Electronic Control of Frustrated Lewis Pair Behavior: Chemistry of a geminal alkylidene-bridged Per-pentafluorophenylated P/B Pair

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Supporting Information

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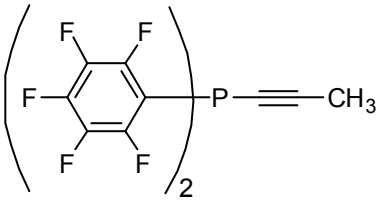
General Information. All reactions were carried out under argon atmosphere with Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds. Elemental analyses: Foss-Heraeus CHNO-Rapid. Mass Spectrometry: Orbitrap LTQ XL (Thermoscientific) for ESI measurements. NMR: Bruker AV 300 (^{1}H: 300 MHz, ^{13}C: 76 MHz, ^{31}P: 122 MHz, ^{19}F: 282 MHz, ^{11}B: 96 MHz), Bruker AV 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{31}P: 162 MHz), Varian 500 MHz INOVA (^{1}H, 500 MHz, ^{13}C, 126 MHz, ^{31}P: 162 MHz, ^{19}F: 470 MHz, ^{11}B: 160 MHz), Varian UNITY plus NMR spectrometer (^{1}H, 600 MHz, ^{13}C, 151 MHz, ^{31}P: 243 MHz, ^{19}F: 564 MHz, ^{11}B: 193 MHz). Assignments of the resonances are supported by 2D experiments. Melting points / decomposition temperature: DSC 2010 (TA-Instruments) apparatus. Determined by the baseline method. Infrared Spectroscopy: Varian 3100 FT-Infrared Spectroscopy (ExcaliburSeries) spectrometer. X-ray diffraction: Data sets were collected with a Nonius KappaCCD-diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction Denzo (Z.Otwinowski, D. Borek, W. Majewski & W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 ((G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997). *R*-values are given for the observed reflections, wR^2-values for all independent ones. All figures are drawn with 50% probability.

Materials. The compounds propynyllithium [K. B. Starowieyski, A. Chwojnowski, Z. Kuśmierek, *J. Organomet. Chem.* **1980**, *192*, 147-154.], bis(pentafluorophenyl)-chlorophosphane (**11)** [G. Mancino, A. J. Ferguson, A. Beeby, N. J. Long, T. S. Jones, *J. Am. Chem. Soc.* **2005**, *127*, 524-525.], and bis(pentafluorophenyl)borane [$HB(C_6F_5)_2$] [Massey, A. G. and Park, A. J. *Organometallic Syntheses,* eds. R. B. King and J. J. Eisch, Elsevier, New York, **1986**, vol. 3, pp. 461-462. Massey, A. G.; Park, A. J. *J. Organomet Chem.* **1964**, *2*, 245-250. Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492-5503. Parks, D. J.; von H. Spence, R. E.; Piers, W. E. *Angew. Chem.* **1995**, *107*, 895-897; *Angew. Chem. Int. Ed.* **1995**, *34*, 809-811.] were prepared according to modified literature procedures.

Preparation of bis(pentafluorophenyl)propynylphosphane (12).



A solution of bis(pentafluorophenyl)chlorophosphane (**11**) (9.81 g, 24.5 mmol, 1 eq) in *n*-pentane (4 mL) was added to a suspension of propynyllithium (1.13 g, 24.5 mmol, 1 eq) in dry THF (80 mL) at –78 °C. The resulting slightly yellow suspension was warmed up to room temperature and stirred for two hours. The solvent of the resulting yellow solution was removed *in vacuo* and the orange-red residue was dissolved in *n*-pentane before filtrated over Celite® to remove the formed lithium chloride. The solvent of the filtrate was removed *in vacuo* and the resulting residue was purified by distillation (p = 0.11 mbar, 97 °C) to get **12** as a colorless oil (4.04 g, 10 mmol, 41%).

^{1}H NMR (400 MHz, [D$_6$]-benzene, 296 K): δ = 1.45 (d, $^{4}J_{P,H}$ = 2.8 Hz, 1H, CH$_3$).

^{13}C{^{1}H} NMR (101 MHz, [D$_6$]-benzene, 296 K): δ = 4.8 (d, $^{3}J_{P,C}$ = 1.2 Hz, CH$_3$), 67.6 (m, ^{P}C≡)^{t}, 107.7 (m br, *i*-C$_6$F$_5$), 109.2 (d, $^{2}J_{P,C}$ = 14.3 Hz, ≡C)^{t}, 137.6 (dm, $^{1}J_{F,C}$ ~ 255 Hz, *o*-C$_6$F$_5$), 142.8 (dm, $^{1}J_{F,C}$ ~ 257 Hz, *p*-C$_6$F$_5$), 147.6 (dm, $^{1}J_{F,C}$ ~ 251 Hz, *m*-C$_6$F$_5$), [^{t} tentative assignment].

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, [D$_6$]-benzene, 297 K): δ^{1}H / δ^{13}C = 1.45 / 4.8 (CH$_3$).

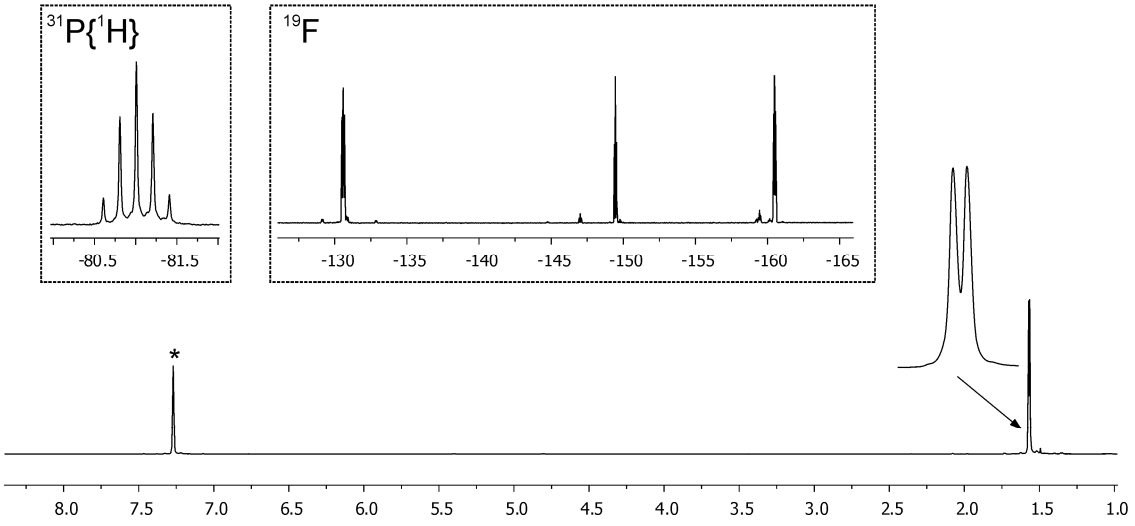
^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, [D$_6$]-benzene, 297 K): δ^{1}H / δ^{13}C = 1.45 / 4.8, 67.6, 107.7, 109.2 (CH$_3$ / CH$_3$, ^{P}C≡, *i*-C$_6$F$_5$, ≡C).

^{19}F{^{1}H} NMR (282 MHz, [D$_6$]-benzene, 296 K): δ = −160.5 (m, 2F, *m*-C$_6$F$_5$), −149.4 (m, 1F, *p*-C$_6$F$_5$), −130.6 (m, 2F, *o*-C$_6$F$_5$).

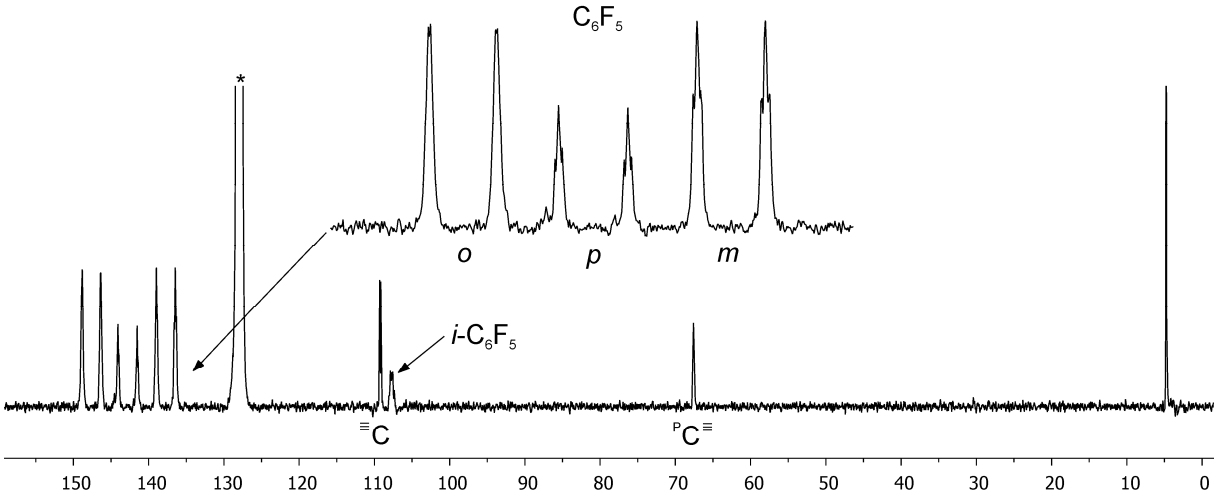
^{31}P{^{1}H} NMR (162 MHz, [D$_6$]-benzene, 298 K): δ = −81.0 (quin, $^{3}J_{P,F}$ = 32.3 Hz).

Elemental Analysis: C$_{15}$H$_3$F$_{10}$P (404.1 g/mol) requires C 44.58, H 0.75, found: C 44.19, H 0.69.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 2197 [st, ν(C≡C)] w, 1640 w, 1514 m, 1470 s, 1386 w, 1290 w, 1086 s, 1045 w, 974 s, 839 w, 760 w, 729 w, 641 w, 568 w.

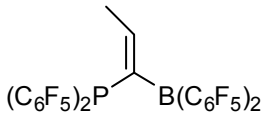


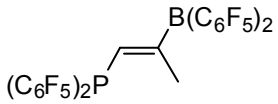
^{1}H NMR (400 MHz, [D$_6$]-benzene*, 296 K), ^{31}P{^{1}H}-NMR (162 MHz, [D$_6$]-benzene, 298 K) and ^{19}F{^{1}H} NMR (282 MHz, [D$_6$]-benzene, 296 K) of **12**.



^{13}C{^{1}H}-NMR (101 MHz, [D$_6$]-benzene*, 296 K) of **12**.

Preparation of compound 13 and compound 14.





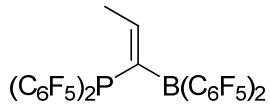
A solution of bis(pentafluorophenyl)propynylphosphane (**12**) and *n*-pentane (10 mL) was added to a suspension of bis(pentafluorophenyl)borane (3.14 g, 9.11 mmol, 1 eq) in *n*-pentane (150 mL) at −78 °C. Upon warming up to room temperature and stirring for two hours the color turned from colorless to slightly yellow. The solvent was removed *in vacuo* and a mixture of the Markovnikov and the anti-Markovnikov product (**13** : **14** = 7 : 1; integral value from the ^{1}H NMR experiment) was obtained as a yellow, viscous foam (5.97 g, 7.96 mmol, 88%).

Elemental Analysis: $C_{27}H_4BF_{20}P$ (750.1 g/mol) requires C 43.23, H 0.54, found: C 43.20, H not detected.

Melting Point: 88 °C.

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 2922 w, 1647 s, 1520 s, 1477 s, 1316 s, 1289 m, 1208 m, 1151 m, 1090 s, 979 s, 873 w, 829 w, 782 w, 694 w, 640 w, 507 w, 420 w.

Major compound **13**.



^{1}H NMR (500 MHz, [D$_6$]-benzene, 298 K): δ = 1.58 (d, $^{3}J_{H,H}$ = 6.9 Hz, 3H, CH$_3$), 6.73 (dq, $^{3}J_{P,H}$ = 24.4 Hz, $^{3}J_{H,H}$ = 6.9 Hz, 1H, CH).

^{13}C{^{1}H} NMR (126 MHz, [D$_6$]-benzene, 298 K): δ = 19.7 (d, $^{3}J_{P,C}$ = 22.6 Hz, CH$_3$), 108.0 (m, *i*-PC$_6$F$_5$), 113.2 (m, *i*-BC$_6$F$_5$), 137.6 (dm, $^{1}J_{F,C}$ ~ 254 Hz, *o*-C$_6$F$_5$), 137.7 (dm, $^{1}J_{F,C}$ ~ 256 Hz, *o*-C$_6$F$_5$), 142.2 (br, $^{B}C^{P}$), 142.9 (dm, $^{1}J_{F,C}$ ~ 258 Hz, *p*-C$_6$F$_5$), 143.7 (dm, $^{1}J_{F,C}$ ~ 255 Hz, *p*-C$_6$F$_5$), 147.1 (dm, $^{1}J_{F,C}$ ~ 247 Hz, *m*-C$_6$F$_5$), 147.7 (dm, $^{1}J_{F,C}$ ~ 253 Hz, *m*-C$_6$F$_5$), 163.8 (d, $^{2}J_{P,C}$ = 22.2 Hz, CH).

^{13}C{^{19}F} (126 MHz, [D$_6$]-benzene, 298 K) : δ [selected resonances] = 108.0 (d, $^{1}J_{P,C}$ = 36.3 Hz, *i*-PC$_6$F$_5$), 113.2 (br, *i*-BC$_6$F$_5$), 137.6 (m, *o*-C$_6$F$_5$), 137.7 (m, *o*-C$_6$F$_5$), 142.9 (s, *p*-C$_6$F$_5$), 143.7 (m, *p*-C$_6$F$_5$), 147.1 (m, *m*-C$_6$F$_5$), 147.7 (m, *m*-C$_6$F$_5$), 163.8 (dm, $^{1}J_{C,H}$ ~ 160 Hz, CH).

$^{13}C\{^{19}F(\delta = -128.5)\}$ NMR (126 MHz, $[D_6]$-benzene, 298 K): δ [selected resonances] = 108.0 (d, $^{1}J_{P,C}$ = 36.3 Hz, *i*-PC_6F_5), 137.6 (m, *o*-C_6F_5), 137.7 (m, *o*-C_6F_5),

$^{13}C\{^{19}F(\delta = -147.1)\}$ NMR (126 MHz, $[D_6]$-benzene, 298 K): δ [selected resonances] = 142.9 (m, *p*-C_6F_5), 143.7 (m, *p*-C_6F_5).

$^{13}C\{^{19}F(\delta = -160.0)\}$ NMR (126 MHz, $[D_6]$-benzene, 298 K): δ [selected resonances] = 147.1 (m, *m*-C_6F_5), 147.7 (m, *m*-C_6F_5).

$^{11}B\{^{1}H\}$ NMR (160 MHz, $[D_6]$-benzene, 298 K): δ = 60.2 ($\nu_{1/2}$ ~ 1400 Hz).

^{19}F NMR (470 MHz, $[D_6]$-benzene, 298 K): δ = −160.2 (2F, *m*), −146.2 (1F, *p*), −128.9 (2F, *o*) (BC_6F_5) [$\Delta\delta^{19}F_{mp}$ =14.0], −159.7 (2F, *m*), −148.0 (1F, *p*), −128.1 (2F, *o*) (PC_6F_5) [$\Delta\delta^{19}F_{mp}$ =11.7] [assignment supported by $^{19}F\{^{31}P\}$ NMR experiment].

$^{1}H\{^{19}F\}$ NOE (500 MHz, $[D_6]$-benzene, 298 K): $\delta^{19}F_{irr}$ / $\delta^{1}H_{res}$ = −128.1 / 1.58, 6.73 (*o*-$C_6F_5^{P}$ / CH_3, CH), −128.9 / 6.73 (*o*- $C_6F_5^{B}$ / CH).

$^{31}P\{^{1}H\}$ NMR (202 MHz, $[D_6]$-benzene, 298 K): δ = −62.8 (m).

$^{31}P\{^{19}F\}$ NMR (202 MHz, $[D_6]$-benzene, 298 K): δ = −62.8 (d, $^{3}J_{P,H}$ = 24.4 Hz).

$^{1}H\{^{1}H\}$ NOE (500 MHz, $[D_6]$-benzene, 298 K): $\delta^{1}H_{irr}$ / $\delta^{1}H_{res}$ = 1.58 / 6.73 (CH_3 / CH), 6.73 / 1.58 (CH / CH_3).

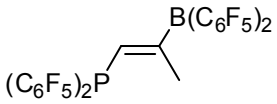
$^{1}H,^{1}H$ GCOSY (500 MHz / 500 MHz, $[D_6]$-benzene, 298 K): $\delta^{1}H$) / $\delta^{1}H$ = 6.73 / 1.58 (CH / CH_3).

$^{1}H,^{13}C$ GHSQC (500 MHz / 126 MHz, $[D_6]$-benzene, 298 K): $\delta^{1}H$) / $\delta^{13}C$ = 1.58 / 19.7 (CH_3), 6.73 / 163.8 (CH).

$^{1}H,^{13}C$ GHMBC (500 MHz / 126 MHz, $[D_6]$-benzene, 298 K): $\delta^{1}H$ / $\delta^{13}C$ = 1.58 / 142.2, 163.8 (CH_3 / CH, $^{P}C^{B}$), 6.73 / 19.7 (CH / CH_3).

$^{19}F,^{19}F$ GCOSY (470 MHz / 470 MHz, $[D_6]$-benzene, 298 K): $\delta^{19}F$ / $\delta^{19}F$ = −160.2 / −146.2, −128.9 (*m* / *p*, *o*), −146.2 / −160.2 (*p* / *m*), −128.9 / −160.2 (*o* / *m*) (BC_6F_5), −159.7 / −148.0, −128.1 (*m* / *p*, *o*), −148.0 / −159.7 (*p* / *m*), −128.1 / −159.7 (*o* / *m*) (PC_6F_5).

Minor Compound **14**



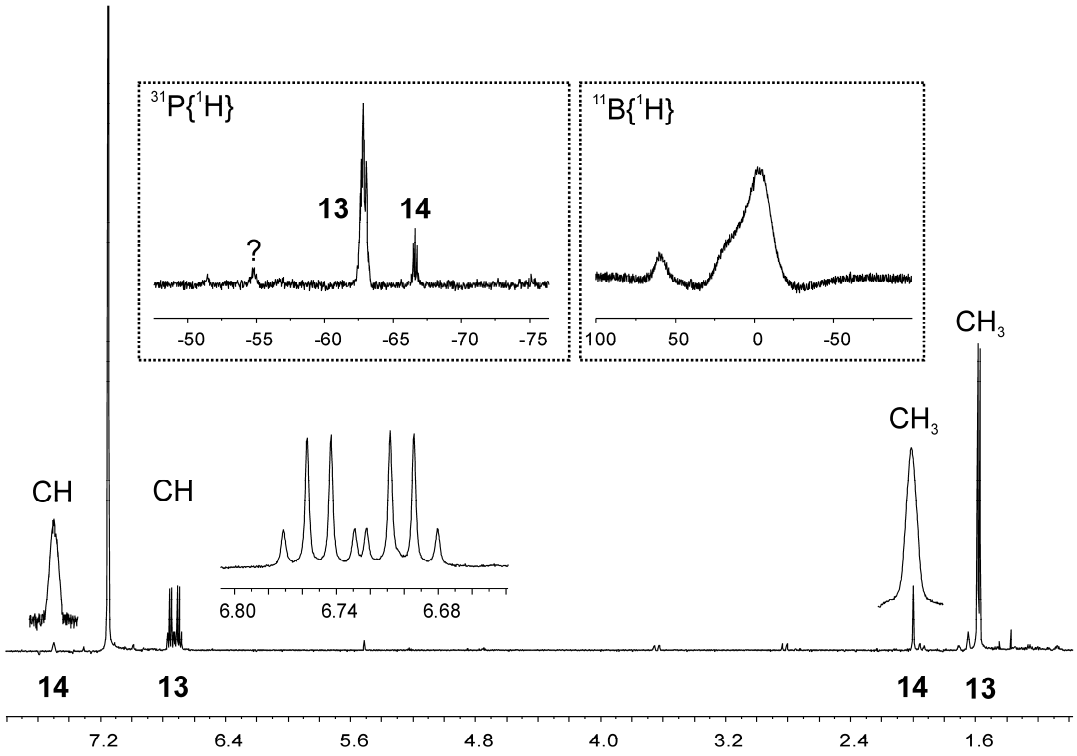
^{1}H NMR (500 MHz, [D_6]-benzene, 298 K): δ = 2.00 (s, 3H, CH_3), 7.50 (s, 1H, CH).

^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 298 K): δ = 18.3 (d, $^{3}J_{P,C}$ = 28.0 Hz, CH_3), 143.1 (d, $^{2}J_{P,C}$ = 22.2 Hz, CH)[a], 161.4 ($^{P}C^{B}$)[b], [[a] from the ghsqc NMR experiment, [b] from the ghmbc NMR experiment].

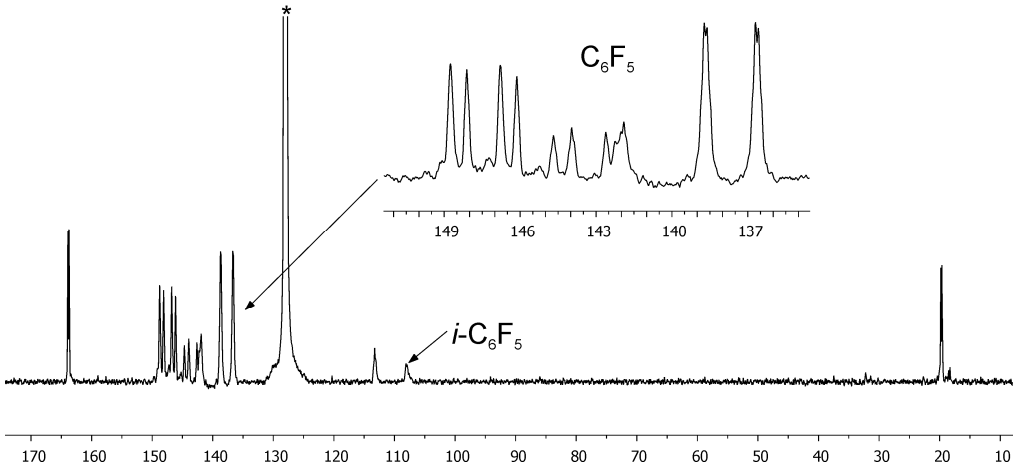
^{19}F NMR (564 MHz, [D_6]-benzene, 298 K): δ = −160.2 (2F, *m*), −144.5 (1F, *p*), −128.9 (2F, *o*) (BC_6F_5), −159.8 (2F, *m*), −148.4 (1F, *p*), −130.4 (2F, *o*) (PC_6F_5), [assignment supported by ^{19}F{^{31}P} and ^{19}F,^{19}F GCOSY NMR experiment].

^{31}P{^{1}H} NMR (202 MHz, [D_6]-benzene, 298 K): δ = −66.6 (quint, $^{3}J_{P,F}$ = 26.4 Hz).

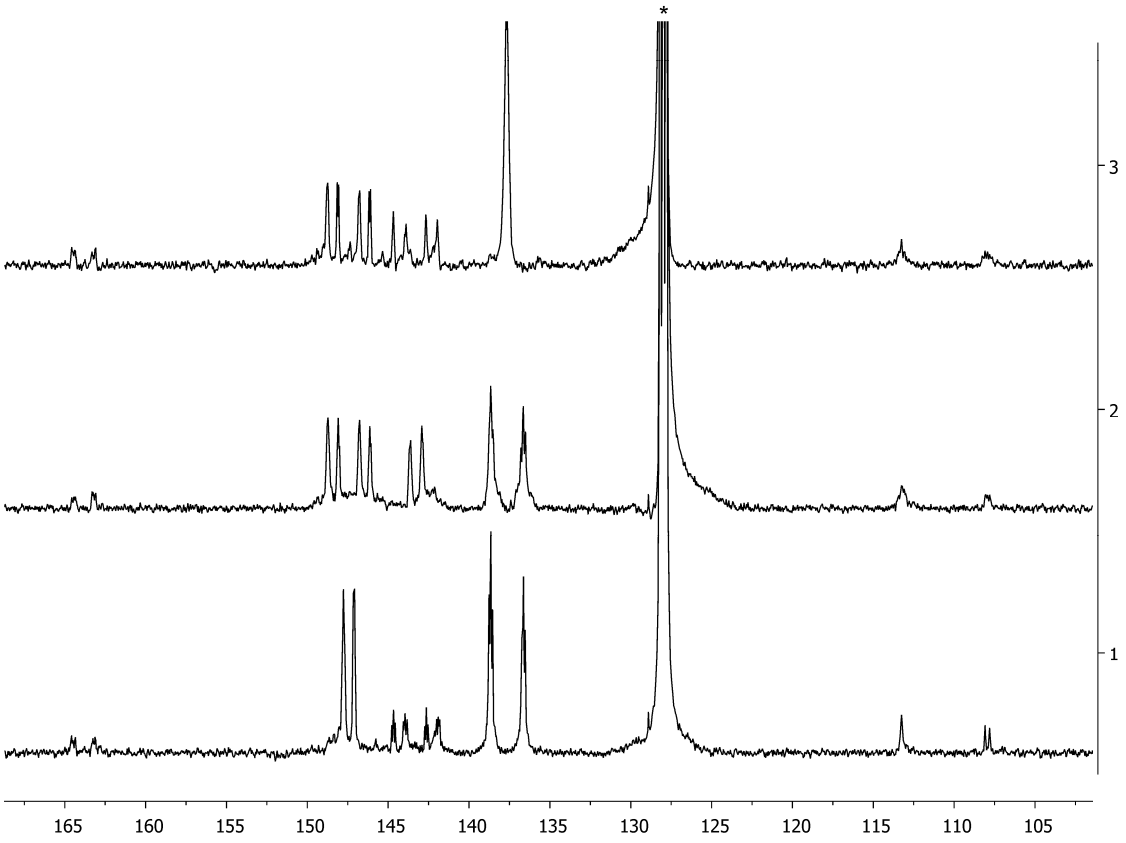
^{31}P{^{19}F} NMR (202 MHz, [D_6]-benzene, 298 K): δ = −66.6 (s, $\nu_{1/2}$ ~ 10 Hz).



