P-C Bond Activation Chemistry: Evidence for 1,1-Carboboration Reactions Proceeding with Phosphorus- Carbon Bond Cleavage

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Supporting Information

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[$] X-ray crystal structure analysis

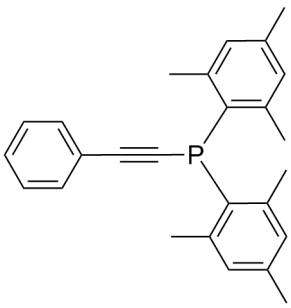
General Procedures. All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried with the procedure according to Grubbs (A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518-1520) or were distilled from appropriate drying agents and stored under an argon atmosphere. NMR spectra were recorded on a *Bruker* AC 200 P (^{1}H: 200 MHz, ^{31}P: 81 MHz, ^{11}B: 64 MHz), a *Bruker* AV 300 (^{1}H: 300 MHz, ^{13}C: 76 MHz, ^{31}P: 122 MHz, ^{11}B: 96 MHz, ^{19}F: 282 MHz), a *Bruker* AV 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{31}P: 162 MHz), 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), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference), ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in D_2O) (external reference). NMR assignments were supported by additional 2D NMR experiments. Elemental analyses were performed on a *Elementar Vario El III*. IR spectra were recorded on a *Varian* 3100 FT-IR (Excalibur Series). Melting points were obtained with a DSC 2010 (*TA Instruments*). HRMS was recorded on GTC Waters Micromass (Manchester, UK).

X-Ray crystal structure analyses. Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122), graphics XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 50 % probability, *R*-values are given for the observed reflections, wR^2-values are given for all reflections.

Materials. Chlorodimesitylphosphine [Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Siegel, G. A. *Inorg. Chem.* **1987**, *26*, 1941-1946.], Diphenyl(phenylethinyl)phosphine (**3b**) [(a) Miller, A. D.; Johnson, S. A.; Tupper, K. A.; McBee, J. L.; Tilley, T. D. *Organometallics* **2009**, *28*, 1252–1262. (b) Samb, A.; Demerseman, B.; Dixneuf, P. H.; Mealli, C. *Organometallics* **1988**, *7*, 26–33.] and $B(C_6F_5)_3$ (**1**) [(a) Wang, C.; Erker, G.; Kehr, G.; Wedeking, K.; Fröhlich, R. *Organometallics*, **2005**, *24*, 4760–4773. (b) Massey, A. G.; Park,

A. J. *J. Organomet. Chem.* **1964**, *2*, 245–250. (c)Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc.* **1963**, 212.] were prepared according to literature procedures. The compounds **3a** [Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Angew. Chem. Int. Ed.* **2008**, *47*, 7543-7546; *Angew. Chem.* **2008**, *120*, 7654-7657.], **3c** [Beletskaya, I. P.; Afanasiev, V. V.; Kazankova, M. A.; Efimova, I. V. *Org. Lett.* **2003**, *5*, 4309-4311.] and **3d** [Synthesis of the lithium salt: Kang, Y. K.; Deria, P.; Caroll, P. J.; Therien, M. J. *Org. Lett.* **2008**, *10*, 1341-1344. See also: Anderson, D. M.; Hitchcock, P. B.; Lappert, M. F. *J. Organomet. Chem.* **1989**, *363*, C7-C11.] were prepared in a similar fashion to **3b**.

Synthesis of 3a.

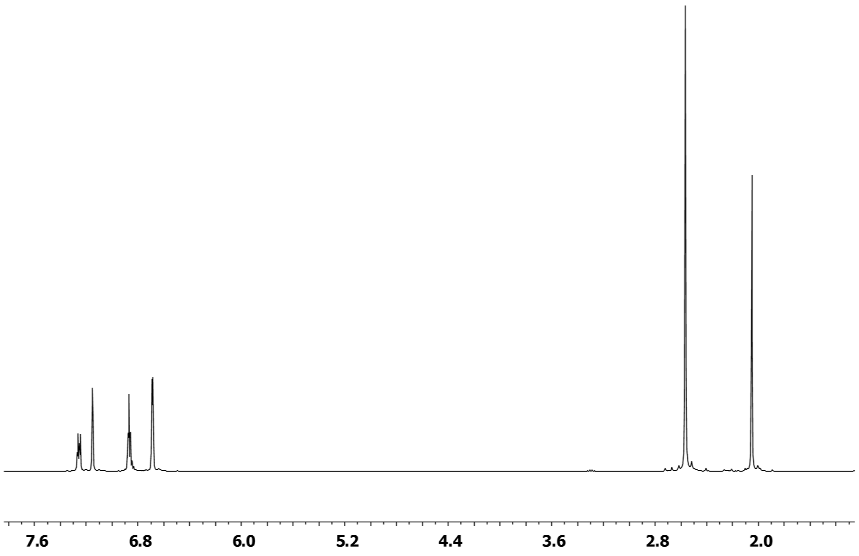


Phenylacetylene (0.20 ml, 1.92 mmol) was dissolved in diethylether (15 ml). Then *n*-butyllithium solution (1.6 M in hexane, 1.2 ml, 1.92 mmol) was added at -78°C. The solution was stirred for 2h at room temperature. Subsequently the reaction mixture was again cooled to -78°C and a solution of chlorodimesitylphosphine (0.586 g, 1.92 mmol) in diethylether(15 ml) was added. The reaction mixture was warmed to room temperature and stirred for 3h. The solvent was removed in vacuum and the residue was extracted with pentane (30 ml). The solution was concentrated to precipitate a yellow solid which was isolated by filtration and washed with pentane several times. The yellow product was crystallized from ethanol at –36 °C (0.290 g, 0.78 mmol, 41%).

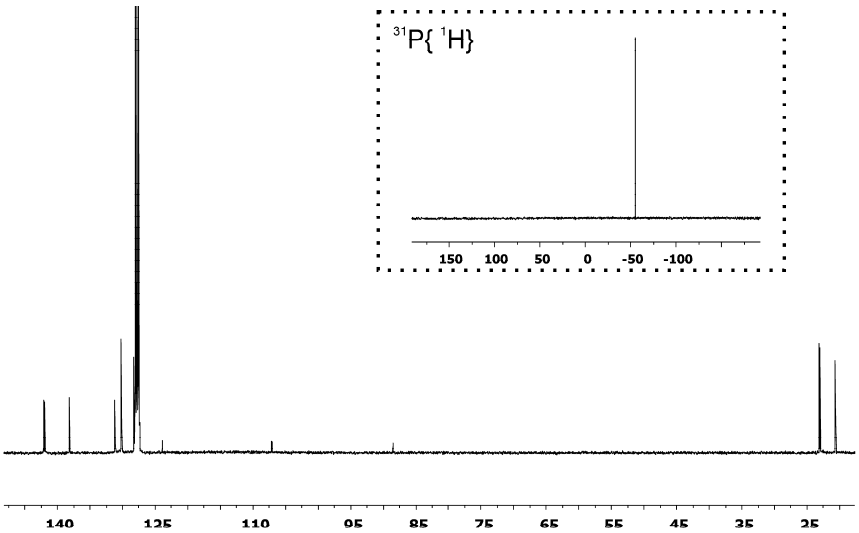
^{1}H NMR (400 MHz, 300 K, C_6D_6): δ = 7.25 (m, 2H, *o*-Ph), 6.87 (m, 3H, *m-, p*-Ph), 6.69 (d, $^{4}J_{PH}$ = 3.0 Hz, 4H, *m*-Mes), 2.56 (s, 12H, *o*-CH_3^{Mes}), 2.05 (s, 6H, *p*-CH_3^{Mes}).

^{13}C{^{1}H} NMR (101 MHz, 300 K, C_6D_6): δ = 142.3 (d, $^{2}J_{PC}$ = 15.4 Hz, *o*-Mes), 138.4 (*p*-Mes), 131.4 (d, $^{4}J_{PC}$ = 2.1 Hz, *o*-Ph), 130.5 (d, $^{1}J_{PC}$ = 12.5 Hz, *i*-Mes), 130.4 (d, $^{3}J_{PC}$ = 3.7 Hz, *m*-Mes), 128.5 (*p*-Ph), 127.6 (*m*-Ph), 124.1 (d, $^{3}J_{PC}$ = 1.4 Hz, *i*-Ph), 107.4 (d, $^{2}J_{PC}$ = 8.4 Hz, $^{Ph}C^{\equiv}$), 88.7 (d, $^{1}J_{PC}$ = 7.5 Hz, $^{\equiv}C^{P}$), 23.3 (d, $^{3}J_{PC}$ = 13.3 Hz, *o*-CH_3^{Mes}), 20.9 (*p*-CH_3^{Mes}).

^{31}P{^{1}H} NMR (81 MHz, 300 K, C_6D_6): δ = -55.2 ($\nu_{1/2}$ ~ 1 Hz).

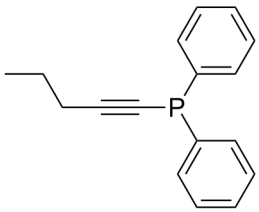


^{1}H NMR (400 MHz, 300 K, C_6D_6) of **3a**.



^{13}C{^{1}H} NMR (101 MHz, 300 K, C_6D_6) and ^{31}P{^{1}H} NMR (81 MHz) of **3a**.

Synthesis of 3c.



Based on the same procedure described for the preparation of **3a** (0.290 g, 41 %) **3c** (2.20 g, 8.73 mmol, 86%) was prepared from 1-pentyne (1.0 ml, 10.1 mmol) and chlordiphenylphosphine (1.8 ml, 10.1 mmol). The pure product could be obtained without recrystallization.

^{1}H NMR (400 MHz, 300 K, C_6D_6): δ = 7.75 (m, 4H, *o*-Ph), 7.08 (m, 4H, *m*-Ph), 7.01 (m, 2H, *p*-Ph), 2.03 (td, $^{3}J_{HH}$ = 6.9 Hz, $^{4}J_{PH}$ = 1.4 Hz, 2H, $^{\equiv}CH_2$), 1.32 (m, 2H, CH_2), 0.79 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, 300 K, C_6D_6): δ = 137.9 (d, $^{1}J_{PC}$ = 8.7 Hz, *i*-Ph), 132.8 (d, $^{2}J_{PC}$ = 20.2 Hz, *o*-Ph), 129.0 (*p*-Ph), 128.8 (d, $^{3}J_{PC}$ = 7.4 Hz, *m*-Ph), 110.5 (d, $^{2}J_{PC}$ = 3.5 Hz, $^{Pr}C^{\equiv}$), 77.0 (d, $^{1}J_{PC}$ = 3.8 Hz, $^{\equiv}C^{P}$), 22.3 (d, $^{3}J_{PC}$ = 14.6 Hz, $^{\equiv}CH_2$), 22.2 (d, $^{4}J_{PC}$ = 0.9 Hz, CH_2) 13.5 (CH_3).

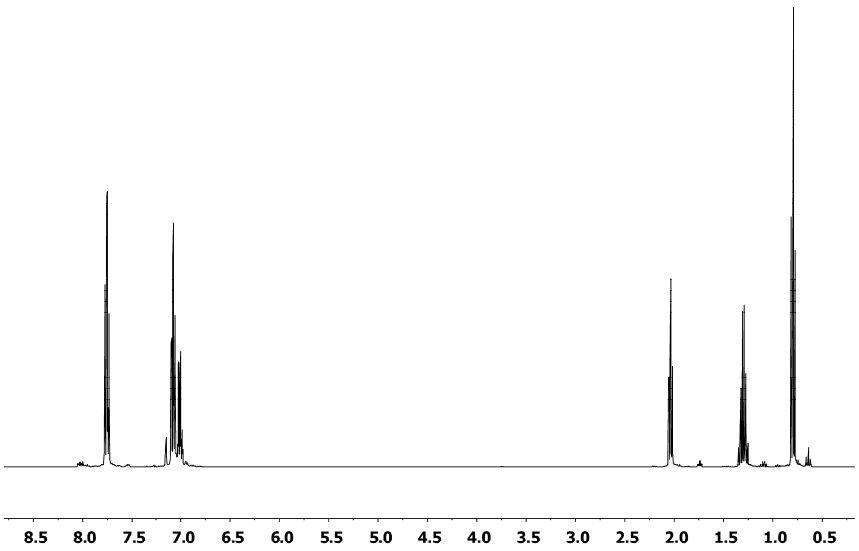
^{31}P{^{1}H} NMR (81 MHz, 300 K, C_6D_6): δ = -32.0 ($\nu_{1/2}$ ~ 2 Hz).

^{1}H,^{1}H GCOSY (400 MHz / 400 MHz, 300 K, C_6D_6): δ^{1}H / δ^{1}H = 7.75 / 7.08 (*o*-Ph / *m*-Ph), 7.08 / 7.75, 7.01 (*m*-Ph / *o*-Ph, *p*-Ph), 2.03 / 1.32 ($^{\equiv}CH_2$ / CH_2), 1.32 / 2.03, 0.79 (CH_2 / $^{\equiv}CH_2$, CH_3), 0.79 / 1.32 (CH_3 / CH_2).

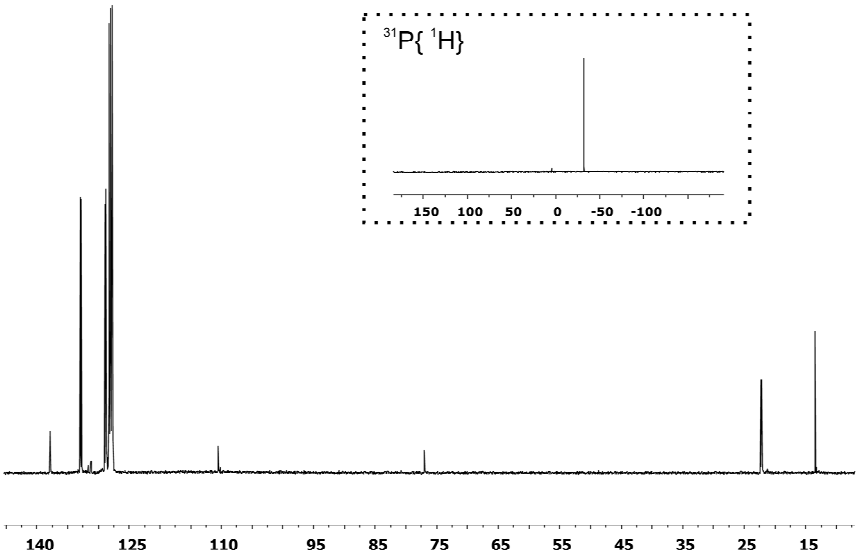
^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 300 K, C_6D_6): δ^{1}H / δ^{13}C = 7.75 / 132.8 (*o*-Ph), 7.08 / 128.8 (*m*-Ph), 7.01 / 129.0 (*p*-Ph), 2.03 / 22.3 ($^{\equiv}CH_2$), 1.32 / 22.2 (CH_2), 0.79 / 13.5 (CH_3).

