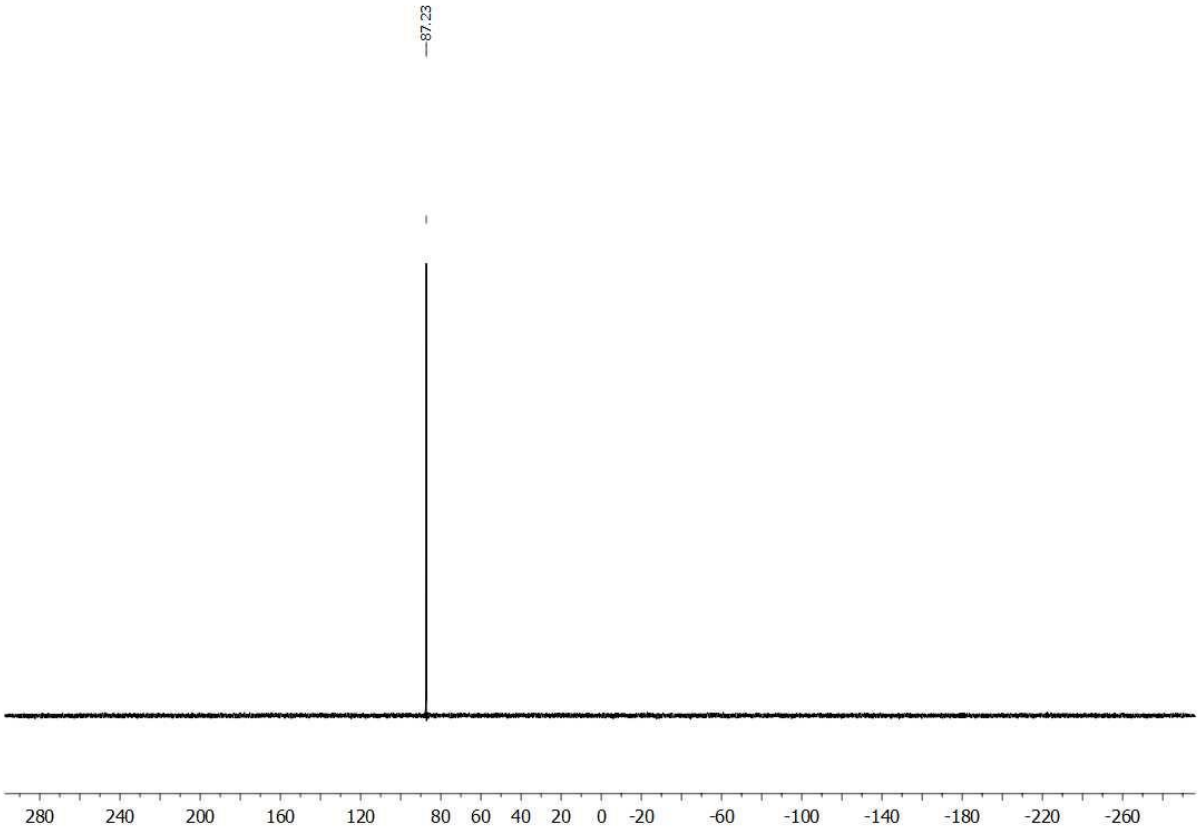


Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of the crude reaction mixture.

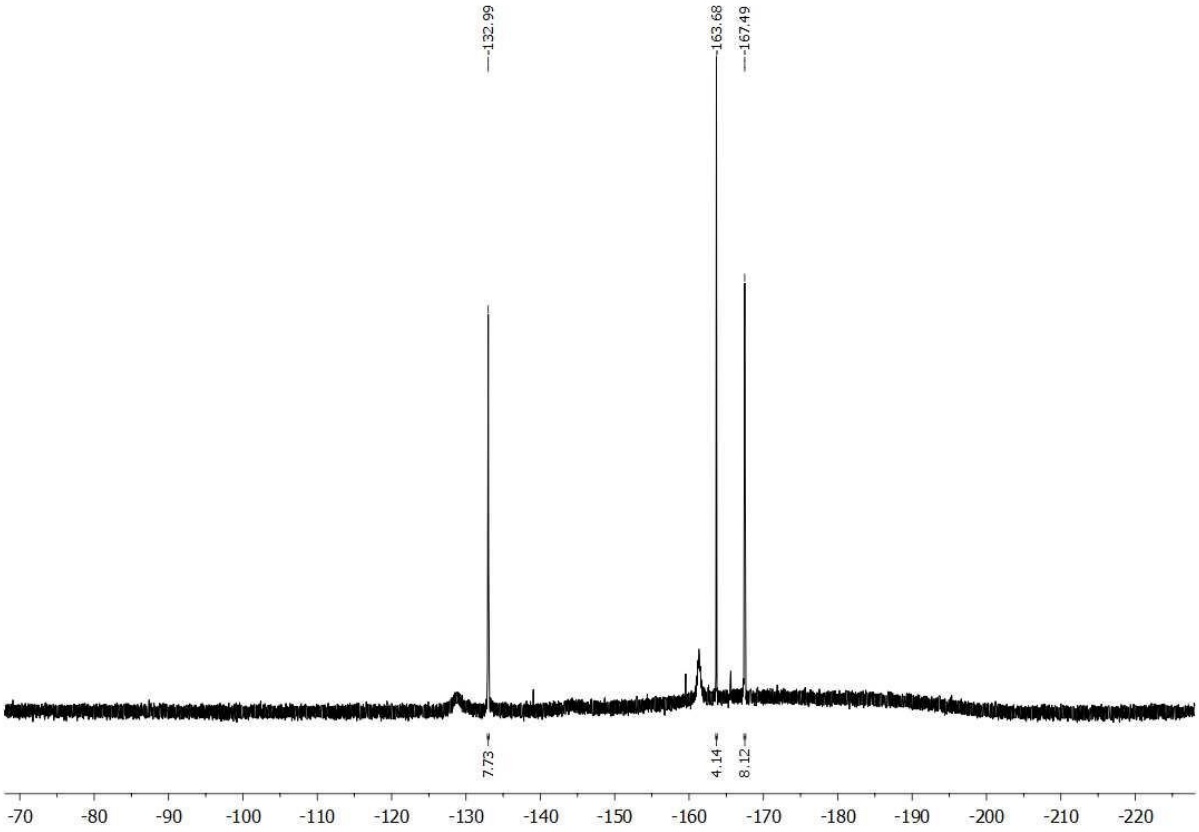


Figure S30. $^{19}F\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of the crude reaction mixture.

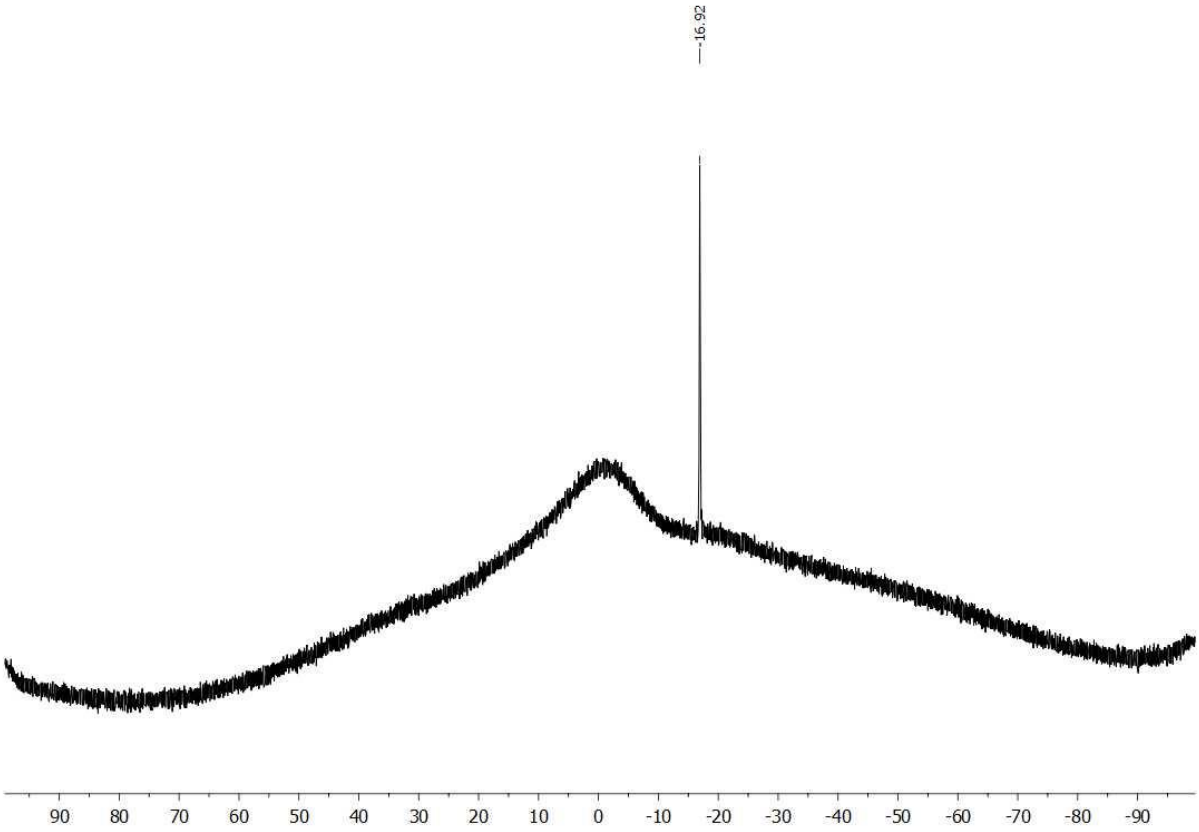


Figure S31. $^{11}B\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of the crude reaction mixture.

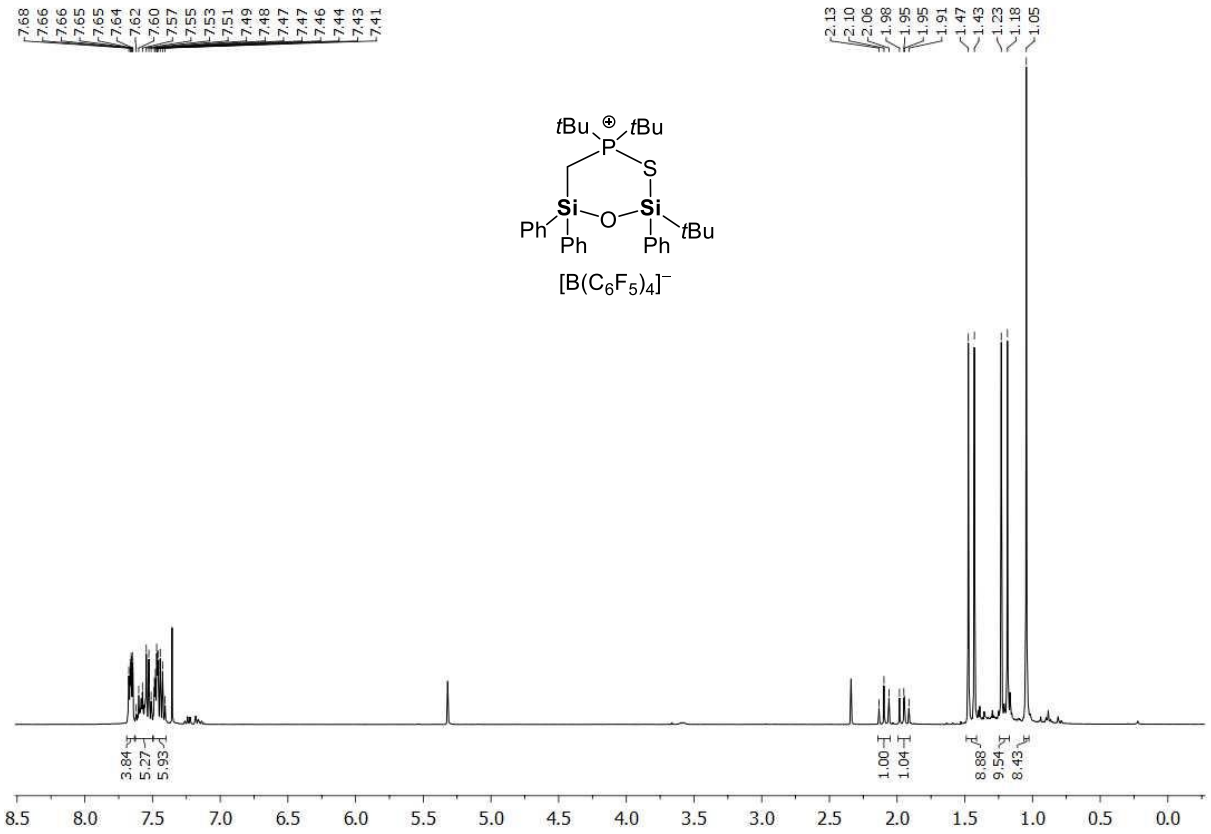


Figure S32. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of isolated compound **7**[$B(C_6F_5)_4$].

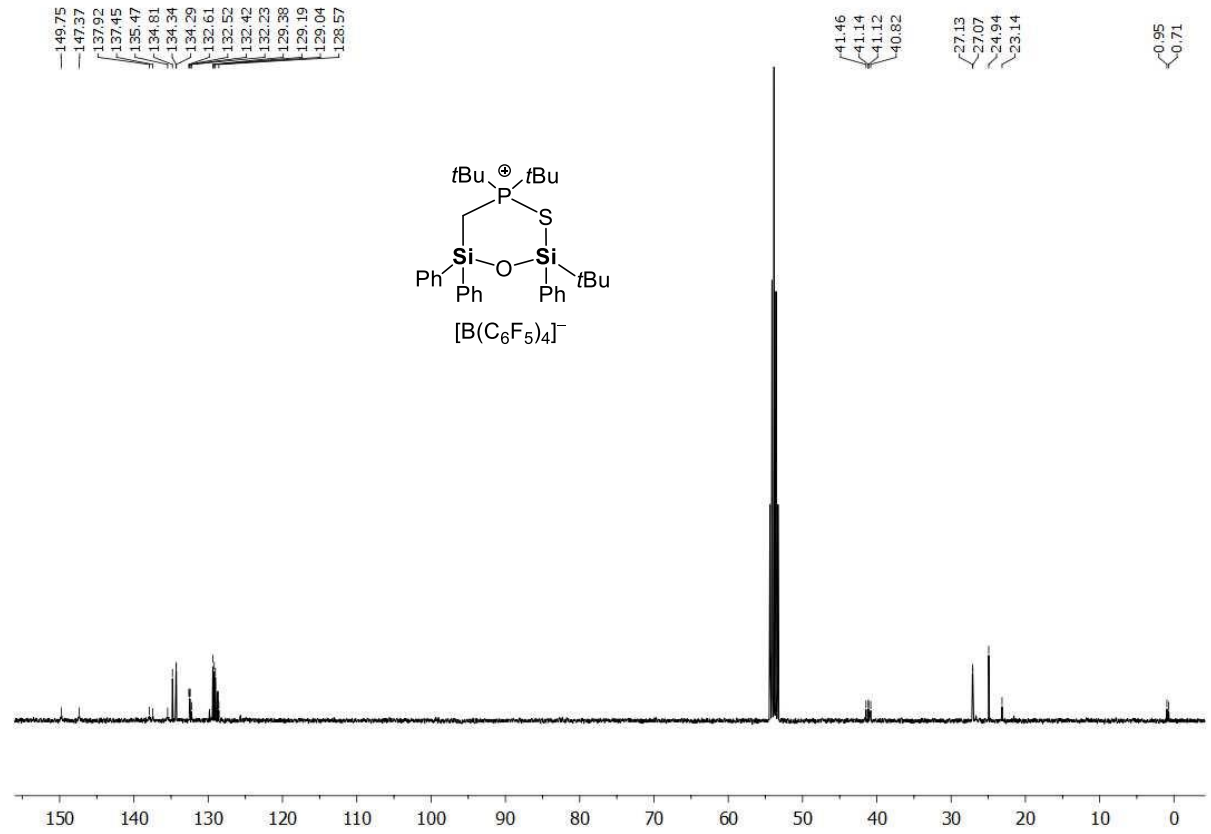


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of isolated compound **7**[$B(C_6F_5)_4$].

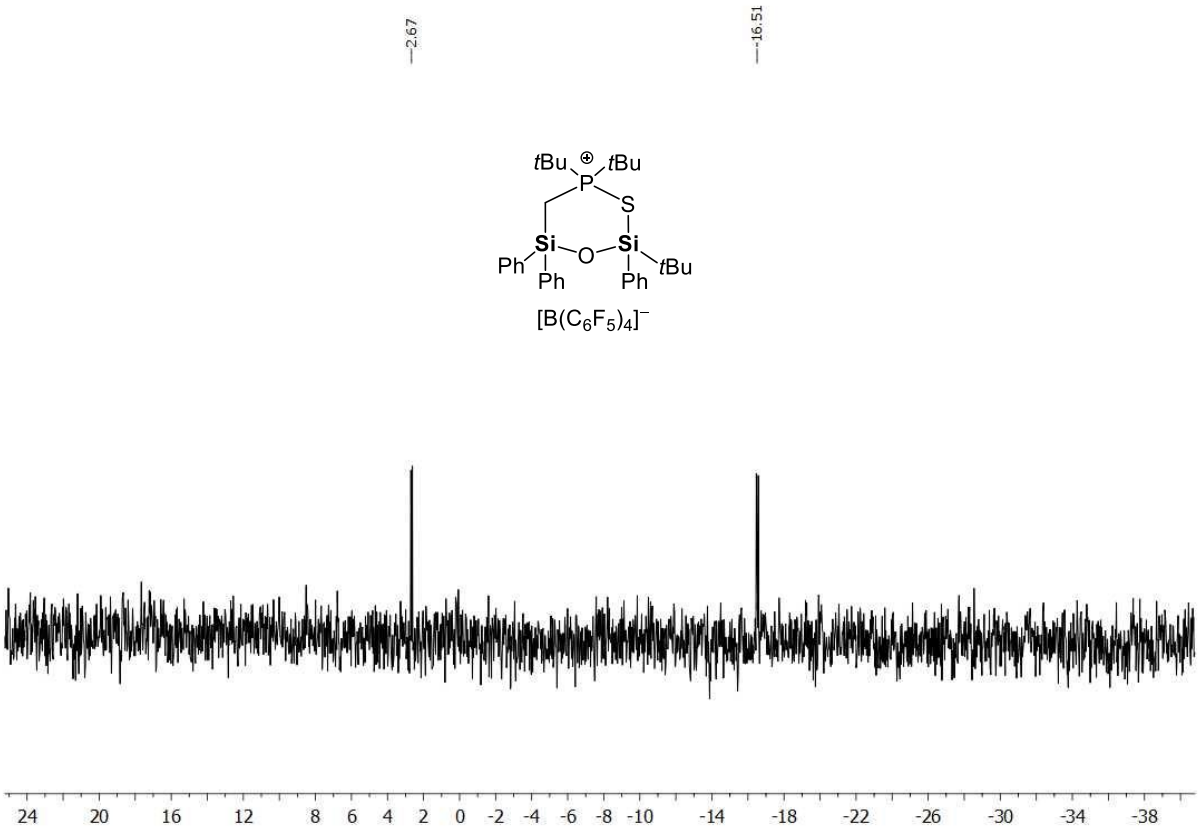


Figure S34. $^{29}Si\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of isolated compound **7**$[B(C_6F_5)_4]$.

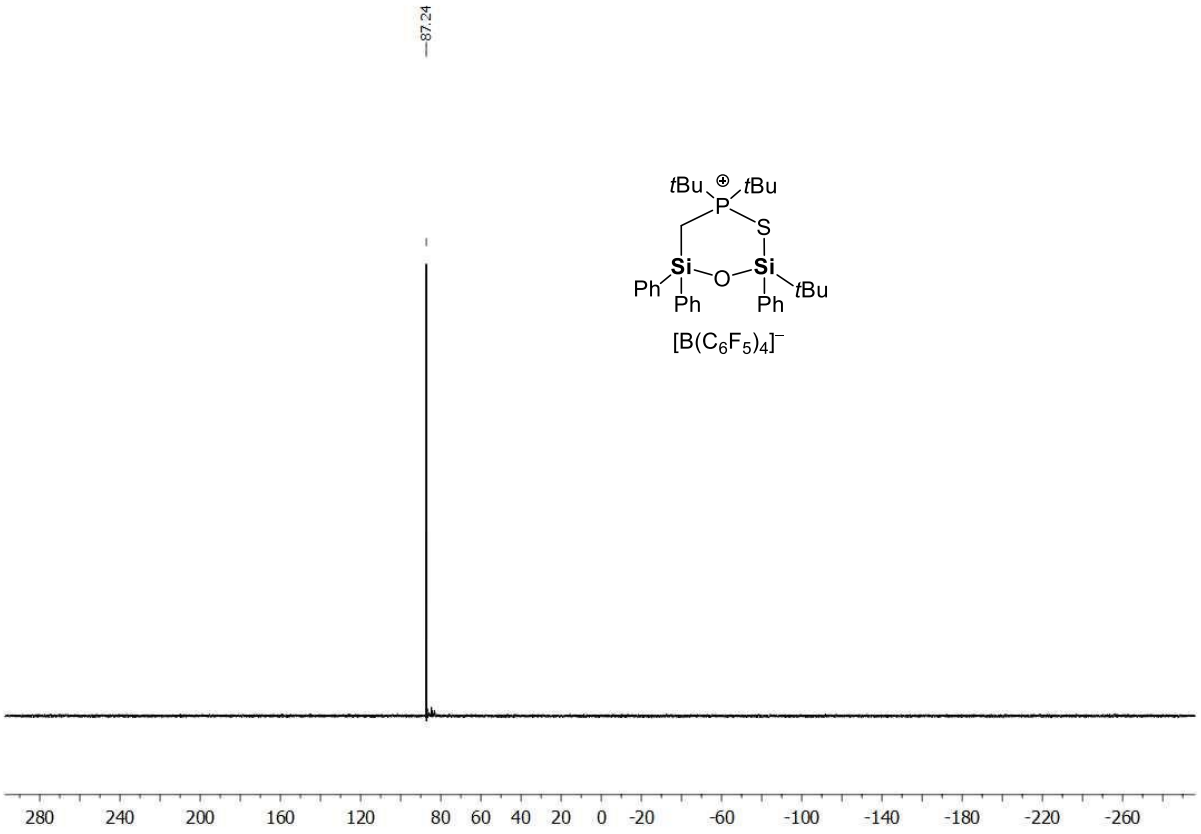


Figure S35. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of isolated compound **7**$[B(C_6F_5)_4]$.

