Electronic supporting information for

"Towards reaction control using an ionic liquid: Biasing outcomes of reactions of benzyl halides"

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Synthesis of 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide ([Bmim][N(CF_3SO_2)$_2$])

The ionic liquid was prepared using a literature procedure through the corresponding chloride.[1] A mixture of 1-methylimidazole (20.6 g, 0.251 mol) and 1-chlorobutane (26.4 g, 0.285 mol) was stirred at reflux at 70°C for four days. Over this period two immiscible layers developed, with the lower layer containing the desired chloride. The lower layer was separated, rinsed with ethyl acetate (3 x 60 mL), and cooled to -18°C to assist crystallisation of the product. Excess ethyl acetate was then removed *in vacuo*, and the solid obtained was dried under reduced pressure at 70°C to afford 1-butyl-3-methylimidazolium chloride as a white amorphous solid (42.4 g, 96%), which was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.31 (m, 2H, $C\underline{H}_2CH_3$), 1.82 (m, 2H, $NCH_2C\underline{H}_2$), 4.08 (s, 3H, $NC\underline{H}_3$), 4.28 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2$), 7.48 and 7.62 (m, 2H, $C\underline{H}C\underline{H}$), 10.42 (s, 1H, $NC\underline{H}N$).

A solution of 1-butyl-3-methylimidazolium chloride (42.37 g, 0.243 mol) in water (50 mL) was added to a solution of lithium *bis*(trifluoromethanesulfonyl)imide (70.81g, 0.246 mol) in water (40 mL). The mixture was stirred for two hours. The ionic liquid **1** was extracted from the mixture using dichloromethane (3 x 40 mL). The organic layers were collected, and rinsed with water (5 x 50 mL) until there was a negative result for chloride anions as determined using the aqueous silver nitrate (*ca.* 0.1 M) test. Excess dichloromethane was removed *in vacuo* and the ionic liquid dried under reduced pressure (1 mbar) at 70°C for 8 hours, to afford 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide (86.0 g, 90%) as a colourless, viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3H, $CH_2C\underline{H}_3$), 1.36 (m, 2H, $C\underline{H}_2CH_3$), 1.82 (m, 2H, $NCH_2C\underline{H}_2$), 4.02 (s, 3H, $NC\underline{H}_3$), 4.21 (t, J = 7.4 Hz, 2H, $NC\underline{H}_2$), 7.46 and 7.60 (m, 2H, $C\underline{H}C\underline{H}$), 8.84 (s, 1H, $NC\underline{H}N$).

Synthesis of 3,4-dimethoxybenzyl bromide **1b**

The electrophile **1b** was prepared by a literature procedure from the corresponding alcohol.[2] Phosphorus tribromide (5.23 g, 1.93 x 10^{-2} mol) was added dropwise to a solution of 3,4-dimethoxybenzyl alcohol **21** (1.28 g, 7.60 x 10^{-3} mol) and dichloromethane (10 mL) at 0°C. The reaction was stirred at 0°C for a further 30 minutes, was then allowed to warm to room temperature and was stirred overnight under nitrogen. The reaction was quenched slowly with water, during which time a deep purple colour developed. Water was added until the solution turned a clear yellow colour. The reaction mixture was then washed with water (3 x 20 mL) and saturated sodium hydrogen carbonate solution (3 x 20 mL). The organic layer was dried using anhydrous magnesium sulfate and excess dichloromethane removed *in vacuo*. The yellow oil obtained was distilled under reduced pressure (6.8 x 10^{-2} mbar, 70°C) using a Kugelröhr apparatus, to afford 3,4-dimethoxybenzyl bromide **1b** as a white crystalline solid (0.24 g, 13%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.88 (s, 3H, $OC\underline{H}_3$), 3.90 (s, 3H, $OC\underline{H}_3$), 4.49 (s, 2H, $C\underline{H}_2Br$), 6.78 – 7.00 (m, 3H, Ar-H).

Synthesis of 1-(1-chloroethyl)-4-methoxybenzene **4**

The electrophile **4** was prepared using a literature procedure through the corresponding alcohol.[3] Sodium borohydride (1.3 g, 3.4 x 10^{-2} mol) was added to a solution of 4-methoxyacetophenone (3.09 g, 2.06 x 10^{-2} mol) in ethanol (40 mL). Sonication was used to assist the dissolution of sodium borohydride and the mixture was then stirred at room temperature for two hours. The solution was slowly acidified to pH 3 using hydrochloric acid (32% w/w), and excess ethanol removed *in vacuo*. Water (15 mL) was added, and the solution was extracted with dichloromethane (3 x 20 mL). The organic extracts were dried with anhydrous magnesium sulfate, and the solvent was removed *in vacuo* to afford 1-(4-methoxyphenyl)-ethanol as a colourless oil (3.10 g, 90%), which was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49 (d, J = 6.8 Hz, 3H, $CHC\underline{H}_3$). 3.83 (s, 3H, $OC\underline{H}_3$), 4.90 (q, J = 6.8 Hz, 1H, $C\underline{H}CH_3$), 6.91 (d, J = 8.8 Hz, 2H, Ar-H), 7.28 (d, J = 8.8 Hz, 2H, Ar-H).

Thionyl chloride (5.72 g, 4.81 x 10^{-3} mol) was added dropwise to a stirring solution of 1-(4-methoxyphenyl)-ethanol (1.86 g, 0.0123 mol) and dichloromethane (20 mL) at -78°C, and was stirred for 45 minutes. The mixture was then allowed to warm to room temperature and was stirred for a further 60 minutes. The reaction mixture was transferred to a Kugelröhr apparatus, and dichloromethane and excess thionyl chloride were removed first, and the compound of interest was distilled under reduced pressure (2.5 mbar, 60°C), to afford 1-(1-chloroethyl)-4-methoxybenzene **4** (1.79 g, 86%) as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85 (d, J = 6.8 Hz, 3H, $CHC\underline{H}_3$). 3.81 (s, 3H, $OC\underline{H}_3$), 5.11 (q, J = 8.8 Hz, 1H, $C\underline{H}CH_3$), 6.88 (d, J = 8.8 Hz, 2H, Ar-H), 7.35 (d, J = 8.8 Hz, 2H, Ar-H).

