Electronic Supplementary Material (ESI) for Chemical Communications

Anomalous Staudinger reaction at intramolecular frustrated P-B Lewis pair frameworks

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Supporting Information

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[‡] X-ray crystal structure analyses

General Procedures. All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried with the procedure according to Grubbs (Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520) or were distilled from appropriate drying agents and stored under an argon atmosphere. NMR spectra were recorded on a *Bruker* AC 200 P (^{1}H: 200 MHz, ^{11}B: 64 MHz, ^{31}P: 81 MHz), a *Bruker* AV 300 (^{1}H: 300 MHz, ^{13}C: 76 MHz, ^{11}B: 96 MHz, ^{19}F: 282 MHz, ^{31}P: 122 MHz), a *Bruker* AV 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{31}P: 162 MHz), a *Varian* Inova 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{11}B:160 MHz, ^{19}F: 470 MHz, ^{31}P: 202 MHz) and on a *Varian* UnityPlus 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{11}B:192 MHz, ^{19}F: 564 MHz, ^{31}P: 243 MHz). ^{1}H NMR and ^{13}C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (external reference), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference), ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in D_2O) (external reference). NMR assignments were supported by additional 2D NMR experiments. Elemental analyses were performed on a *Elementar Vario El III*. IR spectra were recorded on a *Varian* 3100 FT-IR (Excalibur Series). Melting points were obtained with a DSC 2010 (*TA Instruments*). HRMS was recorded on GTC Waters Micromass (Manchester, UK). For irradiation experiments a *Philipps* UV-lamp (type HPK 125 with pyrex filter; λ = 365, 435, 313, 253, 404) was used.

X-Ray crystal structure analyses. Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (Sheldrick, G. M. *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. [CCDC: 902225-902229].

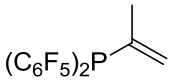
Exceptions and special features: The carbon atoms of the half benzene molecule in the compound **6a** displayed irregular displacement ellipsoids, which were therefore constrained to be more regular using the program commands SIMU and ISOR.

For the compound **5b** one disordered over three positions dichloromethane molecule and one half pentane molecule were found in the asymmetric unit. Several restraints (SIMU, SADI, SAME, ISOR and DFIX) were used in order to improve refinement stability.

Materials. $B(C_6F_5)_3$ [(a) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245-250; (b) Massey, A. G.; Park, A. J.; Stone, F. G. A. *Proc. Chem. Soc.* **1963**, 212], $HB(C_6F_5)_2$ [(a) Parks, D. J.; Spence, R. E.; von, H.; Piers, W. *Angew. Chem.* **1995**, *107*, 895-897; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 809-811; (b) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345-354], $(F_5C_6)_2PCl$ [Magnelli, D. D.; Tesi, G.; Lowe, J. U.; McQuiston, W. E. *Inorg. Chem.* **1966**, *5*, 457-461; Mancino, G.; Ferguson, A. J.; Beeby, A.; Long, N. J.; Jones, T. S. *J. Am. Chem. Soc.* **2005**, *127*, 524-525] and **4** [Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072-5074] were prepared according to literature procedures.

Experimental Procedures:

Preparation of bis(pentafluorophenyl)-2-propenylphosphane (3)



Bis(pentafluorophenyl)chlorophosphane (7.20 g, 18.0 mmol) was dissolved in thf (150 mL) and cooled down to −78 °C. Isopropenylmagnesiumbromide (36.0 mL, 0.5 M in thf, 18.0 mmol) was added dropwise to the reaction mixture which turned brown. The reaction mixture was stirred at rt for two hours before the solvent was removed *in vacuo*. The residue was suspended in *n*-pentane (100 mL) and filtered in a Schlenk-frit over Celite. The filter pad was washed with *n*-pentane (2 x 80 mL). The filtrate was dried *in vacuo.* Purification by column chromatography (SiO_2 : cyclohexane; R_f = 0.67) gave the product **3** (4.69 g, 11.5 mmol, 64%). Crystals were obtained by slow evaporation of an *n*-pentane solution at rt.

^{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, $^{1}J_{FC}$ = 246.7 Hz, C_6F_5), 142.9 (dm, $^{1}J_{FC}$ = 258.1 Hz, C_6F_5), 138.1 (dm, $^{1}J_{FC}$ = 253.3 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).

^{1}H,^{1}H GCOSY (600 MHz, 299 K, CD_2Cl_2): δ = 5.72 / 2.04 ($^{=}CH_{2,trans}$ / CH_3), 2.04 / 5.72 (CH_3 / $^{=}CH_{2,trans}$).

^{1}H,^{13}C GHSQC (600 MHz /151 MHz, 299 K, CD_2Cl_2): δ = 5.72, 5.53 / 128.4 ($^{=}CH_2$), 2.04 / 22.0 (CH_3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, CD_2Cl_2): δ = 5.72 / 22.0 ($^{=}CH_{2,trans}$ / CH_3), 5.53 / 137.5, 22.0 ($^{=}CH_{2,cis}$ / $^{=}C^{P}$, CH_3), 2.04 / 137.5, 128.4 (CH_3 / $^{=}C^{P}$, $^{=}CH_2$).

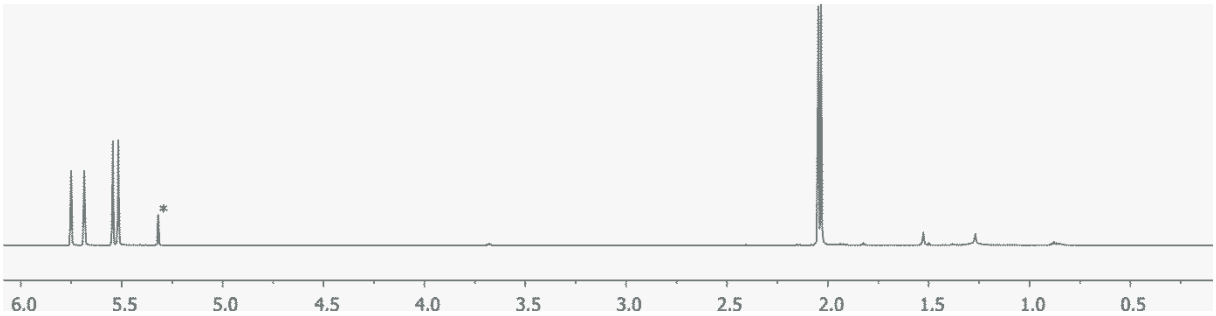
^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −130.3 (m, 2F, *o*-C_6F_5), −150.9 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F, *p*-C_6F_5), −161.4 (m, 2F, *m*-C_6F_5).

^{31}P{^{1}H} NMR (243 MHz, 299 K, CD_2Cl_2): δ = −42.8 (quin, $^{3}J_{PF}$ = 31.0 Hz).

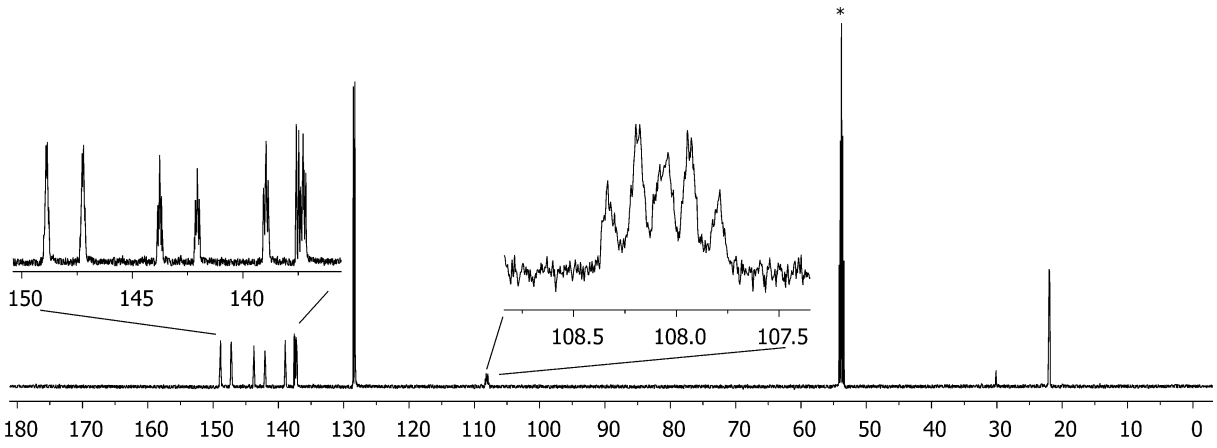
Exact mass calcd. for $C_{15}H_5F_{10}P$: 405.9969 g/mol; found: 405.9984 g/mol.

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).

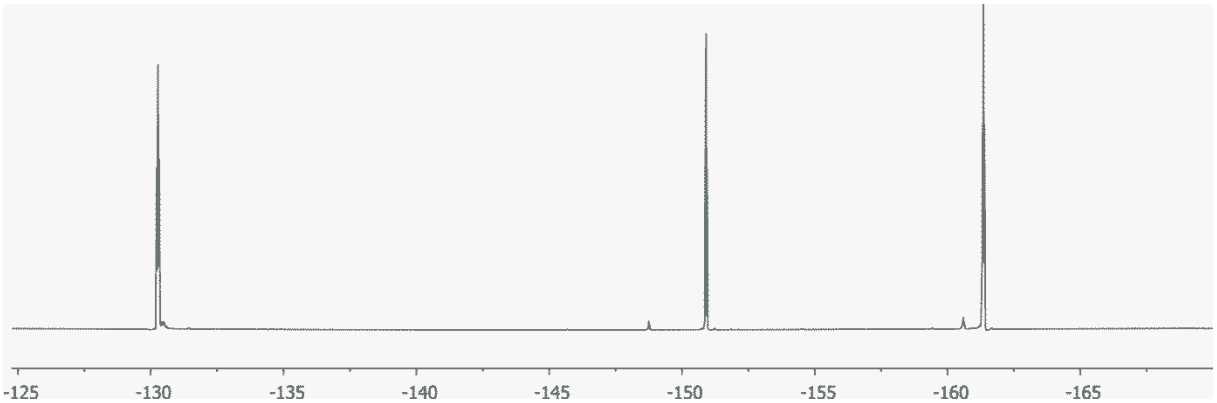
Elemental analysis: calcd. for $C_{15}H_5F_{10}P$ C 44.36, H 1.24; found C 44.46, H 1.20.



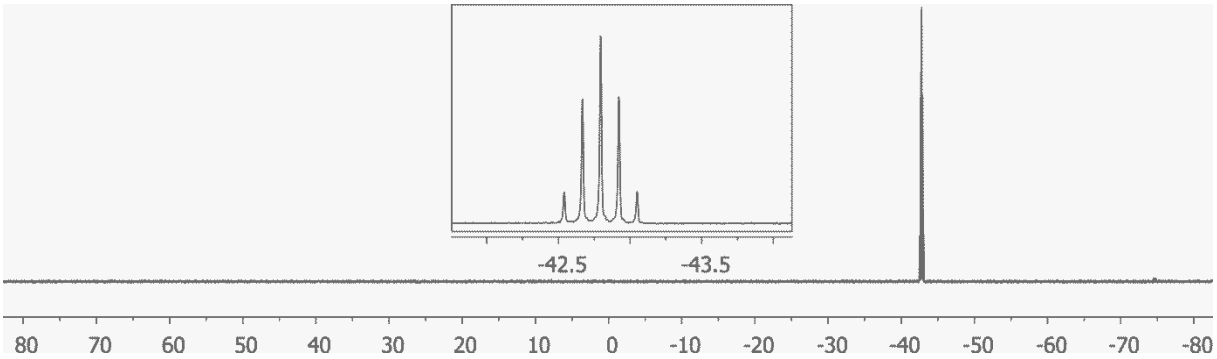
^{1}H NMR (600 MHz, 299 K, CD_2Cl_2(*)).



$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, CD_2Cl_2(*)).

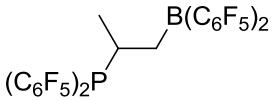


^{19}F NMR (564 MHz, 299 K, CD_2Cl_2).



$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, CD_2Cl_2).

Preparation of FLP 4



Bis(pentafluorophenyl)-2-propenylphosphane (**3**) (25.0 mg, 0.062 mmol) and bis(pentafluorophenyl)borane (21.3 mg, 0.062 mmol) were dissolved in CD_2Cl_2 to get compound **4**. It was studied by NMR experiments (temperature 25 - −85 °C).

For all the following reactions with the FLP **4**, compound **4** was prepared *in situ*.

^{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} MR (192 MHz, 299 K, CD_2Cl_2): δ = 67.8 ($v_{1/2}$ ~ 1160 Hz).

^{19}F NMR (564 MHz, 299 K, CD_2Cl_2): δ = −129.4 (br, 4F, *o*-P), −130.3 (m, 4F, *o*-B), −147.7 (s, 2F, *p*-B), −148.9, −149.7 (each m, each 1F, *p*-P), −160.7 (br, 4F, *m*-P), −161.3 (br, 4F, *m*-B).

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

In situ reaction mixture of **4** with excess of bis(pentafluorophenyl)-2-propenylphosphane (**3**) (NMR scale):

^{1}H NMR (500 MHz, 299 K, C_6D_6): δ = 3.63 (m, 1H, ^{P}CH), 2.22 (m, 1H, ^{B}CH$_2$), 1.67 (m, 1H, ^{B}CH$_2$), 1.10 (dd, $^3J_{PH}$ = 19.2 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, CH$_3$).

^{13}C{^{1}H} NMR (126 MHz, 299 K, C_6D_6): δ = 113.6 (*i*-^{B}C$_6$F$_5$), 35.8 (br d, $^2J_{PC}$ = 20.3 Hz, CH$_2$), 27.4 (m, ^{P}CH), 20.2 (d, $^2J_{PC}$ = 22.8 Hz, CH$_3$); [C$_6$F$_5$ not listed].

^{1}H,^{1}H GCOSY (500 MHz, 299 K, C_6D_6): δ = 3.63 / 2.22, 1.67, 1.10 (^{P}CH / ^{B}CH$_2$, CH$_3$), 2.22 / 3.63, 1.67 (^{B}CH$_2$ / ^{P}CH, ^{B}CH$_2$), 1.67 / 3.63, 2.22, 1.10 (^{B}CH$_2$ / ^{P}CH, ^{B}CH$_2$, CH$_3$), 1.10 / 3.63, 1.67 (CH$_3$ / ^{P}CH, ^{B}CH$_2$).

