# **Electronic Supplementary Information**

# Ethyl-, vinyl- and ethynylcyanoborates: Room temperature borate ionic liquids with saturated and unsaturated hydrocarbon chains

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#### **Experimental Section**

Reactions involving air-sensitive compounds were performed either in 100 or 250 mL roundbottom flasks or in 20 or 60 mL glass tubes equipped with valves with PTFE stems (Rettberg, Göttingen) under argon by using standard Schlenk-line techniques. <sup>11</sup>B, <sup>19</sup>F and <sup>13</sup>C NMR spectra were recorded at 25 °C in (CD<sub>3</sub>)<sub>2</sub>CO on a Bruker Avance I 500 spectrometer. <sup>13</sup>C{<sup>11</sup>B} and <sup>13</sup>C{<sup>11</sup>B, <sup>1</sup>H} spectra were recorded on a Bruker Advance III HD 300 spectrometer. The <sup>13</sup>C{<sup>19</sup>F} NMR spectra were recorded on a Bruker Avance I 500 spectrometer equipped with Prodigy Cyroprobe. The NMR signals were referenced against TMS (<sup>1</sup>H and <sup>13</sup>C), BF<sub>3</sub>·OEt<sub>2</sub> in  $CDCl_3$  with  $\Xi$ <sup>(11</sup>B) = 32.083974 MHz and  $CFCl_3$  with  $\Xi$ <sup>(19</sup>F) = 94.094011 MHz as external standards.<sup>1</sup> <sup>1</sup>H and <sup>13</sup>C chemical shifts were calibrated against the residual solvent signal and the solvent signal, respectively ( $\delta$ <sup>(1</sup>H): (CD<sub>2</sub>H)(CD<sub>3</sub>)CO 2.05 ppm;  $\delta$ (<sup>13</sup>C): (CD<sub>3</sub>)<sub>2</sub>CO 206.26 and 29.84 ppm).<sup>2</sup> IR spectra were measured in the attenuated total reflection (ATR) mode in the region of 4000–400 cm<sup>-1</sup> with an apodized resolution of 2 cm<sup>-1</sup> with a Bruker Alpha spectrometer equipped with a Bruker diamond single reflection ATR system. Raman spectra were recorded at room temperature with a MultiRAM FT-Raman spectrometer using the 1064 nm excitation line of a Nd/YAG laser on crystalline samples contained in melting point capillaries in the region of 3500–100 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> Elemental analyses (C, H, N) were performed with Elementar Varion Micro Cube instrument. Thermal analyses were performed with a DSC 204 F1 Phoenix (Netzsch) in the temperature range of -175 to 550 °C with a heating rate of 10 K min<sup>-1</sup>. Viscosities and densities were measured with a rolling-ball viscometer Lovis 2000 ME combined with DMA 4100 M density meter (Anton Paar) at different angles and temperatures.

All electrochemical studies were performed on the neat ILs under an argon atmosphere with a Metrohm PGSTAT30 potentiostat and a Microcell HC set-up with a Eurotherm temperature controller (rhd instruments). A 0.1 mL Pt-cell TSC-70 closed (rhd instruments) was applied and its cell body served as counter electrode and it was equipped with a glassy carbon working electrode (surface area:  $3.14 \times 10^{-2}$  cm<sup>2</sup>). Specific conductivities ( $\sigma$ ) were determined at different temperatures (20, 40,60, 70 and 80 °C) by impedance spectroscopy from 500 × 10<sup>3</sup> Hz to 800 Hz. The cell constant was determined on a 1413 µS cm<sup>-1</sup> conductivity solution HI 70031 (HANNA instruments). Cyclic voltammetry was conducted at 20 °C with a scan rate of 50 mV s<sup>-1</sup> using the same set-up and an additional Ag/Ag<sup>+</sup> micro reference electrode (acetonitrile, rhd instruments).

Density functional calculations  $(DFT)^3$  using the hybrid functional B3LYP<sup>4-6</sup> and Pople-type basis sets 6-311++G(d,p) were performed with the Gaussian16 program suite. All structures represent true minima with no imaginary frequency on the respective hypersurface.<sup>7</sup>

#### Chemicals

All standard chemicals were obtained from commercial sources. Solvents were dried according to standard protocols and stored in flasks equipped with valves with PTFE stems (Rettberg, Göttingen) under an argon atmosphere.  $K[C_2H_5BF_3]$  and  $K[H_2C=CHBF_3]$  were obtained from ABCR.  $K[HC=CBF_3]$  was synthesized according to known procedures starting from B(OCH<sub>3</sub>)<sub>3</sub> and HC=CMgBr followed by subsequent fluorination with KHF<sub>2</sub>.<sup>8</sup>

#### 1. Syntheses

#### 1.1 Potassium salts

#### 1.1.1 Potassium ethyltricyanoborate

**K**[**C**<sub>2</sub>**H**<sub>5</sub>**B**(**CN**)<sub>3</sub>] (K1): Potassium ethyltrifluoroborate K[C<sub>2</sub>H<sub>5</sub>BF<sub>3</sub>] (7.00 g, 51.5 mmol) was suspended in TMSCN (75 mL, 598 mmol). At room temperature, TMSCI (1.5 mL, 11.8 mmol) was added dropwise, which resulted in a slight warming of the solution. The reaction mixture was stirred for 16 h at 60 °C. The excess TMSCN was distilled off from the dark red suspension. The brown residue was dried under fine vacuum and then dissolved in deionized water (20 mL). The solution was slowly treated with aqueous hydrogen peroxide (20 mL, 30% v/v) followed by the addition of K<sub>2</sub>CO<sub>3</sub> (6 g). The mixture was stirred for two hours to result in a slightly yellow reaction mixture. Potassium disulfite K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> was added until the reaction had ceased. All solvents were removed at 80 °C at a rotary evaporator and the residue was extracted with acetonitrile (3 × 150 mL). The combined solutions were dried with K<sub>2</sub>CO<sub>3</sub>, filtered and the volume was reduced to about 5–10 mL. The addition of Et<sub>2</sub>O (50 mL) resulted in the precipitation of potassium ethyltricyanoborate, which was isolated as a white powdery solid after filtering and drying under fine vacuum. Yield: 4.50 g (28.7 mmol, 56%).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 0.92 (br m, CH<sub>3</sub>, 3H), 0.45 (br m, CH<sub>2</sub>, 2H).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 0.92 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH<sub>3</sub>, 3H), 0.45 (q, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH<sub>2</sub>, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 129.9 (q, <sup>1</sup>J<sub>CB</sub> = 64.2 Hz, *C*N, 3C), 13.0 (q, <sup>1</sup>J<sub>CB</sub> = 45.2 Hz, *C*H<sub>2</sub>, 1C), 11.3 (s, *C*H<sub>3</sub>, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -29.9 (s, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -29.9 (s, 1B).

Anal. calculated for C₅H₅BKN₃: C, 38.25%; H, 3.21%; N, 26.76%. Found: C, 38.30%; H, 3.29%; N, 26.37%.

#### 1.1.2 Potassium ethylfluorodicyanoborate

 $K[C_2H_5BF(CN)_2]$  (K4): Potassium ethyltrifluoroborate  $K[C_2H_5BF_3]$  (5.27 g, 38.8 mmol) was suspended in CH<sub>3</sub>CN (20 mL). TMSCN (9.60 mL, 77.6 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 1 h at 80 °C. All volatiles were removed under reduced pressure, and the slightly coloured crude product was dissolved in water (100 mL) and aqueous H<sub>2</sub>O<sub>2</sub> (1 mL, 30% *v*/*v*) and K<sub>2</sub>CO<sub>3</sub> was added. After stirring for 2 h, K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> was added until no more reaction was observed. The solution was saturated with KCl and extracted with THF (5 x 100 mL). The combined THF solutions were dried with K<sub>2</sub>CO<sub>3</sub>, filtered and evaporated to dryness at a rotary evaporator. The solid remainder was dissolved in THF (5 mL) and colourless K[C<sub>2</sub>F<sub>5</sub>BF(CN)<sub>2</sub>] precipitated upon addition of CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The solid was filtered off and dried under fine vacuum. Yield: 3.15 g (21.0 mmol, 54%).

Colourless single crystals suitable for X-Ray diffraction were obtained from an acetone solution by slow evaporation of the solvent.

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 0.81 (br m, CH<sub>3</sub>, 3H), 0.31 (br m, CH<sub>2</sub>, 2H).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 0.81 (t, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, CH<sub>3</sub>, 3H), 0.31 (dq, <sup>3</sup>J<sub>FH</sub> = 11.2 Hz, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, CH<sub>2</sub>, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 133.7 (dq, <sup>1</sup>J<sub>CB</sub> = 62.9 Hz, <sup>2</sup>J<sub>FC</sub> = 39.3 Hz, *C*N, 2C), 16.1 (dq, <sup>1</sup>J<sub>CB</sub> = 46.6 Hz, <sup>2</sup>J<sub>FC</sub> = 24.3 Hz, *C*H<sub>2</sub>, 1C), 9.1 (d, <sup>2</sup>J<sub>FC</sub> = 4.85 Hz, *C*H<sub>3</sub>, 1C).

