Supporting Information:

Ionic liquid effects on a multistep process: increased product formation due to enhancement of all steps

Sinead T. Keaveney, Ronald S. Haines and Jason B. Harper

Table of Contents

p-Methylbenzaldehyde 2b and Hexan-1-amine 3 ..... **2**
Addition rate constant ($k_{2,A}$) data in [Bmim][N(CF_3SO_2)$_2$] 1 and acetonitrile at 8.1°C **2**
p-Chlorobenzaldehyde 2d and Hexan-1-amine 3 ..... **4**
Addition ($k_{2,A}$), reverse addition ($k_{-1,A}$) and elimination ($k_{1,E}$) data in [Bmim][N(CF_3SO_2)$_2$] 1 and acetonitrile at 8.1°C **4**
p-Trifluoromethylbenzaldehyde 2e and Hexan-1-amine 3 ..... **6**
Addition ($k_{2,A}$), reverse addition ($k_{-1,A}$) and elimination ($k_{1,E}$) data in [Bmim][N(CF_3SO_2)$_2$] 1 and acetonitrile at 8.1°C **6**
p-Nitrobenzaldehyde 2f and Hexan-1-amine 3 ..... **8**
Addition ($k_{2,A}$), reverse addition ($k_{-1,A}$) and elimination ($k_{1,E}$) data in [Bmim][N(CF_3SO_2)$_2$] 1 and acetonitrile at 8.1°C **8**
Hammett Plots: **10**
Acetonitrile using the rate constant of the addition step ($k_{2,A}$) **10**
[Bmim][N(CF_3SO_2)$_2$] 1 and acetonitrile, χ_{IL} = 0.9, using the rate constant of the addition step ($k_{2,A}$) **10**
[Bmim][N(CF_3SO_2)$_2$] 1 and acetonitrile, χ_{IL} = 0.2, using the rate constant of the elimination step ($k_{1,E}$) **11**
[Bmim][N(CF_3SO_2)$_2$] 1 and acetonitrile, χ_{IL} = 0.9, using the rate constant of the elimination step ($k_{1,E}$) **12**
[Bmim][N(CF_3SO_2)$_2$] 1 and acetonitrile, χ_{IL} = 0.2, using the rate constant of the reverse addition step ($k_{-1,A}$) **12**
[Bmim][N(CF_3SO_2)$_2$] 1 and acetonitrile, χ_{IL} = 0.9, using the rate constant of the reverse addition step ($k_{-1,A}$) **13**
[Bmim][N(CF_3SO_2)$_2$] 1 and acetonitrile, χ_{IL} = 0.9, using the rate constant of the overall addition elimination process ($k_{2,app}$) **13**
Activation Parameter Data **14**
***p*-Chlorobenzaldehyde 2d and hexan-1-amine 3, addition step ($k_{2,A}$)** **14**
***p*-Chlorobenzaldehyde 2d and hexan-1-amine 3, elimination step ($k_{1,E}$)** **15**
***p*-Trifluoromethylbenzaldehyde 2e and hexan-1-amine 3, elimination step ($k_{1,E}$)** **16**
***p*-Nitrobenzaldehyde 2f and hexan-1-amine 3, elimination step ($k_{1,E}$)** **17**

p-*Methylbenzaldehyde* ***2b*** *and Hexan-1-amine* ***3***

Addition rate constant ($k_{2,A}$) data in [Bmim][$N(CF_3SO_2)_2$] **1** and acetonitrile at 8.1°C

Mole Fraction of 1	**[Nu] / mol L^{-1}**	$k_{1,A}$ **/ 10^{-4} s^{-1}**	$k_{2,A}$ **/ 10^{-4} L mol^{-1} s^{-1}**	**Average $k_{2,A}$ / 10^{-4} L mol^{-1} s^{-1}**
0	0.140	0.331	2.37	2.70 (0.29)
		0.402	2.88	
		0.400	2.86	
0.11	0.158	1.559	9.86	10.05 (0.88)
		1.740	11.01	
		1.467	9.28	
0.21	0.150	2.296	15.28	14.61 (0.62)
		2.175	14.48	
		2.111	14.05	
0.31	0.146	2.709	18.52	18.67 (0.22)
		2.767	18.92	
		2.717	18.58	
0.42	0.152	2.780	18.33	18.59 (0.39)
		2.791	18.40	
		2.889	19.05	
0.51	0.167	3.455	20.75	20.38 (0.33)
		3.353	20.14	
		3.371	20.24	
0.62	0.147	3.531	24.06	24.42 (1.18)
		3.444	23.46	
		3.776	25.73	
0.70	0.154	4.208	27.38	27.39 (0.25)
		4.248	27.64	
		4.172	27.15	
0.80	0.146	4.566	31.32	30.32 (1.29)
		4.487	30.78	
		4.207	28.86	
0.91	0.144	4.091	28.36	28.33 (0.13)
		4.067	28.19	
		4.105	28.45	

