

## Supporting Information

# Formation of Amidino-borate Derivatives by a Multi-component Reaction

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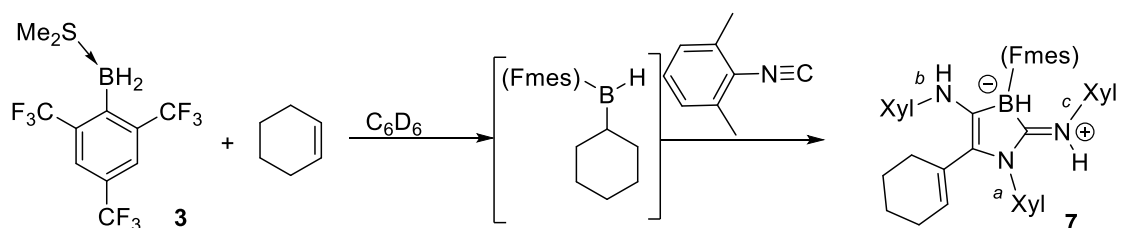
## General Information.

All reactions involving air- or moisture-sensitive compounds were carried out under an inert gas atmosphere (Argon) by using Schlenk-type glassware or in a glovebox. All solvents were dried and degassed before use, if necessary, for the respective reaction. Chemicals: Unless otherwise noted all chemicals were used as purchased. The following instruments were used for physical characterization of the compounds: elemental analyses: Foss–Heraeus CHNO-Rapid; HRMS: Thermo Scientific Orbitrap LTQ XL; NMR: Varian UNITY plus NMR spectrometer ( $^1\text{H}$ , 600 MHz;  $^{13}\text{C}$ , 151 MHz;  $^{11}\text{B}$ , 192 MHz;  $^{19}\text{F}$ , 564 MHz). NMR chemical shifts are given relative to  $\text{SiMe}_4$  and referenced to the respective solvent signal ( $^1\text{H}$  and  $^{13}\text{C}$ ) or an external standard [ $\delta(\text{BF}_3\cdot\text{OEt}_2) = 0$  for  $^{11}\text{B}$  NMR,  $\delta(\text{CFCl}_3) = 0$  for  $^{19}\text{F}$  NMR]. NMR assignments were supported by 2D NMR experiments.

X-Ray diffraction: Data sets for compound **13'** were collected with a Bruker D8 Venture Photon 100 CMOS Diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., **2016**); cell refinement: SAINT V8.37A (Bruker AXS Inc., **2015**); data reduction: SAINT V8.37A (Bruker AXS Inc., **2015**); absorption correction, SADABS V2014/7 (Bruker AXS Inc., **2014**); structure solution *SHELXT-2015* (Sheldrick, G. M. *Acta Cryst.*, **2015**, *A71*, 3-8); structure refinement *SHELXL-2015* (Sheldrick, G. M. *Acta Cryst.*, **2015**, *C71* (1), 3-8). For compounds **7**, **10**, and **13** data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* 1997, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* 2003, *A59*, 228-234); structure solution *SHELXT-2015* (Sheldrick, G. M. *Acta Cryst.*, **2015**, *A71*, 3-8); structure refinement *SHELXL-2015* (Sheldrick, G. M. *Acta Cryst.*, **2015**, *C71* (1), 3-8) and graphics, XP (Version 5.1, Bruker AXS Inc., Madison, Wisconsin, USA, **1998**). *R*-values are given for observed reflections, and  $wR^2$  values are given for all reflections. *Exceptions and special features*: For compound **7** one  $\text{CF}_3$  group, for compound **10** one  $\text{CF}_3$  group and one 2,6-xylyl group and for compound **13** two  $\text{CF}_3$  groups were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For compound **13** a badly disordered half benzene molecule and for compound **13'** a badly disordered half pentane molecule was found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek, A.L. (**2015**). *Acta Cryst.* *C71*, 9-18) as therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecules.

Materials: Borane **3-SMe<sub>2</sub>** and FLP **12** were prepared according to a procedure described in the literature.<sup>8</sup>

## Preparation of Compound 7



Scheme S1.

At room temperature, cyclohexene (16.4 mg, 2 mmol, 1 eq.) was added to a solution of borane **3** (71.2 mg, 2 mmol, 1 eq.) in  $C_6D_6$  (1 mL) under an Argon atmosphere. Then the mixture was stirred overnight at room temperature to give a colorless solution. Subsequently, 2,6-Dimethylphenyl isocyanide (78.6 mg, 6 mmol, 3 equiv.) was added and the resulting solution was stirred at room temperature for 3 days. The volatiles were removed in vacuo, then the residue was dissolved in pentane (3 mL) and stored at  $-35\text{ }^\circ\text{C}$  to give the products as a pale-yellow solid (65 mg, 42 % yield).

**HRMS** for  $C_{42}H_{42}BF_9N_3^+$ ,  $[M+H]^+$ : calc. 770.3323; found: 770.3317.

**$^1\text{H NMR}$**  (600 MHz, methylene chloride- $d_2$ , 253 K):  $\delta$  = [7.90, 7.64](each s, each 1H, *m*-Fmes), [7.22 (t,  $^3J_{\text{HH}}$  = 7.8 Hz, *p*), 7.16 (d,  $^3J_{\text{HH}}$  = 7.8 Hz, *m*), 7.15 (d,  $^3J_{\text{HH}}$  = 7.8 Hz, *m*)](each 1H, Xyl<sup>a</sup>), [6.89 (d,  $^3J_{\text{HH}}$  = 7.5 Hz, *m*), 6.84 (d,  $^3J_{\text{HH}}$  = 7.5 Hz, *m*), 6.79 (t,  $^3J_{\text{HH}}$  = 7.5 Hz, *p*)](each 1H, Xyl<sup>b</sup>), [6.82 (d,  $^3J_{\text{HH}}$  = 7.5 Hz, *m*), 6.73 (t,  $^3J_{\text{HH}}$  = 7.6 Hz, *p*), 6.38 (d,  $^3J_{\text{HH}}$  = 7.5 Hz, *m*)](each 1H, Xyl<sup>c</sup>), 6.07 (s, 1H, NH<sup>c</sup>), 5.34 (br, 1H, CH=), 4.29 (s, 1H, NH<sup>b</sup>), 3.27 (br m, BH), [2.37, 2.33](each s, each 3H, *o*-CH<sub>3</sub><sup>Xyl<sup>a</sup></sup>), [2.30, 2.06](each s, each 3H, *o*-CH<sub>3</sub><sup>Xyl<sup>b</sup></sup>), [2.22, 1.86](each s, each 3H, *o*-CH<sub>3</sub><sup>Xyl<sup>c</sup></sup>), [1.42/1.38, 1.23/1.05, 0.90/0.79, 0.76/0.73](each br m, each 1H, CH<sub>2</sub>).

**$^{13}\text{C}\{^1\text{H}\}$  NMR** (151 MHz, methylene chloride- $d_2$ , 253 K):  $\delta$  = 183.6 (br, NC=N), 151.7 (br, *i*-Fmes), 146.1 (br, BC=), 142.5 (*i*-Xyl<sup>b</sup>), [138.6 (q,  $^2J_{\text{FC}}$  = 27.7 Hz), 135.6 (q,  $^2J_{\text{FC}}$  = 28.6 Hz)](*o*-Fmes), [137.65, 137.60][*o*-Xyl<sup>a</sup>], [137.5, 135.7](*o*-Xyl<sup>c</sup>), 134.89 (*i*-Xyl<sup>c</sup>), [134.85, 134.6](*o*-Xyl<sup>b</sup>), 133.9 (*i*-Xyl<sup>a</sup>), 130.7 (CH=), [129.3, 121.8](C=), [129.2, 129.1, 129.0](*m,p*-Xyl<sup>a</sup>), [128.2, 127.3](*m*-Xyl<sup>c</sup>), [128.0, 127.3](*m*-Xyl<sup>b</sup>), 127.6 (*p*-Xyl<sup>c</sup>), 127.4 (q,  $^2J_{\text{FC}}$  = 33.0 Hz, *p*-Fmes), [124.8, 124.2](each br m, *m*-Fmes), [124.5 (q,  $^1J_{\text{FC}}$  = 273.5 Hz), 123.8 (q,  $^1J_{\text{FC}}$  = 273.2 Hz), 123.5 (q,  $^1J_{\text{FC}}$  = 273.0 Hz)](CF<sub>3</sub>), 123.7 (*p*-Xyl<sup>b</sup>), [27.5, 25.4, 22.4, 21.4](CH<sub>2</sub>), [19.4, 17.6](*o*-CH<sub>3</sub><sup>Xyl<sup>c</sup></sup>), [18.9, 18.2](*o*-CH<sub>3</sub><sup>Xyl<sup>b</sup></sup>), [18.3, 17.8](*o*-CH<sub>3</sub><sup>Xyl<sup>a</sup></sup>).

