Reaction of Strongly Electrophilic Alkenylboranes with Phosphanylalkynes: Rare Examples of Intermolecular 1,1-Alkenylboration Reactions.

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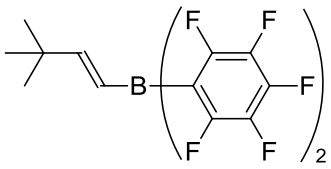
Supporting Information

Materials and Methods. 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* 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 *Agilent* DD2- 500 MHz (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz, ^{31}P: 202 MHz) and on a *Agilent* DD2- 600 MHz (^{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 $CFCl_3$ (δ = 0, external reference), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (δ = 0, external reference), ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in D_2O) (δ = 0, 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 and decomposition 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 (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*.

1990, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: Compound **3a** crystallized with two molecule in the asymmetric unit. In addition were found two toluene molecule, one of this solvent molecule is badly disordered and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek *J. Appl. Cryst.*, **2003**, *36*, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are based on two molecule of toluene per asymmetric unit (one molecule of toluene was squeezed). In compound **3b** one disordered over two position t-Bu group was found in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For the compound **3e** a disordered solvent molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are based on one half molecule of dichloromethane per asymmetric unit.

Materials: $HB(C_6F_5)_2$ [(a) R. E von H. Spence, W. E. Piers, Y. E. Sun, M. Parvez, L. R. MacGillivray and M. J. Zaworotko, *Organometallics*, 1998, **17**, 2459; (b) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492; (c) D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 809; (d) R. E. von H. Spence, D. J. Parks, W. E. Piers, M.-A. McDonald, M. J. Zaworotko and S. J. Rettig, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 1230.], boranes **1a-c** [Daniel J. Parks, Warren E. Piers, and Glenn P. A. Yap, *Organometallics*, 1998, **17**, 5492-5503.] and the P-substituted acetylenes **2a-c** [(a) A. D. Miller, S. A. Johnson, K. A. Tupper, J. L. McBee and T. D. Tilley, *Organometallics*, **2009**, *28*, 1252–1262; (b) A. Samb, B. Demerseman, P. H. Dixneuf and C. Mealli, *Organometallics*, **1988**, *7*, 26–33.] were prepared according to the literature.

Synthesis of compound 1a.



Bis(pentafluorophenyl)borane (0.309 g, 0.894 mmol, 1eq) and *tert*-butylacetylene (0.079 g, 0.967 mmol, 1.1eq) were suspended in toluene (5 ml) and stirred for 3h at room temperature. All volatiles were removed in vacuum and the residue was dissolved in pentane (10 ml). After removal of the solvent *in vacuo* the pure product **1a** (0.304 g, 0.709 mmol, 79%) was isolated as a light yellow solid.

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 6.95 (d, $^{3}J_{HH}$ = 17.5 Hz, 1H, $^{t\mathrm{Bu}}$CH=), 6.81 (d, $^{3}J_{HH}$ = 17.5 Hz, 1H, CH=), 0.92 (m, 9H, CH_3).

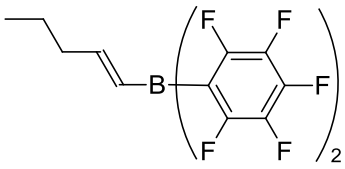
^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ = 180.4 ($^{t\mathrm{Bu}}$CH=), 130.1 (br s, CH=), 36.5 ($^{t\mathrm{Bu}}$C), 28.1 (CH_3) [C_6F_5 not listed].

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 6.95 / 180.4 ($^{t\mathrm{Bu}}$CH=), 6.81 / 130.1 (CH=), 0.92 / 28.1 (CH_3).

^{11}B{^{1}H} NMR (96 MHz, 300 K, C_6D_6): δ = 59 ($\nu_{1/2}$ ~ 600 Hz).

^{19}F{^{1}H} NMR (282 MHz, 300 K, C_6D_6): δ = -129.7 (m, 2F, *o*-C_6F_5), -148.0 (tt, $^{3}J_{FF}$ = 20.8 Hz, $^{4}J_{FF}$ = 4.1 Hz, 1F, *p*-C_6F_5), -161.1 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 13.1].

Synthesis of compound 1b.



1-Pentyne (0.153 g, 2.25 mmol) and $HB(C_6F_5)_2$ (0.625 g, 1.81 mmol) were suspended in toluene (5 ml) and stirred for 3h at room temperature. All volatiles were removed in vacuum and the crude product was suspended in pentane (15 ml). The suspension was filtered *via* cannula filtration, and the filtrate was concentrated and all volatiles were removed *in vacuo* to yield product **1b** (0.523 g, 1.26 mmol, 70%) as a yellow oil. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 2937 (m, =C-H), 1648 (s), 1602 (m), 1520 (s), 1487 (s), 1389 (m), 1154 (m), 974 (s). **HRMS:** Calc. for $C_5H_9B(C_6F_5)_2OH$: 431.06736. Found: 431.07005.

^{1}H NMR (400 MHz, 294 K, C_6D_6): δ = 6.82 (d, $^{3}J_{HH}$ = 17.5 Hz, 1H, $^{\mathrm{Pr}}$CH=), 6.79 (d, $^{3}J_{HH}$ = 17.5 Hz, 1H, CH=), 2.00 (m, 2H, =CH_2), 1.23 (m, 2H, CH_2), 0.75 (t, $^{3}J_{HH}$ = 7.5 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, 294 K, C_6D_6): δ = 172.1 ($^{\mathrm{Pr}}$CH=), 147.6 (dm, $^{1}J_{FC}$ ~ 245 Hz, C_6F_5), 143.1 (dm, $^{1}J_{FC}$ ~ 260 Hz, C_6F_5), 137.6 (dm, $^{1}J_{FC}$ ~ 255 Hz, *m*-C_6F_5), 136.2 (br, CH=), 113.9 (br, *i*-C_6F_5), 38.9 (=CH_2), 21.1 (CH_2), 13.6 (CH_3).

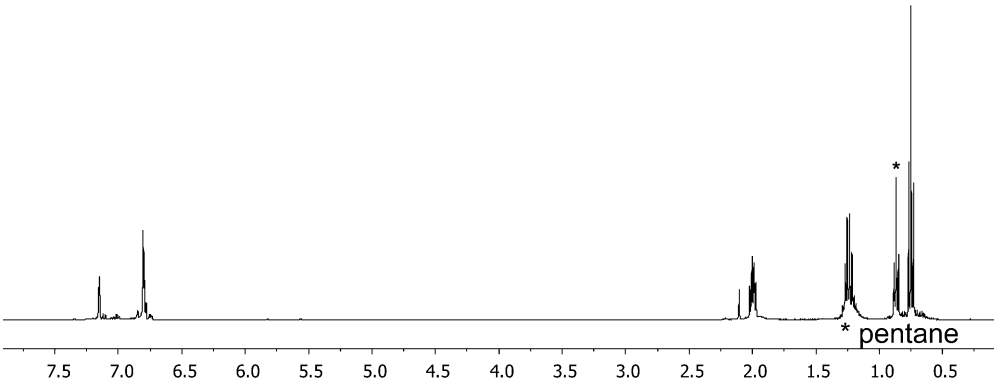
^{11}B{^{1}H} NMR (96 MHz, 300 K, C_6D_6): δ = 59 ($\nu_{1/2}$ ~ 650 Hz).

^{19}F{^{1}H} NMR (282 MHz, 300 K, C_6D_6): δ = -129.8 (m, 2F, *o*-C_6F_5), -148.3 (tt, $^{3}J_{FF}$ = 20.8 Hz, $^{4}J_{FF}$ = 4.1 Hz, 1F, *p*-C_6F_5), -161.2 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 12.9].

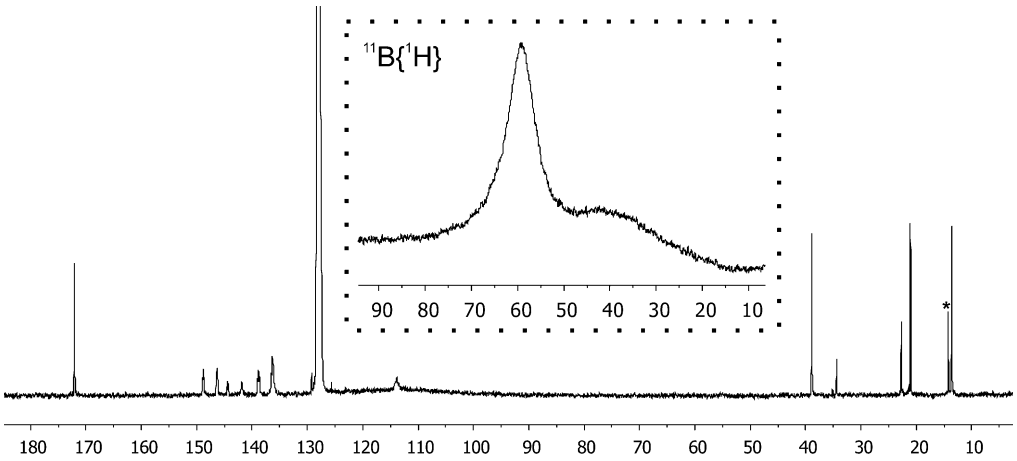
^{1}H, ^{1}H-GCOSY (400 MHz / 400 MHz, 294 K, C_6D_6): δ ^{1}H / δ ^{1}H = 6.79 / 2.00 (CH= / =CH_2), 2.00 / 6.79, 1.23 (=CH_2 / CH=, CH_2), 1.23 / 2.00, 0.75 (CH_2 / =CH_2, CH_3), 0.75 / 1.23 (CH_3 / CH_2).

^{1}H, ^{13}C-GHSQC (400 MHz / 101 MHz, 294 K, C_6D_6): δ ^{1}H / δ ^{13}C = 6.82 / 172.1 (^{Pr}CH=), 6.79 / 136.2 (CH=), 2.00 / 38.9 (=CH_2), 1.23 / 21.1 (CH_2), 0.75 / 13.6 (CH_3).

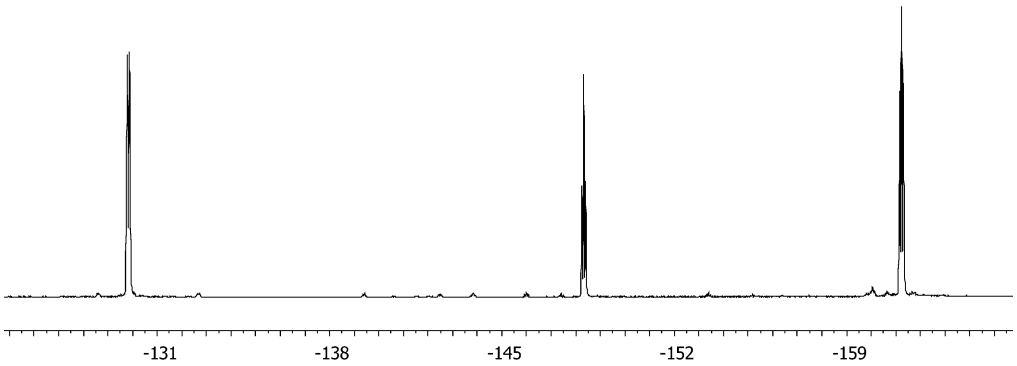
^{1}H, ^{13}C-GHMBC (400 MHz / 101 MHz, 294 K, C_6D_6): δ ^{1}H / δ ^{13}C = 6.79 / 38.9 (CH= / =CH_2), 2.00 / 172.1, 136.2, 21.1, 13.6 (=CH_2 / ^{Pr}CH, CH=, CH_2, CH_3), 1.23 / 172.1, 38.9, 13.6 (CH_2 / ^{Pr}CH, =CH_2, CH_3), 0.75 / 38.9, 21.1 (CH_3 / =CH_2, CH_2).



^{1}H NMR (400 MHz, 294 K, C_6D_6) of **1b**.

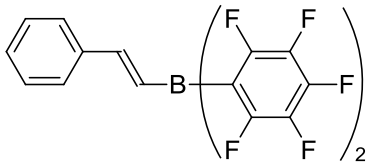


^{13}C{^{1}H} NMR (101 MHz, 294 K, C_6D_6) and **^{11}B{^{1}H} NMR** (96 MHz, 300 K) of **1b**.



^{19}F{^{1}H} NMR (282 MHz, 300 K, C_6D_6) of **1b**.

Synthesis of compound 1c.



Bis(pentafluorophenyl)borane (0.515 g, 1.49 mmol) and phenylacetylene (0.167 g, 1.64 mmol) were suspended in toluene (10 ml) and stirred for 3h at room temperature. Subsequently evaporation of the solvent *in vacuo* the residue was washed with pentane (2×15 ml). After drying in vacuum product **1c** (0.363 g, 0.811 mmol, 54%) was isolated as a light yellow solid.

