

- Supporting Information -

# Cooperative Lewis Acidity in Fluorophosphonium Boranes

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## Table of Content

<b>1. Materials and Methods</b>	S-1
<b>2. Synthesis and Spectroscopic Data</b>	S-2
<b>3. Variable Temperature NMR Studies</b>	S-27
<b>4. Catalysis Studies</b>	S-29

## 1 Materials and Methods

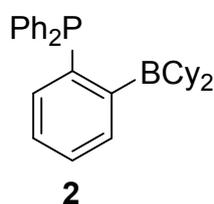
All manipulations were performed in a Glove box MB Unilab produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N<sub>2</sub>. Dry, oxygen-free solvents (CH<sub>2</sub>Cl<sub>2</sub>, *n*-pentane, *n*-hexane, toluene) were prepared using an Innovative Technologies solvent purification system. Deuterated dichloromethane (CD<sub>2</sub>Cl<sub>2</sub>) was purchased from Cambridge Isotope Laboratories Inc., distilled from CaH<sub>2</sub> and stored over molecular sieves (4 Å) for at least two days prior to use. Deuterated bromobenzene (C<sub>6</sub>D<sub>5</sub>Br) was purchased from Cambridge Isotope Laboratories Inc. degassed and stored over molecular sieves (4 Å) for at least two days prior to use. If not stated otherwise commercial reagents were used as received without further purification. Commercial olefin substrates were routinely filtered over silica before use. XeF<sub>2</sub> was purchased from Apollo Scientific and used without further purification. All glassware was oven-dried at temperatures above 180 °C prior to use. NMR spectra were measured on a Bruker AVANCE 400 <sup>1</sup>H (400.03 MHz), <sup>13</sup>C (100.59 MHz), <sup>19</sup>F (376.49 MHz), <sup>31</sup>P (161.94 MHz), <sup>11</sup>B (128.37 MHz) at 25 °C, on an Agilent DD2 500 <sup>1</sup>H (499.7 MHz), <sup>13</sup>C (125.7 MHz) at 27 °C, on an Agilent DD2 500 <sup>1</sup>H (499.9 MHz), <sup>13</sup>C (125.7 MHz), <sup>19</sup>F (470.3 MHz), <sup>31</sup>P (202.4 MHz), <sup>11</sup>B (160.4 MHz) at 25 °C, on an Agilent DD2 600 <sup>1</sup>H (600.0 MHz), <sup>13</sup>C (150.9 MHz), <sup>19</sup>F (564.7 MHz), <sup>31</sup>P (242.9 MHz), <sup>11</sup>B (192.5 MHz) at 26 °C or on an Agilent DD2 700 <sup>1</sup>H (700.0 MHz), <sup>13</sup>C (176.0 MHz), <sup>19</sup>F (658.0 MHz) at 27 °C. Assignments of the carbon atoms in the <sup>13</sup>C spectra were performed via indirect deduction from the cross-peaks in 2D correlation experiments (HMBC; HSQC). Chemical shifts are relative to tetramethylsilane (δ<sup>1</sup>H 0.0, δ<sup>13</sup>C 0.0) and were referenced to the residual proton signal of the deuterated solvent, CFCI<sub>3</sub> (external, δ<sup>19</sup>F 0.0), H<sub>3</sub>PO<sub>4</sub> (85% in H<sub>2</sub>O, external, δ<sup>31</sup>P 0.0), BF<sub>3</sub>·OEt<sub>2</sub> (external, δ<sup>11</sup>B 0.0). Chemical shifts (δ) are reported in ppm, multiplicity is reported as follows (s = singlet, d = doublet, t = triplet, q = quartet, pr.q. = partially

relaxed quartet, p = pentet, m = multiplet, br = broad signal) and coupling constants (J) are reported in Hz. Assignments of individual resonances were done using 2D techniques (HMBC, HSQC, HH-COSY) when necessary. Yields of products in solution were determined by integration of all resonances observed in the respective NMR spectra if not stated otherwise. High-resolution mass spectra (HRMS) were obtained on a micro mass 70S-250 spectrometer (EI), an ABI/Sciex QStar Mass Spectrometer (DART), or on a JOEL AccuTOF-DART (DART).

Compounds **4**,<sup>[S1]</sup> **14**,<sup>[S2]</sup> **15**<sup>[S3]</sup>, **16**<sup>[S3]</sup> and  $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]_2(\text{C}_7\text{H}_8)$ <sup>[S4]</sup> were synthesized according to literature procedures.

## 2 Synthesis and Spectroscopic Data

### 2.1 Synthesis of *o*-Ph<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub> (**2**)



The synthesis was done according to a modified literature procedure for *o*-(*i*Pr)<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>.<sup>[S5]</sup>

To solution of *o*-Ph<sub>2</sub>P(C<sub>6</sub>H<sub>4</sub>)Br (341.1 mg, 1.00 mmol) in 2 ml of THF was added 0.7 ml 1.6 M *n*-BuLi in hexanes at -30 °C. Subsequently a precooled (-30°C) solution of 1M Cy<sub>2</sub>BCl in hexanes diluted with 4 ml THF was added dropwise. After the addition the solution was allowed to warm to room temperature and stirred for 20 h. Volatiles were removed and the residue was extracted with 10 ml of pentane. The resulting suspension was filtered over Celite and a small silica plug. Removal of volatiles gave the title compound **2** as a colorless oil (281.2 mg, 0.43 mmol, 64 %).

**<sup>1</sup>H NMR** (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>1</sup>H 7.35 (m, 1H, C<sub>Ar</sub>H), 7.33 - 7.27 (m, 11H, C<sub>Ar</sub>H), 7.23 (m, 1H, C<sub>Ar</sub>H), 7.01 (m, 1H, C<sub>Ar</sub>H), 1.76 (m, 4H, BCy<sub>2</sub>), 1.62 (m, 6H, BCy<sub>2</sub>), 1.51 (m, 2H, BCy<sub>2</sub>) 1.20 – 1.04 (m, 10H, BCy<sub>2</sub>).

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<sup>S1</sup> T. W. Hudnall, Y. M. Kim, M. W. P. Bebbington, D. Bourissou and F. P. Gabbaï, *J. Am. Chem. Soc.*, 2008, **130**, 10890-10891.

<sup>S2</sup> C. B. Caputo, D. Winkelhaus, R. Dobrovetsky, L. J. Hounjet and D. W. Stephan, *Dalton Trans.*, 2015, **44**, 12256-12264.

<sup>S3</sup> L. J. Hounjet, C. B. Caputo and D. W. Stephan, *Dalton Trans.*, 2013, **42**, 2629-2635.

<sup>S4</sup> J. B. Lambert, S. Zhang, S. M. Ciro, *Organometallics* **1994**, **13**, 2430-2443.

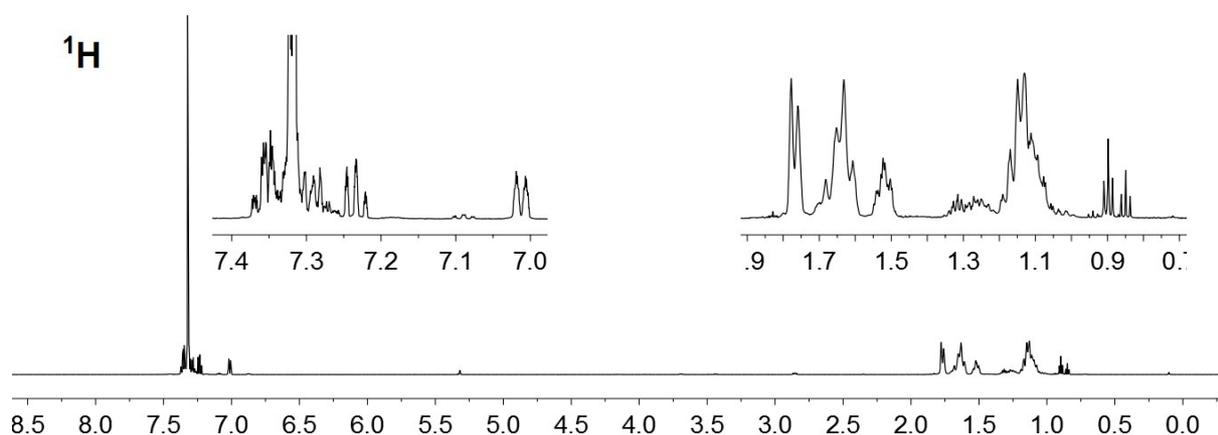
<sup>S5</sup> M. Sircoglou, S. Bontemps, M. Mercy, K. Miqueu, S. Ladeira, N. Saffon, L. Maron, G. Bouhadir and D. Bourissou, *Inorg. Chem.*, 2010, **49**, 3983-3990.

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^{13}\text{C}$  158.8 (d,  $^2J_{\text{PC}} = 51$  Hz, ipso B  $\text{C}_{\text{Ar}}$ ,  $\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2$ ), 138.2 (d,  $^1J_{\text{PC}} = 9$  Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2$ ), 134.6 (d,  $^3J_{\text{PC}} = 2$  Hz,  $\text{C}_{\text{Ar}}\text{H}$ ), 134.1 (d,  $^1J_{\text{PC}} = 20$  Hz,  $\text{C}_{\text{Ar}}$ ,  $\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2$ ), 133.6 (d,  $^2J_{\text{PC}} = 17$  Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{PPh}_2$ ), 133.5 (d,  $^4J_{\text{PC}} = 2$  Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2$ ), 128.8 (s,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{PPh}_2$ ), 128.7 (d,  $^3J_{\text{PC}} = 7$  Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{PPh}_2$ ), 126.6 (d,  $^1J_{\text{PC}} = 21$  Hz,  $\text{C}_{\text{Ar}}$ ,  $\text{PPh}_2$ ), 126.7 (d,  $^3J_{\text{PC}} = 2$  Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2$ ), 37.5 (bs, CH,  $\text{BCy}_2$ ), 28.9 (bs,  $\text{CH}_2$ ,  $\text{BCy}_2$ ), 27.9 (s,  $\text{CH}_2$ ,  $\text{BCy}_2$ ), 26.9 (s,  $\text{CH}_2$ ,  $\text{BCy}_2$ ).

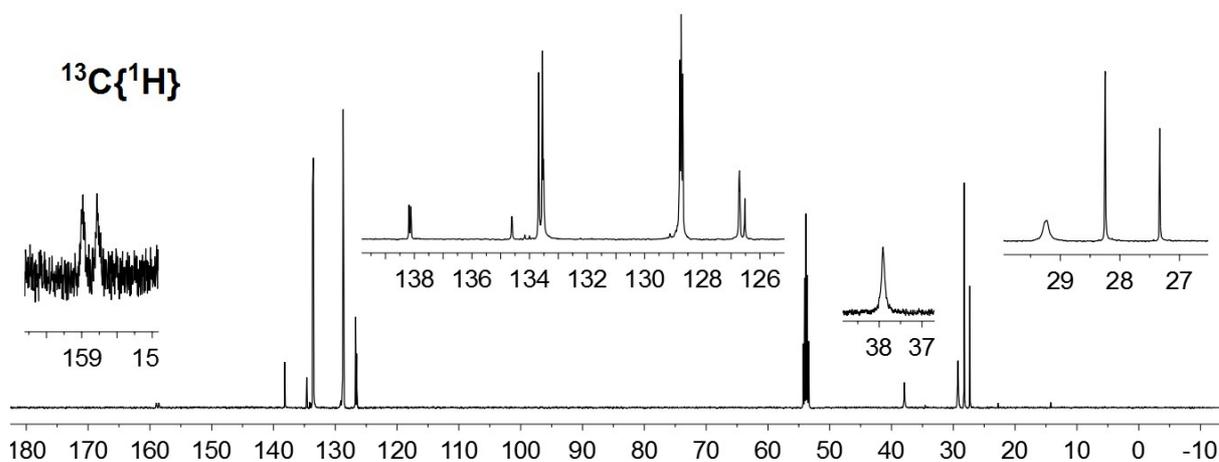
**$^{11}\text{B}\{^1\text{H}\}$  NMR** (192 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ): 80.2 ( $\nu_{1/2} \sim 1250$  Hz).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (243 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ): -8.2 ( $\nu_{1/2} \sim 4$  Hz).

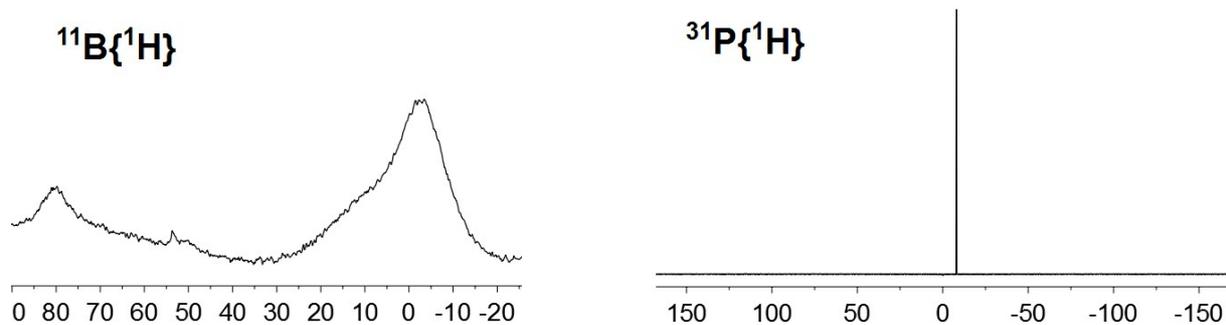
**MS (DART)**  $[\text{M}+\text{H}]^+$   $\text{C}_{30}\text{H}_{37}\text{BP}$  calc. 439.27259 m/z found 439.27405 m/z.



$^1\text{H}$  NMR (600 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of *o*- $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2$  (**2**).

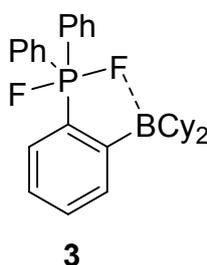


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of *o*- $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2$  (**2**).



$^{11}\text{B}\{^1\text{H}\}$  NMR (192 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of *o*- $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2$  (**2**).

## 2.2 Synthesis of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BCy}_2$ (**3**)



A 20 ml vial was charged with *o*- $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2$  (**2**) (157.3 mg, 0.36 mmol),  $\text{CH}_2\text{Cl}_2$  (5 ml) and a stirring bar.  $\text{XeF}_2$  (60.7 mg, 0.36 mmol, 1 eq.) was added to the stirred solution in small portions. Evolution of gas was observed upon addition. After complete addition the solution was stirred for 20 h at room temperature. Volatiles were removed and the residue recrystallized from 2 ml pentane at  $-30\text{ }^\circ\text{C}$ . The resulting crystals were separated from the mother liquor and dried to give the title compound **3** as colorless solid (140 mg, 0.29 mmol, 82%).

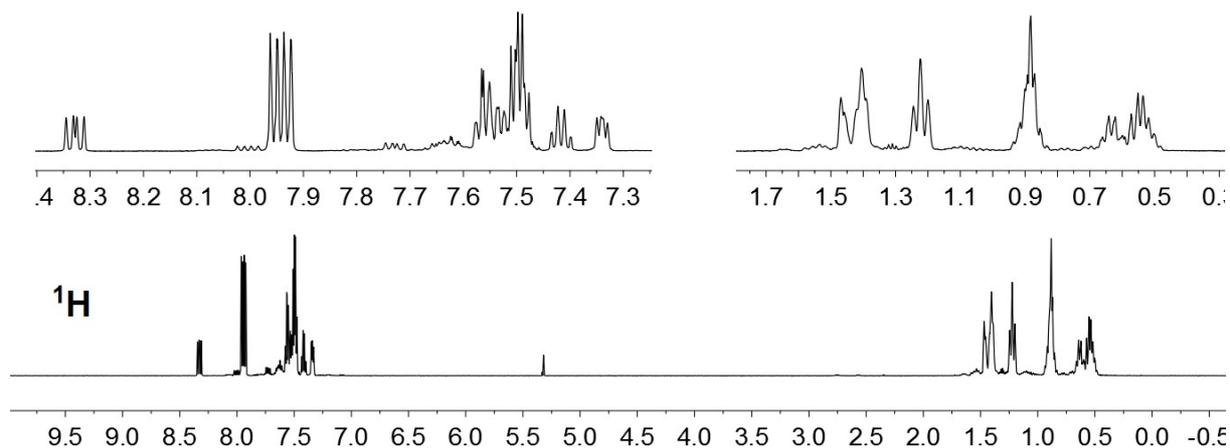
$^1\text{H}$  NMR (600 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^1\text{H}$  8.33 (m, 1H,  $\text{C}_6\text{H}_4$ ), 7.94 (m, 4H, *o*-Ph), 7.60 - 7.46 (m, 7H, *p*-Ph, *m*-Ph,  $\text{C}_6\text{H}_4$ ), 7.42 (m, 1H,  $\text{C}_6\text{H}_4$ ), 7.34 (m, 1H,  $\text{C}_6\text{H}_4$ ), 1.47 (m, 2H,  $\text{BCy}_2$ ), 1.41 (m, 4H,  $\text{BCy}_2$ ), 1.22 (m, 4H,  $\text{BCy}_2$ ), 0.89 (m, 6H), 0.63 (m, 2H  $\text{BCy}_2$ ), 0.54 (m, 4H,  $\text{BCy}_2$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^{13}\text{C}$  167.7 (bm, *ipso*  $\text{C}_{\text{Ar}}$  B,  $\text{PPhBCy}_2$ ), 135.0 (dt,  $^2J_{\text{PC}} = 18$  Hz,  $^3J_{\text{FC}} = 12$  Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{PPhBCy}_2$ ), 134.0 ( $^1J_{\text{PC}} = 157$  Hz,  $^2J_{\text{FC}} = 25$  Hz,  $\text{C}_{\text{Ar}}$ ,  $\text{PPh}_2$ ), 132.6 - 132.3 (m,  $\text{C}_{\text{Ar}}\text{H}$   $\text{PPh}_2$  and  $\text{PPhBCy}_2$ ), 130.1 (dt,  $^3J_{\text{PC}} = 22$  Hz,  $^4J_{\text{FC}} = 7$  Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{PPhBCy}_2$ ), 128.8 (d,  $^3J_{\text{PC}} = 17$  Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{PPh}_2$ ), 126.3 (dt,  $^3J_{\text{PC}} = 17$  Hz,  $^4J_{\text{FC}} = 1.9$  Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{PPhBCy}_2$ ), 124.9 (dt,  $^1J_{\text{PC}} = 156$  Hz,  $^2J_{\text{FC}} = 17$  Hz,  $\text{C}_{\text{Ar}}$ ,  $\text{PPhBCy}_2$ ), 32.4 (bs, CH,  $\text{BCy}_2$ ), 30.0 (m,  $\text{CH}_2$ ,  $\text{BCy}_2$ ), 29.1 (d,  $J_{\text{FC}} = 23$  Hz,  $\text{CH}_2$ ,  $\text{BCy}_2$ ), 27.8 (s,  $\text{CH}_2$ ,  $\text{BCy}_2$ ).

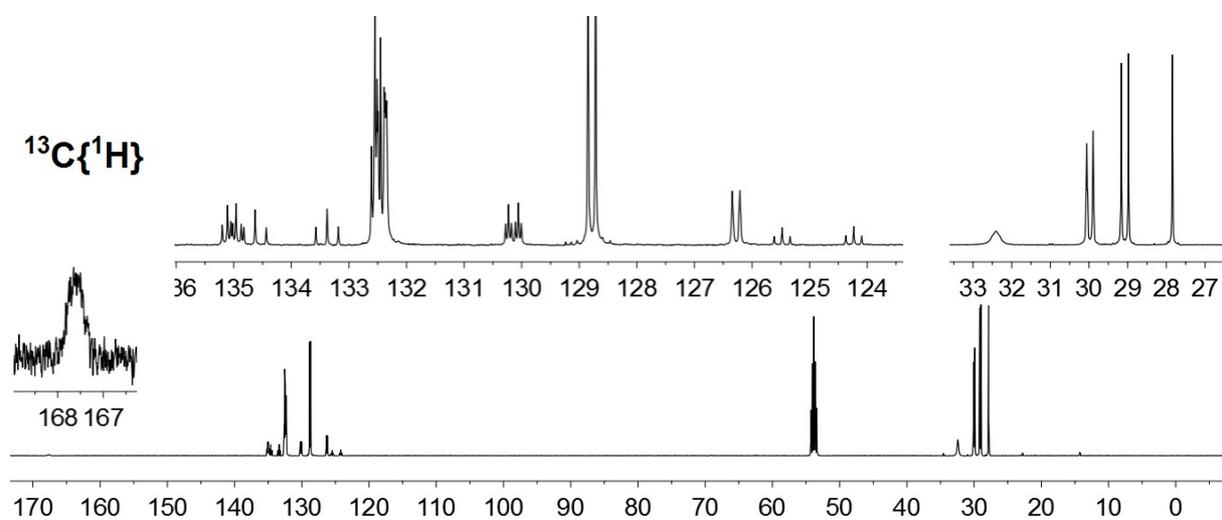
$^{11}\text{B}$  NMR (192 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^{11}\text{B}$  29.7 ( $\nu_{1/2} \sim 710$  Hz).

$^{19}\text{F}$  NMR (564 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ): -76.0 (br), -76.8 (br).

