Electronic supporting information for

"Rational selection of the cation of an ionic liquid solvent to control the reaction outcome of a substitution reaction"

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General experimental

Benzyl bromide was purified through distillation and stored over molecular sieves at 4 °C until use. Pyridine was purified through distillation[1] over calcium hydride and stored over molecular sieves at 4 °C until use. Alkyl halides, amines and sulphides used in the synthesis of the ionic liquids were purified as per literature and were used shortly after.[1] The ionic liquids **2**, **3**, **4**, **5**, **6** and **10** were prepared with reference to literature methods,[2-5] through alkylation of the corresponding heterocycle to form an intermediate halide salt and a salt metathesis to the desired $[N(SO_2CF_3)_2]^-$ anion. Ionic liquid **7** was prepared through adaptation of the above literature methods. Ionic liquid **8** was prepared with reference to literature, through construction of the heterocyclic ring, alkylation and then anion metathesis.[6] The synthesis of ionic liquid **S12** involved synthesis of the heterocyclic ring through literature procedures,[7] followed by alkylation and anion metathesis in adaptations of the above literature procedures. All ionic liquids were dried under reduced pressure (< 0.1 mbar) for at least 3 hours and were found to have < 250 ppm water using Karl Fischer titration methodology. Ion chromatography confirmed < 0.5 mol % residual halide. Full preparation information for all the ionic liquids is below. Where mentioned, *in vacuo* refers to the use of a Heidolph 'Hei-vap precision' rotary evaporator connected to a Vacuubrand PC500 series pump unit. The phrase 'under reduced pressure' refers to use of a Schlenk line, connected to an Edwards oil pump with a measure vacuum of < 0.1 mbar.

^{1}H, ^{13}C, ^{19}F and ^{77}Se NMR spectra for characterisation of synthesised ionic liquids were carried out on either a Bruker Avance III 300, Bruker Avance III 400, Bruker Avance III 400 HD, Bruker Avance III 500 or a Bruker Avance III 600 HD with a BBFO, BBO, TBI or TCI probe. NMR spectra used for characterisation were processed using the Bruker TOPSPIN 3.2 - 4.0 software. ^{19}F and ^{77}Se NMR spectra were referenced to α,α,α-trifluorotoluene (neat) and diphenyl diselenide (*d*-chloroform), respectively (in capillary inserts).

^{1}H NMR spectra for kinetic analyses were carried out on either a Bruker Avance III 400, Bruker Avance III 400 Prodigy, Bruker Avance III 500 or a Bruker Avance III 600 with either a TBI, BBO or BBFO probe. The results were shown to be reproducible between probes and spectrometers.

The Mark Wainwright Analytical Centre Bioanalytical Mass Spectrometry Facility (BMSF) carried out the High Resolution Mass Spectrometry on ionic liquids **7**, **S6** and **S12**. A Thermo Scientific LTQ Orbitrap XL mass spectrometer equipped with a nanospray ionisation source was used to acquire high resolution mass spectra (resolution of 60,000 at *m*/*z* 400). The positive ion mode was used throughout the experiments.

The density and viscosity measurements on ionic liquid **7** were carried out on an Anton Paar DMA 4100 M Density Meter and a Lovis 2000 ME Microviscometer. Fourier Transform Infrared (FTIR) spectra were recorded on a Thermo Scientific Nicolet iS 5 FT-IR spectrometer.

The Thermophysical properties facility (TPF) at the University of Sydney carried out the Differential Scanning Calorimetry and Thermogravimetric Analysis on ionic liquid **7** on a Mettler Toledo DSC823 with a TS0800GC1 gas controller and a TA Instruments Discovery TGA, respectively. The DSC analysis consisted of heating and cooling the sample (between 50 and -160 °C) at a rate of 10 °C min^{-1} under a 50 mL min^{-1} flow of nitrogen, measurements were carried out in duplicate with uncertainties reported as half the range. The TGA consisted of heating the ionic liquid **7** to 300 °C and then holding at that temperature for 20 minutes.

Synthesis of the ionic liquids **2-8**, **10** and **S12**

***S*-Butylthiolanium *bis*(trifluoromethanesulfonyl)imide 2**

A mixture of thiolane (12.0 mL, 0.147 mol), *n*-butyl iodide (23.0 mL, 0.202 mol) and acetonitrile (15 mL) was stirred at 70 °C for 2 days. The acetonitrile was removed under reduced pressure and the resulting yellow solid was triturated in ether (5 x 50 mL). The resulting solid was concentrated *in vacuo* to afford *S*-butylthiolanium iodide **S1** as a yellow solid (34.6 g, 0.127 mol, 93%). m.p. 94-96°C[i] ^{1}H NMR (300 MHz, d_3-acetonitrile) δ 0.96 (t, J = 7.2 Hz, 3H, $CH_2C\underline{H}_3$), 1.47 (m, 2H, $CH_3C\underline{H}_2$), 1.73 (m, 2H, $SCH_2C\underline{H}_2$), 2.26 (m, 4H, $S(CH_2C\underline{H}_2)_2$), 3.14 (m, 2H, $SC\underline{H}_2CH_2$), 3.33 (m, 2H, $S(C\underline{H}_2CH_2)_2$), 3.51 (m, 2H, $S(C\underline{H}_2CH_2)_2$).

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (44.2 g, 0.155 mol) in water (200 mL) was added to a solution of the iodide **S1** (34.6 g, 0.127 mol) in water (200 mL). Immediately two layers formed and the mixture was stirred at room temperature for 60 hours. Dichloromethane (50 mL) was then added, the organic layer separated and then extracted with a saturated aqueous solution of sodium metabisulphite (100 mL) and then water (9 x 100 mL). The organic layer was then concentrated under reduced pressure to yield the title compound **2** as a light yellow viscous liquid (41.9 g, 0.0984 mol, 77%). ^{1}H NMR (300 MHz, d_3-acetonitrile) δ 0.96 (t, J = 7.2 Hz, 3H, $CH_2C\underline{H}_3$), 1.47 (m, 2H, $CH_3C\underline{H}_2$), 1.72 (m, 2H, $SCH_2C\underline{H}_2$), 2.26 (m, 4H, $S(CH_2C\underline{H}_2)_2$), 3.06 (m, 2H, $SC\underline{H}_2CH_2$), 3.27 (m, 2H, $S(C\underline{H}_2CH_2)_2$), 3.46 (m, 2H, $S(C\underline{H}_2CH_2)_2$).

***N*-Butyl-*N*-methylpiperidinium *bis*(trifluoromethanesulfonyl)imide 3**

n-Butyl bromide (11.4 g, 0.0835 mol) was added to a solution of *N*-methylpiperidine (5.75 g, 0.0580 mol) in acetonitrile (10 mL). This mixture was stirred at 50 °C under a nitrogen atmosphere for 3 hours. During this time a light yellow precipitate formed. Acetonitrile (30 mL) was added and this mixture was stirred for a further 2 days. The mixture was then cooled to room temperature, triturated with ethyl acetate (11 x 200 mL) and solid collected through filtration. The solid was dried *in vacuo* to yield *N*-butyl-*N*-methylpiperidinium bromide **S2** (11.1 g, 0.0470 mol, 81 %) as a white solid. m.p. 232-235 °C (dec.) (lit.[8] 241-243 °C). ^{1}H NMR (300 MHz, d_6-acetone) δ 0.98 (t, J = 7.4 Hz, 3H, $C\underline{H}_3CH_2$), 1.37 – 1.50 (m, 2H, $CH_3C\underline{H}_2$), 1.69 – 1.87 (m, 4H, $C\underline{H}_2CH_2N((CH_2CH_2)_2C\underline{H}_2)$), 1.96 (m, 4H, $N((CH_2C\underline{H}_2)_2)CH_2)$), 3.33 (s, 3H, $NC\underline{H}_3$), 3.69 – 3.75 (m, 6H, $C\underline{H}_2N((C\underline{H}_2CH_2)_2)CH_2)$).

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (22.7 g, 0.0790 mol) in water (100 mL) was added to a solution of the bromide **S2** (11.0 g, 0.0464 mol) in water (100 mL). Immediately two layers formed and this mixture was stirred at room temperature for 24 hours. Dichloromethane

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[i] No melting point is recorded in literature.

(100 mL) was then added, the organic layer was separated and was then extracted with water (10 x 60 mL). The organic layer was then concentrated under reduced pressure to yield the title compound **3** as a light yellow, viscous liquid (16.7 g, 0.0382 mol, 82%). ^{1}H NMR (300 MHz, *d*$_6$-acetone) δ 0.98 (t, *J* = 7.4 Hz, 3H, $C\underline{H}_3CH_2$), 1.37 – 1.49 (m, 2H, $CH_3C\underline{H}_2$), 1.68 – 1.77 (m, 2H, $N((CH_2CH_2)_2C\underline{H}_2)$), 1.80 – 1.88 (m, 2H, $C\underline{H}_2CH_2N$), 1.96 – 1.99 (m, 4H, $N((CH_2C\underline{H}_2)_2CH_2)$), 3.21 (s, 3H, $NC\underline{H}_3$), 3.47 – 3.54 (m, 6H, $C\underline{H}_2N((C\underline{H}_2CH_2)_2CH_2)$).

N-Butyl-*N*-methylmorpholinium *bis*(trifluoromethanesulfonyl)imide 4

n-Butyl bromide (31.0 mL, 0.289 mol) was added to a solution of *N*-methylmorpholine (25.0 mL, 0.227 mol) in acetonitrile (25 mL). This mixture was stirred at 45 °C under a nitrogen atmosphere for 15 hours. During this time a white precipitate formed. Acetonitrile (150 mL) was added and this mixture was stirred for a further 5 days. The solvent was removed *in vacuo* and the remaining solid was triturated with ethyl acetate (6 x 150 mL). The solid was then dried *in vacuo* to yield *N*-butyl-*N*-methylmorpholinium bromide **S3** (46.1 g, 0.194 mol, 85 %) as a white solid. m.p. 209-211 °C (lit.[4] 210 °C). ^{1}H NMR (300 MHz, *d*$_3$-acetonitrile) δ 0.98 (t, *J* = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.34-1.43 (m, 2H, $CH_3C\underline{H}_2$), 1.67-1.75 (m, 2H, $NCH_2C\underline{H}_2$), 3.13 (s, 3H, $NC\underline{H}_3$), 3.40-3.46 (m, 6H, $C\underline{H}_2N(C\underline{H}_2CH_2)_2O$), 3.93-3.94 (m, 4H, $CH_2N(CH_2C\underline{H}_2)_2O$).

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (64.5 g, 0.223 mol) in water (100 mL) was added to a solution of the bromide **S3** (45.9 g, 0.193 mol) in water (150 mL). Immediately two layers formed and the mixture was stirred at room temperature for 24 hours. Dichloromethane (100 mL) was then added. The organic layer was separated and was then extracted with water (10 x 100 mL). The organic layer was then concentrated under reduced pressure to give the title compound **4** as colourless, viscous liquid that solidified on standing to give a white solid (68.6 g, 0.157 mol, 81 %). m.p. 32-34 °C (lit.[4] 35 °C). ^{1}H NMR (300 MHz, *d*$_3$-acetonitrile) δ 0.97 (t, *J* = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.32-1.44 (m, 2H, $CH_3C\underline{H}_2$), 1.68-1.76 (m, 2H, $NCH_2C\underline{H}_2$), 3.05 (s, 3H, $NC\underline{H}_3$), 3.30-3.33 (m, 6H, $C\underline{H}_2N(C\underline{H}_2CH_2)_2O$), 3.90-3.92 (m, 4H, $CH_2N(CH_2C\underline{H}_2)_2O$).

N-Butylpyridinium *bis*(trifluoromethanesulfonyl)imide 5

n-Butyl bromide (30.0 mL, 0.278 mol) was added to pyridine (19.0 mL, 0.214 mol) and stirred at room temperature under a nitrogen atmosphere for 2 days. A white solid precipitated and this mixture was triturated with ethyl acetate (5 x 200 mL). The resulting solid was dried *in vacuo* to afford *N*-butylpyridinium bromide **S4** as a white solid (39.7 g, 0.184 mol, 86%). m.p. 95-97 °C (lit.[9] 95-97 °C). ^{1}H NMR (300 MHz, *d*$_6$-acetone) δ 0.97 (t, *J* = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.40-1.52 (m, 2H, $CH_3C\underline{H}_2$), 2.09-2.15 (m, 2H, $NCH_2C\underline{H}_2$), 5.04 (t, *J* = 7.5 Hz, 3H, $NC\underline{H}_2CH_2$), 8.27 (m, 2H, Ar$\underline{H}$3/5), 8.74 (tt, *J* = 7.9 Hz, 1.3 Hz, 1H, Ar$\underline{H}$4), 9.64 (m, 2H, Ar$\underline{H}$2/6).

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (16.1 g, 0.0560 mol) in water (40 mL) was added to a solution of the bromide **S4** (10.3 g, 0.0476 mol) in water (40 mL). Immediately two layers formed and the mixture was stirred at room temperature for 24 hours. Dichloromethane (50 mL) was then added, the organic layer was separated and was then washed with water (10 x 100 mL). The organic layer was then concentrated under reduced pressure to yield the title compound **5** as a colourless, viscous liquid (15.3 g, 0.0368 mol, 77%). ^{1}H NMR (300 MHz, d_6-acetone) δ 0.98 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.39 (m, 2H, $CH_3C\underline{H}_2$), 1.99 (m, 2H, $NCH_2C\underline{H}_2$), 4.61 (t, J = 7.6 Hz, 3H, $NC\underline{H}_2CH_2$), 8.06 (m, 2H, Ar$\underline{H}$3/5), 8.47 (t, J = 7.7 Hz, 1H, Ar$\underline{H}$4), 8.81 (d, J = 5.9 Hz, 2H, Ar$\underline{H}$2/6).

N-Hexylpyridinium *bis*(trifluoromethanesulfonyl)imide 6

n-Hexyl iodide (36.0 mL, 0.242 mol) was added to a solution of pyridine (18.0 mL, 0.186 mol) in acetonitrile (25 mL) and the mixture was stirred at room temperature for five days. The acetonitrile was removed *in vacuo* and the resulting oil was triturated with ethyl acetate (5 x 200 mL) and then with diethyl ether (5 x 200 mL). The resulting white solid was dried *in vacuo* and then under reduced pressure to yield *N*-hexylpyridinium iodide **S5** as a white solid (57.3 g, 0.197 mol, 88%). m.p. 56-58 °C.[ii] ^{1}H NMR (400 MHz, d_6-acetone) δ 0.87 (t, J = 7.2 Hz, 3H, $CH_2C\underline{H}_3$), 1.34 (m, 2H, $CH_2(C\underline{H}_2)_2CH_3$), 1.43 (m, 2H, $C\underline{H}_2(CH_2)_2CH_3$), 2.14 (m, 2H, $NCH_2C\underline{H}_2$), 4.95 (t, J = 7.6 Hz, 3H, $NC\underline{H}_2CH_2$), 8.30 (m, 2H, Ar$\underline{H}$3/5), 8.77 (tt, J = 7.8, 1.3 Hz, 1H, Ar$\underline{H}$4), 9.43 (d, J = 5.7 Hz, 2H, Ar$\underline{H}$2/6).

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (63.0 g, 0.220 mol) in water (100 mL) was added to a solution of the iodide **S5** (56.8 g, 0.195 mol) in water (100 mL). Immediately two layers formed and the mixture was stirred at room temperature for 24 hours. Dichloromethane (100 mL) was then added, the organic layer was separated and then was extracted with a saturated aqueous solution of sodium metabisulphite (100 mL) and water (10 x 150 mL). The organic layer was then concentrated under reduced pressure to yield the title compound **6** as colourless, viscous liquid (83.9 g, 0.189 mol, 97%). ^{1}H NMR (300 MHz, d_6-acetone) δ 0.87 (t, J = 7.3 Hz, 3H, $CH_2C\underline{H}_3$), 1.28-1.47 (m, 6H, $CH_2(C\underline{H}_2)_3CH_3$), 2.15 (m, 2H, $NCH_2C\underline{H}_2$), 4.87 (t, J = 7.6 Hz, 3H, $NC\underline{H}_2CH_2$), 8.30 (m, 2H, Ar$\underline{H}$3/5), 8.76 (t, J = 7.8 Hz, 1H, Ar$\underline{H}$4), 9.21 (d, J = 6.0 Hz, 2H, Ar$\underline{H}$2/6).

[ii] No melting point is recorded in literature.

