Electronic Control in Frustrated Lewis Pair Chemistry: Adduct Formation of Intramolecular FLP Systems with $-P(C_6F_5)_2$ Lewis Base Components

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Supporting Information

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[‡] X-ray crystal structure analyses

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).

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 Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: For compound ***trans*-8** an unidentified disordered solvent molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek J. Appl. Cryst., 2003, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. The half disordered dichloromethane molecule in compound **11** and the disordered pentane molecule in compound **12**, which could not be refined satisfactorily, were removed using the program SQUEEZE. The chemical formula and the molecular mass don't include the squeezed part of the solvent molecules. For the compound **13** one half molecule of pentane was found in the asymmetric unit and is disordered across an inversion centre. Several restraints (SADI, SIMU, SAME and ISOR) were used in order to improve refinement stability. For the compound **14** the n-butyl isocyanide group was found disordered over two positions. Several restraints (SADI, SIMU, ISOR and SAME) were used in order to improve refinement stability. For compound **16b** one

disordered half molecule of benzene, which could not be refined satisfactorily, was removed using the program SQUEEZE.

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

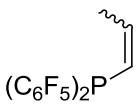
$HB(C_6F_5)_2$ was prepared according to the procedures reported in the literature [a) D. J. Parks, R. E. v. H. Spence and W. E. Piers, *Angew. Chem.*, 1995, **107**, 895-897, (*Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 809-811); b) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492-5503].

$(C_6F_5)_2PCl$ was prepared according to the procedures reported in the literature [D. D. Magnelli, G. Tesi, J. U. Lowe and W. E. McQuistion, *Inorg. Chem.*, 1966, **5**, 457-461; G. Mancino, A. J. Ferguson, A. Beeby, N. J. Long and T. S. Jones, *J. Am. Chem. Soc.*, 2005, **127**, 524-525].

1. Phosphane Precursors

Synthesis of bis(pentafluorophenyl)propenylphosphane (4)

[see: A. Stute, G. Kehr, R. Fröhlich and G. Erker, *Chem. Commun.,* 2011, **47**, 4288-4290]



$(C_6F_5)_2PCl$ (1.00 g, 2.50 mmol) in thf (60 mL) reacted with 1-propenyl-magnesiumbromide (0.5 M solution in thf, 5.00 mL, 2.50 mmol) to get **4** as a red oil (0.994 g, 2.45 mmol, 98%, *E*:*Z* = 0.3:1).

Exact mass: calcd. for $C_{15}H_5F_{10}P + O + Na^+$: 444.98105 m/z; found: 444.98087 m/z.

IR (ATR): ṽ = 1640 (w), 1514 (s), 1466 (s), 1383 (w), 1298 (w), 1084 (s), 971 (s), 835 (w), 762 (w), 736 (w), 699 (w).

Elemental analysis: calcd. for $C_{15}H_5F_{10}P$: C 44.36, H 1.24; found: C 44.46, H 1.17.

Z-Isomer: **^{1}H NMR** (600 MHz, 298 K, C_6D_6): δ = 6.54 (dm, $^3J_{HH,cis}$ = 11.3 Hz, 1H, $^{P}CH^{=}$), 6.15 (ddq, $^3J_{PH}$ = 30.3 Hz, $^3J_{HH,cis}$ = 11.3 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, $^{CH3}CH^{=}$), 1.80 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 298 K, C_6D_6): δ = 147.7 (dm, $^1J_{FC}$ ~ 245 Hz, *p*-C_6F_5), 146.6 (d, $^2J_{PC}$ = 37.4 Hz, $^{CH3}CH^{=}$), 142.3 (dm, $^1J_{FC}$ ~ 255 Hz, *o*-C_6F_5), 137.7 (dm, $^1J_{FC}$ ~ 255 Hz, *m*-C_6F_5), 120.7 (m, $^{P}CH^{=}$), 109.5 (m, *i*-C_6F_5), 16.1 (d, $^3J_{PC}$ = 29.7 Hz, CH_3).

^{19}F NMR (470 MHz, 298 K, C_6D_6): δ = −131.3 (m, 2F, *o*-C_6F_5), −150.7 (tt, $^3J_{FF}$ = 21.0 Hz, $^4J_{FF}$ = 3.7 Hz, 1F, *p*-C_6F_5), −160.9 (m, 2F, *m*-C_6F_5); [$\Delta\delta^{19}F_{p,m}$: 10.2].

^{31}P{^{1}H} NMR (202 MHz, 298 K, C_6D_6): δ = −71.6 (quin, $^3J_{PF}$ = 27.5 Hz).

E-Isomer: **^{1}H NMR** (600 MHz, 298 K, C_6D_6): δ = 6.68 (dm, $^3J_{HH,trans}$ = 16.5 Hz, 1H, $^{P}CH^{=}$), 6.39 (ddq, $^3J_{PH}$ = 21.8 Hz, $^3J_{HH,trans}$ = 16.5 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, $^{CH3}CH^{=}$), 1.51 (dt, $^3J_{HH}$ = 6.5 Hz, $^4J_{PH}$ ~ $^4J_{HH}$ ~ 1.4 Hz, 3H, CH_3).

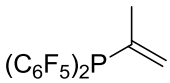
^{13}C{^{1}H} NMR (151 MHz, 298 K, C_6D_6): δ = 149.3 (d, $^2J_{PC}$ = 57.7 Hz, $^{CH3}CH^{=}$), 147.7 (dm, $^1J_{FC}$ ~ 245 Hz, *p*-C_6F_5), 142.3 (dm, $^1J_{FC}$ ~ 255 Hz, *o*-C_6F_5), 137.7 (dm, $^1J_{FC}$ ~ 250 Hz, *m*-C_6F_5), 121.5 (m, $^{P}CH^{=}$), 109.5 (m, *i*-C_6F_5), 20.4 (d, $^3J_{PC}$ = 20.3 Hz, CH_3).

^{19}F NMR (470 MHz, 298 K, C_6D_6): δ = −131.4 (m, 2F, *o*-C_6F_5), −150.8 (tt, $^3J_{FF}$ = 21.4 Hz, $^4J_{FF}$ = 3.5 Hz, 1F, *p*-C_6F_5), −160.9 (m, 2F, *m*-C_6F_5); [$\Delta\delta^{19}F_{p,m}$: 10.1].

^{31}P{^{1}H} NMR (202 MHz, 298 K, C_6D_6): δ = −53.4 (quin, $^3J_{PF}$ = 26.9 Hz).

Synthesis of bis(pentafluorphenyl)-2-propenylphosphane (9)

[see: A. Stute, L. Heletta, R. Fröhlich, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Commun.*, 2012, **48**, 11739-11741]



Chlorobis(pentafluorophenyl)phosphane (7.20 g, 18.0 mmol) in thf (150 mL) reacted with 2-propenylmagnesium bromide (0.5 M in thf, 36.0 mL, 18.0 mmol) at −78 °C to the product (4.69 g, 11.5 mmol, 64%). The product should be kept in the fridge otherwise it slowly decomposes to $(C_6F_5)_2P{-}P(C_6F_5)_2$.

Crystals suitable for crystal structure analysis were obtained by slow evaporation of an *n*-pentane solution at rt.

Exact mass: calcd. for $C_{15}H_5F_{10}P$: 405.9969 m/z; found: 405.9984 m/z.

IR (KBr): ṽ = 2930 (w), 1640 (m), 1514 (s), 1467 (s), 1385 (m), 1290 (m), 1143 (w), 1085 (s), 1016 (w), 972 (s), 941 (m), 839 (m), 764v (w), 729 (w), 637 (w), 587 (w), 515 (m).

Elemental analysis: calcd. for $C_{15}H_5F_{10}P$: C 44.36, H 1.24; found: C 44.46, H 1.20.

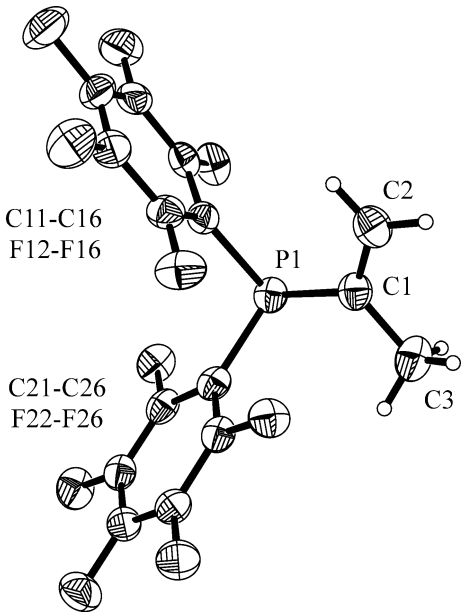
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 5.72 (dm, $^{3}J_{PH}$ = 39.1 Hz, 1H, $^{=}CH_{2,trans}$), 5.53 (dm, $^{3}J_{PH}$ = 16.7 Hz, 1H, $^{=}CH_{2,cis}$), 2.04 (d, $^{3}J_{PH}$ = 8.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = 148.1 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 142.9 (dm, $^{1}J_{FC}$ ~ 260 Hz, C_6F_5), 138.1 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 137.5 (d, $^{1}J_{PC}$ = 17.2 Hz, $^{=}C^{P}$), 128.4 (d, $^{2}J_{PC}$ = 36.8 Hz, $^{=}CH_2$), 108.1 (m, *i*-C_6F_5), 22.0 (dm, $^{2}J_{PC}$ = 14.1 Hz, CH_3).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = −130.3 (m, 2F, *o*-C_6F_5), −150.9 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), −161.4 (m, 2F, *m*-C_6F_5); [$\delta\Delta^{19}F_{p,m}$: 10.5].

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = −42.8 (quin, $^{3}J_{PF}$ = 31.0 Hz).

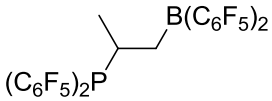
X-ray crystal structure analysis of 9: formula $C_{15}H_5F_{10}P$, *M* = 406.16, colourless crystal, 0.20 x 0.13 x 0.05 mm, *a* = 10.0879(2), *b* = 14.1955(5), *c* = 11.6037(3) Å, *β* = 113.101(2)°, *V* = 1528.44(7) Å^3, ρ_{calc} = 1.765 gcm^{-3}, μ = 2.672 mm^{-1}, empirical absorption correction (0.617 ≤ T ≤ 0.878), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 15206 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 2642 independent (R_{int} = 0.042) and 2233 observed reflections [$I>2\sigma(I)$], 236 refined parameters, *R* = 0.050, wR^2 = 0.142, max. (min.) residual electron density 0.68 (-0.22) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



2. Synthesis of P/B-systems

Hydroboration of bis(pentafluorophenyl)-2-propenylphosphane (9) with bis(pentafluorophenyl)borane to C_2-bridged FLP 10

[see: A. Stute, L. Heletta, R. Fröhlich, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Commun.*, 2012, **48**, 11739-11741]



Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (20.0 mg, 0.049 mmol) and bis(pentafluorophenyl)borane (17.0 mg, 0.049 mmol) were dissolved in deuterated benzene (1 mL) and studied by NMR experiments.[1].

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 3.63 (m, 1H, ^{P}CH), 2.22/1.67 (each m, each 1H, $^{B}CH_2$), 1.10 (dd, $^{3}J_{PH}$ = 19.2 Hz, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ = 35.8 (br d, $^{2}J_{PC}$ = 20.3 Hz, CH_2), 27.4 (m, ^{P}CH), 20.2 (d, $^{2}J_{PC}$ = 22.8 Hz, CH_3); [C_6F_5 not listed].

^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ = 66.0 ($\nu_{1/2}$ ~ 2000 Hz).

[1] Excess of bis(pentafluorophenyl)-2-propenylphosphane is present in the reaction mixture (**9**:**10** ~ 24:76 ^{1}H NMR)

^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = −129.4, −130.0 (each m, each 2F, *o*-$P^{A,B}$), −130.5 (m, 4F, *o*-B), −145.8 (br, 2F, *p*-B), −147.5 (tm, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-P^A), −148.5 (tm, $^3J_{FF}$ = 21.4 Hz, 1F, *p*-P^B), −159.7 (m, 4F, *m*-$P^{A,B}$), −160.4 (m, 4F, *m*-B); [$\Delta\delta^{19}F_{p,m}$: 14.6 (B), 12.2 (P^A), 11.2 (P^B)].

^{31}P{^{1}H} NMR (202 MHz, 299 K, C_6D_6): δ = −34.3 (quin, $^3J_{PF}$ = 30.5 Hz).

^{31}P NMR (202 MHz, 299 K, C_6D_6): δ = −34.3 ($v_{1/2}$ ~ 100 Hz).

Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (25.0 mg, 0.062 mmol) and bis(pentafluorophenyl)borane (21.3 mg, 0.062 mmol) were dissolved in deuterated dichloromethane (1 mL) and studied by DNMR experiments (temperature 26 - −85 °C).

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 3.65 (br, 1H, ^{P}CH), 2.47 (m, 1H, ^{B}CH_2), 1.86 (br, 1H, ^{B}CH_2), 1.22 (dd, $^3J_{PH}$ = 19.7 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3).

^{1}H NMR (600 MHz, 218 K, CD_2Cl_2): δ = 3.60 (br, 1H, ^{P}CH), 2.50 (ddd, $^3J_{PH}$ = 46.4 Hz, J_{HH} = 15.7 Hz, J_{HH} = 10.9 Hz, 1H, ^{B}CH_2), 1.63 (m, 1H, ^{B}CH_2), 1.18 (dd, $^3J_{PH}$ = 19.6 Hz, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 67.8 ($v_{1/2}$ ~ 1200 Hz).

^{11}B{^{1}H} NMR (192 MHz, 228 K, CD_2Cl_2): δ = 53.1 ($v_{1/2}$ ~ 2900 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −129.4 (br, 4F, *o*-B), −130.3 (m, 4F, *o*-P), −147.7 (br, 2F, *p*-B), −148.9, −149.7 (each br, each 1F, *p*-P), −160.7 (br, 4F, *m*-P), −161.3 (br, 4F, *m*-B); [$\Delta\delta^{19}F_{p,m}$: 13.6 (B), 11.0, 11.8 (P)].

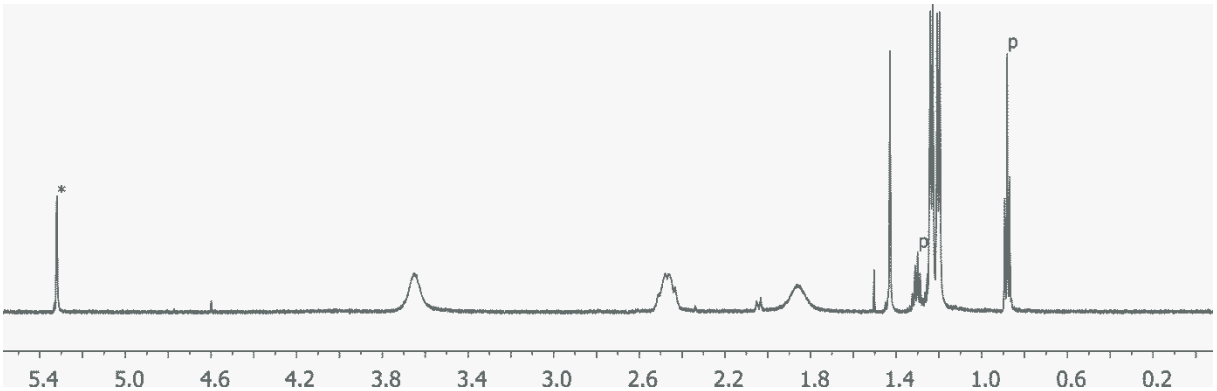
^{19}F NMR (564 MHz, 228 K, CD_2Cl_2): δ = −128.7, −129.5 (each br, each 2F, *o*-P), −130.5 (m, 4F, *o*-B), −147.3, −148.1 (each br, each 1F, *p*-P), −148.7 (br, 2F, *p*-B), −159.8 (m, 4F, *m*-P), −161.4 (m, 4F, *m*-B); [$\Delta\delta^{19}F_{p,m}$: 12.7 (B), 11.7, 12.5 (P)].

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = −32.5 ($v_{1/2}$ ~ 120 Hz).

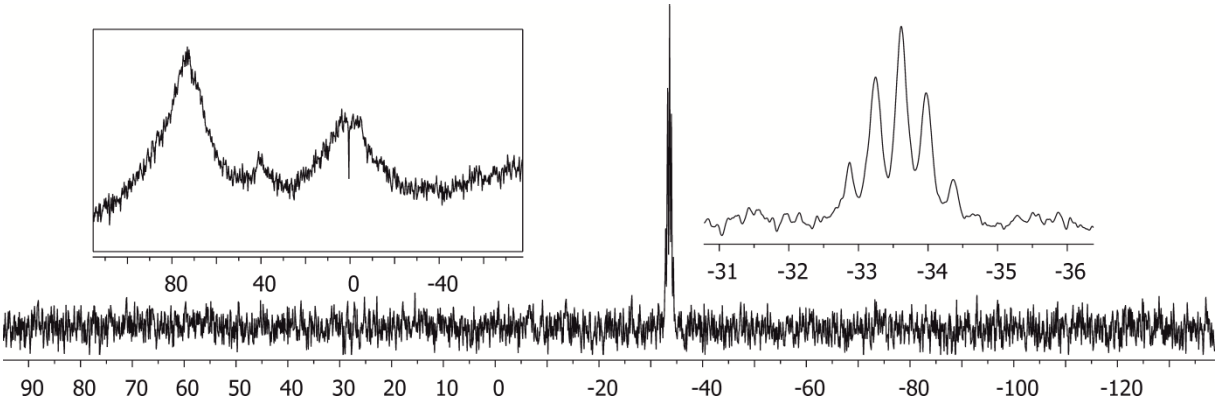
^{31}P{^{1}H} NMR (243 MHz, 228 K, CD_2Cl_2): δ = −28.2 ($v_{1/2}$ ~ 105 Hz).

Exact mass: calcd. for $C_{27}H_6BF_{20}P + H^+$: 753.00536 m/z; found: 753.00662 m/z.[2]

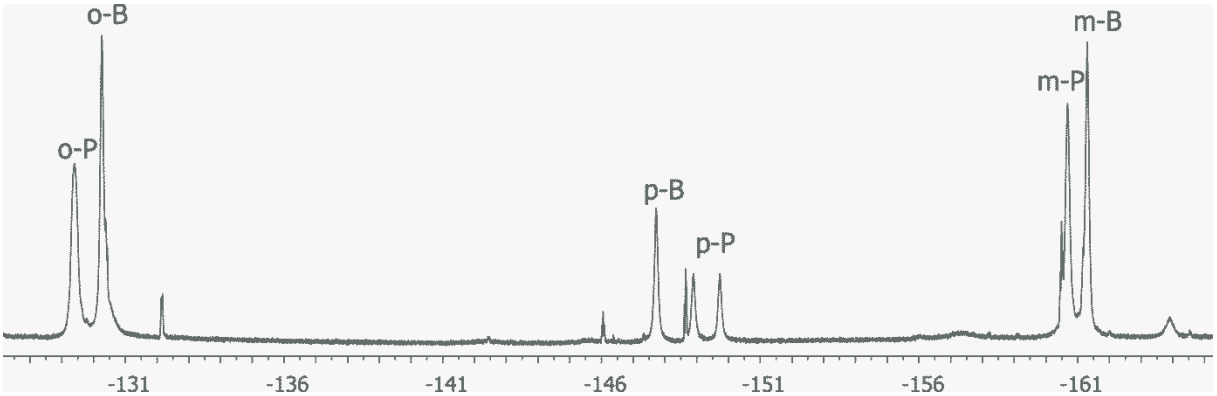
[2] detected during mass spectrometry measurements of acetonitrile adduct **12**.



^{1}H NMR (600 MHz, 299 K, CD_2Cl_2); * CD_2Cl_2; p: pentane.



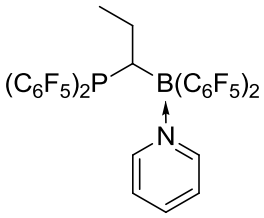
^{31}P{^{1}H} NMR (81 MHz, 300 K, C_6D_6); box: ^{11}B{^{1}H} MR (64 MHz, 300 K, C_6D_6).



^{19}F NMR (564 MHz, 299 K, CD_2Cl_2).

3. Reactions of the C_1-bridged FLP 3

Reaction of C_1-bridged FLP 3 with pyridine to 5



Bis(pentafluorophenyl)propenylphosphane (**4**) (200 mg, 0.49 mmol) and bis(pentafluorophenyl)borane (170 mg, 0.49 mmol) were dissolved in *n*-pentane (30 mL) and stirred for two min. Pyridine (38.9 mg, 0.49 mmol) was added and a white precipitate crushed out immediately. The solid was isolated *via* filter cannula, washed with *n*-pentane (2x20 mL) and dried *in vacuo* to give the product as white powder (228 mg, 0.275 mmol, 56%).

IR (KBr): $\tilde{\nu}$ = 3136 (w), 2973 (w), 2943 (w), 2602 (w), 2363 (w), 1642 (s), 1518 (s), 1460 (s), 1377 (s), 1284 (s), 1165 (w), 1091 (s), 984 (s), 867 (w), 70 (s), 745 (s), 704 (s).

Elemental analysis: calcd. for $C_{32}H_{11}BF_{20}NP$: C 46.24, H 1.33, N 1.69; found: C 46.66, H 1.21, N 1.47.

Mp (DSC): 161 °C.

^{1}H NMR (500 MHz, 298 K, C_7D_8): δ = 8.61 (br, 2H, *o*-py), 6.80 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-py), 6.49 (m, 2H, *m*-py), 4.00 (m, 1H, ^{P}CH^B), 1.26/0.46 (each m, each 1H, CH_2), 0.49 (m, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 298 K, C_7D_8): δ = 146.5 (d, J_{PC} = 16.2 Hz, *o*-py), 141.9 (*p*-py), 124.3 (*m*-py), 24.7 (br, ^{P}CH^B), 23.4 (br d, $^2J_{PC}$ = 3.9 Hz, CH_2), 13.6 (d, $^3J_{PC}$ = 7.9 Hz, CH_3); [C_6F_5 not listed].

^{13}C{^{31}P} NMR (125 MHz, 298 K, C_7D_8): δ = 146.5 (s, *o*-py), 141.9 (*p*-py), 124.3 (*m*-py), 24.7 (br, ^{P}CH^B), 23.4 (s, CH_2), 13.6 (s, CH_3); [C_6F_5 not listed].

^{1}H{^{1}H} TOCSY (500 MHz, 298 K, C_7D_8): δ^1H_{irr} / δ^1H_{res} = 6.80 / 8.61, 6.49 (*p*-py / *o*-py, *m*-py), 6.49 / 8.61, 6.80 (*m*-py / *o*-py, *p*-py), 4.00 / 1.28, 0.49 (^{P}CH^B / CH_2, CH_3), 1.28 / 4.00, 0.49, 0.48 (CH_2 / ^{P}CH^B, CH_3, CH_2), 0.49 / 4.00, 1.28, 0.48 (CH_3 / ^{P}CH^B, CH_2), 0.48 / 4.00, 1.28, 0.49 (CH_2 / ^{P}CH^B, CH_2, CH_3).

^{1}H,^{1}H GCOSY (500 MHz, 298 K, C_7D_8): δ^1H / δ^1H = 8.61 / 6.49 (*o*-py / *m*-py), 6.80 / 6.49 (*p*-py / *m*-py), 6.49 / 8.61, 6.80 (*m*-py / *o*-py, *p*-py), 4.00 / 1.28, 0.49 (^{P}CH^B / CH_2, CH_3), 1.28 / 4.00, 0.49, 0.48 (CH_2 / ^{P}CH^B, CH_3, CH_2), 0.49 / 4.00, 1.28, 0.48 (CH_3 / ^{P}CH^B, CH_2), 0.48 / 1.28, 0.49 (CH_2 / CH_2, CH_3).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, C_7D_8): δ^{1}H / δ^{13}C = 8.61 / 146.5 (*o*-py), 6.80 / 141.9 (*p*-py), 6.49 / 124.3 (*m*-py), 4.00 / 24.7 ($^{P}CH^{B}$), 1.28 / 23.4 (CH_2), 0.49 / 13.6 (CH_3), 0.48 / 23.4 (CH_2).

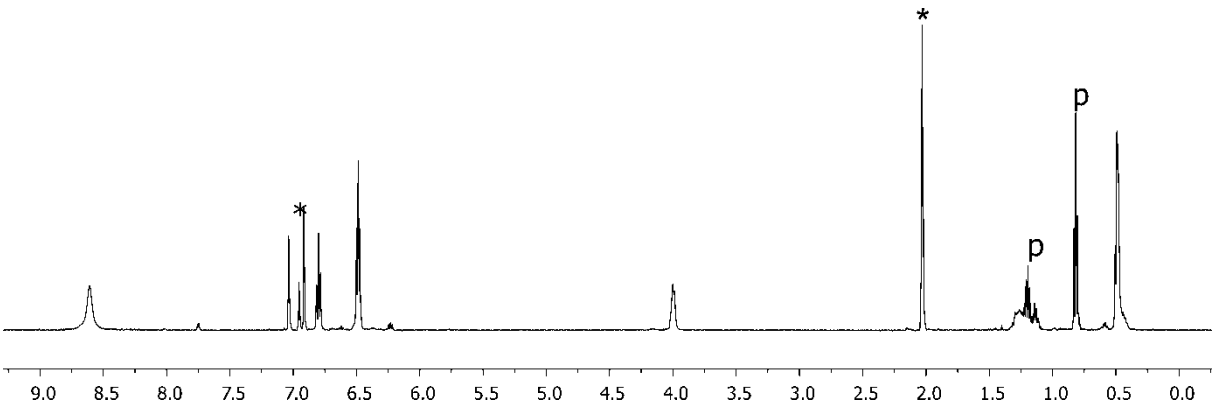
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, C_7D_8): δ^{1}H / δ^{13}C = 6.80 / 146.5 (*p*-py / *o*-py), 6.49 / 146.5 (*m*-py / *o*-py), 0.49 / 23.4 (CH_3 / CH_2), 0.48 / 13.6 (CH_2 / CH_3).

^{11}B{^{1}H} NMR (160 MHz, 298 k, C_7D_8): δ = −0.1 ($v_{1/2}$ ~ 200 Hz).

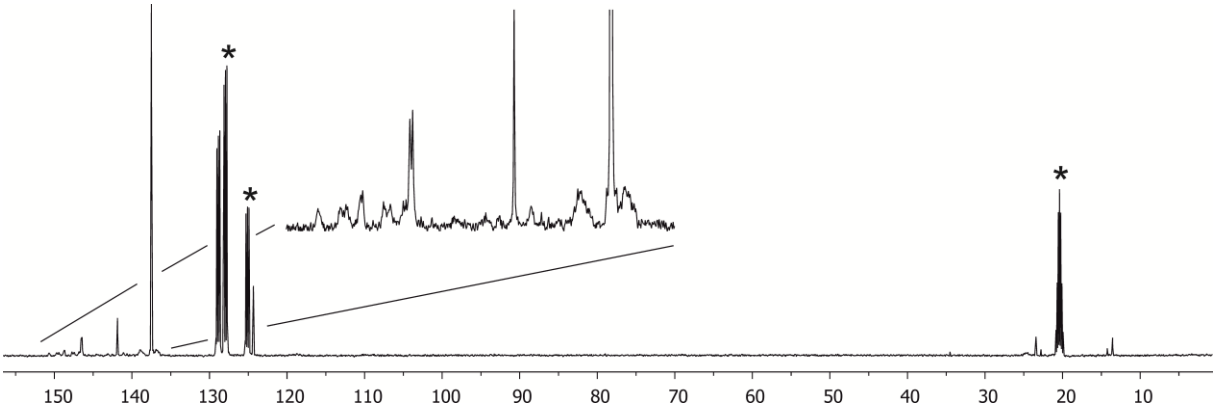
^{19}F NMR (470 MHz, 248 K, C_7D_8): δ = −125.8 (s, 2F, *o*-P^A), −126.9 (s, 1F, *o*-B^A), −128.2 (s, 2F, *o*-B^B), −129.4 (s, 2F, *o*-P^B), −133.1 (s, 1F, *o´*-B^A), −148.0 (s, 1F, *p*-P^A), −149.8 (t, $^{3}J_{FF}$ = 2.8 Hz, 1F, *p*-P^B), −154.8 (t, $^{3}J_{FF}$ = 21.0 Hz, 1F, *p*-B^A), −156.3 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-B^B), −160.4 (m, 2F, *m*-P^B), −160.5 (br, 1F, *m´*-B^A), −161.1 (m, 2F, *m*-P^A), −162.6 (br, 1F, *m*-B^A), −162.9 (m, 2F, *m*-B^B); [$\Delta\delta^{19}F_{p,m}$: 5.7, 7.8 (B^A), 6.6 (B^B), 13.1 (P^A), 10.6 (P^B)].

^{19}F,^{19}F GCOSY (470 MHz, 248 K, C_7D_8): δ^{19}F / δ^{19}F = −125.8 / −161.1 (*o*-P^A / *m*-P^A), −126.9 / −162.6 (*o*-B^A / *m*-B^A), −129.4 / −160.4 (*o*-P^B / *m*-P^B), −133.1 / −160.5, −162.6 (*o´*-B^A / *m´*-B^A, *m*-B^A), −148.0 / −161.1 (*p*-P^A / *m*-P^A), −149.8 / −160.4 (*p*-P^B / *m*-P^B), −154.8 / −160.5, −162.6 (*p*-B^A / *m´*-B^A, *m*-B^A), −156.3 / −162.9 (*p*-B^B / *m*-B^B), −160.4 / −129.4, −149.8 (*m*-P^B / *o*-P^B, *p*-P^B), −160.5 / −133.1, −154.8 (*m´*-B^A / *o´*-B^A, *p*-B^A), −161.1 / −125.8, −148.0 (*m*-P^A / *o*-P^A, *p*-P^A), −162.6 / −126.9, −133.1, −154.8 (*m*-B^A / *o*-B^A, *o´*-B^A, *p*-B^A), −162.9 / −128.2, −156.3 (*m*-B^B / *o*-B^B, *p*-B^B).

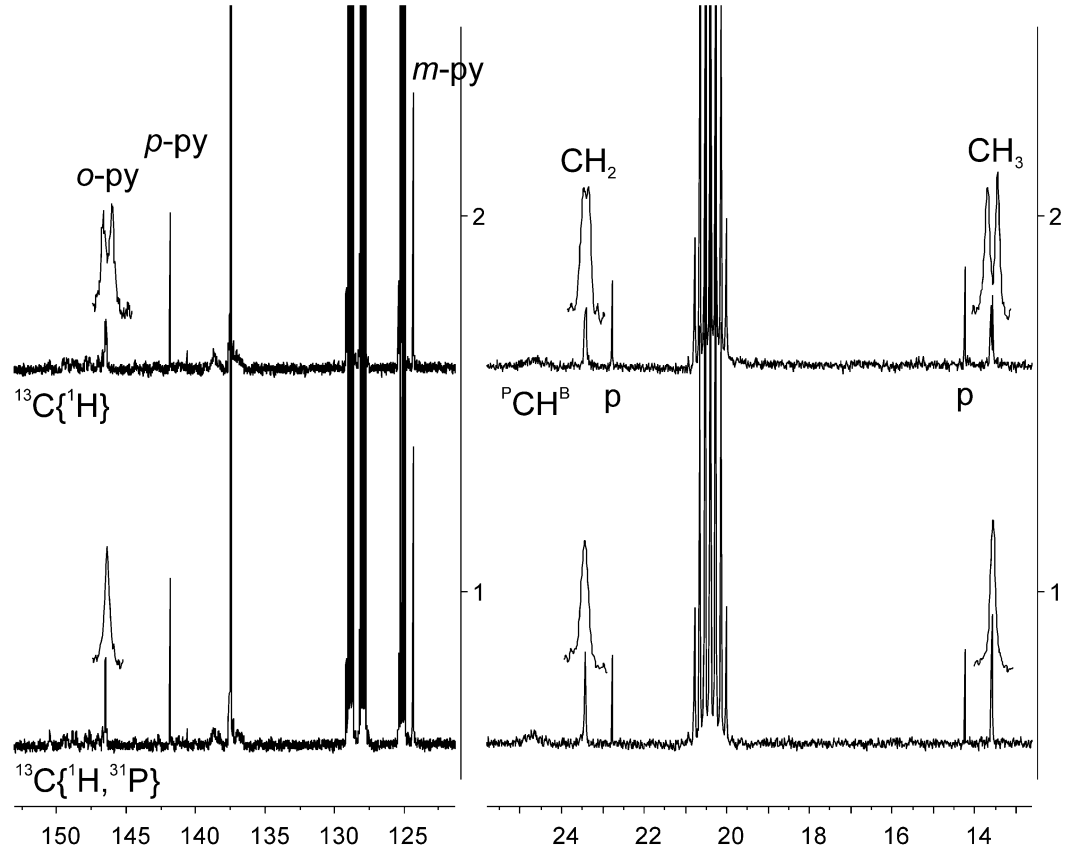
^{31}P{^{1}H} NMR (202 MHz, 298 K, C_7D_8): δ = −51.3 (m, $v_{1/2}$ ~ 120 Hz).



