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Electronic Supporting Information for

"Nitrogen *versus* phosphorus nucleophiles - how changing the nucleophilic heteroatom affects ionic liquid solvent effects in bimolecular nucleophilic substitution processes"

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Synthesis of 1-butyl-3-methylimidazolium *bis*(trifluoromethanesulfonyl)imide ([Bmim][N(SO_2CF_3)$_2$]) **6**

A mixture of 1-bromobutane (9.91 g, 0.121 mol) and 1-methylimidazole (18.7 g, 0.136 mol) was stirred under a nitrogen atmosphere for 2 days at room temperature; during this time a white solid formed. Residual liquid was decanted off and the solid was washed with ethyl acetate (3 x 40 mL) and left overnight at -20 °C covered by a layer of ethyl acetate. Excess ethyl acetate was then removed under reduced pressure and the resulting white bromide salt was used without further purification (24.0 g, 0.110 mol, 91%). m.p. 75-77 ºC (lit.[1] 77-78 ºC). 1H NMR (400 MHz, CD3CN) □ 9.28 (s, 1H, -NCHN-), 7.52 (s, 1H, -NCHCHN-), 7.48 (s, 1H, -NCHCHN-), 4.23 (t, 2H, J = 7.1 Hz, -NCH2-), 3.91 (s, 3H, -NCH3), 1.84 (m, 2H, -NCH2CH2-), 1.35 (m, 2H, -N(CH2)2CH2-), 0.95 (t, 3H, J = 7.3 Hz, -N(CH2)3CH3).

A solution of 1-butyl-3-methylimidazolium bromide (24.0 g, 0.110 mol) in water (23 mL) was added to a solution of lithium *bis*(trifluoromethanesulfonyl)imide (32.0 g, 0.112 mol) in water (18 mL) and the mixture was stirred at room temperature for 24 hours. The reaction mixture was then extracted with dichloromethane (3 x 50 mL), and the combined organic layers were washed with water until a negative silver nitrate test was achieved (5 x 100 mL). Excess organic solvent was then removed *in vacuo* and the resultant liquid was dried under reduced pressure at room temperature for 6 hours to give the ionic liquid **6** as a clear, colourless liquid with a water content < 300 ppm (44.8 g, 0.107 mol, 97%). ^1H NMR (400 MHz, CD_3CN) δ 8.44 (s, 1H, -NC$\underline{H}$N-), 7.40 (s, 1H, -NC$\underline{H}$CHN-), 7.36 (s, 1H, -NCHC$\underline{H}$N-), 4.15 (t, 2H, *J* = 7.3 Hz, -NC$\underline{H}_2$), 3.85 (s, 3H, -NC$\underline{H}_3$), 1.85 (m, 2H, -NCH$_2$C$\underline{H}_2$-), 1.36 (m, 2H,

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[1] A. Hu, G. Cao, *Tetrahedron: Asymm.*, 2011, **22**, 1332-1336

-N(CH_2)$_2$C$\underline{H}_2$-), 0.96 (t, 3H, J = 7.4 Hz, -N(CH_2)$_3$C$\underline{H}_3$).

Reagent and product NMR signals monitored for kinetic studies

Reaction	***NMR method***	***Species followed***	***NMR Chemical Shift / ppm***
Triphenylamine **1** + Benzyl bromide **3**	^{1}H	**3** and **9a**	4.6 and 5.0
Triphenylphosphine **7b** + Benzyl bromide **3**	$^{31}P\{^{1}H\}$	**7b**	-5.5
Triphenylphosphine **7b** + Benzyl chloride **2**	$^{31}P\{^{1}H\}$	**7b**	-5.5
Tributylamine **10a** + Benzyl bromide **3**	^{1}H	**10a** and **12a**	4.6 and 4.5
Tributylphosphine **10b** + Benzyl chloride **2**	$^{31}P\{^{1}H\}$	**11b**	33

General preparation of kinetic samples

All reaction mixtures for kinetic studies were prepared as a stock solution of the chosen electrophile and nucleophile in a mixture containing the desired mole fraction of the ionic liquid **6**, the remaining solvent was deuterated acetonitrile. Stock solutions prepared for the kinetic studies of the reaction of pyridine **1** and benzyl bromide **3** were prepared in a similar manner except the electrophile **3** not included in the stock solutions. Instead *ca.* 4 mg or less of the electrophile was added to 0.5 mL of the prepared stock solution; an appropriate amount to ensure pseudo-first order conditions; immediately before monitoring of the reaction.

For all kinetic analyses there was a minimum of 10-fold molar excess of either the electrophile or nucleophile (dependent on the species being monitored using NMR spectroscopy, as detailed above) such that pseudo-first order conditions were met.

For cases in which more than one stock solution was prepared for a given solvent composition the resultant mole fraction reported was a weighted average value determined from the stock solutions used.

Determination of kinetic and activation parameter data

For the reaction of triphenylamine **7a** and benzyl bromide **3**, which proceeded very slowly, initial rates methodology was employed. The extent of conversion was monitored periodically up to *ca.* 8%. This allowed determination of the observed rate, with the bimolecular rate constants being determined from these data and the concentrations of both starting materials.

For systems in which unidirectional first order kinetics were demonstrated and the concentration of starting material followed, the reaction was monitored to at least 95% conversion of this starting material had occurred and Equation 1 was used to determine the pseudo first order rate constant using the LINEST function in Microsoft Excel. For systems in which the same conditions above were met but with production formation being monitored instead, pseudo first order rate data was obtained using GraphPad Prism 6 software (Equation 2). The bimolecular rate constant was then determined by dividing the pseudo first order rate constant by the concentration of the excess starting material used (Equation 3).

$$\ln[\mathrm{A}] = -k_{obs}t$$

Equation 1: Log form of the integrated first order rate equation; [A] = integral of limiting reagent, k_{obs} = the pseudo first order rate constant and t = time.

$$[C] = 1 - e^{-k_{obs}t}$$

Equation 2: Exponential function used when product formation was monitored for cases where unidirectional first order kinetics were demonstrate; [C] = the integral of the phosphonium salt **X**, k_2 = the pseudo first order rate constant and t = time.

$$k_{obs} = k_2[B]$$

Equation 3: Relationship used to convert pseudo first order rate constants into the corresponding bimolecular rate constants; k_2 = the bimolecular rate constant, k_{obs} = the pseudo first order rate constant and [B] = the concentration of the starting material (in excess).

Systems in which an equilibrium was established were monitored until the extent of conversion had reached a constant value; these kinetic data were analysed through numerically fitting the integration data of all species in the reaction mixture to a model based on the reaction shown in Scheme S1 using Solver in Excel. This provided the bimolecular rate constants for both the forward and reverse reactions.

$$A + B \leftrightharpoons C + D$$

Scheme S1: Reaction to which the reaction progress data was modelled to in cases where non-first order kinetics were observed. Where A and B = starting materials and C and D = products.

The activation enthalpy and entropy, where mentioned, were determined through fitting the obtained rate constants to the bimolecular Eyring equation (Equation 4) using the Microsoft Excel LINEST function.

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

Equation 4: The bimolecular Eyring Equation.[2]

Rate data for the reaction of pyridine **1** and benzyl bromide **3** in different mixtures of [Bmim][$N(SO_2CF_3)_2$] **6** in acetonitrile

Table S1. The composition of stock solutions by mass including resultant mole fractions and concentrations of nucleophile **1** and electrophile **3** for the reaction between pyridine **1** and benzyl bromide **3**.

