Supporting Information:

Developing principles for predicting ionic liquid effects on reaction outcome. A demonstration using a simple condensation reaction

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Representative plots for the determination of rate constants

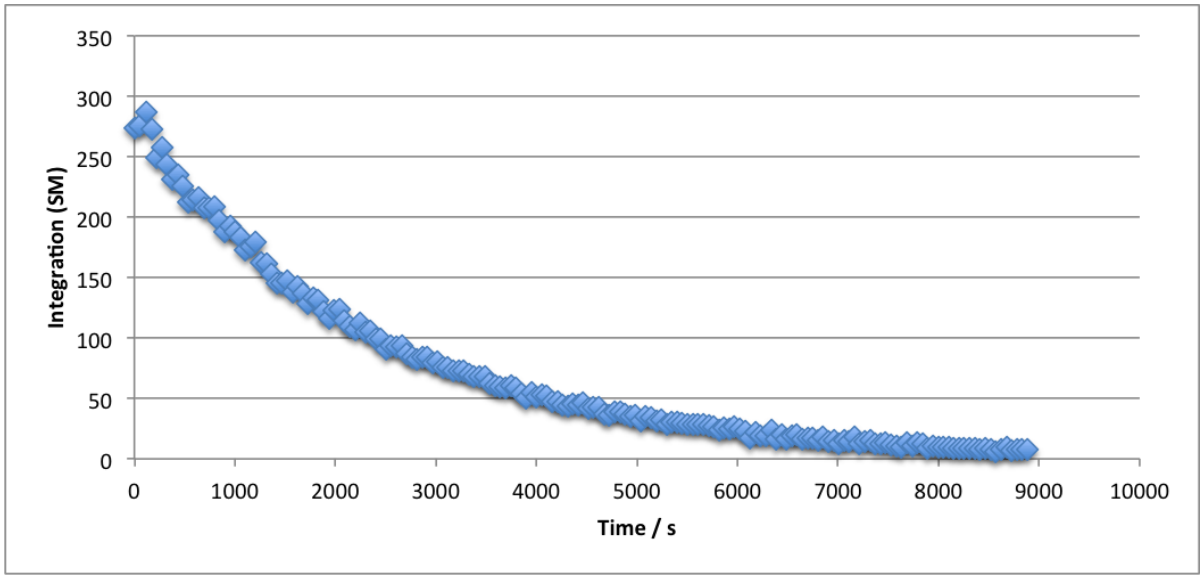

Figure S1: Plot of the integration of the signal due to the starting material **1a** in the ^{1}H NMR spectrum *vs* time for the reaction of species **1a** and **2**, in a mixture of the ionic liquid **4** in acetonitrile at a mole fraction of 0.16 at 8.1°C. Using exponential fitting in Graphpad Prism the R^2 value is 0.998 and the rate constant determined was $(4.17 \pm 0.04) \times 10^{-4}$ s^{-1}.

