Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Rare Olefin 1,1-Carboboration Reaction Opens a Synthetic Pathway to an Unusually Structured Frustrated Lewis Pair

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General information

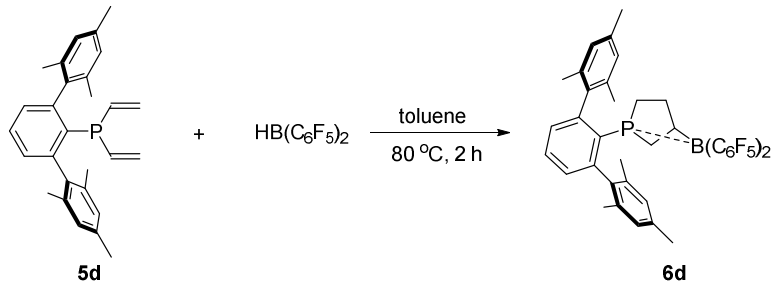
All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Toluene, CH_2Cl_2, pentane and THF were dried using a Grubbs-type solvent purification system with alumina spheres as the drying agent. All solvents were stored under an argon atmosphere. NMR spectra were recorded on a Varian Inova 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{31}P: 243 MHz, ^{19}F: 564 MHz, ^{11}B: 192 MHz). ^{1}H NMR and ^{13}C NMR: chemical shifts δ are given relative to tetramethylsilane (δ^1H = 0, δ^{13}C = 0) and referenced to the solvent signal. ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (external reference, δ^{31}P (H_3PO_4) = 0). ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (external reference, δ^{19}F ($CFCl_3$) = 0). ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference, δ^{11}B ($BF_3{\cdot}Et_2O$) = 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 DSC 2010 (TA-instruments). HRMS was recorded using a Thermo Scientific Orbitrap LTQ XL machine.

X-Ray diffraction:[1-7] Data sets for compounds **5d**, **15** and **19** were collected with a Bruker D8 Venture CMOS diffractometer. For compound **17** 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). For compounds **12** and **16** 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, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution *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) and graphics, *XP* (Version 5.1,

Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compound **12** one C_6F_5 group and for compound **15** one pentane molecule 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 **12** a mixture of badly disordered pentane and dichloromethane molecules was found 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.

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]. Compounds **5a** and **5b** were prepared according to a procedure reported in the literature. [Y. Hasegawa, G. Kehr, S. Ehrlich, S. Gremme, C. G. Daniliuc, G. Erker, *Chem. Sci*. **2018**, *9*, 1544-1550]. Compounds **5c** and **5d** were prepared according to a procedure reported in the literature. [L. Wang, S. Dong, C. G. Daniliuc, L. Liu, S. Gremme, R. Knitsch, H. Eckert, M. R. Hansen, G. Kehr, G. Erker, *Chem. Sci*. **2018**, *9*, 1544-1550].

1. Synthesis of compound 6d and the structure of compound 5d



Scheme S1

In a Schlenk flask (25 mL), compound **5d** (0.796 g, 2.0 mmol, 1.0 equiv.) and $HB(C_6F_5)_2$ (0.69 g, 2.0 mmol, 1.0 equiv.) were mixed and toluene (5 mL) was added. The mixture was stirred at 80 ºC (oil bath temperature) for 2 h to give a clear yellow solution. The solution was filtered and all volatiles were removed in vacuo. The resulting compound **6** was obtained as a light yellow solid (1.42 g, 95%).

Comment: in order to get a purer product, pentane (3 mL) was added to the obtained yellow solid and the resulting suspension was kept at -35 ºC for 24 hours. A white solid (0.9 g, 60 %) was obtained after removal of solvent and washing with cold pentane (3 × 1 mL).

Elemental analysis (%) calc. for $C_{40}H_{32}BF_{10}P$: C, 64.54; H, 4.33. Found: C, 64.31; H, 4.32.

Decomp. point: 168 ºC

NMR data of compound **6d** were obtained from a solution of the isolated white solid in toluene-d_8.

[Mes: mesityl]

^{1}**H NMR** (600 MHz, 299 K, toluene-d_8) δ 6.98 (tm, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-C_6H_3), [6.77, 6.43](each s, each 2H, *m*-Mes), 6.58 (dm, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-C_6H_3), 2.33 (dm, $^3J_{PH}$ = 103.2 Hz, 1H, BCH), 2.12 (s, 6H, *p*-CH_3^{Mes}), [1.91, 1.80](each s, each 6H, *o*-CH_3^{Mes}), [1.63, 1.30](each m, each 1H, PCH_2^{CH}), [1.45, 1.03](each m, each 1H, PCH_2), 1.13 (m, 2H, CH_2).

^{13}**C{^{1}H} NMR** (151 MHz, 299 K, toluene-d_8) δ [147.5 (dm, $^1J_{FC}$ ~ 240 Hz), 140.4 (dm, $^1J_{FC}$ ~ 250 Hz), 137.4 (dm, $^1J_{FC}$ ~ 250 Hz), 116.7 (br)](C_6F_5), 147.4 (d, $^2J_{PC}$ = 8.1 Hz, *o*-C_6H_3), 138.1 (*p*-Mes), 138.0 (d, $^3J_{PC}$ = 3.0 Hz, *i*-Mes), [137.1, 135.8](*o*-Mes), 132.0 (d, $^4J_{PC}$ = 2.7 Hz, *p*-C_6H_3), 130.7 (d, $^3J_{PC}$ = 7.1 Hz, *m*-C_6H_3), 129.5 (d, $^1J_{PC}$ = 6.1 Hz, *i*-C_6H_3), [128.8, 127.9](*m*-Mes), 35.8 (d, $^1J_{PC}$ = 32.4 Hz, PCH_2^{CH}), 29.0 (br, BCH), 24.7

(d, $^{2}J_{PC}$ = 7.5 Hz, CH_2), [21.23, 21.18](*o*-CH_3^{Mes}), 20.9 (*p*-CH_3^{Mes}), 16.7 (d, $^{1}J_{PC}$ = 36.9 Hz, PCH_2).

$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, toluene-d_8) δ 5.5 ($\nu_{1/2}$ ~ 300 Hz).

^{19}F NMR (564 MHz, 299 K, toluene-d_8) δ -130.2 (br, 2F, *o*-C_6F_5), -157.8 (t, $^{3}J_{FF}$ = 20.7 Hz 1F, *p*-C_6F_5), -164.0 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}Fm,p$ = 6.1].

$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, toluene-d_8) δ = 8.8 (m).

^{31}P NMR (243 MHz, 299 K, toluene-d_8) δ 8.8 (dm, $^{3}J_{PH}$ ~ 103 Hz).

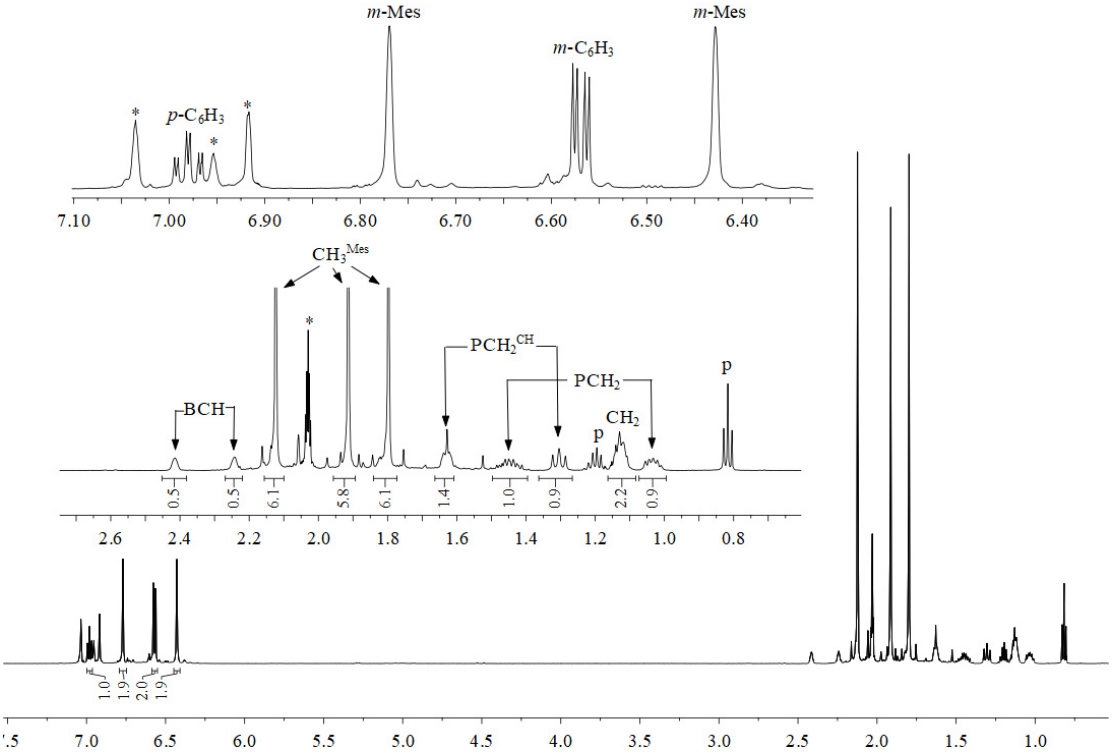


Figure S1. ^{1}H NMR (600 MHz, 299 K, toluene-d_8(*)) spectrum of compound **6d** [admixed with pentane (p)]

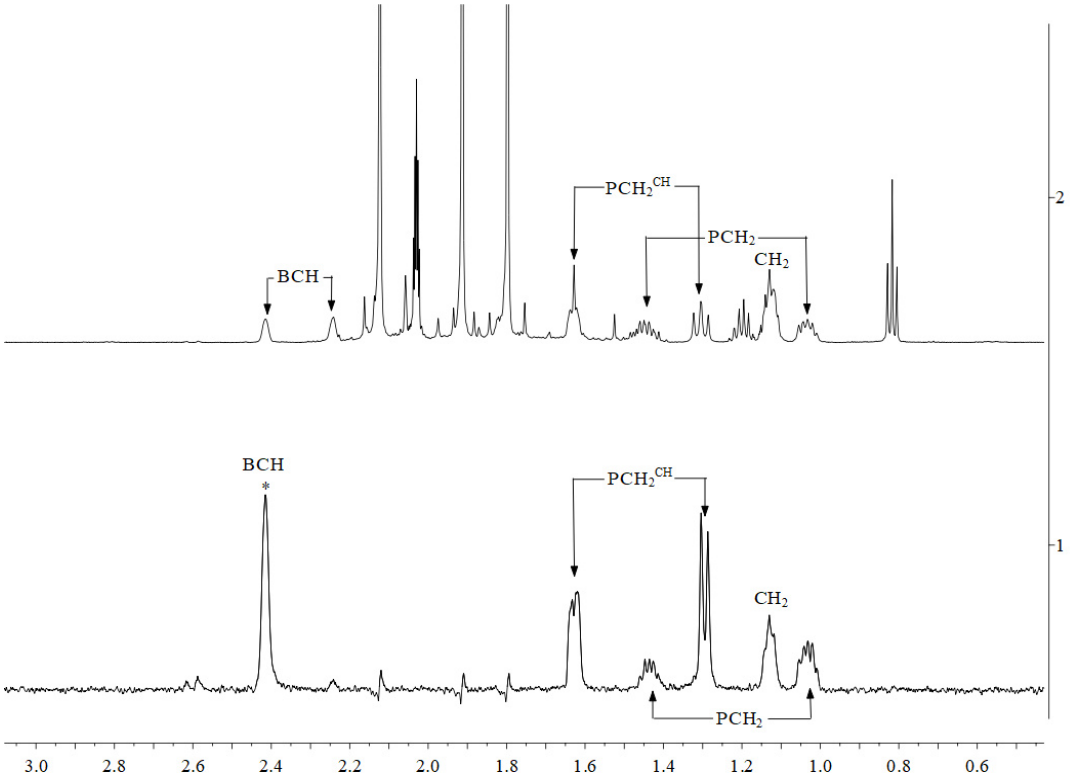


Figure S2. (1) $^{1}H\{^{1}H\}$ 1D-tocsy (600 MHz, 299 K, toluene-d_8) and (2) ^{1}H NMR (600 MHz, 299 K, toluene-d_8) spectra of compound **6d** [* irradiation at $\delta\ ^{1}H_{(irr)} = 2.41$ (BCH)]

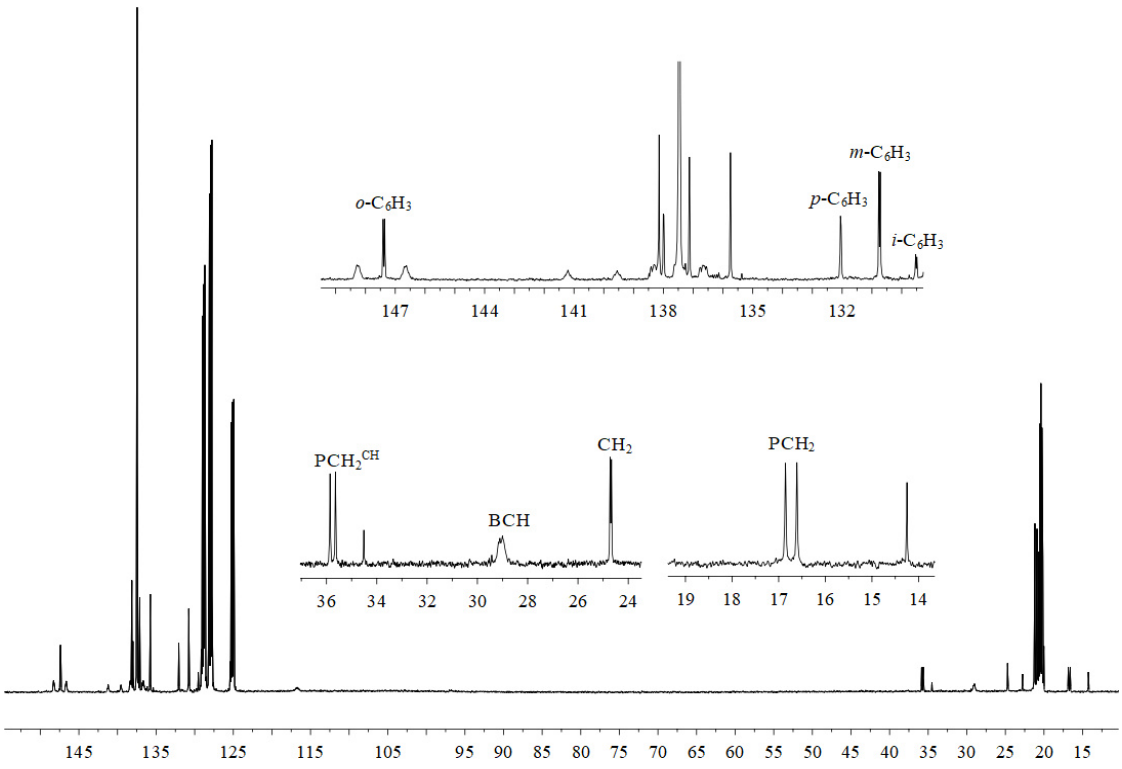


Figure S3. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, toluene-d_8) spectrum of compound **6d**

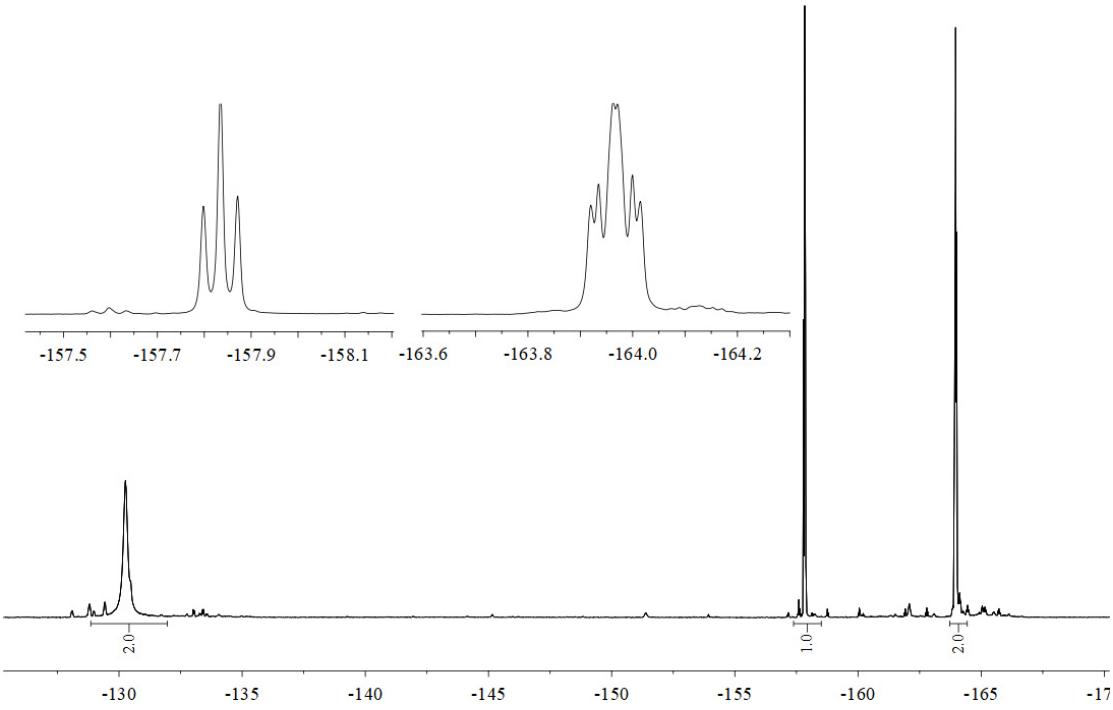


Figure S4. ^{19}F NMR (564 MHz, 299 K, toluene-d_8) spectrum of compound **6d**

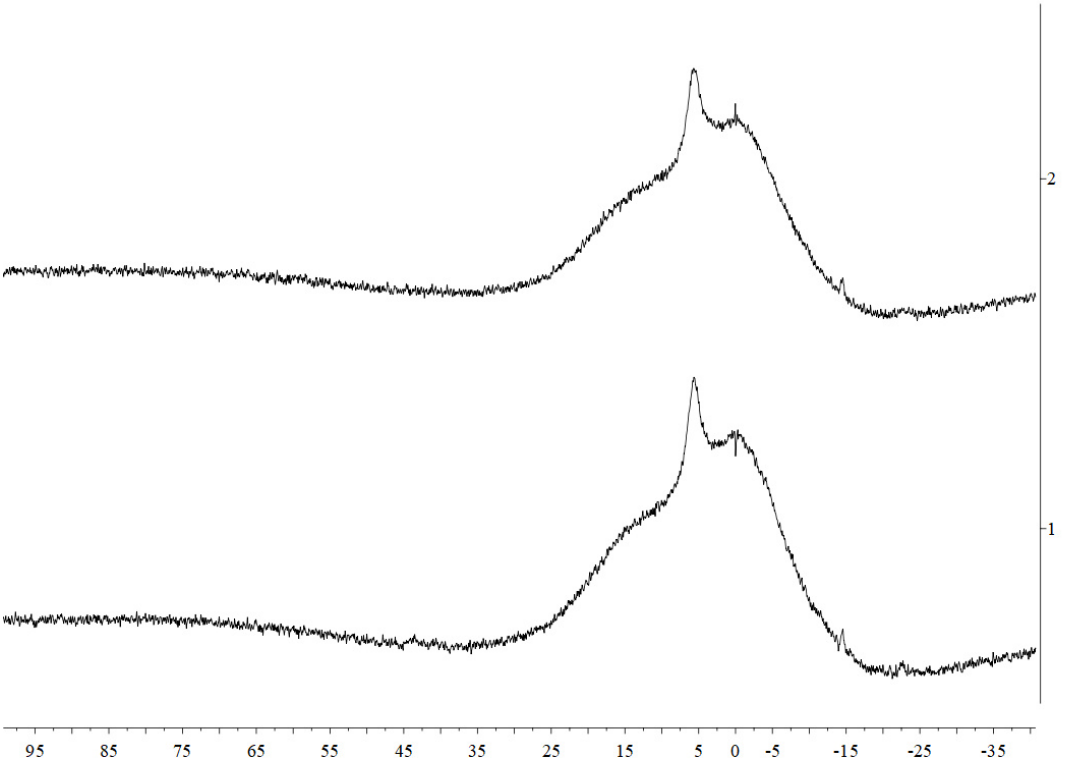


Figure S5. (1) ^{11}B{^{1}H} and (2) ^{11}B NMR (192 MHz, 299 K, toluene-d_8) spectra of compound **6d**

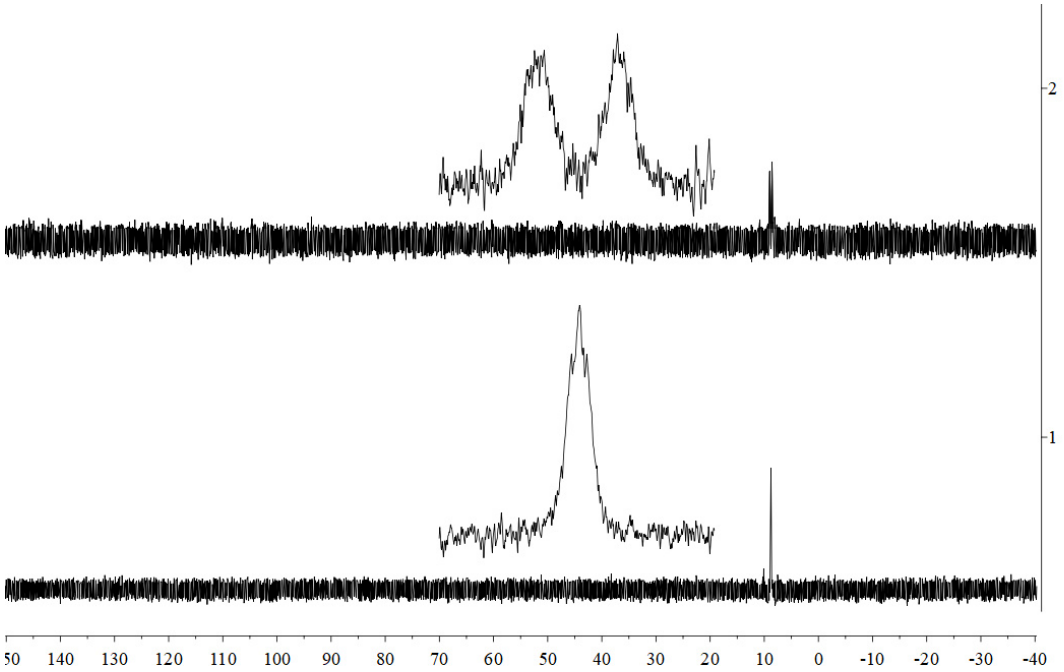


Figure S6. (1) $^{31}P\{^{1}H\}$ and (2) ^{31}P NMR (243 MHz, 299 K, toluene-d_8) spectra of compound **6d**

Crystals suitable for the X-ray crystal structure analysis for compound **5d** were obtained from a solution of compound **5d** in dichloromethane/heptane (v/v ca. 1:5) at room temperature.

X-ray crystal structure analysis of compound 5d (erk9523): A colorless prism-like specimen of $C_{28}H_{31}P$, approximate dimensions 0.162 mm x 0.266 mm x 0.267 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 470 frames were collected. The total exposure time was 2.61 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 21644 reflections to a maximum θ angle of 27.48° (0.77 Å resolution), of which 5318 were independent (average redundancy 4.070, completeness = 99.4%, R_{int} = 4.37%, R_{sig} = 3.47%) and 4688 (88.15%) were greater than $2\sigma(F^2)$. The final cell constants of $\underline{a}$ = 9.0785(3) Å, $\underline{b}$ = 10.6049(4) Å, $\underline{c}$ = 13.1636(5) Å, α = 94.492(2)°, β = 96.6290(10)°, γ = 110.7610(10)°, volume = 1167.39(7) Å^3, are based upon the refinement of the XYZ-centroids of 9964 reflections above 20 σ(I) with 5.096° < 2θ < 54.90°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.905. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9660 and 0.9790. 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, $C_{28}H_{31}P$. The final anisotropic

full-matrix least-squares refinement on F^2 with 268 variables converged at R1 = 4.40%, for the observed data and wR2 = 11.03% for all data. The goodness-of-fit was 1.047. The largest peak in the final difference electron density synthesis was 0.378 $e^-/Å^3$ and the largest hole was -0.280 $e^-/Å^3$ with an RMS deviation of 0.048 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.134 g/cm^3 and F(000), 428 e^-. CCDC number: 1953115.

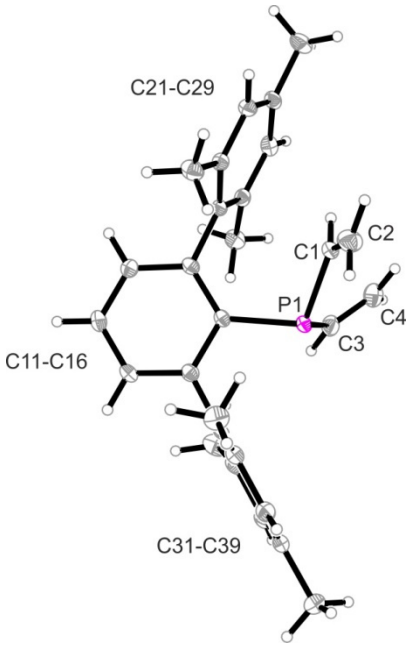
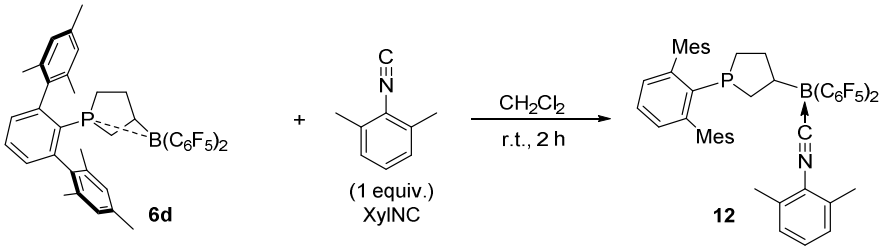


Figure S7: Crystal structure of compound **5d** (thermal ellipsoids: 50% probability).

2. Synthesis of compound 12



Scheme S2

In a vial (4 mL), compound **6d** (74.5 mg, 0.1 mmol, 1.0 equiv.) and XylNC (13.2 mg, 0.1 mmol, 1.0 equiv.) were mixed and CH_2Cl_2 (1 mL) was added. The mixture was stirred at room temperature for 2 h to give a clear light-yellow solution. All volatiles were removed in vacuo and then the residue was carefully washed with cold pentane (2 × 0.5 mL). After storing a solution of the residue in CH_2Cl_2/pentane at -35 °C for 3 days,

compound **12** (75 mg, 86%) was obtained as a white solid.

Elemental analysis (%) calc. for $C_{49}H_{41}BF_{10}NP$: C, 67.21; H, 4.72, N, 1.60. Found: C, 66.81; H, 4.62; N, 1.82.

Decomp. point: 203 °C

IR (KBr): $\tilde{\nu}$ 2255 cm^{-1}

NMR data of compound **12** were obtained from a solution of the isolated white solid in dichloromethane-d_2.

[Mes: mesityl; Xyl: 2,6-dimethylphenyl]

^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) δ 7.40 (t, $^3J_{HH}$ = 7.7 Hz, 1H, *p*-Xyl), 7.26 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-C_6H_3), 7.22 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *m*-Xyl), 6.88 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 2.1 Hz, 2H, *m*-C_6H_3), [6.77, 6.75](each m, each 2H, *m*-Mes), 2.31 (s, 6H, *o*-CH_3^{Xyl}), 2.21 (s, 6H, *p*-CH_3^{Mes}), [1.99, 1.95](each s, each 6H, *o*-CH_3^{Mes}), 1.97 (m, 1H, BCH), [1.69, 0.54](each m, each 1H, PCH_2^{CH}), [1.66 (dm, $^3J_{PH}$ ~ 34 Hz), 0.97 (m)](each 1H, CH_2), [1.38, 0.73](each m, each 1H, PCH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d_2) δ 143.6 (d, $^2J_{PC}$ = 9.8 Hz, *o*-C_6H_3), 141.2 (d, $^1J_{PC}$ = 33.8 Hz, *i*-C_6H_3), 140.3 (d, $^3J_{PC}$ = 1.5 Hz, *i*-Mes), 137.4 (*o*-Xyl), 136.8 (*p*-Mes), [136.6, 136.3](*o*-Mes), 132.2 (*p*-Xyl), 129.6 (d, $^3J_{PC}$ = 1.4 Hz, *m*-C_6H_3), 129.0 (*m*-Xyl), [128.3, 128.1](*m*-Mes), 127.1 (*p*-C_6H_3), 123.4 (br, *i*-Xyl), 32.1 (d, $^2J_{PC}$ = 15.9 Hz, CH_2), 29.1 (br, BCH), 29.1 (d, $^1J_{PC}$ = 10.4 Hz, PCH_2^{CH}), 27.3 (d, $^1J_{PC}$ = 9.0 Hz，PCH_2), [21.06 (d, $^5J_{PC}$ = 5.0 Hz), 20.99 (d, $^5J_{PC}$ = 6.2 Hz)](*o*-CH_3^{Mes}), 20.98 (*p*-CH_3^{Mes}), 18.7 (d, *J* = 4.4 Hz, *o*-CH_3^{Xyl}), [CN not observed, C_6F_5 not listed.].

^{11}B{^{1}H} NMR (192 MHz, 299 K, dichloromethane-d_2) δ -16.1 ($\nu_{1/2}$ ~ 200 Hz).

^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) δ [-131.4, -132.1](each m, each 2F, *o*-C_6F_5), [-158.95, -159.03](each t, $^3J_{FF}$ = 20.2 Hz, each 1F, *p*-C_6F_5), [-164.3, -164.5](each m, each 2F, *m*-C_6F_5).

^{31}P{^{1}H} NMR (243 MHz, 299 K, dichloromethane-d_2) δ -5.6 ($\nu_{1/2}$ ~ 3 Hz).

^{31}P NMR (243 MHz, 299 K, dichloromethane-d_2) δ -5.6 (m).

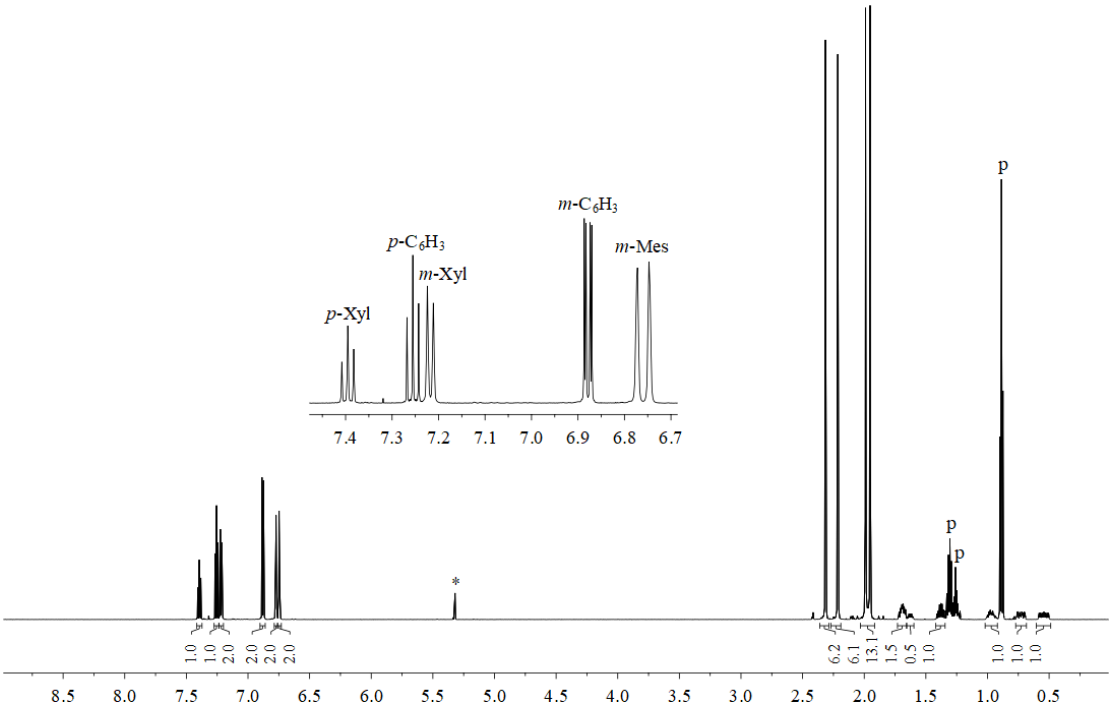


Figure S8a. ^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2(*)) spectrum of compound **12** [admixed with pentane (p)]

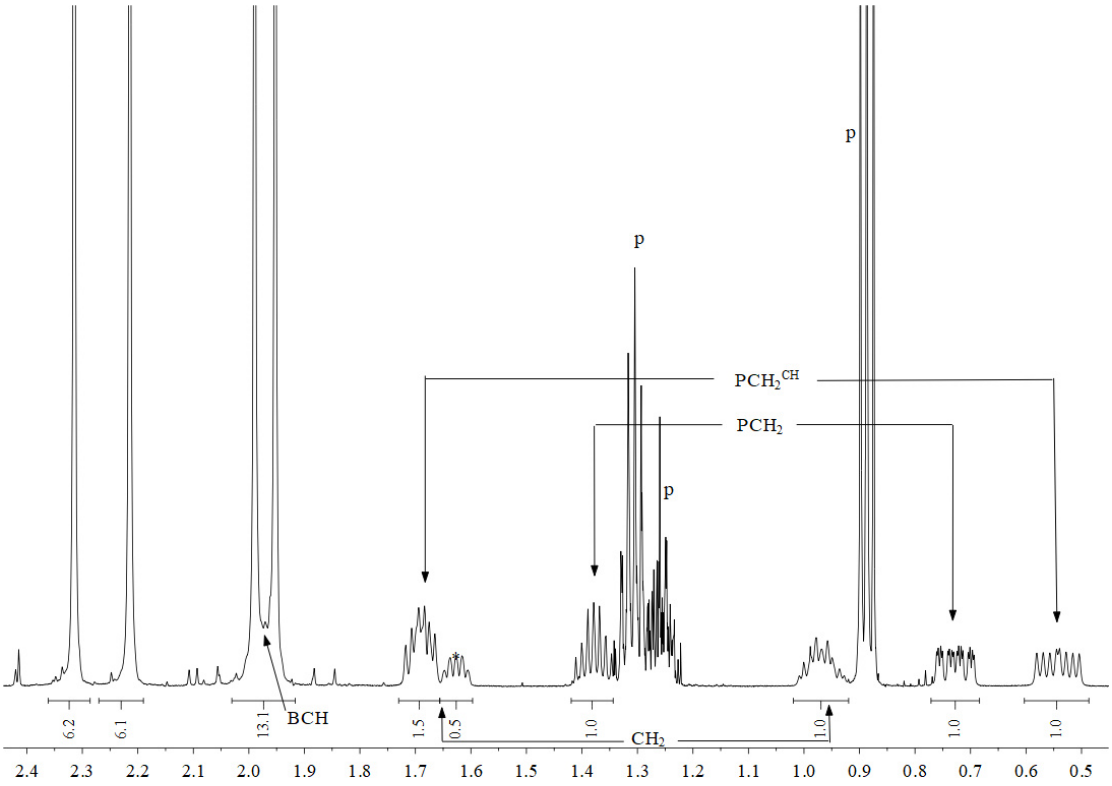


Figure S8b. ^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2(*)) spectrum of compound **12** [admixed with pentane (p)]

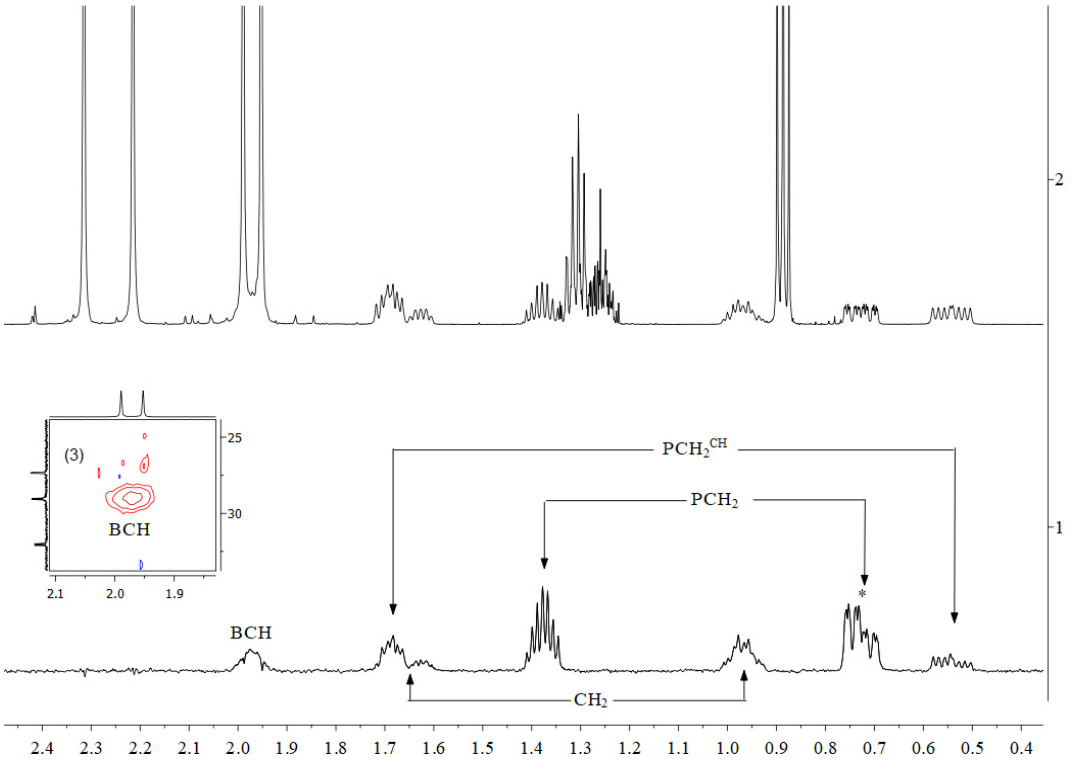


Figure S9. (1) $^{1}H\{^{1}H\}$1D-tocsy (600 MHz, 299 K, dichloromethane-d_2) spectra of compound **12**; (2) ^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) spectra of compound **12** [* irradiation at δ $^{1}H_{(irr)}$ = 0.73 (PCH_2)]; (3) $^{1}H,^{13}C$ gHSQC (600/151 MHz, 299 K, dichloromethane-d_2) spectrum of compound **12** [selected area: BCH].

