Supplementary Material (ESI) for Chemical Communications

Chemistry of a Geminal Frustrated Lewis Pair featuring Electron Withdrawing C_6F_5 Substituents at Both Phosphorus and Boron

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Supporting Information

Experimental Section

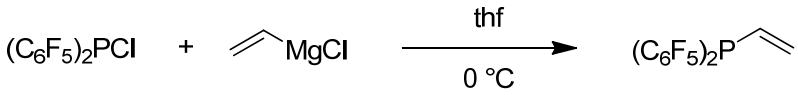
All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. ^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{31}P NMR spectra were recorded on a Varian 500 MHz INOVA or a Varian 600 MHz UNITY plus NMR spectrometer at ambient temperature unless otherwise stated. Chemical shifts are given in ppm relative to solvents (^{1}H and ^{13}C) or an external standard [$\delta(BF_3{\cdot}OEt_2) = 0$ for ^{11}B NMR, $\delta(CFCl_3) = 0$ for ^{19}F NMR and $\delta(85\%\ H_3PO_4) = 0$ for ^{31}P NMR). Coupling constants are in Hz. Elemental analysis data was recorded on Foss-Heraeus CHNO-Rapid. HRMS was recorded on GTC Waters Micromass (Manchester, UK). X-ray structure analysis: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski and W. Minor, *Methods in Enzymology*, 1997, **276**, 307-326), absorption correction Denzo (Z.Otwinowski, D. Borek, W. Majewski and 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). Graphics show the thermal ellipsoids with 50 % probability, *R* values are given for the observed reflections, wR^2 values for all reflections.

$B(C_6F_5)_3$ was prepared according to procedures reported in the literature (caution: the intermediate involved is explosive) [(a) A. G. Massey, A. J. Park, *J. Organomet. Chem.* 1964, **2**, 245-250. (b) C. Wang, G. Erker, G. Kehr, K. Wedeking and R. Fröhlich, *Organometallics*, 2005, **24**, 4760-4773].

$HB(C_6F_5)_2$ was prepared according to the procedures reported in the literature [a) D. J. Parks, R. E. v. H. Spence and W. E. Piers, *Angew. Chem.*, 1995, **107**, 895-897; *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 809-811; b) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492-5503].

$(C_6F_5)_2PCl$ was prepared according to the procedures reported in the literature [D. D. Magnelli, G. Tesi, J. U. Lowe and W. E. McQuistion, *Inorg. Chem.*, 1966, **5**, 457-461; G. Mancino, A. J. Ferguson, A. Beeby, N. J. Long and T. S. Jones, *J. Am. Chem. Soc.*, 2005, **127**, 524-525].

Preparation of compound 4a:



A solution of bis(pentafluorophenyl)chlorophosphine (2.33 g, 5.90 mmol) in thf (100 mL) was cooled to 0 °C. Vinylmagnesiumchloride (1.6 M solution in thf, 1.60 mL, 2.50 mmol) was added slowly and the reaction mixture was stirred for 0.5 h at 0 °C and 0.5 h at rt. The solvent of the red solution was removed *in vacuo* and the red residue was dissolved in pentane (70 mL). The suspension was filtrated over *Celite* and washed with pentane (2x50 mL). The filtrate was removed *in vacuo* to yield a yellow oil (1.63 g, 4.16 mmol, 71%). Single crystals suitable for X-ray structure analysis were obtained by slow evaporation of a solution of **4a** in pentane at 4 °C.

^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 5.56 (ddd, $^{3}J_{PH}$ = 50.8 Hz, $^{3}J_{HH}$ = 11.2 Hz, $^{2}J_{HH}$ = 1.3 Hz, 1H, $^{=}CH_{2(E)}$), 5.80 (ddm, $^{3}J_{PH}$ = 21.6 Hz, $^{3}J_{HH}$ = 18.4 Hz, 1H, $^{=}CH_{2(Z)}$), 6.90 (ddm, $^{3}J_{HH}$ = 18.4 Hz, $^{3}J_{HH}$ = 11.2 Hz, 1H, $^{P}CH^{=}$).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K)[1]: δ 108.9 (m, *i*-C_6F_5), 129.4 (m, $^{P}CH^{=}$), 134.6 (d, $^{2}J_{PC}$ = 48.9 Hz, $^{=}CH_2$), 137.5 (dm, $^{1}J_{FC}$ ~ 254 Hz, *m*-C_6F_5), 142.3 (dm, $^{1}J_{FC}$ ~ 256 Hz, *p*-C_6F_5), 147.4 (dm, $^{1}J_{FC}$ ~ 247 Hz, *o*-C_6F_5).

^{1}H,^{1}H-GCOSY (600 MHz, C_6D_6, 298 K): δ(^{1}H) / δ(^{1}H) 5.56 / 6.90 ($^{=}CH_{2(E)}$ / $^{P}CH^{=}$), 5.80 / 6.90 ($^{=}CH_{2(Z)}$ / $^{P}CH^{=}$), 6.90 / 5.56, 5.80 ($^{P}CH^{=}$ / $^{=}CH_{2(E)}$, $^{=}CH_{2(Z)}$).

^{1}H,^{13}C-GHSQC (600 MHz / 151 MHz, C_6D_6, 298 K): δ(^{1}H) / δ(^{13}C) 5.56, 5.80 / 134.6 ($^{=}CH_2$), 6.90 / 129.4 ($^{P}CH^{=}$).

^{1}H,^{13}C-GHMBC (600 MHz / 151 MHz, C_6D_6, 298 K): δ(^{1}H) / δ(^{13}C) 5.80 / 129.4 ($^{=}CH_{2(Z)}$ / $^{P}CH^{=}$), 6.90 / 134.6 ($^{P}CH^{=}$ / $^{=}CH_2$).

^{19}F NMR (564 MHz, C_6D_6, 298 K): δ −131.9 (m, 2F, *o*-C_6F_5), −151.0 (m, 1F, *p*-C_6F_5), −161.5 (m, 2F, *m*-C_6F_5) [$\Delta\delta_{m,p}$ = 10.5].

^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K): δ −52.5 (quin, $^{3}J_{PF}$ = 27.3 Hz).

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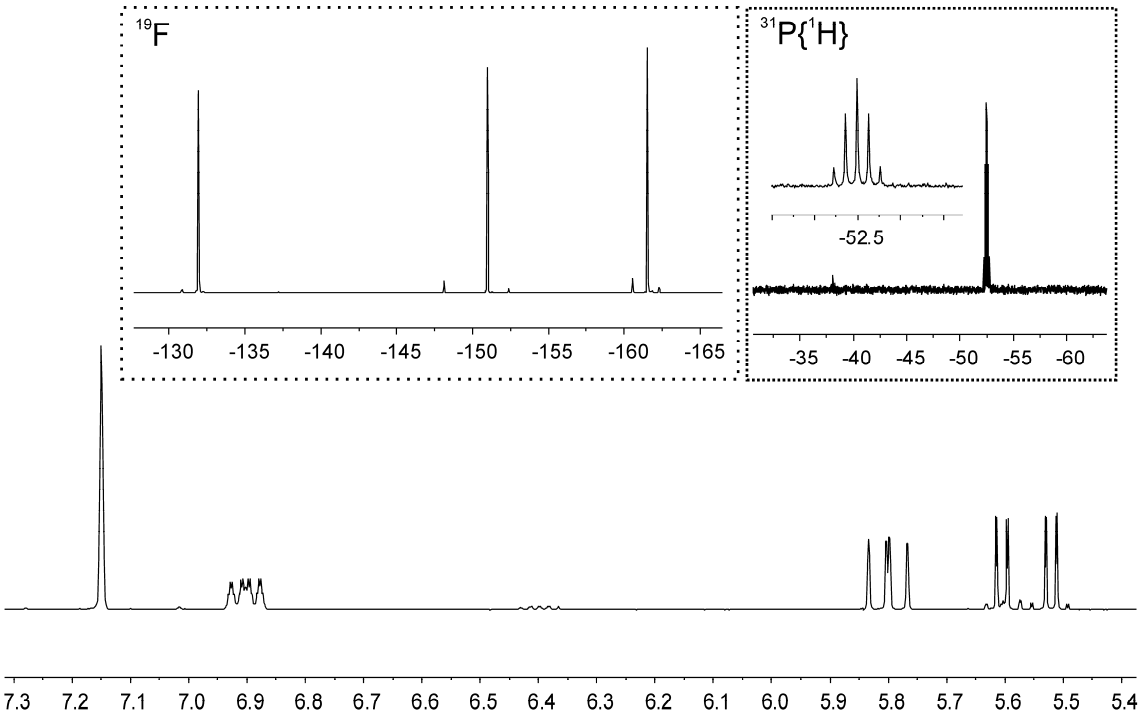
[1] For comparison $P(C_6F_5)_3$: ^{13}C{^{19}F} NMR (126 MHz, CD_2Cl_2, 298 K): δ 105.0 (d, $^{1}J_{PC}$ = 33.9 Hz, *i*-C_6F_5), 138.2 (d, *J* = 1.2 Hz, *m*-C_6F_5), 143.6 (*p*-C_6F_5), 148.2 (d, *J* = 11.8 Hz, *o*-C_6F_5).

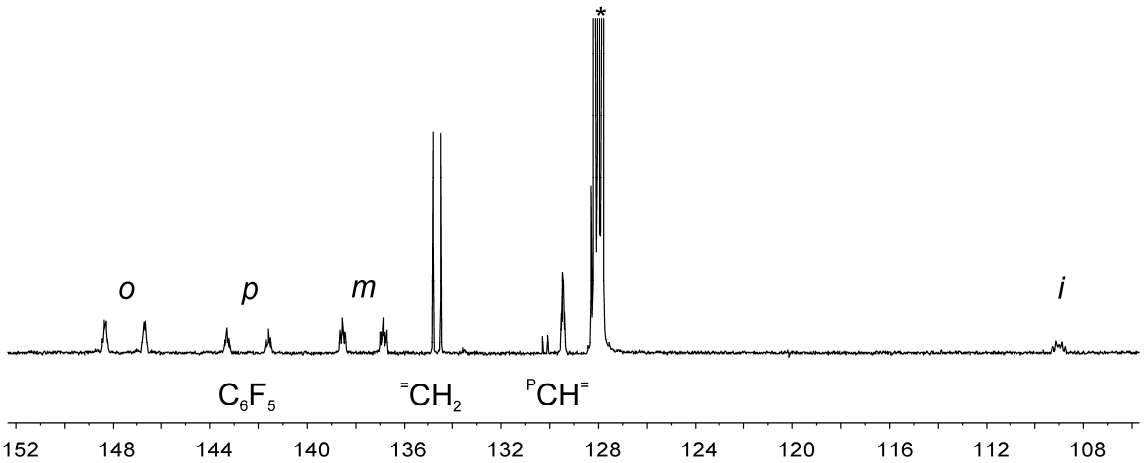
IR (ATR): $\tilde{\nu}$ = 1640 (w), 1514 (s), 1467 (s), 1386 (w), 1290 (w), 1085 (s), 972 (s), 836 (w).

Elemental analysis: calcd. for $C_{14}H_3F_{10}P$: C 42.88; H: 0.77. Found: C 43.22; H: 0.47.

Exact mass calcd. for $C_{14}H_3F_{10}P$: 391.9813 m/z. Found: 391.9808 m/z.

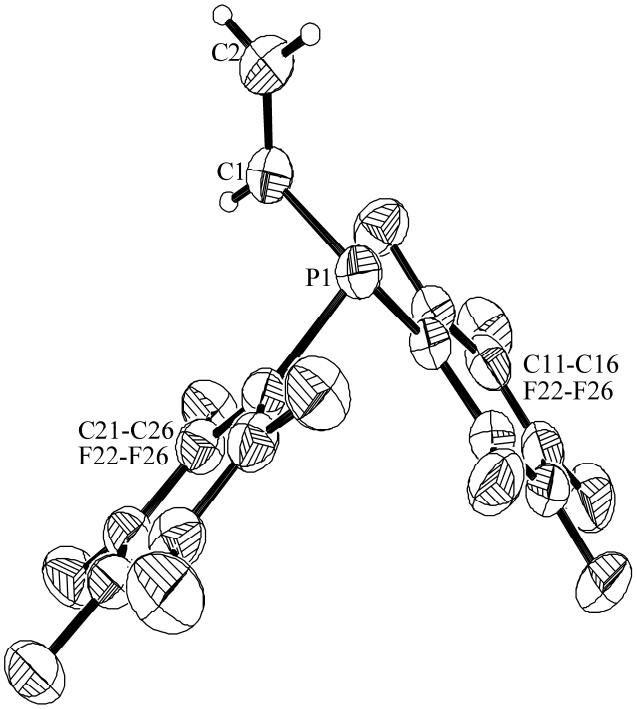


^{1}H NMR (600 MHz, C_6D_6, 298 K), ^{19}F NMR (564 MHz, C_6D_6, 298 K) and ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K).

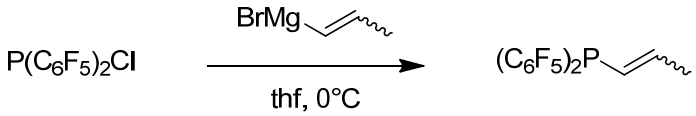


^{13}C{^{1}H} NMR (151 MHz, C_6D_6(*), 298 K).

Crystal data for $C_{14}H_3F_{10}P$ (**4a**), M = 392.58, monoclinic, $C2/c$ (No. 15), a = 19.8040(3), b = 8.1425(1), c = 17.4927(3) Å, β = 96.179(1)°, V = 2804.38(7) Å^3, D_c = 1.858 g cm^{-3}, μ = 2.887 mm^{-1}, *F(000)* = 1536, Z = 8, λ = 1.54178 Å, T = 223(2) K, 18878 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 2470 independent (R_{int} = 0.046), and 2346 observed reflections [I ≥ 2σ(I)], 226 refined parameters, R = 0.034, wR^2 = 0.092, GoF = 1.031.



Preparation of compound 4b:



A solution of bis(pentafluorophenyl)chlorophosphine (1.00 g, 2.50 mmol) in thf (60 mL) was cooled to 0 °C. 1-Propenylmagnesiumbromide (0.5 M solution in thf, 5.00 mL, 2.50 mmol) was added slowly. The solvent of the orange-yellow solution was removed *in vacuo* and the orange residue was dissolved in pentane (50 mL). The suspension was filtrated over *Celite* and washed with pentane (50 mL). The filtrate was removed *in vacuo* to yield a red oil (0.99 g, 98%, *E* : *Z* = 1 : 4).

Z-Isomer: ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 6.54 (dm, $^{3}J_{HH,cis}$ = 11.3 Hz, 1H, CH^{P}), 6.15 (ddq, $^{3}J_{PH}$ = 30.3 Hz, $^{3}J_{HH,cis}$ = 11.3 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1H, CH^{CH3}), 1.80 (d, $^{3}J_{HH}$ = 7.0 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ 147.7 (dm, $^{1}J_{FC}$ ~ 246 Hz, *p*-C_6F_5), 146.6 (d, $^{2}J_{PC}$ = 36.7 Hz, CH^{CH3}), 142.3 (dm, $^{1}J_{FC}$ ~ 257 Hz, *o*-C_6F_5), 137.7 (dm, $^{1}J_{FC}$ ~ 253 Hz, *m*-C_6F_5), 120.7 (m, CH^{P}), 109.5 (m, *i*-C_6F_5), 16.1 (d, $^{3}J_{PC}$ = 29.7 Hz, CH_3).