Mass IL **6** / g	Mass acetonitrile / g	Mass pyridine **1** / g	[Nu] **1a** / mol L^{-1}	χ_6
-	1.6	0.084	0.53	0.0
0.68	1.2	0.084	0.53	0.053
1.1	1.0	0.078	0.49	0.10
1.5	0.80	0.084	0.53	0.16
1.7	0.64	0.082	0.52	0.21
2.0	0.45	0.083	0.52	0.30
2.3	0.30	0.084	0.53	0.41
2.4	0.20	0.081	0.51	0.51
2.5	0.13	0.084	0.53	0.60
2.6	0.07	0.084	0.53	0.70
2.7	0.3	0.081	0.51	0.79
2.8	-	0.057	0.36	0.90[2]
2.8	-	0.058	0.37	0.90[2]

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[2] Values plotted in the mole fraction dependence studies corresponding to the χ_6 0.90 are the average mole fraction and rate data of the two stock solutions prepared.

Table S2. The mole fraction of ionic liquid **6**, concentrations of nucleophile **1**, the observed pseudo-first order rate constants (k_{obs}) and resultant bimolecular rate constants (k_2) for the reaction between pyridine **1** and benzyl bromide **3** in a variety of solvent compositions of the ionic liquid **6** and acetonitrile at 22.2 ºC.

$\chi_{\mathbf{6}}$	[Nu] **1** / mol L^{-1}	k_{obs} / 10^{-9} s^{-1}	k_2 / 10^{-3} L mol^{-1} s^{-1}	Average k_2 / 10^{-3} L mol^{-1} s^{-1}
0.0	0.53	3.1	0.59	0.60 (0.02)
		3.3	0.63	
		3.1	0.59	
0.053	0.53	4.5	0.86	0.88 (0.02)
		4.7	0.88	
		4.7	0.90	
0.10	0.49	4.9	1.0	1.0 (0.0)
		4.9	1.0	
		4.9	1.0	
0.16	0.53	6.0	1.1	1.1 (0.0)
		6.1	1.2	
0.21	0.52	6.6	1.3	1.2 (0.0)
		6.4	1.2	
		6.3	1.2	
0.30	0.52	6.7	1.3	1.3 (0.0)
		6.8	1.3	
		6.9	1.3	
0.41	0.53	7.0	1.3	1.3 (0.0)
		6.9	1.3	
		7.4	1.4	
0.51	0.51	7.1	1.4	1.4 (0.0)
		7.2	1.4	
		7.1	1.4	
0.60	0.53	8.0	1.5	1.5 (0.0)
		7.3	1.4	
		8.0	1.5	
0.70	0.53	7.9	1.5	1.5 (0.0)
		8.0	1.5	
		8.6	1.6	
0.79	0.51	7.7	1.5	1.5 (0.0)
		7.7	1.5	
		7.7	1.5	
0.90	0.36	5.4	1.5	1.4 (0.1)
		4.7	1.3	
		4.9	1.4	
0.90	0.37	5.6	1.5	1.5 (0.2)
		6.4	1.7	
		4.7	1.3	

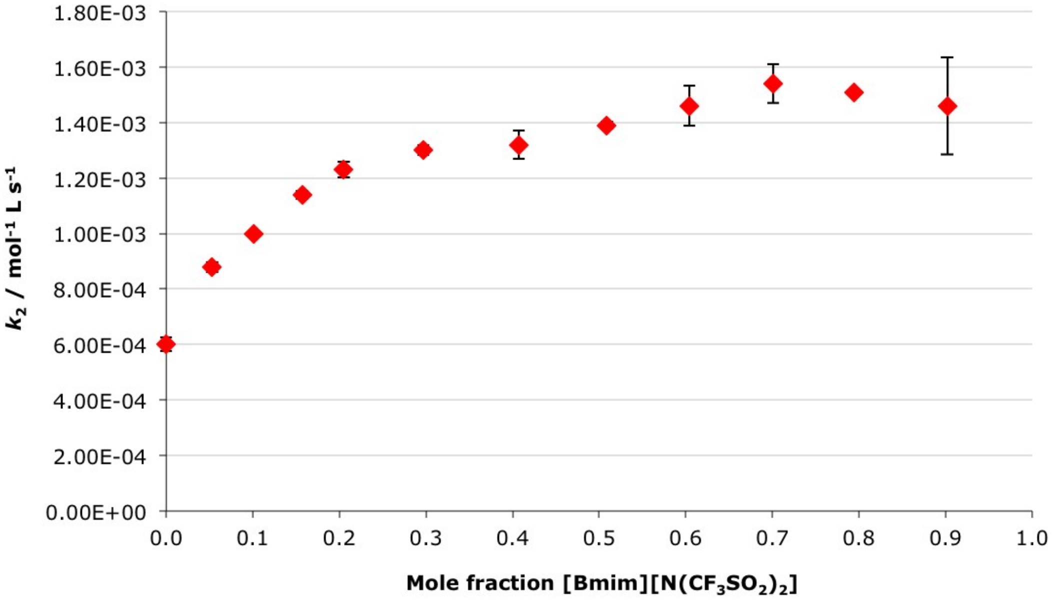

Figure S1. The dependence of the bimolecular rate constant of the reaction between pyridine **1** and benzyl bromide **3** for various mole fractions of the ionic liquid **6** in acetonitrile at 22.2 °C. Uncertainties are reported as the standard deviation of triplicate results (except χ_6 0.16, which was carried out in duplicate); some uncertainties fall within the size of the markers used.

Rate data for reaction between triphenylamine **7a** and benzyl bromide **3** in different mixtures of [Bmim][N(SO_2CF_3)$_2$] **6** in acetonitrile

Table S3. The composition of stock solutions by mass including resultant mole fractions and concentrations of nucleophile **7a** and electrophile **3** for the reaction between triphenylamine **7a** and benzyl bromide **3**.

Mass IL **6** / g	Mass acetonitrile / g	Mass triphenylamine **7a** / g	Mass benzyl bromide **3** / g	[E] **3** / mol L^{-1}	[Nu] **7a** / mol L^{-1}	χ_6
-	1.5	0.025	0.27	0.79	0.052	0
0.98	0.86	0.018	0.29	0.85	0.037	0.09
1.6	0.55	0.024	0.28	0.82	0.048	0.20
1.8	0.37	0.022	0.31	0.91	0.045	0.28
2.0	0.23	0.027	0.28	0.83	0.055	0.39
2.2	0.14	0.018	0.27	0.79	0.037	0.51
2.3	0.074	0.026	0.28	0.81	0.053	0.61
2.4	0.028	0.021	0.29	0.85	0.043	0.70
13	-	0.095	1.4	0.80	0.039	0.78

Table S4. The mole fraction of ionic liquid **6**, concentrations of nucleophile **7a** and electrophile **3**, the observed pseudo-first order rate constants (k_{obs}) and resultant bimolecular rate constants (k_2) for the reaction between triphenylamine **7a** and benzyl bromide **3** in a variety of solvent compositions of the ionic liquid **6** and acetonitrile at 75.0 ºC.

χ_6	[E] **3** / molL^{-1}	[Nu] **7a** / mol L^{-1}	k_{obs} / 10^{-9} s^{-1}	k_2 / 10^{-8} L mol^{-1} s^{-1}	Average k_2 / 10^{-8} L mol^{-1} s^{-1}
0	0.81	0.057	1.2	2.5	3.0 (0.6)
	0.81	0.057	1.3	2.9	
	0.83	0.046	1.4	3.7	
0.09	0.85	0.037	1.2	3.8	5.7 (3.5)
	0.85	0.037	1.1	3.6	
	0.85	0.037	3.1	9.7	
0.20	0.82	0.048	0.95	2.4	4.6 (1.9)
	0.82	0.048	2.3	5.9	
	0.82	0.048	2.1	5.4	
0.28	0.91	0.045	2.9	7.0	7.1 (2.7)
	0.91	0.045	1.8	4.4	
	0.91	0.045	4.1	9.8	
0.39	0.83	0.055	3.9	8.5	12 (3)
	0.83	0.055	6.7	15	
	0.83	0.055	5.3	12	
0.51	0.79	0.037	2.4	8.1	10 (4)
	0.79	0.037	2.4	8.2	
	0.79	0.037	4.3	15	
0.61	0.81	0.053	1.3	3.0	3.9 (1.7)
	0.81	0.053	2.5	5.8	
	0.81	0.053	1.2	2.7	
0.70	0.85	0.04	2.8	7.6	8.7 (2.8)
	0.85	0.04	4.4	12	
	0.85	0.04	2.4	6.6	
0.78	0.80	0.039	17	55	43 (11)
	0.80	0.039	12	39	
	0.80	0.038	11	34	

Table S5. The composition of stock solutions by mass including resultant mole fractions and concentrations of nucleophile **7a** and electrophile **3** for the reaction between triphenylamine **7a** and benzyl bromide **3**.

