Phosphirenium Borate Betaines from Alkynylphosphanes and the Halogeno-B(C_6F_5)$_2$ Reagents

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Supporting Information

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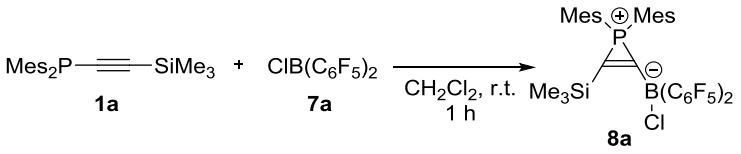
General Information: All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glovebox) under an atmosphere of argon. Solvents were dried and stored under an argon atmosphere. NMR spectra were recorded on a Varian Inova 500 (^{1}H 500 MHz, ^{13}C 126 MHz, ^{19}F 470 MHz, ^{11}B 160 MHz, ^{31}P 202 MHz) and on a 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 shifts δ are given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (external reference, δ = 0), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference, δ = 0), ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in D_2O) (external reference, δ = 0). NMR assignments were supported by additional 2D-NMR experiments. Elemental analyses: Foss–Heraeus CHNO-Rapid.

X-Ray diffraction: For compounds **8b** und **8f** sets were collected with a Nonius Kappa CCD 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). Data sets for compounds **8a** and **8g** were collected with a D8 Venture CMOS diffractometer. For compound **8e** data sets were collected with a Bruker APEX II CCD diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution SHELXT-2015 (Sheldrick, **2015**); structure refinement SHELXL-2015 (Sheldrick, **2015**) and graphics, XP (Bruker AXS Inc., **2015**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compound **8b** a half badly disordered dichloromethane molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek (**2015**) Acta Cryst., C71, 9-18) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule. For compound **8f** one C_6F_5 group and for compound **8e** one half toluene molecule were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. CCDC deposition numbers are 1865543 to 1865547.

Materials: 1) Chloro bis(pentafluorophenyl)borane (**7a**) and Bromo bis(pentafluorophenyl)-borane (**7b**) [A. Ueno, J. Li, C. G. Daniliuc, G. Kehr, G. Erker, *Chem. Eur. J.* **2018**, *24*, 10044-10048.], 2) compound **1a** [A. Ueno, X. Tao, C. G. Daniliuc, G. Kehr, G. Erker, *Organometallics*, 2018, **37**, 2665.], 3) compound **1b** [O. Ekkert, R. Fröhlich, G. Kehr, G. Erker, *J. Am. Chem. Soc.* **2011**, *133*, 4610-4616.], 4) compound **1c** (Mes, tBu) [C. Appelt, H. Westenberg, F. Bertini, A. W.

Ehlers, J. C. Slootweg, K. Lammertsma, W. Uhl, *Angew. Chem. Int. Ed.* **2011**, *50*, 3925-3928.], 5) compound **1d** [J. C. Lee, F. E. Hong, *Organometallics* **2005**, *24*, 5686-5695.] were synthesized according to procedures descripted in the literature.

Preparation of compound 8a:



Scheme S1

A mixture of compound **1a** (36.5 mg, 0.10 mmol) and chloro bis(pentafluorophenyl)borane (**7a**, 38.0 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) was stirred for 1 hour at room temperature. Then, the colorless solution was concentrated *in vacuo* and *n*-pentane (5 mL) was added to the resulting residue. After stirring the obtained suspension for 15 minutes, the white precipitate was collected and dried *in vacuo* to give compound **8a** as a white powder (60.2 mg, 0.08 mmol, 81%).

Melting point: 135 °C

Elemental Analysis calcd for $C_{35}H_{31}BClF_{10}PSi$ (746.94 g/mol): C, 56.28; H, 4.18. Found: C, 56.40; H, 4.43.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 6.92 (m, 4H, *m*-Mes), 2.33 (s, 12H, *o*-Me^{Mes}), 2.30 (s, 6H, *p*-Me^{Mes}), 0.30 (s, $^{2}J_{SiH}$ = 6.8 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 165.3 (br, BC=), 148.0 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 144.1 (d, $^{4}J_{PC}$ = 3.0 Hz, *p*-Mes), 143.1 (d, $^{2}J_{PC}$ = 11.7 Hz, *o*-Mes), 141.5 (d, $^{1}J_{PC}$ = 29.7 Hz, SiC=), 139.9 (dm, $^{1}J_{FC}$ ~ 249 Hz, C_6F_5), 137.3 (dm, $^{1}J_{FC}$ ~ 252 Hz, C_6F_5), 130.7 (d, $^{3}J_{PC}$ = 12.8 Hz, *m*-Mes), 120.9 (d, $^{1}J_{PC}$ = 96.9 Hz, *i*-Mes), 120.8 (i-C_6F_5), 22.4 (d, $^{3}J_{PC}$ = 8.3 Hz, *o*-Me^{Mes}), 21.3 (*p*-Me^{Mes}), -0.5 ($^{1}J_{SiC}$ = 55.5 Hz, $SiMe_3$).

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = -7.8 ($\nu_{1/2}$ ~ 150 Hz).

^{31}P NMR (202 MHz, CD_2Cl_2, 299 K): δ = -151.5 ($\nu_{1/2}$ ~ 17 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -130.5 (m, 2F, *o*-C_6F_5), -159.7 (t, $^{3}J_{FF}$ = 19.2 Hz, 1F, *p*-C_6F_5), -165.4 (m, 2F, *m*-C_6F_5), [$\Delta^{19}F_{m,p}$ = 5.7].

^{29}Si{^{1}H} DEPT (119 MHz, C_6D_6, 299 K): δ = -1.4 (d, $^{2}J_{PSi}$ = 4.8 Hz).

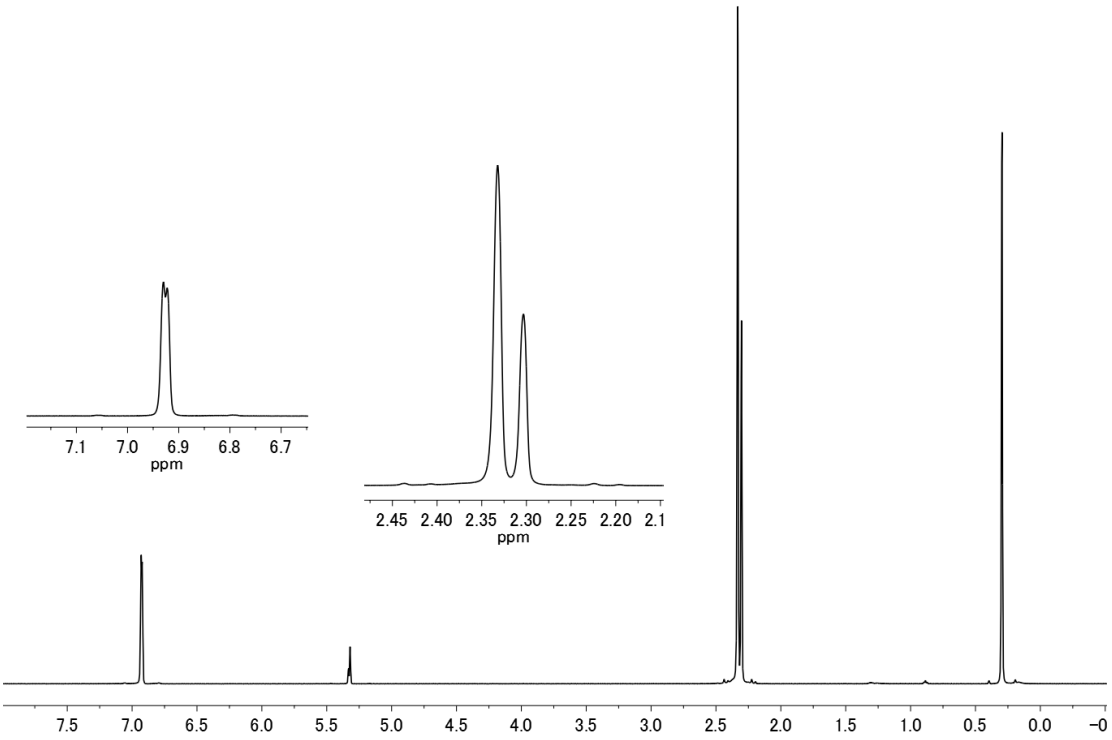


Figure S1 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **8a**.

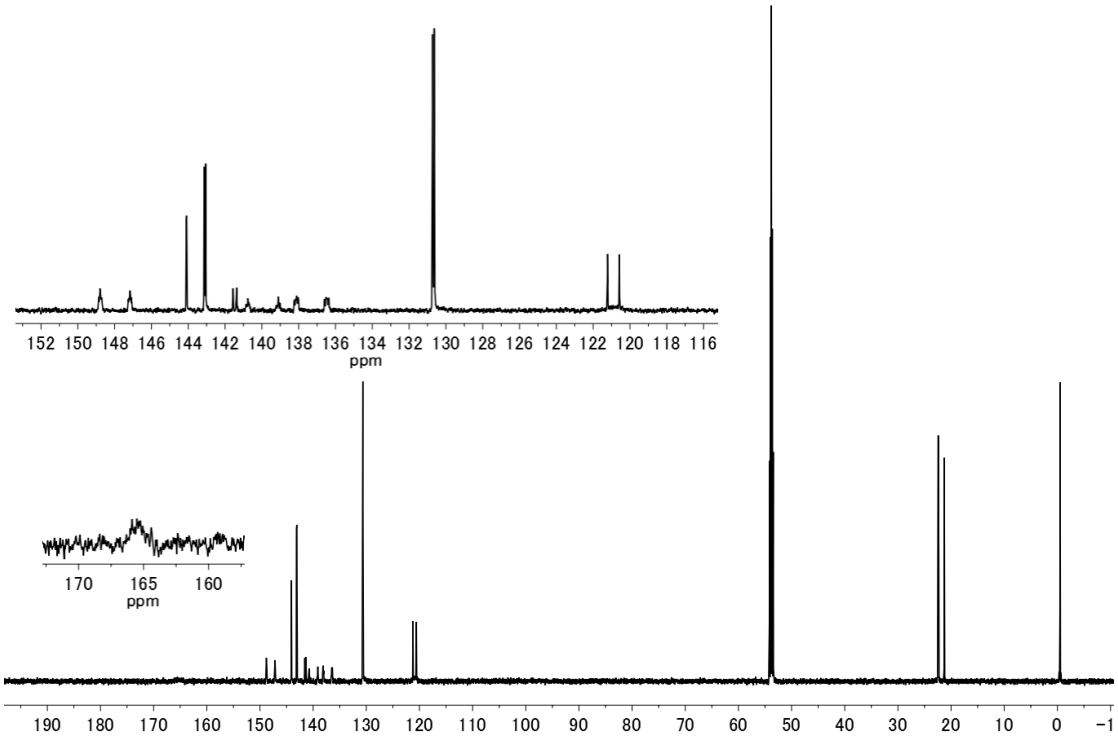


Figure S2 **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **8a**.

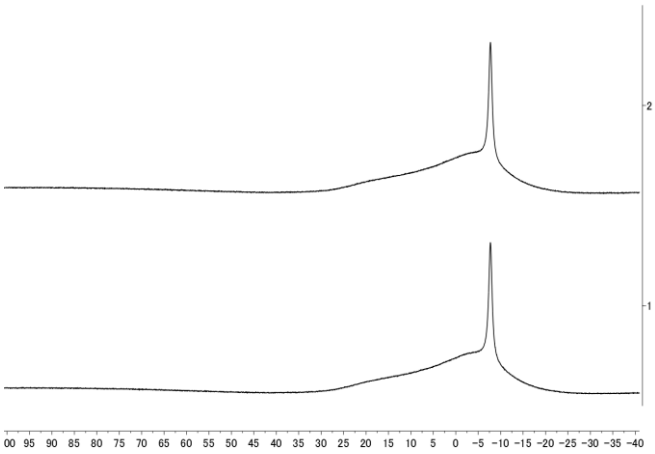


Figure S3 (1) **^{11}B{^{1}H}** and (2) **^{11}B NMR** (192 MHz, CD_2Cl_2, 299 K) spectra of compound **8a**.

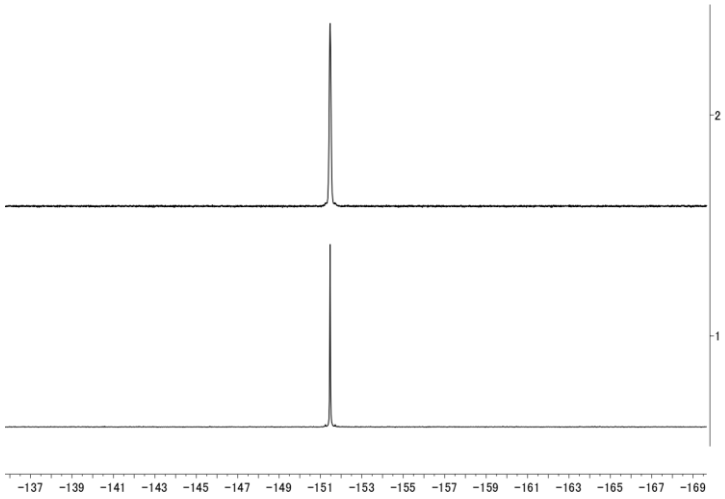


Figure S4 (1) **^{31}P{^{1}H}** and (2) **^{31}P NMR** (202 MHz, CD_2Cl_2, 299K) spectra of compound **8a**.

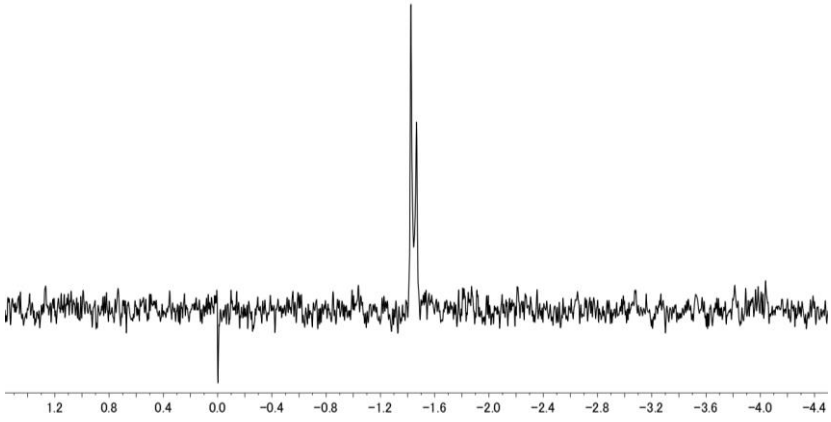


Figure S5 **^{29}Si{^{1}H} DEPT** (119 MHz, CD_2Cl_2, 299 K)) spectra of compound **8a**.

Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a saturated solution of compound **8a** in CH_2Cl_2 at -35 °C.

X-ray crystal structure analysis of compound 8a (erk8890): A colorless prism-like specimen of $C_{35}H_{31}BClF_{10}PSi$, approximate dimensions 0.129 mm x 0.153 mm x 0.187 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1325 frames were collected. The total exposure time was 14.72 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 78562 reflections to a maximum θ angle of 26.73° (0.79 Å resolution), of which 7216 were independent (average redundancy 10.887, completeness = 99.9%, R_{int} = 6.57%, R_{sig} = 3.00%) and 5820 (80.65%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.9107(4) Å, b = 17.0092(6) Å, c = 18.4957(6) Å, β = 97.9540(10)°, volume = 3399.5(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 9969 reflections above 20 σ(I) with 4.750° < 2θ < 54.94°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.933. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9500 and 0.9650. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{35}H_{31}BClF_{10}PSi$. The final anisotropic full-matrix least-squares refinement on F^2 with 451 variables converged at R1 = 3.55%, for the observed data and wR2 = 8.32% for all data. The goodness-of-fit was 1.026. The largest peak in the final difference electron density synthesis was 0.306 $e^-/Å^3$ and the largest hole was -0.318 $e^-/Å^3$ with an RMS deviation of 0.056 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.459 g/cm^3 and F(000), 1528 e^-.

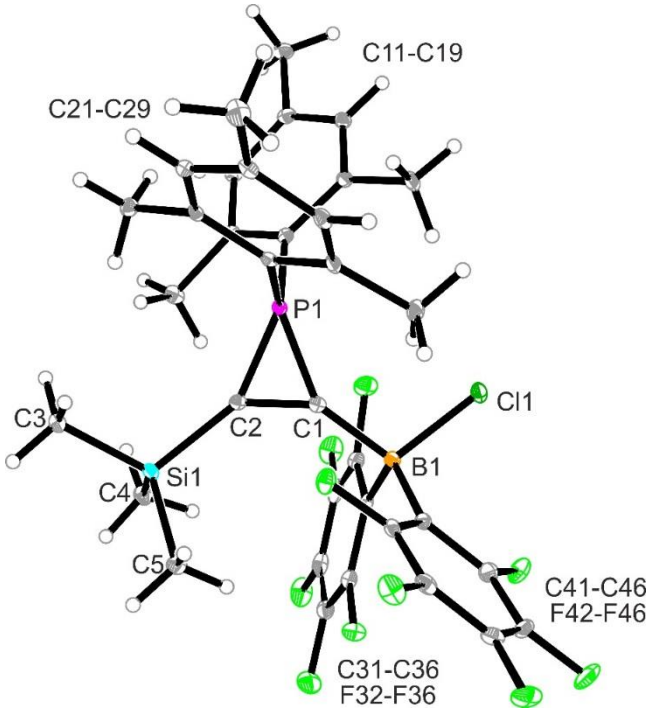
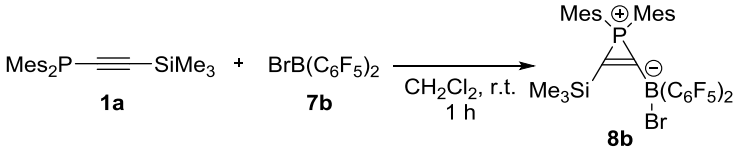


Figure S6: Crystal structure of compound **8a** (thermal ellipsoids: 30% probability).

Preparation of compound 8b:



Scheme S2

A mixture of **1a** (73 mg, 0.20 mmol) and bromo bis(pentafluorophenyl)borane (**7b**, 84 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) was stirred for 1 hour at room temperature. Then, the colorless solution was concentrated *in vacuo* and *n*-pentane (5 mL) was added to the resulting residue. After stirring the obtained suspension for 15 minutes, the white precipitate was collected and dried *in vacuo* to give compound **8b** as a white powder (115 mg, 0.145 mmol, 73%).

Melting point: 145 °C

Elemental Analysis calcd for $C_{35}H_{31}BBrF_{10}PSi$ (791.39 g/mol): C, 53.12; H, 3.95. Found: C, 53.02; H, 4.00.