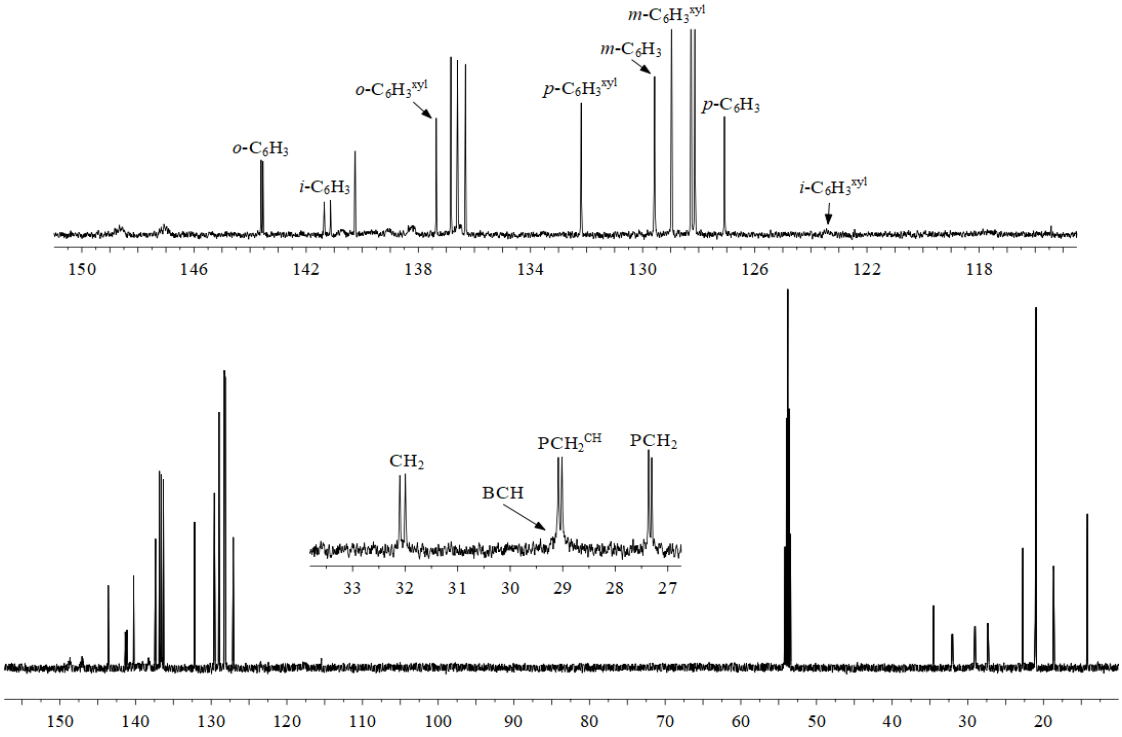


Figure S10. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2) spectrum of compound **12**

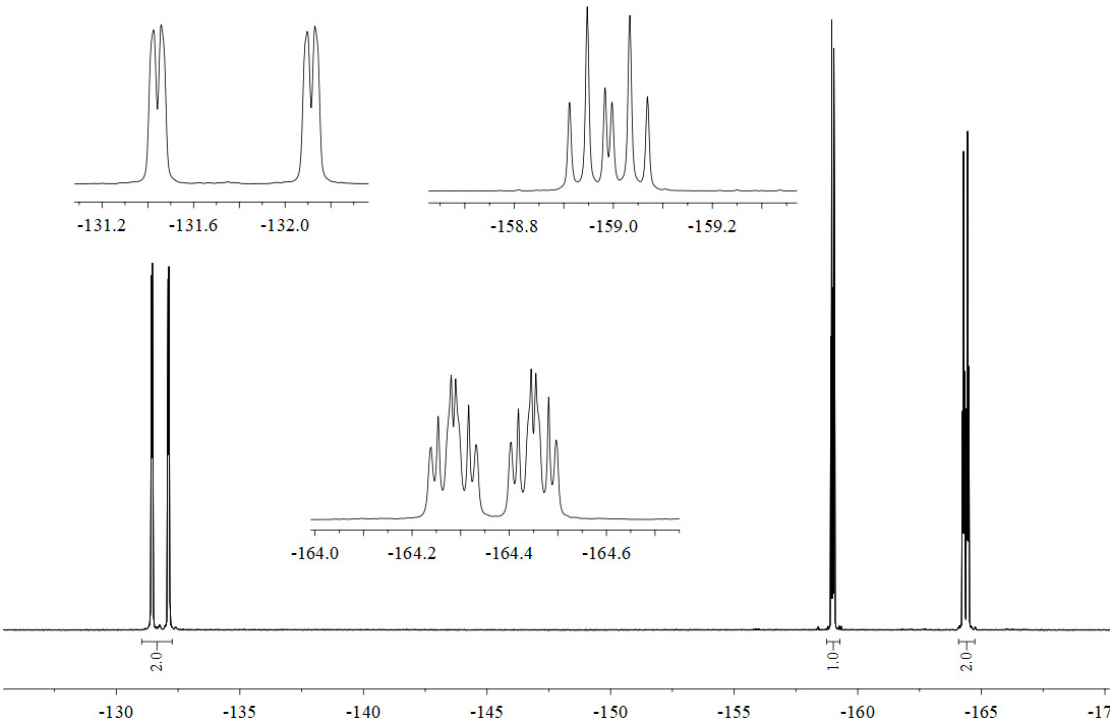


Figure S11.[19]F NMR (564 MHz, 299 K, dichloromethane-d_2) spectrum of compound **12**

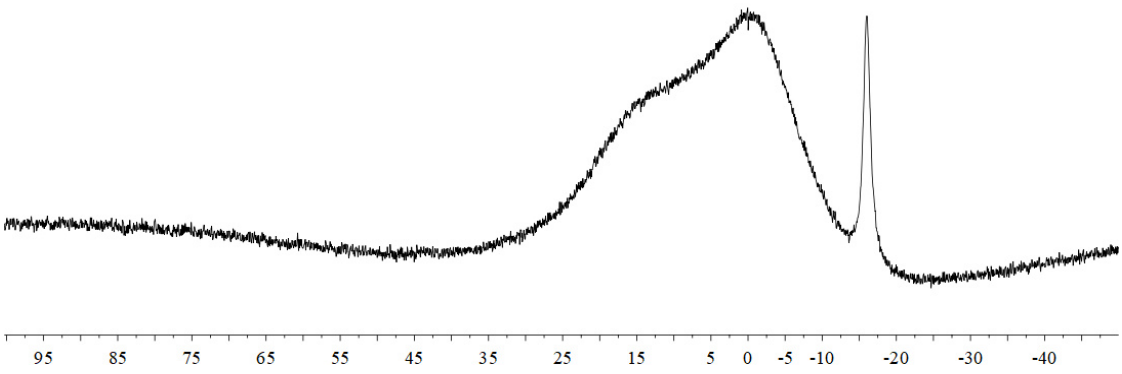


Figure S12.[11]B{[1]H} NMR (192 MHz, 299 K, dichloromethane-d_2) spectrum of compound **12**

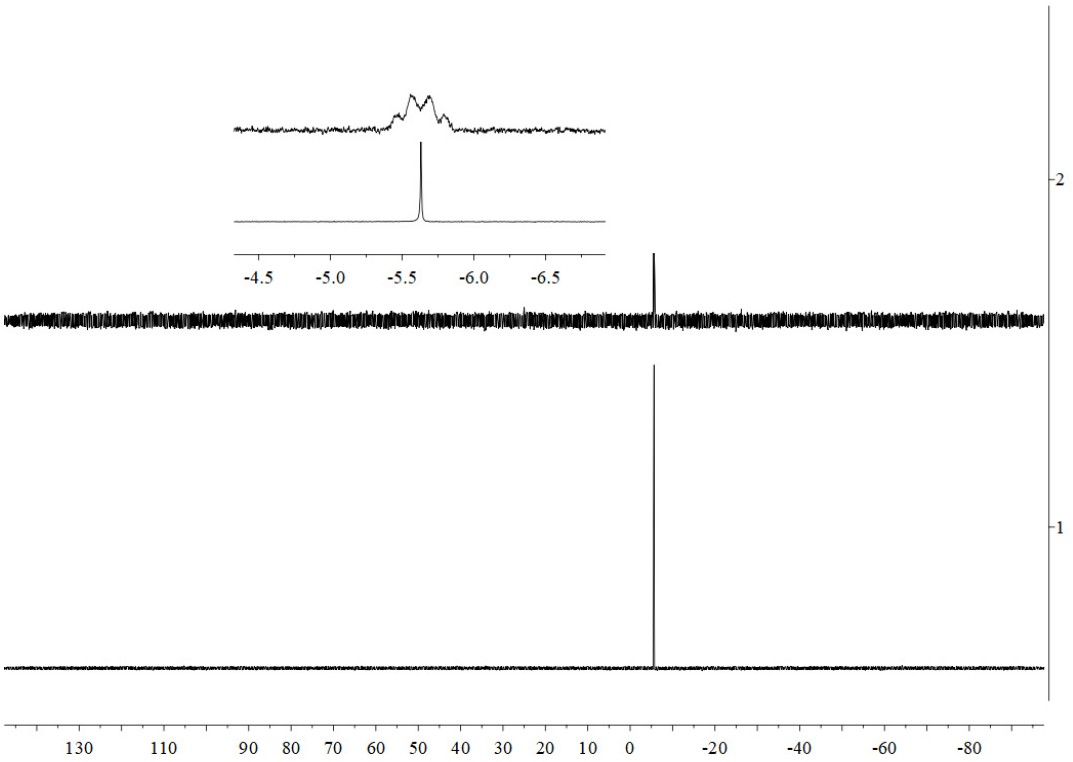


Figure S13. (1) $^{31}P\{^{1}H\}$ and (2) ^{31}P NMR (243 MHz, 299 K, dichloromethane-d_2) spectra of compound **12**

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **12** in dichloromethane/heptane (v/v ca. 1:5) at -35 °C.

X-ray crystal structure analysis of compound 12 (erk9477): A colorless plate-like specimen of $C_{49}H_{41}BF_{10}NP$, approximate dimensions 0.040 mm x 0.080 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a triclinic unit cell yielded a total of 8847 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 8847 were independent (average redundancy 1.000, completeness = 96.6%, R_{int} = 5.48%, R_{sig} = 4.66%) and 6757 (76.38%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.3195(4) Å, b = 12.0466(3) Å, c = 19.8048(8) Å, α = 78.2740(10)°, β = 83.6580(10)°, γ = 79.969(3)°, volume = 2595.93(16) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9840 and 0.9950. 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, $C_{49}H_{41}BF_{10}NP$. The final anisotropic full-matrix least-squares refinement on F^2 with 667 variables converged at R1 = 7.56%, for

the observed data and wR2 = 18.29% for all data. The goodness-of-fit was 1.065. The largest peak in the final difference electron density synthesis was 0.277 $e^-/Å^3$ and the largest hole was -0.298 $e^-/Å^3$ with an RMS deviation of 0.053 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.120 g/cm^3 and F(000), 904 e^-. CCDC number: 1953116.

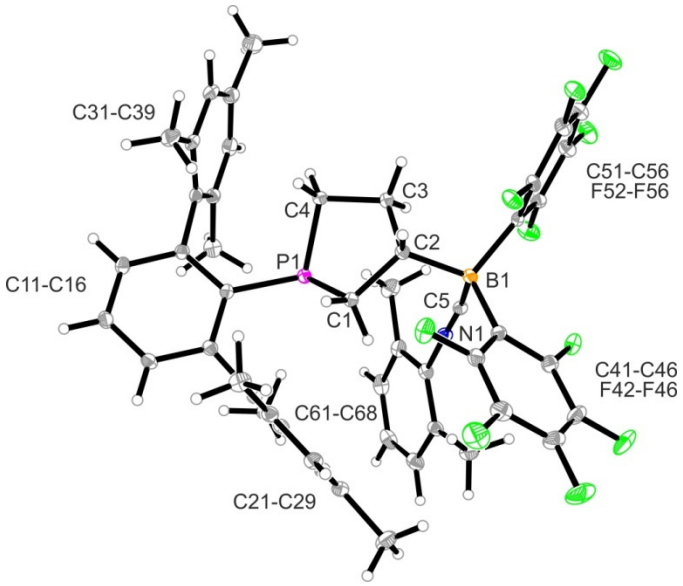
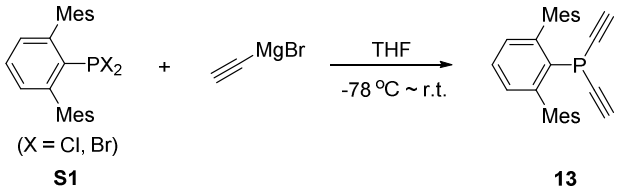


Figure S14: Crystal structure of compound **12** (thermal ellipsoids: 15% probability).

3. Deuterium-labelling experiments

3.1. Synthesis of compound 13



Scheme S3

The *in-situ* generated dihalogeno(2,4-dimesitylphenyl)phosphane (**S1**; ca. 10 mmol) [L. Wang, S. Dong, C. G. Daniliuc, L. Liu, S. Grimme, R. Knitsch, H. Eckert, M. R. Hansen, G. Kehr, G. Erker, *Chem. Sci*. **2018**, *9*, 1544-1550] was dissolved in THF (50 mL) and cooled to -78 °C. Then ethynylmagnesium bromide (44 mL, 22 mmol, 0.5 M THF solution) was added to the solution at -78 °C while vigorously stirring. The reaction mixture was further stirred for 48 h while slowly warming to room temperature. Subsequently all volatiles were removed in vacuo. The obtained residue was dissolved

in pentane (100 mL) and filtered through a pad of Celite. All volatiles were evaporated in vacuo to give a crude brown oil, which was purified by column chromatography using silica gel (pentane : dichloromethane = 10:1 to 4:1). Compound **13** was obtained as a light yellow solid (1.9 g, 50%).

HRMS: *m/z* calc. for $C_{28}H_{27}P[H^+]$ 395.19231, found 395.19208.

NMR data of compound **13** from a solution of the obtained light yellow solid in dichloromethane-d_2.

[Mes: mesityl]

^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2): δ 7.55 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-C_6H_3), 7.08 (dd, $^3J_{HH}$ = 7.6, $^4J_{PH}$ = 3.1 Hz, 2H, *m*-C_6H_3), 6.90 (m, 4H, *m*-Mes), 2.79 (s, 2H, HC≡), 2.34 (s, 6H, *p*-CH_3^{Mes}), 2.02 (s, 12H, *o*-CH_3^{Mes}).

^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d_2) δ 147.7 (d, $^2J_{PC}$ = 21.1 Hz, *o*-C_6H_3), 138.7 (d, $^3J_{PC}$ = 5.7 Hz, *i*-Mes), 137.7 (*p*-Mes), 136.9 (d, $^4J_{PC}$ = 1.2 Hz, *o*-Mes), 131.6 (d, $^4J_{PC}$ = 0.8 Hz, *p*-C_6H_3), 130.3 (d, $^3J_{PC}$ = 4.7 Hz, *m*-C_6H_3), 128.0 (*m*-Mes), 127.5 (d, $^1J_{PC}$ = 3.4 Hz, *i*-C_6H_3), 95.9 (d, $^2J_{PC}$ = 9.8 Hz, HC≡), 77.7 (d, $^1J_{PC}$ = 6.5 Hz, PC≡), 21.3 (d, $^5J_{PC}$ = 2.0 Hz, *o*-CH_3^{Mes}), 21.3 (*p*-CH_3^{Mes}).

^{31}P{^{1}H} NMR (243 MHz, 299 K, dichloromethane-d_2) δ -74.8 ($\nu_{1/2}$ ~ 2 Hz).

^{31}P NMR (243 MHz, 299 K, dichloromethane-d_2) δ -74.8 (t, $^4J_{PH}$ ~ 2.5 Hz).

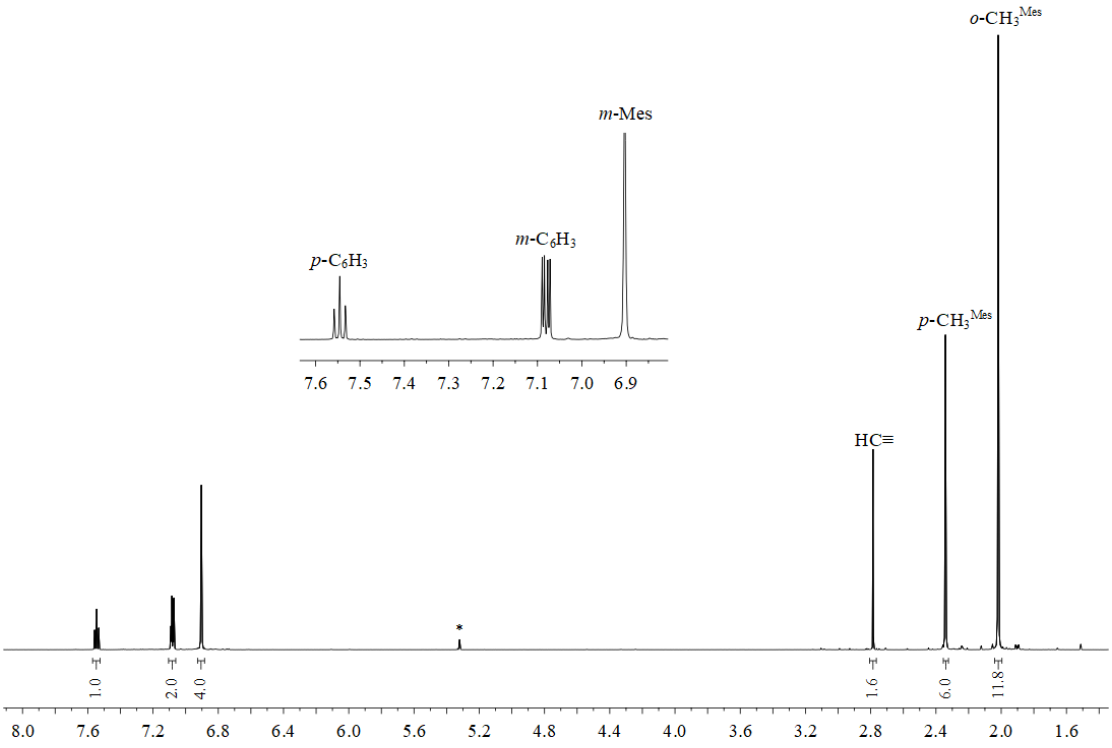


Figure S15.^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2(*)) spectrum of compound **13**

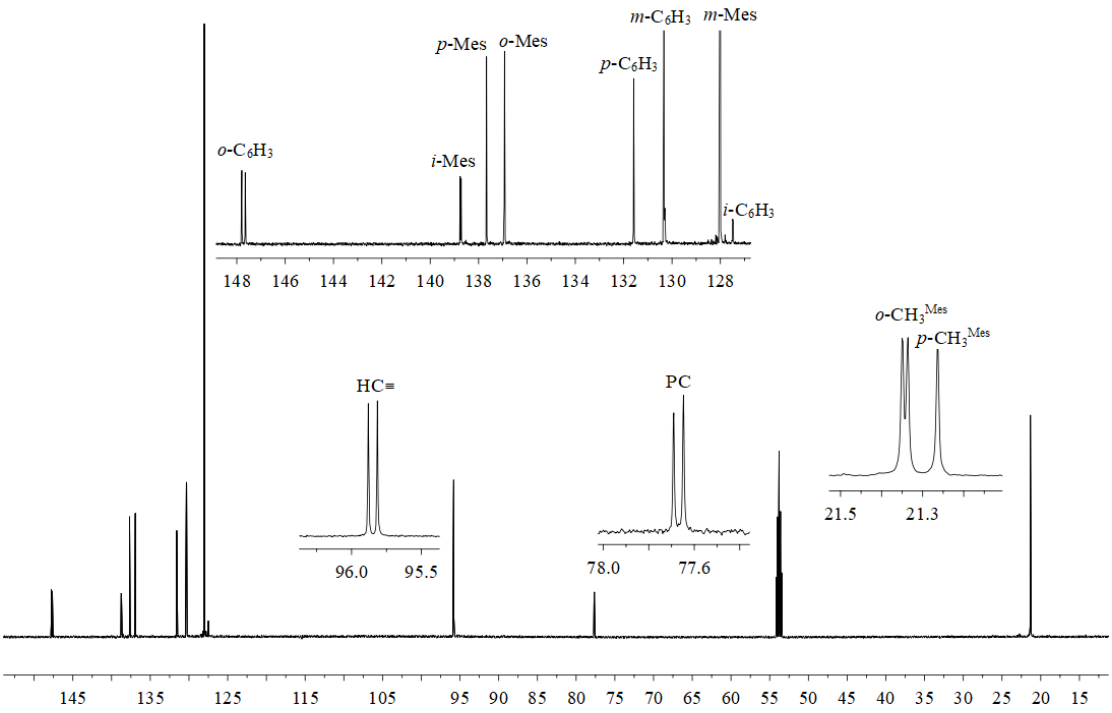


Figure S16. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2) spectrum of compound **13**

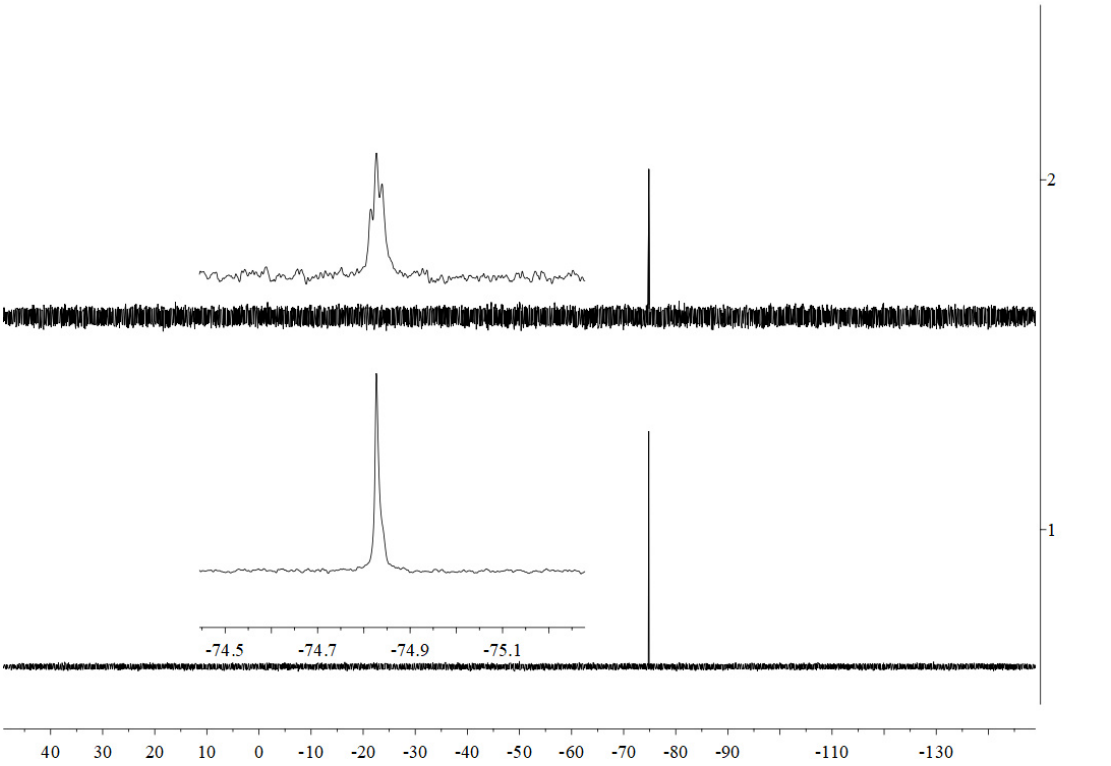
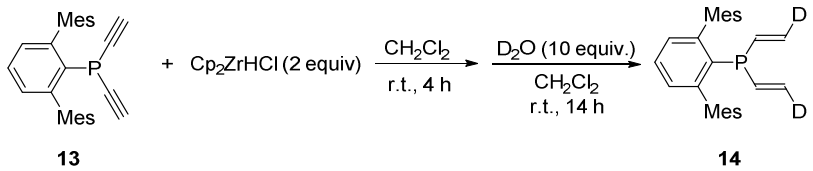


Figure S17. (1) $^{31}P\{^{1}H\}$ and (2) ^{31}P NMR (243 MHz, 299 K, dichloromethane-d_2) spectra of compound **13**

3.2. Synthesis of deuterium-labelled compound 14



Scheme S4

In an oven dry Schlenk tube (25 mL), Cp_2ZrHCl (600 mg, 2.2 mmol) was added and suspended with THF (5 mL). Then a THF (3 mL) solution of compound **13** (440 mg, 1.1 mmol) was added to the suspension and the mixture was stirred at room temperature for 4 h. Then D_2O (0.44 mL) was added and the resulting solution was stirred overnight (ca. 14 h). All volatiles were removed in vacuo and the residue was extracted with pentane (50 mL) and the extract was dried over $MgSO_4$. After filtering through a pad of Celite, the obtained solution was evaporated in vacuo to give a yellow oil. This crude product was purified by column chromatography using silica gel (pentane/dichloromethane = 10:1 to 4:1). The compound **14** was obtained as a white solid (230 mg, 53%).

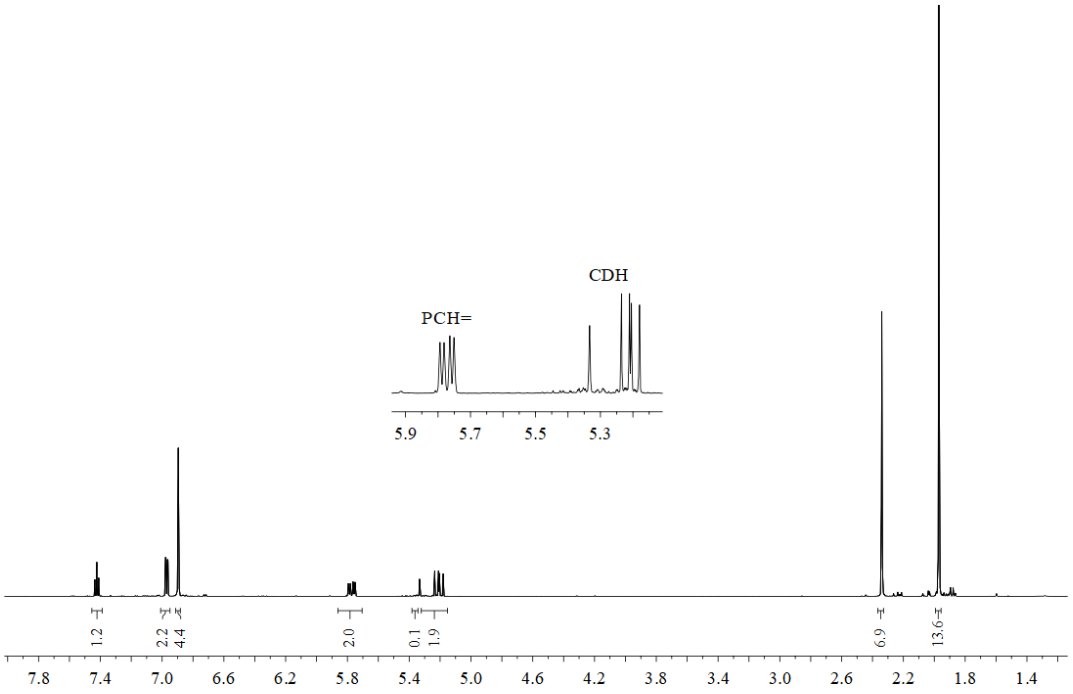


Figure S18. ^{1}H NMR (600 MHz, 299K, dichloromethane-d_2) spectrum of compound **14** [δ^1H: 5.76 (dd, $^3J_{HH}$ = 18.4 Hz, $^2J_{PH}$ = 7.6 Hz, PCH=), 5.19 (dd, $^3J_{HH}$ = 18.4 Hz, $^3J_{PH}$ = 14.9 Hz, =CDH)]

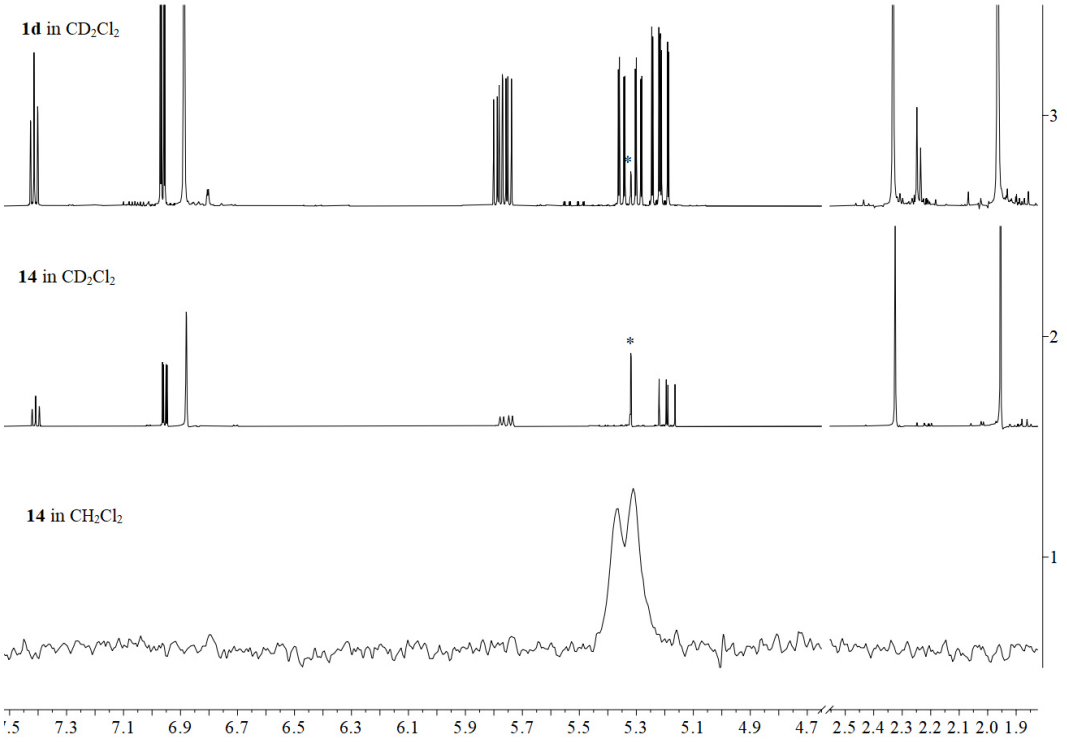
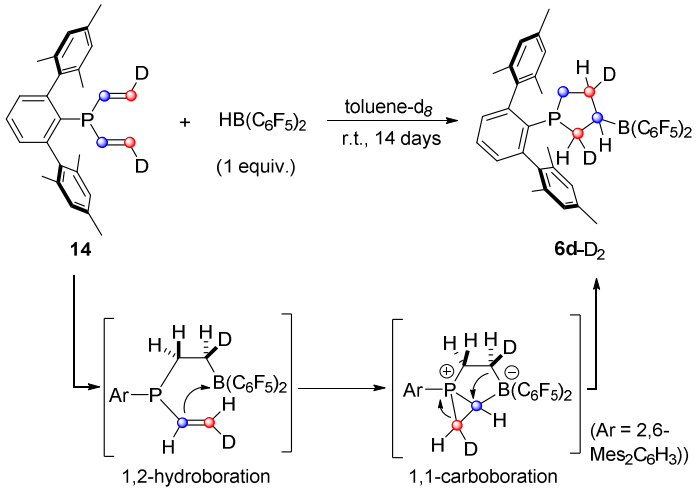


Figure S19. (1) ^{2}H NMR (92 MHz, 299K, dichloromethane) spectrum of compound **14** [δ^{2}H: 5.32 (d, $^{3}J_{PD}$ = 5.4 Hz, =CDH); $\gamma(^{1}H)/\gamma(^{2}H) = J_{PH}/J_{PD} \rightarrow {}^{3}J_{PH} \sim 35$ Hz] (2,3) ^{1}H NMR (600 MHz, 299K, dichloromethane-d_2(*)) spectra (2) of compound **14** and (3) of compound **5d**.

3.3. Reaction of deuterated compound 14



Scheme S5

Compound **14** (79.2 g, 0.2 mmol, 1.0 equiv.) and $HB(C_6F_5)_2$ (69.2 g, 0.2 mmol, 1.0 equiv.) were mixed and toluene (1.0 mL) was added. The mixture was stirred at room temperature for 14 days to give a yellow solution. Then the solution was filtered and all volatiles were removed in vacuo. Subsequently pentane (0.5 mL) was added to the

obtained crude compound **6d**-D_2. The resulting mixture was kept at -35 ºC for 24 hours to give a pale white solid (0.9 g, 60 %).

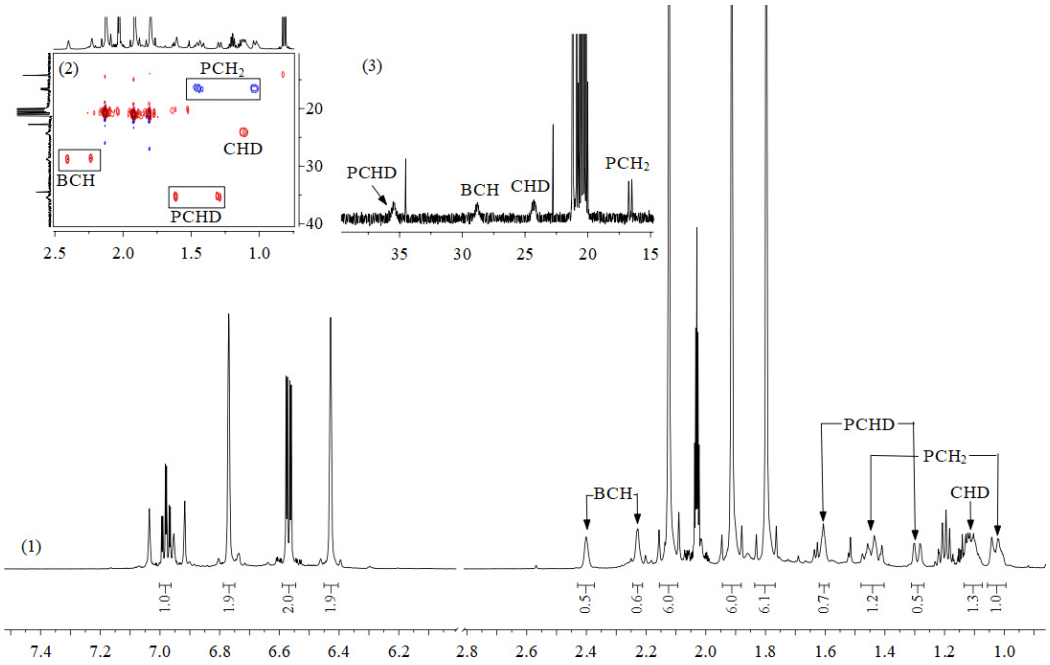


Figure S20. (1) ^{1}H NMR (600 MHz, 299K, toluene-d_8) spectrum of compound **6d**-D_2. (2) ^{1}H,^{13}C gHSQC (600/151 MHz/151MHz, 299K, toluene-d_8) spectrum of compound **6d**-D_2. (3) ^{13}C{^{1}H} NMR (151 MHz, 299K, toluene-d_8) spectrum of compound **6d**-D_2.

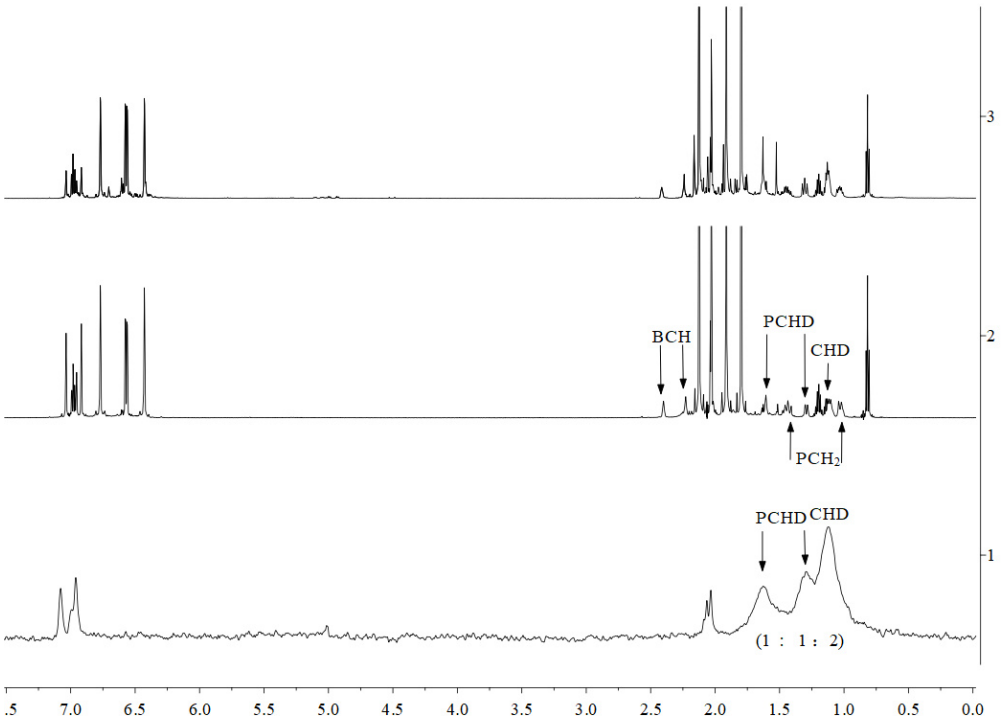


Figure S21. (1) ^{2}H NMR (92 MHz, 299K, toluene) spectrum of compound **6d**-D_2. (2,3) ^{1}H NMR (600 MHz, 299K, toluene-d_8) spectra (2) of compound **6d**-D_2 and (3) of compound **6d**.

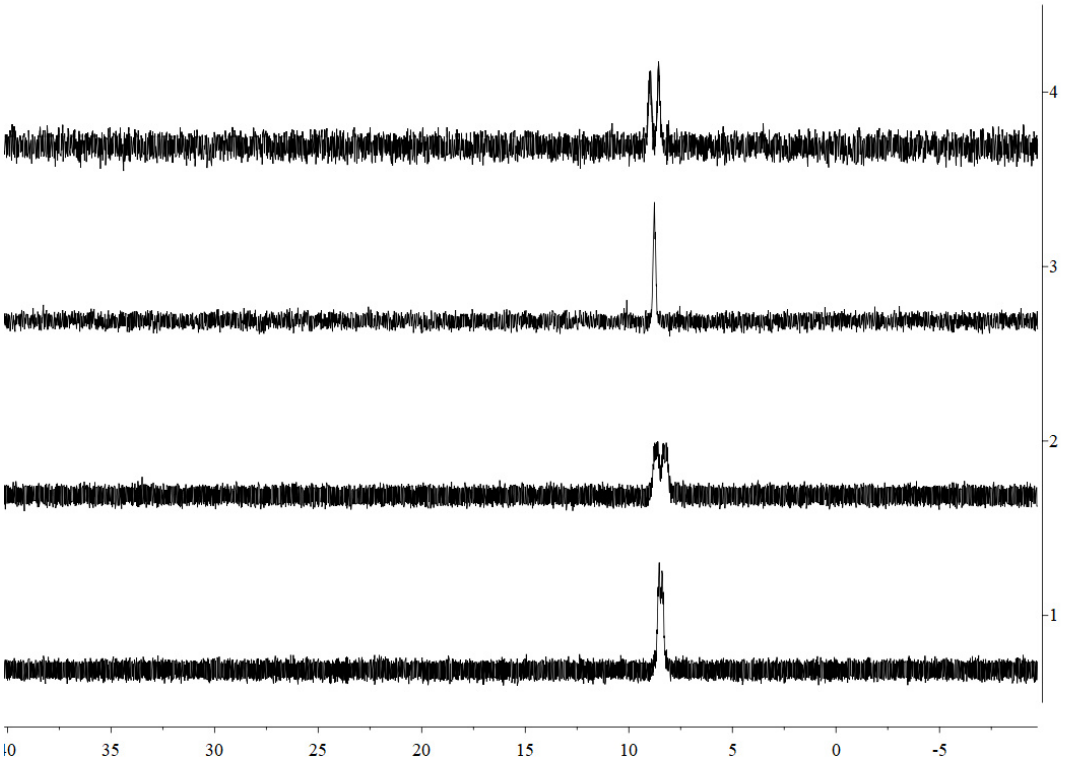
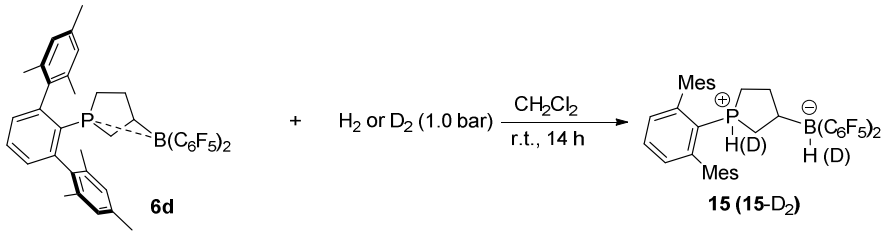


Figure S22. (1) $^{31}P\{^{1}H\}$ and (2) ^{31}P NMR (243 MHz, 299K, toluene) spectra of compound **6d**-D_2. (3) $^{31}P\{^{1}H\}$ and (4) ^{31}P NMR (243 MHz, 299K, toluene) spectra of compound **6d**.

