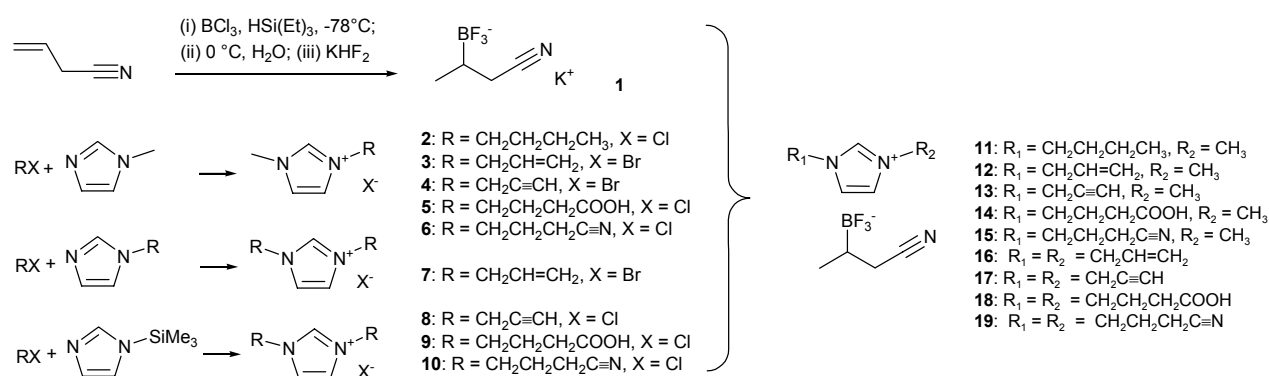


Dual-functionalised ionic liquids: synthesis and characterisation of imidazolium salts with a nitrile-functionalised anion

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Ion chromatography experimental detail, and synthetic details, and IR, NMR, Electrospray mass spectra, and elemental analysis data of new compounds are provided below. The term “mim” denotes 1-methylimidazole, ($\text{C}_4\text{H}_6\text{N}_2$), “im” refers to imidazole, $\text{C}_3\text{H}_3\text{N}_2$.

General remark

The known compounds **2**¹, **4**², **5**³, **6**⁴, **8**⁵, and **9**³ were prepared according to literature methods. All chemicals were purchased from Acros[®] and were used as received without further purification. Syntheses were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques in solvents dried using the appropriate reagents and distilled prior to use. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 system. NMR spectra were measured on a Bruker DMX 400 MHz spectrometer, using SiMe_4 (^1H , ^{13}C), CFCl_3 (^{19}F) and $\text{BF}_3\text{-Et}_2\text{O}$ (^{11}B) as external standards at 20°C . Electrospray ionisation mass

spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ™ Deca XP Plus quadrupole ion trap instrument on samples diluted in methanol or water. Samples were infused directly into the source at 5 $\mu\text{L min}^{-1}$ using a syringe pump and the spray voltage was set at 5 kV and the capillary temperature at 50°C. Elemental analysis was carried out at the EPFL. Melting points of all the liquid compounds were measured using differential scanning calorimeter (DSC) performed with a SETARAM DSC 131 instrument. Viscosities were measured with a Brookfield DV-II+ viscometer on 0.50 ml of sample. The temperature of the samples was maintained at 20 ± 1 °C by means of an external temperature controller. The measurements were performed in duplicate. Ion chromatographic analyses were performed at room temperature using a ICS-90 Dionex equipped with a pre-column (3 mm x 30 mm), an Ion Pac AG14A (3 mm x 150 mm), an Ion Pac AS14A column, and a MMS III suppressor and a DS5 conductivity detector. Ionic liquid samples were prepared by diluting to 1000 ppm in doubly-distilled water and 10 μl was injected. Data were collected on a CHROMELEON work station system. 10 ppm KCl and KBr water solution were used as calibration standards.