^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 6.93 (m, 4H, *m*-Mes), 2.31 (s, 18H, *p*,*o*-Me^{Mes}), 0.37 (s, $^{2}J_{SiH}$ = 6.9 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = 164.0 (br, BC=), 148.0 (dm, $^{1}J_{FC}$ ~ 242 Hz, C_6F_5), 144.2 (d, $^{4}J_{PC}$ = 3.1 Hz, *p*-Mes) 143.1 (d, $^{2}J_{PC}$ = 12.0 Hz, *o*-Mes), 142.8 (d, $^{1}J_{PC}$ = 30.1 Hz, SiC=), 140.0 (dm, $^{1}J_{FC}$ ~ 259 Hz, C_6F_5), 137.3 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 130.6 (d, $^{3}J_{PC}$ = 13.3 Hz, *m*-Mes), 120.8 (d, $^{1}J_{PC}$ = 95.9 Hz, *i*-Mes), 120.2 (i-C_6F_5), 22.5 (d, $^{3}J_{PC}$ = 9.0 Hz, *o*-Me^{Mes}), 21.3 (*p*-Me^{Mes}), -0.2 (d, $^{3}J_{PC}$ = 1.6 Hz, $^{1}J_{SiC}$ = 55.6 Hz, $SiMe_3$).

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = -11.4 ($\nu_{1/2}$ ~ 250 Hz).

^{31}P NMR (243 MHz, CD_2Cl_2, 299 K): δ = -149.3 ($\nu_{1/2}$ ~ 20 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -129.1 (br, 2F, *o*-C_6F_5), -159.4 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), -165.3 (m, 2F, *m*-C_6F_5), [$\Delta^{19}F_{m,p}$ = 5.9].

^{29}Si{^{1}H} DEPT (99 MHz, CD_2Cl_2, 299 K): δ = -1.3 (d, $^{2}J_{PSi}$ = 5.1 Hz).

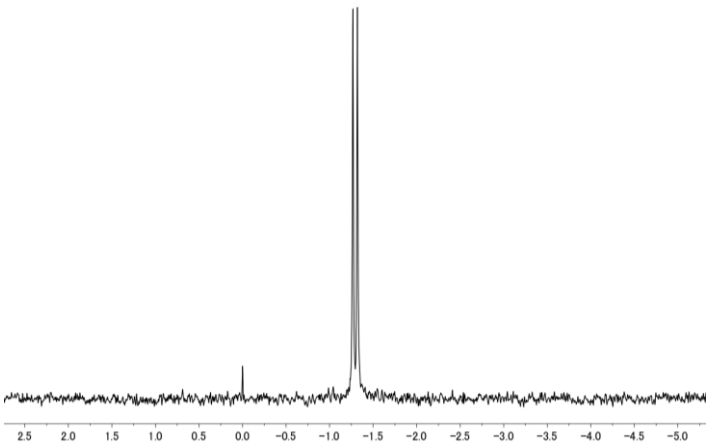


Figure S7 **^{29}Si{^{1}H} DEPT** (99 MHz, CD_2Cl_2, 299 K)) spectrum of compound **8b**.

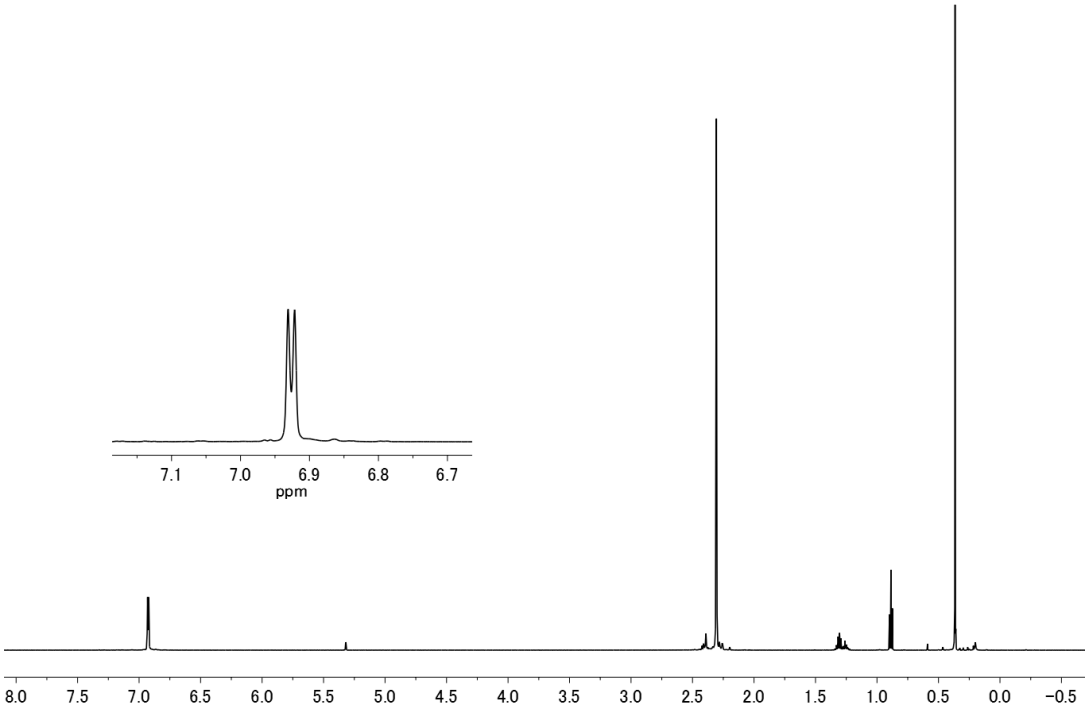


Figure S8 **^{1}H NMR** (500 MHz, CD_2Cl_2, 299K) spectrum of compound **8b**.

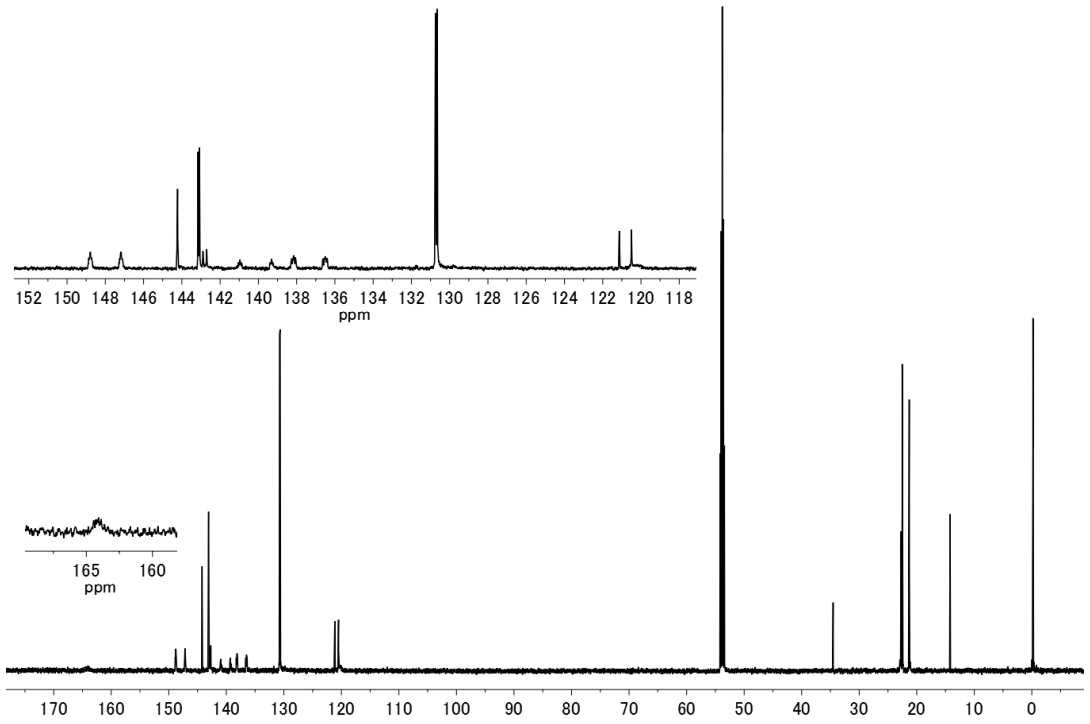


Figure S9 **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2, 299K) spectrum of compound **8b**.

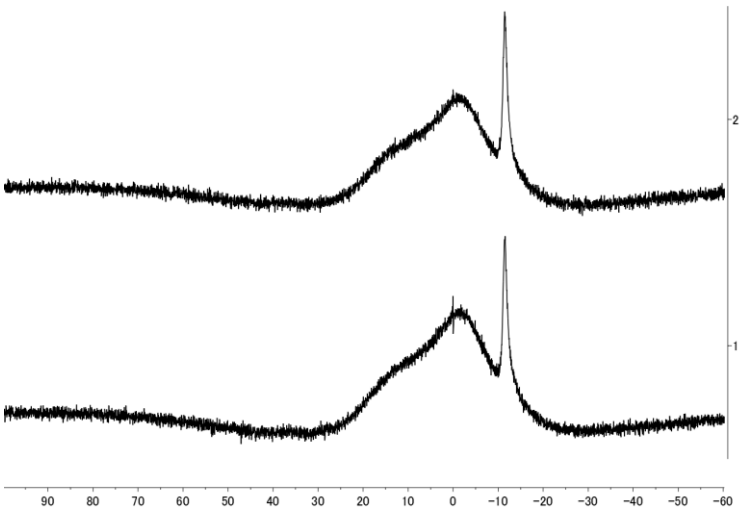


Figure S10 (1) **^{11}B{^{1}H}** and (2) **^{11}B NMR** (192 MHz, CD_2Cl_2, 299 K) spectra of compound **8b**.

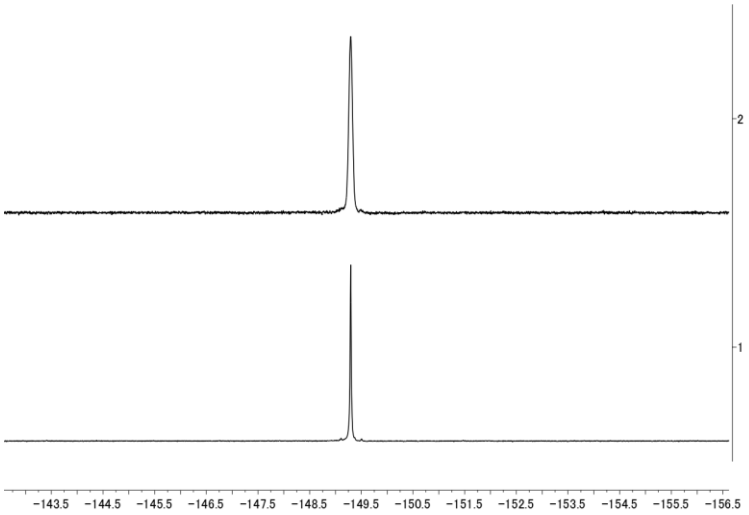


Figure S11 (1) **^{31}P{^{1}H}** and (2) **^{31}P NMR** (243 MHz, CD_2Cl_2, 299K) spectra of compound **8b**.

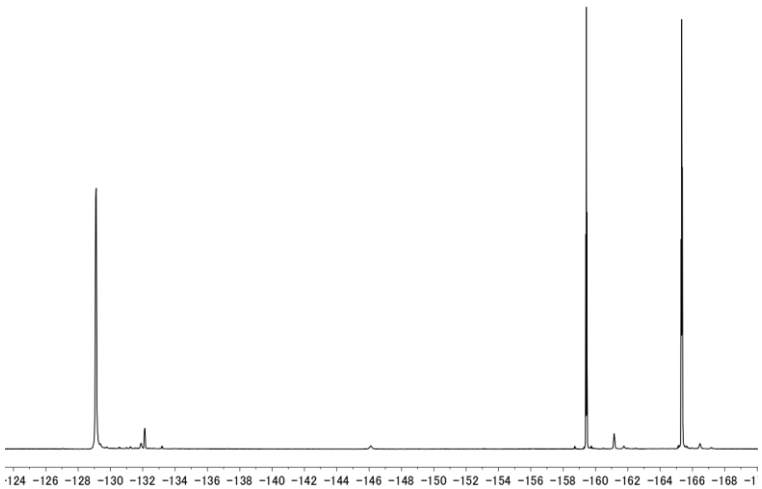


Figure S12 **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **8b**.

Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a saturated solution of compound **8b** in CH_2Cl_2 at -35 °C.

X-ray crystal structure analysis of compound 8b (erk9214): formula $C_{35}H_{31}BBrF_{10}PSi$, M = 791.38, colourless crystal, 0.08 x 0.07 x 0.07 mm, a = 9.6668(2) Å, b = 20.0637(4) Å, c = 19.4399(3) Å, β = 95.326(2)°, V = 3754.12(12) Å^3, ρ_{calc} = 1.400 gcm^{-3}, μ = 1.243 mm^{-1}, empirical absorption correction (0.907 ≤ T ≤ 0.918), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 173(2) K, ω and φ scans, 26502 reflections collected (±h, ±k, ±l), 6527 independent (R_{int} = 0.066) and 5034 observed reflections [I>2σI)], 451 refined parameters, R = 0.051, wR^2 = 0.113, max. (min.) residual electron density 0.48 (-0.39) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

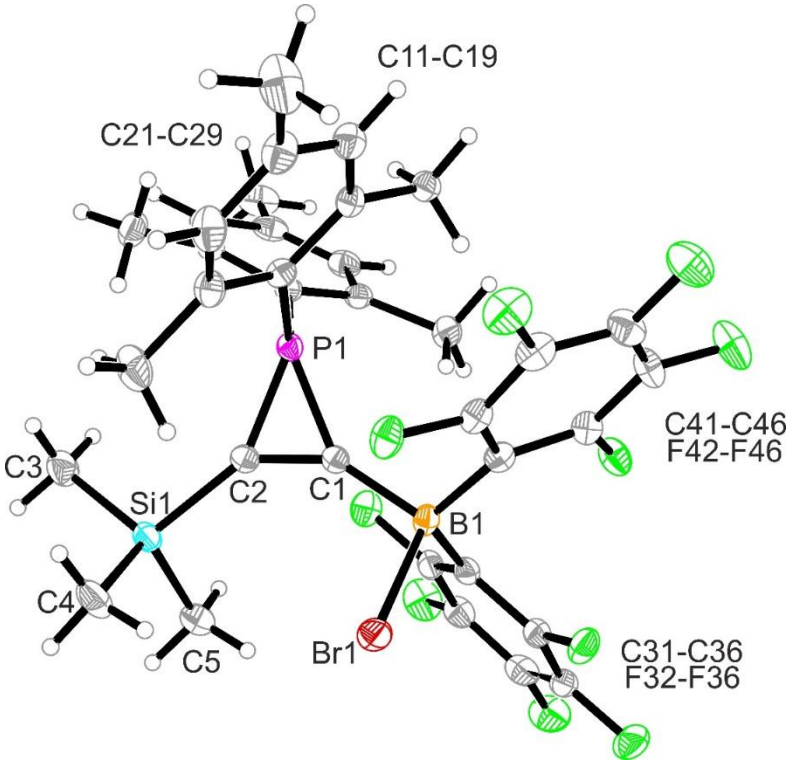
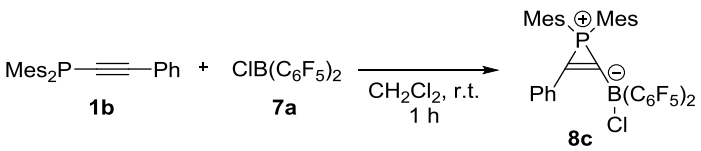


Figure S13: Crystal structure of compound **8b** (thermal ellipsoids: 30% probability).

Preparation of compound 8c



Scheme S3

A mixture of compound **1b** (37 mg, 0.10 mmol) and chlorobis(pentafluorophenyl)borane (**7a**, 38.0 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) was stirred for 1 hour at room temperature. After the colorless solution was concentrated *in vacuo*, *n*-pentane (5 mL) was added to the obtained residue. After stirring the resulting suspension for 15 minutes, the white precipitate was collected and dried *in vacuo* to give compound **8c** as a white powder (65.2 mg, 0.087 mmol, 87%).

Melting point: 125 °C

Elemental Analysis calcd for $C_{38}H_{27}BClF_{10}P$ (750.85 g/mol): C, 60.79; H, 3.62. Found: C, 60.49; H, 3.43.

^{1}H NMR (600 MHz, toluene-d_8, 299 K): δ = 7.69 (m, 2H, *o*-Ph), 6.95 (m, 2H, *m*-Ph), 6.91 (m, 1H, *p*-Ph), 6.41 (m, 4H, *m*-Mes), 2.11 (s, 12H, *o*-Me^{Mes}), 1.88 (s, 6H, *p*-Me^{Mes}).

^{13}C{^{1}H} NMR (151 MHz, toluene-d_8, 299 K): δ = 148.5 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 146.1 (br, BC=), 144.0 (d, $^{4}J_{PC}$ = 1.8 Hz, *p*-Mes), 142.8 (d, $^{2}J_{PC}$ = 11.7 Hz, *o*-Mes), 140.1 (dm, $^{1}J_{FC}$ ~ 245 Hz, C_6F_5), 137.5 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 136.5 (PhC=), 131.6 (*p*-Ph), 131.0 (*o*-Ph), 130.9 (m-Mes), 129.4 (*m*-Ph), 126.8 (d, $^{2}J_{PC}$ = 3.7 Hz, *i*-Ph), 121.3 (*i*-C_6F_5), 120.8 (d, $^{1}J_{PC}$ = 92.5Hz, *i*-Mes), 22.4 (*o*-Me^{Mes}), 20.9 (*p*-Me^{Mes}).

^{11}B NMR (192 MHz, toluene-d_8, 299 K): δ = -8.0 ($\nu_{1/2}$ ~ 350 Hz).

^{31}P NMR (243 MHz, toluene-d_8, 299 K): δ = -140.3 ($\nu_{1/2}$ ~ 20 Hz).

^{19}F NMR (564 MHz, toluene-d_8, 299 K): δ = -130.8 (m, 2F, *o*-C_6F_5), -159.0 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-C_6F_5), -164.6 (m, 2F, *m*-C_6F_5), [$\Delta^{19}F_{m,p}$ = 5.6].