4. Synthesis of compounds 15 and 15-D_2



Scheme S6

H_2 (1.0 bar) atmosphere: In a Schlenk flask (10 mL) compound **6d** (150 mg, 0.2 mmol, 1.0 equiv.) and CH_2Cl_2 (1 mL) were added. The flask was degassed and H_2 (1.0 bar) was introduced. Then the reaction mixture was stirred at room temperature for 14 h (overnight) to give a clear solution. Subsequently all volatiles were removed in vacuo and the residue was carefully washed with cold pentane (2 × 0.5 mL). After storing a solution of the residue in CH_2Cl_2/pentane (v/v 1:5) at -35 °C for several days, compound **15** was obtained as a white solid after drying in vacuo (130 mg, 86%).

Elemental analysis (%) calc. for $C_{40}H_{34}BF_{10}P$: C, 64.36; H, 4.59. Found: C, 63.85; H, 5.02.

HRMS: *m*/*z* calc. for $C_{40}H_{34}BF_{10}P[Na^+]$ 769.22306, found 769.22243.

Melting point: 170 °C (directly followed by decomposition)

NMR data of compound **15** were obtained from a solution of the isolated white solid in dichloromethane-d_2.

[Mes: mesityl]

^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) δ 7.84 (td, $^3J_{HH}$ = 7.7 Hz, $^5J_{PH}$ = 1.8 Hz, 1H, *p*-C_6H_3), 7.33 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{PH}$ = 4.1 Hz, 2H, *m*-C_6H_3), [7.03, 7.00](each m, each 2H, *m*-Mes), 6.12 (dtt, $^1J_{PH}$ = 478.4 Hz, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, PH), 2.35 (s, 6H, *p*-CH_3^{Mes}), [2.16, 1.56](each m, each 1H, PCH_2), [1.97, 1.95](each s, each 6H, *o*-CH_3^{Mes}), [1.80, 1.62](each m, each 1H, PCH_2^{CH}), 1.69 (m, 1H, BCH), [1.37, 1.33](each m, each 1H, CH_2). [BH was not observed]

^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d_2) δ 148.5 (d, $^2J_{PC}$ = 10.3 Hz, *o*-C_6H_3), 140.2 (*p*-Mes), [136.0, 135.8](*o*-Mes), 135.5 (d, $^4J_{PC}$ = 2.7 Hz, *p*-C_6H_3), 135.1 (d, $^3J_{PC}$ = 5.1 Hz, *i*-Mes), 131.3 (d, $^3J_{PC}$ = 9.6 Hz, *m*-C_6H_3), [129.6, 129.4](*m*-Mes), 115.8 (d, $^1J_{PC}$ = 76.4 Hz, *i*-C_6H_3), 32.9 (d, $^2J_{PC}$ = 9.3 Hz, CH_2), 32.3 (br, BCH), 28.1 (d, $^1J_{PC}$ = 43.4 Hz, PCH_2^{CH}), 21.2 (d, $^1J_{PC}$ = 51.7 Hz, PCH_2), 21.1 (*p*-CH_3^{Mes}), 20.9 (*o*-CH_3^{Mes}), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, dichloromethane-d_2) δ -20.6 ($\nu_{1/2}$ ~ 45 Hz).

^{11}B NMR (192 MHz, 299 K, dichloromethane-d_2) δ -20.6 (d, $^1J_{BH}$ ~ 88 Hz).

^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) δ [-132.7, -133.4] [each m, each 2F, *o*-C_6F_5], [-163.7, -164.0] [each t, $^3J_{FF}$ = 20.1 Hz, each 1F, *p*-C_6F_5], [-166.5, -167.0] [each m, each 2F, *m*-C_6F_5)].

^{31}P{^{1}H} NMR (243 MHz, 299 K, dichloromethane-d_2) δ 10.4 ($\nu_{1/2}$ ~ 25 Hz).

^{31}P NMR (243 MHz, 299 K, dichloromethane-d_2) δ 10.4 (br d, $^1J_{PH}$ ~ 480 Hz).

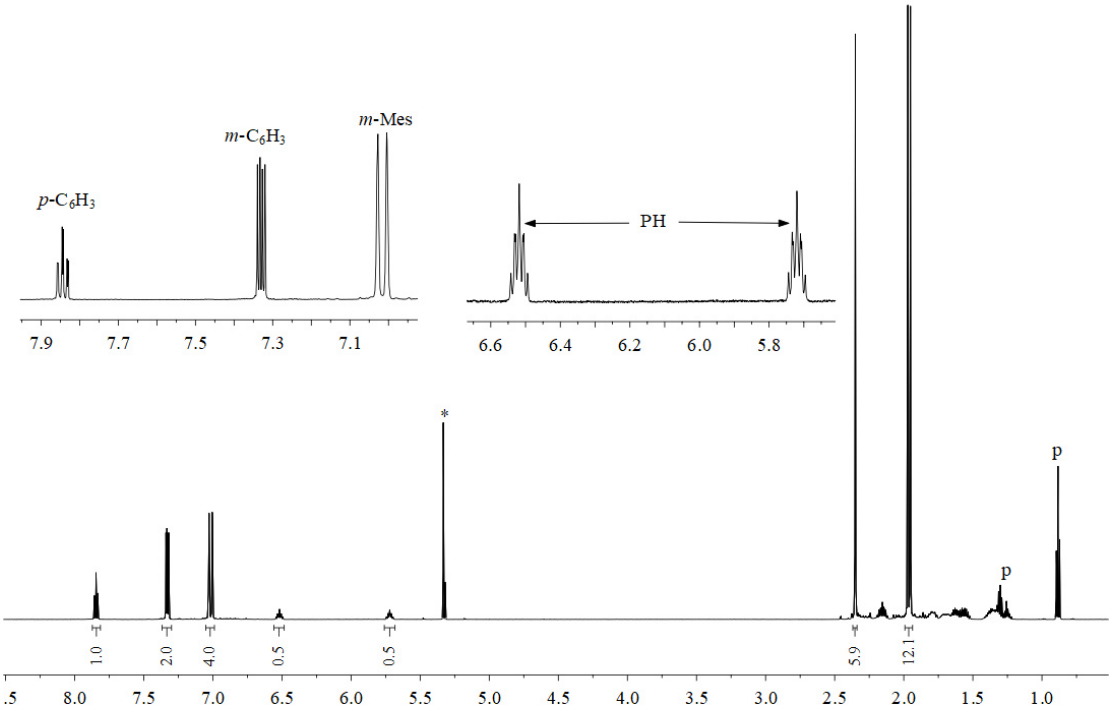


Figure S23a.[1]H NMR (600 MHz, 299 K, dichloromethane-d_2) spectrum of compound **15** [admixed with dichloromethane (*) and pentane (p)]

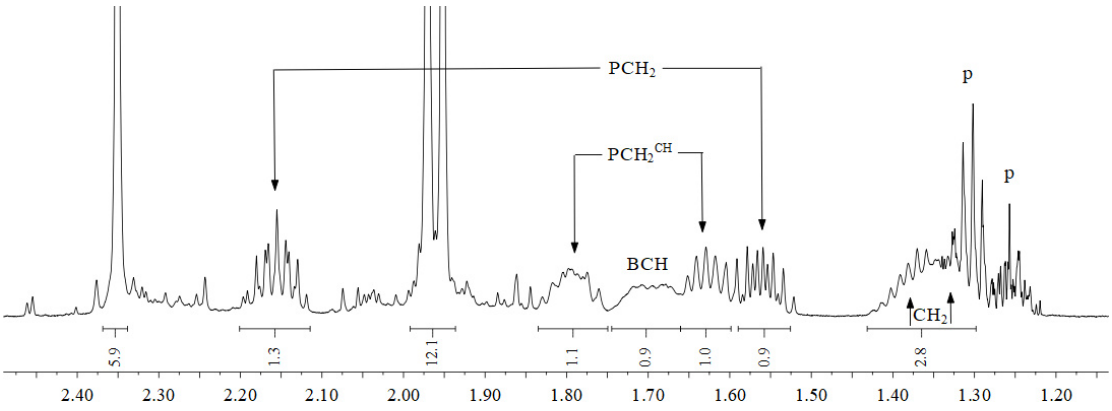


Figure S23b.[1]H NMR (600 MHz, 299 K, dichloromethane-d_2) spectrum of compound **15** [admixed with dichloromethane (*) and pentane (p)]

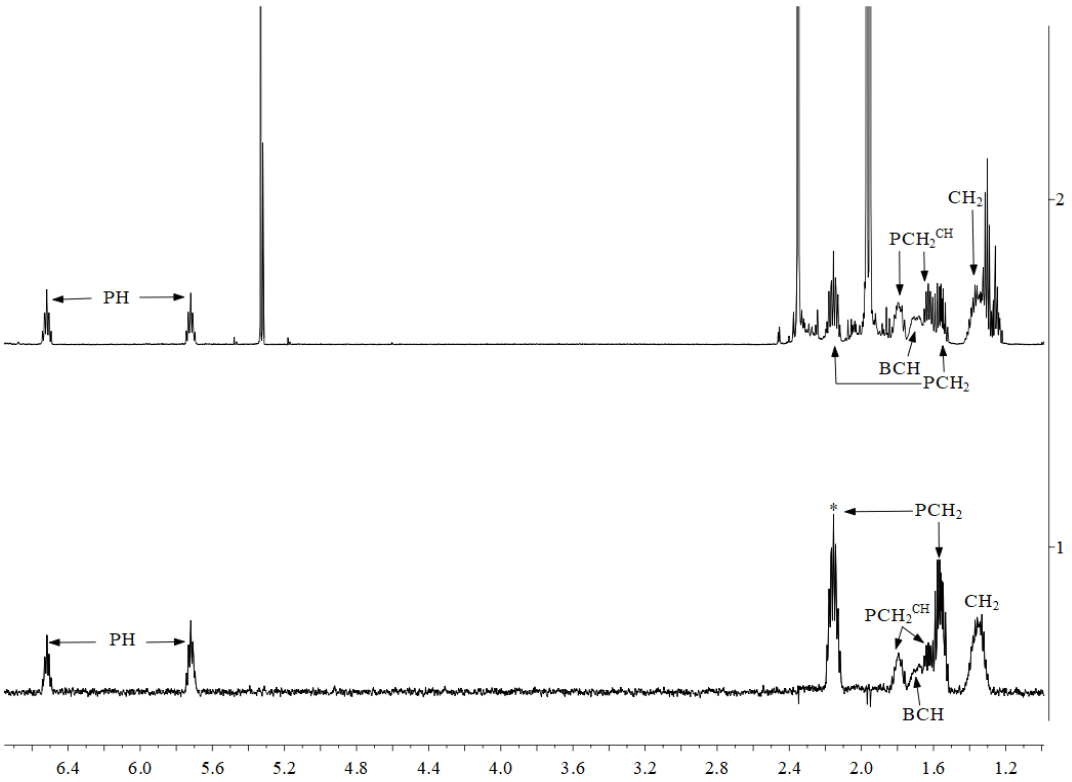


Figure S24. (1) $^{1}H\{^{1}H\}$ 1D-tocsy (600 MHz, 299 K, dichloromethane-d_2) [* irradiation at $\delta\ ^{1}H_{(irr)}$ = 2.16 (PCH_2)] and (2) ^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) spectra of compound **15**

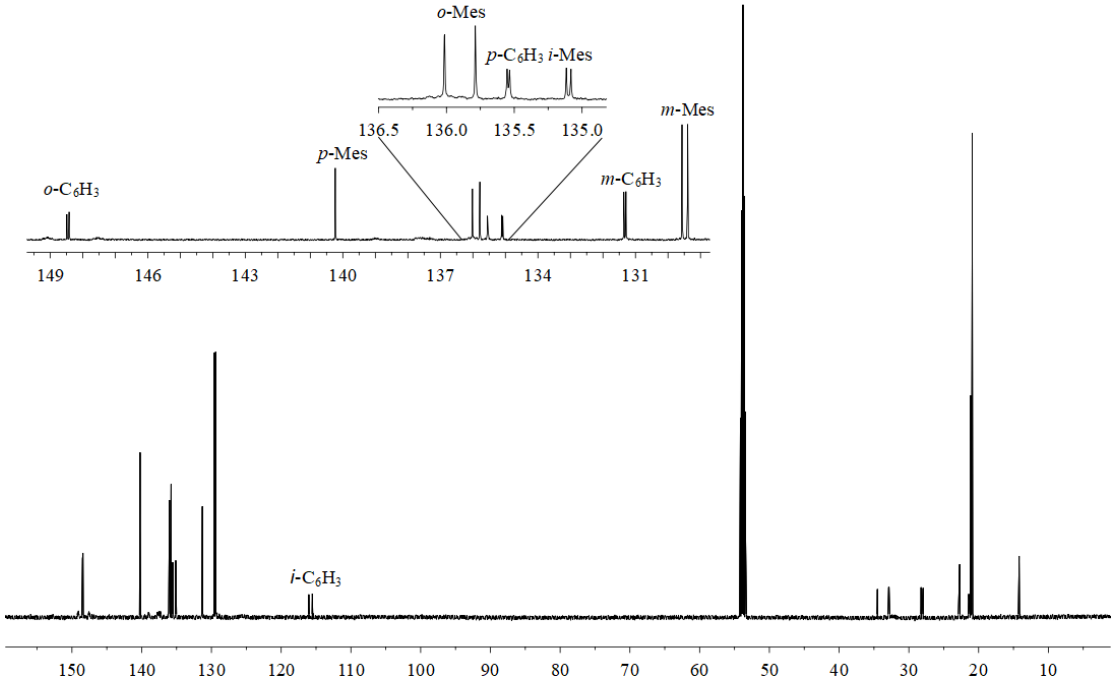


Figure S25a. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2) spectrum of compound **15**

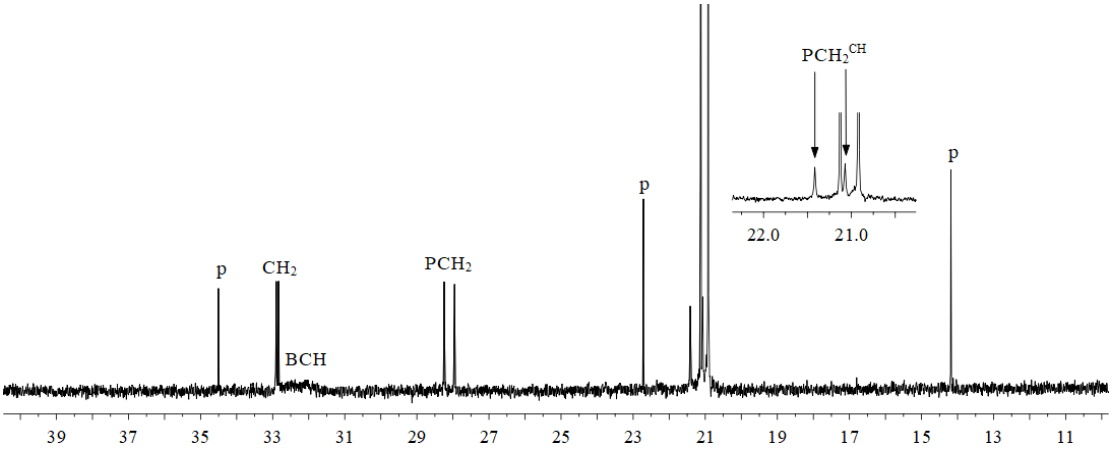


Figure S25b. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2) spectrum of compound **15** [pentane (p)]

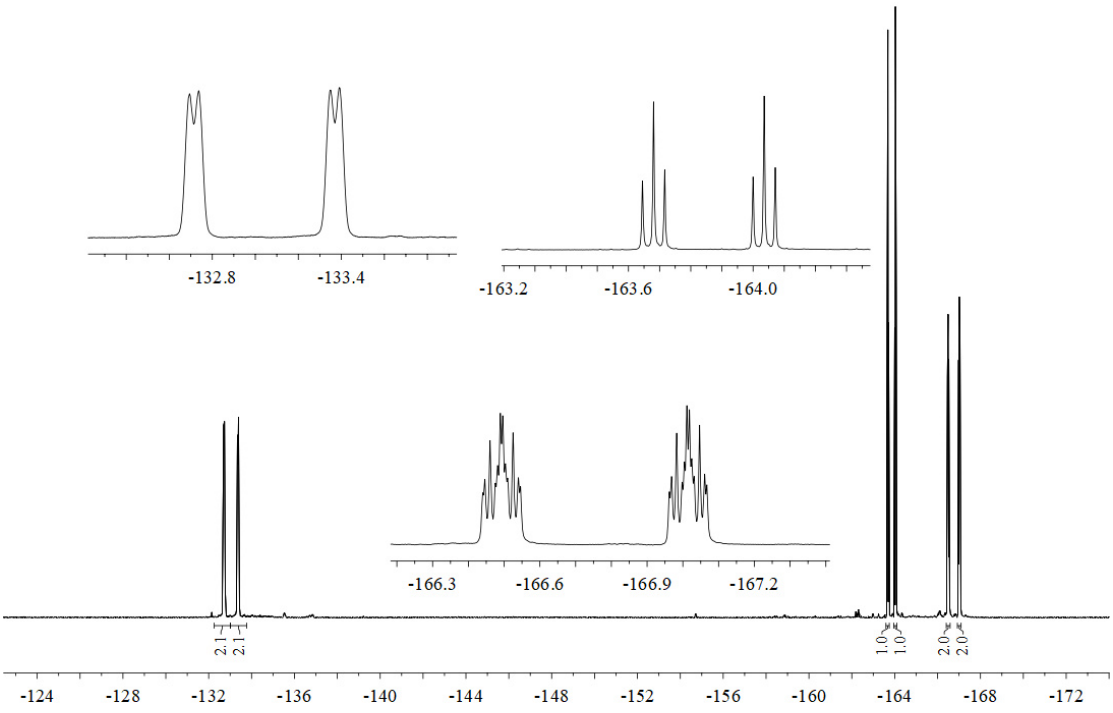


Figure S26.^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) spectrum of compound **15**

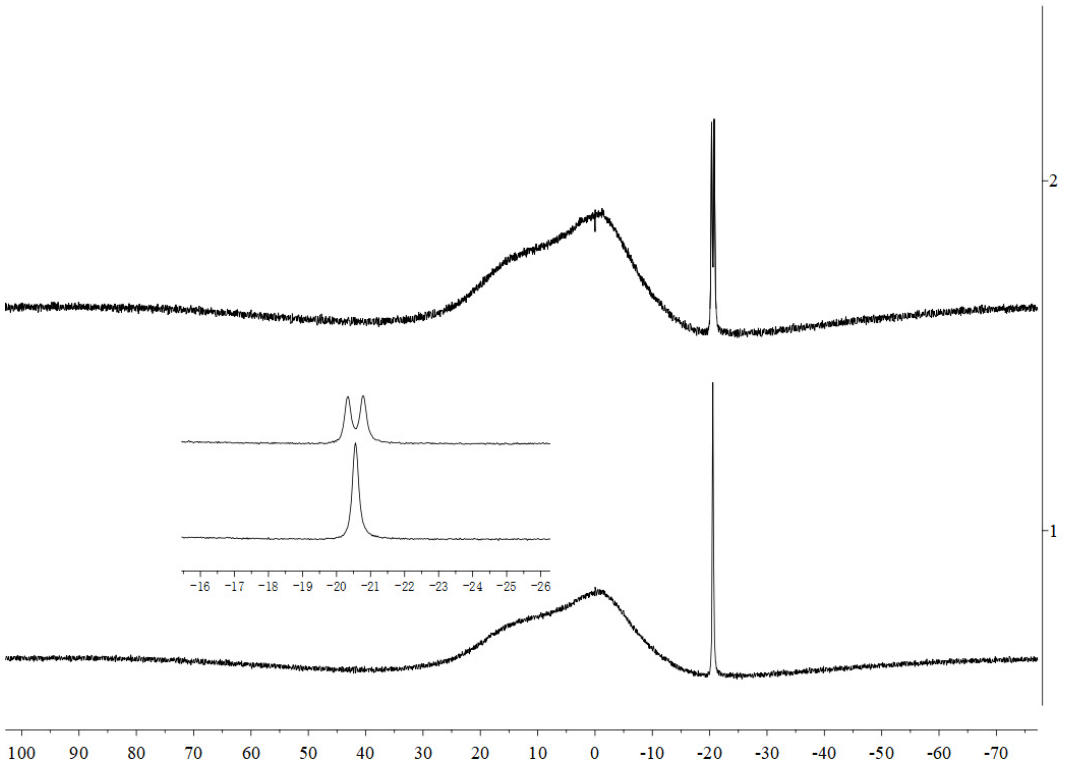


Figure S27. (1) $^{11}B\{^{1}H\}$ and (2) ^{11}B NMR (192 MHz, 299 K, dichloromethane-d_2) spectra of compound **15**

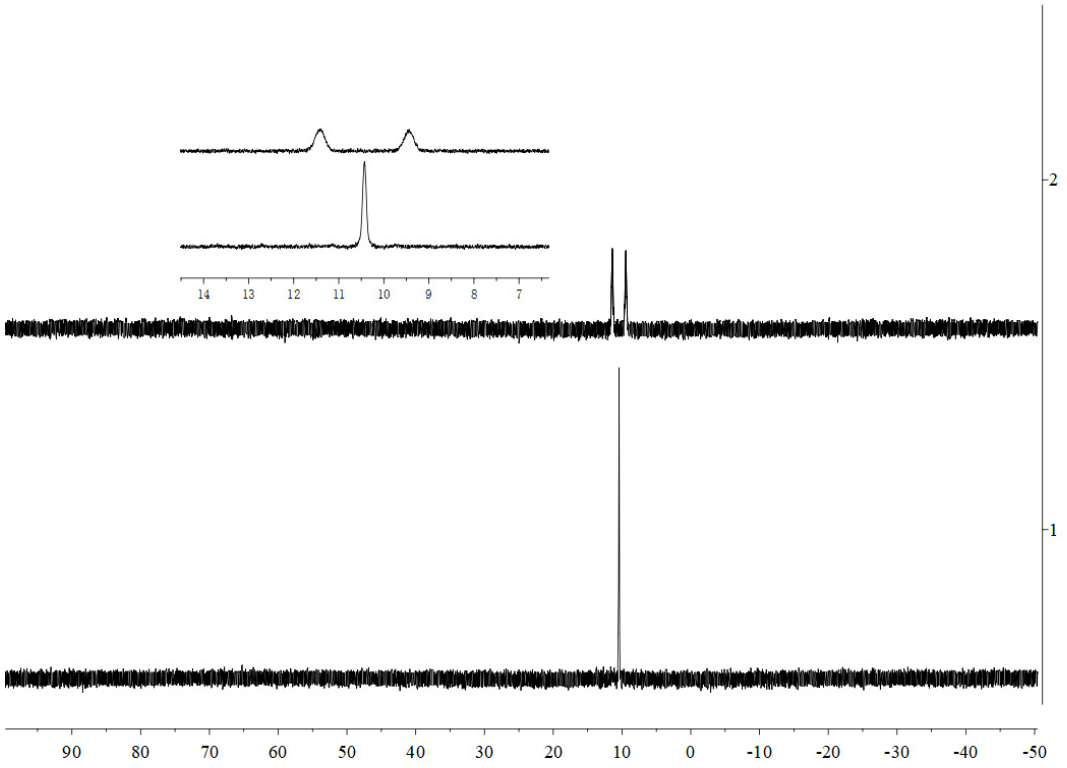


Figure S28. (1) $^{31}P\{^{1}H\}$ and (2) ^{31}P NMR (243 MHz, 299 K, dichloromethane-d_2) spectra of compound **15**

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **15** in dichloromethane/pentane (v/v ca. 1:5) at -35 ºC.

X-ray crystal structure analysis of compound 15 (erk9525): A colorless plate-like specimen of $C_{45}H_{46}BF_{10}P$, approximate dimensions 0.050 mm x 0.186 mm x 0.193 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 440 frames were collected. The total exposure time was 3.67 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 69520 reflections to a maximum θ angle of 27.50° (0.77 Å resolution), of which 9331 were independent (average redundancy 7.450, completeness = 99.8%, R_{int} = 7.04%, R_{sig} = 3.79%) and 7586 (81.30%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.6994(2) Å, b = 23.0965(6) Å, c = 20.3461(6) Å, β = 94.2480(10)°, volume = 4076.82(19) $Å^3$, are based upon the refinement of the XYZ-centroids of 9975 reflections above 20 σ(I) with 5.272° < 2θ < 54.85°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.956. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9730 and 0.9930. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{45}H_{46}BF_{10}P$. The final anisotropic full-matrix least-squares refinement on F^2 with 574 variables converged at R1 = 5.52%, for the observed data and wR2 = 12.99% for all data. The goodness-of-fit was 1.072. The largest peak in the final difference electron density synthesis was 0.480 $e^-/Å^3$ and the largest hole was -0.322 $e^-/Å^3$ with an RMS deviation of 0.051 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.334 g/cm^3 and F(000), 1704 e^-. The hydrogen at B1 and P1 atoms were refined freely. CCDC number: 1953118.

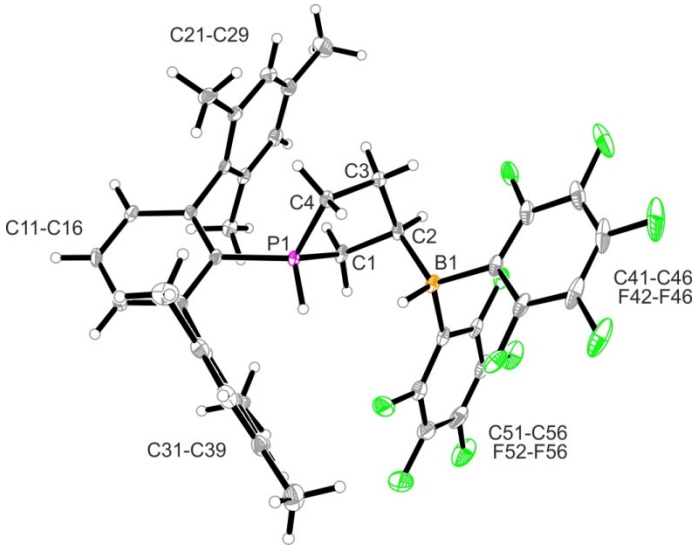


Figure S29: Crystal structure of compound **15** (thermal ellipsoids: 30% probability).

D_2 (1.0 bar) atmosphere: In a Schlenk flask (10 mL) compound **6d** (75 mg, 0.1 mmol, 1.0 equiv.) and CH_2Cl_2 (1 mL) were added. The flask was carefully degassed and D_2 (1.0 bar) was introduced. Then the reaction mixture was stirred at room temperature for 14 h (overnight) to give a clear solution. Subsequently all volatiles were removed in vacuo and the residue was carefully washed with cold pentane (2 × 0.3 mL). After storing a solution of the residue in CH_2Cl_2/pentane (v/v ca. 1:5) at -35 °C for several days, compound **15**-D_2 was obtained as colorless crystals (30 mg, 40 %).

The ^2H NMR spectrum was obtained from a dichloromethane solution of compound **15**-D_2.

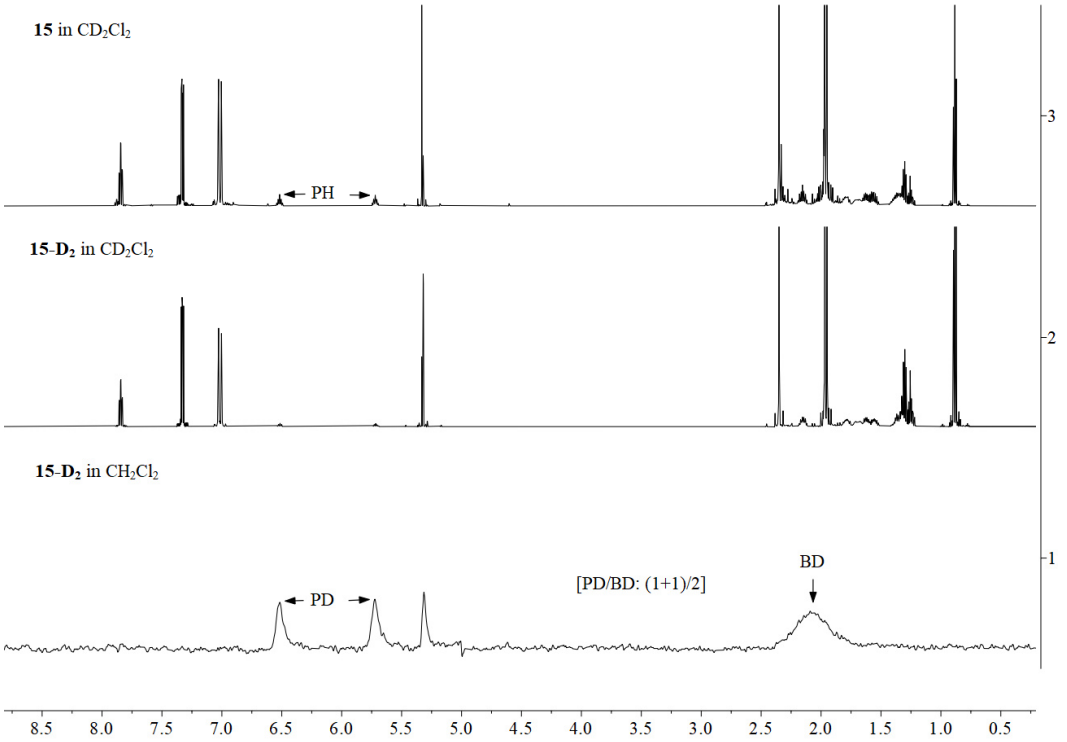
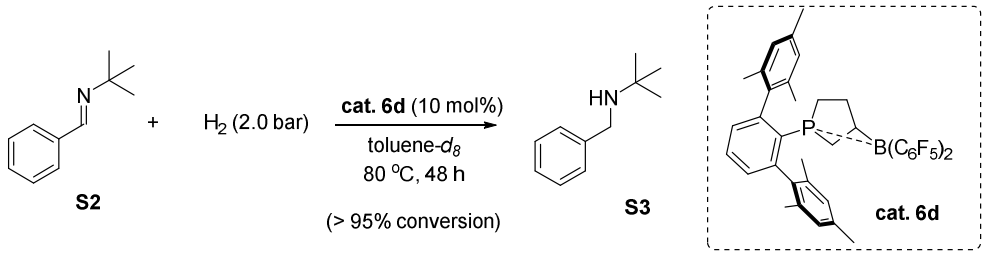


Figure S30. (1) ^{2}H NMR (92 MHz, 299 K, dichloromethane) spectrum of compound **15**-D_2 [δ^{2}H: 6.12 (d, $^{1}J_{PD}$ = 72.9 Hz, 1D, PD), 2.09 (br, 1D, BD); $\gamma(^{1}H)/\gamma(^{2}H) = J_{PH}/J_{PD} \rightarrow {}^{1}J_{PH} \sim 480$ Hz] (2,3) ^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) spectra (2) of compound **15**-D_2 and (3) of compound **15**

5. Hydrogenation of an imine catalysed by compound 6d.



Scheme S7

In an oven-dried Schlenk tube (10 mL) *N*-tert-butyl-1-phenylmethanimine **S2** (32.2 mg, 0.2 mmol, 1 equiv.) and compound **6d** (15.0 mg, 0.02 mmol, 0.1 equiv.) were mixed with toluene-d_8 (1.0 mL). The tube was then carefully degassed and H_2 gas (2.0 bar) was introduced. Then the reaction mixture was stirred at 80 °C for 48 h. The obtained reaction mixture was directly characterized by ^{1}H NMR experiments.

[Comment: the starting imine **S2** was converted into the amine **S3** (> 95%).]

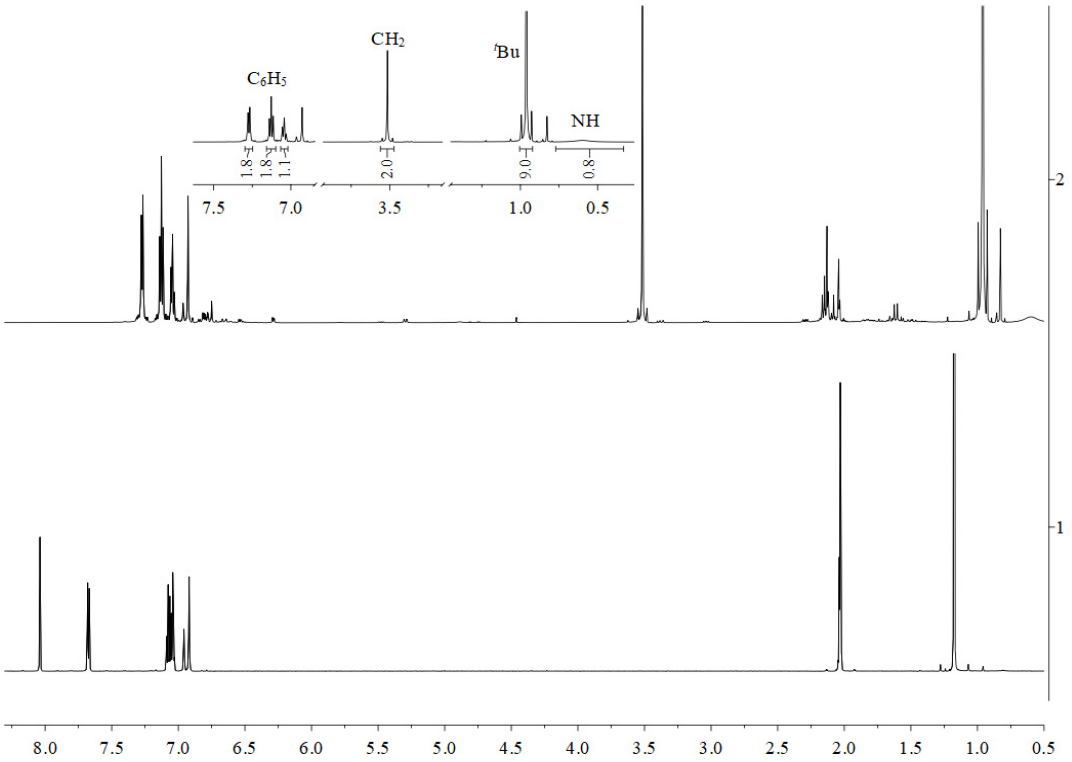
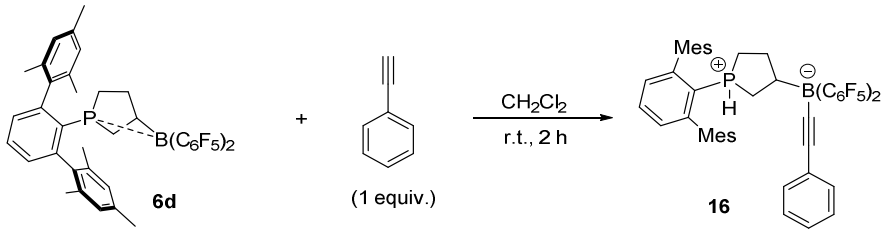


Figure S31. ^{1}H NMR (600 MHz, 299K, toluene-d_8) spectra of (1) imine **S2** and (2) the reaction mixture (**S3**)

6. Synthesis of compound 16



Scheme S8

In a vial (4 mL) compound **6d** (74.5 mg, 0.1 mmol, 1 equiv.) and phenylacetylene (10.2 mg, 0.1 mmol, 1 equiv.) were mixed and CH_2Cl_2 (1 mL) was added. The mixture was stirred at room temperature for 2 h to give a yellow solution. After all volatiles were removed in vacuo, the residue was washed with pentane (3×1 mL) to finally give compound **16** (78 mg, 92%) as a white solid.

Elemental analysis (%) calc. for $C_{48}H_{38}BF_{10}P$: C, 68.10; H, 4.52. Found: C, 67.60; H, 4.22.

HRMS: *m*/*z* calc. for $C_{48}H_{38}BF_{10}P$ [Na^+] 869.25448, found 869.25418.

Melting point: 186 ºC (directly followed by decomposition)

NMR data of compound **16** were obtained from a solution of the isolated white solid in dichloromethane-d_2.

[Mes: mesityl]

^{1}H NMR (600 MHz, 299K, dichloromethane-d_2) δ 7.86 (td, $^{3}J_{HH}$ = 7.7 Hz, $^{5}J_{PH}$ = 1.8 Hz, 1H, *p*-C_6H_3), 7.34 (dd, $^{3}J_{HH}$ = 7.7, $^{4}J_{PH}$ = 4.2 Hz, 2H, *m*-C_6H_3), 7.24 (m, 2H, *m*-Ph), 7.19 (m, 1H, *p*-Ph), 7.16 (m, 2H, *o*-Ph), 6.98 (s, 4H, *m*-Mes), 5.90 (dm, $^{1}J_{PH}$ = 469.8 Hz, 1H, PH), 2.32 (s, 6H, *p*-CH_3^{Mes}), [2.15, 1.95](each m, each 1H, PCH_2^{CH}), [2.08, 1.57](each m, each 1H, PCH_2), [1.96, 1.95](each s, each 6H, *o*-CH_3^{Mes}), [1.79 (dm, $^{3}J_{PH}$ ~ 42 Hz), 1.53 (m)](each 1H, CH_2), 1.52 (m, 1H, BCH).

^{13}C{^{1}H} NMR (151 MHz, 299 K, dichloromethane-d_2) δ 148.5 (d, $^{2}J_{PC}$ = 10.5 Hz, *o*-C_6H_3), 140.3 (*p*-Mes), [136.05, 135.79](*o*-Mes), 135.80 (d, $^{4}J_{PC}$ = 1.7 Hz, *p*-C_6H_3), 135.0 (d, $^{3}J_{PC}$ = 5.1 Hz, *i*-Mes), 131.35 (*o*-Ph), 131.34 (d, $^{3}J_{PC}$ = 9.7 Hz, *m*-C_6H_3), [129.7, 129.4](*m*-Mes), 128.4 (*m*-Ph), 127.2 (*i*-Ph), 126.5 (*p*-Ph), 115.7 (d, $^{1}J_{PC}$ = 75.6 Hz, *i*-C_6H_3), 108.7 (br, BC≡), 95.7 (br, PhC≡), 33.8 (br m, BCH), 31.5 (d, $^{2}J_{PC}$ = 11.7 Hz, CH_2), 25.2 (d, $^{1}J_{PC}$ = 42.7 Hz, PCH_2^{CH}), 24.0 (d, $^{1}J_{PC}$ = 50.2 Hz, PCH_2), 21.1 (*p*-CH_3^{Mes}), [20.9, 20.8](*o*-CH_3^{Mes}), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, dichloromethane-d_2) δ -17.3 ($\nu_{1/2}$ ~ 40 Hz).

^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) δ [-132.3, -132.5](each m, each 2F, *o*-C_6F_5), [-163.2, -163.3](each t, $^{3}J_{FF}$ = 20.3 Hz, each 1F, *p*-C_6F_5), [-166.5, -166.7](each m, each 2F, *m*-C_6F_5).

^{31}P{^{1}H} NMR (243 MHz, 299 K, dichloromethane-d_2) δ 12.3 (m).

^{31}P NMR (243 MHz, 299 K, dichloromethane-d_2) δ 12.3 (dm, $^{1}J_{PH}$ ~ 470 Hz).

