Electronic Supplementary Material (ESI) for Chemical Communications.

Cooperative Reaction Chemistry Derived from a Boratadiene Framework

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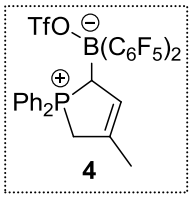
$ X-Ray crystal structure analysis.

Supporting Information

General information

The syntheses involving air- and/or moisture-sensitive compounds were carried out by using Standard Schlenk-type glassware (or at glove box) under an atmosphere of argon. Solvents were purified prior to use and stored under an argon atmosphere. Instruments for NMR spectra recording: Agilent VNMRS 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz, ^{31}P: 202 MHz), Agilent DD2 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz, ^{31}P: 243 MHz). Chemical shift of ^{1}H NMR and ^{13}C NMR were given relative to TMS and referenced to the solvent signal. Chemical shift of ^{19}F NMR was given relative to external reference ($CFCl_3$). Chemical shift of ^{11}B NMR was given relative to external reference ($BF_3{\cdot}Et_2O$). Chemical shift of ^{31}P NMR was given relative to external reference [H_3PO_4 (85% in H_2O)]. NMR assignments were supported by additional 2D NMR experiments. Elemental analyses were performed on a Foss-Heraeus CHNO Rapid machine. Melting points were measured with a DSC 2010 CE (Thermal Advantage Instruments) apparatus and IR spectra were recorded on Varian 3100 FT-IR (Excalibur Series). X-Ray diffraction: Data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski and 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). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: Compound **4** crystallized with a disordered over two positions CF_3 group. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For the compounds **5**, **6**, **7**, **9** and **10** a badly disordered pentane molecule, one badly dichloromethane molecule, one half dichloromethane molecule, one toluene molecule and one dichloromethane molecule were 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.

Synthesis of Compound 4



4

Triflic acid (120 mg, 0.80 mmol) was added to a solution of compound **3** (480 mg, 0.8 mmol) in dichloromethane (6 mL). Then the reaction mixture was stirred at r.t. for 30 min. After removal of all volatiles in vacuo, the obtained residue was washed with pentane (3 × 2 mL) and dried to give compound **4** (400 mg, 0.54 mmol, 67 %) as a light yellow solid. Single crystals of compound **4** suitable for the X-ray crystal structure analysis were obtained by slowly diffusion of pentane into a solution of compound **4** in dichloromethane at -30 °C.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 3064 (w), 2953 (w), 2181 (w), 1647 (m), 1519 (s), 1469 (vs), 1356 (m) 1286 (s), 1201 (s), 1069 (m), 1028 (m), 1004 (m), 973 (m), 806 (w), 745 (m), 688 (m), 637 (m), 530 (w).

Melting point: 179 °C.

Elemental analysis: calc. for $C_{30}H_{17}BF_{13}O_3PS$ (746.28 g/mol): C, 48.28; H, 2.30. Found: C, 48.14; H, 2.29.

^{1}H NMR (500 MHz, 299 K, [D_2]-dichloromethane): δ = 7.79 (m, 1H, p-Ph^{a}), 7.74 (m, 2H, o-Ph^{a}), 7.68 (m, 2H, m-Ph^{a}), 7.65 (m, 1H, p-Ph^{b}), 7.38 (m, 2H, m-Ph^{b}), 7.32 (m, 2H, o-Ph^{b}), 6.11 (br d, $^{3}J_{PH}$ = 35.7 Hz, 1H, =CH), 4.42 (br dm, $^{2}J_{PH}$ = 16.5 Hz, 1H, CH), 4.08 (ddm, $^{2}J_{HH}$ = 18.3 Hz, $^{2}J_{PH}$ = 7.2 Hz, 1H, CH_2), 2.98 (br dd, $^{2}J_{HH}$ = 18.3, $^{2}J_{PH}$ = 10.7 Hz, 1H, CH_2), 1.95 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 299 K, [D_2]-dichloromethane): δ = 134.8 (d, $^{4}J_{PC}$ = 3.0 Hz, p-Ph^{a}), 134.5 (d, $^{2}J_{PC}$ = 11.8 Hz, =C), 134.4 (d, $^{4}J_{PC}$ = 3.2 Hz, p-Ph^{b}), 133.8 (d, $^{3}J_{PC}$ = 10.4 Hz, o-Ph^{b}), 132.5 (d, $^{3}J_{PC}$ = 9.2 Hz, o-Ph^{a}), 130.6 (d, $^{4}J_{PC}$ = 11.8 Hz, m-Ph^{a}), 129.5 (d, $^{4}J_{PC}$ = 12.6 Hz, m-Ph^{b}), 128.9 (m, =CH), 121.9 (d, $^{1}J_{PC}$ = 78.8 Hz, i-Ph^{a}), 119.3 (q, $^{1}J_{CF}$ = 318.2 Hz, CF_3), 119.1 (d, $^{1}J_{PC}$ = 77.4 Hz, i-Ph^{b}), 37.8 (br, CH), 34.9 (d, $^{2}J_{PC}$ = 56.7 Hz, CH_2), 19.3 (d, $^{4}J_{PC}$ = 10.9 Hz, CH_3), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, 299 K, [D_2]-dichloromethane) [selected trace]: δ^{1}H / δ^{1}H = 7.65 / 7.38 (p-Ph^{b} / m-Ph^{b}).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, [D_2]-dichloromethane): δ^{1}H / δ^{13}C = 7.79 / 134.8 (p-Ph^{a}), 7.74 / 132.5 (o-Ph^{a}), 7.68 / 130.6 (m-Ph^{a}), 7.65 / 134.4 (p-Ph^{b}), 7.38 / 129.5 (m-Ph^{b}), 7.32 / 133.8 (o-Ph^{b}), 6.11 / 128.9 (=CH), 4.42 / 37.8 (CH), 4.08, 2.98 / 34.9 (CH_2), 1.95 / 19.3 (CH_3).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, [D_2]-dichloromethane) [selected traces]: δ^{1}H / δ^{13}C = 7.79 / 132.5 (p-Ph^{a} / o-Ph^{a}), 7.68 / 130.6, 121.9 (m-Ph^{a} / m-Ph^{a}, i-Ph^{a}), 7.65 / 133.8 (p-Ph^{b} / o-Ph^{b}), 7.38 / 129.5, 119.1 (m-Ph^{b} / m-Ph^{b}, i-Ph^{b}), 1.95 / 134.5, 128.9 (CH_3 / =C, =CH).

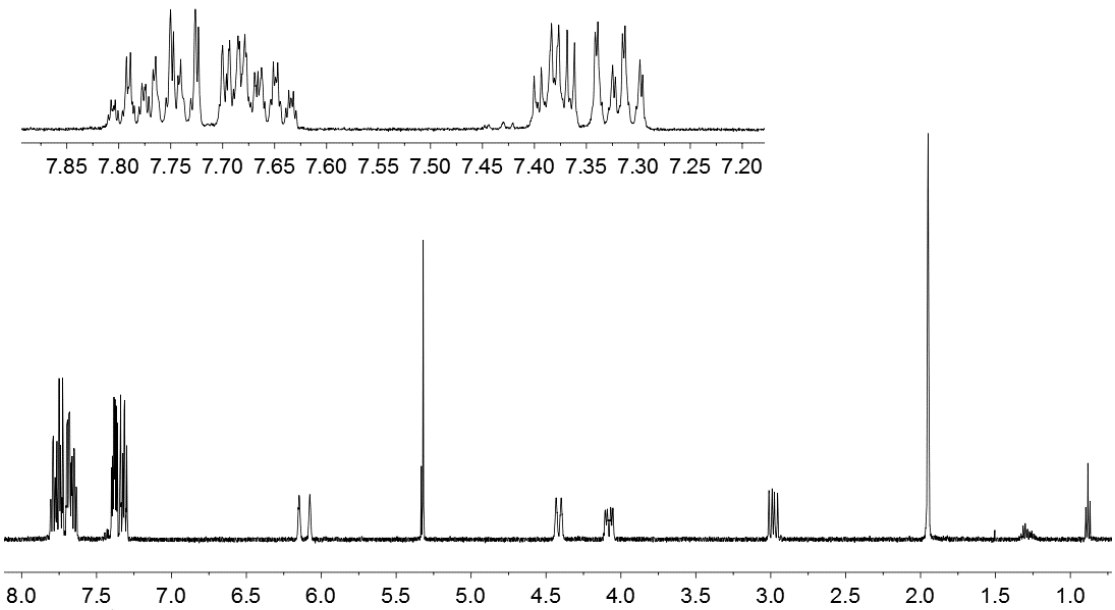
^{11}B{^{1}H} NMR (160 MHz, 299 K, [D_2]-dichloromethane): δ = 2.6 ($\nu_{1/2} \approx$ 300 Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, [D_2]-dichloromethane): δ = 47.9 ($\nu_{1/2} \approx$ 5 Hz).

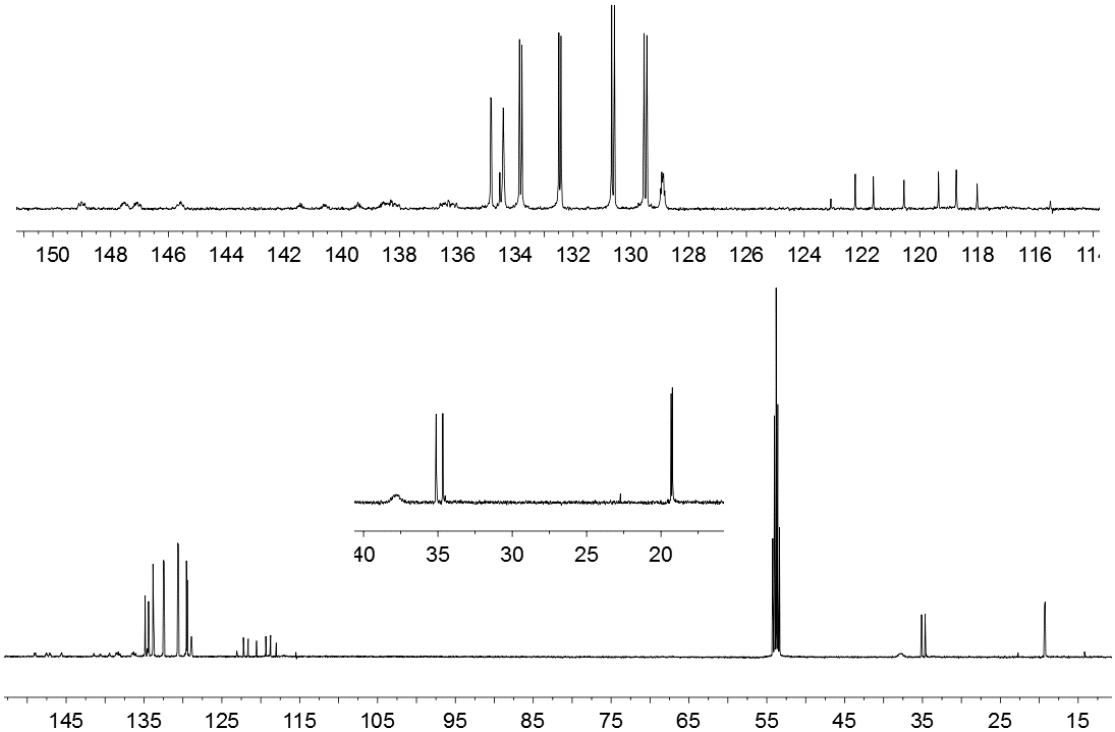
^{19}F NMR (470 MHz, 299 K, [D_2]-dichloromethane): δ = -77.2 (m, 3F, CF_3), -132.7 (br, 2F, o), -158.0 (tm, $^{3}J_{FF}$ = 20.6 Hz, p), -165.1 (m, 2F, m)(C_6F_5)[$\Delta\delta^{19}F_{mp}$ = 7.1], -133.4 (br, 2F, o), -159.4 (t, $^{3}J_{FF}$ = 20.6 Hz, each 1F, p), -165.0 (br, 2F, m)(C_6F_5)[$\Delta\delta^{19}F_{mp}$ = 5.6].

^{19}F NMR (470 MHz, 193 K, [D_2]-dichloromethane): δ = -77.3 (m, 3F, CF_3), -131.0 (br),

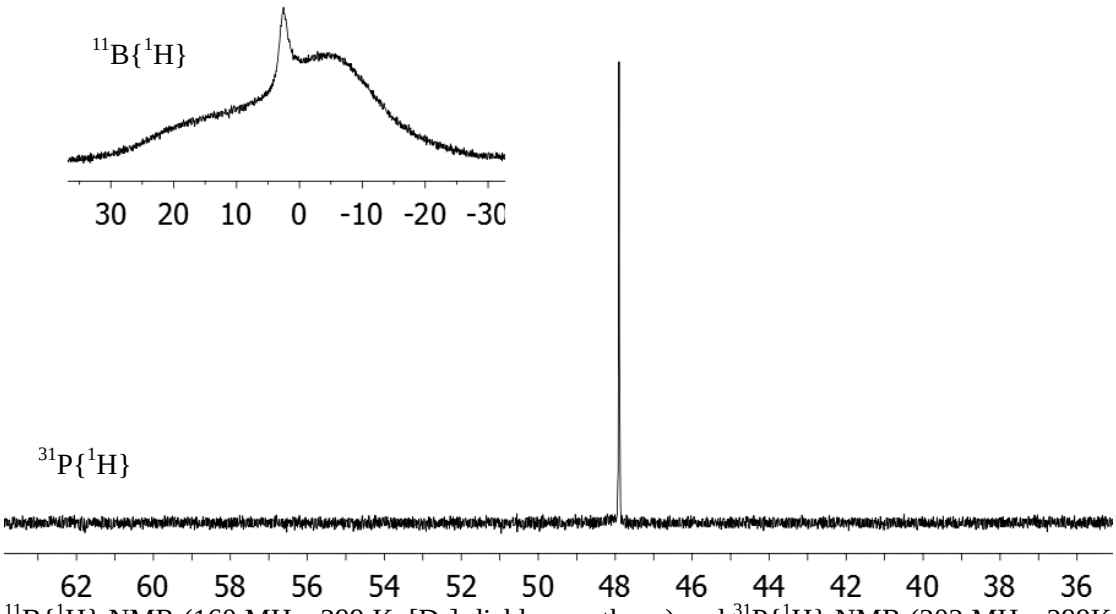
-132.4 (br), -134.7 (br), -135.6 (m)(each 1F, o-C_6F_5), -156.9, -158.6 (each t, $^3J_{FF}$ = 21.4 Hz, each 1F, p-C_6F_5), -163.9 (br m), -164.4 (m), -164.55 (br), -164.64 (m)(each 1F, m-C_6F_5).



