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Electronic Supporting Information for

"Machine learning approaches to understand and predict rate constants for organic processes in mixtures containing ionic liquids"

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Ionic liquids used in the training model



S36 [mTOA][N(SO₂CF₃)₂]

Figure S1. The ionic liquids used in the training models. Abbreviations used throughout this work for cations are based on those commonly used for the 1-alkyl-3-methylimidazolium series;
these are abbreviated [xmim]⁺, where x is the first letter of the name of the alkyl chain, m refers to methyl, and im the imidazolium core. Other, arguably less ambiguous, abbreviations (e.g.
 $[C_xC_yim]^+$ for an imidazolium series with alkyl chains X and Y carbons long) are also used, but the other form is most common and is used here. Abbreviations for other systems are determined
in the same fashion and are introduced as needed. Anions may be abbreviated (for example, $[N(SO_2CF_3)_2]^-$, as either $[NTf_2]^-$ or TFSI) but they are generally referred to with chemical formulae;
this will be consistently used throughout this work.

Table S1. The ILs, their abbreviations, and the number of reactions involving that ionic liquid used in the initial modelling. Detailed data for each reaction is available at the following Figshare repository: 10.25439/rmt.12665651.

	Ionic Liquid	Abbreviation	Number of reactions
S1	1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[emim][N(SO ₂ CF ₃) ₂]	1
S2	1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[bmim][N(SO ₂ CF ₃) ₂]	18
S3	1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[h _x mim][N(SO ₂ CF ₃) ₂]	1
S4	1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[omim][N(SO ₂ CF ₃) ₂]	1
S5	1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[dmim][N(SO ₂ CF ₃) ₂]	1
S6	1-dodecyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[ddmim][N(SO ₂ CF ₃) ₂]	1
S7	1,4-bis(3-methylimidazolium-1-yl)propane bis(trifluoromethanesulfonyl)imide	$[(mim)_2 p_r][N(SO_2 CF_3)_2]_2$	2
S8	1,4-bis(3-methylimidazolium-1-yl)butane bis(trifluoromethanesulfonyl)imide	[(mim) ₂ b][N(SO ₂ CF ₃) ₂] ₂	1
S9	1,4-bis(3-methylimidazolium-1-yl)pentane bis(trifluoromethanesulfonyl)imide	$[(mim)_2 p_e][N(SO_2 CF_3)_2]_2$	18
S10	1,4-bis(3-methylimidazolium-1-yl)hexane bis(trifluoromethanesulfonyl)imide	$[(mim)_2h_x][N(SO_2CF_3)_2]_2$	3
S11	1,4-bis(3-methylimidazolium-1-yl)heptane bis(trifluoromethanesulfonyl)imide	[(mim) ₂ h _p][N(SO ₂ CF ₃) ₂] ₂	1
S12	1,4-bis(3-methylimidazolium-1-yl)octane bis(trifluoromethanesulfonyl)imide	[(mim) ₂ o][N(SO ₂ CF ₃) ₂] ₂	2
S13	1,4-bis(3-methylimidazolium-1-yl)nonane bis(trifluoromethanesulfonyl)imide	[(mim) ₂ n][N(SO ₂ CF ₃) ₂] ₂	2
S15	1,4-bis(3-methylimidazolium-1-yl)decane bis(trifluoromethanesulfonyl)imide	[(mim) ₂ d][N(SO ₂ CF ₃) ₂] ₂	3
S15	1,4-bis(3-methylimidazolium-1-yl)undecane bis(trifluoromethanesulfonyl)imide	[(mim) ₂ u][N(SO ₂ CF ₃) ₂] ₂	2
S16	1,4-bis(3-methylimidazolium-1-yl)dodecane bis(trifluoromethanesulfonyl)imide	$[(mim)_2 dd][N(SO_2 CF_3)_2]_2$	3
S17	1-butyl-3-methylimidazolium dicyanimide	[bmim][N(CN) ₂]	3
S18	1-butyl-3-methylimidazolium hexafluorophoshate	[bmim][PF ₆]	4
S19	1-butyl-3-methylimidazolium tetrafluoroborate	[bmim][BF ₄]	4
S20	1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide	[bm ₂ im][N(SO ₂ CF ₃) ₂]	4
S21	1-butyl-3,4,5-trimethylimidazolium bis(trifluoromethanesulfonyl)imide	[bm ₃ im][N(SO ₂ CF ₃) ₂]	4
S22	1-butyl-2,3,4,5-tetramethylimidazolium bis(trifluoromethanesulfonyl)imide	[bm ₄ im][N(SO ₂ CF ₃) ₂]	4
S23	1-butyl-2-chloro-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[b2Clmim][N(SO ₂ CF ₃) ₂]	4
S24	1-butyl-4-chloro-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[b4Clmim][N(SO ₂ CF ₃) ₂]	8
S25	1-butyl-4,5-dichloro-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[b45Cl ₂ mim][N(SO ₂ CF ₃) ₂]	5
S26	1-(2-methoxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	[(eOm)mim][N(SO ₂ CF ₃) ₂]	1
S27	1-butyl-3-methyl-1,2,3-triazolium bis(trifluoromethanesulfonyl)imide	[bmtr][N(SO ₂ CF ₃) ₂]	7
S28	1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	[bmpyr][N(SO ₂ CF ₃) ₂]	4
S29	1-butylthiolanium bis(trifluoromethanesulfonyl)imide	[btl][N(SO ₂ CF ₃) ₂]	8
S30	1-butyl-1-methylpiperidinium bis(trifluoromethanesulfonyl)imide	[bmpi][N(SO ₂ CF ₃) ₂]	7
S31	1-butyl-1-methylmorpholinium bis(trifluoromethanesulfonyl)imide	[bmmo][N(SO ₂ CF ₃) ₂]	14
S32	1-butylpyridinium bis(trifluoromethanesulfonyl)imide	[bpy][N(SO ₂ CF ₃) ₂]	8
S33	1-hexylpyridinium bis(trifluoromethanesulfonyl)imide	$[h_x py][N(SO_2CF_3)_2]$	3
S34	1-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)pyridinium bis(trifluoromethanesulfonyl)imide	[Fh _x py][N(SO ₂ CF ₃) ₂]	4
S35	tetraoctylammonium bis(trifluoromethanesulfonyl)imide	$[TOA][N(SO_2CF_3)_2]$	4
S36	methyltrioctylammonium bis(trifluoromethanesulfonyl)imide	$[mTOA][N(SO_2CF_3)_2]$	1

Quantitative values of each descriptor used for the ionic liquid constituents

 Table S2. Value of each descriptor used for each cation type.