<sup>13</sup>C{<sup>19</sup>F} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 133.7 (dq, <sup>1</sup>*J*<sub>CB</sub> = 62.9 Hz, <sup>2</sup>*J*<sub>FC</sub> = 39.3 Hz, *C*N, 2C), 16.1 (dq, <sup>1</sup>*J*<sub>CB</sub> = 46.6 Hz, <sup>2</sup>*J*<sub>FC</sub> = 24.3 Hz, *C*H<sub>2</sub>, 1C), 9.1 (d, <sup>2</sup>*J*<sub>FC</sub> = 4.85 Hz, *C*H<sub>3</sub>, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -7.2 (d, <sup>1</sup>J<sub>FB</sub> = 56.8 Hz, 1B).

<sup>11</sup>B{<sup>19</sup>F} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -7.2 (s, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -7.2 (d, <sup>1</sup>J<sub>FB</sub> = 56.8 Hz, 1B).

<sup>19</sup>F NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -207.8 (qt, <sup>1</sup>J<sub>FB</sub> = 56.8 Hz, <sup>3</sup>J<sub>FH</sub> = 11.2 Hz, BF, 1F).

<sup>19</sup>F{<sup>11</sup>B} NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -207.8 (t, <sup>3</sup>*J*<sub>FH</sub> = 11.2 Hz, B*F*, 1F).

Anal. calculated for C<sub>4</sub>H<sub>5</sub>BFKN<sub>2</sub>: C, 32.03%; H, 3.36%; N, 18.68%. Found: C, 32.41%; H, 2.89; N, 18.34%.

#### 1.1.3 Potassium vinyltricyanoborate

**K[H<sub>2</sub>C=CHB(CN)<sub>3</sub>]** (K2): Potassium vinyltrifluoroborate K[H<sub>2</sub>C=CHBF<sub>3</sub>] (8.00 g, 59.7 mmol) was suspended in TMSCN (60 mL, 47.6 g, 480 mmol). TMSCI (6.00 mL, 5.12 g, 47.2 mmol) was added dropwise at room temperature, which was accompanied by strong gas evolution. The reaction mixture was stirred for 2 h at 80 °C. All volatiles were removed under reduced pressure and the dark coloured crude product was dissolved in acetone (100 mL). Brownish coloured K[H<sub>2</sub>C=CHB(CN)<sub>3</sub>] precipitated upon addition of CH<sub>2</sub>Cl<sub>2</sub> (300 mL). The solid was filtered off and dried under vacuum. The crude product was dissolved in water and crystals of the neat compound were obtained by slow evaporation of the solvent. The crystals were separated by decantation from the solution and washed with Et<sub>2</sub>O. This procedure was repeated several times until colourless material was obtained. Yield: 4.81 g (31.0 mmol, 52%).

Colourless single crystals suitable for X-Ray diffraction were obtained from aqueous solution by slow evaporation of the solvent.

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 5.77 (br m, CH, 3H), 5.44 (br m, CH<sub>2</sub>, 1H<sub>trans</sub>), 5.37 (br m, CH<sub>2</sub>, 1H<sub>cis</sub>).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 5.77 (dd, <sup>3</sup>J<sub>HH-trans</sub> = 19.6 Hz, <sup>3</sup>J<sub>HH-cis</sub> = 12.5 Hz, CH, 1H), 5.44 (dd, <sup>3</sup>J<sub>HH-trans</sub> = 19.6 Hz, <sup>2</sup>J<sub>HH</sub> = 3.8 Hz, CH<sub>2</sub>, 1H<sub>trans</sub>), 5.37 (dd, <sup>3</sup>J<sub>HH-cis</sub> = 12.5 Hz, <sup>2</sup>J<sub>HH</sub> = 3.8 Hz, CH<sub>2</sub>, 1H<sub>trans</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 139.7 (q, <sup>1</sup>J<sub>CB</sub> = 55.9 Hz, *C*H, 1C), 128.9 (q, <sup>1</sup>J<sub>CB</sub> = 65.2 Hz, *C*N, 3C), 123.3 (s, *C*H<sub>2</sub>, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -30.5 (m, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -30.5 (s, 1B).

Anal. calculated for C₅H<sub>3</sub>BKN<sub>3</sub>: C, 38.74%; H, 1.95%; N, 27.11%. Found: C, 38.62%; H, 1.97%; N, 27.70%.

#### 1.1.4 Potassium vinylfluorodicyanoborate

 $K[H_2C=CHBF(CN)_2]$  (K5): Potassium vinyltrifluoroborate  $K[H_2C=CHBF_3]$  (4.90 g, 36.6 mmol) was suspended in CH<sub>3</sub>CN (20 mL). TMSCN (8.91 mL, 71.3 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 1 h at room temperature. All volatiles were removed under reduced pressure. The slightly yellowish crude product was dissolved in THF (10 mL). Colourless  $K[H_2C=CHBF(CN)_2]$  precipitated upon addition of  $CH_2Cl_2$  (200 mL) at 0 °C. The solid was filtered off and dried under vacuum. Yield: 3.74 g (25.3 mmol, 69%).

Colourless single crystals suitable for X-Ray diffraction were obtained by slow diffusion of dichloromethane into an acetone solution of K**5**.

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 5.87 (br m, CH, 1H), 5.40 (br m, CH<sub>2</sub>, 1H<sub>trans</sub>), 5.28 (br m, CH<sub>2</sub>, 1H<sub>cis</sub>).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 5.87 (ddd, <sup>3</sup>J<sub>HH-trans</sub> = 19.4 Hz, <sup>3</sup>J<sub>HH-cis</sub> = 12.4 Hz, <sup>3</sup>J<sub>FH</sub> = 7.00 Hz, CH, 1H), 5.40 (ddd, <sup>3</sup>J<sub>HH-trans</sub> = 19.4 Hz, <sup>2</sup>J<sub>HH</sub> = 4.34 Hz, <sup>4</sup>J<sub>FH</sub> = 2.13 Hz, <sup>3</sup>J<sub>HH-trans</sub> = 19.4 Hz, CH<sub>2</sub>, 1H<sub>trans</sub>), 5.28 (dd, <sup>3</sup>J<sub>HH-cis</sub> = 12.4 Hz, <sup>2</sup>J<sub>HH</sub> = 4.34 Hz, CH<sub>2</sub>, 1H<sub>cis</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 145.5 (qd, <sup>1</sup>J<sub>CB</sub> = 65.1 Hz, <sup>2</sup>J<sub>FC</sub> = 25.3 Hz, *C*H, 1C), 132.3 (dq, <sup>1</sup>J<sub>CB</sub> = 64.8 Hz, <sup>2</sup>J<sub>FC</sub> = 39.4 Hz, *C*N, 2C), 120.9 (d, <sup>3</sup>J<sub>FC</sub> = 7.00 Hz, *C*H<sub>2</sub>, 1C).

<sup>13</sup>C{<sup>19</sup>F} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 145.5 (dq, <sup>1</sup>J<sub>CH</sub> = 135.0 Hz, <sup>2</sup>J<sub>CB</sub> = 64.8 Hz, *C*H, 1C), 132.3 (q, <sup>1</sup>J<sub>CB</sub> = 64.8 Hz, *C*N, 2C), 120.9 (td, <sup>1</sup>J<sub>CH</sub> = 153.3 Hz <sup>2</sup>J<sub>CH</sub> = 4.28 Hz, *C*H<sub>2</sub>, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -9.4 (d, <sup>1</sup>*J*<sub>FB</sub> = 54.1 Hz, 1B).

<sup>11</sup>B{<sup>19</sup>F} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -9.4 (m, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  =-9.4 (d, <sup>1</sup>J<sub>FB</sub> = 54.1 Hz, 1B).

<sup>19</sup>F NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -206.8 (q, <sup>1</sup>*J*<sub>FB</sub> = 54.1 Hz, B*F*, 1F).

<sup>19</sup>F{<sup>11</sup>B} NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -206.8 (dd, <sup>3</sup>J<sub>FH</sub> = 7.0 Hz, <sup>4</sup>J<sub>FH</sub> = 2.13 Hz, BF, 1F).

Anal. calculated for C<sub>4</sub>H<sub>5</sub>BFKN<sub>2</sub>: C, 32.46%; H, 2.04%; N, 18.93%. Found: C, 32.06%; H, 1.97%; N, 18.94%.

#### 1.1.5 Potassium ethynyltricyanoborate

**K[HC=CB(CN)<sub>3</sub>]** (K**3**): Potassium ethynyltrifluoroborate K[HC=CBF<sub>3</sub>] (5.70 g, 43.2 mmol) was suspended in TMSCN (60 mL, 47.6 g, 480 mmol). TMSCI (6.00 mL, 5.12 g, 47.2 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 2 d at 80 °C. All volatiles were removed under reduced pressure, the dark coloured crude product was dissolved in water (150 mL) and aqueous  $H_2O_2$  (10 mL, 30% v/v) and  $K_2CO_3$  was added. After stirring for 17 h,  $K_2S_2O_5$  was added until no more reaction was observed. The solution was saturated with KCl and extracted with THF (5 x 100 mL). The combined THF solutions were dried with  $K_2CO_3$ , filtered and evaporated to dryness at a rotary evaporator. The solid remainder was dissolved in THF (10 mL) and off-white K[HC=CB(CN)<sub>3</sub>] precipitated upon addition of CH<sub>2</sub>Cl<sub>2</sub> (200 mL). The solid was filtered off and dried under vacuum. Yield: 4.49 g (29.4 mmol, 68%).

