

**Electronic Supplementary Information (ESI)**

to

**The pentafluoroethyltrihydridoborate anion:  
From shock sensitive salts to stable  
room temperature ionic liquids**

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**General methods:** Reactions involving air-sensitive compounds were carried out under an inert argon atmosphere with glass tubes equipped with valves with PTFE stems (Rettberg, Göttingen / Young, London) using standard Schlenk line techniques.

**Analytical Instruments:**  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra were recorded at 25 °C either in  $(\text{CD}_3)_2\text{CO}$ ,  $\text{CD}_3\text{CN}$ ,  $\text{thf-d}_8$ ,  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$  on a Bruker Avance 500 or a Bruker Avance 400 spectrometer.  $^{13}\text{C}\{^{11}\text{B}, ^1\text{H}\}$  NMR spectra were recorded on a Bruker Avance 300 spectrometer. For the  $^{13}\text{C}$  NMR spectra concentrated samples (100–500 mg in 0.7 mL  $(\text{CD}_3)_2\text{CO}$ ) were used. NMR signals were referenced against TMS ( $^1\text{H}$  and  $^{13}\text{C}$ ),  $\text{BF}_3\cdot\text{OEt}_2$  ( $^{11}\text{B}$ ) and  $\text{CFCl}_3$  ( $^{19}\text{F}$ ), respectively. Chemical shifts were calibrated against the residual solvent signal and the solvent signal respectively ( $\delta(^1\text{H})$ :  $(\text{CD}_2\text{H})(\text{CD}_3)\text{CO}$  2.05 ppm,  $\text{CDHCl}_2$  5.32 ppm,  $\text{CHCl}_3$  7.26 ppm;  $\delta(^{13}\text{C})$ :  $(\text{CD}_3)_2\text{CO}$  206.26 and 29.84 ppm,  $\text{CDCl}_3$  77.16 ppm,  $\text{CD}_2\text{Cl}_2$  53.84 ppm).<sup>1</sup> IR spectra were recorded at room temperature with a Bruker Alpha spectrometer with an apodized resolution of 4  $\text{cm}^{-1}$  in the attenuated total reflection (ATR) mode in the region of 4000–400  $\text{cm}^{-1}$  using an ATR setup with a diamond crystal. Elemental analyses (C, H, N) were performed with an Euro EA3000 instrument (Elementar Analysensysteme, Germany). DSC measurements were carried out with a Netzsch DSC 204 F1 Phoenix in the temperature range of 25 to –180 °C with a cooling and heating rate of 10  $\text{K min}^{-1}$ . The water content of the solvents was determined via Karl-Fischer titration using a 831 KF Coulometer (Metrohm). The water content of the ionic liquids [EMIm]1 and [BMPL]1 could not be determined via Karl-Fischer titration because the ILs decompose during measurement. All electrochemical studies were performed on neat ionic liquids under an argon atmosphere with a Metrohm PGSTAT30 potentiostat (Metrohm Autolab B.V., Netherlands) and a Microcell HC set-up with a Eurotherm temperature controller (rhd instruments, Germany). A 0.1 mL Pt-cell TSC-70-closed from rhd instruments served as counter electrode and was equipped with a glassy carbon working electrode (surface area:  $3.14 \cdot 10^{-2} \text{ cm}^2$ ). Cyclic voltammetry experiments were performed at 20 °C with a scan rate of 50  $\text{mV}\cdot\text{s}^{-1}$  and an  $\text{Ag}/\text{Ag}^+$  micro reference electrode with acetonitrile as solvent from rhd instruments.

**Chemicals:** All standard chemicals were obtained from commercial sources and used without further purification. Pentafluoroethane was obtained from Solvay Fluor GmbH (Germany). Solvents were dried according to standard protocols<sup>2</sup> and stored in flasks equipped with valves with PTFE stems (Young, London, UK or Rettberg, Göttingen, Germany).  $[\text{Me}_4\text{N}]\text{F}$  were synthesized according to known procedures.<sup>3</sup>

### Syntheses:

**Preparation of  $\text{BH}_3\cdot\text{thf}$  solutions.**  $\text{BH}_3\cdot\text{thf}$  was prepared according to two different methods: **Method A:**  $\text{Na}[\text{BH}_4]$  (2.50 g, 66 mmol) was suspended in thf (100 mL).  $\text{TMSCl}$  (7.63 mL, 6.50 g, 60 mmol) was slowly added dropwise. The resulting mixture was vigorously stirred at r.t. for 24 h. The solution was used without further workup. **Method B:**  $\text{Na}[\text{BH}_4]$  (2.50 g, 66 mmol) was suspended in thf (100 mL). Afterwards iodine (8.3 g, 33 mmol) was added at 0 °C in portions. Each portion of iodine was added after the colour of the suspension had been changed from reddish/brown to light yellow.

**Preparation of  $\text{K}[\text{C}_2\text{F}_5\text{BH}_3]$  (K1) as a solution in thf.** Thf (300 ml) was cooled to  $-78$  °C and degassed.  $\text{C}_2\text{F}_5\text{H}$  (7.20 g, 60.0 mmol) was vacuum transferred into the reaction vessel followed by slow, dropwise addition of a solution of  $n\text{BuLi}$  in hexanes ( $2.5 \text{ mol L}^{-1}$ , 22 mL, 55.0 mmol) under vigorous stirring that resulted in the formation of the  $\text{C}_2\text{F}_5\text{Li}$ . A  $\text{BH}_3\cdot\text{thf}$  solution in tetrahydrofuran ( $0.6 \text{ mol L}^{-1}$ , 100 mL, 60.0 mmol), which was prepared according to method A and was cooled to  $-78$  °C, was added to the  $\text{C}_2\text{F}_5\text{Li}$  solution. The reaction mixture was slowly warmed up to room temperature. Subsequently, it was treated with a solution of  $\text{K}_2\text{CO}_3$  (4.20 g, 30.4 mmol) in  $\text{H}_2\text{O}$  (50 mL) and stirred for 15 h at room temperature. The organic layer was separated, and the remaining aqueous phase was extracted with thf (3 x 30 mL). The combined organic phases were dried with  $\text{K}_2\text{CO}_3$  and filtered. K1 was obtained as a solution in thf, which was kept in a refrigerator at 3 °C and was found to be indefinitely stable. Yield: 150 ml,  $0.20 \text{ mol L}^{-1}$  in thf (30.0 mmol, 55%, calculated for  $n\text{BuLi}$ ).

**WARNING! Isolation of neat, colourless  $\text{K}[\text{C}_2\text{F}_5\text{BH}_3]$  (K1) by removal of all volatiles or by precipitation has to be avoided because the solid is highly shock**

**sensitive. Attempted removal of small amounts (<50 mg) of solid K1 with a spatula from a glass frit caused explosions (see shock sensitivity of salts 1).**

$^1\text{H}$  NMR (199.93 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 0.63$  ppm (qtq, 3H,  $^1J(^{11}\text{B}, ^1\text{H}) = 84.7$  Hz,  $^3J(^{19}\text{F}, ^1\text{H}) = 27.8$  Hz,  $^4J(^{19}\text{F}, ^1\text{H}) = 4.0$  Hz,  $\text{BH}_3$ ).

$^{11}\text{B}$  (64.14 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -33.3$  ppm (qt,  $^1J(^{11}\text{B}, ^1\text{H}) = 84.7$  Hz,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz).

$^{11}\text{B}\{^1\text{H}\}$  NMR (64.14 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -33.3$  ppm (t,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz).

$^{19}\text{F}$  NMR (188.12 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -84.4$  (s, 3F,  $\text{CF}_3$ ),  $-110.9$  ppm (qq, 2F,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz,  $^3J(^{19}\text{F}, ^1\text{H}) = 27.8$  Hz,  $\text{CF}_2$ ).

$^{19}\text{F}\{^1\text{H}\}$  NMR (188.12 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -84.4$  (s, 3F,  $\text{CF}_3$ ),  $-110.9$  ppm (q, 2F,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz,  $\text{CF}_2$ ).

**Preparation of  $\text{K}[\text{C}_2\text{F}_5\text{BH}_3]$  (K1) as a solution in  $\text{CH}_3\text{CN}$ .** The synthesis of solutions in acetonitrile have been performed analogously to the preparations of solutions in thf. But the extraction of K1 from aqueous solution was conducted with acetonitrile giving K1 in  $\text{CH}_3\text{CN}$  ( $0.1 \text{ mol L}^{-1}$ ) with a yield of 55% (calculated for  $n\text{BuLi}$ ).

**Preparation of  $\text{Cs}[\text{C}_2\text{F}_5\text{BH}_3]$  (Cs1) as a solution in thf.** Thf (300 mL) was cooled to  $-78$  °C and degassed.  $\text{C}_2\text{F}_5\text{H}$  (7.20 g, 60.0 mmol) was condensed in and a solution of  $n\text{BuLi}$  in hexanes ( $2.5 \text{ mol L}^{-1}$ , 22 mL, 55.0 mmol) was slowly (dropwise) added to the  $\text{C}_2\text{F}_5\text{H}$  solution in thf under vigorous stirring that resulted in the formation of the  $\text{C}_2\text{F}_5\text{Li}$ . A  $\text{BH}_3 \cdot \text{thf}$  solution ( $0.6 \text{ mol L}^{-1}$ , 100 mL, 60.0 mmol), which was synthesized via method A and cooled to  $-78$  °C, was transferred to the  $\text{C}_2\text{F}_5\text{Li}$  solution in thf. The reaction mixture was slowly warmed up to room temperature and subsequently treated with a solution of  $\text{Cs}_2\text{CO}_3$  (8.90 g, 27.3 mmol) in  $\text{H}_2\text{O}$  (50 mL). After further stirring of the reaction mixture for 20 h at room temperature, the organic layer was separated, and the remaining aqueous phase was extracted with thf (3 x 100 mL). The combined organic phases were concentrated under reduced pressure up to a residual volume of approximately 100 mL, which was dried with  $\text{Cs}_2\text{CO}_3$  and filtered.  $\text{Cs}[\text{C}_2\text{F}_5\text{BH}_3]$  was obtained as a solution in thf. Yield: 110 mL,  $0.18 \text{ mol L}^{-1}$  in thf (19.8 mmol, 36%, calculated for  $n\text{BuLi}$ ).

**WARNING! Isolation of neat, colourless Cs[C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>] (Cs1) by removal of all volatiles has to be avoided because the solid is highly shock sensitive (see shock sensitivity of salts 1).**

<sup>1</sup>H NMR (199.93 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 0.63 ppm (qtq, 3H, <sup>1</sup>J(<sup>11</sup>B,<sup>1</sup>H) = 84.7 Hz, <sup>3</sup>J(<sup>19</sup>F,<sup>1</sup>H) = 27.8 Hz, <sup>4</sup>J(<sup>19</sup>F,<sup>1</sup>H) = 4.0 Hz, BH<sub>3</sub>).

<sup>11</sup>B (64.14 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -33.3 ppm (qt, <sup>1</sup>J(<sup>11</sup>B,<sup>1</sup>H) = 84.7 Hz, <sup>2</sup>J(<sup>19</sup>F,<sup>11</sup>B) = 18.3 Hz).

<sup>11</sup>B{<sup>1</sup>H} NMR (64.14 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -33.3 ppm (t, <sup>2</sup>J(<sup>19</sup>F,<sup>11</sup>B) = 18.3 Hz).

<sup>19</sup>F NMR (188.12 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -84.4 (s, 3F, CF<sub>3</sub>), -110.9 ppm (qq, 2F, <sup>2</sup>J(<sup>19</sup>F,<sup>11</sup>B) = 18.3 Hz, <sup>3</sup>J(<sup>19</sup>F,<sup>1</sup>H) = 27.8 Hz, CF<sub>2</sub>).

<sup>19</sup>F{<sup>1</sup>H} NMR (188.12 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -84.4 (s, 3F, CF<sub>3</sub>), -110.9 ppm (q, 2F, <sup>2</sup>J(<sup>19</sup>F,<sup>11</sup>B) = 18.3 Hz, CF<sub>2</sub>).

**Preparation of [nBu<sub>4</sub>N][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>] ([nBu<sub>4</sub>N]1).** C<sub>2</sub>F<sub>5</sub>H (22.8 g, 190.0 mmol) was transferred to thf (200 mL) at -78 °C. A solution of nBuLi in hexanes (2.5 mol L<sup>-1</sup>, 74 mL, 185.0 mmol) was slowly added to the C<sub>2</sub>F<sub>5</sub>H solution in thf under vigorous stirring that resulted in the formation of the C<sub>2</sub>F<sub>5</sub>Li. A solution of BH<sub>3</sub> in thf, which was prepared according to method A (0.85 mol L<sup>-1</sup>, 225 mL, 191.3 mmol) and cooled to -78 °C, was added to the C<sub>2</sub>F<sub>5</sub>Li solution in thf. The reaction mixture was slowly warmed up to room temperature, treated with a solution of K<sub>2</sub>CO<sub>3</sub> (13.8 g, 100 mmol) in H<sub>2</sub>O (50 mL), and stirred at room temperature for 12 h. Most of the thf was removed under reduced pressure. An aqueous solution of [nBu<sub>4</sub>N]Br (190.0 mmol, 61.25 g, 100 mL) was slowly added to residual thf solution. The solid precipitate that had formed was filtered off and dried in a vacuum. [nBu<sub>4</sub>N]1 was obtained as a white solid. Yield: 41.96 g (111.8 mmol, 60%, calculated for nBuLi).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 3.5–3.3 (m, 8H, NCH<sub>2</sub>), 1.8–1.7 (quintet, 8H, <sup>3</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 7.4 Hz, CH<sub>2</sub>), 1.40 (sextet, 8H, <sup>3</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 7.5 Hz, CH<sub>2</sub>), 0.98 (t, 12H, <sup>3</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 7.4 Hz, CH<sub>3</sub>), 0.63 ppm (qtq, 3H, <sup>1</sup>J(<sup>11</sup>B,<sup>1</sup>H) = 84.7 Hz, <sup>3</sup>J(<sup>19</sup>F,<sup>1</sup>H) = 27.8 Hz, <sup>4</sup>J(<sup>19</sup>F,<sup>1</sup>H) = 4.0 Hz, BH<sub>3</sub>).

$^1\text{H}\{^{11}\text{B}\}$  NMR (500.13 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 3.5\text{--}3.3$  (m, 8H,  $\text{NCH}_2$ ), 1.8–1.7 (m, 8H,  $\text{CH}_2$ ), 1.40 (m, 8H,  $^3J(^1\text{H},^1\text{H}) = 7.4$  Hz,  $\text{CH}_2$ ), 0.98 (t, 12H,  $^3J(^1\text{H},^1\text{H}) = 7.4$  Hz,  $\text{CH}_3$ ), 0.63 ppm (tq, 3H,  $^3J(^{19}\text{F},^1\text{H}) = 27.9$  Hz,  $^4J(^{19}\text{F},^1\text{H}) = 3.9$  Hz,  $\text{BH}_3$ ).

$^{11}\text{B}$  (160.46 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -33.3$  ppm (qt,  $^1J(^{11}\text{B},^1\text{H}) = 84.7$  Hz,  $^2J(^{19}\text{F},^{11}\text{B}) = 18.3$  Hz).

$^{11}\text{B}\{^1\text{H}\}$  NMR (160.46 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -33.3$  ppm (t,  $^2J(^{19}\text{F},^{11}\text{B}) = 18.3$  Hz).