**$^{11}\text{B NMR}$**  (192 MHz, methylene chloride- $d_2$ , 299 K):  $\delta$  = -17.0 (d,  $^1J_{\text{BH}}$  ~ 80 Hz).

**$^{11}\text{B NMR}$**  (192 MHz, methylene chloride- $d_2$ , 253 K):  $\delta$  = -17.2 (d,  $^1J_{\text{BH}}$  ~ 80 Hz).

**$^{19}\text{F NMR}$**  (564 MHz, methylene chloride- $d_2$ , 253 K):  $\delta$  = -55.9 (d,  $J_{\text{FH}}$  = 6.2 Hz, 1F, *o*-CF<sub>3</sub>), -58.2 (s, 1F, *o*-CF<sub>3</sub>), -63.5 (s, 1F, *p*-CF<sub>3</sub>).

[Comment: This compound contained an unidentified contaminant, potentially an isomer (ca. 7 mol% ( $^{19}\text{F}$ ))]

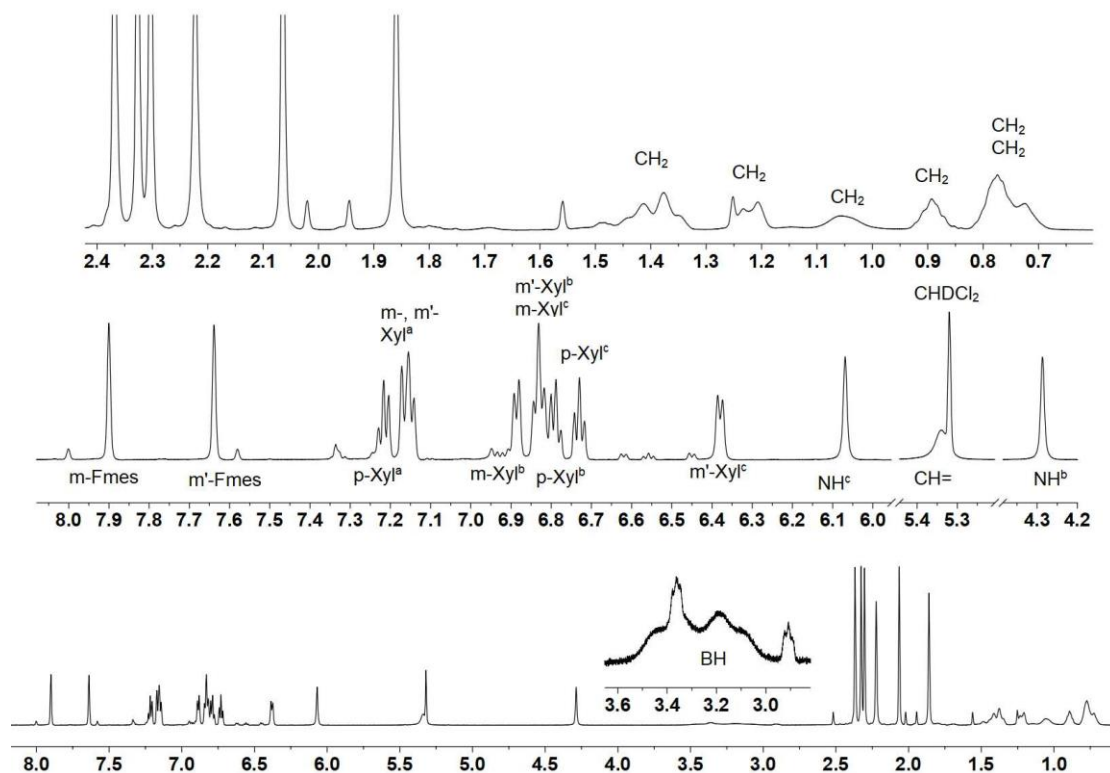


Figure S1.  $^1\text{H}$  NMR (600 MHz, methylene chloride- $d_2$ , 253 K) spectrum of compound 7.

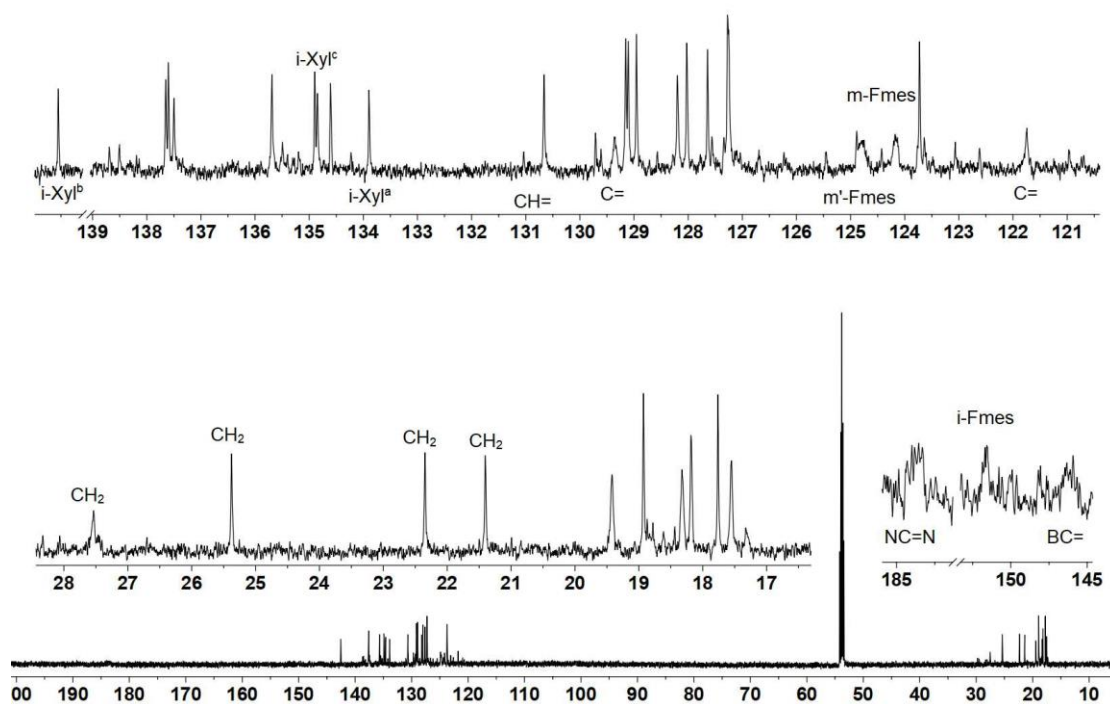


Figure S2.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, methylene chloride- $d_2$ , 253 K) spectrum of compound 7.

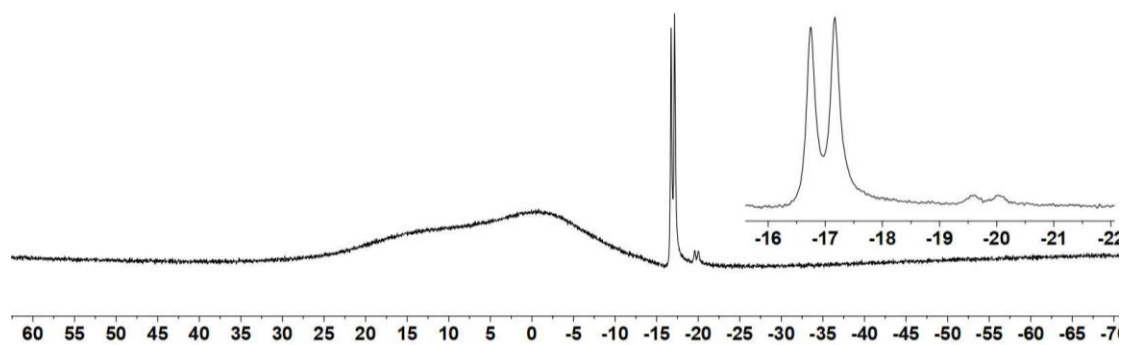


Figure S3.  $^{11}\text{B}$  NMR (192 MHz, methylene chloride- $d_2$ , 299 K) spectrum of compound **7**.