^{1}H,^{1}H GCOSY (500 MHz, C_6D_6, 298 K): δ(^{1}H) / δ(^{1}H) 6.54 / 6.15, 1.80 (CH^{P} / CH^{CH3}, CH_3), 6.15 / 6.54, 1.80 (CH^{CH3} / CH^{P}, CH_3), 1.80 / 6.54, 6.15 (CH_3 / CH^{P}, CH^{CH3}).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, C_6D_6, 298 K): δ(^{1}H) / δ(^{13}C) 6.54 / 120.7 (CH^{P}), 6.15 / 146.6 (CH^{CH3}), 1.80 / 16.1 (CH_3).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, C_6D_6, 298 K): δ(^{1}H) / δ(^{13}C) 6.54 / 16.1 (CH^{P} / CH_3), 6.15 / 16.1 (CH^{CH3} / CH_3), 1.80 / 146.6, 120.7 (CH_3 / CH^{CH3}, CH^{P}).

^{19}F NMR (470 MHz, C_6D_6, 298 K): δ −131.3 (m, 2F, *o*-C_6F_5), −150.7 (tt, $^{3}J_{FF}$ = 21.0 Hz, $^{4}J_{FF}$ = 3.7 Hz, 1F, *p*-C_6F_5), −160.9 (m, 2F, *m*-C_6F_5) [$\Delta\delta_{m,p}$ = 10.2].

^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K): δ −71.6 (quin, $^{3}J_{PF}$ = 27.5 Hz).

E-Isomer: ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ 6.68 (dm, $^{3}J_{HH,trans}$ = 16.5 Hz, 1H, CH^{P}), 6.39 (ddq, $^{3}J_{PH}$ = 21.8 Hz, $^{3}J_{HH,trans}$ = 16.5 Hz, $^{3}J_{HH}$ = 6.5 Hz, 1H, CH^{CH3}), 1.51 (dt, $^{3}J_{HH}$ = 6.5 Hz, $^{4}J_{PH}$ ~ $^{4}J_{HH}$ ~ 1.4 Hz, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6, 298 K): δ 149.3 (d, $^{1}J_{PC}$ = 57.7 Hz, CH^{CH3}), 147.7 (dm, $^{1}J_{FC}$ ~ 246 Hz, *p*-C_6F_5), 142.3 (dm, $^{1}J_{FC}$ ~ 257 Hz, *o*-C_6F_5), 137.7 (dm, $^{1}J_{FC}$ ~ 251 Hz, *m*-C_6F_5), 121.5 (m, CH^{P}), 109.5 (m, *i*-C_6F_5), 20.4 (d, $^{3}J_{PC}$ = 20.3 Hz, CH_3).

$^{1}H,^{1}H$ GCOSY (500 MHz, C_6D_6, 298 K): δ(^{1}H) / δ(^{1}H) 6.68 / 6.39, 1.51 (CH^{P} / CH^{CH3}, CH_3), 6.39 / 6.68, 1.51 (CH^{CH3} / CH^{P}, CH_3), 1.51 / 6.68, 6.39 (CH_3 / CH^{P}, CH^{CH3}).

$^{1}H,^{13}C$ GHSQC (500 MHz / 126 MHz, C_6D_6, 298 K): δ(^{1}H) / δ(^{13}C) 6.68 / 121.5 (CH^{P}), 6.39 / 149.3 (CH^{CH3}), 1.51 / 20.4 (CH_3).

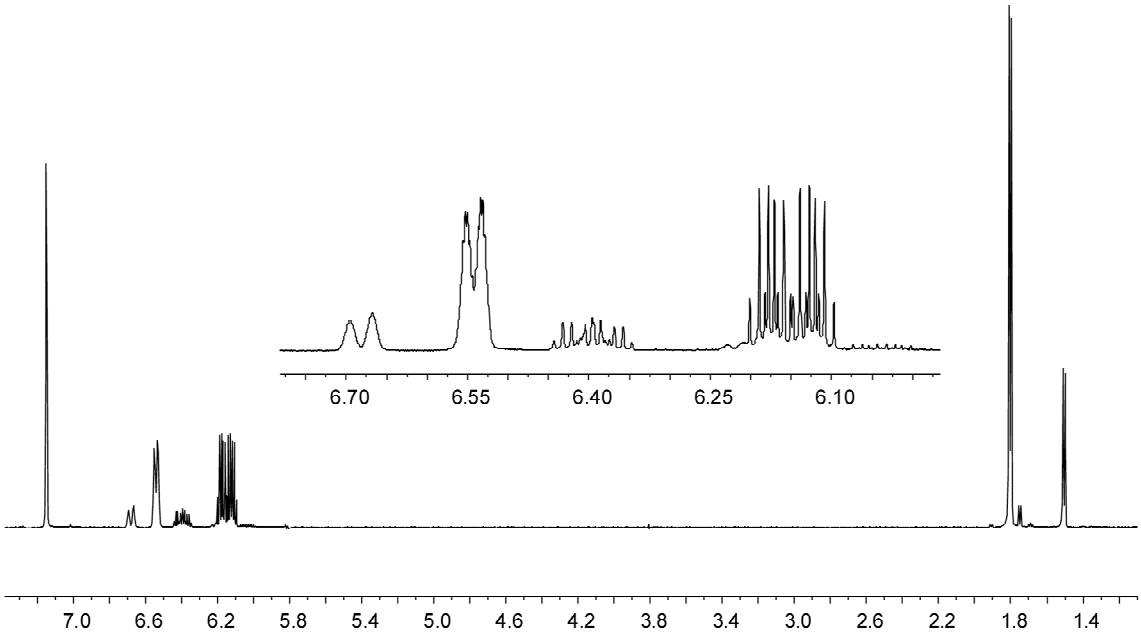
$^{1}H,^{13}C$ GHMBC (500 MHz / 126 MHz, C_6D_6, 298 K): δ(^{1}H) / δ(^{13}C) 6.68 / 20.4 (CH^{P} / CH_3), 6.39 / 20.4 (CH^{CH3} / CH_3), 1.51 / 149.3, 121.5 (CH_3 / CH^{CH3}, CH^{P}).

^{19}F NMR (470 MHz, C_6D_6, 298 K): δ −131.4 (m, 2F, *o*-C_6F_5), −150.8 (tt, $^{3}J_{FF}$ = 21.4 Hz, $^{4}J_{FF}$ = 3.5 Hz, 1F, *p*-C_6F_5), −160.9 (m, 2F, *m*-C_6F_5) [$\Delta\delta_{m,p}$ = 10.1].

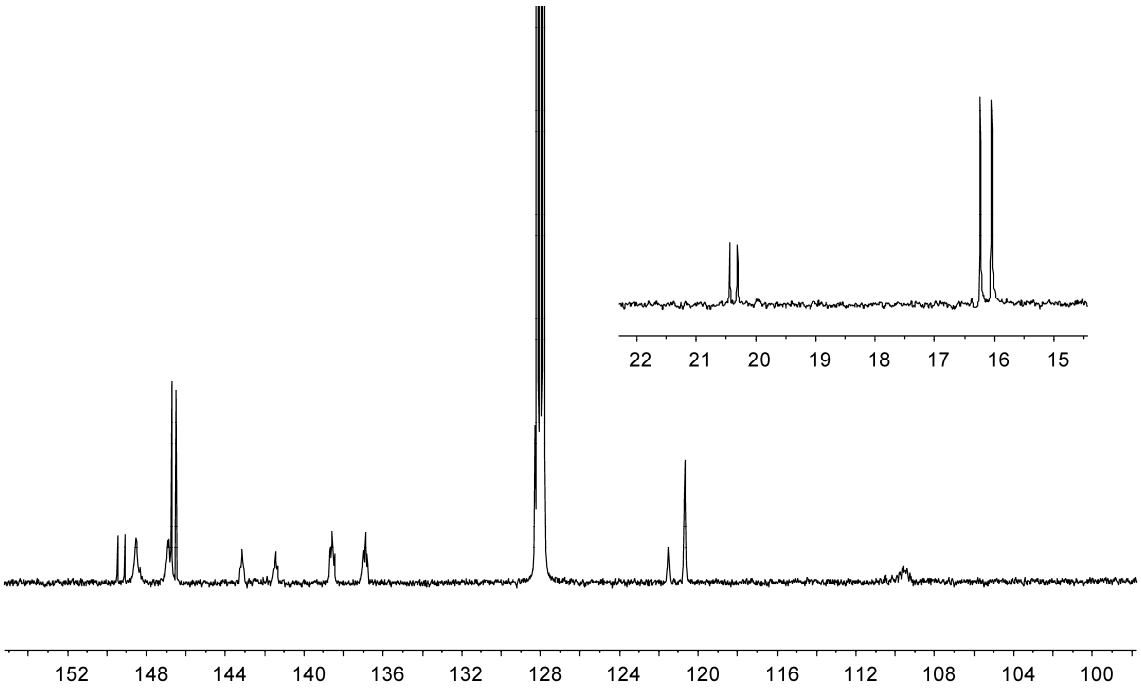
$^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 298 K): δ −53.4 (quin, $^{3}J_{PF}$ = 26.9 Hz).

IR (ATR): $\tilde{\nu}$ = 1640 (w), 1514 (s), 1466 (s), 1383 (w), 1298 (w), 1084 (s), 971 (s), 835 (w), 762 (w), 736 (w), 699 (w).

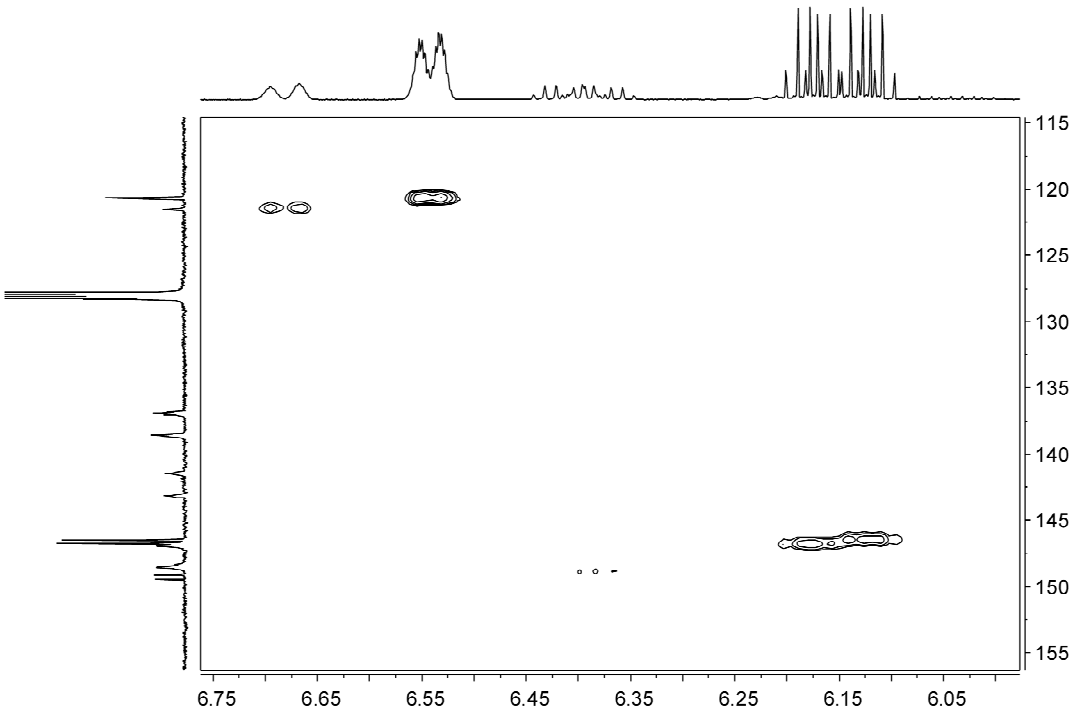
Elemental analysis: calcd. for $C_{15}H_5F_{10}P$: C 44.36; H 1.24. Found: C 44.46; H 1.17.



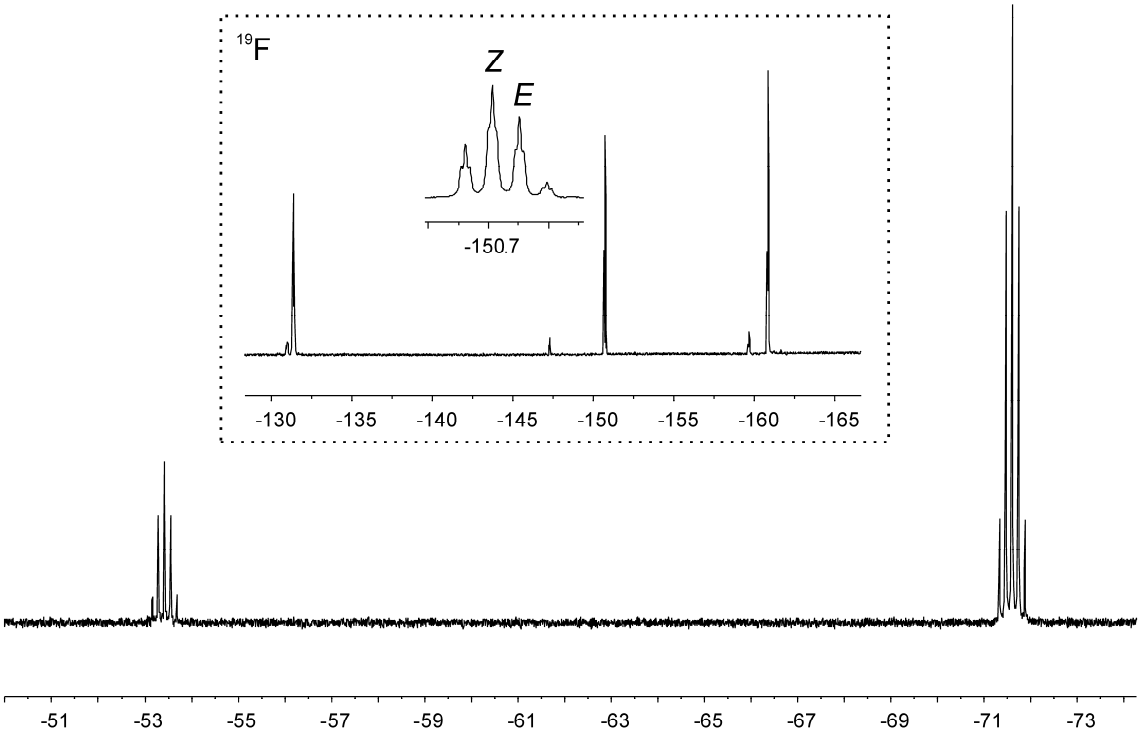
^{1}H NMR (600 MHz, C_6D_6, 298 K).



$^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6, 298 K).