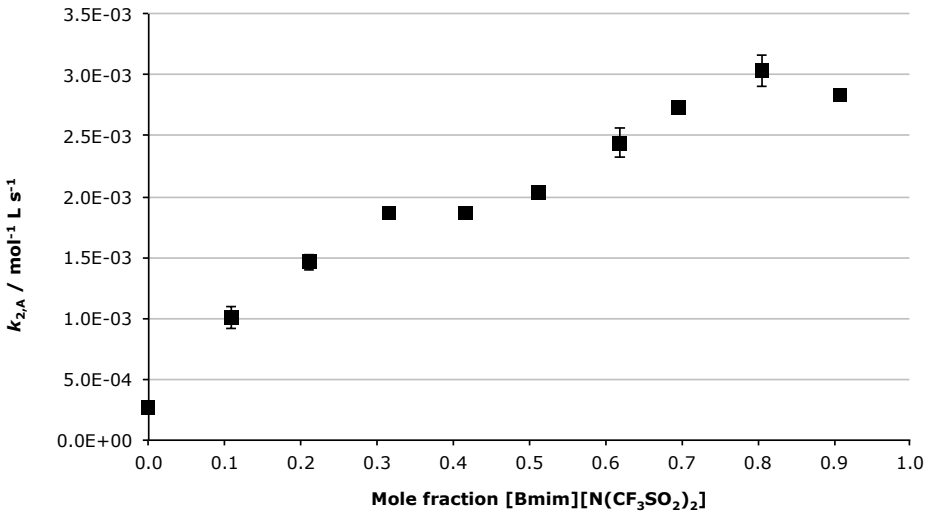

Figure S1: The bimolecular rate constant for the rate-determining addition step ($k_{2,A}$) between 4-methylbenzaldehyde **2b** and the amine **3** in different mole fractions of [Bmim][$N(CF_3SO_2)_2$] **1** in acetonitrile at 281 K. Uncertainties are reported as the standard deviation of three replicates.

*p-Chlorobenzaldehyde **2d** and Hexan-1-amine **3***

Addition ($k_{2,A}$), reverse addition ($k_{-1,A}$) and elimination ($k_{1,E}$) data in [Bmim][$N(CF_3SO_2)_2$] **1** and acetonitrile at 8.1°C

Mole Fraction of 1	**[Nu] / mol L^{-1}**	$k_{1,A}$ **/ 10^{-3} s^{-1}**	$k_{2,A}$ **/ 10^{-3} L mol^{-1} s^{-1}**	$k_{-1,A}$ **/ 10^{-3} s^{-1}**	$k_{1,E}$ **/ 10^{-3} s^{-1}**	$(k_{2,A} \times k_{1,E}) \div (k_{-1,A} + k_{1,E})$ **/ L mol^{-1} s^{-1}**
0	0.147	1.046	7.12	7.42	1.76	1.37
		0.952	6.49	7.64	1.61	1.13
		0.970	6.61	7.46	1.80	1.29
0.22	0.325	11.2	34.6	39.9	2.01	1.66
		10.5	32.3	38.9	1.96	1.55
		10.3	31.7	39.0	2.00	1.55
0.88	0.405	15.9	39.3	38.3	1.76	1.72
		15.2	37.5	38.6	1.53	1.43
		14.3	35.4	38.5	1.90	1.66

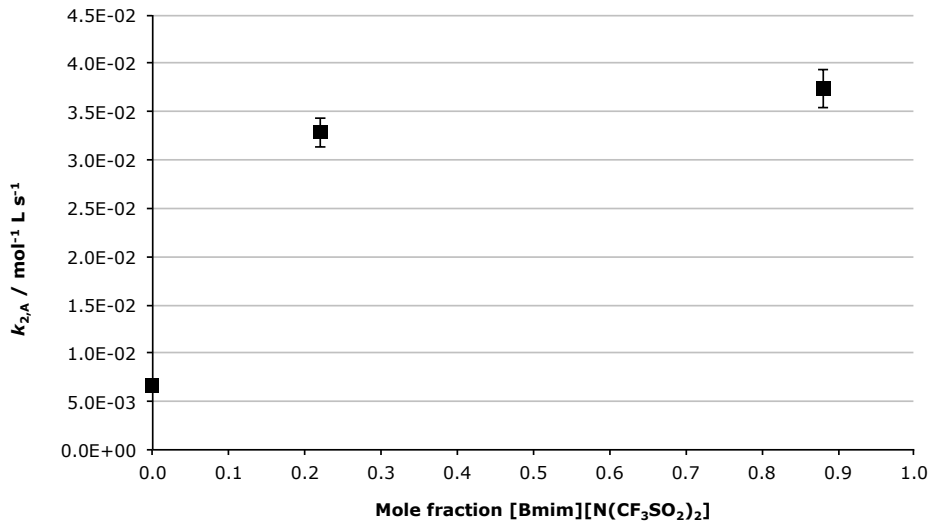

Figure S2: The bimolecular rate constant for the addition step ($k_{2,A}$) of the reaction between 4-chlorobenzaldehyde **2d** and the amine **3** in different mole fractions of [Bmim][$N(CF_3SO_2)_2$] **1** in acetonitrile at 281 K. Uncertainties are reported as the standard deviation of three replicates.

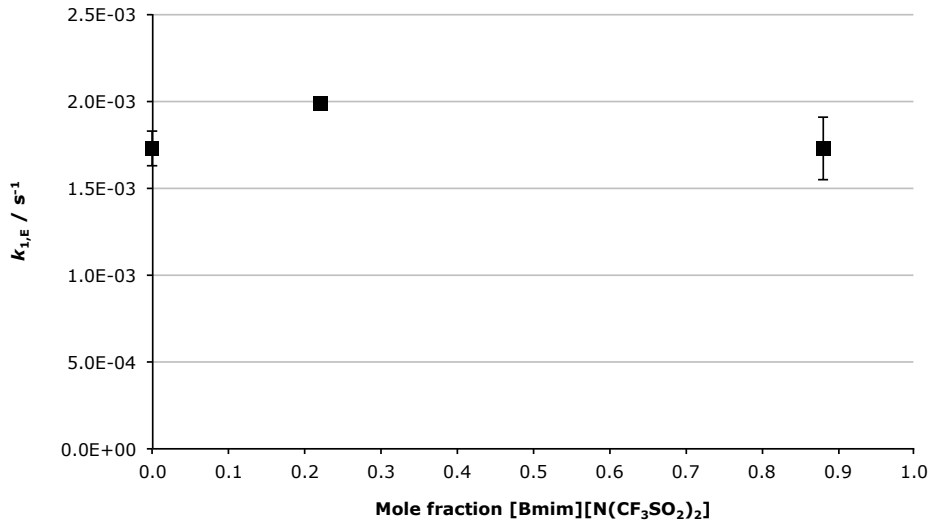

Figure S3: The unimolecular rate constant for the elimination step ($k_{1,E}$) of the reaction between 4-chlorobenzaldehyde **2d** and the amine **3** in different mole fractions of [Bmim][N(CF_3SO_2)$_2$] **1** in acetonitrile at 281 K. Uncertainties are reported as the standard deviation of three replicates.