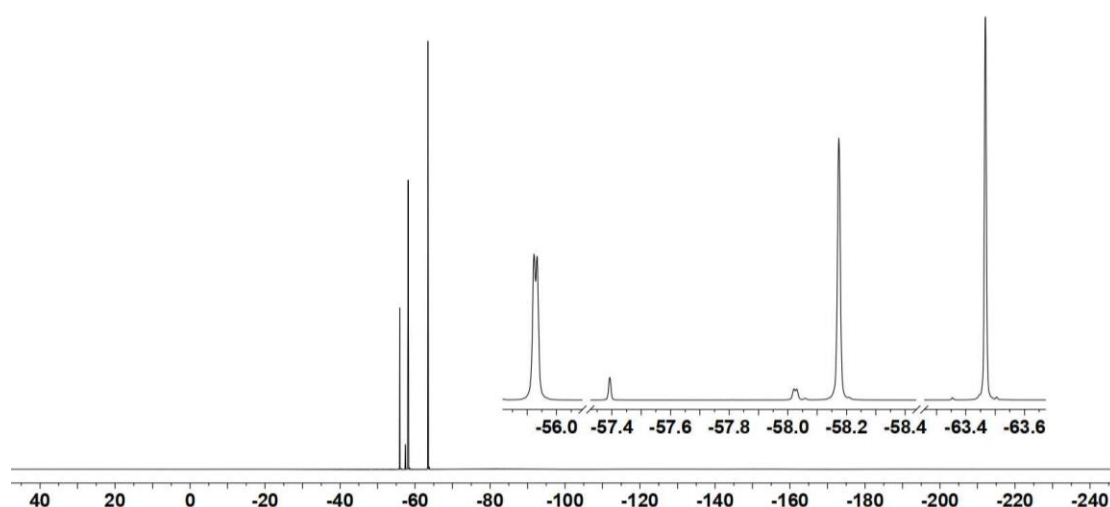


Figure S4.  $^{19}\text{F}$  NMR (564 MHz, methylene chloride- $d_2$ , 253 K) spectrum of compound **7**.

The crystal suitable for the X-ray crystal structure analysis was obtained from a solution of compound **7** in benzene at room temperature.

**X-ray crystal structure analysis of compound 7 (erk9425):** A yellow plate-like specimen of  $\text{C}_{42}\text{H}_{41}\text{BF}_9\text{N}_3$ , approximate dimensions 0.030 mm x 0.070 mm x 0.140 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a triclinic unit cell yielded a total of 6579 reflections to a maximum  $\theta$  angle of  $25.00^\circ$  (0.84 Å resolution), of which 6579 were independent (average redundancy 1.000, completeness = 98.8%,  $R_{\text{sig}} = 3.73\%$ ) and 5240 (79.65%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $\underline{a} = 9.7145(2)$  Å,  $\underline{b} = 11.9901(3)$  Å,  $\underline{c} = 17.9234(6)$  Å,  $\alpha = 103.2820(10)^\circ$ ,  $\beta = 95.2260(10)^\circ$ ,  $\gamma = 109.005(2)^\circ$ , volume =  $1889.60(9)$  Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of reflections above  $20\sigma(I)$ . Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9850 and 0.9970. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group  $P-1$ , with  $Z = 2$  for the formula unit,  $\text{C}_{42}\text{H}_{41}\text{BF}_9\text{N}_3$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 546 variables converged at  $R1 = 7.79\%$ , for the observed data and  $wR2 = 20.64\%$  for all data. The goodness-of-fit was 1.082. The largest peak in the final difference electron density synthesis was  $0.358 \text{ e}^-/\text{Å}^3$  and the largest hole was  $-0.338 \text{ e}^-/\text{Å}^3$  with an RMS

deviation of  $0.065 \text{ e}/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.353 \text{ g}/\text{cm}^3$  and  $F(000)$ ,  $800 \text{ e}^-$ . The hydrogen atoms at B1, N2, N3 and C2 atoms were refined freely. CCDC Nr.: 2064640.

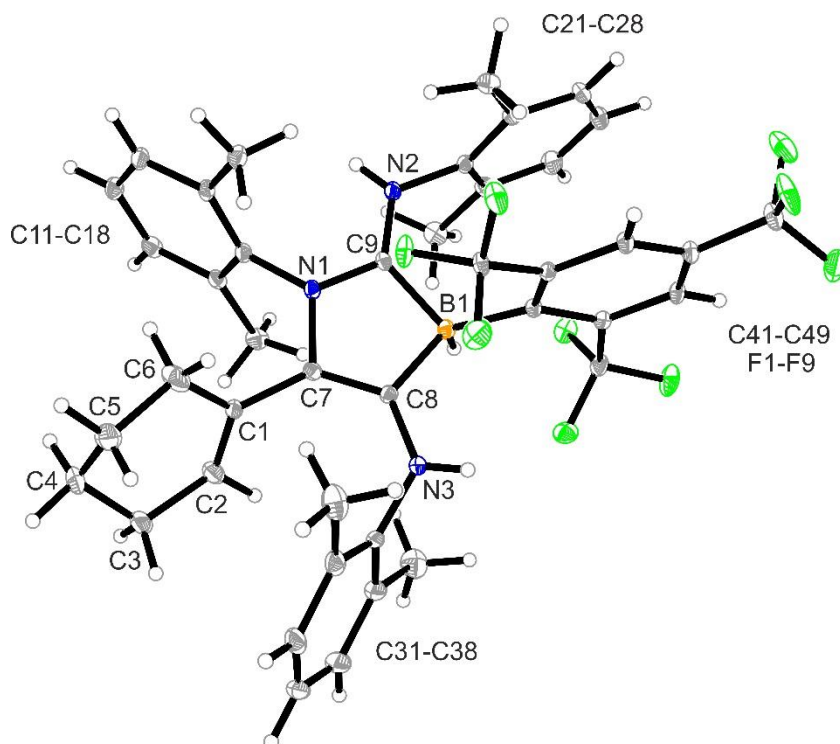
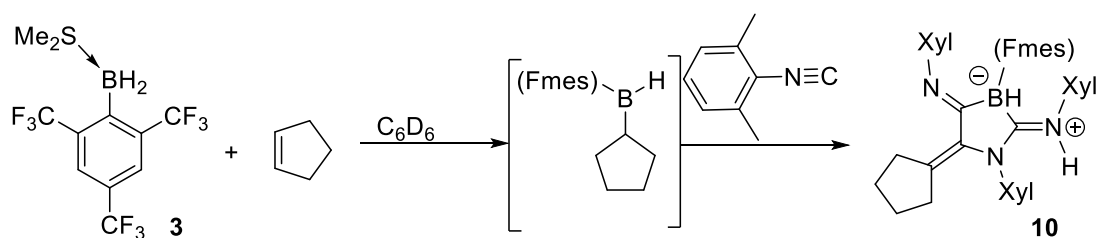


Figure S5. Crystal structure of compound **7** (thermal ellipsoids are set at 15% probability).

## Preparation of compound **10**



Scheme S2.

At room temperature, cyclopentene (13.6 mg, 2 mmol, 1 eq.) was added to the solution of borane **3** (71.2 mg, 2 mmol, 1 eq.) in  $\text{C}_6\text{D}_6$  (1 mL) under Argon atmosphere. Then the mixture was stirred overnight at room temperature to give a colorless solution. 2,6-Dimethylphenyl isocyanide (78.6 mg, 6 mmol, 3 equiv.) was subsequently added and the resulting solution was stirred at room temperature for 3 days. The volatiles were removed in vacuo, the residue was dissolved in pentane (3 mL) and stored at  $-35 \text{ }^\circ\text{C}$  to give the product as a pale-yellow solid (42 mg, 28 % yield).