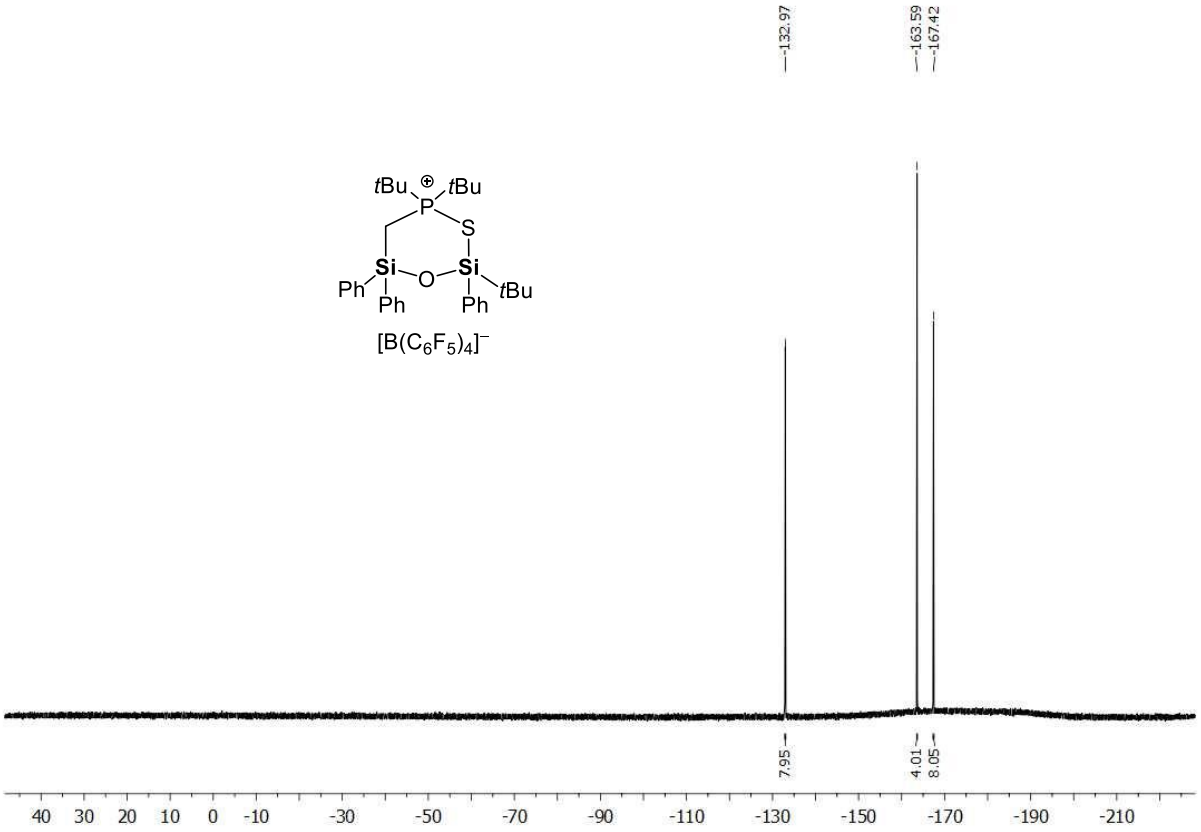


Figure S36. $^{19}F\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of isolated compound **7**$[B(C_6F_5)_4]$.

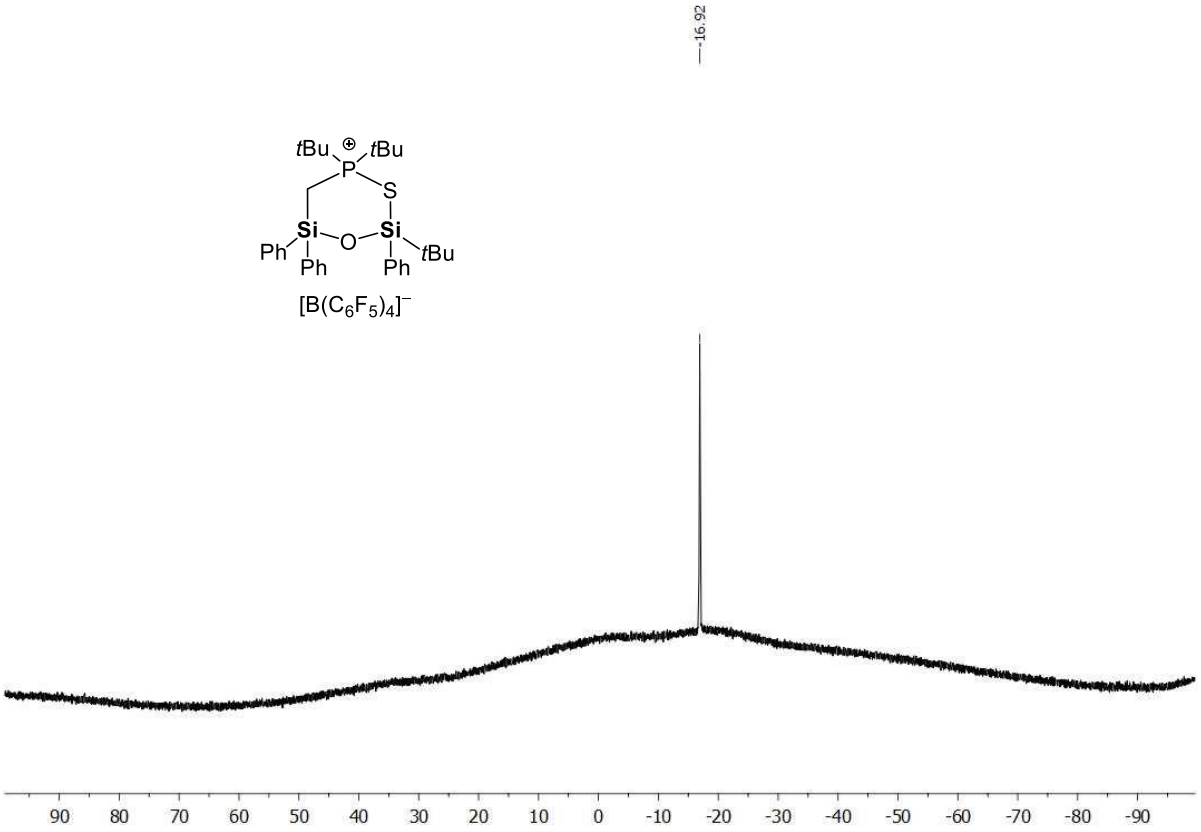
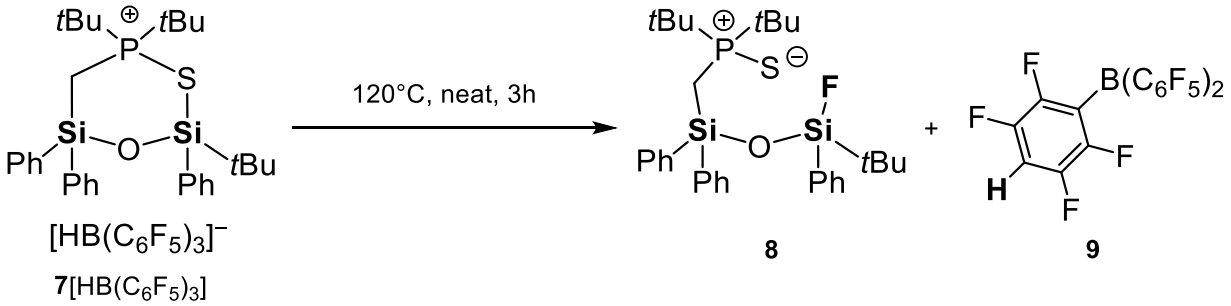


Figure S37. $^{11}B\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of isolated compound **7**$[B(C_6F_5)_4]$.

2.10. Synthesis of (*t*Bu)$_2$P(S)CH$_2$SiPh$_2$OSi(F)Ph*t*Bu (8) and (C$_6$F$_5$)$_2$(C$_6$F$_4$H)B(OH$_2$) (9)



Compound **7**[HB(C$_6$F$_5$)$_3$] (200 mg, 0.188 mmol) was loaded in a Schlenk flask suitable for high pressure reactions (50 ml volume) and sealed under nitrogen atmosphere. The flask was heated up to 120°C for 3 h using an oil bath during which the solid melted while bubbling and turning into a yellow liquid. During the process, thin needles crystallized on the upper part of the flask in a web-like motif (see Figure S38). After 3 h, the vessel was cooled down to room temperature and two thin PTFE cannulas were carefully inserted all the way through the upper layer of the flask, which was covered with the delicate white crystals, to reach the lower half of the flask. Following, DCM was used to extract the yellow residue at the bottom of the flask. After three washings (~10 ml) of the lower part, the organic fractions were collected, dried, and the residue was distilled *via* Kugelrohr distillation (190-200°C oven temperature, 1.0 x 10^{-3} mbar) to yield fluorodisiloxane **8** as a pale-yellow oil (62 mg, 0.109 mmol, 56%). The crystalline compound on the upper part, free of the yellow residue, was extracted with DCM (3 x 5 ml), the extracts were collected and fully dried under vacuum yielding compound **9** as a white solid (86 mg, 0.132 mmol, 70%). Then, the solid was dissolved in the minimum amount of THF, a few drops of water were added and the mixture was stirred for 10 min. After removing all volatiles, the solid residue was suspended in pentane and brought into solution with a few drops of THF. The mixture was stirred over 30 min, then the reaction vessel was sealed and stored overnight at -30°C affording a few co-crystals of **9**·H$_2$O·(THF)$_2$/BCF (1:1) suitable for single-crystal X-ray diffraction analysis (6 mg, 9.14 x 10^{-3} mmol, 4%).

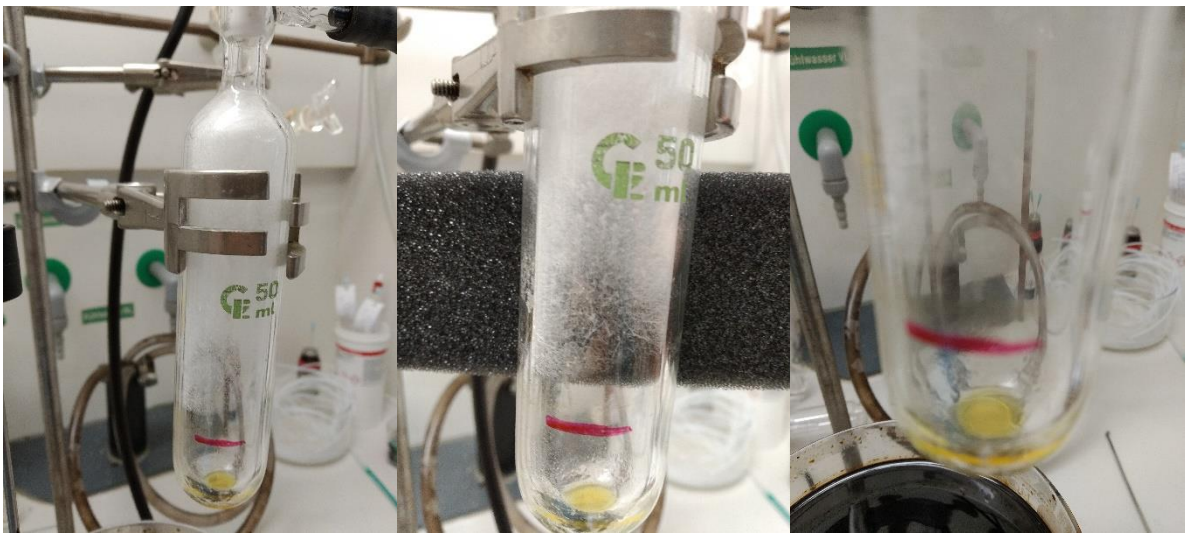


Figure S38. Spontaneous separation of the two product species **8** and **9** under the reaction conditions: Hydrodefluorinated borane **9** (white crystalline solid on the upper part of the vessel) and fluorodisiloxane **8** (yellow oily residue on the bottom part of the vessel).

Characterization of 8:

^{1}H NMR (400.30 MHz, CD_2Cl_2, 298 K): δ =0.95 [d, $^{4}J_{H\text{-}F}$= 0.9 Hz 9H, SiC(CH_3)$_3$], 2.22 [d, $^{3}J_{P\text{-}H}$= 12.2 Hz, 9H, PC(CH_3)$_3$], 1.14 [d, $^{3}J_{P\text{-}H}$= 12.2 Hz, 9H, PC(CH_3)$_3$], 1.87 [dd, J_1= 4.2 Hz, J_2= 12.8 Hz, 2H, SiCH_2P], 7.31–7.34 [m, 6H, H_{Ph}], 7.38–7.42 [m, 3H, H_{Ph}], 7.58 [m, 2H, H_{Ph}], 7.77–7.80 [m, 4H, H_{Ph}]. **^{13}C{^{1}H} NMR** (100.66 MHz, CD_2Cl_2, 298 K): δ = 13.4 [d, $^{1}J_{C\text{-}P}$= 37.8 Hz, SiCH$_2$P], 18.6 [d, $^{2}J_{C\text{-}F}$= 16.5 Hz, SiC(CH$_3$)$_3$], 25.6 [s, SiC(CH$_3$)$_3$], 27.6 [m, PC(CH$_3$)$_3$], 38.6 [d, $^{1}J_{C\text{-}P}$= 43.2 Hz PC(CH$_3$)$_3$], 127.7 [d, $^{4}J_{C\text{-}F}$= 3.7 Hz, C$_{Ph}$], 128.17 [s, C$_{Ph}$], 130.4 [d, $^{5}J_{C\text{-}F}$= 0.9 Hz, C$_{Ph}$], 130.9 [s, C$_{Ph}$], 131.8 [d, $^{2}J_{C\text{-}F}$= 19.5 Hz, C$_{Ph}$], 134.8 [d, $^{5}J_{C\text{-}F}$= 2.6 Hz, C$_{Ph}$], 135.6 [d, $^{4}J_{C\text{-}F}$= 3.4 Hz, C$_{Ph}$], 136.0 [d, $^{3}J_{C\text{-}F}$= 5.6 Hz, C$_{Ph}$]. **^{19}F{^{1}H} NMR** (376.66 MHz, CD_2Cl_2, 298 K): δ = -151.0 [s with satellites, $^{1}J_{F\text{-}Si}$= 298.5 Hz]. **^{29}Si{^{1}H} NMR** (79.49 MHz, CD_2Cl_2, 298 K): δ = -25.2 [d, $^{2}J_{Si\text{-}F}$= 298.4 Hz, PCSiOSiF], -14.9 [s, PCSiOSiF]. **^{31}P{^{1}H} NMR** (162.04 MHz, CD_2Cl_2, 298 K): δ = 73.4 [s]. **CHN Analysis** $C_{31}H_{44}FOPSSi_2$: calculated: C 65.22; H 7.77; found C 64.42, H 7.45. **HR-MS (ESI+)**, calculated. m/z for $C_{32}H_{44}FOPSSi_2^+$ $[M+H]^+$: 571.2451; found: 571.2469.

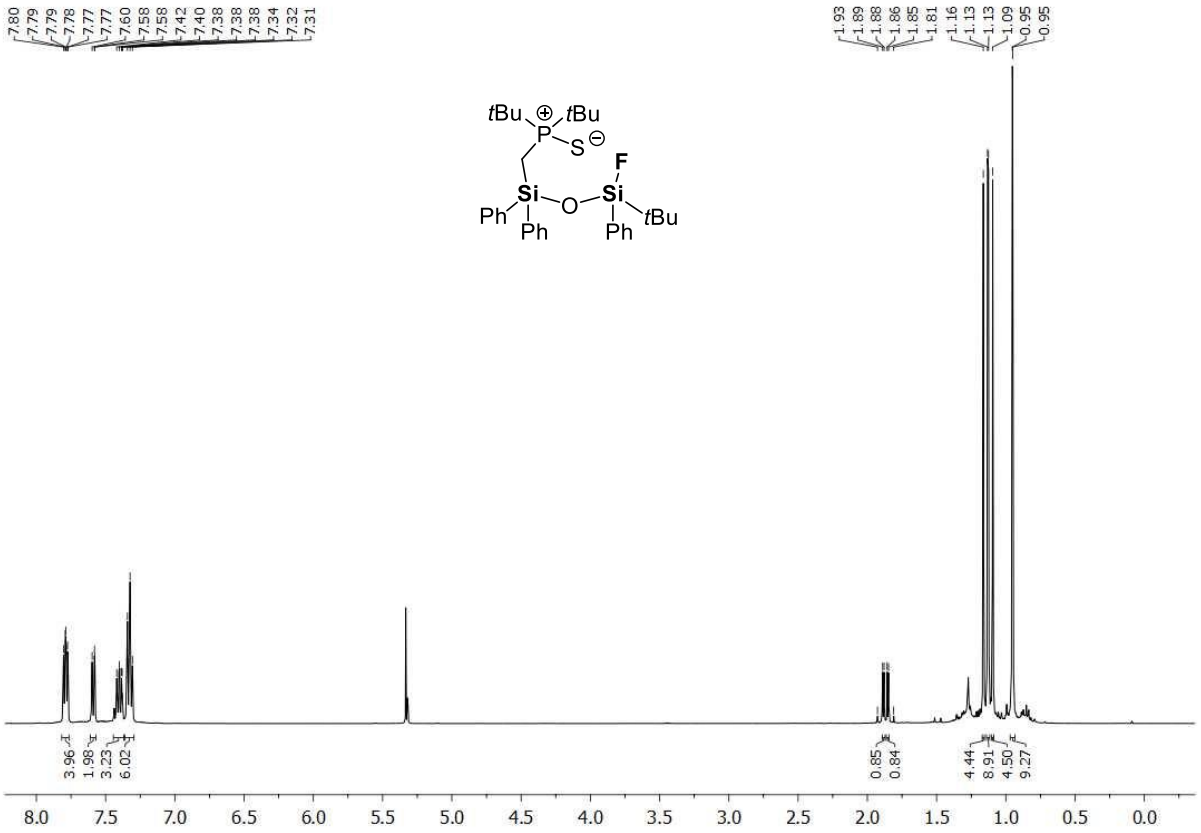


Figure S39. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of compound **8**.

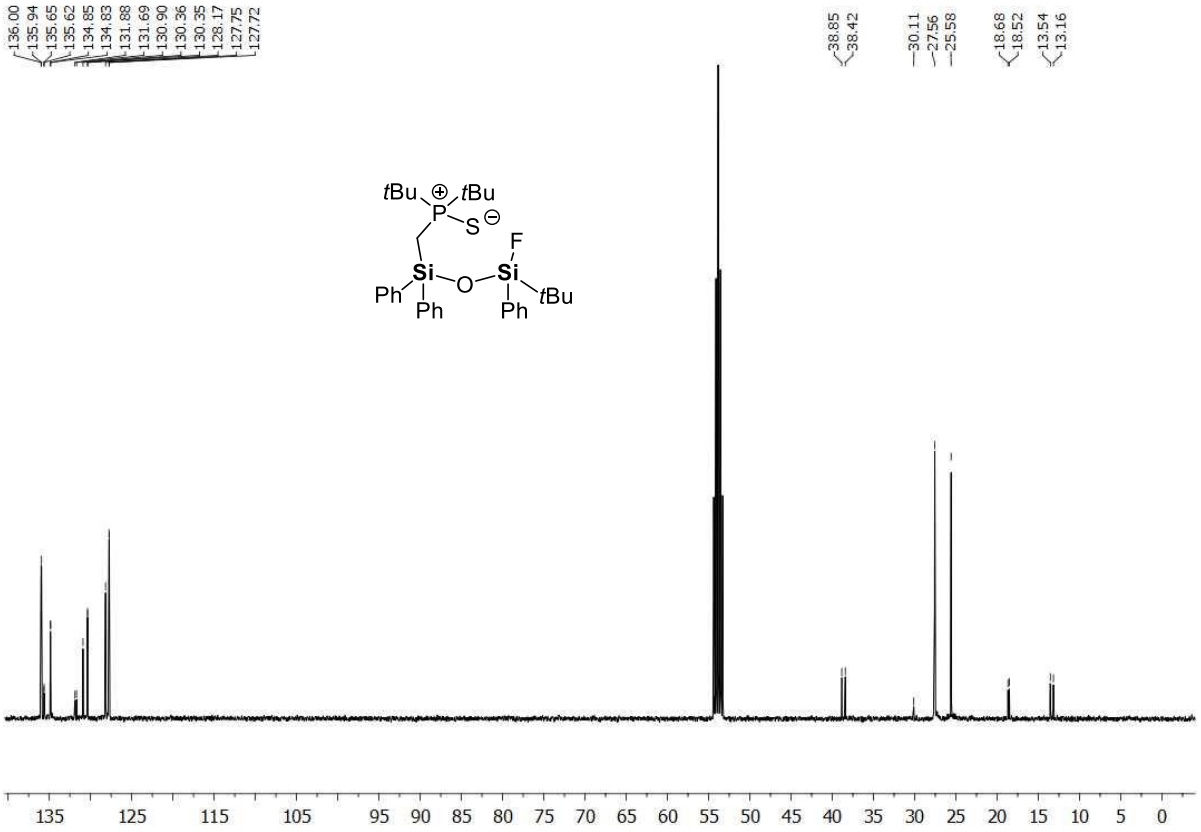


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **8**.

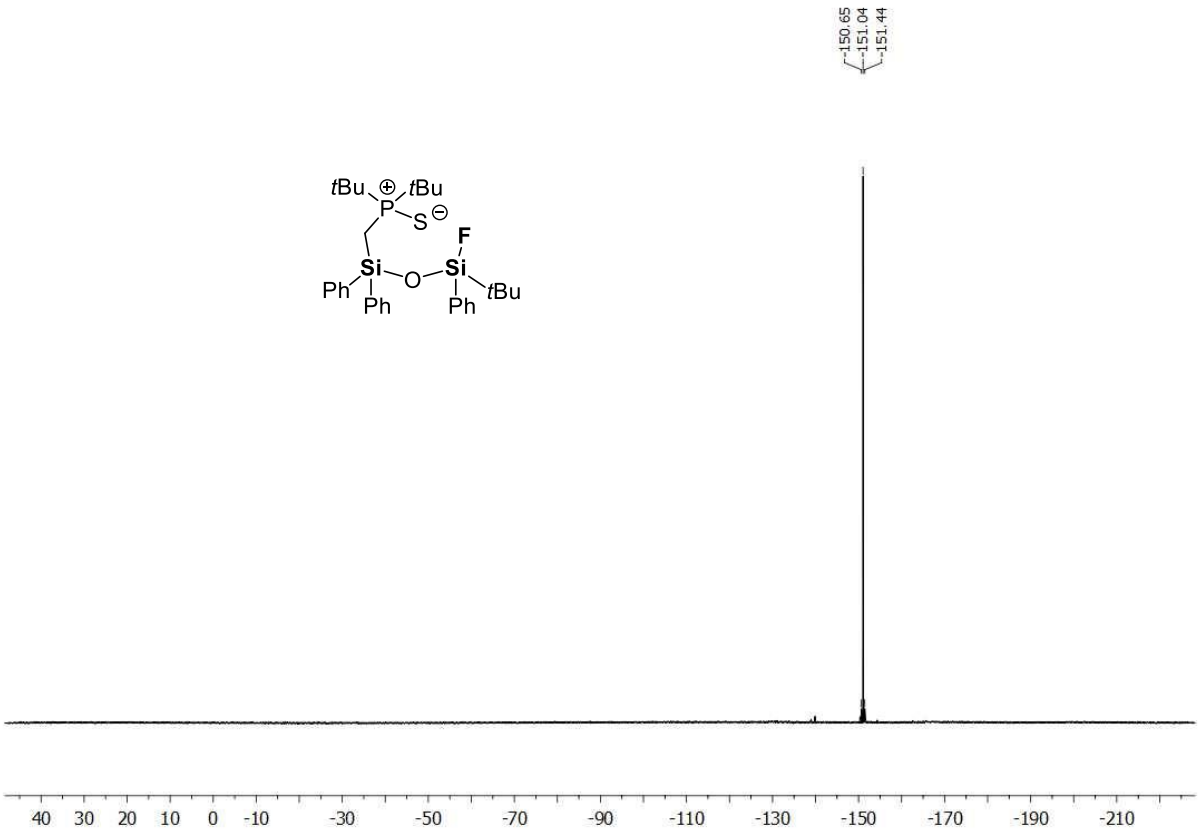


Figure S41. $^{19}F\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **8**.