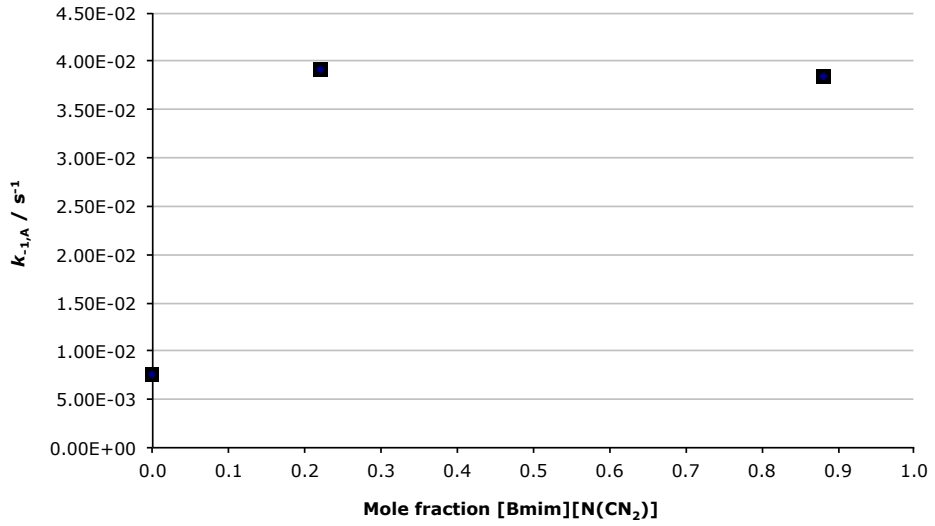

Figure S4: The unimolecular rate constant for the reverse addition step ($k_{-1,A}$) of the reaction between 4-chlorobenzaldehyde **2d** and the amine **3** in different mole fractions of [Bmim][N(CF_3SO_2)$_2$] **1** in acetonitrile at 281 K. Uncertainties are reported as the standard deviation of three replicates.

p-Trifluoromethylbenzaldehyde ***2e*** *and Hexan-1-amine* ***3***

Addition ($k_{2,A}$), reverse addition ($k_{-1,A}$) and elimination ($k_{1,E}$) data in [Bmim][$N(CF_3SO_2)_2$] **1** and acetonitrile at 8.1°C

Mole Fraction of 1	**[Nu] / mol L^{-1}**	$k_{1,A}$ **/ 10^{-3} s^{-1}**	$k_{2,A}$ **/ 10^{-3} L mol^{-1} s^{-1}**	$k_{-1,A}$ **/ 10^{-3} s^{-1}**	$k_{1,E}$ **/ 10^{-3} s^{-1}**	$(k_{2,A} \times k_{1,E}) \div (k_{-1,A} + k_{1,E})$ **/ L mol^{-1} s^{-1}**
0	0.182	6.20	33.98	7.98	0.58	2.30
		5.98	32.77	8.21	0.66	2.46
		5.89	32.31	8.43	0.57	2.04
0.22	0.061	5.73	94.3	24.3	1.42	5.18
		5.59	92.0	25.0	1.35	4.71
0.95	0.151	21.0	139	32.4	2.65	10.5
		20.3	135	33.5	2.75	10.3
		20.1	133	33.2	2.47	9.21

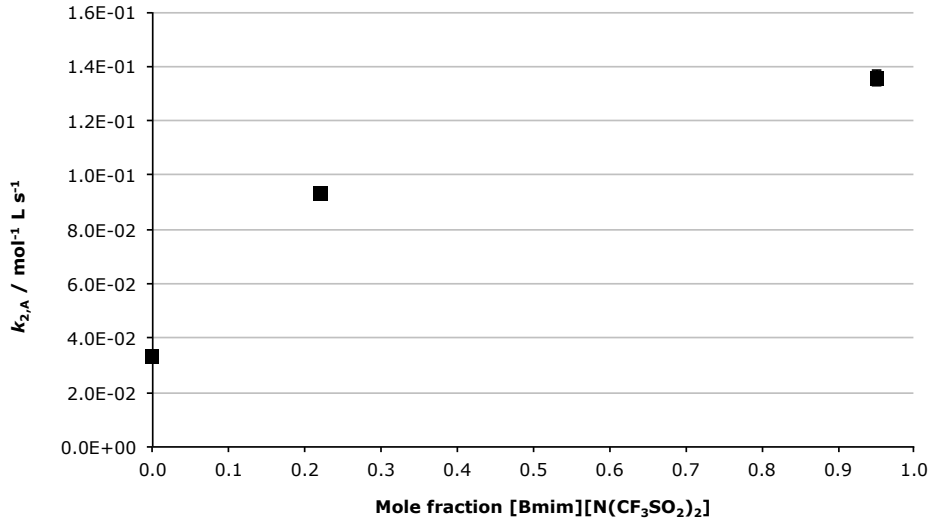

Figure S5: The bimolecular rate constant for the addition step ($k_{2,A}$) of the reaction between 4-trifluoromethylbenzaldehyde **2e** and the amine **3** in different mole fractions of [Bmim][$N(CF_3SO_2)_2$] **1** in acetonitrile at 281 K. Uncertainties are reported as the standard deviation of three replicates.