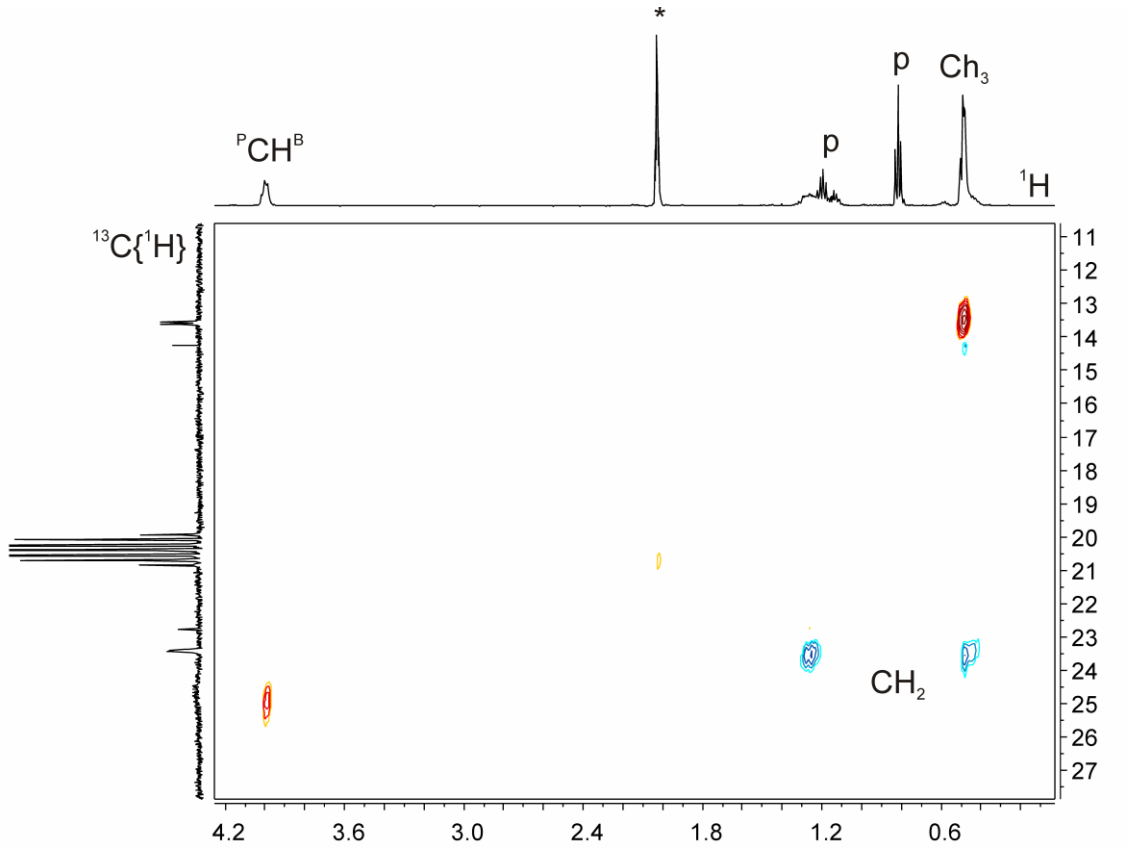
^{1}H NMR (500 MHz, 298 K, C_7D_8(*)); p: pentane.



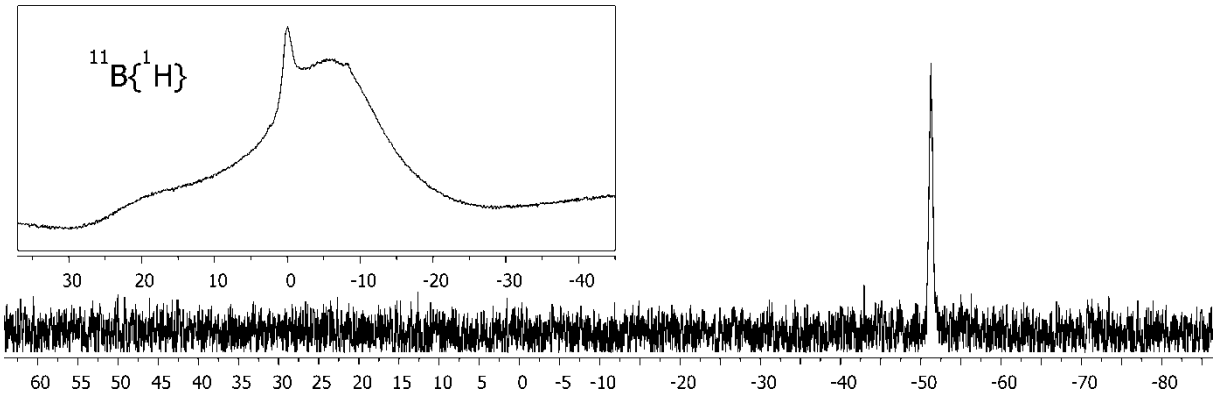
$^{13}C\{^{1}H\}$ NMR (125 MHz, 298 K, C_7D_8(*)).



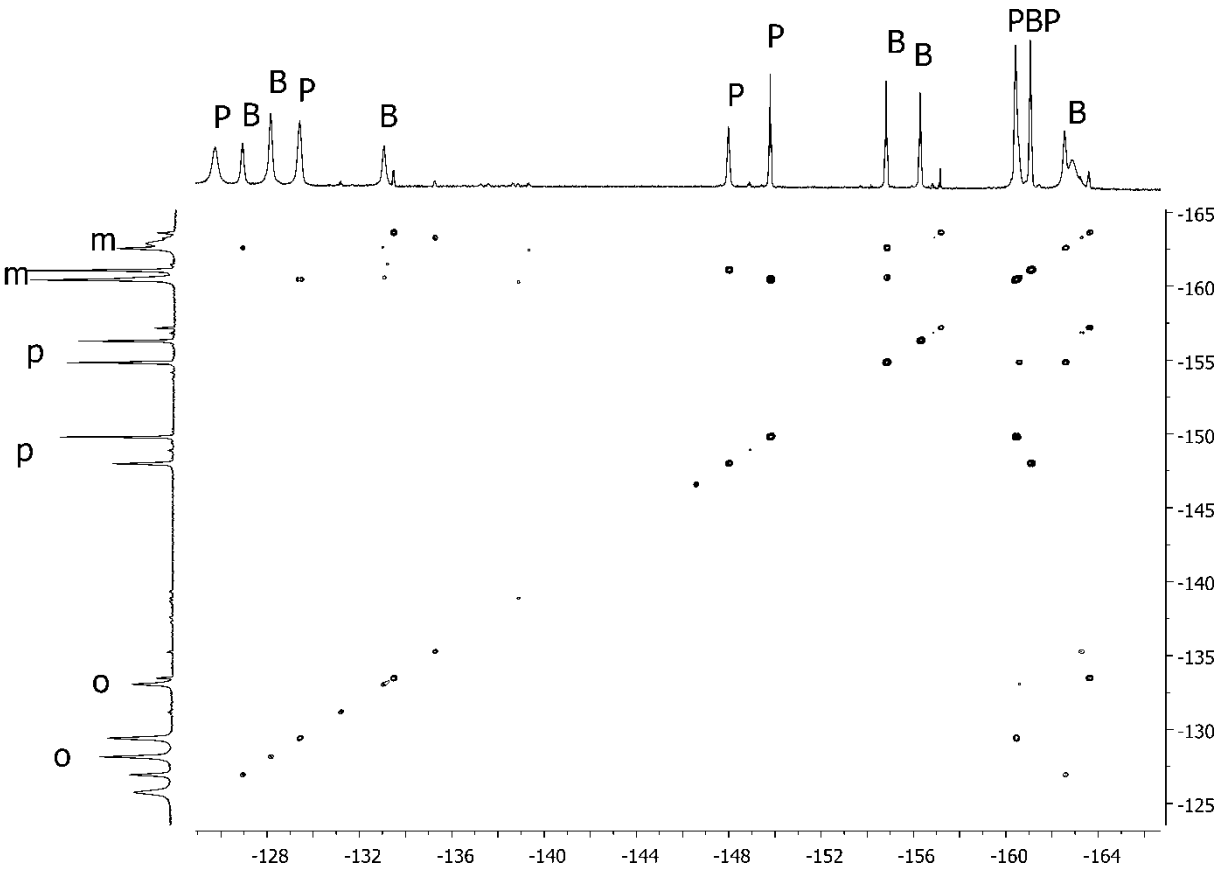
1: $^{13}C\{^{1}H,^{31}P\}$ NMR (126 MHz, 298 K, C_7D_8); 2: $^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, C_7D_8); p: pentane.



^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, C_7D_8(*), projections: ^{1}H and $^{13}C\{^{1}H\}$, respectively); p: pentane.

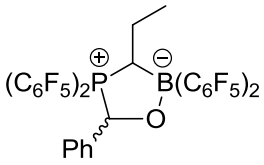


$^{31}P\{^{1}H\}$ NMR (202 MHz, 298 K, C_7D_8); box: $^{11}B\{^{1}H\}$ NMR (160 MHz, 298 k, C_7D_8).



$^{19}F,^{19}F$ GCOSY (470 MHz, 248 K, C_7D_8).

Reaction of C_1-bridged FLP 3 with benzaldehyde to 7



Bis(pentafluorophenyl)propenylphosphane (**4**) (200 mg, 0.49 mmol) and bis(pentafluorophenyl)borane (170.3 mg, 0.49 mmol) were dissolved in *n*-pentane (10 mL) and stirred for five min at rt. Benzaldehyde (52.3 mg, 0.49 mmol) was added and a white precipitate crushed out. The suspension was stirred for 30 min at rt before the solid was isolated on a Schlenk-frit and washed with *n*-pentane (10 mL). Drying *in vacuo* gave the product (190 mg, 0.22 mmol, 45%). According to $^{31}P\{^{19}F\}$ and ^{1}H NMR spectra two isomers in a ratio of 1:0.4 are present in CD_2Cl_2 solution at 258K.

Single crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of compound **7** in dichloromethane at −30 °C.

IR (KBr): ṽ = 2991 (w), 2940 (w), 2885 (w), 1644 (s), 1598 (w), 1519 (s), 1483 (s), 1459 (s), 1381 (m), 1287 (m), 1224 (w), 1185 (w), 1103 (s), 1027 (w), 973 (s), 919 (m), 872 (w), 836 (w), 784 (m), 751 (m), 726 (w), 710 (m), 626 (w), 588 (w), 540 (w), 521 (w).

Elemental analysis: calcd. for $C_{34}H_{12}BF_{20}P$: C 47.58, H 1.41; found: C 47.01, H 0.95.

Mp: 159 °C (DSC); **Dp**: 210 °C (DSC).

Major isomer:

^{1}H NMR (500 MHz, 258 K, CD_2Cl_2): δ = 7.30 (br, 3H, *o*,*p*-Ph), 7.25 (m, 2H, *m*-Ph), 6.36 (d, $^{2}J_{PH}$ = 15.3 Hz, 1H, ^{O}CH), 3.25 (br d, $^{2}J_{PH}$ = 21.8 Hz, 1H, ^{P}CH^{B}), 1.96/1.71 (each br, each 1H, CH_2), 0.91 (br, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 258 K, CD_2Cl_2): δ = 133.9 (*i*-Ph), 130.1 (d, *J* = 4.5 Hz, *p*-Ph)^{t}, 128.7 (*m*-Ph), 126.9 (br, *o*-Ph)^{t}, 85.8 (d, $^{1}J_{PC}$ = 30.8 Hz, ^{O}CH), 34.2 (br, ^{P}CH^{B}), 19.5 (m, CH_2), 16.6 (m, CH_3); [C_6F_5 not listed, ^{t} tentatively assigned].

^{1}H,^{1}H GCOSY (500 MHz, 258 K, CD_2Cl_2): δ^{1}H / δ^{1}H = 6.36 / 1.71 (^{O}CH / CH_2), 3.25 / 1.96, 1.71 (^{P}CH^{B} / CH_2), 1.96 / 1.71, 0.91 (CH_2 / CH_2, CH_3), 1.71 / 3.25, 1.96, 0.91 (CH_2 / ^{P}CH^{B}, CH_2, CH_3), 0.91 / 1.96, 1.71 (CH_3 / CH_2).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 258 K, CD_2Cl_2): δ^{1}H / δ^{13}C = 7.30 / 130.1, 126.9 (*o*-,*p*-Ph), 7.25 / 128.7 (*m*-Ph), 6.36 / 85.8 (^{O}CH), 3.25 / 34.2 (^{P}CH^{B}), 1.96, 1.71 / 19.5 (CH_2), 0.91 / 16.6 (CH_3).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 258 K, CD_2Cl_2): δ^{1}H / δ^{13}C = 7.25 / 133.9, 128.7 (*m*-Ph / *i*-Ph, *m*-Ph), 0.91 / 19.5 (CH_3 / CH_2).

^{11}B{^{1}H} NMR (160 MHz, 258 K, CD_2Cl_2): δ = 1.9 ($\nu_{1/2}$ ~ 120 Hz).

^{19}F NMR (470 MHz, 258 K, CD_2Cl_2): δ = −124.1 (br, 2F, *o*-P^{A}), −132.3 (m, 2F, *o*-B^{A}), n.o. (*o*-P^{B}), −134.5 (m, 2F, *o*-B^{B}), −138.7 (m, 1F, *p*-P^{A}), −140.0 (m, 1F, *p*-P^{B}), −155.4 (m, 2F, *m*-P^{A}), −157.3 (br, 2F, *m*-P^{B}), −157.9 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-B^{A}), −159.6 (t, $^{3}J_{FF}$ = 19.9 Hz, 1F, *p*-B^{B}), −164.0 (m, 2F, *m*-B^{A}), −164.7 (m, 2F, *m*-B^{B}); [$\Delta\delta^{19}F_{p,m}$: 6.1 (B^{A}), 5.1 (B^{B}), 16.7 (P^{A}), 17.3 (P^{B})].

^{19}F,^{19}F GCOSY (470 MHz, 258 K, CD_2Cl_2): δ^{19}F / δ^{19}F = −124.1 / −138.7, −155.4 (*o*-P^{A} / *p*-P^{A}, *m*-P^{A}), −132.3 / −164.0 (*o*-B^{A} / *m*-B^{A}), −134.5 / −164.7 (*o*-B^{B} / *m*-B^{B}), −138.7 / −124.1, −155.4 (*p*-P^{A} / *o*-P^{A}, *m*-P^{A}), −140.0 / −157.3 (*p*-P^{B} / *m*-P^{B}), −155.4 / −124.1, −138.7 (*m*-P^{A} / *o*-P^{A}, *p*-P^{A}), −157.3 / −140.0 (*m*-P^{B} / *p*-P^{B}), −157.9 / −164.0 (*p*-B^{A} / *m*-B^{A}), −159.6 / −164.7 (*p*-B^{B} / *m*-B^{B}), −164.0 / −132.3, −157.9 (*m*-B^{A} / *o*-B^{A}, *p*-B^{A}), −164.7 / −134.5, −159.6 (*m*-B^{B} / *o*-B^{B}, *p*-B^{B}).

$^{31}P\{^{19}F\}$ NMR (202 MHz, 258 K, CD_2Cl_2): δ = 27.9 ($v_{1/2}$ ~ 85 Hz).

Minor isomer (key resonances were listed):

^{1}H NMR (500 MHz, 258 K, CD_2Cl_2): δ = 7.28 (m, 5H, Ph), 6.17 (d, $^{2}J_{PH}$ = 13.9 Hz, 1H, ^{O}CH), 3.70 (br s, 1H, $^{P}CH^{B}$), 2.24 (br d, $^{3}J_{PH}$ ~ 39 Hz)/1.89 (br) (each 1H, CH_2), 0.96 (br, 3H, CH_3).

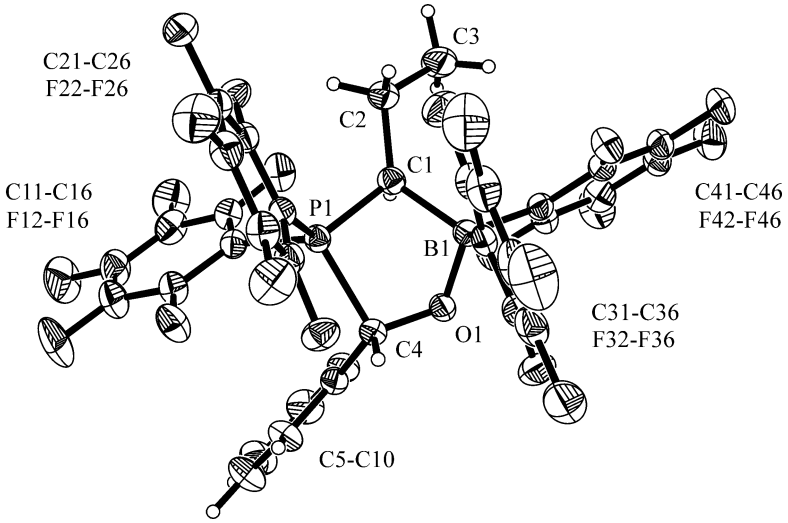
$^{11}B\{^{1}H\}$ NMR (160 MHz, 258 K, CD_2Cl_2): δ = 1.9 ($v_{1/2}$ ~ 120 Hz).

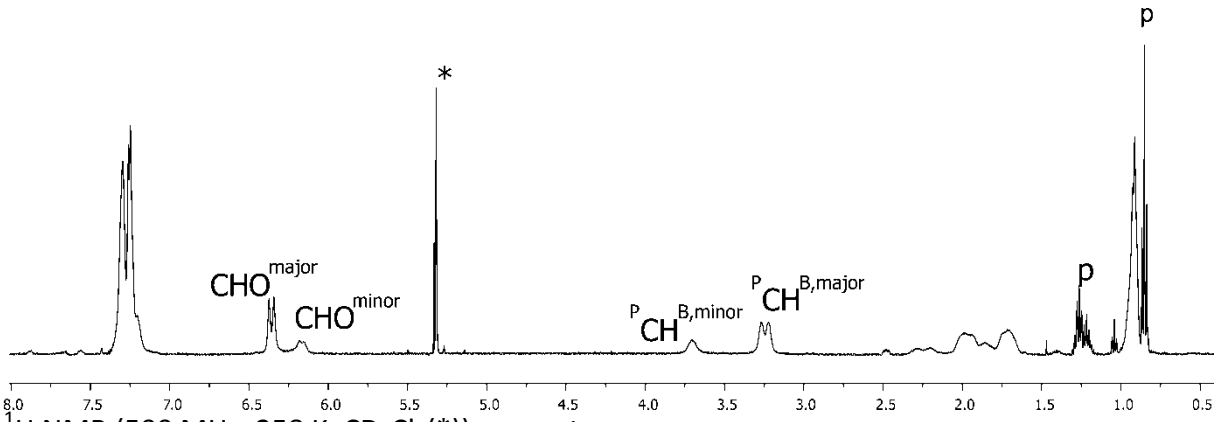
^{19}F NMR (470 MHz, 258 K, CD_2Cl_2): δ = −123.1 (m, 2F, *o*-P^A), −125.4 (m, 2F, *o*-P^B), −138.8 (m, 1F, *p*-P^A), −139.5 (m, 1F, *p*-P^B), −154.9 (m, 2F, *m*-P^B), −157.6 (m, 2F, *m*-P^A), −159.0 (m, 1F, *p*-B^A), −159.5 (m, 1F, *p*-B^B), −164.8 (br, 2F, *m*-B^A), −165.4 (br, 2F, *m*-B^B), n.o. (*o*-B); [$\Delta\delta^{19}F_{p,m}$: 5.8 (B^A), 5.9 (B^B), 18.8 (P^A), 15.4 (P^B)].

$^{19}F,^{19}F$ GCOSY (470 MHz, 258 K, CD_2Cl_2): δ(^{19}F) / δ(^{19}F) = −123.1 / −138.8, −157.6 (*o*-P^A / *p*-P^A, *m*-P^A), −125.4 / −139.5, −154.9 (*o*-P^B / *p*-P^B, *m*-P^B), −138.8 / −123.1, −157.6 (*p*-P^A / *o*-P^A, *m*-P^A), −139.5 / −125.4, −154.9 (*p*-P^B / *o*-P^B, *m*-P^B), −154.9 / −125.4, −139.5 (*m*-P^B / *o*-P^B, *p*-P^B), −157.6 / −123.1, −138.8 (*m*-P^A / *o*-P^A, *p*-P^A), −159.0 / −164.8 (*p*-B^A / *m*-B^A), −159.5 / −165.4 (*p*-B^B / *m*-B^B), −164.8 / −159.0 (*m*-B^A / *p*-B^A), −165.4 / −159.5 (*m*-B^B / *p*-B^B).

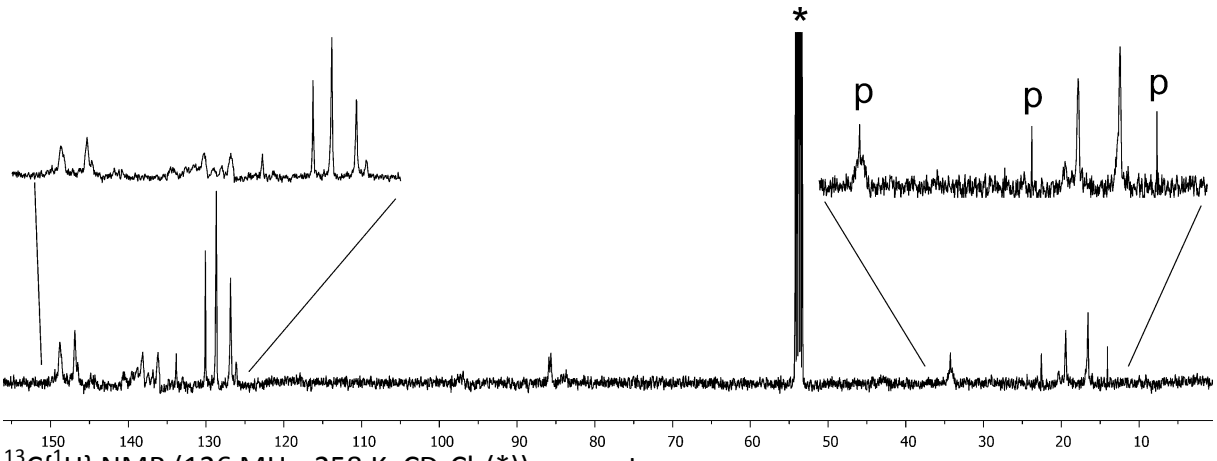
$^{31}P\{^{19}F\}$ NMR (202 MHz, 258 K, CD_2Cl_2): δ = 20.4 ($v_{1/2}$ ~ 90 Hz).

X-ray crystal structure analysis of *trans*-7: formula $C_{34}H_{12}BF_{20}OP$, *M* = 858.22 colourless crystal, 0.27 x 0.05 x 0.02 mm, *a* = 8.8560(4), *b* = 12.7840(6), *c* = 14.4856(12) Å, α = 95.877(4), *β* = 96.842(6), γ = 92.121(3)°, *V* = 1617.74(17) $Å^3$, ρ_{calc} = 1.762 gcm^{-3}, μ = 2.133 mm^{-1}, empirical absorption correction (0.596 ≤ T ≤ 0.958), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 24788 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 $Å^{-1}$, 5522 independent (R_{int} = 0.052) and 4263 observed reflections [$I>2\sigma(I)$], 515 refined parameters, *R* = 0.044, wR^2 = 0.107, max. (min.) residual electron density 0.20 (-0.26) e.$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

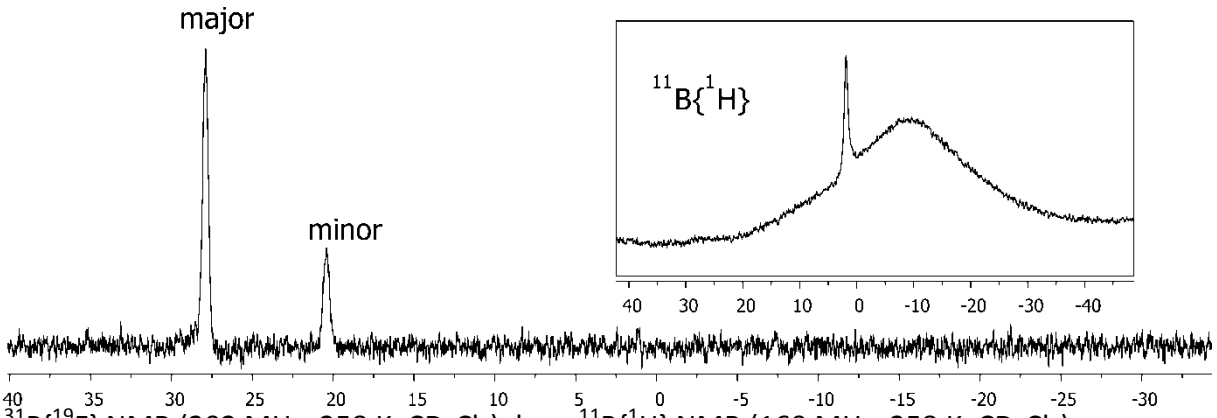




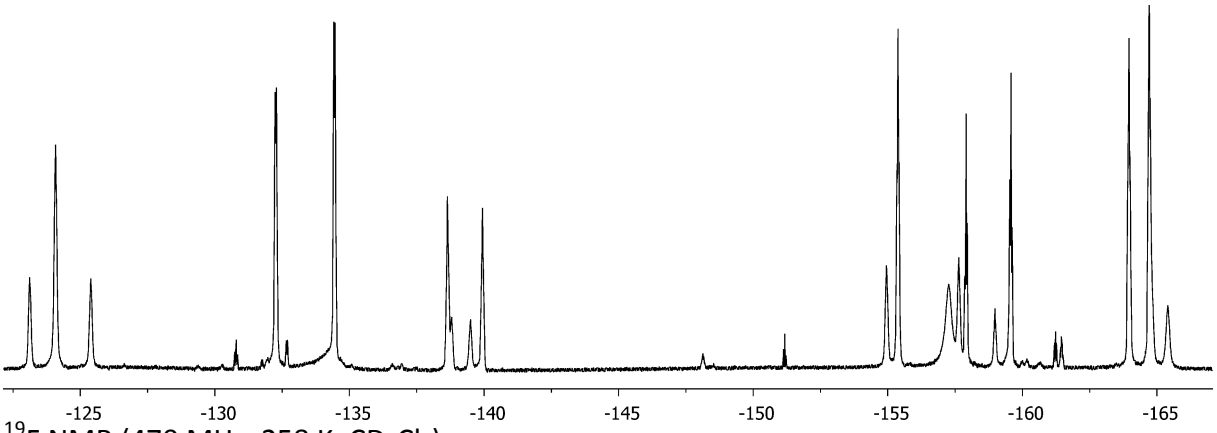
^{1}H NMR (500 MHz, 258 K, CD_2Cl_2(*)); p: pentane.



$^{13}C\{^{1}H\}$ NMR (126 MHz, 258 K, CD_2Cl_2(*)); p: pentane.

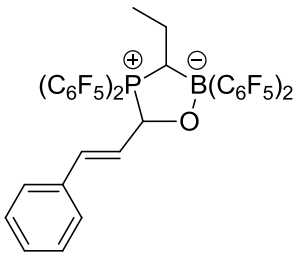


$^{31}P\{^{19}F\}$ NMR (202 MHz, 258 K, CD_2Cl_2); box: $^{11}B\{^{1}H\}$ NMR (160 MHz, 258 K, CD_2Cl_2).



^{19}F NMR (470 MHz, 258 K, CD_2Cl_2).

Reaction of C_1-bridged FLP 3 with cinnamic aldehyde to 8



Bis(pentafluorophenyl)propenylphosphane (**4**) (200 mg, 0.49 mmol) and bis(pentafluorophenyl)borane (170 mg, 0.49 mmol) were dissolved in *n*-pentane (15 mL) and stirred at rt for five min before cinnamic aldehyde (64.8 mg, 0,49 mmol) was added. The solution turned yellow and was stirred at rt for one hour. The reaction mixture was concentrated *in vacuo* until a white precipitate crushed out, which was isolated *via* filter cannula and then dried *in vacuo* to give the product as a white solid (151 mg, 0.171 mmol, 35%).

Single crystals suitable for X-ray crystal structure analysis were obtained from a solution of **8** in C_6D_6.

IR (KBr): $\tilde{\nu}$ = 2964 (w), 2935 (w), 2877 (w), 1644 (m), 1522 (s), 1486 (s), 1464 (s), 1389 (w), 1305 (m), 1293 (m), 1105 (s), 981 (s), 752 (m), 694 (w), 639 (w), 526 (w).

Elemental analysis: calcd. for $C_{36}H_{14}BF_{20}OP$: C48.90, H 1.60; found: C 48.71, H 1.77.

Mp: 90 °C (DSC); **Dp**: 131 °C (DSC).

^{1}H NMR (500 MHz, 298 K, CD_2Cl_2): δ = 7.30 (m, 5H, Ph), 6.97 (dd, $^{3}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 7.4 Hz, 1H, $^{=}CH^{CH}$), 6.33 (d, $^{3}J_{HH}$ = 15.2 Hz, 1H, $^{=}CH^{Ph}$), 5.88 (br d, $^{3}J_{HH}$ = 7.4 Hz, 1H, ^{O}CH), 3.57 (dm, $^{2}J_{PH}$ = 16.8 Hz, 1H, $^{P}CH^{B}$), 1.91/1.65 (each br m, each 1H, CH_2), 0.93 (t, $^{3}J_{HH}$ = 7.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 298 K, CD_2Cl_2): δ = 136.1 (d, $^{2}J_{PC}$ = 13.6 Hz, $^{=}CH^{CH}$), 135.6 (d, $^{4}J_{PC}$ = 4.6 Hz, *i*-Ph), 129.2 (*p*-Ph), 129.1, 127.0 (each Ph), 120.1 (d, $^{3}J_{PC}$ = 5.6 Hz, $^{=}CH^{Ph}$), 83.3 (d, $^{1}J_{PC}$ = 38.1 Hz, ^{O}CH), 34.4 (br, $^{P}CH^{B}$), 21.5 (CH_2), 16.4 (d, $^{3}J_{PC}$ = 6.4 Hz, CH_3); [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, 298 K, CD_2Cl_2): δ^{1}H / δ^{1}H = 6.97 / 6.33, 5.88 ($^{=}CH^{CH}$ / $^{=}CH^{Ph}$, ^{O}CH), 6.33 / 6.97, 5.88 ($^{=}CH^{Ph}$ / $^{=}CH^{CH}$, ^{O}CH), 5.88 / 6.97, 6.33 (^{O}CH / $^{=}CH^{CH}$, $^{=}CH^{Ph}$), 3.57 / 1.91, 1.65 ($^{P}CH^{B}$ / CH_2), 1.91, 1.65 / 3.57, 0.93 (CH_2 / $^{P}CH^{B}$, CH_3), 0.93 / 1.91, 1.65 (CH_3 / CH_2).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, CD_2Cl_2): δ^{1}H / δ^{13}C = 7.30 / 129.2, 129.1, 127.0 (Ph), 6.97 / 136.1 ($^{=}CH^{CH}$), 6.33 / 120.1 ($^{=}CH^{Ph}$), 5.88 / 83.3 (^{O}CH), 1.91, 1.65 / 21.5 (CH_2), 0.93 / 16.4 (CH_3).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, CD_2Cl_2): δ^{1}H / δ^{13}C = 7.30 / 135.6, 129.2, 127.0 (Ph / *i*-Ph, Ph), 1.65 / 16.4 (CH_2 / CH_3), 0.93 / 21.5 (CH_3 / CH_2).