Characterisation of **1** (detailed synthesis described in the note of text)

M.p.: 154°C; ESI-MS (H_2O , m/z): positive ion, 39, $[\text{K}]^+$; negative ion, 136, $[\text{CH}_3\text{CH}(\text{BF}_3)\text{CH}_2\text{CN}]^-$; ^1H NMR (d4-methanol): 2.36 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$ Hz, $^3J(\text{H}, \text{H}) = 4.3$ Hz), 1.93 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$, $^3J(\text{H}, \text{H}) = 10.7$ Hz), 0.91 (d, 3H, $^3J(\text{H}, \text{H}) = 7.3$ Hz), 0.59 (m, 1H); ^{13}C NMR (d4-methanol): 121.8, 28.6, 20.2, 14.8; ^{19}F NMR (d4-methanol): -147.3 (m); ^{11}B NMR (d4-methanol): 7.20 ($^1J(\text{B}, \text{F}) = 60$ Hz); IR (cm^{-1}): 2952, 2873, 2247, 1464, 1374, 1316, 1357, 1226, 1119, 1052, 1014, 983, 892; Anal. Calcd. for $\text{C}_4\text{H}_6\text{NBF}_3\text{K}$ (%): C 27.45, H 3.46, N 8.00; Found: C 28.11, H 3.51, N 7.96.

Synthesis of **3**

A mixture of 1-methylimidazole (8.21 g, 0.10 mol) and propenyl bromide (12.1 g, 0.10 mol) in methanol (50 ml) was stirred at room temperature for 5 days. The solvent was removed under reduced pressure. The resulting pale yellow viscous liquid was washed with diethyl ether (3 x 100 ml) and then dried in vacuum. Yield: 18.67g, 92%; m.p.: - 52.5°C; ESI-MS (H_2O , m/z): positive ion, 123, $[\text{CH}_2\text{CH}=\text{CH}_2\text{mim}]^+$; negative ion, 80, $[\text{Br}]^-$; ^1H NMR (D_2O): δ 8.79 (s, 1H), 7.62 (s, 1H), 7.60 (s, 1H), 6.15 (m, 1H), 5.50 (m, 1H), 4.96 (m, 2H), 4.05 (s,

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3H); ^{13}C NMR (D_2O): 136.1, 130.7, 124.5, 122.8, 121.5, 51.8, 36.3; Anal. Calcd. for $\text{C}_7\text{H}_{11}\text{N}_2\text{Br}$ (%): C 41.40, H 5.46, N, 13.79; Found: C 40.41, H 5.41, N 13.27.

Synthesis of 7

A mixture of 1-allylimidazole (10.8 g, 0.10 mol) and propenyl bromide (12.1 g, 0.10 mol) in methanol (50 ml) was stirred at room temperature for 5 days. The solvent was removed under reduced pressure. The resulting pale yellow viscous liquid was washed with diethyl ether (3 x 30 mL). The product was dried in vacuum for 24 h. Yield: 19.3 g, 95%; m.p.: -26.5°C . ESI-MS (H_2O , m/z): positive ion, 149 [$\text{DiCH}_2\text{CH}=\text{CH}_2\text{im}$] $^+$; negative ion, 80 [Br] $^-$; ^1H NMR (D_2O): δ 9.20 (s, 1H), 7.85 (s, 2H), 6.20 (m, 2H), 5.55 (m, 4H), 5.10 (m, 4H); ^{13}C NMR (D_2O): 135.5, 130.5, 123.1, 122.0, 51.9; Anal. Calcd. for $\text{C}_7\text{H}_{11}\text{N}_2\text{Br}$ (%): C 41.40, H 5.46, N, 13.79. Found: C 40.41, H 5.41, N 13.27.

Synthesis of 10

A mixture of trimethylsilylimidazole (14.03 g, 0.10 mol) and $\text{Cl}(\text{CH}_2)_3\text{CN}$ (24.86 g, 0.24 mol) was stirred at 80°C for 24 h. The resulting white solid was washed with diethyl ether (3 x 30 mL). The product was dried in vacuum for 24 h. Yield: 22.4 g, 94%; m.p.: 100°C . ESI-MS (H_2O , m/z): positive ion, 203 [$\text{Di}(\text{CH}_2)_3\text{C}\equiv\text{Nim}$] $^+$; negative ion, 35, 37 [Cl] $^-$; ^1H NMR (D_2O): δ 8.56 (s, 1H), 7.52 (s, 2H), 4.48 (t, 4H, $^3J(\text{H}, \text{H}) = 7.15$ Hz), 2.66 (m, 4H), 2.35 (t, 4H, $^3J(\text{H}, \text{H}) = 7.15$ Hz); ^{13}C NMR (D_2O): 137.10, 123.4, 119.2, 48.3, 29.3, 25.1; IR (cm^{-1}): 3166, 3075, 2939, 2895, 2839, 2241, 1781, 1669, 1570, 1559; Anal. Calcd for $\text{C}_{11}\text{H}_{15}\text{ClN}_4$ (%): C 55.35, H 6.33, N 23.47. Found: C 54.98, H 6.08, N 23.55.