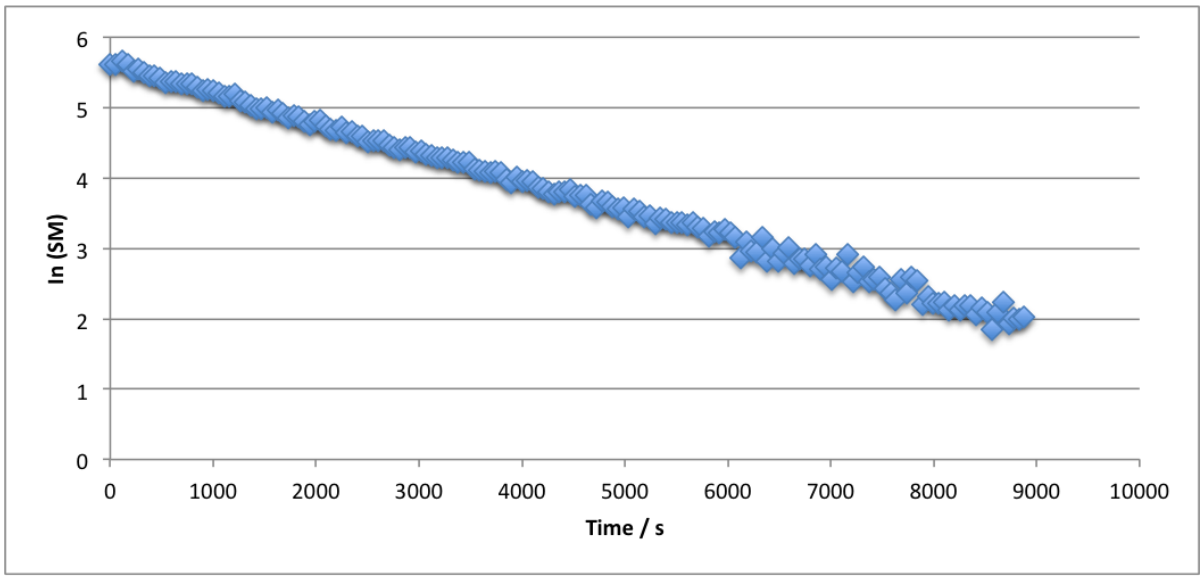

Figure S2: Plot of the natural logarithm of the integration of the signal due to the starting material **1a** in the ^{1}H NMR spectrum *vs* time, for the case shown in Figure S1 above (the reaction of species **1a** and **2** in a mixture of the ionic liquid **4** in acetonitrile at a mole fraction of 0.16 at 8.1°C). Using the LINEST function in Excel, the R^2 value is 0.995 and the rate constant determined was $(4.13 \pm 0.02) \times 10^{-4}$ s^{-1}.