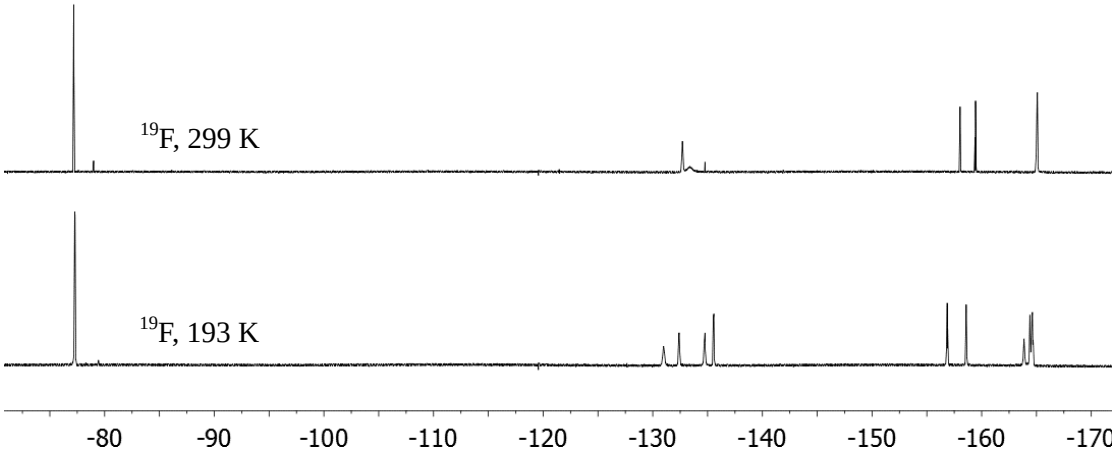
^{1}H NMR (500 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **4**



^{13}C{^{1}H} NMR (126 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **4**

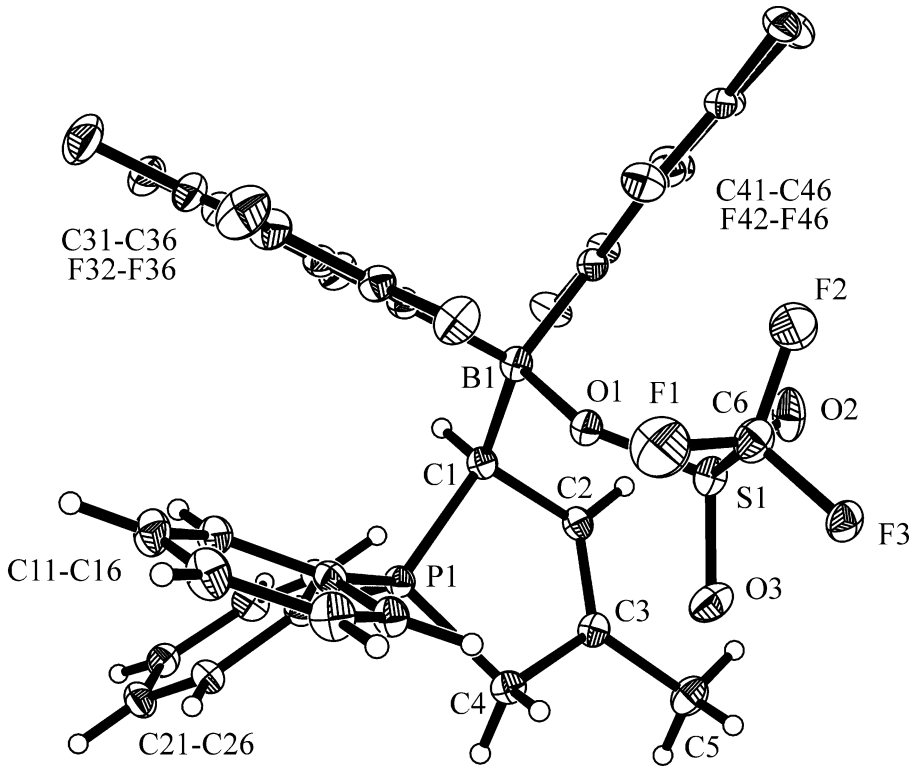


$^{11}B\{^1H\}$ NMR (160 MHz, 299 K, [D_2]-dichloromethane),and $^{31}P\{^1H\}$ NMR (202 MHz, 299K, [D_2]-dichloromethane) spectra of compound **4**

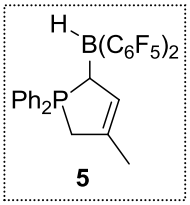


^{19}F NMR (470 MHz, 299 and 193K, [D_2]-dichloromethane) spectra of compound **4**

X-ray crystal structure analysis of compound 4: formula $C_{30}H_{17}BF_{13}O_3PS$, M = 746.28, colourless crystal, 0.12 x 0.03 x 0.02 mm, a = 10.0309(4), b = 16.5754(6), c = 17.7840(7) Å, β = 96.069(2) °, V = 2940.3(2) Å^3, ρ_{calc} = 1.686 gcm^{-3}, μ = 2.583 mm^{-1}, empirical absorption correction ($0.746 \leq T \leq 0.950$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 21204 reflections collected ($\pm h$, $\pm k$, $\pm l$), 5070 independent (R_{int} = 0.068) and 3628 observed reflections [$I>2\sigma(I)$], 471 refined parameters, R = 0.045, wR^2 = 0.111, max. (min.) residual electron density 0.21 (-0.28) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.


C41-C46
F42-F46
C31-C36
F32-F36
F2
B1
O1
F1
C6
O2
C1
C2
S1
F3
C11-C16
P1
O3
C3
C4
C21-C26
C5

Synthesis of Compound 5



5

Excess of chlorodimethylsilane (0.2 mL, 1.8 mmol) was added to a solution of compound **4** (340 mg, 0.46 mmol) in dichloromethane (3 mL). Then the reaction mixture was stirred at 60 °C for 30 min. All volatiles were removed *in vacuo*, the obtained residue was washed with pentane (3 × 2 mL) and dried in vacuo to give compound **5** (200 mg, 0.33 mmol, 73%) as a colorless solid. Single crystals of compound **5** suitable for the X-ray crystal structure analysis were obtained by slowly diffusion of pentane into a solution of compound **5** in dichloromethane at -30 °C.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 2957 (w), 2922, 2374 (s, ν_{BH}), 1641 (w), 1511 (s), 1465 (vs), 1394 (w), 1274 (w), 1166 (w), 1095 (s), 967 (s), 800 (w), 745 (m), 688 (w), 531 (w).

Melting point: 94 °C.

Elemental analysis: calc. for $C_{29}H_{18}BF_{10}P$ (598.22 g/mol): C, 58.22; H, 3.03. Found: C, 58.58; H, 3.06.

^{1}H NMR (600 MHz, 299 K, [D$_2$]-dichloromethane): δ = 7.80 (m, 2H, o-Ph^a), 7.76 (m, 1H, p-Ph^a), 7.65 (m, 2H, m-Ph^a), 7.52 (m, 2H, o-Ph^b), 7.46 (m, 1H, p-Ph^b), 7.29 (m, 2H, m-Ph^b), 5.55 (d, $^3J_{PH}$ = 35.4 Hz, 1H, =CH), 3.98 (br m, 1H, CH), 3.90 (dd, $^2J_{HH}$ = 17.5, $^2J_{PH}$ = 6.3 Hz, 1H, CH$_2$), 2.84 (dd, $^2J_{HH}$ = 17.5, $^2J_{PH}$ = 11.6 Hz, 1H, CH$_2$), 2.78 (q 1:1:1:1 partially relaxed, $^1J_{BH}$ ~ 96 Hz, 1H, BH), 1.79 (s, 3H, CH$_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, [D$_2$]-dichloromethane): δ = 134.3 (d, $^4J_{PC}$ = 2.8 Hz, p-Ph^a), 134.1 (d, $^2J_{PC}$ = 9.4 Hz, o-Ph^b), 133.9 (d, $^4J_{PC}$ = 3.2 Hz, p-Ph^b), 132.9 (d, $^2J_{PC}$ = 8.9 Hz, o-Ph^a), 132.5 (m, =CH), 130.2 (d, $^3J_{PC}$ = 11.4 Hz, m-Ph^a), 128.6 (d, $^3J_{PC}$ = 12.2 Hz, m-Ph^b), 127.0 (d, $^2J_{PC}$ = 12.4 Hz, =C), 122.4 (d, $^1J_{PC}$ = 73.0 Hz, i-Ph^a), 120.1 (d, $^1J_{PC}$ = 79.6 Hz, i-Ph^b), 32.1 (d, $^1J_{PC}$ = 58.9 Hz, CH$_2$), 30.5 (br, CH), 19.1 (d, $^3J_{PC}$ = 10.3 Hz, CH$_3$), [C$_6$F$_5$ not listed].

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 299 K, [D$_2$]-dichloromethane) [selected traces]: δ^{1}H / δ^{1}H = 7.65 / 7.80, 7.76 (m-Ph^a / o-Ph^a, p-Ph^a), 7.29 / 7.52, 7.46 (m-Ph^b / o-Ph^b, p-Ph^b).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, [D$_2$]-dichloromethane): δ^{1}H / δ^{13}C = 7.80 / 132.9 (o-Ph^a), 7.76 / 134.3 (p-Ph^a), 7.65 / 130.2 (m-Ph^a), 7.52 / 134.1 (o-Ph^b), 7.46 / 133.9 (p-Ph^b), 7.29 / 128.6 (m-Ph^b), 5.55 / 132.5 (=CH), 3.98 / 30.5 (CH), 3.90, 2.84 / 32.1 (CH$_2$), 1.79 / 19.1 (CH$_3$).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, [D$_2$]-dichloromethane) [selected traces]: δ^{1}H / δ^{13}C = 7.65 / 132.9, 130.2, 122.4 (m-Ph^a / o-Ph^a, m-Ph^a, i-Ph^a), 7.29 / 134.1, 128.6, 120.1 (m-Ph^b / o-Ph^b, m-Ph^b, i-Ph^b), 3.90 / 132.5, 127.0 (CH$_2$ / =CH, =C).

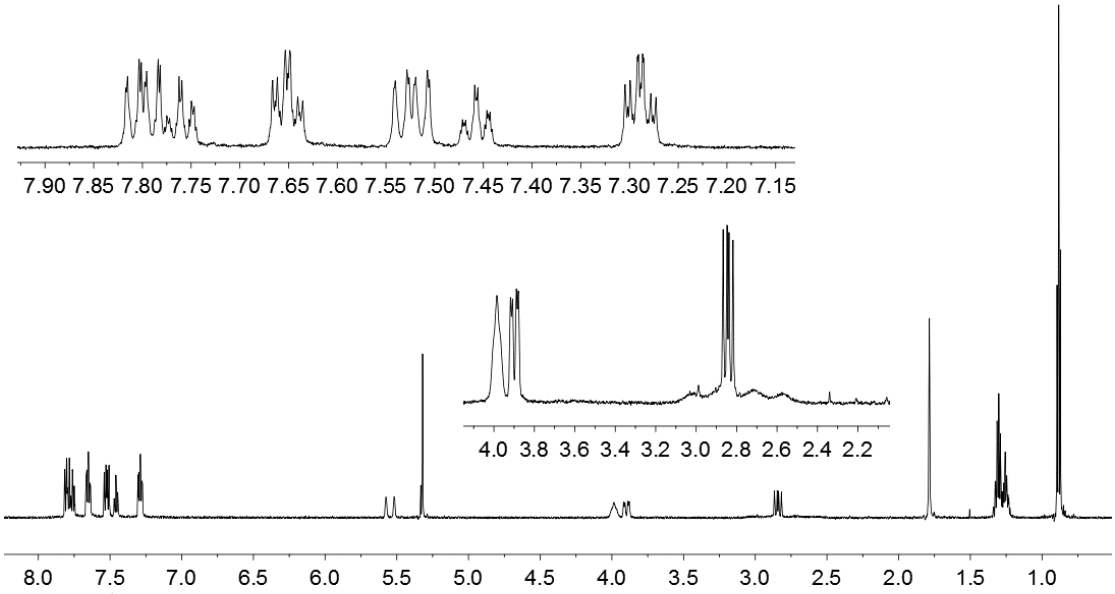
^{11}B NMR (192 MHz, 299 K, [D$_2$]-dichloromethane): δ = -22.1 ($\nu_{1/2}$ ≈ 40 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, [D$_2$]-dichloromethane): δ = -22.1 (d, $^1J_{BH}$ ~ 94 Hz).

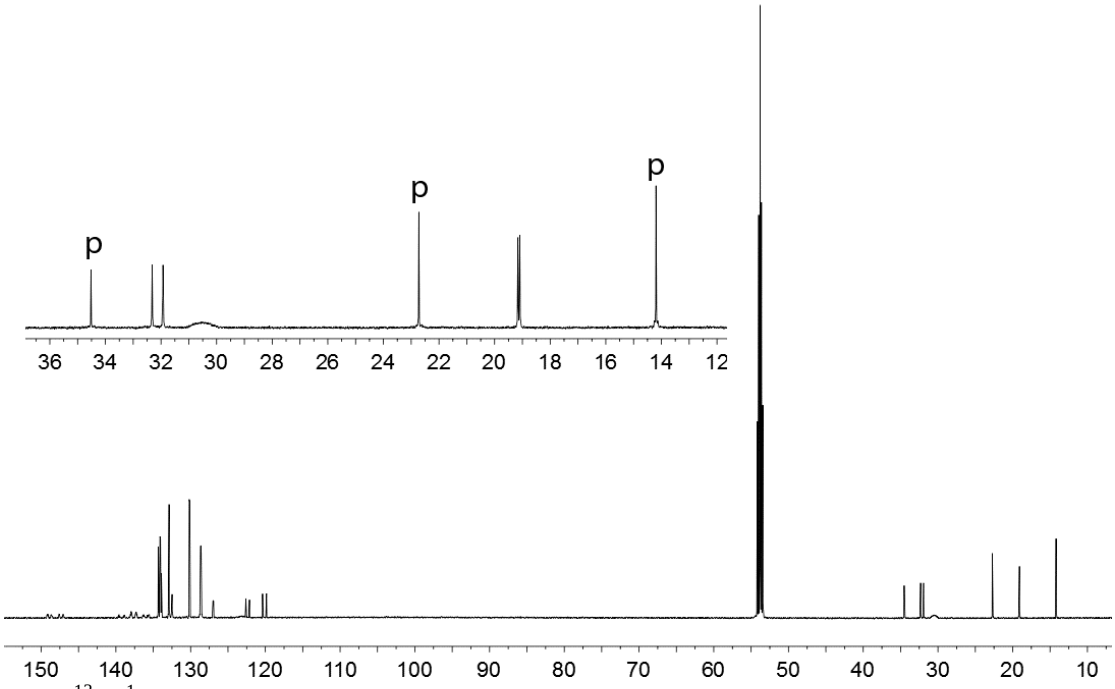
^{31}P{^{1}H} NMR (243 MHz, 299 K, [D$_2$]-dichloromethane): δ = 51.1 ($\nu_{1/2}$ ≈ 3 Hz).

^{19}F NMR (564 MHz, 299 K, [D$_2$]-dichloromethane): δ = -132.7 (m, 2F, o), -163.5 (t, $^3J_{FF}$ = 20.1 Hz, p), -166.9 (m, 2F, m)(C$_6$F$_5$)[$\Delta\delta^{19}F_{mp}$ = 3.4]; -133.1 (m, 2F, o), -162.6 (t, $^3J_{FF}$ = 20.1 Hz, 1F, p), -166.2 (m, 2F, m)(C$_6$F$_5$)[$\Delta\delta^{19}F_{mp}$ =3.6].

