

## Electronic supporting information for

“The effects of an ionic liquid on unimolecular substitution processes:  
the importance of the extent of transition state solvation”

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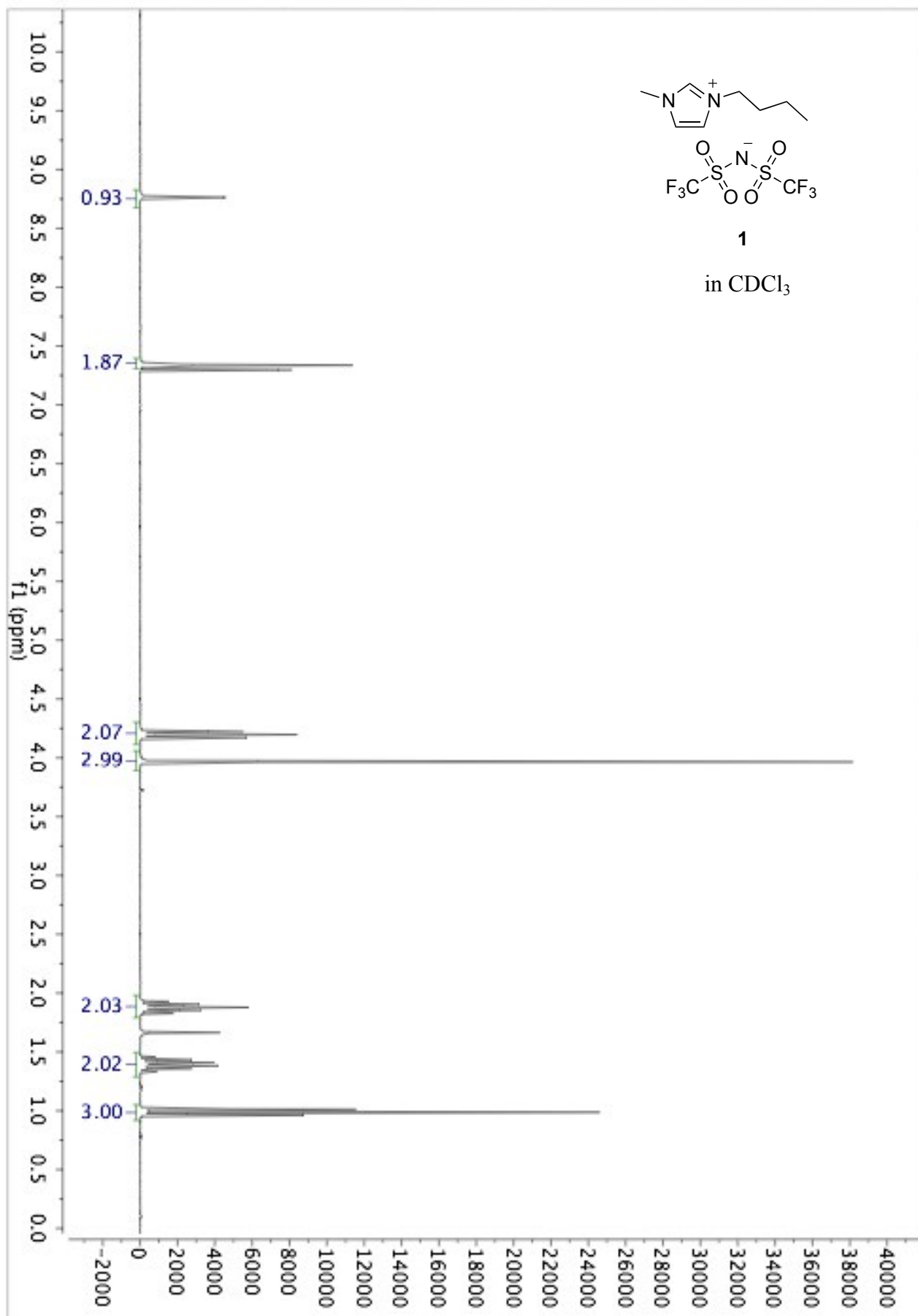
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## Synthesis of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide

### ([Bmim][N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>]**1**)

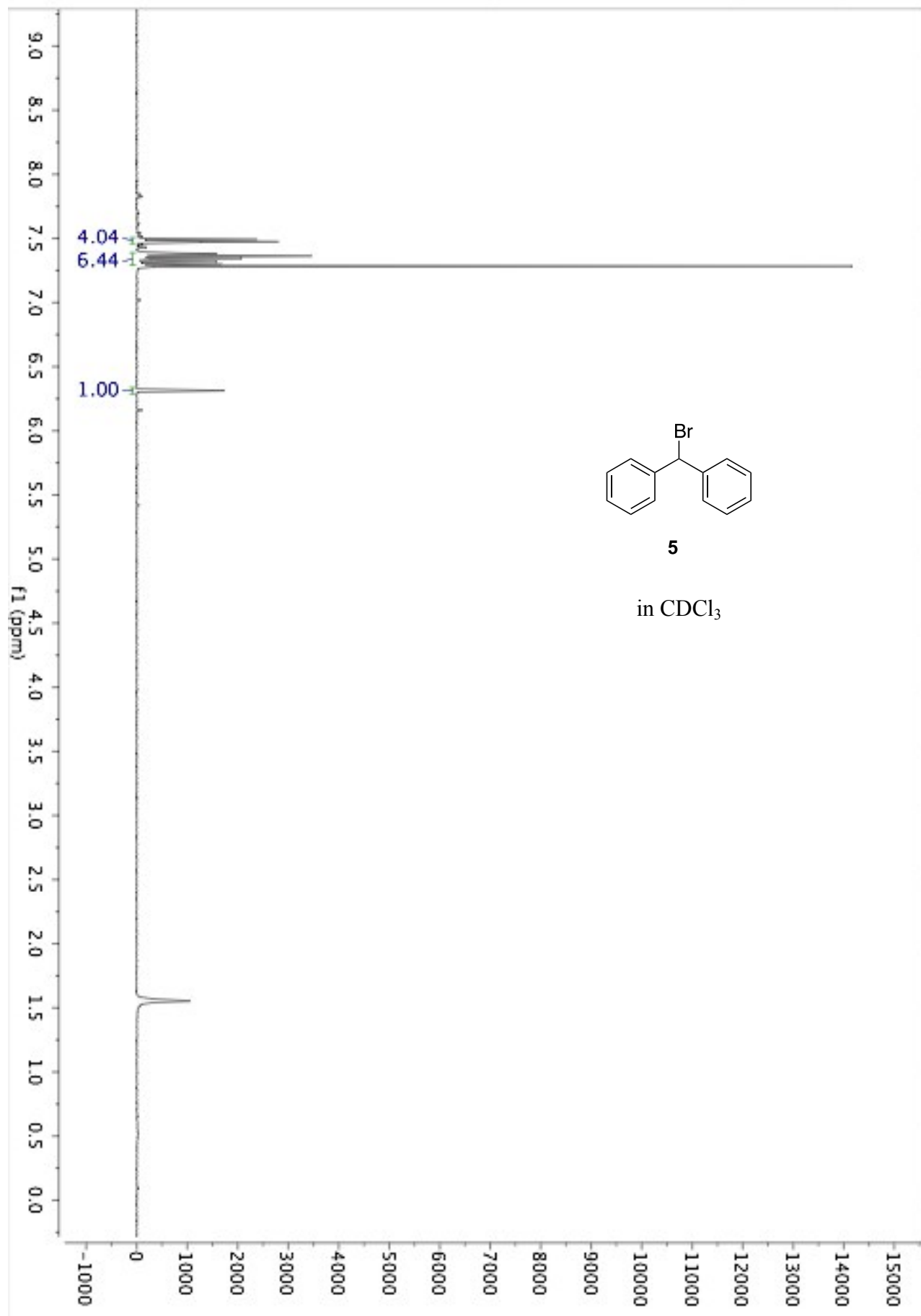
A mixture of 1-methylimidazole (49.5 g, 0.603 mol) and 1-bromobutane (122.0 g, 0.890 mol) was stirred at room temperature for one week under a nitrogen atmosphere. Over this period two immiscible layers developed, with the lower layer containing the intermediate bromide salt. The upper layer was poured off and discarded, and the lower layer shaken with ethyl acetate during which a white solid formed immediately. The white amorphous solid was ground to a fine powder using a mortar and pestle under a layer of ethyl acetate. The solid was then filtered, washed with ethyl acetate, and dried under reduced pressure to obtain the bromide salt as a hygroscopic white solid (130 g, 98%) which was used without further purification. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.89 (t, *J* = 7.4 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.31 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.82 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 4.08 (s, 3H, NCH<sub>3</sub>), 4.28 (t, *J* = 7.4 Hz, 2H, NCH<sub>2</sub>), 7.48 and 7.62 (m, 2H, CHCH), 10.12 (s, 1H, NCHN), which matched the previously reported <sup>1</sup>H NMR data.<sup>1</sup>

1-Butyl-3-methylimidazolium bromide (141.0 g, 0.6430 mol) was dissolved in Milli-Q water (100 mL) and added to a solution of lithium bis(trifluoromethanesulfonyl)imide (176.7 g, 0.6155 mol) in Milli-Q water (150 mL). The mixture was stirred at room temperature overnight, during which two layers developed. The ionic liquid **1** was extracted from the mixture using dichloromethane (2 x 80 mL), the organic extracts were collected and washed with water (8 x 80 mL). Excess dichloromethane was removed *in vacuo*, and the resulting colourless liquid was dried for 8 hours under reduced pressure (< 1 atmosphere) at 70°C, to afford the title compound **1** as a colourless viscous liquid (246.0 g, 92%), which was used without further purification. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 0.92 (t, *J* = 7.4 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.36 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.82 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 4.02 (s, 3H, NCH<sub>3</sub>), 4.21 (t, *J* = 7.4 Hz, 2H, NCH<sub>2</sub>), 7.35 (m, 2H, CHCH), 8.76 (s, 1H, NCHN), which matched the previously reported <sup>1</sup>H NMR data.<sup>2,3</sup>