^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, 300 K, C_6D_6): δ^{1}H / δ^{13}C = 7.75 / 129.0 (*o*-Ph / *p*-Ph), 7.08 / 137.9, 132.8, 129.0 (*m*-Ph / *i*-Ph, *o*-Ph, *p*-Ph), 7.01 / 132.8, 128.8 (*p*-Ph / *o*-Ph, *m*-Ph), 2.03 / 137.9, 110.5, 77.0, 22.2, 13.5 ($^{\equiv}CH_2$ / *i*-Ph, $^{Pr}C^{\equiv}$, $^{\equiv}C^{P}$, CH_2, CH_3), 1.32 /110.5, 22.3, 13.5 (CH_2 / $^{Pr}C^{\equiv}$, $^{\equiv}CH_2$, CH_3), 0.79 / 22.3, 22.2 (CH_3 / $^{\equiv}CH_2$, CH_2).

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 3053 (m), 2962 (s), 2179 (s; C≡C), 1884 (w), 1585 (m), 1434 (s), 1324 (m), 1094 (s), 984, (s), 739 (s), 511 (s).

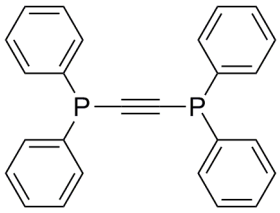


^{1}H NMR (400 MHz, 300 K, C_6D_6) of **3c**.



^{13}C{^{1}H} NMR (101 MHz, 300 K, C_6D_6) and ^{31}P{^{1}H} NMR (81 MHz) of **3c**.

Synthesis of 3d.



N-butyllithium (1.6 M in hexane, 18.8 ml, 30.0 mmol) was dissolved in a mixture of diethylether/tetrahydrofuran and cooled to –78 °C. A solution of trichloroethylene (0.9 ml, 10.0 mmol) in diethylether (10 ml) was added and stirred for 1h at –78 °C. The reaction mixture was stirred overnight at room temperature. The formed suspension was cooled again to -78 °C and added fast to a solution of chlorodiphenylphosphine (3.60 ml, 20.0 mmol) in diethylether (15 ml) at the same temperatur. After stirring overnight at room temperature the solvent was removed by condensation. The residue was extracted with pentane and the product (0.220 g, 0.557 mmol, 7%) could be isolated as a white solid.

^{1}H NMR (400 MHz, 300 K, C_7D_8): δ = 7.54 (m, 2H, *o*-Ph), 6.93 (m, 3H, *m-, p*-Ph).

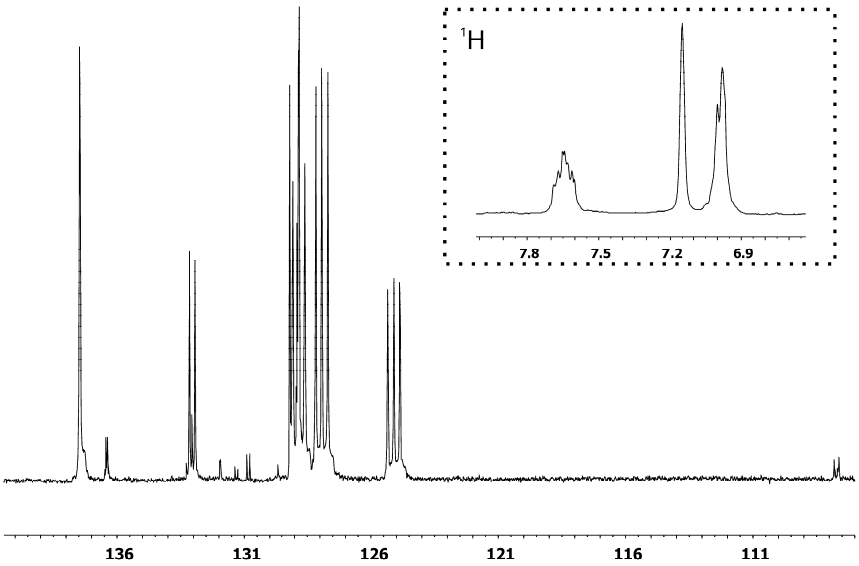
^{13}C{^{1}H} NMR (101 MHz, 300 K, C_7D_8): δ = 136.4 (m, *i*-Ph), 133.0 (m, *o*-Ph), 129.2 (*p*-Ph), 128.9 (m, *m*-Ph), 107.7 (m, $^{P}C^{\equiv}$).

^{31}P{^{1}H} NMR (121 MHz, 300 K, C_7D_8): δ = -32.0 ($\nu_{1/2}$ ~ 3 Hz).

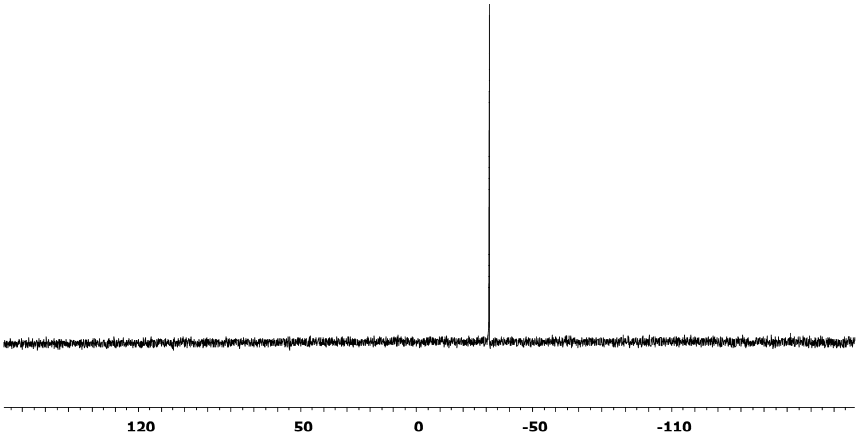
^{1}H,^{1}H GCOSY (400 MHz / 400 MHz, 300 K, C_7D_8): δ^{1}H / δ^{1}H = 7.54 / 6.93 (*o*-Ph / *m-, p*-Ph).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 300 K, C_7D_8): δ^{1}H / δ^{13}C = 7.54 / 133.0 (*o*-Ph), 6.93 / 129.2, 128.9 (*p-, m*-Ph).

^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, 300 K, C_7D_8): δ^{1}H / δ^{13}C = 7.54 / 136.4, 129.2, 128.9 (*o*-Ph / *i*-Ph, *p*-Ph, *m*-Ph), 6.93 / 136.4, 133.0, 129.2, 128.9 (*m-, p*-Ph / *i*-Ph, *o*-Ph, *p*-Ph, *m*-Ph).

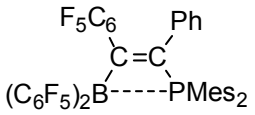


^{1}H NMR (200 MHz, 300 K, C_6D_6) and ^{13}C{^{1}H} NMR (101 MHz, 300 K, C_7D_8) of **3d**.



$^{31}P\{^{1}H\}$ NMR (81 MHz, 300 K, C_6D_6) of **3d**.

Synthesis of 4a.



$B(C_6F_5)_3$ (**1**) (0.400 g, 0.780 mmol) and **3a** (0.290 g, 0.780 mmol) were dissolved in toluene (20 ml) and stirred for 6h at 105 °C. While stirring reaction mixture over night at room temperature, a white solid precipitated. The solid was isolated via cannula filtration and washed twice with pentane (15 ml). Drying under vacuum gave the product (0.406 g, 0.460 mmol, 59%) as a white solid. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **4a** in toluene at –36 °C. **Anal. Calc.** for $C_{44}H_{27}BF_{15}P$: C, 59.89; H, 3.08. Found: C, 59.84; H, 3.14. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3406 (br m), 3026 (w), 2934 (w), 2359 (m), 1639 (s), 1518 (s), 1456 (s), 1287 (m), 1094 (s), 980 (s), 761 (m), 506 (m). Decomp. (DSC): 231 °C.

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 7.04 (m, 2H, *o*-Ph), 6.82 (m, 3H, *m*-, *p*-Ph), 6.43 (d, $^4J_{PH}$ = 3.3 Hz, 4H, *m*-Mes), 2.13 (s, 12H, *o*-CH_3^{Mes}), 1.89 (s, 6H, *p*-CH_3^{Mes}).

^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6): δ = 161.2 (br, $^B\underline{C}^=$), 146.7 (d, $^1J_{PC}$ = 46.8 Hz, $^=\underline{C}^P$), 143.4 (d, $^2J_{PC}$ = 8.8 Hz, *o*-Mes), 142.1 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes), 137.9 (d, $^2J_{PC}$ = 1.9 Hz, *i*-Ph), 131.0 (d, $^3J_{PC}$ = 9.1 Hz, *m*-Mes), 129.0 (*p*-Ph), 128.8 (*m*-Ph), 127.3 (d, $^3J_{PC}$ = 3.6 Hz, *o*-Ph), 123.3 (d, $^1J_{PC}$ = 34.6 Hz, *i*-Mes), 24.0 (d, $^3J_{PC}$ = 5.9 Hz, *o*-CH_3^{Mes}), 20.5 (*p*-CH_3^{Mes}), [C_6F_5 not listed].

^{19}F{^{1}H} NMR (470 MHz, 298 K, C_6D_6): δ = -126.9 (br., 4F, *o*-BC_6F_5), -136.0 (m, 2F, *o*-C_6F_5), -154.1 (t, $^3J_{FF}$ = 21.7 Hz, 1F, *p*-C_6F_5), -156.1 (t, $^3J_{FF}$ = 21.1 Hz, 2F, *p*-BC_6F_5), -162.4 (m, 2F, *m*-C_6F_5), -164.0 (m, 4F, *m*-BC_6F_5) [$\Delta\delta^B$(m, p) = 7.9].

^{11}B{^{1}H} NMR (160 MHz, 298 K, C_6D_6): δ ~ 1 ($\nu_{1/2}$ ~ 700 Hz).

^{31}P{^{1}H} NMR (202 MHz, 298 K, C_6D_6): δ = 15.2 ($\nu_{1/2}$ ~ 40 Hz).

TOCSY (500 MHz, 298 K, C_6D_6): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 7.04 / 6.82 (*o*-Ph / *m*-, *p*-Ph), 6.43 / 2.13, 1.89 (*m*-Mes / *o*-CH_3^{Mes}, *p*-CH_3^{Mes}).

NOE (500 MHz, 298 K, C_6D_6): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 7.04 / 6.82, 2.13 (*o*-Ph / *m*-, *p*-Ph, *o*-CH_3^{Mes}), 6.82 / 7.04 (*m*-, *p*-Ph / *o*-Ph), 6.43 / 2.13, 1.89 (*m*-Mes / *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 2.13 / 7.04, 6.43 (*o*-CH_3^{Mes} / *o*-Ph, *m*-Mes), 1.89 / 6.43 (*p*-CH_3^{Mes} / *m*-Mes).

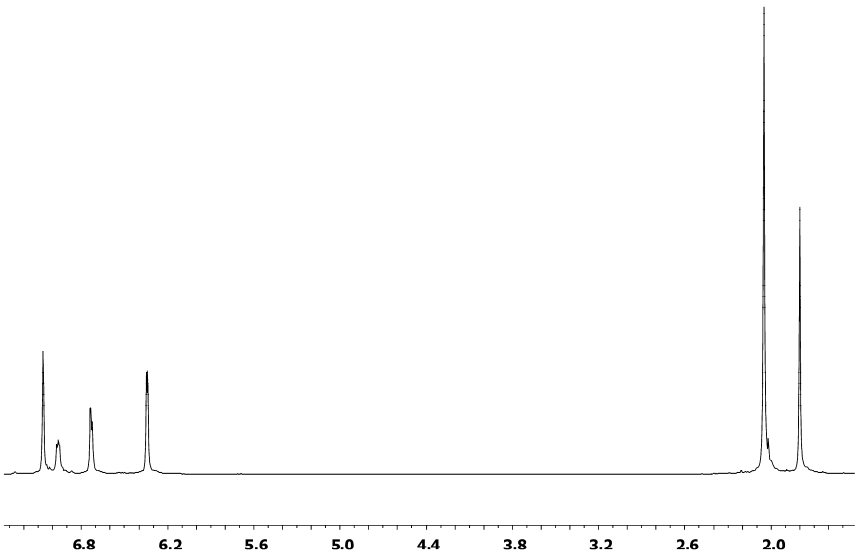
^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, C_6D_6): δ^1H / δ^1H = 7.04 / 6.82 (*o*-Ph / *m*-, *p*-Ph Ph), 6.43 / 2.13, 1.89 (*m*-Mes / *o*-CH_3^{Mes}, *p*-CH_3^{Mes}).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, C_6D_6): δ^1H / $\delta^{13}C$ = 7.04 / 127.3 (*o*-Ph), 6.82 / 128.7 (*m*-, *p*-Ph), 6.43 / 131.0 (*m*-Mes), 2.13 / 24.0 (*o*-CH_3^{Mes}), 1.89 / 20.5 (*p*-CH_3^{Mes}).

