Supplementary Material (ESI) for Chemical Communications

Remarkably Variable Reaction Modes of Frustrated Lewis Pairs with Non-Conjugated Terminal Diacetylenes

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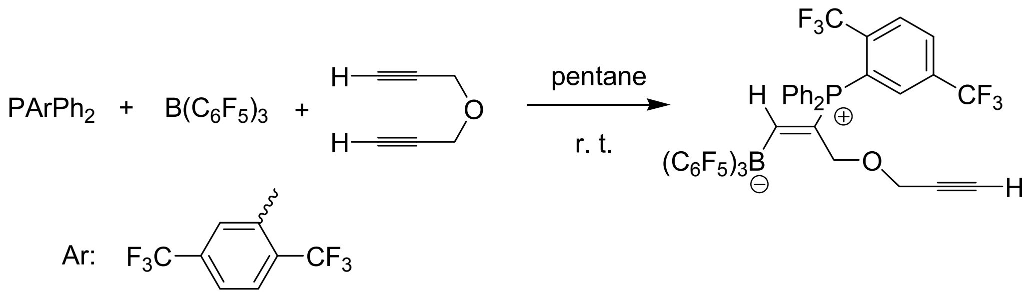
Supporting Information

Experimental Section

All experiments were carried out under a dry Argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. ^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{31}P NMR spectra were recorded on a Varian 500 MHz INOVA or a Varian 600 MHz UNITY plus NMR spectrometer at ambient temperature unless otherwise stated. Chemical shifts are given in ppm relative to solvents (^{1}H and ^{13}C) or an external standard [$\delta(BF_3{\cdot}OEt_2) = 0$ for ^{11}B NMR, $\delta(CFCl_3) = 0$ for ^{19}F NMR and $\delta(85\%\ H_3PO_4) = 0$ for ^{31}P NMR). Coupling constants are in Hz. Elemental analysis data was recorded on Foss-Heraeus CHNO-Rapid. HRMS was recorded on GTC Waters Micromass (Manchester, UK). UV/Vis: UV double-ray spectrometer Uvikon 923 (Kontron Instruments, Zürich, Switzerland), using SUPRASIL Quarz glass (200–2500 nm). X-ray structure analysis: 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 XP (BrukerAXS, 2000). R-value is given for the observed reflections, the weighted R-value is given for all unique reflections. All figures are drawn at the 50% probability level.

$B(C_6F_5)_3$ was prepared according to procedures reported in the literature (caution: the intermediate involved is explosive) [(a) A. G. Massey, A. J. Park. *J. Organomet. Chem.* **1964**, *2*, 245-250. (b) Wang, C.; Erker, G.; Kehr, G.; Wedeking, K.; Fröhlich, R. *Organometallics*, **2005**, *24*, 4760-4773].

Preparation of compound 1:



Dipropargyl ether (9.4 mg, 0.1 mmol) and bis-2,5-(trifluoromethyl)phenyl-diphenylphosphine (39.8 mg, 0.1 mmol) were dissolved in pentane (5 mL). Then a solution of B(C$_6$F$_5$)$_3$ (52 mg, 0.1 mmol) in pentane (5 mL) was added. The reaction mixture was stirred at room temperature overnight. Subsequently all solvent was decanted and the residue was washed with pentane (3×mL). The product was dried overnight and collected as a white, crystalline solid (82 mg, 82%) which was suitable for X-ray crystal structure analysis.

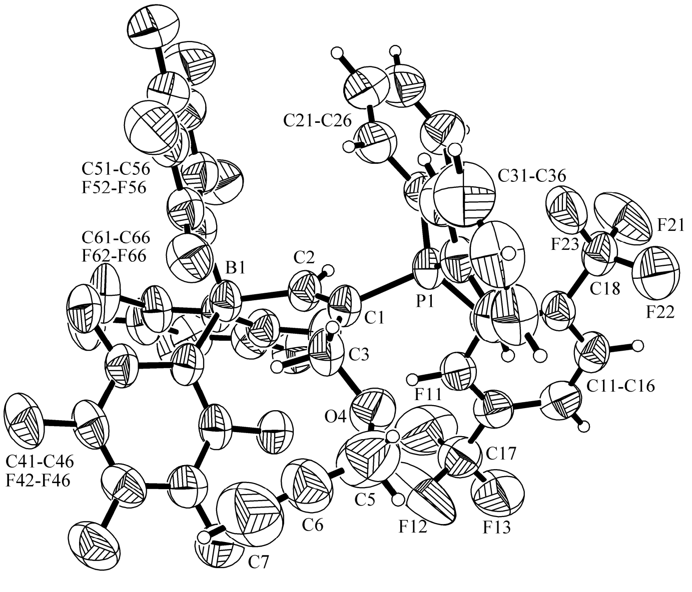
^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298K): δ 8.33 (d, $^3J_{PH}$ = 15.8 Hz, 1H, *o*-Ar), 8.21 (d, $^3J_{HH}$ = 8.1 Hz, 1H, *p*-Ar), 8.11 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{PH}$ = 4.6 Hz, 1H, *m*-Ar), 7.78 (m, 2H, *p*-Ph), 7.70 (d, $^3J_{PH}$ = 35.9 Hz, 1H, $^{=}$CH), 7.63 (md, $^4J_{PH}$ = 3.9 Hz, 4H, *m*-Ph), 7.58 (dm, $^3J_{PH}$ = 12.7 Hz, 4H, *o*-Ph), 4.10 (d, $^3J_{PH}$ = 17.6 Hz, 2H, $^{=}$CH$_2$), 3.49 (d, $^4J_{HH}$ = 2.4 Hz, 2H, $^{\equiv}$CH$_2$), 2.19 (t, $^4J_{HH}$ = 2.4 Hz, 1H, ≡CH). ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$, 298K): δ 186.3 (q(1:1:1:1), $^1J_{CB}$ = 52.5 Hz, $^{=}$CH), 148.1 (dm, $^1J_{FC}$ = 238.7 Hz), 139.1 (dm, $^1J_{FC}$ = 247.5 Hz), 137.1 (dm, $^1J_{FC}$ = 250.6 Hz) (C$_6$F$_5$), 137.2 (qd, $^2J_{FC}$ = 33.7 Hz, $^2J_{PC}$ = 4.3 Hz, *o*-Ar^{CF3}), 136.4 (dq, $^2J_{PC}$ = 12.4 Hz, $^3J_{FC}$ = 3.7 Hz, *o*-Ar^{CH}), 135.1 (qd, $^2J_{FC}$ = 34.6 Hz, $^3J_{PC}$ = 12.8 Hz, *m*-Ar^{CF3}), 135.0 (d, $^4J_{PC}$ = 3.1 Hz, *p*-Ph), 134.3 (d, $^2J_{PC}$ = 9.9 Hz, *o*-Ph), 132.1 (qd, $^3J_{FC}$ = 3.6 Hz, $^4J_{PC}$ = 2.7 Hz, *p*-Ar^{CH}), 131.0 (dq, $^3J_{PC}$ = 8.0 Hz, $^3J_{FC}$ = 4.6 Hz, *m*-Ar^{CH}), 130.1 (d, $^3J_{PC}$ = 13.0 Hz, *m*-Ph), 122.9 (br, *i*-C$_6$F$_5$), 122.79 (q, $^1J_{FC}$ = 273.8 Hz), 122.70 (qd, $^1J_{FC}$ = 275.8 Hz, J_{PC} = 1.7 Hz) (CF$_3$), 121.7 (dq, $^1J_{PC}$ = 79.9 Hz, $^3J_{FC}$ = 1.0 Hz, *i*-Ar), 119.5 (d, $^1J_{PC}$ = 88.7 Hz, *i*-Ph), 118.2 (d, $^1J_{PC}$ = 70.7 Hz, =C^P), 77.8 (-C≡), 75.2

(≡CH), 67.2 (br d, $^{2}J_{PC}$ = 12.3 Hz, $^{=}CH_2$), 57.8 ($^{=}CH_2$). $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 298K): δ -16.1 (d, $^{3}J_{PB} \sim$ 14 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 298K): δ -55.2, -64.2 (each 3F, CF_3), -132.5 (6F, *o*), -161.8 (3F, *p*), -165.9 (6F, *m*) (C_6F_5). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298K): δ 29.3 (partial relaxed q(1:1:1:1), $^{3}J_{PB} \sim$ 14 Hz).

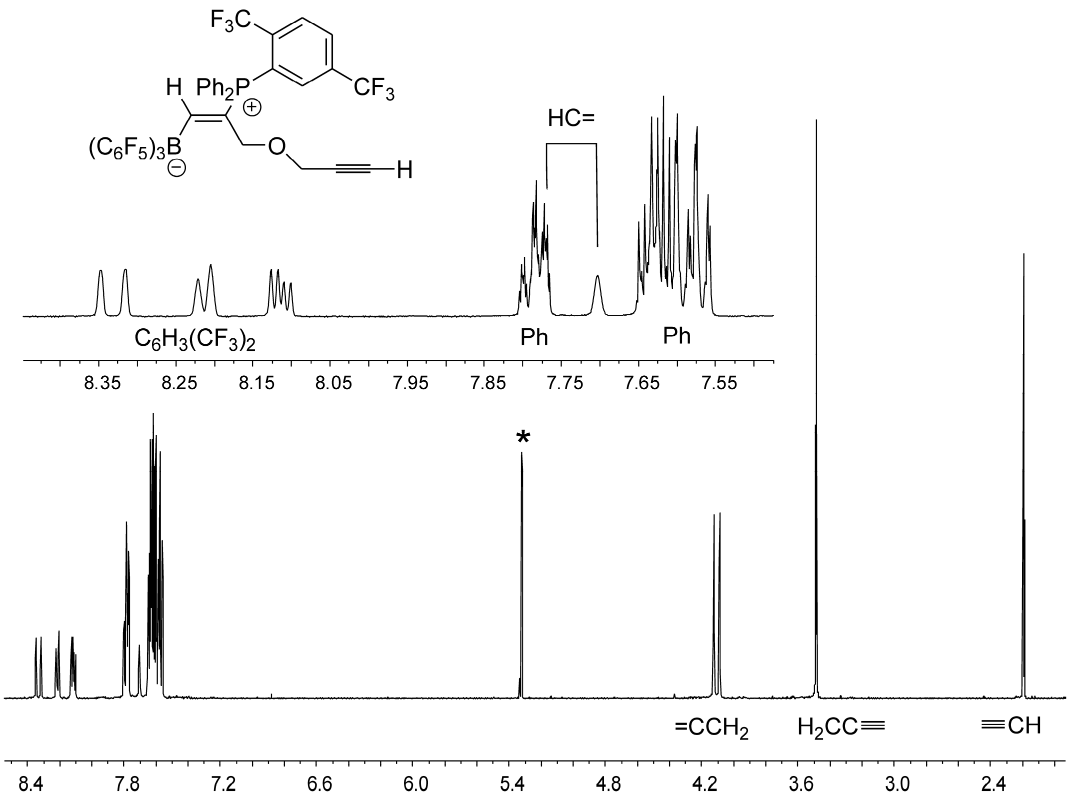
Element analysis: calcd. for $C_{44}H_{19}BF_{21}OP$: C, 52.62; H, 1.91. Found: C, 52.68; H, 1.55.