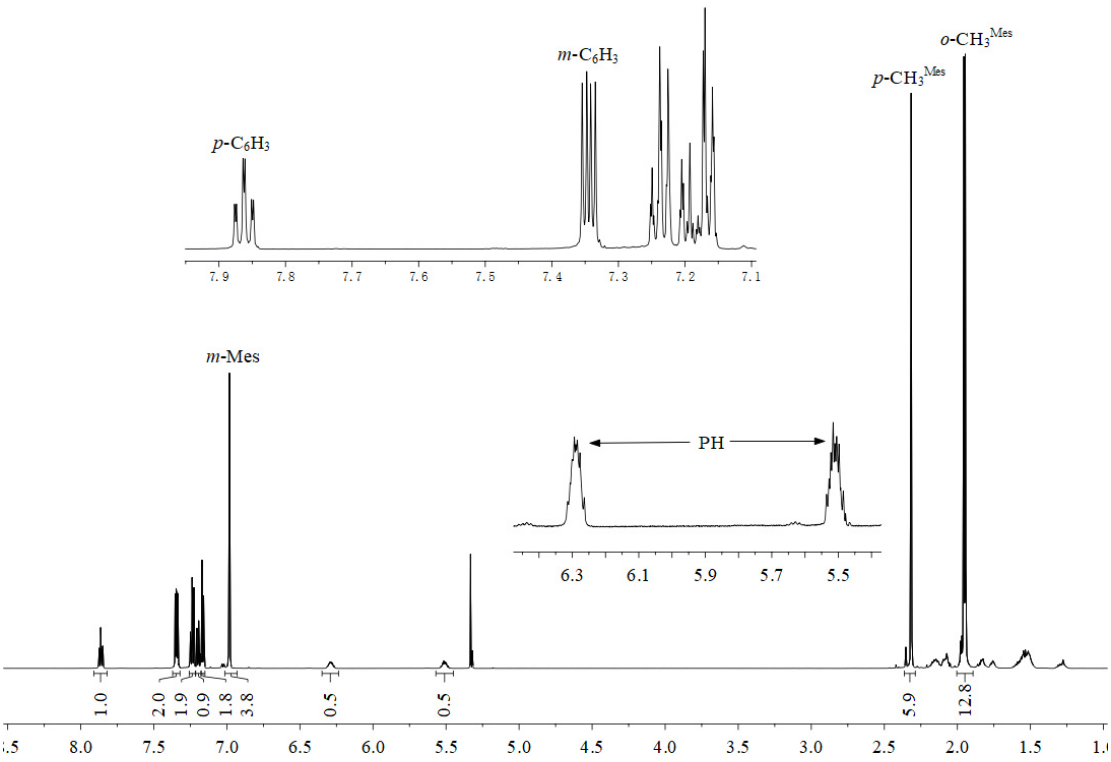


Figure S32a.[1]H NMR (600 MHz, 299 K, dichloromethane-d_2) spectrum of compound **16**

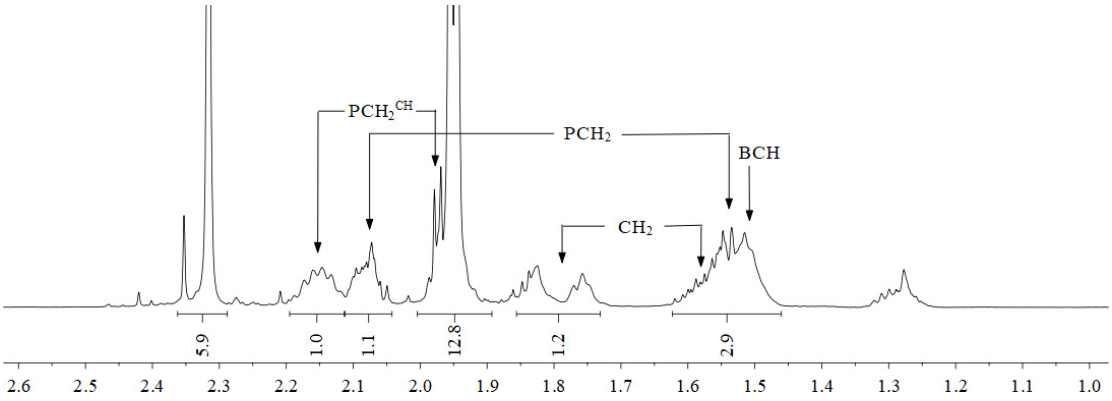


Figure S32b.[1]H NMR (600 MHz, 299 K, dichloromethane-d_2) spectrum of compound **16**

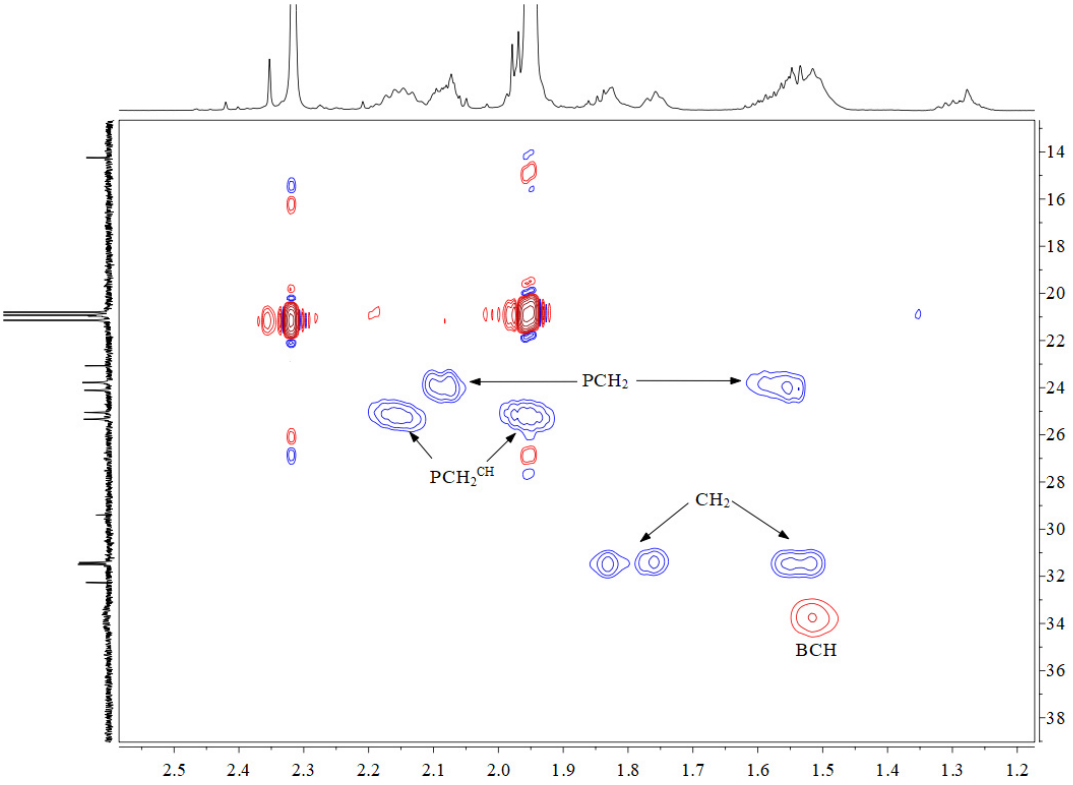


Figure S33. $^{1}H,^{13}C$ gHSQC (600/151 MHz, 299 K, dichloromethane-d_2) spectrum of compound **16** [selected area]

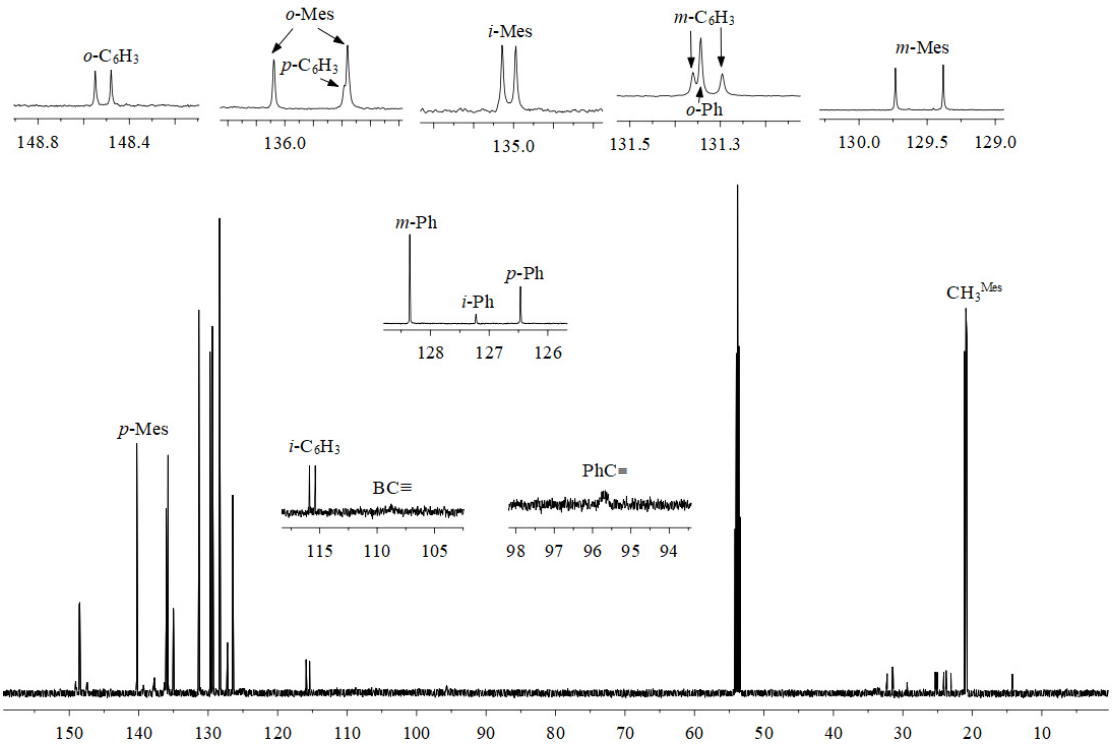


Figure S34a. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2) spectrum of compound **16**

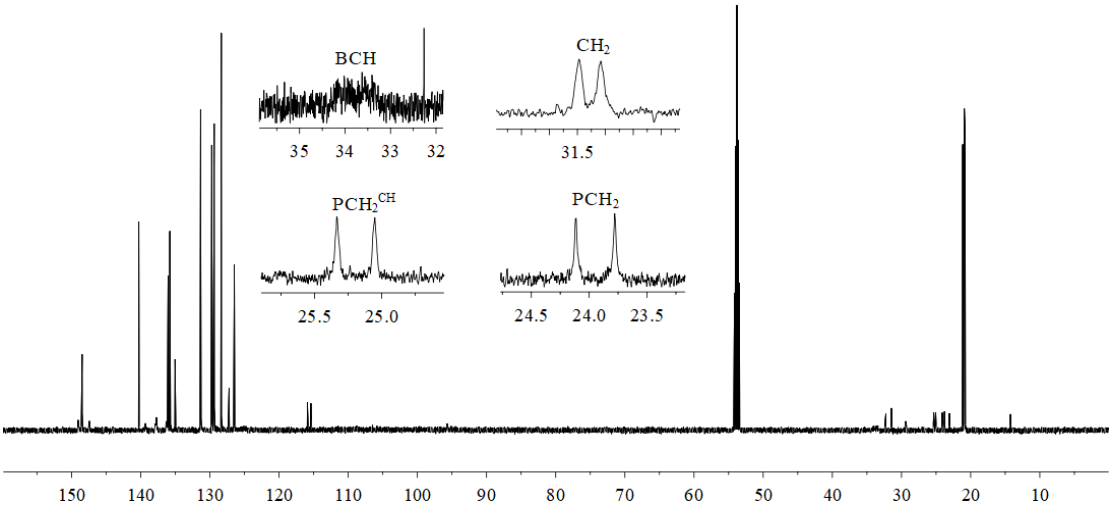


Figure S34b. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2) spectrum of compound **16**

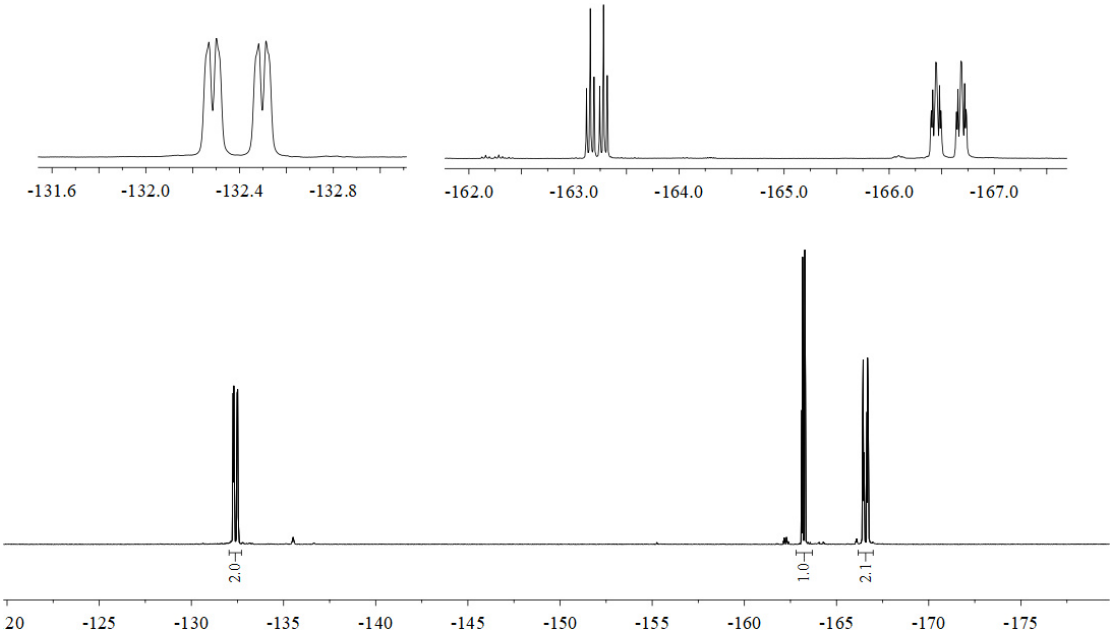


Figure S35. ^{19}F NMR (564 MHz, 299 K, dichloromethane-d_2) spectrum of compound **16**

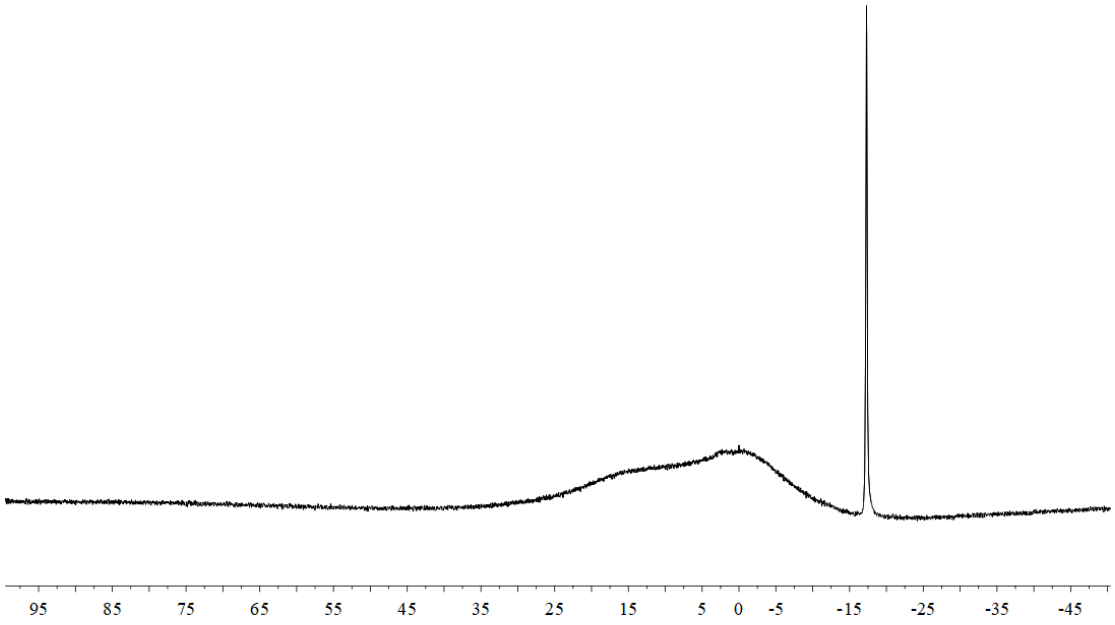


Figure S36. $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, dichloromethane-d_2) spectrum of compound **16**

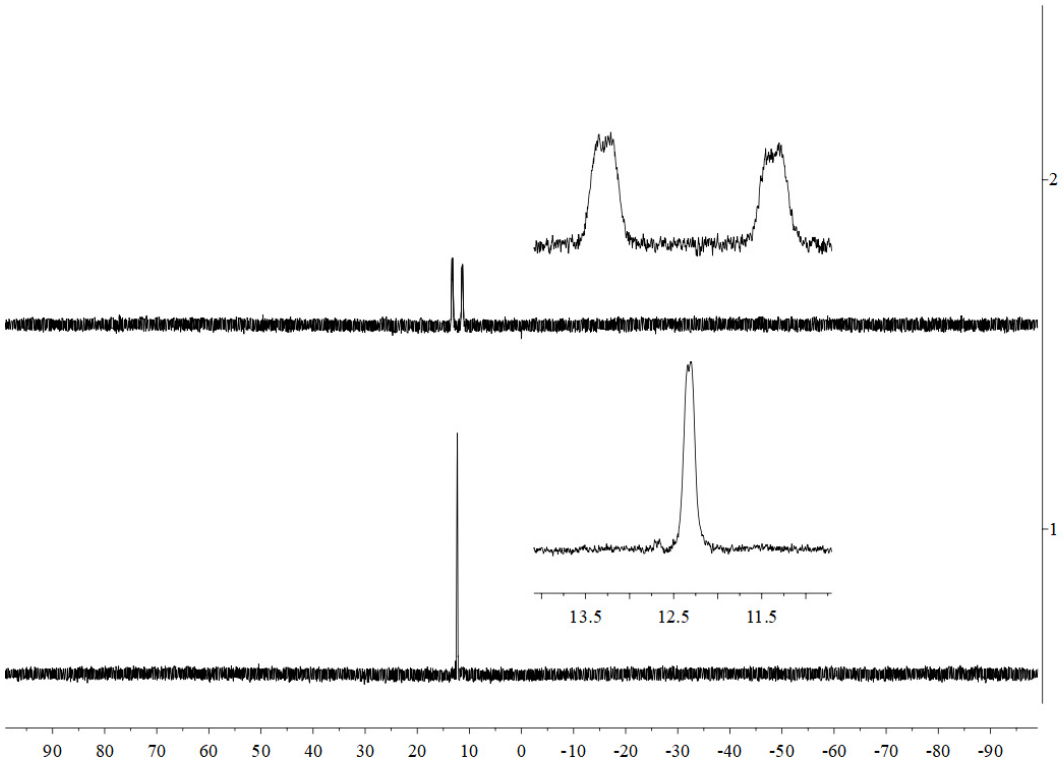


Figure S37. (1) $^{31}P\{^{1}H\}$ and (2) ^{31}P NMR (243 MHz, 299 K, dichloromethane-d_2) spectra of compound **16**

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **16** in dichloromethane/heptane (v/v ca. 1:3) at r.t.

X-ray crystal structure analysis of compound 16 (erk9479): A colorless needle-like specimen of $C_{48}H_{38}BF_{10}P$, approximate dimensions 0.030 mm x 0.100 mm x 0.400 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a triclinic unit cell yielded a total of 6858 reflections to a maximum θ angle of 24.99° (0.84 Å resolution), of which 6858 were independent (average redundancy 1.000, completeness = 97.4%, R_{sig} = 3.78%) and 5698 (83.09%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.0403(3) Å, b = 13.4516(3) Å, c = 13.5382(3) Å, α = 111.4550(10)°, β = 95.2410(10)°, γ = 97.459(2)°, volume = 2000.43(8) $Å^3$, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9420 and 0.9950. 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, $C_{48}H_{38}BF_{10}P$. The final anisotropic full-matrix least-squares refinement on F^2 with 551 variables converged at R1 = 7.34%, for the observed data and wR2 = 19.87% for all data. The goodness-of-fit was 1.088. The largest peak in the final difference electron density synthesis was 0.342 $e^-/Å^3$ and the largest hole was -0.494 $e^-/Å^3$ with an RMS deviation of 0.076 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.405 g/cm^3 and F(000), 872 e^-. The hydrogen at P1 atom was refined freely. CCDC number: 1953119.

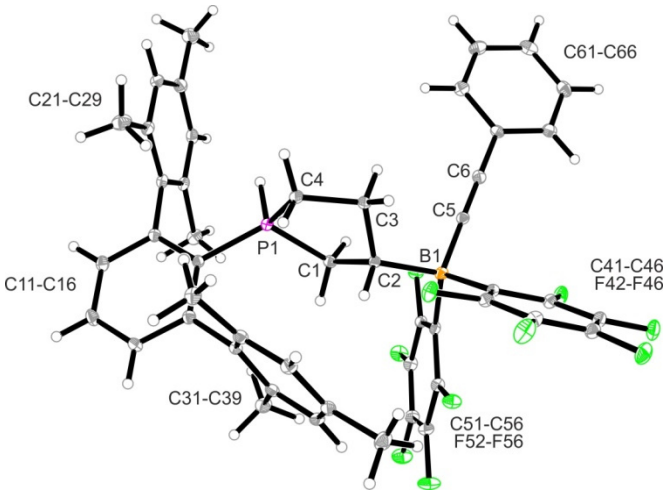
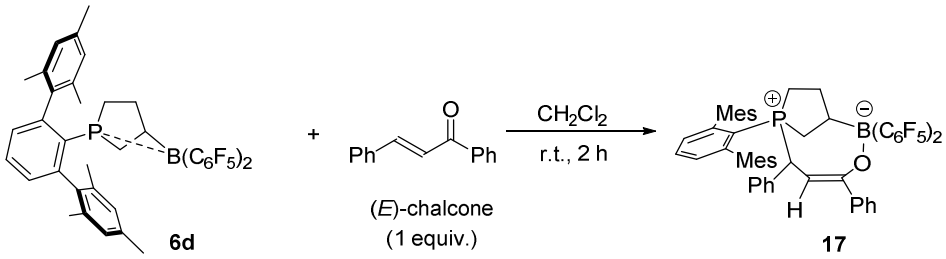


Figure S38: Crystal structure of compound **16** (thermal ellipsoids: 15% probability).

7. Synthesis of compound 17



Scheme S9

In a vial (4 mL) compound **6d** (55.0 mg, 0.074 mmol, 1.0 equiv.) and (*E*)-chalcone (15.4 mg, 0.074 mmol, 1.0 equiv.) were mixed and CH_2Cl_2 (1 mL) was added. The mixture was stirred at room temperature for 2 h to give a light-yellow solution. After all volatiles were removed in vacuo, the residue was washed with pentane (3×1 mL) to finally give compound **17** (72 mg, 98%) as a white solid.

Elemental analysis (%) calc. for $C_{55}H_{44}BF_{10}OP$: C, 69.34; H, 4.66. Found: C, 68.19; H, 4.47.

HRMS: *m*/*z* calc. for $C_{55}H_{44}BF_{10}OP$ [H^+] 953.31450, found 953.31435.

Melting point: 183 ºC.

NMR data of compound **17** were obtained from a solution of the isolated white solid in dichloromethane-d_2 at -40 ºC.

[Mes: mesityl]

^{1}H NMR (600 MHz, 233 K, dichloromethane-d_2) δ 7.79 (td, $^3J_{HH}$ = 7.7 Hz, $^5J_{PH}$ = 1.4 Hz, 1H, *p*-C_6H_3), [7.41, 7.17](each dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 3.6 Hz, 1H, *m*-C_6H_3), [7.34, 6.33](each m, each 1H, *o*-Ph^{CO}), 7.26 (br m, 5H, Ph^{CH}), [7.25/7.02, 6.77/6.73](each s, each 1H, *m*-Mes), [7.05, 6.89](each m, each 1H, *m*-Ph^{CO}), 6.98 (m, 1H, *p*-Ph^{CO}), 4.37 (dd, $^2J_{PH}$ = 19.5, $^3J_{HH}$ = 9.3 Hz, 1H, PCH), 3.80 (dd, $^3J_{PH}$ = 20.5, $^3J_{HH}$ = 9.3 Hz, 1H, HC=), [2.72, 2.64](each m, each 1H, PCH_2^{CH}), [2.39, 2.15](each s, each 3H, *p*-CH_3^{Mes}), [2.31/2.07, 1.93/1.85](each s, each 3H, *o*-CH_3^{Mes}), 2.23 (dm, 1H, $^3J_{PH}$ = 39.4 Hz, BCH), [1.90, 0.67](each m, each 1H, PCH_2), [1.08, 1.03](each m, each 1H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, 233 K, dichloromethane-d_2) δ 162.7 (d, $^3J_{PC}$ = 8.2 Hz, CO), [146.6 (d, $^3J_{PC}$ = 9.5 Hz), 146.4 (d, $^3J_{PC}$ = 7.6 Hz)](*o*-C_6H_3), 140.0 (d, $^4J_{PC}$ = 2.1 Hz, *i*-Ph^{CO}), [139.1, 138.4](*p*-Mes), [137.9, 135.56, 135.54, 134.8](*o*-Mes), [136.2,

135.6](each d, $^{3}J_{PC}$ = 2.8 Hz, *i*-Mes), 135.4 (d, $^{2}J_{PC}$ = 3.5 Hz, *i*-Ph^{CH}), 133.3 (d, $^{4}J_{PC}$ = 2.9 Hz, *p*-C_6H_3), [133.1 (d, $^{3}J_{PC}$ = 9.8 Hz), 131.9 (d, $^{3}J_{PC}$ = 9.5 Hz)](*m*-C_6H_3), [129.7, 128.7 (m), 127.9 (d, *J* = 3.3 Hz)](each br, *o,m,p*-Ph^{CH}), [129.0/128.6, 128.8/ 128.0](*m*-Mes), [127.3, 125.9](each br, *o*-Ph^{CO}), 126.8 (*p*-Ph^{CO}), [126.7, 126.2](each br, *m*-Ph^{CO}), 123.7 (d, $^{1}J_{PC}$ = 60.8 Hz, *i*-C_6H_3), 102.1 (d, $^{2}J_{PC}$ = 6.6 Hz, HC=), 41.6 (d, $^{1}J_{PC}$ = 38.8 Hz, PCH), 36.4 (br, BCH), 32.5 (d, $^{2}J_{PC}$ = 10.0 Hz, CH_2), 32.0 (dd, $^{1}J_{PC}$ = 47.8 Hz, *J* = 13.0 Hz, $PCH_2{}^{CH}$), 23.9 (d, $^{1}J_{PC}$ = 49.7 Hz, PCH_2), [22.1/21.6, 21.4/21.1](*o*-$CH_3{}^{Mes}$), [20.9, 20.7](*p*-$CH_3{}^{Mes}$), [C_6F_5 not listed.]

$^{11}B\{^{1}H\}$ NMR (192 MHz, 233 K, dichloromethane-d_2) δ -0.2 ($\nu_{1/2}$ ~ 800 Hz).

$^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, dichloromethane-d_2) δ -0.1 ($\nu_{1/2}$ ~ 180 Hz).

^{19}F NMR (564 MHz, 233 K, dichloromethane-d_2) δ [-122.7, -133.0, -133.7, -138.7](each m, each 1F, *o*-C_6F_5), [-161.7, -163.2](each t, $^{3}J_{FF}$ = 20.9 Hz, each 1F, *p*-C_6F_5), [-165.5, -165.7, -166.4, -166.8](each m, each 1F, *m*-C_6F_5).

$^{31}P\{^{1}H\}$ NMR (243 MHz, 233K, dichloromethane-d_2) δ 58.3 (m).

^{31}P NMR (243 MHz, 233 K, dichloromethane-d_2) δ 58.3 (br m).

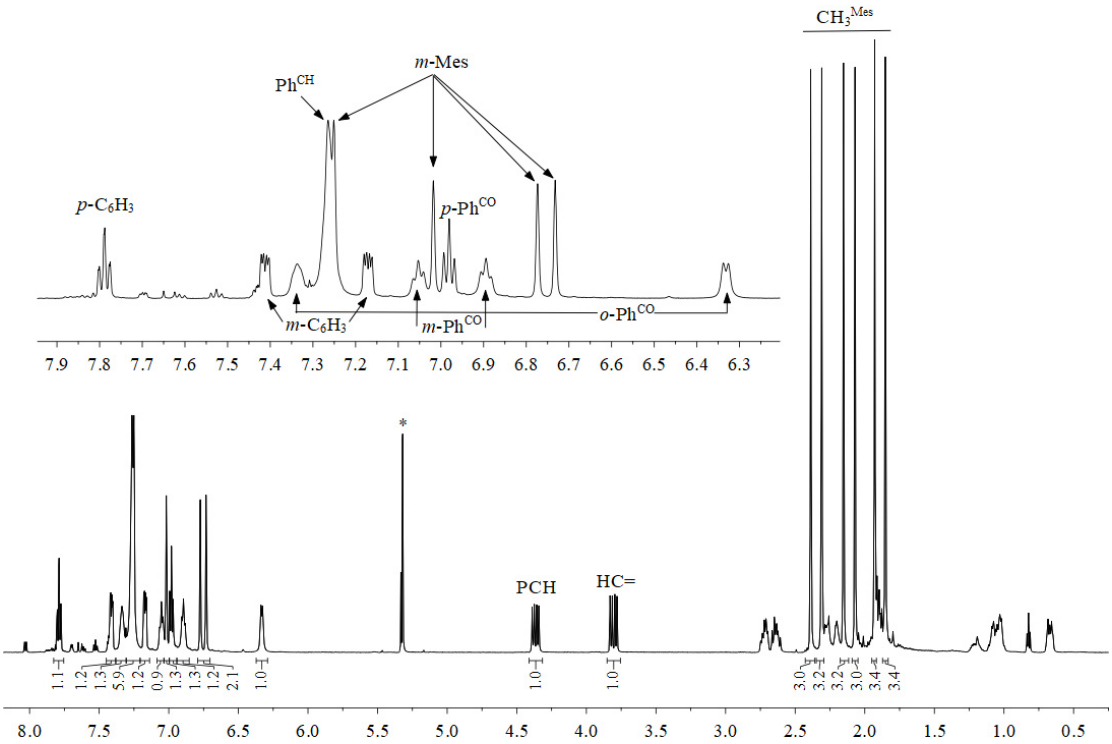


Figure S39a. ^{1}H NMR (600 MHz, 233 K, dichloromethane-d_2(*)) spectrum of compound **17**

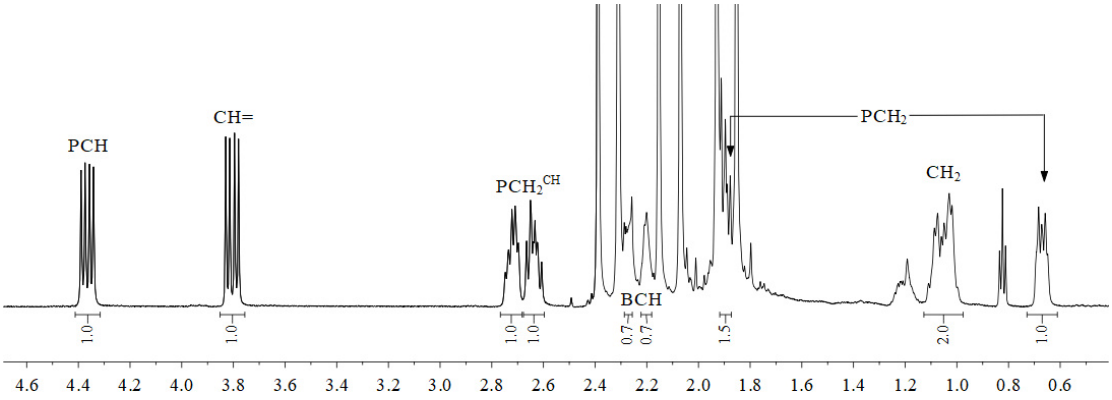


Figure S39b. ^{1}H NMR (600 MHz, 233 K, dichloromethane-d_2) spectrum of compound **17**

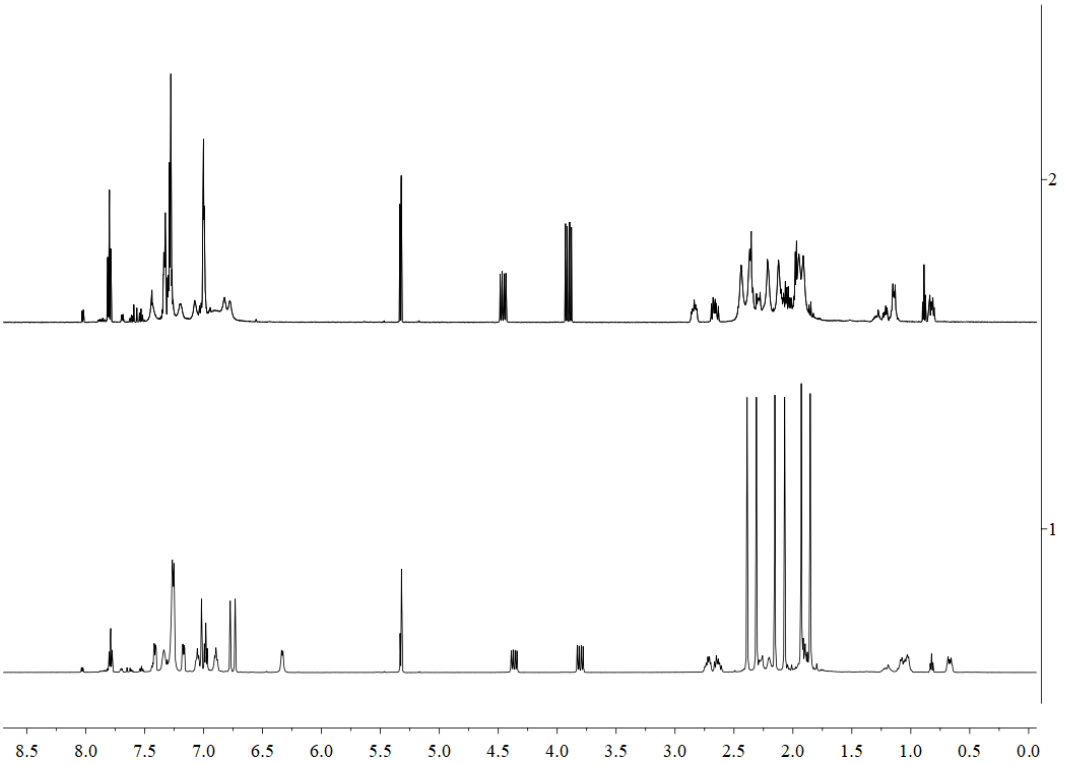


Figure S40. ^{1}H NMR (600 MHz, dichloromethane-d_2) spectra of compound **17** at (1) 233K and (2) 299 K

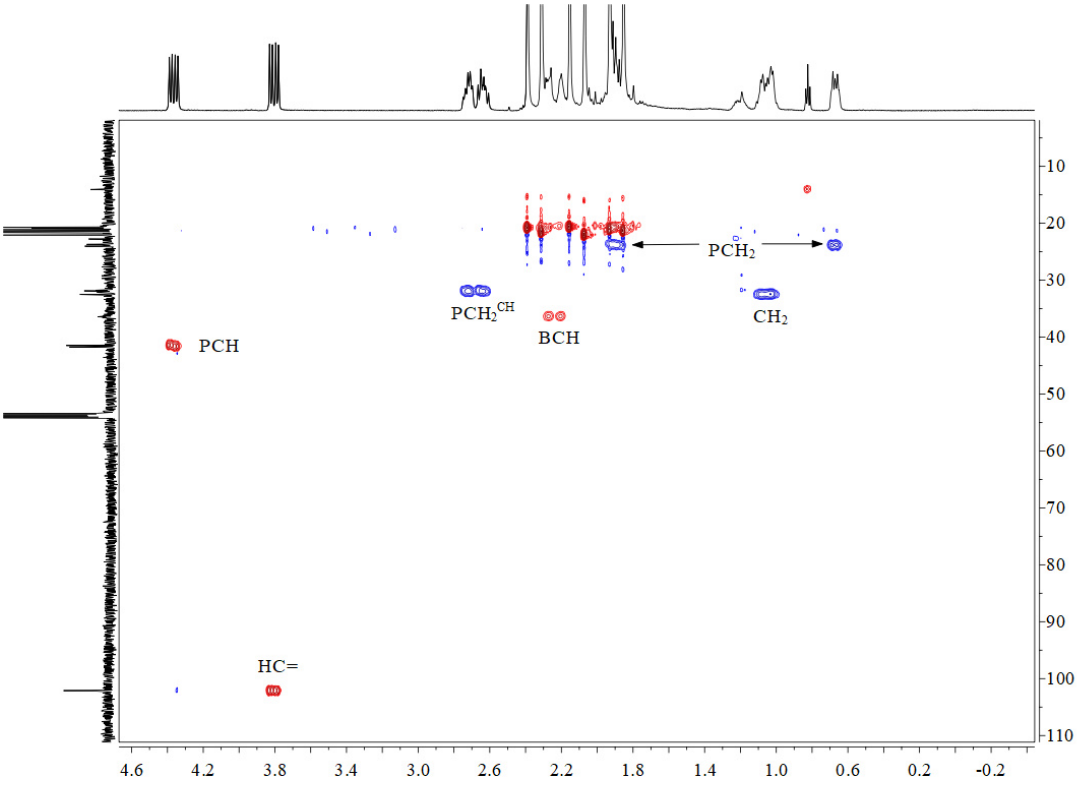


Figure S41. $^{1}H,^{13}C$ gHSQC (600/151 MHz, 233 K, dichloromethane-d_2) spectrum of compound **17** [selected area]

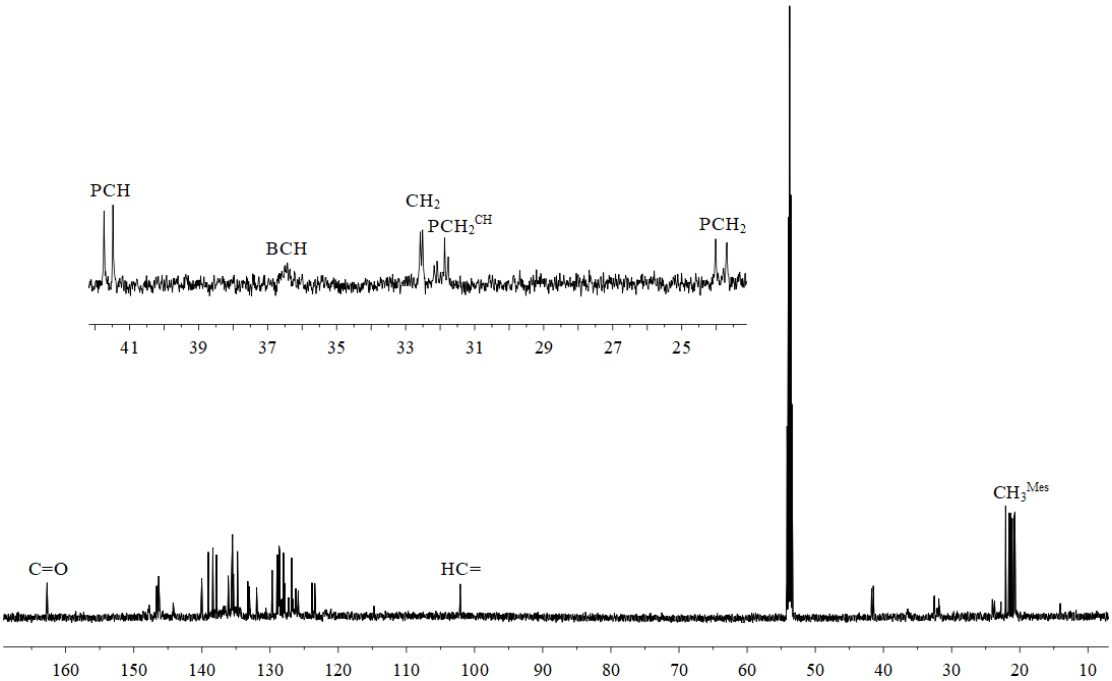


Figure S42a. $^{13}C\{^{1}H\}$ NMR (151 MHz, 233 K, dichloromethane-d_2) spectrum of compound **17**