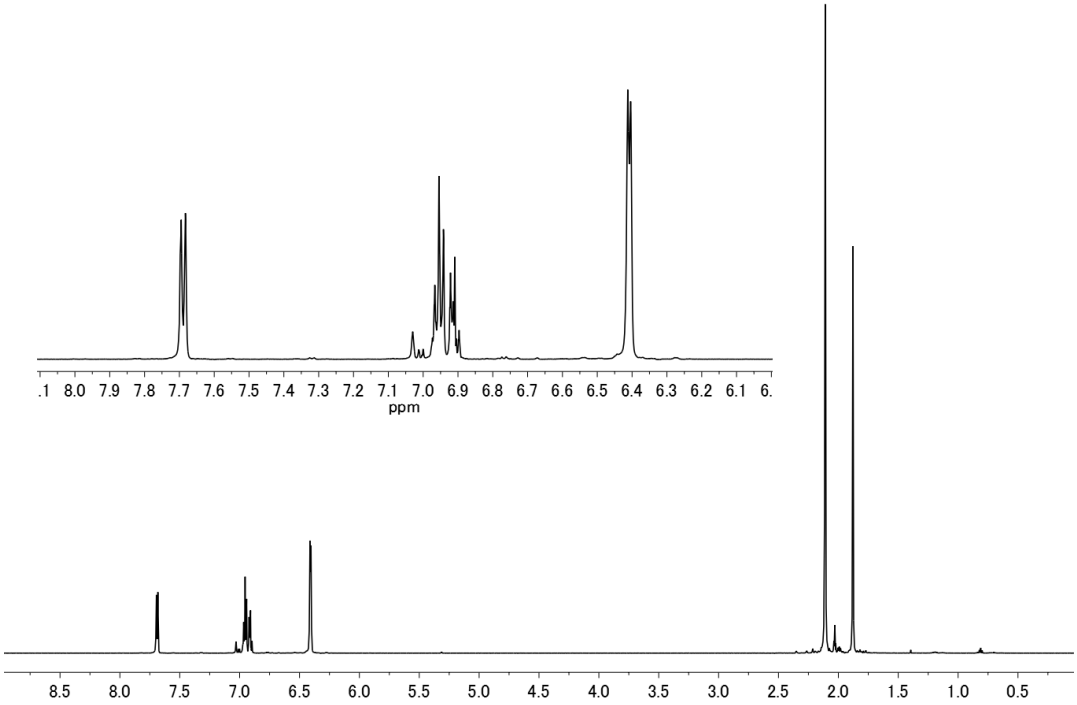


Figure S14 **^{1}H NMR** (600 MHz, toluene-d_8, 299 K) spectrum of compound **8c**.

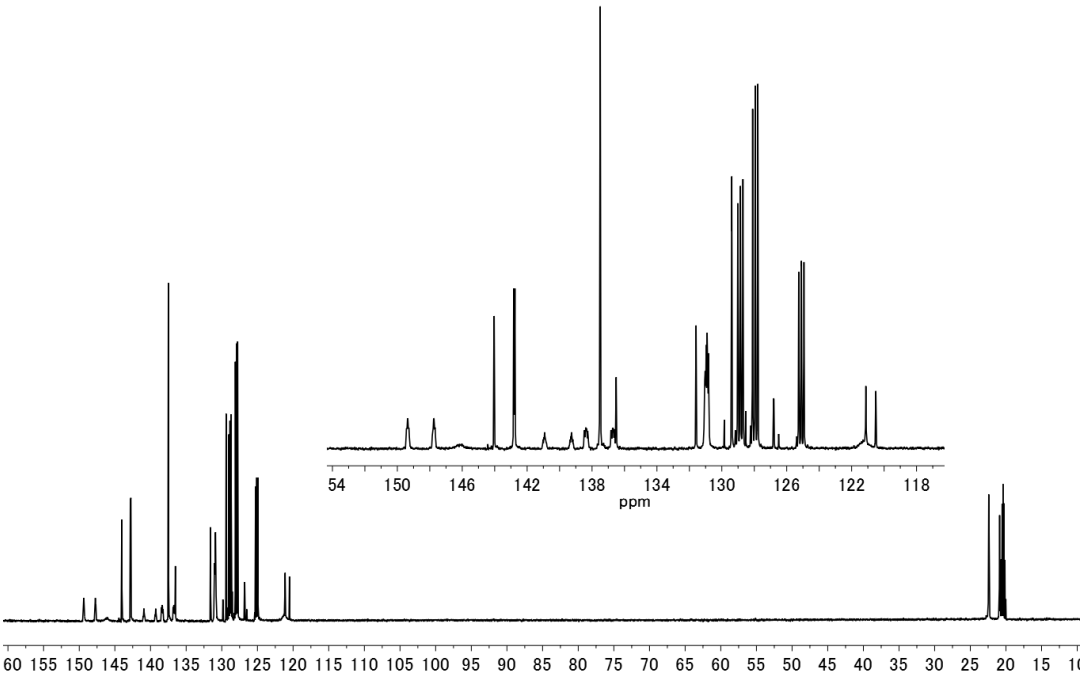


Figure S15 **$^{13}C\{^{1}H\}$ NMR** (151 MHz, toluene-d_8, 299 K) spectrum of compound **8c**.

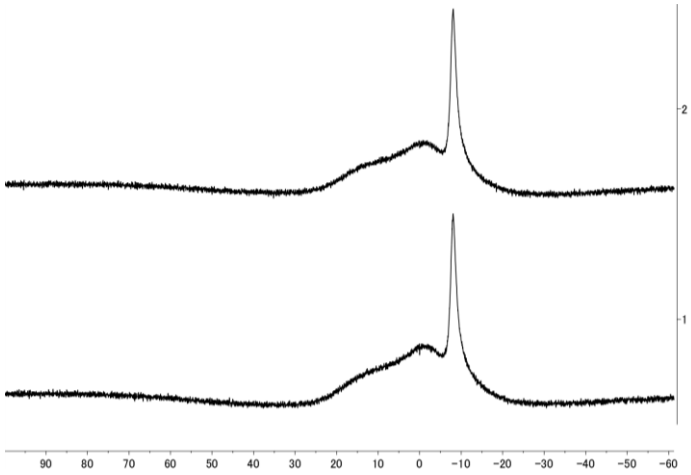


Figure S16 (1) **$^{11}B\{^{1}H\}$** and (2) **^{11}B NMR** (192 MHz, toluene-d_8, 299 K) spectra of compound **8c**.

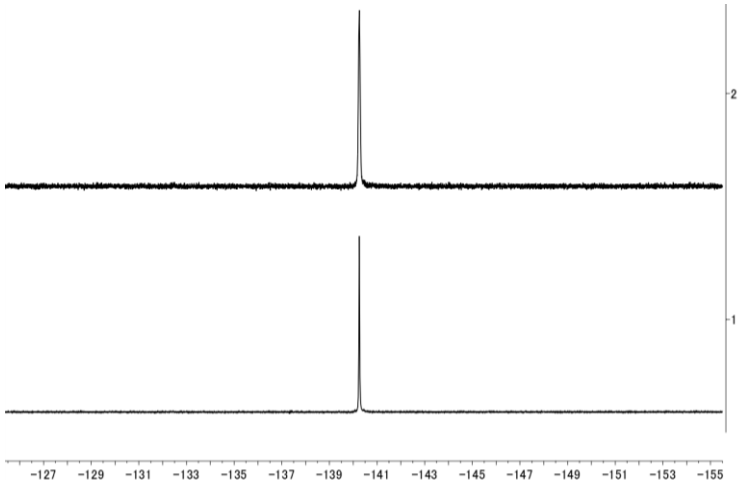


Figure S17 (1) **$^{31}P\{^{1}H\}$** and (2) **^{31}P NMR** (243 MHz, toluene-d_8, 299 K) spectra of compound **8c**.

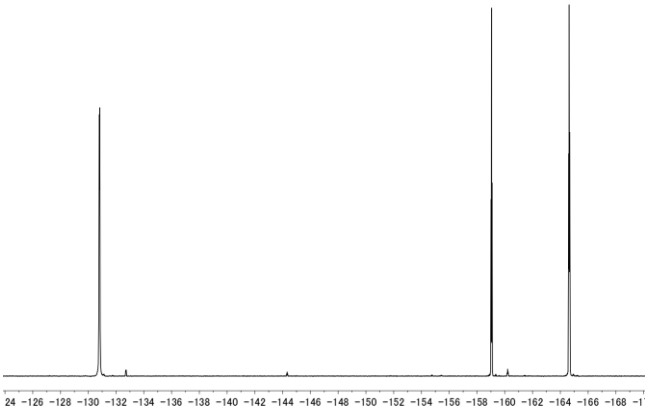
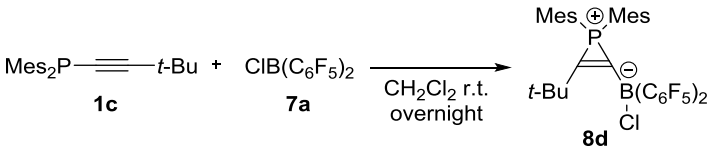


Figure S18 **^{19}F NMR** (564 MHz, toluene-d_8, 299 K) spectrum of compound **8c**.

Preparation of compound 8d:



Scheme S4

A solution of phosphane **1c** (70.1 mg, 0.20 mmol, 1.0 eq.) in CH_2Cl_2 (1 mL) was added to a solution of chlorobis(pentafluorophenyl)borane **7a** (76.1 mg, 0.20 mmol, 1.0 eq.) in CH_2Cl_2 (1 mL). The colorless reaction mixture was stirred at room temperature overnight, then all volatiles were removed *in vacuo*. The residue was suspensed with *n*-pentane (5 mL) and the mixture was filtrated. Subsequently the filtrate was stored at -36 °C whereby compound **8d** was obtained as an offwhite solid (113 mg, 0.15 mmol, 77%).

Melting point: 110 °C.

Elemental Analysis calcd for $C_{36}H_{31}BClF_{10}P$ (730.86 g/mol): C, 59.16; H, 4.28. Found: C, 58.74; H, 4.75.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 6.94 (d, $^4J_{PH}$ = 5.3 Hz, 4H, *m*-Mes), 2.33 (s, 12H, *o*-Me^{Mes}), 2.31 (s, 6H, *p*-Me^{Mes}), 1.33 (s, 9H, *t*-Bu).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = n.o. (br, BC=), 149.0 (d, $^1J_{PC}$ = 10.3 Hz, *t*-BuC=), 147.9 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 143.9 (d, $^4J_{PC}$ = 3.4 Hz, *p*-Mes), 142.6 (d, $^2J_{PC}$ = 11.9 Hz, *o*-Mes), 139.9 (dm, $^1J_{FC}$ ~ 260 Hz, C_6F_5), 137.3 (dm, $^1J_{FC}$ ~ 260 Hz, C_6F_5), 130.8 (d, $^3J_{PC}$ = 13.8 Hz, *m*-Mes), 121.7 (d, $^1J_{PC}$ = 91.9 Hz, *i*-Mes), n.o. (i-C_6F_5), 37.3 (d, $^2J_{PC}$ = 3.6 Hz, $C^{t\text{-Bu}}$), 29.9 (d, $^3J_{PC}$ = 4.9 Hz, $CH_3{}^{t\text{-Bu}}$), 22.3 (m, *o*-Me^{Mes}), 20.9 (*p*-Me^{Mes}).

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = -8.2 ($\nu_{1/2}$ ~ 200 Hz).

^{31}P NMR (243 MHz, CD_2Cl_2, 299 K): δ = -138.7 ($\nu_{1/2}$ ~ 25 Hz).

$^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2, 299 K): δ = -138.7 ($\nu_{1/2}$ ~ 5 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -130.3 (m, 2F, *o*-C_6F_5), -159.8 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F, *p*-C_6F_5), -165.4 (m, 2F, *m*-C_6F_5), [$\Delta^{19}F_{m,p}$ = 5.6].

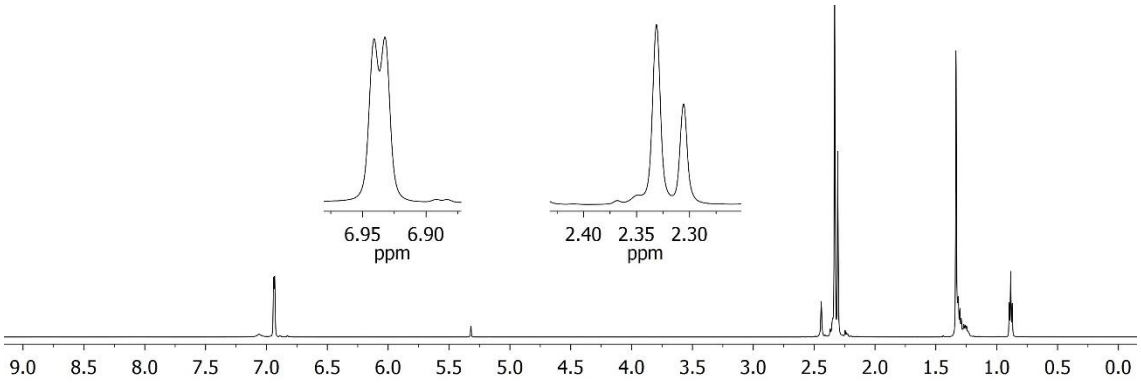


Figure S19 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum of compound **8d**.

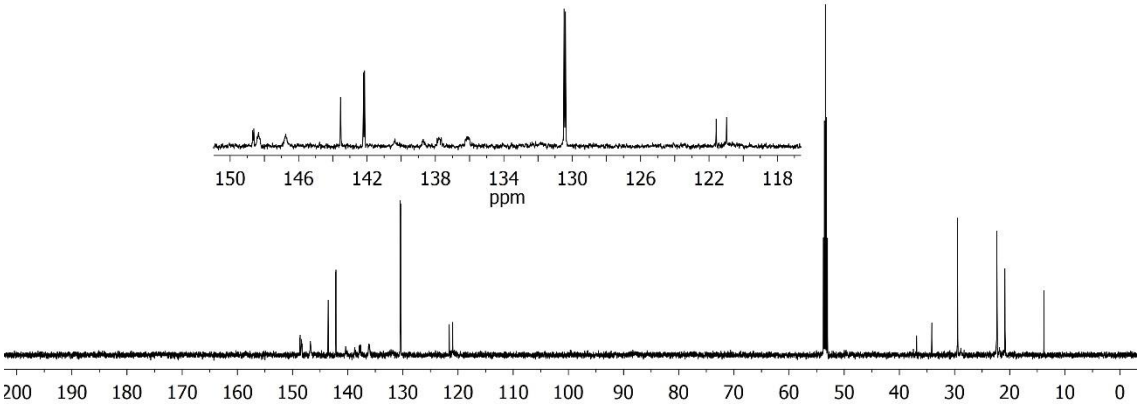


Figure S20 **$^{13}C\{^{1}H\}$ NMR** (151 MHz, CD_2Cl_2, 299 K) spectrum of compound **8d**.

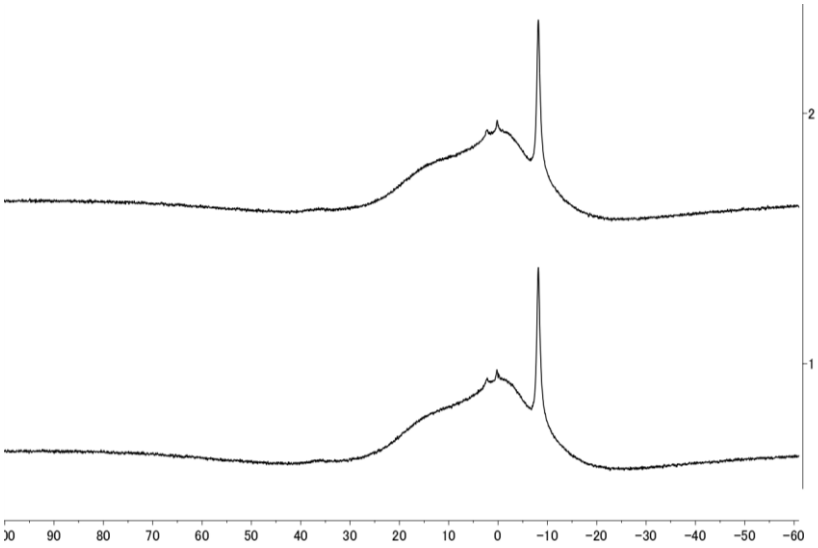


Figure S21 (1) **$^{11}B\{^{1}H\}$** and (2) **^{11}B NMR** (192 MHz, CD_2Cl_2, 299 K) spectra of compound **8d**.

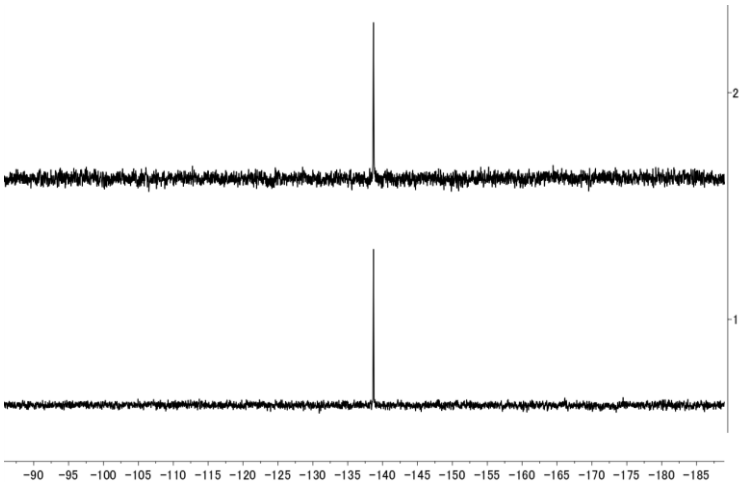


Figure S22 (1) **$^{31}P\{^{1}H\}$** and (2) **^{31}P NMR** (243 MHz, CD_2Cl_2, 299K) spectra of compound **8d**.

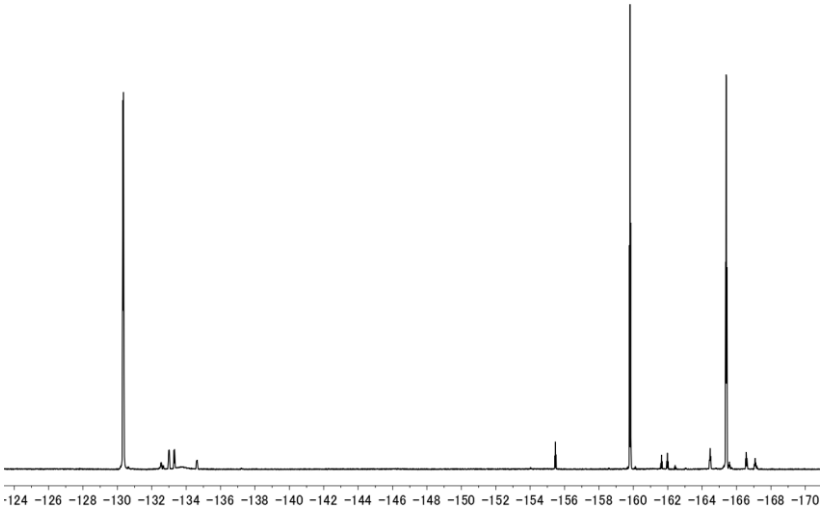
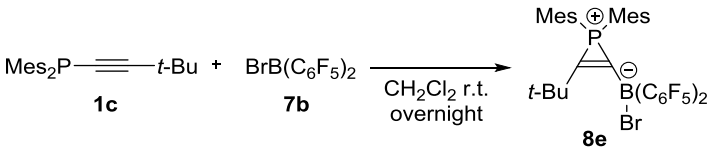


Figure S23 **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **8d**.