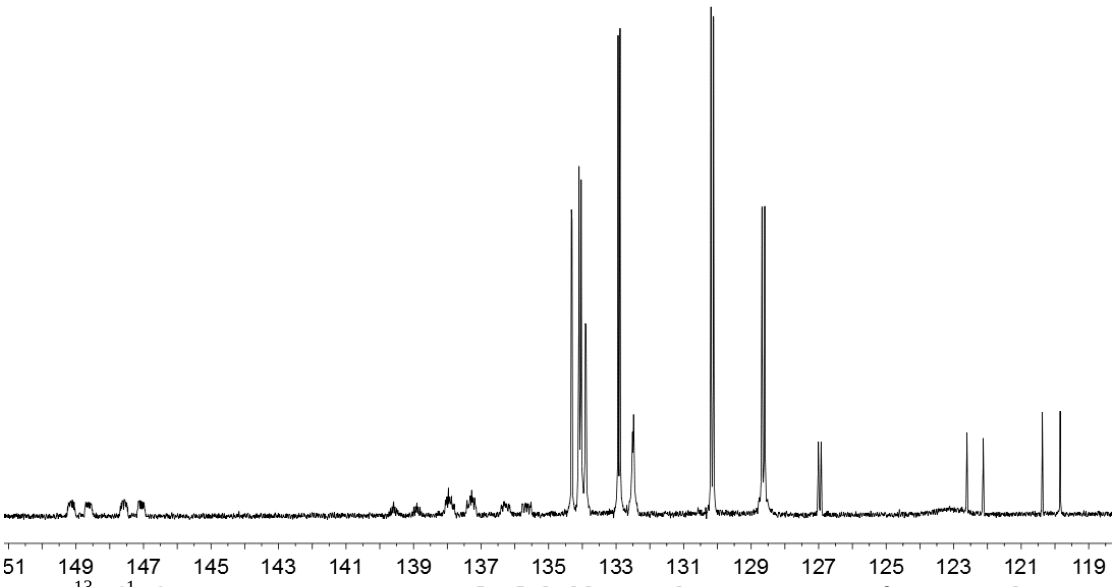
^{19}F,^{19}F GCOSY (564 MHz / 564 MHz, 299 K, [D$_2$]-dichloromethane): δ^{19}F / δ^{19}F = -132.7 / -166.9 (o / m), -163.5 / -166.9 (p / m) (C$_6$F$_5^a$); -133.1 / -166.2 (o / m), -162.6 / -166.2 (p / m) (C$_6$F$_5^b$).



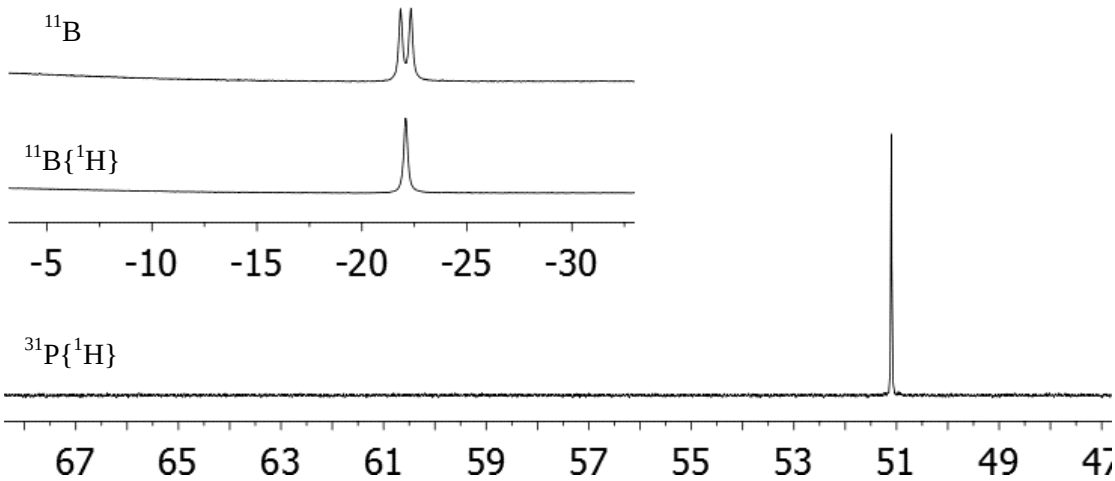
^{1}H NMR (600 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **5**



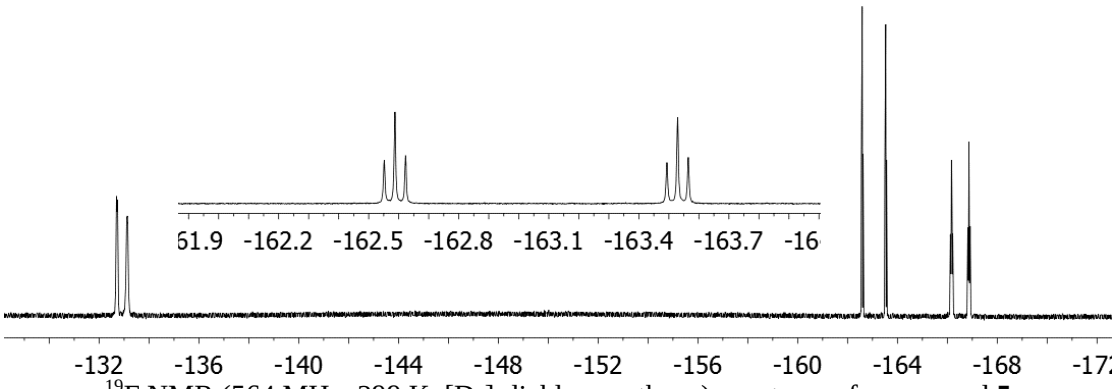
^{13}C{^{1}H} NMR (151 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **5**
(p: pentane)



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **5**

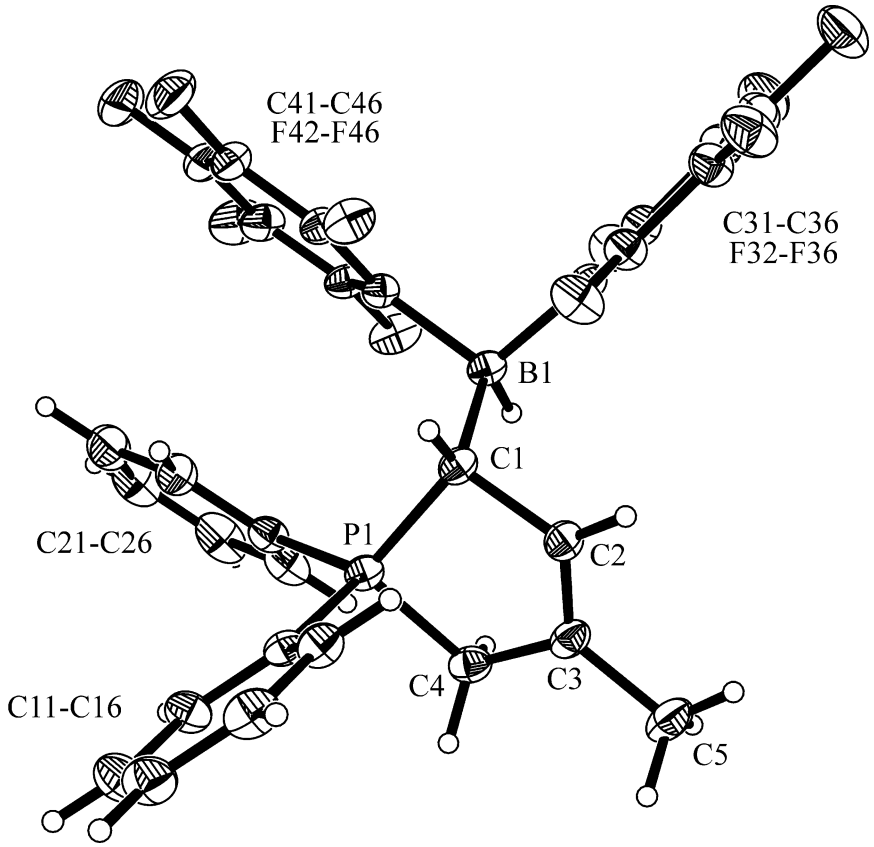


^{11}B , $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, [D_2]-dichloromethane) and $^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, [D_2]-dichloromethane) spectra of compound **5**

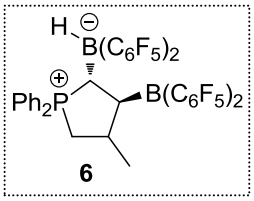


^{19}F NMR (564 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **5**

X-ray crystal structure analysis of compound 5: formula $C_{29}H_{18}BF_{10}P$, M = 598.21, colourless crystal, 0.20 x 0.07 x 0.04 mm, a = 11.8789(6), b = 12.5298(7), c = 12.6592(6) Å, α = 61.284(3), β = 72.907(3), γ = 67.981(3)°, V = 1516.9(1) Å^3, ρ_{calc} = 1.310 gcm^{-3}, μ = 1.519 mm^{-1}, empirical absorption correction (0.751 ≤ T ≤ 0.941), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 17410 reflections collected (±h, ±k, ±l), 4983 independent (R_{int} = 0.047) and 3782 observed reflections [I>2σ(I)], 375 refined parameters, R = 0.049, wR^2 = 0.139, max. (min.) residual electron density 0.29 (-0.19) e.Å^{-3}, the hydrogen at B1 atom was refined freely; others were calculated and refined as riding atoms.



Synthesis of Compound 6



$HB(C_6F_5)_2$ (104 mg, 0.30 mmol) was added to a solution of compound 5 (180 mg, 0.30 mmol) in dichloromethane (6 mL). Then the reaction mixture was stirred at r.t. for 3 h. After concentrating the solution *in vacuo* to 1/3 of the volume, pentane (10 mL) was added to give a suspension. The solid was collected and dried in vacuo to give compound **6** (180 mg, 0.19 mmol, 63%) as a colorless powder. Single crystals of compound **6** suitable for the X-ray crystal structure analysis were obtained by slowly diffusion of pentane into a solution of compound **6** in dichloromethane at -30 °C.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 2921 (w), 2371 (w, ν_{BH}), 1647 (w), 1511 (s), 1466 (vs), 1274 (w), 1164 (w), 1093 (s), 967 (s), 745 (m), 689 (w), 531 (w).

Melting point: 155 °C.

Elemental analysis: calc. for $C_{41}H_{19}B_2F_{20}P$ (944.15 g/mol): C, 52.16; H, 2.03. Found: C, 52.42; H, 2.35.

^{1}H NMR (600 MHz, 299 K, [D_2]-dichloromethane): δ = 7.82 (m, 2H, o-Ph^{a}), 7.76 (m, 1H, p-Ph^{a}), 7.67 (m, 2H, m-Ph^{a}), 7.44 (m, 2H, o-Ph^{b}), 7.41 (m, 1H, p-Ph^{b}), 7.26 (m, 2H, m-Ph^{b}), 3.65 (m, 1H, PCH), 3.06 (m, 1H, BCH), 2.97 (dt, $^{2}J_{HH}$ = 14.7 Hz, $^{2}J_{PH} \sim {}^{3}J_{HH}$ = 12.2 Hz, CH_2), 2.90 (dt, $^{2}J_{HH}$ = 14.7 Hz, $^{2}J_{PH} \sim {}^{3}J_{HH}$ = 5.4 Hz, CH_2), 2.86 (br, 1H, BH), 2.31 (m, 1H, MeCH), 1.34 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, [D_2]-dichloromethane): δ = 134.3 (d, $^{4}J_{PC}$ = 2.9 Hz, p-Ph^{a}), 134.0 (d, $^{2}J_{PC}$ = 9.8 Hz, o-Ph^{b}), 133.8 (d, $^{4}J_{PC}$ = 3.2 Hz, p-Ph^{b}), 132.7 (d, $^{2}J_{PC}$ = 8.8 Hz, o-Ph^{a}), 130.3 (d, $^{3}J_{PC}$ = 11.3 Hz, m-Ph^{a}), 128.7 (d, $^{3}J_{PC}$ = 12.5 Hz, m-Ph^{b}), 121.5 (d, $^{1}J_{PC}$ = 73.8 Hz, i-Ph^{a}), 120.4 (d, $^{1}J_{PC}$ = 79.5 Hz, i-Ph^{b}), 52.2 (br, BCH), 37.9 (d, $^{2}J_{PC}$ = 13.8 Hz, MeCH), 33.7 (d, $^{1}J_{PC}$ = 57.4 Hz, CH_2), 27.8 (br, PCH), 21.9 (d, $^{3}J_{PC}$ = 15.9 Hz, CH_3), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 299 K, [D_2]-dichloromethane) [selected traces]: δ^{1}H / δ^{1}H = 7.67 / 7.82, 7.76 (m-Ph^{a} / o-Ph^{a}, p-Ph^{a}), 7.26 / 7.44, 7.40 (m-Ph^{b} / o-Ph^{b}, p-Ph^{b}).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, [D_2]-dichloromethane): δ^{1}H / δ^{13}C = 7.82 / 132.7 (o-Ph^{a}), 7.76 / 134.3 (p-Ph^{a}), 7.67 / 130.3 (m-Ph^{a}), 7.44 / 134.0 (o-Ph^{b}), 7.41 / 133.8 (p-Ph^{b}), 7.26 / 128.7 (m-Ph^{b}), 3.65 / 27.8 (PCH), 3.06 / 52.2 (BCH), 2.97, 2.90 / 33.7 (CH_2), 2.31 / 37.9 (MeCH), 1.34 / 21.9 (CH_3).

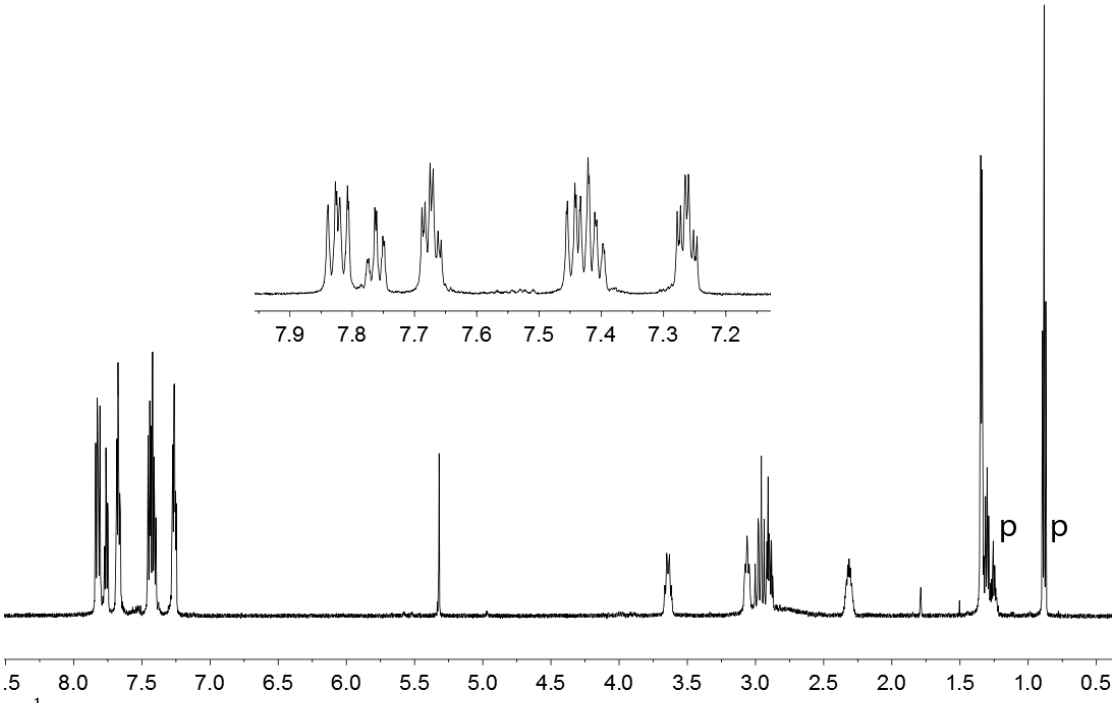
^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, [D_2]-dichloromethane) [selected traces]: δ^{1}H / δ^{13}C = 7.67 / 312.7, 130.3, 121.5 (m-Ph^{a} / m-Ph^{a}, p-Ph^{a}, i-Ph^{a}), 7.26 / 134.0, 128.7, 120.4 (m-Ph^{b} / m-Ph^{b}, p-Ph^{b}, i-Ph^{b}).

