1,1-Alkenylboration of diarylphosphino enynes: convenient synthetic entry to vicinal P/B Lewis pairs at extended conjugated π-frameworks

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$ X-Ray crystal structure analyses.

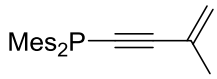
Supporting Information

General Procedure. All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried and stored under an argon atmosphere. NMR spectra were recorded on 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 are given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shifts are given relative to $CFCl_3$ (δ = 0, external reference), ^{11}B NMR: chemical shifts are given relative to $BF_3 \cdot Et_2O$ (δ = 0, external reference), ^{31}P NMR: chemical shifts 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 an 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 (Nonius B.V., 1998); 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). Thermal 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*: For compound **5a** one disordered over two positions t-Bu group was found in the asymmetrical unit. Several restraints (SADI, SIMU, ISOR and SAME) were used in order to improve refinement stability. A half disordered pentane molecule was found in the asymmetrical unit of compound **5c** could not be satisfactorily refined. For the compound **5d** one half dichloromethane and one half pentane molecules were found in the asymmetric unit. 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 not included the squeezed solvent molecule. One CH_2-CH_2 unit disordered over two positions was found in the asymmetrical unit of **7b**. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. In addition a badly disordered dichloromethane molecule was found in the asymmetrical unit 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 not included the squeezed solvent molecule. For compounds **10a** and **11** one disordered over two positions dichloromethane molecule was found in the asymmetrical unit. Several restraints (SADI, SIMU, ISOR and SAME) were used in order to improve refinement stability. CCDC deposition numbers are 1016759 to 1016766.

Materials. Vinylboranes **1a**, **1b** [O. Ekkert, O. Tuschewitzki, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Commun.*, 2013, **49**, 6992-6994; D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492-5503.] and diarylphosphino-enynes **4a** [M. S. Chattha, *J. Chem. Eng. Data.*, 1978, **23**, 95-96] and **6** [C. Charrier, W. Chodkiewicz and P. Cadiot, *Bull. Soc. Chim. Fr.*, 1966, **3**, 1002-1011.] were prepared according to the literature.

Synthesis of compound 4b.



4b

^{n}BuLi (1.6 M / hexane, 16 mmol, 10 mL) was added slowly to a Et_2O solution of 2-methyl-1-buten-3-yne (16 mmol, 1.05 g in 40 mL Et_2O) at -78 °C. After stirring for 1 h at -78°C, the reaction mixture was warmed to r.t. and kept stirring for 1 h. Then it was cooled down to -78 °C and Mes_2PCl (16 mmol, 4.88 g) in Et_2O (40 mL) was added. The reaction mixture was warmed to r.t. and kept stirring for 2 h. Saturated NH_4Cl solution (50 mL) was added and the aqueous layer was extracted with Et_2O (20 × 2 mL). The combined organic layer was washed with $NaHCO_3$ aqueous solution (ca. 20 mL) and dried over $MgSO_4$. After chromatography (silica gel, cyclohexane as eluent) compound **4b** was obtained as a white solid (4.38 g, 82%). **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 2952, 2917, 1605, 1558, 1450, 1373, 1271, 1031, 889, 849. **M.p.**: 73 °C. **Anal. Calc.** for $C_{23}H_{27}P$: C: 82.60; H: 8.14. Found: C: 82.47; H: 8.18.

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2): δ = 6.82 (dm, $^{4}J_{PH}$ = 3.3 Hz, 4H, *m*-Mes), 5.23, 5.22 (each m, each 1H, =CH_2), 2.37 (m, 12H, *o*-CH_3^{Mes}), 2.25 (s, 6H, *p*-CH_3^{Mes}), 1.87 (dd, *J* = 1.6 Hz, *J* = 1.1 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2): δ = 142.3 (d, $^{2}J_{PC}$ = 15.7 Hz, *o*-Mes), 138.8 (*p*-Mes), 130.2 (d, $^{3}J_{PC}$ = 3.7 Hz, *m*-Mes), 130.0 (d, $^{1}J_{PC}$ = 12.1 Hz, *i*-Mes), 127.7 (d, $^{3}J_{PC}$ = 1.7 Hz, =C^{Me}), 121.6 (d, $^{4}J_{PC}$ = 2.8 Hz, =CH_2), 108.4 (d, $^{2}J_{PC}$ = 8.6 Hz, ≡C), 86.9 (d, $^{1}J_{PC}$ = 6.2 Hz, ≡CP), 23.0 (d, $^{3}J_{PC}$ = 14.4 Hz, *o*-CH_3^{Mes}), 22.8 (d, $^{4}J_{PC}$ = 1.4 Hz, CH_3), 21.0 (*p*-CH_3^{Mes}).

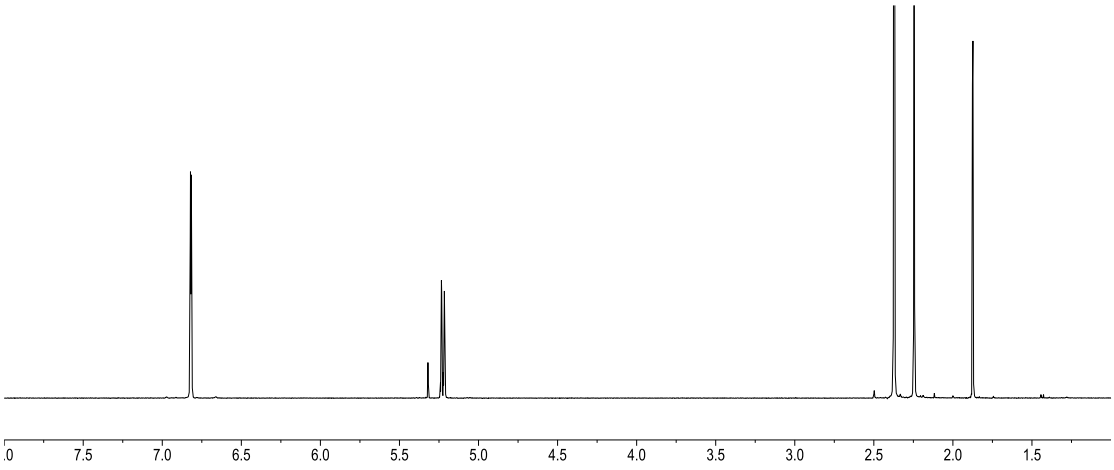
^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2): δ = -56.7 ($\nu_{1/2}$ ~ 1 Hz).

^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{1}H = 6.82 / 2.37,

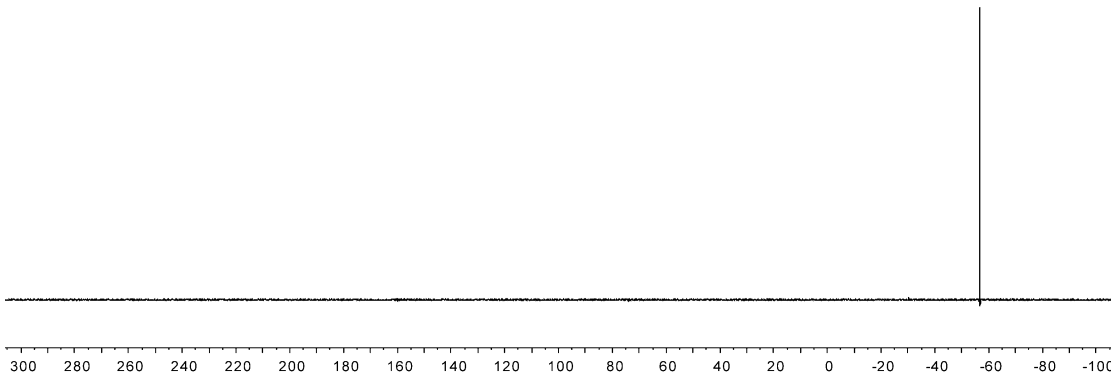
2.25 (*m*-Mes / *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 5.23, 5.22 / 1.87 (=CH_2 / CH_3).

^{1}H, ^{13}C GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 6.82 / 130.2 (*m*-Mes), 5.23 / 121.6 (=CH_2), 5.22 / 121.6 (=CH_2), 2.37 / 23.0 (*o*-CH_3^{Mes}), 2.25 / 21.0 (*p*-CH_3^{Mes}), 1.87 / 22.8 (CH_3).

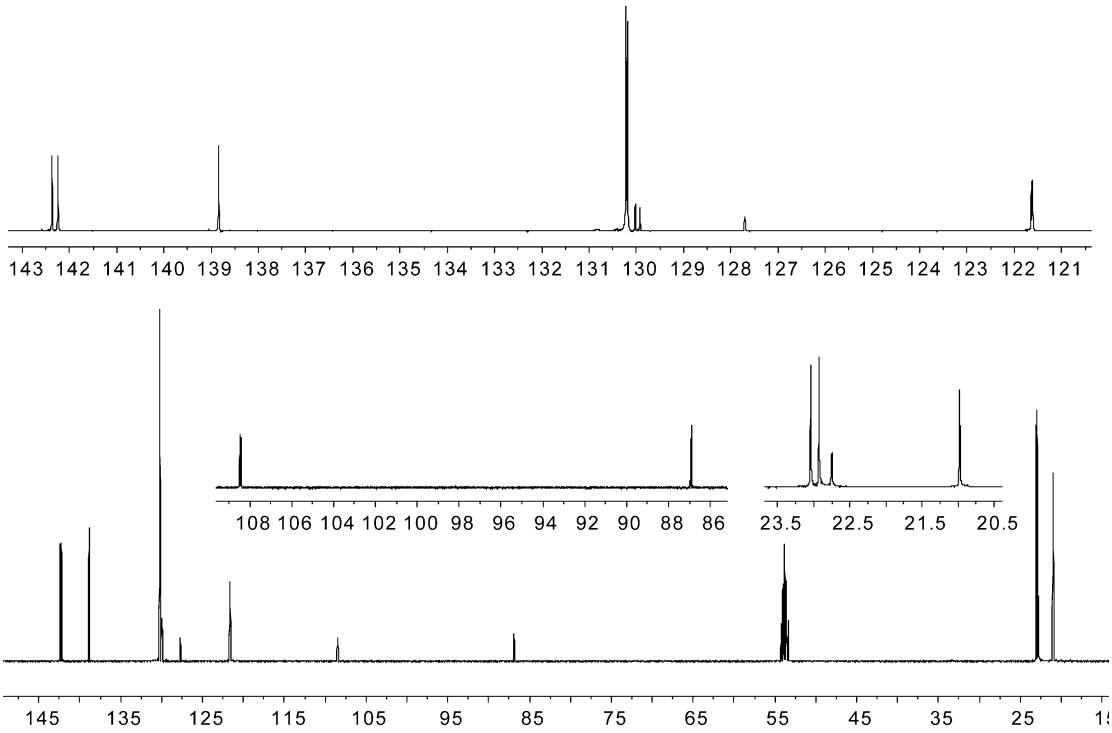
^{1}H, ^{13}C GHMBC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 6.82 / 130.2, 130.0, 23.0, 21.0 (*m*-Mes / *m*-Mes, *i*-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 5.23, 5.22 / 127.7, 108.4, 22.8 (=CH_2, =CH_2 / =C^{Me}, ≡C, CH_3), 2.37 / 142.3, 130.2, 130.0 (*o*-CH_3^{Mes} / *o*-Mes, *m*-Mes, *i*-Mes), 2.25 / 138.8, 130.2 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes), 1.87 / 127.7, 121.6, 108.4 (CH_3 / =C^{Me}, =CH_2, ≡C).



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

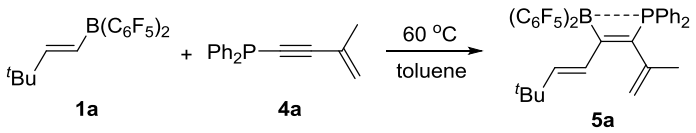


^{31}P{^{1}H} NMR (202 MHz, 299 K, CD_2Cl_2) of compound **4b**



$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) of compound **4b**

Synthesis of compound 5a.



The reaction mixture of the borane **1a** (0.214 g, 0.5 mmol, 1 eq) and the phosphane **4a** (0.125 g, 0.5 mmol, 1 eq) in toluene (5 mL) was heated at 60 °C for 3 d. Then all volatiles were removed in vacuo and the residue was washed with pentane (1 × 3 mL). After drying of the solid in vacuo compound **5a** (0.272 g, 0.40 mmol, 80 %) was obtained as a light yellow solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a dichloromethane solution of compound **5a** at -35 °C. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3055, 2963, 1642, 1622, 1514, 1464, 1378, 1285, 1097, 971, 745, 693. **M.p.**: 152 °C. **Anal. Calc.** for $C_{35}H_{26}BF_{10}P$: C: 61.97; H: 3.86. Found: C: 61.70; H: 3.51.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.31 (m, 4H, *o*-Ph), 6.96 (dd, $^{3}J_{HH}$ = 15.8 Hz, $^{4}J_{PH}$ = 2.0 Hz, 1H, =CH), 6.90 (m, 2H, *p*-Ph), 6.82 (m, 4H, *m*-Ph), 6.18 (d, $^{3}J_{HH}$ = 15.8

Hz, 1H, =CH$^{t\mathrm{Bu}}$), 5.05, 4.91 (each m, each 1H, =CH$_2$), 1.87 (m, 3H, CH$_3$), 0.89 (s, 9H, ^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 177.5 (br, =CB), 155.2 (=CH$^{t\mathrm{Bu}}$), 148.8 (dm, $^1J_{FC}$ ~ 240 Hz, C_6F_5), 140.2 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 140.1 (d, $^2J_{PC}$ = 2.5 Hz, =C^{Me}), 137.5 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 132.2 (d, $^2J_{PC}$ = 9.2 Hz, *o*-Ph), 131.7 (d, $^4J_{PC}$ = 3.0 Hz, *p*-Ph), 129.6 (d, $^1J_{PC}$ = 56.2 Hz, =CP), 128.9 (d, $^3J_{PC}$ = 10.5 Hz, *m*-Ph), 126.2 (d, $^1J_{PC}$ = 40.4 Hz, *i*-Ph), 123.2 (d, $^3J_{PC}$ = 47.2 Hz, =CH), 118.2 (d, $^3J_{PC}$ = 6.6 Hz, =CH$_2$), 117.2 (br, *i*-C_6F_5), 33.8 (d, $^5J_{PC}$ = 0.8 Hz, ^{t}Bu), 28.9 (^{t}Bu), 23.3 (d, $^3J_{PC}$ = 5.4 Hz, CH$_3$).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = -8.3 ($\nu_{1/2}$ ~ 250 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = 10.2 ($\nu_{1/2}$ ~ 75 Hz).

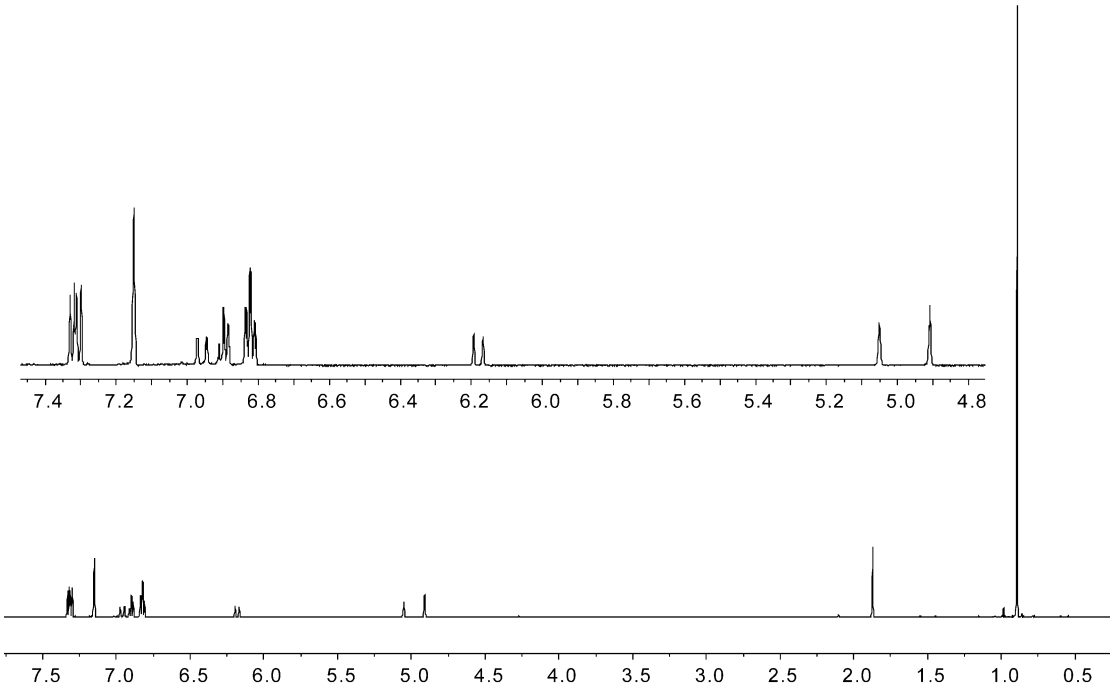
^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -129.2 (m, 2F, *o*-C_6F_5), -157.8 (tm, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), -164.4 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 6.6].

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, C_6D_6)[selective traces]: δ ^{1}H / δ ^{1}H = 7.31 / 6.82 (*o*-Ph / *m*-Ph), 6.96 / 6.18 (=CH / =CH$^{t\mathrm{Bu}}$), 6.90 / 6.82 (*p*-Ph / *m*-Ph), 5.05 / 4.91, 1.87 (=CH$_2$ / =CH$_2$, CH$_3$).

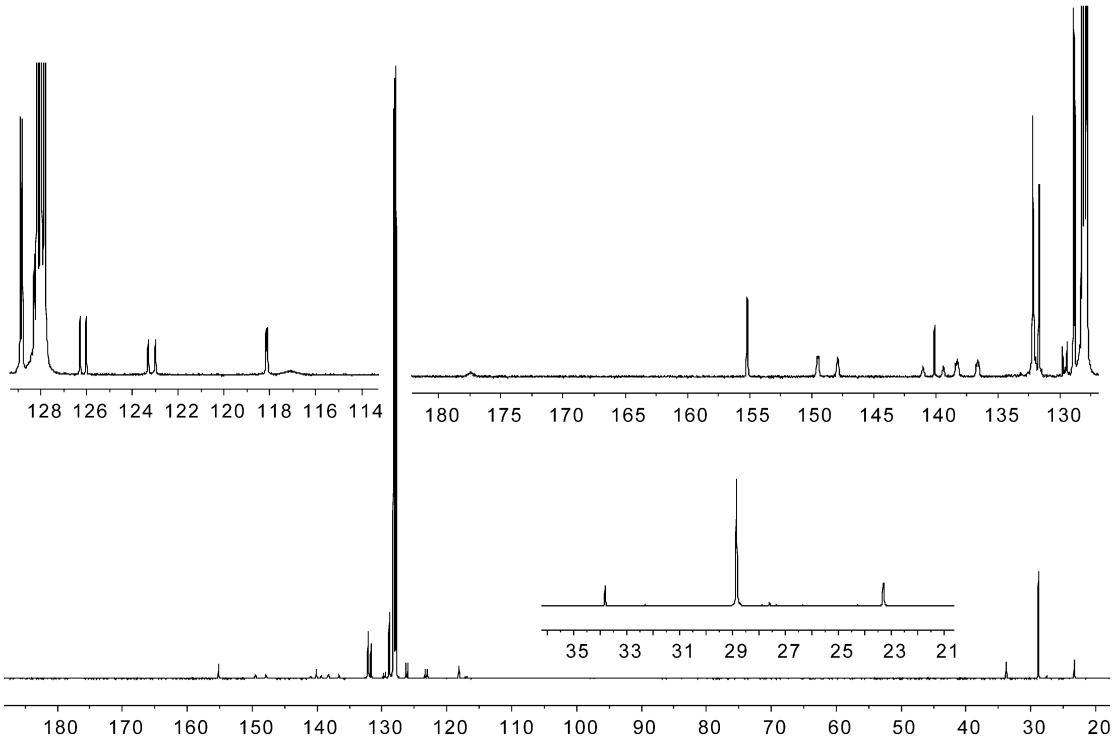
^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.31 / 132.2 (*o*-Ph), 6.96 / 123.2 (=CH), 6.90 / 131.7 (*p*-Ph), 6.82 / 128.9 (*m*-Ph), 6.18 / 155.2 (=CH$^{t\mathrm{Bu}}$), 5.05 / 118.2 (=CH$_2$), 4.91 / 118.2 (=CH$_2$), 1.87 / 23.3 (CH$_3$), 0.89 / 28.9 (^{t}Bu).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6)[selective traces]: δ ^{1}H / δ ^{13}C = 7.31 / 132.2, 131.7 (*o*-Ph / *o*-Ph, *p*-Ph), 6.96 / 129.7, 33.9 (=CH / =CP, ^{t}Bu), 6.82 / 128.9, 126.2 (*m*-Ph / *m*-Ph, *i*-Ph), 6.18 / 177.5, 33.8, 28.9 (=CH$^{t\mathrm{Bu}}$ / =CB, ^{t}Bu, ^{t}Bu), 5.05, 4.91 / 129.6, 23.3 (=CH$_2$ / =CP, CH$_3$), 1.87 / 140.2, 129.6, 118.2 (CH$_3$ / =C^{Me}, =CP, =CH$_2$), 0.89 / 155.2, 33.8, 28.9 (^{t}Bu / =CH$^{t\mathrm{Bu}}$, ^{t}Bu, ^{t}Bu).

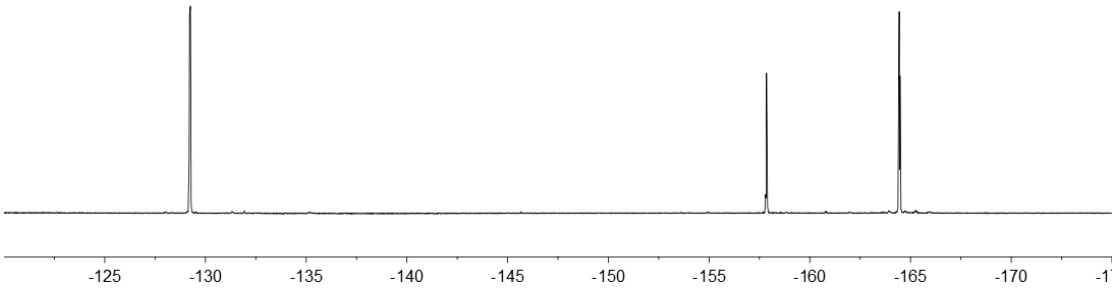
^{19}F, ^{19}F GCOSY (564 MHz / 564 MHz, 299 K, C_6D_6): δ ^{19}F / δ ^{19}F = -129.2 / -164.4 (*o*-C_6F_5 / *m*-C_6F_5), -157.8 / -164.4 (*p*-C_6F_5 / *m*-C_6F_5).



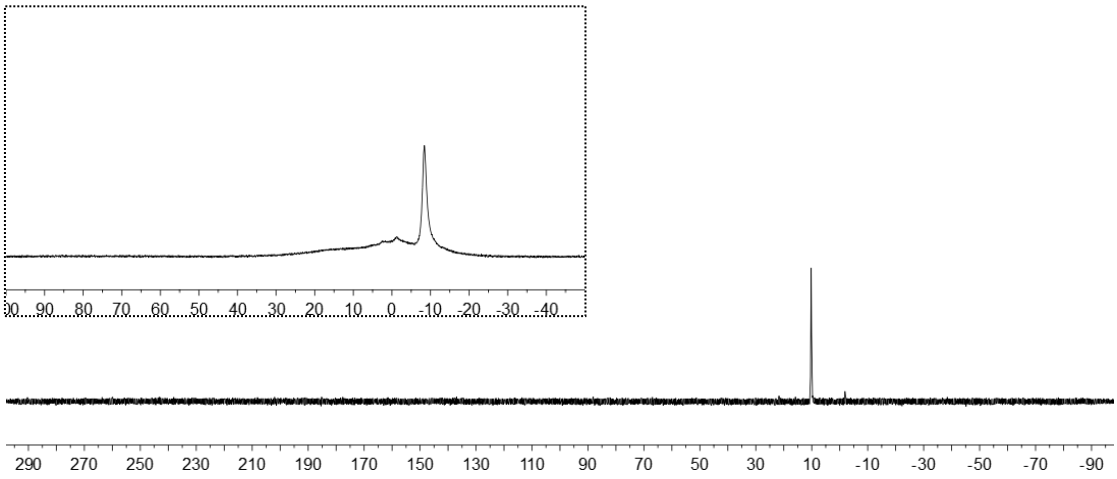
^{1}H NMR (600 MHz, 299 K, C_6D_6) of compound **5a**



^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6) of compound **5a**

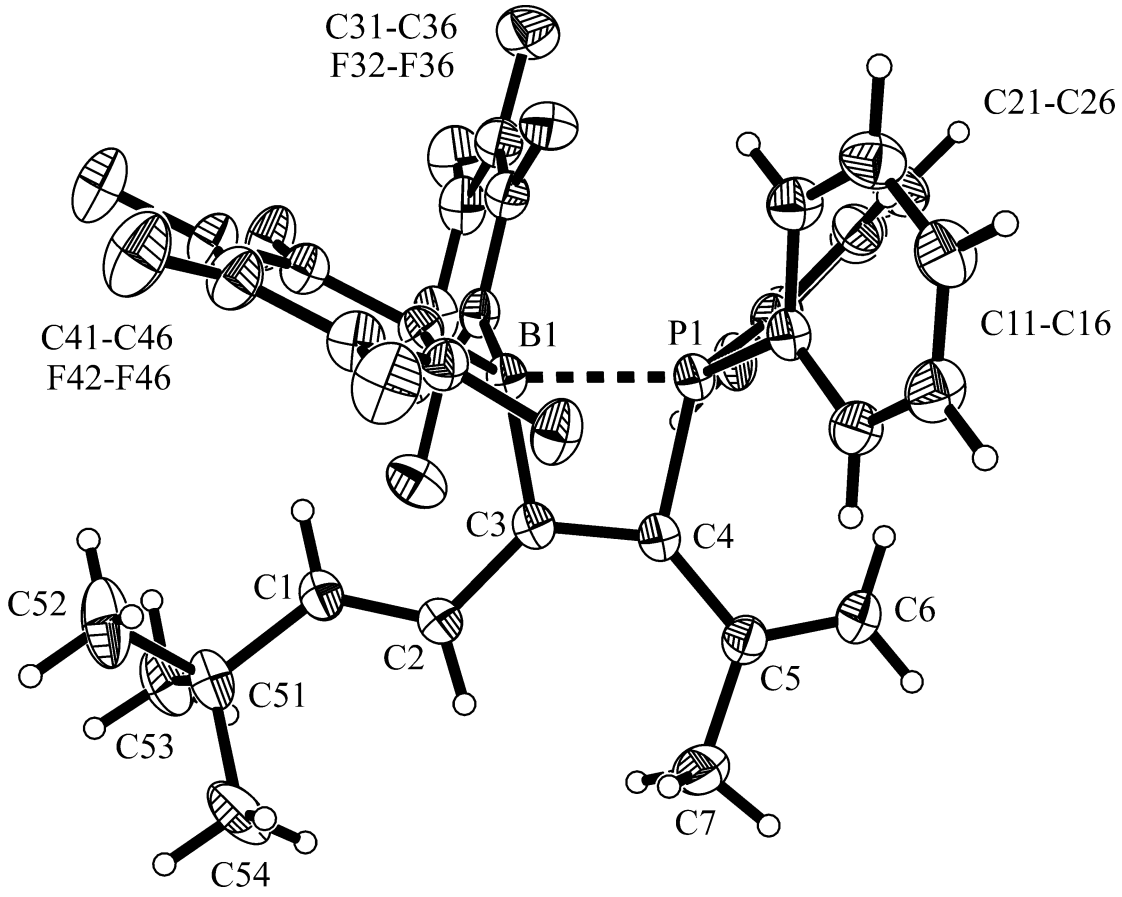


^{19}F NMR (564 MHz, 299 K, C_6D_6) of compound **5a**

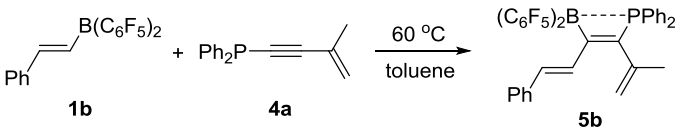


^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6) and **^{31}P{^{1}H} NMR** (243 MHz, 299 K, C_6D_6) of compound **5a**

X-ray crystal structure analysis of compound 5a: formula $C_{35}H_{26}BF_{10}P$, M = 678.34, colourless crystal, 0.24 x 0.19 x 0.14 mm, a = 11.5460(2), b = 12.3600(1), c = 12.7650(2) Å, α = 101.747(1), β = 113.392(2), γ = 95.129(1)°, V = 1607.29(4) Å^3, ρ_{calc} = 1.402 gcm^{-3}, μ = 1.501 mm^{-1}, empirical absorption correction (0.714 ≤ T ≤ 0.817), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 20182 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 5561 independent (R_{int} = 0.045) and 4965 observed reflections [I>2 σ (I)], 459 refined parameters, R = 0.040, wR^2 = 0.106, max. (min.) residual electron density 0.21 (-0.25) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Synthesis of compound 5b.



The reaction mixture of the borane **1b** (0.224 g, 0.5 mmol, 1 eq) and the phosphane **4a** (0.125 g, 0.5 mmol, 1 eq) in toluene (5 mL) was heated at 60 °C for 3 d. Then all volatiles were removed in vacuo and the residue was washed with pentane (1 × 3 mL). After drying in vacuo compound **5b** (0.298 g, 0.43 mmol, 85 %) was obtained as a light yellow solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a dichloromethane solution of compound **5b** at -35 °C. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3053, 2926, 1644, 1598, 1516, 1457, 1382, 1286, 1100, 977, 750, 692. **Decomp.**: 198 °C. **Anal. Calc.** for $C_{37}H_{22}BF_{10}P$: C: 63.64; H: 3.18. Found: C: 63.19; H: 2.89.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.75 (dd, $^{3}J_{HH}$ = 15.8 Hz, $^{4}J_{PH}$ = 2.1 Hz, 1H, =CH), 7.31 (m, 4H, *o*-Ph^{P}), 7.28 (m, 2H, *o*-Ph), 7.08 (d, $^{3}J_{HH}$ = 15.8 Hz, 1H, =CH^{Ph}), 6.98 (m, 2H, *m*-Ph), 6.97 (m, 1H, *p*-Ph), 6.90 (m, 2H, *p*-Ph^{P}), 6.82 (m, 4H, *m*-Ph^{P}), 5.10, 4.96 (each m, each 1H, $=CH_2$), 1.86 (m, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 175.8 (br, =CB), 148.7 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 140.8 (=CH^{Ph}), 140.3 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 140.1 (d, $^{2}J_{PC}$ = 2.3 Hz, =C^{Me}), 137.5 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 136.9 (d, $^{5}J_{PC}$ = 1.2 Hz, *i*-Ph), 132.1 (d, $^{2}J_{PC}$ = 9.2 Hz, *o*-Ph^{P}), 131.8 (d, $^{1}J_{PC}$ = 55.7 Hz, =CP), 131.8 (d, $^{4}J_{PC}$ = 3.0 Hz, *p*-Ph^{P}), 129.1 (*p*-Ph), 129.0 (*m*-Ph), 128.9 (d, $^{3}J_{PC}$ = 10.4 Hz, *m*-Ph^{P}), 127.7 (*o*-Ph), 126.2 (d, $^{3}J_{PC}$ = 48.1 Hz, =CH), 126.0 (d, $^{1}J_{PC}$ = 40.7 Hz, *i*-Ph^{P}), 118.8 (d, $^{3}J_{PC}$ = 6.8 Hz, $=CH_2$), 116.8 (br, *i*-C_6F_5), 23.3 (d, $^{3}J_{PC}$ = 5.1 Hz, CH_3).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = -8.1 ($\nu_{1/2}$ ~ 350 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = 10.6 ($\nu_{1/2}$ ~ 60 Hz).

