Supporting Information

1,1-Carboboration Reactions of Strongly Electrophilic 2-Borylethyl Thioethers

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General Information:

All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried and stored under an argon atmosphere. The following instruments were used for physical characterization of the compounds: *Varian* Inova 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz, ^{31}P: 202 MHz), *Varian* UnityPlus 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz, ^{31}P: 243 MHz). ^{1}H NMR and ^{13}C NMR: chemical shift δ is given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shift δ is given relative to $CFCl_3$ (external reference); ^{11}B NMR: chemical shift δ is given relative to $BF_3{\cdot}Et_2O$ (external reference). NMR assignments are supported by additional 2D NMR experiments. Elemental analyses were performed on a *Elementar Vario El III*. IR spectra were recorded on a *Varian* 2100 FT-IR (Excalibur Series). Melting points were obtained with a DSC Q20 (*TA Instruments*).

X-Ray diffraction: Data sets for compounds **6a** and **7** were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (R. W. W. Hooft, Bruker AXS, **2008**, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). Data sets for compound **4a** were collected with a D8 Venture Dual Source 100 CMOS diffractometer and for compound **4c** with a Kappa CCD APEXII Bruker diffractometer. Programs used: data collection APEX2 V2014.5-0 (Bruker AXS Inc., Madison, Wisconsin, USA, 2014); cell refinement SAINT V8.34A (Bruker AXS Inc., Madison, Wisconsin, USA, 2013); data reduction SAINT V8.34A (Bruker AXS Inc., Madison, Wisconsin, USA, 2013); absorption correction SADABS V2014/2 (Bruker AXS Inc., Madison, Wisconsin, USA, 2014); structure solution SHELXT-2014 (G. M. Sheldrick, *Acta Cryst.*, **2008**, A64**,** 112–122); structure refinement SHELXL-2014 (G. M. Sheldrick, *Acta Cryst.*, **2008**, A64, 112–122) and graphics, XP (G. M. Sheldrick, **1998,** *XP*. Bruker AXS Inc., Madison, Wisconsin, USA). *Exceptions and special features*: Thermal ellipsoids are shown with 50% (**4a, 4b**) and 30% (**6a, 7**) probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections. For compound **4c** one disordered over two positions half dichloromethane molecule was found in the asymmetrical unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

CCDC 1020239 to 1020242 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

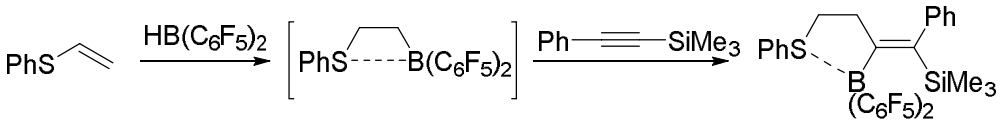
Materials:

The phosphanes were synthesized according to a modified literature procedure: A. Samb, B. Demerseman, P. H. Dixneuf, C. Mealli, *Organometallics* **1988**, *7*, 26-33.

Bis(pentafluorophenyl)borane was synthesized according to a modified literature procedure: D. J. Parks, R. E. von H. Spence, W. E. Piers, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 809-811; W. E. Piers, T. Chivers, *Chem. Soc. Rev.* **1997**, *26*, 345-354.

Phenylvinylsulfide and ethylvinylsulfide were purchased from *Sigma Aldrich* and *TCI*.

Synthesis of compound 4a



Bis(pentafluorophenyl)borane (56.1 mg, 0.162 mmol, 1.0 eq) in toluene (5 mL) was added to a solution of phenylvinylsulfide (22.1 mg, 0.162 mmol, 1.0 eq) in toluene (5 mL) to give a white suspension, which was stirred for 30 min at room temperature. Thereafter trimethylsilylphenylacetylene (28.3 mg, 31.8 µL, 0.162 mmol, 1.0 eq) was added and the light yellow reaction mixture was stirred at 80 °C for overnight. Subsequently all volatiles were removed *in vacuo* and pentane (5 mL) was added to the yellow residue. Then, immediately after the addition of pentane (5 mL), all volatiles were removed *in vacuo* and pentane (5 mL) was added again to finally give a white precipitate. The supernatant solution of the suspension was removed and the white solid was dried *in vacuo* to give compound **4a** (61.4 mg, 0.094 mmol, 58%) as a white powder. Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a dichloromethane solution of compound **6a** at -32°C.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2405 (w), 1700 (w), 1645 (m), 1596 (w), 1519 (s), 1468 (s), 1376 (w), 1292 (m), 1248 (m), 1111 (s), 1089 (m), 1027 (w), 985 (s), 968 (s), 918 (m), 885 (m), 839 (s), 808 (m), 775 (m), 745 (s), 703 (m), 688 (m), 659 (s), 631 (w), 576 (w), 517 (m), 479 (w).

Elemental analysis for $C_{31}H_{23}BF_{10}SSi$: calcd. C 56.72% H 3.53%; found C 56.33% H 3.33%.

Melting point: 198 °C.

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.35 (m, 1H, *p*-Ph^S), 7.31 (m, 2H, *m*-Ph), 7.23 (m, 2H, *m*-Ph^S), 7.17 (m, 1H, *p*-Ph), 7.11 (m, 2H, *o*-Ph^S), 6.96 (m, 2H, *o*-Ph), 3.17 (m, 2H, SCH_2), 3.05 (m, 2H, CH_2), –0.42 (s, $^{2}J_{SiH}$ = 6.6 Hz, 9H, $SiCH_3$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 158.4 (br, BC=), 149.4 (*i*-Ph), 148.9 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 148.1 (br, =CSi), 141.0 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 137.5 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 130.7 (*p*-Ph^S), 130.5 (*i*-Ph^S), 130.0 (*o*-Ph^S), 129.5 (*m*-Ph^S), 128.4 (*m*-Ph), 127.3 (*o*-Ph), 125.2 (*p*-Ph), 116.9 (br, *i*-C_6F_5), 42.3 (CH_2), 38.2 (SCH_2), 0.2 ($^{1}J_{SiC}$ = 52.3 Hz, $SiCH_3$).

^{1}H{^{1}H} 1D-TOCSY (500 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 7.23 / 7.35, 7.11 (*m*-Ph^S / *p*-Ph^S, *o*-Ph^S), 7.17 / 7.31, 6.96 (*p*-Ph / *m*-Ph, *o*-Ph), 3.17 / 3.05 (SCH_2 / CH_2).

^{1}H{^{1}H} NOE-DIFF (500 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 7.11 / 7.23, 3.17, 3.05 (*o*-Ph^{S} / *m*-Ph^{S}, SCH_2, CH_2), 6.96 / 7.31, 3.05, –0.42 (*o*-Ph / *m*-Ph, CH_2, $Si(CH_3)_3$), 3.17 / 7.11, 3.05 (SCH_2 / *o*-Ph^{S}, CH_2), 3.05 / 7.11, 6.96, 3.17 (CH_2 / *o*-Ph^{S}, *o*-Ph, SCH_2), –0.42 / 6.96 ($SiCH_3$ / *o*-Ph).

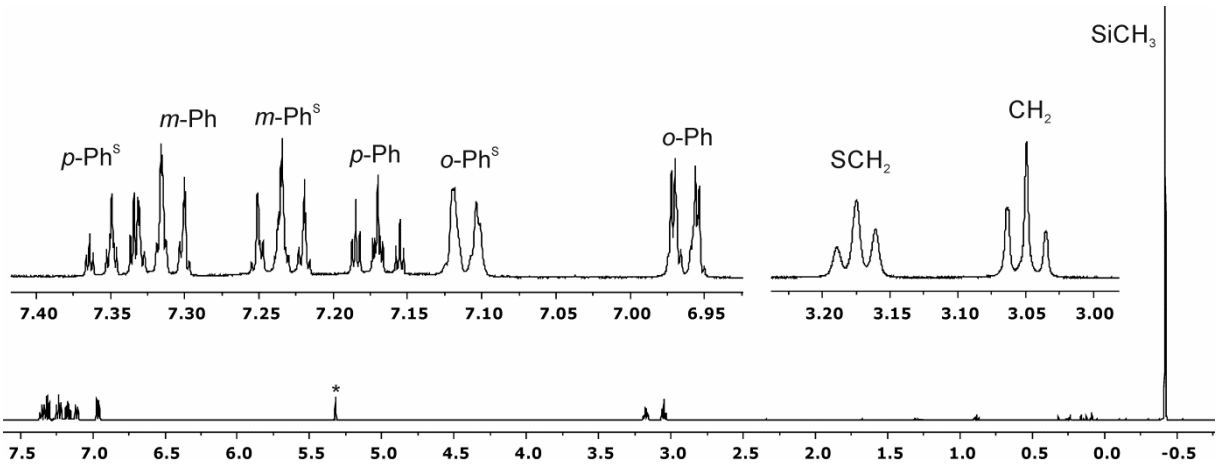
^{1}H, ^{13}C GHSQC (500 MHz / 125 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.35 / 130.7 (*p*-Ph^{S}), 7.31 / 128.4 (*m*-Ph), 7.23 / 129.5 (*m*-Ph^{S}), 7.17 / 125.2 (*p*-Ph), 7.11 / 130.0 (*o*-Ph^{S}), 6.96 / 127.3 (*o*-Ph), 3.17 / 38.2 (SCH_2), 3.05 / 42.3 (CH_2), –0.42 / 0.2 ($SiCH_3$).

^{1}H, ^{13}C GHMBC (500 MHz / 125 MHz, 299 K, CD_2Cl_2)[selected traces]: δ ^{1}H / δ ^{13}C = 7.31 / 149.4, 128.4 (*m*-Ph / *i*-Ph, *m*-Ph), 7.23 / 130.5, 129.5 (*m*-Ph^{S} / *i*-Ph^{S}, *m*-Ph^{S}), 6.96 / 148.1, 127.3, 125.2 (*o*-Ph / =CSi, *o*-Ph, *p*-Ph), 3.17 / 158.4, 130.5, 42.3 (SCH_2 / BC=, *i*-Ph^{S}, CH_2), 3.05 / 158.4, 148.1, 38.2 (CH_2 / BC=, =CSi, SCH_2), –0.42 / 148.1, 0.2 ($SiCH_3$ / =CSi, $SiCH_3$).

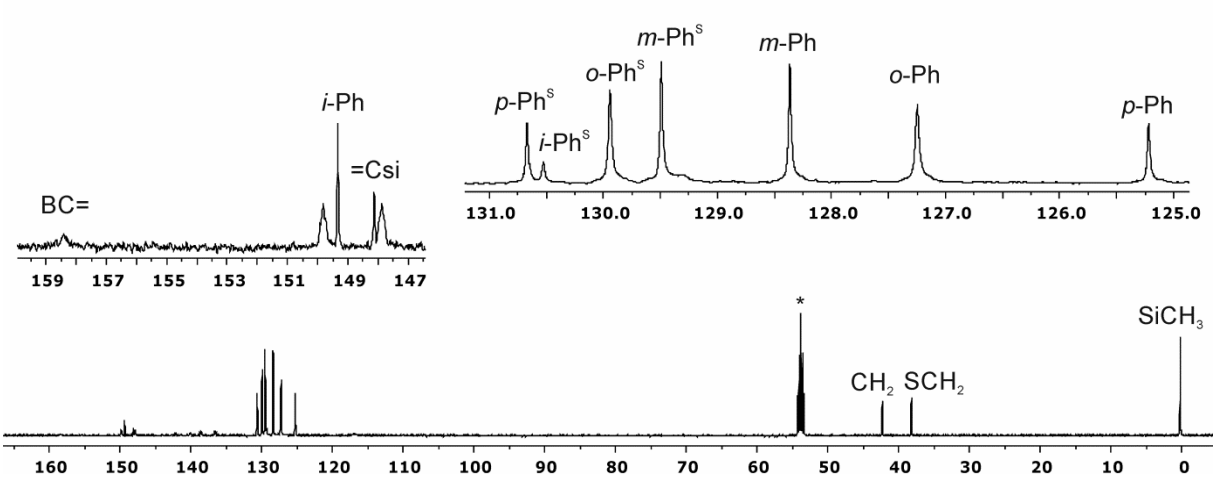
^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = 8.4 ($\nu_{1/2}$~400 Hz)

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = –127.2 (br, 2F, *o*-C_6F_5), –156.4 (tm, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-C_6F_5), –164.5 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 8.1].

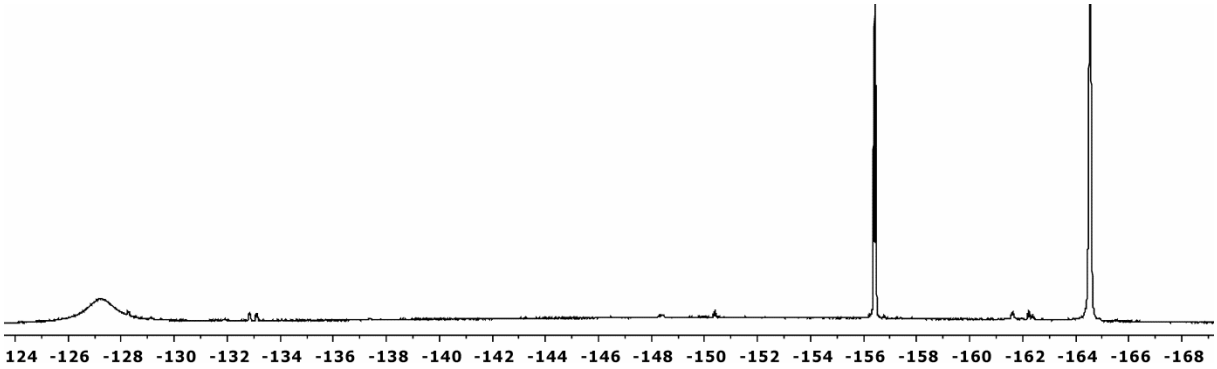
^{29}Si{^{1}H} DEPT (99 MHz, 299 K, CD_2Cl_2): δ = –8.6 ($\nu_{1/2}$~2 Hz).



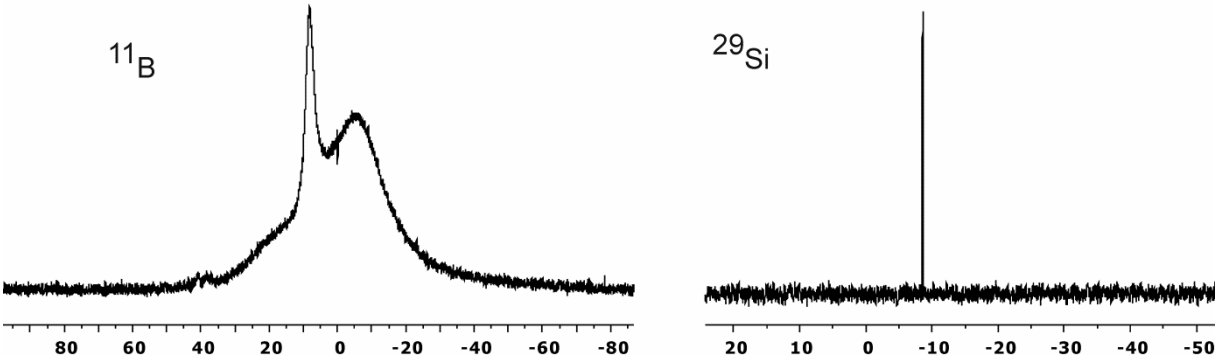
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2 (*)) of **4a**.



^{13}C{^{1}H} NMR (125 MHz, 299 K, CD_2Cl_2 (*))of **4a**.

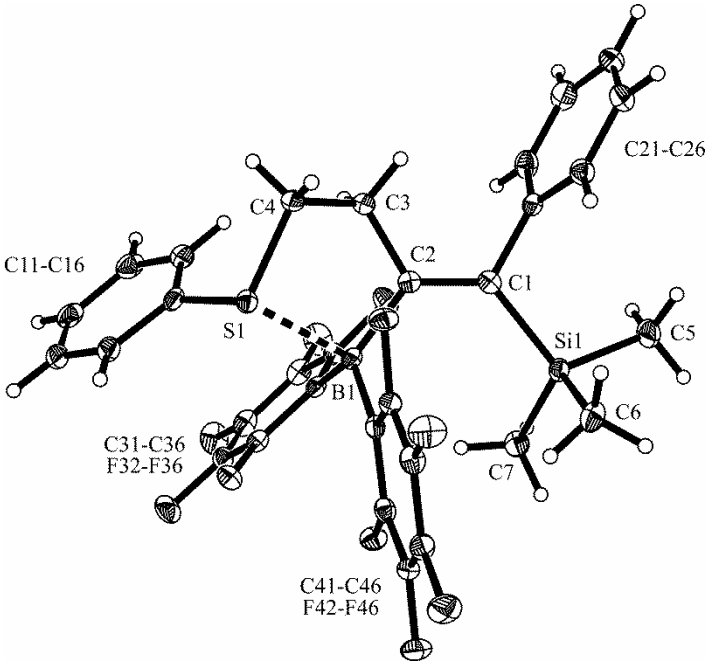


^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of **4a**.

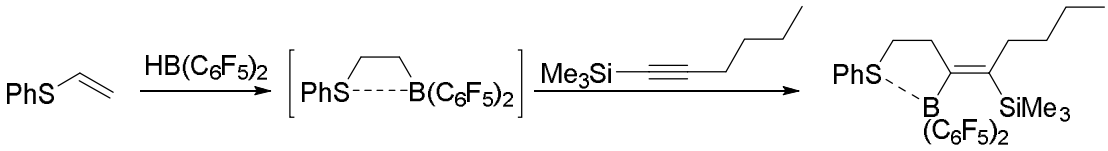


$^{11}B\{^1H\}$ (160 MHz, 299 K, CD_2Cl_2) and $^{29}Si\{^1H\}$ DEPT (99 MHz, 299 K, CD_2Cl_2) of **4a.**

X-ray crystal structure analysis of compound 4a: formula $C_{31}H_{23}BF_{10}SSi$, *M* = 656.45, colourless crystal, 0.20 x 0.20 x 0.10 mm, *a* = 10.8146(3), *b* = 13.0830(3), *c* = 20.1222(5) Å, β = 96.7600(9)°, V = 2827.25(12) $Å^3$, ρcalc = 1.542 g/cm^{-3}, μ = 2.230 mm-1, empirical absorption correction (0.664 ≤ T ≤ 0.808), Z = 4, monoclinic, space group P21/n (No. 14), λ = 1.54178 Å, T = 100(2) K, ω and ϕ scans, 56136 reflections collected to a maximum θ angle of 68.39° (0.83 Å resolution), 5171 independent (Rint = 0.041) and 4758 observed reflections [I>2σ(I)], 400 refined parameters, R = 0.029, wR^2 = 0.076, max. (min.) residual electron density 0.35 (-0.20) $e.Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.