Cation	Abbreviation	ARR	ncic	nCIR	RBN	RBF	nDB	nAB	õ	ncL	nCp	nCs	nCrs	nCar	nHAcc	N-073	N-075	079	Ë	Ηγ	AMR	TPSA	P MLOG
1-ethyl-3-methylimidazolium	[emim]+	0.625	1	1	1	0.053	0	5	0	0	1	0	0	3	0	1	1	0	2.585	-0.71	34.354	8.81	0.468
1-butyl-3-methylimidazolium	[bmim]+	0.5	1	1	3	0.12	0	5	0	0	1	2	0	3	0	1	1	0	2.585	-0.768	43.479	8.81	1.155
1-hexyl-3-methylimidazolium	[h _x mim]+	0.417	1	1	5	0.161	0	5	0	0	1	4	0	3	0	1	1	0	2.585	-0.807	52.681	8.81	1.775
1-octyl-3-methylimidazolium	[omim]+	0.357	1	1	7	0.189	0	5	0	0	1	6	0	3	0	1	1	0	2.585	-0.835	61.883	8.81	3.26
1-decyl-3-methylimidazolium	[dmim]+	0.313	1	1	9	0.209	0	5	0	0	1	8	0	3	0	1	1	0	2.585	-0.856	71.085	8.81	3.795
1-dodecyl-3-methylimidazolium	[ddmim]+	0.278	1	1	11	0.224	0	5	0	0	1	10	0	3	0	1	1	0	2.585	-0.873	80.287	8.81	4.301
1,4-bis(3-methylimidazolium-1-yl)propane	[(mim) ₂ p _r]2+	0.625	2	2	4	0.118	1	10	0	0	0	1	0	6	0	2	2	0	3.585	-0.716	62.109	17.62	0.556
1,4-bis(3-methylimidazolium-1-yl)butane	[(mim) ₂ b]2+	0.588	2	2	5	0.135	1	10	0	0	0	2	0	6	0	2	2	0	3.585	-0.734	66.753	17.62	0.837
1,4-bis(3-methylimidazolium-1-yl)pentane	[(mim) ₂ p _{e2}]+	0.556	2	2	6	0.15	0	10	0	0	0	3	0	6	0	2	2	0	3.459	-0.75	71.354	17.62	1.195
1,4-bis(3-methylimidazolium-1-yl)hexane	[(mim) ₂ h _x]2+	0.526	2	2	7	0.163	0	10	0	0	0	4	0	6	0	2	2	0	3.459	-0.763	75.955	17.62	1.458
1,4-bis(3-methylimidazolium-1-yl)heptane	[(mim) ₂ h _p]2+	0.5	2	2	8	0.174	0	10	0	0	0	5	0	6	0	2	2	0	3.459	-0.776	80.556	17.62	1.715
1,4-bis(3-methylimidazolium-1-yl)octane	[(mim) ₂ o]2+	0.526	2	2	7	0.163	0	10	0	0	0	4	0	6	0	2	2	0	3.459	-0.763	75.955	17.62	1.458
1,4-bis(3-methylimidazolium-1-yl)nonane	[(mim) ₂ n]2+	0.5	2	2	8	0.174	0	10	0	0	0	5	0	6	0	2	2	0	3.459	-0.776	80.556	17.62	1.715
1,4-bis(3-methylimidazolium-1-yl)decane	[(mim) ₂ d]2+	0.435	2	2	11	0.2	0	10	0	0	0	8	0	6	0	2	2	0	3.459	-0.807	94.359	17.62	2.445
1,4-bis(3-methylimidazolium-1-yl)undecane	[(mim) ₂ u]+	0.417	2	2	12	0.207	0	10	0	0	0	9	0	6	0	2	2	0	3.459	-0.815	98.96	17.62	2.677
1,4-bis(3-methylimidazolium-1-yl)dodecane	[(mim) ₂ dd]2+	0.4	2	2	13	0.213	0	10	0	0	0	10	0	6	0	2	2	0	3.459	-0.823	103.561	17.62	2.905
1-butyl-2,3-dimethylimidazolium	[bm ₂ im]+	0.455	1	1	3	0.107	0	5	0	0	2	2	0	3	0	1	1	0	2.585	-0.79	47.92	8.81	1.472
1-butyl-3,4,5-trimethylimidazolium	[bm₃im]+	0.417	1	1	3	0.097	0	5	0	0	3	2	0	3	0	1	1	0	2.585	-0.807	52.912	8.81	1.775
1-butyl-2,3,4,5-tetramethylimidazolium	[bm₄im]+	0.385	1	1	3	0.088	0	5	0	0	4	2	0	3	0	1	1	0	2.585	-0.822	57.353	8.81	2.067
1-butyl-2-chloro-3-methylimidazolium	[b2Clmim]+	0.455	1	1	3	0.12	0	5	0	1	1	2	0	3	0	1	1	0	2.585	-0.702	48.505	8.81	1.74
1-butyl-4-chloro-3-methylimidazolium	[b4Clmim]+	0.455	1	1	3	0.12	0	5	0	1	1	2	0	3	0	1	1	0	2.585	-0.702	49.346	8.81	1.74
1-butyl-4,5-dichloro-3-methylimidazolium	[b45Cl ₂ mim]+	0.417	1	1	3	0.12	0	5	0	2	1	2	0	3	0	1	1	0	2.585	-0.646	54.151	8.81	2.311
1-(2-methoxyethyl)-3-methylimidazolium	[(eOm)mim]+	0.5	1	1	3	0.13	0	5	1	0	0	0	0	3	1	1	1	0	2.585	-0.672	40.65	18.04	-0.015
1-butyl-3-methyl-1,2,3-triazolium	[bmtr]+	0.5	1	1	3	0.125	0	5	0	0	1	2	0	2	1	1	2	0	2.585	-0.672	44.075	21.7	1.203
1-butyl-1-methylpyrrolidinium	[bmpyr]+	0	1	1	3	0.1	0	0	0	0	1	4	2	0	0	0	0	0	0	-0.864	44.2	0	-1.485
1-butylthiolanium	[btl]+	0	1	1	3	0.115	0	0	0	0	1	4	2	0	0	0	0	0	0	-0.848	46.297	0	2.899
1-butyl-1-methylpiperidinium	[bmpi]+	0	1	1	3	0.091	0	0	0	0	1	5	3	0	0	0	0	0	0	-0.877	48.801	0	-1.182
1-butyl-1-methylmorpholinium	[bmmo]+	0	1	1	3	0.097	0	0	1	0	1	2	0	0	1	0	0	0	0	-0.79	45.735	9.23	-2.366
1-butylpyridinium	[bpy]+	0.6	1	1	3	0.125	0	6	0	0	1	2	0	5	0	0	1	0	2.807	-0.864	43.471	3.88	1.85
1-hexylpyridinium	[h _x py]+	0.5	1	1	5	0.167	0	6	0	0	1	4	0	5	0	0	1	0	2.807	-0.888	52.673	3.88	2.445
1-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)pyridinium	[Fh _x py]+	0.286	1	1	5	0.167	0	6	0	0	1	4	0	5	9	0	1	0	2.807	-0.516	53.504	3.88	3.643
tetraoctylammonium	[TOA]+	0	0	0	28	0.28	0	0	0	0	4	24	0	0	0	0	0	1	0	-0.961	151.896	0	5.122
methyltrioctylammonium	[mTOA]+	0	0	0	21	0.266	0	0	0	0	3	18	0	0	0	0	0	1	0	-0.951	119.618	0	3.752

 Table S3. Value of each descriptor used. for each anion type.

Anion	Abbreviation	AnionTotalF	AnionTotalB	AnionTotalP	AnionTotalNsingle	AnionTotalNtriple	AnionTotalS	AnionTotalO	AnionTotalC
bis(triflluoromethanesulfonyl)imide	$[N(SO_2CF_3)_2]$ -	6	0	0	1	0	2	4	2
dicyanimide	[N(CN) ₂]-	4	1	0	0	0	0	0	0
hexafluorophosphate	[PF ₆]-	0	0	0	1	2	0	0	2
1-octyl-3-methylimidazolium	[BF ₄]-	6	0	1	0	0	0	0	0

Table S4. Cross correlation matrix for the 29 descriptors used.