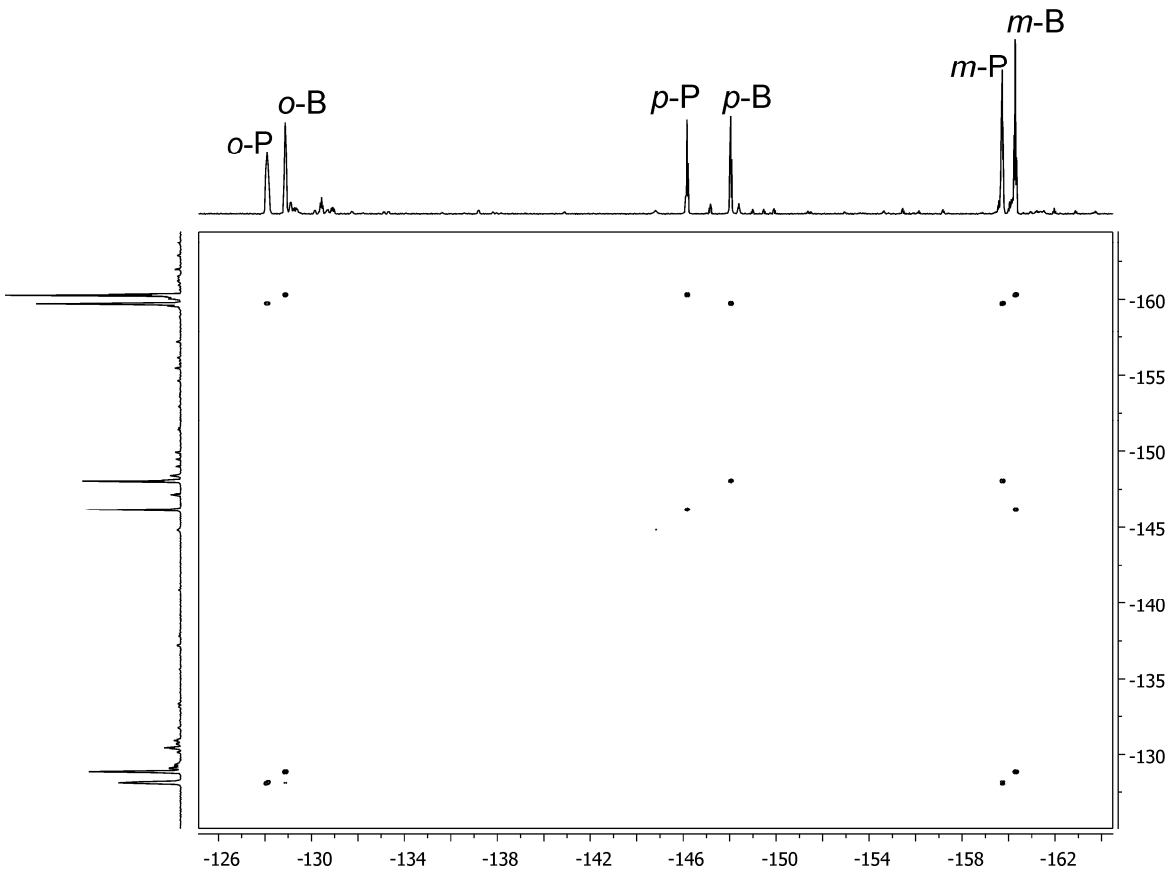
^{1}H NMR (500 MHz, [D_6]-benzene*, 298 K) ^{11}B{^{1}H} NMR (160 MHz, [D_6]-benzene, 298 K) and ^{31}P{^{1}H} NMR (202 MHz, [D_6]-benzene, 298 K) of **13** and **14**.



$^{13}C\{^{1}H\}$ NMR (126 MHz, [D_6]-benzene*, 298 K) of **13** and **14**.



1: $^{13}C\{^{19}F(\delta = -128.5$ ppm)} NMR, 2: $^{13}C\{^{19}F(\delta = -147.1$ ppm)} NMR, 3: $^{13}C\{^{19}F(\delta = -160.0$ ppm) NMR (126 MHz, [D_6]-benzene, 298 K) of **13** and **14**.

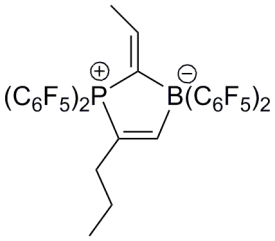


$^{19}F,^{19}F$ GCOSY (470 MHz / 470 MHz, $[D_6]$-benzene, 298 K) of **13** and **14.**

Reaction of 13/14 with small molecules.

General procedure. The mixture **13**/**14** (1 eq) was solved in *n*-pentane (5 mL) and then treated with a solution of the respective substrate (1 eq) in *n*-pentane (1 - 2 mL) at room temperature. Upon stirring the reaction mixture for 12 h at room temperature the resulting precipitate was collected and washed with *n*-pentane (3 × 5-10 mL). Subsequently the obtained solid was dried *in vacuo* to get the respective product.

Preparation of compound 15a.



Mixture **13**/**14** (200 mg, 0.27 mmol, 1 eq) reacted with 1-pentyne (18.0 mg, 0.27 mmol, 1 eq) to obtain **15a** as a white solid (135 mg, 0.165 mmol, 62%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a saturated solution of **15a** in [D_6]-benzene.

^{1}H NMR (500 MHz, [D_6]-benzene, 298 K): δ = 0.73 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, $^{CH2}CH_3$), 1.36 (m, 2H, $CH_2{}^{CH3}$), 1.45 (dd, $^3J_{H,H}$ = 7.1 Hz, $^4J_{P,H}$ = 3.6 Hz, 3H, CH_3), 1.94 (q, $^3J_{P,H}$ = $^3J_{H,H}$ = 7.8 Hz, 2H, CH_2), 7.02 (dq, $^3J_{P,H}$ = 62.3 Hz, $^3J_{H,H}$ = 7.1 Hz, 1H, =CH), 8.27 (d, $^3J_{P,H}$ = 61.5 Hz, 1H, =CH^B).

^{1}H{^{31}P} NMR (500 MHz, [D_6]-benzene, 298 K): δ [selected resonances] = 1.45 (d, $^3J_{H,H}$ = 7.1 Hz, 3H, CH_3), 1.94 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, CH_2), 7.02 (q, $^3J_{H,H}$ = 7.1 Hz, 1H, =CH), 8.27 (s, 1H, =CH^B).

^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 298 K): δ = 13.7 ($^{CH2}CH_3$), 20.8 (d, $^3J_{P,C}$ = 7.8 Hz, $CH_2{}^{CH3}$), 21.9 (d, $^3J_{P,C}$ = 17.2 Hz, CH_3), 31.2 (d, $^2J_{P,C}$ = 16.7 Hz, CH_2), 124.6 (d, $^1J_{P,C}$ = 89.1 Hz, =C^P), 132.9 (br, $^PC^B$), 155.9 (br, =CH), 180.6 (br, =CH^B) [C_6F_5 not listed].

^{11}B NMR (160 MHz, [D_6]-benzene, 298 K): δ = −9.8 (br d, $^3J_{P,B}$ ~ 40 Hz).

^{11}B{^{1}H} NMR (160 MHz, [D_6]-benzene, 298 K): δ = −9.8 (br d, $^3J_{P,B}$ ~ 40 Hz).

^{19}F NMR (470 MHz, [D_6]-benzene, 298 K): δ = −164.2 (m, 2F, *m*), −159.1 (m, 1F, *p*), −132.7 (m, 2F, *o*) (BC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 5.1], −156.7 (m, 2F, *m*), −138.6 (m, 1F, *p*), −130.0 (m, 2F, *o*) (PC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 18.1].

^{31}P{^{1}H} NMR (202 MHz, [D_6]-benzene, 298 K): δ = 0.9 (m, patially relaxed $^3J_{P,B}$).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, [D$_6$]-benzene, 298 K): δ^{1}H / δ^{1}H = 0.73 / 1.36 (^{CH2}CH$_3$ / CH$_2$^{CH3}), 1.36 / 0.73, 1.94 (CH$_2$^{CH3} / ^{CH2}CH$_3$, CH$_2$), 1.45 / 7.02 (CH$_3$ / =CH), 1.94 / 1.36, 8.27 (CH$_2$ / CH$_2$^{CH3}, =CH^{B}), 7.02 / 1.45 (=CH / CH$_3$), 8.27 / 1.94 (=CH^{B} / CH$_2$).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, [D$_6$]-benzene, 298 K): δ^{1}H / δ^{13}C = 0.73 / 13.7 (^{CH2}CH$_3$), 1.36 / 20.8 (CH$_2$^{CH3}), 1.45 / 21.9 (CH$_3$), 1.94 / 31.2 (CH$_2$), 7.02 / 155.9 (=CH), 8.27 / 180.6 (br, =CH^{B}).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, [D$_6$]-benzene, 298 K): δ^{1}H / δ^{13}C = 0.73 / 20.8, 31.2 (^{CH2}CH$_3$ / CH$_2$^{CH3}, CH$_2$), 1.36 / 13.7, 31.2, 124.6 (CH$_2$^{CH3} / ^{CH2}CH$_3$, CH$_2$, =C^{P}), 1.45 / 132.8, 155.9 (CH$_3$ / ^{P}C^{B}, =CH), 1.94 / 13.7, 20.8, 124.6 (CH$_2$ / ^{CH2}CH$_3$, CH$_2$^{CH3}, =C^{P}).

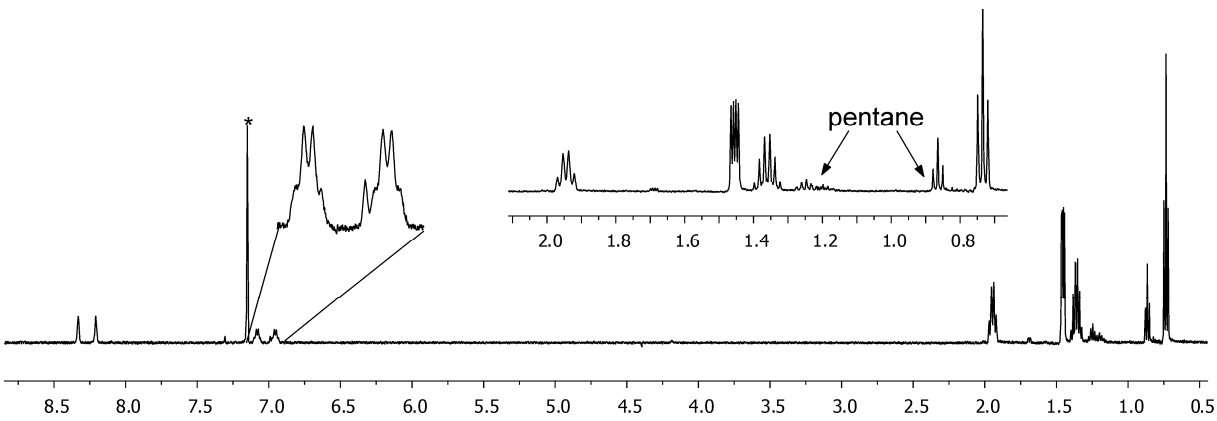
^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, [D$_6$]-benzene, 298 K): δ^{19}F / δ^{19}F = −164.2 7 / −132.7, −159.1 (*m* / *o*, *p*), −159.1 / −164.2 (*p* / *m*), −132.7 / −164.2 (*o* / *m*) (BC$_6$F$_5$), −156.7 / −130.0, −138.6 (*m* / *o*, *p*), −138.6 / −156.7 (*p* / *m*), −130.0 / −156.7 (*o* / *m*) (PC$_6$F$_5$).

^{1}H{^{19}F } NOE (500 MHz, [D$_6$]-benzene, 298 K): $\delta^{19}F_{irr}$ / $\delta^{1}H_{res}$ = −132.7 / 7.02, 8.27 (*o*-C$_6$F$_5$^{B} / $^{=}$CH, $^{=}$CH^{B}), −130.0 / 1.45, 1.94 (*o*-C$_6$F$_5$^{P} / $^{=}$CH$_3$, $^{=}$CH$_2$).

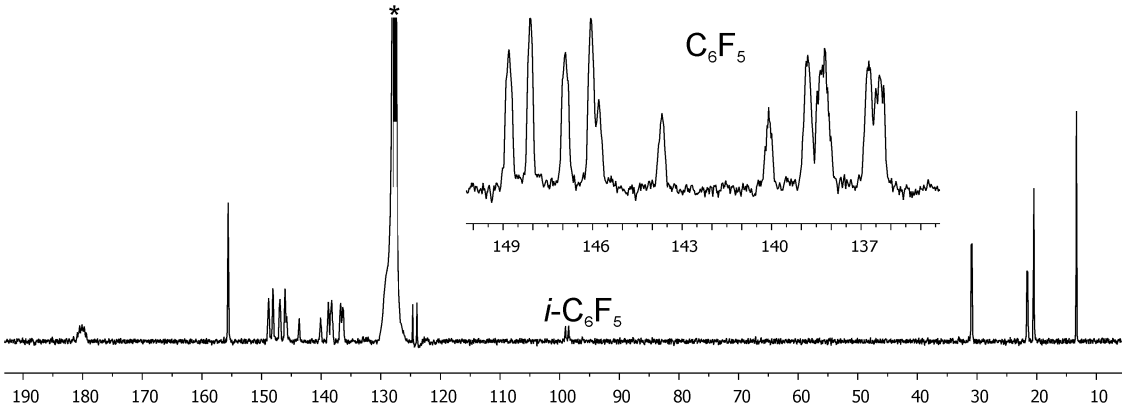
Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 2968 m, 2887 m, 1644 s, 1525 s, 1460 s, 1387 s, 1302 s, 1275 m, 1240 m, 1105 s, 1022 w, 982 s, 940 m, 858 w, 823 m, 767 w, 739 w, 673 m, 640 m, 606 m, 592 m, 565 m.

Elemental Analysis: C$_{32}$H$_{12}$BF$_{20}$P (818.2 g/mol) requires C 46.97, H 1.48, found: C 46.56, H 1.60.

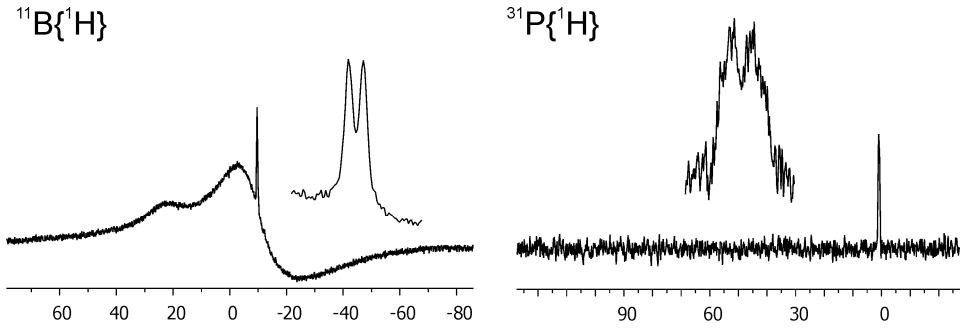
Melting Point: 225 °C.



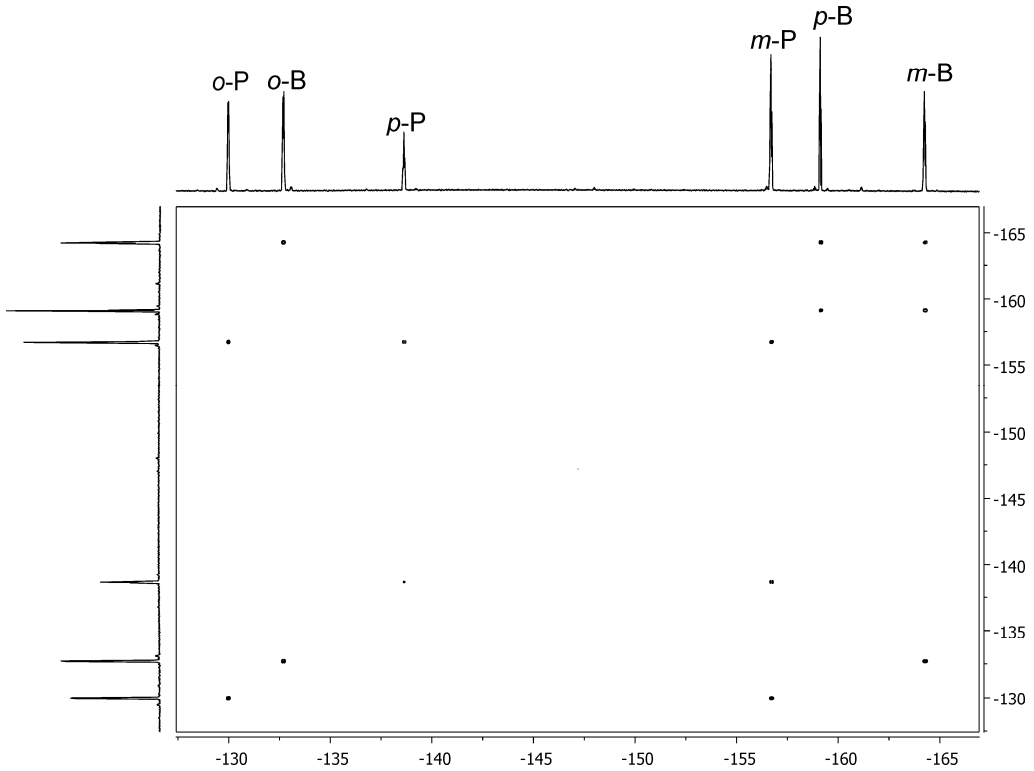
^{1}H NMR (500 MHz, [D$_6$]-benzene*, 298 K) of **15a**.



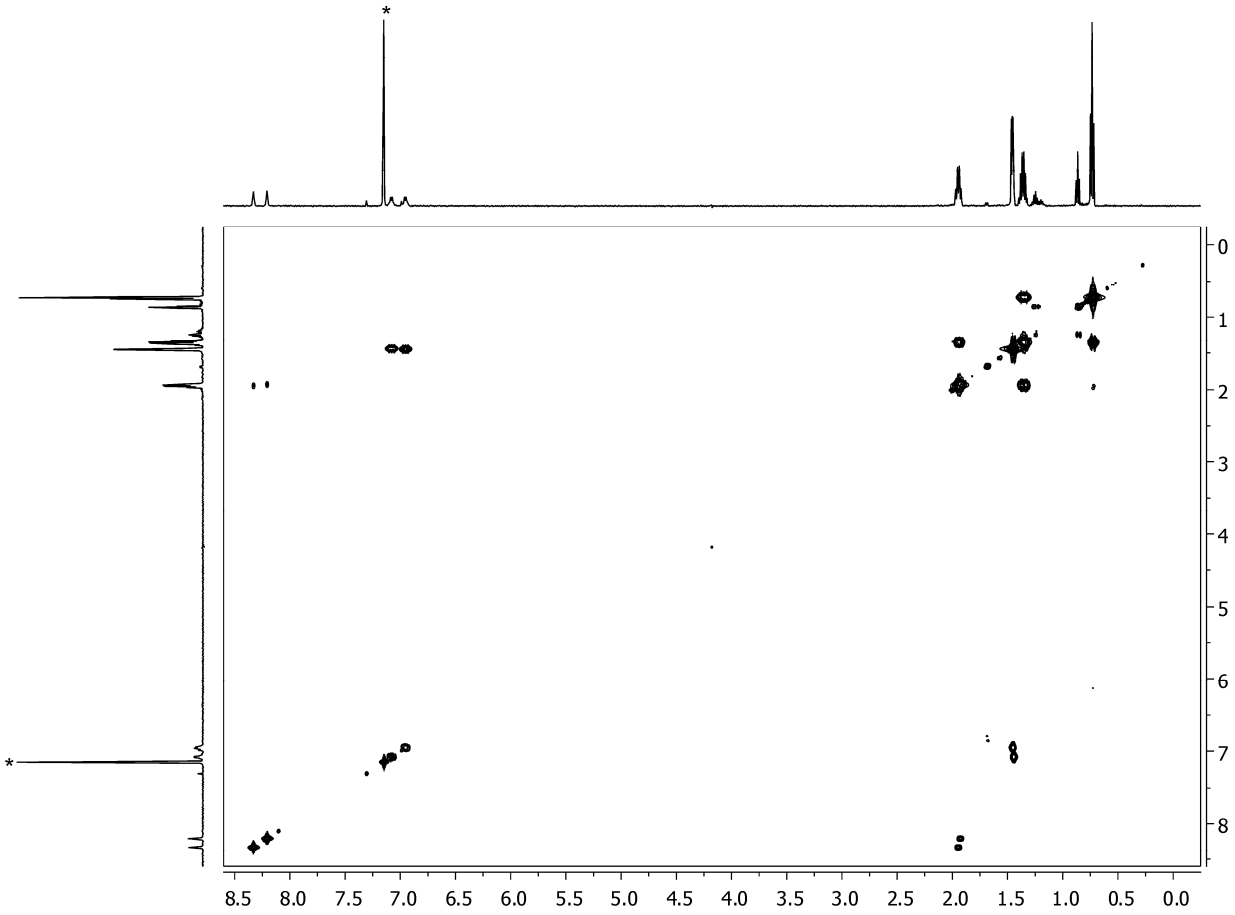
$^{13}C\{^{1}H\}$ NMR (126 MHz, [D_6]-benzene*, 298 K) of **15a**.



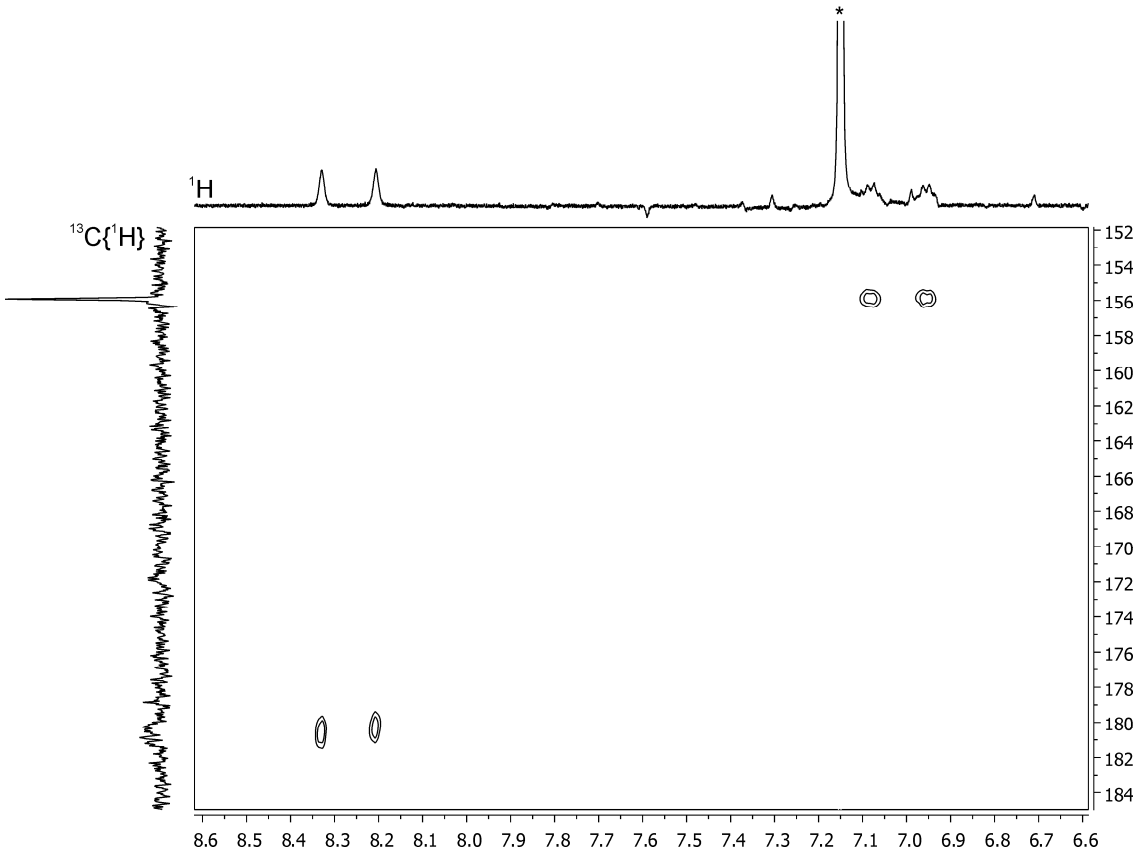
$^{11}B\{^{1}H\}$ (NMR 160 MHz, [D_6]-benzene, 298 K) and $^{31}P\{^{1}H\}$ NMR (202 MHz, [D_6]-benzene, 298 K) of **15a**.