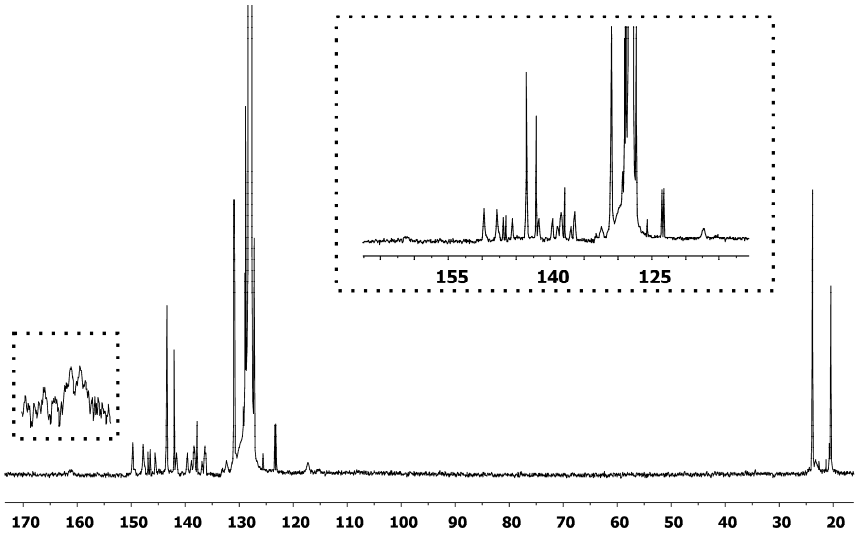
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, C_6D_6): δ^1H / $\delta^{13}C$ = 7.04 / 146.7, 128.9 (*o*-Ph / $^=\underline{C}^P$, *p*-, *m*-Ph), 6.82 / 137.9, 127.3 (*m*-, *p*-Ph / *i*-Ph, *o*-Ph), 6.43 / 123.3, 24.0, 20.5 (*m*-Mes /

i-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 2.13 / 143.4, 131.0, 123.3 (*o*-CH_3^{Mes} / *o*-, *m*-, *i*-Mes), 1.89 / 142.1, 131.0, 123.3 (*p*-CH_3^{Mes} / *m*-, *p*-, *i*-Mes).

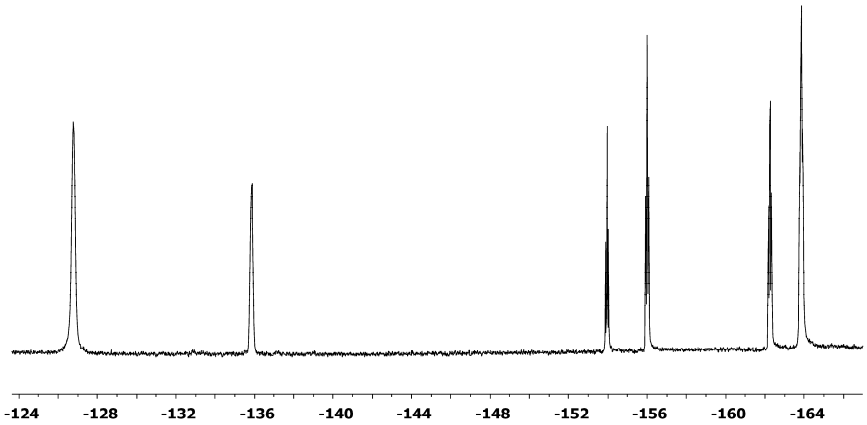
^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, 298 K, C_6D_6): $\delta^{19}F$ / $\delta^{19}F$ = -162.4 / -136.0, -154.1 (*m*-C_6F_5 / *o*-C_6F_5, *p*-C_6F_5), -164.0 / -126.9, -156.1 (*m*-BC_6F_5 / *o*-BC_6F_5, *p*-BC_6F_5).



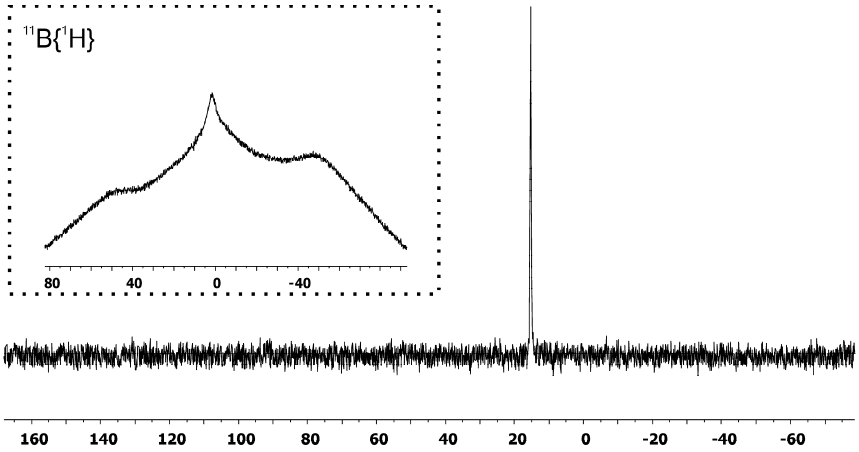
^{1}H NMR (400 MHz, 300 K, C_6D_6) of **4a**.



^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6) of **4a**.(Datei: kb_ole00514_271010_298k_13c.fid/ fid)

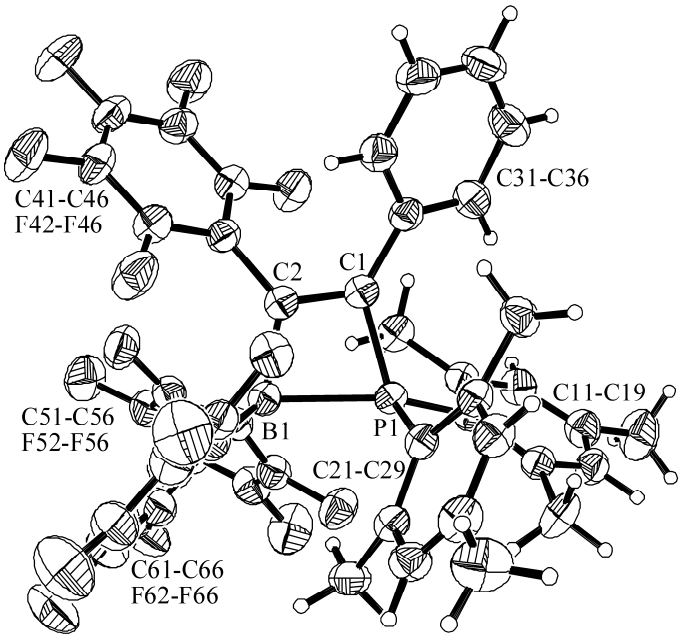


$^{19}F\{^{1}H\}$ NMR (282 MHz, 300 K, C_6D_6) of **4a**.

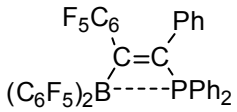


$^{11}B\{^{1}H\}$ NMR (96 MHz, 300 K, C_6D_6) and $^{31}P\{^{1}H\}$ NMR (162 MHz) of **4a**.

X-Ray crystal structure analysis of 4a. formula $C_{44}H_{27}BF_{15}P$, M = 882.44, colorless crystal 0.40 x 0.30 x 0.25 mm, a = 12.2935(3), b = 21.9361(7), c = 14.0308(5) Å, β = 102.427(1)º, V = 3695.1(2) Å^3, ρ_{calc} = 1.586 g cm^{-3}, μ= 1.663 mm^{-1}, empirical absorption correction (0.556 ≤ T ≤ 0.681), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 28710 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6493 independent (R_{int} = 0.044) and 5823 observed reflections [$I \geq 2\ \sigma(I)$], 556 refined parameters, R = 0.044, wR^2 = 0.124, max. (min.) residual electron density 0.32 (-0.28) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.


C41-C46
F42-F46
C31-C36
C2
C1
C11-C19
C51-C56
F52-F56
B1
P1
C21-C29
C61-C66
F62-F66

Synthesis of 4b.



$B(C_6F_5)_3$ (**1**) (0.536 g, 1.05 mmol) and **3b** (0.300 g, 1.05 mmol) were dissolved in toluene (20 ml) and stirred for 6h at 70 °C. Subsequently the solvent was removed and the residue was washed twice with pentane (15 ml) and all volatiles were removed in vacuo to yield **4b** (0.634 g, 0.803 mmol, 77%) as a yellow solid. **Anal. Calc.** for $C_{38}H_{15}BF_{15}P$: C, 57.17; H, 1.89. Found: C, 57.10; H, 2.40. **IR**(KBr) $\tilde{\nu}$ / cm^{-1} = 3406 (br m), 3064 (w), 2360 (m), 1646 (s), 1519 (s), 1463 (s), 1285 (m), 1096 (s), 966 (s), 693 (s), 518 (m). **M.p.** (DSC): 251 °C, decomp. (DSC): 272 °C.

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 7.36 (m, 4H, *o*-Ph^P), 7.12 (m, 2H, *o*-Ph), 6.88 (m, 3H, *p*-Ph / *p*-Ph^P), 6.84 (m, 2H, *m*-Ph), 6.76 (m, 4H, *m*-Ph^P).

^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6): δ = 161.3 (br, $^B\underline{C}^=$), 148.7 (dm, $^1J_{FC}$ ~ 240 Hz), 144.0 (dm, $^1J_{FC}$ ~ 250 Hz), 141.0 (dm, $^1J_{FC}$ ~ 250 Hz), 140.5 (dm, $^1J_{FC}$ ~ 250 Hz), 138.1 (dm, $^1J_{FC}$ ~ 250 Hz), 137.6 (dm, $^1J_{FC}$ = 250 Hz) (C_6F_5), 143.3 (d, $^1J_{PC}$ = 53.0 Hz, $^=\underline{C}^P$), 135.2 (d, $^2J_{PC}$ = 1.9 Hz, *i*-Ph), 132.5 (*p*-Ph^P), 132.1 (d, $^2J_{PC}$ = 9.3 Hz, *o*-Ph^P), 129.7 (*p*-Ph), 129.4 (*m*-Ph), 129.3 (d, $^3J_{PC}$ = 10.4 Hz, *m*-Ph^P), 127.0 (d, $^3J_{PC}$ = 3.2 Hz, *o*-Ph), 124.6 (d, $^1J_{PC}$ = 43.8 Hz, *i*-Ph^P), 115.8 (br, *i*-C_6F_5).

^{19}F{^{1}H} NMR (470 MHz, 298 K, C_6D_6): δ = -129.9 (m, 4F, *o*-BC_6F_5), -138.3 (m, 2F, *o*-C_6F_5), -154.0 (t, $^3J_{FF}$ = 21.5 Hz, 1F, *p*-C_6F_5), -156.1 (m, 2F, *p*-BC_6F_5), -161.7 (m, 2F, *m*-C_6F_5), -163.6 (m, 4F, *m*-BC_6F_5) [$\Delta\delta^B$(m, p) = 7.5].

^{11}B{^{1}H} NMR (160 MHz, 298 K, C_6D_6): δ = -6 ($\nu_{1/2}$ ~ 320 Hz).

^{31}P{^{1}H} NMR (202 MHz, 298 K, C_6D_6): δ = 13.8 ($\nu_{1/2}$ ~ 60 Hz).

TOCSY (500 MHz, 298 K, C_6D_6): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 7.36 / 6.88, 6.76 (*o*-Ph^P / *p*-Ph^P, *m*-Ph^P), 6.88 / 7.12, 6.76 (*p*-Ph / *o*-Ph, *m*-Ph).

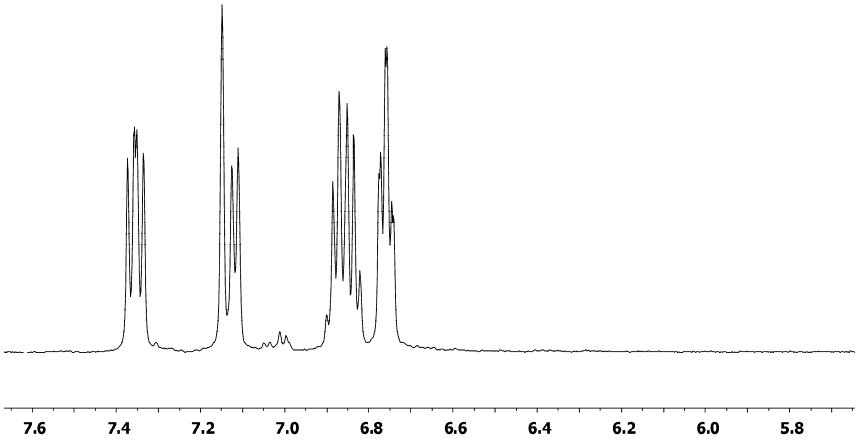
NOE (500 MHz, 298 K, C_6D_6): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 7.36 / 6.76 (*o*-Ph^P / *m*-Ph^P), 7.12 / 6.84 (*o*-Ph / *m*-Ph), 6.88 / 6.76 (*p*-Ph^P/ *m*-Ph^P), 6.76 / 7.36, 6.88 (*m*-Ph^P / *o*-Ph^P, *p*-Ph^P).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, C_6D_6): δ^1H / δ^1H = 7.36 / 6.76 (*o*-Ph^P / *m*-Ph^P), 6.76 / 7.36, 6.88 (*m*-Ph^P / *o*-Ph^P, *p*-Ph^P), 7.12 / 6.84 (*o*-Ph / *m*-Ph), 6.84 / 7.12, 6.88 (*m*-Ph/ *o*-Ph, *p*-Ph).