$^{19}\text{F}$  NMR (470.59 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -84.4$  (s, 3F,  $\text{CF}_3$ ),  $-110.9$  ppm (qq, 2F,  $^2J(^{19}\text{F},^{11}\text{B}) = 18.3$  Hz,  $^3J(^{19}\text{F},^1\text{H}) = 27.8$  Hz,  $\text{CF}_2$ ).

$^{19}\text{F}\{^1\text{H}\}$  NMR (376.75 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -84.4$  (s, 3F,  $\text{CF}_3$ ),  $-110.9$  ppm (q, 2F,  $^2J(^{19}\text{F},^{11}\text{B}) = 18.3$  Hz,  $\text{CF}_2$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.76 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 59.4$  (t, 4C,  $^1J(^{14}\text{N},^{13}\text{C}) = 2.1$  Hz,  $\text{NCH}_2$ ), 24.4 (s, 4C,  $\text{CH}_2$ ), 20.4 (s, 4C,  $\text{CH}_2$ ), 13.8 ppm (s, 4C,  $\text{CH}_3$ ).

$^{13}\text{C}\{^{11}\text{B},^1\text{H}\}$  NMR (75.48 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 134.3$  (tq, 1C,  $\text{CF}_2$ ,  $^1J(^{19}\text{F},^{13}\text{C}) = 256.1$  Hz,  $^3J(^{19}\text{F},^{13}\text{C}) = 35.1$  Hz), 124.3 (qt, 1C,  $\text{CF}_3$ ,  $^1J(^{19}\text{F},^{13}\text{C}) = 284.8$  Hz,  $^3J(^{19}\text{F},^{13}\text{C}) = 35.8$  Hz), 59.4 (t, 4C,  $^1J(^{14}\text{N},^{13}\text{C}) = 2.1$  Hz,  $\text{NCH}_2$ ), 24.4 (s, 4C,  $\text{CH}_2$ ), 20.4 (s, 4C,  $\text{CH}_2$ ), 13.8 ppm (s, 4C,  $\text{CH}_3$ ).

Anal. Calcd for  $\text{C}_{18}\text{H}_{39}\text{BF}_5\text{N}$ : C, 57.60; H, 10.47; N, 3.73%. Found: C, 57.82; H, 10.62; N, 3.67%.

**Preparation of  $[\text{Et}_4\text{N}][\text{C}_2\text{F}_5\text{BH}_3]$  ( $[\text{Et}_4\text{N}]\mathbf{1}$ ).** Thf (250 ml) was cooled to  $-78$  °C and degassed.  $\text{C}_2\text{F}_5\text{H}$  (22.8 g, 190.0 mmol) was condensed to the thf followed by slow, dropwise addition of a solution of  $n\text{BuLi}$  in hexanes ( $2.3$  mol  $\text{L}^{-1}$ , 74 mL, 170.2 mmol) under vigorous stirring that resulted in the formation of the  $\text{C}_2\text{F}_5\text{Li}$ . A solution of  $\text{BH}_3\cdot\text{thf}$  in thf, which was synthesized via method A ( $0.76$  mol  $\text{L}^{-1}$ , 250 mL, 190.0 mmol) and cooled to  $-78$  °C, was added to the solution of  $\text{C}_2\text{F}_5\text{Li}$  in thf. The reaction mixture was slowly warmed up to room temperature. The mixture was treated with a solution of  $\text{K}_2\text{CO}_3$  (13.8 g, 100 mmol) in  $\text{H}_2\text{O}$  (200.0 mL) and stirred at room temperature for 12 h. Most of the thf was removed under reduced pressure and the remaining aqueous phase was slowly mixed with a solution of  $[\text{Et}_4\text{N}]\text{Br}$  (42.0 g, 199.8 mmol) in water (100 mL). A solid precipitate was filtered off and dried in a vacuum (1st crop). The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 30 mL) and the combined organic phases were

dried under reduced pressure (2nd crop). [Et<sub>4</sub>N]1 was obtained as a white solid. Yield: 23.7 g (90.1 mmol, 47% calculated for BH<sub>3</sub>·thf), (1st crop: 16.7 g, 63.5 mmol; 2nd crop: 7.0 g, 26.6 mmol).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 3.1 (q, 8C, <sup>3</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 7.3 Hz, CH<sub>2</sub>), 1.2 (tt, 12C, <sup>3</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 7.3 Hz, <sup>4</sup>J(<sup>15</sup>N,<sup>1</sup>H) = 1.9 Hz, CH<sub>3</sub>), 0.65 ppm (qtq, 3H, <sup>1</sup>J(<sup>11</sup>B,<sup>1</sup>H) = 84.7 Hz, <sup>3</sup>J(<sup>19</sup>F,<sup>1</sup>H) = 27.3 Hz, <sup>4</sup>J(<sup>19</sup>F,<sup>1</sup>H) = 3.7 Hz, BH<sub>3</sub>).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 3.41 (q, 8C, <sup>3</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 7.3 Hz, CH<sub>2</sub>), 1.34 (tt, 12C, <sup>3</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 7.3 Hz, <sup>4</sup>J(<sup>15</sup>N,<sup>1</sup>H) = 1.9 Hz, CH<sub>3</sub>) 0.65 ppm (tq, 3H, <sup>3</sup>J(<sup>19</sup>F,<sup>1</sup>H) = 27.9 Hz, <sup>4</sup>J(<sup>19</sup>F,<sup>1</sup>H) = 3.9 Hz, BH<sub>3</sub>).

<sup>11</sup>B NMR (160.46 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -33.3 ppm (qt, <sup>1</sup>J(<sup>11</sup>B,<sup>1</sup>H) = 84.7 Hz, <sup>2</sup>J(<sup>19</sup>F,<sup>11</sup>B) = 18.3 Hz).

<sup>11</sup>B{<sup>1</sup>H} NMR (160.46 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -33.3 ppm (t, <sup>2</sup>J(<sup>19</sup>F,<sup>11</sup>B) = 18.3 Hz).

<sup>19</sup>F NMR (470.59 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -84.4 (s, 3F, CF<sub>3</sub>), -110.9 ppm (qq, 2F, <sup>2</sup>J(<sup>19</sup>F,<sup>11</sup>B) = 18.3 Hz, <sup>3</sup>J(<sup>19</sup>F,<sup>1</sup>H) = 27.8 Hz, CF<sub>2</sub>).

<sup>19</sup>F{<sup>1</sup>H} NMR (376.75 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -84.7 (s, 3F, CF<sub>3</sub>), -110.9 ppm (q, 2F, <sup>2</sup>J(<sup>19</sup>F,<sup>11</sup>B) = 18.3 Hz, CF<sub>2</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.76 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 134.4 (m, 1C, CF<sub>2</sub>), 124.2 (m, 1C, CF<sub>3</sub>), 52.9 (t, <sup>1</sup>J(<sup>14</sup>N,<sup>13</sup>C) = 3.0 Hz, 4C, NCH<sub>2</sub>), 7.6 ppm (s, 4C, CH<sub>3</sub>).

<sup>13</sup>C{<sup>11</sup>B,<sup>1</sup>H} NMR (75.48 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 134.2 (tq, 1C, CF<sub>3</sub>, <sup>1</sup>J(<sup>19</sup>F,<sup>13</sup>C) = 134.2 Hz, <sup>3</sup>J(<sup>19</sup>F,<sup>13</sup>C) = 34.7 Hz), 124.6 (qt, 1C, CF<sub>2</sub>, <sup>1</sup>J(<sup>19</sup>F,<sup>13</sup>C) = 286.9 Hz, <sup>3</sup>J(<sup>19</sup>F,<sup>13</sup>C) = 35.4 Hz), 52.9 (t, 4C, <sup>1</sup>J(<sup>14</sup>N,<sup>13</sup>C) = 3.0 Hz, NCH<sub>2</sub>), 7.6 ppm (s, 4C, CH<sub>3</sub>).

Anal. Calcd for C<sub>10</sub>H<sub>23</sub>BF<sub>5</sub>N: C, 45.65; H, 8.81; N, 5.32%. Found: C, 43.93; H, 8.54; N, 5.24%.

**Preparation of [Ph<sub>4</sub>P][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>] ([Ph<sub>4</sub>P]1).** A BH<sub>3</sub>·thf solution obtained via method B (1.8 mol L<sup>-1</sup>, 2.3 mL, 4.1 mmol) was cooled to -78 °C and degassed. C<sub>2</sub>F<sub>5</sub>H was (132 mg, 1.1 mmol) condensed to this solution. The mixture was stirred vigorously while a solution of *n*BuLi in hexanes (2.5 mol L<sup>-1</sup>, 0.4 mL, 1.0 mmol) was added dropwise. The reaction mixture was slowly warmed up to room temperature. An aqueous solution of

$\text{K}_2\text{CO}_3$  (1.00 g, 7.2 mmol, 10 mL) was added to the colourless solution and the mixture was stirred for 30 min. A solution of  $[\text{Ph}_4\text{P}]\text{Br}$  (343 mg, 0.8 mmol) in  $\text{H}_2\text{O}$  (5 mL) was added and the mixture was stirred for 15 h. The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 10 mL), the combined organic phases were dried with  $\text{MgSO}_4$  and filtered. All volatile compounds were removed in a vacuum. The remainder was washed with  $\text{H}_2\text{O}$  (10 mL) to give a white solid after drying in a fine vacuum. Yield: 0.29 g (0.6 mmol, 60% calculated for  $n\text{BuLi}$ ).

$^1\text{H}$  NMR (500.13 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  = 8.06-7.94 (m, 4H,  $\text{PPh}_4$ ), 7.94-7.81 (m, 16H,  $\text{PPh}_4$ ), 0.59 ppm (qtq, 3H,  $^1J(^{11}\text{B}, ^1\text{H}) = 84.8$  Hz,  $^3J(^{19}\text{F}, ^1\text{H}) = 28.0$  Hz,  $^4J(^{19}\text{F}, ^1\text{H}) = 3.91$  Hz,  $\text{BH}_3$ ).

$^1\text{H}\{^{11}\text{B}\}$  NMR (500.13 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  = 8.07-7.94 (m, 4H,  $\text{PPh}_4$ ), 7.94-7.78 (m, 16H,  $\text{PPh}_4$ ), 0.71 (tq, 3H,  $^3J(^{19}\text{F}, ^1\text{H}) = 28.0$  Hz,  $^4J(^{19}\text{F}, ^1\text{H}) = 3.94$  Hz,  $\text{BH}_3$ ).

$^{11}\text{B}$  NMR (160.46 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  = -33.3 ppm (qt,  $^1J(^{11}\text{B}, ^1\text{H}) = 84.9$  Hz,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.2$  Hz).

$^{11}\text{B}\{^1\text{H}\}$  NMR (160.46 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  = -33.3 ppm (t,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.2$  Hz).

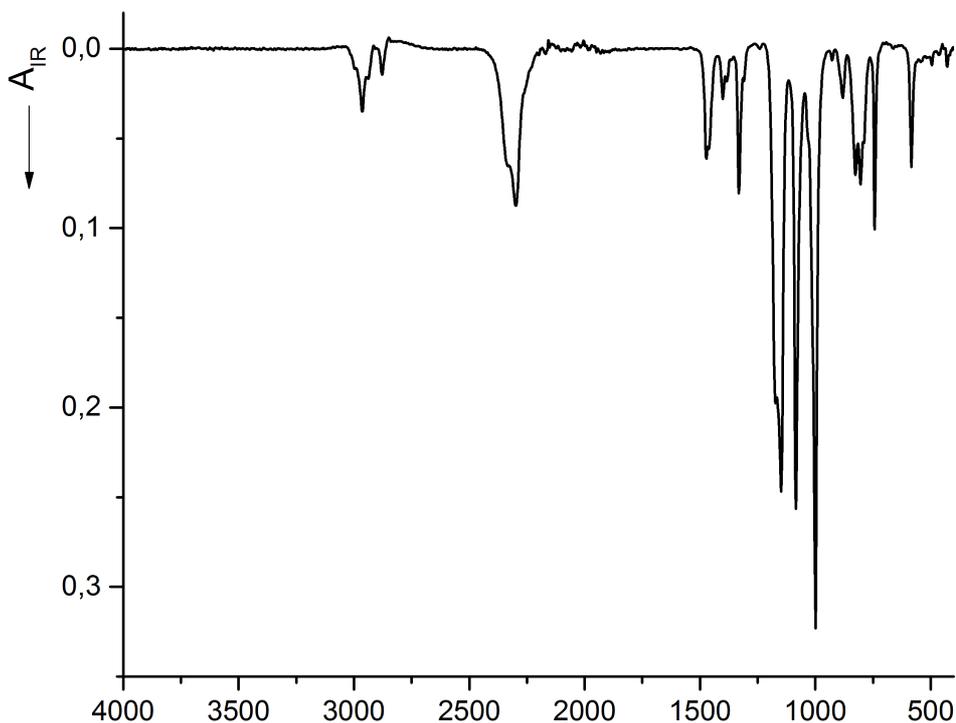
$^{19}\text{F}$  NMR (470.59 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  = -84.4 (s, 3F,  $\text{CF}_3$ ), -110.9 ppm (qq, 2F,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz,  $^3J(^{19}\text{F}, ^1\text{H}) = 27.8$  Hz,  $\text{CF}_2$ ).

$^{19}\text{F}\{^1\text{H}\}$  NMR (376.75 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  = -84.7 (s, 3F,  $\text{CF}_3$ ), -110.9 ppm (q, 2F,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz,  $\text{CF}_2$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.76 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  = 136.4 (d,  $^4J(^{31}\text{P}, ^{13}\text{C}) = 3.2$  Hz, 4C), 135.6 (d, 8C,  $^2J(^{31}\text{P}, ^{13}\text{C}) = 10.4$  Hz), 131.4 ppm (d, 8C,  $^3J(^{31}\text{P}, ^{13}\text{C}) = 12.9$  Hz), 26.2 (d, 4C,  $^1J(^{31}\text{P}, ^{13}\text{C}) = 89.7$  Hz).

$^{13}\text{C}\{^{11}\text{B}, ^1\text{H}\}$  NMR (75.48 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta$  = 136.4 (d, 4C,  $^4J(^{31}\text{P}, ^{13}\text{C}) = 3.2$  Hz), 135.6 (d, 8C,  $^2J(^{31}\text{P}, ^{13}\text{C}) = 10.4$  Hz), 131.4 ppm (d, 8C,  $^3J(^{31}\text{P}, ^{13}\text{C}) = 12.9$  Hz), 26.2 (d, 4C,  $^1J(^{31}\text{P}, ^{13}\text{C}) = 89.7$  Hz).

Anal. Calcd for  $\text{C}_{26}\text{H}_{23}\text{BF}_5\text{P}$ : C, 66.13; H, 4.91%. Found: C, 66.26; H, 4.98%. IR: 2393  $\text{cm}^{-1}$  ( $\nu(\text{B-H})$ ).



