Electronic supporting information for

"The effects of ionic liquids on the ethanolysis of a chloroacenaphthene. Evaluation of the effectiveness of nucleofugality data"

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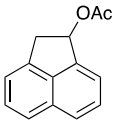
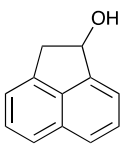
Synthesis of ionic liquids and precursors

1,2-Dihydroacenaphthylen-1-yl acetate



Acenaphthene (2.01 g, 13.0 mmol) was dissolved in glacial acetic acid (200 mL) and the resulting mixture was stirred for thirty minutes at room temperature. To this mixture, lead(II, IV) oxide (10.2 g, 14.9 mmol) was added, and the resultant solution was stirred at 60 ˚C for two hours. The reaction mixture was then allowed to cool to room temperature and the solvent was removed under reduced pressure prior to the addition of water (50 mL) and subsequent extraction with dichloromethane (3 x 100 mL). The combined organic layers were then washed with saturated aqueous sodium bicarbonate solution (100 mL) and dried over magnesium sulfate, before the solvent was removed under reduced pressure. The residue was then purified through distillation (210 ˚C, 14 mbar) (lit.[1] 166-168 ˚C, 5 mm Hg) to give 1,2-dihydroacenaphthylen-1-yl acetate as a yellow oil (2.09 g, 9.80 mmol, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.16 (s, 3H, COC$\underline{H}_3$), 3.38 (d, 1H, J = 18.1, 2.3 Hz, *cis*-C$\underline{H}_2$CHOAc), 3.89 (dd, 1H, J = 18.1, 7.3 Hz, *trans*-C$\underline{H}_2$CHOAc), 6.64 (dd, 1H, J = 7.3, 2.3 Hz, C$\underline{H}$OAc), 7.32 (d, 1H, J = 6.8 Hz, Ar-$\underline{H}$), 7.46-7.58 (m, 3H, Ar-$\underline{H}$), 7.68 (d, 1H, J = 8.3 Hz, Ar-$\underline{H}$), 7.78 (dd, J = 6.8, 2.3 1H, Ar-$\underline{H}$).

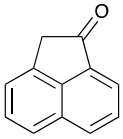
Acenaphthenol



1,2-Dihydroacenaphthylen-1-yl acetate (2.08 g, 9.80 mmol) was dissolved in methanol (20 mL), followed by the addition of potassium carbonate (1.57 g, 11.4 mmol). The reaction mixture was then stirred at room temperature overnight. The solvent was removed under reduced pressure. Water (100 mL) was added to the residue, and the resulting mixture was extracted with dichloromethane (3 x 100 mL) before the organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure to give acenaphthenol as a yellow solid (1.46 g, 8.58 mmol, 88%). m.p. 144

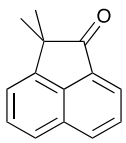
˚C (lit.[1] 144.5-145.5 ˚C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.89 (s, 1H, O<u>H</u>), 3.29 (dd, 1H, J = 17.7, 2.4 Hz, *cis*-C<u>H</u>$_2$CHCOH), 3.83 (dd 1H, J = 17.7, 7.1 Hz, *trans*-C<u>H</u>$_2$CHOH), 5.76 (dd, 1H, J = 7.1, 2.4 Hz, C<u>H</u>OH), 7.32 (d, 1H, J = 6.9 Hz, Ar-<u>H</u>), 7.46-7.58 (m, 3H, Ar-<u>H</u>), 7.68 (d, 1H, J = 6.9 Hz, Ar-<u>H</u>), 7.78 (m, 1H, Ar-<u>H</u>).

Acenaphthenone



Acenaphthenol (1.46 g, 8.58 mmol) was dissolved in THF (30 mL), followed by the dropwise addition of a solution of cerium(IV) ammonium nitrate (9.59 g, 17.5 mmol) in water (50 mL). The resulting mixture was stirred for one hour at room temperature. The THF was then removed under reduced pressure. Water (100 mL) was added to the residue and the resultant mixture was extracted with dichloromethane (3 x 100 mL) before the organic layers were combined and dried over magnesium sulfate. The solvent was removed under reduced pressure to give acenaphthenone as a yellow solid (1.38 g, 8.15 mmol, 95%). m.p. 117 ˚C (lit.[1] 118.5-120.5 ˚C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.83 (s, 2H, C<u>H</u>$_2$), 7.48 (d, 1H, J = 6.8 Ar-<u>H</u>), 7.60 (dd, 1H, J = 8.4, 6.8 Hz, Ar-<u>H</u>), 7.72 (dd, 1H, J = 8.1, 7.1 Hz, Ar-<u>H</u>), 7.83 (d, 1H, J = 8.4 Hz, Ar-<u>H</u>), 7.97 (d, 1H, J = 7.1 Hz, Ar-<u>H</u>), 8.10 (d, 1H, J = 8.1 Hz, Ar-<u>H</u>).

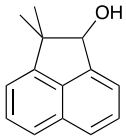
2,2-Dimethyl-1-acenaphthenone



Acenaphthenone (1.38 g, 8.15 mmol) was dissolved in THF (15 mL), followed by the addition of sodium hydride (60% dispersion in mineral oil, 0.698 g, 17.5 mmol) and methyl iodide (2.71 g, 19.1 mmol). The resultant mixture was stirred for 24 hours. The solvent was then removed under reduced pressure. Water (100 mL) was added to the residue and the resultant mixture was extracted with dichloromethane (3 x 100 mL) before

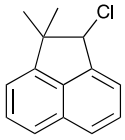
the organic layers were combined and dried over magnesium sulfate. The solvent was then removed under reduced pressure. The crude mixture was passed through a plug of silica with ethyl acetate as the eluent. The filtrate was collected and the solvent was then removed under reduced pressure to give 2,2-dimethyl-1-acenaphthenone as a yellow liquid (1.06 g, 5.40 mmol, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (s, 6H, C$\underline{H}_3$), 7.46 (dd, 1H, J = 0.7, 6.9 Hz, Ar-$\underline{H}$), 7.66 (dd, 1H, J = 6.9, 8.4 Hz, Ar-$\underline{H}$), 7.77 (dd, 1H, J = 6.9, 8.1 Hz, Ar-$\underline{H}$), 7.84 (dd, 1H, J = 0.7, 8.4 Hz, Ar-$\underline{H}$), 7.99 (dd, 1H, J = 0.7, 6.9 Hz, Ar-$\underline{H}$), 8.14 (dd, 1H, J = 0.7, 8.1 Hz, Ar-$\underline{H}$).

2,2-Dimethylacenaphthen-1-ol



2,2-Dimethyl-1-acenaphthenone (0.848 g, 4.32 mmol) was dissolved in methanol (20 mL), followed by the addition of sodium borohydride (0.327 g, 8.65 mmol). The reaction mixture was stirred at room temperature for 4 hours. Acetic acid (3 mL) was added and then the solvent was removed under reduced pressure. Water (15 mL) was then added to the residue and the resultant mixture was extracted with dichloromethane (3 x 10 mL) before the organic layers were combined, washed with an aqueous saturated sodium chloride solution (3 x 10 mL) and dried over magnesium sulfate. The solvent was then removed under reduced pressure. The residue was then recrystalised from hexane to give 2,2-dimethylacenaphthen-1-ol as a yellow solid (0.658 g, 3.32 mmol, 77%). m.p. 88 ˚C (lit.[2] 89-90 ˚C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (s, 3H, C$\underline{H}_3$), 1.47 (s, 3H, C$\underline{H}_3$), 5.20 (s, 1H, C$\underline{H}$OH), 7.23 (d, 1H, J = 6.8 Hz, Ar-$\underline{H}$), 7.46-7.61 (m, 3H, Ar-$\underline{H}$), 7.65 (d, 1H, J = 8.2 Hz, Ar-$\underline{H}$), 7.74 (d, 1H, J = 7.4 Hz, Ar-$\underline{H}$).