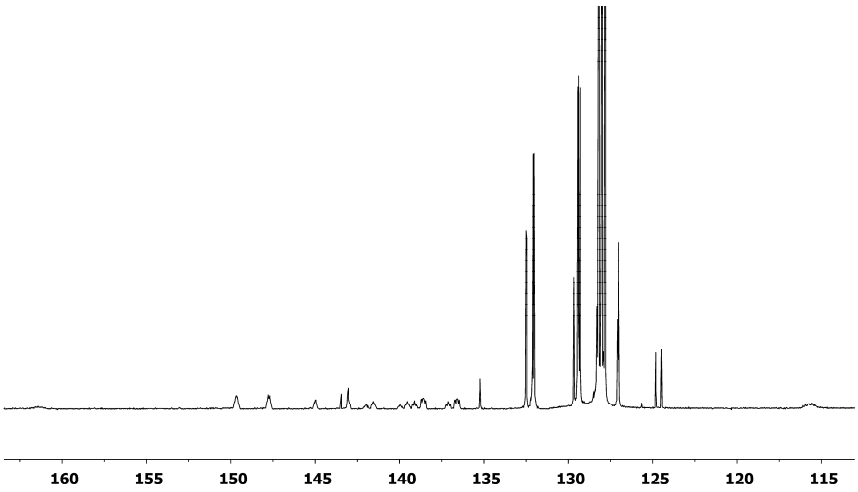
^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, C_6D_6): δ^1H / $\delta^{13}C$ = 7.36 / 132.1 (*o*-Ph^P), 7.12 / 127.1 (*o*-Ph), 6.88 / 132.5, 129.7 (*p*-Ph^P, *p*-Ph), 6.84 / 129.5 (*m*-Ph), 6.76 / 129.3 (*m*-Ph^P).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, C_6D_6): δ^1H / $\delta^{13}C$ = 7.36 / 132.5 (*o*-Ph^P / *p*-Ph^P), 7.12 / 143.3, 129.7 (*o*-Ph / $^=\underline{C}^P$, *p*-Ph), 6.88 / 132.1, 127.0 (*p*-Ph, *p*-Ph^P / *o*-Ph^P, *o*-Ph), 6.84 / 135.2, 129.7 (*m*-Ph / *i*-Ph, *p*-Ph), 6.76 / 132.1, 124.6 (*m*-Ph^P / *o*-Ph^P, *i*-Ph^P).

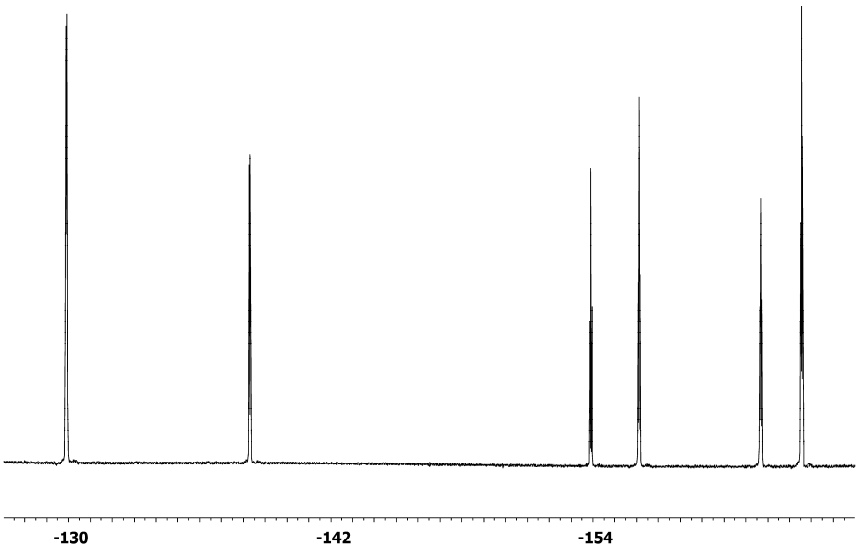
^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, 298 K, C_6D_6): δ^{19}F / δ^{19}F = -161.7 / -138.3, -154,0 (*m*-C_6F_5 / *o*-C_6F_5, *p*-C_6F_5), -163.6 / -129.9, -156.1 (*m*-BC_6F_5 / *o*-BC_6F_5, *p*-BC_6F_5).



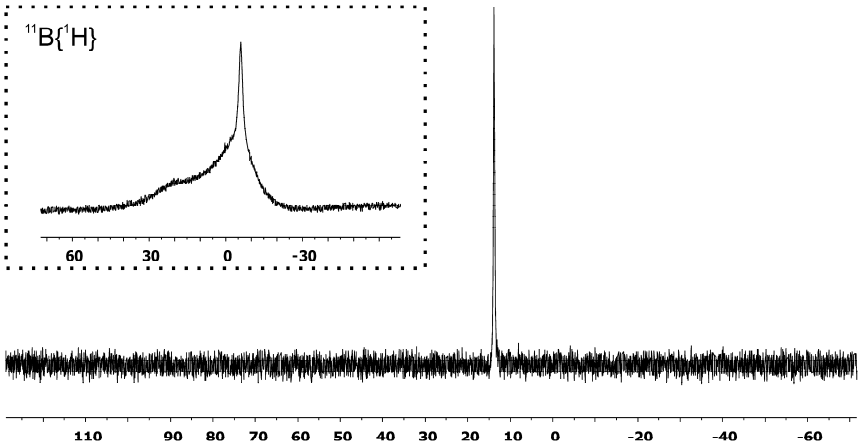
^{1}H NMR (500 MHz, 298 K, C_6D_6) of **4b**.



^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6) of **4b**.



^{19}F{^{1}H} NMR (470 MHz, 298 K, C_6D_6) of **4b**.

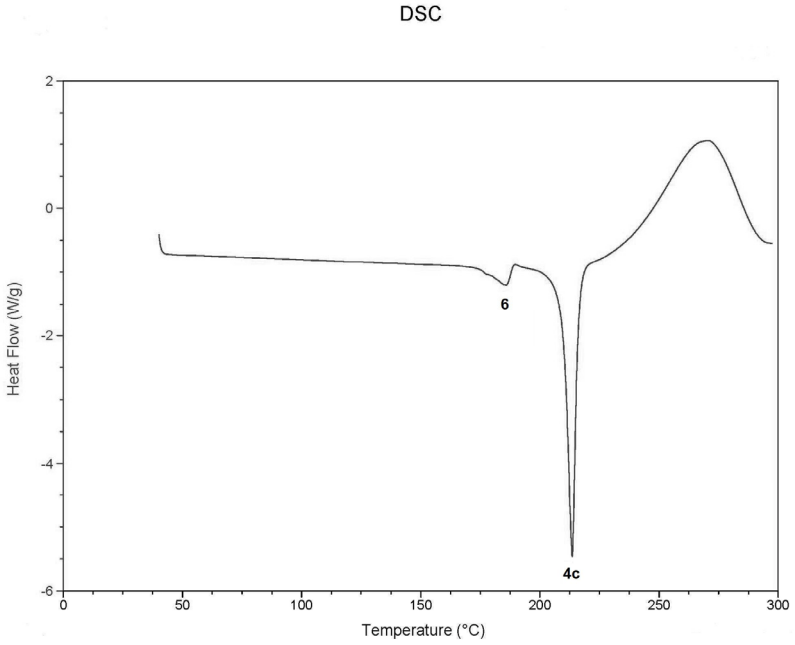


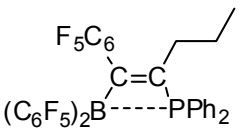
$^{11}B\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6) and $^{31}P\{^{1}H\}$ NMR (202 MHz) of **4b**.

Synthesis of 4c and 6.

$B(C_6F_5)_3$ (**1**) (0.400 g, 0.780 mmol) and **3c** (0.197 g, 0.780 mmol) were dissolved in toluene (20 ml) and stirred 6h at 70 °C. Subsequently the solvent was removed and the residue was washed twice with pentane. The solid was suspended in toluene and filtered via cannula. After removal of toluene in vacuo a mixture of **4c** and **6** (ratio 10:1) (0.333 g, 0.440 mmol, 56%) was obtained as a white solid. Single crystals of **4c** suitable for X-ray crystal structure analysis were obtained by slow diffusion of pentane into a solution of **4c**/**6** in dichloromethane at -36 °C.

4c and **6**: **Anal. Calc.** for $C_{35}H_{17}BF_{15}P$: C, 55.00; H, 2.24. Found: C, 54.51; H, 1.95. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3406 (br m), 3060 (w), 2973 (m), 2880 (w), 2357 (w), 1645 (s), 1518 (s), 1468 (s), 1383 (m), 1288 (m), 1110 (s), 971 (s), 922 (m), 744 (m), 506 (m). **M.p.** (DSC) (**4c**): 214 °C, **m.p.** (DSC) (**6**): 186 °C, decomp. (DSC): 270 °C.





4c: ^{1}H NMR (400 MHz, 300 K, C_6D_6): δ = 7.27 (m, 4H, *o*-Ph), 6.93 (m, 2H, *p*-Ph), 6.86 (m, 4H, *m*-Ph), 2.19 (m, 2H, $^{=}CH_2$), 1.20 (m, 2H, CH_2), 0.55 (m, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, 300 K, C_6D_6): δ = 161.5 (br, $^{B}C^{=}$), 146.7 (d, $^{1}J_{PC}$ = 49.1 Hz, $^{=}C^{P}$), 132.38 (d, $^{2}J_{PC}$ = 8.4 Hz, *o*-Ph), 132.36 (d, $^{4}J_{PC}$ = 3.3 Hz, *p*-Ph), 129.2 (d, $^{3}J_{PC}$ = 10.6 Hz, *m*-Ph), 125.4 (d, $^{1}J_{PC}$ = 42.1 Hz, *i*-Ph), 115.8 (br s, *i*-BC_6F_5), 33.2 ($^{=}CH_2$), 21.3 (d, $^{3}J_{PC}$ = 1.6 Hz, CH_2), 14.0 (CH_3), [C_6F_5 not listed].

$^{19}F\{^1H\}$ NMR (470 MHz, 298 K, C_6D_6): δ = -129.7 (m, 4F, *o*-BC_6F_5), -139.6 (m, 2F, *o*-C_6F_5), -154.5 (t, $^3J_{FF}$ = 21.6 Hz, 1F, *p*-C_6F_5), -156.4 (m, 2F, *p*-BC_6F_5), -161.9 (m, 2F, *m*-C_6F_5), -163.7 (m, 4F, *m*-BC_6F_5) [$\Delta\delta^B$(m, p) = 7.3].

$^{31}P\{^1H\}$ NMR (162 MHz, 300 K, C_6D_6): δ = 15.2 ($\nu_{1/2}$ ~ 80 Hz).

$^{11}B\{^1H\}$ NMR (96 MHz, 300 K, C_6D_6): δ = -6 ($\nu_{1/2}$ ~ 260 Hz).

TOCSY (600 MHz, 300 K, C_6D_6): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 7.27 / 6.93, 6.86 (*o*-Ph / *p*-Ph, *m*-Ph), 2.19 / 1.20, 0.55 ($^{=}CH_2$ / CH_2, CH_3).

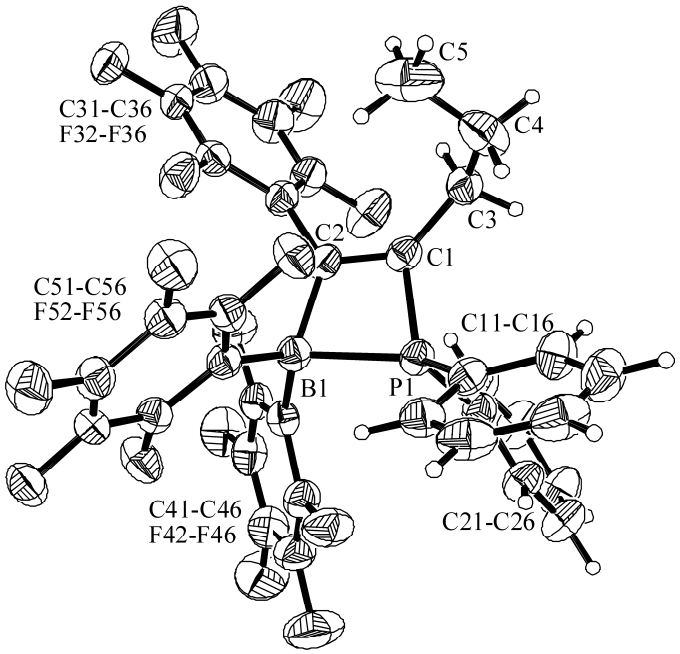
NOE (600 MHz, 300 K, C_6D_6): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 7.27 / 6.86 (*o*-Ph / *m*-Ph), 2.19 / 1.20, 0.55 ($^{=}CH_2$ / CH_2, CH_3).

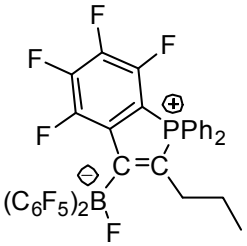
$^1H,^1H$ GCOSY (400 MHz / 400 MHz, 300 K, C_6D_6): δ^1H / δ^1H = 7.27 / 6.86 (*o*-Ph / *m*-Ph), 6.86 / 7.27, 6.93 (*m*-Ph / *o*-Ph, *p*-Ph), 2.19 / 1.20 ($^{=}CH_2$ / CH_2), 1.20 / 2.19, 0.55 (CH_2 / $^{=}CH_2$, CH_3), 0.55 / 1.20 (CH_3 / CH_2).

$^1H,^{13}C$ GHSQC (400 MHz / 101 MHz, 300 K, C_6D_6): δ^1H / $\delta^{13}C$ = 7.27 / 132.38 (*o*-Ph), 6.93 / 132.36 (*p*-Ph), 6.86 / 129.2 (*m*-Ph), 2.19 / 33.2 ($^{=}CH_2$), 1.20 / 21.3 (CH_2), 0.55 /14.0 (CH_3).

$^1H,^{13}C$ GHMBC (400 MHz / 101 MHz, 300 K, C_6D_6): δ^1H / $\delta^{13}C$ = 7.27 / 132.36 (*o*-Ph / *p*-Ph), 6.93 / 132.38 (*p*-Ph / *o*-Ph), 6.86 / 132.38, 132.36, 125.4 (*m*-Ph / *o*-Ph, *p*-Ph, *i*-Ph), 2.19 / 147.0, 21.3, 14.0 ($^{=}CH_2$ / $^{=}C^P$, CH_2, CH_3), 1.20 / 147.0, 33.2, 14.0 (CH_2 / $^{=}C^P$, $^{=}CH_2$, CH_3), 0.55 / 33.2, 21.3 (CH_3 / $^{=}CH_2$, CH_2).

