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Design and preparation of room temperature ionic liquids containing biodegradable side-chains

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Supplementary Data

Methyl bromoacetate, ethyl bromoacetate, propyl bromoacetate were purchased from Aldrich and used without further purification. Ethyl chloroacetate was purchased from Fluka and used without further purification. 1-Methylimidazole (99%, Aldrich) was distilled before use to remove impurities detrimental to all ILs prepared. All organic solvents were dried and distilled before use. ILs were washed with distilled water. Hexyl bromoacetate, octyl bromoacetate, *N,N*-diethyl-2-bromoacetamide, *N*-butyl-2-bromoacetamide and *N*-butyl-*N*-methyl-2-bromoacetamide were prepared by addition of the appropriate amine/alcohol with bromoacetyl bromide. *N*-butyl-*N*-methyl-2-bromoacetamide was prepared as a 1:1.3 mixture of isomers at the amide centre. 3-Methyl-1-(methylacetyl)imidazolium bromide (**3a**) was prepared according to the literature [mp = 131-133°C] (D. S. McGuinness and K. J. Cavell *Organometallics*, 2000, **19**, 741). All NMR spectra were recorded in CD₃CN (Aldrich 15,180-7, 99.8 atom %D). Melting points are uncorrected. All room temperature ionic liquids were placed in the fridge (2°C) and freezer (-18°C) to further evaluate their melting points. Unless indicated in the experimental data below (see **4e** and **5e**) all the room temperature ionic liquids did not crystallise at -18°C. However, the viscosity of the

ionic liquids at this temperature was significantly increased. A study of glass transition temperatures was not attempted with these materials.

3-Methyl-1-(ethylacetyl)imidazolium Bromide (3b)

To a stirred solution of 1-methylimidazole (4.1 g, 4.0 mL, 50 mmol) in THF (50 mL) at -5°C under a nitrogen atmosphere was added dropwise ethyl bromoacetate (10.0 g, 6.7 mL, 60 mmol). The reaction mixture was stirred vigorously at -5°C for 1 h, then at rt for 3 h. The THF top phase was decanted and the IL washed with diethyl ether (3 x 10 mL), then residual solvent removed *in vacuo*. The product was dried at 60°C at 0.01 mmHg for 72 h to give a clear viscous hygroscopic oil in 98 % yield (12.2 g, 49 mmol). ^1H NMR (300 MHz, CD_3CN) 9.38 (s, 1H), 7.64 (s, 1H), 7.51 (s, 1H), 5.30 (s, 2H), 4.23 (q, $J = 7.0$ Hz, 2H), 3.93 (s, 3H), 1.25 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.80, 138.72, 124.82, 124.10, 63.23, 51.06, 37.40, 14.63. MS (ESI): m/z , 169.1 $[\text{M}-\text{Br}^-]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(propylacetyl)imidazolium Bromide (3c)

This compound was prepared analogously to **3b** using 1-methylimidazole (2.11 g, 2.05 mL, 25 mmol) and propyl bromoacetate (5.46 g, 3.90 mL, 30 mmol) to give a clear viscous hygroscopic oil in 96 % yield (6.31 g, 24 mmol). ^1H NMR (300 MHz, CD_3CN) δ 9.57 (s, 1H), 7.78 (s, 1H), 7.63 (s, 1H), 5.42 (s, 2H), 4.10 (q, $J = 7.0$ Hz, 2H), 3.94 (s, 3H), 1.62 (tq, $J = 7.0, 7.0$ Hz, 2H), 0.89 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.93, 138.89, 124.81, 124.40, 68.73, 51.08, 37.40, 22.68, 10.75. MS (ESI): m/z , 183.1 $[\text{M}-\text{Br}^-]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(*N,N*-diethylacetamidyl)imidazolium Bromide (3h)

This compound was prepared analogously to **3b** using 1-methylimidazole (1.05 g, 1.02 mL, 12.8 mmol) and *N,N*-diethyl-2-bromoacetamide (2.98 g, 15.4 mmol) to give a crystalline solid in 99 % yield (3.51g, 12.7 mmol). mp = 66-68°C; ¹H NMR (300 MHz, CD₃CN) δ 9.27 (s, 1H), 7.60 (s, 1H), 7.47 (s, 1H), 5.44 (s, 2H), 3.91 (s, 3H), 3.37 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 7.0 Hz, 2H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.06 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 165.17, 139.25, 125.54, 124.14, 51.80, 42.60, 41.97, 37.55, 14.86, 13.67. MS (ESI): *m/z*, 196.1 [M–Br[–]]⁺; MS (ESI): *m/z*, 79 and 81 [Br[–]].

3-Methyl-1-(ethylacetyl)imidazolium Chloride (8b)

This compound was prepared analogously to **3b** using 1-methylimidazole (4.22 g, 4.10 mL, 50 mmol) and ethyl chloroacetate (7.36 g, 6.4 mL, 60 mmol) to give a clear viscous hygroscopic oil in 94 % yield (8.96 g, 47 mmol). The oil slowly crystallised at room temperature. ¹H NMR (300 MHz, CD₃CN) δ 9.81 (s, 1H), 7.71 (s, 1H), 7.56 (s, 1H), 5.42 (s, 2H), 4.21 (q, *J* = 7.0 Hz, 2H), 3.94 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 168.00, 139.22, 124.66, 124.12, 63.04, 51.82, 37.00, 14.40. MS (ESI): *m/z*, 169.1 [M–Cl[–]]⁺.

