Supporting Information

Reaction of Carbon Oxides with an Ethylene-bridged PH/B Lewis Pair

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General Information

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. Toluene, CH_2Cl_2, pentane and THF were dried using a Grubbs-type solvent purification system with alumina spheres as the drying agent. All solvents were stored under an argon atmosphere. NMR spectra were recorded on a Varian Inova 600 spectrometer (^{1}H: 600 MHz, ^{19}F: 564 MHz, ^{31}P: 243 MHz, ^{11}B: 192 MHz, ^{13}C: 151 MHz). ^{1}H NMR and ^{13}C NMR: chemical shifts δ are given relative to tetramethylsilane (δ^1H = 0, $\delta^{13}C$ = 0) and referenced to the solvent signal. ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (external reference, $\delta^{31}P(H_3PO_4) = 0$). ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (external reference, $\delta\ ^{19}F(CFCl_3) = 0$). ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference, $\delta\ ^{11}B(BF_3{\cdot}OEt_2) = 0$). NMR assignments were supported by additional 1D (NOESY and TOCSY) and 2D (gCOSY, gHSQC and gHMBC) NMR experiments. Elemental analysis data was recorded on Foss-Heraeus CHNO-Rapid machine. Melting points and decomposition points were obtained with a DSC2010 (TA-instruments). HRMS was recorded using a Thermo Scientific Orbitrap LTQ XL machine.

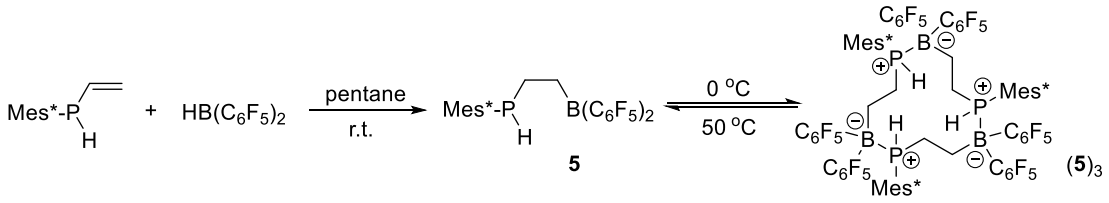
Materials: Unless otherwise noted, all chemicals were purchased from commercially available sources and used as received. $HB(C_6F_5)_2$ (Piers' borane) was prepared according to procedures described in the literature [a) D. J. Parks, R. E. von H. Spence, W. E. Piers, *Angew. Chem. Int. Ed.* **1995**, *34*, 809-811; *Angew. Chem.* **1995**, *107*, 895-897; b) D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492-5503]. (2,4,6-Tri-tert-butylphenyl)(vinyl)phosphane was prepared according to a procedure reported in the literature. [Q. Sun, C. G Daniliuc, C. Mück-Lichtenfeld, K. Bergander, G. Kehr, G. Erker, *J. Am. Chem. Soc.* **2020**, 142, 17260-17264.]

X-Ray diffraction: Data sets for compounds **9**, **11**, **12**, **15** and **16** were collected with a Bruker D8 Venture CMOS diffractometer. For compound **(5)$_3$** and **8** data sets were collected with a Bruker APEX II CCD diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution *SHELXT-2015* (Sheldrick, G. M. *Acta Cryst.,* **2015**, *A71*, 3-8); structure refinement *SHELXL-2015* (Sheldrick, G. M. *Acta Cryst.,* **2015**, *C71* (1), 3-8). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: For compound **(5)$_3$** one pentane molecule, for compound **12** one pentane molecule and for compound **15** one phenyl group were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. Additionally, for compound **9** one and a half heptane molecules, for compound **15** a half heptane molecule and for compound **16** a half pentane molecule were found badly disordered in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek, A.L. (**2015**). Acta Cryst. C71, 9-18) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules.

Warning: Carbon monoxide is a toxic gas; it must be used with due care.

Synthesis of compound 5



Scheme S1

A solution of (2,4,6-tri-tert-butylphenyl)(vinyl)phosphane (60.9 mg, 0.2 mmol) in pentane (1.5 mL) was added dropwise to a solution of $HB(C_6F_5)_2$ (69.2 mg, 0.2 mmol) in pentane (2 mL). The reaction mixture was stirred overnight at room temperature until a pale yellow suspension was obtained. The resulting precipitate was collected by filtration and washed with cold *n*-pentane (3×2 mL) to give a white solid (117.1 mg, 90%).

Characterization of obtained white solid:

Elemental analysis: calc. for $C_{32}H_{34}BF_{10}P$ (650.39 g/mol): C, 59.10; H, 5.27. Found: C, 59.25, H, 5.54.

NMR characterization of the obtained white solid at 50 °C [compound **5**] [*Comment*: **5** : (**5**)$_3$ at 299K ca. 8 : 1 (^{1}H, C_6D_6)]:

^{1}H NMR (600 MHz, 323 K, C_6D_6): δ = 7.51 (d, $^4J_{PH}$ = 2.2 Hz, 2H, *m*-Mes*), 5.33 (br d, $^1J_{PH}$ ~ 247 Hz, 1H, PH), 1.98 (br m, 2H, BCH_2), [1.91, 1.83](each br, each 1H, PCH_2), 1.53 (s, 18H, *o*-^{t}Bu), 1.20 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 323 K, C_6D_6): δ = 155.7 (dm, $^2J_{PC}$ ~ 8 Hz, *o*-Mes*), 150.9 (m, *p*-Mes*), 147.6 (dm, $^1J_{FC}$ ~ 250 Hz, C_6F_5), 143.2 (dm, $^1J_{FC}$ ~ 260 Hz, C_6F_5), 137.6 (dm, $^1J_{FC}$ ~ 260 Hz, C_6F_5), 131.6 (dm, $^1J_{PC}$ ~ 22 Hz, *i*-Mes*), 122.8 (d, $^3J_{PC}$ = 4.7 Hz, *m*-Mes*), 115.2 (*i*-C_6F_5), [38.5, 33.6 (d, $^4J_{PC}$ = 5.9 Hz)](*o*-^{t}Bu), [35.1, 31.2](*p*-^{t}Bu), 27.1 (br, BCH_2), 25.1 (br m, PCH_2).

^{11}B{^{1}H} NMR (192 MHz, 323 K, C_6D_6): δ = 60.7 ($\nu_{1/2}$ ~ 750 Hz).

^{31}P{^{1}H} NMR (243 MHz, 323 K, C_6D_6): δ = -56.2 ($\nu_{1/2}$ ~ 40 Hz).

^{31}P NMR (243 MHz, 323 K, C_6D_6): δ = -56.2 (br d, $^1J_{PH}$ ~ 250 Hz).

^{19}F NMR (564 MHz, 323 K, C_6D_6): δ = -130.1 (m, 2F, *o*-C_6F_5), -149.0 (br t, $^3J_{FF}$ ~ 18 Hz, 1F, *p*-C_6F_5), -161.6 (br m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 12.6].

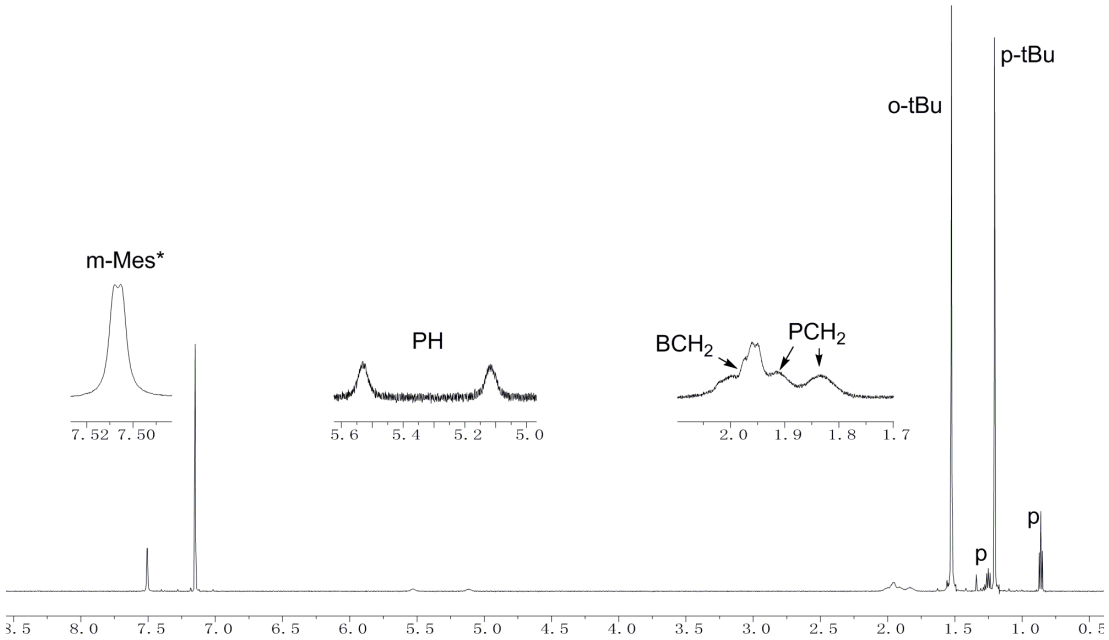


Figure S1. ^{1}H NMR (600 MHz, 323 K, C_6D_6) spectrum of compound **5** [admixed with p: pentane].

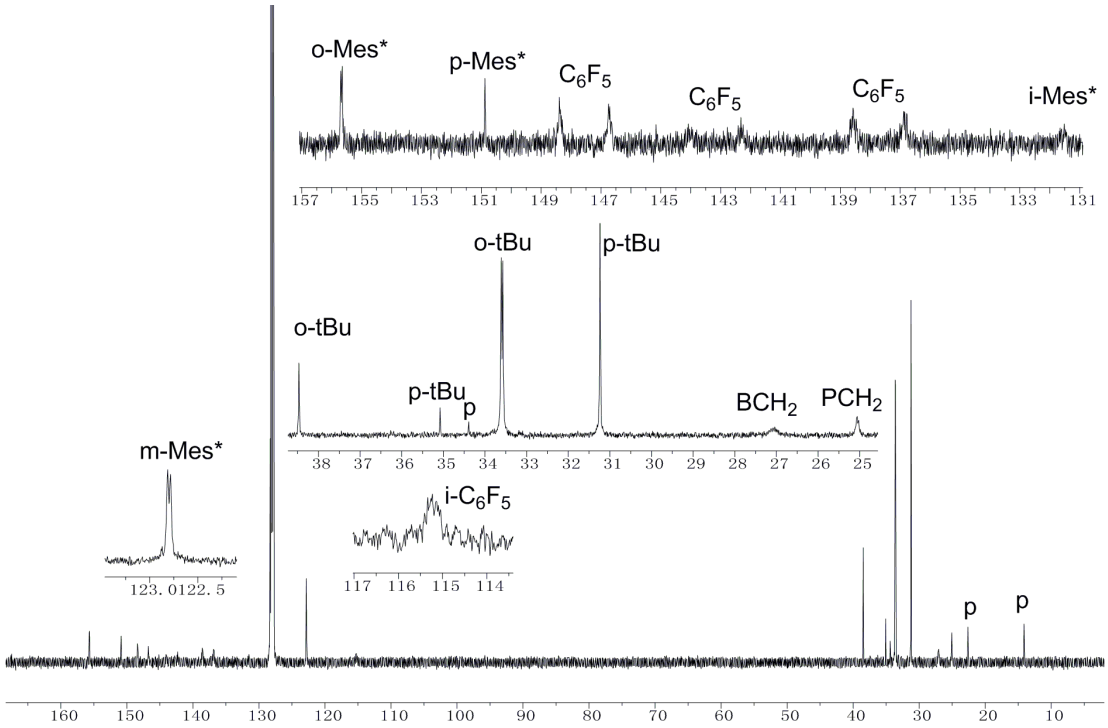


Figure S2. $^{13}C\{^{1}H\}$ NMR (151 MHz, 323 K, C_6D_6) spectrum of compound **5** [admixed with p: pentane].

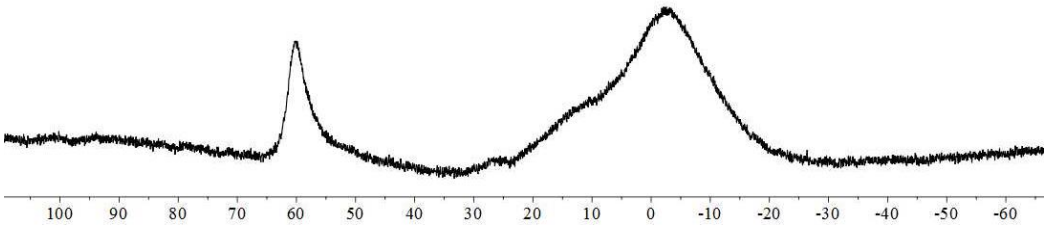


Figure S3. $^{11}B\{^{1}H\}$ NMR (192 MHz, 323 K, C_6D_6) spectrum of compound **5**.

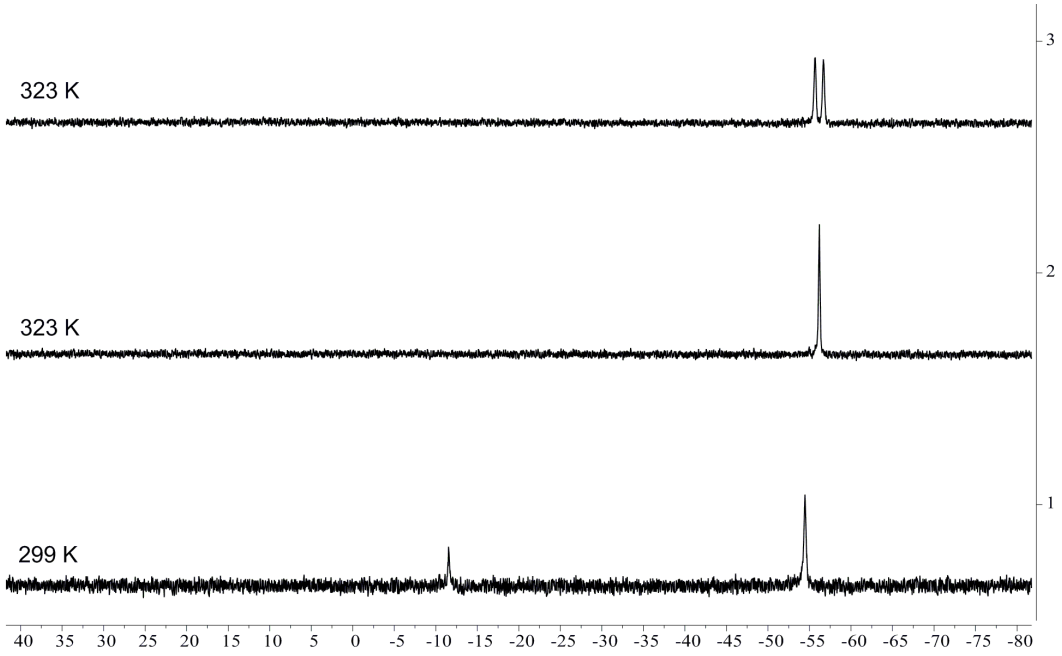


Figure S4. (1) $^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, C_6D_6), (2) $^{31}P\{^{1}H\}$ NMR (243 MHz, 323 K, C_6D_6) and (3) ^{31}P NMR (243 MHz, 323 K, C_6D_6) spectra of compound **5**.

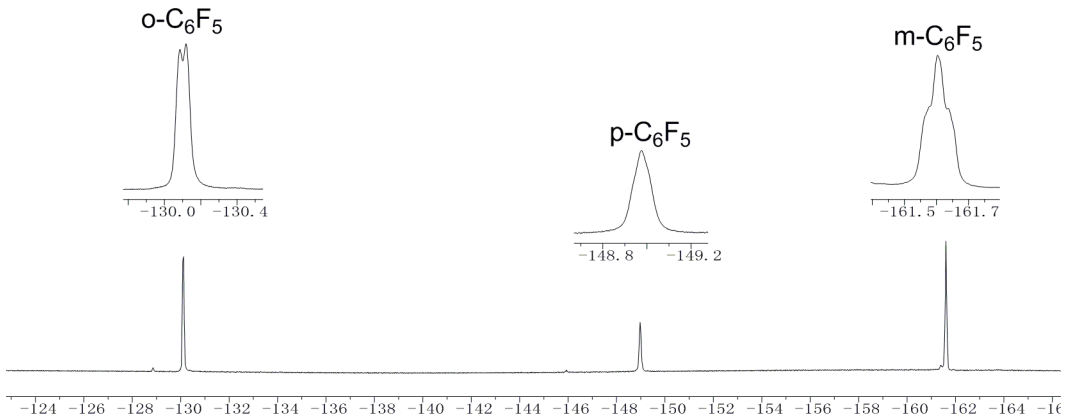


Figure S5. ^{19}F NMR (564 MHz, 323 K, C_6D_6) spectrum of compound **5**.

NMR characterization of the obtained white solid at 0 °C [compound (**5**)$_3$] [*Comment*: **5** : (**5**)$_3$ at 299K ca. 1 : 1 (^{1}H, CD_2Cl_2)]::

^{1}H NMR (600 MHz, 273 K, CD_2Cl_2): δ = [7.20, 7.12](each s, each 1H, *m*-Mes*), 5.92 (dd, $^1J_{PH}$ = 374.9 Hz, $^3J_{HH}$ = 11.6 Hz, 1H, PH), [2.76, 2.49](each m, each 1H, PCH_2), [2.29, 1.91](each br, each 1H, BCH_2), [1.49, 1.04](each s, each 9H, *o*-^{t}Bu), 1.20 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 273 K, CD_2Cl_2): δ = [158.8, 156.9 (br)](*o*-Mes*), 152.8 (m, *p*-Mes*), [124.4, 122.3](each br, *m*-Mes*), 114.8 (br d, $^1J_{PC}$ ~ 36 Hz, *i*-Mes*), [39.7/34.3, 38.2/32.6](*o*-^{t}Bu), [34.9/30.6](*p*-^{t}Bu), 30.5 (br, PCH_2), 26.5 (br, BCH_2), [C_6F_5 not listed].

^{31}P{^{1}H} NMR (243 MHz, 273 K, CD_2Cl_2): δ = -12.8 ($\nu_{1/2}$ ~ 20 Hz).

^{31}P NMR (243 MHz, 273 K, CD_2Cl_2): δ = -12.8 (br d, $^1J_{PH}$ ~ 375 Hz).

^{19}F NMR (564 MHz, 273 K, CD_2Cl_2): δ = [-119.5, -129.0, -132.4, -132.5](each m, each 1F, *o*-C_6F_5), [-157.2 (br t, $^3J_{FF}$ = 21.8 Hz), -159.0 (br t, $^3J_{FF}$ = 17.5 Hz)](each 1F, *p*-C_6F_5), [-162.2, -164.1, -164.9, -165.4](each m, each 1F, *m*-C_6F_5).

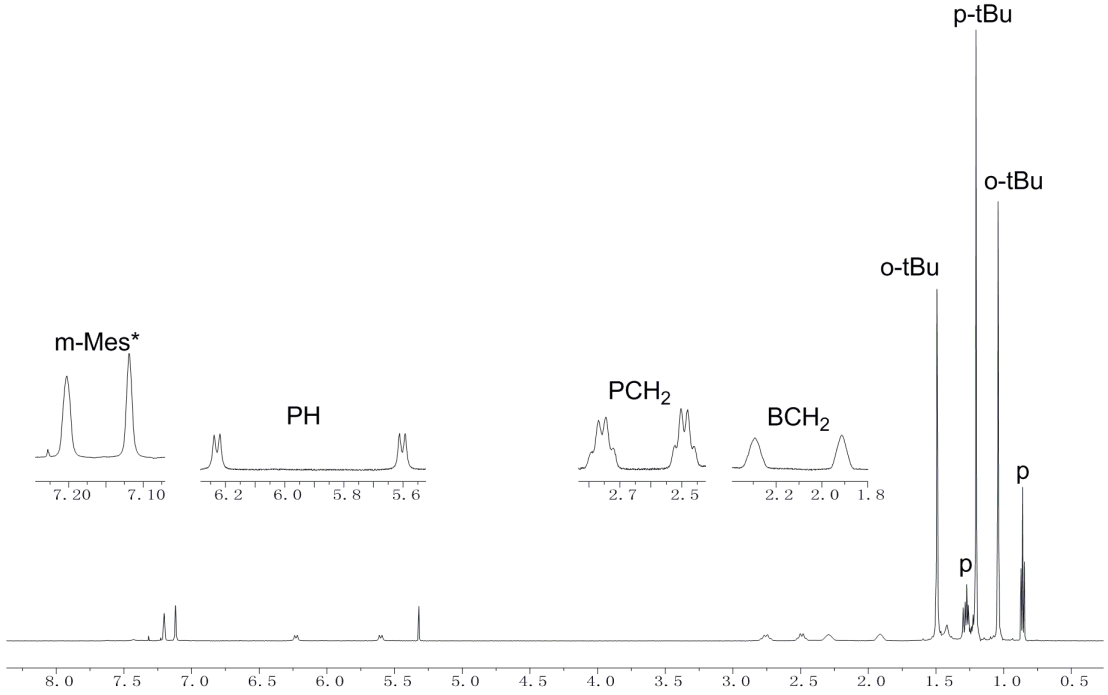


Figure S6. ^{1}H NMR (600 MHz, 273 K, CD_2Cl_2) spectrum of compound (**5**)$_3$ [admixed with p: pentane].

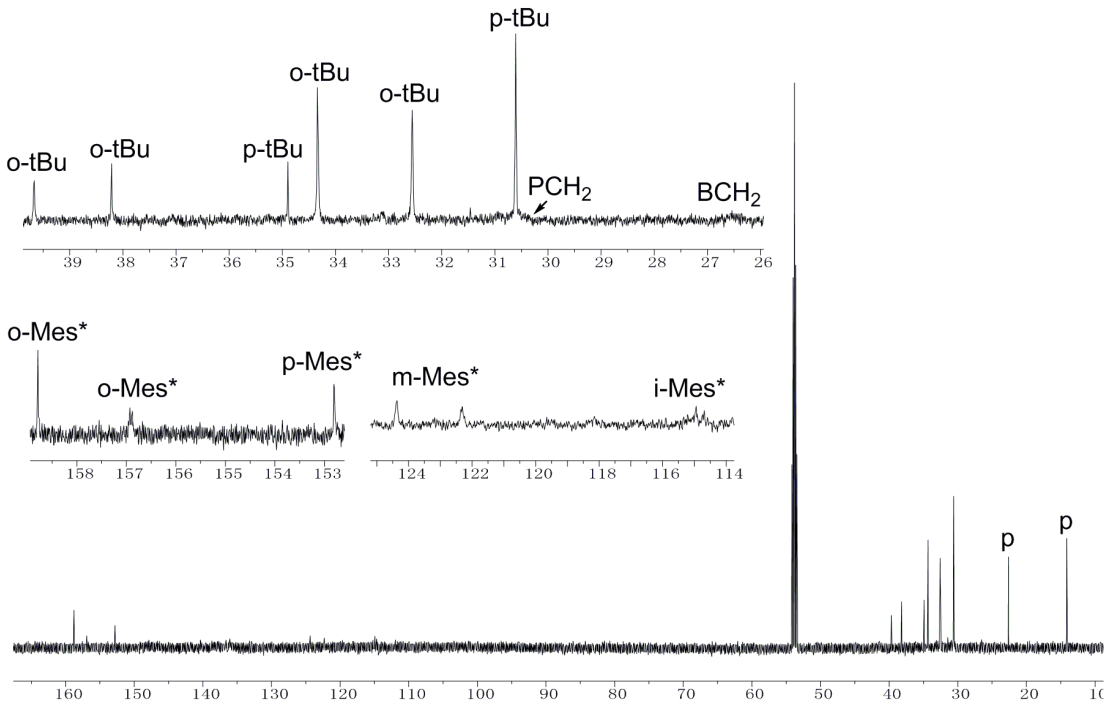


Figure S7. $^{13}C\{^{1}H\}$ NMR (151 MHz, 273 K, CD_2Cl_2) spectrum of compound $(\mathbf{5})_3$ [admixed with p: pentane].

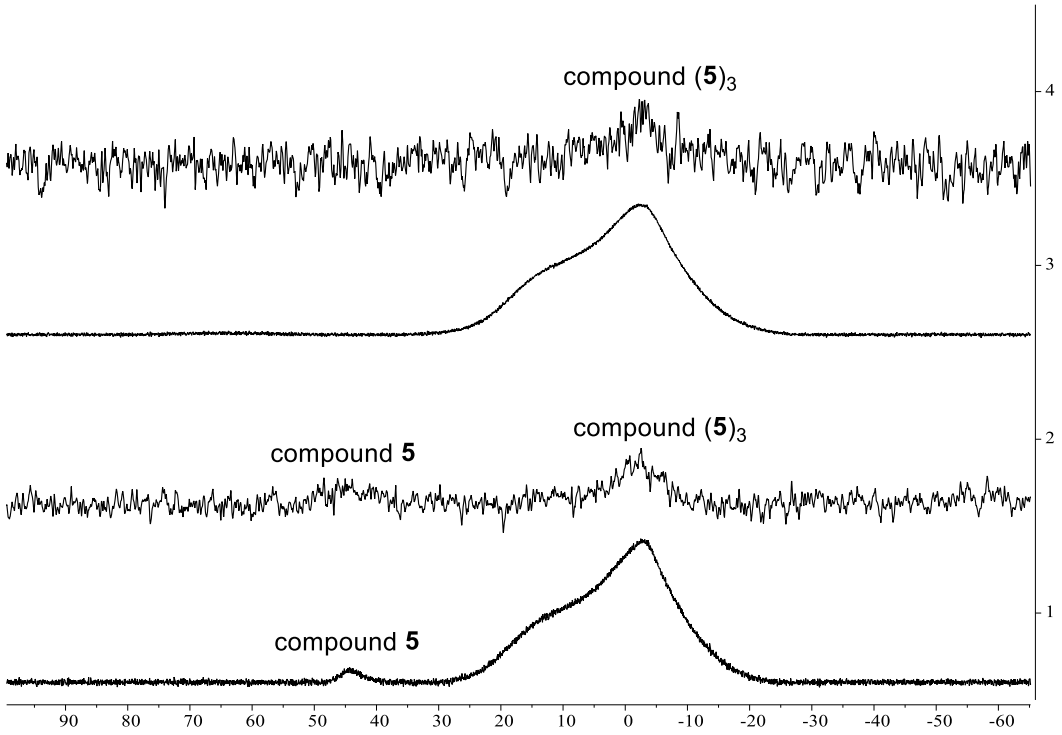


Figure S8. (1) $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) and (2) $^{10}B\{^{1}H\}$ NMR (53.7 MHz, 299 K, CD_2Cl_2) spectra of compound **5** and $(\mathbf{5})_3$, (3) $^{11}B\{^{1}H\}$ NMR (192 MHz, 273 K, CD_2Cl_2) and (4) $^{10}B\{^{1}H\}$ NMR (53.7 MHz, 273 K, CD_2Cl_2) spectra of compound $(\mathbf{5})_3$.