X-Ray crystal structure analysis of 4c. formula $C_{35}H_{17}BF_{15}P$, M = 764.27, colorless crystal 0.30 x 0.07 x 0.01 mm, a = 9.5993(5), b = 11.3438(8), c = 15.4280(15) Å, α = 87.124(5), β = 89.616(4), γ = 70.239(3)°, V = 1579.0(2) Å^3, ρ_{calc} = 1.607 g cm^{-3}, μ= 1.843 mm^{-1}, empirical absorption correction (0.608 ≤ T ≤ 0.982), Z = 2, triclinic, space group P1bar (No. 2), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 23382 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 5445 independent (R_{int} = 0.070) and 4230 observed reflections [$I \geq 2\ \sigma(I)$], 470 refined parameters, R = 0.049, wR^2 = 0.123, max. (min.) residual electron density 0.25 (-0.33) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.





6: [specific resonances are listed; characterization see below] **^{1}H NMR** (400 MHz, 300 K, C_6D_6): δ = 7.26 (m, 4H, *o*-Ph), 7.01 (m, 2H, *p*-Ph), 6.88 (m, 4H, *m*-Ph), 2.95 (m, 2H, $^{=}CH_2$), 1.34 (m, 2H, CH_2), 0.56 (m, 3H, CH_3) [assignment by 2 D NMR experiments].

^{13}C{^{1}H} NMR (101 MHz, 300 K, C_6D_6): δ = 135.7 (*p*-Ph), 133.1 (d, $^{2}J_{PC}$ = 11.4 Hz, *o*-Ph), 130.6 (d, $^{3}J_{PC}$ =13.1 Hz, *m*-Ph), 127.8 (d, $^{1}J_{PC}$ ~ 55 Hz, $^{=}C^{P}$), 30.6 ($^{=}CH_2$), 24.6 (CH_2), 21.2 (CH_3) [assignment by 2 D NMR experiments].

^{19}F{^{1}H} NMR (470 MHz, 298 K, C_6D_6): δ = -123.4 (br s, 1F, C_6F_4), -129.7 (br s, 1F, C_6F_4), -132.9 (m, 4F, *o*-BC_6F_5), -139.1 (m, 1F, C_6F_4), -151.2 (m, 1F, C_6F_4), -159.6 (t, $^{3}J_{FF}$ = 20.6 Hz, 2F, *p*-BC_6F_5), -165.1 (m, 4F, *m*-BC_6F_5), -184.6 (br m, 1F, B-F) [$\Delta\delta^{B}$(m, p) = 5.5].

^{31}P{^{1}H} NMR (162 MHz, 300 K, C_6D_6): δ = 33.9 ($v_{1/2}$ ~ 20 Hz).

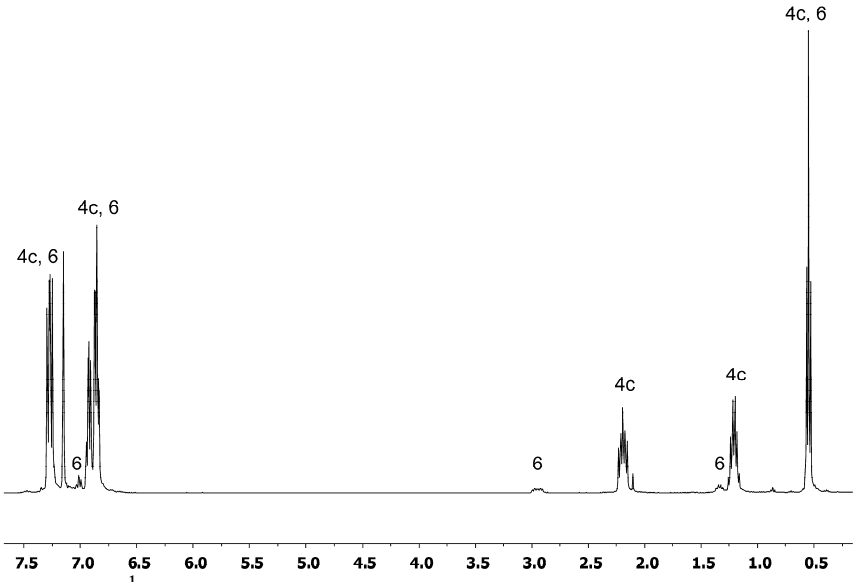
^{11}B{^{1}H} NMR (96 MHz, 300 K, C_6D_6): δ = 0.6 ($v_{1/2}$ ~ 140 Hz).

^{1}H,^{1}H GCOSY (400 MHz / 400 MHz, 300 K, C_6D_6): δ^{1}H / δ^{1}H = 7.01 / 6.88 (*p*-Ph / *m*-Ph), 6.88 / 7.26 (*m*-Ph / *o*-Ph), 2.95 / 1.34 ($^{=}CH_2$ / CH_2), 1.34 / 2.95, 0.56 (CH_2 / $^{=}CH_2$, CH_3).

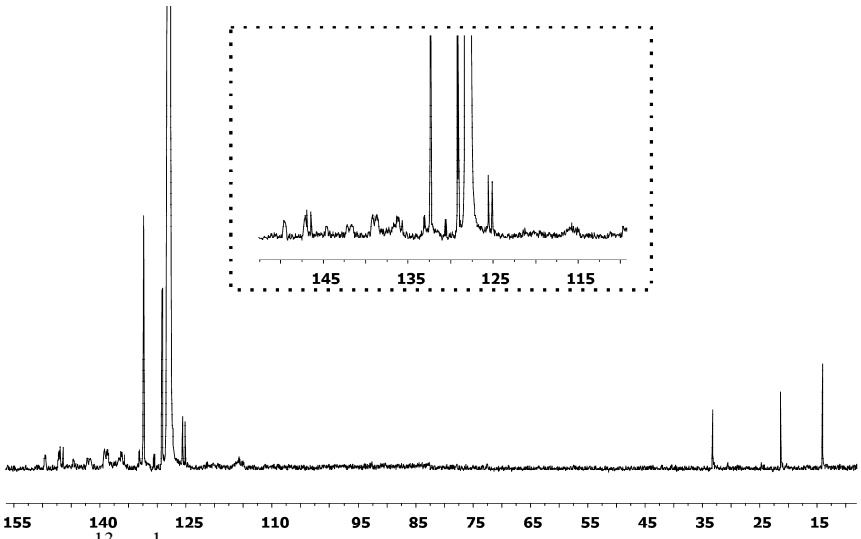
^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, 300 K, C_6D_6): δ^{1}H / δ^{13}C = 7.26 / 133.1 (*o*-Ph), 7.01 / 135.7 (*p*-Ph), 6.88 / 130.6 (*m*-Ph), 2.95 / 30.6 ($^{=}CH_2$), 1.34 / 24.6 (CH_2), 0.56 / 21.2 (CH_3).

^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, 300 K, C_6D_6): δ^{1}H / δ^{13}C = 2.95 / 127.8 ($^{=}CH_2$ / $^{=}C^{P}$).

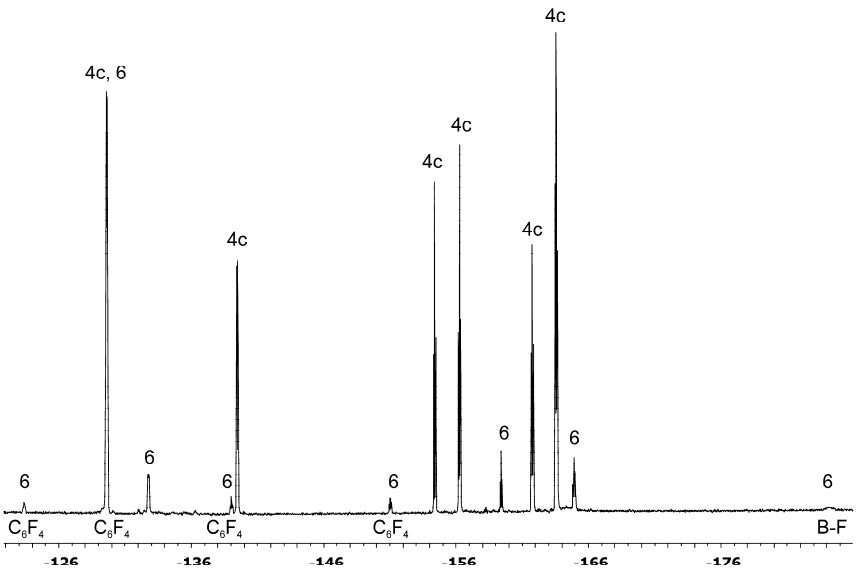
^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, 298 K, C_6D_6): δ^{19}F / δ^{19}F = -132.9 / -165.1 (*o*-BC_6F_5 / *m*-BC_6F_5), -139.1 / -123.4, -151.2 (C_6F_4 / C_6F_4, C_6F_4), -151.2 / -129.7, -139.1 (C_6F_4 / C_6F_4, C_6F_4), -159.6 / -165.1 (*p*-BC_6F_5 / *m*-BC_6F_5).



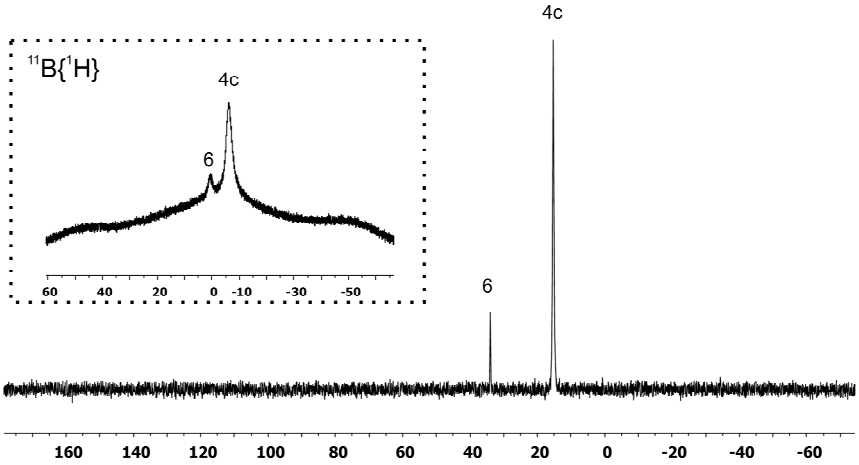
^{1}H NMR (400 MHz, 300 K, C_6D_6) of **4c** and **6**.



$^{13}C\{^{1}H\}$ NMR (101 MHz, 300 K, C_6D_6) of **4c** and **6**.



$^{19}F\{^{1}H\}$ NMR (162 MHz, 300 K, C_6D_6) of **4c** and **6**.



$^{11}B\{^1H\}$ NMR (96 MHz, 300 K, C_6D_6) and $^{31}P\{^1H\}$ NMR (122 MHz) of **4c** and **6**.

NMR-scale reactions:

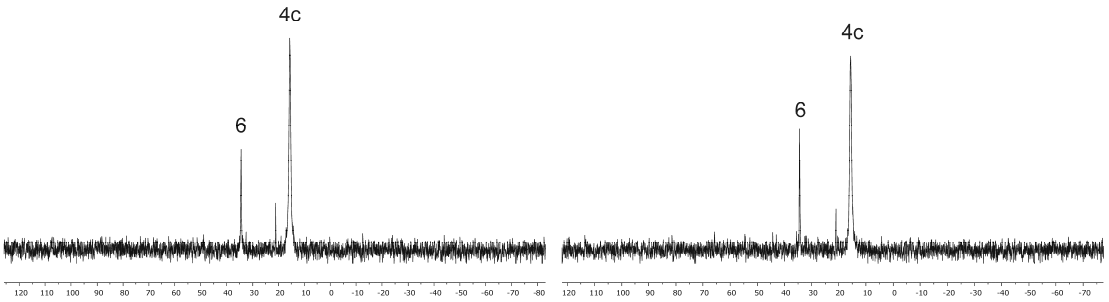
a) Heating of $B(C_6F_5)_3$ (**1**) (81.0 mg, 0.159 mmol) and **3c** (40.2 mg, 0.159 mmol) in d_8-toluene (1 ml) for 2h at 105 °C resulted in a reaction mixture of **4c** and **6** in a 5:1 ratio (monitored by ^{31}P NMR). Continuing heating (105°C) for additional 48h did not change the **4c**/**6** ratio (5:1).

b) Heating of a light protected sample of $B(C_6F_5)_3$ (**1**) (83.2 mg, 0.163 mmol) and **3c** (41.0 mg, 0.163 mmol) in d_8-toluene (1 ml) for 6h at 105 °C resulted in a reaction mixture of **4c** and **6** in a 5:1 ratio (monitored by ^{31}P NMR). The control experiment without light protection ($B(C_6F_5)_3$ (**1**) (82.2 mg, 0.161 mmol), **3c** (40.5 mg, 0.161 mmol), d_8-toluene (1 ml), 6h, 105 °C) resulted in a reaction mixture of **4c** and **6** in a 5:1 ratio.

6: ^1H NMR (500 MHz, 298 K, C_7D_8): δ = 7.29 (m, 4H, *o*-Ph), 7.07 (m, 2H, *p*-Ph), 6.94 (m, 4H, *m*-Ph), 2.87 (m, 2H, $^{=}CH_2$), 1.25 (m, 2H, CH_2), 0.49 (t, $^3J_{HH}$ = 7.3 Hz 3H, CH_3). $^{13}C\{^1H\}$ NMR (126 MHz, 298 K, C_7D_8): δ = 179.4 (br, $^{=}C^B$), 135.9 (d, $^4J_{PC}$ = 3.3 Hz *p*-Ph), 133.3 (d, $^2J_{PC}$ = 11.5 Hz, *o*-Ph), 130.7 (d, $^3J_{PC}$ =13.1 Hz, *m*-Ph), 127.9 (d, $^1J_{PC}$ ~ 65 Hz, $^{=}C^P$)[a], 115.4 (d, $^1J_{PC}$ = 83.0 Hz, *i*-Ph), 30.7 (t, *J* = 13.9 Hz, $^{=}CH_2$), 24.7 (t, *J* = 2.8 Hz, CH_2), 13.95 (CH_3) [C_6F_5 not listed; [a] from the ghmbc experiment]. $^{19}F\{^1H\}$ NMR (470 MHz, 298 K, C_7D_8): δ = -123.8 (br s, 1F, C_6F_4), -129.3 (m, 1F, C_6F_4), -132.8 (m, 4F, *o*-BC_6F_5), -139.9 (m, 1F, C_6F_4), -151.5

(m, 1F, C_6F_4), -160.1 (t, $^3J_{FF}$ = 20.5 Hz, 2F, *p*-BC_6F_5), -165.4 (m, 4F, *m*-BC_6F_5), -184.4 (br m, 1F, B-F) [$\Delta\delta^B$(m, p) = 5.3]. $^{11}B\{^1H\}$ NMR (160 MHz, 298 K, C_7D_8): δ = 0.6 ($\nu_{1/2}$ ~ 140 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, 298 K, C_7D_8): δ = 33.9 ($\nu_{1/2}$ ~ 20 Hz).