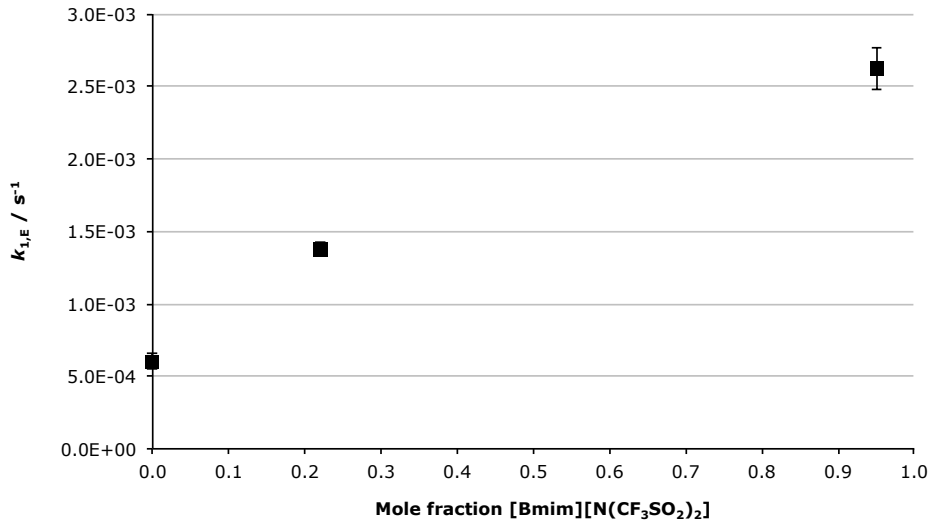

Figure S6: The unimolecular rate constant for the elimination step ($k_{1,E}$) of the reaction between 4-trifluoromethylbenzaldehyde **2e** and the amine **3** in different mole fractions of [Bmim][N(CF_3SO_2)$_2$] **1** in acetonitrile at 281 K. Uncertainties are reported as the standard deviation of three replicates.

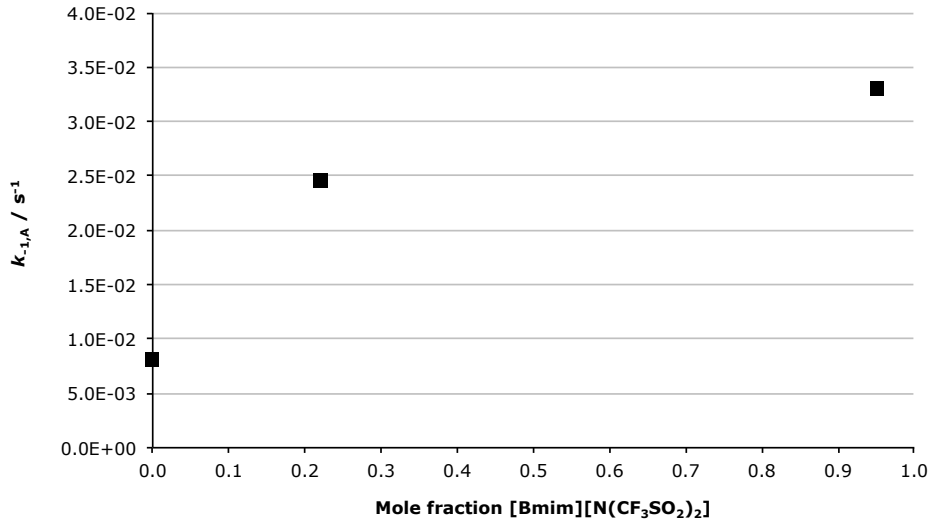

Figure S7: The unimolecular rate constant for the reverse addition step ($k_{-1,A}$) of the reaction between 4-trifluoromethylbenzaldehyde **2e** and the amine **3** in different mole fractions of [Bmim][N(CF_3SO_2)$_2$] **1** in acetonitrile at 281 K. Uncertainties are reported as the standard deviation of three replicates.

*p-Nitrobenzaldehyde **2f** and Hexan-1-amine **3***

Addition ($k_{2,A}$), reverse addition ($k_{-1,A}$) and elimination ($k_{1,E}$) data in [Bmim][$N(CF_3SO_2)_2$] **1** and acetonitrile at 8.1°C

Mole Fraction of 1	**[Nu] / mol L^{-1}**	**$k_{1,A}$ / 10^{-3} s^{-1}**	**$k_{2,A}$ / 10^{-3} L mol^{-1} s^{-1}**	**$k_{-1,A}$ / 10^{-3} s^{-1}**	**$k_{1,E}$ / 10^{-3} s^{-1}**	**($k_{2,A} \times k_{1,E}$) ÷ ($k_{-1,A} + k_{1,E}$) / 10^{-3} L mol^{-1} s^{-1}**
0	0.081	7.56	92.7	6.25	0.22	3.16
		8.42	103	7.43	0.22	2.91
		8.13	99.7	7.41	0.28	3.61
0.06	0.098	13.0	132.4	10.8	0.39	4.65
		12.8	129.5	10.4	0.36	4.38
		12.8	130.2	10.5	0.37	4.44
0.11	0.105	14.31	136	10.20	0.52	6.64
		18.93	179.9	14.05	0.53	6.53
0.21	0.063	9.22	146.9	12.72	0.79	8.61
		7.19	114.5	8.70	0.68	8.28
		8.04	128.2	9.28	0.65	8.36
0.31	0.119	14.86	125.3	9.71	0.73	8.75
		14.53	122.5	9.98	0.69	7.93
0.41	0.087	13.49	154.3	13.24	0.74	8.17
		13.44	153.7	13.37	0.78	8.46
		13.41	153.3	13.65	0.82	8.64
0.51	0.058	9.42	161.5	15.09	1.13	11.29
		8.58	147.2	14.43	1.17	11.07
		8.81	151.1	15.14	1.04	9.69
0.61	0.057	10.14	176.8	16.27	1.55	15.39
		13.10	228.6	22.40	1.31	12.67
		12.74	222.4	22.31	1.28	12.04
0.69	0.070	18.21	259.5	27.85	1.22	10.85
		17.54	250.0	28.74	1.66	13.64
		17.44	248.5	28.42	1.45	12.07
0.78	0.070	18.13	260.3	27.77	1.28	11.45
		18.27	262.2	28.09	1.25	11.17
		19.10	274.1	27.99	1.17	11.00
0.87	0.089	21.33	239.8	29.77	1.32	10.17
		22.27	250.4	27.09	1.28	11.29
		23.10	259.7	29.90	1.20	10.02

