Electronic supporting information for

"Rationalising the effects of ionic liquids on a nucleophilic aromatic substitution reaction"

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Synthesis of the ionic liquids **3-7**

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

n-Bromobutane (50.0 mL, 0.464 mol) was added to *N*-methylpyrrolidine (30.0 mL, 0.288 mol) and stirred at room temperature under a nitrogen atmosphere for 2 days. During this time a white solid formed. This solid was then triturated with ethyl acetate (5 x 200 mL) and any resulting solvent was removed under reduced pressure to yield the bromide salt as a cream solid (59.0 g, 0.265 mol, 92%). m.p. 217-220 °C (lit.[1] 216-217 °C). ^{1}H NMR (400 MHz, CD_3CN): δ 0.97 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.38 (m, 2H, $CH_3C\underline{H}_2$), 1.72 (m, 2H, $NCH_2C\underline{H}_2CH_2CH_3$), 2.15 (m, 4H, $NCH_2C\underline{H}_2C\underline{H}_2CH_2N$), 2.97 (s, 3H, $N(C\underline{H}_3)$), 3.27 (m, 2H, $NC\underline{H}_2CH_2CH_2CH_3$), 3.44 (m, 4H, $NC\underline{H}_2CH_2CH_2C\underline{H}_2N$).

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (26.9 g, 0.0938 mol) in water (100 mL) was added to a solution of *N*-butyl-*N*-methylpyrrolidinium bromide (18.5 g, 0.0834 mol) in water (100 mL). Immediately two layers formed, and this mixture was stirred at room temperature for 20 hours. The aqueous layer was extracted with dichloromethane (3 x 100 mL) and then the combined organic layers were washed with water (15 x 150 mL). The residual solvent was removed under reduced pressure to yield the salt **5** as a light yellow viscous oil (29.1 g, 0.0690 mol, 83%). ^{1}H NMR (300 MHz, CD_3CN): δ 0.96 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.36 (m, 2H, $CH_3C\underline{H}_2$), 1.71 (m, 2H, $NCH_2C\underline{H}_2CH_2CH_3$), 2.15 (m, 4H, $NCH_2C\underline{H}_2C\underline{H}_2CH_2N$), 2.93 (s, 3H, $N(C\underline{H}_3)$), 3.21 (m, 2H, $NC\underline{H}_2CH_2CH_2CH_3$), 3.39 (m, 4H, $NC\underline{H}_2CH_2CH_2C\underline{H}_2N$).

1-Butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide 4

N-Methylimidazole (50.0 mL, 0.627 mol) was added to *n*-bromobutane (82.0 mL, 0.753 mol) and was stirred at room temperature under a nitrogen atmosphere for 7 days. During this time a white precipitate formed. The resulting solid was triturated with ethyl acetate (5 x 200 mL) and any resulting solvent was removed under reduced pressure to yield the bromide salt as a white solid (125 g, 0.571 mol, 91%). m.p. 66-71 °C (lit.[2] 70 °C). ^{1}H NMR (300 MHz, CD_3CN): δ 0.94 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.31 (m, 2H, $CH_3C\underline{H}_2$), 1.81 (m, 2H, $NCH_2C\underline{H}_2CH_2CH_3$), 3.85 (s, 3H, $N(C\underline{H}_3)$), 4.16 (t, J = 7.2 Hz, 2H, $NC\underline{H}_2CH_2CH_3$), 7.40 (m, 2H, $NC\underline{H}C\underline{H}N$), 8.88 (s, 1H, $NC\underline{H}N$).

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (57.8 g, 0.201 mol) in water (50 mL) was added to a solution of the 1-butyl-3-methylimidazolium bromide (34.1 g, 0.155 mol) in water (100 mL), immediately forming two layers that were stirred for 17 hours at room temperature. Dichloromethane (100 mL) was added and the mixture was washed with water (10 x 100 mL). The dichloromethane was removed *in vacuo* to give the salt **4** as a colourless viscous liquid (56.4 g, 0.134 mol, 87%). ^{1}H NMR (400 MHz, CD_3CN): δ 0.94 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.32 (m, 2H, $CH_3C\underline{H}_2$), 1.80 (m, 2H, $NCH_2C\underline{H}_2CH_2CH_3$), 3.81 (s, 3H, $N(C\underline{H}_3)$), 4.11 (t, J = 7.3 Hz, 2H, $NC\underline{H}_2CH_2CH_3$), 7.34 (m, 2H, $NC\underline{H}C\underline{H}N$), 8.39 (s, 1H, $NC\underline{H}N$).

1-Butyl-2,3-dimethylimidazolium *bis*(trifluoromethanesulfonyl)imide 5

n-Chlorobutane (65 mL, 0.622 mol) and acetonitrile (57 mL) were added to 1,2-dimethylimidazole **(**37.4 g, 0.389 mol) and the resulting mixture was heated at 60°C with stirring under a nitrogen atmosphere for 25 days. The resulting yellow reaction mixture was concentrated *in vacuo* and the solvent was removed from the cream solid under reduced pressure. The solid was recrystallised (1:1 acetonitrile/toluene) giving colourless crystals. The crystals were triturated with ethyl acetate (5 x 100 mL) and any remaining solvent removed under reduced pressure, giving 1-butyl-2,3-dimethylimidazolium chloride as white crystalline solid (40.3 g, 0.214 mol, 55%). m.p. 75-80°C (lit.[3] 79 °C). ^{1}H NMR (300 MHz, CD_3CN): δ 0.94 (t, J = 7.3 Hz, 3H, $CH_2C\underline{H}_3$), 1.34 (m, 2H, $CH_3C\underline{H}_2$), 1.74 (m, 2H, $NCH_2C\underline{H}_2CH_2CH_3$), 2.49 (s, 3H, $NC(C\underline{H}_3)NCH_3$), 3.69 (s, 3H, $N(C\underline{H}_3)$, 4.03 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2CH_2CH_2CH_3$), 7.26 (m, 2H, $NC\underline{H}C\underline{H}N$).

A solution of the 1-butyl-2,3-dimethylimidazolium chloride (40.3 g, 0.214 mol) in water (150 mL) was added to lithium *bis*(trifluoromethylsulfonyl)imide (74.3 g, 0.259 mol) in water (150 mL), immediately forming two layers that were stirred for 18 hours at room temperature. Dichloromethane (50 mL) was added and the mixture repeatedly washed with water (11 x 100 mL). The dichloromethane was removed *in vacuo* to give a colourless liquid that was dried under reduced pressure for 36 hours to yield the salt **5** as a colourless, viscous liquid (82.1 g, 0.189 mol, 89%). ^{1}H NMR (300 MHz, CD_3CN): δ 0.94 (t, J = 7.3 Hz, 3H, $CH_2C\underline{H}_3$), 1.33 (m, 2H, $CH_3C\underline{H}_2$), 1.73 (m, 2H, $NCH_2C\underline{H}_2CH_2CH_3$), 2.49 (s, 3H, $NC(C\underline{H}_3)NCH_3$), 3.68 (s, 3H, $NC\underline{H}_3$), 4.02 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2CH_2CH_2CH_3$), 7.24 (m, 2H, $NC\underline{H}C\underline{H}N$).