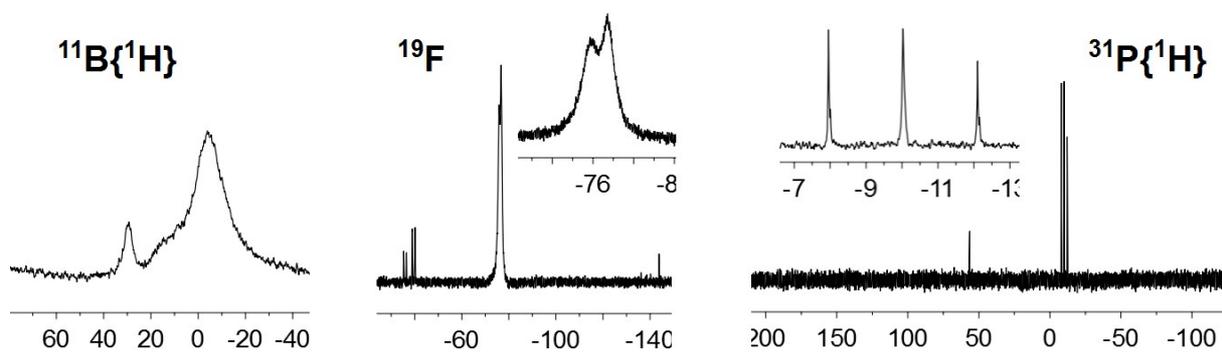
$^{31}\text{P}$  NMR (243 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ): -10.1 (m).



$^1\text{H}$  NMR (600 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BCy}_2$  (**3**).



$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BCy}_2$  (**3**).



$^{11}\text{B}\{^1\text{H}\}$  NMR (192 MHz),  $^{19}\text{F}$  (564 MHz) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz) spectra (298 K,  $\text{CD}_2\text{Cl}_2$ ) of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BCy}_2$  (**3**).

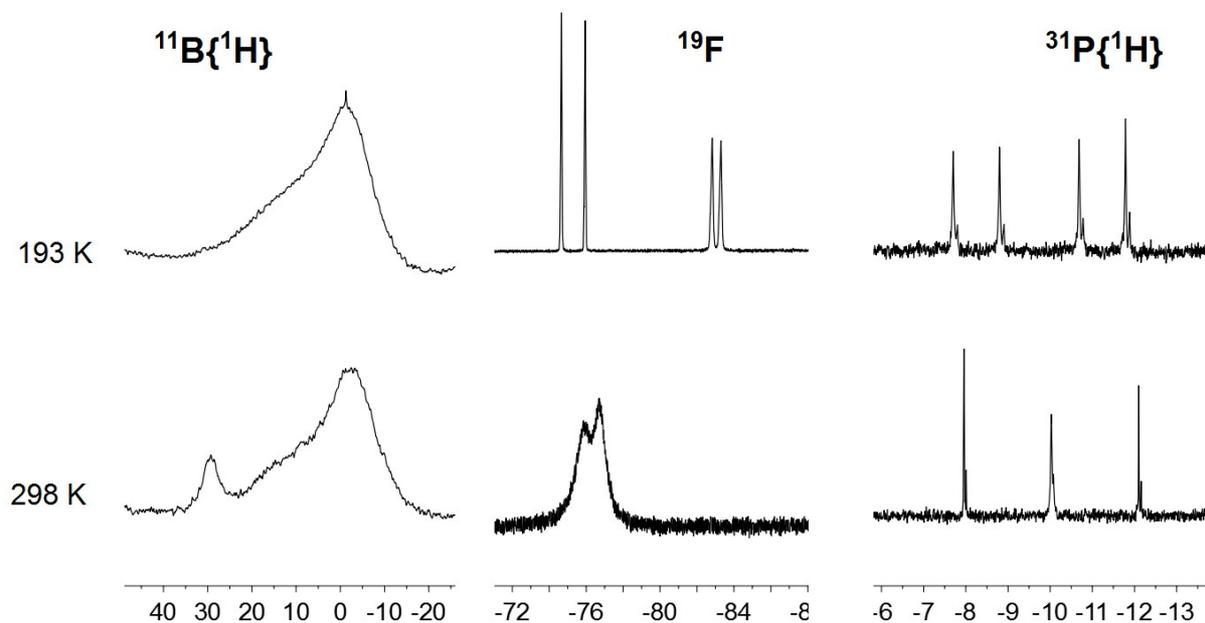
Data at 193 K:

$^{11}\text{B}$  NMR (192 MHz, 193 K,  $\text{CD}_2\text{Cl}_2$ ): n.o.

**$^{19}\text{F}$  NMR** (564 MHz, 193 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^{19}\text{F}$  -75.31 (d,  $J_{\text{PF}} = 725$  Hz,  $\text{FP}_{\text{terminal}}$ ), -83.06 (d,  $J_{\text{PF}} = 267$  Hz,  $\text{FP}_{\text{bridging}}$ ).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (243 MHz, 193 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^{31}\text{P}$  -9.7 (dd,  $J_{\text{PF}} = 725$  Hz,  $J_{\text{PFB}} = 267$  Hz).

MS (DART) [M-F]  $\text{C}_{39}\text{H}_{36}\text{BFP}^+$  calc 457.26317 m/z found. 457.26401 m/z

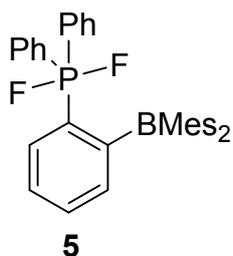


$^{11}\text{B}\{^1\text{H}\}$  NMR (192 MHz,  $\text{CD}_2\text{Cl}_2$ ),  $^{19}\text{F}$  (564 MHz,  $\text{CD}_2\text{Cl}_2$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ ) spectra at 193 K (top) and 298 K (bottom) of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BCy}_2$  (**3**).

Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of a pentane solution of compound **3**.

### 2.3 Synthesis of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BMes}_2$ (**5**)

A 20 ml vial was charged with *o*- $\text{Ph}(\text{C}_6\text{H}_4)\text{BMes}_2$  (**4**) (51.7 mg, 0.101 mmol) and  $\text{CH}_2\text{Cl}_2$  (2 ml).  $\text{XeF}_2$  (17.1 mg, 0.101 mmol) was added in small portions to the stirred solution of **4**. Gas evolution was observed upon addition. The resulting clear solution was then stirred for 6 h at room temperature. Volatiles were removed in vacuum and the resulting colorless powder was washed three times with pentane (2 ml) giving the title compound **5** as colorless powder (48.1 mg, 0.088 mmol, 87%).



**$^1\text{H}$  NMR** (600 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^1\text{H}$  8.13 (m, 1H,  $\text{C}_6\text{H}_4$ ), 7.60 (m, 4H, *o*-Ph)<sup>†</sup>, 7.44 (m, 2\*1H,  $\text{C}_6\text{H}_4$ ), 7.34 (m, 2H, *p*-Ph)<sup>†</sup>, 7.30 (m, 1H,  $\text{C}_6\text{H}_4$ ), 7.20 (m, 4H, *m*-Ph)<sup>†</sup>, 6.45 (br, 4H, *m*-Mes), 2.12 (br, 6H, *p*-Me), 1.81 (br, 12H, *o*-Me).

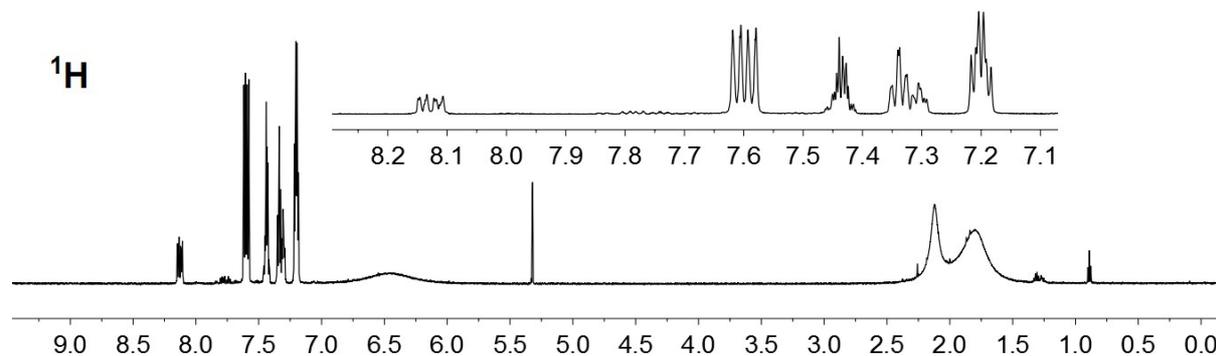
**$^{13}\text{C}\{^1\text{H}\}$  NMR** (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^{13}\text{C}$  157.3 (br, *i*-B- $\text{C}_6\text{H}_4$ ), 140.4 (dt,  $^1J_{\text{PC}} = 182$  Hz,  $^2J_{\text{FC}} = 29$  Hz, *i*-P- $\text{C}_6\text{H}_4$ ), 139.1 (br, Mes), 138.1 (dt,  $^1J_{\text{PC}} = 177$  Hz,  $^2J_{\text{FC}} = 28$  Hz, *i*-Ph), 136.5 (dt,  $J = 17$  Hz,  $J = 11$  Hz,  $\text{C}_6\text{H}_4$ ), 134.3 (d,  $J_{\text{PC}} = 19$  Hz,  $\text{C}_6\text{H}_4$ )<sup>†</sup>, 133.3 (dt,  $^2J_{\text{PC}} = 13$  Hz,  $^3J_{\text{FC}} = 8$  Hz, *o*-Ph)<sup>†</sup>, 131.4 (d,  $J = 4$  Hz,  $\text{C}_6\text{H}_4$ ), 130.3 (d,  $J = 4$  Hz,  $\text{C}_6\text{H}_4$ ), 129.0 (br, *p*-Ph and Mes), 128.1 (d,  $^3J_{\text{PC}} = 17$  Hz, *m*-Ph)<sup>†</sup>, 23.7 (br, *o*-Me), 21.2 (s, *p*-Me). <sup>†</sup> tentatively assigned. Not assigned: Mes.

**$^{11}\text{B}\{^1\text{H}\}$  NMR** (192 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ): 67.6 ( $\nu_{1/2} \sim 1500$  Hz).

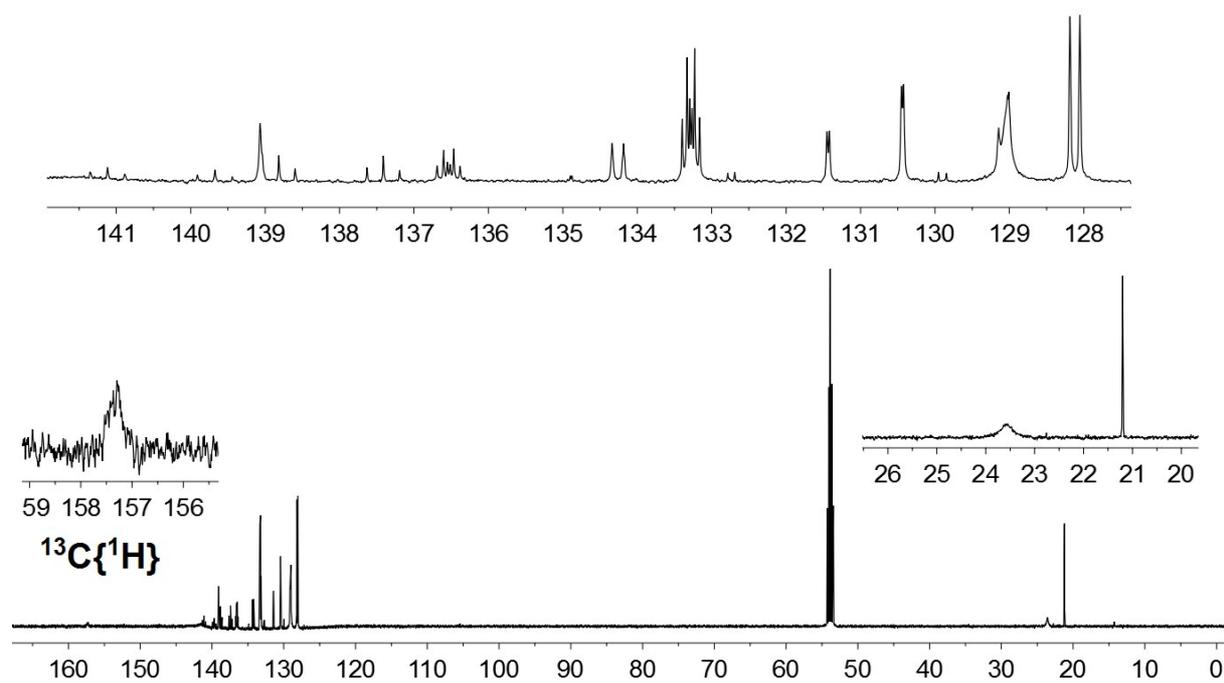
**$^{19}\text{F}$  NMR** (564 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ): -37.2 (d,  $J_{\text{PF}} = 663$  Hz)

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (243 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ): -49.0 (t,  $J_{\text{PF}} = 663$  Hz).

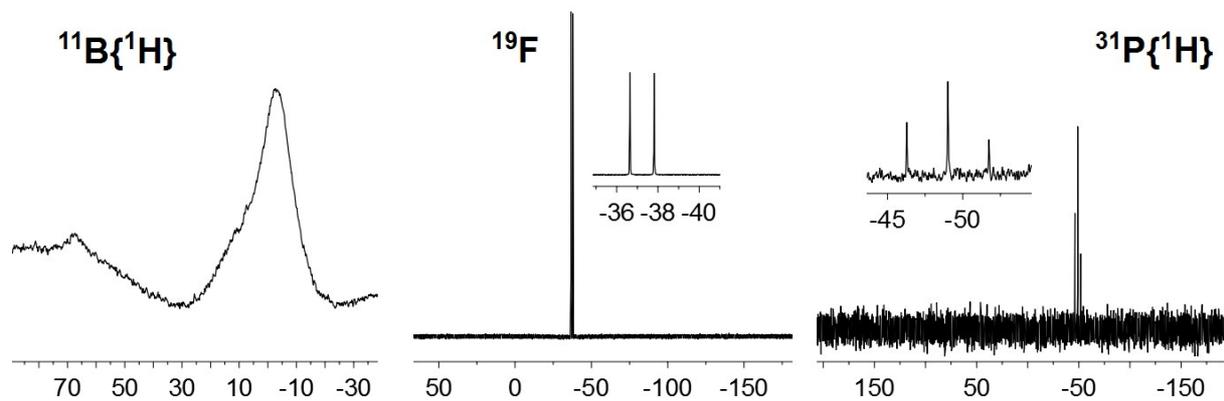
MS (DART) [M-F]  $\text{C}_{36}\text{H}_{36}\text{BFP}^+$  calc. 529.26317 m/z found 529.26267 m/z.



$^1\text{H}$  NMR (600 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BMes}_2$  (**5**).

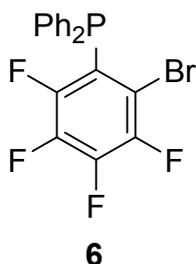


$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BMes}_2$  (5).



$^{11}\text{B}\{^1\text{H}\}$  NMR (192 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $^{19}\text{F}$  (564 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BMes}_2$  (5).

## 2.4 Synthesis of *o*-Ph<sub>2</sub>P(C<sub>6</sub>F<sub>4</sub>)Br (**6**)



1,2-dibromo-tetrafluorobenzene (2.00 g, 6.5 mmol, 1 eq.) was dissolved in Et<sub>2</sub>O (30 ml), cooled to -50 °C and “Turbo-Grignard” solution (iPrMgCl·LiCl, 1.3 M in THF, 5.0 ml, 6.5 mmol, 1 eq.) was added dropwise over 20 min and the resulting colorless solution stirred for 2.5 h allowing to warm to 0 °C. A light, colorless precipitate had formed. The suspension was cooled to -60 °C and Ph<sub>2</sub>PCl was added neat at once to the vigorously stirred suspension. The reaction mixture was allowed to warm to room temperature slowly and stirred overnight. Then, volatiles were removed in vacuum at 50 °C and the residue taken up in hexanes (20 ml) and silica gel (ca. 5 ml) was added. The insoluble components were removed by filtration in a glovebox and washed with pentane (10 ml) twice. The combined mother and wash liquors were evaporated to dryness to give 2.21 g crude product. It was taken up in pentane (5 ml) at room temperature and the suspension allowed to further precipitate at -35 °C. The supernatant was removed by decantation at -35 °C and the precipitate washed with pentane (2 ml) twice at -35 °C. Drying of the precipitate in vacuum gave compound **6** as colorless solid (2.15 g, 5.2 mmol, 84%).

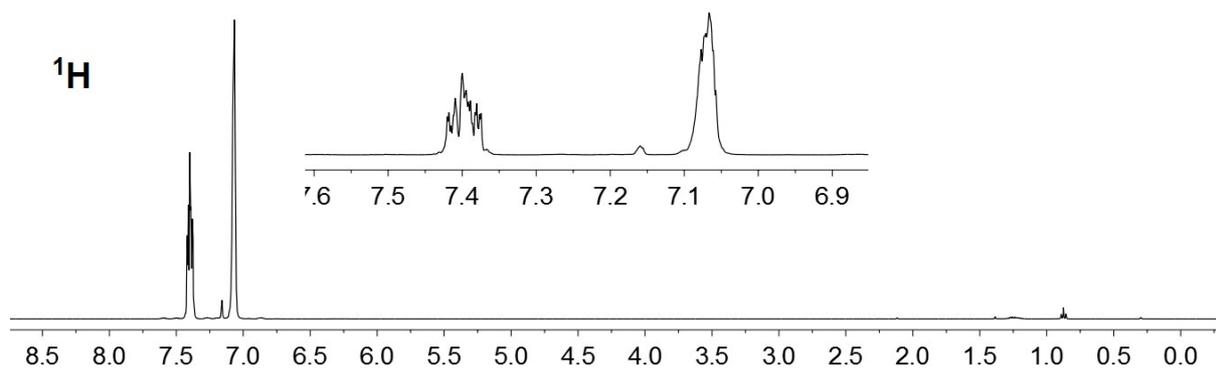
**<sup>1</sup>H NMR** (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>1</sup>H 7.40 (m, 2H, *o*-Ph), 7.07 (m, 3H, *p*-, *m*-Ph).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>13</sup>C 134.4 (dd, *J* = 12.7 Hz, *J* = 3.3 Hz, *i*-Ph), 133.2 (dd, <sup>2</sup>*J*<sub>PC</sub> = 21.2 Hz, *J*<sub>PF</sub> = 1.6 Hz, *o*-Ph), 129.4 (s, *p*-Ph), 128.9 (d, <sup>3</sup>*J*<sub>PC</sub> = 6.8 Hz, *m*-Ph). Not observed: C<sub>6</sub>F<sub>4</sub>Br.

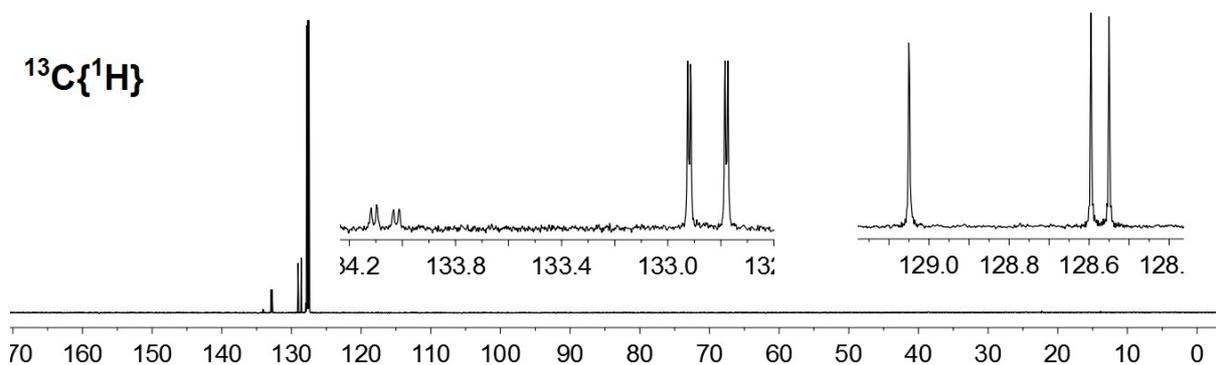
**<sup>19</sup>F NMR** (376 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>19</sup>F -121.6 (m, 1F), -126.1 (m, 1F), -149.4 (m, 1F), -154.4 (m, 1F).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (162 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>31</sup>P -2.5 (ddd, *J*<sub>PF</sub> = 20.7 Hz, 10.5 Hz, 4.5 Hz).

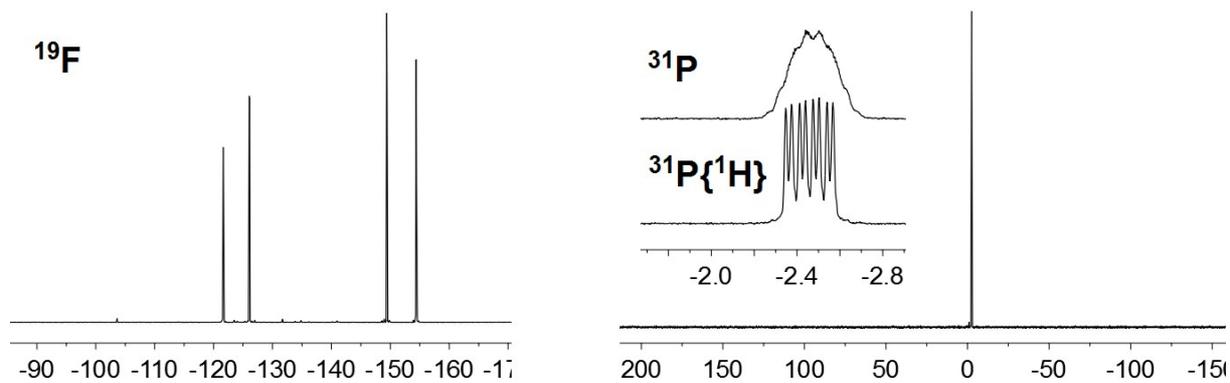
**<sup>31</sup>P NMR** (162 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>31</sup>P -2.5 (m).