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 7.51 (s, 2H, ^{Ph}CH=, CH=), 7.34 (m, 2H, *o*-Ph), 7.05 (m, 1H, *p*-Ph), 7.01 (m, 2H, *m*-Ph).

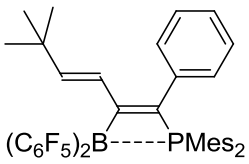
^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ = 163.4 (^{Ph}CH=), 136.2 (*i*-Ph), 132.2 (*p*-Ph), 131.9 (br, CH=), 129.6 (*o*-Ph), 129.3 (*m*-Ph), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (96 MHz, 300 K, C_6D_6): δ = 59 ($\nu_{1/2}$ ~ 760 Hz).

^{19}F{^{1}H} NMR (282 MHz, 300 K, C_6D_6): δ = -129.5 (m, 2F, *o*-C_6F_5), -148.1 (tt, $^{3}J_{FF}$ = 20.9 Hz, $^{4}J_{FF}$ = 4.0 Hz, 1F, *p*-C_6F_5), -161.0 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 12.9].

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.51 / 163.4, 131.9 (^{Ph}CH=, CH=), 7.34 / 129.6 (*o*-Ph), 7.04 / 132.2 (*p*-Ph), 7.02, 7.01 / 129.3 (*m*-Ph).

Synthesis of compound 3a.



Borane **1a** (0.200 g, 0.467 mmol) and dimesityl(phenylethinyl)-phosphane (**2a**) (0.173 g, 0.467 mmol) were dissolved in toluene (15 ml) and stirred for 7 h at 110 °C. After evaporation of the solvent in vacuum the crude product was dissolved in pentane (10 ml) and crystallized at -36 °C to yield compound **3a** (0.211 g, 0.264 mmol, 56%) as light yellow crystals. Crystals suitable for X-ray crystal structure analysis were grown by slow evaporation of a pentane solution of **3a** at -36 °C. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3026 (s, =C-H), 2960, 2866 (each s, C-H). **M.p.** (DSC): 243°C. **Anal. Calc.** for $C_{44}H_{38}BF_{10}P$: C, 66.18; H, 4.80. Found: C, 65.62; H, 4.73.

^{1}H NMR (500 MHz, 193 K, CD_2Cl_2): δ = 7.27 (br m, 3H, Ph), 7.09 (br, 2H, Ph), 7.03 (dm, $^{4}J_{PH}$ = 4.9 Hz, 1H, *m*-Mes^{A}), 6.76 (s, 1H, *m*-Mes^{B}), 6.72 (s, 1H, *m*'-Mes^{A}), 6.36 (dm, $^{4}J_{PH}$ = 3.0 Hz, 1H, *m*'-Mes^{B}), 6.08 (d, $^{3}J_{HH}$ = 15.8 Hz, 1H, =CH), 5.70 (d, $^{3}J_{HH}$ = 15.8 Hz, 1H, $^{t\text{-Bu}}$CH=), 2.51 (br, 3H, *o*-CH_3^{MesA}), 2.47 (s, 3H, *o*-CH_3^{MesB}), 2.24 (s, 3H, *p*-CH_3^{MesA}), 2.08 (s, 3H, *p*-CH_3^{MesB}), 1.69 (s, 3H, *o*'-CH_3^{MesA}), 1.61 (s, 3H, *o*'-CH_3^{MesB}), 0.70 (s, 9H, $CH_3^{t\text{-Bu}}$).

^{13}C{^{1}H} NMR (126 MHz, 193 K, CD_2Cl_2): δ = 168.6 (br d, $^{2}J_{PC}$ = 28.7 Hz, BC=), 153.4 ($^{t\text{-Bu}}$CH=), 143.1 (dd, *J* = 17.9 Hz, *J* = 2.2 Hz, *o*-Mes^{A}), 142.7 (*o*'-Mes^{A}), 142.1 (d, $^{2}J_{PC}$ = 3.1 Hz, *o*-Mes^{B}), 141.3 (d, $^{4}J_{PC}$ = 2.1 Hz, *p*-Mes^{A}), 139.8 (d, $^{4}J_{PC}$ = 2.6 Hz, *p*-Mes^{B}), 139.6 (d, $^{2}J_{PC}$ = 13.9 Hz, *o*'-Mes^{B}), 135.2 (d, $^{2}J_{PC}$ = 4.1 Hz, *i*-Ph)^{t}, 131.6 (d, $^{1}J_{PC}$ = 53.8 Hz, =CP), 130.1 (d, $^{3}J_{PC}$ = 8.0 Hz, *m*-Mes^{B}), 129.7 (d, $^{3}J_{PC}$ = 5.9 Hz, *m*'-Mes^{A}), 129.3 (d, $^{3}J_{PC}$ = 9.4 Hz, *m*-Mes^{A}), 128.9 (d, $^{3}J_{PC}$ = 9.2 Hz, *m*'-Mes^{B}), 127.7, 127.0 (Ph), 123.8 (d, $^{1}J_{PC}$ = 27.2 Hz, *i*-Mes^{A}), 123.6 (d, $^{1}J_{PC}$ = 41.5 Hz, *i*-Mes^{B}), 119.5 (d, $^{3}J_{PC}$ = 45.3 Hz, =CH), 33.3 (d, $^{5}J_{PC}$ = 0.9 Hz, $^{t\text{-Bu}}$C), 27.6 ($CH_3^{t\text{-Bu}}$), 24.9 (dd, *J* = 5.4 Hz, *J* = 2.9 Hz, *o*-CH_3^{MesB}), 23.5 (br d, $^{3}J_{PC}$ = 9.7 Hz, *o*-CH_3^{MesA}), 22.5 (d, $^{3}J_{PC}$ = 2.2 Hz, *o*'-CH_3^{MesA}), 21.8 (dd, *J* = 10.0 Hz, *J* = 3.2 Hz, *o*'-CH_3^{MesB}), 20.6 (d, $^{5}J_{PC}$ = 1.0 Hz, *p*-CH_3^{MesA}), 19.9 (d, $^{5}J_{PC}$ = 1.1 Hz, *p*-CH_3^{MesB}), [C_6F_5 not listed; ^{t} tentatively assigned].

^{11}B{^{1}H} NMR (160 MHz, 299 K, CD_2Cl_2): δ = -0.1 ($\nu_{1/2}$ ~ 350 Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2): δ = 12.0 ($\nu_{1/2}$ ~ 40 Hz).

^{31}P{^{1}H} NMR (202 MHz, 193 K, CD_2Cl_2): δ = 9.3 (d, *J* ~ 28 Hz).

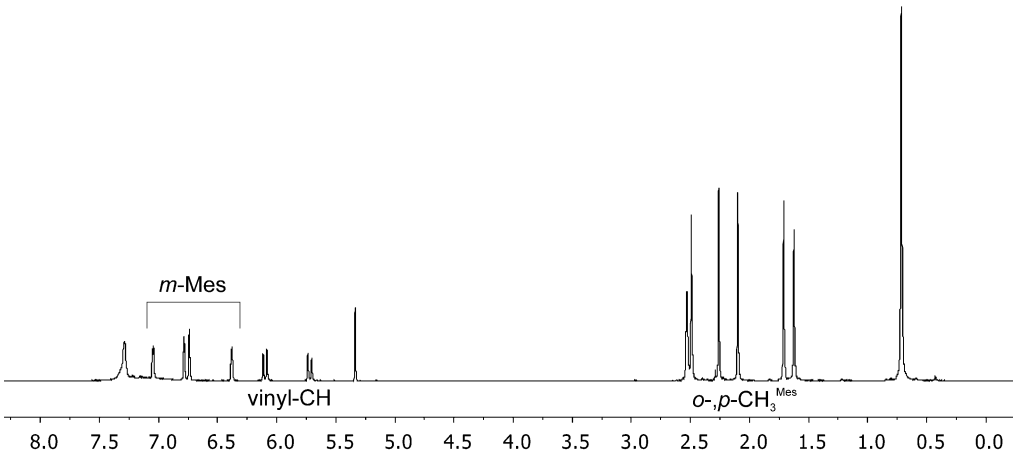
^{19}F NMR (470 MHz, 213 K, CD_2Cl_2): δ = -127.0 (*o*), -131.4 (*o*'), -158.3 (t, $^{3}J_{FF}$ = 21.3 Hz, *p*), -164.5 (*m*), -164.7 (*m*') (each m, each 1F, $^{A}C_6F_5$)[$\Delta\delta^{19}F_{m,p}$ = 6.2, $\Delta\delta^{19}F_{m',p}$ = 6.4], -128.6 (*o*), -130.5 (*o*'), -159.5 (*p*), -165.7 (*m*'), -165.9 (*m*) (each m, each 1F, $^{B}C_6F_5$)[$\Delta\delta^{19}F_{m',p}$ = 6.2, $\Delta\delta^{19}F_{m,p}$ = 6.4].

^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, 193 K, CD_2Cl_2): δ^{1}H / δ^{1}H = 7.03 / 6.72, 2.24, 1.69 (*m*-Mes^{A} / *m*'-Mes^{A}, *p*-, *o*'-CH_3^{MesA}), 6.76 / 6.36, 2.47, 2.08, 1.61 (*m*-Mes^{B} / *m*'-Mes^{B}, *o*-, *p*-, *o*'-CH_3^{MesB}), 6.72 / 7.03, 2.51, 2.24, 1.69 (*m*'-Mes^{A} / *m*-Mes^{A}, *o*- *p*-, *o*'-CH_3^{MesA}), 6.08 / 5.70 (=CH / $^{t\text{-Bu}}$CH=).

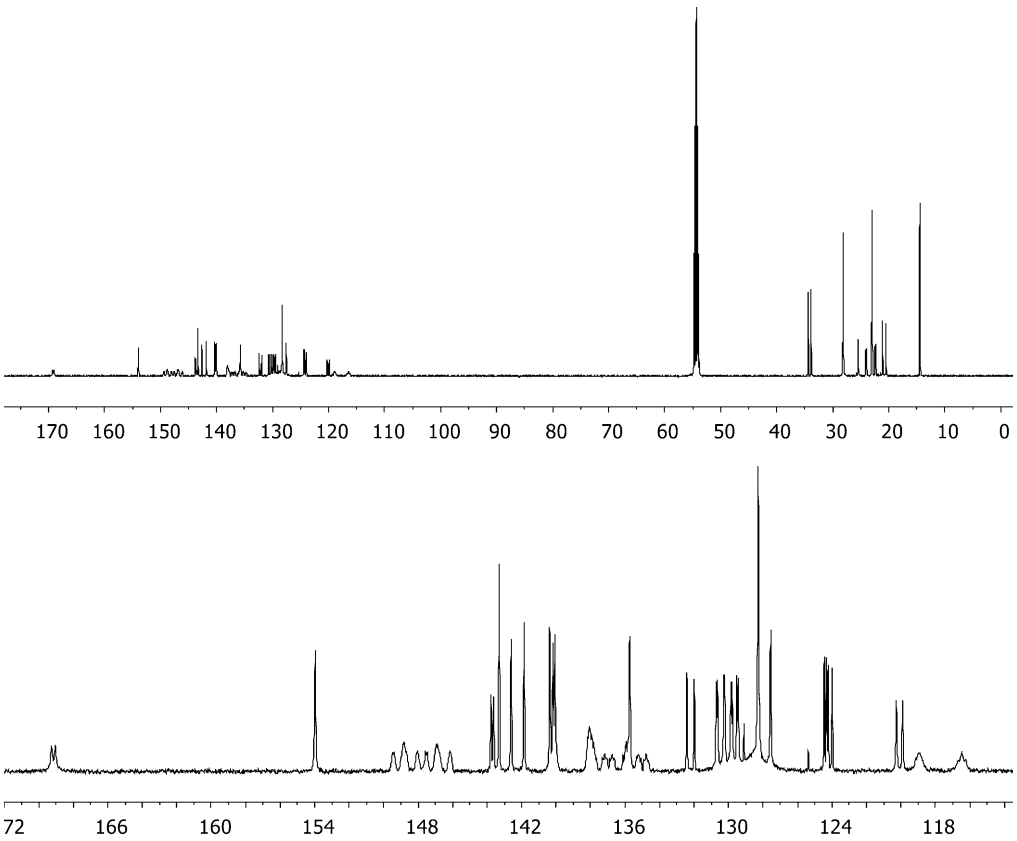
^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, 193 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.27, 7.09 / 127.7 (Ph), 7.27 / 127.0 (Ph), 7.03 / 129.3 (*m*-Mes^{A}), 6.76 / 130.1 (*m*-Mes^{B}), 6.72 / 129.7 (*m*'-Mes^{A}), 6.36 / 128.9 (*m*'-Mes^{B}), 6.08 / 119.5 (=CH), 5.70 / 153.4 ($^{t\text{-Bu}}$CH=), 2.51 / 23.5 (*o*-CH_3^{MesA}), 2.47 / 24.9 (*o*-CH_3^{MesB}), 2.24 / 20.6 (*p*-CH_3^{MesA}), 2.08 / 19.9 (*p*-CH_3^{MesB}), 1.69 / 22.5 (*o*'-CH_3^{MesA}), 1.61 / 21.8 (*o*'-CH_3^{MesB}), 0.70 / 27.6 ($CH_3^{t\text{-Bu}}$).