1-Butyl-2,3,4,5-tetramethylimidazolium *bis*(trifluoromethanesulfonyl)imide 6

n-Bromobutane (43 mL, 0.403 mol) was added to tetramethylimidazole (12.5 g, 0.101 mol) and the resulting mixture was stirred at room temperature under a nitrogen atmosphere for 6 days. During this time a white precipitate formed. The mixture was then triturated with ethyl acetate (5 x 150 mL) and then the residual solvent was removed under reduced pressure to yield the bromide salt as a white solid (21.4 g, 0.0821 mol, 82%). m.p. 86-91°C (lit.[4] 95 °C). ^{1}H NMR (300 MHz, CD_3CN): δ 0.94 (t, J = 7.3 Hz, 3H, $CH_2C\underline{H}_3$), 1.38 (m, 2H, $CH_3C\underline{H}_2$), 1.63 (m, 2H, $NCH_2C\underline{H}_2CH_2CH_3$), 2.18 (s, 3H, $NC(C\underline{H}_3)C(CH_3)N$), 2.20 (s, 3H, $NC(CH_3)C(C\underline{H}_3)N$), 2.51 (s, 3H, $NC(C\underline{H}_3)NCH_3$), 3.55 (s, 3H, $N(C\underline{H}_3)$, 3.97 (m, 2H, $NC\underline{H}_2CH_2CH_2CH_3$).

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (38.5 g, 0.134 mol) in water (100 mL) was added to a solution of the 1-butyl-2,3,4,5-tetramethylimidazolium bromide (28.8 g, 0.110 mol) in water (50 mL), immediately forming two layers that were stirred for 17 hours at room temperature. Dichloromethane (100 mL) was added and the mixture was washed with water (10 x 100 mL). The dichloromethane was removed *in vacuo* to give the salt **6** as a white solid (47.9 g, 0.104 mol, 94%). m.p. 29-32 °C (lit.[5] 31-32 °C). ^{1}H NMR (300 MHz, CD_3CN): δ 0.95 (t, J = 7.3 Hz, 3H, $CH_2C\underline{H}_3$), 1.35 (m, 2H, $CH_3C\underline{H}_2$), 1.63 (m, 2H, $NCH_2C\underline{H}_2CH_2CH_3$), 2.17 (s, 3H,

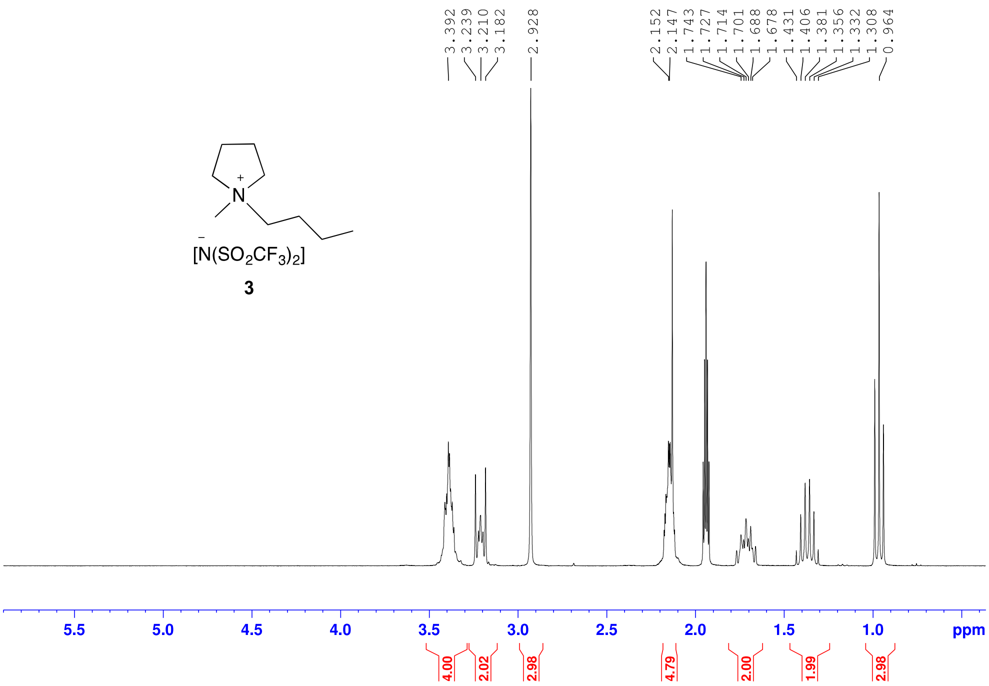
$NC(C\underline{H}_3)C(CH_3)N$), 2.20 (s, 3H, $NC(CH_3)C(C\underline{H}_3)N$), 2.49 (s, 3H, $NC(C\underline{H}_3)NCH_3$), 3.53 (s, 3H, $N(C\underline{H}_3)$), 3.95 (m, 2H, $NC\underline{H}_2CH_2CH_2CH_3$).

Tetraoctylammonium *bis*(trifluoromethanesulfonyl)imide 7

A solution of lithium *bis*(trifluoromethanesulfonyl)imide (8.78 g, 0.0306 mol) in water (50 mL) was added to a solution of tetraoctylammonium bromide (9.18 g, 0.0168 mol) in acetone/water (1/1, 100 mL). Immediately two layers formed and this reaction mixture was stirred for 24 hours. Dichloromethane (75 mL) was added and this was washed with water (10 x 100 mL). The organic layer was then concentrated under reduced pressure to give the salt **7** as a white solid (11.2 g, 0.0150 mol, 89%). m.p. 27-30 °C (lit.[5] 30-31 °C). ^1H NMR (300 MHz, CD_3CN): δ 0.90 (m, 12H, $NCH_2CH_2(CH_2)_5C\underline{H}_3$), 1.31 (m, 40H, $NCH_2CH_2(C\underline{H}_2)_5CH_3$), 1.57 (m, 8H, $NCH_2C\underline{H}_2(CH_2)_5CH_3$), 3.05 (m, 8H, $NC\underline{H}_2CH_2(CH_2)_5CH_3$).