**HRMS** for  $\text{C}_{41}\text{H}_{40}\text{BF}_9\text{N}_3^+$   $[\text{M}+\text{H}]^+$ : calc. 756.3166; found: 756.3164.

**$^1\text{H}$  NMR** (600 MHz, methylene chloride- $d_2$ , 299 K):  $\delta$  = [7.94, 7.51] (each m, each 1H, *m*-Fmes),

[7.38 (t,  $^3J_{\text{HH}} = 7.3$  Hz, *p*), 7.34 (dm,  $^3J_{\text{HH}} = 7.3$  Hz, *m*), 7.30 (dm,  $^3J_{\text{HH}} = 7.3$  Hz, *m'*)](each 1H, Xyl<sup>a</sup>), [6.95 (t,  $^3J_{\text{HH}} = 7.6$  Hz, *p*), 6.93 (dm,  $^3J_{\text{HH}} = 7.6$  Hz, *m*), 6.63 (dm,  $^3J_{\text{HH}} = 7.6$  Hz, *m'*)](each 1H, Xyl<sup>b</sup>), 6.91 (br, 1H, NH)<sup>t</sup>, [6.79 (dm,  $^3J_{\text{HH}} = 7.4$  Hz, *m*), 6.53 (t,  $^3J_{\text{HH}} = 7.4$  Hz, *p*), 6.41 (dm,  $^3J_{\text{HH}} = 7.4$  Hz, *m'*)](each 1H, Xyl<sup>c</sup>), [3.04 (2H), 1.94/1.35 (each 1H), 1.59 (2H), 1.48 (2H)](each m, CH<sub>2</sub>), [2.59, 2.34](each s, each 3H, *o*-CH<sub>3</sub><sup>Xyl<sup>a</sup></sup>), 2.79 (br m, BH), [2.09, 1.70](each s, each 3H, *o*-CH<sub>3</sub><sup>Xyl<sup>b</sup></sup>), [2.04, 1.41](each s, each 3H, *o*-CH<sub>3</sub><sup>Xyl<sup>c</sup></sup>), [t tentative assignment].

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, methylene chloride-*d*<sub>2</sub>, 299 K):  $\delta = [191.7, 189.1]$ (each br, NC=N, BC=), 152.1 (*i*-Xyl<sup>c</sup>), 150.8 (m, *i*-Fmes), [138.6 (q,  $^2J_{\text{FC}} = 29.2$  Hz), 135.9 (q,  $^2J_{\text{FC}} = 28.8$  Hz)](*o*-Fmes), [137.5, 136.98](*o*-Xyl<sup>a</sup>), 137.4 (NC=C), [137.04, 135.8](*o*-Xyl<sup>b</sup>), 135.5 (*i*-Xyl<sup>a</sup>), 134.6 (*i*-Xyl<sup>b</sup>), 130.9 (C=), [130.6, 130.1](*m*-Xyl<sup>a</sup>), 130.4 (*p*-Xyl<sup>a</sup>), [128.9, 128.8, 128.3](*o,p*-Xyl<sup>b</sup>), 127.9 (q,  $^2J_{\text{FC}} = 33.6$  Hz, *p*-Fmes), [127.6, 126.8](*m*-Xyl<sup>c</sup>), [125.8, 125.6](each br m, *m*-Fmes), [125.0, 124.4](*o*-Xyl<sup>c</sup>), [123.8 (q,  $^1J_{\text{FC}} = 271.8$  Hz), 123.2 (q,  $^1J_{\text{FC}} = 271.8$  Hz), 123.2 (q,  $^1J_{\text{FC}} = 271.8$  Hz)](CF<sub>3</sub>), 121.1 (*p*-Xyl<sup>c</sup>), [34.9, 30.7, 27.1, 26.9](CH<sub>2</sub>), [19.0, 17.8 (m)](*o*-CH<sub>3</sub><sup>Xyl<sup>b</sup></sup>), [18.84 (m), 18.6](*o*-CH<sub>3</sub><sup>Xyl<sup>a</sup></sup>), [18.79, 17.7 (m)](*o*-CH<sub>3</sub><sup>Xyl<sup>c</sup></sup>).

**<sup>11</sup>B NMR** (192 MHz, methylene chloride-*d*<sub>2</sub>, 299 K):  $\delta = -19.5$  (d,  $^1J_{\text{BH}} \sim 87$  Hz).

**<sup>19</sup>F NMR** (564 MHz, methylene chloride-*d*<sub>2</sub>, 299 K):  $\delta = -56.6$  (s, 1F, *o*-CF<sub>3</sub>),  $-57.7$  (d,  $J_{\text{FH}} = 5.4$  Hz, 1F, *o*-CF<sub>3</sub>),  $-63.5$  (s, 1F, *p*-CF<sub>3</sub>).

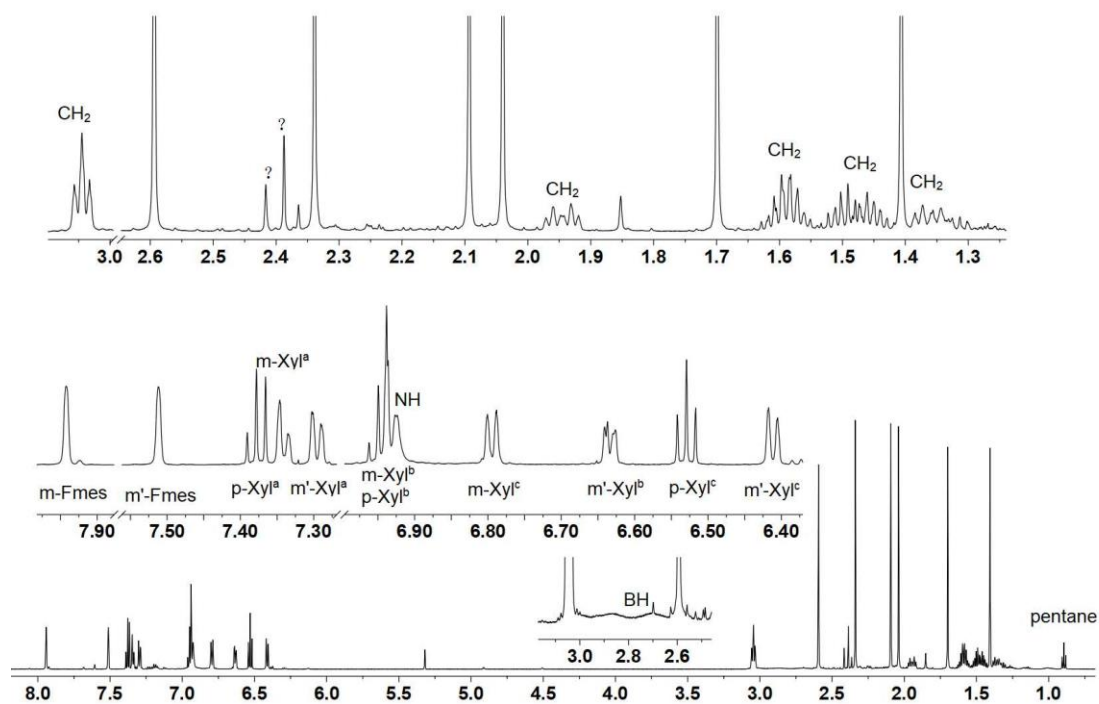


Figure S6. <sup>1</sup>H NMR (600 MHz, methylene chloride-*d*<sub>2</sub>, 299 K) spectrum of compound 10.