**Figure S1:** IR spectrum of  $[\text{PPh}_4][\text{C}_2\text{F}_5\text{BH}_3]$  ( $[\text{PPh}_4]1$ ).

**Preparation of  $[\text{PBnPh}_3][\text{C}_2\text{F}_5\text{BH}_3]$  ( $[\text{PBnPh}_3]1$ ).** Water (20 mL) was added to a solution of K1 in  $\text{CH}_3\text{CN}$  (0.55 g, 3.2 mmol, 20 mL). Most of the acetonitrile was removed under reduced pressure (liquid remainder of approximately 20 mL). An aqueous solution of  $[\text{PBnPh}_3]\text{Br}$  (1.36 g, 3.1 mmol, 50 mL) was added dropwise. A white precipitate formed that was filtered off and dried in a fine vacuum. Yield: 1.06 g (2.2 mmol, 71%).

$^1\text{H}$  NMR (500.13 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 7.97\text{--}7.73$  (m, 15H,  $\text{PPh}_3$ ), 7.39–7.11 (m, 5H, Bn), 5.10 (d, 2H,  $^2J(^{31}\text{P}, ^1\text{H}) = 14.9$  Hz,  $\text{CH}_2$ ), 0.75 ppm (qtq, 3H,  $^1J(^{11}\text{B}, ^1\text{H}) = 84.7$  Hz,  $^3J(^{19}\text{F}, ^1\text{H}) = 27.3$  Hz,  $^4J(^{19}\text{F}, ^1\text{H}) = 3.7$  Hz,  $\text{BH}_3$ ).

$^1\text{H}\{^{11}\text{B}\}$  NMR (500.13 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 7.97\text{--}7.73$  (m, 15H,  $\text{PPh}_3$ ), 7.39–7.11 (m, 5H, Bn), 5.10 (d, 2H,  $^2J(^{13}\text{C}, ^1\text{H}) = 14.9$  Hz), 0.75 ppm (tq, 3H,  $^3J(^{19}\text{F}, ^1\text{H}) = 28.0$  Hz,  $^4J(^{19}\text{F}, ^1\text{H}) = 3.94$  Hz,  $\text{BH}_3$ ).

$^{11}\text{B}$  NMR (160.46 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -33.3$  ppm (qt,  $^1J(^{11}\text{B}, ^1\text{H}) = 84.9$  Hz,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.2$  Hz).

$^{11}\text{B}\{^1\text{H}\}$  NMR (160.46 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -33.3$  ppm (t,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.2$  Hz).

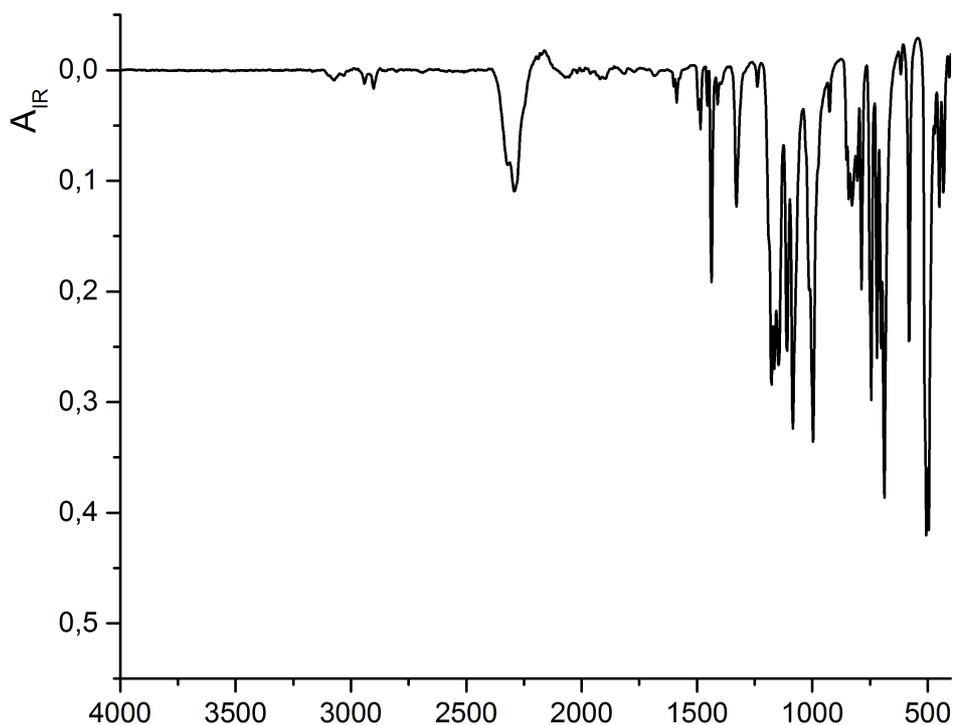
$^{19}\text{F}$  NMR (470.59 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -84.4$  (s, 3F,  $\text{CF}_3$ ),  $-110.9$  ppm (qq, 2F,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz,  $^3J(^{19}\text{F}, ^1\text{H}) = 27.8$  Hz,  $\text{CF}_2$ ).

$^{19}\text{F}\{^1\text{H}\}$  NMR (376.75 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -84.7$  (s, 3F,  $\text{CF}_3$ ),  $-110.9$  ppm (q, 2F,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz,  $\text{CF}_2$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.76 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 136.1$  (d, *p*-CH, 3C), 135.1 (d, 6C, *o*-CH), 131.9 (d, 2C, *o*-CH, Bn-Ring), 131.0 (d, 6C, *m*-CH), 129.7 (d, 1C, *p*-CH, Bn-Ring), 129.4 (d, 2C, *m*-CH, Bn-Ring), 128.4 (d, *i*-CH, 1C, Bn-Ring), 118.6 (d, *i*-CH, 3C), 30.3 ppm (d, 1C,  $\text{CH}_2$ ).

$^{13}\text{C}\{^{11}\text{B}, ^1\text{H}\}$  NMR (75.48 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 136.1$  (d, 3C, *p*-CH), 135.1 (d, 6C, *o*-CH), 131.9 (d, 2C, *o*-CH, Bn-Ring), 131.0 (d, 6C, *m*-CH), 129.7 (d, 1C, *p*-CH, Bn-Ring), 129.4 (d, 2C, *m*-CH, Bn-Ring), 128.4 (d, 1C, *i*-CH, Bn-Ring), 118.6 (d, 3C, *i*-CH), 30.3 ppm (d, 1C,  $\text{CH}_2$ ).

Anal. Calcd for  $\text{C}_{27}\text{H}_{25}\text{BF}_5\text{P}$ : C, 66.69; H, 5.18%. Found: C, 67.00; H, 5.04%. IR: 2291  $\text{cm}^{-1}$  ( $\nu(\text{B-H})$ ).



**Figure S2:** IR spectrum of [PBnPh<sub>3</sub>][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>] ([PBnPh<sub>3</sub>]1).

**Preparation of [EMIm][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>] ([EMIm]1).** A BH<sub>3</sub>·thf solution in thf, synthesized by method A (2.5 mol L<sup>-1</sup>, 33.0 mL, 82.5 mmol) was cooled to -78 °C and degassed. C<sub>2</sub>F<sub>5</sub>H (5.9 g, 49.2 mmol) was condensed into this solution. *n*BuLi in hexanes (2.5 mol L<sup>-1</sup>, 16.4 mL, 41.0 mmol) was slowly added (dropwise) to the mixture of BH<sub>3</sub>·thf and C<sub>2</sub>F<sub>5</sub>H while stirring that resulted in the formation of the C<sub>2</sub>F<sub>5</sub>Li. The reaction mixture was slowly warmed up to room temperature. An aqueous solution of K<sub>2</sub>CO<sub>3</sub> (8.0 g, 57.9 mmol, 80 mL) was added to the colourless solution and the mixture was stirred for 30 min. A solution of [EMIm]Cl (6.0 g, 40.9 mmol) in H<sub>2</sub>O (50 mL) was added. Subsequently, vacuum was applied to remove most of the volatile organic compounds. The liquids remainder was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 40 mL). The combined organic phases were dried with MgSO<sub>4</sub> and filtered. All volatiles were removed under reduced pressure to yield a pale-yellow liquid. Yield: 5.9 g (24.2 mmol, 59% calculated for *n*BuLi).

$^1\text{H}$  NMR (500.13 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 8.96$  (s, 1H, CH), 7.70 (dd, 1H,  $^3J(^1\text{H}, ^1\text{H}) = 1.8$  Hz, CH), 7.62 (dd, 1H, CH,  $^3J(^1\text{H}, ^1\text{H}) = 1.8$  Hz), 4.34 (q, 2H,  $^3J(^1\text{H}, ^1\text{H}) = 7.3$  Hz,  $\text{CH}_2$ ), 3.99 (s, 3H,  $\text{CH}_3$ ), 1.53 (t, 3H,  $^3J(^1\text{H}, ^1\text{H}) = 7.3$  Hz,  $\text{CH}_3$ ), 0.65 ppm (qtq, 3H,  $^1J(^{11}\text{B}, ^1\text{H}) = 84.6$  Hz,  $^3J(^{19}\text{F}, ^1\text{H}) = 27.4$  Hz,  $^4J(^{19}\text{F}, ^1\text{H}) = 3.8$  Hz,  $\text{BH}_3$ ).

$^1\text{H}\{^{11}\text{B}\}$  NMR (500.13 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 8.96$  (s, 1H, CH), 7.70 (dd, 1H,  $^3J(^1\text{H}, ^1\text{H}) = 1.78$  Hz, CH), 7.62 (dd, 1H,  $^3J(^1\text{H}, ^1\text{H}) = 1.78$  Hz, CH), 4.34 (q, 2H,  $^3J(^1\text{H}, ^1\text{H}) = 7.3$ ,  $\text{CH}_2$  Hz), 3.99 (s, 3H,  $\text{CH}_3$ ), 1.53 (t, 3H,  $^3J(^1\text{H}, ^1\text{H}) = 7.3$  Hz,  $\text{CH}_3$ ), 0.57 ppm (tq, 3H,  $^3J(^{19}\text{F}, ^1\text{H}) = 27.4$  Hz,  $^4J(^{19}\text{F}, ^1\text{H}) = 3.8$  Hz,  $\text{BH}_3$ ).

$^{11}\text{B}$  NMR (160.46 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -33.3$  ppm (qt,  $^1J(^{11}\text{B}, ^1\text{H}) = 84.6$  Hz,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.5$  Hz).

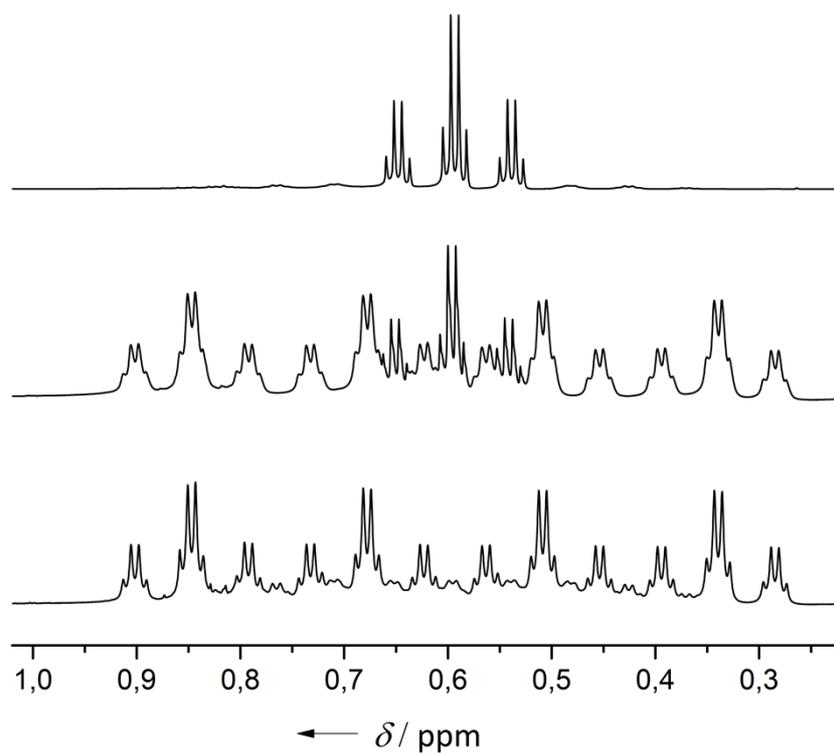
$^{11}\text{B}\{^1\text{H}\}$  NMR (160.46 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -33.3$  ppm (t,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz).

$^{19}\text{F}$  NMR (470.59 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -84.6$  (s, 3F,  $\text{CF}_3$ ),  $-111.1$  ppm (qq, 2F,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.5$  Hz,  $^3J(^{19}\text{F}, ^1\text{H}) = 27.4$  Hz,  $\text{CF}_2$ ).

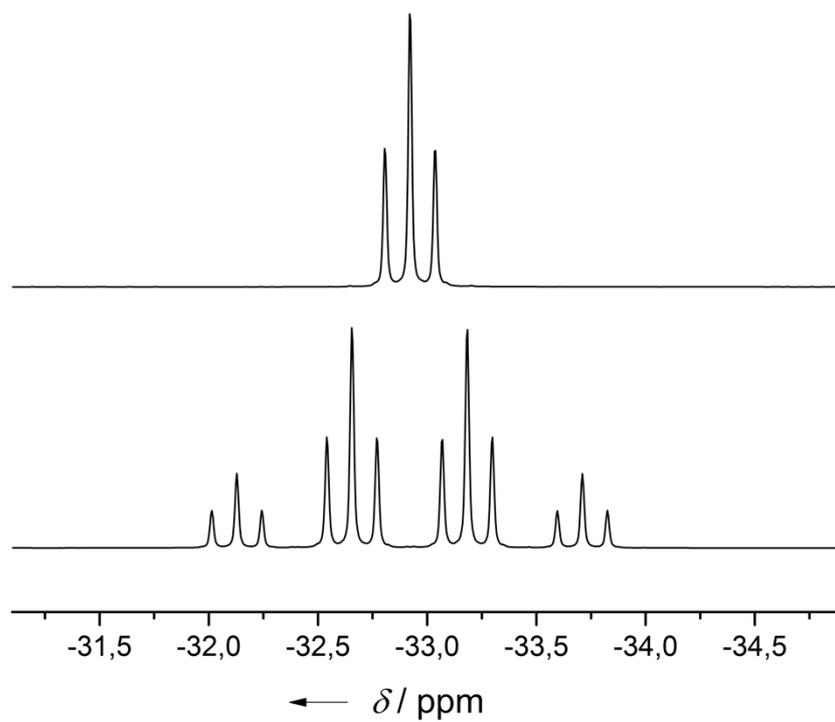
$^{19}\text{F}\{^1\text{H}\}$  NMR (376.76 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -84.7$  (s, 3F,  $\text{CF}_3$ ),  $-110.9$  ppm (q, 2F,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz,  $\text{CF}_2$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.76 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 136.9$  (s, 1C, CH), 133.8 (tqq, 1C,  $^1J(^{19}\text{F}, ^{13}\text{C}) = 242.2$  Hz,  $^2J(^{19}\text{F}, ^{13}\text{C}) = 35.2$  Hz,  $\text{CF}_2$ ), 124.4 (s, 1C, CH), 123.7 (qtq, 1C,  $^1J(^{19}\text{F}, ^{13}\text{C}) = 286.0$  Hz,  $^2J(^{19}\text{F}, ^{13}\text{C}) = 35.3$  Hz,  $^3J(^{19}\text{F}, ^{11}\text{B}) = 3.3$  Hz,  $\text{CF}_3$ ), 122.8 (s, 1C, CH), 45.5 (s, 1C,  $\text{CH}_2$ ), 36.5 (s, 1C,  $\text{CH}_3$ ), 15.4 ppm (s, 1C,  $\text{CH}_3$ ).