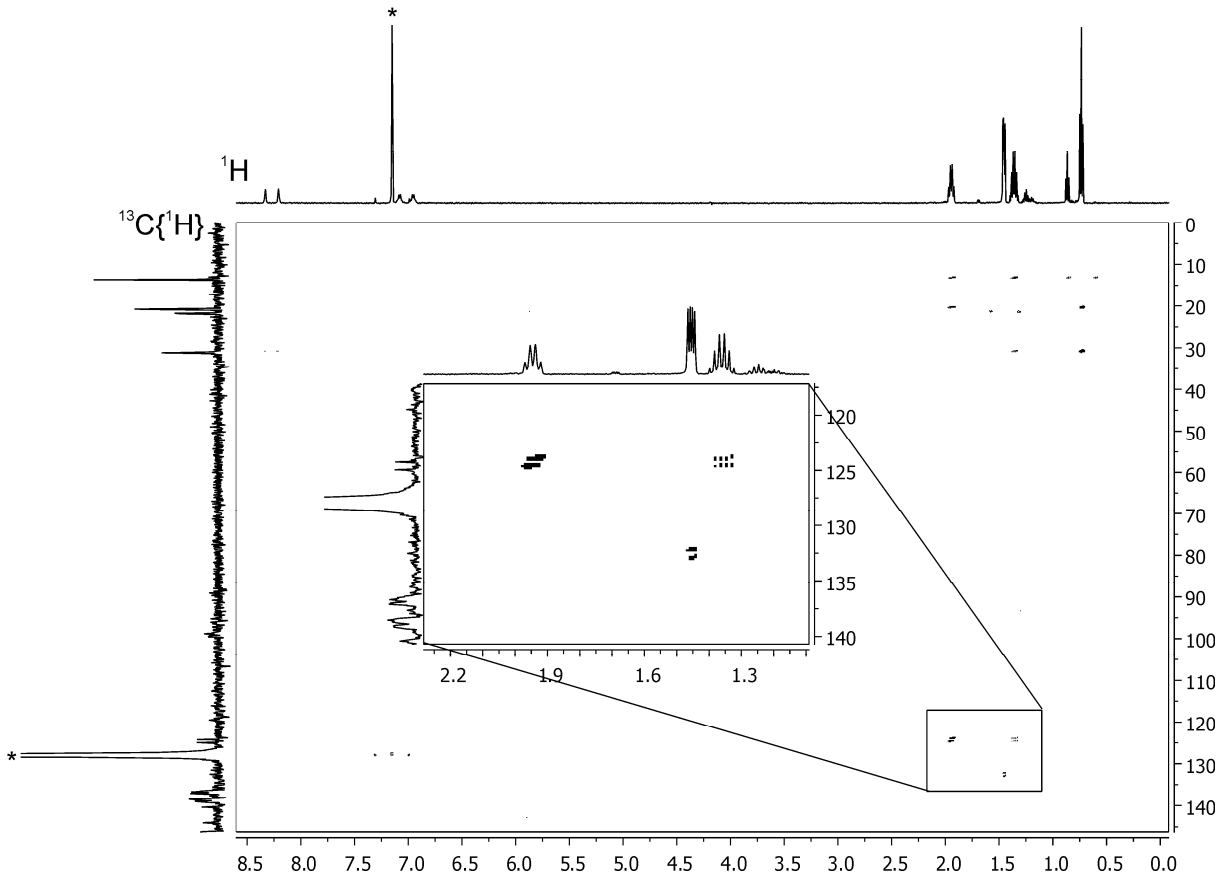
$^{19}F,^{19}F$ GCOSY (470 MHz / 470 MHz, [D_6]-benzene, 298 K) of **15a**.



^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, [D_6]-benzene*, 298 K) of **15a**.

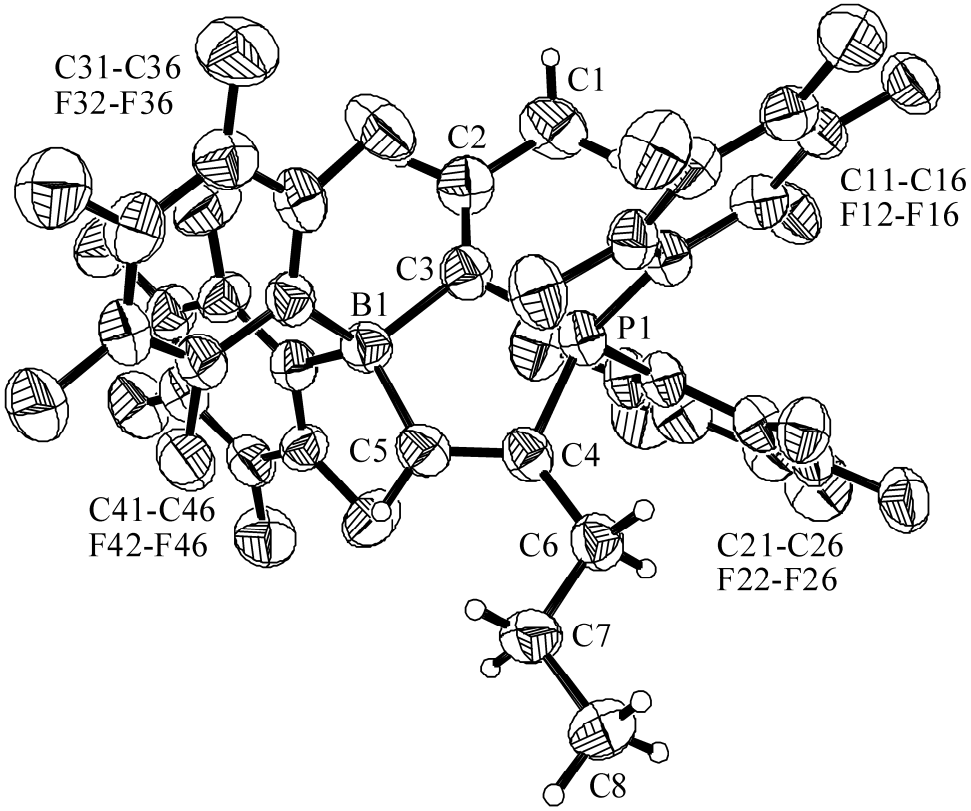


^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, [D_6]-benzene*, 298 K) of **15a**.

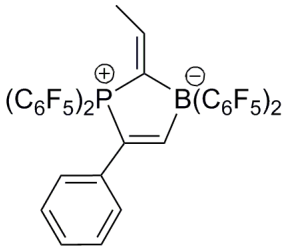


^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, [D_6]-benzene*, 298 K) of **15a**.

X-ray crystal structure analysis of 15a: formula $C_{32}H_{12}BF_{20}P$, M = 818.20, colorless crystal 0.25 x 0.12 x 0.07 mm, a = 11.1848(4), b = 15.8115(6), c = 18.1557(10) Å, β = 103.037(3)°, V = 3128.0(2) Å^3, ρ_{calc} = 1.737 g cm^{-3}, μ = 2.144 cm^{-1}, empirical absorption correction (0.616 ≤ T ≤ 0.864), Z = 4, monoclinic, space group $P2_1$ (No. 4), λ= 1.54178 Å, T = 223 K, ω and φ scans, 28344 reflections collected (±h, -k, -l), [(sinθ)/λ] = 0.60 Å^{-1}, 9090 independent (R_{int} = 0.059) and 7709 observed reflections [$I \geq 2\ \sigma(I)$], 977 refined parameters, R = 0.049, wR^2 = 0.125, Flack parameter 0.04(3), max. residual electron density 0.36 (-0.24) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.


C31-C36
F32-F36
C1
C2
C11-C16
F12-F16
C3
B1
P1
C5
C4
C41-C46
F42-F46
C6
C21-C26
F22-F26
C7
C8

Preparation of compound 15b.



Mixture **13**/**14** (200 mg, 0.27 mmol, 1 eq) reacted with phenylacetylene (28 mg, 0.27 mmol, 1 eq) to get **15b** as a white solid (146 mg, 0.17 mmol, 64%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a saturated solution of **15b** in [D_2]-dichloromethane at −34 °C.

^{1}H NMR (400 MHz, [D_2]-dichloromethane, 296 K): δ = 1.93 (dd, $^{3}J_{H,H}$ = 7.1 Hz, $^{4}J_{P,H}$ = 3.5 Hz, 3H, CH_3), 6.86 (dm, $^{3}J_{P,H}$ = 63.6 Hz, 1H, =CH), 7.20 (m, 2H, *o*-Ph), 7.31 (m, 3H, *m*-, *p*-Ph), 8.73 (dm, $^{3}J_{P,H}$ = 57.3 Hz, 1H, =CH^{B}).

^{13}C{^{1}H} NMR (101 MHz, [D_2]-dichloromethane, 296 K): δ = 21.7 (br d, $^{3}J_{P,C}$ = 18.2 Hz, CH_3), 126.5 (d, $^{2}J_{P,C}$ = 94.8 Hz, ^{P}C=), 127.2 (d, $^{3}J_{P,C}$ = 5.6 Hz, *o*-Ph), 129.2 (d, *J* = 1.1 Hz, *p*-Ph), 129.3 (*m*-Ph), 132.7 (br, $^{P}C^{B}$)^{b}, 133.9 (dm, $^{2}J_{P,C}$ = 18.3 Hz, *i*-Ph), 154.3 (=CH), 184.3 (br, =CH^{B}) [C_6F_5 not listed, ^{b} from the ghmbc NMR experiment].

^{11}B{^{1}H} NMR (160 MHz, [D_2]-dichloromethane, 298 K): δ = −10.1 (d, $^{3}J_{P,B}$ ~ 39 Hz).

^{19}F NMR (470 MHz, [D_2]-dichloromethane, 298 K): δ = −165.3 (2F, *m*), −160.6 (t, $^{3}J_{F,F}$ = 20 Hz, 1F, *p*), −133.2 (2F, *o*) (BC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 4.7], −157.0 (2F, *m*), −140.6 (1F, *p*), −127.9 (2F, *o*) (PC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 16.4].

^{31}P{^{1}H} NMR (202 MHz, [D_2]-dichloromethane, 298 K): δ = −2.8 (1:1:1:1 q, $^{3}J_{P,B}$ ~ 39 Hz).

^{1}H,^{1}H GCOSY (400 MHz / 101 MHz, [D_2]-dichloromethane, 296 K): δ^{1}H / δ^{1}H = 1.93 / 6.86 (CH_3 / =CH), 6.86 / 1.93 (=CH / CH_3), 7.20 / 7.31 (*o*-Ph / *m*-Ph), 7.31 / 7.20 (*m*-Ph / *o*-Ph).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, [D_2]-dichloromethane, 296 K): δ^{1}H / δ^{13}C = 1.93 / 21.7 (CH_3), 6.86 / 154.3 (=CH), 7.20 / 127.2 (*o*-Ph), 7.31 / 129.3 (*m*-Ph).

^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, [D_2]-dichloromethane, 296 K): δ^{1}H / δ^{13}C = 1.93 / 132.7, 154.3 (CH_3 / $^{P}C^{B}$, =CH), 7.20 / 127.2, 129.2 (*o*-Ph / *o*-Ph, *p*-Ph), 7.31 / 127.2, 129.3 (*m*-, *p*-Ph / *o*-Ph, *m*-Ph), 8.73 / 133.9 (=CH^{B} / *i*-Ph).

^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, [D_2]-dichloromethane, 298 K): δ^{19}F / δ^{19}F = −165.3 / −160.6, −133.2 (*m* / *p*, *o*), −160.6 / −165.3 (*p* / *m*), −133.2 / −165.3 (*o* / *m*) (BC_6F_5), −157.0 / −140.6, −127.9 (*m*/ *p, o*), −140.6 / −157.0 (*p* / *m*), −127.9 / −157.0 (*o* / *m*) (PC_6F_5).

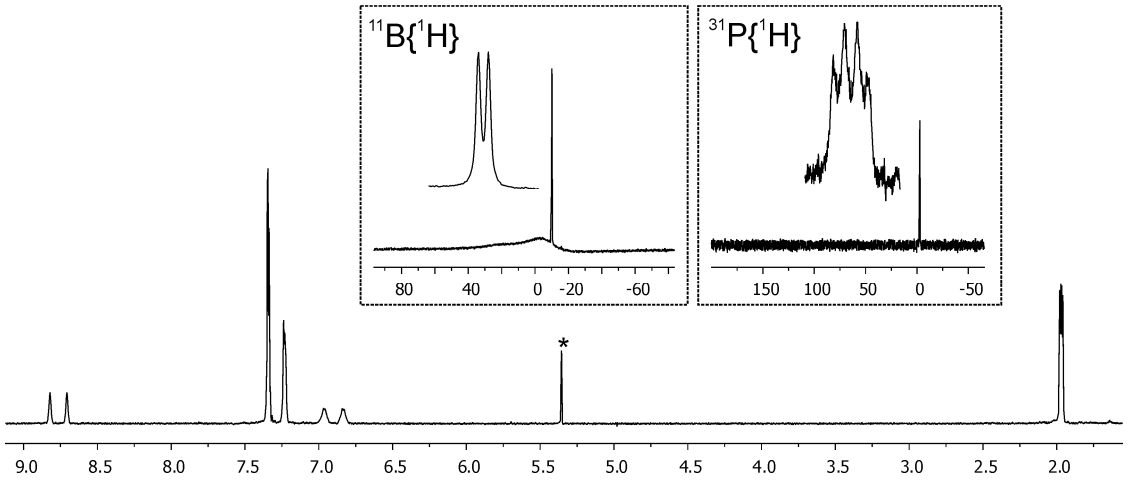
^{1}H{^{19}F } NOE (500 MHz, [D$_2$]- dichloromethane, 298 K): $\delta^{19}F_{irr}$ / δ^1H_{res} = −133.2 / 6.86, 8.73 (*o*-$C_6F_5^B$ / $^{=}$CH, $^{=}$CH^B), −127.9 / 1.93, 7.20 (*o*-$C_6F_5^P$ / CH_3, *o*-Ph).

Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 2924 w, 1644 s, 1525 s, 1485 s, 1461 s, 1387 m, 1303 m, 1275 m, 1238 m, 1152 w, 1105 s, 983 s, 944 m, 898 m, 823 m, 770 m, 730 w, 705 m, 641 w, 627 m, 594 m, 579 w, 560 w, 538 m, 503 w, 460 w.

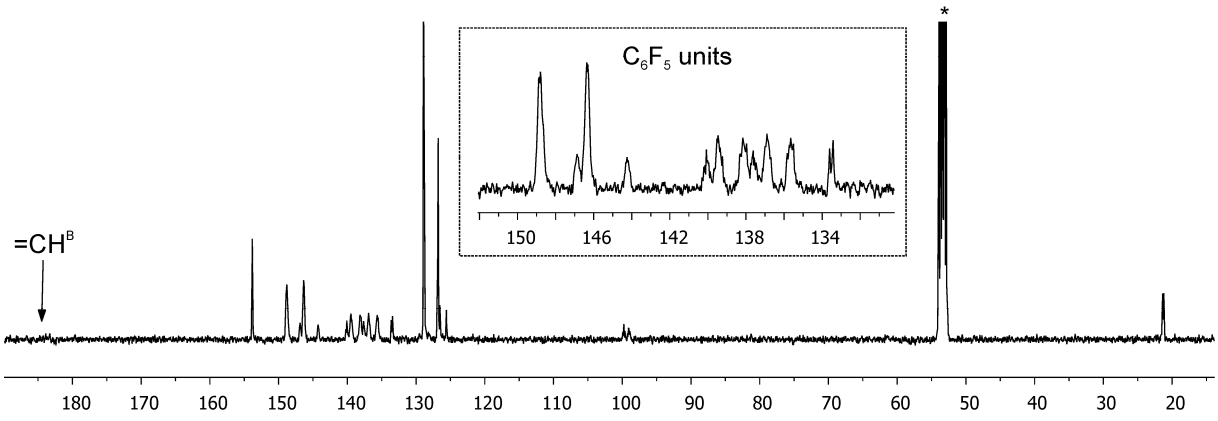
Elemental Analysis: $C_{35}H_{10}BF_{20}P$ (852.2 g/mol) requires C 49.33, H 1.18, found: C 48.71, H 0.79.

MS-ESI-EM: Calcd. for $(C_{35}H_{11}BF_{20}P)H$: 853.0378 g/mol found: 853.03749 g/mol.

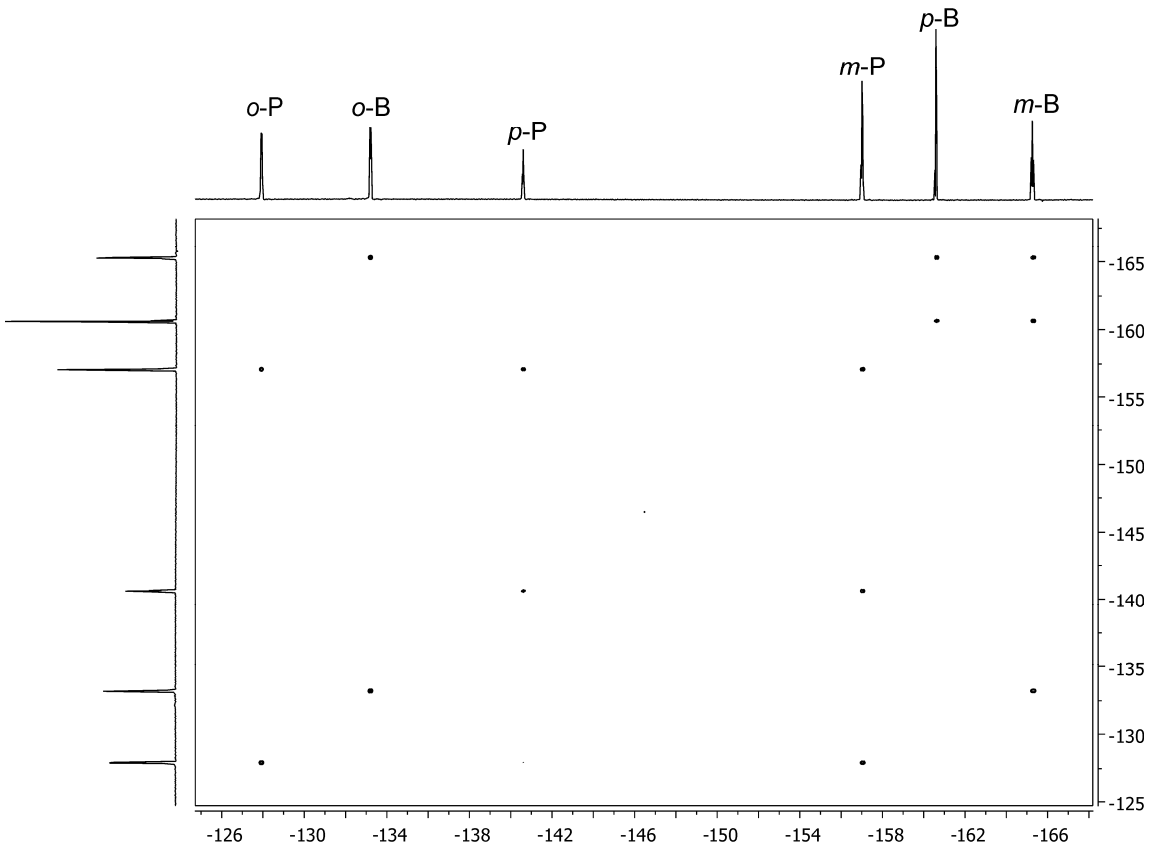
Melting Point: 111 °C.



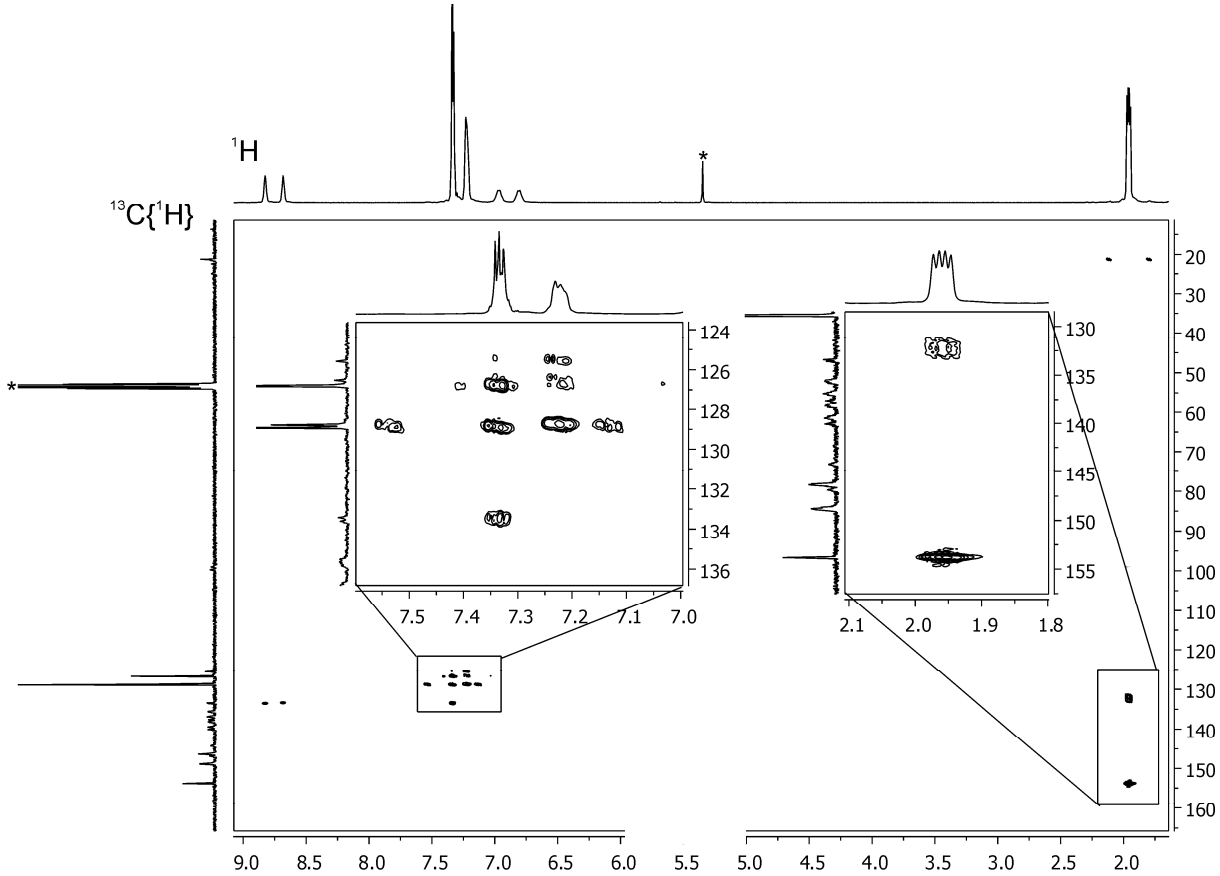
^{1}H NMR (400 MHz, [D$_2$]-dichloromethane*, 296 K), ^{11}B{^{1}H} NMR (160 MHz, [D$_2$]-dichloromethane, 298 K) and ^{31}P{^{1}H} NMR (202 MHz, [D$_2$]-dichloromethane, 298 K) of **15b**.



^{13}C{^{1}H} NMR (101 MHz, [D$_2$]-dichloromethane*, 296 K) of **15b**.

