Supporting Information:

Developing principles for predicting ionic liquid effects on reaction outcome. The importance of the anion in controlling microscopic interactions

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p-*Methoxybenzaldehyde **1** and hexan-1-amine **2***

Mole Fraction of 5	**[Nu] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**	**Average k_2 / 10^{-4} L mol^{-1} s^{-1}**	**k_2 from graph / 10^{-4} L mol^{-1} s^{-1}**
0	0.153	0.185	1.21	1.06 (0.19)	0.83 (0.08)
		0.232	1.52		
	0.427	0.473	1.11		
		0.468	1.09		
		0.386	0.90		
	0.590	0.672	1.14		
		0.521	0.88		
		0.607	1.03		
	0.817	0.840	1.03		
		0.722	0.88		
		0.694	0.85		
0.9	0.292	1.862	6.38	6.83 (0.51)	6.37 (0.46)
		1.916	6.56		
		2.121	7.26		
	0.149	1.169	7.83		
		1.078	7.22		
		2.864	6.88		
	0.416	2.941	7.07		
		2.931	7.04		
	0.358	2.282	6.37		
		2.259	6.31		
		2.232	6.23		

Effect of changing the concentration of **2**: in acetonitrile and [Bmim][N(CF_3SO_2)$_2$] **5**, at 8.1°C

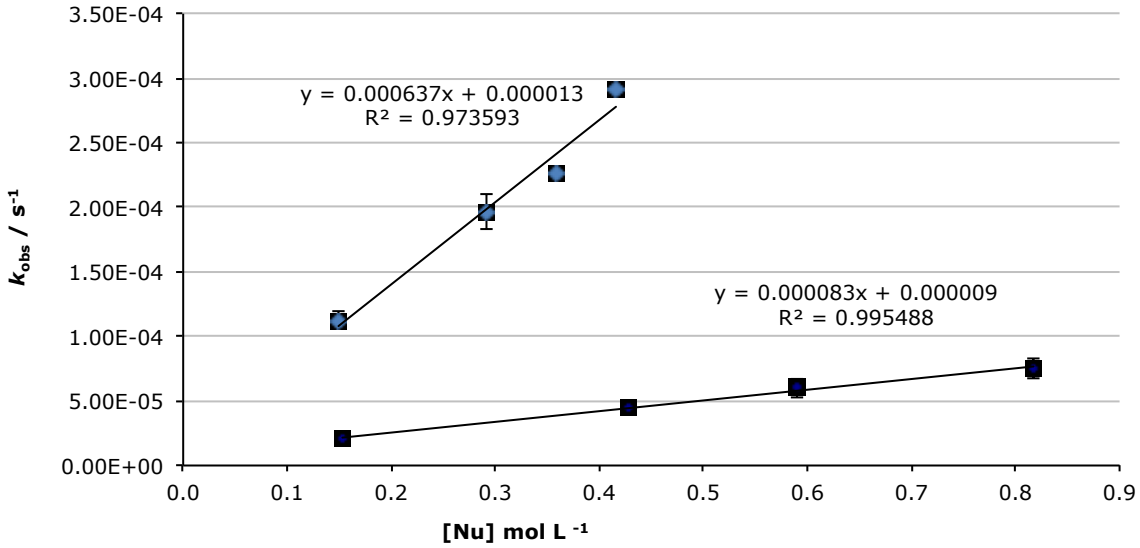

Fig. S1 The observed rate constants for the reaction between benzaldehyde **1** and the amine **2** at different concentrations of the nucleophile **2** in either acetonitrile (black) or [Bmim][$N(CF_3SO_2)_2$ (blue) at 8.1°C.

When changing the concentration of the nucleophile **2** there is a linear change in the observed rate constant, and the slope of the graph of the rate constant *vs* nucleophile concentration corresponds to the bimolecular rate constant as expected. This shows that the rate of the reaction is dependent on the nucleophile, consistent with the initial addition step being rate-determining.