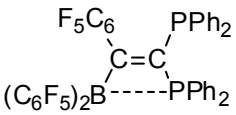
c) Heating of $B(C_6F_5)_3$ (**1**) (82.2 mg, 0.161 mmol) and **3c** (40.5 mg, 0.161 mmol) in d_8-toluene (1 ml) for 3h at 105 °C by simultaneous irradiation (Heraeus Nolelight HPK 125 W, Pyrex filter) resulted in a reaction mixture of **4c** and **6** in a 5:1 ratio (monitored by ^{31}P NMR).



$^{31}P\{^1H\}$ NMR (81 MHz, 300 K, D_8C_7) of reaction *b*

(right: light protection, left: without light protection).

Synthesis of 4d.



$B(C_6F_5)_3$ (**1**) and **3d** (35.5 mg, 0.09 mmol) were dissolved in toluene (20 ml) and stirred 9h at 80 °C. Subsequently toluene was removed and the residue was washed twice with pentane. The solid was dissolved in less toluene to let the impurities precipitate overnight at room temperature. Afterwards the toluene solution was seperated. Removal of all volatiles in vacuo yielded **4d** (0.174 g, 0.19 mmol, 60%) as a white-yellow solid. Crystals suitable for X-ray crystal structure analysis were grown by slow diffusion of pentane into a solution of **4d** in dichloromethane at -36 °C.
Single crystals suitable for X-ray analysis were obtained from a diffusion of pentane into a solution of **4d** in dichloromethane at -36 °C. **HRMS:** Calc. for $BP_2H_{20}C_{44}F_{15}H$: 907.09740. Found: 907.10066. **IR** (ATR): $\tilde{\nu}$ / cm^{-1} = 2383 (br w), 2313 (w), 1646 (w), 1515 (m), 1464 (s), 1384 (w), 1092 (s), 970 (s), 901 (m), 740 (s), 690 (s). **M.p.** (DSC): 258 °C.

^{1}H NMR (500 MHz, 298 K, C_7D_8): δ = 7.26 (m, 2H, *o*-Ph^P), 7.10 (m, 2H, *o*-Ph^{P+}), 6.83 (m, 1H, *p*-Ph^{P+}), 6.71 (m, 3H, *p*-Ph^P, *m*-Ph^{P+}), 6.66 (m, 2H, *m*-Ph^P).

^{13}C{^{1}H} NMR (126 MHz, 298 K, C_7D_8): δ = 173.7 (br, $^B\underline{C}^=$), 146.4 (dd, $^1J_{PC}$ = 53.0 Hz, $^1J_{PC}$ = 32.7 Hz, $^=\underline{C}^P$), 135.0 (d, $^2J_{PC}$ = 22.8 Hz, *o*-Ph^{P+}), 133.1 (d, $^2J_{PC}$ = 10 Hz, *o*-Ph^P), 132.5 (dd, $^1J_{PC}$ = 9.5 Hz, $^3J_{PC}$ = 3.3 Hz, *i*-Ph^{P+}), 132.1 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Ph), 129.9 (d, $^4J_{PC}$ = 1.0 Hz, *p*-Ph^{P+}), 128.8 (d, $^3J_{PC}$ = 11.3 Hz, *m*-Ph^P), 128.7 (d, $^3J_{PC}$ = 9.1 Hz, *m*-Ph^{P+}), 124.8 (d, $^1J_{PC}$ = 44.3 Hz, *i*-Ph^P), [C_6F_5 not listed].

^{19}F{^{1}H} NMR (470 MHz, 298 K, C_7D_8): δ = -128.8 (m, 4F, *o*-BC_6F_5), -138.0 (m, 2F, *o*-C_6F_5), -156.2 (t, $^3J_{FF}$ = 21.3 Hz, 1F, *p*-C_6F_5), -156.4 (t, $^3J_{FF}$ = 21.3 Hz, 2F, *p*-BC_6F_5), -163.1 (m, 2F, *m*-C_6F_5), -163.7 (m, 4F, *m*-BC_6F_5) [$\Delta\delta^B$(m, p) = 7.3].

^{31}P{^{1}H} NMR (202 MHz, 298 K, C_7D_8): δ = -6.3 (td, J_{PF} = 28.4 Hz, $^2J_{PP+}$ = 10.3 Hz, P), 24.2 (br, $\nu_{1/2}$ ~ 70 Hz, P^+).

^{31}P{^{19}F(*δ* -138.0)} NMR (202 MHz, 298 K, C_7D_8): δ = -6.3 (sext., $^2J_{PP+}$ ~ $^3J_{PH}$ ~ 10 Hz, P), 24.2 (br, $\nu_{1/2}$ ~ 70 Hz, P^+).

^{31}P{^{31}P(*δ* 24.2), ^{19}F(*δ* -138.0)} NMR (202 MHz, 298 K, C_7D_8): δ = -6.3 (quint., $^3J_{PH}$ ~ 10 Hz, P).

^{31}P{^{31}P(*δ* 24.2), ^{1}H} NMR (202 MHz, 298 K, C_7D_8): δ = -6.3 (t, J_{PF} = 28.4 Hz, P).

^{11}B{^{1}H} NMR (160 MHz, 298 K, C_7D_8): δ = -5 ($\nu_{1/2}$ ~ 230 Hz).

TOCSY (500 MHz, 298 K, C_7D_8): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 7.26 / 6.71, 6.66 (*o*-Ph^P / *p*-Ph^P, *m*-Ph^P), 7.10 / 6.83, 6.71 (*o*-Ph^{P+} / *p*-Ph^{P+}, *m*-Ph^{P+}).

NOE (500 MHz, 298 K, C_7D_8): $\delta^1H_{irr.}$ / $\delta^1H_{res.}$ = 7.26 / 6.66 (*o*-Ph^P / *m*-Ph^P), 7.10 / 7.26, 6.71 (*o*-Ph^{P+} / *o*-Ph^P, *m*-Ph^{P+}), 6.83 / 6.71 (*p*-Ph^{P+} / *m*-Ph^{P+}), 6.71 / 7.10, 6.83 (*p*-Ph^P, *m*-Ph^{P+} / *o*-Ph^{P+}, *p*-Ph^{P+}), 6.66 / 7.26 (*m*-Ph^P / *o*-Ph^P).

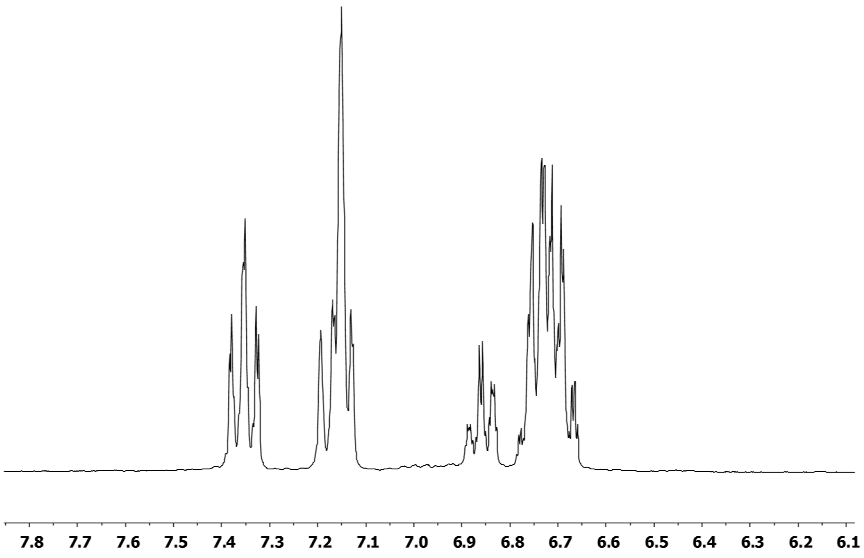
^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, C_7D_8): δ^1H / δ^1H = 7.26 / 6.71, 6.66 (*o*-Ph^P / *p*-Ph^P, *m*-Ph^P), 7.10 / 6.83, 6.71 (*o*-Ph^{P+} / *p*-Ph^{P+}, *m*-Ph^{P+}), 6.83 / 7.10, 6.71 (*p*-Ph^{P+} / *o*-Ph^{P+}, *m*-Ph^{P+}), 6.71 / 7.26, 7.10, 6.83, 6.66 (*p*-Ph^P, *m*-Ph^{P+} / *o*-Ph^P, *o*-Ph^{P+}, *p*-Ph^{P+}, *m*-Ph^P), 6.66 / 7.26, 6.71 (*m*-Ph^P / *o*-Ph^P, *p*-Ph^P).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, C_7D_8): δ^1H / $\delta^{13}C$ = 7.26 / 135.0 (*o*-Ph^P), 7.10 / 133.1 (*o*-Ph^{P+}), 6.83 / 132.1 (*p*-Ph^{P+}), 6.71 / 129.9 (*p*-Ph^P), 6.71 / 128.7 (*m*-Ph^{P+}), 6.66 / 128.6 (*m*-Ph^P).

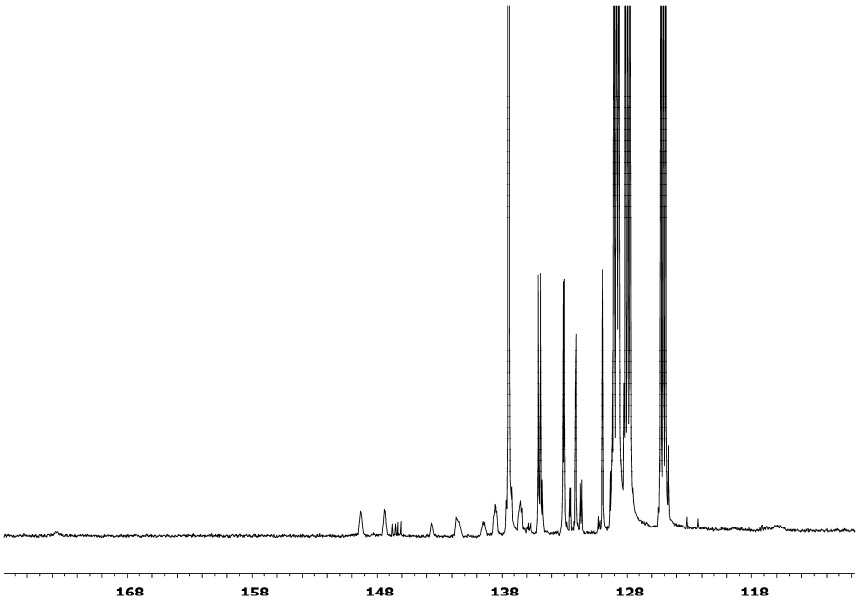
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, C_7D_8): δ^1H / $\delta^{13}C$ = 7.26 / 129.9 (*o*-Ph^P / *p*-Ph^P), 7.10 / 132.1 (*o*-Ph^{P+} / *p*-Ph^{P+}), 6.83 / 133.1 (*p*-Ph^{P+} / *o*-Ph^{P+}), 6.71 / 135.0, 128.7, 124.8 (*p*-Ph^P, *m*-Ph^{P+}/ *o*-Ph^P, *m*-Ph^{P+}, *i*-Ph^{P+}), 6.66 / 135.0, 132.5, 129.9 (*m*-Ph^P / *o*-Ph^P, *i*-Ph^P, *p*-Ph^P).

^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, 298 K, C_7D_8): $\delta^{19}F$ / $\delta^{19}F$ = -128.8 / -163.7 (*o*-BC_6F_5 / *m*-BC_6F_5), -138.0 / -163.1 (*o*-C_6F_5 / *m*-C_6F_5), -156.2 / -163.1 (*p*-C_6F_5 / *m*-C_6F_5), -156.4 / -163.7 (*p*-BC_6F_5 / *m*-BC_6F_5).

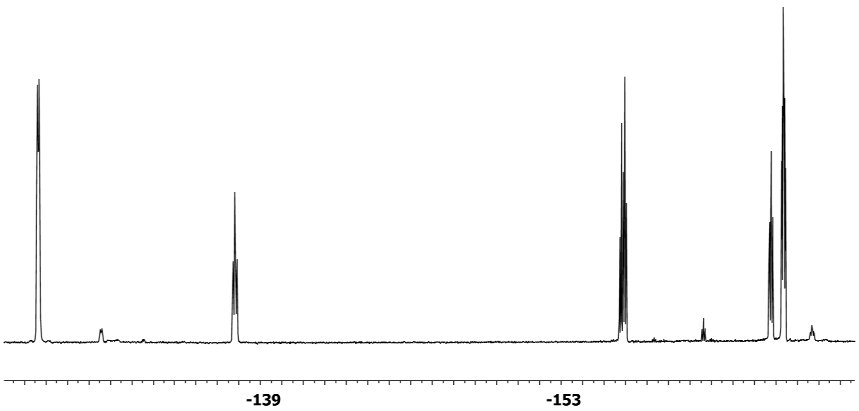
^{1}H,^{31}P GHMBC (500 MHz / 202 MHz, 298 K, C_7D_8): δ^1H / $\delta^{31}P$ = 7.26 / -6.3 (*o*-Ph^P), 7.10 / 24.2 (*o*-Ph^{P+}), 6.68 / -6.3 (*p*-Ph^P), 6.71 / 24.2 (*m*-Ph^{P+}), 6.66 / -6.3 (*m*-Ph^P).