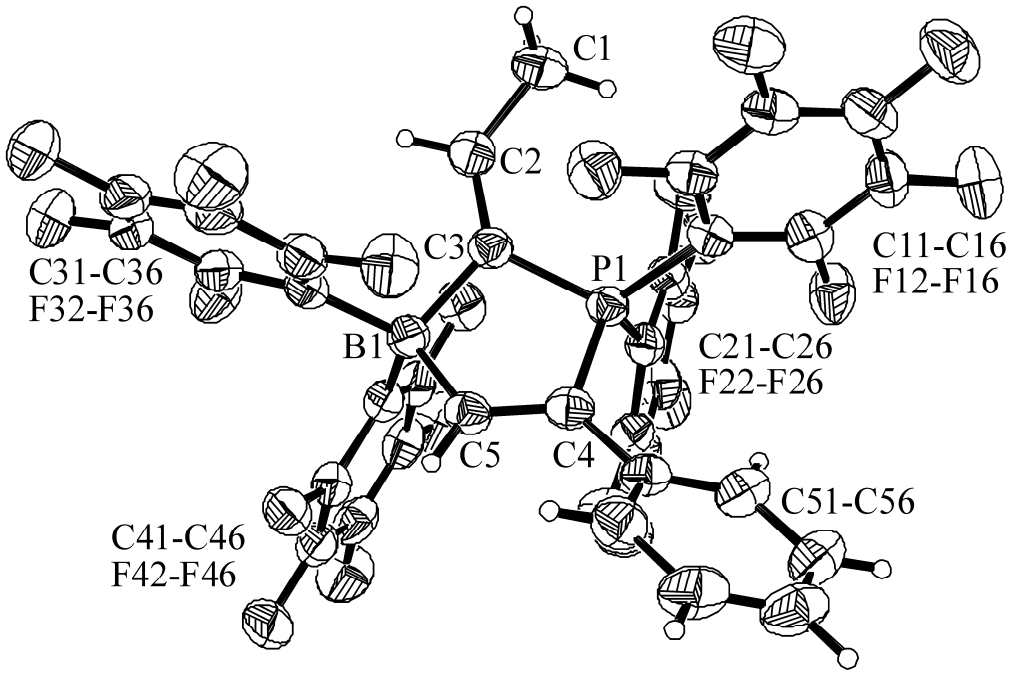


$^{19}F,^{19}F$ GCOSY (470 MHz / 470 MHz, [D_2]-dichloromethane, 298 K) of **15b**.

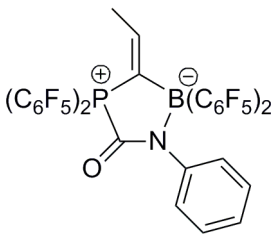


$^{1}H,^{13}C$ GHMBC (400 MHz / 101 MHz, [D_2]-dichloromethane*, 296 K) of **15b**.

X-ray crystal structure analysis of 15b: formula $C_{35}H_{10}BF_{20}P$ * ½ CH_2Cl_2, M = 894.67, colorless crystal 0.35 x 0.20 x 0.10 mm, a = 33.3804(8), b = 40.8995(9), c = 9.9755(4) Å, V = 13619.0(7) Å^3, ρ_{calc} = 1.745 g cm^{-3}, μ = 2.740 cm^{-1}, empirical absorption correction (0.447 ≤ T ≤ 0.771), Z = 16, orthorhombic, space group Fdd2 (No. 43), λ= 1.54178 Å, T = 223 K, ω and φ scans, 14647 reflections collected (±h, -k, -l), [(sinθ)/λ] = 0.60 Å^{-1}, 5675 independent (R_{int} = 0.041) and 5458 observed reflections [$I \geq 2\ \sigma(I)$], 543 refined parameters, R = 0.037, wR^2 = 0.094, Flack parameter 0.47(2), max. residual electron density 0.44 (-0.25) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Preparation of compound 16a.



Mixture **13**/**14** (200 mg, 0.27 mmol, 1 eq) reacted with phenylisocyanate (28.0 mg, 0.27 mmol, 1 eq) to obtain the product **16a** as a white solid (148 mg, 0.17 mmol, 65%).

^{1}H NMR (500 MHz, [D_2]-dichloromethane, 298 K): δ = 2.01 (dd, $^{3}J_{H,H}$ = 7.0 Hz, $^{4}J_{P,H}$ = 3.6 Hz, 3H, CH_3), 7.11 (m, 2H, *o*-Ph), 7.12 (m, 1H, *p*-Ph), 7.16 (dq, $^{3}J_{P,H}$ = 61.3 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 1H, =CH), 7.21 (m, 2H, *m*-Ph).

^{13}C{^{1}H} NMR (126 MHz, [D_2]-dichloromethane, 298 K): δ = 22.7 (br d, $^{4}J_{P,H}$ = 17.9 Hz, CH_3), 125.1 (*o*-Ph), 125.3 (br, =C^{B}), 127.1 (*p*-Ph), 128.9 (*m*-Ph), 140.9 (d, $^{3}J_{P,H}$ = 11.4 Hz, *i*-Ph), 157.3 (=CH), 159.1 (d, $^{1}J_{P,C}$ = 118.8 Hz, C=O) [C_6F_5 not listed].

^{11}B{^{1}H} NMR (192 MHz, [D_2]-dichloromethane, 298 K): δ = −4.7 ($\nu_{1/2}$ ~ 80 Hz).

^{19}F NMR (564 MHz, [D_2]-dichloromethane, 298 K): δ = −164.7 (m, 2F, *m*), −158.1 (m, 1F, *p*), −132.8 (br, 2F, *o*) (BC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 6.6], −155.7 (m, 2F, *m*), −137.4 (m, 1F, *p*), −125.9 (br, 2F, *o*) (PC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 8.3].

^{31}P NMR (243 MHz, [D_2]-dichloromethane, 298 K): δ = −30.1 (dm, $^{3}J_{P,H}$ ~ 61 Hz).

^{31}P{^{1}H} NMR (243 MHz, [D_2]-dichloromethane, 298 K): δ = −30.1 (m, $\nu_{1/2}$ ~ 35 Hz).

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, [D_2]-dichloromethane, 298 K): δ^{1}H / δ^{1}H = 2.01 / 7.16 (CH_3 / $^{=}$CH), 7.11 / 7.21 (*o*-Ph / *m*-Ph), 7.16 / 2.01 ($^{=}$CH / CH_3), 7.21 / 7.11 (*m*-Ph / *o*-Ph).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, [D_2]-dichloromethane, 298 K): δ^{1}H / δ^{13}C = 2.01 / 22.7 (CH_3), 7.11 / 125.1 (*o*-Ph), 7.12 / 127.1 (*p*-Ph), 7.16 / 157.3 (=CH), 7.21 / 128.9 (*m*-Ph).

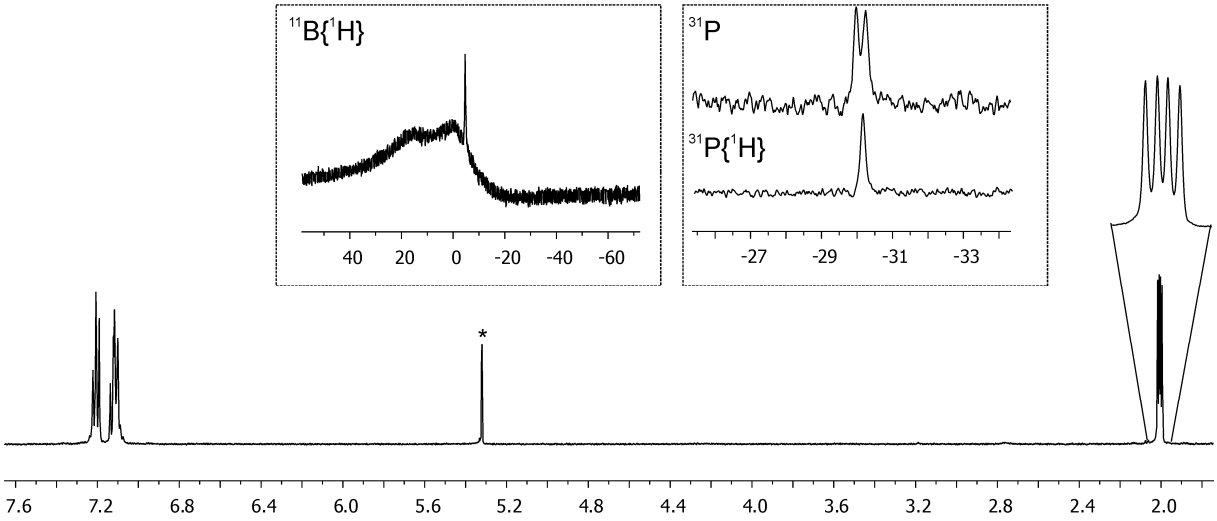
^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, [D_2]-dichloromethane, 298 K): δ^{1}H / δ^{13}C = 2.01 / 157.3 (CH_3 / $^{=}$CH), 7.11 / 127.1 (*o*-Ph / *p*-Ph), 7.12 / 125.1 (*p*-Ph / *o*-Ph), 7.21 / 128.9, 140.9 (*m*-Ph / *m*-Ph, *i*-Ph).

^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, [D_2]-dichloromethane, 298 K): δ^{19}F / δ^{19}F = −164.7 / −132.8, −158.1 (*m* / *o*, *p*), −158.1 / −164.7 (*p* / *m*), −132.8 / −164.7 (*o* / *m*) (BC_6F_5), −155.7 / −125.9, −137.4 (*m* / *o*, *p*), −137.4 / −155.7 (*p* / *m*), −125.9 / −155.7 (*o* / *m*) (PC_6F_5).

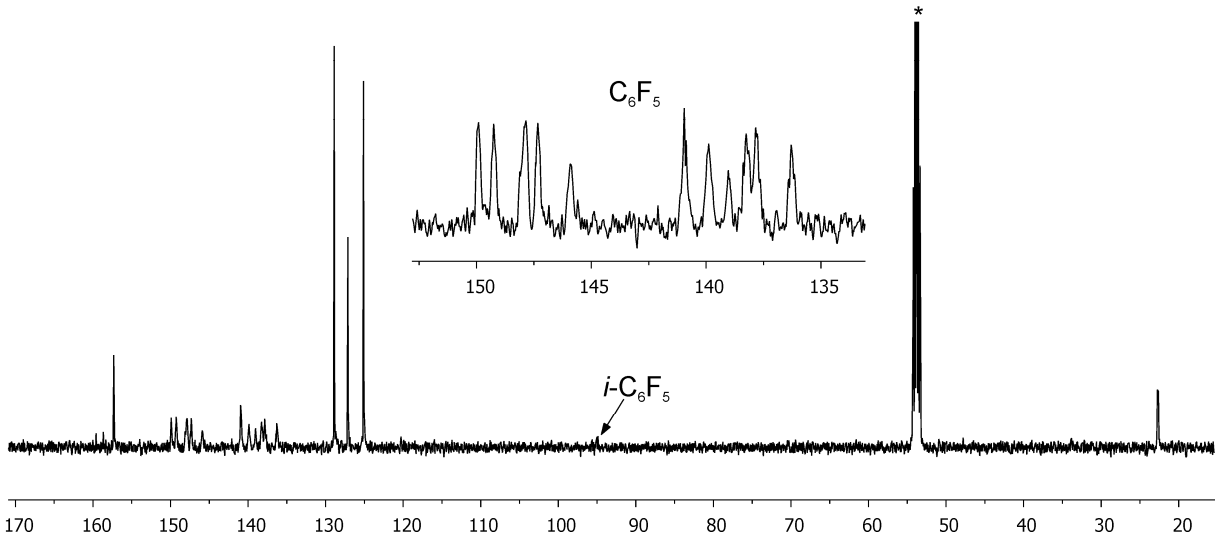
Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 2963 w, 2925 w, 1699 s, 1644 s, 1595 m, 1523 s, 1487 s, 1461 s, 1396 m, 1375 m, 1298 s, 1189 w, 1153 w, 1106 s, 1042 m, 974 s, 843 w, 796 m, 755 m, 709 m, 673 s, 638 w, 607 w, 590 w, 536 m, 519 w, 432 m.

Elemental Analysis: $C_{32}H_{12}BF_{20}P$ (869.2 g/mol) requires C 46.98, H 1.04, N 1.61, found: C 46.87, H 1.22, N 1.54.

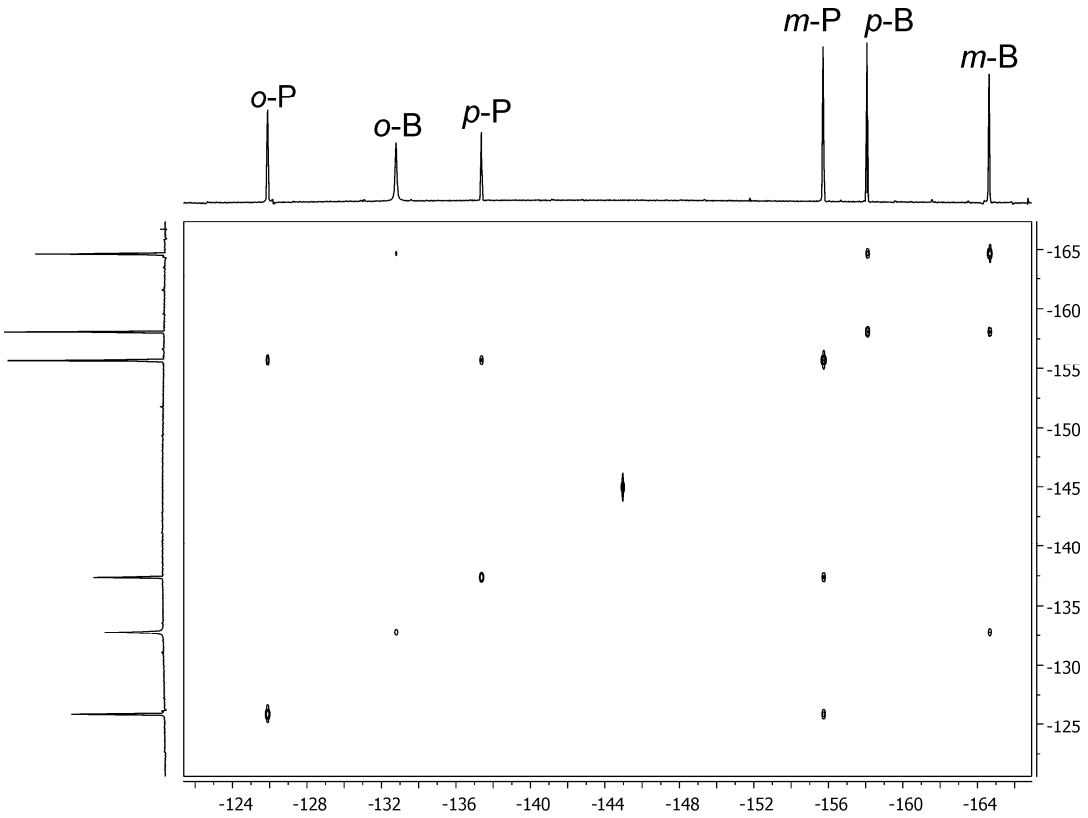
Decomp.: 174 °C.



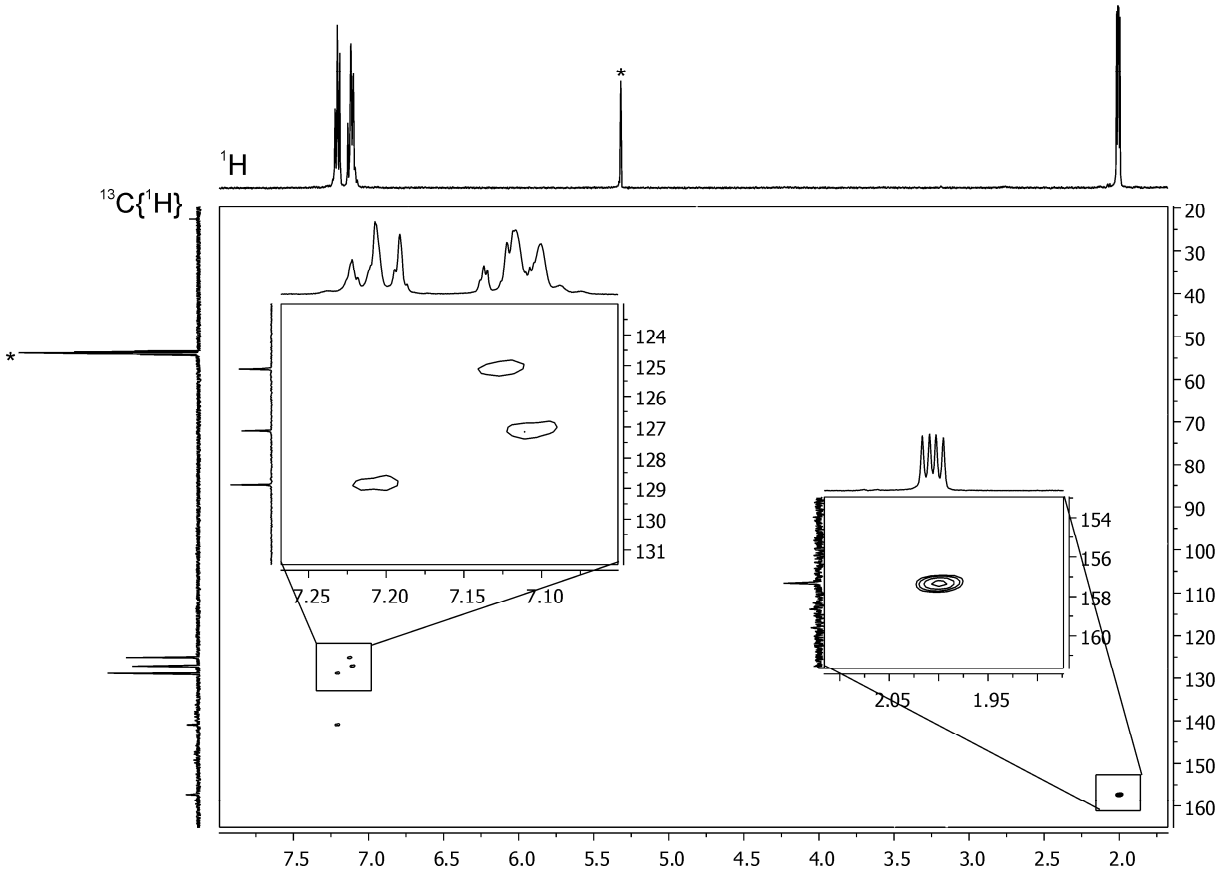
^{1}H NMR (500 MHz, [D_2]-dichloromethane*, 298 K), $^{11}B\{^{1}H\}$NMR (193 MHz, [D_2]-dichloromethane, 298 K), ^{31}P- and $^{31}P\{^{1}H\}$ NMR (243 MHz, [D_2]-dichloromethane, 298 K) of **16a**.



$^{13}C\{^{1}H\}$ NMR (126 MHz, [D_2]-dichloromethane*, 298 K) of **16a**.

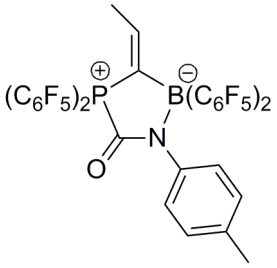


$^{19}F,^{19}F$ GCOSY (470 MHz / 470 MHz, [D_2]-dichloromethane, 298 K) of **16a**.



$^{1}H,^{13}C$ GHMBC (600 MHz / 151 MHz, 298 K, [D_2]-dichloromethane*) of **16a**.

Preparation of compound 16b.



Mixture **13**/**14** (200 mg, 0.27 mmol, 1 eq) reacted with *para*-tolyl-isocyanate (35.0 mg, 0.27 mmol, 1 eq) to yield the product **16b** as a white solid (148 mg, 0.17 mmol, 65%).

^{1}H NMR (500 MHz, [D$_6$]-benzene, 298 K): δ = 1.39 (dd, $^{3}J_{H,H}$ = 6.9, Hz, $^{4}J_{P,H}$ = 3.6 Hz, 3H, CH_3), 1.83 (s, 3H, CH_3^{Tol}), 6.83 (m, 2H, *m*-Tol), 6.87 (dq, $^{3}J_{P,H}$ = 60.6 Hz, $^{3}J_{H,H}$ = 6.9 Hz, 1H, =CH), 7.37 (m, 2H, *o*-Tol).

^{13}C{^{1}H} NMR (126 MHz, [D$_6$]-benzene, 298 K): δ = 20.7 (CH_3^{Tol}), 21.9 (br d, $^{4}J_{P,C}$ = 17.5 Hz, CH_3), 125.1 (*o*-Tol), 126.3 (br, $^{P}C^{B}$)[b], 129.6 (*m*-Tol), 137.2 (*p*-Tol), 138.5 (d, $^{3}J_{P,C}$ = 12.0, Hz, *i*-Tol), 156.4 (m, =CH), 158.7 (d, $^{1}J_{P,C}$ = 115.4 Hz, C=O) [C_6F_5 not listed, [b] from the ghmbc NMR experiment].

^{11}B{^{1}H} NMR (160 MHz, [D$_6$]-benzene, 298 K): δ = −4.5 ($\nu_{1/2}$ ~ 100 Hz).

^{19}F NMR (470 MHz, [D$_6$]-benzene, 298 K): δ = −163.7 (m, 2F, *m*), −156.6 (m, 1F, *p*), −132.2 (br, 2F, *o*) (BC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 7.1], −155.6 (m, 2F, *m*), −136.2 (m, 1F, *p*), −127.0 (br, 2F, *o*) (PC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 19.4].

^{31}P{^{1}H} NMR (202 MHz, [D$_6$]-benzene, 298 K): δ = −32.0 ($\nu_{1/2}$ ~ 30 Hz).

^{1}H,^{1}H GCOSY (500 MHz / 500 MHz [D$_6$]-benzene, 298 K): δ^{1}H / δ^{1}H = 1.39 / 6.87 (CH_3 / =CH), 1.83 / 6.83 (CH_3^{Tol} / *m*-Tol), 6.83 / 1.83, 7.37 (*m*-Tol / CH_3^{Tol}, *o*-Tol), 6.87 / 1.39 (=CH / CH_3), 7.37 / 6.83 (*o*-Tol / *m*-Tol).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, [D$_6$]-benzene, 298 K): δ^{1}H / δ^{13}C = 1.39 / 21.9 (CH_3), 1.83 / 20.7 (CH_3^{Tol}), 6.83 / 129.6 (*m*-Tol), 6.87 / 156.4 (=CH), 7.37 / 125.1 (*o*-Tol).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, [D$_6$]-benzene, 298 K): δ^{1}H / δ^{13}C = 1.39 / 156.4 (CH_3 / =CH), 1.83 / 129.6, 137.2 (CH_3^{Tol} / *m*-Tol, *p*-Tol), 6.83 / 20.7, 138.5 (*m*-Tol / CH_3^{Tol}, *i*-Tol) 7.37 / 137.2 (*o*-Tol / *p*-Tol).

^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, [D$_6$]-benzene, 298 K): δ^{19}F / δ^{19}F = −163.7 / −156.6, −132.2 (*m* / *p*, *o*), −156.6 / −163.7 (*p* / *m*), −132.2 / −163.2 (*o* / *m*) (BC_6F_5), −155.6 / −136.2, −127.0 (*m* / *p*, *o*), −136.2 / −155.6 (*p* / *m*), −127.0 / −155.6 (*o* / *m*) (PC_6F_5).

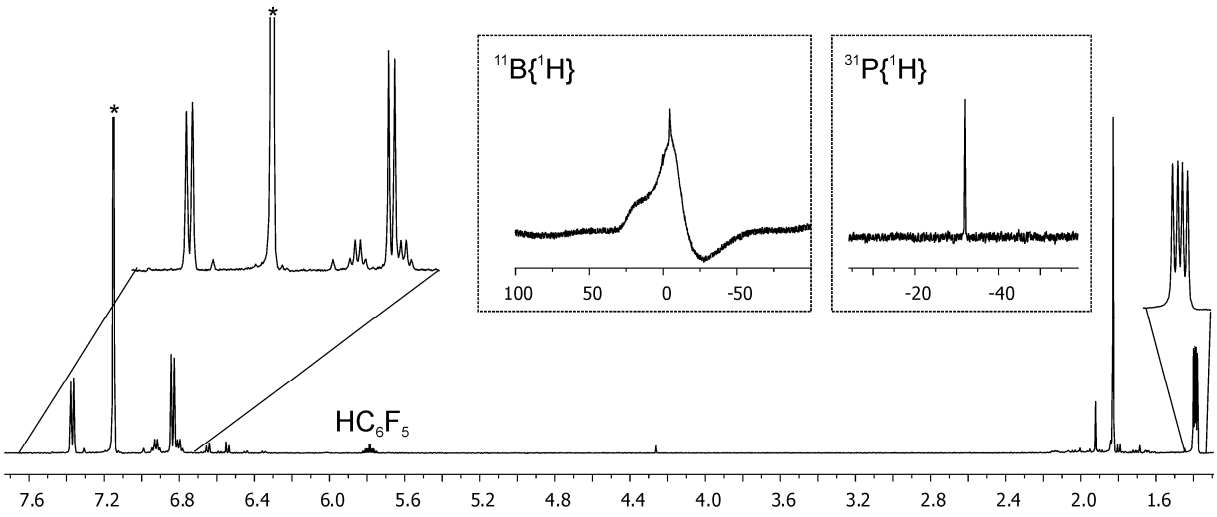
$^{1}H\{^{19}F\}$ NOE (500 MHz, [D$_6$]-benzene, 298 K): $\delta^{19}F_{irr}$ / $\delta^{1}H_{res}$ = −127.0 / 1.39, 7.37 (*o*-P / $^{=}CH_3$, *o*-Tol), −132.1 / 6.87, 7.37 (*o*-B / $^{=}CH$, *o*-Tol).