3-Methyl-1-(hexylacetyl)imidazolium Bromide (3d)

To a stirred solution of 1-methylimidazole (2.11 g, 2.05 mL, 25 mmol) in diethyl ether (25 mL) at –5°C under a nitrogen atmosphere was added dropwise hexyl bromoacetate (6.70 g, 5.31 mL, 30 mmol). The reaction mixture was stirred vigorously at –5°C for 1 h, then at rt for 3 h. The diethyl ether top phase was decanted and the IL washed with diethyl ether (3 x 10 mL) then residual solvent removed *in vacuo*. The product was dried at 60°C at 0.01 mmHg for 72 h to give a clear viscous hygroscopic oil in 92 % yield (7.01 g, 23.0 mmol). ¹H NMR (300 MHz, CD₃CN) δ

9.49 (s, 1H), 7.69 (s, 1H), 7.56 (s, 1H), 5.36 (s, 2H), 4.15 (t, $J = 7.0$ Hz, 2H), 3.93 (s, 3H), 1.67-1.57 (m, 2H), 1.40-1.25 (m, 6H), 0.87 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.95, 139.03, 124.95, 124.54, 67.51, 51.20, 37.50, 32.32, 29.36, 26.35, 23.48, 14.60. MS (ESI): m/z , 225.2 $[\text{M}-\text{Br}^-]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(octylacetyl)imidazolium Bromide (3e) This compound was prepared analogously to **3d** using 1-methylimidazole (0.84 g, 0.82 mL, 10.3 mmol) and octyl bromoacetate (3.01g, 12.0 mmol) to give a clear viscous hygroscopic oil in 95 % yield (3.26 g, 9.8 mmol). ^1H NMR (300 MHz, CD_3CN) δ 9.41 (s, 1H), 7.64 (s, 1H), 7.53 (s, 1H), 5.32 (s, 2H), 4.17 (t, $J = 7.0$ Hz, 2H). 3.94 (s, 3H), 1.70-1.60 (m, 2H), 1.40-1.20 (m, 10H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.97, 139.08, 125.00, 124.59, 67.58, 51.23, 37.52, 32.84, 30.23, 30.18, 29.48, 26.75, 23.68, 14.73. MS (ESI): m/z , 253.3 $[\text{M}-\text{Br}^-]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(*N*-butylacetamidyl)imidazolium Bromide (3f)

This compound was prepared analogously to **3d** using 1-methylimidazole (0.42 g, 0.41 mL, 5.0 mmol) and *N*-butyl-2-bromoacetamide (1.16 g, 6.0 mmol) to give an oil in 94 % yield (1.30 g, 4.7 mmol). The oil slowly crystallised at room temperature. ^1H NMR (300 MHz, CD_3CN) δ 9.11 (s, 1H), 8.39 (bs, 1H, NH), 7.56 (s, 1H), 7.45 (s, 1H), 5.14 (s, 2H), 3.90 (s, 3H), 3.15 (q, $J = 7.0$ Hz, 2H), 1.52-1.40 (m, 2H), 1.40-1.37 (m, 2H), 0.87 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 166.12, 138.89, 124.99, 124.58, 52.70, 40.48, 37.62, 32.55, 21.28, 14.57. MS (ESI): m/z , 196.1 $[\text{M}-\text{Br}^-]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}^-]$.

3-Methyl-1-(*N*-butyl-*N*-methylacetamidyl)imidazolium Bromide (3g)

To a stirred solution of 1-methylimidazole (821 mg, 0.80 mL, 10 mmol) in THF (15 mL) at -5°C under a nitrogen atmosphere was added dropwise *N*-butyl-*N*-methyl-2-bromoacetamide (2.50 g, 12 mmol, 1:1.3 mixture of isomers) in THF (5 mL). The reaction mixture was stirred vigorously at -5°C for 1 h, then at rt for 48 h. The THF top phase was decanted and the IL washed with THF (2 x 5 mL), then residual solvent removed *in vacuo*. The product was dried at 60°C at 0.01 mmHg for 72 h to give a clear viscous hygroscopic oil in 95 % yield (2.76 g, 9.51 mmol). * denotes both isomers. ^1H NMR (300 MHz, CD_3CN) δ 8.78 (s, 1H, minor), 8.74 (s, 1H, major), 7.43-7.35 (m, 2H*), 5.22 (s, 2H, major), 5.19 (s, 2H, minor), 3.90 (s, 3H*), 3.37 (t, $J = 7.0$ Hz, 2H, major), 3.30 (t, $J = 7.0$ Hz, 2H, minor), 3.02 (s, 3H, major), 2.92 (s, 3H, minor), 1.70-1.25 (m, 4H*), 0.99 (t, $J = 7.0$ Hz, 3H, minor), 0.93 (t, $J = 7.0$ Hz, 3H, major). ^{13}C (75 MHz) δ 165.85 (major), 165.53 (minor), 138.89 (minor), 138.72 (major), 125.01 (minor), 124.91 (major), 123.75 (minor), 123.72 (major), 51.70 (major), 51.33 (minor), 49.64 (minor), 48.53 (major), 37.19*, 34.96 (major), 34.24 (minor), 30.86 (minor), 29.94 (major), 20.69 (minor), 20.58 (major), 14.25*. MS (ESI): m/z , 210.2 $[\text{M} - \text{Br}]^+$; MS (ESI): m/z , 79 and 81 $[\text{Br}]^-$.