^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, 193 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.03 / 129.7, 123.8, 23.5, 20.6 (*m*-Mes^{A} / *m*'-Mes^{A}, *i*-Mes^{A}, *o*-, *p*-CH_3^{MesA}), 6.76 / 128.9, 123.6, 24.9, 19.9 (*m*-Mes^{B} / *m*'-Mes^{B}, *i*-Mes^{B}, *o*-, *p*-CH_3^{MesB}), 6.72 / 129.3, 123.8, 22.5, 20.6 (*m*'-Mes^{A} / *m*-Mes^{A}, *i*-Mes^{A}, *o*'-, *p*-CH_3^{MesA}), 6.36 / 130.1, 123.6, 21.8, 19.9 (*m*'-Mes^{B} / *m*-Mes^{B}, *i*-Mes^{B}, *o*'-, *p*-CH_3^{MesB}), 6.08 / 131.6, 33.3 (=CH / =CP, $^{t\text{-Bu}}$C), 5.70 / 168.6, 33.3, 27.6 ($^{t\text{-Bu}}$CH= / BC=, $^{t\text{-Bu}}$C, $CH_3^{t\text{-Bu}}$), 2.51 / 143.1, 129.3, 123.8 (*o*-CH_3^{MesA} / *o*-, *m*-, *i*- Mes^{A}), 2.47 / 142.1, 130.1, 123.6 (*o*-CH_3^{MesB} / *o*-, *m*-, *i*- Mes^{B}), 2.24 / 141.3, 129.7, 129.3 (*p*-CH_3^{MesA} / *p*-, *m*'-, *m*- Mes^{A}), 2.08 / 139.8, 130.1, 128.9 (*p*-CH_3^{MesB} / *p*-, *m*-, *m*'- Mes^{B}), 1.69 / 142.7, 129.7, 123.8 (*o*'-CH_3^{MesA} / *o*'-, *m*'-, *i*- Mes^{A}), 1.61 / 139.6, 128.9, 123.6 (*o*'-CH_3^{MesB} / *o*'-, *m*'-, *i*- Mes^{B}), 0.70 / 153.4, 33.3 ($CH_3^{t\text{-Bu}}$ / $^{t\text{-Bu}}$CH=, $^{t\text{-Bu}}$C).

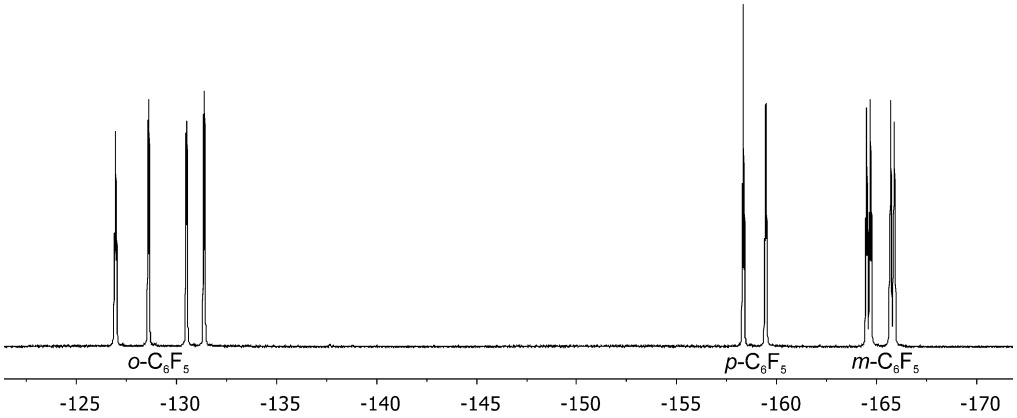
^{19}F / ^{19}F GCOSY (470 MHz / 470 MHz, 213 K, CD_2Cl_2): δ ^{19}F / δ ^{19}F = -127.0 / -164.5 (*o*-, *m*-$^{A}C_6F_5$), -128.6 / -165.9 (*o*-, *m*-$^{B}C_6F_5$), -130.5 / -165.7 (*o*'-, *m*'-$^{B}C_6F_5$), -131.4 / -164.7 (*o*'-, *m*'-$^{A}C_6F_5$), -158.3 / -164.5, -164.7 (*p*- / *m*-, *m*'-$^{A}C_6F_5$), -159.5 / -165.7, -165.9 (*p*- / *m*-, *m*'-$^{B}C_6F_5$), -164.5 / -127.0, -158.3 (*m*- / *o*-, *p*-$^{A}C_6F_5$), -164.7 / -131.4, -158.3 (*m*'- / *o*'-, *p*-$^{A}C_6F_5$), -165.7 / -130.5, -159.5 (*m*- / *o*-, *p*-$^{B}C_6F_5$), -165.9 / -128.6, -159.5 (*m*'- / *o*'-, *p*-$^{B}C_6F_5$).



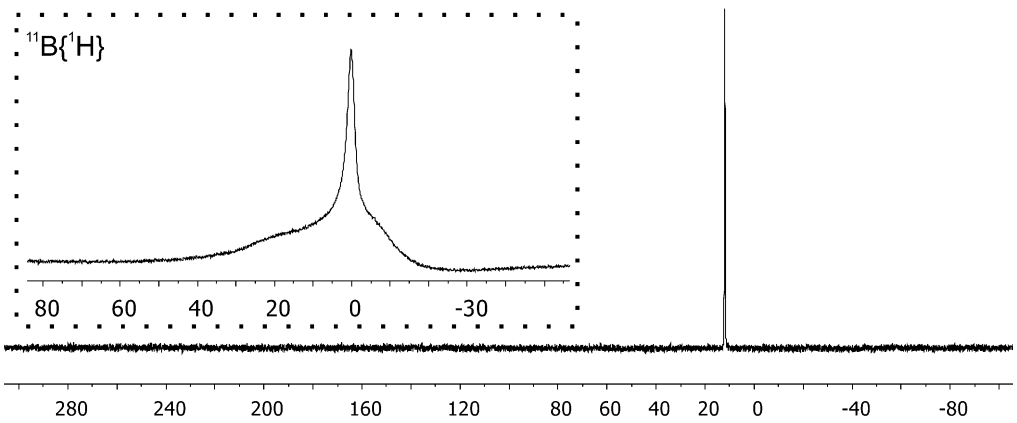
^{1}H NMR (500 MHz, 193 K, CD_2Cl_2) of **3a**.



$^{13}C\{^{1}H\}$ NMR (126 MHz, 193 K, CD_2Cl_2) of **3a**.

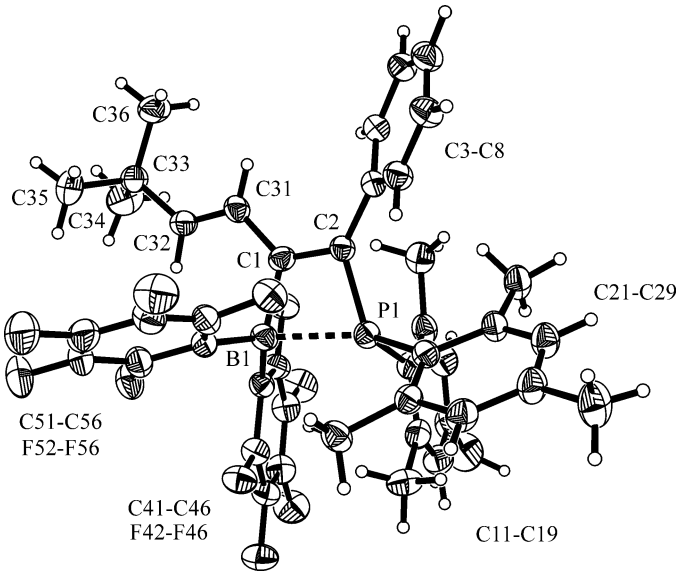


^{19}F NMR (470 MHz, 213 K, CD_2Cl_2) of **3a**.

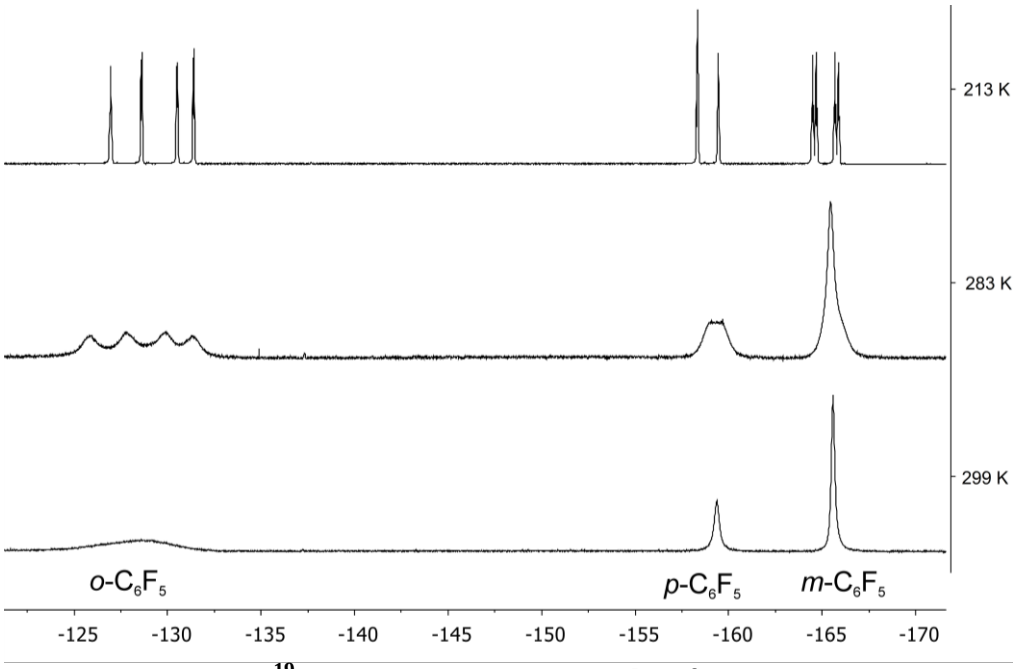


$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) and **$^{31}P\{^{1}H\}$ NMR** (202 MHz) of **3a**.

X-Ray crystal structure analysis of compound **3a**. formula $C_{44}H_{38}BF_{10}P \cdot C_7H_8$, M = 890.66, colourless crystal, 0.10 x 0.07 x 0.03 mm, a = 11.3861(3), b = 17.9307(5), c = 22.8610(6) Å, α = 95.861(4), β = 100.979(5), γ = 92.959(7)°, V = 4511.9(2) Å^3, ρ_{calc} = 1.311 gcm^{-3}, μ = 1.198 mm^{-1}, empirical absorption correction (0.889 ≤ T ≤ 0.964), Z = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å,T = 223(2) K, ω and φ scans, 62853 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 14637 independent (R_{int} = 0.074) and 7434 observed reflections [I>2σ(I)], 1090 refined parameters, R = 0.074, wR^2 = 0.211, max. (min.) residual electron density 0.45 (-0.36) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



Dynamic ^{19}F NMR:



^{19}F NMR (470 MHz, CD_2Cl_2) of **3a**.

$\Delta G^{\neq} = RT_c(22.96 + \ln(T_c/\delta\nu)$ [Jmol^{-1}]
R = 8.314 J(mol K)$^{-1}$
1 cal = 4.187 J

$\Delta G^{\neq}$ (T_c = 283 K; $\Delta\nu$(*p*-BC_6F_5, 213 K) = 530 Hz) = 12.5 kcal/mol

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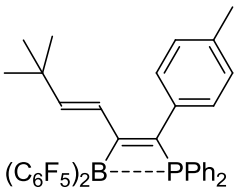
Synthesis of compound 3b.



Borane **1a** (0.200 g, 0.467 mmol) and diphenyl(*p*-tolylethynyl)-phosphane (**2b**) (0.140 g, 0.467 mmol) were dissolved in toluene (10 ml) and stirred for 5 h at 70 °C. Subsequently all volatiles were removed *in vacuo* and the residue was washed with pentane (3×10 ml). After drying in vacuum product **3b** (0.166 g, 0.228 mmol, 49%) was isolated as a light yellow solid. Crystals suitable for X-ray crystal structure analysis were grown by slow evaporation of a deuterated benzene solution of **3b** at room temperature. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3061, 3028 (each w, =C-H), 2963 (m), 2869 (w) (C-H). **M.p.** (DSC): 212°C. **Anal. Calc.** for $C_{39}H_{28}BF_{10}P$: C, 64.31; H, 3.87. Found: C, 64.15; H, 3.68.

