Supplementary Information to accompany

Is it possible to control kinetic rates of radical polymerisation in ionic liquids?

Kaycee Low, Luke Wylie, David Scarbourough, Ekaterina I. Izgorodina

Contents

1 Figure S1

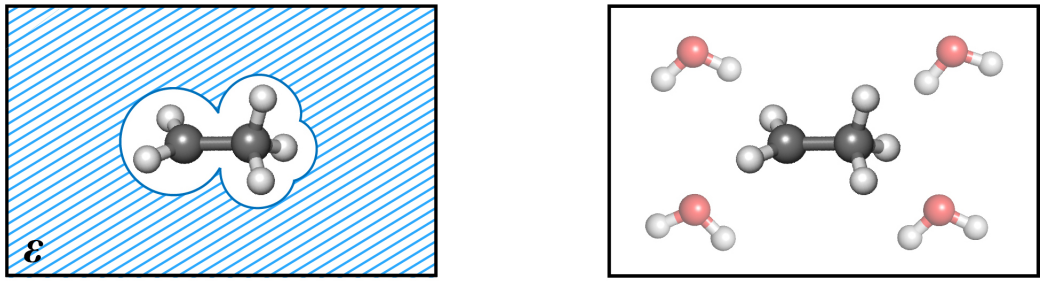


Figure 1 Comparison of implicit and explicit solvent models as used in this study: CPCM solvation (left) and explicit solvation (right) for the ethyl radical in water.

2 Figure S2

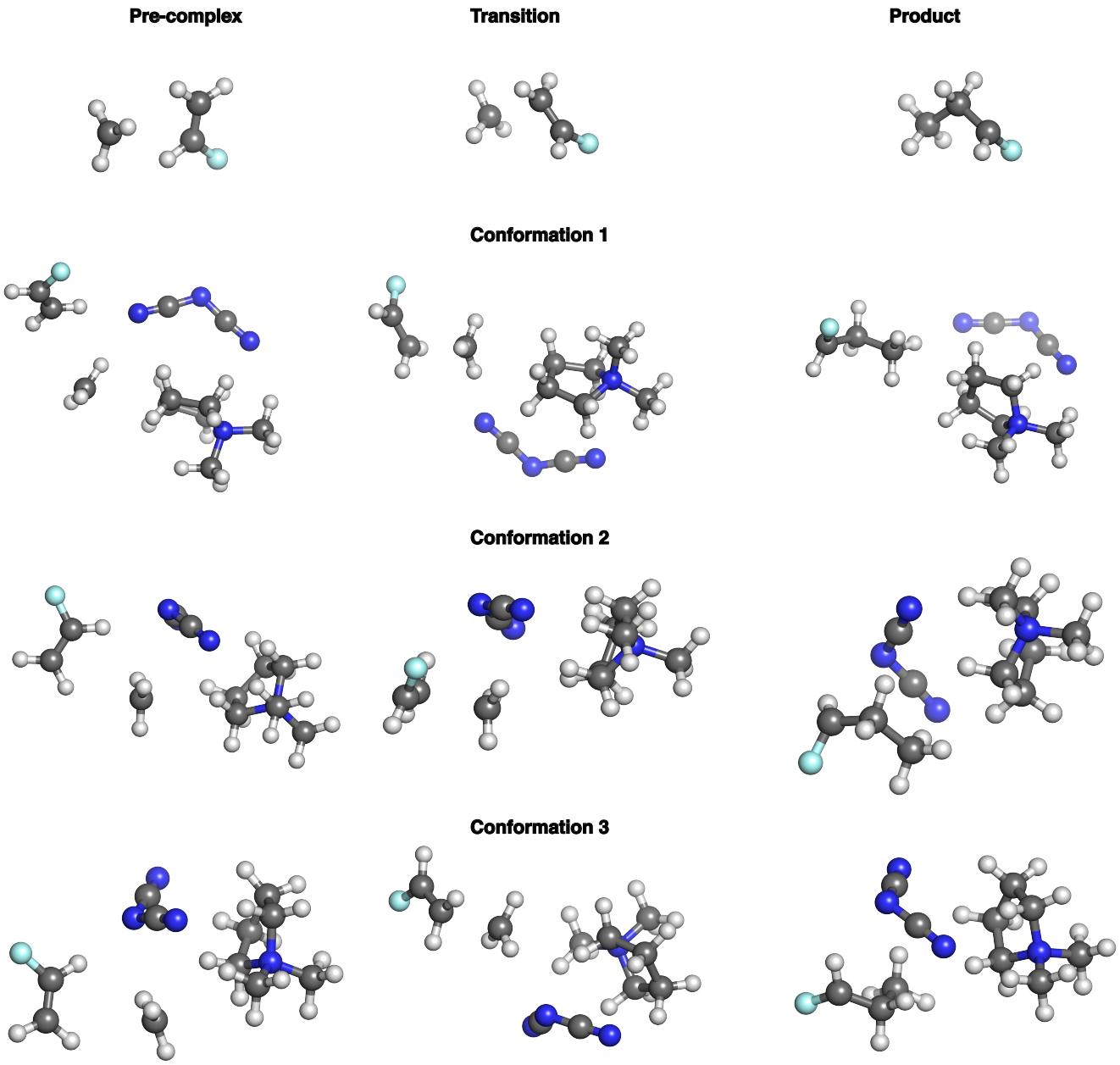
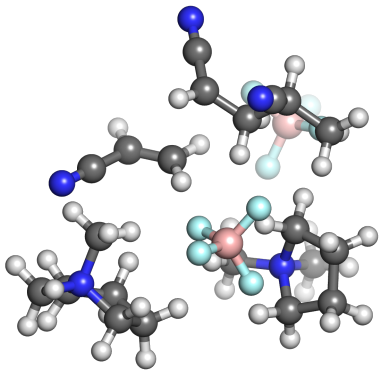
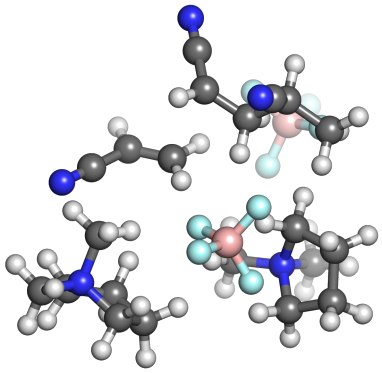