Synthesis of 11

A mixture of **1** (1.0 g, 5.71 mmol) and **2** (1.0 g, 5.71 mmol) was stirred in acetone at room temperature for 24 h. The resulting suspension was filtered and the filtrate dried in vacuum. The resulting ionic liquid was purified by washing with diethyl ether, and the solvents removed *in vacuo*. Yield: 1.32 g, 84%. Pale yellow liquid, m.p.: -84.5°C ; ESI-MS (H_2O , m/z): positive ion, 139, [C_4mim] $^+$; negative ion, 136, [$\text{CH}_3(\text{BF}_3)\text{CHCH}_2\text{CN}$] $^-$; ^1H NMR (d_6 -acetone): δ 8.28 (s, 1H), 7.16 (s, 1H), 7.11 (s, 1H), 4.45 (t, $^3J(\text{H}, \text{H}) = 7.15$ Hz, 2H), 3.85 (s, 3H), 2.35-1.94 (m, 4H), 1.92-1.85 (m, 2H), 1.32 (t, 3H, $^3J(\text{H}, \text{H}) = 6.98$ Hz), 1.20 (m, 2H), 0.89 (d, 3H, $^3J(\text{H}, \text{H}) = 7.3$ Hz), 0.56 (m, 1H); ^{13}C NMR (d_6 -acetone): δ 136.8, 126.3, 124.5, 121.7, 49.0,

35.7, 31.9, 29.2, 20.6, 19.6, 15.5, 13.0; ^{19}F NMR (d6-acetone): -149.8 (m); IR (cm^{-1}): 3154, 3117, 2962, 2872, 2239, 1574; Anal. Calcd. for $\text{C}_{12}\text{H}_{21}\text{BF}_3\text{N}_3$ (%): C 52.39, H 7.69, N, 15.27. Found: C 52.38, H 7.41, N 15.51.

Synthesis of 12

The same method was used as in the synthesis of **11** except **3** (1.16 g, 5.71 mmol) was used in place of **2**. Yield: 1.30 g, 88%. Pale yellow liquid, m. p.: -89.2°C ; ESI-MS (H_2O , m/z): positive ion, 123, $[\text{CH}_2\text{CH}=\text{CH}_2\text{mim}]^+$; negative ion, 136, $[\text{CH}_3(\text{BF}_3)\text{CHCH}_2\text{CN}]^-$; ^1H NMR (d6-acetone): δ 8.89 (s, 1H), 7.67 (s, 1H), 7.66 (s, 1H), 6.07 (m, 1H), 5.58 (m, 1H), 4.92 (m, 1H), 4.61 (s, 3H), 3.95 (s, 2H), 2.34 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$ Hz, $^3J(\text{H}, \text{H}) = 4.3$ Hz), 1.96 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$, $^3J(\text{H}, \text{H}) = 10.7$ Hz), 0.87 (d, 3H, $^3J(\text{H}, \text{H}) = 7.3$ Hz), 0.54 (m, 1H); ^{13}C NMR (d6-acetone): 139.01, 136.7, 124.89, 122.7, 121.5, 121.7, 51.3, 35.9, 28.5, 20.2, 14.8; ^{19}F NMR (d6-acetone): -147.4 (m); IR (cm^{-1}): 3151, 3114, 1647, 2943, 2865, 2238, 1708, 1647, 1574; Anal. Calcd. for $\text{C}_{11}\text{H}_{17}\text{BF}_3\text{N}_3$ (%): C 51.00, H 6.61, N, 16.22; Found: C 51.21, H 6.45, N 16.17.