3-Methyl-1-(methylacetyl)imidazolium BF_4 (4a)

A dry flask was charged with 3-methyl-1-(methylacetyl)imidazolium bromide (**3a**) (702 mg, 3.0 mmol) and acetonitrile (2 mL) under a nitrogen atmosphere. NaBF_4 (362 mg, 3.3 mmol) was added in one portion and the suspension was stirred vigorously for 4 days at rt. The fine white precipitate was filtered quickly in air and washed with dry acetonitrile (2 x 1 mL). The filtrate and washings were combined, solvent removed by rotary evaporation then *in vacuo*. The product was dried at 60°C at 0.01 mmHg for 72 h to give a clear viscous hygroscopic oil in 96 % yield (0.70 g, 2.9 mmol). ^1H NMR

(300 MHz, CD₃CN) δ 8.58 (s, 1H), 7.40 (s, 2H), 5.02 (s, 2H), 3.89 (s, 3H), 3.78 (s, 3H). ¹³C (75 MHz) δ 168.33, 138.75, 125.15, 125.00, 54.33, 51.18, 37.63. ¹⁹F (254 MHz) δ -151.6 (BF₄⁻). MS (ESI): *m/z*, 155.1 [M- BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(ethylacetyl)imidazolium BF₄ (4b)

This compound was prepared analogously to **4a** using 3-methyl-1-(ethylacetyl)imidazolium bromide **3b** (1.79 g, 6.3 mmol) and NaBF₄ (0.69 g, 6.3 mmol) to give a clear viscous hygroscopic oil in 92 % yield (1.51 g, 5.9 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.66 (s, 1H), 7.44 (s, 1H), 7.40 (s, 1H), 5.30 (s, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.83, 138.80, 125.16, 124.93, 63.90, 51.31, 37.64, 14.83. ¹⁹F (254 MHz) δ -151.6 (BF₄⁻). MS (ESI): *m/z*, 169.1 [M- BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(propylacetyl)imidazolium BF₄ (4c)

This compound was prepared analogously to **4a** using 3-methyl-1-(propylacetyl)imidazolium bromide **3c** (722 mg, 2.8 mmol) and NaBF₄ (333 mg, 3.0 mmol) to give a clear viscous hygroscopic oil in 98 % yield (727 mg, 2.7 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.55 (s, 1H), 7.41 (s, 2H), 7.40 (s, 1H), 5.00 (s, 2H), 4.17 (t, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 1.70 (qt, *J* = 7.0, 7.0 Hz, 2H), 0.95 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.90, 138.76, 125.15, 124.9, 69.24, 51.22, 37.58, 23.00, 10.96. ¹⁹F (254 MHz) δ -151.5 (BF₄⁻). MS (ESI): *m/z*, 183.1 [M- BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(hexylacetyl)imidazolium BF₄ (4d)

This compound was prepared analogously to **4a** using 3-methyl-1-(hexylacetyl)imidazolium bromide **3d** (758 mg, 2.25 mmol) and NaBF₄ (247 mg, 2.50 mmol) to give a clear viscous hygroscopic oil in 90 % yield (630 mg, 2.0 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.63 (s, 1H), 7.43 (s, 2H), 7.40 (s, 1H), 5.02 (s, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 1.70-1.60 (m, 2H), 1.42-1.28 (m, 6H), 0.91 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.85, 138.76, 125.17, 124.94, 67.87, 51.30, 37.64, 32.55, 29.56, 26.58, 23.72, 14.77. ¹⁹F (254 MHz) δ -151(BF₄⁻). MS (ESI): *m/z*, 225.2 [M-BF₄⁻]⁺ MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(octylacetyl)imidazolium BF₄ (4e)

This compound was prepared analogously to **4a** using 3-methyl-1-(octylacetyl)imidazolium bromide **3e** (350 mg, 1.05 mmol) and NaBF₄ (127 mg, 1.16 mmol) to give a clear viscous hygroscopic oil in 97 % yield (346 mg, 1.02 mmol). The oil crystallised in the freezer at -18°C. ¹H NMR (300 MHz, CD₃CN) δ 8.50 (s, 1H), 7.40 (s, 2H), 7.38 (s, 1H), 4.98 (s, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 1.70-1.60 (m, 2H), 1.42-1.25 (m, 10H), 0.91 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.87, 138.79, 125.16, 124.95, 67.85, 51.25, 37.60, 33.00, 30.38, 30.32, 29.59, 26.89, 23.83, 14.88. ¹⁹F (254 MHz) δ -151.4 (BF₄⁻). MS (ESI): *m/z*, 253.3 [M-BF₄⁻]⁺; MS (ESI): *m/z*, 87.0 [BF₄⁻].