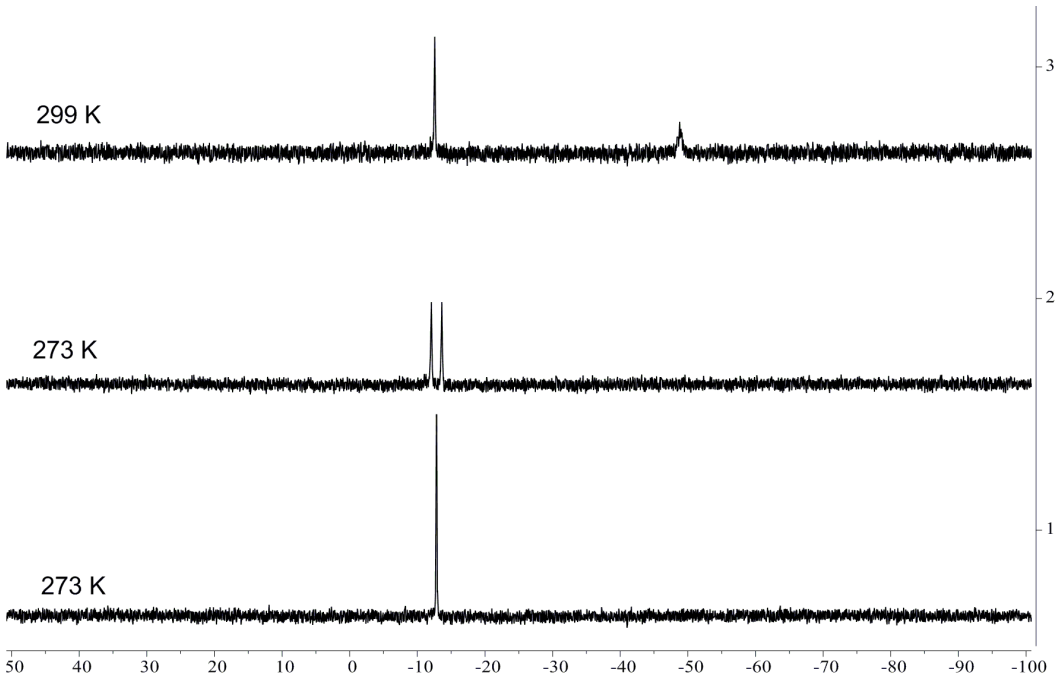


Figure S9. (1) $^{31}P\{^{1}H\}$ NMR (243 MHz, 273 K, CD_2Cl_2), (2) ^{31}P NMR (243 MHz, 273 K, CD_2Cl_2) and $^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compound **5** and $(\mathbf{5})_3$.

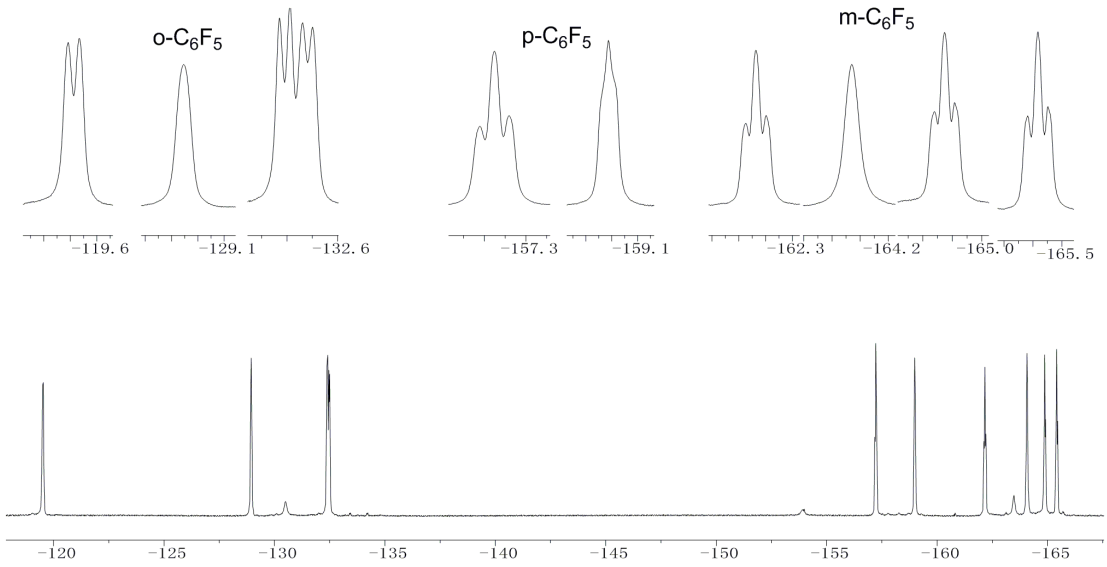
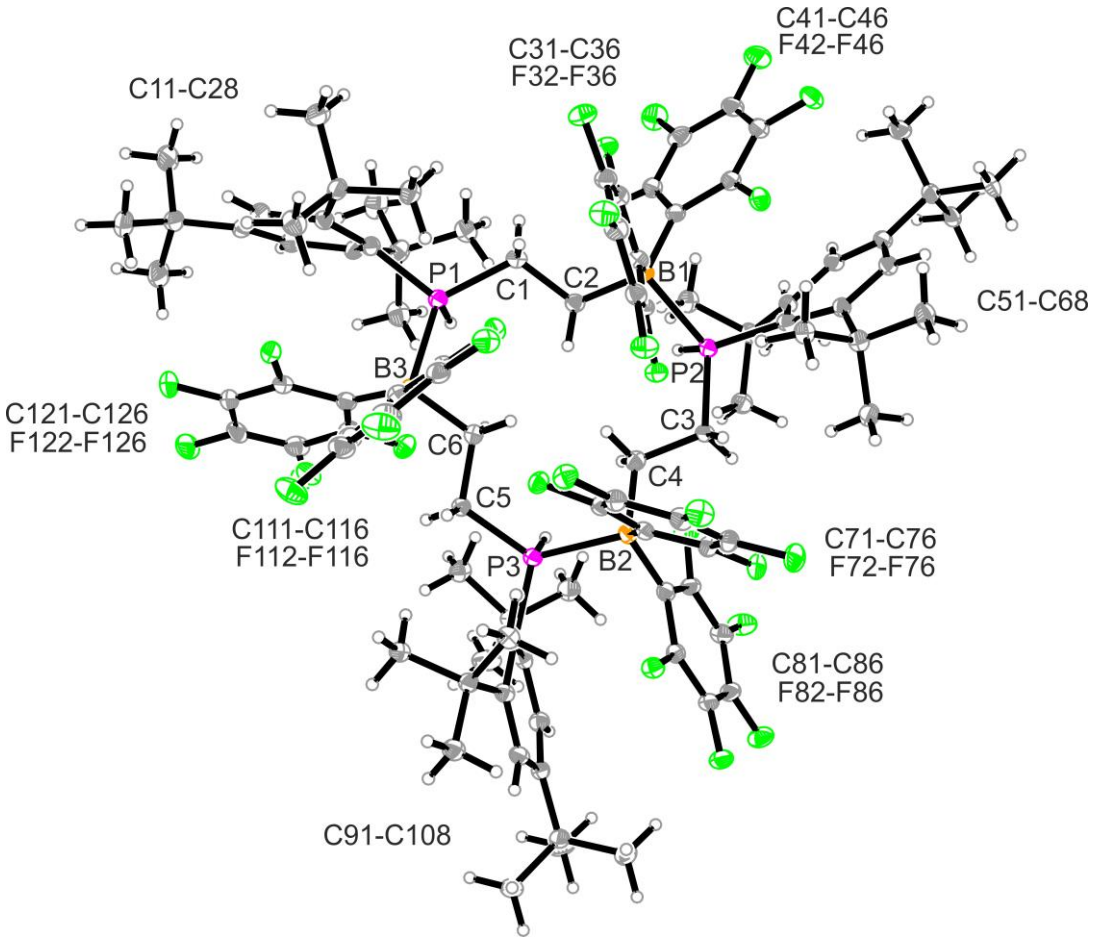


Figure S10. ^{19}F NMR (564 MHz, 273 K, CD_2Cl_2) spectrum of compound $(\mathbf{5})_3$.

Crystals of compound $(\mathbf{5})_3$ suitable for the X-ray crystal structure analysis were obtained from a solution of the obtained white solid in *n*-pentane at room temperature.

X-ray crystal structure analysis of compound $(5)_3$ (erk9811): A colorless plate-like specimen of $C_{106}H_{126}B_3F_{30}P_3$, approximate dimensions 0.030 mm x 0.080 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX II diffractometer system equipped with a fine-focus sealed tube Cu sealed tube (CuK_α, $\lambda = 1.54178$ Å) and a graphite monochromator. A total of 1513 frames were collected. The total exposure time was 21.45 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 72076 reflections to a maximum θ angle of 66.63° (0.84 Å resolution), of which 18149 were independent

(average redundancy 3.971, completeness = 99.7%, R_{int} = 13.79%, R_{sig} = 11.78%) and 11081 (61.06%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.8401(3) Å, b = 19.2176(5) Å, c = 19.5735(5) Å, α = 84.129(2)°, β = 85.038(2)°, γ = 85.211(2)°, volume = 5144.7(2) $Å^3$, are based upon the refinement of the XYZ-centroids of 6092 reflections above 20 σ(I) with 8.207° < 2θ < 132.6°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.882. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8490 and 0.9590. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{106}H_{126}B_3F_{30}P_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 1371 variables converged at R1 = 6.14%, for the observed data and wR2 = 17.36% for all data. The goodness-of-fit was 1.012. The largest peak in the final difference electron density synthesis was 0.630 $e^-/Å^3$ and the largest hole was -0.348 $e^-/Å^3$ with an RMS deviation of 0.075 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.353 g/cm^3 and F(000), 2184 e^-. The hydrogens at P1, P2 and P3 atoms were refined freely, but with one P-H (P1-H1) distance restraints (DFIX). CCDC number: 2054471.



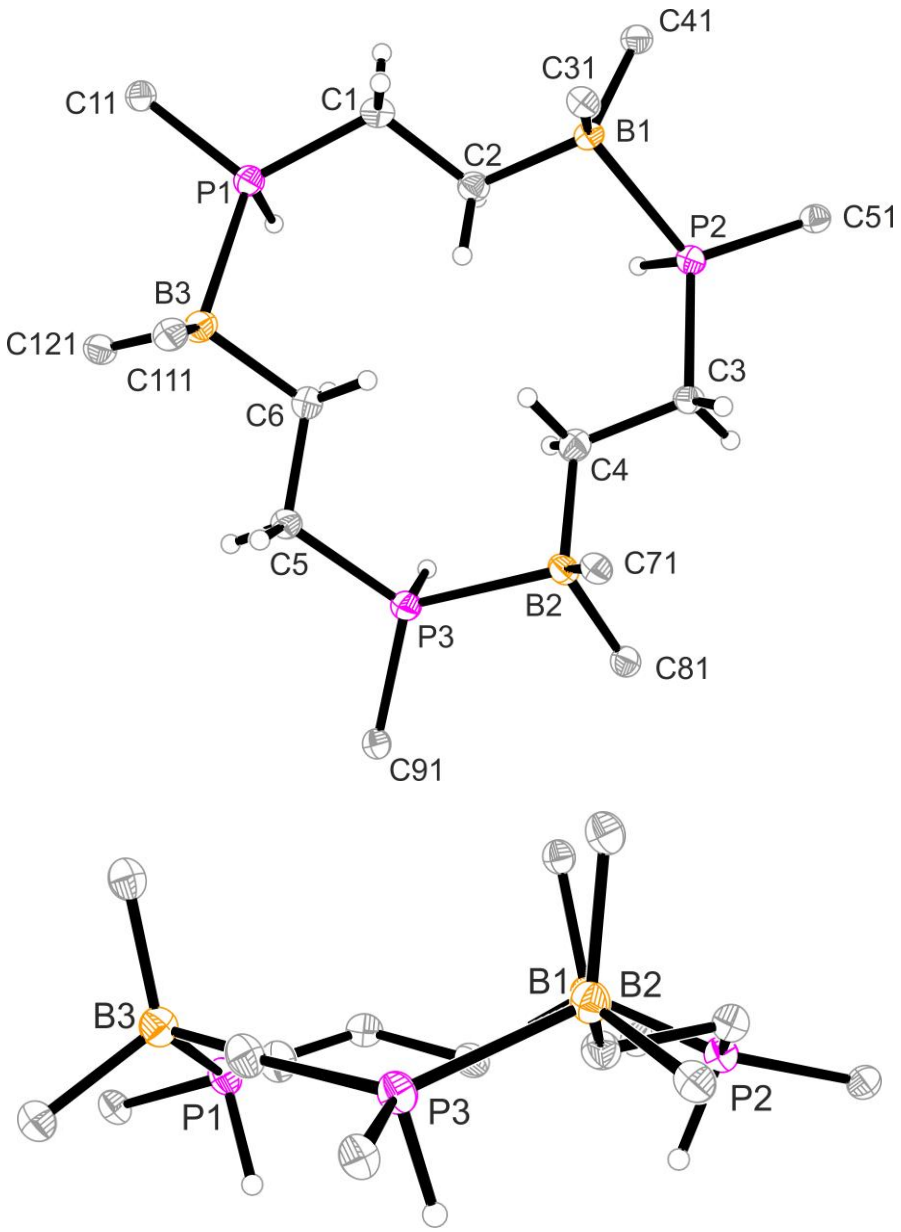
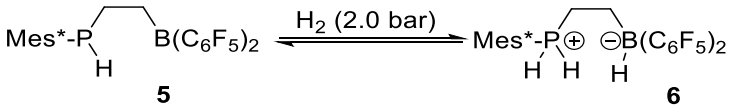


Figure S11. Crystal structure of compound $(\mathbf{5})_3$ (thermal ellipsoids are set at 30% probability).

Reaction of compound 5 with H_2: in situ experiment.



5 **6**

Scheme S2

A solution of compound **5** (13.0 mg 0.02 mmol) in CD_2Cl_2 (0.8 mL) was degassed by freeze-pump-thaw cycles twice at -78 °C. Then the mixture was exposed to a H_2 atmosphere (2.0 bar) at r.t. for 2 hours in a J. Young valve NMR tube. A clear colorless solution was obtained. This colorless solution was then characterized by NMR to give a mixture of compounds **5** : $(\mathbf{5})_3$: **6** ca. 49 : 30 : 20 (^{31}P). NMR characterization of compound **6**:

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.65 (s, 2H, *m*-Mes*), 7.33 (dm, $^{1}J_{PH}$ = 488.3 Hz, 2H PH_2), 2.09 (m, 1H, BH), [2.46, 2.33](br, 4H, CH_2), 1.52 (s, 18H, *o*-^{t}Bu), 1.33 (s, 9H, *p*-^{t}Bu).

^{11}B{^{1}H} NMR (192MHz, 299 K, CD_2Cl_2): δ = -21.6 ($\nu_{1/2}$ ~ 46 Hz).

^{11}B NMR (192 MHz, 299 K, CD_2Cl_2): δ = -21.6 (d, $^{1}J_{BH}$ ~ 85 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -23.7 ($\nu_{1/2}$ ~ 50 Hz).

^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): δ = -23.7 (tm, $^{1}J_{PH}$ ~ 490 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -133.7 (m, 2F, *o*-C_6F_5), -163.4 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F, *p*-C_6F_5), -166.4 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 3.0].

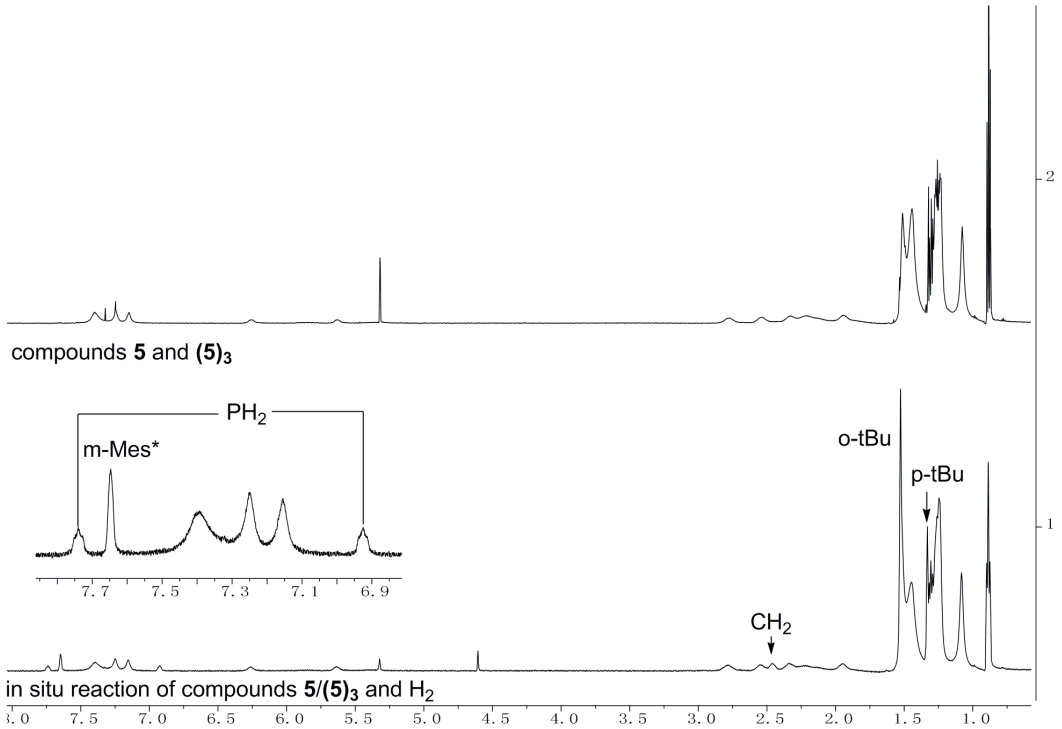


Figure S12. (1) ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of in situ reaction of compounds **5**/$(\mathbf{5})_3$ with H_2 [comment: the marked signal from compound **6**] and (2) ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of the mixture compounds **5** and $(\mathbf{5})_3$.

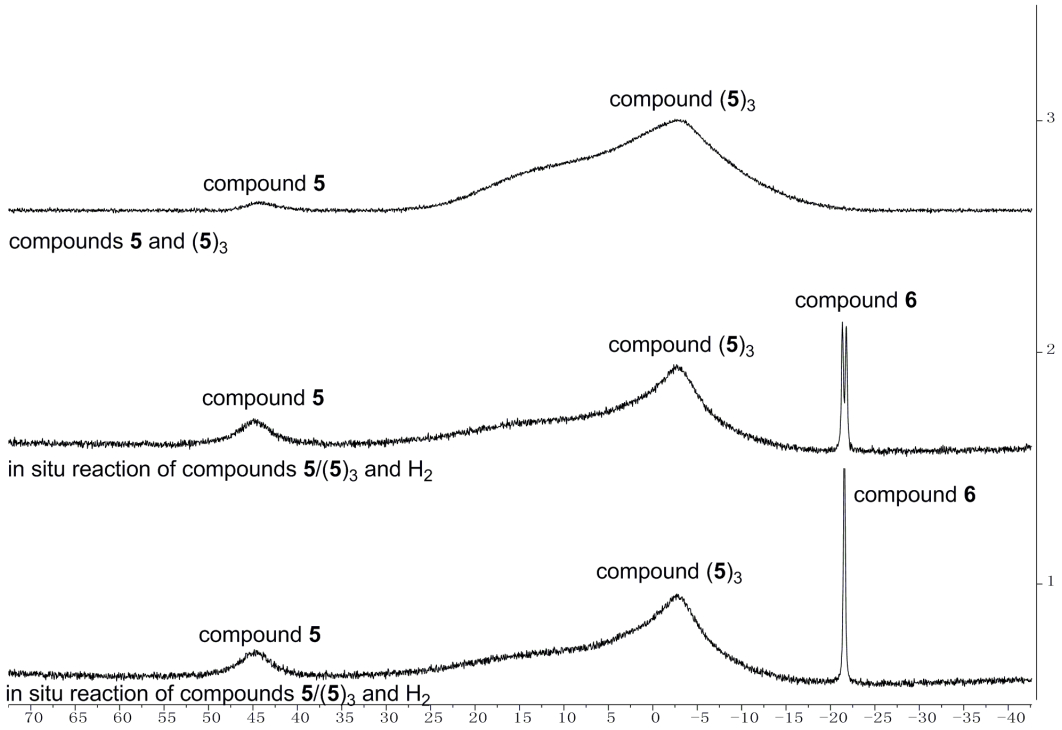


Figure S13. (1) $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of the in situ reaction of compounds **5**/(**5**)$_3$ with H_2, (2) ^{11}B NMR (192 MHz, 299 K, CD_2Cl_2) spectra of the in situ reaction of compounds **5**/(**5**)$_3$ with H_2, (3) $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of the mixture compounds **5** and (**5**)$_3$.

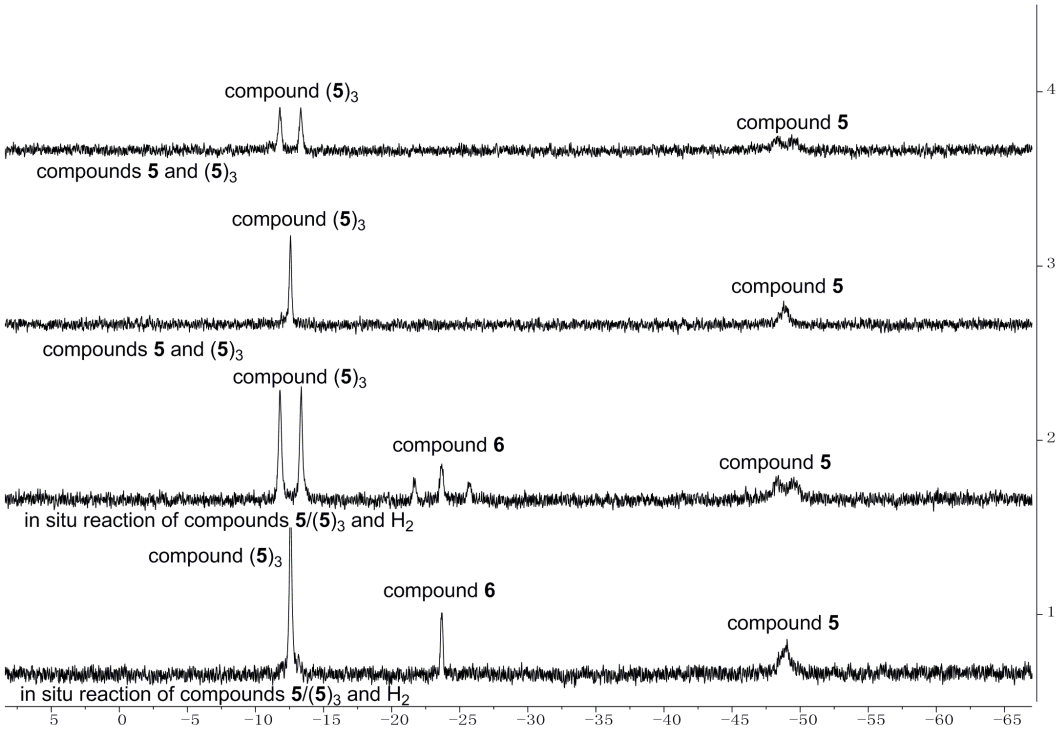


Figure S14. (1) $^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, CD_2Cl_2) spectra of the in situ reaction compound **5**/(**5**)$_3$ with H_2, (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of the in situ reaction compound **5**/(**5**)$_3$ with H_2, (3) $^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compounds **5** and (**5**)$_3$, (4) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compounds **5** and (**5**)$_3$.