Rate data for reaction of compounds **1a** and **2a** in various mole fractions of [Bmim][N(CF_3SO_2)$_2$] in acetonitrile, shown in Figure 1, main text:

Table S1. The mass of each component used prepare the mixtures, and the resultant mole fraction of [Bmim][N(CF_3SO_2)$_2$], and the concentration of the nucleophile **2a** for reactions between benzyl chloride **1a** and pyridine **2a.**

Mass ionic liquid / g	**Mass acetonitrile / g**	**Mass pyridine 2a / g**	**[Nu] / mol L^{-1}**	χ_{IL}
0.00	1.53	0.078	0.492	0.00
0.13	1.44	0.078	0.502	0.01
0.59	1.28	0.076	0.483	0.04
1.24	0.83	0.077	0.487	0.12
1.84	0.56	0.072	0.451	0.23
2.07	0.40	0.077	0.487	0.31
2.40	0.20	0.078	0.490	0.49
2.56	0.08	0.077	0.491	0.66
2.69	0.03	0.078	0.491	0.77
2.76	0.00	0.077	0.490	0.85

Table S2. The rate constants for the reaction between benzyl chloride **1a** and pyridine **2a** in different mole fractions of [Bmim][N(CF_3SO_2)$_2$] in acetonitrile, at 40°C, calculated for each replicate. The final values for k_2 are the average of the observed values and the uncertainty is the standard deviation.

Mole fraction of ionic liquid	**[Nu] / mol L^{-1}**	k_{obs} **/ 10^{-5} s^{-1}**	k_2 **/ 10^{-5} L mol^{-1} s^{-1}**	**Average** k_2 **/ 10^{-5} L mol^{-1} s^{-1}**
0.00	0.492	0.98	1.99	1.968 (0.025)
		0.97	1.97	
		0.95	1.94	
0.01	0.503	1.18	2.35	2.358 (0.038)
		1.21	2.40	
		1.17	2.32	
0.04	0.483	1.53	3.17	3.167 (0.028)
		1.52	3.14	
		1.54	3.19	
0.12	0.488	2.37	4.86	4.896 (0.033)
		2.41	4.93	
0.23	0.452	2.91	6.43	6.460 (0.031)
		2.94	6.49	
		2.92	6.45	
0.31	0.488	3.31	6.78	6.91 (0.12)
		3.38	6.92	

		3.43	7.03	
0.49	0.490	3.77	7.69	7.75 (0.24)
		3.70	7.54	
		3.93	8.02	
0.66	0.491	4.42	9.00	9.025 (0.034)
		4.46	9.07	
		4.42	9.01	
0.77	0.491	4.38	8.91	9.07 (0.17)
		4.45	9.06	
		4.54	9.25	
0.85	0.504	4.06	8.05	8.24 (0.22)
		4.12	8.17	
		4.28	8.49	

Rate data for reaction of compounds **1a** and **2a** used for determination of the activation parameters shown in Table 1, main text:

Table S3. The mass of each component used prepare the mixtures, and the resultant mole fraction of [Bmim][N(CF_3SO_2)$_2$], and the concentration of the nucleophile **2a** for reactions between benzyl chloride **1a** and pyridine **2a** over various temperatures.

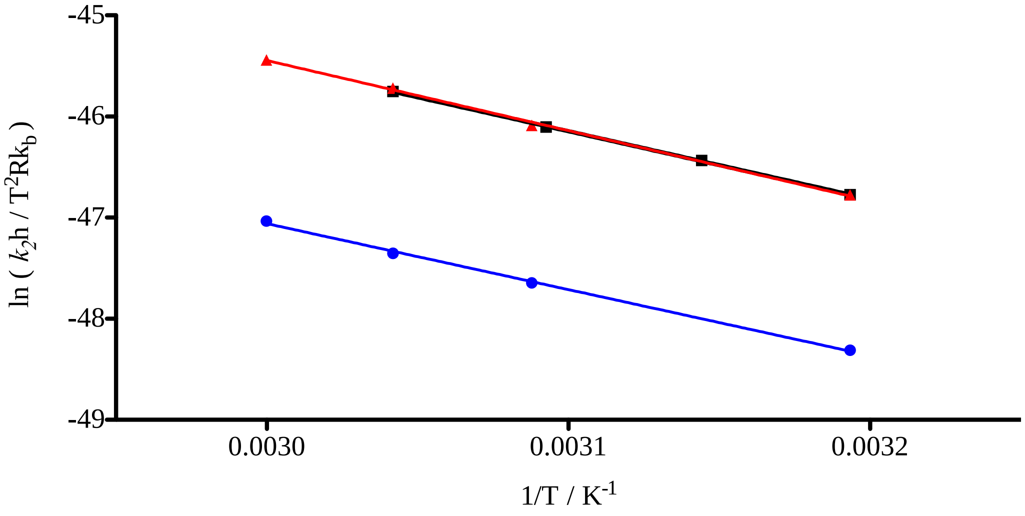
Mass of ionic liquid / g	**Mass acetonitrile / g**	**Mass pyridine 2a / g**	**Mass benzyl chloride 1a / g**	**[Nu] / mol L^{-1}**	χ_{IL}
0.00	7.91	0.43	0.07	0.548	0.00
12.90	0.42	0.41	0.09	0.515	0.66
13.65	0.00	0.40	0.07	0.503	0.85

Table S4. The rate constants for the reaction between benzyl chloride **1a** and pyridine **2a** in different mole fractions of [Bmim][N(CF_3SO_2)$_2$] in acetonitrile, over various temperatures, calculated for each replicate. The final values for k_2 are the average of the observed values and the uncertainty is the standard deviation

Mole fraction of ionic liquid	**Temperature / °C**	**[Nu] / mol L^{-1}**	k_{obs} **/ 10^{-5} s^{-1}**	k_2 **/ 10^{-5} L mol^{-1} s^{-1}**	**Average k_2 / 10^{-5} L mol^{-1} s^{-1}**
0	40.0	0.548	1.00	1.83	1.775 (0.061)
			0.98	1.79	
			0.94	1.71	
	50.7		1.96	3.56	3.69 (0.13)
			2.09	3.82	
			2.03	3.70	
	55.6		2.70	4.92	5.09 (0.15)
			2.85	5.19	
			2.83	5.17	
	60.2		3.93	7.16	7.20 (0.18)
			4.06	7.40	
			3.86	7.04	
0.656	40.0	0.516	4.19	8.12	8.26 (0.12)
			4.29	8.32	
			4.31	8.34	
	44.9		6.18	11.98	11.940 (0.071)
			6.12	11.86	
			6.18	11.98	