***N*-(3,3,4,4,5,5,6,6,6-Nonafluorohexyl)pyridinium *bis*(trifluoromethanesulfonyl)imide 7**

A solution of pyridine (3.00 mL, 0.0320 mol) in acetonitrile (5 mL) was added to 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodohexane (6.00 mL, 0.0330 mol) and the mixture was stirred at room temperature for 3 days. After this time, the temperature was increased to 50 °C and the mixture was stirred for another 14 days. Diethyl ether (40 mL) was then added and a precipitate formed. The precipitate was collected and triturated with diethyl ether (6 x 50 mL). The solid was then dried *in vacuo* to yield the iodide intermediate **S6** as a yellow solid (11.9 g, 0.0263 mol, 81%). m.p. 138-140 °C. ^{1}H NMR (600 MHz, d_3-acetonitrile) δ 3.06 (tt, J = 18.6, 7.4 Hz, 2H, $NCH_2C\underline{H}_2CF_2$), 5.00 (t, J = 7.3 Hz, 2H, $NC\underline{H}_2CH_2CF_2$), 8.11 (m, 2H, Ar$\underline{H}$3/5), 8.60 (t, J = 7.9 Hz, 1H, $\underline{\mathrm{ArH4}}$), 8.99 (d, J = 5.9 Hz, 2H, $\underline{\mathrm{ArH2}}$/6). ^{13}C NMR (600 MHz, d_3-acetonitrile) δ 32.3 (t, J_{CF} = 21 Hz, $NCH_2\underline{C}H_2CF_2$), 54.5 ($N\underline{C}H_2CH_2CF_2$), 109.6 (tqt, J_{CF} = 267, 40, 6 Hz, $CH_2CF_2CF_2\underline{C}F_2CF_3$), 111.0 (ttt, J_{CF} = 256, 35, 31 Hz, $CH_2CF_2\underline{C}F_2CF_2CF_3$), 118.2 (qt, J_{CF} = 288, 34 Hz, $CH_2CF_2CF_2CF_2\underline{C}F_3$), 118.5 (tt, J_{CF} = 256, 33 Hz, $CH_2\underline{C}F_2CF_2CF_2CF_3$), 129.5 (Ar-$\underline{C}$H), 146.2 (Ar-$\underline{C}$H), 147.8 (Ar-$\underline{C}$H). ^{19}F NMR (376 MHz, d_3-acetonitrile) δ -81.1 (tt, J = 9.8, 3.1 Hz, 3F, $CH_2CF_2(CF_2)_2C\underline{F}_3$), -113.3 (tq, J = 13.4, 8.1 Hz, 2F, $CH_2C\underline{F}_2(CF_2)_2CF_3$), -124.2 (m, 2F, $CH_2CF_2(C\underline{F}_2)_2CF_3$), -125.8 (m, 2F, $CH_2CF_2(C\underline{F}_2)_2CF_3$). IR (solid): ν_{max} 3040, 2927, 1634, 1499, 1488, 1217, 1181, 1129, 1090, 957, 873, 832, 775, 747, 707, 675 cm^{-1}. Found HR-MS (ESI) m/z: 326.0580 (100), 327.0610 (12), ([Fhpy], $C_{11}H_9F_9N^+$ requires m/z: 326.0586 (100), 317.0619 (12)). Found: C 29.3; H 2.0; N 2.9%. $C_{11}H_9F_9IN$ requires C 29.2; H 2.0; N 3.1%.

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (9.39 g, 0.0327 mol) in water (100 mL) was added to a solution of the iodide **S6** (11.8 g, 0.0261 mol) in water (150 mL). Immediately two layers formed and the mixture was stirred at room temperature for 24 hours. Dichloromethane (100 mL) was then added, the organic layer was separated and was then extracted with a saturated aqueous solution of sodium metabisulphite (100 mL) and then water (10 x 100 mL). The organic layer was then concentrated under reduced pressure to yield the title compound **7** as a white solid (10.3 g, 0.0170 mol, 65%). m.p. 34-36 °C. ^{1}H NMR (600 MHz, d_3-acetonitrile) δ 2.99 (tt, J = 18.5, 7.4 Hz, 2H, $NCH_2C\underline{H}_2CF_2$), 4.88 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2CH_2CF_2$), 8.08 (m, 2H, Ar$\underline{H}$3/5), 8.57 (t, J = 7.9 Hz, 1H, Ar$\underline{H}$4), 8.77 (d, J = 6.3 Hz, 2H, Ar$\underline{H}$2/6). ^{13}C NMR (600 MHz, d_3-acetonitrile) δ 32.3 (t, J_{CF} = 21 Hz, $NCH_2\underline{C}H_2CF_2$), 54.6 ($N\underline{C}H_2CH_2CF_2$), 109.7 (tq, J_{CF} = 268, 41 Hz, $CH_2CF_2CF_2\underline{C}F_2CF_3$), 111.0 (m, $CH_2CF_2\underline{C}F_2CF_2CF_3$), 118.3 (qt, J_{CF} = 288, 32 Hz, $CH_2CF_2CF_2CF_2\underline{C}F_3$), 118.5 (tt, J_{CF} = 257, 32 Hz, $CH_2\underline{C}F_2CF_2CF_2CF_3$), 120.9 (q, J_{CF} = 321 Hz, $N(SO_2\underline{C}F_3)_2$), 129.7 (Ar-$\underline{C}$H), 146.1 (Ar-$\underline{C}$H), 147.9 (Ar-$\underline{C}$H). ^{19}F NMR (376 MHz, d_3-acetonitrile) δ -79.5 (s, 6F, $N(SO_2C\underline{F}_3)_2$), -81.1 (tt, 9.8, 3.2 Hz, 3F, $CH_2CF_2(CF_2)_2C\underline{F}_3$), -113.3 (m, 2F, $CH_2C\underline{F}_2(CF_2)_2CF_3$), -124.3 (m, 2F, $CH_2CF_2(C\underline{F}_2)_2CF_3$), -125.8 (m, 2F, $CH_2CF_2(C\underline{F}_2)_2CF_3$). IR (solid): ν_{max} 3077, 1638, 1492, 1349, 1181, 1131, 1097, 1048, 1014, 734, 715, 616 cm^{-1}. Found HR-

MS (ESI) m/z: 326.0581 (100), 327.0611 (12), ([Fhpy], $C_{11}H_9F_9N^+$ requires m/z: 326.0586 (100), 317.0619 (12)). Found: C 26.2; H 1.5; N 4.5%. $C_{15}H_9F_{15}N_2O_4S_2$ requires C 25.8; H 1.5; N 4.6%.

1-Butyl-3-methyl-1,2,3-triazolium *bis*(trifluoromethanesulfonyl)imide 8

A mixture of *n*-chlorobutane (30.0 mL, 0.286 mol), sodium azide (16.7 g, 0.258 mol) and dimethylformamide (150 mL) was stirred at 80 °C for 24 hours. It was then cooled to room temperature. Copper(I) iodide (4.97 g, 0.0261 mol) and ethynyltrimethylsilane (42.0 mL, 0.296 mol) was added. The mixture was then heated to 80 °C and stirred at this temperature for 4 days. The solvent was removed *in vacuo* and dichloromethane was added (100 mL). The organic layer was then separated and was then washed with a solution of a saturated aqueous solution of sodium metabisulphite (100 mL) and then water (5 x 100 mL) and filtered through celite. The filtrate was concentrated *in vacuo* to yield a mixture of 1-butyl-4-trimethylsilyl-1,2,3-triazole **S7a** (30.3 g, 0.154 mol, 60%) and 1-butyl-1,2,3-triazole **S7b** (2.76 g, 0.0220 mol, 8%) in a ratio of *ca.* 7:1, which was used without further purification.

A solution of tetrabutylammonium fluoride in tetrahydrofuran (1 M, 275 mL, 0.275 mol) was added dropwise over 15 minutes to a solution of the triazoles **S7** (33.1 g, 0.176 mmol) in tetrahydrofuran (20 mL). This mixture was stirred at room temperature for 16 hours. The solvent was removed *in vacuo* and and the residue purified through repeated column chromatography on silica gel (1:1 ethyl acetate/hexane) to the desired triazole **S7b** as a yellow liquid (16.5 g, 0.131 mol, 71%). ^{1}H NMR (500 MHz, *d*-chloroform) δ 0.94 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.34 (m, 2H, $CH_3C\underline{H}_2$), 1.89 (m, 2H, $NCH_2C\underline{H}_2$), 4.38 (t, J = 7.3 Hz, 3H, $NC\underline{H}_2CH_2$), 7.53 (s, 1H, $NCHC\underline{H}N$), 7.68 (s, 1H, $NC\underline{H}CHN$).

Methyl iodide (7.50 mL, 0.125 mol) was added to a solution of the butyl triazole **S7b** (12.5 g, 0.0995 mol) in ethyl acetate (15 mL). This mixture was stirred at room temperature under a nitrogen atmosphere for 6 days. The solvent was then removed *in vacuo*. Dichloromethane (200 mL) was then added and the solution was extracted with a saturated aqueous solution of sodium metabisulphite (200 mL). The organic phase was then concentrated under reduced pressure. The resulting light yellow solid was triturated with ether (5 x 50 mL) and dried *in vacuo* to afford the iodide salt **S8** as a yellow solid (25.3 g, 0.0947 mol, 95%). mp. 33-35 °C (lit.[6] 42 °C). ^{1}H NMR (300 MHz, d_6-acetone) δ 0.96 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.45 (m, 2H, $CH_3C\underline{H}_2$), 2.06 (m, 2H, $NCH_2C\underline{H}_2$), 4.56 (s, 3H, $NC\underline{H}_3$), 4.88 (t, J = 7.3 Hz, 3H, $NC\underline{H}_2CH_2$), 9.14 (m, 1H, $NCHC\underline{H}N$), 9.25 (m, 1H, $NC\underline{H}CHN$).

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (32.9 g, 0.114 mol) in water (25 mL) was added to a solution of the triazolium iodide **S8** (24.6 g, 0.0922 mol) in water (25 mL). Immediately two layers formed and the mixture was stirred at room temperature for 24 hours. Dichloromethane (50 mL) was then added, the organic layer was separated and then extracted with a saturated aqueous solution of sodium metabisulphite (60 mL) and then water (10 x 80 mL). The organic layer was then concentrated under reduced pressure to yield the title compound **8** as a light yellow, viscous liquid (31.0 g, 0.0737 mol, 80%). ^{1}H NMR (300 MHz, d_3-acetonitrile) δ 0.95 (t, J = 7.4 Hz, 3H, $CH_2\underline{H_3}$), 1.30-1.43 (m, 2H, $CH_3C\underline{H_2}$), 1.88-1.98 (m, 2H, $NCH_2C\underline{H_2}$), 4.23 (s, 3H, $NC\underline{H_3}$), 4.54 (t, J = 7.2 Hz, 3H, $NC\underline{H_2}CH_2$), 8.26 (m, 1H, $NCHC\underline{H}N$), 8.29 (m, 1H, $NC\underline{H}CHN$).

3,3'-(1,5-Pentane-diyl)*bis*(1-methylimidazolium) *bis*(trifluoromethanesulfonyl)imide 10

N-Methylimidazole (24.0 mL, 0.301 mol) was added to a solution of 1,5-dibromopentane (28.9 g, 0.126 mol) in acetonitrile (100 mL) and this solution was stirred at room temperature for 3 days. During this time, a white precipitate was formed. Acetonitrile (100 mL) was then added to the reaction mixture and the solution was stirred at room temperature for another 2 days. The solvent was then removed *in vacuo* and the resulting white solid was triturated with ethyl acetate (5 x 200 mL) and dried *in vacuo* to afford the dibromide salt **S9** as a white solid (46.2 g, 0.117 mol, 93%). mp. 138-141 °C (lit.[5] 136-137 °C). ^{1}H NMR (300 MHz, d_3-acetonitrile) δ 1.28-1.38 (m, 2H, $(NCH_2CH_2)_2C\underline{H_2}$), 1.86-1.91 (m, 4H, $(NCH_2C\underline{H_2})_2CH_2$), 3.87 (s, 6H, $NC\underline{H_3}$), 4.21 (t, J = 7.4 Hz, 3H, $(NC\underline{H_2}CH_2)_2CH_2$), 7.33-7.51 (m, 4H, $NC\underline{H}C\underline{H}N$), 9.23 (m, 2H, $NC\underline{H}N$).

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (37.0 g, 0.129 mol) in water (100 mL) was added to a solution of the dibromide salt **S9** (46.2 g, 0.117 mol) in water (100 mL). Immediately two layers formed and the reaction mixture was stirred at room temperature for 24 hours. The mixture was then extracted with dichloromethane (2 x 50 mL) and subsequently the combined organic phases were washed with water (12 x 150 mL). The dichloromethane was then removed under reduced pressure to yield the title compound **10** as a light yellow, viscous liquid (47.7 g, 0.0601 mol, 51%). ^{1}H NMR (500 MHz, d_6-acetone) δ 1.48-1.54 (m, 2H, $(NCH_2CH_2)_2C\underline{H_2}$), 2.02-2.08 (m, 4H, $(NCH_2C\underline{H_2})_2CH_2$), 4.04 (s, 6H, $NC\underline{H_3}$), 4.38 (t, J = 7.4 Hz, 3H, $(NC\underline{H_2}CH_2)_2CH_2$), 7.70-7.74 (m, 4H, $NC\underline{H}C\underline{H}N$), 8.98 (m, 2H, $NC\underline{H}N$).

Se-Butylselenolanium *bis*(trifluoromethanesulfonyl)imide S12

Selenium powder (8.45 g, 0.107 mol) was added slowly over 3 minutes to a solution of potassium hydroxide (14.3 g, 0.256 mol) in hydrazine monohydrate (50.0 mL). The mixture was stirred at 80 °C for 3 hours. The resulting mixture was then added to water (500 mL). 1,4-Dibromobutane (13.0 mL, 0.109 mol) was then added and the mixture was stirred at 60 °C for 2 hours. The mixture was then cooled, extracted with dichloromethane (200 mL x 3) and the combined organic phases were dried over magnesium sulphate. The dichloromethane was removed *via* distillation and the residue was distilled under vacuum (*ca.* 80°C, *ca.* 120 mbar) to yield the selenolane **S10** as a yellow oil

(0.98 g, 0.00726 mol, 7%). ^{1}H NMR (600 MHz, *d*-chloroform) δ 1.99–2.01 (m, 2H, $\mathrm{Se(CH_2C\underline{H}_2)_2}$), 2.87-2.89 (m, 2H, $\mathrm{Se(C\underline{H}_2CH_2)_2}$).

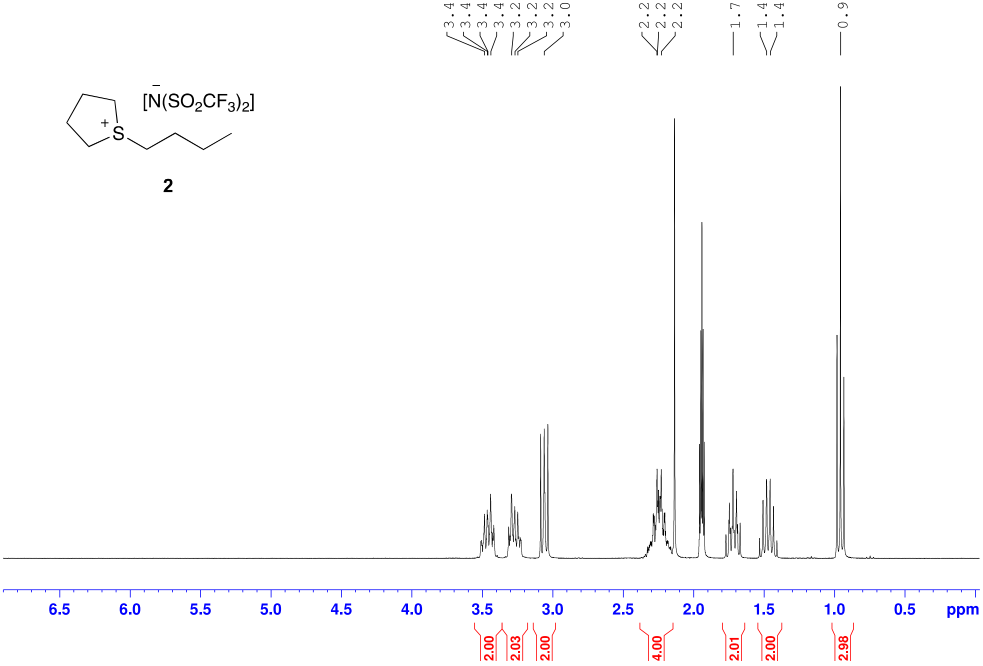
Selenolane **S10** (0.98 g, 0.00726 mol) was added to *n*-iodobutane (3.24 g, 0.0176 mol) and the mixture was stirred at room temperature for 8 days. Acetonitrile (20 mL) was then added and this was mixture was stirred at 50 °C. The reaction was monitored using ^{1}H NMR spectroscopy, with aliquots of the reaction mixture analysed comparing the signals for the selenolane **S10**, with the new signals at δ *ca*. 3.4; the reaction was removed from the heat after 4 days when it had reached 68% conversion. Diethyl ether (20 mL) was added to the cooled reaction mixture and a white precipitate formed. The white precipitate was triturated with diethyl ether (5 x 20 mL) to give the selenolanium iodide **S11** as a white solid that was not isolated and which was used without further purification. ^{1}H NMR (400 MHz, d_3-acetonitrile) δ 0.96 (t, J = 7.4 Hz, 3H, $\mathrm{CH_2C\underline{H}_3}$), 1.46 (m, 2H, $\mathrm{CH_3C\underline{H}_2}$), 1.76 (m, 2H, $\mathrm{SeCH_2C\underline{H}_2}$), 2.27 (m, 4H, $\mathrm{Se(CH_2C\underline{H}_2)_2}$), 3.13 (m, 2H, $\mathrm{SeC\underline{H}_2CH_2}$), 3.30 (m, 2H, $\mathrm{Se(C\underline{H}_2CH_2)_2}$), 3.47 (m, 2H, $\mathrm{Se(C\underline{H}_2CH_2)_2}$). ^{13}C NMR (100 MHz, d_3-acetonitrile) δ 13.6 ($\mathrm{CH_2\underline{C}H_3}$), 23.0 ($\mathrm{CH_3\underline{C}H_2}$), 28.5 ($\mathrm{SeCH_2\underline{C}H_2}$), 31.6 ($\mathrm{Se(\underline{C}H_2CH_2)_2}$), 40.3 ($\mathrm{Se\underline{C}H_2CH_2}$), 43.4 ($\mathrm{Se(CH_2\underline{C}H_2)_2}$). ^{77}Se NMR (76 MHz, *d*-chloroform) δ 425.6.