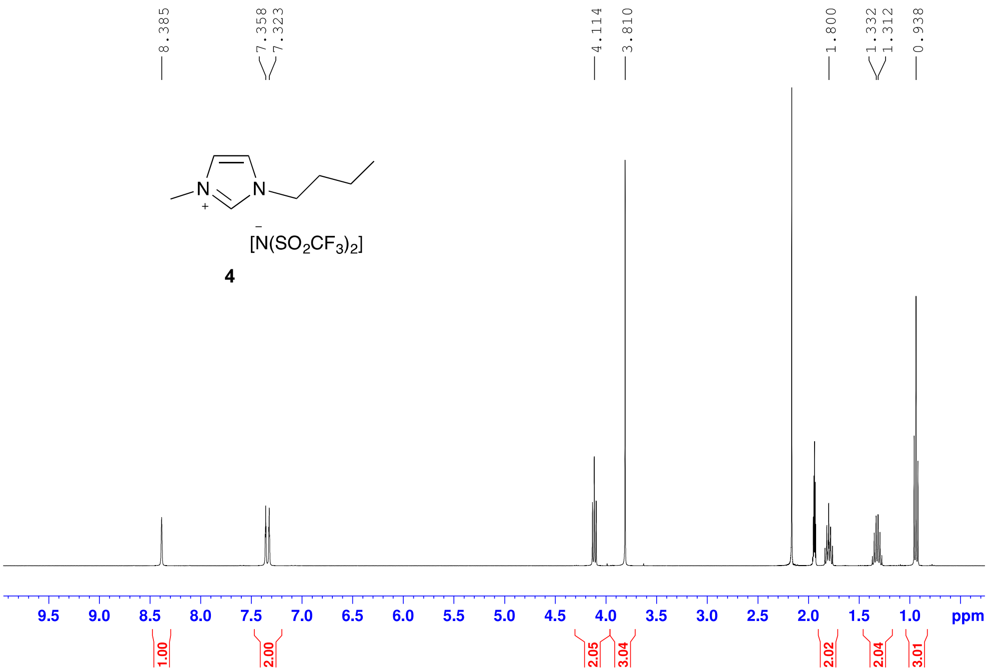
<u>^{1}H NMR spectra of the ionic liquids **3-7**</u>

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



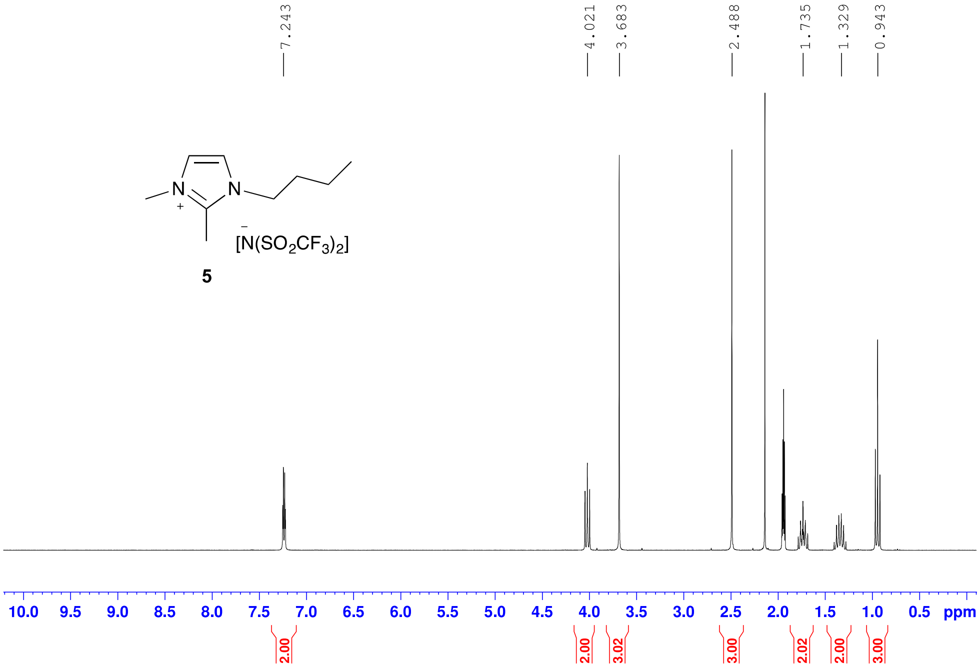
N.B. Residual solvent signal at δ2.15.

1-Butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide **4**



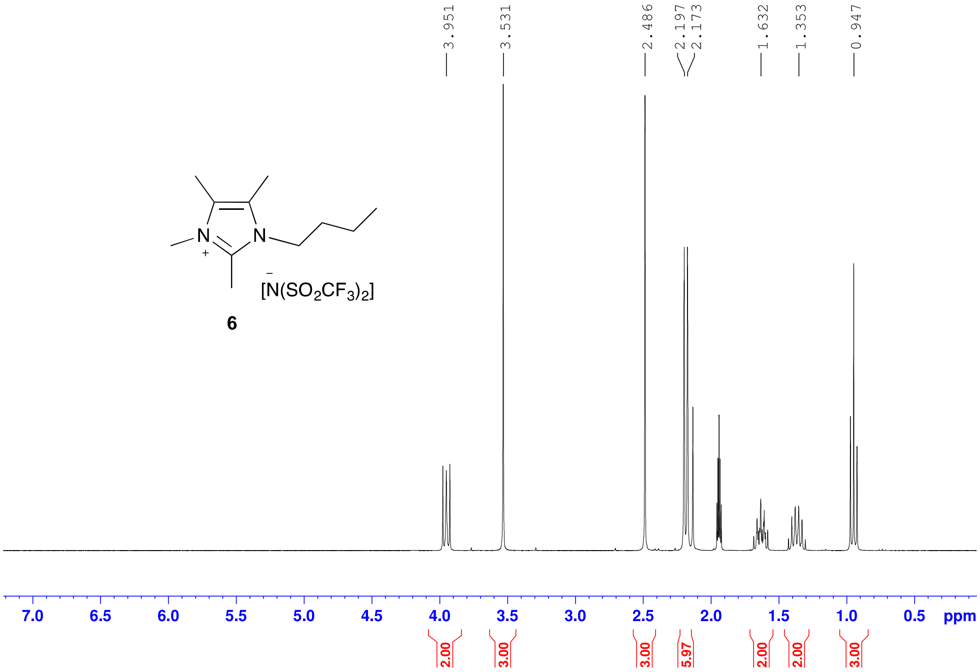
N.B. Residual solvent signal at δ2.15.

1-Butyl-2,3-dimethylimidazolium *bis*(trifluoromethanesulfonyl)imide **5**



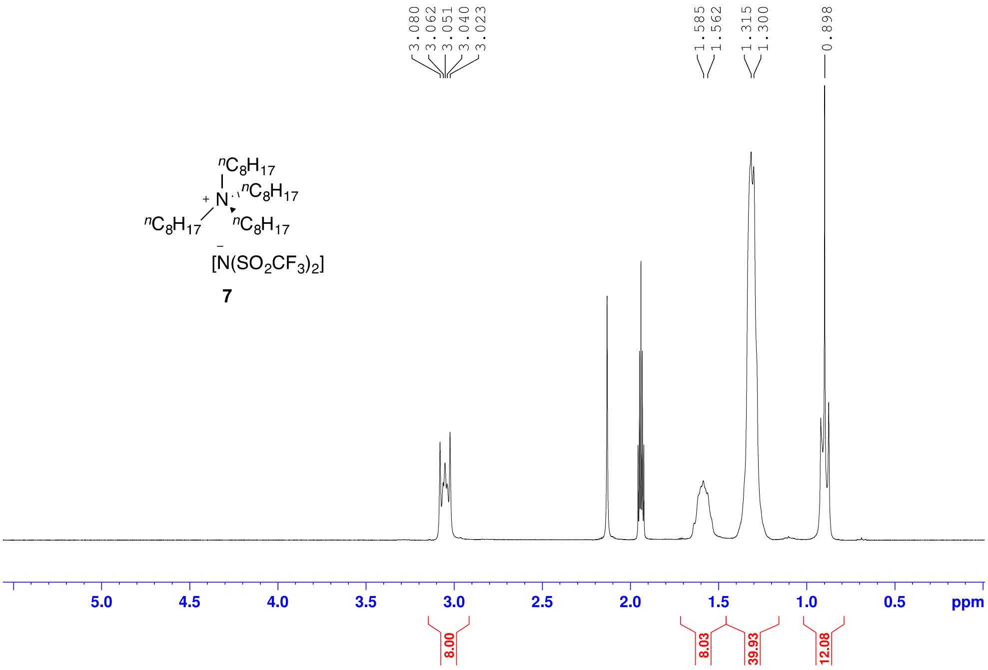
N.B. Residual solvent signal at δ2.15.