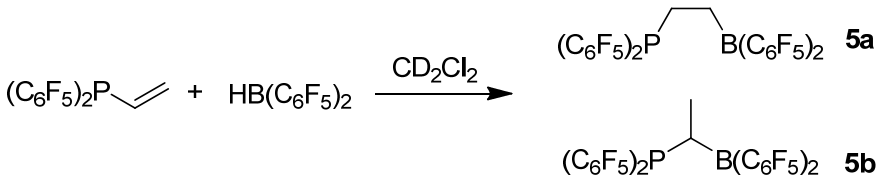


$^{1}H,^{13}C$ GHSQC (600 MHz / 151 MHz, C_6D_6, 298 K; projections: ^{1}H and $^{13}C\{^{1}H\}$ spectrum, respectively).



$^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_6, 298 K) and ^{19}F NMR (470 MHz, C_6D_6, 298 K).

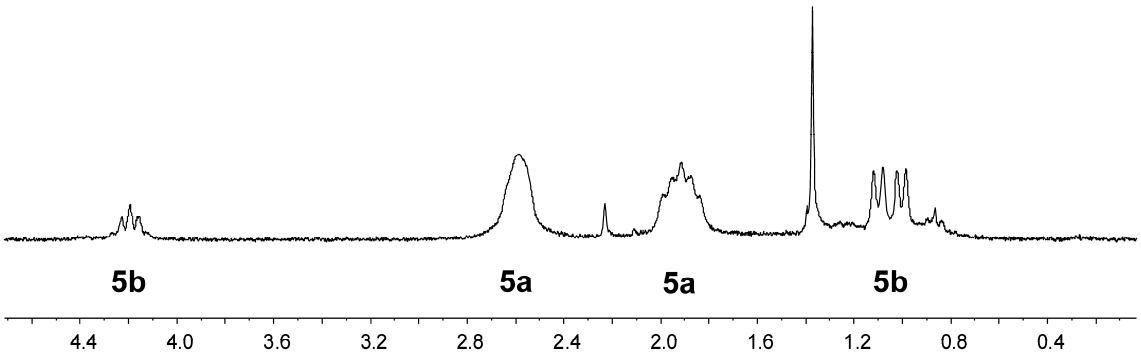
Preparation of compound 5a/5b:



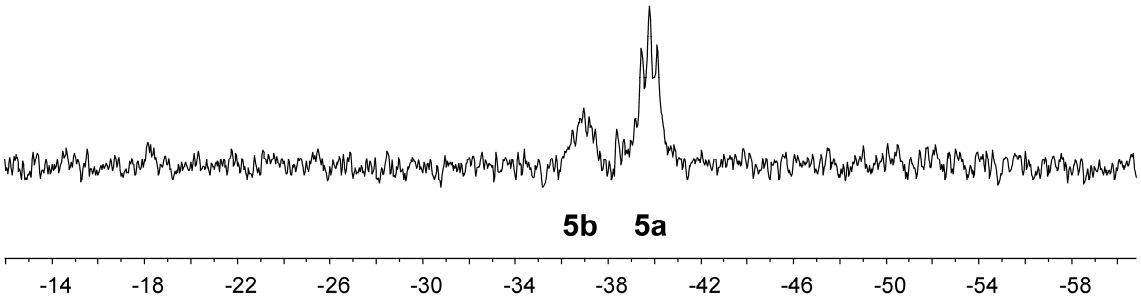
Bis(pentafluorophenyl)vinyl-phosphine (56.0 mg, 0.14 mmol) and bis(pentafluoro-phenyl)borane (49.4 mg, 0.14 mmol) were dissolved in d_6-benzene. The resulting solution was investigated directly by NMR measurements. Due to the ^{1}H and ^{31}P NMR the products are formed in a ratio of **5a** : **5b** = 2.5 : 1.

5a: ^{1}H NMR (200 MHz, C_6D_6, 300 K): δ 2.59 (br m, 2H, $^{P}CH_2$), 1.91 (m, 2H, $^{B}CH_2$).
$^{11}B\{^{1}H\}$ NMR (64 MHz, C_6D_6, 300 K): δ 73 ($\nu_{1/2}$ ~ 2000 Hz). $^{31}P\{^{1}H\}$ NMR (81 MHz, C_6D_6, 300 K): δ −39.8 (m).

5b: ^{1}H NMR (200 MHz, C_6D_6, 300 K): δ 4.19 (quint., $^{2}J_{PH}$ ~ $^{3}J_{HH}$ ~ 7.6 Hz, 1H, CH), 1.51 (dd, $^{3}J_{PH}$ = 19.5 Hz, $^{3}J_{HH}$ = 7.6 Hz, 3H, CH_3).
$^{11}B\{^{1}H\}$ NMR (64 MHz, C_6D_6, 300 K): δ 73 ($\nu_{1/2}$ ~ 2000 Hz). $^{31}P\{^{1}H\}$ NMR (81 MHz, C_6D_6, 300 K): δ −37.1 (m).

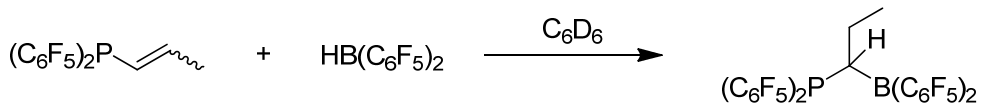


^{1}H NMR (200 MHz, C_6D_6, 300 K)



$^{31}P\{^{1}H\}$ NMR (81 MHz, C_6D_6, 300 K)

Preparation of compound 6:



Bis(pentafluorophenyl)propenyl-phosphine (32.8 mg, 0.08 mmol) and bis(pentafluorophenyl)borane (27.9 mg, 0.08 mmol) were dissolved in d_6-benzene. The resulting yellow solution was investigated directly by NMR measurements.

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 4.40 (m, 1H, CH), 1.84, 1.51 (each m, each 1H, CH_2), 0.69 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (500 MHz, C_6D_6, 298 K): δ 34.1 (br d, $^{1}J_{PC}$ ~ 20 Hz, CH), 22.5 (d, $^{2}J_{PC}$ = 20.3 Hz, CH_2), 15.6 (d, $^{3}J_{PC}$ = 11.4 Hz, CH_3), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, C_6D_6, 298 K): δ 4.40 / 1.84, 1.51 (CH / CH_2), 1.84 / 4.40, 1.51, 0.69 (CH_2 / CH, CH_2, CH_3), 1.51 / 4.40, 1.84, 0.69 (CH_2 / CH, CH_2, CH_3), 0.69 / 1.84, 1.51 (CH_3 / CH_2).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, C_6D_6, 298 K): δ 4.40 / 34.1 (CH), 1.84, 1.51 / 22.5 (CH_2), 0.69 / 15.6 (CH_3).

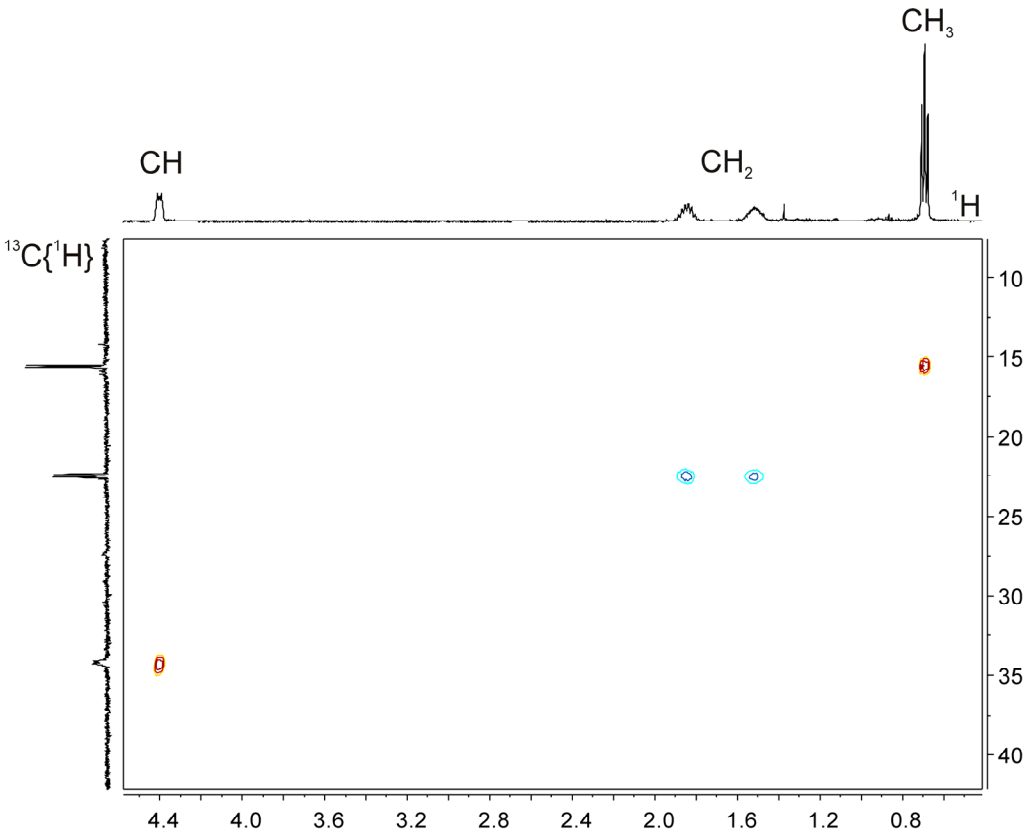
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, C_6D_6, 298 K): δ 4.40 / 22.5, 15.6 (CH / CH_2, CH_3), 1.84 / 15.6 (CH_2 / CH_3), 1.51 / 15.6 (CH_2 / CH_3), 0.69 / 34.1, 22.5 (CH_3 / CH, CH_2).

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 298 K): δ 71 ($\nu_{1/2}$ ~ 1500 Hz).

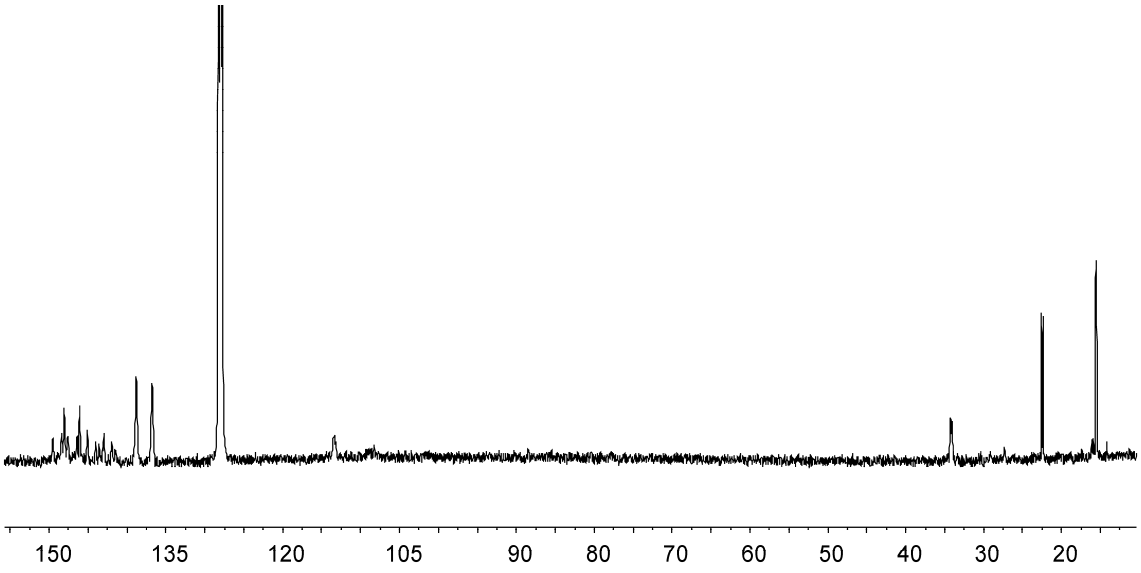
^{19}F NMR (470 MHz, C_6D_6, 298 K): δ −128.7 (m, 4F, *o*), −144.6 (t, $^{3}J_{FF}$ = 19.9 Hz, 2F, *p*), −159.7 (m, 4F, *m*) ($B(C_6F_5)_2$) [$\Delta\delta_{m,p}$ = 15.1], −131.0 (m, 2F, *o*), −147.8 (t, $^{3}J_{FF}$ = 21.5 Hz, 1F, *p*), −159.5 (m, 2F, *m*) ($PC_6F_5^{A}$) [$\Delta\delta_{m,p}$ = 11.7], −130.3 (br m, 2F, *o*),−148.5 (t, $^{3}J_{FF}$ = 20.8 Hz, 1F, *p*), −159.7 (m, 2F, *m*) ($PC_6F_5^{B}$) [$\Delta\delta_{m,p}$ = 11.2].

^{19}F,^{19}F GCOSY (470 MHz, C_6D_6, 298 K) [selected traces]: δ −144.6 / −159.7 (*p*- / *m*-$B(C_6F_5)_2$), −148.5 / −159.7 (*p*- / *m*-$PC_6F_5^{B}$), −159.5 / −131.0, −147.8 (*m*- / *o*-, *p*-$PC_6F_5^{A}$), −159.7 / −130.3 (*m*- / *o*-$PC_6F_5^{B}$), −159.7 / −128.7 (*m*- / *o*-$B(C_6F_5)_2$).

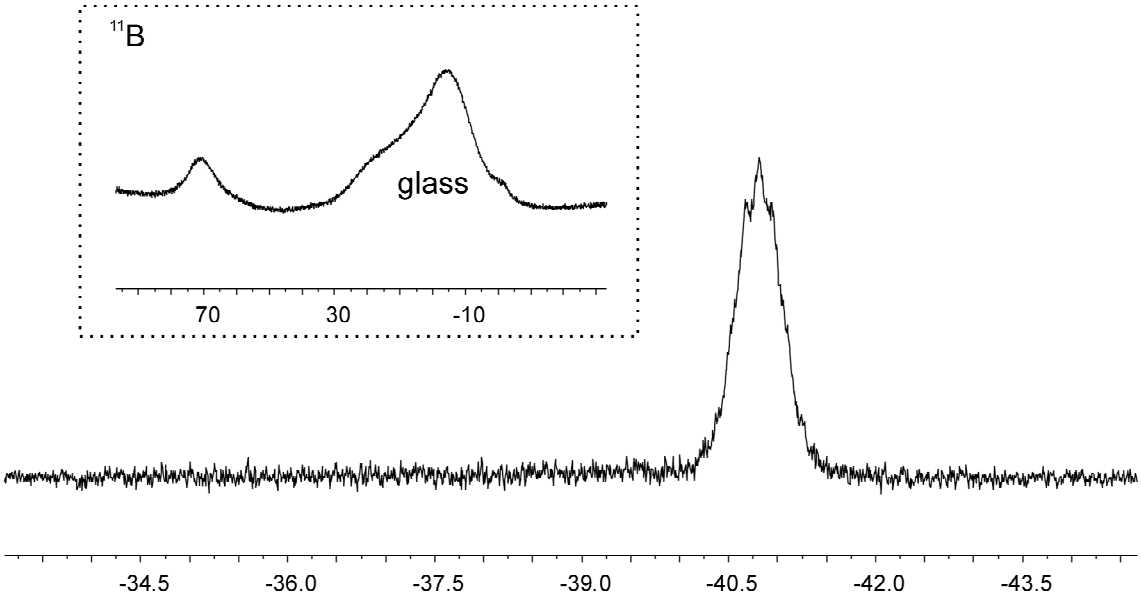
^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K): δ −40.8 (m).