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (2.00 g, 0.00689 mol) in water (20 mL) was added to a solution of the iodide **S11** in water (10 mL). Immediately two layers formed and this mixture was stirred at room temperature for 24 hours. Dichloromethane (10 mL) was then added, the aqueous layer was separated and then extracted with dichloromethane (3 x 10 mL). The combined organic layer was then washed with water (10 x 20 mL). The dichloromethane was removed *via* distillation and the residue was dried under reduced pressure to yield the title compound **S12** as a colourless, viscous liquid (0.692 g, 0.00147 mol, 30%). ^{1}H NMR (400 MHz, *d*-chloroform) δ 0.98 (t, J = 7.4 Hz, 3H, $\mathrm{CH_2C\underline{H}_3}$), 1.48 (m, 2H, $\mathrm{CH_3C\underline{H}_2}$), 1.79 (m, 2H, $\mathrm{SeCH_2C\underline{H}_2}$), 2.38 (m, 4H, $\mathrm{Se(CH_2C\underline{H}_2)_2}$), 3.21 (t, J = 7.8 Hz, 2H, $\mathrm{SeC\underline{H}_2CH_2}$), 3.37 (m, 2H, $\mathrm{Se(C\underline{H}_2CH_2)_2}$), 3.63 (m, 2H, $\mathrm{Se(C\underline{H}_2CH_2)_2}$). ^{13}C NMR (100 MHz, *d*-chloroform) δ 13.4 ($\mathrm{CH_2\underline{C}H_3}$), 22.5 ($\mathrm{CH_3\underline{C}H_2}$), 28.0 ($\mathrm{SeCH_2\underline{C}H_2}$), 31.1 ($\mathrm{Se(CH_2\underline{C}H_2)_2}$), 40.2 ($\mathrm{Se\underline{C}H_2CH_2}$), 42.7 ($J_{\mathrm{CSe}}$ = 49 Hz, $\mathrm{Se(\underline{C}H_2CH_2)_2}$), 119.9 (q, J_{CF} = 321 Hz, $\mathrm{N(SO_2\underline{C}F_3)_2}$). ^{19}F NMR (376 MHz, *d*-chloroform) δ −78.9 ($\mathrm{N(SO_2C\underline{F}_3)_2}$). ^{77}Se NMR (76 MHz, *d*-chloroform) δ 416.3. Found HR-MS (ESI) m/z: 193.0489 (100), 191.0498 (40), 189.0515 (20), 195.0490 (15), 190.0525 (12), 192.0531 (10), 194.0523 (6), ([bse], $\mathrm{C_8H_{17}{}^{76/77/78/80/82}Se^+}$ requires m/z: 193.0490 (100), 191.0498 (48), 189.0517 (19), 195.0492 (18), 190.0524 (15), 194.0524 (9), 192.0531 (4); 668.0164 (30), 670.0157 (3), ($\mathrm{[bse]_2[N(SO_2CF_3)_2]}$, $\mathrm{C_{18}H_{34}F_6NO_4S_2{}^{80/82}Se_2^+}$ requires m/z: 668.0160 (35) and $\mathrm{C_{18}H_{34}F_6NO_4S_2{}^{82/82}Se_2^+}$ requires m/z: 670.0118 (3).

NMR spectra for the salts **2-8**, **10, S6, S11** and **S12**

S-Butylthiolanium *bis*(trifluoromethanesulfonyl)imide **2**

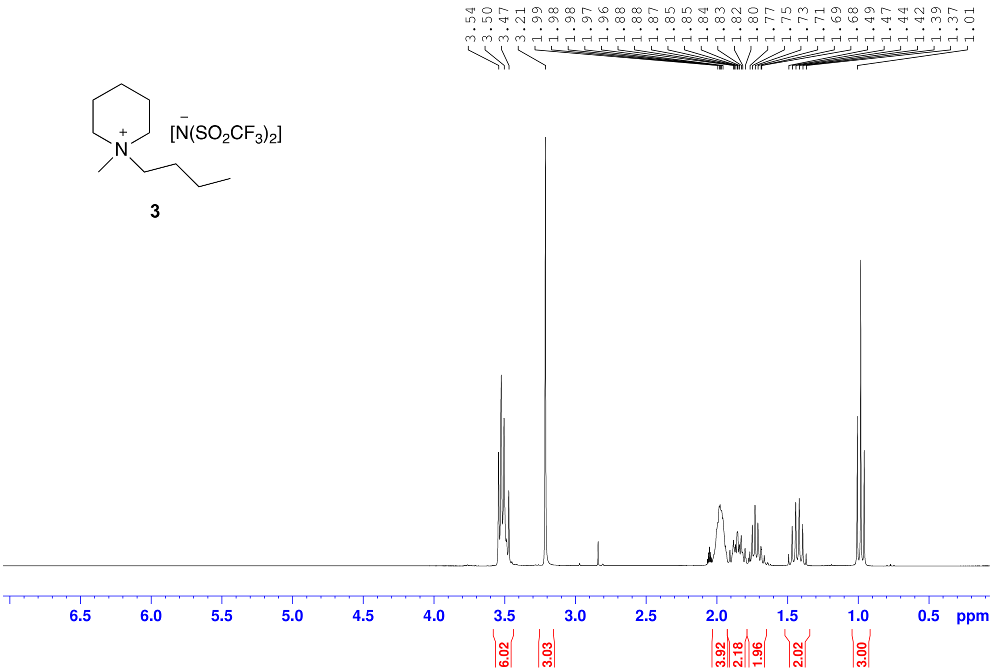
^{1}H (d_3-acetonitrile)



N.B. Water signal at δ2.15.

N-Butyl-*N*-methylpiperidinium *bis*(trifluoromethanesulfonyl)imide **3**

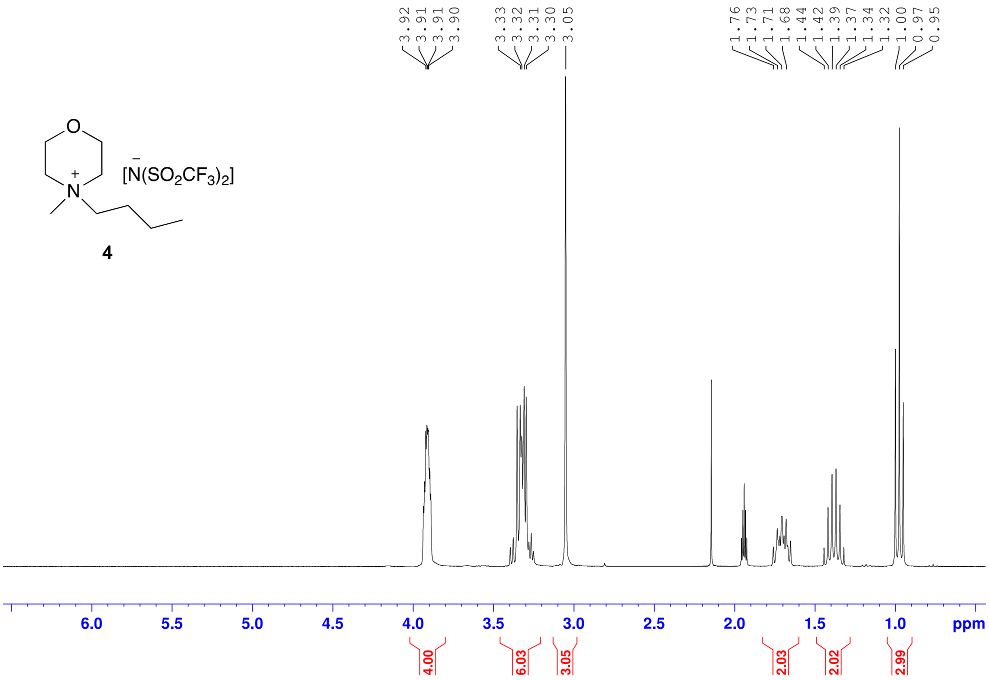
^{1}H (d_3-acetonitrile)



N.B. Water signal at δ2.80.

N-Butyl-*N*-methylmorpholinium *bis*(trifluoromethanesulfonyl)imide **4**

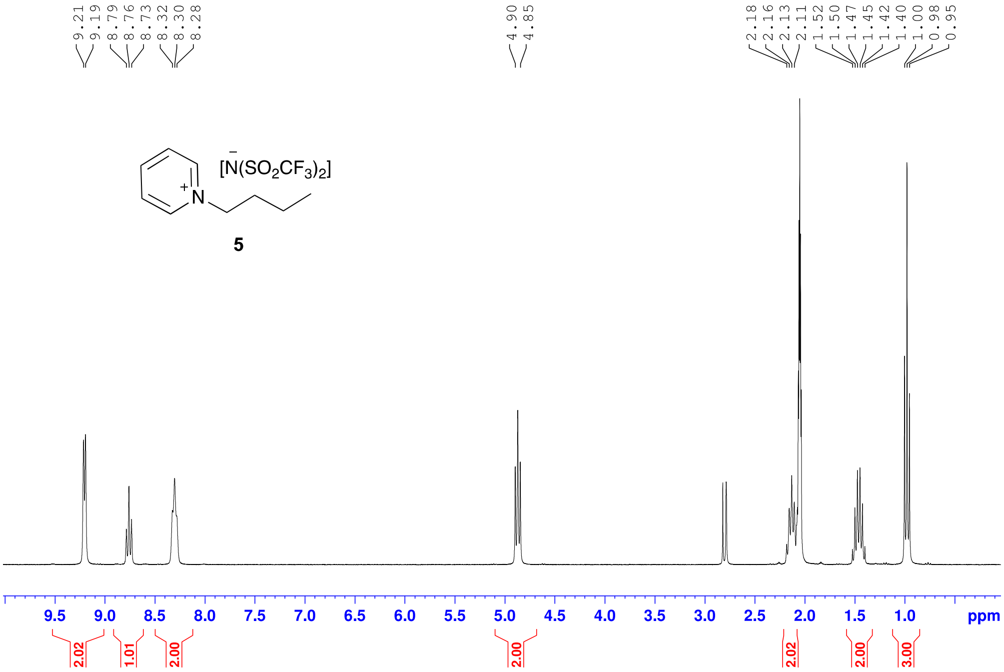
^{1}H (d_3-acetonitrile)



N.B. Water signal at δ 2.15.

N-Butylpyridinium *bis*(trifluoromethanesulfonyl)imide **5**

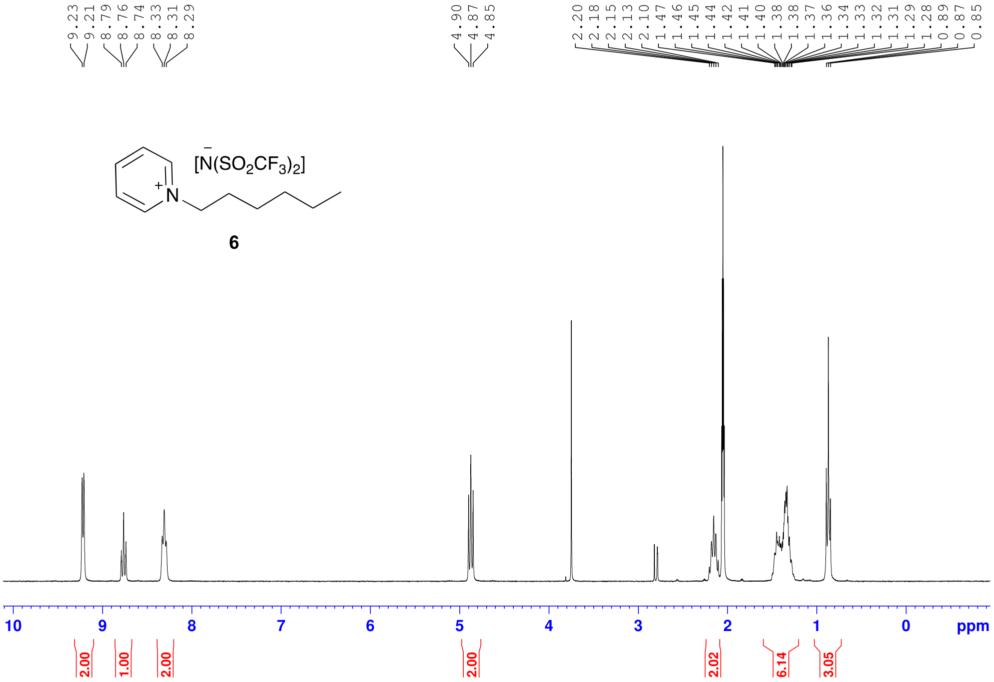
^{1}H (d_6-acetone)



N.B. Water and HOD signals at δ 2.8.

N-Hexylpyridinium *bis*(trifluoromethanesulfonyl)imide **6**

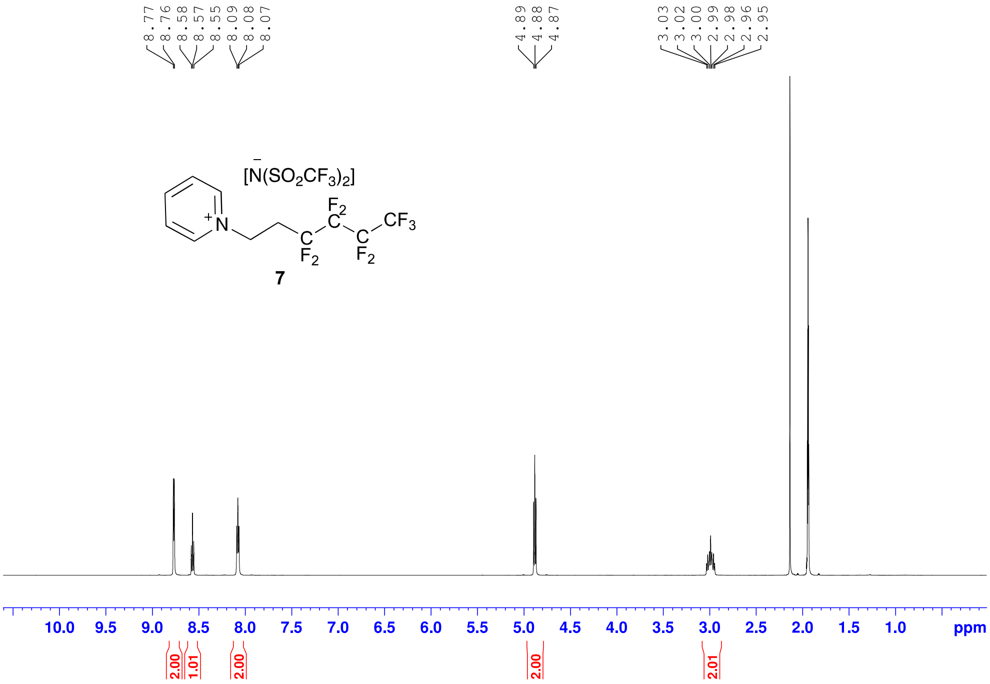
^{1}H (d_6-acetone)



N.B. Water and HOD signals at δ *ca*. 2.8 and 3.8.