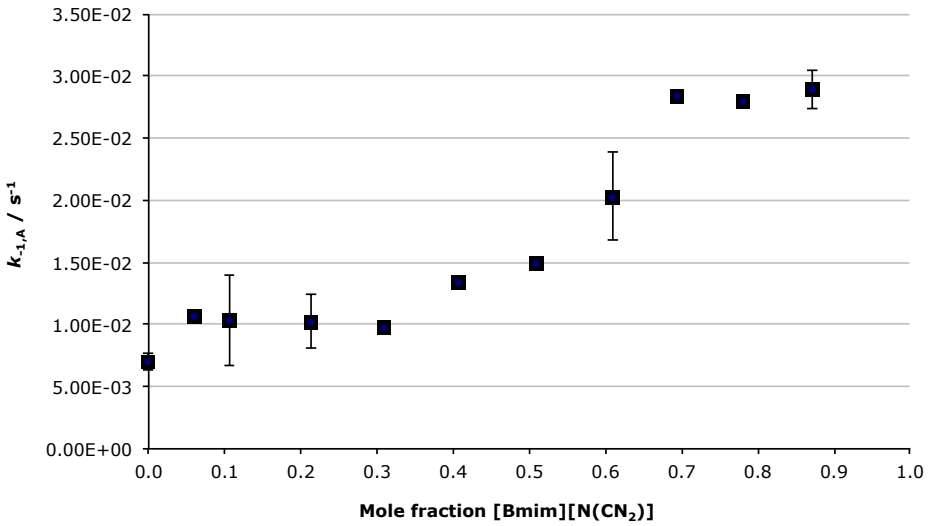

Figure S8: The unimolecular rate constant for the reverse addition step ($k_{-1,A}$) of the reaction between 4-nitrolbenzaldehyde **2f** and the amine **3** in different mole fractions of [Bmim][$N(CF_3SO_2)_2$] **1** in acetonitrile at 281 K. Uncertainties are reported as the standard deviation of three replicates.

Hammett Plots:

Acetonitrile using the rate constant of the addition step ($k_{2,A}$)

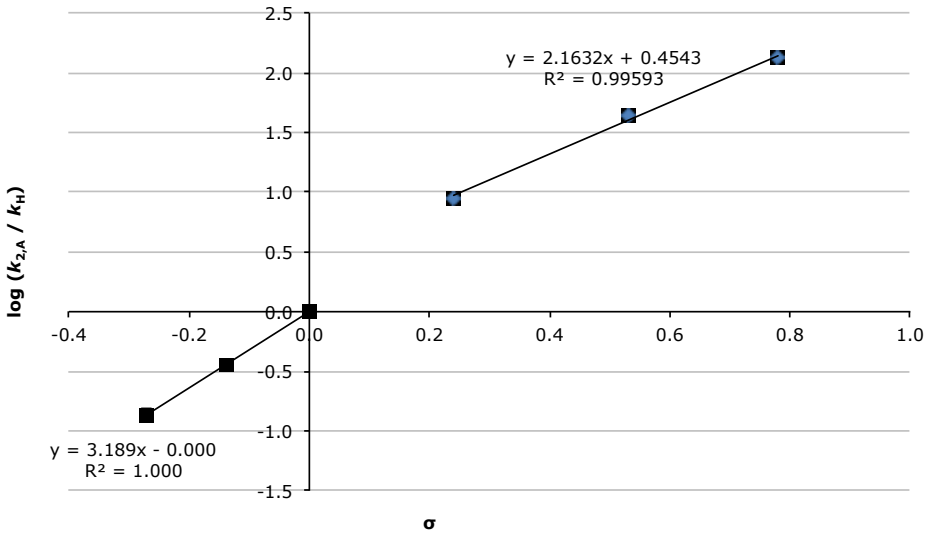

Figure S9: Hammett plot of the second order rate constant for the addition step ($k_{2,A}$) of the reaction between benzaldehydes **2a-f** and the amine **3** in acetonitrile at 281 K. Uncertainties are reported as the standard deviation of three replicates.

[Bmim][$N(CF_3SO_2)_2$] **1** and acetonitrile, χ_{IL} = 0.9, using the rate constant of the addition step ($k_{2,A}$)

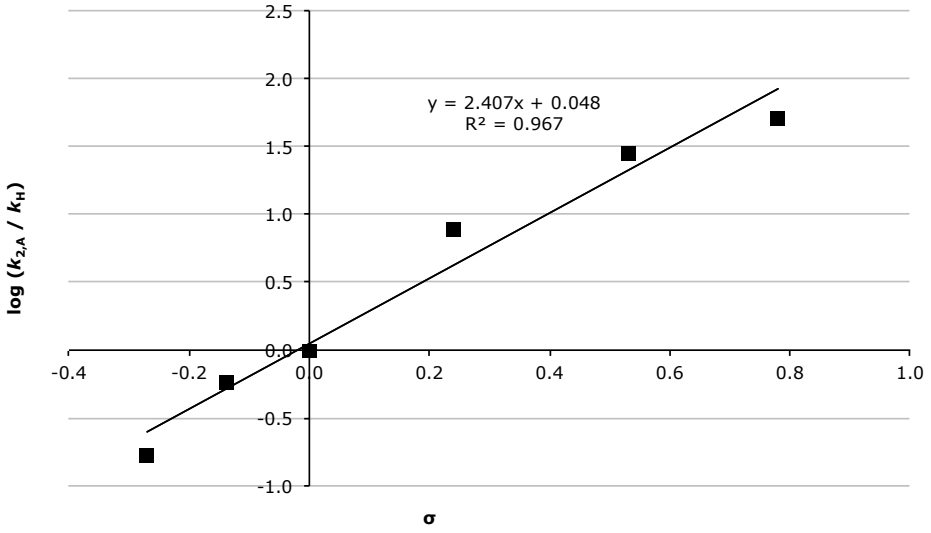

Figure S10: Hammett plots of the second order rate constant for the addition step ($k_{2,A}$) of the reaction between benzaldehydes **2a-f** and the amine **3** in [Bmim][$N(CF_3SO_2)_2$] **1** (χ_{IL} *ca.* 0.9) at 281 K. Uncertainties are reported as the standard deviation of three replicates.