Mass IL **6** / g	Mass acetonitrile / g	Mass triphenylamine **7a** / g	Mass benzyl bromide **3** / g	[E] **3** / mol L^{-1}	[Nu] **7a** / mol L^{-1}	χ_6
-	1.5	0.025	0.27	0.79	0.052	0
-	1.5	0.023	0.28	0.83	0.046	0
-	1.4	0.032	0.27	0.80	0.065	0
-	1.4	0.034	0.29	0.85	0.068	0
-	1.4	0.032	0.31	0.91	0.065	0
2.5	-	0.011	0.30	0.87	0.023	0.77
13	-	0.095	1.4	0.80	0.039	0.78

Table S6. The mole fractions, temperatures, concentrations of nucleophile **7a** and electrophile **3**, the observed pseudo-first order rate constants and the resultant bimolecular rate constants used to determine the activation parameters for the reaction between triphenylamine **7a** and benzyl bromide **3**.

χ_6	Temp / °C	[Nu] **7a** / mol L^{-1}	[E] **3** / mol L^{-1}	k_{obs} / 10^{-8} s^{-1}	k_2 / 10^{-8} L mol^{-1} s^{-1}	Average k_2 / 10^{-8} L mol^{-1} s^{-1}
0.00	50.0	0.065	0.91	0.017	0.29	0.31 (0.02)
		0.065	0.91	0.017	0.30	
		0.065	0.91	0.020	0.33	
	60.0	0.068	0.85	0.059	1.0	0.86 (0.14)
		0.068	0.85	0.044	0.76	
		0.068	0.85	0.047	0.81	
	69.4	0.065	0.80	0.092	1.8	1.8 (0.1)
		0.046	0.83	0.069	1.8	
		0.046	0.83	0.069	1.8	
	75.0	0.046	0.83	0.14	2.5	2.6 (0.2)
		0.057	0.81	0.13	2.9	
		0.057	0.81	0.12	2.5	
0.78	50.0	0.039	0.80	0.078	2.5	3.1 (1.0)
		0.039	0.80	0.13	4.3	
		0.039	0.80	0.079	2.5	
	60.0	0.039	0.80	0.28	9.0	9.9 (1.2)
		0.039	0.80	0.35	11	
		0.039	0.80	0.29	9.3	
	69.4	0.039	0.80	0.50	16	25 (11)
		0.039	0.80	1.2	37	
		0.039	0.80	0.65	21	
	75.0	0.039	0.80	1.1	34	43 (11)
		0.039	0.80	1.2	39	
		0.039	0.80	1.7	55	

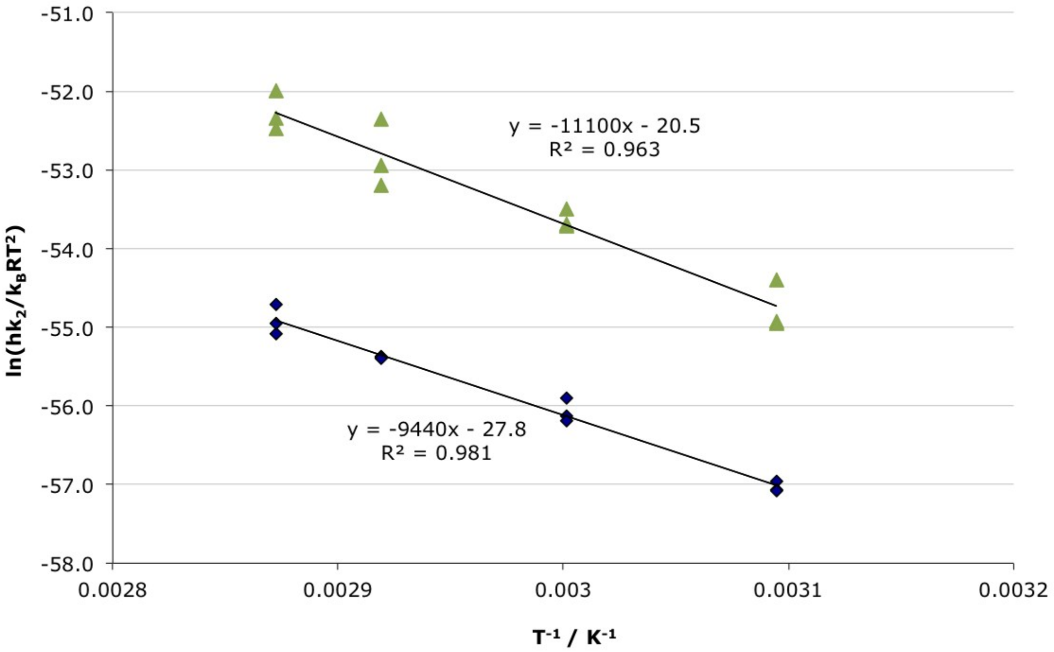

Figure S2. Eyring plots for the reaction between triphenylamine **7a** and benzyl bromide **3** in acetonitrile (χ_6 0, black) and [Bmim][N(SO$_2$CF$_3$)$_2$] **6** (χ_6 0.78, green) from which the activation parameters shown in Table 1 were determined.

Rate data for the reaction between triphenylphosphine **7b** and benzyl bromide **3** in different mixtures of [Bmim][N(SO_2CF_3)$_2$] **6** in acetonitrile

Table S7. The composition of stock solutions by mass including resultant mole fractions and concentration of electrophile **3** for the reaction between triphenylphosphine **7b** and benzyl bromide **3**.

Mass IL **6** / g	Mass acetonitrile / g	Mass triphenylphosphine **7b** / g	Mass benzyl bromide **3** / g	[E] **3** / mol L^{-1}	χ_6
-	1.5	0.015	0.12	0.36	0
1.3	0.90	0.0080	0.096	0.28	0.12
1.7	0.59	0.0088	0.068	0.20	0.21
2.1	0.36	0.0083	0.070	0.21	0.35
2.2	0.26	0.0054	0.072	0.21	0.45
2.4	0.17	0.0050	0.077	0.23	0.56
2.5	0.10	0.0038	0.43	0.13	0.69
2.6	0.041	0.0038	0.065	0.19	0.82
2.6	0.015	0.010	0.10	0.29	0.86
2.7	-	0.0088	0.048	0.14	0.95
2.7	-	0.0063	0.055	0.16	0.95

Table S8. The mole fraction of the ionic liquid **6**, concentration of electrophile **3**, the observed pseudo-first order rate constants (k_{obs}) and resultant bimolecular rate constants (k_2) for the reaction between triphenylphosphine **7b** and benzyl bromide **3** in a variety of solvent compositions of the ionic liquid **6** and acetonitrile at 15.0 ºC.