HMRS: calcd. for $C_{44}H_{19}BF_{21}OP+Na^+$: 1027.0823. Found: 1027.0812.

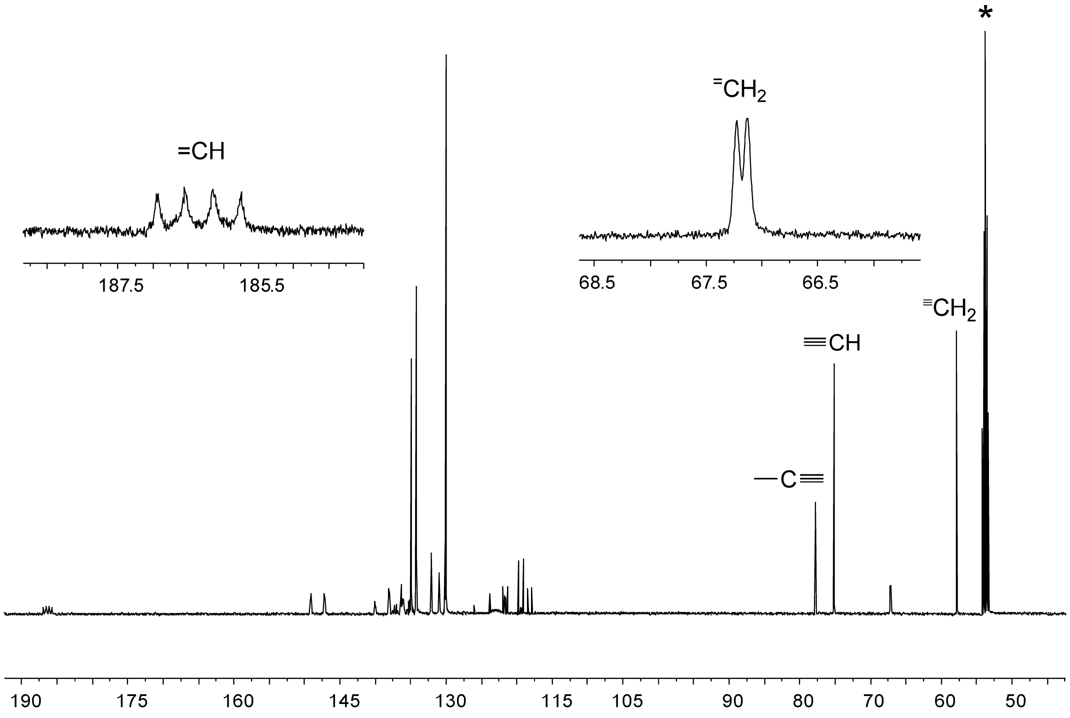
X-ray crystal structure analysis of **1**: formula $C_{44}H_{19}$ $BF_{21}OP$, M = 1004.37, colorless crystal 0.40 x 0.20 x 0.03 mm, a = 9.7019(9), b = 20.5980(13), c = 20.7265(4) Å, β = 97.341(3)°, V = 4106.2(5) Å^3, ρ_{calc} = 1.625 g cm^{-3}, μ = 1.817 mm^{-1}, empirical absorption correction (0.530 ≤ T ≤ 0.948), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 28157 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 6488 independent (R_{int} = 0.101) and 3983 observed reflections [$I \geq 2\,\sigma(I)$], 632 refined parameters, R = 0.066, wR^2 = 0.206, max. (min.) residual electron density 0.44 (-0.30) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, group C5-C6-C7 refined with split positions using geometrical and thermal restraints. (CCDC 759353).



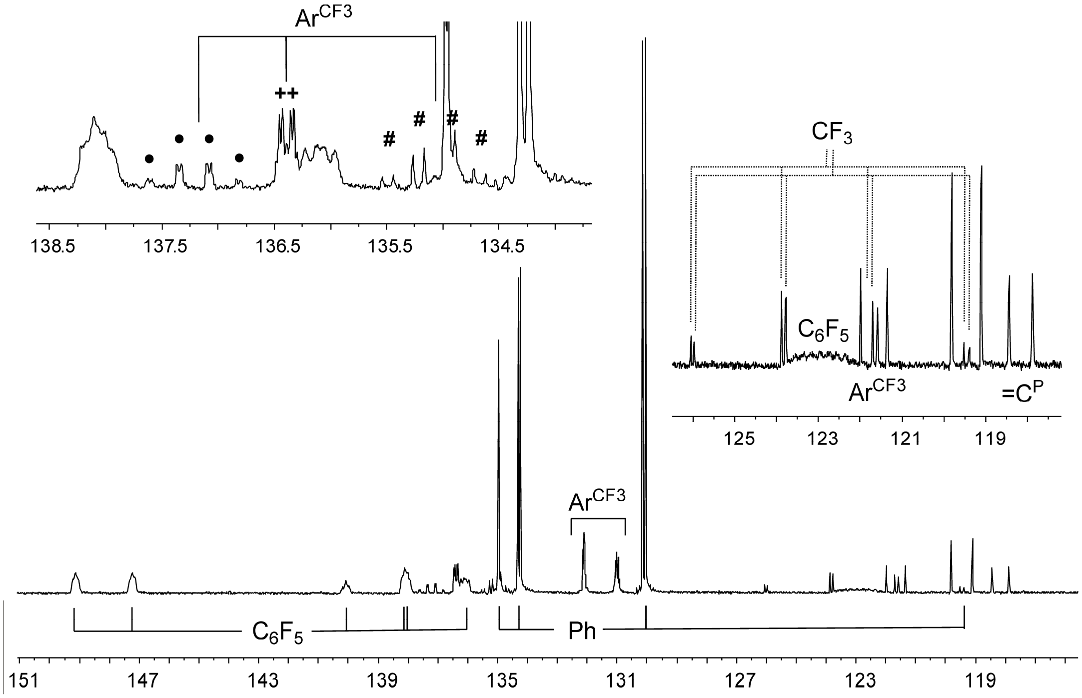
50% probability level



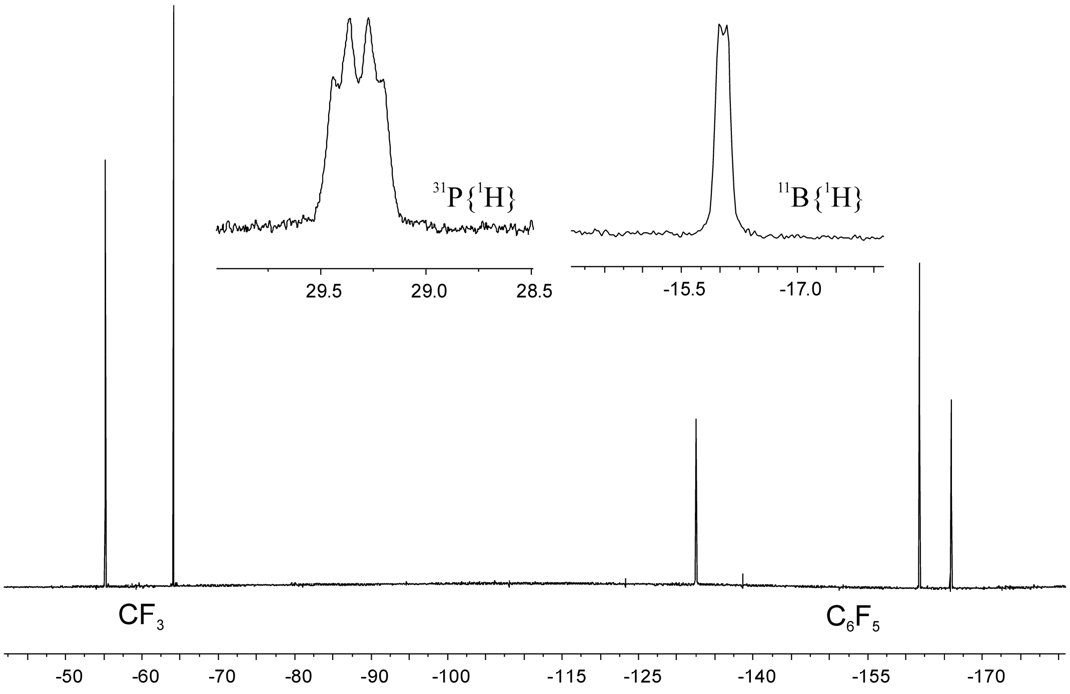
^{1}H NMR (500 MHz, CD_2Cl_2, 298K)



^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298K)

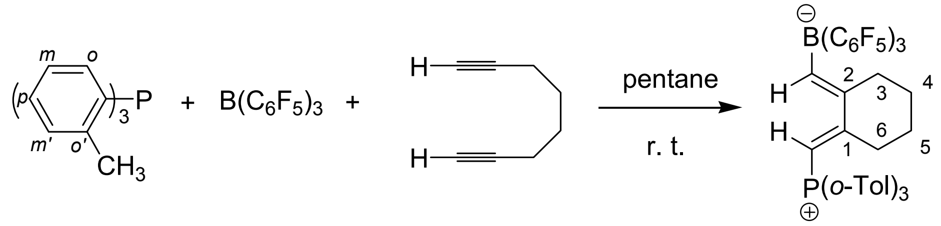


$^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298K)



^{19}F NMR (470 MHz, CD_2Cl_2, 298K)

Preparation of compound 2a:



1,7-Octadiyne (10.6 mg, 0.1 mmol) and tri(*o*-tolyl)phosphine (30.4 mg, 0.1 mmol) were dissolved in pentane (5 mL), and a solution of $B(C_6F_5)_3$ (51.1 mg, 0.1 mmol) in pentane (5 mL) was added. The reaction mixture was stirred overnight at room temperature. Then the solvent was decanted and the residue was washed with pentane (3×1 mL). The crude product was purified via crystallization by slow diffusion of pentane into the dichloromethane solution (46 mg, 49%) at -20 ^{o}C. The obtained crystals were suitable for X-ray structure analysis.