1-Butyl-2,3,4,5-tetramethylimidazolium *bis*(trifluoromethanesulfonyl)imide **6**



N.B. Residual solvent signal at δ2.15.

Tetraoctylammonium *bis*(trifluoromethanesulfonyl)imide **7**



N.B. Residual solvent signal at δ2.15.

Kinetic analyses

Examining the kinetics of the nucleophilic aromatic substitution reaction between the fluorodinitrobenzene 1 and ethanol, in ethanol and the ionic liquids 3-7

To determine the rate constants of the reaction of ethanol with benzene **1** in mixtures containing different amounts of each of the ionic liquids **3-7**, standard solutions were prepared containing triethylamine (*ca.* 0.35 mol L^{-1}) and varying concentrations of ethanol dissolved in one of the ionic liquids **3-7** to the desired mole fraction (See Tables S1-S6 for exact quantities).

To determine the activation parameters for the reaction in the molecular solvent, ethanol, a standard solution was prepared containing triethylamine (*ca.* 0.35 mol L^{-1}) in ethanol (total volume, 10 mL). To determine the activation parameters for the ionic liquid solvents **3-7**, standard solutions were prepared containing triethylamine (*ca.* 0.35 mol L^{-1}) and ethanol (*ca.* 0.50 mol L^{-1}) dissolved in one of the ionic liquids **3-7** to a total volume of 10 mL (See Tables S7-S13 for exact quantities).

The probe in the NMR spectrometer was equilibrated to the desired temperature. 1-Fluoro-2,4-dinitrobenzene **1** (*ca.* 3 mg, 0.02 mmol) was added to a 5 mm NMR tube followed by an aliquot of a standard solution (0.50 mL). Reaction progress was followed using ^{19}F NMR spectroscopy to observe the depletion of the starting material **1** signal at δ *ca.* -110. The pseudo first order rate constant (k_{obs}) and, using the concentration of ethanol (Equation S1), the second order rate constant (k_2) were determined from the change in integration of this signal. These data were used in the bimolecular form of the Eyring equation (Equation S2) to create an Eyring plot and calculate the activation parameters in each case.

$$k_{obs} = k_2[EtOH] \qquad \text{(S1)}$$

$$\ln\left(\frac{k_2 h}{k_B R T^2}\right) = \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \qquad \text{(S2)}$$

Rate data for the mole fraction dependence plots shown in Figures 1 and 2

Table S1. Masses used to prepare reaction mixtures, mole fraction of ionic liquid and concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in mixtures containing [bmim][N(SO_2CF_3)$_2$] **4** at 324 K.

Mole fraction	**Masses**			**Concentrations**		**Rate constants**	
IL 4	**IL / g**	**NEt_3 / g**	**EtOH / g**	**[NEt_3] / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-5} L mol^{-1} s^{-1}**
0	0	0.0700	1.51	0.346	16.4	1.12	0.684
						1.32	0.804
						0.949	0.578
0.102	1.02	0.0706	0.956	0.349	10.4	4.06	3.91
						3.92	3.78
						3.84	3.70
0.202	1.59	0.0714	0.654	0.353	7.10	4.29	6.04
						3.78	5.32
						4.16	5.86
0.301	1.93	0.0714	0.461	0.352	5.00	4.22	8.45
						4.24	8.49
						4.13	8.26
0.400	2.17	0.0715	0.325	0.353	3.52	4.56	13.0
						3.99	11.3
						3.97	11.3
0.502	2.36	0.0715	0.225	0.353	2.44	3.81	15.6
						4.07	16.7
						4.24	17.4
0.545	2.41	0.0723	0.188	0.357	2.04	4.01	19.7
						3.92	19.2
						3.94	19.3
0.599	2.47	0.0711	0.150	0.351	1.62	3.75	23.1
						3.62	22.3
						4.21	25.9
0.666	2.55	0.0710	0.108	0.351	1.18	3.17	26.9
						3.29	28.0
						2.72	23.1
0.692	2.59	0.0740	0.0927	0.366	1.01	3.11	30.9
						3.19	31.7
						3.11	30.9
0.754	2.64	0.0712	0.0624	0.352	0.677	2.70	39.8
						2.21	32.6
						2.52	37.3
0.791	2.68	0.0710	0.0451	0.351	0.489	2.25	45.9
						2.01	41.2
						2.15	43.9
0.801	2.69	0.0697	0.0416	0.344	0.452	1.85	41.1
						1.96	43.4
						1.58	35.0

Table S2. Masses used to prepare reaction mixtures, mole fraction of ionic liquid and concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in mixtures containing [bmpyr][N(SO_2CF_3)$_2$] **3** at 324 K.

Mole fraction	**Masses**			**Concentrations**		**Rate constants**	
IL 3	**IL / g**	**NEt_3 / g**	**EtOH / g**	**[NEt_3] / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-5} L mol^{-1} s^{-1}**
0.104	1.03	0.0717	0.931	0.354	10.1	4.54	4.49
						5.19	5.13
						4.62	4.58
0.198	1.54	0.0719	0.645	0.355	7.00	3.89	5.56
						4.04	5.77
						3.80	5.43
0.306	1.91	0.0713	0.440	0.352	4.78	4.78	10.0
						4.52	9.46
						5.00	10.5
0.394	2.11	0.0718	0.321	0.355	3.48	4.09	11.7
						4.21	12.1
						4.30	12.3
0.501	2.29	0.0712	0.217	0.352	2.35	4.53	19.3
						4.59	19.5
						4.66	19.8
0.546	2.36	0.0717	0.181	0.354	1.97	4.03	20.5
						4.33	23.3
0.594	2.41	0.0699	0.148	0.354	1.61	3.92	24.4
						4.12	25.7
						4.42	27.5
0.665	2.49	0.0703	0.105	0.347	1.14	4.01	35.1
						4.59	40.2
						3.33	29.1
0.688	2.53	0.0711	0.0925	0.351	1.00	4.07	40.5
						3.61	35.9
						3.50	34.8
0.745	2.56	0.0713	0.0630	0.352	0.684	3.01	43.9
						2.26	33.1
						2.25	32.9
0.745	2.56	0.0705	0.0645	0.348	0.700	3.18	45.4
						2.85	40.7
0.785	2.57	0.0708	0.0446	0.350	0.484	2.46	50.9
						2.48	51.2
0.785[i]	12.9	0.341	0.218	0.337	0.472	2.31	48.9
						2.10	44.5

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[i] Duplicate mole fraction as these data are a subset of the temperature dependent data; solution was prepared to 10 mL rather than 2 mL.