Colourless single crystals suitable for X-Ray diffraction were obtained by slow diffusion of dichloromethane into an acetone solution of K**3**.

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 2.35 (q, <sup>3</sup>J<sub>BH</sub> = 2.50 Hz, 1H).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 2.35 (s, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 126.6 (q, <sup>1</sup>J<sub>CB</sub> = 67.2 Hz, CN, 3C), 86.8 (q, <sup>1</sup>J<sub>CB</sub> = 80.5 Hz, BCCH, 1C), 84.9 (q, <sup>2</sup>J<sub>CB</sub> = 16.9 Hz, BCCH, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -36.9 (d, <sup>3</sup>J<sub>BH</sub> = 2.50 Hz, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -36.9 (s, 1B).

Anal. calculated for C₅HBKN<sub>3</sub>: C, 39.25%; H, 0.66%; N, 27.47%. Found: C, 38.18%; H, 0.89%; N, 27.60%.

#### 1.1.6 Potassium ethynylfluorodicyanoborate

**K[HC=CBF(CN)**<sub>2</sub>] (K6): Potassium ethynyltrifluoroborate K[HC=CBF<sub>3</sub>] (4.55 g, 34.5 mmol) was suspended in CH<sub>3</sub>CN (20 mL) and TMSCN (8.62 mL, 69.0 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 17 h at room temperature. All volatiles were removed under reduced pressure. The slightly coloured crude product was dissolved in water (100 mL) and aqueous H<sub>2</sub>O<sub>2</sub> (3 mL, 30% *v*/*v*) and K<sub>2</sub>CO<sub>3</sub> was added. After stirring for 2 h, K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> was added until no more reaction was observed. The solution was saturated with KCl and extracted with THF (5 x 100 mL). The combined solutions were dried with K<sub>2</sub>CO<sub>3</sub>, filtered and evaporated to dryness at a rotary evaporator. The solid remainder was dissolved in THF (10 mL) and colourless K[HC=CBF(CN)<sub>2</sub>] precipitated upon addition of CH<sub>2</sub>Cl<sub>2</sub> (200 mL). The solid was filtered off and dried under vacuum. Yield: 3.88 g (26.5 mmol, 77%).

Colourless single crystals suitable for X-Ray diffraction were obtained from an acetonitrile solution by slow evaporation of the solvent.

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 2.32 (br m, CCH, 1H).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 2.32 (d, <sup>4</sup>J<sub>FH</sub> = 3.19 Hz, CCH, 1H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 130.4 (qd, <sup>1</sup>J<sub>CB</sub> = 69.9 Hz, <sup>2</sup>J<sub>FC</sub> = 39.9 Hz, CN, 2C), 93.3 (qd, <sup>1</sup>J<sub>CB</sub> = 84.5 Hz, <sup>2</sup>J<sub>FC</sub> = 34.4 Hz, BCCH, 1C), 83.3 (qd, <sup>2</sup>J<sub>CB</sub> = 18.1 Hz, <sup>3</sup>J<sub>FC</sub> = 6.3 Hz, BCCH, 1C).

<sup>13</sup>C{<sup>19</sup>F} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 130.4 (q, <sup>1</sup>*J*<sub>CB</sub> = 69.9 Hz, *C*N, 2C), 93.3 (qd, <sup>1</sup>*J*<sub>CB</sub> = 84.5 Hz, <sup>2</sup>*J*<sub>CH</sub> = 43.0 Hz, BCCH, 1C), 83.3 (dq, <sup>1</sup>*J*<sub>CH</sub> = 236.7 Hz, <sup>2</sup>*J*<sub>CB</sub> = 18.1 Hz, BCCH, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -15.9 (d, <sup>1</sup>*J*<sub>FB</sub> = 47.4 Hz, 1B).

<sup>11</sup>B{<sup>19</sup>F} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -15.9 (s, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -15.9 (d, <sup>1</sup>J<sub>FB</sub> = 47.4 Hz, 1B).

<sup>19</sup>F NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -204.9 (q, <sup>1</sup>*J*<sub>FB</sub> = 47.4 Hz, B*F*, 1F).

<sup>19</sup>F{<sup>11</sup>B} NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -204.9 (d, <sup>4</sup>*J*<sub>FH</sub> = 3.19 Hz, B*F*, 1F).

Anal. calculated for C<sub>4</sub>HBFKN<sub>2</sub>: C, 32.91%; H, 0.69%; N, 19.19%. Found: C, 32.25%; H, 0.62%; N, 18.64%.

## 1.2 [EMIm]<sup>+</sup> salts

All [EMIm]<sup>+</sup> salts were synthesized by salt metatheses using the corresponding potassium salt and [EMIm]Cl as starting materials following the general procedure described below.

#### General procedure for the synthesis of [EMIm]<sup>+</sup> salts:

The potassium borate was dissolved in deionized water (50–100 mL) and an aqueous solution of [EMIm]Cl (1.1 eq., 4.63 M) was added. The solution was stirred at room temperature for 30 min. The aqueous solution was extracted with  $CH_2Cl_2$  (3 x 100 mL) and the combined organic phases were washed with deionized water (10 x 5 mL). The solvent was removed at a rotary evaporator. The ionic liquid was dried under fine vacuum at 50 °C overnight.

#### 1.2.1 1-Ethyl-3-methylimidazolium ethyltricyanoborate

**[EMIm][C**<sub>2</sub>**H**<sub>5</sub>**B(CN)**<sub>3</sub>**]** ([EMIm]**1**): The general procedure was employed for the preparation of [EMIm]**1** using K**1** (3.00 g, 19.1 mmol) and [EMIm]Cl (2.94 g, 20.1 mmol) to yield [EMIm]**1** as a colourless ionic liquid. Yield: 3.89 g (17.0 mmol, 89%).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 8.99 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.74 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.67 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 4.39 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.05 (s, CH<sub>3</sub>, 3H), 1.57 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H), 0.90 (br m, CH<sub>3</sub>, 3H), 0.43 (br m, CH<sub>2</sub>, 2H).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 8.99 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.74 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$ <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.67 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 4.39 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.05 (s, CH<sub>3</sub>, 3H), 1.57 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H), 0.90 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH<sub>3</sub>, 3H), 0.43 (q, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH<sub>2</sub>, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 136.76 (s, *C*H, 1C), 130.5 (q, <sup>1</sup>*J*<sub>CB</sub> = 64.2 Hz, *C*N, 3C), 124.47 (s, *C*H, 1C), 122.81 (s, *C*H, 1C), 45.47 (s, *C*H<sub>2</sub>, 1C), 36.38 (s, *C*H<sub>3</sub>, 1C), 15.32 (s, *C*H<sub>3</sub>, 1C), 13.0 (q, <sup>1</sup>*J*<sub>CB</sub> = 45.2 Hz, CH<sub>2</sub>, 1C), 11.3 (s, CH<sub>3</sub>, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -30.0 (s, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -30.0 (s, 1B).

Anal. calculated for C<sub>11</sub>H<sub>16</sub>BN<sub>5</sub>: C, 57.67%; H, 7.04%; N, 30.57% Found: C, 57.28%; H, 7.31%; N, 30.90%.

#### 1.2.2 1-Ethyl-3-methylimidazolium vinyltricyanoborate

**[EMIm][H<sub>2</sub>C=CHB(CN)<sub>3</sub>]** ([EMIm]**2**): The general procedure was employed for the preparation of [EMIm]**2** using K**2** (2.30 g, 14.8 mmol) and [EMIm]Cl (2.28 g, 15.6 mmol) to yield [EMIm]**2** as a colourless ionic liquid. Yield: 2.89 g (12.7 mmol, 86%).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 9.00 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.75 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.68 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 5.77 (br m, CH, 1H), 5.44 (br m, CH<sub>2</sub>, 1H<sub>trans</sub>), 5.37 (br m, CH<sub>2</sub>, 1H<sub>cis</sub>), 4.40 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.05 (s, CH<sub>3</sub>, 3H), 1.57 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 9.00 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.75 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$ <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.68 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 5.77 (dd, <sup>3</sup>J<sub>HH-trans</sub> = 19.6 Hz, <sup>3</sup>J<sub>HH-cis</sub> = 12.5 Hz, CH, 1H), 5.44 (dd, <sup>3</sup>J<sub>HH-trans</sub> = 19.6 Hz, <sup>2</sup>J<sub>HH</sub> = 3.8 Hz, CH<sub>2</sub>, 1H<sub>trans</sub>), 5.37 (dd, <sup>3</sup>J<sub>HH-cis</sub> = 12.5 Hz, <sup>2</sup>J<sub>HH</sub> = 3.8 Hz, CH<sub>2</sub>, 1H<sub>cis</sub>), 4.39 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.05 (s, CH<sub>3</sub>, 3H), 1.57 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 139.7 (q, <sup>1</sup>*J*<sub>CB</sub> = 55.9 Hz, *C*H, 1C), 136.8 (s, *C*H, 1C), 128.9 (q, <sup>1</sup>*J*<sub>CB</sub> = 65.2 Hz, *C*N, 3C), 124.47 (s, *C*H, 1C), 123.3 (s, *C*H<sub>2</sub>, 1C), 122.9 (s, *C*H, 1C), 45.5 (s, *C*H<sub>2</sub>, 1C), 36.5 (s, *C*H<sub>3</sub>, 1C), 15.4 (s, *C*H<sub>3</sub>, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -30.5 (m, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -30.5 (s, 1B).