	InverseT	Ilmole fraction	Anion TotalF	AnionTotal Nsingle	Anion TotalS	Anion TotalO	Anion TotalC	ARR	nCIC	nCIR	RBN	RBF	nAB	nO	nCL	nCp	nCs	nCrs	nCar	nHAcc	N-073	N-075	N-079	Ui	Ну	AMR	TPSA	k2
InverseT	1	0.26	-0.186	-0.167	-0.223	-0.223	-0.167	0.012	-0.06	-0.06	-0.395	-0.294	-0.118	-0.104	0.054	-0.23	-0.319	0.255	-0.088	0.047	-0.196	-0.097	-0.321	-0.063	0.089	-0.431	-0.171	-0.086
Ilmolefraction	0.26	1	-0.17	-0.2	-0.239	-0.239	-0.2	-0.05	-0.362	-0.362	-0.126	-0.194	-0.261	-0.232	0.21	0.301	-0.024	0.229	-0.277	-0.22	-0.206	-0.206	0.041	-0.143	-0.123	-0.183	-0.273	0.112
AnionTotalF	-0.186	-0.17	1	0.222	0.691	0.691	0.222	-0.113	0.076	0.076	0.078	0.059	-0.002	0.06	0.061	0.003	0.079	0.069	0.006	0.048	-0.03	0.005	0.034	-0.061	-0.025	0.119	0.023	0.009
AnionTotalNsingle	-0.167	-0.2	0.222	1	0.844	0.844	1	-0.138	0.093	0.093	0.096	0.072	-0.002	0.074	0.074	0.003	0.096	0.085	0.007	0.058	-0.037	0.006	0.041	-0.075	-0.03	0.145	0.028	0.011
AnionTotalS	-0.223	-0.239	0.691	0.844	1	1	0.844	-0.164	0.11	0.11	0.113	0.085	-0.002	0.087	0.088	0.004	0.114	0.1	0.009	0.069	-0.044	0.007	0.049	-0.088	-0.036	0.172	0.033	0.013
AnionTotalO	-0.223	-0.239	0.691	0.844	1	1	0.844	-0.164	0.11	0.11	0.113	0.085	-0.002	0.087	0.088	0.004	0.114	0.1	0.009	0.069	-0.044	0.007	0.049	-0.088	-0.036	0.172	0.033	0.013
AnionTotalC	-0.167	-0.2	0.222	1	0.844	0.844	1	-0.138	0.093	0.093	0.096	0.072	-0.002	0.074	0.074	0.003	0.096	0.085	0.007	0.058	-0.037	0.006	0.041	-0.075	-0.03	0.145	0.028	0.011
ARR	0.012	-0.05	-0.113	-0.138	-0.164	-0.164	-0.138	1	0.453	0.453	-0.165	0.084	0.848	-0.493	0.103	-0.31	-0.363	-0.622	0.835	-0.141	0.696	0.835	-0.302	0.95	0.411	-0.07	0.603	0.336
nCIC	-0.06	-0.362	0.076	0.093	0.11	0.11	0.093	0.453	1	1	-0.07	0.112	0.794	-0.13	-0.131	-0.733	-0.25	-0.149	0.743	-0.103	0.798	0.748	-0.46	0.595	0.239	0.169	0.716	-0.068
nCIR	-0.06	-0.362	0.076	0.093	0.11	0.11	0.093	0.453	1	1	-0.07	0.112	0.794	-0.13	-0.131	-0.733	-0.25	-0.149	0.743	-0.103	0.798	0.748	-0.46	0.595	0.239	0.169	0.716	-0.068
RBN	-0.395	-0.126	0.078	0.096	0.113	0.113	0.096	-0.165	-0.07	-0.07	1	0.903	0.076	-0.134	-0.135	0.276	0.96	-0.154	0.069	-0.036	0.103	0.053	0.863	-0.048	-0.381	0.96	-0.001	0.51
RBF	-0.294	-0.194	0.059	0.072	0.085	0.085	0.072	0.084	0.112	0.112	0.903	1	0.335	-0.27	-0.101	0.012	0.821	-0.292	0.344	0.077	0.264	0.302	0.656	0.234	-0.183	0.884	0.16	0.661
nAB	-0.118	-0.261	-0.002	-0.002	-0.002	-0.002	-0.002	0.848	0.794	0.794	0.076	0.335	1	-0.437	0.003	-0.494	-0.154	-0.538	0.976	-0.041	0.881	0.953	-0.261	0.946	0.376	0.26	0.749	0.351
nO	-0.104	-0.232	0.06	0.074	0.087	0.087	0.074	-0.493	-0.13	-0.13	-0.134	-0.27	-0.437	1	-0.104	-0.028	-0.146	-0.119	-0.431	0.144	-0.356	-0.431	-0.058	-0.503	-0.015	-0.175	0.013	-0.675
nCL	0.054	0.21	0.061	0.074	0.088	0.088	0.074	0.103	-0.131	-0.131	-0.135	-0.101	0.003	-0.104	1	-0.004	-0.136	-0.119	-0.01	-0.082	0.052	-0.009	-0.058	0.105	0.416	-0.086	-0.039	0.151
nCp	-0.23	0.301	0.003	0.003	0.004	0.004	0.003	-0.31	-0.733	-0.733	0.276	0.012	-0.494	-0.028	-0.004	1	0.378	-0.005	-0.473	-0.008	-0.456	-0.474	0.551	-0.357	-0.343	0.161	-0.49	0.245
nCs	-0.319	-0.024	0.079	0.096	0.114	0.114	0.096	-0.363	-0.25	-0.25	0.96	0.821	-0.154	-0.146	-0.136	0.378	1	0.077	-0.15	-0.028	-0.115	-0.169	0.884	-0.261	-0.497	0.88	-0.232	0.475
nCrs	0.255	0.229	0.069	0.085	0.1	0.1	0.085	-0.622	-0.149	-0.149	-0.154	-0.292	-0.538	-0.119	-0.119	-0.005	0.077	1	-0.53	-0.094	-0.442	-0.529	-0.066	-0.627	-0.402	-0.174	-0.568	-0.246
nCar	-0.088	-0.277	0.006	0.007	0.009	0.009	0.007	0.835	0.743	0.743	0.069	0.344	0.976	-0.431	-0.01	-0.473	-0.15	-0.53	1	0.039	0.767	0.882	-0.258	0.93	0.335	0.235	0.621	0.382
nHAcc	0.047	-0.22	0.048	0.058	0.069	0.069	0.058	-0.141	-0.103	-0.103	-0.036	0.077	-0.041	0.144	-0.082	-0.008	-0.028	-0.094	0.039	1	-0.257	-0.05	-0.046	-0.014	0.562	-0.081	-0.081	0.093
N-073	-0.196	-0.206	-0.03	-0.037	-0.044	-0.044	-0.037	0.696	0.798	0.798	0.103	0.264	0.881	-0.356	0.052	-0.456	-0.115	-0.442	0.767	-0.257	1	0.887	-0.215	0.801	0.344	0.306	0.834	0.213
N-075	-0.097	-0.206	0.005	0.006	0.007	0.007	0.006	0.835	0.748	0.748	0.053	0.302	0.953	-0.431	-0.009	-0.474	-0.169	-0.529	0.882	-0.05	0.887	1	-0.257	0.915	0.443	0.224	0.863	0.316
N-079	-0.321	0.041	0.034	0.041	0.049	0.049	0.041	-0.302	-0.46	-0.46	0.863	0.656	-0.261	-0.058	-0.058	0.551	0.884	-0.066	-0.258	-0.046	-0.215	-0.257	1	-0.305	-0.411	0.74	-0.276	0.396
Ui	-0.063	-0.143	-0.061	-0.075	-0.088	-0.088	-0.075	0.95	0.595	0.595	-0.048	0.234	0.946	-0.503	0.105	-0.357	-0.261	-0.627	0.93	-0.014	0.801	0.915	-0.305	1	0.468	0.091	0.677	0.419
Ну	0.089	-0.123	-0.025	-0.03	-0.036	-0.036	-0.03	0.411	0.239	0.239	-0.381	-0.183	0.376	-0.015	0.416	-0.343	-0.497	-0.402	0.335	0.562	0.344	0.443	-0.411	0.468	1	-0.308	0.477	0.028
AMR	-0.431	-0.183	0.119	0.145	0.172	0.172	0.145	-0.07	0.169	0.169	0.96	0.884	0.26	-0.175	-0.086	0.161	0.88	-0.174	0.235	-0.081	0.306	0.224	0.74	0.091	-0.308	1	0.164	0.497
TPSA	-0.171	-0.273	0.023	0.028	0.033	0.033	0.028	0.603	0.716	0.716	-0.001	0.16	0.749	0.013	-0.039	-0.49	-0.232	-0.568	0.621	-0.081	0.834	0.863	-0.276	0.677	0.477	0.164	1	-0.029
k2	-0.086	0.112	0.009	0.011	0.013	0.013	0.011	0.336	-0.068	-0.068	0.51	0.661	0.351	-0.675	0.151	0.245	0.475	-0.246	0.382	0.093	0.213	0.316	0.396	0.419	0.028	0.497	-0.029	1

Comparison of the predicted vs experimental values for k_2 and $log(k_2)$ for other models considered



Figure S2. a) Predicted k_2 versus experimental k_2 for the reaction shown in Scheme 1 as analysed by MLR, and b) predicted $log(k_2)$ versus experimental $log(k_2)$ for the reaction shown in Scheme 1 as analysed by MLR. The training set is shown by the circles and the test set by the triangles.