### Synthesis of bromodiphenylmethane **5**

Benzhydrol (0.36 g, 0.0016 mol) was dissolved in dry dichloromethane (30 mL), the mixture was cooled to 0°C and phosphorus(III) bromide (1.0 mL, 0.030 mol) was added slowly. The mixture was protected from water in the atmosphere with a drying tube and was stirred at room temperature overnight. Excess phosphorus(III) bromide was quenched through slow addition of water, with vigorous stirring, until gas evolution ceased. The organic layer was then washed with water (3 x 40 mL) and saturated sodium bicarbonate solution (3 x 30 mL), then the organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to afford the compound **5** as a pale yellow oil. The oil was cooled to -20°C overnight to assist with crystallisation, to obtain the compound **5** as a white amorphous solid (0.34 g, 70%), which was used without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.29 (s, 1H, BrCH), 7.21 – 7.53 (m, 10H, Ar-H), which matched the previously reported <sup>1</sup>H NMR data.<sup>4</sup>



### Determination of a suitable reaction to analyse

Initially the reaction of the diphenyl species **5** with pyridine **6c** was considered; the observed rate constants were determined over a range of concentrations of the nucleophile **6c** and both the first and second order rate constants calculated. In this system, the bimolecular pathway dominated and the resulting large uncertainties in  $k_1$  made the process unsuitable for studies of the type considered here.

The unimolecular process might be favoured relative to the bimolecular pathway in three ways. The first is through stabilisation of the intermediate carbocation using electron donating groups on the phenyl rings of the substrate. Unfortunately, though perhaps not surprisingly,<sup>5</sup> the 4',4''-dimethoxy and 4',4''-dimethyl derivatives of substrate **5** were found to be very reactive and readily decomposed. A second method might be through incorporating a better leaving group, though given the instability of the substituted derivatives, this was not considered.

Alternatively, deactivation of the nucleophile through addition of an electron-withdrawing group might be used to disfavour the bimolecular process. This was initially examined using 2-chloropyridine **6b** and, although the overall rate of reaction was seen to decrease relative to the pyridine **6c** case as expected, the system was complicated as both (a) an equilibrium was established and (b) multiple products were observed; the latter is consistent with that seen previously for similar deactivated nucleophiles and is likely due to the ready polymerisation of 2- and 4-substituted pyridines.<sup>5</sup>

In contrast, the reaction of the bromide **5** with 3-chloropyridine **6a** proceeded readily to give the salt **7a**. An overall reduction in the observed rate constant was seen (by a factor of two) relative to that for the reaction of species **5** and **6c**, and there was an increase in the ratio of the first order rate constant to the second. The result was that the first order rate constants could be obtained with sufficient accuracy, allowing the effect of an ionic liquid on the unimolecular substitution process to be examined. Hence, this nucleophile was used for all further kinetic studies.

## Experimental details for the kinetic analyses

Reaction progress was monitored using  $^1\text{H}$  NMR spectroscopy on either a Bruker Avance III 400, Bruker Avance III 500 or Bruker Avance III 600 spectrometer with either a BBFO or TBI probe using *ca.* 0.5 mL of reaction mixture (details below) in a 5 mm NMR tube. Results were shown to be reproducible between the different spectrometers.

Kinetic analyses were carried out in solutions containing the electrophile **5** (*ca.* 0.01 mol L<sup>-1</sup>) and the nucleophile of interest (at either *ca.* 0.1, 0.2, 0.3 or 0.4 mol L<sup>-1</sup>, see ESI for further details) at a given temperature and specific mole fraction of the ionic liquid, with the remaining solvent being made up by deuterated acetonitrile. For all kinetic analyses there was at least a 10-fold molar excess of the nucleophile, so all reactions were under pseudo-first order conditions.

For all reactions between bromodiphenylmethane **5** and pyridine **6c**, the reactions of nucleophile **6a** conducted in the ionic liquid **1** and for the higher temperature reactions of nucleophile **6a** in acetonitrile, each reaction was monitored *in situ* until more than 90% of the electrophile **5** was consumed, with the spectrometer set to the desired temperature for the duration of the reaction and all kinetic analyses performed in triplicate. For the lower temperature reactions of reagents **5** and **6a** conducted in acetonitrile, and all reactions of species **5** and **6b** (in which the reactions proceeded much slower) NMR samples containing the reaction mixture were incubated in a water bath set to the desired temperature and were periodically analysed (at 275 K, to halt the reaction) using  $^1\text{H}$  NMR spectroscopy. Once again the reaction was monitored until more than 90% of the electrophile **5** was consumed, and each reaction was performed in triplicate.

NMR spectra were processed using either the Bruker TOPSPIN 1.3 software or the MestReNova 7.1.1 software. For each case the observed pseudo-first order rate constant ( $k_{\text{obs}}$ ) for the reaction was calculated using integrations of the signal corresponding to the benzylic proton in the electrophile **5** at  $\delta$  *ca.* 6.5, obtained from the processed  $^1\text{H}$  NMR spectra, by fitting the natural logarithm of the integrations to a linear function using the Microsoft Excel 14.4.3 LINEST function. An exemplar stacked  $^1\text{H}$  NMR plot showing the reaction progress over time, and the resulting first order decay plot from which the pseudo-first order rate constants could be determined, are included below.