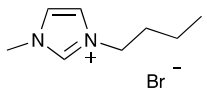
2-Chloro-1,1-dimethylacenaphthene 1



1

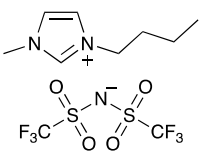
2,2-Dimethylacenaphthen-1-ol (0.450 g, 3.32 mmol) was dissolved in thionyl chloride (4.5 mL) at 0 ºC. The resultant mixture was allowed to warm to room temperature and was then stirred for two hours. The solvent was then removed under reduced pressure to yield 2-chloro-1,1-dimethylacenaphthene **1** as a yellow liquid (0.446 g, 2.06 mmol, 91%). ^{1}H NMR (600 MHz, DMSO-d_6) δ 1.45 (s, 3H, C$\underline{H}_3$), 1.47 (s, 3H, C$\underline{H}_3$), 5.72 (s, 1H, C$\underline{H}$OH), 7.40 (d, 1H, J = 6.9 Hz, Ar-$\underline{H}$), 7.54 (d, 1H, J = 6.9 Hz, Ar-$\underline{H}$), 7.57 (dd, 1H, J = 6.9, 8.2 Hz, Ar-$\underline{H}$), 7.63 (dd, 1H, J = 6.9, 8.2 Hz, Ar-$\underline{H}$), 7.75 (d, 1H, J = 8.2 Hz, Ar-$\underline{H}$), 7.84 (d, 1H, J = 8.2 Hz, Ar-$\underline{H}$).

1-Butyl-3-methylimidazolium bromide



1-Methylimidazole (5.95 g, 72.4 mmol) and 1-bromobutane (11.2 g, 81.4 mmol) were combined, and the resulting mixture was stirred at room temperature for 5 days under a nitrogen atmosphere. During this time, the mixture formed two layers. The top layer was poured off and ethyl acetate (50 mL) was added to the bottom layer. This mixture was stored at -18 ˚C for 18 hours until a white solid formed. The ethyl acetate was decanted, and the remaining white solid was crushed and then washed with ethyl acetate (3 x 100 mL). Residual ethyl acetate was removed under reduced pressure, then *in vacuo* to give 1-butyl-3-methylimidazolium bromide as a white solid (15.2 g, 69.5 mmol, 96%) m.p. 69 ˚C (lit.[3] 70 ˚C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.36-1.51 (m, 2H, C$\underline{H}_2CH_3$), 1.86-1.99 (m, 2H, C$\underline{H}_2CH_2CH_3$), 4.15 (s, 3H, NC$\underline{H}_3$), 4.35 (t, J = 7.4 Hz, 2H, NC$\underline{H}_2$), 7.24-7.33 (m, 2H, C$\underline{H}$C$\underline{H}$), 10.68 (s, 1H, NC$\underline{H}$N).

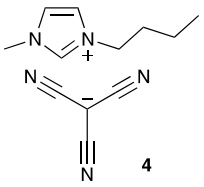
1-Butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide 3



3

1-Butyl-3-methylimidazoium bromide (39.0 g, 178 mmol) was dissolved in water (75 mL) and the resulting solution was added to a solution of lithium *bis*(trifluoromethanesulfonyl)imide (62.4 g, 217 mmol) in water (75 mL). The resulting mixture was stirred for 24 hours at room temperature. During this time, the reaction mixture separated into two phases. The aqueous layer was extracted with dichloromethane (3 x 100 mL). The combined organic layers were washed with water (3 x 100 mL) before volatile components were removed under reduced pressure to give the ionic liquid **3** as a colourless, viscous liquid (70.0 g, 167 mmol, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.35-1.42 (m, 2H, $C\underline{H}_2CH_3$), 1.84-1.92 (m, 2H, $C\underline{H}_2CH_2CH_3$), 3.98 (s, 3H, $NC\underline{H}_3$), 4.21 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2$), 7.28-7.31 (m, 2H, C<u>H</u>C<u>H</u>), 8.84 (s, 1H, NC<u>H</u>N).

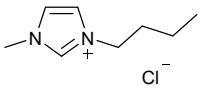
1-Butyl-3-methylimidazolium tricyanomethanide 4



4

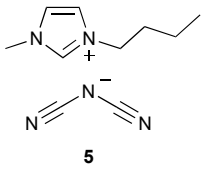
1-Butyl-3-methylimidazoium bromide (10.0 g, 45.9 mmol) was dissolved in water (50 mL) and the resulting solution was added to a solution of sodium tricyanomethanide (5.74 g, 50.8 mmol) in water (50 mL). The resulting mixture was stirred for 24 hours at room temperature. During this time, the reaction mixture separated into two phases. The aqueous layer was extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed with water (8 x 50 mL) before volatile components were removed under reduced pressure to give the ionic liquid **4** as a colourless, viscous liquid (6.66 g, 29.1 mol, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.29 – 1.44 (m, 2H, $C\underline{H}_2CH_3$), 1.77 – 1.92 (m, 2H, $C\underline{H}_2CH_2CH_3$), 3.84 (s, 3H, $NC\underline{H}_3$), 4.14 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2$), 7.34-7.40 (m, 2H, C<u>H</u>C<u>H</u>), 8.42 (s, 1H, NC<u>H</u>N).

1-Butyl-3-methylimidazolium chloride



1-Methylimidazole (5.90 g, 71.9 mmol) and 1-chlorobutane (7.32 g, 79.0 mmol) were combined and the mixture was stirred at room temperature for 5 days under a nitrogen atmosphere; during this time, a white solid formed. The ethyl acetate was decanted, and the remaining white solid was crushed and then washed with ethyl acetate (3 x 100 mL). Residual ethyl acetate was removed under reduced pressure, then *in vacuo* to give 1-butyl-3-methylimidazolium chloride as a white solid (10.2 g, 58.4 mmol, 81%) which was used without further purification. m.p. 64 ˚C (lit.[3] 65 ˚C). ^{1}H NMR (300 MHz, CD_3CN) δ 0.92 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.26 – 1.45 (m, 2H, $C\underline{H}_2CH_3$), 1.74 – 1.93 (m, 2H, $C\underline{H}_2CH_2CH_3$), 3.93 (s, 3H, $NC\underline{H}_3$), 4.25 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2$), 7.46-7.69 (m, 2H, C<u>H</u>C<u>H</u>), 9.73 (s, 1H, NC<u>H</u>N).

1-Butyl-3-methylimidazolium dicyanimide 5

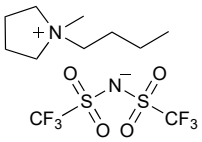


5

1-Butyl-3-methylimidazoium chloride (3.93 g, 22.5 mmol) was dissolved in acetone (25 mL) and the resulting solution was added to a solution of sodium dicyanimide (2.65 g, 29.8 mmol) in acetone (25 mL). The resulting mixture was stirred for 24 hours at room temperature. The solvent was removed under reduced pressure and dichloromethane (50 mL) was added. Sodium chloride formed as a white precipitate and was collected through filtration and discarded. The solution was stored at -20 ˚C overnight. This process was repeated ten times to ensure complete removal of sodium chloride. Ion chromatography confirmed the chloride content as <20 ppm. The solvent was removed under reduced pressure to give the ionic liquid **5** as a pale yellow liquid (3.83 g, 18.7 mmol, 83 %). ^{1}H NMR (300 MHz, CD_3CN) δ 0.86 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$),

1.23 – 1.38 (m, 2H, C<u>H</u>$_2$CH$_3$), 1.69 – 1.90 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_3$), 3.98 (s, 3H, NC<u>H</u>$_3$), 4.29 (t, J = 7.4 Hz, 2H, NC<u>H</u>$_2$), 7.58-7.75 (m, 2H, C<u>H</u>C<u>H</u>), 9.06 (s, 1H, NC<u>H</u>N).