Preparation of compound 8e:



Scheme S5

A solution of phosphane **1c** (70.1 mg, 0.20 mmol, 1.0 eq.) in CH_2Cl_2 (1 mL) was added to a solution of bromobis(pentafluorophenyl)borane (**7b**) (85.0 mg, 0.20 mmol, 1.0 eq.) in CH_2Cl_2 (1 mL). After the colorless reaction mixture was stirred at room temperature overnight, all volatiles were removed *in vacuo*. The residue was washed with *n*-pentane (5 mL) and dried *in*

vacuo. Compound **8e** was obtained as white solid (116 mg, 0.15 mmol, 75%).

Melting point: 126 °C.

Elemental Analysis calcd for $C_{36}H_{31}BBrF_{10}P$ (775.32 g/mol): C, 55.77; H, 4.03. Found: C, 56.21; H, 4.61.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 6.94 (d, $^{4}J_{PH}$ = 5.3 Hz, 4H, *m*-Mes), 2.33 (s, 12H, *o*-Me^{Mes}), 2.31 (s, 6H, *p*-Me^{Mes}), 1.36 (s, 9H, *t*-Bu).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 149.8 (d, $^{1}J_{PC}$ = 10.5 Hz, *t*-BuC=), 147.7 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 144.3 (br, BC=), 144.0 (d, $^{4}J_{PC}$ = 3.0 Hz, *p*-Mes), 142.7 (d, $^{2}J_{PC}$ = 11.6 Hz, *o*-Mes), 140.1 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 137.3 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 130.8 (d, $^{3}J_{PC}$ = 13.8 Hz, *m*-Mes), 121.5 (d, $^{1}J_{PC}$ = 90.9 Hz, *i*-Mes), 120.7 (br, *i*-C_6F_5), 37.4 (d, $^{2}J_{PC}$ = 3.1 Hz, $C^{t\text{-Bu}}$), 30.0 (d, $^{4}J_{PC}$ = 4.1 Hz, $CH_3{}^{t\text{-Bu}}$), 22.9 (d, $^{4}J_{PC}$ = 7.9 Hz, *o*-Me^{Mes}), 20.3 (*p*-Me^{Mes}).

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = -11.9 ($\nu_{1/2}$ ~ 200 Hz).

^{31}P NMR (243 MHz, CD_2Cl_2, 299 K): δ = -136.9 ($\nu_{1/2}$ ~ 30 Hz).

^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = -136.9 ($\nu_{1/2}$ ~ 20 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -128.7 (m, 2F, *o*-C_6F_5), -159.5 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F, *p*-C_6F_5), -165.3 (m, 2F, *m*-C_6F_5), [$\Delta^{19}F_{m,p}$ = 5.8].

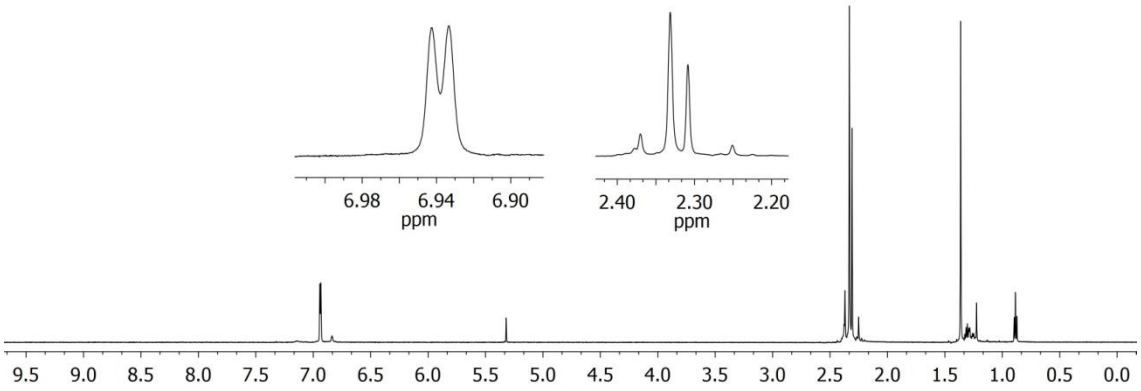


Figure S24 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299K) spectrum of compound **8e**.

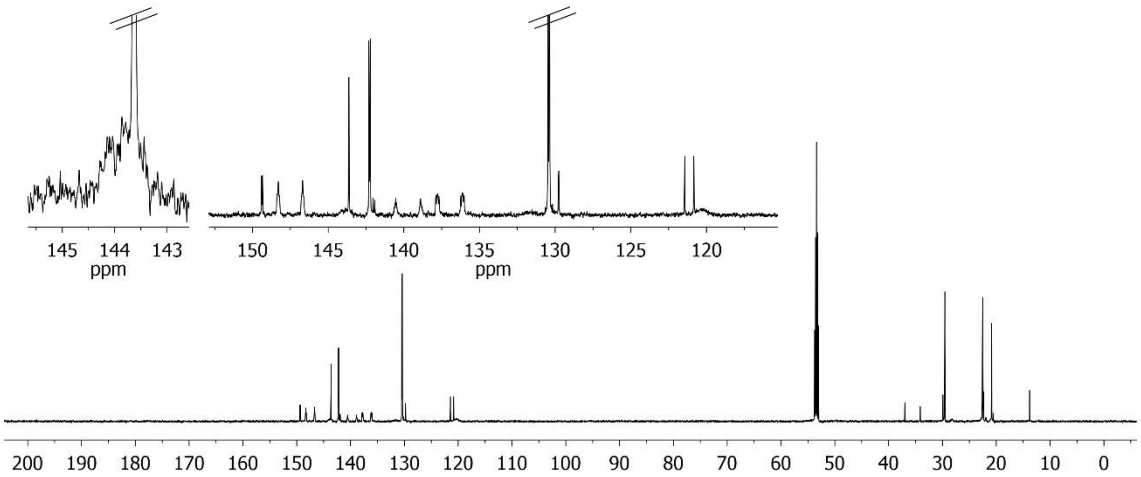


Figure S25 **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 299K) spectrum of compound **8e**.

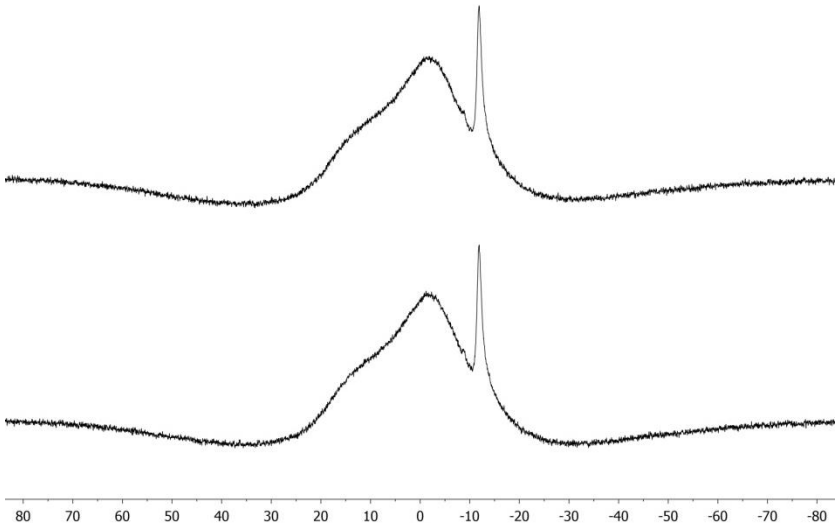


Figure S26 (1) **$^{11}B\{^{1}H\}$** and (2) **^{11}B NMR** (192 MHz, CD_2Cl_2, 299 K) spectra of compound **8e**.

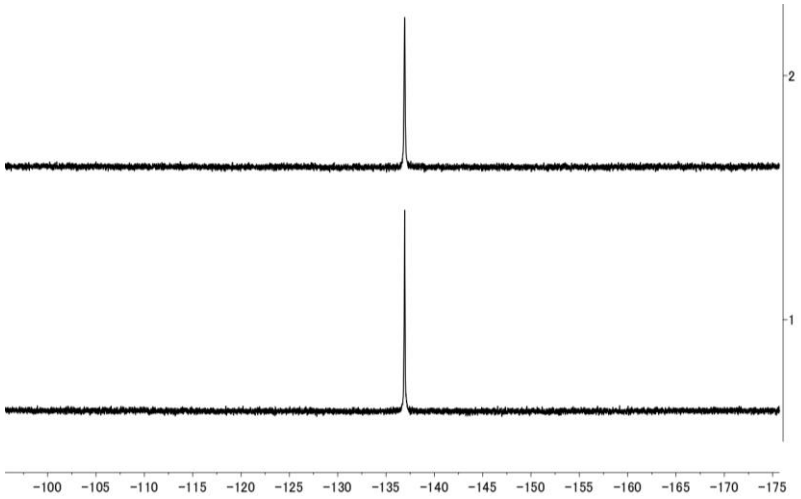


Figure S27 (1) **$^{31}P\{^{1}H\}$** and (2) **^{31}P NMR** (243 MHz, CD_2Cl_2, 299K) spectra of compound **8e**.

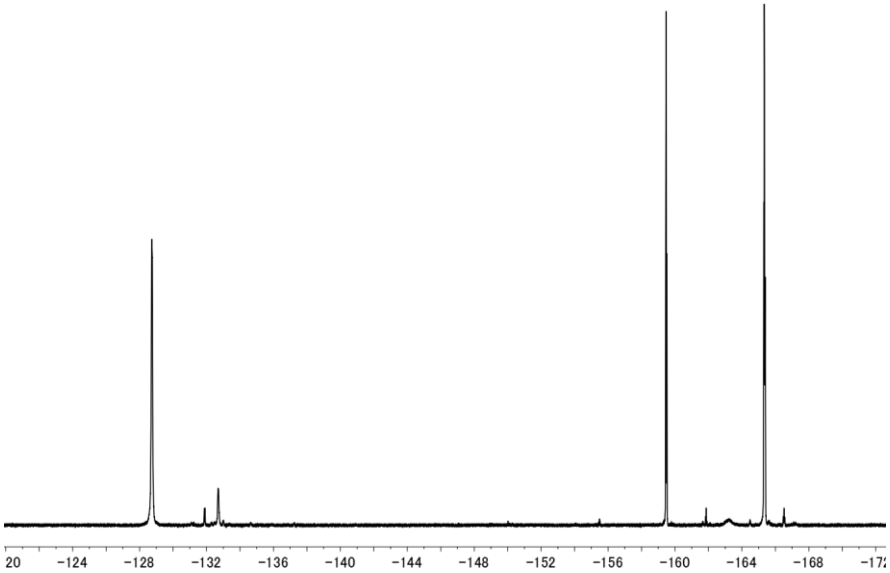


Figure S28 **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **8e**.

Crystals suitable for the X-ray crystal structure analysis were obtained from a saturated solution of compound **8e** in toluene at -36 °C.

X-ray crystal structure analysis of compound 8e (erk9236): A colorless plate-like specimen of $C_{36}H_{31}BBrF_{10}P \cdot 0.5$ x C_7H_8, approximate dimensions 0.030 mm x 0.100 mm x 0.180 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1586 frames were collected. The total exposure time was 21.94 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 24093 reflections to a maximum θ angle of 66.69° (0.84 Å resolution), of which 6361 were independent (average redundancy 3.788, completeness = 97.7%, R_{int} = 4.14%, R_{sig} = 3.69%) and 5558 (87.38%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.5895(3) Å, b = 10.8563(3) Å, c = 18.7360(5) Å, α = 82.3630(10)°, β = 76.1530(10)°, γ = 76.8730(10)°, volume = 1837.99(9) $Å^3$, are based upon the refinement of the XYZ-centroids of 9893 reflections above 20 σ(I) with 9.351° < 2θ < 133.3°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.782. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6480 and 0.9250. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P\bar{1}$, with Z = 2 for the formula unit, $C_{36}H_{31}BBrF_{10}P \cdot 0.5$ x C_7H_8. The final anisotropic full-matrix least-squares refinement on F^2 with 515 variables converged at R1 = 3.22%, for the observed data and wR2 = 8.33% for all data. The goodness-of-fit was 1.039. The largest peak in the final difference electron density synthesis was 0.360 $e^-/Å^3$ and the largest hole was -0.324 $e^-/Å^3$ with an RMS deviation of 0.058 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.484 g/cm^3 and F(000), 834 e^-.

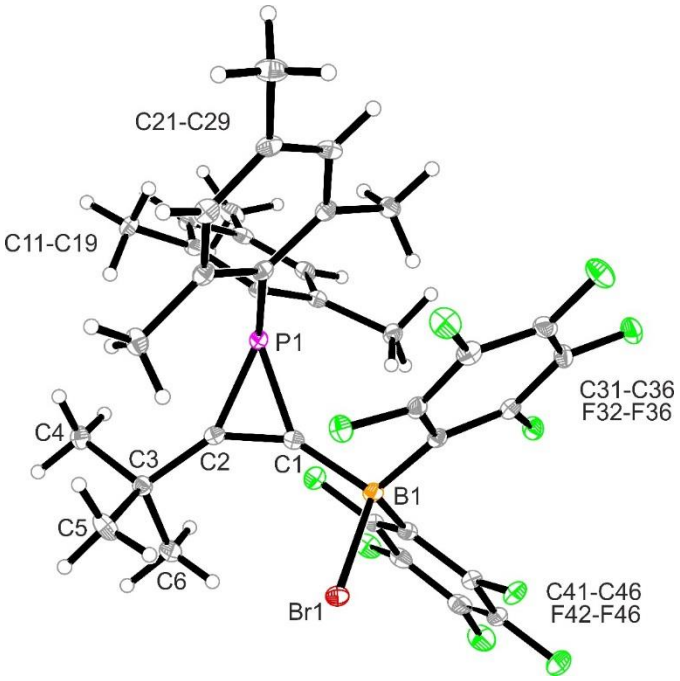
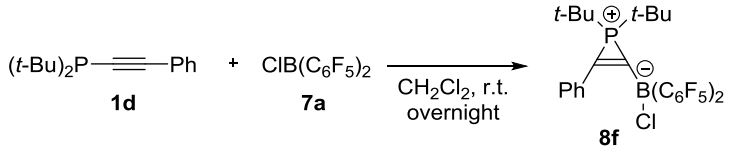


Figure S29: Crystal structure of compound **8e** (thermal ellipsoids: 30% probability).

Preparation of compound 8f:



Scheme S6

A solution of phosphane **1d** (49.3 mg, 0.20 mmol, 1.0 eq.) in CH_2Cl_2 (1 mL) was added to a solution of chlorobis(pentafluorophenyl)borane **7a** (76.1 mg, 0.20 mmol, 1.0 eq.) in CH_2Cl_2 (1 mL). The yellow reaction mixture was stirred at room temperature overnight then all volatiles were removed *in vacuo*. The obtained residue was washed with *n*-pentane (5 mL) and dried *in vacuo*. Compound **8f** was obtained as a yellow solid (77.5 mg, 0.12 mmol, 62%).

Melting point: 178 °C

Elemental Analysis calcd for $C_{28}H_{23}BClF_{10}P$ (626.71 g/mol): C, 53.66; H, 3.70. Found: C, 53.33; H, 3.70.

^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.60 (m, 2H, *o*-Ph), 7.53 (m, 1H, *p*-Ph), 7.51 (m, 2H, *m*-Ph), 1.42 (d, $^{3}J_{PH}$ = 20.0 Hz, 18H, *t*-Bu).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = n.o. (BC=), 148.1 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 139.9 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 137.5 (dm, $^{1}J_{FC}$ ~ 251 Hz, C_6F_5), 132.02 (*p*-Ph), 131.98 (d, $^{3}J_{PC}$ = 7.2 Hz, *o*-Ph), 131.7 (br d, $^{1}J_{PC}$ = 7.2 Hz, PhC=), 129.7 (*m*-Ph), 125.9 (d, $^{2}J_{PC}$ = 6.4 Hz, *i*-Ph), n.o. (*i*-C_6F_5), 39.5 (d, $^{1}J_{PC}$ = 25.1 Hz, $C^{t\text{-Bu}}$), 29.9 ($CH_3{}^{t\text{-Bu}}$).

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = -8.0 ($\nu_{1/2}$ ~ 120 Hz).

^{31}P NMR (202 MHz, CD_2Cl_2, 299 K): δ = -86.3 (m).

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = -86.3 ($\nu_{1/2}$ ~ 5 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -132.5 (m, 2F, *o*-C_6F_5), -159.3 (t, $^{3}J_{FF}$ = 20.6 Hz, 1F, *p*-C_6F_5), -164.8 (m, 2F, *m*-C_6F_5), [$\Delta^{19}F_{m,p}$ = 5.5].

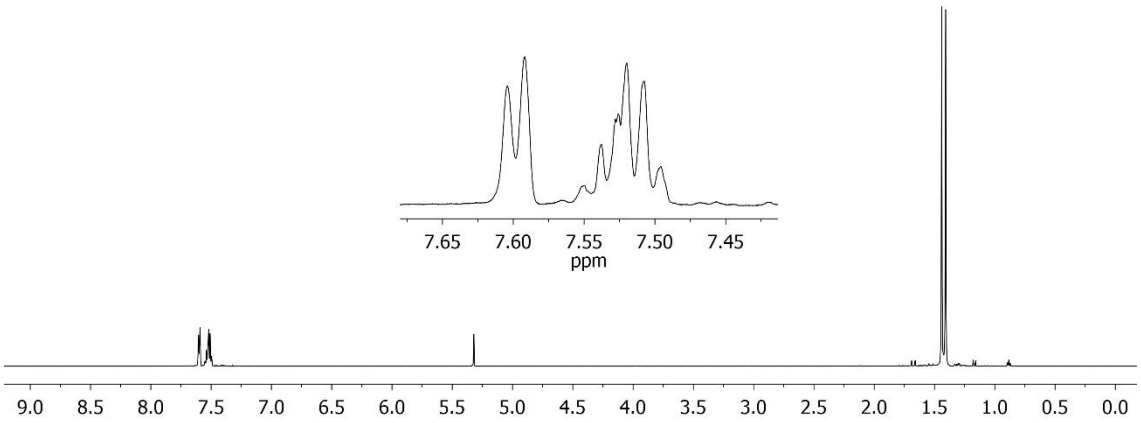


Figure S30 **^{1}H NMR** (500 MHz, CD_2Cl_2, 299K) spectrum of compound **8f**.