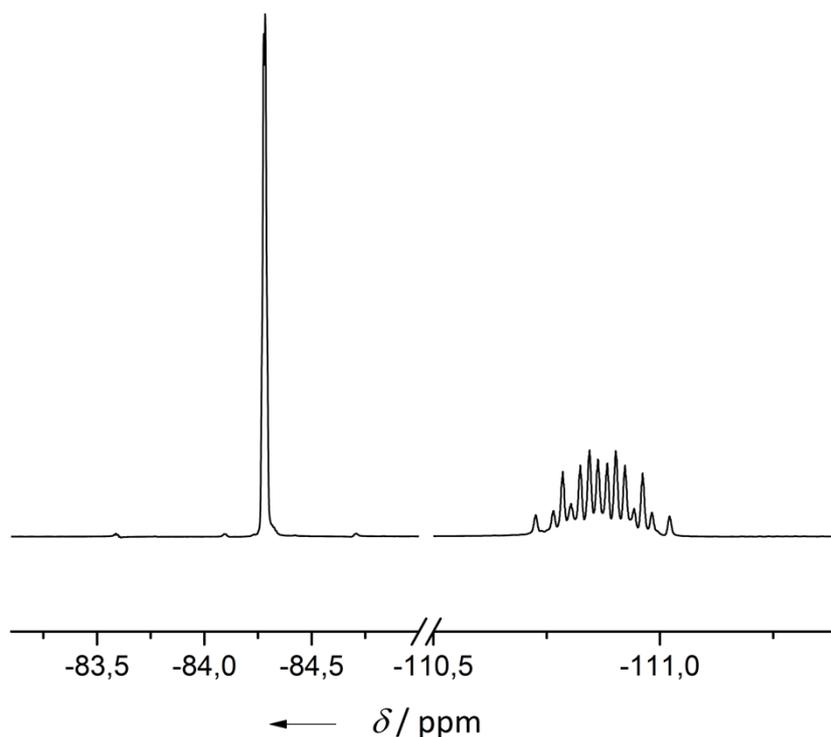
Anal. Calcd for  $\text{C}_8\text{H}_{14}\text{BF}_5\text{N}_2$ : C, 39.38; H, 5.78; N, 11.48%. Found: C, 39.84, H, 5.84; N, 11.90%. IR:  $2297\text{ cm}^{-1}$  ( $\nu(\text{B-H})$ ).



**Figure S3:** The signal of the  $[\text{C}_2\text{F}_5\text{BH}_3]^-$  anion in the  $^1\text{H}$  (bottom),  $^1\text{H}\{^{10}\text{B}\}$  (middle), and  $^1\text{H}\{^{11}\text{B}\}$  NMR (top) spectrum of  $[\text{EMIm}][\text{C}_2\text{F}_5\text{BH}_3]$ .



**Figure S4:**  $^{11}\text{B}$  (bottom) and  $^{11}\text{B}\{^1\text{H}\}$  NMR (top) spectrum of  $[\text{EMIm}][\text{C}_2\text{F}_5\text{BH}_3]$ .



**Figure S5:**  $^{19}\text{F}$  NMR spectrum of  $[\text{EMIm}][\text{C}_2\text{F}_5\text{BH}_3]$ .

**Preparation of  $[\text{BMPL}][\text{C}_2\text{F}_5\text{BH}_3]$  ( $[\text{BMPL}1]$ ).** Tetrahydrofuran (1 mL) was cooled to  $-78\text{ }^\circ\text{C}$  and degassed.  $\text{C}_2\text{F}_5\text{H}$  (164 mg, 1.37 mmol) was condensed in and a solution of  $n\text{BuLi}$  in hexanes ( $2.5\text{ mol L}^{-1}$ , 0.50 mL, 1.25 mmol) was slowly added dropwise under vigorous stirring that resulted in the formation of the  $\text{C}_2\text{F}_5\text{Li}$ . A solution of  $\text{BH}_3\cdot\text{thf}$ , which was synthesized according to method A ( $1.8\text{ mol L}^{-1}$ , 0.80 mL, 1.44 mmol), was added and the reaction mixture was slowly warmed up to room temperature.  $\text{K}_2\text{CO}_3$  (1.0 g, 7.24 mmol) in  $\text{H}_2\text{O}$  (10 mL) was added to the colourless solution and the mixture was stirred for 12 h. A solution of  $[\text{BMPL}]\text{Cl}$  (0.22 g, 1.24 mmol) in  $\text{H}_2\text{O}$  (1 mL) was added. Most of the thf was removed under reduced pressure. The remaining aqueous solution was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 10 mL), the combined organic phases were dried with  $\text{MgSO}_4$  and filtered. Most of the volatiles were removed under reduced pressure and the residue was dried in a fine vacuum to give a pale-yellow liquid. Yield: 0.13 g (0.47 mmol, 38% calculated for  $n\text{BuLi}$ ).

$^1\text{H}$  NMR (500.13 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 3.7\text{--}3.6$  (m, 4H,  $\text{CH}_2$ ),  $3.5\text{--}3.5$  (m, 2H,  $\text{CH}_2$ ), 3.20 (s, 3H,  $\text{CH}_3$ ), 2.3-2.2 (m, 4H,  $\text{CH}_2$ ), 1.9-1.8 (m, 2H,  $\text{CH}_2$ ), 1.5-1.4 (m, 2H,  $\text{CH}_2$ ), 0.97 (t, 3H,  $^3J(^1\text{H},^1\text{H}) = 7.40\text{ Hz}$ ,  $\text{CH}_3$ ), 0.58 ppm (qtq, 3H,  $^1J(^{11}\text{B},^1\text{H}) = 84.6\text{ Hz}$ ,  $^3J(^{19}\text{F},^1\text{H}) = 27.8\text{ Hz}$ ,  $^4J(^{19}\text{F},^1\text{H}) = 3.8\text{ Hz}$ ,  $\text{BH}_3$ ).

$^1\text{H}\{^{11}\text{B}\}$  NMR (500.13 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 3.7\text{-}3.6$  (m, 4H,  $\text{CH}_2$ ), 3.5-3.5 (m, 2H,  $\text{CH}_2$ ), 3.20 (s, 3H,  $\text{CH}_3$ ), 2.3-2.2 (m, 4H,  $\text{CH}_2$ ), 1.9-1.8 (m, 2H,  $\text{CH}_2$ ), 1.5-1.4 (m, 2H,  $\text{CH}_2$ ), 0.97 (t, 3H,  $^3J(^1\text{H}, ^1\text{H}) = 7.40$  Hz,  $\text{CH}_3$ ), 0.58 ppm (tq, 3H,  $^3J(^{19}\text{F}, ^1\text{H}) = 27.7$  Hz,  $^4J(^{19}\text{F}, ^1\text{H}) = 3.8$  Hz,  $\text{BH}_3$ ).

$^{11}\text{B}$  NMR (160.46 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -33.3$  ppm (qt,  $^1J(^{11}\text{B}, ^1\text{H}) = 84.7$  Hz,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz).

$^{11}\text{B}\{^1\text{H}\}$  NMR (160.46 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -33.3$  ppm (t,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz).

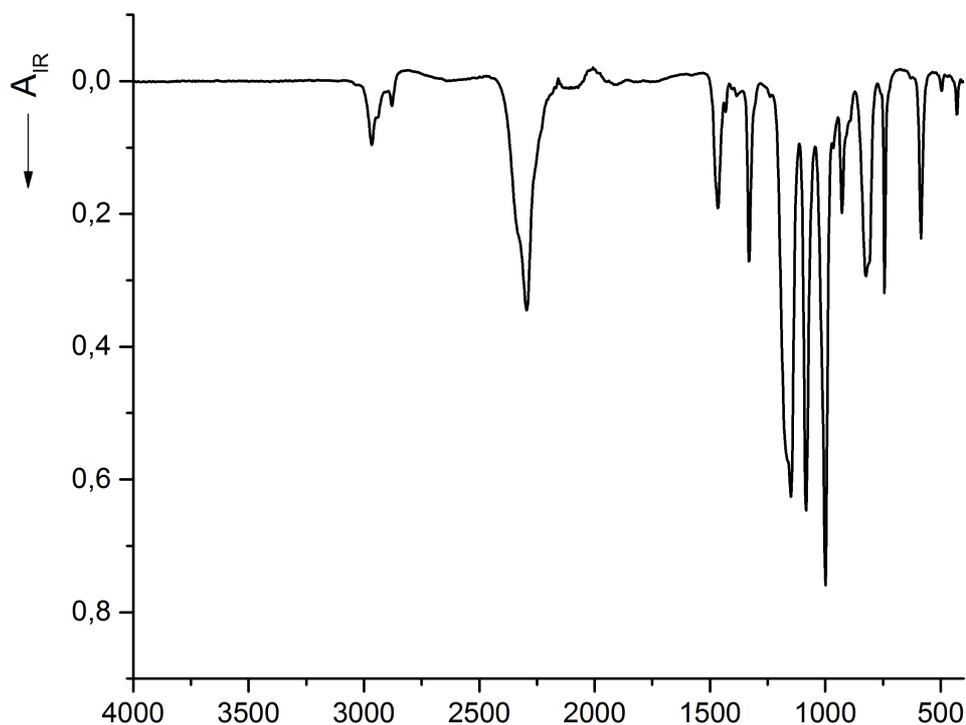
$^{19}\text{F}$  NMR (470.59 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -84.6$  (s, 3F,  $\text{CF}_3$ ), -111.1 ppm (qq, 2F,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.5$  Hz,  $^3J(^{19}\text{F}, ^1\text{H}) = 27.4$  Hz,  $\text{CF}_2$ ).

$^{19}\text{F}\{^1\text{H}\}$  NMR (376.76 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -84.7$  (s, 3F,  $\text{CF}_3$ ), -110.9 ppm (q, 2F,  $^2J(^{19}\text{F}, ^{11}\text{B}) = 18.3$  Hz,  $\text{CF}_2$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.76 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 65.1$  (t, 2C,  $^1J(^{14}\text{N}, ^{13}\text{C}) = 3.2$  Hz,  $\text{CH}_2$ ), 64.8 (t, 1C,  $^1J(^{14}\text{N}, ^{13}\text{C}) = 3.0$  Hz,  $\text{CH}_2$ ), 48.9 (t, 1C,  $^1J(^{14}\text{N}, ^{13}\text{C}) = 4.0$  Hz,  $\text{CH}_3$ ), 26.2 (s, 1C,  $\text{CH}_2$ ), 22.2 (s, 2C,  $\text{CH}_2$ ), 20.3 (t, 1C,  $^1J(^{14}\text{N}, ^{13}\text{C}) = 1.5$  Hz,  $\text{CH}_2$ ), 13.8 ppm (s, 1C,  $\text{CH}_3$ ).

IR:  $2294\text{ cm}^{-1}$  ( $\nu(\text{B-H})$ ).

Anal. Calcd for  $\text{C}_{11}\text{H}_{23}\text{BF}_5\text{N}$ : C, 48.02; H, 8.43; N, 5.09%. Found: C, 48.23; H, 8.73; N, 5.45%.



**Figure S6:** IR spectrum of [BMPL][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>] ([BMPL]1).

**Preparation of C<sub>2</sub>F<sub>5</sub>BH<sub>2</sub>(NCCH<sub>3</sub>) (3).** [*n*Bu<sub>4</sub>N][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>] (10.00 g, 26.6 mmol) was dissolved in CH<sub>3</sub>CN (100 mL) and the solution was cooled to 0 °C. Elemental I<sub>2</sub> (3.35 g, 13.2 mmol) was slowly added in portions and the reaction mixture was stirred for 12 h. After addition of each portion of iodine, the colour of the reaction mixture turned orange, immediately. The subsequent portion of I<sub>2</sub> was added when the colour had turned pale-yellow. After complete addition of iodine, all volatiles were removed under reduced pressure. The solid residue was suspended in Et<sub>2</sub>O (100 mL). The mixture was filtered, and the filtrate was dried in a vacuum to give **3** as a pale-yellow solid. Yield: 2.96 g (17.1 mmol, 64% calculated for [*n*Bu<sub>4</sub>N][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>]).

<sup>1</sup>H NMR (500.13 MHz, CD<sub>3</sub>CN): δ = 2.00 ppm (s, 3H, CH<sub>3</sub>CN). The signal of the BH<sub>2</sub> group was not observed.

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, CD<sub>3</sub>CN): δ = 1.99 (m, 2H, BH<sub>2</sub>), 2.00 ppm (s, 3H, CH<sub>3</sub>CN).

$^{11}\text{B}$  NMR (160.46 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = -20.7$  ppm (t,  $^1J(^{11}\text{B}, ^1\text{H}) = 104.1$  Hz).

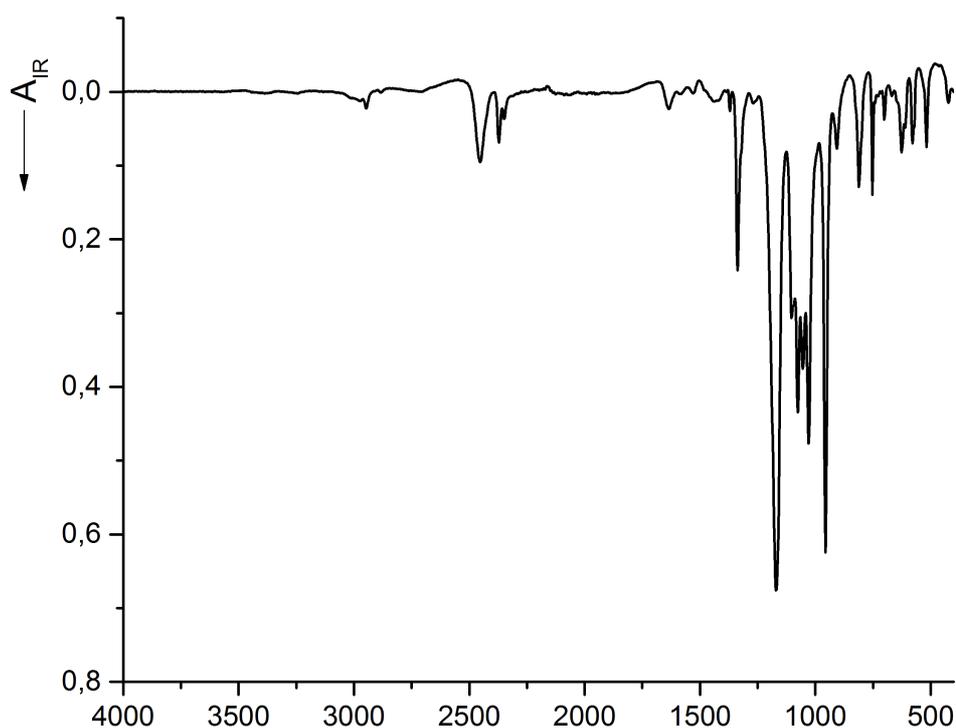
$^{11}\text{B}\{^1\text{H}\}$  NMR (160.46 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = -20.7$  (s).