Table S3. Masses used to prepare reaction mixtures, mole fraction of ionic liquid and concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in mixtures containing [bm$_2$im][N(SO$_2$CF$_3$)$_2$] **5** at 324 K.

Mole fraction	**Masses**			**Concentrations**		**Rate constants**	
IL 5	**IL / g**	**NEt$_3$ / g**	**EtOH / g**	**[NEt$_3$] / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-5} L mol^{-1} s^{-1}**
0.0730	0.774	0.0707	1.01	0.349	10.9	4.13	3.77
						5.41	4.94
						3.98	3.63
0.142	1.23	0.0700	0.758	0.346	8.23	5.11	6.21
						5.62	6.83
						5.21	6.33
0.241	1.65	0.0716	0.520	0.354	5.65	4.80	8.50
						3.70	6.56
						5.58	9.89
0.341	1.94	0.0703	0.366	0.347	3.97	4.86	12.3
						5.14	12.9
0.351	2.04	0.0704	0.368	0.348	4.00	4.83	12.1
						4.73	11.8
						4.75	11.9
0.461	2.19	0.0710	0.240	0.351	2.61	4.04	15.5
						5.00	19.2
						4.89	18.8
0.527	2.37	0.0698	0.194	0.345	2.11	5.20	24.6
						4.87	23.2
						4.94	23.4
0.569	2.40	0.0725	0.160	0.358	1.74	5.53	31.8
						5.35	30.8
0.571	2.41	0.0739	0.159	0.365	1.72	5.39	31.2
						3.96	23.0
						3.38	19.6
0.618	2.37	0.0733	0.122	0.362	1.32	5.61	42.4
						4.85	36.7
						6.25	47.2
0.705	2.44	0.0722	0.0758	0.357	0.823	4.02	48.8
						4.09	49.7
						4.24	51.6
0.817[ii]	13.2	0.350	0.154	0.346	0.335	2.29	68.5
						2.27	67.7
						2.19	65.4

[ii] These data are a subset of the temperature dependent data; solution was prepared to 10 mL rather than 2 mL.

Table S4. Masses used to prepare reaction mixtures, mole fraction of ionic liquid and concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in mixtures containing [bm$_4$im][N(SO$_2$CF$_3$)$_2$] **6** at 324 K.

Mole fraction	**Masses**			**Concentrations**		**Rate constants**	
IL 6	**IL / g**	**NEt$_3$ / g**	**EtOH / g**	**[NEt$_3$] / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-5} L mol^{-1} s^{-1}**
0.102	1.06	0.0700	0.902	0.346	9.79	4.60	4.70
						4.24	4.32
						4.53	4.63
0.212	1.65	0.0680	0.584	0.336	6.33	4.75	7.50
						4.63	7.30
						4.96	7.84
0.295	1.90	0.0700	0.420	0.346	4.56	5.77	12.7
						4.52	9.91
						3.81	8.36
0.408	2.17	0.0652	0.285	0.322	3.09	5.21	16.9
						4.88	15.8
						4.52	14.6
0.486	2.25	0.0700	0.205	0.346	2.23	5.66	26.5
						5.27	24.7
						5.40	25.3
0.499	2.29	0.0716	0.197	0.354	2.14	6.00	28.1
						5.54	25.9
0.603	2.42	0.0688	0.128	0.340	1.38	5.03	36.4
						4.88	35.3
						4.83	34.9
0.689	2.45	0.0727	0.0773	0.359	0.839	4.57	54.4
						4.21	50.1
						4.13	49.2
0.694	2.50	0.0724	0.0767	0.358	0.832	4.61	55.4
						4.80	57.7
0.795	2.56	0.0768	0.0311	0.379	0.338	2.04	60.4
						2.06	60.9
0.798	2.52	0.0700	0.0320	0.346	0.347	2.61	75.1
						2.79	80.3
						2.48	71.3
0.793[iii]	12.7	0.340	0.176	0.336	0.382	2.70	70.8
						2.86	74.9
						2.38	62.4

[iii] Duplicate mole fraction as these data are a subset of the temperature dependent data; solution was prepared to 10 mL rather than 2 mL.

Table S5. Masses used to prepare reaction mixtures, mole fraction of ionic liquid and concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in mixtures containing [TOA][N(SO_2CF_3)$_2$] **7** at 324 K.

Mole fraction	**Masses**			**Concentrations**		**Rate constants**	
IL 7	**IL / g**	**NEt_3 / g**	**EtOH / g**	**[NEt_3] / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-5} L mol^{-1} s^{-1}**
0.071	0.994	0.0723	0.775	0.357	8.41	4.36	5.18
						3.60	4.28
						3.28	3.89
0.148	1.40	0.0730	0.464	0.361	5.03	5.34	10.6
						5.48	10.9
						5.49	10.9
0.220	1.52	0.0704	0.301	0.348	3.27	4.57	14.0
						6.18	18.9
						5.06	15.5
0.308	1.67	0.0715	0.198	0.353	2.15	6.10	28.4
						4.77	22.2
						6.15	28.7
0.374	1.82	0.0720	0.155	0.356	1.69	4.78	28.4
						4.98	29.5
						2.79	16.5
0.442	1.88	0.0711	0.114	0.351	1.24	3.81	30.9
						5.62	45.5
						6.75	54.6
0.510	1.92	0.0712	0.0810	0.352	0.879	4.33	49.3
						4.37	49.7
						4.86	55.2
0.583	1.86	0.0711	0.0496	0.351	0.538	3.43	63.8
						3.93	73.0
						3.92	72.9
0.661[iv]	9.85	0.300	0.174	0.297	0.379	3.23	85.3
						3.51	92.7
						3.25	85.8

[iv] These data are a subset of the temperature dependent data; solution was prepared to 10 mL rather than 2 mL.

Table S6. Masses used to prepare reaction mixtures, mole fraction of ionic liquid and concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in mixtures containing Li[N(SO_2CF_3)$_2$] at 324 K.

Mole fraction	**Masses**			**Concentrations**		**Rate constants**	
SALT	**SALT / g**	**NEt_3 / g**	**EtOH / g**	**[NEt_3] / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-5} L mol^{-1} s^{-1}**
0.014	0.130	0.0706	1.44	0.349	15.7	3.49	2.23
						3.41	2.18
						4.00	2.55
0.033	0.300	0.0767	1.37	0.379	14.9	7.03	4.72
						8.67	5.82
						9.58	6.43
0.055	0.488	0.0740	1.30	0.366	14.1	25.8	18.3
						12.5	8.88
						14.2	10.1
0.089	0.778	0.0883	1.23	0.436	13.4	37.2	27.8
						24.9	18.6
						20.7	15.5
0.122	0.987	0.0746	1.10	0.369	12.0	34.1	28.4
						32.4	27.1
						24.9	20.7
0.155[v]	5.90	0.350	5.00	0.346	10.9	37.2	34.3
						34.5	31.8
						31.9	29.4

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[v] These data are a subset of the temperature dependent data; solution was prepared to 10 mL rather than 2 mL.