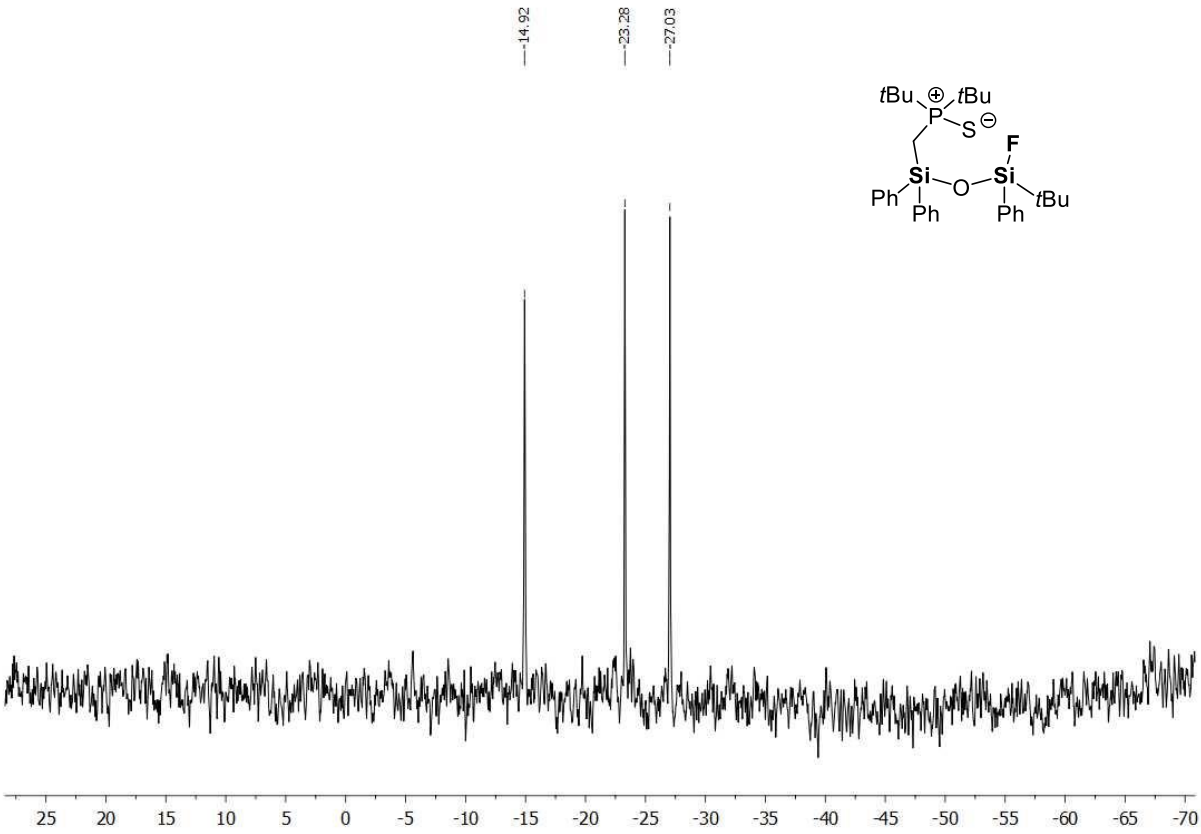


Figure S42. $^{29}Si\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **8**.

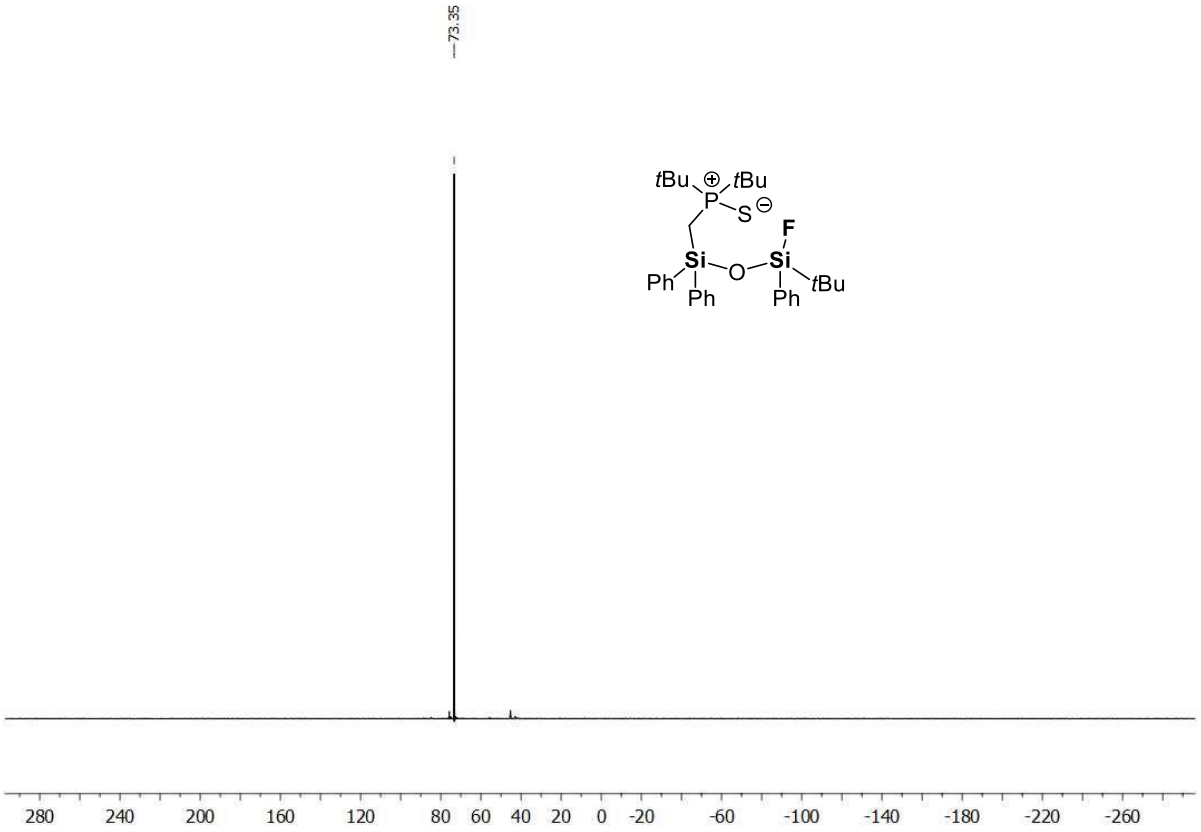


Figure S43. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **8**.

Characterization of 9·H_2O·$(THF)_2$:

^{1}H NMR (400.30 MHz, CD_2Cl_2, 298 K): δ =2.06 [s, 8H, OCH_2CH_2], 4.15 [s, 8H, OCH_2CH_2], 7.02 [m, 1H, $B(C_6F_4H)$], 10.24 [bs, 1H BOH_2]. **^{11}B{^{1}H} NMR** (128.43 MHz, CD_2Cl_2, 298 K): δ = -2.4 [bs]. **^{13}C{^{1}H} NMR** (100.66 MHz, CD_2Cl_2, 298 K): δ = 25.2 [s, OCH_2CH_2], 75.2 [s, OCH_2CH_2], 105.6 [bs, $B(C_5F_4CH)$], 137.6 [bd, $^1J_{C\text{-}F}$ = 237.7 Hz, $C_{Ar\text{-}borate}$], 139.6 [bs, $C_{Ar\text{-}borate}$], 143.6 [bd, $^1J_{C\text{-}F}$ = 290.8 Hz, $C_{Ar\text{-}borate}$], 148.2 [d, $^1J_{C\text{-}F}$= 250.0 Hz $C_{Ar\text{-}borate}$]. **^{19}F{^{1}H} NMR** (376.66 MHz, CD_2Cl_2, 298 K): δ = -164.5 [bm, 6F], -157.9 [bm, 1F], -157.7 [bm, 2F], -141.6 [bm, 1F], -135.1 [bm, 1F], -135.1 [bm, 6F]. **CHN Analysis** $C_{26}H_{19}BF_{14}O_3$: calculated: C 47.59; H 2.92; found C 47.19, H 2.79. **HR-MS (ESI-)**, calculated. m/z for $C_{18}HBF_{14}O$ [M, -H]$^-$: 510.9981; found: 510.9993.

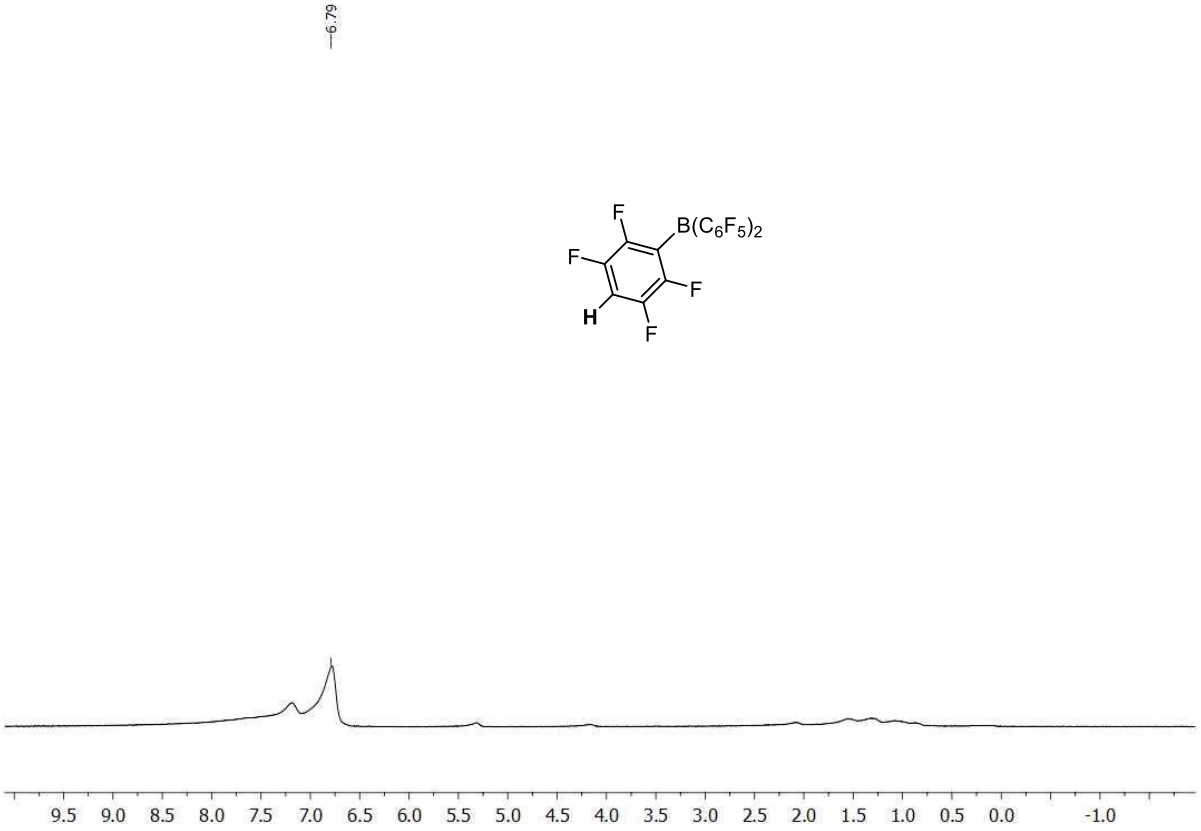


Figure S44. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of the isolated crystalline sublimate.

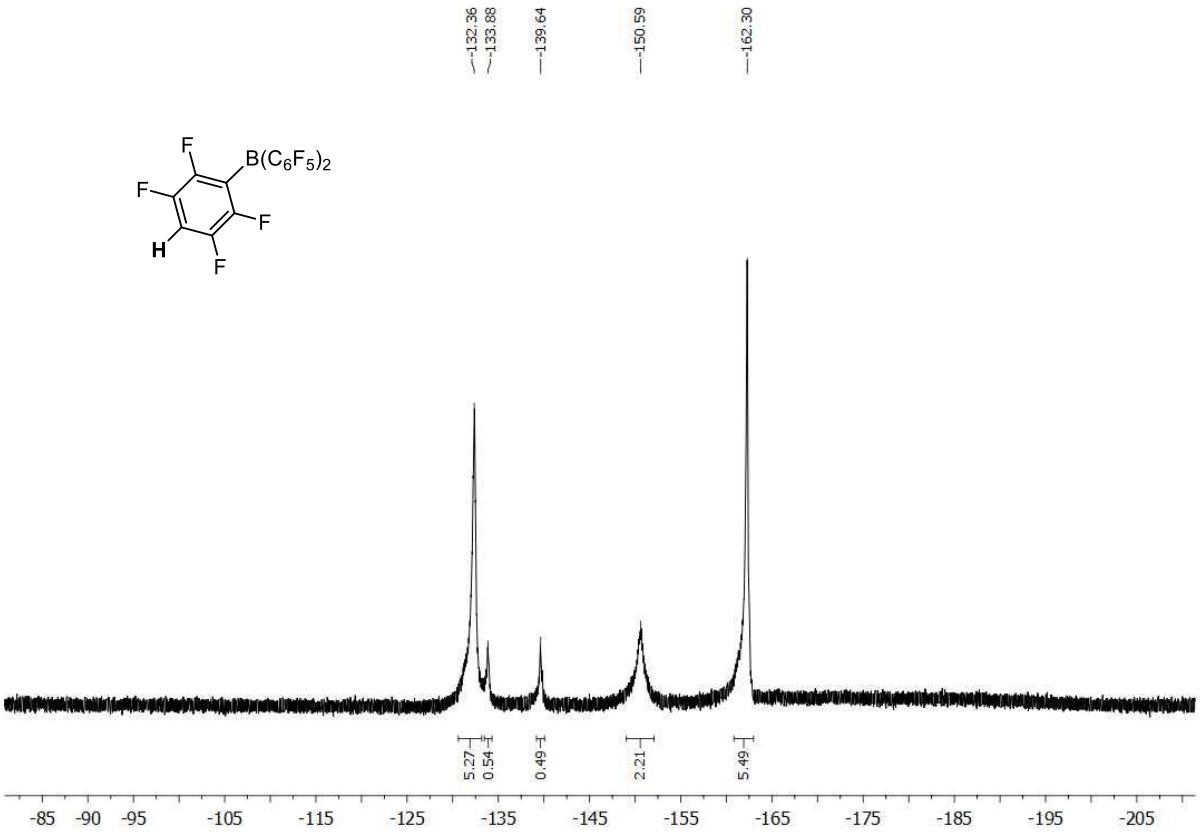


Figure S45. $^{19}F\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of the isolated crystalline sublimate.

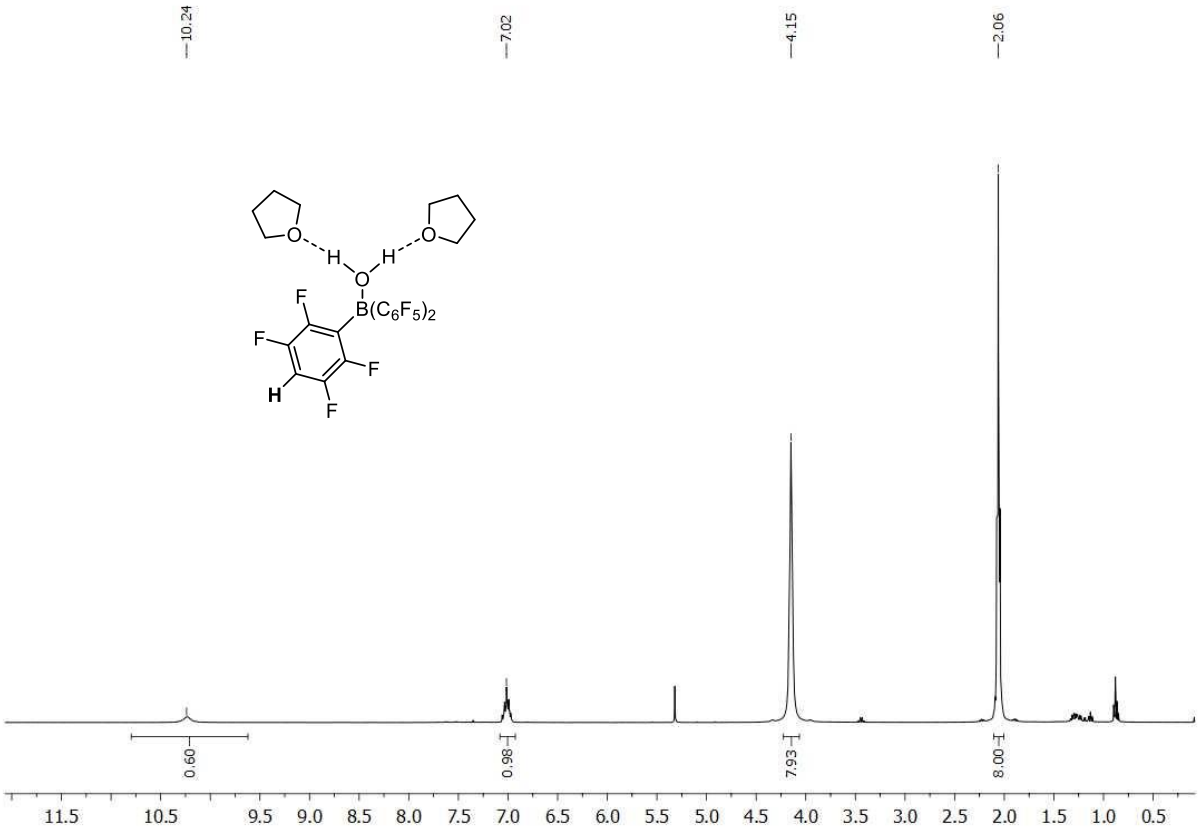


Figure S46. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of compound **9**·H_2O·$(THF)_2$.

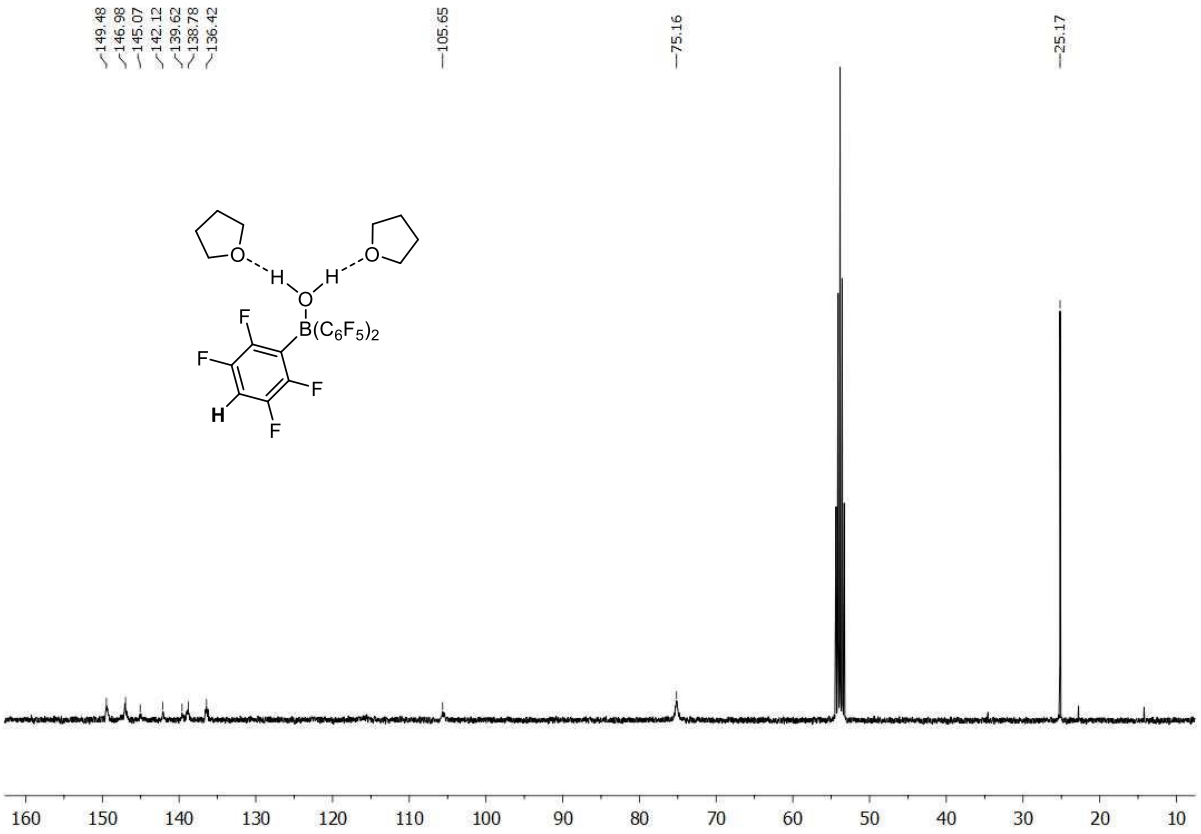


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **9**·H_2O·$(THF)_2$.