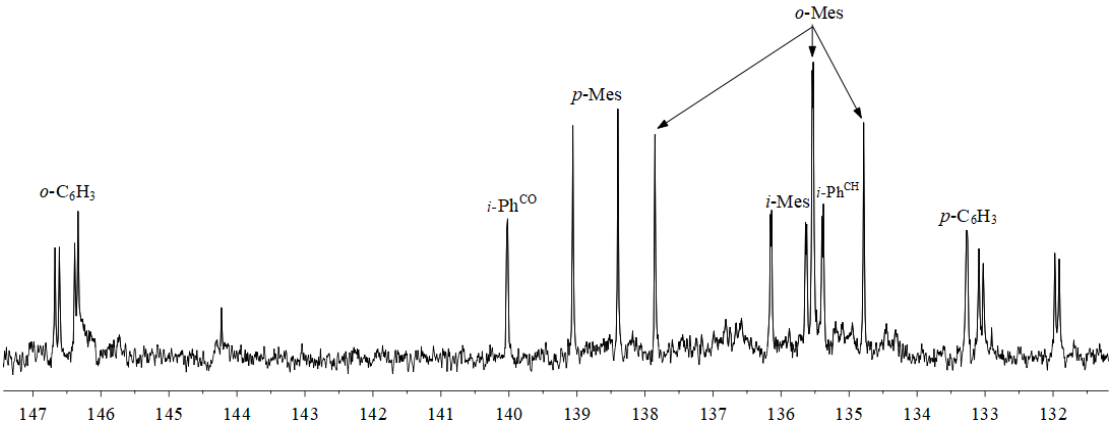


Figure S42b. $^{13}C\{^{1}H\}$ NMR (151 MHz, 233 K, dichloromethane-d_2) spectrum of compound **17**

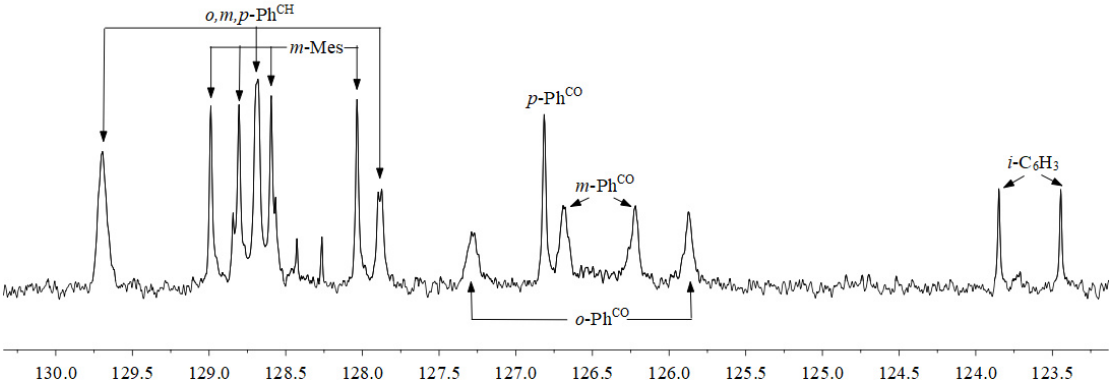


Figure S42c. $^{13}C\{^{1}H\}$ NMR (151 MHz, 233 K, dichloromethane-d_2) spectrum of compound **17**

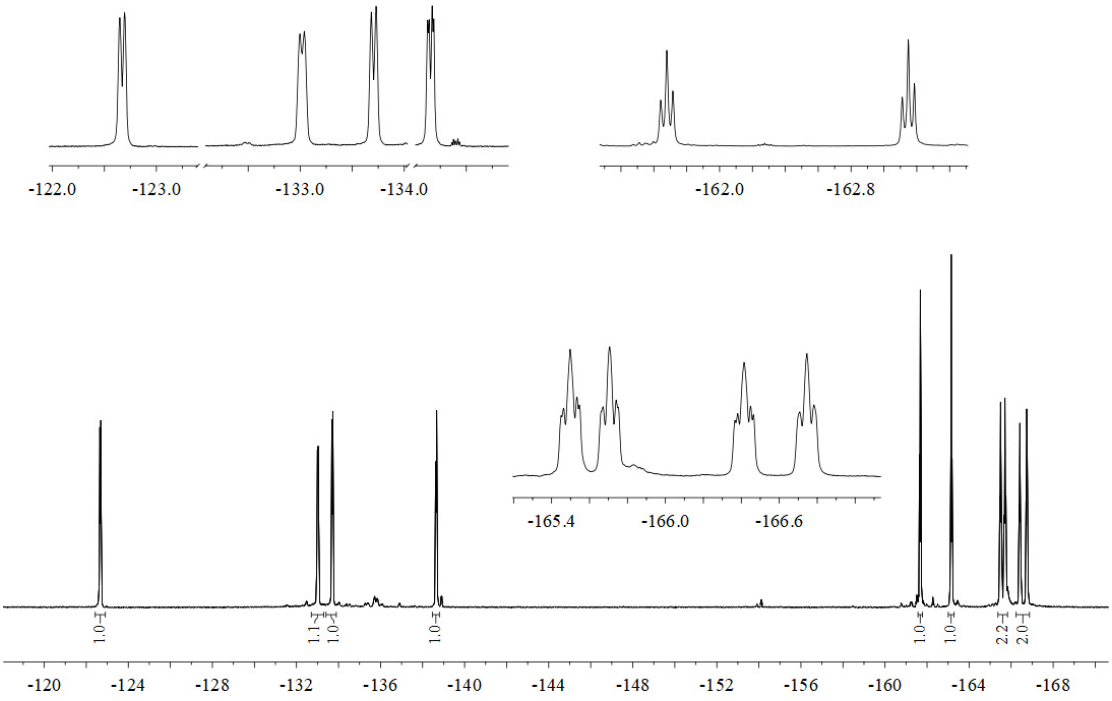


Figure S43. ^{19}F NMR (564 MHz, 233 K, dichloromethane-d_2) spectrum of compound **17**

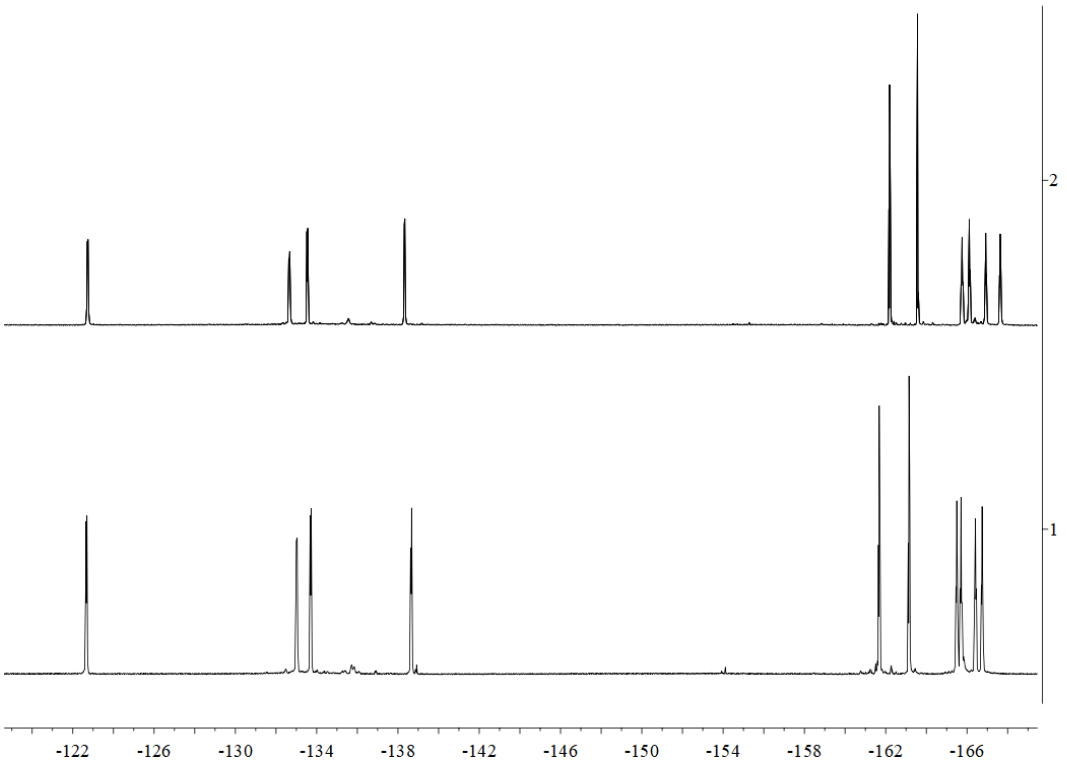


Figure S44. ^{19}F NMR (564 MHz, dichloromethane-d_2) spectra of compound **17** at (1) 233K and (2) 299 K.

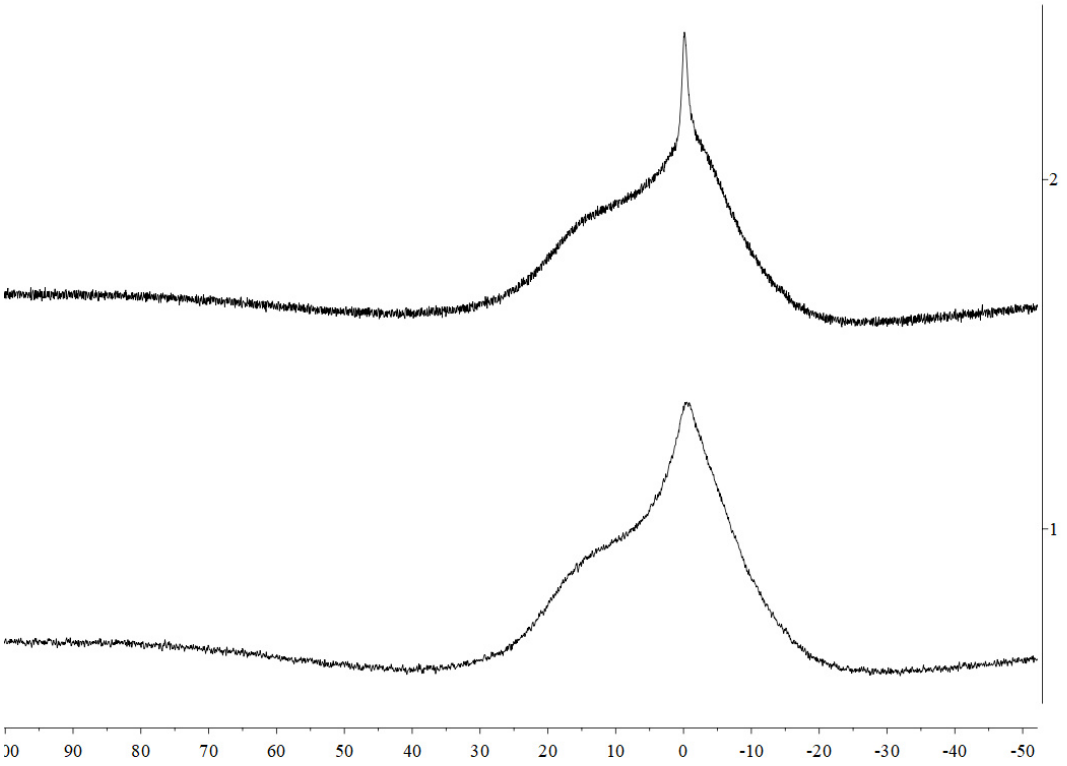


Figure S45. (1) $^{11}B\{^1H\}$ NMR (192 MHz, dichloromethane-d_2) spectra of compound **17** at (1) 233K and (2) 299 K.

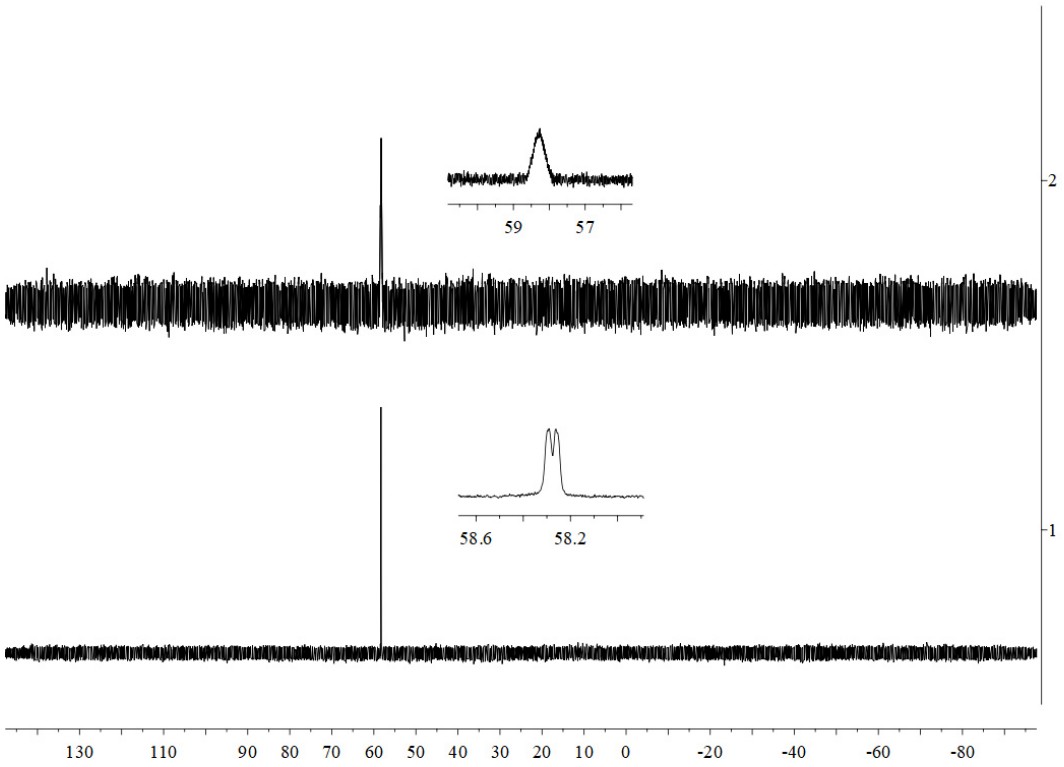


Figure S46. (1) $^{31}P\{^{1}H\}$ and (2) ^{31}P NMR (243 MHz, 233 K, dichloromethane-d_2) spectra of compound **17**

Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of compound **17** in dichloromethane/heptane (v/v ca. 1:3) at r.t.

X-ray crystal structure analysis of compound 17 (erk9472): A colorless plate-like specimen of $C_{55}H_{44}BF_{10}OP$, approximate dimensions 0.040 mm x 0.140 mm x 0.240 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1926 frames were collected. The total exposure time was 22.01 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 62367 reflections to a maximum θ angle of 66.74° (0.84 Å resolution), of which 7865 were independent (average redundancy 7.930, completeness = 99.6%, R_{int} = 6.49%, R_{sig} = 3.62%) and 6395 (81.31%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.0862(3) Å, b = 17.6699(4) Å, c = 21.1798(5) Å, β = 99.9670(10)°, volume = 4454.93(18) $Å^3$, are based upon the refinement of the XYZ-centroids of 9919 reflections above 20 σ(I) with 6.555° < 2θ < 133.1°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.870. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7500 and 0.9510. The structure was solved and

refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{55}H_{44}BF_{10}OP$. The final anisotropic full-matrix least-squares refinement on F^2 with 619 variables converged at R1 = 3.95%, for the observed data and wR2 = 10.21% for all data. The goodness-of-fit was 1.065. The largest peak in the final difference electron density synthesis was 0.308 $e^-/Å^3$ and the largest hole was -0.334 $e^-/Å^3$ with an RMS deviation of 0.050 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.420 g/cm^3 and F(000), 1968 e^-. CCDC number: 1953120.

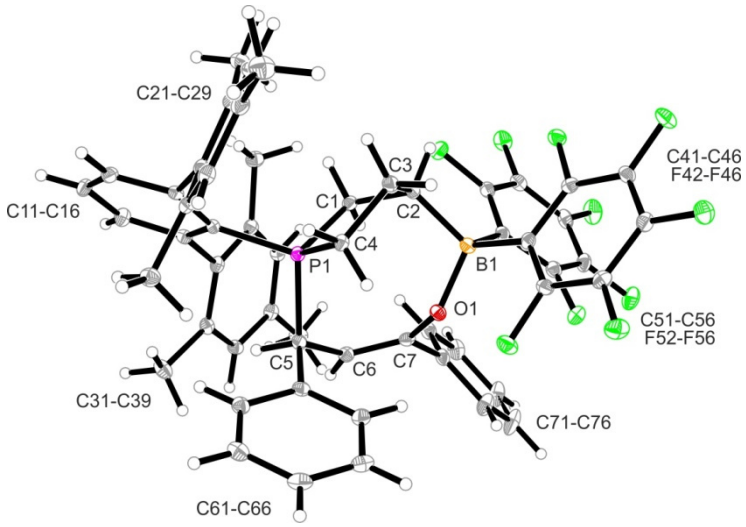
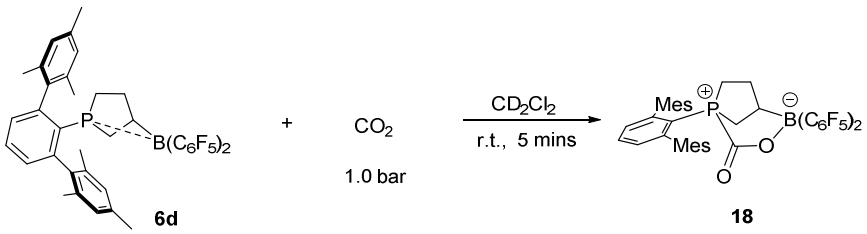


Figure S47: Crystal structure of compound **17** (thermal ellipsoids: 30% probability).

8. Synthesis of compound 18



Scheme S10

In a *J*-Young NMR tube compound **6d** (74.5 mg, 0.1 mmol, 1.0 equiv.) was added and dissolved with CD_2Cl_2 (0.6 mL). Then the NMR tube was degassed and CO_2 (1.0 bar) was introduced. Subsequently the NMR tube was shaken at room temperature for 5 minutes to give a pale yellow solution.

[Comment: compound **18** was not isolated due to the release of CO_2 while working-up. It was analyzed by *in situ* NMR experiments.]

NMR data of *in situ* generated compound **18** were obtained from a solution in dichloromethane-d_2 at -20 °C.

[Mes: mesityl]

^{1}H NMR (600 MHz, 253 K, dichloromethane-d_2) δ 7.87 (td, $^{3}J_{HH}$ = 7.7, $^{5}J_{PH}$ = 1.5 Hz, 1H, *p*-C_6H_3), [7.33, 7.31](each dd, $^{3}J_{HH}$ = 7.8, $^{4}J_{PH}$ = 4.4 Hz, each 1H, *m*-C_6H_3), [6.99/6.89, 6.80/6.78](each s, each 1H, *m*-Mes), 2.40 (dm, $^{3}J_{PH}$ = 37.9 Hz, 1H, BCH), [2.29, 2.08](each s, each 3H, *p*-CH_3^{Mes}), [2.21/1.86, 2.00/1.83](each s, each 3H, *o*-CH_3^{Mes}), [2.03, 1.13](each m, each 1H, PCH_2^{CH}), [1.91, 1.66](each m, each 1H, CH_2), [1.63, 1.26](each m, each 1H, PCH_2).

^{13}C{^{1}H} NMR (151 MHz, 253 K, dichloromethane-d_2) δ 161.1 (d, $^{1}J_{PC}$ = 91.4 Hz, C=O), [149.6 (d, $^{2}J_{PC}$ = 9.0 Hz), 148.6 (d, $^{2}J_{PC}$ = 11.4 Hz)](*o*-C_6H_3), 139.3 (*p*-Mes), [137.2/136.2, 136.7/136.4](*o*-Mes), 135.8 (d, $^{4}J_{PC}$ = 2.9 Hz, *p*-C_6H_3), [135.7 (d, $^{3}J_{PC}$ = 3.3 Hz), 135.5 (d, $^{3}J_{PC}$ = 4.5 Hz)](*i*-Mes), [131.6 (d, $^{3}J_{PC}$ = 10.7 Hz), 131.0 (d, $^{3}J_{PC}$ = 10.4 Hz)](*m*-C_6H_3), [129.4/128.1, 129.0/128.2](*m*-Mes), 115.0 (d, $^{1}J_{PC}$ = 71.7 Hz，*i*-C_6H_3), 28.4 (d, $^{1}J_{PC}$ = 37.6 Hz, PCH_2^{CH}), 25.8 (br, BCH), 23.5 (d, $^{2}J_{PC}$ = 6.0 Hz, CH_2), [21.0, 20.5](*p*-CH_3^{Mes}), [21.2/20.5, 21.1/20.2](*o*-CH_3^{Mes}), 21.1 (d, $^{1}J_{PC}$ = 36.4 Hz, PCH_2).

^{11}B{^{1}H} NMR (192 MHz, 253 K, dichloromethane-d_2) δ 2.5 ($\nu_{1/2}$ ~ 700 Hz).

^{11}B{^{1}H} NMR (192 MHz, 299 K, dichloromethane-d_2) δ 2.6 ($\nu_{1/2}$ ~ 260 Hz).

^{19}F NMR (564 MHz, 253 K, dichloromethane-d_2) δ [-133.6 (m), -134.5 (br)](each 2F, *o*-C_6F_5), [-159.9, -160.4](each t, $^{3}J_{FF}$ = 20.6 Hz, each 1F, *p*-C_6F_5), [-164.4, -165.1](each br m, each 2F, *m*-C_6F_5).

^{31}P{^{1}H} NMR (243 MHz, 253K, dichloromethane-d_2) δ 17.7 ($\nu_{1/2}$ ~ 10 Hz).

^{31}P NMR (243 MHz, 253 K, dichloromethane-d_2) δ 17.7 (br m).

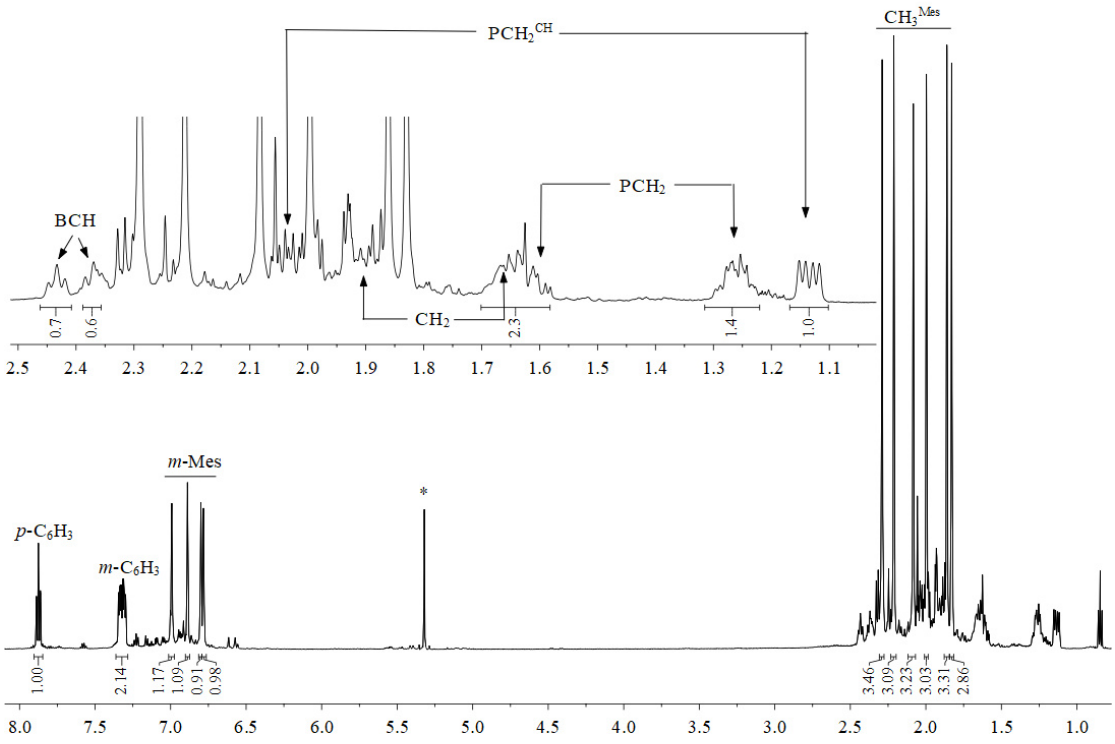


Figure S48. ^{1}H NMR (600 MHz, 253 K, dichloromethane-d_2(*)) spectrum of compound **18**

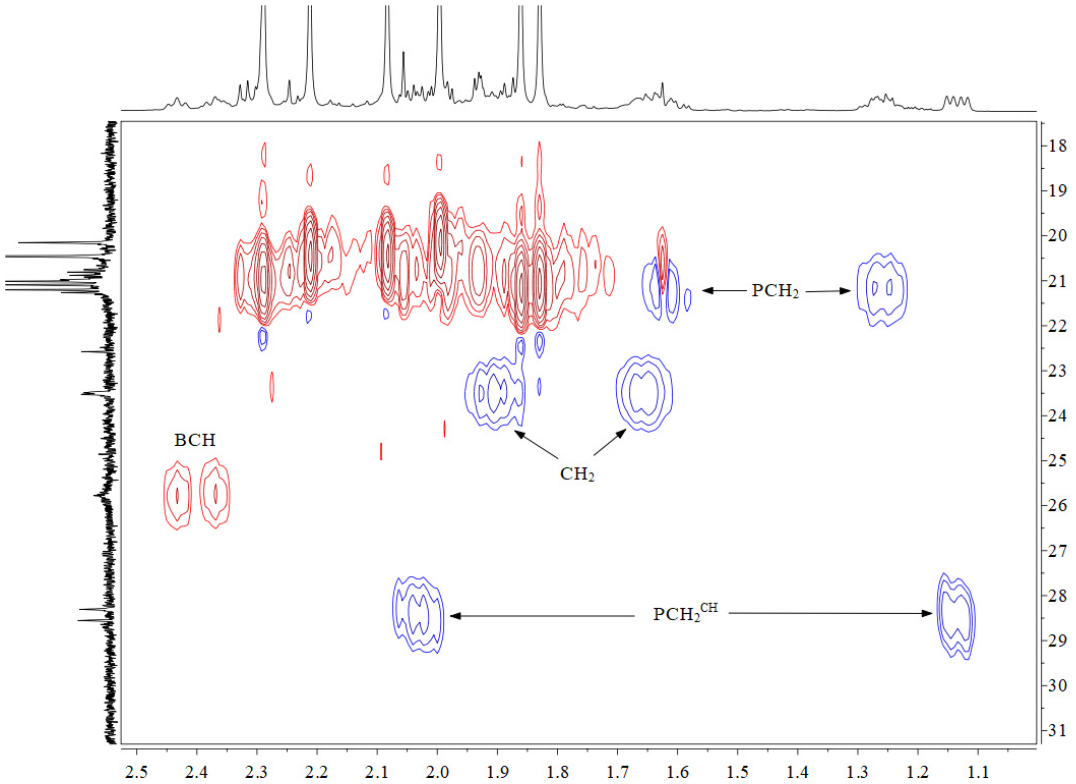


Figure S49. ^{1}H,^{13}C gHSQC (600/151 MHz, 253 K, dichloromethane-d_2) spectrum of compound **18** [selected area].

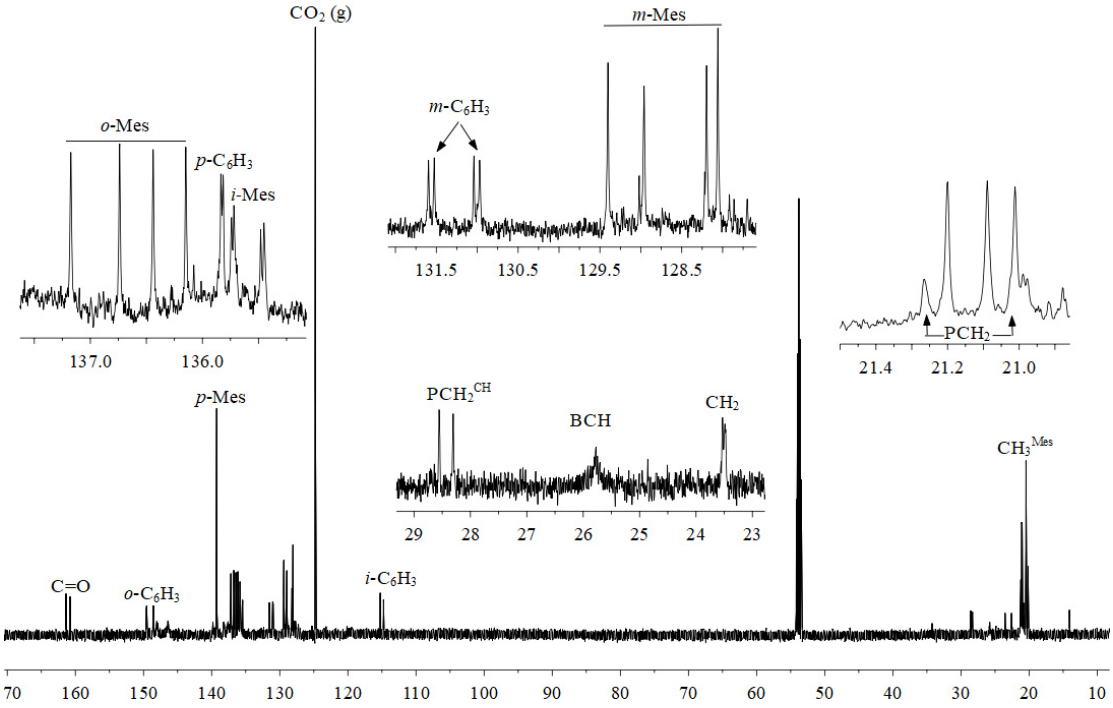


Figure S50. $^{13}C\{^{1}H\}$ NMR (151 MHz, 253 K, dichloromethane-d_2) spectrum of compound **18**

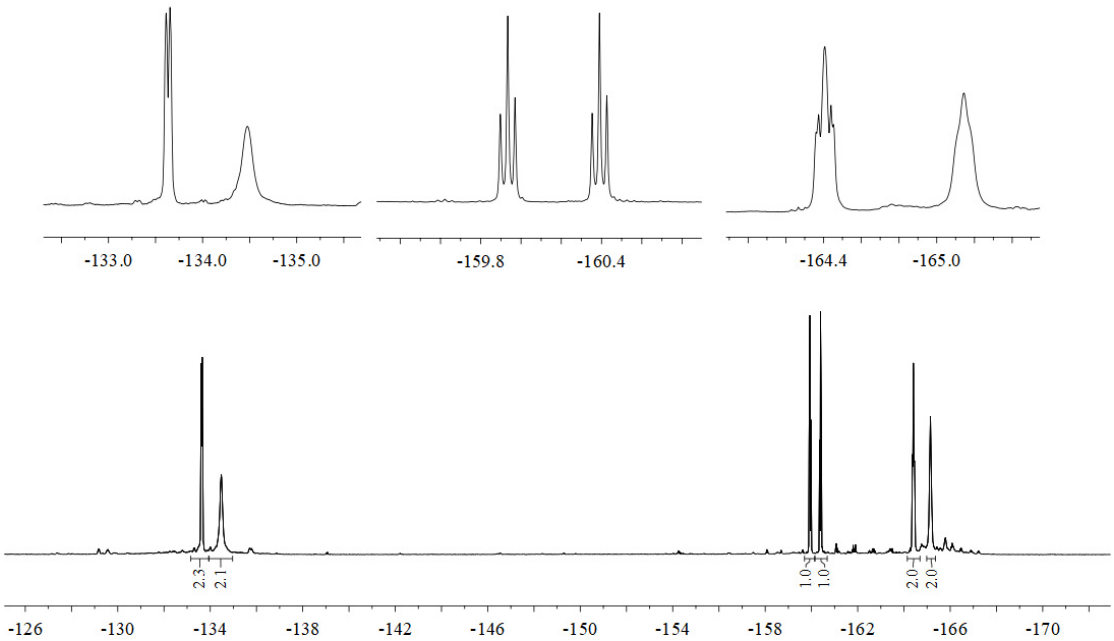


Figure S51. ^{19}F NMR (564 MHz, 253 K, dichloromethane-d_2) spectrum of compound **18**

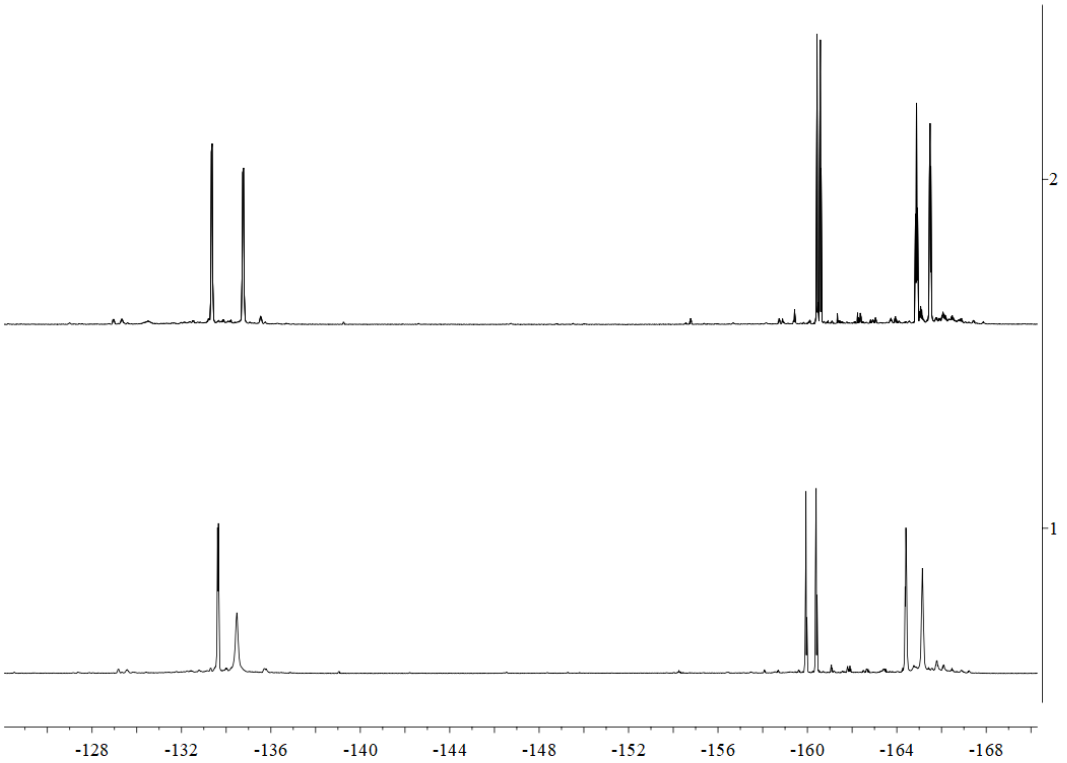


Figure S52. ^{19}F NMR (564 MHz, dichloromethane-d_2) spectra of compound **18** at (1) 253K and (2) 299 K.

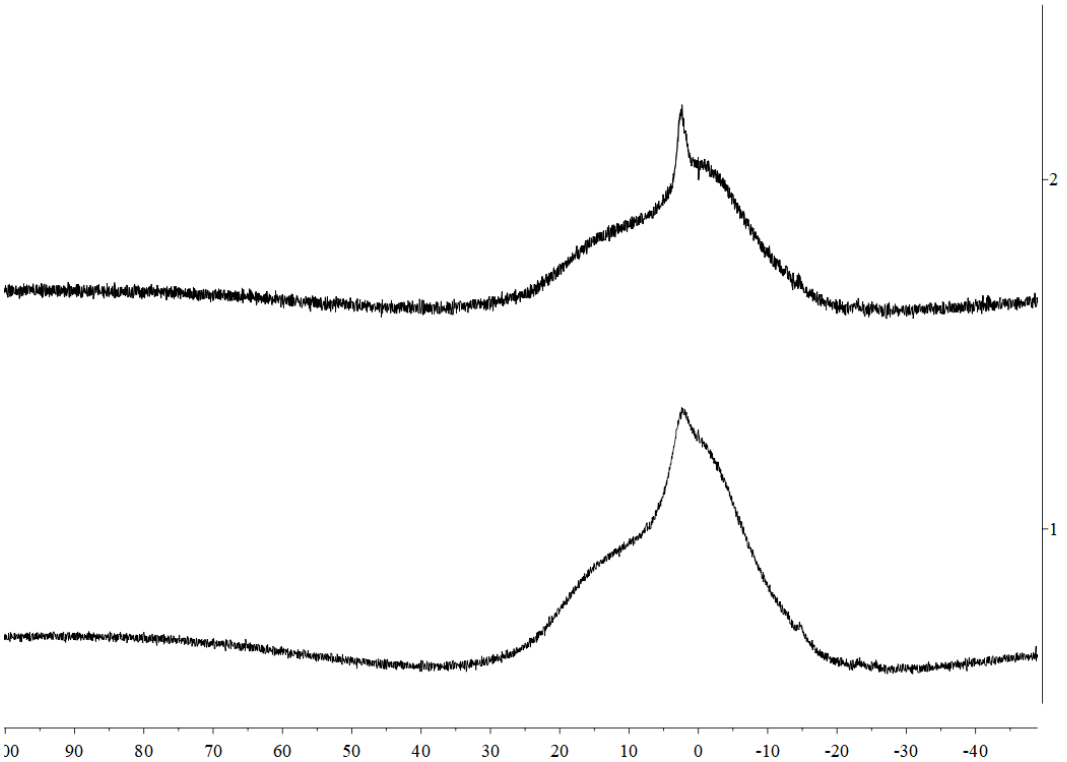


Figure S53. (1) $^{11}B\{^1H\}$ NMR (192 MHz, dichloromethane-d_2) spectra of compound **18** at (1) 253K and (2) 299 K.