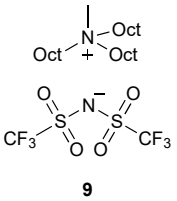
1-Butyl-1-methylpyrrolidinium *bis*(trifluoromethanesulfonyl)imide 8



8

1-Butyl-1-methylpyrrolidinium bromide* (14.8 g, 59.2 mmol) was dissolved in water (50 mL) and the resulting solution was added to a solution of lithium *bis*(trifluoromethanesulfonyl)imide (21.6 g, 75.3 mmol) in water (50 mL). The resulting mixture was stirred for 24 hours at room temperature. During this time, the reaction mixture separated into two phases. The aqueous layer was extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed with water (10 x 50 mL) before volatile components were removed under reduced pressure to give the ionic liquid **8** as a colourless, viscous liquid (24.8 g, 55.1 mmol, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (t, J = 7.3 Hz, 3H, CH$_2$C<u>H</u>$_3$), 1.40 – 1.53 (m, 2H, C<u>H</u>$_2$CH$_3$), 1.72 – 1.84 (m, 2H, C<u>H</u>$_2$CH$_2$CH$_3$), 2.32 (s, 4H, NCH$_2$C<u>H</u>$_2$), 3.10 (s, 3H, NC<u>H</u>$_3$), 3.30 – 3.42 (m, 2H, NC<u>H</u>$_2$), 3.49 – 3.66 (m, 4H, NC<u>H</u>$_2$CH$_2$)

Methyltrioctylammonium *bis*(trifluoromethanesulfonyl)imide 9



9

Methyltrioctylammonium bromide (16.0 g, 32.6 mmol) was dissolved in acetone (75 mL) and the resulting solution was added to a solution of lithium *bis*(trifluoromethanesulfonyl)imide (12.6 g, 44.0 mmol) in water (75 mL). The resulting mixture was stirred for 24 hours at room temperature. The acetone was removed under reduced pressure to leave two immiscible layers. The aqueous layer was extracted with dichloromethane (3 x 50 mL). The combined organic layers were washed with

* The bromide salt was the generous gift of Dr Alyssa Gilbert.[3]

water (10 x 100 mL) before volatile components were removed under reduced pressure to give the ionic liquid **9** as a yellow, viscous liquid (21.6 g, 31.3 mmol, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 6.8 Hz, 9H, $C\underline{H}_3$), 1.26 – 1.45 (m, 30H, $C\underline{H}_2$), 1.63 – 1.79 (m, 6H, $NCH_2C\underline{H}_2$), 3.07 (s, 3H, $NC\underline{H}_3$), 3.15 – 3.33 (m, 6H, $NC\underline{H}_2CH_2$).

Experimental details for kinetic analyses

Stock solutions were each prepared with a fixed amount of triethylamine (*ca.* 8 mg) in mixtures containing the desired mole fraction of one of the ionic liquids **3-10** in ethanol (for exact compositions, see Tables S1-S4). The chloride **1** (*ca*. 5 mg) was placed into an empty NMR tube prior to mixing with an aliquot (0.5 mL) of the appropriate stock solution. All kinetic experiments were monitored in a Bruker Avance III 500 spectrometer with a TBI probe. NMR spectra were processed using MestReNova (V. 14.2.0) software. The desired temperature was set on the NMR spectrometer *via* external thermocouple.

All cases were monitored using ^{1}H NMR spectroscopy by following the depletion of the signal representing the benzylic proton at *ca*. 5.5 ppm over time at the desired temperature. For cases where the reaction spanned prohibitively long time periods which prevented efficient use of NMR resources, samples were kept in a water bath at a consistent temperature (40˚C for all cases barring temperature dependent kinetic analyses). In the cases where spectra were obtained over multiple separate occasions, the signal integrations were normalised using a signal associated with a species of unchanging concentration in solution.

Where reasonable (reaction complete in less than 8 h), the reaction was followed until at least 90% of the starting material was consumed. In all other cases, the reaction was monitored up to *ca*. 10% completion with the rate constant being obtained using initial rates methodology.

Nucleophile dependent kinetic studies to confirm that the reaction proceeded through an S_N1 pathway were performed as detailed above in mixtures of acetonitrile and ethanol over a range of concentrations of ethanol. All cases were followed to *ca*. 10% *via* initial rates methodology.

Temperature dependent kinetic studies to determine activation parameters were performed as detailed above in mixtures of ionic liquid **3** and ethanol at either χ_{IL} = 0.15 or 0.80, as well as

in neat ethanol. Temperatures chosen for this study were 20˚C, 30˚C, 50˚C, and 60˚C. As above, cases were followed until at least 90% of starting material was consumed, or *ca*. 10% *via* initial rates methodology, depending on the time required for the reaction to progress.

Stock solution compositions and rate constant data for nucleophile dependence studies

Table S1. The concentration of ethanol, the mass of acetonitrile, ethanol, triethylamine and the chloride **1**, and the first order rate constant (k_1) for the ethanolysis of the chloride **1** in each 2 mL stock solution.

[EtOH] / molL^{-1}	Mass acetonitrile / g	Mass ethanol / g	Mass triethylamine / g	Mass chloride 1 / g	k_1 / 10^{-7} s^{-1}	Average[a]
1.025	1.4659	0.0944	0.0132	0.0060	6.98	6.7 (0.5)
				0.0052	6.15	
				0.0064	6.87	
2.009	1.3744	0.1851	0.0107	0.0056	7.11	6.7 (0.7)
				0.0062	7.03	
				0.0054	5.95	
2.994	1.2818	0.2759	0.0100	0.0062	6.76	7.0 (0.6)
				0.0064	6.51	
				0.0057	7.57	
4.0004	1.1908	0.3686	0.0091	0.0068	7.65	7.2 (0.6)
				0.0052	6.56	
				0.0066	7.35	

[a]The reported uncertainty is the standard deviation of the individual results.

Stock solution compositions and rate constant data for ionic liquid mole fraction dependence studies

Table S2. The mole fraction of [bmim][$N(SO_2CF_3)_2$] **3**, the exact amounts of ionic liquid **3**, ethanol, triethylamine and the chloride **1**, and the first order rate constant (k_1) for the ethanolysis of the chloride **1** in each 2 mL stock solution.

χ_3	Mass ionic liquid 3 / g	Mass ethanol / g	Mass triethylamine / g	Mass chloride 1 / g	k_1 / 10^{-5} s^{-1}	Average[a]
0	-	1.5526	0.0094	0.0050	0.76	0.74 (0.03)
				0.0053	0.71	
				0.0055	0.76	
0.05	0.5940	1.234	0.0100	0.0060	1.78	1.77 (0.05)
				0.0057	1.75	
				0.0055	1.78	
0.10	1.0061	0.9980	0.0119	0.0048	1.85	1.92 (0.08)
				0.0052	1.97	
				0.0053	1.94	
0.15	1.3391	0.8167	0.0100	0.0054	2.16	2.09 (0.08)
				0.0051	2.08	
				0.0054	2.06	
	1.3364	0.8211	0.0094	0.0053	2.01	
				0.0054	2.06	
				0.0047	2.11	
0.20	1.5884	0.6869	0.0095	0.0047	1.95	1.89 (0.08)
				0.0055	1.83	
				0.0045	1.88	
0.30	1.9544	0.4807	0.0092	0.0047	1.54	1.43 (0.09)
				0.0049	1.36	
				0.0045	1.39	
0.40	2.1898	0.3477	0.0133	0.0048	0.742	0.73 (0.07)
				0.0054	0.743	
				0.0056	0.694	
0.50	2.3731	0.2648	0.0107	0.055	0.458	0.462
				0.0057	0.478	(0.015)
				0.0054	0.451	
0.60	2.5129	0.1800	0.0117	0.0051	0.252	0.247
				0.0055	0.244	(0.015)
				0.0061	0.245	
0.70	2.6268	0.1173	0.0102	0.0054	0.1128	0.114
				0.0052	0.1161	(0.007)
				0.0062	0.1137	
0.80	2.7183	0.0677	0.0088	0.0054	0.112	0.102
				0.0046	0.100	(0.011)
				0.0055	0.106	
	2.7154	0.0670	0.0135	0.0054	0.0900	
				0.0052	0.0906	

[a]The reported uncertainty is the standard deviation of the individual results.

Stock solution compositions and rate constant data for the determination of rate constant in mixtures containing ionic liquids 4-10

Table S3. Mass of each component contributing to the stock solutions for each of the ionic liquids **4-10** at χ_{IL} *ca.* 0.80 used to measure the first order rate constant (k_1) for the ethanolysis of the chloride **1** in each 2 mL stock solution.