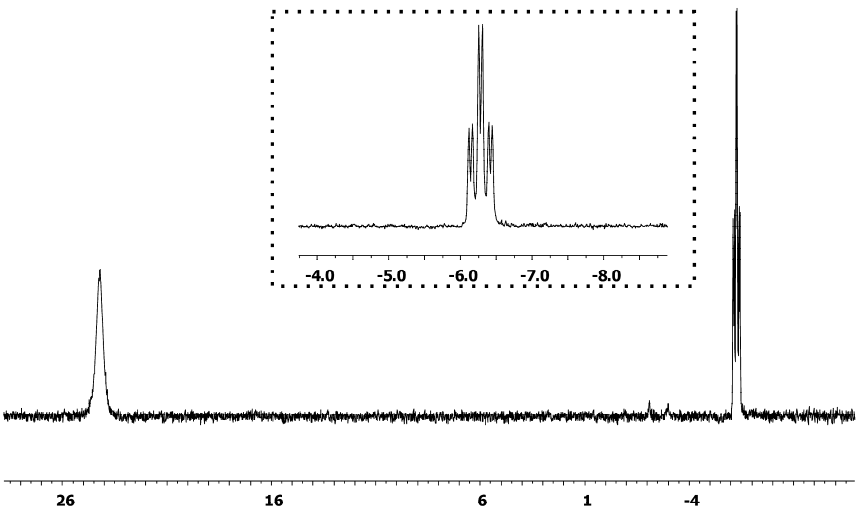
^{1}H NMR (300 MHz, 300 K, C_6D_6) of **4d**.



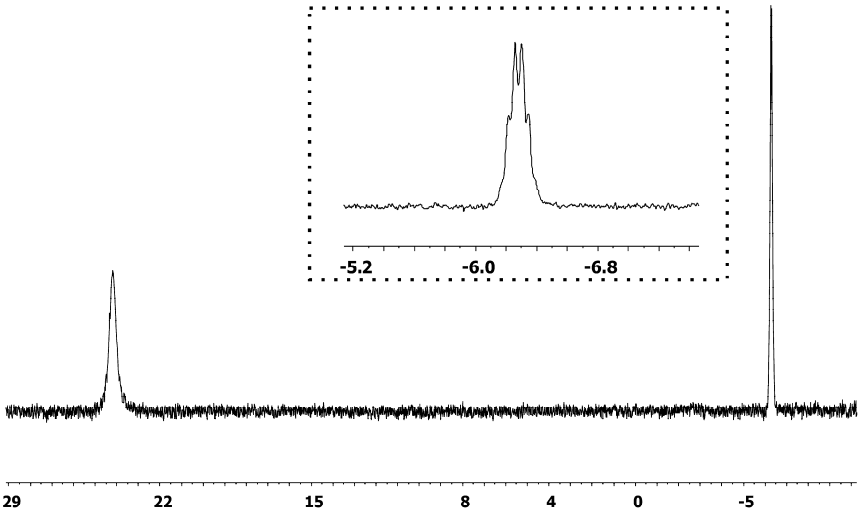
$^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, C_7D_8) of **4d**.



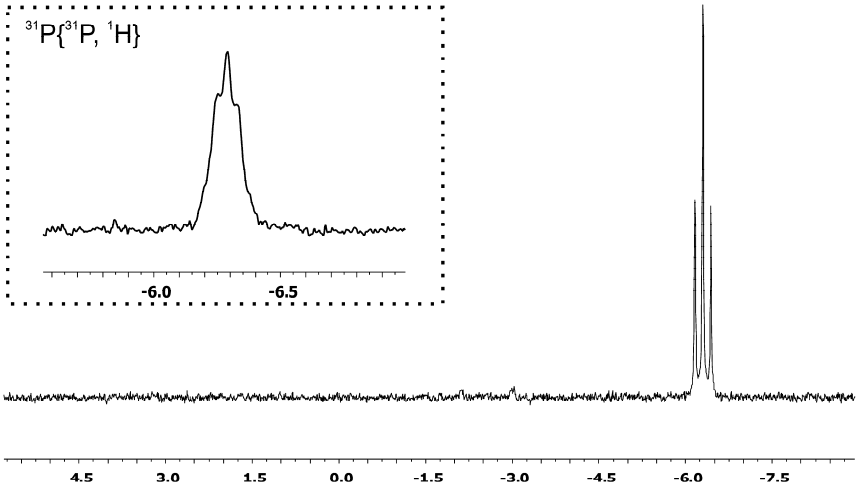
$^{19}F\{^{1}H\}$ NMR (282 MHz, 300 K, C_6D_6) of **4d**.



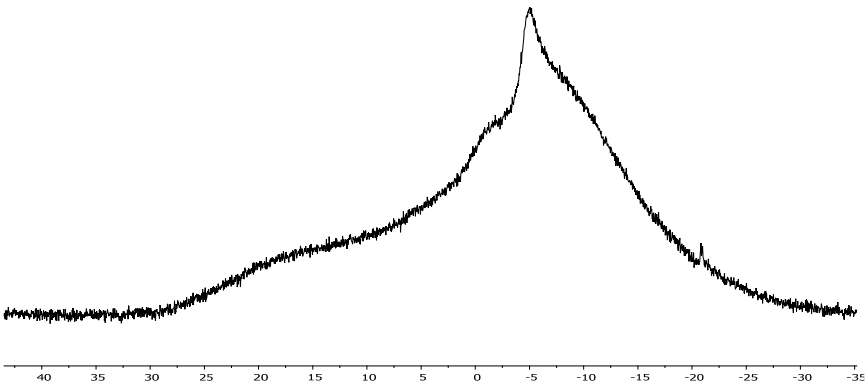
$^{31}P\{^{1}H\}$ NMR (202 MHz, 298 K, C_7D_8) of **4d**.



$^{31}P\{^{19}F(\delta\ -138.0)\}$ NMR (202 MHz, 298 K, C_7D_8) of **4d**.

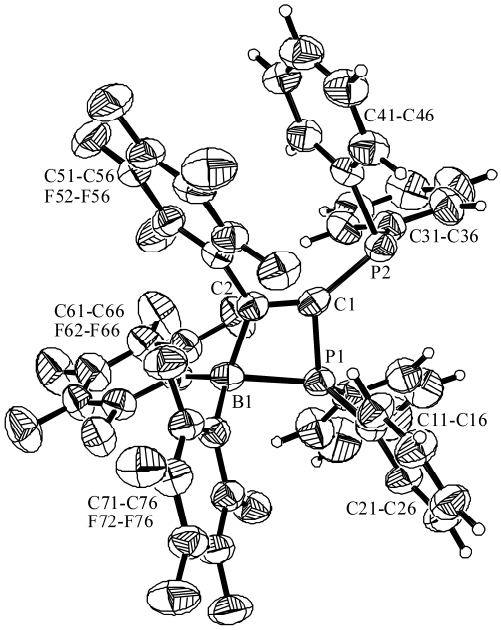


$^{31}P\{^{31}P(\delta\ 24.2), ^{1}H\}$ NMR (202 MHz, 298 K, C_7D_8) and $^{31}P\{^{31}P(\delta\ 24.2), ^{19}F(\delta\ -138.0)\}$ NMR (202 MHz) of **4d**.

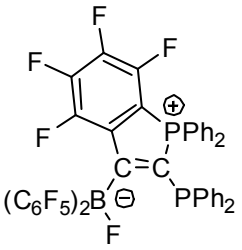


$^{11}B\{^{1}H\}$ NMR (160 MHz, 298 K, C_7D_8) of **4d**.

X-Ray crystal structure analysis of 4d. formula $C_{44}H_{20}BF_{15}P_2$ * CH_2Cl_2, M = 991.28, colorless crystal 0.10 x 0.10 x 0.04 mm, a = 9.7976(2), b = 10.8460(4), c = 21.1870(7) Å, α = 95.231(2), β = 102.492(2), γ = 104.305(2)°, V = 2104.94(11) Å^3, ρ_{calc} = 1.564 g cm^{-3}, μ= 3.023 mm^{-1}, empirical absorption correction (0.752 ≤ T ≤ 0.889), Z = 2, triclinic, space group P1bar (No. 2), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 25965 reflections collected (±h, ± k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6932 independent (R_{int} = 0.110) and 4337 observed reflections [I ≥ 2 σ(I)], 596 refined parameters, R = 0.077, wR^2 = 0.224, max. (min.) residual electron density 0.70 (-0.82) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Synthesis of 7.



Heating **4d** (0.08 mmol, 72.4 mg) for 3d at 105 °C in toluene followed by cooling at room temperature gave the precipitated product **7** (0.028 mmol, 25.1 mg, 35%) as orange crystals. These crystals suitable for X-ray analysis, after filtration via cannula and washing with very small amount of toluene. **HRMS:** Calc. for $C_{44}H_{20}BF_{15}P_2H$: 907.09665. Found: 907.09354. **IR** (ATR): $\tilde{\nu}$ / cm^{-1} = 1666 (w), 1588 (w), 1514 (m), 1493 (m), 1453 (s), 1379 (w), 1274 (m), 1091 (br s), 955 (m), 743 (s), 691 (s). Decomp. (DSC): 276 °C.

^{1}H NMR (500 MHz, 298 K, CD_2Cl_2): δ = 7.82 (m, 2H, *p*-Ph^{P+}), 7.64 (m, 4H, *m*-Ph^{P+}), 7.62 (m, 4H, *o*-Ph^{P+}), 7.19 (m, 4H, *o*-Ph^{P}), 7.11 (m, 2H, *p*-Ph^{P}), 6.92 (m, 4H, *m*-Ph^{P}).

^{13}C{^{1}H} NMR (126 MHz, 298 K, CD_2Cl_2): δ = 189.7 (br, $^{=}C^{B}$), 135.8 (d, $^4J_{PC}$ = 2.5 Hz, *p*-Ph^{P+}), 135.7 (d, $^2J_{PC}$ = 23.2 Hz, *o*-Ph^{P}), 133.6 (d, $^2J_{PC}$ = 12.3 Hz, *o*-Ph^{P+}), 130.8 (d, $^3J_{PC}$ = 13.3 Hz, *m*-Ph^{P+}), 129.5 (d, $^4J_{PC}$ = 0.8 Hz, *p*-Ph^{P}), 128.2 (d, $^3J_{PC}$ = 8.4 Hz, *m*-Ph^{P}), 115.5 (d, $^1J_{PC}$ = 84.6 Hz, *i*-Ph^{P+}), n.o. ($^{=}C^{P}$, *i*-Ph^{P}), [C_6F_4, C_6F_5 not listed].

^{19}F{^{1}H} NMR (470 MHz, 298 K, CD_2Cl_2): δ = -123.5 (br, 1F, C_6F_4), -129.5 (m, 1F, C_6F_4), -133.3 (m, 4F, *o*-BC_6F_5), -141.8 (m, 1F, C_6F_4), -152.4 (m, 1F, C_6F_4), -161.1 (t, $^3J_{FF}$ = 20.5 Hz, 2F, *p*-BC_6F_5), -166.2 (m, 4F, *m*-BC_6F_5), -171.5 (br, 1F, B-F) [$\Delta\delta^B$(m, p) = 5.1].

^{19}F{^{11}B} NMR (470 MHz, 298 K, CD_2Cl_2): δ = -171.5 (br d, J_{PF} ~ 180 Hz, B-F) [selected resonance].

^{31}P{^{1}H} NMR (202 MHz, 298 K, CD_2Cl_2): δ = 39.1 ($\nu_{1/2}$ ~ 30 Hz, P^+), -2.5 (dd, J_{PF} = 177.8 Hz, $^2J_{PP+}$ = 7.1 Hz, P).

^{31}P{^{19}F(*δ* -171.5)} NMR (202 MHz, 298 K, CD_2Cl_2): δ = 39.1 ($\nu_{1/2}$ ~ 50 Hz, P^+), -2.5 (sext., $^2J_{PP+}$ ~ $^3J_{HH}$ ~ 7 Hz, P).

^{11}B{^{1}H} NMR (160 MHz, 298 K, CD_2Cl_2): δ = 0.3 ($\nu_{1/2}$ ~ 150 Hz).

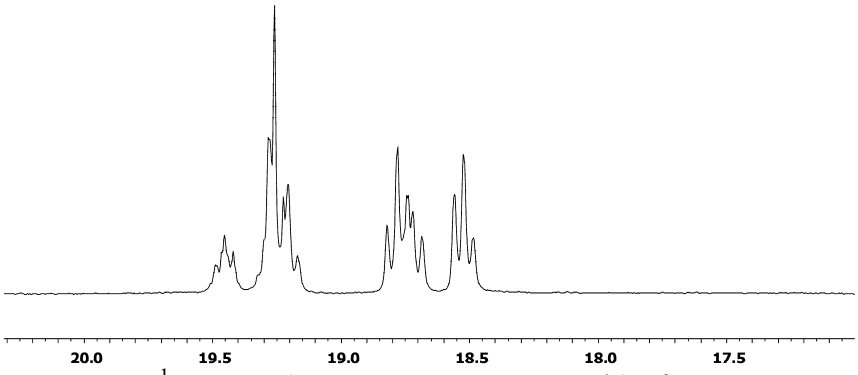
^{11}B{^{19}F(*δ* -171.5)} NMR (160 MHz, 298 K, CD_2Cl_2): δ = 0.3 ($\nu_{1/2}$ ~ 100 Hz).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 298 K, CD_2Cl_2): δ^1H / δ^1H = 7.82 / 7.64 (*p*-Ph^{P+}/ *m*-Ph^{P+}), 7.64 / 7.82, 7.62 (*m*-Ph^{P+}/ *p*-Ph^{P+}, *o*-Ph^{P+}), 7.19 / 6.92 (*o*-Ph^{P} / *m*-Ph^{P}), 7.11 / 6.92 (*p*-Ph^{P} / *m*-Ph^{P}), 6.92 / 7.19, 7.11 (*m*-Ph^{P} / *o*-Ph^{P}, *p*-Ph^{P}).