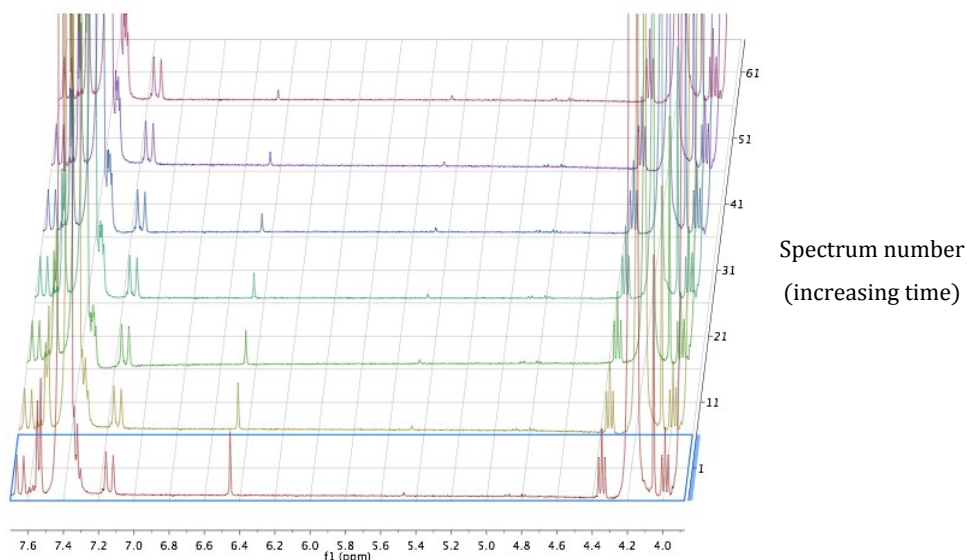
The obtained pseudo first order rate constants were plotted against the nucleophile concentration, allowing the unimolecular and bimolecular rate constants ( $k_1$  and  $k_2$ , respectively) to be determined according to Equation S1.

$$k_{\text{obs}} = k_1 + k_2[\text{Nu}] \quad (\text{S1})$$

Where carried out, the activation enthalpy and entropy were then determined through fitting the obtained rate constants to either the unimolecular or bimolecular Eyring equations<sup>6, 7</sup> (Equations S2 and S3, respectively) using the Microsoft Excel 14.4.3 LINEST function.

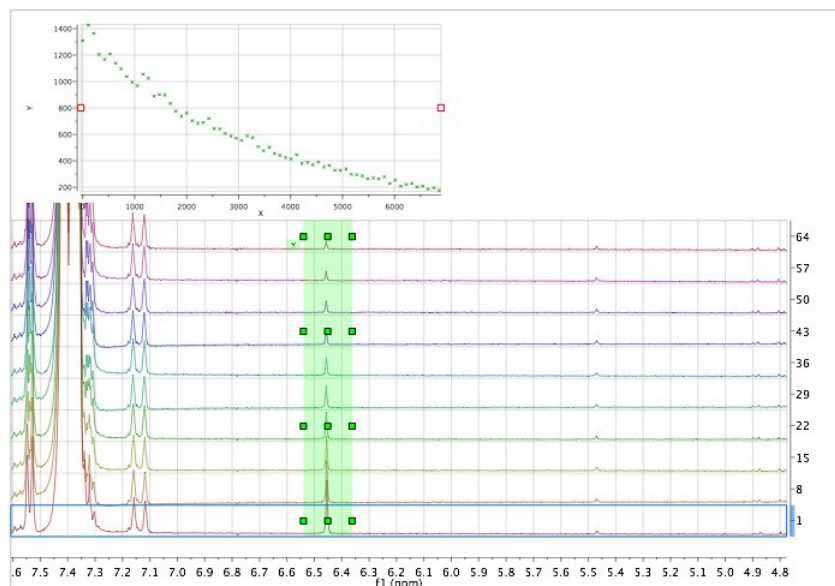
$$\ln\left(\frac{k_1 h}{k_B T}\right) = \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (\text{S2})$$

$$\ln\left(\frac{k_2 h}{k_B R T^2}\right) = \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (\text{S3})$$