	50.2		8.76	16.97	17.20 (0.56)
			8.66	16.79	
			9.20	17.83	
	55.6		13.15	25.48	25.27 (0.20)
			13.03	25.26	
			12.94	25.07	
0.853	40.0	0.504	4.06	8.05	8.24 (0.23)
			4.12	8.17	
			4.28	8.49	
	50.7		8.98	17.82	17.52 (0.32)
			8.84	17.54	
			8.66	17.19	
	55.6		13.35	26.48	26.11 (0.74)
			13.40	26.59	
			12.73	25.25	
	60.2		17.47	34.67	35.5 (1.2)
			18.30	36.32	

Figure S1. Eyring plot plot from which the activation parameters were determined for the reaction between benzyl chloride **1a** and pyridine **2a** in acetonitrile (blue), and mole fractions of [Bmim][N(CF_3SO_2)$_2$] in acetonitrile of 0.66 (black) and 0.85 (red). The error bars represent half the range of three replicate experiments.



Rate data for the reaction of compounds **1b** and **2b** in various mole fractions of [Bmim][N(CF_3SO_2)$_2$] in acetonitrile, shown in Figures 2, 3 and 4, main text:

Table S5. The mass of each component used prepare the mixtures, and the resultant mole fraction of [Bmim][N(CF_3SO_2)$_2$], and the concentration of the nucleophile **2b** for reactions between 3,4-dimethoxybenzyl bromide **1b** and 3-chloropyridine **2b.**

Mass of ionic liquid / g	**Mass acetonitrile /g**	**Mass 3-chloropyridine 1b / g**	**Mass substrate 2b / g**	**[Nu] / mol L^{-1}**	χ_{IL}
0	1.5884	0.0315	0.0055	0.139	0.00
0	1.5597	0.0493	0.0055	0.217	0.00
0	1.5274	0.0767	0.0060	0.338	0.00
0	1.5345	0.0754	0.0050	0.332	0.00
0	1.5280	0.1001	0.0051	0.441	0.00
0.2957	1.3939	0.0255	0.0040	0.112	0.02
0.2790	1.4130	0.0489	0.0080	0.215	0.02
0.2776	1.3969	0.0756	0.0093	0.333	0.02
0.2848	1.3564	0.0988	0.0088	0.435	0.02
0.5800	1.2433	0.0269	0.0068	0.118	0.04
0.5864	1.2000	0.0615	0.0067	0.271	0.04
0.5840	1.2012	0.0800	0.0055	0.352	0.04
0.5819	1.1810	0.1020	0.0068	0.449	0.04
1.1412	0.9204	0.0300	0.0042	0.132	0.11
1.1425	0.8749	0.0627	0.0076	0.276	0.11
1.1426	0.8592	0.0916	0.0068	0.403	0.11
1.1436	0.8653	0.1134	0.0104	0.499	0.11
1.8014	0.5397	0.0308	0.0080	0.136	0.24
2.3333	0.6548	0.0760	0.0055	0.257	0.25
1.7995	0.4734	0.0855	0.0048	0.377	0.26
1.7919	0.4595	0.1040	0.0073	0.458	0.26
1.7953	0.5311	0.0444	0.0056	0.196	0.24
2.0539	0.3676	0.0249	0.0040	0.110	0.35
2.0562	0.3513	0.0576	0.0086	0.254	0.35
2.0541	0.3587	0.0777	0.0050	0.342	0.34
2.0549	0.3281	0.0943	0.0055	0.415	0.36
2.3021	0.2324	0.0270	0.0045	0.119	0.48
2.3155	0.2264	0.0424	0.0057	0.187	0.48
2.3024	0.2099	0.0584	0.0069	0.257	0.49
2.3019	0.2027	0.0705	0.0052	0.310	0.50
2.5888	0.0822	0.0309	0.0045	0.136	0.73
2.5834	0.0741	0.0420	0.0049	0.185	0.74
2.5941	0.0626	0.0478	0.0042	0.210	0.76
2.5898	0.0630	0.0553	0.0098	0.244	0.75
2.5988	0.0760	0.0623	0.0042	0.274	0.72

Table S6. The rate constants for the reaction between 3,4-dimethoxybenzyl bromide **1b** and 3-chloropyridine **2b** in different mole fractions of [Bmim][N(CF_3SO_2)$_2$] in acetonitrile, at 40°C, calculated for each replicate. The final values for k_2 are the average of the observed values and the uncertainty is the standard deviation.

χ_{IL}	**[Nu] / mol L^{-1}**	**k_{obs} / x 10^{-5} s^{-1}**	**k_1 / x 10^{-6} s^{-1}**	**k_2 / x 10^{-4} L mol^{-1} s^{-1}**
0	0.139	19.10	14 (10)	13.49 (0.34)
		20.22		
		19.48		
	0.217	31.05		
		30.63		
		30.55		
	0.338	47.12		
		50.04		
	0.332	47.81		
		45.19		
	0.441	58.59		
		61.04		
		60.31		
0.02	0.112	29.46	119.8 (9.3)	14.93 (0.31)
		28.56		
		29.56		
	0.215	43.33		
		45.02		
		42.32		
	0.333	61.79		
		62.08		
		60.48		
	0.435	76.12		
		75.89		
		79.75		
0.04	0.118	34.93	88 (14)	22.78 (0.44)
		35.64		
		36.37		
	0.271	67.47		
		73.21		
		71.82		
	0.352	87.95		
		89.24		
		89.17		
	0.449	108.46		
		113.69		
		111.17		

0.11	0.132	52.78	134 (20)	30.11 (0.60)
		52.20		
		52.34		
	0.276	95.08		
		95.35		
		98.95		
	0.403	136.29		
		138.24		
		138.36		
	0.499	162.52		
		158.74		
0.25	0.136	64.35	160 (22)	37.67 (0.75)
		66.25		
		63.94		
	0.196	92.03		
		92.72		
		94.83		
	0.257	112.05		
		111.11		
	0.458	188.43		
		191.75		
		184.58		
0.35	0.110	61.06	143 (23)	41.52 (0.77)
		60.08		
		59.40		
	0.254	123.87		
		115.81		
		119.71		
	0.342	151.92		
		158.29		
		153.84		
	0.415	185.16		
		191.79		
		186.98		
0.48	0.119	61.78	63 (31)	45.7 (1.3)
		63.52		
		63.95		
	0.187	85.83		
		87.19		
		91.01		
	0.257	120.32		
		124.40		
		125.07		
	0.310	148.51		
		153.10		

		147.58		
0.74	0.136	76.87	117 (25)	49.4 (1.2)
		79.12		
		79.44		
	0.185	105.09		
		103.62		
		102.42		
	0.210	112.53		
		118.74		
	0.244	134.75		
		130.29		
	0.274	147.63		
		144.05		
		148.66		

Rate data for reaction of compounds **4** and **2b** in in various mole fractions of [Bmim][N(CF_3SO_2)$_2$] in acetonitrile, shown in Figures 5 and 6, main text:

Table S7. The mass of each component used prepare the mixtures, and the resultant mole fraction of [Bmim][N(CF_3SO_2)$_2$], and the concentration of the nucleophile **2b** for reactions between 1-(1-chloroethyl)-4-methoxybenzene **4** and 3-chloropyridine **2b**.