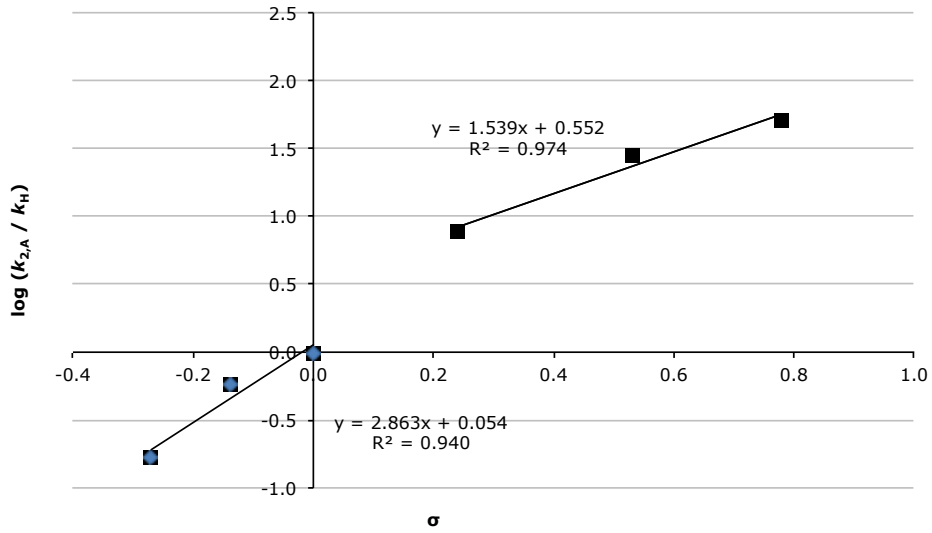

Figure S11: Hammett plots of the second order rate constant for the addition step ($k_{2,A}$) of the reaction between benzaldehydes **2a-f** and the amine **3** in [Bmim][$N(CF_3SO_2)_2$] **1** (χ_{IL} *ca.* 0.9) at 281 K. Uncertainties are reported as the standard deviation of three replicates.

[Bmim][$N(CF_3SO_2)_2$] **1** and acetonitrile, χ_{IL} = 0.2, using the rate constant of the elimination step ($k_{1,E}$)

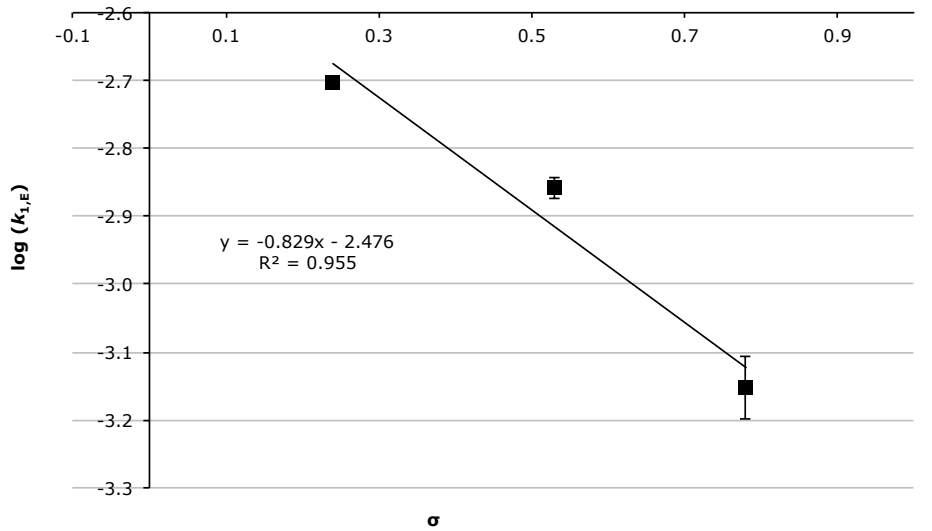

Figure S12: Log plot of the first order rate constant for the elimination step ($k_{1,E}$) of the reaction between benzaldehydes **2c-f** and the amine **3** in [Bmim][$N(CF_3SO_2)_2$] **1** / acetonitrile (χ_{IL} *ca.* 0.2) at 281 K. Uncertainties are reported as the standard deviation of three replicates

[Bmim][$N(CF_3SO_2)_2$] **1** and acetonitrile, χ_{IL} = 0.9, using the rate constant of the elimination step ($k_{1,E}$)