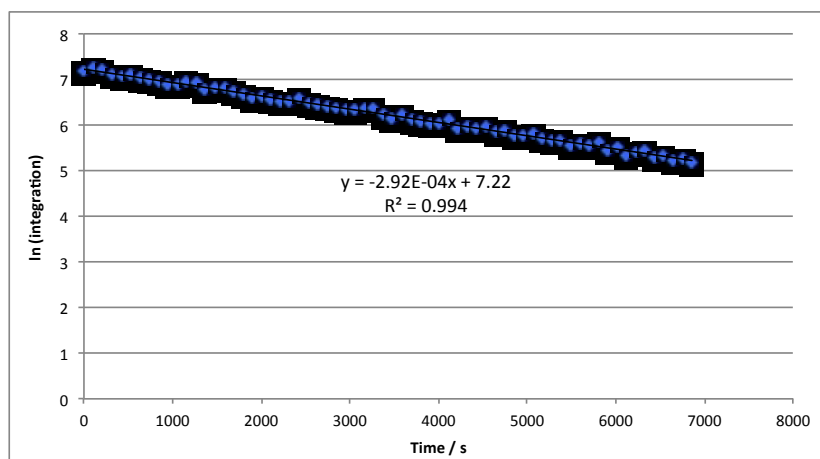


**Figure 1:** A stacked plot of the <sup>1</sup>H NMR spectra obtained over time, showing the disappearance of the benzylic proton of the starting material bromodiphenylmethane **5**, at  $\delta$  ca. 6.5. Only part of the spectrum is shown to allow the <sup>1</sup>H NMR signal of interest to be seen, as the rest of the spectrum is dominated by the ionic liquid **1** (which is present in a much larger concentration than reagent **5**).





**Figure 2:** A stacked plot of the  $^1\text{H}$  NMR spectra over time, showing the change in the integration of the signal corresponding to the benzylic proton at  $\delta$  ca. 6.5 in bromodiphenylmethane **5** as the reaction proceeds.



**Figure 3:** A plot of the natural logarithm of the integration of the benzylic signal of bromodiphenylmethane **5** at  $\delta$  ca. 6.5 over time. The pseudo first order rate constant of the reaction was determined from the slope of this plot.

Temperature dependent rate data for the reaction of bromodiphenylmethane **5** and 3-chloropyridine **6a** in acetonitrile

**Table S1.** The mass of each component used to prepare the mixtures, the resultant mole fraction of [Bmim][N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>] **1** and the concentration of the nucleophile **6a** for reactions between bromodiphenylmethane **5** and pyridine **6a**.

Temperature / °C	Mass of ionic liquid / g	Mass acetonitrile / g	Mass pyridine <b>6a</b> / g	Mass bromide <b>5</b> / g	[Nu] / mol L <sup>-1</sup>	χ <sub>IL</sub>
39.4	0	1.5031	0.0966	0.0034	0.425	0
	0	1.5249	0.0741	0.0036	0.326	0
	0	1.5636	0.0474	0.0033	0.209	0
	0	1.5797	0.0285	0.0040	0.126	0
47.5	0	1.5342	0.0970	0.0027	0.427	0
	0	1.5555	0.0769	0.0032	0.339	0
	0	1.5729	0.0471	0.003	0.207	0
	0	1.5759	0.0285	0.0029	0.126	0
52.0	0	1.5368	0.0965	0.0025	0.425	0
	0	1.5393	0.0745	0.0017	0.328	0
	0	1.564	0.0519	0.0032	0.229	0
	0	1.5772	0.0263	0.0031	0.116	0
56.2	0	1.5360	0.094	0.0039	0.414	0
	0	1.5370	0.0743	0.0041	0.327	0
	0	1.5552	0.0482	0.0043	0.212	0
	0	1.5772	0.0267	0.0034	0.118	0
	0	1.5283	0.1101	0.0021	0.485	0
63.5	0	1.5323	0.0972	0.0014	0.428	0
	0	1.5432	0.0744	0.0054	0.328	0
	0	1.5398	0.0543	0.0026	0.239	0
	0	1.5668	0.0288	0.0015	0.127	0

**Table S2.** The exact temperature, nucleophile concentration, the observed pseudo-first order rate constant ( $k_{\text{obs}}$ ) and the resultant  $k_1$  and  $k_2$  values, used for calculating the activation parameters for the reaction between bromodiphenylmethane **5** and pyridine **6a** in acetonitrile.

Temperature / °C	$\chi_{\text{IL}}$	[Nu] / mol L <sup>-1</sup>	$k_{\text{obs}} / 10^{-5} \text{ s}^{-1}$	$k_1 / 10^{-5} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
39.4	0	0.425	4.40	0.95 (0.14)	0.788 (0.046)
			4.04		
			4.06		
		0.326	3.57		
			3.72		
			3.75		
		0.209	2.68		
			2.75		
			2.68		
		0.126	1.83		
			1.74		
			1.84		
47.5	0	0.427	8.69	1.92 (0.28)	1.516 (0.094)
			7.76		
			8.80		
		0.339	6.40		
			7.43		
			7.35		
		0.207	4.94		
			4.89		
			5.10		
		0.126	3.99		
			4.00		
			3.67		
52.0	0	0.425	11.92	2.65 (0.38)	2.24 (0.13)
			12.53		
			9.41		
		0.328	9.83		
			10.07		
			7.95		
		0.229	8.53		
			7.61		
			4.75		
		0.116	5.40		
56.2	0	0.414	19.80	4.35 (1.31)	2.84 (0.39)
			17.58		

			17.23		
		0.327	13.55		
			12.56		
			16.63		
		0.212	12.47		
			10.27		
			9.04		
		0.118	6.57		
			6.81		
			7.28		
		0.485	15.46		
			17.54		
			15.19		
63.5	0	0.428	28.05	6.65 (0.97)	4.92 (0.32)
			28.82		
			28.32		
		0.328	23.19		
			23.44		
			19.69		
		0.239	17.05		
			18.23		
			18.11		
		0.127	13.86		
			13.00		
			13.66		

Temperature dependent rate data for the reaction of bromodiphenylmethane **5** and 3-chloropyridine **6a** in [Bmim][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] ( $\chi_{IL} = 0.20$ )

**Table S3.** The mass of each component used to prepare the mixtures, the resultant mole fraction of [Bmim][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] **1** and the concentration of the nucleophile **6a** for reactions between bromodiphenylmethane **5** and pyridine **6a**.