Mass of ionic liquid / g	Mass acetonitrile / g	Mass 3-chloropyridine 2b / g	Mass substrate 4 / g	[Nu] / mol L^{-1}	χ_{IL}
0	1.567	0.0471	0.004	0.207	0
0	1.545	0.0765	0.005	0.337	0
0	1.554	0.0925	0.006	0.407	0
0	1.505	0.1019	0.006	0.449	0
0.2821	1.404	0.0517	0.005	0.228	0.02
0.2822	1.392	0.0729	0.005	0.321	0.02
0.2833	1.377	0.0886	0.005	0.390	0.02
0.2840	1.358	0.1020	0.007	0.449	0.02
1.1408	0.921	0.0341	0.005	0.150	0.11
1.1401	0.904	0.0530	0.005	0.233	0.11
1.1407	0.900	0.0656	0.005	0.289	0.11
1.1412	0.882	0.0897	0.005	0.395	0.11
1.8498	0.515	0.0320	0.005	0.141	0.26
1.8488	0.497	0.0420	0.005	0.185	0.26
1.8484	0.508	0.0516	0.005	0.227	0.26
1.8439	0.503	0.0964	0.007	0.425	0.25
2.3038	0.237	0.0475	0.005	0.209	0.47
2.3024	0.219	0.0675	0.013	0.297	0.48
2.3003	0.216	0.0827	0.005	0.364	0.48
2.3019	0.205	0.1052	0.005	0.463	0.48
2.4281	0.141	0.0375	0.005	0.165	0.60
2.4257	0.144	0.0618	0.005	0.272	0.59
2.4041	0.143	0.0821	0.006	0.362	0.58
2.6202	0.038	0.0539	0.005	0.237	0.82
2.5870	0.034	0.0615	0.008	0.271	0.82
2.6140	0.027	0.0777	0.005	0.342	0.82
2.7112	0.000	0.0948	0.011	0.417	0.88

The reactions between 1-(1-chloroethyl)-4-methoxybenzene **4** and 3-chloropyridine **2b** were followed using the ratio between the signals corresponding to the starting material **4** (at δ *ca*. 5.1) and both the substitution product **5** (at δ *ca*. 6.2) and elimination product **6** (at δ *ca*. 6.8). By fitting the change in integration over time to Equations (1) and (2),[i] the rate constant that is observed for both cases is in fact the sum of the rate constants due to the substitution and elimination pathways ($k_S + k_E$). The individual rate constants can be obtained using this data.

$$[S] = \frac{k_S}{k_S + k_E} \times [A]_o \times \left(1 - e^{-(k_S + k_E)t}\right) \qquad (1)$$

$$[E] = \frac{k_E}{k_S + k_E} \times [A]_o \times \left(1 - e^{-(k_S + k_E)t}\right)$$

(2)

Where: S = the substitution product ***5****,*

E = the elimination product ***6***

A = the starting material ***4***

The substitution case will be used as an example; by dividing the integration of the substitution product over time by the sum of the integration[ii] of both the substitution and elimination products over time, gives the ratio $k_S /(k_S + k_E)$. This ratio is then multiplied by the observed rate constant (recall that $k_{obs} = k_S + k_E$), to give k_S as shown in Equation (3)

$$k_S = \frac{[S]}{[S]+[E]} \times (k_S + k_E) \quad \text{and} \quad k_E = \frac{[E]}{[S]+[E]} \times (k_S + k_E) \qquad (3) \text{ and } (4)$$

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[i] Which is essentially a pseudo first order rate curve

[ii] The integrations for all spectra obtained across three half lives are deterrmined (which will remain constant), and the ratio used in the calculation is the average of these.

$$k_{\mathrm{obs}} = k_1 + k_2[\mathrm{Nu}] \qquad (5)$$

This can be then repeated for the elimination pathway (Equation (4)). This was the method used to obtain the respective overall rate constants for the substitution and elimination pathways. The unimolecular and bimolecular components of each pathway was determined by plotting this observed rate (that is, k_S or k_E) against the nucleophile concentration (Table S7) the value of both the unimolecular and bimolecular rate constants were determined. As shown in Equation (5) the slope of the linear fit is k_2 and the y-intercept, where the theoretical nucleophile concentration is zero, is k_1. The rate constants for the substitution and elimination pathways are summarised in Table S7 and S8, respectively.

Table S7. The rate constants for the substitution reaction between 1-(1-chloroethyl)-4-methoxybenzene **4** and 3-chloropyridine **2b** in different mole fractions of [Bmim][$N(CF_3SO_2)_2$] in acetonitrile, at 41.3°C. The values for k_1 and k_2 are from the intercept and slope of the linear regression of k_S *vs* [Nu], respectively. The uncertainty is the error from the linear regression. Where N/A is given values were physically unrealistic, even incorporating uncertainty.