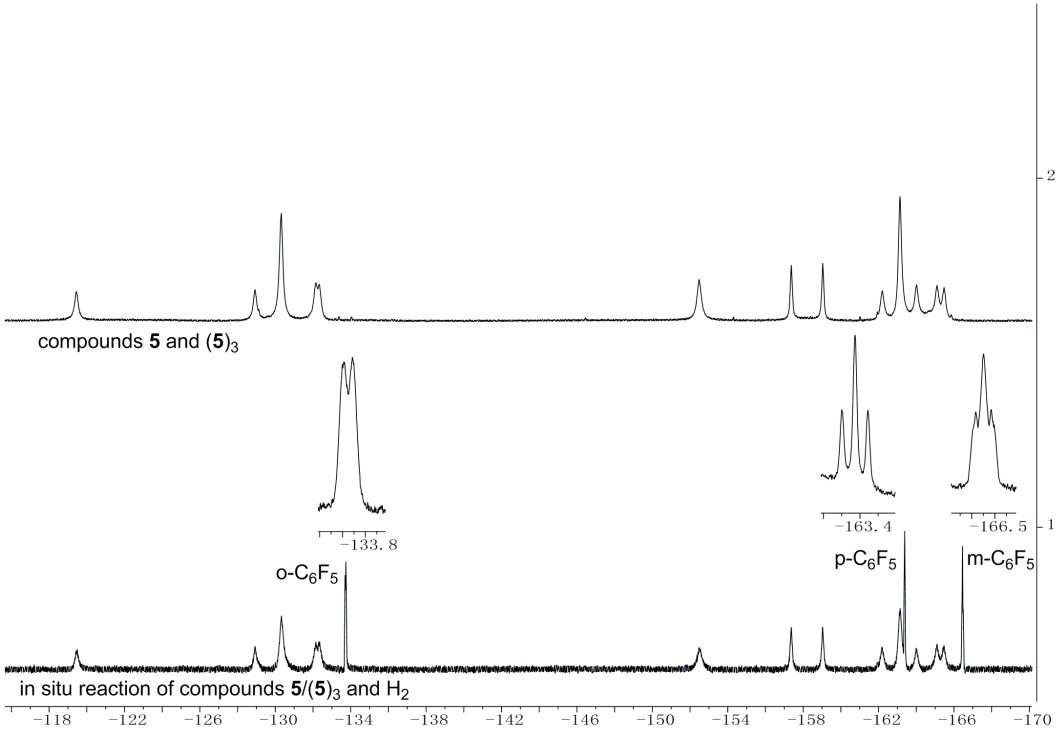
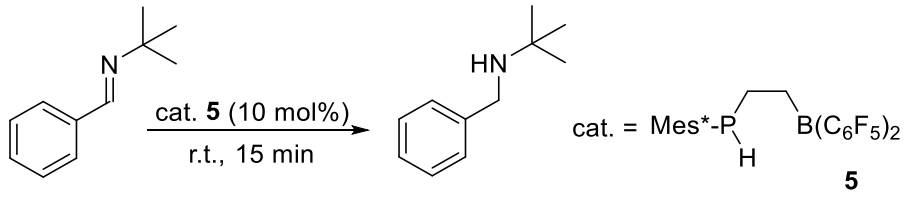


Figure S15. (1) ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of the in situ reaction of compounds **5**/(**5**)$_3$ with H_2 [comment: the marked signal from compound **6**], (2) ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compounds **5** and (**5**)$_3$.

Catalytic hydrogenation of *N*-tert-butyl-1-phenylmethanimine with compound 5



5

Scheme S3

In a glovebox with an argon atmosphere, a mixture of compound **5** (13.0 mg, 0.02 mmol, 0.1 equiv.) and the *N*-tert-butyl-1-phenylmethanimine (32.2 mg, 0.2 mmol, 1.0 equiv) were dissolved in CD_2Cl_2 (0.8 mL). Then the obtained solution was transferred to a J. Young valve NMR tube. The mixture was exposed to a H_2 atmosphere (1.5 bar) at r.t. for 15 minutes. The obtained reaction mixture was characterized by ^1H NMR experiments to give the respective amine in ca. 99% NMR yield.

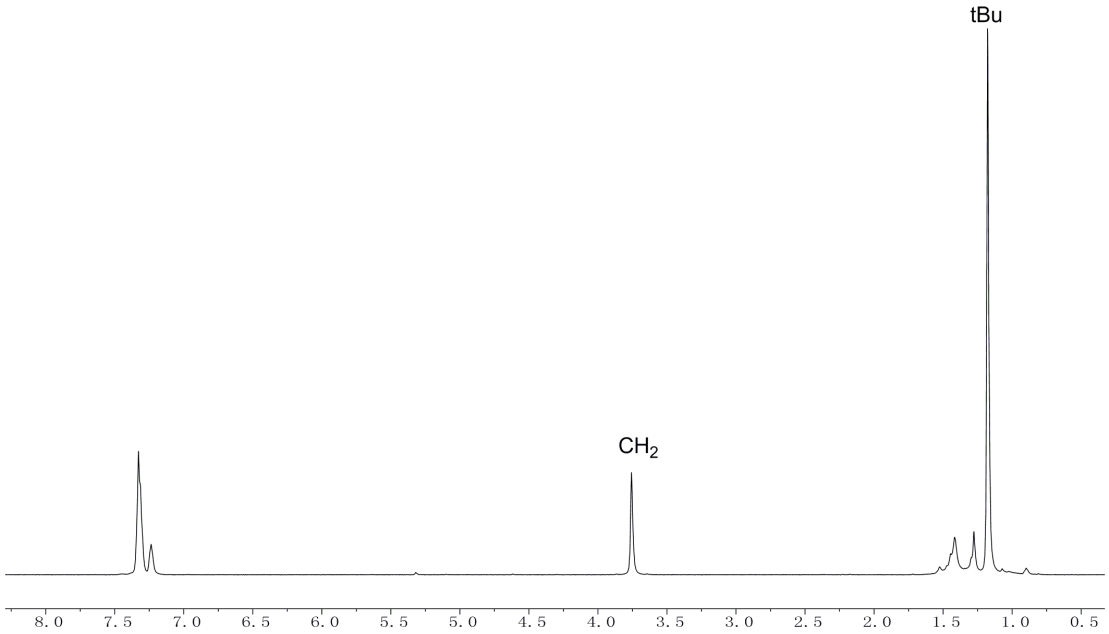
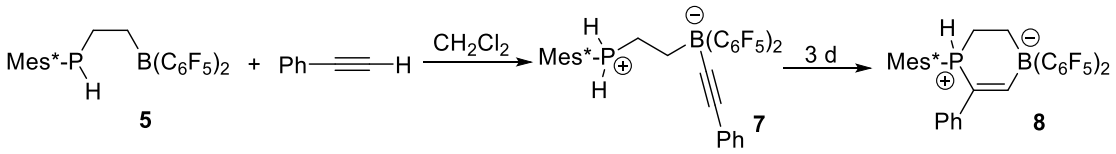


Figure S16. ^1H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of catalytic hydrogenation of *N*-tert-butyl-1-phenylmethanimine.

Synthesis of compound 8



Scheme S4

A solution of phenylacetylene (10.2 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL) was dropwise added to the solution of compound **5** (65.0 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL). After 0.5 h at r.t., a clear colorless solution was obtained. All volatiles were removed in *vacuo*. *n*-Pentane (2 mL) was added to the residue and the suspension was vigorously stirred for 0.5 h. The precipitate was collected by filtration and washed with *n*-pentane (3×2 mL) to give compound **7** as a white solid (71.4 mg, 95%). A solution of compound **7** (37.6 mg, 0.05 mmol, 0.6 mL) in pentane and CH_2Cl_2 (ca. 3:1) was kept at r.t for 3 days. During this time, colorless crystals had formed, which were collected by filtration and washed with *n*-pentane (2×1 mL) to give compound **8** (35.7 mg, 95%).

Characterization of compound **7**:

Elemental analysis: calc. for $C_{40}H_{40}BF_{10}P$ (752.53 g/mol): C, 63.84; H, 5.36. Found: C, 63.04, H, 5.17.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.63 (d, $^4J_{PH}$ = 4.7 Hz, 2H, *m*-Mes*), 7.32 (m, 2H, *o*-Ph), 7.31 (ddd, $^1J_{PH}$ = 479.8 Hz, J = 8.4 Hz, J = 6.1 Hz, 2H, PH_2), 7.23 (m, 2H, *m*-Ph), 7.18 (m, 1H, *p*-Ph), 2.64 (m, 2H, PCH_2), 1.55 (br m, 2H, BCH_2), 1.51 (d, $^5J_{PH}$ = 0.9 Hz, 18H, *o*-^{t}Bu), 1.32 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299K, CD_2Cl_2): δ = 158.4 (d, $^4J_{PC}$ = 3.4 Hz, *p*-Mes*), 158.0 (d, $^2J_{PC}$ = 7.5 Hz, *o*-Mes*), 131.5 (*o*-Ph), 128.5 (*m*-Ph), 127.0 (*i*-Ph), 126.8 (*p*-Ph), 125.4 (d, $^3J_{PC}$ = 12.1 Hz, *m*-Mes*), n.o. (BC≡), 106.5 (d, $^1J_{PC}$ = 65.4 Hz, *i*-Mes*), 97.1 (br, PhC≡), [38.6 (d, $^3J_{PC}$ = 3.3 Hz), 33.7 (d, $^4J_{PC}$ = 1.0 Hz)](*o*-^{t}Bu), [36.0 (d, $^5J_{PC}$ = 0.9 Hz), 30.8](*p*-^{t}Bu), 24.4 (d, $^1J_{PC}$ = 40.9 Hz, PCH_2), 21.2 (br, BCH_2), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2) δ = -18.1 (br d, J ~ 18 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -21.8 (m).

^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): δ = -21.8 (tm, $^1J_{PH}$ ~ 480 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = -133.1 (m, 2F, *o*-C_6F_5), -162.9 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*-C_6F_5), -166.3 (m, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{m,p}$ = 3.4].

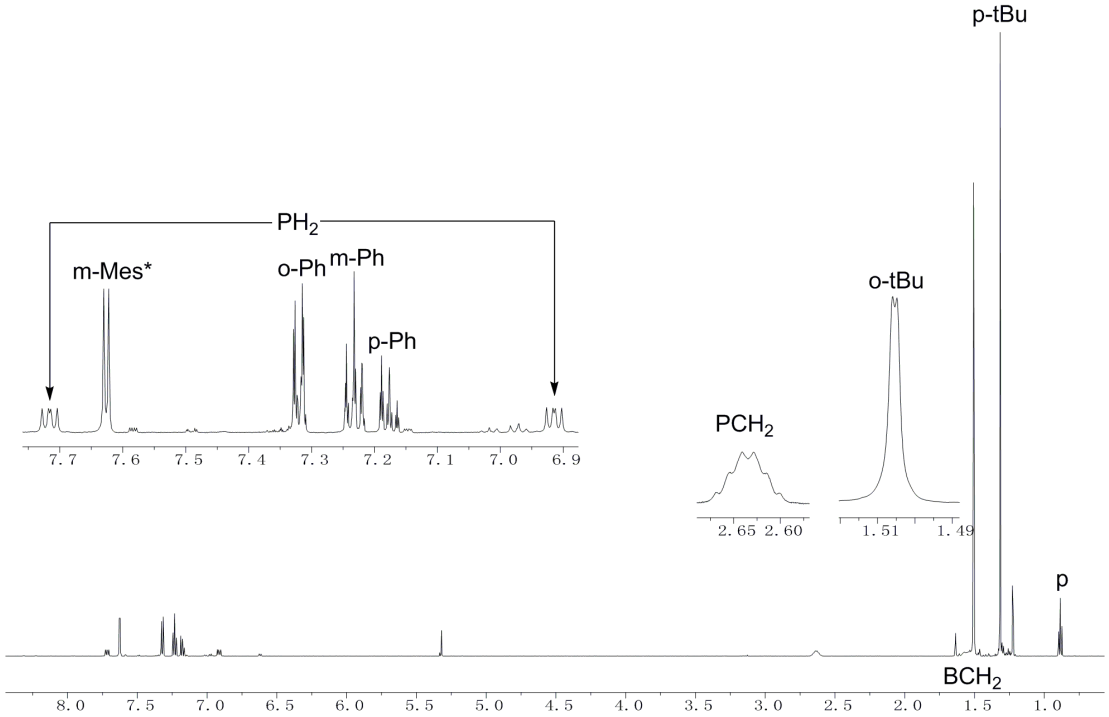


Figure S17. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **7** [admixed with p: pentane].

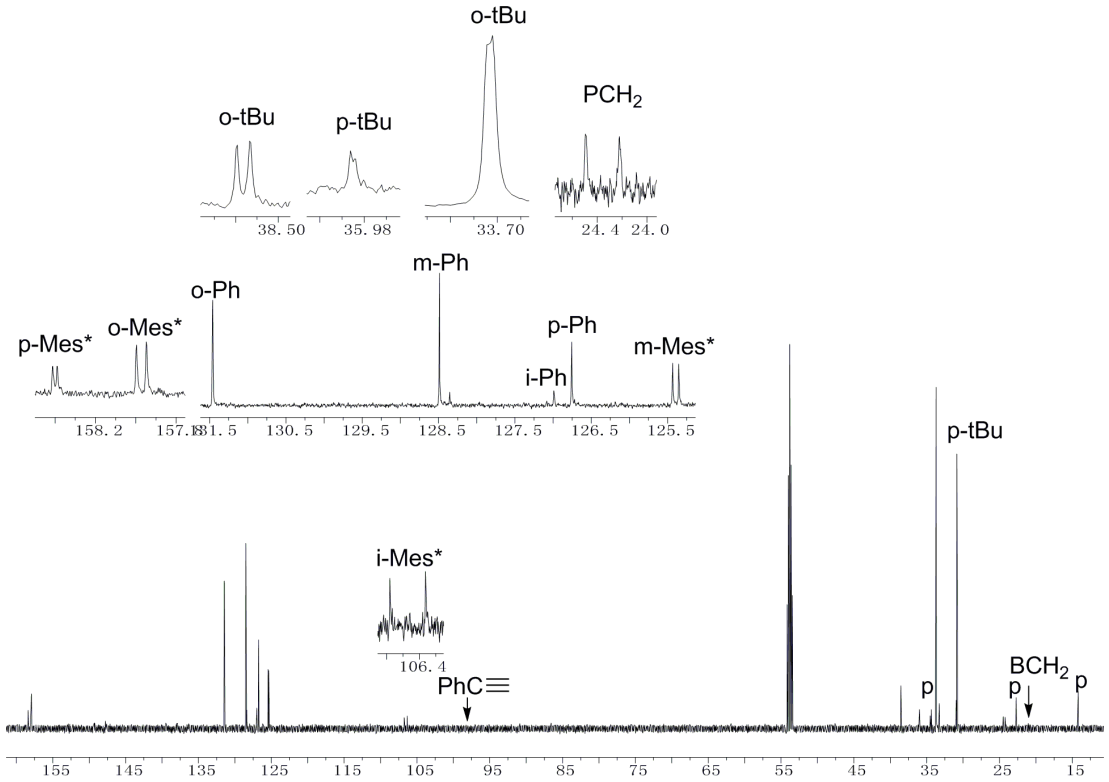


Figure S18. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **7** [admixed with p: pentane].

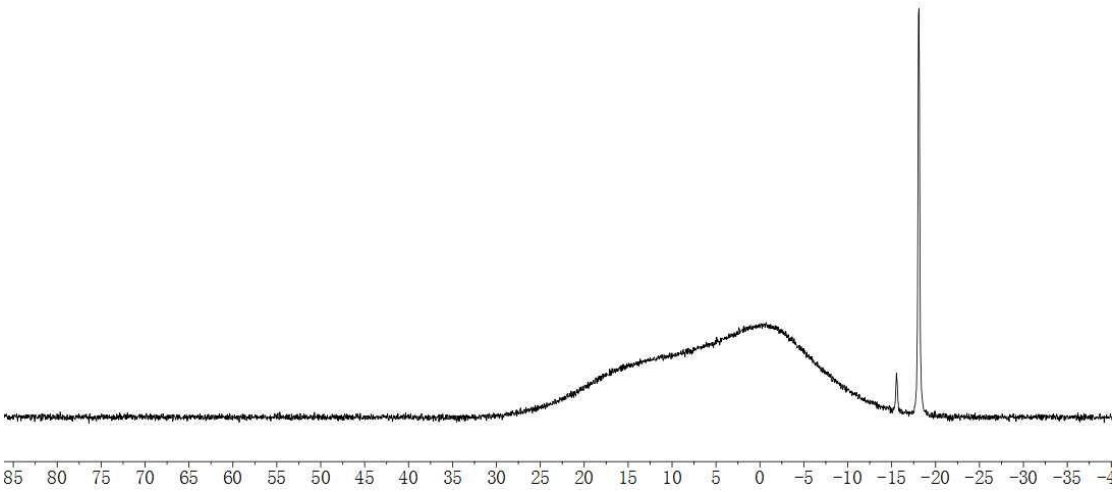


Figure S19. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectra of compound **7**.

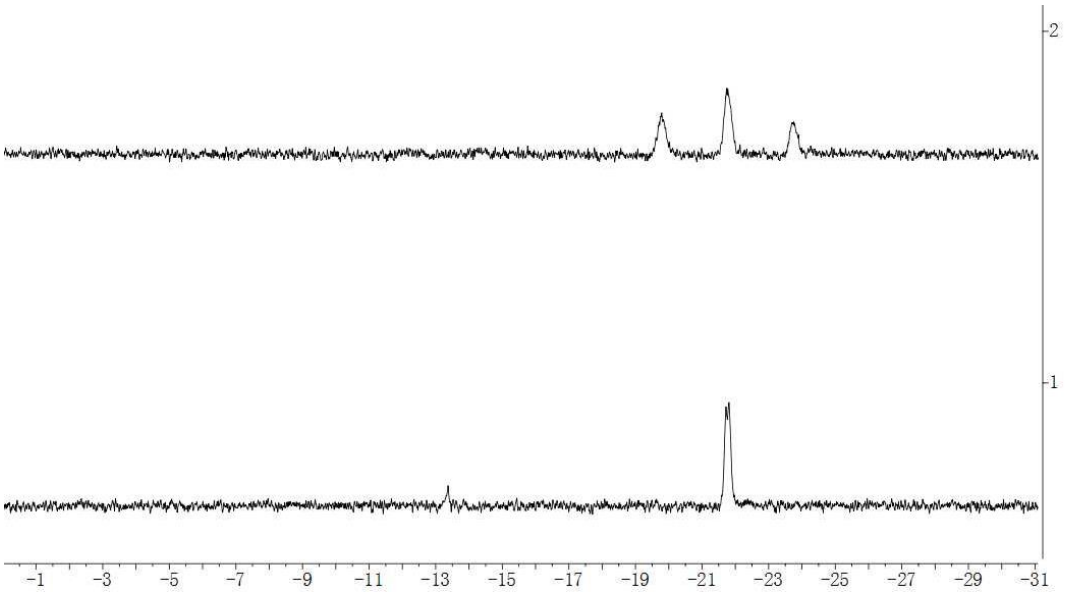


Figure S20. (1) $^{31}P\{^{1}H\}$ NMR and (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2), spectra of compound **7**.

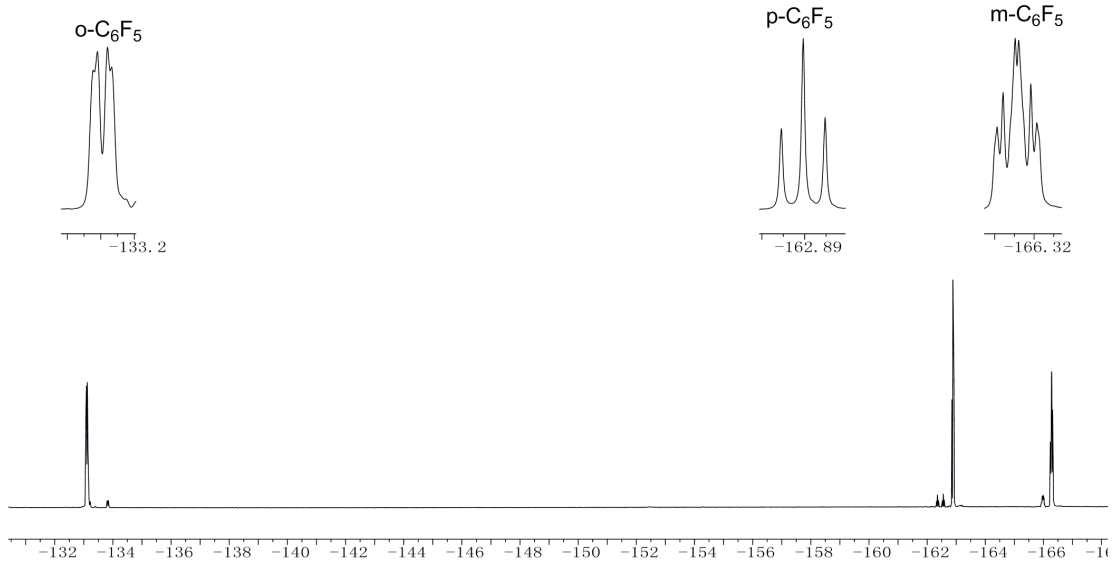


Figure S21. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectra of compound **7**.

Characterization of compound **8**:

Elemental analysis: calc. for $C_{40}H_{40}BF_{10}P$ (752.53 g/mol): C, 63.84; H, 5.36. Found: C, 65.65, H, 5.37.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 8.27 (d, $^{3}J_{PH}$ = 52.6 Hz, 1H, BCH=), 7.58 (dm, $^{1}J_{PH}$ = 456.8 Hz, 1H, PH), [7.58 (dd, $^{4}J_{HH}$ = 4.3 Hz, $^{4}J_{PH}$ = 2.1 Hz), 7.14 (dd, $^{4}J_{HH}$ = 4.3 Hz, $^{4}J_{PH}$ = 2.0 Hz)](each 1H, *m*-Mes*), 7.02 (m, 1H, *p*-Ph), 6.97 (m, 2H, *m*-Ph), 6.62 (m, 2H, *o*-Ph), [3.17, 3.14](each m, each 1H, PCH_2), [1.91, 1.61](each m, each 1H, BCH_2), [1.63 (d, $^{5}J_{PH}$ = 1.1 Hz), 1.22 (s)](each 9H, *o*-^{t}Bu), 1.23 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299K, CD_2Cl_2): δ = 179.4 (br, BCH=), [161.0 (d, $^{2}J_{PC}$ = 6.0 Hz), 159.6](*o*-Mes*), 156.8 (*p*-Mes*), 139.3 (d, $^{2}J_{PC}$ = 12.5 Hz, *i*-Ph), 128.4 (*m*-Ph), 127.1 (*p*-Ph), 126.7 (d, $^{3}J_{PC}$ = 5.2 Hz, *o*-Ph), [126.1, 125.3](each d, $^{3}J_{PC}$ = 12.2 Hz, *m*-Mes*), 121.6 (d, $^{1}J_{PC}$ = 74.8 Hz, PC=). 109.6 (d, $^{1}J_{PC}$ = 73.1 Hz, *i*-Mes*), [39.6/34.4, 39.3/33.3](*o*-^{t}Bu), [35.3, 31.0](*p*-^{t}Bu), 23.9 (d, $^{1}J_{PC}$ = 44.2, PCH_2), 17.0 (br, BCH_2), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2) δ = -15.6 ($\nu_{1/2}$ ~ 40 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -13.4 (m).

^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): δ = -13.4 (dm, $^{1}J_{PH}$ ~ 460 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = [-133.2, -133.8](each m, each 2F, *o*-C_6F_5), [-162.4, -162.6](each t, $^{3}J_{FF}$ = 20.2 Hz, each 1F, *p*-C_6F_5), -166.0 (m, 4F, *m*-C_6F_5).

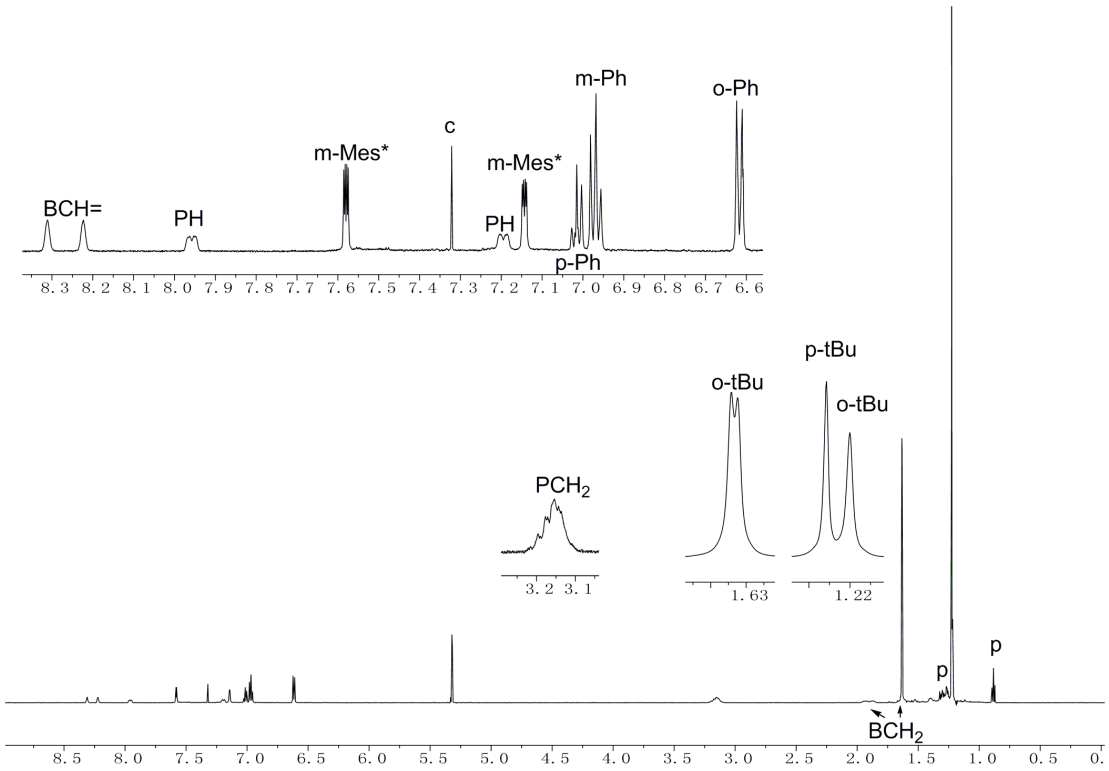


Figure S22. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **8** [admixed with p: pentane, c: chloroform].