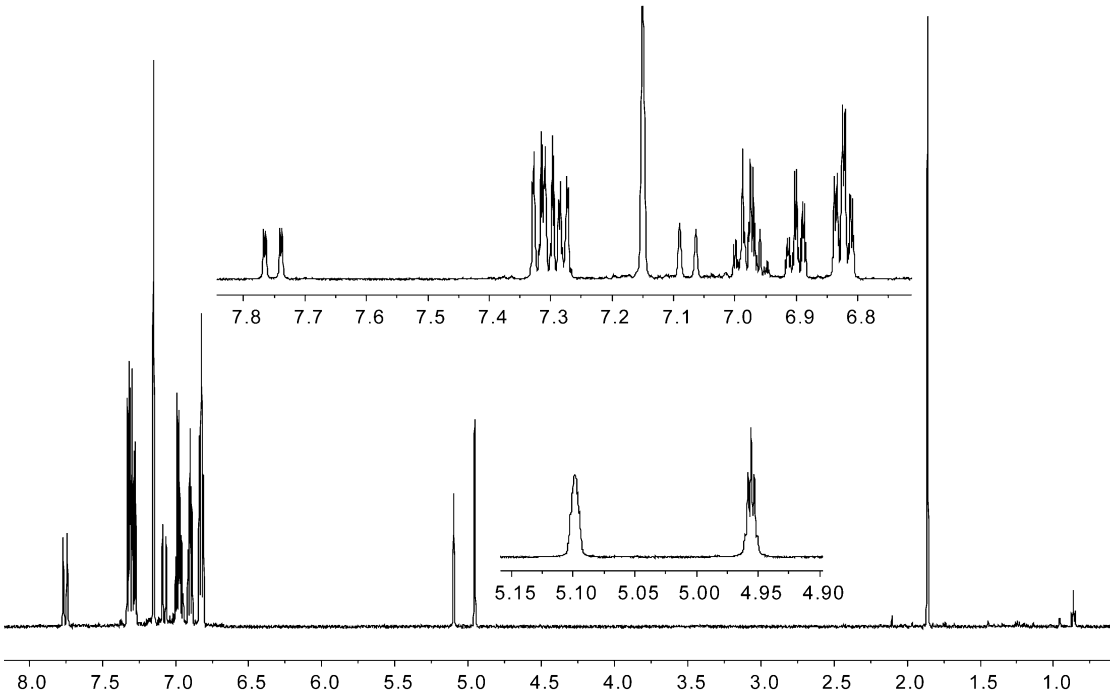
^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -129.2 (m, 2F, *o*-C_6F_5), -157.3 (tm, $^{3}J_{FF}$ = 20.8 Hz, 1F, *p*-C_6F_5), -164.0 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 6.7].

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 299 K, C_6D_6)[selective traces]: δ ^{1}H / δ ^{1}H = 7.75 / 7.08 (=CH / =CH^{Ph}), 7.31 / 6.90, 6.82 (*o*-Ph^{P} / *p*-Ph^{P}, *m*-Ph^{P}), 7.28 / 6.97 (*o*-Ph / *m*-Ph, *p*-Ph), 5.10 / 4.96, 1.86 ($=CH_2$ / $=CH_2$, CH_3).

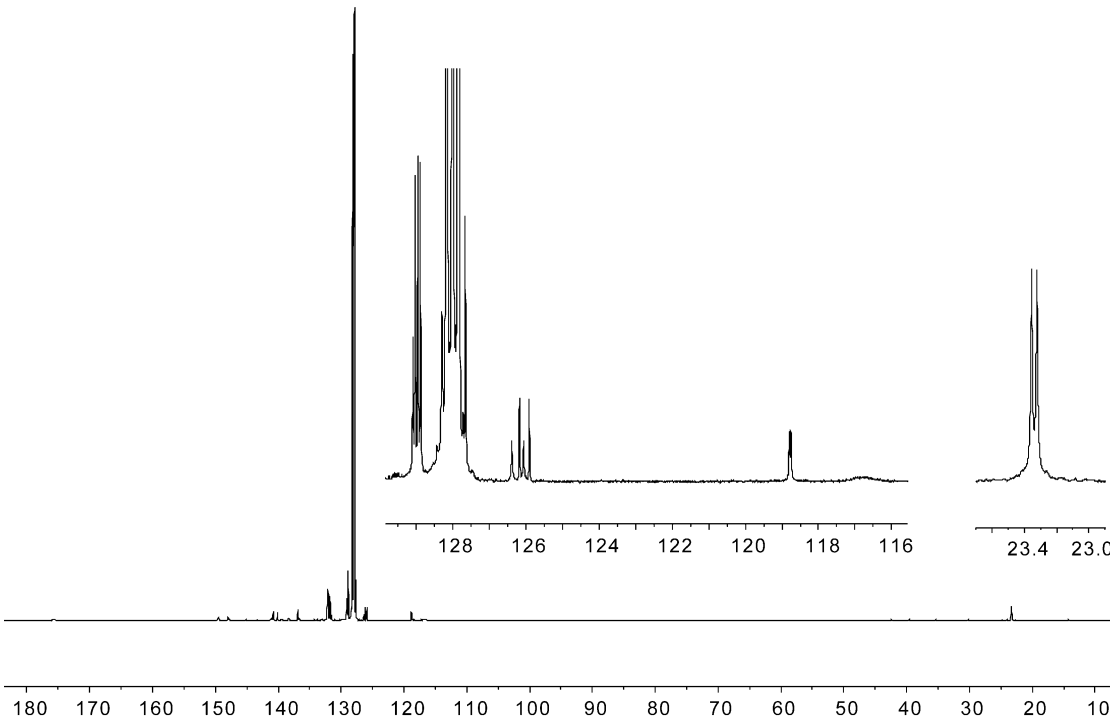
^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.75 / 126.2 (=CH), 7.31 / 132.1 (*o*-Ph^{P}), 7.28 / 127.7 (*o*-Ph), 7.08 / 140.8 (=CH^{Ph}), 6.97 / 129.1 (*p*-Ph), 6.97 / 129.0 (*m*-Ph), 6.90 / 131.8 (*p*-Ph^{P}), 6.82 / 128.9 (*m*-Ph^{P}), 5.10, 4.96 / 118.8 ($=CH_2$), 1.86 / 23.3 (CH_3).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6)[selective traces]: δ ^{1}H / δ ^{13}C = 7.75 / 136.9, 131.8 (=CH / *i*-Ph, =CP), 7.31 / 132.1, 131.8 (*o*-Ph^{P} / *o*-Ph^{P}, *p*-Ph^{P}), 7.28 / 140.8, 129.1, 127.7 (*o*-Ph / =CH^{Ph}, *p*-Ph, *o*-Ph), 7.08 / 175.8, 136.9, 127.7 (=CH^{Ph} / =CB, *i*-Ph, *o*-Ph), 6.97 / 136.9, 129.0 (*m*-Ph / *i*-Ph, *m*-Ph), 6.82 / 128.9, 126.0 (*m*-Ph^{P} / *m*-Ph^{P}, *i*-Ph^{P}), 5.10, 4.96 / 131.8, 23.3 ($=CH_2$ / =CP, CH_3), 1.86 / 140.1, 131.8, 118.8 (CH_3 / =C^{Me}, =CP, $=CH_2$).

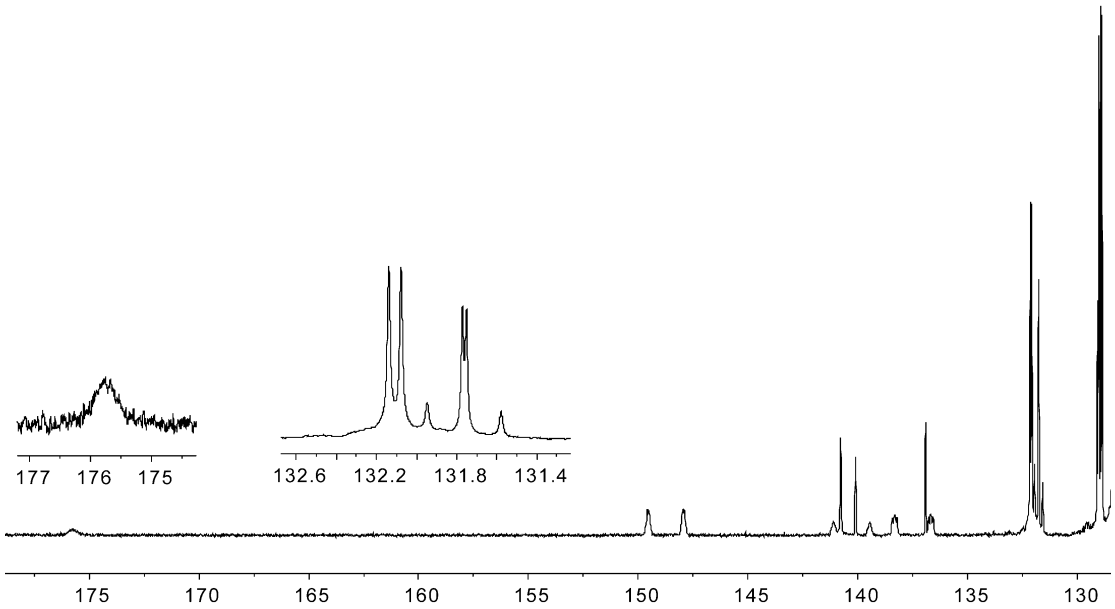
^{19}F, ^{19}F GCOSY (564 MHz / 564 MHz, 299 K, C_6D_6): δ ^{19}F / δ ^{19}F = -129.2 / -164.0 (*o*-C_6F_5 / *m*-C_6F_5), -157.3 / -164.0 (*p*-C_6F_5 / *m*-C_6F_5).



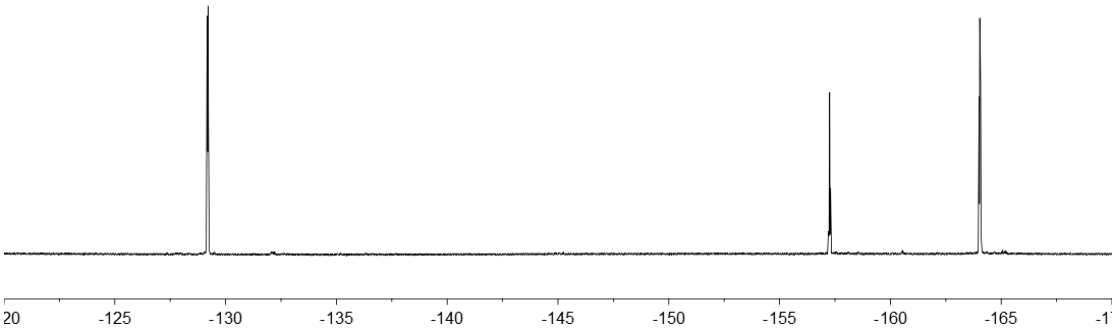
^{1}H NMR (600 MHz, 299 K, C_6D_6) of compound **5b**



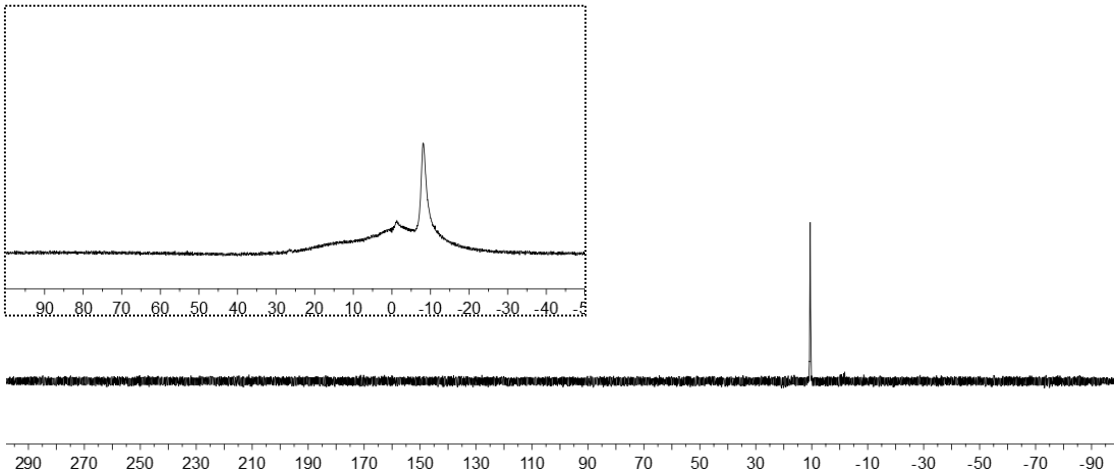
^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6) of compound **5b**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) of compound **5b**

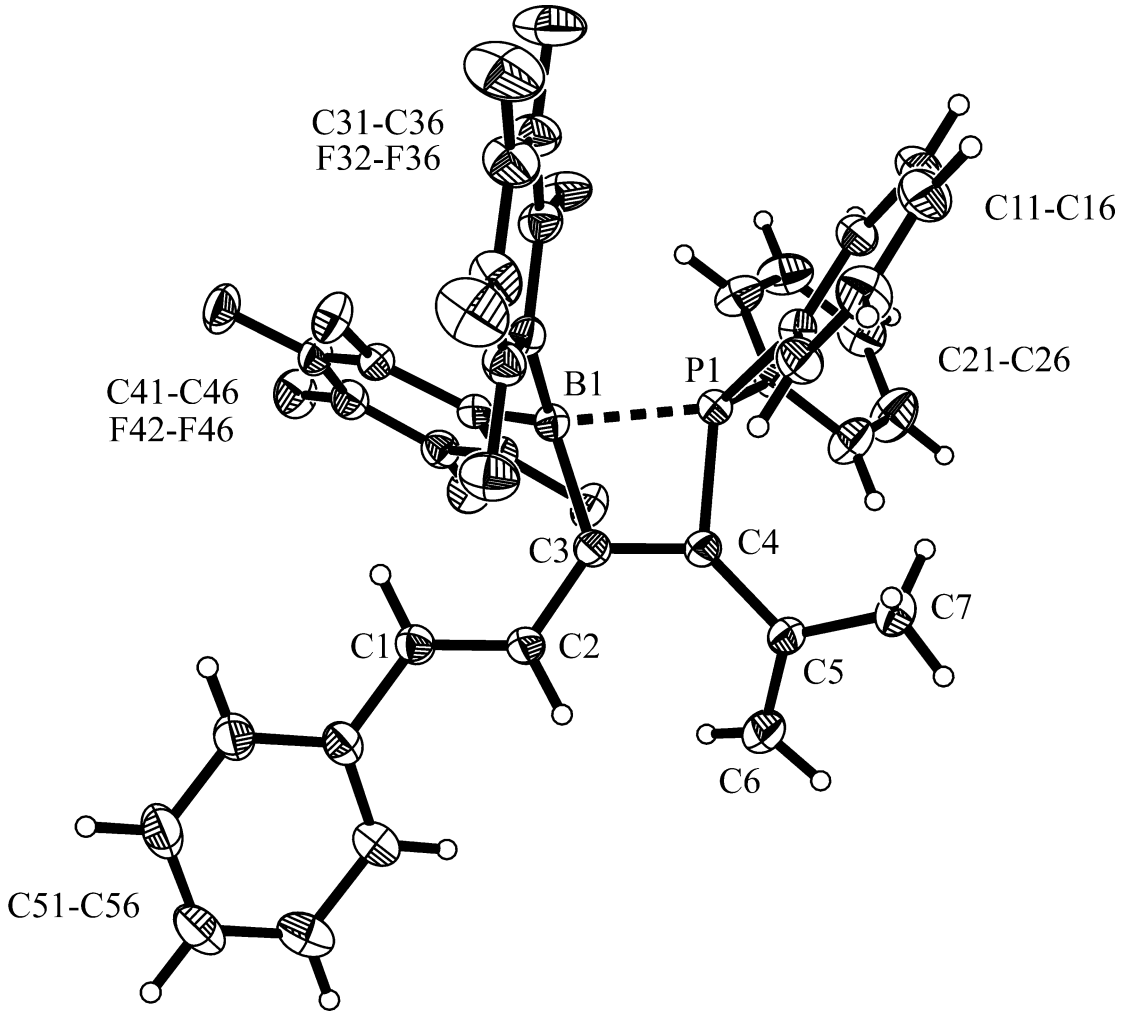


^{19}F NMR (564 MHz, 299 K, C_6D_6) of compound **5b**

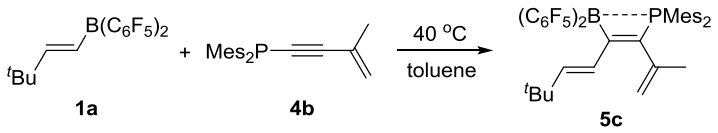


$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, C_6D_6) and **$^{31}P\{^{1}H\}$ NMR** (243 MHz, 299 K, C_6D_6) of compound **5b**

X-ray crystal structure analysis of compound 5b: formula $C_{37}H_{22}BF_{10}P \cdot 0.5 \times CH_2Cl_2$, M = 740.79, colourless crystal, 0.24 x 0.16 x 0.08 mm, a = 23.2576(5), b = 18.1844(5), c = 16.9234(5) Å, β = 111.378(2)°, V = 6664.9(3) Å^3, ρ_{calc} = 1.477 gcm^{-3}, μ = 2.224 mm^{-1}, empirical absorption correction (0.617 ≤ T ≤ 0.842), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 24503 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 5865 independent (R_{int} = 0.046) and 5223 observed reflections [I>2σ(I)], 465 refined parameters, R = 0.051, wR^2 = 0.140, max. (min.) residual electron density 1.17 (-0.75) e.Å^{-3}, the hydrogen atom at C6 was refined freely; others were calculated and refined as riding atoms.



Synthesis of compound 5c.



The reaction mixture of the borane **1a** (0.214 g, 0.5 mmol, 1 eq) and the phosphane **4b** (0.167 g, 0.5 mmol, 1 eq) in toluene (5 mL) was heated at 40 °C for 3 d. Then all volatiles were removed in vacuo and the residue was washed with pentane (1 × 3 mL). After drying in vacuo compound **5c** (0.270 g, 0.35 mmol, 71 %) was obtained as a light yellow solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a dichloromethane solution of compound **5c** at -35 °C. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3023, 2962, 2866, 1642, 1605, 1516, 1469, 1380, 1287, 1107, 975. **M.p.**: 173 °C. **Anal. Calc.** for $C_{41}H_{38}BF_{10}P$: C: 64.58; H: 5.02. Found: C: 64.35; H: 4.58.

^{1}H NMR (600 MHz, 213 K, CD_2Cl_2): δ = 6.96 (m, 1H, *m*-Mes^A), 6.80 (m, 1H, *m*'-Mes^A), 6.77 (m, 1H, *m*-Mes^B), 6.36 (m, 1H, *m*'-Mes^B), 6.19 (d, $^3J_{HH}$ = 16.0 Hz, 1H, =CH), 5.65 (d, $^3J_{HH}$ = 16.0 Hz, 1H, =CH^{tBu}), 5.27, 4.99 (each br m, each 1H, =CH_2), 2.54 (s, 3H, *o*-CH_3^{MesB}), 2.45 (br s, 3H, *o*-CH_3^{MesA}), 2.22 (s, 3H, *p*-CH_3^{MesA}), 2.16 (s, 3H, *o*'-CH_3^{MesA}), 2.10 (s, 3H, *p*-CH_3^{MesB}), 1.58 (s, 3H, *o*'-CH_3^{MesB}), 1.53 (s, 3H, CH_3), 0.75 (s, 9H, ^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 213 K, CD_2Cl_2): δ = 168.6 (d, $^2J_{PC}$ = 28.7 Hz, =CB), 152.6 (=CH^{tBu}), 143.3 (d, $^2J_{PC}$ = 17.7 Hz, *o*-Mes^A), 142.9 (*o*'-Mes^A), 142.5 (d, $^2J_{PC}$ = 3.3 Hz, *o*-Mes^B), 141.2 (d, $^4J_{PC}$ = 2.3 Hz, *p*-Mes^A), 139.8 (d, $^4J_{PC}$ = 2.5 Hz, *p*-Mes^B), 139.72 (d, $^2J_{PC}$ = 13.8 Hz, *o*'-Mes^B), 139.67 (d, $^2J_{PC}$ = 2.9 Hz, =C^{Me}), 134.7 (d, $^1J_{PC}$ = 52.4 Hz, =CP), 130.2 (d, $^3J_{PC}$ = 8.2 Hz, *m*-Mes^B), 129.6 (d, $^3J_{PC}$ = 5.8 Hz, *m*'-Mes^A), 129.4 (d, $^3J_{PC}$ = 9.1 Hz, *m*-Mes^A), 129.2 (m, *m*'-Mes^B), 125.1 (d, $^1J_{PC}$ = 25.8 Hz, *i*-Mes^A), 124.4 (d, $^1J_{PC}$ = 40.2 Hz, *i*-Mes^B), 120.1 (dm, $^3J_{PC}$ = 45.3 Hz, =CH), 118.7 (*i*-C_6F_5), 118.0 (m, =CH_2), 116.4 (*i*-C_6F_5), 33.4 (^{t}Bu), 27.9 (^{t}Bu), 24.8 (*o*-CH_3^{MesB}), 23.6 (*o*-CH_3^{MesA}), 22.6 (*o*'-CH_3^{MesA}), 22.0 (m, *o*'-CH_3^{MesB}), 21.9 (CH_3), 20.7 (*p*-CH_3^{MesA}), 20.1 (*p*-CH_3^{MesB}), [C_6F_5 not listed]

^{11}B{^{1}H} NMR (192 MHz, 213 K, CD_2Cl_2): δ = -2.0 ($\nu_{1/2}$ ~ 1800 Hz).

$^{11}B\{^1H\}$ NMR (192 MHz, 213 K, CD_2Cl_2): δ = -0.5 ($\nu_{1/2}$ ~ 380 Hz).

$^{31}P\{^1H\}$ NMR (243 MHz, 213 K, CD_2Cl_2): δ = 11.3 (partial relaxed 1:1:1:1 q, J_{PB} ~ 25 Hz).

$^{31}P\{^1H\}$ NMR (243 MHz, 299 K, CD_2Cl_2): δ = 12.8 ($\nu_{1/2}$ ~ 40 Hz).

^{19}F NMR (564 MHz, 213 K, CD_2Cl_2): δ = -125.9 (m, *o*), -131.3 (m, *o*'), -158.5 (t, $^3J_{FF}$ = 21.4 Hz, *p*), -164.7 (m, *m*), -164.8 (m, *m*')(each 1F, $C_6F_5{}^A$) [$\Delta\delta^{19}F_{m,p}$ = 6.2, 6.3], -128.7 (m, *o*), -130.6 (m, *o*'), -159.7 (br t, $^3J_{FF}$ = 19.8 Hz, *p*), -165.8 (m, *m*'), -166.0 (m, *m*)(each 1F, $C_6F_5{}^B$) [$\Delta\delta^{19}F_{m,p}$ = 6.1, 6.3].

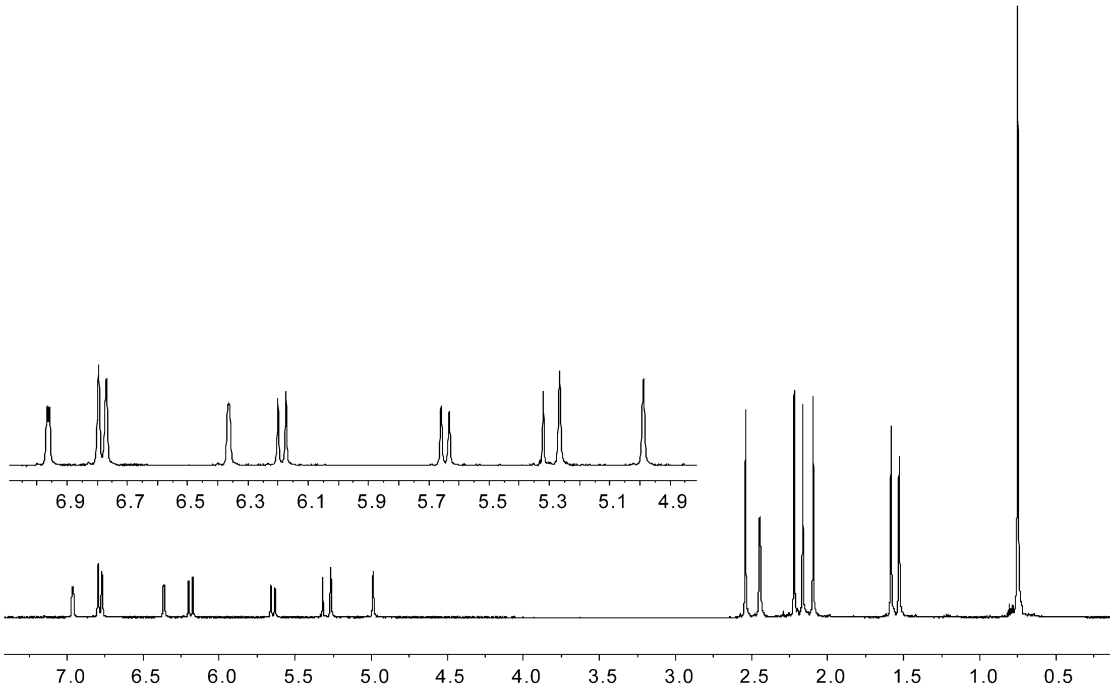
^1H, ^1H GCOSY (600 MHz / 600 MHz, 213 K, CD_2Cl_2)[selected traces]: δ ^1H / δ ^1H = 6.96 / 6.80, 2.45, 2.22, 2.16 (*m*-Mes^A / *m*'-Mes^A, *o*-$CH_3{}^{MesA}$, *p*-$CH_3{}^{MesA}$, *o*'-$CH_3{}^{MesA}$), 6.77 / 6.36, 2.54, 2.10, 1.58 (*m*-Mes^B / *m*'-Mes^B, *o*-$CH_3{}^{MesB}$, *p*-$CH_3{}^{MesB}$, *o*'-$CH_3{}^{MesB}$), 6.19 / 5.65 (=CH / =CH$^{t\text{Bu}}$), 5.27 / 4.99, 1.53 (=CH_2 / =CH_2, CH_3).

^1H, ^{13}C GHSQC (600 MHz / 151 MHz, 213 K, CD_2Cl_2): δ ^1H / δ ^{13}C = 6.96 / 129.4 (*m*-Mes^A), 6.80 / 129.6 (*m*'-Mes^A), 6.77 / 130.2 (*m*-Mes^B), 6.36 / 129.2 (*m*'-Mes^B), 6.19 / 120.1 (=CH), 5.65 / 152.6 (=CH$^{t\text{Bu}}$), 5.27, 4.99 / 118.0 (=CH_2), 2.54 / 24.8 (*o*-$CH_3{}^{MesB}$), 2.45 / 23.6 (*o*-$CH_3{}^{MesA}$), 2.22 / 20.7 (*p*-$CH_3{}^{MesA}$), 2.16 / 22.6 (*o*'-$CH_3{}^{MesA}$), 2.10 / 20.1 (*p*-$CH_3{}^{MesB}$), 1.58 / 22.0 (*o*'-$CH_3{}^{MesB}$), 1.53 / 21.9 (CH_3), 0.75 / 27.9 (^{t}Bu).

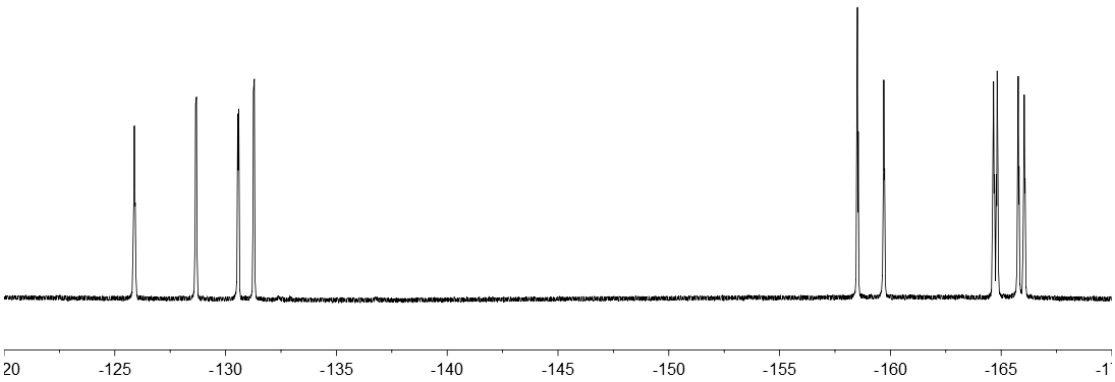
^1H, ^{13}C GHMBC (600 MHz / 151 MHz, 213 K, CD_2Cl_2): δ ^1H / δ ^{13}C = 6.96 / 129.6, 125.1, 23.6, 20.7 (*m*-Mes^A / *m*'-Mes^A, *i*-Mes^A, *o*-$CH_3{}^{MesA}$, *p*-$CH_3{}^{MesA}$), 6.80 / 129.4, 125.1, 22.6, 20.7 (*m*'-Mes^A / *m*-Mes^A, *i*-Mes^A, *o*'-$CH_3{}^{MesA}$, *p*-$CH_3{}^{MesA}$), 6.77 / 129.2, 124.4, 24.8, 20.0 (*m*-Mes^B / *m*'-Mes^B, *i*-Mes^B, *o*-$CH_3{}^{MesB}$, *p*-$CH_3{}^{MesB}$), 6.36 / 130.2, 124.4, 22.0, 20.0 (*m*'-Mes^B / *m*-Mes^B, *i*-Mes^B, *o*'-$CH_3{}^{MesB}$, *p*-$CH_3{}^{MesB}$), 6.19 / 134.7, 33.5 (=CH / =CP, ^{t}Bu), 5.65 / 168.6, 33.5, 27.9 (=CH$^{t\text{Bu}}$ / =CB, ^{t}Bu, ^{t}Bu), 5.27, 4.99 / 134.7, 21.9 (=CH_2 / =CP, CH_3), 2.54 / 142.5, 130.2, 124.4 (*o*-$CH_3{}^{MesB}$ / *o*-Mes^B, *m*-Mes^B, *i*-Mes^B), 2.45 / 143.3, 129.4, 125.1 (*o*-$CH_3{}^{MesA}$ / *o*-Mes^A, *m*-Mes^A, *i*-Mes^A), 2.22 / 141.2, 129.6, 129.4 (*p*-$CH_3{}^{MesA}$ / *p*-Mes^A, *m*'-Mes^A, *m*-Mes^A), 2.16 / 142.9, 129.6, 125.1 (*o*'-$CH_3{}^{MesA}$ / *o*'-Mes^A, *m*'-Mes^A, *i*-Mes^A), 2.10 / 139.8, 130.2, 129.2 (*p*-$CH_3{}^{MesB}$ / *p*-Mes^B, *m*-Mes^B, *m*'-Mes^B), 1.58 / 139.72, 129.2, 124.5 (*o*'-$CH_3{}^{MesB}$ / *o*'-Mes^B, *m*'-Mes^B, *i*-Mes^B), 1.53 / 139.67, 134.7, 118.0 (CH_3 / =C^{Me}, =CP, =CH_2),

0.75 / 152.6, 33.5, 27.9 (^{t}Bu / =CH^{tBu}, ^{t}Bu, ^{t}Bu).

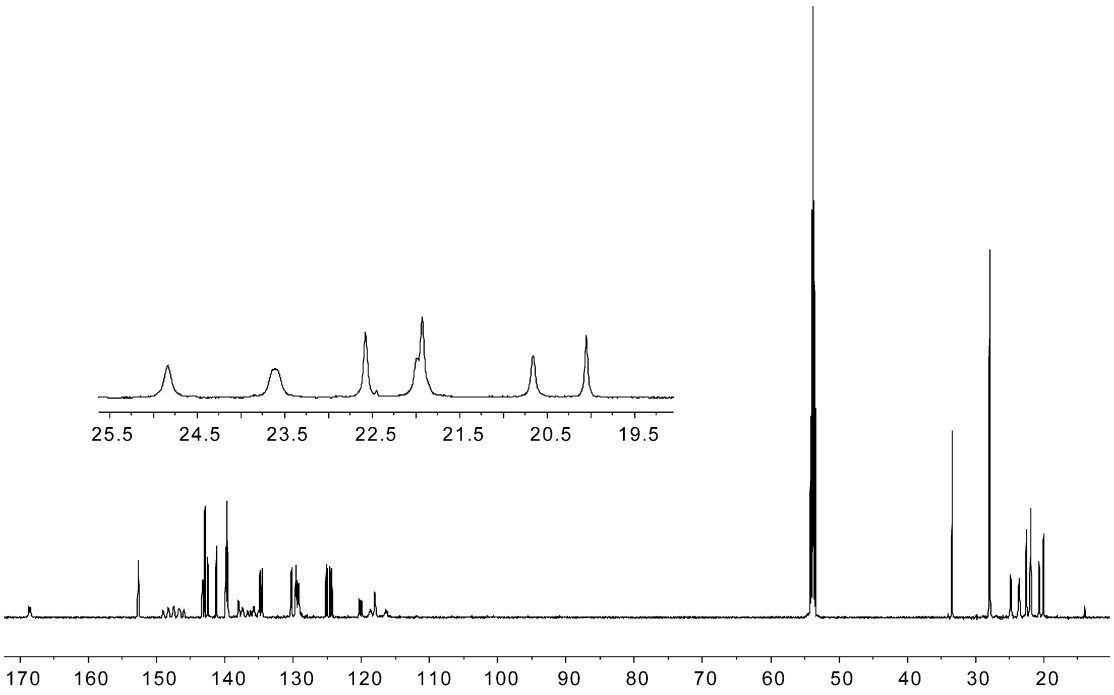
^{19}F, ^{19}F GCOSY (564 MHz / 564 MHz, 213 K, CD_2Cl_2): δ ^{19}F / δ ^{19}F = -125.9 / 164.7 (*o*-$C_6F_5^A$ / *m*-$C_6F_5^A$), -128.7 / -166.0 (*o*-$C_6F_5^B$ / *m*-$C_6F_5^B$), -130.6 / -165.8 (*o*'-$C_6F_5^B$ / *m*'-$C_6F_5^B$), -131.3 / -164.8 (*o*'-$C_6F_5^A$ / *m*'-$C_6F_5^A$), -158.5 / -164.7, -164.8 (*p*-$C_6F_5^A$ / *m*-$C_6F_5^A$, *m*'-$C_6F_5^A$), -159.7 / -165.8, -166.0 (*p*-$C_6F_5^B$ / *m*'-$C_6F_5^B$, *m*-$C_6F_5^B$).