$^{19}\text{F}$  NMR (470.59 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = -85.2$  (m, 3F,  $\text{CF}_3$ ),  $-125.2$  ppm (m, 2F,  $\text{CF}_2$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.76 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = 118.3$  (s, 1C,  $\text{CH}_3\text{CN}$ ), 1.77 ppm (s, 3C,  $\text{CH}_3\text{CN}$ ). The signals of the pentafluoroethyl group were not observed.

$^{13}\text{C}\{^{11}\text{B}, ^1\text{H}\}$  NMR (75.48 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta = 123.8$  (tq,  $^1J(^{19}\text{F}, ^{13}\text{C}) = 255.9$  Hz,  $^3J(^{19}\text{F}, ^{13}\text{C}) = 36.8$  Hz,  $\text{CF}_2$ ), 122.6 (qt,  $^1J(^{19}\text{F}, ^{13}\text{C}) = 284.9$  Hz,  $^3J(^{19}\text{F}, ^{13}\text{C}) = 32.7$  Hz,  $\text{CF}_3$ ), 118.3 (s, 1C,  $\text{CH}_3\text{CN}$ ), 1.77 (s, 3C,  $\text{CH}_3\text{CN}$ ) ppm.

Anal. Calcd for  $\text{C}_4\text{H}_5\text{BF}_5\text{N}$ : C, 27.79; H, 2.92; N, 8.10%. Found: C, 28.27, H, 3.31; N, 8.49%. IR:  $2371\text{ cm}^{-1}$ ,  $2453\text{ cm}^{-1}$  ( $\nu(\text{B-H})$ ).



**Figure S7:** IR spectrum of  $\text{C}_2\text{F}_5\text{BH}_2(\text{NCCH}_3)$  (**3**).

**Example for the preparation of a solution of  $\text{C}_2\text{F}_5\text{BH}_2(\text{thf})$  (**4**) in thf.**  $[\textit{n}\text{Bu}_4\text{N}][\text{C}_2\text{F}_5\text{BH}_3]$  (20.0 g, 53.3 mmol) was taken up into thf (400 mL) and the mixture

was cooled to 0 °C. Elemental I<sub>2</sub> (6.7 g, 26.4 mmol) was slowly added in portions as described for the synthesis of **3** and the reaction mixture was stirred for 48 h. The reaction mixture was concentrated at reduced pressure up to a residual volume of 280 mL and kept at -30 °C for 48 h. The mixture was filtered, and the resulting solution was stored at 4 °C. This solution of **4** was used as a source for the free borane C<sub>2</sub>F<sub>5</sub>BH<sub>2</sub> without further purification. Yield: 280 mL, 0.18 mol L<sup>-1</sup> in thf (50.4 mmol, 95 % calculated for [nBu<sub>4</sub>N][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>]).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 3.58 (m, thf), 1.73 (m, thf) ppm. The signal of the BH<sub>2</sub> moiety was not observed.

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 3.58 (m, thf), 2.46 (tq, <sup>3</sup>J(<sup>1</sup>H, <sup>19</sup>F) = 18.3 Hz, <sup>4</sup>J(<sup>1</sup>H, <sup>19</sup>F) = 2.3 Hz), 1.73 (m, thf) ppm.

<sup>11</sup>B NMR (160.46 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -2.4 (t, <sup>1</sup>J(<sup>11</sup>B, <sup>1</sup>H) = 110.1 Hz) ppm.

<sup>11</sup>B{<sup>1</sup>H} NMR (160.46 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -2.4 (s) ppm.

<sup>19</sup>F NMR (470.59 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -85.8 (m, CF<sub>3</sub>, 3F), -127.9 ppm (m, 2F, CF<sub>2</sub>).

<sup>19</sup>F{<sup>11</sup>B} NMR (470.59 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -85.8 (m, CF<sub>3</sub>, 3F), -127.9 ppm (tq, 2F, <sup>3</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 18.3 Hz, <sup>3</sup>J(<sup>19</sup>F, <sup>19</sup>F) = 1.3 Hz, CF<sub>2</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.76 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 25.7 (s, thf), 67.3 ppm (s, thf).

**Preparation of C<sub>2</sub>F<sub>5</sub>BH<sub>2</sub>(py) (5).** [nBu<sub>4</sub>N][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>] (2.40 g, 6.39 mmol) was dissolved in pyridine (20 mL) and the mixture was cooled to 0 °C. Iodine (0.8 g, 3.15 mmol) was slowly added in portions as described for the preparation of **3** and the reaction mixture was stirred for 12 h. All volatiles were removed under reduced pressure. The remaining solid residue was suspended in Et<sub>2</sub>O (100 mL) and the suspension was filtered. The filtrate was concentrated under reduced pressure to 5 mL. Pentane (55 mL) was added that resulted in the formation of two layers, which were separated. The ethereal phase was washed with a saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (3 x 2 mL). The diethyl ether and all volatile compounds were removed in a vacuum to result in **5** as a pale-yellow liquid. Yield: 0.20 g (0.95 mmol, 15% calculated for [nBu<sub>4</sub>N][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>]).

<sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>): δ = 8.62 (m, 2H, CH), 8.16 (m, 1H, CH), 7.70 (m, 2H, CH), 2.73 ppm (m, 2H, BH<sub>2</sub>, not resolved).

$^1\text{H}\{^{11}\text{B}\}$ -NMR (500.13 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.62$  (m, 2H, CH), 8.16 (m, 1H, CH), 7.70 (m, 2H, CH), 2.73 ppm (tq, 2H,  $^3J(^{19}\text{F}, ^1\text{H}) = 20.1$  Hz,  $^4J(^{19}\text{F}, ^1\text{H}) = 2.3$  Hz,  $\text{BH}_2$ ).

$^{11}\text{B}$  NMR (160.46 MHz,  $\text{CDCl}_3$ ):  $\delta = -9.46$  ppm (t,  $^1J(^{11}\text{B}, ^1\text{H}) = 101.2$  Hz).

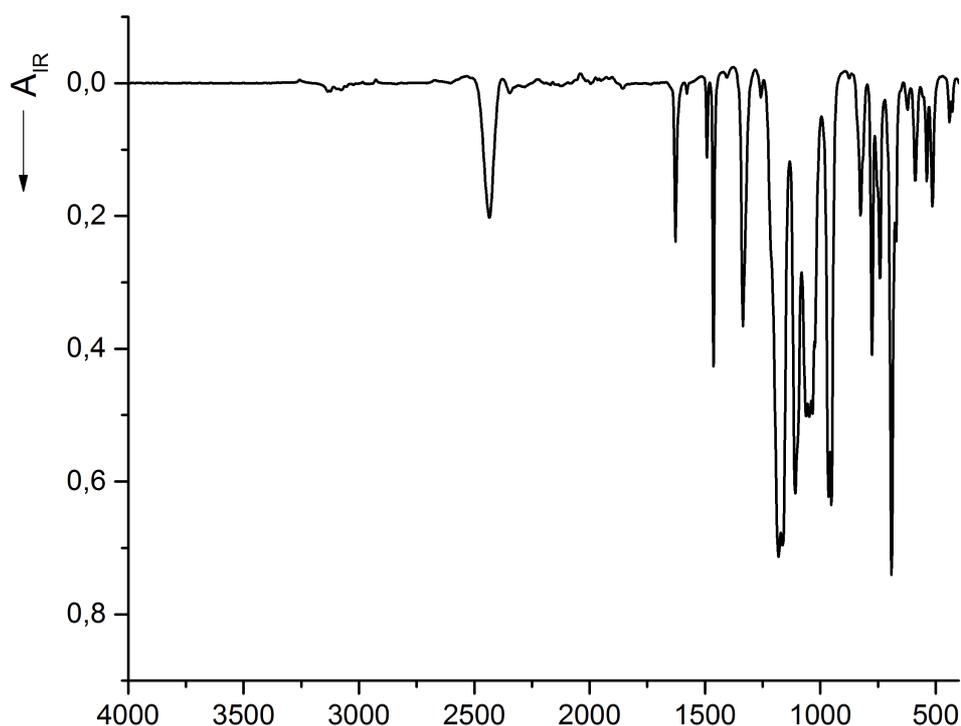
$^{11}\text{B}\{^1\text{H}\}$  NMR (160.46 MHz,  $\text{CDCl}_3$ ):  $\delta = -9.46$  ppm (s).

$^{19}\text{F}$  NMR (470.59 MHz,  $\text{CDCl}_3$ ):  $\delta = -83.8$  (m, 3F,  $\text{CF}_3$ ),  $-125.8$  ppm (m, 2F,  $\text{CF}_2$ ).

$^{19}\text{F}\{^1\text{H}\}$  NMR (376.76 MHz,  $\text{CDCl}_3$ ):  $\delta = -85.4$  (s, 3F,  $\text{CF}_3$ , not resolved),  $-127.3$  ppm (m, 2F,  $\text{CF}_2$ , not resolved).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.76 MHz,  $\text{CDCl}_3$ ):  $\delta = 148.7$  (s, 2C, CH), 141.4 (s, 1C, CH), 125.9 (s, 2C, CH), 121.7 ppm (qt,  $^1J(^{19}\text{F}, ^{13}\text{C}) = 284.9$  Hz,  $^3J(^{19}\text{F}, ^{13}\text{C}) = 33.0$  Hz).

Anal. Calcd for  $\text{C}_7\text{H}_7\text{BF}_5\text{N}$ : C, 39.86; H, 3.34; N, 6.64%. Found: C, 40.17; H, 3.66; N, 7.16. IR:  $2348\text{ cm}^{-1}$ ,  $2434\text{ cm}^{-1}$  ( $\nu(\text{B-H})$ ).



**Figure S8:** IR spectrum of  $\text{C}_2\text{F}_5\text{BH}_2(\text{py})$  (**5**).

**Preparation of C<sub>2</sub>F<sub>5</sub>BH<sub>2</sub>(4-NC-py) (6).** [*n*Bu<sub>4</sub>N][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>] (1.00 g, 2.66 mmol) and 4-cyanopyridine (0.28 g, 2.66 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The solution was cooled to 0 °C and I<sub>2</sub> (0.34 mg, 1.34 mmol) was slowly added in portions. The mixture was stirred for 3 d. Then, all volatiles were removed under reduced pressure and the remaining residue was suspended in Et<sub>2</sub>O (20 mL). After filtration, the filtrate was concentrated under reduced pressure to 2 mL. The Et<sub>2</sub>O phase was washed with a saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (3 x 2 mL). The ether was removed under reduced pressure to give **6** as pale-yellow solid. Yield: 0.08 g (0.34 mmol, 13% calculated for [*n*Bu<sub>4</sub>N][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>]).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 8.98 (d, 2H, <sup>3</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 6.7 Hz, CH), 8.39 (d, 2H, <sup>3</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 6.8 Hz, CH), 2.72 ppm (m, BH<sub>2</sub>).

<sup>1</sup>H{<sup>11</sup>B}-NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 8.98 (d, 2H, CH, <sup>3</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 6.7 Hz), 8.39 (d, 2H, <sup>3</sup>J(<sup>1</sup>H,<sup>1</sup>H) = 6.8 Hz, CH), 2.74 ppm (t, 2H, <sup>3</sup>J(<sup>19</sup>F,<sup>1</sup>H) = 19.9 Hz, BH<sub>2</sub>).

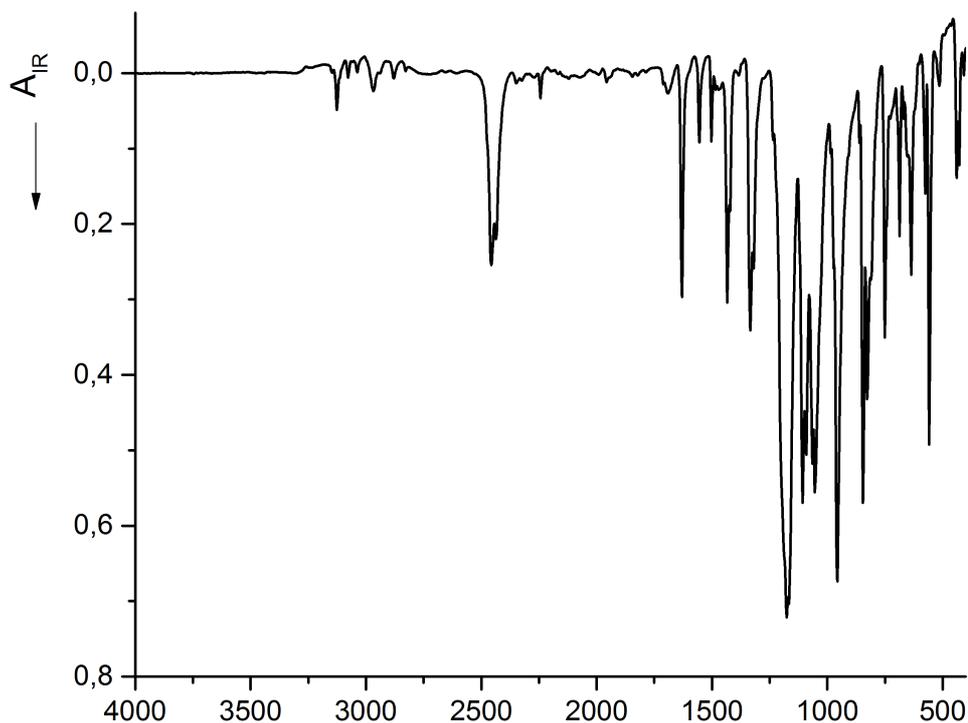
<sup>11</sup>B NMR (160.46 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -9.24 ppm (t, <sup>1</sup>J(<sup>11</sup>B,<sup>1</sup>H) = 100.16 Hz).

<sup>11</sup>B{<sup>1</sup>H} NMR (160.46 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -9.24 ppm (s).

<sup>19</sup>F NMR (470.59 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -84.6 (m, 3F, CF<sub>3</sub>), -126.1 ppm (m, 2F, CF<sub>2</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (125.76 MHz, CDCl<sub>3</sub>): δ = 150.8 (s, 1C, CN), 130.2 (s, 1C, C-CN), 126.7 (s, 2C, CH<sub>2</sub>), 115.7 (s, 2C, CH<sub>2</sub>).

Anal. Calcd for C<sub>8</sub>H<sub>6</sub>BF<sub>5</sub>N<sub>2</sub>: C, 40.72; H, 2.56; N, 11.87. Found: C, 40.71; H, 2.71; N, 10.52%. IR: 2435 cm<sup>-1</sup>, 2456 cm<sup>-1</sup> (ν(B-H)).



**Figure S9:** IR spectrum of  $C_2F_5BH_2(4\text{-NC-py})$  (**6**).

**Preparation of  $C_2F_5BH_2(PPh_3)$  (**7**).** Triphenylphosphane (0.53 g, 2.02 mmol) was taken up into a solution of **4** in thf (30.0 mL, 0.1 mol L<sup>-1</sup>, 3.00 mmol) and stirred at room temperature for 7 d. All volatiles were removed under reduced pressure and the residual solid was suspended in pentane (20 mL). The mixture was filtered, and all volatiles were removed under reduced pressure. **7** was obtained as a pale-yellow solid. Yield: 0.20 g (0.51 mmol, 25% calculated for PPh<sub>3</sub>).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 7.7–7.5 ppm (m, CH, PPh<sub>3</sub>). The signal of the BH<sub>2</sub> group was not resolved.