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 7.40 (m, 2H, *o*-Tol), 7.31 (m, 4H, *o*-Ph), 7.03 (dd, $^3J_{HH}$ = 15.9 Hz, $^4J_{PH}$ = 2.0 Hz, 1H, =CH), 6.88 (m, 2H, *m*-Tol), 6.85 (m, 2H, *p*-Ph), 6.77 (m,

4H, *m*-Ph), 6.30 (d, $^{3}J_{HH}$ = 15.9 Hz, 1H, $^{t\text{-Bu}}$CH=), 2.02 (s, 3H, *p*-CH_3^{Tol}), 0.91 (s, 9H, $CH_3^{t\text{-Bu}}$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ = 176.9 (br, BC=), 155.3 ($^{t\text{-Bu}}$CH=), 148.7 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 140.2 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 138.2 (d, $^{5}J_{PC}$ = 1.1 Hz, *p*-Tol), 137.5 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 132.9 (d, $^{2}J_{PC}$ = 3.2 Hz, *i*-Tol), 132.2 (d, $^{2}J_{PC}$ = 9.2 Hz, *o*-Ph), 131.7 (d, $^{4}J_{PC}$ = 3.0 Hz, *p*-Ph), 129.9 (*m*-Tol), 128.9 (d, $^{3}J_{PC}$ = 10.4 Hz, *m*-Ph), 128.7 (d, $^{3}J_{PC}$ = 5.5 Hz, *o*-Tol), 126.9 (d, $^{1}J_{PC}$ = 40.2 Hz, *i*-Ph), 122.8 (d, $^{3}J_{PC}$ = 46.6 Hz, =CH), 117.3 (br, *i*-C_6F_5), 33.9 (d, $^{5}J_{PC}$ = 0.9 Hz, $^{t\text{-Bu}}$C), 28.9 ($CH_3^{t\text{-Bu}}$), 21.1 (*p*-CH_3^{Tol}), n.o. (=CP).

^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ = -7.6 ($\nu_{1/2}$ ~ 260 Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, C_6D_6): δ = 13.4 ($\nu_{1/2}$ ~ 60 Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = -129.1 (m, 2F, *o*-C_6F_5), -157.8 (td, $^{3}J_{FF}$ = 20.9 Hz, $^{4}J_{FF}$ = 5.1 Hz, 1F, *p*-C_6F_5), -164.3 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 6.5].

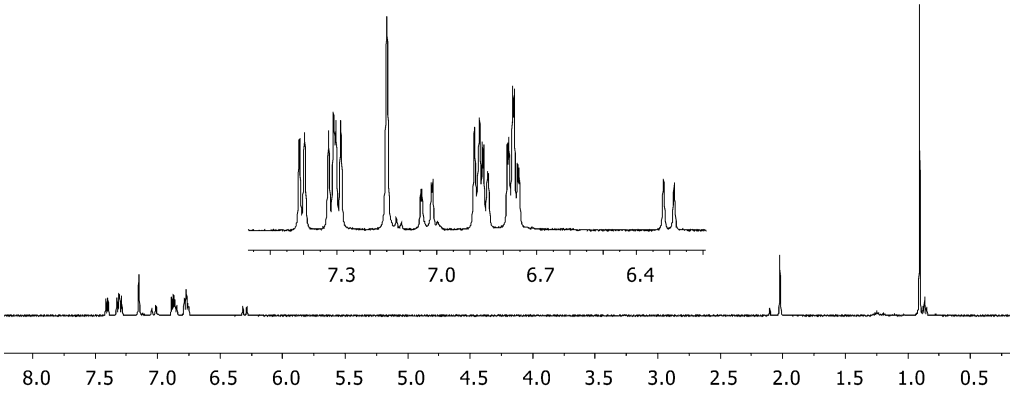
^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{1}H = 7.40 / 6.88, 2.02 (*o*-Tol / *m*-Tol, *p*-CH_3^{Tol}), 7.31 / 6.77 (*o*-Ph / *m*-Ph), 7.03 / 6.30, 0.91 (=CH / $^{t\text{-Bu}}$CH=, $CH_3^{t\text{-Bu}}$), 6.85 / 6.77 (*p*-Ph / *m*-Ph), 6.77 / 7.31, 6.85 (*m*-Ph / *o*-, *p*-Ph) 6.30 / 7.03 ($^{t\text{-Bu}}$CH= / CH=).

TOCSY (500 MHz, 299 K, C_6D_6): δ $(^{1}H)_{irr.}$ / δ $(^{1}H)_{res.}$ = 7.40 / 6.88, 2.02 (*o*-Tol / *m*-Tol, *p*-CH_3^{Tol}), 7.31 / 6.85, 6.77 (*o*-Ph / *p*-, *m*-Ph), 7.03 / 6.30, 0.91 ($^{t\text{-Bu}}$CH= / =CH, $CH_3^{t\text{-Bu}}$).

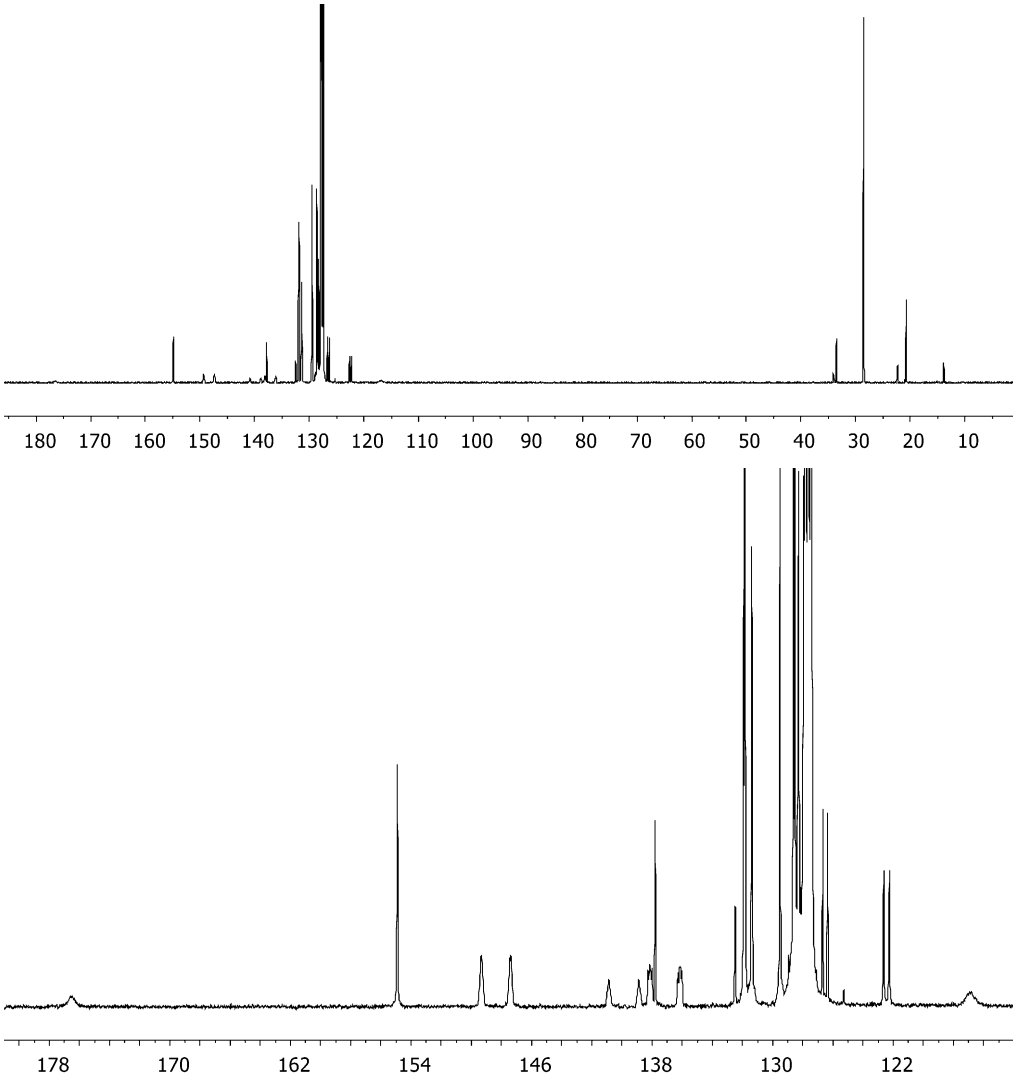
NOE (500 MHz, 299 K, C_6D_6): δ $(^{1}H)_{irr.}$ / δ $(^{1}H)_{res.}$ = 7.40 / 7.31, 7.03, 6.88 (*o*-Tol / *o*-Ph, $^{t\text{-Bu}}$CH=, *m*-Tol), 7.31 / 7.40, 6.77 (*o*-Ph / *o*-Tol, *m*-Ph), 7.03 / 7.40, 6.30, 0.91 (=CH / *o*-Tol, $^{t\text{-Bu}}$CH=, $CH_3^{t\text{-Bu}}$), 6.88 / 7.40, 6.77, 2.02 (*m*-Tol / *o*-Tol, *m*-Ph, *p*-CH_3^{Tol}), 6.85 / 6.77 (*p*-Ph / *m*-Ph), 6.77 / 7.31 (*m*-Ph / *o*-Ph), 6.30 / 7.03, 0.91 ($^{t\text{-Bu}}$CH= / =CH, $CH_3^{t\text{-Bu}}$), 2.02 / 6.88 (*p*-CH_3^{Tol} / *m*-Tol), 0.91 / 7.03, 6.30 ($CH_3^{t\text{-Bu}}$ / =CH, $^{t\text{-Bu}}$CH=).

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.40 / 128.7 (*o*-Tol), 7.31 / 132.2 (*o*-Ph), 7.03 / 122.8 (=CH), 6.88 / 129.9 (*m*-Tol), 6.85 / 131.7 (*p*-Ph), 6.77 / 128.9 (*m*-Ph), 6.30 / 155.3 ($^{t\text{-Bu}}$CH=), 2.02 / 21.1 (*p*-CH_3^{Tol}), 0.91 / 28.9 ($CH_3^{t\text{-Bu}}$).

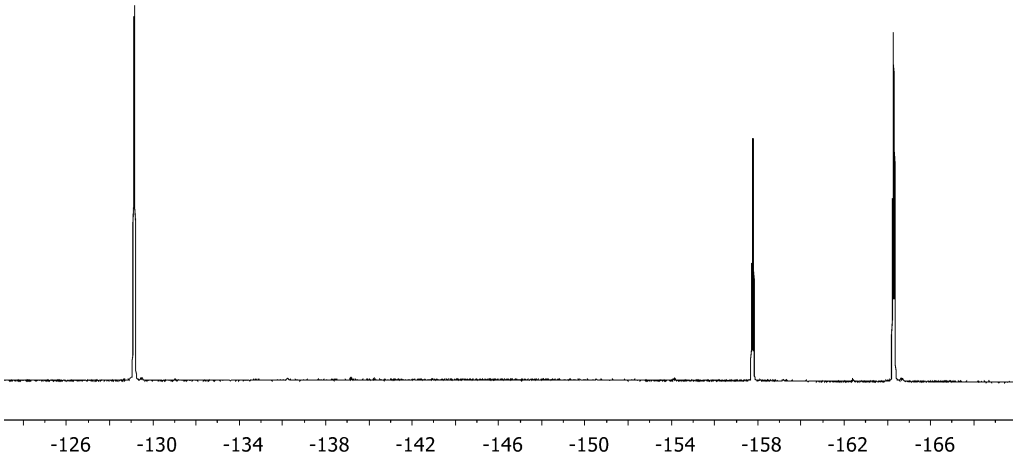
^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.40 / 138.2 (*o*-Tol / *p*-Tol), 7.31 / 131.7, 128.9 (*o*-Ph / *p*-Ph, *m*-Ph), 7.03 / 33.5 (=CH / $^{t\text{-Bu}}$C), 6.88 / 132.9, 128.7, 21.1 (*m*-Tol / *i*-Tol, *o*-Tol, *p*-CH_3^{Tol}), 6.85 / 132.2 (*p*-Ph / *o*-Ph), 6.77 / 132.2, 126.9 (*m*-Ph / *o*-, *i*-Ph), 6.30 / 176.9, 33.9, 28.9 ($^{t\text{-Bu}}$CH= / BC=, $^{t\text{-Bu}}$C, $CH_3^{t\text{-Bu}}$), 2.02 / 138.2, 129.9, 128.7 (*p*-CH_3^{Tol} / *p*-, *m*-, *o*-Tol), 0.91 / 155.3, 33.9 ($CH_3^{t\text{-Bu}}$ / $^{t\text{-Bu}}$CH=, $^{t\text{-Bu}}$C).