Ionic liquid	Mass ionic liquid / g	Mass ethanol / g	Mass triethylamine / g	Mass chloride 1 / g	k_1 / 10^{-6} s^{-1}	Average[a]
[bmim][$C(CN)_3$] **4**	2.0134	0.0570	0.0122	0.0049	5.66	6.5 (0.7)
				0.0052	6.73	
				0.0042	7.03	
[bmim][$N(CN)_2$] **5**	2.0439	0.0551	0.0112	0.0065	4.06	4.2 (0.2)
				0.0048	4.43	
				0.0049	4.21	
[bmim][PF_6] **6**	2.6085	0.0671	0.0091	0.0055	3.38	3.8 (0.3)
				0.0046	3.81	
				0.0057	3.99	
[bmim][BF_4] **7**	2.3124	0.0616	0.0126	0.0055	1.18	1.170
				0.0061	1.17	(0.011)
				0.0058	1.16	
[bmpyr] [$N(SO_2CF_3)_2$] **8**	2.6249	0.0640	0.0100	0.0054	0.82	0.84
				0.0056	0.83	(0.02)
				0.0052	0.86	
[mTOA] [$N(SO_2CF_3)_2$] **9**	2.2065	0.0537	0.0101	0.0051	0.24	0.22
				0.0042	0.21	(0.02)
				0.0047	0.21	
[Li(G3)] [$N(SO_2CF_3)_2$] **10**	2.5732	0.1624	0.0127	0.0049	0.99	1.10
				0.0065	1.14	(0.08)
				0.0040	1.16	

[a]The reported uncertainty is the standard deviation of the individual results.

Eyring analyses

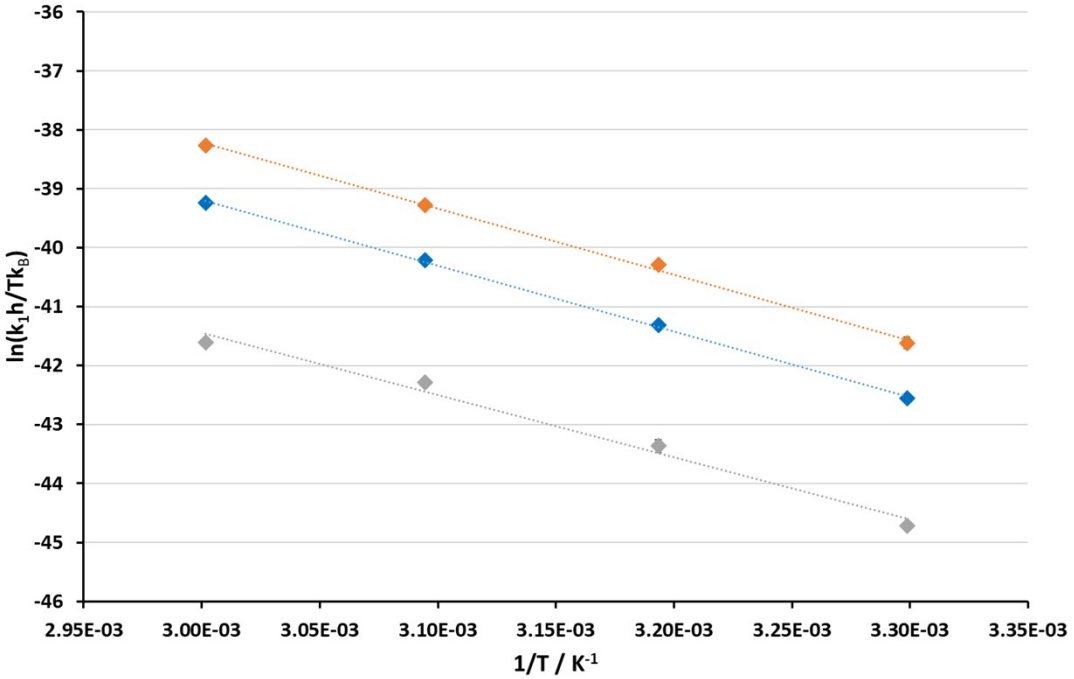


Figure S1. The Eyring plot from which the activation parameters were determined for the unimolecular substitution reaction between the chloride **1** and ethanol in either neat ethanol (◆) or a mixture of the ionic liquid **3** and ethanol (χ = 0.15, ◆; χ = 0.80, ◆).

Stock solution compositions and rate constant data for temperature dependent kinetic studies

Table S4. The exact amounts of ionic liquid **3**, ethanol, triethylamine and the chloride **1**, and the first order rate constant (k_1) for the ethanolysis of the chloride **1** at the temperature specified.

χ_3	Temperature / °C	Mass ionic liquid 3 / g	Mass ethanol / g	Mass triethylamine / g	Mass chloride 1 / g	k_1 / 10^{-5} s^{-1}	Average[a]
0	30	-	1.5427	0.0106	0..0048	0.199	0.208
					0.0050	0.213	(0.014)
					0.0047	0.213	
	50	-	1.5576	0.0083	0.0055	2.30	2.33 (0.14)
					0.0048	2.49	
					0.0056	2.20	
	60	-	1.5482	0.0091	0.0047	6.23	6.3 (0.4)
					0.0044	5.98	
					0.0049	6.72	
0.15	30	1.3422	0.8142	0.0097	0.0045	0.496	0.51 (0.06)
					0.005	0.576	
					0.0055	0.441	
	50	1.3423	0.8162	0.0094	0.0051	5.58	5.90 (0.31)
					0.0052	6.09	
					0.0048	5.96	
	60	1.3425	0.8244	0.0095	0.0046	16.34	16.7 (0.7)
					0.0051	16.26	
					0.0048	17.42	
0.80	30	2.7121	0.0630	0.0110	0.0049	0.0231	0.026
					0.0048	0.0265	(0.002)
					0.0048	0.0274	
	50	2.7152	0.0664	0.0092	0.0054	0.297	0.304
					0.0048	0.324	(0.018)
					0.0047	0.290	
	60	2.7186	0.0741	0.0105	0.0047	0.581	0.584
					0.0048	0.596	(0.033)
					0.0047	0.574	

[a]The reported uncertainty is the standard deviation of the individual results.

Multivariate regression analyses for Kamlet-Taft correlations

Analyses were carried out as previously,[3-6] based on the methods of Welton *et al.*[7] These analyses have used a linear combination of Kamlet-Taft parameters as outlined below in each case. They are presented in the form

$$\ln(k_1) = \text{intercept} + a\alpha + b\beta + c\pi^*$$

with *p*-values in parentheses after each parameter. The coefficient of determination (R^2) is given at the end to give further evidence of the general poorness of the correlations shown; where the intercept is included this is sufficient. When no intercept is included, the adjusted R^2, which takes into account the number of independent variables.

Combination of α, β and π^* with intercept

$\ln(k_1) = -19.64(0.17) + 11.94(0.28)\alpha + 11.78(0.50)\beta - 5.93(0.79)\pi^*$ $R^2 = 0.53$

Combination of α and β with intercept

$\ln(k_1) = -22.43(0.010) + 10.98(0.21)\alpha + 7.55(0.18)\beta$ $R^2 = 0.52$

Combination of α and π^* with intercept

$\ln(k_1) = -25.65(0.022) + 9.29(0.30)\alpha + 8.62(0.26)\pi^*$ $R^2 = 0.44$

Combination of β and π^* with intercept

$\ln(k_1) = -18.74(0.19) + 3.96(0.81)\beta + 3.81(0.86)\pi^*$ $R^2 = 0.26$

Combination of α and intercept

$\ln(k_1) = -17.94(0.010) + 9.38(0.31)\alpha$ $R^2 = 0.19$

Combination of β and intercept

$\ln(k_1) = -16.62(1.3 \times 10^{-3}) + 6.62(0.25)\beta$ $R^2 = 0.25$

Combination of π* and intercept

$\ln(k_1) = -21.19(0.020) + 7.35(0.46)\pi^*$ $R^2 = 0.15$

Combination of α, β and π*

$\ln(k_1) = 10.92(0.39)\alpha + 31.99\ (0.07)\beta - 38.19(0.03)\pi^*$ $R^2 = 0.99$; Adjusted $R^2 = 0.74$

Combination of α and β

$\ln(k_1) = -20.47(0.07)\alpha - 6.59(0.49)\beta$ $R^2 = 0.98$; Adjusted $R^2 = 0.77$

Combination of α and π*

$\ln(k_1) = -6.03(0.65)\alpha - 11.49(0.15)\pi^*$ $R^2 = 0.99$; Adjusted $R^2 = 0.78$