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 7.7–7.5 (m, CH, PPh<sub>3</sub>), 2.21 ppm (dtq, 2H, <sup>2</sup>J(<sup>1</sup>H, <sup>31</sup>P) = 20.3 Hz, <sup>3</sup>J(<sup>1</sup>H, <sup>19</sup>F) = 22.2 Hz, <sup>4</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 2.5 Hz, BH<sub>2</sub>).

<sup>11</sup>B NMR (160.46 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -28.6 ppm (dt, <sup>1</sup>J(<sup>31</sup>P, <sup>11</sup>B) = 71.1 Hz, <sup>1</sup>J(<sup>11</sup>B, <sup>1</sup>H) = 87.9 Hz).

$^{11}\text{B}\{^1\text{H}\}$  NMR (160.46 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -28.6$  ppm (d,  $^1J(^{31}\text{P}, ^{11}\text{B}) = 71.1$  Hz).

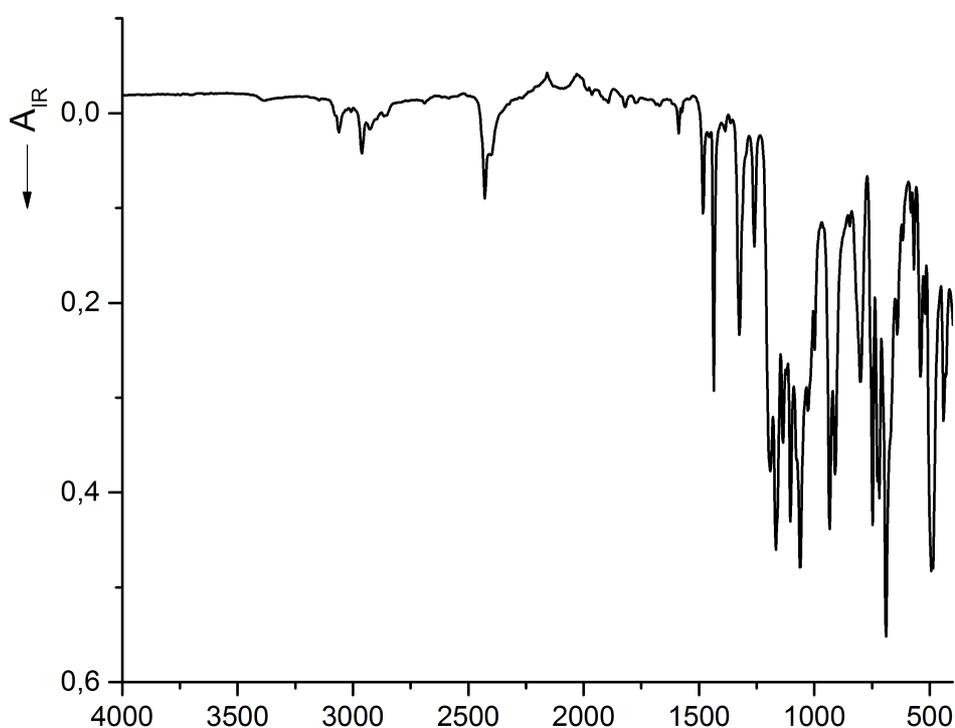
$^{19}\text{F}$  NMR (470.59 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = -85.8$  (m,  $\text{CF}_3$ , 3F),  $-112.1$  ppm (m,  $\text{CF}_2$ , 2F).

$^{31}\text{P}$  NMR (202.45 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 12.1$  ppm (m).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202.45 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 12.1$  ppm (m).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 134.2$  (d, 3C,  $^2J(^{31}\text{P}, ^{13}\text{C}) = 9.7$  Hz, *i*-CH, Ph),  
133.0 (d, 6C,  $^2J(^{31}\text{P}, ^{13}\text{C}) = 2.7$  Hz, *o*-CH, Ph), 130.0 ppm (d. 9C, *m*-, *p*-CH, Ph).

Anal. Calcd for  $\text{C}_{20}\text{H}_{17}\text{BF}_5\text{P}$ : C, 60.95; H, 4.35%. Found: C, 60.19; H, 4.21%. IR: 2401  $\text{cm}^{-1}$ , 2429  $\text{cm}^{-1}$  ( $\nu(\text{B-H})$ ).



**Figure S10:** IR spectrum of  $\text{C}_2\text{F}_5\text{BH}_2(\text{PPh}_3)$  (**7**).

### Preparation of C<sub>2</sub>F<sub>5</sub>BH<sub>2</sub>(OPEt<sub>3</sub>)

Triethylphosphane oxide was dissolved in a solution of C<sub>2</sub>F<sub>5</sub>BH<sub>2</sub>·thf (1.00 mmol, 0.1 mol L<sup>-1</sup> in thf, 10 mL) and stirred for two hours. All volatiles were removed under reduced pressure.

<sup>31</sup>P{<sup>1</sup>H} NMR (202.45 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 82.6 ppm (m).

**Preparation of [Me<sub>4</sub>N][CF<sub>3</sub>BH<sub>3</sub>] ([Me<sub>4</sub>N]2).** A solution of BH<sub>3</sub>·thf in tetrahydrofuran (2.0 mol L<sup>-1</sup>, 0.43 mL, 0.86 mmol) was added to a solution of TMSCF<sub>3</sub> (Ruppert-Prakash reagent) (0.10 mL, 0.68 mmol) in Et<sub>2</sub>O (1.0 mL). The reaction mixture was cooled to -90 °C and [Me<sub>4</sub>N]F (64 mg, 0.69 mmol) was added. The mixture was slowly warmed up to room temperature and stirred for 24 h. Since [Me<sub>4</sub>N]2 is almost insoluble in thf, a few drops of water had to be added to dissolve the salt and to enable a characterization by NMR spectroscopy. According to the <sup>11</sup>B and the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum, **2** was formed with a selectivity of 80%. All attempts to isolate pure [Me<sub>4</sub>N]2 remained unsuccessful, so far. Thus, anion **2** was characterized by NMR spectroscopy in solution, only.

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 3.41 (m, 3H, NCH<sub>3</sub>), 0.67 ppm (qq, 3H, <sup>1</sup>J(<sup>11</sup>B, <sup>1</sup>H) = 83.6 Hz, <sup>3</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 18.2 Hz, BH<sub>3</sub>),

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = 3.41 (m, 3H, NCH<sub>3</sub>), 0.67 ppm (q, 3H, <sup>3</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 18.2 Hz, BH<sub>3</sub>).

<sup>11</sup>B NMR (160.46 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -31.6 ppm (qq, <sup>1</sup>J(<sup>11</sup>B, <sup>1</sup>H) = 83.6 Hz, <sup>2</sup>J(<sup>19</sup>F, <sup>11</sup>B) = 28.0 Hz).

<sup>11</sup>B{<sup>1</sup>H} NMR (160.46 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -31.6 ppm (q, <sup>2</sup>J(<sup>19</sup>F, <sup>11</sup>B) = 28.0 Hz).

<sup>19</sup>F NMR (470.59 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -47.9 ppm (qq, <sup>2</sup>J(<sup>19</sup>F, <sup>11</sup>B) = 28.2 Hz, <sup>3</sup>J(<sup>19</sup>F, <sup>11</sup>B) = 17.9 Hz).

<sup>19</sup>F{<sup>1</sup>H} NMR (376.76 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -47.9 ppm (q, <sup>2</sup>J(<sup>19</sup>F, <sup>11</sup>B) = 28.2 Hz).

<sup>19</sup>F{<sup>11</sup>B} NMR (470.59 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -47.7 ppm (q, <sup>3</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 18.2 Hz).

<sup>19</sup>F{<sup>10</sup>B} NMR (470.59 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ = -47.7 (q, <sup>2</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 18.2 Hz, <sup>10</sup>BH), -47.8 (qq, <sup>2</sup>J(<sup>19</sup>F, <sup>11</sup>B) = 28.1 Hz, <sup>3</sup>J(<sup>19</sup>F, <sup>1</sup>H) = 18.2 Hz).

$^{13}\text{C}\{^{19}\text{F}\}$  NMR (125.76 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 55.9$  (m,  $\text{NCH}_3$ ), 147.2 ppm (qq,  $^1J(^{13}\text{C}, ^{11}\text{B}) = 66.3$  Hz,  $^2J(^{13}\text{C}, ^1\text{H}) = 5.8$  Hz).

### Shock sensitivity of salts of 1

#### Explosions of K1 / Cs1

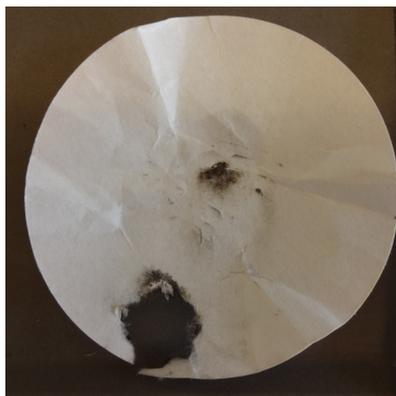
A solution of K1 (50 ml,  $0.50 \text{ mol L}^{-1}$ ) in thf was concentrated using a rotary evaporator to a volume of ca. 5 mL. The addition of  $\text{Et}_2\text{O}$  (100 mL) resulted in the precipitation of K1.

The precipitate was filtered off using a fine glass frit. The colourless solid was dried in air and a small portion was carefully removed from the glass frit. Attempted removal of a larger amount of the solid (< 50 mg) from the glass frit by scratching with a spatula caused an explosion.



**Fig. S11:** Explosion of a glass frit.

In further attempts, K1 or Cs1 were dried in air on a filter paper. The colourless solids were transferred into a dry box with an argon atmosphere. A gentle hit with a hammer caused explosions.



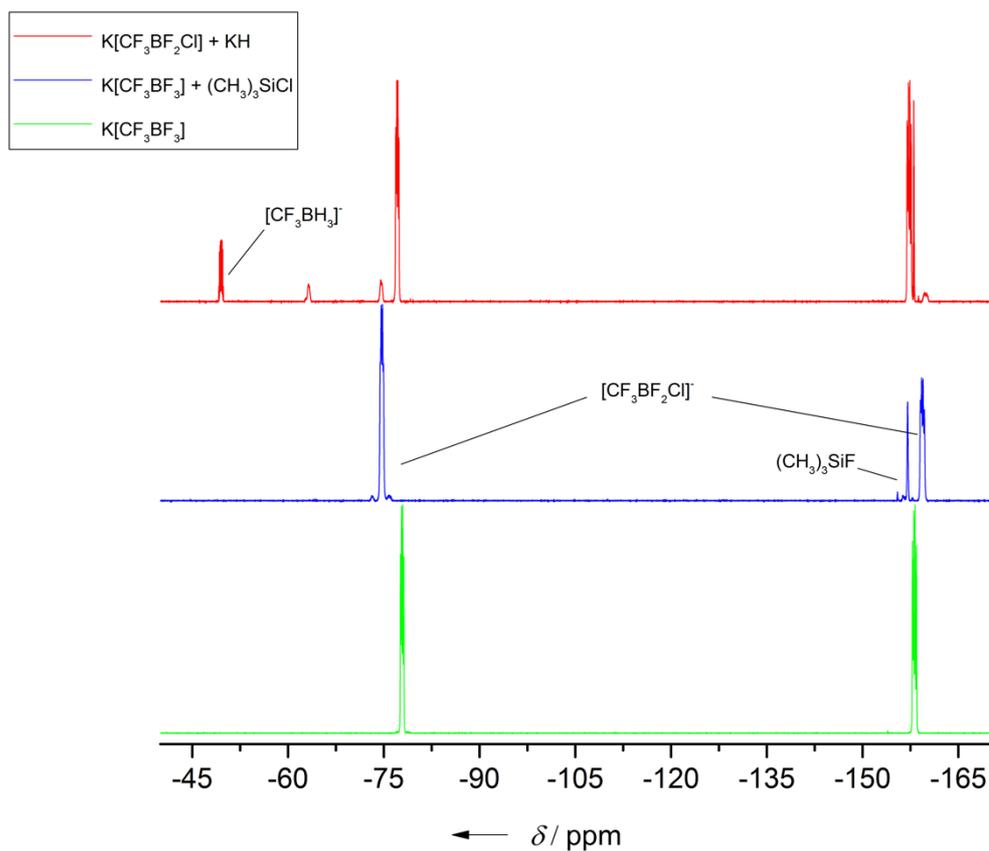
**Fig. S12:** Filter paper after explosion.

Explosion behaviour of organic salts of **1**:

A sample of any isolated salt of **1** with an organic counterion that is described in this contribution was hit with a hammer, as well. None of these salts exploded.

#### **Reactions of $K[CF_3BF_3]$ with KH and $Li[AlH_4]$**

$K[CF_3BF_3]$  (250 mg, 1.42 mmol) was dissolved in thf (2 mL) and treated with TMSCl (0.25 mL, 0.21 g, 1.97 mmol). The reaction mixture was stirred over night at 50 °C and  $[CF_3BF_2Cl]^-$  had formed. KH (253 mg, 6.31 mmol) was added and the suspension was stirred at room temperature for 24 h. The anion  $[CF_3BH_3]^-$  was observed by NMR spectroscopy in ca. 13 % yield. The suspension was poured into a solution of  $[nBu_4N]Br$  (451 mg, 1.40 mmol) in water (5 mL) and thf was removed in vacuo. Water (45 mL) was added to the mixture and the suspension was stirred overnight. The precipitate was filtered off and dried in fine vacuum. Only  $[nBu_4N][CF_3BF_3]$  was obtained.



**Fig. S13:**  $^{19}\text{F}$  NMR spectra of the stepwise reaction of  $\text{K}[\text{CF}_3\text{BF}_3]$  with  $(\text{CH}_3)_3\text{SiCl}$  followed by treatment with  $\text{KH}$ .

$\text{K}[\text{CF}_3\text{BF}_3]$  (40 mg, 0.23 mmol) was dissolved in thf (0.8 mL) and  $\text{Li}[\text{AlH}_4]$  (40 mg, 1.05 mmol) was added. No reaction was observed during 2 h.  $\text{TMSCl}$  was added in portions (4 x 0.1 mL). In the  $^{11}\text{B}$  NMR spectrum only the signal of the  $[\text{CH}_3\text{BH}_3]^-$  anion was present.

## Crystal Structure Determinations

Colourless single crystals suitable for a X-ray diffraction study of  $[n\text{Bu}_4\text{N}][\text{C}_2\text{F}_5\text{BH}_3]$  ( $[n\text{Bu}_4\text{N}]\mathbf{1}$ ),  $\text{C}_2\text{F}_5\text{BH}_2(4\text{-NC-py})$  (**6**) and  $\text{C}_2\text{F}_5\text{BH}_2(\text{PPh}_3)$  (**7**) were obtained from acetone, acetone/pentane and pentane, respectively. Data collection was performed on a Bruker X8-Apex II diffractometer with a CCD area detector and multi-layer mirror or graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by intrinsic phasing methods (SHELXT),<sup><Sheldrick, 2014 #1593><sup>4</sup> and refinements are based on full-matrix least-squares calculations on  $F^2$  (SHELXL).<sup>4-5</sup> All non-hydrogen atoms were refined anisotropically. H atoms bonded to boron were refined without any restraints. For CH, idealized bond lengths and angles were used. Calculations were carried out using the ShelXle graphical interface.<sup>6</sup> Molecular structure diagrams were drawn with the program Diamond 4.5.1.<sup>7</sup> Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Experimental details, crystal data, and CCDC numbers are collected in Table S1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).</sup>

**Table S1.** Selected crystal data and details of the refinements of the structures of  $[n\text{Bu}_4\text{N}][\text{C}_2\text{F}_5\text{BH}_3]$  ( $[n\text{Bu}_4\text{N}]\mathbf{1}$ ),  $\text{C}_2\text{F}_5\text{BH}_2(4\text{-NC-py})$  ( $\mathbf{6b}$ ) and  $\text{C}_2\text{F}_5\text{BH}_2(\text{PPh}_3)$  ( $\mathbf{5}$ ).