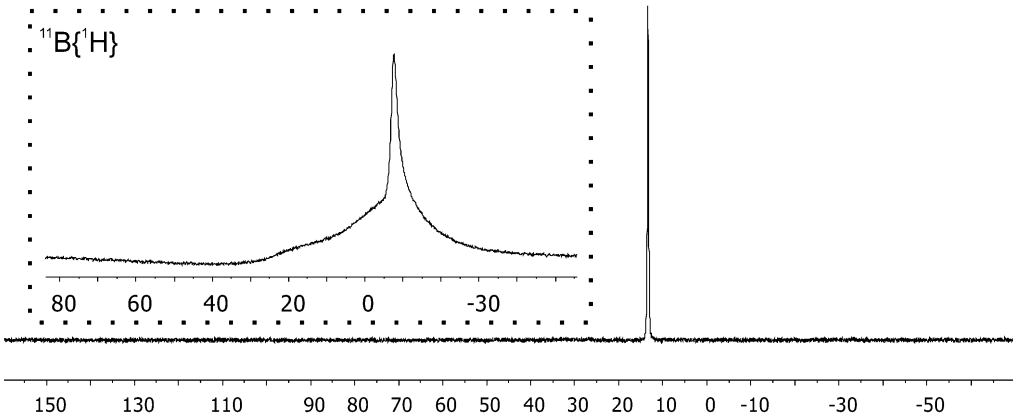
^{1}H NMR (500 MHz, 299 K, C_6D_6) of **3b**.



^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6) of **3b**.

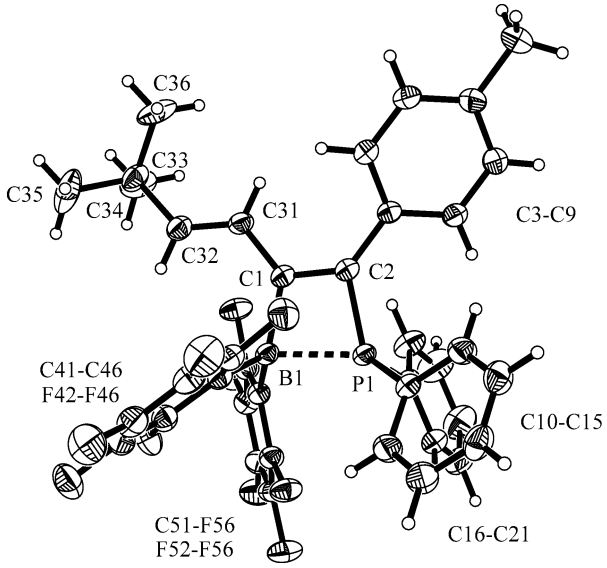


^{19}F NMR (470 MHz, 299 K, C_6D_6) of **3b**.

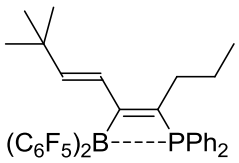


^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6) and **^{31}P{^{1}H} NMR** (202 MHz) of **3b**.

X-Ray crystal structure analysis of compound **3b**. formula $C_{39}H_{28}BF_{10}P$, M = 728.39, colourless crystal, 0.25 x 0.23 x 0.10 mm, a = 11.6685(2), b = 13.0796(5), c = 13.1348(7) Å, α = 102.092(4), β = 100.916(2), γ = 111.060(3)°, V = 1750.60(12) Å^3, ρ_{calc} = 1.382 gcm^{-3}, μ = 1.420 mm^{-1}, empirical absorption correction (0.717 ≤ T ≤ 0.871), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å,T = 223(2) K, ω and φ scans, 23167 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6007 independent (R_{int} = 0.033) and 5717 observed reflections [I>2σ(I)], 498 refined parameters, R = 0.039, wR^2 = 0.108, max. (min.) residual electron density 0.17 (-0.24) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.



Synthesis of compound 3c.



Borane **1a** (0.177 g, 0.701 mmol, 1eq) and diphenyl(1-pentinyl)-phosphane (**2c**) (0.300 g, 0.701 mmol, 1eq) were dissolved in toluene (10 ml) and heated up at 110 °C for 7 h. After removal of all volatiles *in vacuo* the residue was extracted with pentane (15 ml) *via* filter cannula. The solvent was removed to yield **3c** (0.299 g, 0.439 mmol, 63%) as a light green solid. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3066, 3013 (each w, =C-H), 2957, 2870 (each m, C-H). **M.p.** (DSC): 150°C. **Anal. Calc.** for $C_{35}H_{28}BF_{10}P$: C, 61.79; H, 4.15. Found: C, 61.73; H, 4.19.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.16 (m, 4H, *o*-Ph), 6.90 (m, 2H, *p*-Ph), 6.83 (m, 4H, *m*-Ph), 6.65 (dd, $^{3}J_{HH}$ = 15.8 Hz, $^{4}J_{PH}$ = 2.3 Hz, 1H, =CH), 6.12 (d, $^{3}J_{HH}$ = 15.8 Hz, 1H, $^{t\text{-Bu}}$CH=), 2.36 (m, 2H, $^{=}CH_2$), 1.40 (m, 2H, CH_2), 0.93 (s, 9H, $CH_3{}^{t\text{-Bu}}$), 0.77 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 177.5 (br, BC=), 153.9 ($^{t\text{-Bu}}$CH=), 148.6 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 140.1 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 137.4 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 132.3 (d, $^{2}J_{PC}$ = 9.2 Hz, *o*-Ph), 131.6 (d, $^{4}J_{PC}$ = 2.9 Hz, *p*-Ph), 130.8 (d, $^{1}J_{PC}$ = 54.1 Hz, =CP), 128.8 (d, $^{3}J_{PC}$ = 10.2 Hz, *m*-Ph), 127.7 (d, $^{1}J_{PC}$ = 39.6 Hz, *i*-Ph), 121.4 (d, $^{3}J_{PC}$ = 48.5 Hz, =CH), 117.4 (br, *i*-C_6F_5), 33.7 (d, $^{5}J_{PC}$ = 1.2 Hz, $^{t\text{-Bu}}$C), 30.8 (d, $^{2}J_{PC}$ = 2.8 Hz, $^{=}CH_2$), 29.0 ($CH_3{}^{t\text{-Bu}}$), 22.8 (d, $^{3}J_{PC}$ = 2.8 Hz, CH_2), 14.3 (CH_3).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = -7.4 ($\nu_{1/2}$ ~ 300 Hz).

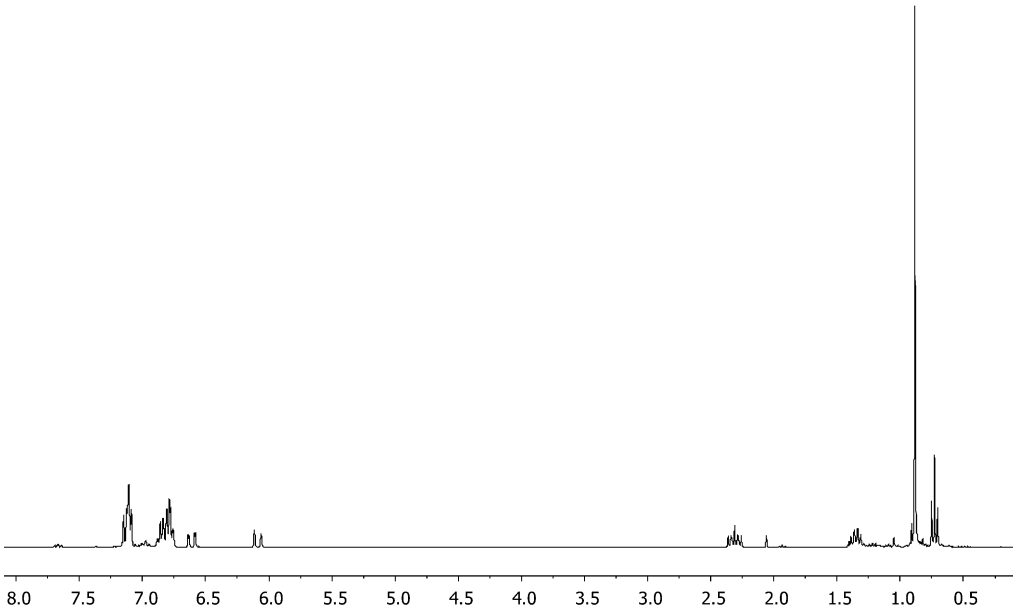
^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = 14.3 ($\nu_{1/2}$ ~ 60 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -129.4 (m, 2F, *o*-C_6F_5), -158.1 (td, $^3J_{FF}$ = 20.9 Hz, $^4J_{FF}$ = 5.1 Hz,1F, *p*-C_6F_5), -164.5 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 6.4].

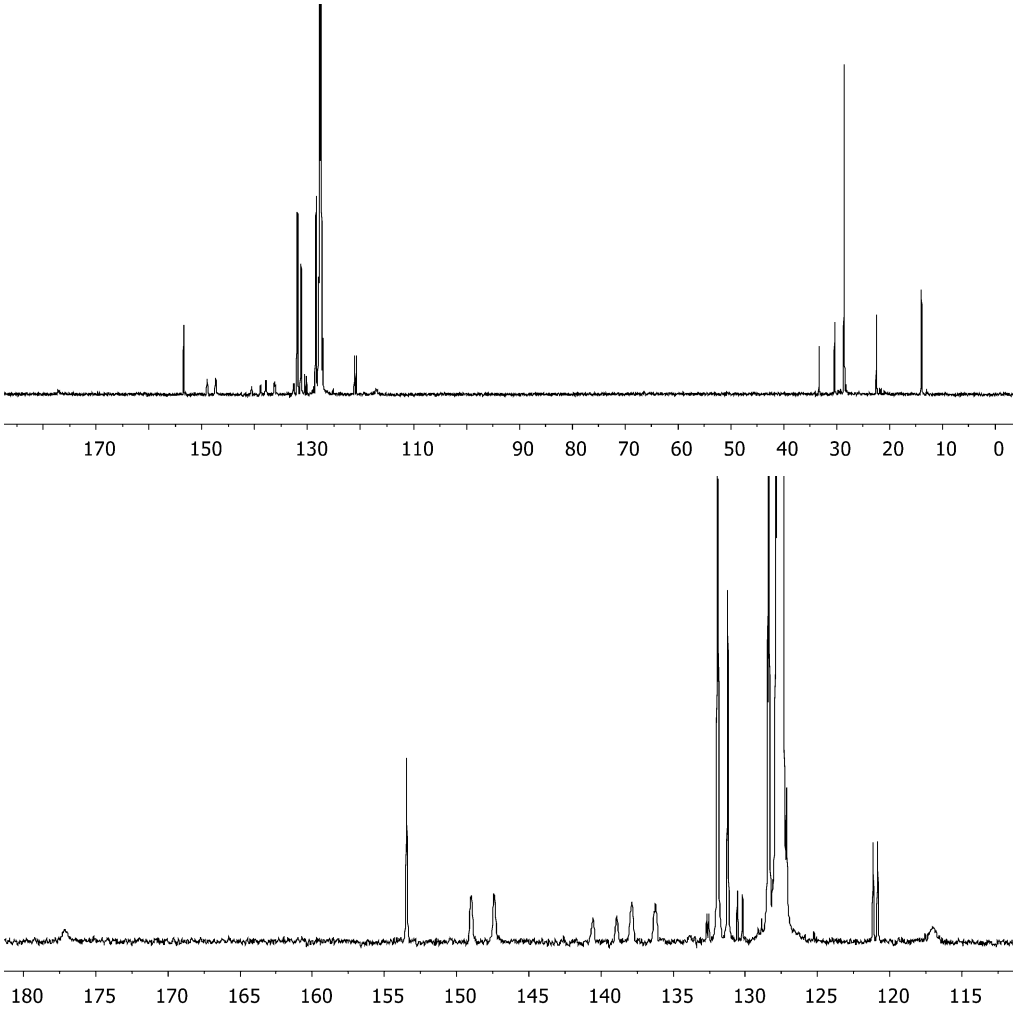
^{1}H, ^{1}H-GCOSY (600 MHz / 600 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{1}H = 7.16 / 6.83 (*o*-Ph / *m*-Ph), 6.90 / 6.83 (*p*-Ph / *m*-Ph), 6.83 / 7.16, 6.90 (*m*-Ph / *o*-, *p*-Ph), 6.65 / 6.12, 0.93 (=CH / $^{t\text{-Bu}}$CH=, $CH_3{}^{t\text{-Bu}}$), 6.12 / 6.65 ($^{t\text{-Bu}}$CH= / =CH), 2.36 / 1.40 ($^{=}CH_2$ / CH_2), 1.40 / 2.36, 0.77 (CH_2 / $^{=}CH_2$, CH_3), 0.77 / 1.40 (CH_3 / CH_2).