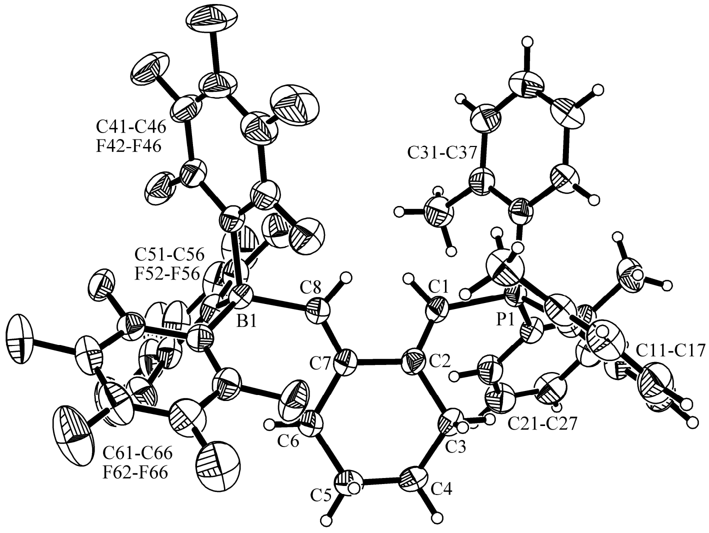
^{1}H NMR (600 MHz, CD_2Cl_2, 213K): δ 7.92 (*o*), 7.70 (*p*), 7.57 (*m*), 7.39 (*m'*) (each m, each 1H, ^{A}Tol), 7.67 (*p*), 7.58 (*m'*), 7.35 (*m*), 7.26 (*o*) (each m, each 1H, ^{C}Tol), 7.58 (*p*), 7.38 (*o*), 7.37 (*m'*), 7.32 (*m*) (each m, each 1H, ^{B}Tol), 6.70 (br s, 1H, =CH^{B}), 5.78 (d, $^2J_{PH}$ = 26.8 Hz, 1H, =CH^{P}), 2.45 (s, 3H, ^{C}Tol^{CH3}), 2.32, 1.64 (each m, each 1H, 3-CH_2), 2.08 (s, 3H, ^{B}Tol^{CH3}), 1.88, 1.44 (each m, each 1H, 6-CH_2), 1.73 (s, 3H, ^{A}Tol^{CH3}), 1.45, 1.23 (each m, each 1H, 4-CH_2), 1.38, 1.31 (each m, each 1H, 5-CH_2). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 213K): 177.2, 142.2 (d, J_{PC} = 17.1 Hz) (1,2-C), 151.0 (br, =CH^{B}), 147.4 (dm, $^1J_{FC}$ = 239.6 Hz), 137.4 (dm, $^1J_{FC}$ = 244.2 Hz), 135.8 (dm, $^1J_{FC}$ = 247.0 Hz) (C_6F_5), 144.1 (d, $^2J_{PC}$ = 8.7 Hz, *o'*-^{C}Tol), 143.0 (d, $^2J_{PC}$ = 8.5 Hz, *o'*-^{A}Tol), 142.4 (d, $^2J_{PC}$ = 9.1 Hz, *o'*-^{B}Tol), 134.8 (d, $^2J_{PC}$ = 14.2 Hz, *o*-^{A}Tol), 134.7 (d, $^4J_{PC}$ = 3.1 Hz, *p*-^{A}Tol), 134.36 (d, $^4J_{PC}$ = 2.9 Hz, *p*-^{C}Tol), 134.37 (d, $^2J_{PC}$ = 12.6 Hz, *o*-^{C}Tol), 134.1 (d, $^4J_{PC}$ = 2.2 Hz, *p*-^{B}Tol), 134.0 (d, $^2J_{PC}$ = 12.1 Hz, *o*-^{B}Tol), 133.44 (d, $^3J_{PC}$ = 10.9 Hz, *m'*-^{A}Tol), 133.40 (d, $^3J_{PC}$ = 11.1 Hz, *m'*-^{C}Tol), 133.3 (d, $^3J_{PC}$ = 11.3 Hz, *m'*-^{B}Tol), 127.6 (d, $^3J_{PC}$ = 13.2 Hz, *m*-^{A}Tol), 127.4 (d, $^3J_{PC}$ = 13.0 Hz, *m*-^{C}Tol), 126.7 (d, $^3J_{PC}$ = 12.8 Hz, *m*-^{B}Tol), 125.1 (br, *i*-C_6F_5), 118.0 (d, $^1J_{PC}$ = 87.2 Hz, *i*-^{B}Tol), 116.3 (d, $^1J_{PC}$ = 85.2 Hz, *i*-^{A}Tol), 116.1 (d, $^1J_{PC}$ = 85.6 Hz, *i*-^{C}Tol), 95.1 (d, $^1J_{PC}$= 86.6 Hz, =CH^{P}), 34.2 (d, $^3J_{PC}$= 7.7 Hz, 6-CH_2), 30.4 (3-

CH_2), 25.0 (5-CH_2), 24.2 (4-CH_2), 23.3 (d, ${}^3J_{PC}$ = 4.5 Hz, ${}^{C}Tol^{CH3}$), 22.6 (d, ${}^3J_{PC}$ = 4.3 Hz, ${}^{A}Tol^{CH3}$), 21.0 (d, ${}^3J_{PC}$ = 4.3 Hz, ${}^{B}Tol^{CH3}$). ${}^{11}B\{{}^1H\}$ NMR (160 MHz, CD_2Cl_2, 213K): δ -17.2 ($\nu_{1/2}$ ~ 230 Hz). ${}^{19}F$ NMR (470 MHz, CD_2Cl_2, 213K): δ -133.2 (2F, *o*), -163.5 (1F, *p*), -166.7 (2F, *m*) (C_6F_5). ${}^{31}P\{{}^1H\}$ NMR (202 MHz, CD_2Cl_2, 213K): δ 11.7 (s, $\nu_{1/2}$ ~ 3 Hz).

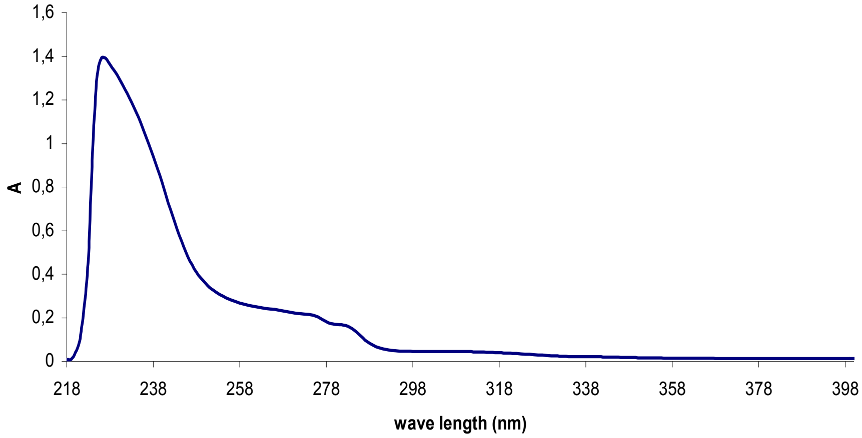
Element analysis: calcd. for $C_{47}H_{31}BF_{15}P \cdot 0.5CH_2Cl_2 \cdot C_5H_{12}$: C, 59.99; H, 3.83. Found: C, 59.95; H, 3.52.

HMRS: calcd. for $C_{47}H_{31}BF_{15}P$ +Na^+: 945.1915. Found: 945.1909.