Eyring plot for the data shown in Table 2 in the main text

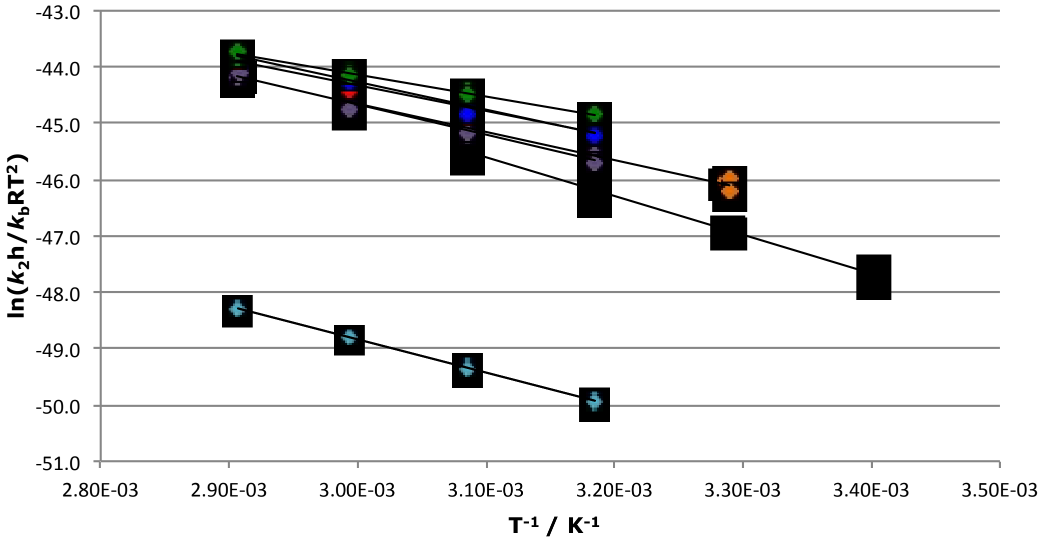

Figure S1. The Eyring plot for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol in mixtures containing either no added salt (◆), [bmpyr][$N(SO_2CF_3)_2$] **3** (◆), [bmim][$N(SO_2CF_3)_2$] **4** (◆), [bm$_2$im][$N(SO_2CF_3)_2$] **5** (◆), [bm$_4$im][$N(SO_2CF_3)_2$] **6** (◆), [TOA][$N(SO_2CF_3)_2$] **7** (◆) or Li[$N(SO_2CF_3)_2$] (◆) at the highest mole fraction used.

Rate data for the Eyring plot shown in Figure S1

Table S7. Masses used to prepare reaction mixtures, concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in ethanol.

Masses			**Concentrations**			**Rate constants**	
IL / g	**NEt_3 / g**	**EtOH / g**	**$[NEt_3]$ / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-5} s^{-1}**	**k_2 / 10^{-5} L mol^{-1} s^{-1}**
0	0.350	7.54	0.346	16.4	314.0	5.93	0.363
					314.0	5.60	0.342
					314.0	5.74	0.351
					324.0	11.5	0.701
					324.0	11.3	0.691
					324.0	10.8	0.658
					334.0	20.0	1.22
					334.0	20.1	1.23
					334.0	20.3	1.24
					344.0	36.3	2.22
					344.0	35.5	2.17
					344.0	35.4	2.16

Table S8. Masses used to prepare reaction mixtures, concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in [bmim][$N(SO_2CF_3)_2$] **4** ($\chi_{IL} = 0.796$).

Masses			**Concentrations**			**Rate constants**	
IL / g	**NEt_3 / g**	**EtOH / g**	**$[NEt_3]$ / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
13.2	0.352	0.214	0.346	0.465	314.0	1.29	2.77
					314.1	1.18	2.53
					314.0	1.10	2.37
					324.1	2.33	5.01
					324.1	1.96	4.23
					324.0	2.05	4.41
					334.0	4.15	8.93
					334.0	3.65	7.86
					334.0	3.26	7.01
					344.1	6.43	13.8
					344.1	6.05	13.0
					343.9	6.54	14.1

Table S9. Masses used to prepare reaction mixtures, concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in [bmpyr][N(SO_2CF_3)$_2$] **3** (χ_{IL} = 0.784).

Masses			**Concentrations**			**Rate constants**	
IL / g	**NEt_3 / g**	**EtOH / g**	**[NEt_3] / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
12.9	0.341	0.22	0.337	0.472	304.3	0.786	1.66
					304.0	0.809	1.71
					304.0	0.658	1.39
					314.0	1.14	2.40
					314.0	1.36	2.89
					314.0	1.31	2.78
					324.0	1.86	3.94
					324.0	2.25	4.76
					334.0	4.29	9.08
					334.0	4.43	9.37
					334.0	4.02	8.51

Table S10. Masses used to prepare reaction mixtures, concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in [bm$_2$im][N(SO_2CF_3)$_2$] **5** (χ_{IL} = 0.811).

Masses			**Concentrations**			**Rate constants**	
IL / g	**NEt_3 / g**	**EtOH / g**	**[NEt_3] / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
13.2	0.350	0.154	0.346	0.335	314.1	1.46	4.36
					314.0	1.43	4.27
					314.0	1.44	4.30
					324.1	1.96	5.85
					324.0	2.27	6.78
					324.0	2.29	6.85
					334.0	3.88	11.6
					334.0	4.00	12.0
					334.0	3.36	10.0
					344.0	6.03	18.0
					344.1	5.96	17.8
					344.0	6.05	18.1

Table S11. Masses used to prepare reaction mixtures, concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in $[bm_4im][N(SO_2CF_3)_2]$ **6** (χ_{IL} = 0.786).

Masses			**Concentrations**			**Rate constants**	
IL / g	**NEt_3 / g**	**EtOH / g**	**$[NEt_3]$ / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
12.7	0.340	0.176	0.336	0.382	314.1	1.67	4.37
					314.0	1.60	4.19
					314.1	1.48	3.87
					324.1	2.70	7.08
					324.0	2.86	7.49
					324.0	2.38	6.24
					334.1	4.91	12.9
					334.0	4.85	12.7
					334.0	4.35	11.4
					344.1	7.18	18.8
					344.1	7.30	19.1
					344.0	7.39	19.4

Table S12. Masses used to prepare reaction mixtures, concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in $[TOA][N(SO_2CF_3)_2]$ **7** (χ_{IL} = 0.651).