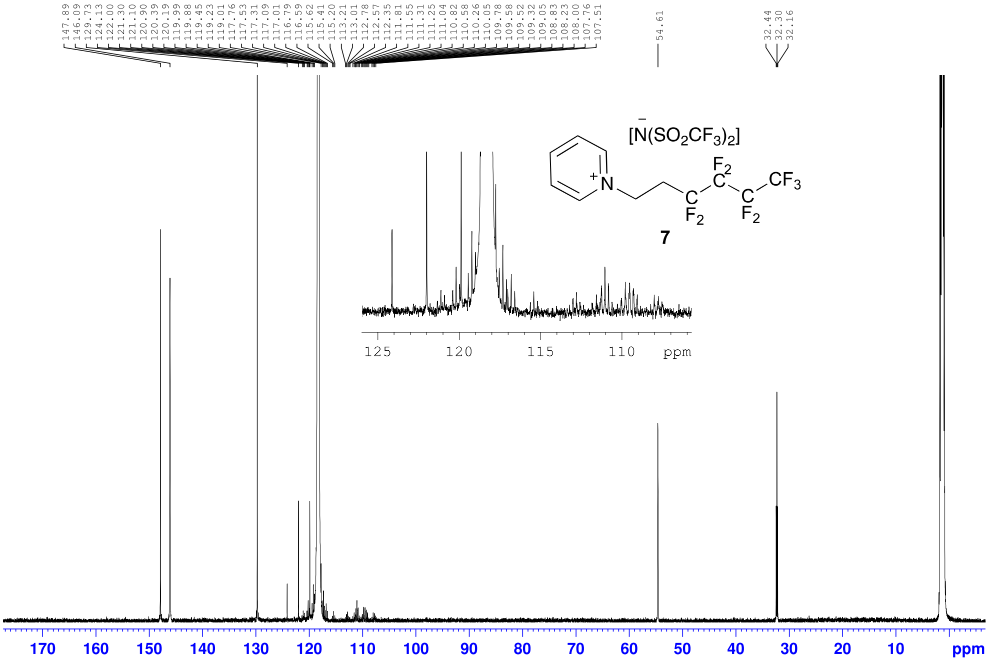
N-(3,3,4,4,5,5,6,6,6-Nonafluorohexyl)pyridinium *bis*(trifluoromethanesulfonyl)imide **7**

^{1}H (d_3-acetonitrile)

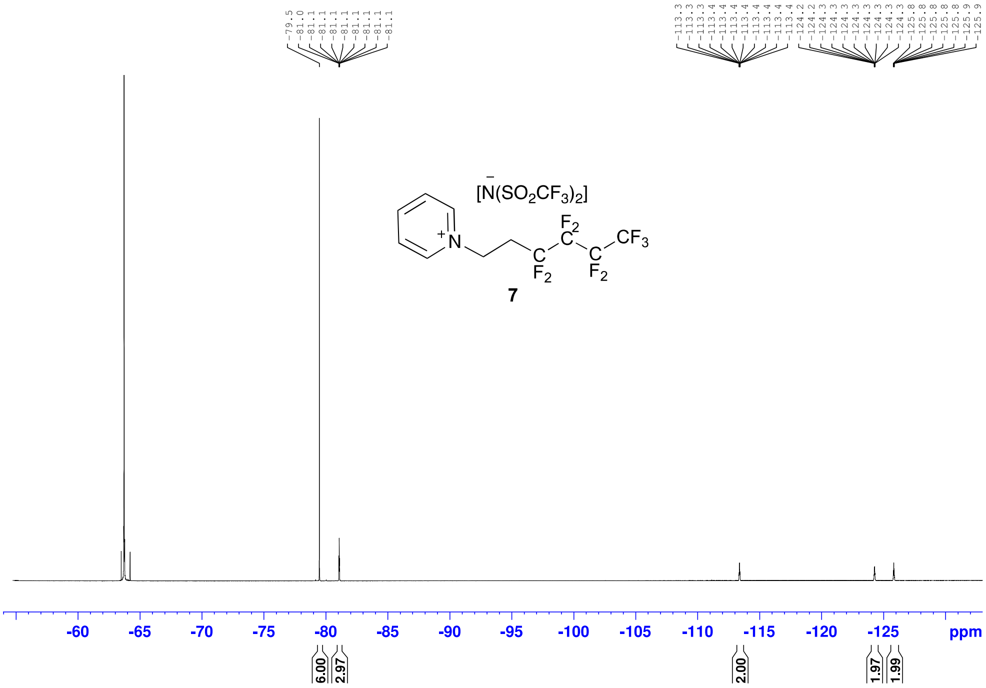


N.B. Water signal at δ *ca*. 2.15.

^{13}C (d_3-acetonitrile)



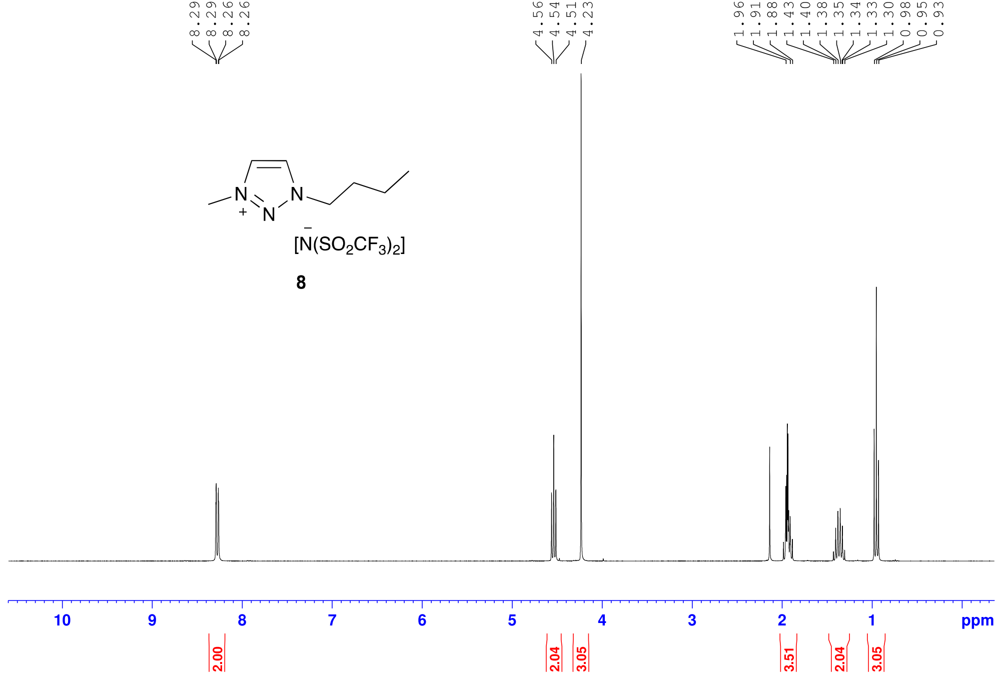
^{19}F (d_3-acetonitrile)



N.B. Externally referenced to α,α,α-trifluorotoluene at δ -63.72.

1-Butyl-3-methyl-1,2,3-triazolium *bis*(trifluoromethanesulfonyl)imide **8**

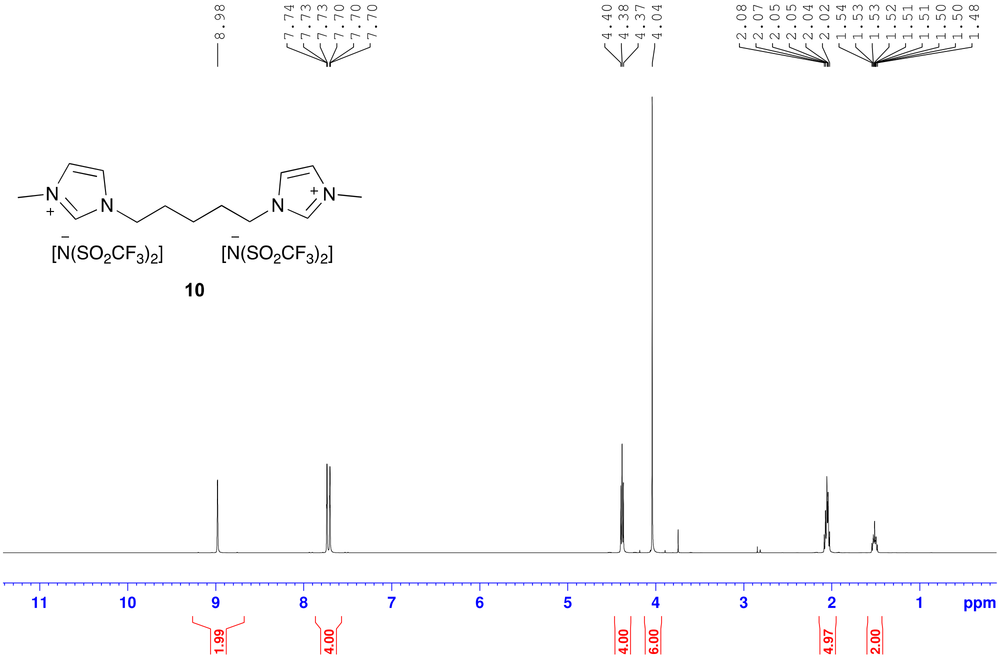
^{1}H (d_3-acetonitrile)



N.B. Water signal at δ *ca*. 2.15.

3,3'-(1,5-Pentane-diyl)-*bis*(1-methylimidazolium) *bis*(trifluoromethanesulfonyl)imide **10**

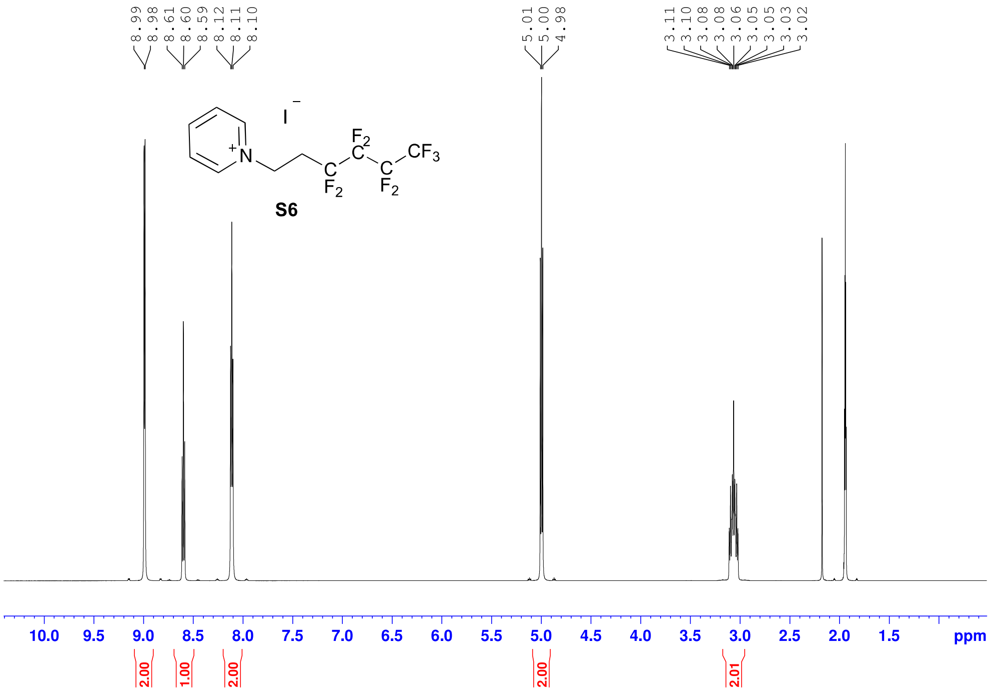
^{1}H (d_6-acetone)



N.B. Water and HOD signals at δ *ca*. 2.8 and 3.8.

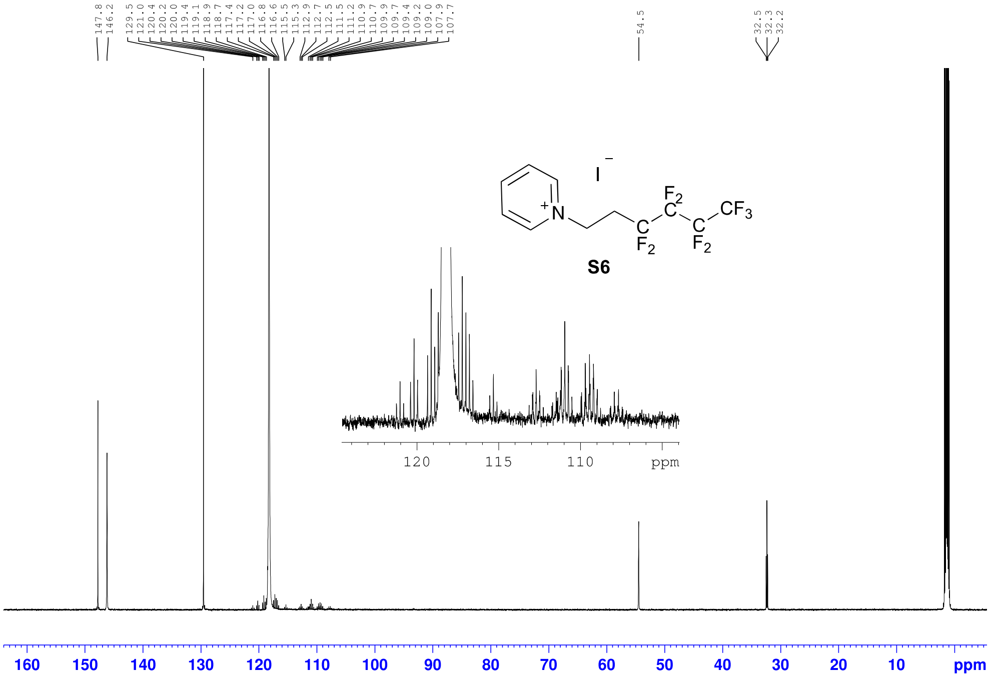
N-Nonafluorohexylpyridinium iodide **S6**

^{1}H (d_3-acetonitrile)

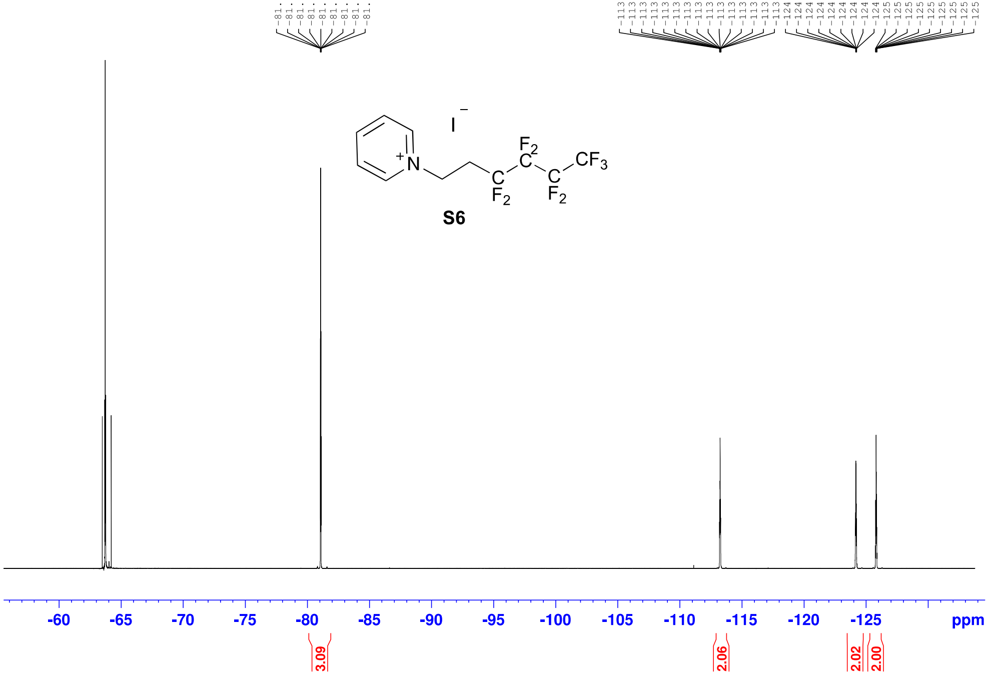


N.B. Water signal at δ *ca*. 2.15.

^{13}C (d_3-acetonitrile)



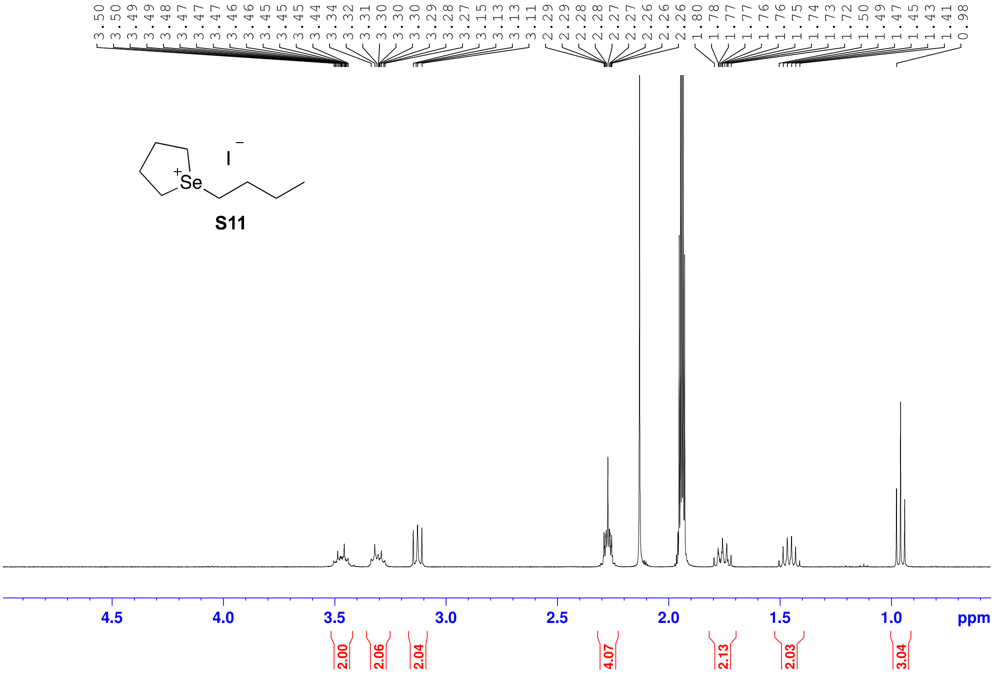
^{19}F (d_3-acetonitrile)



N.B. Externally referenced to α,α,α-trifluorotoluene at δ -63.72.