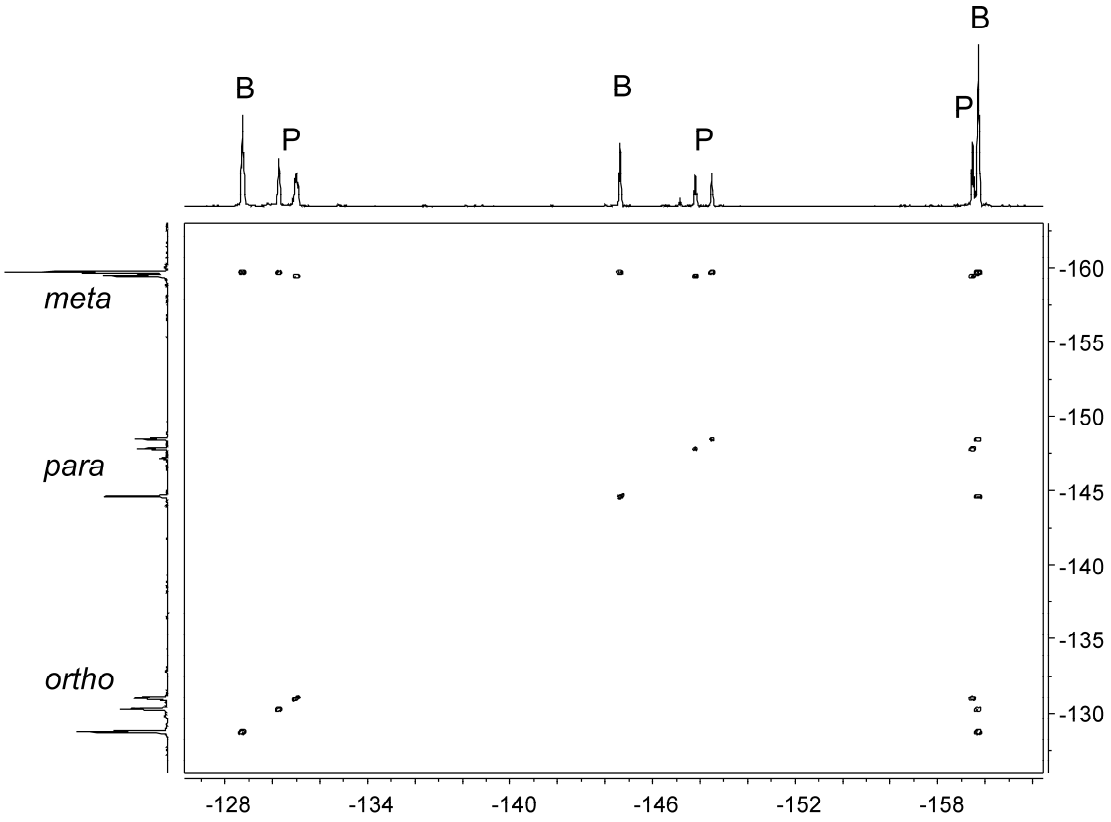
$^{1}H,^{13}C$ GHSQC (500 MHz / 126 MHz, C_6D_6, 298 K; projections: ^{1}H and $^{13}C\{^{1}H\}$ spectrum, respectively).



$^{13}C\{^{1}H\}$ NMR (500 MHz, C_6D_6, 298 K)

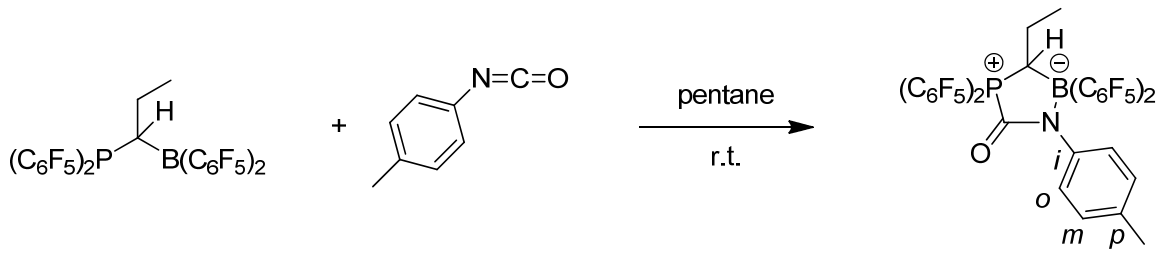


^{31}P NMR (202 MHz, C_6D_6, 298 K) and ^{11}B NMR (160 MHz, C_6D_6, 298 K).



^{19}F,^{19}F GCOSY (470 MHz, C_6D_6, 298 K; projections: ^{19}F spectrum).

Preparation of compound 7:



Bis(pentafluorophenyl)propenyl-phosphine (200 mg, 0.49 mmol) and bis(pentafluorophenyl)borane (170 mg, 0.49 mmol) were dissolved in pentane (30 mL) and stirred for 10 min. *p*-Tolylisocyanate (64.9 mg, 0.49 mmol) was added to the solution. After stirring 30 min at room temperature the precipitate was isolated *via* filtration and washed with pentane (20 mL). The white powder (339 mg ,0.38 mmol, 78%) was dried *in vacuo*. Single crystals suitable for X-ray structural analysis were obtained by slow diffusion of pentane in a solution of the compound in dichloromethane at -30 °C.

^{1}H NMR (500 MHz, CD_2Cl_2, 188 K): δ 6.93 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H, *m*-tol), 6.82 (br, 2H, *o*-tol), 4.02 (br, 1H, CH), 2.15 (s, 3H, $^{tol}CH_3$), 2.04 (br d, $^{3}J_{PH}$ ~ 50 Hz), 1.84 (br) (each 1H, CH_2), 0.91 (br t, $^{3}J_{HH}$ = 6.0 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 188 K): δ 158.9 (br d, $^{1}J_{PC}$ ~ 105 Hz, C=O), 136.9 (d, $^{3}J_{PC}$ = 12.6 Hz, *i*-tol), 136.5 (*p*-tol), 128.9 (*m*-tol), 124.1 (*o*-tol), 118.1, 115.4 (each br, *i*-$B(C_6F_5)_2$), 96.7 (br d, $^{1}J_{PC}$ ~ 75 Hz), 92.7 (br d, $^{1}J_{PC}$ ~ 65 Hz) (*i*-$P(C_6F_5)_2$), 40.3 (br, CH), 20.5 ($^{tol}CH_3$), 19.2 (br, CH_2), 16.3 (br d, $^{3}J_{PC}$ ~ 8 Hz, CH_3), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, CD_2Cl_2, 188 K): δ(^{1}H) / δ(^{1}H) 6.93 / 6.82 (*m*-tol / *o*-tol), 6.82 / 6.93 (*o*-tol / *m*-tol), 2.04 / 0.91 (CH_2 / CH_3), 1.84 / 0.91 (CH_2 / CH_3), 0.91 / 2.04, 1.84 (CH_3 / CH_2).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, CD_2Cl_2, 188 K): δ(^{1}H) / δ(^{13}C) 6.93 / 128.9 (*m*-tol), 6.82 / 124.1 (*o*-tol), 2.15 / 20.5 ($^{tol}CH_3$), 2.04, 1.84 / 19.2 (CH_2), 0.91 / 16.3 (CH_3).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, CD_2Cl_2, 188 K): δ(^{1}H) / δ(^{13}C) 6.93 / 136.5, 128.9, 20.5 (*m*-tol / *p*-tol, *m*-tol, $^{tol}CH_3$), 2.15 / 136.5, 128.9 ($^{tol}CH_3$ / *p*-tol, *m*-tol).

^{19}F NMR (470 MHz, CD_2Cl_2, 188 K): δ −121.8 (2F, *o*), −136.0 (1F, *p*), −155.1 (2F, *m*) (each br, $PC_6F_5^{A}$) [$\Delta\delta_{m,p}$ = 19.1], −125.5 (*o*), −139.6 (*o*'), −156.6 (*p*), −162.0 (*m*), −163.8

(*m*') (each br, each 1F, $BC_6F_5^A$) [$\Delta\delta_{m,p}$ = 5.4, 7.2], −126.7 (2F, *o*), −137.1 (1F, *p*), −154.3 (2F, *m*) (each br, $PC_6F_5^B$) [$\Delta\delta_{m,p}$ = 17.2], −128.3 (*o*), −137.6 (*o*'), −156.5 (*p*), −163.7 (*m*), −163.9 (*m*') (each br, each 1F, $BC_6F_5^B$) [$\Delta\delta_{m,p}$ = 7.2, 7.4].

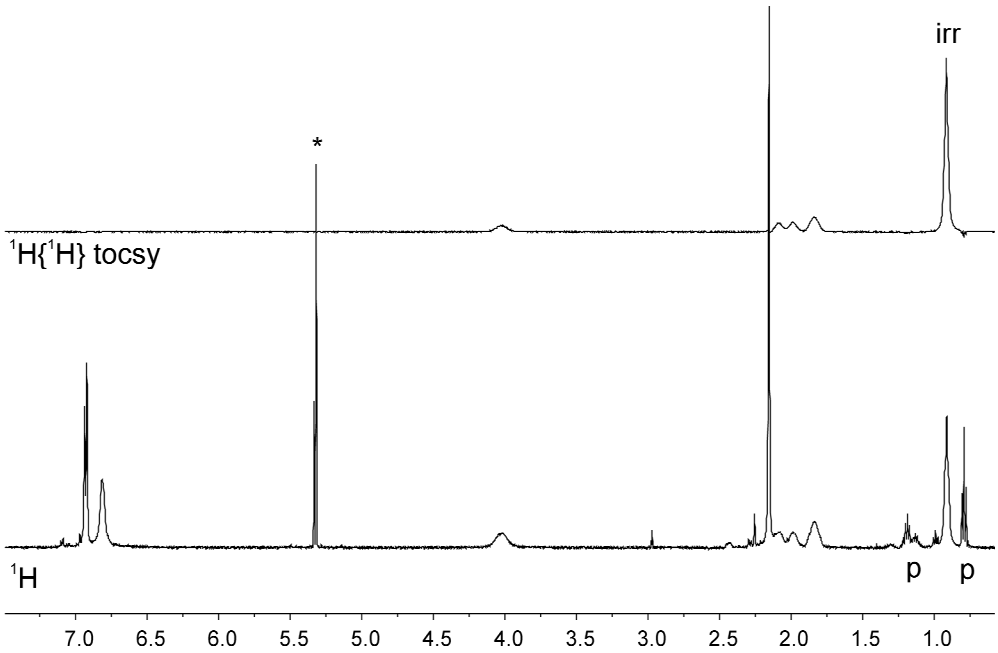
$^{19}F,^{19}F$ GCOSY (470 MHz, CD_2Cl_2, 188 K) [selected traces]: $\delta(^{19}F)$ / $\delta(^{19}F)$ −125.5 / −139.6, −162.0 (*o*- / *o*'-, *m*-$BC_6F_5^A$), −137.6 / −163.9 (*o*'- / *m*'-$BC_6F_5^B$), −139.6 / −163.8 (*o*'- / *m*'-$BC_6F_5^A$), −154.3 / −126.7, −137.1 (*m*- / *o*-, *p*-$PC_6F_5^B$), −155.1 / −121.8, −136.0 (*m*- / *o*-, *p*-$PC_6F_5^A$), −162.0 / −125.5, −156.6 (*m*- / *o*-, *p*-$BC_6F_5^A$), −163.7 / −128.3, −137.6, −156.5 (*m*- / *o*-, *o*'-, *p*-$BC_6F_5^B$).

$^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 188 K): δ −2.8 ($\nu_{1/2}$ ~ 50 Hz).

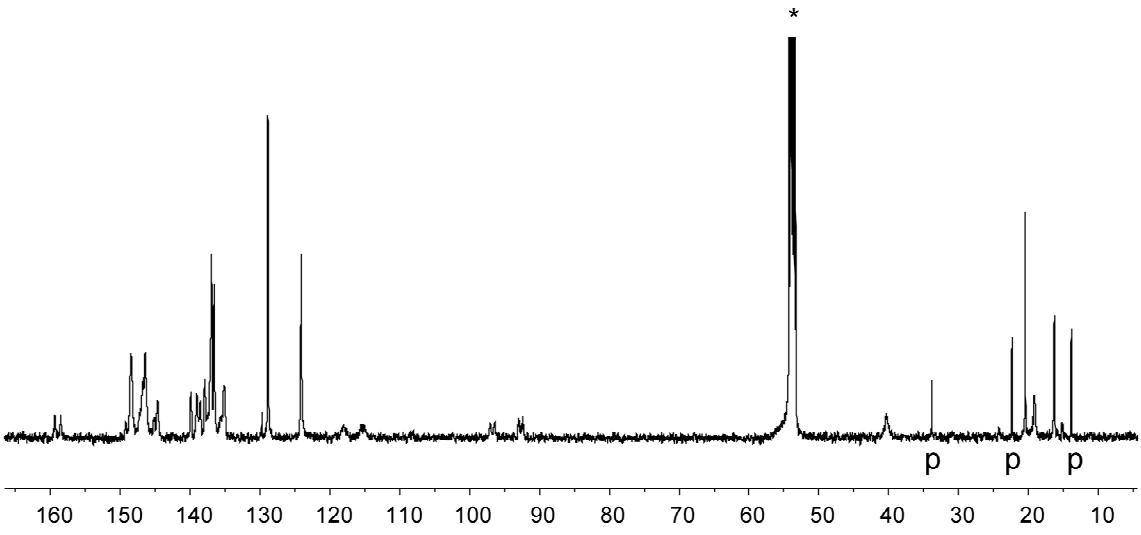
Melting point: 144.9 °C

IR (KBr): $\tilde{\nu}$ = 2968 (w), 2930 (w), 2873 (w), 1700 (s), 1645 (s), 1522 (s), 1487 (s), 1456 (s), 1394 (w), 1291 (s), 1112 (s), 1030 (w), 978 (s), 811 (w), 784 (w).