$^1\text{H}$  NMR (400 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of *o*- $\text{Ph}_2\text{P}(\text{C}_6\text{F}_4)\text{Br}$  (**6**).

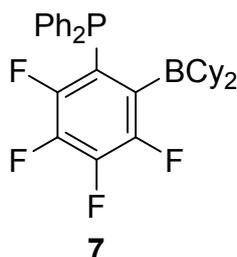


$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of *o*- $\text{Ph}_2\text{P}(\text{C}_6\text{F}_4)\text{Br}$  (**6**).



$^{19}\text{F}$  NMR (376 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) and  $^{31}\text{P}$  NMR (162 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectra of *o*- $\text{Ph}_2\text{P}(\text{C}_6\text{F}_4)\text{Br}$  (**6**).

## 2.5 Synthesis of *o*-Ph<sub>2</sub>P(C<sub>6</sub>F<sub>4</sub>)BCy<sub>2</sub> (**7**)



*o*-Ph<sub>2</sub>P(C<sub>6</sub>F<sub>4</sub>)Br (**6**) (750 mg, 1.82 mmol, 1 eq.) was dissolved in Et<sub>2</sub>O (20 ml), cooled to -60 °C and “Turbo-Grignard” solution (*i*PrMgCl·LiCl, 1.3 M in THF, 1.4 ml, 1.82 mmol, 1 eq.) was added dropwise over 15 min, the resulting colorless solution stirred for 2 h allowing to warm to -20 °C and another 2 h maintaining the temperature between -30 °C and -20 °C. A light, colorless precipitate had formed. The suspension was cooled to -50 °C and Cy<sub>2</sub>BCl (1 M in hexanes, 1.9 ml, 1.9 mmol, 1.05 eq) was added at once to the vigorously stirred suspension. The reaction mixture was allowed to warm to room temperature slowly and stirred overnight. Then, volatiles were removed in vacuum at 40 °C and the residue taken up in pentane (30 ml) at room temperature. The insoluble components were removed by filtration over *Celite* in a glovebox and washed with pentane (10 ml) twice. The combined, colorless filtrates were concentrated in vacuum to ca. 5 ml and cooled to -35 °C. Then, a seed crystal of **7** was added and the product allowed to crystallize overnight at -35 °C. The supernatant was removed by decantation at -35 °C and the residue washed with cold pentane (1 ml) at -35 °C three times. Drying of the precipitate in vacuum afforded compound **7** as colorless solid (835 mg, 1.64 mmol, 90%).

**<sup>1</sup>H NMR** (400 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>1</sup>H 7.44 (m, 4H, *o*-Ph), 7.04 (m, 6H, *p*-, *m*-Ph), 1.92 (m, 4H, BCy<sub>2</sub>), 1.76 (m, 2H, BCy<sub>2</sub>), 1.68 (m, 4H, BCy<sub>2</sub>), 1.65 (m, 2H, B-CH), 1.34 (m, 2H, BCy<sub>2</sub>), 1.21 (m, 8H, BCy<sub>2</sub>).

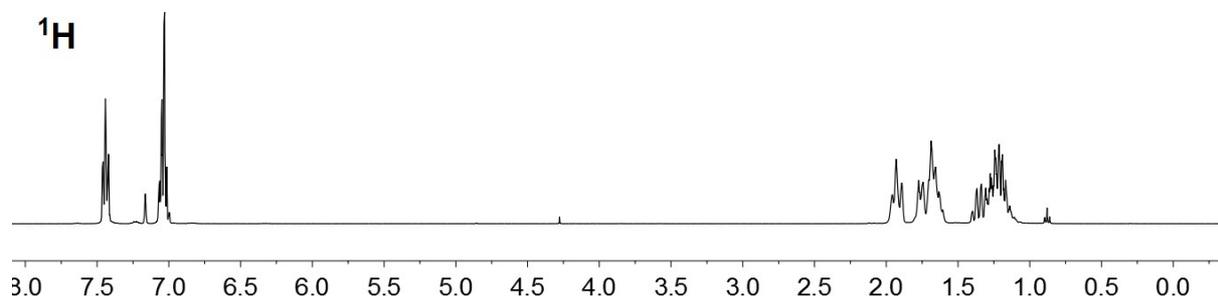
**<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>13</sup>C 134.4 (d, *J* = 3.3 Hz, *i*-Ph), 133.2 (dd, <sup>2</sup>*J*<sub>PC</sub> = 16.9 Hz, *J*<sub>PF</sub> = 2.1 Hz, *o*-Ph), 129.6 (s, *p*-Ph), 128.9 (d, <sup>3</sup>*J*<sub>PC</sub> = 7.5 Hz, *m*-Ph), 37.5 (br s, BCH), 30.2 (d, *J* = 9.0 Hz), 29.3 (d, *J* = 4.5 Hz), 28.3 (s), 28.2 (s), 27.2 (s). Not observed: C<sub>6</sub>F<sub>4</sub>.

**<sup>11</sup>B{<sup>1</sup>H} NMR** (128 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>11</sup>B 76.7 (*v*<sub>1/2</sub> ~ 2000 Hz).

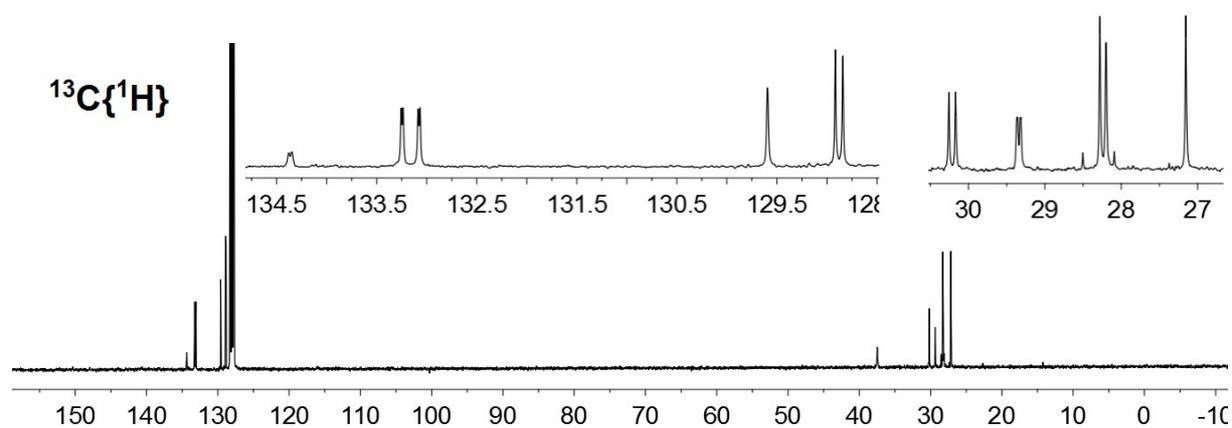
**<sup>19</sup>F NMR** (376 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>19</sup>F -125.4 (m, 1F), -132.5 (m, 1F), -150.4 (m, 1F), -155.5 (m, 1F).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (162 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>31</sup>P -5.8 (d, *J*<sub>PF</sub> = 15.0 Hz).

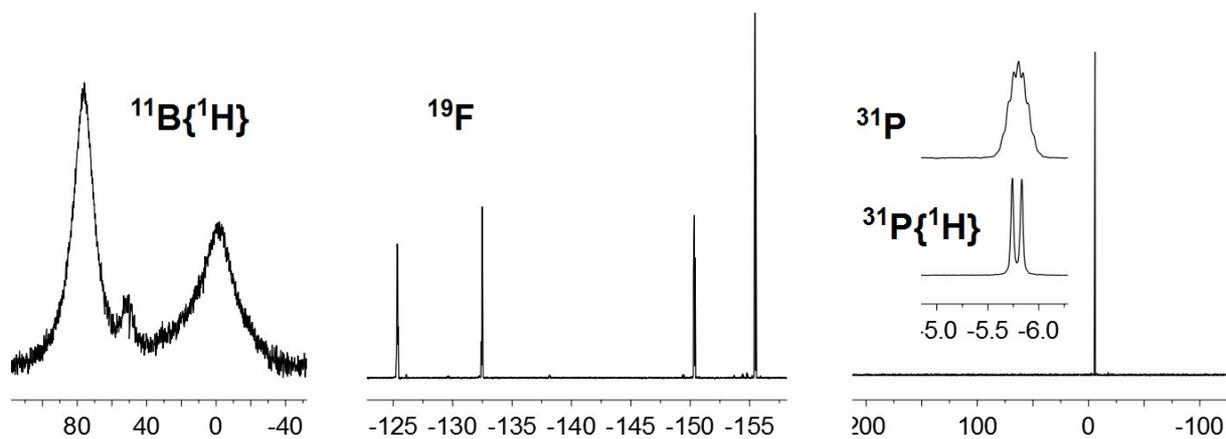
**<sup>31</sup>P NMR** (162 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>31</sup>P -5.8 (m).



$^1\text{H}$  NMR (400 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of *o*- $\text{Ph}_2\text{P}(\text{C}_6\text{F}_4)\text{BCy}_2$  (**7**).

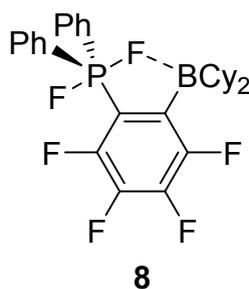


$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectrum of *o*- $\text{Ph}_2\text{P}(\text{C}_6\text{F}_4)\text{BCy}_2$  (**7**).



$^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz, 298 K,  $\text{C}_6\text{D}_6$ ),  $^{19}\text{F}$  NMR (376 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) and  $^{31}\text{P}$  NMR (162 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) spectra of *o*- $\text{Ph}_2\text{P}(\text{C}_6\text{F}_4)\text{BCy}_2$  (**7**).

## 2.6 Synthesis of *o*-Ph<sub>2</sub>PF<sub>2</sub>(C<sub>6</sub>F<sub>4</sub>)BCy<sub>2</sub> (**8**)



*o*-Ph<sub>2</sub>P(C<sub>6</sub>F<sub>4</sub>)BCy<sub>2</sub> (**7**) (375 mg, 0.73 mmol, 1 eq.) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 ml) in a glovebox and pre-cooled to -35 °C before addition of XeF<sub>2</sub> (122 mg, 0.72 mmol, 0.98 eq) in portions in the glovebox cold well. The resulting clear solution was stirred for 1 h at -35 °C, then the cooling was removed, the solution allowed to warm to room temperature and stirred another 3 h at room temperature. Then, the solution was saturated in vacuum (to ca. 1 ml) and pentane (3 ml) was added, which resulted in heavy colorless precipitation. The product was allowed to fully precipitate at -35 °C overnight. The supernatant was removed by decantation at -35 °C and the residue washed with cold pentane (1 ml) twice at -35 °C. Drying of the precipitate in vacuum gave the title compound **8** as colorless solid (375 mg, 0.68 mmol, 95%).

**<sup>1</sup>H NMR** (400 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>1</sup>H 8.02 (m, 4H, *o*-Ph), 7.63 (m, 2H, *p*-Ph), 7.55 (m, 4H, *m*-Ph), 1.43 (m, 6H, BCy<sub>2</sub>), 1.17 (m, 4H, BCy<sub>2</sub>), 0.89 (m, 6H, BCy<sub>2</sub>), 0.59 (m, 4H, BCy<sub>2</sub>), 0.49 (m, 2H, BCy<sub>2</sub>).

**<sup>1</sup>H NMR** (700 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>1</sup>H 7.81 (m, 4H, *o*-Ph), 7.02 (m, 2H, *p*-Ph), 6.99 (m, 4H, *m*-Ph), 1.69 (m, 2H, BCy<sub>2</sub>), 1.17 (m, 4H, BCy<sub>2</sub>), 1.66 (m, 4H, BCy<sub>2</sub>), 1.48 (m, 2H, BCy<sub>2</sub>), 1.44 (m, 2H, BCy<sub>2</sub>), 1.20 (m, 2H, BCy<sub>2</sub>), 1.14 (m, 2H, BCy<sub>2</sub>), 1.06 (m, 2H, BCy<sub>2</sub>), 0.87 (m, 2H, BCH)<sup>a</sup>, 0.84 (m, 2H, BCy<sub>2</sub>), 0.72 (m, 2H, BCy<sub>2</sub>). <sup>a</sup> from ghsqc

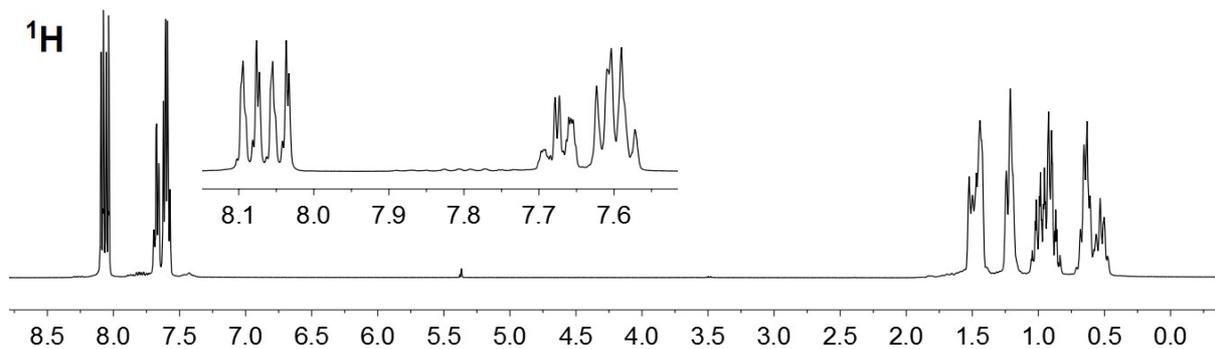
**<sup>13</sup>C{<sup>1</sup>H} NMR** (176 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>): δ<sup>13</sup>C 133.0 (dt, <sup>1</sup>J<sub>PC</sub> = 163.9 Hz, <sup>2</sup>J<sub>FC</sub> = 24.9 Hz, *i*-Ph), 132.8 (m, *o*-Ph, *p*-Ph), 128.8 (d, <sup>3</sup>J<sub>PC</sub> = 17.1 Hz, *m*-Ph), 31.4 (br s, BCH), 30.2 (s, BCy<sub>2</sub>), 30.0 (s, BCy<sub>2</sub>), 29.1 (s, BCy<sub>2</sub>), 29.0 (s, BCy<sub>2</sub>), 27.8 (s, BCy<sub>2</sub>). Not assigned: C<sub>6</sub>F<sub>4</sub>.

**<sup>11</sup>B{<sup>1</sup>H} NMR** (128 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>11</sup>B 30.7 (*v*<sub>1/2</sub> ~ 740 Hz).

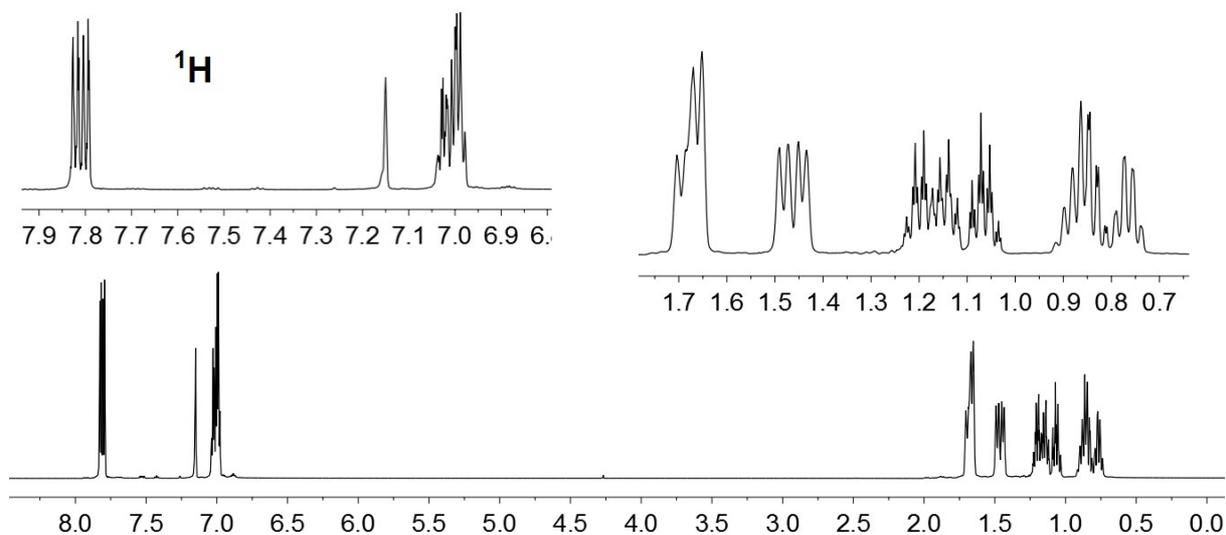
**<sup>19</sup>F NMR** (376 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>19</sup>F -66.6 (dd, <sup>1</sup>J<sub>PF</sub> = 545.4 Hz, J<sub>FF</sub> = 70.8 Hz, 2F, PF<sub>2</sub>), -125.9 (tm, J<sub>FF</sub> = 70.8 Hz, 1F), -130.4 (m, 1F), -147.4 (m, 1F), -157.7 (m, 1F).

**<sup>31</sup>P{<sup>1</sup>H} NMR** (162 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>31</sup>P -9.8 (t, <sup>1</sup>J<sub>PF</sub> = 545.4 Hz).

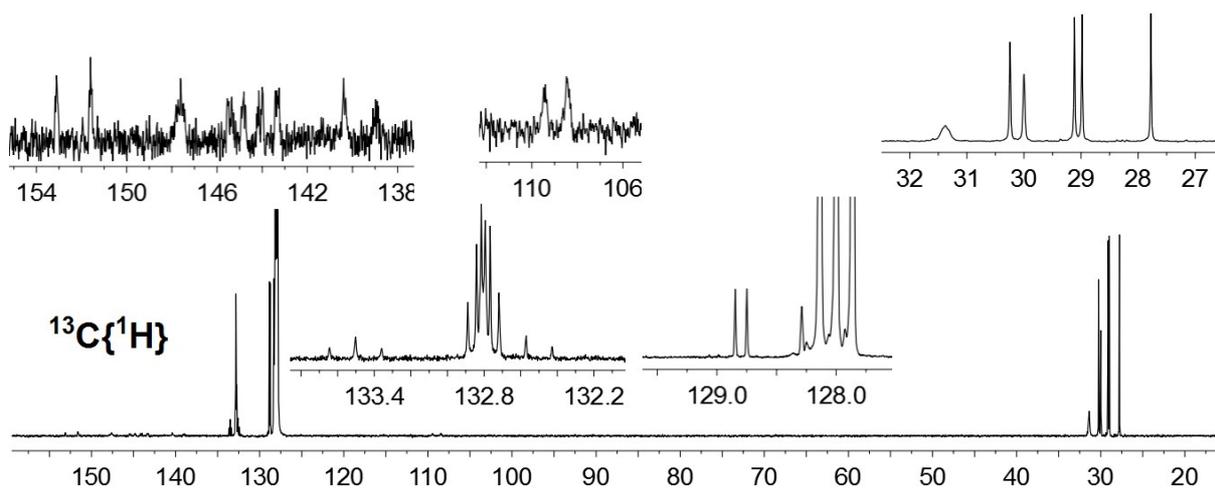
**<sup>31</sup>P NMR** (162 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>31</sup>P -9.8 (m).



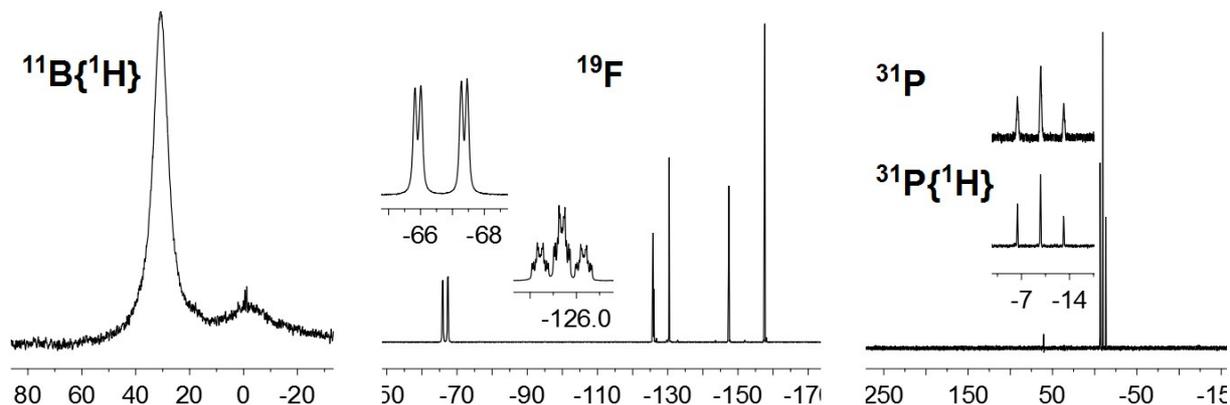
$^1\text{H}$  NMR (400 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{F}_4)\text{BCy}_2$  (**8**).



$^1\text{H}$  NMR (700 MHz, 300 K,  $\text{C}_6\text{D}_6$ ) spectrum of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{F}_4)\text{BCy}_2$  (**8**).



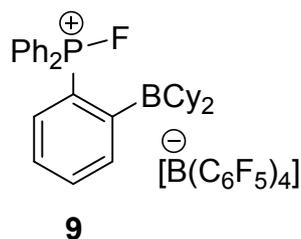
$^{13}\text{C}\{^1\text{H}\}$  NMR (176 MHz, 300 K,  $\text{C}_6\text{D}_6$ ) spectrum of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{F}_4)\text{BCy}_2$  (**8**).