Masses			**Concentrations**			**Rate constants**	
IL / g	**NEt_3 / g**	**EtOH / g**	**$[NEt_3]$ / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
9.85	0.300	0.174	0.297	0.379	314.0	2.17	5.73
					314.0	2.09	5.52
					314.1	2.19	5.79
					324.0	3.24	8.56
					324.0	3.26	8.62
					324.1	3.43	9.07
					334.0	5.17	13.7
					334.1	5.07	13.4
					334.0	4.71	12.4
					344.0	6.92	18.3
					344.1	7.64	20.2
					344.1	8.35	22.1

Table S13. Masses used to prepare reaction mixtures, concentrations of reagents in the reaction mixture, and rate constants for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) in mixtures containing Li[N(SO_2CF_3)$_2$] (χ_{salt} = 0.155).

Masses			**Concentrations**			**Rate constants**	
Salt / g	**NEt_3 / g**	**EtOH / g**	**[NEt_3] / mol L^{-1}**	**[EtOH] / mol L^{-1}**	**Temperature / K**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**
5.90	0.350	5.00	0.346	10.9	294.0	2.94	0.271
					294.0	2.94	0.271
					294.0	3.71	0.342
					304.1	7.59	0.699
					304.1	7.82	0.721
					304.0	7.48	0.689
					314.0	19.1	1.76
					314.0	14.4	1.32
					314.0	13.9	1.28
					324.0	37.2	3.43
					324.0	34.5	3.18
					324.0	31.9	2.94

The change in the activation parameters from χ_{IL} 0 → 0.5, χ_{IL} 0.5 → 0.8 and χ_{IL} 0 → 0.8

Table S14. The change in the enthalpy ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) on changing solvent composition

Solvent	□□□□ □□□□□□□□ **s**	**$\Delta(\Delta H^{\ddagger})$ / kJ mol^{-1} ^{a}**	**$\Delta(\Delta S^{\ddagger})$ / J K^{-1} mol^{-1} ^{a}**
[bmpyr][N(SO_2CF_3)$_2$] **3**	χ_{IL} 0 → 0.5	-3.3 ± 2.0	19 ± 6
[bmim][N(SO_2CF_3)$_2$] **4**		0.5 ± 0.7	30 ± 3
[bm$_2$im][N(SO_2CF_3)$_2$] **5**		0.0 ± 3.9	36 ± 12
[bm$_4$im][N(SO_2CF_3)$_2$] **6**		1.5 ± 1.8	38 ± 5
[TOA][N(SO_2CF_3)$_2$] **7**		-8.0 ± 2.7	7 ± 8
[bmpyr][N(SO_2CF_3)$_2$] **3**	χ_{IL} 0.5 → 0.8	-2.7 ± 3.1	-2 ± 10
[bmim][N(SO_2CF_3)$_2$] **4**		-4.9 ± 2.0	-9 ± 6
[bm$_2$im][N(SO_2CF_3)$_2$] **5**		-10.6 ± 4.4	-30 ± 14
[bm$_4$im][N(SO_2CF_3)$_2$] **6**		-9.5 ± 2.4	-24 ± 7
[TOA][N(SO_2CF_3)$_2$] **7**		-8.6 ± 2.9	-18 ± 9
[bmpyr][N(SO_2CF_3)$_2$] **3**	χ_{IL} 0 → 0.8	-6.0 ± 2.4	17 ± 7
[bmim][N(SO_2CF_3)$_2$] **4**		-4.4 ± 1.9	21 ± 6
[bm$_2$im][N(SO_2CF_3)$_2$] **5**		-10.6 ± 2.0	6 ± 6
[bm$_4$im][N(SO_2CF_3)$_2$] **6**		-8.0 ± 1.6	14 ± 5
[TOA][N(SO_2CF_3)$_2$] **7**		-16.6 ± 1.1	-11 ± 3

[a] Errors are the compounded uncertainty of the activation parameters at both molefractions.

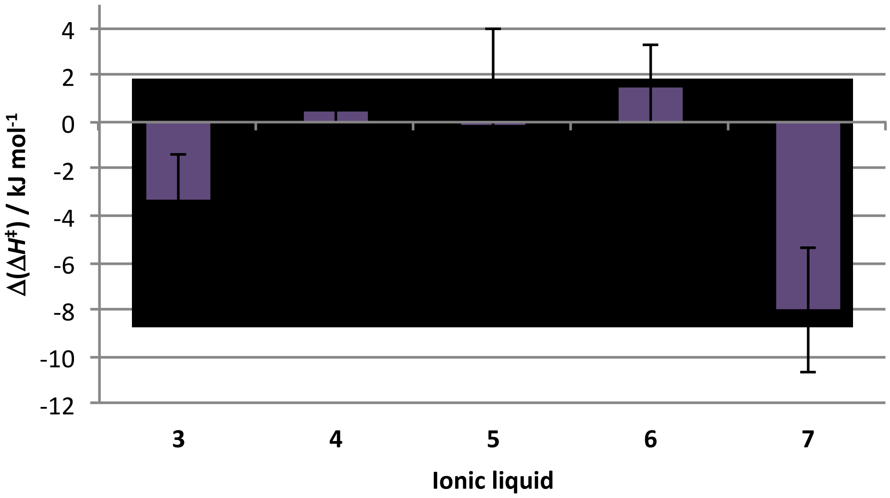

Figure S2. The change in the enthalpy of activation (Δ$H^‡$) for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) on moving from χ_{IL} 0 → 0.5 for each of the ionic liquids **3-7**.

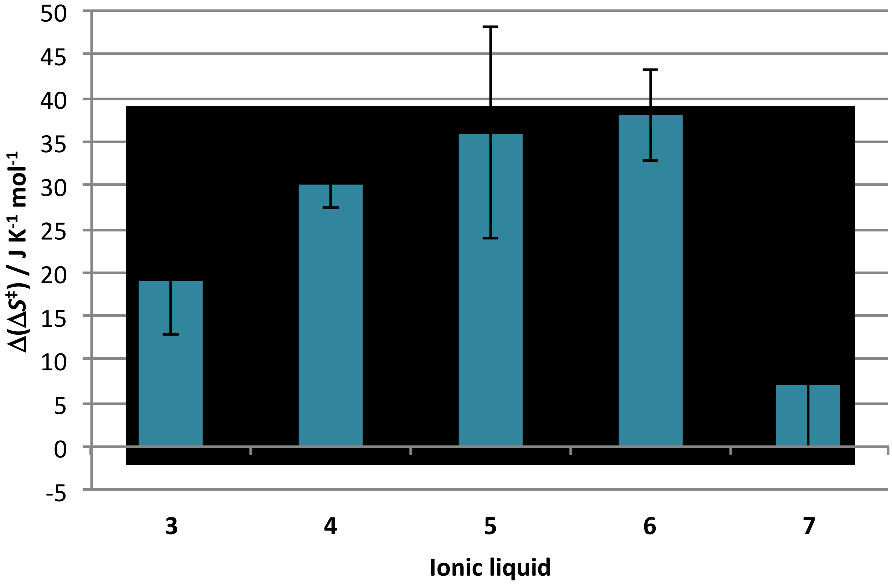

Figure S3. The change in the entropy of activation (Δ$S^‡$) for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) on moving from χ_{IL} 0 → 0.5 for each of the ionic liquids **3-7**.