χ_6	[E] **3**/ mol L^{-1}	k_{obs} / 10^{-3} s^{-1}	k_2 / 10^{-2} L mol^{-1} s^{-1}	Average k_2 / 10^{-2} L mol^{-1} s^{-1}
0	0.36	0.93	0.26	0.22 (0.03)
		0.73	0.20	
		0.74	0.21	
0.12	0.28	0.91	0.32	0.32 (0.01)
		0.90	0.32	
		0.85	0.30	
0.21	0.20	0.79	0.40	0.38 (0.01)
		0.75	0.38	
		0.73	0.37	
0.35	0.21	0.86	0.42	0.43 (0.01)
		0.91	0.44	
		0.90	0.44	
0.45	0.21	0.79	0.38	0.37 (0.01)
		0.77	0.37	
		0.77	0.37	
0.56	0.23	0.67	0.30	0.31 (0.01)
		0.71	0.32	
		0.72	0.32	
0.69	0.13	0.40	0.32	0.30 (0.01)
		0.37	0.30	
		0.36	0.28	
0.82	0.19	0.54	0.28	0.30 (0.01)
		0.57	0.30	
		0.59	0.31	
0.86	0.29	1.0	0.36	0.38 (0.03)
		1.2	0.41	
		1.1	0.37	
0.95	0.14	0.59	0.43	0.44 (0.03)
		0.66	0.47	
	0.16	0.66	0.41	

Table S9. The composition of stock solutions by mass including resultant mole fractions and concentration of electrophile **3** for the reaction between triphenylphosphine **7b** and benzyl bromide **3**.

Mass IL **6** / g	Mass acetonitrile / g	Mass triphenylphosphine **7b** / g	Mass benzyl bromide **3** / g	[E] **3** / mol L^{-1}	χ_6
-	1.5	0.015	0.12	0.36	0
-	1.5	0.015	0.13	0.38	0
-	1.5	0.014	0.11	0.34	0
-	1.6	0.018	0.12	0.32	0
-	0.81	0.0070	0.055	0.36	0
-	0.81	0.0079	0.061	0.35	0
2.1	0.36	0.0083	0.070	0.21	0.35
2.0	0.36	0.0043	0.045	0.13	0.35
2.1	0.33	0.010	0.097	0.28	0.37
2.1	0.29	0.020	0.15	0.44	0.38
2.5	0.10	0.0038	0.43	0.13	0.69
2.5	0.085	0.011	0.077	0.22	0.70
2.5	0.073	0.014	0.14	0.40	0.69
2.5	0.053	0.0096	0.17	0.49	0.72
2.7	-	0.0041	0.044	0.13	0.96
2.7	-	0.0038	0.044	0.13	0.96
2.7	-	0.0088	0.048	0.14	0.95
2.7	-	0.0063	0.055	0.16	0.95
2.8	-	0.0043	0.036	0.10	0.97
1.4	-	0.0029	0.018	0.11	0.97[a]
1.4	-	0.0031	0.019	0.11	0.97[a]

Table S10. The mole fractions, temperatures, concentration of electrophile **3**, the observed pseudo-first order rate constants and the resultant bimolecular rate constants used to determine the activation parameters for the reaction between triphenylphosphine **7b** and benzyl bromide **3**.

χ_6	Temp / °C	[E] **3** / 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	5.0	0.35	0.21	0.59	0.52 (0.06)
		0.32	0.15	0.48	
		0.34	0.17	0.50	
	9.4	0.35	0.30	0.85	0.85 (0.11)
		0.35	0.34	0.96	
		0.36	0.26	0.73	
	16.1	0.34	0.49	1.4	1.2 (0.2)
		0.34	0.36	1.1	
		0.38	0.46	1.2	
	24.4	0.36	0.74	2.1	2.2 (0.3)
		0.36	0.73	2.0	
		0.36	0.94	2.6	
0.36	5.0	0.44	0.36	0.81	0.81 (0.02)
			0.36	0.83	
			0.35	0.80	
	15.0	0.28	0.51	1.8	1.8 (0.1)
			0.48	1.7	
			0.52	1.8	
	24.4	0.21	0.90	4.4	4.3 (0.1)
			0.91	4.4	
			0.86	4.2	
	35.0	0.13	1.3	9.7	11 (1)
			1.5	12	
			1.5	11	
0.70	5.0	0.49	0.36	0.73	0.72 (0.03)
			0.33	0.68	
			0.36	0.74	
	15.0	0.41	0.88	2.2	2.2 (0.1)
			0.89	2.2	
			0.88	2.2	
	24.4	0.13	0.36	2.8	3.0 (0.2)
			0.37	3.0	
			0.40	3.2	
	35.0	0.22	1.5	6.8	6.8 (0.1)
			1.5	6.8	
			1.5	6.8	
0.96	-1.8	0.13	0.051	0.40	0.38 (0.01)
		0.16	0.062	0.38	
		0.11	0.040	0.37	
	5.0	0.13	0.090	0.70	0.80 (0.09)
		0.10	0.088	0.84	
		0.10	0.090	0.85	
	9.4	0.13	0.14	1.1	1.1 (0.1)
		0.10	0.12	1.1	
		0.11	0.11	1.1	
	24.4	0.14	0.59	4.3	4.4 (0.3)
		0.14	0.66	4.7	
		0.16	0.66	4.1	

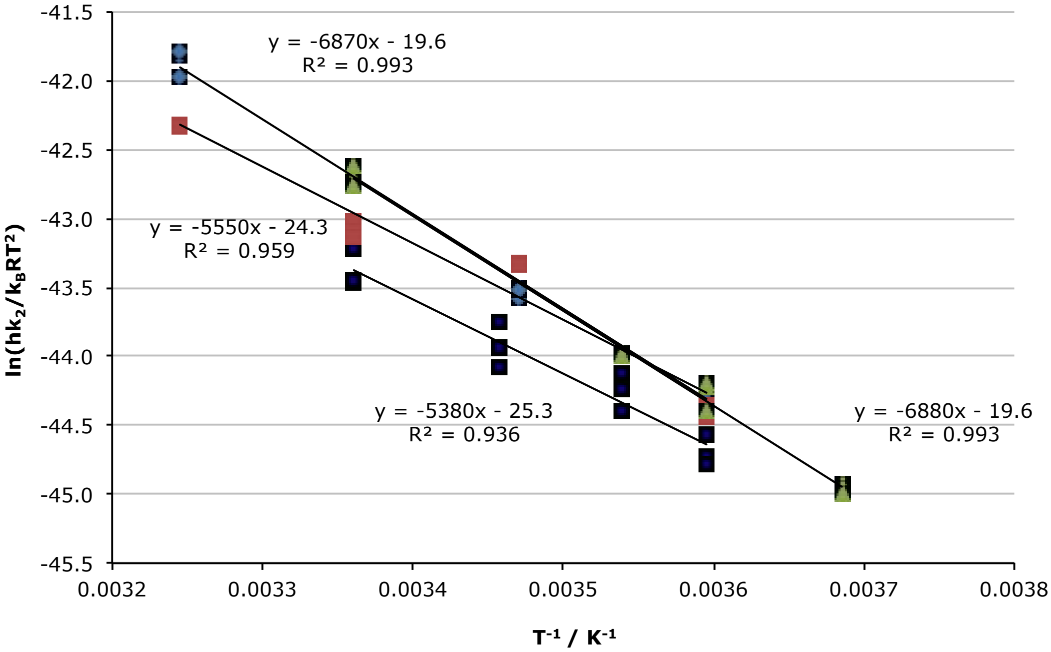

Figure S3. Eyring plots for the reaction between triphenylphosphine **7b** and benzyl bromide **3** in acetonitrile (χ_6 0, black), mixtures of acetonitrile and [Bmim][N(SO_2CF_3)$_2$] **6** (χ_6 0.36, blue, and χ_6 0.70, red) and [Bmim][N(SO_2CF_3)$_2$] **6** (χ_6 0.96, green) from which the activation parameters shown in Table 2 were determined.