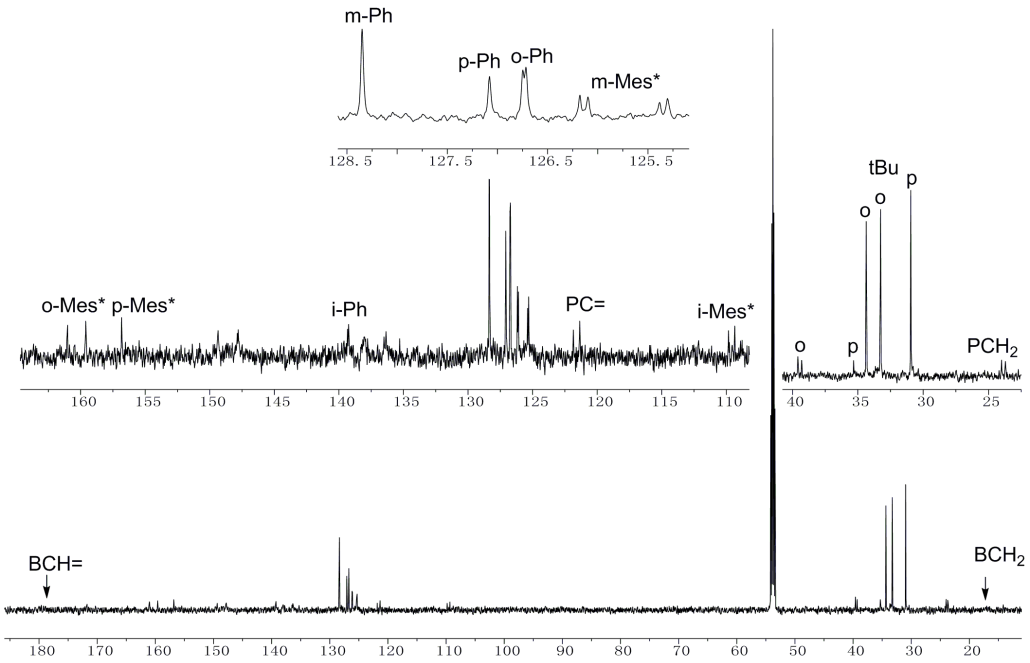


Figure S23. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **8**.

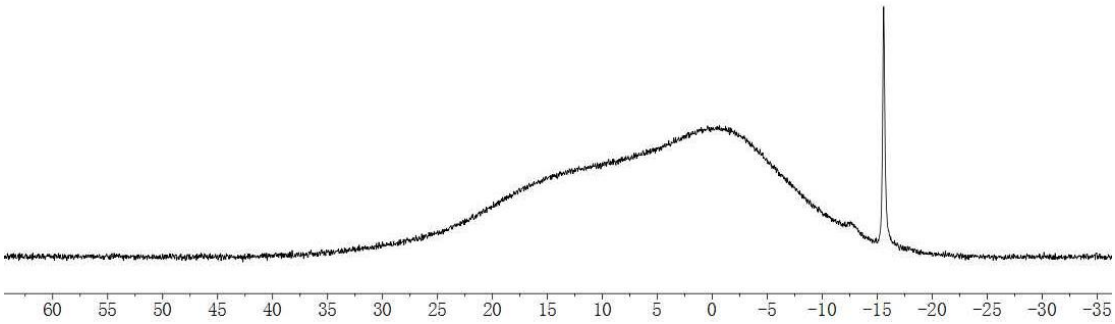


Figure S24. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **8**.

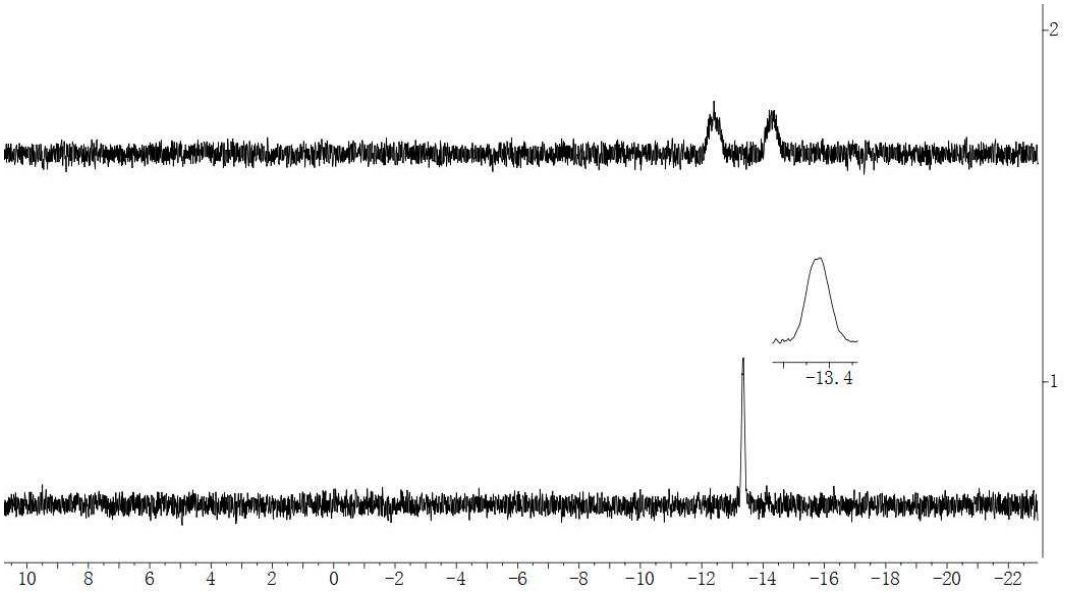


Figure S25. (1) $^{31}P\{^{1}H\}$ and (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) NMR spectra of compound **8**.

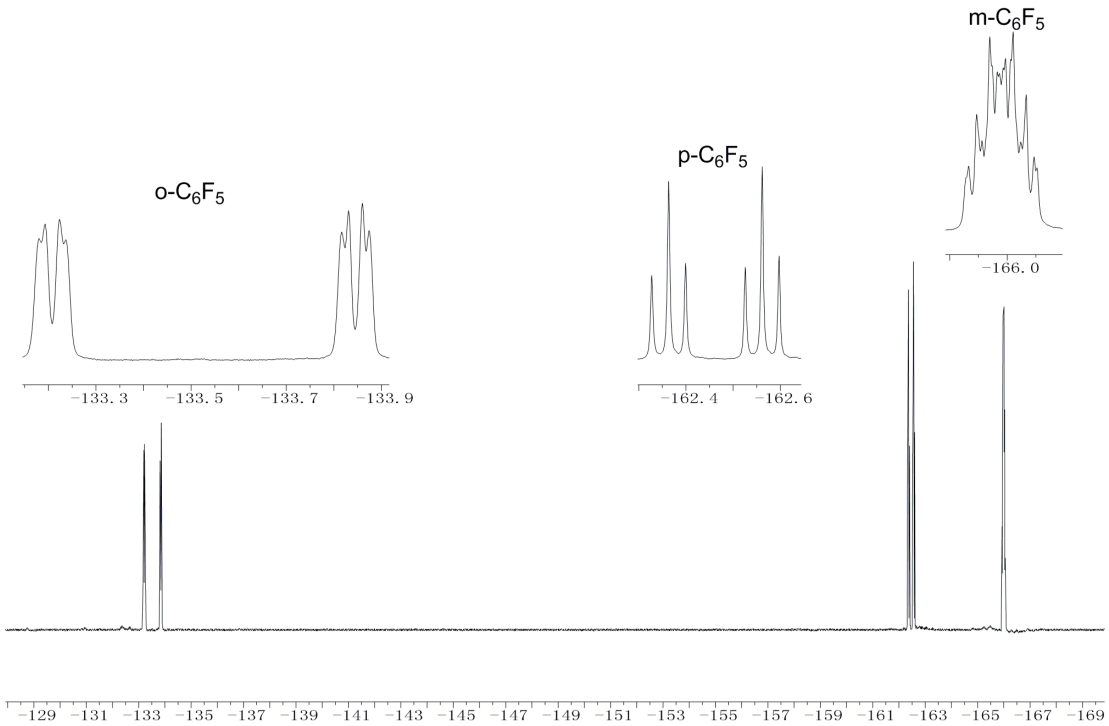


Figure S26. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **8**.

Crystals of compound **8** suitable for the X-ray crystal structure analysis were obtained from a solution of the obtained white solid in dichloromethane and pentane (ratio ca.: 1:3) at room temperature.

X-ray crystal structure analysis of compound 8 (erk9838): A colorless plate-like specimen of $C_{40}H_{40}BF_{10}P$, approximate dimensions 0.040 mm x 0.120 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX II diffractometer system equipped with a fine-focus sealed tube Cu sealed tube (CuK_α, λ = 1.54178 Å) and a graphite monochromator. A total of 1311 frames were collected. The total exposure time was 18.85 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 24096 reflections to a maximum θ angle of 66.65° (0.84 Å resolution), of which 6274 were independent (average redundancy 3.841, completeness = 99.7%, R_{int} = 5.11%, R_{sig} = 4.09%) and 5193 (82.77%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.4244(2) Å, b = 12.6791(2) Å, c = 12.8790(2) Å, α = 75.8800(10)°, β = 79.1700(10)°, γ = 84.3520(10)°, volume = 1774.24(5) Å^3, are based upon the refinement of the XYZ-centroids of 8623 reflections above 20 σ(I) with 7.891° < 2θ < 133.1°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.874. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8270 and 0.9460. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{40}H_{40}BF_{10}P$. The final anisotropic full-matrix least-squares refinement on F^2 with 482 variables converged at R1 = 3.78%, for the observed data and wR2 = 9.65% for all data. The goodness-of-fit was 1.029. The largest peak in the final difference electron density synthesis was 0.306 e^-/Å^3 and the largest hole was -0.281 e^-/Å^3 with an RMS deviation of 0.050 e^-/Å^3. On the basis of the final model, the calculated density was 1.409 g/cm^3 and F(000), 780 e^-. The hydrogen at P1 atom was refined freely. CCDC number: 2054472.

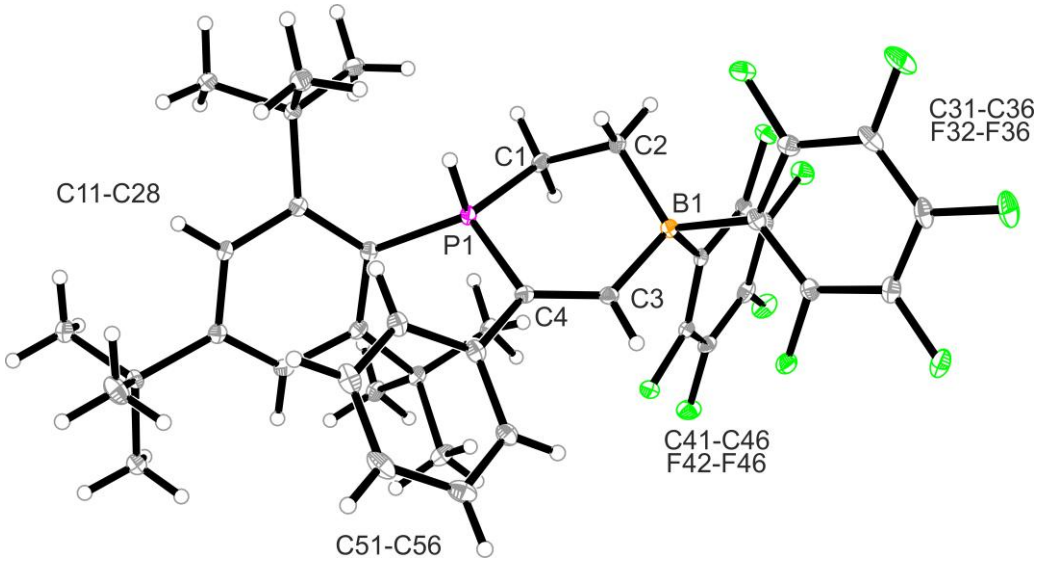
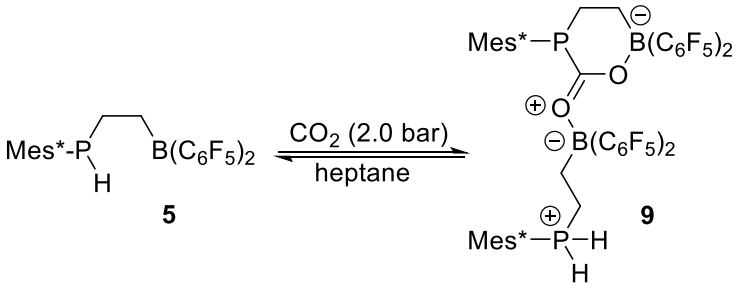


Figure S27. Crystal structure of compound **8** (thermal ellipsoids are set at 30% probability).

Synthesis of compound 9



Scheme S5

A solution of compound **5** (65.0 mg, 0.1 mmol) in heptane (1 mL) was degassed by freeze-pump-thaw cycles twice at -78°C. Then the mixture was exposed to a CO_2 atmosphere (2.0 bar) at r.t. After the reaction mixture was stirred at 80 °C for 15 minutes, a clear colorless solution was obtained. The solution was left in the oil bath, which was slowly cooled to room temperature. The formed colorless crystals were collected by filtration and washed with *n*-pentane (2×2 mL) to finally give compound **9** as a white solid (60.5 mg, 90%).

Characterization of compound **9** in an CO_2 atmosphere:

A solution of the obtained white solid in CD_2Cl_2 (0.8 mL) was degassed by freeze-pump-thaw cycles for two times at -78°C using a J. Young valved NMR tube. After the mixture was exposed to a CO_2 atmosphere (2.0 bar) at room temperature, the obtained clear colorless solution was characterized by NMR experiments at 299K.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.65 (d, $^4J_{PH}$ = 4.9 Hz, 2H, *m*-Mes*^{PH2}), 7.45 (d, $^4J_{PH}$ = 2.8 Hz, 2H, *m*-Mes*), 7.02 (dm, $^1J_{PH}$ = 475.7 Hz, 2H, PH_2), 2.31 (m, 2H, PCH_2), 2.18 (m, 2H, PCH_2^{PH2}), 1.69 (m, 2H, BCH_2^{PH2}), 1.49 (s, 18H, *o*-^{t}Bu^{PH2}), 1.44 (m, 2H, BCH_2), 1.42 (s, 18H, *o*-^{t}Bu), 1.33 (s, 9H, *p*-^{t}Bu^{PH2}), 1.28 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299K, CD_2Cl_2): δ = 196.0 (d, $^1J_{PC}$ = 37.4 Hz, C=O), 159.1 (d, $^2J_{PC}$ = 14.9 Hz, *o*-Mes*), 158.6 (d, $^2J_{PC}$ = 7.9 Hz, *o*-Mes*^{PH2}), 159.0 (d, $^4J_{PC}$ = 2.7 Hz, *p*-Mes*^{PH2}), 152.7 (d, $^4J_{PC}$ = 2.6 Hz, *p*-Mes*), 125.7 (d, $^3J_{PC}$ = 12.4 Hz, *m*-Mes*^{PH2}), 125.3 (CO_2),[1] 124.0 (d, $^3J_{PC}$ = 9.0 Hz, *m*-Mes*), 122.5 (d, $^1J_{PC}$ = 25.7 Hz, *i*-Mes*), 104.6 (d, $^1J_{PC}$ = 67.3 Hz, *i*-Mes*^{PH2}), [39.4 (d, $^3J_{PC}$ = 4.9 Hz), 33.8 (d, $^4J_{PC}$ = 5.8 Hz)](*o*-^{t}Bu), [38.6 (d, $^3J_{PC}$ = 3.2 Hz), 33.6](*o*-^{t}Bu^{PH2}), [36.1, 30.8](*p*-^{t}Bu^{PH2}), [35.2, 31.0](*p*-^{t}Bu), 22.7 (d, $^1J_{PC}$ = 7.2 Hz, PCH_2), 22.3 (d, $^1J_{PC}$ = 42.7 Hz, PCH_2^{PH2}), 18.2 (br, BCH_2^{PH2}), 15.2 (br, BCH_2), [C_6F_5 not listed]. [[1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics*, **2010**, *29*, 2176-2179]

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 1.7 ($\nu_{1/2}$ ~ 600 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -20.8 ($\nu_{1/2}$ ~ 10 Hz, PH_2), -21.5 (m, P).

^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): δ = -20.8 (tm, $^1J_{PH}$ ~ 475 Hz, 1P, PH_2), -21.5 (m, 1P, P).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = [-132.4, 134.0](each m, each 2F, *o*-C_6F_5), [-160.8, -160.9](each t, $^3J_{FF}$ = 20.2 Hz, each 1F, *p*-C_6F_5), [-165.8, -165.9](each m, each 2F, *m*-C_6F_5).

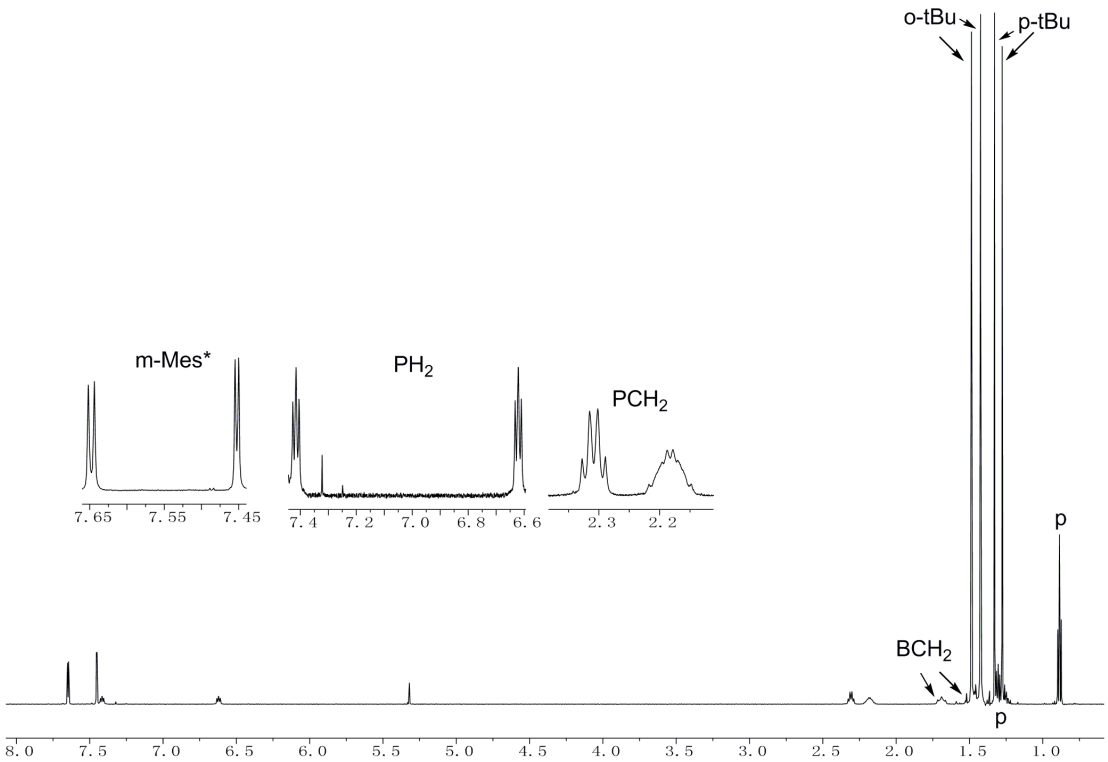


Figure S28. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of the compound **9** [admixed with p: pentane].

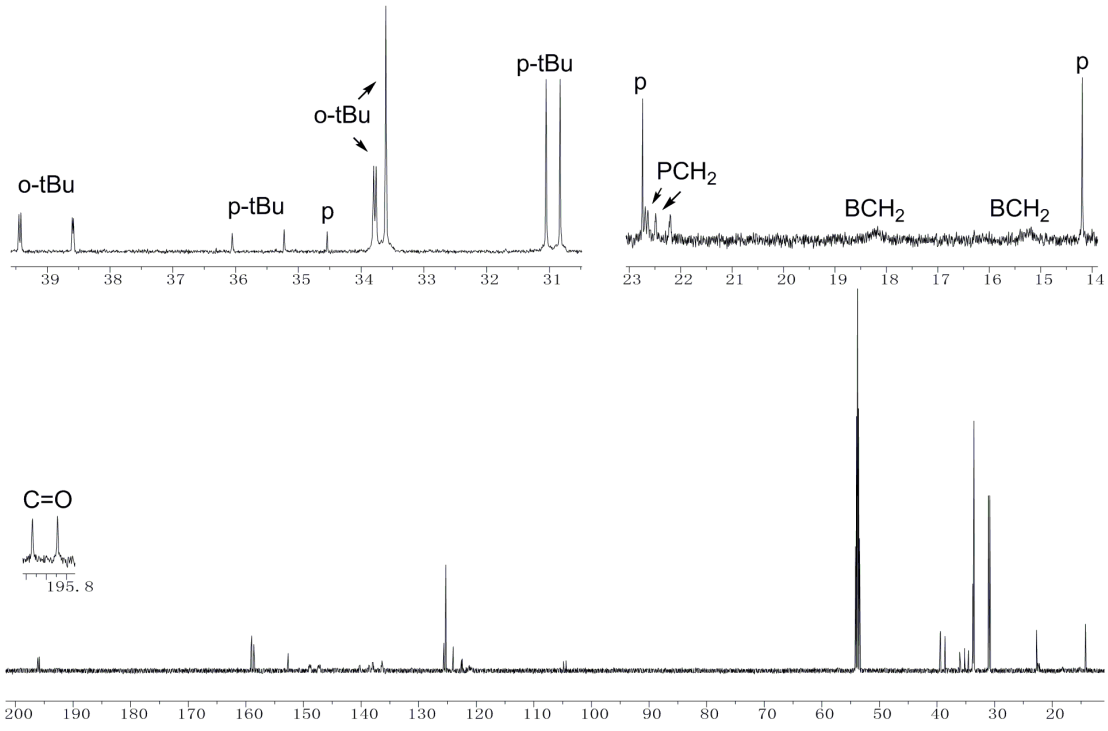


Figure S29a. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **9** [admixed with p: pentane].

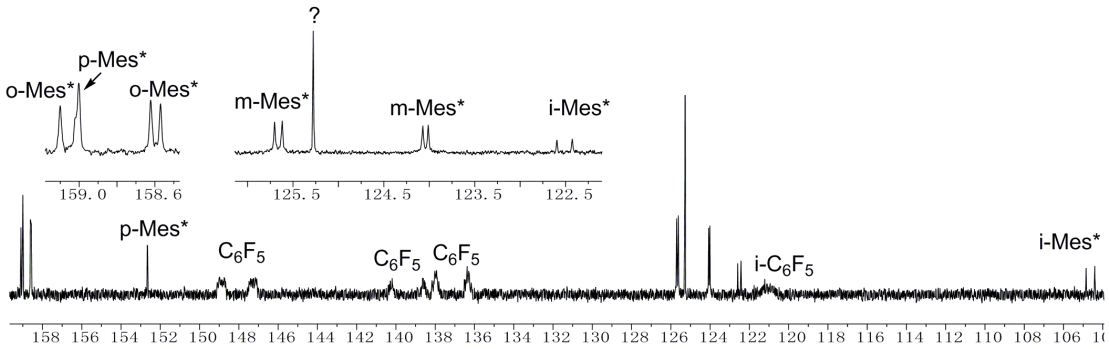


Figure S29b. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **9** [?:$^{13}CO_2$].

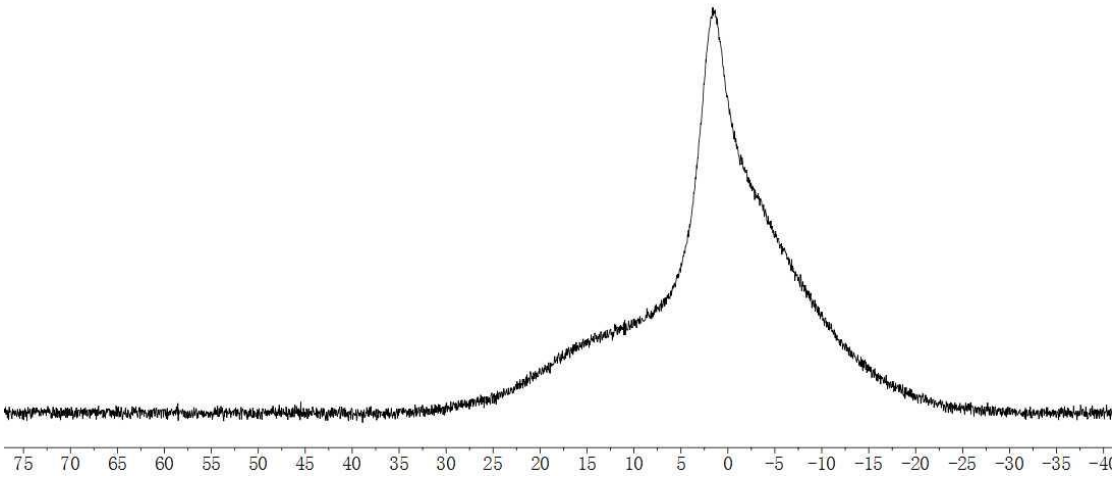


Figure S30. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **9**.