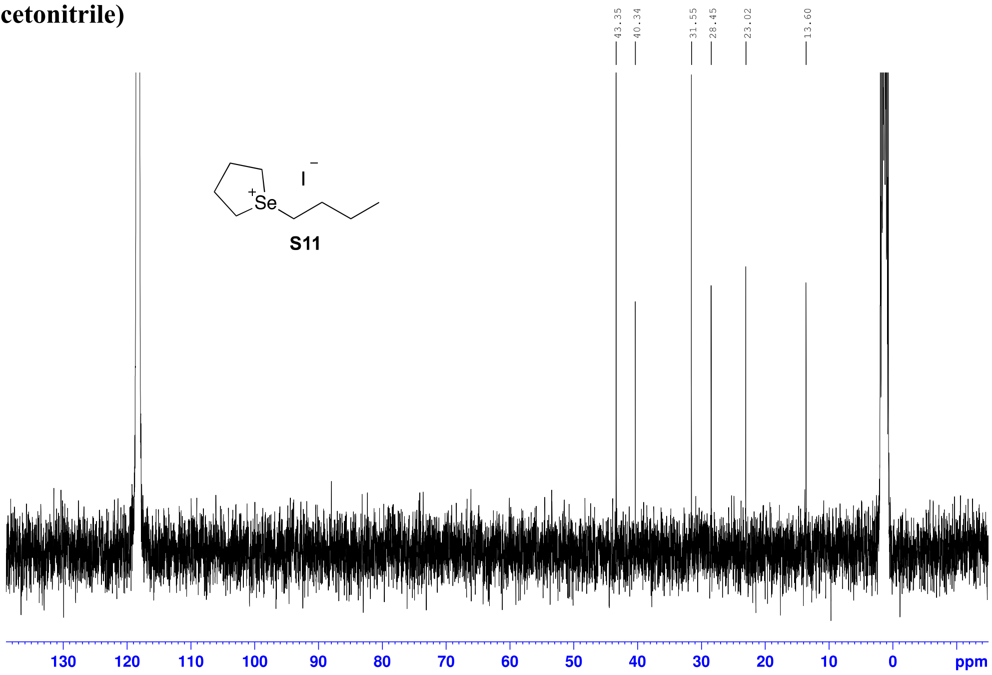
Se-Butylselenolanium iodide **S11**

^{1}H (d_3-acetonitrile)

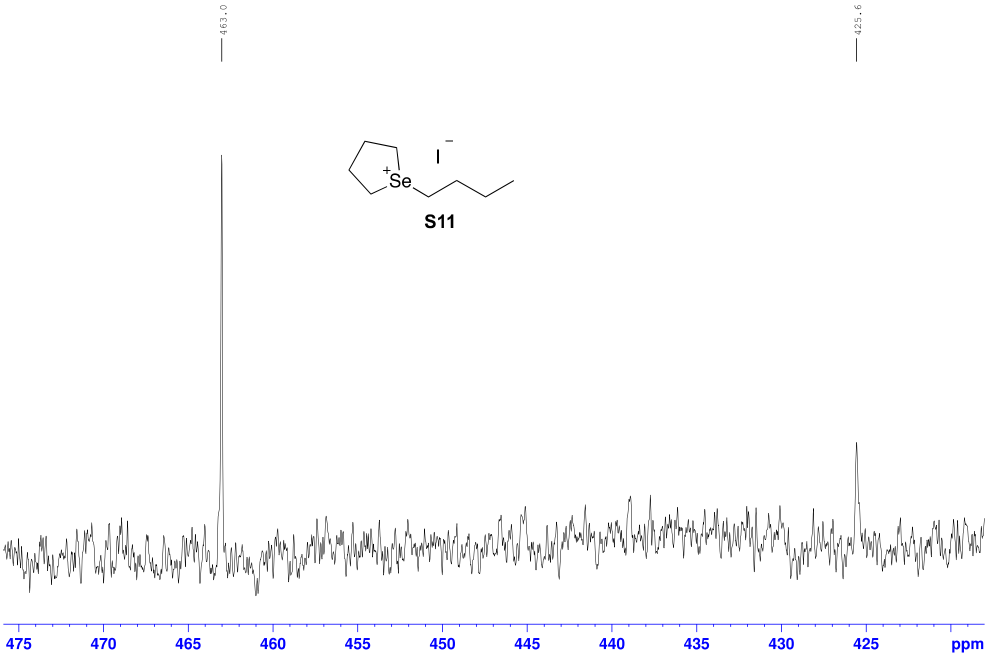


N.B. Water signal at δ *ca*. 2.15.

^{13}C (d_3-acetonitrile)



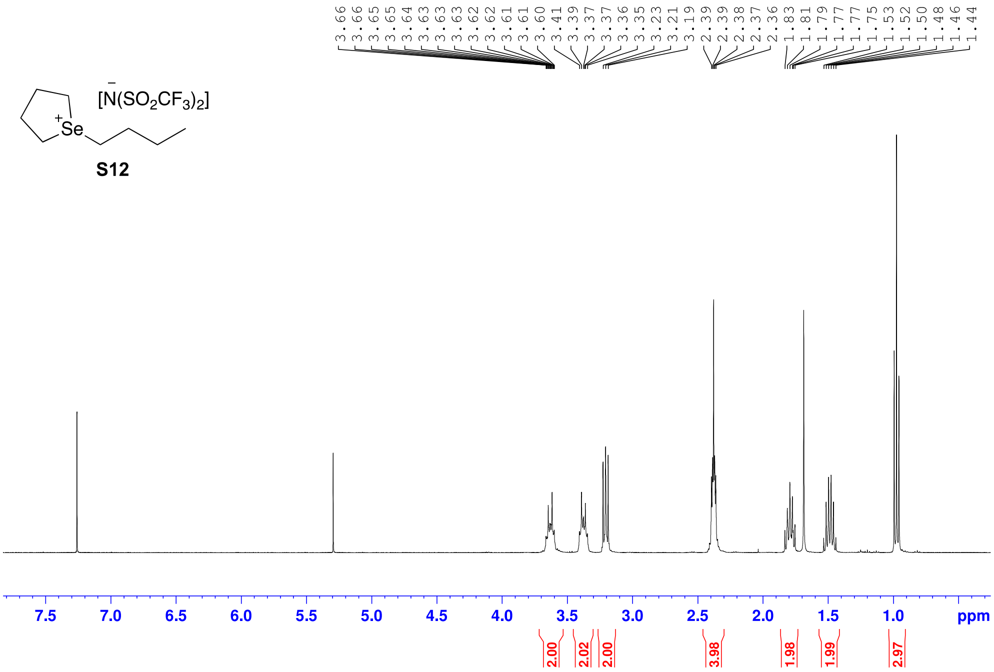
^{77}Se (*d*-chloroform)



N.B. Externally referenced to diphenyl diselenide in *d*-chloroform at δ 463.

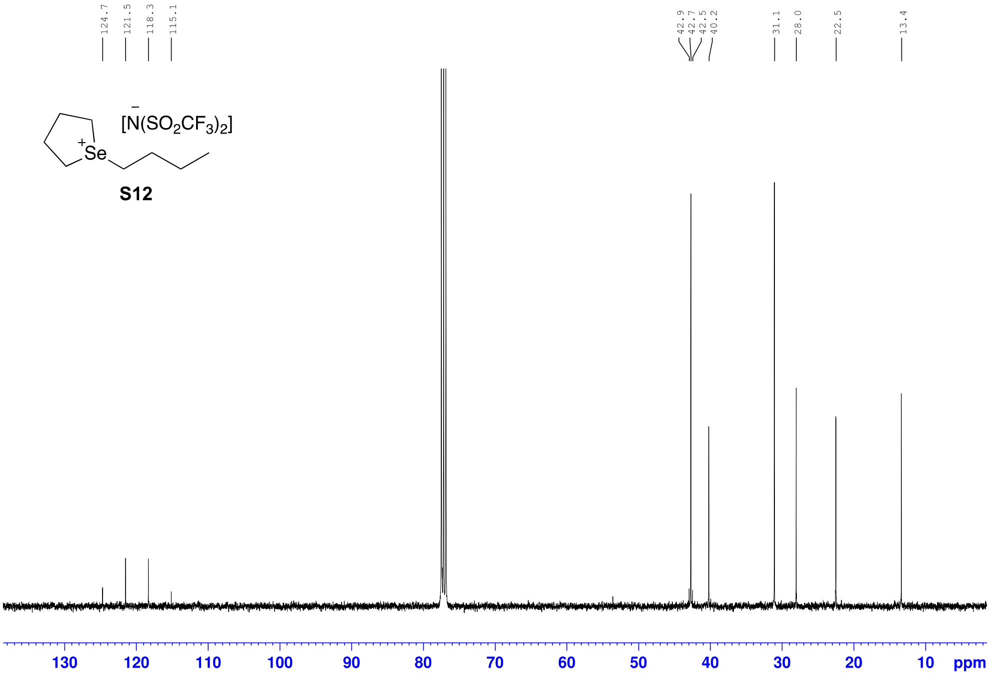
Se-Butylselenolanium *bis*(trifluoromethanesulfonyl)imide **S12**

^{1}H (*d*-chloroform)

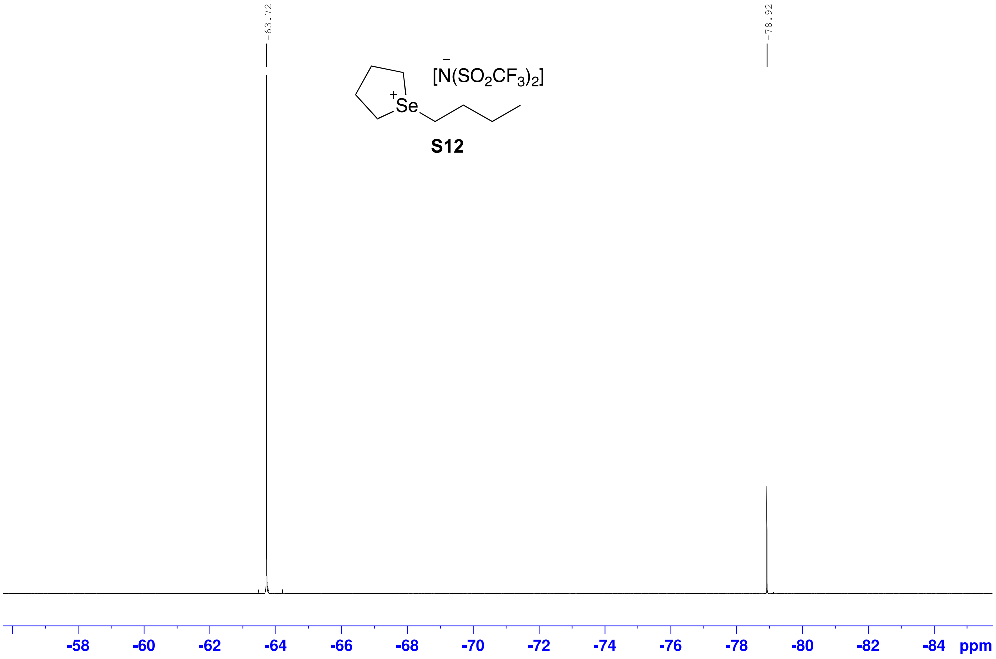


N.B. Solvent signals at *δ ca*. 1.7 and 5.3.

^{13}C (*d*-chloroform)

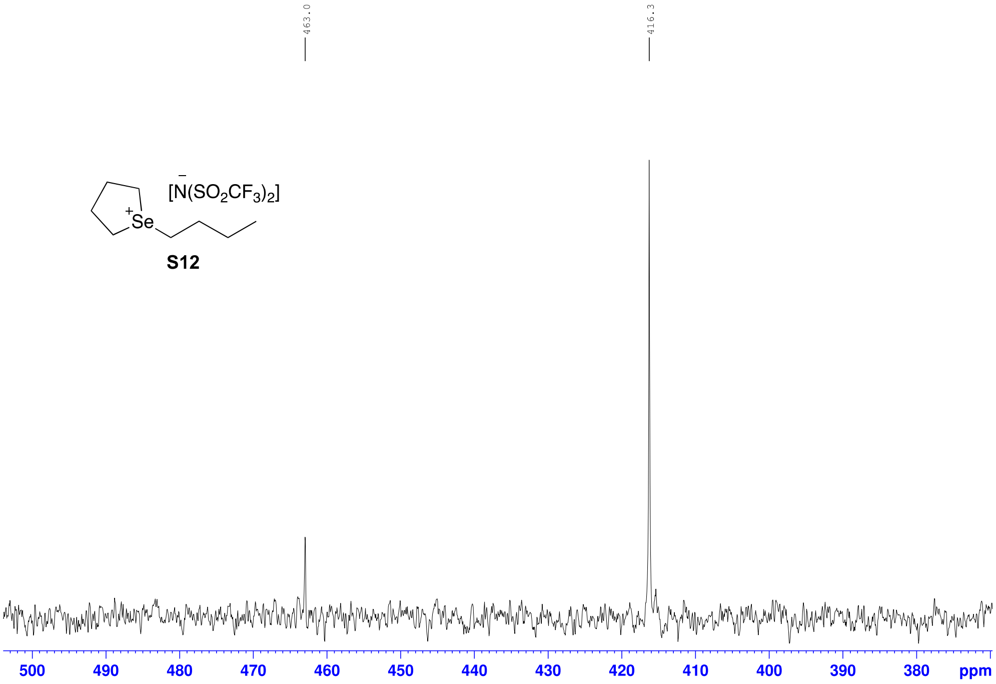


^{19}F (*d*-chloroform)



N.B. Externally referenced to neat α,α,α-trifluorotoluene at δ -63.72.

^{77}Se (*d*-chloroform)



N.B. Externally referenced to diphenyl diselenide in *d*-chloroform at δ 463.

Physicochemical properties of the ionic liquid **7**

Thermophysical properties of the ionic liquid [Fhpy][N(SO_2CF_3)$_2$] 7

Table S1. The glass transition, crystallisation, melting and decomposition temperatures for the salt **7** based on the data presented in Figures S1 and S2. The measurements were run in duplicate with uncertainties calculated as half the range presented to one significant figure.

Ionic liquid	**T_g / K**	**T_c / K**	**T_m / K**	**T_d / K**
[Fhpy][N(SO_2CF_3)$_2$] **7**	151 ± 1	270.0 ± 0.8	314.7 ± 0.2	678 ± 1

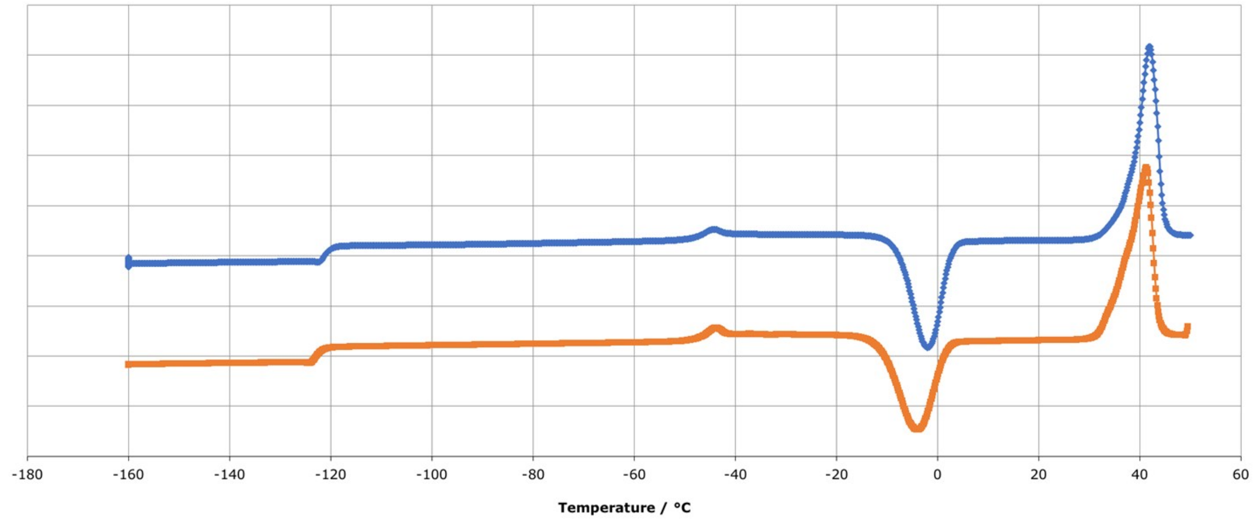


Figure S1. The differential scanning calorimetry traces of ionic liquid **7**.