$^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $^{19}\text{F}$  NMR (376 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) and  $^{31}\text{P}$  NMR (162 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{F}_4)\text{BCy}_2$  (**8**).

Crystals suitable for X-ray structure analysis were obtained by cooling of a saturated solution of compound **8** in pentane to  $-35\text{ }^\circ\text{C}$ .

## 2.7 Synthesis of [*o*- $\text{Ph}_2\text{PF}(\text{C}_6\text{H}_4)\text{BCy}_2$ ][ $\text{B}(\text{C}_6\text{F}_5)_4$ ] (**9**)



To a solution of *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BCy}_2$  (**3**) (119.1 mg, 0.25 mmol) in toluene (4 ml) was added freshly prepared  $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4] \cdot 2\text{C}_7\text{H}_8$  (220.1 mg, 0.225 mmol, 0.9 eq.). The resulting suspension was stirred at room temperature for 20 min. The resulting suspension separated into a yellow oil and colorless supernatant upon standing. The supernatant was removed by decantation and the oil was treated with 3 x 2 ml of pentane. The resulting white powder was dried and then recrystallized by taking it up in  $\text{CH}_2\text{Cl}_2$  (1 ml) and precipitation with pentane (3 ml). The resulting solid was washed three times with pentane (2 ml) and dried in vacuum. Finally, the solid was re-dissolved in  $\text{CH}_2\text{Cl}_2$  (1 ml) and the volatiles were removed in order to get rid of co-crystallizing pentane. Compound **9** was obtained as colorless solid (193.4 mg, 0.17 mmol, 76%).

$^1\text{H}$  NMR (500 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^1\text{H}$  8.05 (m, 2H, *p*-Ph)<sup>†</sup>, 7.94 (m, 1H,  $\text{C}_6\text{H}_4$ ), 7.81 (m, 4H, *m*-Ph)<sup>†</sup>, 7.73 (m, 4H, *o*-Ph)<sup>†</sup>, 7.62 (m, 1H,  $\text{C}_6\text{H}_4$ ), 7.52 (m, 1H,  $\text{C}_6\text{H}_4$ ), 7.43 (m, 1H,  $\text{C}_6\text{H}_4$ ), 1.64 (br m, 10H,  $\text{BCy}_2$ ), 1.40 (m, 2H,  $\text{BCH}$ ), 1.07 (m, 10H,  $\text{BCy}_2$ ). <sup>†</sup> tentatively assigned.

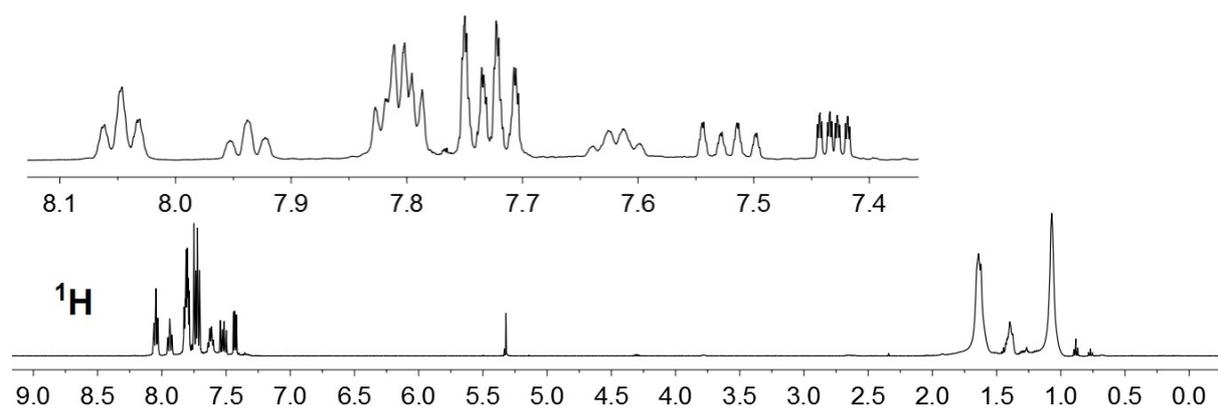
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^{13}\text{C}$  156.1 (p.r. quart., *i*-B- $\text{C}_6\text{H}_4$ ), 148.5 (d,  $^1J_{\text{FC}} \sim 245$  Hz, *o*- $\text{C}_6\text{F}_5$ )<sup>†</sup>, 139.1 (s, *p*-Ph)<sup>†</sup>, 138.6 (d,  $^1J_{\text{FC}} \sim 245$  Hz, *p*- $\text{C}_6\text{F}_5$ )<sup>†</sup>, 136.8 (d,  $^1J_{\text{FC}} \sim 245$  Hz, *m*- $\text{C}_6\text{F}_5$ )<sup>†</sup>, 136.1 (d,  $J$

= 3.5 Hz, C<sub>6</sub>H<sub>4</sub>), 134.3 (dd, <sup>3</sup>J<sub>PC</sub> = 13.4 Hz, <sup>4</sup>J<sub>FC</sub> = 1.3 Hz, *m*-Ph)<sup>†</sup>, 133.9 (dd, *J* = 21.8 Hz, *J* = 3.5 Hz, C<sub>6</sub>H<sub>4</sub>), 131.3 (d, <sup>2</sup>J<sub>PC</sub> = 14.4 Hz, *o*-Ph), 128.5 (m, C<sub>6</sub>H<sub>4</sub>), 128.3 (m, C<sub>6</sub>H<sub>4</sub>), 124.5 (br, *i*-C<sub>6</sub>F<sub>5</sub>), 118.0 (dd, <sup>1</sup>J<sub>PC</sub> = 104.9 Hz, <sup>2</sup>J<sub>FC</sub> = 14.2 Hz, *i*-Ph), 113.3 (dd, <sup>1</sup>J<sub>PC</sub> = 110.3 Hz, <sup>2</sup>J<sub>FC</sub> = 13.9 Hz, *i*-P-C<sub>6</sub>H<sub>4</sub>), 38.1 (m, CH, BCy<sub>2</sub>), 28.5 (br m, BCy<sub>2</sub>), 27.8 (br, BCy<sub>2</sub>), 26.8 (br, BCy<sub>2</sub>). <sup>†</sup> tentatively assigned.

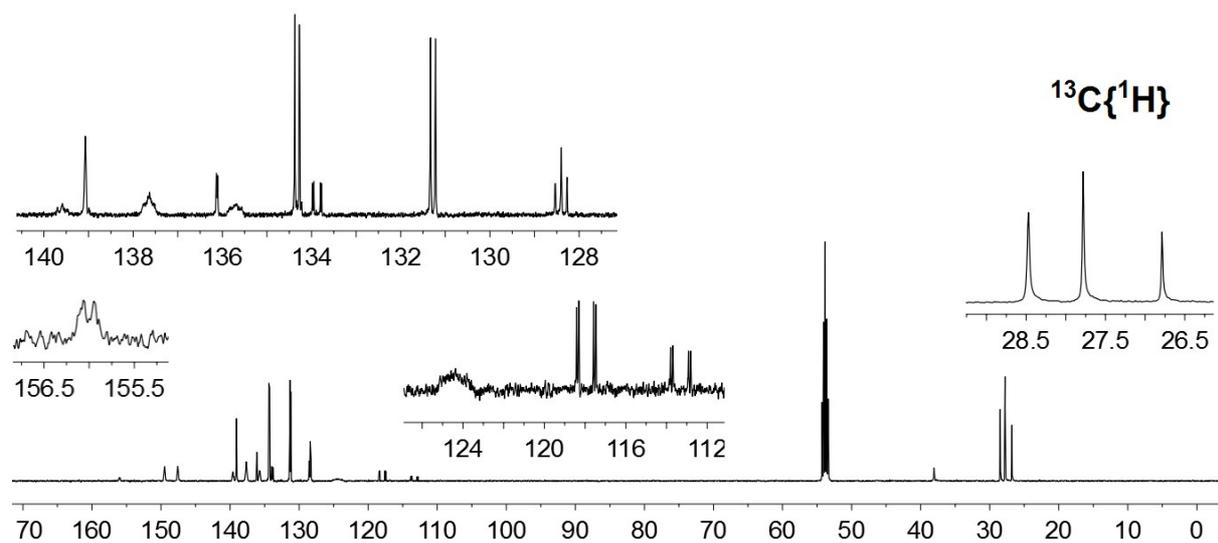
<sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>11</sup>B 83.5 (*v*<sub>1/2</sub> ~ 1500 Hz).

<sup>19</sup>F NMR (376 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>19</sup>F -129.6 (d, *J*<sub>PF</sub> = 980 Hz, FP), -133.1 (m, 8F, *o*-C<sub>6</sub>F<sub>5</sub>), -163.8 (m, 4F, *p*-C<sub>6</sub>F<sub>5</sub>), -167.7 (m, 8F, *m*-C<sub>6</sub>F<sub>5</sub>).

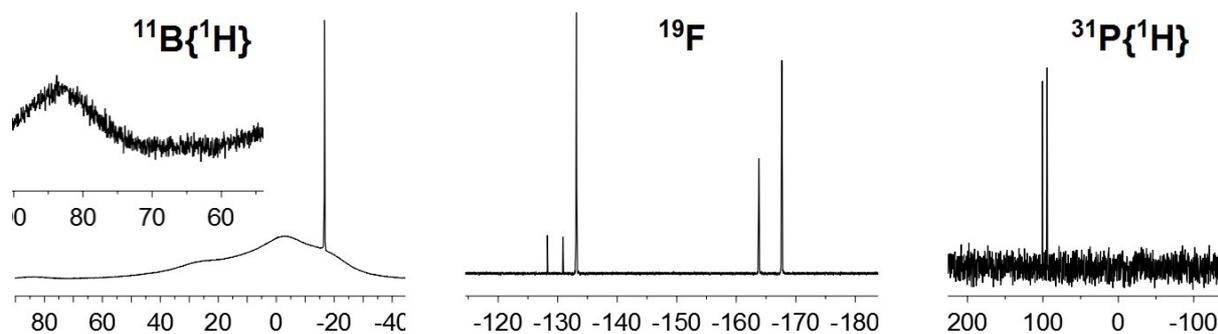
<sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>31</sup>P 97.5 (d, *J*<sub>PF</sub> = 980 Hz).



<sup>1</sup>H NMR (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of [*o*-Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**9**).



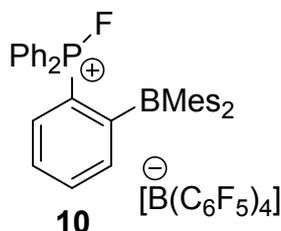
<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of [*o*-Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**9**).



$^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $^{19}\text{F}$  (376 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**9**).

Crystal suitable for X-ray crystal structure analysis were obtained by crystallization from 3:1 mixture of pentane :  $\text{CH}_2\text{Cl}_2$ .

## 2.8 Synthesis of $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{H}_4)\text{BMes}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**10**)



To a solution of  $\text{o-Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BMes}_2$  (**5**) (34.7 mg, 0.063 mmol) in toluene (2 ml) was added freshly prepared  $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]\cdot 2\text{C}_7\text{H}_8$  (57.7 mg, 0.059 mmol, 0.95 eq.). The resulting suspension was stirred at room temperature for 20 min. The suspension separated into a yellow oil and colorless supernatant upon standing. The supernatant was removed by decantation and the oil was treated with 3 x 2 ml of pentane. The resulting white powder was dried in vacuum, yielding the title compound **10** (58.1 mg, 0.048 mmol, 82%).

$^1\text{H}$  NMR (600 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^1\text{H}$  7.93 (m, 3H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.79 (m, 1H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.74 (m, 1H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.63 (m, 4H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.53 (m, 1H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.32 (bs, 4H,  $\text{C}_{\text{Ar}}\text{H}$ ), 6.94 (bs, 1H,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{BMes}_2$ ), 6.88 (bs, 1H,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{BMes}_2$ ), 6.73 (bs, 1H  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{BMes}_2$ ), 5.79 (bs, 1H,  $\text{C}_{\text{Ar}}\text{H}$   $\text{BMes}_2$ ), 2.33 (bs, 3H,  $p\text{-CH}_3$   $\text{BMes}_2$ ), 2.33 (bs, 3H,  $o\text{-CH}_3$   $\text{BMes}_2$ ), 2.19 (bs, 3H,  $o\text{-CH}_3$   $\text{BMes}_2$ ), 2.09 (bs, 3H,  $p\text{-CH}_3$   $\text{BMes}_2$ ), 2.01 (bs, 3H,  $o\text{-CH}_3$   $\text{BMes}_2$ ), 1.95 (bs, 3H,  $p\text{-CH}_3$   $\text{BMes}_2$ ), 1.33 (bs, 3H,  $o\text{-CH}_3$   $\text{BMes}_2$ ). The mesityl rings are not equivalent, probably due to a hindered rotation because of the steric bulk of the Mes groups.

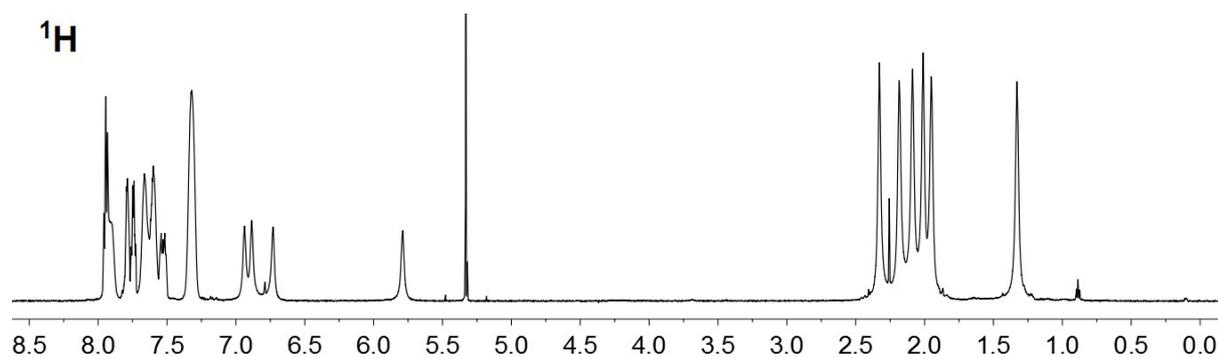
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^{13}\text{C}$  157.3 (m, *ipso* B-CAr,  $\text{P}(\text{C}_6\text{H}_4)\text{B}$ ), 148.5 (d,  $^1J_{\text{FC}} = 240.9$  Hz,  $\text{B}(\text{C}_6\text{F}_5)_4$ ), 142.4 (bs,  $\text{C}_{\text{Ar}}$ ), 142.2 (bs,  $\text{C}_{\text{Ar}}$ ), 141.9 (bs,  $\text{C}_{\text{Ar}}$ ), 141.2 (d,  $^1J_{\text{FC}} = 211.1$  Hz,  $\text{B}(\text{C}_6\text{F}_5)_4$ ), 138.6 (d,  $^1J_{\text{FC}} = 244.4$  Hz,  $\text{B}(\text{C}_6\text{F}_5)_4$ ), 138.7 (bs,  $\text{FPPH}_2$ ), 137.5 (d,  $^4J_{\text{C-P}} = 3$  Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{P}(\text{C}_6\text{H}_4)\text{B}$ ) 134.5 (m,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{FPPH}_2$ ), 137.1 (dd,  $J = 6.6$  z, 1.7 Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{P}(\text{C}_6\text{H}_4)\text{B}$ ), 137.0 (bs,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{P}(\text{C}_6\text{H}_4)\text{B}$ ), 136.6 (bs,  $\text{C}_{\text{Ar}}$ ) 131.1 (dd,  $J = 6.6$  z, 1.7 Hz,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{P}(\text{C}_6\text{H}_4)\text{B}$ ), 130.6 (m,  $\text{C}_{\text{Ar}}\text{H}$ ,  $\text{FPPH}_2$ ), 130.7 (bs,  $\text{C}_{\text{Ar}}$ ) 129.3 (bs,  $\text{C}_{\text{Ar}}\text{H}$ , Mes, 4C), 124.4 (m,  $\text{B}(\text{C}_6\text{F}_5)_4$ ), 121.1 (m, *ipso*  $\text{C}_{\text{Ar}}$ , Mes), 102.8 (m, *ipso*  $\text{C}_{\text{Ar}}$ ), 118.5 (dd,  $^1J_{\text{PC}} = 105$  Hz,  $^2J_{\text{FC}} = 11.5$  Hz, *ipso*  $\text{Ph}_2\text{PF}$ ), 24.3 (bs,  $o\text{-CH}_3$ ,  $\text{BMes}_2$ ), 23.8 (bs,  $o\text{-CH}_3$ ,  $\text{BMes}_2$ ), 22.9 (bs,  $p\text{-CH}_3$ ,  $\text{BMes}_2$ ).

CH<sub>3</sub>, BMes<sub>2</sub>, 2C), 21.4 (bs, *o*-CH<sub>3</sub>, BMes<sub>2</sub>), 21.2 (bs, *o*-CH<sub>3</sub>, BMes<sub>2</sub>). Mesityl rings are not equivalent, giving 7 different signals as the CH carbons overlap. Not all quaternary carbons could be assigned due to the complexity and overlapping peaks.

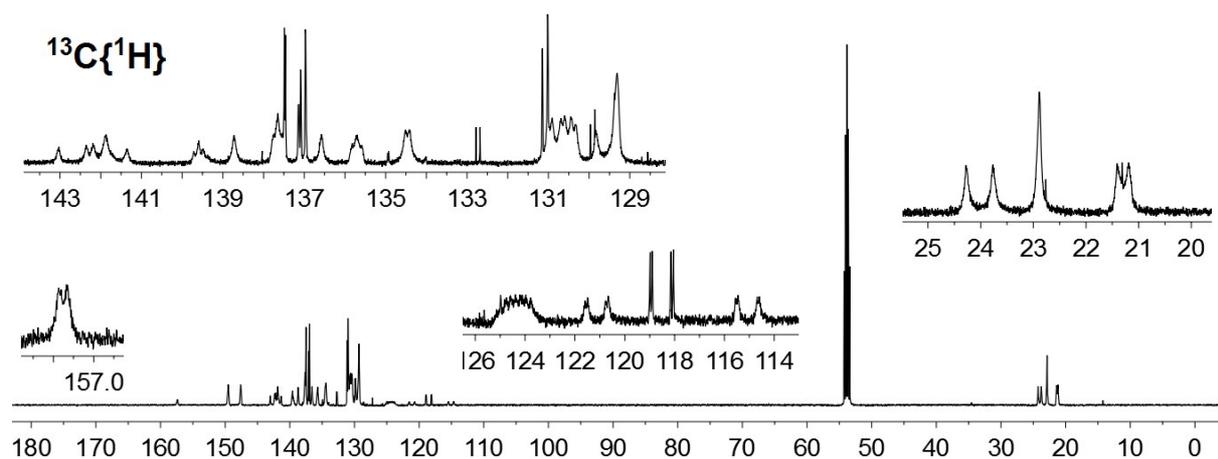
**<sup>11</sup>B NMR** (192 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>11</sup>B 73.5 (ν<sub>1/2</sub> ~ 2000 Hz, BMes<sub>2</sub>), -16.7 (ν<sub>1/2</sub> ~ 50 Hz [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>).

**<sup>19</sup>F NMR** (564 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>19</sup>F -126.7 (d, J<sub>PF</sub> = 999.5 Hz, PF), -133.1 (m, 8F, *o*-F, [B(C<sub>6</sub>F<sub>6</sub>)<sub>4</sub>]), 163.8 (t, J = 20 Hz, 4F, *p*-F, [B(C<sub>6</sub>F<sub>6</sub>)<sub>4</sub>]), -167.7 (m, 8F, *m*-F [B(C<sub>6</sub>F<sub>6</sub>)<sub>4</sub>]).

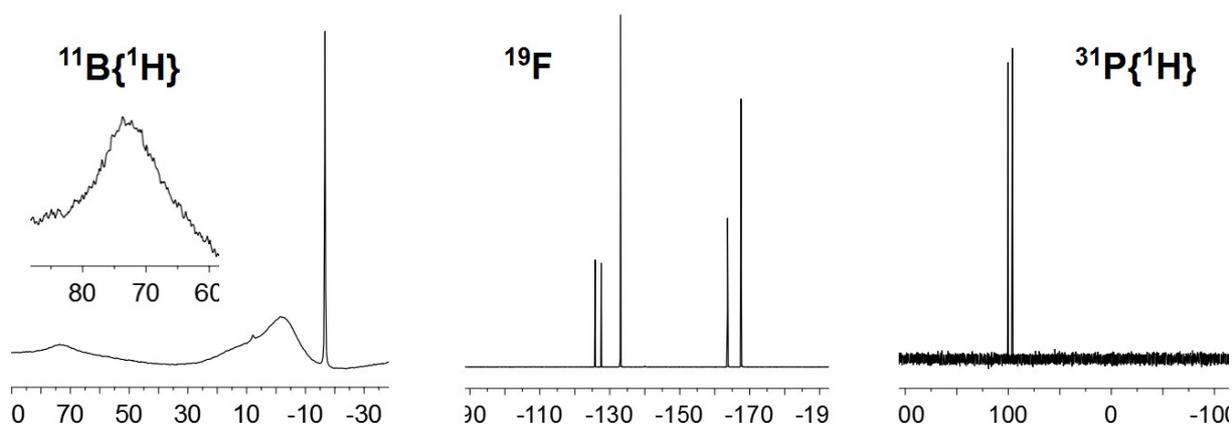
**<sup>31</sup>P{<sup>1</sup>H} NMR** (243 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>31</sup>P -98.2 (d, J<sub>PF</sub> = 999.5 Hz).



<sup>1</sup>H NMR (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of [o-Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BMes<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>(**10**).