Figure S3. a) Predicted k_2 versus experimental k_2 , and b) predicted $log(k_2)$ versus experimental $log(k_2)$ for the reaction shown in Scheme 1 as analysed by BRANNLP. The training set is shown by the circles and the test set by the triangles.

Analysis of MLREM model using 18 descriptors



Figure S4. MLREM coefficients for the 18 descriptors (intercept not included) used to assess the reaction shown in Scheme 1, using $log(k_2)$ as the output, averaged for the three training sets.

General experimental

Unless otherwise stated all chemicals were purified prior to use as according to standard protocols. Where water is mentioned Milli-Q[™] water was used unless otherwise stated. The terms 'under reduced pressure' and '*in vacuo*' refer to the use of a Heidolph 'Hei-vac precision' rotary evaporator connected to a Vacuubrand PC500 series pump unit and the use of a Schlenk line apparatus connected to an Edwards oil pump with a measured vacuum <0.2 mbar, respectively. The ionic liquids **1-5**, **9** and **12** were available within the research group, having been prepared previously,¹⁻⁵ as were the precursors 1-dodecyl-3-methylimidazolium bromide, 1,5-*bis*(3-methylimidazolium-1-yl)pentane dibromide and 1-butyl-1-methylpiperidinium bromide.^{2, 5, 6} The remaining precursors, tetraoctylammonium bromide and methyltrioctylammonium bromide, were commercially available.

Before use in the kinetic studies, all ionic liquids were dried *in vacuo* (< 0.3 mbar) at room temperature until a constant, sustained pressure was obtained unless otherwise stated. Under these conditions the water content of all the ionic liquids considered was < 300 ppm as measured by Karl-Fischer titrimetry. Ion chromatography showed that all the ionic liquids contained < 1% halide content.

NMR spectra for the characterisation of the synthesised ionic liquids and their precursor halides was conducted on a Bruker Avance III 400 (400 MHz, ¹H; 100 MHz, ¹³C{¹H}; 376 MHz, ¹⁹F) spectrometer. Multiplicities are reported as singlet (s), triplet (t), pentet (p), hextet (h), triplet of triplets (tt) and multiplet (m). ¹H NMR spectra used in the kinetic studies were conducted on either a Bruker Avance III 400 (400 MHz, ¹H), a Bruker Avance III 500 (500 MHz, ¹H) or a Bruker Avance III 600 (600 MHz, ¹H) spectrometer equipped with either a BBO, BBFO or TBI probe. The results were shown to be reproducible regardless of the NMR spectrometer and probe used.

The reaction mixtures for the kinetic studies were prepared under pseudo first order conditions such that they contained at least a 10-fold excess of pyridine (*ca.* 0.08 g, 0.5 mol L⁻¹) relative to benzyl bromide (< 0.017 g, 0.05 mol L⁻¹). All stock solutions for the kinetic studies were prepared in a 2 mL volumetric flask with addition of pyridine and the appropriate proportions of acetonitrile and the chosen ionic liquid to achieve the desired mole fraction of ionic liquid in the reaction mixture for the kinetic studies. Benzyl bromide (< 0.004 g) was weighed into an empty 5 mm NMR tube and 0.5 mL of the aforementioned stock solution was added to the NMR tube immediately before insertion in an NMR spectrometer for the *in situ* kinetic studies. The NMR spectrometer was calibrated to the desired temperature for the kinetic studies. Kinetic studies of the probe using a thermocouple in an ethanol solution. Kinetic studies did not commence until the desired temperature had been achieved and stabilised for at least 15 minutes

Reaction progress was monitored using ¹H NMR spectroscopy following depletion of the signal corresponding benzylic protons of benzyl bromide at approximately 4.0 ppm. The reactions were monitored until > 95% completion. The pseudo first order rate constants were obtained using Equation S1 and the software MestReNova and the second order rate constant was determined using Equation S2 in the LINEST function in Microsoft Excel. There were two exceptions, the first occurring for the ionic liquid [bmpi][PF₆] **11**, where reaction progress was monitored using ¹H NMR spectroscopy following formation of the signal corresponding to the benzylic protons of the product at approximately 5.6 ppm. In this instance Equation S3 and the three-parameter linear regression fit in MestReNova were used to determine the pseudofirst order rate constant and the second order rate constant was determined in the same manner as for the other ionic liquids using Equation S2. The other exception was for the ionic liquid [bmim][PF₆] **2** where initial rates methodology was employed to determine the rate constant of the reaction. In this instance reaction progress was monitored up to 10% completion and the bimolecular rate constant was determined using the slope of a graph of concentration *vs* time to determine the observed pseudo-first order rate constant. The second order rate constant was then determined using Equation S2.

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

Equation S1: Log form of the integrated first order rate equation; [A] = integral of benzyl bromide, k_{obs} = the pseudo first order rate constant and t = time.

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

Equation S2: 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 pyridine.

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

Equation S3: Exponential function used to determine the observed pseudo first order rate constant through monitoring product formation; [C] = the integral of the product, k_{obs} = the pseudo first order rate constant and t = time.

1-Dodecyl-3-methylimidazolium dicyanimide [ddmim][N(CN)₂] 6

Sodium dicyanimide (1.49 g, 1.67 mmol) was rinsed with dichloromethane (60 mL) into ⁶ [ddmim][N(CN)₂] Sodium dicyanimide (1.49 g, 1.67 mmol) was rinsed with dichloromethane (60 mL) into ^{1-dodecyl-3-methylimidazolium bromide (4.91 g, 1.45 mmol) and the mixture was stirred under ambient conditions for 1.5 h. The white solid was removed by gravity filtration, the dichloromethane was collected, concentrated under reduced pressure and the resultant colourless liquid was diluted with dichloromethane (30 mL) prior to storage at -18 °C for a minimum of 4 h. This process was repeated a further 9 times}

before the residual dichloromethane was removed from the recovered title compound *in vacuo* at 60 °C as a white solid (2.85 g, 0.844 mmol, 58%). m.p. 38-41 °C (lit.⁷ not reported). ¹H NMR (400 MHz, acetonitrile- d_3) δ 9.58 (s, 1H, -NC<u>H</u>N-), 7.64 (m, 2H, -N(C<u>H</u>)₂N-), 4.25 (t, 2H, J = 7.3 Hz, $-NC\underline{H}_2(CH_2)_{10}CH_3$), 3.93 (s, 3H, -N (CH₂)₁₁C<u>H</u>₃), 1.84 (m, 2H, -NCH₂C<u>H₂(CH₂)₉CH₃), 1.26 (m, 18H, -N(CH₂)₂(C<u>H₂)₉CH₃), 0.85 (m, 3H, -N(CH₂)₁₁C<u>H</u>₃). ¹³C{¹H} NMR (100 MHz, acetonitrile- d_3) δ 136.9 (-NCHN-), 123.6 (-NCHCHN-), 122.3 (-NCHCHN-), 49.3 (-NCH₃), 36.0 (-NCH₂(CH₂)₁₀CH₃), 31.7 (-NCH₂CH₂(CH₂)₉CH₃), 29.9 (-N(CH₂)₂CH₂(CH₂)₈CH₃), 29.4 (-N(CH₂)₃(CH₂)₂(CH₂)₆CH₃), 29.3 (-N(CH₂)₅CH₂(CH₂)₅CH₃), 29.2 (-N(CH₂)₆CH₂(CH₂)₄CH₃), 29.1 (-N(CH₂)₇CH₂(CH₂)₃CH₃), 28.8 (-N(CH₂)₈CH₂(CH₂)₂CH₃), 25.8 (-N(CH₂)₉CH₂CH₂CH₃), 22.4 (-N(CH₂)₁₀CH₃), 13.5 (-N(CH₂)₁₁CH₃).</u></u>

1,5-bis(3-Methylimidazolium-1-yl)pentane bis(trifluoromethanesulfonyl)imide [(mim)₂p][N(SO₂CF₃)₂] 7