3-Methyl-1-(*N,N*-diethylacetamidyl)imidazolium BF₄ (4h)

This compound was prepared analogously to **4a** using 3-methyl-1-(*N,N*-diethylacetamidyl)imidazolium bromide **3h** (552 mg, 2.0 mmol) and NaBF₄ (242 mg, 2.2 mmol) to give a clear viscous hygroscopic oil in 92 % yield (520 mg, 1.84 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.55 (s, 1H), 7.38 (s, 2H), 5.10 (s, 2H), 3.83 (s, 3H),

3.30 (m, 4H), 1.19 (t, $J = 7.0$ Hz), 1.07 (t, $J = 7.0$ Hz). ^{13}C (75 MHz) δ 163.72, 137.68, 124.10, 122.95, 50.22, 41.12, 40.58, 36.01, 13.25, 12.21. ^{19}F (254 MHz) δ -150.8 (BF_4^-). MS (ESI): m/z , 196.1 [$\text{M} - \text{BF}_4^-$] $^+$; MS (ESI): m/z , 87.0 [BF_4^-].

3-Methyl-1-(*N*-butyl-*N*-methylacetamidyl)imidazolium BF_4 (4g)

This compound was prepared analogously to **4a** using 3-methyl-1-(*N*-butyl-*N*-methylacetamidyl)imidazolium bromide **3g** (256 mg, 0.88 mmol, 1:1.3 mixture of isomers) and NaBF_4 (107 mg, 0.97 mmol) to give a clear viscous hygroscopic oil in 98 % yield (256 mg, 0.86 mmol, 1:1.3 mixture of isomers). * denotes both isomers. ^1H NMR (300 MHz, CD_3CN) δ 8.46 (s, 1H, minor), 8.44 (s, 1H, major), 7.40-7.30 (m, 2H*), 5.08 (s, 2H, minor), 5.05 (s, 2H, major), 3.88 (s, 3H*), 3.37 (t, $J = 7.0$ Hz, 2H, major), 3.28 (t, $J = 7.0$ Hz, 2H, minor), 3.00 (s, 3H, major), 2.92 (s, 3H, minor), 1.70-1.25 (m, 4H*), 0.99 (t, $J = 7.0$ Hz, 3H, minor), 0.93 (t, $J = 7.0$ Hz, 3H, major). ^{13}C (75 MHz) δ 166.05 (major), 165.79 (minor), 139.14 (minor), 139.04 (major), 125.48 (minor), 125.44 (major), 124.43*, 121.42* (q, $J = 320$ Hz, CF_3), 51.76 (major), 51.51 (minor), 50.01 (minor), 49.15 (major), 37.41*, 35.07 (major), 34.65 (minor), 31.21 (minor), 30.35 (major), 21.10 (minor), 21.09 (major), 14.74 (major), 14.69 (minor). ^{19}F (254 MHz) δ -152.10 (BF_4^-). MS (ESI): m/z , 210.2 [$\text{M} - \text{BF}_4^-$] $^+$; MS (ESI): m/z , 87.0 [BF_4^-].

3-Methyl-1-(*N*-butylacetamidyl)imidazolium BF_4 (4f)

This compound was prepared analogously to **4a** using 3-methyl-1-(*N*-butylacetamidyl)imidazolium bromide **3f** (128 mg, 0.45 mmol) and NaBF_4 (50 mg, 0.50 mmol) in acetonitrile (1 mL) to give a clear viscous hygroscopic oil in 86 % yield (110 mg, 0.39 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.55 (s, 1H), 7.39 (s, 1H),

7.35 (s, 1H), 7.05 (bs, 1H, NH), 4.85 (s, 2H), 3.86 (s, 3H), 3.20 (q, $J = 7.0$ Hz, 2H), 1.55-1.40 (tt, $J = 7.0, 7.0$ Hz, 2H), 1.40-1.28 (qt, $J = 7.0, 7.0$ Hz, 2H), 0.92 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 165.73, 138.65, 125.10, 124.59, 52.39, 20.54, 37.50, 32.52, 21.11, 14.45. ^{19}F (254 MHz) δ -151.7 (BF_4^-). MS (ESI): m/z , 196.1 [$\text{M} - \text{BF}_4^-$] $^+$; MS (ESI): m/z , 87.0 [BF_4^-].

3-Methyl-1-(methylacetyl)imidazolium NTf₂ (6a)

A flask was charged with 3-methyl-1-(methylacetyl)imidazolium bromide **3a** (702 mg, 3.0 mmol) and distilled water (2 mL). LiNTf₂ (947 mg, 3.3 mmol) in distilled water (1 mL) was added in one portion and the suspension was stirred vigorously for 4 h at rt. The top aqueous layer was removed, the IL washed with water (3 x 1 mL) then the solvent removed *in vacuo*. The product was dried at 60°C at 0.01 mmHg for 72 h to give a clear viscous hygroscopic oil in 93 % yield (1.21 g, 2.8 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.49 (s, 1H), 7.39 (bs, 2H), 4.99 (s, 2H), 3.88 (s, 3H), 3.79 (s, 3H). ^{13}C (75 MHz) δ 168.23, 138.59, 125.22, 125.09, 121.39 (q, $J = 320$ Hz, CF_3), 54.31, 51.19, 37.64. ^{19}F (254 MHz) δ -80.15 (CF_3). MS (ESI): m/z , 155.1 [$\text{M} - \text{NTf}_2^-$] $^+$; MS (ESI): m/z , 279.9 [NTf_2^-].