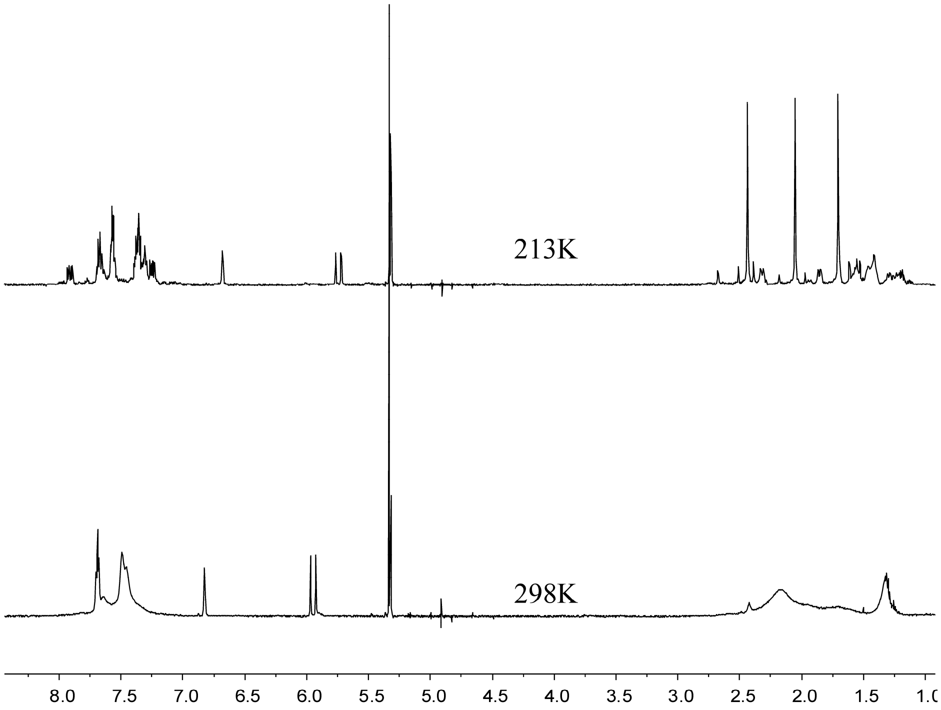
X-ray crystal structure analysis of **2a**: formula $C_{47}H_{31}BF_{15}P \times \frac{1}{2} CH_2Cl_2$, M = 964.96, colorless crystal 0.35 x 0.20 x 0.20 mm, a = 12.3976(5), b = 13.8705(4), c = 15.1225(6) Å, α = 108.590(1), β = 99.318(2), γ = 112.299(2)°, V = 2158.56(14) Å^3, ρ_{calc} = 1.485 g cm^{-3}, μ = 2.031 mm^{-1}, empirical absorption correction ($0.537 \le T \le 0.687$), Z = 2, triclinic, space group P1bar (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 26830 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 7574 independent (R_{int} = 0.039) and 7062 observed reflections [$I \ge 2\,\sigma(I)$], 607 refined parameters, R = 0.050, wR^2 = 0.142, max. (min.) residual electron density 1.04 (-0.59) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. (CCDC 759354).



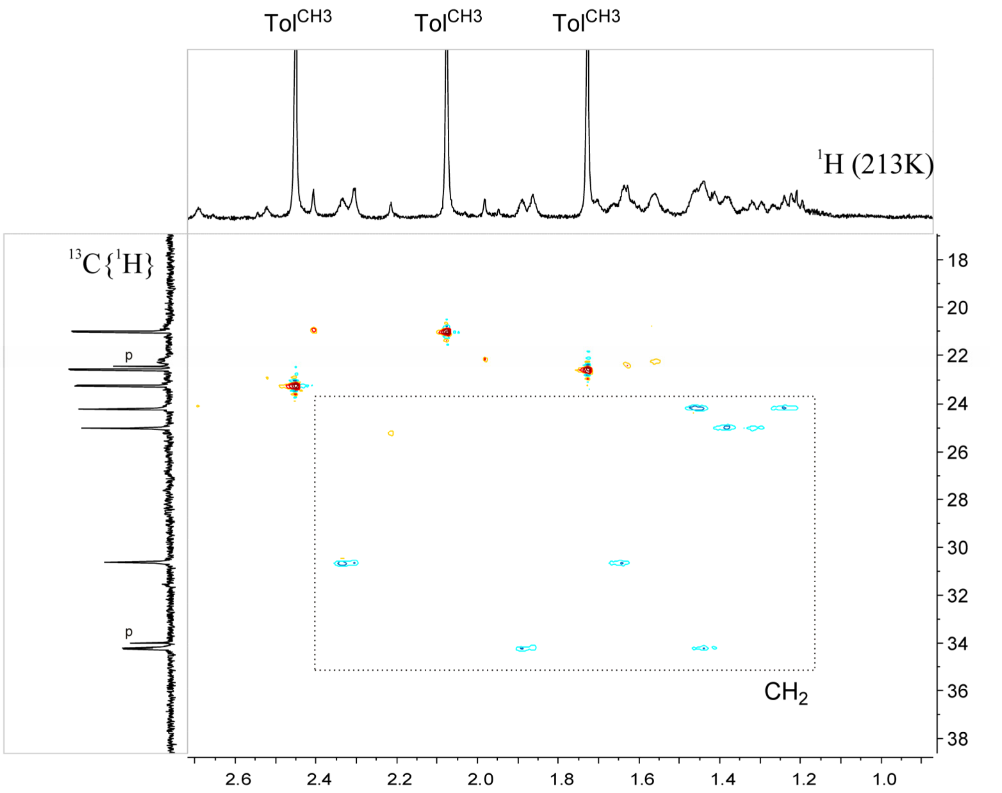
50% probability level



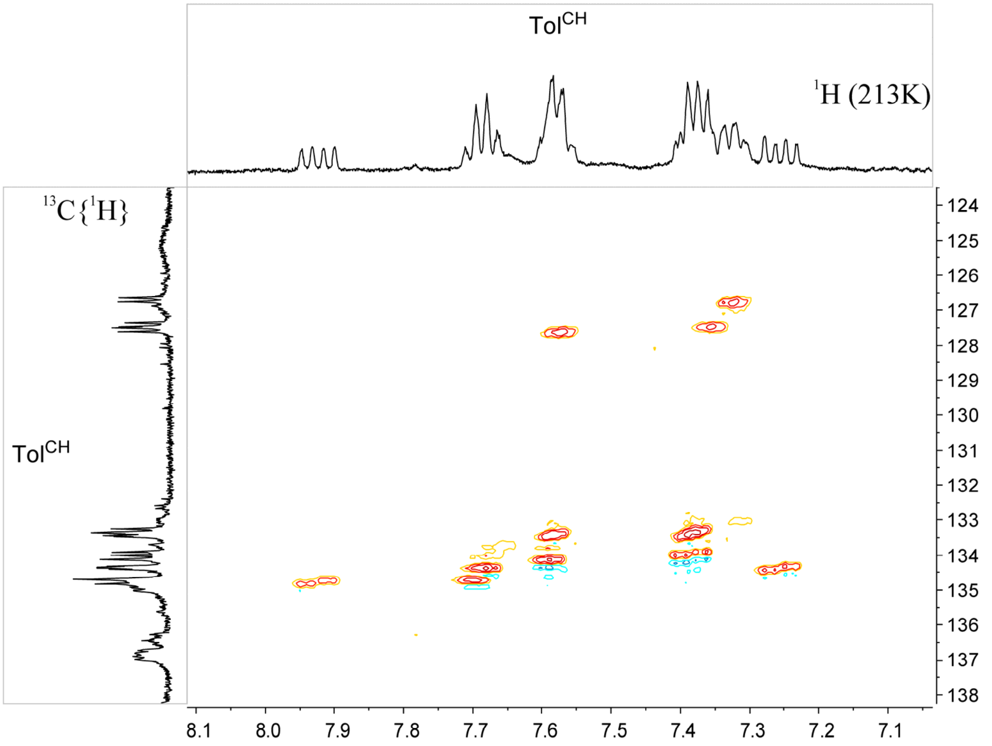
UV-vis spectra of compound **2a** (dichlormethane).



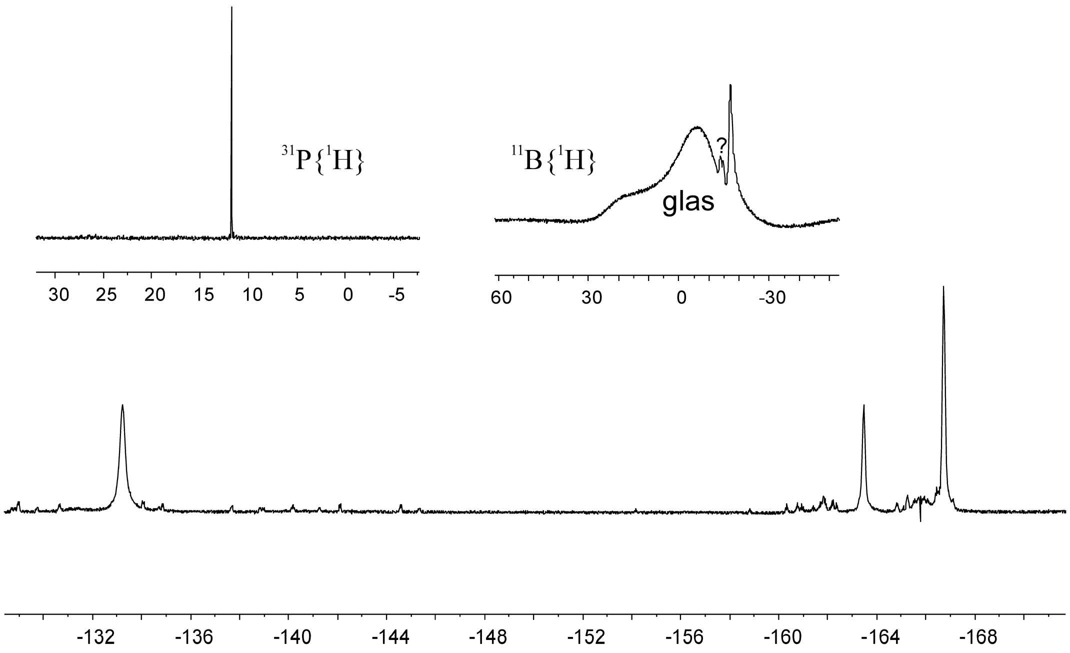
^{1}H NMR (600 MHz, CD_2Cl_2)



^{1}H / ^{13}C ghsqc NMR experiment (500 / 126 MHz, CD_2Cl_2, 213K) (p = pentane)

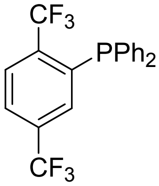


^{1}H / ^{13}C ghsqc NMR experiment (500 / 126 MHz, CD_2Cl_2, 213K)