Combination of β and π*

$\ln(k_1) = 23.96(0.07)\beta - 27.90(4.5 \times 10^{-3})\pi^*$ $R^2 = 0.99$; Adjusted $R^2 = 0.79$

α only

$\ln(k_1) = -27.03(5.1 \times 10^{-6})\alpha$ $R^2 = 0.97$; Adjusted $R^2 = 0.81$

β only

$\ln(k_1) = -27.03(3.2 \times 10^{-5})\beta$ $R^2 = 0.95$; Adjusted $R^2 = 0.79$

π* only

$\ln(k_1) = -14.74(1.4 \times 10^{-6})\pi^*$ $R^2 = 0.98$; Adjusted $R^2 = 0.82$

Estimation of acenaphthyl electrofugality value and accounting for temperature

As there is no reported E_f value for the acenaphthyl species, an estimation of the E_f must be made. The phenylethyl species was used as a starting point for this estimation, with an E_f of -8.48.[8]

The addition of a second aromatic ring (that is, going from a phenylethyl species to a naphthylethyl species) would be expected to stabilise the positive charge of the carbocation, and as such, it is reasonable to expect a notable increase in E_f. Based on the effect seem in related systems (comparing a naphthyl(*tert*-butyl)methyl carbocation to a phenyl(*tert*-butyl)methyl carbocation)[8] this change would be expected to be about +2. It should be noted this effect is likely to be larger in this case than in literature (1-naphthyl *vs* 2-naphthyl),[8] we increase this estimate to +3.

However, this increase in stability is tempered by the addition of two methyl groups on the α-carbon (going from a naphthylethyl species to a naphthylmethylpropyl species). Whilst nominally these might be expected to stabilise the carbocation, previous results[8] have shown that adding in these methyl groups *decreases* the E_f, postulating that this is a steric effect. The effect on reactivity is shown to be *ca.* -1 in E_f on this change (comparing the phenyl(dimethyl)methyl cation and the pheny(methyl)isopropylmethyl cation). [8]

The final transformation to get to the acenaphthyl carbocation is to ring-close the naphthylmethylpropyl species. Evidence using benzyhydrylium and fluorene cations suggest the effect is large (-2),[9] but the ring closed system in this case is antiaromatic (*cf.* system here). As such, any decrease in stability (as a result of decreased stabilisation through inefficient electron delocalisation on ring closure) is likely to be less than that, so we estimate the change in E_f at -1.

Overall, the sum of these changes give E_f for the acenapthene system considered as -7.5.

With these data, the rate constant for the process considered here could be calculated in each of the mixtures considered using the equation below.

$$log_{10}(k_1)_{25^oC} = s_f(N_f + E_f)$$

It should be noted that this gives data for the process at 25 °C; the reaction was carried out at 40 °C. Fortunately, the activation parameters for the process are known and the enthalpy of activation does not change in the presence of ionic liquid **3**. Assuming it does not change in other systems and noting that it is large (90 kJ mol^{-1}), the resulting effect on rate constant of changing temperature is (using $E_a = \Delta H^{\ddagger}$ - RT) is to multiply by a factor of 5.70.

Predicted *vs* experimental log(k_1) values for ionic liquids 3-10 at χ_{IL} = 0.8

Table S5. The predicted log(k_1) values for salts **3-10** and their corresponding experimental values at χ_{IL} = 0.8

Ionic liquid	Predicted log(k_1)	Experimental log(k_1)	Absolute Error
[bmim] [$N(SO_2CF_3)_2$] **3**	-6.18	-5.99	0.19
[bmim][$C(CN)_3$] **4**	-5.47	-5.19	0.29
[bmim][$N(CN)_2$] **5**	-5.50	-5.37	0.13
[bmim][PF_6] **6**	-5.73	-5.43	0.30
[bmim][BF_4] **7**	-6.16	-5.93	0.22
[bmpyr][$N(SO_2CF_3)_2$] **8**	-6.45	-6.08	0.37
[mTOA][$N(SO_2CF_3)_2$] **9**	-7.13	-6.66	0.48
[Li(G3)][$N(SO_2CF_3)_2$] **10**	-6.60	-5.96	0.64

Mean absolute error (all data) = 0.33

Mean absolute error (excluding **10**) = 0.28

Predicted *vs* experimental log(k_1) values for ionic liquid 3 at varying mole fractions

Table S6. The predicted log(k_1) values for salt **3** and their corresponding experimental values at varying mole fractions.

χ_3	Predicted log(k_1)	Experimental log(k_1)	Absolute error
0	-4.96	-5.13	0.17
0.05	-4.65	-4.75	0.10
0.1	-4.61	-4.72	0.11
0.2	-4.69	-4.72	0.04
0.3	-4.80	-4.84	0.04
0.5	-5.17	-5.34	0.16
0.8	-6.18	-6.01	0.18

Mean absolute error (all data) = 0.11

Estimating E_f from a linear fit

The predicted values for the rate constants in mixtures containing each of the salts **3-10** in ethanol at χ_{IL} = 0.80 were initially calculated as above. The Solver function of Microsoft Excel was then used to vary the value of E_f such that the sum of the square of the errors was minimised. This process resulted in an E_f of -7.17 (corresponding to an MAE of 0.11). When this process was repeated for the rate constant date for mixtures containing different mole fractions of the salt **3**, the result was a value of E_f of -7.60 of and an MAE of 0.08.

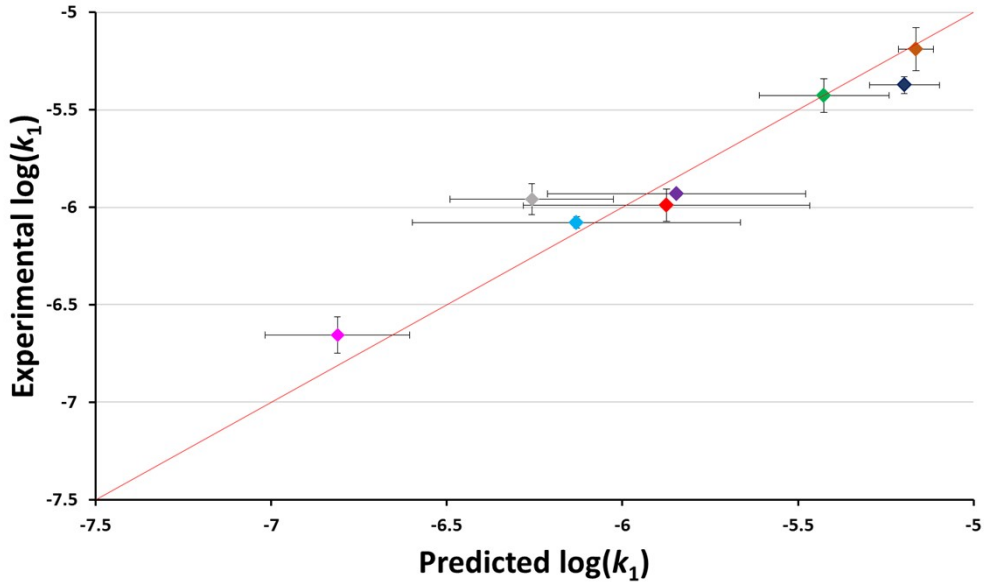


Figure S2. The log of experimentally determined rate constant for the reaction between the chloride **1** and ethanol (Scheme 1) in mixtures containing ethanol and either [bmim][$N(SO_2CF_3)_2$] **3** (◆), [bmim][$C(CN)_3$] **4** (◆), [bmim][$N(CN)_2$] **5** (◆), [bmim][PF_6] **6** (◆), [bmim][BF_4] **7** (◆), [bmpyr][$N(SO_2CF_3)_2$] **8** (◆), [mTOA][$N(SO_2CF_3)_2$] **9** (◆), and [Li(G3)][$N(SO_2CF_3)_2$] **10** (◆) at χ_{IL} = 0.80 at 40 °C plotted against the corresponding predicted value based on reported nucleofugality data and E_f = -7.17. Uncertainties are the standard deviation of at least triplicate results for experimental data and are compounded from uncertainties in the reported nucleofugality data for the predicted values; some error bars are smaller than the markers used in the former case. The line shown is y = x and is present to guide the eye only.

Table S7. The predicted log(k_1) values for salts **3-10** and their corresponding experimental values at χ_{IL} = 0.80 with E_f = -7.17.