^{1}H,^{13}C GHSQC (500 MHz / 126 MHz, 299 K, C_6D_6): δ = 3.63 / 27.4 (^{P}CH), 2.22, 1.67 / 35.8 (^{B}CH$_2$), 1.10 / 20.2 (CH$_3$).

^{1}H,^{13}C GHMBC (500 MHz / 126 MHz, 299 K, C_6D_6): δ = 2.22, 1.67 / 113.6, 27.4, 20.2 (^{B}CH$_2$ / *i*-^{B}C$_6$F$_5$, ^{P}CH, CH$_3$), 1.10 / 35.8, 27.4 (CH$_3$ / ^{B}CH$_2$, ^{P}CH).

$^{11}B\{^{1}H\}$ NMR (160 MHz, 299 K, C_6D_6): δ = 66.0 ($v_{1/2}$ ≈1600 Hz).

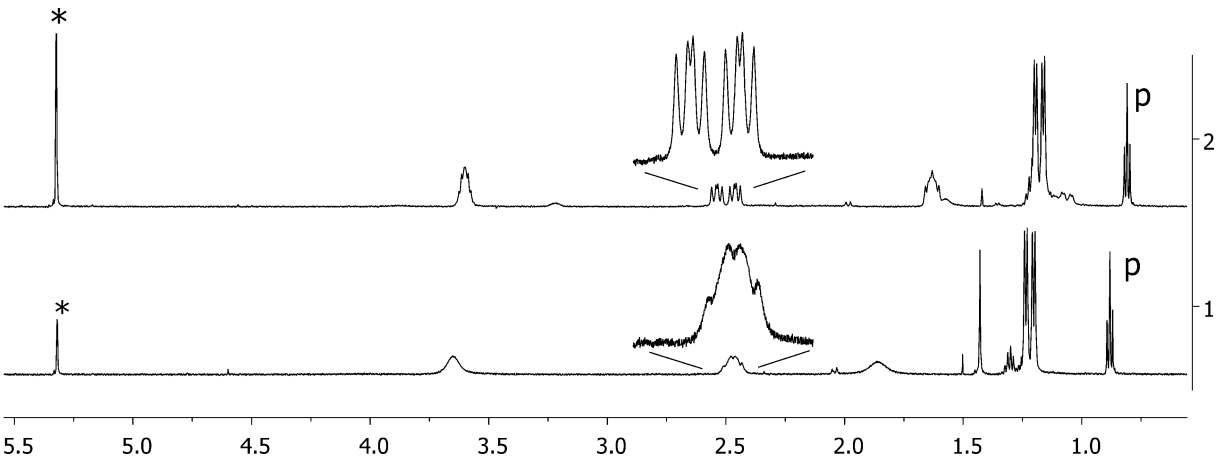
^{19}F NMR (470 MHz, 299 K, C_6D_6): δ = −129.4 (m, 2F, *o*-P^A), −130.0 (m, 2F, *o*-P^B), −130.5 (m, 4F, *o*-B), −145.8 (br, 2F, *p*-B), −147.5 (tm, $^3J_{FF}$ = 21.1 Hz, 1F, *p*-P^A), −148.5 (tm, $^3J_{FF}$ = 21.4 Hz, 1F, *p*-P^B), −159.7 (m, 4F, *m*-P^{A+B}), −160.4 (m, 4F, *m*-B).

$^{19}F,^{19}F$ GCOSY (470 MHz, 299 K, C_6D_6): δ = −129.4 / −147.5, −159.7 (*o*-P^A / *p*-P^A, *m*-P^{A+B}), −130.0 / −148.5, −159.7 (*o*-P^B / *p*-P^B, *m*-P^{A+B}), −130.5 / −160.4 (*o*-B / *m*-B), −145.8 / −145.8 (*o*-B / *m*-B), −147.5 / −159.7 (*p*-P^A / *m*-P^{A+B}), −148.5 / −159.7 (*p*-P^B / *m*-P^{A+B}), −159.7 / −130.0, −147.5, −148.5 (*m*-P^{A+B} / *o*-P^B, *p*-P^A, *p*-P^B), −160.4 / −130.5 (*m*-B / *o*-B).

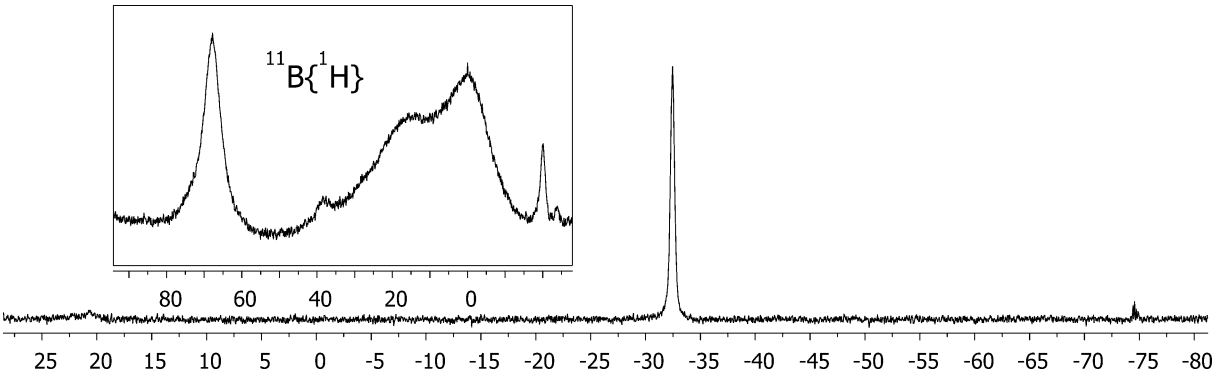
$^{31}P\{^{1}H\}$ NMR (202 MHz, 299 K, C_6D_6): δ = −34.3 (quin, $^3J_{PF}$ = 30.5 Hz).

^{31}P NMR (202 MHz, 299 K, C_6D_6): δ = −34.3 ($v_{1/2}$ = 85 Hz).

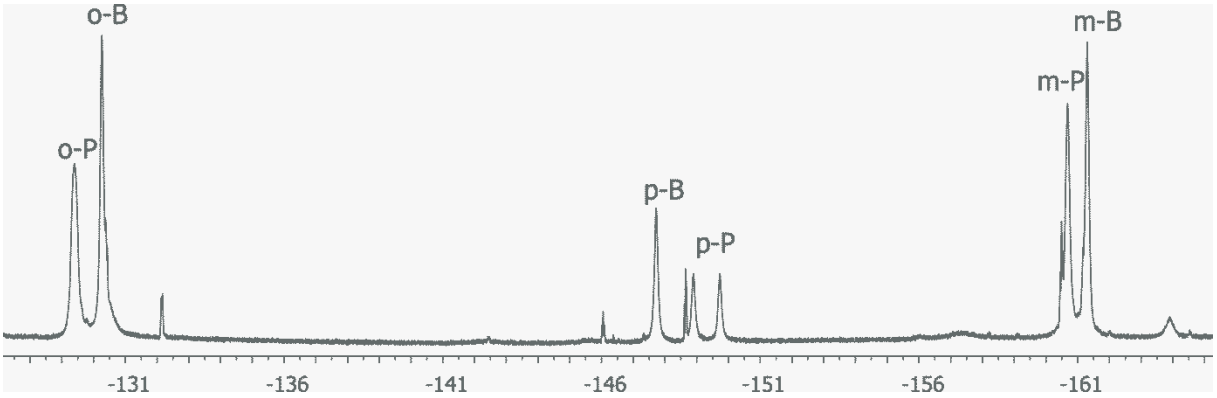
Exact mass calcd. for $C_{27}H_6BF_{20}P + H^+$: 753.00536 g/mol; found: 753.00662 g/mol.



^{1}H NMR (600 MHz, CD_2Cl_2(*)); p: pentane; 2: 218 K; 1: 299 K.

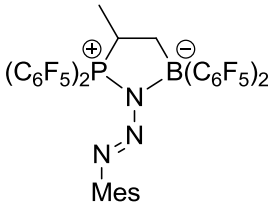


$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, CD_2Cl_2); box: $^{11}B\{^{1}H\}$ MR (192 MHz, 299 K, CD_2Cl_2).



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

Reaction of FLP 4 with mesityl azide to phosphazide 5a



Bis(pentafluorophenyl)-2-propenylphosphane (**3**) (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 minutes the reaction mixture turned cloudy. Mesityl azide (40.0 mg, 0.246 mmol) was added to the reaction mixture which was stirred for one hour at rt. The solution turned slightly yellow and a white solid crushed out. After the solid was isolated *via* filter cannula, washed with *n*-pentane (5 mL) and dried *in vacuo*, **5a** was obtained as a white solid (205.2 mg, 0.255 mmol, 61%).

The solid is stable at rt, but a solution of the product in CD_2Cl_2 turned yellow after a couple of hours at rt. According to NMR measurements the subsequent reaction to **6a** and **7** starts at rt after 30 minutes.

Crystals suitable for X-ray crystal structure analysis were obtained by layering a cold solution of bis(pentafluorophenyl)isopropenylphosphane and bis(pentafluorophenyl)borane in CH_2Cl_2 with a cold solution of mesitylazide in *n*-pentane and subsequent slow diffusion at −30 °C.

^{1}H NMR (600 MHz, 203 K, CD_2Cl_2): δ = 6.75 (br, 2H, *m*-Mes), 3.54 (br m, 1H, ^{P}CH), 2.15 (s, 3H, *p*-CH_3^{Mes}), 1.88/1.80 (each m, each 1H, $^{B}CH_2$), 1.72 (s, 6H, *o*-CH_3^{Mes}), 1.21 (br d, $^{3}J_{PH}$ = 22.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 203 K, CD_2Cl_2): δ = 142.5 (*i*-Mes), 137.3 (*p*-Mes), 130.4 (*o*-Mes), 129.1 (*m*-Mes), 31.0 (br d, $^{1}J_{PC}$ = 59.7 Hz, ^{P}CH), 27.7 (br, $^{B}CH_2$), 20.4 (*p*-CH_3^{Mes}), 17.8 (br, *o*-CH_3^{Mes}), 14.1 (br, CH_3), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz, 203 K, CD_2Cl_2): δ = 6.75 / 2.15, 1.72 (*m*-Mes / *p*-CH_3^{Mes}, *o*-CH_3^{Mes}), 3.54 / 1.88, 1.80 (^{P}CH / $^{B}CH_2$), 1.88 / 3.54 ($^{B}CH_2$ / ^{P}CH), 1.21 / 3.54 (CH_3 / ^{P}CH).

^{1}H,^{13}C GHSQC (600 / 151 MHz, 203 K, CD_2Cl_2): δ = 6.75 / 129.1 (*m*-Mes), 3.54 / 31.0 (^{P}CH), 2.15 / 20.4 (*p*-CH_3^{Mes}), 1.88, 1.80 / 27.7 ($^{B}CH_2$), 1.72 / 17.8 (*o*-CH_3^{Mes}), 1.21 / 14.1 (CH_3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 203 K, CD_2Cl_2): δ = 6.75 / 142.5, 129.1, 20.4, 17.8 (*m*-Mes / *i*-Mes, *m*-Mes, *p*-CH_3^{Mes}, *o*-CH_3^{Mes}), 2.15 / 137.3, 129.1 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes), 1.72 / 142.5, 130.4, 129.1 (*o*-CH_3^{Mes} / *i*-Mes, *o*-Mes, *m*-Mes), 1.21 / 31.0 (CH_3 / ^{P}CH).

^{11}B{^{1}H} NMR (192 MHz, 203 K, CD_2Cl_2): δ = −5.9 ($\nu_{1/2}$ ≈ 1500 Hz).

^{19}F NMR (564 MHz, 253 K, CD_2Cl_2): δ = −122.2, −126.0, −127.7, −134.9 (each br, each 1F, *o*-P), −131.5, −135.8 (each br, each 2F, *o*-B), −138.6, −139.7 (each m, each 1F, *p*-P), −155.7 (1F), −156.6 (3F) (each br, *m*-P), −159.4 (t, $^{3}J_{FF}$ = 20.1 Hz, 1F *p*-B), −160.6 (t, $^{3}J_{FF}$ = 20.0 Hz, 1F, *p*-B), −165.3 (m, 4F, *m*-B).

^{19}F,^{19}F GCOSY (564 MHz, 253 K, CD_2Cl_2): δ = −159.4 / −165.3 (*p*-B / *m*-B), −160.6 / −165.3 (*p*-B / *m*-B), −165.3 / −159.4, −160.6 (*m*-B / *p*-B).

^{31}P{^{1}H} NMR (243 MHz, 203 K, CD_2Cl_2): δ = 18.1 ($\nu_{1/2}$ ≈ 25 Hz).

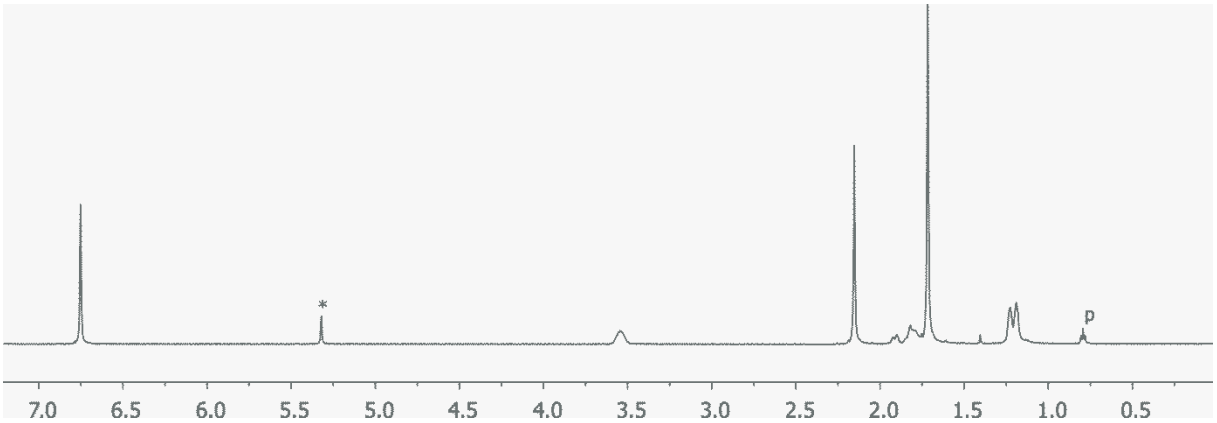
^{31}P NMR (243 MHz, 203 K, CD_2Cl_2): δ = 18.1 ($\nu_{1/2}$ ≈ 90Hz).