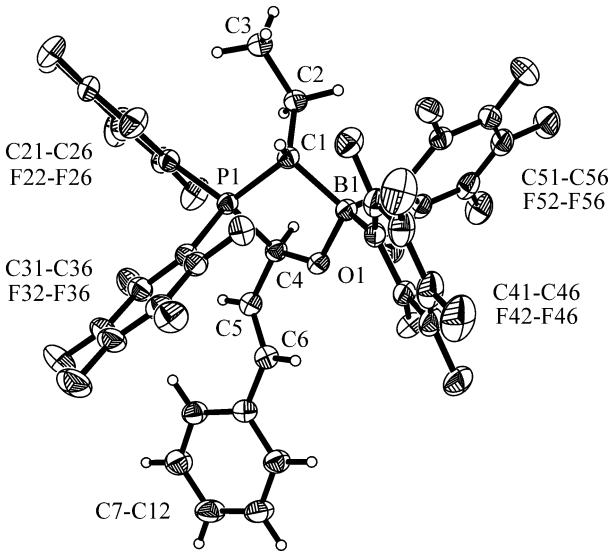
^{11}B{^{1}H} NMR (160 MHz, 298 K, CD_2Cl_2): δ = 2.6 ($\nu_{1/2}$ ~ 70 Hz).

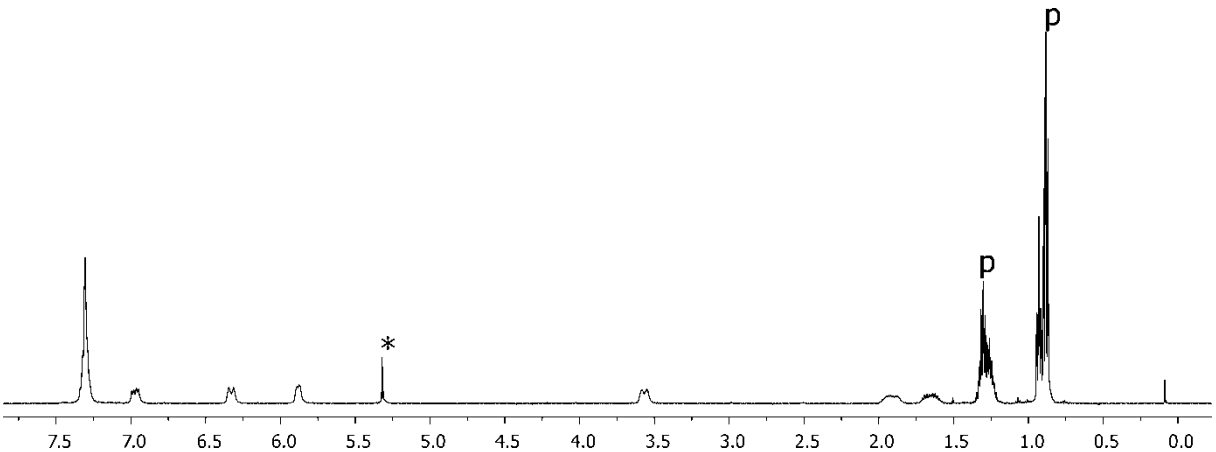
^{19}F NMR (470 MHz, 298 K, CD_2Cl_2): δ = −124.5 (br, 2F, *o*-P^{A}), −125.8 (br, 2F, *o*-P^{B}), −133.7 (m, 4F, *o*-$B^{A,B}$), −138.8 (m, 1F, *p*-P^{A}), −139.4 (m, 1F, *p*-P^{B}), −155.8 (br, 2F, *m*-P^{A}), −156.7 (br, 2F, *m*-P^{B}), −159.0 (br, 1F, *p*-B^{A}), −159.8 (br, 1F, *p*-B^{B}), −164.6 (br, 2F, *m*-B^{A}), −165.2 (br, 2F, *m*-B^{B}); [$\Delta\delta^{19}F_{p,m}$: 5.6 (B^{A}), 5.4 (B^{B}), 17.0 (P^{A}), 17.3 (P^{B})].

^{19}F,^{19}F GCOSY (470 MHz, 298 K, CD_2Cl_2): δ^{19}F / δ^{19}F = −124.5 / −155.8 (*o*-P^{A} / *m*-P^{A}), −125.8 / −156.7 (*o*-P^{B} / *m*-P^{B}), −133.7 / −164.6, −165.2 (*o*-$B^{A,B}$ / *m*-B^{A}, *m*-B^{B}), −138.8 / −155.8 (*p*-P^{A} / *m*-P^{A}), −139.4 / −156.7 (*p*-P^{B} / *m*-P^{B}), −155.8 / −124.5, −138.8 (*m*-P^{A} / *o*-P^{A}, *p*-P^{A}), −156.7 / −125.8, −139.4 (*m*-P^{B} / *o*-P^{B}, *p*-P^{B}), −159.0 / −164.6 (*p*-B^{A} / *m*-B^{A}), −159.8 / −165.2 (*p*-B^{B} / *m*-B^{B}), −164.6 / −133.7, −159.0 (*m*-B^{A} / *o*-$B^{A,B}$, *p*-B^{A}), −165.2 / −133.7, −159.8 (*m*-B^{B} / *o*-$B^{A,B}$, *p*-B^{B}).

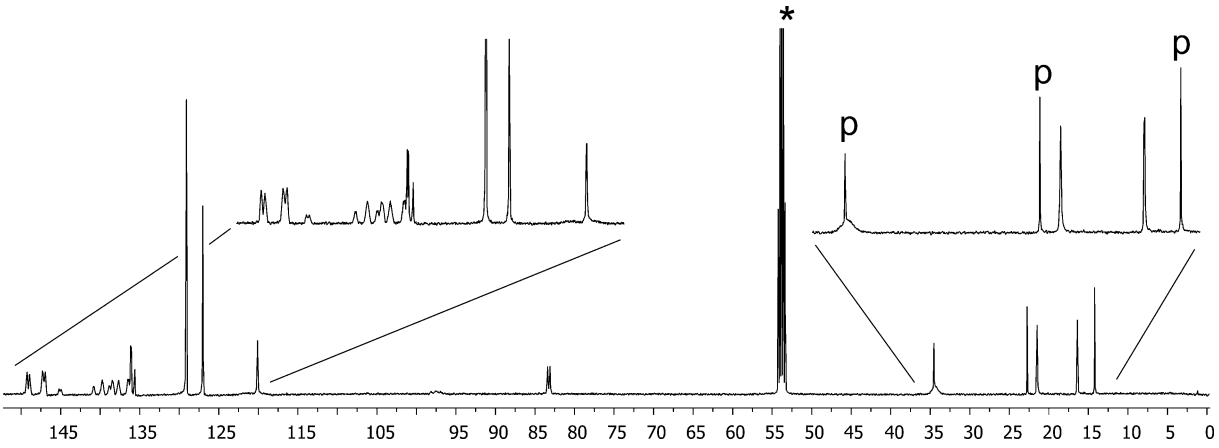
^{31}P{^{1}H} NMR (202 MHz, 298 K, CD_2Cl_2): δ = 23.5 ($\nu_{1/2}$ ~ 60 Hz).

X-ray crystal structure analysis of *trans*-8: formula $C_{36}H_{14}BF_{20}OP$ * 1.5 C_6H_6, M = 1001.41 colourless crystal, 0.25 x 0.20 x 0.20 mm, a = 13.5250(20), b = 13.9090(30), c = 14.5825(11) Å, α = 111.609(7), β = 113.015(11), γ = 94.428(12)°, V = 2267.7(6) Å^3, ρ_{calc} = 1.467 gcm^{-3}, μ = 1.609 mm^{-1}, empirical absorption correction (0.689 ≤ T ≤ 0.739), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 33792 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 7795 independent (R_{int} = 0.039) and 6896 observed reflections [I>2σ(I)], 614 refined parameters, R = 0.041, wR^2 = 0.122, max. (min.) residual electron density 0.20 (-0.20) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

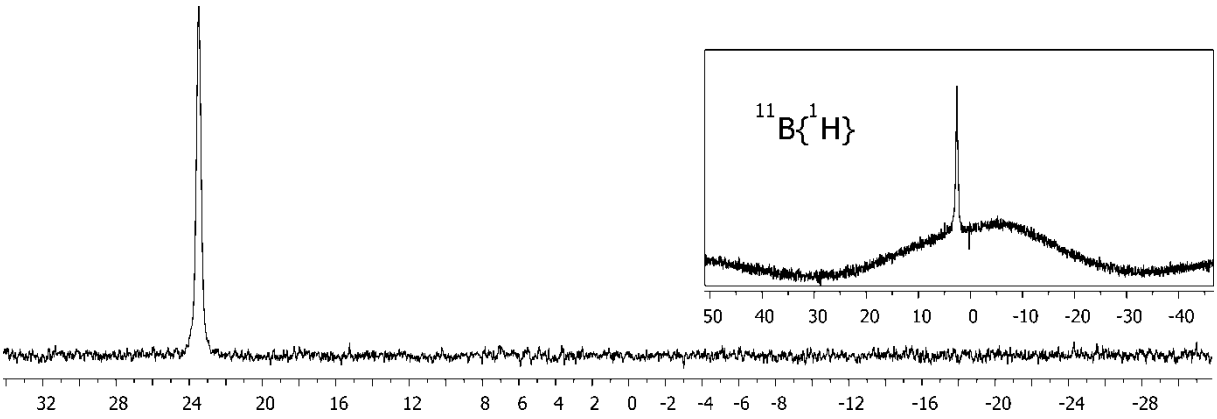




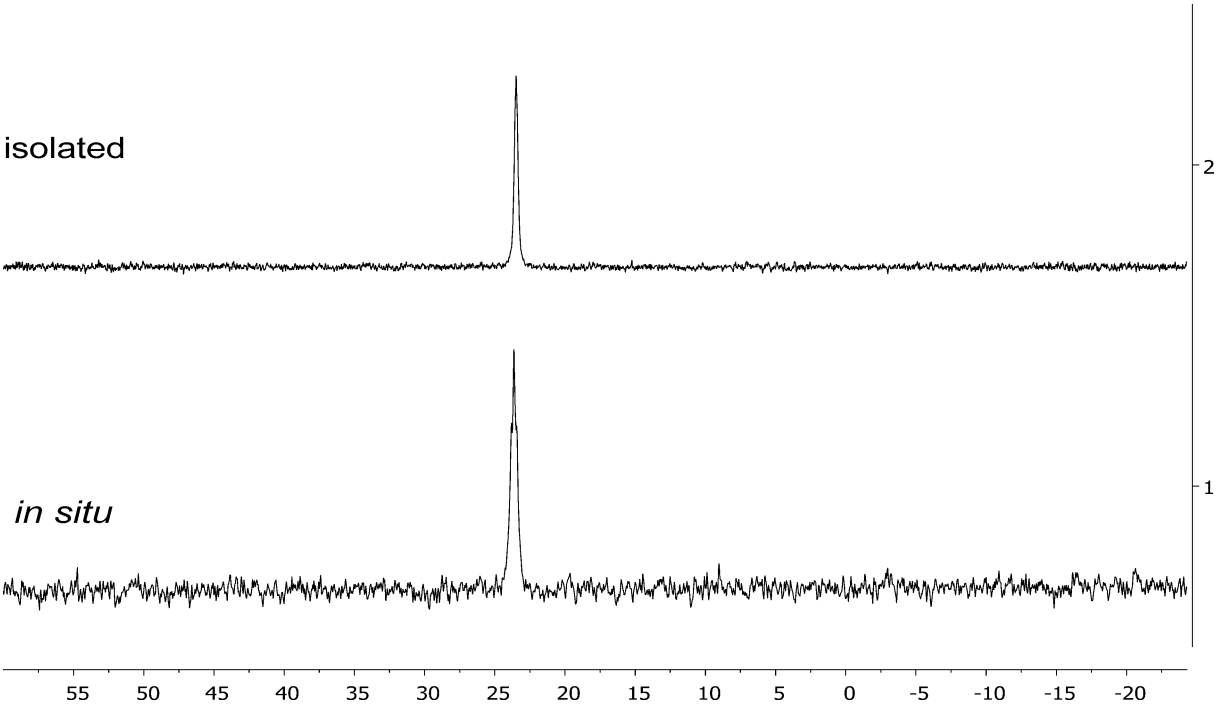
^{1}H NMR (500 MHz, 298 K, CD_2Cl_2(*)); p: pentane.



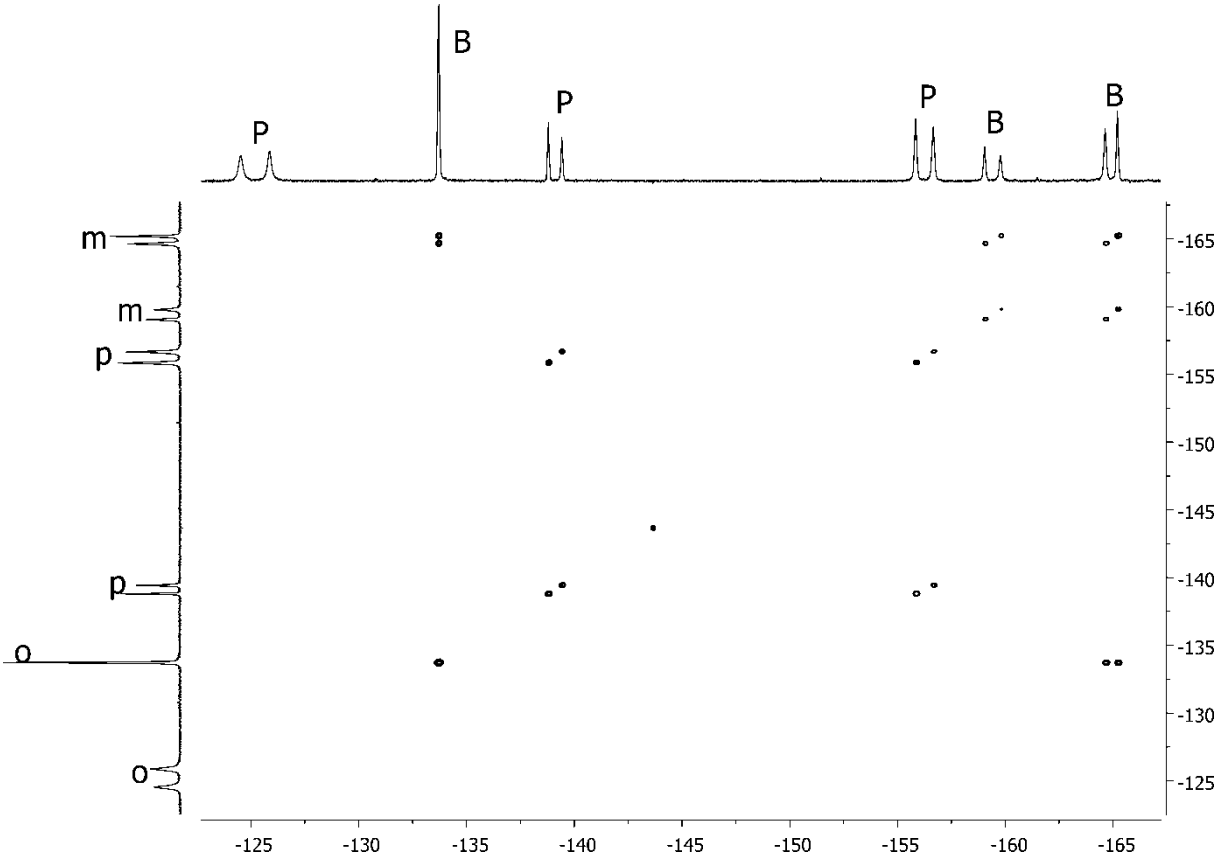
$^{13}C\{^{1}H\}$ NMR (126 MHz, 298 K, CD_2Cl_2(*)).



$^{31}P\{^{1}H\}$ NMR (202 MHz, 298 K, CD_2Cl_2); box: $^{11}B\{^{1}H\}$ NMR (160 MHz, 298 K, CD_2Cl_2).

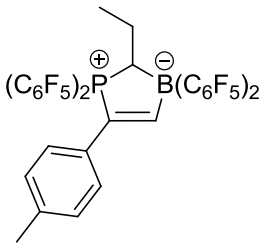


2: $^{31}P\{^{1}H\}$ NMR (202 MHz, 298 K, CD_2Cl_2) of isolated compound **8**; 1: $^{31}P\{^{1}H\}$ NMR (81 MHz, 300 K, C_6D_6) of *in situ* prepared compound **8**.



$^{19}F,^{19}F$ GCOSY (470 MHz, 298 K, CD_2Cl_2).

Reaction of C_1-bridged FLP 3 with *p*-tolylacetylene to 6



Bis(pentafluorophenyl)propenylphosphane (**4**) (200 mg, 0.49 mmol) and bis(pentafluorophenyl)borane (169.5 mg, 0.49 mmol) were dissolved in *n*-pentane (10 mL) and stirred for one hour at rt. *p*-Tolylacetylene (56.9 mg, 0.49 mmol) was added to the reaction mixture which turned red-orange. After stirring for one hour at rt the solvent was removed *in vacuo* to give a brown residue. The crude product was suspended in *n*-pentane again and the solvent was removed *via* filter cannula. The remaining product was then dried *in vacuo* to give a white solid (299 mg, 0.34 mmol, 70%).

IR (KBr): $\tilde{\nu}$ = 3442 (w), 3029 (w), 2970 (w), 2934 (w), 2879 (w), 1644 (s), 1523 (s), 1488(s), 1462 (s), 1106 (s), 984 (s), 816 (m).

Elemental analysis: calcd. for $C_{36}H_{14}BF_{20}P$: C 49.80, H 1.63; found: C 49.54, H 1.23.

Mp: 170 °C (DSC).

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 9.08 (d, $^{3}J_{PH}$ = 64.3 Hz, 1H, $^{=}$CH), 7.05 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, *o*-tol), 6.80 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, *m*-tol), 3.40 (m, 1H, ^{P}CH^{B}), 1.90 (s, 3H, *p*-CH_3^{tol}), 1.79 (dm, $^{3}J_{PH}$ = 29.1 Hz, 1H, CH_2), 1.66 (m, 1H, CH_2), 0.75 (t, $^{3}J_{HH}$ = 7.3 Hz, CH_3).

^{1}H{^{31}P} NMR (500 MHz, 298 K, C_6D_6): δ = 9.08 (s, 1H, $^{=}$CH), 7.05 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, *o*-tol), 6.80 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, *m*-tol), 3.40 (m, 1H, ^{P}CH^{B}), 1.90 (s, 3H, *p*-CH_3^{tol}), 1.79 (m, 1H, CH_2), 1.66 (m, 1H, CH_2), 0.75 (t, $^{3}J_{HH}$ = 7.3 Hz, CH_3).

^{1}H{^{1}H} NOE (500 MHz, 298 K, C_6D_6): $\delta^{1}H_{irr}$ / $\delta^{1}H_{res}$ = 7.05 / 9.08, 6.80 (*o*-tol / $^{=}$CH, *m*-tol), 6.80 / 7.05, 1.90 (*m*-tol / *o*-tol, *p*-CH_3^{tol}); [selected traces].

^{13}C{^{1}H} NMR (126 MHz, 298 K, C_6D_6): δ = 183.6 (br, $^{=}$CH), 139.2 (*p*-tol), 130.8 (d, $^{2}J_{PC}$ = 16.6 Hz, *i*-tol), 129.9 (*m*-tol), 126.6 (d, $^{3}J_{PC}$ = 5.9 Hz, *o*-tol), 125.5 (d, $^{1}J_{PC}$ = 84.1 Hz, $^{=}$C^{tol}), 39.5 (br, ^{P}CH^{B}), 21.6 (CH_2), 20.8 (*p*-CH_3^{tol}), 16.2 (d, $^{3}J_{PC}$ = 9.0 Hz, CH_3); [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, 298 K, C_6D_6): $\delta^{1}H$ / $\delta^{1}H$ = 7.05 / 6.80, 1.90 (*o*-tol / *m*-tol, *p*-CH_3^{tol}), 6.80 / 7.05, 1.90 (*m*-tol / *o*-tol, *p*-CH_3^{tol}), 3.40 / 1.79, 1.66 (^{P}CH^{B} / CH_2), 1.90 / 6.80 (*p*-CH_3^{tol} / *m*-tol), 1.79, 1.66 / 3.40, 0.75 (CH_2 / ^{P}CH^{B}, CH_3), 0.75 / 1.79, 1.66 (CH_3 / CH_2).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 298 K, C_6D_6): $\delta^{1}H$ / $\delta^{13}C$ = 9.08 / 183.6 ($^{=}$CH), 7.05 / 126.6 (*o*-tol), 6.80 / 129.9 (*m*-tol), 3.40 / 39.5 (^{P}CH^{B}), 1.90 / 20.8 (*p*-CH_3^{tol}), 1.79, 1.66 / 21.6 (CH_2), 0.75 / 16.2 (CH_3).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 298 K, C_6D_6): $\delta^{1}H$ / $\delta^{13}C$ = 9.08 / 130.8 ($^{=}$CH / *i*-tol), 7.05 / 139.2, 126.6, 125.5 (*o*-tol / *p*-tol, *o*-tol, $^{=}$C^{tol}), 6.80 / 130.8, 129.9, 20.8 (*m*-tol / *i*-tol, *m*-tol, *p*-CH_3^{tol}), 1.90 / 139.2, 129.9 (*p*-CH_3^{tol} / *p*-tol, *m*-tol), 0.75 / 21.6 (CH_3 / CH_2).

^{11}B{^{1}H} NMR (160 MHz, 298 K, C_6D_6): δ = −8.2 ($\nu_{1/2}$ ~ 50 Hz).

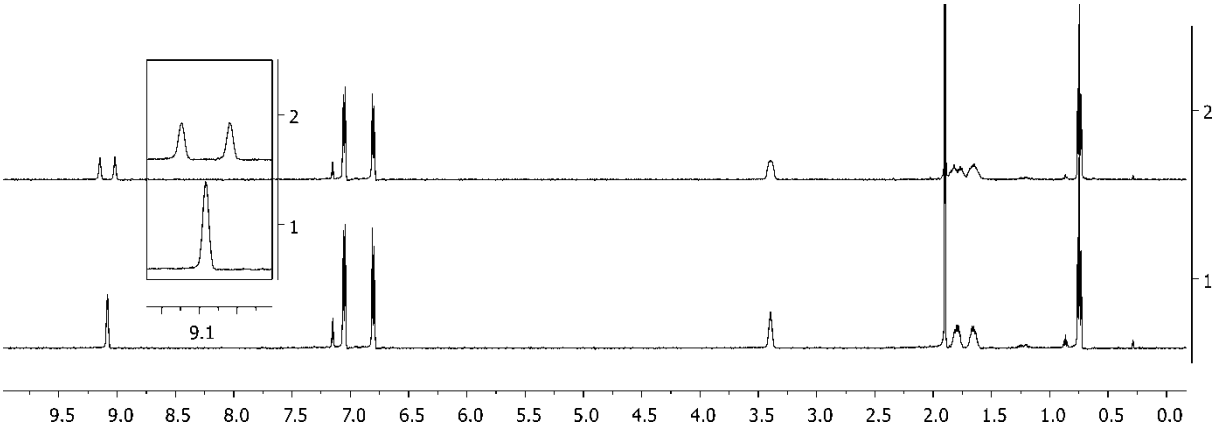
^{19}F NMR (470 MHz, 298 K, C_6D_6): δ = −127.3 (m, 2F, *o*-P^{A}), −127.6 (m, 2F, *o*-P^{B}), −131.7 (m, 2F, *o*-B^{A}), −132.0 (m, 2F, *o*-B^{B}), −138.1 (tm, $^{3}J_{FF}$ = 22.0 Hz, 1F, *p*-P^{B}), −139.4 (tm, $^{3}J_{FF}$ = 22.3 Hz, 1F, *p*-P^{A}), −156.4 (m, 2F, *m*-P^{B}), −157.0 (m, 2F, *m*-P^{A}), −157.6 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F, *p*-B^{A}), −158.2 (t, $^{3}J_{FF}$ = 20.7 Hz, 1F, *p*-B^{B}), −163.5 (m, 2F, *m*-B^{A}), −163.7 (m, 2F, *m*-B^{B}); [$\Delta\delta^{19}F_{p,m}$: 5.9 (B^{A}), 5.5 (B^{B}), 17.6 (P^{A}), 18.3 (P^{B})].

^{19}F,^{19}F GCOSY (470 MHz, 298 K, C_6D_6): $\delta^{19}F$ / $\delta^{19}F$ = −127.3 / −139.4, −157.0 (*o*-P^{A} / *p*-P^{A}, *m*-P^{A}), −127.6 / −138.1, −156.4 (*o*-P^{B} / *p*-P^{B}, *m*-P^{B}), −131.7 / −163.5 (*o*-B^{A} / *m*-B^{A}), −132.0 / −163.7 (*o*-B^{B} / *m*-B^{B}), −138.1 / −127.6, −156.4 (*p*-P^{B} / *o*-P^{B}, *m*-P^{B}), −139.4 / −127.3, −157.0 (*p*-

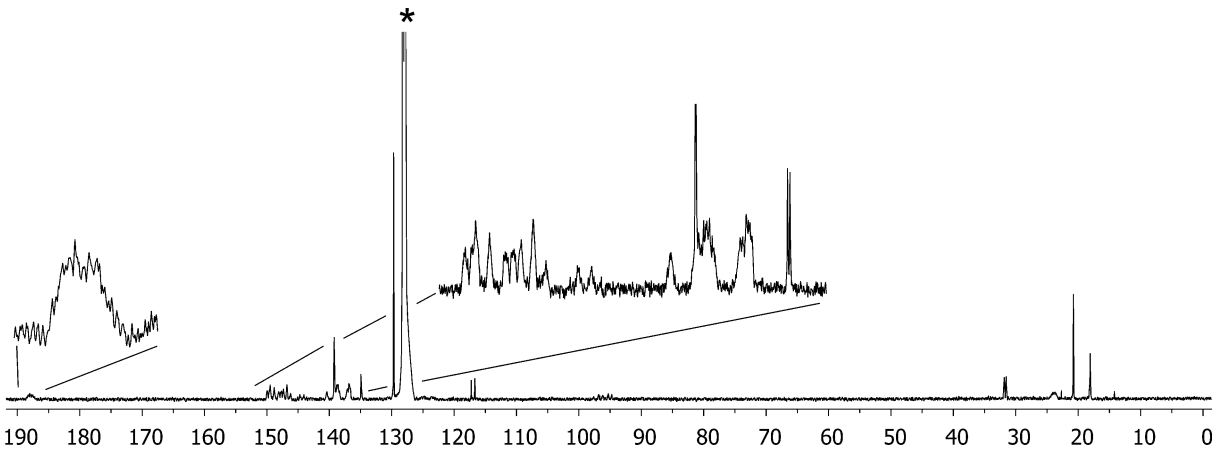
P^A / *o*-P^A, *m*-P^A), −156.4 / −127.6, −138.1 (*m*-P^B / *o*-P^B, *p*-P^B), −157.0 / −127.3, −139.4 (*m*-P^A / *o*-P^A, *p*-P^A), −157.6 / −163.5 (*p*-B^A / *m*-B^A), −158.2 / −163.7 (*p*-B^B / *m*-B^B), −163.5 / −131.7, −157.6 (*m*-B^A / *o*-B^A, *p*-B^A), −163.7 / −132.0, −158.2 (*m*-B^B / *o*-B^B, *p*-B^B).

$^{31}P\{^1H\}$ NMR (202 MHz, 298 K, C_6D_6): δ = 25.2 ($v_{1/2}$ ~ 50 Hz).

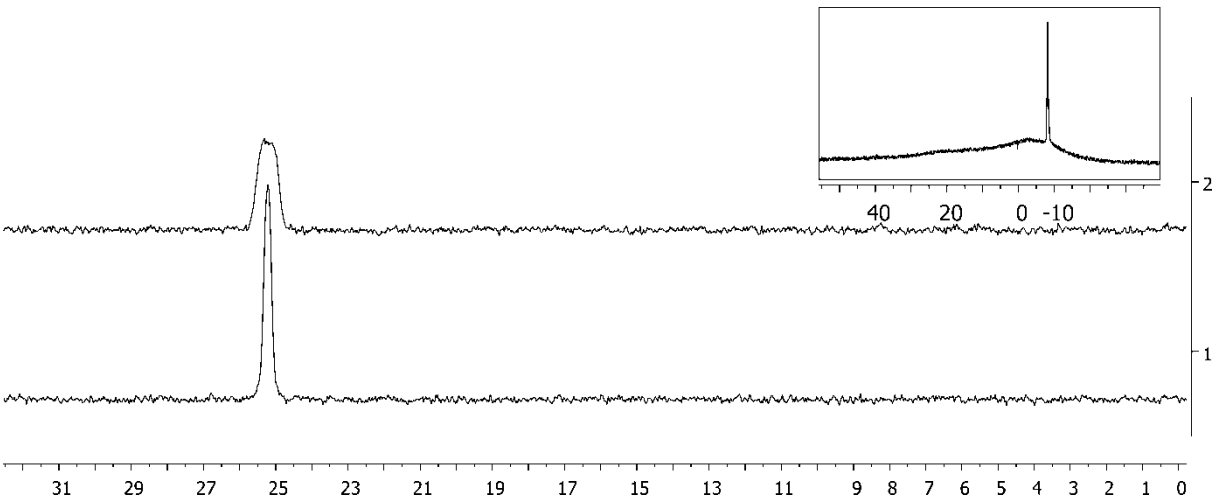
^{31}P NMR (202 MHz, 298 K, C_6D_6): δ = 25.2 ($v_{1/2}$ ~ 140 Hz).



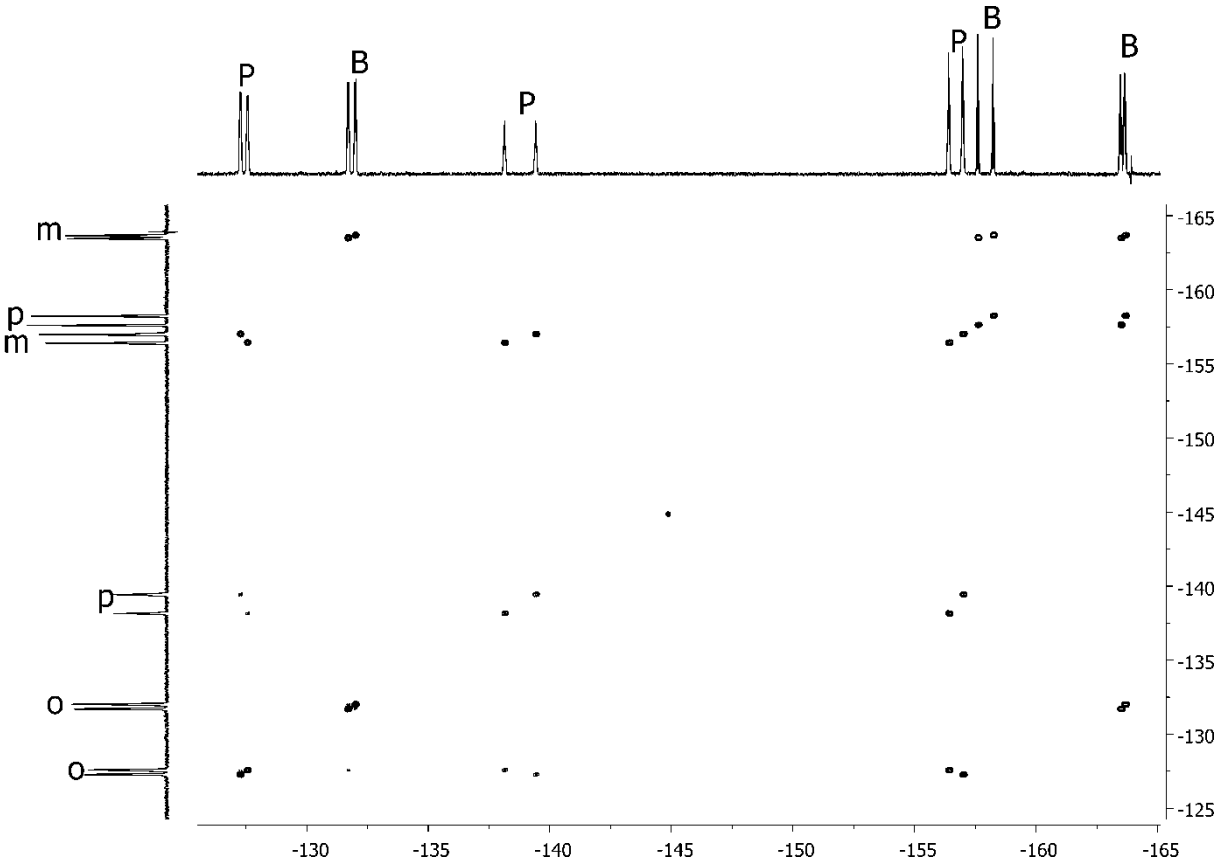
1: ^1H NMR (500 MHz, 298 K, C_6D_6); 2: $^1H\{^{31}P\}$ NMR (500 MHz, 298 K, C_6D_6).