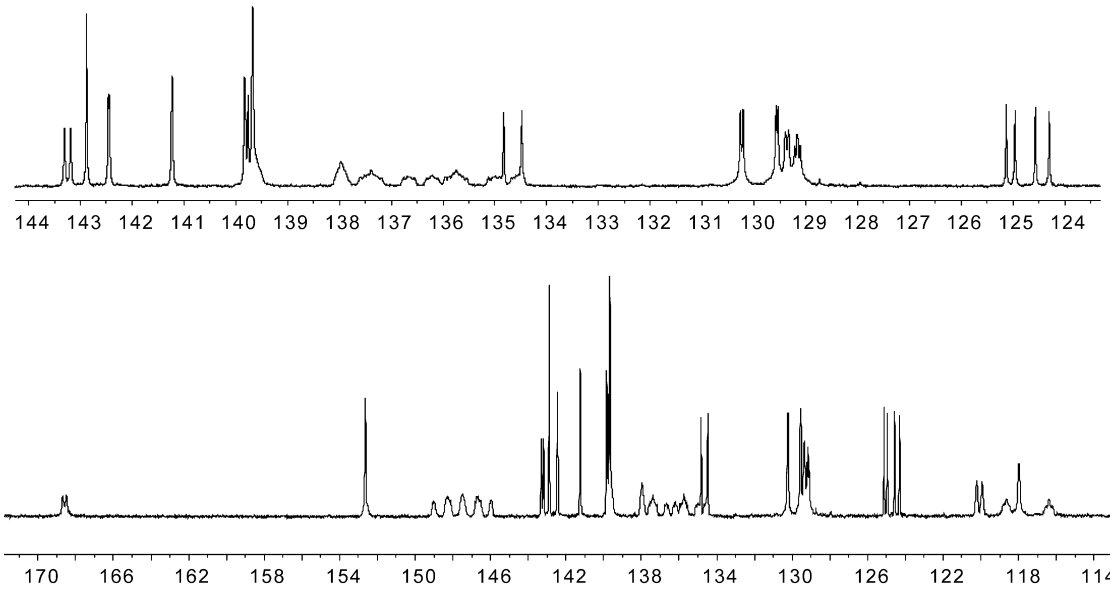
^{1}H NMR (600 MHz, 213 K, CD_2Cl_2) of compound **5c**



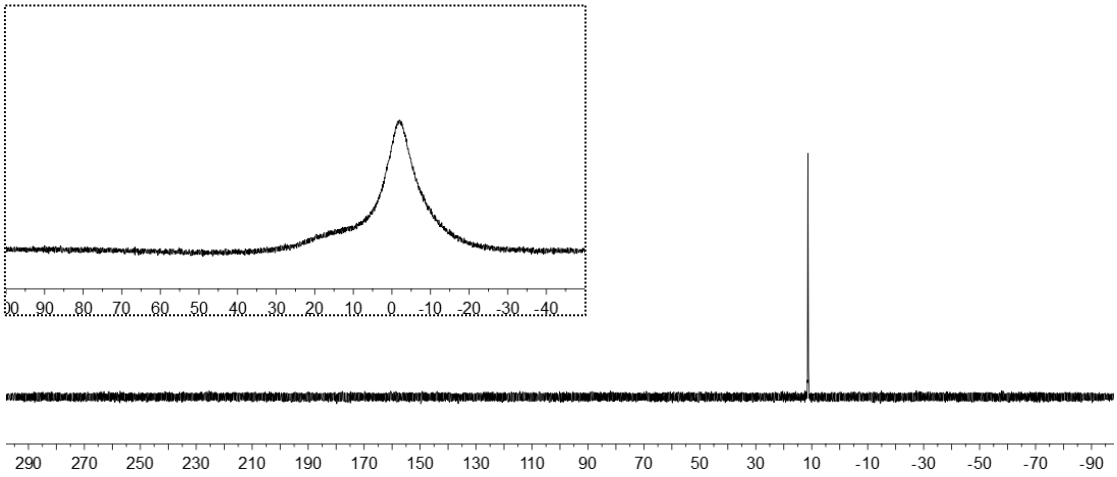
^{19}F NMR (564 MHz, 213 K, CD_2Cl_2) of compound **5c**



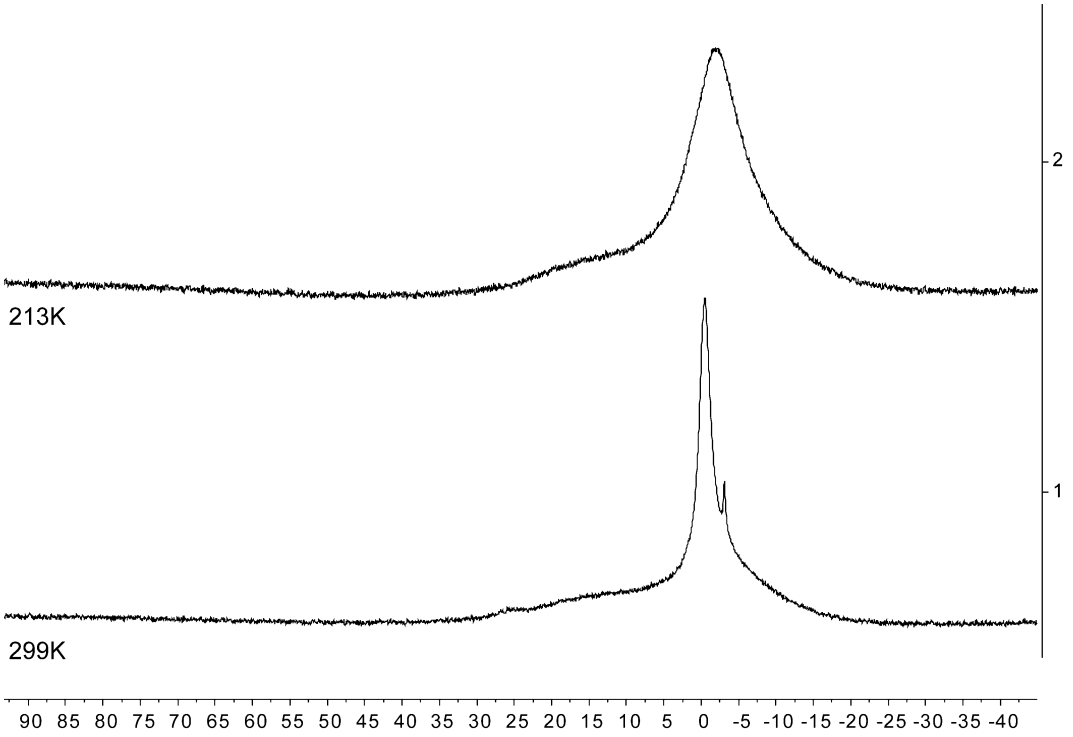
$^{13}C\{^{1}H\}$ NMR (151 MHz, 213 K, CD_2Cl_2) of compound **5c**



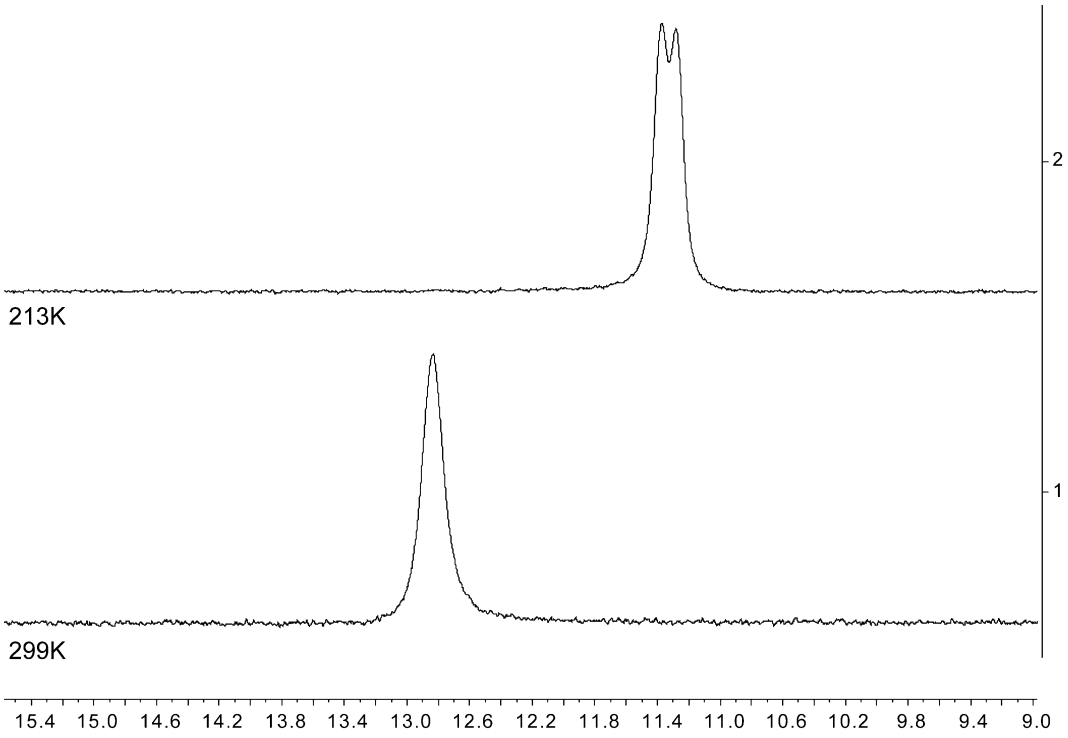
$^{13}C\{^{1}H\}$ NMR (151 MHz, 213 K, CD_2Cl_2) of compound **5c**



$^{11}B\{^{1}H\}$ NMR (192 MHz, 213 K, CD_2Cl_2) and **$^{31}P\{^{1}H\}$ NMR** (243 MHz, 213 K, CD_2Cl_2) of compound **5c**

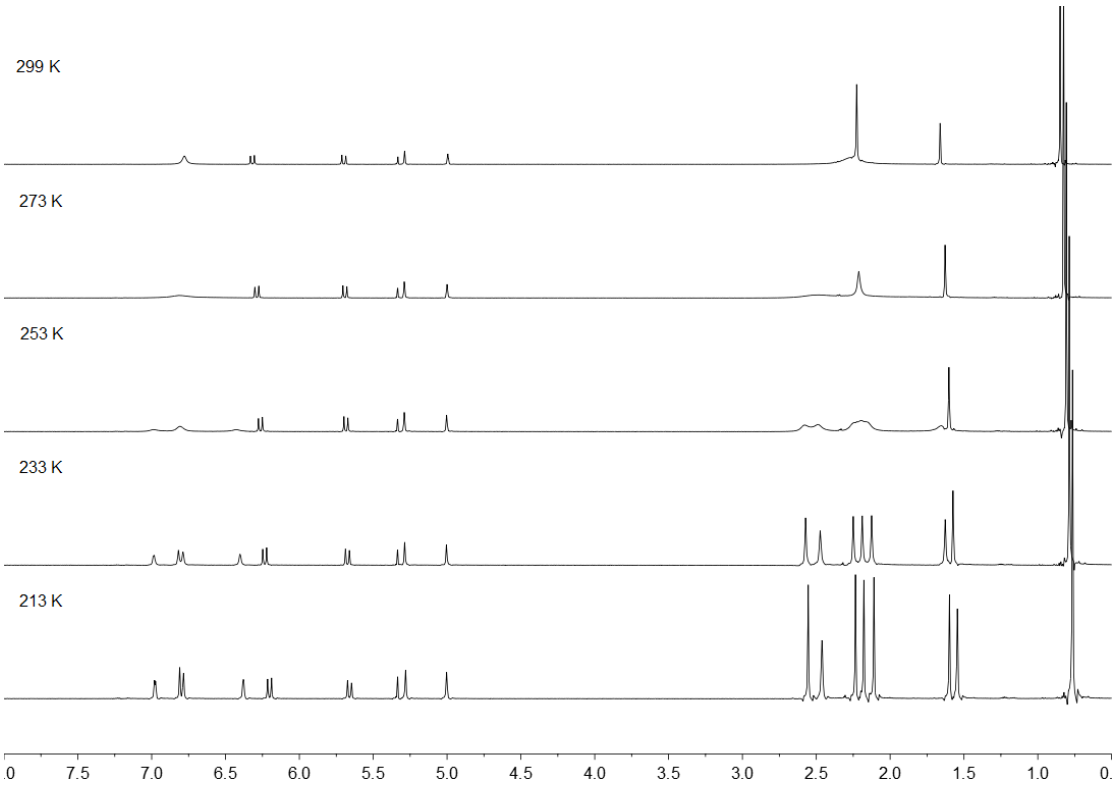


$^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2) of compound **5c** at 299K (1) and 213K (2)

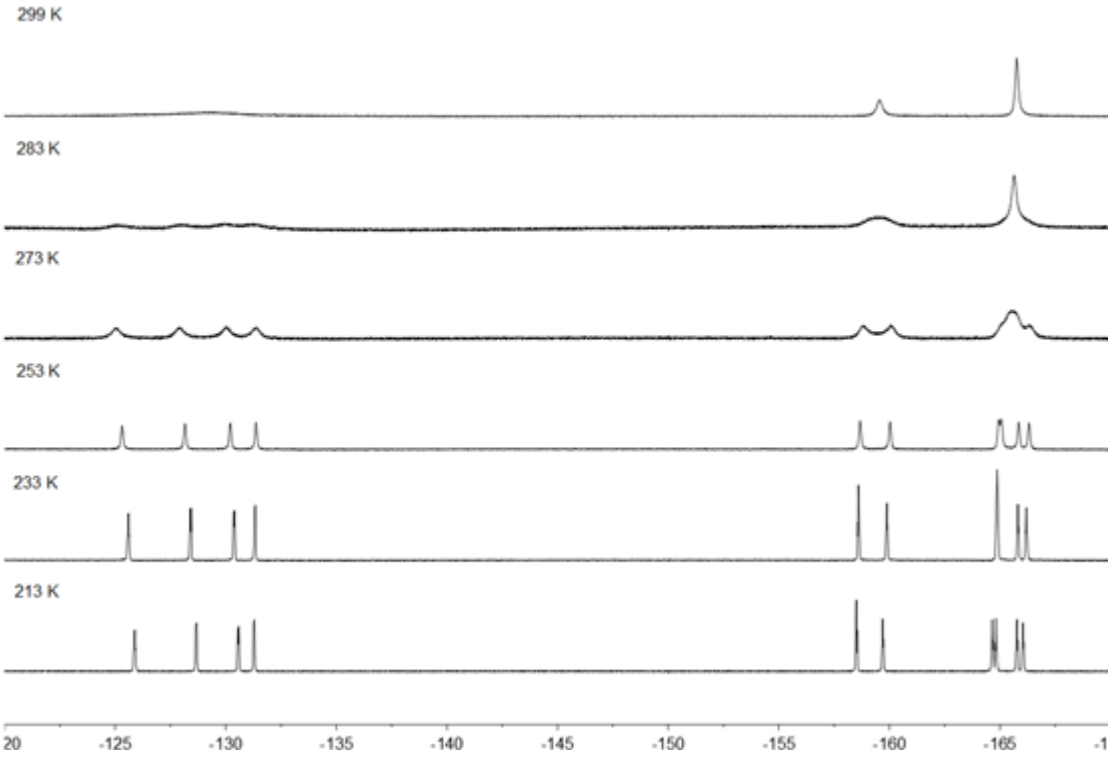


$^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2) of compound **5c** at 299K (1) and 213K (2)

Dynamic ^{1}H NMR (600 MHz, CD_2Cl_2):



Dynamic ^{19}F NMR (564 MHz, CD_2Cl_2)



$\Delta G^{\ddagger}[T_c, \Delta\nu(T)] = RT_c(22.96 + \ln(T_c/\Delta\nu))$ [J/mol]

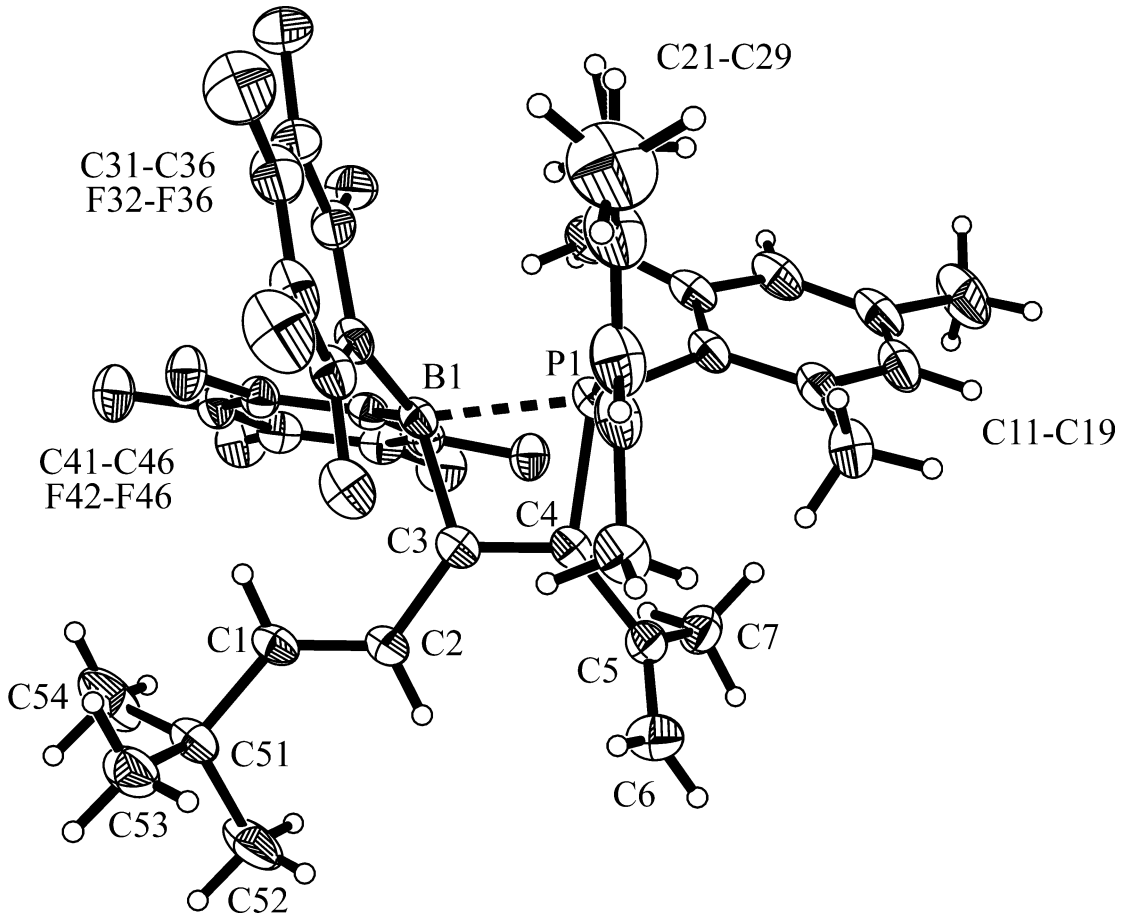
T_c = coalescence temperature [K]: 278 K (^{19}F, *p*-BC_6F_5)

$\Delta\nu$ = chemical shift difference [Hz] (^{19}F, *p*-BC_6F_5, 213 K): 675 Hz

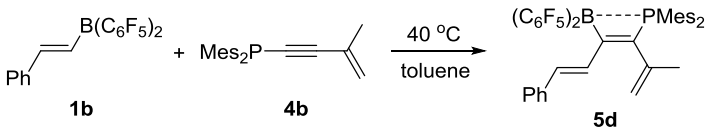
R = 8.314 J/(mol·K); 1 J = 0.239 cal

$\Delta G^{\ddagger}$[278K, $\Delta\nu$(213 K) = 675 Hz] = 51017 J/mol = 12.2 ± 0.3 kcal/mol

X-ray crystal structure analysis of compound 5c: formula $C_{41}H_{38}BF_{10}P$, *M* = 762.49, colourless crystal, 0.18 x 0.11 x 0.07 mm, *a* = 22.3123(3), *b* = 15.8067(2), *c* = 23.2517(4) Å, β = 106.554(1)° , *V* = 7860.6(2) Å^3, ρ_{calc} = 1.289 gcm^{-3}, μ = 0.145 mm^{-1}, empirical absorption correction (0.974 ≤ T ≤ 0.989), *Z* = 8, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, *T* = 223(2) K, ω and ϕ scans, 58267 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.62 Å^{-1}, 15885 independent (R_{int} = 0.069) and 9981 observed reflections [$I>2\sigma(I)$], 975 refined parameters, *R* = 0.073, wR^2 = 0.182, max. (min.) residual electron density 0.40 (-0.26) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Synthesis of compound 5d.



The reaction mixture of the borane **1b** (0.224 g, 0.5 mmol, 1 eq) and the phosphane **4b** (0.167 g, 0.5 mmol, 1 eq) in toluene (5 mL) was heated at 40 °C for 3 d. Then all volatiles were removed in vacuo and the residue was washed with pentane (1 × 3 mL). After drying in vacuo compound **5d** (0.304 g, 0.39 mmol, 78 %) was obtained as a light yellow solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a dichloromethane solution of compound **5d** at -35 °C. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3026, 2965, 2927, 1643, 1606, 1517, 1465, 1381, 1288, 1113, 978. **Decomp**.: 190 °C. **Anal. Calc.** for $C_{43}H_{34}BF_{10}P$: C: 66.00; H: 4.38. Found: C: 66.06; H: 4.09.

^{1}H NMR (600 MHz, 213 K, CD_2Cl_2): δ = 7.28 (m, 2H, *o*-Ph), 7.23 (m, 2H, *m*-Ph), 7.18 (m, 1H, *p*-Ph), 7.17 (d, $^{3}J_{HH}$ = 16.3 Hz, 1H, =CH), 6.98 (m, 1H, *m*-Mes^{A}), 6.82 (m, 1H, *m*'-Mes^{A}), 6.79 (m, 1H, *m*-Mes^{B}), 6.42 (d, $^{3}J_{HH}$ = 16.3 Hz, 1H, =CH^{Ph}), 6.40 (m, 1H, *m*'-Mes^{B}), 5.38, 5.12 (each m, each 1H, =CH_2), 2.57 (s, 3H, *o*-CH_3^{MesB}), 2.45 (br s, 3H, *o*-CH_3^{MesA}), 2.23 (s, 3H, *p*-CH_3^{MesA}), 2.20 (s, 3H, *o*'-CH_3^{MesA}), 2.11 (s, 3H, *p*-CH_3^{MesB}), 1.63 (s, 3H, *o*'-CH_3^{MesB}), 1.58 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 213 K, CD_2Cl_2): δ = 166.9 (d, $^{2}J_{PC}$ = 29.2 Hz, =CB), 143.3 (d, $^{2}J_{PC}$ = 17.8 Hz, *o*-Mes^{A}), 142.9 (*o*'-Mes^{A}), 142.4 (d, $^{2}J_{PC}$ = 3.2 Hz, *o*-Mes^{B}), 141.4 (d, $^{4}J_{PC}$ = 2.3 Hz, *p*-Mes^{A}), 140.0 (d, $^{4}J_{PC}$ = 2.7 Hz, *p*-Mes^{B}), 139.84 (d, $^{2}J_{PC}$ = 13.9 Hz, *o*'-Mes^{B}), 139.78 (d, $^{2}J_{PC}$ = 2.9 Hz, =C^{Me}), 137.8 (d, $^{1}J_{PC}$ = 51.9 Hz, =CP), 137.0 (br, =CH^{Ph}), 136.0 (*i*-Ph), 130.3 (d, $^{3}J_{PC}$ = 8.3 Hz, *m*-Mes^{B}), 129.6 (d, $^{3}J_{PC}$ = 5.9 Hz, *m*'-Mes^{A}), 129.4 (d, $^{3}J_{PC}$ = 9.3 Hz, *m*-Mes^{A}), 129.3 (m, *m*'-Mes^{B}), 128.35 (*m*-Ph), 128.29 (*p*-Ph), 126.7 (*o*-Ph), 124.8 (d, $^{1}J_{PC}$ = 26.2 Hz, *i*-Mes^{A}), 124.3 (d, $^{1}J_{PC}$ = 40.4 Hz, *i*-Mes^{B}), 124.2 (d, $^{3}J_{PC}$ = 46.4 Hz, =CH), 118.4 (m, =CH_2), 117.9 (br, *i*-C_6F_5), 116.1 (br, *i*-C_6F_5), 24.9 (m, *o*-CH_3^{MesB}), 23.7 (m, *o*-CH_3^{MesA}), 22.6 (m, *o*'-CH_3^{MesA}), 22.0 (CH_3, *o*'-CH_3^{MesB}), 20.7 (*p*-CH_3^{MesA}), 20.1 (*p*-CH_3^{MesB}), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 213 K, CD_2Cl_2): δ = -1.1 ($\nu_{1/2}$ ~ 1800 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 0.1 ($\nu_{1/2}$ ~ 500 Hz).

^{31}P{^{1}H} NMR (243 MHz, 213 K, CD_2Cl_2): δ = 12.4 (partial relaxed 1:1:1:1 q, J_{PB} ~ 25 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = 13.8 ($\nu_{1/2}$ ~ 35 Hz).

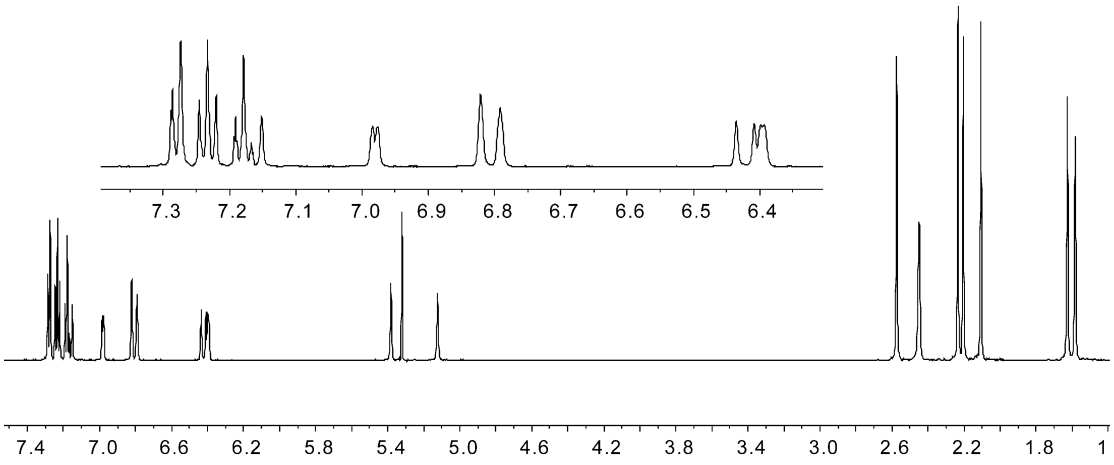
^{19}F NMR (564 MHz, 213 K, CD_2Cl_2): δ = -125.5 (m, *o*), -131.7 (m, *o*'), -157.8 (t, $^{3}J_{FF}$ = 21.3 Hz, *p*), -163.7 (m, *m*'), -164.5 (m, *m*)(each 1F, $C_6F_5^{A}$) [$\Delta\delta^{19}F_{m,p}$ = 5.9, 6.7], -128.3 (m, *o*), -130.5 (m, *o*'), -159.2 (br t, $^{3}J_{FF}$ ~ 20 Hz, *p*), -165.4 (m, *m*'), -165.8 (m, *m*)(each 1F, $C_6F_5^{B}$) [$\Delta\delta^{19}F_{m,p}$ = 6.2, 6.6].

^{1}H, ^{1}H GCOSY (600 MHz / 600 MHz, 213 K, CD_2Cl_2)[selected traces]: δ ^{1}H / δ ^{1}H = 7.28 / 7.23 (*o*-Ph / *m*-Ph), 7.23 / 7.18 (*m*-Ph / *p*-Ph), 7.17 / 6.42 (=CH / =CH^{Ph}), 6.98 / 6.82, 2.45, 2.23, 2.20 (*m*-Mes^{A} / *m*'-Mes^{A}, *o*-CH_3^{MesA}, *p*-CH_3^{MesA}, *o*'-CH_3^{MesA}), 6.79 / 6.40, 2.57, 2.11, 1.63 (*m*-Mes^{B} / *m*'-Mes^{B}, *o*-CH_3^{MesB}, *p*-CH_3^{MesB}, *o*'-CH_3^{MesB}), 5.38 / 5.12, 1.58 (=CH_2 / =CH_2, CH_3).

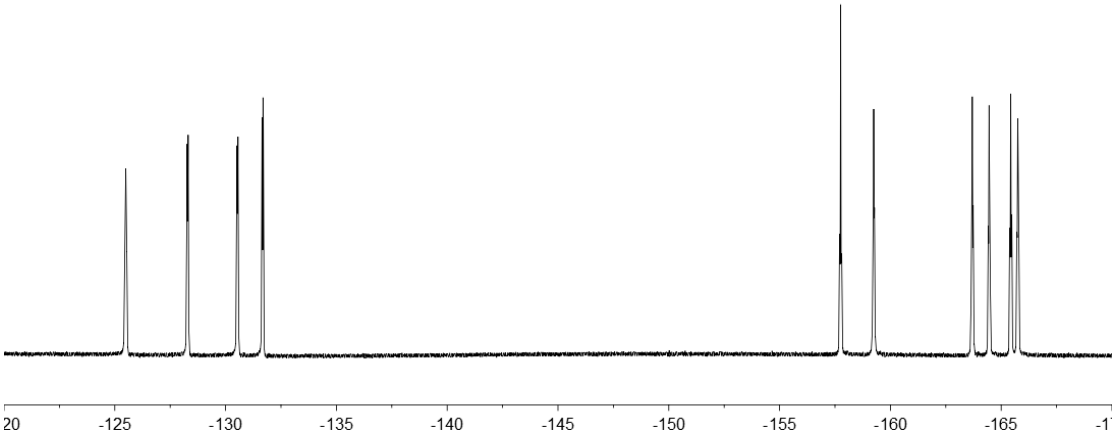
^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 213 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.28 / 126.7 (*o*-Ph), 7.23 / 128.35 (*m*-Ph), 7.18 / 128.29 (*p*-Ph), 7.17 / 124.2 (=CH), 6.98 / 129.4 (*m*-Mes^{A}), 6.82 / 129.6 (*m*'-Mes^{A}), 6.79 / 130.3 (*m*-Mes^{B}), 6.42 / 137.0 (=CH^{Ph}), 6.40 / 129.3 (m, 1H, *m*'-Mes^{B}), 5.38 / 118.4 (=CH_2), 5.12 / 118.4 (=CH_2), 2.57 / 24.9 (*o*-CH_3^{MesB}), 2.45 / 23.7 (*o*-CH_3^{MesA}), 2.23 / 20.7 (*p*-CH_3^{MesA}), 2.20 / 22.6 (*o*'-CH_3^{MesA}), 2.11 / 20.1 (*p*-CH_3^{MesB}), 1.63 / 22.0 (*o*'-CH_3^{MesB}), 1.58 / 22.0 (CH_3).