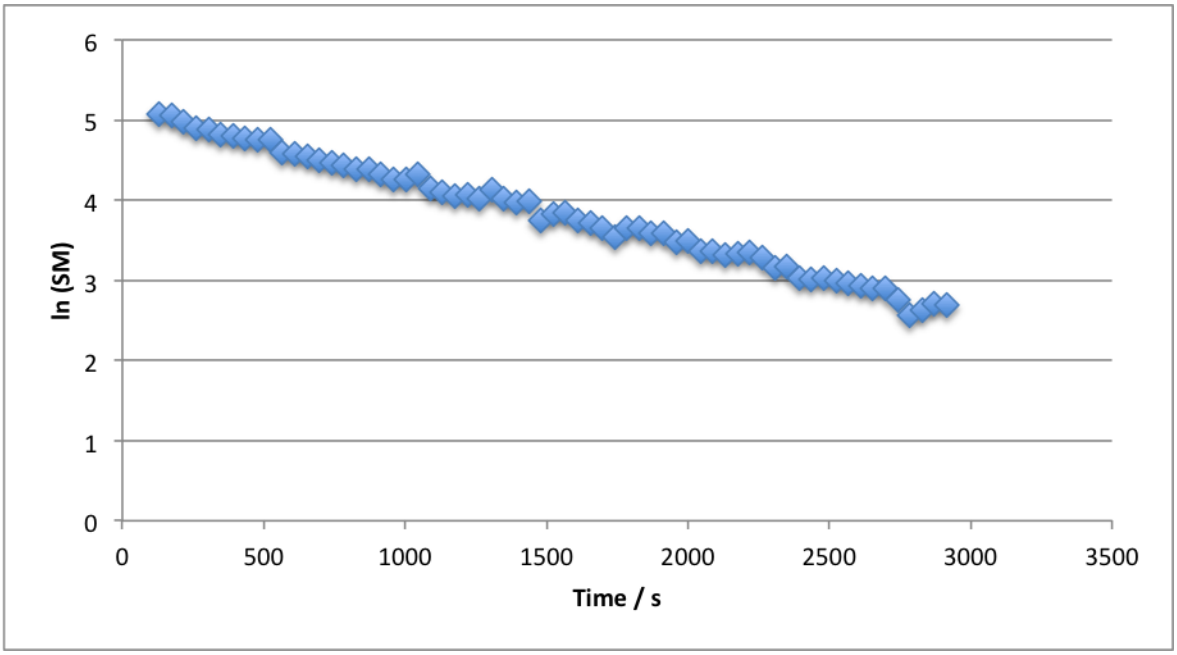

Figure S3: Plot of the integration of the signal due to the starting material **1a** in the ^{1}H NMR spectrum *vs* time for the reaction of species **1a** and **2**, in a mixture of the ionic liquid **4** in acetonitrile at a mole fraction of 0.90 at 8.1°C Using the LINEST function in Excel, the R^2 value is 0.994 and the rate constant determined was (8.49 ± 0.08) x 10^{-4} s^{-1}.

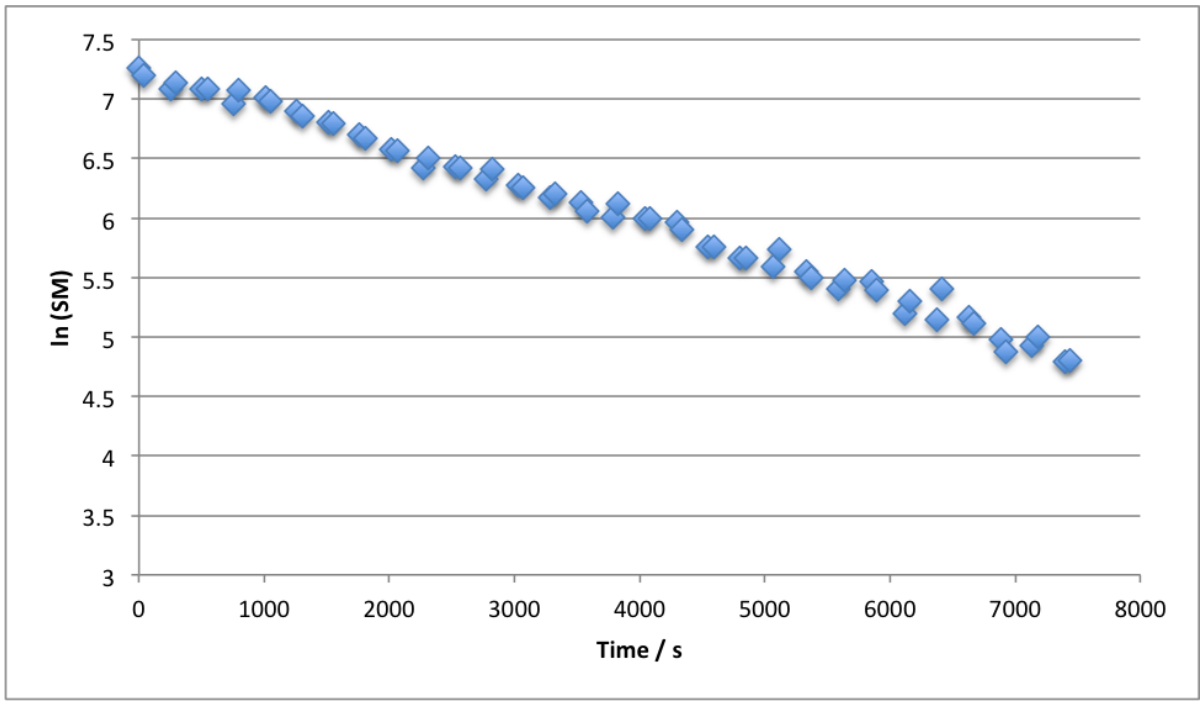

Figure S4: Plot of the integration of the signal due to the starting material **1b** in the ^{1}H NMR spectrum *vs* time for the reaction of species **1b** and **2**, in a mixture of the ionic liquid **8** at a mole fraction of 0.87 (diluted only by reagents) at 36.6°C Using the LINEST function in Excel, the R^2 value is 0.993 and the rate constant determined was (3.23 ± 0.04) x 10^{-4} s^{-1}.