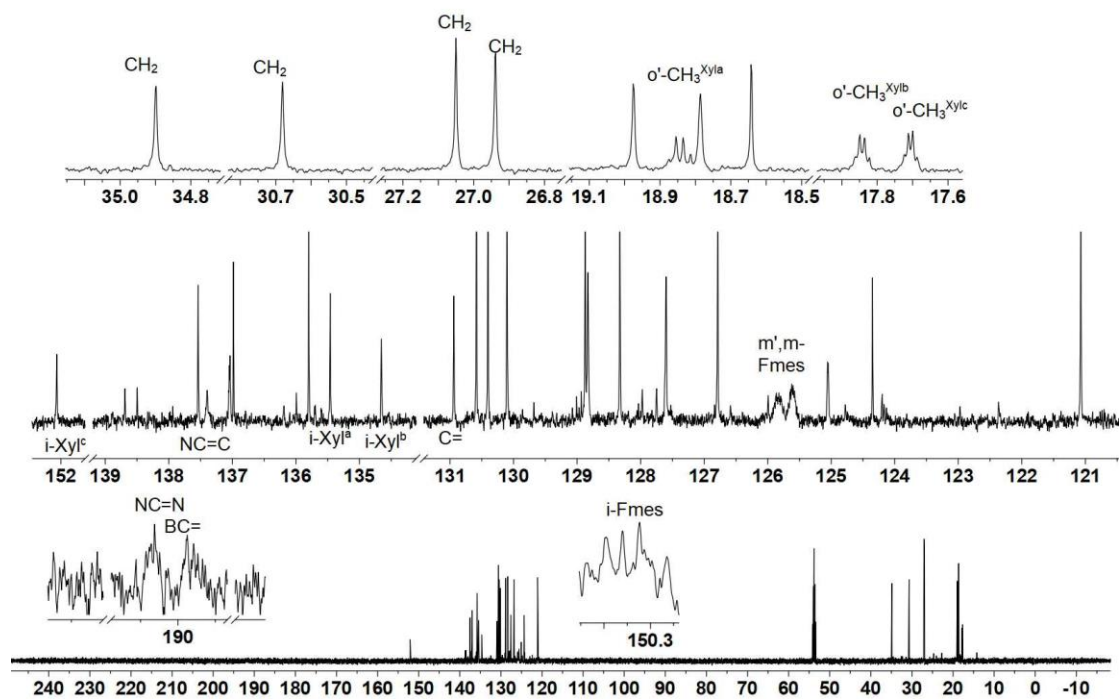


Figure S7.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, methylene chloride- $d_2$ , 299 K) spectrum of compound **10**.

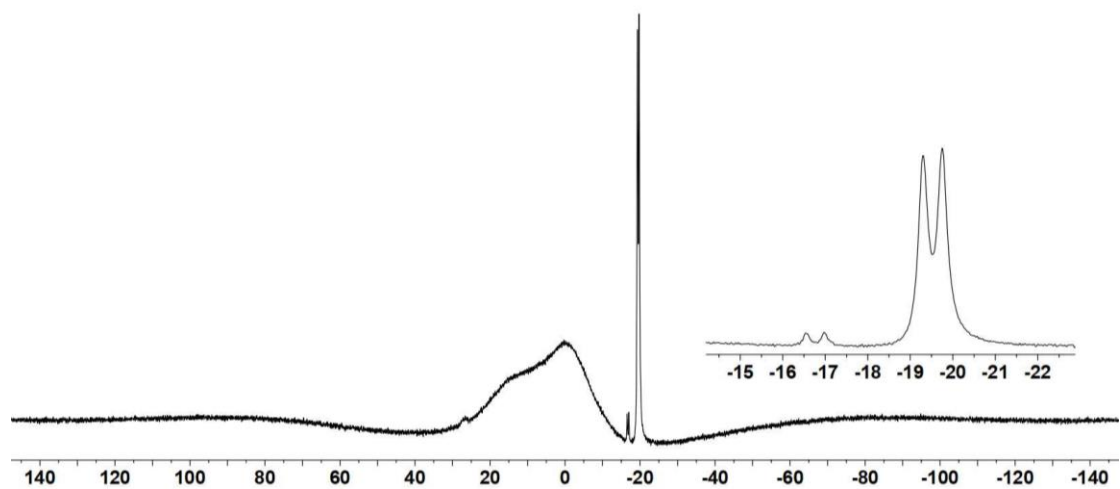


Figure S8.  $^{11}\text{B}$  NMR (192 MHz, methylene chloride- $d_2$ , 299 K) spectrum of compound **10**.



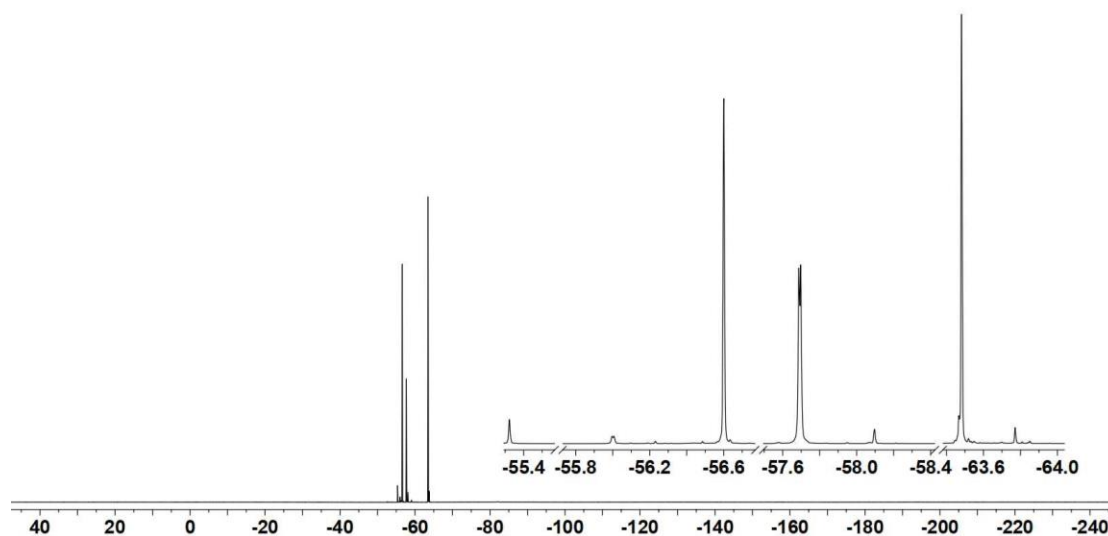


Figure S9.  $^{19}\text{F}$  NMR (564 MHz, methylene chloride- $d_2$ , 253 K) spectrum of compound **10**.

The crystal suitable for X-ray crystal structure analysis was obtained from a solution of compound **10** in pentane at  $-35\text{ }^\circ\text{C}$ .

**X-ray crystal structure analysis of compound 10 (erk9465):** A yellow plate-like specimen of  $\text{C}_{41}\text{H}_{39}\text{BF}_9\text{N}_3$ , approximate dimensions  $0.040\text{ mm} \times 0.090\text{ mm} \times 0.100\text{ mm}$ , was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using an orthorhombic unit cell yielded a total of 6341 reflections to a maximum  $\theta$  angle of  $25.00^\circ$  ( $0.84\text{ \AA}$  resolution), of which 6341 were independent (average redundancy 1.000, completeness = 99.1%,  $R_{\text{sig}} = 4.56\%$ ) and 5202 (82.04%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $\underline{a} = 20.6283(7)\text{ \AA}$ ,  $\underline{b} = 8.9160(2)\text{ \AA}$ ,  $\underline{c} = 19.7224(4)\text{ \AA}$ , volume =  $3627.38(16)\text{ \AA}^3$ , are based upon the refinement of the XYZ-centroids of reflections above  $20\sigma(I)$ . Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9890 and 0.9950. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group  $P2_12_12_1$ , with  $Z = 4$  for the formula unit,  $\text{C}_{41}\text{H}_{39}\text{BF}_9\text{N}_3$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 600 variables converged at  $R1 = 7.81\%$ , for the observed data and  $wR2 = 20.25\%$  for all data. The goodness-of-fit was 1.097. The largest peak in the final difference electron density synthesis was  $0.352\text{ e}^-/\text{\AA}^3$  and the largest hole was  $-0.250\text{ e}^-/\text{\AA}^3$  with an RMS deviation of  $0.060\text{ e}^-/\text{\AA}^3$ . On the basis of the final model, the calculated density was  $1.384\text{ g/cm}^3$  and  $F(000)$ , 1568  $e^-$ . The hydrogen atoms at B1 and N2 atoms were refined freely. CCDC Nr.: 2064641.