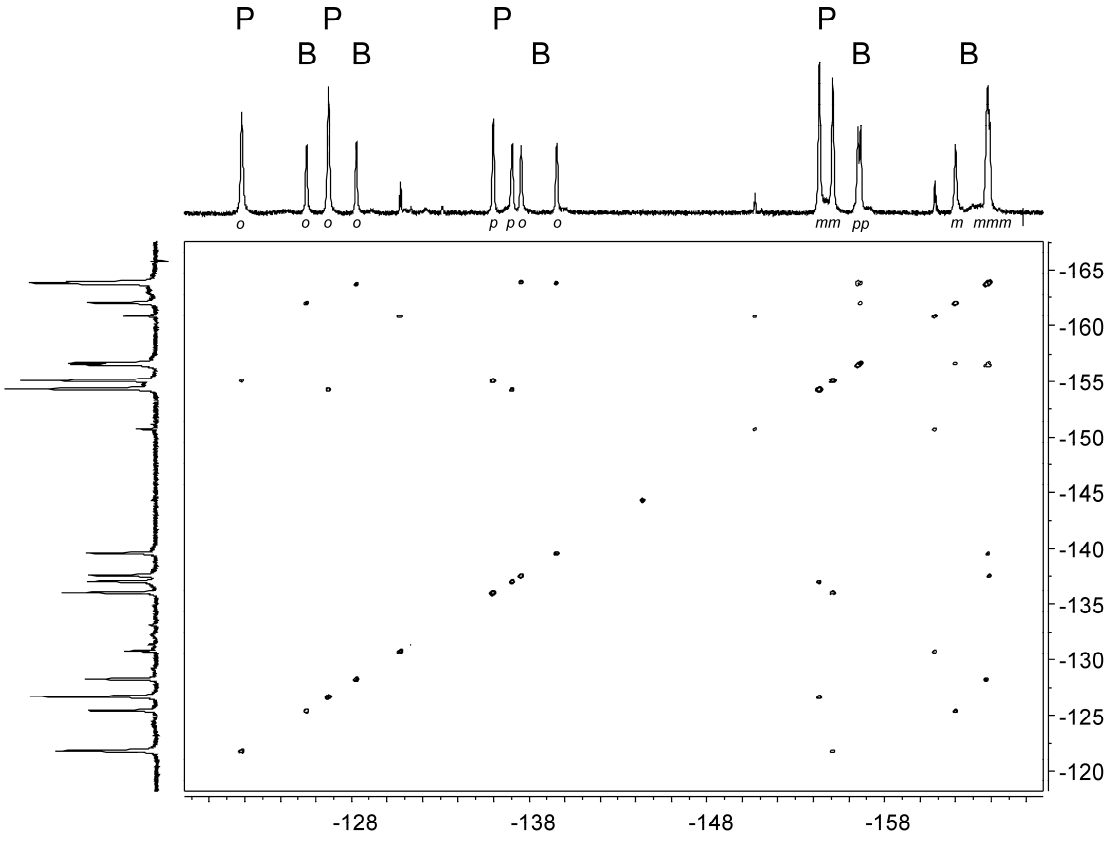
Elemental analysis calcd. for $C_{35}H_{13}BF_{20}NOP$: C 47.49; H 1.48; N 1.58. Found: C 46.72; H 1.19; N 1.34.



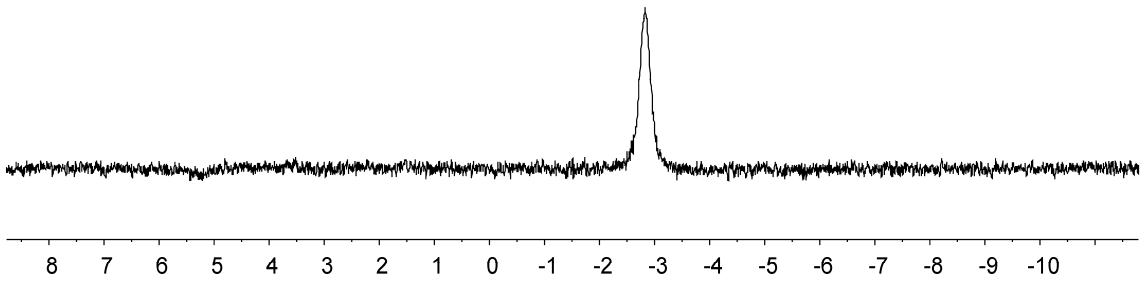
^1H NMR (500 MHz, CD_2Cl_2(*), 188 K) and $^1H\{^1H\}$ tocsy (irr: irradiation resonance) [p: pentane].



$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2(*), 188 K) [p: pentane].

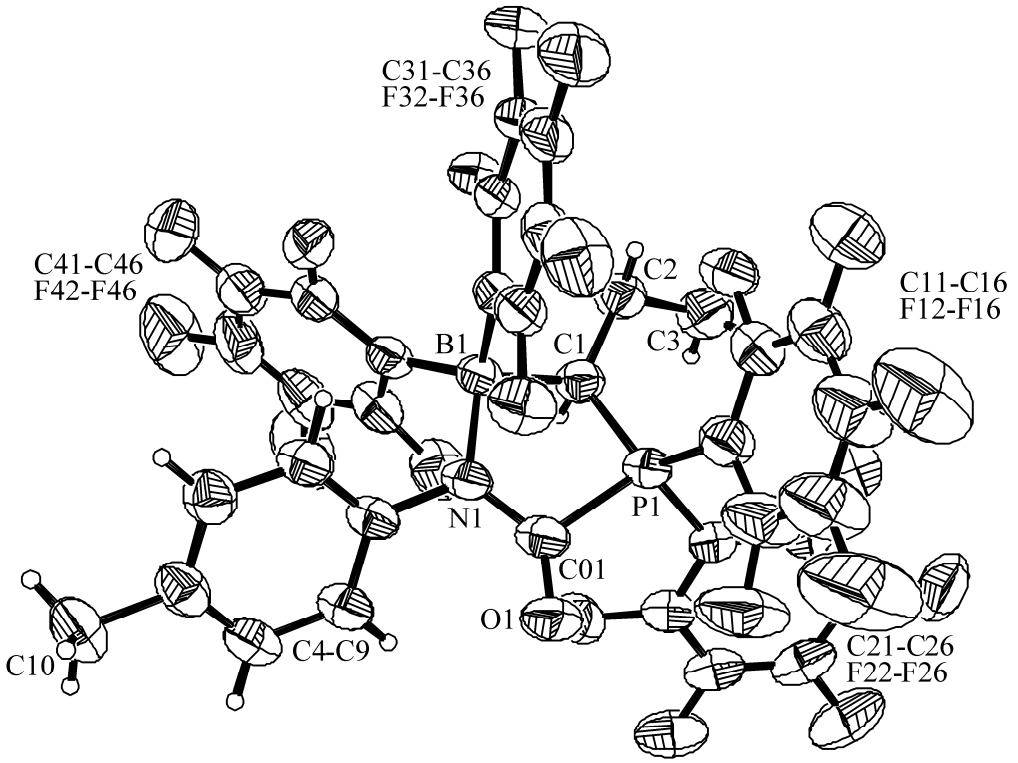


$^{19}F,^{19}F$ GCOSY (470 MHz, CD_2Cl_2, 188 K; projections: ^{19}F spectrum).

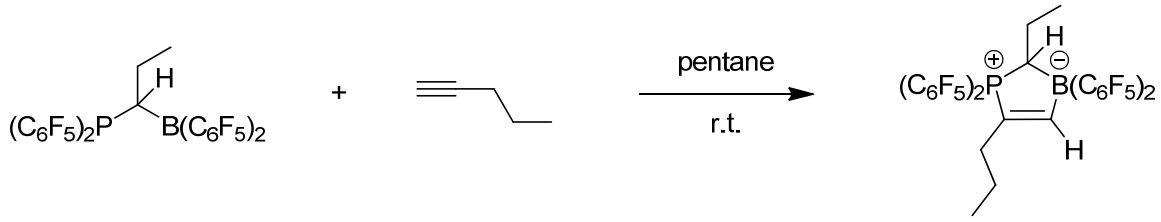


$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 188 K).

Crystal data for $C_{35}H_{13}BF_{20}NOP$ * 0.75 CH_2Cl_2 (**7**), M = 948.94, monoclinic, $C2/c$ (No. 15), a = 24.3493(10), b = 8.8572(2), c = 34.2513(11) Å, β = 92.683(3)°, V = 7378.8(4) Å^3, D_c = 1.708 g cm^{-3}, μ = 2.921 mm^{-1}, *F(000)* = 3756, Z = 8, λ = 1.54178 Å, T = 223(2) K, 31219 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6421 independent (R_{int} = 0.063), and 5002 observed reflections [I ≥ 2σ(I)], 561 refined parameters, R = 0.069, wR^2 = 0.202, GoF = 1.029.



Preparation of compound 8:



Bis(pentafluorophenyl)propenyl-phosphine (200 mg, 0.49 mmol) and bis(pentafluorophenyl)borane (170 mg, 0.49 mmol) were dissolved in pentane (30 mL) and stirred for 1 h. 1-Pentyne (33.5 mg, 0.49 mmol) was added and the solution was stirred 1 h at room temperature. The solvent was removed *in vacuo* and a white powder was isolated (181 mg, 0.22 mmol, 45%).

^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.33 (d, $^{3}J_{PH}$ = 67.9 Hz, 1H, $^{=}CH^{B}$), 3.26 (m, 1H, $^{P}CH^{B}$), 2.20, 2.12 (each m, each 1H, $^{=}CH_2^{Pr}$), 1.80 (d, $^{3}J_{PH}$ ~ 32 Hz), 1.72 (m) (each 1H, CH_2), 1.65 (m, 2H, CH_2^{Pr}), 0.92 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, CH_3^{Pr}), 0.89 (t, $^{3}J_{HH}$ = 7.8 Hz, 3H, CH_3).

^{1}H{^{31}P} NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.33 (s, 1H, $^{=}CH^{B}$), 3.26 (br, 1H, $^{P}CH^{B}$), 2.20, 2.12 (each m, each 1H, $^{=}CH_2^{Pr}$), 1.80, 1.72 (each m, each 1H, CH_2), 1.65 (m, 2H, CH_2^{Pr}), 0.92 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, CH_3^{Pr}), 0.89 (t, $^{3}J_{HH}$ = 7.8 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ 181.7 (br m, $^{=}CH^{B}$), 124.9 (d, $^{1}J_{PC}$ = 75.9 Hz, ^{P}C=), 123.3, 120.9 (each br, *i*-$B(C_6F_5)_2$), 101.0 (dm, $^{1}J_{PC}$ = 64.5 Hz), 98.5 (dm, $^{1}J_{PC}$ = 63.4 Hz) (*i*-$P(C_6F_5)_2$), 37.1 (m, $^{P}CH^{B}$), 31.8 (br d, $^{2}J_{PC}$ = 14.5 Hz, $^{=}CH_2^{Pr}$), 21.4 (d, $^{2}J_{PC}$ = 7.3 Hz, CH_2), 21.3 (br, CH_2^{Pr}), 16.2 (d, $^{3}J_{PC}$ = 8.9 Hz, CH_3), 13.7 (CH_3^{Pr}), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, CD_2Cl_2, 298 K): δ(^{1}H) / δ(^{1}H) 8.33 / 2.20, 2.12 ($^{=}CH^{B}$ / $^{=}CH_2^{Pr}$), 3.26 / 1.80, 1.72 ($^{P}CH^{B}$ / CH_2), 2.20 / 8.33, 1.65 ($^{=}CH_2^{Pr}$ / $^{=}CH^{B}$, CH_2^{Pr}), 2.12 / 8.33, 1.65 ($^{=}CH_2^{Pr}$ / $^{=}CH^{B}$, CH_2^{Pr}), 1.80 / 0.89 (CH_2 / CH_3), 1.72 / 0.89 (CH_2 / CH_3), 1.65 / 2.20, 2.12, 0.92 (CH_2^{Pr} / $^{=}CH_2^{Pr}$, CH_3^{Pr}), 0.92 / 1.65 (CH_3^{Pr} / CH_2^{Pr}), 0.89 / 1.80, 1.72 (CH_3 / CH_2).

$^{1}H,^{13}C$ GHSQC (500 MHz / 126 MHz, CD_2Cl_2, 298 K): δ(^{1}H) / δ(^{13}C) 3.26 / 37.1 ($^{P}CH^{B}$), 2.20, 2.12 / 31.8 ($^{=}CH_2^{Pr}$), 1.80, 1.72 / 21.4 (CH_2), 1.65 / 21.3 (CH_2^{Pr}), 0.92 / 13.7 (CH_3^{Pr}), 0.89 / 16.2 (CH_3).

$^{1}H,^{13}C$ GHMBC (500 MHz / 126 MHz, CD_2Cl_2, 298 K): δ(^{1}H) / δ(^{13}C) 1.65 / 124.9, 31.8, 13.7 (CH_2^{Pr} / $^{P}C^{=}$, $^{=}CH_2^{Pr}$, CH_3^{Pr}), 0.92 / 31.8, 21.3 (CH_3^{Pr} / $^{=}CH_2^{Pr}$, CH_2^{Pr}), 0.89 / 21.4 (CH_3 / CH_2).

$^{1}H\{^{1}H\}$ TOCSY (500 MHz, CD_2Cl_2, 298 K): $\delta(^{1}H)_{irr.}$ / $\delta(^{1}H)_{res.}$ 8.33 / 0.92 ($^{=}CH^{B}$ / CH_3), 3.26 / 0.89 ($^{P}CH^{B}$ / CH_3), 2.20 / 1.65, 0.92 ($^{=}CH_2^{Pr}$ / CH_2^{Pr}, CH_3^{Pr}), 2.12 / 1.65, 0.92 ($^{=}CH_2^{Pr}$ / CH_2^{Pr}, CH_3^{Pr}), 1.80 / 0.89 (CH_2 / CH_3), 1.72 / 0.89 (CH_2 / CH_3), 0.92 / 3.26, 2.20, 2.12, 1.80, 1.72, 1.65 (CH_3^{Pr} / $^{P}CH^{B}$, $^{=}CH_2^{Pr}$, CH_2, CH_2^{Pr})[1], 0.89 / 3.26, 2.20, 2.12, 1.80, 1.72, 1.65 (CH_3 / $^{P}CH^{B}$, $^{=}CH_2^{Pr}$, CH_2, CH_2^{Pr})[1] [[1] irradiation points at 0.92 and 0.89 are too close for the irradiation pulse, therefore unselective exitation].

$^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): δ −8.6 (d, J ~ 14 Hz).

^{19}F NMR (470 MHz, CD_2Cl_2, 298 K)[1]: δ −127.7 (2F, *o*), −141.4 (1F, *p*), −157.1 (2F, *m*) (each br, $PC_6F_5^{A}$) [$\Delta\delta_{m,p}$ = 15.7], −127.9 (2F, *o*), −140.5 (1F, *p*), −156.8 (2F, *m*) (each br, $PC_6F_5^{B}$) [$\Delta\delta_{m,p}$ = 16.3], −131.8 (2F, *o*)[t], −160.1 (1F, *p*), −165.2 (2F, *m*) (each br, $BC_6F_5^{A}$) [$\Delta\delta_{m,p}$ = 5.1], −132.9 (2F, *o*)[t], −160.6 (1F, *p*), −165.2 (2F, *m*) (each br, $BC_6F_5^{B}$) [$\Delta\delta_{m,p}$ = 4.6] [[1].assignment supported by $^{19}F\{^{31}P\}$ NMR] [[t].tentative assignment].

$^{19}F,^{19}F$ COSY (470 MHz, CD_2Cl_2, 298 K) [selected traces]: δ(^{19}F) / δ(^{19}F) −131.8 / −165.2 (*o*-$BC_6F_5^{A}$ / *m*-$BC_6F_5^{A+B}$), −132.9 / −165.2 (*o*-$BC_6F_5^{B}$ / *m*-$BC_6F_5^{A+B}$), −156.8 / −127.9, −140.5 (*m*- / *o*-, *p*-$PC_6F_5^{B}$), −157.1 / −127.7, −141.4 (*m*- / *o*-, *p*-$PC_6F_5^{A}$), −160.1 / −165.2 (*p*-$BC_6F_5^{A}$ / *m*-$BC_6F_5^{A+B}$), −160.6 / −165.2 (*p*-$BC_6F_5^{B}$ / *m*-$BC_6F_5^{A+B}$), −165.2 / −131.8, −132.9, −160.1, −160.6 (*m*-$BC_6F_5^{A+B}$ / *o*-$BC_6F_5^{A}$, *o*-$BC_6F_5^{B}$, *p*-$BC_6F_5^{A}$, *p*-$BC_6F_5^{B}$).