	$[n\text{Bu}_4\text{N}]\mathbf{1}$	$\mathbf{6b}$	$\mathbf{5}$
Formula	$\text{C}_{18}\text{H}_{39}\text{BF}_5\text{N}$	$\text{C}_8\text{H}_6\text{BF}_5\text{N}_2$	$\text{C}_{20}\text{H}_{17}\text{BF}_5\text{P}$
$M_w$	375.31	235.96	394.11
$T$ (K)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$I2/a$	$P-1$
$a$ [Å]	8.8965(16)	9.7492(10)	8.943(3)
$b$ [Å]	16.170(3)	8.9386(9)	10.057(4)
$c$ [Å]	15.312(3)	22.528(3)	10.567(4)
$\alpha$ [°]			96.064(9)
$\beta$ [°]	98.429(6)	93.546(3)	101.313(9)
$\gamma$ [°]			95.583(10)
volume [Å <sup>3</sup> ]	2178.9(7)	1959.4(4)	920.0(6)
$Z$	4	8	2
$\rho$ (calcd) [Mg m <sup>-3</sup> ]	1.144	1.600	1.423
$\mu$ [mm <sup>-1</sup> ]	0.095	0.163	0.199
$F(000)$	816	944	404
No. of collected reflections	27674	11419	11995
No. of unique reflections	4355	1922	3607
$R(\text{int})$	0.0335	0.0382	0.0656
No. of parameters/restraints	292 / 0	151 / 0	252 / 0
$R1$ ( $I > 2\sigma(I)$ )	0.0468	0.0331	0.0407
$wR2$ (all)	0.1241	0.0891	0.0978
GOF on $F^2$	1.032	1.063	1.065
Largest diff. peak / hole / e Å <sup>-3</sup>	0.368 / -0.244	0.385 / -0.288	0.314 / -0.376
CCDC no.	1842548	1842550	1842549

## Viscosity Studies

Viscosities and densities of neat [EMIm]1 (Table S2) and [BMPL]1 (Table S3) were measured with a rolling-ball viscometer Lovis 2000 ME using capillaries with different inner diameters at different angles combined with a DMA 4100 M density meter (Anton Paar GmbH, Austria).

**Table S2.** Densities, viscosities and further selected data of the viscosity study of neat [EMIm]1.

$T$ [°C]	$\rho$ [g cm <sup>-3</sup> ]	$\eta$ [mPa s]	$\nu$ [mm <sup>2</sup> s <sup>-1</sup> ]	$\dot{\gamma}$ [1 s <sup>-1</sup> ]	angle [°]
20.00	1.2158	37.7	31.0	68.3	80
		37.1	30.6	64.2	70
		37.0	30.4	57.6	60
		37.0	30.5	49.4	50
		37.0	30.5	40.5	40
		37.1	30.5	31.0	30
		37.4	30.7	20.9	20
23.00	1.2134	33.8	27.8	76.4	80
		33.4	27.5	71.5	70
		33.1	27.3	64.4	60
		33.2	27.4	55.2	50
		33.3	27.4	45.1	40
		33.4	27.5	34.5	30
		33.7	27.7	23.2	20
25.00	1.2118	31.3	25.9	82.3	80
		31.1	25.7	76.7	70
		30.8	25.4	69.3	60
		30.9	25.5	59.3	50
		31.0	25.6	48.4	40
		31.1	25.7	37.0	30
		31.4	25.9	24.9	20
30.00	1.2079	26.6	22.0	96.9	80
		26.3	21.8	90.8	70
		26.0	21.5	82.0	60
		26.2	21.7	70.1	50
		26.3	21.8	57.2	40
		26.4	21.8	43.6	30
		26.5	22.0	29.4	20
40.00	1.2001	18.2	15.2	37.2	80
		18.6	15.5	34.6	70
		19.2	16.0	30.9	60
		19.4	16.2	27.0	50
		19.6	16.4	22.5	40
		20.1	16.8	17.1	30
		---	---	---	20
50.00	1.1923	14.1	11.8	48.0	80
		14.4	12.1	44.6	70
		14.9	12.5	39.9	60
		15.0	12.6	34.9	50
		15.1	12.7	29.1	40
		15.2	12.8	22.5	30
		15.5	13.0	15.1	20

**Table S2 continued.** Densities, viscosities and further selected data of the viscosity study of neat [EMIm]1.

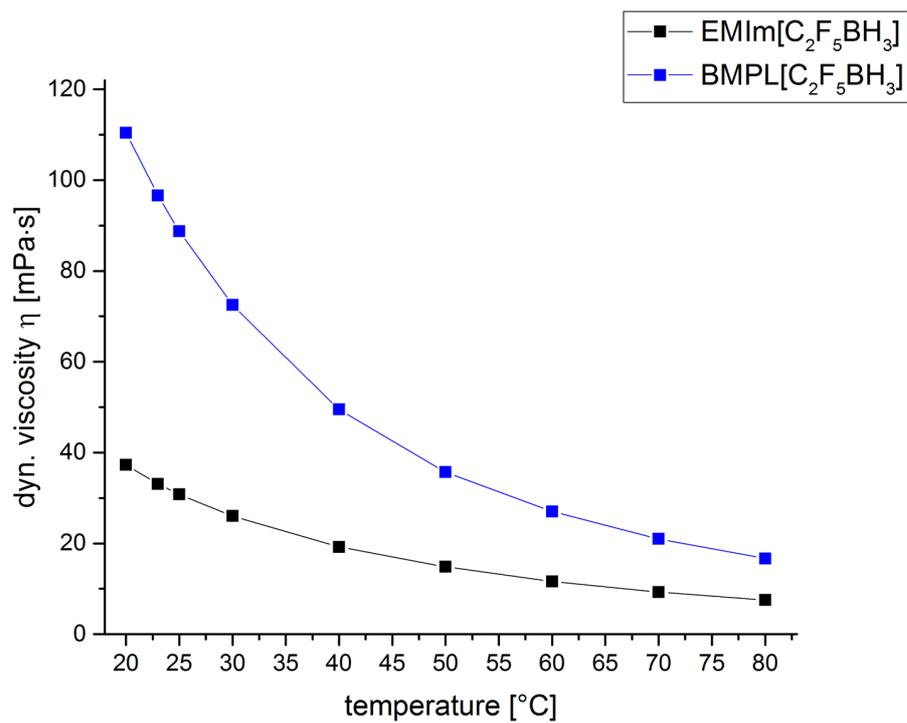
$T$ [°C]	$\rho$ [g cm <sup>-3</sup> ]	$\eta$ [mPa s]	$\nu$ [mm <sup>2</sup> s <sup>-1</sup> ]	$\dot{\gamma}$ [1 s <sup>-1</sup> ]	angle [°]
60.00	1.1846	10.9	9.2	61.6	80
		11.2	9.5	57.1	70
		11.6	9.8	51.0	60
		11.7	9.9	44.7	50
		11.8	9.9	37.3	40
		11.9	10.0	28.8	30
		12.1	10.2	19.3	20
70.00	1.1770	8.8	7.4	76.8	80
		9.0	7.6	71.2	70
		9.3	7.9	63.7	60
		9.3	7.9	55.9	50
		9.4	8.0	46.6	40
		9.5	8.1	35.9	30
		9.7	8.2	24.1	20
80.00	1.1695	7.1	6.1	93.8	80
		7.4	6.3	86.8	70
		7.6	6.5	77.7	60
		7.6	6.5	68.1	50
		7.7	6.6	56.8	40
		7.8	6.6	43.8	30
		7.9	6.8	29.4	20

**Table S3.** Densities, viscosities and further selected data of the viscosity study of neat [BMPL]1.

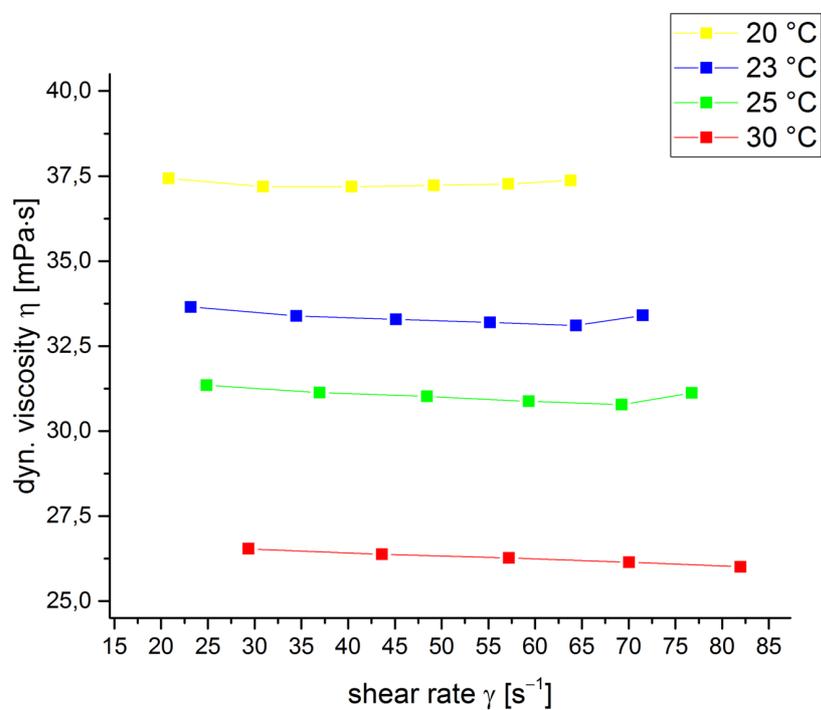
$T$ [°C]	$\rho$ [g cm <sup>-3</sup> ]	$\eta$ [mPa s]	$\nu$ [mm <sup>2</sup> s <sup>-1</sup> ]	$\dot{\gamma}$ [1 s <sup>-1</sup> ]	angle [°]
20.00	1.1228	113.0	100.6	23.1	80
		112.3	100.0	21.5	70
		110.4	98.3	19.6	60
		110.1	98.1	16.9	50
		111.3	99.1	13.7	40
		112.6	100.3	10.4	30
		114.1	101.6	6.9	20
23.00	1.1207	99.1	88.5	26.4	80
		98.4	87.8	24.6	70
		96.8	86.4	22.3	60
		96.7	86.3	19.2	50
		97.8	87.3	15.6	40
		99.0	88.3	11.8	30
		100.1	89.3	7.9	20
25.00	1.1193	91.1	81.4	28.7	80
		90.2	80.6	26.9	70
		88.7	79.3	24.7	60
		89.	79.5	20.9	50
		89.9	80.3	17.0	40
		90.9	81.2	12.8	30
		91.9	82.1	8.6	20

**Table S3 continued.** Densities, viscosities and further selected data of the viscosity study of neat [BMPL]1.

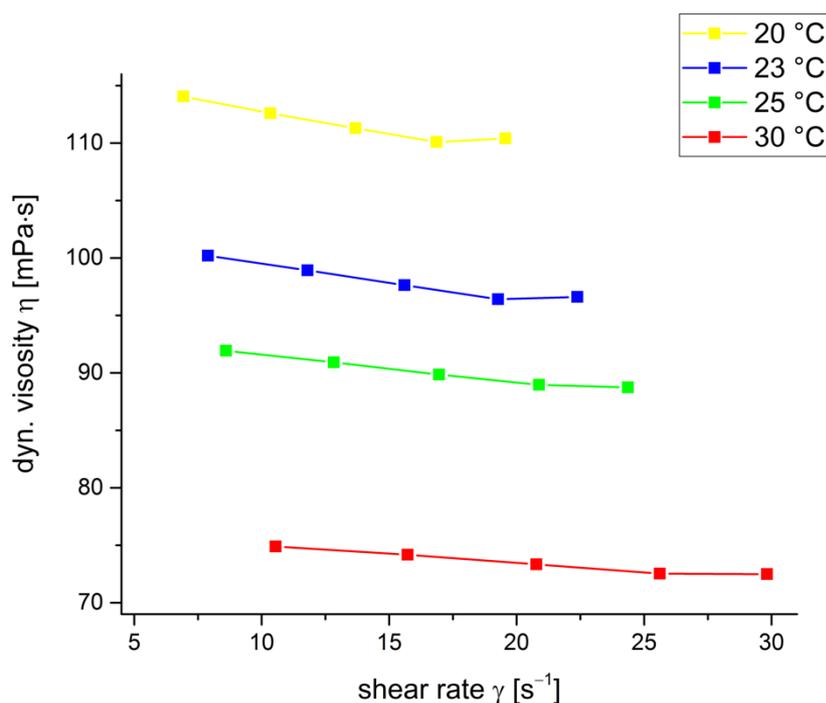
$T$ [°C]	$\rho$ [g cm <sup>-3</sup> ]	$\eta$ [mPa s]	$\nu$ [mm <sup>2</sup> s <sup>-1</sup> ]	$\dot{\gamma}$ [1 s <sup>-1</sup> ]	angle [°]
30.00	1.1159	74.3	66.6	35.2	80
		73.7	66.0	32.9	70
		72.5	65.0	29.8	60
		72.5	65.0	25.6	50
		73.3	65.7	20.8	40
		74.2	66.5	15.7	30
		74.9	67.1	10.6	20
40.00	1.1091	51.1	46.1	51.2	80
		50.5	45.5	47.9	70
		49.5	44.6	43.6	60
		49.8	44.9	37.2	50
		50.4	45.4	30.2	40
		50.9	45.9	22.9	30
		51.5	46.4	15.3	20
50.00	1.1023	36.6	33.2	71.4	80
		36.2	32.9	66.6	70
		35.2	32.0	60.9	60
		35.6	32.3	51.8	50
		36.0	32.7	42.1	40
		36.4	33.0	31.9	30
		36.8	33.4	21.4	20
60.00	1.0956	27.5	25.1	95.2	80
		27.5	25.1	88.1	70
		27.0	24.7	79.6	60
		27.0	24.6	68.3	50
		27.1	24.7	55.9	40
		27.2	24.9	42.7	30
		27.5	25.1	28.8	20
70.00	1.0890	21.0	19.3	124.8	80
		21.0	19.3	115.0	70
		21.0	19.3	102.5	60
		20.9	19.1	88.4	50
		20.7	19.0	73.2	40
		20.7	19.0	56.3	30
		20.8	19.1	38.0	20
80.00	1.0824	16.5	15.3	158.6	80
		16.6	15.3	146.1	70
		16.7	15.4	128.8	60
		16.4	15.2	112.1	50
		16.2	14.9	93.5	40
		16.1	14.9	72.3	30
		16.2	14.9	48.9	20