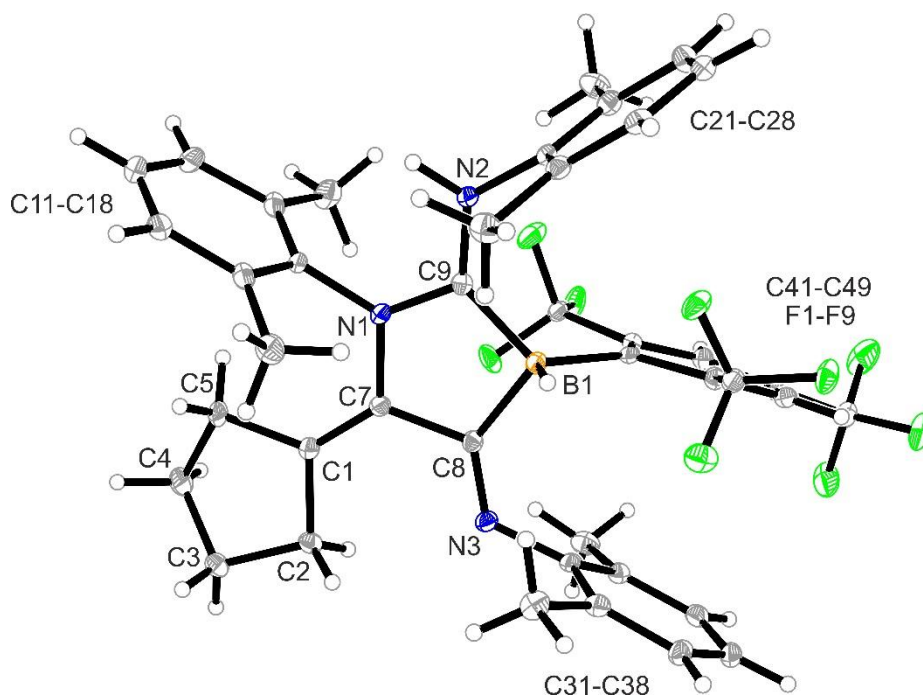
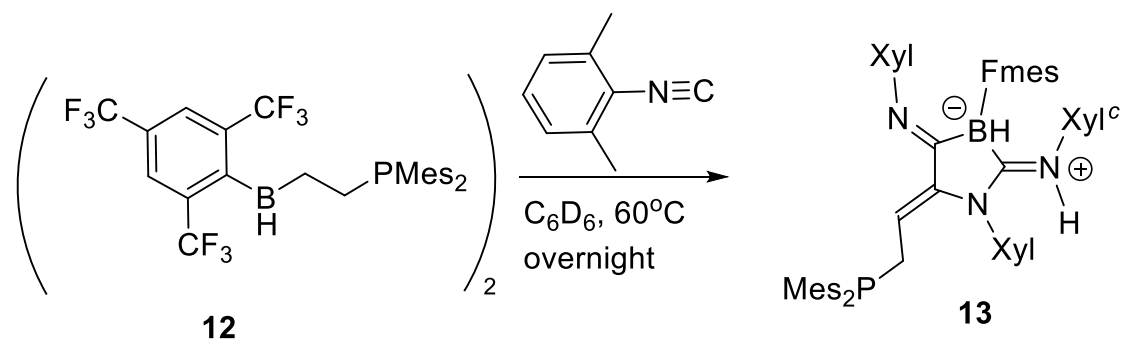


Figure S10. Crystal structure of compound **10** (thermal ellipsoids are shown at 15% probability).

## Preparation of compound **13**



Scheme 3.

At room temperature, 2,6-dimethylphenyl isocyanide (117.9 mg, 9 mmol, 3 eq.) was added to a solution of compound **12** (177 mg, 3 mmol, 1 eq.) in  $C_6D_6$  (2 mL) under an Argon atmosphere. Then the mixture was stirred overnight at 60 °C to give a red solution. The volatiles were removed in vacuo and the residue was washed with pentane (3 \*10 mL) to give the product as a light-yellow solid (183 mg, 62 % yield)

**HRMS** for  $C_{56}H_{57}BF_9N_3P^+$   $[M+H]^+$ : calc. 984.4234; found: 984.4239.

**$^1H$  NMR** (600 MHz, methylene chloride- $d_2$ , 243 K):  $\delta$  = [7.88, 7.42](each s, each 1H, *m*-Fmes), [7.38 (*p*), 7.35 (*m*), 7.33 (*m*)](each m, each 1H, Xyl<sup>a</sup>), 7.07 (m, 1H, NH), [6.90 (m, 2H, *m,p*), 6.58 (d,  $^3J_{HH}$  = 7.1 Hz, 1H, *m*)](Xyl<sup>c</sup>), [6.74 (d,  $^3J_{HH}$  = 7.4 Hz), *m*), 6.51 (t,  $^3J_{HH}$  = 7.4 Hz, *p*), 6.36 (d,  $^3J_{HH}$  = 7.4 Hz, *m*)](each 1H, Xyl<sup>b</sup>), [6.73, 6.70](each s, each 2H, *m*-Mes), 5.77 (td,  $^3J_{HH}$  =  $^3J_{PH}$  = 9.6 Hz,  $^3J_{HH}$  = 7.8 Hz,

1H, HC=), [2.76 (dd,  $^2J_{\text{HH}} = 12.7$  Hz,  $^3J_{\text{HH}} = 7.8$  Hz), 2.70 (dd,  $^2J_{\text{HH}} = 12.7$  Hz,  $^3J_{\text{HH}} = 9.6$  Hz)](each 1H, CH<sub>2</sub>P), [2.47, 2.25](each s, each 3H, *o*-CH<sub>3</sub><sup>Xyl<sup>a</sup></sup>), [2.18, 2.16](each s, each 3H, *p*-Mes), [2.10, 1.65](each s, each 3H, *o*-CH<sub>3</sub><sup>Xyl<sup>c</sup></sup>), [2.013, 2.008](each s, each 6H, *o*-CH<sub>3</sub><sup>Mes</sup>), [1.96, 1.39](each s, each 3H, *o*-CH<sub>3</sub><sup>Xyl<sup>b</sup></sup>),

**<sup>13</sup>C{<sup>1</sup>H} NMR** (151 MHz, methylene chloride-*d*<sub>2</sub>, 243 K):  $\delta = 191.6$  (br, NC=NH), 185.3 (br, BC=), 150.8 (*i*-Xyl<sup>b</sup>), 149.2 (br, *i*-Fmes), 142.7 (d,  $^3J_{\text{PC}} = 12.9$  Hz, C=), [141.8 (d,  $^2J_{\text{PC}} = 13.6$  Hz), 141.5 (d,  $^2J_{\text{PC}} = 13.5$  Hz)](*o*-Mes), [137.7, 137.6](*p*-Mes), [137.4 (q,  $^2J_{\text{FC}} = 28.9$  Hz), 135.0 (q,  $^2J_{\text{FC}} = 29.6$  Hz)](*o*-Fmes), [137.2, 136.6](*o*-Xyl<sup>a</sup>), [136.7, 135.0](*o*-Xyl<sup>c</sup>), 133.7 (*i*-Xyl<sup>a</sup>), 133.4 (*i*-Xyl<sup>c</sup>), [132.5 (d,  $^1J_{\text{PC}} = 25.0$  Hz), 132.1 (d,  $^1J_{\text{PC}} = 24.7$  Hz)](*i*-Mes), [130.7, 129.69](*m'*-Xyl<sup>a</sup>), 130.6 (*p*-Xyl<sup>a</sup>), [129.8 (d,  $^3J_{\text{PC}} = 2.7$  Hz), 129.67 (d,  $^3J_{\text{PC}} = 3.3$  Hz)](*m*-Mes), 128.6 (*p*-Xyl<sup>c</sup>), [128.4, 127.8](*m*-Xyl<sup>c</sup>), 127.2 (q,  $^2J_{\text{FC}} = 33.8$  Hz, *p*-Fmes), [126.9, 126.2](*m*-Xyl<sup>b</sup>), [125.6, 124.7](*o*-Xyl<sup>b</sup>), [125.5, 125.1](br m, *m*-Fmes), [124.4 (q,  $^1J_{\text{FC}} = 275.3$  Hz), 123.2 (q,  $^1J_{\text{FC}} = 273.3$  Hz), 122.7 (q,  $^1J_{\text{FC}} = 275.3$  Hz)](CF<sub>3</sub>), 120.8 (*p*-Xyl<sup>b</sup>), 104.2 (d,  $^2J_{\text{PC}} = 16.2$  Hz, HC=), 24.1 (d,  $^1J_{\text{PC}} = 16.0$  Hz, CH<sub>2</sub>P), [22.9 (d,  $^3J_{\text{PC}} = 12.6$  Hz), 22.7 (d,  $^3J_{\text{PC}} = 13.1$  Hz)](*o*-CH<sub>3</sub><sup>Mes</sup>), [20.59, 20.55](*p*-CH<sub>3</sub><sup>Mes</sup>), [19.2, 17.6 (m)](*o*-CH<sub>3</sub><sup>Xyl<sup>c</sup></sup>), [18.5, 17.8](each br m, *o*-CH<sub>3</sub><sup>Xyl<sup>a</sup></sup>), [18.4, 17.1](*o*-CH<sub>3</sub><sup>Xyl<sup>b</sup></sup>).