^{1}H, ^{13}C GHMBC (600 MHz / 151 MHz, 213 K, CD_2Cl_2)[selected traces]: δ ^{1}H / δ ^{13}C = 7.28 / 137.0, 128.29, 126.7 (*o*-Ph / =CH^{Ph}, *p*-Ph, *o*-Ph), 7.23 / 136.0, 128.35 (*m*-Ph / *i*-Ph, *m*-Ph), 7.17 / 137.8, 136.0 (=CH / =CP, *i*-Ph), 6.98 / 129.6, 124.8, 23.7, 20.7 (*m*-Mes^{A} / *m*'-Mes^{A}, *i*-Mes^{A}, *o*-CH_3^{MesA}, *p*-CH_3^{MesA}), 6.82 / 129.4, 124.8, 22.6, 20.7 (*m*'-Mes^{A} / *m*-Mes^{A}, *i*-Mes^{A}, *o*'-CH_3^{MesA}, *p*-CH_3^{MesA}), 6.79 / 129.3, 124.3, 24.9, 20.1 (*m*-Mes^{B} / *m*'-Mes^{B}, *i*-Mes^{B}, *o*-CH_3^{MesB}, *p*-CH_3^{MesB}), 6.42 / 166.9, 136.0, 126.6 (=CH^{Ph} / =CB, *i*-Ph, *o*-Ph), 6.40 / 130.3, 124.3, 22.0, 20.1 (*m*'-Mes^{B} / *m*-Mes^{B}, *i*-Mes^{B}, *o*'-CH_3^{MesB}, *p*-CH_3^{MesB}), 5.38, 5.12 / 137.8, 22.0 (=CH_2 / =CP, CH_3), 2.57 / 142.4, 130.3, 124.3 (*o*-CH_3^{MesB} / *o*-Mes^{B}, *m*-Mes^{B}, *i*-Mes^{B}), 2.45 / 143.3, 129.4, 124.8 (*o*-CH_3^{MesA} / *o*-Mes^{A}, *m*-Mes^{A}, *i*-Mes^{A}), 2.23 / 141.4, 129.6, 129.4 (*p*-CH_3^{MesA} / *p*-Mes^{A}, *m*'-Mes^{A}, *m*-Mes^{A}), 2.20 / 142.9, 129.6, 124.8 (*o*'-CH_3^{MesA} / *o*'-Mes^{A}, *m*'-Mes^{A}, *i*-Mes^{A}), 2.11 / 140.0, 130.3, 129.3 (*p*-CH_3^{MesB} / *p*-Mes^{B}, *m*-Mes^{B}, *m*'-Mes^{B}), 1.63 / 139.84, 129.3, 124.3 (*o*'-CH_3^{MesB} / *o*'-Mes^{B}, *m*'-Mes^{B}, *i*-Mes^{B}), 1.58 / 139.78, 137.8, 118.4 (CH_3 / =C^{Me}, =CP, =CH_2).

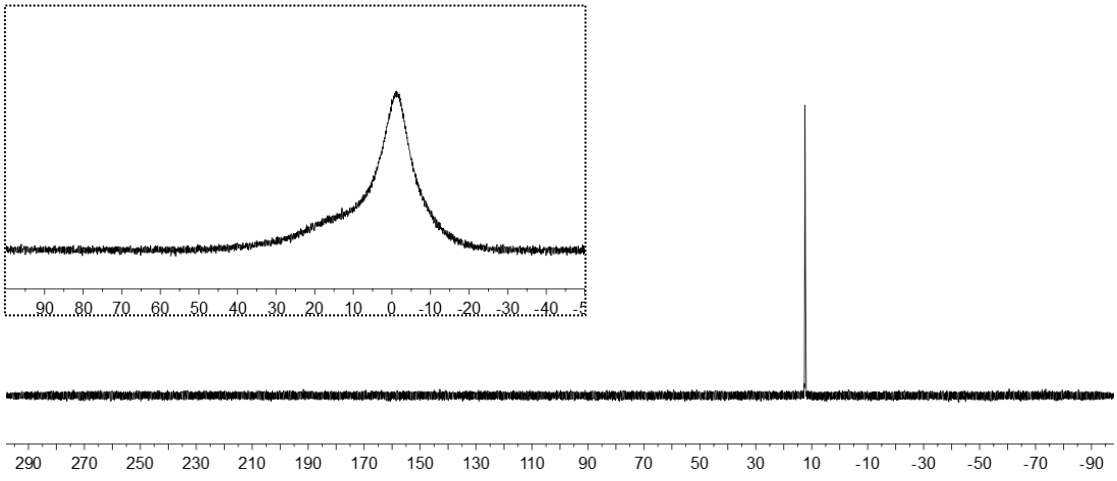
^{19}F, ^{19}F GCOSY (564 MHz / 564 MHz, 213 K, CD_2Cl_2): δ ^{19}F / δ ^{19}F = -125.5 / 164.4 (*o*-$C_6F_5^{A}$ / *m*-$C_6F_5^{A}$), -128.3 / -165.8 (*o*-$C_6F_5^{B}$ / *m*-$C_6F_5^{B}$), -130.5 / -165.4 (*o*'-$C_6F_5^{B}$ / *m*'-$C_6F_5^{B}$), -131.7 / -163.7 (*o*'-$C_6F_5^{A}$ / *m*'-$C_6F_5^{A}$), -157.8 / -163.7, -164.4 (*p*-$C_6F_5^{A}$ / *m*'-$C_6F_5^{A}$, *m*-$C_6F_5^{A}$), -159.2 / -165.4, -165.8 (*p*-$C_6F_5^{B}$ / *m*'-$C_6F_5^{B}$, *m*-$C_6F_5^{B}$).



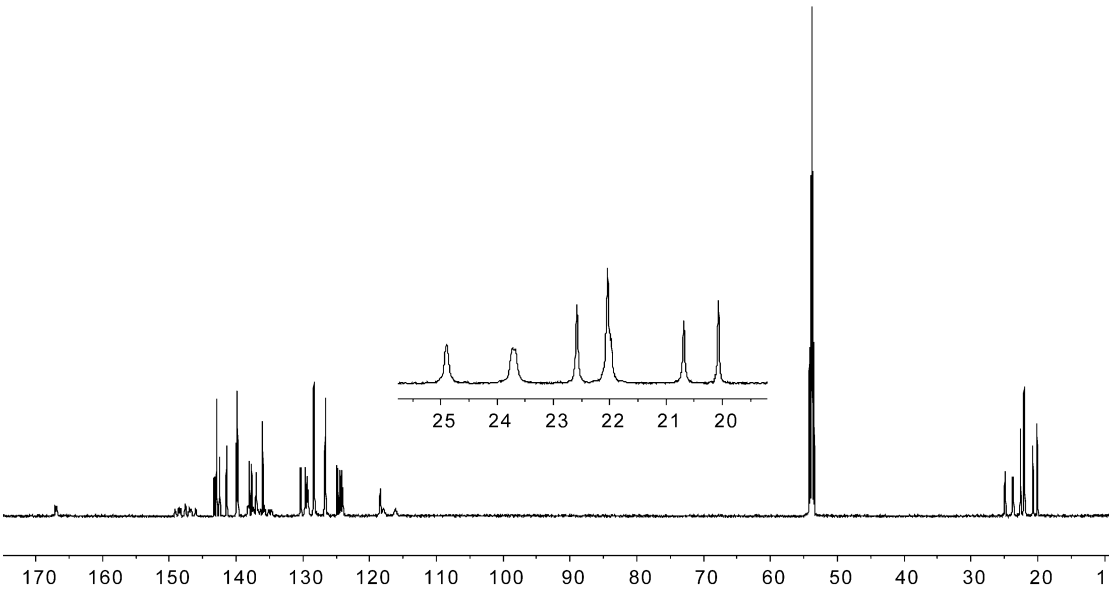
^{1}H NMR (600 MHz, 213 K, CD_2Cl_2) of compound **5d**



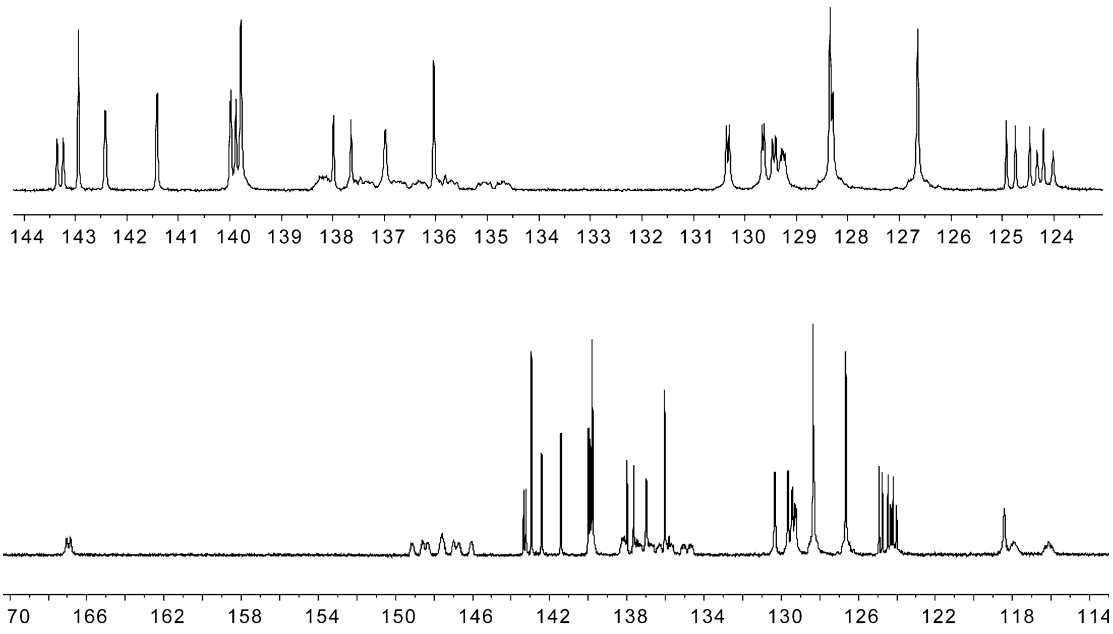
^{19}F NMR (564 MHz, 213 K, CD_2Cl_2) of compound **5d**



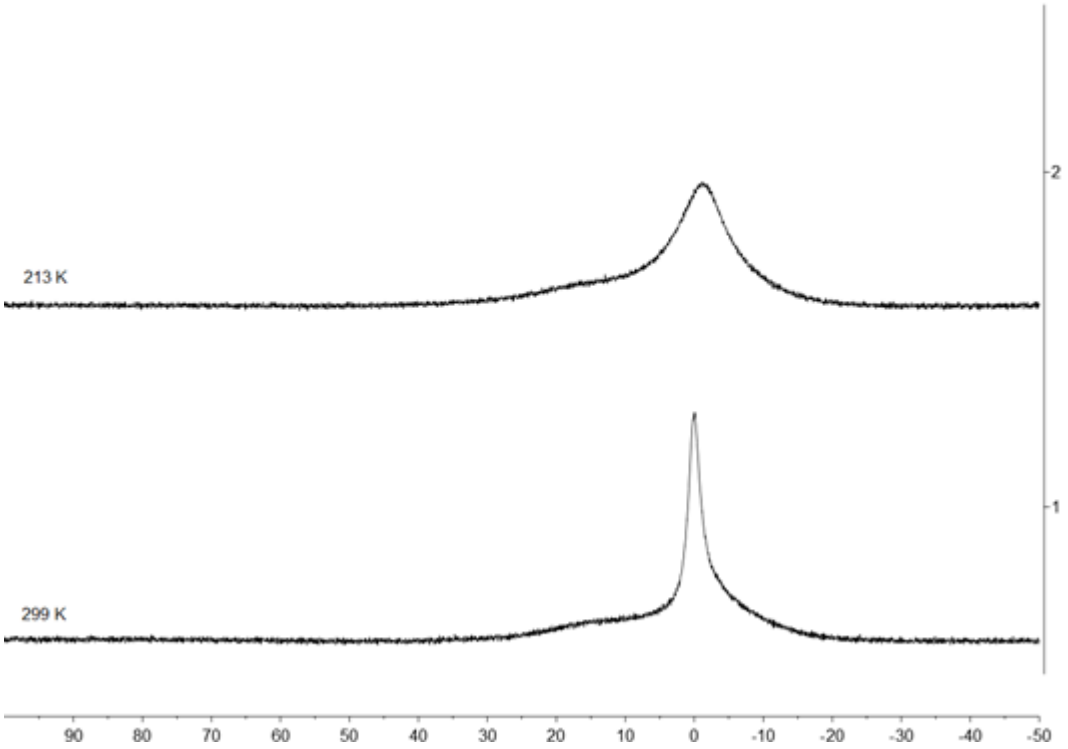
^{11}B{^{1}H} NMR (192 MHz, 213 K, CD_2Cl_2) and **^{31}P{^{1}H} NMR** (243 MHz, 213 K, CD_2Cl_2) of compound **5d**



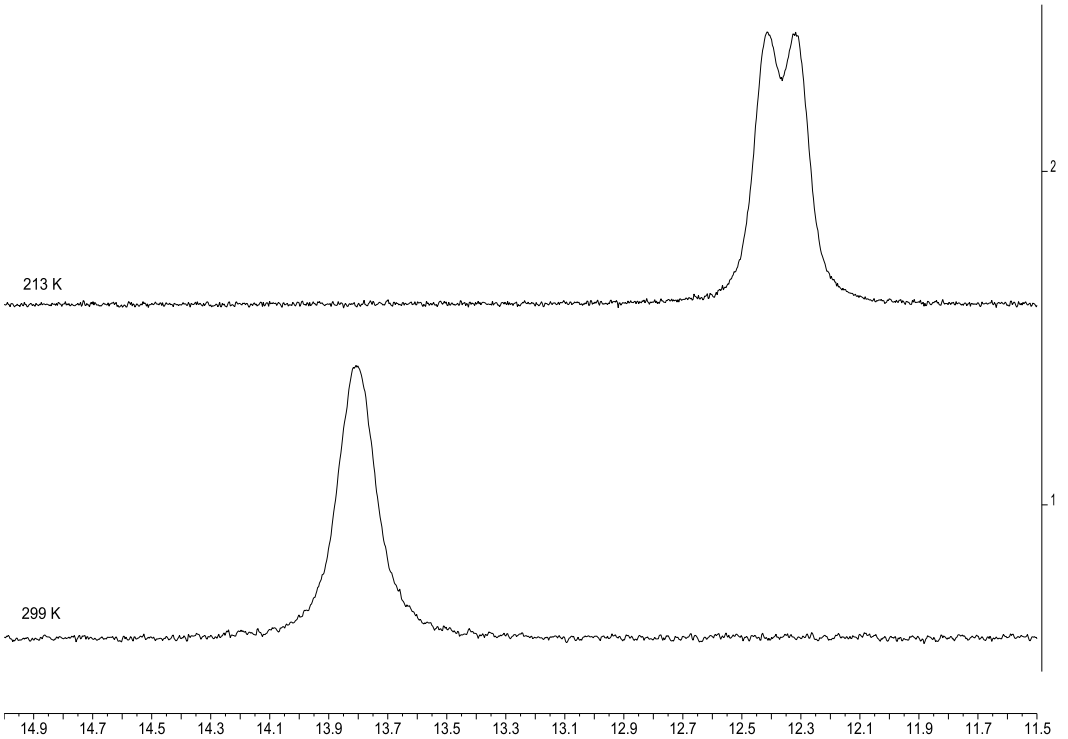
$^{13}C\{^{1}H\}$ NMR (151 MHz, 213 K, CD_2Cl_2) of compound **5d**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 213 K, CD_2Cl_2) of compound **5d**

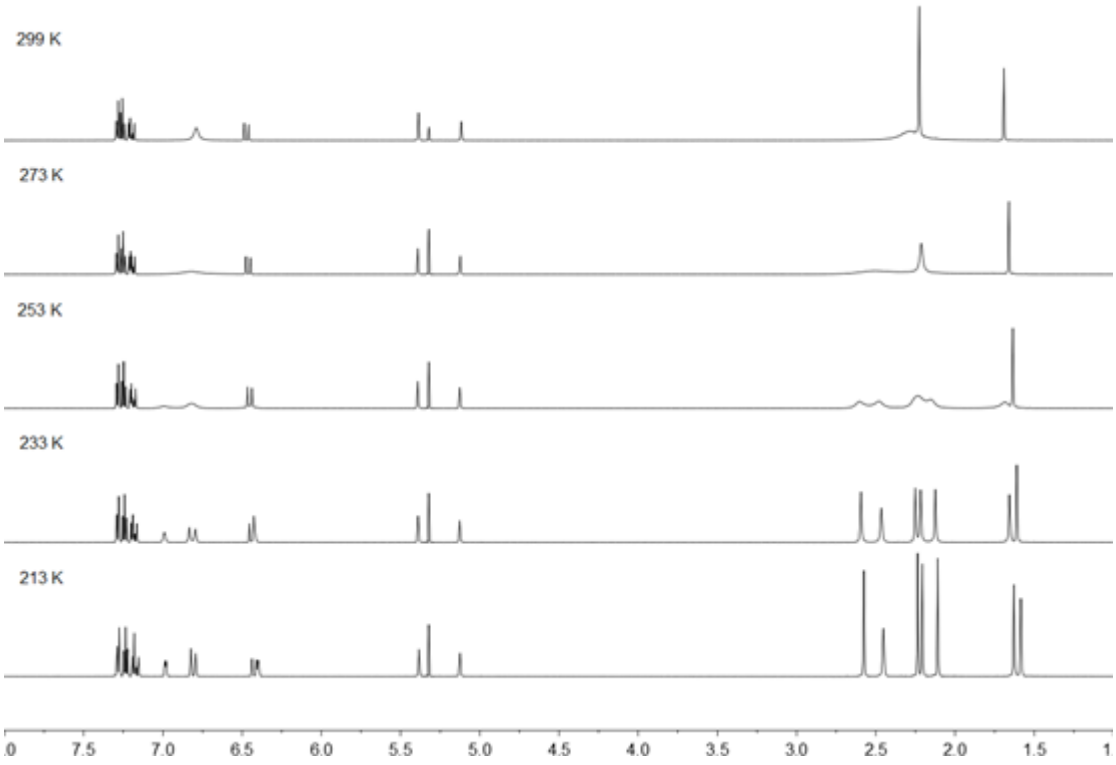


$^{11}B\{^{1}H\}$ NMR (192 MHz, CD_2Cl_2) of compound **5d** at 299K (1) and 213K (2)

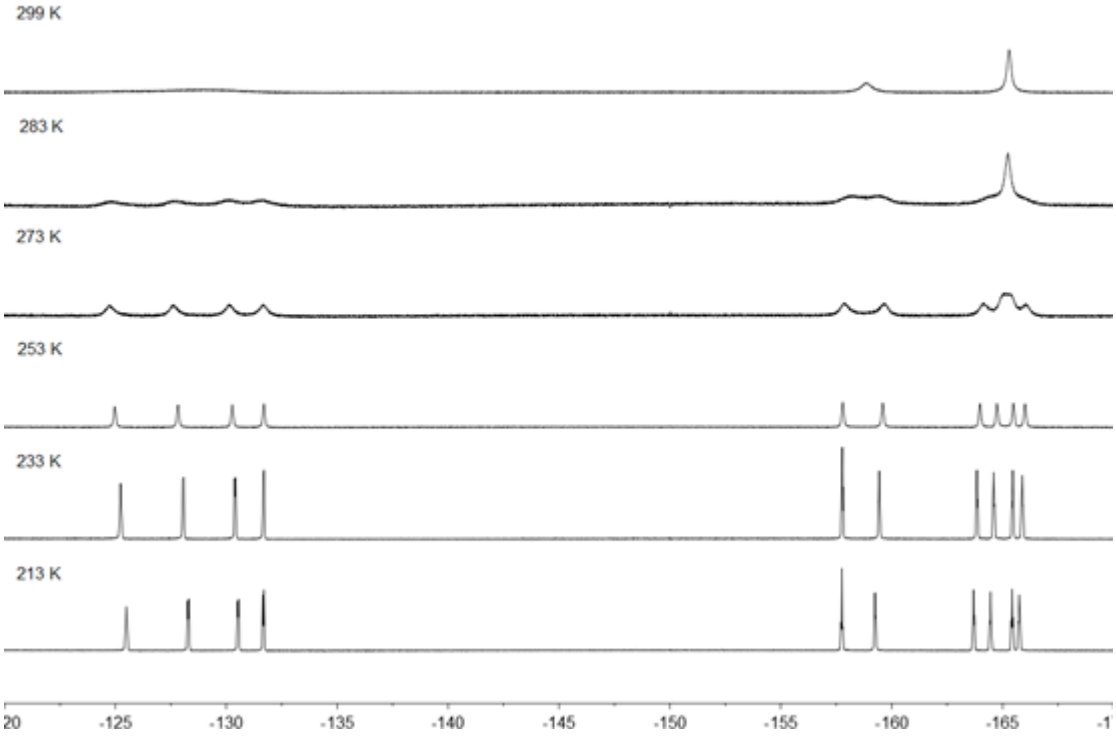


$^{31}P\{^{1}H\}$ NMR (243 MHz, CD_2Cl_2) of compound **5d** at 299K (1) and 213K (2)

Dynamic ^{1}H NMR (600 MHz, CD_2Cl_2):



Dynamic ^{19}F NMR (564 MHz, CD_2Cl_2):



$\Delta G^{\ddagger}[T_c, \Delta\nu(T)] = RT_c(22.96 + \ln(T_c/\Delta\nu))$ [J/mol]

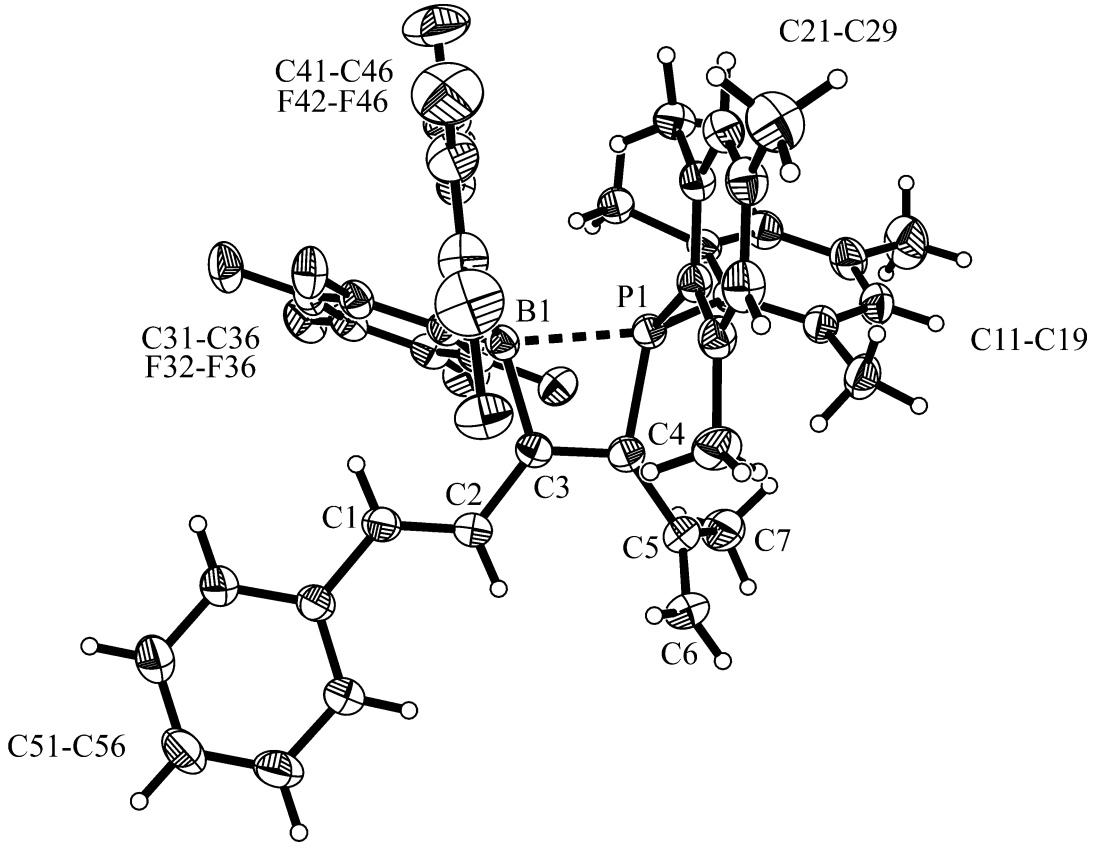
T_c = coalescence temperature [K]: 290 K (^{19}F, *p*-BC_6F_5)

$\Delta\nu$ = chemical shift difference [Hz] (^{19}F, *p*-BC_6F_5, 213 K): 842 Hz

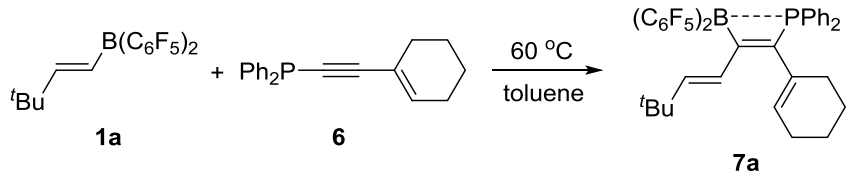
R = 8.314 J/(mol·K); 1 J = 0.239 cal

$\Delta G^{\ddagger}$[290K, $\Delta\nu$(213 K) = 842 Hz] = 57928 J/mol = 13.8 ± 0.3 kcal/mol

X-ray crystal structure analysis of compound 5d: formula $C_{43}H_{34}BF_{10}P$, *M* = 782.48, colourless crystal, 0.20 x 0.13 x 0.10 mm, *a* = 21.8974(5), *b* = 20.2120(5), *c* = 20.4155(7) Å, β = 108.587(1)°, *V* = 8564.4(4) Å^3, ρ_{calc} = 1.214 gcm^{-3}, μ = 1.195 mm^{-1}, empirical absorption correction (0.796 ≤ T ≤ 0.889), *Z* = 8, monoclinic, space group *C*2/*c* (No. 15), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 29400 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 7537 independent (R_{int} = 0.049) and 5941 observed reflections [*I*>2σ(*I*)], 503 refined parameters, *R* = 0.045, wR^2 = 0.130, max. (min.) residual electron density 0.21 (-0.23) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Synthesis of compound 7a.



The reaction mixture of the borane **1a** (0.214 g, 0.5 mmol, 1 eq) and the phosphane **6** (0.145 g, 0.5 mmol, 1 eq) in toluene (5 mL) was heated at 60 °C for 3 d. Then all volatiles were removed in vacuo and the residue was washed with pentane (1 × 3 mL). After drying in vacuo compound **7a** (0.293 g, 0.41 mmol, 82 %) was obtained as a light yellow solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to dichloromethane solution of compound **7a** at -35 °C. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 2952, 2864, 1639, 1516, 1457, 1384 1282, 1097, 972, 749, 693. **M.p.**: 155 °C. **Anal. Calc.** for $C_{38}H_{30}BF_{10}P$: C: 63.53; H: 4.21. Found: C: 63.32; H: 3.87.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.35 (m, 4H, *o*-Ph), 6.97 (dd, $^{3}J_{HH}$ = 15.8 Hz, $^{4}J_{PH}$ = 2.1 Hz, 1H, =CH), 6.91 (m, 2H, *p*-Ph), 6.85 (m, 4H, *m*-Ph), 6.16 (d, $^{3}J_{HH}$ = 15.8 Hz, 1H, =CH^{tBu}), 5.92 (m, 1H, =CH^{cy}), 2.25 (2H), 1.84 (2H), 1.39 (4H)(each m, CH_2^{cy}), 0.92 (s, 9H, ^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 175.0 (br, =CB), 154.2 (=CH^{tBu}), 148.7 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 140.1 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 137.4 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 134.1 (d, $^{2}J_{PC}$ = 2.4 Hz, =C^{cy}), 132.1 (d, $^{2}J_{PC}$ = 9.1 Hz, *o*-Ph), 131.6 (d, $^{4}J_{PC}$ = 3.0 Hz, *p*-Ph), 130.7 (d, $^{1}J_{PC}$ = 55.3 Hz, =CP), 130.4 (d, $^{3}J_{PC}$ = 7.2 Hz, =CH^{cy}), 128.8 (d, $^{3}J_{PC}$ = 10.4 Hz, *m*-Ph), 126.7 (d, $^{1}J_{PC}$ = 49.7 Hz, *i*-Ph), 123.5 (d, $^{3}J_{PC}$ = 47.9 Hz, =CH), 117.4 (br, *i*-C_6F_5), 33.8 (d, $^{5}J_{PC}$ = 0.9 Hz, ^{t}Bu), 29.4 (d, $^{3}J_{PC}$ = 5.0 Hz), 25.8, 22.9, 22.0 (CH_2^{cy}), 29.0 (^{t}Bu),.

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = -8.5 ($\nu_{1/2}$ ~ 300 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = 10.1 ($\nu_{1/2}$ ~ 65 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -129.2 (m, 2F, *o*-C_6F_5), -158.1 (tm, $^{3}J_{FF}$ = 20.8 Hz, 1F, *p*-C_6F_5), -164.6 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 6.5].

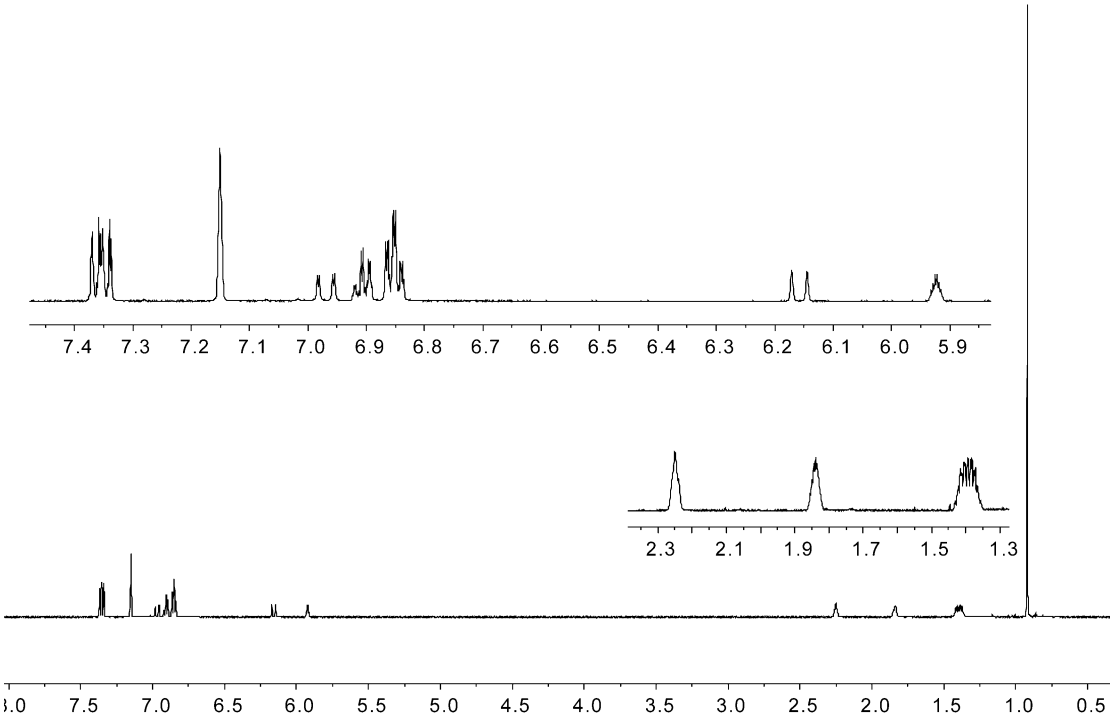
^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = 10.1 ($\nu_{1/2}$ ~ 60 Hz).

^{1}H, ^{1}H-GCOSY (600 MHz / 600 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{1}H = 7.35 / 6.85 (*o*-Ph / *m*-Ph), 6.97 / 6.16 (=CH / =CH^{tBu}), 6.91 / 6.85 (*p*-Ph / *m*-Ph), 5.92 / 2.25, 1.84 (=CH$^{2\text{-cy}}$ / $CH_2^{6\text{-cy}}$, $CH_2^{3\text{-cy}}$), 2.25 / 1.84, 1.39 ($CH_2^{6\text{-cy}}$ / $CH_2^{3\text{-cy}}$, $CH_2^{5\text{-cy}}$), 1.84 / 1.39 ($CH_2^{3\text{-cy}}$ / $CH_2^{4\text{-cy}}$).