Rate data for the reaction between triphenylphosphine **7b** and benzyl chloride **2** in different mixtures of [Bmim][N(SO_2CF_3)$_2$] **6** in acetonitrile

Table S11. The composition of stock solutions by mass including resultant mole fractions, concentration of electrophile **2** for the reaction between triphenylphosphine **7b** and benzyl chloride **2**.

Mass IL **6** / g	Mass acetonitrile / g	Mass triphenylphosphine **7b** / g	Mass benzyl chloride **2** / g	[E] **2** / mol L^{-1}	χ_6
-	7.8	0.18	1.0	0.81	0
0.77	1.1	0.035	0.26	1.0	0.060
1.1	0.88	0.023	0.14	0.55	0.10
1.6	0.59	0.021	0.14	0.53	0.20
0.81	0.31	0.014	0.063	0.50	0.19
1.9	0.40	0.022	0.13	0.53	0.29
1.9	0.41	0.020	0.13	0.51	0.29
2.2	0.26	0.022	0.13	0.49	0.42
2.2	0.19	0.022	0.13	0.51	0.49
2.4	0.12	0.022	0.13	0.52	0.59
2.4	0.064	0.022	0.13	0.52	0.68
2.6	0.030	0.022	0.12	0.47	0.78
2.5	-	0.018	0.16	0.62	0.82

Table S12. The mole fraction of the ionic liquid **6**, concentration of electrophile **2**, the observed pseudo-first order rate constants (k_{obs}) and resultant bimolecular rate constants (k_2) for the reaction between triphenylphosphine **7b** and benzyl chloride **2** in a variety of solvent compositions of the ionic liquid **6** and acetonitrile at 63.6 ºC.

χ_6	[E] **2** / 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	0.81	0.85	1.1	1.1 (0.02)
		0.86	1.1	
		0.84	1.0	
0.060	1.0	2.0	2.0	1.97 (0.10)
		1.9	1.9	
		2.1	2.1	
0.10	0.55	1.7	3.1	3.22 (0.24)
		1.9	3.5	
		1.7	3.1	
0.20	0.53	2.1	4.0	3.8 (0.3)
		2.1	4.0	
		1.7	3.4	
0.29	0.52	2.1	4.0	3.94 (0.10)
		2.1	4.0	
		2.0	3.8	
0.42	0.49	2.1	4.3	4.26 (0.08)
		2.1	4.3	
		2.1	4.2	
0.49	0.51	2.5	4.8	4.57 (0.25)
		2.2	4.3	
		2.4	4.6	
0.59	0.52	2.6	4.9	5.07 (0.19)
		2.7	5.3	
		2.6	5.0	
0.68	0.52	2.6	4.9	5.09 (0.38)
		2.9	5.5	
		2.5	4.8	
0.78	0.47	2.4	5.2	5.11 (0.25)
		2.3	4.8	
		2.5	5.3	
0.82	0.62	3.3	5.3	4.84 (0.43)
		2.9	4.7	
		2.8	4.5	

Table S13. The composition of stock solutions by mass including resultant mole fractions, concentration of electrophile **2** for the reaction between triphenylphosphine **7b** and benzyl chloride **2**.

Mass IL **6** / g	Mass acetonitrile / g	Mass triphenylphosphine **7b** / g	Mass benzyl chloride **2** / g	[E] **2** / mol L^{-1}	χ_6
-	7.80	0.175	1.02	0.807	0.00
8.14	3.55	0.149	1.02	0.807	0.20
13.2	-	0.138	1.03	0.814	0.79

Table S14. The mole fractions, temperatures, concentration of electrophile **2**, the observed pseudo-first order rate constants and the resultant bimolecular rate constants used to determine the activation parameters for the reaction between triphenylphosphine **7b** and benzyl chloride **2**.

χ_6	Temp / °C	[E] **2** / 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	54.8	0.81	0.53	0.43	0.40 (0.03)
			0.47	0.38	
			0.47	0.38	
	63.6		0.85	0.68	0.69 (0.01)
			0.86	0.70	
			0.84	0.68	
	67.7		1.0	0.84	0.89 (0.07)
			1.2	0.97	
			1.1	0.87	
	74.2		1.6	1.3	1.3 (0.1)
			1.5	1.2	
			1.6	1.3	
0.20	54.8	0.81	1.3	1.6	1.7 (0.1)
			1.4	1.8	
			1.4	1.8	
	63.6		2.8	3.5	3.3 (0.1)
			2.6	3.3	
			2.7	3.3	
	67.7		3.4	4.2	4.3 (0.1)
			3.6	4.4	
			3.6	4.4	
	74.2		5.2	6.4	6.6 (0.2)
			5.4	6.7	
			5.3	6.5	
0.79	54.8	0.81	1.8	2.3	2.3 (0.1)
			1.9	2.3	
			1.9	2.3	
	63.6		3.6	4.4	4.3 (0.2)
			3.3	4.1	
			3.5	4.3	
	67.7		5.1	6.3	5.9 (0.4)
			4.6	5.7	
			4.6	5.6	
	74.2		6.7	8.2	8.7 (0.6)
			6.9	8.5	
			7.6	9.3	

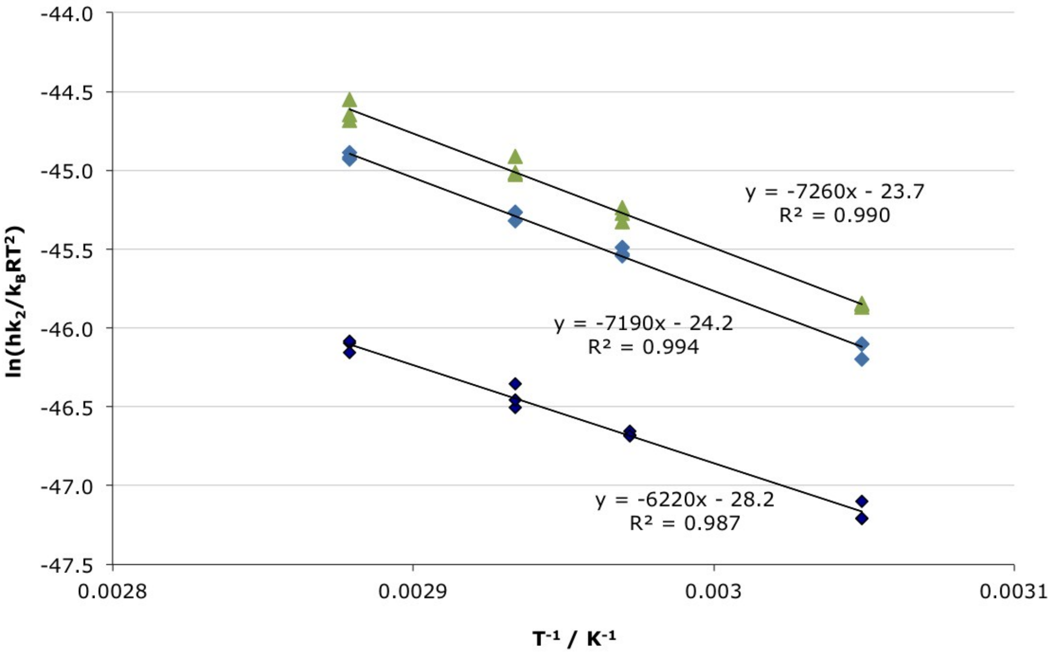

Figure S4. Eyring plots for the reaction between triphenylphosphine **7b** and benzyl chloride **2** in acetonitrile (χ_6 0, black), a mixture of acetonitrile and [Bmim][N(SO_2CF_3)$_2$] **6** (χ_6 0.20, blue) and [Bmim][N(SO_2CF_3)$_2$] **6** (χ_6 0.78, green) from which the activation parameters shown in Table 3 were determined.