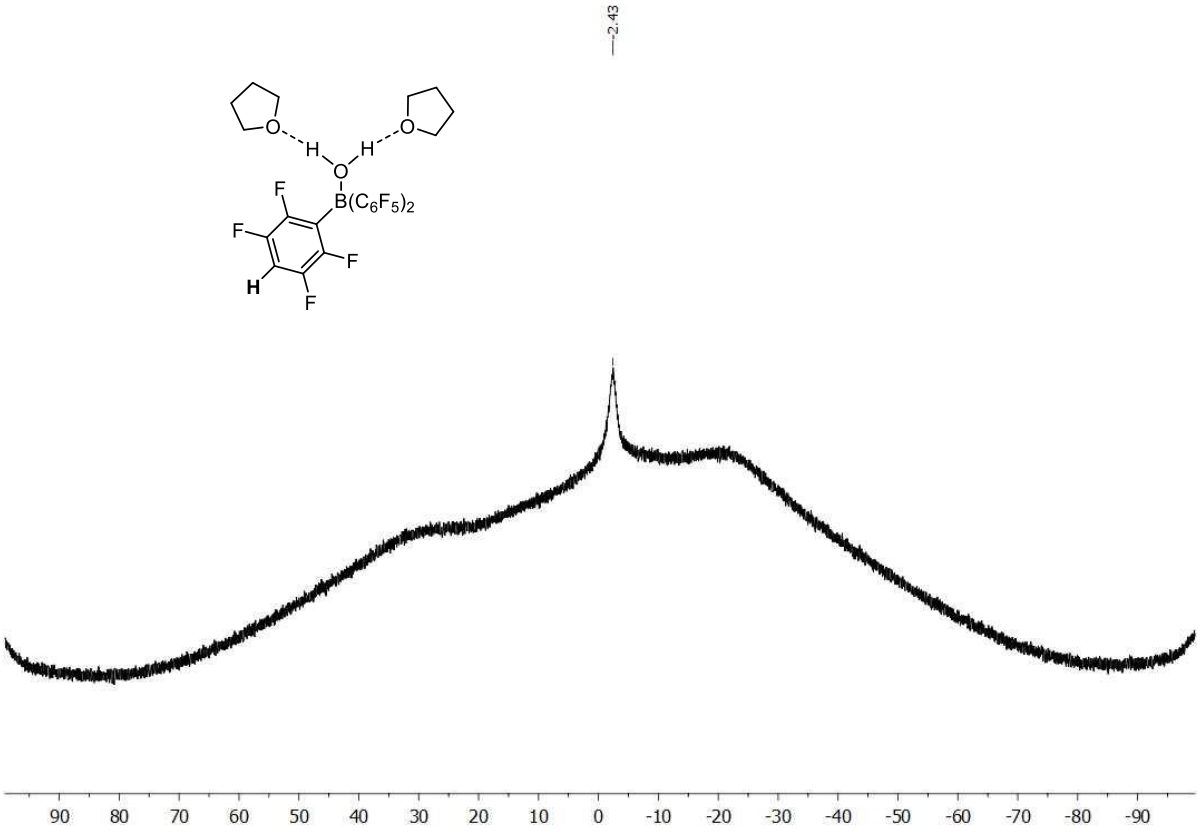


Figure S48. $^{11}B\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **9**·H_2O·$(THF)_2$.

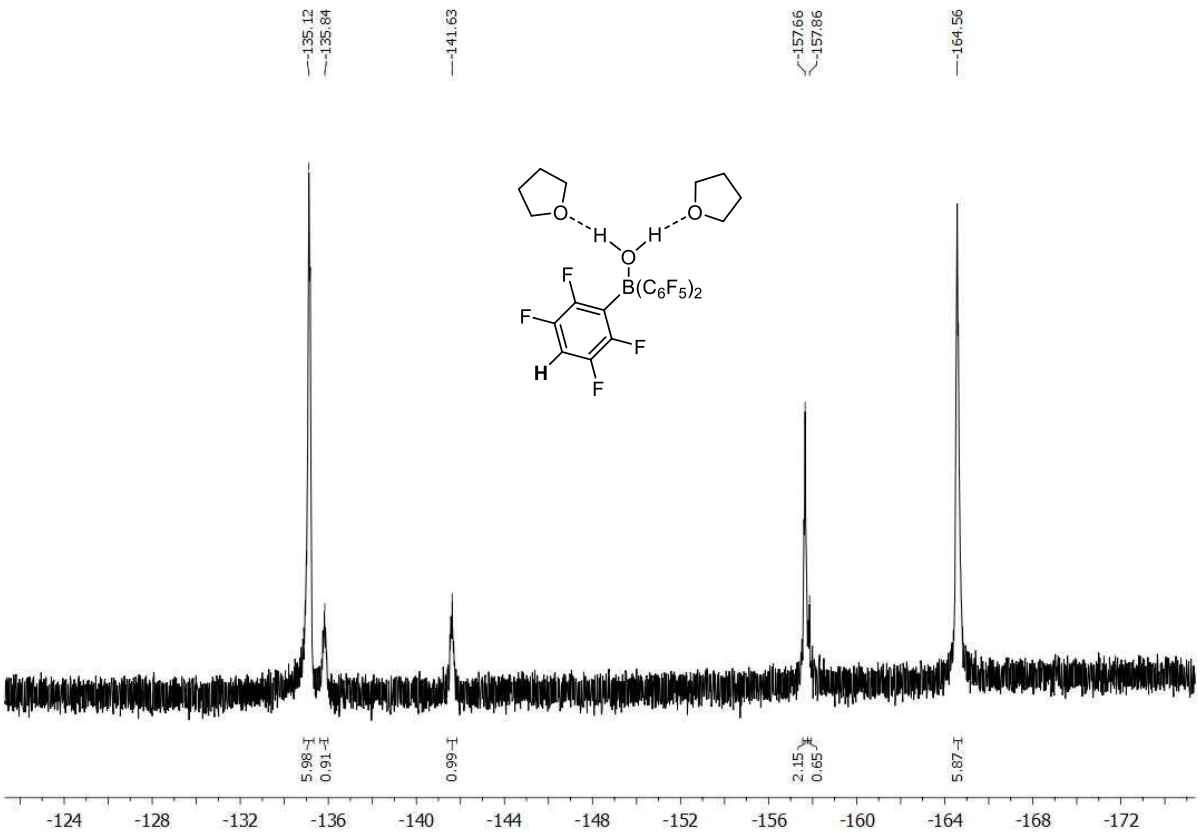


Figure S49. $^{19}F\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K) of compound **9**·H_2O·$(THF)_2$.

3. X-Ray Crystallographic Details

The crystals were selected and measured on a SuperNova Dualflex diffractometer equipped with a TitanS2 detector {**6**, **7**[$B(C_6F_5)_4$]} or on a XtaLAB Synergy R, DW system equipped with a HyPix-Arc 150 detector (**9**). The crystals were kept at T = 123(1) K during data collection. Data collection and reduction were performed with **CrysAlisPro** (Version 1.171.41.90a).[5] An analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R. C. Clark & J. S. Reid[6] and an empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm, was applied for all compounds. Using **Olex2**,[7] the structures were solved with **ShelXT**[8] and a least-square refinement on F^2 was carried out with **ShelXL**[9] or **olex2.refine**[10], respectively. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were located in idealized positions and refined isotropically according to the riding model. Figures were created with **Olex2**[7] and **Mercury 4.1.0**.[11]

Compound 6: The asymmetric unit contains one molecule of (tBu)$_2$P(S)CH$_2$Si(Ph)$_2$OSi(H)PhtBu. The hydrogen atom on the Si atom was located from the difference Fourier map and refined without restraints. The tBu group at the Si atom shows a disorder over two positions with an occupancy of 0.6 for the main part and 0.4 for the minor part. To describe this disorder the SIMU restraint was applied.

Compound 7[$B(C_6F_5)_4$]: The asymmetric unit contains one molecule of the cation [(tBu)$_2$P(S)CH$_2$Si(Ph)$_2$OSiPhtBu]$^+$ and one molecule of the anion [$B(C_6F_5)_4$]$^-$.

Compound 9·H_2O·$(THF)_2$: The asymmetric unit contains one molecule of $B(C_6F_5)_2(C_6HF_4)\cdot(H_2O)$ and two THF solvent molecules. The hydrogen atom located in para position at the C_6HF_4 substituent is only partly occupied (0.5) and distributed over the para positions of the three phenyl substituents (0.1:0.2:0.2). Consequently $B(C_6F_5)_2(C_6HF_4)\cdot(H_2O)$ co-crystalizes with $B(C_6F_5)_3\cdot(H_2O)$ in a 1:1 ratio. Additionally, the two THF molecules are disordered over two positions, which were described using the restraints SADI and SIMU.

CCDC-2107143 (**6**), CCDC-2107144 {**7**[$B(C_6F_5)_4$]}, and CCDC-2107145 [**9**·H_2O·$(THF)_2$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

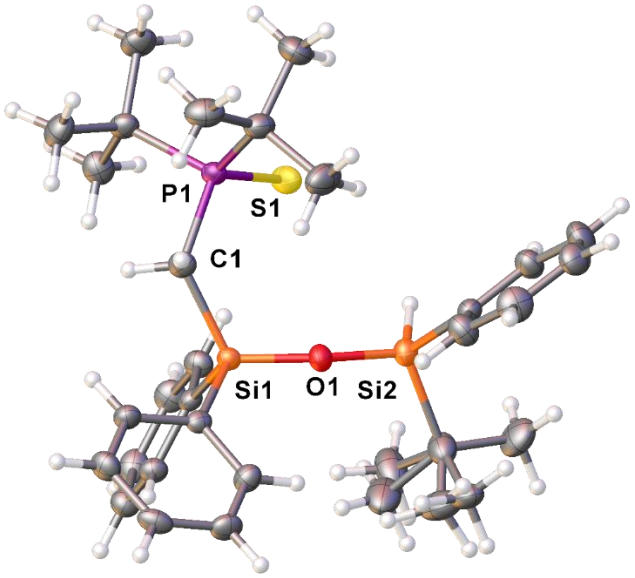
Structural details concerning compound 7[$B(C_6F_5)_4$]:

The Si2 atom in cation **7** exhibits an almost ideal tetrahedral coordination geometry. In comparison with the same bonds in siloxane **6**, the Si1–O1 bond in cation **7** is slightly elongated and the Si2–O1 bond slightly shortened. The Si–O–Si angle decreases from 156.83(16)° in **6** to 139.60(11)° in **7**, while the heterocyclic Si–S–P angle with 107.86(3)° is close to the tetrahedral angle.

Table S1. Crystallographic data for compounds **6**, **7**[$B(C_6F_5)_4$], and **9**·H_2O·$(THF)_2$.

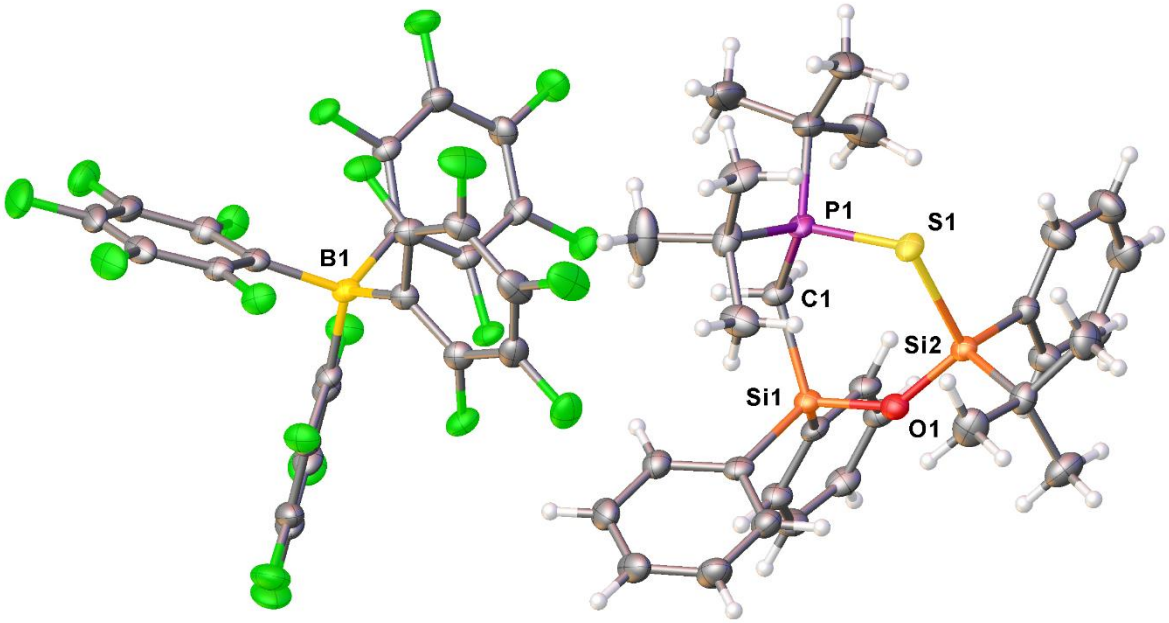
Compound	**6**	**7[$B(C_6F_5)_4$]**	**9·H_2O·$(THF)_2$**
Data set (internal naming)	**nf_719_2b_GV**	**nf_693_1**	**nf_771_subl_thf_2**
CCDC number	2107143	2107144	2107145
Formula	$C_{31}H_{45}OPSSi_2$	$C_{55}H_{44}BF_{20}OPSSi_2$	$C_{26}H_{18.5}BF_{14.5}O_3$
Dcalc	1.167	1.528	1.666
μ/mm^{-1}	2.276	2.247	0.175
Formula Weight	552.913	1230.92	665.236
Colour	colourless	colourless	colourless
Shape	block-shaped	block-shaped	plate-shaped
Size/mm^3	0.12×0.10×0.08	0.35×0.24×0.21	0.44×0.12×0.08
T/K	123.0(1)	123.0(1)	123.01(10)
Crystal System	monoclinic	triclinic	monoclinic
Space Group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a/Å	8.3897(2)	9.9141(2)	9.2436(3)
b/Å	35.0632(6)	14.3805(2)	29.8297(7)
c/Å	11.2062(2)	19.1892(3)	9.9706(3)
α/°	90	101.2990(10)	90
β/°	107.304(2)	90.3210(10)	105.288(3)
γ/°	90	93.8460(10)	90
V/Å^3	3147.32(11)	2676.24(8)	2651.94(14)
Z	4	2	4
Z'	1	1	1
Wavelength/Å	1.54184	1.54184	0.71073
Radiation type	Cu K$_\alpha$	Cu K$_\alpha$	Mo K$_\alpha$
θ_{min}/°	4.32	4.278	2.22
θ_{max}/°	66.60	66.647	32.62
Measured Refl's.	35994	41863	44425
Indep't Refl's	5524	9402	9629
Refl's I≥2 σ(I)	5124	8248	7025
R_{int}	0.0563	0.0812	0.0289
Parameters	359	739	436
Restraints	42	0	59
Largest Peak	0.5996	0.640	0.6516
Deepest Hole	-0.4918	-0.605	-0.5345
GooF	1.0223	1.024	1.0261
wR_2 (all data)	0.1286	0.1342	0.1263
wR_2	0.1267	0.1286	0.1156
R_1 (all data)	0.0623	0.0561	0.0690
R_1	0.0588	0.0491	0.0463

3.1. Compound 6



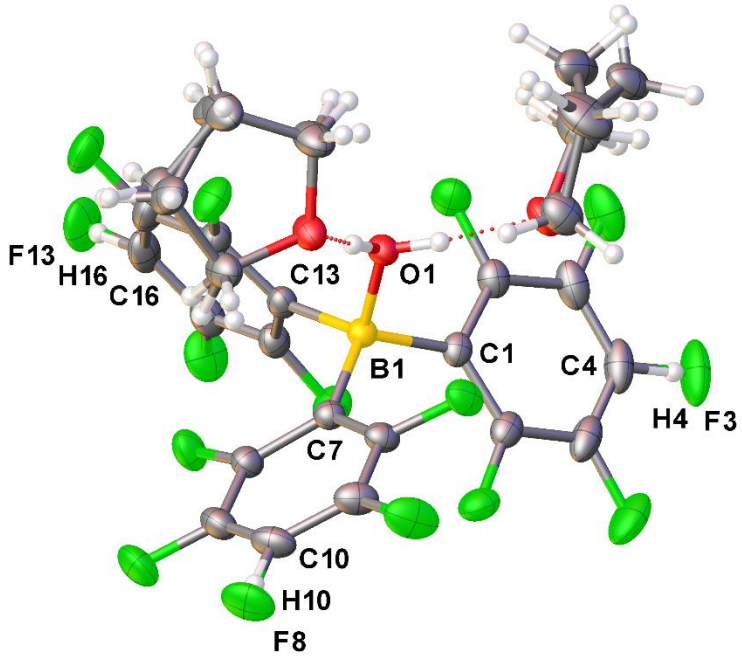
Selected Bond Lengths in Å		Selected Bond Angles in °	
P1–S1	1.9671(12)	**S1–P1–C1**	114.38(11)
P1–C1	1.818(3)	**P1–C1–Si1**	125.15(18)
C1–Si1	1.891(3)	**C1–Si1–O1**	115.52(14)
Si1–O1	1.614(2)	**Si1–O1–Si2**	156.83(16)
Si2–O1	1.644(2)		

3.2. Compound 7[B(C_6F_5)$_4$]



Selected Bond Lengths in Å		Selected Bond Angles in °	
P1–S1	2.0678(9)	**S1–P1–C1**	114.11(9)
P1–C1	1.803(2)	**P1–C1–Si1**	124.60(13)
C1–Si1	1.899(2)	**C1–Si1–O1**	106.42(10)
Si1–O1	1.6381(18)	**Si1–O1–Si2**	139.60(11)
O1–Si2	1.6265(18)	**O1–Si2–S1**	109.26(7)
Si2–S1	2.1940(8)	**Si2–S1–P1**	107.86(3)

3.3. Compound 9·H_2O·$(THF)_2$



Selected Bond Lengths in Å		Selected Bond Angles in °	
B1–O1	1.5502(15)	**O1–B1–C1**	104.01(9)
B1–C1	1.6365(17)	**O1–B1–C7**	106.18(9)
B1–C7	1.6383(18)	**O1–B1–C13**	107.70(9)
B1–C13	1.6359(17)	**C1–B1–C7**	116.35(10)
		C1–B1–C13	109.74(9)
		C7–B1–C13	112.14(9)

4. Quantum Chemical Calculations

Optimization and additional harmonic vibrational frequency analyses were performed with the software package Gaussian 09 (Revision E.01) either at the B3LYP/6-311+G(d,p) or the B3LYP/6-31G(d) level of theory without symmetry restrictions.[12] The GJF input files and the figures of the optimized structures were created with the program GaussView version 5.0.9.[13] For the ground state structures, the vibrational frequency analysis showed no imaginary frequency in the harmonical approximation. Natural bond orbital (NBO) analysis has been performed at the B3LYP/6-311+G(d,p) level of theory with the Gaussian NBO Version 3.1. The total (SCF) and zero-point-corrected (ZPE) energies of the calculated systems can be found in Table S2. The results of the NBO analysis can be found in Table S3. A mechanistic proposal is given in Scheme S50. The optimized structures can be found in Figures S51–S65. The calculated standard orientations of the optimized structures can be found in Tables S4–S18. The Hartree units can be converted as follows:[14] 1 Hartree = 2625.4995 kJ·mol^{-1}, 1 cal = 4.184 J.

Table S2. Total (SCF) and zero-point-corrected (ZPE) energies of the optimized structures.

Optimized structure	Method/Basis	SCF [Hartree]	ZPE [Hartree]
6	B3LYP/6-311+G(d,p)	–2602.77036406	–2602.087217
7-Cat-S	B3LYP/6-311+G(d,p)	–2601.98833969	–2601.311959
7-Cat-Ar	B3LYP/6-311+G(d,p)	–2601.92295396	–2601.246927
7-Cat-free	B3LYP/6-311+G(d,p)	–2601.92048049	–2601.245066
6-C	B3LYP/6-311+G(d,p)	–2566.76138254	–2566.055163
7-C-Cat-S	B3LYP/6-311+G(d,p)	–2565.98204034	–2565.282543
7-C-Cat-Ar	B3LYP/6-311+G(d,p)	–2565.92074226	–2565.221776
7[HB(C_6F_5)$_3$]	B3LYP/6-31G(d)	–4810.55379635	–4809.707548
Int-1	B3LYP/6-31G(d)	–4810.50524685	–4809.660073
Int-2	B3LYP/6-31G(d)	–4810.55774210	–4809.711035
Int-3	B3LYP/6-31G(d)	–2108.81960768	–2108.663675
Int-3	B3LYP/6-311+G(d,p)	–2109.48067241	–2109.325350
8	B3LYP/6-31G(d)	–2701.64176243	–2700.957034
9	B3LYP/6-31G(d)	–2109.01278044	–2108.850989
9	B3LYP/6-311+G(d,p)	–2109.67379911	–2109.512775

Table S3. Results of the natural bond orbital (NBO) calculations [B3LYP/6-311+G(d,p)].

Property	**6**	**7-Cat-S**	**7-Cat-Ar**	**7-Cat-free**	**6-C**	**7-C-Cat-S**	**7-C-Cat-Ar**
i_{Si2S}[a]	—	0.506	—	—	—	0.496	—
i_{SP}[a]	0.026	0.128	0.039	0.034	0.030	0.129	0.036
i_{PC1}[a]	0.256	0.221	0.271	0.277	0.251	0.226	0.271
i_{C1Si1}[a]	0.500	0.527	0.489	0.496	0.493	0.520	0.471
i_{Si1C2}[a]	—	—	—	—	0.455	0.469	0.491
i_{C2Si2}[a]	—	—	—	—	0.459	0.491	0.497
Q_{Si1}[b]	2.004	1.999	2.020	2.020	1.768	1.765	1.783
Q_{O}[b]	–1.266	–1.280	–1.296	–1.286	—	—	—
Q_{Si2}[b]	1.759	1.978	2.226	2.256	1.483	1.747	2.003

Q_S[b]	–0.629	–0.451	–0.611	–0.604	–0.632	–0.431	–0.597
Q_P[b]	1.421	1.519	1.439	1.434	1.426	1.526	1.429
Q_{C1}[b]	–1.275	–1.271	–1.288	–1.288	–1.252	–1.258	–1.260
Q_{C2}[b]	—	—	—	—	–1.410	–1.444	–1.451
h_O (% s)[c]	$sp^{0.08}$ (92.5)	$sp^{0.14}$ (87.7)	$sp^{0.25}$ (80.1)	$sp^{0.14}$ (87.3)	—	—	—
h_{Si2} (% s)[c]	$sp^{8.39}$ (10.6)	$sp^{9.17}$ (9.7)	$sp^{10.0}$ (9.0)	$sp^{7.57}$ (11.5)	$sp^{2.85}$ (25.8)	$sp^{2.57}$ (27.8)	$sp^{2.18}$ (31.2)
h_{C2} (% s)[c]	—	—	—	—	$sp^{2.49}$ (28.7)	$sp^{2.35}$ (29.9)	$sp^{2.47}$ (28.8)
occ. n_O'[d]	1.916	1.914	1.923	1.930	—	—	—
occ. n_O''[d]	1.907	1.904	1.900	1.841	—	—	—
hc loss n_O[e]	0.177	0.182	0.177	0.229	—	—	—
rel. hc loss n_O[f]	0 %	2.8 %	0 %	29.4 %	—	—	—
$E^{(2)}$ (n_O'' → p_{Si2})[g]	—	—	—	–29.98	—	—	—

[a] Bond ionicities (i_{AB}) of the A–B bonds ($i_{AB} = |c_A^2 – c_B^2|$ with c_A and c_B being NBO polarization coefficients). [b] Natural atomic charges (Q_A) at atoms A. [c] Natural hybrid types (h_O, h_{Si2}, h_{C2}) and their % s character at atoms O, Si2, and C2 in the O–Si2 and C2–Si2 bonds, respectively (h_O corresponds to the lone electron pair-like natural hybrid at oxygen that makes the greatest contribution to the O–Si2 bond). [d] Oxygen lone electron pair occupancies (occ. n_O', occ. n_O''). [e] Net hyperconjugative electronic loss of oxygen lone electron pairs (hc loss n_O). [f] hc loss n_O relative to compound **6** (rel. hc loss n_O). [g] Hyperconjugative stabilization energy estimates ($E^{(2)}$ in kcal mol^{-1}) from the second order perturbation theory analysis for the n_O'' → p_{Si2} interaction.