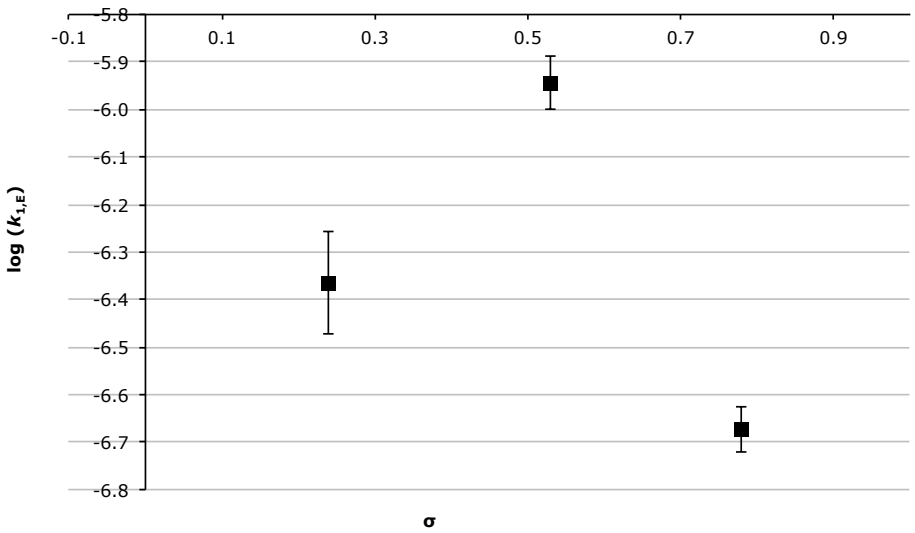

Figure S13: Log plot of the first order rate constant for the elimination step ($k_{1,E}$) of the reaction between benzaldehydes **2c-f** and the amine **3** in [Bmim][$N(CF_3SO_2)_2$] **1** (χ_{IL} *ca.* 0.9) at 281 K. Uncertainties are reported as the standard deviation of three replicates

[Bmim][$N(CF_3SO_2)_2$] **1** and acetonitrile, χ_{IL} = 0.2, using the rate constant of the reverse addition step ($k_{-1,A}$)

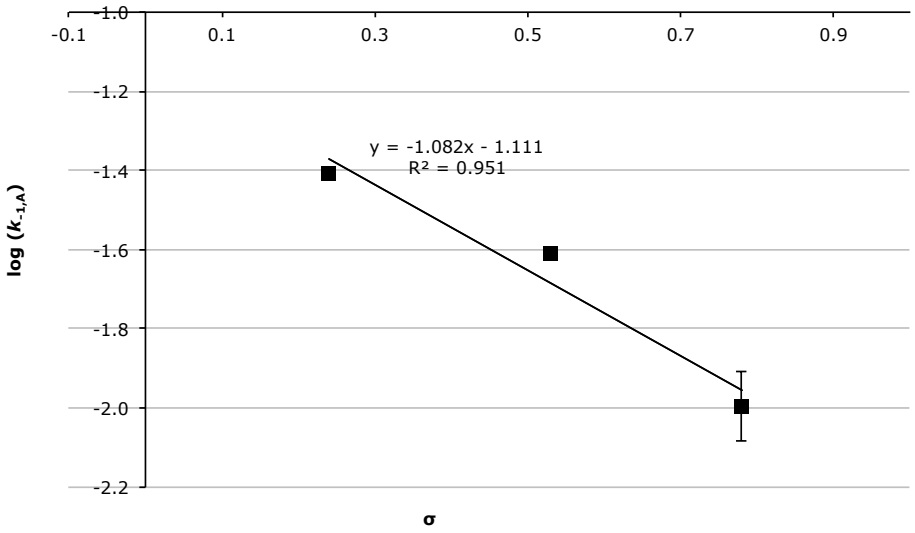

Figure S14: Log plot of the first order rate constant for the reverse of the addition step ($k_{-1,A}$) of the reaction between benzaldehydes **2c-f** and the amine **3** in [Bmim][$N(CF_3SO_2)_2$] **1** / acetonitrile (χ_{IL} *ca.* 0.2) at 281 K. Uncertainties are reported as the standard deviation of three replicates

[Bmim][$N(CF_3SO_2)_2$] **1** and acetonitrile, χ_{IL} = 0.9, using the rate constant of the reverse addition step ($k_{-1,A}$)

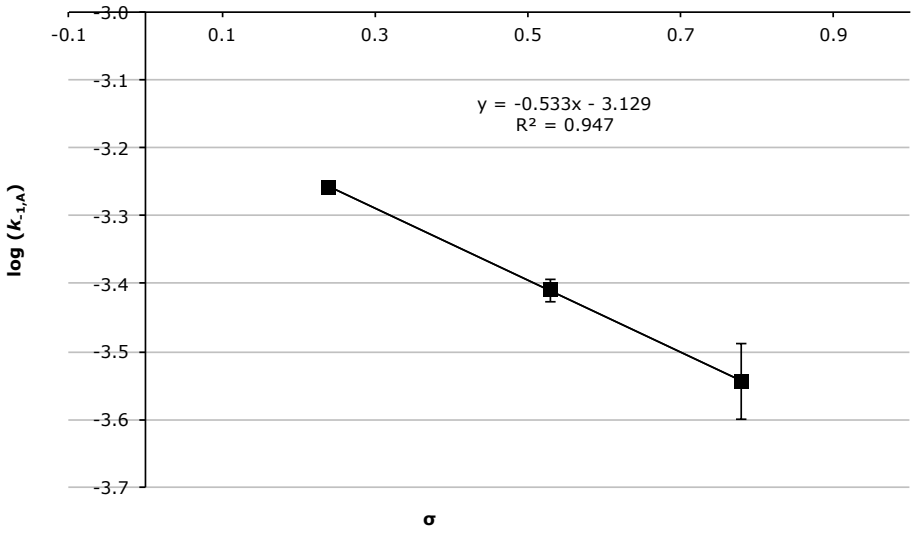

Figure S15: Log plot of the first order rate constant for the reverse of the addition step ($k_{-1,A}$) of the reaction between benzaldehydes **2c-f** and the amine **3** in [Bmim][$N(CF_3SO_2)_2$] **1** (χ_{IL} *ca.* 0.9) at 281 K. Uncertainties are reported as the standard deviation of three replicates

[Bmim][$N(CF_3SO_2)_2$] **1** and acetonitrile, χ_{IL} = 0.9, using the rate constant of the overall addition elimination process ($k_{2,app}$)