Ionic liquid	Predicted log(k_1)	Experimental log(k_1)	Absolute Error
[bmim] [$N(SO_2CF_3)_2$] **3**	-5.87	-5.99	0.12
[bmim][$C(CN)_3$] **4**	-5.16	-5.19	0.02
[bmim][$N(CN)_2$] **5**	-5.20	-5.37	0.18
[bmim][PF_6] **6**	-5.43	-5.43	0.00
[bmim][BF_4] **7**	-5.85	-5.93	0.09
[bmpyr][$N(SO_2CF_3)_2$] **8**	-6.13	-6.08	0.05
[mTOA][$N(SO_2CF_3)_2$] **9**	-6.81	-6.66	0.16
[Li(G3)][$N(SO_2CF_3)_2$] **10**	-6.26	-5.96	0.30

Mean absolute error = 0.11

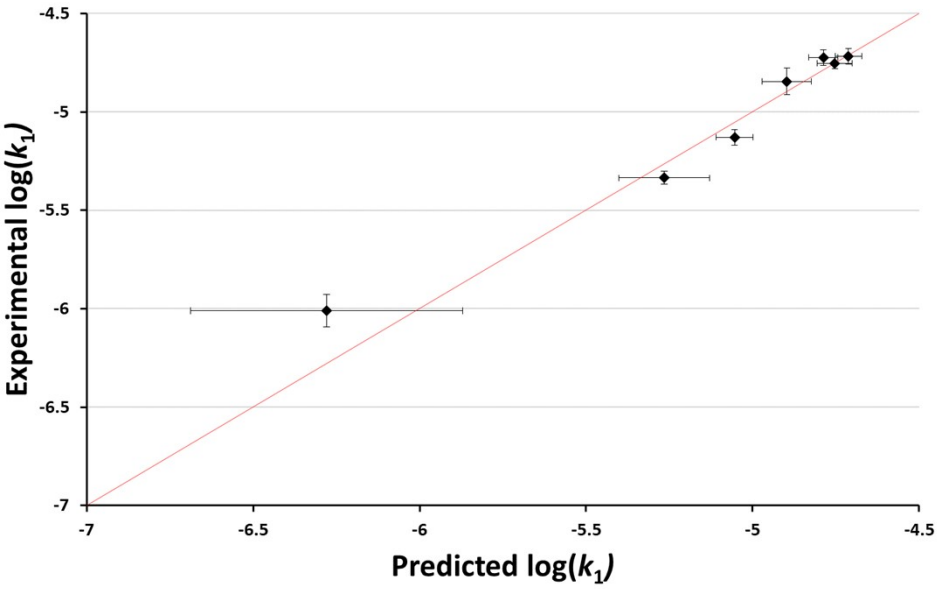


Figure S3. The log of experimentally determined rate constant for the reaction between the chloride **1** and ethanol (Scheme 1) in mixtures containing ethanol and [bmim][$N(SO_2CF_3)_2$] **3** (◆) at 40 °C plotted against the corresponding predicted based on reported nucleofugality data E_f = -7.60. Uncertainties are the standard deviation of at least triplicate results for the experimental data are compounded from uncertainties in the reported nucleofugality data for the predicted values; some error bars are smaller than the markers used in the former case. The line shown is y = x and is present to guide the eye only.

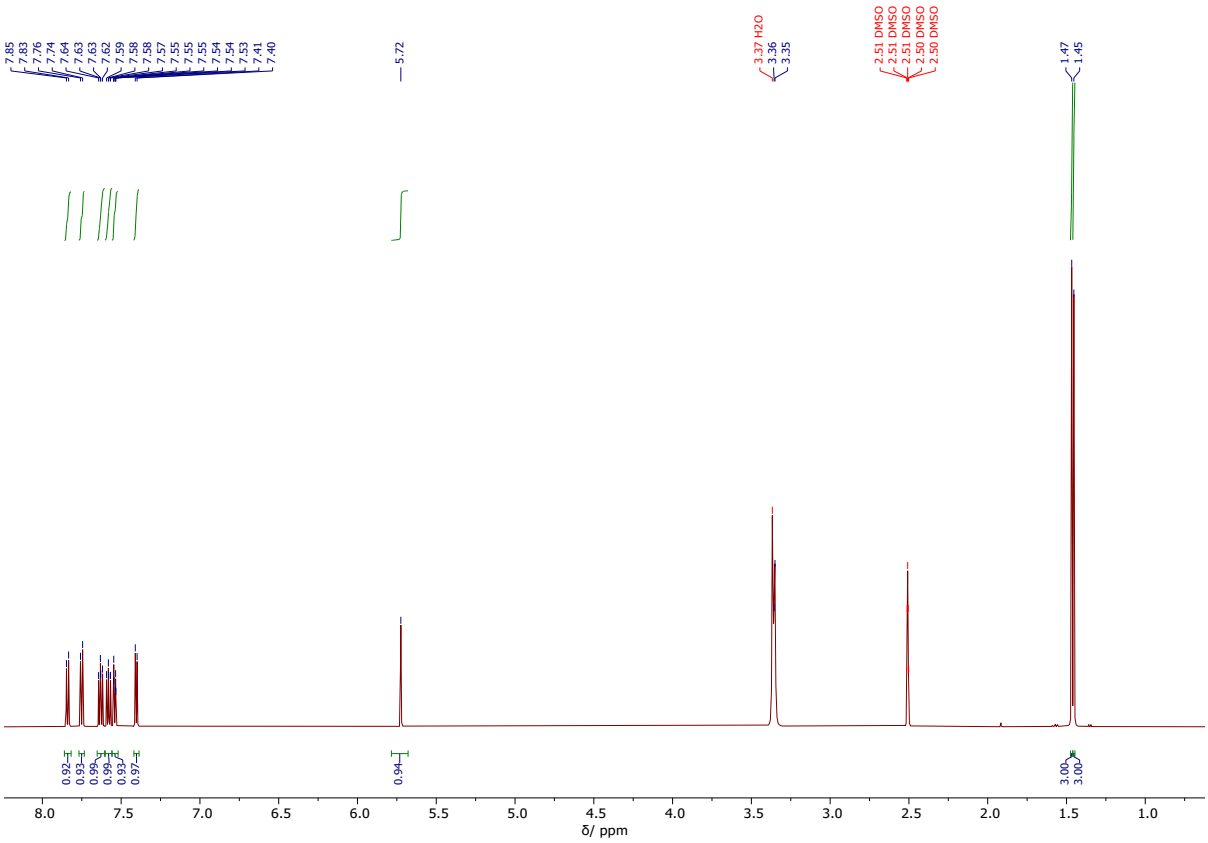
Table S8. The predicted log(k_1) values for salt **3** and their corresponding experimental values at varying mole fractions of salt **3** in ethanol.

χ_3	**Predicted log(k_1)**	**Experimental log(k_1)**	**Absolute error**
0	-5.05	-5.13	0.08
0.05	-4.75	-4.75	0.00
0.1	-4.71	-4.72	0.01
0.2	-4.79	-4.72	0.07
0.3	-4.90	-4.84	0.06
0.5	-5.27	-5.34	0.07
0.8	-6.28	-6.01	0.27