^{11}B NMR (192 MHz, 299 K, [D_2]-dichloromethane): δ = 65.1 ($\nu_{1/2} \approx$ 1600 Hz), -16.3 (d, $^{1}J_{BH} \sim$ 77 Hz).

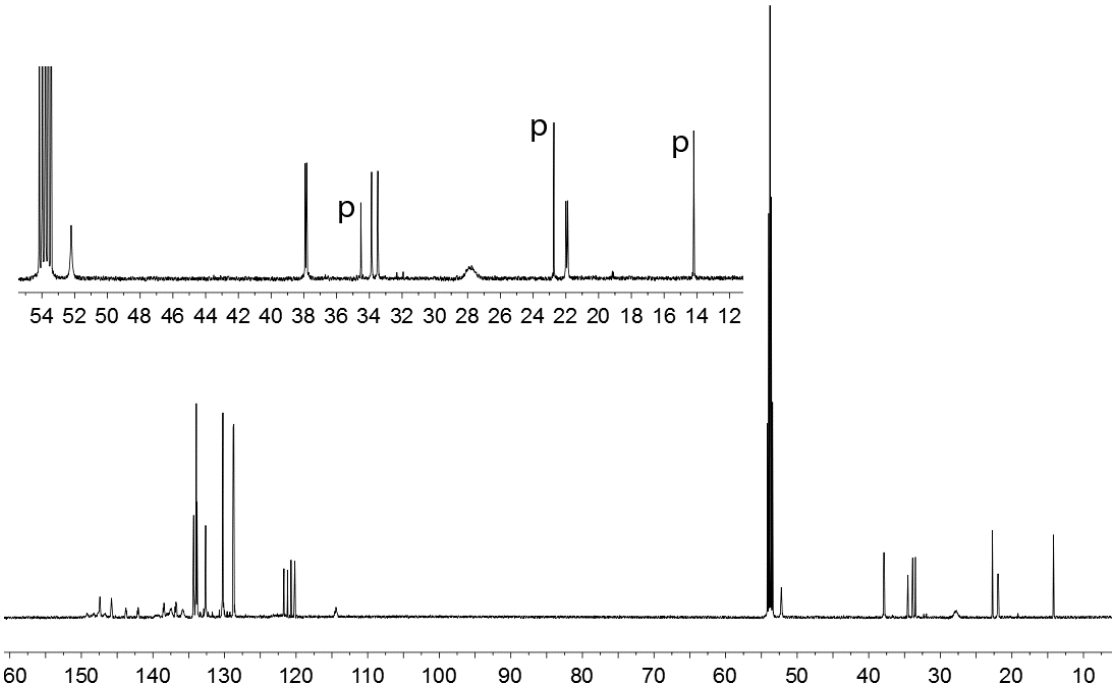
^{11}B{^{1}H} NMR (192 MHz, 299 K, [D_2]-dichloromethane): δ = 65.1 ($\nu_{1/2} \approx$ 1600 Hz), -16.3 ($\nu_{1/2} \approx$ 15 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, [D_2]-dichloromethane): δ = 48.6 ($\nu_{1/2} \approx$ 5 Hz).

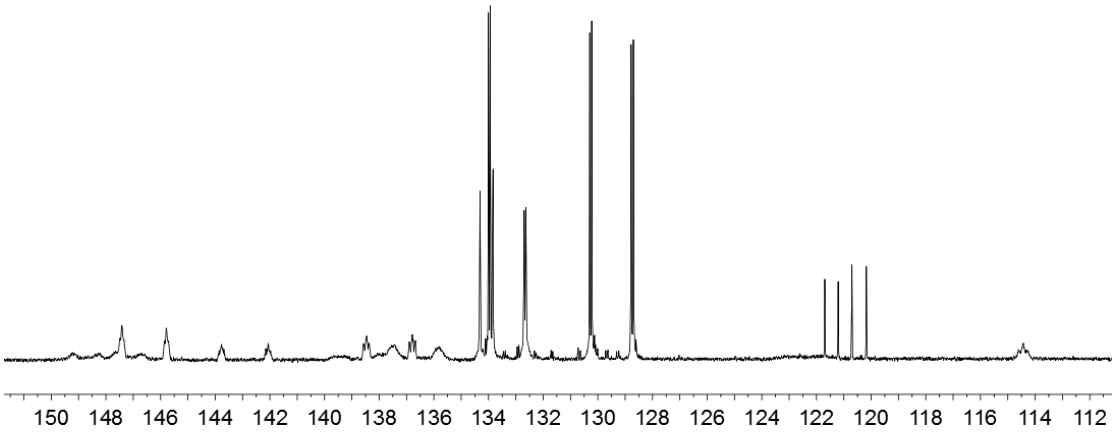
^{19}F NMR (564 MHz, 299 K, [D_2]-dichloromethane): δ = -128.0 (m, 4F, o), -149.7 (t, $^{3}J_{FF}$ = 20.3 Hz, 2F, p), -161.7 (m, 4F, m)($B(C_6F_5)_2$)[$\Delta\delta^{19}F_{mp}$ = 12.0], -131.5, -131.9 (each 2F, o), -161.0, -162.3 (each br, each 1F, p), -165.4, -166.1 (each br, each 2F, m)($HB(C_6F_5)_2$).



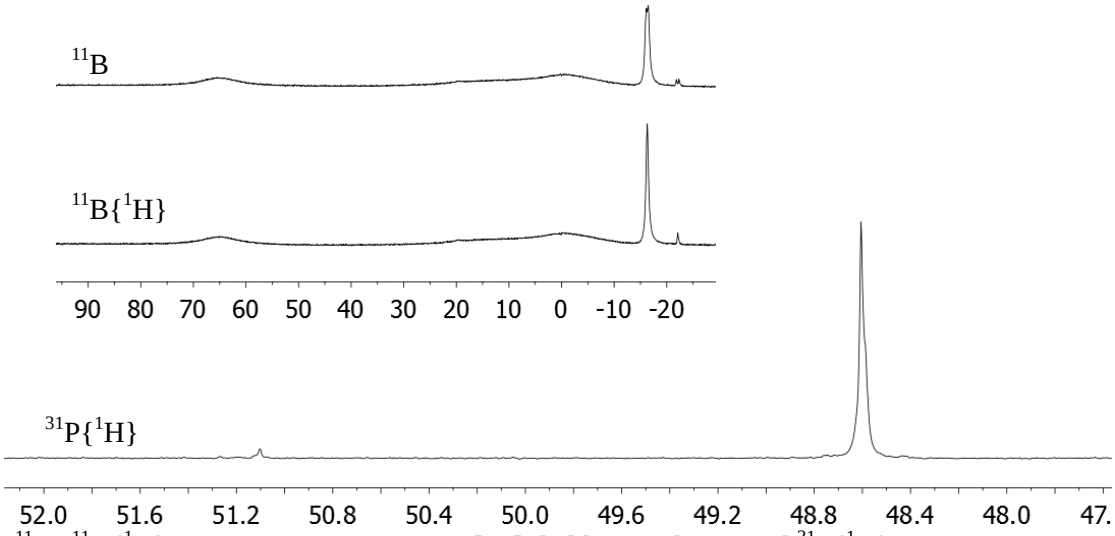
^{1}H NMR (600 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **6** (p: pentane)



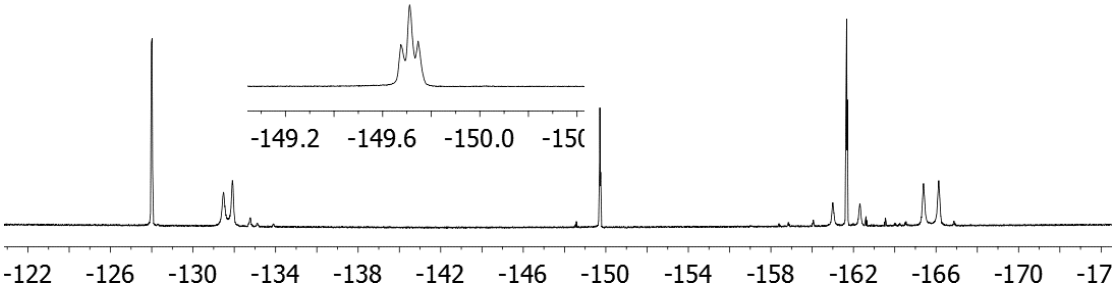
^{13}C{^{1}H} NMR (151 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **6** (p: pentane)



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $[D_2]$-dichloromethane) spectrum of compound **6**

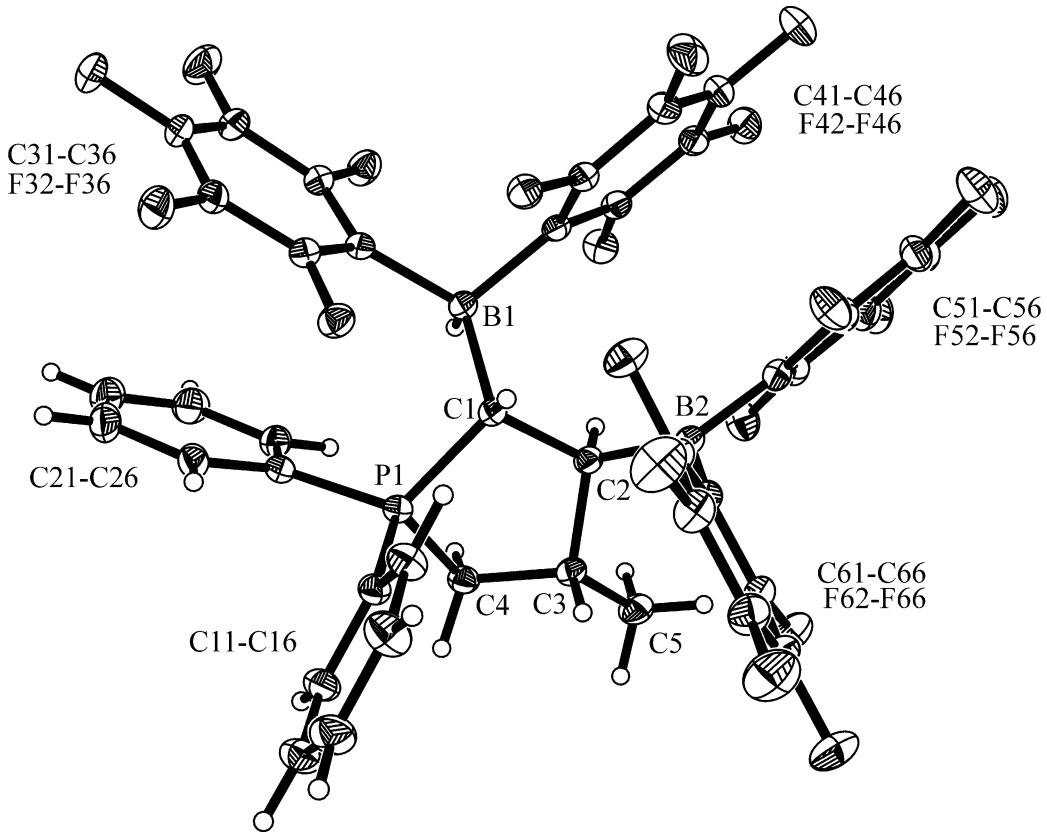


^{11}B , $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, $[D_2]$-dichloromethane) and $^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, $[D_2]$-dichloromethane) spectra of compound **6**

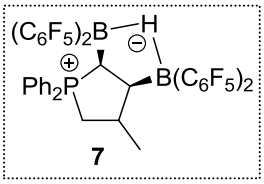


^{19}F NMR (564 MHz, 299 K, $[D_2]$-dichloromethane) spectrum of compound **6**

X-ray crystal structure analysis of compound 6: formula $C_{41}H_{19}B_2F_{20}P$, M = 944.15, colourless crystal, 0.16 x 0.08 x 0.03 mm, a = 12.7173(3), b = 24.4025(6), c = 16.3076(4) Å, β = 111.724(1) °, V = 4701.4(2) Å^3, ρ_{calc} = 1.334 gcm^{-3}, μ = 1.499 mm^{-1}, empirical absorption correction ($0.795 \leq T \leq 0.956$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 43736 reflections collected ($\pm h$, $\pm k$, $\pm l$), 8056 independent (R_{int} = 0.063) and 5963 observed reflections [$I>2\sigma(I)$], 582 refined parameters, R = 0.054, wR^2 = 0.179, max. (min.) residual electron density 0.24 (-0.38) e.Å^{-3}, the hydrogen at B1 atom was refined freely; others were calculated and refined as riding atoms.



Synthesis of Compound 7



7

A solution of compound **6** (120 mg, 0.13 mmol) in dichloromethane was stirred at 80 °C for 3 h. Subsequently, all volatiles were removed *in vacuo*. The obtained residue was washed with pentane (3 × 2 mL) and dried in vacuo to give compound **7** (100 mg, 0.11 mmol, 81%) as a colorless solid. Single crystals of compound **7** suitable for the X-ray crystal structure analysis were obtained by storing a solution of compound **7** in pentane at room temperature for several days.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 3065 (w), 2963 (w), 2930 (w), 1646 (m), 1518 (s), 1466 (vs), 1360 (w), 1288 (w), 1217 (w), 1096 (s), 972 (s), 743 (w), 689 (w), 625 (w).

Melting point: 144 °C.

Elemental analysis: calc. for $C_{41}H_{19}B_2F_{20}P$ (944.15 g/mol): C, 52.16; H, 2.03. Found: 52.42, H, 2.57.

^{1}H NMR (600 MHz, 299 K, [D_2]-dichloromethane): δ = 7.74 (m, 3H, o,p-Ph^a), 7.68 (m, 2H, m-Ph^a), 7.59 (m, 1H, p-Ph^b), 7.37 (m, 2H, m-Ph^b), 7.24 (m, 2H, o-Ph^b), 4.44 (m, 1H, PCH), 3.17, 2.35 (each m, each 1H, CH_2), 3.11 (m, MeCH), 2.78 (m, 1H, BCH), 2.12 (br, 1H, BHB), 0.99 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, [D_2]-dichloromethane): δ = 134.3 (p-Ph^{a,b}), 132.3 (d, $^2J_{PC}$ = 9.6 Hz, o-Ph^b), 131.7 (d, $^2J_{PC}$ = 9.3 Hz, o-Ph^a), 130.7 (d, $^3J_{PC}$ = 11.7 Hz, m-Ph^a), 129.7 (d, $^3J_{PC}$ = 12.0 Hz, m-Ph^b), 124.7 (d, $^1J_{PC}$ = 77.5 Hz, i-Ph^a), 121.2 (d, $^1J_{PC}$ = 74.2 Hz, i-Ph^b), 47.4 (br, BCH), 36.7 (MeCH), 34.6 (d, $^1J_{PC}$ = 58.4 Hz, CH_2), 27.2 (br, PCH), 22.8 (d, $^3J_{PC}$ = 8.9 Hz, CH_3), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 299 K, [D_2]-dichloromethane) [selected traces]: δ^{1}H / δ^{1}H = 7.68 / 7.74 (m-Ph^a / o,p-Ph^a), 7.37 / 7.59, 7.24 (m-Ph^a / o-Ph^a, p-Ph^a).