Temperature / °C	Mass of ionic liquid / g	Mass acetonitrile / g	Mass pyridine <b>6a</b> / g	Mass bromide <b>5</b> / g	[Nu] / mol L <sup>-1</sup>	$\chi_{IL}$
39.4	1.5775	0.6207	0.1014	0.0026	0.447	0.201
	1.5653	0.6313	0.0774	0.0018	0.341	0.199
	1.5671	0.6465	0.0567	0.0027	0.250	0.197
	1.5954	0.6627	0.0303	0.0015	0.133	0.199
47.5	1.5564	0.6196	0.1103	0.0020	0.486	0.198
	1.6267	0.6300	0.0757	0.0029	0.333	0.206
	1.5739	0.6304	0.0758	0.0027	0.334	0.200
	1.6098	0.6446	0.0500	0.0039	0.220	0.203
	1.5944	0.6611	0.0265	0.0018	0.117	0.200
52.0	1.5348	0.6233	0.1013	0.0020	0.446	0.196
	1.5798	0.6330	0.0767	0.0023	0.338	0.200
	1.5653	0.6453	0.0524	0.0028	0.231	0.198
	1.5238	0.6653	0.0368	0.0025	0.162	0.191
56.2	1.5867	0.6207	0.0980	0.0026	0.432	0.202
	1.5684	0.6309	0.0745	0.0030	0.328	0.200
	1.5746	0.6470	0.0530	0.0027	0.233	0.198
	1.5893	0.6602	0.0293	0.0023	0.129	0.199

**Table S4.** The exact temperature, nucleophile concentration, the observed pseudo-first order rate constant ( $k_{\text{obs}}$ ) and the resultant  $k_1$  and  $k_2$  values, used for calculating the activation parameters for the reaction between bromodiphenylmethane **5** and pyridine **6a** in acetonitrile and [Bmim][N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>] **1** ( $\chi_{\text{IL}} = 0.20$ )

Temperature / °C	$\chi_{\text{IL}}$	[Nu] / mol L <sup>-1</sup>	$k_{\text{obs}} / 10^{-5} \text{ s}^{-1}$	$k_1 / 10^{-5} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$			
39.4	0.201	0.447	30.46	15.0 (1.4)	3.37 (0.45)			
			31.31					
			32.46					
	0.199	0.341	23.24					
			26.99					
			24.59					
	0.197	0.250	23.48					
			20.88					
			23.28					
	0.199	0.133	20.15					
			20.75					
			20.81					
	47.5	0.198	0.486			67.19	24.9 (1.7)	8.93 (0.51)
						70.62		
						71.12		
0.200		0.334	53.00					
			51.08					
			50.58					
0.206		0.333	56.49					
			45.01					
0.203		0.220	45.75					
			37.48					
0.200		0.117	34.81					
			35.67					
			88.74					
52.0		0.196	0.446	89.51	36.4 (0.93)	12.1 (0.30)		
				91.17				
	78.00							
	0.200	0.338	76.14					
			79.01					
			65.03					
	0.198	0.231	65.25					
			63.34					
			56.09					
	0.191	0.162	55.21					
			55.22					

56.2	0.202	0.432	139.06	54.6 (3.7)	17.9 (1.2)
			136.65		
			127.13		
	0.200	0.328	108.50		
			115.15		
			105.03		
	0.198	0.233	98.26		
			97.60		
			92.98		
	0.199	0.129	76.52		
			79.87		
			80.54		

Temperature dependent rate data for the reaction of bromodiphenylmethane **5** and 3-chloropyridine **6a** in [Bmim][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] ( $\chi_{IL} = 0.88$ )

**Table S5.** The mass of each component used to prepare the mixtures, the resultant mole fraction of [Bmim][N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>] **1** and the concentration of the nucleophile **6a** for reactions between bromodiphenylmethane **5** and pyridine **6a**.