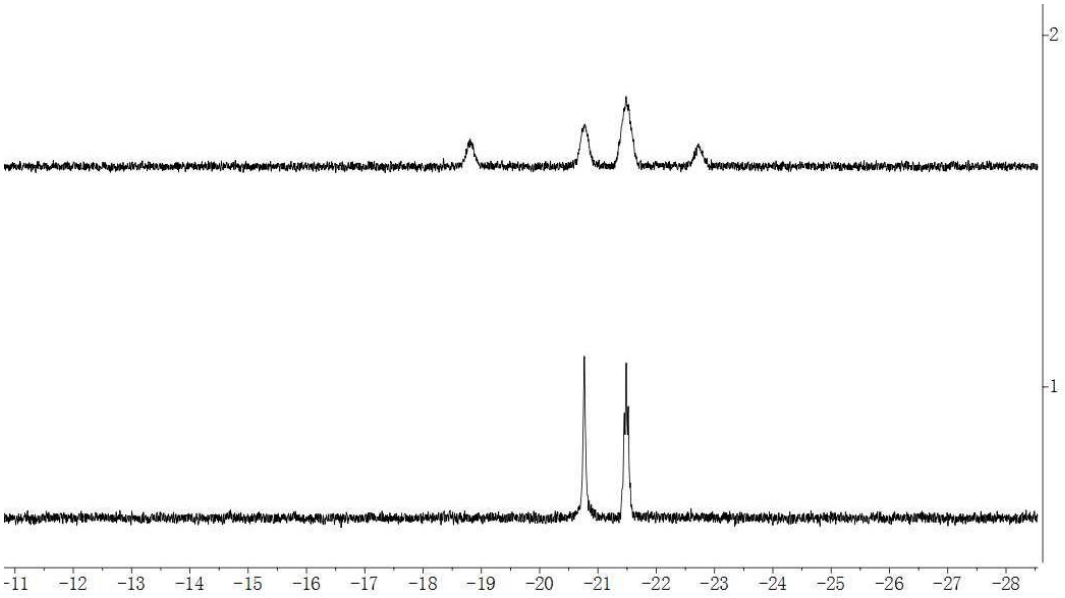


Figure S31. (1) $^{31}P\{^{1}H\}$ NMR and (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compound **9**.

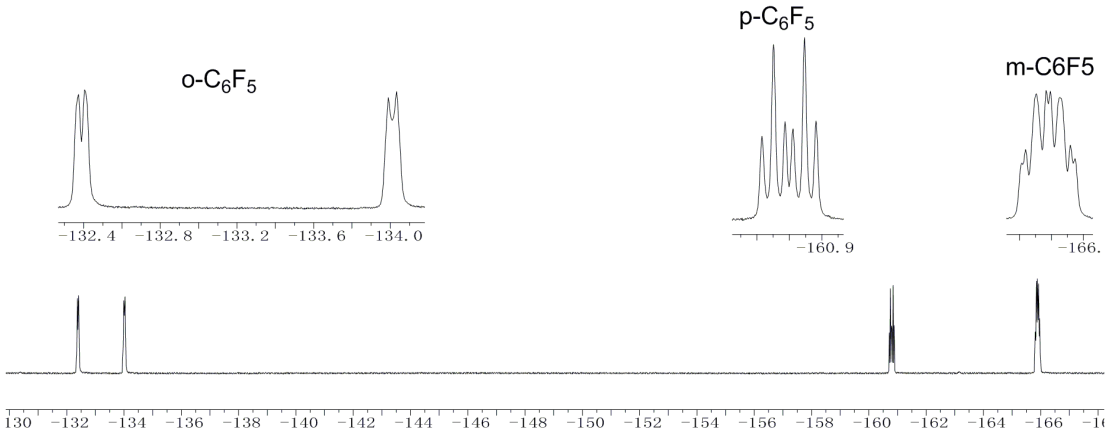


Figure S32. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **9**

Crystals of compound **9** suitable for the X-ray crystal structure analysis were obtained from a solution of compound **5** exposed to a CO_2 atmosphere (2.0 bar) in heptane.

X-ray crystal structure analysis of compound 9 (erk9863): A colorless prism-like specimen of $C_{65}H_{68}B_2F_{20}O_2P_2$, approximate dimensions 0.114 mm x 0.143 mm x 0.261 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Mo Ims (MoK_α, $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 1092 frames were collected. The total exposure time was 5.74 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 142399 reflections to a maximum θ angle of 25.35° (0.83 Å resolution), of which 14076 were independent (average redundancy 10.116, completeness = 99.8%, R_{int} = 10.93%, R_{sig} = 4.76%) and 10118 (71.88%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.4236(5) Å, b = 18.8115(9) Å, c = 19.7580(8) Å, α = 109.926(2)°, β = 104.169(2)°, γ = 91.101(2)°, volume = 3845.7(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9951 reflections above 20 σ(I) with 4.551° < 2θ < 52.86°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.941. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9640 and 0.9840. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{65}H_{68}B_2F_{20}O_2P_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 846 variables converged at R1 = 4.25%, for the observed data and wR2 = 12.14% for all data. The goodness-of-fit was 1.027. The largest peak in the final difference electron density synthesis was 0.242 $e^-/Å^3$ and the largest hole was -0.307 $e^-/Å^3$ with an RMS deviation of 0.053 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.161 g/cm^3 and F(000), 1388 e^-. The hydrogens at P2 atom were refined freely. CCDC number: 2054473.

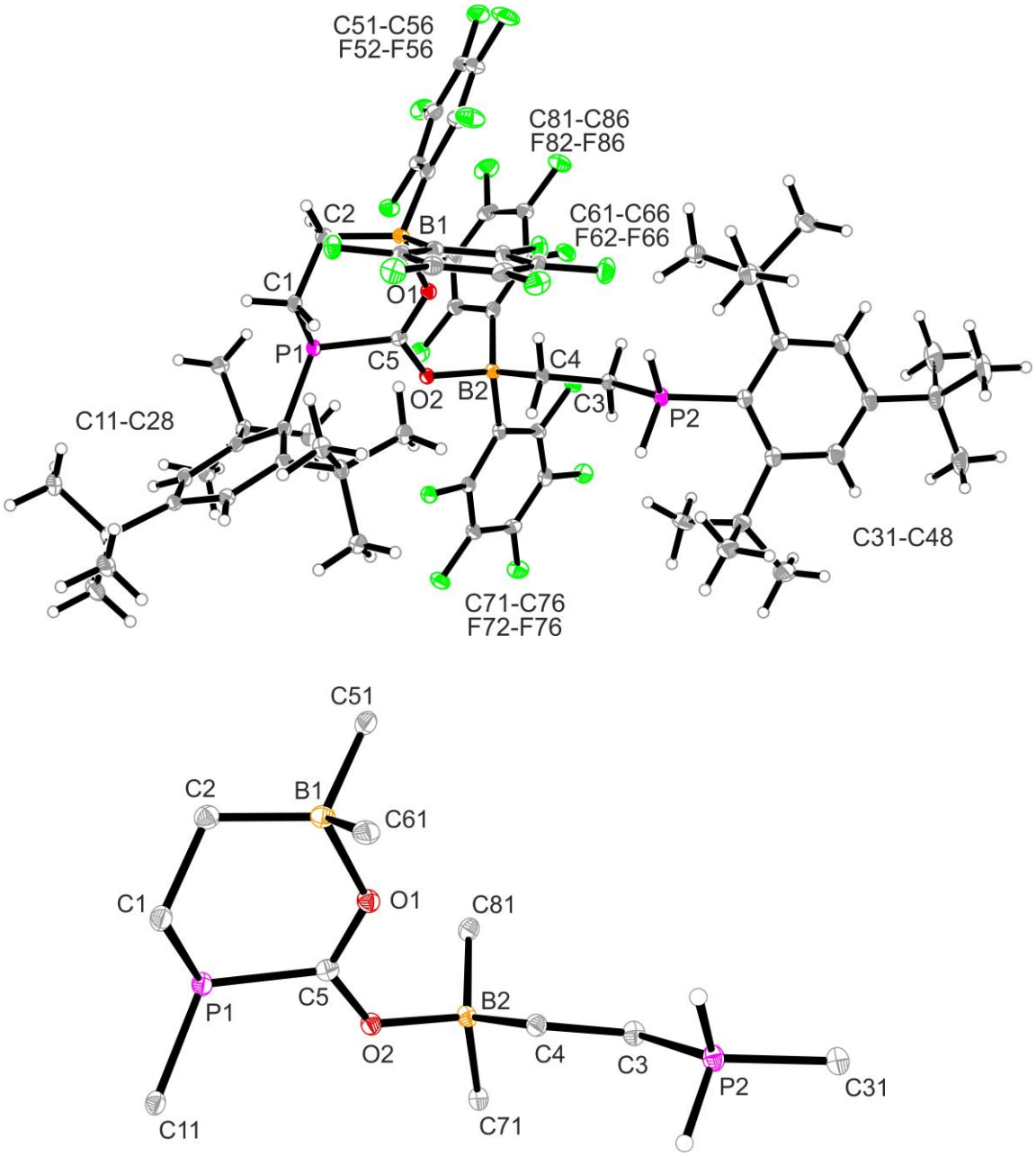
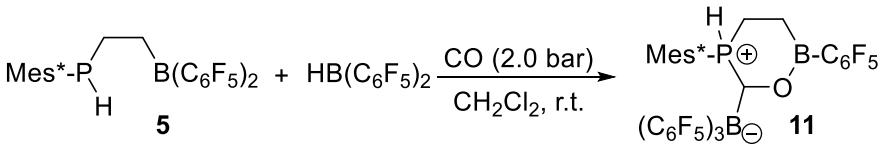


Figure S33. Crystal structure of compound **9** (thermal ellipsoids are set at 30% probability).

Synthesis of compound 11



Scheme S6

A solution of compound **5** (65.0 mg, 0.1 mmol) and $HB(C_6F_5)_2$ (34.5 mg, 0.1 mmol) in CH_2Cl_2 (0.8 mL) was degassed by freeze-pump-thaw cycles twice at -78°C. Then the mixture was exposed to a CO atmosphere (2.0 bar) at r.t. After the reaction mixture was stirred at r.t. for 12 hours, a suspension was obtained. Then all volatiles were removed in *vacuo*. *n*-Pentane (2 mL) was added to the residue and the suspension was vigorously stirred for 0.5 h. The precipitate was collected by filtration and washed with *n*-pentane (3×2 mL) to give compound **11** as a white solid (93.4 mg, 95%).

Characterization of compound **11**:

Elemental analysis: calc. for $C_{45}H_{35}B_2F_{20}OP$ (1024.34 g/mol): C, 52.77; H, 3.44. Found: C, 51.93, H, 3.35.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = [7.76, 7.48](each dd, J = 4.8, 1.9 Hz, each 1H, *m*-Mes*), 6.87 (br d, $^1J_{PH}$ ~ 487 Hz, 1H, PH), 6.31 (br m, 1H, CH), [2.82, 2.66](each m, each 1H, PCH_2), [1.65, 0.50](each m, each 1H, BCH_2), [1.55, 1.25](each s, each 9H, *o*-^{t}Bu), 1.39 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299K, CD_2Cl_2): δ = [161.2 (d, $^2J_{PC}$ = 8.2 Hz), 159.5 (d, $^2J_{PC}$ = 8.0 Hz)](*o*-Mes*), 157.5 (d, $^4J_{PC}$ = 4.0 Hz, *p*-Mes*), [128.7 (d, $^3J_{PC}$ = 12.9 Hz), 125.6 (d, $^3J_{PC}$ = 12.7 Hz)](*m*-Mes*), 110.4 (d, $^1J_{PC}$ = 75.2 Hz, *i*-Mes*), 69.0 (br, PCH), [39.6 (d, $^3J_{PC}$ = 2.6 Hz), 39.5 (d, $^3J_{PC}$ = 4.0 Hz), 33.7, 33.2](*o*-^{t}Bu), [35.5, 30.7](*p*-^{t}Bu), 15.4 (d, $^1J_{PC}$ = 36.9 Hz, PCH_2), 9.8 (br, BCH_2), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 43.6 ($\nu_{1/2}$ ~ 1100 Hz, BO), -11.5 ($\nu_{1/2}$ ~ 16 Hz, $B(C_6F_5)_3$).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -19.5 ($\nu_{1/2}$ ~ 30 Hz).

^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): δ = -19.5 (dm, $^1J_{PH}$ ~ 485 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = {[-126.6, -127.4, -127.6, -129.5, -133.0, -139.1](each br, each 1F, *o*), [-157.6, -159.5, -161.6](each br, each 1F, *p*), [-163.3 (br), -163.4 (br m), -165.8 (br)](each 2F, *m*)]}($BC_6F_5)_3$), -132.2 (m, 2F, *o*), -150.6 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*), -162.5 (m, 2F, *m*](OB(C_6F_5)).

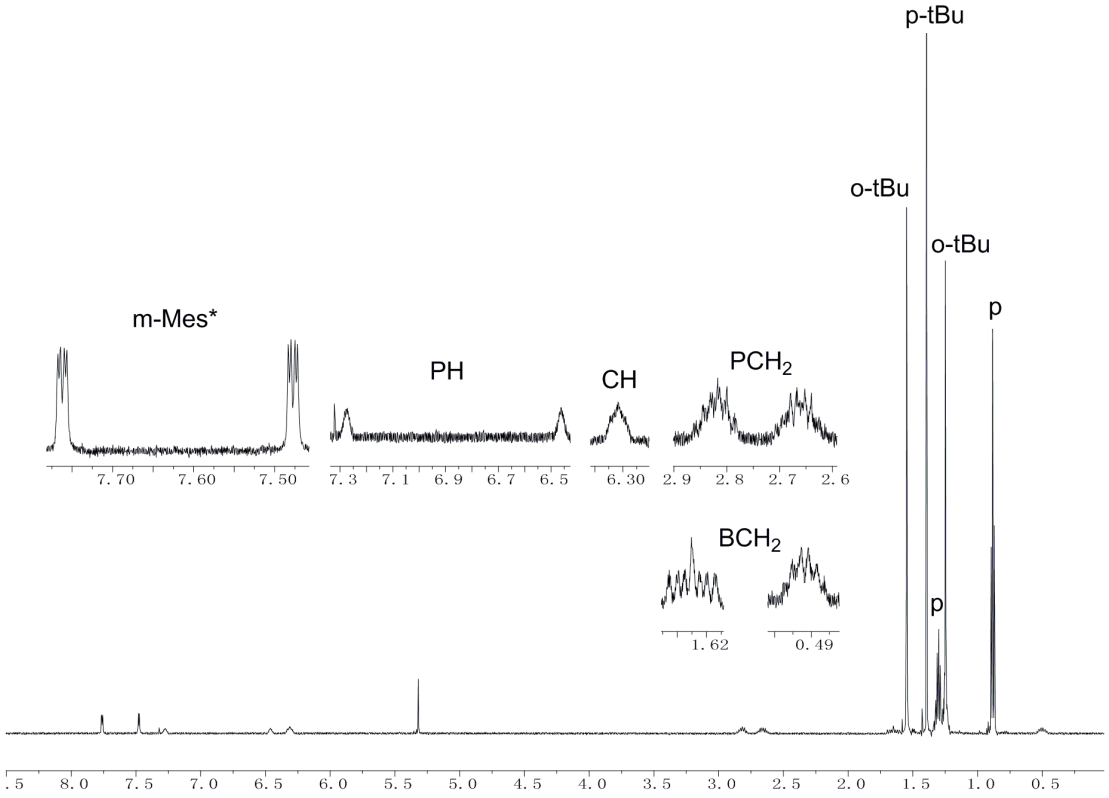


Figure S34. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **11** [admixed with p: pentane].

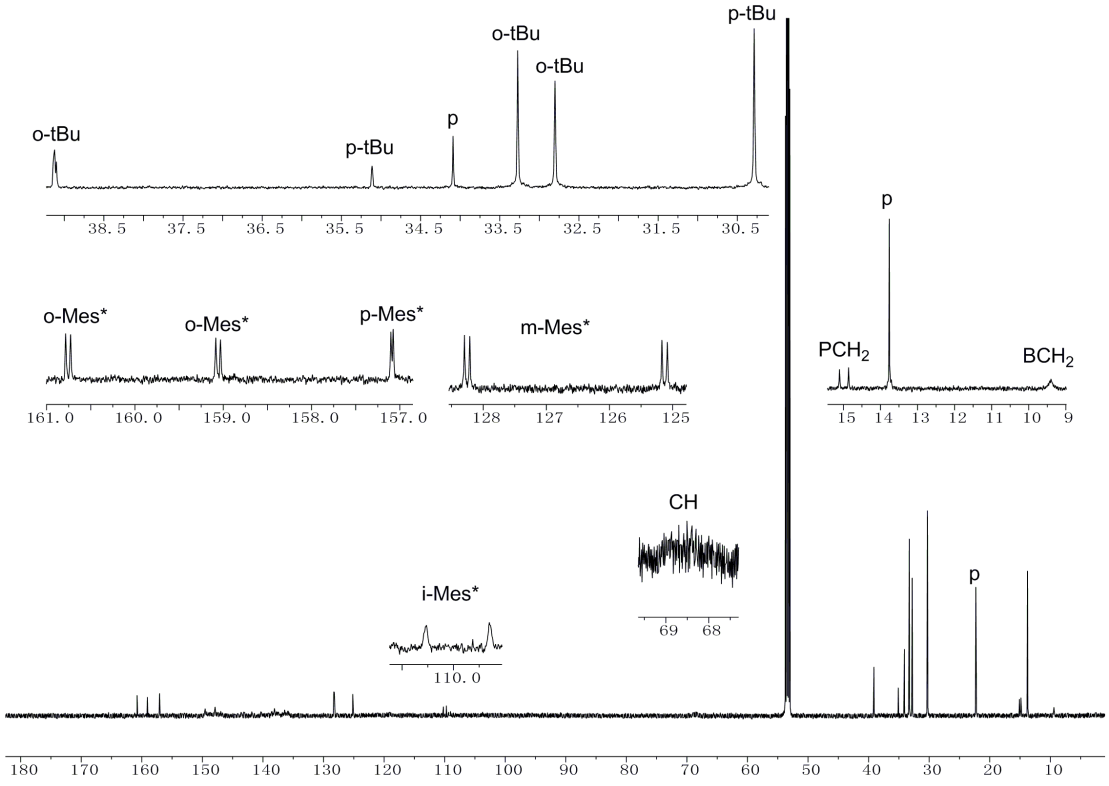


Figure S35. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **11** [admixed with p: pentane].

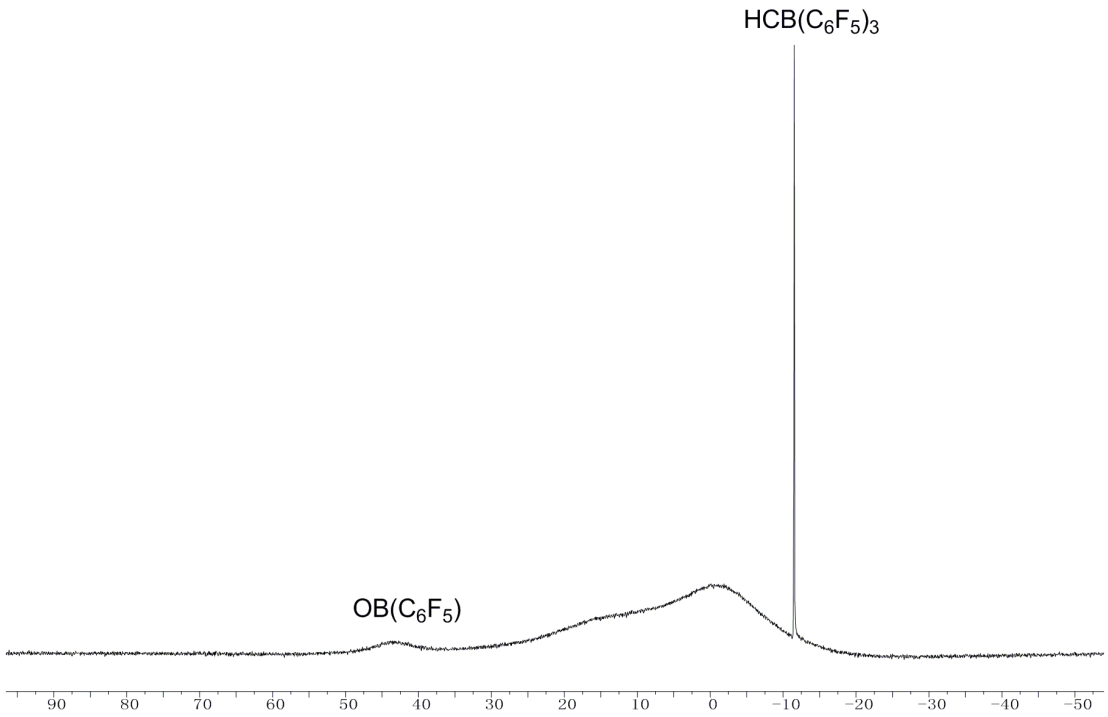


Figure S36. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **11**.

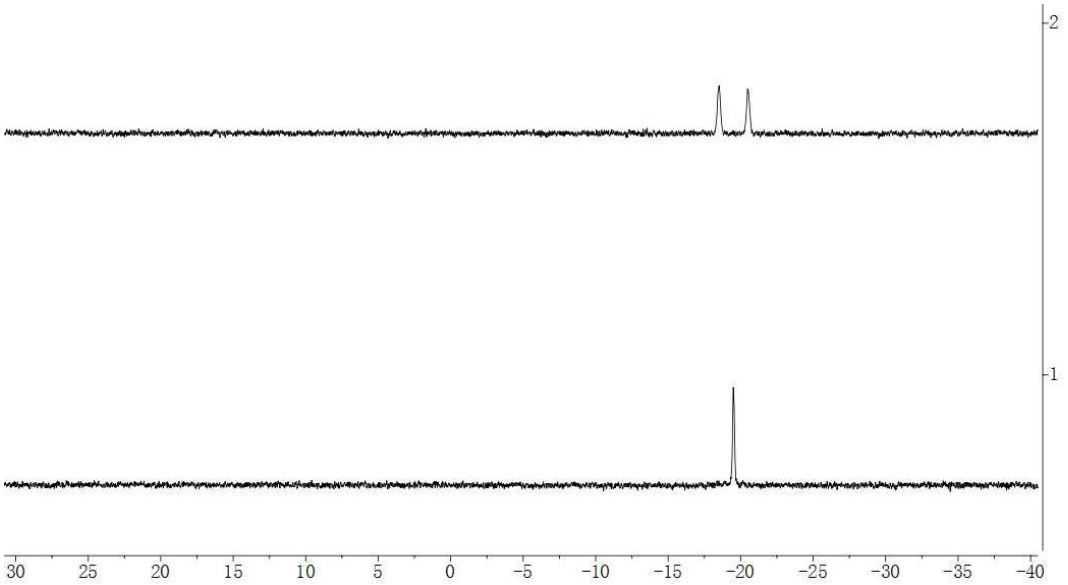


Figure S37. (1) $^{31}P\{^{1}H\}$ NMR and (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of compound **11**.

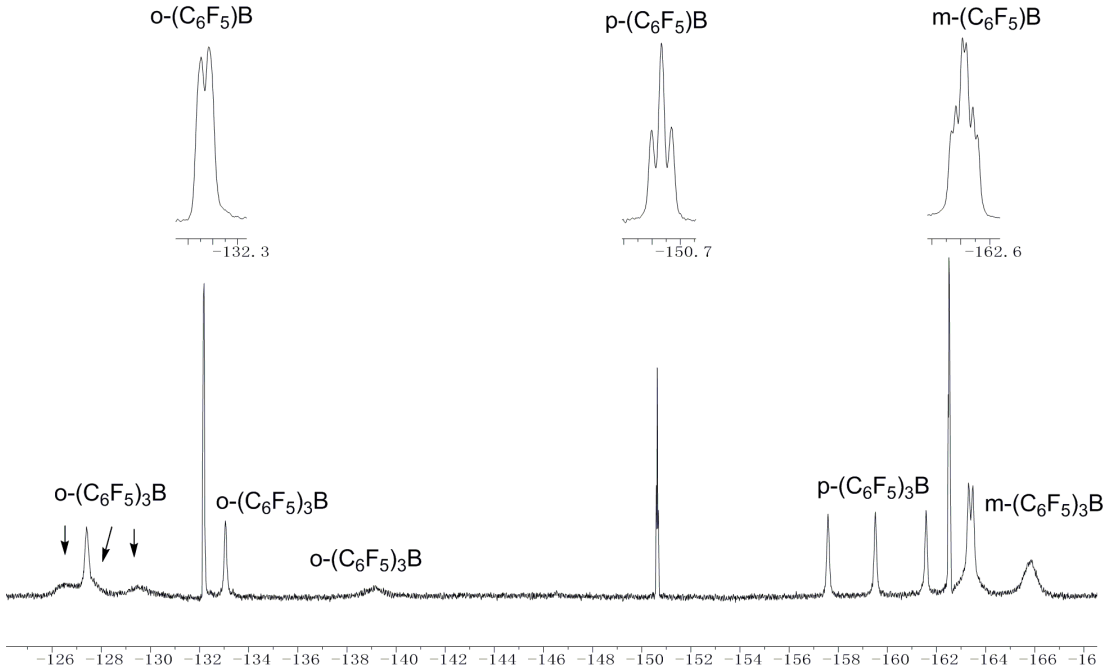


Figure S38. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **11**.

Crystals of compound **11** suitable for the X-ray crystal structure analysis were obtained from a solution of the obtained white solid in dichloromethane and pentane (ratio ca.: 1:1) at room temperature.

X-ray crystal structure analysis of compound 11 (erk9851): A colorless plate-like specimen of $C_{45}H_{35}B_2F_{20}OP$, approximate dimensions 0.041 mm x 0.109 mm x 0.143 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Cu Ims (CuK_α, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1879 frames were collected. The total exposure time was 23.15 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 248626 reflections to a maximum θ angle of 68.36° (0.83 Å resolution), of which 15697 were independent (average redundancy 15.839, completeness = 99.7%, R_{int} = 14.31%, R_{sig} = 4.94%) and 10869 (69.24%) were greater than $2\sigma(F^2)$. The final cell constants of a = 18.1083(4) Å, b = 19.6312(4) Å, c = 25.0061(5) Å, β = 105.1040(10)°, volume = 8582.3(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9973 reflections above 20 σ(I) with 5.054° < 2θ < 136.6°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.839. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7930 and 0.9330. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 8 for the formula unit, $C_{45}H_{35}B_2F_{20}OP$. The final anisotropic full-matrix least-squares refinement on F^2 with 1270 variables converged at R1 = 6.51%, for the observed data and wR2 = 19.54% for all data. The goodness-of-fit was 1.020. The largest peak in the final difference electron density synthesis was 0.580 $e^-/Å^3$ and the largest hole was -0.518 $e^-/Å^3$ with an RMS deviation of 0.114 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.586 g/cm^3 and F(000), 4144 e^-. The hydrogens at P1A and P1B atoms were refined freely. CCDC number: 2054474.