*Benzaldehyde **1a** and hexan-1-amine **2***

Mole fraction plot: [Bmim][$N(CF_3SO_2)_2$] **4** in acetonitrile, at 8.1°C

Mole Fraction of 4	**[Nu] / mol L^{-1}**	**k_{obs} / 10^{-3} s^{-1}**	**k_2 / 10^{-3} L mol^{-1} s^{-1}**	**Average k_2 / 10^{-3} L mol^{-1} s^{-1}**
0.00	0.144	0.099	0.69	0.75 (0.06)
		0.115	0.80	
		0.110	0.76	
0.01	0.151	0.187	1.24	1.17 (0.08)
		0.178	1.18	
		0.162	1.07	
0.05	0.156	0.349	2.23	2.22 (0.08)
		0.360	2.30	
		0.335	2.14	
0.16	0.131	0.435	3.31	3.18 (0.11)
		0.408	3.10	
		0.413	3.14	
0.25	0.129	0.586	4.56	4.48 (0.31)
		0.610	4.75	
		0.533	4.15	
0.39	0.129	0.679	5.28	5.40 (0.11)
		0.708	5.50	
		0.697	5.42	
0.49	0.151	0.706	4.67	4.79 (0.10)
		0.734	4.85	
		0.732	4.84	
0.51	0.134	0.589	4.40	4.42 (0.25)
		0.626	4.68	
		0.559	4.18	
0.65	0.126	0.770	6.10	6.01 (0.15)
		0.737	5.84	
		0.769	6.09	
0.80	0.143	0.858	6.01	6.02 (0.23)
		0.893	6.25	
		0.828	5.80	
0.91	0.131	0.903	6.90	6.72 (0.21)
		0.849	6.48	
		0.888	6.78	
0.97	0.099	0.694	7.02	6.80 (0.20)
		0.657	6.64	
		0.667	6.74	

Mole fraction plot: [Bmpy][$N(CF_3SO_2)_2$] **5** in acetonitrile, at 8.1°C

Mole Fraction of 5	**[Nu] / mol L^{-1}**	**k_{obs} / 10^{-3} s^{-1}**	**k_2 / 10^{-3} L mol^{-1} s^{-1}**	**Average k_2 / 10^{-3} L mol^{-1} s^{-1}**
0.00	0.144	0.099	0.69	0.75 (0.06)
		0.115	0.80	
		0.110	0.76	
0.06	0.148	0.343	2.32	2.35 (0.04)
		0.354	2.39	
		0.346	2.33	
0.13	0.152	0.635	4.18	4.19 (0.04)
		0.629	4.15	
		0.642	4.23	
0.24	0.164	0.974	5.93	6.16 (0.24)
		0.991	6.03	
		1.024	6.23	
		1.062	6.46	
0.28	0.276	1.343	4.86	4.88 (0.02)
		1.349	4.88	
		1.355	4.91	
0.41	0.209	1.528	7.33	7.15 (0.29)
		1.421	6.81	
		1.525	7.31	
0.51	0.203	1.764	8.71	8.72 (0.09)
		1.749	8.63	
		1.785	8.81	
0.61	0.215	2.448	11.39	12.34 (1.00)
	0.200	2.452	12.26	
		2.677	13.38	
0.71	0.177	2.122	12.00	12.02 (0.38)
		2.196	12.41	
		2.060	11.64	
0.79	0.203	2.726	13.46	14.18 (0.81)
		3.051	15.06	
		2.843	14.03	
0.86	0.215	2.842	13.19	13.28 (0.28)
		2.813	13.06	
		2.928	13.59	
0.91	0.178	3.137	17.59	17.33 (0.56)
		2.976	16.69	
		3.159	17.71	
0.94	0.189	4.168	22.00	21.33 (0.65)
		4.029	21.27	
		3.924	20.71	