7 [(mim)₂ p_e][N(SO₂CF₃)₂]

1,5-*bis*(3-Methylimidazolium-1-yl)pentane dibromide (3.41 g, 8.66 mmol) and lithium *bis*(trifluoromethanesulfonyl)imide (2.94 g, 10.2 mmol) were combined and dissolved in water (60 mL). The resultant reaction mixture was stirred for 16 h under ambient conditions. The aqueous reaction mixture was extracted with dichloromethane (3 x 50

mL), the organic extracts were collected and combined before being extracted with

water (10 x 100 mL) until a negative silver nitrate test result was achieved. Excess dichloromethane was removed under reduced pressure and then dried *in vacuo* at room temperature until a constant pressure reading was achieved. The resultant ionic liquid **7** was obtained as a pale yellow highly viscous liquid (3.33 g, 4.20 mmol, 96%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.08 (s, 2H, (-NC<u>H</u>N-)₂), 7.73 (m, 4H, (-N(C<u>H</u>)₂N-)₂), 4.16 (t, 4H, *J* = 7.3 Hz, -NC<u>H</u>₂(CH₂)₃C<u>H</u>₂N-), 3.85 (s, 6H, -NC<u>H</u>₃), 1.82 (p, 4H, *J* = 7.4 Hz, -NCH₂CH₂CH₂CH₂CH₂N-), 1.23 (m, 2H, -N(CH₂)₂C<u>H</u>₂(CH₂)₂N-). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆) δ 136.5 (-NCHN-), 124.0 (-NCHCHN-), 122.6 (-NCHCHN-), 49.2 (-NCH₃), 35.8 (-NCH₂(CH₂)₃CH₂N-), 29.3 (-NCH₂CH₂CH₂CH₂N-), 22.5 (-N(CH₂)₂CH₂(CH₂)₂N-. ¹⁹F NMR (376 MHz, acetone-*d*₆) δ 79.9 (-C<u>F</u>₃).

1,10-bis(3-Methylimidazolium-1-yl)decane tetrafluoroborate [(mim)2d][BF4]28



Sodium tetrafluoroborate (2.06 g, 18.8 mmol) was rinsed with water (85 mL) into a solution of 1,10-*bis*(3-methylimidazolium-1-yl)decane dibromide (3.71 g, 8.82 mmol) in water (15 mL). The aqueous reaction was stirred for 4 h before extraction with dichloromethane (5 x 100 mL) until a negative silver nitrate test was confirmed. The dichloromethane was removed under reduced

8 [(mim)₂d][N(SO₂CF₃)₂]₂

combined and back extracted first with dichloromethane (3 x 150 mL) and then ethyl acetate (3 x 150 mL). Concentration of these organic phases only marginally improved the yield of the recovered ionic liquid. The water from the water washings was then concentrated under reduced pressure and the resulting oil was triturated with acetonitrile (50 mL), then allowed to sit. The resulting white solid was filtered off and the filtrate was combined with the recovered ionic liquid from previous. The remaining acetonitrile was removed *in vacuo* to give the title ionic liquid as a pale yellow, highly viscous oil (3.62 g, 8.33 mmol, 94%). ¹H NMR (400 MHz, acetone- d_6) δ 9.07 (s, 2H, (-NC<u>H</u>N-)₂), 7.75 (m, 4H, (-N(C<u>H</u>₂)₂N-)₂), 4.35 (t, 4H, J = 7.2 Hz, -NC<u>H₂(CH₂)₈CH₂N-), 4.05 (s, 6H, -NC<u>H₃</u>), 1.95 (m, 4H, -NCH₂C<u>H₂(CH₂)₆CH₂CH₂N-), 1.33 (m, 12H, -N(CH₂)₂(C<u>H₂)₆(CH₂)₂N-). ¹³C{¹H} NMR (100 MHz, acetone- d_6) δ 136.7 (-NC<u>H</u>N-), 124.0 (-NC<u>H</u>CHN-), 122.4 (-NCHC<u>H</u>N-), 49.5 (-NC<u>H₃</u>), 35.6 (-NC<u>H₂(CH₂)₈CH₂N-), 29.8 (-NCH₂CH₂(CH₂)₆CH₂CH₂)-(CH₂)₄CH₂)CH₂(CH₂)₄CH₂)-N-), 29.8 (-NCH₂C₂H₂(CH₂)-N-), 28.8 (-N(CH₂)₂CH₂(CH₂)₄CH₂)-N-), 28.5 (-N(CH₂)₃CH₂(CH₂)₃N-), 25.7 (-N(CH₂)₄(CH₂)₂(CH₂)₄N-). ¹⁹F NMR (376 MHz, acetone- d_6) δ -151.4 (^BE₄).</u></u></u></u>

1-Butyl-1-methylpiperidinium chloride [bmpi]Cl S37



1-Chlorobutane (5.86 g, 63.3 mmol) and 1-methylpiperidine (5.18 g, 52.2 mmol) were combined and stirred in acetonitrile (20 mL) at 50 °C under nitrogen for 3 weeks during which time the reaction mixture became progressively more yellow in colouration. Any excess volatile organic components were removed from the

reaction mixture under reduced pressure and the resulting yellow solid was titrated with ethyl acetate (5 x 70 mL). The yellow solid was then dried *in vacuo* to give the title compound (10.7 g, 55.8 mmol, 88%) which was used without further purification. ¹H NMR (400 MHz, DMSO- d_6) δ 3.29 (m, 6H, CH₂(CH₂)₂(CH₂)₂NCH₂-), 2.98 (s, 3H, -NCH₃), 1.78 (m, 4H, CH₂(CH₂)₂(CH₂)₂N-), 1.64 (m, 2H, CH₂(CH₂)₄N-), 1.54 (m, 2H, -NCH₂CH₂-), 1.33 (h, 2H, *J* = 7.5 Hz, -N(CH₂)₂CH₂-), 0.95 (t, 3H, *J* = 7.4 Hz, -N(CH₂)₃CH₃).

1-Butyl-1-methylpiperidinium tetrafluoroborate [bmpi][BF₄] 10



10 [bmpi][BF₄]

1-Butyl-1-methylpiperidinium chloride (6.65 g, 3.47 mmol) and sodium tetrafluoroborate (10.6 g, 9.65 mmol) were combined and dissolved together in dichloromethane (60 mL) with the resultant reaction mixture being stirred together under ambient conditions for 18 h. The solid formed during this time removed by gravity filtration and the filtrate was collected and concentrated. The

resultant yellow solid was redissolved in dichloromethane (50 mL) and stored at -18 °C for a minimum of 4 h before the process was repeated a further 10 times. One the last repeat the dichloromethane was removed *in vacuo* until a constant pressure reading was obtained resulting in a yellow solid (6.60 g, 2.38 mmol, 68%). m.p. 138–142 °C (lit.⁸ not reported).

¹H NMR (400 MHz, acetonitrile-*d*₃) δ 3.26 (m, 6H, CH₂(CH₂)₂(CH₂)₂NCH₂-), 2.96 (s, 3H, -NCH₃), 1.85 (m, 4H, CH₂(CH₂)₂(CH₂)₂(CH₂)₂N-), 1.67 (m, 4H, CH₂(CH₂)₄NCH₂-), 1.39 (h, 2H, *J* = 7.5 Hz, -N(CH₂)₂CH₂-), 0.99 (t, 3H, *J* = 7.4 Hz, -N(CH₂)₃CH₃). ¹³C{¹H} NMR (100 MHz, acetonitrile-*d*₃) δ 63.3 (CH₂(CH₂)₂(CH₂)₂N-), 60.9 (-NCH₂(CH₂)₂CH₃), 47.7 (-NCH₃), 23.3 (CH₂(CH₂)₂(CH₂)₂(CH₂)₂N-), 20.6 (-NCH₂CH₂CH₂CH₃), 19.5 (CH₂(CH₂)₂(CH₂)₂N-), 19.4 (-N(CH₂)₂CH₂CH₃), 12.8 (-N(CH₂)₃CH₃). ¹⁹F NMR (376 MHz, acetonitrile-*d*₃) δ -151.5 (⁻BF₄).