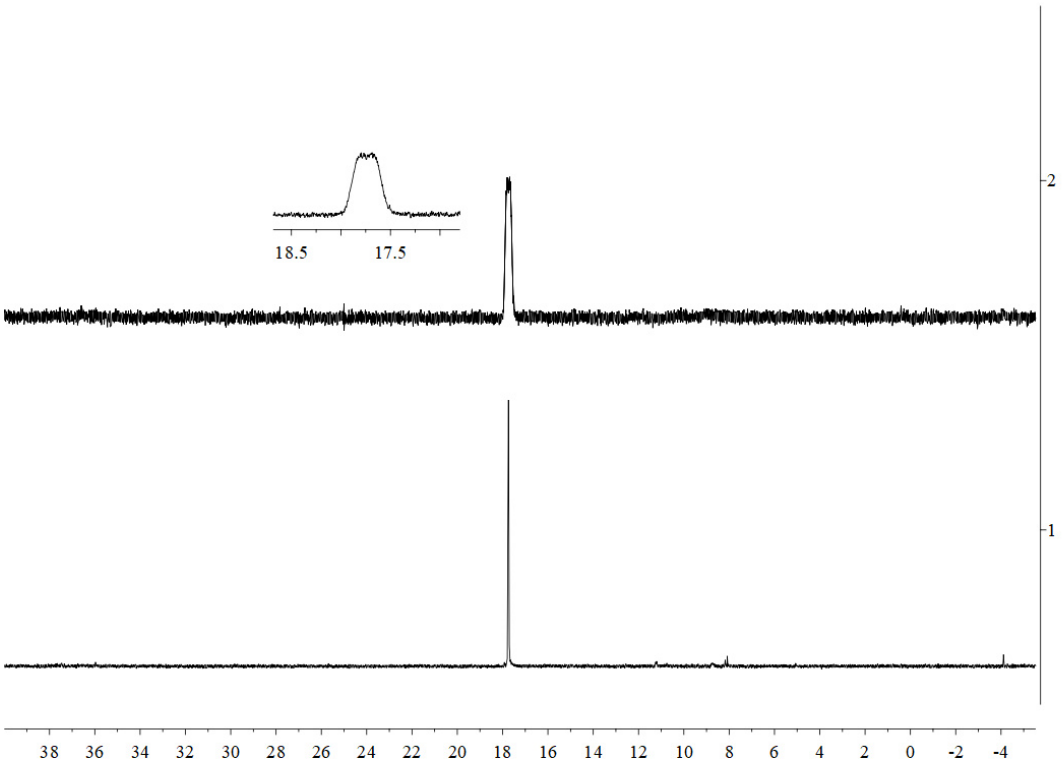
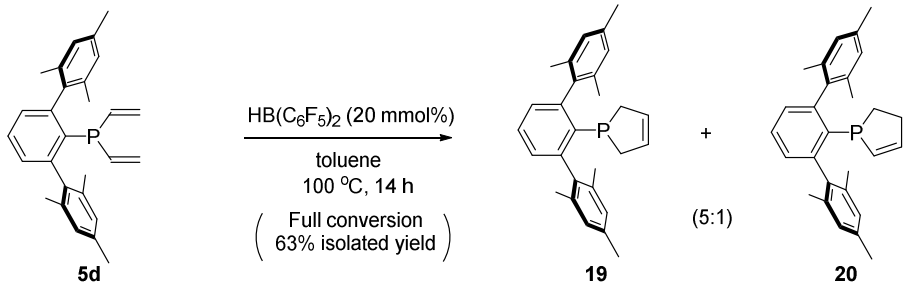


Figure S54. (1) $^{31}P\{^{1}H\}$ and (2) ^{31}P NMR (243 MHz, 233 K, dichloromethane-d_2) spectra of compound **18**.

9. Catalytic synthesis of compound 19 and compound 20



Scheme S11

Step 1: In a Schlenk flask (10 mL) compound **5d** (79.6 g, 0.2 mmol, 1 equiv.) and $HB(C_6F_5)_2$ (14 mg, 0.04 mmol, 0.2 equiv.) were mixed and toluene-d_8 (1 mL) was added. The mixture was stirred at 100 °C (oil bath temperature) overnight (ca. 14 h) to give a light-yellow solution. The obtained reaction mixture was directly characterized by an ^{1}H NMR experiment [Comment: full conversion of compound **5d** to compound **19** and **20** was observed.]

Step 2: Then all volatiles of the reaction mixture were removed in vacuo and the remaining residue was purified by a flash column chromatography (SiO_2) with

pentane/dichloromethane (10/1 to 5:1) to finally give a white solid (50 mg, 63% yield).
Elemental analysis (%) calc. for $C_{28}H_{31}P$: C, 84.39; H, 7.84. Found: C, 83.16; H, 8.97.
HRMS: *m*/*z* calc. for $C_{28}H_{31}P$ [H^+] 399.22361, found 399.22355.
NMR data of compound **19** and **20** were obtained from a solution of the isolated white solid in dichloromethane-d_2, which showed a mixture of compounds **19** and **20** (**19** : **20** ca. 83 : 17 (^{1}H))
[Mes: mesityl]
^{1}**H NMR** (600 MHz, 299 K, dichloromethane-d_2)
Compound 19: δ 7.33 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-C_6H_3), 6.94 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 2.1 Hz, 2H, *m*-C_6H_3), 6.90 (m, 4H, *m*-Mes), 5.42 (m, 2H, HC=), 2.32 (s, 6H, *p*-CH_3^{Mes}), [2.14 (ddm, $^2J_{HH}$ = 14.1 Hz, $^2J_{PH}$ = 7.8 Hz), 1.39 (ddm, $^2J_{PH}$ = 21.6 Hz, $^2J_{HH}$ = 14.1 Hz)](each 2H, CH_2), 2.07 (s, 12H, *o*-CH_3^{Mes}).
Compound 20 [selected resonances]: δ 7.32 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-C_6H_3), [6.93, 6.88](each m, each 2H, *m*-Mes), [5.59 (ddt, J_{PH} = 15.9 Hz, $^3J_{HH}$ = 7.8 Hz, J_{HH} = 2.7 Hz), 4.59 (ddt, J_{PH} = 38.8 Hz, $^3J_{HH}$ = 7.8 Hz, J_{HH} = 2.2 Hz)](each 1H, PCH=CH), [2.38/2.04, 1.73/1.39](each m, each 1H, PCH_2CH_2), 2.33 (s, 6H, *p*-CH_3^{Mes}), [2.04, 2.01](each s, each 6H, *o*-CH_3^{Mes}).
^{13}**C{^{1}H} NMR** (151 MHz, 299 K, dichloromethane-d_2)
Compound 19: δ 144.3 (d, $^2J_{PC}$ = 11.0 Hz, *o*-C_6H_3), 139.8 (d, $^3J_{PC}$ = 2.3 Hz, *i*-Mes), 139.2 (d, $^1J_{PC}$ = 33.3 Hz, *i*-C_6H_3), 137.2 (*p*-Mes), 136.4 (*o*-Mes), 129.8 (d, $^3J_{PC}$ = 1.5 Hz, *m*-C_6H_3), 129.5 (d, $^2J_{PC}$ = 7.0 Hz, HC=), 128.4 (*m*-Mes), 127.7 (*p*-C_6H_3), 29.4 (d, $^1J_{PC}$ = 13.2 Hz, CH_2), 21.18 (d, $^5J_{PC}$ = 4.9 Hz, *o*-CH_3^{Mes})^t, 21.18 (*p*-CH_3^{Mes})^t. [^{t} tentatively assigned].
Compound 20 [selected resonances]: δ [137.0 (d, J_{PC} = 8.5 Hz), 128.6 (d, J_{PC} = 15.9 Hz)](PCH=CH), [33.3, 25.0 (d, J_{PC} = 11.0 Hz)](PCH_2CH_2).
^{31}**P{^{1}H} NMR** (243 MHz, 299 K, dichloromethane-d_2)
Compound 19 (83 mol%): δ -5.2 ($\nu_{1/2}$ ~ 1 Hz).
Compound 20 (17 mol%): δ 8.4 ($\nu_{1/2}$ ~ 1 Hz).

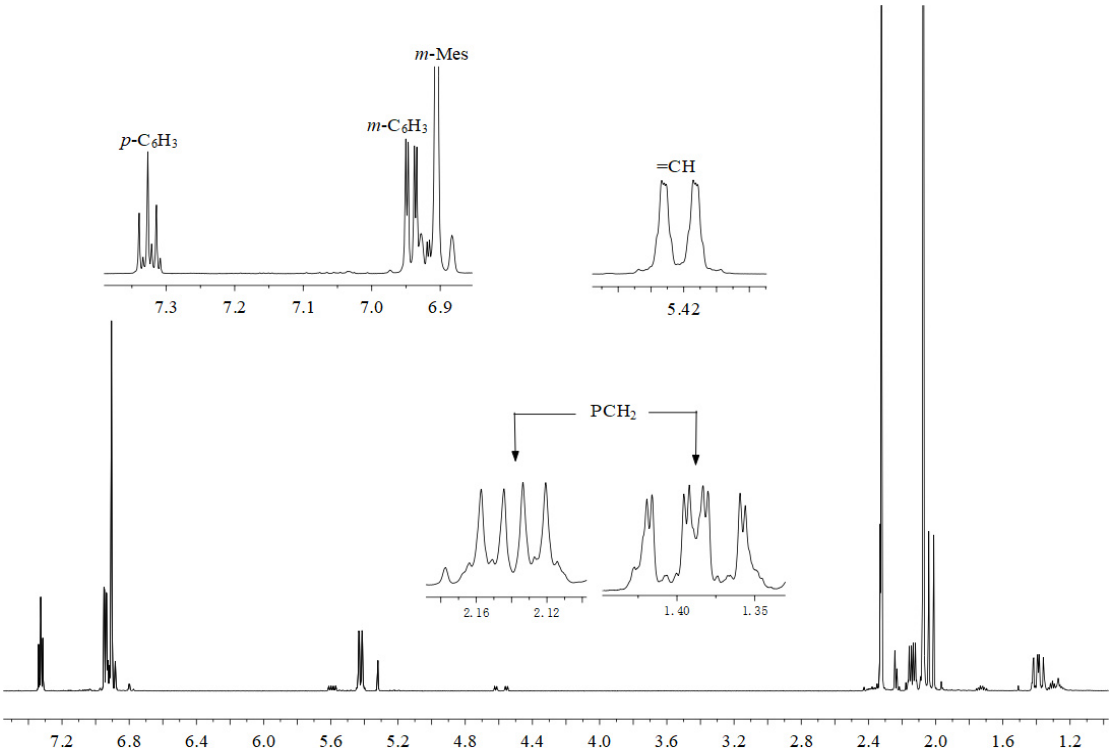


Figure S55a. ^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) spectrum of the obtained mixture [selected traces of compound **19**]

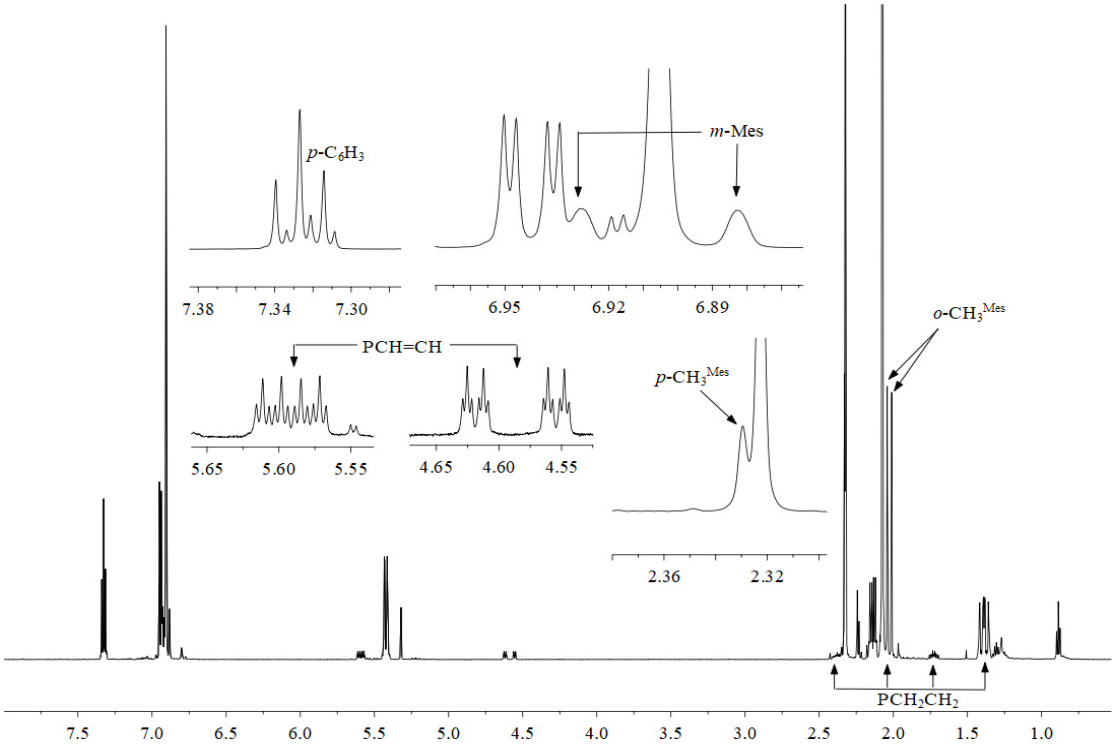


Figure S55b.^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) spectrum of the obtained mixture [selected traces of compound **20**]

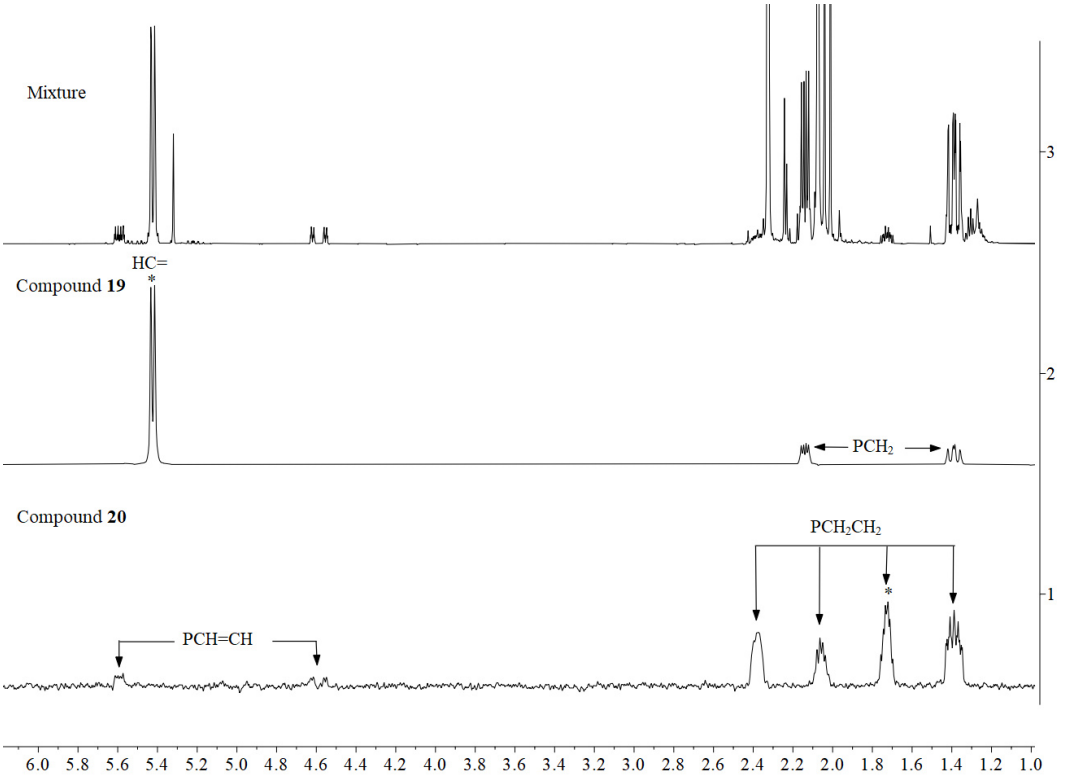


Figure S56. (1, 2) $^{1}H\{^{1}H\}$1D-tocsy (600 MHz, 299 K, dichloromethane-d_2) spectra of the obtained mixture: (1) * irradiation at δ $^{1}H_{(irr)}$ = 1.73 (PCH_2, **20**). (2) * irradiation at δ $^{1}H_{(irr)}$ = 5.42 (HC=, **19**)]. (3) ^{1}H NMR (600 MHz, 299 K, dichloromethane-d_2) spectrum of the obtained mixture.

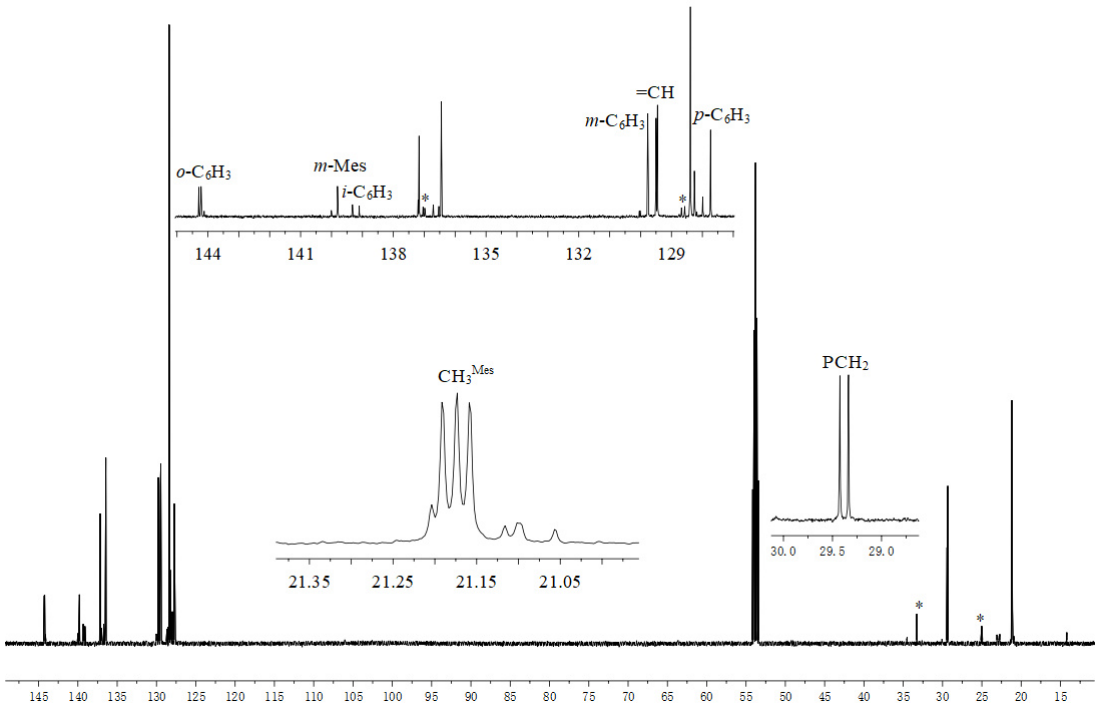


Figure S57. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, dichloromethane-d_2) spectrum of the obtained mixture [assignment selected for compound **19**; * compound **20**]

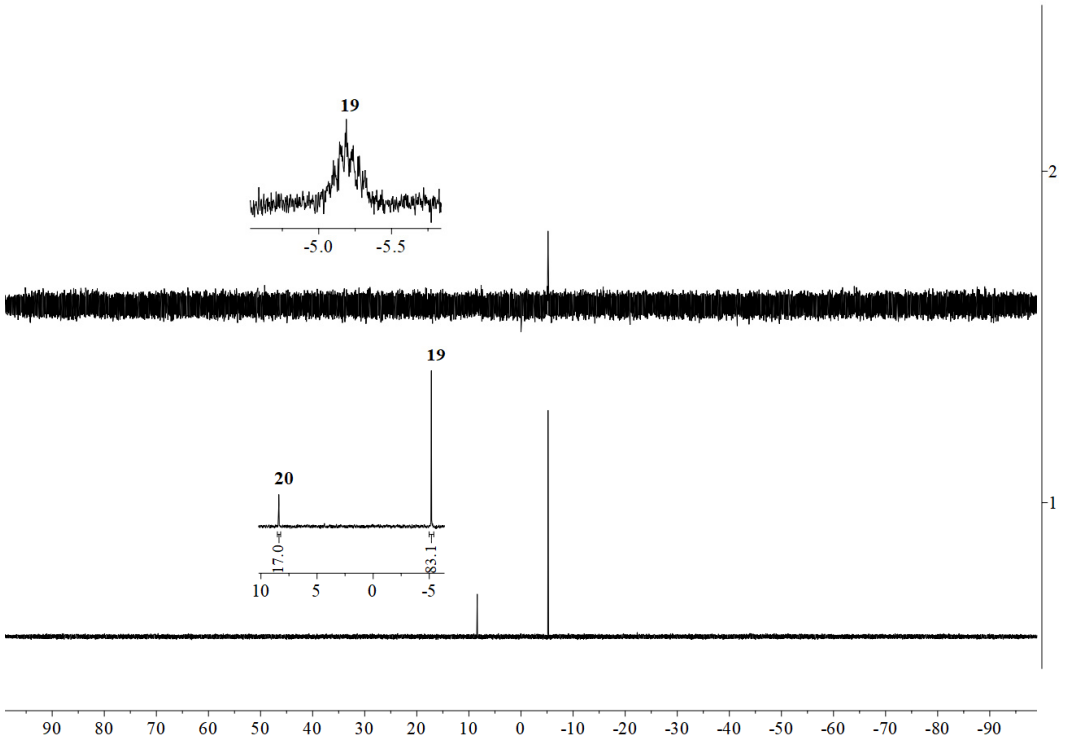


Figure S58. (1) $^{31}P\{^{1}H\}$ and (2) ^{31}P NMR (243 MHz, 299 K, dichloromethane-d_2) spectra of the obtained mixture.

Crystals suitable for the X-ray crystal structure analysis for compound **19** were obtained from a solution of the obtained white solid in dichloromethane/pentane (v/v ca. 1:5) at room temperature.

X-ray crystal structure analysis of compound 19 (erk9555): A colorless prism-like specimen of $C_{28}H_{31}P$, approximate dimensions 0.118 mm x 0.174 mm x 0.202 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 446 frames were collected. The total exposure time was 3.10 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 41145 reflections to a maximum θ angle of 27.48° (0.77 Å resolution), of which 5143 were independent (average redundancy 8.000, completeness = 99.7%, R_{int} = 6.37%, R_{sig} = 3.29%) and 4479 (87.09%) were greater than $2\sigma(F^2)$. The final cell constants of a = 8.1976(4) Å, b = 18.0312(7) Å, c = 15.7056(7) Å, β = 104.521(2)°, volume = 2247.33(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9934 reflections above 20 σ(I) with 5.133° < 2θ < 54.71°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.953. The calculated minimum and maximum transmission

coefficients (based on crystal size) are 0.9730 and 0.9840. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{28}H_{31}P$. The final anisotropic full-matrix least-squares refinement on F^2 with 268 variables converged at R1 = 4.30%, for the observed data and wR2 = 10.87% for all data. The goodness-of-fit was 1.013. The largest peak in the final difference electron density synthesis was 0.365 $e^-/Å^3$ and the largest hole was -0.282 $e^-/Å^3$ with an RMS deviation of 0.052 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.178 g/cm^3 and F(000), 856 e^-. CCDC number: 1953117.

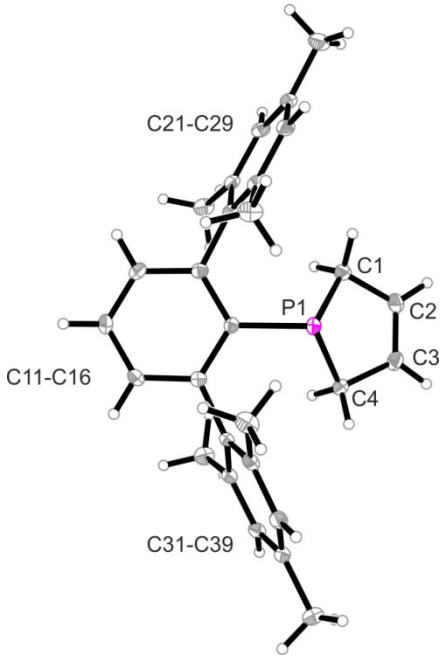
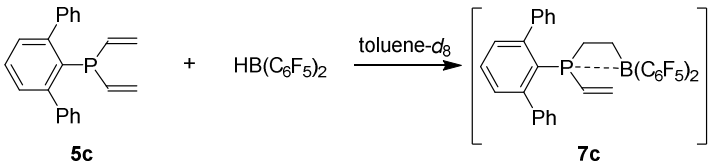


Figure S59: Crystal structure of compound **19** (thermal ellipsoids: 50% probability).

10. Generation of compound 7c



Scheme S12

In a Young NMR tube, compound **5c** (31.4 mg, 0.1 mmol, 1.0 equiv.) [Comment: compound **5c** was synthesized by the same procedure as described for compound **5d**] and $HB(C_6F_5)_2$ were mixed and toluene-d_8 was added. The NMR tube was rotated at r.t.

for 2 hours to give a yellow solution. Then the sample was directly characterized by NMR experiments and the generation of compound **7c** was confirmed.

Characterization of compound **7c**

^{1}H NMR (600 MHz, 299 K, toluene-d_8)[selected resonances] δ [6.29 (ddd, $^{2}J_{PH}$ = 25.4, $^{3}J_{HH}$ = 18.2, $^{3}J_{HH}$ = 12.2 Hz), 5.53 (dd, $^{3}J_{PH}$ = 35.9, $^{3}J_{HH}$ = 12.2 Hz), 5.27 (dd, $^{3}J_{PH}$ = 18.8 Hz, $^{3}J_{HH}$ = 18.2 Hz)](each 1H, PCH=CH_2), [1.80 (m), 1.58 (m), 1.26 (dm, $^{3}J_{PH}$ = 80.2 Hz), 0.87 (m)](each 1H, PCH_2CH_2B).

^{11}B{^{1}H} NMR (192 MHz, 299 K, toluene-d_8) δ 0.3 ($\nu_{1/2}$ ~ 380 Hz).

^{19}F NMR (564 MHz, 299 K, toluene-d_8) δ -129.3 (m, 2F, *o*-C_6F_5), -158.4 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-C_6F_5), -164.1 (m, 2F, *m*-C_6F_5), [$\Delta\delta^{19}Fm,p$ = 5.7].

^{31}P{^{1}H} NMR (243 MHz, 299K, toluene-d_8) δ 10.3 ($\nu_{1/2}$ ~ 43 Hz).

^{31}P NMR (243 MHz, 299 K, toluene-d_8) δ 10.3 (dm, $^{3}J_{PH}$ ~ 80 Hz).

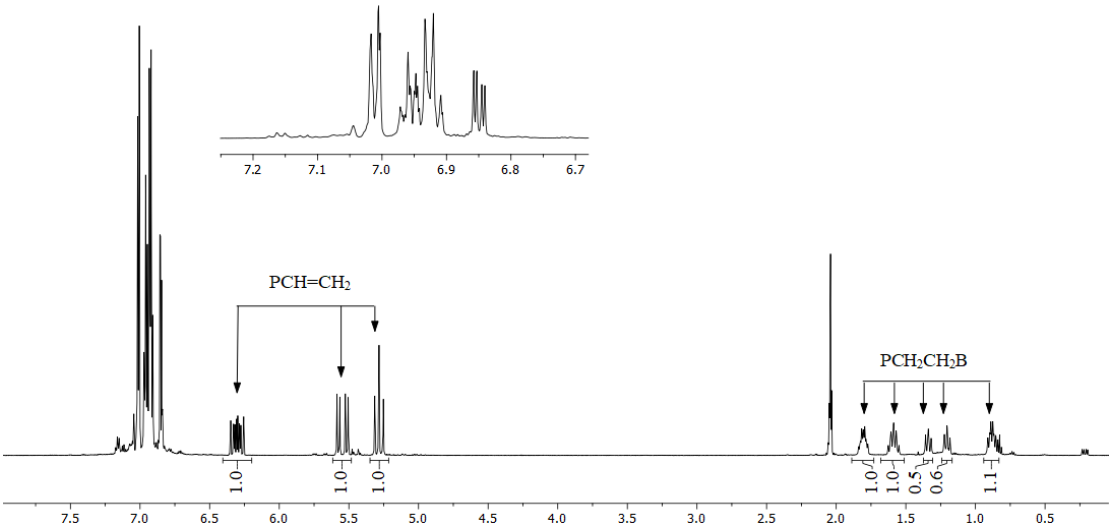


Figure S60. ^{1}H NMR (600 MHz, 299 K, toluene-d_8) spectrum of the reaction mixture

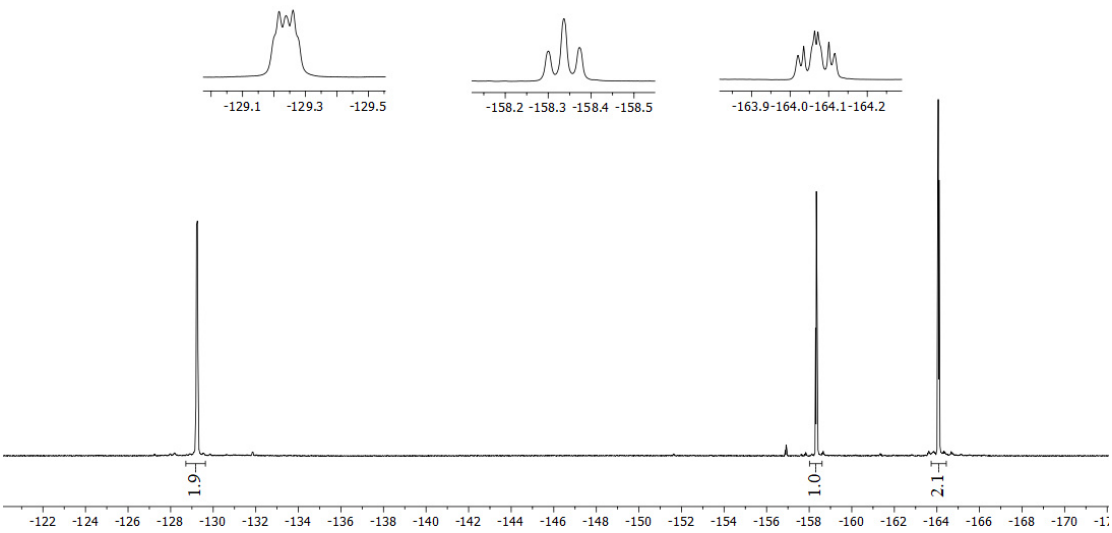


Figure S61. ^{19}F NMR (564 MHz, 299 K, toluene-d_8) spectrum of the reaction mixture

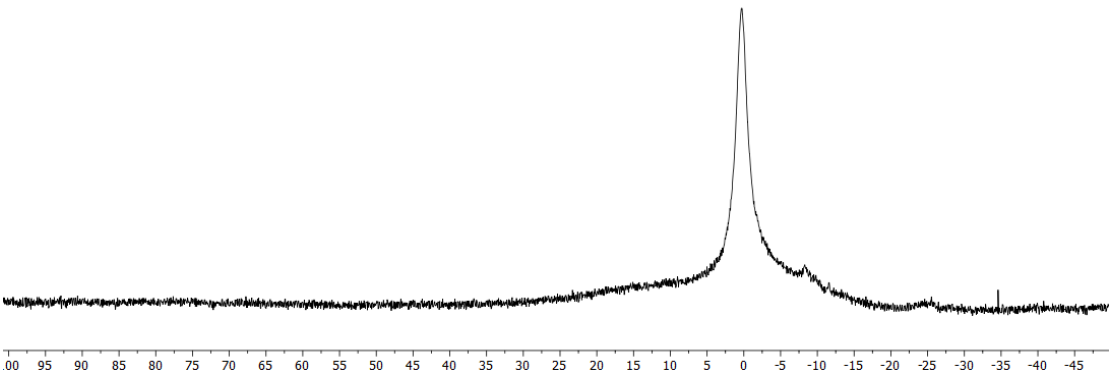


Figure S62. $^{11}B\{^1H\}$ NMR (192 MHz, 299K, toluene-d_8) spectrum of the reaction mixture

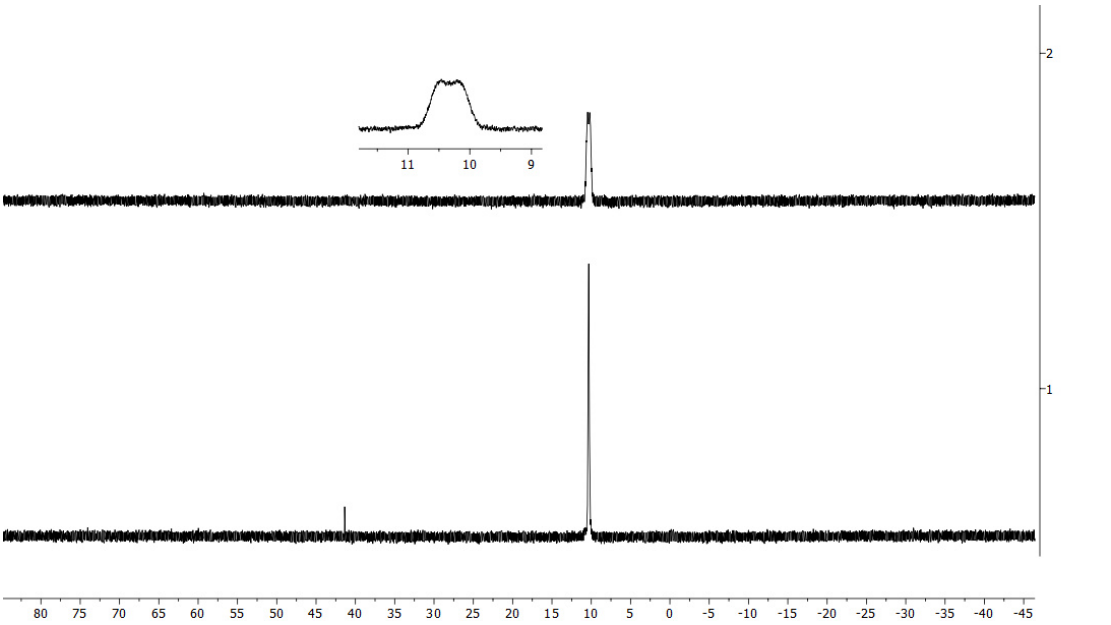


Figure S63. (1) $^{31}P\{^1H\}$ and (2) ^{31}P NMR (243 MHz, 299 K, toluene-d_8) spectra of the reaction mixture

Characterization of compound **5c**

HRMS: *m*/*z* calc. for $C_{22}H_{19}P$ [H^+] 315.12971, found 315.12969.

^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2) δ 7.43 (tm, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-C_6H_3), 7.36 (m, 10H, Ph), 7.27 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 2.3 Hz, 2H, *m*-C_6H_3), 5.93 (dt, $^3J_{HH}$ = 18.3 Hz, $^2J_{PH}$ = $^3J_{HH}$ = 11.8 Hz, 2H, PCH=), [5.31 (ddd, $^3J_{PH}$ = 32.3 Hz, $^3J_{HH}$ = 11.8 Hz, $^2J_{HH}$ = 1.9 Hz), 5.16 (ddd, $^3J_{HH}$ = 18.3 Hz, $^3J_{PH}$ = 13.4 Hz, $^2J_{HH}$ = 1.9 Hz)](each 2H, =CH_2).

^{13}C{^{1}H} NMR (125 MHz, 299 K, dichloromethane-d_2) δ 149.7 (d, $^2J_{PC}$ = 15.0 Hz, *o*-C_6H_3), 143.7 (d, $^3J_{PC}$ = 4.7 Hz, *i*-Ph), 137.5 (d, $^1J_{PC}$ = 14.7 Hz, PCH=), 133.9 (d, $^1J_{PC}$ = 20.5 Hz, *i*-C_6H_3), 130.5 (d, $^4J_{PC}$ = 2.1 Hz, *o*-Ph), 130.3 (d, $^3J_{PC}$ = 2.9 Hz, *m*-C_6H_3), 128.7 (*p*-C_6H_3), 127.8 (*m*-Ph), 127.5 (*p*-Ph), 125.1 (d, $^2J_{PC}$ = 25.9 Hz, =CH_2).

^{31}P{^{1}H} NMR (202 MHz, 299K, dichloromethane-d_2) δ -18.0 ($\nu_{1/2}$ ~ 1 Hz).

^{31}P NMR (202 MHz, 299 K, dichloromethane-d_2) δ -18.0 (m).

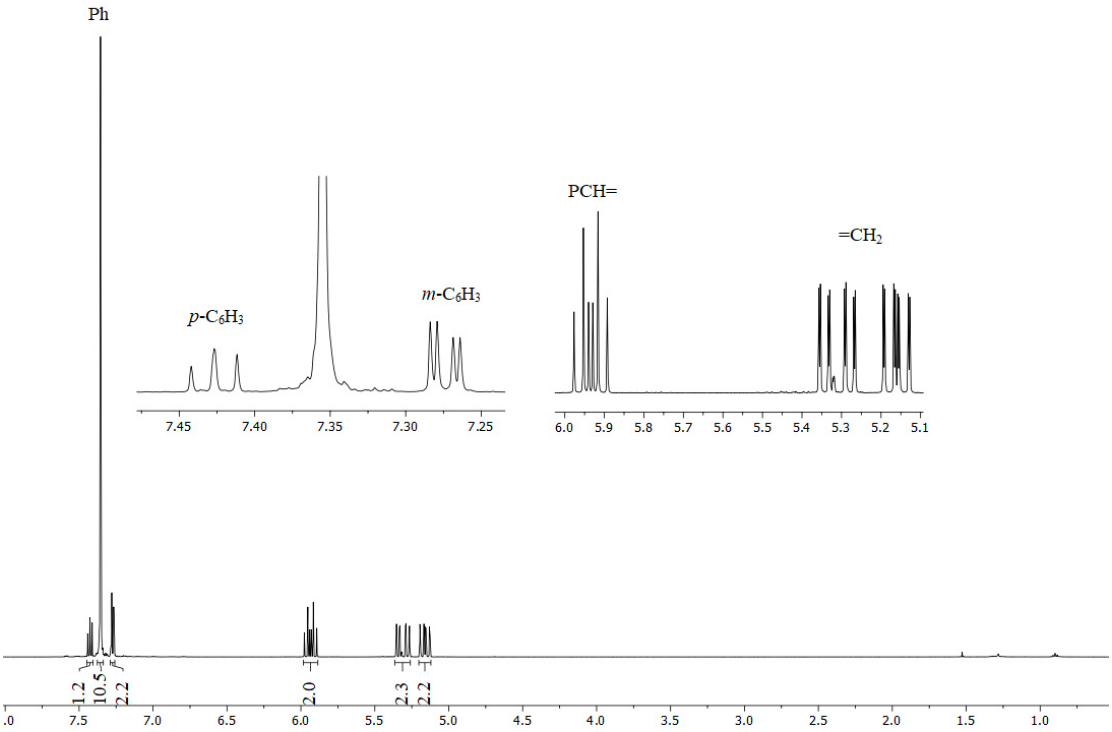


Figure S64. ^{1}H NMR (500 MHz, 299 K, dichloromethane-d_2) spectrum of compound **5c**

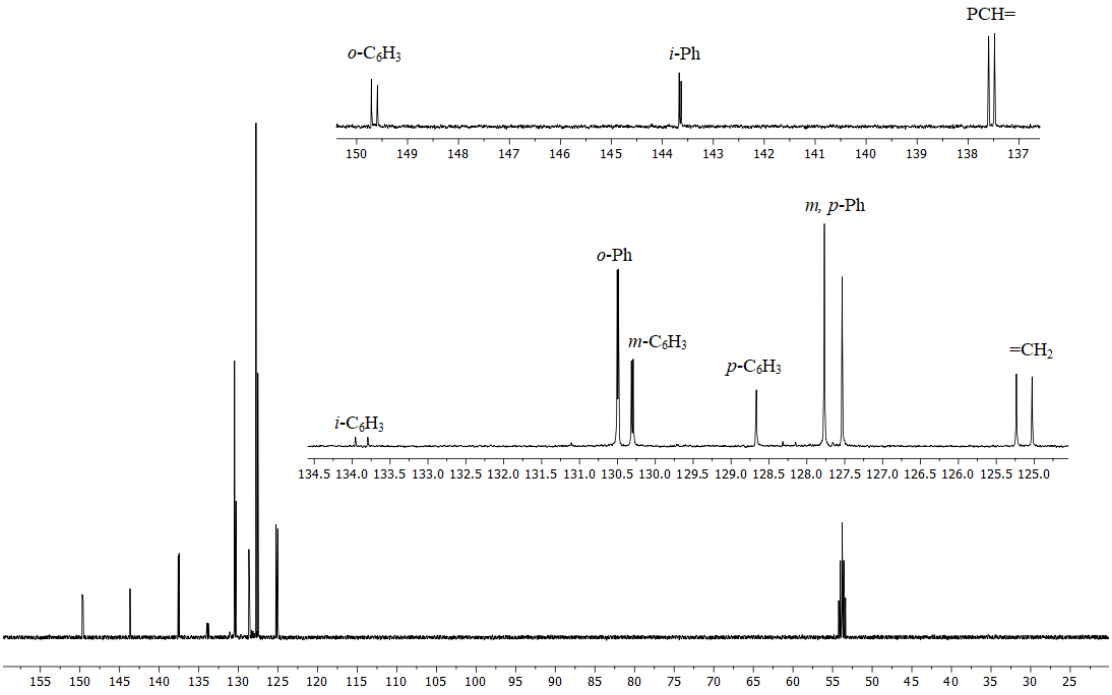


Figure S65. $^{13}C\{^{1}H\}$ NMR (125 MHz, 299 K, dichloromethane-d_2) spectrum of compound **5c**

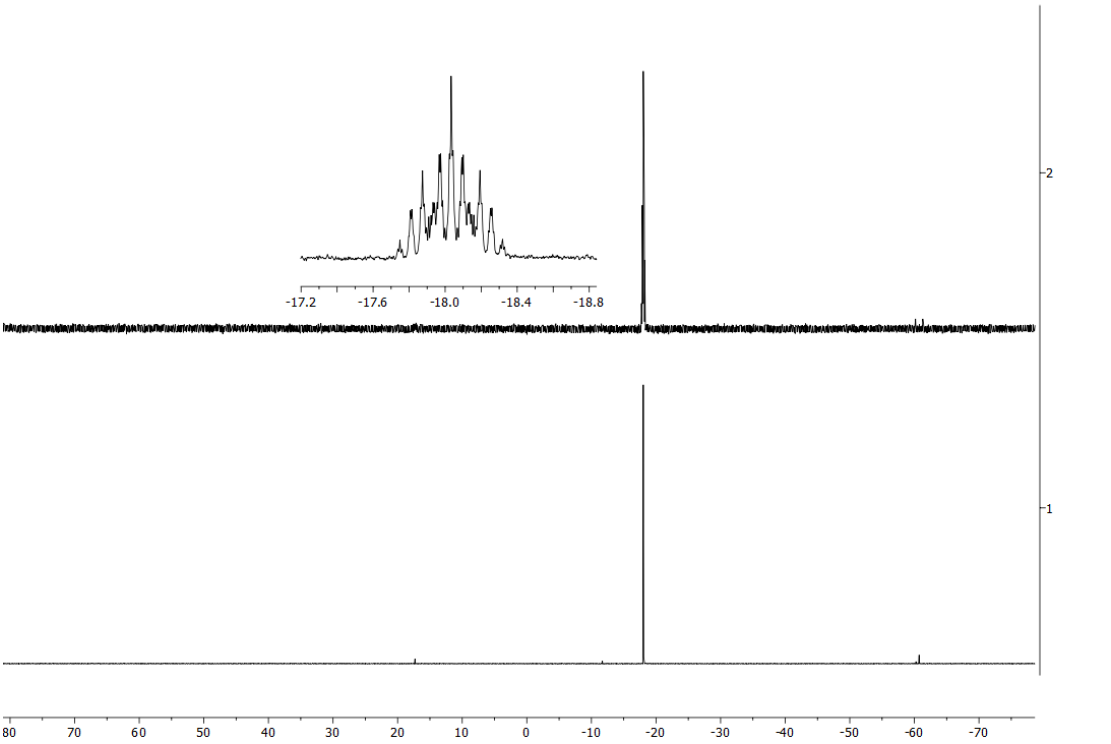
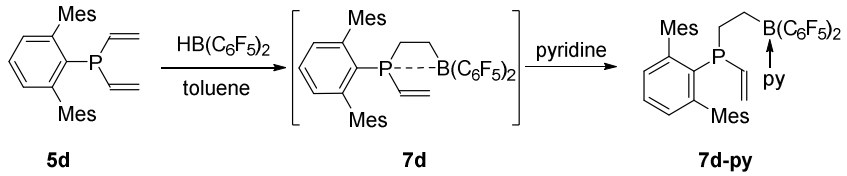


Figure S66. (1) $^{31}P\{^{1}H\}$ and (2) ^{31}P NMR (202 MHz, 299 K, dichloromethane-d_2) spectra of compound **5c**

11. Synthesis of compound 7d-py



5d **7d** **7d-py**

Scheme S13

In a vial (20 mL), compound **5d** (79.8 mg, 0.2 mmol, 1.0 equiv.) and $HB(C_6F_5)_2$ (69.0 mg, 0.2 mmol, 1.0 equiv.) were mixed and toluene (2 mL) was added. The mixture was stirred at r.t. for 10 min. Then pyridine (15 mg, 0.2 mmol, 1.0 equiv.) was added and the resulted mixture was further stirred at r.t. for 10 min to give a clear light-yellow solution. Subsequently all volatiles were removed in vacuo and then the residue was carefully washed with cold pentane (2 × 0.5 mL). After storing a solution of the residue in CH_2Cl_2/pentane solution at -35 °C for 3 days, compound **7d-py** (120 mg, 73%) was obtained as a white solid.