Exact mass calcd. for $C_{36}H_{17}BF_{20}N_3P + H^+$: 914.10128 g/mol; found: 914.10144 g/mol;
$C_{36}H_{17}BF_{20}N_3P + Na^+$:936.08322 g/mol; found: 936.08378 g/mol;
$C_{36}H_{17}BF_{20}N_3P + K^+$: 952.05716 g/mol; found: 952.05777 g/mol.

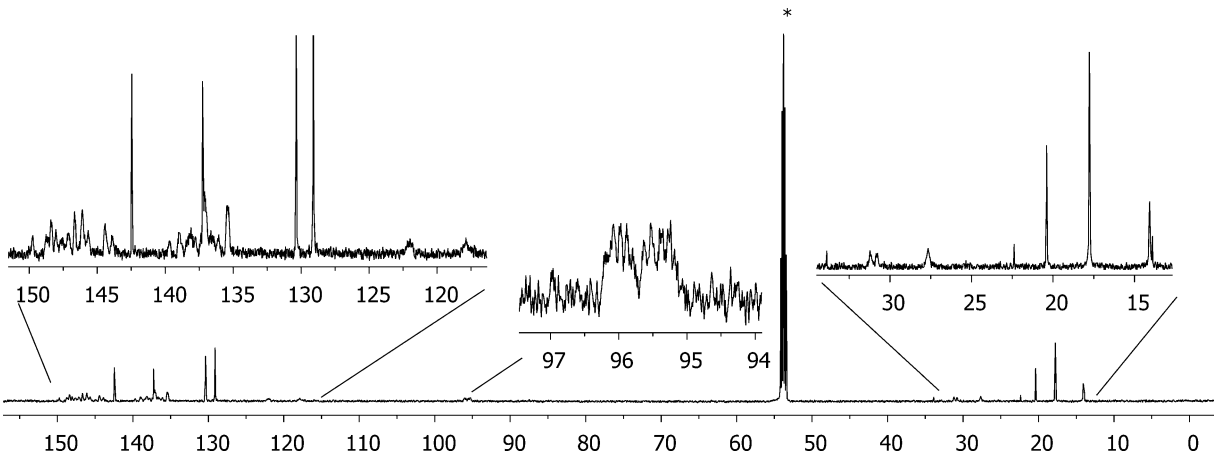
IR (KBr): $\tilde{\nu}$ = 2962 (w), 2928 (w), 1772 (w), 1734 (w), 1700 (w), 1645 (m), 1616 (w), 159 (w), 1520 (s), 1478 (s), 1386 (m), 1304 (m), 1279 (m), 1263 (m), 1228 (w), 1108 (s), 1036 (m), 982 (m), 881 (w), 838 (w), 814 (m), 729 (w), 686 (w), 652 (w), 629 (w), 592 (w), 574 (w), 546 (w).

Elemental analysis: calcd. for $C_{36}H_{17}BF_{20}N_3P$ C 47.34, H 1.88, N 4.06; found C 47.23, H 1.51, N 4.51.

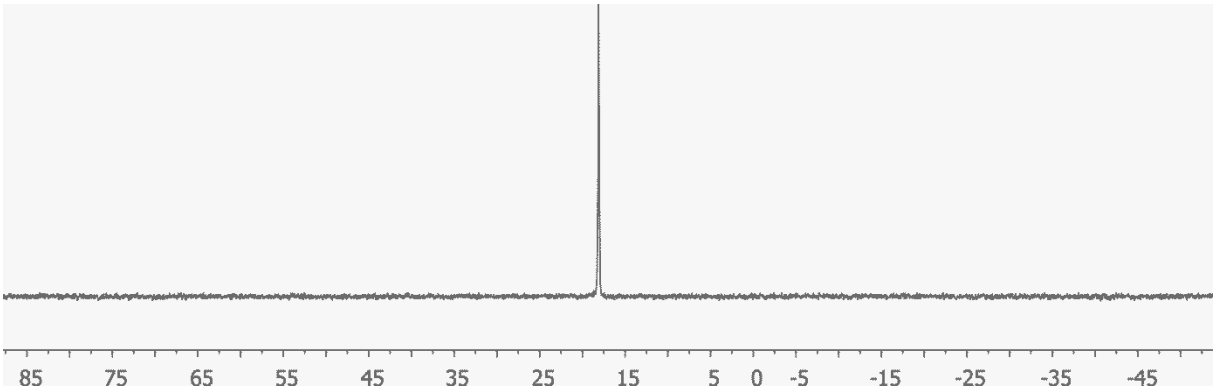
Decomposition point: 135 °C.



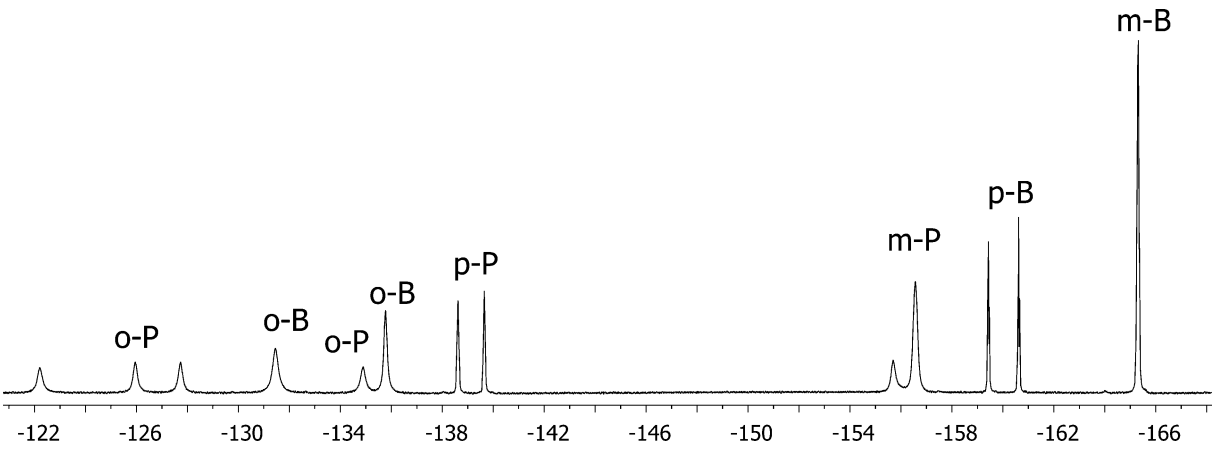
^{1}H NMR (600 MHz, 203 K, CD_2Cl_2(*)); p: pentane.



$^{13}C\{^{1}H\}$ NMR (151 MHz, 203 K, CD_2Cl_2(*)).

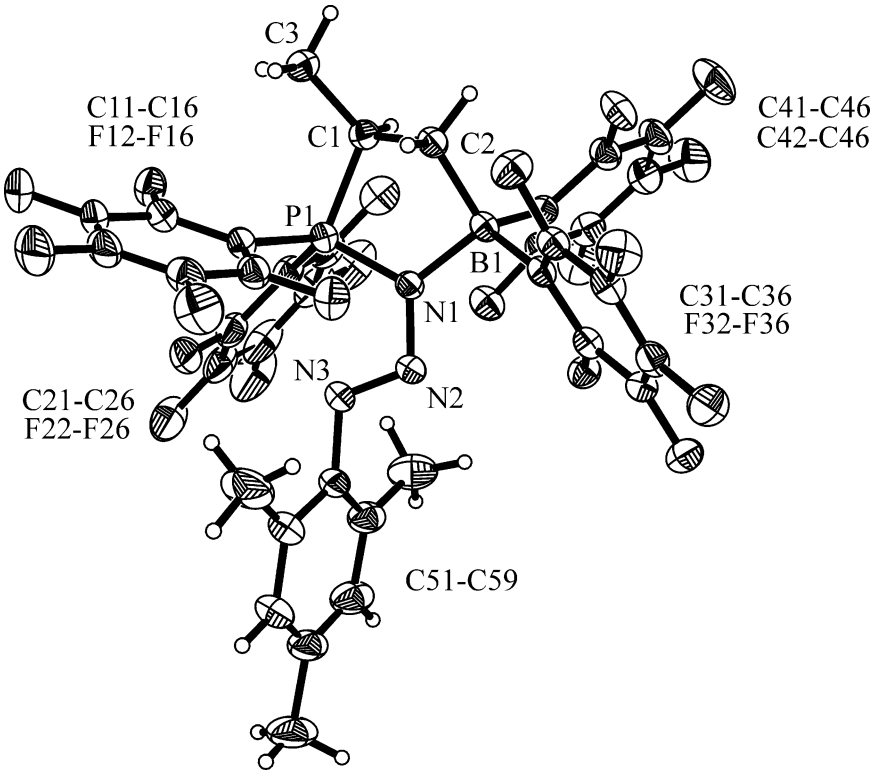


$^{31}P\{^{1}H\}$ NMR (243 MHz, 203 K, CD_2Cl_2).

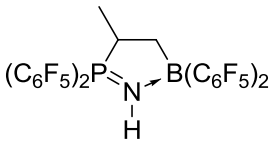


^{19}F NMR (564 MHz, 253 K, CD_2Cl_2).

X-ray crystal structure analysis of 5a: formula $C_{36}H_{17}BF_{20}N_3P$, M = 913.31, colourless crystal, 0.25 x 0.25 x 0.04 mm, a = 38.3358(8), b = 11.6945(6), c = 17.4973(5) Å, β = 111.156(2) °, V = 7315.7(5) Å^3, ρ_{calc} = 1.658 gcm^{-3}, μ = 1.930 mm^{-1}, empirical absorption correction (0.644 ≤ T ≤ 0.926), Z = 8, monoclinic, space group $C2/c$ (No. 15), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 41872 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 6388 independent (R_{int} = 0.052) and 5475 observed reflections [I>2σ(I)], 554 refined parameters, R = 0.037, wR^2 = 0.101, max. (min.) residual electron density 0.21 (-0.24) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Preparation of phosphinimine 6a and indazole 7



5a (58.0 mg, 0.064 mmol) was placed into a small Schlenk and closed with a cooling finger. Heating to 150 °C under vacuum for one hour gave an orange residue and a white/pale yellow solid at the cooling finger (**7**: 4.97 mg, 0.034 mmol, 53%). The residue was purified by column chromatography (SiO_2 : CH_2Cl_2:*n*-pentane = 1:4; R_f = 0.35) to give the product as a white solid (49.3 mg, 0.064 mmol, 75%).

Crystals suitable for X-ray crystal structure analysis were obtained by layering a solution of the starting material **5a** in C_6D_6 and CD_2Cl_2 with *n*-pentane at rt.

Initiating the reaction by UV irradiation of the starting material **5a** gave no conversion in the solid state, but full conversion in solution (CD_2Cl_2) after 4.5 h.

^{1}H NMR (600 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 3.81 (d, $^2J_{PH}$ = 9.3 Hz, 1H, NH), 3.17 (m, 1H, ^{P}CH), 2.14 (ddd, $^3J_{PH}$ = 35.3 Hz, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 6.0 Hz, ^{B}CH$_2^a$), 1.62 (td, $^3J_{PH} \approx {}^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 10.8 Hz, 1H, ^{B}CH$_2^b$), 0.99 (dd, $^3J_{PH}$ = 24.5 Hz, $^3J_{HH}$ = 6.9 Hz, CH_3).

^{1}H{^{31}P} NMR (600 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 3.81 (s, 1H, NH), 3.17 (m, 1H, ^{P}CH), 2.14 (dd, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 6.0 Hz, ^{B}CH$_2^a$), 1.62 (dd, $^2J_{HH}$ = 14.7 Hz, $^3J_{HH}$ = 10.8 Hz, 1H, ^{B}CH$_2^b$), 0.99 (d, $^3J_{HH}$ = 6.9 Hz, CH_3).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 122.7 (br, *i*-$C_6F_5^B$), 104.2 (dt, $^1J_{PC}$ = 85.4 Hz, $^2J_{FC}$ = 20.5 Hz, *i*-$C_6F_5^P$), 100.4 (dt, $^1J_{PC}$ = 83.9 Hz, $^2J_{FC}$ = 17.5 Hz, *i*-$C_6F_5^P$), 36.3 (d, $^1J_{PC}$ = 65.0 Hz, ^{P}CH), 28.1 (br, ^{B}CH$_2$), 15.1 (CH_3); [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 3.17 / 2.14, 1.62, 0.99 (^{P}CH / ^{B}CH$_2^a$, ^{B}CH$_2^b$, CH_3), 2.14 / 3.17, 1.62 (^{B}CH$_2^a$ / ^{P}CH, ^{B}CH$_2^b$), 1.62 / 3.17, 2.14 (^{B}CH$_2^b$ / ^{P}CH, ^{B}CH$_2^a$), 0.99 / 3.17 (CH_3 / ^{P}CH).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 3.17 / 36.3 (^{P}CH), 2.14, 1.62 / 28.1 (^{B}CH$_2$), 0.99 / 15.1 (CH_3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 3.81 / 36.3, 28.1 (NH / ^{P}CH, $^{B}CH_2$), 2.14, 1.62 / 36.3, 15.1 ($^{B}CH_2$ / ^{P}CH, CH_3), 0.99 / 36.3, 28.1 (CH_3 / ^{P}CH, $^{B}CH_2$).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = −4.8 ($v_{1/2}$ ≈ 150 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = −131.1 (m, 2F, *o*-P^A), −132.4 (m, 2F, *o*-P^B), −135.0 (m, 2F, *o*-B^A), −136.3 (m, 2F, *o*-B^B), −138.9 (m, 1F, *p*-P^B), −139.7 (m, 1F, *p*-P^A), −155.8 (m, 2F, *m*-P^A), −156.0 (m, 2F, *m*-P^B), −159.53 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-B^B), −159.54 (t, $^{3}J_{FF}$ = 20.5 Hz, 1F, *p*-B^A), −163.9 (m, 2F, *m*-B^B), −164.3 (m, 2F, *m*-B^A); [$\delta\Delta^{19}F_{p,m}$: 4.4 (B^B), 4.8 (B^A), 16.1 (P^A), 17.1 (P^B)].

^{19}F,^{19}F GCOSY (564 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = −131.1 / −139.7, −155.8 (*o*-P^A / *p*-P^A, *m*-P^A), −132.4 / −138.9, −156.0 (*o*-P^B / *p*-P^B, *m*-P^B), −135.0 / −164.3 (*o*-B^A / *m*-B^A), −136.3 / −163.9 (*o*-B^B / *m*-B^B), −138.9 / −132.4, −156.0 (*p*-P^B / *o*-P^B, *m*-P^B), −139.7 / −131.1, −155.8 (*p*-P^A / *o*-P^A, *m*-P^A), −155.8 / −131.1, −139.7 (*m*-P^A / *o*-P^A, *p*-P^A), −156.0 / −132.4, −138.9 (*m*-P^B / *o*-P^B, *p*-P^B), −159.53 / −163.9 (*p*-B^B / *m*-B^B), −159.54 / −164.3 (*p*-B^A / *m*-B^A), −163.9 / −136.3, −159.53 (*m*-B^B / *o*-B^B, *p*-B^B), −164.3 / −135.0, −159.54 (*m*-B^A / *o*-B^A, *p*-B^A).