Rate data for the reaction involving tributylamine **10a** and benzyl bromide **3** in different mixtures of [Bmim][$N(SO_2CF_3)_2$] **6** in acetonitrile

Table S15. The composition of stock solutions by mass including resultant mole fractions, concentrations of nucleophile **10a** and electrophile **3** for the reaction between tributylamine **10a** and benzyl bromide **3**.

Mass IL **6** / g	Mass acetonitrile / g	Mass tributylamine **10a** / g	Mass benzyl bromide **3** / g	[Nu] **10a** / mol L^{-1}	[E] **3** / mol L^{-1}	χ_6
0.00	3.64	0.48	0.032	0.51	0.04	0.00
0.75	0.85	0.19	0.016	0.50	0.05	0.08
1.61	0.55	0.11	0.010	0.30	0.03	0.22
1.93	0.38	0.12	0.011	0.31	0.03	0.32
2.02	0.33	0.14	0.012	0.38	0.03	0.35
2.10	0.23	0.14	0.013	0.39	0.04	0.44
2.31	0.18	0.14	0.014	0.37	0.04	0.52
2.35	0.10	0.17	0.014	0.47	0.04	0.62
1.20	0.05	0.09	0.007	0.46	0.04	0.62
2.42	0.04	0.16	0.014	0.42	0.04	0.75
13.0	0.00	0.80	-	0.43	-	0.87

Table S16. The mole fraction of the ionic liquid **6**, concentration of nucleophile **10a**, the observed pseudo-first order rate constants (k_{obs}) and resultant bimolecular rate constants (k_2) for the reaction between tributylamine **10a** and benzyl bromide **3** in a variety of solvent compositions of the ionic liquid **6** and acetonitrile at 45.0 ºC.

χ_6	[Nu] **10a** / 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	0.51	0.79	1.6	1.5 (0.1)
		0.78	1.5	
		0.77	1.5	
0.08	0.50	1.2	2.3	2.6 (0.4)
		1.5	3.0	
		1.2	2.4	
0.22	0.30	1.0	3.4	3.0 (0.4)
		0.91	3.0	
		0.80	2.7	
0.32	0.31	0.69	2.2	2.3 (0.1)
		0.70	2.2	
		0.76	2.4	
0.35	0.38	0.77	2.0	1.9 (0.1)
		0.68	1.8	
		0.75	2.0	
0.44	0.39	0.96	2.5	2.3 (0.2)
		0.83	2.1	
		0.82	2.1	
0.52	0.37	0.44	1.2	1.5 (0.3)
		0.58	1.6	
		0.65	1.8	
0.62	0.47	0.46	0.97	1.2 (0.2)
		0.59	1.3	
	0.46	0.56	1.2	
0.75	0.42	0.38	0.89	0.96 (0.20)
		0.50	1.2	
		0.34	0.80	
0.87	0.43	0.41	0.95	0.98 (0.14)
		0.49	1.1	
		0.37	0.86	

Table S17. The mole fraction of the ionic liquid **6**, concentrations of nucleophile **10a** and electrophile **3**, the reverse bimolecular rate constants (k_{-2}) for the reaction the salt **6** to tributylamine **10a** and benzyl bromide **3** in a variety of solvent compositions of the ionic liquid **6** and acetonitrile at 45.0 ºC.

χ_6	[Nu] **10a** / mol L^{-1}	[E] **3** / mol L^{-1}	k_{-2} / 10^{-3} L mol^{-1} s^{-1}	Average k_{-2} / 10^{-3} L mol^{-1} s^{-1}
0.52	0.37	0.039	3.3	3.2 (0.4)
			2.8	
			3.5	
0.62	0.47	0.040	5.1	4.9 (0.7)
			4.2	
	0.46	0.042	5.4	
0.75	0.42	0.040	8.3	7.1 (1.1)
			6.1	
			7.0	
0.87	0.43	0.0050	11	9.8 (1.1)
			9.1	
			9.1	

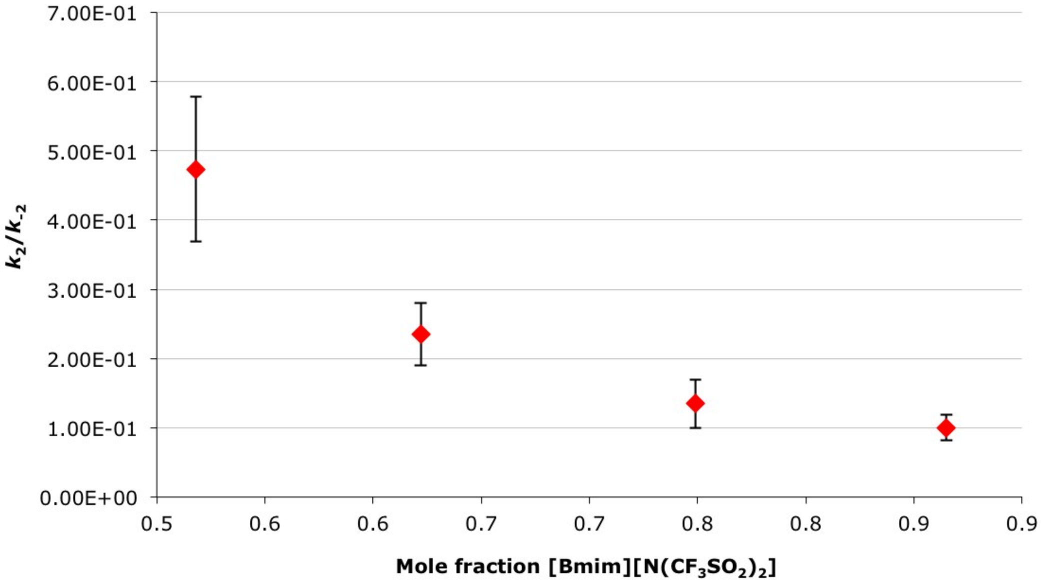

Figure S5. Ratio of the forward and reverse rate constants for the reaction between tributylamine **10a** and benzyl bromide **3** in various mixtures of the ionic liquid **6** in acetonitrile. Uncertainties are reported as the compounded standard deviation of triplicate results from both the forwards and reverse rate constants.

Table S18. The composition of stock solutions by mass including resultant mole fractions, concentrations of nucleophile **10a** and electrophile **3** for the reaction between tributylamine **10a** and benzyl bromide **3**.

Mass IL **6** / g	Mass acetonitrile / g	Mass tributylamine **10a** / g	Mass benzyl bromide **3** / g	[Nu] **10a** / mol L^{-1}	[E] **3** / mol L^{-1}	χ_6
-	0.73	0.094	0.0079	0.51	0.046	0.00
-	7.07	0.92	0.094	0.50	0.055	0.00
-	3.64	0.45	0.032	0.51	0.037	0.00
1.5	0.55	0.11	0.010	0.30	0.030	0.22
1.59	0.56	0.12	0.011	0.32	0.032	0.21
1.61	0.55	0.12	0.010	0.32	0.030	0.22
1.62	0.55	0.12	0.011	0.31	0.031	0.21
13.0	0.00	0.80	-	0.43	0.044	0.87
6.49	0.00	0.40	-	0.44	0.042	0.87

Table S19. The mole fractions, temperatures, concentration of nucleophile **10a**, the observed pseudo-first order rate constants and the resultant bimolecular rate constants used to determine the activation parameters for the reaction between tributylamine **10a** and benzyl bromide **3**.