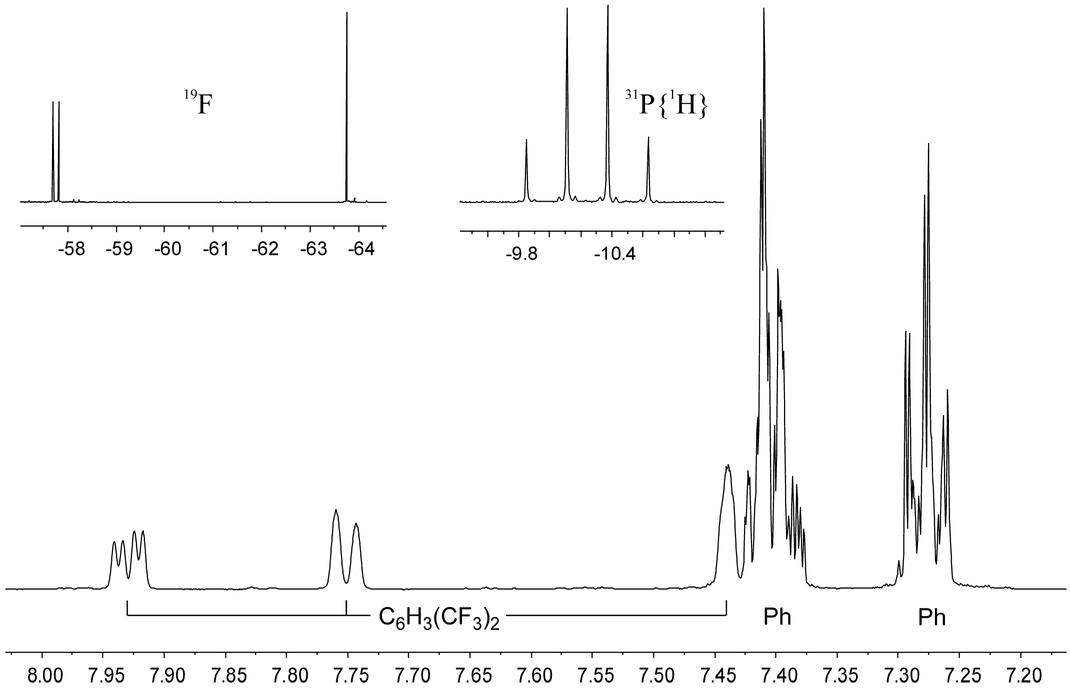


^{19}F NMR (470 MHz, CD_2Cl_2, 213K)

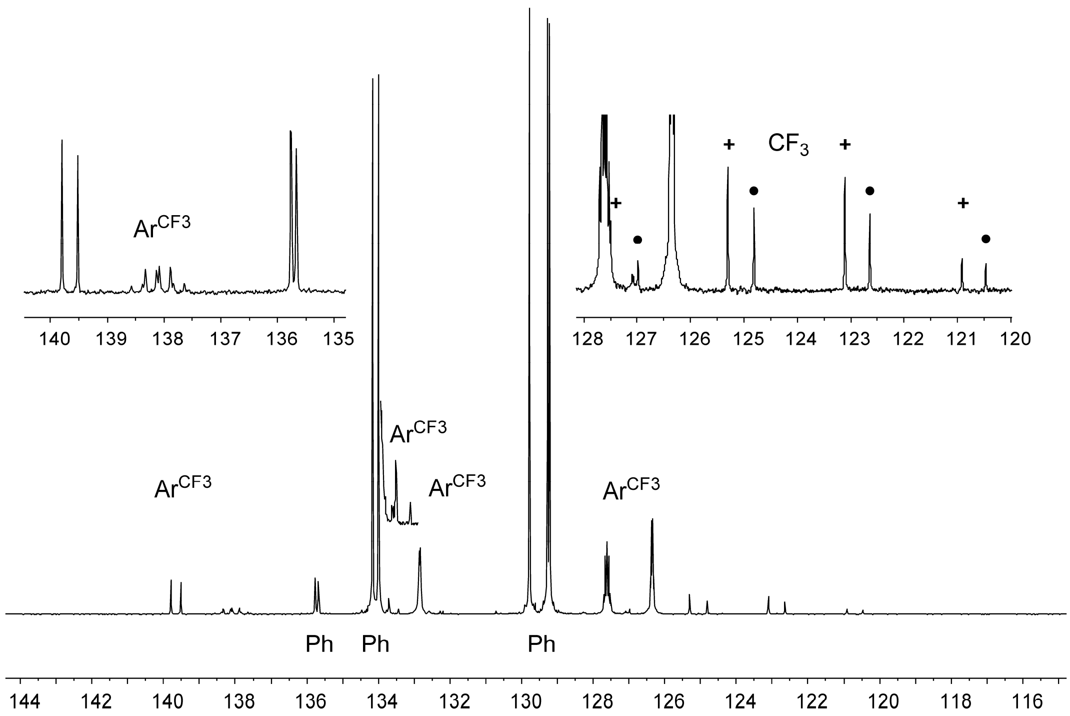
Preparation of $PPh_2(2,5\text{-}(CF_3)_2C_6H_3)$:



Bis(trifluoromethyl)benzene (4.8 mL, 6.42 g, 30 mmol) was dissolved in ether (60 mL) and cooled to 0 °C under argon amosphere. Then BuLi (20 mL, 1.6 M in hexane, 32 mmol) was added dropwise. Afterwards, the solution was allowed to stir for 1 h at room temperature and reflux for further 4 h. The resulting solution was cooled to 0 °C and $ClPPh_2$ (5.6 mL, 30 mmol) was added via syringe. The suspension was stirred at room temperature overnight, before it was quenched with brine (20 mL). The organic phase was separated, dried over $MgSO_4$ and filtered. Finally the solvent was removed. The obtained crude product was first purified by column chromatography (pentane : DCM = 10 : 1) and subsequently crystallized from pentane (10.1 g, 85%, colorless crystal). ^1H NMR (500 MHz, CD_2Cl_2, 298K): δ 7.93 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{PH}$ = 3.4 Hz, 1H, *m*-Ar), 7.75 (dm, $^3J_{HH}$ = 8.3 Hz, 1H, *p*-Ar), 7.44 (br m, 1H, *o*-Ar), 7.41 (m, 2H, *p*-Ph), 7.39 (m, 4H, *m*-Ph), 7.28 (m, 4H, *o*-Ph). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298K): δ 139.7 (d, $^1J_{PC}$ = 35.2 Hz, *i*-Ar), 138.1 (qd, $^2J_{FC}$ = 30.8 Hz, $^3J_{PC}$ = 24.8 Hz, *m*-Ar^{CF3}), 135.7 (d, $^1J_{PC}$ = 11.7 Hz, *i*-Ph), 134.1 (d, $^2J_{PC}$ = 20.8 Hz, *o*-Ph), 133.9 (q, $^2J_{FC}$ = 32.8 Hz, *o*-Ar^{CF3}), 132.8 (m, *o*-Ar^{CH}), 129.8 (*p*-Ph), 129.2 (d, $^3J_{PC}$ = 7.0 Hz, *m*-Ph), 127.6 (sept, $^3J_{FC} \sim {}^3J_{PC}$ = 5.4 Hz, *m*-Ar^{CH}), 126.4 (q, $^3J_{FC}$ = 3.4 Hz, *p*-Ar^{CH}), 124.2 (q, $^1J_{FC}$ = 275.9 Hz, *o*-CF_3), 123.7 (q, $^1J_{FC}$ = 273.2 Hz, *m*-CF_3). ^{19}F NMR (470 MHz, CD_2Cl_2, 298K): δ -57.8 (d, $^4J_{PF}$ = 53.0 Hz, *o*-CF_3,), -63.8 (*m*-CF_3). $^{31}P\{1H\}$ NMR (CD_2Cl_2, 298K): δ -10.2 (q, $^4J_{PF}$ = 53.0 Hz).
Element analysis: calcd. for $C_{20}H_{13}BF_6$: C, 60.31; H, 3.28. Found: C, 60.16; H, 3.26.
HMRS: calcd. for $C_{20}H_{13}F_6P$: 398.0659. Found: 398.0659.

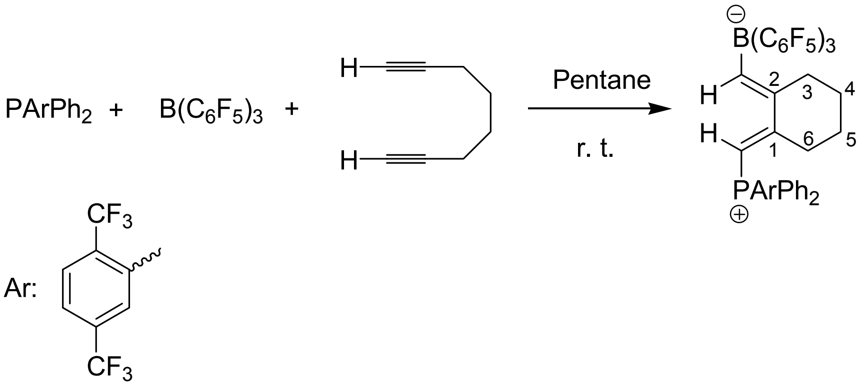


^{1}H NMR (500 MHz, CD_2Cl_2, 298K)



^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298K)

Preparation of compound 2b:



1,7-Octadiyne (10.6 mg, o.1 mmol) and bis-2,5-(trifluoromethyl)phenyl-diphenylphosphine (39.8 mg, 0.1 mmol) were dissolved in pentane (5 mL). Then a solution of $B(C_6F_5)_3$ (52 mg, 0.1 mmol) in pentane (5 mL) was added. The reaction mixture was stirred overnight at room temperature. Subsequently the solvent was decanted and the residue was washed with pentane (3×1 mL). The crude product was purified via crystallization by slow diffusion of pentane into a solution of **2b** in dichloromethane (48 mg, 48%). Crystals suitable for crystal structure analysis were obtained form a solution of **2b** in dichloromethane by slow evaporation of the solvent.