$^{13}C\{^1H\}$ NMR (126 MHz, 298 K, C_6D_6(*)).



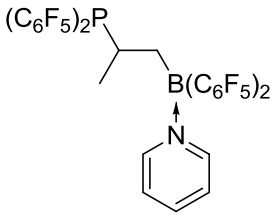
1: $^{31}P\{^{1}H\}$ NMR (202 MHz, 298 K, C_6D_6); 2: ^{31}P NMR (202 MHz, 298 K, C_6D_6); box: $^{11}B\{^{1}H\}$ NMR (160 MHz, 298 K, C_6D_6).



$^{19}F,^{19}F$ GCOSY (470 MHz, 298 K, C_6D_6).

4. Reactions of the C_2-bridged FLP 10

Reaction of C_2-bridged FLP 10 with pyridine to 11



Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (150 mg, 0.369 mmol) and bis(pentafluorophenyl)borane (127.8 mg, 0.369 mmol) were dissolved in *n*-pentane (10 mL) and stirred for ten min at rt to give a white suspension. Pyridine (29.2 mg, 0.369 mmol) was added and a white precipitate crushed out. After stirring for 45 min at rt all volatiles were removed *in vacuo*, the residue was washed with *n*-pentane (3x2 mL) and dried *in vacuo* to give the product as white solid (226 mg, 0.272 mmol, 74%). Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product **11** in dichloromethane at −30 °C.

Exact mass: calcd. for $C_{32}H_{11}BF_{20}NP + H^+$: 832.04811 m/z; found: 832.04798 m/z;
$C_{32}H_{11}BF_{20}NP+Ag^+$: 939.94542 m/z; found: 939.94469 m/z;
$2[C_{32}H_{11}BF_{20}NP]+Ag^+$: 1770.98661 m/z; found: 1770.98733 m/z.

IR (KBr): $\tilde{\nu}$ = 3433 (br), 2973 (w), 2936 (w), 1642 (s), 1518 (s), 1469 (s), 1380 (s), 1284 (s), 1224 (m), 1190 (w), 1088 (s), 976 (s), 841 (m), 809 (m), 693 (s), 626 (m), 577 (w), 506 (w).

Elemental analysis: calcd. for $C_{32}H_{11}BF_{20}NP$: C 46.24, H 1.33, N 1.69; found: C 46.43, H 1.29, N 1.77.

Mp: 200 °C (DSC).

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 8.08 (m, 2H, *o*-py), 6.46 (m, 1H, *p*-py), 6.18 (m, 2H, *m*-py), 3.10 (m, 1H, ^{P}CH), 2.10 (m, 1H, ^{B}CH$_2$), 1.29 (dd, $^3J_{PH}$ = 21.5 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3), 1.00 (m, 1H, ^{B}CH$_2$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ = 144.7 (*o*-py), 140.9 (*p*-py), 125.6 (*m*-py), 120.2 (br, *i*-$C_6F_5{}^B$), 108.9 (m, *i*-$C_6F_5{}^P$), 26.4 (br, ^{B}CH$_2$), 26.2 (m, ^{P}CH), 17.5 (d, $^2J_{PC}$ = 25.2 Hz, CH_3); [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, 299 K, C_6D_6): δ^1H / δ^1H = 8.08 / 6.46, 6.18 (*o*-py / *p*-py, *m*-py), 6.46 / 8.08, 6.18 (*p*-py / *o*-py, *m*-py), 6.18 / 8.08, 6.46 (*m*-py / *o*-py, *p*-py), 3.10 / 2.10, 1.29 (^{P}CH / $^{B}CH_2$, CH_3), 1.29 / 3.10 (CH_3 / ^{P}CH), 1.00 / 3.10, 2.10, 1.29 ($^{B}CH_2$ / ^{P}CH, $^{B}CH_2$, CH_3).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6): δ^1H / δ^{13}C = 8.08 / 144.7 (*o*-py), 6.46 / 140.9 (*p*-py), 6.18 / 125.6 (*m*-py), 3.10 / 26.2 (^{P}CH), 2.10 / 26.4 ($^{B}CH_2$), 1.29 / 17.5 (CH_3), 1.00 / 26.4 ($^{B}CH_2$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, C_6D_6): δ^1H / δ^{13}C = 8.08 / 144.7, 140.9, 125.6 (*o*-py / *o*-py, *p*-py, *m*-py), 6.46 / 144.7 (*p*-py / *o*-py), 6.18 / 144.7, 125.6 (*m*-py / *o*-py, *m*-py), 2.10 / 120.2, 26.2, 17.5 ($^{B}CH_2$ / *i*-$C_6F_5^{B}$, ^{P}CH, CH_3), 1.29 / 26.4 or 26.2 (CH_3 / $^{B}CH_2$ or ^{P}CH), 1.00 / 120.2, 26.2 ($^{B}CH_2$ / *i*-$C_6F_5^{B}$, ^{P}CH).

^{11}B{^{1}H} NMR (64 MHz, 300 K, C_6D_6): δ = −1.5 ($v_{1/2}$ ~ 430 Hz).

^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = −129.6 (m, 2F, *o*-P^A), −130.25 (m, 2F, *o*-P^B), −130.33 (m, 2F, *o*-B^A), −132.1 (m, 2F, *o*-B^B), −148.9 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-P^A), −149.9 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-P^B), −155.9 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-B^A), −156.5 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-B^B), −160.1 (m, 2F, *m*-P^B), −160.5 (m, 2F, *m*-P^A), −162.8 (m, 4F, *m*-$B^{A,B}$); [$\Delta\delta^{19}F_{p,m}$: 6.9 (B^A), 6.3 (B^B), 11.6 (P^A), 10.2 (P^B)].

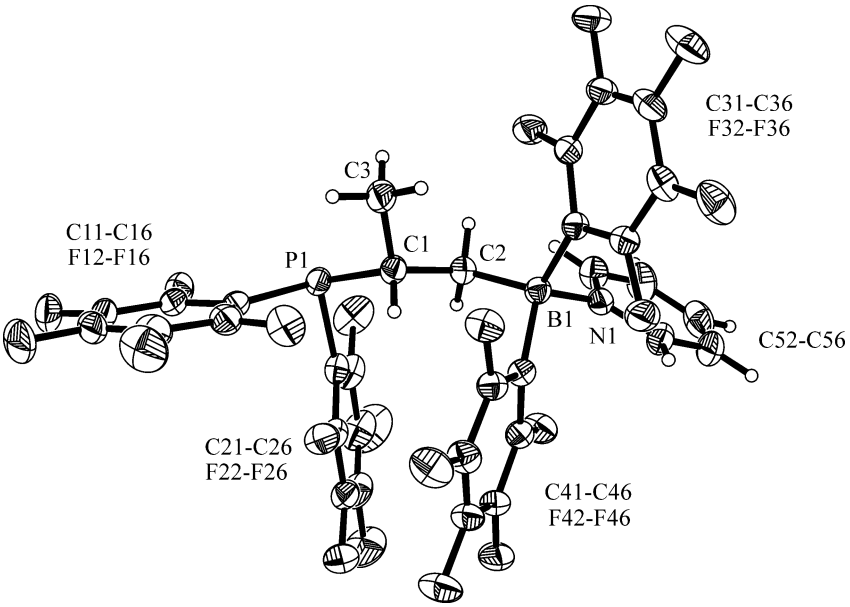
^{19}F,^{19}F GCOSY (470 MHz, 299 K, C_6D_6): δ^{19}F / δ^{19}F = −129.6 / −148.9, −160.5 (*o*-P^A / *p*-P^A, *m*-P^A), −130.25 / −149.9, −160.1 (*o*-P^B / *p*-P^B, *m*-P^B), −130.33 / −155.9, −162.8 (*o*-B^A / *p*-B^A, *m*-$B^{A,B}$), −132.1 / −156.5, −162.8 (*o*-B^B / *p*-B^B, *m*-$B^{A,B}$), −148.9 / −129.6, −160.5 (*p*-P^A / *o*-P^A, *m*-P^A), −149.9 / −130.25, −160.1 (*p*-P^B / *o*-P^B, *m*-P^B), −155.9 / −130.33, −162.8 (*p*-B^A / *o*-B^A, *m*-$B^{A,B}$), −156.5 / −132.1, −162.8 (*p*-B^B / *o*-B^B, *m*-$B^{A,B}$), −160.1 / −130.25, −149.9 (*m*-P^B / *o*-P^B, *p*-P^B), −160.5 / −129.6, −148.9 (*m*-P^A / *o*-P^A, *p*-P^A), −162.8 / −130.33, −132.1, −155.9, −156.5 (*m*-$B^{A,B}$ / *o*-B^A, *o*-B^B, *p*-B^A, *p*-B^B).

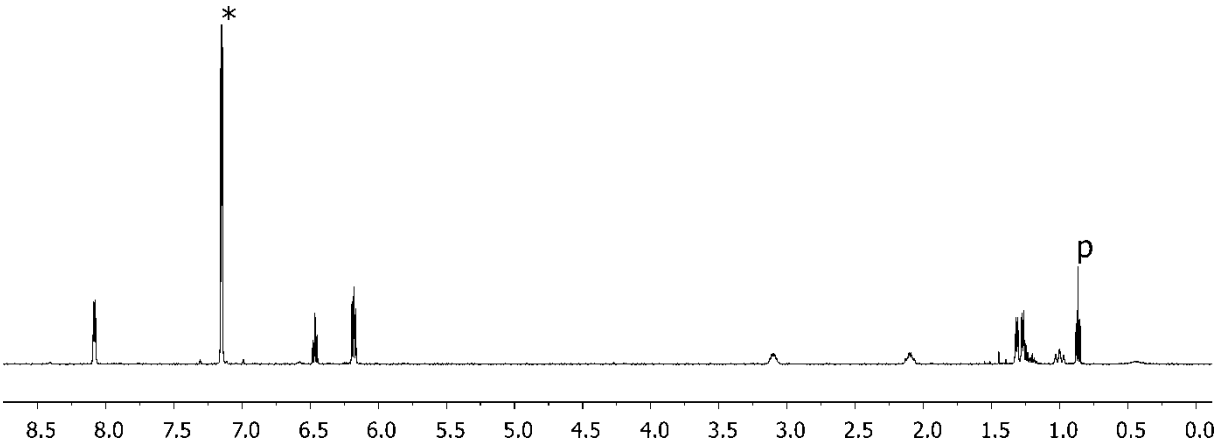
^{31}P{^{1}H} NMR (202 MHz, 299 K, C_6D_6): δ = −36.3 (quin, $^3J_{FF}$ = 31.1 Hz).

^{31}P NMR (202 MHz, 299 K, C_6D_6): δ = −36.3 ($v_{1/2}$ ~ 110 Hz).

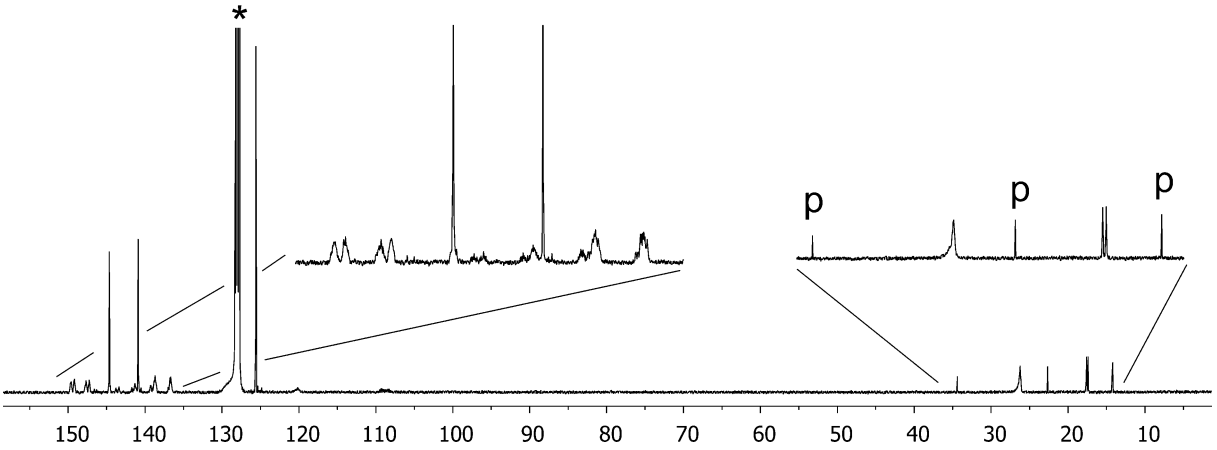
X-ray crystal structure analysis of 11: formula $C_{32}H_{11}BF_{20}NP$, *M* = 831.20, colourless crystal, 0.33 x 0.10 x 0.08 mm, *a* = 9.4074(2), *b* = 15.6502(6), *c* = 22.7817(10) Å, *β* = 96.343(2)°, *V* = 3333.6(2) Å^3, ρ_{calc} = 1.656 gcm^{-3}, μ = 2.032 mm^{-1}, empirical absorption correction (0.553 ≤ T ≤ 0.854), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 19676 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 5697 independent (R_{int} =

0.041) and 4614 observed reflections [$I>2\sigma(I)$], 497 refined parameters, R = 0.042, wR^2 = 0.113, max. (min.) residual electron density 0.18 (-0.27) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

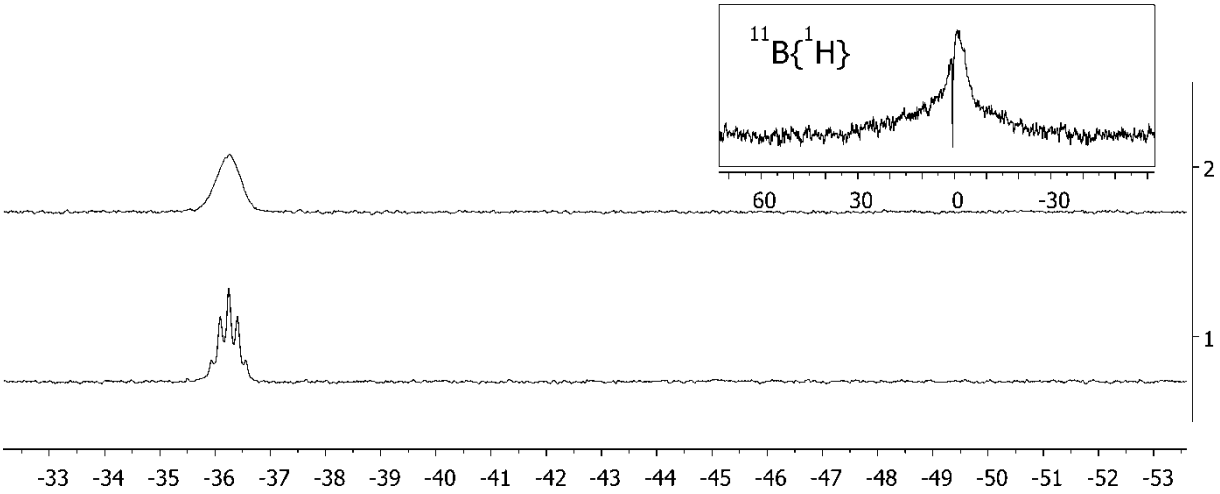




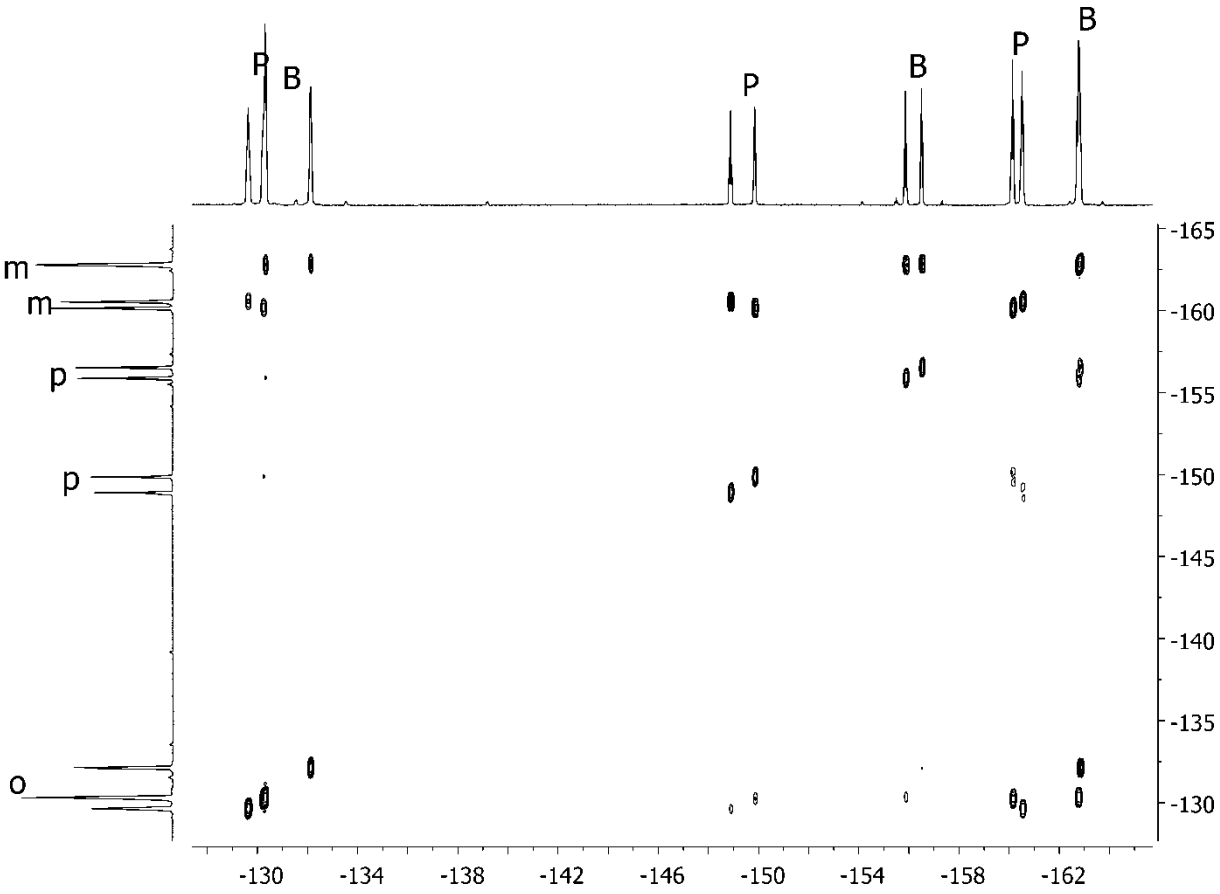
^{1}H NMR (500 MHz, 299 K, C_6D_6(*)); p: pentane.



^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6(*)); p: pentane.

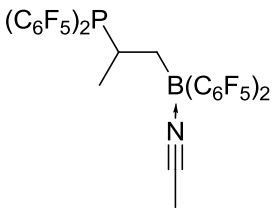


1: $^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, C_6D_6); 2: ^{31}P NMR (202 MHz, 299 K, C_6D_6), box: $^{11}B\{^{1}H\}$ NMR (64 MHz, 300 K, C_6D_6).



$^{19}F,^{19}F$ GCOSY (470 MHz, 299 K, C_6D_6).

Reaction of C_2-bridged FLP 10 with acetonitrile to 12



Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (100 mg, 0.246 mmol) and bis(pentafluorophenyl)borane (85.3 mg, 0.246 mmol) were dissolved in *n*-pentane (5 mL) and after stirring for five min the reaction mixture turned cloudy. Acetonitrile (22.8 mg, 0.246 mmol) was added to the reaction and a white solid crushed out instantly. After stirring the suspension for one hour at rt the solid was isolated *via* filter cannula. The product (144 mg, 0.180 mmol, 73%) was washed with *n*-pentane (5 mL) and dried *in vacuo*.

Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product **12** in dichloromethane.

IR (KBr): ṽ = 2941 (w), 2363 (m), 1647 (m), 1519 (s), 1469 (s), 1381 (m), 1287 (m), 1092 (s), 977 (s), 888 (w), 855 (w), 819 (w), 768 (w), 744 (w), 675 (w), 511 (w), 426 (w).

Elemental analysis: calcd. for $C_{29}H_9BF_{20}NP$: C 43.92, H 1.14, N 1.77; found: C 43.96, H 1.16, N 1.60.

Mp: 76 °C (DSC).

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 3.26 (br m, 1H, ^{P}CH), 1.54 (m, 2H, $^{B}CH_2$), 0.99 (dd, $^3J_{PH}$ = 20.9 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 0.57 (s, 3H, $^{NC}CH_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 114.9 (^{N}C), 25.7 (br, ^{P}CH), 25.5 (br, $^{B}CH_2$), 18.7 (d, $^2J_{PC}$ = 24.2 Hz, CH_3), −0.5 ($^{NC}CH_3$); [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz, 299 K, C_6D_6): δ^{1}H / δ^{1}H = 3.26 / 1.54, 0.99 (^{P}CH / $^{B}CH_2$, CH_3), 1.54 / 3.26 ($^{B}CH_2$ / ^{P}CH), 0.99 / 3.26 (CH_3 / ^{P}CH).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ^{1}H / δ^{13}C = 3.26 / 25.8 (^{P}CH), 1.54 / 25.6 ($^{B}CH_2$), 0.99 / 18.7 (CH_3), 0.57 / −0.5 ($^{NC}CH_3$).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6): δ^{1}H / δ^{13}C = 1.54 / 25.8, 18.7 ($^{B}CH_2$ / ^{P}CH, CH_3), 0.99 / 25.8, 25.6 (CH_3 / ^{P}CH, $^{B}CH_2$), 0.57 / 114.9 ($^{NC}CH_3$ / ^{N}C).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = −6.8 ($\nu_{1/2}$ ~ 450 Hz).

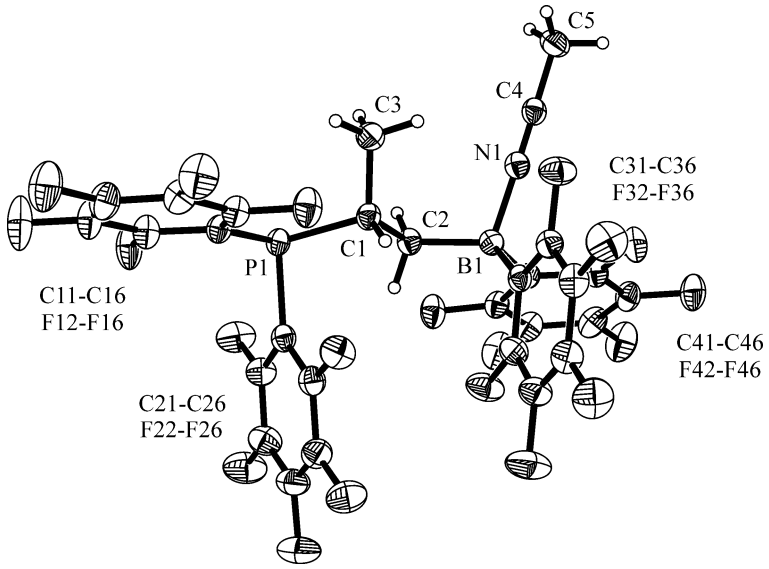
^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = −130.1 (m, 4F, *o*-$P^{A,B}$), −134.5 (br, 4F, *o*-B), −148.9 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-P^{A}), −149.4 (t, $^3J_{FF}$ = 21.3 Hz, 1F, *p*-P^{B}), −156.2 (t, $^3J_{FF}$ = 21.0 Hz, 2F, *p*-B),

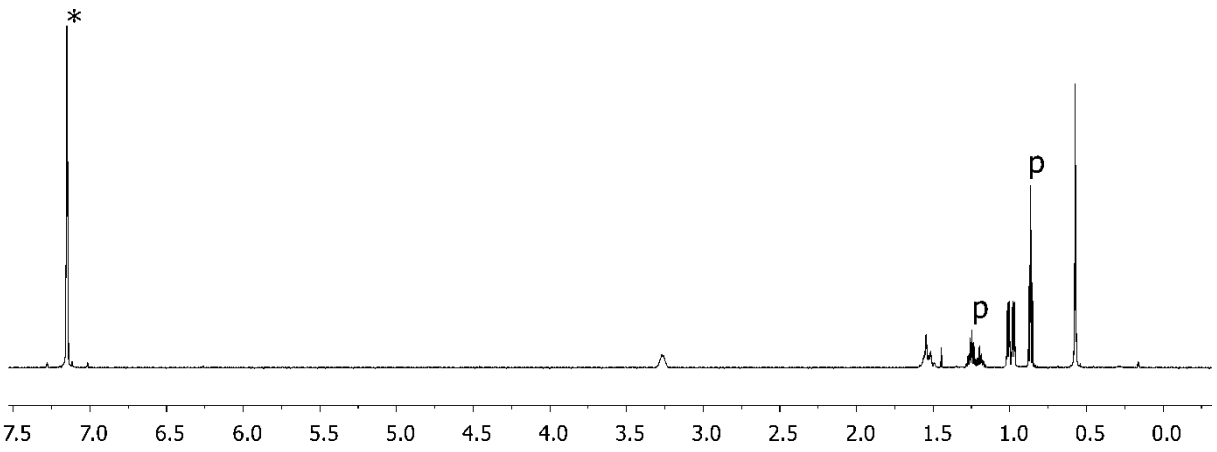
−160.2 (m, 2F, *m*-P^B), −160.3 (m, 2F, *m*-P^A), −163.0 (m, 4F, *m*-B); [$\Delta\delta^{19}F_{p,m}$: 6.8 (B), 11.4 (P^A), 10.8 (P^B)].

$^{19}F,^{19}F$ GCOSY (564 MHz, 299 K, C_6D_6): $\delta^{19}F$ / $\delta^{19}F$ = −130.1 / −148.9, −149.4, −160.2, −160.3 (*o*-$P^{A,B}$ / *p*-P^A, *p*-P^B, *m*-P^B, *m*-P^A), −134.5 / −163.0 (*o*-B / *m*-B), −148.9 / −130.1, −160.3 (*p*-P^A / *o*-$P^{A,B}$, *m*-P^A), −149.4 / −130.1, −160.2 (*p*-P^B / *o*-$P^{A,B}$, *m*-P^B), −156.2 / −163.0 (*p*-B / *m*-B), −160.2 / −130.1, −149.4 (*m*-P^B / *o*-$P^{A,B}$, *p*-P^B), −160.3 / −130.1, −148.9 (*m*-P^A / *o*-$P^{A,B}$, *p*-P^A), −163.0 / −134.5, −156.2 (*m*-B / *o*-B, *p*-B).

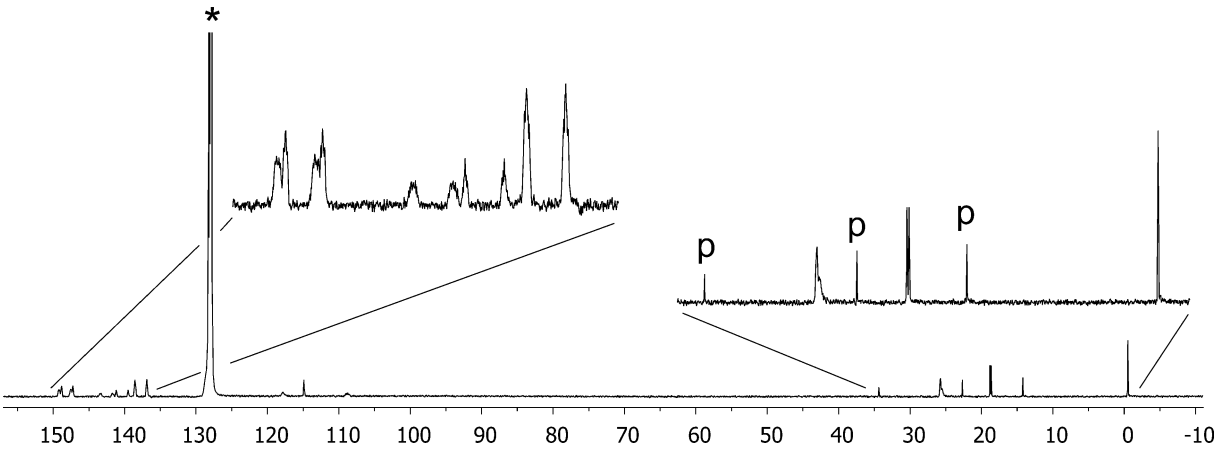
$^{31}P\{^1H\}$ NMR (243 MHz, 299 K, C_6D_6): δ = −36.3 (quin, $^3J_{PF}$ = 29.7 Hz).