Synthesis of 13

The same method was used as in the synthesis of **11** except **4** (1.15 g, 5.71 mmol) was used in place of **2**. Yield: 1.20 g, 82%. Pale yellow liquid, m.p.: -80.4°C ; ESI-MS (H_2O , m/z): positive ion, 121, $[\text{CH}_2\text{C}\equiv\text{CHmim}]^+$; negative ion, 136, $[\text{CH}_3(\text{BF}_3)\text{CHCH}_2\text{CN}]^-$; ^1H NMR (d6-acetone): δ 9.49 (s, 1H), 7.87 (s, 1H), 7.58 (s, 1H), 5.40 (d, 2H, $^4J(\text{H}, \text{H}) = 2.80$ Hz), 4.37 (s, 3H), 3.21 (d, 4H, $^4J(\text{H}, \text{H}) = 2.80$ Hz); 2.36 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$ Hz, $^3J(\text{H}, \text{H}) = 4.3$ Hz), 1.91 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$, $^3J(\text{H}, \text{H}) = 10.7$ Hz), 0.89 (d, 3H, $^3J(\text{H}, \text{H}) = 7.3$ Hz), 0.54 (m, 1H); ^{13}C NMR (acetone): δ 137.2, 124.2, 122.2, 121.2, 78.2, 75.2, 35.9, 29.3, 28.7, 20.5, 15.1; ^{19}F NMR (d6-acetone): -148.8 (m); IR (cm^{-1}): 3252, 3156, 3116, 2960, 2867, 2238, 2131, 1697, 1625, 1576, 1459, 1425; Anal. Calcd. for $\text{C}_{11}\text{H}_{15}\text{BF}_3\text{N}_3$ (%): C 51.40, H 5.88, N, 16.35. Found: C 51.21, H 5.75, N 16.32.

Synthesis of 14

The same method was used as synthesis of **11** except **5** (1.17 g, 5.71 mmol) was used in place of **2**. Yield: 1.53 g, 88%. Colourless liquid, m.p.: -58.6°C ; ESI-MS (H_2O , m/z): positive ion, 169, $[\text{CH}_2\text{CH}_2\text{CH}_2\text{COOHmim}]^+$; negative ion, 136, $[\text{CH}_3(\text{BF}_3)\text{CHCH}_2\text{CN}]^-$; ^1H NMR (d6-

acetone): δ 10.33 (br, 1H), 9.01 (s, 1H), 7.75 (s, 1H), 7.72 (s, 1H), 4.35 (t, 2H, $^3J(\text{H}, \text{H}) = 7.05$ Hz), 4.00 (s, 3H), 2.17 (t, 2H, $^3J(\text{H}, \text{H}) = 7.05$), 2.39-1.96 (m, 2H), 0.89 (d, 3H, $^3J(\text{H}, \text{H}) = 7.3$ Hz), 0.55 (m, 1H); ^{13}C NMR (d6-acetone): $\delta = 173.7, 136.0, 124.6, 121.1, 48.46, 35.1, 30.9, 28.9, 20.5, 15.1$; ^{19}F NMR (d6-acetone): -148.8 (m); IR (cm^{-1}): 3155, 3117, 2943, 2867, 2238, 1728, 1566, 1460; Anal. Calcd. for $\text{C}_{12}\text{H}_{19}\text{BF}_3\text{N}_3\text{O}_2$ (%): C 47.24, H 6.28, N, 13.77; Found: C 47.12, H 6.75, N 13.32.