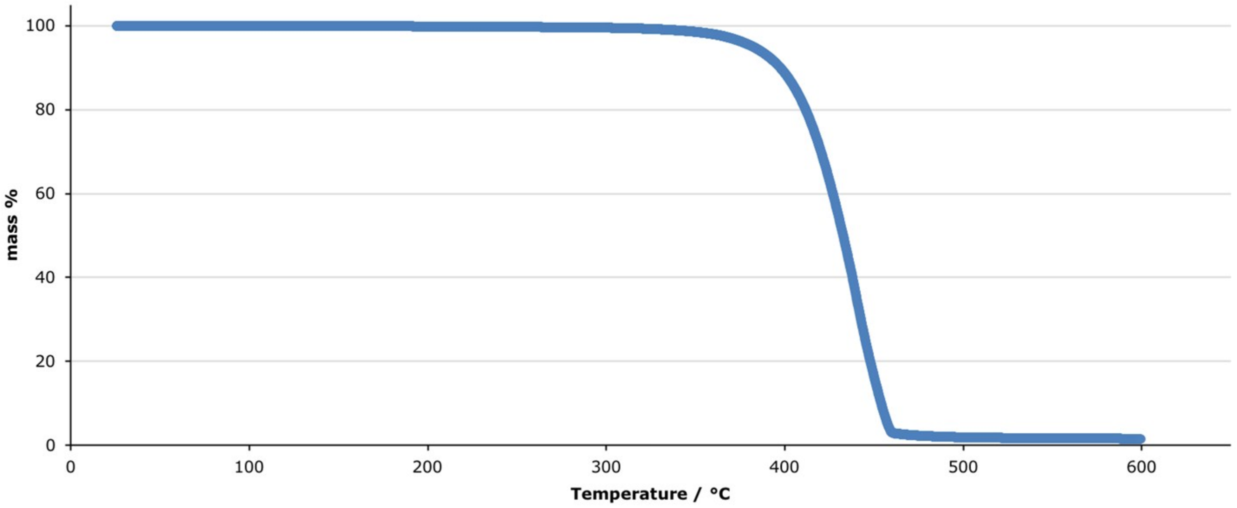


Figure S2. The thermogravimetric analysis trace of ionic liquid **7**, where the ionic liquid was ramped up to 600 °C.

Density and viscosity of ionic liquid [Fhpy][N(SO_2CF_3)$_2$] 7 at multiple temperatures

Table S2. The density and viscosity of ionic liquid **7** across a range of temperatures. Uncertainties reported are the standard deviation of triplicate measurements.

Temperature / °C	**Density / g cm^{-3}**	**Dynamic Viscosity / mPa s**
40.0	1.6800 ± 0.0001	355 ± 17
45.0	1.6742 ± 0.0001	259 ± 11
50.0	1.6686 ± 0.0003	200.8 ± 4.0
55.0	1.6627 ± 0.0004	152.9 ± 2.8
60.0	1.6569 ± 0.0003	118.9 ± 1.9
65.0	1.6511 ± 0.0003	92.2 ± 4.5
70.0	1.6453 ± 0.0003	75.7 ± 1.3

Solubility of ionic liquid [Fhpy][N(SO_2CF_3)$_2$] 7 in common solvents

To test the solubility of ionic liquid **7**, *ca.* 1 g was added to a 5 mL measuring cylinder, then the appropriate solvent (1 mL) was added. The measuring cylinder was inverted three times and the mixture was left to stand for 3 minutes. The appearance of the mixture (number of phases, relative volume of phases) was then noted. If the solid **7** did not dissolve to this point, another aliquot (3 mL) of solvent was added. The appearance of the mixture was then noted; results are presented in Table S3.

Table S3. The solubility of ionic liquid **7** in a variety of common solvents. The ratio for the partially soluble ionic liquid refers to the ratio of volumes of ionic liquid phase : molecular solvent phase.

Solvent	[Fhpy][N(SO_2CF_3)$_2$] **7**
water	insoluble
ethanol	soluble
acetone	soluble
dichloromethane	partially soluble (1: 2.5)
chloroform	partially soluble (1:5.3)
diethyl ether	partially soluble (1:3.3)
ethyl acetate	soluble
tetrahydrofuran	soluble
toluene	partially soluble (1:2.6)
hexane	insoluble

Details of the kinetic analyses

To determine the activation parameters for the reaction between benzyl bromide and pyridine in the ionic liquids **2**, **3**, **5**, **8** and **10**, standard solutions were prepared containing pyridine (*ca.* 0.4 g, 0.005 mol) dissolved in one of the salts **2**, **3**, **5**, **8** and **10** (total volume, 10 mL). For ionic liquids **4**, **6** and **7**, standard solutions were prepared containing pyridine (*ca.* 0.4 g, 0.005 mol) dissolved in a mixture of one of the salts **4**, **6** and **7** and acetonitrile (total volume, 10 mL). The probe in the NMR spectrometer was equilibrated to the desired temperature. Benzyl bromide (*ca.* 3.0 mg, 0.018 mmol) was added to an NMR tube followed by an aliquot of a standard solution (0.5 mL).

To determine the rate constants of the reaction between benzyl bromide and pyridine in mixtures containing different amounts of each of the ionic liquids **4** and **10**, standard solutions were prepared containing pyridine (*ca*. 0.08 g, 0.001 mol) and mixtures of acetonitrile dissolved and each of the ionic liquids **4** and **10** (total volume, 2 mL) at the desired mole fraction (see Tables S11-S12 for exact values). The probe in the NMR spectrometer was equilibrated to the desired temperature. Benzyl bromide (*ca.* 3.0 mg, 0.018 mmol) was added to an NMR tube followed by an aliquot of a standard solution (0.5 mL).

Reaction progress was followed using ^{1}H NMR spectroscopy to observe either the depletion of the signal due to the benzyl bromide at *ca.* δ 4.5 or the appearance of the signal due to the product at *ca.* δ 6.0. The pseudo first order rate constant and, using the concentration of pyridine, second order rate constant was determined from the change in integration of this signal. These data were used in an Eyring plot to calculate the activation parameters.

Eyring plots for the data shown in Table 1, main text

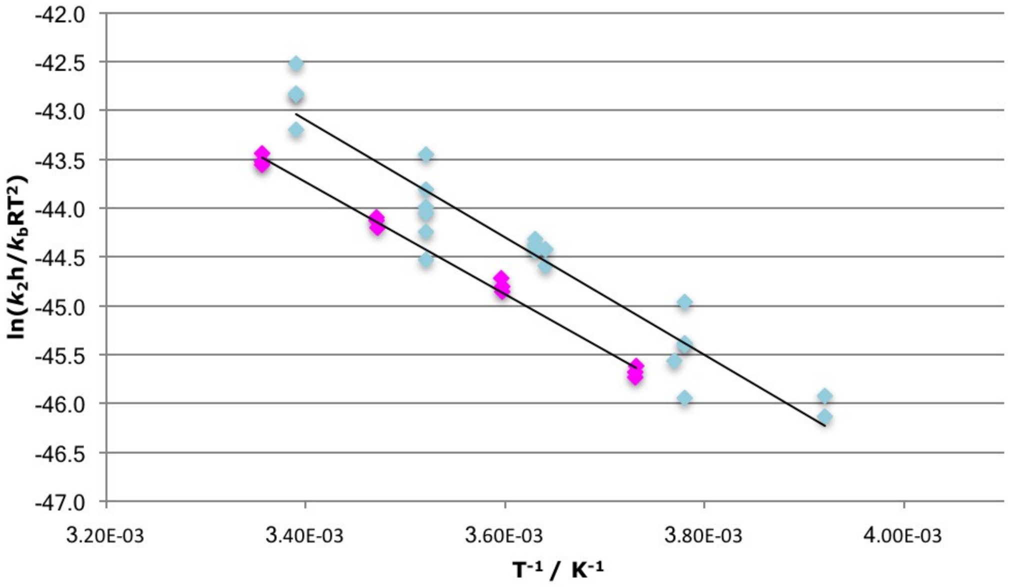


Figure S3. The Eyring plot for the reaction between benzyl bromide and pyridine (Scheme 1) in mixtures containing [btl][$N(SO_2CF_3)_2$] **2** (◆) at a mole fraction of *ca*. 0.85. Data for [bmpyr][$N(SO_2CF_3)_2$] **1** (◆) at a mole fraction of *ca*. 0.85 is shown here for comparison and is reproduced from Tanner *et al*.[10]

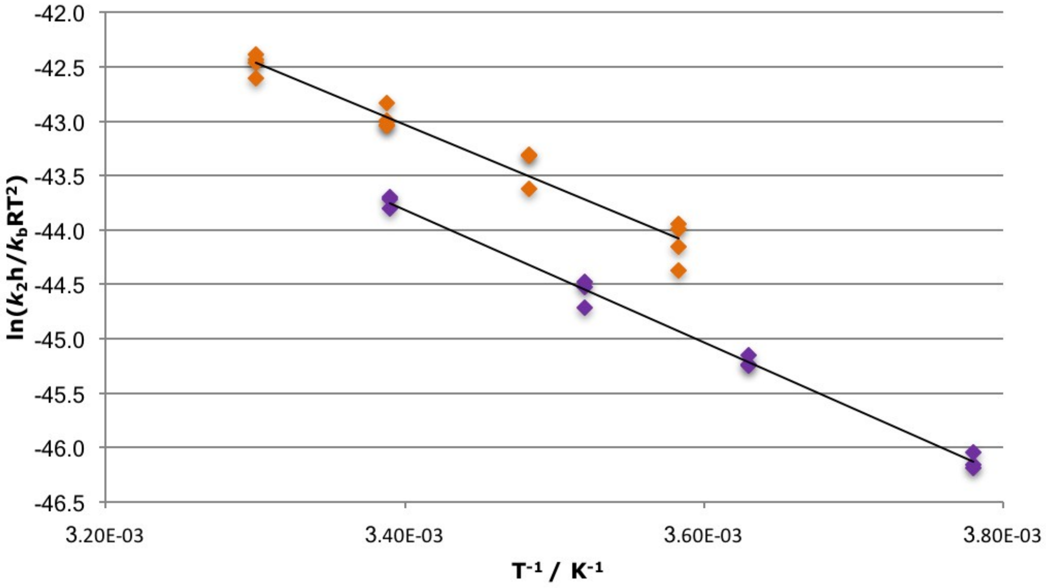


Figure S4. The Eyring plot for the reaction between benzyl bromide and pyridine (Scheme 1) in mixtures containing [bmpi][$N(SO_2CF_3)_2$] **3** (◆) and [bmmo][$N(SO_2CF_3)_2$] **4** (◆) at a mole fraction of *ca*. 0.85 and *ca.* 0.70, respectively.

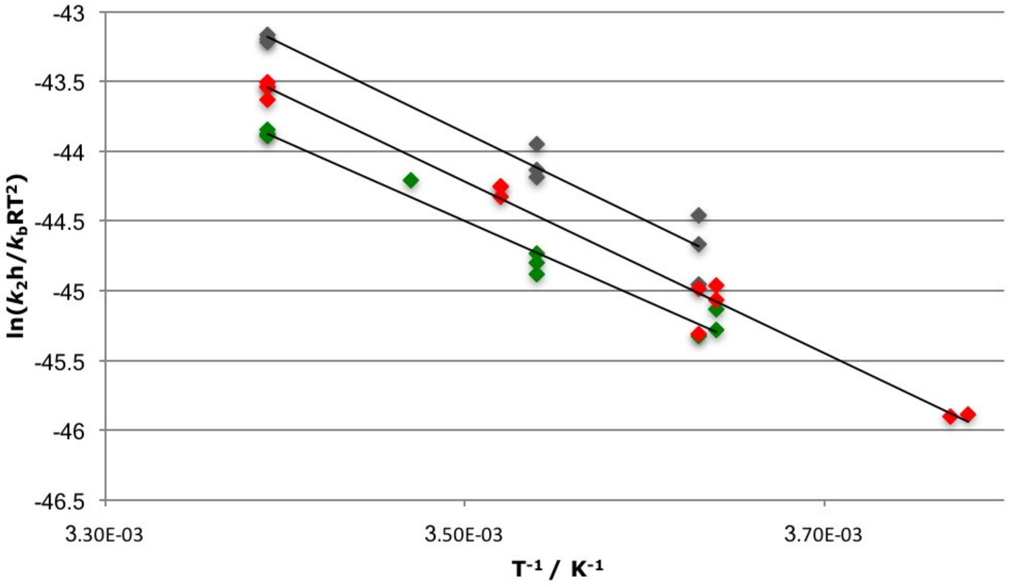


Figure S5. The Eyring plot for the reaction between benzyl bromide and pyridine (Scheme 1) in mixtures containing [bpy][$N(SO_2CF_3)_2$] **5** (◆), [hpy][$N(SO_2CF_3)_2$] **6** (◆) and [Fhpy][$N(SO_2CF_3)_2$] **6** (◆) at a mole fraction of either *ca.* 0.85 (ionic liquid **5**) or *ca.* 0.36 (ionic liquids **6** and **7**).

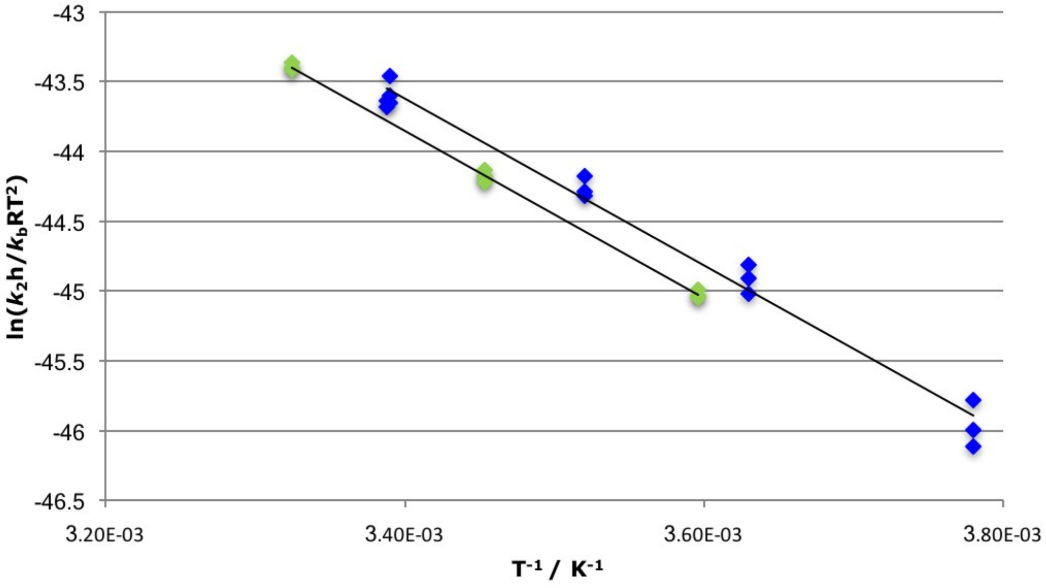


Figure S6. The Eyring plot for the reaction between benzyl bromide and pyridine (Scheme 1) in mixtures containing [bmtr][$N(SO_2CF_3)_2$] **8** (◆) at a mole fraction of *ca*. 0.85. Data for [bmim][$N(SO_2CF_3)_2$] **9** (◆) at a mole fraction of *ca*. 0.85 is shown here for comparison and is reproduced from Yau *et al.*[11]

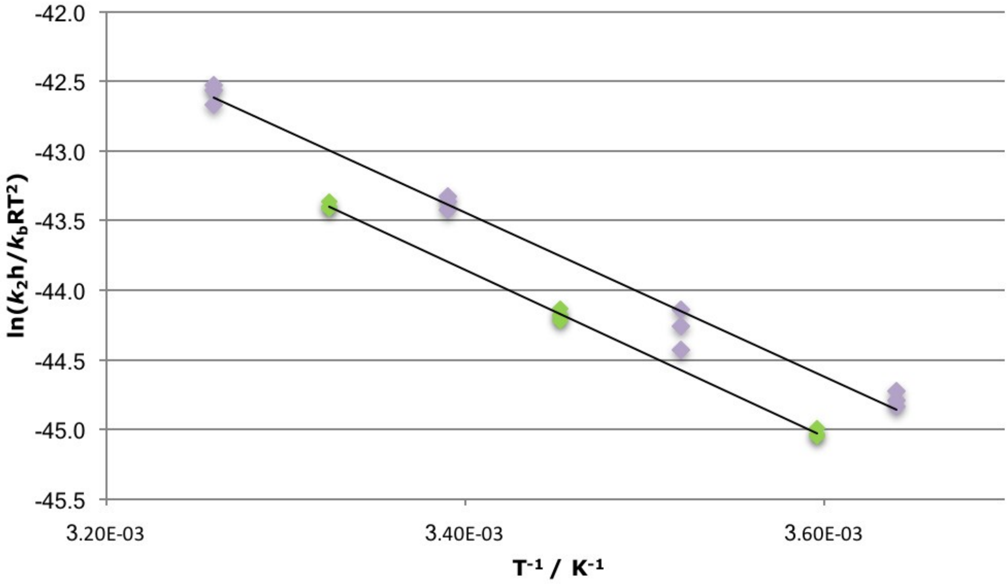


Figure S7. The Eyring plot for the reaction between benzyl bromide and pyridine (Scheme 1) in mixtures containing [p_e(mim)$_2$][N(SO$_2$CF$_3$)$_2$]$_2$ **10** (◆) at a mole fraction of *ca*. 0.85. Data for [bmim][N(SO$_2$CF$_3$)$_2$] **9** (◆) at a mole fraction of *ca*. 0.85 is shown here for comparison and is reproduced from Yau *et al*.[11]

Rate data for the Eyring plots shown in Figure **S3-S7**

Table S4. Masses used to prepare reaction mixtures, concentration of nucleophile in the reaction mixture, and rate constants for the reaction between benzyl bromide and pyridine (Scheme 1) in the ionic liquid [btl][N(SO_2CF_3)$_2$] **2**.