1-Butyl-1-methylpiperidinium hexafluorophosphate [bmpi][PF₆] 11



11 [bmpi][PF₆]

Potassium hexafluorophosphate (4.61 g, 25.0 mmol) was rinsed with water (80 mL) into a solution of 1-butyl-1-methylpiperidinium bromide (5.73 g, 24.3 mmol) in water (20 mL). The reaction mixture was stirred under ambient conditions for 18 h before extraction with dichloromethane (3 x 70 mL). The organic layers were combined and extracted with water (8 x 100 mL). The organic

layer was concentrated under reduced pressure and dried *in vacuo* until a constant pressure reading was observed yielding the title compound as a white powder (2.35 g, 7.76 mmol, 32%). m.p. 71-73 °C (lit.⁷ not reported), ¹H NMR (400 MHz, acetone- d_6) δ 3.59 (m, 6H, CH₂(CH₂)₂(CH₂)₂NCH₂-), 3.29 (s, 3H, -NCH₃), 2.02 (m, 4H, CH₂(CH₂)₂(CH₂)₂N-), 1.91 (m, 2H, CH₂(CH₂)₄N-), 1.76 (m, 2H, -NCH₂CH₂-), 1.46 (h, 2H, *J* = 7.5 Hz, -N(CH₂)₂CH₂-), 1.01 (t, 3H, *J* = 7.4 Hz, -N(CH₂)₃CH₃). ¹³C{¹H} NMR (100 MHz, acetone- d_6) δ 63.3 (CH₂(CH₂)₂(CH₂)₂N-), 61.1 (-NCH₂(CH₂)₂CH₃), 47.7 (-NCH₃), 23.3 (CH₂(CH₂)₂(CH₂)₂N-), 20.7 (-NCH₂CH₂CH₂CH₂CH₃), 19.6 (CH₂(CH₂)₂(CH₂)₂N-), 19.4 (-N(CH₂)₂CH₂CH₃), 12.8 (-N(CH₂)₃CH₃) ¹⁹F NMR (376 MHz, acetone- d_6) δ -71.7 (d, 3F, ⁻PE₆), -73.5 (d, 3F, ⁻PF₆).

1-Butylpyridinium chloride [bpy]Cl S38

1-Butylpyridinium dicyanimide [bpyr][N(CN)₂] 13



Sodium dicyanimide (1.01 g, 11.2 mmol) was rinsed with dichloromethane (25 mL) into a solution of 1-butylpyridinium chloride (1.56 g, 9.10 mmol) in dichloromethane (25 mL). The resultant reaction mixture was stirred under ambient conditions for 1.5 h. The reaction mixture was filtered to remove 13 [bpy][N(CN)2] the white solid, the dichloromethane filtrate was collected, concentrated under reduced pressure and the resulting liquid was diluted by dichloromethane (30 mL) and stored at -18 °C for a minimum of 4 h. This process was repeated a further 9 times before the dichloromethane was removed in vacuo at 50 °C until a constant pressure reading was obtained, giving the title compounds as a light beige, non-viscous liquid (1.26 g, 6.23 mmol, 69%). ¹H NMR (400 MHz, DMSO- d_6) δ 8.89 (m, 2H, CH(CH)₂(CH)₂N-), 8.56 (m, 1H, CH(CH)₂(CH)₂N-), 8.07 (t, 2H, J = 6.9 Hz, CH(CH)₂(CH)₂N-), 4.60 (t, 2H, J = 4.6 Hz, $-NCH_2(CH_2)_2CH_3$, 1.95 (m, 2H, $-NCH_2CH_2CH_2CH_3$), 1.35 (h, 2H, J = 7.4 Hz, $-N(CH_2)_2CH_2CH_3$), 0.92 (t, 3H, J = 7.4 Hz, $-N(CH_2)_2CH_3$), 0.92 (t, 3H, $-N(CH_2)_2CH_3$), 0.92 (t, 3H, -N(CH_2)_2CH_3), 0.92 (t, 3H, -N(CH_2)_2CH_3), 0 7.4 Hz, -N(CH₂)₃CH₃). ¹³C{¹H} NMR (100 MHz, acetone-d₆) δ 145.8 (CH(CH)₂(CH)₂N-), 144.6 (CH(CH)₂(CH)₂N-), 128.5 (CH(<u>C</u>H)₂(CH)₂N-), 119.7 (⁻N(<u>C</u>N)₂), 117.7 (<u>C</u>H(CH)₂(CH)₂N-), 61.5 (-N<u>C</u>H₂(CH₂)₂CH₃), 33.0 (-NCH₂<u>C</u>H₂CH₂CH₂CH₃), 19.0 $(-N(CH_2)_2CH_2CH_3), 13.0 (-N(CH_2)_3CH_3).$

4-Butyl-4-methylmorpholinium chloride [bmmo]Cl S39



1-Chlorobutane (17.97 g, 194 mmol) and 4-methylmorpholine (10.78 g, 107 mmol) were combined and stirred in acetonitrile (50 mL) at 50 °C under nitrogen for 3 weeks. Any excess volatile organic components were removed from the reaction mixture under reduced pressure and the tan residue was recrystallised from ethyl acetate / acetonitrile (1:1). The resulting solid was triturated with ethyl acetate (3 x 100 mL)

and dried in vacuo to give the title chloride as an off-white solid (19.2 g, 99.1 mmol, 93%). that was used without further purification. m.p. 188-190 °C (lit.⁷ not reported). ¹H NMR (400 MHz, acetonitrile- d_3) δ 3.93(m, 4H, -CH₂OCH₂-), 3.42 (m, 6H, -CH₂NCH₂-, -NCH₂(CH₂)₂CH₃), 3.12 (s, 3H, -NCH₃), 1.70 (m, 2H, -NCH₂CH₂CH₂CH₂CH₃), 1.38 (m, 2H, -N(CH₂)₂CH₃CH₃), 0.98 $(t, 3H, J= 7.4 Hz, -N(CH_2)_3CH_3).$

4-Butyl-4-methylmorpholinium dicyanimide [bmmo][N(CN)₂] 14



14 [bmmo][N(CN)₂]

Sodium dicyanimide (4.10 g, 46.1 mmol) was dissolved in dichloromethane (20 mL) and added to a solution of 4-butyl-4-methylmorpholinium chloride (8.67 g, 44.8 mmol) in dichloromethane (20 mL). This reaction mixture was stirred under ambient conditions for 27 h after which the white

solid formed was removed by gravity filtration resulting in a colourless liquid. This liquid was concentrated under reduced pressure resultant white solid was redissolved in dichloromethane (30 mL) before being stored at -18 °C for a minimum of 6 h. This process was repeated a further 9 times before the white solid was dried in vacuo at 50 °C until a constant pressure reading was obtained for the title compound (5.44 g, 24.3 mmol, 54%). m.p. 184-190 °C (lit.⁷ not reported °C). ¹H NMR (400 MHz, acetone-*d*₃) δ 4.13 (m, 4H, -C<u>H</u>₂OC<u>H</u>₂-), 3.80 (m, 2H, -NC<u>H</u>₂(CH₂)₂CH₃), 3.75 (m, 4H, -CH₂NCH₂-), 3.48 (s, 3H, -NCH₃), 1.94 (m, 2H, -NCH₂CH₂CH₂CH₂CH₃), 1.48 (h, 2H, J = 7.4 Hz, -N(CH₂)₂CH₂CH₃), 1.02

(t, 3H, J= 7.4 Hz, -N(CH₂)₃CH₃). ¹³C{¹H} NMR (100 MHz, acetone- d_3) δ 60.4 (-<u>C</u>H₂O<u>C</u>H₂-), 59.9 (-<u>C</u>H₂N<u>C</u>H₂-), 46.7 (-N(<u>C</u>N)₂), 23.3 (-N<u>C</u>H₃), 19.5 (-N(<u>C</u>H₂)₃CH₃), 13.1 (-N(CH₂)₃CH₃).