NMR data of compound **7d-py** were obtained from a solution of the isolated white solid in toluene-d_8, [Mes: mesityl; Py: pyridine].

^{1}H NMR (600 MHz, 299 K, toluene-d_8) δ [7.88 (m, 2H, *o*), 6.58 (m, 1H, *p*), 6.24 (m, 2H, *m*)](Py), 7.05 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-C_6H_3), [6.80, 6.79](each m, each 2H, *m*-Mes), 6.73 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 1.9 Hz, 2H, *m*-C_6H_3), [5.64 (ddd, $^3J_{HH}$ = 18.2 Hz, $^3J_{PH}$ = 16.2 Hz, $^2J_{HH}$ = 3.0 Hz), 5.32 (ddd, $^3J_{PH}$ = 40.2 Hz, $^3J_{HH}$ = 11.0 Hz, $^2J_{HH}$ = 3.0 Hz)](each 1H, =CH_2), 5.52 (dd, $^3J_{HH}$ = 18.2 Hz, $^3J_{HH}$ = 11.0 Hz, 1H, =CH), 2.21 (s, 6H, *p*-Me^{Mes}), [2.04, 1.94](each s, each 6H, *o*-Me^{Mes}), [1.38, 1.17](each m, each 1H, PCH_2), [1.10, 0.94](each m, each 1H, BCH_2).

^{13}C{^{1}H} NMR (151 MHz, 299 K, toluene-d_8) δ 147.0 (d, $^2J_{PC}$ = 15.9 Hz, *o*-C_6H_3), [145.5 (*o*), 140.4 (*p*), 125.2 (*m*)](Py), 140.5 (d, $^3J_{PC}$ = 4.2 Hz, *i*-Mes), 138.5 (d, $^1J_{PC}$ = 18.9 Hz, =CH), 136.6 (p-Mes), [136.3, 136.0](*m*-Mes), 129.7 (d, $^2J_{PC}$ = 41.9 Hz, =CH_2), 129.6 (d, $^3J_{PC}$ = 3.0 Hz, *m*-C_6H_3), 137.1 (d, $^1J_{PC}$ = 26.2 Hz, *i*-C_6H_3), 129.3 (d, $^4J_{PC}$ = 2.9 Hz, *p*-C_6H_3), [128.2, 128.1](*m*-Mes), 23.2 (br d, $^1J_{PC}$ = 11.3 Hz, PCH_2), 21.5 (br, BCH_2), [21.39 (d, *J* = 4.7 Hz), 21.37](*o*-Me^{Mes}), 21.1 (*p*-Me^{Mes}), [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, 299 K, toluene-d_8) δ -0.7 ($\nu_{1/2}$ ~ 450 Hz).

^{19}F NMR (564 MHz, 299 K, toluene-d_8) δ [-131.4, -132.0] (each m, each 2F, *o*-C_6F_5), [-157.8, -158.0] (each t, $^3J_{FF}$ = 20.6 Hz, each 1F, *p*-C_6F_5), [-163.4, -163.7](each m, each 2F, *m*-C_6F_5).

$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, toluene-d_8) δ -12.9 ($\nu_{1/2}$ ~ 7 Hz).

^{31}P NMR (243 MHz, 299 K, toluene-d_8) δ -12.9 (br d, $^{3}J_{PH}$ ~ 40 Hz).

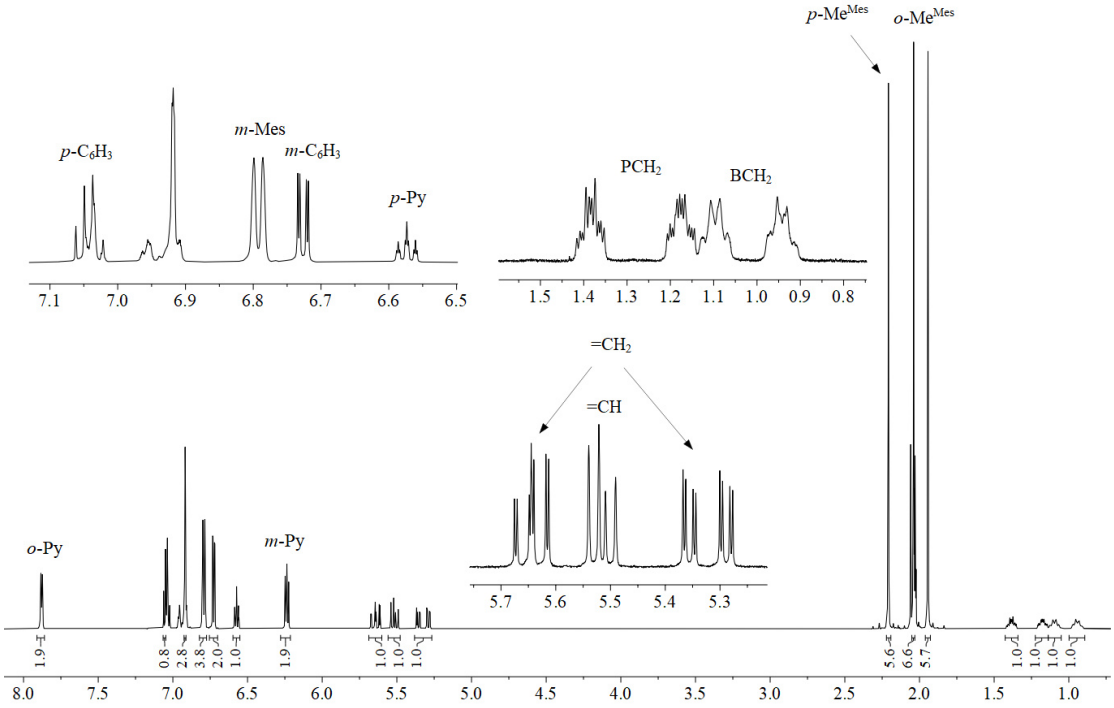


Figure S67. ^{1}H NMR (600 MHz, 299 K, toluene-d_8) spectrum of compound **7d-py**

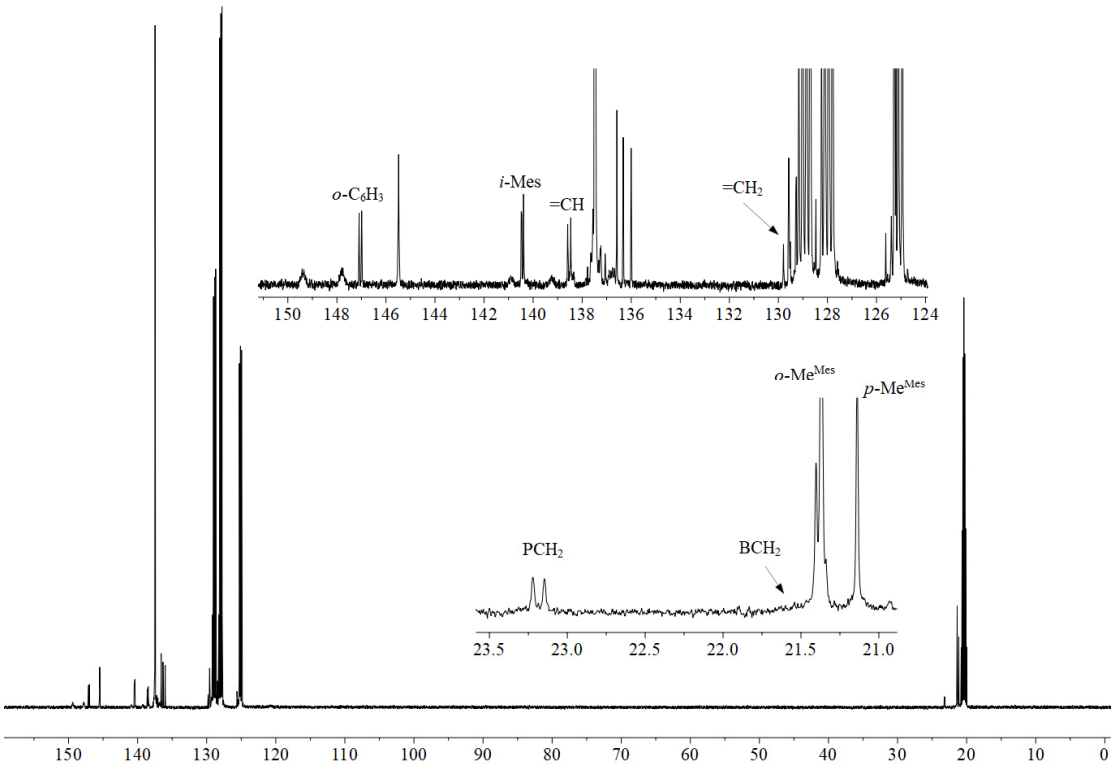


Figure S68. $^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, toluene-d_8) spectrum of compound **7d-py**

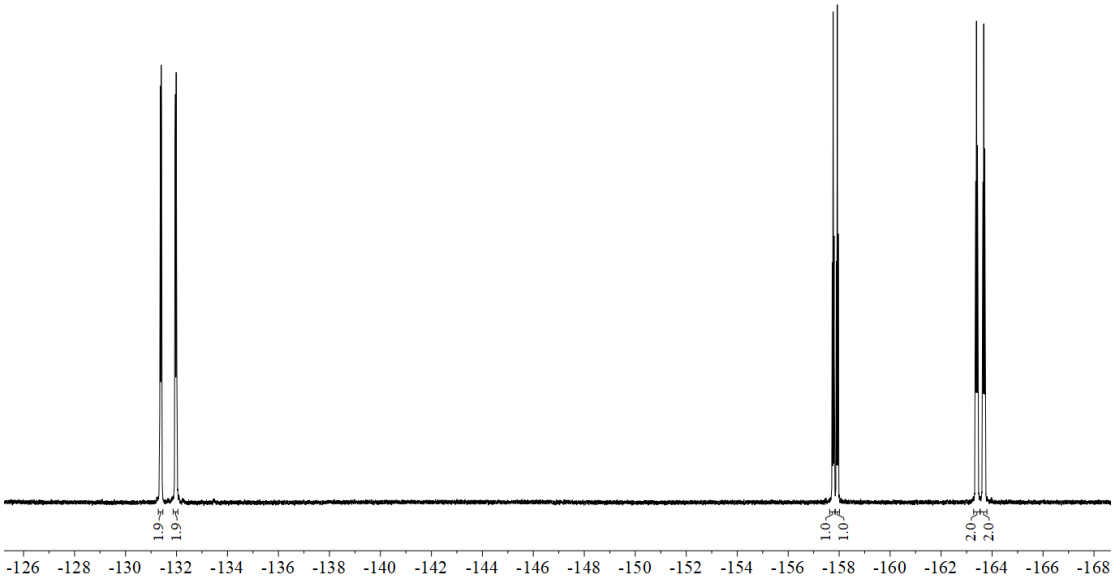


Figure S69.[19]F NMR (564 MHz, 299 K, toluene-d_8) spectrum of compound **7d-py**

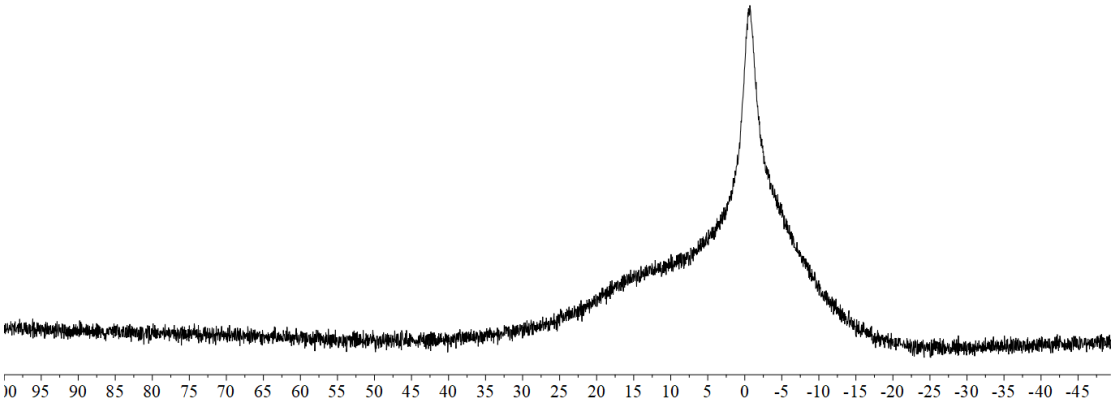


Figure S70.[11]B{[1]H} NMR (192 MHz, 299 K, toluene-d_8) spectrum of compound **7d-py**

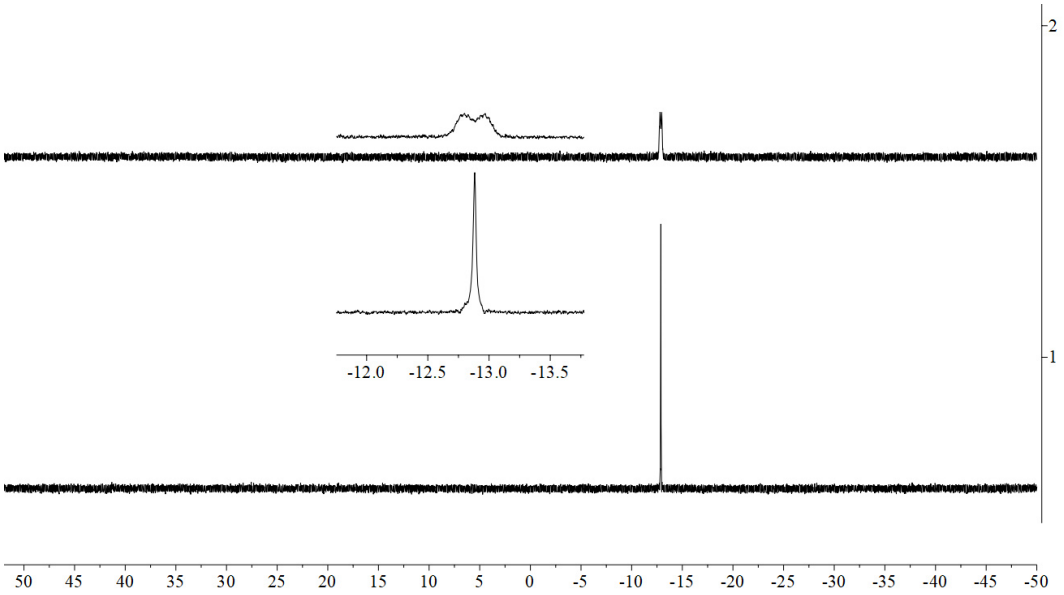


Figure S71. (1) [31]P{[1]H} and (2) [31]P NMR (243 MHz, 299 K, toluene-d_8) spectrum of compound **7d-py**

12. DFT Calculations

12.1 Methods

All calculations were performed with the TURBOMOLE 7.4.1 program.[8] The structures were optimized without any geometry constraints using the TPSS functional[9] and an atom-pairwise dispersion correction (D3).[10] A flexible triple zeta basis set (def2-TZVP)[11] was used in all calculations. For the calculation of free energy contributions of translation, rotations and harmonic vibrations (G^{RRHO}_{298}), a rotor approximation was applied for vibrational modes with wave numbers below 100 cm^{-1}.[12] Single point calculations were performed with the hybrid functional PW6B95(-D3).[13] Free energies of solvation were obtained with the COSMO-RS model[14] for 298 K using CH_2Cl_2 as solvent.

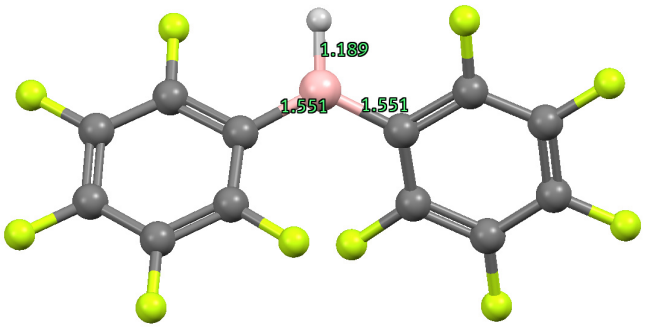
12.2 Results

Energies and molecular structures of all intermediates are reported in Table S1 and Figure S72, respectively.

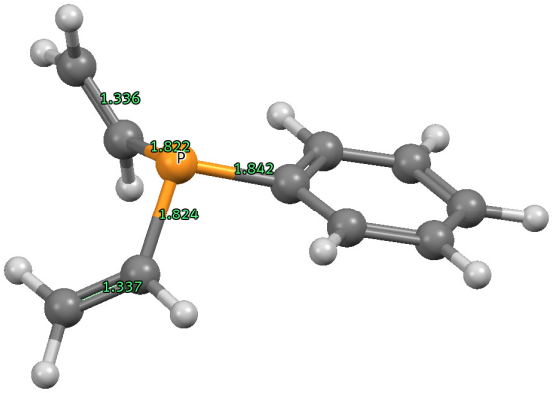
	E(TPSS-D3) [E_h]	E(PW6B95-D3) [E_h]	G^{RRHO}_{298} [kcal/mol]	$G^{COSMO-RS}_{298}$ (CH_2Cl_2) [kcal/mol]	ΔG(298) (gas phase) [kcal/mol]	$\Delta G(298)_{solv}$ (CH_2Cl_2) [kcal/mol]
$HB(C_6F_5)_2$	-1481.8871490	-1483.3949301	40.005	-4.604	--	**--**
5e_Ph	-729.2651205	-729.9507596	86.123	-5.845	0.0	**0.0**
9e_Ph	-2211.2022177	-2213.3981289	143.482	-12.432	-15.6	**-17.5**
7e_Ph	-2211.2176908	-2213.4140154	145.005	-12.302	-24.0	**-25.9**
10e_Ph	-2211.1992407	-2213.3952673	144.535	-12.126	-12.7	**-14.4**
11e_Ph	-2211.2065085	-2213.4044264	146.679	-16.507	-16.3	**-22.4**
6e_Ph	-2211.2413772	-2213.4407388	147.769	-13.392	-38.0	**-40.9**
5d_Dmesp	-1427.7043419	-1429.1460838	273.909	-14.802	0.0	**0.0**
9d_Dmesp	-2909.6438433	-2912.5978735	334.345	-19.786	-15.2	**-15.6**
7d_Dmesp	-2909.6602020	-2912.6148406	336.340	-19.583	-23.9	**-24.1**
10d_Dmesp	-2909.6408310	-2912.5921572	333.921	-19.421	-12.1	**-12.1**
11d_Dmesp	-2909.6622190	-2912.6180936	335.692	-22.990	-26.6	**-30.2**
6d_Dmesp	-2909.6873650	-2912.6458881	338.479	-20.408	-41.2	**-42.2**

[a] all calculations were performed with the def2-TZVP basis set

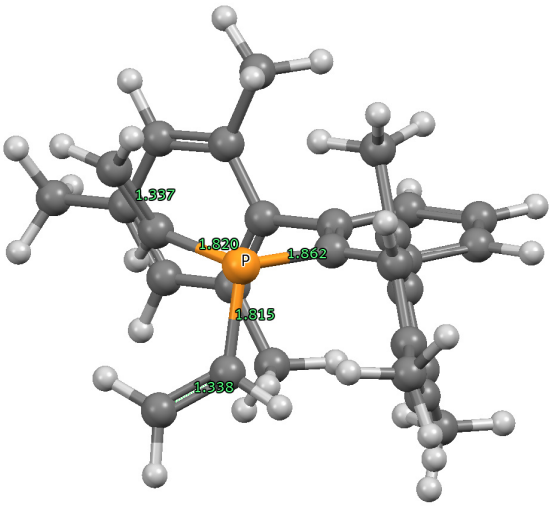
Table S1 Relative energies of intermediates in Scheme 3 as calculated with DFT[a]. The relative free energy with respect to compound **5** and **$HB(C_6F_5)_2$** is $\Delta G(298)_{solv} = \Delta E$(PW6B95-D3//TPSS-D3/def2-TZVP) + ΔG^{RRHO}_{298} + $\Delta G^{COSMO-RS}_{298}$



$HB(C_6F_5)_2$

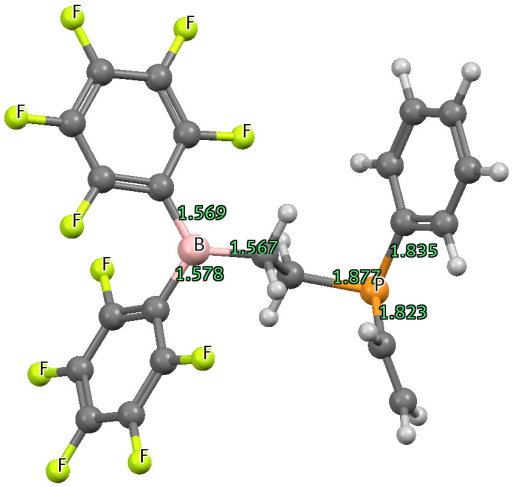


5e_Ph

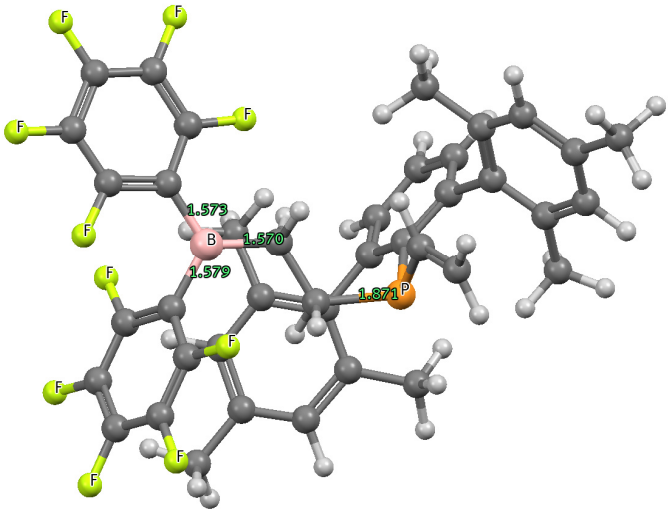


5d_Dmesp

Figure S72 (continued)

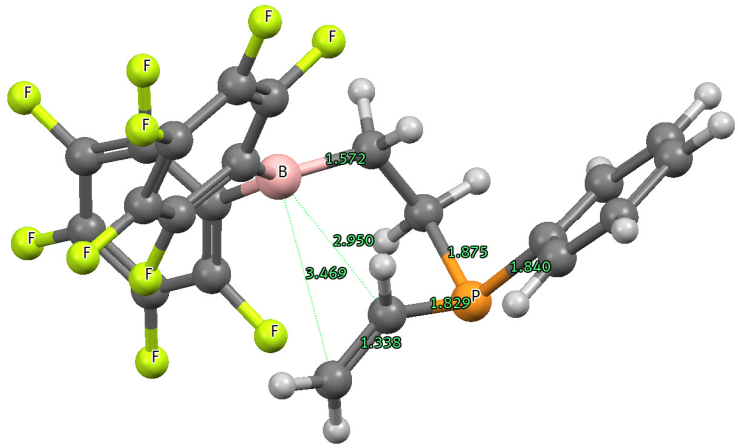


9e_Ph

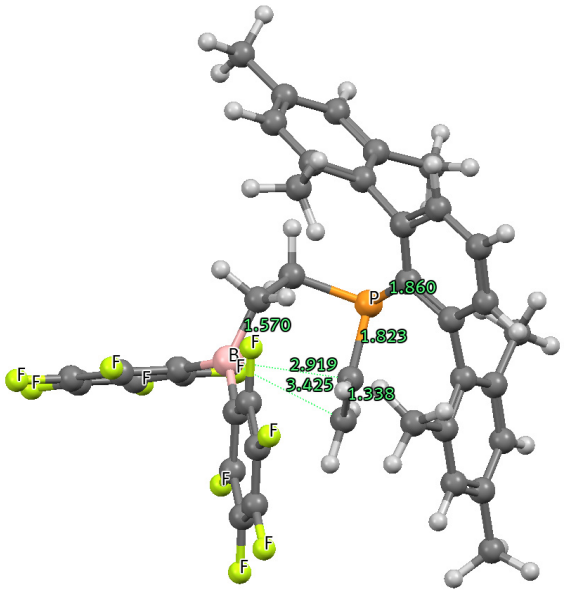


9e_Dmesp

Figure S72 (continued)

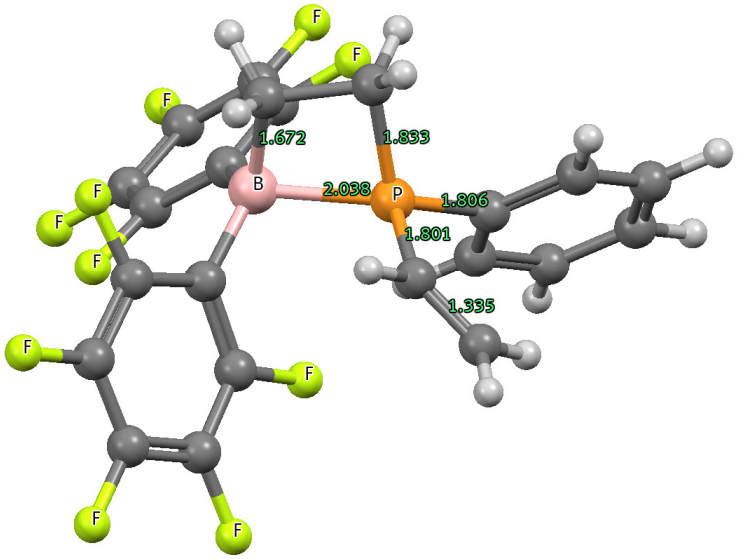


10e_Ph

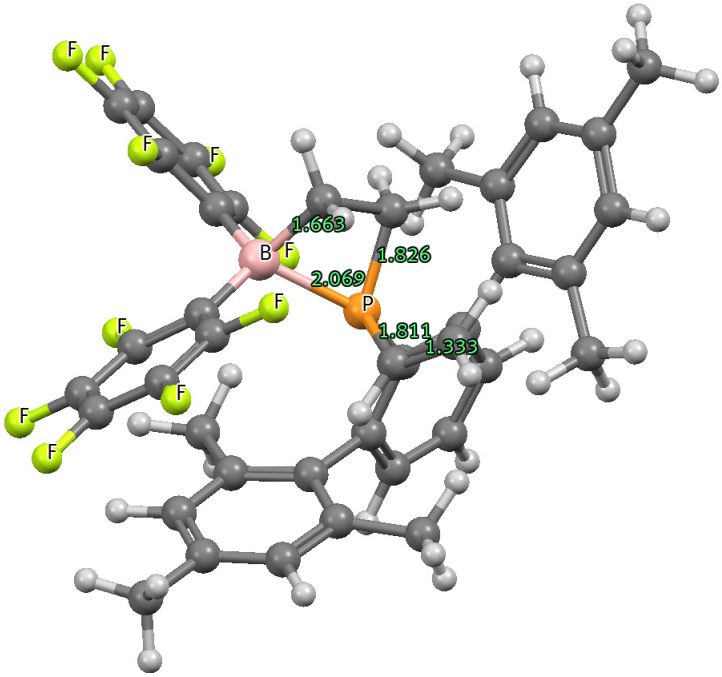


10d_Dmesp

Figure S72 (continued)

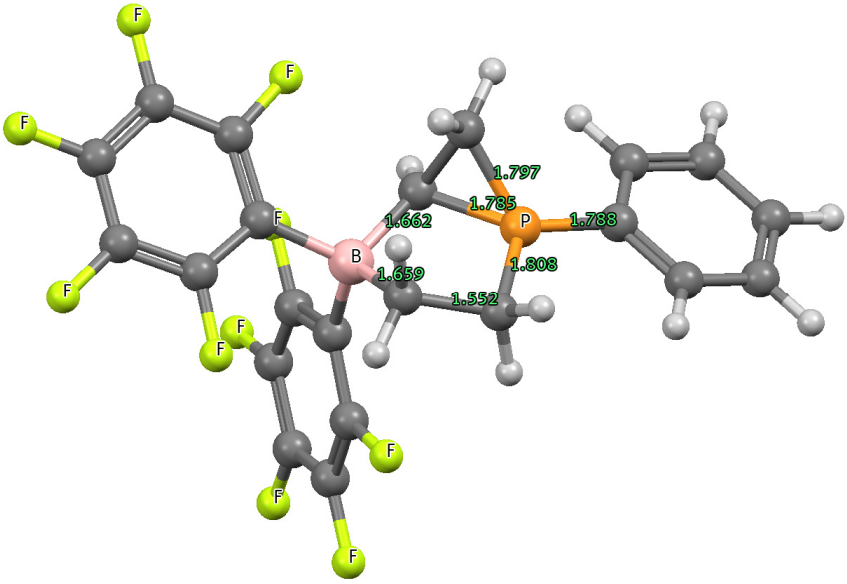


7e_Ph

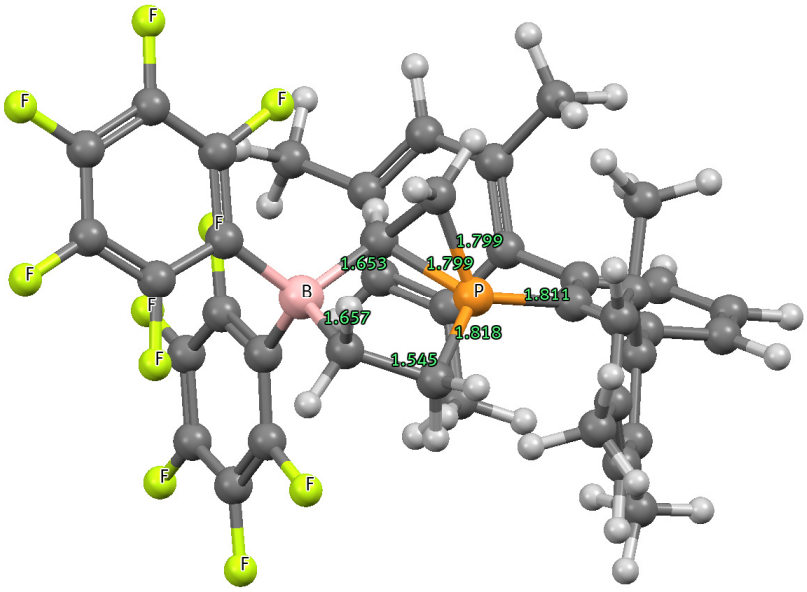


7d_Dmesp

Figure S72 (continued)

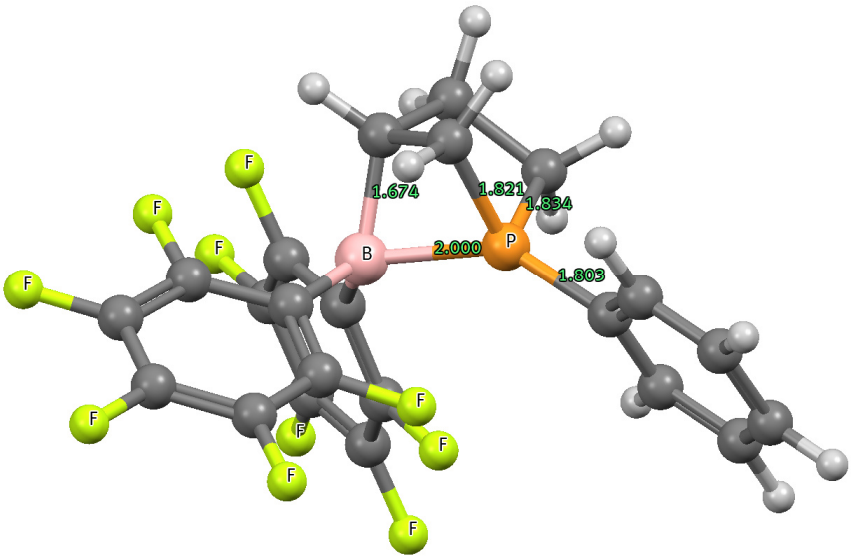


11e_Ph

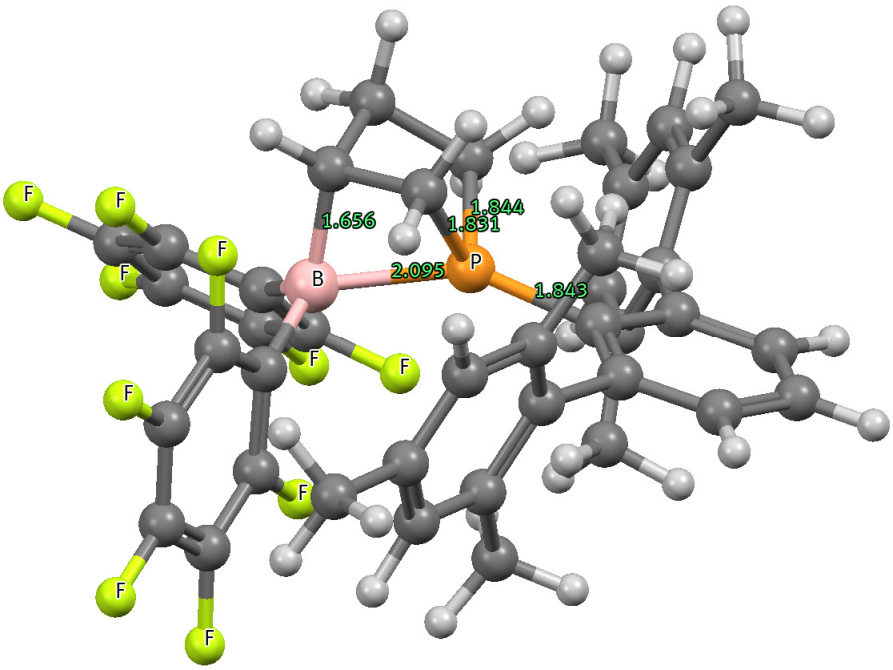


11d_Dmesp

Figure S72 (continued)



6e_Ph



6d_Dmesp

Figure S72 DFT-optimized Intermediates in Scheme 3.