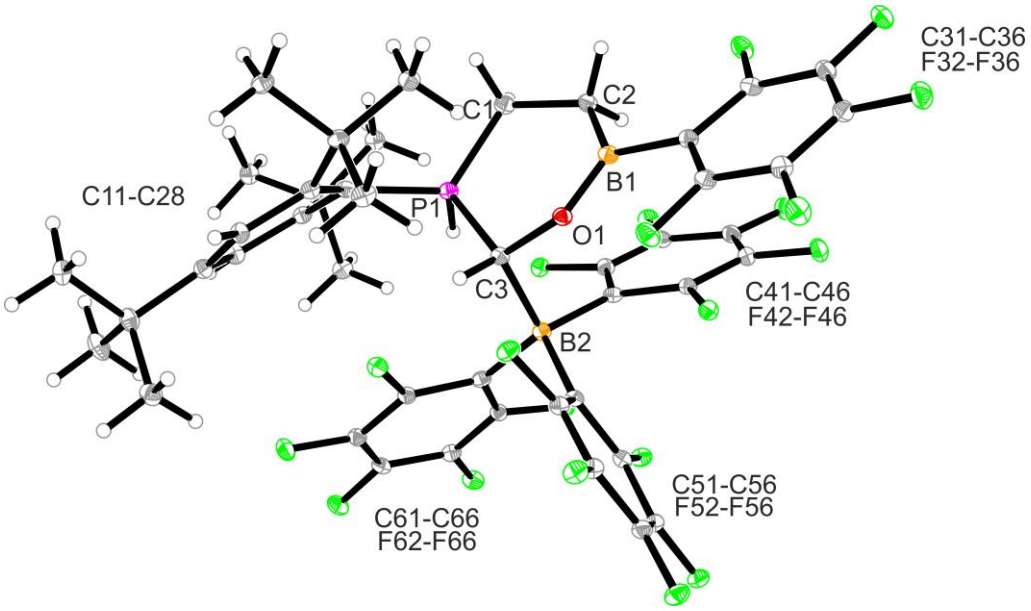
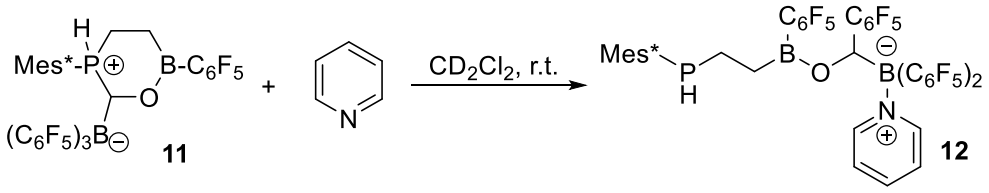


Figure S39. Crystal structure of compound **11**. (Only one molecule (Molecule "A") of two found in the asymmetric unit is shown. Thermal ellipsoids are set at 15% probability).

Synthesis of compound 12



Scheme S7

A solution of pyridine (7.9 mg, 0.1 mmol) in CD_2Cl_2 (0.5 mL) was added dropwise to a solution of compound **11** (102.4 mg, 0.1 mmol) in CD_2Cl_2 (0.5 mL) at r.t. After the reaction mixture was stirred at r.t. for 2 h, a clear colorless solution was obtained. After all volatiles were removed in *vacuo*, *n*-pentane (1 mL) was added to the residue and the solution was kept under argon for 2 h at r.t. to give compound **12** as a colorless crystalline solid (88.2 mg, 80%).

Characterization of compound **12**:

Elemental analysis: calc. for $C_{50}H_{40}B_2F_{20}NOP$ (1103.44 g/mol): C, 54.43; H, 3.65; N, 1.27. Found: C, 55.04, H, 4.18; N, 1.07.

Comment: The solution of the obtained white solid in CD_2Cl_2 showed a mixture of two isomers (ratio ca. 56 : 44 (^{1}H NMR)).

^{1}H NMR (600 MHz, 213 K, CD_2Cl_2) major isomer: δ = [8.25 (m, 3H), 7.62 (m, 2H)](pyr), [7.31, 7.21](each br, each 1H, *m*-Mes*), 6.74 (s, 1H, CH), 4.34 (ddd, $^1J_{PH}$ = 221.5 Hz, J = 11.4 Hz, J = 5.1 Hz, 1H, PH), [1.47, 1.04](each m, each 1H, PCH_2), [1.42, 1.04](each m, each 1H, BCH_2), [1.35, 1.30](each s, each 9H, *o*-^{t}Bu), 1.18 (s, 9H, *p*-^{t}Bu).

^{1}H NMR (600 MHz, 213 K, CD_2Cl_2) minor isomer: δ = [8.25 (m, 3H), 7.62 (m, 2H)](pyr), [7.28 (br), 7.26 (br d, $^4J_{PH}$ = 3.7 Hz)](each 1H, *m*-Mes*), 6.79 (s, 1H, CH), 4.62 (ddd, $^1J_{PH}$ = 221.5 Hz, J = 11.5, J = 5.9 Hz, 1H, PH), [1.47, 1.04](each m, each 1H, PCH_2), [1.50, 0.92](each m, each 1H, BCH_2), [1.48, 1.27](each s, each 9H, *o*-^{t}Bu), 1.18 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 213 K, CD_2Cl_2) major isomer: δ = [154.1 (d, $^2J_{PC}$ = 21.1 Hz), 153.2](each m, *o*-Mes*), 148.9 (d, $^4J_{PC}$ = 1.6 Hz, *p*-Mes*), [146.1, 143.0, 124.5](pyr), 132.8 (dm, $^1J_{PC}$ ~ 30 Hz, *i*-Mes*), [122.4, 121.9](each m, *m*-Mes*), 69.4 (br, CH), [37.80, 37.78, 32.2 (d, J = 14.0 Hz), 32.1](*o*-^{t}Bu), [34.5/30.5](*p*-^{t}Bu), 21.7 (dm, $^1J_{PC}$ ~ 31 Hz), 15.8 (br, BCH_2), [C_6F_5 not listed].

^{13}C{^{1}H} NMR (151 MHz, 213 K, CD_2Cl_2) minor isomer: δ = [154.3 (d, $^2J_{PC}$ = 20.5 Hz), 153.1](each m, *o*-Mes*), 148.8 (*p*-Mes*), [146.1, 143.0, 124.5](pyr), 133.0 (dm, $^1J_{PC}$ ~ 30 Hz, *i*-Mes*), [122.3, 121.8](each m, *m*-Mes*), 69.4 (br, CH), [38.0/32.5 (d, J = 13.8 Hz), 37.7/32.0](*o*-^{t}Bu), [34.5/30.5](*p*-^{t}Bu), 21.8 (dm, $^1J_{PC}$ ~ 29 Hz), 15.7 (br, BCH_2), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 47.9 ($\nu_{1/2}$ ~ 1200 Hz, B-O), -0.9 ($\nu_{1/2}$ ~ 200 Hz, B-pyr).

^{11}B{^{1}H} NMR (192 MHz, 213 K, CD_2Cl_2): δ = -1.1 (B-pyr).

^{31}P{^{1}H} NMR (243 MHz, 213 K, CD_2Cl_2): δ = -69.6 (dm, $^1J_{PH}$ ~ 222 Hz, ca. 55 mol%), -69.0 (dm, $^1J_{PH}$ ~ 222 Hz, ca. 45 mol%).

^{19}F NMR (564 MHz, 213 K, CD_2Cl_2): δ = [-127.0 (br, 2F), -128.5 (br, 1F), {-133.9, -134.0, -134.2}(each br, 3F), -140.9 (br, 2F)](*o*-C_6F_5), [-152.8 (m, 1F), {-155.7, -155.9}(each t, each $^3J_{FF}$ = 22.2 Hz, 1F), -156.3 (m, 1F), -156.8 (m, 1F)](*p*-C_6F_5), [-161.7 (2F), -162.5 (3F), -163.1 (3F)](each m, *m*-C_6F_5).

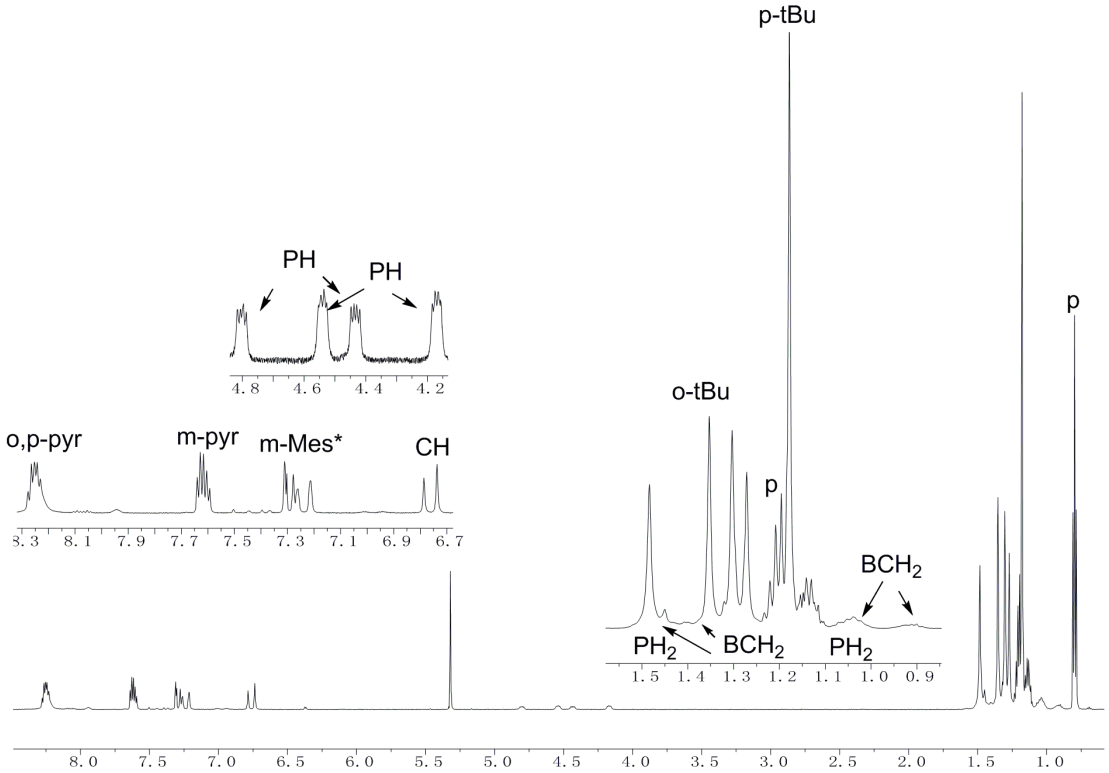


Figure S40. ^{1}H NMR (600 MHz, 213 K, CD_2Cl_2) spectrum of compound **12** [admixed with p: pentane].

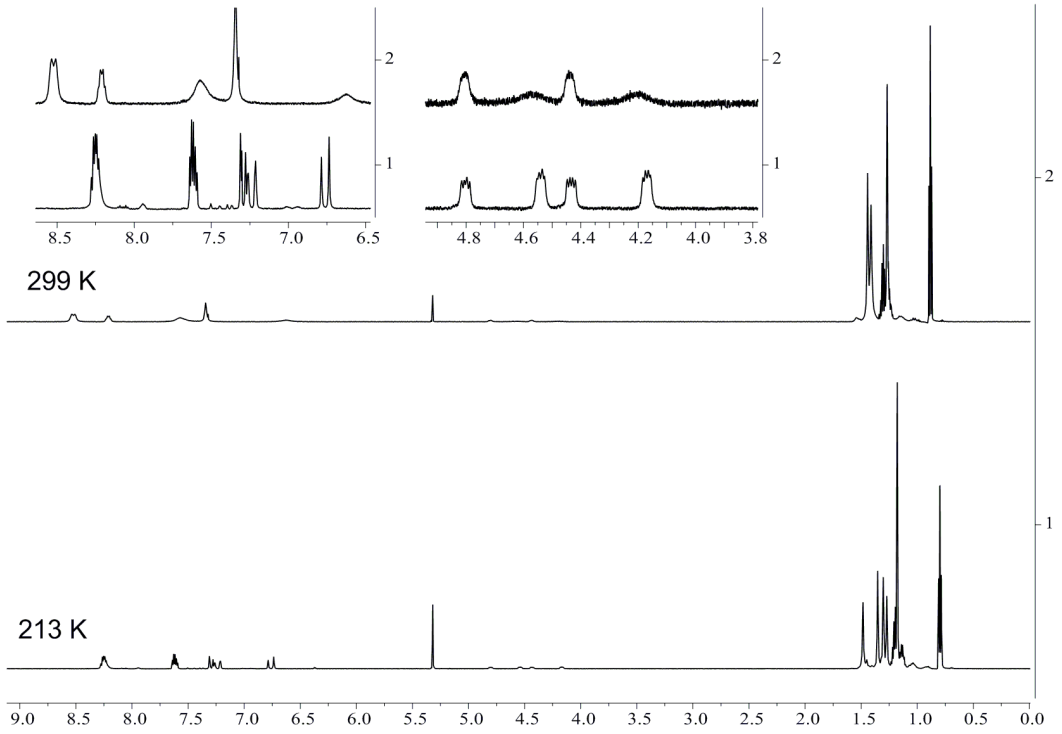


Figure S41. (1) ^{1}H NMR (600 MHz, 213 K, CD_2Cl_2) and (2) ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectra of compound **12** [admixed with p: pentane].

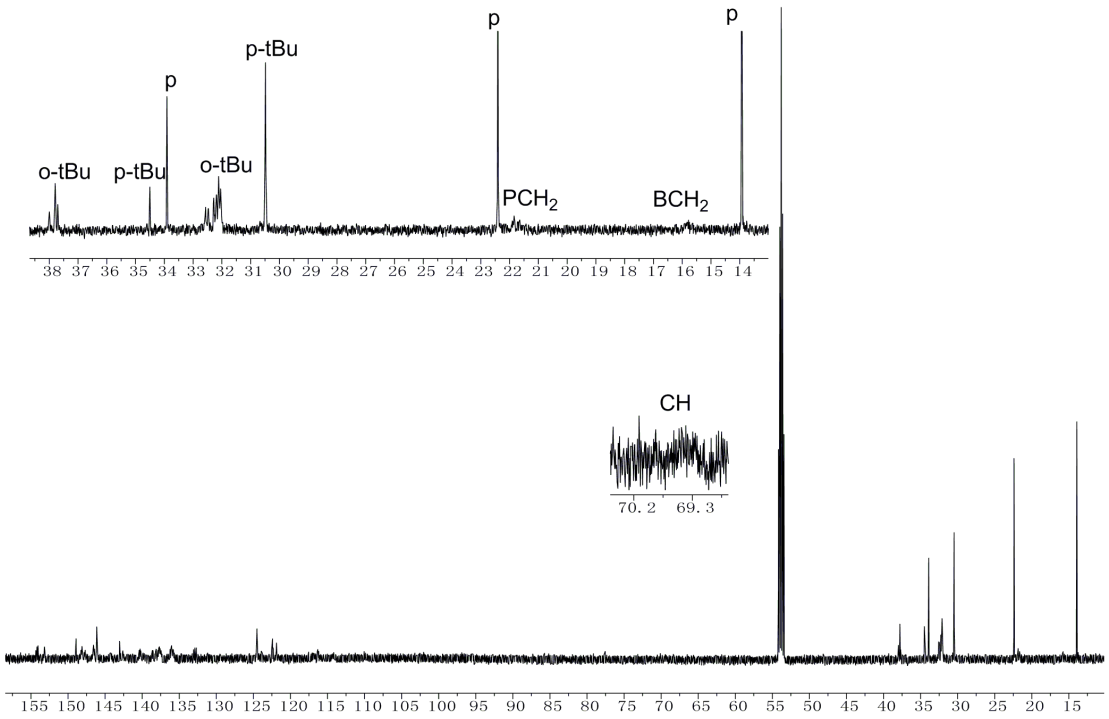


Figure S42a. $^{13}C\{^{1}H\}$ NMR (151 MHz, 213 K, CD_2Cl_2) spectrum of compound **12**[admixed with p: pentane].

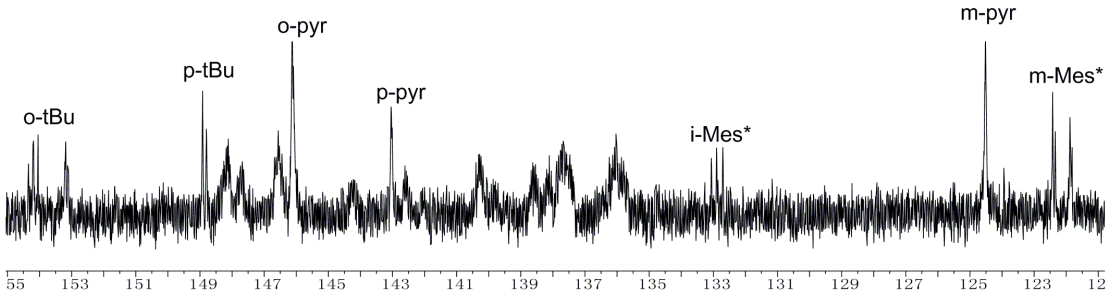


Figure S42b. $^{13}C\{^{1}H\}$ NMR (151 MHz, 213 K, CD_2Cl_2) spectrum of compound **12**.

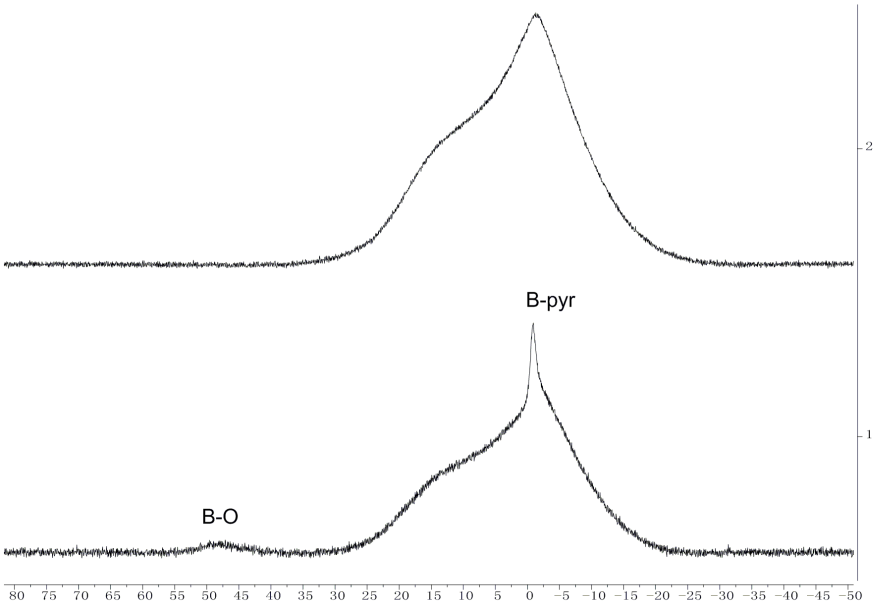


Figure S43. (1) $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) and (2) $^{11}B\{^{1}H\}$ NMR (192 MHz, 213 K, CD_2Cl_2) spectra of compound **12**.

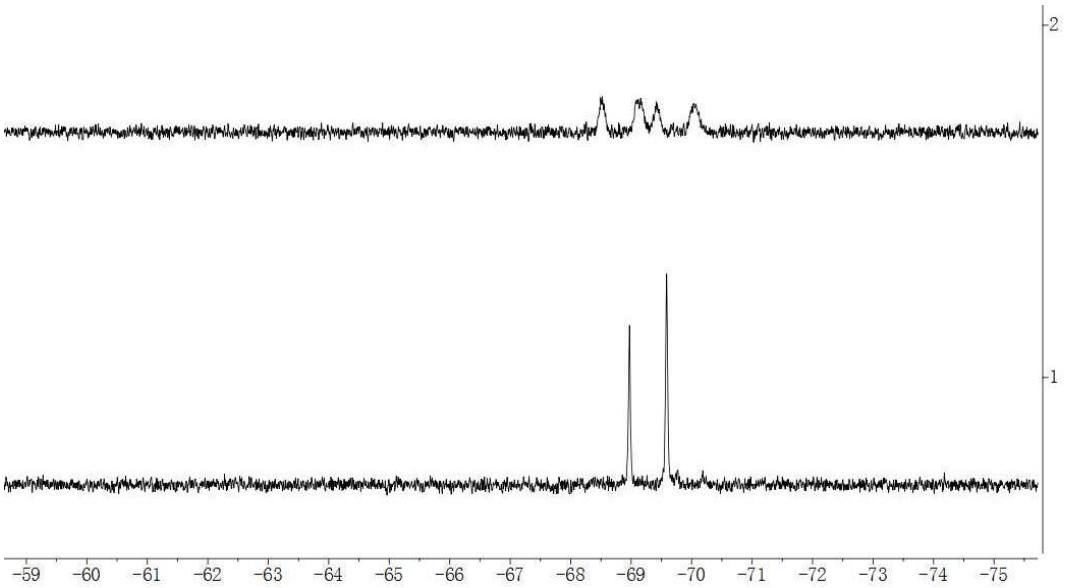


Figure S44. (1) $^{31}P\{^{1}H\}$ NMR and (2) ^{31}P NMR (243 MHz, 213 K, CD_2Cl_2) spectrum of compound **12**.

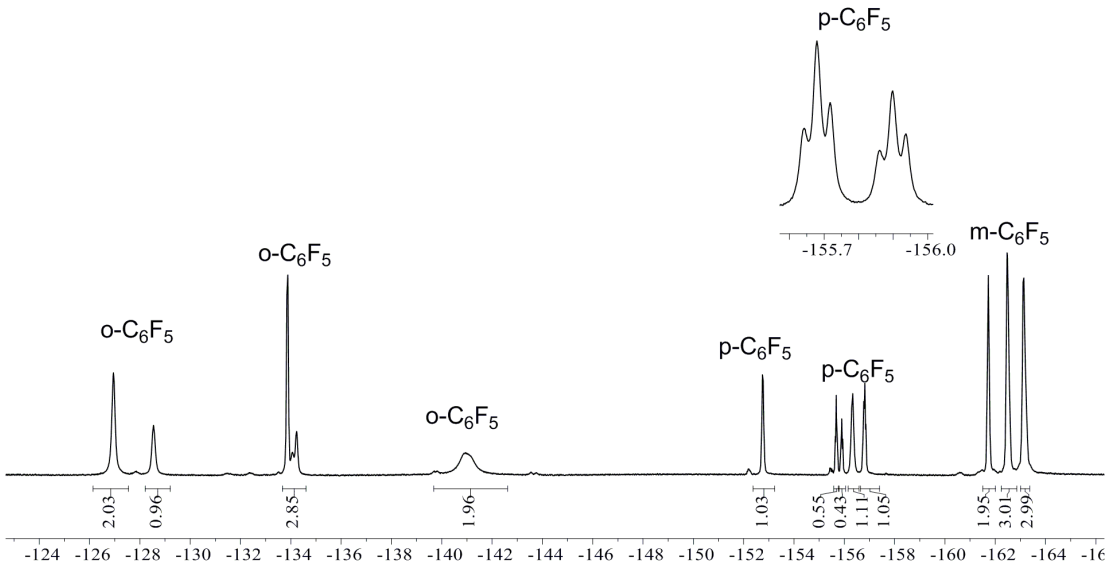


Figure S45. ^{19}F NMR (564 MHz, 213 K, CD_2Cl_2) spectrum of compound **12**.

Crystals of compound **12** suitable for the X-ray crystal structure analysis were obtained from a solution of the obtained white solid in *n*-pentane at room temperature.

X-ray crystal structure analysis of compound 12 (erk9804): A colorless needle-like specimen of $C_{55}H_{52}B_2F_{20}NOP$, approximate dimensions 0.064 mm x 0.109 mm x 0.240 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Mo ImS (MoK_α, $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 510 frames were collected. The total exposure time was 7.08 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 54600 reflections to a maximum θ angle of 26.74° (0.79 Å resolution), of which 11528 were independent (average redundancy 4.736, completeness = 99.8%, $R_{int} = 6.86\%$, $R_{sig} = 4.68\%$) and 8012 (69.50%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.4179(5) Å, b = 15.1109(6) Å, c = 17.2639(6) Å, α = 112.9100(10)°, β = 99.4230(10)°, γ = 106.4220(10)°, volume = 2721.35(18) $Å^3$,

are based upon the refinement of the XYZ-centroids of 9105 reflections above 20 σ(I) with 4.835° < 2θ < 53.35°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.904. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9630 and 0.9900. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{55}H_{52}B_2F_{20}NOP$. The final anisotropic full-matrix least-squares refinement on F^2 with 784 variables converged at R1 = 4.29%, for the observed data and wR2 = 11.44% for all data. The goodness-of-fit was 1.009. The largest peak in the final difference electron density synthesis was 0.292 $e^-/Å^3$ and the largest hole was -0.388 $e^-/Å^3$ with an RMS deviation of 0.054 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.435 g/cm^3 and F(000), 1204 e^-. The hydrogen at P1 atom was refined freely. CCDC number: 2054475.