Mole fraction plot: [Bm_2im][$N(CF_3SO_2)_2$] **6** in acetonitrile, at 8.1°C

Mole Fraction of 6	**[Nu] / mol L^{-1}**	**k_{obs} / 10^{-3} s^{-1}**	**k_2 / 10^{-3} L mol^{-1} s^{-1}**	**Average k_2 / 10^{-3} L mol^{-1} s^{-1}**
0.00	0.144	0.099	0.69	0.75 (0.06)
		0.115	0.80	
		0.110	0.76	
0.10	0.160	0.410	2.57	2.55 (0.04)
		0.399	2.50	
		0.411	2.58	
0.20	0.112	0.378	3.38	3.34 (0.07)
		0.378	3.37	
		0.365	3.26	
0.30	0.136	0.655	4.82	4.65 (0.15)
		0.621	4.57	
		0.618	4.55	
0.39	0.151	0.779	5.15	5.16 (0.03)
		0.786	5.20	
		0.776	5.14	
0.49	0.167	0.740	4.43	4.49 (0.05)
		0.758	4.54	
		0.749	4.49	
0.60	0.138	0.782	5.65	5.68 (0.09)
		0.775	5.60	
		0.800	5.78	
0.67	0.159	0.968	6.08	6.04 (0.04)
		0.955	6.00	
		0.959	6.03	
0.86	0.166	1.052	6.33	6.31 (0.03)
		1.045	6.29	
0.95	0.157	1.062	6.76	6.89 (0.34)
		1.145	7.28	
		1.045	6.64	

Mole fraction plot: [Bm_4im][$N(CF_3SO_2)_2$] **7** in acetonitrile, at 8.1°C

Mole Fraction of 7	**[Nu] / mol L^{-1}**	**k_{obs} / 10^{-3} s^{-1}**	**k_2 / 10^{-3} L mol^{-1} s^{-1}**	**Average k_2 / 10^{-3} L mol^{-1} s^{-1}**
0.00	0.144	0.099	0.69	0.75 (0.06)
		0.115	0.80	
		0.110	0.76	
0.05	0.150	0.696	4.64	4.60 (0.05)
		0.696	4.64	
		0.682	4.54	
0.12	0.150	1.383	9.21	9.47 (0.24)
		1.452	9.67	
		1.433	9.54	

Eyring Data: Acetonitrile

Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}
8.1	0.144	0.099	0.69
		0.095	0.66
		0.110	0.76
21.2		0.188	1.31
		0.188	1.35
		0.204	1.46
27.8		0.240	1.67
		0.245	1.70
		0.264	1.89
15.4		0.166	1.19
		0.142	1.01
		0.171	1.22

Eyring Data: [Bmim][$N(CF_3SO_2)_2$] **4** in acetonitrile

Mole Fraction of 4	Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}
0.23	21.4	0.139	1.028	7.42
			1.021	7.37
			1.033	7.45
			1.032	7.45
	15.4		0.759	5.48
			0.745	5.37
			0.768	5.54
	8.1		0.494	3.56
			0.503	3.63
			0.494	3.56
	2.3		0.338	2.44
			0.334	2.41
			0.339	2.44
0.50	21.1	0.148	1.522	10.29
			1.631	11.03
			1.661	11.23
			1.655	11.19
	15.3		1.120	7.57
			1.191	8.05
			1.200	8.11
	8.1		0.780	5.27
			0.769	5.20
			0.827	5.59
	1.7		0.551	3.73
			0.548	3.71
			0.558	3.77
0.97	15.4	0.099	1.011	10.22
			0.929	9.39
			0.987	9.97
	21.4		1.281	12.94
			1.311	13.25
			1.524	15.40
	8.1		0.694	7.02
			0.657	6.64
			0.667	6.74
	0		0.416	4.20
			0.432	4.36
			0.391	3.95

Activation parameters: Benzaldehyde **1a** and hexan-1-amine **2** in [Bmim][$N(CF_3SO_2)_2$] **4** / acetonitrile mixtures

Mole Fraction [Bmim][$N(CF_3SO_2)_2$] 4 in acetonitrile	**$\Delta H^{\ddagger}$ / kJ mol^{-1}**	**$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}**
0	27.2 (2.5)	-272.1 (8.6)
0.23	34.5 (0.5)	-233.2 (1.7)
0.50	32.4 (0.8)	-237.0 (2.8)
0.97	32.4 (1.3)	-235.2 (4.6)