Mole fraction of ionic liquid	**[Nu] / mol L^{-1}**	**k_{obs} / x 10^{-4} s^{-1}**	**[S]/ ([S]+[E])**	**k_S / x 10^{-4} s^{-1}**	**k_1 / x 10^{-4} s^{-1}**	**k_2 / x 10^{-4} L mol^{-1} s^{-1}**
0	0.207	1.66	0.561	0.93	0.635 (0.067)	1.11 (0.19)
		1.57	0.534	0.84		
		1.68	0.533	0.89		
	0.337	1.50	0.587	0.88		
		1.70	0.584	0.99		
		1.77	0.582	1.03		
	0.407	1.98	0.566	1.12		
		1.84	0.576	1.06		
		1.94	0.545	1.05		
	0.449	1.96	0.589	1.16		
		2.04	0.601	1.22		
		1.86	0.603	1.12		
0.02	0.228	4.68	0.818	3.83	4.66 (0.73)	N/A
		4.49	0.829	3.72		
		4.53	0.826	3.74		
	0.321	5.09	0.833	4.24		
		5.56	0.835	4.64		
		5.29	0.836	4.43		
	0.390	4.51	0.844	3.81		
		5.29	0.840	4.45		
		3.91	0.840	3.28		
	0.449	2.94	0.858	2.52		
		4.67	0.847	3.95		
		3.97	0.831	3.30		
0.11	0.150	17.14	0.920	15.76	9.7 (1.4)	42.9 (5.0)
		18.91	0.915	17.31		
		19.17	0.919	17.62		
	0.233	19.88	0.929	18.48		
		22.46	0.932	20.92		
		19.84	0.923	18.31		
	0.289	21.97	0.925	20.31		
		21.71	0.931	20.21		
	0.395	30.69	0.948	29.09		
		28.20	0.943	26.59		
		28.39	0.937	26.60		

0.26	0.141	20.19	0.888	17.94	17.1 (1.5)	14.4 (5.6)
		19.16	0.891	17.08		
		20.94	0.886	18.56		
	0.185	24.27	0.895	21.73		
		23.71	0.922	21.87		
		25.40	0.940	23.89		
	0.227	21.64	0.910	19.70		
		20.86	0.904	18.86		
		19.12	0.919	17.58		
	0.425	26.14	0.922	24.11		
		25.96	0.908	23.57		
		23.81	0.924	21.99		
0.48	0.209	26.95	0.884	23.81	15.3 (2.7)	40.5 (7.6)
		27.71	0.891	24.70		
	0.297	32.03	0.899	28.78		
		28.84	0.899	25.93		
		28.73	0.895	25.70		
	0.364	33.08	0.935	30.94		
		33.89	0.932	31.58		
		30.13	0.920	27.73		
	0.463	37.53	0.939	35.25		
		40.74	0.918	37.40		
		31.28	0.959	29.98		
0.58	0.165	16.66	0.872	14.53	12.4 (1.0)	17.8 (3.7)
		17.87	0.864	15.43		
		18.40	0.848	15.61		
	0.272	20.78	0.869	18.07		
		20.13	0.865	17.41		
		20.33	0.873	17.75		
	0.362	19.84	0.888	17.61		
		20.44	0.889	18.17		
		22.89	0.882	20.19		
0.83	0.237	21.86	0.871	19.05	24.2 (3.7)	-5 (11)
		24.10	0.853	20.55		
		23.38	0.899	21.02		
	0.271	28.53	0.869	24.80		
		30.39	0.885	26.89		
		29.72	0.886	26.33		
	0.342	24.96	0.856	21.38		
		27.40	0.902	24.72		
		23.37	0.860	20.10		
	0.417	24.86	0.869	21.60		
		25.84	0.872	22.53		
		22.80	0.873	19.91		

Table S8. The rate constants for the elimination reaction between 1-(1-chloroethyl)-4-methoxybenzene **4** and 3-chloropyridine **2b** in different mole fractions of [Bmim][N(CF_3SO_2)$_2$] in acetonitrile, at 41.3°C. The values for k_1 and k_2 are from the intercept and slope of the linear regression of k_E *vs* [Nu], respectively. The uncertainty is the error from the linear regression. Where N/A is given values were physically unrealistic, even incorporating uncertainty.

Mole Fraction [Bmim][N(CF_3SO_2)$_2$]	**[Nu] / mol L^{-1}**	**k_{obs} / x 10^{-4} s^{-1}**	**[E]/ ([S]+[E])**	**k_E / x 10^{-4} s^{-1}**	**k_1 / x 10^{-4} s^{-1}**	**k_2 / x 10^{-4} L mol^{-1} s^{-1}**
0	0.207	1.66	0.439	0.73	0.664 (0.078)	0.29 (0.22)
		1.57	0.466	0.73		
		1.68	0.467	0.78		
	0.337	1.50	0.413	0.62		
		1.70	0.416	0.71		
		1.77	0.418	0.74		
	0.407	1.98	0.434	0.86		
		1.84	0.424	0.78		
		1.94	0.455	0.88		
	0.449	1.96	0.411	0.80		
		2.04	0.399	0.81		
		1.86	0.397	0.74		
0.02	0.228	4.68	0.182	0.85	1.08 (0.14)	N/A
		4.49	0.171	0.77		
		4.53	0.174	0.79		
	0.321	5.09	0.167	0.85		
		5.56	0.165	0.92		
		5.29	0.164	0.87		
	0.390	4.51	0.156	0.71		
		5.29	0.160	0.84		
		3.91	0.160	0.62		
	0.449	2.94	0.142	0.42		
		4.67	0.153	0.72		
		3.97	0.169	0.67		
0.11	0.150	17.14	0.080	1.38	1.375 (0.087)	0.70 (0.31)
		18.91	0.085	1.60		
		19.17	0.081	1.55		
	0.233	19.88	0.071	1.40		
		22.46	0.068	1.54		
		19.84	0.077	1.53		
	0.289	21.97	0.075	1.66		
		21.71	0.069	1.50		
	0.395	30.69	0.052	1.60		
		28.20	0.057	1.61		
		28.39	0.063	1.79		

0.26	0.141	20.19	0.112	2.25	2.06 (0.24)	-0.1 (0.9)
		19.16	0.109	2.08		
		20.94	0.114	2.38		
	0.185	24.27	0.105	2.54		
		23.71	0.078	1.84		
		25.40	0.060	1.51		
	0.227	21.64	0.090	1.94		
		20.86	0.096	2.00		
		19.12	0.081	1.54		
	0.425	26.14	0.078	2.03		
		25.96	0.092	2.39		
		23.81	0.076	1.82		
0.48	0.209	26.95	0.116	3.14	3.44 (0.57)	N/A
		27.71	0.109	3.01		
	0.297	32.03	0.101	3.25		
		28.84	0.101	2.91		
		28.73	0.105	3.03		
	0.364	33.08	0.065	2.14		
		33.89	0.068	2.31		
		30.13	0.080	2.40		
	0.463	37.53	0.061	2.28		
		40.74	0.082	3.34		
0.58	0.165	16.66	0.128	2.13	2.56 (0.31)	-0.2 (1.1)
		17.87	0.136	2.44		
		18.40	0.152	2.79		
	0.272	20.78	0.131	2.71		
		20.13	0.135	2.72		
		20.33	0.127	2.58		
	0.362	19.84	0.112	2.23		
		20.44	0.111	2.27		
		22.89	0.118	2.70		
0.83	0.237	21.86	0.129	2.81	3.16 (0.59)	0.1 (1.8)
		24.10	0.147	3.55		
		23.38	0.101	2.36		
	0.271	28.53	0.131	3.73		
		30.39	0.115	3.50		
		29.72	0.114	3.39		
	0.342	24.96	0.144	3.58		
		27.40	0.098	2.68		
		23.37	0.140	3.27		
	0.417	24.86	0.131	3.26		
		25.84	0.128	3.31		
		22.80	0.127	2.89		