12.3 Energies and Cartesian Coordinates (in Å) of DFT-optimized Intermediates

$HB(C_6F_5)_2$

E(TPSS-D3/def2-TZVP) = -1481.887148983 (conv)
Lowest Freq. = 24.33 cm^-1
24
HBCF (HBCF/c1/tpss-d3.def2-TZVP)

B	3.1516215	1.0928787	-2.9973646
F	1.0163090	2.6787577	-1.9757498
C	0.7798891	2.0434225	-3.1378678
C	-0.4747525	2.2139488	-3.7105864
F	-1.4097227	2.9763422	-3.1244597
C	-0.7592880	1.5752988	-4.9176968
F	-1.9621078	1.7184059	-5.4802521
C	0.2083000	0.7826884	-5.5368293
F	-0.0835370	0.1553814	-6.6858733
C	1.4587632	0.6543745	-4.9456701
F	2.3436102	-0.1509146	-5.5632681
C	1.7985865	1.2783932	-3.7334861
F	7.7255996	-0.7565969	-2.8412769
C	6.7987695	-0.0643164	-3.5198110
C	5.5299241	0.1490457	-2.9948353
F	5.2714042	-0.3730860	-1.7822365
C	4.5200593	0.8441113	-3.6843689
C	4.8837172	1.3498837	-4.9440545
F	4.0085044	2.0830991	-5.6575759
C	6.1485009	1.1761993	-5.4916448
F	6.4629516	1.6921160	-6.6891688
C	7.1068646	0.4565407	-4.7766506
F	8.3233397	0.2702131	-5.2953536
H	3.1391633	1.1476431	-1.8097891

5e_Ph

E(TPSS-D3/def2-TZVP) = -729.2651204667 (conv)
Lowest Freq. = 31.17 cm^-1
22
5_Ph (001/c1/tpss-d3.def2-TZVP)

H	2.0387395	-0.1029891	1.7226464
C	1.4108551	0.0429942	0.8480364
C	0.0612939	-0.3081411	0.9018470
H	-0.3471430	-0.7300692	1.8162914
C	-0.7591712	-0.1235625	-0.2101350
H	-1.8089155	-0.3993447	-0.1681318

C	-0.2232169	0.4261862	-1.3764133
H	-0.8556150	0.5821885	-2.2462261
C	1.1218698	0.7840083	-1.4289865
H	1.5179239	1.2287853	-2.3390727
C	1.9616752	0.5836797	-0.3216185
P	3.7111495	1.1553143	-0.4021313
C	4.2838716	0.1767500	-1.8308174
C	4.4712158	0.2108116	0.9582278
C	5.4369758	-0.4959545	-1.9021685
H	6.1186738	-0.5614192	-1.0575356
H	5.7404024	-1.0021738	-2.8151012
H	3.6389244	0.2273567	-2.7079860
C	5.1785693	0.8105227	1.9193064
H	5.3135595	1.8896137	1.9319839
H	5.6460599	0.2469882	2.7241737
H	4.3538122	-0.8742253	0.9559209

5d_Dmesp

E(TPSS-D3/def2-TZVP) = -1427.704341848 (conv)

Lowest Freq. = 11.73 cm^-1

60

5_Dmesp (005/c1/tpss-d3.def2-TZVP)

C	1.4727171	0.3950581	0.9442406
C	0.0812688	0.4403739	1.1116516
H	-0.3343646	0.1231907	2.0648077
C	-0.7580365	0.8600452	0.0853437
H	-1.8340989	0.8861921	0.2331842
C	-0.2055329	1.2353297	-1.1358507
H	-0.8439290	1.5543018	-1.9555835
C	1.1791024	1.2204595	-1.3285253
C	2.0398401	0.8042566	-0.2826745
P	3.8527770	0.9806732	-0.6685584
C	4.2084424	-0.5799131	-1.5244675
C	4.7902686	0.7653422	0.8763805
C	5.2502830	-1.3860716	-1.2881799
H	5.9431059	-1.2120946	-0.4688481
H	5.4493678	-2.2484644	-1.9198624
H	3.5590214	-0.7822044	-2.3734691
C	5.5045475	1.7916290	1.3505209
H	5.5095256	2.7581321	0.8511705
H	6.0976294	1.7016216	2.2581395
H	4.8179779	-0.1969717	1.3837960
C	2.2789338	-0.1323050	2.0830006
C	2.6314569	-1.4951571	2.1073585
C	2.6584200	0.7168222	3.1377933
C	3.4216200	0.1969252	4.1860112
C	3.3996344	-1.9756269	3.1711233
C	3.8094284	-1.1448203	4.2183988
H	3.7298078	0.8610670	4.9918501
H	3.6827557	-3.0269284	3.1817142
C	1.7186827	1.6180602	-2.6654462
C	2.1967069	2.9280428	-2.8806186
C	1.6949784	0.6941852	-3.7264012
C	2.2006984	1.0777322	-4.9734542
C	2.6830834	3.2730151	-4.1411978
C	2.7063121	2.3580275	-5.1994510
H	2.1952335	0.3554156	-5.7881329
H	3.0556140	4.2836410	-4.3005043
C	4.6172730	-1.6916863	5.3703093
H	3.9597990	-2.0902062	6.1535703

H	5.2360348	-0.9120093	5.8250574
H	5.2707244	-2.5069096	5.0444098
C	2.2052617	-2.4212789	0.9953088
H	2.6814403	-2.1413362	0.0493487
H	1.1219151	-2.3768827	0.8380957
H	2.4828729	-3.4538576	1.2250086
C	2.3006886	2.1806311	3.1094892
H	2.7837374	2.6769161	2.2586346
H	2.6269176	2.6783843	4.0268603
H	1.2217852	2.3298751	2.9954563
C	1.1077340	-0.6871078	-3.5483198
H	1.4958914	-1.3737983	-4.3066642
H	0.0152685	-0.6628351	-3.6488682
H	1.3215501	-1.0975407	-2.5568415
C	2.1926250	3.9372081	-1.7624514
H	2.4636503	4.9297275	-2.1328529
H	2.9165027	3.6467872	-0.9895648
H	1.2105747	3.9963945	-1.2809725
C	3.2689066	2.7478843	-6.5444872
H	2.8447111	3.6964912	-6.8922234
H	3.0590258	1.9823073	-7.2971414
H	4.3568202	2.8782844	-6.4913197

9e_Ph

E(TPSS-D3/def2-TZVP) = -2211.202217691 (conv)

Lowest Freq. = 2.61 cm^-1

46

9_Ph (002/c1/tpss-d3.def2-TZVP)

H	1.7736156	-1.1523599	2.5980882
C	0.9415941	-0.5824985	2.1935113
C	-0.3632941	-1.0349803	2.3936049
H	-0.5340568	-1.9545152	2.9469741
C	-1.4429951	-0.3155613	1.8830092
H	-2.4581501	-0.6709173	2.0345962
C	-1.2109697	0.8694774	1.1812148
H	-2.0452917	1.4404560	0.7831534
C	0.0901525	1.3270204	0.9912562
H	0.2527592	2.2563581	0.4516456
C	1.1878345	0.5992358	1.4801698
P	2.8781902	1.2786360	1.2570728
C	2.9337080	1.4372957	-0.6125606
C	3.8927250	-0.2189776	1.4812346
C	2.5088047	0.1794527	-1.4279210
C	5.0116886	-0.1942594	2.2114399
H	5.3349395	0.7109061	2.7206724
H	5.6417136	-1.0738676	2.3258190
H	3.5900272	-1.1476712	0.9945290
H	2.3056911	2.2970892	-0.8690137
H	3.9663356	1.7223429	-0.8456387
B	2.7413623	0.4859391	-2.9469219
H	3.1483474	-0.6531888	-1.1183348
H	1.4764899	-0.0768252	-1.1784642
F	0.1958070	1.7823092	-2.2690501
C	0.3508214	1.3533216	-3.5390733
C	-0.7178410	1.5717258	-4.4003233
F	-1.8444957	2.1596671	-3.9684198
C	-0.6104828	1.1737334	-5.7319368
F	-1.6321599	1.3626329	-6.5727261
C	0.5657975	0.5770692	-6.1832578
F	0.6647071	0.1847820	-7.4625376
C	1.6207321	0.3983800	-5.2957220
F	2.7268988	-0.1957191	-5.7901047
C	1.5611580	0.7670619	-3.9411196
F	7.4330700	-1.2002061	-3.3232695
C	6.5290359	-0.2496153	-3.6079575
C	5.2108949	-0.3630552	-3.1779919

F 4.8911184 -1.4824241 -2.4900935
C 4.2260681 0.5876355 -3.4716860
C 4.6573776 1.6849673 -4.2272543
F 3.7815676 2.6655909 -4.5443791
C 5.9691950 1.8486883 -4.6571497
F 6.3384803 2.9296125 -5.3618657
C 6.9106869 0.8684473 -4.3474325
F 8.1767388 1.0000748 -4.7594534

9d_Dmesp

E(TPSS-D3/def2-TZVP) = -2909.643843343 (conv)

Lowest Freq. = 8.20 cm^-1

84

9_Dmesp (006/c1/tpss-d3.def2-TZVP)

C 1.0000556 -0.4779488 2.2467957
C -0.3667897 -0.6834847 2.4707338
H -0.6674307 -1.5365520 3.0735477
C -1.3221756 0.1887791 1.9619336
H -2.3788284 0.0220306 2.1506187
C -0.9007129 1.2941443 1.2326944
H -1.6260955 2.0091561 0.8541772
C 0.4571982 1.5307284 0.9853703
C 1.4387023 0.6194490 1.4621235
P 3.2454353 1.0045363 1.2618718
C 3.4778720 1.3586371 -0.5610192
C 4.0917166 -0.6116774 1.2702645
C 2.8763946 0.3371925 -1.5309625
C 5.2520452 -0.7634494 1.9151359
H 5.6646485 0.0318413 2.5316516
H 5.8182555 -1.6900549 1.8611360
H 3.7036197 -1.4338445 0.6728334
H 3.1054845 2.3646746 -0.7683273
H 4.5674885 1.3933722 -0.6507259
B 2.9401486 0.6074933 -3.0763518
H 3.2699893 -0.6699219 -1.3294263
H 1.8045027 0.2344849 -1.2999360
F 0.9877629 -1.5531852 -2.4992458
C 1.4498655 -1.4435311 -3.7606675
C 0.9293376 -2.3549831 -4.6726077
F 0.0290983 -3.2738275 -4.2908477
C 1.3568716 -2.3156767 -5.9979317
F 0.8776244 -3.1926783 -6.8838396
C 2.2936445 -1.3624176 -6.3917772

F	2.7187849	-1.3336607	-7.6638028
C	2.7755469	-0.4544374	-5.4559528
F	3.6915954	0.4230635	-5.9099901
C	2.3785137	-0.4425131	-4.1042275
F	6.4959457	4.0937300	-3.3877480
C	5.2506435	3.6961382	-3.6935748
C	4.7862652	2.4402394	-3.3168381
F	5.6569665	1.6227660	-2.6806599
C	3.5041152	1.9785348	-3.6188611
C	2.7124774	2.8475529	-4.3714519
F	1.4662156	2.4665961	-4.7433079
C	3.1272422	4.1171486	-4.7532938
F	2.3107461	4.9335331	-5.4410409
C	4.4062249	4.5461023	-4.4053083
F	4.8244786	5.7681029	-4.7603531
C	1.9369778	-1.4304085	2.9127390
C	2.1320205	-2.7190402	2.3789420
C	2.5926776	-1.0493151	4.0979304
C	3.4757085	-1.9465937	4.7002911
C	3.0265306	-3.5860127	3.0085249
C	3.7163734	-3.2152081	4.1659845
H	3.9969952	-1.6426680	5.6065248
H	3.1984329	-4.5708312	2.5770935
C	0.8059299	2.7732627	0.2366845
C	0.4459662	2.9071689	-1.1201905
C	1.4516721	3.8429364	0.8973698
C	1.8211930	4.9704992	0.1612054
C	0.8297810	4.0584257	-1.8166085
C	1.5436032	5.0889807	-1.2037996
H	2.3241872	5.7876503	0.6758511
H	0.5542370	4.1525914	-2.8647251
C	4.6674768	-4.1724763	4.8413694
H	5.4637753	-3.6355600	5.3661225
H	5.1273034	-4.8519712	4.1168699
H	4.1416865	-4.7883844	5.5823988
C	1.4257949	-3.1440724	1.1142112
H	1.8299375	-4.0907461	0.7446284
H	1.5263454	-2.3883258	0.3269280
H	0.3502795	-3.2750687	1.2805194
C	2.3923763	0.3249535	4.6859804
H	2.8845504	1.0873338	4.0674284
H	2.8159880	0.3799651	5.6926956
H	1.3310079	0.5890617	4.7350872
C	-0.3724122	1.8599436	-1.8423288

H -0.2421445 0.8633038 -1.4153170
H -0.1137443 1.8305644 -2.9043036
H -1.4421486 2.0959059 -1.7762301
C 1.7128897 3.8155009 2.3847292
H 0.9154985 3.2884734 2.9167827
H 1.7803624 4.8357617 2.7739987
H 2.6529965 3.2992816 2.6128194
C 1.9828438 6.3056787 -1.9809339
H 1.6932587 7.2290170 -1.4672579
H 1.5420620 6.3177932 -2.9814567
H 3.0739495 6.3283513 -2.0921849

10e_Ph

E(TPSS-D3/def2-TZVP) = -2211.199240660 (conv)
Lowest Freq. = 9.44 cm^-1
46
10_Ph (003/c1/tpss-d3.def2-TZVP)
H 0.7727699 0.4333686 2.9889726
C 0.4153638 1.2647426 2.3868841
C -0.9454349 1.5698058 2.3855844
H -1.6310556 0.9683990 2.9763709
C -1.4252084 2.6391189 1.6300546
H -2.4853693 2.8747686 1.6251194
C -0.5300182 3.4086807 0.8856657
H -0.8909407 4.2489643 0.2988643
C 0.8301190 3.1063866 0.8909433
H 1.5092048 3.7280776 0.3134926
C 1.3248464 2.0187561 1.6284434
P 3.1309964 1.6807206 1.7197959
C 3.5762210 1.7748122 -0.0987943
C 3.0679173 -0.1356102 1.9211326
C 2.9596078 0.6426310 -0.9440910
C 4.0204407 -0.8321241 2.5528257
H 4.8810592 -0.3424821 3.0002635
H 3.9777308 -1.9152017 2.6360101
H 2.2034289 -0.6620936 1.5151928
H 3.2319187 2.7534147 -0.4503658
H 4.6667046 1.7887803 -0.1599028
B 3.6735524 -0.7565974 -0.8983118
H 1.8898032 0.5810718 -0.7296305
H 3.0388955 0.9333194 -2.0094027
F 6.1473021 0.1572032 0.6676393
C 6.3153548 -0.4201297 -0.5436062

C 7.6300092 -0.5710855 -0.9785832
F 8.6540818 -0.1365479 -0.2263192
C 7.8829648 -1.1788737 -2.2054999
F 9.1410263 -1.3180527 -2.6430617
C 6.8170434 -1.6366918 -2.9771667
F 7.0490349 -2.2142474 -4.1666412
C 5.5221265 -1.4815951 -2.4955276
F 4.5118414 -1.9301853 -3.2817686
C 5.2155655 -0.8723028 -1.2735467
F -0.4028967 -3.5660066 -1.5766348
C 0.8502063 -3.4589162 -1.1092016
C 1.5582744 -2.2674281 -1.2265433
F 0.9255826 -1.2529146 -1.8501379
C 2.8779449 -2.1090994 -0.7755843
C 3.4491922 -3.2521315 -0.1941869
F 4.7083233 -3.2084974 0.2917875
C 2.7669072 -4.4530040 -0.0367742
F 3.3499137 -5.5069452 0.5558837
C 1.4575165 -4.5572925 -0.5031451
F 0.7881330 -5.7072911 -0.3729600

10d_Dmesp

E(TPSS-D3/def2-TZVP) = -2909.640831040 (conv)
Lowest Freq. = 7.00 cm^-1
84
10_Dmesp (007/c1/tpss-d3.def2-TZVP)
C 0.5255183 1.2661186 2.5724614
C -0.8238283 1.6331863 2.6322263
H -1.4794472 1.0805395 3.3000152
C -1.3196232 2.6902365 1.8777813
H -2.3679423 2.9680350 1.9385983
C -0.4466633 3.4012770 1.0635456
H -0.8041923 4.2482488 0.4841403
C 0.9108544 3.0666043 0.9805412
C 1.4186979 1.9624110 1.7130749
P 3.2296333 1.5425738 1.7746738
C 3.8998111 1.6998288 0.0381312
C 3.1804460 -0.2798653 1.7845021
C 3.2131249 0.7594998 -0.9792110
C 4.1403685 -1.0256128 2.3441554
H 4.9685352 -0.5739989 2.8831218
H 4.1257188 -2.1101092 2.2890681
H 2.3494242 -0.7669430 1.2827290

H	3.8430873	2.7405068	-0.2807364
H	4.9601231	1.4600456	0.1589051
B	3.7542494	-0.7127261	-1.0445406
H	2.1335597	0.8050472	-0.8277373
H	3.4006754	1.1718545	-1.9867534
F	6.3905161	-0.3258084	0.5165943
C	6.4365632	-0.7598874	-0.7628729
C	7.7041156	-1.0169048	-1.2814118
F	8.8024507	-0.8148431	-0.5342726
C	7.8334364	-1.4874042	-2.5852981
F	9.0474527	-1.7261033	-3.1005021
C	6.6907473	-1.7025984	-3.3524987
F	6.8026807	-2.1450089	-4.6158013
C	5.4455880	-1.4480310	-2.7890001
F	4.3558094	-1.6576454	-3.5711078
C	5.2633306	-0.9710444	-1.4868206
F	-0.6436678	-2.9885057	-1.7289692
C	0.6313218	-3.0602720	-1.3150744
C	1.4739910	-1.9579449	-1.4039939
F	0.9425331	-0.8427819	-1.9485418
C	2.8139753	-1.9770037	-0.9891027
C	3.2615240	-3.2086474	-0.4862898
F	4.5320635	-3.3419963	-0.0499984
C	2.4437255	-4.3252929	-0.3566076
F	2.9128787	-5.4684512	0.1688616
C	1.1173516	-4.2495518	-0.7767915
F	0.3139176	-5.3134676	-0.6621691
C	0.9625474	0.1466662	3.4599222
C	0.5958771	-1.1794626	3.1454065
C	1.7122482	0.4116235	4.6217749
C	2.1550556	-0.6618258	5.3991014
C	1.0597857	-2.2219881	3.9460363
C	1.8580033	-1.9856496	5.0698406
H	2.7513493	-0.4554879	6.2862554
H	0.8049669	-3.2461360	3.6777670
C	1.7689638	3.9322265	0.1215880
C	2.6773549	4.8318376	0.7204897
C	1.6595255	3.8719198	-1.2806500
C	2.5242288	4.6472168	-2.0614554
C	3.5111582	5.5972075	-0.0959618
C	3.4677896	5.5025688	-1.4911950
H	2.4568449	4.5776522	-3.1459189
H	4.2125997	6.2866591	0.3710179
C	2.0563132	1.8234575	5.0274880

H 2.8808289 2.2155463 4.4180294
H 2.3650172 1.8562459 6.0761979
H 1.2038832 2.4959152 4.8897895
C -0.2467330 -1.4850904 1.9305090
H -1.2963385 -1.2132835 2.0915194
H -0.2094858 -2.5522731 1.6947063
H 0.0869877 -0.9168867 1.0552154
C 2.3462555 -3.1287427 5.9250561
H 3.2173371 -2.8350240 6.5180079
H 2.6207802 -3.9932448 5.3118166
H 1.5647086 -3.4573950 6.6219462
C 2.7557604 4.9781531 2.2209663
H 3.2689710 4.1221075 2.6777888
H 1.7573325 5.0294174 2.6667659
H 3.3076894 5.8837167 2.4880034
HBCFC 0.6332925 2.9985490 -1.9642746
H -0.3059116 3.5470612 -2.1104504
H 0.3951966 2.1082081 -1.3783139
H 0.9876319 2.6851769 -2.9506737
C 4.4115473 6.3078728 -2.3503055
H 4.1301582 6.2517045 -3.4057528
H 5.4400540 5.9383190 -2.2558315
H 4.4170509 7.3620155 -2.0518479

7e_Ph

E(TPSS-D3/def2-TZVP) = -2211.217690814 (conv)
Lowest Freq. = 6.37 cm^-1
46
7_Ph (003/c3/tpss-d3.def2-TZVP)
H 2.1533935 4.2499423 -3.2585298
C 1.8336968 4.6593345 -2.3054305
C 1.1790624 5.8887158 -2.2490831
H 0.9898939 6.4410716 -3.1646370
C 0.7624434 6.4031488 -1.0210526
H 0.2476862 7.3586385 -0.9801735
C 1.0008772 5.6908252 0.1565245
H 0.6726361 6.0906870 1.1114529
C 1.6584053 4.4640150 0.1083437
H 1.8440829 3.9099902 1.0245224
C 2.0786904 3.9453106 -1.1249095
P 2.9015997 2.3407060 -1.2284355
C 2.1583749 0.9521550 -0.2906406
C 4.5640453 2.5678496 -0.5737240

C 2.5081227 -0.0666544 -1.4289924
C 5.1328849 3.7546570 -0.3504514
H 4.6003962 4.6860475 -0.5215927
H 6.1565786 3.8290057 0.0065514
H 5.1204171 1.6451700 -0.4150499
H 2.6047419 0.7613637 0.6885476
H 1.0855325 1.1053720 -0.1732887
B 2.8862698 0.9403004 -2.7090480
H 3.3656979 -0.6739948 -1.1317415
H 1.6785244 -0.7520485 -1.6265899
F 0.1324874 1.8090470 -2.1984465
C 0.4460473 1.5789689 -3.5032292
C -0.5755175 1.7953304 -4.4201032
F -1.7913982 2.2095543 -4.0182502
C -0.3262160 1.5764336 -5.7720067
F -1.2925573 1.7724247 -6.6821736
C 0.9368043 1.1452692 -6.1634387
F 1.1870887 0.9171322 -7.4650178
C 1.9306053 0.9482379 -5.2045259
F 3.1179767 0.5119926 -5.6837437
C 1.7398277 1.1642567 -3.8331682
F 7.1001933 -1.5789418 -3.8510015
C 6.4449432 -0.4047730 -3.7983815
C 5.1241287 -0.3422827 -3.3585852
F 4.5421281 -1.5207335 -3.0257748
C 4.3949059 0.8448356 -3.2839336
C 5.0808962 1.9793592 -3.7189057
F 4.4421118 3.1822302 -3.7239573
C 6.3987770 1.9716919 -4.1601674
F 7.0091066 3.1066946 -4.5496832
C 7.0898401 0.7628896 -4.1976734
F 8.3633912 0.7233035 -4.6220195

7d_Dmesp

E(TPSS-D3/def2-TZVP) = -2909.660201999 (conv)

Lowest Freq. = 14.73 cm^-1

84

7_Dmesp (006/c2/tpss-d3.def2-TZVP)

C 3.0344098 1.0618504 1.2679025
C 3.5807033 1.3862176 2.5158965
C 2.7847886 1.8709146 3.5485103
C 1.4262239 2.0773486 3.3294918
C 0.8389329 1.7593982 2.1010925

C	1.6405740	1.2118776	1.0712883
P	0.8182349	0.6103522	-0.4661655
C	0.3509344	2.0808439	-1.4153803
C	1.0453706	2.5685154	-2.4430496
H	1.9800300	2.1253949	-2.7755245
H	0.6899375	3.4321893	-2.9993419
H	-0.5876833	2.5377376	-1.1137884
C	1.7831354	-0.4061625	-1.6359119
C	0.4721387	-0.8243092	-2.3607192
H	0.2187303	-0.0975781	-3.1299604
H	0.5548654	-1.8099878	-2.8288526
B	-0.5529031	-0.8240453	-1.0511973
C	-0.3706731	-2.2644937	-0.3247842
C	-0.9850078	-3.3654223	-0.9315634
C	-0.8813980	-4.6700792	-0.4604850
C	-0.1161966	-4.9252507	0.6756406
C	0.5243839	-3.8669835	1.3106193
C	0.3830673	-2.5787866	0.7998387
F	1.0383681	-1.5973726	1.4797527
F	1.2748564	-4.0939725	2.4068256
F	0.0064541	-6.1773235	1.1463863
F	-1.5030337	-5.6848260	-1.0882399
F	-1.7350507	-3.1762423	-2.0453269
C	-2.0817389	-0.3156857	-1.1342439
C	-3.0271915	-0.6610096	-0.1599674
C	-4.3619999	-0.2723638	-0.1920841
C	-4.8183741	0.5219375	-1.2369829
C	-3.9253587	0.9005146	-2.2324590
C	-2.6000535	0.4763532	-2.1670624
F	-1.8195517	0.8769751	-3.2003263
F	-4.3510811	1.6698183	-3.2532051
F	-6.0981872	0.9275704	-1.2779110
F	-5.2096483	-0.6338368	0.7919335
F	-2.6684058	-1.4175146	0.9048282
H	2.5787940	0.0668391	-2.2128474
H	2.2019595	-1.2475505	-1.0808439
C	-0.6081124	2.0744684	1.9012382
C	-0.9656161	3.2849918	1.2676717
C	-2.3173516	3.5768369	1.0736285
C	-3.3271192	2.7275418	1.5353244
C	-2.9503422	1.5793604	2.2340213
C	-1.6089980	1.2407702	2.4366502
C	-1.2573494	0.0331771	3.2684384
H	-2.1204924	-0.6270134	3.3748104

H -0.9418217 0.3430587 4.2729753
H -0.4318523 -0.5331192 2.8354446
H -3.7200281 0.9187845 2.6266443
C -4.7813362 3.0646999 1.3170481
H -4.9717721 3.3415294 0.2746559
H -5.4259972 2.2190672 1.5702240
H -5.0822274 3.9163471 1.9395711
H -2.5862230 4.5010537 0.5645309
C 0.0802843 4.3053980 0.8848970
H -0.3075342 4.9993474 0.1337106
H 0.9891986 3.8421562 0.4948098
H 0.3716366 4.8916641 1.7658507
H 0.8005636 2.4988496 4.1112071
H 3.2267147 2.1125454 4.5109620
H 4.6512988 1.2660462 2.6572005
C 3.9744857 0.6756261 0.1724506
C 4.5128836 -0.6178896 0.0720133
C 5.3770294 -0.9110181 -0.9914254
C 5.7284615 0.0420507 -1.9448623
C 5.2261700 1.3404190 -1.7917413
C 4.3698346 1.6771337 -0.7441873
C 3.9255539 3.1085394 -0.5654633
H 2.8355803 3.1995777 -0.5461687
H 4.3068194 3.7340474 -1.3772120
H 4.2950040 3.5125311 0.3844197
H 5.5245067 2.1155675 -2.4956599
C 6.6262445 -0.3073133 -3.1058936
H 6.0468291 -0.3997394 -4.0330401
H 7.3821414 0.4679273 -3.2706733
H 7.1386045 -1.2585891 -2.9368064
H 5.7813232 -1.9186325 -1.0731407
C 4.1710953 -1.7126303 1.0542492
H 3.5572215 -2.4873396 0.5789887
H 5.0838167 -2.2017227 1.4112405
H 3.6182976 -1.3359100 1.9151706

11e_Ph

E(TPSS-D3/def2-TZVP) = -2211.206508525 (conv)
Lowest Freq. = 17.42 cm^-1
46
11_Ph (003/c4/tpss-d3.def2-TZVP)
C -1.7319053 -0.3347184 2.4120501

C	-2.6501919	-0.9887503	3.2266851
H	-2.5237033	-0.9647596	4.3047143
C	-3.7249724	-1.6800241	2.6614223
H	-4.4359640	-2.1923729	3.3023419
C	-3.8827170	-1.7179347	1.2764280
H	-4.7150988	-2.2578438	0.8356806
C	-2.9715477	-1.0626692	0.4497948
C	-1.8946728	-0.3660483	1.0179054
P	-0.7184612	0.4496599	-0.0531419
C	-0.7671027	0.2302501	-1.8473798
C	0.9826541	0.8416258	0.3211424
C	0.5735103	0.8918521	-2.2656432
C	-0.0023710	2.0216922	0.4406765
H	0.0509207	2.8160422	-0.2994071
H	-0.2662535	2.3580958	1.4408946
H	1.4140734	0.4894911	1.2531453
H	-0.7685918	-0.8444737	-2.0540897
H	-1.6598845	0.6806465	-2.2915771
B	1.7572850	0.6270036	-1.1331932
H	0.8390853	0.5374241	-3.2622947
H	0.4046575	1.9726683	-2.3548832
F	3.3576717	0.7162282	-3.5228079
C	3.6944996	1.6390519	-2.5842053
C	4.7543202	2.4833499	-2.9011802
F	5.3923463	2.3861977	-4.0837139
C	5.1556297	3.4438147	-1.9763409
F	6.1726977	4.2766663	-2.2578606
C	4.4906932	3.5302704	-0.7578841
F	4.8730738	4.4530203	0.1476220
C	3.4369890	2.6583380	-0.4877982
F	2.8549407	2.8042463	0.7342057
C	2.9879713	1.6844031	-1.3788244
F	4.8309462	-2.7063227	0.9892443
C	3.9351214	-2.4678109	0.0120207
C	3.3213665	-1.2256402	-0.1130898
F	3.6873929	-0.2865594	0.8002343
C	2.3815727	-0.9003688	-1.0981495
C	2.0982672	-1.9506249	-1.9718612
F	1.2048578	-1.7950557	-2.9885251
C	2.6826668	-3.2143172	-1.8905760
F	2.3572492	-4.1817642	-2.7705812
C	3.6109381	-3.4775599	-0.8899761
F	4.1847779	-4.6887068	-0.7928451
H	-0.8897799	0.1896591	2.8542977

H	-3.0969251	-1.0931673	-0.6285436

11d_Dmesp

E(TPSS-D3/def2-TZVP) = -2909.662218981 (conv)

Lowest Freq. = 5.54 cm^-1

84

11_Dmesp (007/c2/tpss-d3.def2-TZVP)

C	2.1116249	1.1980389	3.2295506
C	1.0928024	0.6678074	4.0295245
H	1.3672585	0.1758471	4.9581104
C	-0.2427433	0.7565550	3.6468991
H	-1.0178325	0.3362299	4.2813611
C	-0.5863944	1.3868037	2.4528944
H	-1.6269351	1.4690542	2.1524029
C	0.3975316	1.9369308	1.6284067
C	1.7530490	1.8348813	2.0219639
P	3.0081745	2.5635453	0.9392216
C	3.0083472	2.3242728	-0.8626813
C	4.7147610	2.9943772	1.3118678
C	4.3546433	2.9577653	-1.2806359
C	3.7133175	4.1599366	1.3774866
H	3.7582571	4.9268240	0.6082796
H	3.4484458	4.5277748	2.3651645
H	5.1388463	2.6872772	2.2610757
H	2.9819408	1.2469521	-1.0490187
H	2.1305724	2.7830108	-1.3206401
B	5.5206898	2.7847800	-0.1157193
H	4.6468993	2.5465621	-2.2484607
H	4.1817532	4.0299286	-1.4408777
F	7.1116501	2.9736346	-2.5121691
C	7.3808156	3.9254707	-1.5799042
C	8.3716363	4.8455027	-1.9098550
F	9.0060779	4.7905210	-3.0979702
C	8.7076428	5.8377391	-0.9931906
F	9.6571632	6.7441981	-1.2871355
C	8.0497795	5.8775573	0.2311939
F	8.3730748	6.8282201	1.1322450
C	7.0672801	4.9301288	0.5142153
F	6.4983245	5.0311463	1.7466012
C	6.6811172	3.9233659	-0.3700050
F	8.9919630	-0.1866368	1.9349723
C	8.0031976	-0.0721995	1.0236112
C	7.2976744	1.1167218	0.8744776
F	7.6664694	2.1331196	1.6962154
C	6.2563616	1.3095005	-0.0398528
C	5.9648902	0.1794856	-0.8031572

F	4.9714091	0.2001571	-1.7353591
C	6.6297757	-1.0404167	-0.6829716
F	6.2793476	-2.0956993	-1.4462685
C	7.6620090	-1.1692587	0.2384862
F	8.3132767	-2.3379692	0.3788602
C	3.5270794	1.0874002	3.6808316
C	4.3525502	0.0712904	3.1658908
C	4.0238808	1.9972503	4.6326383
C	5.3554487	1.8863124	5.0398018
C	5.6699824	-0.0188191	3.6188317
C	6.1962258	0.8848751	4.5463111
H	5.7455914	2.6016666	5.7611850
H	6.3042478	-0.8117068	3.2299976
C	0.0280917	2.6108962	0.3516258
C	-0.2770038	1.8230722	-0.7792443
C	0.0246120	4.0149331	0.2615346
C	-0.2378656	4.6096088	-0.9783681
C	-0.5483151	2.4579613	-1.9907152
C	-0.5177801	3.8522193	-2.1161009
H	-0.2273738	5.6955193	-1.0514441
H	-0.7673413	1.8485262	-2.8653190
C	0.2423182	4.8907438	1.4724212
H	-0.7225177	5.1724168	1.9129329
H	0.7625102	5.8130033	1.1985265
H	0.8175237	4.3831005	2.2492899
C	-0.2652417	0.3156629	-0.6989840
H	-0.3911063	-0.1235735	-1.6916669
H	-1.0685929	-0.0591655	-0.0547552
H	0.6755982	-0.0530156	-0.2748106
C	-0.7583046	4.5112538	-3.4513735
H	-1.5849773	4.0323755	-3.9860242
H	0.1316165	4.4329026	-4.0881369
H	-0.9910389	5.5731575	-3.3328509
C	3.1449192	3.0823436	5.2089916
H	3.7509452	3.8501797	5.6970189
H	2.4500240	2.6772260	5.9548476
H	2.5317425	3.5613257	4.4380753
C	7.6384702	0.8038830	4.9768388
H	8.2646388	1.4266652	4.3277621
H	8.0152654	-0.2205408	4.9091080
H	7.7647993	1.1574014	6.0047493
C	3.8396583	-0.8908047	2.1234655
H	4.5493187	-1.7064500	1.9661345
H	3.7030200	-0.3861463	1.1585211

H 2.8708634 -1.3161200 2.4063293

6e_Ph

E(TPSS-D3/def2-TZVP) = -2211.241377194 (conv)

Lowest Freq. = 9.16 cm^-1

46

6d_Ph (004/c2/tpss-d3.def2-TZVP)

H -3.6335233 0.5709956 0.3975254
C -3.7773787 0.4008143 -0.6656142
C -4.9876617 0.7374053 -1.2688704
H -5.7868944 1.1655285 -0.6711183
C -5.1688570 0.5299052 -2.6364948
H -6.1111623 0.7970742 -3.1056261
C -4.1374478 -0.0141754 -3.4045615
H -4.2745906 -0.1682802 -4.4707509
C -2.9259911 -0.3546665 -2.8087589
H -2.1207160 -0.7606521 -3.4136505
C -2.7436645 -0.1543882 -1.4320880
P -1.1709820 -0.5736589 -0.6574212
C -0.8014949 -2.3650848 -0.7960946
C 0.4832049 -1.0110306 0.8226025
C 0.3054576 -2.4564838 0.3008812
C -0.9722703 -0.5267391 1.1518169
H -0.9825728 0.4969536 1.5300723
H -1.5966390 -1.1851572 1.7626474
H 1.1868865 -0.9238725 1.6523004
H -1.6837666 -2.9738889 -0.5855307
H -0.4346261 -2.6100641 -1.7955625
B 0.7347623 0.0065600 -0.4827399
H -0.0171176 -3.1278515 1.1042345
H 1.2352145 -2.8488171 -0.1126312
F -1.1067901 2.3497842 -1.0878560
C 0.0350401 2.6021287 -0.3975990
C 0.2522028 3.9324680 -0.0439466
F -0.6332169 4.8887925 -0.3804934
C 1.3983982 4.2714646 0.6683108
F 1.6264324 5.5467088 1.0194361
C 2.3050225 3.2728290 1.0161614
F 3.4159756 3.5892568 1.7053707
C 2.0425723 1.9579929 0.6431452
F 2.9592637 1.0282813 1.0007527
C 0.9071321 1.5626931 -0.0713354

F 1.8791409 -0.1778231 -5.3472393
C 2.2209103 -0.5006116 -4.0859586
C 1.4182627 -0.1396465 -3.0088395
F 0.2801547 0.5462088 -3.2959187
C 1.7089539 -0.4550848 -1.6803694
C 2.8955184 -1.1666580 -1.4910373
F 3.2845277 -1.5278884 -0.2458118
C 3.7356018 -1.5454654 -2.5370481
F 4.8675652 -2.2319715 -2.2986911
C 3.3954049 -1.2100556 -3.8447666
F 4.1897428 -1.5699516 -4.8651243

6d_Dmesp

E(TPSS-D3/def2-TZVP) = -2909.687364999 (conv)
Lowest Freq. = 7.58 cm^-1
84
6d_Dmesp (008/c2/tpss-d3.def2-TZVP)
C -3.7335212 -0.0699214 -0.4547219
C -5.0687892 -0.0954262 -0.8732309
H -5.8356700 0.2119305 -0.1677927
C -5.4109035 -0.4838578 -2.1631761
H -6.4514368 -0.4975930 -2.4748852
C -4.4046032 -0.8249565 -3.0597308
H -4.6490891 -1.0942720 -4.0834850
C -3.0565295 -0.8167228 -2.6832212
C -2.7115439 -0.4728624 -1.3500414
P -1.0011340 -0.6066504 -0.6766117
C 0.0269480 -1.8143026 -1.6180552
C 0.7227727 -1.2980390 0.6889773
C 1.0988141 -2.1473483 -0.5398619
C -0.7991312 -1.5307781 0.8913841
H -1.1924131 -0.9744456 1.7392509
H -1.1439424 -2.5693147 0.9053703
H 1.3312243 -1.5106016 1.5682781
H -0.5623541 -2.6861706 -1.8973319
H 0.4349815 -1.3716235 -2.5262874
B 0.6707328 0.2883226 0.2148978
H 1.0717049 -3.2166144 -0.3020725
H 2.1013322 -1.9074165 -0.9028045
F 0.1361723 3.0565527 -0.3735183
C 0.1703608 2.7405084 0.9427755
C 0.0186878 3.7967701 1.8325724

F	-0.1813605	5.0535366	1.3904149
C	0.0545142	3.5421613	3.2002089
F	-0.1107171	4.5421668	4.0822024
C	0.2369313	2.2371402	3.6406623
F	0.2732999	1.9778333	4.9616284
C	0.3727799	1.2075657	2.7120180
F	0.5522381	-0.0270450	3.2400253
C	0.3503561	1.4061795	1.3280288
F	2.6045092	1.9183365	-4.1792200
C	2.8013472	1.5017189	-2.9124702
C	1.7236818	1.1836020	-2.0898987
F	0.4902339	1.3290260	-2.6282224
C	1.8589910	0.7381234	-0.7792666
C	3.1756519	0.6495634	-0.3215398
F	3.4101951	0.2332250	0.9480056
C	4.2860210	0.9627523	-1.1001105
F	5.5336200	0.8551738	-0.6071431
C	4.0953170	1.3904022	-2.4126498
F	5.1503833	1.6944098	-3.1865270
C	-2.0584153	-1.1258731	-3.7478664
C	-1.4532315	-0.0633356	-4.4473898
C	-1.7799860	-2.4576808	-4.1024941
C	-0.8173298	-2.7089116	-5.0838303
C	-0.4911277	-0.3562170	-5.4160693
C	-0.1438238	-1.6724687	-5.7349692
H	-0.5780538	-3.7406882	-5.3349812
H	0.0008269	0.4670539	-5.9303101
C	-3.4763420	0.4428796	0.9239398
C	-3.6748713	-0.3863290	2.0447633
C	-3.1776251	1.8075456	1.0954764
C	-3.0656120	2.3158466	2.3927763
C	-3.5212022	0.1537857	3.3225147
C	-3.2234431	1.5066615	3.5187791
H	-2.8543885	3.3746521	2.5235789
H	-3.6503496	-0.4954984	4.1867057
C	-4.0702559	-1.8334941	1.8761469
H	-3.8268385	-2.4101888	2.7729023
H	-3.5708120	-2.2913817	1.0176117
H	-5.1498129	-1.9246391	1.7016578
C	-3.0423632	2.7235043	-0.0955651
H	-3.9882733	2.7872108	-0.6467001
H	-2.2867335	2.3620418	-0.7993200
H	-2.7582937	3.7305495	0.2188432
C	-3.1030604	2.0762922	4.9104523

H	-4.0787341	2.0876440	5.4115228
H	-2.7245923	3.1017027	4.8872869
H	-2.4253790	1.4764418	5.5262122
C	-1.8842820	1.3639336	-4.2127997
H	-1.1689687	2.0626996	-4.6515292
H	-1.9861597	1.5956241	-3.1501078
H	-2.8646182	1.5399207	-4.6739262
C	-2.4975816	-3.6061172	-3.4335048
H	-3.5116376	-3.7221709	-3.8358142
H	-2.6072955	-3.4461381	-2.3553531
H	-1.9635258	-4.5465803	-3.5959842
C	0.9137115	-1.9597641	-6.7725170
H	1.8293245	-1.3939992	-6.5674094
H	0.5705044	-1.6704996	-7.7734230
H	1.1645108	-3.0241704	-6.7966909

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