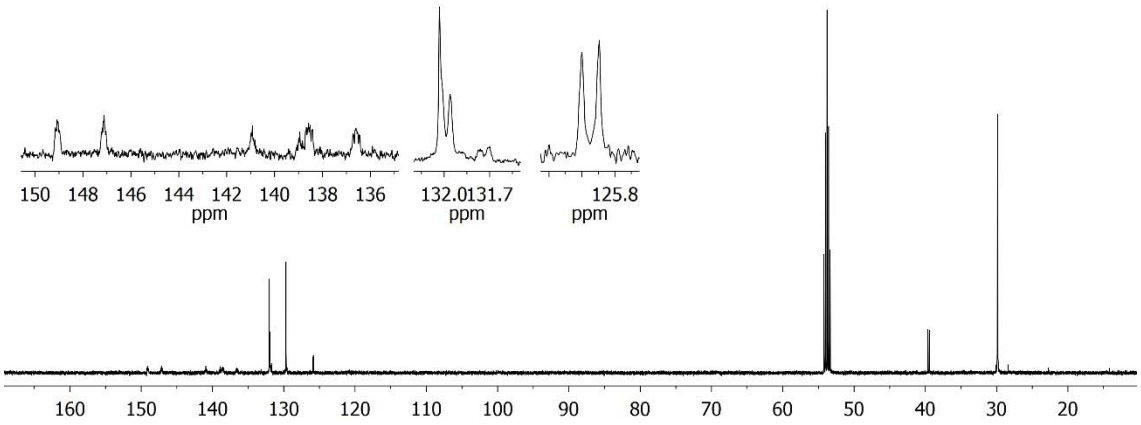


Figure S31 **$^{13}C\{^{1}H\}$ NMR** (126 MHz, CD_2Cl_2, 299K) spectrum of compound **8f**.

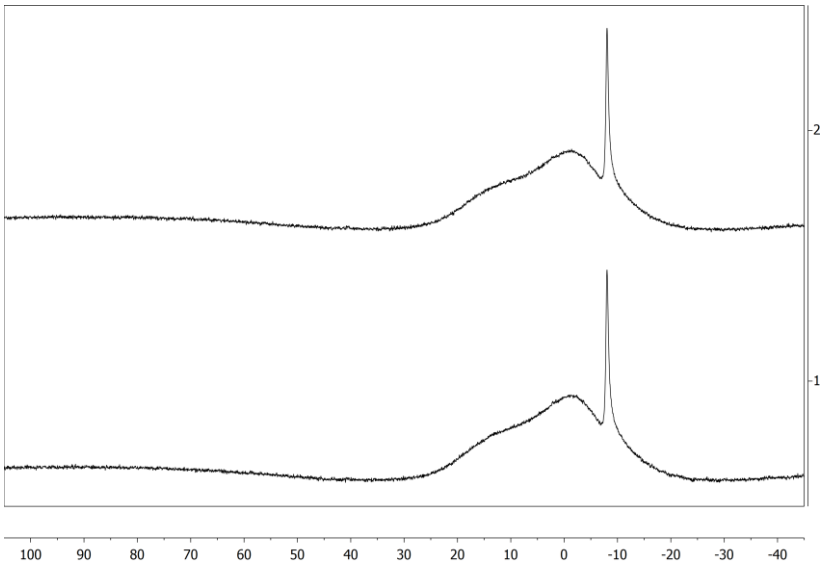


Figure S32 (1) **$^{11}B\{^{1}H\}$** and (2) **^{11}B NMR** (192 MHz, CD_2Cl_2, 299 K) spectra of compound **8f**.

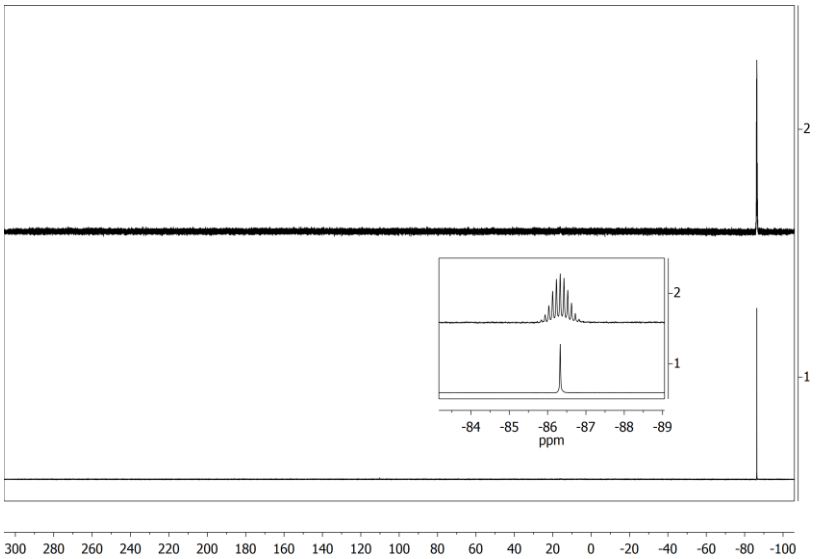


Figure S33 (1) **$^{31}P\{^{1}H\}$** and (2) **^{31}P NMR** (202 MHz, CD_2Cl_2, 299 K) spectra of compound **8f**.

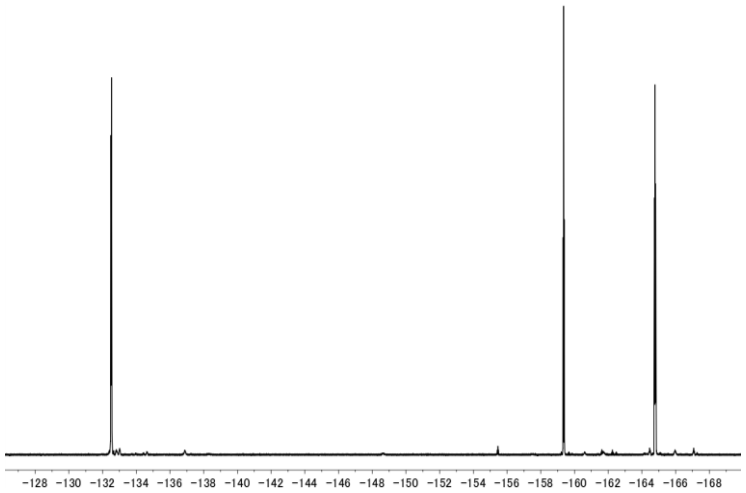


Figure S34 **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **8f**.

Crystals suitable for the X-ray crystal structure analysis were obtained from a saturated solution of compound **8f** in *n*-pentane at -36 °C.

X-ray crystal structure analysis of compound 8f (erk9235): formula $C_{28}H_{23}BClF_{10}P$, M = 626.69, colourless crystal, 0.18 x 0.06 x 0.03 mm, a = 9.2115(2) Å, b = 22.0031(5) Å, c = 14.1968(4) Å, β = 97.690(1)°, V = 2851.55(12) Å^3, ρ_{calc} = 1.460 gcm^{-3}, μ = 0.273 mm^{-1}, empirical absorption correction (0.953 ≤ T ≤ 0.992), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 173(2) K, ω and φ scans, 13796 reflections collected ($\pm h$, $\pm k$, $\pm l$), 4909 independent (R_{int} = 0.057) and 3453 observed reflections [$I>2\sigma I$)], 476 refined parameters, R = 0.079, wR^2 = 0.160, max. (min.) residual electron density 0.34 (-0.28) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

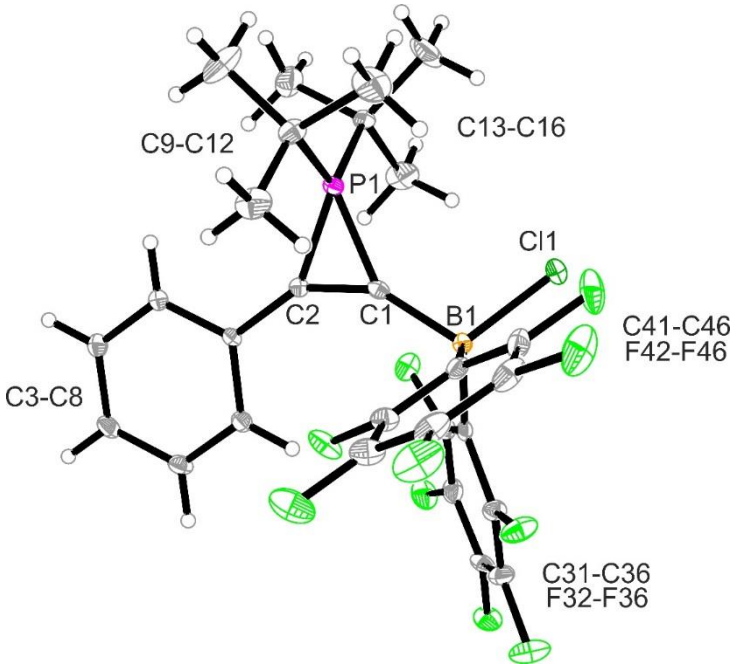
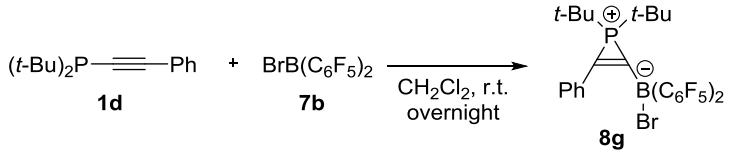


Figure S35: Crystal structure of compound **8f** (thermal ellipsoids: 15% probability).

Preparation of compound 8g:



Scheme S7

A solution of phosphane **1d** (49.3 mg, 0.20 mmol, 1.0 eq.) in CH_2Cl_2 (1 mL) was added to a solution of bromobis(pentafluorophenyl)borane **7b** (85.0 mg, 0.20 mmol, 1.0 eq.) in CH_2Cl_2 (1 mL). The colorless reaction mixture was stirred at room temperature overnight then all volatiles were removed *in vacuo*. The resulting residue was washed with *n*-pentane (5 mL) and dried *in vacuo*. Compound **8g** was obtained as white solid (101 mg, 0.15 mmol, 75%).

Melting point: 168 °C

Elemental Analysis calcd for $C_{28}H_{23}BBrF_{10}P$ (671.16 g/mol): C, 50.11; H, 3.45. Found: C, 49.83; H, 3.51.

^{1}H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 7.62 (m, 2H, *o*-Ph), 7.54 (m, 1H, *p*-Ph), 7.51 (m, 2H, *m*-Ph), 1.44 (d, $^{3}J_{PH}$ = 20.0 Hz, 18H, *t*-Bu).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 299 K): δ = n.o. (BC=), 148.0 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 140.1 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 137.6 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 132.21 (br d, $^{1}J_{PC}$ = 6.5 Hz, PhC=), 132.11 (d, $^{3}J_{PC}$ = 7.5 Hz, *o*-Ph), 132.08 (*p*-Ph), 129.7 (*m*-Ph), 125.9 (d, $^{2}J_{PC}$ = 6.7 Hz, *i*-Ph), 120.1 (br, *i*-C_6F_5), 39.7 (d, $^{1}J_{PC}$ = 24.3 Hz, $C^{t\text{-Bu}}$), 29.9 ($CH_3^{t\text{-Bu}}$).

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = -11.6 ($\nu_{1/2}$ ~ 200 Hz).

^{31}P NMR (202 MHz, CD_2Cl_2, 299 K): δ = -85.4 (m).

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 299 K): δ = -85.4 ($\nu_{1/2}$ ~ 5 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -131.5 (m, 2F, *o*-C_6F_5), -159.1 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), -164.6 (m, 2F, *m*-C_6F_5), [$\Delta^{19}F_{m,p}$ = 5.5].

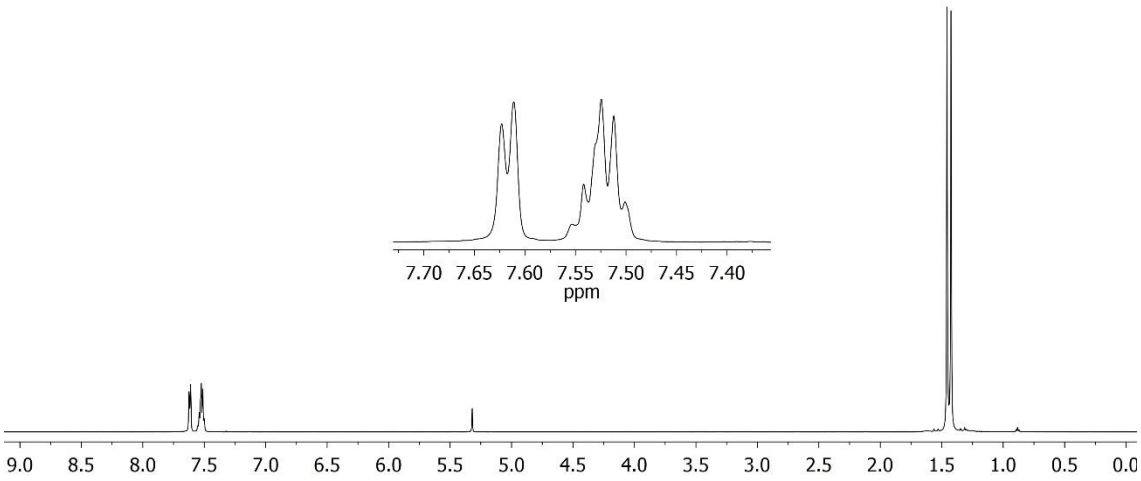


Figure S36 **^{1}H NMR** (500 MHz, CD_2Cl_2, 299 K) spectrum of compound **8g**.

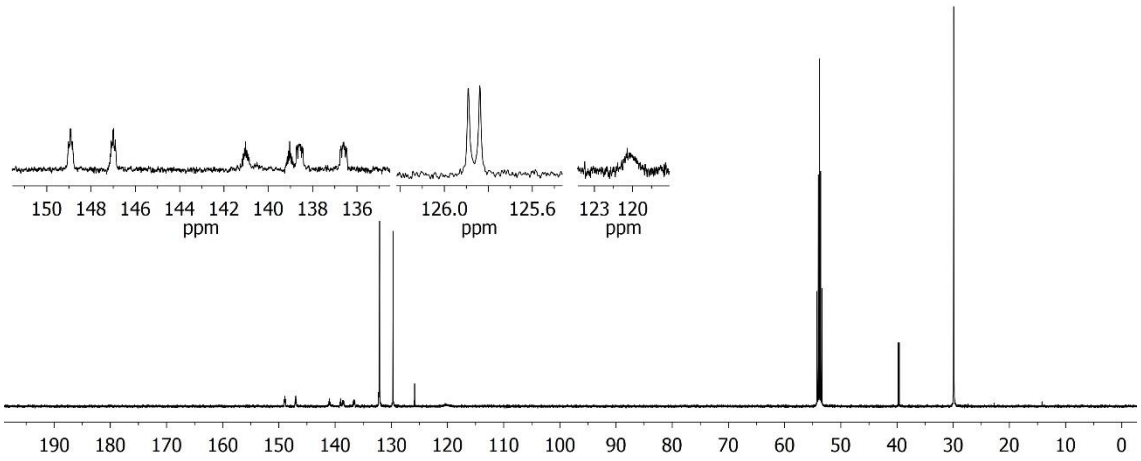


Figure S37 **$^{13}C\{^{1}H\}$ NMR** (126 MHz, CD_2Cl_2, 299 K) spectrum of compound **8g**.

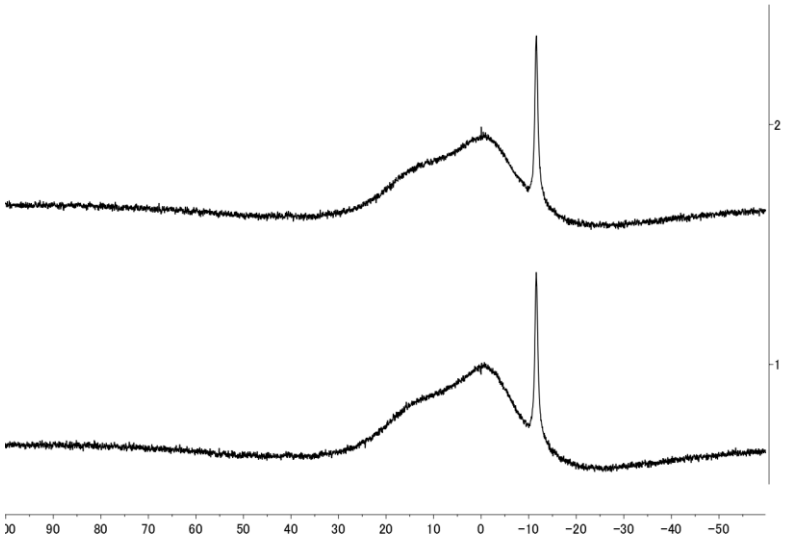


Figure S38 (1) **$^{11}B\{^{1}H\}$** and (2) **^{11}B NMR** (192 MHz, CD_2Cl_2, 299 K) spectra of compound **8g**.

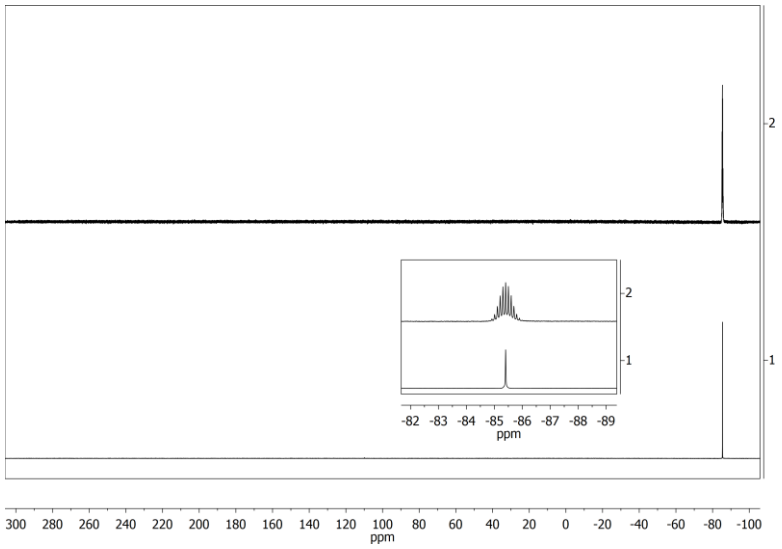


Figure S39 (1) **$^{31}P\{^{1}H\}$** and (2) **^{31}P NMR** (202 MHz, CD_2Cl_2, 299 K) spectra of compound **8g**.