Elemental Analysis: $C_{35}H_{11}BF_{20}OP$ (883.2 g/mol) requires C 47.60, H 1.26, N 1.59, found: C 47.48, H 0.61, N 1.79.

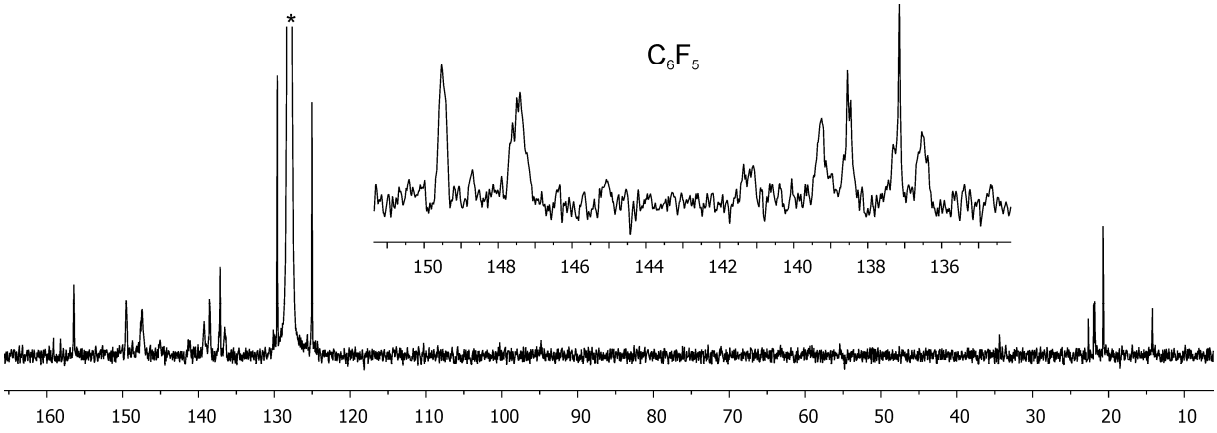
Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3441 m, 1699 m, 1644 m, 1522 s, 1491 s, 1466 s, 1395 w, 1293 m, 1248 w, 1155 w, 1110 s, 1034 w, 976 s, 916 w, 795 m, 745 w, 674 m, 641 w, 543 w, 432 w.

MS-ESI-EM: Calcd. for $(C_{35}H_{11}BF_{20}OP)H$: 884.0436 g/mol found: 884.04350 g/mol.

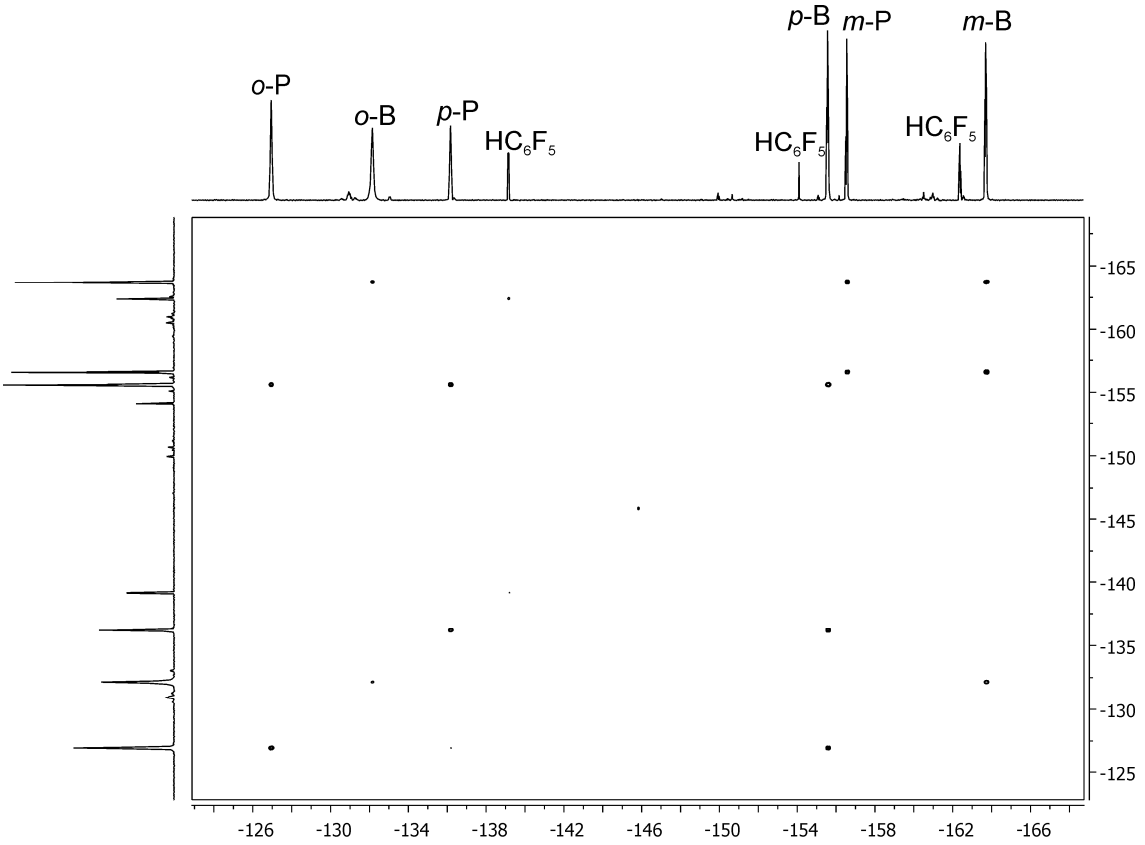
Decomp.: 184 °C.



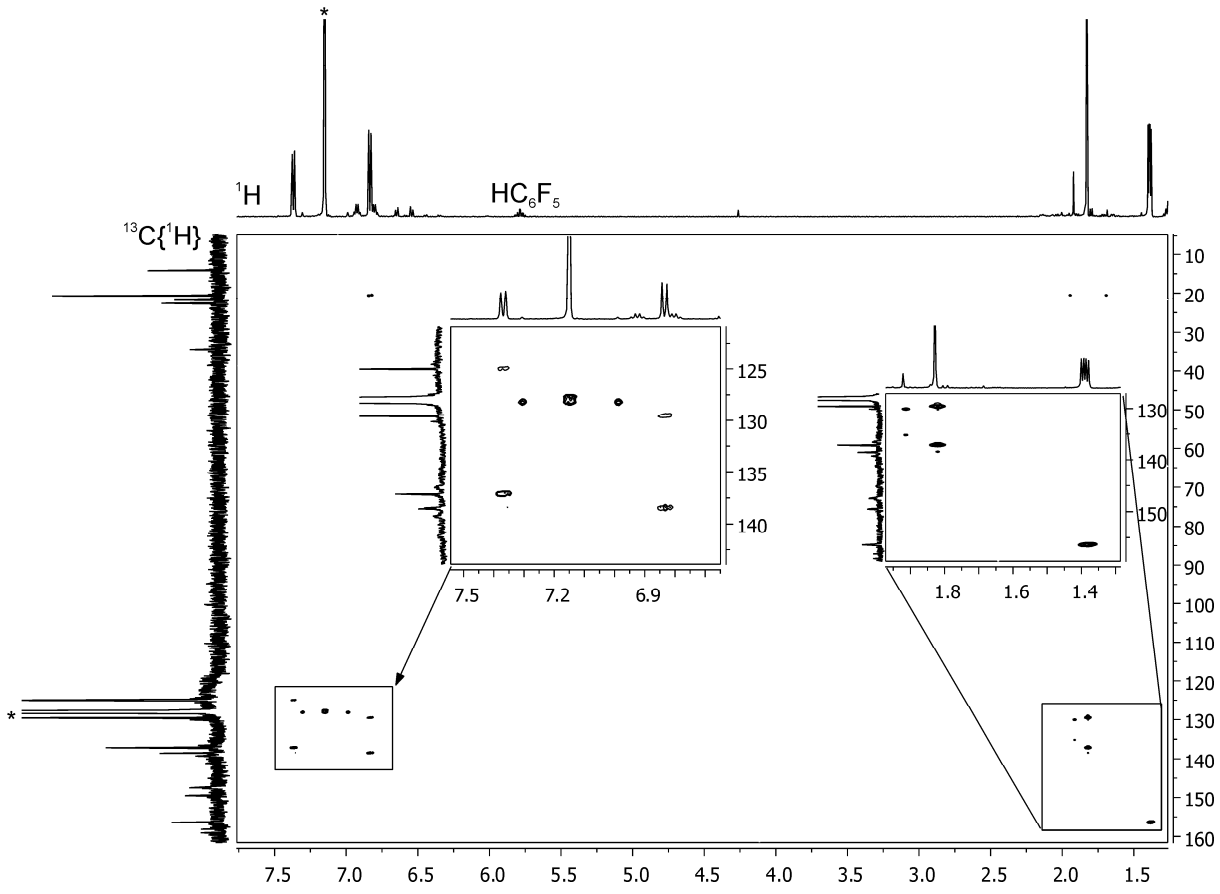
^{1}H NMR (500 MHz, [D$_6$]-benzene*, 298 K), $^{11}B\{^{1}H\}$ NMR (160 MHz, [D$_6$]-benzene, 298 K) and $^{31}P\{^{1}H\}$ NMR (202 MHz, [D$_6$]-benzene, 298 K) of **16b**.



$^{13}C\{^{1}H\}$ NMR (126 MHz, [D$_6$]-benzene*, 298 K) of **42b**.

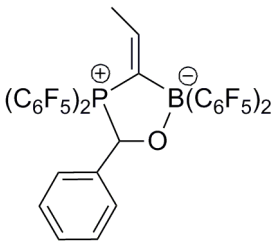


$^{19}F,^{19}F$ GCOSY (470 MHz / 470 MHz, [D_6]-benzene, 298 K) of **16b**.



$^{1}H,^{13}C$ GHMBC (500 MHz / 126 MHz, [D_6]-benzene*, 298 K) of **16b**.

Preparation of compound 17.



Mixture **13**/**14** (200 mg, 0.27 mmol, 1 eq) reacted with benzaldehyde (28.0 mg, 0.27 mmol, 1 eq) to a slightly yellow reaction solution. After 12 h the product **17** was obtained as a white solid (148 mg, 0.172 mmol, 65%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a saturated solution of **17** in [D_2]-dichloromethane at −34 °C.

^{1}H NMR (500 MHz, [D_2]-dichloromethane, 298 K): δ = 1.95 (dd, $^{3}J_{H,H}$ = 7.0 Hz, $^{4}J_{P,H}$ = 3.5 Hz, 3H, CH_3), 6.34 (d, $^{2}J_{P,H}$ = 15.3 Hz, 1H, CH), 7.23 (m, 2H, *o*-Ph), 7.27 (m, 2H, *m*-Ph), 7.28 (dq, $^{3}J_{P,H}$ = 61.5 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 1H, =CH), 7.36 (m, 1H, *p*-Ph).

^{1}H{^{31}P} NMR (500 MHz, [D_2]-dichloromethane, 298 K): δ = 1.95 (d, 3H, $^{3}J_{H,H}$ = 7.0 Hz, CH_3), 6.34 (s, 1H, CH), 7.23 (m, 2H, *o*-Ph), 7.27 (m, 2H, *m*-Ph), n.o. (=CH), 7.36 (m, 1H, *p*-Ph).

^{13}C{^{1}H} NMR (151 MHz, [D_2]-dichloromethane, 298 K): δ = 22.9 (br d, $^{3}J_{P,C}$ = 15.0 Hz, CH_3), 85.5 (br d, $^{1}J_{P,C}$ = 40.9 Hz, CH), 126.7 (d, $^{3}J_{P,C}$ = 5.7 Hz, *o*-Ph), 129.0 (d, *J* = 4.0 Hz, *m*-Ph), 130.4 (d, *J* = 4.8 Hz, *p*-Ph), 133.6 (d, $^{2}J_{P,C}$ = 3.6 Hz, *i*-Ph), 133.8 (br, $^{P}C^{B}$)^{b}, 158.0 (br, =CH) [C_6F_5 not listed, ^{b} from the ghmbc NMR experiment].

^{11}B{^{1}H} NMR (160 MHz, [D_2]-dichloromethane, 298 K): δ = 0.7 ($\nu_{1/2}$ ~ 80 Hz).

^{19}F NMR (470 MHz, [D_2]-dichloromethane, 298 K): δ = −165.4 (m, 2F, *m*), −160.4 (m, 1F, *p*), −135.1 (m, 2F, *o*) ($BC_6F_5^{A}$) [$\Delta\delta^{19}F_{mp}$ = 5.0], −165.4 (m, 2F, *m*), −159.4 (m, 1F, *p*), −132.5 (m, 2F, *o*) ($BC_6F_5^{B}$) [$\Delta\delta^{19}F_{mp}$ = 6.0], −158.2 (m, 2F, *m*), −139.6 (m, 1F, *p*), −126.6 (m, 2F, *o*), ($PC_6F_5^{A}$) [$\Delta\delta^{19}F_{mp}$ = 18.6], −155.4 (m, 2F, *m*), −139.4 (m, 1F, *p*), −124.6 (m, 2F, *o*) ($PC_6F_5^{A}$) [$\Delta\delta^{19}F_{mp}$ = 16.0].

^{19}F NMR (470 MHz, [D_2]-dichloromethane, 283 K): δ = −165.2 (m, 2F, *m*), −160.4 (m, 1F, *p*), −135.1 (m, 2F, *o*) ($BC_6F_5^{A}$) [$\Delta\delta^{19}F_{mp}$ = 4.8], −165.2 (m, 2F, *m*), −159.3 (m, 1F, *p*), −132.5 (m, 2F, *o*) ($BC_6F_5^{B}$) [$\Delta\delta^{19}F_{mp}$ = 5.9], −158.1 (m, 2F, *m*), −139.4 (m, 1F, *p*), −126.8 (m, 2F, *o*) ($PC_6F_5^{A}$) [$\Delta\delta^{19}F_{mp}$ = 18.7], −155.3 (m, 2F, *m*), −139.2 (m, 1F, *p*), −124.6 (m, 2F, *o*) ($PC_6F_5^{B}$) [$\Delta\delta^{19}F_{mp}$ = 15.1].

^{31}P NMR (202 MHz, [D_2]-dichloromethane, 298 K): δ = −5.5 (dm, $^{3}J_{P,H}$ ~ 62 Hz).

$^{31}P\{^{1}H\}$ NMR (202 MHz, [D_2]-dichloromethane, 298 K): $\delta = -5.5$ ($\nu_{1/2} \sim 60$ Hz).

$^{1}H,^{1}H$ GCOSY (500 MHz / 500 MHz, [D_2]-dichloromethane, 298 K): $\delta^{1}H$ / $\delta^{1}H$ = 1.95 / 7.28 (CH_3 / =CH), 7.27 / 7.36 (*m*-Ph / *p*-Ph), 7.28 / 1.95 (=CH / CH_3), 7.36 / 7.27 (*p*-Ph / *m*-Ph).

$^{1}H,^{13}C$ GHSQC (600 MHz / 151 MHz, [D_2]-dichloromethane, 298 K): $\delta^{1}H$ / $\delta^{13}C$ = 1.95 / 22.9 (CH_3), 6.34 / 85.5 (CH), 7.23 / 126.7 (*o*-Ph), 7.27 / 129.0 (*m*-Ph), 7.28 / 158.0 (=CH), 7.36 / 130.4 (*p*-Ph).

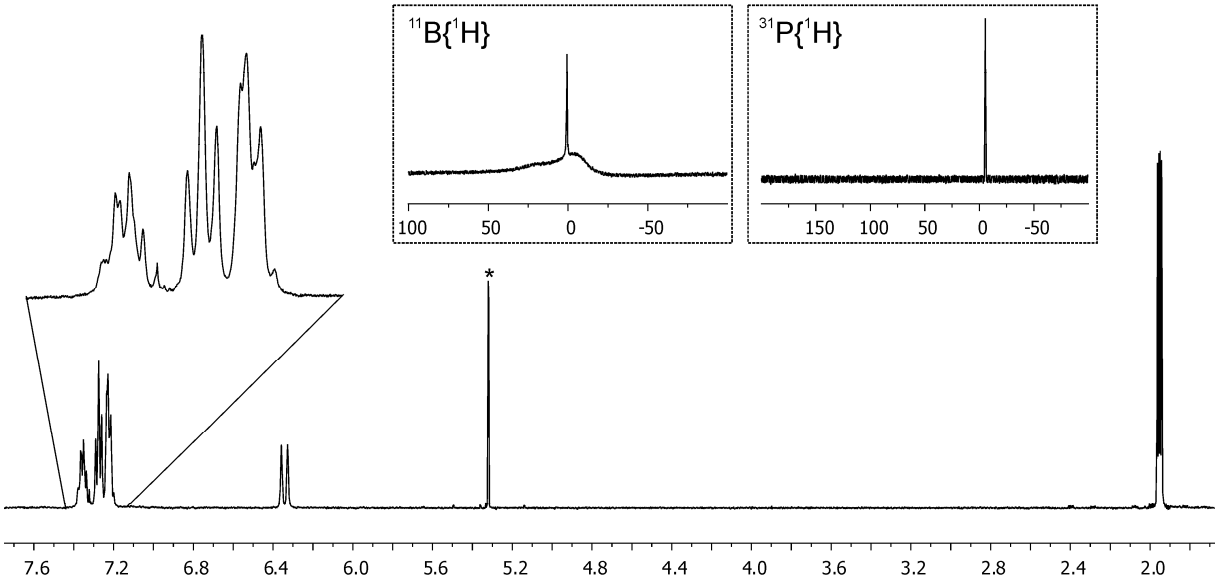
$^{1}H,^{13}C$ GHMBC (600 MHz / 151 MHz, [D_2]-dichloromethane, 298 K): $\delta^{1}H$ / $\delta^{13}C$ = 1.95 / 22.9, 158.0 (CH_3 / CH_3, =CH), 6.34 / 126.7, 133.8 (CH / *o*-Ph, *i*-Ph), 7.23 / 126.7, 130.4 (*o*-Ph / *o*-Ph, *p*-Ph), 7.27 / 129.0, 133.8 (*m*-Ph / *m*-Ph, *i*-Ph), 7.36 / 126.7 (*p*-Ph / *o*-Ph).

$^{19}F,^{19}F$ GCOSY (470 MHz / 470 MHz, [D_2]-dichloromethane, 283 K): $\delta^{19}F$ / $\delta^{19}F$ = −165.2 / −160.4, −135.1 (*m* / *p*, *o*), −159.3 / −165.2 (*p* / *m*), −132.5 / −165.2 (*o* / *m*) ($BC_6F_5^{A}$), −165.2 / −159.3, −132.5 (*m* / *p*, *o*), −160.4 / −165.2 (*p* / *m*), −135.1 / −165.2 (*o* / *m*) ($BC_6F_5^{B}$), −158.1 / −139.4, −126.8 (*m* / *p*, *o*), −139.4 / −158.1 (*p* / *m*), −126.8 / −158.1 (*o* / *m*) ($PC_6F_5^{A}$), −155.3 / −139.2, −124.6 (*m* / *p*, *o*), −139.2 / −155.3 (*p* / *m*), −124.6 / −155.3 (*o* / *m*) ($PC_6F_5^{B}$).

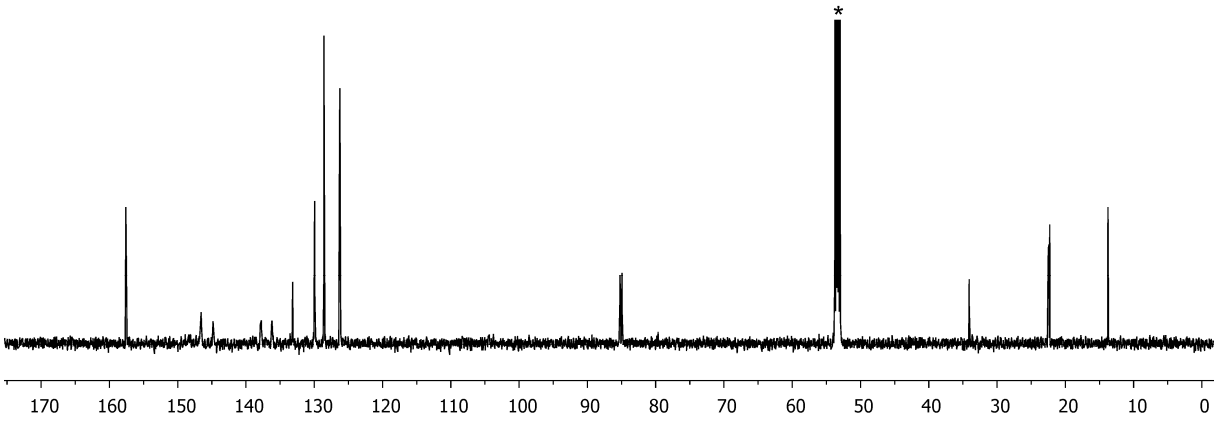
Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 3430 w, 2963 w, 2924 w, 2861 w, 1644 s, 1523 s, 1486 s, 1465 s, 1394 m, 1304 m, 1281 m, 1227 w, 1152 w, 1105 s, 978 s, 931 m, 909 m, 819 m, 769 w, 744 w, 700 s, 671 w, 652 m, 623 w, 577 w, 519 w, 456 w, 413 w.

Elemental Analysis: $C_{35}H_{10}BF_{20}P$ (856.2 g/mol) requires C 47.70, H 1.18, found: C 47.98, H 1.39.

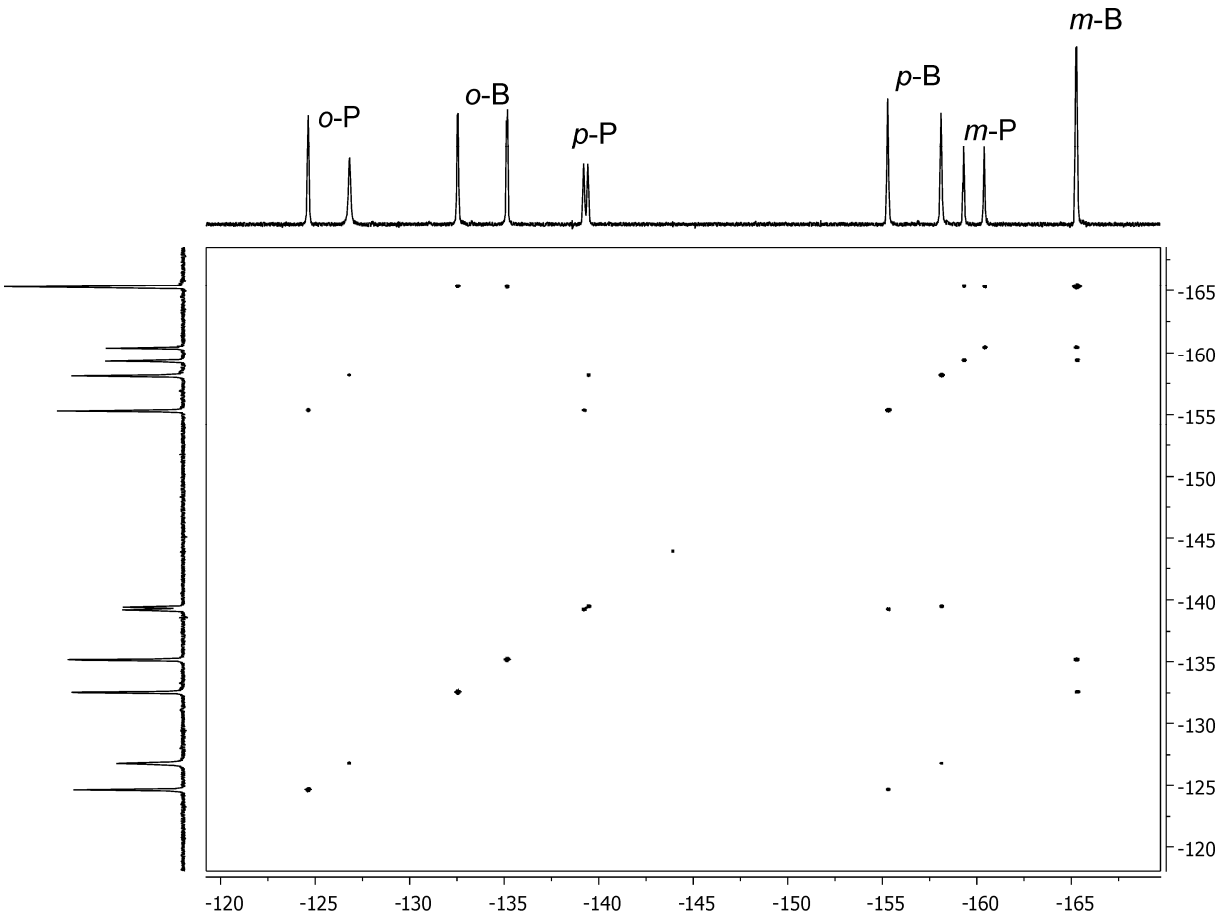
Melting Point: 95 °C.