Anal. calculated for C<sub>11</sub>H<sub>14</sub>BN<sub>5</sub>: C, 58.18%; H, 6.21%; N, 30.84%. Found: C, 57.86%; H, 6.60%; N, 30.99%.

#### 1.2.3 1-Ethyl-3-methylimidazolium ethynyltricyanoborate

**[EMIm][HC≡CB(CN)**<sub>3</sub>] ([EMIm]**3**): The general procedure was employed for the preparation of [EMIm]**3** using K**3** (2.50 g, 16.3 mmol) and [EMIm]Cl (2.52 g,17.2 mmol) to yield [EMIm]**3** as a colourless ionic liquid. Yield: 3.04 g (13.5 mmol, 83%).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 9.00 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.75 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.68 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 4.40 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.05 (s, CH<sub>3</sub>, 3H), 2.35 (q, <sup>3</sup>J<sub>BH</sub> = 2.50 Hz, HCC, 1H), 1.57 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 9.00 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.75 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$ <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.68 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 4.40 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.05 (s, CH<sub>3</sub>, 3H), 2.35 (s, HCC, 1H), 1.57 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 136.7 (s, CH, 1C), 126.6 (q, <sup>1</sup>*J*<sub>CB</sub> = 67.2 Hz, CN, 3C), 124.5 (s, CH, 1C), 122.8 (s, CH, 1C), 86.8 (q, <sup>1</sup>*J*<sub>CB</sub> = 80.5 Hz, BCCH, 1C), 84.9 (q, <sup>2</sup>*J*<sub>CB</sub> = 16.9 Hz, BCCH, 1C), 45.5 (s, CH<sub>2</sub>, 1C), 36.4 (s, CH<sub>3</sub>, 1C), 15.3 (s, CH<sub>3</sub>, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -36.9 (d, <sup>3</sup>J<sub>BH</sub> = 2.50 Hz, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -36.9 (s, 1B).

Anal. calculated for C<sub>11</sub>H<sub>12</sub>BN<sub>5</sub>: C, 58.70%; H, 5.37%; N, 31.12%. Found: C, 58.25%; H, 5.59%; N, 30.62%.

#### 1.2.4 1-Ethyl-3-methylimidazolium ethylfluorodicyanoborate

[EMIm][C<sub>2</sub>H<sub>5</sub>BF(CN)<sub>2</sub>] ([EMIm]4): The general procedure was employed for the preparation of [EMIm]4 using K4 (3.70 g, 24.7 mmol) and [EMIm]Cl (3.80 g, 25.9 mmol) to yield [EMIm]4 as a colourless ionic liquid. Yield: 5.00 g (22.5 mmol, 91%).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 8.96 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.73 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.66 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 4.38 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.04 (s, CH<sub>3</sub>, 3H), 1.56 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H), 0.81 (br m, CH<sub>3</sub>, 3H), 0.31 (br m, CH<sub>2</sub>, 2H).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 8.96 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.73 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$ <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.66 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 4.38 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.04 (s, CH<sub>3</sub>, 3H), 1.56 (t, CH<sub>3</sub>,  ${}^{3}J_{HH}$  = 7.40 Hz, 3H), 0.81 (t,  ${}^{3}J_{HH}$  = 7.7 Hz, CH<sub>3</sub>, 3H), 0.31 (dq,  ${}^{3}J_{FH}$  = 11.2 Hz,  ${}^{3}J_{HH}$  = 7.7 Hz, CH<sub>2</sub>, 2H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 136.6 (s, CH, 1C), 133.7 (dq, <sup>1</sup>*J*<sub>CB</sub> = 62.9 Hz, <sup>2</sup>*J*<sub>FC</sub> = 39.3 Hz, *C*N, 2C), 124.3 (s, *C*H, 1C), 122.6 (s, *C*H, 1C), 45.3 (s, *C*H<sub>2</sub>, 1C), 36.2 (s, *C*H<sub>3</sub>, 1C), 16.1 (dq, <sup>1</sup>*J*<sub>CB</sub> = 46.6 Hz, <sup>2</sup>*J*<sub>FC</sub> = 24.3 Hz, CH<sub>2</sub>, 1C), 15.1 (s, *C*H<sub>3</sub>, 1C), 9.1 (d, <sup>2</sup>*J*<sub>FC</sub> = 4.85 Hz, CH<sub>3</sub>, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -7.2 (d, <sup>1</sup>J<sub>FB</sub> = 56.8 Hz, 1B).

<sup>11</sup>B{<sup>19</sup>F} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -7.2 (s, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -7.2 (d, <sup>1</sup>J<sub>FB</sub> = 56.8 Hz, 1B).

<sup>19</sup>F NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -207.9 (qt, <sup>1</sup>J<sub>FB</sub> = 56.8 Hz, <sup>3</sup>J<sub>FH</sub> = 11.2 Hz, BF, 1F).

<sup>19</sup>F{<sup>11</sup>B} NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -207.9 (t, <sup>3</sup>J<sub>FH</sub> = 11.2 Hz, BF, 1F).

Anal. calculated for C<sub>10</sub>H<sub>16</sub>BFN<sub>4</sub>: C, 54.09%; H, 7.26%; N, 25.23%. Found: C, 53.53%; H, 7.55%; N, 26.28%.

#### 1.2.5 1-Ethyl-3-methylimidazolium vinylfluorodicyanoborate

[EMIm][H<sub>2</sub>C=CHBF(CN)<sub>2</sub>] ([EMIm]5): The general procedure was employed for the preparation of [EMIm]5 using K5 (3.30 g, 22.3 mmol) and [EMIm]Cl (3.43 g, 23.4 mmol) to yield [EMIm]5 as a colourless ionic liquid. Yield: 4.42 g (20.1 mmol, 90%).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 8.89 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.69 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.62 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 5.87 (br m, CH, 1H), 5.40 (br m, CH<sub>2</sub>, 1H<sub>trans</sub>), 5.28 (br m, CH<sub>2</sub>, 1H<sub>cis</sub>), 4.35 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.01 (s, CH<sub>3</sub>, 3H), 1.55 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 8.89 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.69 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.62 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 5.87 (ddd, <sup>3</sup>J<sub>HH-trans</sub> = 19.4 Hz, <sup>3</sup>J<sub>HH-cis</sub> = 12.4 Hz, <sup>3</sup>J<sub>FH</sub> = 7.00 Hz, CH, 1H), 5.40 (ddd, <sup>3</sup>J<sub>HH-trans</sub> = 19.4 Hz, <sup>2</sup>J<sub>HH</sub> = 4.34 Hz, <sup>4</sup>J<sub>FH</sub> = 2.13 Hz, <sup>3</sup>J<sub>HH-trans</sub> = 19.4 Hz, CH<sub>2</sub>, 1H<sub>trans</sub>), 5.28 (dd, <sup>3</sup>J<sub>HH-cis</sub> = 12.4 Hz, <sup>2</sup>J<sub>HH</sub> = 4.34 Hz, CH<sub>2</sub>, 1H<sub>cis</sub>), 4.35 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.01 (s, CH<sub>3</sub>, 3H), 1.55 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 145.5 (qd, <sup>1</sup>J<sub>CB</sub> = 65.1 Hz, <sup>2</sup>J<sub>FC</sub> = 25.3 Hz, *C*H, 1C), 136.2 (s, *C*H, 1C), 132.4 (dq, <sup>1</sup>J<sub>CB</sub> = 64.8 Hz, <sup>2</sup>J<sub>FC</sub> = 39.4 Hz, *C*N, 2C), 124.0 (s, *C*H, 1C), 122.4 (s, *C*H, 1C), 120.9 (d, <sup>3</sup>J<sub>FC</sub> = 7.00 Hz, *C*H<sub>2</sub>, 1C), 45.1 (s, *C*H<sub>2</sub>, 1C), 36.0 (s, *C*H<sub>3</sub>, 1C), 14.9 (s, *C*H<sub>3</sub>, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -9.4 (d, <sup>1</sup>J<sub>FB</sub> = 54.1 Hz, 1B).

<sup>11</sup>B{<sup>19</sup>F} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -9.4 (m, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): 
$$\delta$$
 =-9.4 (d, <sup>1</sup>*J*<sub>FB</sub> = 54.1 Hz, 1B).

<sup>19</sup>F NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -206.8 (q, <sup>1</sup>J<sub>FB</sub> = 54.1 Hz, BF, 1F).

<sup>19</sup>F{<sup>11</sup>B} NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -206.8 (dd, <sup>3</sup>J<sub>FH</sub> = 7.0 Hz, <sup>4</sup>J<sub>FH</sub> = 2.13 Hz, BF, 1F).

Anal. calculated for C<sub>10</sub>H<sub>14</sub>BFN<sub>4</sub>: C, 54.58%; H, 6.41%; N, 25.46%. Found, [%]: C, 54.97%; H, 6.69%; N, 25.60%.