X-ray crystal structure analysis of 12: formula $C_{29}H_9BF_{20}NP$, *M* = 793.15 colourless crystal, 0.37 x 0.21 x 0.21 mm, *a* = 10.7188(3), *b* = 12.7599(6), *c* = 13.1819(5) Å, α = 78.178(4), *β* = 78.512(3), γ = 80.597(3)°, *V* = 1715.13(11) $Å^3$, ρ_{calc} = 1.536 gcm^{-3}, μ = 1.944 mm^{-1}, empirical absorption correction (0.533 ≤ T ≤ 0.685), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 24911 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 $Å^{-1}$, 5920 independent (R_{int} = 0.043) and 5299 observed reflections [*I*>2σ(*I*)], 471 refined parameters, *R* = 0.040, wR^2 = 0.111, max. (min.) residual electron density 0.19 (-0.24) e.$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

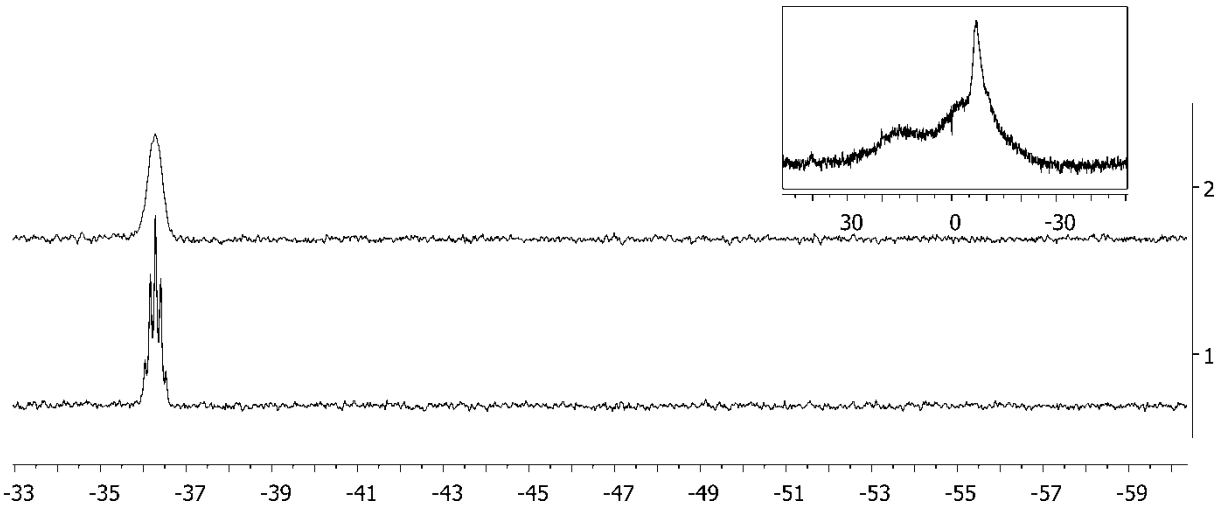




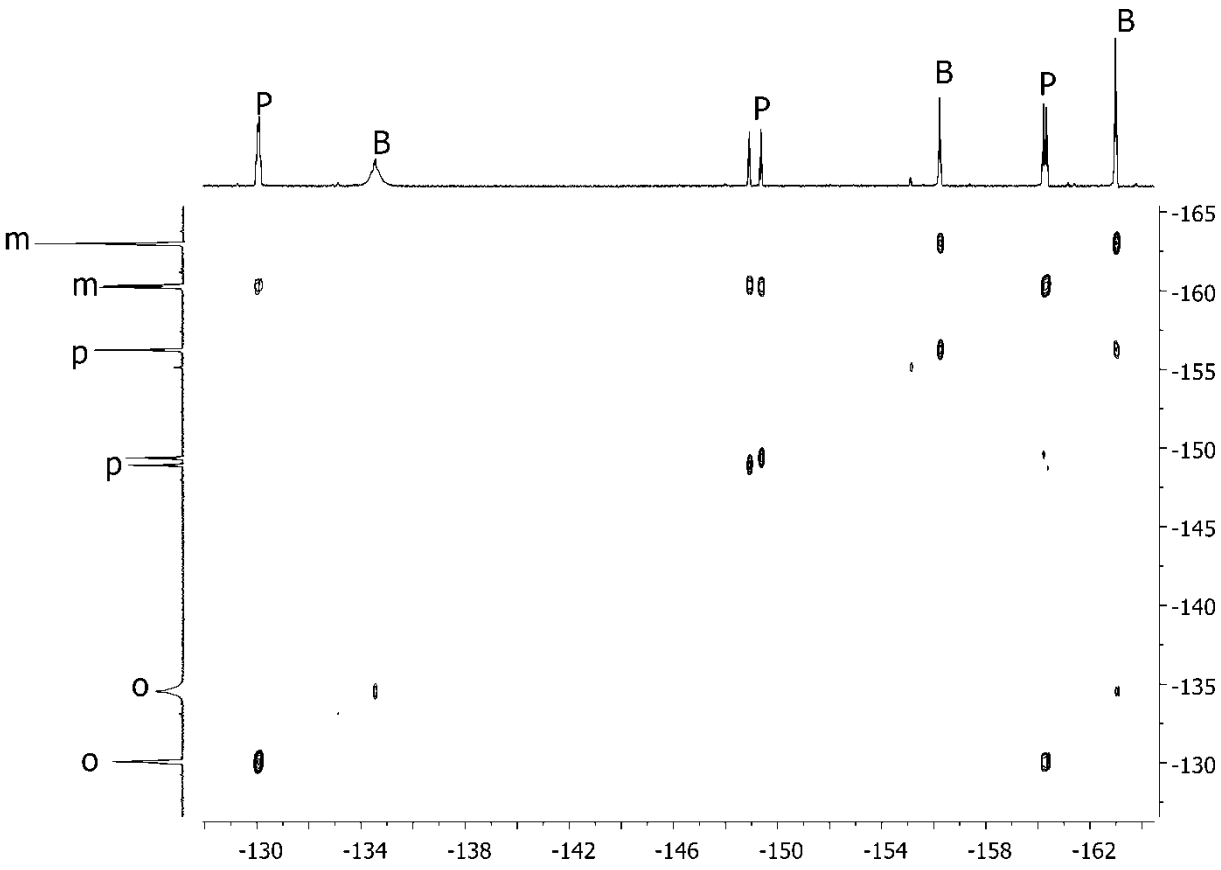
^{1}H NMR (600 MHz, 299 K, C_6D_6(*)); p: pentane.



^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6(*)); p: pentane.



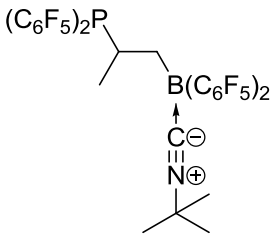
1: ^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6); 2: ^{31}P NMR (243 MHz, 299 K, C_6D_6); box: ^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6).



$^{19}F,^{19}F$ GCOSY (564 MHz, 299 K, C_6D_6).

Reaction of C_2-bridged FLP 10 with *t*-butylisonitrile to 13

Caution: many isonitriles are toxic and must handled with due care.



Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (100 mg, 0.246 mmol) and bis(pentafluorophenyl)borane (85.3 mg, 0.246 mmol) were dissolved in *n*-pentane (5 mL) and stirred for two hours at rt to give a cloudy solution. *t*-Butylisonitrile (20.5 mg, 0.246 mmol) was added to give a clear reaction mixture. After stirring at rt for ten min the reaction mixture was cooled to −78 °C and stirred for 30 min at that temperature while a white solid crushed out. The solvent was removed by filter cannula and the residue was dried *in vacuo* to give a white solid (158 mg, 0.189 mmol, 77%). (little impurities of $HB(C_6F_5)_2$*CN^tBu ($\delta^{11}B\{^1H\}$: −30.8) are visible in the NMR spectra; unknown

species with –P(C_6F_5)$_2$ moiety present in the ^{31}P NMR spectrum ($\delta^{31}P\{^1H\}$:−74.3 (quin, J_{PF} ~ 35 Hz, 9%))).

Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product **13** in dichloromethane at −30 °C.

IR (KBr): $\tilde{\nu}$ = 3433 (br), 2996 (w), 2930 (w), 2874 (w), 2291 (m), 1643 (m), 1517 (s), 1474 (s), 1379 (m), 1240 (s), 1186 (m), 1140 (m), 1092 (s), 978 (s), 908 (w), 838 (w), 810 (w), 777 (w), 753 (w), 733 (w), 662 (w), 637 (w), 536 (w), 514 (w).

^{1}H NMR (500 MHz, 299 K, $CDCl_3$): δ = 3.10 (m, 1H, ^{P}CH), 1.66 (s, 9H, C(CH_3)$_3$), 1.29 (m, 2H, ^{B}CH_2), 1.05 (dd, $^3J_{PH}$ = 21.4 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 299 K, $CDCl_3$): δ = 126.9 (br, ^{N}C), 116.9 (*i*-$C_6F_5^B$), 108.6 (m, *i*-$C_6F_5^P$), 60.6 (*C*(CH_3)$_3$), 28.9 (C(*C*H_3)$_3$), 26.2 (m, ^{P}CH), 22.9 (br, ^{B}CH_2), 18.2 (d, $^2J_{PC}$ = 25.5 Hz, CH_3); [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, 299 K, $CDCl_3$): δ^1H / δ^1H = 3.10 / 1.29, 1.05 (^{P}CH / ^{B}CH_2, CH_3), 1.29 / 3.10 (^{B}CH_2 / ^{P}CH), 1.05 / 3.10 (CH_3 / ^{P}CH).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, $CDCl_3$): δ^1H / δ^{13}C = 3.10 / 26.2 (^{P}CH), 1.66 / 28.9 (C(*C*H_3)$_3$), 1.29 / 22.9 (^{B}CH_2), 1.05 / 18.2 (CH_3).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, $CDCl_3$): δ^1H / δ^{13}C = 3.10 / 18.2 (^{P}CH / CH_3), 1.66 / 60.6, 28.9 (C(CH_3)$_3$ / *C*(CH_3)$_3$, C(*C*H_3)$_3$), 1.29 / 126.9, 116.9, 26.2, 18.2 (^{B}CH_2 / *i*-$C_6F_5^B$, ^{P}CH, CH_3), 1.05 / 26.2, 22.9 (CH_3 / ^{P}CH, ^{B}CH_2).

^{11}B{^{1}H} NMR (160 MHz, 299 K, $CDCl_3$): δ = −19.3 ($v_{1/2}$ ~ 200 Hz).

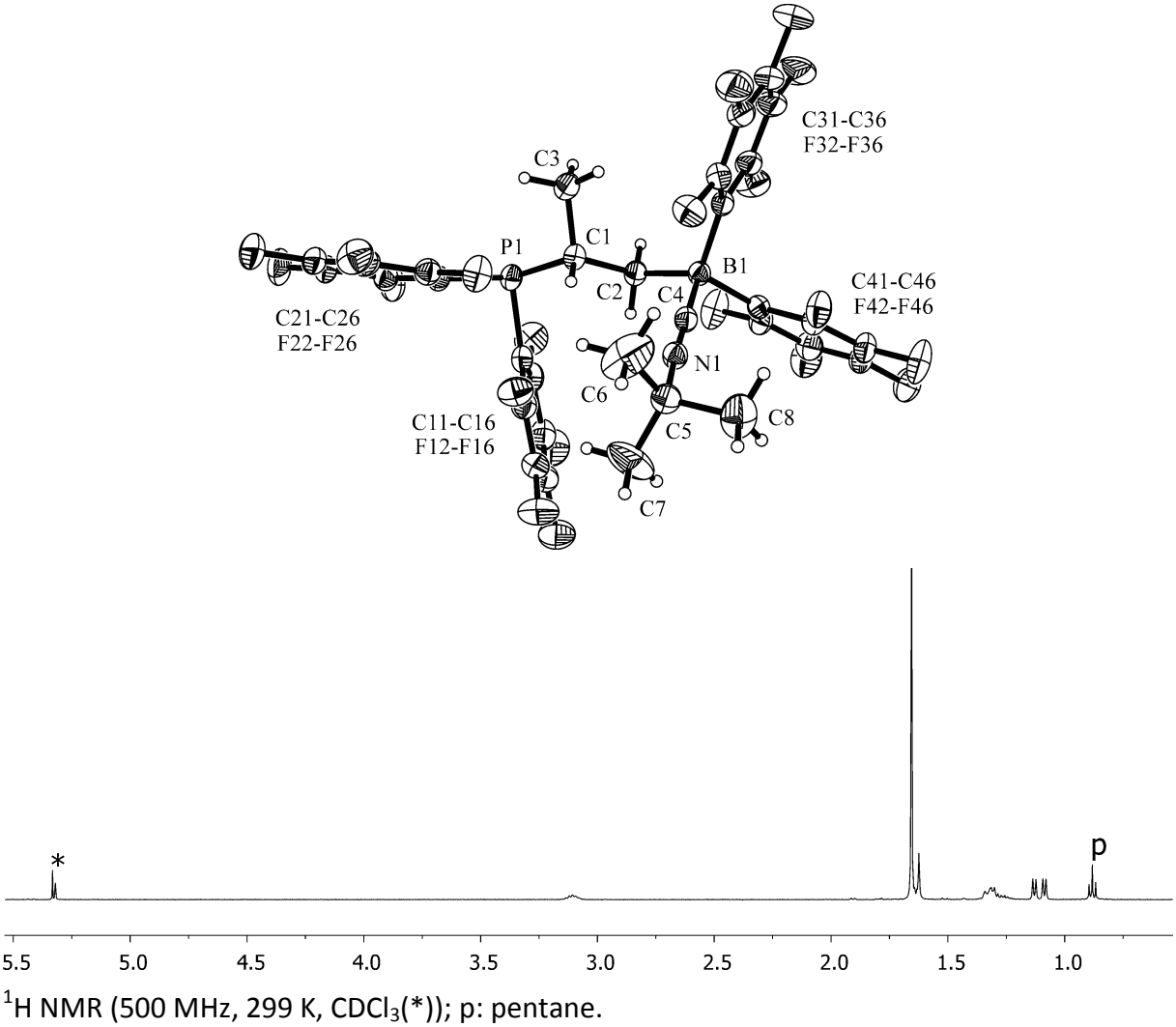
^{19}F NMR (470 MHz, 299 K, $CDCl_3$): δ = −129.4, −129.6 (each m, each 2F, *o*-P^{A,B}), −132.6, −133.2 (each m, each 2F, *o*-B^{A,B}), −149.3 (tm, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-P^A), −149.9 (tm, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-P^B), −156.9 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-B^A), −157.1 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-B^B), −160.2 (m, 4F, *m*-P^{A,B}), −163.0 (m, 4F, *m*-B^{A,B}); [$\Delta\delta^{19}F_{p,m}$: 6.1 (B^A), 5.9 (B^B), 10.9 (P^A), 10.3 (P^B)].

^{19}F,^{19}F GCOSY (470 MHz, 299 K, $CDCl_3$): δ^{19}F / δ^{19}F = −129.4 / −149.3, −160.2 (*o*-P^{A,B} / *p*-P^A, *m*-P^{A,B}), −129.6 / −149.9, −160.2 (*o*-P^{A,B} / *p*-P^B, *m*-P^{A,B}), −132.6 / −156.9, −163.0 (*o*-B^{A,B} / *p*-B^A, *m*-B^{A,B}), −133.2 / −157.1, −163.0 (*o*-B^{A,B} / *p*-B^B, *m*-B^{A,B}), −149.3 / −129.4, −160.2 (*p*-P^A / *o*-P^{A,B}, *m*-P^{A,B}), −149.9 / −129.6, −160.2 (*p*-P^B / *o*-P^{A,B}, *m*-P^{A,B}), −156.9 / −163.0 (*p*-B^A / *m*-B^{A,B}), −157.1 / −163.0 (*p*-B^B / *m*-B^{A,B}), −160.2 / −129.4, −129.6, −149.3, −149.9 (*m*-P^{A,B} / *o*-P^{A,B}, *p*-P^A, *p*-P^B), −163.0 / −132.6, −133.2, −156.9, −157.1 (*m*-B^{A,B} / *o*-B^{A,B}, *p*-B^A, *p*-B^B).

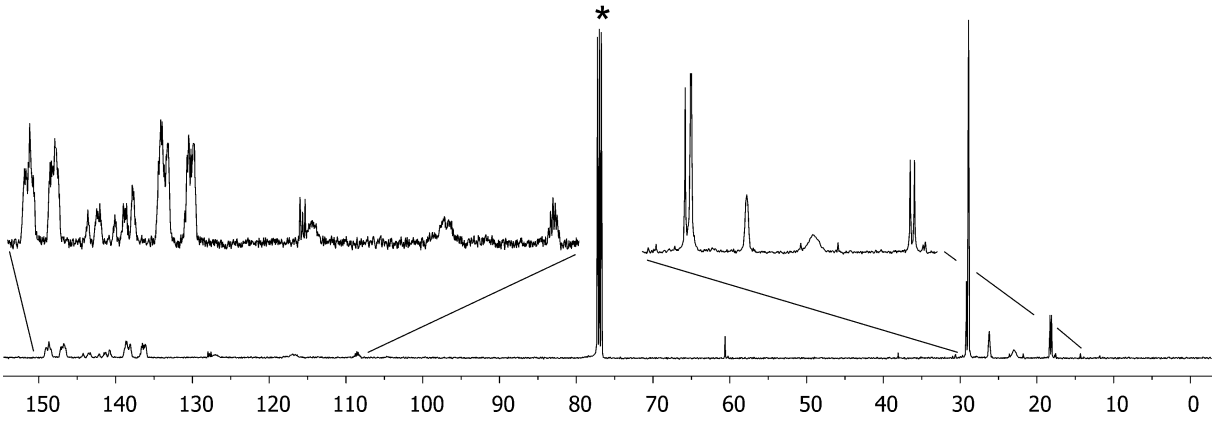
$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, $CDCl_3$): δ = −37.3 (quin, $^{3}J_{PF}$ = 30.0 Hz).

^{31}P NMR (202 MHz, 299 K, $CDCl_3$): δ = −37.3 ($v_{1/2}$ ~ 100 Hz).

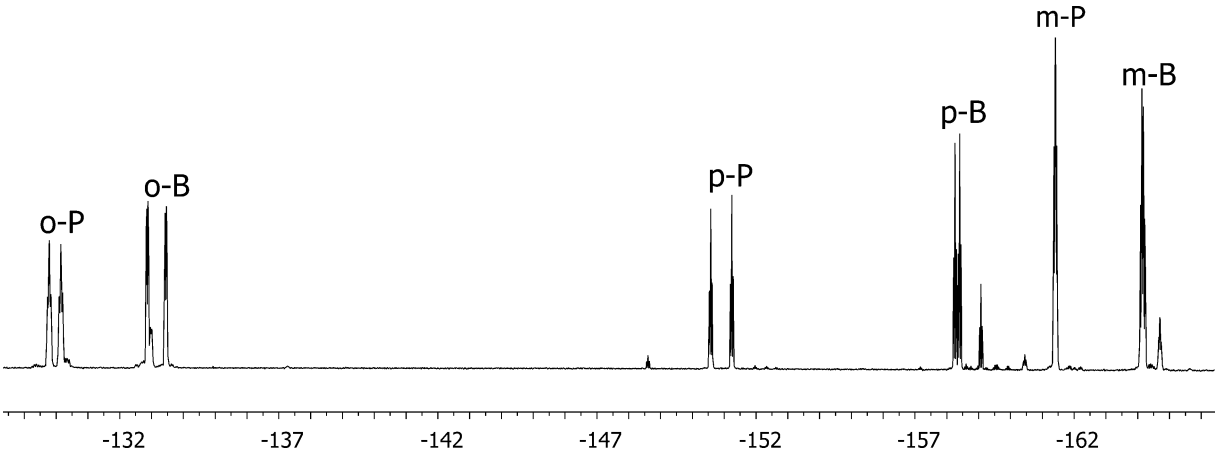
X-ray crystal structure analysis of 13: formula $C_{32}H_{15}BF_{20}NP$ * ½ C_5H_{12}, *M* = 871.30, colourless crystal, 0.27 x 0.10 x 0.10 mm, *a* = 27.4280(7), *b* = 20.0877(8), *c* = 15.7738(4) Å, *β* = 124.926(2)°, *V* = 7125.5(4) Å^3, ρ_{calc} = 1.624 gcm^{-3}, μ = 1.928 mm^{-1}, empirical absorption correction (0.624 ≤ T ≤ 0.830), *Z* = 8, monoclinic, space group *C*2/*c* (No. 15), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 17145 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 5948 independent (R_{int} = 0.038) and 4883 observed reflections [*I*>2σ(*I*)], 547 refined parameters, *R* = 0.050, wR^2 = 0.135, max. (min.) residual electron density 0.30 (-0.24) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



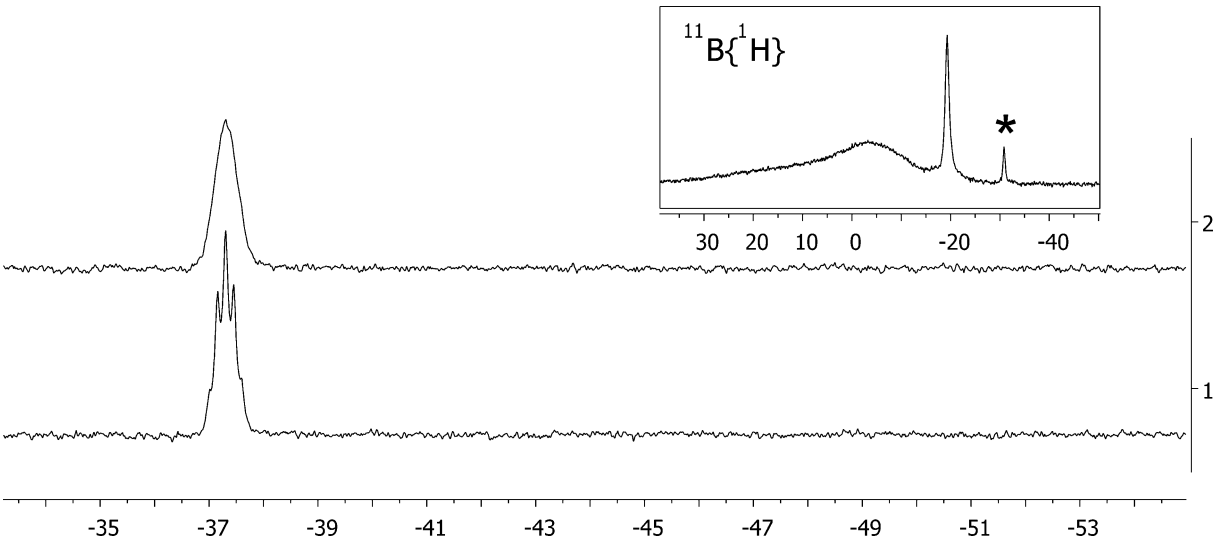
^{1}H NMR (500 MHz, 299 K, $CDCl_3$(*)); p: pentane.



$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, $CDCl_3$(*)).



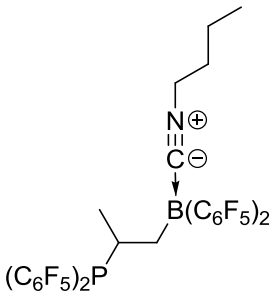
^{19}F NMR (470 MHz, 299 K, $CDCl_3$).



1: $^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, $CDCl_3$);2: ^{31}P NMR (202 MHz, 299 K, $CDCl_3$); box: $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, $CDCl_3$); *: $HB(C_6F_5)_2$*CN^tBu.

Reaction of C_2-bridged FLP 10 with *n*-butylisonitrile 14

Caution: many isonitriles are toxic and must handled with due care.



Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (100 mg, 0.246 mmol) and bis(pentafluorophenyl)borane (85.3 mg, 0.246 mmol) were dissolved in *n*-pentane (10 mL) and stirred for two hours at rt to give a clear solution. *n*-Butylisonitrile (20.5 mg, 0.246 mmol) was added and the reaction mixture was cooled to −78 °C and stirred for one hour at that temperature while a white solid precipitated. The solvent was removed by filter cannula and the residue was dried *in vacuo* to give a white solid (128 mg, 0.153 mmol, 62%). (small amounts of impurities of $HB(C_6F_5)_2$*CN^nBu are visible in the NMR spectra ($\delta^{11}B\{^1H\}$: −30.7).

Single crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of an n-pentane solution of **14** at rt.

^{1}H NMR (500 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 3.25 (m, 1H, ^{P}CH), 2.49 (td, $^3J_{HH}$ = 6.7 Hz, *J* = 1.4 Hz, 2H, $^{N}CH_2$), 1.68/1.60 (each br m, each 1H, $^{B}CH_2$), 1.07 (dd, $^3J_{PH}$ = 20.7 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, $^{CH}CH_3$), 0.97 (m, 2H, $^{CH2}CH_2{}^{CH2}$), 0.85 (m, 2H, $^{CH3}CH_2$), 0.54 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $^{CH2}CH_3$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 128.7 (br, ^{N}C), 117.1 (br, *i*-$C_6F_5{}^{B}$), 108.8 (br, *i*-$C_6F_5{}^{P}$), 43.6 ($^{N}CH_2$), 29.2 ($^{CH2}CH_2{}^{CH2}$), 26.8 (m, ^{P}CH), 23.9 (br, $^{B}CH_2$), 19.3 ($^{CH3}CH_2$), 18.6 (d, $^2J_{PC}$ = 25.1 Hz, $^{CH}CH_3$), 12.6 ($^{CH2}CH_3$); [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (500 MHz, 299 K, C_6D_6/CD_2Cl_2): δ^1H / δ^1H = 3.25 / 1.68, 1.60, 1.07 (^{P}CH / $^{B}CH_2$, $^{CH}CH_3$), 2.49 / 0.97 ($^{N}CH_2$ / $^{CH2}CH_2{}^{CH2}$), 1.68, 1.60 / 3.25 ($^{B}CH_2$ / ^{P}CH), 1.07 / 3.25, 1.68 ($^{CH}CH_3$ / ^{P}CH, $^{B}CH_2$), 0.97 / 2.49, 0.85 ($^{CH2}CH_2{}^{CH2}$ / $^{N}CH_2$, $^{CH3}CH_2$), 0.85 / 0.97, 0.54 ($^{CH3}CH_2$ / $^{CH2}CH_2{}^{CH2}$, $^{CH2}CH_3$).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6/CD_2Cl_2): δ^1H / $\delta^{13}C$ = 3.25 / 26.8 (^{P}CH), 2.49 / 43.6 ($^{N}CH_2$), 1.68, 1.60 / 23.9 ($^{B}CH_2$), 1.07 / 18.6 ($^{CH}CH_3$), 0.97 / 29.2 ($^{CH2}CH_2{}^{CH2}$), 0.85 / 19.3 ($^{CH3}CH_2$), 0.54 / 12.6 ($^{CH2}CH_3$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, C_6D_6/CD_2Cl_2): δ^1H / $\delta^{13}C$ = 2.49 / 128.7, 29.2, 19.3 ($^{N}CH_2$ / ^{N}C, $^{CH2}CH_2{}^{CH2}$, $^{CH3}CH_2$), 1.68, 1.60 / 128.7, 117.1, 26.8, 18.6 ($^{B}CH_2$ / ^{N}C, *i*-$C_6F_5{}^{B}$, ^{P}CH, $^{CH}CH_3$), 1.07 / 26.8, 23.9 ($^{CH}CH_3$ / ^{P}CH, $^{B}CH_2$), 0.97 / 43.6, 19.3, 12.6 ($^{CH2}CH_2{}^{CH2}$ / $^{N}CH_2$, $^{CH3}CH_2$,

$^{CH2}CH_3$), 0.85 / 43.6, 29.2, 12.6 ($^{CH3}CH_2$ / $^{N}CH_2$, $^{CH2}CH_2{}^{CH2}$, $^{CH2}CH_3$), 0.54 / 29.2, 19.3 ($^{CH2}CH_3$ / $^{CH2}CH_2{}^{CH2}$, $^{CH3}CH_2$).

^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = −19.1 ($v_{1/2}$ ~ 250 Hz).

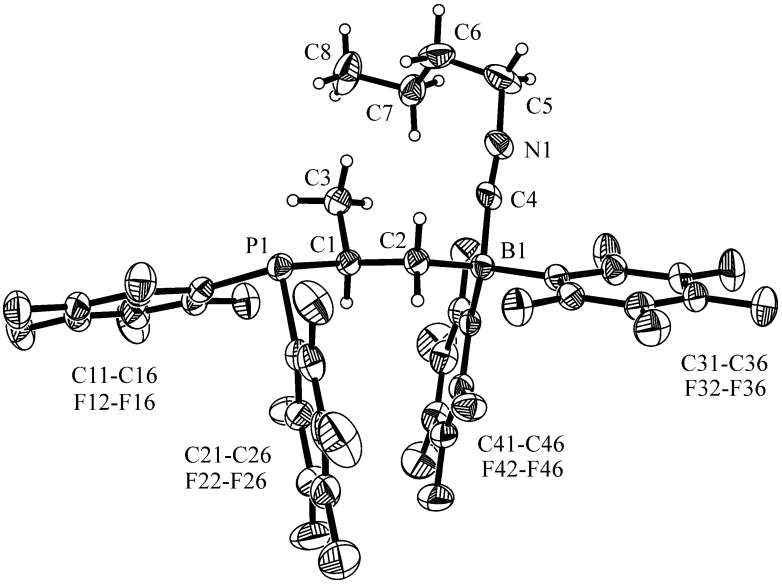
^{19}F NMR (470 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = −130.1 (m, 4F, *o*-$P^{A,B}$), −132.6 (m, 2F, *o*-B^{A}), −133.4 (m, 2F, *o*-B^{B}), −148.8 (tm, $^{3}J_{FF}$ = 20.9 Hz, 1F, *p*-P^{A}), −149.5 (tm, $^{3}J_{FF}$ = 20.9 Hz, 1F, *p*-P^{B}), −156.2 (tm, $^{3}J_{FF}$ = 20.0 Hz, 2F, *p*-$B^{A,B}$), −160.3 (m, 4F, *m*-$P^{A,B}$), −162.7 (m, 4F, *m*-$B^{A,B}$); [$\Delta\delta^{19}F_{p,m}$: 6.5 (B), 11.5 (P^{A}), 10.8 (P^{B})].

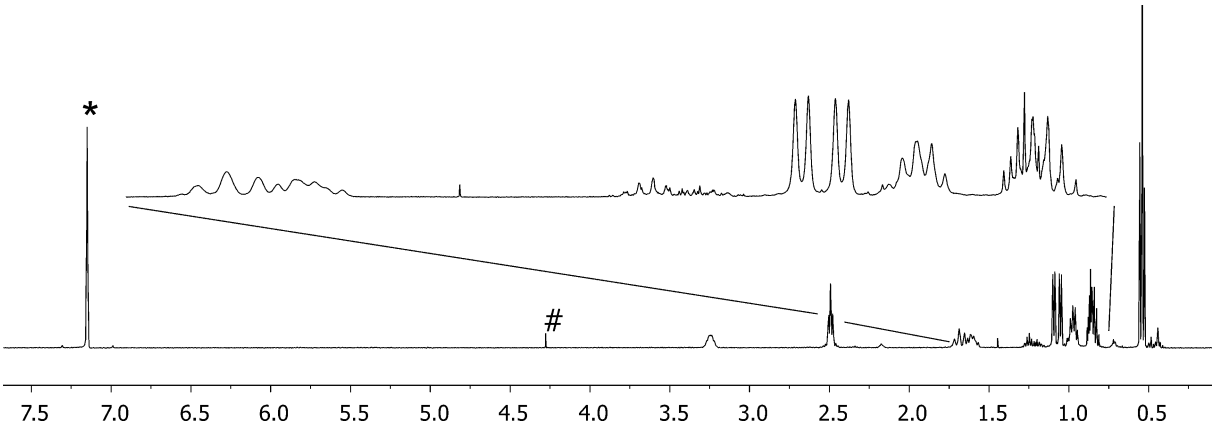
^{19}F,^{19}F GCOSY (470 MHz, 299 K, C_6D_6/CD_2Cl_2): δ^{19}F / δ^{19}F = −130.1 / −148.8, −149.5, −160.3 (*o*-$P^{A,B}$ / *p*-P^{A}, *p*-P^{B}, *m*-$P^{A,B}$), −132.6 / −156.2, −162.7 (*o*-B^{A} / *p*-$B^{A,B}$, *m*-$B^{A,B}$), −133.4 / −156.2, −162.7 (*o*-B^{B} / *p*-$B^{A,B}$, *m*-$B^{A,B}$), −148.8 / −130.1, −160.3 (*p*-P^{A} / *o*-$P^{A,B}$, *m*-$P^{A,B}$), −149.5 / −130.1, −160.3 (*p*-P^{B} / *o*-$P^{A,B}$, *m*-$P^{A,B}$), −156.2 / −132.6, −133.4, −162.7 (*p*-$B^{A,B}$ / *o*-B^{A}, *o*-B^{B}, *m*-$B^{A,B}$), −160.3 / −130.1, −148.8, −149.5 (*m*-$P^{A,B}$ / *o*-$P^{A,B}$, *p*-P^{A}, *p*-P^{B}), −162.7 / −132.6, −133.4, −156.2 (*m*-$B^{A,B}$ / *o*-B^{A}, *o*-B^{B}, *p*-$B^{A,B}$).

^{31}P{^{1}H} NMR (202 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = −36.9 (quin, $^{3}J_{PF}$ = 30.5 Hz).