3-Methyl-1-(ethylacetyl)imidazolium NTf₂ (6b)

This compound was prepared analogously to **6a** using 3-methyl-1-(ethylacetyl)imidazolium bromide **3b** (0.53 g, 2.1 mmol) and LiNTf₂ (0.60 g, 2.1 mmol) to give a clear viscous hygroscopic oil in 90 % yield (0.85 g, 1.9 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.46 (s, 1H), 7.39 (s, 2H), 4.96 (s, 2H), 4.26 (q, $J = 7.0$ Hz, 2H), 3.88 (s, 3H), 1.29 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.70, 138.66, 125.19, 124.98, 123.53 (q, $J = 320$ Hz, CF_3), 63.98, 51.33, 37.64, 14.81. ^{19}F (254

MHz) δ -80.05 (CF₃). MS (ESI): m/z , 169.1 [M- NTf₂⁻]⁺; MS (ESI): m/z , 279.9 [NTf₂⁻].

3-Methyl-1-(propylacetyl)imidazolium NTf₂ (6c)

This compound was prepared analogously to **6a** using 3-methyl-1-(propylacetyl)imidazolium bromide **3c** (0.95 g, 3.6 mmol) and LiNTf₂ (1.15 g, 4.0 mmol) to give a clear viscous hygroscopic oil in 92 % yield (1.55 g, 3.4 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.49 (s, 1H), 7.39 (s, 2H), 4.99 (s, 2H), 4.17 (t, J = 7.0 Hz, 2H), 3.87 (s, 3H), 1.68 (tq, J = 7.0, 7.0 Hz, 2H), 0.95 (t, J = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.89, 138.82, 125.27, 125.02, 121.44 (q, J = 320 Hz, CF₃), 69.44, 51.32, 37.63, 23.03, 11.03. ¹⁹F (254 MHz) δ -80.06 (CF₃). MS (ESI): m/z , 183.1 [M- NTf₂⁻]⁺; MS (ESI): m/z , 279.9 [NTf₂⁻].

3-Methyl-1-(hexylacetyl)imidazolium NTf₂ (6d)

This compound was prepared analogously to **6a** using 3-methyl-1-(hexylacetyl)imidazolium bromide **3d** (680 mg, 2.0 mmol) and LiNTf₂ (637 mg, 2.2 mmol) to give a clear viscous hygroscopic oil in 89 % yield (0.90 g, 1.8 mmol). ¹H NMR (300 MHz, CD₃CN) δ 8.47 (s, 1H), 7.39 (s, 2H), 4.97 (s, 2H), 4.19 (t, J = 7.0 Hz, 2H), 3.87 (s, 3H), 1.70-1.60 (m, 2H), 1.40-1.30 (m, 6H), 0.90 (t, J = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.74, 138.60, 125.16, 124.97, 121.39 (q, J = 320 Hz, CF₃), 67.90, 51.30, 37.65, 32.53, 29.55, 26.57, 23.70, 14.74. ¹⁹F (254 MHz) δ -80.20 (CF₃). MS (ESI): m/z , 225.2 [M- NTf₂⁻]⁺; MS (ESI): m/z , 279.9 [NTf₂⁻].

3-Methyl-1-(octylacetyl)imidazolium NTf₂ (6e)

This compound was prepared analogously to **6a** using 3-methyl-1-(octylacetyl)imidazolium bromide **3e** (548 mg, 1.64 mmol) and LiNTf₂ (520 mg, 1.81

mmol) to give a clear viscous hygroscopic oil in 93 % yield (0.81 g, 1.52 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.48 (s, 1H), 7.39 (s, 2H), 4.97 (s, 2H), 4.20 (t, $J = 7.0$ Hz, 2H), 3.88 (s, 3H), 1.70-1.60 (m, 2H), 1.40-1.20 (m, 10H), 0.90 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.76, 138.72, 125.21, 124.27, 121.20 (q, $J = 320$ Hz, CF_3), 67.95, 51.28, 37.60, 33.06, 30.43, 30.40, 29.62, 26.96, 23.89, 14.95. ^{19}F (254 MHz) δ -80.05 (CF_3); MS (ESI): m/z , 253.3 [$\text{M} - \text{NTf}_2^-$] $^+$; MS (ESI): m/z , 279.9 [NTf_2^-].

3-Methyl-1-(*N,N*-diethylacetamidyl)imidazolium NTf₂ (6h)

This compound was prepared analogously to **6a** using 3-methyl-1-(*N,N*-diethylacetamidyl)imidazolium bromide **3h** (828 mg, 3.0 mmol) and LiNTf_2 (947 mg, 3.3 mmol) to give a crystalline solid in 83 % yield (1.18 g, 2.48 mmol). mp = 43-45°C; ^1H NMR (300 MHz, CD_3CN) δ 8.47 (s, 1H), 7.34 (s, 2H), 5.06 (s, 2H), 3.88 (s, 3H), 3.37 (q, $J = 7.0$ Hz, 2H), 3.34 (q, $J = 7.0$ Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 3H), 1.10 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 164.81, 138.89, 125.47, 124.33, 121.39 (q, $J = 320$ Hz, CF_3), 51.72, 42.51, 42.00, 37.53, 14.65, 13.55. ^{19}F (254 MHz) δ -80.03 (CF_3); MS (ESI): m/z , 196.1 [$\text{M} - \text{NTf}_2^-$] $^+$; MS (ESI): m/z , 279.9 [NTf_2^-].