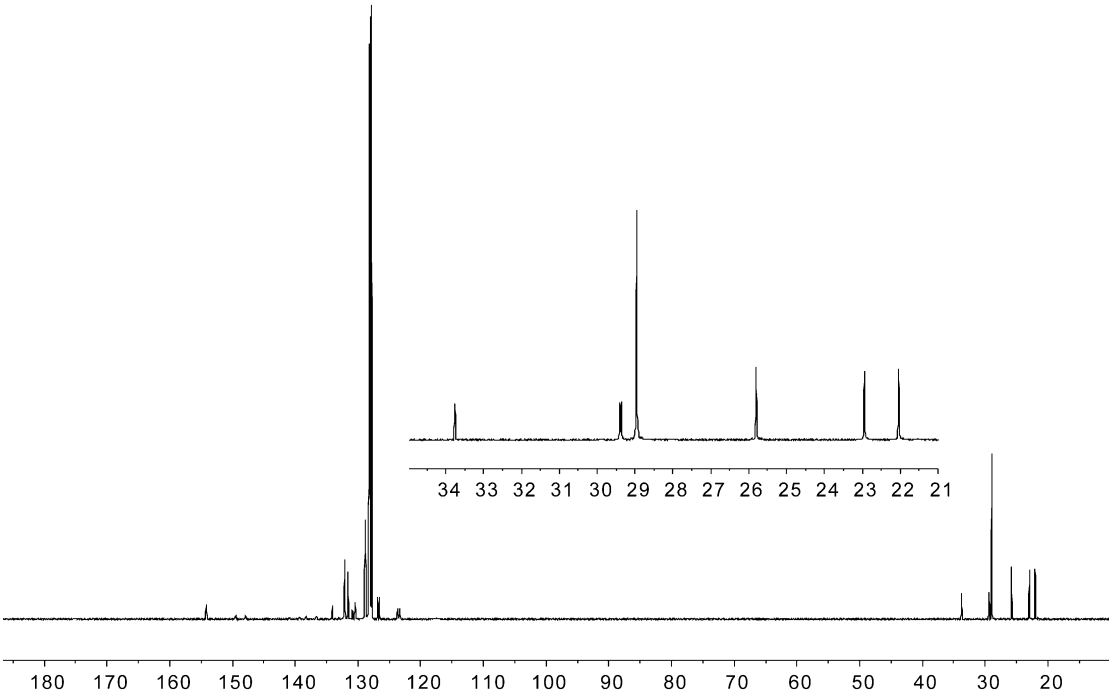
^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.35 / 132.1 (*o*-Ph), 6.97 / 123.5 (=CH), 6.91 / 131.6 (*p*-Ph), 6.85 / 128.8 (*m*-Ph), 6.16 / 154.2 (=CH^{tBu}), 5.92 / 130.4 (=CH^{cy}), 2.25 / 29.4 ($CH_2^{6\text{-cy}}$), 1.84 / 25.8 ($CH_2^{3\text{-cy}}$), 1.39 / 22.9 ($CH_2^{5\text{-cy}}$), 1.39 / 22.0 ($CH_2^{4\text{-cy}}$), 0.92 / 29.0 (^{t}Bu).

^{1}H, ^{13}C-GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6)[selected traces]: δ ^{1}H / δ ^{13}C = 7.35 / 132.1, 131.6 (*o*-Ph / *o*-Ph, *p*-Ph), 6.97 / 130.8, 33.8 (=CH / =CP, ^{t}Bu), 6.85 / 128.8, 126.7 (*m*-Ph / *m*-Ph, *i*-Ph), 6.16 / 175.0, 33.8, 29.0 (=CH^{tBu} / =CB, ^{t}Bu, ^{t}Bu), 5.92 / 25.8, 22.0 (=CH^{cy} / $CH_2^{3\text{-cy}}$, $CH_2^{4\text{-cy}}$), 2.25 / 134.1, 130.4, 22.9, 22.0 ($CH_2^{6\text{-cy}}$ / =C^{cy}, =CH^{cy}, $CH_2^{5\text{-cy}}$, $CH_2^{4\text{-cy}}$), 0.92 / 154.2, 33.8, 29.0 (^{t}Bu / =CH^{tBu}, ^{t}Bu, ^{t}Bu).

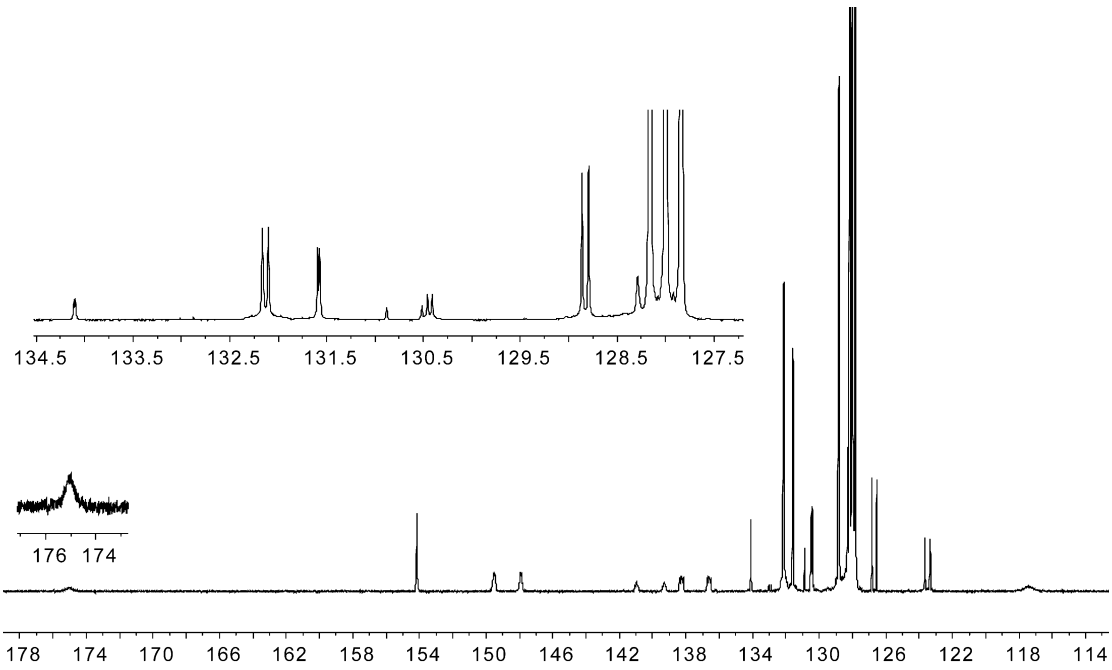
^{19}F, ^{19}F-GCOSY (564 MHz / 564 MHz, 299 K, C_6D_6): δ ^{19}F / δ ^{19}F = -129.2 / -164.6 (*o*-C_6F_5 / *m*-C_6F_5), -158.1 / -164.4 (*p*-C_6F_5 / *m*-C_6F_5).



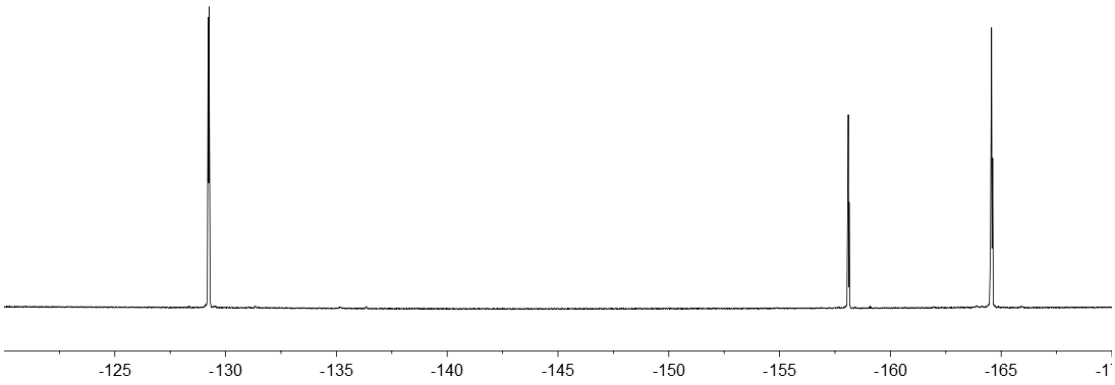
^{1}H NMR (600 MHz, 299 K, C_6D_6) of compound **7a**



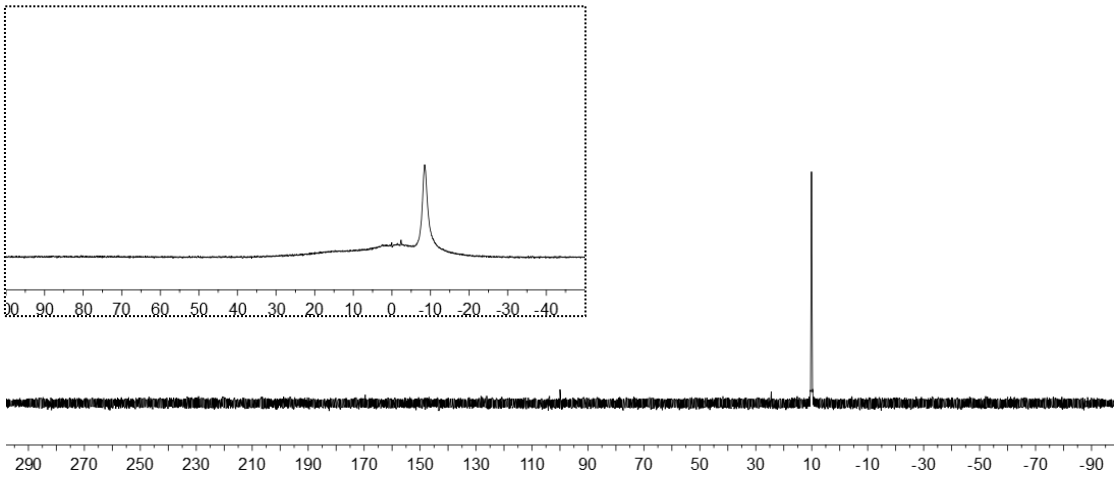
$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) of compound **7a**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) of compound **7a**

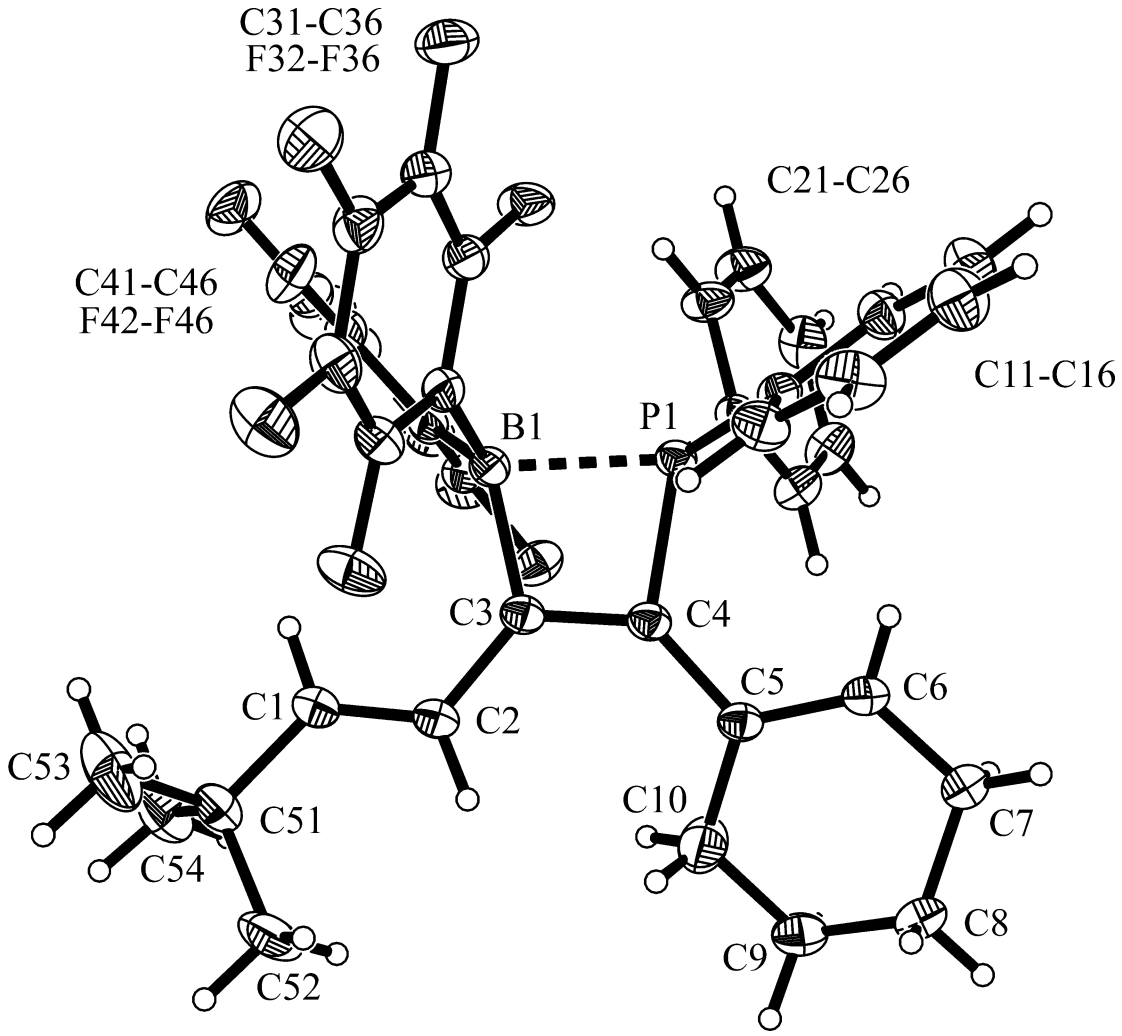


^{19}F NMR (564 MHz, 299 K, C_6D_6) of compound **7a**

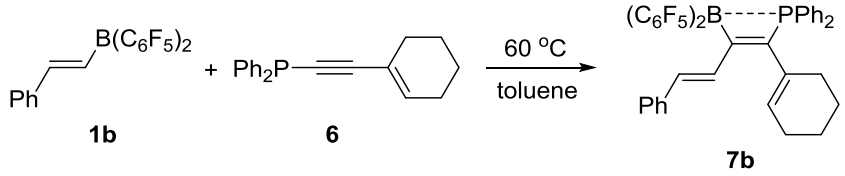


^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6) and **^{31}P{^{1}H} NMR** (243 MHz, 299 K, C_6D_6) of compound **7a**

X-ray crystal structure analysis of compound 7a: formula $C_{38}H_{30}BF_{10}P$, M = 718.40, colourless crystal, 0.27 x 0.20 x 0.17 mm, a = 10.1386(2), b = 10.9523(2), c = 16.0070(4) Å, α = 94.704(1), β = 90.060(1), γ = 104.481(2)°, V = 1714.74(6) Å^3, ρ_{calc} = 1.391 gcm^{-3}, μ = 0.162 mm^{-1}, empirical absorption correction (0.957 ≤ T ≤ 0.973), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 16073 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 6788 independent (R_{int} = 0.039) and 6089 observed reflections [I>2 σ (I)], 454 refined parameters, R = 0.049, wR^2 = 0.129, max. (min.) residual electron density 0.37 (-0.34) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Synthesis of compound 7b.



The reaction mixture of the borane **1b** (0.224 g, 0.5 mmol, 1 eq) and the phosphane **6** (0.145 g, 0.5 mmol, 1 eq) in toluene (5 mL) was heated at 60 °C for 3 d. Then all volatiles were removed in vacuo and the residue was washed with pentane (1 × 3 mL). After drying in vacuo compound **7b** (0.318 g, 0.43 mmol, 86 %) was obtained as a light yellow solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to dichloromethane solution of compound **7b** at

-35 °C. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3059, 2933, 2859, 1641, 1516, 1456, 1381, 1287, 1102, 972, 743, 693. **Decomp**.: 183 °C. **Anal. Calc.** for $C_{40}H_{26}BF_{10}P$: C: 65.06; H: 3.55. Found: C: 64.72; H: 3.21.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 7.77 (dd, $^{3}J_{HH}$ = 16.0 Hz, $^{4}J_{PH}$ = 2.2 Hz, 1H, =CH), 7.35 (m, 4H, *o*-Ph^{P}), 7.32 (m, 2H, *o*-Ph), 7.07 (d, $^{3}J_{HH}$ = 16.0 Hz, 1H, =CH^{Ph}), 6.99 (m, 2H, *m*-Ph), 6.96 (m, 1H, *p*-Ph), 6.91 (m, 2H, *p*-Ph^{P}), 6.85 (m, 4H, *m*-Ph^{P}), 5.96 (m, 1H, =CH^{cy}), 2.23 (2H), 1.85 (2H), 1.40 (4H)(each m, CH_2^{cy}).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 173.4 (br, =CB), 148.8 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 140.2 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 139.9 (=CH^{Ph}), 137.4 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 137.2 (d, $^{5}J_{PC}$ = 1.2 Hz, *i*-Ph), 134.2 (d, $^{2}J_{PC}$ = 2.0 Hz, =C^{cy}), 132.9 (d, $^{1}J_{PC}$ = 54.7 Hz, =CP), 132.1 (d, $^{2}J_{PC}$ = 9.1 Hz, *o*-Ph^{P}), 131.7 (d, $^{4}J_{PC}$ = 3.0 Hz, *p*-Ph^{P}), 131.3 (dm, $^{3}J_{PC}$ = 7.5 Hz, =CH^{cy}), 129.0 (*m*-Ph), 128.89 (d, $^{3}J_{PC}$ = 10.4 Hz, *m*-Ph^{P}), 128.86 (*p*-Ph), 127.6 (*o*-Ph), 126.8 (d, $^{3}J_{PC}$ = 48.8 Hz, =CH), 126.5 (d, $^{1}J_{PC}$ = 40.1 Hz, *i*-Ph^{P}), 117.1 (br, *i*-C_6F_5), 29.5 (d, $^{3}J_{PC}$ = 4.8 Hz), 25.9, 22.9, 22.0 (CH_2^{cy}).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = -8.2 ($\nu_{1/2}$ ~ 350 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = 10.4 ($\nu_{1/2}$ ~ 50 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = -129.2 (m, 2F, *o*-C_6F_5), -157.5 (tm, $^{3}J_{FF}$ = 20.8 Hz, 1F, *p*-C_6F_5), -164.2 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 6.7].

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = 10.4 ($\nu_{1/2}$ ~ 50 Hz).

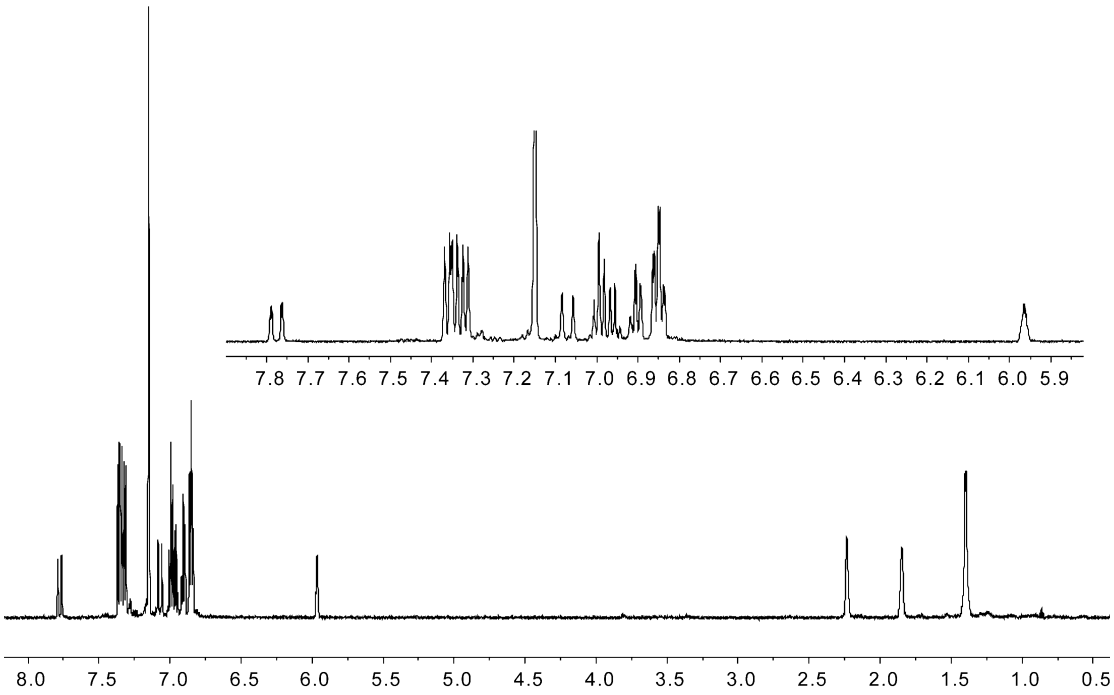
^{1}H, ^{1}H-GCOSY (600 MHz / 600 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{1}H = 7.77 / 7.07 (=CH / =CH^{Ph}), 7.35 / 6.85 (*o*-Ph^{P} / *m*-Ph^{P}), 7.32 / 6.99 (*o*-Ph / *m*-Ph), 6.99 / 6.96 (*m*-Ph / *p*-Ph), 6.91 / 6.85 (*p*-Ph^{P} / *m*-Ph^{P}), 5.96 / 2.23, 1.85 (=CH^{cy} / $CH_2^{6\text{-}cy}$, $CH_2^{3\text{-}cy}$), 2.23 / 1.84, 1.40 ($CH_2^{6\text{-}cy}$ / $CH_2^{3\text{-}cy}$, $CH_2^{5\text{-}cy}$), 1.85 / 1.40 ($CH_2^{3\text{-}cy}$ / $CH_2^{4\text{-}cy}$).

^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ ^{1}H / δ ^{13}C = 7.77 / 126.8 (=CH), 7.35 / 132.1 (*o*-Ph^{P}), 7.32 / 127.6 (*o*-Ph), 7.07 / 139.9 (=CH^{Ph}), 6.99 / 129.0 (*m*-Ph), 6.96 / 128.86 (*p*-Ph), 6.91 / 131.7 (*p*-Ph^{P}), 6.85 / 128.89 (*m*-Ph^{P}), 5.96 / 131.3 (=CH^{cy}), 2.23 / 29.5 ($CH_2^{6\text{-}cy}$), 1.85 / 25.9 ($CH_2^{3\text{-}cy}$), 1.40 / 22.9 ($CH_2^{5\text{-}cy}$), 1.40 / 22.0 ($CH_2^{4\text{-}cy}$).

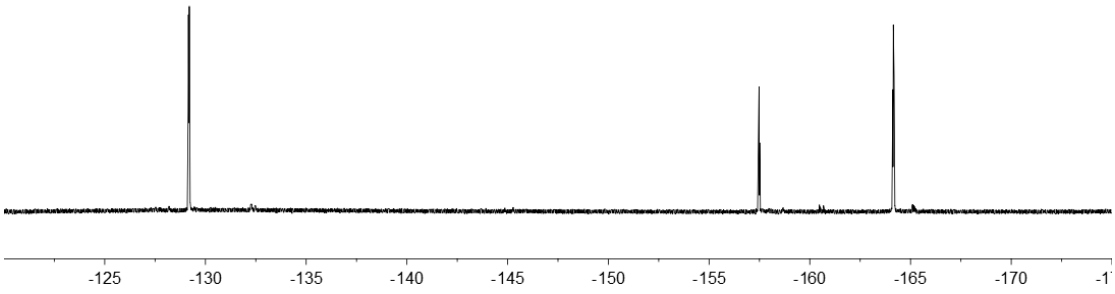
^{1}H, ^{13}C-GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6)[selected traces]: δ ^{1}H / δ ^{13}C = 7.77 / 137.2, 132.9 (=CH / *i*-Ph, =CP), 7.35 / 132.1, 131.7 (*o*-Ph^{P} / *o*-Ph^{P}, *p*-Ph^{P}), 7.32

/ 139.9, 128.86, 127.6 (*o*-Ph / =CH^{Ph}, *p*-Ph, *o*-Ph), 7.07 / 173.4, 122.6 (=CH^{Ph} / =CB, *o*-Ph), 6.99 / 137.2, 129.0 (*m*-Ph / *i*-Ph, *m*-Ph), 6.85 / 128.89, 126.5 (*m*-Ph^{P} / *m*-Ph^{P}, *i*-Ph^{P}), 5.96 / 25.9, 22.0 (=CH^{cy} / $CH_2^{3\text{-}cy}$, $CH_2^{4\text{-}cy}$), 2.23 / 134.2, 131.3, 22.9, 22.0 ($CH_2^{6\text{-}cy}$ / $=C^{cy}$, $=CH^{cy}$, $CH_2^{5\text{-}cy}$, $CH_2^{4\text{-}cy}$),.

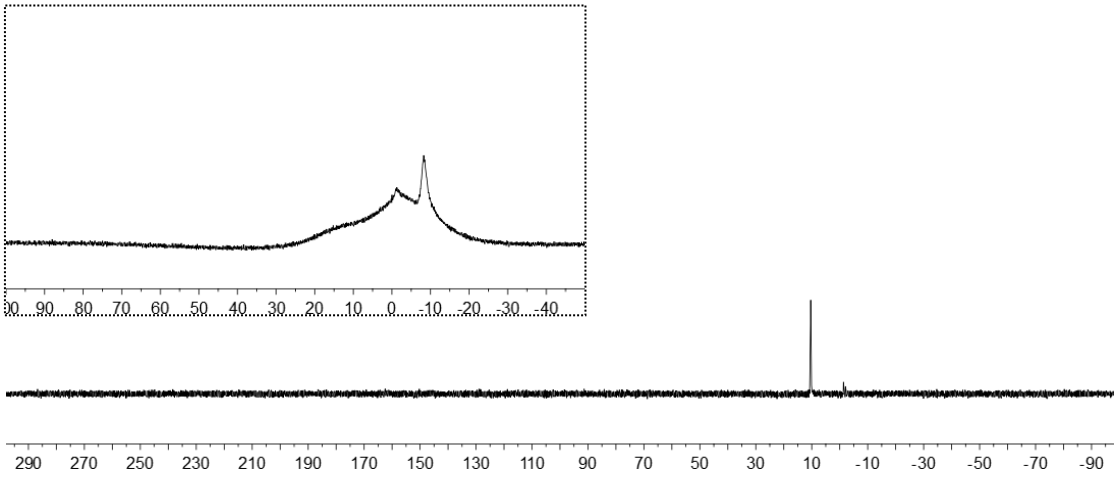
^{19}F, ^{19}F-GCOSY (564 MHz / 564 MHz, 299 K, C_6D_6): δ ^{19}F / δ ^{19}F = -129.2 / -164.2 (*o*-C_6F_5 / *m*-C_6F_5), -157.5 / -164.2 (*p*-C_6F_5 / *m*-C_6F_5).



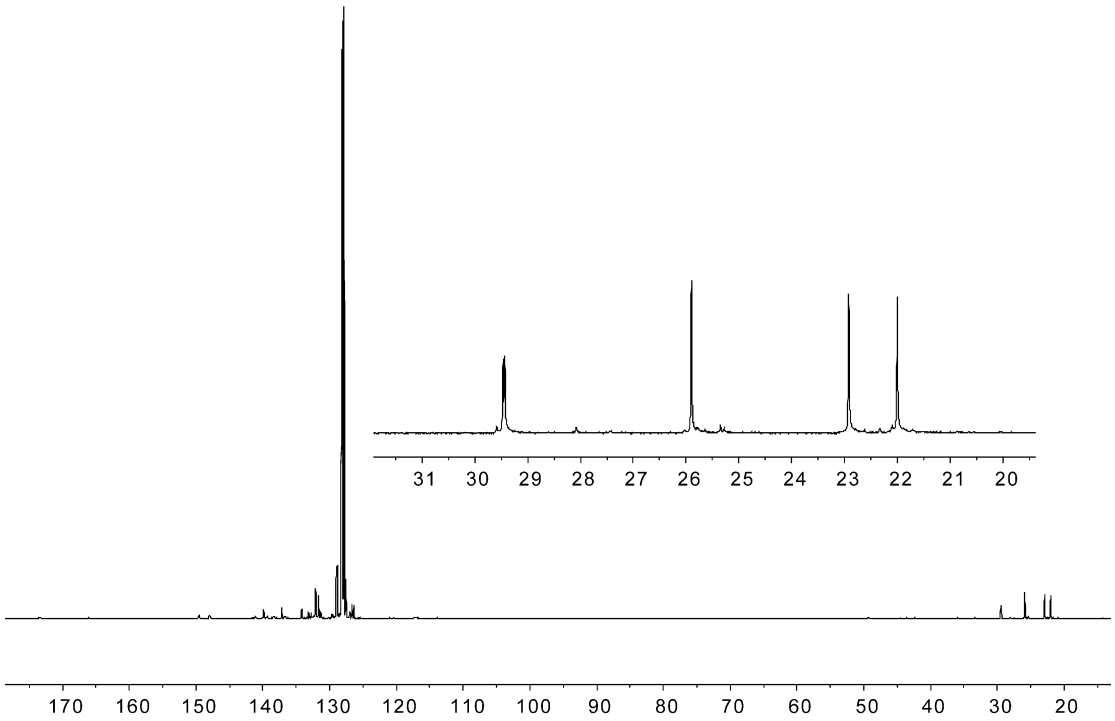
^{1}H NMR (600 MHz, 299 K, C_6D_6) of compound **7b**



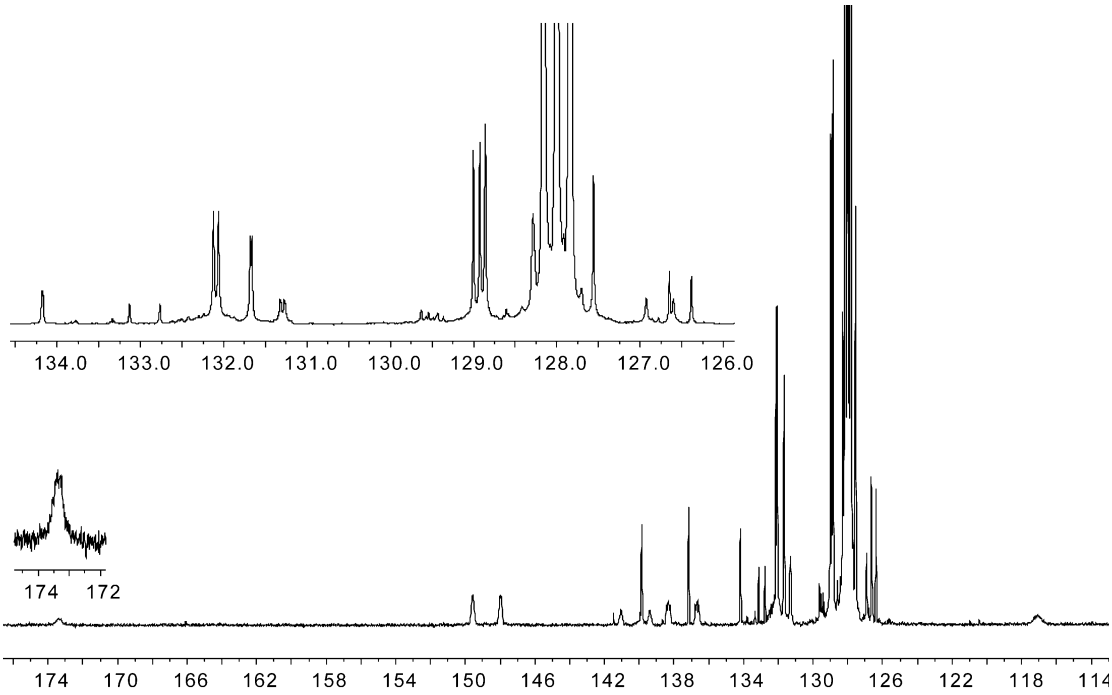
^{19}F NMR (564 MHz, 299 K, C_6D_6) of compound **7b**



^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6) and **^{31}P{^{1}H} NMR** (243 MHz, 299 K, C_6D_6) of compound **7b**

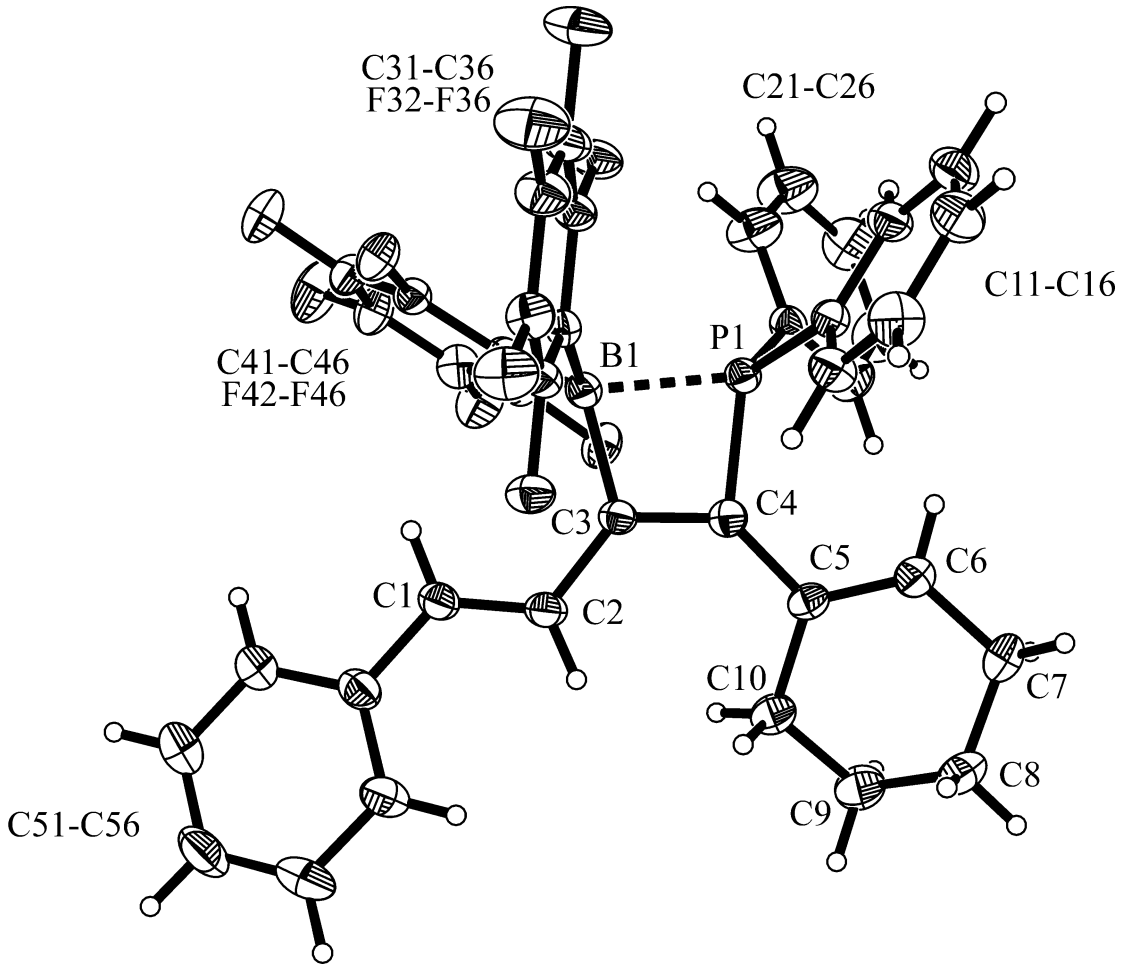


^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6) of compound **7b**

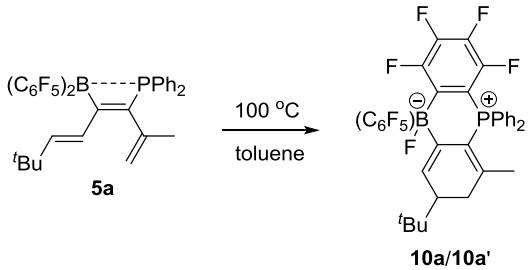


$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6) of compound **7b**

X-ray crystal structure analysis of compound 7b: formula $C_{40}H_{26}BF_{10}P$, M = 738.39, colourless crystal, 0.35 x 0.20 x 0.08 mm, a = 12.0744(3), b = 28.1047(6), c = 11.3117(2) Å, β = 99.395(1)° , V = 3787.1(1) Å^3, ρ_{calc} = 1.295 gcm^{-3}, μ = 0.149 mm^{-1}, empirical absorption correction (0.949 ≤ T ≤ 0.988), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 17587 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 6486 independent (R_{int} = 0.056) and 5195 observed reflections [I>2 σ (I)], 488 refined parameters, R = 0.073, wR^2 = 0.211, max. (min.) residual electron density 0.48 (-0.34) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Synthesis of compounds 10a/10a'.