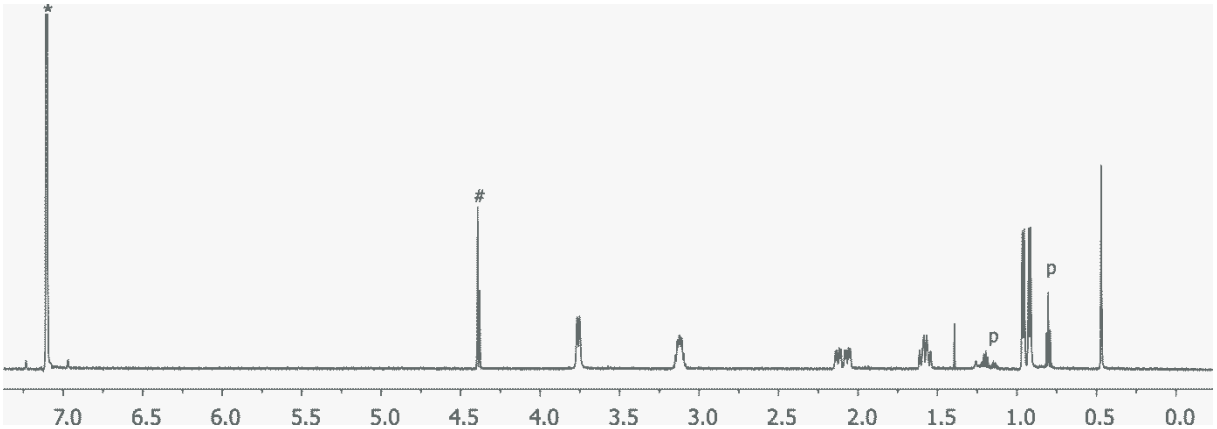
^{31}P NMR (243 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 36.6 ($v_{1/2}$ ≈ 80 Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6/CD_2Cl_2): δ = 36.6 ($v_{1/2}$ ≈ 20 Hz).

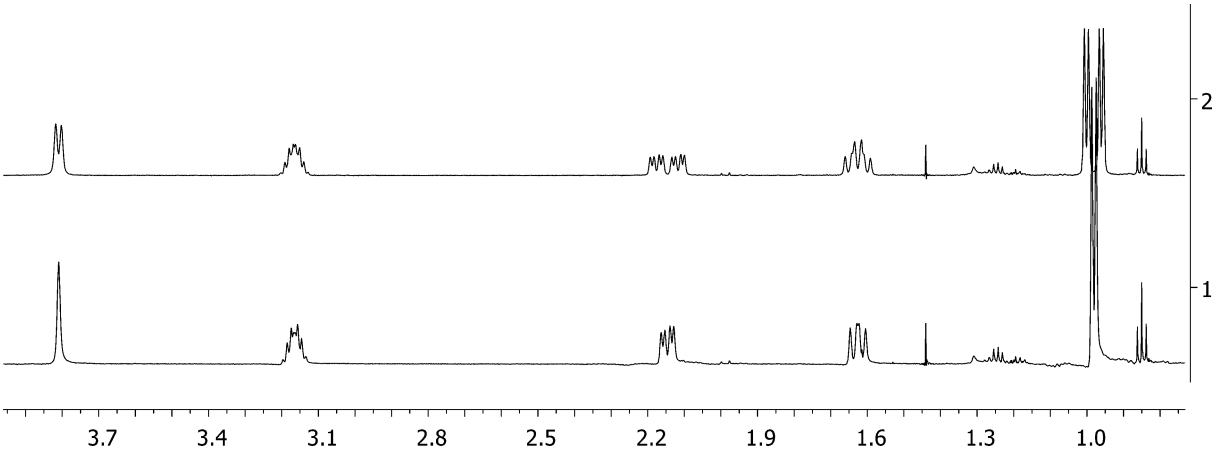
Exact mass calcd. for $C_{27}H_7BF_{20}NP + BF_4^-$: 854.01336 g/mol; found: 854.01652 g/mol;
$C_{27}H_7BF_{20}NP + Cl^-$: 801.97886 g/mol; found: 801.98292 g/mol.

IR (KBr): ṽ = 1646 (m), 1515 (m), 1483 (s), 1459 (s), 1386 (m), 1306 (m), 1279 (w), 1234 (w), 1197 (m), 1085 (s), 983 (s), 955 (s), 916 (m), 818 (w), 785 (w), 745 (w), 730 (w), 689 (w), 649 (w), 593 (w), 565 (w), 536 (m).

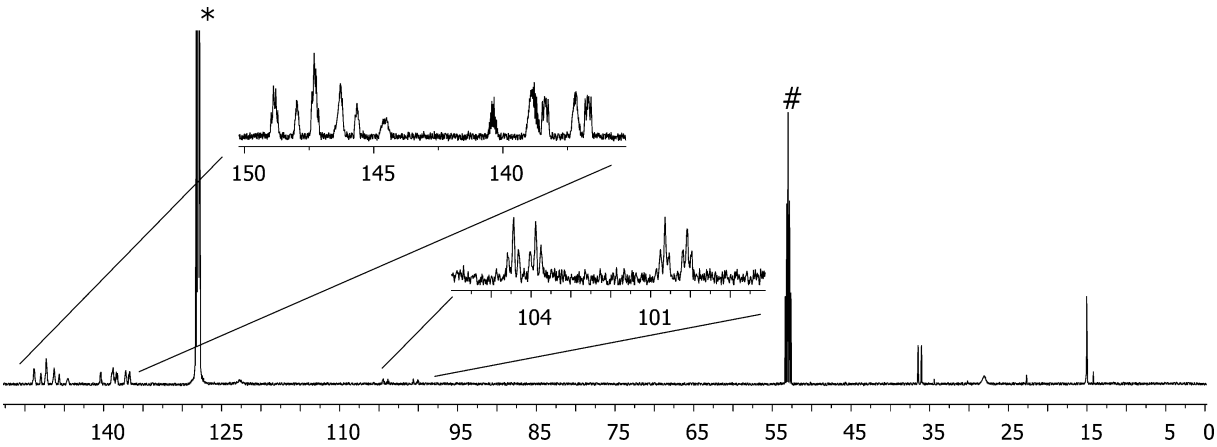
Melting Point: 204 °C.



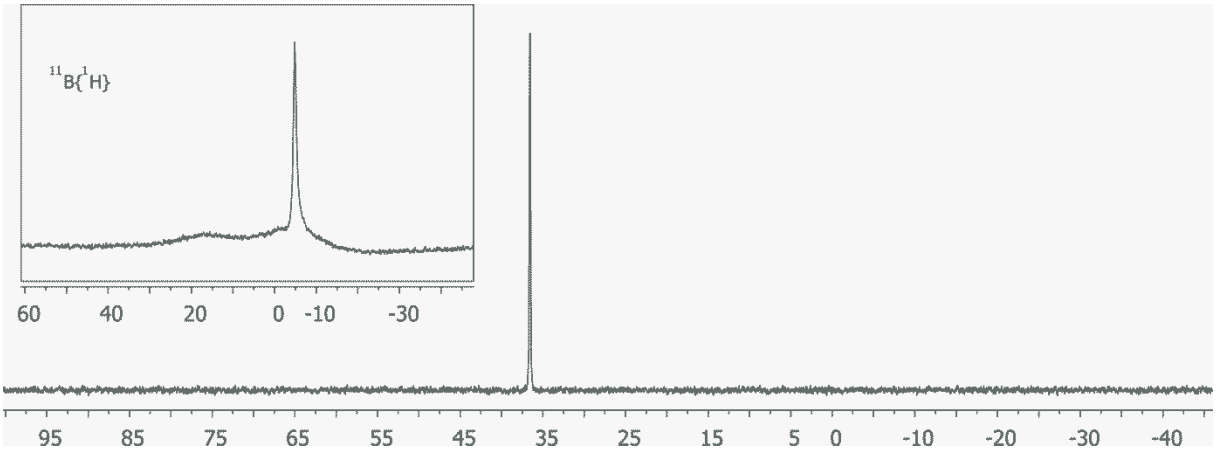
^{1}H NMR (600 MHz, 299 K, C_6D_6(*)/CD_2Cl_2(#)); p: pentane.



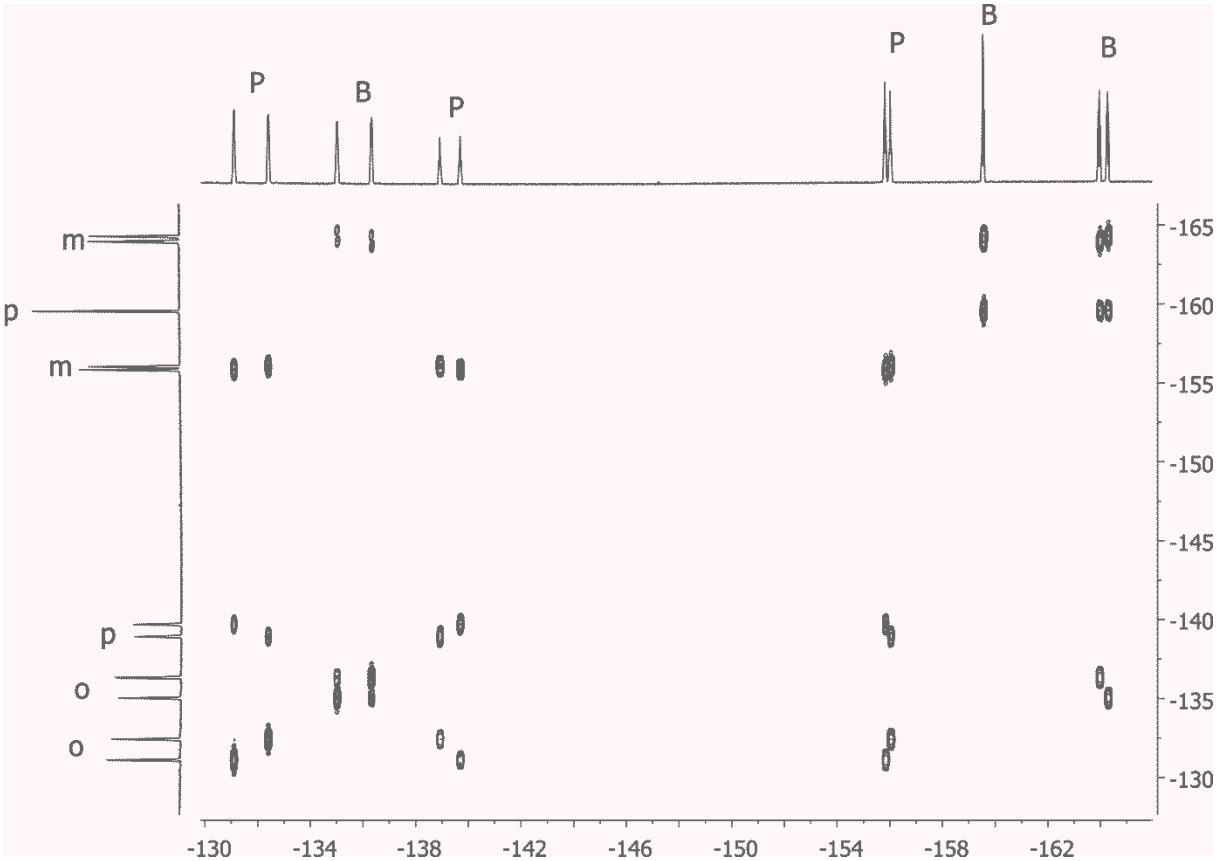
2: ^{1}H NMR (600 MHz, 299 K, C_6D_6/CD_2Cl_2); 1: ^{1}H{^{31}P} NMR (600 MHz, 299 K, C_6D_6/CD_2Cl_2).



^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6(*)/CD_2Cl_2(#)).



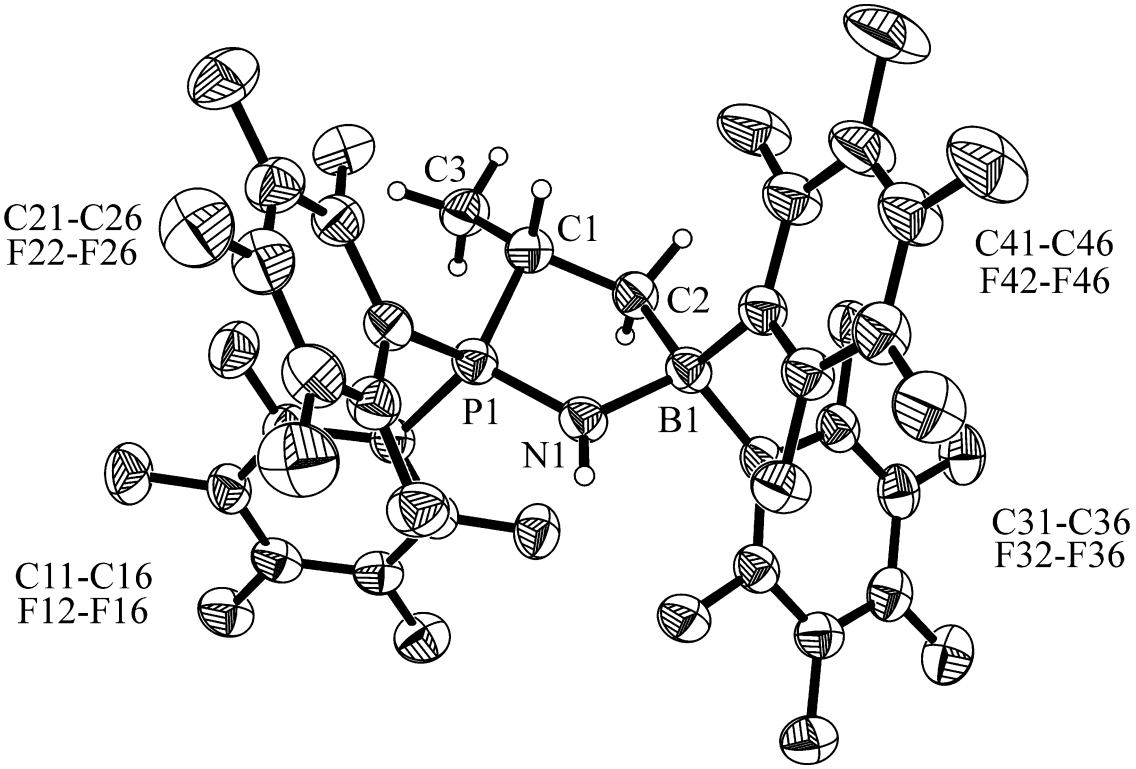
$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, C_6D_6/CD_2Cl_2); box: $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, C_6D_6/CD_2Cl_2).