3-Methyl-1-(*N*-butyl-*N*-methylacetamidyl)imidazolium NTf₂ (6g)

This compound was prepared analogously to **6a** using 3-methyl-1-(*N*-butyl-*N*-methylacetamidyl)imidazolium bromide **3g** (302 mg, 1.04 mmol, 1:1.3 mixture of isomers) and LiNTf_2 (329 mg, 1.15 mmol) to give a clear viscous hygroscopic oil in 80 % yield (410 mg, 0.84 mmol, 1:1.3 mixture of isomers). * denotes both isomers. ^1H NMR (300 MHz, CD_3CN) δ 8.42 (s, 1H, minor), 8.40 (s, 1H, major), 7.40-7.30 (m, 2H*), 5.06 (s, 2H, minor), 5.02 (s, 2H, major), 3.88 (s, 3H*), 3.37 (t, $J = 7.0$ Hz, 2H, major), 3.28 (t, $J = 7.0$ Hz, 2H, minor), 3.00 (s, 3H, major), 2.92 (s, 3H, minor), 1.70-

1.25 (m, 4H*), 0.99 (t, $J = 7.0$ Hz, 3H, minor), 0.93 (t, $J = 7.0$ Hz, 3H, major). ^{13}C (75 MHz) δ 165.72 (major), 165.47 (minor), 139.01 (minor), 138.93 (major), 125.55 (minor), 125.48 (major), 124.38*, 121.42* (q, $J = 320$ Hz, CF_3), 51.90 (major), 51.65 (minor), 50.07 (minor), 49.24 (major), 37.49*, 35.07 (major), 34.62 (minor), 31.29 (minor), 30.36 (major), 21.10*, 14.67 (major), 14.61 (minor). ^{19}F (254 MHz) δ -79.90 (CF_3); MS (ESI): m/z , 210.2 [$\text{M} - \text{NTf}_2^-$] $^+$; MS (ESI): m/z , 279.9 [NTf_2^-].

3-Methyl-1-(methylacetyl)imidazolium PF_6 (**5a**)

A flask was charged with 3-methyl-1-(methylacetyl)imidazolium bromide **3a** (702 mg, 3.0 mmol) and distilled water (2 mL). KPF_6 (607 mg, 3.3 mmol) in distilled water (1 mL) was added in one portion and the suspension was stirred vigorously for 4 h at rt. The top aqueous layer was removed, the IL washed with water (3 x 1 mL) then the solvent removed *in vacuo*. The product was dried at 60°C at 0.01 mmHg for 72 h to give a crystalline solid in 67 % yield (0.61 g, 2.0 mmol). mp = 76-78°C; ^1H NMR (300 MHz, CD_3CN) δ 8.49 (s, 1H), 7.39 (s, 2H), 4.99 (s, 2H), 3.88 (s, 3H), 3.79 (s, 3H). ^{13}C (75 MHz) δ 168.32, 138.67, 125.14, 125.02, 54.35, 51.18, 37.64; ^{19}F (254 MHz) δ -73.0 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-); MS (ESI): m/z , 155.1 [$\text{M} - \text{PF}_6^-$] $^+$; MS (ESI): m/z , 144.9 [PF_6^-].

3-Methyl-1-(ethylacetyl)imidazolium PF_6 (**5b**)

This compound was prepared analogously to **5a** using 3-methyl-1-(ethylacetyl)imidazolium bromide **3b** (0.55 g, 2.2 mmol) and KPF_6 (0.41 g, 2.2 mmol) to give a clear viscous hygroscopic oil in 68 % yield (0.47 g, 1.5 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.47 (s, 1H), 7.39 (s, 2H), 4.97 (s, 2H), 4.26 (q, $J = 7.0$ Hz, 2H), 3.88 (s, 3H), 1.29 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.80, 138.65, 125.18,

125.00, 63.98, 51.30, 37.63, 14.84. ^{19}F (254 MHz) δ -72.5 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-).