Mole fraction data: [Bmim][$N(CF_3SO_2)_2$] **5**, at 8.1°C

Mole Fraction of 5	**[Nu] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**	**Average k_2 / 10^{-4} L mol^{-1} s^{-1}**
0	0.153	0.185	1.21	1.31 (0.20)
	0.196	0.303	1.54	
		0.232	1.18	
0.11	0.177	0.609	3.44	3.31 (0.21)
		0.544	3.07	
		0.608	3.43	
0.21	0.151	0.742	4.91	4.87 (0.15)
		0.712	4.71	
		0.756	5.00	
0.32	0.155	0.912	5.88	5.85 (0.03)
		0.909	5.86	
		0.904	5.82	
0.41	0.159	1.052	6.61	6.63 (0.03)
		1.051	6.60	
		1.061	6.67	
0.51	0.176	1.101	6.24	6.28 (0.07)
		1.100	6.24	
		1.122	6.36	
0.62	0.148	0.979	6.63	6.91 (0.28)
		1.018	6.89	
		1.063	7.20	
0.70	0.154	1.074	6.96	6.93 (0.04)
		1.062	6.89	
		1.071	6.95	
0.80	0.156	1.183	7.58	7.87 (0.45)
		1.311	8.40	
		1.194	7.65	
0.91	0.145	1.223	8.45	8.12 (0.36)
		1.120	7.74	
		1.184	8.18	

Mole fraction data: [Bmim][PF_6] **6**, at 8.1°C

Mole Fraction of 6	**[Nu] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**	**Average k_2 / 10^{-4} L mol^{-1} s^{-1}**
0	0.153	0.185	1.21	1.31 (0.20)
	0.196	0.303	1.54	
		0.232	1.18	
0.15	0.379	0.723	1.91	2.00 (0.14)
		0.818	2.15	
		0.734	1.94	
0.21	0.499	0.764	1.53	1.64 (0.10)
		0.852	1.71	
		0.842	1.69	
0.34	0.399	0.738	1.85	1.74 (0.10)
		0.678	1.70	
		0.666	1.67	
0.40	0.252	0.487	1.94	1.97 (0.09)
		0.522	2.08	
		0.480	1.91	
0.51	0.279	0.565	2.02	2.07 (0.04)
		0.581	2.08	
		0.584	2.09	
0.60	0.364	0.588	1.62	1.62 (0.03)
		0.578	1.59	
		0.597	1.64	
0.70	0.395	0.644	1.63	1.64 (0.09)
		0.612	1.55	
		0.684	1.73	
0.81	0.407	0.774	1.90	1.99 (0.08)
		0.831	2.04	
		0.829	2.04	
0.91	0.399	0.720	1.81	1.78 (0.10)
		0.669	1.68	
		0.746	1.87	

Mole fraction data: [Bmim][BF_4] **7**, at 8.1°C

Mole Fraction of 7	**[Nu] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**	**Average k_2 / 10^{-4} L mol^{-1} s^{-1}**
0	0.153	0.185	1.21	1.31 (0.20)
	0.196	0.303	1.54	
		0.232	1.18	
0.11	0.247	0.953	3.86	3.76 (0.11)
		0.899	3.64	
		0.935	3.78	
0.23	0.231	1.276	5.52	5.60 (0.07)
		1.309	5.66	
		1.298	5.61	
0.30	0.347	1.735	5.00	4.95 (0.05)
		1.702	4.91	
		1.719	4.96	
0.40	0.360	2.360	6.55	6.37 (0.16)
		2.263	6.28	
		2.258	6.27	
0.52	0.299	2.280	7.61	7.49 (0.11)
		2.217	7.40	
		2.228	7.44	
0.61	0.308	2.418	7.84	8.04 (0.17)
		2.522	8.18	
		2.494	8.09	
0.70	0.274	2.168	7.92	7.95 (0.19)
		2.235	8.16	
		2.131	7.78	
0.83	0.329	2.603	7.91	7.94 (0.04)
		2.621	7.96	
0.93	0.332	2.920	8.80	8.83 (0.60)
		2.674	8.06	
		2.978	8.98	
		3.152	9.50	

Mole fraction data: [Bmim][$N(CN)_2$] **8** at 8.1°C

Mole Fraction of 8	**[Nu] / mol L^{-1}**	**k_{obs} / 10^{-4} s^{-1}**	**k_2 / 10^{-4} L mol^{-1} s^{-1}**	**Average k_2 / 10^{-4} L mol^{-1} s^{-1}**
0	0.153	0.185	1.21	1.31 (0.20)
	0.196	0.303	1.54	
		0.232	1.18	
0.10	0.338	0.770	2.27	2.46 (0.17)
		0.843	2.49	
		0.883	2.61	
0.22	0.269	0.807	3.00	3.13 (0.12)
		0.873	3.25	
		0.842	3.13	
0.30	0.310	1.137	3.67	3.72 (0.18)
		1.216	3.92	
		1.107	3.57	
0.41	0.296	1.327	4.48	4.46 (0.03)
		1.329	4.48	
		1.314	4.43	
0.51	0.316	1.634	5.17	4.79 (0.42)
		1.538	4.86	
		1.369	4.33	
0.60	0.329	1.586	4.83	4.73 (0.14)
		1.578	4.80	
		1.501	4.57	
0.71	0.297	1.752	5.89	5.46 (0.42)
		1.620	5.45	
		1.504	5.05	
0.84	0.292	1.679	5.76	5.52 (0.21)
		1.573	5.40	
		1.573	5.40	
0.93	0.285	1.473	5.17	5.42 (0.23)
		1.565	5.49	
		1.598	5.61	