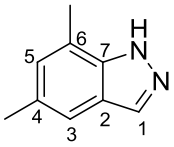
$^{19}F,^{19}F$ GCOSY (564 MHz, 299 K, C_6D_6/CD_2Cl_2).

X-ray crystal structure analysis of 6a: formula $C_{27}H_7BF_{20}NP$ * ½ C_6H_6, *M* = 806.17, colourless crystal, 0.20 x 0.13 x 0.03 mm, *a* = 10.1955(5), *b* = 11.4489(5), *c* = 14.1284(5) Å, α = 66.764(2), *β* = 78.902(3), γ = 89.099(3)°, *V* = 1483.74(11) $Å^3$, ρ_{calc} = 1.804 gcm^{-3}, μ = 2.259 mm^{-1}, empirical absorption correction (0.660 ≤ T ≤ 0.935), *Z* = 2, triclinic, space group $P\bar{1}$ (No.

2), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 16479 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 $Å^{-1}$, 4959 independent (R_{int} = 0.067) and 3735 observed reflections [*I*>2σ(*I*)], 498 refined parameters, *R* = 0.058, wR^2 = 0.164, max. (min.) residual electron density 0.49 (-0.45) e.$Å^{-3}$, hydrogen atom at N1 was refined freely, others hydrogen atoms were calculated and refined as riding atoms.



Residue from cooling finger after thermolysis of **5a**, compound **7**:



^{1}H NMR (400 MHz, 294 K, C_6D_6): δ = 7.97 (s, 1H, 1-H), 7.16 (s, 1H, 3-H), 6.75 (s, 1H, 5-H), 2.26 (s, 3H, 4-CH_3), 2.14 (s, 3H, 6-CH_3), [NH not detected].

$^{13}C\{^{1}H\}$ NMR (101 MHz, 294 K, C_6D_6): δ = 139.5 (C7), 134.4 (d, $^{1}J_{CH}$ = 187.5 Hz, C1)[a], 130.4 (C4), 128.9 (d, $^{1}J_{CH}$ = 154.4 Hz, C5)[a], 123.9 (C2), 119.5 (C6), 117.6 (d, $^{1}J_{CH}$ = 159.9 Hz, C3)[a], 21.3 (4-CH_3), 16.7 (6-CH_3), [a from proton coupled $^{1}H,^{13}C$ GHSQC NMR experiment].

$^{13}C\{DEPT90\}$ NMR (101 MHz, 294 K, C_6D_6) δ = 134.4 (CH, C1), 128.9 (CH, C5), 117.6 (CH, C3).

$^{13}C\{DEPT135\}$ NMR (101 MHz, 294 K, C_6D_6): δ = 134.4 (CH, C1), 128.9 (CH, C5), 117.6 (CH, C3), 21.3 (CH_3, 4-CH_3), 16.7 (CH_3, 6-CH_3).

$^{1}H,^{1}H$ GCOSY (400 MHz, 294 K, C_6D_6): δ = 7.16 / 6.75, 2.26, 2.14 (3-H / 5-H, 4-CH_3, 6-CH_3), 6.75 / 7.16, 2.26, 2.14 (5-H / 3-H, 4-CH_3, 6-CH_3), 2.26 / 7.16 (4-CH_3 / 3-H), 2.14 / 6.75 (6-CH_3 / 5-H).

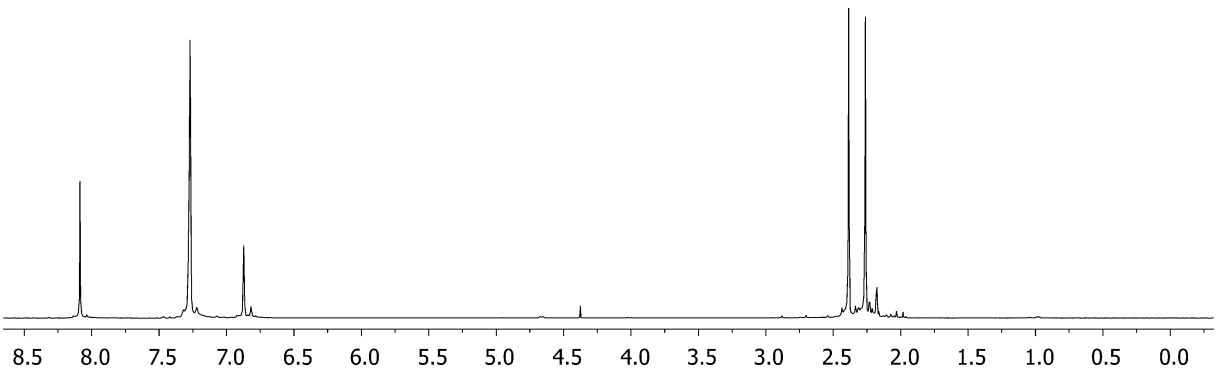
$^{1}H,^{13}C$ GHSQC (400 MHz / 101 MHz, 294 K, C_6D_6): δ = 7.97 / 134.4 (1-H / C1), 7.16 / 117.6 (3-H / C3), 6.75 / 128.9 (5-H / C5), 2.26 / 21.3 (4-CH_3), 2.14 / 16.7 (6-CH_3).

$^{1}H,^{13}C$ GHMBC (400 MHz / 101 MHz, 294 K, C_6D_6): δ = 7.97 / 139.5, 123.9 (1-H / C7, C2), 7.16 / 139.5, 128.9, 21.3 (3-H / C7, C5, 4-CH_3), 6.75 / 139.5, 117.6, 21.3, 16.7 (5-H / C7, C3, 4-CH_3, 6-CH_3), 2.26 / 130.4, 128.9, 117.6 (4-CH_3 / C4, C5, C3), 2.14 / 139.5, 128.9, 119.5 (6-CH_3 / C7, C5, C6).

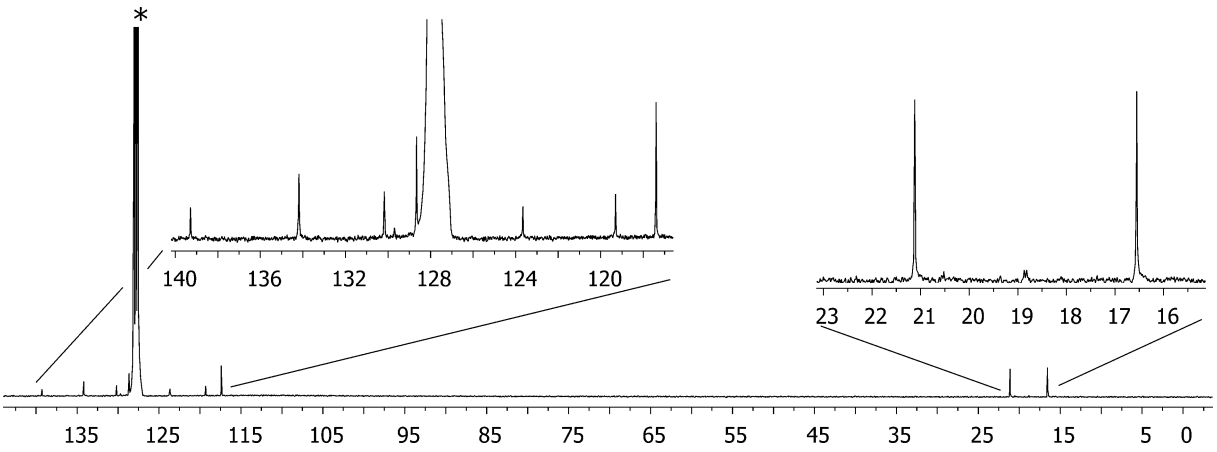
Exact mass calcd. for 2 $[C_9H_{10}N_2]$ + Ag^+: 399.07334 g/mol; found: 399.07269 g/mol.

IR (ATR): ṽ = 3162 (s), 3079 (m), 2971 (w), 2939 (s), 2859(m), 1642 (w), 1515 (s), 1476 (s), 1374 (w), 1354 (m), 1318 (m), 1255 (w), 1217 (w), 1149 (w), 1084 (s), 976 (s), 951 (s), 851 (s), 824 (m), 804 (m), 784 (m), 748 (s).

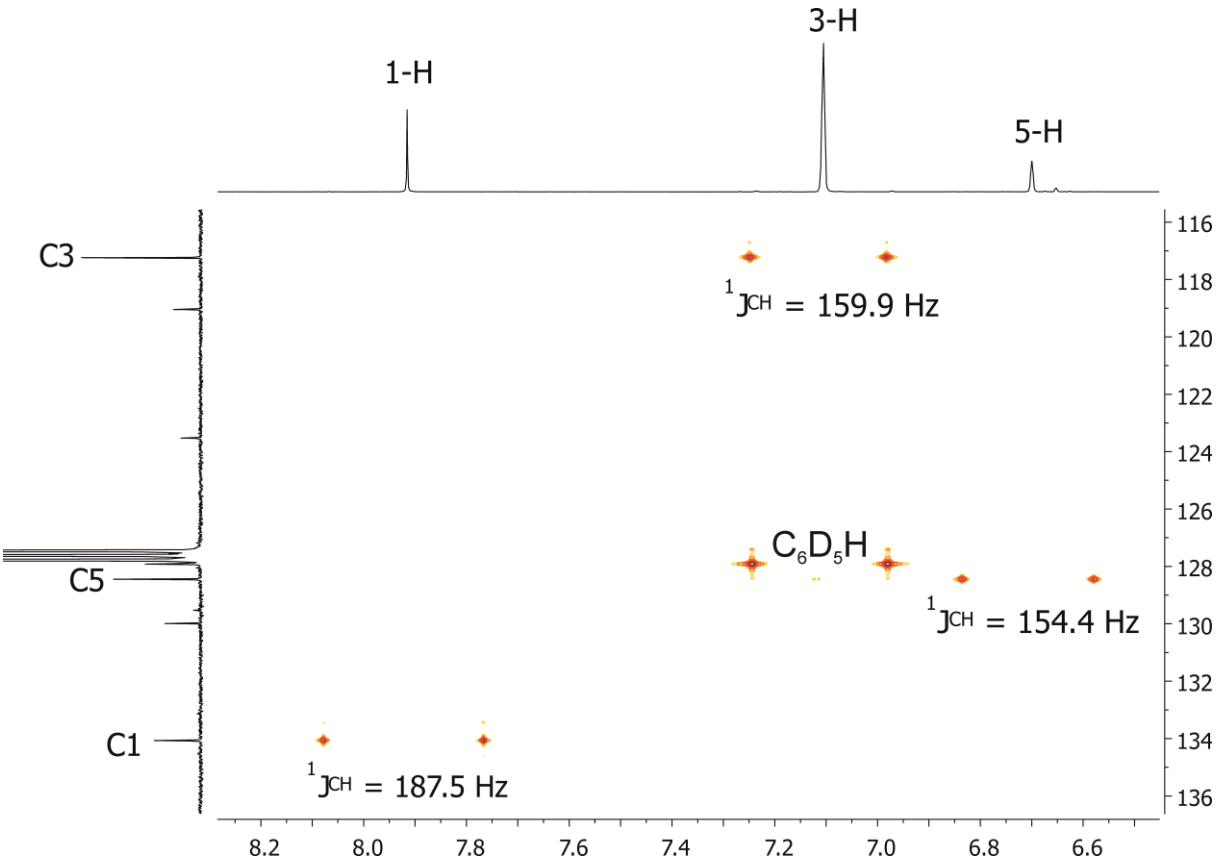
Melting Point: 121 °C.



^{1}H NMR (400 MHz, 294 K, C_6D_6).

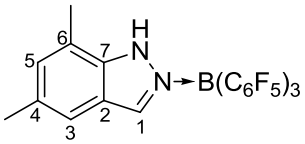


$^{13}C\{^{1}H\}$ NMR (101 MHz, 294 K, C_6D_6(*)).



proton-coupled ^{1}H, ^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6).

Preparation of adduct 7·B(C$_6$F$_5$)$_3$



4,6-Dimethylindazole (**7**) (20.9 mg, 0.143 mmol) and tris(pentafluorophenyl)borane (73.2 mg, 0.143 mmol) were dissolved in CD_2Cl_2 and investigated by NMR spectroscopy. The NMR solution was layered with *n*-pentane and a white solid precipitated. Removal of the solvent, washing of the residue with *n*-pentane, isolating the solid and drying *in vacuo* gave the product **7·B(C$_6$F$_5$)$_3$** as white solid (75.0 mg, 0.114 mmol, 80%).

Crystals suitable for crystal structure analysis were obtained by slow diffusion of *n*-pentane into a solution of compound **7·B(C$_6$F$_5$)$_3$** in CH_2Cl_2 at −30 °C.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 9.72 (s, 1H, NH), 7.83 (s, 1H, H-1), 6.72 (s, 1H, H-3), 6.49 (s, 1H, H-5), 1.96 (s, 3H, 4-CH_3), 1.46 (s, 3H, 6-CH_3).

^{1}H{^{1}H} NOE (600 MHz, 299 K, C_6D_6): δ = 6.72 / 1.96 (H-3 / 4-CH_3), 6.49 / 1.96, 1.46 (H-5 / 4-CH_3, 6-CH_3), 1.96 / 6.72, 6.49 (4-CH_3 / H-3, H-5), 1.46 / 6.49 (6-CH_3 / H-5).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 148.5 (dm, $^1J_{FC}$ ~ 243 Hz, C_6F_5), 140.8 (dm, $^1J_{FC}$ ~252 Hz, C_6F_5), 139.7 (C-7), 137.7 (dm, $^1J_{FC}$ ~ 251 Hz, C_6F_5), 136.1 (C-1), 135.0 (C-5), 134.8 (C-4), 121.2 (C-2), 120.0 (C-6), 118.5 (C-3), 117.4 (br, *i*-C_6F_5), 20.9 (4-CH_3), 15.1 (6-CH_3).