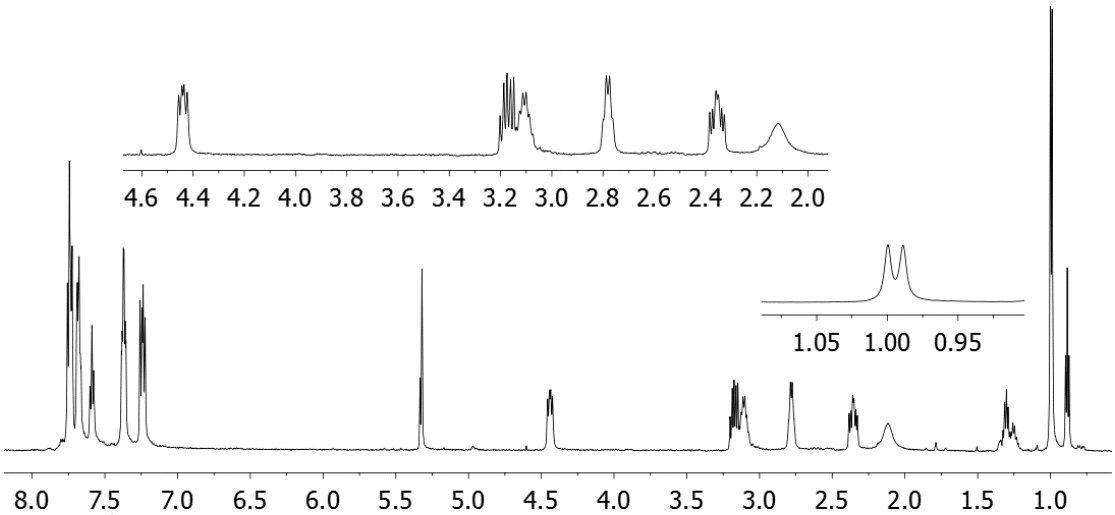
^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, [D_2]-dichloromethane): δ^{1}H / δ^{13}C = 7.74 / 131.7 (o-Ph^a), 7.74 / 134.3 (p-Ph^a), 7.68 / 130.7 (m-Ph^a), 7.59 / 134.3 (p-Ph^b), 7.37 / 129.7 (m-Ph^b), 7.24 / 132.3 (o-Ph^b), 4.44 / 27.2 (PCH), 3.17, 2.35 / 34.6 (CH_2), 3.11 / 36.7 (MeCH), 2.78 / 47.4 (BCH), 0.99 / 22.8 (CH_3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, [D_2]-dichloromethane) [selected traces]: δ^{1}H / δ^{13}C = 7.68 / 130.7, 124.7 (m-Ph^a / m-Ph^a, i-Ph^a), 7.37 / 129.7, 121.2 (m-Ph^b / m-Ph^b, i-Ph^b).

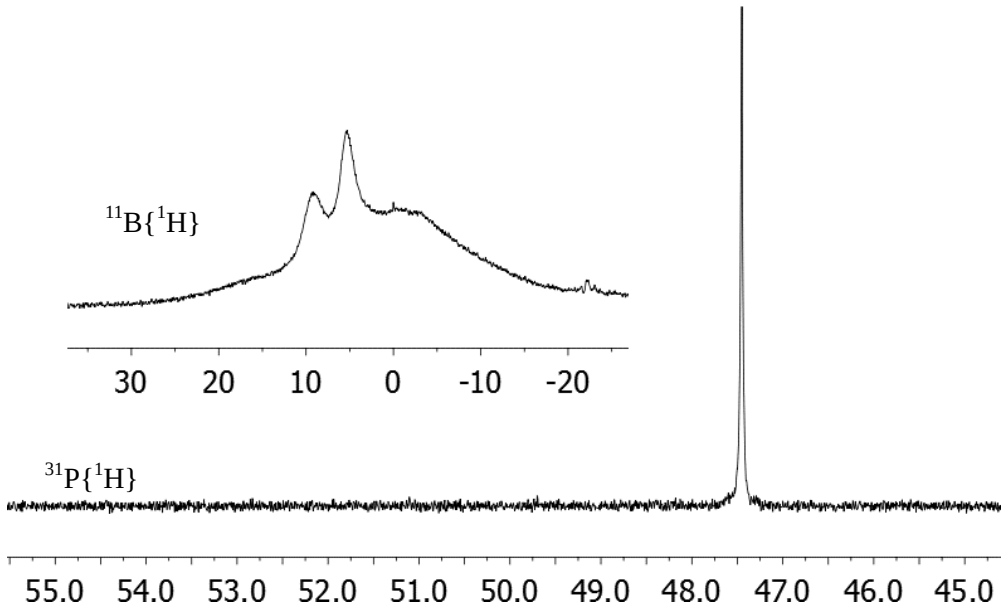
^{11}B{^{1}H} NMR (192 MHz, 299 K, [D_2]-dichloromethane): δ = 9.4 ($\nu_{1/2}$ ≈ 500 Hz), 5.5 ($\nu_{1/2}$ ≈ 300 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, [D_2]-dichloromethane): δ = 47.5 ($\nu_{1/2}$ ≈ 10 Hz).

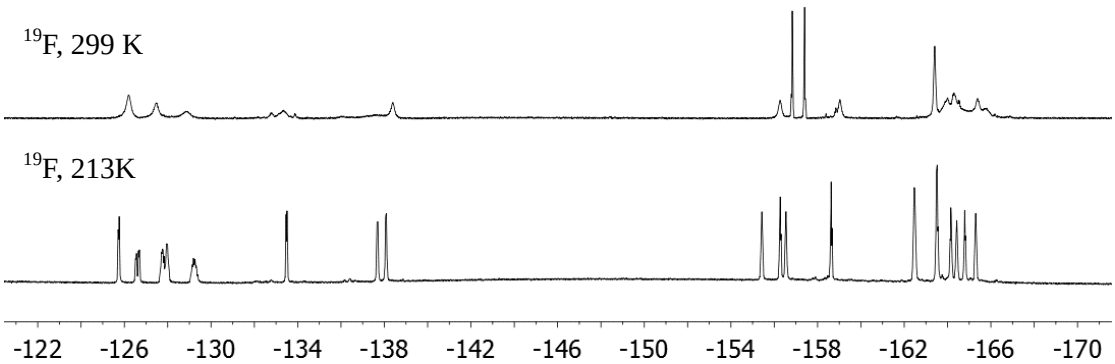
^{19}F NMR (564 MHz, 213 K, [D_2]-dichloromethane): δ = -125.8, -126.7, -127.7, -127.9, -129.2, -133.5, -137.8, -138.0 (each m, each 1F, o-C_6F_5), -155.6 (t, $^3J_{FF}$ = 20.0 Hz), -156.4 (t, $^3J_{FF}$ = 20.4 Hz), -156.7 (t, $^3J_{FF}$ = 20.0 Hz), -158.7 (t, $^3J_{FF}$ = 20.4 Hz)(each 1F, p-C_6F_5), -162.6, -162.7, -163.5, -163.6, -164.2, -164.6, -164.8, -165.4 (each m, each 1F, m-C_6F_5).



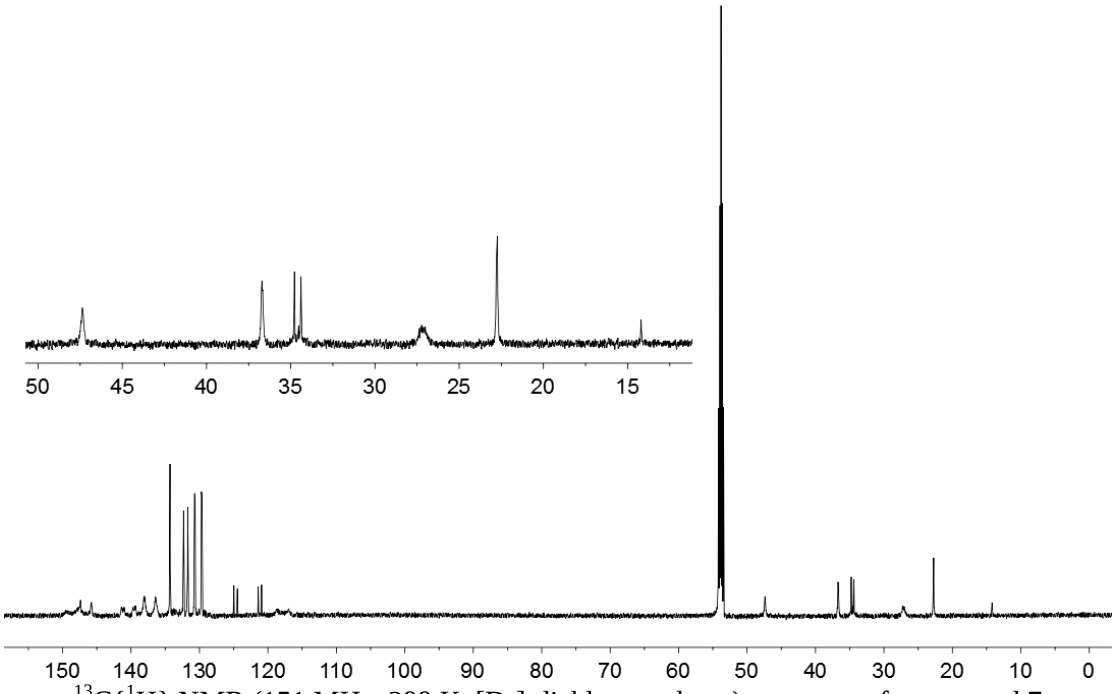
^{1}H NMR (600 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **7**



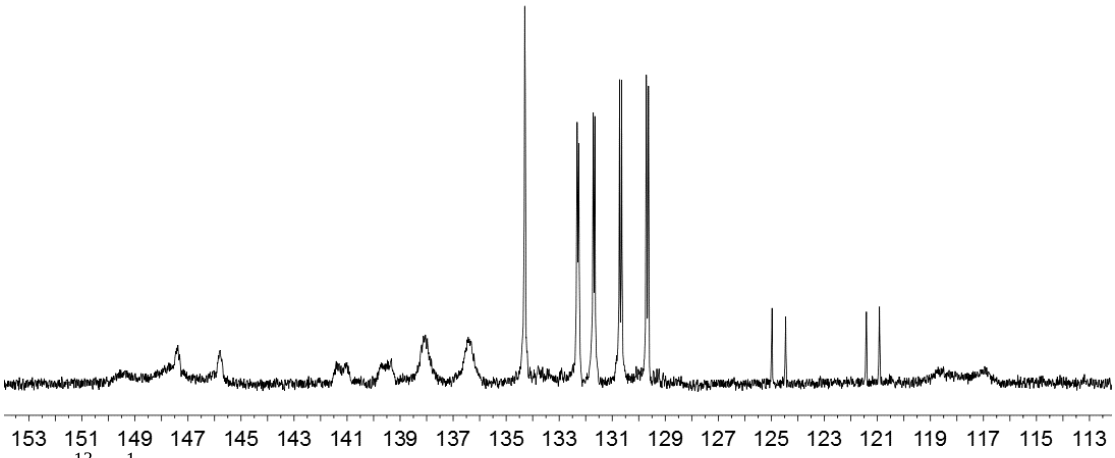
^{11}B{^{1}H} NMR (192 MHz, 299 K, [D_2]-dichloromethane) and ^{31}P{^{1}H} NMR (243 MHz, 299 K, [D_2]-dichloromethane) spectra of compound **7**



^{19}F NMR (564 MHz, 299 and 213 K, [D_2]-dichloromethane) spectra of compound **7**

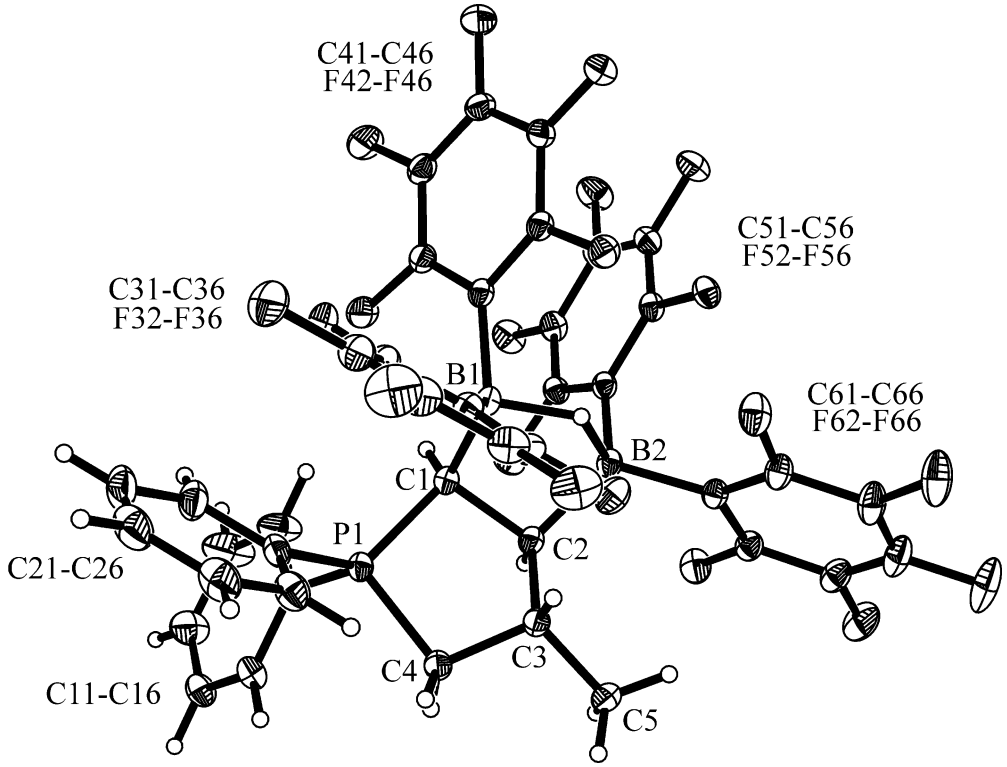


$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **7**

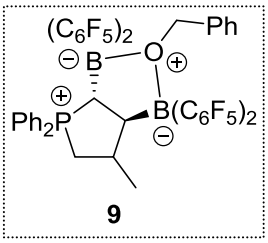


$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **7**

X-ray crystal structure analysis of compound 7: formula $C_{41}H_{19}B_2F_{20}P$, M = 944.15, colourless crystal, 0.22 x 0.12 x 0.10 mm, a = 12.6726(5), b = 20.3084(6), c = 19.6095(6) Å, β = 124.093(1) °, V = 8136.8(4) Å^3, ρ_{calc} = 1.541 gcm^{-3}, μ = 1.733 mm^{-1}, empirical absorption correction ($0.701 \leq T \leq 0.845$), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 32709 reflections collected ($\pm h$, $\pm k$, $\pm l$), 7075 independent (R_{int} = 0.042) and 6125 observed reflections [$I>2\sigma(I)$], 582 refined parameters, R = 0.046, wR^2 = 0.135, max. (min.) residual electron density 0.32 (-0.27) e.Å^{-3}, the hydrogen between B1 and B2 atoms was refined freely; others were calculated and refined as riding atoms.