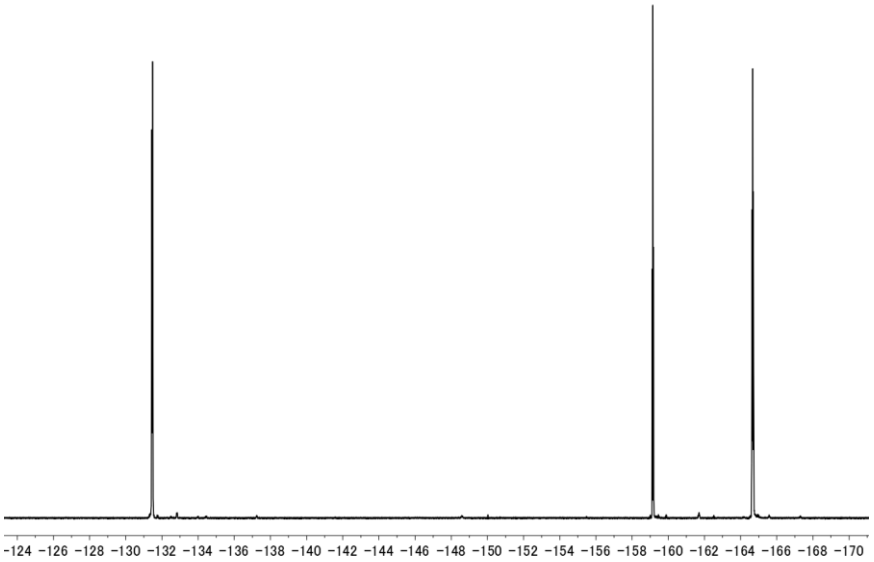


Figure S40 **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **8g**.

Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a saturated solution of compound **8g** in CH_2Cl_2 at -36 °C.

X-ray crystal structure analysis of compound 8g (erk9221): A colorless needle-like specimen of $C_{28}H_{23}BBrF_{10}P$, approximate dimensions 0.046 mm x 0.055 mm x 0.168 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1908 frames were collected. The total exposure time was 28.37 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 46108 reflections to a maximum θ angle of 72.39° (0.81 Å resolution), of which 5453 were independent (average redundancy 8.456, completeness = 99.5%, R_{int} = 5.81%, R_{sig} = 3.10%) and 4799 (88.01%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.9577(2) Å, b = 18.6647(5) Å, c = 16.5940(4) Å, β = 91.4580(10)°, volume = 2773.50(12) Å^3, are based upon the refinement of the XYZ-centroids of 9794 reflections above 20 σ(I) with 7.129° < 2θ < 144.2°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.855. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6030 and 0.8610. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{28}H_{23}BBrF_{10}P$. The final anisotropic full-matrix least-squares refinement on F^2 with 376 variables converged at R1 = 3.48%, for the observed data and wR2 = 7.92% for all data. The goodness-of-fit was 1.105. The largest peak in the final difference electron density synthesis was 0.378 e$^-$/Å^3 and the largest hole was -0.419 e$^-$/Å^3 with an RMS deviation of 0.062 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.607 g/cm^3 and F(000), 1344 e$^-$.

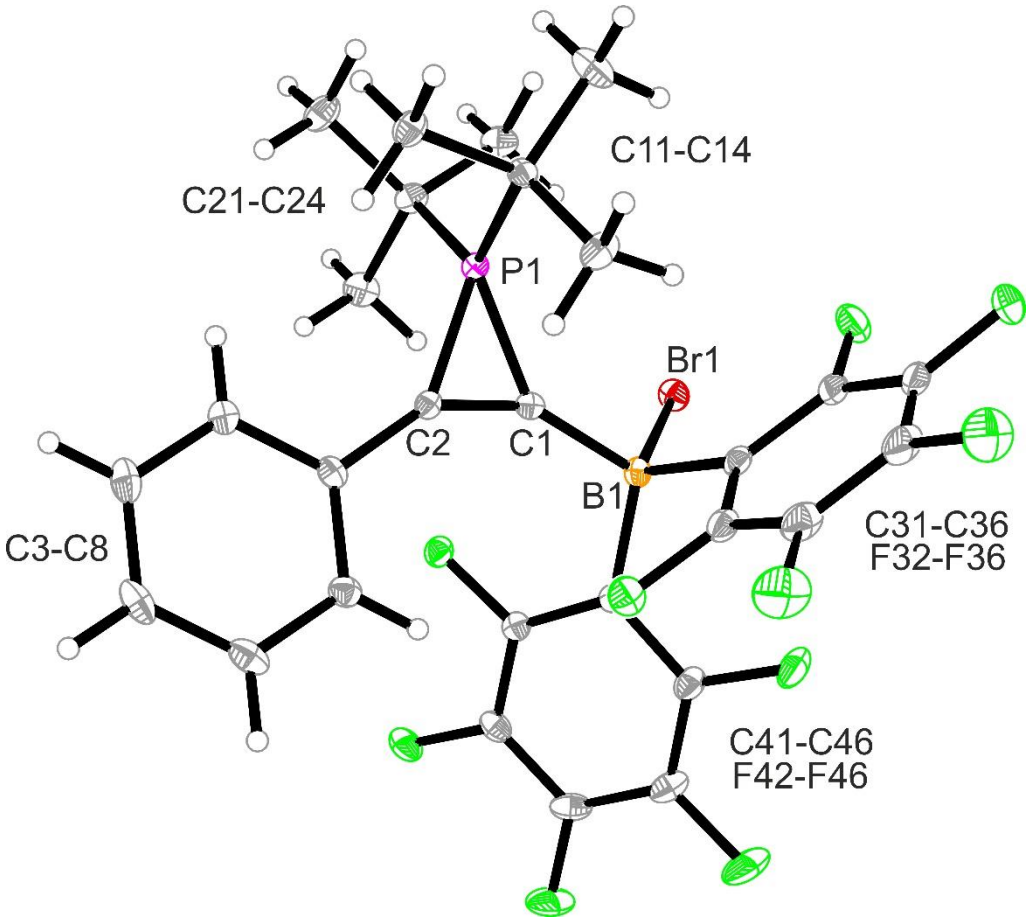
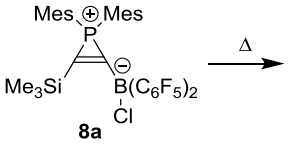


Figure S41: Crystal structure of compound **8g** (thermal ellipsoids: 30% probability).

Heating of compound 8a:



Scheme S8

A solution of the phosphirenium **8a** (ca. 25.0 mg) in toluene (0.5 mL) was sealed in a NMR tube. Subsequently, it was heated to 70 °C (4 h) and 100 °C (2 h). Each temperature step was monitored by NMR experiments.

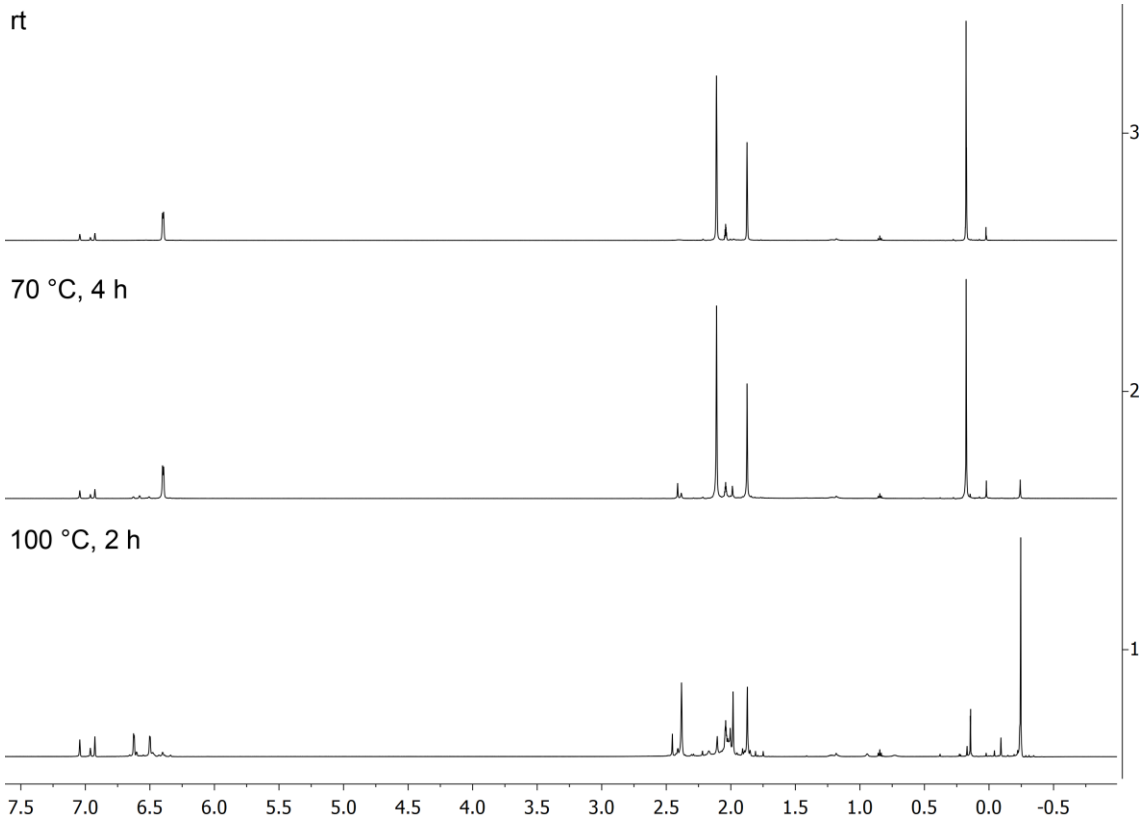
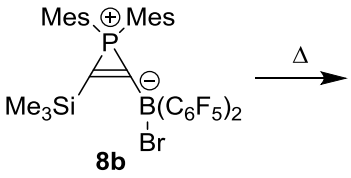


Figure S42 **^{1}H NMR** (600 MHz, toluene-d_8) spectra of compound **8a** at (1) at 100 °C for 2 h, (2) at 70 °C for 4 h, and (3) at room temperature.

Heating of compound 8b



8b

Scheme S9

A solution of the phosphirenium **8b** (ca. 25.0 mg) in toluene (0.5 mL) was sealed in a NMR tube. Subsequently, it was heated to 70 °C (4 h) and 100 °C (2 h). Each temperature step was monitored by NMR experiments.

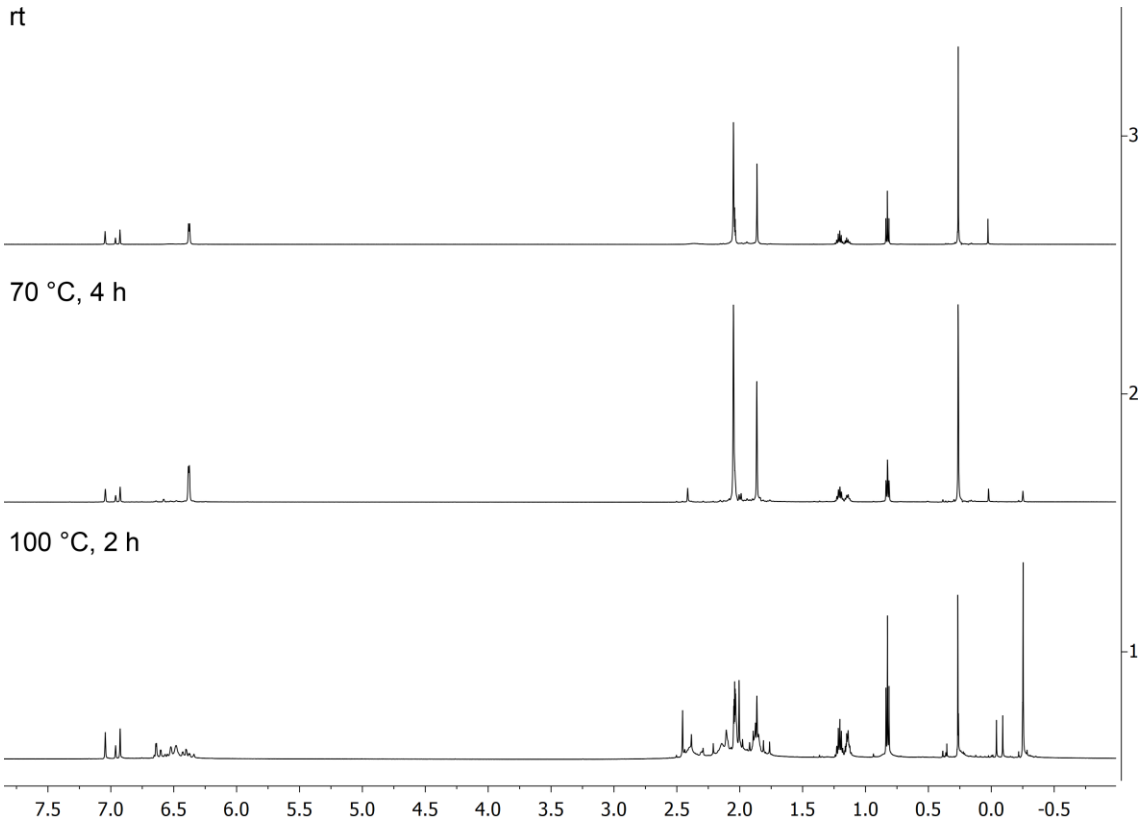
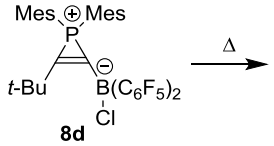


Figure S43 **^{1}H NMR** (600 MHz, toluene-d_8) spectra of compound **8b** (1) at 100 °C for 2 h, (2) at 70 °C for 4 h, and (3) at room temperature.

Heating of compound 8d:



8d

Scheme S10

A solution of the phosphirenium **8d** (ca. 25.0 mg) in CD_2Cl_2 (1 mL) was sealed in a NMR tube. Subsequently, it was heated in an autoclave to 70 °C (1 h), 100 °C (1 h), 120 °C (24 h). Each temperature step was monitored by NMR experiments.

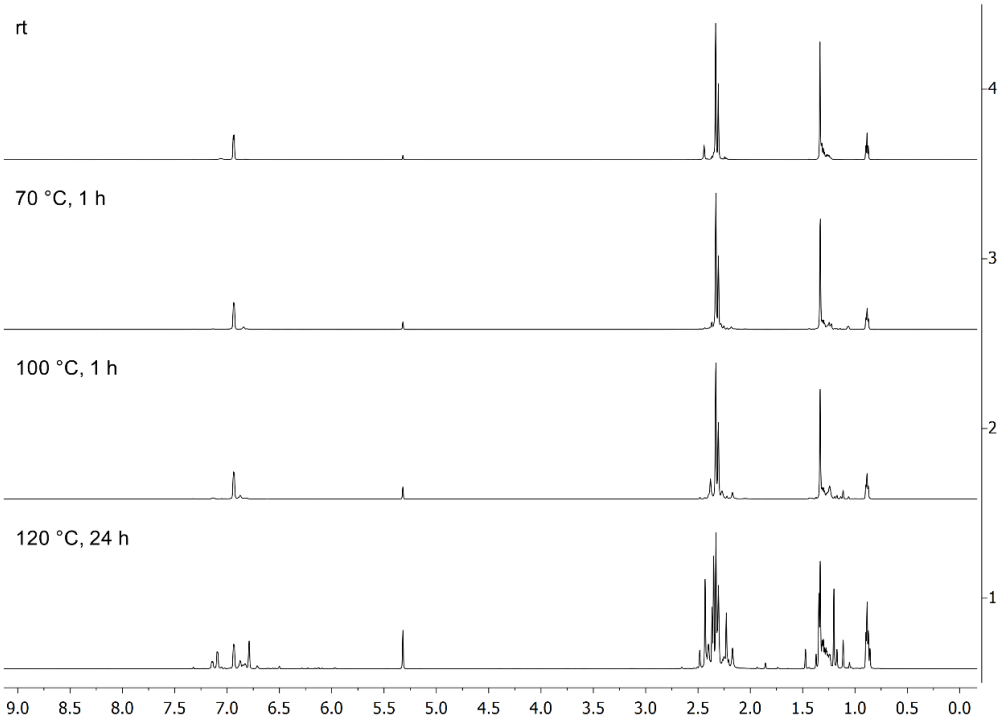
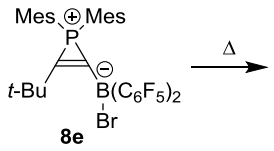


Figure S44 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectra of compound **8d** (1) at 120 °C for 24 h, (2) at 100 °C for 1 h, (3) at 70 °C for 1 h, and (5) at room temperature

Heating of compound 8e:



8e

Scheme S11

A solution of the phosphirenium **8e** (ca. 25.0 mg) in CD_2Cl_2 (1 mL) was sealed in a NMR tube. Subsequently, it was heated in an autoclave to 70 °C (1 h), 100 °C (1 h), 120 °C (24 h). Each temperature step was monitored by NMR experiments.

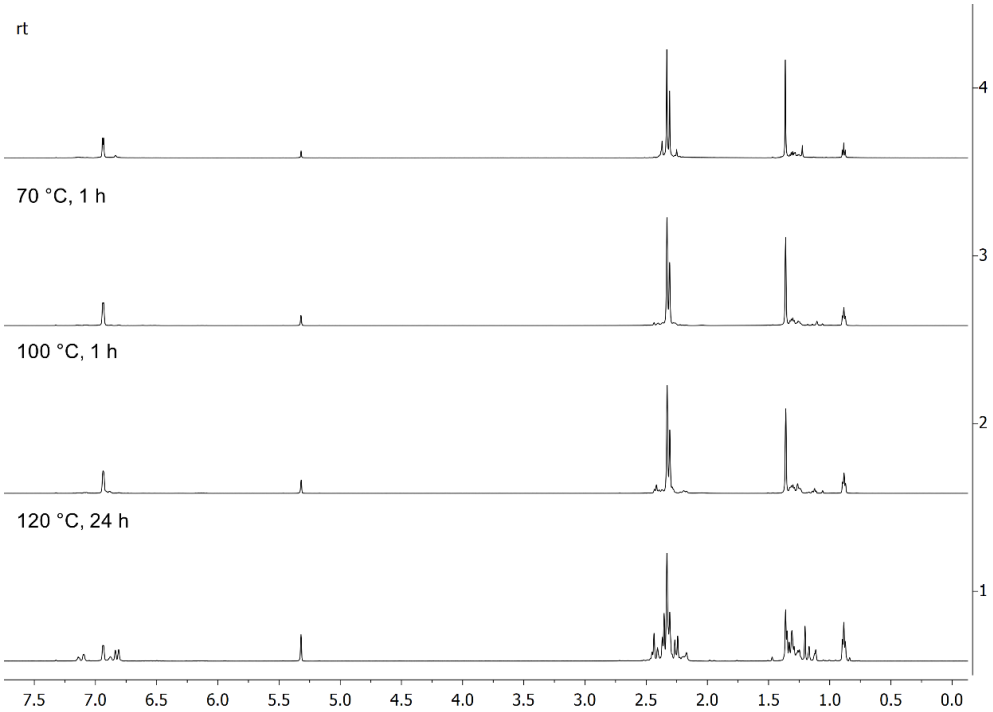
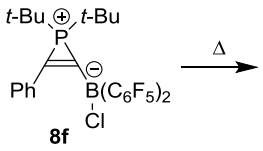


Figure S45 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectra of compound **8e** (1) at 120 °C for 24 h, (2) at 100 °C for 1 h, (3) at 70 °C for 1 h, and (5) at room temperature.