**<sup>11</sup>B NMR** (192 MHz, methylene chloride-*d*<sub>2</sub>, 299 K):  $\delta = -19.5$  (br d,  $^1J_{\text{BH}} \approx 90$  Hz).

**<sup>11</sup>B NMR** (192 MHz, methylene chloride-*d*<sub>2</sub>, 243 K):  $\delta = -19.7$  ( $\nu_{1/2} \approx 260$  Hz).

**<sup>31</sup>P NMR** (243 MHz, methylene chloride-*d*<sub>2</sub>, 243 K):  $\delta = -22.3$  ( $\nu_{1/2} \approx 25$  Hz).

**<sup>19</sup>F NMR** (564 MHz, methylene chloride-*d*<sub>2</sub>, 243 K):  $\delta = -55.6, -57.5$  (each s, each 1F, *o*-CF<sub>3</sub><sup>Fmes</sup>), -63.2 (s, 1F, *p*-CF<sub>3</sub><sup>Fmes</sup>).

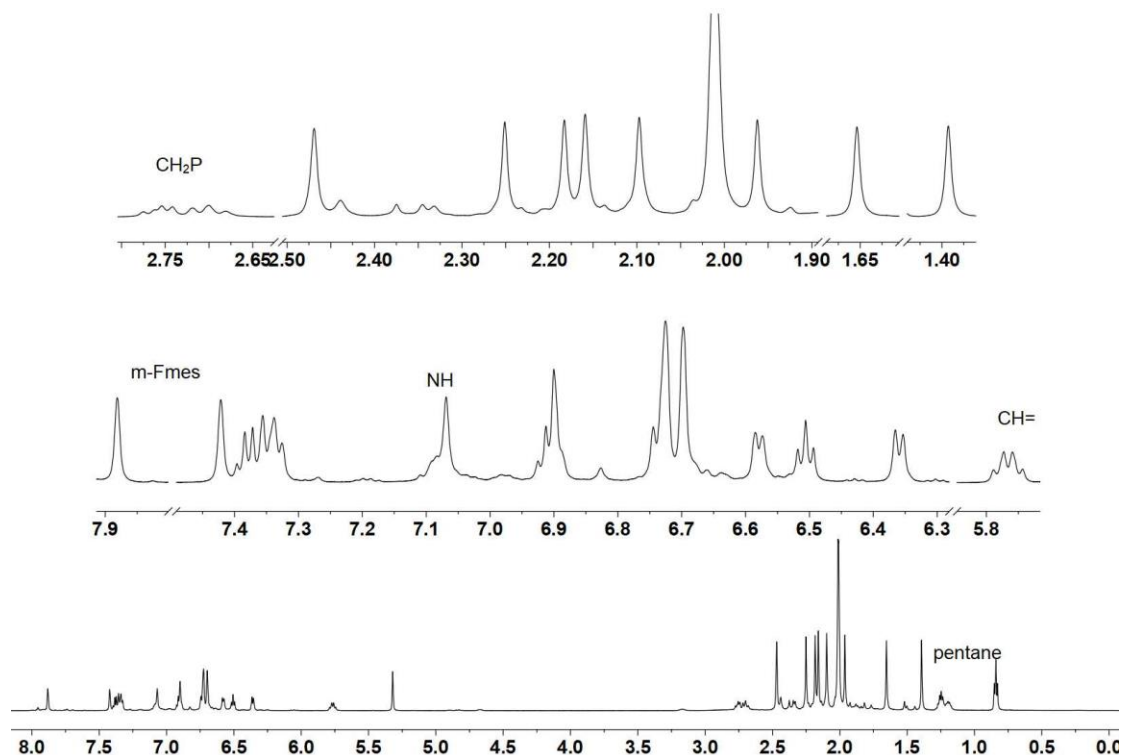


Figure 11. <sup>1</sup>H NMR (600 MHz, methylene chloride-*d*<sub>2</sub>, 243 K) spectrum of compound **13**.

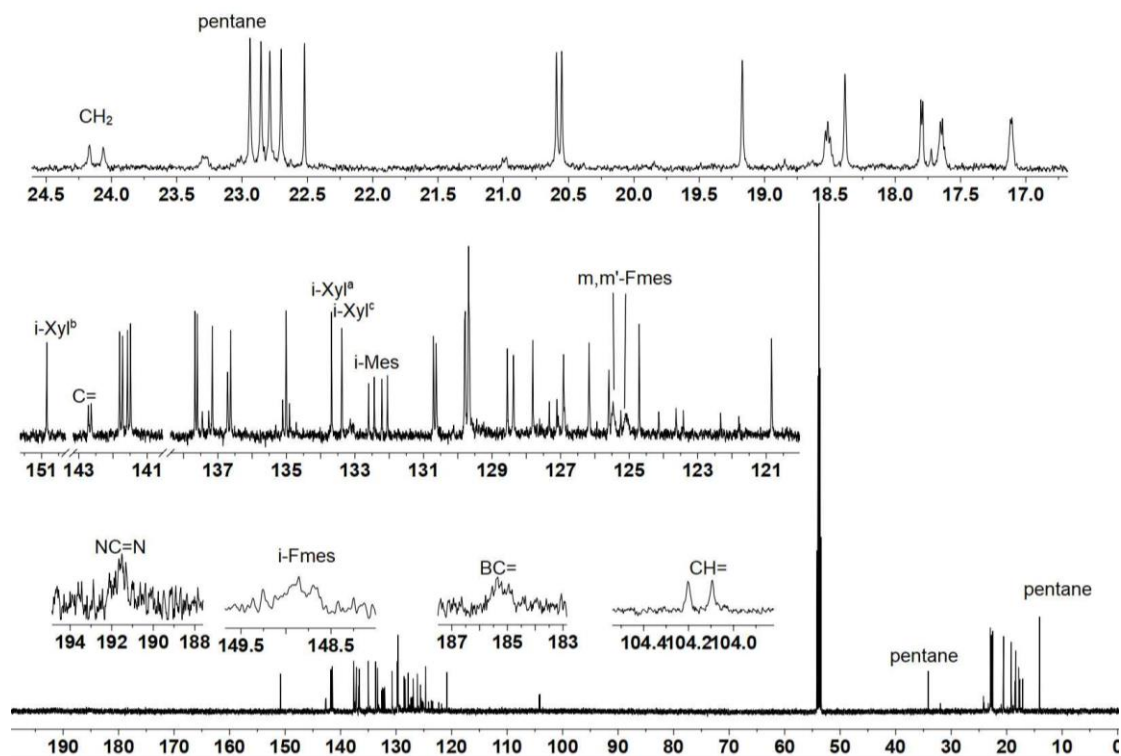


Figure 12.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, methylene chloride- $d_2$ , 243 K) spectrum of compound **13**.