Synthesis of 15

The same method was used as in the synthesis of **11** except **6** (1.06 g, 5.71 mmol) was used in place of **2**. Yield: 1.39 g, 85%. Pale yellow liquid, m.p.: -76.6°C ; ESI-MS (H_2O , m/z): positive ion, 150 [$\text{CH}_2\text{CH}_2\text{CH}_2\text{CNmim}$] $^+$; negative ion, 136, [$\text{CH}_3(\text{BF}_3)\text{CHCH}_2\text{CN}$] $^-$; ^1H NMR (d6-acetone): $\delta = 8.75$ (s, 1H), 7.44 (s, 1H), 7.39 (s, 1H), 4.45 (t, 2H, $^3J(\text{H}, \text{H}) = 7.15$ Hz), 4.00 (s, 3H), 2.64 (t, 2H, $^3J(\text{H}, \text{H}) = 7.15$ Hz), 2.31 (t, 2H, $^1J(\text{H}, \text{H}) = 7.14$ Hz), 2.30 (m, 1H), 1.98 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$, $^3J(\text{H}, \text{H}) = 10.7$ Hz), 0.87 (d, 3H, $^3J(\text{H}, \text{H}) = 7.3$ Hz), 0.55 (m, 1H); ^{13}C NMR (d6-acetone): δ 134.11, 130.49, 120.0, 121.5, 116.1, 48.0, 30.8, 28.9, 25.9, 20.5, 13.6, 9.8; ^{19}F NMR (d6-acetone): -148.8 (m); IR (cm^{-1}): 3156, 3116, 2960, 2866, 2239, 1631, 1575, 1566, 1459, 1425; Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{BF}_3\text{N}_4$ (%): C 50.38, H 6.34, N, 19.58; Found: C 50.21, H 6.45, N 19.32.

Synthesis of 16

The same method was used as in the synthesis of **11** except **7** (1.31 g, 5.71 mmol) was used in place of **2**. Yield: 1.43 g, 88%. Pale yellow liquid, m.p.: -87.3°C ; ESI-MS (H_2O , m/z): positive ion, 149 [$\text{DiCH}_2\text{CH}=\text{CH}_2\text{im}$] $^+$; negative ion, 136, [$\text{CH}_3(\text{BF}_3)\text{CHCH}_2\text{CN}$] $^-$; ^1H NMR (d6-acetone): δ 9.25 (s, 1H), 7.86 (s, 2H), 6.11 (m, 2H), 5.45-5.35 (m, 4H), 4.99 (m, 4H), 2.31 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$ Hz, $^3J(\text{H}, \text{H}) = 4.3$ Hz), 1.95 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$, $^3J(\text{H}, \text{H}) = 10.7$ Hz), 1.20 (m, 2H), 0.88 (d, 3H, $^3J(\text{H}, \text{H}) = 7.3$ Hz), 0.56 (m, 1H); ^{13}C NMR (d6-acetone): δ 136.0, 131.7, 122.07, 121.7, 120.8, 51.4, 29.4, 20.6, 15.3; ^{19}F NMR (d6-acetone): -149.8 (m); IR (cm^{-1}): 3143, 3087, 2943, 2866, 2238, 1646, 1562, 1451, 1424; Anal. Calcd. for $\text{C}_{13}\text{H}_{19}\text{BF}_3\text{N}_3$ (%): C 54.76, H 6.72, N, 14.74. Found: C 54.21, H 6.85, N 14.41.

Synthesis of 17

The same method was used as in the synthesis of **11** except **8** (1.03 g, 5.71 mmol) was used in place of **2**. Yield: 1.38 g, 86%. Pale yellow liquid, m.p.: -55.1°C ; ESI-MS (H_2O , m/z): positive ion, 145 $[\text{DiCH}_2\text{C}\equiv\text{CHim}]^+$; negative ion, 136, $[\text{CH}_3(\text{BF}_3)\text{CHCH}_2\text{CN}]^-$; ^1H NMR (D_2O): $\delta = 9.36$ (s, 1H), 7.90 (s, 2H), 5.97 (d, 4H, $^4J(\text{H}, \text{H}) = 4.0$ Hz), 3.36 (t, 2H, $^4J(\text{H}, \text{H}) = 4.0$ Hz), 2.35 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$ Hz, $^3J(\text{H}, \text{H}) = 4.3$ Hz), 1.94 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$, $^3J(\text{H}, \text{H}) = 10.7$ Hz), 0.89 (d, 3H, $^3J(\text{H}, \text{H}) = 7.3$ Hz), 0.56 (m, 1H); ^{13}C NMR (D_2O): δ 138.9, 125.7, 121.7, 81.1, 74.8, 42.5, 29.2, 20.5, 15.4; ^{19}F NMR (d6-acetone): -149.8 (m); IR (cm^{-1}): 3255, 3145, 2944, 2867, 2239, 2131, 1559, 1445; Anal. Calcd. for $\text{C}_{13}\text{H}_{15}\text{BF}_3\text{N}_3$ (%): C 55.55, H 5.38, N, 14.95; Found: C 55.21, H 5.45, N 14.69.