Synthesis of compound 4b



NMR-Scale Experiment:

Bis(pentafluorophenyl)borane (28.0 mg, 0.081 mmol, 1.0 eq) in toluene-d_8 (0.5 mL) was added to a solution of phenylvinylsulfide (11.0 mg, 0.081 mmol, 1.0 eq) in toluene-d_8 (0.5 mL) to give a suspension, which was stirred for 20 min at room temperature. Thereafter trimethylsilylhexyne (12.6 mg, 16.4 µL, 0.081 mmol, 1.0 eq) was added and the light yellow reaction mixture was stirred at 50 °C for 15 h and then at 90 °C for 4 h. Thereafter the reaction mixture was characterized by NMR-experiments.

^{1}H NMR (600 MHz, 299 K, C_7D_8): δ = 6.69 (m, 1H, *p*-Ph), 6.59 (m, 4H, *o*,*m*-Ph), 2.94 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, CH_2), 2.55 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, SCH_2), 2.23 (m, 2H, $^{=}CH_2^{Bu}$), 1.35 (m, 4H, CH_2^{Bu}), 0.95 (m, 3H, CH_3^{Bu}), −0.21 (s, $^{2}J_{SiH}$ = 6.4 Hz, 9H, $SiCH_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_7D_8): δ = 156.4 (br, BC=), 149.0 (dm, $^{1}J_{FC}$ ~ 242 Hz, C_6F_5), 144.4 (=CSi), 141.2 (dm, $^{1}J_{FC}$ ~ 251 Hz, C_6F_5), 137.7 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 130.7 (*i*-Ph), 130.0 (*p*-Ph), 129.4 (*o*-Ph), 129.0 (*m*-Ph), 117.1 (br, *i*-C_6F_5), 38.7 (CH_2), 37.3 (SCH_2), 36.2 ($^{=}CH_2^{Bu}$), 32.1, 23.5 (CH_2^{Bu}), 14.2 (CH_3^{Bu}), 0.6 ($SiCH_3$).

^{1}H{^{1}H} NOE-DIFF (600 MHz, 299 K, C_7D_8)[selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 6.59 / 2.94, 2.55 (*o*-,*m*-Ph / CH_2, SCH_2), 2.23 / 2.94, 1.35, 0.95, −0.21 ($^{=}CH_2^{Bu}$ / CH_2, CH_2^{Bu}, CH_3^{Bu}, $SiCH_3$), −0.21 / 2.23, 1.35 ($SiCH_3$ / $^{=}CH_2^{Bu}$, CH_2^{Bu}).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, C_7D_8)[selective traces]: δ ^{1}H / δ ^{1}H = 6.69 / 6.59 (*p*-Ph / *o*-,*m*-Ph), 2.94 / 2.55 (CH_2 / SCH_2), 2.23 / 1.35 ($^{=}CH_2^{Bu}$ / CH_2^{Bu}), 1.35 / 2.23, 0.95 (CH_2^{Bu} / $^{=}CH_2^{Bu}$, CH_3^{Bu}).

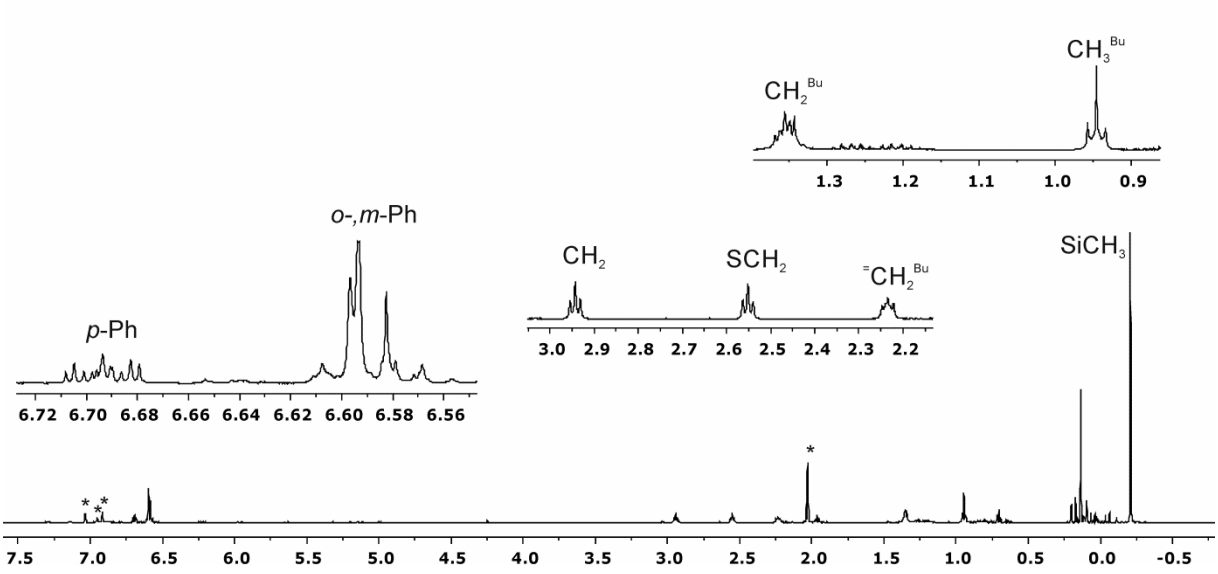
^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_7D_8): δ ^{1}H / δ ^{13}C = 6.69 / 130.0 (*p*-Ph), 6.59 / 129.4, 129.0 (*o*-,*m*-Ph), 2.94 / 38.7 (CH_2), 2.55 / 37.3 (SCH_2), 2.23 / 36.2 ($^{=}CH_2^{Bu}$), 1.35 / 32.1, 23.5 (CH_2^{Bu}), 0.95 / 14.2 (CH_3^{Bu}), −0.21 / 0.6 ($SiCH_3$).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_7D_8)[selected traces]: δ ^{1}H / δ ^{13}C = 6.64 / 130.6, 130.0, 129.0 (*o*-,*m*-Ph / *i*-Ph, *p*-Ph, *m*-Ph), 2.94 / 156.4, 144.4, 37.3 ($CH_2^{=}$ / BC=, =CSi, SCH_2), 2.55 / 156.4, 130.7, 38.7 (SCH_2 / BC=, *i*-Ph, CH_2), 2.23 / 156.4, 144.4, 32.1, 23.5 ($^{=}CH_2^{Bu}$ / BC=, =CSi, CH_2, CH_2), −0.21 / 144.4, 14.2 ($SiCH_3$ / =CSi, CH_3^{Bu}).

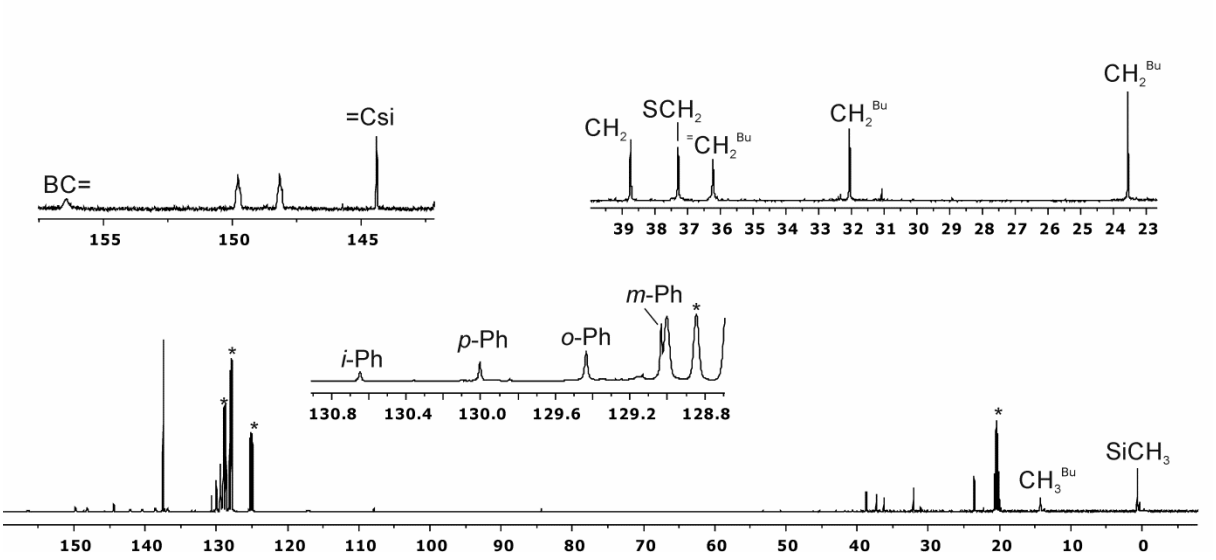
^{11}B{^{1}H} NMR (192 MHz, 299 K, C_7D_8) : δ = 10.5 ($v_{1/2}$~600 Hz)

^{19}F NMR (564 MHz, 299 K, C_7D_8): δ = –126.7 (br, 2F, *o*-C_6F_5), –155.7 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), –164.1 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 8.4].

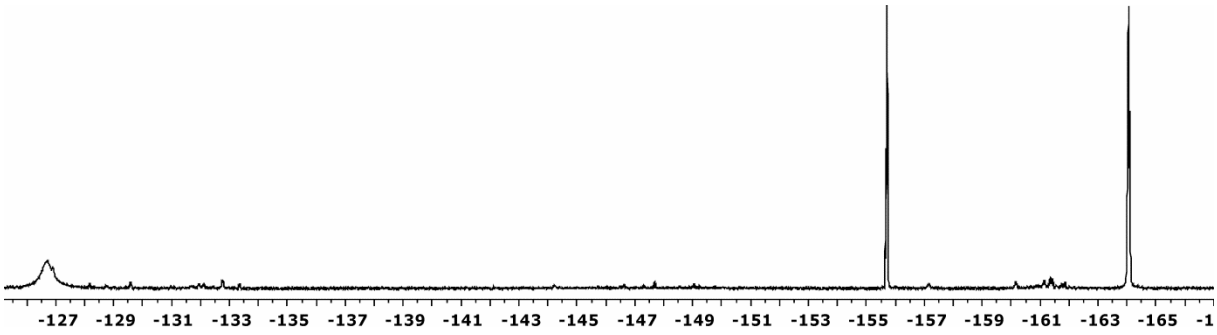
^{29}Si{^{1}H} DEPT (119 MHz, 299 K, C_7D_8): δ = –6.8 ($v_{1/2}$ ~ 4 Hz).



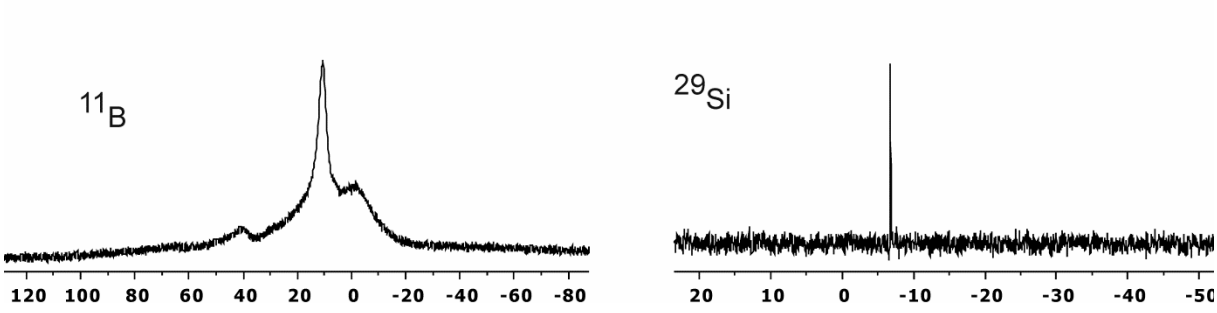
^{1}H NMR (600 MHz, 299 K, C_7D_8 (*)) of **4b** admixed with traces of vinylsulfide and trimethylsilylhexyne



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_7D_8 (*))of **4b**.

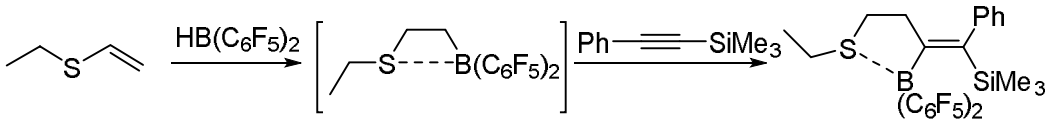


^{19}F NMR (564 MHz, 299 K, C_7D_8) of **4b**.



$^{11}B\{^{1}H\}$ (192 MHz, 299 K, C_7D_8) and $^{29}Si\{^{1}H\}$ DEPT (119 MHz, 299 K, C_7D_8) of **4b.**

Synthesis of compound 4c



Bis(pentafluorophenyl)borane (80.0 mg, 0.231 mmol, 1.0 eq) was dissolved in toluene (2 mL) and added to a solution of ethylvinylsulfid (20.4 mg, 0.231 mmol, 1.0 eq) in toluene (10 mL). After the resulting suspension was stirred for 30 min trimethylsilylphenylacetylene (40.3 mg, 0.231 mmol, 1.0 eq) was added. The brownish reaction mixture was stirred at 80 °C for overnight. Then all volatiles were removed *in vacuo* and the obtained residue was extracted with pentane (5 mL) to give a white precipitated. The supernatant solution of the suspension was removed and the residue was dried *in vacuo* to give a white powder (66.2 mg). The supernatant solution was stored at -32 °C for 3 d to give a white solid (27.0 mg). The two solid fractions were combined to give compound **4c** (93.2 mg, 0.153 mmol, 66%).

Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a dichloromethane solution of compound **6a** at -32 °C.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2400 (w), 2347 (w), 2096 (w), 1645 (m), 1596 (w), 1560 (w), 1518 (s), 1468 (s), 1379 (m), 1285 (m), 1247 (m), 1200 (w), 1105 (s), 1027 (w), 982 (s), 968 (s), 917 (m), 886 (m), 852 (m), 834 (s), 809 (m), 771 (m), 739 (m), 702 (s), 671 (m), 630 (w), 567 (w), 523 (m), 469 (w).

Elemental analysis for $C_{27}H_{23}BF_{10}SSi$: calcd. C 53.30% H 3.81%; found C 53.10% H 3.51%.

Melting point: 167 °C.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.29 (m, 2H, *m*-Ph), 7.15 (m, 1H, *p*-Ph), 6.92 (m, 2H, *o*-Ph), 2.75 (br, 2H, SCH_2), 2.69 (m, 2H, CH_2), 2.18 (q, $^{3}J_{HH}$ = 7.4 Hz, 2H, CH_2^{Et}), 1.25 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH_3^{Et}), –0.44 (s, $^{2}J_{SiH}$ = 6.6 Hz, 9H, $SiCH_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 158.4 (br, BC=), 149.3 (*i*-Ph), 149.1 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 146.7 (=CSi), 140.9 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 137.7 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 128.3 (*m*-Ph), 127.4 (br, *o*-Ph), 125.1 (*p*-Ph), 116.7 (br, *i*-C_6F_5), 38.9 (CH_2), 34.1 (SCH_2), 30.2 (CH_2^{Et}), 12.8 (CH_3^{Et}), 0.2 ($^{1}J_{SiC}$ = 52.3 Hz, $SiCH_3$).

^{1}H{^{1}H} NOE-DIFF (600 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 6.92 / 7.29, 2.69, 1.25, –0.44 (*o*-Ph / *m*-Ph, CH_2, CH_3^{Et}, $SiCH_3$), 1.25 / 2.75, 2.69, 2.18 (CH_3^{Et} / SCH_2, CH_2, CH_2^{Et}), –0.44 / 7.29, 6.92 ($SiCH_3$ / *m*-Ph, *o*-Ph).

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2)[selected traces]: δ ^{1}H / δ ^{1}H = 7.29 / 7.15, 6.92 (*m*-Ph / *p*-Ph, *o*-Ph), 2.75 / 2.69 (SCH_2 / CH_2), , 2.18 / 1.25 (CH_2^{Et} / CH_3^{Et}).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.29 / 128.3 (*m*-Ph), 7.15 / 125.1 (*p*-Ph), 6.92 / 127.4 (*o*-Ph), 2.75 / 34.1 (SCH_2), 2.69 / 38.9 (CH_2), 2.18 / 30.2 (CH_2^{Et}), 1.25/ 12.8 (CH_3^{Et}), –0.44 / 0.2 ($SiCH_3$).

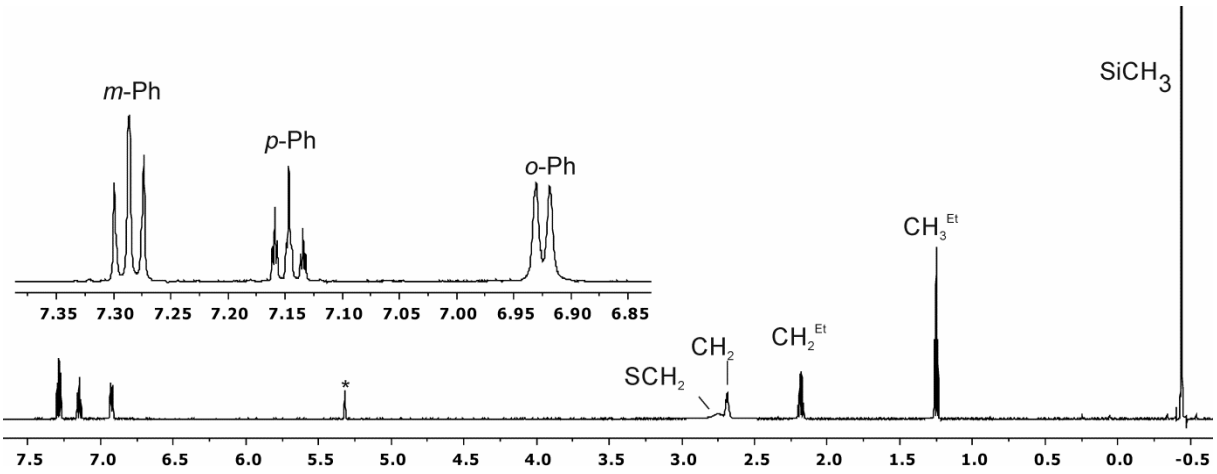
^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2)[selected traces]: δ ^{1}H / δ ^{13}C = 7.29 / 149.3, 128.3, 127.4, 125.1 (*m*-Ph / *i*-Ph, *m*-Ph, *o*-Ph, *p*-Ph), 6.92 / 146.7, 128.3, 127.4, 125.1 (*o*-Ph / =CSi, *m*-

Ph, *o*-Ph, *p*-Ph), 2.69 / 158.4, 146.7, 34.1 (CH_2 / BC=, =CSi, SCH_2), 2.18 / 34.1, 12.8 (CH_2^{Et} / SCH_2, CH_3^{Et}), −0.44 / 146.7, 0.2 ($SiMe_3$ / =CSi, $SiMe_3$).