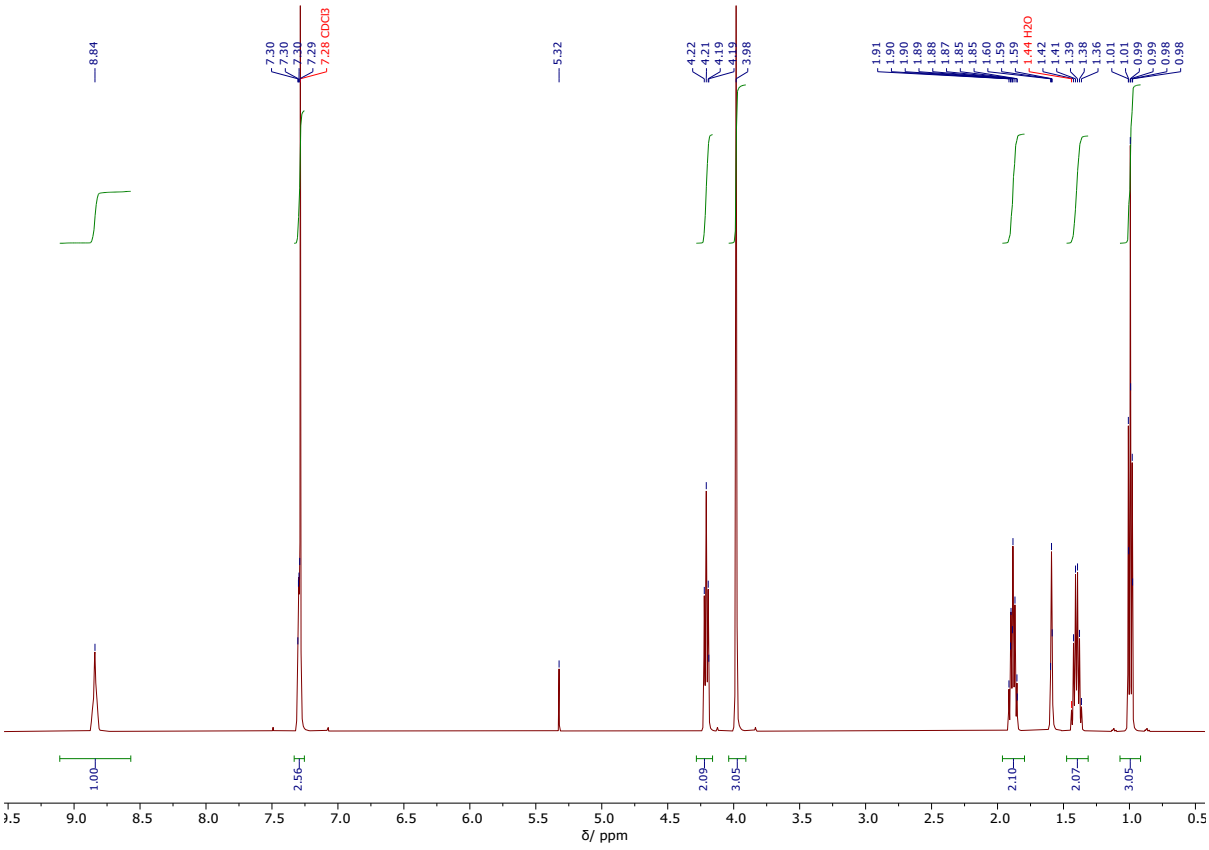
Mean absolute error (all data) = 0.08

NMR spectra for prepared compounds

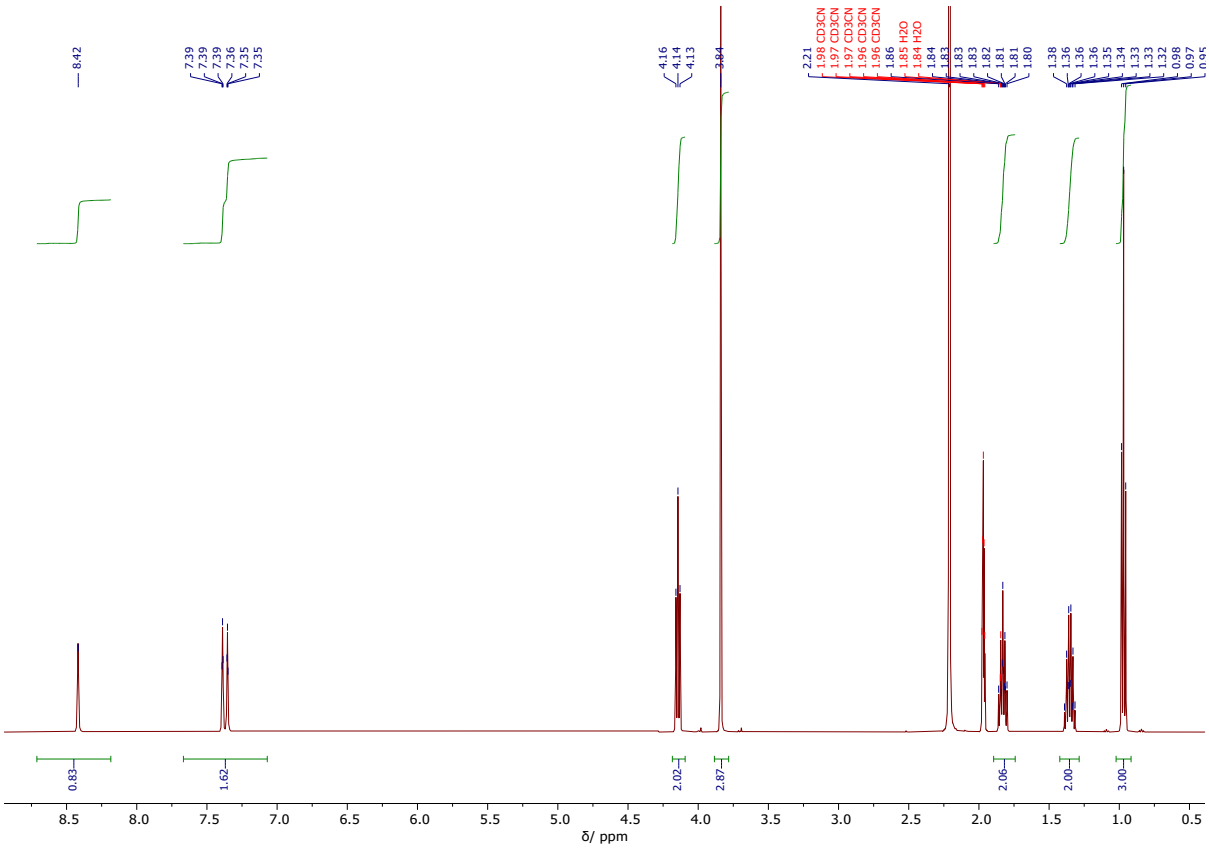
^{1}H NMR spectrum (600 MHz, DMSO) of 2-chloro-1,1-dimethylacenaphthene **1**



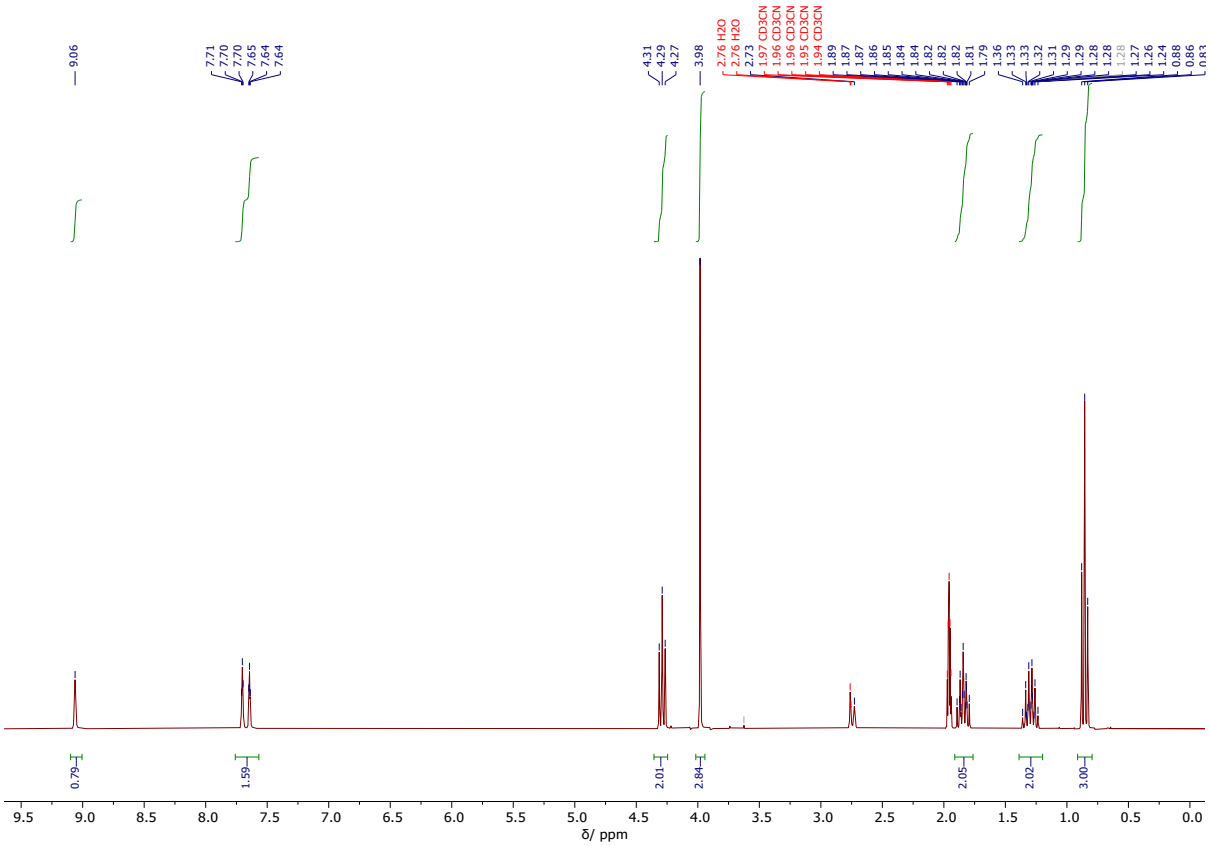
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide **3**