C41-C46
F42-F46
C51-C56
F52-F56
C31-C36
F32-F36
B1
C61-C66
F62-F66
B2
C1
C2
P1
C21-C26
C4
C3
C11-C16
C5

Synthesis of Compound 9



9

Excess of benzaldehyde (40 mg, 0.38 mmol) was added to a solution of compound **6** (150 mg, 0.16 mmol) in dichloromethane (10 mL). Then the reaction mixture was stirred at r.t. for one hour. After removing all volatiles of the solution *in vacuo*, the residue was dissolved in hot pentane (5 mL). The solution was kept at r.t. for one day to give some colorless crystalline material. The solid was collected and dried in vacuo to give compound **9** (130 mg, 0.12 mmol, 77%). Single crystals of compound **9** suitable for the X-ray crystal structure analysis were obtained by storing a solution of compound **9** in dichloromethane at room temperature for several days.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 3065 (w), 2929 (w), 1644 (m), 1519 (s), 1456 (vs), 1283 (w), 1095 (s), 971 (s), 854, 750 (m), 691 (m), 531 (w).

Melting point: 189 °C.

Elemental analysis: calc. for $C_{48}H_{25}B_2F_{20}OP$ (1050.27 g/mol): C, 54.89; H, 2.40. Found: C, 54.83; H, 2.38.

^{1}H NMR (500 MHz, 299 K, [D_2]-dichloromethane) δ = 7.79 (m, 1H, p-Ph^{a}), 7.67 (m, 2H, o-Ph^{a}), 7.62 (m, 2H, m-Ph^{a}), 7.49 (m, 1H, p-Ph^{b}), 7.32 (m, 2H, m-Ph^{b}), 7.12 (m, 1H, p-bzl), 7.10 (m, 1H, o-Ph^{b}), 7.00 (m, 2H, m-bzl), 6.88 (m, 2H, o-bzl), 5.01, 4.97 (AB, $^{2}J_{HH}$ = 13.5 Hz, each 1H, CH_2), 3.39 (ddd, $^{2}J_{HH}$ = 16.6, $^{3}J_{HH}$ = 10.1, $^{2}J_{PH}$ = 6.8 Hz, 1H, PCH_2), 3.31 (br, 1H, BCH), 3.14 (m, 1H, PCH), 2.37 (ddd, $^{2}J_{HH}$ = 16.6, $^{2}J_{PH}$ = 13.0, $^{3}J_{HH}$ = 8.0 Hz, 1H, PCH_2), 1.91 (m, 1H, MeCH), 1.38 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 299 K, [D_2]-dichloromethane): δ = 134.6 (d, $^{4}J_{PC}$ = 2.9 Hz, p-Ph^{a}), 134.5 (i-bzl), 133.8 (d, $^{2}J_{PC}$ = 9.0 Hz, o-Ph^{a}), 133.1 (d, $^{2}J_{PC}$ = 9.2 Hz, o-Ph^{b}), 133.0 (d, $^{4}J_{PC}$ = 3.2 Hz, p-Ph^{b}), 130.7 (o-bzl), 130.0 (d, $^{3}J_{PC}$ = 11.8 Hz, m-Ph^{a}), 129.4 (d, $^{3}J_{PC}$ = 11.8 Hz, m-Ph^{b}), 128.7 (p-bzl), 127.6 (m-bzl), 124.1 (d, $^{1}J_{PC}$ = 73.1 Hz, ^{i}Ph^{b}), 120.4 (d, $^{1}J_{PC}$ = 78.2 Hz, i-Ph^{a}), 74.1 (CH_2), 46.6 (br, BCH), 40.2 (d, $^{1}J_{PC}$ = 60.9 Hz, PCH_2), 39.6 (br m, PCH), 36.1 (d, $^{2}J_{PC}$ = 3.2 Hz, MeCH), 21.4 (m, CH_3), [C_6F_5 not listed].

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, [D_2]-dichloromethane): δ^{1}H / δ^{13}C = 7.79 / 134.6 (p-Ph^{a}), 7.67 / 133.8 (o-Ph^{a}), 7.62 / 130.0 (m-Ph^{a}), 7.49 / 133.0 (p-Ph^{b}), 7.32 / 129.4 (m-Ph^{b}), 7.10 / 133.1 (o-Ph^{b}), 7.10 / 128.7 (p-bzl), 7.00 / 127.6 (m-bzl), 6.88 / 130.7 (o-bzl), 5.01, 4.97 / 74.1 (CH_2), 3.39, 2.27 / 40.2 (PCH_2), 3.31 / 46.6 (BCH), 3.14 / 39.6 (PCH), 1.91 / 36.1 (MeCH), 1.38 / 21.4 (CH_3).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, [D_2]-dichloromethane) [selected traces]: δ^{1}H / δ^{13}C = 7.62 / 134.6, 130.0, 120.4 (m-Ph^{a} / p-Ph^{a}, m-Ph^{a}, i-Ph^{a}), 7.32 / 133.0, 129.4, 124.1 (m-Ph^{b} / p-Ph^{b}, m-Ph^{b}, i-Ph^{b}), 7.00 / 134.5, 127.6 (m-bzl / i-bzl, m-bzl), 3.14 / 124.1, 120.4 (PCH / i-Ph^{b}, i-Ph^{b}).

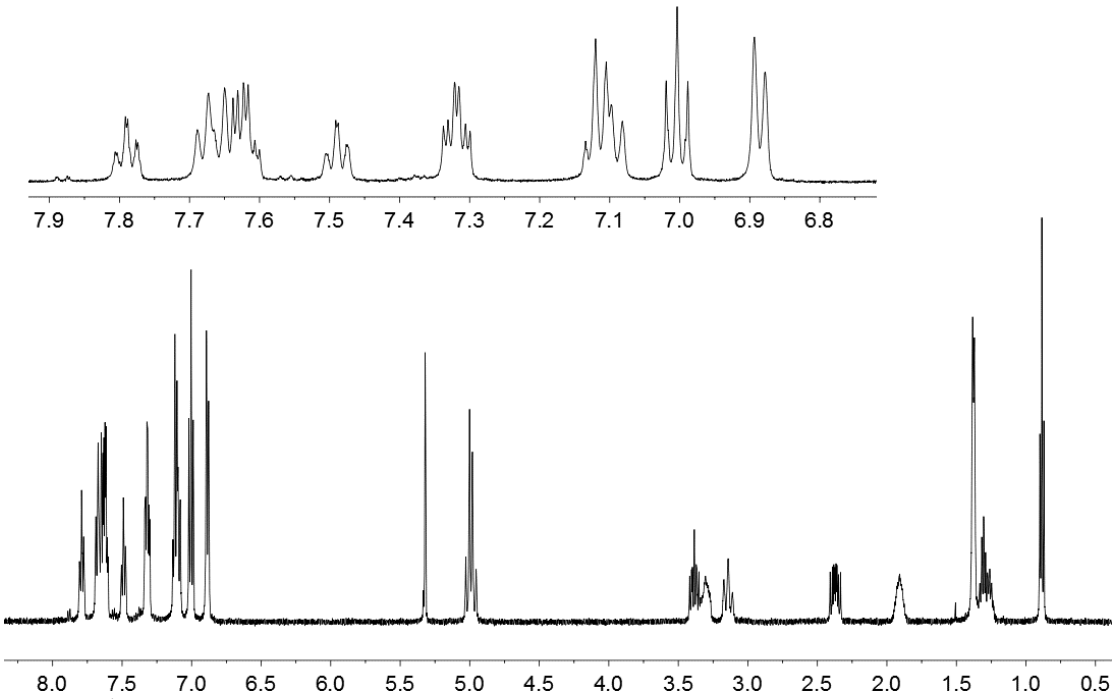
^{11}B{^{1}H} NMR (160 MHz, 299 K, [D_2]-dichloromethane): δ = 5.8 ($\nu_{1/2} \approx$ 400 Hz), 3.5 ($\nu_{1/2} \approx$ 300 Hz).

^{31}P{^{1}H} NMR (202 MHz, 299 K, [D_2]-dichloromethane): δ = 42.1 ($\nu_{1/2} \approx$ 10 Hz).

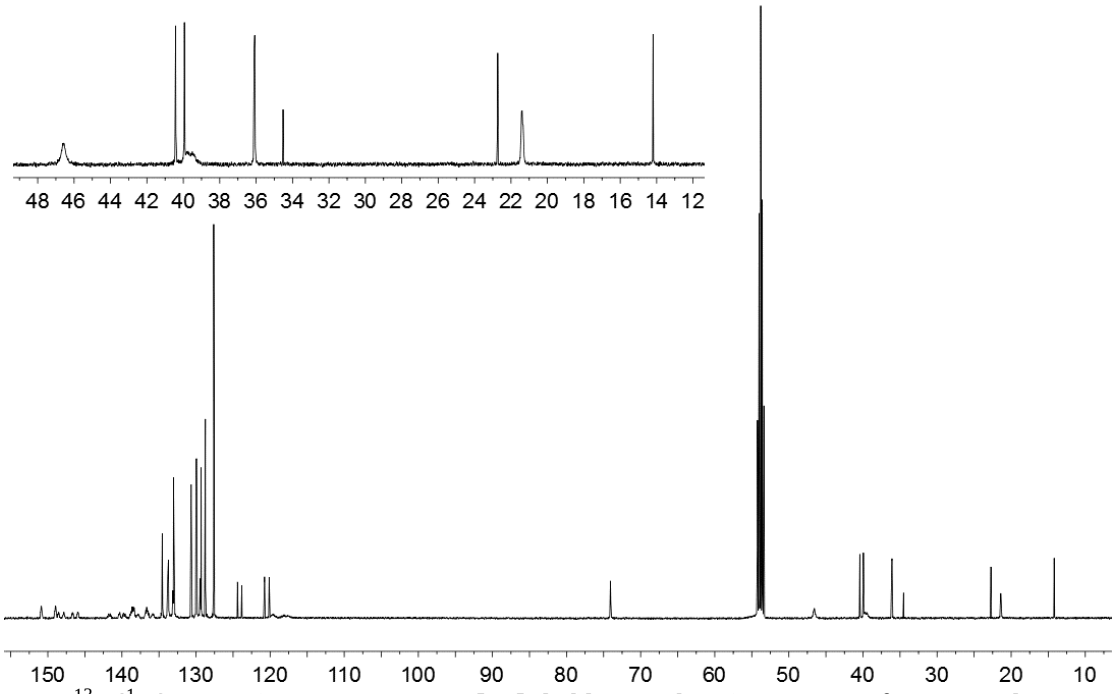
^{19}F NMR (564 MHz, 198 K, [D_2]-dichloromethane): δ = -123.4 (m, 1F, o), -126.4(m, 1F, o'), -155.5 (br d, $^{1}J_{FF}$ = 21.7 Hz, 1F, p), -163.4 (m, 1F, m), -164.1 (m, 1F, m')(C_6F_5)[$\Delta\delta^{19}F_{mp}$ = 7.9, 8.6], -121.0 (m, 1F, o), -126.72 (m, 1F, o'), -157.1 (br d, $^{1}J_{FF}$ = 21.4 Hz, 1F, p), -164.0 (m, 1F,

m'), -164.44 (m, 1F, m)(C_6F_5)[$\Delta\delta^{19}F_{mp}$ = 6.9, 7.3], -126.66 (o), -134.1 (m, 1F, o'), -158.9 (br d, $^1J_{FF}$ = 21.6 Hz, 1F, p), -161.0 (m, 1F, m), -163.9 (m, 1F, m')(C_6F_5)[$\Delta\delta^{19}F_{mp}$ = 2.1, 5.0], -127.3 (m, 1F, o), -132.9 (m, 1F, o'), -159.2 (br d, $^1J_{FF}$ = 21.2 Hz, 1F, p), -164.36 (m, 1F, m'), -164.8 (m, 1F, m)(C_6F_5)[$\Delta\delta^{19}F_{mp}$ = 5.2, 5.6].

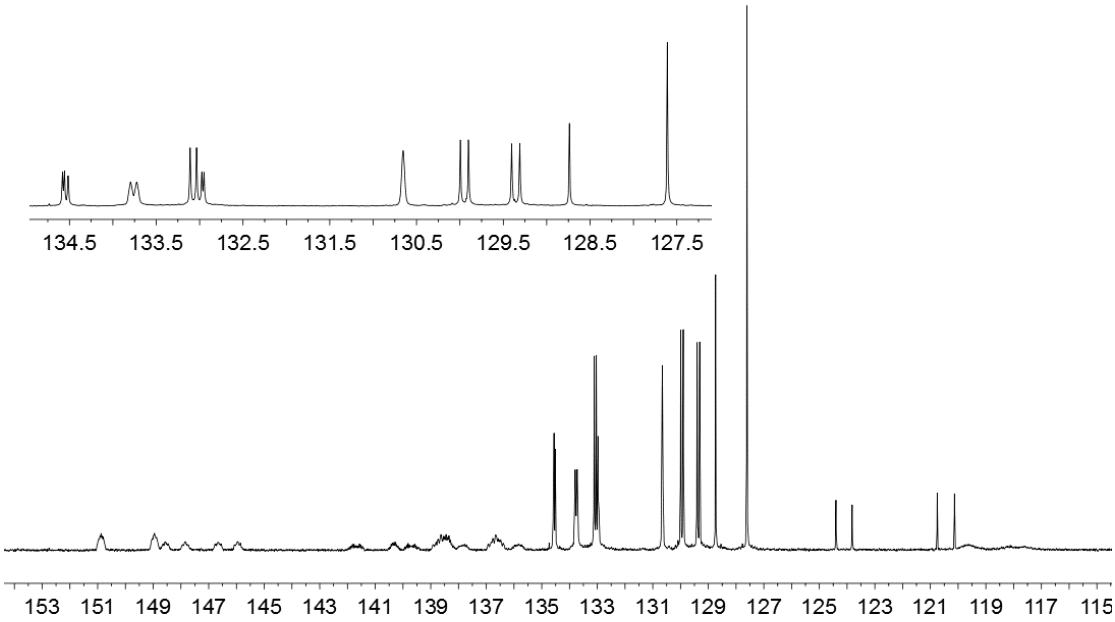
^{19}F,^{19}F GCOSY (564 MHz / 564 MHz, 198 K, [D_2]-dichloromethane): δ^{19}F / δ^{19}F = -163.4 / -123.4, -155.5 (m / o, p), -126.4 (m, 1F, o'), -155.5 (br d, $^1J_{FF}$ = 21.7 Hz, 1F, p), -164.1 / -126.4, -155.5 (m' / o', p)(C_6F_5), -121.0 (m, 1F, o), -157.1 (br d, $^1J_{FF}$ = 21.4 Hz, 1F, p), -164.44 / -121.0, -157.1 (m / o, p), -126.72 (m, 1F, o'), -157.1 (br d, $^1J_{FF}$ = 21.4 Hz, 1F, p), -164.0 / -126.72, -157.1 (m' / o', p)(C_6F_5), -126.66 (o), -158.9 (br d, $^1J_{FF}$ = 21.6 Hz, 1F, p), -161.0 / -126.66, -158.9 (m / o, p), -163.9 / -134.1, -158.9 (m, 1F, m' / o', p)(C_6F_5), -164.8 / -127.3, -159.2 (m / o, p), -164.36 / -132.9, -159.2 (m, 1F, m'/ o', p), (C_6F_5).