A solution of compound **5a** (0.271 g, 0.4 mmol) in toluene (4 mL) was heated at 100 °C for 3 d. Then all volatiles were removed in vacuo and the residue was washed with pentane (1 × 3 mL). After drying in vacuo a light yellow solid (0.244 g, 90 %) was obtained. In CD_2Cl_2 solution two isomers were observed (ca. 80:20 [^{1}H]).

*Major isomer **10a**.*

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2)[selected resonances]: δ = 6.33 (m, 1H, =CH),

2.34 (td, $^{2}J_{HH}$ = 17.4 Hz, $^{4}J_{PH}$ = 5.2 Hz, 1H, CH_2), 2.25 (dd, $^{2}J_{HH}$ = 17.0 Hz, $^{3}J_{HH}$ = 6.5 Hz, 1H, CH_2), 2.02 (ddm, $^{3}J_{HH}$ = 17.7 Hz, $^{3}J_{HH}$ = 6.5 Hz, 1H, CH), 1.56 (d, $^{4}J_{PH}$ = 2.9 Hz, 3H, CH_3), 0.99 (s, 9H, ^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 160.3 (dd, $^{2}J_{PC}$ = 8.9 Hz, $^{5}J_{FC}$ = 1.8 Hz, $=C^{Me}$), 134.5 (d, $^{4}J_{PC}$ = 3.1 Hz), 134.1 (d, $^{4}J_{PC}$ = 3.2 Hz)(*p*-Ph), 133.0 (dd, $^{2}J_{PC}$ = 11.2 Hz, $^{5}J_{FC}$ = 1.9 Hz), 132.6 (dd, $^{2}J_{PC}$ = 11.5 Hz, $^{5}J_{FC}$ = 2.3 Hz)(*o*-Ph), 130.3 (d, $^{3}J_{PC}$ = 13.3 Hz), 130.0 (d, $^{3}J_{PC}$ = 13.1 Hz)(*m*-Ph), 127.8 (m, =CH), 125.1 (dd, $^{1}J_{PC}$ = 87.0 Hz, $^{4}J_{FC}$ = 4.1 Hz), 119.2 (d, $^{1}J_{PC}$ = 85.2 Hz)(*i*-Ph), 114.3 (dd, $^{1}J_{PC}$ = 85.1 Hz, $^{4}J_{FC}$ = 6.2 Hz, =CP), 42.9 (d, $^{4}J_{PC}$ = 2.1 Hz, CH), 35.6 (d, $^{3}J_{PC}$ = 13.2 Hz, CH_2), 32.5 (^{t}Bu), 27.6 (^{t}Bu), 25.1 (d, $^{3}J_{PC}$ = 9.1 Hz, CH_3). [C_6F_5, C_6F_4 not listed]

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = -1.5 ($\nu_{1/2}$ ~ 200 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -1.5 ($\nu_{1/2}$ ~ 20 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -126.8, -131.4, -147.1, -158.9 (each m, each 1F, C_6F_4), -132.8 (m, 2F, *o*), -161.0 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*), -165.8 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.8], -199.2 (br, 1F, BF).

^{1}H, ^{1}H-GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{1}H = 7.70 / 7.57 (*p*-Ph^A / *m*-Ph^A), 7.67 / 7.49 (*o*-Ph^B / *m*-Ph^B), 6.33 / 2.25, 2.02, 1.56 (=CH / CH_2, CH, CH_3), 2.34 / 2.25, 1.56 (CH_2 / CH_2, CH_3), 2.25 / 2.02 (CH_2 / CH).

^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.70 / 134.1 (*p*-Ph^A), 7.67 / 134.5 (*p*-Ph^B), 7.57 / 132.6, 130.3 (*o*-,*m*-Ph^A / *o*-Ph^A, *m*-Ph^A), 7.49 / 133.0, 130.0 (*o*-,*m*-Ph^B / *o*-Ph^B, *m*-Ph^B), 6.33 / 127.8 (=CH), 2.34 / 35.6 (CH_2), 2.25 / 35.6 (CH_2), 2.02 / 42.9 (CH), 1.56 / 25.1 (CH_3), 0.99 / 27.6 (^{t}Bu).

^{1}H, ^{13}C-GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2)[selected traces]: δ ^{1}H / δ ^{13}C = 7.57 / 134.1, 132.6 (*o*-Ph^A / *p*-Ph^A, *o*-Ph^A), 7.57 / 130.3, 125.4 (*m*-Ph^A / *m*-Ph^A, *i*-Ph^A), 7.49 / 134.5, 133.0 (*o*-Ph^B / *p*-Ph^B, *o*-Ph^B), 7.49 / 130.0, 119.2 (*m*-Ph^B / *m*-Ph^B, *i*-Ph^B), 2.25 / 160.3, 127.8, 114.3, 42.9, 32.5, 25.1 (CH_2 / $=C^{Me}$, =CH, =CP, CH, ^{t}Bu, CH_3), 0.99 / 42.9, 32.5, 27.6 (^{t}Bu / CH, ^{t}Bu, ^{t}Bu).

^{19}F, ^{19}F-GCOSY (564 MHz / 564 MHz, 299 K, CD_2Cl_2): δ ^{19}F / δ ^{19}F = -126.8 / -147.1, 158.9 (C_6F_4 / C_6F_4, C_6F_4), -131.4 / -147.1 (C_6F_4 / C_6F_4), -132.8 / -165.8 (*o*-C_6F_5 / *m*-C_6F_5), -147.1 / -158.9 (C_6F_4 / C_6F_4), -161.0 / -165.8 (*p*-C_6F_5 / *m*-C_6F_5).

*Minor isomer **10a'**.*

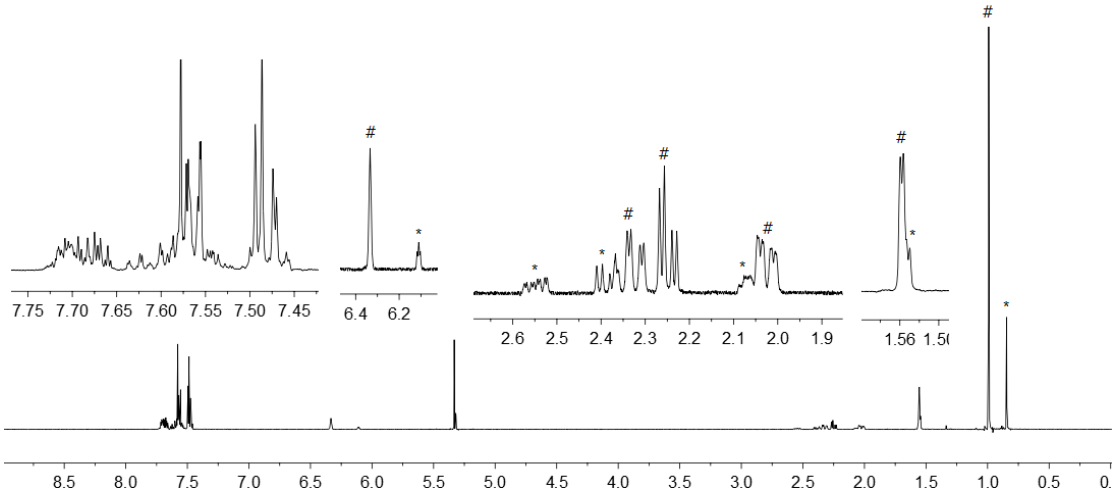
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2)[selected resonances]: δ = 6.11 (m, 1H, =CH), 2.55 (dddm, $^{2}J_{HH}$ = 17.8 Hz, $^{3}J_{HH}$ = 9.8 Hz, $^{4}J_{PH}$ = 3.4 Hz, 1H, CH_2), 2.39 (dd, $^{2}J_{HH}$ = 17.8 Hz, $^{3}J_{HH}$ = 7.6 Hz, 1H, CH_2), 2.07 (m, 1H, CH), 1.55 (d, $^{4}J_{PH}$ = 2.9 Hz, 3H, CH_3), 0.85 (s, 9H, ^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = n.o. (=CB), 159.2 (dd, $^{2}J_{PC}$ = 9.0 Hz, $^{5}J_{FC}$ = 0.8 Hz, =C^{Me}), 134.3 (d, $^{4}J_{PC}$ = 3.2 Hz), 134.2 (d, $^{4}J_{PC}$ = 3.2 Hz)(*p*-Ph), 132.89 (dd, $^{2}J_{PC}$ = 11.2 Hz, $^{5}J_{FC}$ = 1.6 Hz), 132.87 (dd, $^{2}J_{PC}$ = 11.6 Hz, $^{5}J_{FC}$ = 2.2 Hz)(*o*-Ph), 130.2 (d, $^{3}J_{PC}$ = 13.3 Hz), 130.1 (d, $^{3}J_{PC}$ = 13.0 Hz)(*m*-Ph), 128.0 (m, =CH), 123.7 (dd, $^{1}J_{PC}$ = 86.6 Hz, $^{4}J_{FC}$ = 3.1 Hz), 121.0 (d, $^{1}J_{PC}$ = 85.9 Hz)(*i*-Ph), 113.9 (dd, $^{1}J_{PC}$ = 85.8 Hz, $^{4}J_{FC}$ = 4.2 Hz, =CP), 42.2 (d, $^{4}J_{PC}$ = 1.9 Hz, CH), 35.5 (d, $^{3}J_{PC}$ = 13.2 Hz, CH_2), 34.0 (^{t}Bu), 27.4 (^{t}Bu), 25.0 (d, $^{3}J_{PC}$ = 9.2 Hz, CH_3). [C_6F_5, C_6F_4 not listed]

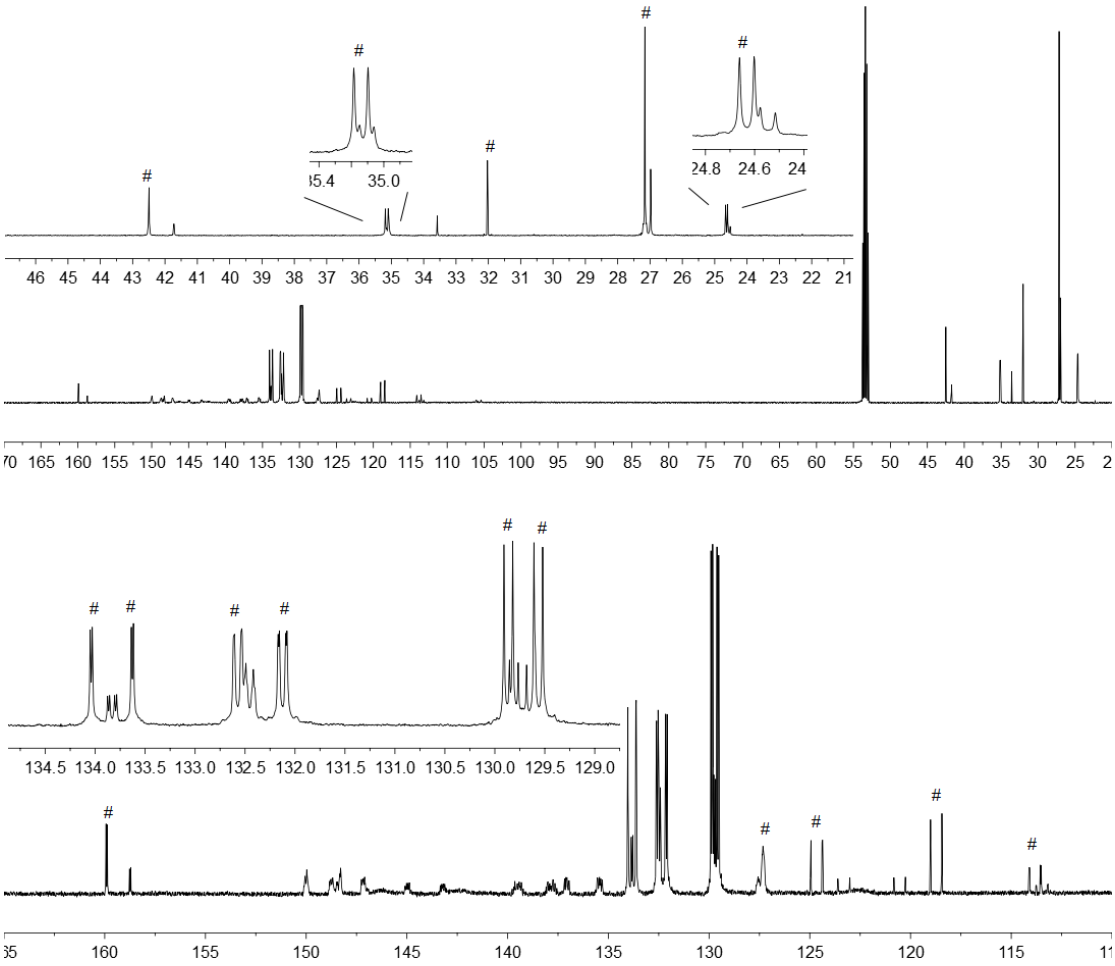
^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = -1.5 ($\nu_{1/2}$ ~ 200 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -0.9 ($\nu_{1/2}$ ~ 20 Hz).

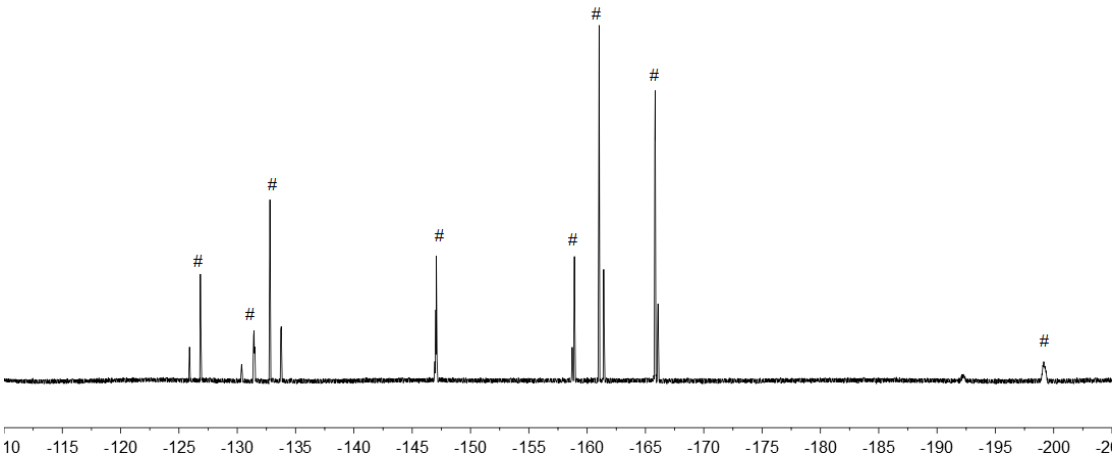
^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -125.9, -130.4, -147.0, -158.7 (each m, each 1F, C_6F_4), -133.7 (m, 2F, *o*), -161.4 (t, $^{3}J_{FF}$ = 20.1 Hz,1F, *p*), -166.1 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.7], -192.3 (br, 1F, BF).



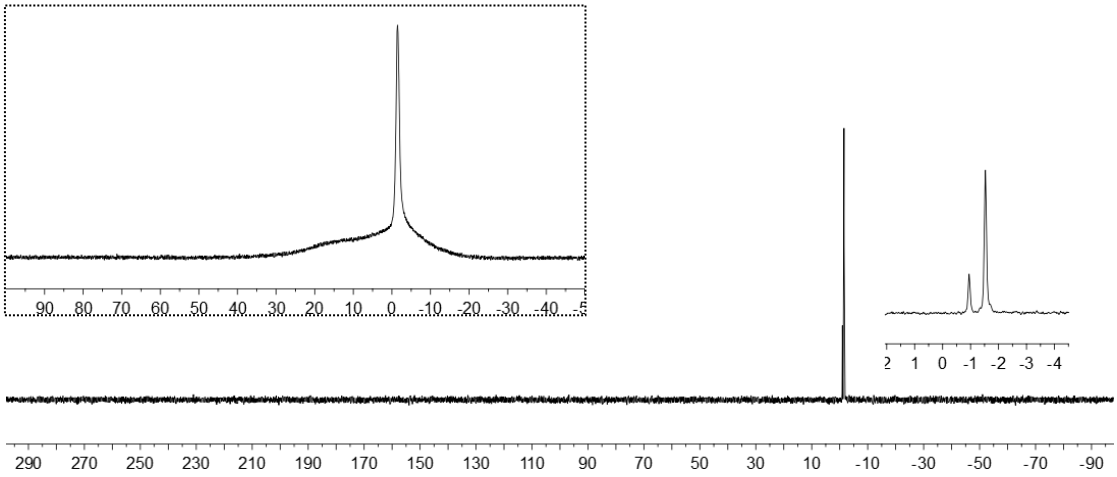
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) of **10a/10a'** (# major isomer, * minor isomer)



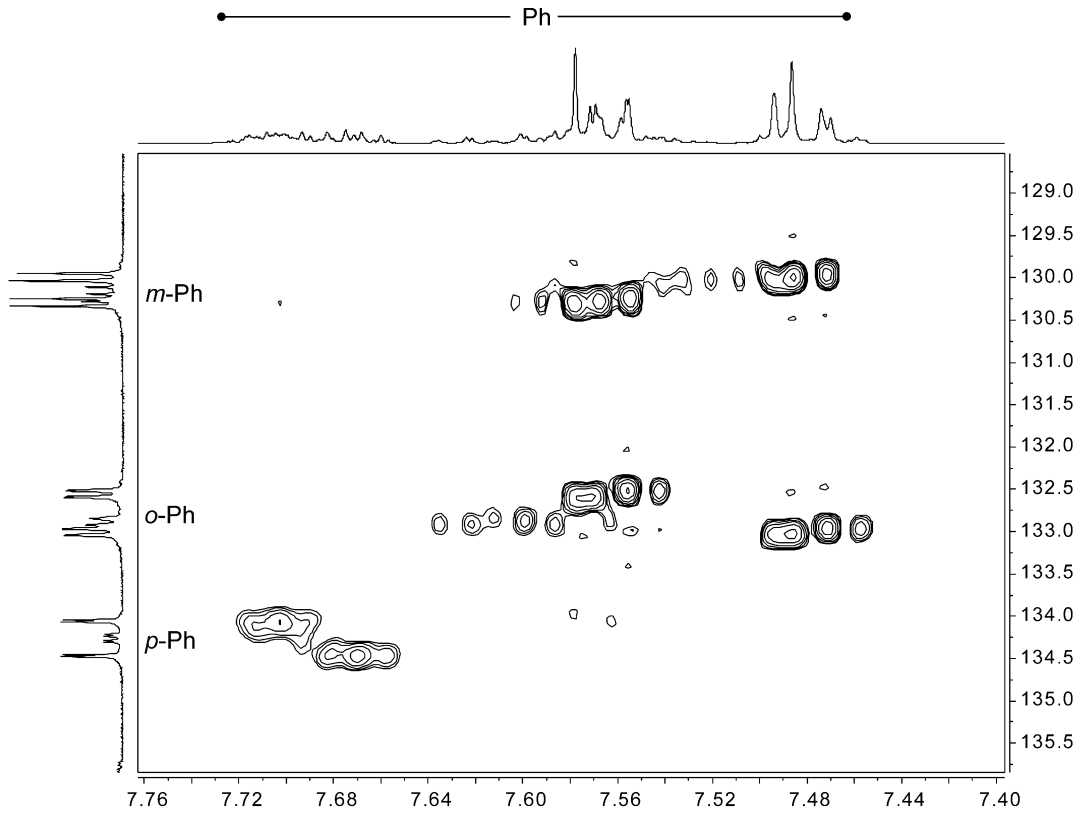
$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) of compounds **10a/10a'** (# major isomer)



^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compounds **10a/10a'** (# major isomer)



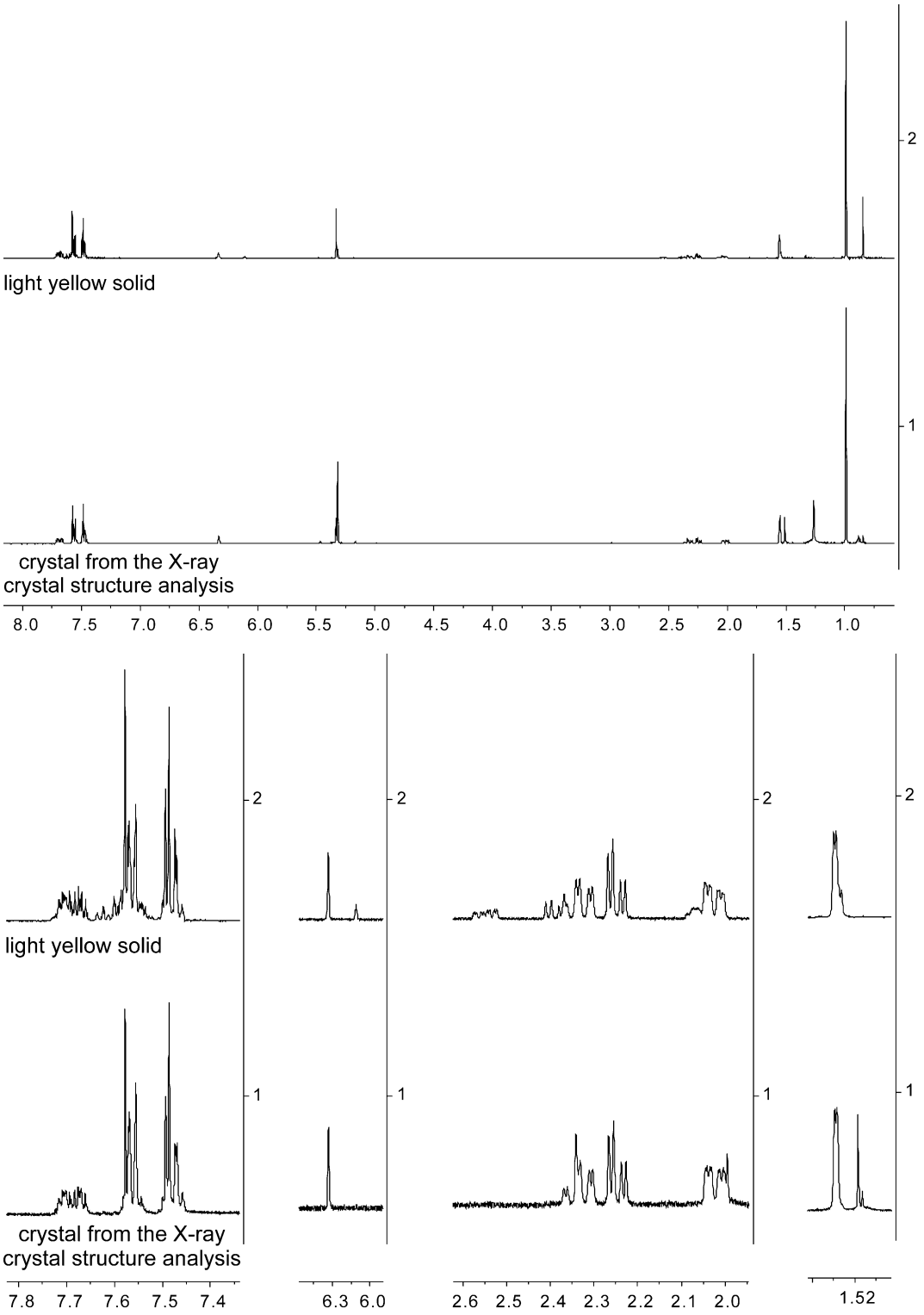
^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2) and **^{31}P{^{1}H} NMR** (243 MHz, 299 K, CD_2Cl_2) of compounds **10a/10a'**



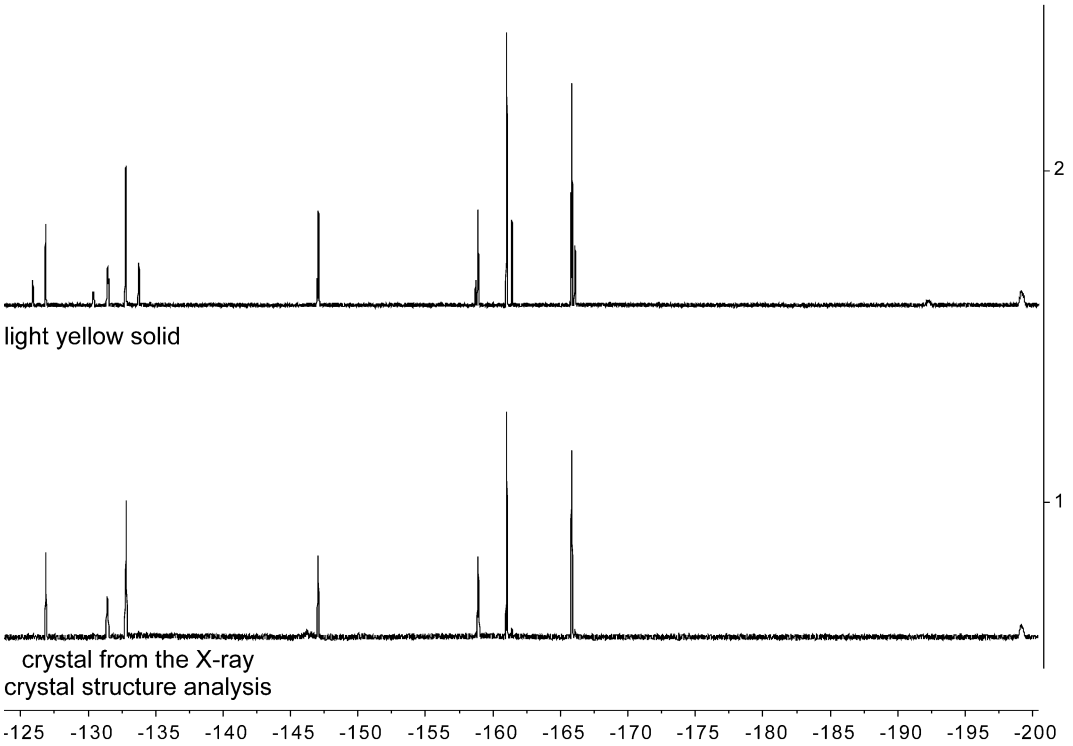
^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2) of compounds **10a/10a'**

Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a dichloromethane solution of the yellow solid at -35 °C.

The ^{1}H and ^{19}F NMR data obtained from a solution of the crystal from the X-ray crystal structure analysis in CD_2Cl_2 are consistent with those listed for the major isomer **10a** (see above).

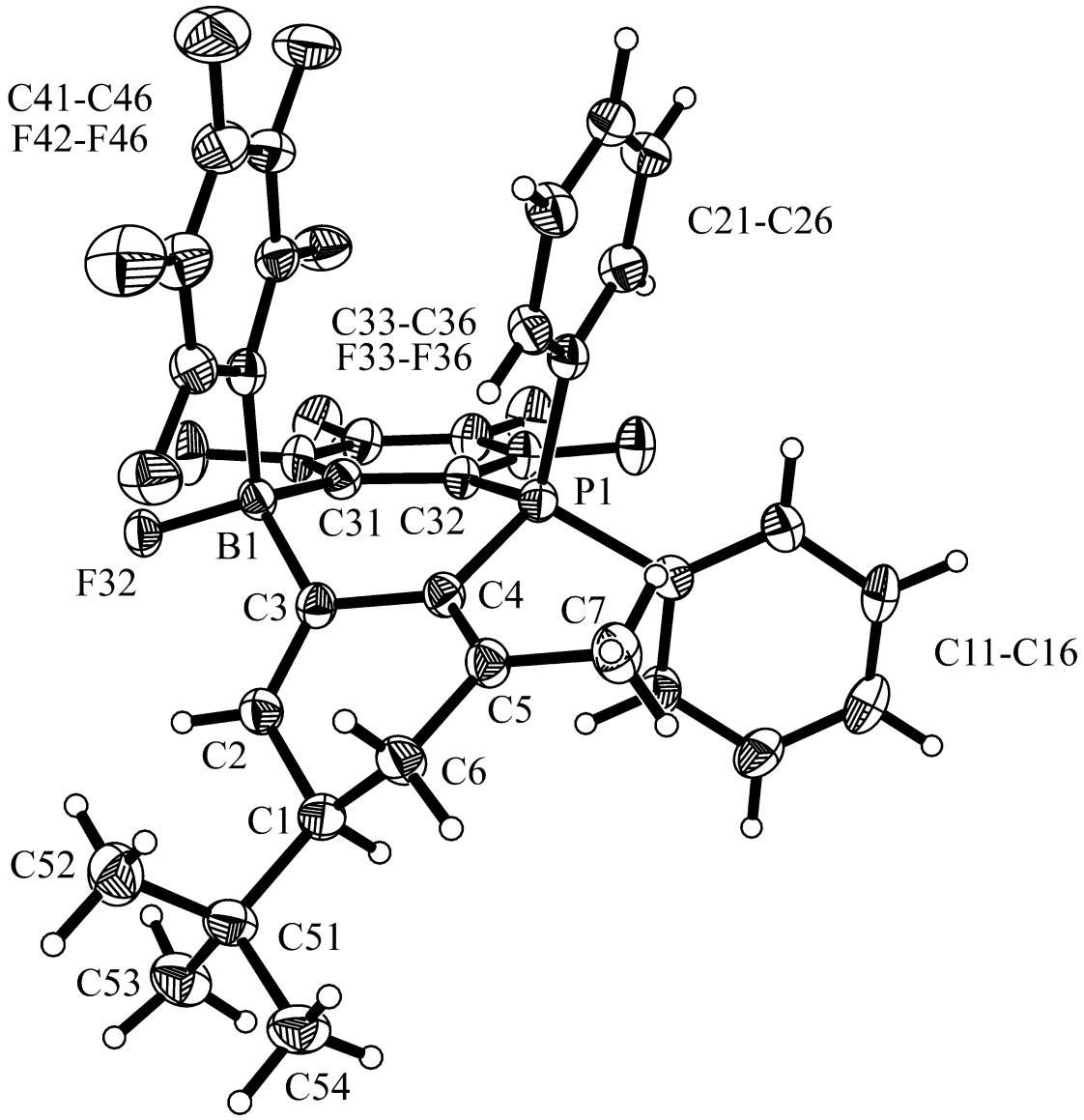


^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) of (2) isomer mixure **10a/10a'** [light yellow solid, see above)] and (1) the crystal from the X-ray crystal structure analysis.