#### 1.2.6 1-Ethyl-3-methylimidazolium ethynylfluorodicyanoborate

[EMIm][HC=CBF(CN)<sub>2</sub>] ([EMIm]6): The general procedure was employed for the preparation of [EMIm]6 using K6 (2.20 g, 15.1 mmol) and [EMIm]Cl (2.32 g, 15.8 mmol) to yield [EMIm]6 as a colourless ionic liquid. Yield: 2.79 g (12.8 mmol, 85%).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 8.99 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.74 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.67 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 4.39 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.05 (s, CH<sub>3</sub>, 3H), 2.32 (m, CCH, 1H), 1.57 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 8.99 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.74 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$ <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.67 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 4.39 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.05 (s, CH<sub>3</sub>, 3H), 2.32 (d, <sup>4</sup>J<sub>FH</sub> = 3.19 Hz, CCH, 1H), 1.57 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 136.2 (s, *C*H, 1C), 130.4 (qd, <sup>1</sup>J<sub>CB</sub> = 69.9 Hz, <sup>2</sup>J<sub>FC</sub> = 39.9 Hz, *C*N, 2C), 124.0 (s, *C*H, 1C), 122.3 (s, *C*H, 1C), 93.3 (qd, <sup>1</sup>J<sub>CB</sub> = 84.5 Hz, <sup>2</sup>J<sub>FC</sub> = 34.4 Hz, BCCH, 1C), 83.3 (qd, <sup>2</sup>J<sub>CB</sub> = 18.1 Hz, <sup>3</sup>J<sub>FC</sub> = 6.3 Hz, BCCH, 1C), 45.1 (s, *C*H<sub>2</sub>, 1C), 36.0 (s, *C*H<sub>3</sub>, 1C), 14.9 (s, *C*H<sub>3</sub>, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -15.9 (d, <sup>1</sup>J<sub>FB</sub> = 47.4 Hz, 1B).

<sup>11</sup>B{<sup>19</sup>F} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -15.9 (s, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -15.9 (d, <sup>1</sup>J<sub>FB</sub> = 47.4 Hz, 1B).

<sup>19</sup>F NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -204.9 (q, <sup>1</sup>J<sub>FB</sub> = 47.4 Hz, BF, 1F).

<sup>19</sup>F{<sup>11</sup>B} NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -204.9 (d, <sup>4</sup>*J*<sub>FH</sub> = 3.19 Hz, B*F*, 1F).

Anal. calculated for C<sub>10</sub>H<sub>12</sub>BFN<sub>4</sub>: C, 55.09%; H, 5.55%; N, 25.70%. Found: C, 55.39%; H, 5.68%; N, 26.04%.

#### 1.2.7 1-Ethyl-3-methylimidazolium ethynyltrifluoroborate

**[EMIm][HC=CBF**<sub>3</sub>]: The general procedure was employed for the preparation of [EMIm] [HC=CBF<sub>3</sub>] using K[HC=CBF<sub>3</sub>] (5.50 g, 41.7 mmol) and [EMIm]Cl (6.73 g, 45.9 mmol) to yield [EMIm][HC=CBF<sub>3</sub>] as a colourless ionic liquid. Yield: 5.70 g (27.9 mmol, 67%).

<sup>1</sup>H NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 8.94 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.73 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$  <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.65 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 4.35 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.00 (s, CH<sub>3</sub>, 3H), 1.86 (m, CCH, 1H), 1.52 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H).

<sup>1</sup>H{<sup>11</sup>B} NMR (500.13 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 8.94 (t, CH, <sup>4</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.73 (t, CH, <sup>4</sup>J<sub>HH</sub>  $\approx$ <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, 1H), 7.65 (t, CH, <sup>3</sup>J<sub>HH</sub>  $\approx$  <sup>4</sup>J<sub>HH</sub> = 1.7 Hz, 1H), 4.35 (t, CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, 2H), 4.00 (s, CH<sub>3</sub>, 3H), 1.86 (q, <sup>4</sup>J<sub>FH</sub> = 1.13 Hz, CCH, 1H), 1.57 (t, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 7.40 Hz, 3H).

<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = 136.3 (s, CH, 1C), 123.7 (s, CH, 1C), 122.1 (s, CH, 1C), 98.0 (qq, <sup>1</sup>*J*<sub>CB</sub> = 103.5 Hz, <sup>2</sup>*J*<sub>FC</sub> = 68.9 Hz, BCCH, 1C), 77.6 (qq, <sup>2</sup>*J*<sub>CB</sub> = 19.8 Hz, <sup>3</sup>*J*<sub>FC</sub> = 9.7 Hz, BCCH, 1C), 44.7 (s, CH<sub>2</sub>, 1C), 35.8 (s, CH<sub>3</sub>, 1C), 14.8 (s, CH<sub>3</sub>, 1C).

<sup>11</sup>B NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -1.97 (q, <sup>1</sup>J<sub>FB</sub> = 36.5 Hz, 1B).

<sup>11</sup>B{<sup>19</sup>F} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -1.97 (s, 1B).

<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -1.97 (q, <sup>1</sup>J<sub>FB</sub> = 36.5 Hz, 1B).

<sup>19</sup>F NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = –133.8 (q, <sup>1</sup>*J*<sub>FB</sub> = 36.5 Hz, B*F*, 3F).

<sup>19</sup>F{<sup>11</sup>B} NMR (471 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  = -133.8 (s, B*F*, 3F).

Anal. calculated for C<sub>8</sub>H<sub>12</sub>BF<sub>3</sub>N<sub>2</sub>: C, 47.10%; H, 5.93%; N, 13.73%. Found: C, 46.72%; H, 6.13%; N, 13.90%.

# 2. NMR spectroscopic details

	<sup>11</sup> B	2.	24	<sup>19</sup> F			<sup>1</sup> Η		2.	2.	2/4+			<sup>13</sup> C			<sup>1</sup> <i>J</i> <sub>CB</sub>	1J <sub>CB</sub>	24
Anion	δ	2J <sub>BH</sub>	зЈ <sub>ВН</sub>	δ (BF)	J <sub>FB</sub>	δ (–CH <sub>2</sub> –)	δ (–CH₃)	δ (–CH)	зJ <sub>НН</sub>	-Э <sub>нн</sub>	<sup>3/4</sup> J <sub>FH</sub>	δ (– CH <sub>2</sub> –)	δ (–CH₃)	δ (–CH)	δ (–СВ)	δ (–CN)	(BCN)	(CCB)	2J <sub>FC</sub>
	[ppm]		[Hz]	[ppm]	[Hz]		[ppm]			[Hz]				[pp	m]			[Hz]	
[C <sub>2</sub> H <sub>5</sub> B(CN) <sub>3</sub> ] <sup>−</sup>	-29.9	6.0	-	-	-	0.45	0.92	-	7.6	-	-	13.0	11.3	-	-	129.9	64.2	45.2	-
[H <sub>2</sub> C=CHB(CN) <sub>3</sub> ] <sup>−</sup>	-30.5	-	-	-	-	5.39	-	5.77	19.6 ( <i>trans</i> ) 12.5 ( <i>cis</i> )	3.8	-	123.3	-	139.7	-	128.9	65.2	55.9	-
[HC≡CB(CN) <sub>3</sub> ] <sup>−</sup>	-36.9	-	2.5	-	-	-	-	2.35	-	-	-	-	-	84.9	86.8	126.6	67.2	80.5	-
$[C_2H_5BF(CN)_2]^-$	-7.2	-	-	-207.8	56.8	0.31	0.81	-	7.7	-	11.2	16.1	9.1	-	-	133.7	62.9	46.6	39.3 ( <i>C</i> N) 24.3 ( <i>C</i> C)
[H <sub>2</sub> C=CHBF(CN) <sub>2</sub> ] <sup>-</sup>	-9.4	-	-	-206.8	54.1	5.32	-	5.87	19.4 (trans) 12.4 (cis)	4.34	7.0	120.9	-	145.5	-	132.3	64.8	64.8	39.4 ( <i>C</i> N) 25.3 ( <i>C</i> C)
[HC=CBF(CN) <sub>2</sub> ] <sup>-</sup>	-15.9	-	-	-204.9	47.4	-	-	2.32	-	-	3.2	-	-	83.3	93.3	130.4	69.9	84.5	39.9 ( <i>C</i> N) 34.3 ( <i>C</i> C)