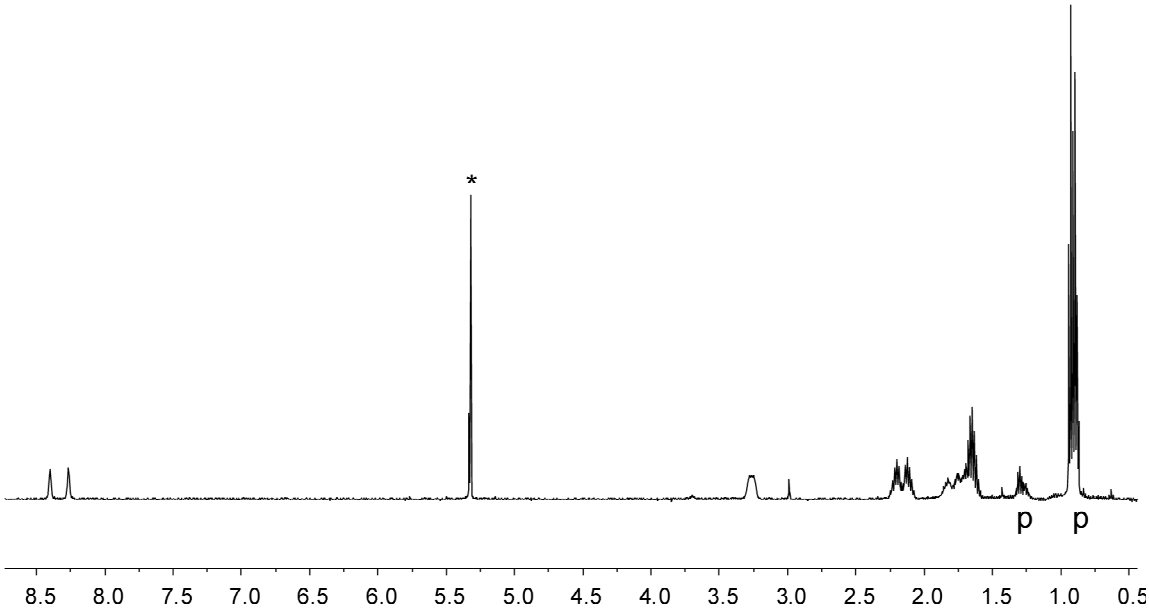
$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): δ 29.8 (br m).

$^{31}P\{^{19}F\}$ NMR (202 MHz, CD_2Cl_2, 298 K): δ 29.8 (br, $\nu_{1/2}$ ~ 135 Hz).

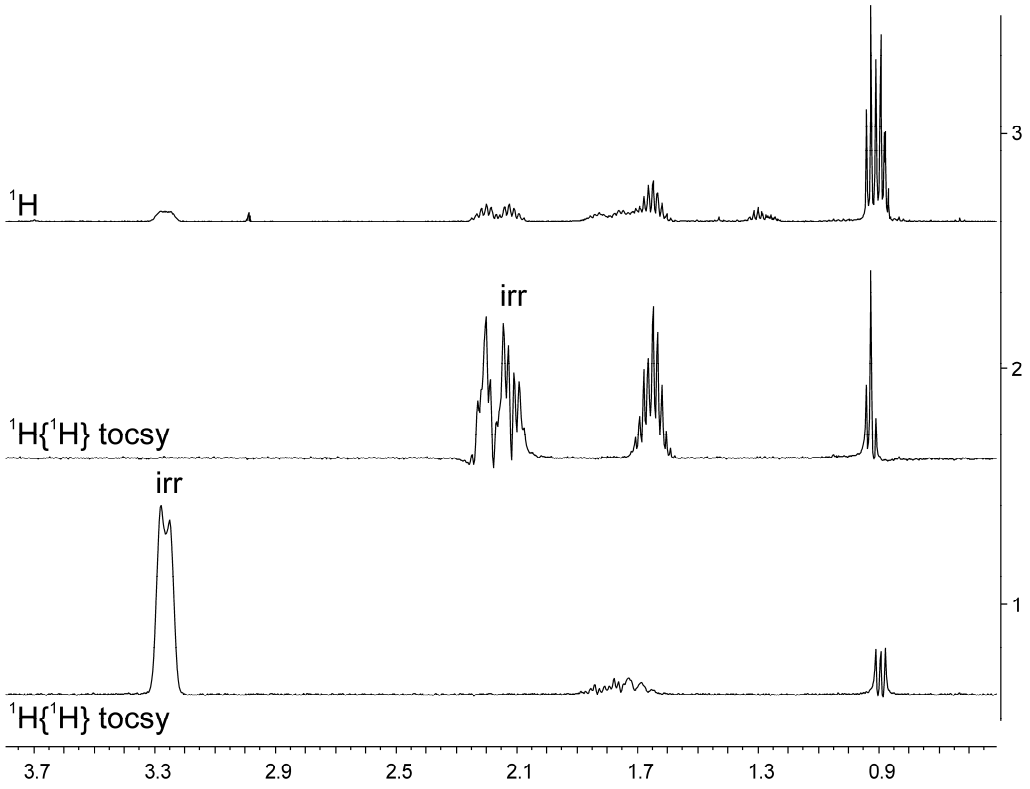
Melting point: 132.7 °C

IR (KBr): $\tilde{\nu}$ = 2977 (w), 2940 (w), 2882 (w), 1644 (s), 1522 (s), 1482 (s), 1459 (s), 1394 (w), 1302 (w), 1281 (w), 1102 (s), 979 (s), 782 (w), 674 (w), 548 (w).

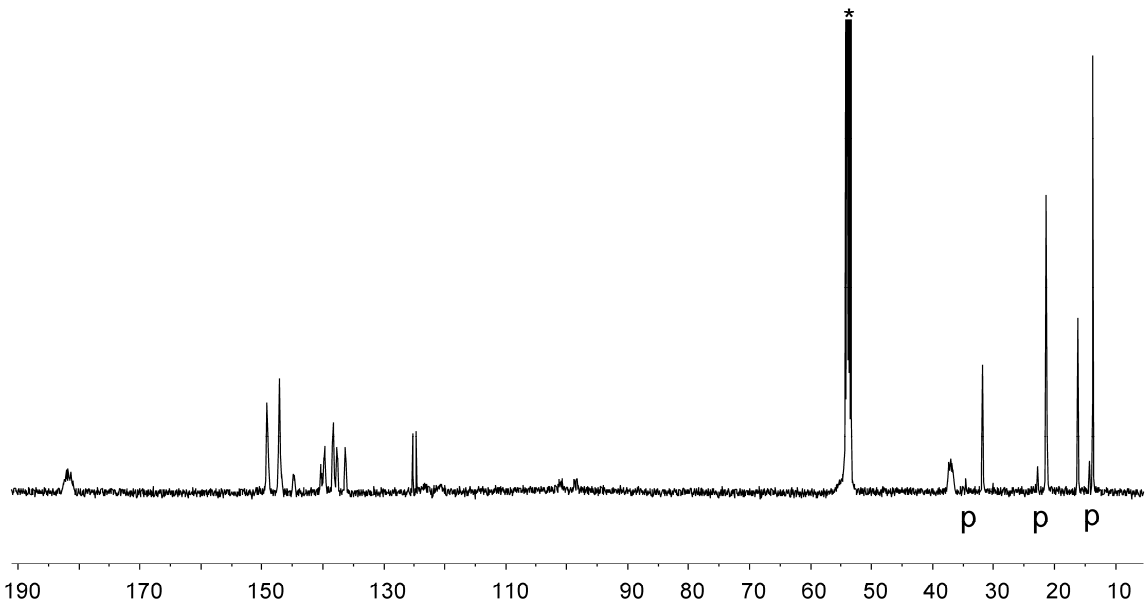
Elemental analysis calcd. for $C_{32}H_{14}BF_{20}P$: C 46.86; H 1.72. Found: C 45.93; H 1.34.



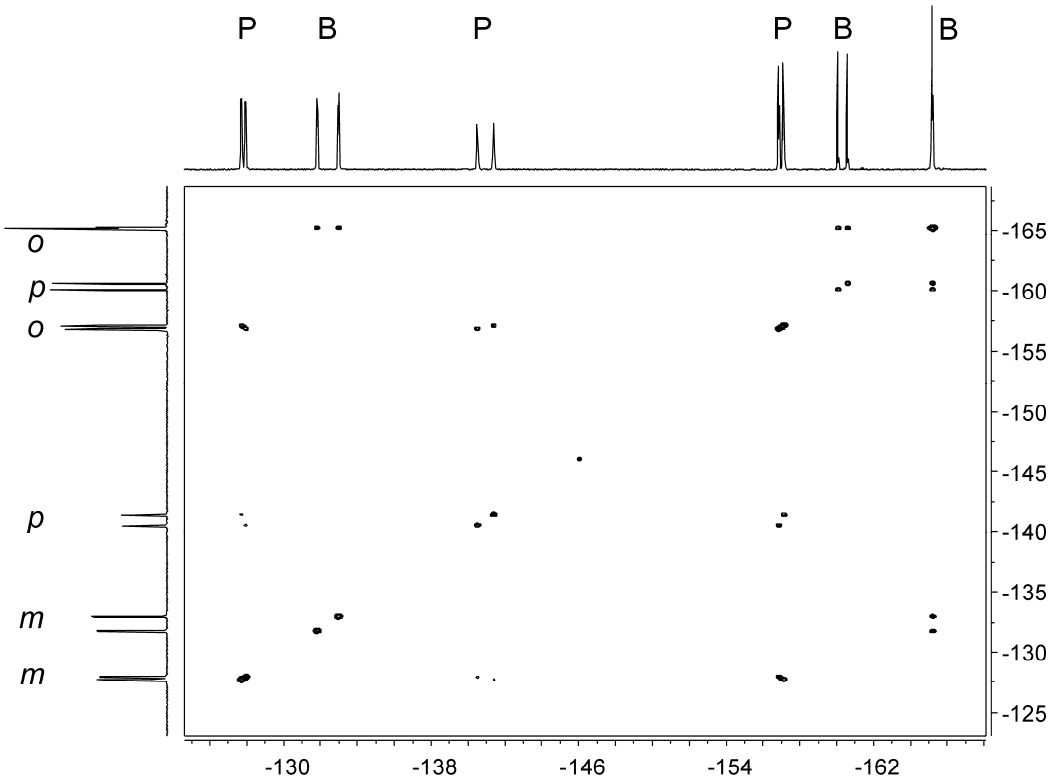
^{1}H NMR (500 MHz, CD_2Cl_2(*), 298 K) [p: pentane].



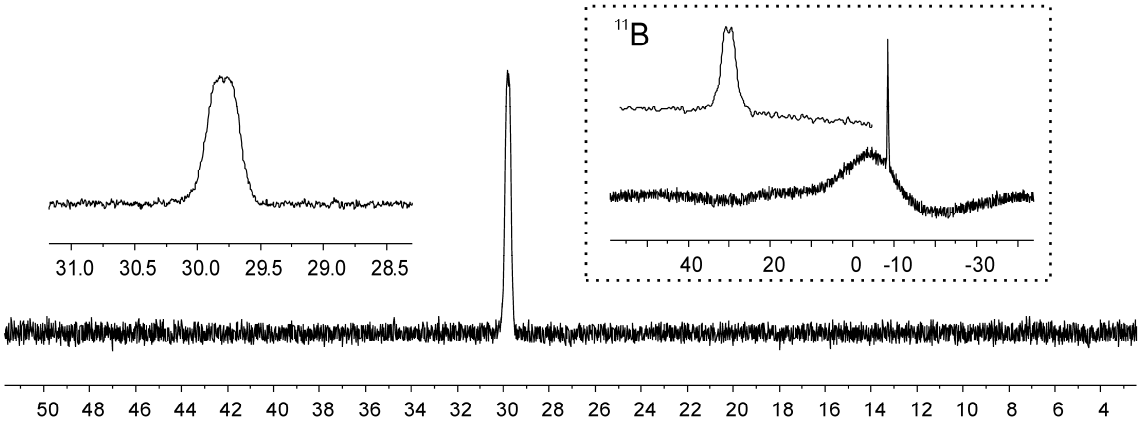
^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) and ^{1}H{^{1}H} tocsy
(irr: irradiation resonance at 3.26 (1) and 2.12 (2), respectively).



$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2(*), 298 K) [p: pentane].



$^{19}F,^{19}F$ COSY (470 MHz, CD_2Cl_2, 298 K; projections: ^{19}F spectrum).



$^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298 K) and $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 298 K).

Preparation of compound 9:

Bis(pentafluorophenyl)propenyl-phosphine (170 mg, 0.42 mmol) and bis(pentafluorophenyl)borane (148 mg, 0.49 mmol) were dissolved in pentane (10 mL) and stirred for 5 min. The flask was evacuated and ethylene (2 bar) was pressed on the solution and the reaction mixture was stirred for 4 days at room temperature. The white precipitate was isolated by filtration. The product was dried *in vacuo* to yield a white powder (55.1 mg, 0.07 mmol, 17%).

^{1}H NMR(500 MHz, $CDCl_3$, 298 K): δ 3.38, 2.91 (each m, each 1H, $^{P}CH_2$), 3.31 (m, 1H, CH), 2.05 (dm, $^{3}J_{PH}$ = 42.3 Hz), 1.40 (m) (each 1H, $^{B}CH_2$), 1.75 (dm, $^{3}J_{PH}$ = 32.7 Hz), 1.23 (m) (each 1H, CH_2), 0.82 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR(126 MHz, $CDCl_3$ 298 K): δ 32.8 (br, CH), 27.8 (d, $^{1}J_{PC}$ = 52.3 Hz, $^{P}CH_2$), 23.1 (d, $^{2}J_{PC}$ = 3.9 Hz, CH_2), 16.5 (br, $^{B}CH_2$), 15.4 (d, $^{3}J_{PC}$ = 4.5 Hz, CH_3), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, $CDCl_3$, 298 K): δ(^{1}H) / δ(^{1}H) 3.38 / 2.91, 1.40 ($^{P}CH_2$ / $^{P}CH_2$, $^{B}CH_2$), 3.31 / 1.23 (CH / CH_2), 2.91 / 3.38, 2.05, 1.40 ($^{P}CH_2$ / $^{P}CH_2$, $^{B}CH_2$), 2.05 / 2.91, 1.40 ($^{B}CH_2$ / $^{P}CH_2$, $^{B}CH_2$), 1.75 / 3.31, 0.82 (CH_2 / CH, CH_3), 1.40 / 3.38, 2.91, 2.05 ($^{B}CH_2$ / $^{P}CH_2$, $^{B}CH_2$), 1.23 / 3.31, 1.75, 0.82 (CH_2 / CH, CH_2, CH_3), 0.82 / 1.75, 1.23 (CH_3 / CH_2).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, $CDCl_3$, 298 K): δ(^{1}H) / δ(^{13}C) 3.38 / 27.8 ($^{P}CH_2$), 3.31 / 32.8 (CH), 2.91 / 27.8 ($^{P}CH_2$), 2.05 / 16.5 ($^{B}CH_2$), 1.75 / 23.1 (CH_2), 1.40 / 16.5 ($^{B}CH_2$), 1.23 / 23.1 (CH_2), 0.82 / 15.4 (CH_3).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, $CDCl_3$, 298 K): δ(^{1}H) / δ(^{13}C) 1.23 / 15.4 (CH_2 / CH_3), 0.82 / 23.1 (CH_3 / CH_2).