MS (ESI): m/z , 169.1 $[\text{M} - \text{PF}_6^-]^+$; MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(propylacetyl)imidazolium PF_6 (5c)

This compound was prepared analogously to **5a** using 3-methyl-1-(propylacetyl)imidazolium bromide **3c** (0.60 g, 2.3 mmol) and KPF_6 (464 mg, 2.5 mmol) to give a clear viscous hygroscopic oil in 78 % yield (585 mg, 1.8 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.47 (s, 1H), 7.39 (s, 2H), 4.98 (s, 2H), 4.17 (t, $J = 7.0$ Hz, 2H), 3.88 (s, 3H), 1.69 (qt, $J = 7.0, 7.0$ Hz, 2H), 0.95 (t, $J = 7.0$ Hz, 3H); ^{13}C (75 MHz) δ 167.84, 138.65, 125.18, 124.99, 69.32, 51.28, 37.64, 23.03, 10.98; ^{19}F (254 MHz) δ -72.7 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-); MS (ESI): m/z , 183.1 $[\text{M} - \text{PF}_6^-]^+$; MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(hexylacetyl)imidazolium PF_6 (5d)

This compound was prepared analogously to **5a** using 3-methyl-1-(hexylacetyl)imidazolium bromide **3d** (762 mg, 2.3 mmol) and KPF_6 (458 mg, 2.5 mmol) to give a clear viscous hygroscopic oil in 89 % yield (0.76 g, 2.1 mmol). ^1H NMR (300 MHz, CD_3CN) δ 8.49 (s, 1H), 7.39 (s, 2H), 4.98 (s, 2H), 4.20 (t, $J = 7.0$ Hz, 2H), 3.88 (s, 3H), 1.70-1.60 (m, 2H), 1.40-1.30 (m, 6H), 0.90 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 167.78, 138.62, 125.17, 124.97, 67.89, 51.28, 37.62, 32.54, 29.56, 26.57, 23.71, 14.77. ^{19}F (254 MHz) δ -71.94 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-). MS (ESI): m/z , 225.2 $[\text{M} - \text{PF}_6^-]^+$ MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(octylacetyl)imidazolium PF_6 (5e)

This compound was prepared analogously to **5a** using 3-methyl-1-(octylacetyl)imidazolium bromide **3e** (528 mg, 1.58 mmol) and KPF_6 (321 mg, 1.74

mmol) to give a colourless oil in 81 % yield (508 mg, 1.27 mmol). The oil crystallised in the fridge at 2°C. ¹H NMR (300 MHz, CD₃CN) δ 8.46 (s, 1H), 7.39 (s, 2H), 4.96 (s, 2H), 4.19 (t, *J* = 7.0 Hz, 2H), 3.88 (s, 3H), 1.72-1.60 (m, 2H), 1.42-1.25 (m, 10H), 0.90 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.77, 138.57, 125.15, 124.96, 67.88, 51.26, 37.62, 32.99, 30.38, 30.31, 29.58, 26.89, 23.84, 14.86. ¹⁹F (254 MHz) δ -72.67 (d, *J*_{P-F} = 707 Hz, PF₆⁻); MS (ESI): *m/z*, 253.3 [M- PF₆⁻]⁺; MS (ESI): *m/z*, 144.9 [PF₆⁻].

3-Methyl-1-(*N,N*-diethylacetamidyl)imidazolium PF₆ (5h)

This compound was prepared analogously to **5a** using 3-methyl-1-(*N,N*-diethylacetamidyl)imidazolium bromide **3h** (828 mg, 3.0 mmol) and KPF₆ (607 mg, 3.3 mmol) to give a crystalline solid in 66 % yield (0.68 g, 2.0 mmol). mp = 64-66°C; ¹H NMR (300 MHz, CD₃CN) δ 8.43 (s, 1H), 7.33 (s, 2H), 5.04 (s, 2H), 3.88 (s, 3H), 3.37 (q, *J* = 7.0 Hz, 2H), 3.34 (q, *J* = 7.0 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.10 (t, *J* = 7.0 Hz, 3H); ¹³C (75 MHz) δ 164.80, 138.85, 125.47, 124.34, 51.71, 42.50, 42.00, 37.54, 14.65, 13.55; ¹⁹F (254 MHz) δ -72.8 (d, *J*_{P-F} = 707 Hz, PF₆⁻); MS (ESI): *m/z*, 196.1 [M- PF₆⁻]⁺; MS (ESI): *m/z*, 144.9 [PF₆⁻].

3-Methyl-1-(*N*-butyl-*N*-methylacetamidyl)imidazolium PF₆ (5g)

This compound was prepared analogously to **5a** using 3-methyl-1-(*N*-butyl-*N*-methylacetamidyl)imidazolium bromide **3g** (265 mg, 0.91 mmol, 1:1.3 mixture of isomers) and KPF₆ (185 mg, 1.0 mmol) to give a crystalline solid in 70 % yield (225 mg, 0.63 mmol, 1:1.3 mixture of isomers). mp = 62-64°C; * denotes both isomers. ¹H NMR (300 MHz, CD₃CN) δ 8.42 (s, 1H, minor), 8.40 (s, 1H, major), 7.40-7.30 (m, 2H*), 5.06 (s, 2H, major), 5.03 (s, 2H, minor), 3.88 (s, 3H*), 3.37 (t, *J* = 7.0 Hz, 2H,

major), 3.28 (t, $J = 7.0$ Hz, 2H, minor), 3.00 (s, 3H, major), 2.92 (s, 3H, minor), 1.70-1.25 (m, 4H*), 0.99 (t, $J = 7.0$ Hz, 3H, minor), 0.93 (t, $J = 7.0$ Hz, 3H, major); ^{13}C (75 MHz) δ 165.75 (major), 165.48 (minor), 138.93 (minor), 138.85 (major), 125.51 (minor), 125.45 (major), 124.42*, 51.86 (major), 51.61 (minor), 50.00 (minor), 49.18 (major), 37.50*, 35.05 (major), 34.59 (minor), 31.28 (minor), 30.36 (major), 21.11*, 14.69 (major), 14.65 (minor). ^{19}F (254 MHz) δ -72.38 (d, $J_{\text{P-F}} = 710$ Hz, PF_6^-); MS (ESI): m/z , 210.2 $[\text{M} - \text{PF}_6^-]^+$; MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(*N*-butylacetamidyl)imidazolium PF_6 (5f)