Eyring Data: [Bmpy][$N(CF_3SO_2)_2$] **5** in acetonitrile

Mole Fraction of 5	Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 /10^{-3} L mol^{-1} s^{-1}
0.24	8.1	0.164	0.974	5.93
			0.991	6.03
			1.024	6.23
			1.062	6.46
	1.6		0.660	4.02
			0.670	4.08
			0.662	4.03
	-5.2		0.405	2.47
			0.395	2.41
			0.396	2.41
	-12.7		0.247	1.51
			0.246	1.50
			0.246	1.50
0.94	8.1	0.189	4.168	22.00
			4.029	21.27
			3.924	20.71
	2.4		2.110	11.14
			2.758	14.56
			2.328	12.29
	-4.6		1.420	7.50
			1.330	7.02
			1.415	7.47
	-12.6		0.729	3.85
			0.736	3.88
			0.729	3.85

Activation parameters: Benzaldehyde **1a** and hexan-1-amine **2** in [Bmpy][$N(CF_3SO_2)_2$] **5** / acetonitrile mixtures

Mole Fraction [Bmpy][$N(CF_3SO_2)_2$] 5 in acetonitrile	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}
0	27.2 (2.5)	-272.1 (8.6)
0.24	37.3 (0.6)	-218.7 (2.4)
0.94	45.3 (1.7)	-180.2 (6.2)

Eyring Data: [Bm_2im][$N(CF_3SO_2)_2$] **6** in acetonitrile

Mole Fraction of 6	Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}
0.20	16.0	0.112	0.592	5.29
			0.612	5.46
			0.578	5.16
	8.1		0.378	3.38
			0.378	3.37
			0.365	3.26
	-8.1		0.143	1.28
			0.139	1.24
			0.136	1.21
	0.0		0.219	1.95
			0.212	1.90
			0.222	1.98
0.95	8.1	0.157	1.045	6.64
			1.062	6.76
			1.145	7.28
	1.1		0.755	4.80
			0.763	4.85
			0.798	5.08
	-5		0.533	3.39
			0.563	3.58
			0.513	3.26
	-12.5		0.313	1.99
			0.312	1.99
			0.315	2.00

Activation parameters: Benzaldehyde **1a** and hexan-1-amine **2** in [Bm_2im][$N(CF_3SO_2)_2$] **6** / acetonitrile mixtures

Mole Fraction [bm_2im][$N(CF_3SO_2)_2$] 6 in acetonitrile	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}
0	27.2 (2.5)	-272.1 (8.6)
0.20	34.1 (0.8)	-234.9 (2.7)
0.95	32.3 (1.1)	-235.2 (4.1)

Eyring Data: [TOA][$N(CF_3SO_2)_2$] **8**

Mole Fraction of #	Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}
0.87	36.1	0.200	0.938	4.70
			1.113	5.57
			1.195	5.99
	41.7		1.233	6.18
			1.558	7.81
			1.570	7.87
	47.4		1.742	8.73
			2.049	10.26
			1.776	8.90
	53.8		2.377	11.91
			2.432	12.18
			2.110	10.57

Activation parameters: Benzaldehyde and hexan-1-amine **2** in [TOA][$N(CF_3SO_2)_2$] **8**

Mole Fraction [TOA][$N(CF_3SO_2)_2$] **8**	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}
0	27.2 (2.5)	-272.1 (8.6)
0.87	30.8 (3.7)	-254.1 (11.8)

Activation Parameter Summary:

Solvent	Mole Fraction	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}
Acetonitrile	-	27.2 (2.5)	-272.1 (8.6)
[TOA][$N(CF_3SO_2)_2$] **8**	0.87	30.8 (3.7)	-254.1 (11.8)
[Bm_2im][$N(CF_3SO_2)_2$] **6**	0.20	34.1 (0.8)	-234.9 (2.7)
	0.95	32.3 (1.1)	-235.2 (4.1)
[Bmim][$N(CF_3SO_2)_2$] **4**	0.23	34.5 (0.5)	-233.2 (1.7)
	0.50	32.4 (0.8)	-237.0 (2.8)
	0.97	32.4 (1.3)	-235.2 (4.6)
[Bmpy][$N(CF_3SO_2)_2$] **5**	0.24	37.3 (0.6)	-218.7 (2.4)
	0.94	45.3 (1.7)	-180.2 (6.2)