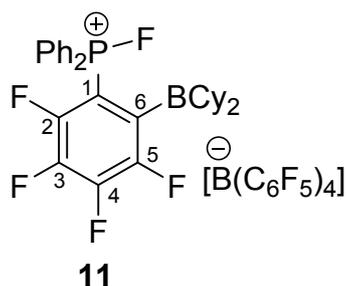


<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of [o-Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BMes<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>(**10**).



<sup>11</sup>B{<sup>1</sup>H} NMR (192 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>), <sup>19</sup>F (564 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) and <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) spectra of [o-Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BMes<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>(**10**).

## 2.9 Synthesis of [*o*-Ph<sub>2</sub>PF(C<sub>6</sub>F<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**11**)



In a glovebox, [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (400 mg, 0.43 mmol, 0.95 eq.) was dissolved in toluene (5 ml) and triethylsilane (160 mg, 1.37 mmol, 3 eq) was added to the stirred deep red solution. The solution turns into an almost colorless suspension quickly which was stirred for 1 h at room temperature. Then the suspended red oil was left to settle and was separated from the supernatant solution with a pipette and added dropwise to a solution of *o*-Ph<sub>2</sub>PF<sub>2</sub>(C<sub>6</sub>F<sub>4</sub>)BCy<sub>2</sub> (**8**) (250 mg, 0.46 mmol, 1 eq) in toluene (5 ml) at -35 °C. The resulting suspension was stirred at room temperature for 1 h at -35 °C and another 3 h at room temperature. Then pentane (5 ml) was added and the resulting suspension separated into a pale-orange oil and colorless supernatant upon standing. The supernatant was removed by decantation and the oil was washed with pentane (2 ml) twice. The oily residue was then taken up in CH<sub>2</sub>Cl<sub>2</sub> and stirred for 2 h at room temperature to ensure full consumption of the in-situ generated [Et<sub>3</sub>Si][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] before precipitation with pentane (10 ml). The oily phase of the biphasic mixture was allowed to solidify at -35 °C before removing the supernatant by decantation and washing of the residue with pentane (2 ml) twice. Drying in vacuum yields the title compound **11** as colorless foamy powder (486 mg, 0.40 mmol, 93%).

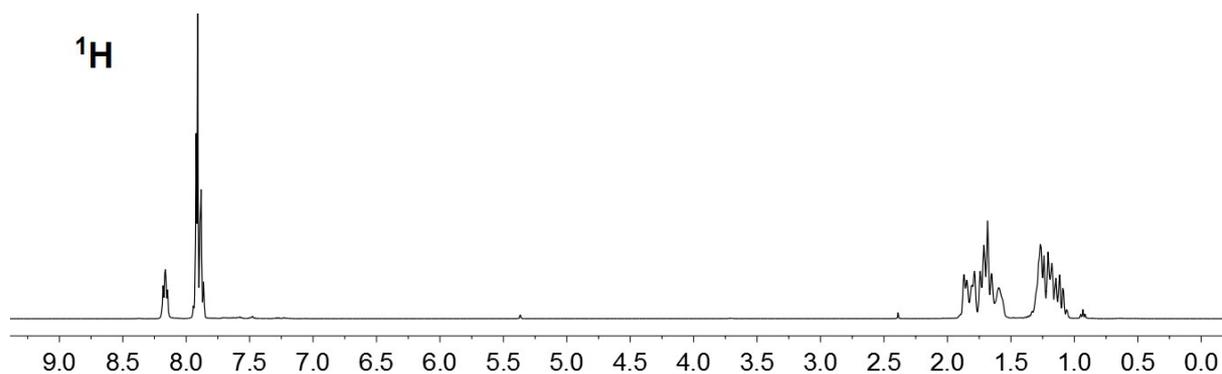
**<sup>1</sup>H NMR** (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>1</sup>H 8.11 (m, 2H, *p*-Ph), 7.85 (m, 8H, *o*-, *m*-Ph), 1.77 (m, 4H, CH<sub>2</sub>, BCy<sub>2</sub>), 1.65 (m, 6H, CH<sub>2</sub>, BCy<sub>2</sub>), 1.55 (br, 2H, CH, BCy<sub>2</sub>), 1.14 (m, 10H, CH<sub>2</sub>, BCy<sub>2</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR** (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>13</sup>C 151.4 (br m, C6), 148.4 (d, <sup>1</sup>J<sub>FC</sub> = 240 Hz, *o*-C<sub>6</sub>F<sub>5</sub>), 146.8 (dm, <sup>1</sup>J<sub>FC</sub> ~ 275 Hz, C4)<sup>†</sup>, 145.2 (ddd, <sup>1</sup>J<sub>FC</sub> ~ 243 Hz, *J* ~ 24 Hz, *J* ~ 11 Hz, C2)<sup>†</sup>, 140.3 (t, <sup>4</sup>J<sub>PC</sub> ~ <sup>5</sup>J<sub>FC</sub> = 2.4 Hz, *p*-Ph), 140.2 (dm, <sup>1</sup>J<sub>FC</sub> = 260 Hz, C3)<sup>†</sup>, 139.1 (dm, <sup>1</sup>J<sub>FC</sub> = 274 Hz, C5)<sup>†</sup>, 138.6 (dm, <sup>1</sup>J<sub>FC</sub> ~ 245 Hz, *p*-C<sub>6</sub>F<sub>5</sub>), 136.6 (dm, <sup>1</sup>J<sub>FC</sub> ~ 241 Hz, *m*-C<sub>6</sub>F<sub>5</sub>), 134.1 (dt, <sup>2</sup>J<sub>PC</sub> = 14.4 Hz, <sup>3</sup>J<sub>FC</sub> ~ <sup>5</sup>J<sub>FC</sub> = 1.5 Hz, *o*-Ph), 131.7 (dd, <sup>3</sup>J<sub>PC</sub> = 15.1 Hz, <sup>3</sup>J<sub>FC</sub> = 0.7 Hz, *m*-Ph), 124.4 (br, *i*-C<sub>6</sub>F<sub>5</sub>), 115.4 (dd, <sup>1</sup>J<sub>PC</sub> = 107.7 Hz, <sup>2</sup>J<sub>FC</sub> = 13.2 Hz, *i*-Ph), 99.8 (dm, <sup>1</sup>J<sub>PC</sub> ~ 120 Hz, C1), 38.3 (br, BCH), 29.2 (d, *J* = 1.8 Hz, CH<sub>2</sub>, BCy<sub>2</sub>), 28.6 (m, CH<sub>2</sub>, BCy<sub>2</sub>), 27.8 (CH<sub>2</sub>, BCy<sub>2</sub>), 27.6 (CH<sub>2</sub>, BCy<sub>2</sub>), 26.6 (CH<sub>2</sub>, BCy<sub>2</sub>).

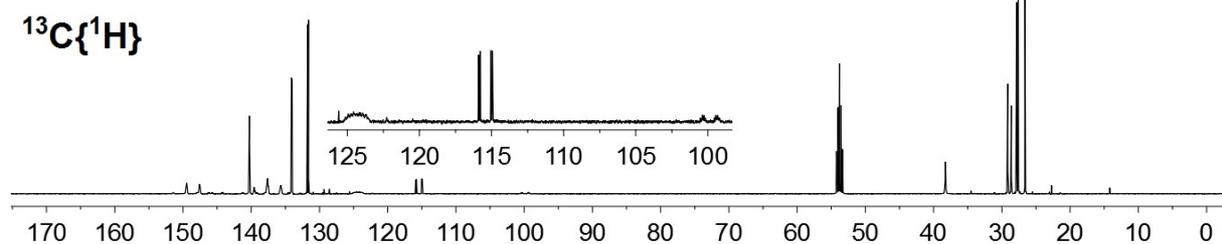
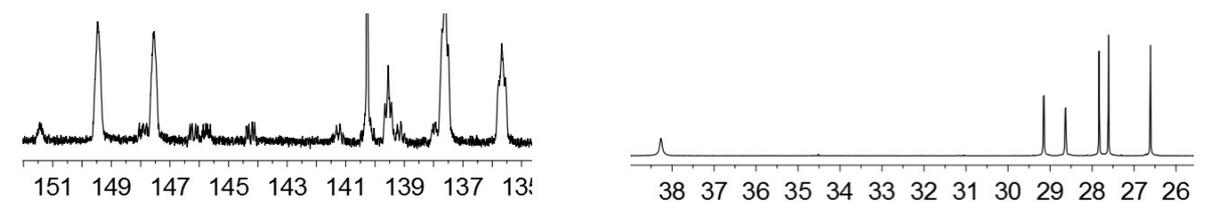
**<sup>11</sup>B{<sup>1</sup>H} NMR** (128 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>11</sup>B 84.8 (*v*<sub>1/2</sub> ~ 1500 Hz).

**<sup>19</sup>F NMR** (376 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>19</sup>F -119.0 (m, 1F, C<sub>6</sub>F<sub>4</sub>), -122.8 (m, 1F, C<sub>6</sub>F<sub>4</sub>), -128.2 (dm, <sup>1</sup>J<sub>PF</sub> = 977 Hz, PF), -133.1 (m, 8F, *o*-C<sub>6</sub>F<sub>5</sub>), -135.9 (m, 1F, C<sub>6</sub>F<sub>4</sub>), -150.4 (m, 1F, C<sub>6</sub>F<sub>4</sub>), -163.8 (t, <sup>3</sup>J<sub>FF</sub> = 20.4 Hz, 4F, *p*-C<sub>6</sub>F<sub>5</sub>), -167.6 (m, 8F, *m*-C<sub>6</sub>F<sub>5</sub>).

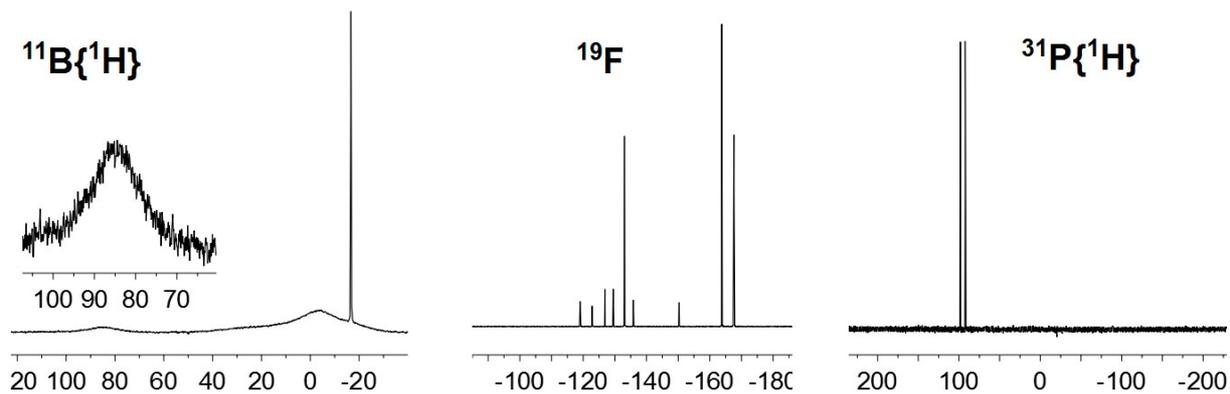
**<sup>31</sup>P{<sup>1</sup>H} NMR** (162 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): δ<sup>31</sup>P 95.3 (dm, *J*<sub>PF</sub> = 977 Hz).



$^1\text{H}$  NMR (400 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{F}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**11**).



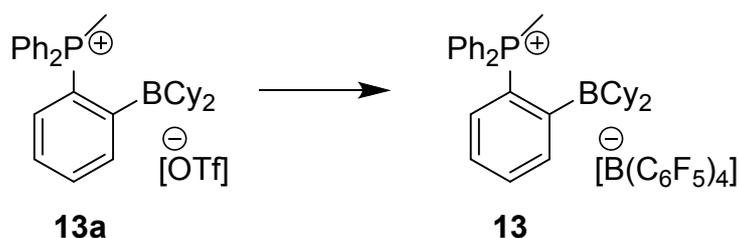
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{F}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**11**).



$^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $^{19}\text{F}$  (376 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{F}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**11**).

Crystal suitable for X-ray crystal structure analysis were obtained by slow diffusion of pentane into a concentrate solution of compound **11** in  $\text{CH}_2\text{Cl}_2$ .

## 2.10 Synthesis of $[o\text{-Ph}_2\text{PMe}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**13**) in two steps



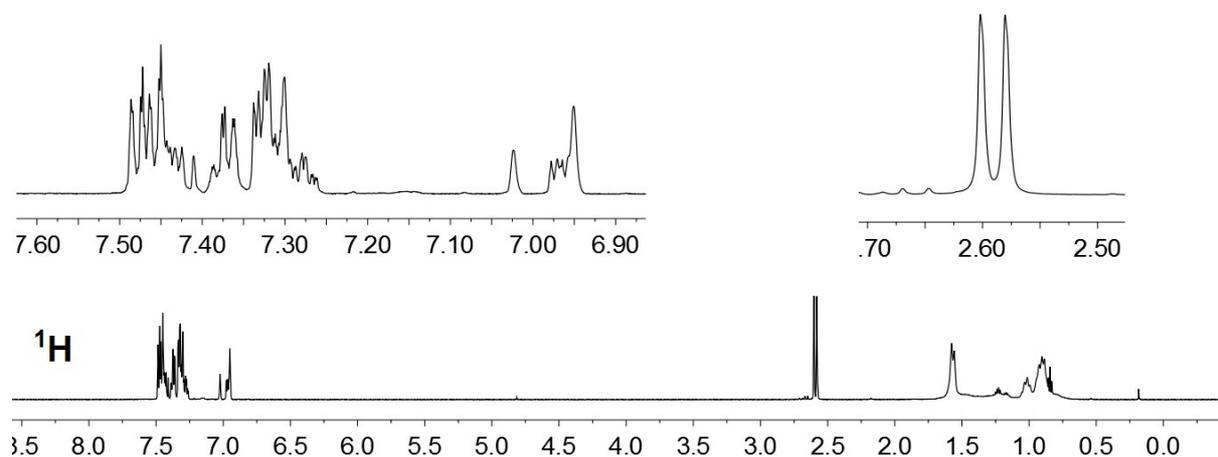
### Step 1: Methylation of $o\text{-Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2$ (**2**) with MeOTf

A 20 ml vial was charged with  $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4)\text{BCy}_2$  (**2**) (87.7 mg, 0.2 mmol) dissolved in 3 ml pentane. To this was added a solution of MeOTf (49.2 mg, 0.3 mmol, 1.5 eq.) in 2 ml pentane. The colorless solution was then stirred for 14.5 h after which a white precipitate was formed. The supernatant removed by decantation and the colorless residue washed with pentane (3 x 2 ml) giving  $[o\text{-Ph}_2\text{PMe}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{OTf}]$  (**13a**) (79.7 mg, 0.13 mmol) in 66% yield. The triflate salt was used without further purification for the next step.

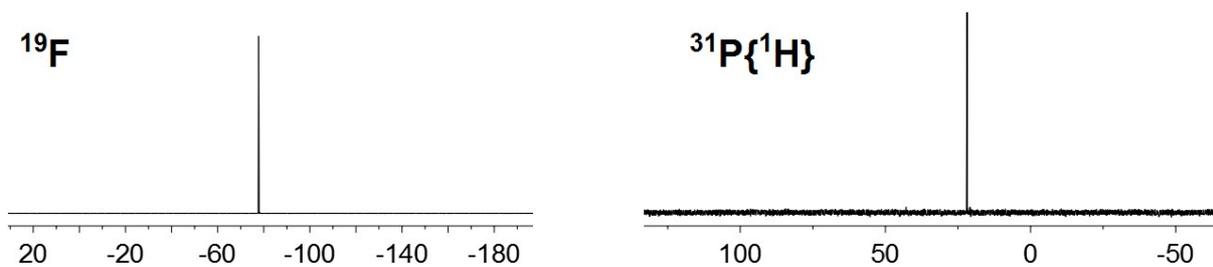
**$^1\text{H}$  NMR** (600 MHz, 298 K,  $\text{C}_6\text{D}_5\text{Br}$ ): 7.49 – 7.40 (m, 6H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.40 – 7.35 (m,  $\text{C}_{\text{Ar}}\text{H}$ , 2H), 7.34 – 7.30 (m, 4H,  $\text{C}_{\text{Ar}}\text{H}$ ), 7.28 (m, 1H,  $\text{C}_{\text{Ar}}\text{H}$ ), 6.97 (m, 1H,  $\text{C}_{\text{Ar}}\text{H}$ ), 2.59 (d,  $^1J_{\text{PC}} = 12.9$  Hz, 3H,  $\text{CH}_3$ ), 1.57 (m, 8H,  $\text{CH}_2$ ,  $\text{BCy}_2$ ), 1.23 (m, 2H,  $\text{CH}$ ,  $\text{BCy}_2$ ) 1.08 – 0.71 (m, 12H,  $\text{CH}_2$ ;  $\text{BCy}_2$ ).

**$^{19}\text{F}$  NMR** (564 MHz, 298 K,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta^{19}\text{F}$  -77.8 ( $\nu_{1/2} \sim 2$  Hz).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** (243 MHz, 298 K,  $\text{C}_6\text{D}_5\text{Br}$ ):  $\delta^{31}\text{P}$  21.9 ( $\nu_{1/2} \sim 3$  Hz).



$^1\text{H}$  NMR (600 MHz, 298 K,  $\text{C}_6\text{D}_5\text{Br}$ ) spectrum of  $[o\text{-Ph}_2\text{PMe}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{OTf}]$  (**13a**).



$^{11}\text{B}\{^1\text{H}\}$  NMR (192 MHz, 298 K,  $\text{C}_6\text{D}_5\text{Br}$ ),  $^{19}\text{F}$  (564 MHz, 298 K,  $\text{C}_6\text{D}_5\text{Br}$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz, 298 K,  $\text{C}_6\text{D}_5\text{Br}$ ) spectra of  $[o\text{-Ph}_2\text{PMe}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{OTf}]$  (**13a**).

### Step 2: Anion exchange with $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]\cdot 2\text{C}_7\text{H}_8$ .

To  $[o\text{-Ph}_2\text{PMe}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{OTf}]$  (**13a**) (60.2 mg, 0.1 mmol) in toluene (2 ml) was added freshly prepared  $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]\cdot 2\text{C}_7\text{H}_8$  (92.9 mg, 0.095 mmol, 0.95 eq.) and the reaction was stirred for 1 h at room temperature. After this a colorless oil separated upon standing. The toluene phase was decanted and the oil washed with pentane (3 x 2 ml). Drying in vacuum yielded compound **13** as a colorless powder (66.0 mg, 0.058 mmol, 61%).

$^1\text{H}$  NMR (600 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^1\text{H}$  7.87 (m, 2H,  $p\text{-Ph}$ )<sup>†</sup>, 7.81 (tdd,  $J = 7.5, 2.4, 1.2$  Hz 1H,  $\text{C}_6\text{H}_4$ ), 7.71 (m, 4H,  $m\text{-Ph}$ )<sup>†</sup>, 7.56 (m, 1H,  $\text{C}_6\text{H}_4$ ), 7.51 (m, 4H,  $o\text{-Ph}$ )<sup>†</sup>, 7.49 (m, 1H,  $\text{C}_6\text{H}_4$ ), 7.30 (m, 1H,  $\text{C}_6\text{H}_4$ ), 2.46 (d,  $^2J_{\text{PH}} = 12.7$  Hz, 3H,  $\text{CH}_3$ ), 1.75 - 1.34 (m, 10H,  $\text{BCy}_2$ ), 1.16 - 0.91 (m, 12H,  $\text{BCy}_2$ ). <sup>†</sup> tentatively assigned.

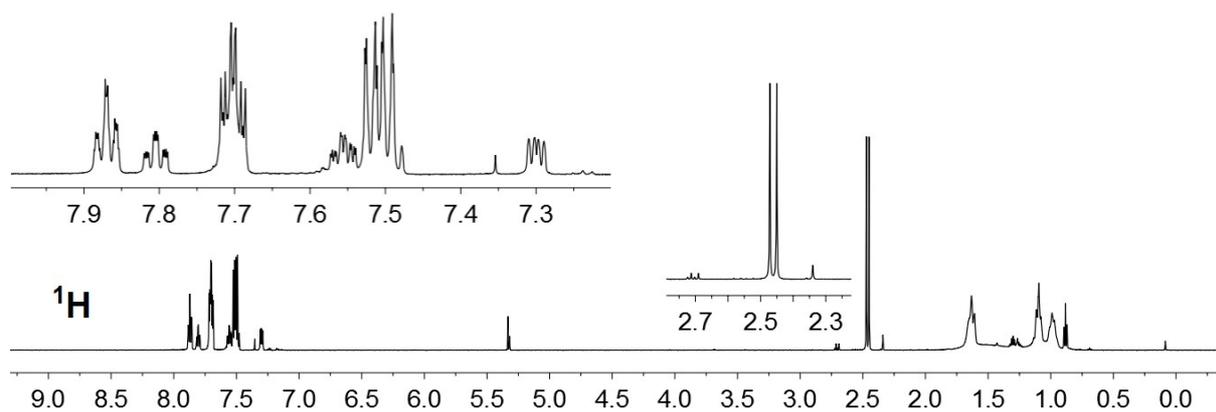
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^{13}\text{C}$  154.8 (p.r. quart.,  $i\text{-B-C}_6\text{H}_4$ ), 148.5 (dm,  $^1J_{\text{FC}} \sim 245$  Hz,  $o\text{-C}_6\text{F}_5$ )<sup>†</sup>, 138.8 (d,  $^1J_{\text{FC}} \sim 245$  Hz,  $p\text{-C}_6\text{F}_5$ )<sup>†</sup>, 136.9 (d,  $^1J_{\text{FC}} \sim 245$  Hz,  $m\text{-C}_6\text{F}_5$ )<sup>†</sup>, 136.1 (d,  $^4J_{\text{PC}} = 3$  Hz,  $p\text{-Ph}$ )<sup>†</sup>, 135.1 (d,  $J = 14$  Hz,  $\text{C}_6\text{H}_4$ ), 134.0 (d,  $J = 3$  Hz,  $\text{C}_6\text{H}_4$ ), 133.3 (d,  $^3J_{\text{PC}} = 11$  Hz,  $m\text{-Ph}$ )<sup>†</sup>, 131.1 (d,  $^2J_{\text{PC}} = 13$  Hz,  $o\text{-Ph}$ )<sup>†</sup>, 128.8 (d,  $J = 13$  Hz,  $\text{C}_6\text{H}_4$ ), 128.8 (d,  $J = 13$  Hz,  $\text{C}_6\text{H}_4$ ), 128.3 (d,  $J = 16$  Hz,  $\text{C}_6\text{H}_4$ ), 124.2 (br,  $i\text{-C}_6\text{F}_5$ ), 120.6 (d,  $^1J_{\text{PC}} = 88$  Hz,  $i\text{-Ph}$ ), 117.0 (d,  $^1J_{\text{PC}} = 90$  Hz,  $i\text{-C}_6\text{H}_4$ ), 38.8 (br,  $\text{BCH}$ ), 29.3 (br,  $\text{BCy}_2$ ), 28.0 (br,  $\text{BCy}_2$ ), 26.8 (s,  $\text{BCy}_2$ ), 11.6 (d,  $^1J_{\text{PC}} = 58.8$  Hz,  $\text{CH}_3$ ) <sup>†</sup> tentatively assigned.