Details on bond polarity parameters:

The formal exchange of the siloxane oxygen atom by a CH_2 group led to the analogous cations **7-C-Cat-S** and **7-C-Cat-Ar**, the latter being 38.2 kcal mol^{-1} higher in energy. The Si–O–Si linkage leads to an increased Lewis acidity in comparison to the Si–CH_2–Si system. The O–Si2 σ bonds of all calculated disiloxane species have a high s character in the lone electron pair-like natural hybrids at oxygen (h_O) and a high p character in h_{Si2} in accordance with Bent's rule (Table S3).[15] The consistently higher positive charge on the Si2 atom of the disiloxane-based cations (**7-Cat-S**: Q_{Si2} = 1.978; **7-Cat-Ar**: Q_{Si2} = 2.226; **7-Cat-free**: Q_{Si2} = 2.256) compared to the respective methylene-bridged analogs (**7-C-Cat-S**: Q_{Si2} = 1.747; **7-C-Cat-Ar**: Q_{Si2} = 2.003) also reflects the high ionicity in the O–Si σ bonds (Table S3). The C2–Si2 bonds can be classified as polar covalent σ bonds.

Further mechanistic considerations on the ion pair reaction:

An alternative route starting from intermediate **Int-1** *via* fluoride abstraction with the formation of a free zwitterionic intermediate (**Int-3**) appears unlikely in view of the additional energy of 24.6 kcal mol^{-1} required for this step (Figure S50). Intermolecular mechanisms might explain the traces of tris(pentafluorophenyl)borane (BCF) found in the cocrystals of compound **9** (for details, see chapter 3).

It should also be noted that electrostatically-driven, attractive σ-hole-type C(phenyl)–H···F–C(aryl) interactions between the phenyl groups of the cation and the perfluorinated aryl groups of the counterion could play an important role for the formation of a reactive encounter complex.[16] This is strongly suggested by the optimized structures **7[HB(C_6F_5)$_3$]** (Figure S58), **Int-1** (Figure S59), and **Int-2** (Figure S62).

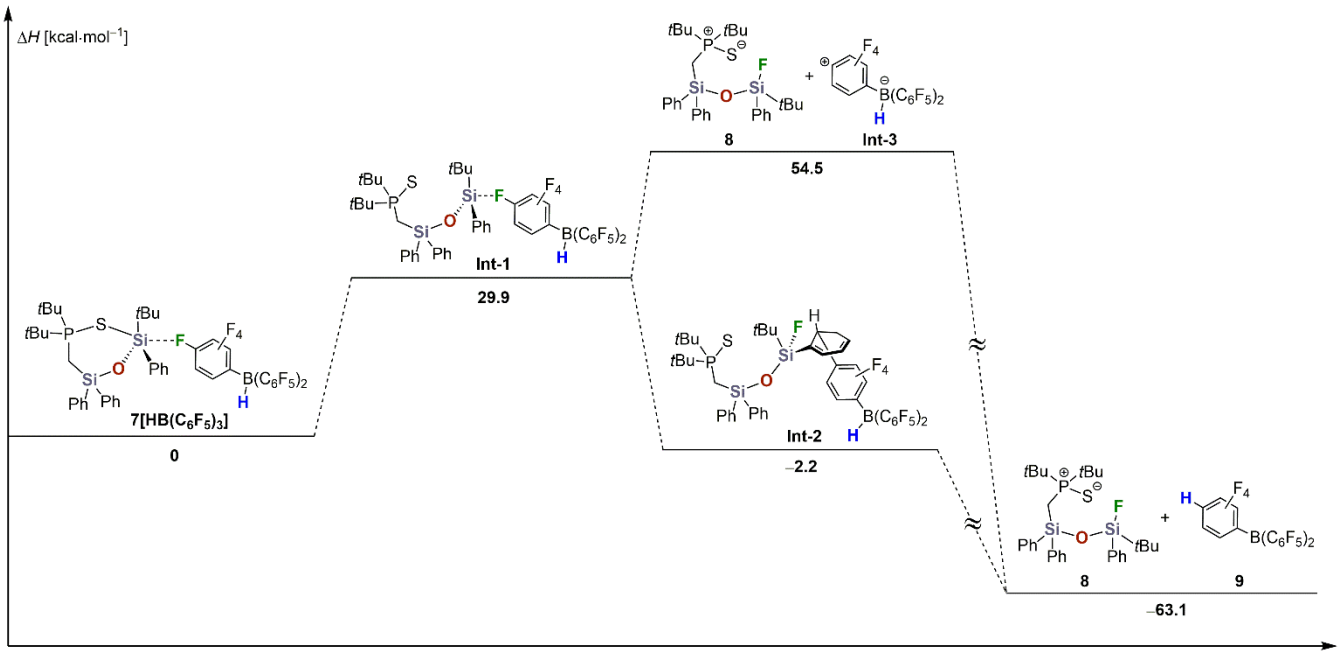


Figure S50. Conceivable reaction paths for the *para*-C(sp^2)–F hydrodefluorination calculated on the B3LYP/6-31G(d) level of theory. Formal charges, except for product **8** and intermediate **Int-3**, are omitted for clarity. The zwitterion **Int-3** is 117.6 kcal mol^{-1} higher in energy than borane **9**. The suitability of the moderate DFT level for an appropriate thermodynamic description of the reaction was confirmed by the fact that the energy difference between zwitterion **Int-3** and borane **9** was exactly the same based on the structures optimized at the B3LYP/6-311+G(d,p) level of theory.

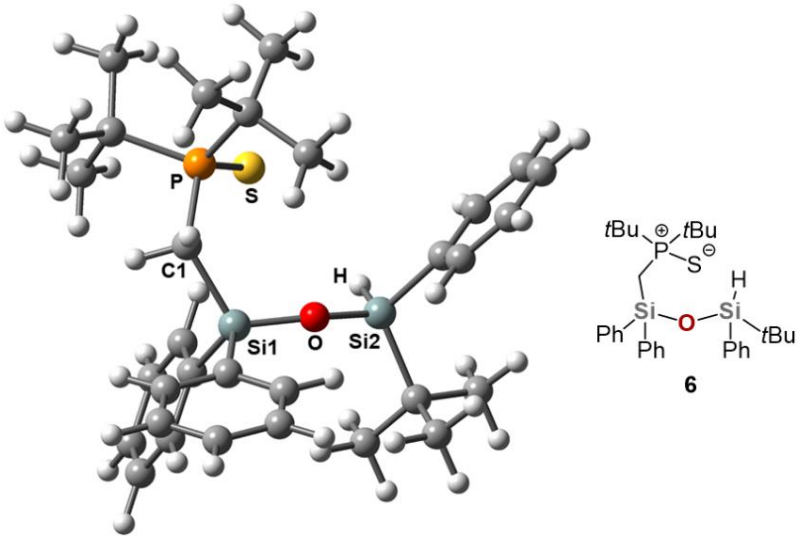


Figure S51. Optimized structure of compound **6** [B3LYP/6-311+G(d,p)]. Selected bond lengths [Å] and angles [°]: P–S 1.996, Si1–O 1.649, Si2–O 1.669, Si1–O–Si2 152.9.

Table S4. Standard orientation of **6** [B3LYP/6-311+G(d,p)].

Atomic symbol	x	y	z
C	–0.69870100	3.18636900	4.58302800
C	0.45819600	3.52036700	3.87927000
C	–1.60631200	2.28678800	4.02853900
C	0.70045600	2.95523500	2.62882600
C	–1.35794400	1.72594100	2.77540000
C	–0.20276000	2.04780400	2.04732900

C	3.08394100	–2.55619300	2.21621600
C	–3.41971300	–3.56542700	1.51219300
C	–3.02380200	–2.31699100	1.03616700
C	–3.50612400	–4.64984100	0.63930300
C	0.70301400	–2.54251800	1.42733900
C	5.02935100	–0.22512100	0.71910000
C	2.17524000	–2.61138900	0.97498000
C	1.82309500	0.33583800	0.66929300
C	2.38928300	–3.94721400	0.23836800
C	0.06966100	3.90339900	–0.70867000
C	–2.70583000	–2.11973200	–0.31793400
C	–3.18993300	–4.47896200	–0.70697300
C	4.30428700	–0.76360100	–0.53030900
C	0.38291700	2.55614000	–0.95701700
C	0.20677700	4.87293000	–1.70185200
C	–2.79285200	–3.22711300	–1.17645000
C	5.02149800	–2.02473700	–1.04509500
C	–3.76394100	0.68404900	–1.25218000
C	4.36439200	0.31594100	–1.63166200
C	0.83711900	2.21415700	–2.24379000
C	0.65891300	4.51325600	–2.96960500
C	–4.74719000	–0.06615900	–2.17817800
C	0.97218600	3.18134400	–3.23823600
H	–0.89023900	3.62503400	5.55617300
H	1.16904500	4.22131700	4.30353900
H	–2.50835200	2.02238000	4.57000700
H	1.60652700	3.23684000	2.09995300
H	–3.65914500	–3.69379400	2.56253800
H	2.75333200	–3.32548500	2.92215800
H	3.03456700	–1.59807000	2.73966400
H	–2.07135600	1.02703700	2.35447400
H	4.12680100	–2.76759100	1.97544000
H	–2.95129000	–1.48991600	1.73503500
H	1.87863300	0.11160300	1.73802400
H	–3.81370400	–5.62251200	1.00773500
H	0.47897700	–3.43599300	2.01881700
H	5.07556200	–0.94754700	1.53207700
H	0.49804000	–1.67570100	2.05881800
H	4.57860300	0.69211200	1.10376000
H	6.06049200	0.01790900	0.44102400
H	–0.28949400	4.20443400	0.26954600

H	2.55879700	1.12752700	0.49912600
H	2.12989300	–4.76466200	0.91931400
H	0.01742100	–2.52298500	0.58096100
H	3.42335000	–4.09238100	–0.07587600
H	5.14403400	–2.77814000	–0.26457600
H	–0.04198100	5.90643900	–1.48560800
H	–3.24583200	–5.32005300	–1.38964300
H	1.75269500	–4.01747300	–0.64392200
H	3.85994600	1.24143500	–1.34176000
H	6.02289600	–1.74821100	–1.39135100
H	5.41497700	0.55978200	–1.82211300
H	4.48602000	–2.47243800	–1.88470900
H	–2.53515700	–3.11597100	–2.22514600
H	–5.11146100	–0.99305000	–1.72628500
H	3.91476000	–0.03708100	–2.55953600
H	–1.61572500	–0.63883800	–2.34804500
H	1.08161400	1.18114100	–2.47245800
H	–5.61919700	0.56611800	–2.38691200
H	0.76481900	5.26534700	–3.74405000
H	–4.29183600	–0.31800400	–3.14181200
H	1.32116000	2.89344600	–4.22419700
O	–1.13450700	0.26904300	0.03324600
P	2.44377100	–1.15166000	–0.24013000
S	1.53331400	–1.51509400	–1.97922300
Si	0.15594600	1.23778200	0.37540400
Si	–2.22884800	–0.43378200	–1.01326500
C	–3.34276100	2.00149900	–1.93600800
C	–4.46943700	1.00454100	0.07986900
H	–3.81809900	1.55769900	0.76229400
H	–5.35308500	1.62925300	–0.10386700
H	–4.81184400	0.09959200	0.59065000
H	–2.84924600	1.82383100	–2.89634700
H	–4.22727300	2.62169500	–2.12974300
H	–2.65969700	2.58839900	–1.31713200

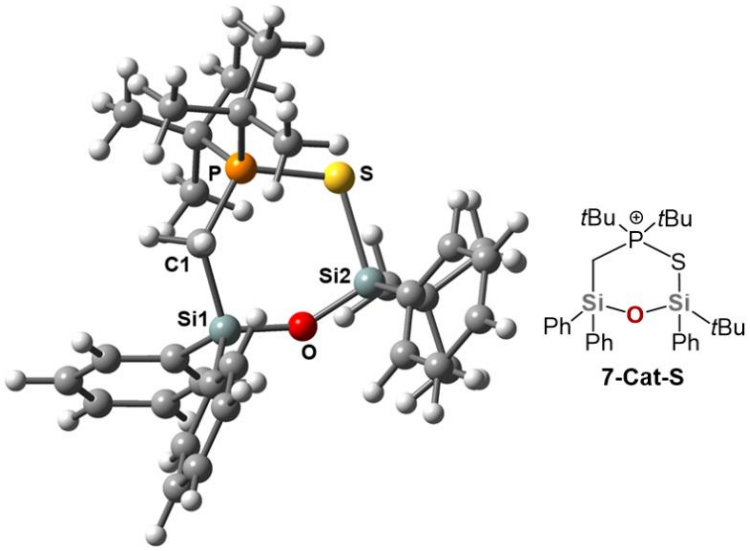


Figure S51. Optimized structure of compound **7-Cat-S** [B3LYP/6-311+G(d,p)]. Selected bond lengths [Å] and angles [°]: P–S 2.108, Si1–O 1.663, Si2–O 1.647, Si1–O–Si2 144.5, Si2–S 2.259.

Table S5. Standard orientation of **7-Cat-S** [B3LYP/6-311+G(d,p)].

Atomic symbol	x	y	z
Si	–1.04309400	1.12388600	–0.21645900
O	0.08144400	0.84073500	0.97601000
Si	1.38221900	–0.07576000	1.40185400
C	–1.01843700	–0.42487400	–1.37261000
C	–2.71859100	1.37230500	0.57318800
P	–0.45501200	–2.10197500	–0.89541400
C	–0.57798200	2.59138500	–1.28541800
C	1.53590000	–0.24143700	3.28812400
C	2.93065900	0.53455400	0.55142700
S	0.93841900	–2.17104500	0.68459500
C	–1.95406500	–3.09028100	–0.25987600
C	0.43981400	–2.81506200	–2.42213000
C	–1.51200900	–4.42232700	0.37682800
C	–2.62631400	–2.22248400	0.82236200
C	–2.95514900	–3.36699200	–1.39929700
C	1.73309600	–1.99873300	–2.62969900
C	–0.44538500	–2.68115100	–3.67890100
C	0.81015600	–4.29135100	–2.19037000
C	–3.87401600	1.47774100	–0.22181900
C	–5.12572800	1.68240400	0.35348900
C	–5.24489800	1.79498500	1.73877300
C	–4.11033100	1.70592300	2.54258200
C	–2.85941300	1.49574100	1.96387200
C	0.46958000	2.53272900	–2.22222200
C	0.81769900	3.64223600	–2.98729500

C	0.12358900	4.84170200	–2.82959500
C	–0.91348900	4.92570200	–1.90352400
C	–1.26061800	3.81189100	–1.14059600
C	3.05758200	1.90050700	0.24447500
C	4.23775600	2.40443700	–0.29972600
C	5.31227800	1.55268200	–0.54705300
C	5.20457100	0.19418100	–0.25047200
C	4.02555000	–0.30880800	0.29378900
C	0.23118100	–0.76294800	3.92181600
C	1.84503900	1.17382700	3.83589300
C	2.70008600	–1.19123200	3.64556500
H	–0.40216600	–0.14647700	–2.22962200
H	–2.40367400	–4.91135800	0.77892700
H	–1.05892200	–5.10787300	–0.33781000
H	–0.81908800	–4.26973900	1.20439000
H	–3.44947100	–2.79897800	1.25331400
H	–3.04818900	–1.29911100	0.42629200
H	–1.93880200	–1.97440200	1.63261500
H	–2.58100500	–4.10317400	–2.11134600
H	–3.86375700	–3.78160400	–0.95404300
H	–3.25077900	–2.46803100	–1.94512800
H	2.22846300	–2.37955000	–3.52701000
H	2.42515600	–2.10010400	–1.79455900
H	1.54603800	–0.93557500	–2.79570800
H	0.12295300	–3.06574400	–4.53040400
H	–1.36564100	–3.25996700	–3.61756100
H	–0.70133400	–1.64502100	–3.90739800
H	1.36296400	–4.43926800	–1.26040100
H	–0.06378800	–4.94329900	–2.19167800
H	1.45679400	–4.61570900	–3.01039000
H	–3.80470700	1.41448600	–1.30449600
H	–6.00480400	1.76245800	–0.27577100
H	–6.21774800	1.95855100	2.18795400
H	–4.19891500	1.80227100	3.61874600
H	–1.98370600	1.43276300	2.59943300
H	1.04170000	1.61930100	–2.35346800
H	1.62856600	3.57363900	–3.70356900
H	0.39121300	5.70610600	–3.42646000
H	–1.45425400	5.85641600	–1.77590100
H	–2.07463700	3.89649900	–0.42935500
H	2.23200100	2.57917900	0.42741400

H	4.31722200	3.46114700	–0.52803300
H	6.23133900	1.94503100	–0.96714900
H	6.03906300	–0.47114100	–0.44066200
H	3.96446500	–1.36932400	0.51593700
H	0.33632700	–0.77973400	5.01204900
H	–0.00223800	–1.78104500	3.60027800
H	–0.62426200	–0.12572100	3.68545700
H	1.95867700	1.12206000	4.92421500
H	2.77475000	1.58074400	3.42954100
H	1.04002400	1.88288500	3.62338800
H	2.52631300	–2.21280800	3.29300300
H	3.65495600	–0.84594500	3.24131500
H	2.80655900	–1.24138700	4.73457400
H	–2.03114800	–0.55825000	–1.76632900

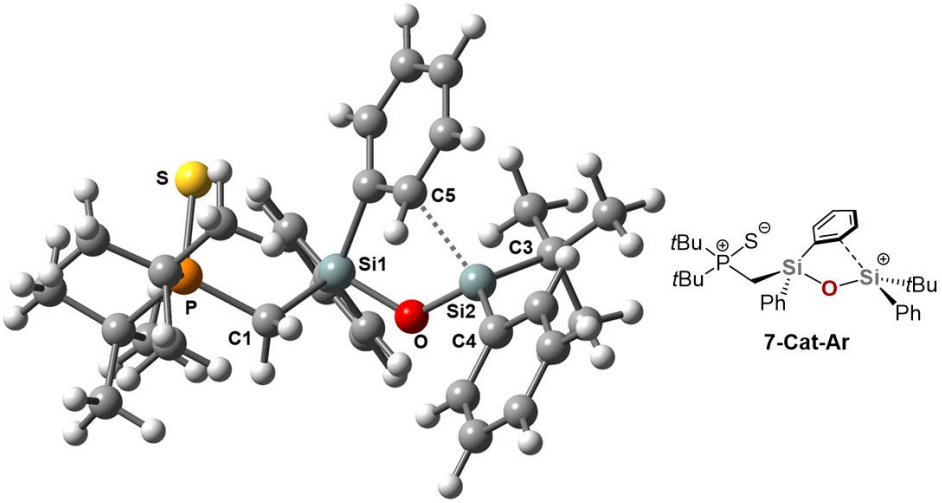


Figure S53. Optimized structure of compound **7-Cat-Ar** [B3LYP/6-311+G(d,p)]. Selected bond lengths [Å] and angles [°]: P–S 2.012, Si1–O 1.721, Si2–O 1.638, Si1–O–Si2 124.3, Si2–C5 2.285, O–Si2–C3 116.2, O–Si2–C4 110.6, C3–Si2–C4 118.4 (Σ angles around Si2: 345.2°).

Table S6. Standard orientation of **7-Cat-Ar** [B3LYP/6-311+G(d,p)].

Atomic symbol	x	y	z
C	–1.37590900	5.09961900	–1.48368600
C	–1.94295900	4.57391300	–0.32369200
C	–0.49863700	4.32356700	–2.23831900
C	–1.63952200	3.27573000	0.08011200
C	–0.18232000	3.03026900	–1.82710600
C	–0.74838800	2.48130500	–0.66139300
C	–2.68086400	–3.73618400	–0.53381700
C	3.13001600	–3.35904000	–2.53692600
C	2.67661700	–2.14539000	–2.02543100
C	4.18180700	–4.02952800	–1.91514700

C	–1.70206400	–2.96605900	1.64008900
C	–4.49128600	–1.41066100	–2.20055000
C	–2.88077100	–2.78342000	0.66108200
C	–1.33973900	–0.68550000	–0.80626400
C	–4.18801200	–3.12915400	1.39804300
C	0.43168400	1.43998700	2.59492800
C	3.28148000	–1.57472700	–0.89000000
C	4.78413200	–3.48443500	–0.78145300
C	–4.34639300	–0.45597500	–1.00195700
C	0.53781000	0.54083700	1.53457600
C	1.25129000	1.32417100	3.71840700
C	4.34128200	–2.26591100	–0.27506300
C	–5.65836000	–0.41358800	–0.19521400
C	3.87231100	1.48822000	–0.06342900
C	–4.05443600	0.96761000	–1.51914100
C	1.53299300	–0.48592700	1.63560000
C	2.21008900	0.30768300	3.82336000
C	5.09035100	1.08996600	0.79352500
C	2.33615800	–0.61286600	2.79895300
H	–1.61910900	6.10774200	–1.79939300
H	–2.63025200	5.17241700	0.26345400
H	–0.05869300	4.72458000	–3.14441200
H	–2.12022400	2.86846900	0.96149500
H	2.66417800	–3.78001000	–3.42045100
H	–2.56644900	–4.75352100	–0.14672100
H	–1.78066000	–3.51190000	–1.11136200
H	0.51146000	2.44393100	–2.41940000
H	–3.52850600	–3.74658600	–1.21642400
H	1.85672300	–1.63156200	–2.51442700
H	–0.74380200	–1.60014200	–0.75825200
H	4.53226000	–4.97509100	–2.31243700
H	–1.70174800	–4.00313400	1.98814900
H	–4.88303500	–2.38497000	–1.90866500
H	–0.73412400	–2.78788300	1.16342300
H	–3.55532700	–1.56058300	–2.74544700
H	–5.20653900	–0.97563800	–2.90519400
H	–0.29520000	2.24100700	2.55269400
H	–1.55610300	–0.52033500	–1.86549700
H	–4.08330200	–4.11671400	1.85709100
H	–1.78968700	–2.31007600	2.50588600
H	–5.04096300	–3.17703000	0.72009300

H	–5.98287400	–1.40053200	0.13311400
H	1.14561500	2.03933000	4.52690000
H	5.60025400	–4.00654900	–0.29579600
H	–4.40803300	–2.41295600	2.19225000
H	–3.16877500	1.01824700	–2.15578300
H	–6.44535000	–0.00578600	–0.83657600
H	–4.90575800	1.29134000	–2.12492500
H	–5.56840400	0.23063000	0.68062600
H	4.82884700	–1.86155600	0.60482300
H	5.65060400	0.25865500	0.36054200
H	–3.93529400	1.67818800	–0.70150700
H	1.40016700	–1.39699000	1.05013100
H	5.77547200	1.94213700	0.85213300
H	2.82384500	0.22901400	4.71248700
H	4.80995300	0.82943000	1.81760300
H	3.02140800	–1.44845500	2.88864300
P	–2.90061000	–0.93635100	0.15286000
S	–2.84599700	0.25736900	1.77176700
Si	–0.24950900	0.74235500	–0.19583900
Si	2.64071300	0.06237200	–0.28580600
C	3.20519100	2.74557000	0.52495100
C	4.34175700	1.78337300	–1.51598700
H	3.52101400	2.11640400	–2.15660300
H	5.08147900	2.59048900	–1.48517400
H	4.82047800	0.91992500	–1.98598400
H	2.90521900	2.59941200	1.56381200
H	3.92375300	3.57193900	0.50312100
H	2.32935600	3.06108200	–0.04600900
O	1.22781600	0.43676200	–1.02431200

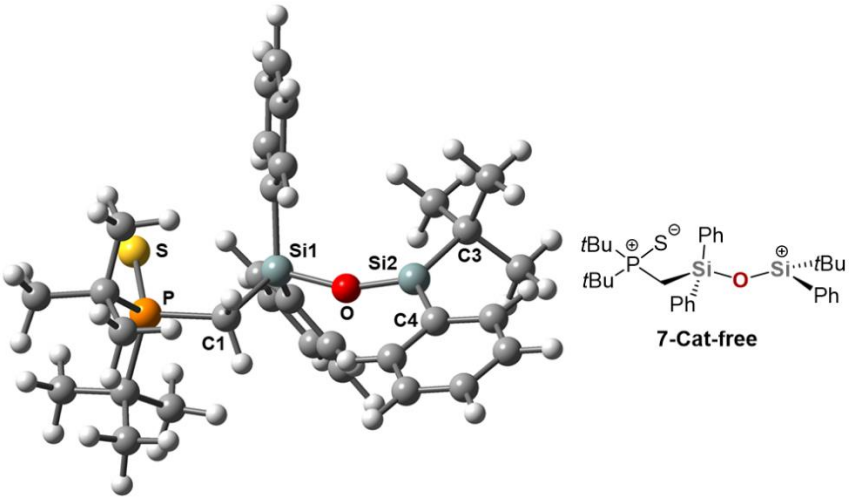


Figure S54. Optimized structure of compound **7-Cat-free** [B3LYP/6-311+G(d,p)]. Selected bond lengths [Å] and angles [°]: P–S 2.001, Si1–O 1.767, Si2–O 1.582, Si1–O–Si2 157.0, O–Si2–C3 122.1, O–Si2–C4 113.5, C3–Si2–C4 124.4 (Σ angles around Si2: 360.0°).