#### Table S1: Selected NMR spectroscopic data of ethyl-, vinyl- and ethynylcyanoborate anions.

#### Table S2: Selected calculated<sup>a</sup> NMR spectroscopic data of ethyl-, vinyl- and ethynylcyanoborate anions.

1	<sup>11</sup> B	2.	24	<sup>19</sup> F	1.		<sup>1</sup> H		24					<sup>13</sup> C			1J <sub>CB</sub>	1 <sub>J<sub>CB</sub></sub>	24
Anion	δ	2 <b>Ј</b> ВН	∍Ј <sub>ВН</sub>	δ (B <i>F</i> )	±J <sub>FB</sub>	δ (–CH <sub>2</sub> –)	$\delta$ (–CH <sub>3</sub> )	δ (–CH)	∍Јнн	∠ <b>ј</b> <sub>НН</sub> зј	∘J <sub>FH</sub>	δ (–CH <sub>2</sub> –)	δ (–CH <sub>3</sub> )	δ (–CH)	δ (–CB)	δ (–CN)	(BCN)	(C <i>CB</i> )	<sup>2</sup> J <sub>FC</sub>
	[ppm]		[Hz]	[ppm]	[Hz]		[ppm]		[Hz	]				[pp	m]			[Hz]	
[C <sub>2</sub> H <sub>5</sub> B(CN) <sub>3</sub> ] <sup>−</sup>	-36.6	-4.4	4.5	-	-	0.44	0.93	-	6.9	-	-	20.3	12.2	-	-	134.8	68.1	43.1	-
[H <sub>2</sub> C=CHB(CN) <sub>3</sub> ] <sup>-</sup>	-38.7	2.8	7.6	-	-	5.51	-	6.53	16.8 (trans) 12.4 (cis)	3.1	-	125.3	-	157.0	-	134.7	68.8	54.8	-
[HC=CB(CN) <sub>3</sub> ] <sup>-</sup>	-43.0	-	2.7	-	-	-	-	1.11	-	-	-	-	-	77.9	96.2	130.9	70.8	80.6	-
[C <sub>2</sub> H <sub>5</sub> BF(CN) <sub>2</sub> ] <sup>-</sup>	-13.0	-1.6	3.9	-254.4	-108.2	0.30	0.83	-	6.9	- 11	1.8	22.8	10.5	-	-	138.1	69.9	51.4	35.1
[H <sub>2</sub> C=CHBF(CN) <sub>2</sub> ] <sup>-</sup>	-15.6	5.02	6.2	-259.4	-103.5	5.22	-	6.38	16.3 (trans) 12.1 (cis)	4.8		114.8	-	162.4	-	136.5	70.8	61.7	34.6
[HC≡CBF(CN) <sub>2</sub> ] <sup>−</sup>	-21.2	-	2.8	-241.8	-100.2	-	-	1.09	-	:	-3.5	-	-	75.5	103.0	135.1	74.9	87.4	35.5

<sup>a</sup> B3LYP/6-311++G(2d,p)//B3LYP/6-311++G(d,p).



Figure S1: <sup>11</sup>B NMR spectra of ethynylborate anions  $[HC \equiv CBF_n(CN)_{3-n}]^-$ .



<sup>13</sup>C NMR

Figure S2: Sections of the <sup>13</sup>C, <sup>13</sup>C{<sup>19</sup>F}, <sup>13</sup>C{<sup>11</sup>B,<sup>1</sup>H} and <sup>13</sup>C{<sup>11</sup>B} NMR spectra of ethyl-, vinyl- and ethynylcyanoborates.

# 2. Vibrational spectroscopy

	<i>ν</i> ̈́ (C≡N)									
anion		IR	Rai	man						
	K+	[EMIm]*	K+	[EMIm] <sup>+</sup>	calc.					
[C <sub>2</sub> H <sub>5</sub> B(CN) <sub>3</sub> ] <sup>-</sup>	2214	2203	2218	2205	2295					
[H₂C=CHB(CN)₃]⁻	2219	2205	2221	2208	2300					
[HC=CB(CN) <sub>3</sub> ] <sup>-</sup>	2226	2213	2228	2216	2308					
[C <sub>2</sub> H <sub>5</sub> BF(CN) <sub>2</sub> ] <sup>-</sup>	2200	2194	2204	2197	2285					
[H <sub>2</sub> C=CHBF(CN) <sub>2</sub> ] <sup>-</sup>	-	2198	2215	2199	2287					
[HC=CBF(CN) <sub>2</sub> ] <sup>-</sup>	-	2203	2224	2208	2297					

Table S3: Selected experimental and calculated vibrational spectroscopic data of ethyl, vinyl- and ethynylcyanoborates.



Figure S3: IR and Raman spectra of the potassium salts of the ethyl-, vinyl- and ethynylcyanoborate anions.

**Table S4**: Experimental and calculated C≡C and CH stretching band positions of Potassium salts and EMIm-ILs of ethynyl borate anions.

			ν̃ (C≡C)				i	ῦ (CH)		
anion		IR	Ra	aman			IR		Raman	
	K⁺	[EMIm]⁺	K+	[EMIm]+	calc.	K+	[EMIm]+	K⁺	[EMIm]+	calc.
[HC≡CBF <sub>3</sub> ] <sup>-</sup>	2068	2056	2070	2059	2131	3280	n.d.	3282	n.d.	3467
[HC≡CBF(CN) <sub>2</sub> ] <sup>-</sup>	2068	2064	2070	2065	2147	3284	n.d.	3287	n.d.	3471
[HC≡CB(CN)₃] <sup>−</sup>	2077	2073	2078	2074	2157	3275	n.d.	3278	n.d.	3474



Figure S4: IR and Raman spectra of the potassium salts of the ethynylborate anions.

# 3. Thermal properties

anion	K⁺ salt		[EMIm] <sup>+</sup> salt			
	<i>T</i> <sub>mp</sub> [°C]	T <sub>dec</sub> [°C]	<i>T</i> <sub>fp</sub> [°C]	<i>T</i> <sub>g</sub> [°C]	<i>T</i> <sub>mp</sub> [°C]	T <sub>dec</sub> [°C]
[C₂H₅B(CN)₃] <sup>-</sup>	242	410	-	-95	-	388
[H <sub>2</sub> C=CHB(CN) <sub>3</sub> ] <sup>-</sup>	230	290	-69	-96	-17	344
[HC=CB(CN)₃]⁻	251	285	-	-91	-	296
[C <sub>2</sub> H <sub>5</sub> BF(CN) <sub>2</sub> ]⁻	93	170	-	-111	-	229
[H <sub>2</sub> C=CHBF(CN) <sub>2</sub> ] <sup>-</sup>	-	160	-	-112	-	190
[HC≡CBF(CN) <sub>2</sub> ] <sup>-</sup>	179	180	-	-104	-	219

Table S5: Thermal properties of potassium salts and EMIm-ILs of ethyl-, vinyl- and ethynylcyanoborate anions



Figure S5. DSC curve of K1.



Figure S6. DTA/TG curves of K1.



Figure S7. DSC curve of K2.



Figure S8. DTA/TG curves of K2.



Figure S9. DSC curve of K3.



Figure S10. DTA/TG curves of K3.



Figure S11. DSC curve of K4.



Figure S12. DTA/TG curves of K4.



Figure S13. DSC curve of K5.



Figure S14. DTA/TG curves of K5.







Figure S16. DTA/TG curves of K6.



Figure S17. DSC curve of [EMIm]1 in the temperature range from 40 °C to -170 °C.



Figure S18. DSC curve of [EMIm]1 in the temperature range from 20 °C to 550 °C.



Figure S19. DTA/TG curves of [EMIm]1.



Figure S20. DSC curve of [EMIm]2 in the temperature range from 40 °C to -175 °C.



Figure S21. DSC curve of [EMIm]2 in the temperature range from 20 °C to 550 °C.



Figure S22. DTA/TG curves of [EMIm]2.



Figure S23. DSC curve of [EMIm]3 in the temperature range from 40 °C to -175 °C.



Figure S24. DSC curve of [EMIm]3 in the temperature range from 20 °C to 550 °C.







Figure S26. DSC curve of [EMIm]4 in the temperature range from 40 °C to -175 °C.



Figure S27. DSC curve of [EMIm]4 in the temperature range from 20 °C to 550 °C.



Figure S28. DTA/TG curves of [EMIm]4.



Figure S29. DSC curve of [EMIm]5 in the temperature range from 40 °C to -175 °C.



Figure S30. DSC curve of [EMIm]5 in the temperature range from 20 °C to 550 °C.







Figure S32. DSC curve of [EMIm]6 in the temperature range from 40 °C to -175 °C.



Figure S33. DSC curve of [EMIm]6 in the temperature range from 20 °C to 550 °C.



Figure S34. DTA/TG curves of [EMIm]6.



Figure S35. DSC curve of  $[EMIm][HC=CBF_3]$  in the temperature range from 40 °C to -175 °C.



Figure S36. DSC curve of [EMIm][HC=CBF<sub>3</sub>] in the temperature range from 20 °C to 550 °C.