^{1}H,^{1}H GCOSY (600 MHz, 299 K, C_6D_6): δ = 9.72 / 7.83, 6.72 (NH / H-1, H-3), 7.83 / 9.72, 1.96 (H-1 / NH, 4-CH_3), 6.72 / 9.72, 6.49, 1.96, 1.46 (H-3 / NH, 5-H, 4-CH_3, 6-CH_3), 6.49 / 6.72, 1.96, 1.46 (H-5 / H-3, 4-CH_3, 6-CH_3), 1.96 / 6.72, 6.49, 1.46 (4-CH_3 / H-3, H-5, 6-CH_3), 1.46 / 6.72, 6.49, 1.96 (6-CH_3 / 3-H, 5-H, 4-CH_3).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ = 7.83 / 136.1 (H-1 / C-1), 6.72 / 118.5 (H-3 / C-3), 6.49 / 135.0 (H-5 / C-5), 1.96 / 20.9 (4-CH_3), 1.46 / 15.1 (6-CH_3).

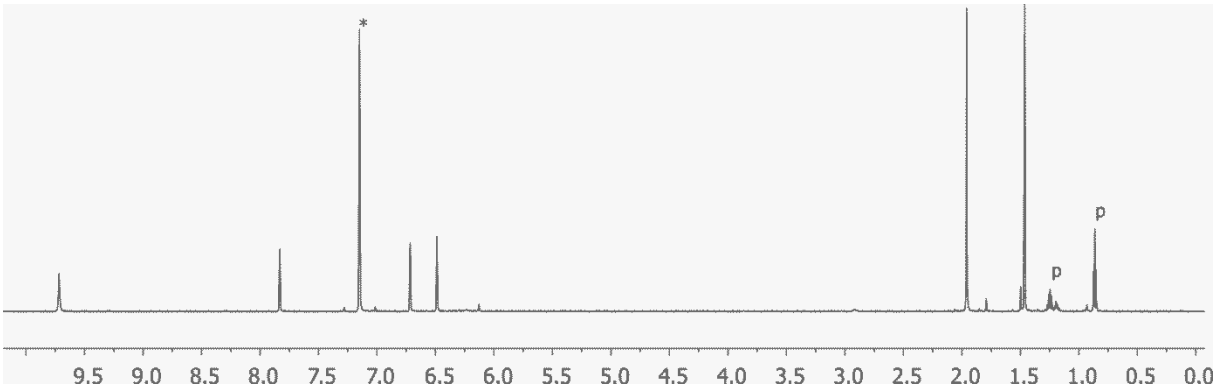
^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6): δ = 9.72 / 139.7, 136.1, 121.2 (NH / C-7, C-1, C-2), 7.83 / 139.7, 121.2 (H-1 / C-7, C-2), 6.72 / 139.7, 135.0 or 134.8, 121.2, 20.9 (H-3 / C-7, C-4 or C-5, C-2, 4-CH_3), 6.49 / 139.7, 118.5, 15.1 (H-5 / C-7, C-3, 6-CH_3), 1.96 / 134.8, 118.5 (4-CH_3 / C-4 C-3), 1.46 / 139.7, 135.0, 120.0 (6-CH_3 / C-7, C-5, C-6).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = −6.4 ($\nu_{1/2}$ ≈ 200 Hz).

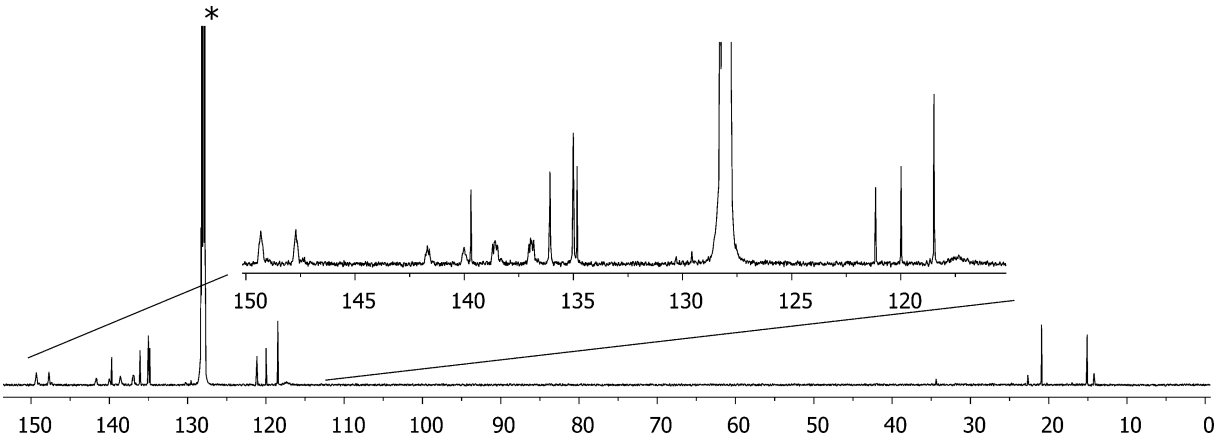
^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = −132.7 (m, 2F, *o*-C_6F_5), −155.0 (t, $^3J_{FF}$ = 20.9 Hz, 1F, *p*-C_6F_5), −162.5 (m, 2F, *m*-C_6F_5); [$\delta\Delta^{19}F_{p,m}$: 7.5].

Exact mass calcd. for $C_{27}H_{10}BF_{15}NP - H^+$: 657.06248 g/mol; found: 657.05966 g/mol.

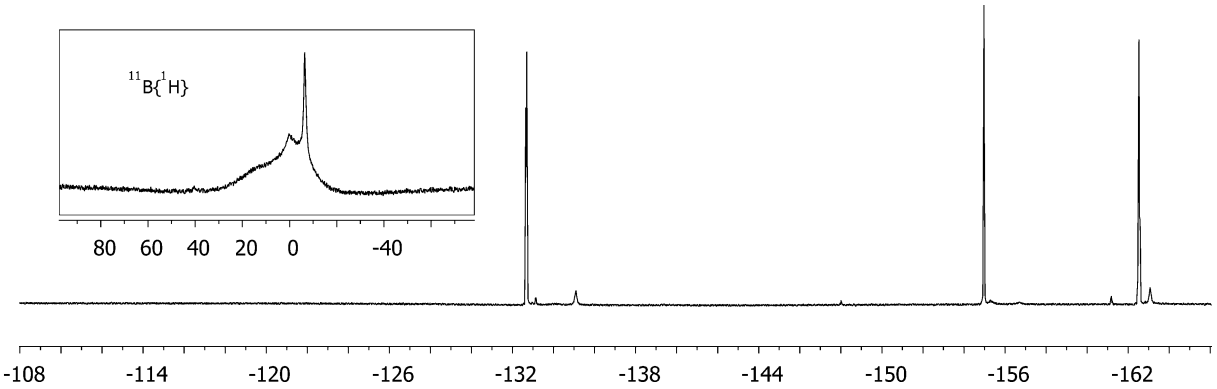
IR (KBr): ṽ = 3448 (s), 2961 (w), 2929 (w), 2873 (w), 1647 (m), 1606 (w), 1520 (s), 1469 (s), 1384 (m), 1333 (w), 1288 (m), 1109 (s), 984 (s), 870 (w), 792 (w), 775 (w), 683 (m), 678 (m), 602 (w), 578 (w).



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

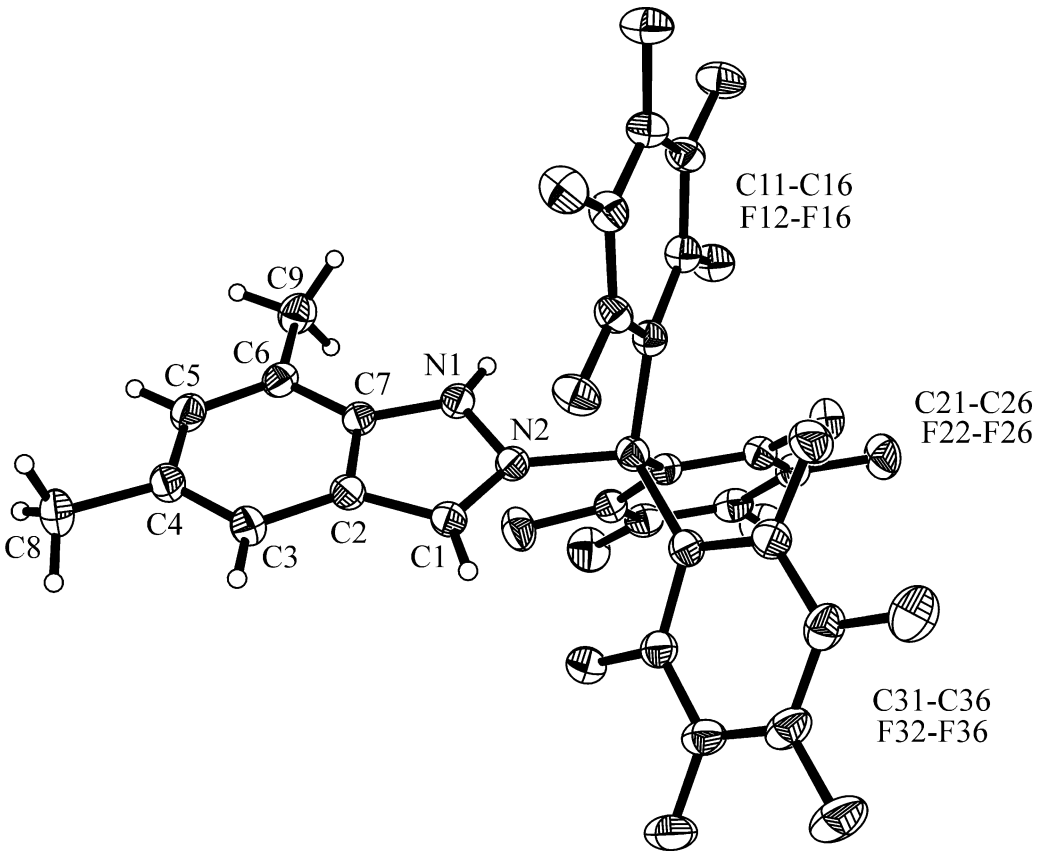


^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6(*)).

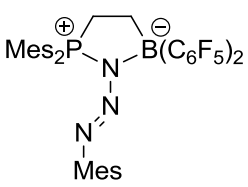


^{19}F NMR (564 MHz, 299 K, C_6D_6); box: ^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6).

X-ray crystal structure analysis of 7·B(C$_6$F$_5$)$_3$: formula $C_{27}H_{10}BF_{15}N_2$, *M* = 658.18, colourless crystal, 0.28 x 0.25 x 0.10 mm, *a* = 11.8538(4), *b* = 16.1096(5), *c* = 13.2359(3) Å, *β* = 91.891(2) °, *V* = 2526.15(13) Å^3, ρ_{calc} = 1.731 gcm^{-3}, μ = 1.630 mm^{-1}, empirical absorption correction (0.658 ≤ T ≤ 0.854), *Z* = 4, monoclinic, space group *P*2$_1$/*n* (No. 14), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 19408 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 4383 independent (R_{int} = 0.041) and 3848 observed reflections [*I*>2σ(*I*)], 412 refined parameters, *R* = 0.039, wR^2 = 0.102, max. (min.) residual electron density 0.20 (-0.21) e.Å^{-3}, hydrogen atom at N1 was refined freely, others hydrogen atoms were calculated and refined as riding atoms.



Reaction of FLP 8 with mesityl azide to phosphazide 5b



Dimesitylvinylphosphane (100 mg, 0.337 mmol) and bis(pentafluorophenyl)borane (116.7 mg, 0.337 mmol) were dissolved in *n*-pentane (10 mL) to give a yellow solution. After stirring for five minutes at rt mesitylazide (54.4 mg, 0.337 mmol) was added to the reaction mixture to obtain a colourless solution. After stirring for 1.5 h at rt the solution was concentrated (5 mL) and stored in the freezer. The white/pale yellow precipitate was isolated by filter cannula and the obtained solid was dried *in vacuo* to get the product **5b** as white solid (185 mg, 0.230 mmol, 68%).

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 6.60 (s, 2H, *m*-Mes^N), 6.43 (d, $^{4}J_{PH}$ = 4.3 Hz, 4H, *m*-Mes^P), 2.85 (m, 2H, $^{P}CH_2$), 1.98 (s, 3H, *p*-CH_3^{MesN}), 1.90 (m, 2H, $^{B}CH_2$), 1.88 (br s, 12H, *o*-CH_3^{MesP}), 1.86 (s, 6H, *p*-CH_3^{MesP}), 1.83 (s, 6H, *o*-CH_3^{MesN}).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 146.6 (*i*-Mes^N), 143.1 (d, $^{4}J_{PC}$ = 2.9 Hz, *p*-Mes^P), 142.0 (br d, $^{2}J_{PC}$ = 9.1 Hz, *o*-Mes^P), 136.1 (*p*-Mes^N), 131.9 (d, $^{3}J_{PC}$ = 11.5 Hz, *m*-Mes^P), 130.2 (*o*-Mes^N), 129.9 (*m*-Mes^N), 125.4 (d, $^{1}J_{PC}$ = 85.3 Hz, *i*-Mes^P), 30.5 (d, $^{1}J_{PC}$ = 66.2 Hz, $^{P}CH_2$), 22.8 (d, $^{3}J_{PC}$ = 4.9 Hz, *o*-CH_3^{MesP}), 20.71 (d, $^{5}J_{PC}$ = 1.4 Hz, *p*-CH_3^{MesP}), 20.67 (*p*-CH_3^{MesN}), 19.8 (br, $^{B}CH_2$), 17.7 (*o*-CH_3^{MesN}), [C_6F_5 not listed].