^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ 8.22 (br m, 2H, *m,p*-Ar), 7.60 (br d, $^3J_{PH}$ = 15.9 Hz, 1H, *o*-Ar), 7.87 (m, 2H, *p*-Ph), 7.73 (m, 4H, *m*-Ph), 7.60 (m, 4H, *o*-Ph), 6.96 (br, 1H, $=CH^B$), 6.07 (d, $^2J_{PH}$ = 26.7 Hz, 1H, $=CH^P$), 2.17 (br m, 2H, 3-CH_2), 1.92 (br m, 2H, 6-CH_2), 1.54 (br, 2H, 4-CH_2), 1.38 (m, 2H, 5-CH_2), 1.35 (m, 2H, 4-CH_2). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298K): δ 183.3, 142.8 (d, J_{PC} = 17.7 Hz) (1,2-C), 152.7 (br, $=CH^B$), 148.4 (dm, $^1J_{FC}$ = 241.9 Hz), 138.3 (dm, $^1J_{FC}$ = 250.3 Hz), 136.6 (dm, $^1J_{FC}$ = 247.8 Hz) (C_6F_5), 135.8 (*p*-Ph), 133.7 (d, $^2J_{PC}$ = 10.7 Hz, *o*-Ph), 133.6, 132.7, 132.2 (each m, Ar^{CH}), 131.0 (d, $^3J_{PC}$ = 13.2 Hz, *m*-Ph), 126.1 (br, *i*-C_6F_5), 122.62 (q, $^1J_{FC}$ = 275.9 Hz), 122.54 (q, $^1J_{FC}$ = 273.5 Hz) (CF_3), 122.4 (d, $^1J_{PC}$ = 83.8 Hz, *i*-Ar), 119.7 (d, $^1J_{PC}$ = 89.9 Hz, *i*-Ph), 93.3 (d, $^1J_{PC}$ = 88.7 Hz, $=CH^P$), 36.1 (d, $^3J_{PC}$ = 7.3 Hz, 6-CH_2), 31.2 (3-CH_2), 26.0 (5-CH_2), 24.5 (4-CH_2), n.o. (*o,m*-Ar^{CF3}). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298K): δ -16.5 ($\nu_{1/2}$ ~ 60 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 298K): δ -55.9, -64.1 (each 3F, CF_3), -132.7

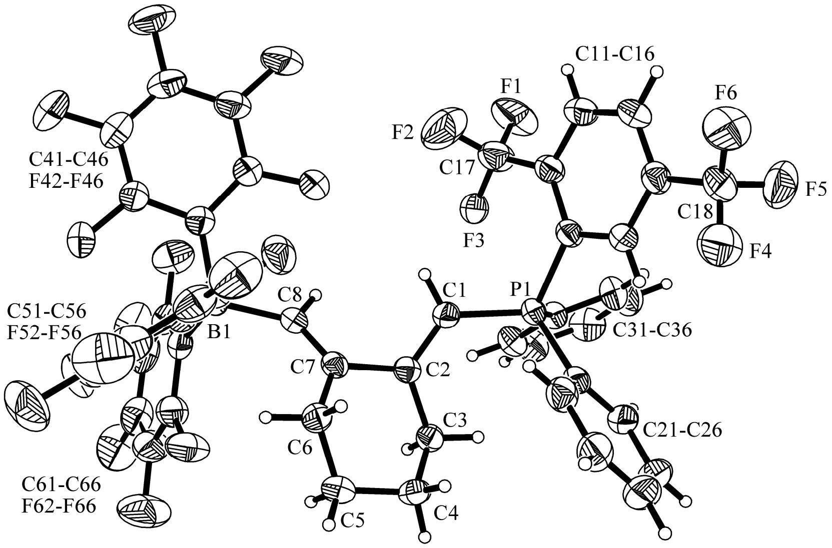
(6F, *o*), -164.0 (3F, *p*), -167.4 (6F, *m*) (C_6F_5). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298K): δ 16.8 ($\nu_{1/2}$ ~ 10 Hz),.

Element analysis: calcd. for $C_{46}H_{23}BF_{21}P$: C, 54.36; H, 2.28. Found: C, 53.45; H, 2.60.

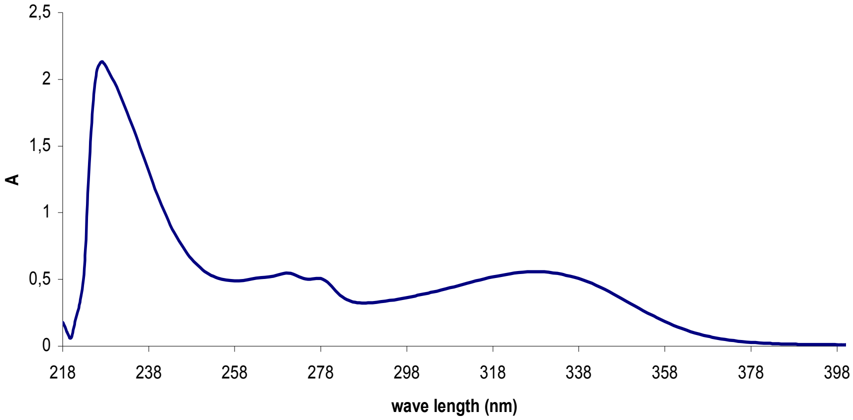
HMRS: calcd. for $C_{46}H_{23}BF_{21}P+Na^+$: 1039.1187. Found: 1039.1185.

X-ray crystal structure analysis of **2b**: formula $C_{46}H_{23}BF_{21}P$, M = 1016.42, colorless crystal 0.25 x 0.25 x 0.05 mm, a = 10.9971(5), b = 11.1320(5), c = 18.0736(7) Å, α = 80.920(2), β = 75.060(2), γ = 75.741(2)°, V = 2061.38(15) Å^3, ρ_{calc} = 1.638 g cm^{-3}, μ = 1.798 mm^{-1}, empirical absorption correction ($0.662 \leq T \leq 0.916$), Z = 2, triclinic, space group P1bar (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 29925 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 7197 independent (R_{int} = 0.054) and 6259 observed reflections [$I \geq 2\,\sigma(I)$], 642 refined parameters, R = 0.057, wR^2 = 0.150, max. (min.) residual electron density 1.08 (-0.90) e Å^{-3}, both CF_3-groups are disordered, refined with split positions using thermal and geometrical restraints, hydrogen atoms calculated and refined as riding atoms. (CCDC 759355).

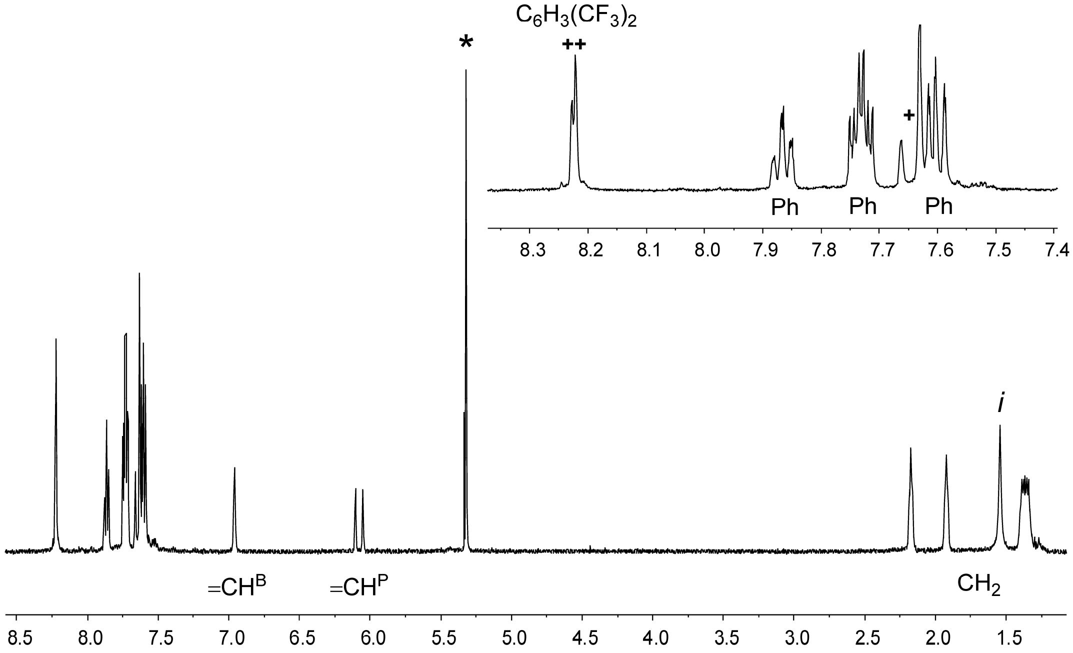
In the figure of **2b** for both CF_3-groups the major component is shown.



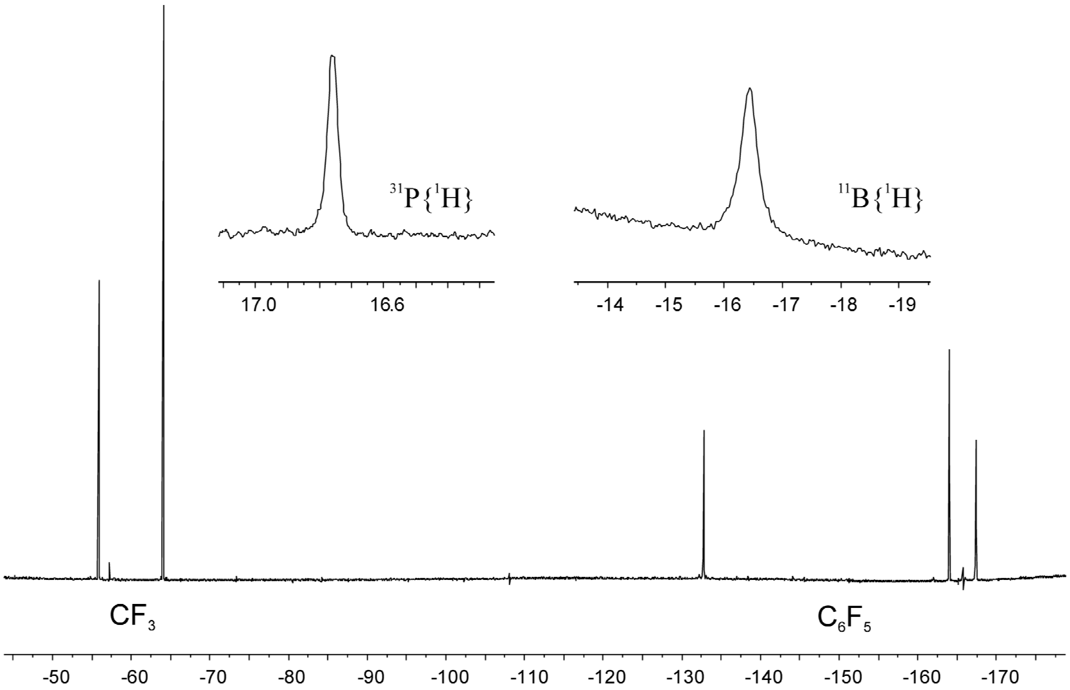
50% probability level



UV-vis spectra of compound **2b** (dichlormethane).