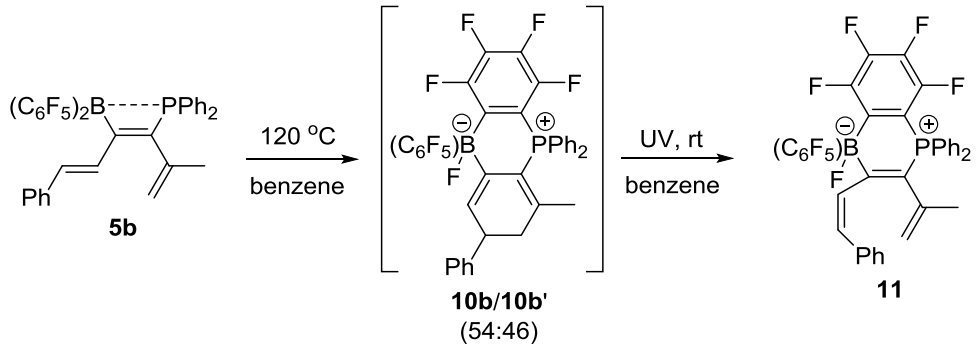


^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of (2) isomer mixure **10a/10a**' [light yellow solid, see above)] and (1) the crystal from the X-ray crystal structure analysis.

X-ray crystal structure analysis of compound 10a: formula $C_{35}H_{26}BF_{10}P \cdot CH_2Cl_2$, M = 763.26, colourless crystal, 0.18 x 0.04 x 0.02 mm, a = 20.7710(9), b = 10.2846(5), c = 18.6572(9) Å, β = 120.235(4)°, V = 3443.4(3) Å^3, ρ_{calc} = 1.472 gcm^{-3}, μ = 2.862 mm^{-1}, empirical absorption correction (0.626 ≤ T ≤ 0.945), Z = 4, monoclinic, space group *Cc* (No. 9), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 12481 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 5034 independent (R_{int} = 0.060) and 4282 observed reflections [I>2σ(I)], 484 refined parameters, R = 0.054, wR^2 = 0.137, max. (min.) residual electron density 0.35 (-0.27) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Synthesis of compound 11.



A solution of compound **5b** (0.175 g, 0.25 mmol) in benzene (5 mL) was heated at 120 °C for 1 d. After cooling to room temperature, the reaction mixture was photolyzed (UV lamp: HPK 125, Pyrex filter) for 1 d. Then all volatiles of the

reaction mixture were removed in vacuo and the residue was washed with pentane (1 × 3 mL). After drying in vacuo compound **11** (0.145 g, 82 %) was obtained as a light yellow solid. Crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane to a dichloromethane solution of compound **11** at -35 °C. **IR** (KBr): $\tilde{\nu}$ / cm^{-1} = 3062, 1636, 1559, 1512, 1500, 1460, 1429, 1318, 1273, 1108, 1085, 1054, 962. **Decomp**.: 250 °C. **Anal. Calc.** for $C_{37}H_{22}BF_{10}P$: C: 63.64; H: 3.18. Found: C: 63.34; H: 3.12.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.80, 7.69 (each m, each 1H, *p*-Ph^{P}), 7.79, 7.75 (each m, each 2H, *o*-Ph^{P}), 7.64, 7.54 (each m, each 2H, *m*-Ph^{P}), 7.42 (br m, 2H, *o*-Ph), 7.26 (m, 2H, *m*-Ph), 7.20 (m, 1H, *p*-Ph), 6.43 (dd, $^{3}J_{HH}$ = 12.7 Hz, $^{5}J_{PH}$ = 1.2 Hz, 1H, =CH^{Ph}), 6.15 (br d, $^{3}J_{HH}$ = 12.7 Hz, 1H, =CH), 4.61, 3.53 (each m, each 1H, =CH_2), 1.20 (m, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 180.4 (br, =CB), 139.6 (d, $^{2}J_{PC}$ = 13.4 Hz, =C^{Me}), 138.8 (*i*-Ph), 134.8 (d, $^{4}J_{PC}$ = 3.0 Hz), 134.4 (d, $^{4}J_{PC}$ = 3.1 Hz)(*p*-Ph^{P}), 134.14 (d, $^{2}J_{PC}$ = 10.0 Hz), 134.09(dd, $^{2}J_{PC}$ = 10.9 Hz, *J* = 1.3 Hz)(*o*-Ph^{P}), 133.6 (d, $^{3}J_{PC}$ = 21.8 Hz, =CH), 130.4 (br, =CH^{Ph}), 129.9 (d, $^{3}J_{PC}$ = 12.7 Hz), 129.8 (d, $^{3}J_{PC}$ = 12.9 Hz)(*m*-Ph^{P}), 128.8 (d, *J* = 3.2 Hz, *o*-Ph), 128.2 (*m*-Ph), 127.1 (*p*-Ph), 121.8 (d, $^{1}J_{PC}$ = 90.2 Hz), 118.3 (d, $^{1}J_{PC}$ = 90.1 Hz)(*i*-Ph^{P}), 121.2 (d, $^{3}J_{PC}$ = 6.3 Hz, =CH_2), 117.5 (dd, $^{1}J_{PC}$ = 83.7 Hz, $^{3}J_{FC}$ = 4.4 Hz,=CP), 23.9 (d, $^{3}J_{PC}$ = 2.5 Hz, CH_3), [C_6F_5, C_6F_4 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = -1.9 (d, $^{1}J_{BF}$ ~ 50 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -5.9 ($\nu_{1/2}$ ~ 30 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -125.0, -129.0, -147.0, -157.6 (each m, each 1F, C_6F_4), -135.8 (br, 2F, *o*), -161.1 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*), -165.6 (br m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.5], -197.0 (br, 1F, BF).

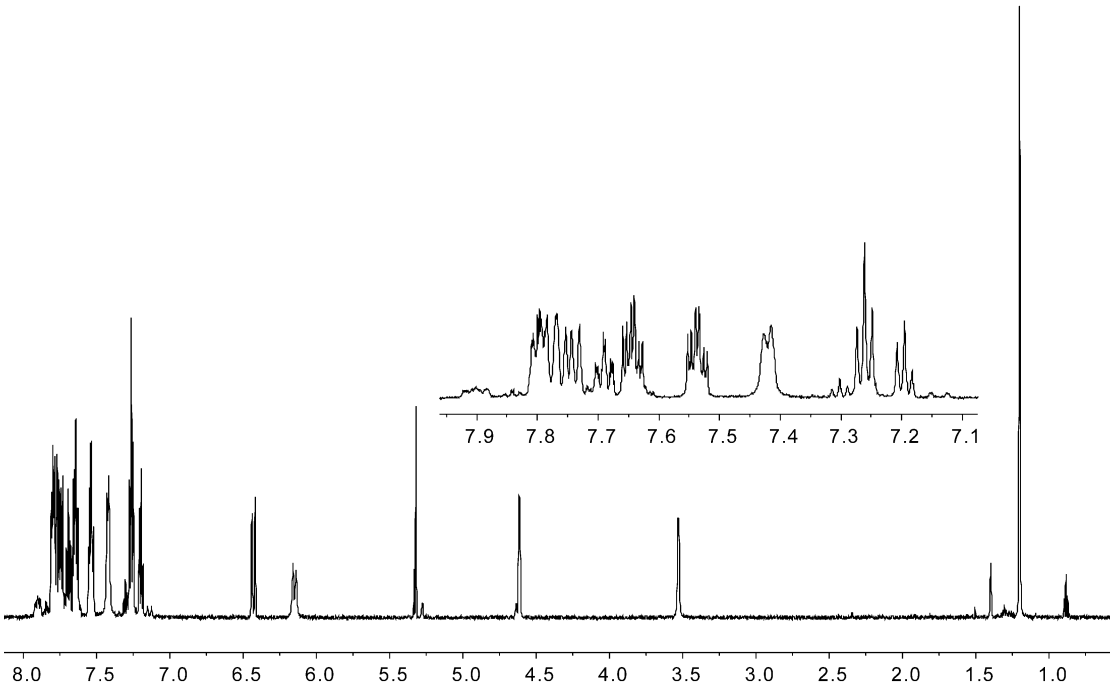
^{1}H, ^{1}H-GCOSY (600 MHz / 600 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{1}H = 7.80 / 7.64 (*p*-Ph^{PB} / *m*-Ph^{PB}), 7.79 / 7.64 (*o*-Ph^{PB} / *m*-Ph^{PB}), 7.75 / 7.54 (*o*-Ph^{PA} / *m*-Ph^{PA}), 7.69 / 7.54 (*p*-Ph^{PA} / *m*-Ph^{PA}), 7.42 / 7.26 (*o*-Ph / *m*-Ph), 7.26 / 7.20 (*m*-Ph / *p*-Ph), 6.43 / 6.15 (=CH^{Ph} / =CH), 4.61 / 3.53, 1.20 (=CH_2 / =CH_2, CH_3), 3.53 / 1.20 (=CH_2 / CH_3).

^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 7.80 / 134.8

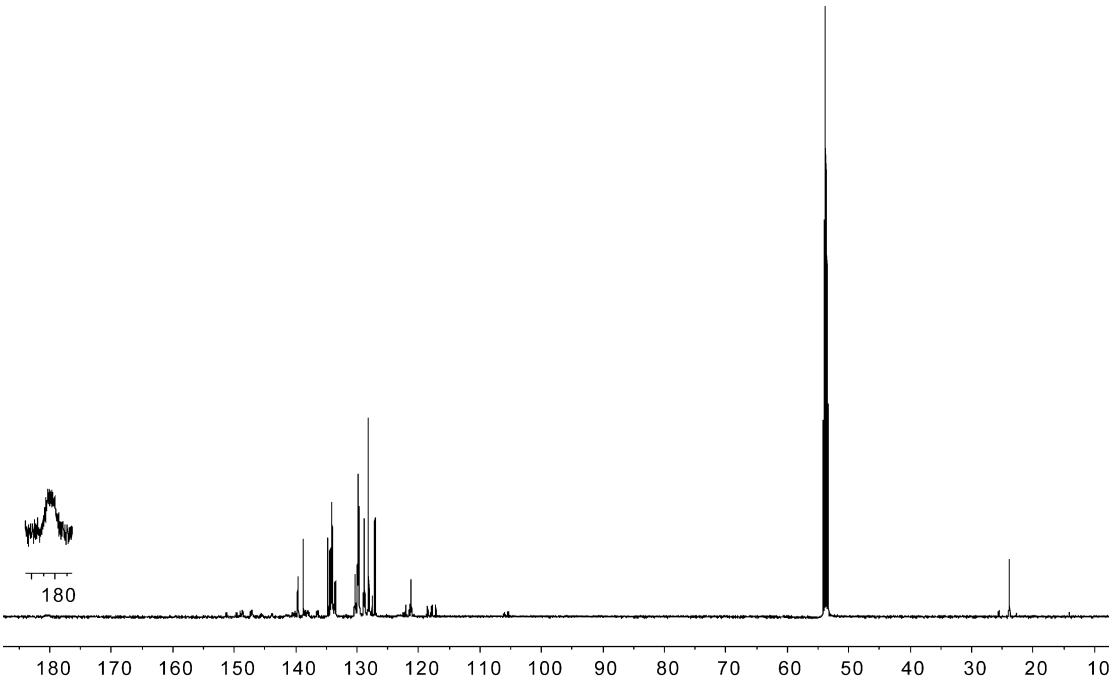
(*p*-Ph^{PB}), 7.79 / 134.14 (*o*-Ph^{PB}), 7.75 / 134.09 (*o*-Ph^{PA}), 7.69 / 134.4 (*p*-Ph^{PA}), 7.64 / 129.9 (*m*-Ph^{PB}), 7.54 / 129.8 (*m*-Ph^{PA}), 7.42 / 128.8 (*o*-Ph), 7.26 / 128.2 (*m*-Ph), 7.20 / 127.1 (*p*-Ph), 6.43 / 130.4 (=CH^{Ph}), 6.15 / 133.6 (=CH), 4.61, 3.53 / 121.2 (=CH_2), 1.20 / 23.9 (CH_3).

^{1}H, ^{13}C-GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2)[selected traces]: δ ^{1}H / δ ^{13}C = 7.79 / 134.8 (*o*-Ph^{PB} / *p*-Ph^{PB}),7.75 / 134.4 (*o*-Ph^{PA} / *p*-Ph^{PA}), 7.64 / 134.14, 129.9, 118.3 (*m*-Ph^{PB} / *o*-Ph^{PB}, *m*-Ph^{PB}, *i*-Ph^{PB}), 7.54 / 134.09, 129.8, 121.8 (*m*-Ph^{PA} / *o*-Ph^{PA}, *m*-Ph^{PA}, *i*-Ph^{PA}), 7.42 / 128.8, 128.2, 127.1 (*o*-Ph / *o*-Ph, *m*-Ph, *p*-Ph), 7.26 / 138.8, 128.8, 128.2 (*m*-Ph / *i*-Ph, *o*-Ph, *m*-Ph), 6.43 / 180.4, 128.8 (=CH^{Ph} / =CB, *o*-Ph), 4.61, 3.53 / 117.5, 23.9 (=CH_2 / =CP, CH_3), 1.20 / 139.6, 121.2, 117.5 (CH_3 / =C^{Me}, =CH_2, =CP).

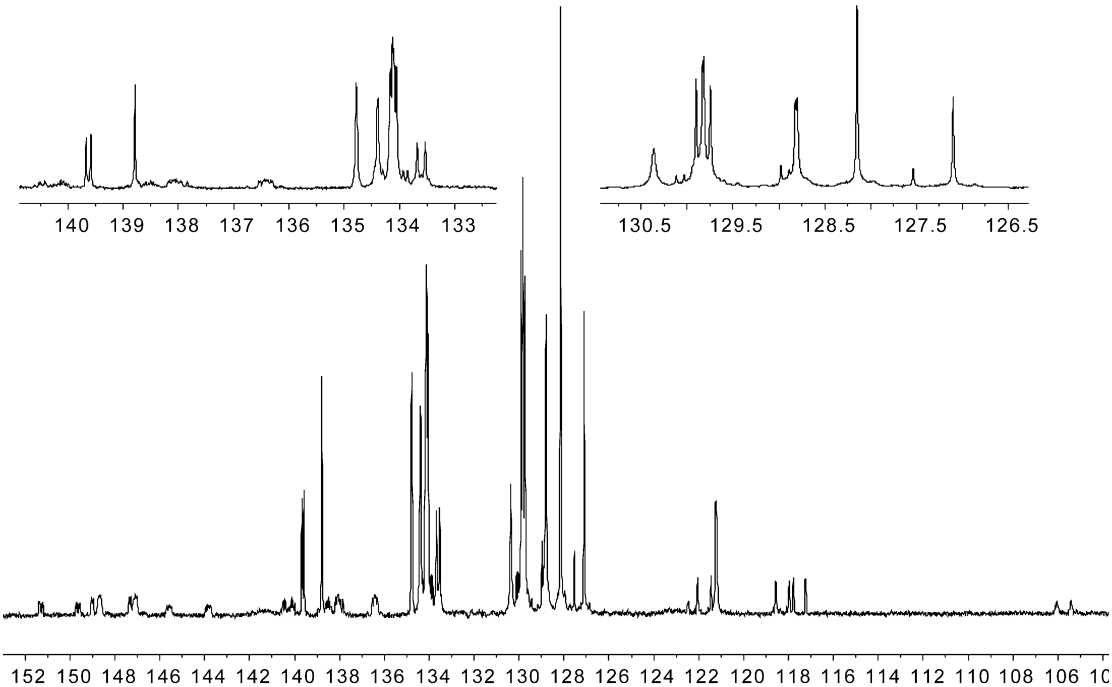
^{19}F, ^{19}F-GCOSY (564 MHz / 564 MHz, 299 K, CD_2Cl_2): δ ^{19}F / δ ^{19}F = -125.0 / 157.6 (C_6F_4 / C_6F_4), -129.0 / -147.0 (C_6F_4 / C_6F_4), -161.1 / -165.6 (*p*-C_6F_5 / *m*-C_6F_5).



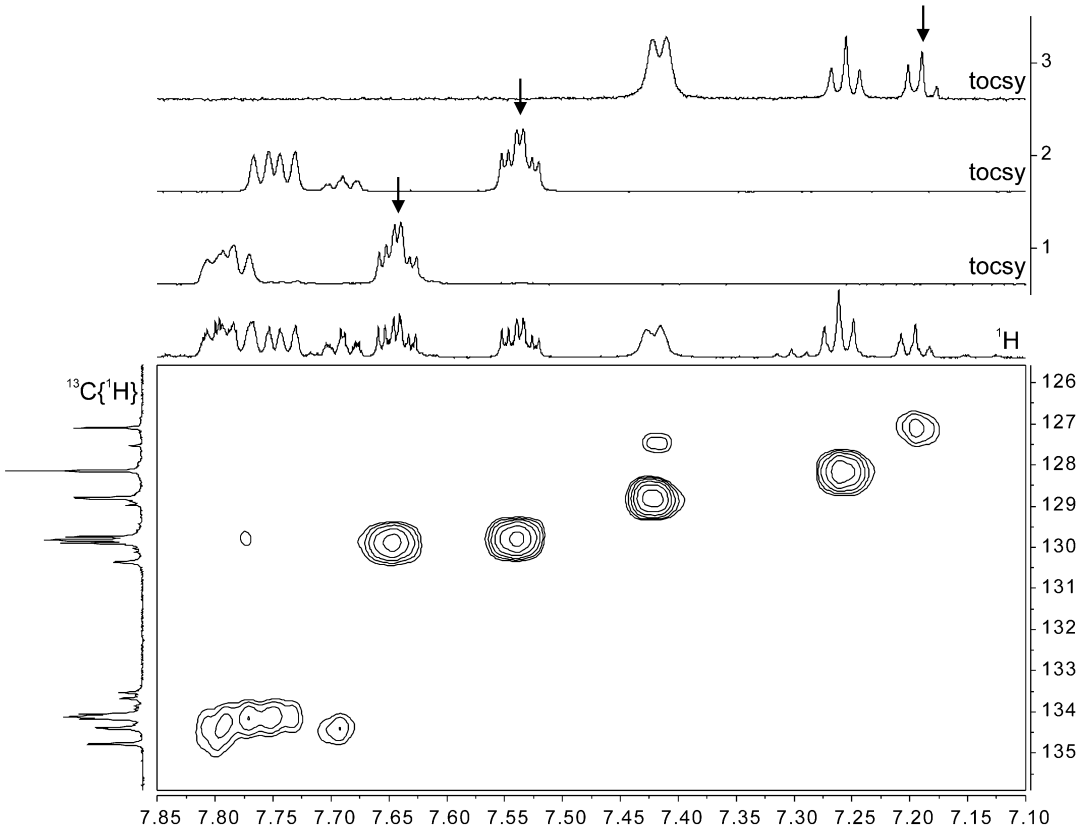
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) of **11**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) of compound **11**

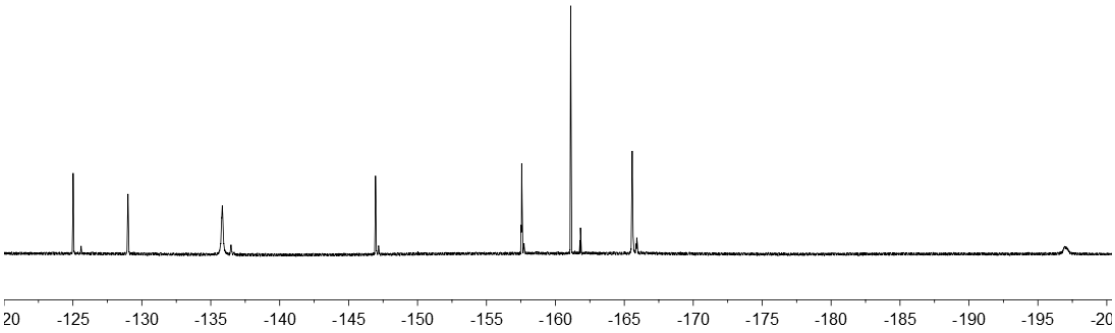


$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) of compound **11**

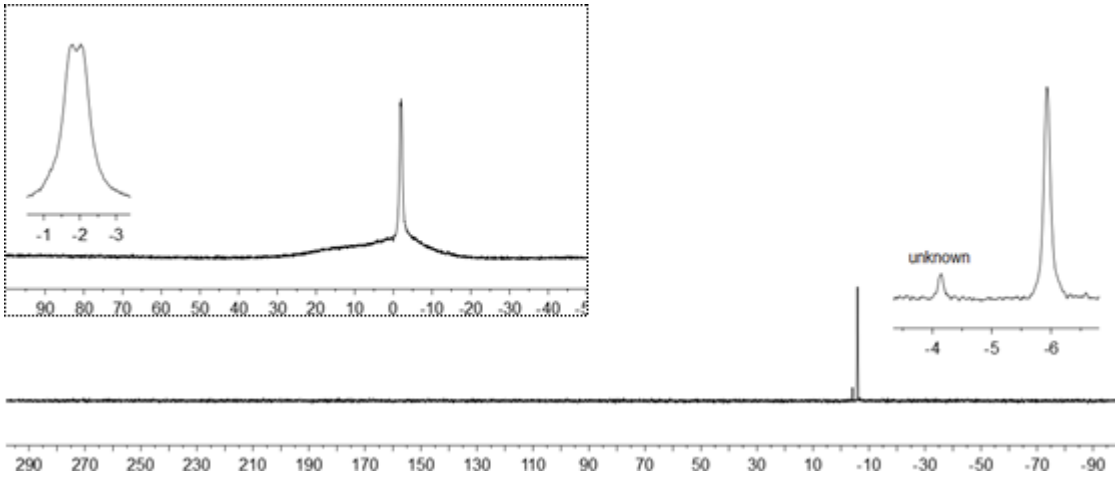


^{1}H, ^{13}C-GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2) of compound **11**:

(1) $\delta^{1}H_{irr}$: 7.64 (*m*-Ph^{P}). (2) $\delta^{1}H_{irr}$: 7.54 (*m*-Ph^{P}). (3) $\delta^{1}H_{irr}$: 7.20 (*p*-Ph).

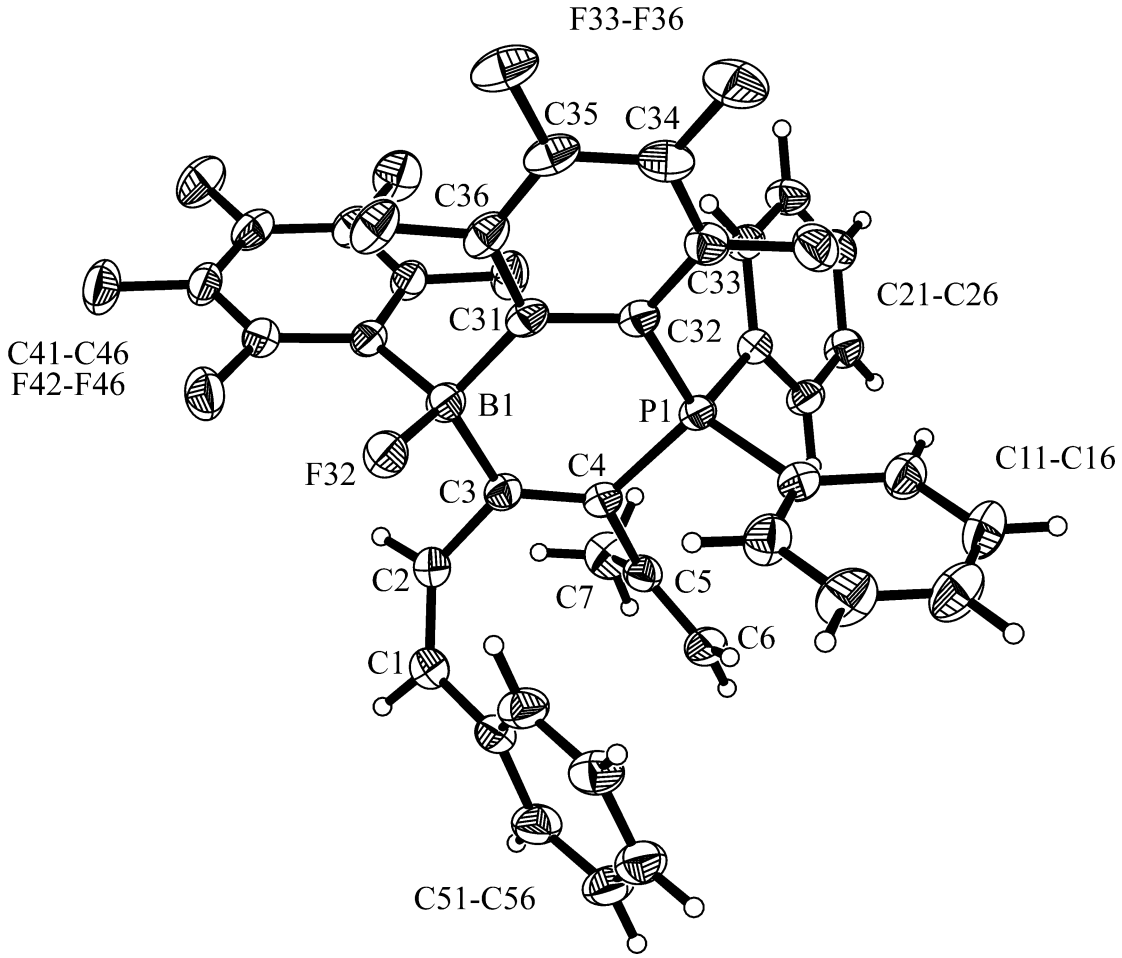


^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compound **11**



$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) and **$^{31}P\{^{1}H\}$ NMR** (243 MHz, 299 K, CD_2Cl_2) of compound **11**

X-ray crystal structure analysis of compound 11: formula $C_{37}H_{22}BF_{10}P \cdot CH_2Cl_2$, M = 783.25, colourless crystal, 0.14 x 0.11 x 0.06 mm, a = 16.2406(5), b = 10.2753(3), c = 21.4263(8) Å, β = 102.915(2)°, V = 3485.1(2) Å^3, ρ_{calc} = 1.493 gcm^{-3}, μ = 2.848 mm^{-1}, empirical absorption correction (0.691 ≤ T ≤ 0.847), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 26271 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 5989 independent (R_{int} = 0.087) and 4390 observed reflections [I>2σ(I)], 506 refined parameters, R = 0.050, wR^2 = 0.137, max. (min.) residual electron density 0.22 (-0.31) e.Å^{-3}, the hydrogen atoms at C1 and C2 were refined freely; others were calculated and refined as riding atoms.



Generation of compounds 10b/10b'

A solution of compound **5b** (135.6 mg, 0.2 mmol) in toluene (2 mL) was heated at 120 °C for 1 d. Then all volatiles of the reaction mixture were removed in vacuo and the residue was washed with pentane (3 × 1 mL). After drying in vacuo a light yellow solid (117.4 mg, 86 %) was obtained. **Anal. Calc.** for $C_{37}H_{22}BF_{10}P$: C: 63.64; H: 3.18. Found: C: 63.56; H: 3.10.

In CD_2Cl_2 solution two isomers were observed (ca. 54:46 [^{1}H]). After characterization of the reaction mixture by NMR experiments the solution was photolyzed (UV lamp: HPK 125, Pyrex filter) at room temperature for 1 day to finally give compound **11**.

*Major isomer **10b***

^{1}H NMR (500 MHz, 299 K, CD_2Cl_2)[selected resonaces]: δ = 6.41 (m, 1H, =CH), 3.62 (br dm, $^3J_{HH}$ = 16.5 Hz, 1H, CH), 2.73 (br ddd, $^2J_{HH}$ = 17.1 Hz, $^3J_{HH}$ = 16.5 Hz,

$^{4}J_{PH}$ = 4.1 Hz), 2.52 (dd, $^{2}J_{HH}$ = 17.1 Hz, $^{3}J_{HH}$ = 6.8 Hz)(each 1H, CH_2), 1.59 (d, $^{4}J_{PH}$ = 2.8 Hz, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2)[selected resonaces]: δ = 158.9 (d, $^{2}J_{PC}$ = 9.0 Hz, $=C^{Me}$), 129.7 (m, =CH), 114.9 (dm, $^{1}J_{PC}$ = 85.8 Hz, =CP), 42.7 (d, $^{3}J_{PC}$ = 13.3 Hz, CH_2), 39.5 (d, $^{4}J_{PC}$ = 2.0 Hz, CH), 24.9 (d, $^{3}J_{PC}$ = 9.0 Hz, CH_3).

$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2): δ = -1.4 ($\nu_{1/2}$ ~ 200 Hz).

$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, CD_2Cl_2): δ = -1.0 ($\nu_{1/2}$ ~ 20 Hz).

^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = -126.6, -130.7, -146.6, -158.47 (each m, each 1F, C_6F_4), -132.8 (m, 2F, *o*), -160.72 (t, $^{3}J_{FF}$ = 19.7 Hz, 1F, *p*), -165.5 (m, 2F, *m*)(C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 4.78], -197.7 (br, 1F, BF).

^{1}H, ^{1}H-GCOSY (500 MHz / 500 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{1}H = 6.41 / 3.62, 2.52, 1.59 (=CH / CH_2, CH_3), 3.62 / 2.73, 2.52 (CH / CH_2, CH_2), 2.73 / 2.52, 1.59 (CH_2 / CH_2, CH_3). [Ph not listed]

^{1}H, ^{13}C-GHSQC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 6.41 / 129.7 (=CH), 3.62 / 39.5 (CH), 2.73 / 42.7 (CH_2) , 2.52 / 42.7 (CH_2) , 1.59 / 24.9 (CH_3). [Ph not listed]

^{1}H, ^{13}C-GHMBC (500 MHz / 126 MHz, 299 K, CD_2Cl_2): δ ^{1}H / δ ^{13}C = 2.73 / 158.9, 129.7 (CH_2 / $=C^{Me}$, =CH), 2.52 / 158.9, 129.7, 114.9, 39.5, 24.9 (CH_2 / $=C^{Me}$, =CH, =CP, CH, CH_3), 1.59 / 158.9, 114.9, 42.7 (CH_3 / $=C^{Me}$, =CP, CH_2). [Ph not listed]

^{19}F, ^{19}F-GCOSY (470 MHz / 470 MHz, 299 K, CD_2Cl_2): δ ^{19}F / δ ^{19}F = -126.6 / 158.5 (C_6F_4 / C_6F_4), -130.7 / -146.6 (C_6F_4 / C_6F_4), -132.8 / -165.5 (*o*-C_6F_5 / *m*-C_6F_5).

*Minor isomer **10b**'*

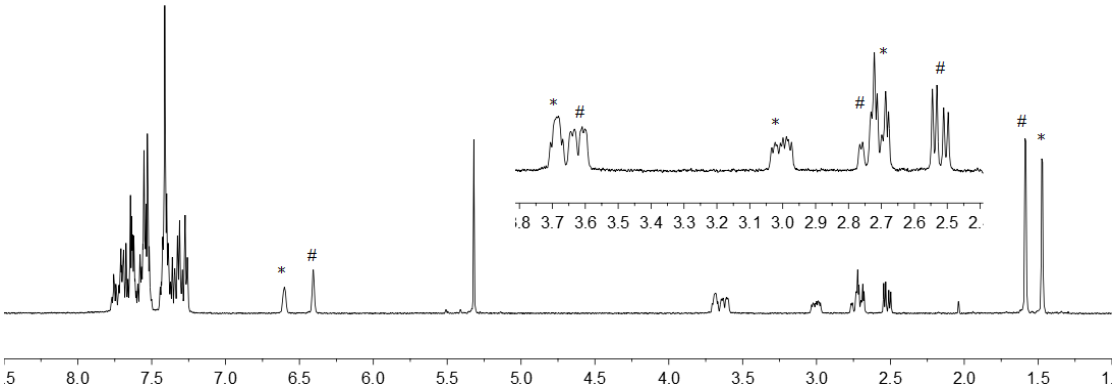
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2)[selected resonances]: δ = 6.60 (m, 1H, =CH), 3.69 (m, 1H, CH), 3.00 (m), 2.70 (dd, $^{2}J_{HH}$ = 17.2 Hz, $^{3}J_{HH}$ = 4.7 Hz)(each 1H, CH_2), 1.47 (d, $^{4}J_{PH}$ = 2.9 Hz, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2)[selected resonaces]: δ = 158.1 (d, $^{2}J_{PC}$ = 8.8 Hz, $=C^{Me}$), 127.3 (m, =CH), 114.9 (dm, $^{1}J_{PC}$ = 86.8 Hz, =CP), 41.0 (d, $^{3}J_{PC}$ = 13.2 Hz, CH_2), 36.0 (d, $^{4}J_{PC}$ = 2.0 Hz, CH), 25.5 (d, $^{3}J_{PC}$ = 9.1 Hz, CH_3).