^{1}H{^{1}H} NOE (500 MHz, $CDCl_3$, 298 K): δ (^{1}H)$_{irr.}$ / δ (^{1}H)$_{res.}$ 3.38 / 2.91 ($^{P}CH_2$ / $^{P}CH_2$), 3.31 / 0.82 (CH / CH_3), 2.91 / 3.38 ($^{P}CH_2$ / $^{P}CH_2$), 2.05 / 1.40 ($^{B}CH_2$ / $^{B}CH_2$), 1.75 / 1.23 (CH_2 / CH_2), 1.40 / 2.05 ($^{B}CH_2$ / $^{B}CH_2$), 1.23 / 1.75 (CH_2 / CH_2), 0.82 / 3.31 (CH_3 / CH).

$^{1}H\{^{1}H\}$ TOCSY (500 MHz, $CDCl_3$, 298 K): δ ($^{1}H)_{irr.}$ / δ ($^{1}H)_{res.}$ 3.38 / 2.91, 2.05, 1.40 ($^{P}CH_2$ / $^{P}CH_2$, $^{B}CH_2$), 3.31 / 1.75, 1.23, 0.82 (CH / CH_2, CH_3), 2.91 / 3.38, 2.05, 1.40 ($^{P}CH_2$ / $^{P}CH_2$, $^{B}CH_2$), 2.05 / 3.38, 2.91, 1.40 ($^{B}CH_2$ / $^{P}CH_2$, $^{B}CH_2$), 1.75 / 3.31, 1.23 (CH_2 / CH, CH_2), 1.40 / 3.38, 2.91, 2.05 ($^{B}CH_2$ / $^{P}CH_2$, $^{B}CH_2$), 1.23 / 3.31, 1.75, 0.82 (CH_2 / CH, CH_2, CH_3), 0.82 / 1.75, 1.23 (CH_3 / CH_2).

$^{11}B\{^{1}H\}$ NMR(160 MHz, $CDCl_3$, 298 K): δ −8.7 ($\nu_{1/2}$ ~ 55 Hz).

^{19}F NMR (470 MHz, $CDCl_3$ 298 K): δ −124.3 (2F, *o*), −139.2 (1F, *p*), −156.3 (2F, *m*) (each br, $PC_6F_5{}^{A}$) [$\Delta\delta_{m,p}$ = 17.1], −126.2 (2F, *o*), −138.5 (1F, *p*), −154.9 (2F, *m*) (each br, $PC_6F_5{}^{B}$) [$\Delta\delta_{m,p}$ = 16.4], −131.7 (2F, *o*), −159.8 (1F, *p*), −164.3 (2F, *m*) (each br, $BC_6F_5{}^{A}$) [$\Delta\delta_{m,p}$ = 4.5], −132.2 (2F, *o*), −159.0 (1F, *p*), −164.2 (2F, *m*) (each br, $BC_6F_5{}^{B}$) [$\Delta\delta_{m,p}$ = 4.2].

$^{19}F,^{19}F$ GCOSY (470 MHz, $CDCl_3$, 298 K) [selected traces]: δ(^{19}F) / δ(^{19}F) −154.9 / −126.2, −138.5 (*m*- / *o*-, *p*-$PC_6F_5{}^{B}$), −156.3 / −124.3, −139.2 (*m*- / *o*-, *p*-$PC_6F_5{}^{A}$), −164.2 / −132.2, −159.0 (*m*- / *o*-, *p*-$BC_6F_5{}^{B}$), −164.3 / −131.7, −159.8 (*m*- / *o*-, *p*-$BC_6F_5{}^{A}$).

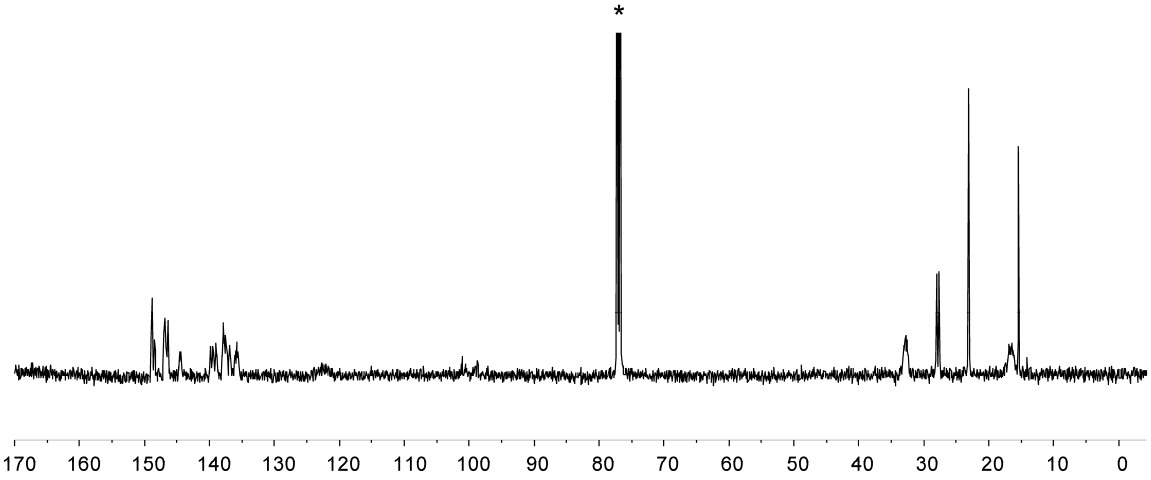
$^{31}P\{^{1}H\}$ NMR(202 MHz, $CDCl_3$, 298 K): δ 37.5 ($\nu_{1/2}$ ~ 50 Hz).

Melting point: 161.5 °C

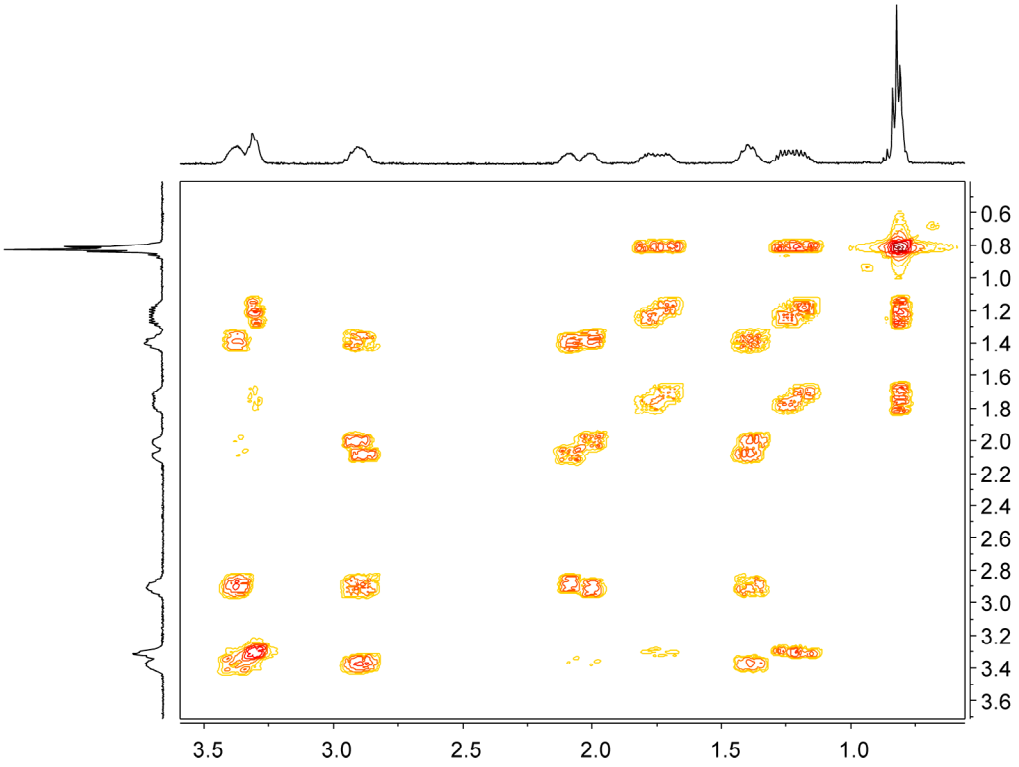
IR (KBr): $\tilde{\nu}$ = 2983(w), 2946 (w), 2867 (w), 1645 s), 1522 (s), 1491 (s), 1463 (s), 1389 (w), 1305 (w), 1275 (w), 1103 (s), 1082 (s), 989 (s), 922 (w), 772 (w), .

Elemental analysis calcd. for $C_{29}H_{10}BF_{20}P$: C 44.65; H 1.29. Found: C 43.56; H 1.14.

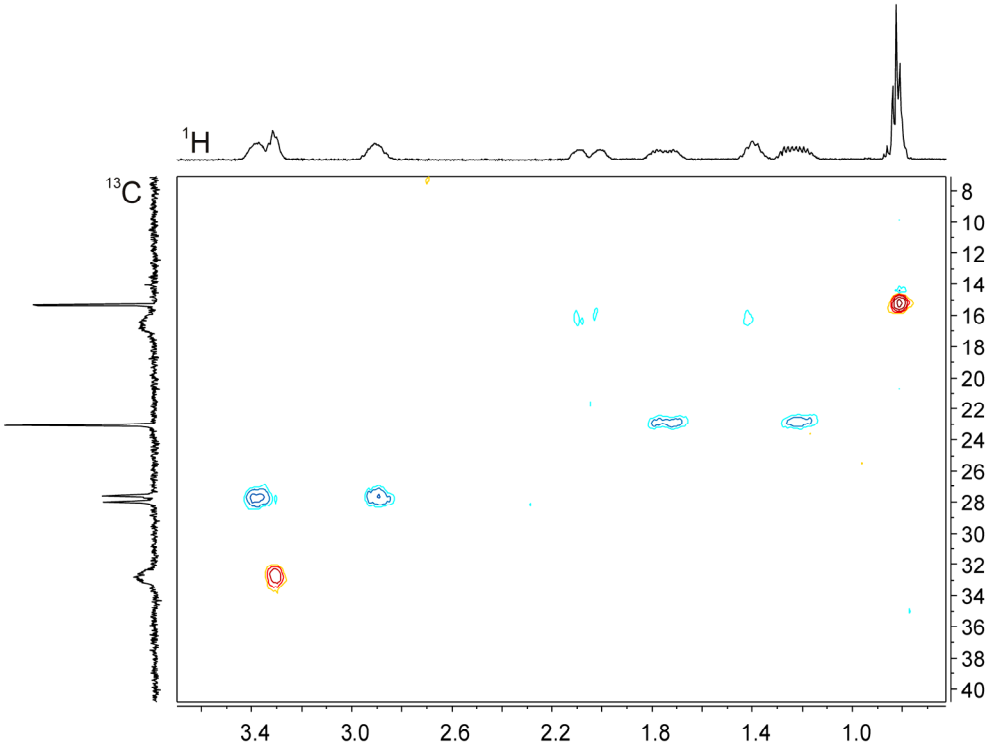
Exact mass calcd. for $C_{29}H_{10}BF_{20}P+Cl^{-}$: 814.99887 m/z. Found: 814.99929 m/z.



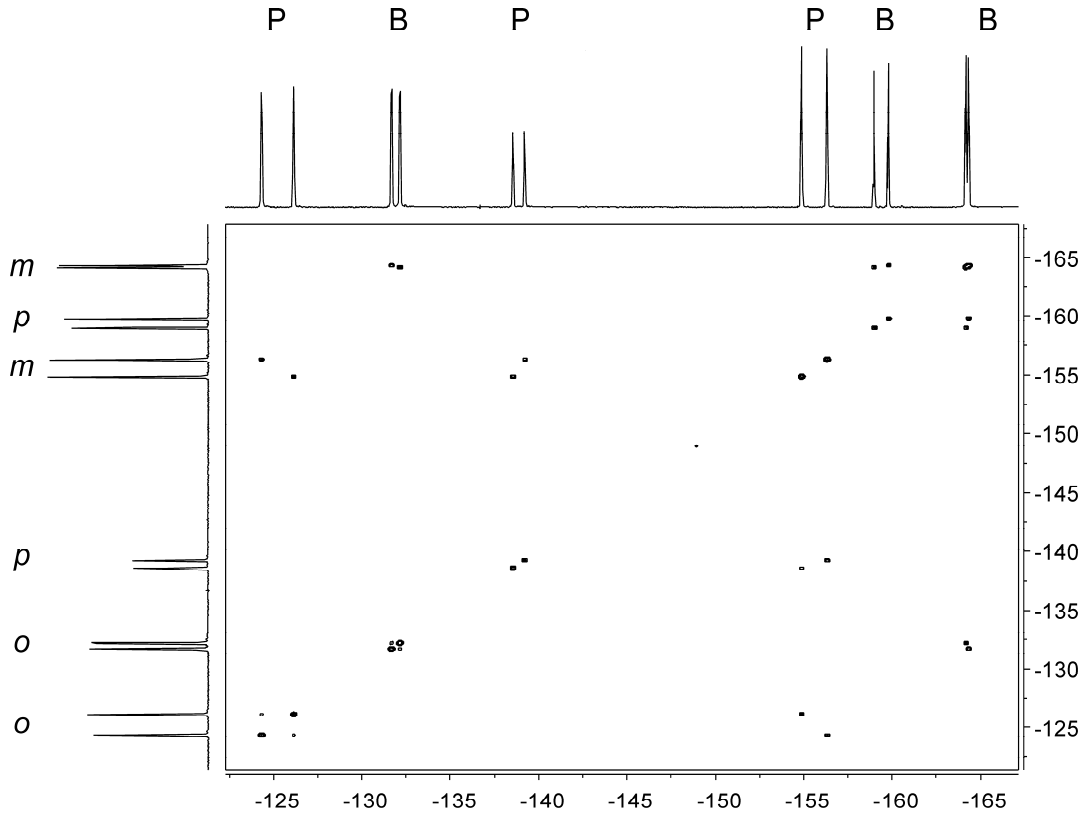
$^{13}C\{^{1}H\}$ NMR(126 MHz, $CDCl_3$(*), 298 K).



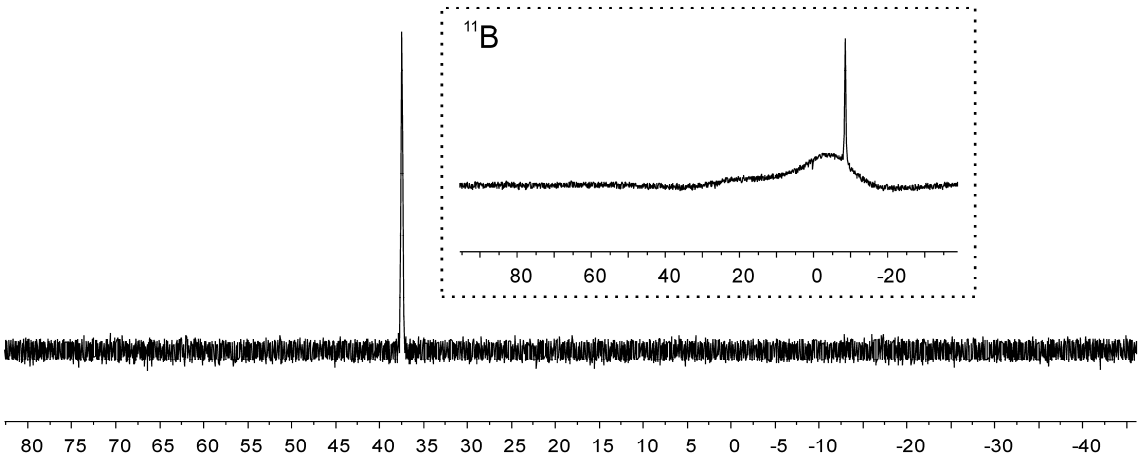
$^{1}H,^{1}H$ GCOSY (500 MHz, $CDCl_3$, 298 K; projections: ^{1}H spectrum).