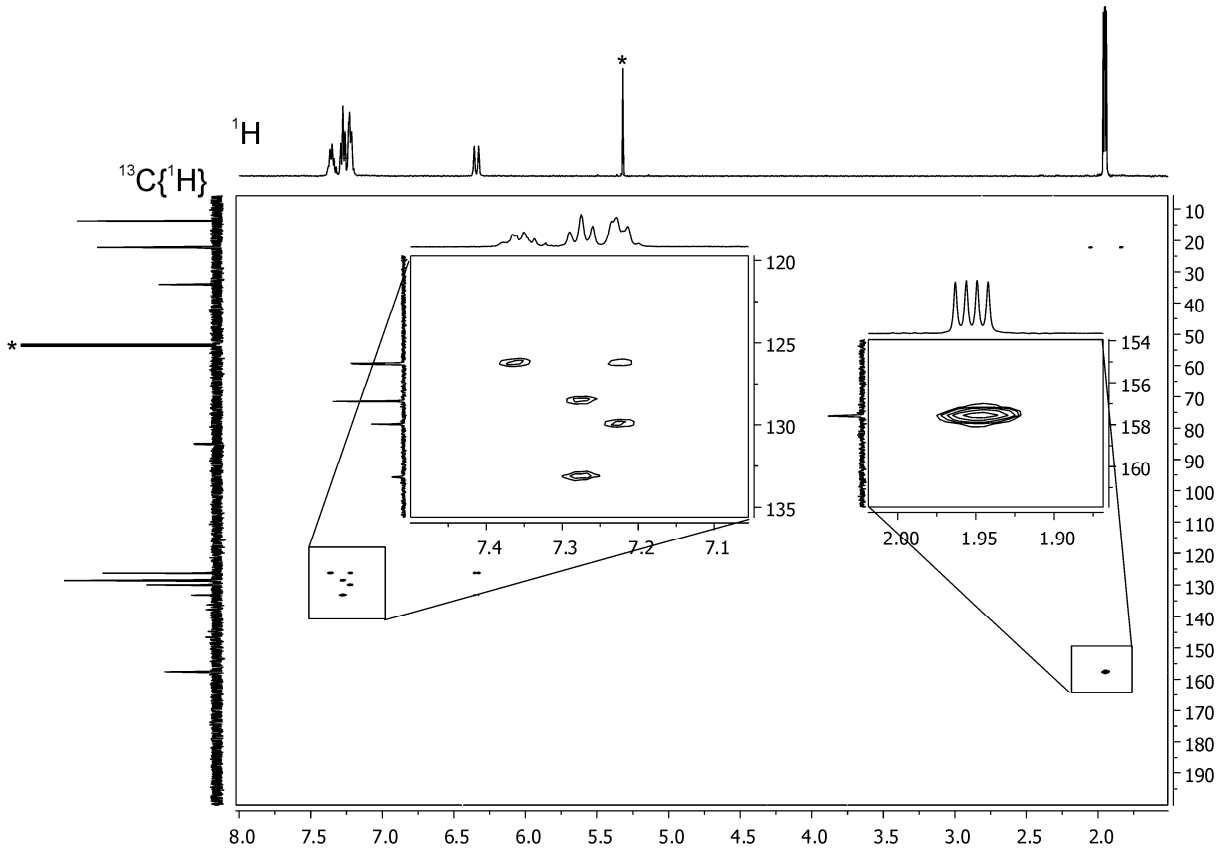
^{1}H NMR (500 MHz, [D$_2$]-dichloromethane*, 298 K), ^{11}B{^{1}H} NMR (160 MHz, [D$_2$]-dichloromethane, 298 K) and ^{31}P{^{1}H} NMR (202 MHz, [D$_2$]-dichloromethane, 298 K) of **17**.



^{3}C{^{1}H} NMR (151 MHz, [D$_2$]-dichloromethane*, 298 K) of **17**.



$^{19}F,^{19}F$ GCOSY (470 MHz / 470 MHz, [D_2]-dichloromethane, 283 K) of **17**.



$^{1}H,^{13}C$ GHMBC (600 MHz / 151 MHz, [D_2]-dichloromethane*, 298 K) of **17**.

Dynamic ^{19}F NMR:

$\Delta G^{\neq} = RT_c(22.96 + \ln(T_c/\delta\nu)$ [Jmol^{-1}]

R = 8.314 J(mol K)$^{-1}$

1 cal = 4.187 J

$\Delta G^{\neq}_{diss}$ (T_c = 333 K; $\Delta\nu$(*o*-P, 298 K) = 920 Hz) = 14.5 kcal/mol

$\Delta G^{\neq}_{diss}$ (T_c = 333 K; $\Delta\nu$(*o*-B, 298 K) = 1200 Hz) = 14.3 kcal/mol
$\Delta G^{\neq}_{diss}$ (T_c = 343 K; $\Delta\nu$(*o*-B, 298 K) = 1200 Hz) = 14.8 kcal/mol
average value: $\Delta G^{\neq}_{diss}$(*o*-B) = 14.6 ± 0.3 kcal/mol

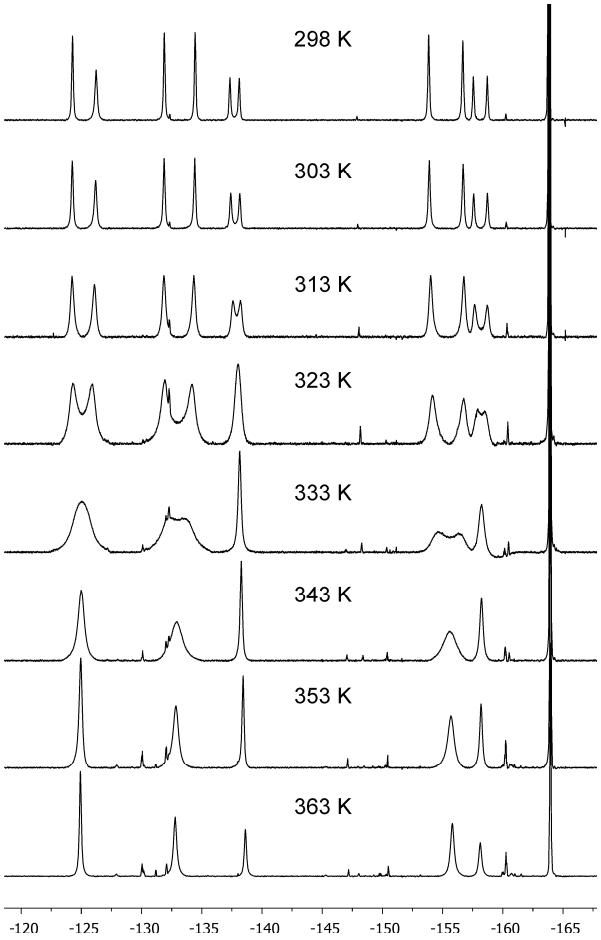
$\Delta G^{\neq}_{diss}$(T_c= 333 K; $\Delta\nu$(*m*-P, 298 K) = 1330 Hz) = 14.3 kcal/mol
$\Delta G^{\neq}_{diss}$(T_c= 343 K; $\Delta\nu$(*m*-P, 298 K) = 1330 Hz) = 14.7 kcal/mol
average value: $\Delta G^{\neq}_{diss}$(*m*-P) = 14.5 ± 0.2 kcal/mol

$\Delta G^{\neq}_{diss}$(T_c= 313 K; $\Delta\nu$(*p*-P, 298 K) = 360 Hz) = 14.2 kcal/mol
$\Delta G^{\neq}_{diss}$(T_c= 323 K; $\Delta\nu$(*p*-P, 298 K) = 360 Hz) = 14.7 kcal/mol
average value: $\Delta G^{\neq}_{diss}$(*p*-P) = 14.5 ± 0.3 kcal/mol

$\Delta G^{\neq}_{diss}$(T_c= 323 K; $\Delta\nu$(*p*-B, 298 K) = 540 Hz) = 14.4 kcal/mol
$\Delta G^{\neq}_{diss}$(T_c= 333 K; $\Delta\nu$(*p*-B, 298 K) = 540 Hz) = 14.9 kcal/mol
average value: $\Delta G^{\neq}_{diss}$(*p*-B) = 14.7 ± 0.3 kcal/mol

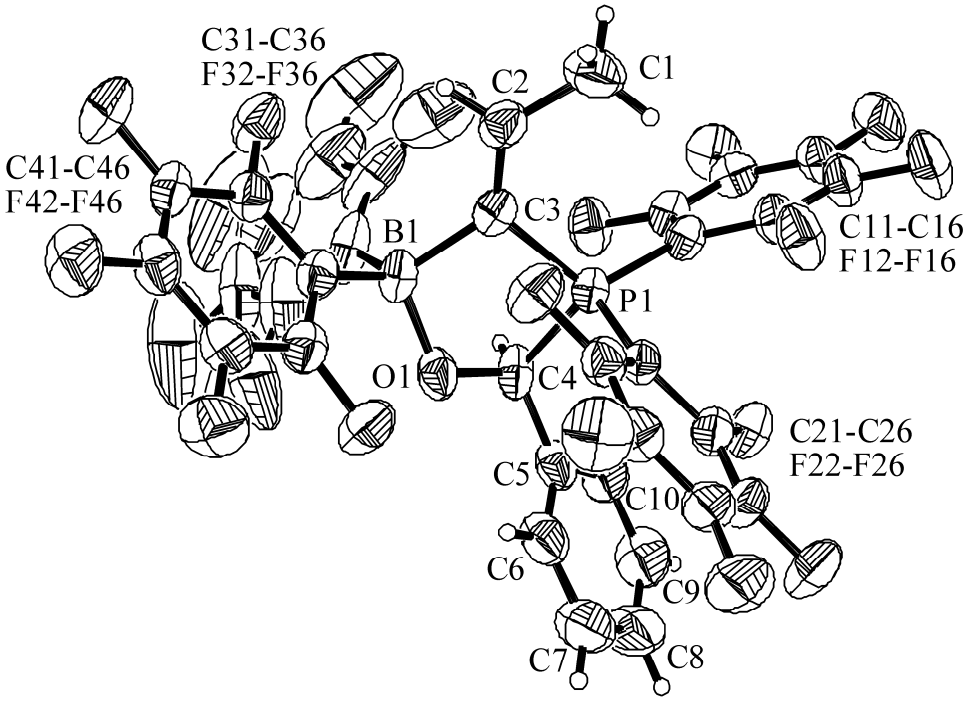
average value:

$\Delta G^{\neq}_{diss}$ = 14.6 ± 0.3 kcal/mol

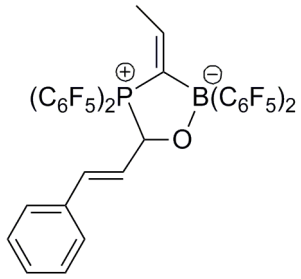


^{19}F NMR (470 MHz, [D_2]-tetrachloro-ethane) of **18**.

X-ray crystal structure analysis of 17: formula $C_{34}H_{10}BF_{20}OP$, M = 856.20, colorless crystal 0.25 x 0.15 x 0.05 mm, a = 10.6020(3), b = 17.5414(6), c = 18.9734(6) Å, β = 90.290(2)°, V = 3528.5(2) Å^3, ρ_{calc} = 1.612 g cm^{-3}, μ = 1.955 cm^{-1}, empirical absorption correction (0.641 ≤ T ≤ 0.909), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ= 1.54178 Å, T = 223 K, ω and φ scans, 19821 reflections collected (±h, -k, -l), [(sinθ)/λ] = 0.60 Å^{-1}, 5790 independent (R_{int} = 0.068) and 4198 observed reflections [$I \geq 2\,\sigma(I)$], 515 refined parameters, R = 0.085, wR^2 = 0.259, solvent molecules couldn't be identified, therefore the SQUEEZE routine was used, group C31 – C36 refined with thermal restraints (ISOR), max. residual electron density 0.85 (-0.72) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Preparation of compound 18.



Mixture **13**/**14** (100 mg, 0.13 mmol, 1 eq) reacted with cinnamic aldehyde (17.5 mg, 0.13 mmol, 1 eq) to a bright yellow reaction solution. The product **18** was obtained as a white solid (85 mg, 0.098 mmol, 74%). Crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a saturated solution of **18** in [D_2]-dichloromethane at −34 °C.

^{1}H NMR (400 MHz, [D_2]-dichloromethane, 295 K): δ = 1.96 (dd, $^{3}J_{H,H}$ = 7.0 Hz, $^{4}J_{P,H}$ = 3.5 Hz, 3H, CH_3), 5.91 (br d, $^{3}J_{H,H}$ = 7.1 Hz, CH), 6.29 (br d, $^{3}J_{H,H}$ = 15.8 Hz, 1H, $=CH^{Ph}$), 6.91 (dd, $^{3}J_{H,H}$ = 15.8 Hz, $^{3}J_{H,H}$ = 7.5 Hz, 1H, $=CH^{CH}$), 7.26 (dq, $^{3}J_{P,H}$ = 63.3 Hz, $^{3}J_{H,H}$ = 7.0 Hz, 1H, =CH), 7.30 (m, 2H, *m*-Ph), 7.32 (m, 3H, *o*-, *p*-Ph).

^{13}C{^{1}H} NMR (101 MHz, [D_2]-dichloromethane, 295 K): δ = 23.1 (br d, $^{3}J_{P,C}$ = 15.7 Hz, CH_3), 84.0 (br d, $^{1}J_{P,C}$ = 43.5 Hz, CH), 120.2 (m, $=CH^{Ph}$), 127.0 (br, *m*-Ph), 129.15 (*o*-Ph), 129.24 (*p*-Ph), 133.7 (br, $^{P}C^{B}$)[b], 135.5 (m, *i*-Ph), 136.1 (m, $=CH^{CH}$)[a], 158.1 (=CH) [C_6F_5 not listed, [a] from the ghsqc NMR experiment, [b] from the ghmbc NMR experiment].

^{11}B NMR (96 MHz, [D_2]-dichloromethane, 296 K): δ = 0.9 (s, $\nu_{1/2}$ ~ 100 Hz).

^{19}F NMR (470 MHz, [D_2]-dichloromethane, 298 K): δ = −165.3 (m, 2F, *m*), −159.8 (br, 1F, *p*), −133.8 (br, 2F, *o*) (BC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 5.5], −156.6 (br, 2F, *m*), −139.3 (br, 1F, *p*), −125.9 (br, 2F, *o*) (PC_6F_5) [$\Delta\delta^{19}F_{mp}$ = 17.3].

^{19}F NMR (470 MHz, [D_2]-dichloromethane, 233 K): δ = −164.9 (m, 2F, *m*), −160.0 (m, 1F, *p*), −135.1 (m, 2F, *o*) ($BC_6F_5^{A}$) [$\Delta\delta^{19}F_{mp}$ = 5.5], −164.9 (m, 2F, *m*), −159.0 (m, 1F, *p*), −132.7 (m, 2F, *o*) ($BC_6F_5^{B}$) [$\Delta\delta^{19}F_{mp}$ = 5.9], −157.4 (m, 2F, *m*), −138.8 (m, 1F, *p*), −126.9 (m, 2F, *o*) ($PC_6F_5^{A}$) [$\Delta\delta^{19}F_{mp}$ = 18.6], −155.4 (m, 2F, *m*), −138.6 (m, 1F, *p*), −125.0 (m, 2F, *o*) ($PC_6F_5^{B}$) [$\Delta\delta^{19}F_{mp}$ = 16.6].

^{31}P{^{1}H} NMR (243 MHz, [D_2]-dichloromethane, 296 K): δ = −6.9 (br, $\nu_{1/2}$ ~ 70 Hz).

^{1}H,^{1}H GCOSY (400 MHz / 400 MHz, [D_2]-dichloromethane, 295 K): δ^{1}H / δ^{1}H = 1.96 / 7.26 (CH_3 / =CH), 5.91 / 6.29 (CH / $=CH^{Ph}$), 6.29 / 5.91, 6.91 ($=CH^{Ph}$ / CH, $=CH^{CH}$), 6.91 / 6.29 ($=CH^{CH}$ / $=CH^{Ph}$), 7.26 / 1.96 (=CH / CH_3).

^{1}H,^{13}C GHSQC (400 MHz / 101 MHz, [D$_2$]-dichloromethane, 295 K): δ^{1}H / δ^{13}C = 1.96 / 23.1 (CH_3), 5.91 / 84.0 (CH), 6.29 / 120.2 (=CH^{Ph}), 6.91 / 136.1 (=CH^{CH}), 7.26 / 158.1 (=CH), 7.30 / 127.0 (*m*-Ph), 7.32 / 129.15, 129.24 (*o*- or *p*-Ph).

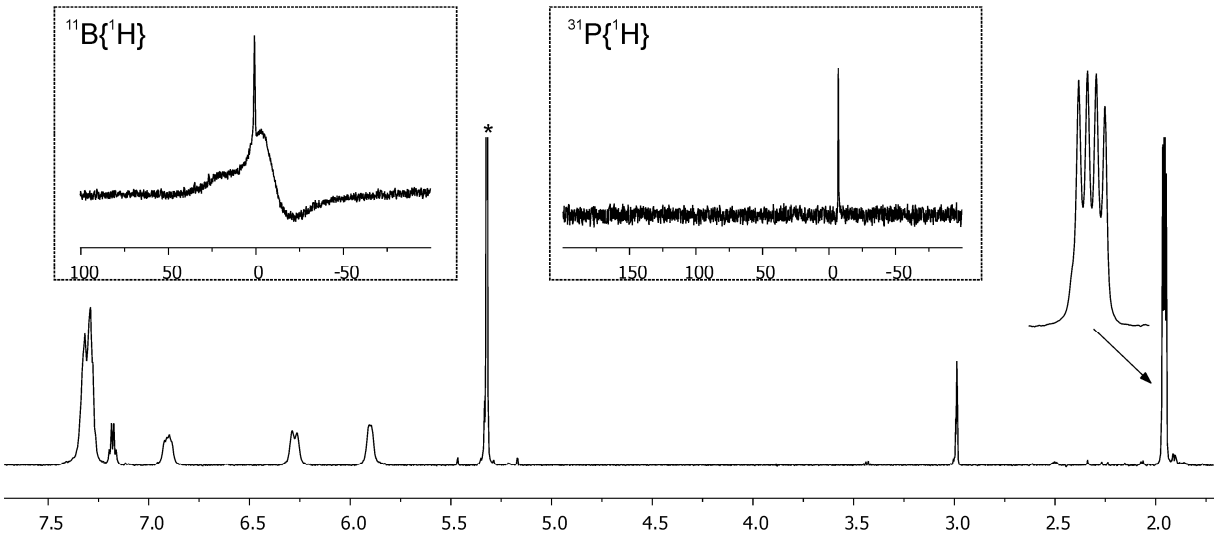
^{1}H,^{13}C GHMBC (400 MHz / 101 MHz, [D$_2$]-dichloromethane, 296 K): δ^{1}H / δ^{13}C = 1.96 / 23.1, 158.1 (CH_3 / CH_3, =CH), 7.26 / 23.1 (=CH / CH_3), 7.30 / 129.15, 129.24 (*m*-Ph / *o*-, *p*-Ph), 7.32 / 127.2, 135.5 (*o*- or *p*-Ph / *m*-Ph, *i*-Ph).

^{19}F,^{19}F GCOSY (470 MHz / 470 MHz, [D$_2$]-dichloromethane, 233 K): δ^{19}F / δ^{19}F = −164.9 / −160.0, −135.1 (*m* / *p*, *o*), −160.0 / −164.9 (*p* / *m*), −135.1 / −164.9 (*o* / *m*) ($BC_6F_5^A$), −164.9 / −159.0, −132.7 (*m* / *p*, *o*), −159.0 / −164.9 (*p* / *m*), −132.7 / −164.9 (*o* / *m*) ($BC_6F_5^B$), −157.4 / −138.8, −126.9 (*m* / *p*, *o*), −138.8 / −157.4 (*p* / *m*), −126.9 / −157.4 (*o* / *m*) ($PC_6F_5^A$), −155.4 / −138.6, −125.0 (*m* / *p*, *o*), −138.6 / −155.4 (*p* / *m*), −125.0 / −155.4 (*o* / *m*) ($PC_6F_5^B$).

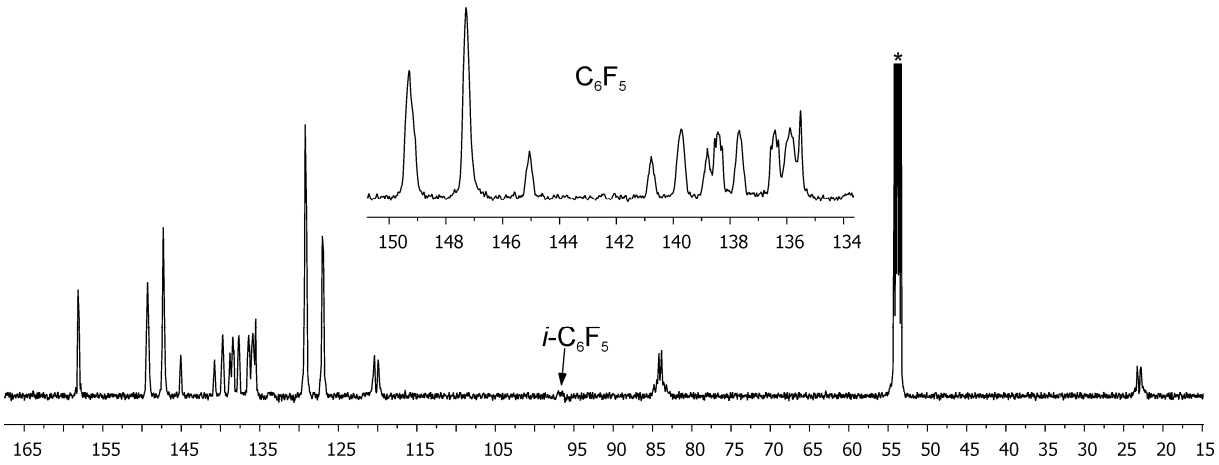
Infrared Spectroscopy $\tilde{\nu}$ (KBr) / cm^{-1} = 1700 w, 1646 m, 1559 m, 1522 s, 1484 s, 1464 s, 1385 m, 1304 m, 1282 m, 1246 w, 1105 s, 1105 s, 981 m, 818 w, 753 w, 683 w, 637 w.

Elemental Analysis: $C_{36}H_{12}BF_{20}OP$ (864.2 g/mol) requires C 49.01, H 1.37, found: C 49.17, H 1.49.