$^{11}\text{B}$  NMR (192 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ): -16.9 [ $\nu_{1/2} \sim 50$  Hz,  $\text{B}(\text{C}_6\text{F}_5)_4$ ]<sup>-</sup>,  $\text{BCy}_2$  was not observed.

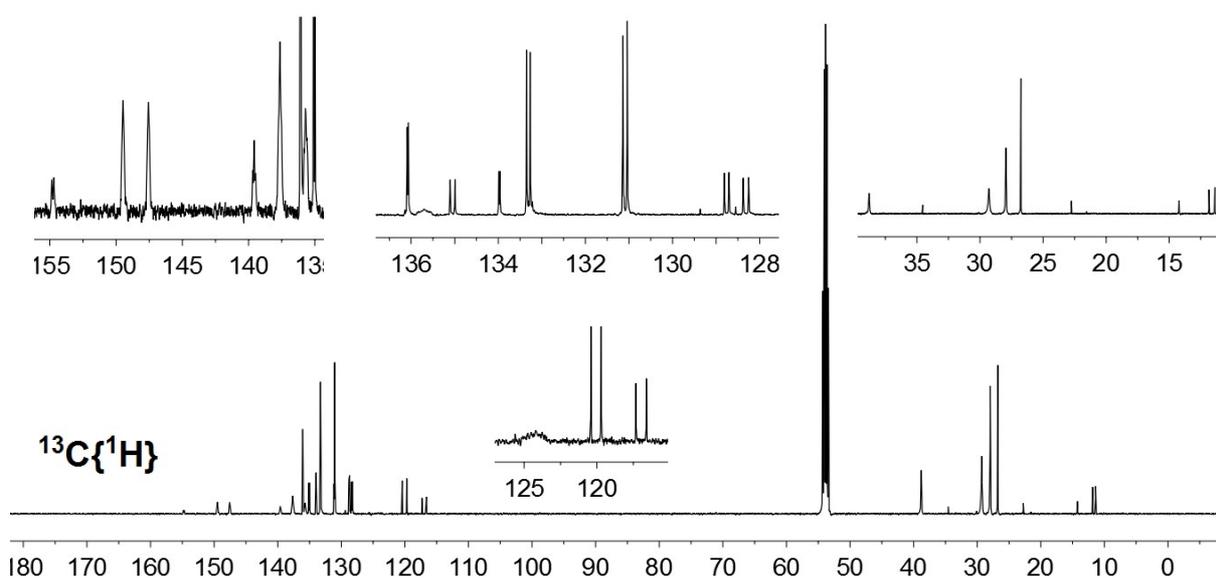
$^{19}\text{F}$  NMR (564 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta^{19}\text{F}$  -133.2 (m, 8F,  $o\text{-C}_6\text{F}_5$ ), 163.8 (t,  $J = 20.4$  Hz, 4F,  $p\text{-F}[\text{B}(\text{C}_6\text{F}_5)_4]$ ), 167.7 (m, 8F,  $m\text{-C}_6\text{F}_5$ ). Ca. 5% of remaining  $[\text{OTf}]^-$  anion (-78.9 ppm) was observed.

$^{31}\text{P}$  NMR (243 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ): 21.4 ( $\nu_{1/2} \sim 2$  Hz).

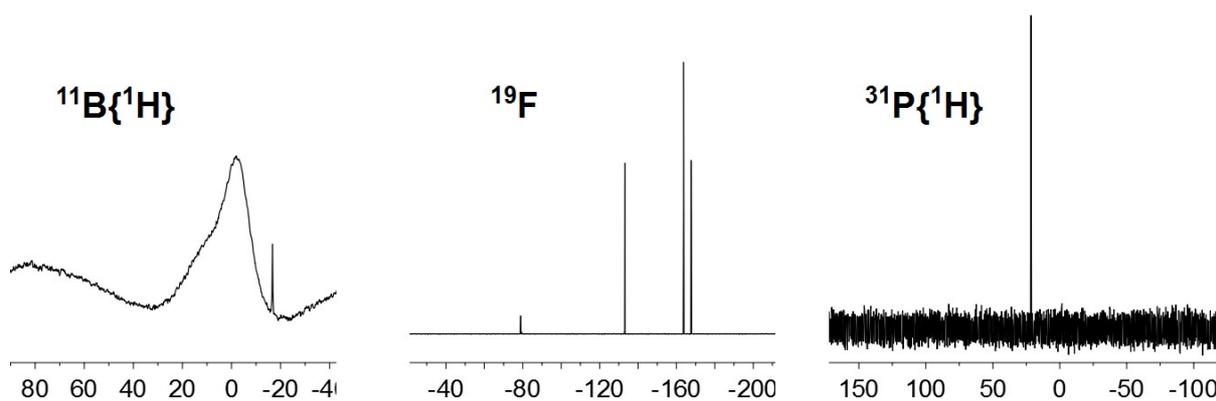
MS (ESI) [M]  $\text{C}_{31}\text{H}_{39}\text{BP}^+$  calc. 453.2877 m/z. found 453.2889 m/z.



$^1\text{H}$  NMR (600 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of  $[\text{o-Ph}_2\text{PMe}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**13**).



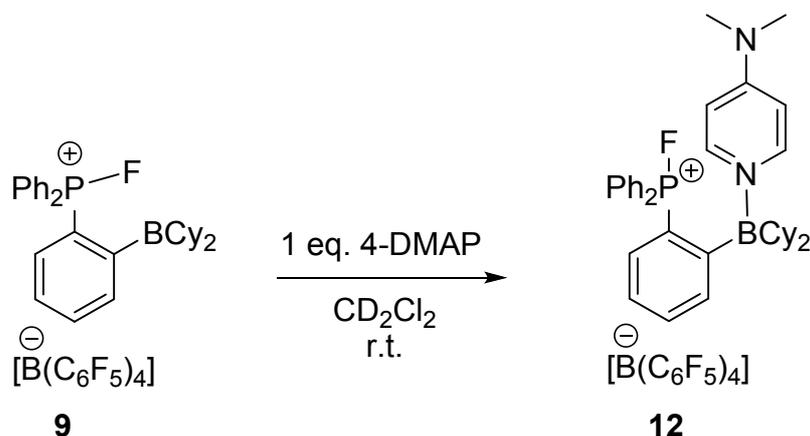
$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectrum of  $[\text{o-Ph}_2\text{PMe}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**13**).



$^{11}\text{B}\{^1\text{H}\}$  NMR (192 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $^{19}\text{F}$  (564 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of  $[\text{o-Ph}_2\text{PMe}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**13**).

## 2.11 Adduct Formation of compound 9 with 4-DMAP

A 5 ml vial was charged with [*o*-Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**9**) (11.4 mg, 0.01 mmol) and 4-DMAP (1.2 mg, 0.01 mmol) and both reagents were dissolved with 0.25 ml CD<sub>2</sub>Cl<sub>2</sub>. The solution was transferred to a 3 mm tube and analyzed by NMR evidencing B-N adduct formation.



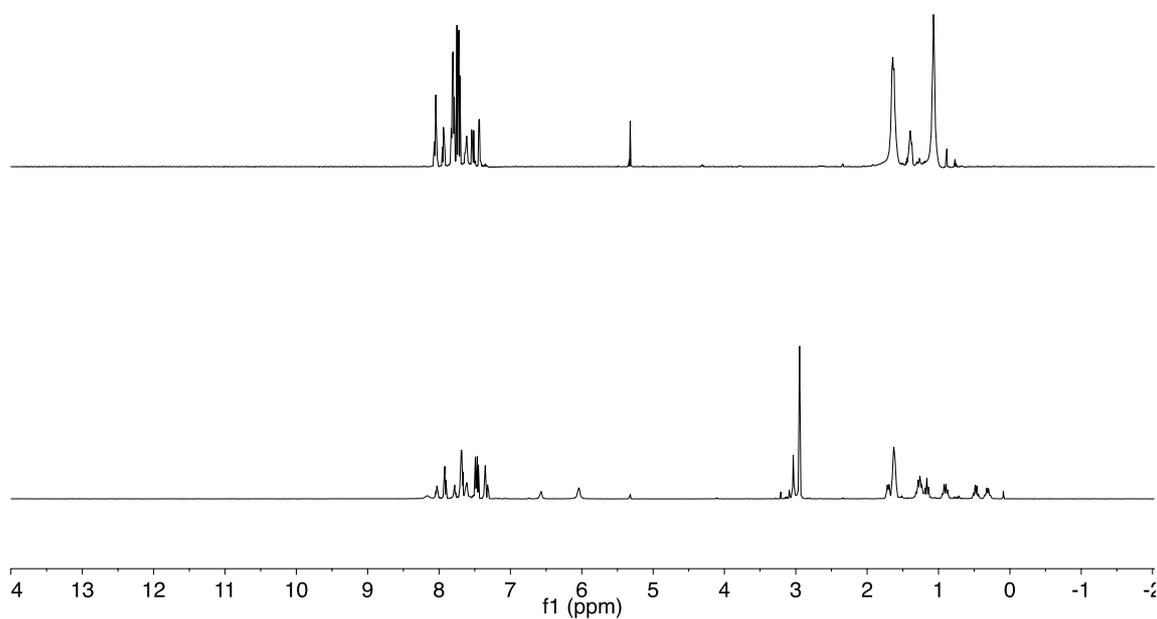
*Adduct formation with of compound 9 with 4-DMAP.*

**<sup>1</sup>H NMR** (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): 8.03 (m, 1H, C<sub>Ar</sub>H, [Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>]), 7.92 (m, 2H, C<sub>Ar</sub>H, [Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>]), 7.79 (m, 4H, C<sub>Ar</sub>H, [Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>]), 7.69 (m, 4H, C<sub>Ar</sub>H, [Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>]), 7.62 (bs, 2H, C<sub>Ar</sub>H, 4-DMAP), 7.47 (m, 1H, C<sub>Ar</sub>H, [Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>]), 7.35 (m, 1H, C<sub>Ar</sub>H, [Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>]), 7.32 (m, 1H, C<sub>Ar</sub>H, [Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>]), 6.57 (bs, 1H, C<sub>Ar</sub>H, 4-DMAP), 6.09 (bs, 2H, C<sub>Ar</sub>H, 4-DMAP), 2.95 (s, 6H, CH<sub>3</sub> 4-DMAP), 1.71 (d, *J* = 12.9 Hz, 2H, BCy<sub>2</sub>), 1.63 (m, 8H, BCy<sub>2</sub>), 1.26 (m, 4H, BCy<sub>2</sub>), 1.16 (m, 2H, BCy<sub>2</sub>), 0.91 (m, 2H, BCy<sub>2</sub>), 0.48 (m, 2H, BCy<sub>2</sub>), 0.31 (m, 2H, BCy<sub>2</sub>).

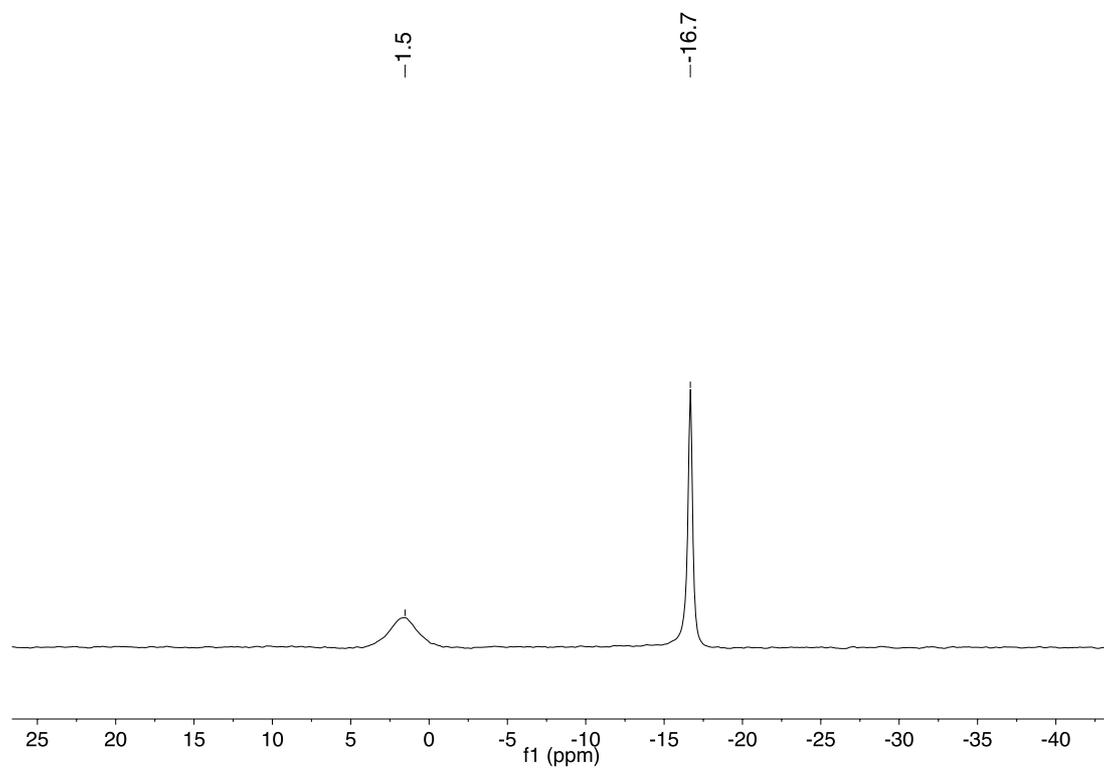
**<sup>11</sup>B{<sup>1</sup>H} NMR** (160 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): 1.5 (BCy<sub>2</sub>), -16.7 ([B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).

**<sup>19</sup>F NMR** (564 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>): -123.0 (d, *J*<sub>PF</sub> = - 1025 Hz, 1F, [Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>]), -132.9 (m, 8F, *o*-F [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]), -163.6 (t, *J* = 20.5 Hz, 4F, *o*-F [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]), -167.4 (m, 8F, *m*-F [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).

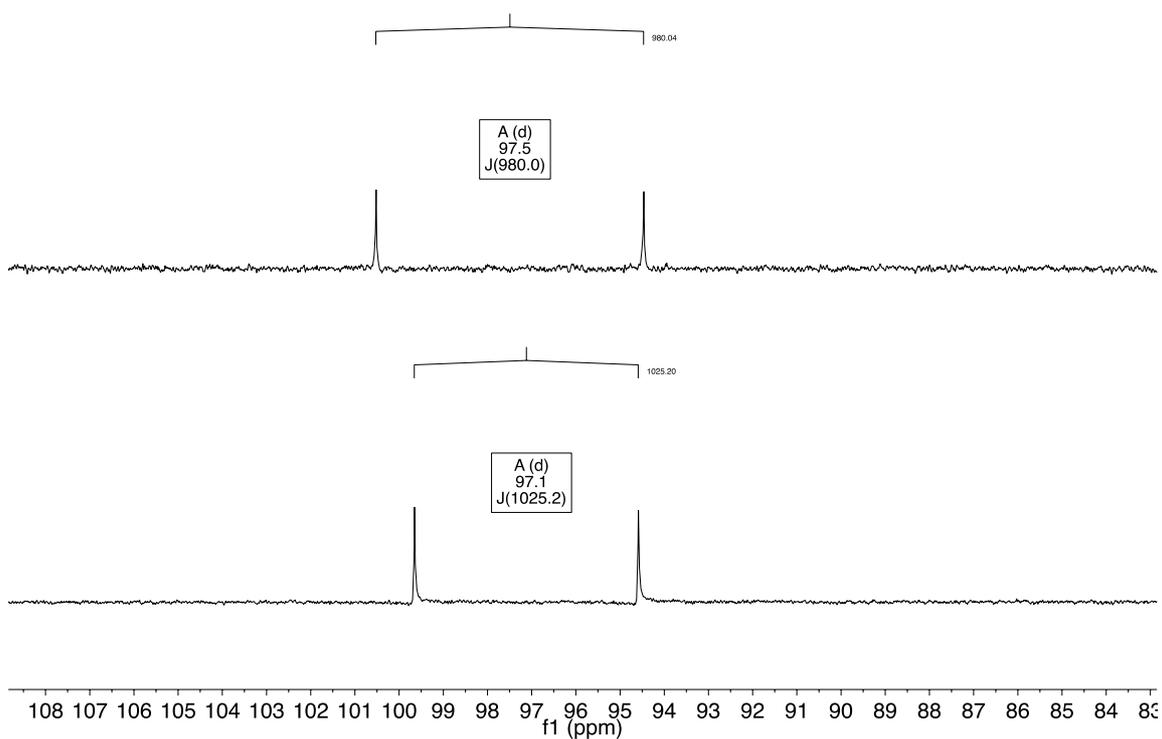
**<sup>31</sup>P{<sup>1</sup>H} NMR** (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>): 97.1 (d, *J*<sub>PF</sub> = 1025 Hz).



$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) of free  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (top) and 1:1 mixture of  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  and 4-DMAP (bottom). Some excess of 4-DMAP is observed.



$^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ ) of 1:1 mixture of  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  and 4-DMAP.

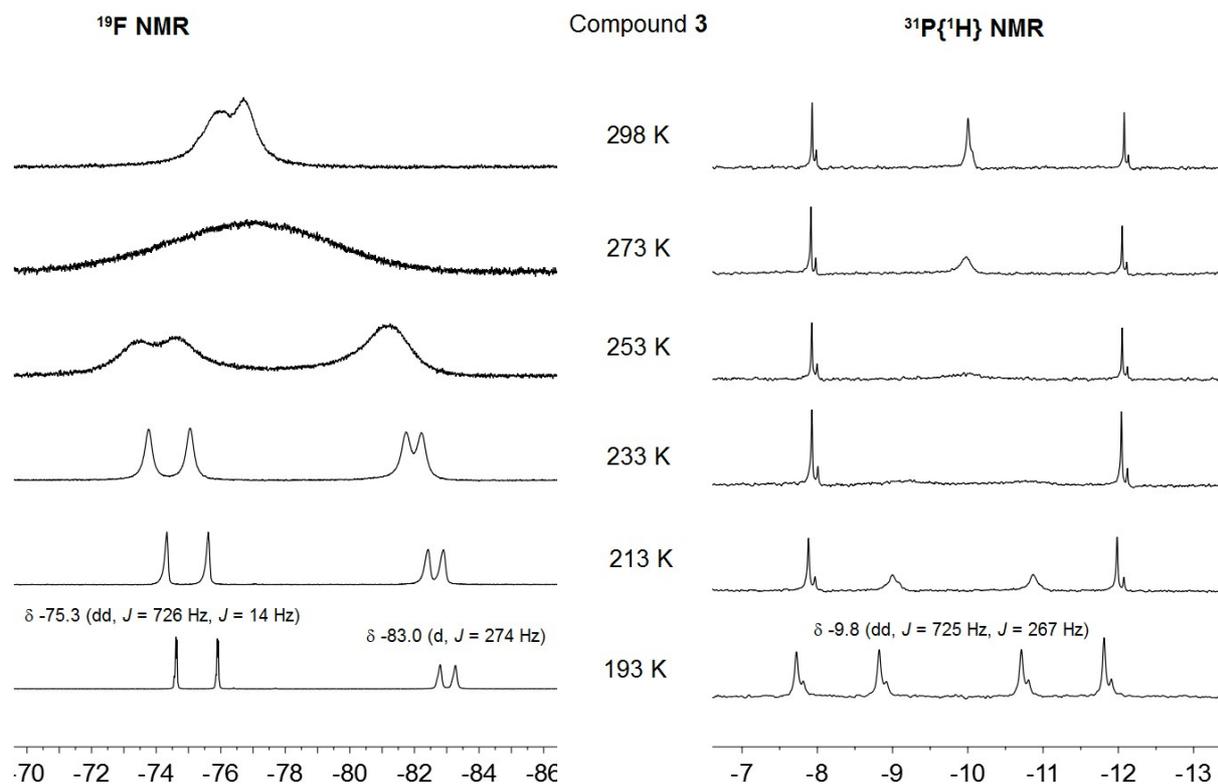


$^{31}\text{P}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ ) of free **9** (top) and  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ ) 1:1 of mixture of [*o*- $\text{Ph}_2\text{PF}(\text{C}_6\text{H}_4)\text{BCy}_2$ ][ $\text{B}(\text{C}_6\text{F}_5)_4$ ] and 4-DMAP (bottom).