Rate data used for determination of the activation parameters for the reaction of compounds **4** and **2b,** parts of which are shown in Table 2, main text:

Table S9. The mass of each component used prepare the mixtures, and the resultant mole fraction of [Bmim][N(CF_3SO_2)$_2$], and the concentration of the nucleophile **2b** for reactions between1-(1-chloroethyl)-4-methoxybenzene **4** and 3-chloropyridine **2b**.

Temperature / °C	**Mass of ionic liquid / g**	**Mass acetonitrile /g**	**Mass pyridine 2b / g**	**Mass chlorid 4 / g**	**[Nu] / mol L^{-1}**	**χ_{IL}**
27.7	0	1.5762	0.0467	0.005	0.206	0
	0	1.5616	0.0588	0.004	0.259	0
	0	1.5746	0.0738	0.005	0.325	0
34.7	0	1.5752	0.0408	0.006	0.180	0
	0	1.5616	0.0519	0.005	0.229	0
	0	1.5540	0.0754	0.005	0.332	0
	0	1.5428	0.1110	0.007	0.489	0
41.3	0	1.567	0.0471	0.004	0.207	0
	0	1.545	0.0765	0.005	0.337	0
	0	1.554	0.0925	0.006	0.407	0
	0	1.505	0.1019	0.006	0.449	0
20.4	2.4410	0.1436	0.0455	0.005	0.200	0.60
	2.4135	0.1400	0.0606	0.005	0.267	0.59
	2.4254	0.1427	0.0708	0.005	0.312	0.58
	2.3770	0.1406	0.0998	0.005	0.439	0.57
27.7	2.4559	0.1397	0.0468	0.007	0.206	0.60
	2.4238	0.1406	0.0634	0.005	0.279	0.59
	2.4002	0.1428	0.0840	0.013	0.370	0.57
	2.3999	0.1412	0.1015	0.005	0.447	0.57
34.7	2.4664	0.1408	0.0436	0.005	0.192	0.61
	2.4386	0.1408	0.0625	0.005	0.275	0.59
	2.3893	0.1440	0.0822	0.005	0.362	0.57
	2.3564	0.1420	0.1060	0.006	0.467	0.56
41.3	2.4281	0.1409	0.0375	0.005	0.165	0.60
	2.4257	0.1438	0.0618	0.008	0.272	0.59
	2.4041	0.1430	0.0821	0.005	0.362	0.58

Table S10. The rate constants for the unimolecular component of reaction between 1-(1-chloroethyl)-4-methoxybenzene **4** and 3-chloropyridine **2b** in mole fractions of [Bmim][N(CF_3SO_2)$_2$], in acetonitrile of 0 and 0.58, over different temperatures. The k_1 values are from the intercept of the linear regression of k_{obs} vs [Nu], respectively. The uncertainty is the error from the linear regression.

Mole Fraction [Bmim][N(CF_3SO_2)$_2$]	**Temperature / °C**	**[Nu] / mol L^{-1}**	**k_{obs} / x 10^{-4} s^{-1}**	**k_1 / x 10^{-4} s^{-1}**
0	27.7	0.206	0.40	0.318 (0.033)
			0.40	
			0.35	
		0.259	0.40	
			0.39	
			0.41	
		0.325	0.42	
			0.43	
			0.41	
0	34.7	0.180	0.91	0.734 (0.051)
			0.88	
			0.76	
		0.229	0.94	
			0.92	
			0.88	
		0.332	0.89	
			0.93	
			0.92	
		0.489	1.01	
			1.14	
0	41.3	0.207	1.66	1.30 (0.13)
			1.57	
			1.68	
		0.337	1.50	
			1.70	
			1.77	
		0.407	1.98	
			1.84	
			1.94	
		0.449	1.96	
			2.04	
			1.86	
0.58	20.4	0.200	2.23	1.71 (0.13)
			2.11	
			2.26	

		0.267	2.24	
			2.27	
			2.29	
		0.312	2.21	
			2.19	
			2.50	
		0.439	2.69	
			2.85	
			2.56	
0.58	27.7	0.206	4.38	3.276 (0.090)
			4.33	
			4.37	
		0.279	4.80	
			4.71	
			4.61	
		0.370	5.33	
			5.32	
			5.14	
		0.447	5.68	
			5.59	
			5.50	
0.58	34.7	0.192	8.47	6.06 (0.51)
			9.36	
			8.71	
		0.275	9.79	
			9.81	
			9.66	
		0.362	11.85	
			10.60	
		0.467	13.47	
			11.98	
			12.41	
0.58	41.3	0.165	16.66	15.0 (1.3)
			17.87	
			18.40	
		0.272	20.78	
			20.13	
			20.33	
		0.362	19.84	
			20.44	
			22.89	

Figure S2. The Eyring plot from which the activation parameters were determined for the unimolecular component of reaction between 1-(1-chloroethyl)-4-methoxybenzene **4** and 3-chloropyridine **2b** in mole fractions of [Bmim][N(CF_3SO_2)$_2$], in acetonitrile of 0 (black) and 0.58 (blue).