**Figure S37**: Decomposition temperature ( $T_{dec}$ ) of EMIm-ILs of ethyl-, vinyl- and ethynylcyanoborates anions.

# 4. Viscosity and density

 Table S6. Selected electrochemical parameters of [EMIm]<sup>+</sup> salts in the temperature range of 293–353 K.

anion	М		density $ ho$				dynamic viscosity $\eta$					СС	oncentra	ation <i>c</i>	= ρ · M	-1
		20 °C	40°C	60 °C	70 °C	80 °C	20 °C	40 °C	60 °C	70 °C	80 °C	20 °C	40 °C	60 °C	70 °C	80 °C
	[g·mol <sup>−1</sup> ]			[g∙mL <sup>-1</sup>	]				[mPa∙s]				[	mol·L <sup>-1</sup>	]	
[C₂H₅B(CN)₃] <sup>−</sup>	229.09	0.99	0.98	0.96	0.96	0.95	24.9	12.5	7.5	6.0	5.2	4.32	4.28	4.19	4.19	4.15
[H <sub>2</sub> C=CHB(CN) <sub>3</sub> ] <sup>−</sup>	227.08	1.01	0.99	0.98	0.97	0.97	16.2	9.1	5.8	4.8	4.0	4.45	4.36	4.32	4.27	4.27
[HC≡CB(CN) <sub>3</sub> ] <sup>−</sup>	225.06	1.02	1.01	0.99	0.99	0.98	24.7	12.3	7.3	5.9	4.9	4.53	4.49	4.40	4.40	4.35
$[C_2H_5BF(CN)_2]^-$	222.07	1.03	1.01	1.00	0.99	0.98	19.5	10.7	6.8	5.6	4.7	4.64	4.55	4.50	4.46	4.41
$[H_2C=CHBF(CN)_2]^-$	220.06	1.05	1.03	1.02	1.01	1.01	13.3	7.9	5.2	4.4	3.8	4.77	4.68	4.64	4.59	4.59
[HC≡CBF(CN) <sub>2</sub> ] <sup>−</sup>	218.04	1.06	1.05	1.03	1.03	1.02	18.1	10.1	6.5	5.4	4.6	4.86	4.82	4.72	4.72	4.67
[HC≡CBF <sub>3</sub> ] <sup>−</sup>	204.00	1.19	1.18	1.16	1.16	1.15	34.5	17.9	11.0	8.8	7.3	5.83	5.78	5.69	5.69	5.64
[B(CN) <sub>4</sub> ] <sup>-</sup> <i>e</i>	226.05	1.04	1.02	1.01	1.00	0.99	22.6	11.4	7.0	5.7	4.7	4.60	4.53	4.46	4.43	4.40



Figure S38: Dynamic viscosities (η) of EMIm-ILs of ethyl, vinyl- and ethynylcyanoborate anions at 25 °C. Values for [EMIm][C<sub>2</sub>H<sub>5</sub>BF<sub>3</sub>] and [EMIm][H<sub>2</sub>C=CHBF<sub>3</sub>] were taken from the literature.<sup>9</sup>



**Figure S39**: Dynamic viscosities ( $\eta$ ) of EMIm-ILs of ethyl-, vinyl- and ethynylcyanoborate anions at 20 °C.

#### Table S6 continued.

anion	S	pecific	condu	ctivity a	σ		I	og(A <sub>imp</sub> )	a				$\log(\eta^{-1})$		
	20 °C	40 °C	60 °C	70 °C	80 °C	20 °C	40 °C	60 °C	70 °C	80 °C	20 °C	40 °C	60 °C	70 °C	80 °C
		[r	nS∙cm⁻	<sup>-1</sup> ]			[log(	S·cm²·mo	ol <sup>-1</sup> )]			[lo	g(cm·s·g⁻	<sup>-1</sup> )]	
$[C_2H_5B(CN)_3]^-$	5.6	9.4	13.8	17.4	18.4	0.1127	0.3417	0.5177	0.6183	0.6468	0.6038	0.9031	1.1249	1.2218	1.2840
$[H_2C=CHB(CN)_3]^-$	7.7	12.3	17.8	20.0	22.4	0.2381	0.4504	0.6149	0.6706	0.7198	0.7904	1.0410	1.2366	1.3188	1.3979
[HC≡CB(CN) <sub>3</sub> ] <sup>−</sup>	6.5	11.4	16.7	19.6	22.6	0.1568	0.4047	0.5793	0.6488	0.7156	0.6073	0.9101	1.1367	1.2291	1.3098
$[C_2H_5BF(CN)_2]^-$	12.8	19.9	29.7	34.7	38.4	0.4407	0.6408	0.8195	0.8910	0.9399	0.7010	0.9706	1.1675	1.2518	1.3279
$[H_2C=CHBF(CN)_2]^-$	13.0	19.1	26.1	30.8	32.4	0.4354	0.6108	0.7501	0.8267	0.8487	0.8761	1.1024	1.2840	1.3565	1.4202
[HC≡CBF(CN) <sub>2</sub> ] <sup>-</sup>	11.5	17.2	23.9	27.1	29.9	0.3747	0.5527	0.7074	0.7590	0.8062	0.7423	0.9957	1.1871	1.2676	1.3372
[HC≡CBF <sub>3</sub> ] <sup>−</sup>	7.96	13.4	20.1	22.85	26.2	0.134	0.365	0.548	0.604	0.667	0.462	0.747	0.959	1.056	1.137
[B(CN) <sub>4</sub> ] <sup>-</sup> <i>e</i>	12.1	20.7	31.0	36.6	42.4	0.4211	0.6588	0.8410	0.9171	0.9845	0.6612	0.9582	1.1791	1.2705	1.3520

 $^{a}\Lambda_{imp} = \sigma \cdot c^{-1}$ .



Figure S40: Conductivities ( $\sigma$ ) of EMIm-ILs of ethyl-, vinyl- and ethynylcyanoborate anions at 25 °C. Values for [EMIm][C<sub>2</sub>H<sub>5</sub>BF<sub>3</sub>] and [EMIm][H<sub>2</sub>C=CHBF<sub>3</sub>] were taken from the literature.<sup>9</sup>



Figure S41: Conductivities (*o*) of EMIm-ILs of ethyl-, vinyl- and ethynylcyanoborate anions at 20 °C

#### Table S6 continued.

anion	D <sup>+ b</sup>			<b>D</b> <sup>- c</sup>			$\Lambda_{\rm NMR}{}^d$		$arLambda_{imp}$			$I = \Lambda_{\rm imp} \cdot \Lambda_{\rm NMR}^{-1}$								
	20 °C	40 °C	60 °C	80°C	20 °C	40 °C	60 °C	80°C	20 °C	40 °C	60 °C	80°C	20 °C	40 °C	60 °C	80°C	20 °C	40 °C	60 °C	80°C
		[10 <sup>-11</sup> ·	m²∙s <sup>−1</sup> ]			[10 <sup>-11</sup> ·	m²⋅s <sup>−1</sup> ]			[cm²·S·	mol <sup>–1</sup> ]		l	[cm²·S·	mol <sup>-1</sup> ]			[-	·]	
[C <sub>2</sub> H <sub>5</sub> B(CN) <sub>3</sub> ] <sup>−</sup>	5.6	11.7	19.7	31.6	4.2	8.9	15.3	24.4	3.74	7.35	11.7	17.7	1.30	2.20	3.29	4.43	0.35	0.30	0.28	0.25
$[H_2C=CHB(CN)_3]^-$	8.9	17.0	27.0	42.5	7.0	13.4	21.3	33.5	6.06	10.9	16.2	24.1	1.73	2.82	4.12	5.24	0.28	0.26	0.25	0.22
[HC≡CB(CN)₃]⁻	6.1	11.7	19.8	34.3	4.5	8.6	14.7	25.7	4.04	7.25	11.6	18.9	1.43	2.54	3.80	5.19	0.35	0.35	0.33	0.27
$[C_2H_5BF(CN)_2]^-$	7.4	14.5	23.9	36.3	5.7	11.2	18.9	29.3	5.00	9.17	14.4	20.8	2.76	4.37	6.60	8.71	0.55	0.48	0.49	0.42
[H <sub>2</sub> C=CHBF(CN) <sub>2</sub> ] <sup>-</sup>	11.0	19.9	32.2	45.5	8.7	16.0	26.2	37.5	7.51	12.8	19.6	26.3	2.73	4.08	5.63	7.06	0.36	0.31	0.28	0.27
[HC≡CBF(CN) <sub>2</sub> ] <sup>-</sup>	8.6	16.5	27.3	41.0	6.2	11.9	19.8	29.8	5.64	10.1	15.8	22.4	2.37	3.57	5.06	6.40	0.42	0.35	0.32	0.29
[HC≡CBF <sub>3</sub> ] <sup>−</sup>	5.0	n.d	n.d	n.d	3.3	n.d	n.d	n.d	3.16	n.d	n.d	n.d	1.36	2.32	3.53	4.64	0.43	n.d	n.d	n.d
[B(CN) <sub>4</sub> ] <sup>-</sup> <i>e</i>	6.3	13.3	22.5	n.d.	5.4	11.8	20.1	n.d.	4.47	8.98	14.3	n.d.	2.64	4.56	6.93	n.d.	0.59	0.51	0.48	n.d.

<sup>b</sup>  $D^+$  was determined by <sup>1</sup>H NMR DOSY, mean value of all signals. <sup>c</sup>  $D^-$  was determined by <sup>1</sup>H and <sup>19</sup>F NMR DOSY, mean value of all signals. <sup>d</sup> calcd. by:  $\Lambda_{NMR} = (D^+ + D^-) \cdot N_A \cdot e^2 \cdot k_B^{-1} \cdot T^{-1} \cdot e^2$  Lit.<sup>10</sup>



Figure S42: Plots of molar conductivities of EMIm-ILs versus temperature ( $\Lambda_{NMR}$ : calculated from diffusion constants derived from DOSY NMR experiments;  $\Lambda_{imp}$ : measured via impedance spectroscopy).