### 3 Variable temperature NMR studies

#### 3.1 Temperature dependent $^{19}\text{F}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compound **3**.

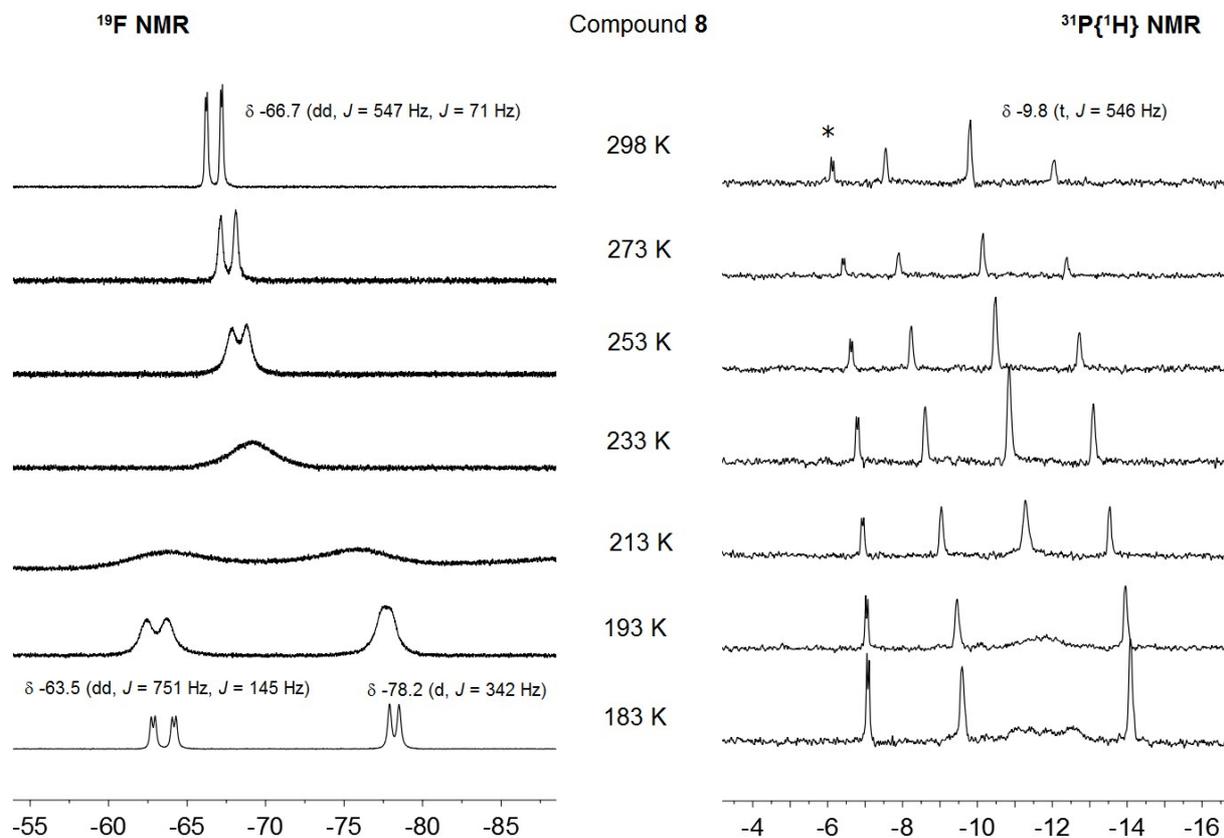
For the NMR experiment, compound **3** (10 mg, 0.02 mmol) were dissolved in  $\text{CD}_2\text{Cl}_2$  (ca. 0.5 ml) in a glove box, filled into a J-Young NMR tube and subjected to the NMR analysis.



$^{19}\text{F}$  NMR (564 MHz,  $\text{CD}_2\text{Cl}_2$ , left) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ , right) spectra of the difluorophosphorane *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{H}_4)\text{BCy}_2$  (**3**) at variable temperatures.

### 3.2 Temperature dependent $^{19}\text{F}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compound **8**.

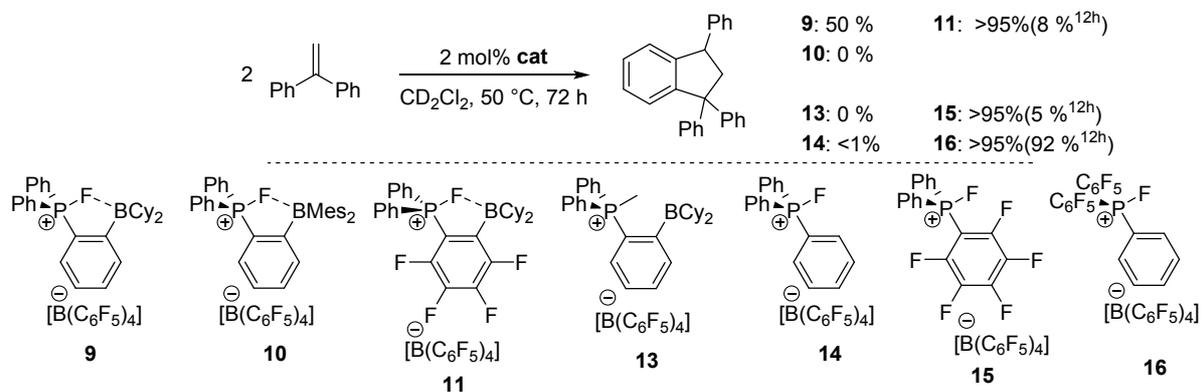
For the NMR experiment, compound **8** (10 mg, 0.02 mmol) were dissolved in  $\text{CD}_2\text{Cl}_2$  (ca. 0.5 ml) in a glove box, filled into a J-Young NMR tube and subjected to the NMR analysis.



$^{19}\text{F}$  NMR (564 MHz,  $\text{CD}_2\text{Cl}_2$ , left) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ , right) spectra of the difluorophosphorane *o*- $\text{Ph}_2\text{PF}_2(\text{C}_6\text{F}_4)\text{BCy}_2$  (**8**) at variable temperatures. \* the investigated sample contained some residual starting material **7**.

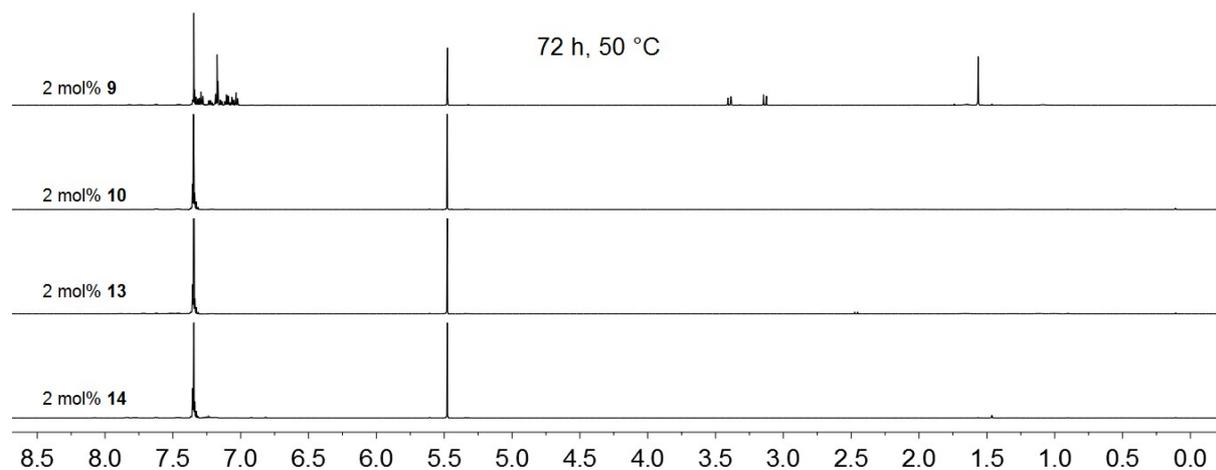
## 4 Catalytic Reactions

### 4.1 Dimerization of 1,1-Diphenylethylene

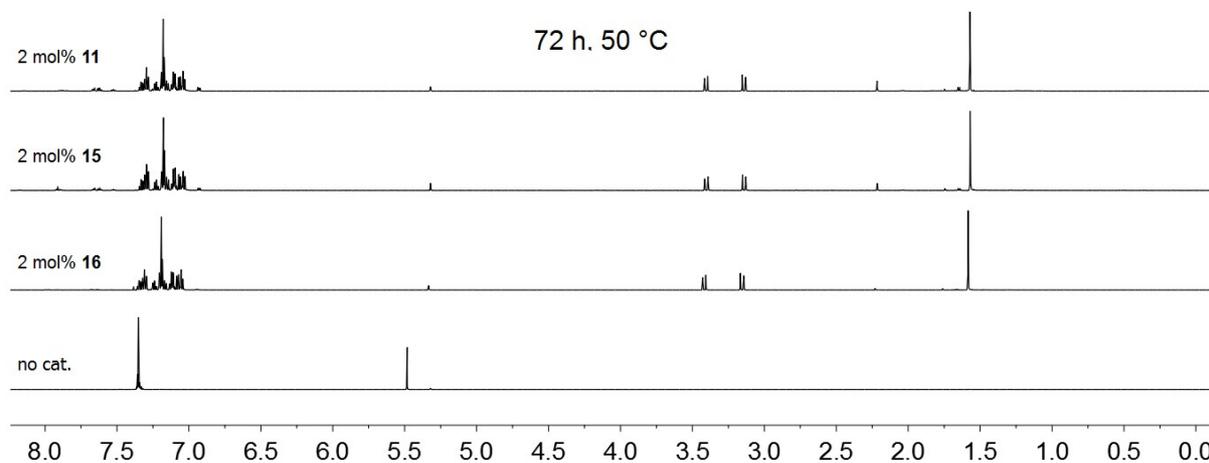


Reaction conditions: 0.1 mmol substrate, 0.7 ml solvent. Conversion determined by  $^1\text{H}$  NMR integration.

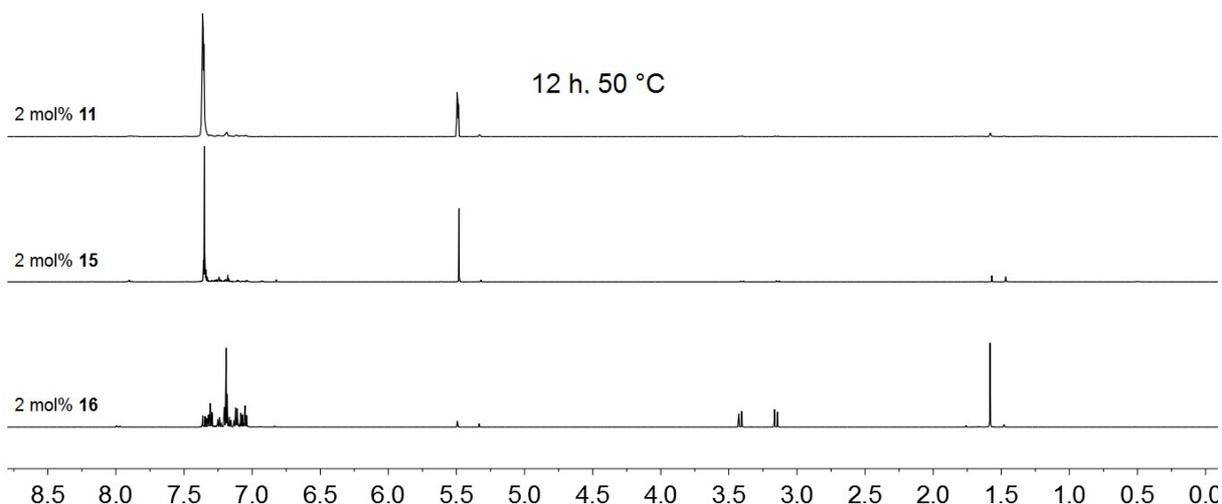
A 1-dram vial was charged with 0.002 mmol of the respective phosphonium borane (**9-11**, **13-16**). To this was added 0.7 ml of a 0.14 M stock solution of 1,1-diphenylethylene in  $\text{CD}_2\text{Cl}_2$ . The resulting solution was transferred to a J-Young tube and heated for 72 h at 50 °C. The reaction was monitored by  $^1\text{H}$  NMR.



Stacked  $^1\text{H}$  NMR (600 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of the reaction solutions from the catalytic dimerization of 1,1-diphenylethylene after 72 h at 50 °C employing [o-Ph<sub>2</sub>PF(C<sub>6</sub>F<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**11**), [Ph<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**15**) and [Ph(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**16**) as well as the spectrum of the control experiment with no added catalyst. (top to bottom).

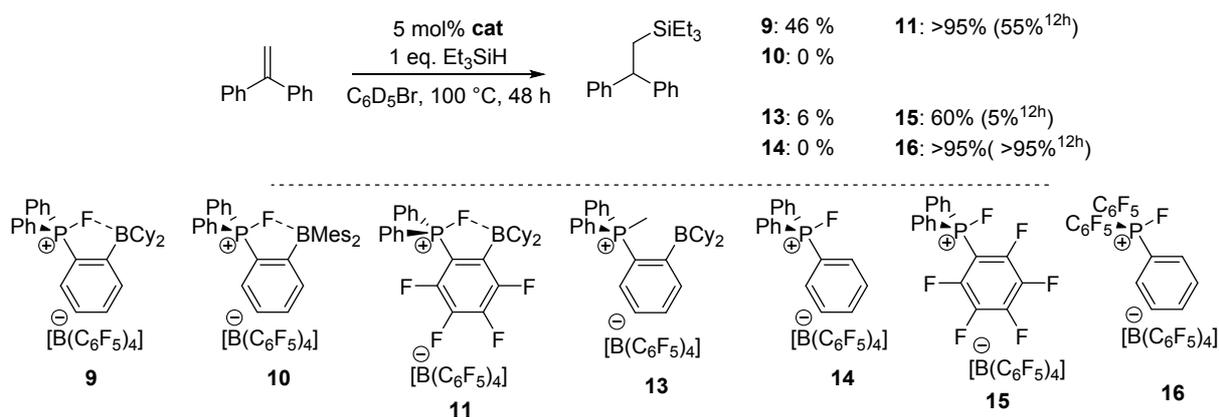


Stacked  $^1\text{H}$  NMR (600 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of the reaction solutions from the catalytic dimerization of 1,1-diphenylethylene after 72 h at 50 °C employing [o-Ph<sub>2</sub>PF(C<sub>6</sub>F<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**11**), [Ph<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**15**) and [Ph(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**16**) as well as the spectrum of the control experiment with no added catalyst. (top to bottom).

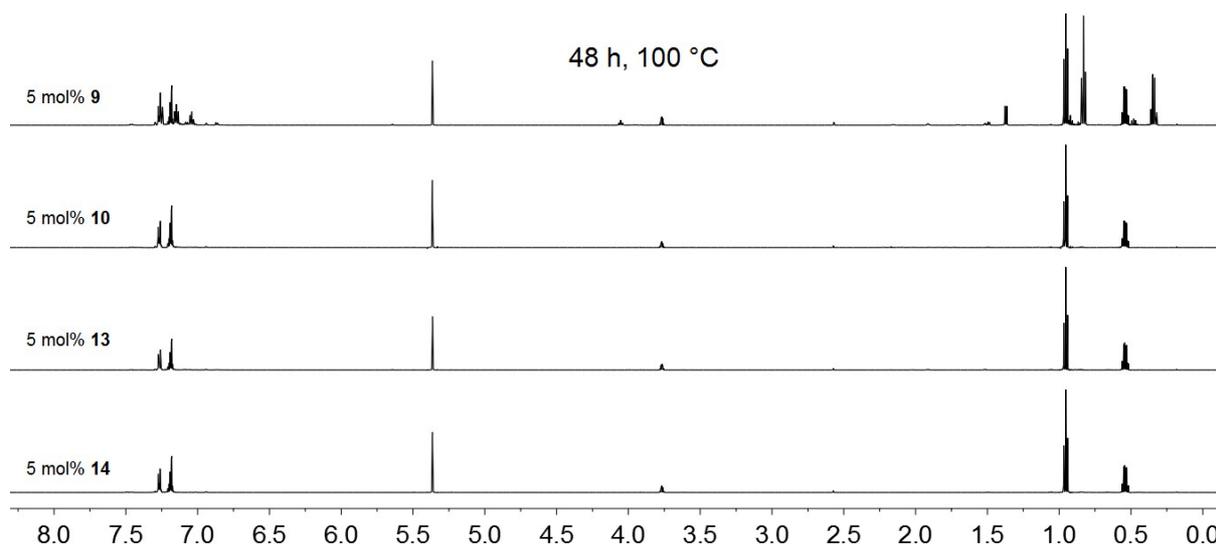


Stacked  $^1\text{H}$  NMR (600 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) spectra of the reaction solutions from the catalytic dimerization of 1,1-diphenylethylene after 12 h at 50 °C employing [o-Ph<sub>2</sub>PF(C<sub>6</sub>F<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**11**), [Ph<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**15**) and [Ph(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**16**). (top to bottom).

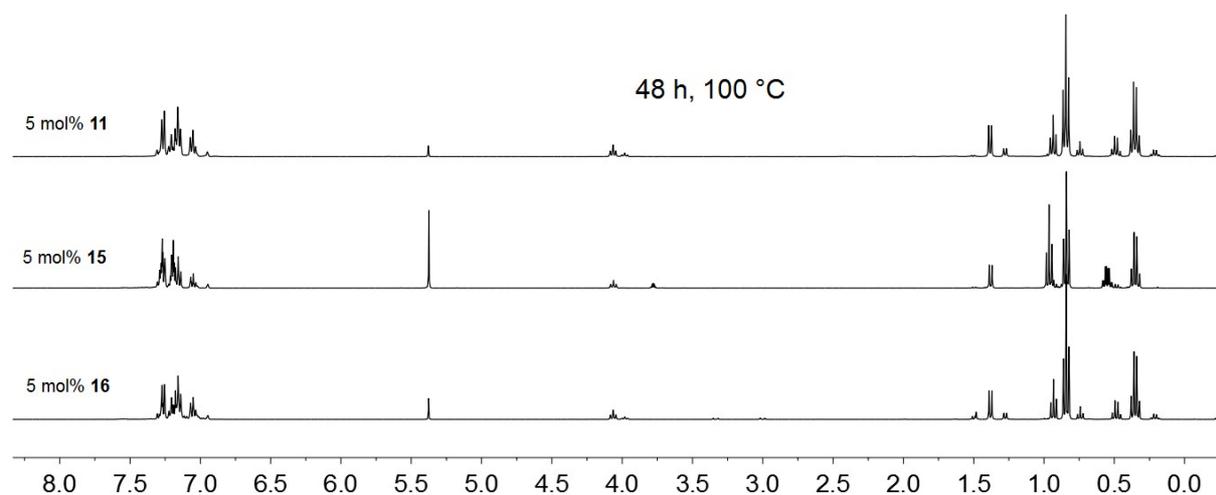
## 4.2 Hydrosilylation of 1,1-Diphenylethylene with Et<sub>3</sub>SiH



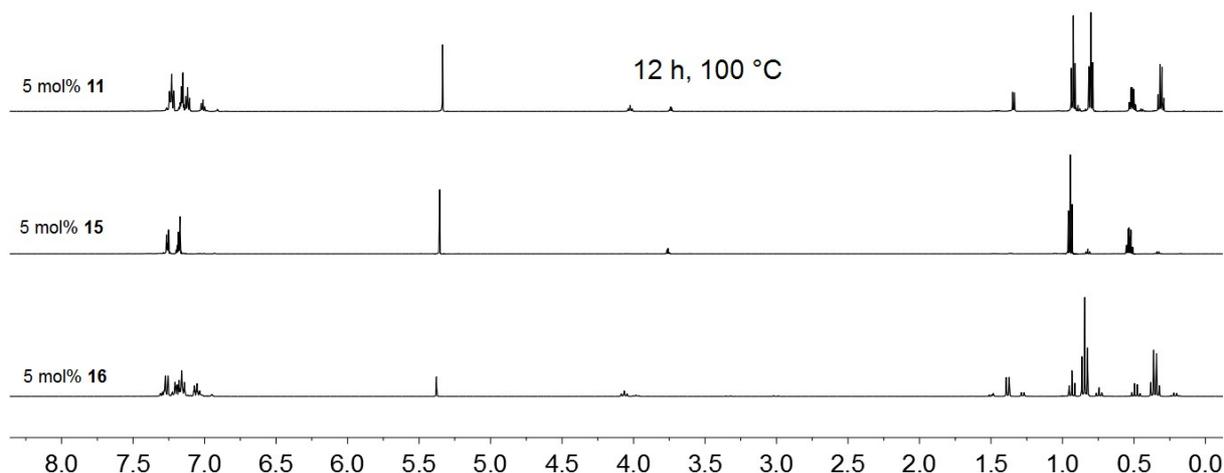
A 1-dram vial was charged with 0.005 mmol of the respective phosphonium borane (**9-11**, **13-16**). In a separate vial 1,1-diphenylethylene (18.1 mg, 0.1 mmol) and Et<sub>3</sub>SiH (11.6 mg, 0.1 mmol) were dissolved in 0.5 ml C<sub>6</sub>D<sub>5</sub>Br. The resulting solution was transferred to the catalyst vial and then to a J-Young tube, which was heated for 48 h at 100 °C. The reaction was monitored by  $^1\text{H}$  NMR.



Stacked  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ) spectra of the reaction solutions from the catalytic hydrosilylation of 1,1-diphenylethylene after 48 h at 100 °C employing [o-Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**9**), [o-Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BMes<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**10**), [o-Ph<sub>2</sub>PMe(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**13**) and [Ph<sub>3</sub>PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**14**) (top to bottom).