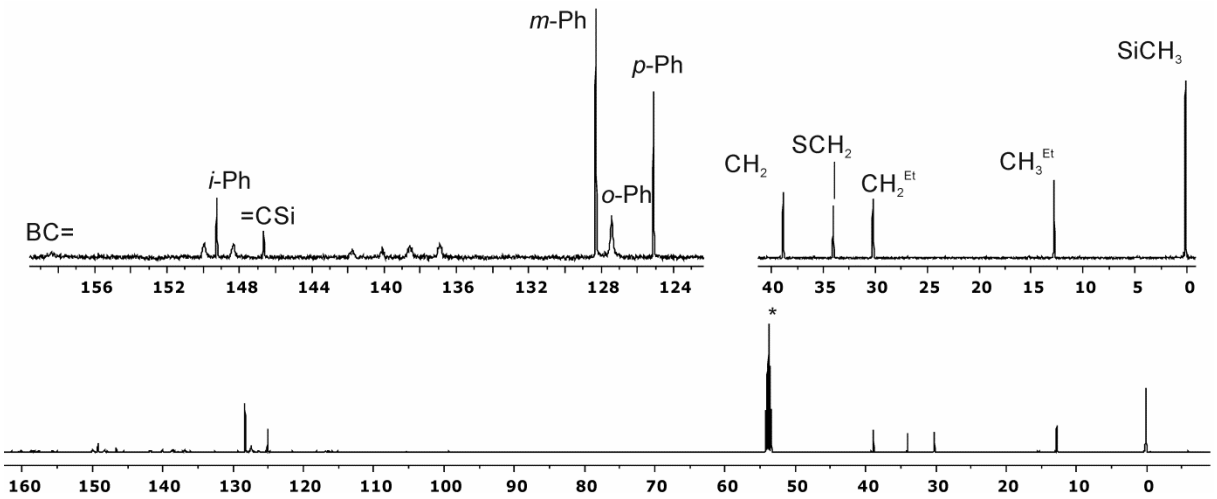
$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2): δ = 1.6 ($\nu_{1/2}$ ~ 350 Hz)

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -126.3, –127.9, -129.5 (each br, Σ4F, *o*-C_6F_5), -156.0, –156.9 (each br, each 1F, *p*-C_6F_5), –164.2 (br, 4F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 7.8].

$^{29}Si\{^1H\}$ DEPT (119 MHz, 299 K, CD_2Cl_2): δ = –8.9 ($\nu_{1/2}$ ~ 1 Hz).

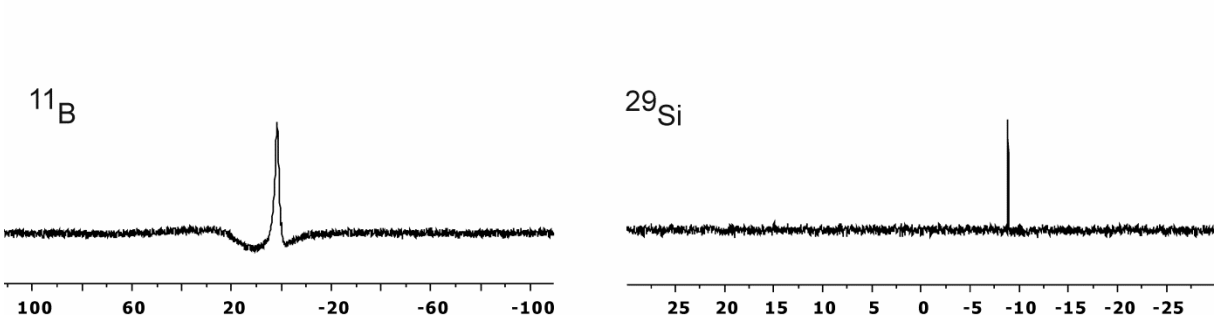


^1H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) of **4c**.



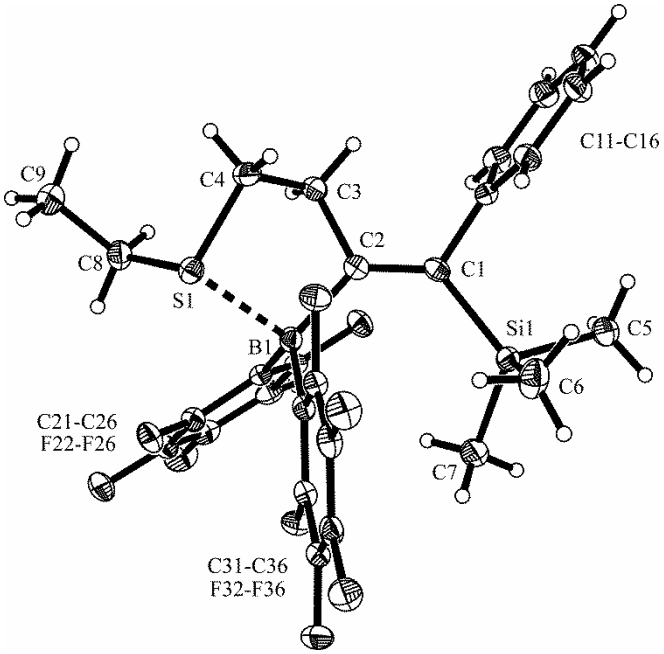
$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2 (*))of **4c**.

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of **4c**.

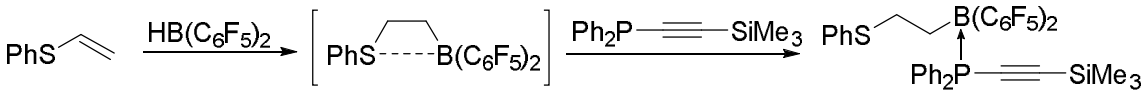


$^{11}B\{^1H\}$ (192 MHz, 299 K, CD_2Cl_2) and $^{29}Si\{^1H\}$ DEPT (119 MHz, 299 K, CD_2Cl_2) of **4c.**

X-ray crystal structure analysis of compound 4c: formula $C_{27}H_{23}BF_{10}SSi$ ⍰ 0.5 x CH_2Cl_2, M = 650.88, colourless crystal, 0.20 x 0.10 x 0.05 mm, a = 25.364(3), b = 21.164(2), c = 10.3848(11) Å, V = 5574.6(10) $Å^3$, ρ_{calc} = 1.551 g/cm^{-3}, μ = 3.113 mm^{-1}, empirical absorption correction (0.575 ≤ T ≤ 0.860), Z = 8, orthorhombic, space group *P*bcn, λ = 1.54178 Å, T = 100(2) K, ω and ϕ scans, 115437 reflections collected to a maximum θ angle of 66.59° (0.84 Å resolution), 4927 independent (R_{int} = 0.109) and 4245 observed reflections [I>2σ(I)], 389 refined parameters, R = 0.036, wR^2 = 0.093, max. (min.) residual electron density 0.81 (-0.63) e.$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.



Synthesis of compound 5



NMR Scale Experiment:

A solution of bis(pentafluorophenyl)borane (28.0 mg, 0.081 mmol, 1.0 eq) in CD_2Cl_2 (0.5 mL) was added to a solution of phenylvinylsulfide (11.0 mg, 0.081 mmol, 1.0 eq) in CD_2Cl_2 (0.5 mL), whereupon a suspension was formed which was stirred for 10 min at room temperature. Thereafter trimethylsilyldiphenylethinylphosphane (22.9 mg, 0.081 mmol, 1.0 eq) was added and immediately the colour of the reaction mixture turned to brown/yellow. Subsequently, 10 min after the addition of the phosphane, the reaction solution was characterized by NMR experiments.

[Comment: the reaction mixture contained ca. 88% of compound **5** and ca. 12% of a 2nd compound *tentatively assigned as* the *$HB(C_6F_5)_2/PPh_2P–C\equiv C–SiMe_3$-adduct]*

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.53 (m, 4H, *o*-Ph^P), 7.50 (m, 2H, *p*-Ph^P), 7.39 (m, 4H, *m*-Ph^P), 7.20 (m, 2H, *m*-Ph^S), 7.14 (m, 2H, *o*-Ph^S), 7.11 (m, 1H, *p*-Ph^S), 2.73 (m, 2H, SCH_2), 1.69 (m, 2H, BCH_2), 0.26 (s, $^2J_{SiH}$ = 7.2 Hz, 9H, $SiCH_3$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 148.5 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 139.9 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 138.0 (*i*-Ph^S), 137.4 (d, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 132.7 (d, $^2J_{PC}$ = 11.6 Hz, *o*-Ph^P), 132.2 (br, *p*-Ph^P), 129.2 (d, $^3J_{PC}$ = 10.5 Hz, *m*-Ph^P), 129.1 (*o*-Ph^S), 129.0 (*m*-Ph^S), 128.8 (br d, $^1J_{PC}$ ~ 90 Hz, *i*-Ph^P)^t, 125.7 (*p*-Ph^S), 123.6 (br, ≡CSi)^t, 117.8 (br, *i*-C_6F_5), 32.5 (SCH_2), 23.1 (br, BCH_2), –0.9 ($^1J_{SiC}$ = 57.1 Hz, $SiCH_3$), n.o. (PC≡), [^{t} tentative assignment].

^{1}H{^{1}H} 1D-TOCSY (500 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 7.53 / 7.50, 7.39 (*o*-Ph^P / *p*-Ph^P, *m*-Ph^P), 7.20 / 7.14, 7.11 (*m*-Ph^S / *o*-Ph^S, *p*-Ph^S), 2.73 / 1.69 (SCH_2 / BCH_2).

^{1}H{^{1}H} NOE-DIFF (500 MHz, 299 K, CD_2Cl_2) [selected experiments]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 7.14 / 7.20, 7.11, 2.73 (*o*-Ph^S / *m*-Ph^S, *p*-Ph^S, SCH_2), 2.73 / 7.14, 1.69 (SCH_2 / *o*-Ph^S, BCH_2), 1.69 / 7.53, 7.14, 2.73, 0.26 (BCH_2 / *o*-Ph^P, *o*-Ph^S, $^SCH_2$, $SiCH_3$).

^{1}H, ^{13}C GHSQC (500 MHz / 125 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.53 / 132.7 (*o*-Ph^P), 7.50 / 132.2 (*p*-Ph^P), 7.39 / 129.2 (*m*-Ph^P), 7.20 / 129.2 (*m*-Ph^S), 7.14 / 129.1 (*o*-Ph^S), 7.11 / 125.7 (*p*-Ph^S), 2.73 / 32.5 (SCH_2), 1.69 / 23.1 (BCH_2), 0.26 / –0.9 ($SiCH_3$).

^{1}H, ^{13}C GHMBC (500 MHz / 125 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ ^{1}H / δ ^{13}C = 7.20 / 138.2, 129.1 (*m*-Ph^S / *i*-Ph^S, *m*-Ph^S), 2.73 / 138.0, 23.1 (SCH_2 / *i*-Ph^S, BCH_2), 1.69 / 118.0, 2.73 (BCH_2 / *i*-C_6F_5, SCH_2), 0.26 / 123.6, –0.9 ($SiCH_3$ / ≡CSi , $SiCH_3$).

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = –8.7 ($\nu_{1/2}$ ~ 300 Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = –127.7 (m, 2F, *o*-C_6F_5), –158.4 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), –164.4 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 6.1].

^{1}H, ^{29}Si GHMQC (600 MHz / 119 MHz, 299 K, CD_2Cl_2): δ = −14.0.

^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2): δ = –1.1 (br, $\nu_{1/2}$ ~ 350 Hz)

Selcted resonances of the $HB(C_6F_5)_2/PPh_2P–{\equiv}–SiMe_3$-adduct:

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2)[selected resonances]: δ = 7.67 (m, 2H, *o*-Ph^P), 7.50 (m, 2H, *p*-Ph^P), 7.45 (m, 2H, *m*-Ph^P), 0.33 (m, 9H, $SiCH_3$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2)[selected resonances]: δ 132.2 (d, $^{2}J_{PC}$ = 9.9 Hz, *o*-Ph^P), 132.6 (d, $^{4}J_{PC}$ = 2.8 Hz, *p*-Ph^P), 129.5 (d, $^{3}J_{PC}$ = 11.4 Hz, *m*-Ph^P), 125.9 (d, $^{1}J_{PC}$ = 70.2 Hz, *i*-Ph^P), 124.2 (br d, $^{2}J_{PC}$ = 8.6 Hz, ≡CSi), –1.0 ($^{1}J_{SiC}$ = 56.6 Hz, $SiCH_3$).

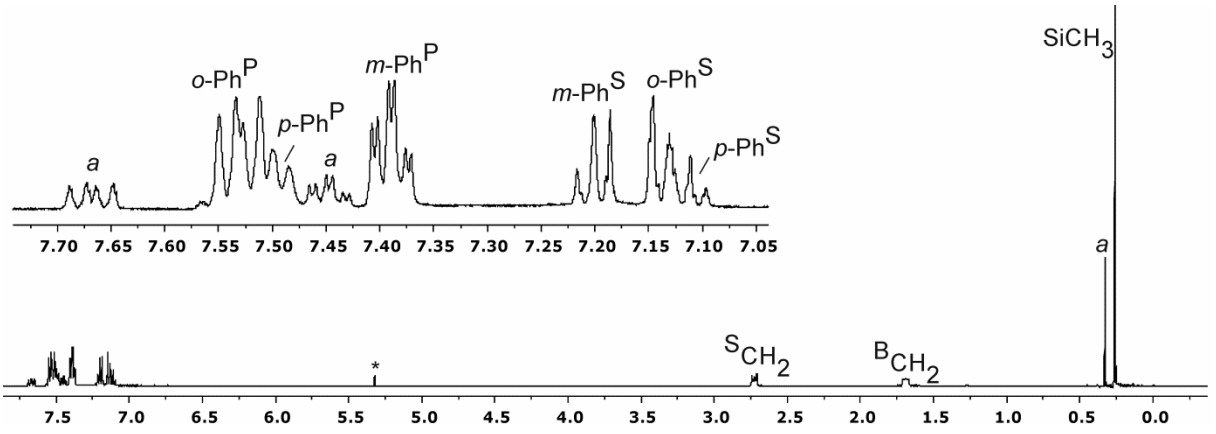
^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = –23.3 (d, $^{1}J_{PB}$ ~ 65 Hz).

^{11}B NMR (160 MHz, 299 K, CD_2Cl_2): δ = –23.3 (t, $^{1}J_{PB}$ ~ $^{1}J_{BH}$ ~ 65 Hz).

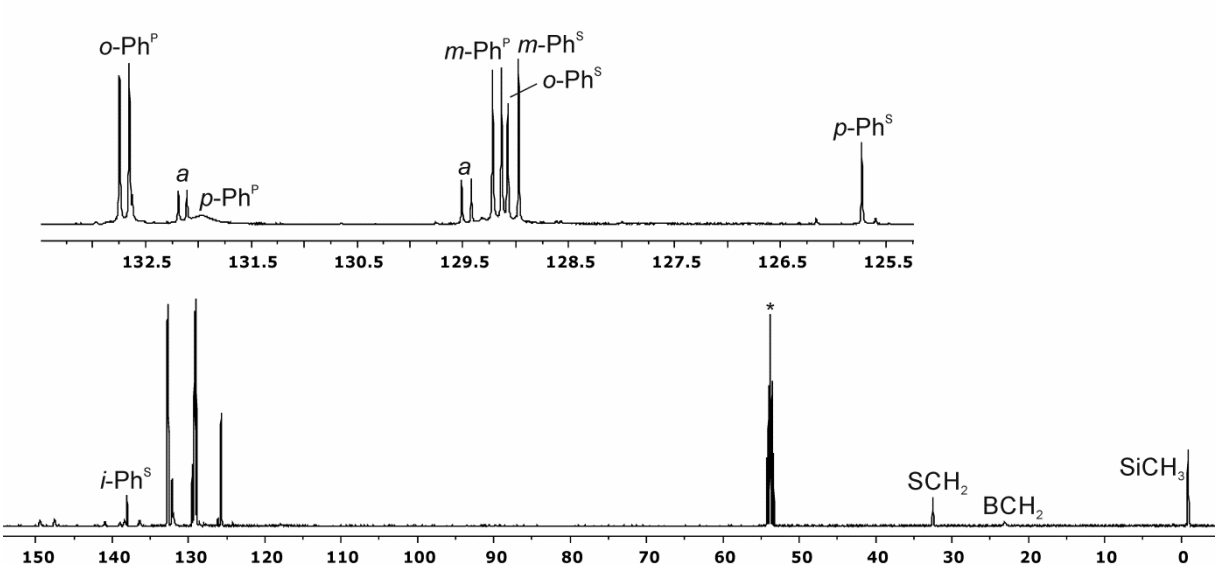
^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = –128.5 (m, 2F, *o*-C_6F_5), –158.8 (tm, $^{3}J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), –165.1 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 6.3].

^{29}Si{^{1}H} DEPT (99 MHz, 299 K, CD_2Cl_2): δ = –13.4 (d, $^{2}J_{PSi}$ = 2.6 Hz).