^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.16 / 132.3 (*o*-Ph), 6.90 / 131.6 (*p*-Ph), 6.83 / 128.8 (*m*-Ph), 6.65 / 121.4 (=CH), 6.12 / 153.9 ($^{t\text{-Bu}}$CH=), 2.36 / 30.8 ($^{=}CH_2$), 1.40 / 22.8 (CH_2), 0.93 / 29.0 ($CH_3{}^{t\text{-Bu}}$), 0.77 / 14.3 (CH_3).

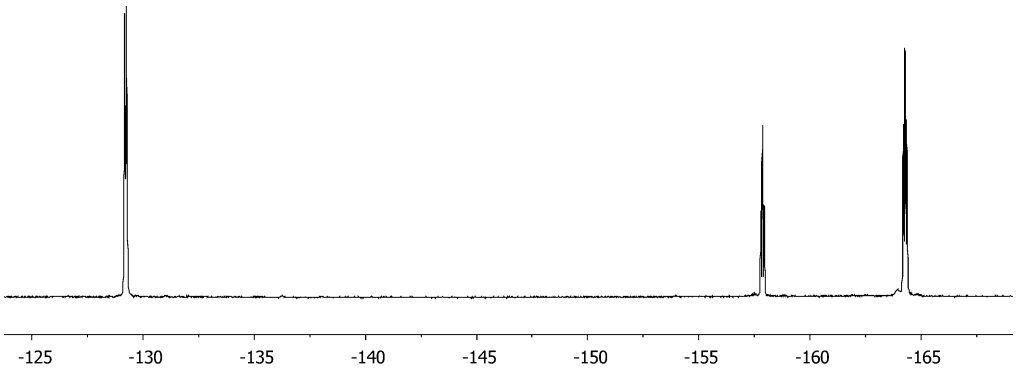
^{1}H, ^{13}C-GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.16 / 131.6 (*o*-Ph / *p*-Ph), 6.90 / 132.3 (*p*-Ph / *o*-Ph), 6.83 / 132.3, 127.7 (*m*-Ph / *o*-, *i*-Ph), 6.65 / 130.8, 33.7 (=CH / =CP, $^{t\text{-Bu}}$C), 6.12 / 177.5, 33.7, 29.0 ($^{t\text{-Bu}}$CH= / BC=, $^{t\text{-Bu}}$C, $CH_3{}^{t\text{-Bu}}$), 2.36 / 177.5, 130.8, 22.8, 14.3 ($^{=}CH_2$ / BC=, =CP, CH_2, CH_3), 1.40 / 130.8, 30.8, 14.3 (CH_2 / =CP, $^{=}CH_2$, CH_3), 0.93 / 153.9, 121.4, 33.7 ($CH_3{}^{t\text{-Bu}}$ / $^{t\text{-Bu}}$CH=, =CH, $^{t\text{-Bu}}$C), 0.77 / 30.8, 22.8 (CH_3 / $^{=}CH_2$, CH_2).



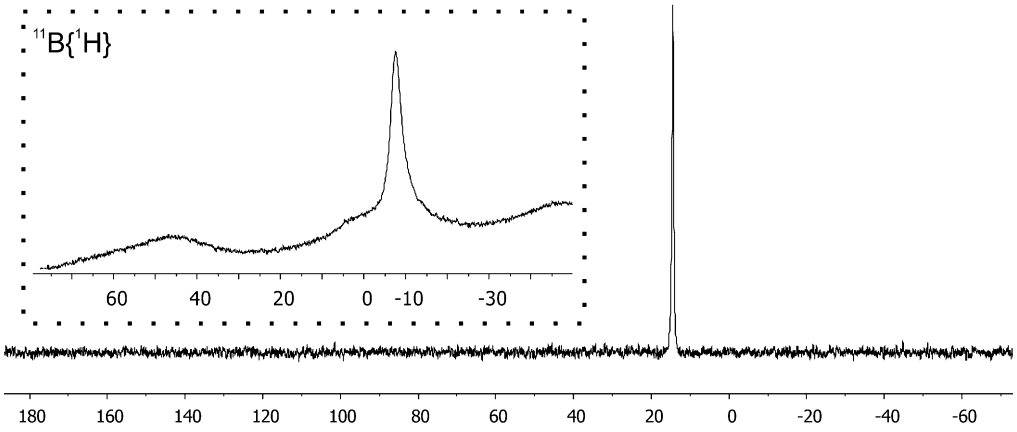
^{1}H NMR (300 MHz, 300 K, C_6D_6) of **3c**.



^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6) of **3c**.

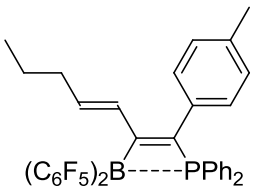


^{19}F NMR (282 MHz, 300 K, C_6D_6) of **3c**.



$^{11}B\{^{1}H\}$ NMR (96 MHz, 300 K, C_6D_6) and **$^{31}P\{^{1}H\}$ NMR** (121 MHz) of **3c**.

Synthesis of compound 3d.



Borane **1b** (0.235 g, 0.567 mmol) and diphenyl(*p*-tolylethynyl)phosphane (**2b**) (0.170 g, 0.567 mmol) were dissolved in toluene (10 ml) and stirred for 5h at 70 °C. After removal of the solvent in vacuum the crude product was washed with pentane (3×10 ml) to yield **3d** (0.152 g, 0.213 mmol, 38%) as a light yellow solid. Crystals suitable for X-ray crystal structure analysis were grown by slow evaporation of a deuterated benzene solution of **3d** at room temperature. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3062, 3013 (each w, =C-H), 2973, 2927, 2862 (each m, C-H). **M.p.** (DSC): 188°C. **Anal. Calc.** for $C_{39}H_{28}BF_{10}P$: C: 63.89; H: 3.67. Found: C: 63.82; H: 3.37.

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 7.39 (m, 2H, *o*-Tol), 7.29 (m, 4H, *o*-Ph), 7.05 (dm, $^{3}J_{HH}$ = 15.5 Hz, 1H, =CH), 6.89 (m, 2H, *m*-Tol), 6.85 (m, 2H, *p*-Ph), 6.77 (m, 4H, *m*-Ph), 6.27 (dm, $^{3}J_{HH}$ = 15.5 Hz, 1H, ^{Pr}CH=), 2.03 (s, 3H, *p*-CH_3^{Tol}), 1.94 (m, 2H, $^{=}CH_2$), 1.22 (m, 2H, CH_2), 0.73 (t, $^{3}J_{HH}$ = 7.4 Hz, CH_3).

$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, C_6D_6): δ = 176.6 (br, BC=), 148.7 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 144.8 (^{Pr}CH=), 140.2 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 138.2 (d, $^{5}J_{PC}$ = 1.1 Hz, *p*-Tol), 137.5 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 132.9 (d, $^{2}J_{PC}$ = 3.1 Hz, *i*-Tol), 132.2 (d, $^{2}J_{PC}$ = 9.1 Hz, *o*-Ph), 131.7 (d, $^{4}J_{PC}$ = 3.0 Hz, *p*-Ph), 129.8 (*m*-Tol), 128.9 (d, $^{3}J_{PC}$ = 10.4 Hz, *m*-Ph), 128.7 (d, $^{3}J_{PC}$ = 5.5 Hz, *o*-Tol), 128.4 (=CH)[1], 126.9 (d, $^{1}J_{PC}$ = 40.2 Hz, *i*-Ph), 117.1 (br, *i*-C_6F_5), 35.6 (d, $^{5}J_{PC}$ = 1.1 Hz, $^{=}CH_2$), 22.3 (CH_2), 21.1 (*p*-CH_3^{Tol}), 13.5 (CH_3), n.o. (PC=), [[1] assigned from the ghsqc experiment]

$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6): δ = -7.6 ($\nu_{1/2}$ ~ 300 Hz).

$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, C_6D_6): δ = 13.6 ($\nu_{1/2}$ ~ 60 Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = -129.1 (m, 2F, *o*-C_6F_5), -157.7 (t, $^{3}J_{FF}$ = 20.8 Hz, 1F, *p*-C_6F_5), -164.3 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 6.6].

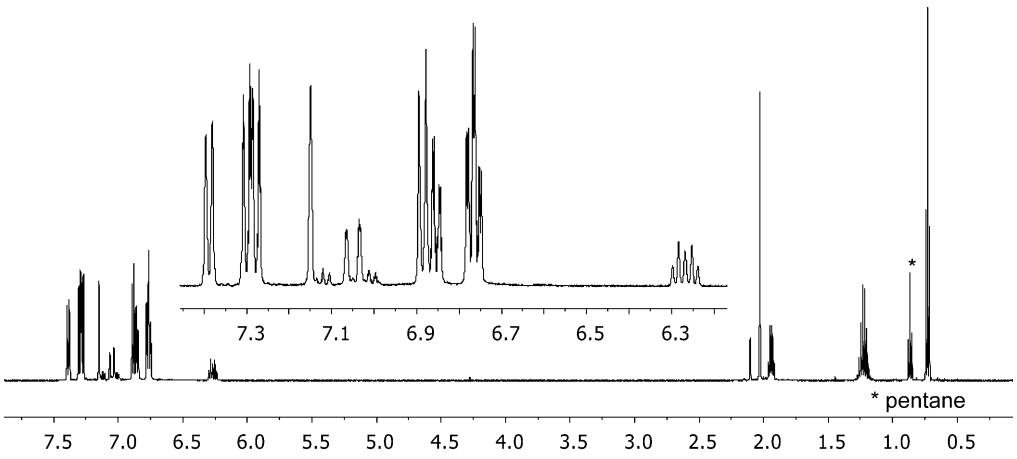
^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{1}H = 7.39 / 6.89, 2.03 (*o*-Tol / *m*-Tol, *p*-CH_3^{Tol}), 7.29 / 6.85, 6.77 (*o*-Ph / *p*-, *m*-Ph), 7.05 / 6.27, 1.94 (=CH / ^{Pr}CH=, $^{=}CH_2$), 1.94 / 7.05, 6.27, 1.22 ($^{=}CH_2$ / =CH, ^{Pr}CH=, CH_2), 1.22 / 1.94, 0.73 (CH_2 / $^{=}CH_2$, CH_3), 0.73 / 1.22 (CH_3 / CH_2).

TOCSY (500 MHz, 299 K, C_6D_6): δ $(^{1}H)_{irr.}$ / δ $(^{1}H)_{res.}$ = 7.39 / 6.89, 2.03 (*o*-Tol / *m*-Tol, *p*-CH_3^{Tol}), 7.29 / 6.85, 6.77 (*o*-Ph / *p*-, *m*-Ph), 7.05 / 6.27, 1.94, 1.22, 0.73 (=CH / ^{Pr}CH=, $^{=}CH_2$, CH_2, CH_3).

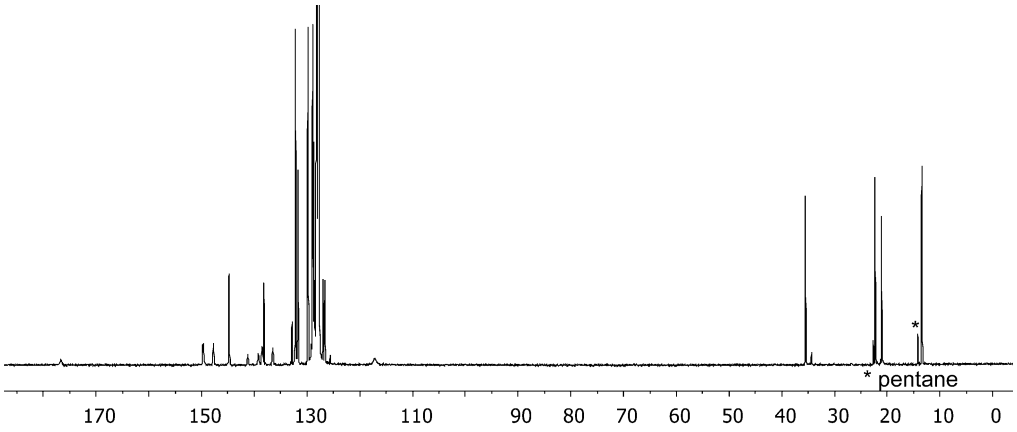
NOE (500 MHz, 299 K, C_6D_6): δ $(^{1}H)_{irr.}$ / δ $(^{1}H)_{res.}$ = 7.39 / 7.29, 7.05, 6.89 (*o*-Tol / *o*-Ph, =CH, *m*-Tol), 7.29 / 7.39, 6.77 (*o*-Ph / *o*-Tol, *m*-Ph), 7.05 / 7.39, 6.27, 1.94 (=CH / *o*-Tol, ^{Pr}CH=, $^{=}CH_2$), 6.89 / 7.39, 2.03 (*m*-Tol / *o*-Tol, *p*-CH_3^{Tol}), 6.85 / 6.77 (*p*-Ph / *m*-Ph), 6.77 / 7.29, 6.85 (*m*-Ph / *o*-, *p*-Ph), 6.27 / 1.94, 1.22 (^{Pr}CH= / $^{=}CH_2$, CH_2), 2.03 / 6.89 (*p*-CH_3^{Tol} / *m*-Tol), 1.94 / 7.05, 6.27, 1.22, 0.73 ($^{=}CH_2$ / =CH, ^{Pr}CH=, CH_2, CH_3), 1.22 / 1.94, 0.73 (CH_2 / $^{=}CH_2$, CH_3), 0.73 / 1.94, 1.22 (CH_3 / $^{=}CH_2$, CH_2).