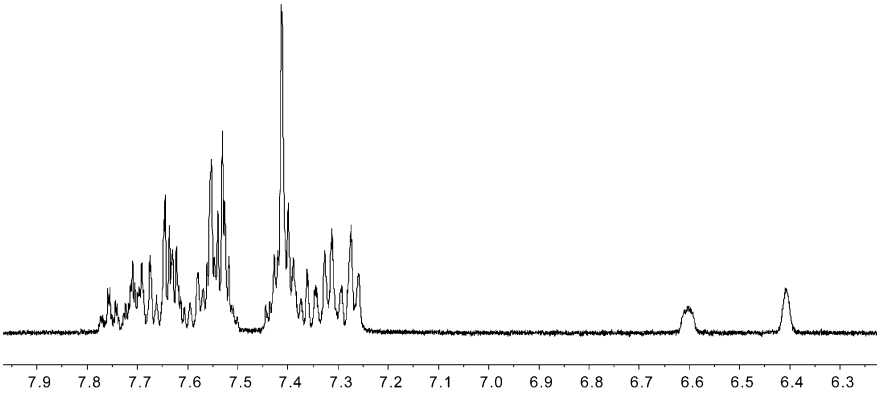
$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2): δ = -1.4 ($\nu_{1/2}$ ~ 200 Hz).

$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, CD_2Cl_2): δ = -1.1 ($\nu_{1/2}$ ~ 20 Hz).

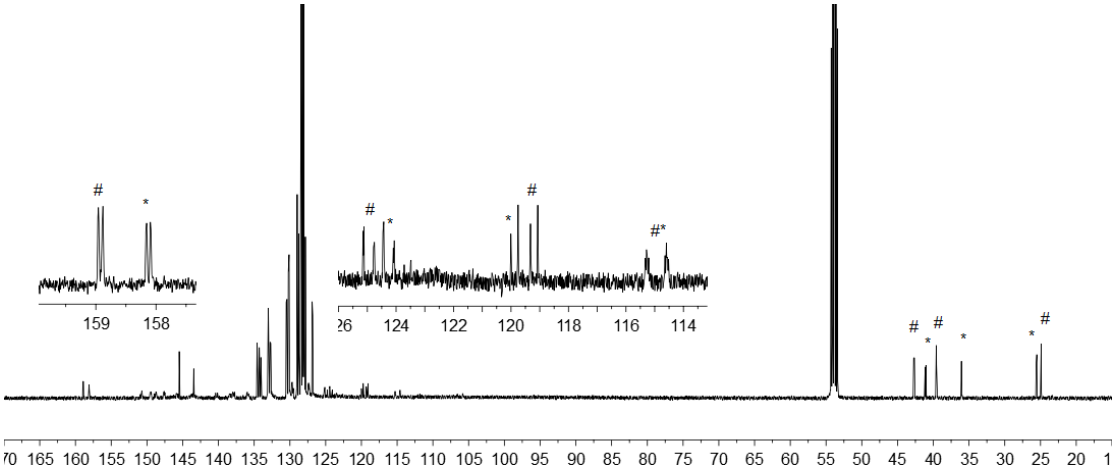
^{19}F NMR (470 MHz, 299 K, CD_2Cl_2): δ = -126.6, -130.7, -146.6, -158.53 (each m, each 1F, C_6F_4), -133.1 (m, 2F, *o*), -160.67 (t, $^3J_{FF}$ = 19.8 Hz, 1F, *p*), -165.5 (m, 2F, *m*)(C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 4.83], -197.6 (br, 1F, BF).



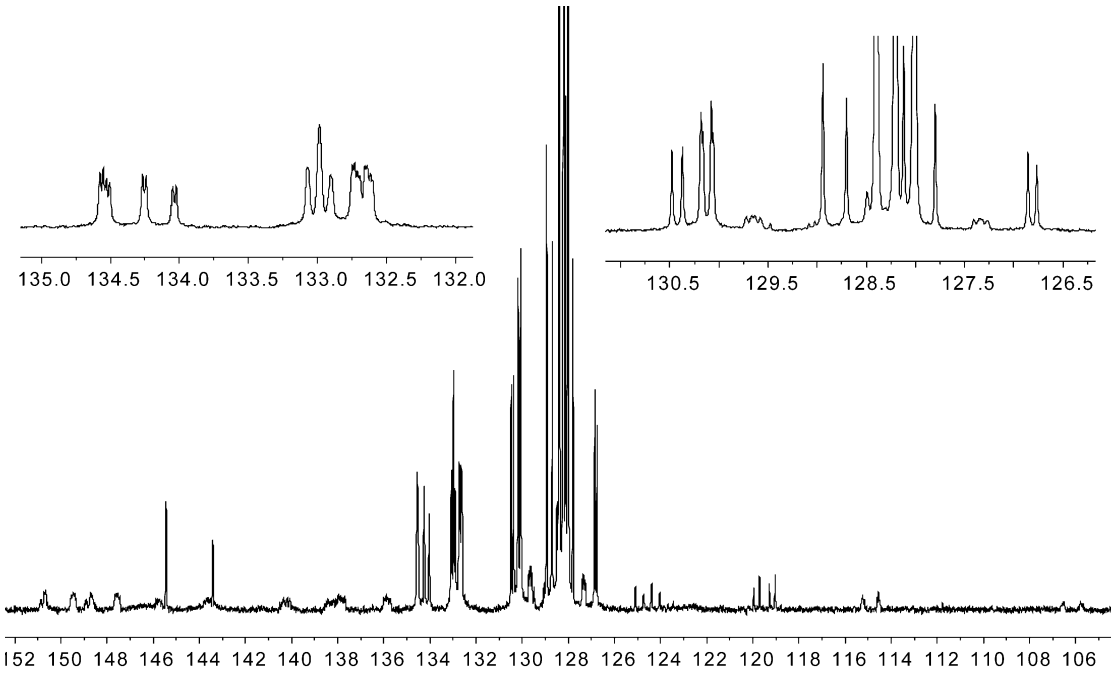
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) of compounds **10b/10b'** (# major isomer, * minor isomer)



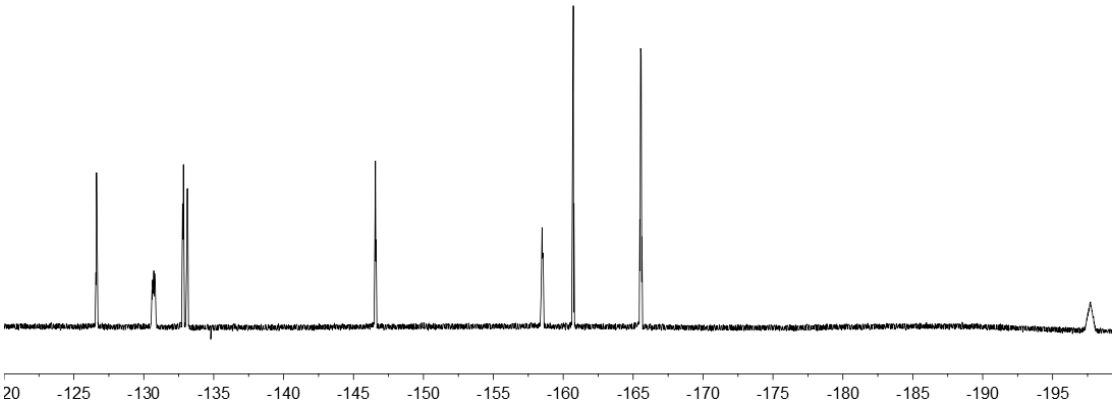
^{1}H NMR (500 MHz, 299 K, CD_2Cl_2) of compounds **10b/10b'**



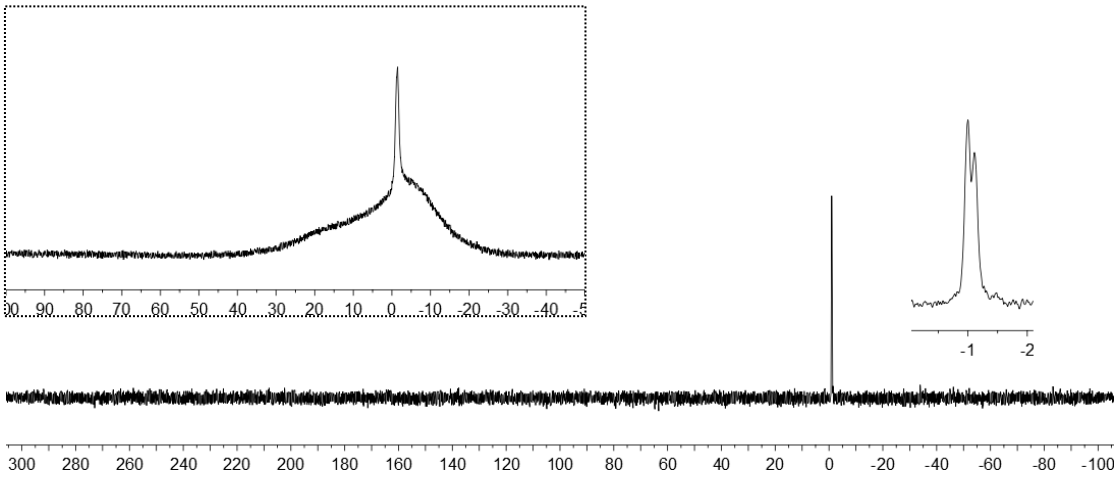
^{13}C{^{1}H} NMR (126 MHz, 299 K, CD_2Cl_2) of compounds **10b/10b'** (# major isomer, * minor isomer)



$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, CD_2Cl_2) of compounds **10b/10b'**



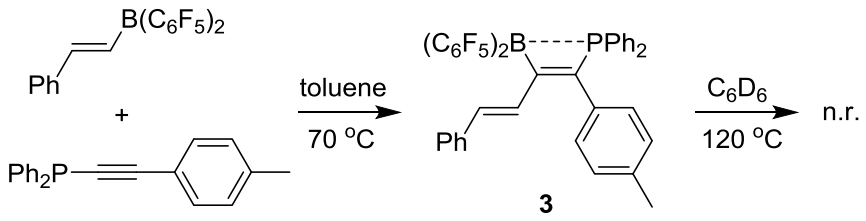
^{19}F NMR (470 MHz, 299 K, CD_2Cl_2) of compounds **10b/10b'**

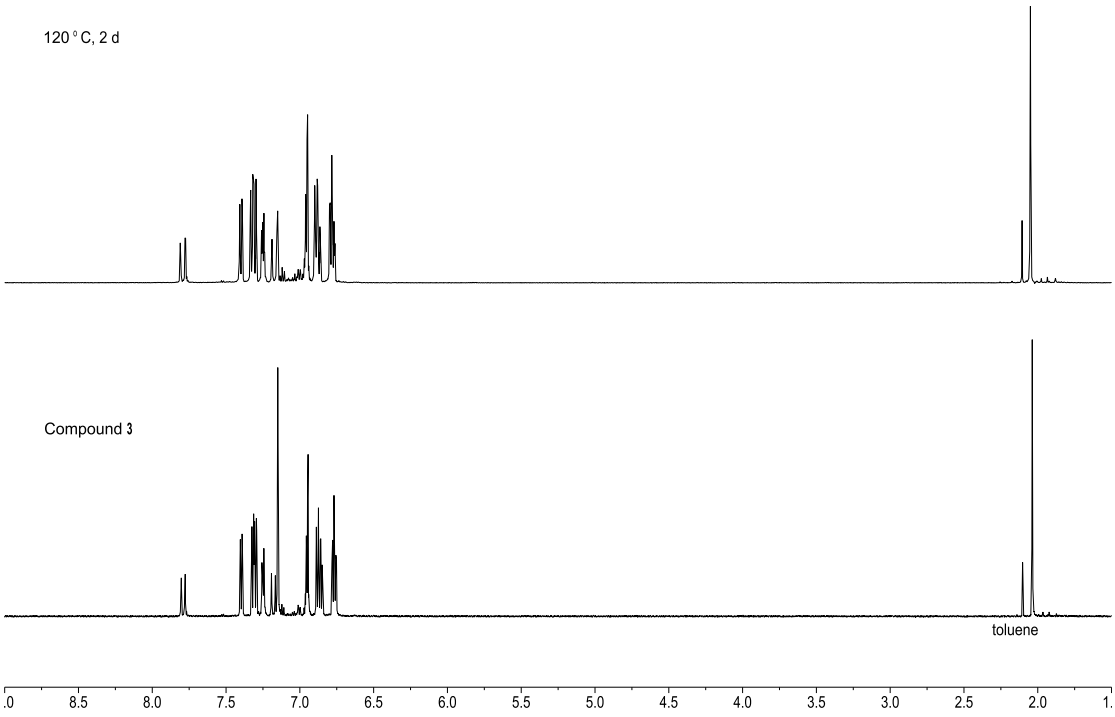


$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, CD_2Cl_2) and **$^{31}P\{^{1}H\}$ NMR** (202 MHz, 299 K, CD_2Cl_2) of compounds **10b/10b'**

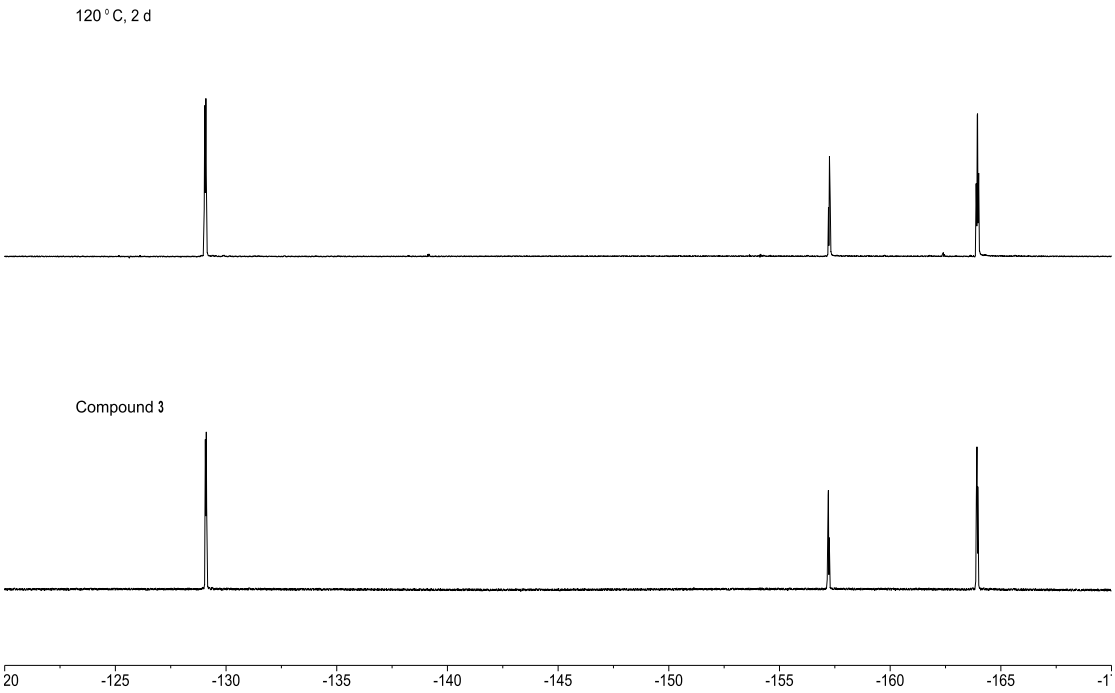
Control experiment

1) We have synthesized a selected example of compounds **3** according to reference [10]. Then a solution of compound **3** in C_6D_6 was heated at 120 ^oC for 2 days. No nucleophilic substitution of the PPh_2 substituent to a C_6F_5 ring at boron was observed.

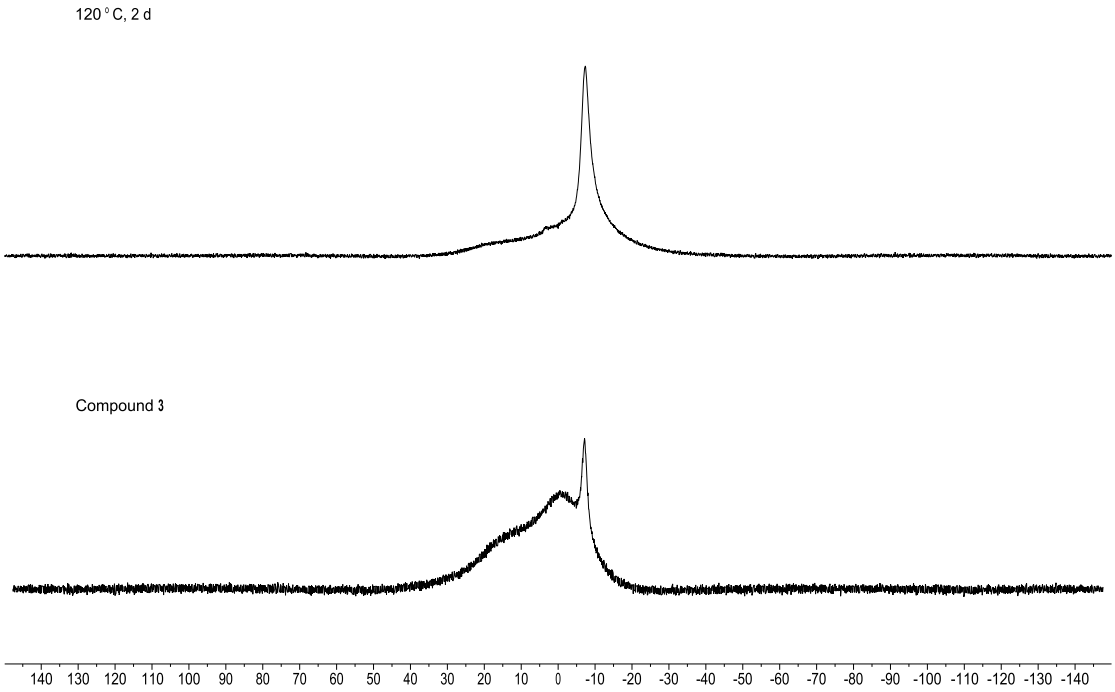




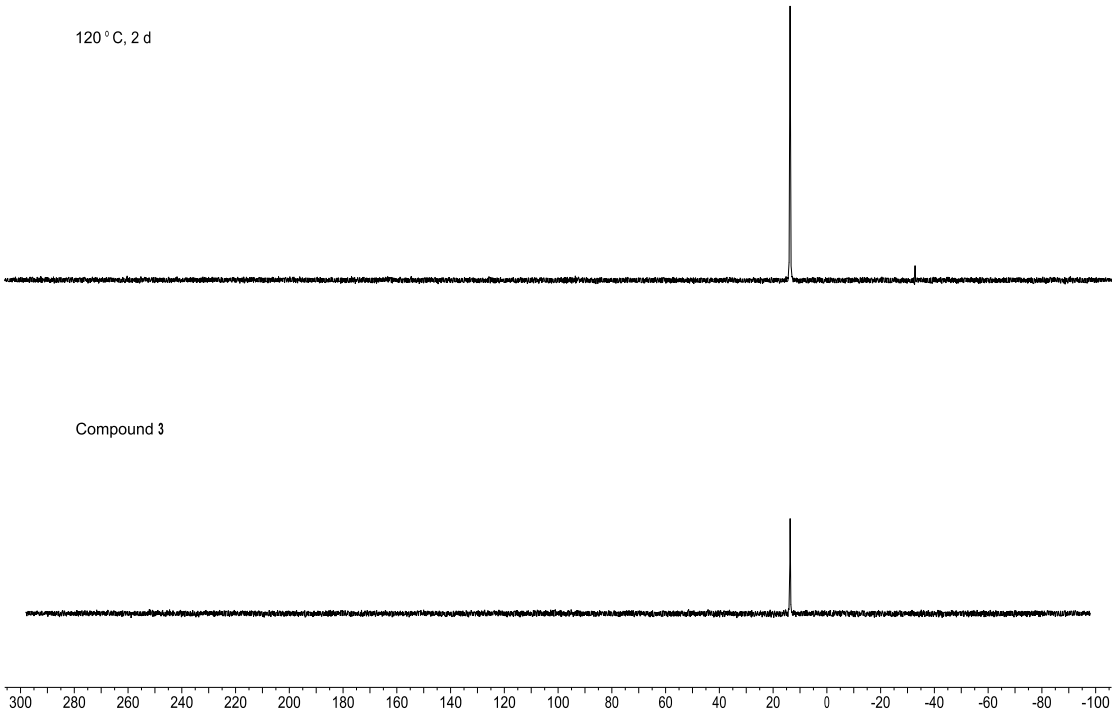
^{1}H NMR (299 K, C_6D_6) of compound **3** (600 MHz, bottom) and after heating (500 MHz, top)



^{19}F NMR (299 K, C_6D_6) of compound **3** (470 MHz, bottom) and after heating (564 MHz, top)

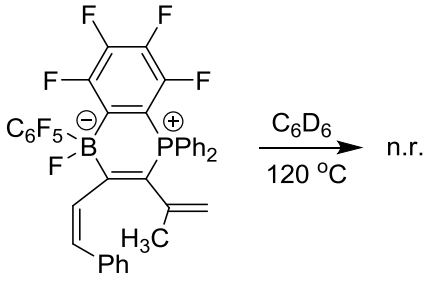


^{11}B NMR (299 K, C_6D_6) of compound **3** (192 MHz, bottom) and after heating (160 MHz, top)

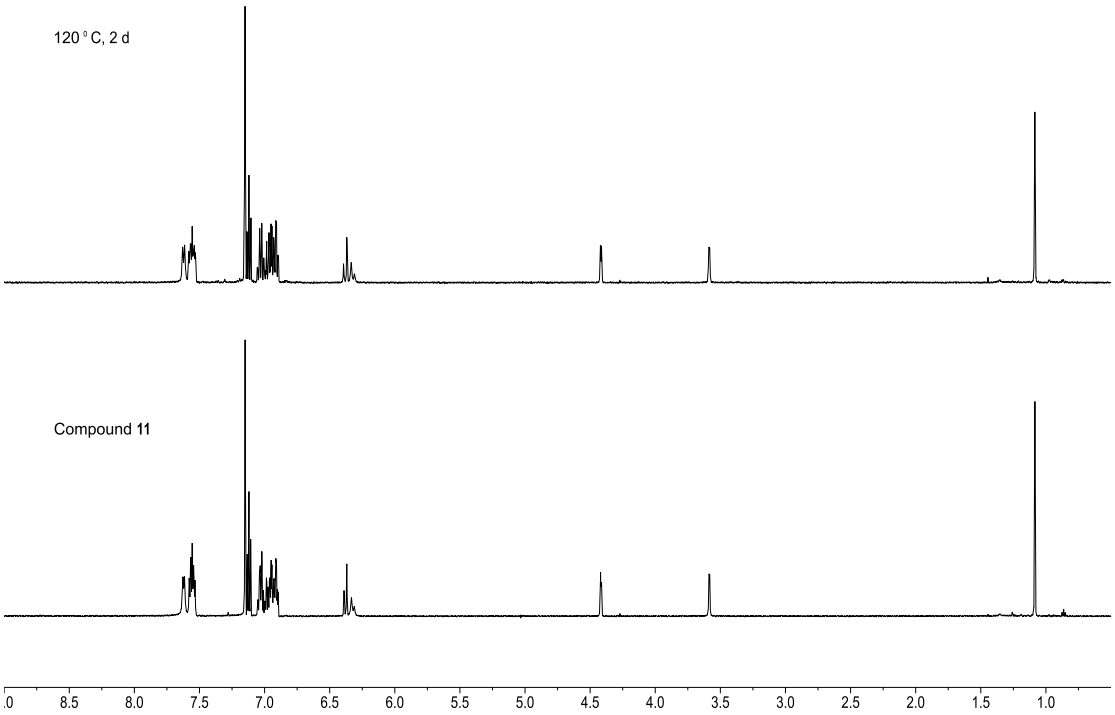


^{31}P NMR (299 K, C_6D_6) of compound **3** (243 MHz, bottom) and after heating (202 MHz, top)

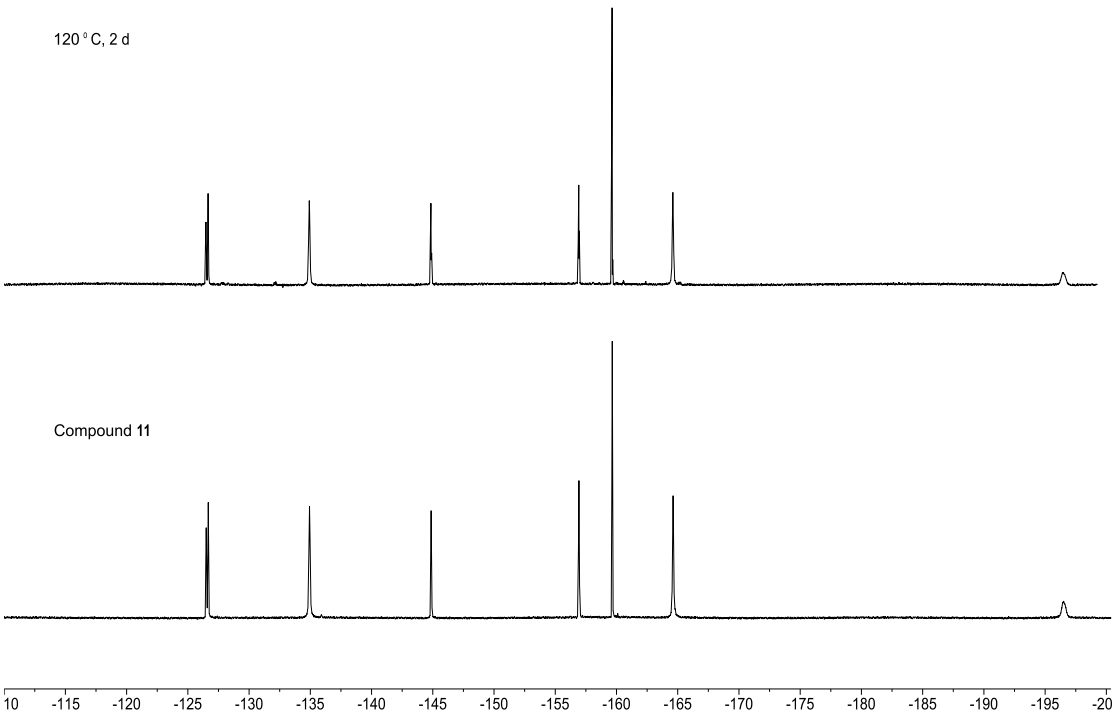
2) A solution of compound **11** in C_6D_6 was heated at 120 ^{o}C for 2 days. No reaction was observed.



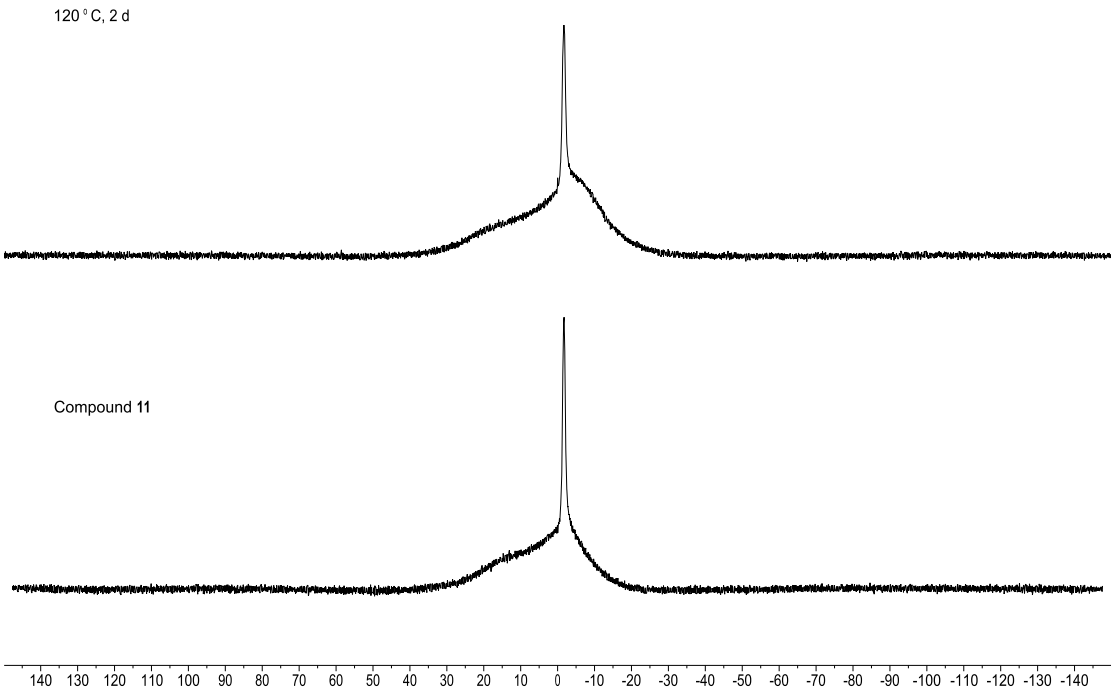
11



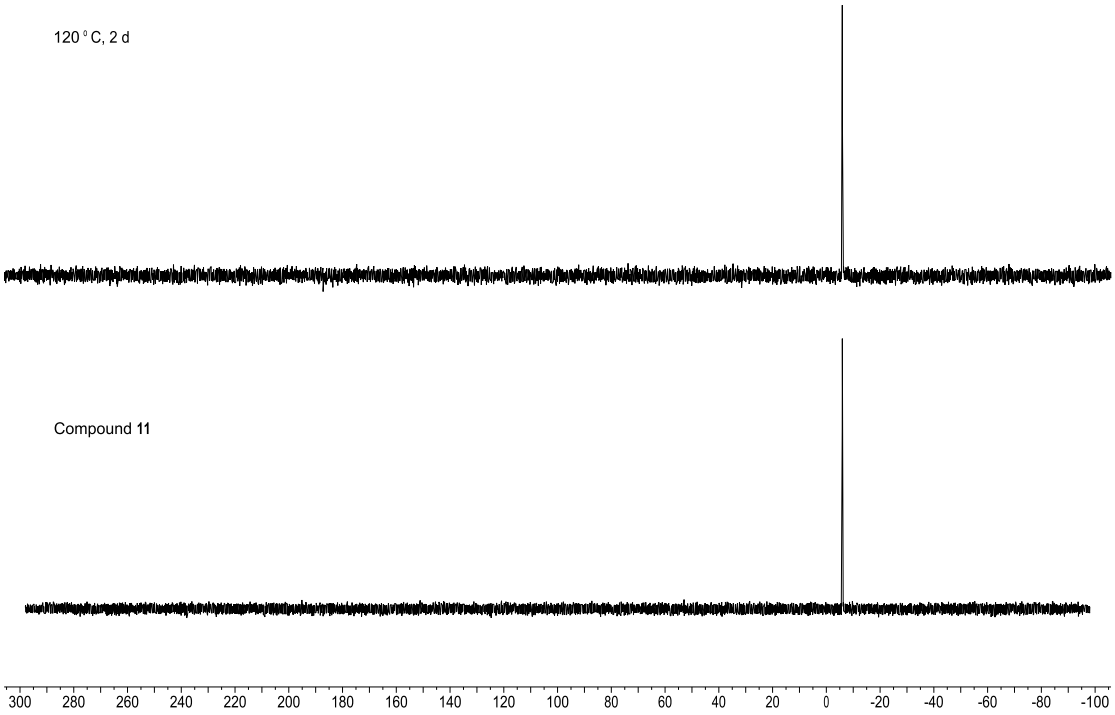
^{1}H NMR (299 K, C_6D_6) of compound **11** (600 MHz, bottom) and after heating (500 MHz, top)



^{19}F NMR (299 K, C_6D_6) of compound **11** (564 MHz, bottom) and after heating (470 MHz, top)



^{11}B NMR (299 K, C_6D_6) of compound **11** (192 MHz, bottom) and after heating (160 MHz, top)



^{31}P NMR (299 K, C_6D_6) of compound **11** (243 MHz, bottom) and after heating (202 MHz, top)