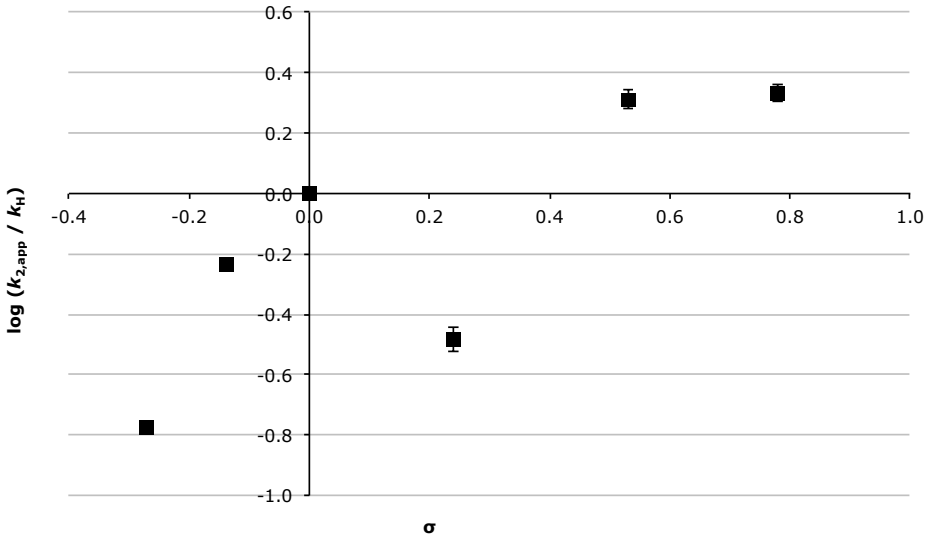

Figure S16: Hammett plot of the observed second order rate constant ($k_{2,app}$) for the reaction between benzaldehydes **2a-f** and the amine **3** in [Bmim][$N(CF_3SO_2)_2$] **1** (χ_{IL} *ca.* 0.9) at 281 K. Uncertainties are reported as the standard deviation of three replicates.

Activation Parameter Data

p-Chlorobenzaldehyde **2d** and hexan-1-amine **3**, addition step ($k_{2,A}$)

Mole Fraction of 1	Temperature / °C	[Nu] / mol L^{-1}	$k_{1,A}$ / 10^{-3} s^{-1}	$k_{2,A}$ / 10^{-3} L mol^{-1} s^{-1}
0	1.6	0.187	0.704	3.77
			0.883	4.72
	14.5		2.749	14.69
			1.987	10.62
			1.905	10.18
	8.1	0.147	1.046	7.12
			0.952	6.49
			0.970	6.61
	-3.4	0.157	0.439	2.79
			0.443	2.82
0.22	8.1	0.325	11.247	34.56
			10.514	32.31
			10.318	31.71
	2.6		8.133	24.99
			7.470	22.96
			7.297	22.42
	-3.6		3.496	10.74
			3.447	10.59
	-9.9		2.559	7.86
			2.664	8.19
			2.282	7.01

p-Chlorobenzaldehyde **2d** and hexan-1-amine **3**, elimination step ($k_{1,E}$)

Mole Fraction of 1	**Temperature / °C**	**[Nu] / mol L^{-1}**	**$k_{1,E}$ / 10^{-3} s^{-1}**
0	8.1	0.146	1.76
			1.61
			1.80
	1.6	0.187	0.51
			0.61
			0.47
	14.5		2.40
			2.91
			2.20
	-3.7		0.20
			0.23
			0.17
0.22	8.1	0.325	2.01
			1.96
			2.00
	2.6		1.11
			1.13
			1.21
	-3.6		0.46
			0.46
			0.51
	-9.9		0.27
			0.24
			0.22

p-Trifluoromethylbenzaldehyde **2e** and hexan-1-amine **3**, elimination step ($k_{1,E}$)

Mole Fraction of 1	Temperature / °C	[Nu] / mol L^{-1}	$k_{1,E}$ / 10^{-3} s^{-1}
0	8.1	0.182	0.58
			0.66
			0.57
	18.9		1.74
			1.49
			1.46
	14.5		0.96
			0.84
			0.86
	24.8		2.23
			2.30
			2.21
0.22	8.1	0.061	1.42
			1.35
			1.17
	14.3		2.93
			2.49
			2.70
	1.4	0.095	0.81
			0.79
			0.82
	-3.6	0.154	0.33
			0.31
			0.32
0.95	13.0	0.151	3.86
			3.85
			4.38
	8.1		2.65
			2.75
			2.47
	-3.6		0.66
			0.66
			0.76
	2.3		1.28
			1.22
			1.28

p-Nitrobenzaldehyde **2f** and hexan-1-amine **3**, elimination step ($k_{1,E}$)

Mole Fraction of 1	**Temperature / °C**	**[Nu] / mol L^{-1}**	**$k_{1,E}$ / 10^{-3} s^{-1}**
0	8.1	0.082	0.221
			0.215
			0.278
	13.0		0.342
			0.452
			0.392
	23.7		0.935
			0.798
	18.2		0.594
			0.621
			0.542
	-0.6	0.078	0.124
			0.138
0.06	8.1	0.099	0.393
			0.363
			0.372
	13.7		0.686
			0.694
			0.752
	-3.6		0.099
			0.092
			0.093
	2.5		0.238
			0.153
			0.208
0.22	8.1	0.082	0.520
			0.472
			0.474
			0.504
	23.3		2.927
			3.372
			3.024
	15.8		1.528
			1.368
			1.646
	2.4		0.230
			0.198
			0.237

Mole Fraction of 1	Temperature / °C	[Nu] / mol L^{-1}	$k_{1,E}$ / 10^{-3} s^{-1}
0.88	8.1	0.089	1.318
			1.280
			1.200
	2.3	0.082	0.393
			0.577
			0.527
	14.7		1.623
			1.800
			1.648
	-3.3		0.258
			0.297
			0.248
			1.318