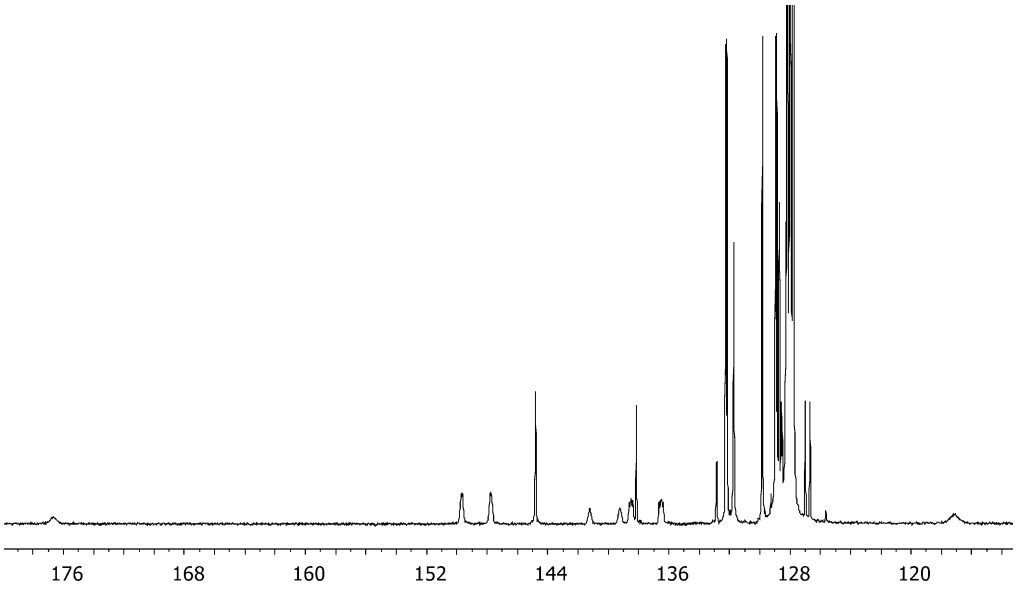
^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.39 / 128.7 (*o*-Tol), 7.29 / 132.2 (*o*-Ph), 7.05 / 128.3 (=CH), 6.89 / 129.8 (*m*-Tol), 6.85 / 131.7 (*p*-Ph), 6.77 / 128.9 (*m*-Ph), 6.27 / 144.8 (^{Pr}CH=), 2.03 / 21.1 (*p*-CH_3^{Tol}), 1.94 / 35.6 ($^{=}CH_2$), 1.22 / 22.3 (CH_2), 0.73 / 13.5 (CH_3).

^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.39 / 138.2 (*o*-Tol / *p*-Tol), 7.05 / 35.6 (=CH / $^{=}CH_2$), 6.89 / 132.9, 21.1 (*m*-Tol / *i*-Tol, *p*-CH_3^{Tol}), 6.85 / 132.2 (*p*-Ph / *o*-Ph), 6.77 / 132.2, 126.9 (*m*-Ph / *o*-, *i*-Ph), 6.27 / 176.6, 35.6, 22.3 (^{Pr}CH= / BC=, $^{=}CH_2$, CH_2), 2.03 / 138.2, 129.8 (*p*-CH_3^{Tol} / *p*-, *m*-Tol), 1.94 / 144.8, 128.3, 22.3, 13.5 ($^{=}CH_2$ / ^{Pr}CH=, =CH, CH_2, CH_3), 1.22 / 144.8, 35.6, 13.5 (CH_2 / ^{Pr}CH=, $^{=}CH_2$, CH_3), 0.73 / 35.6, 22.3 (CH_3 / $^{=}CH_2$, CH_2).

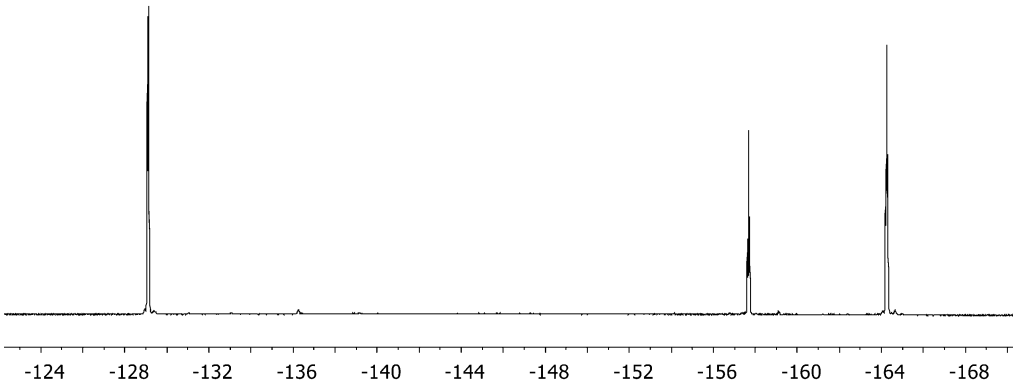


^{1}H NMR (500 MHz, 299 K, C_6D_6) of **3d**.

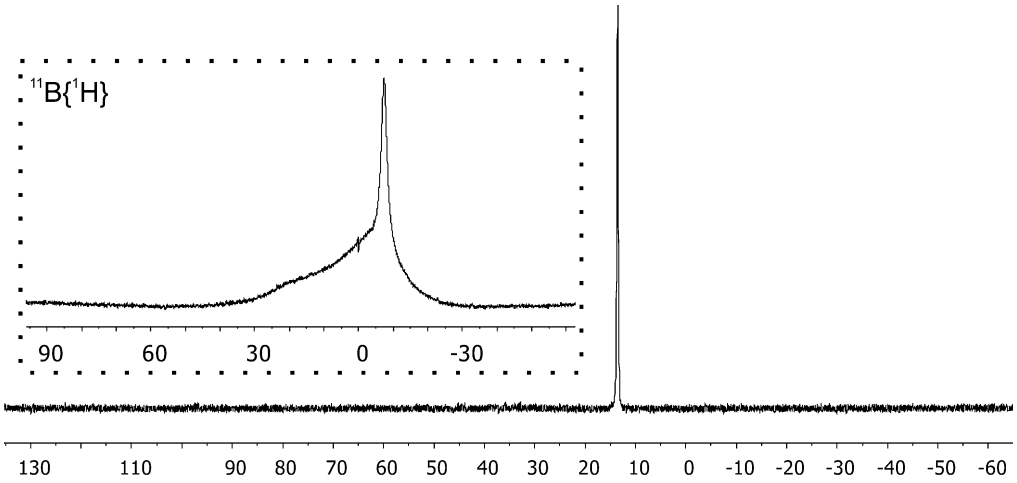




^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6) of **3d**.

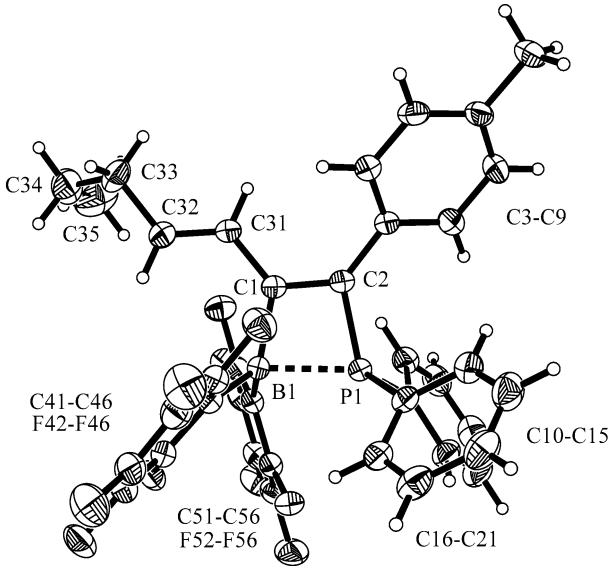


^{19}F NMR (470 MHz, 299 K, C_6D_6) of **3d**.

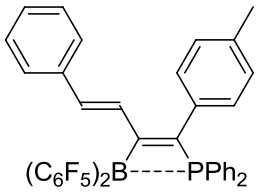


^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6) and **^{31}P{^{1}H} NMR** (202 MHz) of **3d**.

X-Ray crystal structure analysis of compound **3d**. formula $C_{38}H_{26}BF_{10}P$, M = 714.37, pale yellow crystal, 0.20 x 0.15 x 0.04 mm, a = 31.8747(6), b = 21.7074(5), c = 9.5693(2) Å, V = 6621.2(2) Å^3, ρ_{calc} = 1.433 gcm^{-3}, μ = 1.490 mm^{-1}, empirical absorption correction (0.754≤ T ≤ 0.942), Z = 8, orthorhombic, space group *A*ba2 (No. 41), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 26345 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 5588 independent (R_{int} = 0.046) and 5232 observed reflections [I>2σ(I)], 454 refined parameters, R = 0.033, wR^2 = 0.089, max. (min.) residual electron density 0.20 (-0.19) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms. Flack parameter: 0.37(2).



Synthesis of compound 3e.



Borane **1c** (0.300 g, 0.670 mmol) and diphenyl(*p*-tolylethynyl)-phosphane (**2b**) (0.205 g, 0.670 mmol) were dissolved in toluene (10 ml) and stirred for 5 h at 70 °C. Subsequently all volatiles were removed *in vacuo* and the residue was washed with pentane (3×20 ml). After drying in vacuum product **3e** (0.143 g, 0.324 mmol, 48%) was isolated as a light yellow solid. Crystals suitable for X-ray crystal structure analysis were grown by slow evaporation of a deuterated benzene solution of **3e** at room temperature. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3061 (w), 3026 (m) (=C-H), 2924 (w, C-H). **M.p.** (DSC): 240°C. **Anal. Calc.** for $C_{41}H_{24}BF_{10}P$: C, 65.80; H, 3.23. Found: C, 65.51; H, 3.29.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.79 (dd, $^{3}J_{HH}$ = 15.9 Hz, $^{4}J_{PH}$ = 2.2 Hz, 1H, =CH), 7.40 (m, 2H, *o*-Tol), 7.31 (m, 4H, *o*-^{P}Ph), 7.25 (m, 2H, *o*-Ph), 7.18 (d, $^{3}J_{HH}$ = 15.9 Hz, 1H, ^{Ph}CH=), 6.95 (m, 3H, *p*-,*m*-Ph), 6.88 (m, 2H, *m*-Tol), 6.86 (m, 2H, *p*-^{P}Ph), 6.77 (m, 4H, *m*-^{P}Ph), 2.04 (s, 3H, *p*-CH_3^{Tol}).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 175.2 (br, BC=), 148.8 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 140.8 (^{Ph}CH=), 140.3 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 138.5 (d, $^{5}J_{PC}$ = 1.1 Hz, *p*-Tol), 137.5 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 136.9 (d, $^{5}J_{PC}$ = 1.4 Hz, *i*-Ph), 132.8 (d, $^{2}J_{PC}$ = 3.0 Hz, *i*-Tol), 132.2 (d, $^{2}J_{PC}$ = 9.2 Hz, *o*-^{P}Ph), 131.8 (d, $^{4}J_{PC}$ = 3.0 Hz, *p*-^{P}Ph), 130.7 (d, $^{1}J_{PC}$ = 56.4 Hz, =CP), 130.0 (*m*-Tol), 129.02 (*p*-Ph)^{t}, 129.00 (*m*-Ph)^{t}, 128.99 (d, $^{3}J_{PC}$ = 10.5 Hz, *m*-^{P}Ph)^{t}, 128.8 (d, $^{3}J_{PC}$ = 5.6 Hz, *o*-Tol), 127.7 (*o*-Ph), 126.7 (d, $^{1}J_{PC}$ = 40.8 Hz, *i*-^{P}Ph), 125.9 (d, $^{3}J_{PC}$ = 47.5 Hz, =CH), 116.9 (br, *i*-C_6F_5), 21.1 (*p*-CH_3^{Tol}), [^{t} tentatively assigned].

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = -7.4 ($\nu_{1/2}$ ~ 400 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = 13.7 ($\nu_{1/2}$ ~ 50 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -129.1 (m, 2F, *o*-C_6F_5), -157.2 (td, $^{3}J_{FF}$ = 20.9 Hz, $^{4}J_{FF}$ = 4.6 Hz, 1F, *p*-C_6F_5), -163.9 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 6.7].