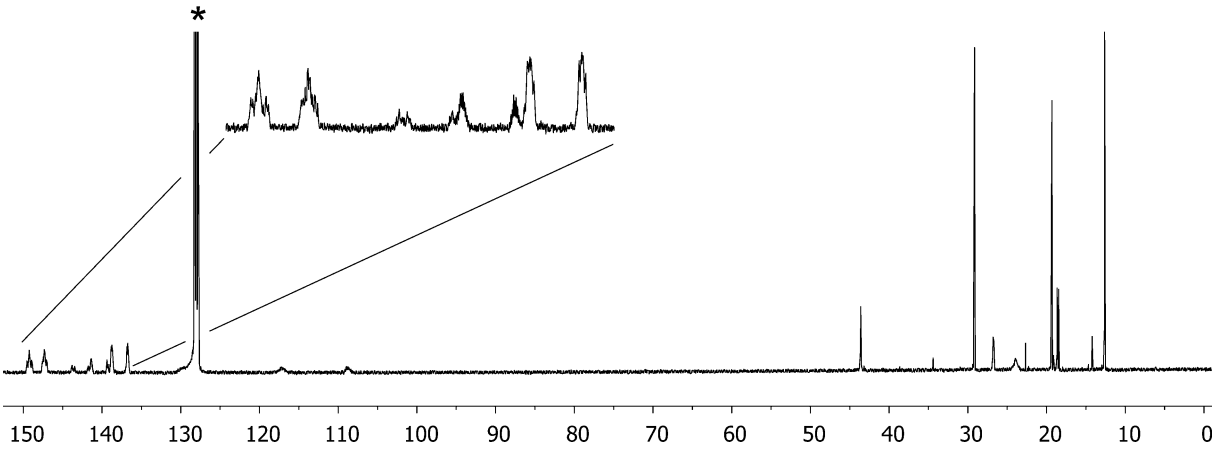
^{31}P NMR (202 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = −36.9 ($v_{1/2}$ ~ 100 Hz).

X-ray crystal structure analysis of 14: formula $C_{32}H_{15}BF_{20}NP$, *M* = 835.23 colourless crystal, 0.42 x 0.36 x 0.12 mm, *a* = 9.1649(2), *b* = 11.6030(2), *c* = 16.2616(4) Å, α = 75.183(1), *β* = 75.375(1), γ = 85.283(2)°, *V* = 1617.31(6) $Å^3$, ρ_{calc} = 1.715 gcm^{-3}, μ = 0.228 mm^{-1}, empirical absorption correction (0.910 ≤ T ≤ 0.973), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.71073 Å, *T* = 223(2) K, ω and ϕ scans, 15281 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.59 $Å^{-1}$, 5516 independent (R_{int} = 0.037) and 4873 observed reflections [*I*>2σ(*I*)], 552 refined parameters, *R* = 0.048, wR^2 = 0.120, max. (min.) residual electron density 0.33 (-0.30) e.$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

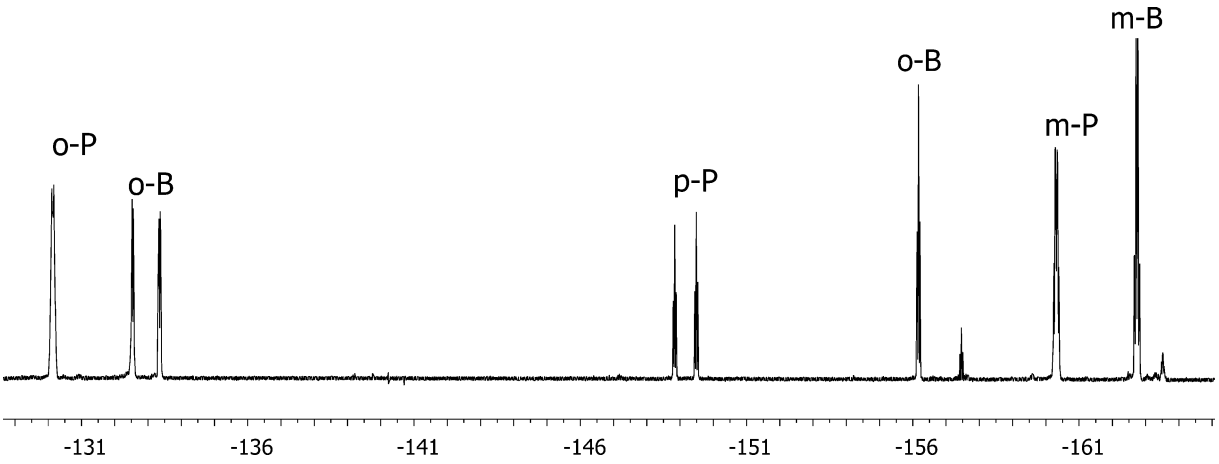




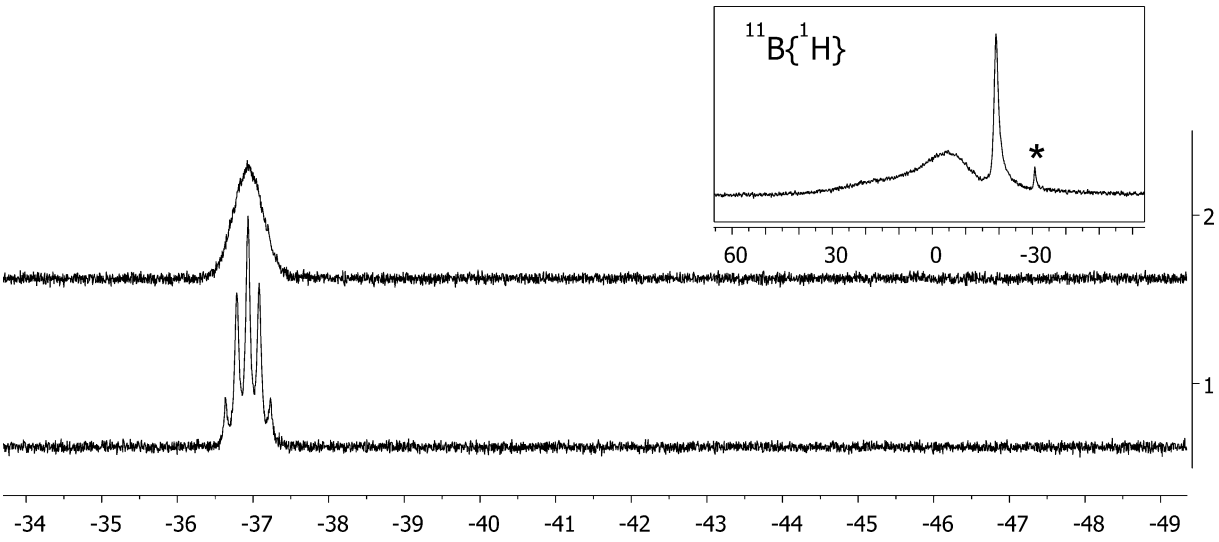
^{1}H NMR (500 MHz, 299 K, C_6D_6(*)/CD_2Cl_2(#)).



$^{13}C\{^{1}H\}$ NMR (126 MHz, 299 K, C_6D_6(*)/CD_2Cl_2).

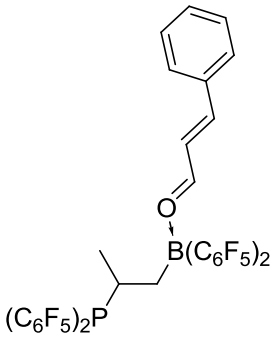


^{19}F NMR (470 MHz, 299 K, C_6D_6/CD_2Cl_2).



1: $^{31}P\{^1H\}$ NMR (202 MHz, 299 K, C_6D_6/CD_2Cl_2); 2: ^{31}P NMR (202 MHz, 299 K, C_6D_6/CD_2Cl_2); box: $^{11}B\{^1H\}$ NMR (160 MHz, 299 K, C_6D_6/CD_2Cl_2); *: $HB(C_6F_5)_2$*CN^nBu.

Reaction of C_2-bridged FLP 10 with cinnamic aldehyde to 15



Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (150 mg, 0.375 mmol) and bis(pentafluorophenyl)borane (130 mg, 0.375 mmol) were dissolved in *n*-pentane (5 mL) and after stirring for five min the reaction mixture turned cloudy. Cinnamic aldehyde (50.0 mg, 0.375 mmol) was added to the reaction mixture which turned green-yellow and a white solid precipitated. The solid was isolated *via* filter cannula, washed with *n*-pentane (15 mL) and dried

in vacuo (158 mg, 0.179 mmol, 48%).

Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product **15** in dichloromethane.

IR (KBr): ṽ = 3434 (br), 2966 (w), 2917 (w), 1643 (m), 1611 (s), 1586 (s), 1518 (s), 1461 (s), 1386 (m), 1330 (w), 1288 (m), 1267 (w), 1223 (w), 1197 (m), 1090 (s), 975 (s), 896 (w), 861 (w), 812 (m), 755 (w), 713 (w), 682 (w), 634 (w), 564 (w).

Elemental analysis: calcd. for $C_{36}H_{14}BF_{20}OP$: C 48.90, H 1.60; found: C 48.21, H 1.84.

Mp: 165 °C (DSC).

^{1}H NMR (600 MHz, 299 K, C_6D_6) : δ = 8.20 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H, CHO), 6.96 (m, 1H, *p*-Ph), 6.82 (m, 2H, *m*-Ph), 6.76 (m, 2H, *o*-Ph), 6.72 (d, $^{3}J_{HH}$ = 15.5 Hz, 1H, ^{Ph}CH), 6.56 (dd, $^{3}J_{HH}$ = 15.5 Hz, $^{3}J_{HH}$ = 8.6 Hz, 1H, ^{CHO}CH), 3.54 (m, 1H, ^{P}CH), 1.73/1.60 (each m, each 1H, $^{B}CH_2$), 1.28 (dd, $^{3}J_{PH}$ = 21.2 Hz, $^{3}J_{HH}$ = 6.7 Hz, 3H, CH_3).

^{1}H{^{1}H} TOCSY (600 MHz, 299 K, C_6D_6): $\delta^{1}H_{irr}$ / $\delta^{1}H_{res}$ = 8.20 / 6.72, 6.56 (CHO / ^{Ph}CH, ^{CHO}CH), 6.96 / 6.82, 6.76 (*p*-Ph / *m*-Ph, *o*-Ph), 6.82 / 6.96, 6.76 (*m*-Ph / *p*-Ph, *o*-Ph), 6.76 / 8.20, 6.96, 6.82, 6.56 (*o*-Ph / CHO, *p*-Ph, *m*-Ph, ^{CHO}CH), 6.72 / 8.20, 6.96, 6.82, 6.56 (^{Ph}CH / CHO, *p*-Ph, *m*-Ph, ^{CHO}CH), 6.56 / 8.20, 6.72 (^{CHO}CH / CHO, ^{Ph}CH), 3.54 / 1.28 (^{P}CH / CH_3), 1.73, 1.60 / 1.28 (CH_2 / CH_3), 1.28 / 3.54, 1.73, 1.60 (CH_3 / ^{P}CH, $^{B}CH_2$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ = 193.8 (CHO), 166.7 (br, ^{Ph}CH), 135.2 (*p*-Ph), 132.6 (*i*-Ph), 131.2 (*o*-Ph), 129.4 (*m*-Ph), 123.3 (^{CHO}CH), 28.6 (br, $^{B}CH_2$), 25.9 (^{P}CH), 19.5 (d, $^{2}J_{PC}$ = 23.8 Hz, CH_3); [C_6F_5 not listed]

^{1}H,^{1}H GCOSY (600 MHz, 299 K, C_6D_6): $\delta^{1}H$ / $\delta^{1}H$ = 8.20 / 6.56 (CHO / ^{CHO}CH), 6.96 / 6.82, 6.76 (*p*-Ph / *m*-Ph, *o*-Ph), 6.82 / 6.96, 6.76 (*m*-Ph / *p*-Ph, *o*-Ph), 6.76 / 6.96, 6.82 (*o*-Ph / *p*-Ph, *m*-Ph), 6.72 / 6.56 (^{Ph}CH / ^{CHO}CH), 6.56 / 8.20, 6.72 (^{CHO}CH / CHO, ^{Ph}CH), 3.54 / 1.73, 1.60, 1.28 (^{P}CH / $^{B}CH_2$, CH_3), 1.73, 1.60 / 3.54 ($^{B}CH_2$ / ^{P}CH), 1.28 / 3.54 (CH_3 / ^{P}CH).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): $\delta^{1}H$ / $\delta^{13}C$ = 8.20 / 193.8 (CHO), 6.96 / 135.2 (*p*-Ph), 6.82 / 129.4 (*m*-Ph), 6.76 / 131.2 (*o*-Ph), 6.72 / 166.7 (^{Ph}CH), 6.56 / 123.3 (^{CHO}CH), 3.54 / 25.9 (^{P}CH), 1.73, 1.60 / 28.6 ($^{B}CH_2$), 1.28 / 19.5 (CH_3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6) : $\delta^{1}H$ / $\delta^{13}C$ = 6.96 / 131.2 (*p*-Ph / *o*-Ph), 6.82 / 132.6, 129.4 (*m*-Ph / *i*-Ph, *m*-Ph), 6.76 / 166.7, 135.2, 131.2 (*o*-Ph / ^{Ph}CH, *p*-Ph, *o*-Ph),

6.72 / 193.8, 131.2, 123.3 (^{Ph}CH / CHO, *o*-Ph, ^{CHO}CH), 6.56 / 132.5 (^{CHO}CH / *i*-Ph), 1.73 / 19.5 ($^{B}CH_2$ / CH_3), 1.28 / 28.6, 25.9 (CH_3 / $^{B}CH_2$, ^{P}CH).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = 8.3 ($v_{1/2}$ ~ 700 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = −129.3 (m, 2F, *o*-P^A), −129.8 (m, 2F, *o*-P^B), −133.2 (br, 4F, *o*-B), −148.6 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-P^A), −149.6 (t, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-P^B), −155.7 (br, 2F, *p*-B), −160.2 (m, 4F, *m*-$P^{A,B}$), −162.6 (br, 4F, *m*-B); [$\Delta\delta^{19}F_{p,m}$: 6.9 (B), 11.6 (P^A), 10.6 (P^B)].

^{19}F,^{19}F GCOSY (470 MHz, 299 K, C_6D_6) : δ^{19}F / δ^{19}F = −129.3 / −148.6, −160.2 (*o*-P^A / *p*-P^A, *m*-$P^{A,B}$), −129.8 / −149.6, −160.2 (*o*-P^B / *p*-P^B, *m*-$P^{A,B}$), −148.6 / −129.3, −160.2 (*p*-P^A / *o*-P^A, *m*-$P^{A,B}$), −149.6 / −129.8, −160.2 (*p*-P^B / *o*-P^B, *m*-$P^{A,B}$), −160.2 / −129.3, −129.8, −148.6, −149.6 (*m*-$P^{A,B}$ / *o*-P^A, *o*-P^B, *p*-P^A, *p*-P^B).

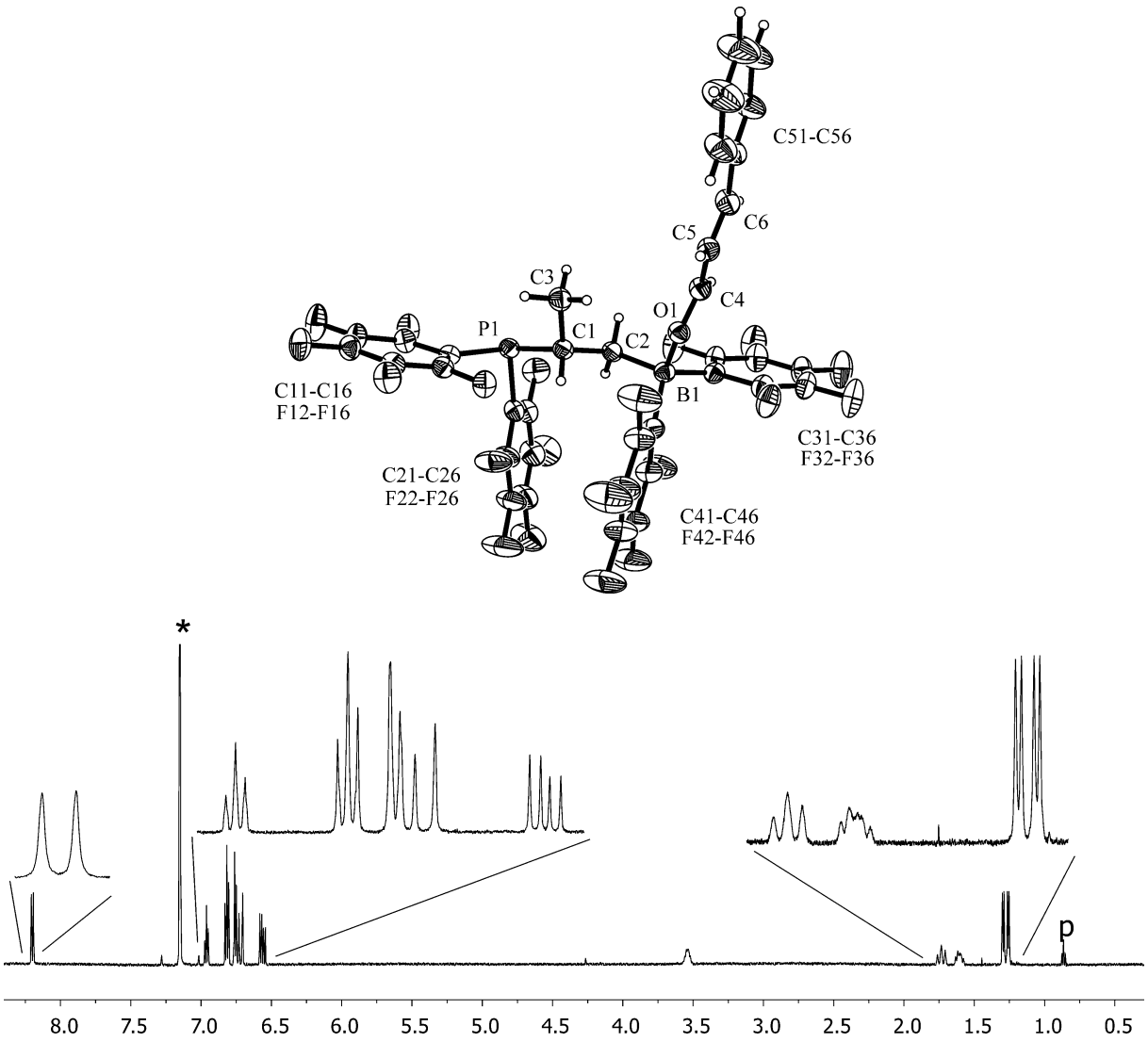
^{19}F NMR (564 MHz, 248 K, CD_2Cl_2): δ = −129.0, −129.3 (each br, each 2F, *o*-P), −132.7, −135.3 (each m, each 2F, *o*-B), −148.7, −149.6 (each br, each 1F, *p*-P), −157.2 (t, $^3J_{FF}$ = 20.4 Hz, 1H, *p*-B), −158.9 (t, $^3J_{FF}$ = 20.5 Hz, 1F, *p*-B), −160.6 (br m, 4F, *m*-P), −163.7, −164.6 (each m, 2F, *m*-B).

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = −34.8 (quin, $^3J_{PF}$ = 28.5 Hz).

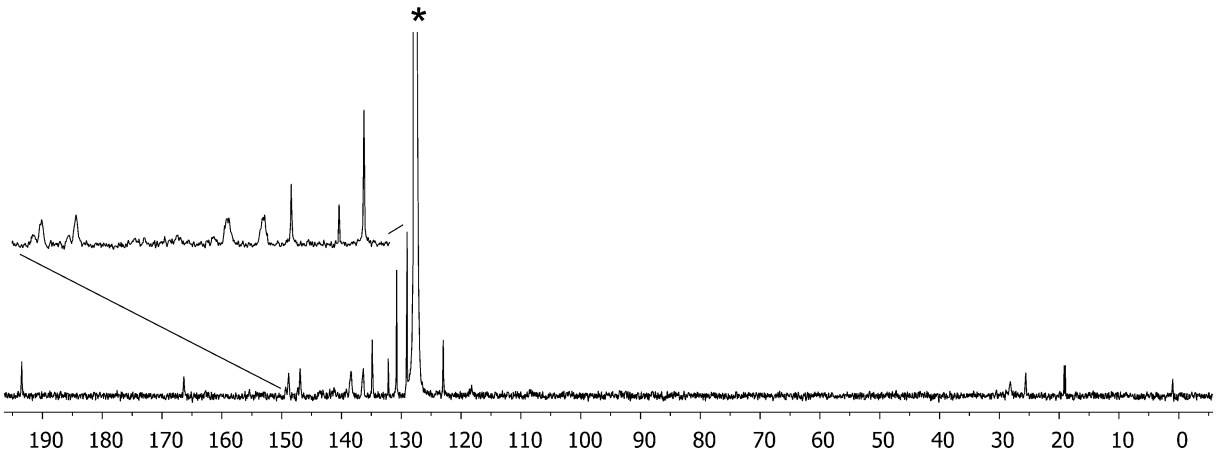
^{31}P NMR (243 MHz, 299 K, C_6D_6): δ = −34.8 ($v_{1/2}$ ~ 90 Hz).

^{31}P{^{1}H} NMR (243 MHz, 188 K, CD_2Cl_2): δ = −40.7 (br, $v_{1/2}$ ~ 1000 Hz, ~ 66%), 3.5 (br, $v_{1/2}$ ~ 700 Hz, ~ 16%), 12.2 (br, $v_{1/2}$ ~ 2500 Hz, ~ 18%).

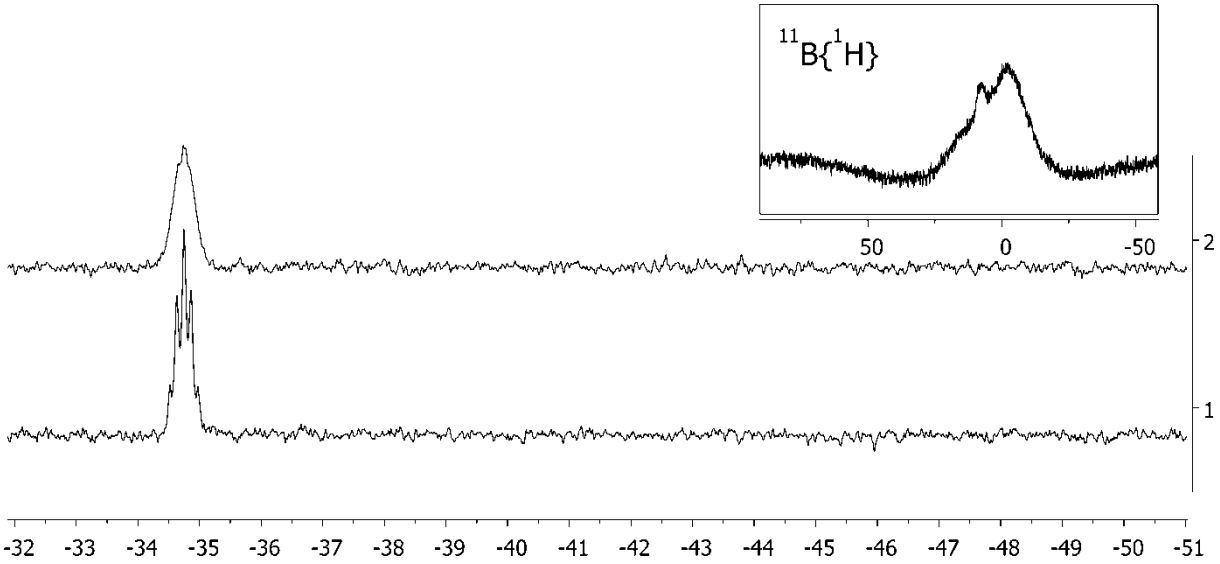
X-ray crystal structure analysis of 15: formula $C_{36}H_{14}BF_{20}OP$, *M* = 884.25, colourless crystal, 0.15 x 0.13 x 0.04 mm, *a* = 10.7451(3), *b* = 24.4031(8), *c* = 14.3508(6) Å, *β* = 110.583(2)°, *V* = 3522.8(2) Å^3, ρ_{calc} = 1.667 gcm^{-3}, μ = 1.979 mm^{-1}, empirical absorption correction (0.755 ≤ T ≤ 0.925), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 30969 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 6115 independent (R_{int} = 0.049) and 4880 observed reflections [*I*>2σ(*I*)], 534 refined parameters, *R* = 0.053, wR^2 = 0.144, max. (min.) residual electron density 0.33 (-0.30) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



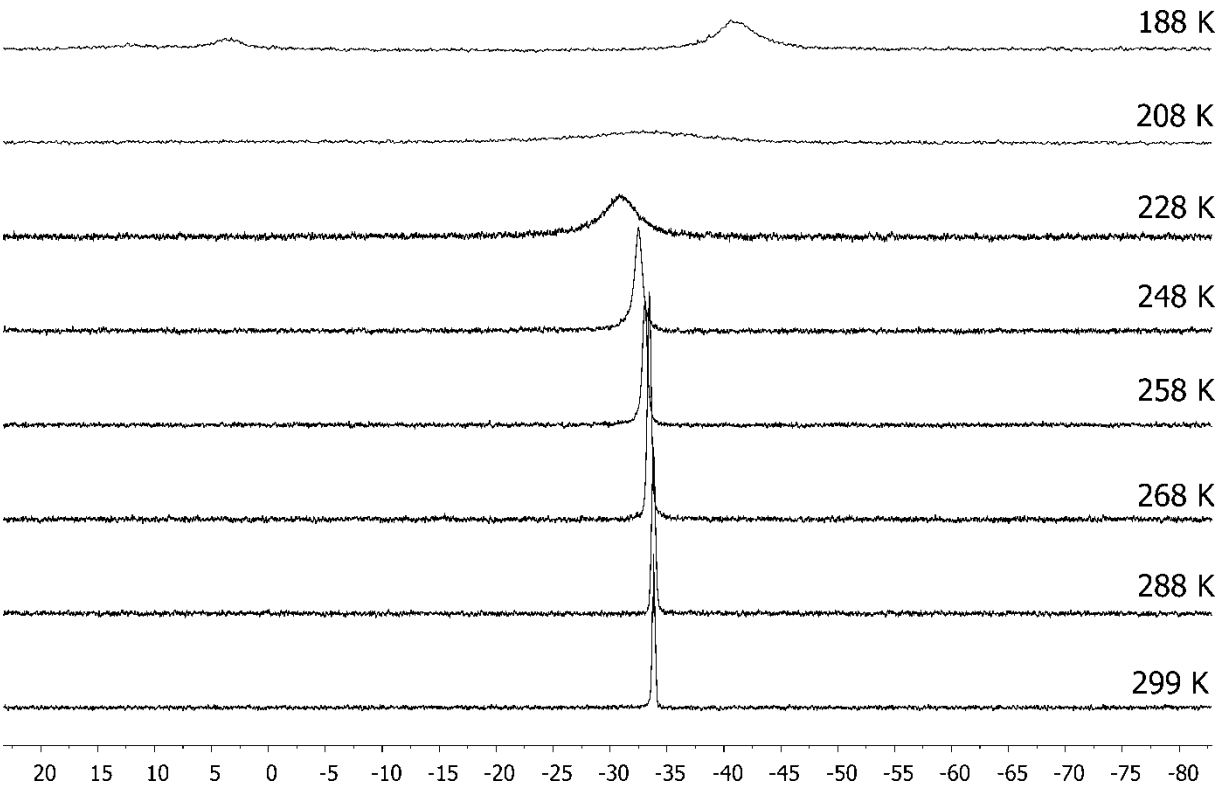
^{1}H NMR (600 MHz, 299 K, C_6D_6(*)); p: pentane.



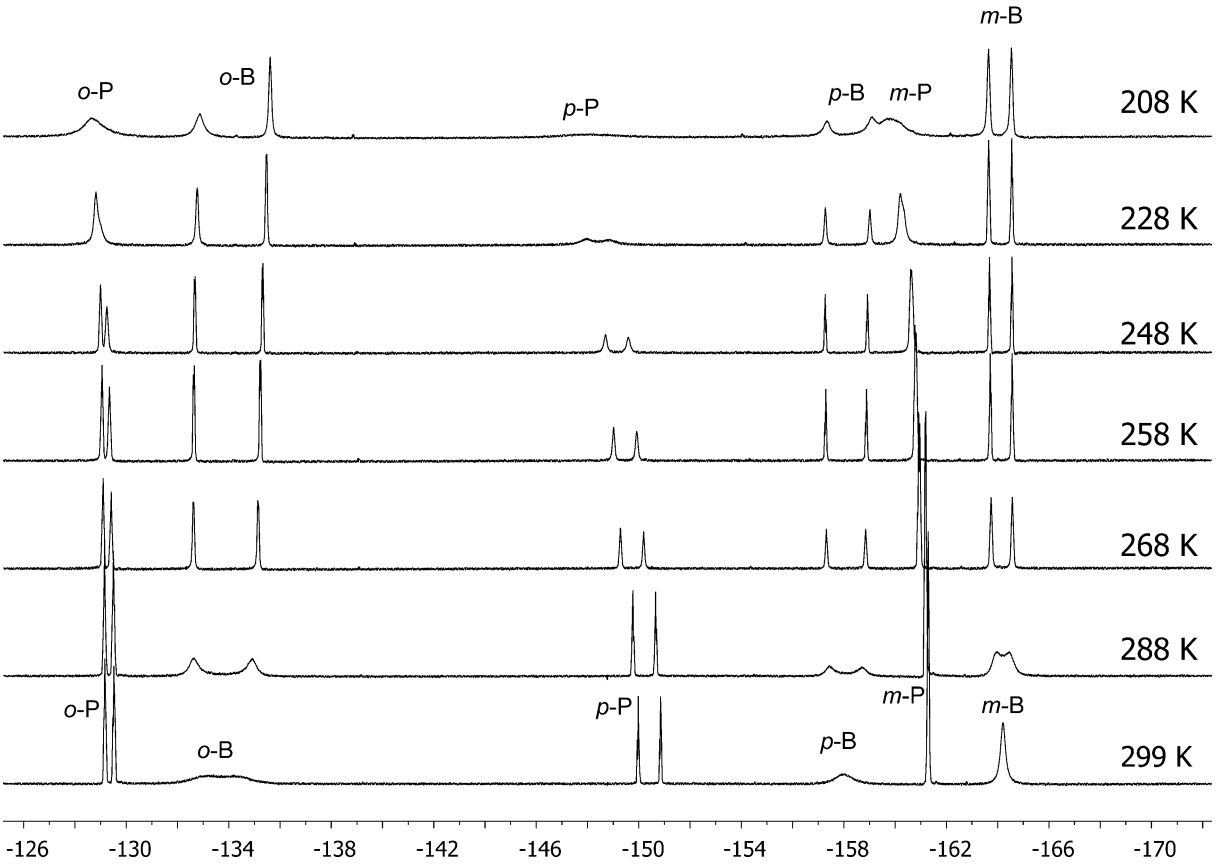
^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6(*)).



1: $^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, C_6D_6); 2: ^{31}P NMR (243 MHz, 299 K, C_6D_6); box: $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, C_6D_6).

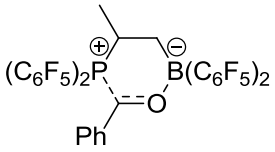


$^{31}P\{^{1}H\}$ VT-NMR (243 MHz, CD_2Cl_2).



^{19}F VT-NMR (564 MHz, CD_2Cl_2).

Reaction of C_2-bridged FLP 10 with benzaldehyde to 16



Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (250 mg, 0.62 mmol) and bis(pentafluorophenyl)borane (212.9 mg, 0.62 mmol) were dissolved in *n*-pentane (10 mL) and stirred for ten min before benzaldehyde (65.3 mg, 0.62 mmol) was added. A white solid precipitated. After stirring overnight the precipitate was isolated *via* filter cannula and the residue was dried *in vacuo* to give the product (392 mg, 0.457 mmol, 74%).

Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product **16** in dichloromethane at −30 °C.

Exact mass: calcd. for $C_{34}H_{12}BF_{20}OP + Na^+$: 881.03085 m/z; found: 881.03027 m/z.

IR (KBr): ṽ = 3437 (br), 2981 (w), 2935 (w), 1644 (s), 1598 (m), 1576 (m), 1524 (s), 1483 (s), 1463 (s), 1394 (m), 1307 (m), 1279 (m), 1230 (w), 1178 (w), 1103 (s), 1010 (m), 984 (s), 921 (m), 849 (w), 792 (m), 766 (w), 728 (w), 701 (m), 680 (m), 643 (w), 568 (w), 511 (w).

Elemental analysis: calcd. for $C_{34}H_{12}BF_{20}OP$: C 47.58, H 1.41; found: C 47.38, H 1.04.

Mp: 149 °C (DSC); **Dp**: 220 °C (DSC).