Mole fraction data: [Bmim][I] **9**, at 8.1°C

Mole Fraction of 8	[Nu] / mol L^{-1}	k_{obs} / 10^{-4} s^{-1}	k_2 / 10^{-4} L mol^{-1} s^{-1}	Average k_2 / 10^{-4} L mol^{-1} s^{-1}
0	0.153	0.18	1.2	1.3 (0.2)
	0.196	0.30	1.5	
		0.23	1.2	
0.11	0.189	11.33	59.9	61.5 (2.8)
		11.36	60.0	
		12.25	64.8	
0.23	0.253	41.11	162.5	172.3 (8.7)
		45.37	179.4	
		44.26	175.0	
0.33	0.194	23.07	119.1	118.5 (1.1)
		23.09	119.2	
		22.72	117.3	
0.70	0.206	88.84	431.8	432 (43)*

- As only one replicate was able to be used, error is assumed to be 10%

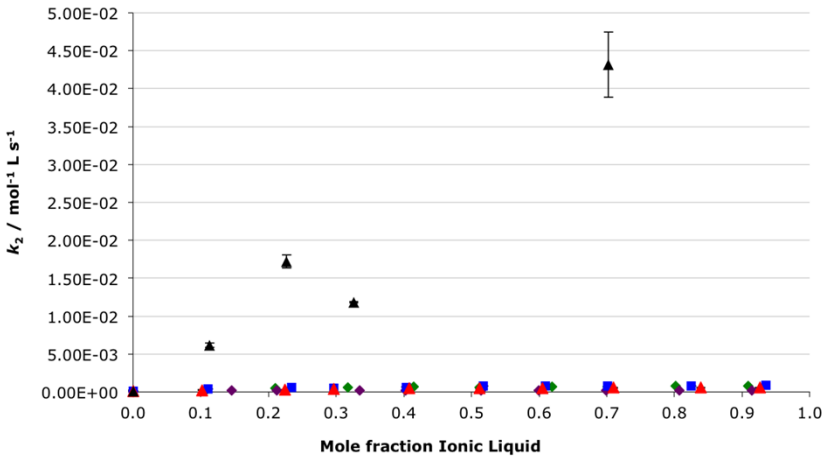

Fig. S2 The bimolecular rate constants for the reaction between benzaldehyde **1** and the amine **2** in different mole fractions of [Bmim][I] **9** (□) in acetonitrile, at 282 K. Uncertainties are reported as the standard deviation of three replicates, except for χ_{IL} 0.7 which represents one data point, and the error was estimated as ± 10%. [Bmim][$N(CF_3SO_2)_2$] **5** (◆), [Bmim][PF_6] **6** (◆), [Bmim][BF_4] **7** (■) and [Bmim][$N(CN)_2$] **8** (□) in acetonitrile are included for perspective.

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][$N(CF_3SO_2)_2$] **5**

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}**
0.22	20.3	0.200	0.185	0.92
			0.164	0.82
			0.196	0.98
	28.7		0.286	1.43
			0.281	1.40
			0.285	1.42
	8.1		0.079	0.40
			0.080	0.40
			0.082	0.41
	42.7		0.600	3.00
			0.553	2.76
			0.584	2.92
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: [Bmim][PF_6] **6**

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}
0.21	41.8	0.499	0.665	1.33
			0.585	1.17
			0.503	1.01
	31		0.293	0.59
			0.290	0.58
			0.327	0.66
	20.1		0.177	0.36
			0.191	0.38
			0.180	0.36
	8.1		0.076	0.15
			0.085	0.17
			0.084	0.17
0.91	18.9	0.399	0.134	0.34
			0.146	0.37
			0.141	0.35
	29.0		0.266	0.67
			0.281	0.70
			0.256	0.64
	8.1		0.072	0.18
			0.067	0.17
			0.075	0.19
	36.3		0.389	0.97
			0.365	0.91
			0.340	0.85