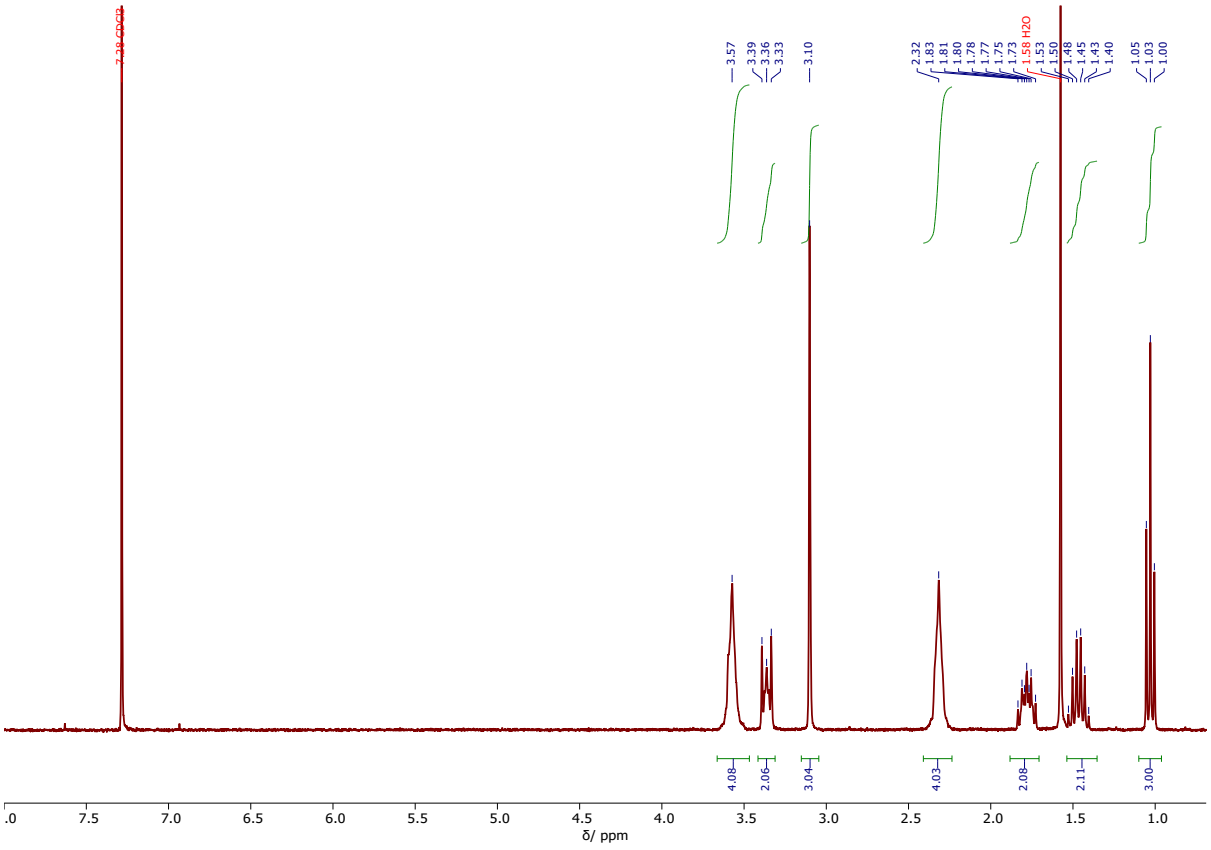
^{1}H NMR spectrum (500 MHz, CD_3CN) of 1-butyl-3-methylimidazolium tricyanomethanide **4**



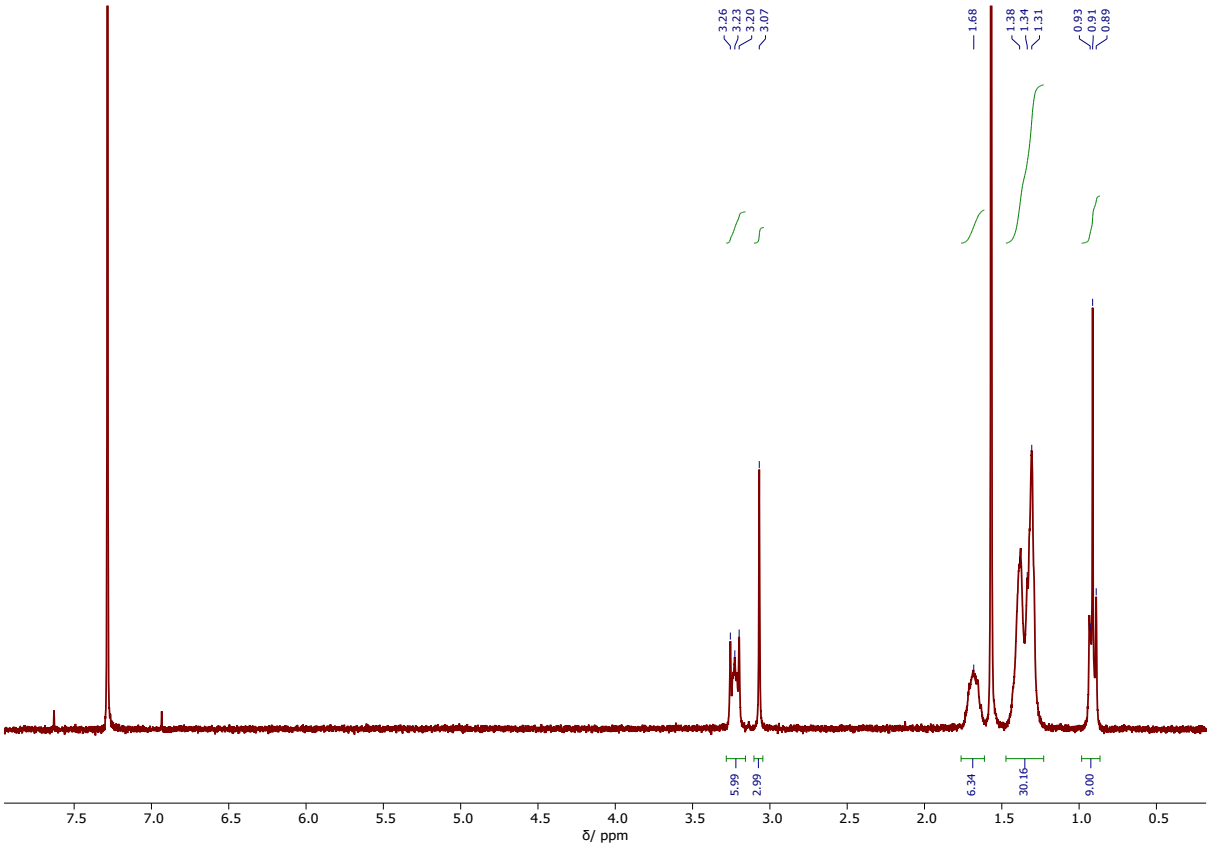
^{1}H NMR spectrum (300 MHz, CD_3CN) of 1-butyl-3-methylimidazolium dicyanimide **5**



^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 1-butyl-1-methylpyrrolidinium *bis*(trifluoromethanesulfonyl)imide **8**



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of methyltrioctylammonium *bis*(trifluoromethanesulfonyl)imide **9**



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