**Figure S14.** Temperature-dependent dynamic viscosities of [EMIm]1 and [BMPL]1.



**Figure S15.** Temperature-dependent dynamic viscosities and shear rates of [EMIm]1.



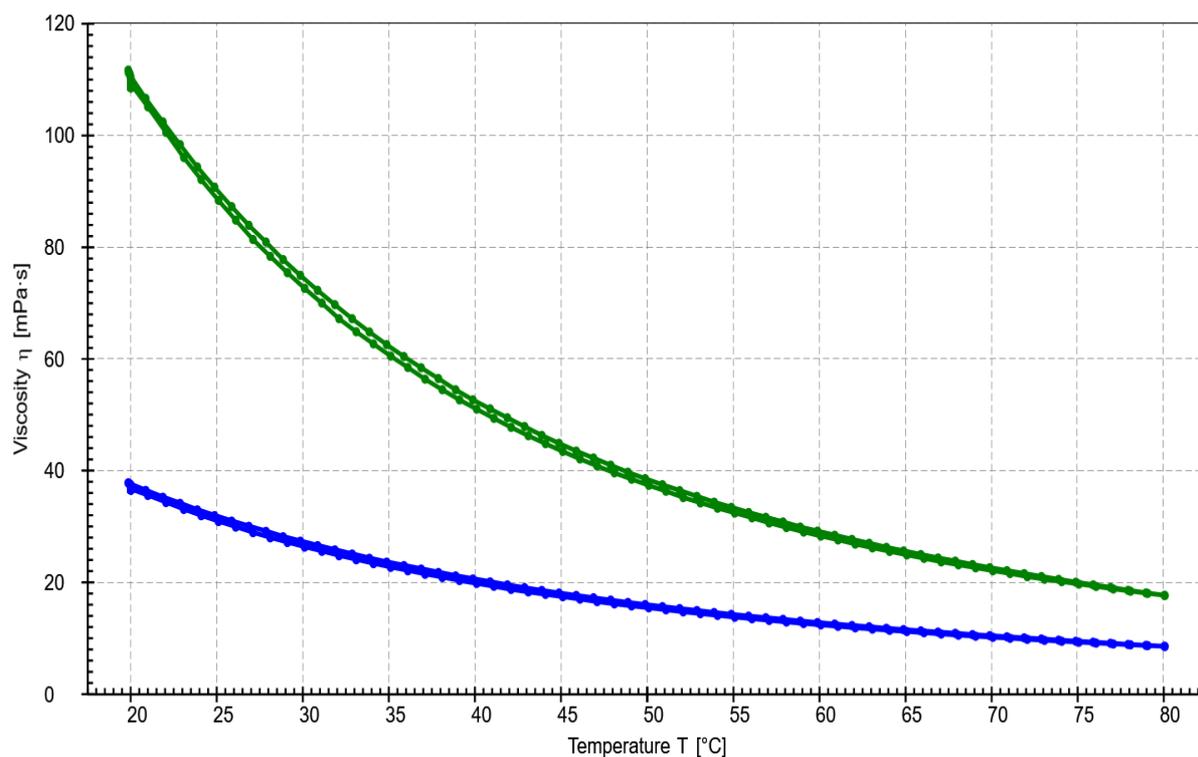
**Figure S16.** Temperature-dependent dynamic viscosities and shear rates of [BMPL]1.

### Rheological Studies

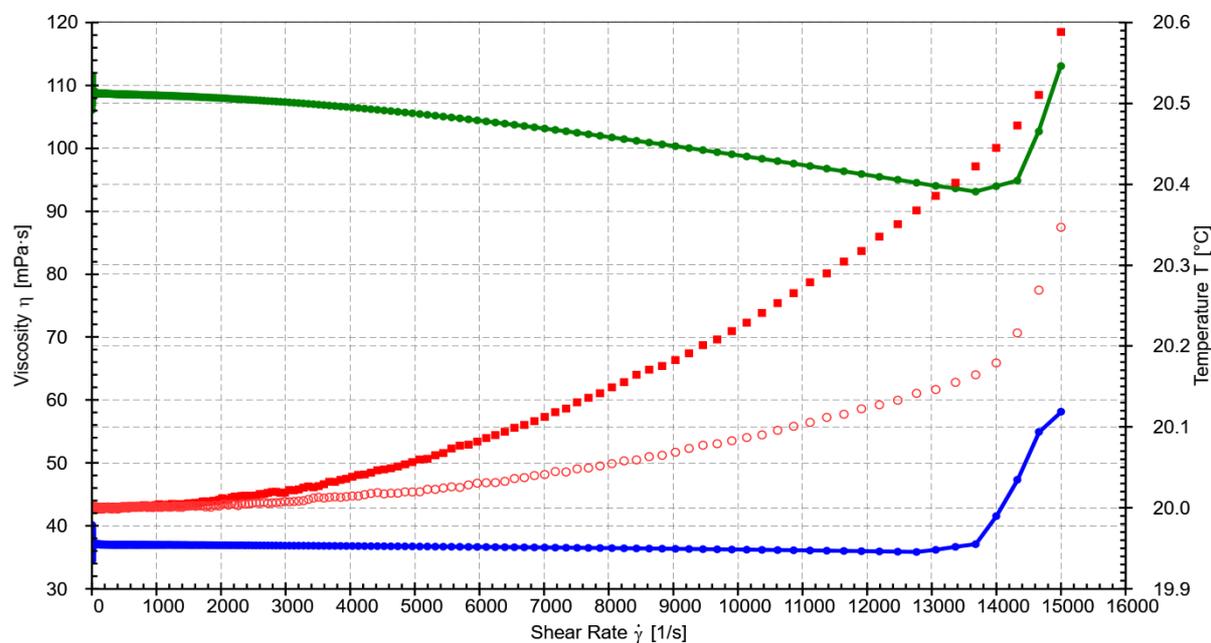
Rheological studies on [EMIm][1] and [BMPL][1] were performed with a Modular Compact Rheometer 302 (MCR 302, Anton Paar Germany GmbH) with a cone plate (Peltier-controlled) system in a glass cabin under inert conditions (Ar, 200 mL min<sup>-1</sup>).

Both, [EMIm][1] and [BMPL][1] show slightly shear warming lower than 0.5 °C while increasing the shear rate up to 13000 s<sup>-1</sup> (Figure S18). While [EMIm][1] shows nearly Newtonian behaviour in this shear-rate range, however [BMPL][1] shows significant shear thinning of more than 10 mPa s. Such a decrease in viscosity corresponds to an increase in temperature of more than 3 °C as known from table S3 and figure S17. Therefore this decrease is not correlated to the temperature. This shear thinning effect was observed in furthermore experiments under different conditions.

Above 13000 s<sup>-1</sup> [EMIm][1] and [BMPL][1] show a shear thickening behaviour which presumably is caused by a crossing from laminar into turbulent flow. The observed shear thinning and thickening behaviour was fully reversible and none of the ILs show any decomposition upon this mechanical stress as confirmed by NMR spectroscopy after the rheological measurements.



**Figure S17.** Dynamic viscosity of [EMIm][1] (blue) and [BMPL][1] (green) in the temperature range from 20 to 80 °C and back at a shear rate of 500 s<sup>-1</sup>.



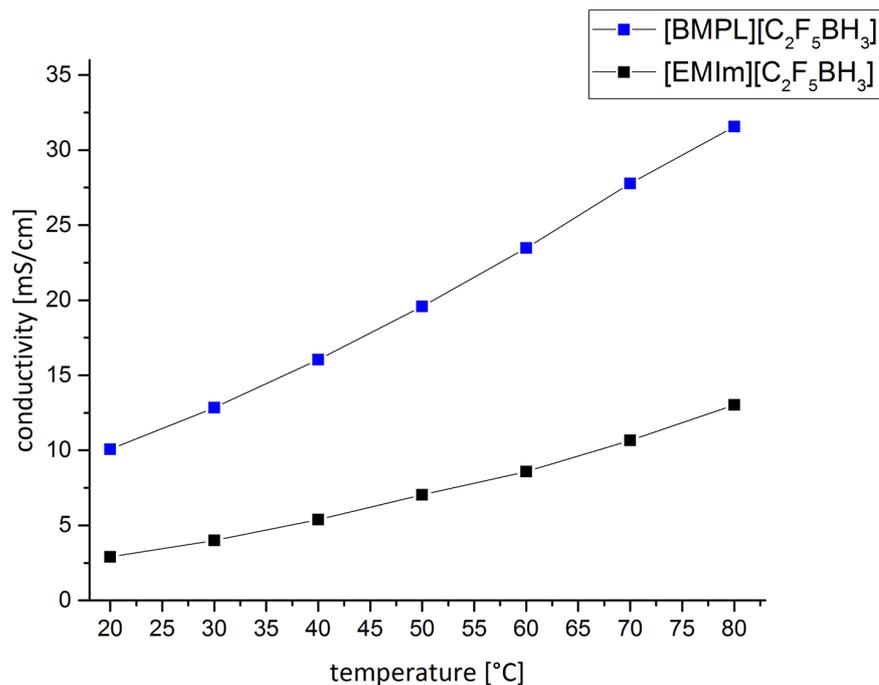
**Figure S18.** Dynamic viscosity [EMIm][1] (blue) and [BMPL][1] (green) in the shear-rate range up to 15000 s<sup>-1</sup>. (▪ T [°C] of [BMPL][1], ○ T [°C] of [EMIm][1],) at 20 °C.

## Conductivity Measurements

Conductivity measurements were carried out with neat ionic liquids under an argon atmosphere with a Metrohm PGSTAT30 potentiostat (Metrohm Autolab B.V., Netherlands) and a Microcell HC set-up with a Eurotherm temperature controller (rhd instruments, Germany) in the temperature range of 20–80 °C (Table S4). The measurements were performed with a TSC 70 closed Pt-cell (rhd instruments, Germany) that contained 0.1 mL of the sample. Conductivity measurements of neat [EMIm][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>] ([EMIm]1) and [BMPL][C<sub>2</sub>F<sub>5</sub>BH<sub>3</sub>] ([BMPL]1) were performed by electrochemical impedance spectroscopy (EIS) in the frequency range from 500kHz to 800 MHz with a cell constant of  $C = 1.787788 \text{ cm}^{-1}$ . The cell constant was determined by measuring a standard solution (1.278 mS cm<sup>-1</sup> at 20 °C, HI 70031, Hanna Instruments Deutschland GmbH, Germany).

**Table S4.** Specific conductivity ( $\sigma$ ) of neat [EMIm]1 and [BMPL]1 at different temperatures.

IL	$\sigma$ (20 °C)	$\sigma$ (30 °C)	$\sigma$ (40 °C)	$\sigma$ (50 °C)	$\sigma$ (60 °C)	$\sigma$ (70 °C)	$\sigma$ (80 °C)
[EMIm]1	10.1	12.8	16.0	19.6	23.5	27.8	31.6
[BMPL]1	2.9	4.0	5.4	7.0	8.6	10.7	13.0



**Figure S19.** Conductivity of neat [EMIm]1 and [BMPL]1 at different temperatures.

### DFT Calculations

Density functional calculations (DFT)<sup>8</sup> were carried out using Becke's three-parameter hybrid functional and the Lee-Yang-Parr correlation functional (B3LYP)<sup>9</sup> using the Gaussian09 program suite.<sup>10</sup> Geometries were optimized and energies were calculated with the 6-311++G(d,p) (SDD for iodine) basis sets. Diffuse functions were incorporated because improved energies are obtained for anions.<sup>11</sup> Structures represent true minima with no imaginary frequency on the respective hypersurface. Energies, enthalpies and Gibbs free energies are collected in Table S5. Calculated DFT-GIAO-NMR chemical shifts and coupling constants were calibrated to diborane(6) with  $\delta(^{11}\text{B}) = 16.6$  ppm and  $\text{CFCl}_3$  with  $\delta(^{19}\text{F}) = 0$  ppm.

**Table S5.** Calculated energies and free energies at the B3LYP/6-311+G(d,p) level of theory.

species	symmetry	$E(298\text{ K})$ [au]	$H$ [au]	$G$ [au]
F <sup>-</sup>		-99.888693	-99.886333	-99.902852
H <sup>-</sup>		-0.534164	-0.531803	-0.544163
thf	$C_1$	-232.402649	-232.396725	-232.431228
C <sub>2</sub> F <sub>5</sub> BH <sub>2</sub>	$C_s$	-601.590059	-601.581060	-601.622917
BBr <sub>3</sub>	$D_{3h}$	-7747.393885	-7747.387890	-7747.424743
BCl <sub>3</sub>	$D_{3h}$	-1405.649718	-1405.644382	-1405.677246
BF <sub>3</sub>	$D_{3h}$	-324.652044	-324.647571	-324.676527
BH <sub>3</sub>	$D_{3h}$	-26.595002	-26.591172	-26.612548
BI <sub>3</sub>	$D_{3h}$	-59.170212	-59.163778	-59.203463
C <sub>2</sub> F <sub>5</sub> BH <sub>2</sub> -thf	$C_1$	-834.034320	-834.020191	-834.076013
[C <sub>2</sub> F <sub>5</sub> BH <sub>3</sub> ] <sup>-</sup>	$C_1$	-602.286548	-602.277609	-602.319106
[C <sub>2</sub> F <sub>5</sub> BH <sub>2</sub> F] <sup>-</sup>	$C_1$	-701.623195	-701.613507	-701.657635
[BBr <sub>3</sub> F] <sup>-</sup>	$C_{3v}$	-7847.433724	-7847.426268	-7847.466844
[BCl <sub>3</sub> F] <sup>-</sup>	$C_{3v}$	-1505.681593	-1505.674936	-1505.711294
[BF <sub>4</sub> ] <sup>-</sup>	$T_d$	-424.666025	-424.660623	-424.691361
[BI <sub>3</sub> F] <sup>-</sup>	$C_{3v}$	-159.221053	-159.213079	-159.256754
[BBr <sub>3</sub> H] <sup>-</sup>	$C_{3v}$	-7748.089929	-7748.083430	-7748.122082
[BCl <sub>3</sub> H] <sup>-</sup>	$C_{3v}$	-1406.334023	-1406.328180	-1406.362715
[BF <sub>3</sub> H] <sup>-</sup>	$C_{3v}$	-325.302670	-325.297878	-325.328116
[BI <sub>3</sub> H] <sup>-</sup>	$C_{3v}$	-59.881135	-59.874200	-59.915771

**Table S6.** Calculated and measured NMR chemical shifts at the B3LYP/6-311++G(2d,p) level of theory.<sup>a</sup>

anion	measured				calculated			
	$\delta(^{11}\text{B})$	$^1J(^{11}\text{B},^1\text{H})$	$\delta(^{19}\text{F})$ CF <sub>3</sub> / CF <sub>2</sub>	$^2J(^{19}\text{F},^{11}\text{B})$	$\delta(^{11}\text{B})$	$^1J(^{11}\text{B},^1\text{H})$	$\delta(^{19}\text{F})$ CF <sub>3</sub> / CF <sub>2</sub>	$^2J(^{19}\text{F},^{11}\text{B})$
[CF <sub>3</sub> BH <sub>3</sub> ] <sup>-</sup>	-31.6	83.6	-47.9	28.2	-39.9	80.7	-71.3	24.7
[C <sub>2</sub> F <sub>5</sub> BH <sub>3</sub> ] <sup>-</sup>	-33.3	84.7	-84.4 / -110.9	18.3	-39.8	81.2	-103.9 <sup>b</sup> / -135.0	15.6

<sup>a</sup>  $\delta$  in [ppm];  $J$  in Hz. <sup>b</sup> Mean value.

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