Heating of compound 8f:



8f

Scheme S12

A solution of the phosphirenium **8f** (ca. 25.0 mg) in CD_2Cl_2 (1 mL) was sealed in a NMR tube. Subsequently, it was heated in an autoclave to 70 °C (1 h), 100 °C (1 h, 12 h), 120 °C (12 h) and 170 °C (24 h). Each temperature step was monitored by NMR experiments.

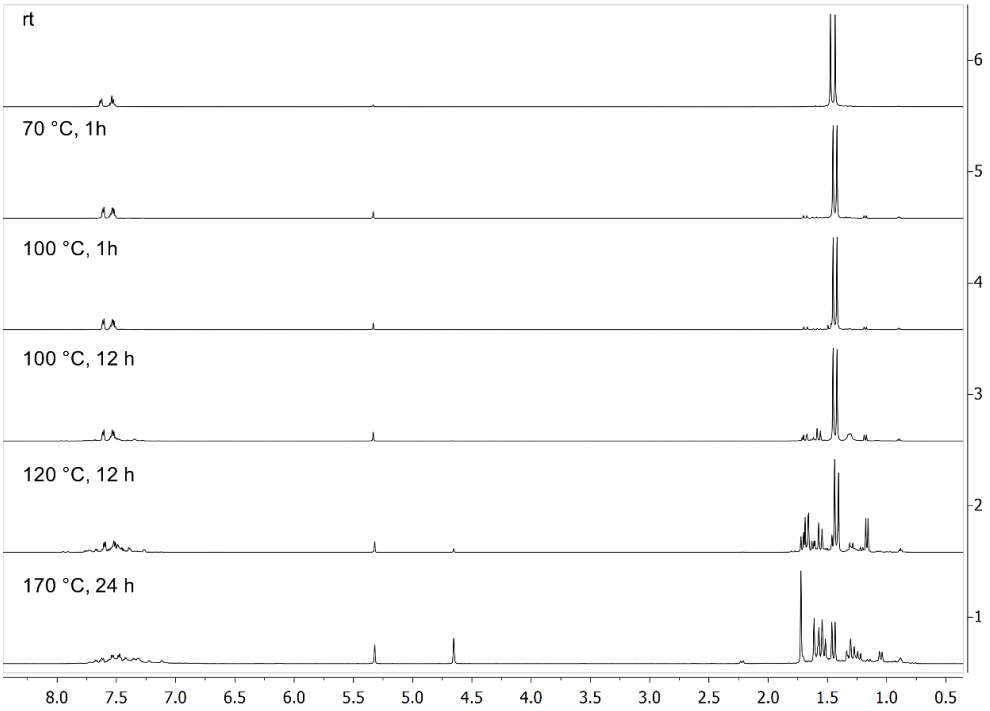
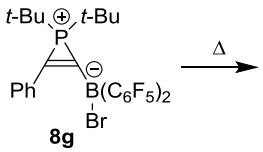


Figure S46 **^{1}H NMR** (600 MHz, CD_2Cl_2) spectra of compound **8f** (1) at 170 °C for 24 h, (2) at 120 °C for 12 h, (3) at 100 °C for 12 h, (4) at 100 °C for 1 h, (5) at 70 °C for 1 h, and (6) at room temperature.

Heating of compound 8g:



8g

Scheme S13

A solution of the phosphirenium **8g** (ca. 25.0 mg) in CD_2Cl_2 (1 mL) was sealed in a NMR tube. Subsequently, it was heated in an autoclave to 70 °C (1 h), 100 °C (1 h, 12 h), 120 °C (12 h) and 170 °C (24 h). Each temperature step was monitored by NMR experiments.

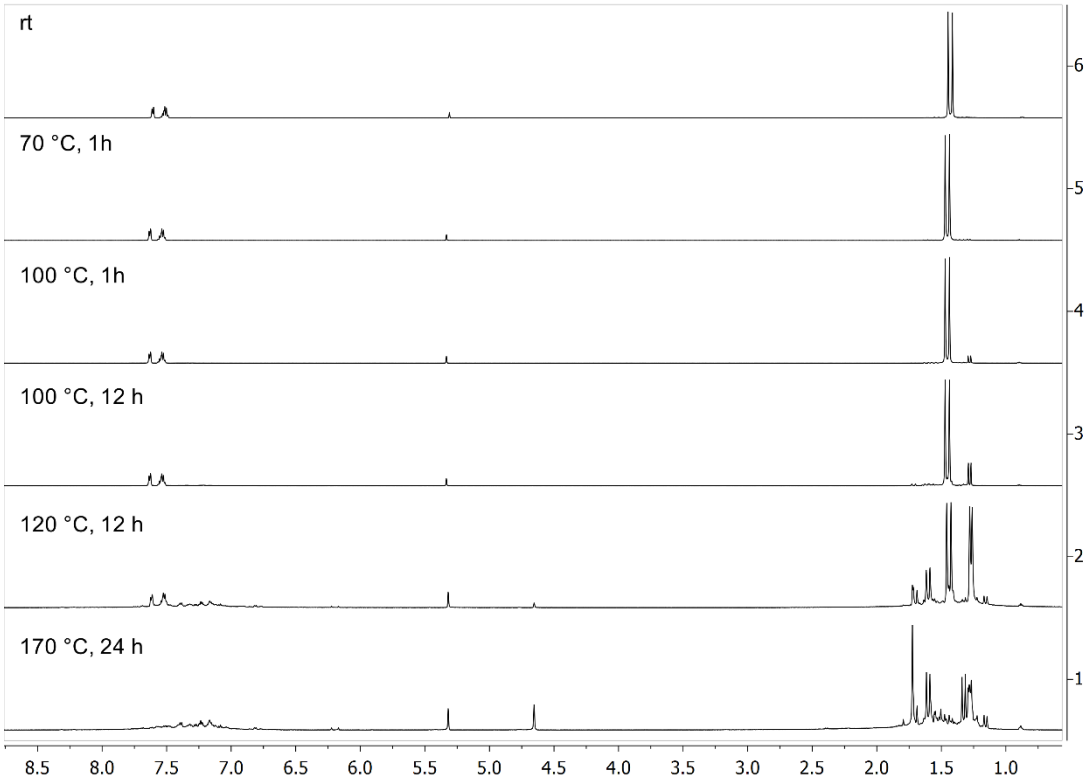
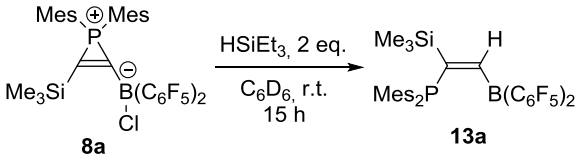


Figure S47 **^{1}H NMR** (600 MHz, CD_2Cl_2) spectra of compound **8g** (1) at 170 °C for 24 h, (2) at 120 °C for 12 h, (3) at 100 °C for 12 h, (4) at 100 °C for 1 h, (5) at 70 °C for 1 h, and (6) at room temperature.

Preparation of compound 13a



Scheme S14

1st Step: A mixture of compound **8a** (74.6 mg, 0.10 mmol) and triethylsilane (32 μL, 0.20 mmol) in C_6D_6 (1 mL) was stirred for 15 hours at room temperature. Then the obtained reaction mixtion was characterized by NMR experiments. [Comment: the obtained NMR data are in good agreement with the reported data of compound **13a** [A. Ueno, X. Tao, C. G. Daniliuc, G. Kehr, G. Erker, *Organometallics*, 2018, **37**, 2665.].

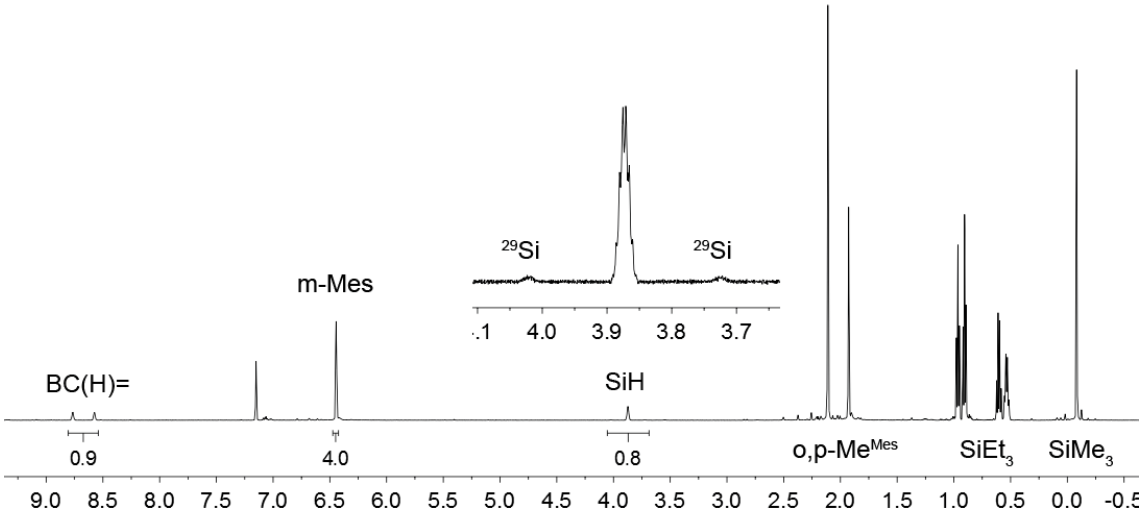


Figure S48 **^{1}H NMR** (600 MHz, C_6D_6, 299 K) spectrum of the obtained reaction mixture [δ^{1}H: 3.87 (m, $^{1}J_{SiH}$ = 177.5 Hz, HSi)]

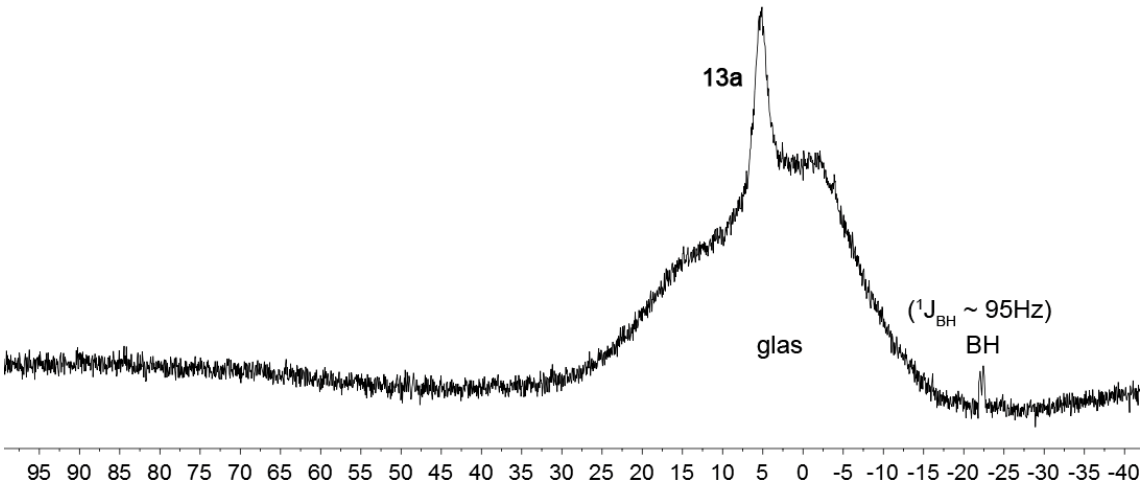


Figure S49 **^{11}B NMR** (192 MHz, C_6D_6, 299 K) spectrum of the obtained reaction mixture.

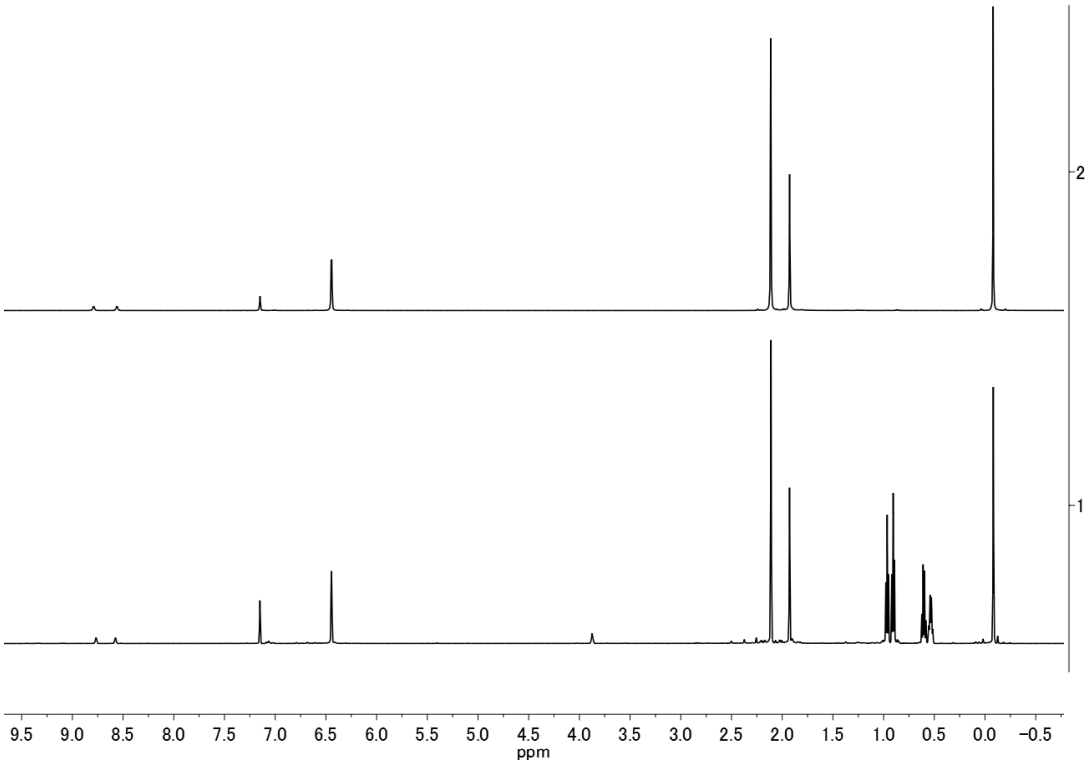
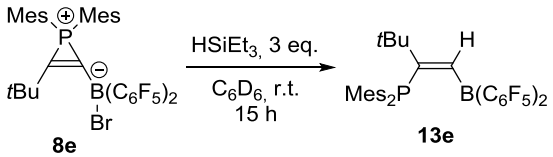


Figure S50 **^{1}H NMR** (600 MHz, C_6D_6, 299 K) spectra of (1) the obtained reaction mixture and (2) the compound **13a**.

2nd Step: Then, all volatiles were removed *in vacuo*. The remaining pale yellow solid was collected and washed with *n*-pentane (2×2 mL) to finally give compound **13a** as a white powder (65.3 mg, 0.091 mmol, 91%).

The obtained NMR data are consistent with those published in the literature: A. Ueno, X. Tao, C. G. Daniliuc, G. Kehr, G. Erker, *Organometallics*, 2018, **37**, 2665.

Generation of compound 13e (NMR scale, *in situ* reaction)



Scheme S15

The mixture of **8e** (38.0 mg, 0.05 mmol) and triethylsilane (24 μL, 0.15 mmol) in C_6D_6 (0.5 mL) was stirred for 15 hours at room temperature. The reaction was monitored by NMR analysis.

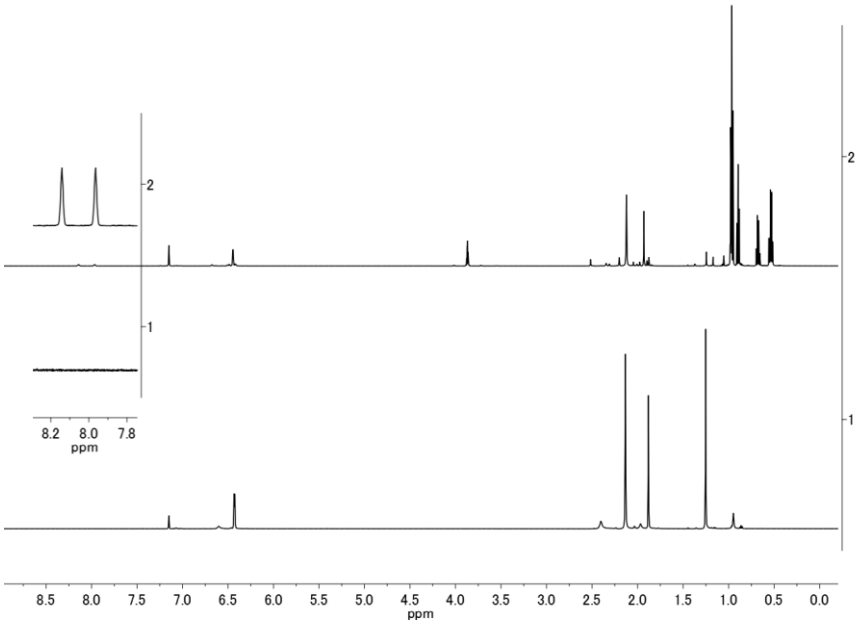


Figure S51 **^{1}H NMR** (600 MHz, C_6D_6, 299 K) spectra of (1) compound **8e** and (2) after treatment with $HSiEt_3$.