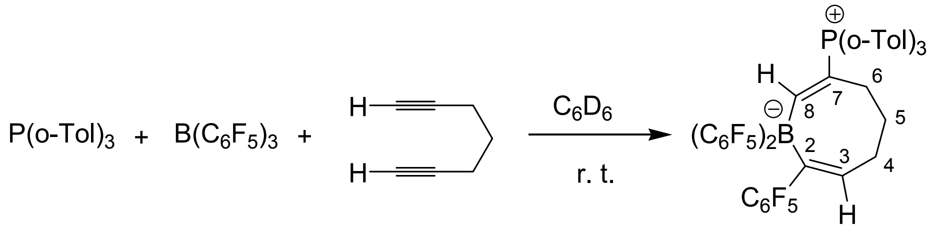


^{1}H NMR (500 MHz, CD_2Cl_2, 298K) [*i* : impurity]



^{19}F NMR (470 MHz, CD_2Cl_2, 298K)

Preparation of compound 4:



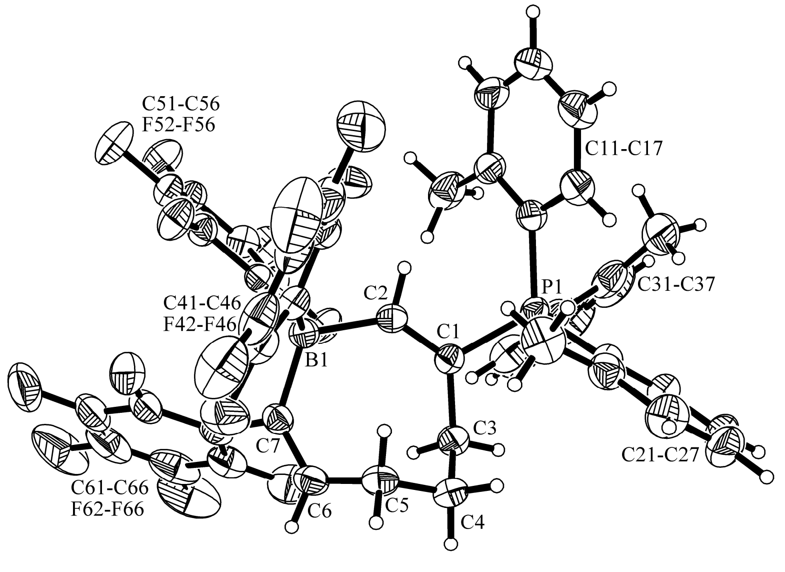
Method 1: 1,6-Heptadiyne (10.6 mg, 0.1 mmol) and tri(*o*-tolyl)phosphine (30.0 mg, 0.1 mmol) were dissolved in C_6D_6 (0.3 mL). Subsequently a solution of $B(C_6F_5)_3$ (52 mg, 0.1 mmol) in C_6D_6 (0.5 mL) was added. The reaction mixture was kept for 1week at room temperature. Then all the solvent was decanted and the residue was quickly washed with cold ether (2×1 mL). The product was collected as colorless crystals (65 mg, 71%).

Method 2: 1,7-Heptadiyne (10.6 mg, 0.1 mmol) and tri(*o*-tolyl)phosphine (30.0 mg, 0.1 mmol) were dissolved in pentane (5 mL). Subsequently a solution of $B(C_6F_5)_3$ (52 mg, 0.1 mmol) in pentane (5 mL) was added. The mixture was stirred overnight at room temperature. Then all the solvent was decanted and the residue was washed with pentane. The crude product was purified via crystallization by slow diffusion of pentane into a solution of **4** in dichloromethane at -20 ^{o}C (43 mg, 48%). Crystals suitable for X-ray structure analysis were obtained from a solution of **4** in benzene after one week.

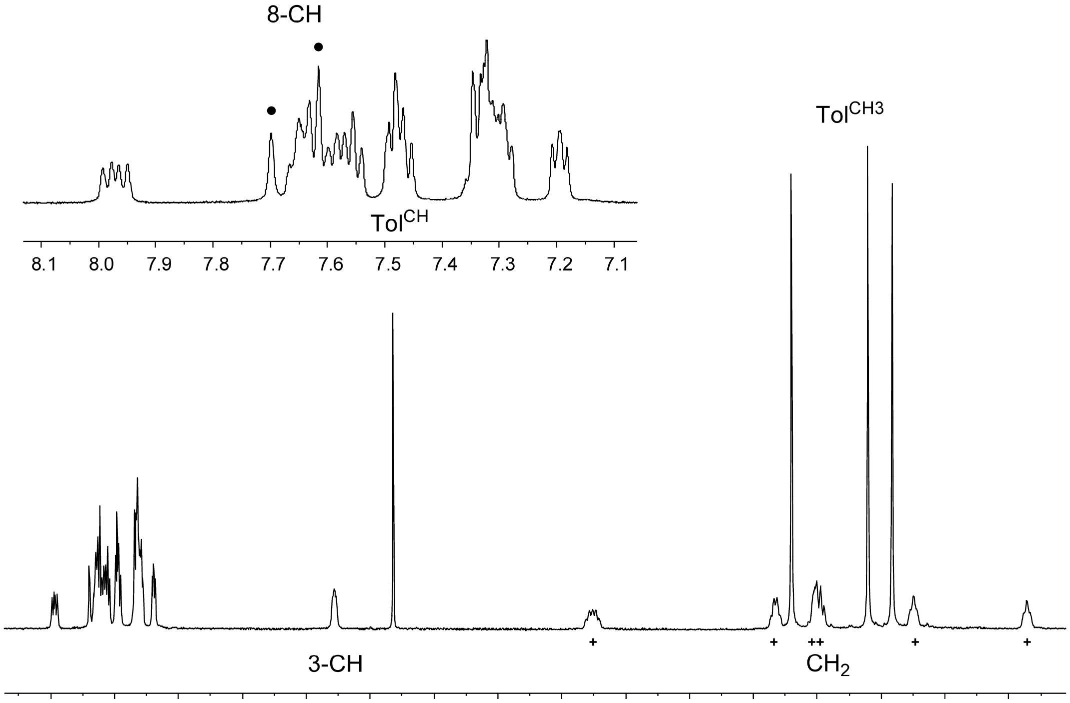
^{1}H NMR (500 MHz, CD_2Cl_2, 193K): δ 7.97 (*o*), 7.63 (*p*), 7.59 (*m*), 7.30 (*m'*) (each m, each 1H, ^{B}Tol), 7.65, 7.48 (m'), 7.34 (*m*), 7.34 (*o*) (each m, each 1H, ^{C}Tol), 7.56 (*p*), 7.48 (*o*), 7.32 (*m*), 7.20 (*m'*) (each m, each 1H, ^{A}Tol), 7.66 (d, $^{3}J_{PH}$ = 41.8 Hz, 1H, 8-CH), 5.79 (br, 1H, 3-CH), 3.77, 1.98 (each br, each 1H, 6-CH_2), 2.33, 2.02 (each br, each 1H, 4-CH_2), 2.21 (s, 3H, ^{C}Tol^{CH3}), 1.61 (s, 3H, ^{B}Tol^{CH3}), 1.42 (s, 3H, ^{A}Tol^{CH3}), 1.25, 0.36 (each br, each 1H, 5-CH_2). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 193K): δ 177.8 (br, 8-C), n.o. (C_6F_5), 144.5 (d, $^{2}J_{PC}$ = 9.7 Hz, *o'*-^{C}Tol), 143.7 (d, $^{2}J_{PC}$ = 7.9 Hz, *o'*-^{A}Tol), 143.1 (d, $^{2}J_{PC}$ = 6.7 Hz, *o'*-^{B}Tol), 141.9 (br, 2-C), 139.8 (3-CH), 135.3 (d, $^{2}J_{PC}$ = 12.4 Hz, *o*-^{B}Tol), 134.9 (d, $^{2}J_{PC}$ = 11.8 Hz, *o*-^{A}Tol), 134.7 (d, $^{2}J_{PC}$ = 11.8 Hz, *o*-^{C}Tol), 133.71, 133.67 (*p*-^{B,C}Tol), 133.4 (*p*-^{A}Tol), 132.9 (d, $^{3}J_{PC}$ = 10.7 Hz, *m'*-^{C}Tol), 132.8 (d, $^{3}J_{PC}$ = 9.4 Hz, *m'*-^{B}Tol), 132.5 (d, $^{3}J_{PC}$ = 10.4 Hz, *m'*-^{A}Tol), 126.9 (d, $^{3}J_{PC}$ = 12.1 Hz, *m*-^{B}Tol), 126.8 (d, $^{3}J_{PC}$ = 10.7 Hz, *m*-^{C}Tol), 126.0 (d, $^{3}J_{PC}$ = 12.4 Hz, *m*-^{A}Tol), 124.3 (t, $^{2}J_{FC}$ = 20.2 Hz, *i*-C_6F_5), 122.7 (br, *i*-BC_6F_5), 118.5 (d, $^{1}J_{PC}$ = 82.0 Hz, *i*-^{B}Tol), 116.1 (d, $^{1}J_{PC}$ = 84.1 Hz, *i*-^{A}Tol), 115.5 (d,