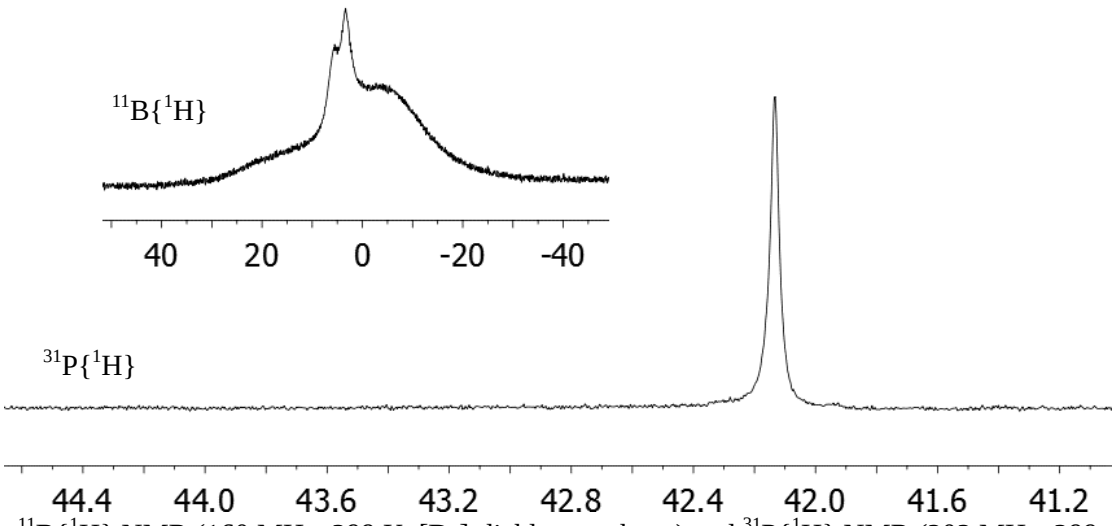
^{1}H NMR (500 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **9**



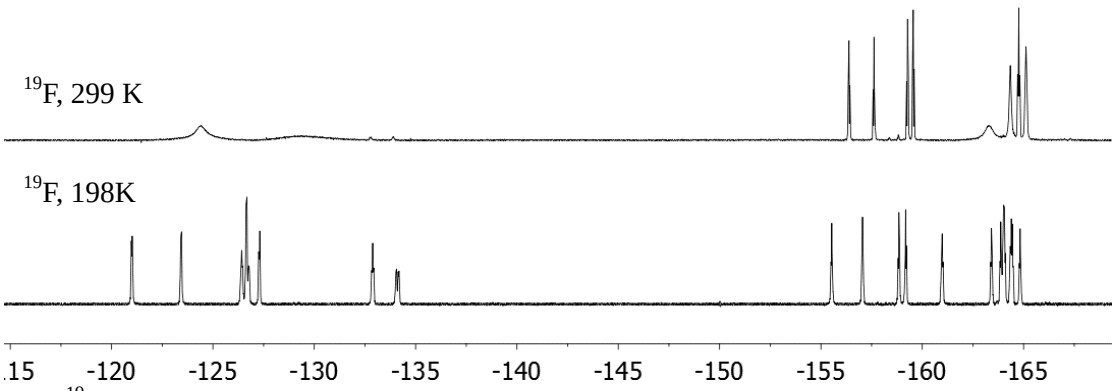
$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **9**



$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **9**

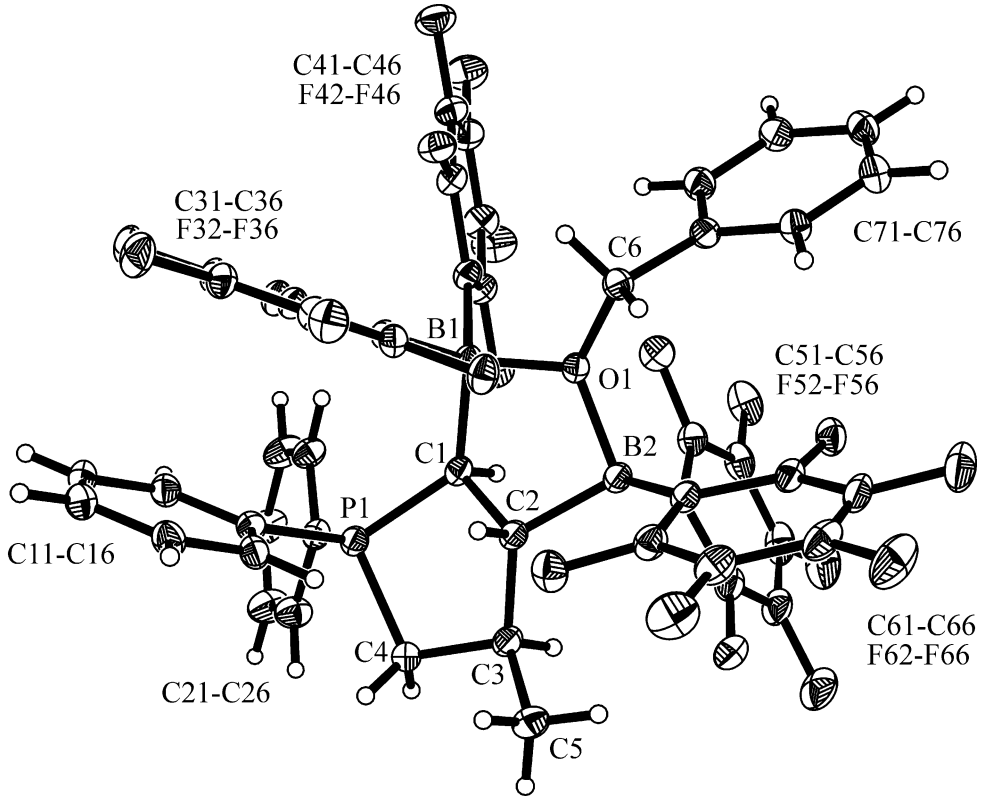


$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, $[D_2]$-dichloromethane) and $^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, $[D_2]$-dichloromethane) spectra of compound **9**

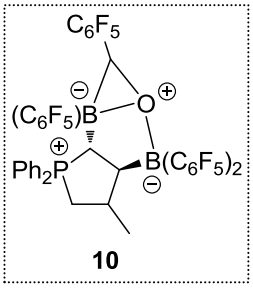


^{19}F NMR (470 MHz, 299 K and 564 MHz, 198 K, $[D_2]$-dichloromethane) spectra of compound **9**

X-ray crystal structure analysis of compound 9: formula $C_{48}H_{25}B_2F_{20}OP$, M = 1050.27, colourless crystal, 0.33 x 0.10 x 0.02 mm, a = 13.2593(4), b = 22.2116(7), c = 19.2412(7) Å, β = 101.101(2) °, V = 5560.7(3) $Å^3$, ρ_{calc} = 1.255 gcm^{-3}, μ = 1.335 mm^{-1}, empirical absorption correction ($0.667 \leq T \leq 0.973$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 40993 reflections collected ($\pm h$, $\pm k$, $\pm l$), 9383 independent (R_{int} = 0.075) and 6308 observed reflections [$I>2\sigma(I)$], 650 refined parameters, R = 0.053, wR^2 = 0.159, max. (min.) residual electron density 0.20 (-0.26) $e.Å^{-3}$, the hydrogen at B1 atom was refined freely; others were calculated and refined as riding atoms.


C41-C46
F42-F46
C31-C36
F32-F36
C6
C71-C76
B1
O1
C51-C56
F52-F56
C1
B2
P1
C2
C11-C16
C61-C66
F62-F66
C4
C3
C21-C26
C5

Synthesis of Compound 10



10

A solution of compound **6** (120 mg, 0.17 mmol) in dichloromethane (5 mL) was degassed and then exposed to a CO atmosphere (2.5 bar). After stirring the reaction mixture at r.t. for 30 min, all volatiles were removed *in vacuo*. The obtained residue was washed with cold dichloromethane (4 mL) and dried in vacuo to give compound **10** (104 mg, 0.11 mmol, 63%) as a colorless solid. Single crystals of compound **10** suitable for the X-ray crystal structure analysis were obtained by slowly diffusion of pentane to a solution of compound **10** in dichloromethane at room temperature.

IR (KBr): $\tilde{\nu}$ / cm^{-1} = 3021 (w), 2987 (w), 2933 (w), 1647 (m), 1519 (s), 1497 (m), 1468 (vs), 1247 (m), 1069 (m), 971 (s), 737 (w), 544 (w).

Melting point: 176 °C.

Elemental analysis: calc. for $C_{42}H_{19}B_2F_{20}OP$ (972.16 g/mol): C, 51.89; H, 1.97. Found: C, 52.10; H, 1.89.

^{1}H NMR (600 MHz, 299 K, [D_2]-dichloromethane) δ = 8.02 (m, 2H, o-Ph^{a}), 7.85 (m, 1H, p-Ph^{a}), 7.74 (m, 2H, m-Ph^{a}), 7.67 (m, 1H, p-Ph^{b}), 7.52 (m, 2H, m-Ph^{b}), 7.41 (m, 2H, o-Ph^{b}), 4.29 (s, 1H, OCH), 3.11 (ddd, $^{2}J_{HH}$ = 16.3 Hz, $^{3}J_{HH}$ = 9.0 Hz, $^{2}J_{PH}$ = 7.4 Hz, 1H, CH_2), 2.81 (ddd, $^{2}J_{HH}$ = 16.3 Hz, $^{2}J_{PH}$ = 12.4 Hz, $^{3}J_{HH}$ = 7.3 Hz, 1H, CH_2), 2.67 (dd, $^{2}J_{PH}$ = 17.4 Hz, $^{3}J_{HH}$ = 15.0 Hz, 1H, PCH), 2.27 (m, 1H, BCH), 2.19 (br, 1H, MeCH), 1.22 (d, $^{3}J_{HH}$ = 6.0 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, [D_2]-dichloromethane) δ = 134.9 (d, $^{4}J_{PC}$ = 3.0 Hz, p-Ph^{a}), 134.3 (d, $^{4}J_{PC}$ = 3.1 Hz, p-Ph^{b}), 133.6 (d, $^{2}J_{PC}$ = 9.6 Hz, o-Ph^{a}), 132.1 (d, $^{2}J_{PC}$ = 9.8 Hz, o-Ph^{b}), 130.5 (d, $^{3}J_{PC}$ = 12.2 Hz, m-Ph^{a}), 130.1 (d, $^{3}J_{PC}$ = 12.2 Hz, m-Ph^{b}), 123.3 (d, $^{1}J_{PC}$ = 76.5 Hz, i-Ph^{b}), 119.9 (d, $^{1}J_{PC}$ = 81.2 Hz, i-Ph^{a}), 60.8 (br, OCH), 45.9 (br, BCH), 41.8 (d, $^{1}J_{PC}$ = 60.4 Hz, CH_2), 36.9 (br m, PCH), 36.1 (MeCH), 21.1 (br, CH_3), [C_6F_5 not listed].

^{1}H{^{1}H} TOCSY (600 MHz, 299 K, [D_2]-dichloromethane) [selected experiment]: $\delta^{1}H_{irr}$ / $\delta^{1}H_{res}$ = 3.11 / 2.81, 2.67, 2.27, 2.19, 1.22 (CH_2 / CH_2, PCH, BCH, MeCH, CH_3).

^{1}H,^{1}H COSY (600 MHz / 600 MHz, 299 K, [D_2]-dichloromethane) [selected traces]: $\delta^{1}H$ / $\delta^{1}H$ = 7.74 / 8.02, 7.85 (m-Ph^{a} / o-Ph^{a}, p-Ph^{a}), 7.52 / 7.67, 7.41 (m-Ph^{b} / p-Ph^{b}, o-Ph^{b}), 1.22 / 2.19 (CH_3 / MeCH).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, [D_2]-dichloromethane) [selected traces]: $\delta^{1}H$ / $\delta^{13}C$ = 8.02 / 134.9, 133.6 (o-Ph^{a} / p-Ph^{a}, o-Ph^{a}), 7.85 / 133.6 (p-Ph^{a} / o-Ph^{a}), 7.74 / 130.5, 119.9 (m-Ph^{a} / m-Ph^{a}, i-Ph^{a}), 7.67 / 132.1 (p-Ph^{b} / o-Ph^{b}), 7.52 / 130.1, 123.3 (m-Ph^{b} /, m-Ph^{b}, i-Ph^{b}), 7.41 / 134.3, 132.1 (o-Ph^{b} / p-Ph^{b}, o-Ph^{b}), 4.29 / 144.8, 113.8, 36.9 (OCH / o-C_6F_5, i-C_6F_5, PCH), 3.11 / 119.9, 45.9, 36.1 (CH_2 / i-Ph^{a}, BCH, MeCH), 2.81 / 119.9, 36.1, 21.1 (CH_2 / i-Ph^{a}, MeCH, CH_3), 2.67 / 119.9, 60.8, 45.9 (PCH / i-Ph^{a}, OCH, BCH), 1.22 / 45.9, 41.8, 36.1 (CH_3 / BCH, CH_2, MeCH).

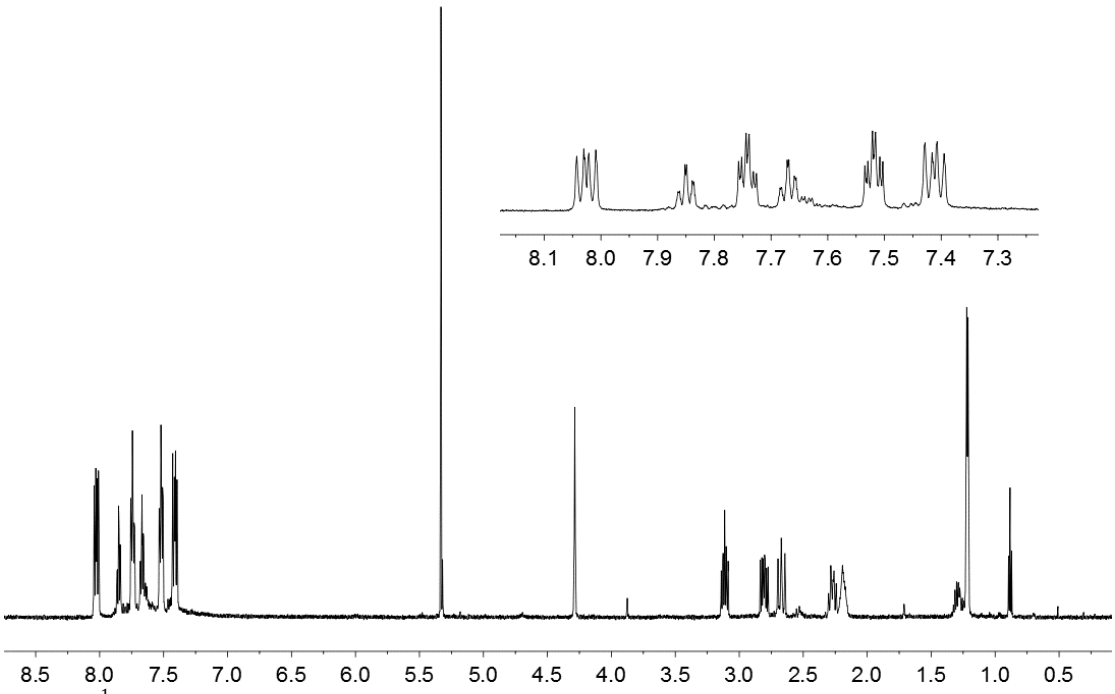
^{11}B{^{1}H} NMR (192 MHz, 299 K, [D_2]-dichloromethane): δ = 4.2 ($\nu_{1/2} \approx$ 500 Hz), -3.5 ($\nu_{1/2} \approx$ 500 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, [D_2]-dichloromethane) δ = 38.9 ($\nu_{1/2} \approx$ 15 Hz).