$^{1}H,^{13}C$ GHSQC (500 MHz / 126 MHz, $CDCl_3$, 298 K; projections: ^{1}H and $^{13}C\{^{1}H\}$ spectrum, respectively).

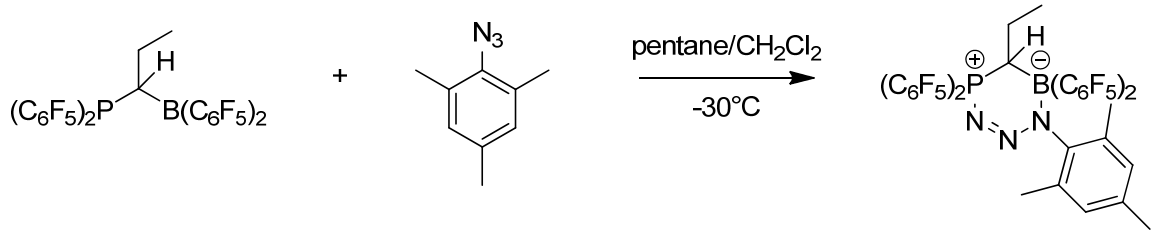


$^{19}F,^{19}F$ GCOSY (470 MHz, $CDCl_3$, 298 K; projections: ^{19}F spectrum).



^{31}P NMR(202 MHz, $CDCl_3$, 298 K) and ^{11}B NMR(160 MHz, $CDCl_3$, 298 K).

Preparation of compound 10:



Bis(pentafluorophenyl)propenyl-phosphine (200 mg, 0.49 mmol) and bis(pentafluorophenyl)borane (170 mg, 0.49 mmol) were dissolved in pentane (30 mL) and stirred for 5 min. Mesitylazide (79.4 mg, 0.49 mmol) was added and a white precipitate is formed immediately. The solution was stirred for 10 min at room temperature. The white precipitate was isolated by filtration and dried *in vacuo* (222 mg, 0.24 mmol, 50%). The product could be stored as a white solid but it slowly decomposed in CD_2Cl_2 solution (T > -10 °C).

Single crystals suitable for X-ray structural analysis were obtained by slow diffusion of mesitylazide in pentane in a solution of bis(pentafluorophenyl)propenyl-phosphine and bis(pentafluorophenyl)borane in dichloromethane at -30 °C.

^{1}H NMR (500 MHz, CD_2Cl_2, 218 K): δ 6.72, 6.58 (each br, each 1H, *m*-Mes), 3.57 (br, 1H, $^{P}CH^{B}$), 2.12, 1.97, 1.96 (each br, each 3H, CH_3^{Mes}), 2.04 (br d, $^3J_{PH}$ ~ 40 Hz), 1.83 (br) (each 1H, CH_2), 0.82 (br, CH_3).

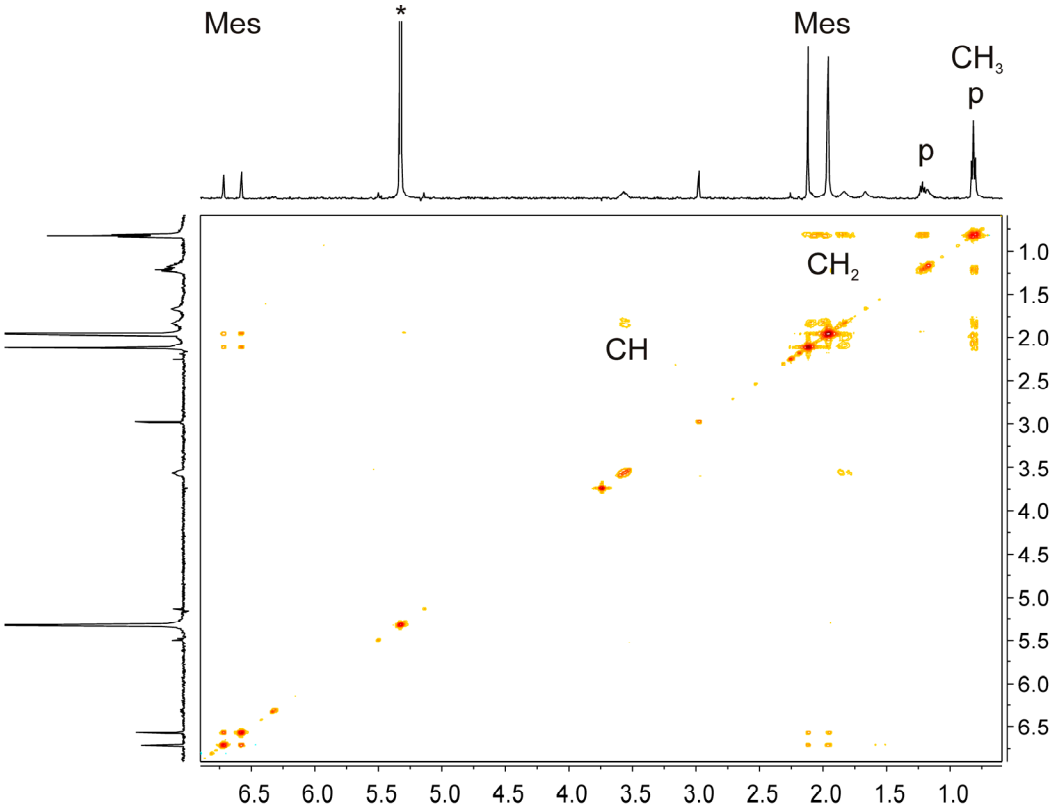
^{1}H,^{1}H GCOSY (500 MHz / 126 MHz, CD_2Cl_2, 218 K): δ(^{1}H) / δ(^{1}H) 6.72 / 6.58, 2.12, 1.97, 1.96 (*m*-Mes / *m*-Mes, CH_3^{Mes}), 6.58 / 6.72, 2.12, 1.97, 1.96 (*m*-Mes / *m*-Mes, CH_3^{Mes}), 3.57 / 1.83 ($^{P}CH^{B}$ / CH_2), 2.12 / 6.72, 6.58, 0.82 (CH_3^{Mes} / *m*-Mes, CH_3), 1.97 / 6.72, 6.58, 0.82 (CH_3^{Mes} / *m*-Mes, CH_3), 1.96 / 6.72, 6.58, 0.82 (CH_3^{Mes} / *m*-Mes, CH_3), 1.83 / 3.57, 0.82 (CH_2 / $^{P}CH^{B}$, CH_3), 0.82 / 2.12, 1.97, 1.96, 1.83 (CH_3 / CH_3^{Mes}, CH_2).

^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): δ −9.3 ($\nu_{1/2}$ ~ 100 Hz).

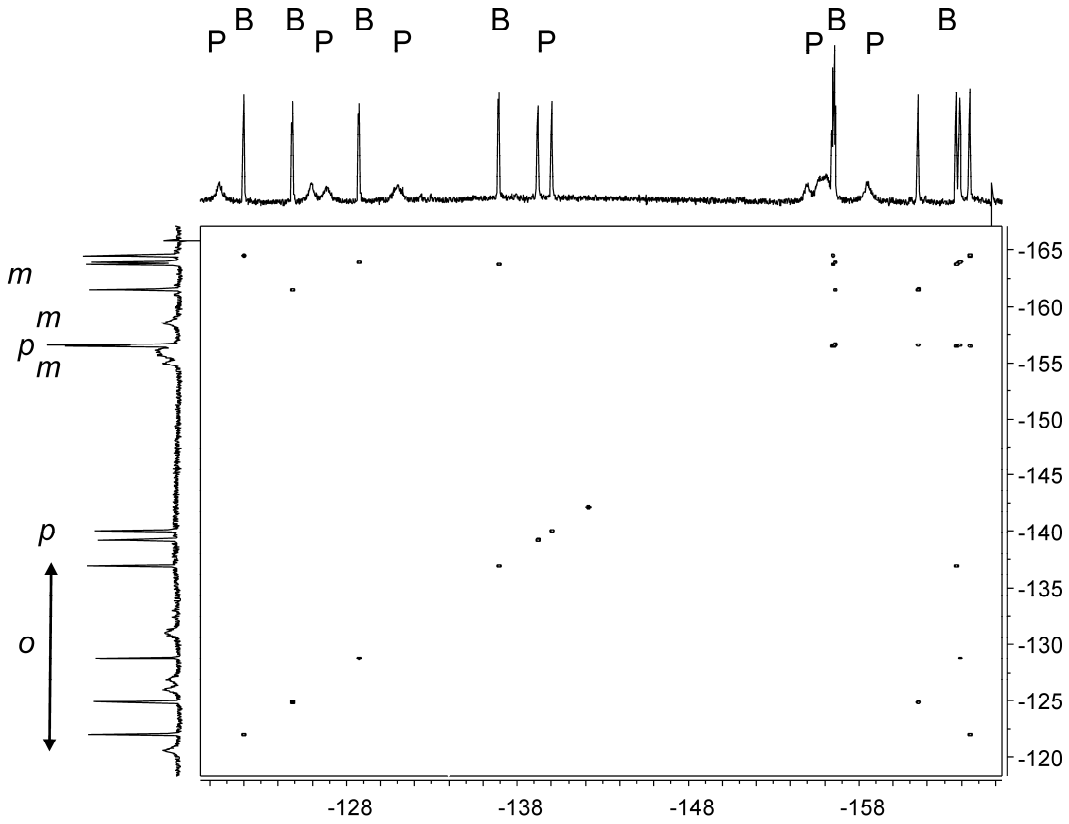
^{19}F NMR (470 MHz, CD_2Cl_2, 218 K): δ −120.6, −125.9, −126.9, −131.0 (*o*), −139.2, −140.0 (*p*), −154.9, −155.7, −156.1, −158.5 (*m*) (each br, each 1F, $P(C_6F_5)_2$), −122.0 (*o*), −136.9 (*o*'), −156.5 (*p*), −163.7 (*m*'), −164.5 (*m*) (each br, each 1F, $BC_6F_5^{A}$) [$\Delta\delta_{m,p}$ = 7.2, 8.0], −124.8 (*o*), −128.8 (*o*'), −156.6 (*p*), −161.5 (*m*), −163.9 (*m*') (each br, each 1F, $BC_6F_5^{B}$) [$\Delta\delta_{m,p}$ = 4.9, 7.3].

$^{19}F,^{19}F$ GCOSY (470 MHz, CD_2Cl_2, 218 K) [selected traces]: δ(^{19}F) / δ(^{19}F) −161.5 / −124.8, −156.6 (*m*- / *o*-, *p*-$BC_6F_5^B$), −163.7 / −136.9, −156.5 (*m*'- / *o*'-, *p*-$BC_6F_5^A$), −163.9 / −128.8, −156.6 (*m*'- / *o*'-, *p*-$BC_6F_5^B$), −164.5 / −122.0, −156.5 (*m*- / *o*-, *p*-$BC_6F_5^A$).
$^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 4.0 (218 K, $\nu_{1/2}$ ~ 50 Hz), 4.6 (298K, m).

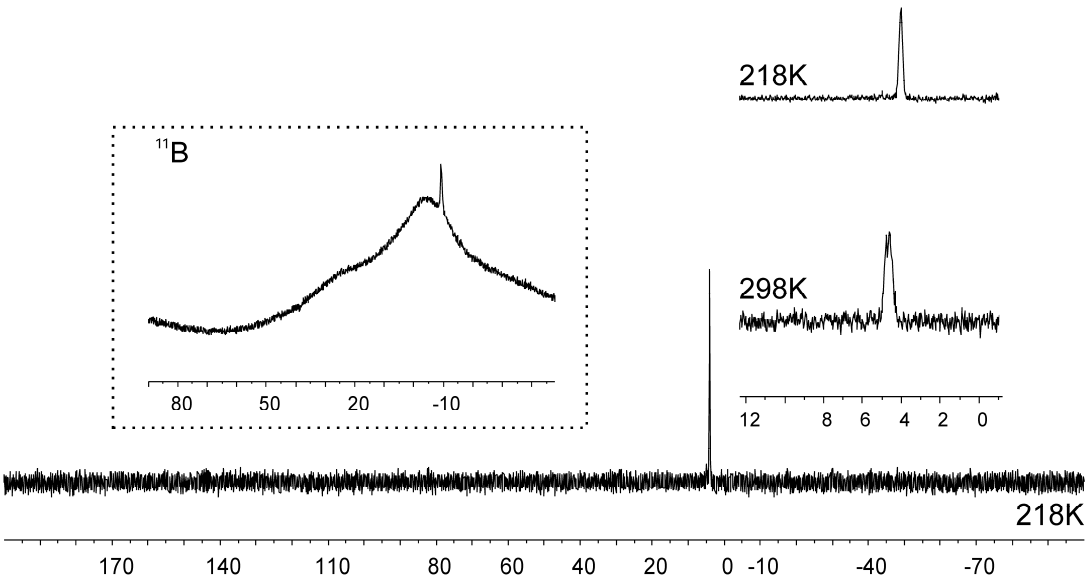
Decomposition point: 125.9 °C
IR (KBr): $\tilde{\nu}$ = 2984(w), 2956 (w), 2936 (w), 2878 (w), 2123 (w), 1645 (s), 1526 (s), 1487 (s), 1456 (s), 1384 (m), 1323 (s), 1300 (s), 1226 (w), 1104 (s), 984 (s), 936 (w), 915 (w),
Elemental analysis calcd. for $C_{36}H_{17}BF_{20}N_3P$: C 47.34; H 1.88; N 4.60. Found: C 47.05; H 2.20; N 4.10.



$^1H,^1H$ GCOSY (500 MHz / 126 MHz, CD_2Cl_2, 218 K; projections: ^1H spectrum) [p: pentane].



$^{19}F,^{19}F$ GCOSY (470 MHz, CD_2Cl_2, 218 K; projections: ^{19}F spectrum).



$^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 218 K/298 K) and $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298 K).

Crystal data for $C_{36}H_{17}BF_{20}N_3P$ (**10**), M = 913.31, monoclinic, $P2_1/n$ (No. 14), a = 9.7940(3), b = 13.5562(5), c = 26.7495(9) Å, β = 97.441(2)°, V = 3521.6(2) Å^3, D_c = 1.723 g cm^{-3}, μ = 2.005 mm^{-1}, F(000) = 1816, Z = 4, λ = 1.54178 Å, T = 223(2) K, 29109 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6200 independent (R_{int} = 0.055), and 5057 observed reflections [I ≥ 2σ(I)], 554 refined parameters, R = 0.045, wR^2 = 0.129, GoF = 1.013.