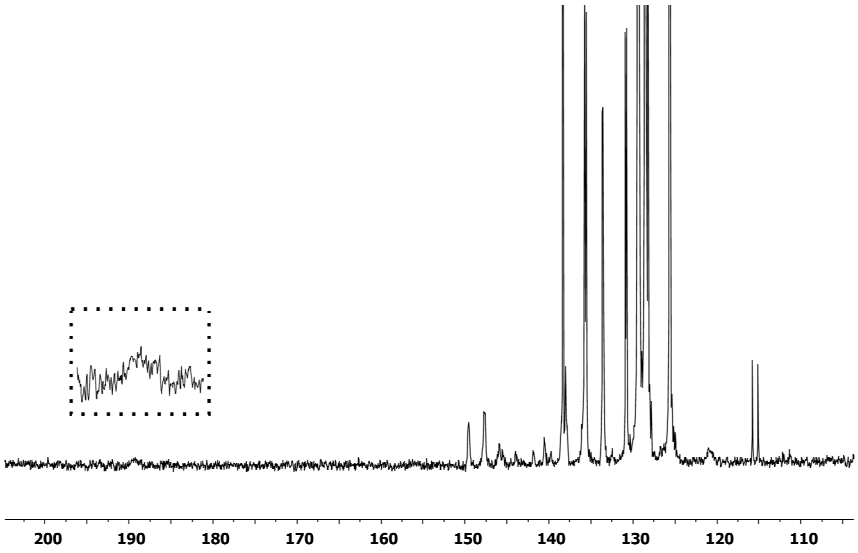
^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, CD_2Cl_2): δ^1H / δ^{13}C = 7.82 / 135.8 (*p*-Ph^{P+}), 7.64 / 130.8 (*m*-Ph^{P+}), 7.62 / 133.6 (*o*-Ph^{P+}), 7.19 / 135.8 (*o*-Ph^{P}), 7.11 / 129.5 (*p*-Ph^{P}), 6.92 / 128.2 (*m*-Ph^{P}).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, CD_2Cl_2): δ^1H / δ^{13}C = 7.82 / 133.6 (*p*-Ph^{P+}/ *o*-Ph^{P+}), 7.64 / 135.8, 115.5 (*m*-Ph^{P+}/ *p*-Ph^{P+}, *i*-Ph^{P+}), 7.11 / 135.7 (*p*-Ph^{P} / *o*-Ph^{P}), 6.92 / 135.7 (*m*-Ph^{P} / *o*-Ph^{P}).

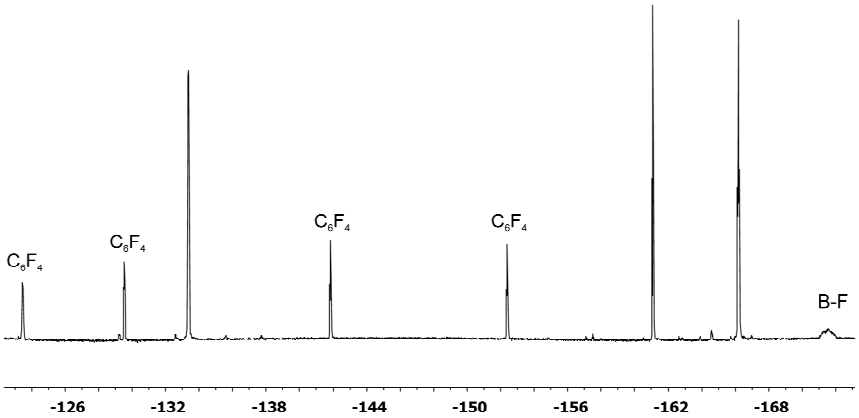
^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, 298 K, CD_2Cl_2): $\delta^{19}F$ / $\delta^{19}F$ = -123.5 / -141.8 (C_6F_4 / C_6F_4), -129.5 / -152.4 (C_6F_4 / C_6F_4), -133.3 / -166.2 (*o*-BC_6F_5 / *m*-BC_6F_5), -161.1 / -166.2 (*p*-BC_6F_5 / *m*-BC_6F_5), -166.2 / -161.1, -133.3 (*m*-BC_6F_5 / *p*-BC_6F_5, *o*-BC_6F_5).



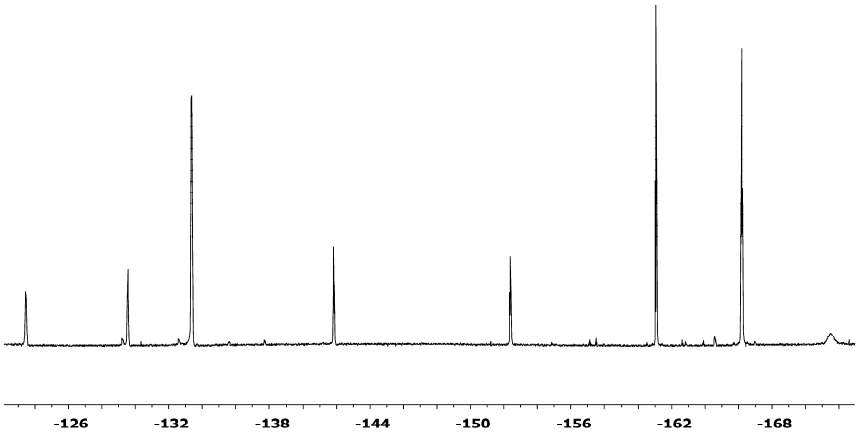
^{1}H NMR (200 MHz, 300 K, CD_2Cl_2) of **7**.



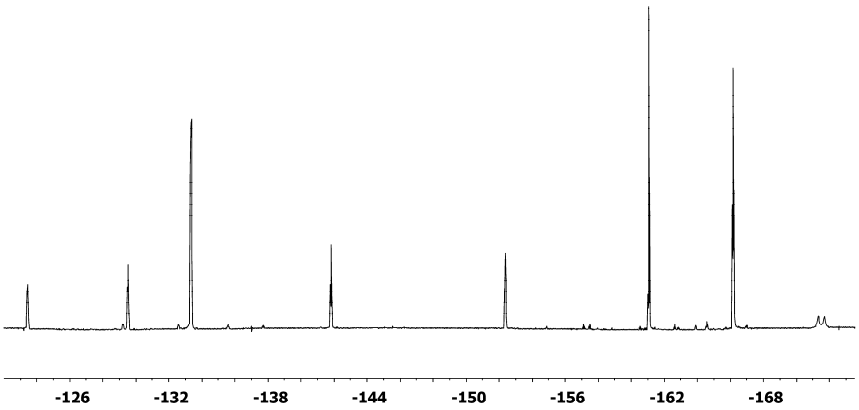
^{13}C{^{1}H} NMR (126 MHz, 298 K, CD_2Cl_2) of **7**.



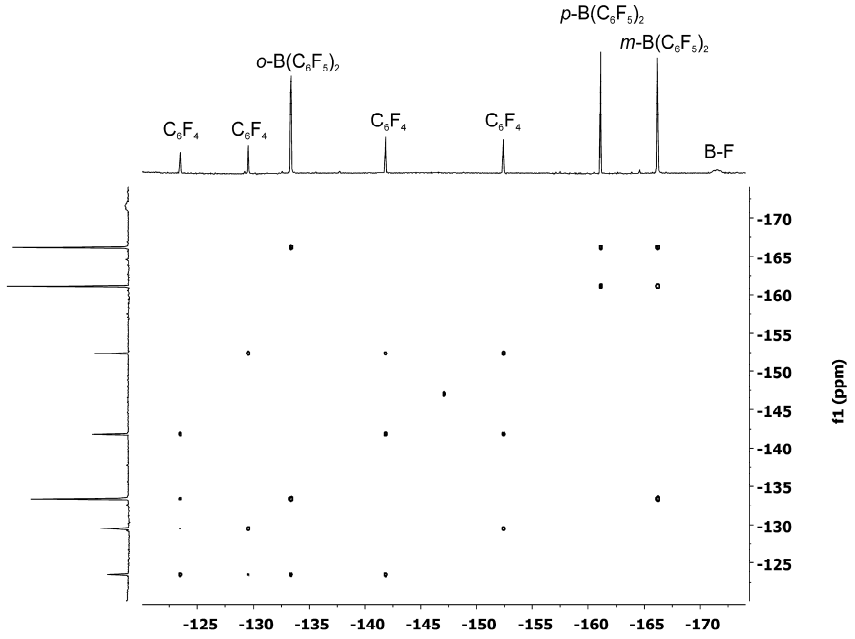
^{19}F{^{1}H} NMR (470 MHz, 298 K, CD_2Cl_2) of **7**.



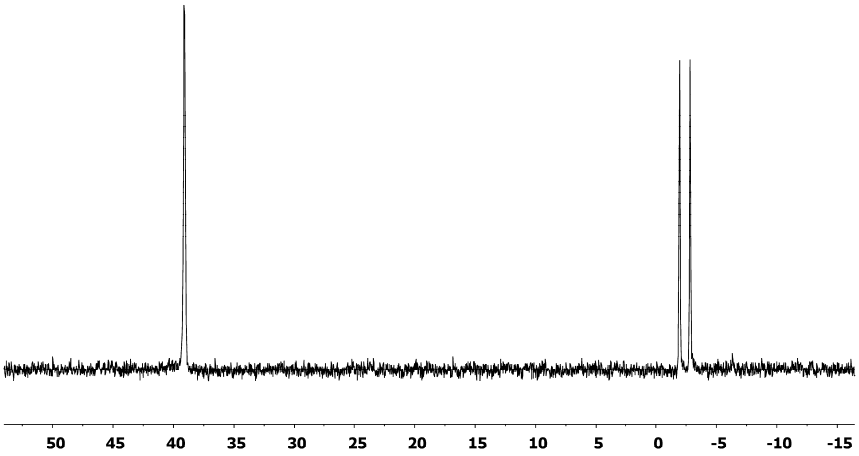
$^{19}F\{^{31}P(\delta\ -2.5)\}$ NMR (470 MHz, 298 K, CD_2Cl_2) of **7**.



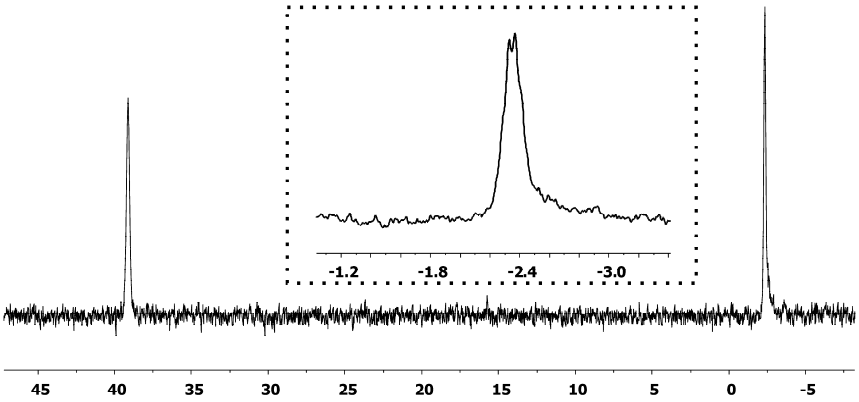
$^{19}F\{^{11}B\}$ NMR (470 MHz, 298 K, CD_2Cl_2) of **7**.



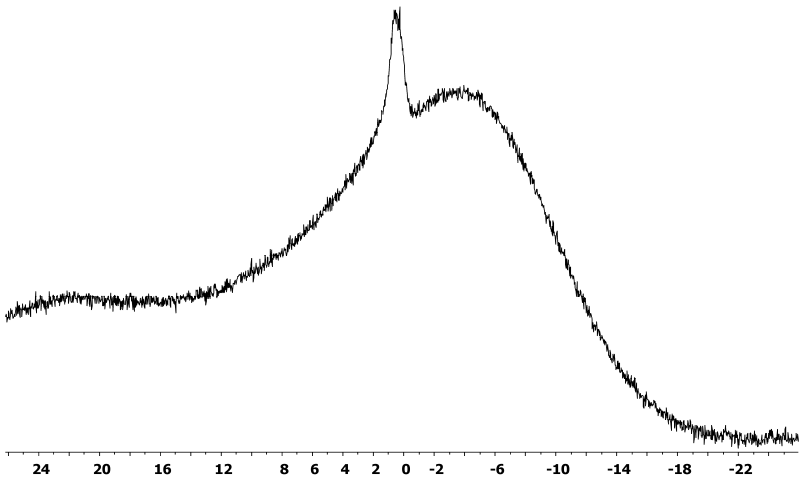
$^{19}F,^{19}F$ GCOSY (470 MHz / 470 MHz, 298 K, CD_2Cl_2) of **7**.



$^{31}P\{^{1}H\}$ NMR (202 MHz, 298 K, CD_2Cl_2) of **7**.



$^{31}P\{^{19}F(\delta$ -171.5 $)\}$ NMR (202 MHz, 298 K, CD_2Cl_2) of **7**.



$^{11}B\{^{1}H\}$ NMR (160 MHz, 298 K, CD_2Cl_2) of **7**.

X-Ray crystal structure analysis of 7. formula $C_{44}H_{20}BF_{15}P_2$ * C_7H_8, M = 998.48, orange crystal 0.30 x 0.23 x 0.15 mm, a = 10.4606(4), b = 13.1363(5), c = 16.4911(7) Å, α = 91.614(2), β = 103.553(2), γ = 95.609(3)°, V = 2189.39(15) Å^3, ρ_{calc} = 1.515 g cm^{-3}, μ= 1.816 mm^{-1}, empirical absorption correction ($0.612 \leq T \leq 0.772$), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ= 1.54178 Å, T = 223(2) K, ω and φ scans, 29350 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 7643 independent (R_{int} = 0.043) and 7024 observed reflections [$I \geq 2\,\sigma(I)$], 610 refined parameters, R = 0.050, wR^2 = 0.142, max. (min.) residual electron density 0.79 (-0.55) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.