Table S7. Standard orientation of **7-Cat-free** [B3LYP/6-311+G(d,p)].

Atomic symbol	x	y	z
C	0.34765400	–3.86822200	–3.35071400
C	1.08151800	–4.06009200	–2.18194600
C	–0.41407600	–2.71148900	–3.50279600
C	1.05552400	–3.10301200	–1.16958100
C	–0.45031600	–1.76366700	–2.48203200
C	0.27876700	–1.93877300	–1.29117100
C	3.06785800	3.43929100	0.94747200
C	–3.07990100	4.21620700	–1.04253200
C	–2.66274900	2.91373900	–0.80163100
C	–4.43861900	4.53225300	–0.99594900
C	2.97148200	1.61027100	2.65806900
C	3.72804300	2.37329100	–2.21639200
C	3.56923900	2.02464100	1.29733700
C	1.20373000	0.94965400	–0.19059500
C	5.10452600	2.02573500	1.41799600
C	0.13705900	–2.47666700	2.27588100
C	–3.60540400	1.90320600	–0.51253300
C	–5.38432200	3.54657200	–0.71043900
C	3.81458100	0.92521500	–1.70433800
C	–0.07062800	–1.16274100	1.83050700
C	–0.10910100	–2.83431400	3.59968200
C	–4.97491800	2.24078100	–0.47159800
C	5.28431900	0.46448400	–1.66347300
C	–4.11500500	–1.27833600	0.12634500
C	3.05129300	–0.00310200	–2.67084500
C	–0.53783100	–0.22006200	2.76388200

C	–0.56734400	–1.88390600	4.51049400
C	–4.91702900	–1.01192500	1.42761200
C	–0.78192400	–0.57255600	4.09049400
H	0.37604600	–4.60977200	–4.14082400
H	1.68669400	–4.95124100	–2.06079600
H	–0.97500500	–2.54531300	–4.41577800
H	1.67386500	–3.25096500	–0.29432000
H	–2.35097500	4.98590200	–1.26631500
H	3.36642300	4.11829300	1.75232000
H	1.97882800	3.49475400	0.87435800
H	–1.04619700	–0.86911000	–2.63204500
H	3.49218700	3.82846400	0.02370000
H	–1.60770300	2.67080300	–0.83870500
H	0.86146600	1.67806100	0.54905200
H	–4.76197200	5.54969600	–1.18321000
H	3.27715600	2.34762500	3.40668700
H	4.40029700	3.04329000	–1.67956200
H	1.87884700	1.58713000	2.64914400
H	2.71525800	2.78289000	–2.16588600
H	4.03045000	2.39037700	–3.26816200
H	0.49882000	–3.23298000	1.59099200
H	0.99240700	1.37993100	–1.17324700
H	5.38895000	2.63013100	2.28465600
H	3.32625400	0.62883800	2.97157700
H	5.58853700	2.46485900	0.54425100
H	5.91211000	1.11161400	–1.05193800
H	0.06341700	–3.85492700	3.92167200
H	–6.43755200	3.79760600	–0.67555000
H	5.49824900	1.01884100	1.57167500
H	2.01732700	0.30910300	–2.83208400
H	5.68224500	0.48676300	–2.68270600
H	3.55170100	0.02687500	–3.64330100
H	5.37073400	–0.55555200	–1.28672100
H	–5.72470000	1.49061900	–0.25291200
H	–5.55464000	–0.12713500	1.36697100
H	3.05279700	–1.03642300	–2.32279600
H	–0.70354600	0.81238500	2.46695500
H	–5.56929700	–1.87194000	1.61090200
H	–0.75091700	–2.16202500	5.54191800
H	–4.26524100	–0.90713300	2.29910400
H	–1.12884600	0.17504300	4.79515700

O	–1.42504300	0.07483800	–0.27832400
P	3.02897000	0.69700500	0.02786200
S	3.35231900	–1.15204100	0.72213700
Si	0.16543300	–0.62409200	0.04681800
Si	–3.00044200	0.20590100	–0.20605100
C	–3.26608000	–2.55578000	0.29276500
C	–5.08208300	–1.44993900	–1.07483900
H	–4.55012100	–1.66432400	–2.00584700
H	–5.73378600	–2.30538800	–0.86998800
H	–5.72461800	–0.58258800	–1.23997900
H	–2.58414800	–2.49087600	1.14215900
H	–3.94234900	–3.39776100	0.47210900
H	–2.68021300	–2.78542900	–0.59975300

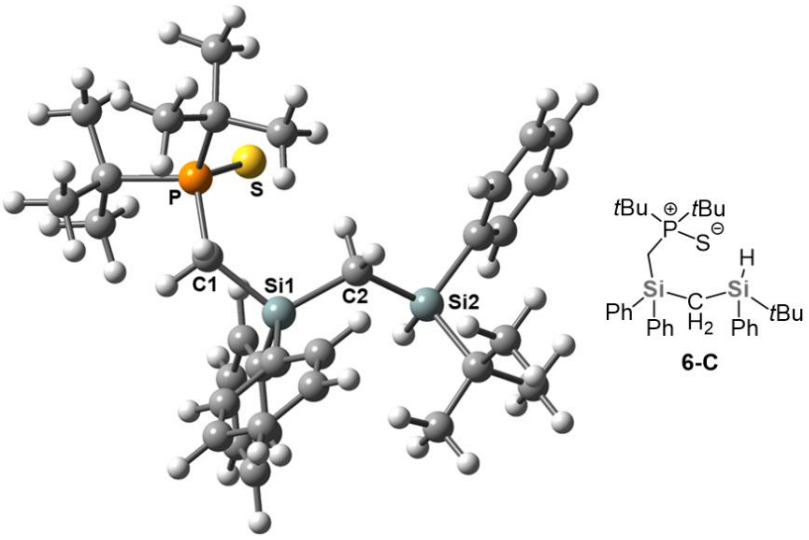


Figure S55. Optimized structure of compound **6-C** [B3LYP/6-311+G(d,p)]. Selected bond lengths [Å] and angles [°]: P–S 1.999, Si1–C2 1.886, Si2–C2 1.902, Si1–C2–Si2 123.4.

Table S8. Standard orientation of **6-C** [B3LYP/6-311+G(d,p)].

Atomic symbol	x	y	z
C	–0.33336400	4.79838200	–2.98942500
C	–1.04211000	4.83558500	–1.78918000
C	0.42804600	3.67492800	–3.30168800
C	–0.98420600	3.75551100	–0.91063700
C	0.48057200	2.59800000	–2.41604400
C	–0.21838800	2.61086900	–1.19888700
C	–3.99383000	–1.27888100	–2.65892200
C	3.79555200	–4.03523600	–1.24965100
C	3.30707000	–2.73669500	–1.11566500
C	4.37652700	–4.67814100	–0.15750900

C	–1.55723700	–1.84755900	–2.47156800
C	–5.29577100	0.18655300	0.12541500
C	–2.93367600	–1.97546600	–1.78683700
C	–2.09169600	0.50085400	–0.32661300
C	–3.26639900	–3.47510800	–1.66935900
C	0.43655800	2.92904400	2.08636800
C	3.38724500	–2.04477600	0.10456700
C	4.46250200	–4.01544500	1.06508600
C	–4.44806700	–0.89993000	0.81607900
C	–0.10544800	1.67483500	1.75836000
C	0.59464600	3.32683300	3.41390300
C	3.97259100	–2.71575300	1.19074900
C	–5.24517900	–2.21488100	0.88335600
C	4.05722400	0.97242200	–0.37971200
C	–4.14012700	–0.44085200	2.25652100
C	–0.47501200	0.82789900	2.81869400
C	0.21505700	2.47439800	4.44841400
C	5.39385700	0.70155100	0.34508600
C	–0.31792000	1.22239700	4.14631800
H	–0.37485500	5.63802100	–3.67447000
H	–1.63813100	5.70610700	–1.53676200
H	0.98385100	3.63630800	–4.23239900
H	–1.54297600	3.81191200	0.01843800
H	3.71946300	–4.54689700	–2.20329600
H	–3.91807300	–1.66910600	–3.67953000
H	–3.85635300	–0.19634900	–2.71771000
H	1.08276000	1.73743100	–2.68600800
H	–5.00868700	–1.48078700	–2.31376600
H	2.85102800	–2.26265100	–1.97958900
H	–2.35163200	0.77718200	–1.35227900
H	4.75363000	–5.69005300	–0.25781000
H	–1.60220400	–2.35607300	–3.44023400
H	–5.58257300	–0.07745600	–0.89127800
H	–1.27850000	–0.80911800	–2.66240000
H	–4.79534000	1.15645400	0.09752800
H	–6.21903800	0.31887000	0.69960100
H	0.74428600	3.60960900	1.30051900
H	–2.68000500	1.16852900	0.30826500
H	–3.22453400	–3.92084700	–2.66885200
H	–0.77277300	–2.31946500	–1.87883300
H	–4.26559000	–3.65382600	–1.27149700

H	–5.63106300	–2.51297400	–0.09340200
H	1.01498200	4.30147300	3.63832200
H	4.90523200	–4.51167000	1.92214900
H	–2.54767500	–3.99039600	–1.03117500
H	–3.55775000	0.48345400	2.28964300
H	–6.10657900	–2.07395100	1.54458600
H	–5.08818900	–0.25063000	2.77047400
H	–4.64041500	–3.02918500	1.28740200
H	4.04068100	–2.22016200	2.15425800
H	5.76881500	–0.30674900	0.15084600
H	–3.59265100	–1.20507400	2.80820400
H	2.63835400	–0.02578600	1.76786500
H	–0.87618900	–0.15853500	2.60781600
H	6.15668300	1.41211900	0.00176800
H	0.33711100	2.78173000	5.48147100
H	5.29916400	0.82265500	1.42893100
H	–0.60821300	0.54786500	4.94480400
P	–2.75053700	–1.20494400	–0.03669600
S	–1.59595400	–2.37721500	1.09857100
Si	–0.27263700	1.09921600	–0.04131600
Si	2.74967500	–0.26902400	0.30408800
C	3.62727700	2.42402500	–0.08680600
C	4.26894300	0.79209600	–1.89570900
H	3.35585500	0.98693200	–2.46634600
H	5.03139900	1.49396000	–2.25735100
H	4.61158400	–0.21733200	–2.14079200
H	3.46596300	2.59066700	0.98235600
H	4.41090400	3.12010200	–0.41363600
H	2.71053300	2.70139600	–0.61280700
C	1.02687900	–0.18925800	–0.49761300
H	1.12760300	–0.23591500	–1.58788100
H	0.57217000	–1.14410400	–0.20318100

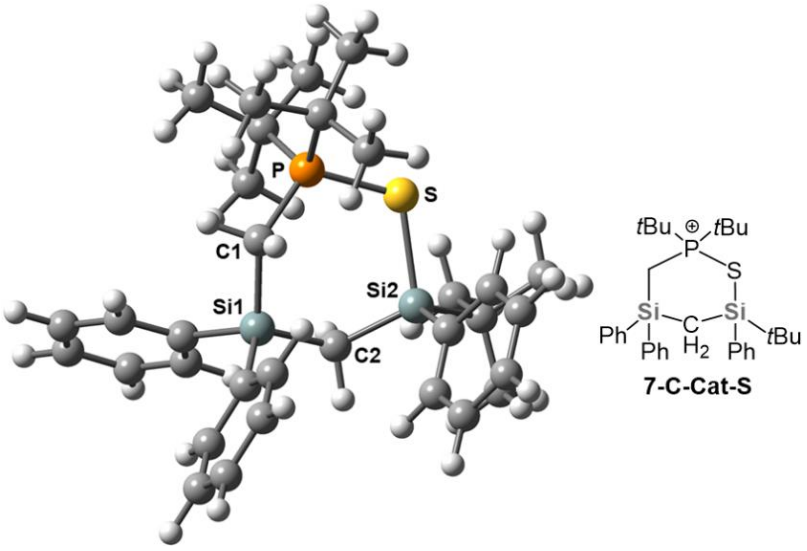


Figure S56. Optimized structure of compound **7-C-Cat-S** [B3LYP/6-311+G(d,p)]. Selected bond lengths [Å] and angles [°]: P–S 2.104, Si1–C2 1.890, Si2–C2 1.880, Si1–C2–Si2 121.6, Si2–S 2.257.

Table S9. Standard orientation of **7-C-Cat-S** [B3LYP/6-311+G(d,p)].

Atomic symbol	x	y	z
Si	–1.20929000	1.02389100	0.14401600
Si	1.65108700	–0.07633900	1.34580300
C	–1.00193500	–0.37951800	–1.17575700
C	–2.99181100	1.02768700	0.76621400
P	–0.33669300	–2.05635400	–0.90177900
C	–0.91831200	2.63580300	–0.79706200
C	2.47163300	–0.53729400	3.02172400
C	2.82957400	0.85983500	0.22197300
S	1.25533800	–2.11974800	0.47183900
C	–1.68076100	–3.18877100	–0.16832400
C	0.37143900	–2.61557100	–2.58656400
C	–1.08426900	–4.53942200	0.27632000
C	–2.25293400	–2.47652500	1.07292300
C	–2.81236200	–3.42457600	–1.18792500
C	1.62259000	–1.76250800	–2.88161500
C	–0.66433600	–2.38339300	–3.70765800
C	0.78412300	–4.09827500	–2.54600400
C	–4.04831900	1.06972400	–0.16215100
C	–5.37697100	1.10537800	0.25291300
C	–5.68145600	1.11041200	1.61413900
C	–4.65230000	1.08417500	2.55202400
C	–3.32310600	1.04290600	2.13029600
C	–0.00818400	2.76791000	–1.85900900
C	0.17658100	3.98631300	–2.50922600
C	–0.54250200	5.10906400	–2.10422100

C	–1.44476500	5.00612300	–1.04736500
C	–1.63267000	3.78323000	–0.40633400
C	2.78677300	2.26410200	0.17411800
C	3.73328400	2.98958100	–0.54749200
C	4.74208300	2.32487200	–1.24063700
C	4.80186100	0.93182100	–1.20938900
C	3.85748600	0.20995000	–0.48413000
C	1.49081600	–1.28945600	3.94446200
C	2.88215200	0.79324500	3.69809600
C	3.73395200	–1.39867300	2.80584200
H	–0.36194900	0.04187800	–1.95403200
H	–1.88304300	–5.11363800	0.75406900
H	–0.70680900	–5.13561400	–0.55219400
H	–0.28628600	–4.41366800	1.00901100
H	–2.97501500	–3.14997600	1.54293000
H	–2.78198700	–1.55649000	0.82740200
H	–1.48034100	–2.26104300	1.81329500
H	–2.49847400	–4.05322900	–2.02120900
H	–3.62247500	–3.95052700	–0.67515300
H	–3.23523300	–2.49764300	–1.58167400
H	1.99120300	–2.04171100	–3.87247000
H	2.41932300	–1.94321600	–2.16185400
H	1.41781700	–0.69022100	–2.90691500
H	–0.21099300	–2.70027300	–4.65113200
H	–1.57659800	–2.96384000	–3.57809100
H	–0.93332400	–1.33165100	–3.81921400
H	1.44476900	–4.32317500	–1.70599700
H	–0.07446200	–4.76917300	–2.51288700
H	1.33473400	–4.32499600	–3.46322200
H	–3.83948900	1.09495800	–1.22818700
H	–6.17322200	1.13885700	–0.48209300
H	–6.71466700	1.14231300	1.94022400
H	–4.88225400	1.09884100	3.61136300
H	–2.54321300	1.02739300	2.88418500
H	0.58585700	1.92186100	–2.18867000
H	0.88189700	4.05890600	–3.32933900
H	–0.40210800	6.05725500	–2.61045700
H	–2.00914700	5.87459600	–0.72733100
H	–2.35565200	3.72366800	0.40010800
H	2.01004000	2.80933800	0.69875600
H	3.67996000	4.07196900	–0.56806500

H	5.48010300	2.88824800	–1.80010000
H	5.58715100	0.40979600	–1.74440600
H	3.92743100	–0.87231600	–0.46722000
H	1.98738200	–1.52122400	4.89303400
H	1.15725200	–2.23612100	3.51145100
H	0.60699100	–0.69189200	4.18492600
H	3.35450700	0.57694400	4.66268000
H	3.60294000	1.35695000	3.10058700
H	2.02304800	1.44060200	3.89979800
H	3.50269100	–2.37340700	2.36599200
H	4.46909900	–0.90084600	2.16881800
H	4.21547500	–1.58827000	3.77162000
H	–1.98026300	–0.52624900	–1.64476700
C	–0.00656500	0.77860500	1.58171000
H	0.18739600	1.76625000	2.01786700
H	–0.52496500	0.20481900	2.35701200

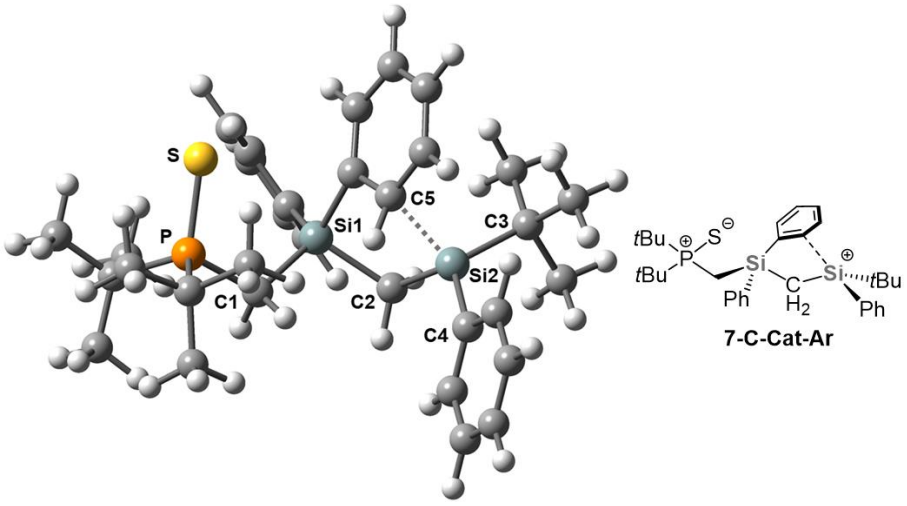


Figure S57. Optimized structure of compound **7-C-Cat-Ar** [B3LYP/6-311+G(d,p)]. Selected bond lengths [Å] and angles [°]: P–S 2.007, Si1–C2 1.915, Si2–C2 1.882, Si1–C2–Si2 109.9, Si2–C5 2.219, C2–Si2–C3 114.2, C2–Si2–C4 114.2, C3–Si2–C4 114.7 (Σ angles around Si2: 343.1°).

Table S10. Standard orientation of **7-C-Cat-Ar** [B3LYP/6-311+G(d,p)].