χ_6	Temp / °C	[Nu] **10a** / mol L^{-1}	k_{obs} / 10^{-8} s^{-1}	k_2 / 10^{-8} L mol^{-1} s^{-1}	Average k_2 / 10^{-8} L mol^{-1} s^{-1}
0	13.0	0.51	0.19	0.37	0.41 (0.05)
		0.50	0.23	0.46	
		0.51	0.22	0.42	
	25.0	0.50	0.42	0.89	0.83 (0.10)
		0.50	0.36	0.73	
		0.51	0.47	0.92	
	35.6	0.50	0.63	1.27	1.2 (0.1)
		0.50	0.59	1.19	
		0.50	0.51	1.02	
	45.0	0.51	0.79	1.55	1.5 (0.1)
		0.51	0.78	1.52	
		0.51	0.76	1.47	
0.22	15.0	0.32	0.19	0.59	0.66 (0.07)
		0.31	0.22	0.71	
		0.31	0.22	0.69	
	25.0	0.32	0.40	1.26	1.2 (0.1)
		0.31	0.37	1.19	
		0.31	0.37	1.17	
	35.6	0.32	0.61	1.89	1.9 (0.1)
		0.32	0.62	1.94	
		0.32	0.57	1.78	
	45.0	0.30	1.02	3.40	3.0 (0.4)
		0.30	0.91	3.04	
		0.30	0.80	2.68	
0.87	15.0	0.58	0.11	0.26	0.28 (0.02)
		0.48	0.11	0.26	
		0.57	0.13	0.30	
	25.0	0.57	0.20	0.45	0.47 (0.04)
		0.58	0.19	0.44	
		0.51	0.22	0.51	
	35.6	0.48	0.38	0.88	0.75 (0.11)
		0.59	0.31	0.71	
		0.55	0.30	0.67	
	45.0	0.45	0.41	0.95	1.0 (0.1)
		0.54	0.49	1.13	
		0.56	0.44	1.02	

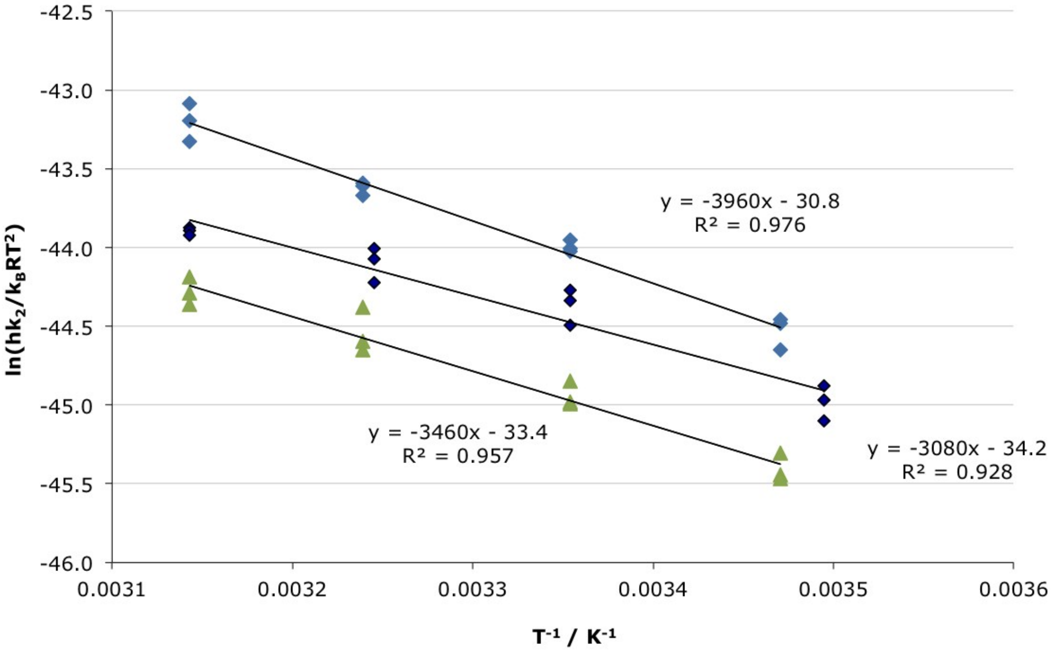

Figure S6. Eyring plots for the reaction between tributylamine **10a** and benzyl bromide **3** in acetonitrile (χ_6 0, black), a mixture of acetonitrile and [Bmim][N(SO_2CF_3)$_2$] **6** (χ_6 0.22, blue) and [Bmim][N(SO_2CF_3)$_2$] **6** (χ_6 0.87, green) from which the activation parameters shown in Table 4 were determined.

Table S20. The mole fraction, temperature, concentrations of nucleophile **10a** and electrophile **3** and the reverse bimolecular rate constants used to determine the activation parameters for the reaction of the salt **12a** to tributylamine **10a** and benzyl bromide **3**.

χ_6	Temp / °C	[Nu] **10a** / mol L^{-1}	[E] **3** / mol L^{-1}	k_{-2} / 10^{-8} L mol^{-1} s^{-1}	Average k_{-2} / 10^{-8} L mol^{-1} s^{-1}
0.87	15.0	0.58	0.0042	2.72	2.7 (0.1)
		0.48	0.0043	2.80	
		0.57	0.0044	2.65	
	25.0	0.57	0.0043	4.74	4.7 (0.1)
		0.58	0.0042	4.72	
		0.51	0.0046	4.76	
	35.6	0.48	0.0042	6.47	7.5 (1.1)
		0.59	0.0057	7.46	
		0.55	0.0042	8.69	
	45.0	0.45	0.0041	11.1	9.8 (1.2)
		0.54	0.0050	9.11	
		0.56	0.0051	9.13	

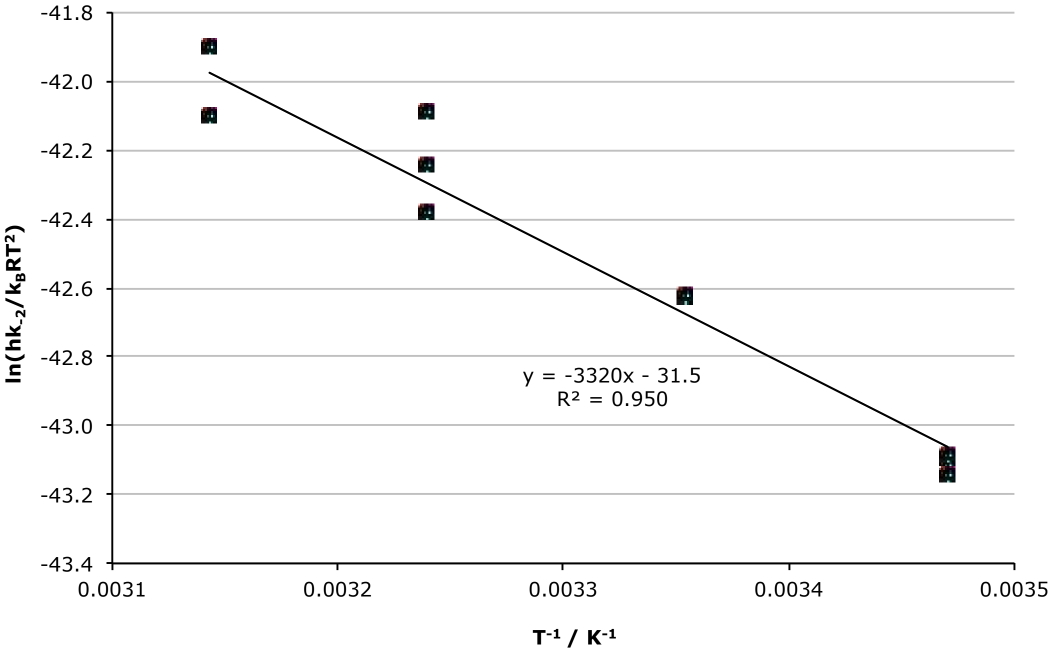

Figure S7. Eyring plots for the reaction of salt **11a** to give tributylamine **7b** and benzyl bromide **3** in [Bmim][N(SO_2CF_3)$_2$] **6** (χ_6 0.87) from which the activation parameters shown in Table S20 were determined.