*4-Methoxybenzaldehyde **1b** and hexan-1-amine **2***

Eyring Data: Acetonitrile

Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}
8.1	0.196	0.0303	0.154
		0.0232	0.118
	0.153	0.0185	0.121
63.6		0.0708	0.463
		0.0744	0.486
		0.0831	0.543
47.8		0.0574	0.375
		0.0493	0.322
		0.0552	0.361
36.6		0.0349	0.228
		0.0461	0.301
		0.0388	0.254
54.0		0.0644	0.421
		0.0672	0.439
		0.0621	0.406

Eyring Data: [Bmim][$N(CF_3SO_2)_2$] **4**

Mole Fraction of 4	Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}
0.93	29.4	0.237	0.578	2.44
			0.543	2.29
			0.536	2.26
	36.6		0.930	3.93
			0.932	3.94
			0.858	3.62
	44.3		1.131	4.78
			1.275	5.39
			1.264	5.34
	19.3		0.333	1.41
			0.316	1.33
			0.329	1.39

Eyring Data: [Bmpy][$N(CF_3SO_2)_2$] **5**

Mole Fraction of 5	Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}
0.93	22.3	0.227	0.798	3.51
			0.823	3.62
			0.776	3.41
	29.4		1.144	5.03
			1.133	4.98
			1.389	6.11
	14.5		0.450	1.98
			0.511	2.25
			0.471	2.07
	36.6		1.895	8.33
			2.033	8.94

Eyring Data: [Bm_2im][$N(CF_3SO_2)_2$] **6**

Mole Fraction of 6	Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}
0.95	36.6	0.147	0.958	6.52
			1.062	7.22
			1.010	6.87
	48.1		1.934	13.16
			1.832	12.46
			1.921	13.07
	17.7		0.476	3.24
			0.442	3.01
			0.446	3.04
	63.6		4.146	28.21
			4.191	28.52
			3.592	24.45

Eyring Data: [Bm_4im][$N(CF_3SO_2)_2$] **7**

Mole Fraction of 7	Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}
0.94	36.6	0.171	5.707	33.38
			5.561	32.52
			5.595	32.72
	41.6		7.248	42.40
			6.519	38.13
			6.536	38.23
	25.9		3.477	20.33
			3.541	20.71
			3.426	20.04
	30.5		4.241	24.80
			4.194	24.53
			3.969	23.22

Eyring Data: [TOA][$N(CF_3SO_2)_2$] **8**

Mole Fraction of 8	Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}
0.87	54.0	0.165	0.349	2.12
		0.176	0.476	2.70
			0.394	2.29
	63.6		0.524	3.05
			0.578	3.36
			0.532	3.10
	47.8		0.388	2.21
			0.448	2.60
			0.433	2.52
	36.6		0.235	1.37
			0.263	1.53
			0.323	1.88

Activation Parameter Summary:

Solvent	**Mole Fraction**	**$\Delta H^{\ddagger}$ / kJ mol^{-1}**	**$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}**
Acetonitrile	-	14.2 (1.0)	-333.1 (3.3)
[TOA][N(CF_3SO_2)$_2$] **8**	0.87	15.8 (3.2)	-312.9 (10.0)
[Bm_4im][N(CF_3SO_2)$_2$] **7**	0.94	28.8 (1.4)	-246.1 (4.6)
[Bm_2im][N(CF_3SO_2)$_2$] **6**	0.95	33.3 (1.3)	-243.4 (4.0)
[Bmim][N(CF_3SO_2)$_2$] **4**	0.93	36.8 (1.5)	-238.5 (5.0)
[Bmpy][N(CF_3SO_2)$_2$] **5**	0.93	41.9 (1.9)	-214. 8 (6.5)