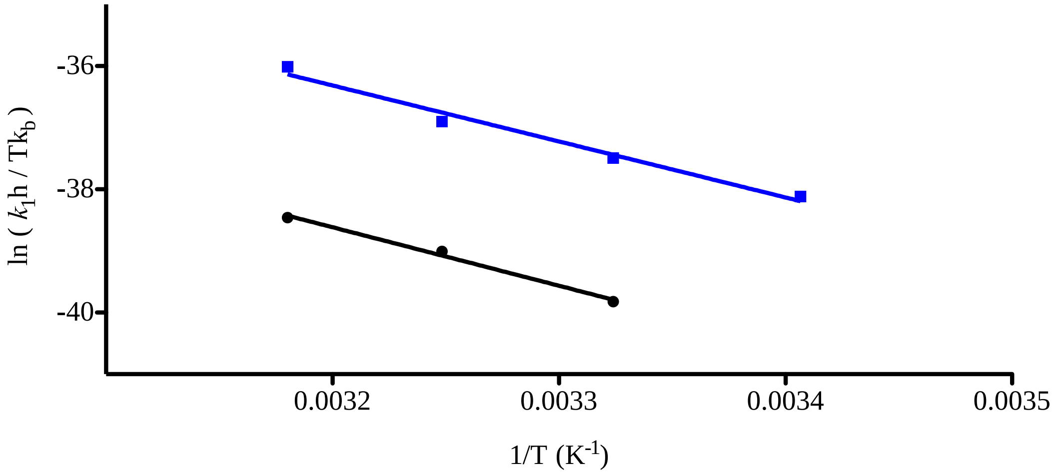

Table S11. The rate constants for the bimolecular substitution component of reaction between 1-(1-chloroethyl)-4-methoxybenzene **4** and 3-chloropyridine **2b** in mole fractions of [Bmim][N(CF_3SO_2)$_2$], in acetonitrile of 0 and 0.58, over different temperatures. The k_2 values are from the slope of the linear regression of k_{obs} vs [Nu], respectively. The uncertainty is the error from the linear regression.

Mole Fraction [Bmim][N(CF_3SO_2)$_2$]	**Temperature / °C**	**[Nu] / mol L^{-1}**	**k_{obs} / x 10^{-4} s^{-1}**	**[S]/ ([S]+[E])**	**k_S / x 10^{-4} s^{-1}**	**k_2 / x 10^{-4} s^{-1}**
0						0.356
	27.7	0.206	0.40	0.587	0.23	(0.057)
			0.40	0.574	0.23	
			0.35	0.603	0.21	
		0.259	0.40	0.621	0.25	
			0.39	0.634	0.25	
			0.41	0.627	0.26	
		0.325	0.42	0.636	0.27	
			0.43	0.624	0.27	
			0.41	0.655	0.27	

0						0.558
	34.7	0.180	0.91	0.526	0.48	(0.104)
			0.88	0.524	0.46	
			0.76	0.541	0.41	
		0.229	0.94	0.576	0.54	
			0.92	0.583	0.54	
			0.88	0.651	0.57	
		0.332	0.89	0.608	0.54	
			0.93	0.632	0.59	
			0.92	0.627	0.57	
		0.489	1.01	0.625	0.63	
			1.14	0.576	0.66	
0						1.125
	41.3	0.207	1.66	0.561	0.93	(0.186)
			1.57	0.534	0.84	
			1.68	0.533	0.89	
		0.337	1.50	0.587	0.88	
			1.70	0.584	0.99	
			1.77	0.582	1.03	
		0.407	1.98	0.566	1.12	
			1.84	0.576	1.06	
			1.94	0.545	1.05	
		0.449	1.96	0.589	1.16	
			2.04	0.601	1.22	
			1.86	0.603	1.12	
0.58						2.15
	20.4	0.200	2.23	0.881	1.97	(0.37)
			2.11	0.884	1.87	
			2.26	0.889	2.01	
		0.267	2.24	0.896	2.00	
			2.27	0.890	2.02	
			2.29	0.891	2.04	
		0.312	2.21	0.905	1.99	
			2.19	0.918	2.01	
			2.50	0.903	2.25	
		0.439	2.69	0.907	2.44	
			2.85	0.917	2.61	
			2.56	0.897	2.29	
0.58						5.36
	27.7	0.206	4.38	0.863	3.78	(0.27)
			4.33	0.864	3.74	
			4.37	0.862	3.76	
		0.279	4.80	0.880	4.22	
			4.71	0.893	4.21	
			4.61	0.879	4.06	

		0.370	5.33	0.892	4.75	
			5.32	0.892	4.74	
			5.14	0.892	4.58	
		0.447	5.68	0.909	5.16	
			5.59	0.899	5.02	
			5.50	0.896	4.92	
0.58	34.7	0.192	8.47	0.858	7.26	13.8 (1.4)
			9.36	0.860	8.06	
			8.71	0.859	7.48	
		0.275	9.79	0.856	8.39	
			9.81	0.862	8.46	
			9.66	0.863	8.34	
		0.362	11.85	0.877	10.39	
			10.60	0.882	9.35	
		0.467	13.47	0.900	12.12	
			11.98	0.892	10.68	
			12.41	0.896	11.12	
0.58	41.3	0.165	16.66	0.872	14.53	17.8 (3.7)
			17.87	0.864	15.43	
			18.40	0.848	15.61	
		0.272	20.78	0.869	18.07	
			20.13	0.865	17.41	
			20.33	0.873	17.75	
		0.362	19.84	0.888	17.61	
			20.44	0.889	18.17	
			22.89	0.882	20.19	

Figure S3. The Eyring plot from which the activation parameters were determined for the bimolecular subsitution component of reaction between 1-(1-chloroethyl)-4-methoxybenzene **4** and 3-chloropyridine **2b** in mole fractions of [Bmim][N(CF_3SO_2)$_2$], in acetonitrile of 0 (black) and 0.58 (blue).