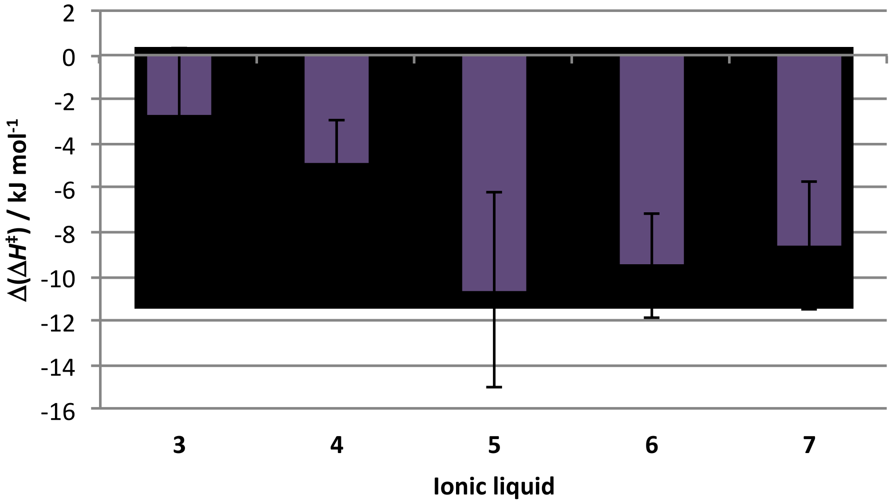

Figure S4. The change in the enthalpy of activation ($\Delta H^{\ddagger}$) for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) on moving from χ_{IL} 0.5 → 0.8 for each of the ionic liquids **3-7**.

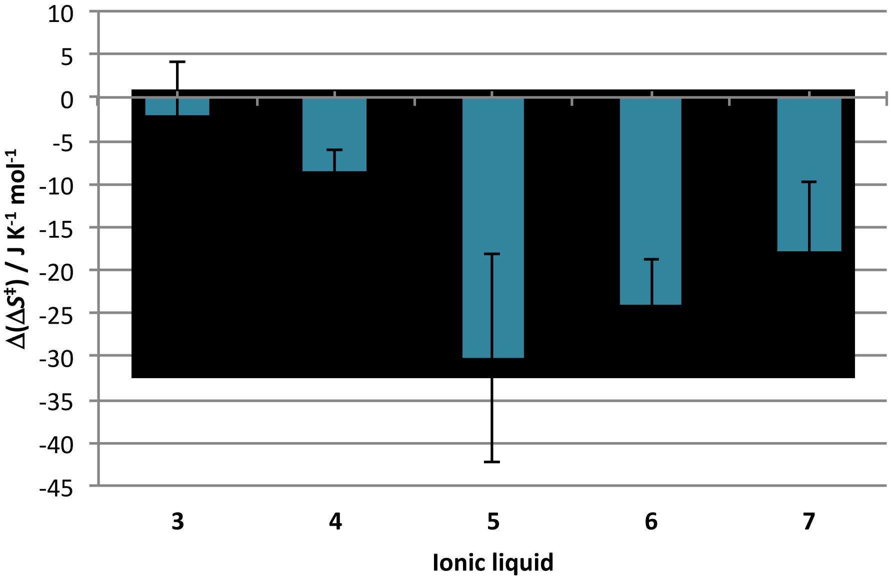

Figure S5. The change in the entropy of activation ($\Delta S^{\ddagger}$) for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) on moving from χ_{IL} 0.5 → 0.8 for each of the ionic liquids **3-7**.

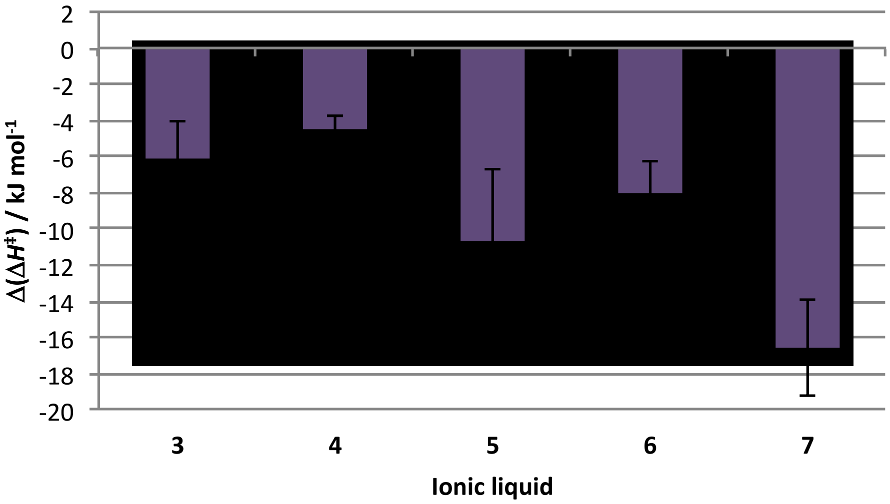

Figure S6. The change in the enthalpy of activation ($\Delta H^{\ddagger}$) for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) on moving from χ_{IL} 0 → 0.8 for each of the ionic liquids **3-7**.

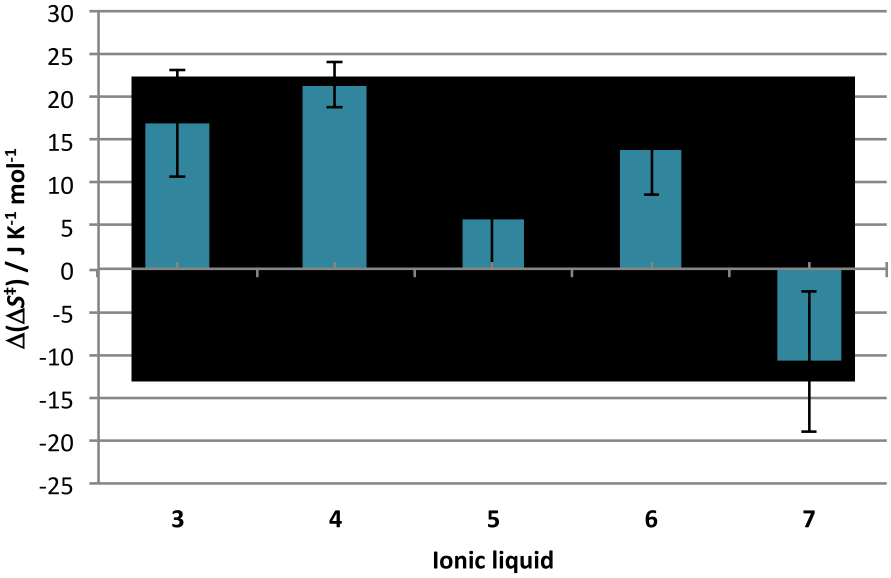

Figure S7. The change in the entropy of activation ($\Delta S^{\ddagger}$) for the reaction between 1-fluoro-2,4-dinitrobenzene **1** and ethanol (Scheme 1) on moving from χ_{IL} 0 → 0.8 for each of the ionic liquids **3-7**.

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