Synthesis of 18

The same method was used as in the synthesis of **11** except **9** (1.58 g, 5.71 mmol) was used in place of **2** as waxy solid. Yield: 1.83 g, 85%. ESI-MS (H_2O , m/z): positive ion, 241, $[\text{DiCH}_2\text{CH}_2\text{CH}_2\text{COOHim}]^+$; negative ion, 136, $[\text{CH}_3(\text{BF}_3)\text{CHCH}_2\text{CN}]^-$; ^1H NMR (d6-acetone): δ 8.76 (s, 1H), 7.44 (s, 2H), 4.08 (t, 4H, $^3J(\text{H}, \text{H}) = 7.05$ Hz), 2.38-2.30 (m, 1H) 2.37 (t, 4H, $^3J(\text{H}, \text{H}) = 7.05$ Hz), 2.08 (m, 4H), 1.97 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$, $^3J(\text{H}, \text{H}) = 10.7$ Hz), 1.21 (m, 2H), 0.90 (d, 3H, $^3J(\text{H}, \text{H}) = 7.3$ Hz), 0.59 (m, 1H); ^{13}C NMR (d6-acetone): δ 179.7, 138.5, 125.5, 121.8, 51.6, 33.1, 28.4, 27.5, 20.3, 14.9; ^{19}F NMR (d6-acetone): -149.8 (m); IR (cm^{-1}): 3607, 3454, 3151, 2946, 2873, 2246, 1727, 1651, 1565, 1460, 1421, 1308; Anal. Calcd. for $\text{C}_{15}\text{H}_{23}\text{BF}_3\text{N}_3\text{O}_4$ (%): C 47.77, H 6.15, N, 11.14. Found: C 47.35, H 6.25, N 11.38.

Synthesis of 19

The same method was used as in the synthesis of **11** except **10** (1.39 g, 5.71 mmol) was used in place of **2**. Yield: 1.68 g, 87%. Colourless liquid, m.p.: -69.8°C ; ESI-MS (H_2O , m/z): positive ion, 203 $[\text{Di}(\text{CH}_2)_3\text{C}\equiv\text{Nim}]^+$; negative ion, 136, $[\text{CH}_3(\text{BF}_3)\text{CHCH}_2\text{CN}]^-$; ^1H NMR (d6-acetone): δ 9.30 (s, 1H), 7.83 (s, 2H), 4.46 (t, 4H, $^3J(\text{H}, \text{H}) = 7.10$ Hz), 2.66 (m, 4H), 2.32 (t, 4H, $^3J(\text{H}, \text{H}) = 7.00$ Hz), 2.34 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$ Hz, $^3J(\text{H}, \text{H}) = 4.3$ Hz), 1.99 (dd, 1H, $^2J(\text{H}, \text{H}) = -17.1$ Hz, $^3J(\text{H}, \text{H}) = 10.7$ Hz), 0.91 (d, 3H, $^3J(\text{H}, \text{H}) = 7.3$ Hz), 0.58 (m, 1H); ^{13}C NMR (d6-acetone): 137.0, 123.4, 121.9, 119.2, 48.3, 29.3, 29.1, 25.1, 20.6, 13.6; ^{19}F NMR (d6-acetone): -148.8 (m); IR (cm^{-1}): 3148, 3117, 2967, 2247, 1567, 1461, 1425; Anal. Calcd. for $\text{C}_{15}\text{H}_{21}\text{BF}_3\text{N}_5$ (%): C 53.12, H 6.24, N, 20.65. Found: C 52.97, H 6.25, N 20.34.

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The stability of the nitrile-functionalised anion towards catalytic hydrogenation was tested by pressurising a solution of $\text{K}[\text{CH}_3\text{CH}(\text{BF}_3)\text{CH}_2\text{CN}]$ (8 mg) and $\text{RuCl}_2(\text{PMe}_3)_4$ (1 mg) in acetone (0.4 ml) with H_2 (40 bar) at 35 °C. No reduction was observed even after 48 hours.

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