^{1}H,^{1}H GCOSY (600 MHz, 299 K, C_6D_6): δ = 6.60 / 1.98, 1.83 (*m*-Mes^N / *p*-CH_3^{MesN}, *o*-CH_3^{MesN}), 6.43 / 1.88, 1.86 (*m*-Mes^P / *o*-CH_3^{MesP}, *p*-CH_3^{MesP}), 2.85 / 1.90 ($^{P}CH_2$ / $^{B}CH_2$), 1.98 / 6.60, 1.83 (*p*-CH_3^{MesN} / *m*-Mes^N, *o*-CH_3^{MesN}), 1.90 / 2.85 ($^{B}CH_2$ / $^{P}CH_2$), 1.88 / 6.43 (*o*-CH_3^{MesP} / *m*-Mes^P), 1.86 / 6.43 (*p*-CH_3^{MesP} / *m*-Mes^P), 1.83 / 6.60, 1.98 (*o*-CH_3^{MesN} / *m*-Mes^N, *p*-CH_3^{MesN}).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ = 6.60 / 129.9 (*m*-Mes^N), 6.43 / 131.9 (*m*-Mes^P), 2.85 / 30.5 ($^{P}CH_2$), 1.98 / 20.67 (*p*-CH_3^{MesN}), 1.90 / 19.8 ($^{B}CH_2$), 1.88 / 22.8 (*o*-CH_3^{MesP}), 1.86 / 20.71 (*p*-CH_3^{MesP}), 1.83 / 17.7 (*o*-CH_3^{MesN}).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6): δ = 6.60 / 146.6, 129.9, 20.67, 17.7 (*m*-Mes^N / *i*-Mes^N, *m*-Mes^N, *p*-CH_3^{MesN}, *o*-CH_3^{MesN}), 6.43 / 142.0, 131.9, 125.4, 22.8, 20.71 (*m*-Mes^P / *o*-Mes^P, *m*-Mes^P, *i*-Mes^P, *o*-CH_3^{MesP}, *p*-CH_3^{MesP}), 1.98 / 136.1, 129.9 (*p*-CH_3^{MesN} / *p*-Mes^N, *m*-Mes^N), 1.90 / 30.5 ($^{B}CH_2$ / $^{P}CH_2$), 1.88 / 142.0, 131.9 (*o*-CH_3^{MesP} / *o*-Mes^P, *m*-Mes^P), 1.86 / 143.1, 131.9 (*p*-CH_3^{MesP} / *p*-Mes^P, *m*-Mes^P), 1.83 / 146.6, 130.2 (*o*-CH_3^{MesN} / *i*-Mes^N, *o*-Mes^N).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = −5.9 ($\nu_{1/2}$ ≈ 300 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = −130.9 (br, 2F, *o*-C_6F_5), −160.8 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-C_6F_5), −165.2 (m, 2F, *m*-C_6F_5); [$\delta\Delta^{19}F_{p,m}$: 4.4].

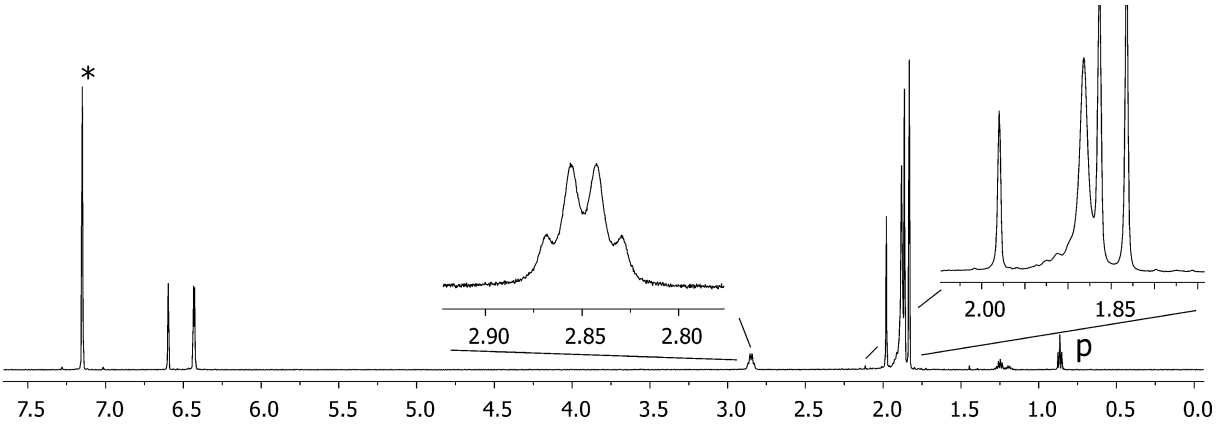
^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = 54.6 ($\nu_{1/2}$ ≈ 110 Hz).

Exact mass calcd. for $C_{41}H_{37}BF_{10}N_3P + Na^+$: 826.25649 g/mol; found: 826.25567 g/mol;

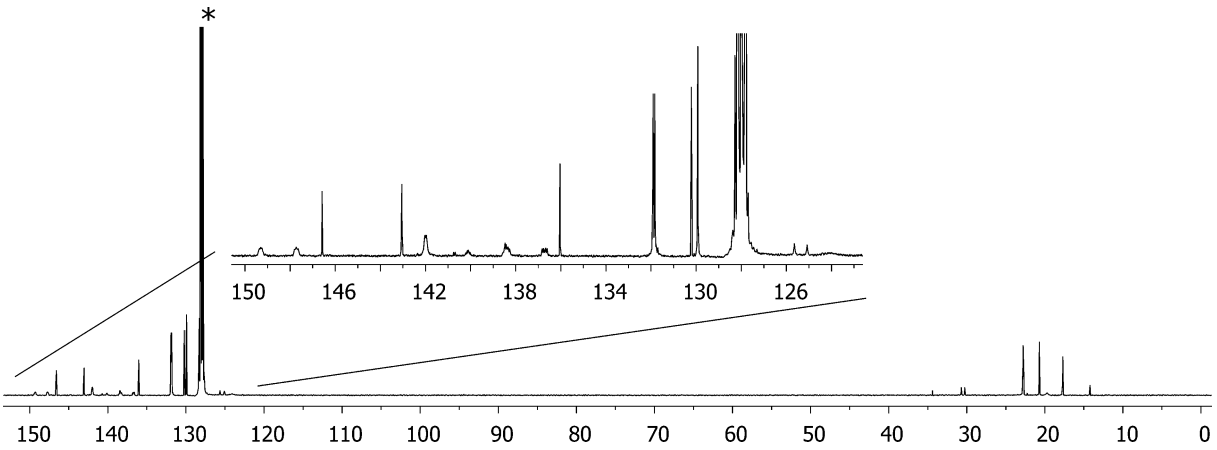
IR (KBr): $\tilde{\nu}$ = 1643 (w), 1606 (w), 1514 (m), 1450 (s), 1380 (w), 1279 (m), 1085 (s), 974 (s), 893 (w), 853 (m), 814 (w), 772 (w), 731 (w), 707 (w), 676 (w), 623 (m), 577 (w), 554 (w).

Elemental analysis: calcd. for C $_{41}H_{37}BF_{10}N_3P$ C 61.29, H 4.64, N 5.23; found C 60.68, H 4.48, N 5.03.

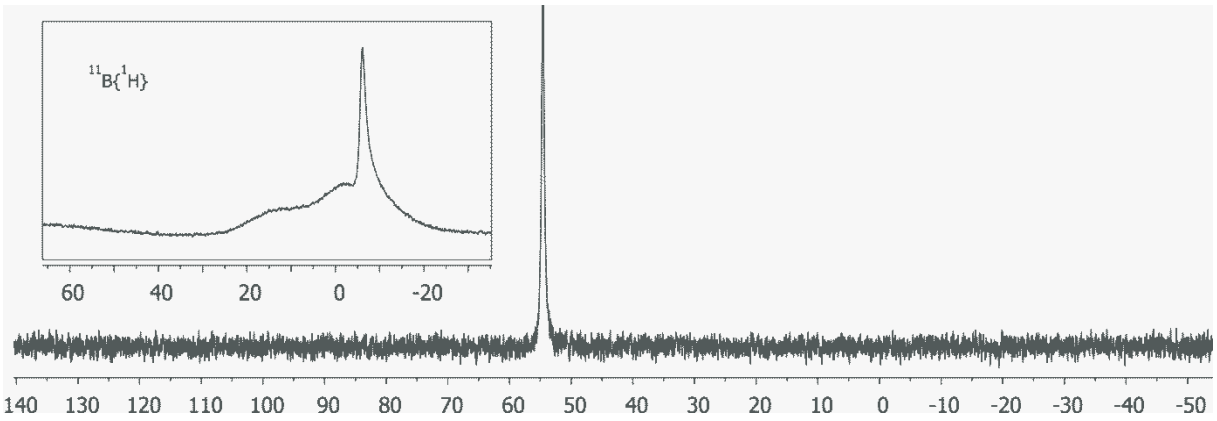
Decomposition point: 150 °C.



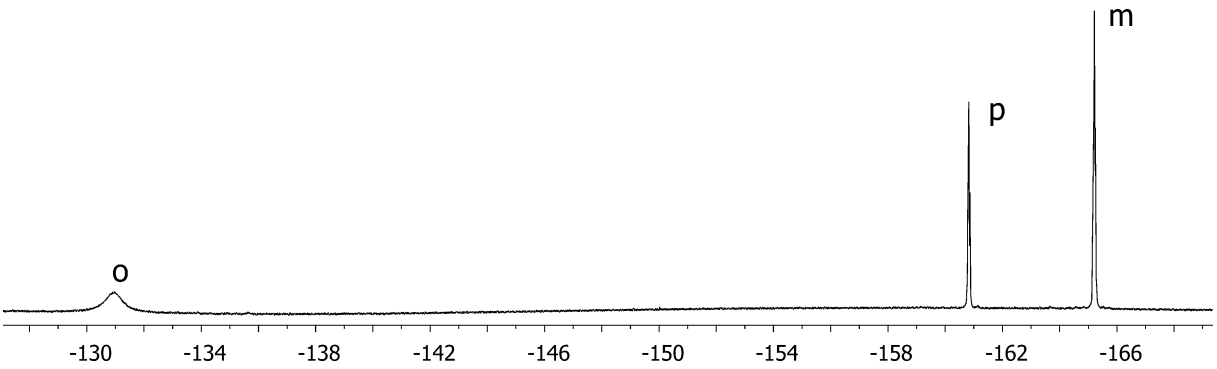
^{1}H NMR (600 MHz, 299 K, C_6D_6(*)); p: pentane.



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

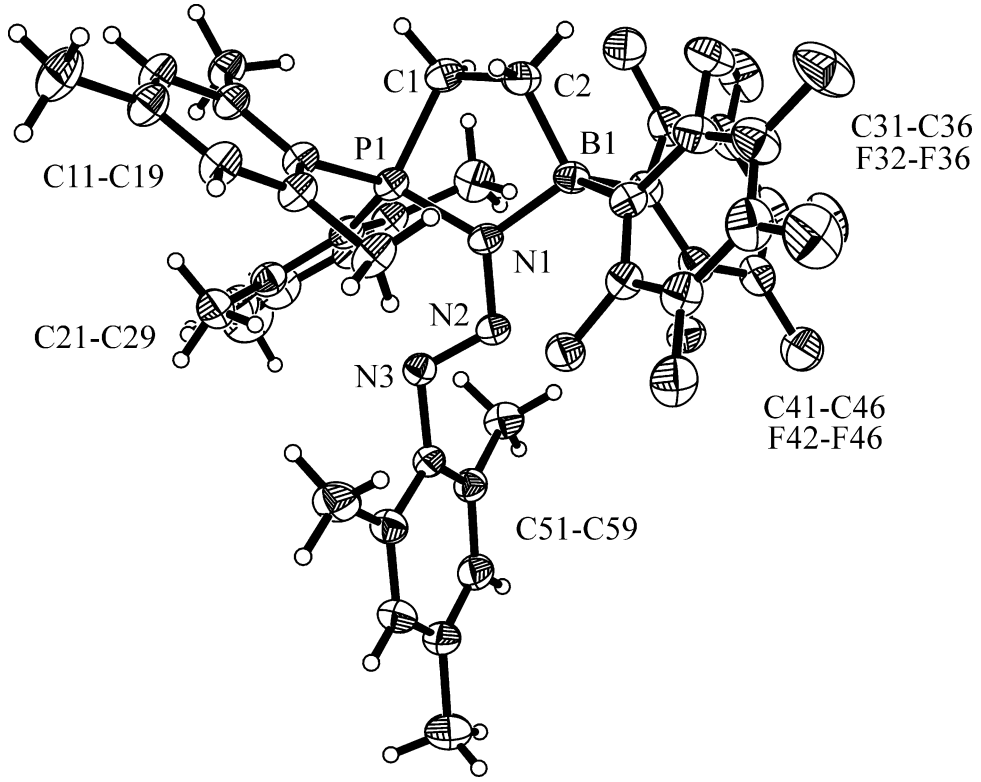


$^{31}P\{^{1}H\}$ NMR (243 MHz, 299 K, C_6D_6); box: $^{11}B\{^{1}H\}$ NMR (192 MHz, 299 K, C_6D_6).

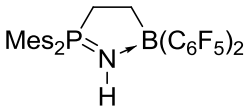


^{19}F NMR (564 MHz, 299 K, C_6D_6).

X-ray crystal structure analysis of 5b: formula $C_{41}H_{37}BF_{10}N_3P$ * ½ C_5H_{12} * CH_2Cl_2, M = 924.52, colourless crystal, 0.60 x 0.30 x 0.10 mm, a = 10.3617(1), b = 12.6512(1), c = 19.2962(2) Å, α = 78.926(1), β = 84.773(1), γ = 74.640(1)°, V = 2391.57(4) Å^3, ρ_{calc} = 1.284 gcm^{-3}, μ = 2.168 mm^{-1}, empirical absorption correction (0.356 ≤ T ≤ 0.812), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 23344 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 7889 independent (R_{int} = 0.071) and 6945 observed reflections, space group [I>2σ(I)], 595 refined parameters, R = 0.071, wR^2 = 0.208, max. (min.) residual electron density 0.48 (-0.57) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.



Preparation of phosphinimine 6b



Dimesitylvinylphosphane (577.5 mg, 1.95 mmol) and bis(pentafluorophenyl)borane (674.2 mg, 1.95 mmol) were dissolved in *n*-pentane (20 mL) until a clear yellow solution was formed. Mesitylazide (314.2 mg, 1.95 mmol) in *n*-pentane (1 mL) was added to the reaction mixture; the colour changed to orange and a white-yellow solid precipitated. After stirring for one hour at rt the solvent was removed by filter cannula and the solid was dissolved in CH_2Cl_2 (20 mL) to give a clear yellow solution. The reaction mixture was exposed to UV light and the reaction was controlled by NMR measurements. Completion of the reaction was reached after four days. Then the solvent was removed *in vacuo* and the crude (compound **7** was identified but not isolated) was purified by column chromatography (SiO_2 : CH_2Cl_2:*n*-pentane = 1:4; R_f = 0.36). The product **6b** was isolated as white solid (1.114 g, 1.69 mmol, 87%).

Crystals suitable for X-ray structure analysis were obtained by slow diffusion of *n*-pentane into a solution of the product in CH_2Cl_2 at 4 °C.

Initiating the reaction by thermolysis (165 °C, *in vacuo*) of the neat starting material **5b** gave also **6b** as main product (71%) along with two unidentified side products (δ ^{31}P: 55.2 (15%); 31.5 (14%)) according to ^{31}P NMR measurements.