4-Butyl-4-methylmorpholinium hexafluorophosphate [bmmo][PF₆] 15



15 [bmmo][PF₆]

Potassium hexafluorophosphate (3.34 g, 18.1 mmol) was dissolved in water (35 mL) and added to a solution of 4-butyl-4-methylmorpholinium chloride (3.61 g, 16.5 mmol) in water (6 mL). Additional water (30 mL) and dichloromethane (50 mL) were added to this reaction mixture before it was stirred under ambient conditions for 18 h. The aqueous layer was extracted with

dichloromethane (3 x 50 mL) and the organic extracts were combined and washed with water (8 x 200 mL). The combined water washings were then concentrated under reduced pressure (200 mL) and were extracted with dichloromethane (4 x 200 mL). All dichloromethane washings were combined, concentrated under reduced pressure and then dried *in vacuo* at 50 °C until a constant pressure reading was noted to give the title compound as a white solid (1.23 g, 4.05 mmol, 25%). m.p. 187-190 °C (lit.¹⁰ not reported). ¹H NMR (400 MHz, acetone-*d*₆) δ 4.12 (m, 4H, -CH₂OCH₂-), 3.68 (m, 6H, O(CH₂)₂(CH₂)₂NCH₂-), 3.42 (s, 3H, -NCH₃), 1.94 (m, 2H, -NCH₂CH₂CH₂CH₃), 1.47 (h, 2H, *J* = 7.4 Hz, -N(CH₂)₂CH₂CH₃), 1.01 (t, 3H, *J* = 7.4 Hz, -N(CH₂)₃CH₃). ¹³C{¹H} NMR (100 MHz, acetone-*d*₆) δ 60.4 (-CH₂OCH₂-), 59.9 (-CH₂NCH₂-), 23.2 (-NCH₃), 19.4 (-N(CH₂)₃CH₃), 13.0 (-N(CH₂)₃CH₃) ¹⁹F NMR (376 MHz, acetone-*d*₆). δ -71.5 (d, 3F, PF₆), -73.3 (d, 3F, PF₆).

Tetraoctylammonium tetrafluoroborate [TOA][BF₄] 16



Sodium tetrafluoroborate (1.44 g, 13.1 mmol) was rinsed with dichloromethane (13 mL) into tetraoctylammonium bromide (6.92 g, 12.7 mmol). The resultant reaction mixture was stirred under ambient conditions for 24 h. During this time a solid formed, which was removed by gravity filtration. The filtrate was collected, concentrated under reduced pressure and the

resulting white solid was redissolved in dichloromethane (30 mL) prior to storage at -18 °C for a minimum of 6 h. This process was repeated twice. The organic mixture was then extracted with water (7 x 25 mL) until a negative silver nitrate test was observed. The water extracts were combined and back-extracted with dichloromethane (3 x 100 mL). All organic extracts were then combined, concentrated under reduced pressure and then dried *in vacuo* until a constant pressure reading was noted yielding the title compound as a white solid (4.14 g, 7.48 mmol, 59%). m.p. 117-120 °C (lit.¹¹ 122-125 °C) ¹H NMR (400 MHz, acetone- d_6) δ 3.49 (m, 8H, N(CH₂(CH₂)₆CH₃)₄), 1.88 (m, 8H, N(CH₂CH₂(CH₂)₅CH₃)₄), 1.37 (m, 40H, N(CH₂)₂(CH₂)₅CH₃)₄), 0.89 (m, 12H, N((CH₂)₇CH₃)₄) ¹³C{¹H} NMR (100 MHz, acetone- d_6) δ 58.5 (N(CH₂(CH₂)₆CH₃)₄), 31.4 (N(CH₂)₂CH₂(CH₂)₅CH₃)₄), 28.7 (N((CH₂)₂CH₂(CH₂)₄CH₃)₄), 28.6 (N((CH₂)₃CH₂(CH₂)₃CH₃)₄), 25.8 (N((CH₂)₄CH₂(CH₂)₂CH₃)₄), 22.4 (N((CH₂)₅CH₃)₄), 21.3 (N(CH₂)₆CH₂CH₃)₄), 13.4 (N(CH₂)₇CH₃) ¹⁹F NMR (376 MHz, acetone- d_6) δ -151.8 (⁻BE₄).

Methyltrioctylammonium hexafluorophosphate [mTOA][PF₆] 17



17 [mTOA][PF₆]

Potassium hexafluorophosphate (1.90 g, 10.3 mmol) was rinsed into methyltrioctylammonium bromide (4.03 g, 8.99 mmol) with water (100 mL) and the resulting reaction mixture was stirred under ambient conditions for 16 h. The aqueous reaction mixture was washed with dichloromethane ($3 \times 100 \text{ mL}$) and the organic extracts were collected and combined. The organic

extracts were extracted with water (8 x 200 mL) until a negative silver nitrate test was observed. The dichloromethane was removed under reduced pressure and then *in vacuo* at 50 °C until a constant pressure reading was obtained. The resulting ionic liquid was obtained as a beige solid (4.32 g, 7.80 mmol, 87%). m.p. 74 °C (lit.⁷ not reported). ¹H NMR (400 MHz, DMSO-*d*₆) δ 3.18 (m, 6H, -N(CH₂(CH₂)₆CH₃)₃), 2.93 (s, 3H, -NCH₃), 1.61 (m, 6H, -N(CH₂CH₂(CH₂)₅CH₃)₃), 1.29 (m, 30H, -N(CH₂CH₂(CH₂)₅CH₃)₃). ¹³C{¹H} NMR (100 MHz, DMSO-*d*₆) δ 61.0 (-NCH₃), 48.0 (-NCH₂(CH₂)₆CH₃), 31.7 (-NCH₂CH₂(CH₂)₅CH₃), 28.9 (-N(CH₂)₂CH₂(CH₂)₄CH₃), 28.8 (-N(CH₂)₃CH₂(CH₂)₃CH₃), 26.2 (-N(CH₂)₄CH₂(CH₂)₂CH₃), 22.5(-N(CH₂)₅CH₃), 21.8 (-N(CH₂)₆CH₂CH₃), 14.4 (-N(CH₂)₇CH₃). ¹⁹F NMR (377 MHz, acetone-*d*₃) δ -71.6 (d, 3F), -73.4 (d, 3F).

Stock solution composition

Ionic liquid	Mass ionic liquid / g	Mass acetonitrile / g	Mass pyridine / g	[pyridine] / mol L ⁻¹	ℋ℩ւ
[bmim][N(CN) ₂] 1	1.87	0.121	0.0818	0.517	0.69
[bmim][PF ₆] 2	1.40	0.696	0.0802	0.507	0.21
[bm ₂ im][BF ₄] 3	1.68	0.391	0.0799	0.505	0.40
[b45Cl ₂ mim][N(SO ₂ CF ₃) ₂] 4	2.17	0.407	0.0797	0.504	0.29
[h _x mim][N(SO ₂ CF ₃) ₂] 5	1.61	0.538	0.0796	0.503	0.19
[ddmim][N(CN) ₂] 6	1.69	0.256	0.0808	0.511	0.42
[(mim) ₂ p _e][N(SO ₂ CF ₃) ₂] ₂ 7	1.69	0.657	0.0816	0.516	0.11
[(mim) ₂ p _e][BF ₄] ₂ 8	2.20	0.138	0.0810	0.512	0.51
[bmtr][N(SO ₂ CF ₃) ₂] 9	1.30	0.811	0.0823	0.520	0.21
[bmtr][N(SO ₂ CF ₃) ₂] 9	2.68	0.059	0.0861	0.544	0.71
[bmpi][BF ₄] 10	1.39	0.550	0.0877	0.554	0.28
[bmpi][PF ₆] 11	0.85	0.991	0.0814	0.515	0.10
[bmpyr][PF ₆] 12	2.20	0.258	0.0794	0.502	0.50
[bpy][N(CN) ₂] 13	0.76	0.946	0.0803	0.508	0.13
[bmmo][N(CN) ₂] 14	0.75	1.08	0.0887	0.561	0.11
[bmmo][N(CN) ₂] 14	0.73	1.01	0.0812	0.513	0.11
[Bmmo][PF ₆] 15	1.05	0.922	0.0807	0.510	0.12
[TOA][BF ₄] 16	1.02	0.595	0.0800	0.506	0.11
[TOA][BF ₄] 16	1.01	0.673	0.0816	0.516	0.10
[mTOA][PF ₆] 17	1.71	0.131	0.0826	0.522	0.42

Table S5. Composition of stock solutions by mass, including resultant mole fraction and concentration of the pyridine, for the kinetic studies of the reaction between pyridine and benzyl bromide in mixtures of acetonitrile and an ionic liquid.