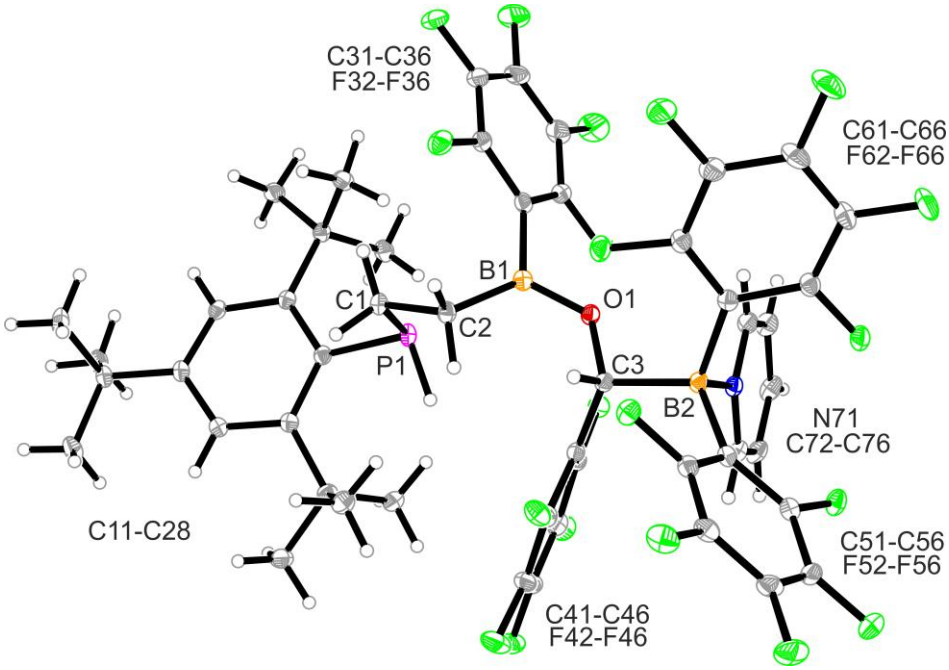
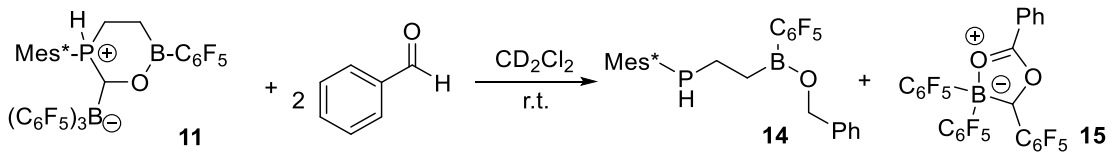


Figure S46. Crystal structure of compound **12** (thermal ellipsoids are set at 30% probability).

Synthesis of compounds 14 and 15



Scheme S8

*1st Experiment: in situ reaction of compound **11** with benzaldehyde:*

A solution of benzaldehyde (21.2 mg, 0.2 mmol) in CD_2Cl_2 (0.5 mL) was dropwise added to the solution of compound **11** (102.4 mg, 0.1 mmol) in CD_2Cl_2 (0.5 mL). After the reaction mixture was transferred into a *J*-Young valve NMR tube, it was stored at r.t. for 48 hours. The obtained light yellow solution was then characterized by NMR experiments.

Comment: A mixture of compound **14** and compound **15** were detected (conversion ca. 90%, ratio ca. 41 : 59 (^{1}H)).

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) of compound **14**: δ = 7.38 (s, 2H, *m*-Mes*), 7.35 (m, 2H, *m*-Ph), 7.31 (m, 3H, *p*,*o*-Ph), 5.10 (s, 2H, OCH_2), 4.77 (ddd, $^1J_{PH}$ = 221.1 Hz, J = 10.5 Hz, J = 6.1 Hz, 1H, PH), [1.68, 1.42](each m, each 1H, PCH_2), 1.52 (s, 18H, *o*-^{t}Bu), [1.41, 1.31](each m, each 1H, BCH_2)^t, 1.29 (s, 9H, *p*-^{t}Bu), [^{t} tentatively assigned]

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) of compound **15**: δ = 8.31 (m, 2H, *o*-Ph), 7.93 (m, 1H, *p*-Ph), 7.68 (m, 2H, *m*-Ph), 6.89 (s, 1H, CH).

^{13}C{^{1}H} NMR (151 MHz, 299K, CD_2Cl_2) of compound **14**: δ = 155.0 (d, $^2J_{PC}$ = 8.0 Hz, *o*-Mes*), 149.7 (*p*-Mes*), 138.2 (*i*-Ph), 133.7 (dm, $^1J_{PC}$ ~ 31 Hz, *i*-Mes*), 128.9 (*m*-Ph), 128.3 (*p*-Ph), 127.1 (*o*-Ph), 122.5 (d, $^3J_{PC}$ = 3.9 Hz, *m*-Mes*), 70.5 (br, OCH_2), [38.7, 33.6 (d, $^4J_{PC}$ = 7.0 Hz)](*o*-^{t}Bu), [35.2, 31.4](*p*-^{t}Bu), 21.6 (d, $^1J_{PC}$ = 13.0 Hz, PCH_2), 19.5 (br, BCH_2), [C_6F_5 not listed].

^{13}C{^{1}H} NMR (151 MHz, 299K, CD_2Cl_2) of compound **15**: δ = 180.7 (C=O), 139.0 (*p*-Ph), 132.7 (*o*-Ph), 130.2 (*m*-Ph), 121.2 (*i*-Ph), 80.7 (br, CH), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 48.1 ($\nu_{1/2}$ ~ 600 Hz, compound **14**), 4.7 ($\nu_{1/2}$ ~ 250 Hz, compound **15**).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -65.9 ($\nu_{1/2}$ ~ 33 Hz, compound **14**).

^{31}P NMR (243 MHz, 299 K, CD_2Cl_2): δ = -65.9 (br d, $^1J_{PH}$ ~ 222 Hz, compound **14**).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compound **14** (40 mol%): δ = -133.0 (m, 2F, *o*-C_6F_5), -153.5 (t, $^3J_{FF}$ = 20.2 Hz, *p*-C_6F_5), -162.3 (br, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{m,p}$ = 8.8].

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) of compound **15** (60 mol%): δ = [-134.4, -134.9, -141.7](each m, each 2F, *o*-C_6F_5), [-153.4 (t, $^3J_{FF}$ = 20.8 Hz), -156.4 (t, $^3J_{FF}$ = 20.2 Hz), -157.0 (t, $^3J_{FF}$ = 20.1 Hz)](each 1F, *p*-C_6F_5), [-162.1, -163.8, -163.9](each m, each 2F, *m*-C_6F_5).

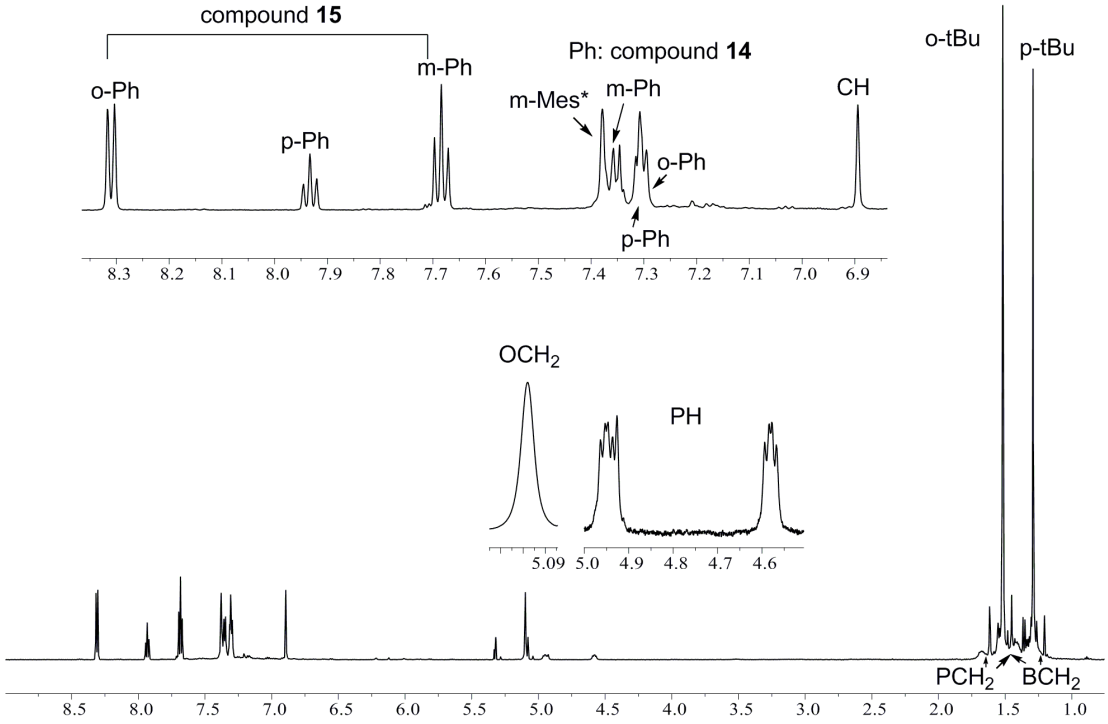


Figure S47. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of the reaction of compound **11** and benzaldehyde.

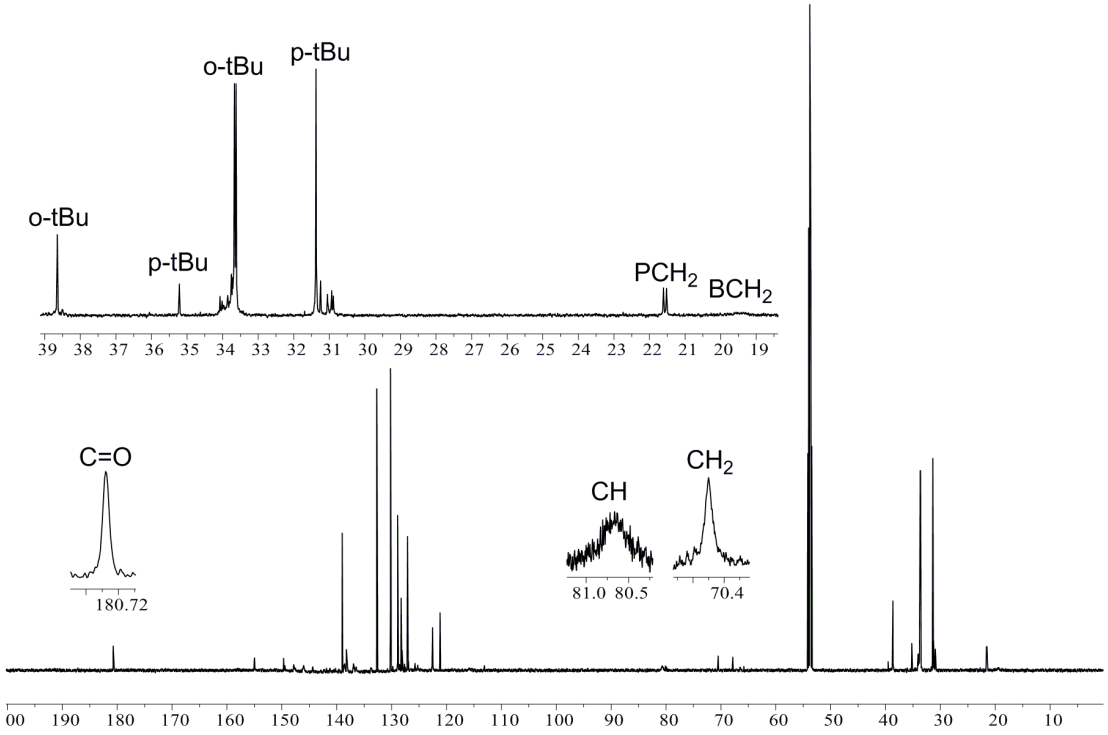


Figure S48a. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of the reaction of compound **11** and benzaldehyde.

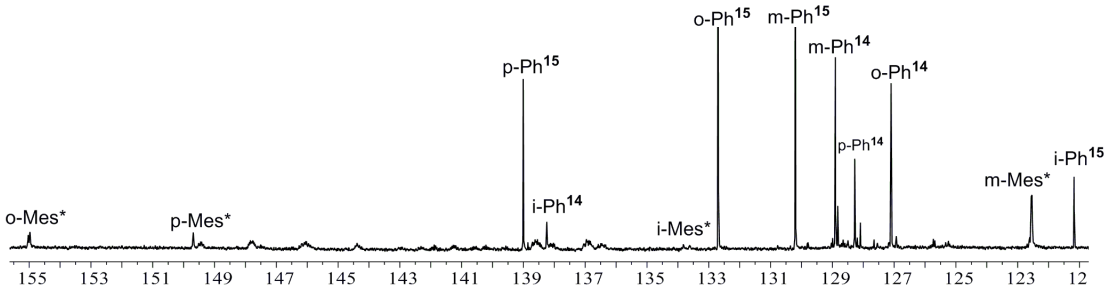


Figure S48b. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of the reaction of compound **11** and benzaldehyde.

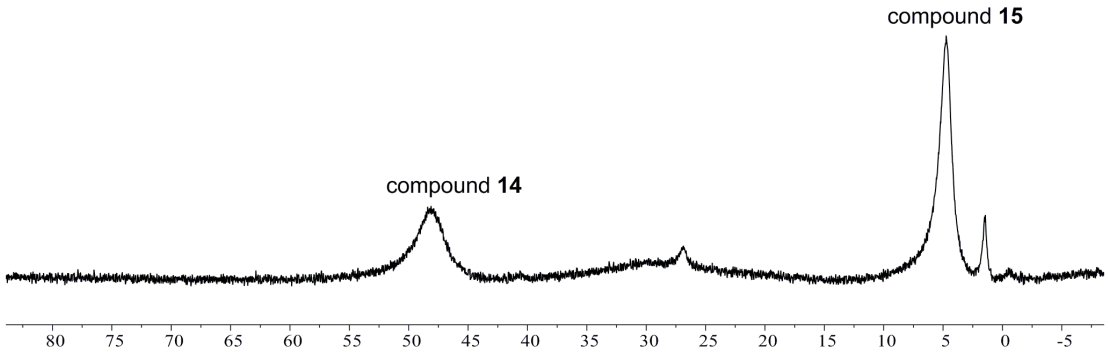


Figure S49. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of the reaction of compound **11** and benzaldehyde.

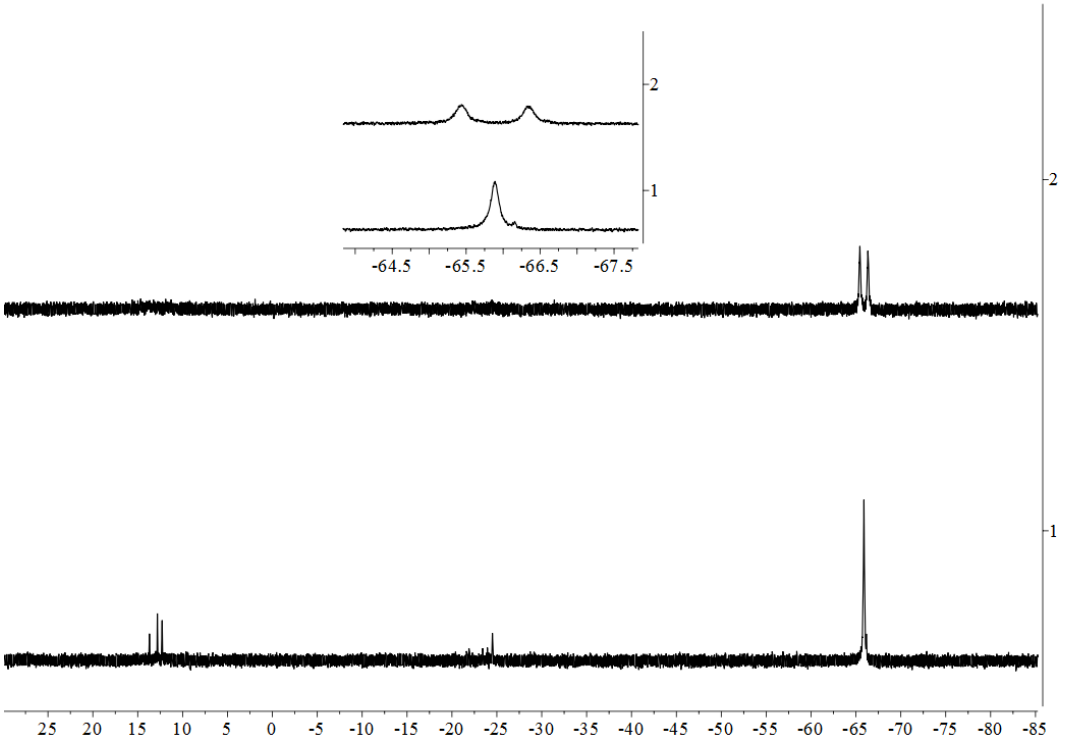


Figure S50. (1) $^{31}P\{^{1}H\}$ NMR and ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectra of the reaction of compound **11** and benzaldehyde.

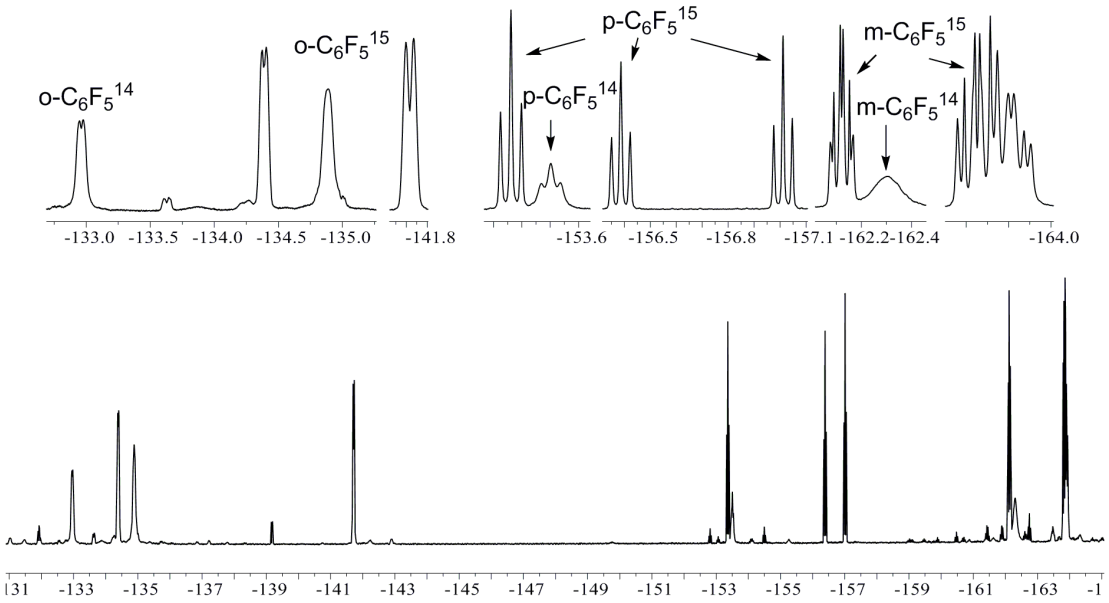


Figure S51. $^{19}F\{^{1}H\}$ NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of the reaction of compound **11** and benzaldehyde.

2nd Experiment: *synthesis of compound **15**:*

A solution of benzaldehyde (21.2 mg, 0.2 mmol) in CH_2Cl_2 (0.5 mL) was dropwise added to the solution of compound **11** (116.6 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL). After the reaction mixture was stirred at r.t. for 48 h, a clear colorless solution was obtained. All volatiles were removed in *vacuo*. *n*-Pentane (1 mL) was added to the residue and the solution was kept at r.t. to give compound **15** as a colorless crystalline solid (51.0 mg, 79%).

Characterization of compound **15**:

Elemental analysis: calc. for $C_{26}H_6BF_{15}O_2$ (646.12 g/mol): C, 48.33; H, 0.94. Found: C, 49.43, H, 1.37.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 8.30 (m, 2H, *o*-Ph), 7.93 (m, 1H, *p*-Ph), 7.68 (m, 2H, *m*-Ph), 6.88 (s, 1H, CH).

^{13}C{^{1}H} NMR (151 MHz, 299K, CD_2Cl_2): δ = 180.7 (C=O), 139.0 (*p*-Ph), 132.7 (*o*-Ph), 130.2 (*m*-Ph), 121.2 (*i*-Ph), 80.6 (br, CH), [C_6F_5 not listed]

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 4.4 ($\nu_{1/2}$ ~ 150 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = [-134.4, -134.9, -141.8](each m, each 2F, *o*-C_6F_5), [-153.4 (t, $^{3}J_{FF}$ = 20.8 Hz), -156.4 (t, $^{3}J_{FF}$ = 20.2 Hz), -157.0 (t, $^{3}J_{FF}$ = 20.1 Hz)](each 1F, *p*-C_6F_5), [-162.1, -163.87, -163.93](each m, each 2F, *m*-C_6F_5).

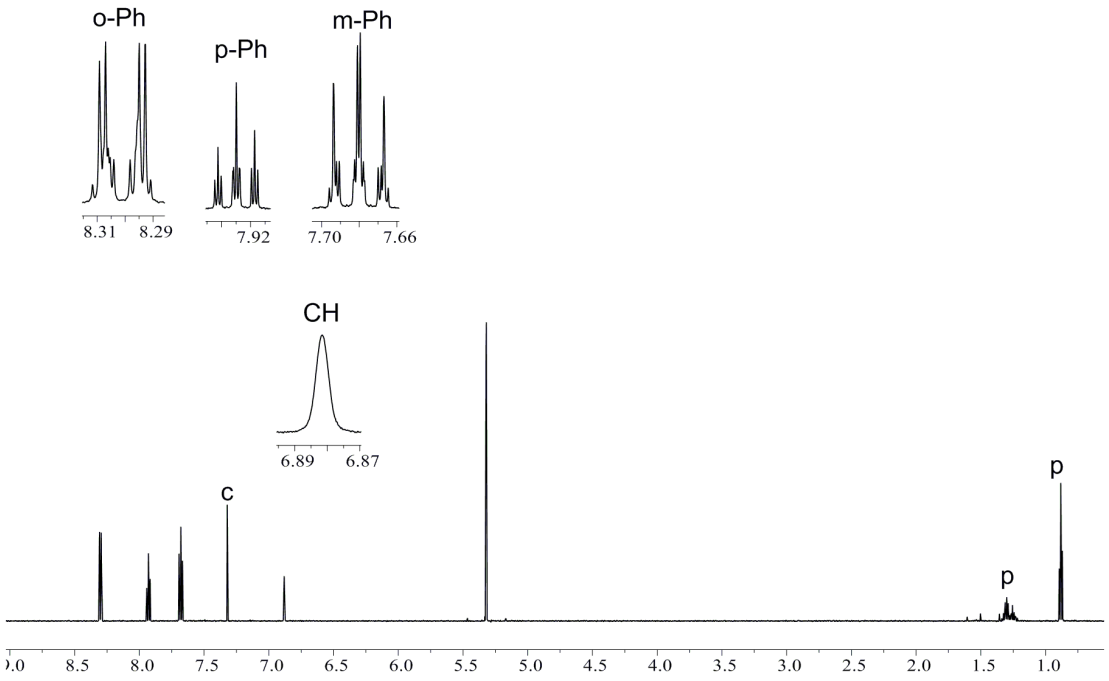


Figure S52. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **15** [admixed with c: chloroform, p: pentane].

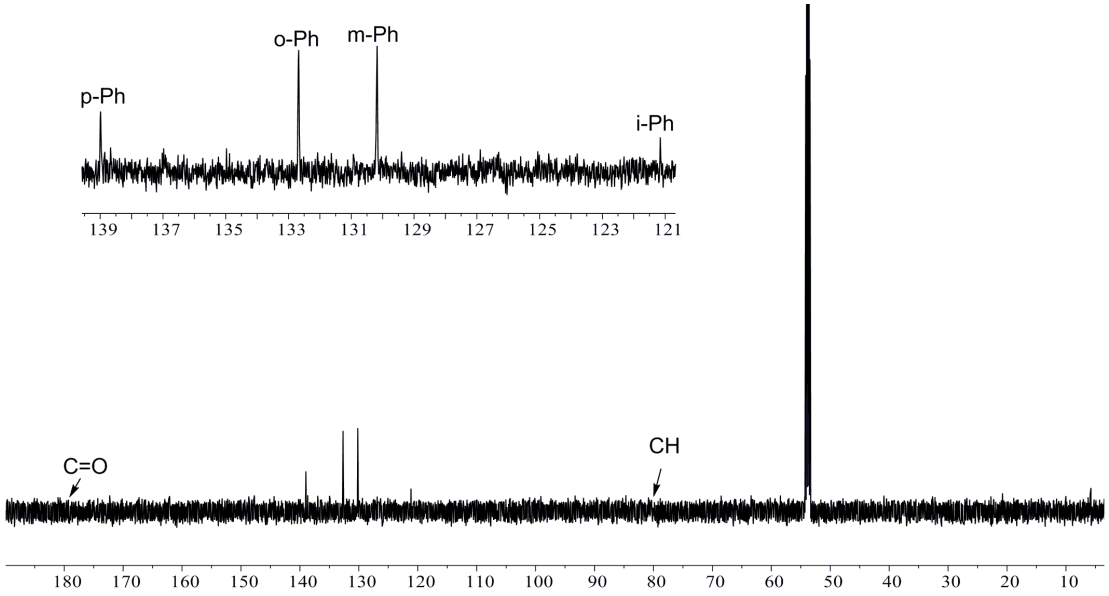


Figure S53. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **15**.

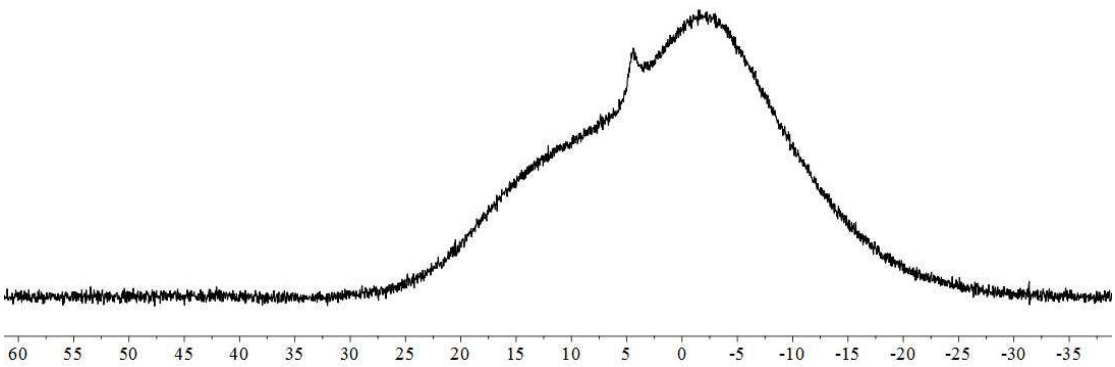


Figure S54. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **15**.