Temperature / °C	Mass of ionic liquid / g	Mass acetonitrile / g	Mass pyridine <b>6a</b> / g	Mass bromide <b>5</b> / g	[Nu] / mol L <sup>-1</sup>	$\chi_{IL}$
39.4	2.6004	0	0.0977	0.0062	0.430	0.875
	2.6177	0.0095	0.0751	0.0053	0.331	0.874
	2.6443	0.0168	0.048	0.0036	0.211	0.885
	2.6942	0.0264	0.0264	0.0034	0.116	0.884
43.7	2.6450	0	0.0983	0.0028	0.433	0.878
	2.5932	0.0085	0.0745	0.0032	0.328	0.878
	2.6605	0.0184	0.0483	0.0053	0.213	0.880
	2.6567	0.0257	0.0277	0.0037	0.122	0.883
47.5	2.5684	0	0.0976	0.003	0.430	0.875
	2.5772	0.0075	0.0752	0.0047	0.331	0.878
	2.6107	0.0176	0.0491	0.0045	0.216	0.880
	2.6426	0.0181	0.0481	0.0031	0.212	0.882
	2.6713	0.0246	0.0264	0.0030	0.116	0.888
	2.6443	0.0252	0.0277	0.0032	0.122	0.884
52.0	2.6700	0	0.0972	0.0037	0.428	0.880
	2.6578	0.0074	0.0755	0.0043	0.332	0.882
	2.6571	0.0170	0.0481	0.0058	0.212	0.884
	2.6294	0.0262	0.0289	0.0037	0.127	0.879
56.2	2.6421	0	0.0997	0.0046	0.439	0.875
	2.6970	0.0076	0.0745	0.0043	0.328	0.884
	2.7017	0.0141	0.0477	0.0044	0.210	0.895
	2.6618	0.0252	0.0267	0.0037	0.118	0.885



**Table S6.** The exact temperature, nucleophile concentration, the observed pseudo-first order rate constant ( $k_{\text{obs}}$ ) and the resultant  $k_1$  and  $k_2$  values, used for calculating the activation parameters for the reaction between bromodiphenylmethane **5** and pyridine **6a** in acetonitrile and [Bmim][N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>] **1** ( $\chi_{\text{IL}} = 0.88$ )

Temperature / °C	$\chi_{\text{IL}}$	[Nu] / mol L <sup>-1</sup>	$k_{\text{obs}} / 10^{-5} \text{ s}^{-1}$	$k_1 / 10^{-5} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$			
39.4	0.875	0.430	27.09	6.42 (2.02)	5.33 (0.68)			
			27.87					
			33.78					
	0.874	0.331	25.62					
			22.67					
			26.65					
	0.885	0.211	16.15					
			14.29					
			14.40					
	0.884	0.116	14.85					
			12.06					
			15.84					
	43.7	0.878	0.433			39.94	9.9 (1.8)	7.37 (0.58)
						41.09		
						41.43		
0.878		0.328	33.76					
			33.74					
			39.90					
0.884		0.214	24.15					
			25.00					
			25.12					
0.883		0.122	19.37					
			18.28					
47.5		0.875	0.430	64.17	12.5 (2.3)	11.16 (0.83)		
				56.13				
				58.10				
	0.878	0.331	44.75					
			53.74					
			53.59					
	0.880	0.216	39.80					
			0.882	0.212			35.64	
			38.70					
			32.89					
	0.888	0.116	22.64					
			21.86					
	0.884	0.122	27.10					

			29.39		
52.0	0.880	0.428	97.79	14.1 (3.3)	17.6 (1.1)
			84.38		
			85.90		
	0.882	0.332	72.22		
			66.20		
			75.55		
	0.884	0.212	52.99		
			55.50		
			53.77		
	0.879	0.127	34.15		
			36.28		
			34.08		
56.2	0.875	0.439	131.81	18.1 (6.2)	23.4 (2.1)
			119.41		
			121.26		
	0.884	0.328	105.41		
			82.36		
			79.25		
	0.895	0.210	72.08		
			75.72		
			61.91		
	0.885	0.118	44.16		
			45.72		
			47.83		

Rate data for the reaction of bromodiphenylmethane **5** and 3-chloropyridine **6a** in different mole fractions of [Bmim][N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>] **1** in acetonitrile

**Table S7.** The mass of each component used prepare the mixtures, the resultant mole fraction of [Bmim][N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>] **1** and the concentration of the nucleophile **6a** for reactions between bromodiphenylmethane **5** and pyridine **6a**.