Rate constant data

Table S6. Rate constants determined for the kinetic studies for the reaction between pyridine and benzyl bromide in mixtures of acetonitrile and an ionic liquid. Also included are the corresponding mole fractions, temperatures and concentrations of pyridine. Errors are reported as the standard deviation of at least three replicates.

Ionic liquid	ХIL	Temperature / K	[pyridine] / mol L ⁻¹	<i>k</i> _{obs} / 10 ⁻⁴ s ⁻¹	<i>k</i> ₂ / 10 ⁻⁴ L mol ⁻¹ s ⁻¹	Average <i>k</i> 2 / 10 ⁻⁴ L mol ⁻¹ s ⁻¹
[bmim][N(CN) ₂] 1	0.69	260	0.517	0.630	1.22	1.27 (0.05)
				0.684	1.32	()
				0.660	1.28	
[bmim][PF ₆] 2	0.21	260	0.507	0.328	0.648	0.67 (0.05)
[][6] =	0.22		0.007	0.322	0.634	
				0.364	0.719	
[bm2im][BF4] 3	0.38	290	0.505	7.19	14.2	14.7 (0.5)
				7.39	14.6	()
				7.67	15.2	
$[b45Cl_{2}mim][N(SO_{2}CE_{2})_{2}]$	0.29	330	0.504	40.8	81.0	100 (20)
	0.20		0.001	55.1	109	200 (20)
				59.3	118	
$[h_mim][N(SO_2CE_2)_2]$ 5	0 19	280	0 503	1 35	2 69	2 70(0 08)
	0.15	200	0.000	1 40	2 78	2.7 0(0.00)
				1 32	2.62	
[ddmim][N(CN)] 6	0.42	290	0 511	3.76	7 37	8 2 (1 2)
	0.42	250	0.511	4 92	9.63	0.2 (1.2)
				3 93	7.69	
[(mim) n][N(SO_CE_)] 7	0 11	300	0.516	11 /	7.05	21.6 (0.3)
	0.11	300	0.510	11.4	22.0	21.0 (0.3)
				11.0	21.4	
	0.51	200	0 512	24.0	46.0	19 (7)
	0.51	500	0.312	24.0	40.9	40 (2)
				25.0	40.4 E0.1	
	0.21	210	0.520	25.7	22.4	24 2 (1 2)
$[BIIIII][N(SO_2CF_3)_2]$	0.21	310	0.520	17.4	33.4 25.9	34.3 (1.3)
				10.0	22.0 22.0	
	0.71	210	0 5 4 4	20.2	53.9	F1 (2)
$[\text{DITIT}][N(SO_2CF_3)_2]$	0.71	310	0.544	28.3	52.1	51 (3)
				29.1	53.5	
	0.20	200	0.554	20.0	47.7	C 2F (0.01)
	0.28	280	0.554	3.52	0.30	6.35 (0.01)
				3.51	0.33	
	0.10	200	0.545	3.52	0.35	22 (2)
	0.10	300	0.515	12.8	24.9	22 (3)
				10.3	20.1	
[has as w1[D5 1] 42	0.50	200	0.502	2.00	21.5	C 2 (0 2)
	0.50	280	0.502	3.09	6.15	6.3 (0.3)
				3.05	6.07	
	0.42	270	0.500	3.282	6.54	2.0.(0.2)
$[DPY][N(CN)_2]$ 13	0.13	270	0.508	1.16	2.28	2.0 (0.2)
				0.944	1.86	
	0.14	220	0.564	1.08	1.99	24(7)
$[\text{bmmo}][N(CN)_2]$ 14	0.11	320	0.561	11.3	20.1	24 (7)
	0.44	220	0.542	10.3	18.3	-
	0.11	320	0.513	19.7	38.283	
[Deces 2105.145	0.42	200	0.540	9.83	19.148	14.0 (0.0)
[BWW0][64] 12	0.13	290	0.510	7.14 C.C.7	13.999	14.0 (0.9)
				0.6/	13.077	
	0.11	220	0.500	/.5/	14.846	2 4 2 (2 1)
[IOA][BF ₄] 16	0.11	320	0.506	1.39	2.75	3.18 (0.4)
				1.70	3.36	
				1.74	3.44	

[TOA][BF ₄] 16	0.10	330	0.516	3.83	7.42	6.97 (0.4)
				3.46	6.72	
				3.50	6.78	
[mTOA][PF ₆] 1	7 0.42	310	0.522	9.58	18.3	17.9 (0.5)
				9.36	17.9	
				9.08	17.4	

Comparison of rate constant data with predictions

Table S7. Comparison between the rate constants for the new data in Table S5 and the predicted data from the MLREM and BRANNLP models, using predicted data from $log(k_2)$ models.

Ionic liquid	XIL	Temperature / K	k ₂ / 10 ⁻⁴ L mol ⁻¹ s ⁻¹	MLREM k ₂ / 10 ⁻⁴ L mol ⁻¹ s ⁻¹	BANNLP <i>k</i> ₂ / 10 ⁻⁴ L mol ⁻¹ s ⁻¹	% diff MLREM	%diff BRANNLP
[bmim][N(CN) ₂] 1	0.69	260	1.27 (0.05)	1.40	1.67	-10.2	-31.5
[bmim][PF ₆] 2	0.21	260	0.67 (0.05)	0.48	0.839	28.1	-25.8
[bm ₂ im][BF ₄] 3	0.40	290	14.7 (0.5)	8.48	12.87	42.3	12.4
[b45Cl ₂ mim][N(SO ₂ CF ₃) ₂] 4	0.29	330	100 (20)	103.54	96.16	-0.9	6.3
[h _x mim][N(SO ₂ CF ₃) ₂] 5	0.19	280	2.70(0.08)	2.44	2.17	9.5	19.5
[ddmim][N(CN) ₂] 6	0.42	290	8.2 (1.2)	11.68	16.69	-41.9	-102.8
[(mim) ₂ p _e][N(SO ₂ CF ₃) ₂] ₂ 7	0.11	300	21.6 (0.3)	22.44	20.72	-3.8	4.1
[(mim) ₂ p _e][BF ₄] ₂ 8	0.51	300	48 (2)	33.8	42.14	29.3	11.9
[bmtr][N(SO ₂ CF ₃) ₂] 9	0.21	310	34.3 (1.3)	39.87	42.55	-16.0	-23.8
[bmtr][N(SO ₂ CF ₃) ₂] 9	0.71	310	51 (3)	53.01	56.87	-3.8	-11.3
[bmpi][BF ₄] 10	0.28	280	6.35 (0.01)	5.44	6.91	14.3	-8.8
[bmpi][PF ₆] 11	0.10	300	22 (3)	15.09	27.42	31.9	-23.8
[bmpyr][PF ₆] 12	0.50	280	6.3 (0.3)	4.96	6.53	20.7	-4.4
[bpy][N(CN) ₂] 13	0.13	270	2.0 (0.2)	3.34	4.33	-63.6	-112.4
[bmmo][N(CN) ₂] 14	0.11	320	24 (7)	263.24	170.43	-998.2	-611.1
[Bmmo][PF ₆] 15	0.12	290	14.0 (0.9)	13.98	25.2	-0.1	-80.3
[TOA][BF ₄] 16	0.11	320	3.18 (0.4)	16.03	29.16	-403.6	-816.1
[TOA][BF ₄] 16	0.10	330	6.97 (0.4)	30.06	51.49	-331.1	-638.4
[mTOA][PF ₆] 17	0.42	310	17.9 (0.5)	12.37	10.41	30.8	41.8

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