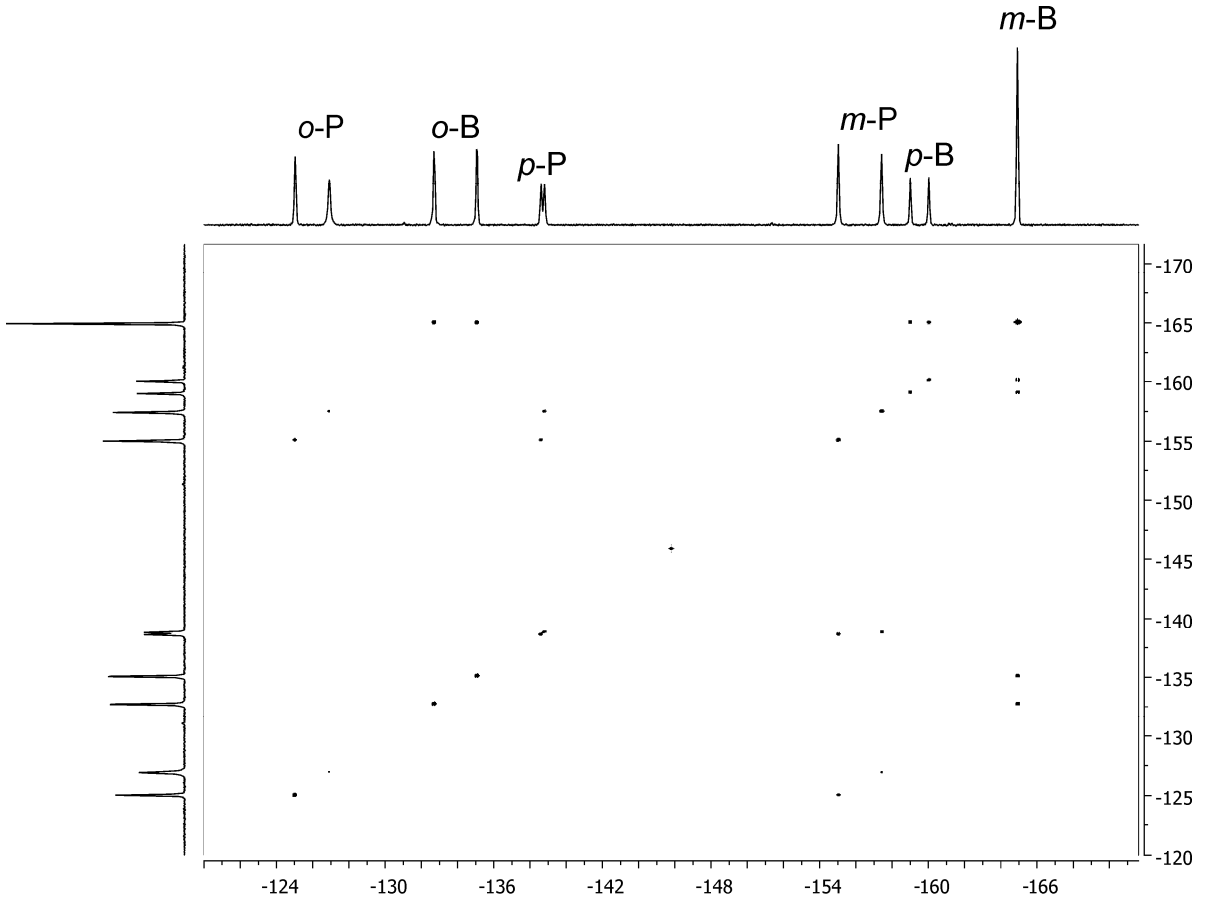
Decomp.: 140 °C.



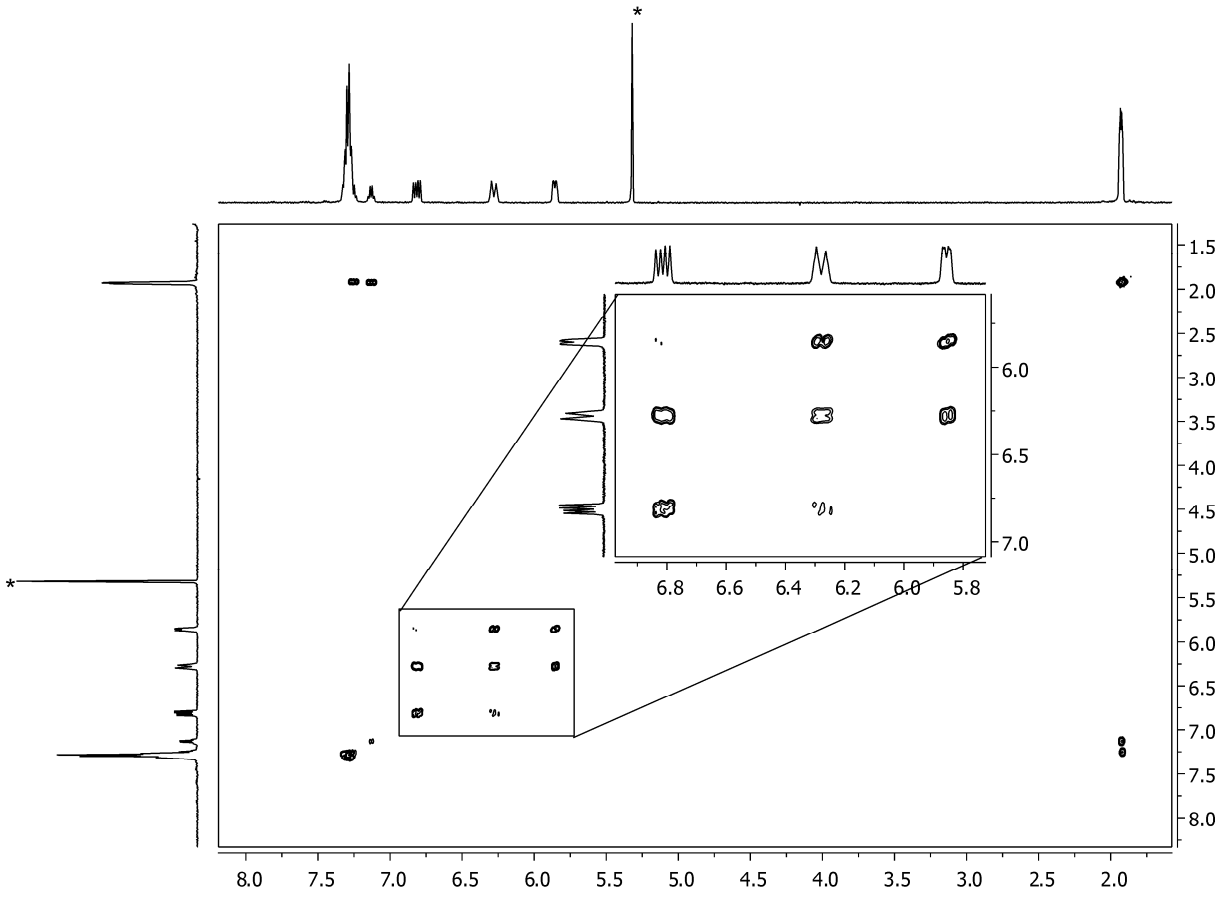
^{1}H NMR (400 MHz, [D$_2$]-dichloromethane*, 295 K), ^{11}B{^{1}H} NMR (96 MHz, [D$_2$]-dichloromethane, 296 K) and ^{31}P{^{1}H} NMR (298 MHz, [D$_2$]-dichloromethane, 296 K) of **18**.



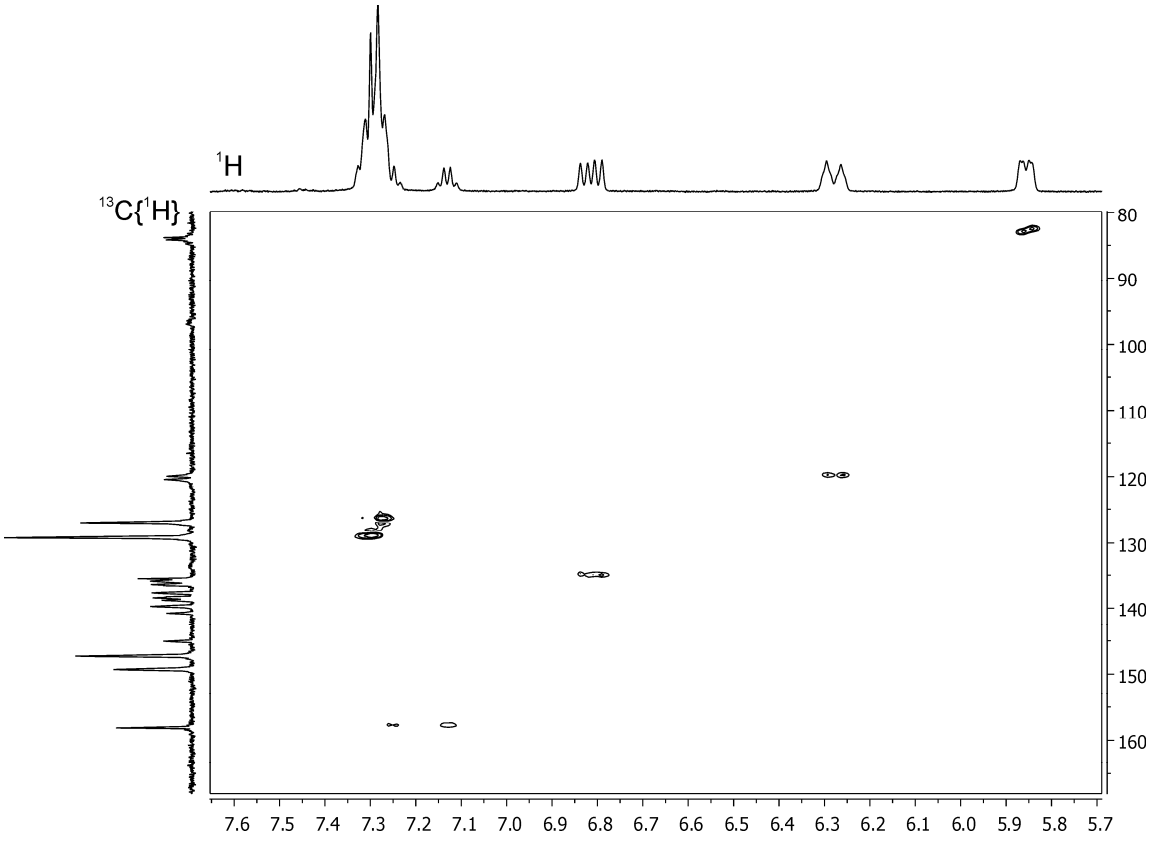
$^{13}C\{^{1}H\}$ NMR (101 MHz, [D_2]-dichloromethane*, 295 K) of **18**.



$^{19}F,^{19}F$ GCOSY (470 MHz / 470 MHz, [D_2]-dichloromethane, 233 K) of **18**.



^{1}H,^{1}H GCOSY (500 MHz / 500 MHz, [D_2]-dichloromethane*, 243 K) of **18**.



^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, [D_6]-benzene*, 243 K) of **18**.

Dynamic ^{19}F NMR:

$\Delta G^{\neq} = RT_c(22.96 + \ln(T_c/\delta\nu)$ [Jmol^{-1}]

R = 8.314 J(mol K)$^{-1}$

1 cal = 4.187 J

$\Delta G^{\neq}_{diss}$ (T_c = 273 K; $\Delta\nu$(*o*-P, 223 K) = 900 Hz) = 11.8 kcal/mol

$\Delta G^{\neq}_{diss}$ (T_c = 273 K; $\Delta\nu$(*o*-B, 223 K) = 1120 Hz) = 11.7 kcal/mol
$\Delta G^{\neq}_{diss}$ (T_c = 283 K; $\Delta\nu$(*o*-B, 223 K) = 1120 Hz) = 12.1 kcal/mol
average value: $\Delta G^{\neq}_{diss}$(*o*-B) = 11.9 ± 0.2 kcal/mol

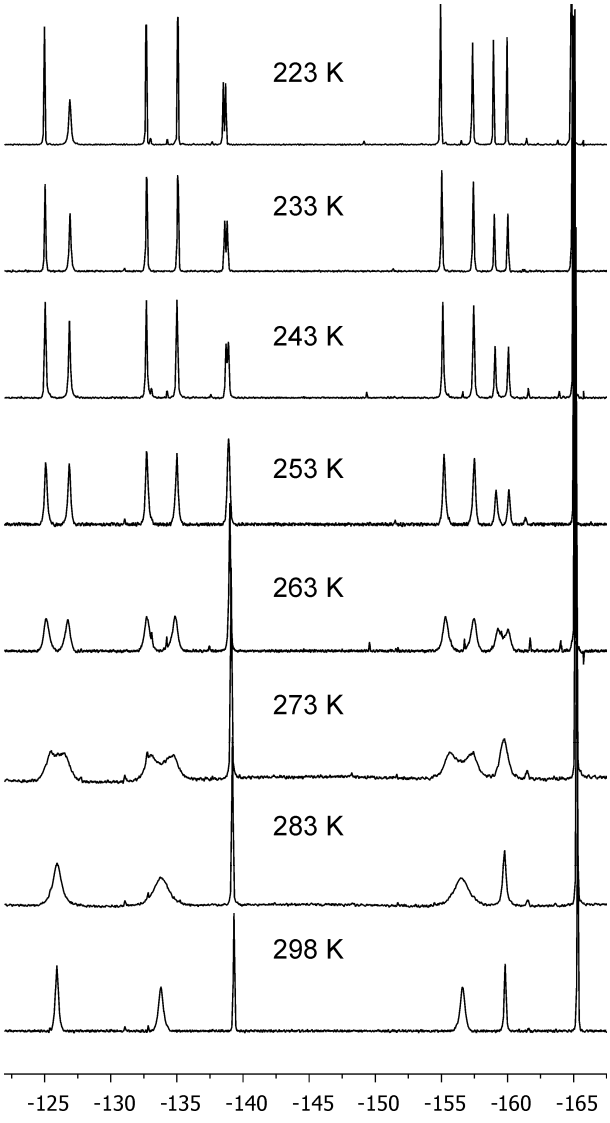
$\Delta G^{\neq}_{diss}$ (T_c= 273 K; $\Delta\nu$(*m*-P, 223 K) = 1140 Hz) = 11.7 kcal/mol
$\Delta G^{\neq}_{diss}$ (T_c= 283 K; $\Delta\nu$(*m*-P, 223 K) = 1140 Hz) = 12.1 kcal/mol
average value: $\Delta G^{\neq}_{diss}$(*m*-P) = 11.9 ± 0.2 kcal/mol

$\Delta G^{\neq}_{diss}$ (T_c= 243 K; $\Delta\nu$(*p*-P, 223 K) = 80 Hz) = 11.6 kcal/mol
$\Delta G^{\neq}_{diss}$ (T_c= 253 K; $\Delta\nu$(*p*-P, 223 K) = 80 Hz) = 12.1 kcal/mol
average value: $\Delta G^{\neq}_{diss}$(*p*-P) = 11.9 ± 0.3 kcal/mol

$\Delta G^{\neq}_{diss}$ (T_c= 263 K; $\Delta\nu$(*p*-B, 223 K) = 480 Hz) = 11.7 kcal/mol
$\Delta G^{\neq}_{diss}$ (T_c= 273 K; $\Delta\nu$(*p*-B, 223 K) = 480 Hz) = 12.1 kcal/mol
average value: $\Delta G^{\neq}_{diss}$(*p*-B) = 11.9 ± 0.2 kcal/mol

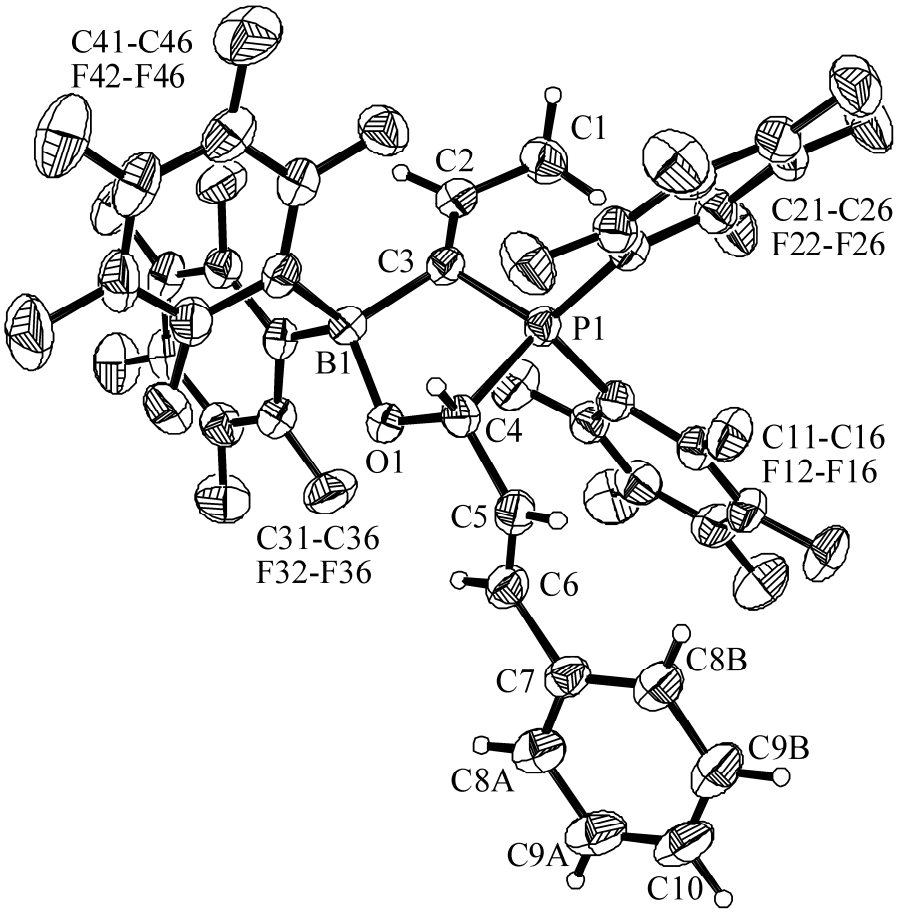
overall average value:

$\Delta G^{\neq}_{diss}$ = 11.9 ± 0.2 kcal/mol

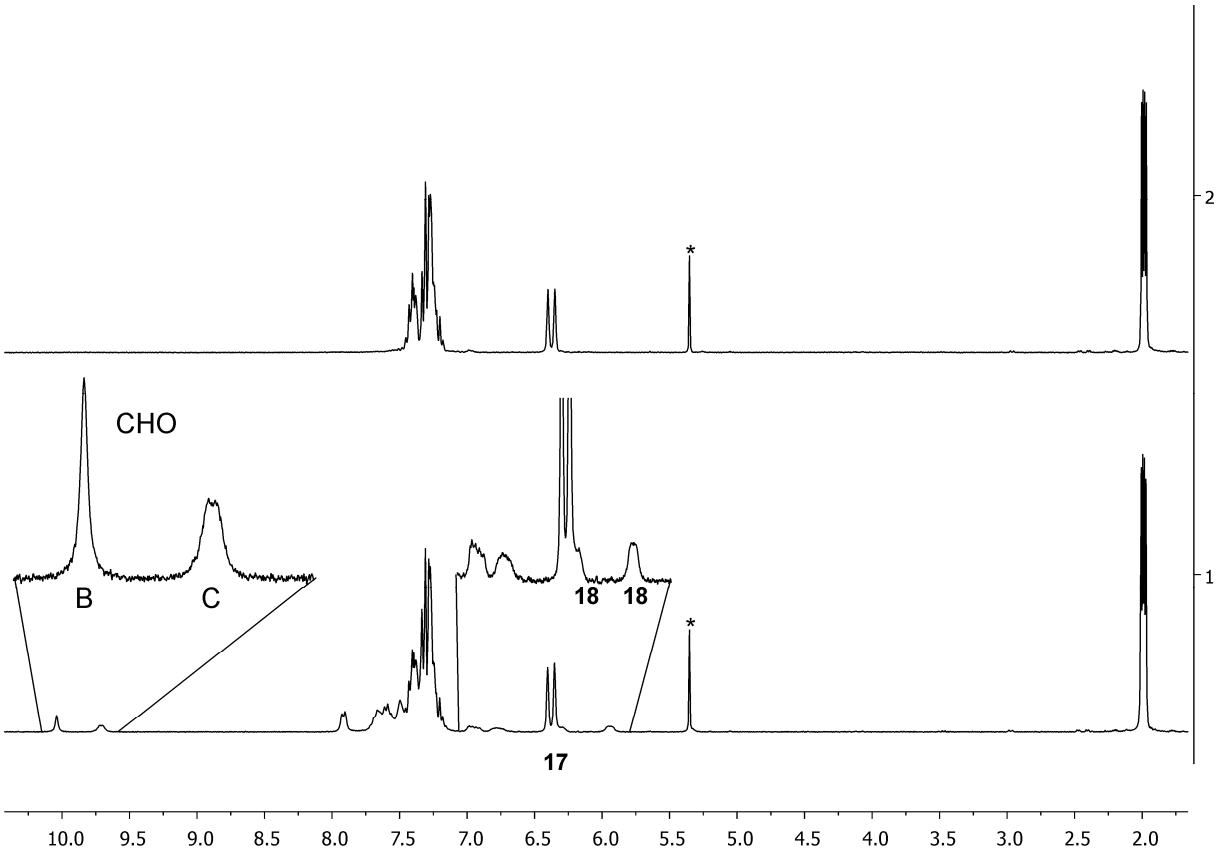


^{19}F NMR (470 MHz, [D_2]-dichloromethane) of **18**.

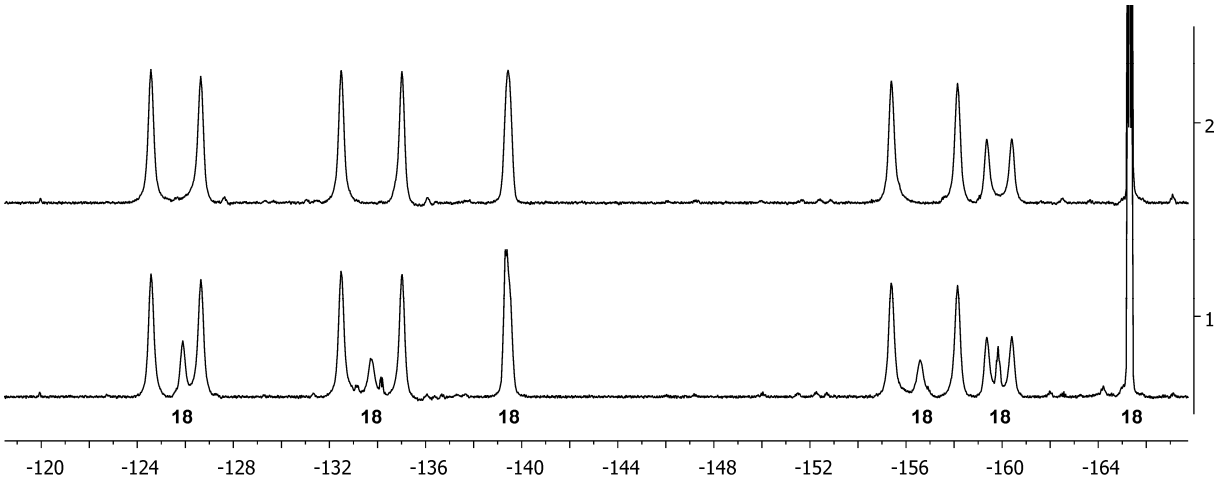
X-ray crystal structure analysis of 18: formula $C_{36}H_{12}BF_{20}OP$ * 2 CH_2Cl_2, M = 1052.09, colorless crystal 0.23 x 0.20 x 0.14 mm, a = 10.9273(4), b = 11.9928(4), c = 16.7507(8) Å, α = 70.979(5), β = 89.996(4), γ = 73.451(5)°, V = 1978.89(14) Å^3, ρ_{calc} = 1.766 g cm^{-3}, μ = 4.303 cm^{-1}, empirical absorption correction (0.438 ≤ T ≤ 0.584), Z = 2, triclinic, space group P1bar (No. 2), λ= 1.54178 Å, T = 223 K, ω and φ scans, 26239 reflections collected (±h, -k, -l), [(sinθ)/λ] = 0.60 Å^{-1}, 6850 independent (R_{int} = 0.049) and 5901 observed reflections [$I \geq 2\sigma(I)$], 587 refined parameters, R = 0.044, wR^2 = 0.113, max. residual electron density 0.33 (-0.41) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



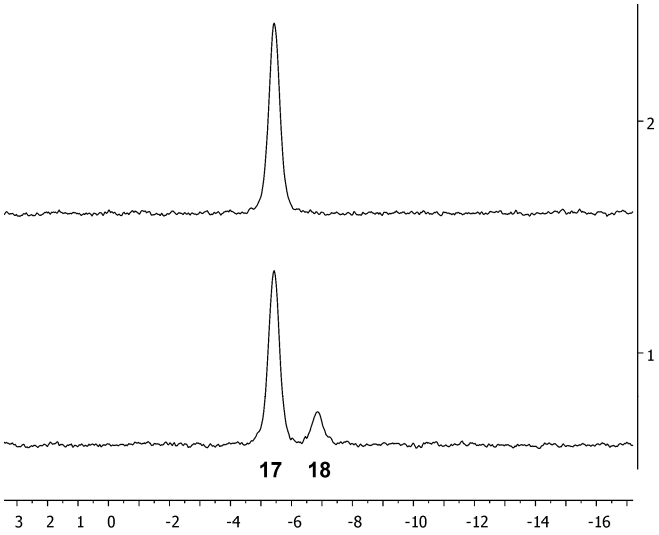
Crossover experiment of 17 and cinnamic aldehyde (NMR scale). The reaction of compound **17** (40 mg, 0.046 mmol, 1 eq) in [D_2]-dichloromethane (3 mL) with cinnamic aldehyde (1.7 mg, 0.013 mmol, 0.3 eq) resulted after 22h at r. t. in a mixture of **17**, **18**, benzaldehyde and cinnamic aldehyde (**17** : **18** : benzaldehyde : cinnamic aldehyde ~ 6 : 1 : 1 : 1).



(2) ^{1}H NMR (300 MHz, [D_2]-dichloromethane(*), 297 K) of **17**. (1) After additon of cinnamic aldehyde (22h, r.t): ^{1}H NMR (300 MHz, [D_2]-dichloromethane(*), 297 K) of the mixture of **17**, **18**, benzaldehyde (B) and cinnamic aldehyde (C).