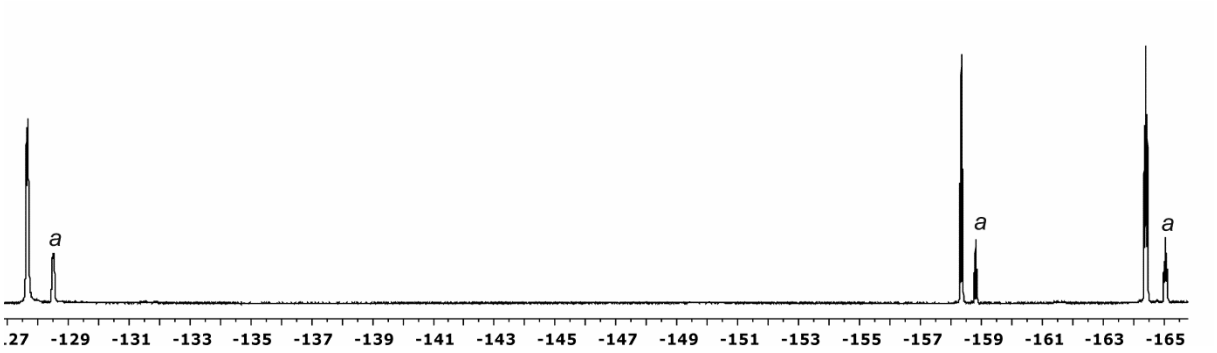
^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2): δ = –2.7 (br, $\nu_{1/2}$ ~ 250 Hz)



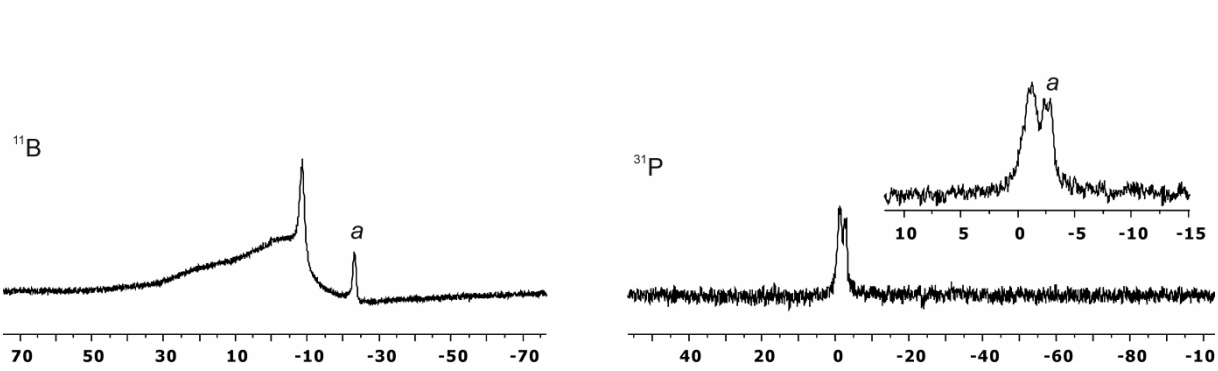
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2 (*)) of **5** [*a* = adduct].



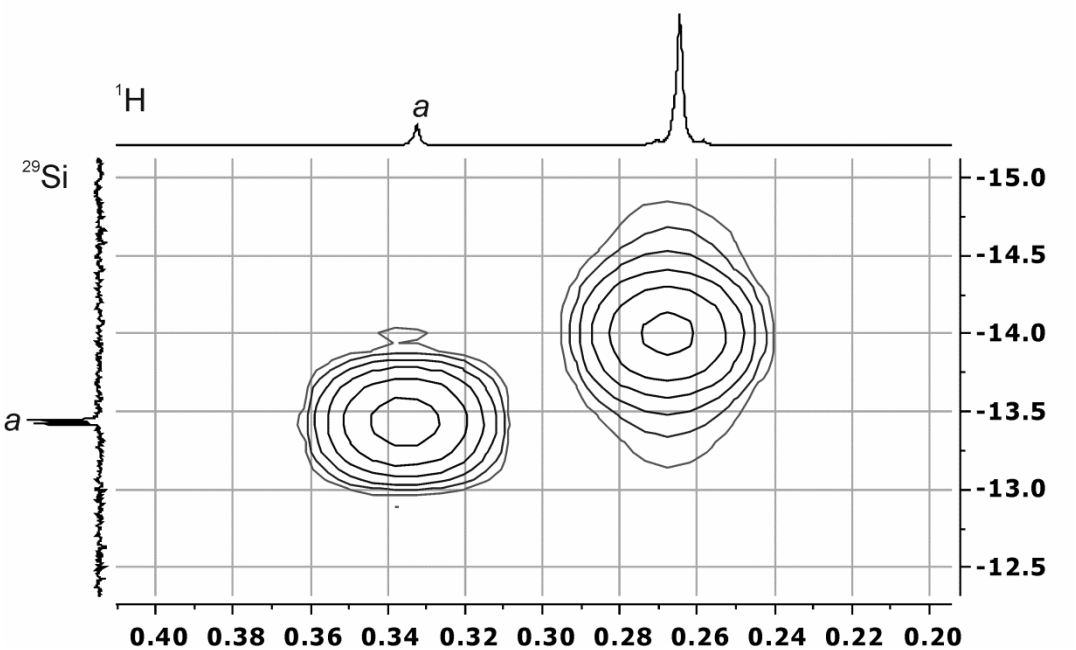
$^{13}C\{^{1}H\}$ NMR (125 MHz, 299 K, CD_2Cl_2 (*)) of **5** [*a*= adduct].



^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of **5** [*a* = adduct]



$^{11}B\{^{1}H\}$ (160 MHz, 299 K, CD_2Cl_2)and $^{31}P\{^{1}H\}$ (202 MHz, 299 K, CD_2Cl_2) of **5** [*a* = adduct]**.**



^{1}H, ^{29}Si GHMQC (600 MHz /119 MHz, 299 K, CD_2Cl_2) of **5** [*a* = adduct]**.**

Control experiment: generation of the $HB(C_6F_5)_2/PPh_2P{-}{\equiv}{-}SiMe_3$-adduct

Bis(pentafluorophenyl)borane (28.0 mg, 0.081 mmol, 1.0 eq) and trimethylsilyldiphenylethinylphosphane (22.9 mg, 0.081 mmol, 1.0 eq) were mixed in CD_2Cl_2 (1 mL) and directly characterized by NMR experiments.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2)δ = 7.67 (m, 4H, *o*-Ph^P), 7.55 (m, 2H, *p*-Ph^P), 7.45 (m, 4H, *m*-Ph^P), 0.33 (m, $^{2}J_{SiH}$ = 7.2 Hz, 9H, $SiCH_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 132.6 (d, $^{4}J_{PC}$ = 2.6 Hz, *p*-Ph^P), 132.2 (d, $^{2}J_{PC}$ = 10.1 Hz, *o*-Ph^P), 129.5 (d, $^{3}J_{PC}$ = 11.6 Hz, *m*-Ph^P), 125.9 (d, $^{1}J_{PC}$ = 70.4 Hz, *i*-Ph^P), 124.2 (br d, $^{2}J_{PC}$ = 7.9 Hz, ≡CSi), 90.3 (d, $^{1}J_{PC}$ = 105.1 Hz, PC≡), –1.0 ($^{1}J_{SiC}$ = 56.9 Hz, $SiCH_3$).

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = –23.3 (d, $^{1}J_{PB}$ ~ 65 Hz).

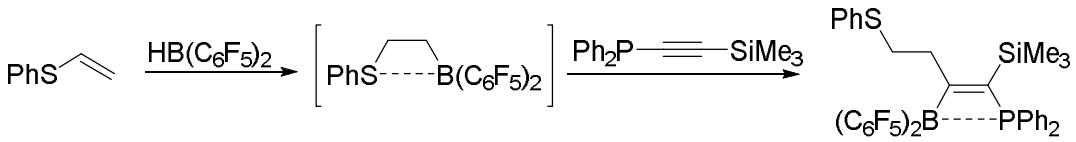
^{11}B NMR (160 MHz, 299 K, CD_2Cl_2): δ = –23.3 (t, $^{1}J_{PB}$ ~ $^{1}J_{BH}$ ~ 65 Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = –128.5 (m, 2F, *o*-C_6F_5), –158.8 (tm, $^{3}J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), –165.1 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 6.3].

^{29}Si{^{1}H} DEPT (99 MHz, 299 K, CD_2Cl_2): δ = –13.4 (d, $^{2}J_{PSi}$ = 2.6 Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2): δ = –2.7 (br, $\nu_{1/2}$ ~ 250 Hz)

Synthesis of compound 6a



Bis(pentafluorophenyl)borane (56.1 mg, 0.162 mmol, 1.0 eq) in toluene (2 mL) was added to a solution of phenylvinylsulfide (22.1 mg, 0.162 mmol, 1.0 eq) in toluene (10 mL) to give a suspension which was stirred for further 1 h at room temperature. Thereafter trimethylsilyldiphenylethinyl-phosphane (45.7 mg, 0.162 mmol, 1.0 eq) was added. The brownish/yellow reaction mixture was stirred at 80 °C for overnight. After cooling to room temperature all volatiles were removed *in vacuo* and the obtained residue was dissolved in pentane (3 mL). Then all volatiles were removed *in vacuo* again and the resulting residue was dissolved in hexane (3 mL). The hexane solution was stored at -32 °C and after 4 days a white precipitate was formed. The precipitate was collected and dried *in vacuo* to give compound **6a** (44.0 mg, 0.058 mmol, 36%) as a white powder.

Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a pentane solution of compound **6a** at -32°C.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2596 (w), 2495 (w), 2343 (w), 2209 (w), 2096 (w), 1965 (w), 1890 (w), 1816 (w), 1772 (w), 1645 (m), 1582 (w), 1514 (s), 1467 (s), 1384 (m), 1287 (m), 1253 (m), 1202 (w), 1090 (s), 1026 (w), 969 (s), 906 (w), 843 (s), 776 (m), 743 (s), 692 (s), 639 (w), 591 (w), 561 (w), 542 (m), 500 (m).

Elemental analysis for $C_{37}H_{28}BF_{10}PSSi$: calcd. C 58.18% H 3.69%; found C 58.67% H 3.46%.

Melting point: 135 °C.

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 7.50 (m, 2H, *p*-Ph^P), 7.38 (m, 4H, *m*-Ph^P), 7.31 (m, 4H, *o*-Ph^P), 7.27 (m, 2H, *m*-Ph^S), 7.24 (m, 2H, *o*-Ph^S), 7.19 (m, 1H, *p*-Ph^S), 3.12 (m, 2H, CH_2), 2.88 (m, 2H, SCH_2), 0.10 (s, $^2J_{SiH}$ = 6.7 Hz, 9H, $SiCH_3$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 205.6 (br, BC=), 147.9 (dm, $^1J_{FC}$ = ~ 240 Hz, C_6F_5), 140.0 (dm, $^1J_{FC}$ = ~ 250 Hz, C_6F_5), 139.1 (d, $^1J_{PC}$ = 27.2 Hz, =CP), 137.3 (dm, $^1J_{FC}$ = ~ 250 Hz, C_6F_5), 136.2 (*i*-Ph^S), 132.3 (d, $^2J_{PC}$ = 9.1 Hz, *o*-Ph^P), 131.8 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Ph^P), 130.1 (*o*-Ph^S), 129.2 (*m*-Ph^S), 129.1 (d, $^3J_{PC}$ = 10.3 Hz, *m*-Ph^P), 126.9 (d, $^1J_{PC}$ = 39.3 Hz, *i*-Ph^P), 126.7 (*p*-Ph^S), 116.9 (br, *i*-C_6F_5), 40.2 (br d, $^3J_{PC}$ = 50.0 Hz, CH_2), 32.8 (SCH_2), 0.1 (d, $^3J_{PC}$ = 2.2 Hz, $^1J_{SiC}$ = 53.3 Hz, $SiCH_3$).

^{1}H{^{1}H} 1D-TOCSY (500 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 7.50 / 7.38, 7.31 (*p*-Ph^P / *m*-Ph^P, *o*-Ph^P), 7.27 / 7.24, 7.19 (*m*-Ph^S / *o*-Ph^S, *p*-Ph^S), 2.88 / 3.12 (SCH_2 / CH_2).

^{1}H{^{1}H} NOE-DIFF (500 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 7.31 / 7.38, 0.10 (*o*-Ph^P / *m*-Ph^P, $SiCH_3$), 3.12 / 2.88, 0.10 (CH_2 / SCH_2, $SiCH_3$), 2.88 / 7.24, 3.12, 0.10 (SCH_2 / *o*-Ph^S, CH_2, $SiCH_3$), 0.10 / 7.31, 3.12, 2.88 ($SiCH_3$ / *o*-Ph^P, CH_2, SCH_2).

^{1}H, ^{13}C GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.50 / 131.8 (*p*-Ph^P), 7.38 / 129.1 (*m*-Ph^P), 7.31 / 132.3 (*o*-Ph^P), 7.27 / 129.2 (*m*-Ph^S), 7.24 / 130.1 (*o*-Ph^S), 7.19 / 126.7 (*p*-Ph^S), 3.12 / 40.2 (CH_2), 2.88 / 32.8 (SCH_2), 0.10 / 0.1 ($SiCH_3$).

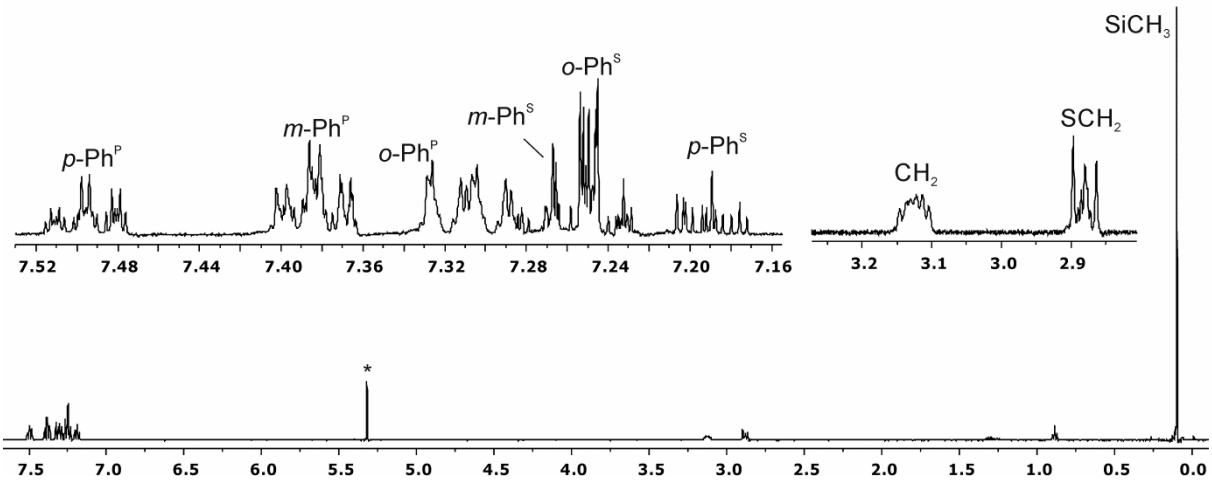
^{1}H, ^{13}C GHMBC (500 MHz / 126 MHz, 299 K, CD_2Cl_2)[selected traces]: δ ^{1}H / δ ^{13}C = 7.38 / 132.3, 129.1, 126.9 (*m*-Ph^P / *o*-Ph^P, *m*-Ph^P, *i*-Ph^P), 7.27 / 136.2, 129.2 (*m*-Ph^S / *i*-Ph^S, *m*-Ph^S), 3.12 / 205.6, 139.1, 32.8 (CH_2 / BC=, =CP, SCH_2), 2.88 / 205.6, 136.2, 40.2 (SCH_2 / BC=, *i*-Ph^S, CH_2), 0.10 / 139.3, 0.1 ($SiCH_3$ / =CP, $SiCH_3$).

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = –6.7 ($\nu_{1/2}$ ~ 200 Hz).

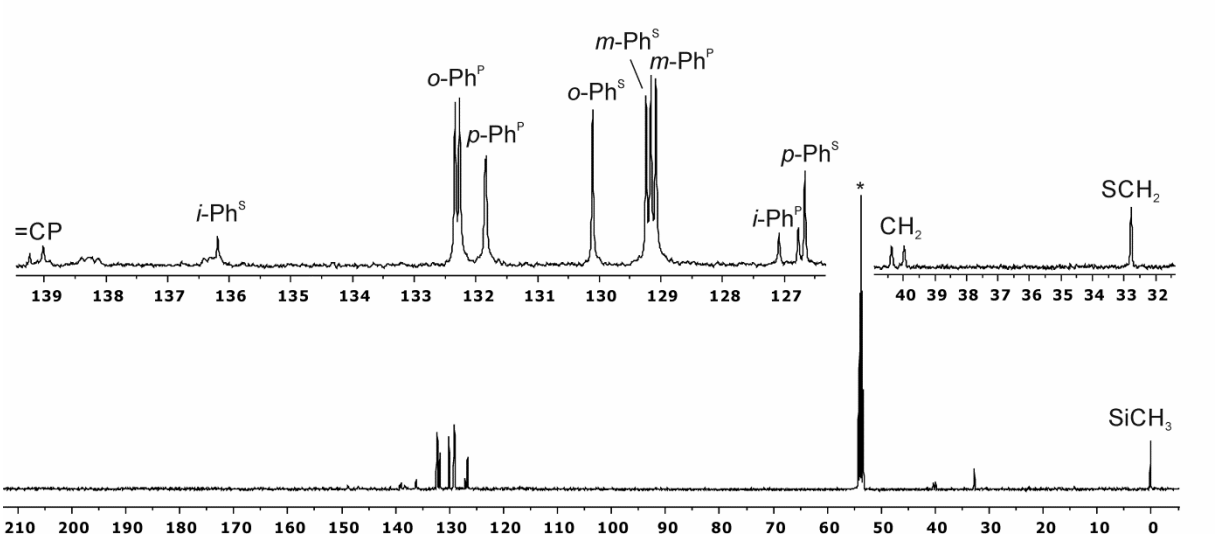
^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = –130.1 (m, 2F, *o*-C_6F_5), –158.4 (tm, $^{3}J_{FF}$ = 20.2 Hz, 1F, *p*-C_6F_5), –164.9 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 6.4].