# 6. Cyclic voltammograms

anion	E <sub>a</sub> [V]	<i>E</i> <sub>c</sub> [V]	<b>⊿E</b> [V] <sup>[a]</sup>
[C₂H₅B(CN)₃] <sup>−</sup>	2.5	-2.4	4.9
[H <sub>2</sub> C=CHB(CN) <sub>3</sub> ] <sup>-</sup>	2.7	-2.4	5.1
[HC≡CB(CN) <sub>3</sub> ]⁻	2.5	-2.4	4.9
[C₂H₅BF(CN)₂]⁻	2.4	-2.4	4.8
[H₂C=CHBF(CN)₂] <sup>−</sup>	3.3	-2.4	5.8
[HC≡CBF(CN) <sub>2</sub> ]⁻	3.1	-2.4	5.5
[HC≡CBF <sub>3</sub> ] <sup>−</sup>	0.9	-2.4	3.1
[B(CN) <sub>4</sub> ]-	2.0	-2.4	4.4

**Table S7**. Cathodic limit  $E_c$ , anodic limit  $E_a$  and electrochemical window  $\Delta E = E_a - E_c$  of neat EMIm-salts.



Figure S43: Cyclic voltammograms of neat EMIm-ILs of ethynylborate anions.

### 8. Single Crystal X-ray Diffraction

Crystals of K2, K3, K4, K5 and K6 were investigated with a XtaLAB Synergy, Dualflex, Hypix diffractometer using Cu-K<sub> $\alpha$ </sub> radiation (micro-focus sealed X-Ray tube,  $\lambda = 1.54184$  Å) or Mo-K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å). All structures were solved by direct methods,<sup>11</sup> and refinements are based on full-matrix-least-squares calculations on  $F^2$ . All non-hydrogen atoms were refined anisotropically. The positions of all H atoms were located from electron density difference maps. In the final steps of the refinements, idealized bond lengths and angles were introduced for most of the H atoms.

All calculations were performed with the ShelXle graphical interface.<sup>12</sup> Molecular structure diagrams were drawn with the programm Diamond 4.6.3.<sup>13</sup> Selected experimental details, crystal data and the CCDC numbers are collected in Table S8 and selected bond parameters are summarized in Table S9.

Table S8: Selected crystal data and experi	mental details for the structure determinations of	f the notassium ethyl vinyl- a	nd ethynylcyanohorates
Table 36. Selected ci ystal data and experi		i the polassium ethyl, vinyl- a	nu etnynyicyanoborates.

compound	К <b>2</b>	К <b>З</b>	К <b>4</b>	К5	К <b>6</b>	K[HC≡CBF <sub>3</sub> ]
Formula	$C_5H_3BKN_3$	C <sub>5</sub> HBKN <sub>3</sub>	$C_4H_5BFKN_2$	$C_{24}H_{18}B_6F_6K_6N_{12}$	C <sub>4</sub> HBFKN <sub>2</sub>	C <sub>2</sub> HBF <sub>3</sub> K
<i>Mw</i> [g mol <sup>-1</sup> ]	155.01	153.00	150.01	887.96	145.98	131.94
<i>T</i> [K]	100	100	100	100	100	100
Colour	colourless	colourless	colourless	colourless	colourless	colourless
Crystal size [mm <sup>3</sup> ]	0.371 x 0.265 x 0.186	0.325 x 0.293 x 0.244	0.140 x 0.050 x 0.030	0.330 x 0.250 x 0.150	0.340 x 0.270 x 0.160	0.080 x 0.070 x 0.020
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic
Space group	P21/c	P21/c	P21/c	ΡĪ	P21/c	Pbca
a [Å]	8.5049(2)	7.4162(1)	10.7130(4)	9.7205(1)	7.0120(1)	6.9337(1)
b [Å]	12.8513(2)	13.6940(2)	8.4048(2)	13.8586(3)	12.1801(3)	7.0937(2)
<i>c</i> [Å]	7.1205(2)	7.4904(1)	7.9608(3)	15.5058(2)	7.7061(2)	18.3067(5)
α[°]				74.003(2)		
β[°]	94.550(2)	105.738(1)	104.381	89.658(1).	95.232(2)	
γ[°]				82.480(1)		
<i>V</i> [ų]	775.81(3)	732.19(2)	694.33(4)	1989.68(6)	655.41(3)	900.43(4)
Ζ	4	4	4	2	4	8
$ ho_{ m calc}$ [Mg m <sup>-3</sup> ]	1.327	1.388	1.435	1.482	1.479	1.947
μ[mm <sup>-1</sup> ]	5.368	5.687	6.134	0.721	6.497	9.876
Absorption correction	Gaussian	Gaussian	Gaussian	Gaussian	Gaussian	Gaussian
<i>F</i> (000) [e]	312	304	304	888	288	512
Device, radiation,	XtaLAB Synergy, Dualflex,	XtaLAB Synergy, Dualflex,	XtaLAB Synergy, Dualflex,	, XtaLAB Synergy, Dualflex,	XtaLAB Synergy, Dualflex,	XtaLAB Synergy, Dualflex,
wavelength	HyPix, (CuKα = 1.54184 Å)	HyPix, (CuKα = 1.54184 Å)	HyPix, (CuKα = 1.54184 Å)	HyPix, (MoKα = 0.71073 Å)	HyPix, (CuKα = 1.54184 Å)	HyPix, (CuKα = 1.54184 Å)
Theta range [°]	5.217 to 74.332	6.200 to 77.409	4.2603 to 77.3813	2.114 to 31.353	6.339 to 77.095	4.831 to 77.667
reflections collected /	8371 / 1583	7738 / 1530	5056 / 1422	56118 / 10981	6001 / 1368	5015 / 917
independent	837171383	//38/1550	50507 1422	504487 10584	050171508	50457 547
refelctions observed	1503	1/0/	1277	9031	1342	880
$[l > 2\sigma(l)]$	1905	1494	1277	5031	1342	880
R(int)	0.0468	0.0346	0.0462	0.0358	0.0235	0.0330
Data / restraints / parameters	1583/0/91	1530 / 0 / 95	1422/0/83	10984 / 6 / 569	1368 / 0 / 86	947 / 0 / 68
$R1[I > 2\sigma(I)]$	0.0343	0.0283	0.0409	0.0331	0.0231	0.0260
wR2 (all data)	0.0969	0.0767	0.1092	0.0872	0.0633	0.0700
Goodness-of-fit F <sup>2</sup>	1.064	1.061	1.075	1.059	1.065	1.084
$\Delta ho_{max}$ / $\Delta ho_{min}$ [e Å <sup>-3</sup> ]	0.522 /0.223	0.266 / -0.457	0.561/-0.367	1.194 / -0.540	0.235 / -0.276	0.752 /0.337
CCDC no.	2121278	2121277	2121281	2121280	2121279	2121276



Figure S44. Crystallographically-determined solid-state structures of K1, K2, K3, K4, K5 and K6. Atomic displacement ellipsoids depicted at the 50% probability level and the cation was omitted for clarity.

anion	d(B–CN)	d(B-F)	d(C-N)	d(B-CC)	d(CC)	≰ (B–C–N)	≰ (B−C−C)	Reference
[C₂H₅B(CN)₃]⁻	1.603(5)	-	1.142(4)	1.615(5)	1.527(4)	178.4(4)	113.2(3)	14
	1.600	-	1.158	1.644	1.535	177.2	115.0	this work
[H₂C=CHB(CN)₃] <sup>−</sup>	1.605(2)	-	1.144(2)	1.609(3)	1.320(3)	177.4(2)	125.7(2)	this work
	1.600	-	1.157	1.631	1.334	178.1	125.9	this work
[HC≡CB(CN)₃]⁻	1.603(2)	-	1.145(2)	1.570(2)	1.195(2)	178.7(1)	174.9(1)	this work
	1.602	-	1.156	1.582	1.208	179.4	180.0	this work
[C₂H₅BF(CN)₂]⁻	1.625(3)	1.444(3)	1.150(3)	1.600(3)	1.521(3)	176.6(2)	115.9(2)	this work
	1.619	1.442	1.159	1.629	1.536	177.4	113.8	this work
[H₂C=CHBF(CN)₂]⁻	1.623(2)	1.431(2)	1.148(2)	1.598(2)	1.323(2)	176.4(2)	126.6(2)	this work
	1.620	1.432	1.158	1.613	1.335	177.9	124.5	this work
[HC=CBF(CN)₂]⁻	1.617(2)	1.423(2)	1.146(2)	1.586(2)	1.194(2)	176.7(1)	179.1(1)	this work
	1.617	1.430	1.157	1.590	1.201	179.2	179.7	this work
[HC≡CBF₃]⁻	-	1.414(2)	-	1.588(2)	1.198(2)	-	178.9(2)	this work
	-	1.422	-	1.616	1.213		180.0	this work
[B(CN)₄]⁻	1.595(1)	-	1.142(1)	-	-	178.68(9)	-	10
	1.596	-	1.156	-	-	180.0	-	10

**Table S9**: Selected experimental and calculated<sup>*a*</sup> bond parameters<sup>*b*</sup> of ethyl-, vinyl- and ethynylcyanoborate anions in their K<sup>+</sup> salts.

<sup>a</sup> B3LYP/6-311++G(d,p); calculated values in italics. <sup>b</sup> Bond length in Å and bond angles in °; mean values where applicable.

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