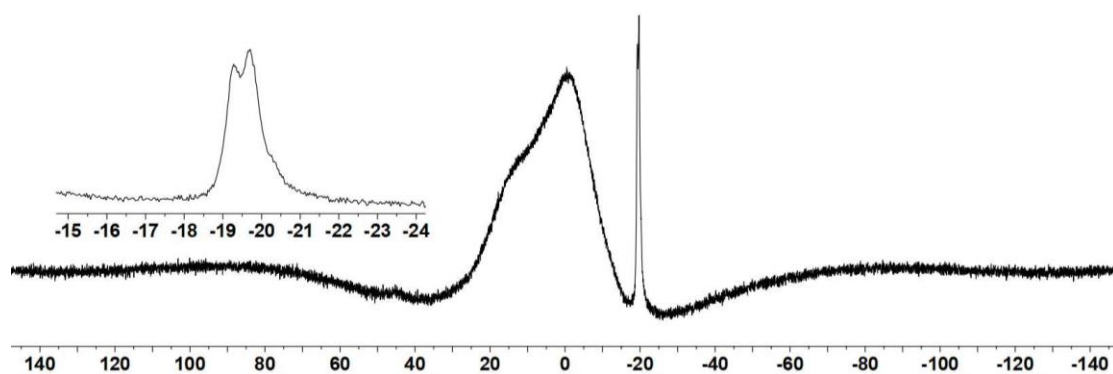


Figure 13.  $^{11}\text{B}$  NMR (192 MHz, methylene chloride- $d_2$ , 299 K) spectrum of compound **13**.

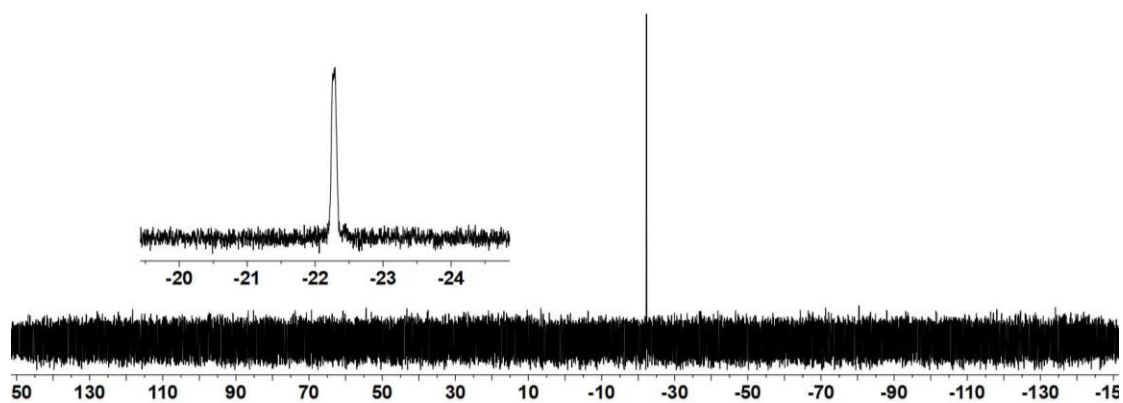


Figure 14.  $^{31}\text{P}$  NMR (192 MHz, methylene chloride- $d_2$ , 243 K) spectrum of compound **13**.

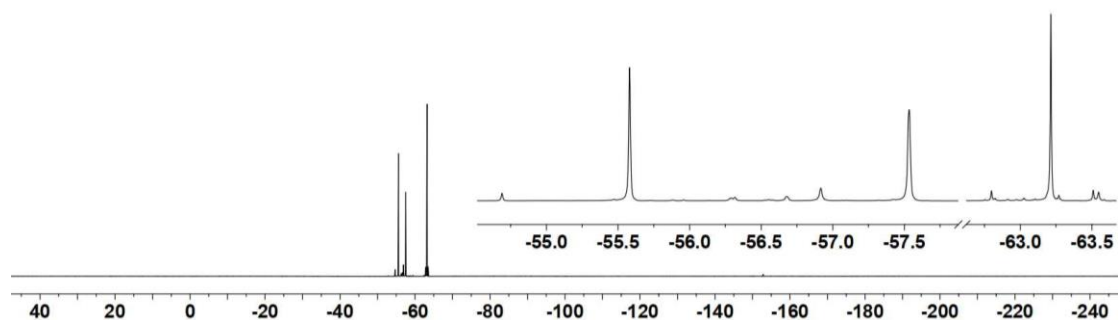


Figure 15.  $^{19}\text{F}$  NMR (564 MHz, methylene chloride- $d_2$ , 243 K) spectrum of compound **13**.

The crystal suitable for X-ray crystal structure analysis was obtained from a solution of compound **13** in pentane.

**X-ray crystal structure analysis of compound 13 (erk9338):** A yellow plate-like specimen of  $\text{C}_{56}\text{H}_{56}\text{BF}_9\text{N}_3\text{P}$ , approximate dimensions 0.040 mm x 0.100 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 17308 reflections to a maximum  $\theta$  angle of  $25.00^\circ$  (0.84 Å resolution), of which 9214 were independent (average redundancy 1.878, completeness = 99.3%,  $R_{\text{int}} = 4.98\%$ ,  $R_{\text{sig}} = 5.76\%$ ) and 6297 (68.34%) were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 13.5769(2)$  Å,  $b = 17.0284(4)$  Å,  $c = 23.6162(5)$  Å,  $\beta = 104.9690(10)^\circ$ , volume =  $5274.62(19)$  Å<sup>3</sup>, are based upon the refinement of the XYZ-centroids of reflections above  $20 \sigma(I)$ . Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9850 and 0.9950. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group  $P2_1/c$ , with  $Z = 4$  for the formula unit,  $\text{C}_{56}\text{H}_{56}\text{BF}_9\text{N}_3\text{P}$ . The final anisotropic full-matrix least-squares refinement on  $F^2$  with 707 variables converged at  $R1 = 6.18\%$ , for the observed data and  $wR2 = 15.64\%$  for all data. The goodness-of-fit was 1.033. The largest peak in the final difference electron density synthesis was  $0.236 \text{ e}^-/\text{Å}^3$  and the largest hole was  $-0.311 \text{ e}^-/\text{Å}^3$  with an RMS deviation of  $0.043 \text{ e}^-/\text{Å}^3$ . On the basis of the final model, the calculated density was  $1.239 \text{ g/cm}^3$  and  $F(000)$ , 2056  $e^-$ . The hydrogens at B1 and N2 atoms were refined freely. CCDC Nr.: 2064642.

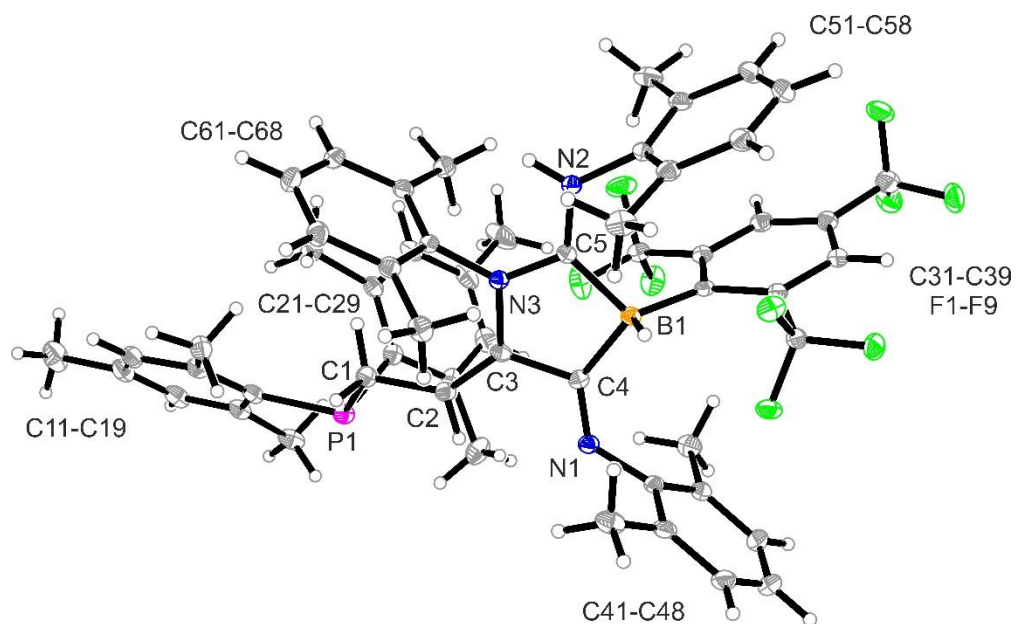


Figure S11. Crystal structure of compound **13** (thermal ellipsoids are shown at 15% probability).

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