^{29}Si{^{1}H} DEPT (99 MHz, 299 K, CD_2Cl_2): δ = –10.8 (d, $^{2}J_{PSi}$ = 6.9 Hz).

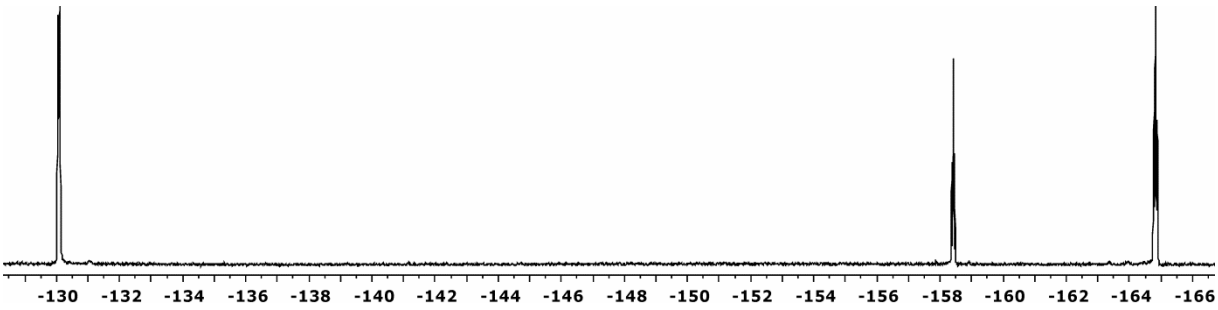
^{31}P{^{1}H} NMR (202 MHz, 299 K CD_2Cl_2): δ = 14.3 ($\nu_{1/2}$ ~ 100 Hz).



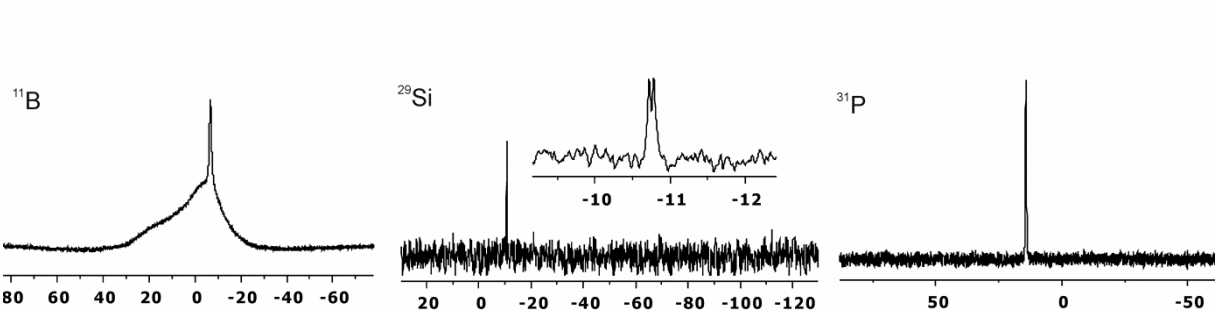
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2 (*)) of **6a.**



$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2 (*))of **6a**.



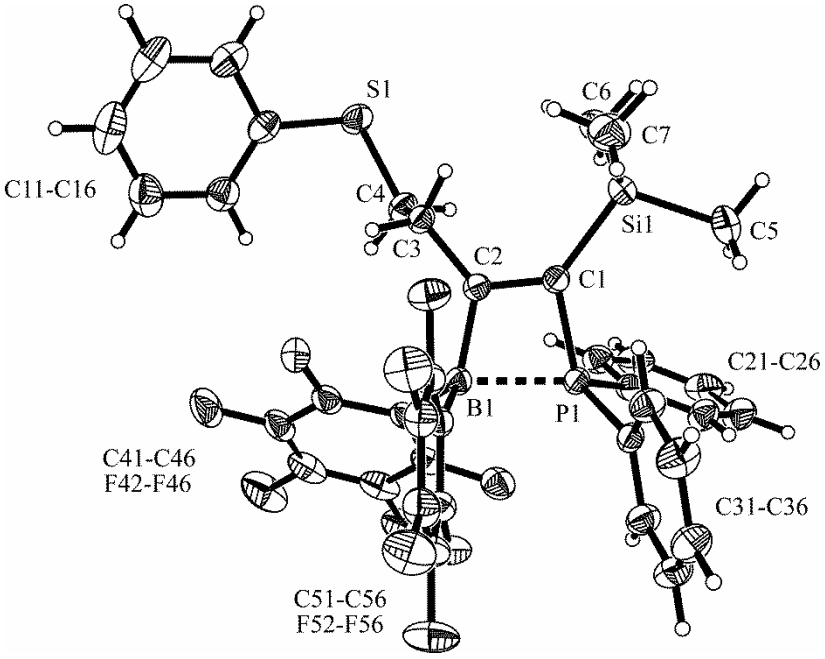
^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of **6a**.



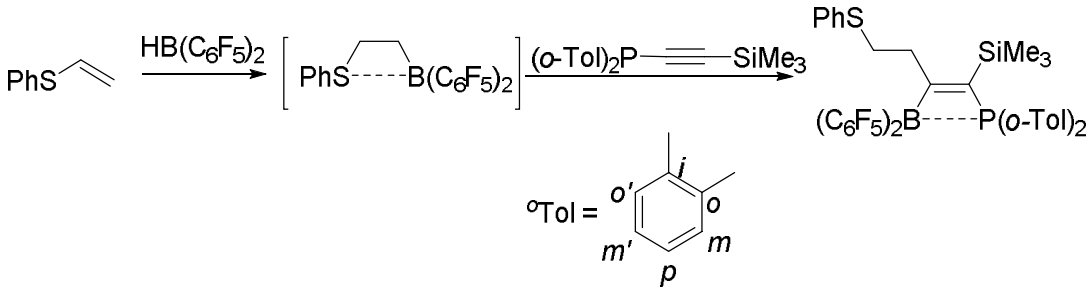
$^{11}B\{^{1}H\}$ (192 MHz, 299 K, CD_2Cl_2), $^{29}Si\{^{1}H\}$ DEPT (119 MHz, 299 K, CD_2Cl_2) and $^{31}P\{^{1}H\}$ (243 MHz, 299 K, CD_2Cl_2) of **6a.**

X-ray crystal structure analysis of compound 6a: formula $C_{37}H_{28}BF_{10}PSSi$, *M* = 764.52, colourless crystal, 0.20 x 0.14 x 0.05 mm, *a* = 9.7415(2), *b* = 12.0320(2), *c* = 16.4943(4) Å, α = 73.727(1), *β* = 75.481(1), γ = 82.657(2)°, *V* = 1794.9(1) Å^3, ρ_{calc} = 1.415 gcm^{-3}, μ = 0.247 mm^{-1}, empirical absorption correction (0.952 ≤ T ≤ 0.987), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 16082 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.62 Å^{-1}, 7151 independent (R_{int} =

0.041) and 6214 observed reflections [$I>2\sigma(I)$], 463 refined parameters, R = 0.052, wR^2 = 0.130, max. (min.) residual electron density 0.40 (-0.27) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Synthesis of compound 6b



A solution of bis(pentafluorophenyl)borane (80.0 mg, 0.231 mmol, 1.0 eq) in toluene (2 mL) was added to a solution of phenylvinylsulfide (31.5 mg, 0.231 mmol, 1.0 eq) in toluene (2 mL). After thehe resulting suspension was stirred for 30 min trimethylsilyldi-ortho-tolylethinylphosphane (71.7 mg, 0.231 mmol, 1.0 eq) was added. The orange solution was stirred for 2.5 d at 80 °C. After cooling to room temperature all volatiles were removed in *vacuo*. The residue was dissolved in pentane (3 mL) and a white precipitate was formed after 5 min. The supernatant solution was removed and the residue was dried in *vacuo* to give compound **6b** (88.5 mg, 0.112 mmol, 48%) as a white powder.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 1948 (w), 1699 (w), 1643 (m), 1592 (w), 1514 (s), 1467 (s), 1386 (m), 1282 (m), 1254 (m), 1201 (w), 1089 (s), 1025 (w), 968 (s), 905 (w), 843 (s), 804 (w), 776 (m), 759 (s), 743(s), 715 (w), 692 (m), 669 (w), 638 (w), 592 (w), 570 (m), 532 (w), 513 (w), 488 (m), 455 (w).

Elemental analysis for $C_{39}H_{32}BF_{10}PSSi$: calcd. C 59.01% H 4.07%; found C 57.55% H 3.64%.

Melting point: 182 °C.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.41 (m, 2H, *o*-Ph), 7.38 (m, 2H, *p*-^{o}Tol), 7.31 (m, 2H, *m*-Ph), 7.24 (m, 1H, *p*-Ph), 7.22 (m, 2H, *m*-^{o}Tol)[a], 7.21 (m, 2H, *o'*-^{o}Tol)[a], 7.18 (m, 2H, *m'*-^{o}Tol), 3.04 (br, 2H, CH_2), 2.91 (m, 2H, SCH_2), 2.28 (s, 6H, *o*-CH_3^{Tol}), −0.02 (s, $^{2}J_{SiH}$ = 6.6 Hz, 9H, $SiCH_3$), [[a] from the ghsqc experiment].

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 202.1 (br, =CB), 147.8 (dm, $^{1}J_{FC}$ ~235 Hz, C_6F_5), 142.4 (d, $^{2}J_{PC}$ = 11.3 Hz, *o*-^{o}Tol), 140.0 (d, $^{1}J_{PC}$ = 27.1 Hz, =CP), 139.9 (dm, $^{1}J_{FC}$ ~249 Hz, C_6F_5), 137.1 (dm, $^{1}J_{FC}$ ~250 Hz, C_6F_5), 135.7 (*i*-Ph), 134.0 (d, $^{3}J_{PC}$ = 6.0 Hz, *o'*-^{o}Tol), 131.80 (d, $^{4}J_{PC}$ = 2.0 Hz, *p*-^{o}Tol), 131.76 (br, *m*-^{o}Tol), 131.6 (*o*-Ph), 129.3 (*m*-Ph), 127.2 (*p*-Ph), 126.4 (d, $^{3}J_{PC}$ = 8.5 Hz, *m'*-^{o}Tol), 126.2 (d, $^{1}J_{PC}$ = 36.1 Hz, *i*-^{o}Tol), 117.8 (br, *i*-C_6F_5), 40.9 (d, $^{3}J_{PC}$ = 52.3 Hz, CH_2), 33.0 (d, $^{4}J_{PC}$ = 3.2 Hz, SCH_2), 22.3 (d, $^{3}J_{PC}$ = 4.6 Hz, *o*-CH_3^{oTol}), 0.0 (d, $^{3}J_{PC}$ = 1.5 Hz, $^{1}J_{SiC}$ = 52.6 Hz, $SiCH_3$).

^{1}H{^{1}H} 1D-TOCSY (600 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 7.41 / 7.31, 7.24 (*o*-Ph / *m*-Ph, *p*-Ph), 7.22, 7.21 / 7.38, 7.22, 7.21, 7.18, 2.28 (*o'*-^{o}Tol, *m*-^{o}Tol / *p*-^{o}Tol, *o'*-^{o}Tol, *m*-^{o}Tol, *m'*-^{o}Tol, *o*-CH_3^{Tol}), 3.04 / 2.91 (CH_2 / SCH_2).

^{1}H{^{1}H} NOE-DIFF (600 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 7.41 / 7.31, 2.91, −0.02 (*o*-Ph / *p*-Ph, SCH_2, $SiCH_3$), 7.38 / 7.22, 7.18, −0.02 (*p*-^{o}Tol / *o'*-^{o}Tol, *m*-^{o}Tol, *m'*-^{o}Tol, $SiCH_3$), 3.04 / 2.91, −0.02 (CH_2 / SCH_2, $SiCH_3$), 2.91/ 3.04, –0.02 (SCH_2 / CH_2, $SiCH_3$), –0.02 / 7.41, 7.22, 7.18, 3.04, 2.91, 2.28 ($SiCH_3$ / *o*-Ph, *o'*-^{o}Tol, *m*-^{o}Tol, *m'*-^{o}Tol, CH_2, SCH_2, *o*-CH_3^{Tol}).

^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ ^{1}H / δ ^{13}C = 7.41 / 131.6 (*o*-Ph), 7.38 / 131.80 (*p*-^{o}Tol), 7.31 / 129.3 (*m*-Ph), 7.24 / 127.2 (*p*-Ph), 7.22 / 131.76 (*m*-^{o}Tol), 7.21 / 134.0 (*o'*- ^{o}Tol), 7.18 / 126.4 (*m'*-^{o}Tol), 3.04 / 40.9 (CH_2), 2.91 / 33.0 (SCH_2), 2.28 / 22.3 (*o*-CH_3^{Tol}), –0.02 / 0.0 ($SiCH_3$).

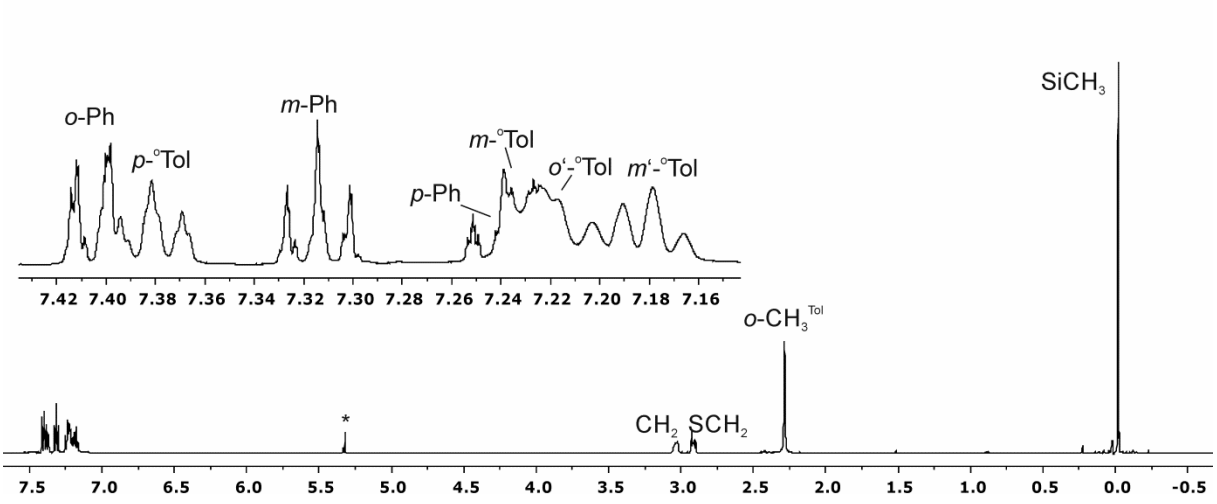
^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ ^{1}H / δ ^{13}C = 7.38 / 142.4, 134.0 (*p*-^{o}Tol / *o*-^{o}Tol, *o'*-^{o}Tol), 7.31 / 135.7, 129.3 (*m*-Ph / *i*-Ph, *m*-Ph), 7.18 / 131.75, 126.1 (*m'*-^{o}Tol / *m*-^{o}Tol, *i*-^{o}Tol), 3.04 / 202.1, 140.0, 33.0 (CH_2 / =CB, =CP, SCH_2), 2.28 / 142.4, 131.76, 126.1 (*o*-CH_3^{Tol} / *o*-^{o}Tol, *m*-^{o}Tol, *i*-^{o}Tol), –0.02 / 140.0, 0.0 ($SiCH_3$ / =CP, $SiCH_3$).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = −2.7 ($\nu_{1/2}$ ~ 250 Hz).

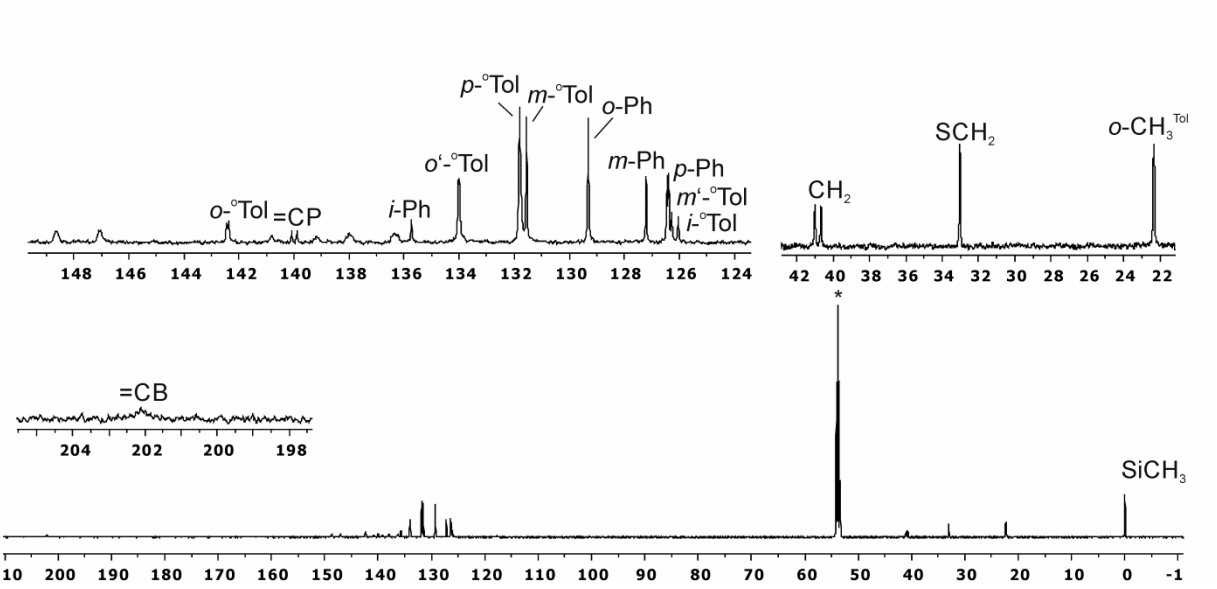
^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −129.4 (br, 2F, *o*-C_6F_5), −158.3 (br t, $^{3}J_{FF}$ = 19.8 Hz, 1F, *p*-C_6F_5), −164.7 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 6.4].

^{29}Si{^{1}H} DEPT (99 MHz, 299 K, CD_2Cl_2): δ = −10.9 (d, $^{2}J_{PC}$ = 6.0 Hz,).