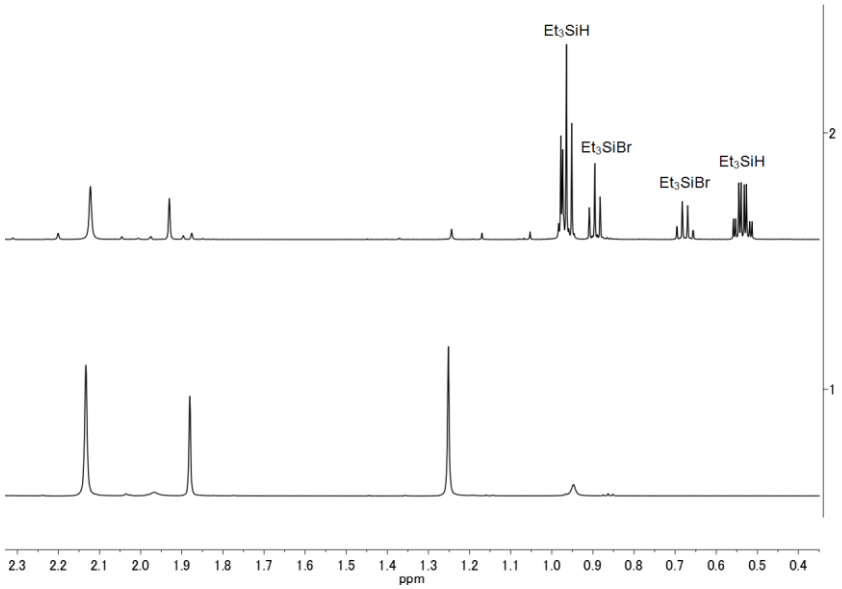


Figure S52 **^{1}H NMR** (600 MHz, C_6D_6, 299 K) spectra of (1) compound **8e** and (2) after treatment with $HSiEt_3$ (0.4 to 2.3 ppm).

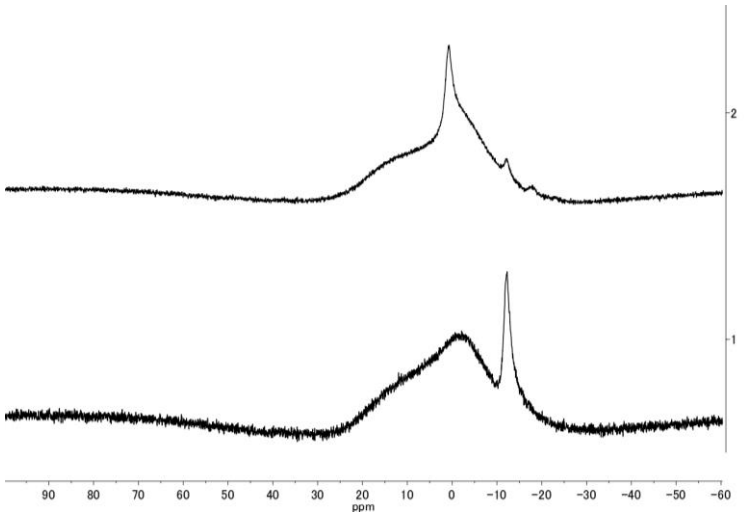


Figure S53 **^{11}B NMR** (192 MHz, C_6D_6, 299 K) spectra of (1) compound **8e** and (2) after treatment with $HSiEt_3$.

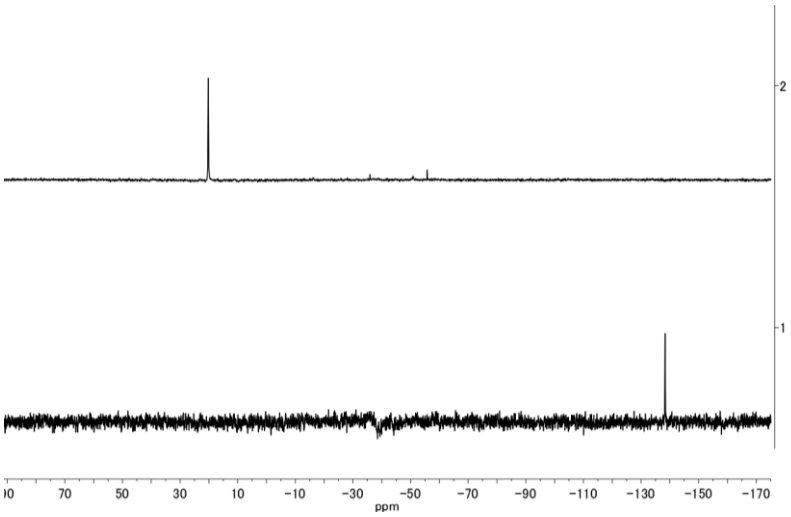


Figure S54 **^{31}P{^{1}H} NMR** (243 MHz, C_6D_6, 299 K) spectra of (1) compound **8e** and (2) after treatment with $HSiEt_3$.

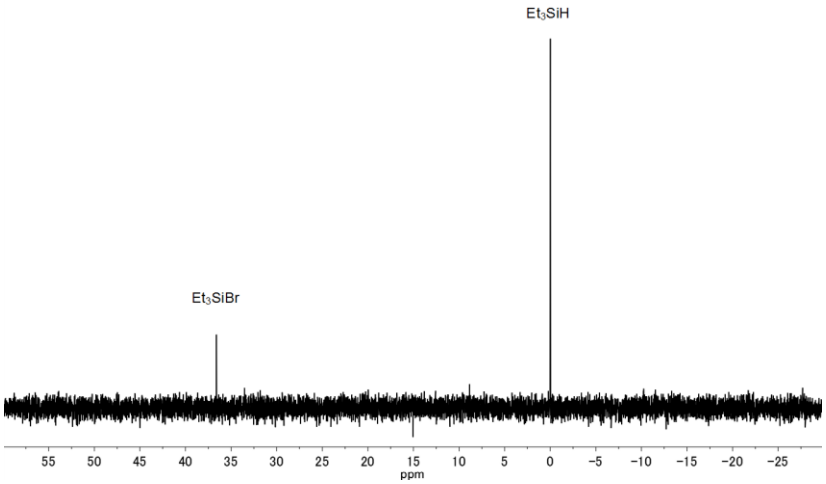
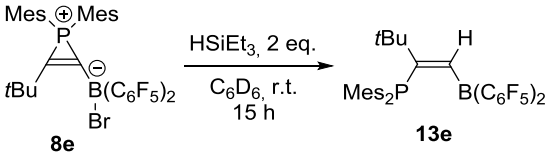


Figure S55 **^{29}Si{^{1}H} DEPT** (119 MHz, C_6D_6, 299 K) spectrum of the reaction mixture.

Preparation of compound 13e



Scheme S16

The mixture of **8e** (119 mg, 0.15 mmol) and triethylsilane (49 μL, 0.30 mmol) in C_6D_6 (1 mL) was stirred for 15 hours at room temperature. Then, all volatiles were removed *in vacuo* and the oily orange material was collected and washed with *n*-pentane (2×2 mL). The white precipitate was dried *in vacuo* to give compound **13e** as a white powder (61 mg, 0.089 mmol, 58%).

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 8.06 (d, $^{3}J_{PH}$ = 106.6 Hz, 1H, BCH=), 6.44 (d, $^{3}J_{PH}$ = 2.0 Hz, 4H, *m*-Mes), 2.13 (s, 12H, *o*-CH_3^{Mes}), 1.92 (s, 6H, *p*-CH_3^{Mes}), 0.97 (m, *t*-Bu).
^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 166.1 (br, BCH=), 152.8 (d, $^{1}J_{PC}$ = 35.1 Hz, *t*BuC=), 147.8 (dm, $^{1}J_{FC}$ ~ 243 Hz, C_6F_5), 141.1 (d, $^{2}J_{PC}$ = 8.4 Hz, *o*-Mes), 140.7 (d, $^{4}J_{PC}$ = 2.7 Hz, *p*-Mes), 140.3 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 137.2 (dm, $^{1}J_{FC}$ ~ 248 Hz, C_6F_5), 131.0 (d, $^{3}J_{PC}$ = 8.2 Hz, *m*-Mes), 125.8 (d, $^{1}J_{PC}$ = 27.9 Hz, *i*-Mes), 36.3 (d, $^{2}J_{PC}$ = 3.3 Hz, C^{tBu}), 30.8 (d, $^{3}J_{PC}$ = 3.2 Hz, CH_3^{tBu}), 23.5 (d, $^{3}J_{PC}$ = 5.8, *o*-CH_3^{Mes}), 20.5 (*p*-CH_3^{Mes}).
^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = 0.7 ($\nu_{1/2}$ ~ 330 Hz).
^{11}B NMR (192 MHz, 299 K, C_6D_6): δ = 0.7 ($\nu_{1/2}$ ~ 340 Hz).
^{31}P NMR (243 MHz, 299 K, C_6D_6): δ = 20.2 (d, $^{3}J_{PH}$ ~ 106 Hz).
^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = 20.2 ($\nu_{1/2}$ ~ 30 Hz).
^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = [-124.8, -133.4](each br, each 1F, *o*-C_6F_5), -158.2 (t, $^{3}J_{FF}$ = 20.4 Hz, 1F, *p*-C_6F_5), -164.1 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 5.9].

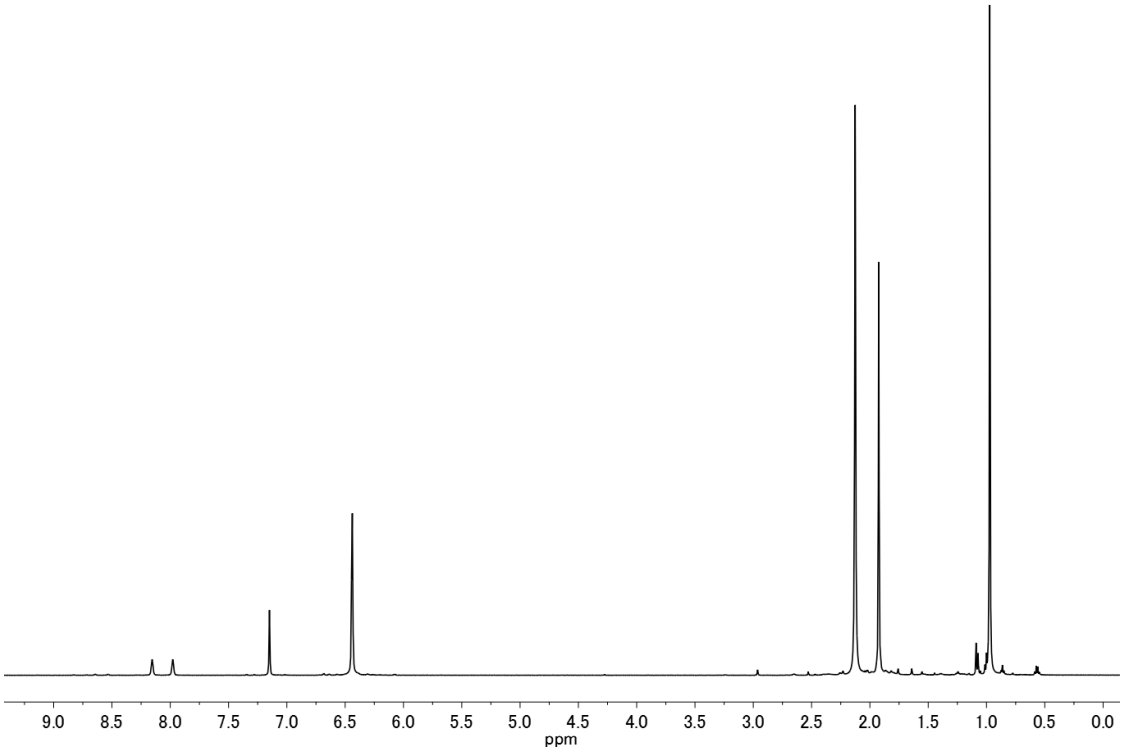


Figure S56 **^{1}H NMR** (600 MHz, C_6D_6, 299K) spectrum of compound **13e**.

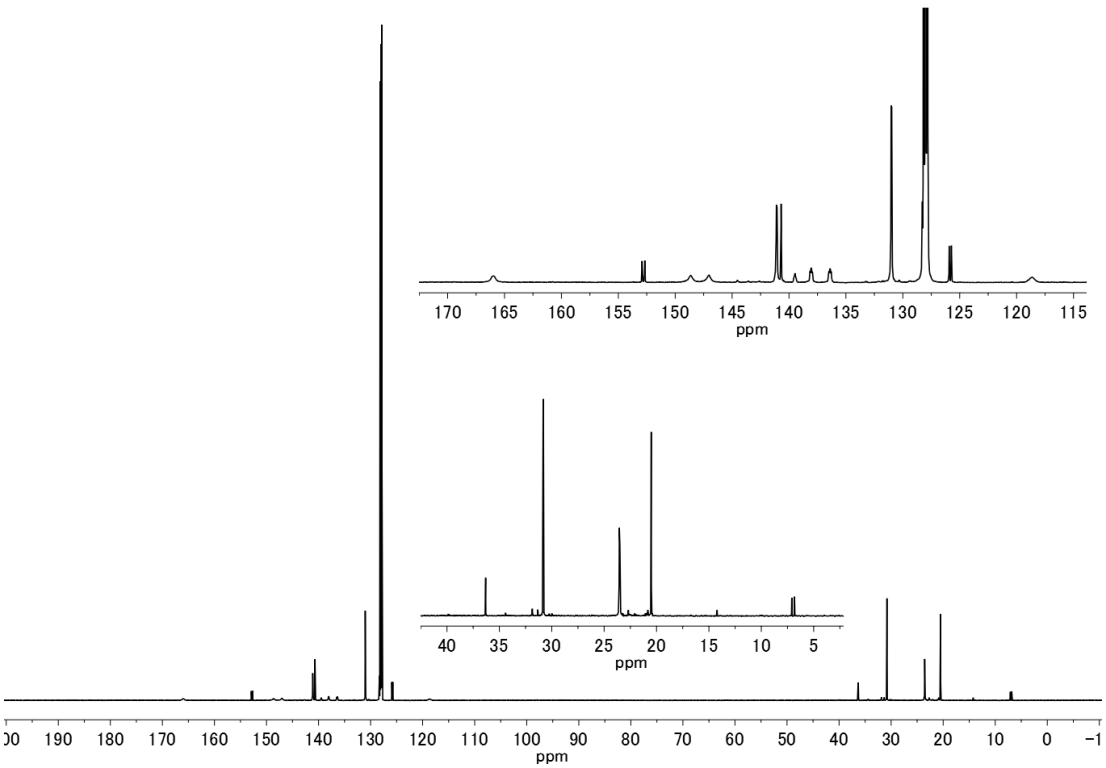


Figure S57 **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6, 299K) spectrum of compound **13e**.

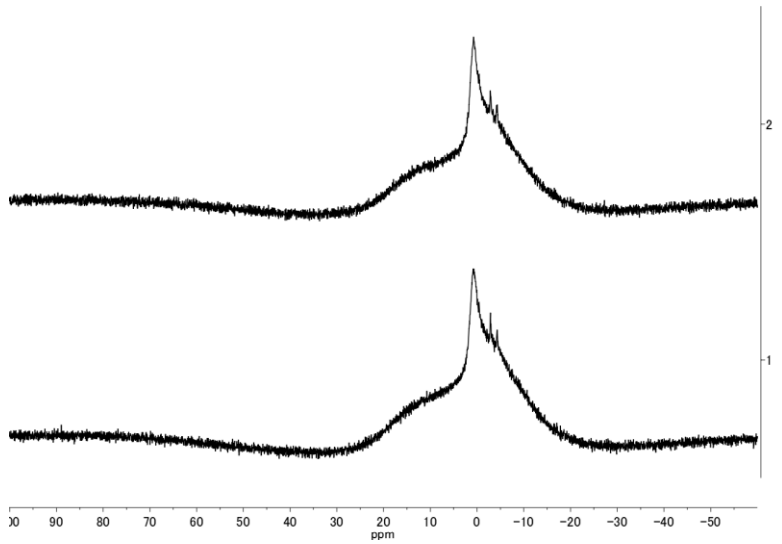


Figure S58 (1) **$^{11}B\{^{1}H\}$** and (2) **^{11}B NMR** (192 MHz, C_6D_6, 299 K) spectra of compound **13e**.

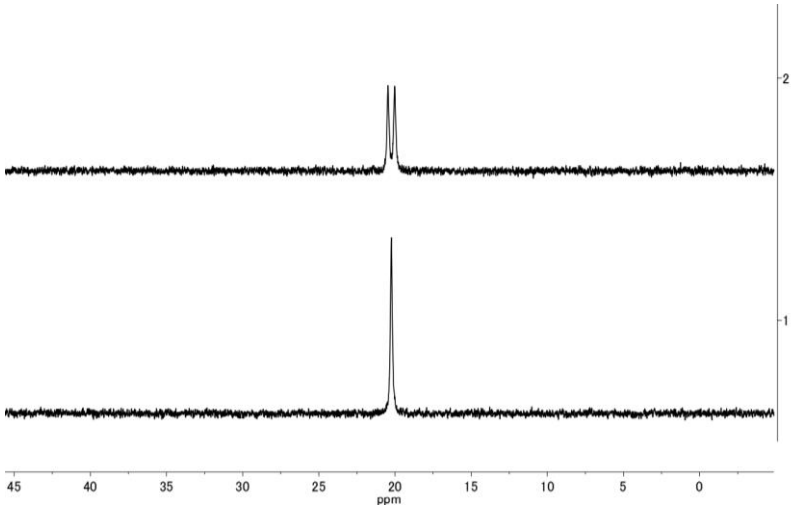


Figure S59 (1) **$^{31}P\{^{1}H\}$** and (2) **^{31}P NMR** (243 MHz, C_6D_6, 299K) spectra of compound **13e**.

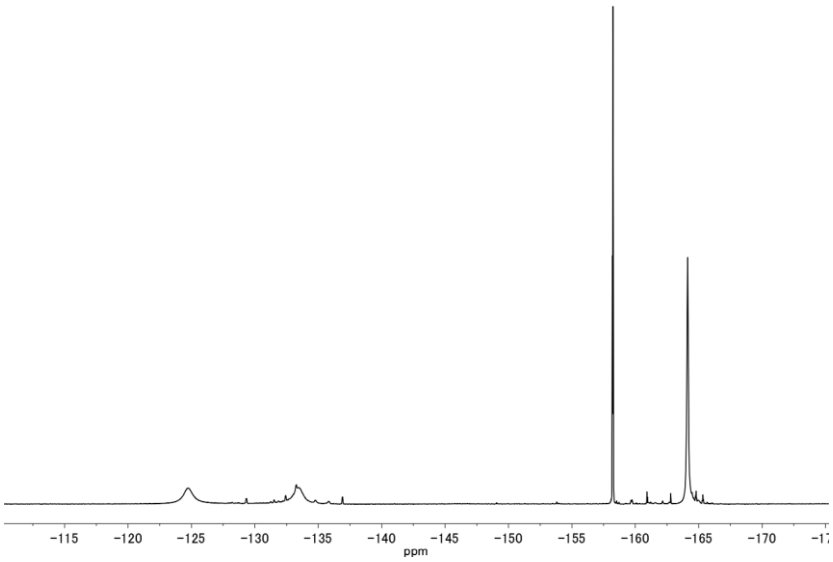


Figure S60 **^{19}F NMR** (564 MHz, C_6D_6, 299 K) spectrum of compound **13e**.