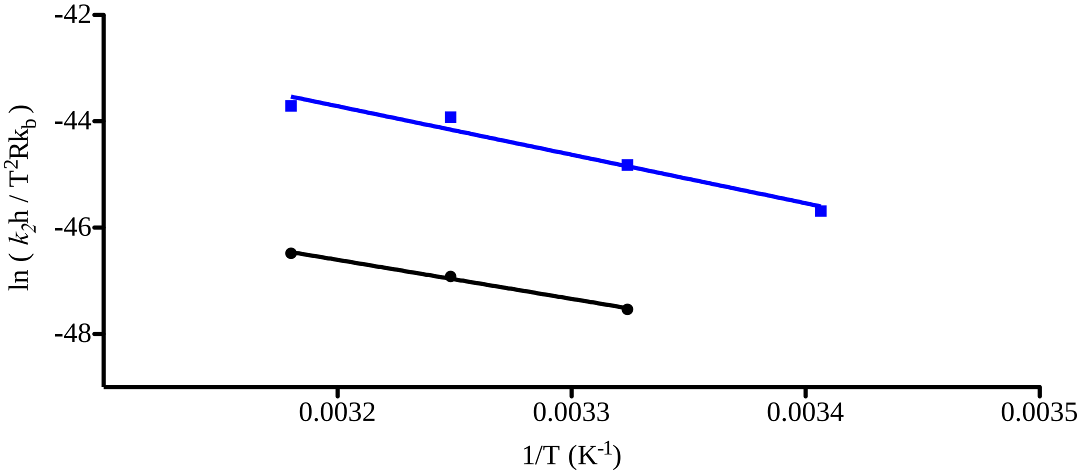

Table S12. The rate constants for the bimolecular elimination component of reaction between 1-(1-chloroethyl)-4-methoxybenzene **4** and 3-chloropyridine **2b** in mole fractions of [Bmim][N(CF_3SO_2)$_2$], in acetonitrile of 0 and 0.58, over different temperatures. The k_2 values are from the slope of the linear regression of k_{obs} vs [Nu], respectively. The uncertainty is the error from the linear regression. Where N/A is given values were physically unrealistic, even incorporating uncertainty.

Mole fraction of ionic liquid	Temperature / °C	[Nu] / mol L^{-1}	k_{obs} / x 10^{-4} s^{-1}	[E]/ ([S]+[E])	k_E / x 10^{-4} s^{-1}	k_2 / x 10^{-4} s^{-1}
0						-0.049
	27.7	0.206	0.40	0.413	0.17	(0.081)
			0.40	0.426	0.17	
			0.35	0.397	0.14	
		0.259	0.40	0.379	0.15	
			0.39	0.366	0.14	
			0.41	0.373	0.15	
		0.325	0.42	0.364	0.15	
			0.43	0.376	0.16	
			0.41	0.345	0.14	
0	34.7	0.180	0.91	0.474	0.43	0.10 (0.14)
			0.88	0.476	0.42	
			0.76	0.459	0.35	
		0.229	0.94	0.424	0.40	
			0.92	0.417	0.38	
			0.88	0.349	0.31	

		0.332	0.89	0.392	0.35	
			0.93	0.368	0.34	
			0.92	0.373	0.34	
		0.489	1.01	0.375	0.38	
			1.14	0.424	0.48	
0	41.3	0.207	1.66	0.439	0.73	0.29 (0.21)
			1.57	0.466	0.73	
			1.68	0.467	0.78	
		0.337	1.50	0.413	0.62	
			1.70	0.416	0.71	
			1.77	0.418	0.74	
		0.407	1.98	0.434	0.86	
			1.84	0.424	0.78	
			1.94	0.455	0.88	
		0.449	1.96	0.411	0.80	
			2.04	0.399	0.81	
			1.86	0.397	0.74	
0.58	20.4	0.200	2.23	0.119	0.27	-0.010 (0.081)
			2.11	0.116	0.24	
			2.26	0.111	0.25	
		0.267	2.24	0.104	0.23	
			2.27	0.110	0.25	
			2.29	0.109	0.25	
		0.312	2.21	0.095	0.21	
			2.19	0.082	0.18	
			2.50	0.097	0.24	
		0.439	2.69	0.093	0.25	
			2.85	0.083	0.24	
			2.56	0.103	0.26	
0.58	27.7	0.206	4.38	0.137	0.60	N/A
			4.33	0.136	0.59	
			4.37	0.138	0.60	
		0.279	4.80	0.120	0.58	
			4.71	0.107	0.50	
			4.61	0.121	0.56	
		0.370	5.33	0.108	0.58	
			5.32	0.108	0.58	
			5.14	0.108	0.56	
		0.447	5.68	0.091	0.52	
			5.59	0.101	0.57	
			5.50	0.104	0.57	
0.58	34.7	0.192	8.47	0.142	1.21	0.18 (0.22)
			9.36	0.140	1.31	
			8.71	0.141	1.23	

		0.275	9.79	0.144	1.41	
			9.81	0.138	1.36	
			9.66	0.137	1.32	
		0.362	11.85	0.123	1.46	
			10.60	0.118	1.25	
		0.467	13.47	0.100	1.35	
			11.98	0.108	1.30	
			12.41	0.104	1.29	
0.58	41.3	0.165	16.66	0.128	2.13	-0.2 (1.1)
			17.87	0.136	2.44	
			18.40	0.152	2.79	
		0.272	20.78	0.131	2.71	
			20.13	0.135	2.72	
			20.33	0.127	2.58	
		0.362	19.84	0.112	2.23	
			20.44	0.111	2.27	
			22.89	0.118	2.70	

Ratio of the substitution and elimination products **5** and **6** in the reaction compounds **4** and **2b** at an arbitrary concentration of nucleophile **2b** in various mole fractions of [Bmim][N(CF_3SO_2)$_2$] in acetonitrile, shown in Figure 7, main text:

The ratio of the integrations of the signals due to the benzylic proton in the elimination and substitution products **5** and **6**, at δ *ca.* 6.2 and δ *ca.* 6.6, respectively was examined for all spectra obtained over *ca.* 3 half lives (*ca.* 100 spectra for each replicate)[iii] with three replicates at each mole fraction of the ionic liquid. The data is obtained from the reactions described in Table S7 for nucleophile concentrations *ca.* 0.2 mol L^{-1}.

Table S13. The ratio between the integrations of the signals due to the substitution product **5** and the elimination product **6** for the reaction between the chloride **4** and pyridine **2b** ([Nu] *ca.* 0.2 mol L^{-1}) across various mole fractions of [Bmim][N(CF_3SO_2)$_2$] in acetonitrile at 314 K.

Mole fraction of ionic liquid	Ratio product 5 / product 6	Average (half the range)
0.00	1.2809	1.194
0.00	1.1495	(0.065)
0.00	1.1528	
0.02	4.5216	4.71
0.02	4.8512	(0.16)
0.02	4.7566	
0.11	13.375	13.3
0.11	14.470	(1.1)
0.11	12.271	
0.26	10.169	10.4
0.26	9.4691	(1.0)
0.26	11.455	
0.47	8.1576	8.78
0.47	8.4887	(0.76)
0.47	9.6873	
0.63	6.8560	8.8
0.63	8.2660	(1.3)
0.63	9.4087	
0.82	6.8145	7.2
0.82	5.8494	(1.6)
0.82	8.9581	

[iii] The ratio should remain consistent throughout the course of the reaction; this was observed, confirming no reaction of either of the products.

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