$^{1}J_{PC}$ = 79.2 Hz, *i*-^{C}Tol), 114.9 (d, $^{1}J_{PC}$ = 60.1 Hz, 7-C), 27.6 (br d, $^{2}J_{PC}$ = 14.9 Hz, 6-CH$_2$), 26.9 (4-CH$_2$), 24.8 (5-CH$_2$), 22.34 (d, $^{3}J_{PC}$ = 4.3 Hz, ^{C}Tol^{CH3}), 22.28 (d, $^{3}J_{PC}$ = 3.7 Hz, ^{B}Tol^{CH3}), 20.7 (d, $^{3}J_{PC}$ = 2.8 Hz, ^{A}Tol^{CH3}). ^{11}B{^{1}H} NMR (160 MHz, CD$_2$Cl$_2$, 193K): δ -13.6 ($\nu_{1/2}$ ~ 210 Hz). ^{19}F NMR (470 MHz, CD$_2$Cl$_2$, 193K): δ -129.7, -134.2 (*o*), -162.1 (*p*), -165.0, -167.3 (*m*) (each br, each 1F, BC$_6$F$_5$^{A}), -130.8, -134.7 (*o*), -160.6 (*p*), -164.4, -166.1 (*m*) (each br, each 1F, BC$_6$F$_5$^{B}), -140.0, -145.2 (*o*), -161.8 (*p*), -164.6, -166.0 (*m*) (each br, each 1F, C$_6$F$_5$). ^{31}P{^{1}H} NMR (202 MHz, CD$_2$Cl$_2$, 213K): δ 28.5 ($\nu_{1/2}$ ~ 30 Hz). Element analysis: calcd. for $C_{46}H_{29}BF_{15}P$: C, 60.81; H, 3.22. Found: C, 60.33; H, 3.26. HMRS: calcd. for $C_{46}H_{29}BF_{15}P$+Na^{+}: 931.1758. Found: 931.1753.

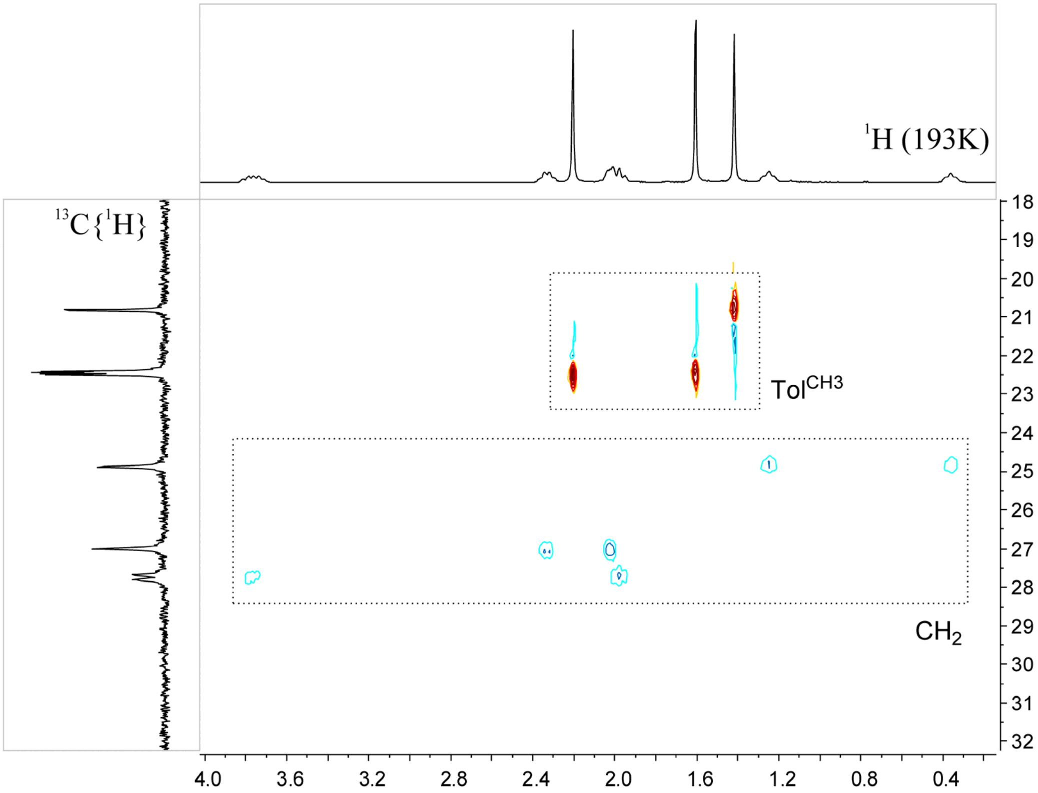
X-ray crystal structure analysis of **4**: formula $C_{46}H_{29}BF_{15}P \times C_6H_6$, *M* = 986.58, colorless crystal 0.30 x 0.15 x 0.10 mm, *a* = 10.6583(3), *b* = 12.9039(5), *c* = 17.8377(10) Å, *α* = 106.182(2), *β* = 103.094(4), *γ* = 98.528(4)°, *V* = 2235.44(16) Å^3, ρ_{calc} = 1.466 g cm^{-3}, μ = 1.439 mm^{-1}, empirical absorption correction (0.672 ≤ *T* ≤ 0.869), *Z* = 2, triclinic, space group *P*1bar (No. 2), λ = 1.54178 Å, *T* = 223(2) K, ω and φ scans, 29409 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.59 Å^{-1}, 7651 independent (R_{int} = 0.052) and 6557 observed reflections [*I* ≥ 2 σ(*I*)], 625 refined parameters, *R* = 0.043, *wR*^{2} = 0.113, max. (min.) residual electron density 0.25 (-0.33) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms. (CCDC 759356).



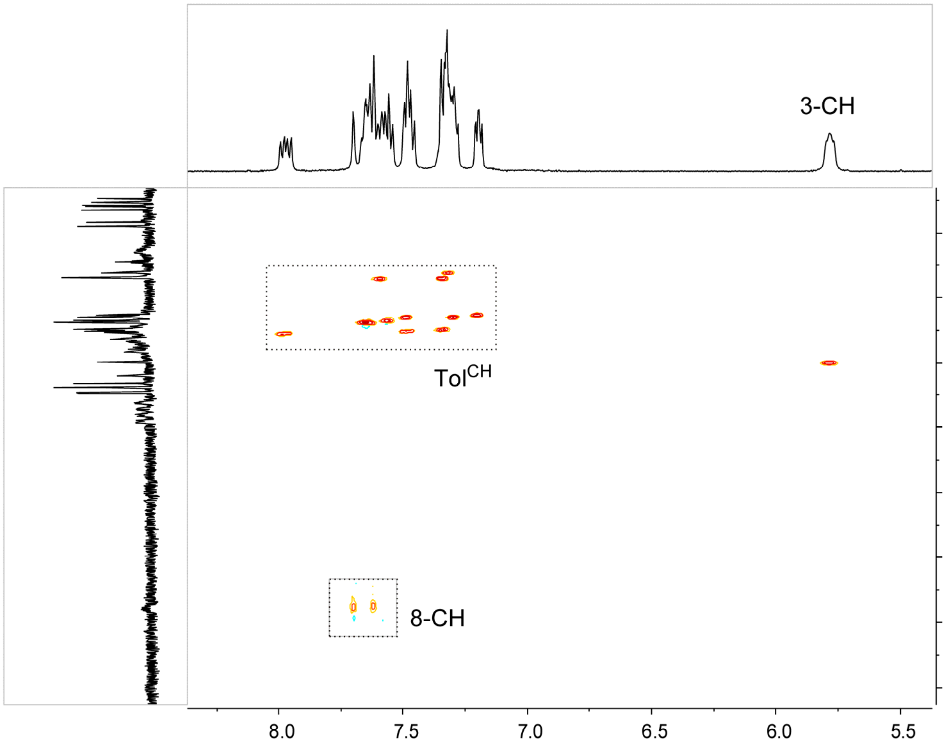
50% probability level



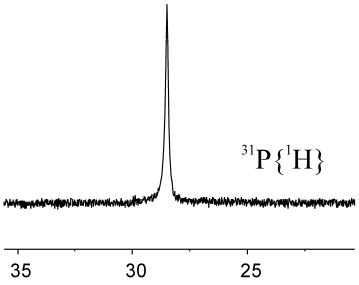
^{1}H NMR (500 MHz, CD_2Cl_2, 193K)

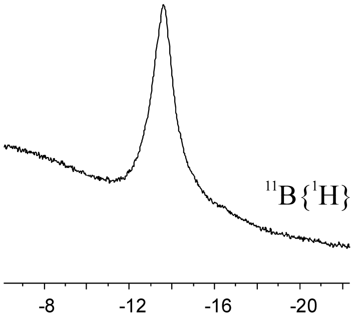


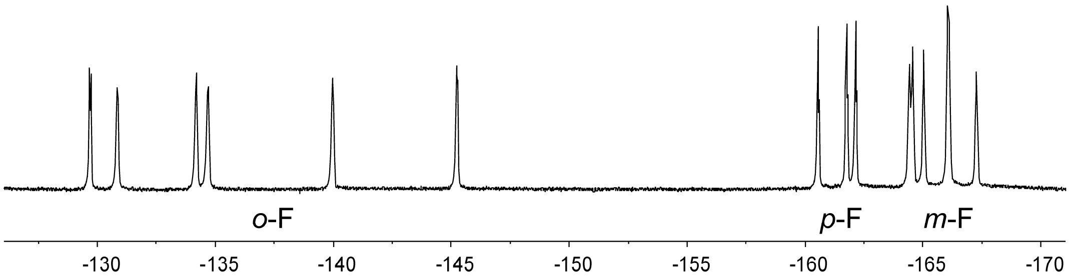
^{1}H / ^{13}C ghsqc NMR experiment (500 / 126 MHz, CD_2Cl_2, 193K)



^{1}H / ^{13}C ghsqc NMR experiment (500 / 126 MHz, CD_2Cl_2, 193K)
(intensity of cosspeak 8-CH was increased)







^{19}F NMR (470MHz, CD_2Cl_2, 193K)