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2): δ = 7.82 (br s, 1H, ^{O}CH), 7.68 (m, 2H, *o*-Ph), 7.64 (m, 1H, *p*-Ph), 7.48 (m, 2H, *m*-Ph), 3.50 (m, 1H, ^{P}CH), 1.66 (ddd, $^{3}J_{PH}$ = 30.5 Hz, J_{HH} = 15.5 Hz, J_{HH} = 7.4 Hz), 1.43 (m) (each 1H, $^{B}CH_2$), 1.24 (dd, $^{3}J_{PH}$ = 22.1 Hz, $^{3}J_{HH}$ = 6.8 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, CD_2Cl_2): δ = n.o. (^{O}CH), 135.4 (br, *p*-Ph), 133.3 (*i*-Ph), 130.3 (br, *o*-Ph), 129.9 (*m*-Ph), 120.5 (br, *i*-$C_6F_5{}^{B}$), 101.1, 100.8 (each br, *i*-$C_6F_5{}^{P}$), 28.6 (br d, $^{1}J_{PC}$ = 13.3 Hz, ^{P}CH), 25.3 (br, $^{B}CH_2$), 19.1 (d, $^{2}J_{PC}$ = 7.1 Hz, CH_3); [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz, 299 K, CD_2Cl_2): δ^{1}H / δ^{1}H = 7.68 / 7.64, 7.48 (*o*-Ph / *p*-Ph, *m*-Ph), 7.64 / 7.68, 7.48 (*p*-Ph / *o*-Ph, *m*-Ph), 7.48 / 7.68, 7.64 (*m*-Ph / *o*-Ph, *p*-Ph), 3.50 / 1.66, 1.43, 1.24 (^{P}CH / $^{B}CH_2$, CH_3), 1.66 / 3.50, 1.43 ($^{B}CH_2$ / ^{P}CH, $^{B}CH_2$), 1.43 / 3.50, 1.66 ($^{B}CH_2$ / ^{P}CH, $^{B}CH_2$), 1.24 / 3.50 (CH_3 / ^{P}CH).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^{1}H / δ^{13}C = 7.68 / 130.3 (*o*-Ph), 7.64 / 135.4 (*p*-Ph), 7.48 / 129.9 (*m*-Ph), 3.50 / 28.6 (^{P}CH), 1.66, 1.43 / 25.3 ($^{B}CH_2$), 1.24 / 19.1 (CH_3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ^{1}H / δ^{13}C = 7.68 / 135.4, 130.3 (*o*-Ph / *p*-Ph, *o*-Ph), 7.64 / 130.3 (*p*-Ph / *o*-Ph), 7.48 / 133.3, 129.9 (*m*-Ph / *i*-Ph, *m*-Ph), 3.50 / 19.1 (^{P}CH / CH_3), 1.66, 1.43 / 28.6, 19.1 ($^{B}CH_2$ / ^{P}CH, CH_3), 1.24 / 28.6, 25.3 (CH_3 / ^{P}CH, $^{B}CH_2$).

^{11}B{^{1}H} NMR (192 MHz, 299 K, CD_2Cl_2): δ = 4.6 ($v_{1/2}$ ~ 350 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −125.7 (m, 2F, *o*-P^{A}), −126.9 (m, 2F, *o*-P^{B}), −134.6 (br, 4F, *o*-B), −143.9 (br, 1F, *p*-P^{A}), −144.1 (br, 1F, *p*-P^{B}), −158.0 (m, 2F, *m*-P^{A}), −158.7 (m, 2F, *m*-P^{B}), −159.4 (br, 2F, *p*-B), −164.9 (br, 4F, *m*-B); [$\Delta\delta^{19}F_{p,m}$: 5.5 (B), 14.1 (P^{A}), 14.3 (P^{B})].

^{19}F,^{19}F GCOSY (564 MHz, 299 K, CD_2Cl_2): δ^{19}F / δ^{19}F = −125.7 / −158.0 (*o*-P^{A} / *m*-P^{A}), −126.9 / −158.7 (*o*-P^{B} / *m*-P^{B}), −143.9 / −158.0 (*p*-P^{A} / *m*-P^{A}), −144.1 / −158.7 (*p*-P^{B} / *m*-P^{B}), −158.0 / −125.7 (*m*-P^{A} / *o*-P^{A}), −158.7 / −126.9 (*m*-P^{B} / *o*-P^{B}).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = −5.9 ($v_{1/2}$ ~ 70 Hz).

low temperature NMR measurements:

^{1}H NMR (600 MHz, 248 K, CD_2Cl_2): δ = 7.40 (1H), 7.31 (each br m, 4H)(Ph), 6.79 (br d, $^{2}J_{PH}$ = 14.3 Hz, 1H, $^{P}CH^{O}$), 3.60 (m, 1H, ^{P}CH), 1.79 (dd, $^{3}J_{PH}$ = 43.7 Hz, $^{3}J_{HH}$ = 15.4 Hz, 1H, $^{B}CH_2$), 1.37 (m, 1H, $^{B}CH_2$), 1.28 (dd, $^{3}J_{PH}$ = 22.7 Hz, $^{3}J_{HH}$ = 6.9 Hz, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR (151 MHz, 248 K, CD_2Cl_2): δ = 133.2 (*i*), 131.4 (*p*), 128.9, 127.2 (Ph), 29.4 (br, ^{P}CH), 22.5 (br, $^{B}CH_2$), 18.5 (CH_3); [C_6F_5 not listed, $^{P}CH^{O}$ not observed].

$^{11}B\{^{1}H\}$ NMR (192 MHz, 248 K, CD_2Cl_2): δ = 0.7 ($v_{1/2}$ ~ 460 Hz).

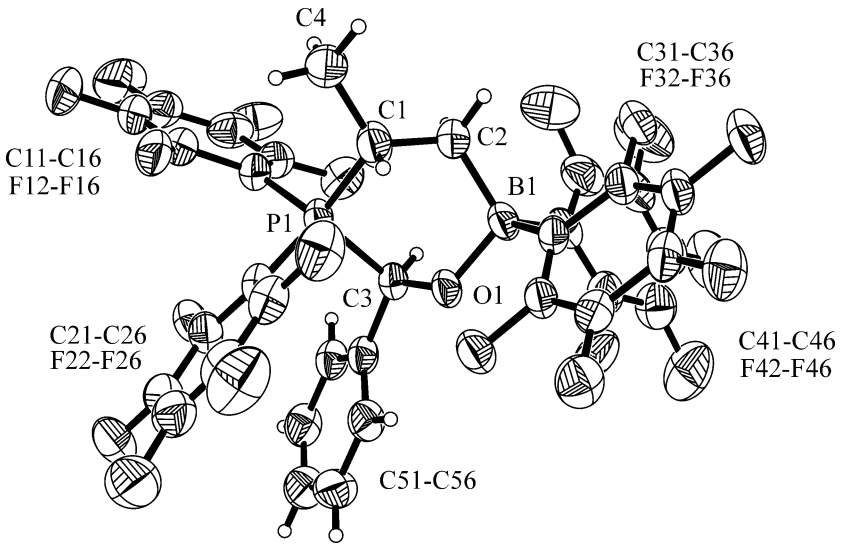
^{19}F NMR (564 MHz, 258 K, CD_2Cl_2): δ = −123.8, −125.6 (each m, each 2F, *o*-P), −134.9 (m, 2F, *o*-B^A), −135.6 (m, 2F, *o*-B^B), −140.1, −140.6 (each m, each 1F, *p*-P), −156.1, −157.2 (each m, each 2F, *m*-P), −159.8 (m, 1F, *p*-B^A), −160.8 (m, 1F, *p*-B^B), −164.9 (m, 2F, *m*-B^A), −165.4 (m, 2F, *m*-B^B); [$\Delta\delta^{19}F_{p,m}$: 5.1 (B^A), 4.6 (B^B), 15.5-17.1 (P)].

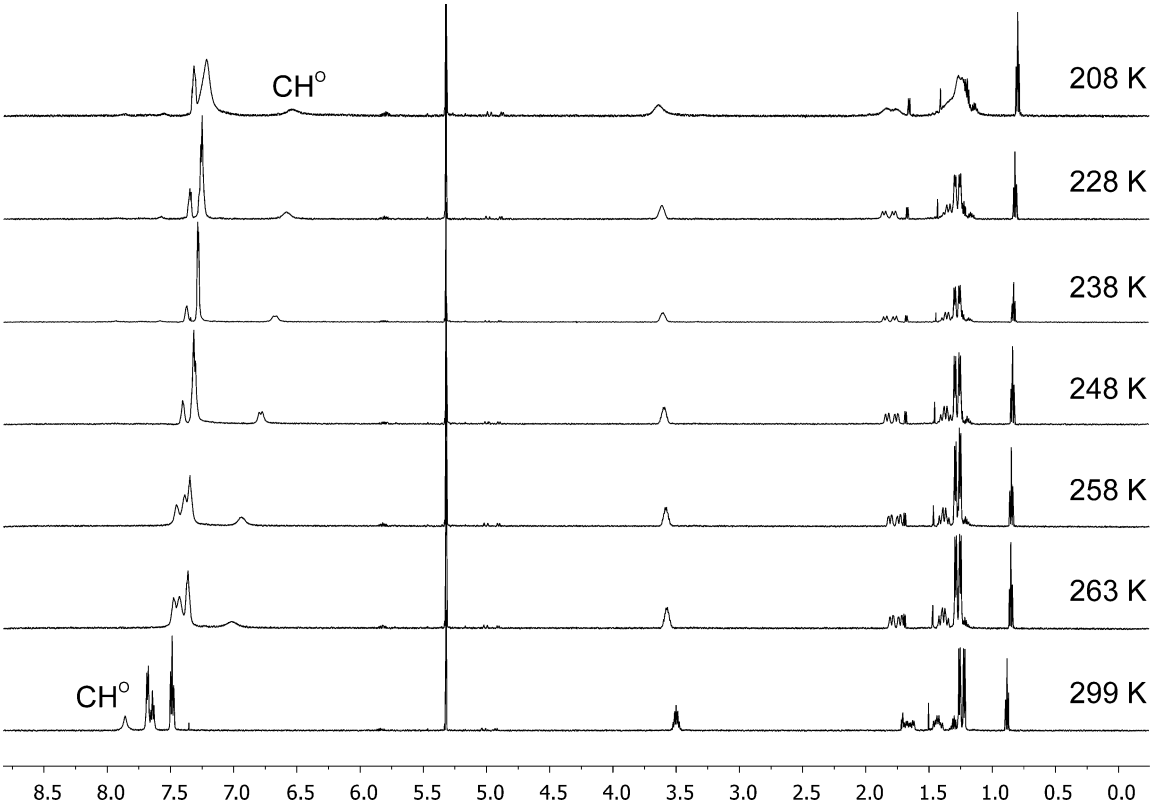
$^{19}F,^{19}F$ GCOSY (564 MHz, 258 K, CD_2Cl_2): $\delta^{19}F$ / $\delta^{19}F$ = −135.6 / −165.4 (*o*-B^B / *m*-B^B), −159.8 / −164.9 (*p*-B^A / *m*-B^A), −160.8 / −165.4 (*p*-B^B / *m*-B^B), −164.9 / −134.9, −159.8 (*m*-B^A / *o*-B^A, *p*-B^A), −165.4 / −135.6, −160.8 (*m*-B^B / *o*-B^B, *p*-B^B).

$^{31}P\{^{1}H\}$ NMR (243 MHz, 248 K, CD_2Cl_2): δ = 10.3 ($v_{1/2}$ ~ 450 Hz).

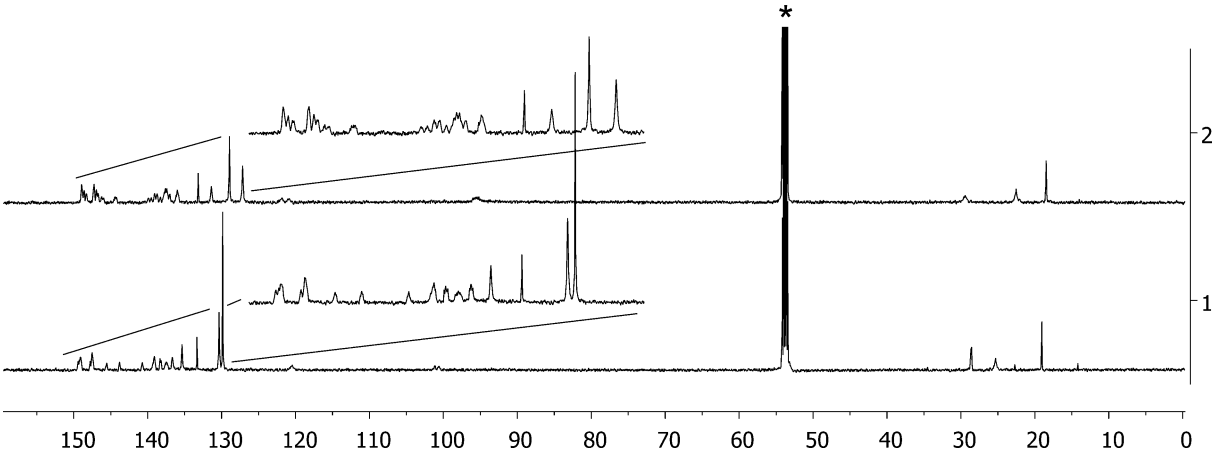
$^{31}P\{^{1}H\}$ NMR (243 MHz, 208 K, CD_2Cl_2): δ = 20.5 ($v_{1/2}$ ~ 350 Hz, 80%), 5.7 ($v_{1/2}$ ~ 200 Hz, 20%).

X-ray crystal structure analysis of 16B (quality of the crystals are too poor for discussion)**:** formula $C_{34}H_{12}BF_{20}OP$, *M* = 858.22, colourless crystal, 0.12 x 0.05 x 0.03 mm, *a* = 10.9643(8), *b* = 17.5853(9), *c* = 18.1387(15) Å, *β* = 90.951(7)°, *V* = 3496.9(4) $Å^3$, ρ_{calc} = 1.630 gcm^{-3}, μ = 1.973 mm^{-1}, empirical absorption correction (0.797 ≤ T ≤ 0.943), *Z* = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 23338 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 $Å^{-1}$, 5664 independent (R_{int} = 0.071) and 3593 observed reflections [$I>2\sigma(I)$], 515 refined parameters, *R* = 0.090, wR^2 = 0.279, max. (min.) residual electron density 0.78 (-0.39) e.$Å^{-3}$, hydrogen atoms calculated and refined as riding atoms.

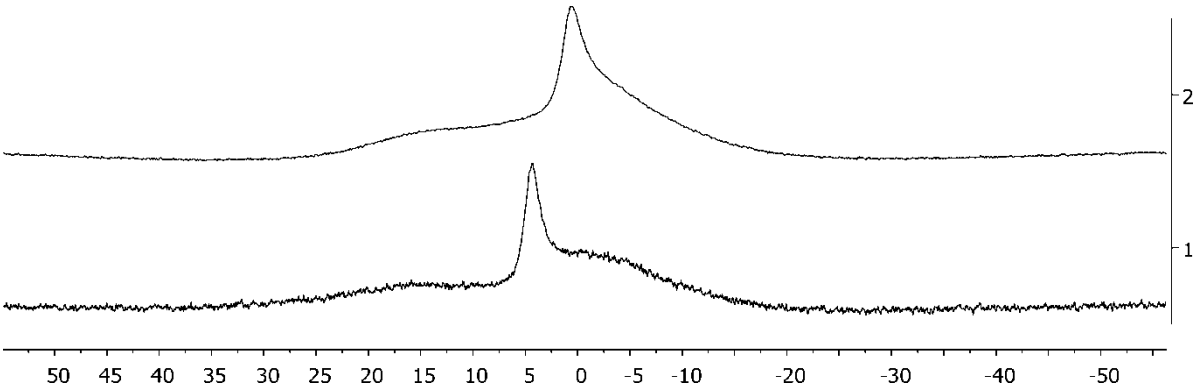




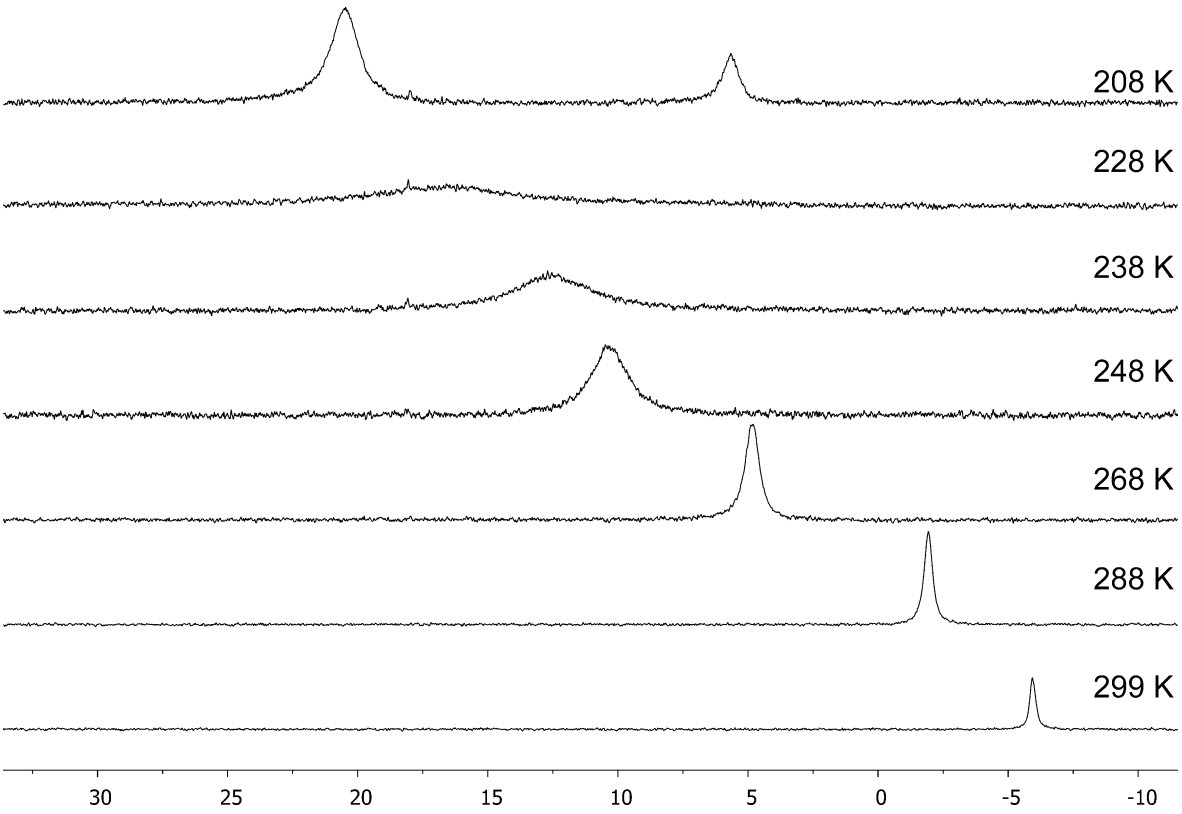
^{1}H VT-NMR (600 MHz, CD_2Cl_2).



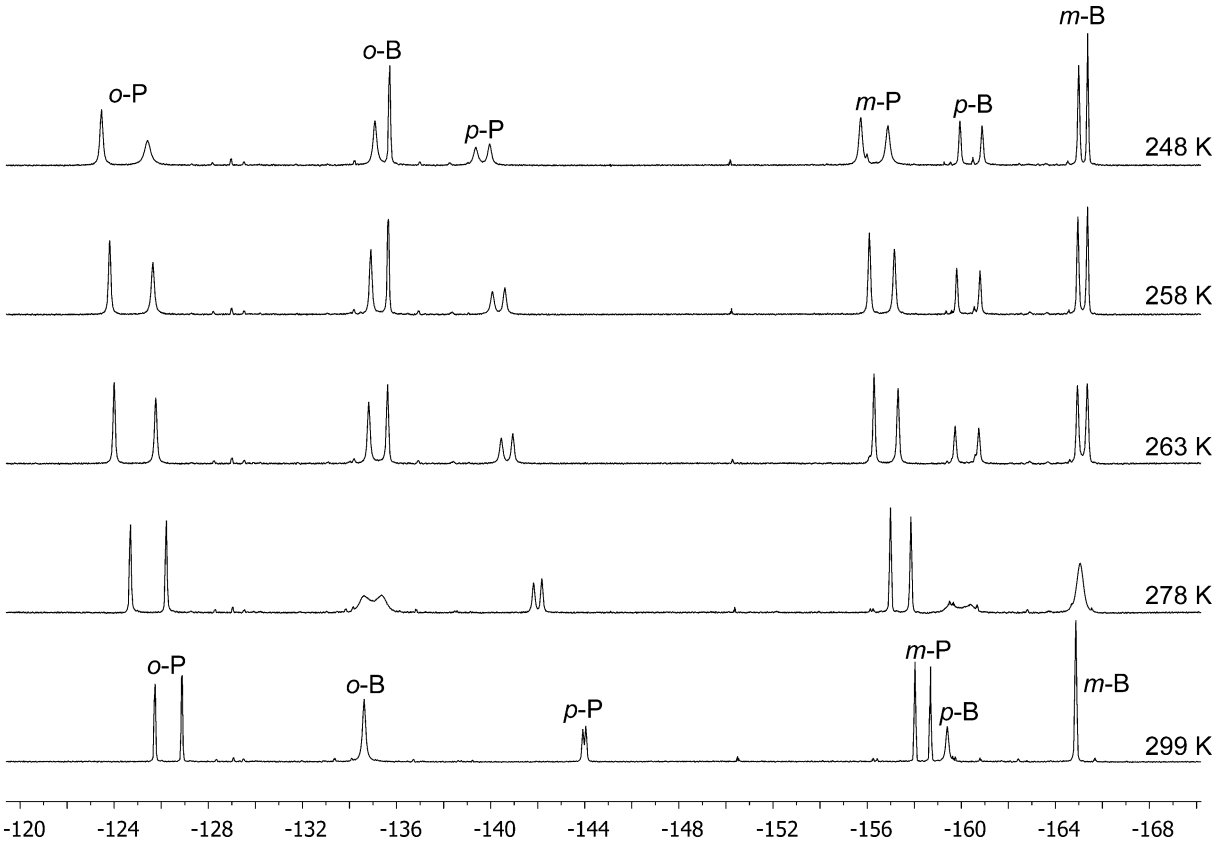
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) top: 248 K, bottom: 299 K.



^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2) top: 248 K, bottom 299 K.

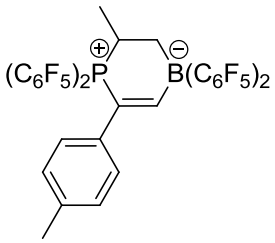


$^{31}P\{^{1}H\}$ VT-NMR (243 MHz, CD_2Cl_2).



^{19}F VT-NMR (564 MHz, CD_2Cl_2).

Reaction of C_2-bridged FLP 10 with *p*-tolylacetylene to 17



Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (100 mg, 0.246 mmol) and bis(pentafluorophenyl)borane (85.3 mg, 0.246 mmol) were dissolved in *n*-pentane (5 mL) and after stirring for five min the reaction mixture turned cloudy. *p*-Tolylacetylene (28.6 mg, 0.246 mmol) was added to the solution which turned orange immediately and after one hour a white solid precipitated. The white solid was isolated *via* filter cannula, washed with *n*-pentane (5 mL) and dried *in vacuo* (114 mg, 0.13 mmol, 52%).

Exact mass: calcd. for $C_{36}H_{14}BF_{20}P + Na^+$: 891.05052 m/z; found: 891.05089 m/z.

IR (KBr): $\tilde{\nu}$ = 2960 (w), 1936 (w), 1644 (m), 1525 (s), 1484 (s), 1460 (s), 1395 (m), 1306 (m), 1267 (m), 1111 (s), 1083 (s), 985 (s), 966 (s), 891 (w), 862 (w), 816 (m), 779 (w), 738 (w), 694 (m), 674 (w), 636 (w), 593 (w), 571 (w), 526 (w).

Elemental analysis: calcd. for $C_{36}H_{14}BF_{20}P$: C 49.80, H 1.63; found: C 49.40, H 1.48.

Mp: 216 °C (DSC).

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 8.92 (d, $^3J_{PH}$ = 64.1 Hz, 1H, $^{=}$CH), 6.84 (m, 2H, *o*-tol), 6.69 (m, 2H, *m*-tol), 3.47 (m, 1H, ^{P}CH), 1.99 (dd, $^3J_{PH}$ = 43.9 Hz, $^3J_{HH}$ = 15.6 Hz, 1H, $^{B}CH_2$), 1.84 (s, 3H, *p*-CH_3^{tol}), 1.57 (m, 1H, $^{B}CH_2$), 0.93 (dd, $^3J_{PH}$ = 22.8 Hz, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6) : δ = 187.9 (br, $^{=}$CH), 139.2 (d, $^5J_{PC}$ = 2.1 Hz, *p*-tol), 134.9 (d, $^2J_{PC}$ = 13.7 Hz, *i*-tol), 129.7 (d, $^4J_{PC}$ = 1.1 Hz, *m*-tol), 127.8 (*o*-tol), 116.9 (d, $^1J_{PC}$ = 71.0 Hz, $^{=}C^{tol}$), 31.7 (d, $^1J_{PC}$ = 39.1 Hz, ^{P}CH), 23.8 (br, $^{B}CH_2$), 20.8 (*p*-CH_3^{tol}), 18.1 (br, CH_3).

^{1}H,^{1}H GCOSY (500 MHz, 299 K, C_6D_6) : δ^{1}H / δ^{1}H = 8.92 / 1.99 ($^{=}$CH / $^{B}CH_2$), 6.84 / 6.69, 1.84 (*o*-tol / *m*-tol, *p*-CH_3^{tol}), 6.69 / 6.84, 1.84 (*m*-tol / *o*-tol, *p*-CH_3^{tol}), 3.47 / 1.99, 1.57, 0.93 (^{P}CH / $^{B}CH_2$, CH_3), 1.99 / 8.92, 3.47, 1.57 (CH_2 / $^{=}$CH, ^{P}CH, $^{B}CH_2$), 1.84 / 6.69 (*p*-CH_3^{tol} / *m*-tol), 1.57 / 3.47, 1.99, 0.93 ($^{B}CH_2$ / ^{P}CH, $^{B}CH_2$, CH_3), 0.93 / 3.47 (CH_3 / ^{P}CH).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6) : δ^{1}H / δ^{13}C = 8.92 / 187.9 ($^{=}$CH), 6.84 / 127.5 (*o*-tol), 6.69 / 129.7 (*m*-tol), 3.47 / 31.7 (^{P}CH), 1.99 / 23.8 ($^{B}CH_2$), 1.84 / 20.8 (*p*-CH_3^{tol}), 1.57 / 23.8 ($^{B}CH_2$), 0.93 / 18.1 (CH_3).

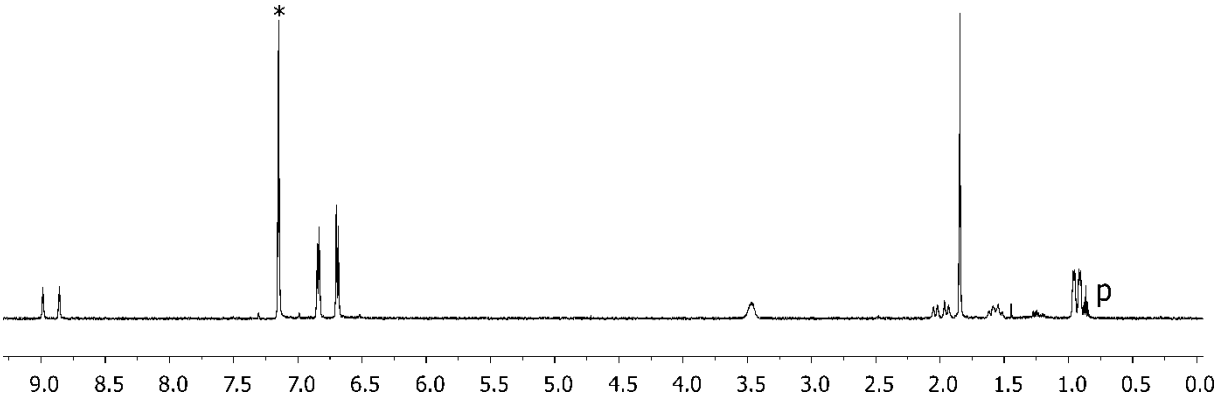
^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, C_6D_6) : δ^{1}H / δ^{13}C = 8.92 / 134.9, 23.8 ($^{=}$CH / *i*-tol, $^{B}CH_2$), 6.84 / 139.2, 129.7, 116.9 (*o*-tol / *p*-tol, *m*-tol, $^{=}C^{tol}$), 6.69 / 134.9, 127.5, 20.8 (*m*-tol / *i*-tol, *o*-tol, *p*-CH_3^{tol}), 1.84 / 139.2, 129.7 (*p*-CH_3^{tol} / *p*-tol, *m*-tol), 0.93 / 31.7, 23.8 (CH_3 / ^{P}CH, $^{B}CH_2$).

^{11}B{^{1}H} NMR (160 MHz, 299 K, C_6D_6): δ = −14.6 ($v_{1/2}$ ~ 50 Hz).

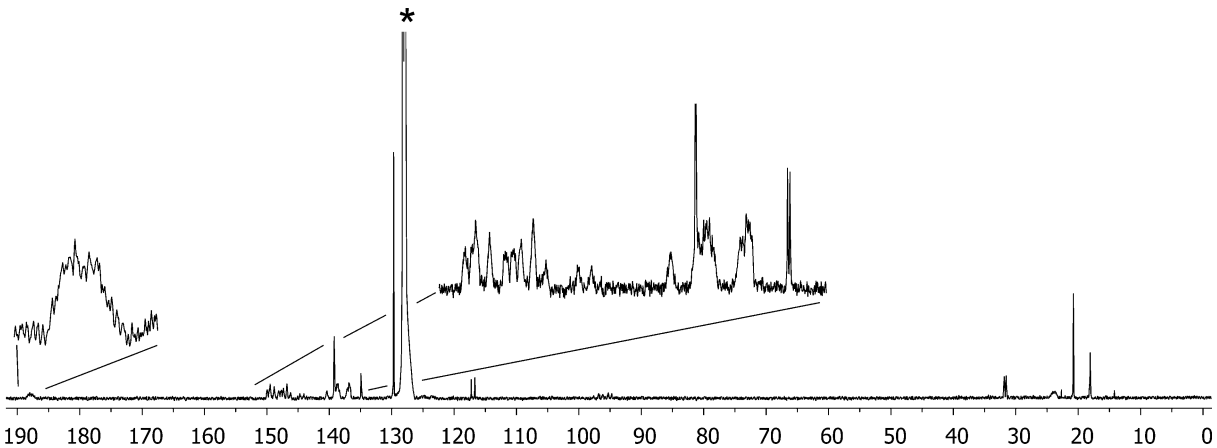
^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = −126.1, −127.1 (each br, each 2F, *o*-P), −132.8 (m, 2F, *o*-B^A), −133.9 (m, 2F, *o*-B^B), −135.2, −138.3 (each m, each 1F, *p*-P), −155.8, −156.1 (each m, each 2F, *m*-P), −159.2 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*-B^A), −159.9 (t, $^{3}J_{FF}$ = 20.6 Hz, 1F, *p*-B^B), −163.8 (m, 2F, *m*-B^A), −164.4 (m, 2F, *m*-B^B); [$\Delta\delta^{19}F_{p,m}$: 4.6 (B^A), 4.5 (B^B), 17.5-20.9 (P)].

^{19}F,^{19}F GCOSY (470 MHz, 299 K, C_6D_6): δ^{19}F / δ^{19}F = −132.8 / −163.8 (*o*-B^A / *m*-B^A), −133.9 / −164.4 (*o*-B^B / *m*-B^B), −159.2 / −163.8 (*p*-B^A / *m*-B^A), −159.9 / −164.4 (*p*-B^B / *m*-B^B), −163.8 / −132.8, −159.2 (*m*-B^A / *o*-B^A, *p*-B^A), −164.4 / −133.9, −159.9 (*m*-B^B / *o*-B^B, *p*-B^B).