A dry flask was charged with 3-methyl-1-(*N*-butylacetamidyl)imidazolium bromide **3f** (120 mg, 0.43 mmol) and acetonitrile (1 mL) under a nitrogen atmosphere. KPF_6 (96 mg, 0.52 mmol) was added in one portion and the suspension was stirred vigorously for 4 days at rt. The fine white precipitate was filtered quickly in air and washed with dry acetonitrile (2 x 1 mL). The filtrate and washings were combined, solvent removed by rotary evaporation then *in vacuo*. The product was dried at 60°C at 0.01 mmHg for 72 h to give a clear crystalline solid in 99 % yield (145 mg, 0.42 mmol). mp = 64-66°C; ^1H NMR (300 MHz, CD_3CN) δ 8.46 (s, 1H), 7.36 (s, 2H), 6.78 (bs, 1H, NH), 4.80 (s, 2H), 3.87 (s, 3H), 3.21 (q, $J = 7.0$ Hz, 2H), 1.60-1.30 (m, 4H), 0.93 (t, $J = 7.0$ Hz, 3H). ^{13}C (75 MHz) δ 165.87, 138.66, 125.15, 124.69, 52.36, 40.68, 37.51, 32.53, 21.14, 14.55. ^{19}F (254 MHz) δ -72.46 (d, $J_{\text{P-F}} = 707$ Hz, PF_6^-); MS (ESI): m/z , 196.1 $[\text{M} - \text{PF}_6^-]^+$; MS (ESI): m/z , 144.9 $[\text{PF}_6^-]$.

3-Methyl-1-(ethylacetyl)imidazolium (NCNCN) (7b)

A dry flask was charged with 3-methyl-1-(ethylacetyl)imidazolium bromide (**3b**) (1.50 g, 6.0 mmol) and acetonitrile (3 mL) under a nitrogen atmosphere. NaN CNCN

(641 mg, 7.2 mmol) was added in one portion and the suspension was stirred vigorously for 4 days at rt. The fine white precipitate was filtered quickly in air and washed with dry acetonitrile (2 x 1 mL). The filtrate and washings were combined, solvent removed by rotary evaporation then *in vacuo*. The product was dried at 60°C at 0.01 mmHg for 72 h to give a clear viscous hygroscopic oil in 96 % yield (1.35 g, 5.73 mmol). ¹H NMR (300 MHz, CD₃CN) δ 9.06 (s, 1H), 7.53 (s, 1H), 7.45 (s, 1H), 5.18 (s, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.92 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 3H). ¹³C (75 MHz) δ 167.90, 138.99, 125.02, 124.64, 63.67, 51.26, 37.53, 14.77. Peaks for NCNCN⁻ not cited. MS (ESI): *m/z*, 169.1 [M- NCNCN]⁺; MS (ESI): *m/z*, 66.0 [NCNCN⁻].

3-Methyl-1-(*N*-butyl-*N*-methylacetamidyl)imidazolium (NCNCN) (7g)

This compound was prepared analogously to **7b** using 3-methyl-1-(*N*-butyl-*N*-methylacetamidyl)imidazolium bromide **3g** (208 mg, 0.71 mmol, 1:1.3 mixture of isomers) and NaNCNCN (77 mg, 0.86 mmol) to give a clear viscous hygroscopic oil in 96 % yield (189 mg, 0.68 mmol, 1:1.3 mixture of isomers). * denotes both isomers. ¹H NMR (300 MHz, CD₃CN) δ 8.75 (s, 1H, minor), 8.71 (s, 1H, major), 7.50-7.35 (m, 2H*), 5.20 (s, 2H, major), 5.18 (s, 2H, minor), 3.90 (s, 3H*), 3.37 (t, *J* = 7.0 Hz, 2H, major), 3.30 (t, *J* = 7.0 Hz, 2H, minor), 3.02 (s, 3H, major), 2.92 (s, 3H, minor), 1.70-1.25 (m, 4H*), 0.99 (t, *J* = 7.0 Hz, 3H, minor), 0.93 (t, *J* = 7.0 Hz, 3H, major). ¹³C (75 MHz) δ 165.85 (major), 165.54 (minor), 138.99 (minor), 138.85 (major), 125.19 (minor), 125.11 (major), 123.94*, 51.78 (major), 51.43 (minor), 49.78 (minor), 48.75 (major), 37.29*, 35.03 (major), 34.36 (minor), 31.02 (minor), 30.09 (major), 20.85 (minor), 20.77 (major), 14.41*. Peaks for NCNCN⁻ not cited. MS (ESI): *m/z*, 210.2 [M- NCNCN]⁺; MS (ESI): *m/z*, 66.0 [NCNCN⁻].