(2) $^{19}F\{^{1}H\}$ NMR (282 MHz, $[D_2]$-dichloromethane, 297 K) of **17**. (1) After additon of cinnamic aldehyde (22h, r.t): $^{19}F\{^{1}H\}$ NMR (282 MHz, $[D_2]$-dichloromethane, 297 K) of the mixture of **17**, **18**, benzaldehyde and cinnamic aldehyde.



(2) $^{31}P\{^{1}H\}$ NMR (122 MHz, $[D_2]$-dichloromethane, 297 K) of **17.** (1) After additon of cinnamic aldehyde (22h, r.t): $^{31}P\{^{1}H\}$ NMR (122 MHz, $[D_2]$-dichloromethane, 297 K) of the mixture of **17**, **18**, benzaldehyde and cinnamic aldehyde.

Theoretical Methods and Technical Details of the Computations

The quantum chemical calculations have been performed with the TURBOMOLE suite of programs.[1] As Gaussian AO basis, large triple-zeta (denoted as def2-TZVP) sets of Ahlrichs et al.[2] have been employed. All geometries have been fully optimized at the DFT level using the TPSS density functional[3]. We included our standard atom pair-wise correction for intra- and inter-molecular dispersion (also called van der Waals) interactions[4] (dubbed TPSS-D3(BJ) in the following). For a detailed description of this dispersion correction, that is of great importance in studies of large molecules, including many illustrative examples see Ref.[5], for the most recent chemical applications of this method see Ref.[6] In all DFT treatments, the RI-approximation has been used[7] for the Coulomb integrals which speeds the computations up significantly without any significant loss of accuracy. The numerical quadrature grid *m4* (*m5* for PWPB95, see below) has been employed for the integration of the exchange-correlation contribution. All reported energies are pure electronic values *without* zero-point vibrational and thermal corrections.

Single-point energy calculations for selected thermochemical properties were also performed at the higher dispersion-corrected PWPB95[9] double-hybrid functional level. For the non-local perturbation part (all electrons correlated) in these calculations also the RI approximation using matching auxiliary basis functions[10] has been employed. This final theoretical level which should provide relative energies with an estimated accuracy of about 1-2 kcal/mol[9,11]. Covalent bond orders are calculated according to Wiberg[12] from the TPSS Kohn-Sham determinants.

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Optimized cartesian coordinates in Bohr and electronic energies in Hartree (TPSS-D3(BJ)/def2-TZVP)

13A E(TPSS-D3(BJ)/def2-TZVP)=-3395.88468

0.39374753046240	2.38486554097569	-3.51603009945267	p
-0.43055037970728	1.02028915006600	1.99587763034744	b
-0.24129114247203	3.03299589035185	-0.14549763228496	c
3.50684671290985	0.82317666539234	-3.68540683395177	c
4.70720474083107	-0.59681665662206	-1.81801611863515	c
7.18974805794479	-1.42526490536109	-2.01930758136408	c
8.55903083081588	-0.87023150063089	-4.19999460536831	c
7.42437991373529	0.50218174746797	-6.13866839095517	c
4.94248436569534	1.32666453197296	-5.85376553458348	c
-1.82678791080894	-0.17181738494021	-4.38082911335673	c
-4.18372377350913	0.65632498067108	-5.27128453971614	c
-6.06151770209070	-0.98446218621240	-6.09821327036022	c
-5.60200104562041	-3.57745965209463	-6.07506009232105	c
-3.28303301012704	-4.47967888147150	-5.21683416509279	c
-1.44597690231584	-2.78838974518490	-4.38902850792165	c
1.10757421424559	1.33861587020434	4.51371445453401	c
3.46588132245178	2.55902244158309	4.60382265247470	c
4.83479615701892	2.88850393271832	6.82009391001730	c
3.83285469899222	2.02352243507558	9.09800649249587	c
1.48549494533925	0.83118341017852	9.12249044848130	c
0.18934526097319	0.50180937595534	6.86093799455814	c
-2.35818369805808	-1.22846121432464	1.70188322155886	c
-4.80383067828003	-0.82971075973325	0.77246537516347	c
-6.53468596288250	-2.76955848429656	0.39993843277890	c
-5.82341511979484	-5.24684409260742	0.94149754310667	c
-3.42038884585598	-5.73789721884777	1.90273556179769	c
-1.76513728368428	-3.73674435817293	2.30487951680538	c
3.44078995862355	-1.29266471993373	0.28647744190125	f
10.94697103988875	-1.66693727094914	-4.43541508488180	f
3.92478398297904	2.64985487830043	-7.77666744081034	f
-4.70225678619055	3.14890667543920	-5.31610840095501	f
-7.38598730123215	-5.19339889525551	-6.84631130239586	f
0.72465220483396	-3.81188792734963	-3.53396295712055	f
4.55464921190202	3.43589536924956	2.47276414186358	f
7.09919379189882	4.03130896497942	6.79643371986100	f
5.11569256473967	2.34490127884769	11.24959704205535	f
0.50673836390574	0.02120588221494	11.31714005877805	f
-2.09256955810356	-0.62432642437202	7.02754509971980	f
-5.60445801978680	1.54089549952110	0.25978697852288	f
-8.86591703384744	-2.29008145053931	-0.48618486753548	f
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0.51193036817072	-4.30808982359162	3.29249026514734	f
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-2.85332989677196	-6.98110902056637	-5.15030702131810	f
-0.69964058606497	5.52678551338171	0.19264062802617	c
-1.44055318033506	6.81274446692425	2.59797326175951	c
-0.61186857228006	6.76213151349581	-1.45964562053516	h
-1.52382358424756	5.52886427629324	4.21023628359775	h
-3.30189612522228	7.69897134214170	2.36652291547844	h
-0.10775764842893	8.34371755478745	3.02409279420462	h

13B E(TPSS-D3(BJ)/def2-TZVP)=-3395.88321

-1.34709897966861	-2.38765376529821	1.58614836584053	p
-1.29815349162736	1.79076585433562	-1.79749658176699	b
-1.16344041680242	-1.13613070594930	-1.65668391881565	c
1.26477797704025	-0.94584327303548	3.40332673551730	c
3.20735205100565	0.61815929537707	2.54027303399759	c
4.90039406042330	1.80773823263140	4.16491460224337	c
4.70594629508576	1.41540819939732	6.76000288716516	c
2.81589112069267	-0.16039041393238	7.70167930242942	c
1.14196051144593	-1.29586338647864	6.02632978392233	c
-0.12357638735163	-5.63280433463106	1.26460573217378	c
2.32287744252243	-6.24407570273064	0.46411969050144	c
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-5.98593998732191	3.54836489066531	3.60978465919365	c
-4.63934469638413	5.38239612114517	4.93798994804662	c
-2.27275890145112	6.15789292885285	4.07659853103977	c
-1.29232747798604	5.08297072413105	1.89017225467850	c
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6.72525125036600	3.31106873789218	3.24961503275429	f
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-1.97307213060746	-2.17805189159986	-6.30621225169336	c
-1.33358675527599	-4.80155118190967	-3.20038950970177	h
-2.25101703910493	-0.16476473465254	-6.64877580592940	h
-3.68234822282398	-3.18856698420692	-6.90731495404541	h
-0.42984856674164	-2.86120061203633	-7.51310323722913	h

H2 E(TPSS-D3(BJ)/def2-TZVP)=-1.17969

0.00000000000000	0.00000000000000	0.70251513755511	h
0.00000000000000	0.00000000000000	-0.70251513755511	h

Ph-N=C=O E(TPSS-D3(BJ)/def2-TZVP)=-399.97358

-1.47208778385914	2.11141398695344	0.00000000000000	c
-3.54388303480824	0.48780326294055	0.00000000000000	c
-3.19467680974810	-2.12567541104392	0.00000000000000	c
-0.74798434863520	-3.11366160846202	0.00000000000000	c

1.33864445016156	-1.51225068737024	0.00000000000000	c
0.97513424414603	1.11209555405996	0.00000000000000	c
3.01308610427020	2.80052297285937	0.00000000000000	n
5.30002063508245	2.71365318336970	0.00000000000000	c
7.51665016219616	2.91015712213278	0.00000000000000	o
-1.71801825482300	4.14706016679760	0.00000000000000	h
-5.44005815278197	1.27314496673545	0.00000000000000	h
-4.81452884637265	-3.38464110723052	0.00000000000000	h
-0.45714432749103	-5.14562440159395	0.00000000000000	h
3.24484596266289	-2.27399800014811	0.00000000000000	h

Ph-CH=O E(TPSS-D3(BJ)/def2-TZVP)=-345.77899

-1.18534434641039	2.00999948693169	0.00000000000000	c
-3.23462771468103	0.36931265146042	0.00000000000000	c
-2.83670389540065	-2.24601455650925	0.00000000000000	c
-0.38687277076705	-3.22362785469126	0.00000000000000	c
1.66951678487790	-1.58020263557055	0.00000000000000	c
1.28198122973833	1.03838147363627	0.00000000000000	c
3.49018031393356	2.74852655371941	0.00000000000000	c
3.37707313588425	5.04852555396384	0.00000000000000	o
-1.43746300721444	4.04677430218935	0.00000000000000	h
-5.14818217718594	1.11192920557474	0.00000000000000	h
-4.44476709521728	-3.52250650142744	0.00000000000000	h
-0.08833308130081	-5.25408502011129	0.00000000000000	h
3.59097668912550	-2.31278403507496	0.00000000000000	h
5.35256593461801	1.76577137590906	0.00000000000000	h

Ph-CH=CH-CH=O E(TPSS-D3(BJ)/def2-TZVP)=-423.23020

-2.43510404934365	0.30478809445480	0.00000000000000	c
-4.35341999856570	-1.48602678740902	0.00000000000000	c
-3.77217552047034	-4.06475973085096	0.00000000000000	c
-1.25278304188387	-4.84046036456459	0.00000000000000	c
0.67064571547759	-3.04657334086241	0.00000000000000	c
0.11877899400243	-0.44545415604683	0.00000000000000	c
2.20182494810308	1.35155849446635	0.00000000000000	c
2.07749603416998	3.90328188363702	0.00000000000000	c
4.38936585667032	5.40677972568420	0.00000000000000	c
4.45676774448316	7.71600859853495	0.00000000000000	o
-2.91128613078078	2.30040982087799	0.00000000000000	h
-6.31395779848948	-0.87846411681611	0.00000000000000	h
-5.27961572618104	-5.45762868854593	0.00000000000000	h
-0.78937011623133	-6.83976038145227	0.00000000000000	h
2.63590732362239	-3.64674158962526	0.00000000000000	h
4.08571533742100	0.50866683830056	0.00000000000000	h
0.30210941954459	4.93677218431319	0.00000000000000	h
6.16910100845167	4.27760351590425	0.00000000000000	h

H2+13 reaction product E(TPSS-D3(BJ)/def2-TZVP)=-3397.07602

0.31970170231322	2.47475235568061	1.63769863013235	p
-2.05447748624080	-1.20298362374346	-0.84890156385341	b
-0.10728760653686	1.16284589588646	-1.38159000667671	c
1.57695008363035	0.16784804440529	3.78480006172623	c
0.29721472354567	-0.48798648342997	6.00279577680184	c
1.06365960207990	-2.52270331295299	7.47807320008794	c
3.16613553435910	-3.93180113566356	6.73864135422664	c
4.49798211967976	-3.30266484353995	4.54879020219864	c
3.68576084315193	-1.27648128805549	3.09689210110278	c
2.11576232905886	5.40409091870364	1.78178617804375	c
0.91788431771740	7.54987273392820	0.78708691227815	c
2.07604891792461	9.90510548851972	0.71270711269116	c
4.52412954307796	10.15453078586483	1.66094369499526	c
5.76961951033381	8.06442240891703	2.67351104780744	c
4.56579237115644	5.72503864801784	2.72373962894094	c
-4.36250482727088	-1.16844583258070	-2.86986730917319	c
-5.99870956696685	0.90150813638830	-2.86886892962294	c
-8.05540975010841	1.15353242041518	-4.48270366467223	c
-8.54845562052675	-0.75765527898461	-6.22543685436128	c
-6.97540837282373	-2.86295175138750	-6.30889507116139	c
-4.93323367327474	-3.02557975880604	-4.65001801237227	c
-0.59538388871831	-3.86850110328413	-0.38800649715430	c
1.45947626177403	-4.72822796373115	-1.79650928714716	c
2.79332219685523	-6.92977879618630	-1.25133167002336	c
2.05531843924409	-8.40565810140459	0.79851353510252	c
-0.00336182879954	-7.64895453585634	2.25072763736239	c
-1.27492243080170	-5.42975988499676	1.62944550881041	c
-1.73913466310952	0.83627694916063	6.73895586367008	f
3.91963253777072	-5.88290401304877	8.13870444000908	f

4.97282221524492	-0.69557756298590	0.99090334466931 f
-1.44888090452692	7.33836063728661	-0.11704701152793 f
5.67278486652959	12.39615500148188	1.60488780374638 f
5.84450888999764	3.78608896199621	3.74341064953892 f
-5.59678152048209	2.82386273706712	-1.20220397904851 f
-9.56854982832012	3.19990550251129	-4.38422048960909 f
-10.52316919950011	-0.56537071862100	-7.81189918086334 f
-7.43524097455224	-4.71114268210235	-7.99747109705805 f
-3.46606087955058	-5.11612578996493	-4.86596581750193 f
2.25737825579158	-3.39180102065712	-3.83339419679170 f
4.77645966010953	-7.64925562388368	-2.67390112697300 f
3.31864132847516	-10.53146391983200	1.37267475021646 f
-0.71856477863456	-9.05143285396700	4.25505146281392 f
-3.24895404909670	-4.80189471310044	3.14442145785560 f
-0.19137593646920	-3.13759581955893	9.58226386865529 f
6.52526915934799	-4.65178331400833	3.87390848180321 f
0.87868360595592	11.91223548830496	-0.24830708659127 f
8.10942385415277	8.32155260940085	3.59685516613557 f
0.87576507839104	2.33340891603157	-3.41212757290126 c
0.48932657044246	1.53993969827452	-6.09067379508436 c
2.05361417998903	4.01147971614749	-3.15561832732354 h
-0.74162196450119	-0.10207833896594	-6.24080950116908 h
2.31784926959397	1.08754589245845	-6.95853838425887 h
-0.32049907908504	3.10959231632019	-7.17862602407057 h
-1.99787241887146	3.15195463538337	2.69148298286774 h
-2.99105671892652	-0.67334683325194	1.20325960270066 h

16 E(TPSS-D3(BJ)/def2-TZVP)=-3795.88384

2.31310559653232	1.22808684950030	0.36630047598178 p
-1.10629978537363	-1.73517410900492	-2.07332035092839 b
1.69687703583270	-0.40225193595259	-2.46231867305241 c
4.58136311901690	-0.55469740717067	2.21154464870930 c
3.87073788819509	-2.39114699363860	3.97654450422934 c
5.65943555552064	-3.87645586794542	5.20908981665624 c
8.21817422868115	-3.54877449173891	4.67770399364557 c
8.98155078289343	-1.75190654139961	2.90379617202692 c
7.16141977470501	-0.30144515811703	1.69548499410959 c
3.30650587610612	4.49168912667883	0.43679893878981 c
3.21850966348478	6.07239793404050	-1.68629682592560 c
3.74539933028964	8.64359176410597	-1.51425296404670 c
4.36948325096029	9.69405178249737	0.81838166504815 c
4.48152699595224	8.16801693827008	2.96410003043310 c
3.95853530063209	5.60371913622251	2.75493098627790 c
-2.87877411428009	-0.85923118451186	-4.44282168448943 c
-3.52053006701872	1.68833061977444	-4.71270992879942 c
-5.00003204108823	2.63407483629469	-6.66705161921048 c
-5.89934317129449	0.98064183636673	-8.50683270124967 c
-5.28392198237744	-1.57059754670157	-8.35227069975311 c
-3.79537020470161	-2.42513085449186	-6.35478822678888 c
-1.08868070349091	-4.74716857525595	-1.41961123389446 c
1.01971873749391	-6.29490182432277	-1.11594139642988 c
0.88872801786124	-8.80943847952875	-0.33963653614672 c
-1.45191022617718	-9.88566855612210	0.16927906241579 c
-3.62305492663324	-8.41941829496513	-0.09439254617266 c
-3.39302423333187	-5.91797433965259	-0.86050305854031 c
1.43175839356666	-2.81392921067572	4.50545342809864 f
9.94193373395123	-4.96849524603855	5.84797321440323 f
7.93661138430409	1.38735684521916	-0.05626849515309 f
2.63134738684305	5.15993266324039	-3.97433242107129 f
4.87262636612600	12.15816200604208	0.99778670191493 f
4.12783657214488	4.19683466460561	4.85821723646445 f
-2.65197744684799	3.41585657732878	-3.01545900445744 f
-5.55126235077037	5.11359454429156	-6.81277481603764 f
-7.32280870269337	1.84431432390375	-10.42136732439613 f
-6.12264914264964	-3.18104268336569	-10.13367925865390 f
-3.21862793502216	-4.92545150816696	-6.37970289374763 f
3.40078671409922	-5.40633199462882	-1.54454206977550 f
3.01014015321500	-10.19197968597756	-0.05771422526830 f
-1.61934047442497	-12.30440590536338	0.91588474065966 f
-5.89997292436411	-9.43919611232992	0.39386539376990 f
-5.56671666199629	-4.58080148231481	-1.06534371874242 f
4.93659384428494	-5.61481350401359	6.89543777841529 f
11.43882530807283	-1.45629976665165	2.37484092383269 f
3.66359750471248	10.10723855575864	-3.57559867075038 f
5.08571070416544	9.18053859662591	5.20318563389245 f
3.29666813587864	-0.49940552617710	-4.43315907221751 c
2.89664885553133	-2.07199740245655	-6.73895057415205 c

-0.87282191935316	1.05684738659007	1.67591099985763	c
-2.25423018526461	-0.52257197301865	0.32922677991532	o
-3.74436725680049	2.61694705667985	4.76480210515259	c
-3.90300314327738	4.38044181446134	6.74731490335370	c
-6.14783281445915	4.71486936460742	8.06849087678717	c
-8.27431975072492	3.28258074476747	7.43970385880816	c
-8.13047970108038	1.51924605644101	5.48226272759620	c
-5.89326925843104	1.17093030054189	4.14138186681778	c
-1.38227678727729	2.46229943485694	3.57178300777132	n
5.03300489217619	0.60883397813992	-4.41597353409006	h
1.27934588844363	-3.33498066158938	-6.56163047419721	h
2.62314002667123	-0.85320070390143	-8.39715699161095	h
4.59328807229496	-3.20480253092845	-7.10807636874347	h
-2.22231609070804	5.46135185919363	7.21379674118371	h
-6.24245889838420	6.08841788314468	9.59113672694549	h
-10.03031826092166	3.53472581811052	8.47200667311493	h
-9.77959717726607	0.40031094678047	4.98864448418888	h
-5.79934675215453	-0.20514418696392	2.63141626722550	h

17 E(TPSS-D3(BJ)/def2-TZVP)=-3741.70440

-1.66424203950278	-0.86053300017033	0.63108937840787	p
3.35148839356829	-0.26476181752048	-0.27131022660199	b
1.65845510247430	1.80825629710959	-1.28085448526104	o
4.82873919304653	-0.86246475171631	-5.10557277172161	c
6.40387198705837	-1.85881144790402	-6.96760170704952	c
1.27493661731932	-2.46649048733702	0.56588945109074	c
1.60624915114817	-4.94623560235768	0.97101705293643	c
8.40585323234401	-3.42062654966425	-6.28791098365800	c
-0.33168955904422	-6.95864797256795	1.36367920241145	c
8.79404312964544	-3.96896896210179	-3.74575087327860	c
7.17245395053016	-2.93157179234869	-1.95543453704088	c
5.14817496143585	-1.33933924898569	-2.52824409055137	c
-0.18682605373757	2.45268212229607	0.44453374168896	c
6.61476282749826	2.96557600173521	1.52246638402036	c
-1.93613595349498	4.47994337580921	-0.45823362242523	c
-2.17675482123673	4.97145016016900	-3.04442501619906	c
8.08798712498475	4.19189132877878	3.32311290755946	c
-3.85773707732222	6.82258984303910	-3.87495323693240	c
7.99985501702838	3.37624087184939	5.82366795549526	c
-5.30018444949139	8.18294123646534	-2.13591543151059	c
6.44719084375395	1.35440073927314	6.46200742541624	c
-5.03736321118885	7.71393294229786	0.44753926242034	c
5.01043140812552	0.18369115565607	4.59056468292603	c
-3.35554504090457	5.87122115725946	1.28485315220082	c
5.02097260482565	0.92617479214026	2.06272405555339	c
-3.68042952399589	-1.61862613565071	3.31049666268669	c
-5.74091873201830	-3.27922463098107	3.19538263829578	c
-2.71322927640849	-2.20085654474571	-4.42568633426106	c
-7.22763622137621	-3.82233412039732	5.29139715077622	c
-4.05543650125366	-2.00369425046088	-6.68160860161717	c
-6.67179706509660	-2.69542181437490	7.60726405106498	c
-6.32833062789850	-0.67607508510446	-6.74017716094533	c
-4.63397621257309	-1.03734598151702	7.79933225596285	c
-7.26188232380527	0.43945568754902	-4.54251710584574	c
-3.18164359792015	-0.52400875234295	5.67059201991112	c
-5.88319322730255	0.23699909419950	-2.32274872373466	c
-3.57685209799929	-1.06158739502212	-2.19482371562778	c
2.92061094320727	0.61744375664481	-5.96355741294677	f
-1.25406933331018	1.11053083158729	5.94092752963797	f
-9.45182459020068	1.70677831467991	-4.59532635098224	f
-4.10095486246235	0.05974015129491	10.01350926911567	f
-7.62542941285037	-0.48836001781413	-8.89529751728737	f
-8.08690875485472	-3.20225769476427	9.63141484379554	f
-3.18872905518666	-3.10886059835241	-8.78425569371392	f
-9.17781103495165	-5.42396227349732	5.10233815427173	f
-0.58026776006621	-3.55564429771362	-4.47414519411163	f
-6.34757599999736	-4.44709711659467	1.01471396270637	f
-6.84282486409801	1.32171070058814	-0.23203343418529	f
3.56347706021490	-1.78819794866972	5.38382700027556	f
6.00030743671201	-1.33072866685497	-9.42562116038265	f
6.34425641761914	0.55262500864545	8.87812950677335	f
9.93504583942136	-4.39995277038837	-8.06322930858073	f
9.39584721331091	4.53348163485154	7.60085981343475	f
10.71151922298214	-5.49301914617256	-3.05259538999783	f
9.58840738550513	6.14530200950955	2.68524339387517	f
7.63504146936925	-3.57374549045515	0.49581950241200	f
6.78551895239117	3.83847446029994	-0.87692282447081	f

-3.13651886806731	5.51139010395069	3.29616848312568	h
0.04679832613125	-8.55634654118358	0.09859182241798	h
0.54976968615174	2.84985549978921	2.34345906176125	h
-0.22686016305661	-7.70267706676491	3.29884334044307	h
-1.01086502969180	3.92372863122667	-4.36674587895346	h
-2.25430409856800	-6.30091568136010	1.00779092729829	h
-4.03243447586978	7.21170073168467	-5.88285509721957	h
3.55866299734905	-5.60618210744983	0.99908172132935	h
-6.60858667723147	9.62294180283625	-2.78888747624326	h
-6.13295990111798	8.79242331809125	1.80691359983895	h

17(open) E(TPSS-D3(BJ)/def2-TZVP)=-3741.68253

-2.77453932013400	-0.21818450055220	0.75992980898152	p
2.61394198122327	-0.65659723345203	-0.45965521846104	b
1.78400128840235	2.21841647707919	-0.76241844114116	o
1.79611563760075	-1.54560453770294	-5.28433625273642	c
2.17685710771516	-2.68117054769271	-7.62104306354981	c
0.10246006394929	-2.14076498790926	0.48482685894380	c
0.26450821912335	-4.61659313052354	1.02012312131249	c
4.27486563697105	-4.23520670580553	-7.95118393094654	c
-1.72744067638983	-6.40454969090108	1.90424015570955	c
5.92520749648582	-4.60835942296352	-5.93773792445286	c
5.46682765006949	-3.41026095356544	-3.63673995324175	c
3.40471456868870	-1.82039916646828	-3.20808784779033	c
2.25137974590186	3.67955646303595	-2.56887125640665	c
7.06318761608892	1.04289227915423	0.84435906135802	c
1.39493902284606	6.25354835601790	-2.53631289865976	c
-0.08855470220911	7.17319153672125	-0.52175138886355	c
9.10335346822107	1.57204746660464	2.40687168268286	c
-0.91777587774284	9.65746609729565	-0.57098976288452	c
9.04962512303387	0.71472162715703	4.89379492376573	c
-0.27718066954464	11.22876153203782	-2.60325621131666	c
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-7.39455921570874	-3.67498276366118	9.01937115780659	f
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