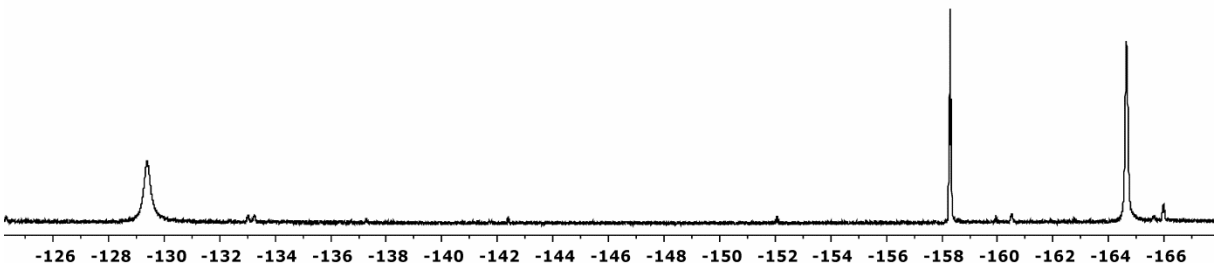
$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, CD_2Cl_2): δ = 18.4 ($\nu_{1/2}$ ~ 70 Hz).



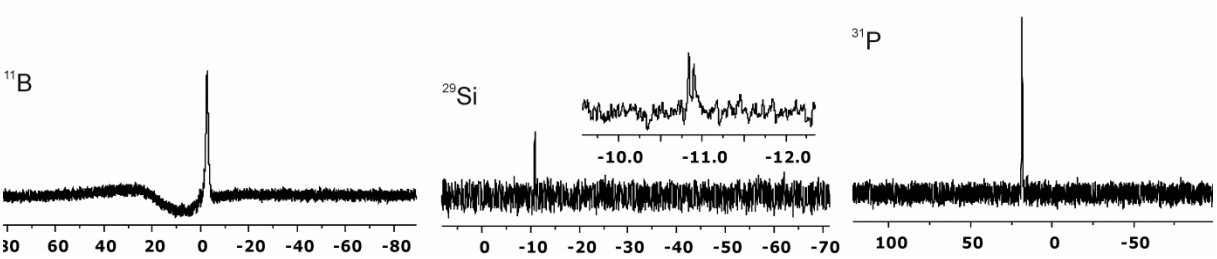
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) of **6b.**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2 (*))of **6b**.

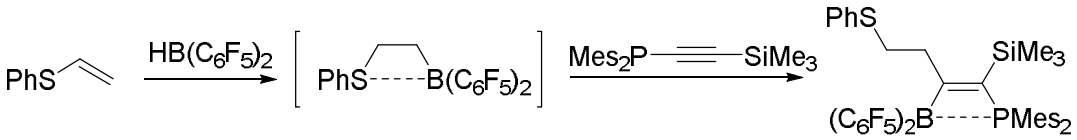


^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of **6b**.



$^{11}B\{^1H\}$ (192 MHz, 299 K, CD_2Cl_2), $^{29}Si\{^1H\}$ DEPT (99 MHz, 299 K, CD_2Cl_2) and $^{31}P\{^1H\}$ (202 MHz, 299 K, CD_2Cl_2) of **6b.**

Synthesis of compound 6c



A solution of bis(pentafluorophenyl)borane (80.0 mg, 0.231 mmol, 1.0 eq) in toluene (2 mL) was added to a solution of phenylvinylsulfide (31.5 mg, 0.231 mmol, 1.0 eq) in toluene (2 mL). After 30 min stirring of the resulting suspension trimethylsilyldimesitylethinylphosphane (84.8 mg, 0.231 mmol, 1.0 eq) was added. The yellow reaction mixture was stirred at 80 °C for overnight. Then all volatiles were removed *in vacuo* and the residue was dissolved in pentane (3 mL). The solvent was removed *in vacuo* and the residue was dissolved in pentane (3 mL) and the obtained solution was stored for 3 d at -32 °C. The supernatant solution of the obtained suspension was removed and the residue was dried *in vacuo* to give compound **6c** (66.8 mg, 0.079 mmol, 34%) as a white powder.

IR (KBr) $\tilde{\nu}$ [cm^{-1}] = 2397 (w), 2282 (w), 1645 (m), 1605 (w), 1516 (s), 1465 (s), 1384 (m), 1286 (m), 1252 (m), 1091 (s), 1026 (w), 972 (s), 843 (m), 748 (w), 691 (w), 652 (w), 553 (w), 467 (w).
Elemental analysis for $C_{43}H_{40}BF_{10}PSSi$: calcd. C 60.85% H 4.75%; found C 61.18% H 4.60%.
Melting point: 183 °C.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.35 (m, 2H, *o*-Ph), 7.29 (m, 2H, *m*-Ph), 7.22 (m, 1H, *p*-Ph), 6.77 (br, 4H, *m*-Mes), 2.99 (s, 2H, CH_2), 2.83 (m, 2H, SCH_2), 2.22 (s, 6H, *p*-CH_3^{Mes}), 2.19 (br, 12H, *o*-CH_3^{Mes}), 0.01 (s, $^2J_{SiH}$ = 6.6 Hz, 9H, $SiCH_3$).
$^{13}C\{^1H\}$ NMR (151 MHz, 299 K, CD_2Cl_2): δ = 196.5 (br, BC=), 147.7 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 144.8 (d, $^1J_{PC}$ = 24.2 Hz,=CP), 141.9 (br, *o*-Mes)^t, 141.2 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Mes), 140.0 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 137.1 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 135.8 (*i*-Ph), 131.4 (*o*-Ph), 130.9 (br, *m*-Mes), 129.3 (*m*-Ph), 127.1 (*p*-

Ph), 125.4 (br, i-Mes), 119.0 (br, *i*-C_6F_5), 40.4 (d, $^3J_{PC}$ = 51.8 Hz, CH_2), 32.6 (d, $^4J_{PC}$ = 3.3 Hz, SCH_2), 23.9 (br, *o*-CH_3^{Mes}), 20.8 (d, $^5J_{PC}$ = 1.2 Hz, *p*-CH_3^{Mes}), 0.6 (d, $^3J_{PC}$ = 2.0 Hz, $^1J_{SiC}$ = 52.9 Hz, $SiCH_3$), [^{t} tentative assignment].

$^1H\{^1H\}$ 1D-TOCSY (600 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 7.35 / 7.29, 7.22 (*o*-Ph / *m*-Ph, *p*-Ph), 6.77 / 2.22, 2.19 (*m*-Mes / *p*-CH_3^{Mes}, *o*-CH_3^{Mes}), 2.99 / 2.83 (CH_2 / SCH_2).

$^1H\{^1H\}$ NOE-DIFF (600 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ $^1H_{irr}$ / δ $^1H_{res}$ = 2.99 / 2.83, 0.01 (CH_2 / SCH_2, $SiCH_3$), 0.01 / 7.35, 2.99, 2.83, 2.22, 2.19 ($SiCH_3$ / *o*-Ph, CH_2, SCH_2, *p*-CH_3^{Mes} *o*-CH_3^{Mes}).

^1H, ^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^1H / δ ^{13}C = 7.35 / 131.4 (*o*-Ph), 7.29 / 129.3 (*m*-Ph), 7.22 / 127.1 (*p*-Ph), 6.77 / 130.9 (*m*-Mes), 2.99 / 40.4 (CH_2), 2.83 / 32.6 (SCH_2), 2.22 / 23.9, 20.8 (*p*-CH_3^{Mes}, *o*-CH_3^{Mes}), 0.01 / 0.6 ($SiCH_3$).

^1H, ^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ ^1H / δ ^{13}C = 7.29 / 135.8, 129.3 (*m*-Ph / *i*-Ph, *m*-Ph), 2.99 / 196.5, 144.8, 32.6 (CH_2 / BC=, =CP, SCH_2), 2.83 / 196.6, 138.5, 40.4 (SCH_2 / BC=, *i*-Ph, CH_2), 0.01 / 144.8, 0.6 ($SiMe_3$ / =CP, $SiMe_3$).

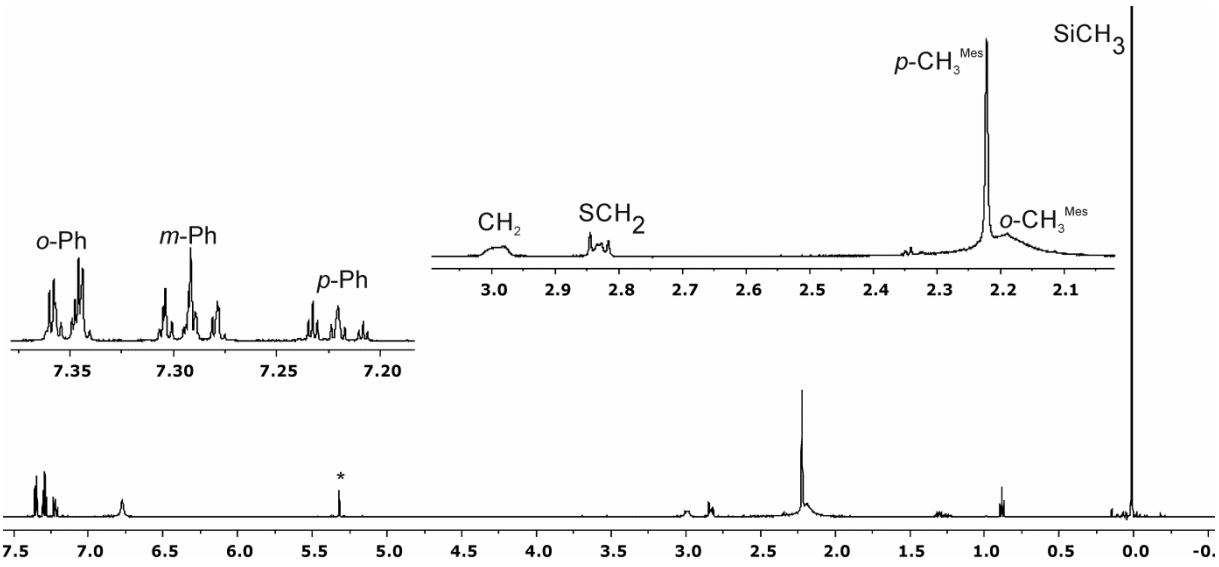
$^{11}B\{^1H\}$ NMR (192 MHz, 299 K, CD_2Cl_2): δ = 0.5 ($\nu_{1/2}$ ~ 350 Hz)

^{19}F NMR (564 MHz, 193 K, CD_2Cl_2): δ = –125.6, –126.6, –131.8, –132.9 (each br m, each 1F, *o*-C_6F_5), –158.2, –158.8 (each br m, each 1F, *p*-C_6F_5), –163.5, –164.9 (each br m, each 2F, *m*-C_6F_5).

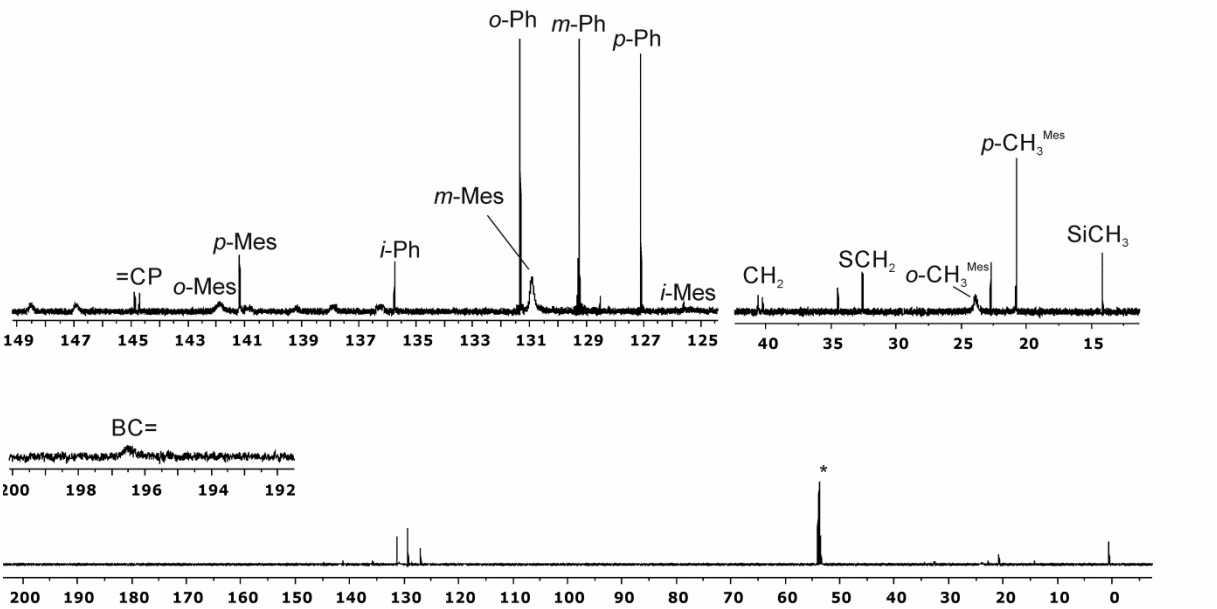
$^{29}Si\{^1H\}$ DEPT (119 MHz, 299 K, CD_2Cl_2): δ = –10.0 (d, $^2J_{PSi}$ = 7.4 Hz).

$^{31}P\{^1H\}$ NMR (243 MHz, 299 K, CD_2Cl_2): δ = 10.0 ($\nu_{1/2}$ ~ 60 Hz).

$^{31}P\{^1H\}$ NMR (202 MHz, 193 K, CD_2Cl_2): δ = 9.0 ($\nu_{1/2}$ ~ 40 Hz).

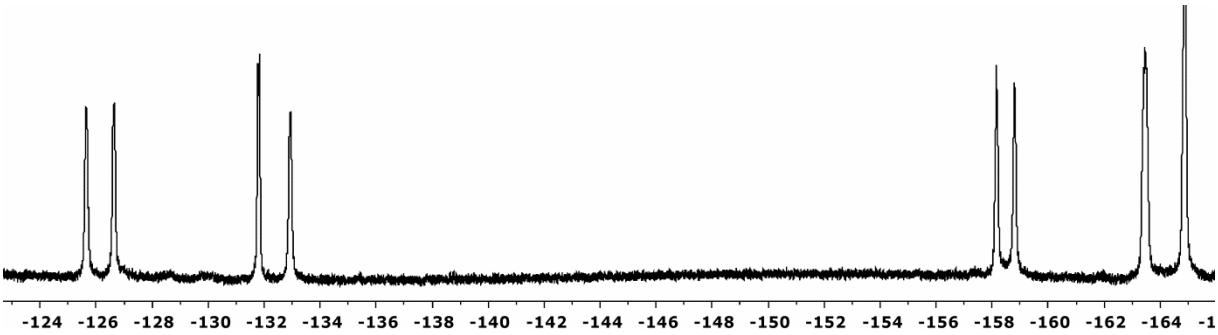


^1H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) of **6c.**

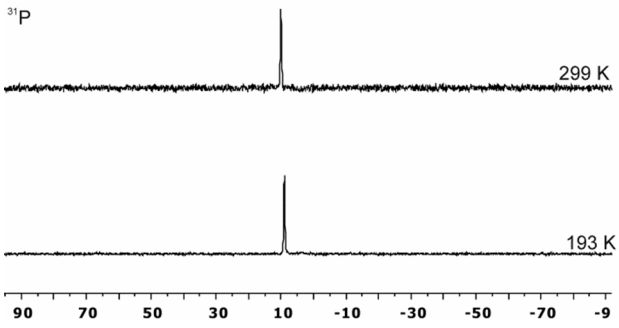


$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2 (*))of **6c**.

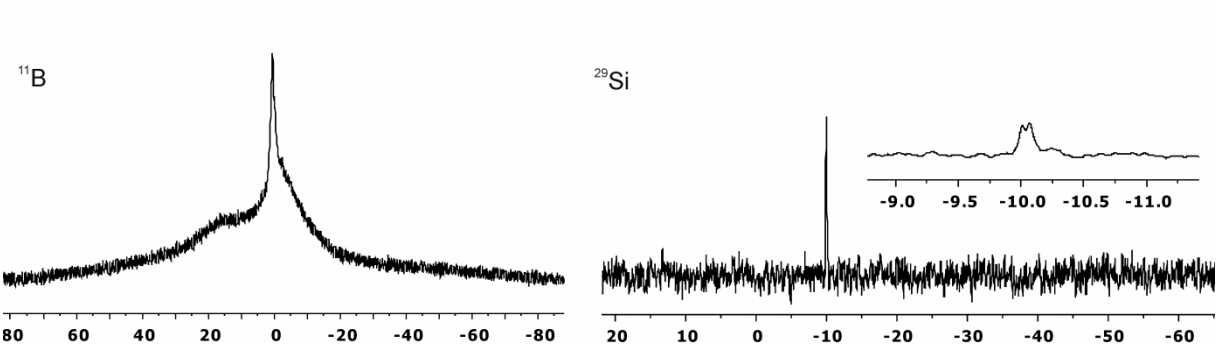
^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of **6c.**



^{19}F NMR (564 MHz, 193 K, CD_2Cl_2) of **6c**.

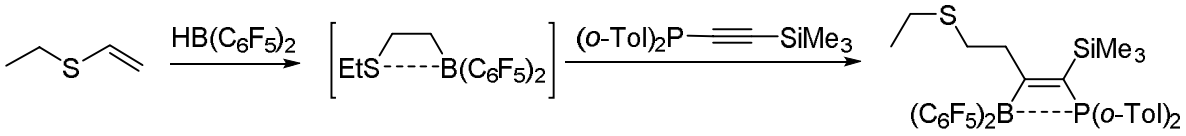


$^{31}P\{^{1}H\}$ (243 MHz, VT, CD_2Cl_2) of **6c.**



$^{11}B\{^{1}H\}$ (192 MHz, 299 K, CD_2Cl_2) and $^{29}Si\{^{1}H\}$ DEPT (119 MHz, 299 K, CD_2Cl_2) of **6c.**

Synthesis of compound 6d



A solution of bis(pentafluorophenyl)borane (80.0 mg, 0.231 mmol, 1.0 eq) in toluene (2 mL) was added to a solution of ethylvinylsulfide (20.4 mg, 0.231 mmol, 1.0 eq) in toluene (2 mL). After the resulting supsension was stirred for 30 min at room temperature trimethylsilyldi-ortho-tolylethinylphosphane (71.7 mg, 0.231 mmol, 1.0 eq) was added. The obtained yellow reaction mixture was stirred at 80 °C for two days. After cooling to room temperature all volatiles were removed *in vacuo* and the residue was dissolved in pentane (2 mL). The solution was stored at −32 °C for 4 days and a white precipitated was formed. The supernatant solution of the suspension was removed and the residue was dried *in vacuo* to give compound **6d** (69.4 mg, 0.093 mmol, 40%) as a white powder.