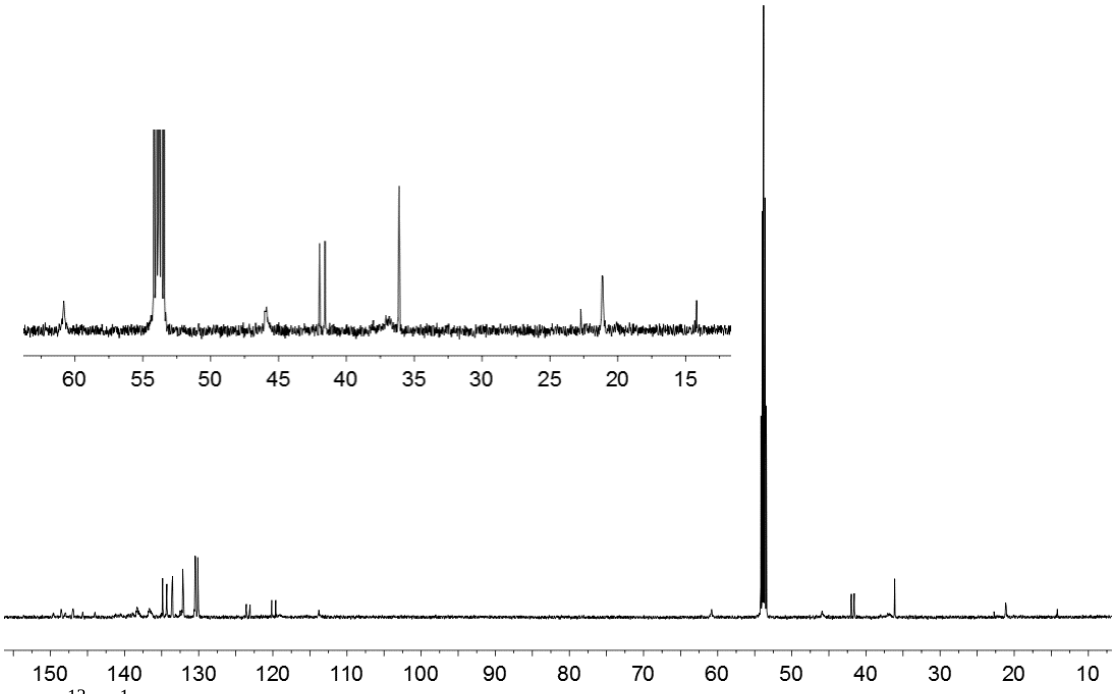
^{19}F NMR (564 MHz, 299 K, [D_2]-dichloromethane) δ = -130.6 (m, 2F, o), -159.6 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, p), -164.8 (m, 2F, m)(BC_6F_5)[$\Delta\delta^{19}F_{mp}$ = 5.2], -131.2 (m, 2F, o), -159.0 (t, $^{3}J_{FF}$ =

20.2 Hz, 1F, p), -165.3 (m, 2F, m)(BC_6F_5)[$\Delta\delta^{19}F_{mp}$ = 6.3], -142.8 (m, 2F, o); -158.3 (t, $^3J_{FF}$ = 20.9 Hz, 1F, p), -164.0 (m, 2F, m)(C_6F_5)[$\Delta\delta^{19}F_{mp}$ = 5.7], -131.5 (m, 2F, o), -156.8 (t, $^3J_{FF}$ = 20.2 Hz, 1F, p), -164.1 (m, 2F, m)(BC_6F_5)[$\Delta\delta^{19}F_{mp}$ = 7.3].

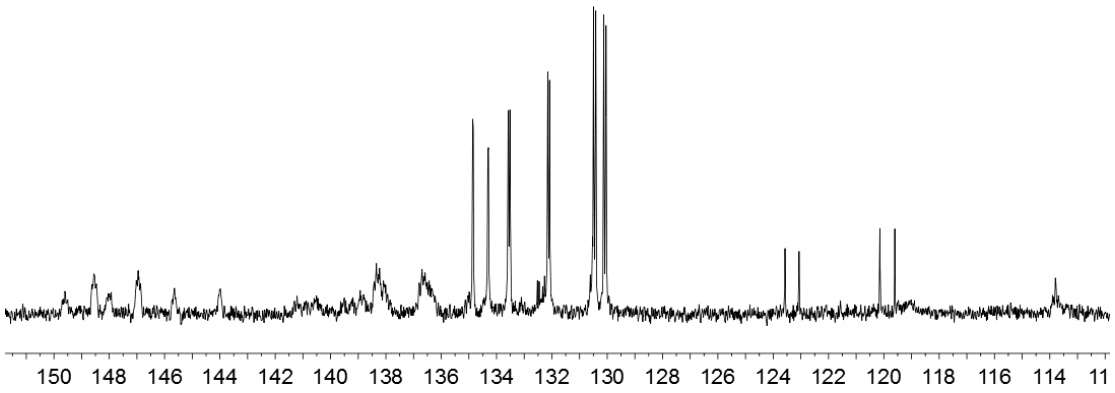
^{19}F,^{19}F GCOSY (564 MHz / 564 MHz, 299 K, [D_2]-dichloromethane): $\delta^{19}F$ / $\delta^{19}F$ = -164.8 / -130.6, -159.6 (m / o, p) (BC_6F_5), -131.2 (m, 2F, o), -159.0 (t, $^3J_{FF}$ = 20.2 Hz, 1F, p), -165.3 / -131.2, -19.0 (m / o, p) (BC_6F_5), -142.8 (m, 2F, o); -158.3 (t, $^3J_{FF}$ = 20.9 Hz, 1F, p), -164.0 / -142.8, -158.3 (m / o, p) (C_6F_5), -131.5 (m, 2F, o), -164.1 / -131.5, -156.8 (m / o, p) (BC_6F_5).



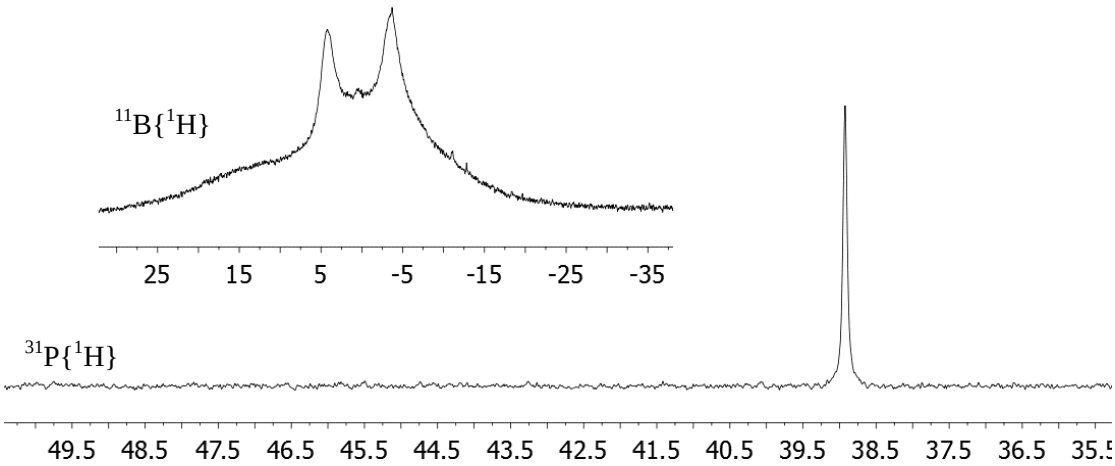
^{1}H NMR (600 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **11**



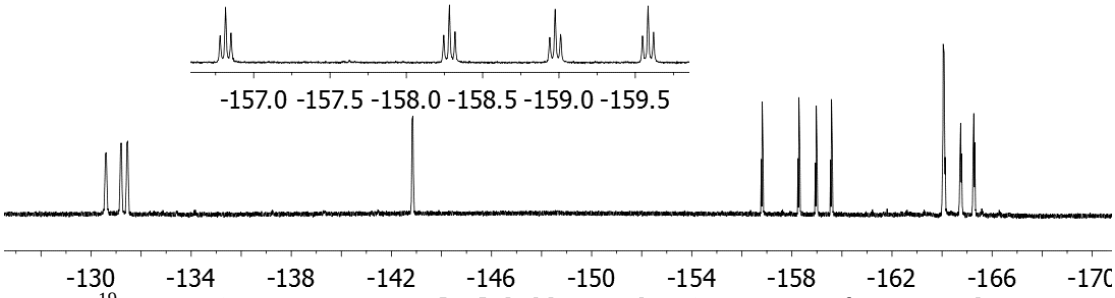
$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $[D_2]$-dichloromethane) spectrum of compound **11**



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, $[D_2]$-dichloromethane) spectrum of compound **11**

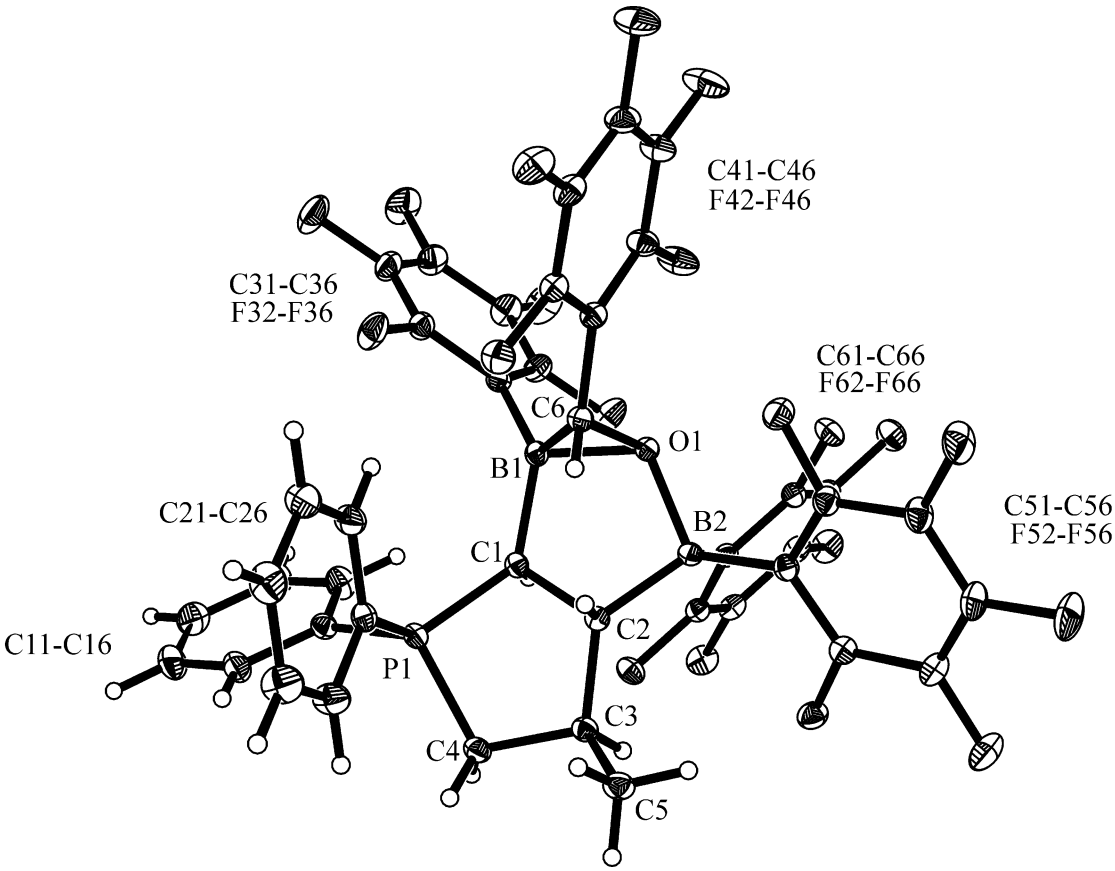


$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, $[D_2]$-dichloromethane) and $^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, $[D_2]$-dichloromethane) spectra of compound **11**



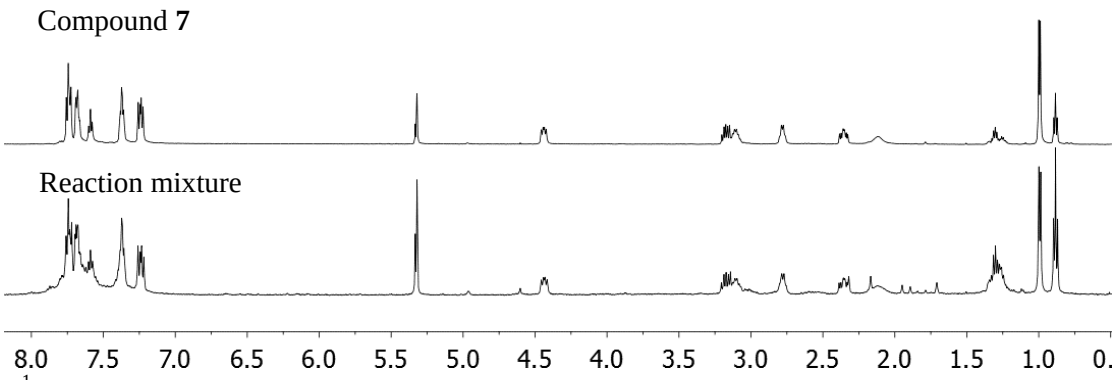
^{19}F NMR (562 MHz, 299 K, [D_2]-dichloromethane) spectrum of compound **11**

X-ray crystal structure analysis of compound 10: formula $C_{41}H_{19}B_2F_{20}OP$, M = 972.16, colourless crystal, 0.26 x 0.20 x 0.13 mm, a = 11.3678(4), b = 11.6324(4), c = 16.8035(7) Å, α = 70.245(2), β = 82.445(2), γ = 79.967(3)°, V = 2052.9(1) Å^3, ρ_{calc} = 1.573 gcm^{-3}, μ = 1.755 mm^{-1}, empirical absorption correction (0.658 ≤ T ≤ 0.804), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 26975 reflections collected (±h, ±k, ±l), 7091 independent (R_{int} = 0.036) and 6631 observed reflections [I>2σ(I)], 596 refined parameters, R = 0.046, wR^2 = 0.137, max. (min.) residual electron density 0.53 (-0.28) e.Å^{-3}, the hydrogen at B1 atom was refined freely; others were calculated and refined as riding atoms.



Reaction of Compound 7 with CO

A solution of compound **7** (24 mg, 0.034 mmol) in [D_2]-dichloromethane (2 mL) was degassed and then exposed to a CO atmosphere (2.5 bar). After stirring the reaction mixture at r.t. for 30 min, the solution was transferred to an NMR tube and characterized by NMR experiments.



^{1}H NMR (500 MHz, 299 K, [D_2]-dichloromethane) spectra of compound **7** and the reaction mixture after the reaction of compound **7** and CO