<b>Mass of ionic liquid / g</b>	<b>Mass acetonitrile / g</b>	<b>Mass pyridine 6a / g</b>	<b>Mass bromide 5 / g</b>	<b>[Nu] / mol L<sup>-1</sup></b>	<b>χ<sub>IL</sub></b>
0	1.5342	0.0970	0.0027	0.427	<b>0</b>
0	1.5555	0.0769	0.0032	0.339	<b>0</b>
0	1.5729	0.0471	0.003	0.207	<b>0</b>
0	1.5759	0.0285	0.0029	0.126	<b>0</b>
0.6696	1.1578	0.0967	0.0022	0.426	<b>0.056</b>
0.6560	1.1644	0.0765	0.0032	0.337	<b>0.055</b>
0.6531	1.1787	0.0507	0.0033	0.223	<b>0.054</b>
0.7025	1.1945	0.0272	0.0025	0.120	<b>0.058</b>
1.1092	0.9125	0.0971	0.0022	0.428	<b>0.109</b>
1.0922	0.9240	0.0768	0.0018	0.338	<b>0.107</b>
1.1287	0.9350	0.0509	0.0021	0.224	<b>0.110</b>
1.0983	0.9510	0.0289	0.0025	0.127	<b>0.107</b>
1.5564	0.6196	0.1103	0.0020	0.486	<b>0.198</b>
1.6267	0.6300	0.0757	0.0029	0.333	<b>0.206</b>
1.5739	0.6304	0.0758	0.0027	0.334	<b>0.200</b>
1.6098	0.6446	0.0500	0.0039	0.220	<b>0.203</b>
1.5944	0.6611	0.0265	0.0018	0.117	<b>0.200</b>
1.9344	0.4098	0.1003	0.0018	0.442	<b>0.312</b>
1.9178	0.4121	0.0968	0.0035	0.426	<b>0.309</b>
1.9420	0.4242	0.0747	0.0026	0.329	<b>0.310</b>
1.9237	0.4417	0.0483	0.0030	0.213	<b>0.305</b>
1.9781	0.4480	0.0269	0.0015	0.118	<b>0.312</b>
2.2782	0.1890	0.0017	0.1004	0.442	<b>0.512</b>
2.3189	0.1894	0.0024	0.1033	0.455	<b>0.514</b>
2.2810	0.2006	0.0030	0.0754	0.332	<b>0.510</b>
2.2758	0.2126	0.0021	0.0492	0.217	<b>0.507</b>
2.3442	0.2234	0.0028	0.0268	0.118	<b>0.512</b>
2.3330	0.2316	0.0019	0.0293	0.129	<b>0.502</b>
2.4996	0.0766	0.0018	0.0992	0.437	<b>0.695</b>
2.5455	0.0871	0.0024	0.0781	0.344	<b>0.694</b>
2.5347	0.0959	0.0027	0.0502	0.221	<b>0.697</b>
2.5239	0.1038	0.0015	0.0287	0.126	<b>0.697</b>
2.5684	0	0.0030	0.0976	0.430	<b>0.875</b>
2.5772	0.0075	0.0047	0.0752	0.331	<b>0.878</b>

2.6107	0.0176	0.0045	0.0491	0.216	<b>0.880</b>
2.6426	0.0181	0.0031	0.0481	0.212	<b>0.882</b>
2.6713	0.0246	0.0030	0.0264	0.116	<b>0.888</b>
2.6443	0.0252	0.0032	0.0277	0.122	<b>0.884</b>

**Table S8.** The mole fraction of ionic liquid **1**, the nucleophile concentration, the observed pseudo-first order rate constant ( $k_{\text{obs}}$ ) and the resultant  $k_1$  and  $k_2$  values, for the reaction between bromodiphenylmethane **5** and pyridine **6a** across a number of mixtures of acetonitrile and [Bmim][N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>] **1**.

$\chi_{\text{IL}}$	[Nu] / mol L <sup>-1</sup>	$k_{\text{obs}} / 10^{-5} \text{ s}^{-1}$	$k_1 / 10^{-6} \text{ s}^{-1}$	$k_2 / 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
<b>0</b>	0.427	8.69	1.92 (0.28)	1.516 (0.094)
		7.76		
		8.80		
	0.339	6.40		
		7.43		
		7.35		
	0.207	4.94		
		4.89		
		5.10		
	0.126	3.99		
		4.00		
		3.67		
<b>0.05</b>	0.426	37.89	17.9 (0.92)	4.92 (0.30)
		40.41		
		38.65		
	0.337	36.23		
		34.56		
		32.51		
	0.223	28.37		
		29.16		
		24.97		
	0.120	23.85		
		22.94		
<b>0.11</b>	0.428	51.51	21.6 (0.77)	6.97 (0.26)
		50.06		
		53.51		
	0.338	44.85		

		44.30		
	0.224	37.54		
		36.89		
		36.97		
	0.127	29.62		
		30.94		
		31.35		
<b>0.20</b>	0.486	67.19	24.9 (1.7)	8.93 (0.51)
		70.62		
		71.12		
	0.334	53.00		
		51.08		
		50.58		
	0.333	56.49		
	0.220	45.01		
		45.75		
	0.117	37.48		
		34.81		
		35.67		
<b>0.31</b>	0.426	64.49	24.5 (1.7)	9.55 (0.60)
		64.52		
		65.99		
	0.329	54.24		
		57.27		
		56.24		
	0.213	43.94		
		50.53		
		41.60		
	0.118	35.85		
		33.28		
		37.07		
<b>0.51</b>	0.455	63.62	16.3 (1.5)	11.15 (0.51)
		65.99		
	0.442	69.27		
	0.332	51.78		
		53.79		
	0.217	43.53		
		42.76		
		41.26		
	0.118	30.15		
		27.67		
	0.129	29.07		
		29.43		
<b>0.70</b>	0.437	59.46	10.0 (1.8)	11.73 (0.60)
		59.04		

		63.86		
	0.344	55.30		
		51.79		
		46.16		
	0.221	35.91		
		35.95		
		35.79		
	0.126	24.52		
		24.00		
		25.49		
<b>0.88</b>	0.430	64.17	12.5 (2.3)	11.16 (0.83)
		56.13		
		58.10		
	0.331	44.75		
		53.74		
		53.59		
	0.216	39.80		
	0.212	35.64		
		38.70		
		32.89		
	0.116	22.64		
		21.86		
	0.122	27.10		
		29.39		

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