Elemental analysis for $C_{35}H_{32}BF_{10}PSSi$: calcd. C 56.46% H 4.33%; found C 56.78% H 4.30%.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.38 (m, 2H, *p*-^{o}Tol), 7.24 (m, 4H, *o'*,*m*-^{o}Tol), 7.19 (m, 2H, *m'*-^{o}Tol), 3.04 (br, 2H, CH_2), 2.59 (q, $^{3}J_{HH}$ = 7.0 Hz, 2H, CH_2^{Et}), 2.54 (m, 2H, SCH_2), 2.30 (s, 6H, *o*-CH_3^{Tol}), 1.24 (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, CH_3^{Et}), 0.06 (s, $^{2}J_{SiH}$ = 6.7 Hz, 9H, $SiCH_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 202.8 (br, =CB), 147.8 (dm, $^{1}J_{FC}$ ~235 Hz, C_6F_5), 142.4 (d, $^{2}J_{PC}$ = 11.4 Hz, *o*-^{o}Tol), 139.9 (dm, $^{1}J_{FC}$ ~249 Hz, C_6F_5), 139.3 (d, $^{1}J_{PC}$ = 29.5 Hz, =CP), 137.1 (dm, $^{1}J_{FC}$~250 Hz, C_6F_5), 134.0 (d, $^{3}J_{PC}$ = 6.0 Hz, *o'*-^{o}Tol), 131.82 (br, *m*-^{o}Tol), 131.79 (d, $^{4}J_{PC}$ = 2.7 Hz, *p*-^{o}Tol), 126.4 (d, $^{3}J_{PC}$ = 8.6 Hz, *m'*-^{o}Tol), 126.2 (d, $^{1}J_{PC}$ = 36.1 Hz, *i*-^{o}Tol), 118.0 (br, *i*-C_6F_5), 41.3 (d, $^{3}J_{PC}$ = 50.2 Hz, CH_2), 29.8 (d,

$^{4}J_{PC}$ = 3.2 Hz, SCH_2), 25.9 (CH_2^{Et}), 22.4 (br d, $^{3}J_{PC}$ = 5.0 Hz, *o*-CH_3^{oTol}), 15.0 (CH_3^{Et}), 0.1 (d, $^{3}J_{PC}$ = 2.1 Hz, $^{1}J_{SiC}$ = 52.7 Hz, $SiCH_3$).

^{1}H{^{1}H} NOE (600 MHz, 299 K, CD_2Cl_2)[selected experiments]: δ $^{1}H_{irr}$ / δ $^{1}H_{res}$: 7.24 / 2.30, 0.06 (*o'*,*m*-^{o}Tol / *o*-CH_3^{Tol}, $SiCH_3$), 3.04 / 2.59, 2.54, 1.24, 0.06 (CH_2 / CH_2^{Et}, SCH_2, CH_3^{Et}, $SiCH_3$), 2.59 / 1.24, 0.06 (CH_2^{Et} / CH_3^{Et}, $SiCH_3$), 0.06 / 7.24, 3.04, 2.58, 2.30, 1.24 ($SiCH_3$ / *o'*,*m*-^{o}Tol, CH_2, SCH_2, *o*-CH_3^{Tol}, CH_3^{Et}).

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2)[selected traces]: δ ^{1}H / δ ^{1}H = 7.38 / 7.24, 7.19, 2.30 (*p*-^{o}Tol / *o'*,m-^{o}Tol *m'*-^{o}Tol, *o*-CH_3^{Tol}), 3.04 / 2.58 (CH_2 / SCH_2), 2.59 / 1.24 (CH_2^{Et} / CH_3^{Et}).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.38 / 131.79 (*p*-^{o}Tol), 7.24 / 134.0, 131.82 (*o'*-^{o}Tol, *m*-^{o}Tol), 7.19 / 126.4 (*m'*-^{o}Tol), 3.04 / 41.3 (CH_2), 2.59 / 25.9 (CH_2^{Et}), 2.54 / 29.8 (SCH_2), 2.30 / 22.4 (*o*-CH_3^{Tol}), 1.24 / 15.0 (CH_3^{Et}), 0.06 / 0.1 ($SiCH_3$).

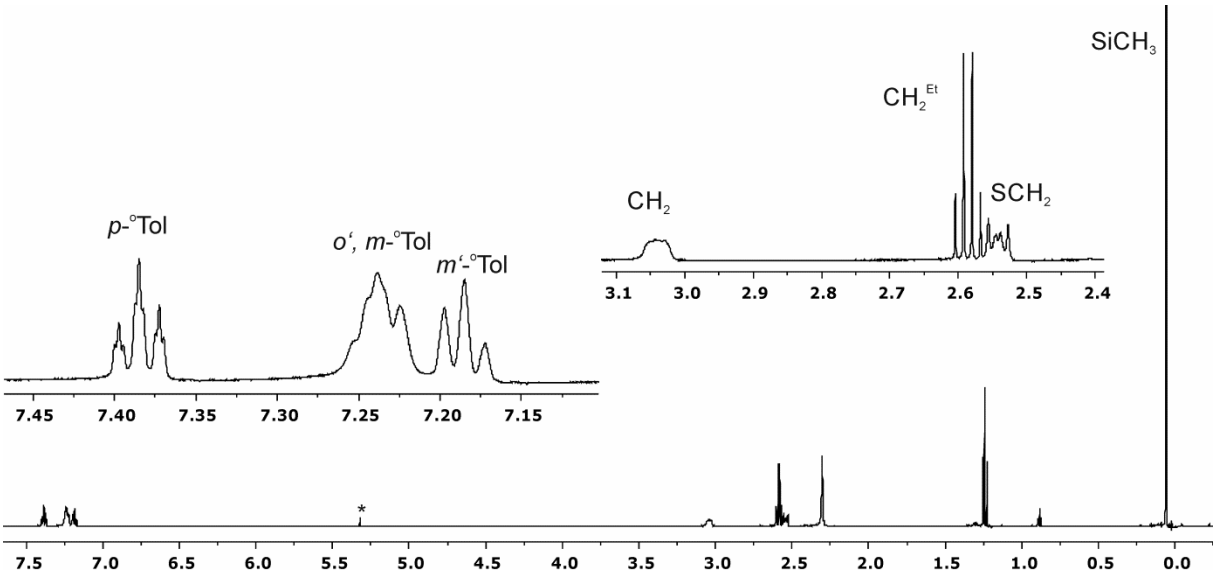
^{1}H,^{13}C GHMBC (600 MHz / 126 MHz, 299 K, CD_2Cl_2)[selected traces]: δ ^{1}H / δ ^{13}C = 7.38 / 142.4, 134.0 (*p*-^{o}Tol / *o*-^{o}Tol, *o'*-^{o}Tol), 7.19 / 131.82, 126.2 (*m'*-^{o}Tol / *m*-^{o}Tol, *i*-^{o}Tol), 3.04 / 202.8, 139.3, 29.8 (CH_2 /=CB, =CP, SCH_2), 2.59 / 29.8, 15.0 (CH_2^{Et} / SCH_2, CH_3^{Et}), 2.30 / 142.4, 131.82, 126.2 (*o*-CH_3^{Tol} / *o*-^{o}Tol, *m*-^{o}Tol, *i*-^{o}Tol), 0.06 / 139.3, 0.1 ($SiCH_3$ / =CP, $SiCH_3$).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −129.5 (br, 2F, *o*-C_6F_5), −158.4 (br t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), −164.8 (br, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 6.3].

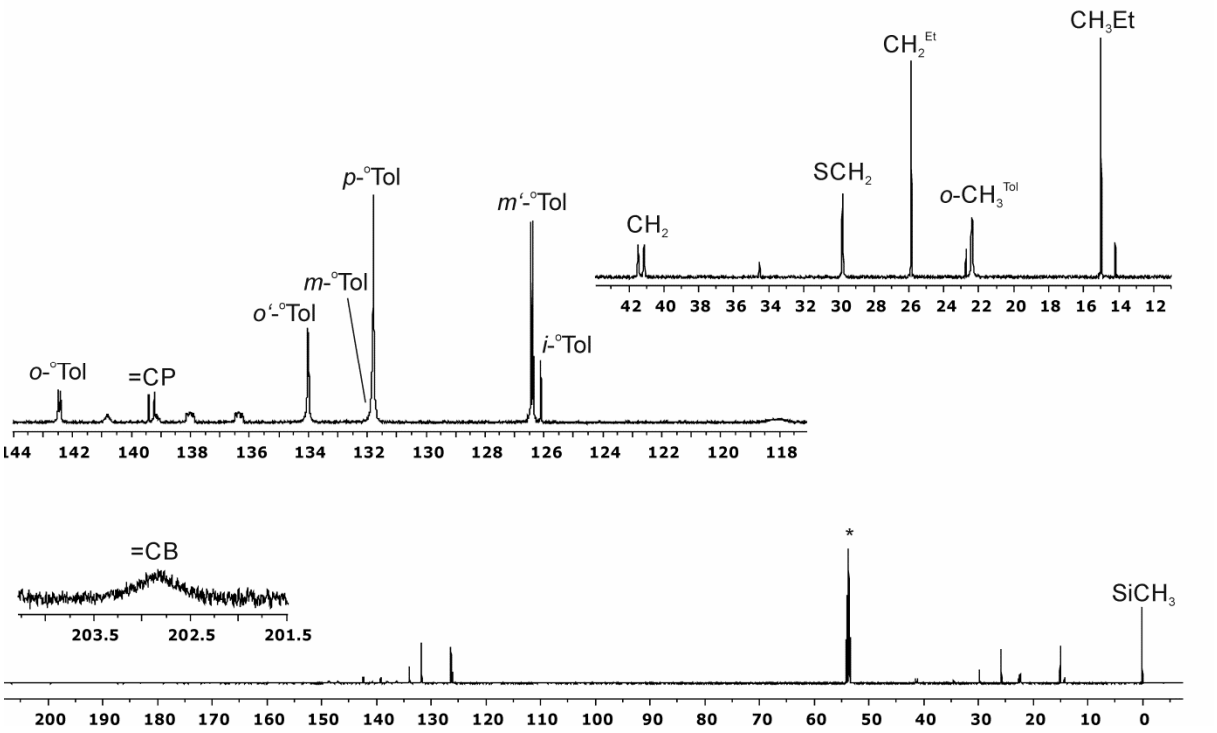
^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = −2.8 ($\nu_{1/2}$ ~ 250 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 18.6 ($\nu_{1/2}$ ~ 70 Hz).

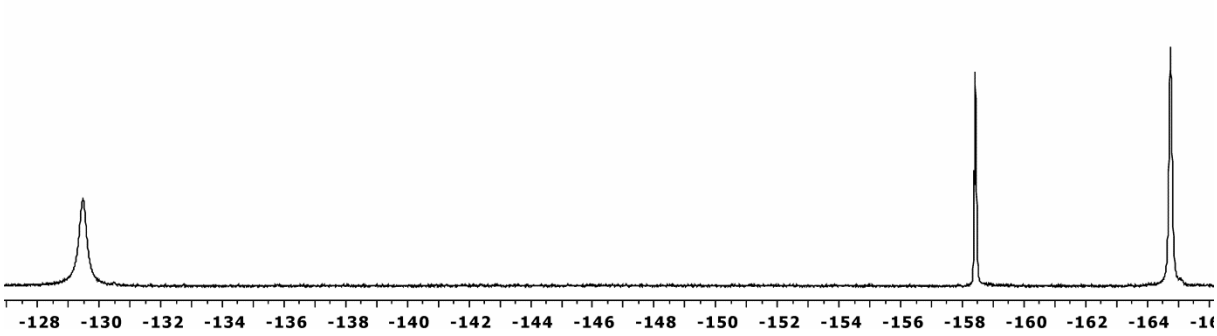
^{29}Si{^{1}H} DEPT (119 MHz, 299 K, CD_2Cl_2): δ = −10.9 (d, $^{2}J_{PSi}$ = 6.4 Hz,).



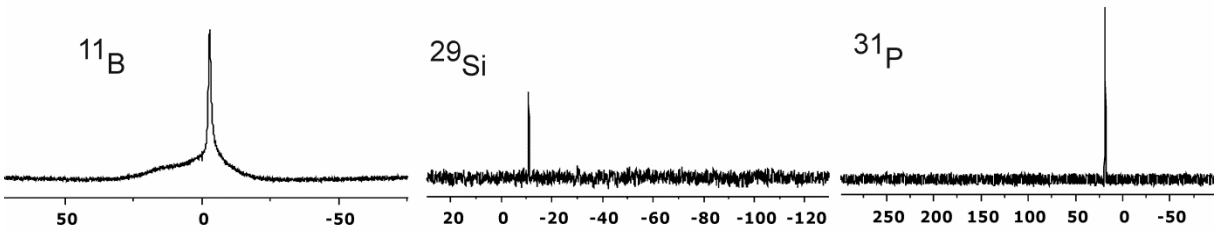
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2 (*)) of **6d.**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2 (*))of **6d**.

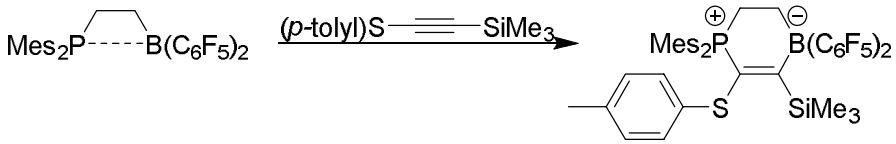


^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of **6d**.



$^{11}B\{^{1}H\}$ (192 MHz, 299 K, CD_2Cl_2), $^{29}Si\{^{1}H\}$ DEPT (119 MHz, 299 K, CD_2Cl_2) and $^{31}P\{^{1}H\}$ (243 MHz, 299 K, CD_2Cl_2) of **6d.**

Synthesis of compound 7



Dimesitylvinylphosphane (48.0 mg, 0.162 mmol, 1.0 eq.) and bis(pentafluorophenyl)borane (56.1 mg, 0.162 mmol, 1.0 eq.) were dissolved in pentane (4 mL) and stirred 30 min at room temperature. Then *p*-tolyl[(trimethylsilyl)ethenyl]sulfide (35.7 mg, 0.162 mmol, 1.0 eq.) was added. Immediately the reaction mixture turned yellow and a white solid precipitated. Stirring of the suspension was continued for overnight. Subsequently the supernatant solution was removed and the resulting residue was washed with pentane (5 mL). The obtained white solid was dried in vacuo to give compound **7** (65.5 mg, 0.076 mmol, 47%) as a white powder.

Crystals suitable for the X-ray crystal structure analysis were obtained from a pentane solution of compound **7** at -32°C.

IR (KBr) $\tilde{\nu}$ [cm^{-1}]= 2098 (w), 1734 (w), 1638 (m), 1607 (m), 1559 (w), 1510 (s), 1444 (s), 1387 (m), 1274 (m), 1243 (m), 1181 (w), 1110 (m), 1083 (s), 1034 (w), 977 (s), 956 (s), 913 (m), 886 (w), 834 (s), 805 (s), 782 (m), 735 (m), 700 (s), 647 (m), 621 (w), 576 (w), 550 (w), 499 (w), 481 (w), 459 (w), 434 (w), 412 (w).

Elemental analysis for $C_{45}H_{46}BF_{10}PSSi$: calcd. C 61.50% H 5.28%; found C 59.45% H 4.45%.

Melting point (DSC): 190 °C

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 6.82 (m, 2H, *o*-Tol), 6.65 (d, $^{4}J_{PH}$ = 2.3 Hz, 1H, *m*-Mes^{a}), 6.43 (m, 2H, *m*-Tol), 6.38 (d, $^{4}J_{PH}$ = 2.9 Hz, 1H, *m*'-Mes^{a}), 6.08 (s, 1H, *m*-Mes^{b}), 5.87 (d, $^{4}J_{PH}$ = 3.2 Hz, 1H, *m*'-Mes^{b}), 2.99 (s, 3H, *o*-$CH_3^{Mes,a}$), 2.89, 2.15 (each m, each 1H, PCH_2), 1.90 (s, 3H, *p*-$CH_3^{Mes,a}$), 1.89 (s, 3H, *p*-CH_3^{Tol}), 1.86 (s, 3H, *o*-$CH_3^{Mes,b}$), 1.85 (s, 3H, *o*'-$CH_3^{Mes,b}$), 1.76, 1.57 (each m, each 1H, BCH_2), 1.66 (s, 3H, *p*-$CH_3^{Mes,b}$), 1.45 (s, 3H, *o*'-$CH_3^{Mes,a}$), 0.39 (s, 9H, $SiCH_3$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ = 226.0 (br, BC=), 144.7 (d, $^{2}J_{PC}$ = 7.2 Hz, *o*-Mes^{b}), 144.3 (d, $^{2}J_{PC}$ = 7.6 Hz, *o*-Mes^{a}), 142.4 (d, $^{4}J_{PC}$ = 7.9 Hz, *p*-Mes^{b}), 142.3 (d, $^{4}J_{PC}$ = 7.8 Hz, *p*-Mes^{a}), 141.8 (d, $^{2}J_{PC}$ = 12.9 Hz, *o*'-Mes^{b}), 140.5 (d, $^{2}J_{PC}$ = 10.0 Hz, *o*'-Mes^{a}), 135.1 (*p*-Tol), 134.4 (*i*-Tol), 132.3 (d, $^{3}J_{PC}$ = 10.6 Hz, *m*-Mes^{a}), 132.2 (d, $^{3}J_{PC}$ = 10.3 Hz, *m*-Mes^{b}), 131.9 (d, $^{3}J_{PC}$ = 10.8 Hz, *m*'-Mes^{a}), 131.7 (d, $^{3}J_{PC}$ = 11.2 Hz, *m*'-Mes^{b}), 128.5 (*m*-Tol), 127.4 (*o*-Tol), 125.1 (d, $^{1}J_{PC}$ = 76.3 Hz, *i*-Mes^{a}), 120.5 (d, $^{1}J_{PC}$ = 76.6 Hz, *i*-Mes^{b}), 117.0 (d, $^{1}J_{PC}$ = 58.8 Hz, PC=)^{t}, 29.0 (d, $^{1}J_{PC}$ = 41.6 Hz, PCH_2), 24.9 (d, $^{3}J_{PC}$ = 5.4 Hz, *o*'-$CH_3^{Mes,b}$), 24.5 (d, $^{3}J_{PC}$ = 3.4 Hz, *o*-$CH_3^{Mes,b}$), 23.4 (d, $^{3}J_{PC}$ = 4.7 Hz, *o*'-$CH_3^{Mes,a}$), 22.9 (br, *o*-$CH_3^{Mes,a}$), 20.7 (*p*-CH_3^{Tol}),

20.6 (*p*-$CH_3^{Mes,a}$), 20.3 (*p*-$CH_3^{Mes,b}$), 15.5 (br, BCH_2), 3.1 ($^1J_{SiC}$ = 52.5 Hz, $SiCH_3$), [C_6F_5 not listed; ^{t} tentative assignment].