^{1}H NMR (600 MHz, 299 K, C_6D_6): δ = 6.36 (d, $^{4}J_{PH}$ = 3.9 Hz, 4H, *m*-Mes), 2.80 (d, $^{2}J_{PH}$ = 12.1 Hz, 1H, NH), 2.43 (q, $^{2}J_{PH} \approx {}^{3}J_{HH} \approx$ 6.8 Hz, 2H, $^{P}CH_2$), 1.95 (s, 12H, *o*-CH_3^{Mes}), 1.91 (dt, $^{3}J_{PH}$ = 23.9 Hz, $^{3}J_{HH}$ = 6.9 Hz, 2H, $^{B}CH_2$), 1.86 (s, 6H, *p*-CH_3^{Mes}).

^{13}C{^{1}H} NMR (151 MHz, 299 K, C_6D_6): δ = 148.3 (dm, $^{1}J_{FC}$ ~ 240 Hz, C_6F_5), 142.4 (d, $^{4}J_{PC}$ = 2.7 Hz, *p*-Mes), 140.7 (d, $^{2}J_{PC}$ = 10.5 Hz, *o*-Mes), 139.3 (dm, $^{1}J_{FC}$ ~ 255 Hz, C_6F_5), 137.4 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 131.8 (d, $^{3}J_{PC}$ = 11.1 Hz, *m*-Mes), 126.0 (d, $^{1}J_{PC}$ = 87.4 Hz, *i*-Mes), 124.5 (br, *i*-C_6F_5), 32.9 (d, $^{1}J_{PC}$ = 65.3 Hz, $^{P}CH_2$), 22.3 (d, $^{3}J_{PC}$ = 5.3 Hz, *o*-CH_3^{Mes}), 20.7 (d, $^{5}J_{PC}$ = 1.4 Hz, *p*-CH_3^{Mes}), 19.2 (br, $^{B}CH_2$).

^{1}H,^{1}H GCOSY (600 MHz, 299 K, C_6D_6): δ = 6.36 / 1.95 (*m*-Mes / *o*-CH_3^{Mes}), 2.43 / 1.91 ($^{P}CH_2$ / $^{B}CH_2$), 1.91 / 2.43 ($^{B}CH_2$ / $^{P}CH_2$).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 299 K, C_6D_6): δ = 6.36 / 131.8 (*m*-Mes), 2.43 / 32.9 ($^{P}CH_2$), 1.95 / 22.3 (*o*-CH_3^{Mes}), 1.91 / 19.2 ($^{B}CH_2$), 1.86 / 20.7 (*p*-CH_3^{Mes}).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 299 K, C_6D_6): δ = 6.36 / 131.8, 126.0, 22.3, 20.7 (*m*-Mes / *m*-Mes, *i*-Mes, *o*-CH_3^{Mes}, *p*-CH_3^{Mes}), 1.95 / 140.7, 131.8, 126.0 (*o*-CH_3^{Mes} / *o*-Mes, *m*-Mes, *i*-Mes), 1.86 / 142.4, 131.8 (*p*-CH_3^{Mes} / *p*-Mes, *m*-Mes).

^{11}B{^{1}H} NMR (192 MHz, 299 K, C_6D_6): δ = −4.6 ($\nu_{1/2}$ ~ 140 Hz).

^{19}F NMR (564 MHz, 299 K, C_6D_6): δ = −134.9 (m, 2F, *o*-C_6F_5), −160.2 (t, $^{3}J_{FF}$ = 20.8 Hz, 1F, *p*-C_6F_5), −164.3 (m, 2F, *m*-C_6F_5); [$\delta\Delta^{19}F_{p,m}$: 4.1].

^{31}P NMR (243 MHz, 299 K, C_6D_6): δ = 50.7 (s, $\nu_{1/2}$ ~ 55Hz).

^{31}P{^{1}H} NMR (243 MHz, 299 K, C_6D_6): δ = 50.7 ($\nu_{1/2}$ ~ 12 Hz).

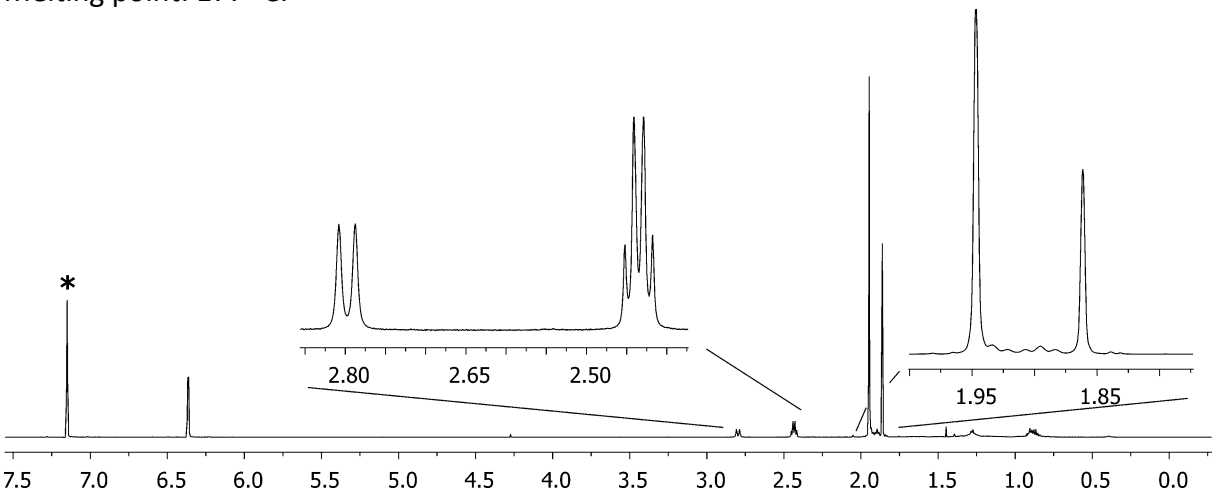
Exact mass calcd. for $C_{32}H_{27}BF_{10}NP + Na^+$: 680.1712 g/mol; found: 680.1710 g/mol;

$2[C_{32}H_{27}BF_{10}NP]+Na^+$:1337.3541 g/mol; found: 1337.3485 g/mol.

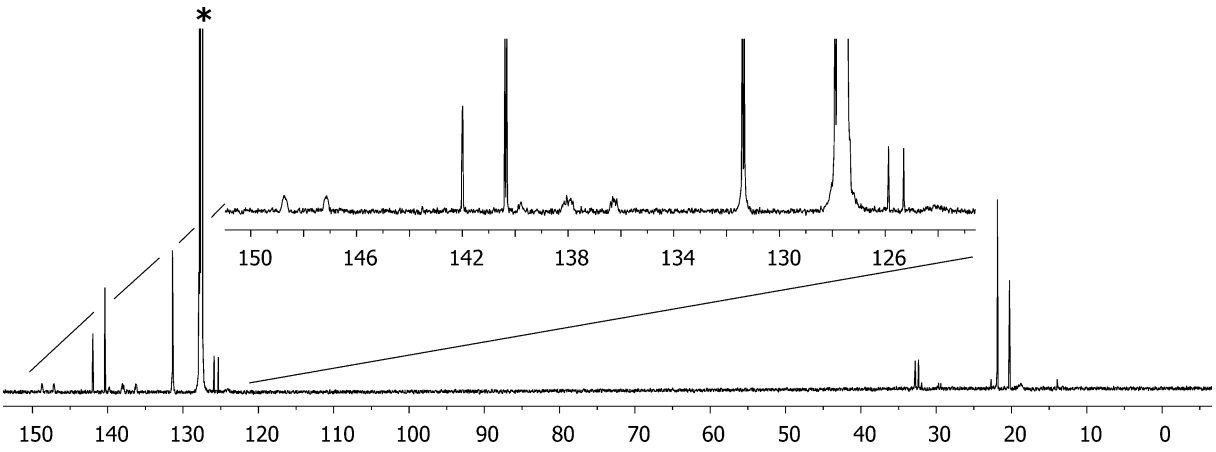
IR (KBr): $\tilde{\nu}$ = 1641 (w), 1608 (w), 1510 (m), 1457 (s), 1384 (w), 1273 (w), 1248 (w), 1213 (m), 1086 (s), 1035 (w), 968 (s), 923 (m), 853 (w), 811 (w), 783 (w), 751 (w), 710 (w), 668 (w), 640 (w), 607 (w), 572 (w).

Elemental analysis: calcd. for $C_{32}H_{27}BF_{10}NP$ C 58.47, H 4.14, N 2.13; found C 58.84, H 4.10, N 2.08.

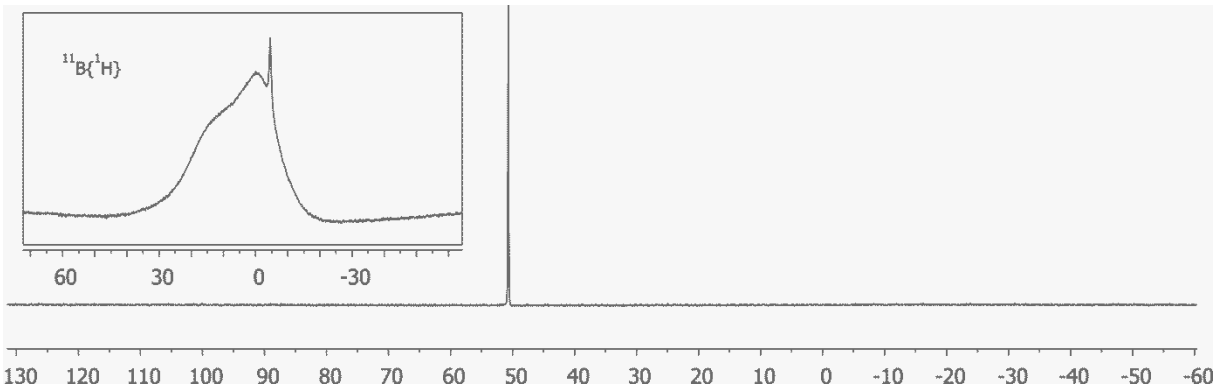
Melting point: 177 °C.



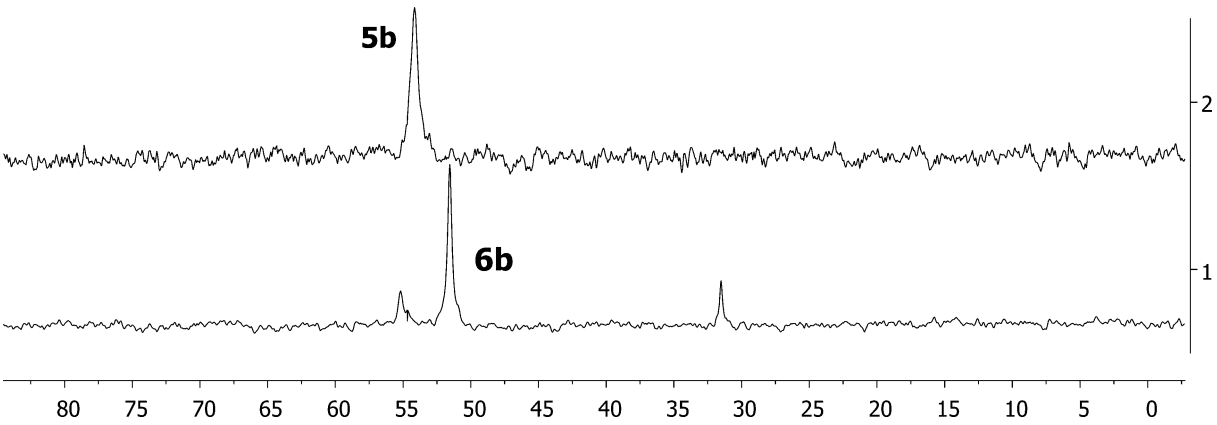
^{1}H NMR (600 MHz, 299 K, C_6D_6(*)).



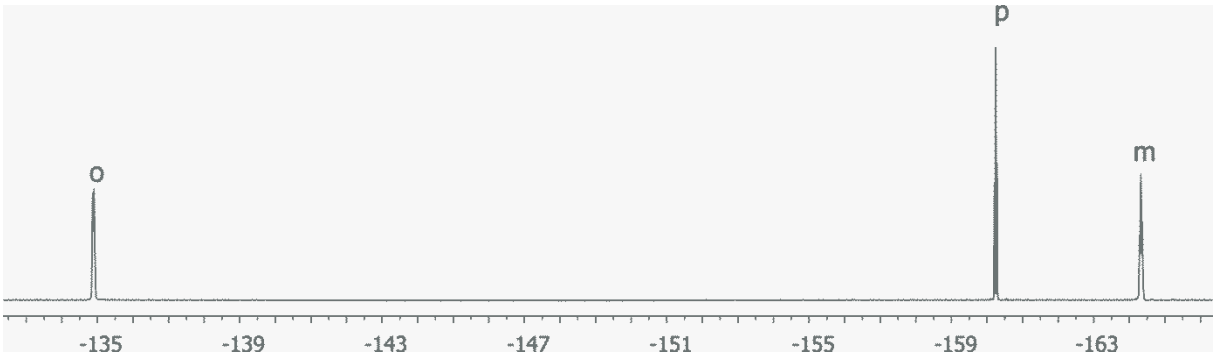
$^{13}C\{^{1}H\}$ NMR (151 MHz, 299 K, C_6D_6(*)).



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



$^{31}P\{^{1}H\}$ NMR (81 MHz, 300 K, C_6D_6), 1: before thermolysis of **5b**; 2: after thermolysis of **5b** (165 °C, *in vacuo*).



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

X-ray crystal structure analysis of 6b: formula $C_{32}H_{27}BF_{10}NP$, M = 657.33, colourless crystal, 0.15 x 0.15 x 0.12 mm, a = 11.1667(4), b = 14.5051(8), c = 18.7777(10) Å, β = 100.307(2) °, V = 2992.4(3) Å^3, ρ_{calc} = 1.459 gcm^{-3}, μ = 1.600 mm^{-1}, empirical absorption correction (0.795 ≤ T ≤ 0.831), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 29490 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.60 Å^{-1}, 5195 independent (R_{int} = 0.058) and 4279 observed reflections [I>2σ(I)], 415 refined parameters, R = 0.050, wR^2 = 0.141, max. (min.) residual electron density 0.25 (-0.34) e.Å^{-3}, hydrogen atom at N1 was refined freely, but with fixed U-value; others hydrogen atoms were calculated and refined as riding atoms.