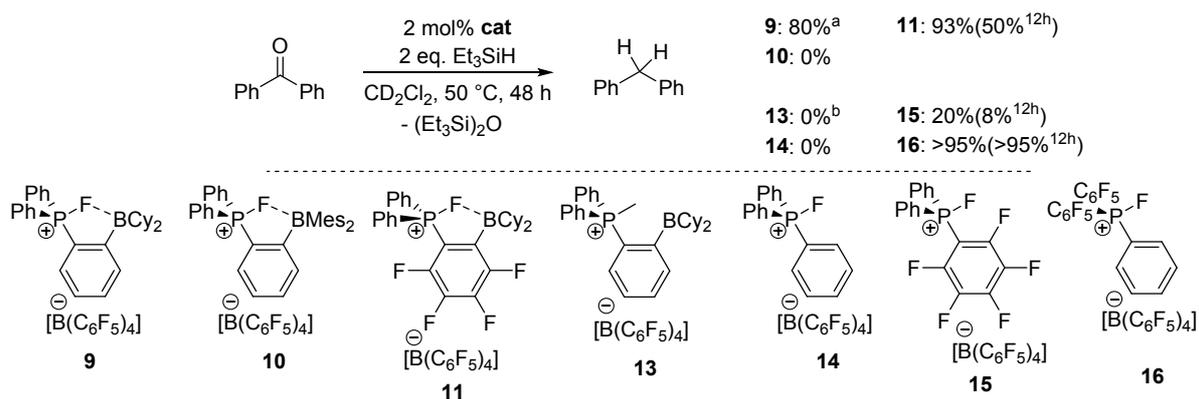


Stacked  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ) spectra of the reaction solutions from the catalytic hydrosilylation of 1,1-diphenylethylene after 48 h at 100 °C employing [o-Ph<sub>2</sub>PF(C<sub>6</sub>F<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**11**), [Ph<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**15**) and [Ph(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**16**) as well as the spectrum of the control experiment with no added catalyst. (top to bottom).



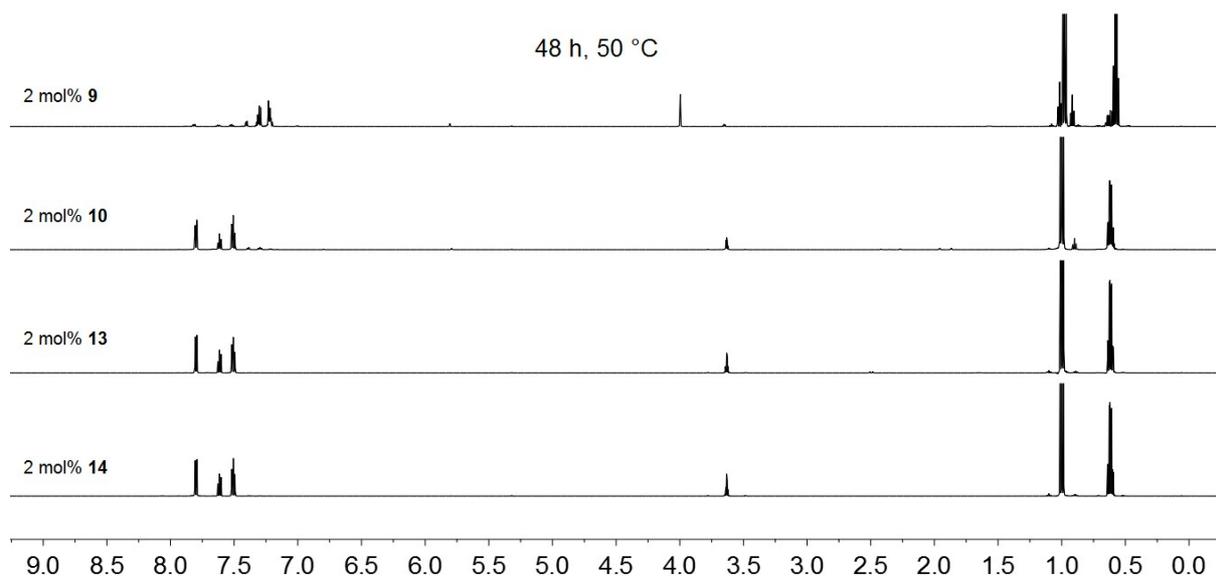
Stacked  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ) spectra of the reaction solutions from the catalytic hydrosilylation of 1,1-diphenylethylene after 12 h at 100 °C employing  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{F}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**11**),  $[\text{Ph}_2(\text{C}_6\text{F}_5)\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$  (**15**) and  $[\text{Ph}(\text{C}_6\text{F}_5)_2\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$  (**16**). (top to bottom).

### 4.3 Deoxygenation of benzophenone with $\text{Et}_3\text{SiH}$

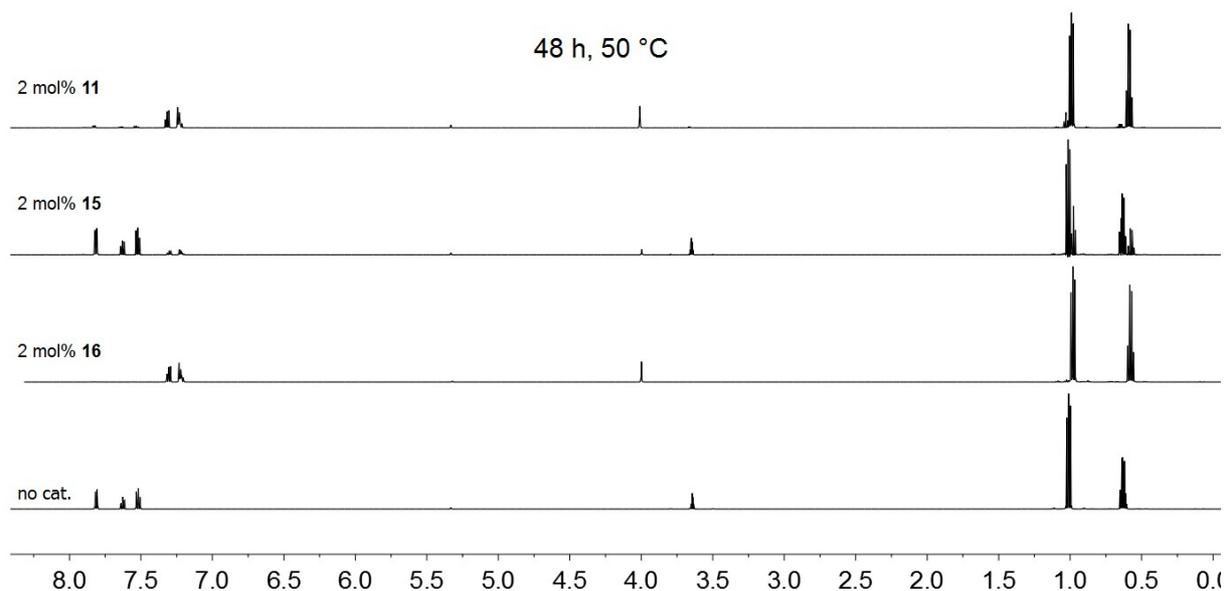


<sup>a</sup> 15% of  $\text{Ph}_2\text{CHOSiEt}_3$  were observed. <sup>b</sup> 8% of  $\text{Ph}_2\text{CHOSiEt}_3$  were observed.

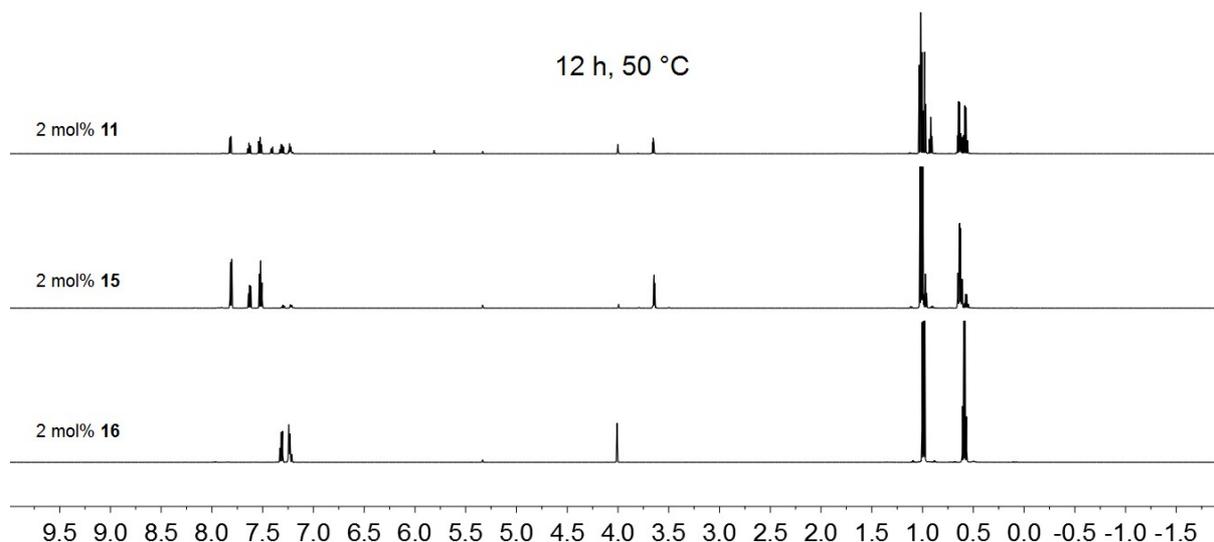
A 1-dram vial was charged with 0.002 mmol of the respective phosphonium borane (**9-11**, **13-16**). In a separate vial benzophenone (18.2 mg, 0.1 mmol) and  $\text{Et}_3\text{SiH}$  (23.2 mg, 0.2 mmol) were dissolved in 0.5 ml  $\text{CD}_2\text{Cl}_2$ . The resulting solution was transferred to the catalyst vial and then to a J-Young tube, which was heated for 48 h at 50 °C. The reaction was monitored by  $^1\text{H}$  NMR spectroscopy.



Stacked <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectra of the reaction solutions from the catalytic deoxygenation of benzophenone with triethylsilane after 48 h at 50 °C employing [o-Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**9**), [o-Ph<sub>2</sub>PF(C<sub>6</sub>H<sub>4</sub>)BMes<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**10**), [o-Ph<sub>2</sub>PMe(C<sub>6</sub>H<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**13**) and [Ph<sub>3</sub>PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**14**) (top to bottom).

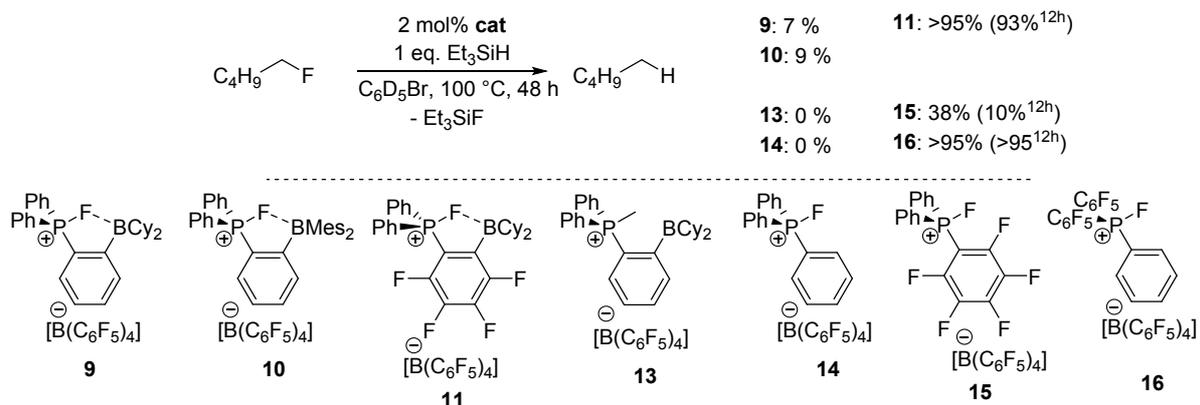


Stacked <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>5</sub>Br) spectra of the reaction solutions from the catalytic deoxygenation of benzophenone with triethylsilane after 48 h at 50 °C employing [o-Ph<sub>2</sub>PF(C<sub>6</sub>F<sub>4</sub>)BCy<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**11**), [Ph<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**15**) and [Ph(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>PF][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>](**16**) as well as the spectrum of the control experiment with no added catalyst. (top to bottom).

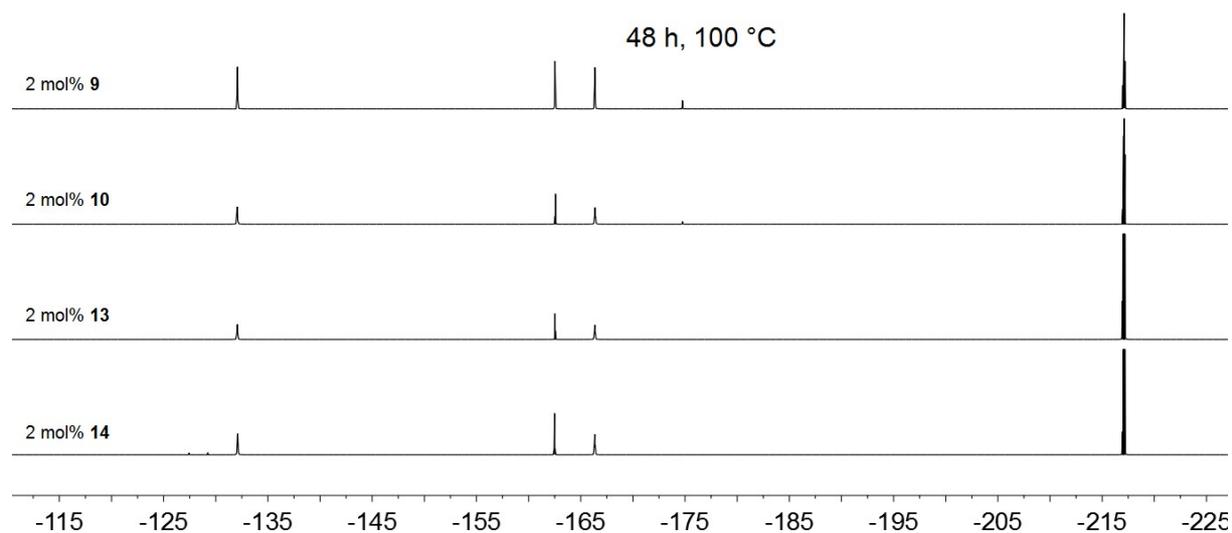


Stacked  $^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ) spectra of the reaction solutions from the catalytic deoxygenation of benzophenone with triethylsilane after 12 h at 50 °C employing  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{F}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**11**),  $[\text{Ph}_2(\text{C}_6\text{F}_5)\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$  (**15**) and  $[\text{Ph}(\text{C}_6\text{F}_5)_2\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$  (**16**). (top to bottom).

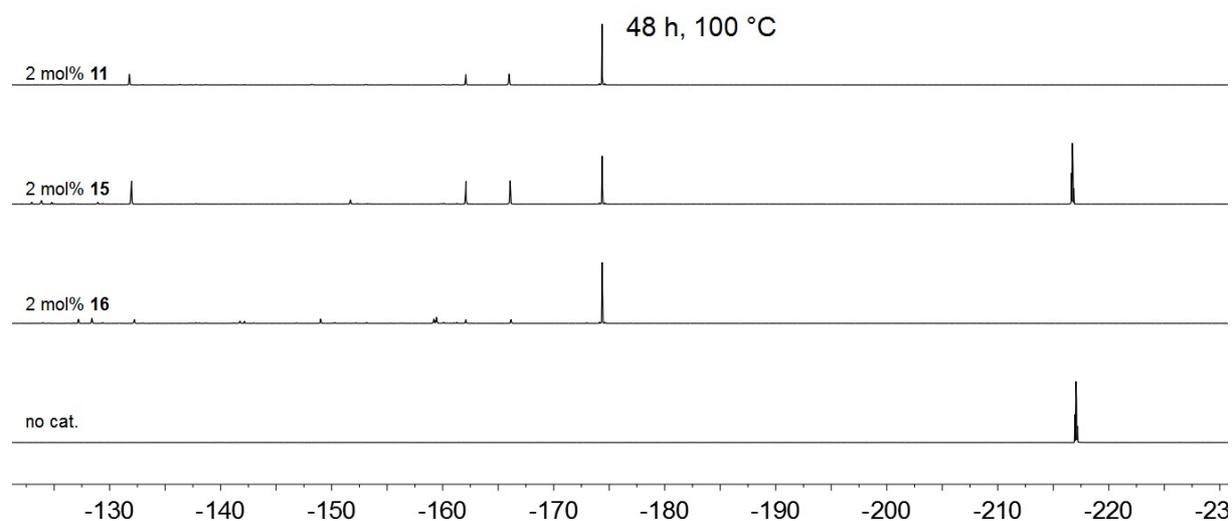
#### 4.4 Hydrodefluorination of 1-fluoropentane with $\text{Et}_3\text{SiH}$



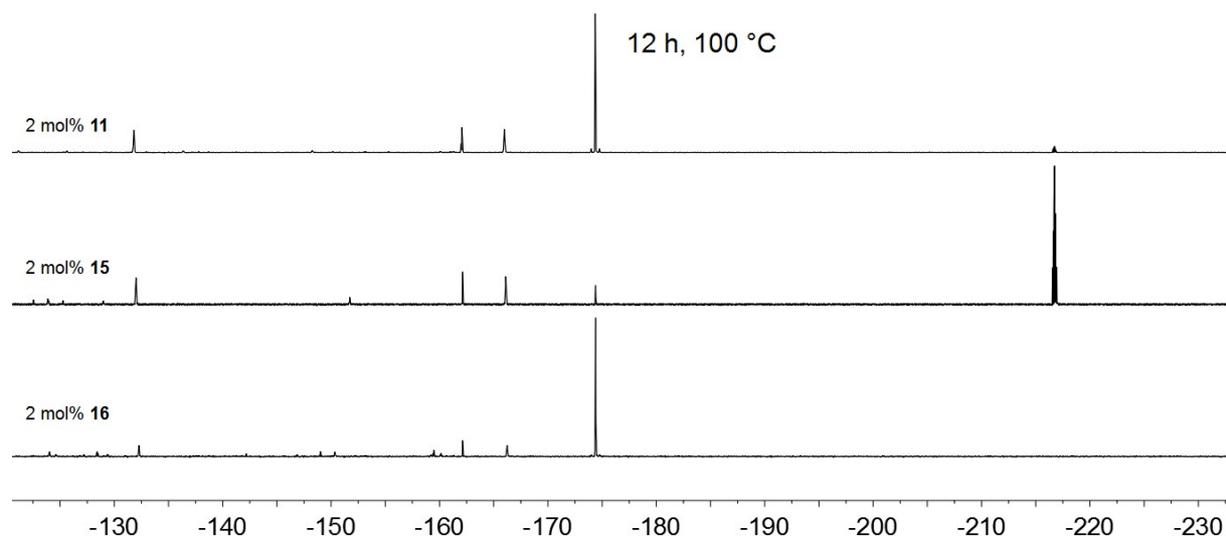
A 1-dram vial was charged with 0.005 mmol of the respective phosphonium borane (**9-11**, **13-16**). In a separate vial 1-fluoropentane (9.0 mg, 0.1 mmol) and  $\text{Et}_3\text{SiH}$  (11.6 mg, 0.1 mmol) were dissolved in 0.5 ml  $\text{C}_6\text{D}_5\text{Br}$ . The resulting solution was transferred to the catalyst vial and then to a J-Young tube, which was heated for 48 h at 100 °C. The reaction was monitored by  $^{19}\text{F}$  NMR.



Stacked  $^{19}\text{F}$  NMR (564 MHz, 298 K,  $\text{C}_6\text{D}_5\text{Br}$ ) spectra of the reaction solutions from the catalytic hydrodefluorination of 1-fluoropentane with triethylsilane after 48 h at 100 °C employing  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**9**),  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{H}_4)\text{BMes}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**10**),  $[\text{o-Ph}_2\text{PMe}(\text{C}_6\text{H}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**13**) and  $[\text{Ph}_3\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$  (**14**) (top to bottom).



Stacked  $^{19}\text{F}$  NMR (564 MHz, 298 K,  $\text{C}_6\text{D}_5\text{Br}$ ) spectra of the reaction solutions from the catalytic hydrodefluorination of 1-fluoropentane with triethylsilane after 48 h at 100 °C employing  $[\text{o-Ph}_2\text{PF}(\text{C}_6\text{F}_4)\text{BCy}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (**11**),  $[\text{Ph}_2(\text{C}_6\text{F}_5)\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$  (**15**) and  $[\text{Ph}(\text{C}_6\text{F}_5)_2\text{PF}][\text{B}(\text{C}_6\text{F}_5)_4]$  (**16**) as well as the spectrum of the control experiment with no added catalyst. (top to bottom).



Stacked  $^{19}\text{F}$  NMR (564 MHz, 298 K,  $\text{C}_6\text{D}_5\text{Br}$ ) spectra of the reaction solutions from the catalytic hydrodefluorination of 1-fluoropentane with triethylsilane after 48 h at 100 °C employing [*o*- $\text{Ph}_2\text{PF}(\text{C}_6\text{F}_4)\text{BCy}_2$ ][ $\text{B}(\text{C}_6\text{F}_5)_4$ ] (**11**), [ $\text{Ph}_2(\text{C}_6\text{F}_5)\text{PF}$ ][ $\text{B}(\text{C}_6\text{F}_5)_4$ ] (**15**) and [ $\text{Ph}(\text{C}_6\text{F}_5)_2\text{PF}$ ][ $\text{B}(\text{C}_6\text{F}_5)_4$ ] (**16**) (top to bottom).