Table S21. The activation parameters obtained for the reaction of salt **11a** to give tributyllamine **7a** and benzyl bromide **3** in [Bmim][N(SO_2CF_3)$_2$] **6** (χ_6 0.87).

χ_6	$\Delta H^{\ddagger}$ / kJ mol^{-1} [a]	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1} [a]
0.87	27.6 ± 2.0	-262 ± 7

[a] Errors reported are from the fit of the linear regression.

Rate data for the reaction between tributylphosphine **10b** and benzyl chloride **2** in different mixtures of [Bmim][N(SO_2CF_3)$_2$] **6** in acetonitrile

Table S22. The composition of stock solutions by mass including resultant mole fractions, concentration of electrophile **2** for the reaction between tributylphosphine **10b** and benzyl chloride **2**.

Mass IL **6** / g	Mass acetonitrile / g	Mass tributylphosphine **10b** / g	Mass benzyl chloride **2** / g	[E] **2** / mol L^{-1}	χ_6
0.00	1.47	0.015	0.14	0.55	0.00
0.29	1.29	0.016	0.15	0.58	0.08
0.65	1.15	0.015	0.13	0.52	0.19
0.94	0.93	0.013	0.14	0.55	0.28
1.27	0.76	0.015	0.15	0.61	0.38
1.68	0.49	0.012	0.14	0.55	0.53
2.08	0.37	0.012	0.15	0.59	0.62
2.30	0.20	0.023	0.19	0.73	0.68
2.62	0.00	0.014	0.14	0.54	0.85
2.62	0.00	0.017	0.15	0.59	0.83

Table S23. The mole fraction of ionic liquid **6**, concentration of electrophile **2**, the observed pseudo-first order rate constants (k_{obs}) and resultant bimolecular rate constants (k_2) for the reaction between tributylphosphine **10b** and benzyl chloride **2** in a variety of solvent compositions of the ionic liquid **6** and acetonitrile at 45.0 ºC.

χ_6	[E] **2** / 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	0.54	0.32	0.59	0.60 (0.04)
		0.35	0.65	
		0.31	0.57	
0.08	0.58	0.48	0.82	0.78 (0.04)
		0.44	0.76	
		0.44	0.76	
0.19	0.52	0.54	1.0	1.0 (0.1)
		0.51	0.98	
		0.54	1.0	
0.32	0.55	0.62	1.1	0.97 (0.15)
		0.49	0.89	
		0.49	0.88	
0.38	0.61	0.77	1.3	1.3 (0.1)
		0.68	1.1	
		0.85	1.4	
0.52	0.55	0.86	1.6	1.6 (0.1)
		0.87	1.6	
		0.81	1.5	
0.62	0.59	0.94	1.6	1.6 (0.1)
		0.92	1.6	
		1.00	1.7	
0.68	0.73	1.52	2.1	1.9 (0.2)
		1.38	1.9	
		1.23	1.7	
0.84	0.54	0.90	1.7	1.8 (0.2)
	0.59	1.08	1.8	
		1.12	2.0	

Table S24. The composition of stock solutions by mass including resultant mole fractions, concentration of electrophile **2** for the reaction between tributylphosphine **10b** and benzyl chloride **2**.

Mass IL **6** / g	Mass acetonitrile / g	Mass tributylphosphine **10a** / g	Mass benzyl chloride **2** / g	[E] **2** / mol L^{-1}	χ_6
0.00	1.50	0.015	0.13	0.52	0.00
0.00	1.50	0.014	0.14	0.54	0.00
0.00	1.47	0.015	0.14	0.55	0.00
0.00	1.51	0.014	0.13	0.52	0.00
0.00	1.49	0.012	0.13	0.52	0.00
2.62	0.00	0.014	0.14	0.54	0.85
2.62	0.00	0.017	0.15	0.59	0.83
2.60	0.00	0.021	0.15	0.60	0.83
2.49	0.00	0.019	0.18	0.70	0.80
2.62	0.00	0.017	0.15	0.59	0.83

Table S25. The mole fractions, temperatures, concentration of electrophile **2**, the observed pseudo-first order rate constants and the resultant bimolecular rate constants used to determine the activation parameters for the reaction between tributylphosphine **10b** and benzyl chloride **2**.

χ_6	Temp / ºC	[E] **2** / 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	5.0	0.54	0.14	0.25	0.23 (0.02)
		0.52	0.12	0.24	
		0.52	0.11	0.24	
	15.0	0.55	0.32	0.59	0.60 (0.04)
			0.35	0.65	
			0.31	0.57	
	25.0	0.54	0.55	1.0	0.94 (0.10)
			0.44	0.83	
			0.52	0.97	
	35.6	0.52	1.2	2.3	2.2 (0.2)
			1.0	2.0	
			1.2	2.2	
0.83	0.0	0.60	0.35	0.58	0.55 (0.04)
			0.33	0.55	
		0.70	0.36	0.51	
	7.0	0.59	0.57	0.96	1.0 (0.1)
		0.60	0.64	1.1	
			0.64	1.1	
	15.0	0.54	0.90	1.7	1.8 (0.2)
		0.59	1.1	1.8	
			1.1	2.0	
	20.0	0.54	1.7	3.1	2.8 (0.4)
			1.6	3.0	
		0.59	1.4	2.5	

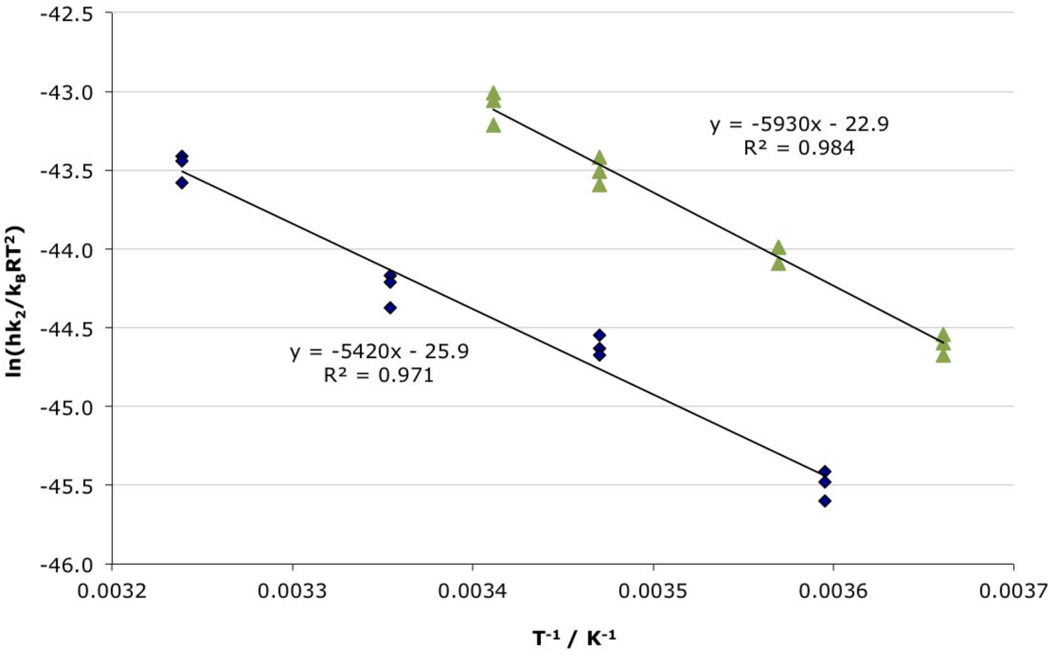

Figure S8. Eyring plots for the reaction between tributylphosphine **10b** and benzyl chloride **2** in acetonitrile (χ_6 0, black) and [Bmim][N(SO_2CF_3)$_2$] **6** (χ_6 0.83, green) from which the activation parameters shown in Table 5 were determined.