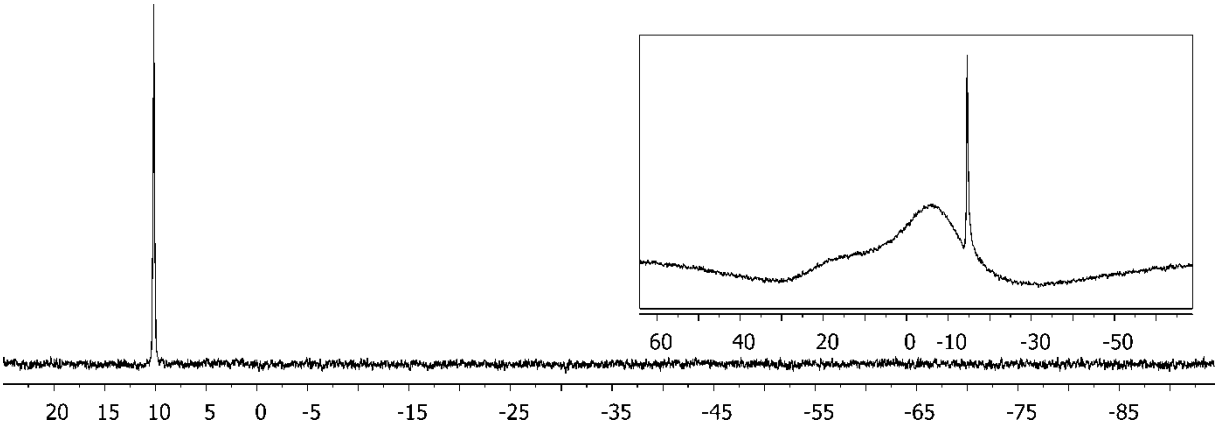
^{31}P{^{1}H} NMR (202 MHz, 299 K, C_6D_6): δ = 10.2 ($v_{1/2}$ ~ 35 Hz).



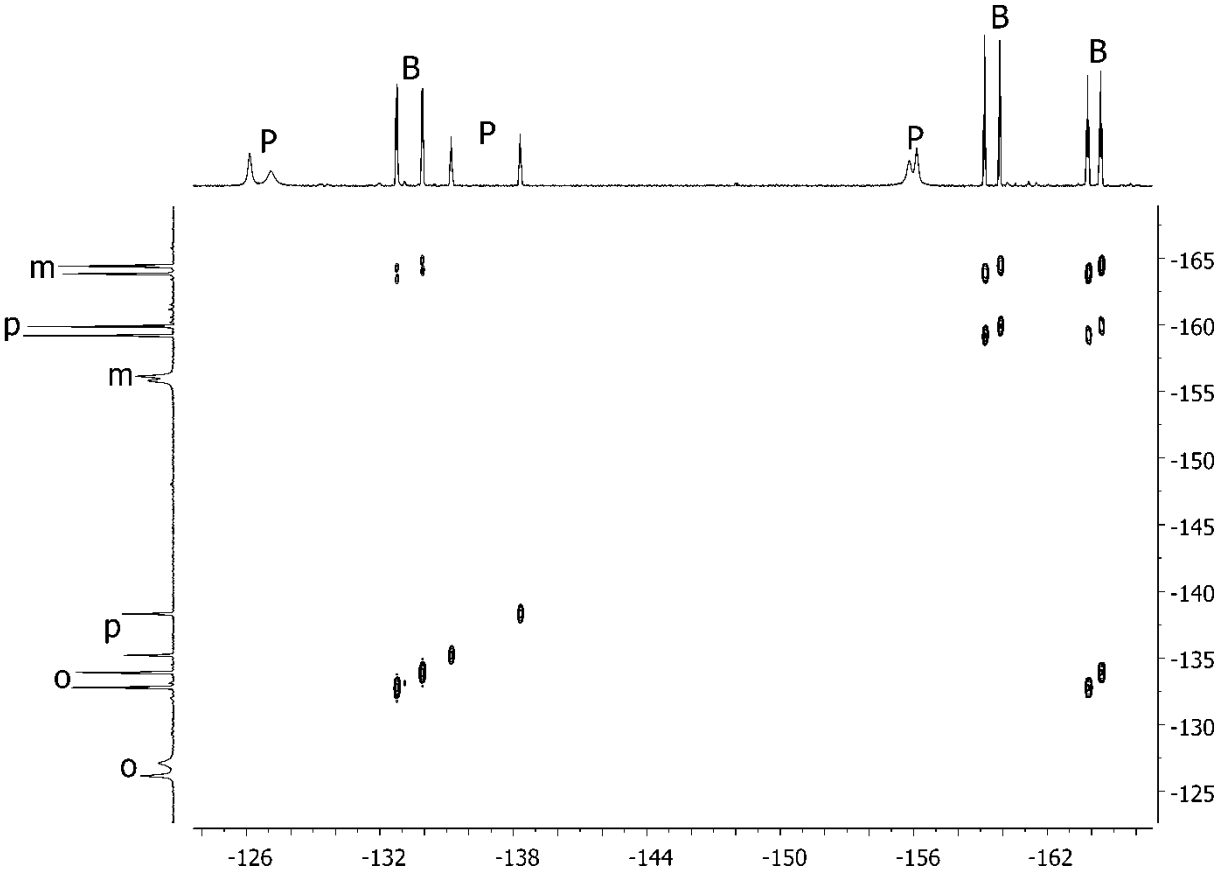
^{1}H NMR (500 MHz, 299 K, C_6D_6(*)); p: pentane.



^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6(*)).

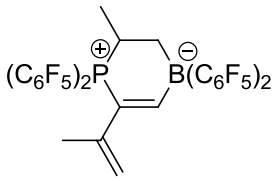


$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, C_6D_6); box: $^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6).

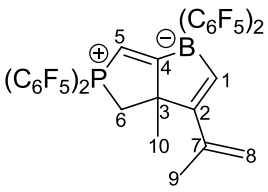


$^{19}F,^{19}F$ GCOSY (470 MHz, 299 K, C_6D_6).

Reaction of C_2-bridged FLP 10 with 3-methylbut-3-en-1-yne to 18 and a minor product



18



minor product

Bis(pentafluorophenyl)-2-propenylphosphane (**9**) (120 mg, 0.295 mmol) and bis(pentafluorophenyl)borane (102.2 mg, 0.295 mmol) were dissolved in *n*-pentane (5 mL) and stirred for 15 min at rt to give a cloudy solution. 2-Methylbut-1-en-3-yne (19.5 mg, 0.295 mmol) was added and the reaction mixture was stirred for 90 min at rt. The white precipitate was isolated from the yellow solution by filter cannula. The residue was washed with *n*-pentane (2x10 mL) and then dried *in vacuo* to give a white solid (127 mg, 0.154 mmol, 52%).

According to ^{1}H and ^{31}P NMR spectra two main compounds are formed in a ratio of major product **18** : minor product = 5 : 1 (also present in the reaction mixture: propene (δ^{1}H: 5.63 (ddq), 4.89 (ddq), 4.82 (ddq), 1.49 (ddd), compare to: A. A. Bothner-By, C. Naar-Colin, *J. Am. Chem. Soc.* 1961, **83**, 231-236; and compound **10** δ ^{31}P −34.1 (quin, $^{3}J_{PF}$ = 29.6 Hz)).

Crystals of **18** suitable for X-ray crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product mixture in dichloromethane at −30 °C.

Exact mass: calcd. for $C_{32}H_{12}BF_{20}P + Na^{+}$: 841.03425 m/z; found: 841.03588 m/z;

$2[C_{32}H_{12}BF_{20}P] + Na^{+}$: 1659.07928 m/z; found: 1659.08408 m/z;

$C_{32}H_{12}BF_{20}P + Cl^{-}$: 853.01370 m/z; found: 853.01259 m/z.

Exact mass: calcd. for $C_{34}H_{12}BF_{20}P + H^{+}$: 843.05290 m/z; found: 843.05320 m/z;

$C_{34}H_{12}BF_{20}P + Cl^{-}$: 877.01392 m/z; found: 877.01250 m/z.

Major product **18**:

^{1}H NMR (600 MHz, 299 K, C_7D_8): δ = 8.66 (d, $^{3}J_{PH}$ = 65.9 Hz, 1H, $^{=}$CH^{B}), 4.55 (m, 1H, $^{=}$CH$_2$), 4.35 (m, 1H, $^{=}$CH$_2$), 3.26 (m, 1H, ^{P}CH), 1.76 (dd, $^{3}J_{PH}$ = 42.6 Hz, $^{3}J_{HH}$ = 15.5 Hz, 1H, ^{B}CH$_2$), 1.53 (s, 3H, $^{=}$CH$_3$), 1.24 (br m, 1H, ^{B}CH$_2$), 0.93 (dm, $^{3}J_{PH}$ = 22.8 Hz, ^{CH}CH$_3$).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_7D_8): δ = 185.0 (br, $^{=}$CH^{B}), 142.5 (d, $^{2}J_{PC}$ = 12.5 Hz, ^{CH3}C$^{=}$), 117.9 (d, $^{1}J_{PC}$ = 71.0 Hz, ^{P}C$^{=}$), 114.5 (d, $^{3}J_{PC}$ = 5.8 Hz, $^{=}$CH$_2$), 31.7 (d, $^{1}J_{PC}$ = 41.1 Hz, ^{P}CH), 23.6 (br, ^{B}CH$_2$), 22.8 (d, $^{3}J_{PC}$ = 4.2 Hz, $^{=}$CH$_3$), 18.2 (^{CH}CH$_3$); [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz, 299 K, C_7D_8): δ^1H / δ^1H = 4.55 / 1.53 ($^{=}CH_2$ / $^{=}CH_3$), 4.35 / 1.53 ($^{=}CH_2$ / $^{=}CH_3$), 3.26 / 1.24, 0.93 (^{P}CH / $^{B}CH_2$, $^{CH}CH_3$), 1.76 / 8.66, 1.24 ($^{B}CH_2$ / $^{=}CH^{B}$, $^{B}CH_2$), 1.53 / 4.55 ($^{=}CH_3$ / $^{=}CH_2$), 1.24 / 3.26, 1.76 ($^{B}CH_2$ / ^{P}CH, $^{B}CH_2$), 0.93 / 3.26 ($^{CH}CH_3$ / ^{P}CH).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_7D_8): δ^1H / δ^{13}C = 8.66 / 185.0[3] ($^{=}CH^{B}$), 4.55, 4.35 / 114.5 ($^{=}CH_2$), 3.26 / 31.7 (^{P}CH), 1.76 / 23.6 ($^{B}CH_2$), 1.53 / 22.8 ($^{=}CH_3$), 1.24 / 23.6 ($^{B}CH_2$), 0.93 / 18.2 ($^{CH}CH_3$).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_7D_8): δ^1H / δ^{13}C = 8.66 / 142.5, 23.6 ($^{=}CH^{B}$ / $^{CH3}C^{=}$, $^{B}CH_2$), 4.55, 4.35 / 117.9, 22.8 ($^{=}CH_2$ / $^{P}C^{=}$, $^{=}CH_3$), 3.26 / 18.2 (^{P}CH / $^{CH}CH_3$), 1.76 / 18.2 ($^{B}CH_2$ / $^{CH}CH_3$), 1.53 / 142.5, 117.9, 114.5 ($^{=}CH_3$ / $^{CH3}C^{=}$, $^{P}C^{=}$, $^{=}CH_2$), 1.24 / 31.7 ($^{B}CH_2$ / ^{P}CH), 0.93 / 31.7, 23.6 ($^{CH}CH_3$ / ^{P}CH, $^{B}CH_2$).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_7D_8): δ = −14.8 ($v_{1/2}$ ~ 50 Hz).

^{19}F NMR (564 MHz, 299 K, C_7D_8): δ = −125.8 (br, 2F, *o*-P^A), −127.2 (br, 2F, *o*-P^B), −133.2 (m, 2F, *o*-B^A), −133.9 (m, 2F, *o*-B^B), −136.4 (m, 1F, *p*-P^A), −138.7 (m, 1F, *p*-P^B), −156.1 (m, 2F, *m*-P^B), −156.3 (m, 2F, *m*-P^A), −160.0 (t, $^3J_{FF}$ = 20.2 Hz, 1F, *p*-B^A), −160.5 (t, $^3J_{FF}$ = 20.4 Hz, 1F, *p*-B^B), −164.3 (m, 2F, *m*-B^A), −164.8 (m, 2F, *m*-B^B); [$\Delta\delta^{19}F_{p,m}$: 4.3 (B^A), 4.3 (B^B), 20.0 (P^A), 17.4 (P^B)].

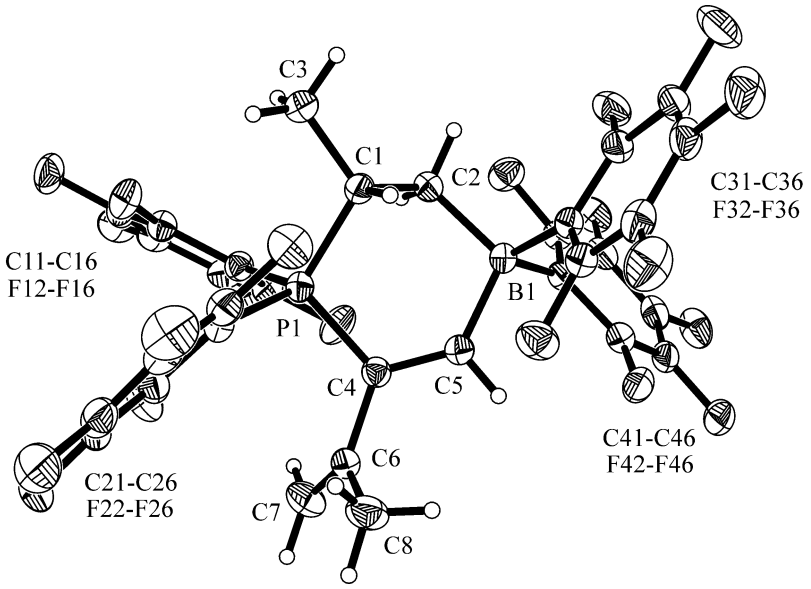
^{19}F,^{19}F GCOSY (564 MHz, 299 K C_7D_8): δ^{19}F / δ^{19}F = −133.2 / −164.3 (*o*-B^A / *m*-B^A), −133.9 / −164.8 (*o*-B^B / *m*-B^B), −136.4 / −156.4 (*p*-P^A / *m*-P^A), −138.7 / −156.1 (*p*-P^B / *m*-P^B), −160.0 / −164.3 (*p*-B^A / *m*-B^A), −160.5 / −164.8 (*p*-B^B / *m*-B^B), −164.3 / −133.2, −160.0 (*m*-B^A / *o*-B^A, *p*-B^A), −164.8 / −133.9, −160.5 (*m*-B^B / *o*-B^B, *p*-B^B).

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_7D_8): δ = 8.8 ($v_{1/2}$ ~ 40 Hz).

X-ray crystal structure analysis of 18: formula $C_{32}H_{12}BF_{20}P$, M = 818.20, colourless crystal, 0.20 x 0.05 x 0.04 mm, a = 12.6350(4), b = 18.8200(7), c = 12.7955(4) Å, β = 99.880(3)°, V = 2997.53(17) Å^3, ρ_{calc} = 1.813 gcm^{-3}, μ = 2.237 mm^{-1}, empirical absorption correction (0.663 ≤ T ≤ 0.915), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 25276 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 5175 independent (R_{int} = 0.043) and 4252 observed reflections [I>2σ(I)], 497 refined parameters, R = 0.041, wR^2 =

[3] from GHSQC at 228 K.

0.105, max. (min.) residual electron density 0.21 (-0.26) e.Å^{-3}, the hydrogen atoms at C7 were refined freely, others were calculated and refined as riding atoms.



Minor product:

^{1}H NMR (600 MHz, 299 K, C_7D_8): δ = 7.32 (br, 1H, H-1), 6.25 (d, $^{2}J_{PH}$ = 46.6 Hz, 1H, H-5), 4.95 (s, 1H, H-8$_{cis}$), 4.81 (s, 1H, H-8$_{trans}$), 3.45 (dd, $^{2}J_{HH}$ = 15.5 Hz, $^{2}J_{PH}$ = 5.6 Hz), 3.06 (dd, $^{2}J_{HH}$ = 15.5 Hz, $^{2}J_{PH}$ = 12.8 Hz) (each 1H, H-6), 2.01 (m, 3H, H-9), 1.40 (s, 3H, H-10).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_7D_8): δ = 229.2 (C4)[4], 149.2 (br m, C1), 147.9 (br, C2), 140.9 (C7), 110.3 (C8), 95.1 (br d, $^{1}J_{PC}$ ~ 76 Hz, C5), 67.0 (br, C3), 38.9 (d, $^{1}J_{PC}$ = 59.9 Hz, C6), 27.9 (C10), 22.6 (C9); [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz, 299 K, C_7D_8): δ^{1}H / δ^{1}H = 4.95, 4.81 / 2.01 (H-8$_{cis}$, H-8$_{trans}$ / H-9), 3.45 / 3.06 (H-6 / H-6), 3.06 / 3.45, 1.40 (H-6 / H-6, H-10), 2.01 / 4.95 (H-9 / H-8$_{cis}$).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_7D_8): δ^{1}H / δ^{13}C = 7.32 / 149.2 (H-1 / C1), 6.25 / 95.1 (H-5 / C5), 4.95, 4.81 / 110.3 (H-8$_{cis}$, H-8$_{trans}$ / C8), 3.45, 3.06 / 38.9 (H-6 / C6), 2.01 / 22.6 (H-9 / C9), 1.40 / 27.9 (H-10 / C10).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_7D_8): δ^{1}H / δ^{13}C = 7.32 / 140.9 (H-1 / C7), 4.95, 4.81 / 147.9, 22.6 (H-8 / C2, C9), 3.45 / 229.2, 95.1, 27.9 (H-6 / C4, C5, C10), 3.06 / 27.9 (H-6 / C10), 2.01 / 147.9, 140.9, 110.3 (H-9 / C2, C7, C8), 1.40 / 229.2, 147.9, 67.0, 38.9 (H-10 / C4, C2, C3, C6).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_7D_8): δ = −13.2 ($\nu_{1/2}$ ~ 50 Hz).

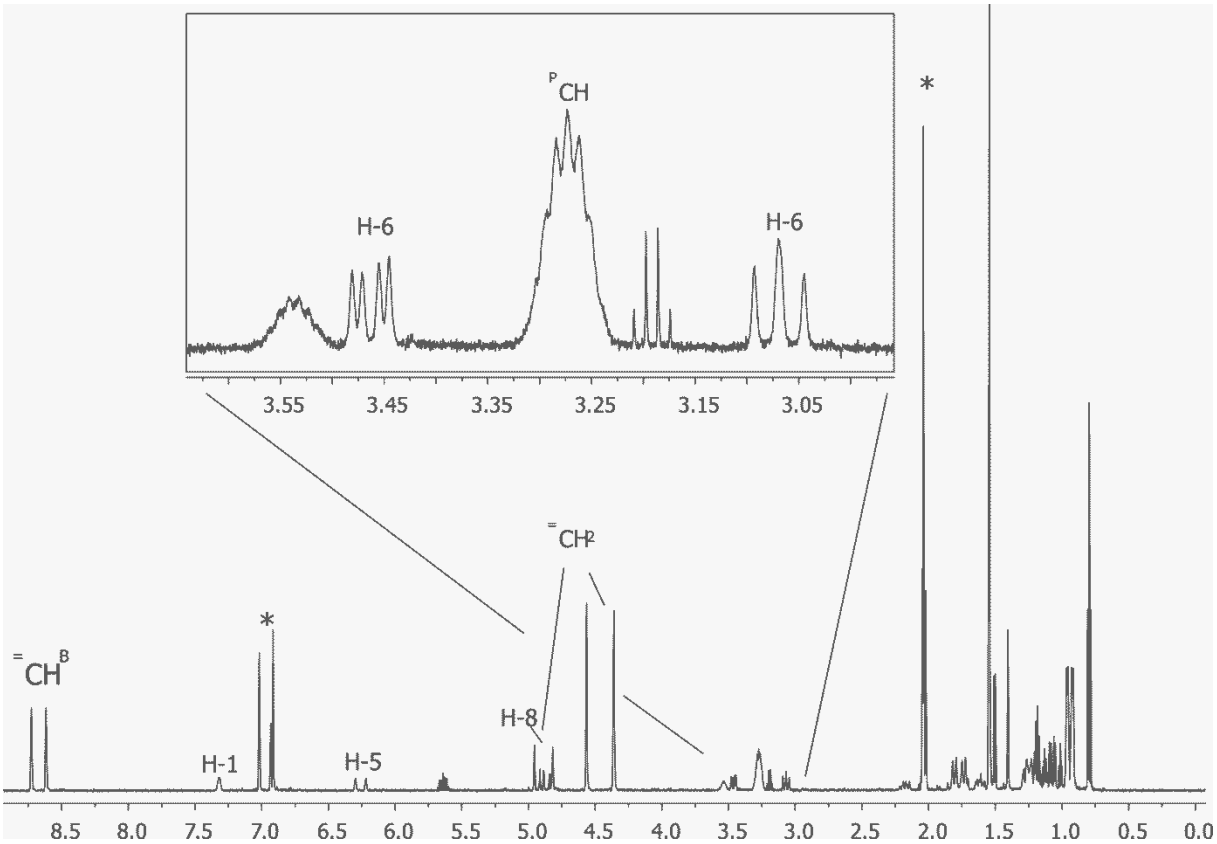
[4] detected from ghmbc

^{19}F NMR (564 MHz, 299 K, C_7D_8): δ = −128.9 (br, 2F, *o*-P^A), −129.2 (br, 2F, *o*-P^B), n.o. (*o*-B^B), −132.1 (m, 2F, *o*-B^A), −137.0 (m, 1F, *p*-P^B), −138.2 (m, 1F, *p*-P^A), −154.7 (m, 2F, *m*-P^B), −155.0 (m, 2F, *m*-P^A), −160.4 (t, $^3J_{FF}$ = 19.8 Hz, 1F, *p*-B^A), −161.0 (t, $^3J_{FF}$ = 20.9 Hz, *p*-B^B), −164.7 (m, 2F, *m*-B^A), −165.0 (br, 2F *m*-B^B)^t; [$\Delta\delta^{19}F_{p,m}$: 4.3 (B^A), 4.0 (B^B), 16.8 (P^A), 17.7 (P^B), ^{t} tentatively assigned]

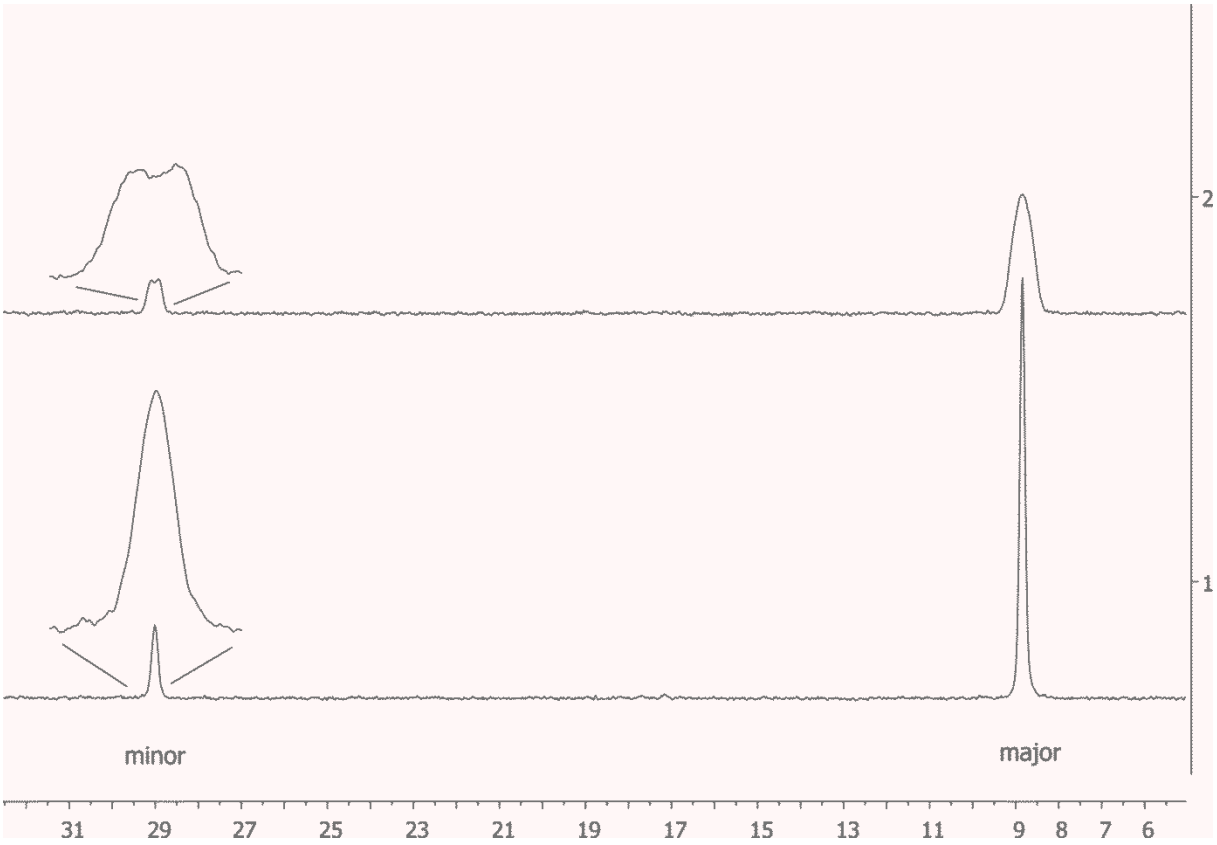
^{19}F,^{19}F GCOSY (564 MHz, 299 K, C_7D_8): $\delta^{19}F$ / $\delta^{19}F$ = −128.9 / −155.0 (*o*-P^A / *m*-P^A), −129.2 / −154.7 (*o*-P^B / *m*-P^B), −130.5 / −161.0 (*o*-B^B / *p*-B^B), −132.1 / −160.4, −164.7 (*o*-B^A / *p*-B^A, *m*-B^A), −137.0 / −154.7 (*p*-P^B / *m*-P^B), −138.2 / −155.0 (*p*-P^A/ *m*-P^A), −154.7 / −129.2, −137.0 (*m*-P^B / *o*-P^B, *p*-P^B), −155.0 / −128.9, −138.2 (*m*-P^A / *o*-P^A, *p*-P^A), −160.4 / −164.7 (*p*-B^A / *m*-B^A), −161.0 / −130.5 (*p*-B^B / *o*-B^B), −164.7 / −132.1, −160.4 (*m*-B^A / *o*-B^A, *p*-B^A).

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_7D_8): δ = 29.0 ($v_{1/2}$ ~40 Hz).

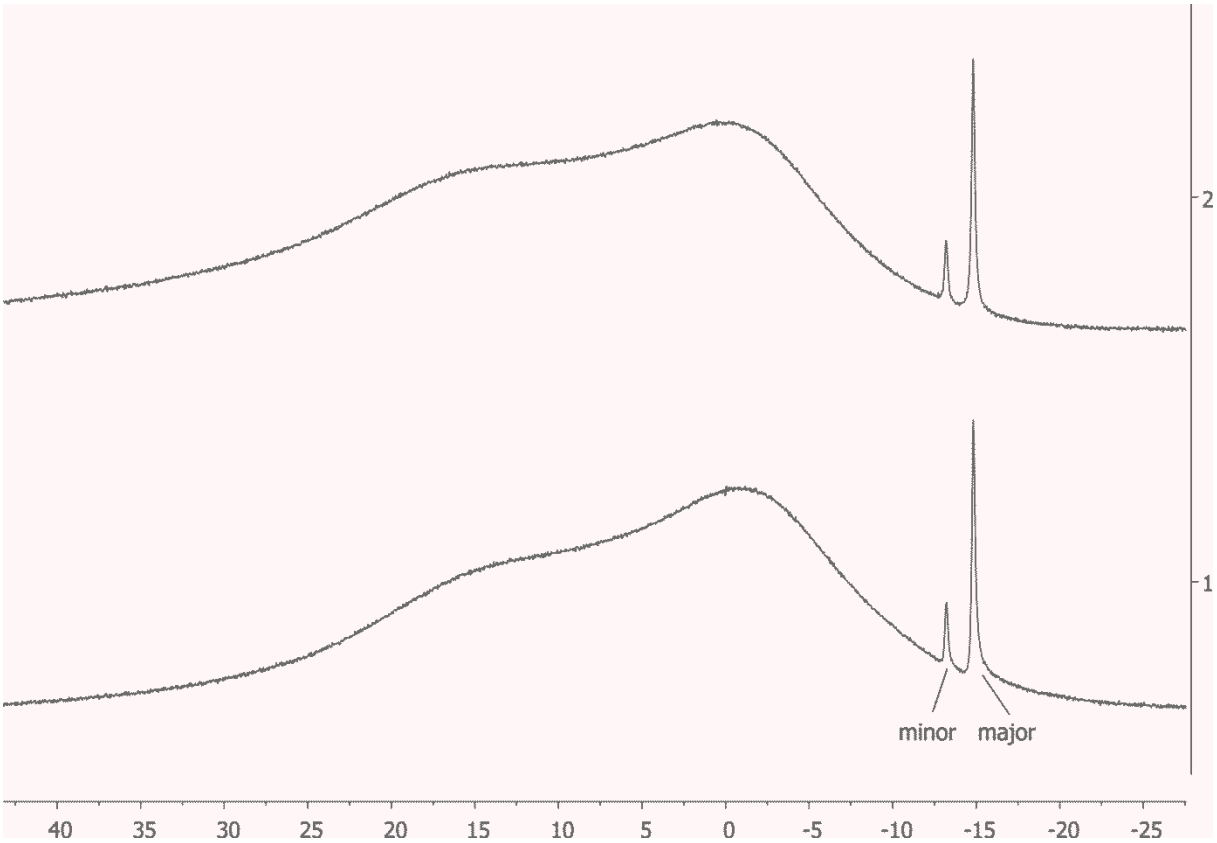
^{31}P NMR (243 MHz, 299 K, C_7D_8): δ = 29.0 (br d, $^2J_{PH}$ ~ 47 Hz).



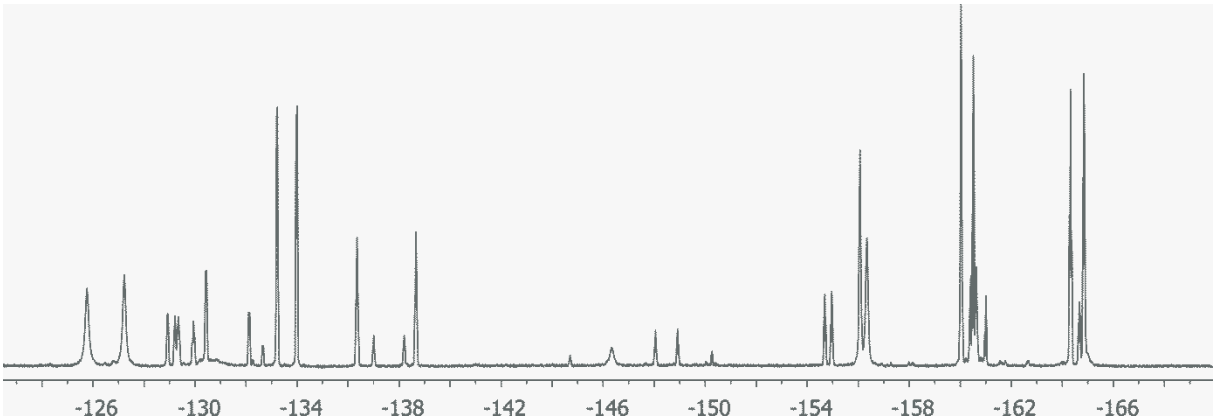
^{1}H NMR (600 MHz, 299 K, C_7D_8(*)).



1: $^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, C_7D_8); 2: ^{31}P NMR (243 MHz, 299 K, C_7D_8).



1: $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, C_7D_8); 2: ^{11}B NMR (192 MHz, 299 K, C_7D_8).



^{19}F NMR (564 MHz, 299 K, C_7D_8).