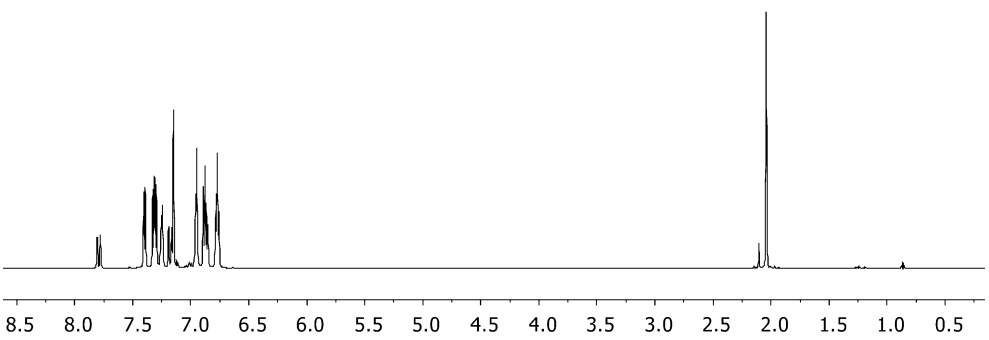
^{1}H, ^{1}H-GCOSY (600 MHz / 600 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{1}H = 7.79 / 7.18 (=CH / ^{Ph}CH=), 7.40 / 6.88 (*o*-Tol / *m*-Tol, *p*-CH_3^{Tol}), 7.31 / 6.77 (*o*-^{P}Ph / *m*-^{P}Ph), 7.25 / 6.95 (*o*-Ph / *p*-, *m*-Ph), 6.86 / 6.77 (*p*-^{P}Ph / *m*-^{P}Ph), 6.77 / 7.31, 6.86 (*m*-^{P}Ph / *o*-, *p*-^{P}Ph).

TOCSY (600 MHz, 299 K, C_6D_6): δ $^{1}H_{irr.}$ / δ $^{1}H_{res.}$ = 7.79 / 7.18 (CH= / ^{Ph}CH=), 7.40 / 6.88, 2.04 (*o*-Tol / *m*-Tol, *p*-CH_3^{Tol}), 7.31 / 6.86, 6.77 (*o*-^{P}Ph / *p*-, *m*-^{P}Ph), 7.25 / 6.95 (*o*-Ph / *p*-, *m*-Ph).

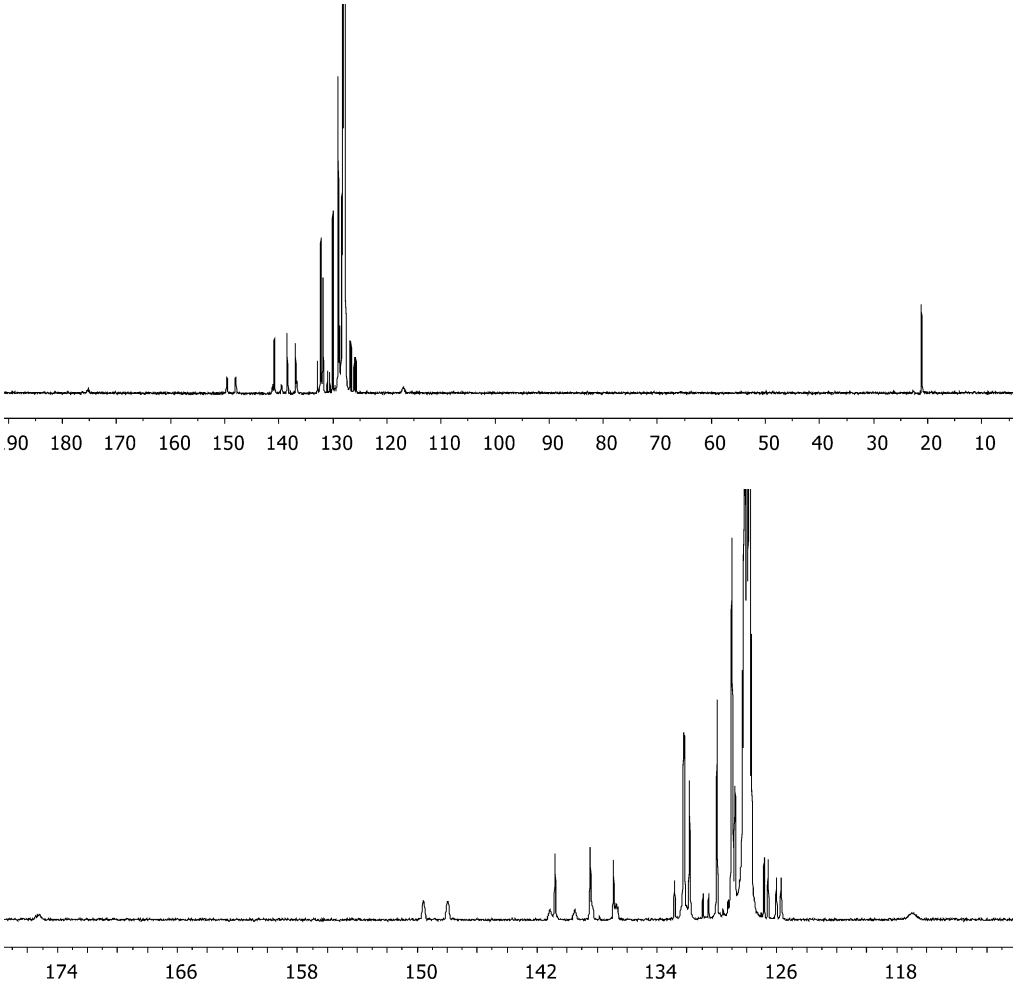
NOE (600 MHz, 299 K, C_6D_6): δ $^{1}H_{irr.}$ / δ $^{1}H_{res.}$ = 7.79 / 7.40, 7.25 (=CH / *o*-Tol, *o*-Ph), 7.40 / 7.79, 6.88 (*o*-Tol / CH=, *m*-Tol), 7.31 / 6.77 (*o*-^{P}Ph / *m*-^{P}Ph), 7.25 / 7.79, 7.18, 6.95 (*o*-Ph / CH=, ^{Ph}CH=, *p*-, *m*-Ph), 7.18 / 7.25 (^{Ph}CH= / *o*-Ph), 6.95 / 7.25 (*p*-, *m*-Ph / *o*-Ph), 6.88 / 7.40, 6.77, 2.04 (*m*-Tol / *o*-Tol, *m*-^{P}Ph, *p*-CH_3^{Tol}), 6.86 / 7.40, 7.31, 6.77, 2.04 (*p*-Ph / *o*-Tol, *o*-, *m*-^{P}Ph, *p*-CH_3^{Tol}), 6.77 / 7.31 (*m*-^{P}Ph / *o*-^{P}Ph), 2.04 / 6.88 (*p*-CH_3^{Tol} / *m*-Tol).

^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.79 / 125.9 (=CH), 7.40 / 128.8 (*o*-Tol), 7.31 / 132.2 (*o*-^{P}Ph), 7.25 / 127.7 (*o*-Ph), 7.18 / 140.8 (^{Ph}CH=), 6.95 / 129.02, 129.00 (*p*-, *m*-Ph), 6.88 / 130.0 (*m*-Tol), 6.86 / 131.8 (*p*-^{P}Ph), 6.77 / 128.99 (*m*-^{P}Ph), 2.04 / 21.1 (*p*-CH_3^{Tol}).

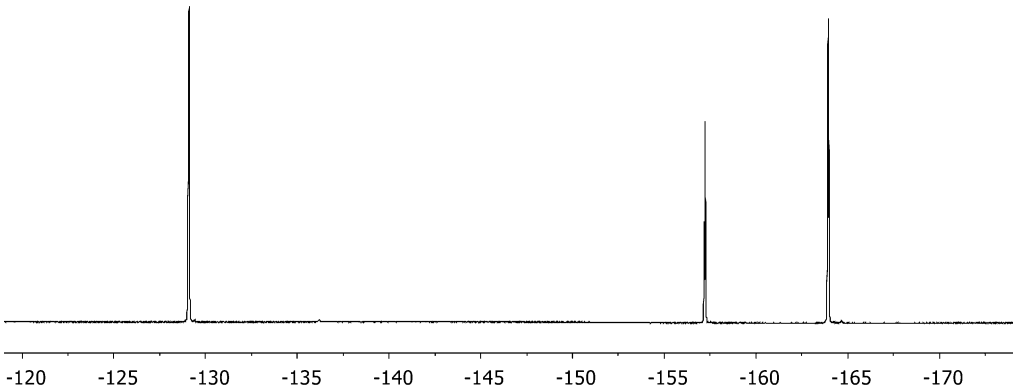
^{1}H, ^{13}C-GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.79 / 136.9, 130.7 (=CH / *i*-Ph, =CP), 7.40 / 138.5, 130.7 (*o*-Tol / *p*-Tol, =CP), 7.31 / 131.8, 128.99 (*o*-^{P}Ph / *p*-, *m*-^{P}Ph), 7.25 / 140.8, 129.02, 129.00 (*o*-Ph / ^{Ph}CH=, *p*-, *m*-Ph), 7.18 / 175.2, 136.9, 132.2, 127.7 (^{Ph}CH= / BC=, *i*-Ph, *o*-^{P}Ph, *o*-Ph), 6.95 / 136.9, 127.7 (*p*-, *m*-Ph / *i*-, *o*-Ph), 6.88 / 132.8, 21.1 (*m*-Tol / *i*-Tol, *p*-CH_3^{Tol}), 6.86 / 132.2 (*p*-^{P}Ph / *o*-^{P}Ph), 6.77 / 132.2, 126.7 (*m*-^{P}Ph / *o*-, *i*-^{P}Ph), 2.04 / 138.5, 130.0 (*p*-CH_3^{Tol} / *p*-, *m*-Tol).



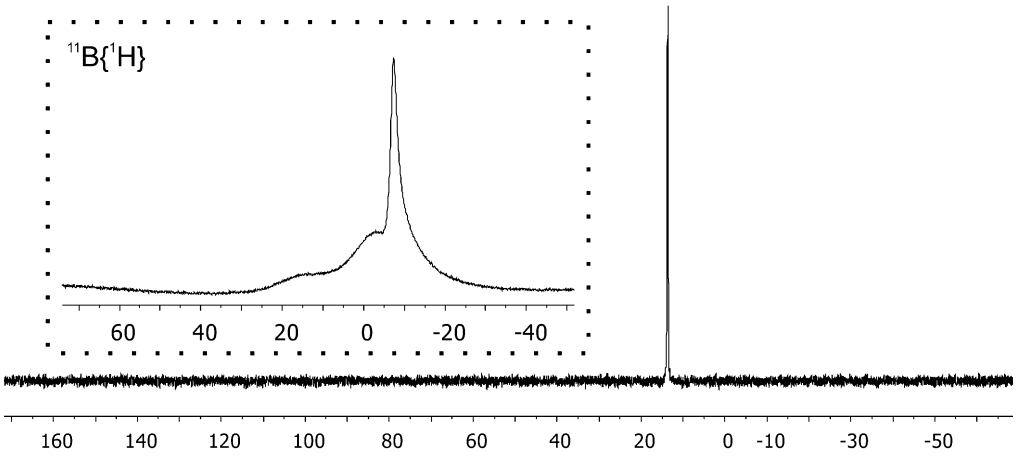
^{1}H NMR (600 MHz, 299 K, C_6D_6) of **3e**.



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) of **3e**.



^{19}F NMR (564 MHz, 299 K, C_6D_6) of **3e**.



$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, C_6D_6) and **$^{31}P\{^{1}H\}$ NMR** (243 MHz) of **3e**.

X-Ray crystal structure analysis of compound **3e**. formula $C_{41}H_{24}BF_{10}P \cdot 0.5$ x CH_2Cl_2 , M = 790.84, colourless crystal, 0.27 x 0.12 x 0.05 mm, a = 13.8469(4), b = 18.4534(4), c = 14.8031(7) Å, β = 106.575(2)°, V = 3625.3(2) $Å^3$, ρ_{calc} = 1.449 gcm^{-3}, μ = 2.084 mm^{-1}, empirical absorption correction ($0.603 \leq T \leq 0.903$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 27693 reflections collected ($\pm h$, $\pm k$, $\pm l$), [$(\sin\theta)/\lambda$] = 0.60 $Å^{-1}$, 6278 independent (R_{int} = 0.043) and 5284 observed reflections [$I > 2\sigma(I)$], 479 refined parameters, R = 0.040, wR^2 = 0.103, max. (min.) residual electron density 0.24 (-0.26) e.$Å^{-3}$, hydrogen atoms were calculated and refined as riding atoms.