Atomic symbol	x	y	z
C	–2.66061000	4.99794700	–1.25060200
C	–2.90661900	4.28615000	–0.07744600
C	–1.75588700	4.49867800	–2.18465700
C	–2.25092000	3.08080200	0.16201300
C	–1.09064300	3.29890800	–1.93780800
C	–1.32162800	2.56558800	–0.76055300
C	–1.99121400	–3.89825800	–0.82098300

C	3.64422400	–3.11250900	–2.47472900
C	3.10803700	–1.88034400	–2.10401000
C	4.41868700	–3.83680200	–1.57216900
C	–0.90479000	–3.17930800	1.31382000
C	–4.47318200	–1.90228800	–1.90257800
C	–2.20943400	–3.12309600	0.49347000
C	–1.30004900	–0.65158300	–0.91828000
C	–3.33153300	–3.78433200	1.31523900
C	0.33276200	1.87713700	2.25857700
C	3.34321500	–1.33935200	–0.82677000
C	4.66148200	–3.32225300	–0.29898500
C	–4.30098100	–0.99580500	–0.67093700
C	0.43918000	0.90478200	1.26237100
C	1.12501700	1.81948900	3.40333200
C	4.13332900	–2.08741200	0.06635600
C	–5.45687800	–1.22767200	0.32151900
C	3.98772200	1.69581800	–0.07739900
C	–4.34336700	0.47850600	–1.11775600
C	1.45658400	–0.09829100	1.41993100
C	2.06282900	0.79333000	3.59835600
C	5.06740900	1.25750300	0.92999700
C	2.21413700	–0.17393700	2.62723900
H	–3.17430500	5.93401900	–1.43743600
H	–3.61628200	4.66571500	0.64907400
H	–1.56564800	5.04253700	–3.10289500
H	–2.48461100	2.52209100	1.06150400
H	3.45682500	–3.50402800	–3.46792800
H	–1.66338800	–4.91214500	–0.57086200
H	–1.21234800	–3.45804000	–1.44842600
H	–0.38907900	2.93683500	–2.68231600
H	–2.89598700	–3.99184400	–1.41799200
H	2.51296500	–1.33905100	–2.83095400
H	–0.54272900	–1.43635600	–0.99894600
H	4.83394500	–4.79594700	–1.85875900
H	–0.69003600	–4.22550200	1.55043700
H	–4.64504600	–2.94365400	–1.62958500
H	–0.04702700	–2.80053100	0.75024500
H	–3.62470700	–1.85788400	–2.59051600
H	–5.35429400	–1.56730700	–2.45841400
H	–0.38742900	2.67873300	2.15643500
H	–1.70270300	–0.52982000	–1.92906400

H	–3.00115700	–4.77937400	1.62817300
H	–0.98792600	–2.62256700	2.24728600
H	–4.24377000	–3.91605300	0.73233900
H	–5.54579400	–2.26847400	0.63118600
H	1.00726900	2.58063100	4.16725300
H	5.26647000	–3.88039700	0.40618800
H	–3.56732100	–3.21157200	2.21439200
H	–3.59194800	0.71933600	–1.87234400
H	–6.39397800	–0.94933800	–0.16993300
H	–5.32284700	0.67257900	–1.56466800
H	–5.34508200	–0.61176900	1.21486900
H	4.35079200	–1.70792100	1.05835600
H	5.57790300	0.34431800	0.61625400
H	–4.21981800	1.15947600	–0.27640200
H	1.29928900	–1.05186200	0.91308400
H	5.82780300	2.04218400	1.00737700
H	2.64189900	0.75252900	4.51280800
H	4.66068400	1.10259400	1.93210900
H	2.88904300	–1.00745000	2.78321200
P	–2.62850600	–1.26885200	0.22217200
S	–2.56051500	–0.25503500	1.95345800
Si	–0.38630500	0.96500700	–0.46299900
Si	2.65984200	0.35367100	–0.38947100
C	3.36382100	3.03089800	0.37421800
C	4.65136500	1.88524600	–1.46894500
H	3.94453600	2.22823600	–2.23000300
H	5.43025500	2.65090300	–1.38594800
H	5.13002300	0.97120700	–1.83056300
H	2.92297200	2.96010900	1.36955600
H	4.14436700	3.79847000	0.41359500
H	2.59421300	3.39323500	–0.31285900
C	1.23452500	0.91606500	–1.48223100
H	1.47041100	1.92824200	–1.82375100
H	1.14038700	0.29510700	–2.37609000

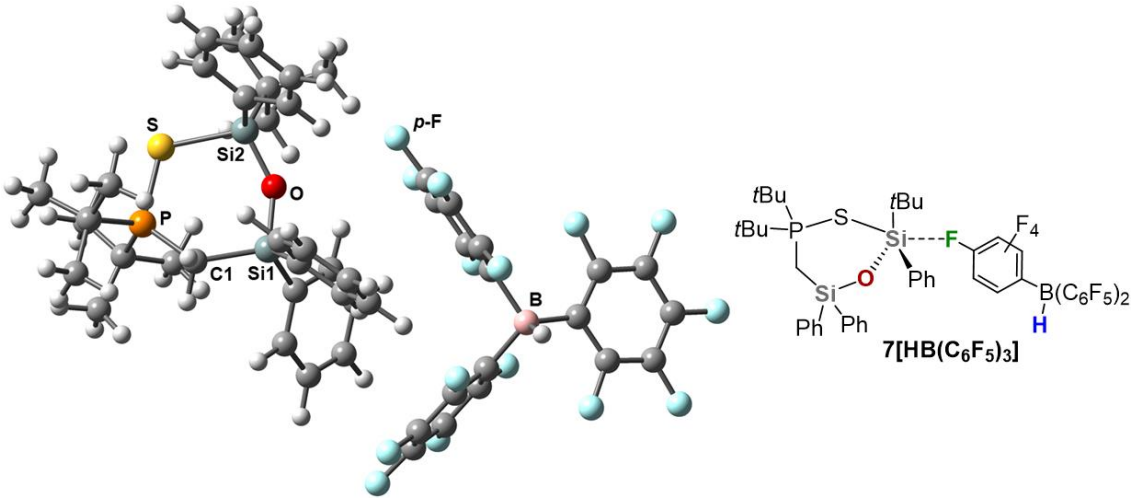


Figure S58. Optimized structure of compound **7[HB(C_6F_5)$_3$]** [B3LYP/6-31G(d)]. Selected bond lengths [Å]: Si1–O 1.669, Si2–O 1.638, Si2–S 2.271, Si2–(*p*-F) 4.049. Formal charges are omitted for clarity.

Table S11. Standard orientation of **7[HB(C_6F_5)$_3$]** [B3LYP/6-31G(d)].

Atomic symbol	x	y	z
Si	2.21236400	0.67255000	0.35968900
O	2.62430500	–0.65277700	–0.56762600
Si	3.85349400	–1.60093900	–1.09160800
C	3.86316200	1.64457700	0.67904600
C	0.97594500	1.70066600	–0.57534800
P	5.35437800	1.57121200	–0.38092800
C	1.59166400	0.17144700	2.04671600
C	3.50737800	–2.36525400	–2.79695800
C	4.40198000	–2.80942800	0.22664200
S	5.59108900	–0.19309000	–1.48918800
C	5.25122500	2.96142200	–1.68142400
C	6.84605000	1.65437000	0.80903100
C	6.36120100	2.81831500	–2.74307700
C	3.88117700	2.81695600	–2.37711800
C	5.34836200	4.35000500	–1.01589700
C	6.85712300	0.34630500	1.63150300
C	6.70706200	2.84925200	1.77804800
C	8.16932500	1.76235700	0.02728600
C	0.69150200	3.02857800	–0.19765900
C	–0.31760600	3.75435300	–0.82962000
C	–1.07092100	3.16072100	–1.84664600
C	–0.81067300	1.84470200	–2.22891100
C	0.20750100	1.12372300	–1.60272400
C	2.42722400	–0.45407800	2.99494800
C	1.93385900	–0.85541200	4.23439400
C	0.58944400	–0.64076100	4.55208900

C	–0.25673300	–0.02237700	3.63240200
C	0.24321100	0.38169000	2.39240000
C	3.44047900	–3.37834600	1.08633700
C	3.81047900	–4.33579100	2.03310300
C	5.14075700	–4.74403400	2.13763400
C	6.10591500	–4.19506600	1.29029400
C	5.73849500	–3.23774300	0.34484400
C	3.04614900	–1.29420000	–3.80661400
C	2.38503200	–3.41720800	–2.61716000
C	4.77995000	–3.06667300	–3.32271200
H	4.19020400	1.33278000	1.67543000
H	6.21690300	3.60993900	–3.48748200
H	7.36556100	2.93565100	–2.33112900
H	6.30772500	1.85957900	–3.26480300
H	3.83400300	3.55333100	–3.18798600
H	3.03883800	3.01176800	–1.71007300
H	3.74864500	1.82746600	–2.82383000
H	6.35723200	4.56808200	–0.65539200
H	5.10240800	5.10548600	–1.77079400
H	4.64347200	4.48408900	–0.18901600
H	7.69147100	0.40005500	2.34039500
H	7.00114500	–0.53612200	1.00479200
H	5.94496400	0.20312600	2.21962200
H	7.55213500	2.81819400	2.47553500
H	6.73942200	3.81579900	1.27161100
H	5.79291800	2.80234800	2.37705700
H	8.26541000	0.98352300	–0.73553500
H	8.29256700	2.73994200	–0.44645600
H	8.99949700	1.63692700	0.73208800
H	1.23887000	3.50002800	0.61816800
H	–0.55313300	4.76222600	–0.50046900
H	–1.88897500	3.70982900	–2.30197100
H	–1.42175800	1.36265600	–2.98565300
H	0.37194700	0.09143500	–1.89243500
H	3.47169000	–0.65604400	2.76136400
H	2.59266400	–1.34226800	4.94881300
H	0.20152900	–0.96091900	5.51522800
H	–1.30464300	0.13923000	3.85962700
H	–0.43351400	0.85567200	1.68767800
H	2.39693200	–3.08850300	1.01710800
H	3.05417100	–4.76166800	2.68634900

H	5.42523600	–5.49007500	2.87483700
H	7.14256500	–4.51257600	1.36533300
H	6.50398300	–2.82031700	–0.30526600
H	2.79090900	–1.77520500	–4.76027900
H	3.83112800	–0.55703500	–4.01183100
H	2.15509400	–0.76101600	–3.45930300
H	2.19649600	–3.90442900	–3.58339000
H	2.66387700	–4.20074900	–1.90373300
H	1.44433600	–2.97245200	–2.28276500
H	5.60553400	–2.36435000	–3.49504000
H	5.13205600	–3.84921000	–2.64079600
H	4.56014000	–3.54716600	–4.28531200
H	3.60333200	2.70691300	0.76494200
F	0.33354200	–3.30268100	–0.03852400
C	–0.82982500	–2.64480100	0.18207800
C	–1.41628700	–2.65988500	1.43830400
C	–1.43182900	–1.92736100	–0.84449300
C	–2.60290100	–1.95279700	1.64619600
C	–2.60329300	–1.22402500	–0.58756300
C	–3.24943100	–1.21727100	0.65102100
B	–4.61796000	–0.34832300	0.94632100
H	–4.94530400	–0.55832100	2.09027700
C	–5.91240100	–0.75112800	0.02402500
C	–7.08038300	0.01518900	0.10512700
C	–6.03421000	–1.87426700	–0.79560000
C	–8.26046100	–0.27569700	–0.57176500
C	–7.19524700	–2.20946300	–1.49367400
C	–8.32014900	–1.40354800	–1.38397500
C	–4.19942200	1.24469100	0.85568200
C	–3.55498700	1.85171900	1.93606600
C	–4.38597700	2.08579100	–0.24346100
C	–3.12665000	3.17761600	1.95189100
C	–3.99008700	3.42186700	–0.26813200
C	–3.34719100	3.97155900	0.83326800
F	–0.84733300	–1.89789000	–2.06859200
F	–3.11861800	–0.52266600	–1.62092800
F	–3.09087900	–2.00447100	2.90132200
F	–0.81981700	–3.33158700	2.44142400
F	–5.00191800	–2.73826500	–0.95680500
F	–7.23469200	–3.30952300	–2.26923900
F	–9.44869900	–1.70895200	–2.04726500

F	–7.10379700	1.12067300	0.88463400
F	–9.34201600	0.51534600	–0.44720000
F	–4.16157700	4.17397400	–1.37699200
F	–4.97038700	1.62929300	–1.37001900
F	–3.28973800	1.13685400	3.05842600
F	–2.48902300	3.69037100	3.02256900
F	–2.89830900	5.24256100	0.79637100

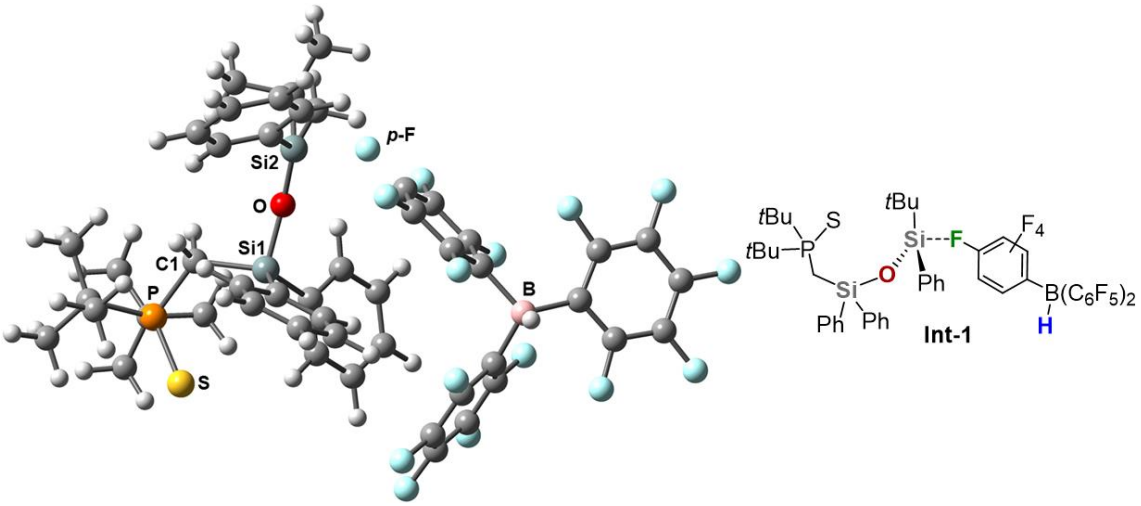


Figure S59. Optimized structure of compound **Int-1** [B3LYP/6-31G(d)]. Selected bond lengths [Å]: Si1–O 1.738, Si2–O 1.595, Si2–(*p*-F) 1.946. Formal charges are omitted for clarity.

Table S12. Standard orientation of **Int-1** [B3LYP/6-31G(d)].

Atomic symbol	x	y	z
Si	–2.49211800	–0.24950500	–0.18602700
O	–2.28558000	1.36010000	–0.80957500
Si	–2.19163900	2.95253900	–0.80807000
C	–4.35468800	–0.44284800	–0.57914000
C	–1.25436700	–1.27706700	–1.13569700
P	–5.22787100	–2.07939900	–0.39692400
C	–2.09001000	–0.17671900	1.63665100
C	–2.45216500	3.77827800	–2.48373900
C	–2.81636900	3.84341000	0.68943000
C	–6.94322200	–1.59421000	0.32854500
C	–5.37450400	–2.78353500	–2.17760900
C	–7.89177100	–2.80751200	0.26704800
C	–6.72202100	–1.23513900	1.81345100
C	–7.59932600	–0.38605700	–0.37196900
C	–3.96269000	–2.75626400	–2.79891700
C	–6.32993300	–1.98041600	–3.08059500
C	–5.83335300	–4.25462000	–2.11362500

C	–0.90407500	–2.56696800	–0.68614800
C	0.08967000	–3.30439800	–1.32973400
C	0.75971400	–2.76856700	–2.43231900
C	0.41904300	–1.49907800	–2.90004600
C	–0.58011300	–0.76423500	–2.25891300
C	–3.00933300	0.26981600	2.60397200
C	–2.64834600	0.38314500	3.94537300
C	–1.35321100	0.05263600	4.35062500
C	–0.42070300	–0.38985000	3.41203900
C	–0.78963000	–0.50225700	2.07035400
C	–2.10046400	4.87192500	1.33044700
C	–2.65882800	5.56093700	2.40612700
C	–3.94264200	5.24333600	2.85251200
C	–4.67002100	4.23075700	2.22456000
C	–4.11061900	3.53507100	1.15406300
C	–1.80282100	2.98083000	–3.63286400
C	–1.90893300	5.22467100	–2.46401100
C	–3.99123000	3.81165100	–2.68418300
H	–4.52465100	–0.05442100	–1.59083200
H	–8.79190500	–2.58806600	0.85479900
H	–8.21666300	–3.02997800	–0.75360400
H	–7.42494400	–3.70192000	0.69068900
H	–7.69155100	–0.98340400	2.26149700
H	–6.06769600	–0.36576000	1.94034200
H	–6.28387100	–2.06734000	2.36837400
H	–7.83485200	–0.57212900	–1.42116200
H	–8.54402300	–0.15914700	0.13828000
H	–6.98219800	0.51699900	–0.31732900
H	–4.00422900	–3.24742000	–3.77921700
H	–3.23567700	–3.29285400	–2.18493600
H	–3.58938500	–1.74068600	–2.96117000
H	–6.24090100	–2.35758500	–4.10715300
H	–7.37706900	–2.09346200	–2.78677800
H	–6.09122800	–0.91099200	–3.10967900
H	–5.17785700	–4.84573600	–1.46925300
H	–6.85791600	–4.36387200	–1.75026800
H	–5.79462200	–4.67619000	–3.12587300
H	–1.40923700	–2.99596500	0.17404100
H	0.36534800	–4.28376300	–0.95000300
H	1.56238200	–3.32986200	–2.90062700
H	0.94495800	–1.06989500	–3.74832500

H	–0.81378300	0.22946600	–2.62641100
H	–4.02453200	0.53081300	2.31673100
H	–3.37805700	0.72363200	4.67541500
H	–1.07230500	0.13722500	5.39698500
H	0.58817700	–0.65387100	3.71169000
H	–0.05325100	–0.85898900	1.35645100
H	–1.09481100	5.12525100	1.01161700
H	–2.08763800	6.34220700	2.89885300
H	–4.37473100	5.78238400	3.69084400
H	–5.66834800	3.97951600	2.57115600
H	–4.69062300	2.74537400	0.68178100
H	–2.03237100	3.47045700	–4.58821900
H	–2.18566400	1.95624900	–3.68449900
H	–0.71493100	2.93192400	–3.53656700
H	–2.17184000	5.72313000	–3.40568600
H	–2.33599600	5.81901500	–1.64825100
H	–0.81760500	5.25078900	–2.37462000
H	–4.42483000	2.80464900	–2.71920500
H	–4.50316300	4.38305700	–1.90121400
H	–4.21685600	4.29546800	–3.64327900
H	–4.85808500	0.25577100	0.10066000
F	–0.28903100	3.31002400	–0.60827400
C	0.81842700	2.49189200	–0.19615500
C	1.14411600	2.44769900	1.14607200
C	1.54455700	1.83322900	–1.17343800
C	2.26143300	1.68920500	1.50534900
C	2.63647200	1.08260700	–0.75007000
C	3.04907800	0.99163800	0.58416500
B	4.31764400	0.04716900	1.07124300
H	4.55668000	0.33372700	2.21898400
C	5.70166900	0.28925600	0.23241600
C	6.73984300	–0.64754500	0.26082300
C	6.02088100	1.46153600	–0.45428200
C	7.97365200	–0.46587700	–0.35851300
C	7.23955200	1.69135100	–1.09032700
C	8.22826800	0.71680400	–1.04477100
C	3.73117200	–1.49040700	1.04430000
C	3.02318300	–1.98803700	2.14098100
C	3.79960100	–2.36733000	–0.04095400
C	2.42112300	–3.24457800	2.18028800
C	3.22131700	–3.63388600	–0.04459600

C	2.51995100	–4.07530300	1.07066200
F	1.18407400	1.92082000	–2.46626200
F	3.30766800	0.43670300	–1.71444500
F	2.53618500	1.66814900	2.81716700
F	0.40378200	3.11192000	2.04513300
F	5.12632700	2.48192100	–0.53245500
F	7.46672700	2.84778100	–1.74020800
F	9.41135800	0.91504700	–1.64818300
F	6.58124100	–1.81317500	0.92619100
F	8.92173500	–1.41638000	–0.29495800
F	3.27590500	–4.41559700	–1.14193300
F	4.43838100	–2.00876100	–1.17389100
F	2.85361900	–1.22327500	3.24795800
F	1.73382800	–3.64628800	3.26376600
F	1.90498400	–5.27104000	1.05072000
S	–4.27160200	–3.33852800	0.80861200

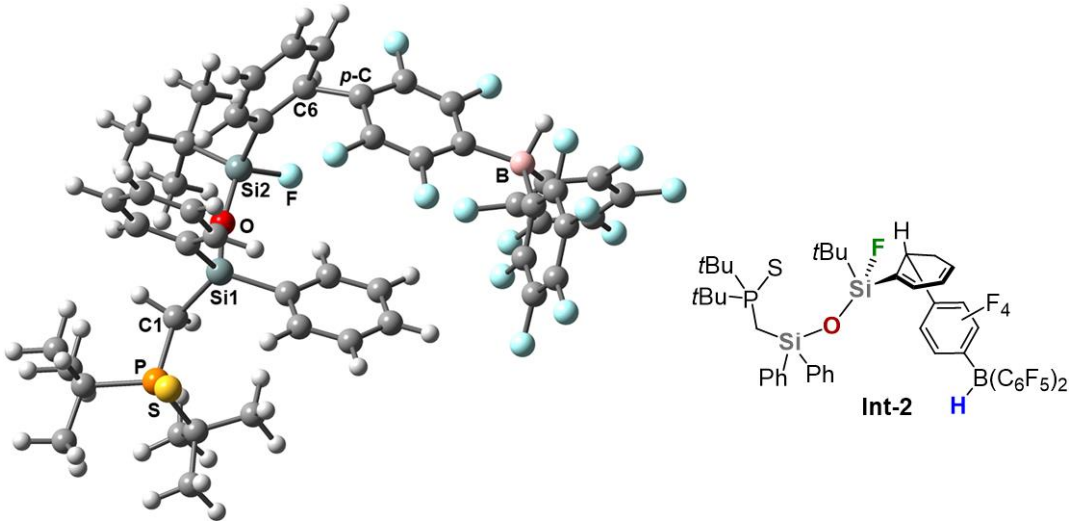


Figure S62. Optimized structure of compound **Int-2** [B3LYP/6-31G(d)]. Selected bond lengths [Å]: Si1–O 1.688, Si2–O 1.623, Si2–F 1.626, C6–(*p*-C) 1.621. Formal charges are omitted for clarity.

Table S15. Standard orientation of **Int-2** [B3LYP/6-31G(d)].