Eyring Data: [Bmim][BF_4] **7**

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}**
0.23	19.2	0.231	0.238	1.03
			0.260	1.13
			0.261	1.13
	27.8		0.372	1.61
			0.384	1.66
			0.375	1.62
	8.1		0.128	0.55
			0.131	0.57
			0.130	0.56
	36.8		0.585	2.53
			0.634	2.74
			0.623	2.69
0.93	27.7	0.332	0.714	2.15
			0.770	2.32
			0.733	2.21
	20.8		0.574	1.73
			0.564	1.70
			0.597	1.80
	14.2		0.354	1.07
			0.384	1.16
			0.375	1.13
	8.1		0.292	0.88
			0.267	0.81
			0.298	0.90
			0.315	0.95

Eyring Data: [Bmim][$N(CN)_2$] **8**

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}
0.22	18.9	0.269	0.141	0.52
			0.144	0.54
			0.148	0.55
	29.8		0.234	0.87
			0.240	0.89
			0.254	0.95
	40.1		0.343	1.28
			0.339	1.26
			0.332	1.24
	8.1		0.081	0.30
			0.087	0.33
			0.084	0.31
0.93	23.5	0.285	0.262	0.92
			0.282	0.99
			0.267	0.94
	15.7		0.199	0.70
			0.215	0.76
	29.9		0.345	1.21
			0.373	1.31
			0.362	1.27
	8.1		0.147	0.52
			0.157	0.55
			0.160	0.56

Eyring Data: [Bmim][I] **9**

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}
0.23	0.6	0.253	2.912	11.51
			2.923	11.56
			2.723	10.77
	8.1		4.111	16.25
			4.537	17.94
			4.426	17.50
	-6.3		2.296	9.08
			2.261	8.94
			2.305	9.11
	-12		1.810	7.16
			1.790	7.08
			1.809	7.15

Eyring Data: [Bmim][Br]/[$N(CF_3SO_2)_2$]

Mole Fraction of 9 in 4	Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}
0.32/0.60	30.1	0.285	0.597	2.09
			0.506	1.78
			0.553	1.94
	22.1		0.410	1.44
			0.381	1.34
			0.392	1.38
	35.4		0.605	2.12
			0.541	1.90
			0.551	1.93
	40.8		0.633	2.22
			0.627	2.20
			0.656	2.30

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)
[Bmim][N(CF_3SO_2)$_2$] **5**	0.22	37.0 (0.9)	-242.1 (3.1)
	0.93	36.8 (1.5)	-238.5 (5.0)
[Bmim][PF_6] **6**	0.21	37.1 (1.5)	-249.4 (5.1)
	0.91	37.7 (1.2)	-246.5 (4.1)
[Bmim][BF_4] **7**	0.24	34.0 (0.8)	-250.3 (2.6)
	0.93	29.7 (1.7)	-262.1 (5.8)
[Bmim][N(CN)$_2$] **8**	0.22	27.3 (0.9)	-278.6 (2.9)
	0.93	22.2 (1.1)	-292.6 (3.7)
[Bmim][I] **9**	0.23	21.6 (1.3)	-266.3 (4.9)
[Bmim][Br]/[N(CF_3SO_2)$_2$]	0.32/0.60	14.1 (2.4)	-316.4 (7.8)

Gibbs free energy *vs* β

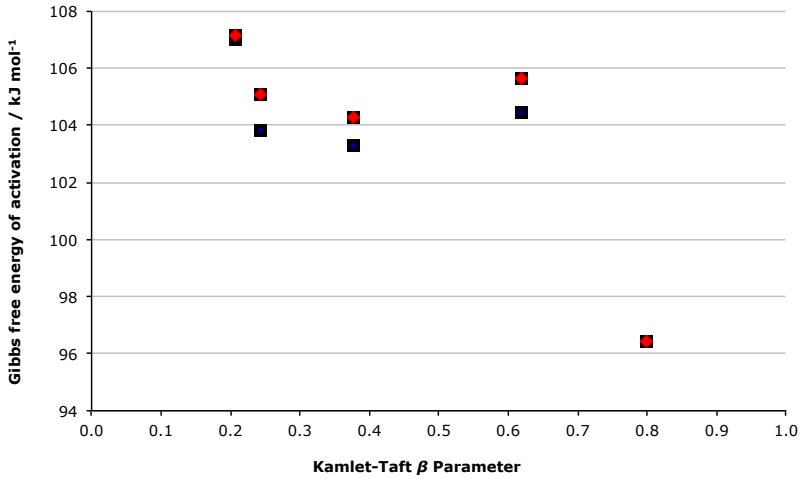

Fig. S3 The relationship between the Gibbs free energy of activation at 281K and the Kamlet-Taft β parameter for the ionic liquids **5-9** (Table 1) at a mole fraction of 0.2 (◆) and 0.9 (◆). The linear correlations were poor (having an R^2 value of 0.624 and 0.141, respectively) so the trendlines are not included in the figure.