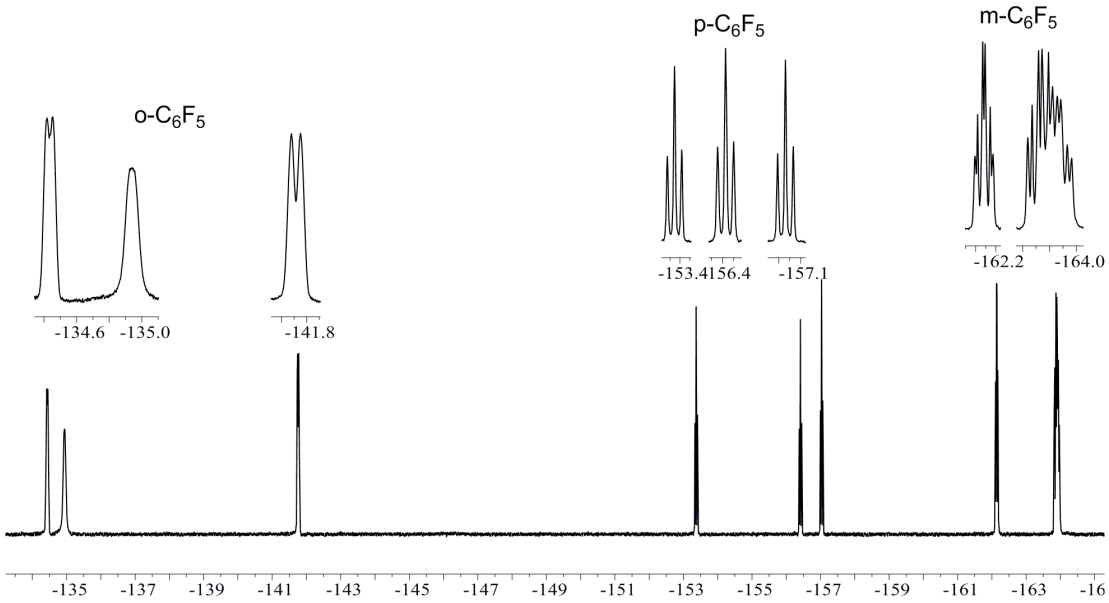


Figure S55. $^{19}F\{^{1}H\}$ NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **15**.

Crystals of compound **15** suitable for the X-ray crystal structure analysis were obtained from a solution of the obtained crystalline material in *n*-pentane at room temperature.

X-ray crystal structure analysis of compound 15 (erk9778): A colorless prism-like specimen of $C_{26}H_6BF_{15}O_2$, approximate dimensions 0.066 mm x 0.143 mm x 0.282 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Mo Ims (MoK_α, $\lambda = 0.71073$ Å) and a MX mirror monochromator. A total of 510 frames were collected. The total exposure time was 5.67 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 49237 reflections to a maximum θ angle of 26.73° (0.79 Å resolution), of which 10393 were independent (average redundancy 4.738, completeness = 97.8%, $R_{int} = 2.97\%$, $R_{sig} = 2.11\%$) and 9046 (87.04%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.4022(2) Å, b = 12.8441(2) Å, c = 15.9843(3) Å, α = 87.8420(10)°, β = 87.6030(10)°, γ = 79.3800(10)°, volume = 2499.25(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 9835 reflections above 20 σ(I) with 6.871° < 2θ < 53.45°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.962. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9500 and 0.9880. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 4 for the formula unit, $C_{26}H_6BF_{15}O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 848 variables converged at R1 = 3.80%, for the observed data and wR2 = 9.82% for all data. The goodness-of-fit was 1.042. The largest peak in the final difference electron density synthesis was 0.426 $e^-/Å^3$ and the largest hole was -0.227 $e^-/Å^3$ with an RMS deviation of 0.043 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.717 g/cm^3 and F(000), 1272 e^-. CCDC number: 2054476.

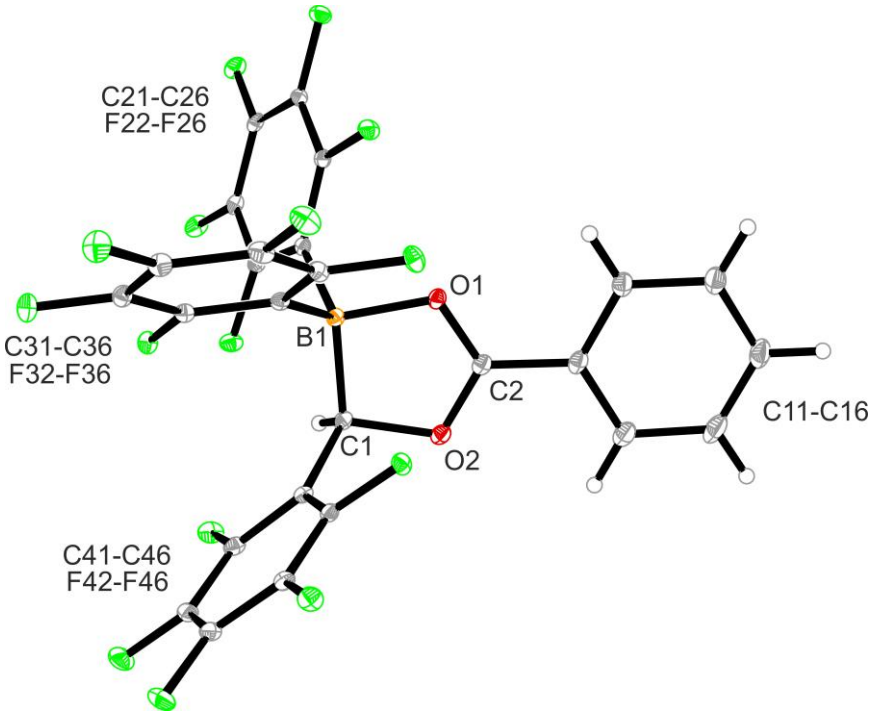
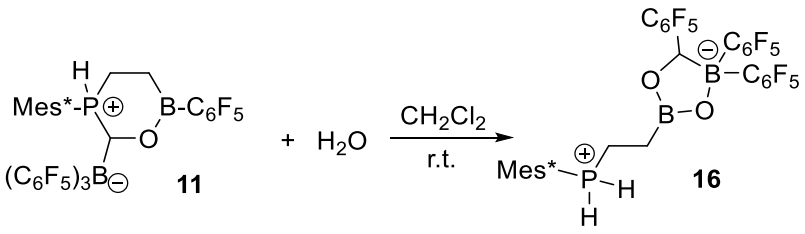


Figure S56. Crystal structure of compound **15** (Only one molecule (molecule "A") of two found in the asymmetric unit is shown. Thermal ellipsoids are set at 15% probability).

Synthesis of compound 16



Scheme S9

A solution of water (1.8 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise to a solution of compound **11** (102.4 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL) at r.t. After the reaction mixture was stirred at r.t. for 48 h, a clear colorless solution was obtained. Then all volatiles were removed in *vacuo*, *n*-pentane (1 mL) was added to the residue and the solution was kept at r.t. to give a colorless crystalline solid (63.3 mg, 75%).

Characterization of compound **16**:

HRMS for $C_{39}H_{37}B_2F_{15}O_2P$ $[M+H]^+$: calc. 875.24723; found: 875.24797.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = [7.98 (ddd, $^1J_{PH}$ = 521.7 Hz, J = 10.3 Hz, J = 3.4 Hz), 7.70 (dd, $^1J_{PH}$ = 510.0, J = 10.3 Hz)](each 1H, PH), 7.70 (d, $^4J_{PH}$ = 4.5 Hz, *m*-Mes*), 6.11 (s, 1H, CH), [2.64, 2.53](each m, each 1H, PCH_2), 1.61 (s, 18H, *o*-^{t}Bu), [1.47, 1.42](each m, each 1H, BCH_2), 1.36 (s, 9H, *p*-^{t}Bu).

^{13}C{^{1}H} NMR (151 MHz, 299K, CD_2Cl_2): δ = 158.2 (m, *p*-Mes*), 158.0 (m, *o*-^{t}Bu), 125.3 (dm, $^3J_{PC}$ ~ 13 Hz, *m*-Mes*), 107.8 (br d, $^1J_{PC}$ ~ 63 Hz, *i*-Mes*), 71.6 (br, CH), [38.5 (m), 33.8](*o*-^{t}Bu), [36.1, 30.9](*p*-^{t}Bu), 21.4 (dm, $^1J_{PC}$ ~ 54 Hz, PCH_2), 8.3 (br, BCH_2), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 33.8 ($\nu_{1/2}$ ~ 800 Hz, BO_2), 1.3 ($\nu_{1/2}$ ~ 90 Hz, BO).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -24.5 (m).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = -24.5 (tm, $^1J_{PH}$ ~ 520 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = [134.3 (m), -135.8 (br), -142.9 (m)](each 2F, *o*-C_6F_5), [-160.5 (t, $^3J_{FF}$ = 20.8 Hz), -161.4 (t, $^3J_{FF}$ = 20.7 Hz), -161.5 (t, $^3J_{FF}$ = 20.7 Hz)](each 1F, *p*-C_6F_5), [-165.5, -165.7, -166.0](each m, each 2F, *m*-C_6F_5).

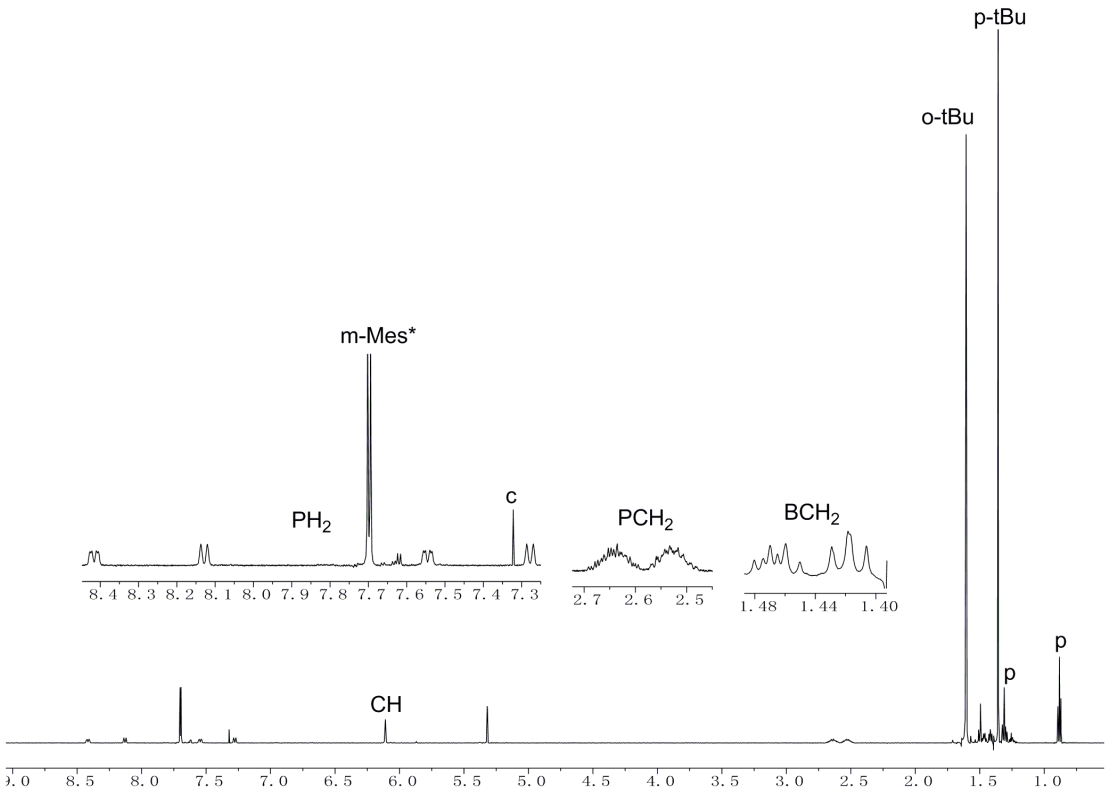


Figure S57. ^{1}H NMR (600 MHz, 299 K, CD_2Cl_2) spectrum of compound **16** [admixed with c: chloroform and p: pentane].

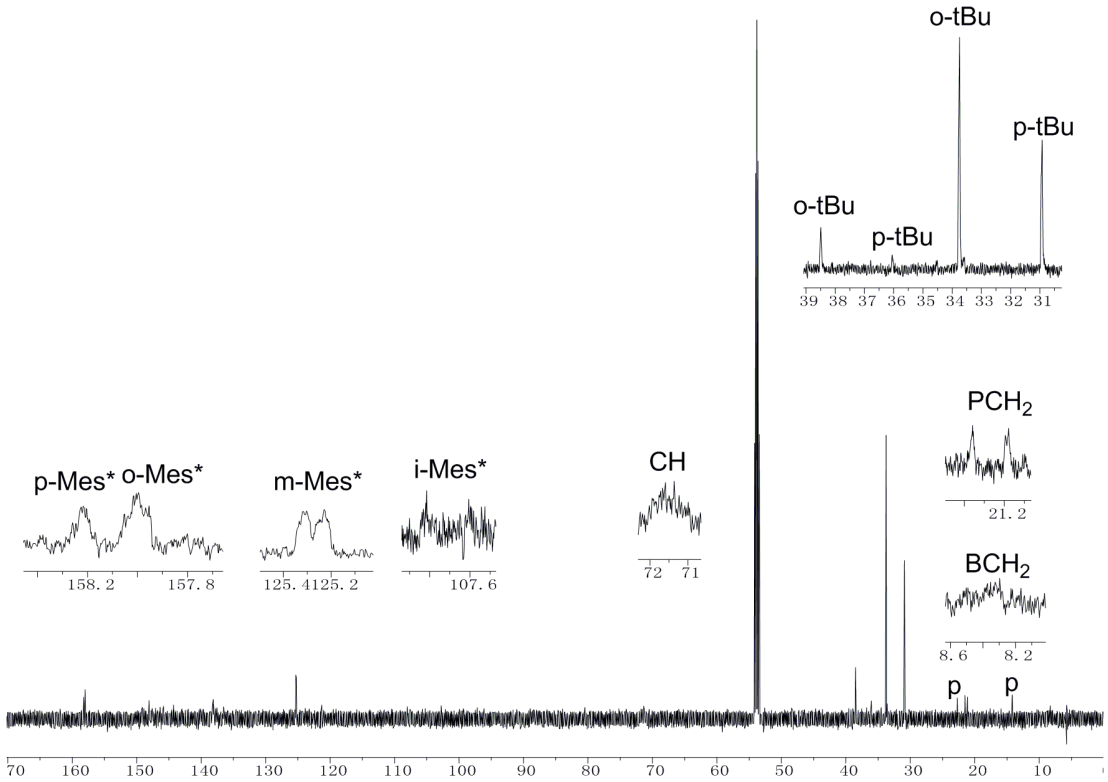


Figure S58. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2) spectrum of compound **16** [admixed with p: pentane].

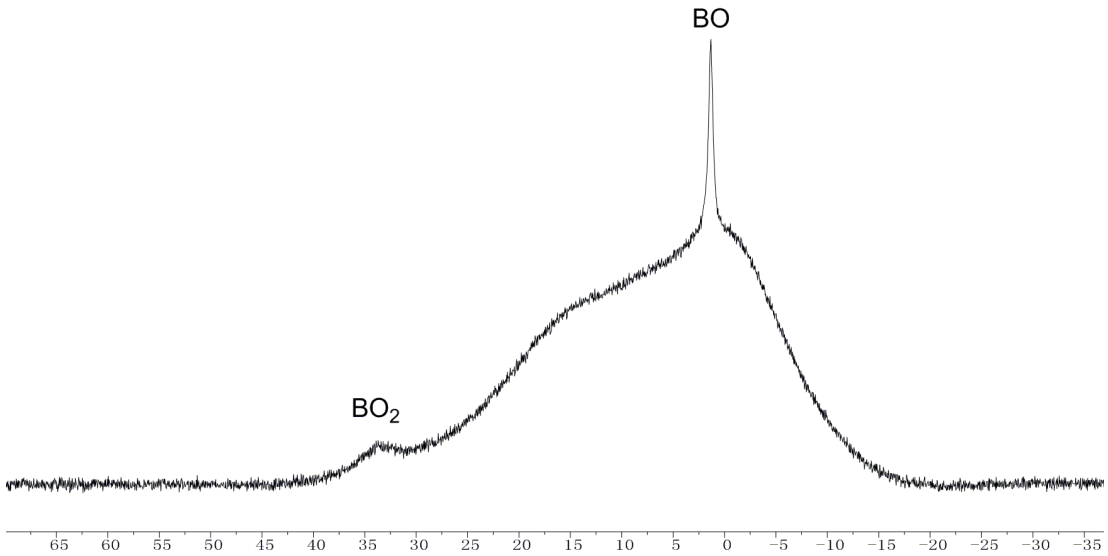


Figure S59. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, CD_2Cl_2) spectrum of compound **16**.

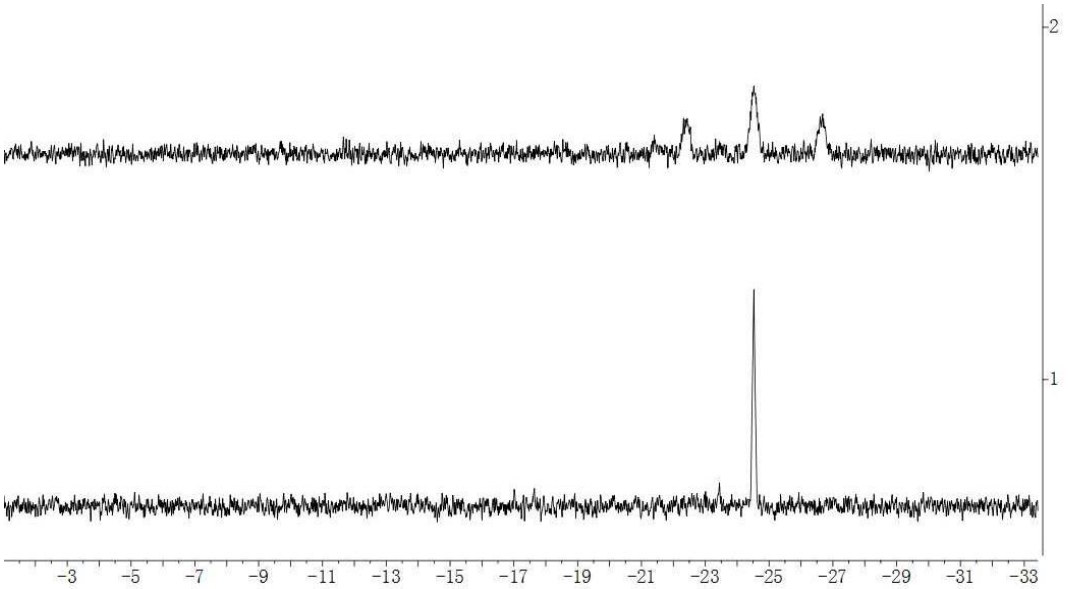


Figure S60. (1) $^{31}P\{^{1}H\}$ NMR and (2) ^{31}P NMR (243 MHz, 299 K, CD_2Cl_2) spectrum of compound **16**.

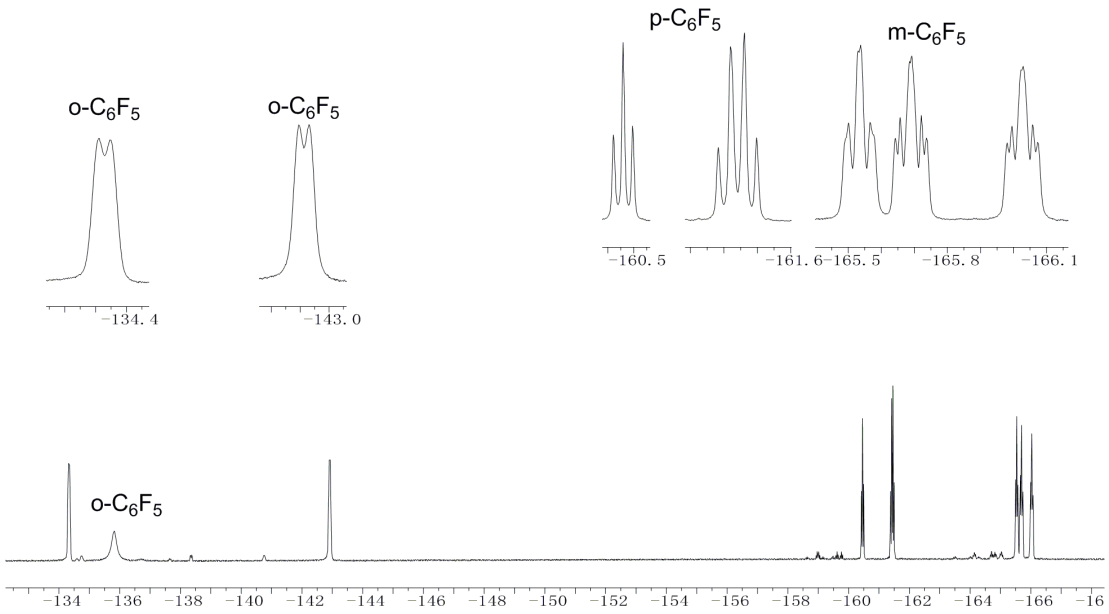


Figure S61. ^{19}F NMR (564 MHz, 299 K, CD_2Cl_2) spectrum of compound **16**.

Crystals of compound **16** suitable for the X-ray crystal structure analysis were obtained from a solution of the obtained crystalline material in *n*-pentane at room temperature.

X-ray crystal structure analysis of compound 16 (erk9773): A colorless needle-like specimen of $C_{39}H_{36}B_2F_{15}O_2P$, approximate dimensions 0.074 mm x 0.087 mm x 0.226 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture PHOTON III Diffractometer system equipped with a micro focus tube Cu Ims (CuK_α, λ = 1.54178 Å) and a MX mirror monochromator. A total of 1540 frames were collected. The total exposure time was 21.21 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 34069 reflections to a maximum θ angle of 66.59° (0.84 Å resolution), of which 7008 were independent (average redundancy 4.861, completeness = 95.7%, R_{int} = 4.37%, R_{sig} = 3.33%) and 6074 (86.67%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.7803(2) Å, b = 14.9792(3) Å, c = 15.1373(3) Å, α = 119.3560(10)°, β = 99.0210(10)°, γ = 93.5650(10)°, volume = 2076.51(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 9829 reflections above 20 σ(I) with 6.810° < 2θ < 136.4°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.894. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7280 and 0.8970. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{39}H_{36}B_2F_{15}O_2P$. The final anisotropic full-matrix least-squares refinement on F^2 with 549 variables converged at R1 = 3.41%, for the observed data and wR2 = 8.66% for all data. The goodness-of-fit was 1.064. The largest peak in the final difference electron density synthesis was 0.275 $e^-/Å^3$ and the largest hole was -0.312 $e^-/Å^3$ with an RMS deviation of 0.044 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.398 g/cm^3 and F(000), 892 e^-. The hydrogens at P1 atom were refined freely. CCDC number: 2054477.

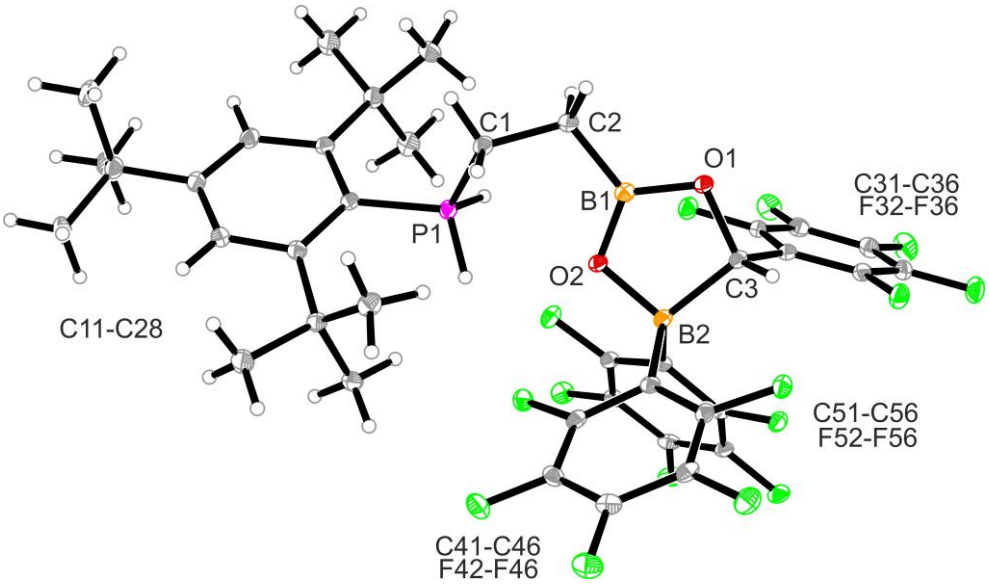


Figure S62. Crystal structure of compound **16** (thermal ellipsoids are set at 30% probability).

Reference

1. *APEX3* (**2016**), *SAINT* (**2015**) and *SADABS* (**2015**), Bruker AXS Inc., Madison, Wisconsin, USA.
2. G. M. Sheldrick, *SHELXT – Integrated space-group and crystal-structure determination*, *Acta Cryst.,* 2015, **A71**, 3-8.
3. G.M. Sheldrick, *Crystal structure refinement with SHELXL*, *Acta Cryst.*, 2015, **C71 (1)**, 3-8.