Atomic symbol	x	y	z
Si	3.36504700	–0.09772600	–0.15046000
O	2.95354300	1.36394800	0.58619900
Si	2.16174100	2.74786300	0.88912700
C	4.82049100	–0.60651700	0.97981400
C	1.84216200	–1.18600700	–0.15249700
P	5.76090600	–2.18987400	0.74186500
C	3.92127000	0.36286200	–1.89071700

C	3.31142700	4.03632900	1.65970700
C	1.23878400	3.34287300	–0.64771700
C	7.59815500	–1.66462200	0.97996700
C	5.15848600	–3.35908900	2.14061100
C	8.48642000	–2.91907300	1.09472200
C	8.01180700	–0.89357000	–0.29220500
C	7.83287100	–0.74955300	2.20003900
C	3.61687000	–3.38604100	2.08419800
C	5.59653000	–2.90451800	3.54533900
C	5.66763700	–4.78940600	1.87230600
C	1.77551600	–2.36690700	–0.91980100
C	0.61476500	–3.14126100	–0.94424900
C	–0.50644700	–2.75614300	–0.20659200
C	–0.45872300	–1.59491900	0.56702900
C	0.70410900	–0.82195900	0.59414200
C	5.05082900	1.17941500	–2.09244400
C	5.41763600	1.61659000	–3.36587100
C	4.65661400	1.24294300	–4.47629100
C	3.53062400	0.43739100	–4.30127600
C	3.16673300	0.00753100	–3.02310700
C	–0.10703900	3.92745200	–0.48989700
C	–0.81481700	4.44178300	–1.67893800
C	–0.15287500	4.33411800	–2.97525000
C	1.08850200	3.79611400	–3.06672500
C	1.78299300	3.30345200	–1.89940300
C	4.45570300	4.38338400	0.68408200
C	3.90236900	3.45317600	2.96292200
C	2.50724100	5.31430700	1.98693800
H	4.45917900	–0.54690600	2.01375800
H	9.53994900	–2.61913900	1.02832500
H	8.35573000	–3.43427500	2.05129800
H	8.28682800	–3.62760500	0.28485700
H	9.06379600	–0.59618900	–0.19567600
H	7.42403300	0.01971200	–0.43620500
H	7.90016100	–1.50741800	–1.18845000
H	7.60335900	–1.23187600	3.15159100
H	8.89397200	–0.47005700	2.22461000
H	7.25922800	0.18124100	2.14449400
H	3.25546800	–4.12632100	2.80890500
H	3.24940300	–3.67557300	1.09716800
H	3.16475000	–2.42585500	2.34995700

H	5.08595400	–3.52681100	4.29099200
H	6.67133700	–3.02657300	3.70488000
H	5.32980500	–1.86334600	3.75804900
H	5.36748500	–5.13543800	0.87994700
H	6.75475300	–4.87150100	1.94619800
H	5.23139400	–5.46279100	2.62083000
H	2.64400500	–2.69281200	–1.48572500
H	0.58603700	–4.04753100	–1.54381800
H	–1.41334400	–3.35159100	–0.23435800
H	–1.32765100	–1.28760000	1.14026500
H	0.71810100	0.07204000	1.21144400
H	5.66035700	1.48684200	–1.24505900
H	6.29858000	2.24069900	–3.49304200
H	4.94385300	1.57408700	–5.47097500
H	2.93520800	0.13871100	–5.16028700
H	2.28262900	–0.61230400	–2.90829200
H	–0.32932900	4.38730700	0.46820800
H	–1.52761300	5.25122100	–1.55211300
H	–0.65732600	4.74540900	–3.84417400
H	1.59377100	3.74809200	–4.02683000
H	2.77953400	2.89769400	–2.04676700
H	5.12397600	5.12943900	1.13564800
H	4.08169900	4.80763500	–0.25587700
H	5.06203400	3.50395700	0.43838100
H	4.57487800	4.18457200	3.43215000
H	3.11996900	3.20811500	3.69018400
H	4.48140300	2.54266800	2.77151900
H	2.07824900	5.77131300	1.08579600
H	1.69052700	5.11386700	2.69020800
H	3.16206000	6.06545700	2.44915600
H	5.54045900	0.21316900	0.87265000
C	–1.44144400	3.12194900	–0.93541300
C	–2.60604500	3.41459300	–0.14301000
C	–1.43735700	1.80767800	–1.51082800
C	–3.62495400	2.51916300	0.02985000
C	–2.48376100	0.93112000	–1.32120800
C	–3.62921300	1.22744000	–0.55143400
B	–4.95264500	0.30409700	–0.38886700
H	–5.79322700	1.02719000	–0.89406400
C	–5.38269300	0.09997100	1.17319600
C	–6.72260000	–0.10553000	1.50895100

C	–4.49764300	0.06993800	2.24848700
C	–7.16077800	–0.32483600	2.81348200
C	–4.88699800	–0.14380700	3.56771100
C	–6.23444200	–0.34194400	3.85217800
C	–4.94243900	–1.10824800	–1.19992600
C	–5.60195100	–1.26679900	–2.42026600
C	–4.31121000	–2.25815000	–0.72766900
C	–5.64115700	–2.47160200	–3.12290300
C	–4.31397100	–3.47720300	–1.39604200
C	–4.98742700	–3.58637800	–2.60890100
F	–0.39580200	1.42077100	–2.24028700
F	–2.35317700	–0.26433500	–1.91208400
F	–4.66548400	2.91506300	0.77324800
F	–2.67120100	4.62925600	0.42153400
F	–3.16778200	0.26135100	2.03953700
F	–3.98268400	–0.15774400	4.56107100
F	–6.63597000	–0.54716400	5.11459000
F	–7.66488900	–0.10432800	0.54647600
F	–8.46242500	–0.51549900	3.07956000
F	–3.64767900	–4.53597200	–0.89736000
F	–3.61700900	–2.21724400	0.43639000
F	–6.23783900	–0.22520700	–2.99387200
F	–6.29128000	–2.56303200	–4.29430700
F	–5.00075000	–4.74957700	–3.27446300
S	5.48691200	–3.00995500	–1.05456600
F	0.95918100	2.47783200	1.94976600

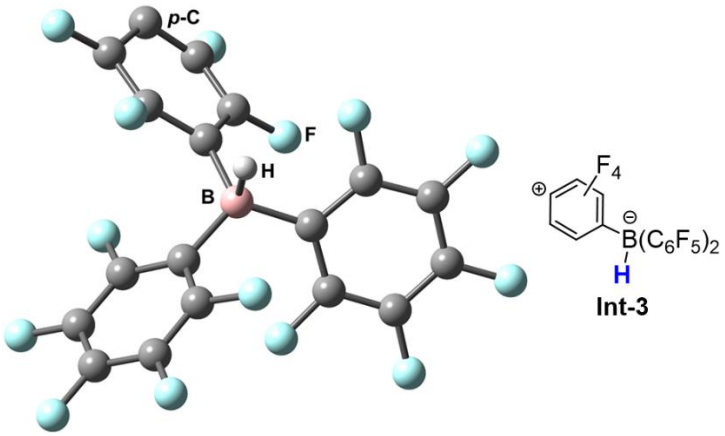


Figure S60. Optimized structure of compound **Int-3** [B3LYP/6-31G(d)].

Table S13. Standard orientation of **Int-3** [B3LYP/6-31G(d)].

Atomic symbol	x	y	z
C	2.85448700	2.17447500	0.83802100
C	3.98280000	1.67198500	0.18759500
C	1.61774500	1.57475800	0.62688700
C	–3.44424600	1.11443200	0.85980200
C	3.85880000	0.57066500	–0.65668300
C	–2.32243800	0.32259400	0.63465000
C	–3.58571700	2.31160900	0.15964700
C	1.43414600	0.46881100	–0.21513700
C	2.60485000	0.00125400	–0.83763400
C	–1.30474200	0.66282000	–0.25859500
C	–2.60129400	2.69606500	–0.74755500
C	0.83148100	–2.55499300	0.48383600
C	0.53096900	–3.91362400	0.75856000
C	–1.49696900	1.87232900	–0.93899900
C	–0.09674900	–1.78284600	–0.18835900
C	–0.47153100	–4.58804600	0.08012400
C	–1.19882500	–2.53887500	–0.71003200
C	–1.51739100	–3.90649600	–0.42640400
B	0.01827500	–0.21438700	–0.54842200
F	2.97918800	3.22140000	1.66061300
F	5.17357800	2.23839000	0.38194400
F	–4.38355300	0.74147300	1.73771100
F	0.57895000	2.10012500	1.30090000
F	–2.24620800	–0.82377900	1.35435800
F	4.93828600	0.07903000	–1.27652100
F	1.86388700	–2.02763300	1.14655400
F	1.13195200	–4.47180500	1.79738700
F	–2.73037200	3.84295700	–1.42521500
F	2.53806300	–1.06730800	–1.65501800
F	–0.57333500	2.28784100	–1.82449000
F	–1.86063700	–2.04209600	–1.73514300
F	–2.54854400	–4.43480000	–1.08419300
H	0.03017500	–0.39552900	–1.77989000
F	–4.65834500	3.08131300	0.35707300

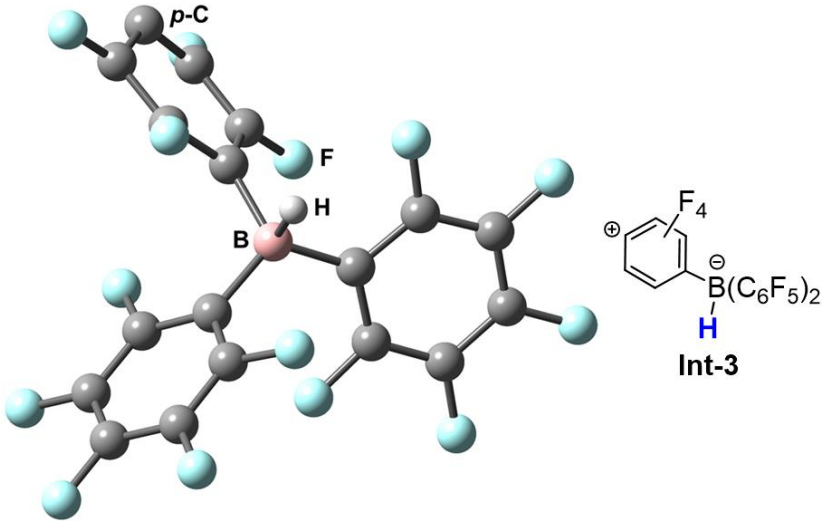


Figure S61. Optimized structure of compound **Int-3** [B3LYP/6-311+G(d,p)].

Table S14. Standard orientation of **Int-3** [B3LYP/6-311+G(d,p)].

Atomic symbol	x	y	z
C	–3.25343900	–1.21060700	–1.06387900
C	–3.56291800	–2.27591500	–0.22593100
C	–2.13380000	–0.43741700	–0.78991400
C	0.34945000	3.83927900	–0.88875800
C	–2.74488700	–2.55200000	0.86504300
C	0.71545200	2.50652100	–0.57859700
C	–0.60004700	4.51697300	–0.14970000
C	–1.27990100	–0.67489600	0.28722100
C	–1.63342600	–1.75510800	1.09932600
C	–0.11148300	1.75521300	0.22719700
C	–1.56107400	3.85077500	0.50675100
C	1.66558600	–1.57145900	–0.57502000
C	2.90897100	–2.14604800	–0.79502700
C	–1.17814500	2.50802400	0.82364300
C	1.46813300	–0.46667400	0.26204700
C	4.03071700	–1.61890800	–0.15976900
C	2.63276700	0.02606700	0.87093200
C	3.89174900	–0.51969800	0.68131900
B	0.04435100	0.19629200	0.60513200
F	–4.03104700	–0.94742900	–2.12012000
F	–4.63654400	–3.02836300	–0.46658800
F	0.79899000	4.35130900	–2.02039500
F	–1.86825300	0.56997400	–1.65547200
F	1.68778600	1.96240300	–1.31098100
F	–3.04139200	–3.57588200	1.67199600
F	0.63003300	–2.11934300	–1.23543400

F	3.04758000	–3.19283600	–1.61303400
F	–2.53456500	4.39863700	1.22950200
F	–0.87025100	–2.06771700	2.16243200
F	5.22914100	–2.15988400	–0.36249100
F	–1.69763700	2.05607800	1.94286400
F	2.55235300	1.09553800	1.68600300
F	4.96705400	–0.00667000	1.28737600
H	0.05676900	0.35145700	1.83211500

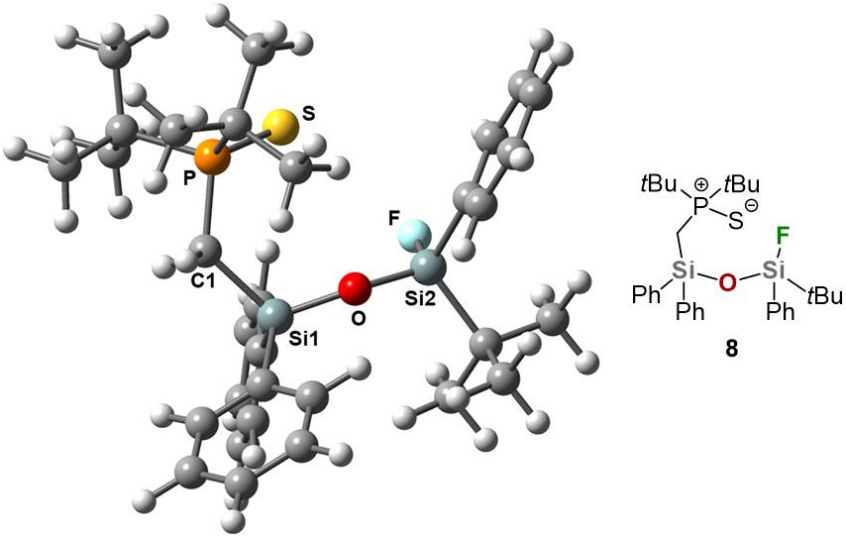


Figure S63. Optimized structure of compound **8** [B3LYP/6-31G(d)]. Selected bond lengths [Å] and angles [°]: P–S 1.990, Si1–O 1.660, Si2–O 1.654, Si1–O–Si2 148.7, Si2–F 1.620.

Table S16. Standard orientation of **8** [B3LYP/6-31G(d)].

Atomic symbol	x	y	z
C	0.73340700	–3.52972600	4.41885200
C	–0.18851300	–4.04998500	3.50793400
C	1.43803600	–2.36821300	4.10085100
C	–0.39969800	–3.40940800	2.28623600
C	1.22365700	–1.73353000	2.87527700
C	0.30525200	–2.24038000	1.93892600
C	–3.59630100	1.63780600	2.36065400
C	2.46920000	4.21532900	1.60215500
C	2.40515500	2.87570000	1.21649300
C	2.34461600	5.22315800	0.64368300
C	–1.16180000	1.96365200	1.86128800
C	–5.08459700	–0.61295600	0.31687900
C	–2.58199100	2.00015600	1.25934800
C	–1.87077200	–0.78396100	0.45696900
C	–2.85712100	3.43057900	0.75489400

C	0.62154600	–3.80242700	–1.03142500
C	2.21679200	2.51192500	–0.13025400
C	2.15290600	4.88493500	–0.69674500
C	–4.36990000	0.26277700	–0.73318500
C	0.11760600	–2.49488100	–1.16172000
C	0.74101200	–4.64533600	–2.13843700
C	2.09038100	3.54363400	–1.07814800
C	–5.21379400	1.51732500	–1.02974800
C	3.89915500	–0.10213600	–0.63186300
C	–4.23892800	–0.55323500	–2.03820100
C	–0.25686200	–2.05721000	–2.44845900
C	0.36107600	–4.19411400	–3.40293100
C	4.85935300	0.73539400	–1.50845600
C	–0.13537100	–2.89771800	–3.55577900
H	0.90001700	–4.02708600	5.37091000
H	–0.74161900	–4.95438400	3.74883800
H	2.15520000	–1.95580200	4.80621900
H	–1.12041600	–3.83647400	1.59119400
H	2.61375400	4.47267200	2.64853400
H	–3.42219300	2.29109000	3.22532900
H	–3.49190500	0.60542300	2.71209900
H	1.77459700	–0.82662500	2.64302500
H	–4.63136700	1.79274700	2.04275700
H	2.49239200	2.10662400	1.98098400
H	–2.15249000	–0.84751400	1.51470900
H	2.39386600	6.26758100	0.94145100
H	–1.08456700	2.74991000	2.62313800
H	–5.24854000	–0.09923800	1.26580200
H	–0.94191300	1.01086900	2.35405000
H	–4.54583300	–1.54350800	0.52101700
H	–6.07054400	–0.89238900	–0.07640100
H	0.92854000	–4.16989700	–0.05576900
H	–2.40702600	–1.59913900	–0.04341900
H	–2.77080200	4.12501400	1.60046200
H	–0.39324800	2.14998000	1.10865300
H	–3.86060100	3.53997700	0.33491100
H	–5.46545200	2.07332900	–0.12135400
H	1.13329300	–5.65155100	–2.01300100
H	2.04709800	5.66559000	–1.44576000
H	–2.13510700	3.72500700	–0.01049100
H	–3.62565300	–1.45262000	–1.91193200

H	–6.15886400	1.21246200	–1.49740500
H	–5.23968400	–0.87779700	–2.35133500
H	–4.69829100	2.19118900	–1.72115500
H	1.92794000	3.29410600	–2.12278400
H	4.95175400	1.76601600	–1.14613700
H	–3.79679300	0.04344800	–2.83888000
H	–0.63272900	–1.04585200	–2.58771500
H	5.86383000	0.28894300	–1.49844500
H	0.45424200	–4.84844200	–4.26622500
H	4.52474300	0.77439600	–2.55144300
H	–0.42601000	–2.53769900	–4.53943000
O	1.08070400	–0.11212300	0.21843800
P	–2.58814400	0.78442600	–0.22423100
S	–1.60920900	1.54156000	–1.78262700
Si	–0.03487800	–1.33740500	0.31566400
Si	2.18742300	0.72376100	–0.68337700
C	3.81973100	–1.53465700	–1.20139200
C	4.44978600	–0.15681200	0.80872000
H	3.81473400	–0.76237300	1.46585600
H	5.45056900	–0.61210000	0.81195900
H	4.54590200	0.84234000	1.25037100
H	3.42596500	–1.54725300	–2.22370800
H	4.82265100	–1.98523600	–1.22357500
H	3.18182300	–2.18461800	–0.59286300
F	1.74320700	0.72349100	–2.24128400

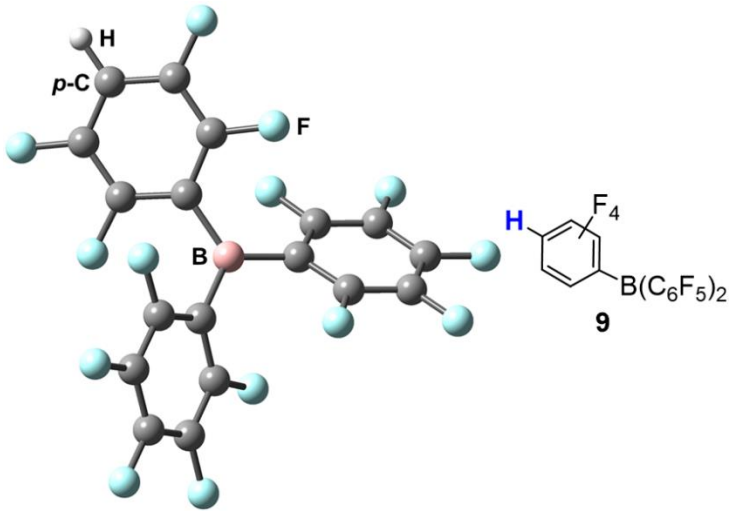


Figure S64. Optimized structure of compound **9** [B3LYP/6-31G(d)].

Table S17. Standard orientation of **9** [B3LYP/6-31G(d)].

Atomic symbol	x	y	z
C	–3.82980500	–1.99682600	0.00848800
C	–3.69724700	–0.81526800	0.73467700
C	–2.74762600	–2.49057700	–0.71723700
C	–2.48347900	–0.13768800	0.71452400
C	–1.54333600	–1.79684700	–0.69703600
C	–1.36016900	–0.59704400	0.00863600
C	–0.91652900	2.50031600	–0.75509500
C	–0.00033200	1.75444600	0.00001700
C	–0.91458000	3.89167100	–0.76733900
C	1.36045900	–0.59652600	–0.00860000
C	0.91551300	2.50073400	0.75514500
C	1.54417700	–1.79611900	0.69729200
C	–0.00098000	4.60275700	0.00001400
C	2.48349400	–0.13691600	–0.71476900
C	0.91293600	3.89208800	0.76737900
C	2.74872500	–2.48940200	0.71745700
C	3.69750600	–0.81405600	–0.73496300
C	3.83061100	–1.99540800	–0.00853900
B	–0.00000500	0.18351800	0.00003400
F	–4.98843900	–2.65339900	0.00867800
F	–4.73220800	–0.34677200	1.43921300
F	–2.87682400	–3.61994700	–1.42068400
F	–2.41082900	0.98796100	1.44280200
F	–0.53891500	–2.31372900	–1.42367400
F	–1.82363900	1.87292500	–1.52593100
F	–1.80900600	4.54259400	–1.52564400
F	0.54006600	–2.31322100	1.42419800
F	2.41032400	0.98853200	–1.44330300
F	1.82288500	1.87376200	1.52601300
F	1.80705500	4.54342000	1.52569300
F	2.87844400	–3.61857600	1.42112100
F	4.73218400	–0.34533800	–1.43976700
F	4.98948400	–2.65155800	–0.00877100
H	–0.00122600	5.68652200	0.00001200

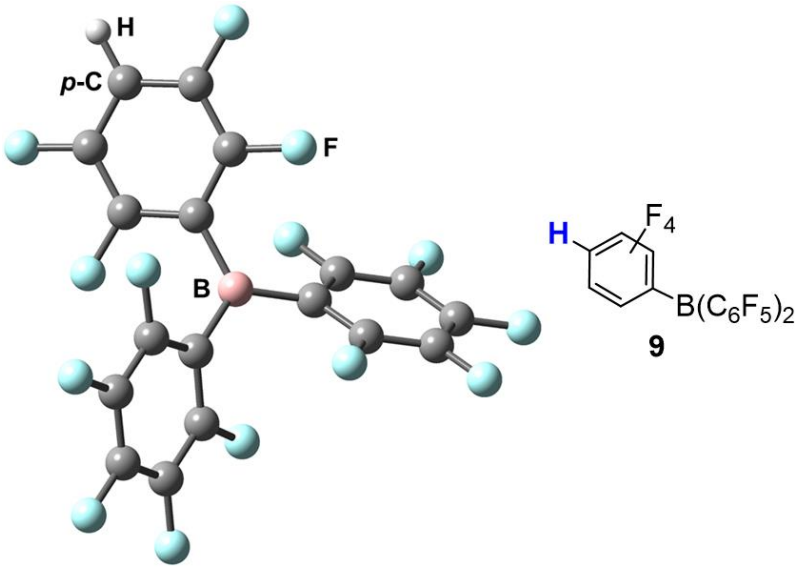


Figure S65. Optimized structure of compound **9** [B3LYP/6-311+G(d,p)].

Table S18. Standard orientation of **9** [B3LYP/6-311+G(d,p)].

Atomic symbol	x	y	z
C	–3.82494100	–1.98816600	0.00516500
C	–3.66882100	–0.84932700	0.78776600
C	–2.76744000	–2.44329800	–0.77506700
C	–2.45780400	–0.17357000	0.76786900
C	–1.56294300	–1.75654400	–0.75114600
C	–1.36038100	–0.59769700	0.00842200
C	–0.86330900	2.49400100	–0.81203100
C	0.00067900	1.75141800	–0.00002600
C	–0.85680000	3.88163200	–0.82378400
C	1.35979000	–0.59876100	–0.00850500
C	0.86538000	2.49317900	0.81196700
C	1.56124000	–1.75809300	0.75060700
C	0.00198800	4.59076600	0.00002000
C	2.45777100	–0.17508700	–0.76738300
C	0.86014000	3.88081600	0.82377800
C	2.76520900	–2.44577100	0.77458100
C	3.66828800	–0.85174500	–0.78721600
C	3.82329800	–1.99107900	–0.00511400
B	0.00001400	0.18123800	–0.00006600
F	–4.98303800	–2.64099700	0.00344000
F	–4.68095400	–0.42084500	1.54528900
F	–2.92207900	–3.53111400	–1.53309800
F	–2.35601400	0.91290000	1.55039100
F	–0.57735800	–2.23260300	–1.52981500
F	–1.71580600	1.86119600	–1.63967900

F	–1.69502800	4.53921100	–1.63976800
F	0.57503800	–2.23374900	1.52874400
F	2.35704200	0.91187900	–1.54935700
F	1.71733600	1.85955400	1.63954500
F	1.69899500	4.53759300	1.63976400
F	2.91879000	–3.53405100	1.53216000
F	4.68099100	–0.42365100	–1.54419700
F	4.98090400	–2.64478000	–0.00332200
H	0.00248500	5.67288400	0.00003700

5. References

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