Masses				**Rate constants**	
IL / g	**Pyridine / g**	**[Pyridine] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
13.9	0.406	0.514	264.9	1.85	3.60
			264.9	0.697	1.37
			275.1	3.44	6.70
			275.1	2.89	5.63
			275.2	3.58	6.97
			284.1	6.72	13.1
			284.1	3.29	6.41
			284.1	4.36	8.48
			284.1	5.30	10.3
			295.1	19.3	37.6
			295.1	19.5	38.0
			295.2	26.5	51.6
13.9	0.412	0.520	254.9	0.656	1.28
			254.9	0.541	1.04
			264.9	1.22	2.36
			265.0	1.03	1.97
			264.9	1.20	2.31
			275.2	3.40	6.54
			275.2	3.87	7.44
			284.1	9.84	18.9
			284.1	5.72	11.0
			295.2	13.7	26.3

Table S5. Masses used to prepare reaction mixtures, concentration of nucleophile in the reaction mixture, and rate constants for the reaction between benzyl bromide and pyridine (Scheme 1) in the ionic liquid [bmpi][N(SO_2CF_3)$_2$] **3**.

Masses				**Rate constants**	
IL / g	**Pyridine / g**	**[Pyridine] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
13.2	0.410	0.518	264.9	0.550	1.06
			264.9	0.634	1.22
			264.9	0.566	1.09
			275.2	1.67	3.22
			275.3	1.52	2.94
			275.2	1.51	2.92
			284.2	3.33	6.42
			284.1	2.76	5.32
			284.1	3.49	6.75
			295.3	7.75	15.0
			295.2	7.90	15.3

Table S6. Masses used to prepare reaction mixtures, concentration of nucleophile in the reaction mixture, and rate constants for the reaction between benzyl bromide and pyridine (Scheme 1) in the ionic liquid [bmmo][N(SO_2CF_3)$_2$] **4**.

Masses					**Rate constants**	
IL / g	**CD_3CN / g**	**Pyridine / g**	**[Pyridine] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
2.68	0.0928	0.0392	0.496	287.1		21.9
				295.2		32.1
				295.2		31.0
2.68	0.0915	0.0404	0.511	279.1		11.1
2.70	0.0906	0.0398	0.503	287.1		16.2
				287.1		22.2
				303.0		57.7
2.67	0.0928	0.0408	0.516	303.0		62.3
2.67	0.0895	0.0416	0.526	279.1		7.23
				303.0		49.8
2.65	0.103	0.0393	0.497	279.1		10.6
				279.1		8.97
				295.2		37.6
2.68	0.0916	0.0392	0.496	295.2		30.6
				303.0		59.2

Table S7. Masses used to prepare reaction mixtures, concentration of nucleophile in the reaction mixture, and rate constants for the reaction between benzyl bromide and pyridine (Scheme 1) in the ionic liquid [bpy][$N(SO_2CF_3)_2$] **5**.

Masses				**Rate constants**	
IL / g	**Pyridine / g**	**[Pyridine] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
13.8	0.455	0.575	265.0	0.811	1.41
			264.9	0.820	1.43
			275.1	2.24	3.89
			275.2	2.19	3.82
			275.1	2.01	3.51
			275.2	1.58	2.75
			284.1	4.85	8.44
			284.1	4.51	7.84
			284.1	4.84	8.41
			295.1	10.7	18.6
			295.1	9.71	16.9
			295.2	11.0	19.2
			295.1	10.7	18.5

Table S8. Masses used to prepare reaction mixtures, concentration of nucleophile in the reaction mixture, and rate constants for the reaction between benzyl bromide and pyridine (Scheme 1) in the ionic liquid [hpy][$N(SO_2CF_3)_2$] **6**.

Masses					**Rate constants**	
IL / g	**CD_3CN / g**	**Pyridine / g**	**[Pyridine] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
10.5	1.60	0.442	0.559	275.2	1.52	2.72
				275.1	1.84	3.29
				275.1	1.59	2.84
				282.3	2.49	4.45
				282.3	2.88	5.16
				282.3	2.69	4.82
				288.6	5.10	9.13
				295.2	7.31	13.1
				295.2	7.41	13.3
				295.2	7.65	13.7
2.10	0.321	0.0873	0.552	288.6	4.40	7.97
				288.7	4.95	8.97

Table S9. Masses used to prepare reaction mixtures, concentration of nucleophile in the reaction mixture, and rate constants for the reaction between benzyl bromide and pyridine (Scheme 1) in the ionic liquid [Fhpy][N(SO_2CF_3)$_2$] **7**.

Masses					Rate constants	
IL / g	**CD_3CN / g**	**Pyridine / g**	**[Pyridine] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
6.38	0.560	0.450	1.14	275.2	7.33	6.44
				275.2	5.94	5.22
				275.2	4.46	3.92
				282.3	10.7	9.37
				282.3	12.8	11.3
				282.3	10.1	8.91
				295.2	30.8	27.1
				295.2	29.2	25.7
				295.2	29.8	26.2

Table S10. Masses used to prepare reaction mixtures, concentration of nucleophile in the reaction mixture, and rate constants for the reaction between benzyl bromide and pyridine (Scheme 1) in the ionic liquid [bmtr][N(SO_2CF_3)$_2$] **8**.

Masses				Rate constants	
IL / g	**Pyridine / g**	**[Pyridine] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
14.0	0.418	0.528	264.9	0.841	1.59
			264.9	0.601	1.14
			264.9	0.676	1.28
			275.2	1.95	3.69
			275.2	2.39	4.52
			275.2	2.17	4.10
			284.1	4.19	7.93
			284.1	4.18	8.12
			284.2	4.82	9.11
			295.1	9.23	17.5
			295.2	10.6	20.1
			295.2	8.79	16.6
			295.2	8.30	16.1
			295.2	8.67	16.8

Table S11. Masses used to prepare reaction mixtures, concentration of nucleophile in the reaction mixture, and rate constants for the reaction between benzyl bromide and pyridine (Scheme 1) in the ionic liquid $[p_e(mim)_2][N(SO_2CF_3)_2]_2$ **10**.

Masses				**Rate constants**	
IL / g	**Pyridine / g**	**[Pyridine] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
14.9	0.408	0.515	275.1	2.28	4.43
			275.1	2.38	4.63
			275.1	2.55	4.95
			284.1	3.66	7.10
			284.1	4.34	8.41
			284.1	4.88	9.47
			295.2	11.9	23.1
			295.2	11.4	22.1
			295.2	10.8	20.9
			306.3	28.4	55.0
			306.3	24.7	47.9
			306.3	27.3	53.0

Rate data for the mole fraction dependence plot shown in Figure 3, main text

Table S12. Masses used to prepare reaction mixtures, mole fraction of ionic liquid and concentrations of nucleophile in the reaction mixture, and rate constants for the reaction between benzyl bromide and pyridine (Scheme 1) in mixtures containing [bmmo][N(SO$_2$CF$_3$)$_2$] **4** at 295.2 K.

	Masses				**Rate constants**	
χ_{IL}	**IL / g**	**CD$_3$CN / g**	**Pyridine / g**	**[Pyridine] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
0.040	0.528	1.24	0.0606	0.383	3.99	10.4
					3.86	10.1
					3.80	9.92
0.104	1.14	0.960	0.0602	0.381	5.52	14.5
					5.65	14.8
					5.91	15.5
0.145	1.41	0.801	0.0621	0.393	6.78	17.3
					6.48	16.5
					6.88	17.5
0.204	1.71	0.637	0.0631	0.399	8.33	20.9
					8.37	21.0
					8.18	20.5
0.309	2.08	0.443	0.0430	0.272	6.93	25.5
					6.63	24.4
					6.68	24.6
0.401	2.28	0.320	0.0402	0.254	7.30	28.7
					7.21	28.4
					7.17	28.2
0.490	2.43	0.230	0.0432	0.273	7.80	28.6
					8.34	30.5
					8.08	29.6
0.600	2.58	0.150	0.0399	0.252	8.24	32.7
					7.64	30.3
					7.99	31.7
0.702	2.68	0.0928	0.0392	0.248	7.96	32.1
					7.69	31.0

Table S13. Masses used to prepare reaction mixtures, mole fraction of ionic liquid and concentrations of nucleophile in the reaction mixture, and rate constants for the reaction between benzyl bromide and pyridine (Scheme 1) in mixtures containing $[p_e(mim)_2][N(SO_2CF_3)_2]_2$ **10** at 295.2 K.

	Masses				**Rate constants**	
χ_{IL}	**IL / g**	**CD_3CN / g**	**Pyridine / g**	**[Pyridine] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
0.019	0.478	1.34	0.0800	0.506	5.01	9.92
					5.35	10.6
					5.60	11.1
0.047	0.989	1.06	0.0838	0.530	7.12	13.4
					6.99	13.2
					5.81	11.0
0.102	1.62	0.748	0.0812	0.513	8.26	16.1
					10.3	20.0
					8.68	16.9
0.194	2.14	0.449	0.0818	0.517	10.5	20.2
					8.02	15.5
					9.38	18.1
0.296	2.47	0.280	0.0819	0.518	9.25	17.9
					12.3	23.8
					12.0	23.2
0.357	2.59	0.214	0.0814	0.515	13.0	25.2
					10.4	20.1
					10.2	19.8
0.446	2.71	0.140	0.0844	0.534	9.45	17.7
					10.9	20.4
					12.5	23.4
0.525	2.81	0.0949	0.0824	0.521	11.5	22.0
					12.0	23.0
					12.2	23.4
0.591	2.88	0.0622	0.0871	0.551	11.7	21.3
					14.2	25.7
					13.4	24.4
0.677	2.91	0.0294	0.0852	0.539	12.1	22.5
					15.0	27.8
0.783	14.8	0	0.408	0.515	12.2	23.7
					12.0	23.2
					12.3	23.9

Characteristics determining the 'overall best' ionic liquid for the reaction

Table S14. Stability, cost analysis and qualitative discussion of ease of synthesis of the ionic liquids **2**, **4**, **7** or **10**. Blocks highlighted in red indicate a feature which significantly limits the applicability of the ionic liquid.

Ionic liquid	Stability	Cost / \$AUD g^{-1} [a]	Ease of synthesis[b]
[btl][$N(SO_2CF_3)_2$] **2**	Reacts with pyridine[c]	4.20	Starting material is volatile sulphur containing species with strong odour; difficult to work with
[bmmo][$N(SO_2CF_3)_2$] **4**	T_d = 671 K[4]	3.72	-
[Fhpy][$N(SO_2CF_3)_2$] **7**	T_d = 678 K	13.5	Perfluorinated starting material has reduced reactivity, making preparation slow and difficult
[$p_e(mim)_2$][$N(SO_2CF_3)_2$]$_2$ **10**	T_d = 638 K[12]	4.36	-

[a] Cost analysis for the ionic liquids was determined based on materials purchased from Sigma-Aldrich. [b] Whilst this is a subjective term, highlighted are problems that make preparation of the ionic liquid difficult. [c] Even given this reactivity, this ionic liquid has a markedly lower decomposition temperature (T_d = 553 K[3]) than the others listed.

Normalised mole fraction dependence plots for ionic liquids **9** and **10**

Ionic liquid **10** had a higher rate constant across the range of mole fractions examined than ionic liquid **9** (see Figure 3, main text). This effect is likely due to greater interaction of pyridine with the cation of the ionic liquid **10**, perhaps due to some level of cooperatively between charged centres, but it is unclear the exact nature of those interactions. As ionic liquid **10** has two charged centres, it is possible for those centres to act either independently (*i.e.* behave as 'double' the amount of a mono-cationic ionic liquid) or dependently (*i.e.* the nature of an interaction between pyridine and one of the imidazolium moieties effects the interaction of the other imidazolium moiety, either with the same pyridine or another). By normalising the mole fraction dependence plot (Figure 3) using Equation S1, where χ_{IL} is the rate constant at the mole fraction of ionic liquid, χ_0 is the rate constant at without any ionic liquid present and χ_{HIGH} is the extreme of rate enhancement seen for salt **9**, the nature of the interactions can be investigated.

$$(S1) \qquad Normalised\ rate\ constant = \frac{\chi_{IL} - \chi_0}{\chi_{HIGH} - \chi_0}$$

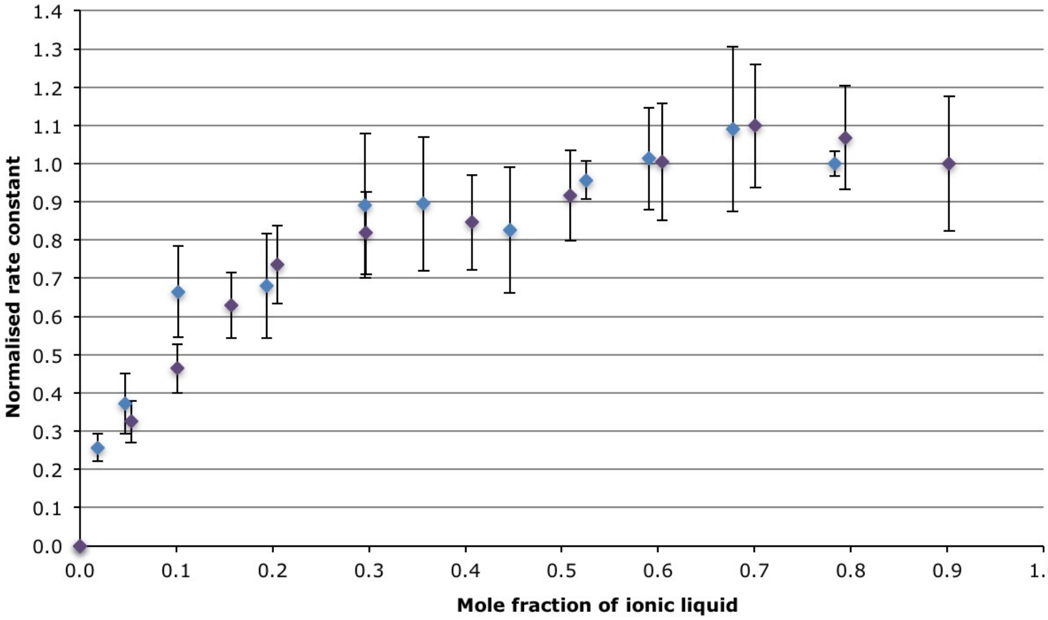


Figure S8. The rate constants for the reaction between benzyl bromide and pyridine in varying proportions of ionic liquids **9** (◆) and **10** (◆), normalised to the lowest and highest mole fraction as shown in Equation S1.

Immediately both the trends in the mole fraction dependence of the rate constant for the reaction shown in Scheme 1, main text, are similar in ionic liquids **9** and **10**, which suggests that the interactions of the cations with pyridine in both these cases are similar. Looking at the region below $\chi = 0.2$ the effect of the ionic liquid **10** might be considered to be greater than that for ionic liquid **9**, which may suggest that the charged centres are behaving independently (so the effect of salt **10** is the same as if twice the amount of ionic liquid **9** were used). However, it is difficult to make such comparisons given the uncertainties.