^{1}H, ^{1}H GCOSY (500 MHz / 500 MHz, 299 K, C_6D_6)[selective traces]: δ ^{1}H / δ ^{1}H = 6.82 / 6.43, 1.89 (*o*-Tol / *m*-Tol, *p*-CH_3^{Tol}), 6.65 / 6.38, 2.99, 1.90, 1.45 (*m*-Mes^a / *m*'-Mes^a, *o*-$CH_3^{Mes,a}$, *p*-$CH_3^{Mes,a}$, *o*'- $CH_3^{Mes,a}$), 6.08 / 5.87, 1.86, 1.85, 1.66 (*m*-Mes^b / *m*'-Mes^b, *o*-$CH_3^{Mes,b}$, *o'*-$CH_3^{Mes,b}$, *p*-$CH_3^{Mes,b}$), 2.89 / 2.15, 1.76, 1.53 (PCH_2 / PCH_2, BCH_2, BCH_2).

^{1}H, ^{13}C GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 6.82 / 127.4 (*o*-Tol), 6.65 / 132.3 (*m*-Mes^a), 6.43 / 128.5 (*m*-Tol), 6.38 / 131.9 (*m*'-Mes^a), 6.08 / 132.2 (*m*-Mes^b), 5.87 / 131.7 (*m*'-Mes^b), 2.99 / 22.9 (*o*-$CH_3^{Mes,a}$), 2.89 / 29.0 (PCH_2), 2.15 / 29.0 (PCH_2), 1.90 / 20.6 (*p*-$CH_3^{Mes,a}$), 1.89 / 20.7 (*p*-CH_3^{Tol}), 1.86 / 24.5 (*o*-$CH_3^{Mes,b}$), 1.85 / 24.9 (*o*'-$CH_3^{Mes,b}$), 1.76 / 15.5 (BCH_2), 1.66 / 20.3 (*p*- $CH_3^{Mes,b}$), 1.57 / 15.6 (BCH_2), 1.45 / 23.4 (*o*'- $CH_3^{Mes,a}$), 0.39 / 3.1 ($SiCH_3$).

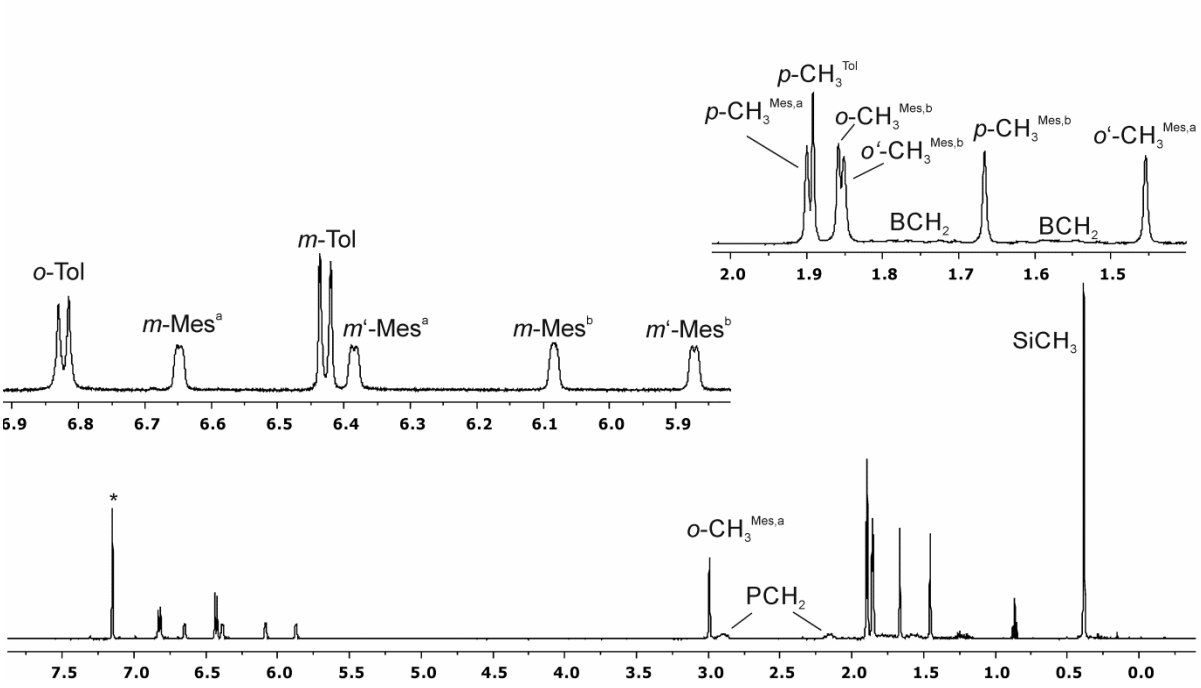
^{1}H, ^{13}C GHMBC (500 MHz / 126 MHz, 299 K, C_6D_6)[selective traces]: δ ^{1}H / δ ^{13}C = 6.65 / 131.9, 125.1, 22.9, 20.6 (*m*-Mes^a / *m*'-Mes^a, *i*-Mes^a, *o*-$CH_3^{Mes,a}$, *p*-$CH_3^{Mes,a}$), 6.43 / 134.4, 128.5, 127.4, 20.7 (*m*-Tol / *i*-Tol, *m*-Tol, *o*-Tol, *p*-CH_3^{Tol}), 6.38 / 132.3, 125.1, 23.4, 20.6 (*m*'-Mes^a / *m*-Mes^a, *i*-Mes^a, *o*'-$CH_3^{Mes,a}$, *p*-$CH_3^{Mes,a}$), 6.08 / 131.7, 120.5, 24.5, 20.4 (*m*-Mes^b / *m*'-Mes^b, *i*-Mes^b, *o*-$CH_3^{Mes,b}$, *p*-$CH_3^{Mes,b}$), 5.87 / 132.2, 120.5, 24.9, 20.3 (*m*'-Mes^b / *m*-Mes^b, *i*-Mes^b, *o*'-$CH_3^{Mes,b}$, *p*-$CH_3^{Mes,b}$), 2.99 / 144.3, 132.3, 125.1 (*o*-$CH_3^{Mes,a}$ / *o*-Mes^a, *m*-Mes^a, *i*-Mes^a), 1.90 / 142.3, 132.3 (*p*-$CH_3^{Mes,a}$ / *p*-Mes^a, *m*-Mes^a), 1.89 / 135.1, 128.5 (*p*-CH_3^{Tol} / *p*-Tol, *m*-Tol), 1.86 / 144.7, 132.2 (*o*-$CH_3^{Mes,b}$ / *o*-Mes^b, *m*-Mes^b), 1.85 / 141.8, 131.7, (*o*'- $CH_3^{Mes,b}$ / *o*'-Mes^b, *m*'-Mes^b), 1.66 / 144.3, 132.2, 131.7 (*p*- $CH_3^{Mes,b}$ / *o*-Mes^a, *m*-Mes^b, *m*'-Mes^b), 1.45 / 140.5, 131.9, 125.1 (*o*'-$CH_3^{Mes,a}$ / *o*'-Mes^a, *m*'-Mes^a, *i*-Mes^a), 0.39 / 226.0, 3.1 ($SiCH_3$ / BC=, $SiCH_3$).

^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ = –12.4 ($v_{1/2}$ ~ 60 Hz)

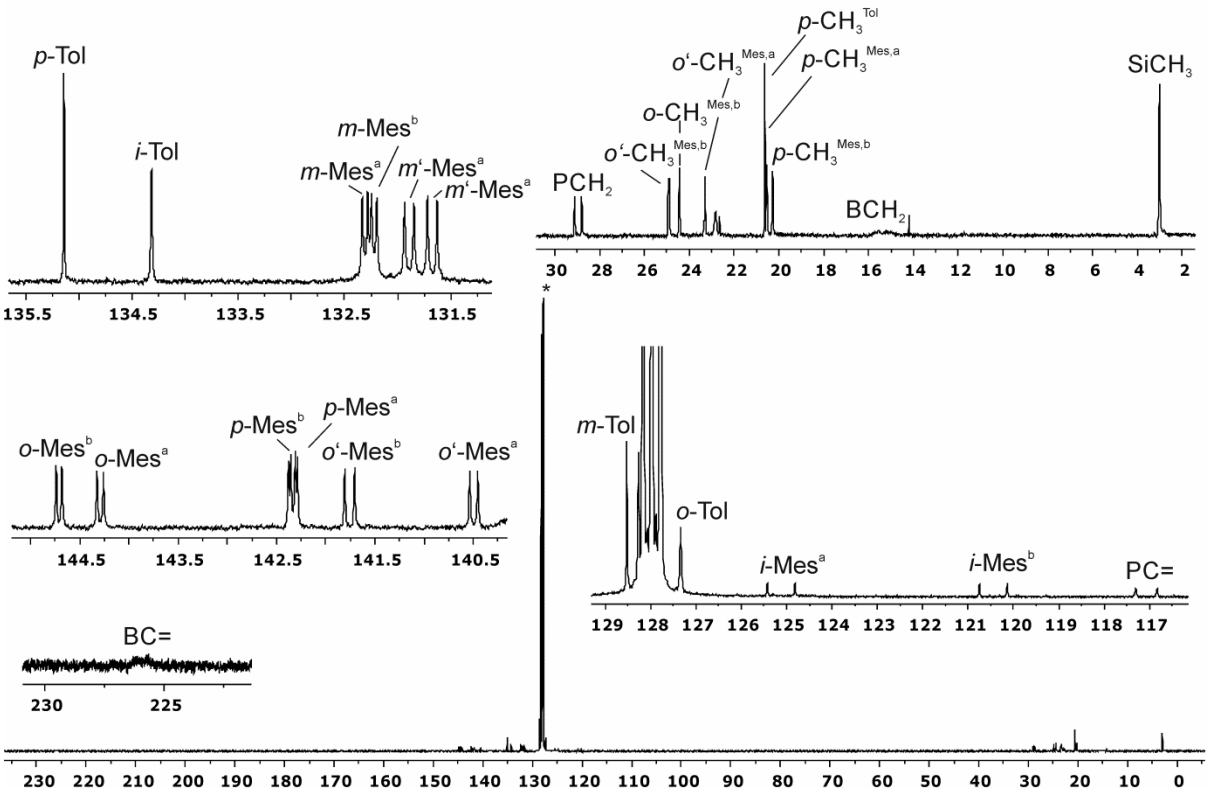
^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = –124.0, -127.0, -128.4, -128.9 (each br, each 1F, *o*-C_6F_5), –160.29 (t, $^3J_{FF}$ = 20.8 Hz), -160.34 (t, $^3J_{FF}$ = 21.1 Hz) (each 1F, *p*-C_6F_5), –164.1 (2F), -165.3 (1F), -165.6 (1F)(each br, 4F, *m*-C_6F_5).

^{29}Si{^{1}H} DEPT (99 MHz, 299 K, C_6D_6): δ = −3.0 (dm, $^3J_{PSi}$ = 25.0 Hz,).

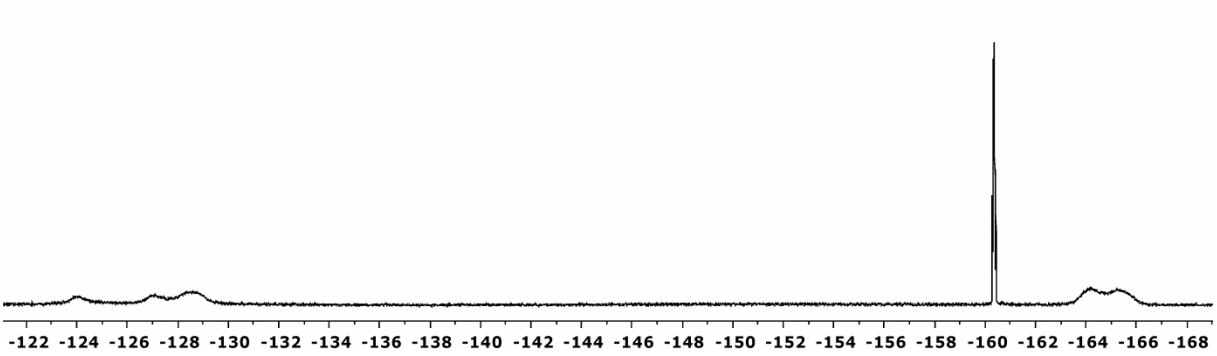
^{31}P{^{1}H} NMR (202 MHz, 299 K, C_6D_6): δ = 5.1 ($v_{1/2}$ ~ 20 Hz).



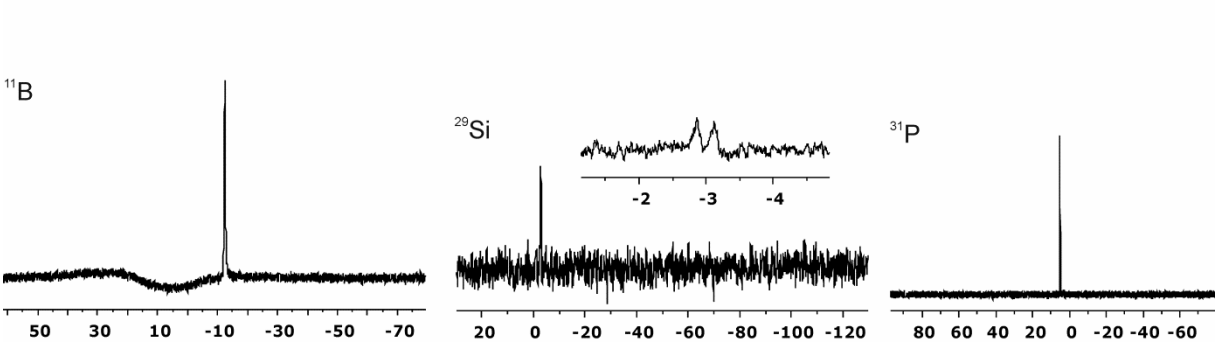
^{1}H NMR (500 MHz, 299 K, C_6D_6 (*)) of **7.**



^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6 (*)) of **7.**.

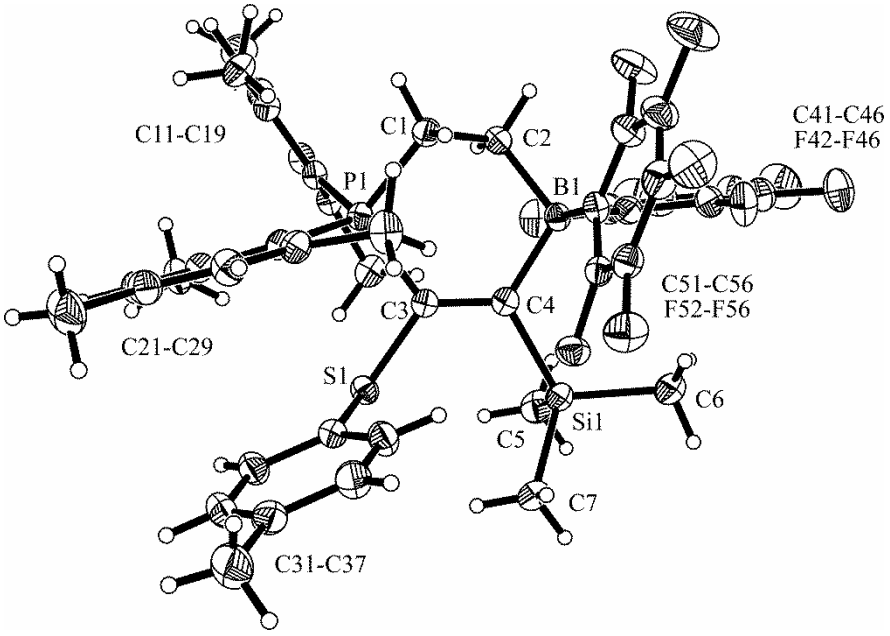


^{19}F NMR (470 MHz, 299 K, C_6D_6) of **7.**



^{11}B{^{1}H} (160 MHz, 299 K, C_6D_6), ^{29}Si{^{1}H} DEPT (99 MHz, 299 K, C_6D_6) and ^{31}P{^{1}H} (202 MHz, 299 K, C_6D_6) of **7.**

X-ray crystal structure analysis of compound 7: formula $C_{44}H_{42}BF_{10}PSSi$, M = 862.71, colourless crystal, 0.10 x 0.05 x 0.02 mm, a = 16.1212(4), b = 12.6187(4), c = 21.1518(7) Å, β = 108.148(1)°, V = 4088.8(2) Å^3, ρ_{calc} = 1.401 gcm^{-3}, μ = 2.037 mm^{-1}, empirical absorption correction (0.822 ≤ T ≤ 0.960), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 41584 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 7206 independent (R_{int} = 0.073) and 5489 observed reflections [I>2σ(I)], 533 refined parameters, R = 0.045, wR^2 = 0.125, max. (min.) residual electron density 0.31 (-0.29) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.


C11-C19
C1
C2
C41-C46
F42-F46
P1
B1
C51-C56
F52-F56
C3
C4
C21-C29
S1
C6
Si1
C5
C7
C31-C37