To examine this feature further the mole fraction of positively charged centres in solution was calculated (Equation S3) from the mole fractions of ionic liquid **10** examined. If you consider the calculation for mole fraction (Equation S2) where IL is the amount of ionic liquid and Z is the amount of everything else present. Then if there are two charged species, the updated mole fraction can be calculated through Equation S3. The updated mole fraction dependence for ionic liquid **10** is compared with ionic liquid **9** in Figure S9.

$$(S2) \qquad Mole\ fraction\ of\ ionic\ liquid\ (\chi_{IL}) = \frac{IL}{IL + Z}$$

$$(S3) \qquad Mole\ fraction\ of\ charged\ species = \frac{2\,\chi_{IL}}{2\,\chi_{IL} + \chi_{Z}}$$

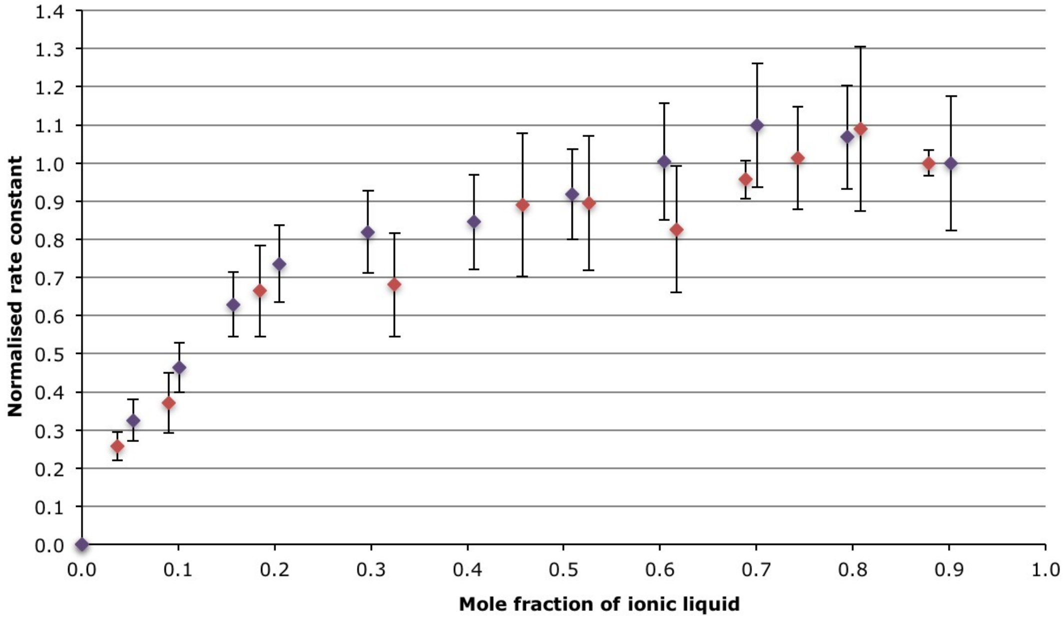


Figure S9. The rate constants for the reaction between benzyl bromide and pyridine in varying proportions of ionic liquids **9** (◆) and proportions of charged species in the cation of ionic liquid **10** (◆), normalised to the lowest and highest mole fraction as shown in Equation S3.

The shape of the mole fraction dependence of the rate constant for the reaction shown in Scheme 1, main text in the two ionic liquids **9** and **10** (Figure S9) are again, very similar, and the anomalies noted above are not present. This outcome would suggest that there is not any difference between the interactions of the charged centre of the ionic liquids with pyridine whether the cation has two imidazolium moieties or not. However, the enhanced rate constant over all the mole fractions of ionic liquid examined would suggest some level of cooperativity. Otherwise it would be expected, that both ionic liquids **9** and **10** would have very similar rate constants.

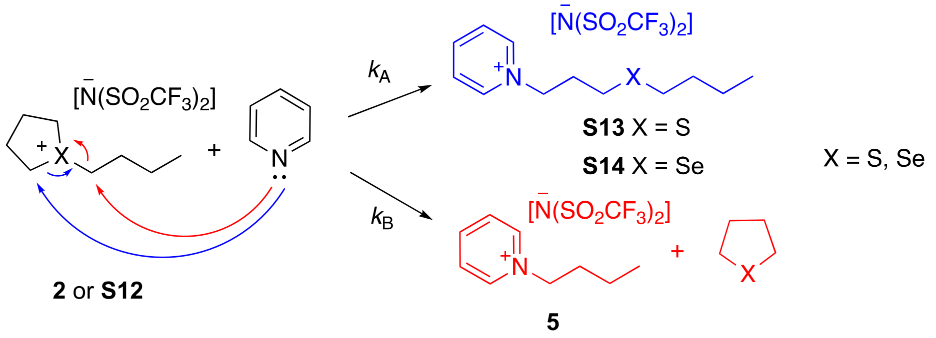
Details for the decomposition of salts **2** and **S12** with pyridine

To determine the rate constants for the reactions between each of the ionic liquids **2** and **S12** and pyridine, standard solutions were prepared containing pyridine (*ca.* 0.04 g, 0.5 mmol) dissolved in mixtures containing one of the ionic liquids **2** and **S12** (*ca.* 0.65 g, 1.5 mmol) in acetonitrile (total volume 1 mL). To compare the rate constant for the reaction between ionic liquid **2** and pyridine and the rate constant for the reaction between benzyl bromide and pyridine in the ionic liquid **2**, a standard solution was prepared containing pyridine (*ca.* 0.04 g, 0.5 mmol) dissolved in ionic liquid **2** up to a total volume of 1 mL. Masses, mole fractions and concentrations of reagents are presented in Table S15.

Table S15. Masses used, mole fractions and concentrations of reagents in the reaction mixture for the reaction between pyridine and either [btl][N(SO$_2$CF$_3$)$_2$] **2** or [bse][N(SO$_2$CF$_3$)$_2$] **S12** at 298 K.

Ionic liquid	χ_{IL}	**Masses**			**Concentrations**	
		IL / g	**Py / g**	**CD$_3$CN / g**	**[IL] / mol L^{-1}**	**[Py] / mol L^{-1}**
S12	0.12	0.692	0.0417	0.439	1.47	0.527
2	0.13	0.647	0.0432	0.439	1.50	0.546
	0.86	1.40	0.0414	0	3.29	0.523

To identify the products of the reaction, the reaction mixtures were left at room temperature for an extended period of time. Leaving the reaction mixture for such periods allowed for significant extents of conversion of the salts **2** and **S12,** and thus product determination to be practical. The proposed mechanism is that the pyridine reacts at two sites, the methylene adjacent to the charged centre on the heterocyclic ring, allowing for ring opening to form products **S13** and **S14** (Scheme S1) but also at the methylene adjacent to the charged centre on the butyl chain of the ionic liquid **S12** forming ionic liquid **5** and the starting selenolane **S10**.[iii]



Scheme S1. The proposed mechanism for the reaction between each of the ionic liquids **2** and **S12** and pyridine.

[iii] There is not any reaction observed between ionic liquid **2** and pyridine that forms ionic liquid **5** and thiolane at any of the conditions examined.

The ^{1}H spectra for the reaction mixtures containing both **2** and **S12**, and products **S13** and **S14** are below (Figures S10 and 11). For Figure S12 it is important to note not only the signals associated with selenolane **S10** at *δ ca.* 1.9 and *ca.* 2.9, but also the signals associated with the pyridinium-based ionic liquid **5** at *δ ca.* 0.8, *ca.* 1.4, *ca.* 1.7 and *ca.* 4.6, some of which are under some of the signals for **S14**.

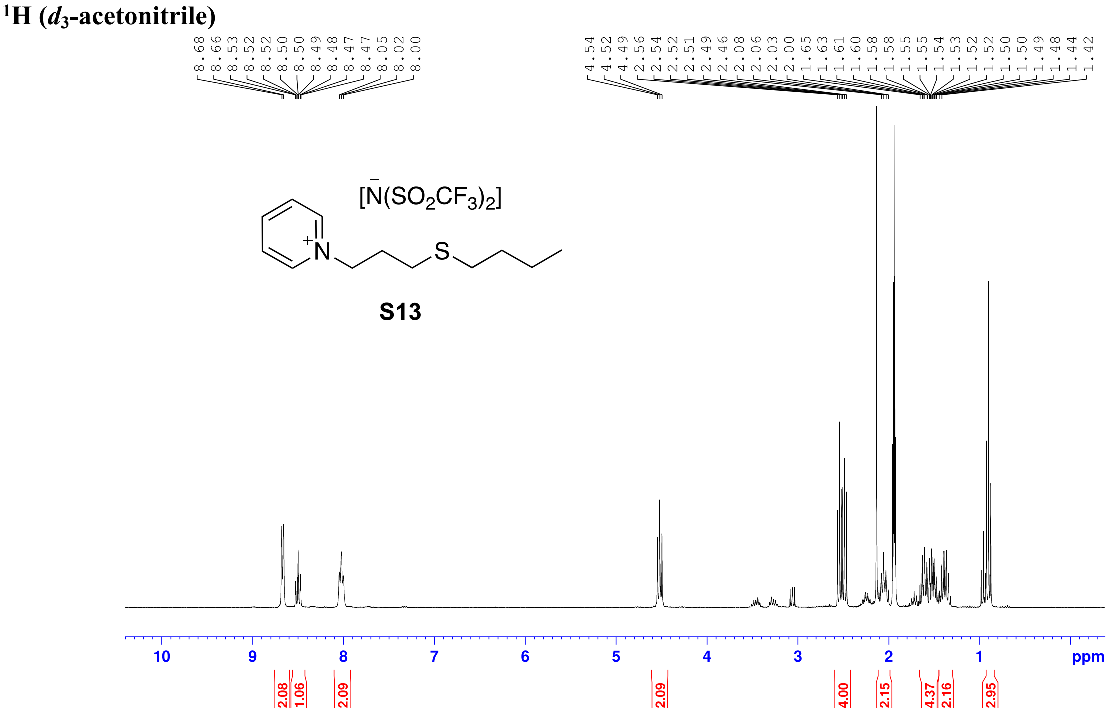


Figure S10. The ^{1}H NMR spectrum for the reaction mixture containing ionic liquid **2** and pyridine at 100% conversion. Only the chemical shifts and integrals for the product **S13** is presented.

^{1}H (d_3-acetonitrile)

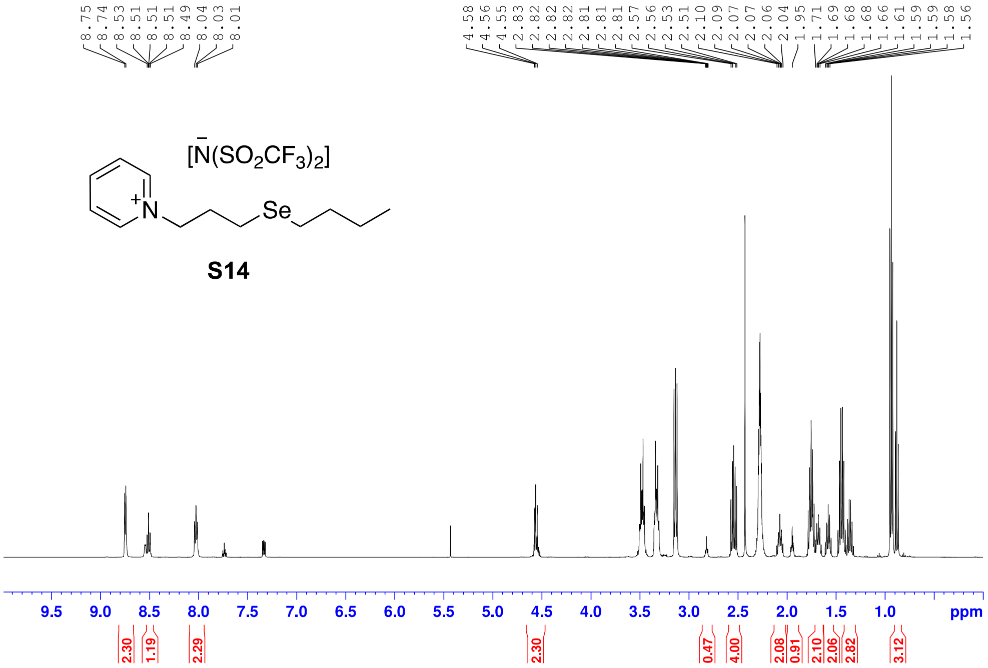


Figure S11. The ^{1}H NMR spectrum for the reaction mixture containing ionic liquid **S12** and pyridine at *ca.* 80% conversion. Only the chemical shifts and integrals for the products **S10** and **S14** are presented.

Reaction progress was followed using ^{1}H NMR spectroscopy to observe the depletion of the signal due to the pyridine at *ca.* δ 7.3, or the appearance of the signal due to the products at *ca.* δ 4.6 (Figure S12). For ionic liquid **S12**, to get both the rate constants (k_A and k_B) the reaction was also followed observing the signals at *ca.* δ 2.6 and 2.8. The rate constant for each of the processes was determined using initial rate methodology at 298 K.[iv]

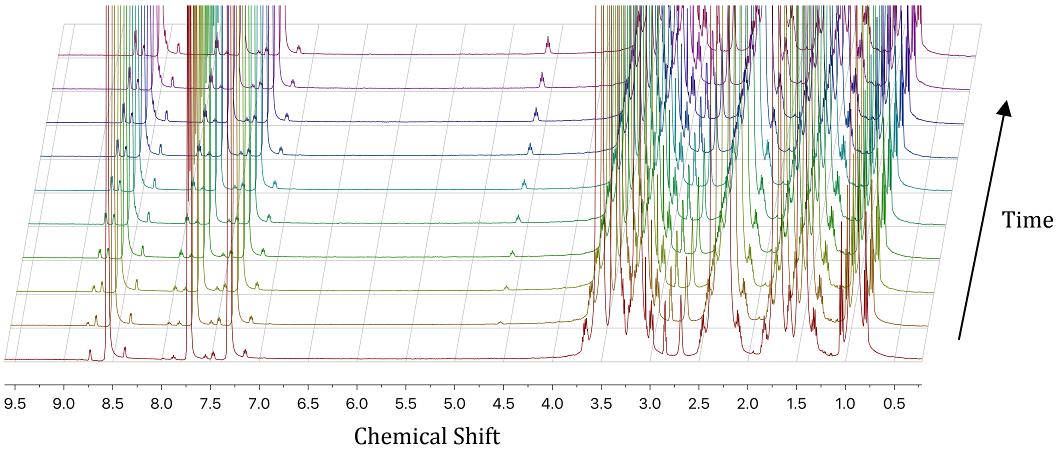


Figure S12. The stacked spectra over time for the reaction between pyridine and ionic liquid **2** showing the appearance of a signal at *ca.* δ 4.6.

[iv] This temperature is slightly higher than that of the reaction between benzyl bromide and pyridine at 295.2 K. However, this would not make significant difference in the rate constants determined.

The determined rate constants are presented in Table S16. The rate constants for the reaction between benzyl bromide and pyridine in ionic liquid **2** is also there for comparison.

Table S16. Mole fractions and concentrations of reagents in the reaction mixture, and rate constants for the reaction between pyridine and either [btl][$N(SO_2CF_3)_2$] **2** or [bse][$N(SO_2CF_3)_2$] **S12** at 298 K. Also, for comparison the mole fraction and concentration of reagents in the reaction mixture, and rate constants for the reaction between benzyl bromide and pyridine in ionic liquid **2** at 295.2 K.

Ionic liquid	χ_{IL}	**Concentrations**		**Electrophile**	**Rate constants**		
		[IL] / mol L^{-1}	**[Py] / mol L^{-1}**		$k_A + k_B$ **/ 10^{-7} L mol^{-1} s^{-1}**	k_A **/ 10^{-7} L mol^{-1} s^{-1}**	k_B **/10^{-7} L mol^{-1} s^{-1}**
S12	0.12	1.47	0.527	**S12**	4.23	3.51	0.666
2	0.13	1.50	0.546	**2**	-	0.602 0.639	-
	0.86	3.29	0.523	**2**	-	0.899 0.935	-
2	0.85	3.27	0.517	Benzyl bromide		26,300 37,600 38,000 51,600	

It is interesting to note the differences in the rate constants of reaction of the cations of the ionic liquids **2** and **S12**. The rate constant of the decomposition in the presence of pyridine is higher for ionic liquid **S12** containing the selenium-based cation, than in ionic liquid **2** with the sulfur-based cation.

To confirm that the decomposition is significantly slow enough that it will not affect the reaction being studied between benzyl bromide and pyridine (Scheme 1), comparison of the rate constants at the same mole fraction is necessary. The rate constant for the reaction between benzyl bromide and pyridine in ionic liquid **2** is *ca.* 40,000 times faster than that of the reaction between ionic liquid **2** and pyridine. This suggests that there is negligible effect of this side reaction on the reaction (Scheme 1) being examined.

For the case of ionic liquid **S12**, as the rate constant for the side reaction is significantly higher, and this may cause problems in trying to determine the rate constants and activation parameters for the reaction in Scheme 1.

Representative viscosities of reaction mixtures and associated rate constants

Table S17. Mole fractions, dynamic viscosities and rate constants for the reaction mixtures in either the ionic liquids **4**, **5**, **9** or **S15**.

Ionic liquid	χ_{IL}	**Dynamic Viscosity (η) / mPa s** [a]	**k_2 / 10^{-3} L mol^{-1} s^{-1}** [a]
[bmmo][N(SO_2CF_3)$_2$] **4**	0.67	95.3 ± 0.5	3.3 ± 0.3
[bpy][N(SO_2CF_3)$_2$] **5**	0.85	43.0 ± 0.2	1.83 ± 0.10
[bmim][N(SO_2CF_3)$_2$] **9**	0.85	35.54 ± 0.02	1.45 ± 0.05 [b]
[TOA][N(SO_2CF_3)$_2$] **S15**	0.73	287 ± 2	0.29 ± 0.04 [c]

[a] Uncertainties are the standard deviation of triplicate measurements and are reported to one significant figure with values rounded to the same level of accuracy. [b] Data reproduced from Yau *et al.*[11] [c] Data reproduced from Tanner *et al.*[10]

Table S17 shows the rate constants and viscosities for three of the ionic liquids discussed in this manuscript, along with the tetraoctylammonium salt **S15**. From these data it is evident that the rate constant is not limited by the viscosity of the solvent; there is no correlation. This can also be observed in the mole fraction dependence of the both the rate constant[13] and the diffusion of species in the mixture[14] reported previously.

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