Figure 2 Different conformations of the pre-complex, transition state, and product forms for the methyl radical addition to CH_2=CHF.

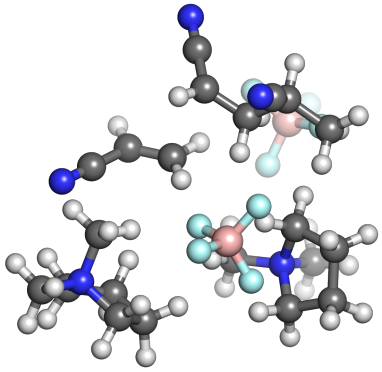
3 Figure S3



(a) Pre-complex



(b) Propagation transition state



(c) Polymer trimer

Figure 3 Method used to locate transition states structures for radical propagation studies: first, a three-monomer polymer was optimised. Bond length was extended to locate a transition state, and then a pre-complex was constructed. The propagation of acrylonitrile is shown in 2 ion pairs of $[C_1mpyr][BF_4]$.

4 Figures S4 and S5

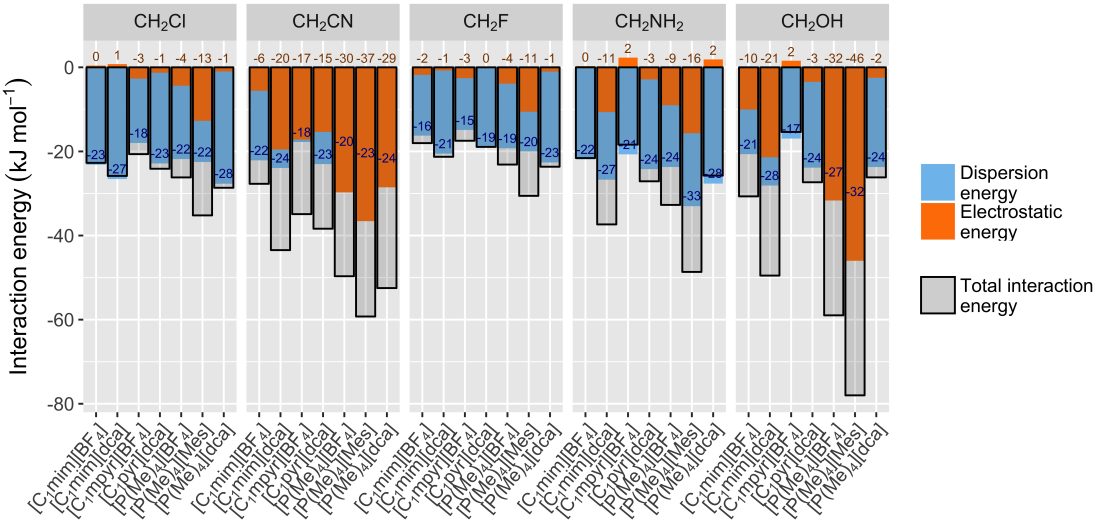


Figure 4 Average interaction energies (in $\mathrm{kJ\,mol^{-1}}$) across all system conformations for model radical interaction with 1 ion pair of ionic liquid. Contributions from dispersion forces are shown in blue, contributions from electrostatic forces in orange.

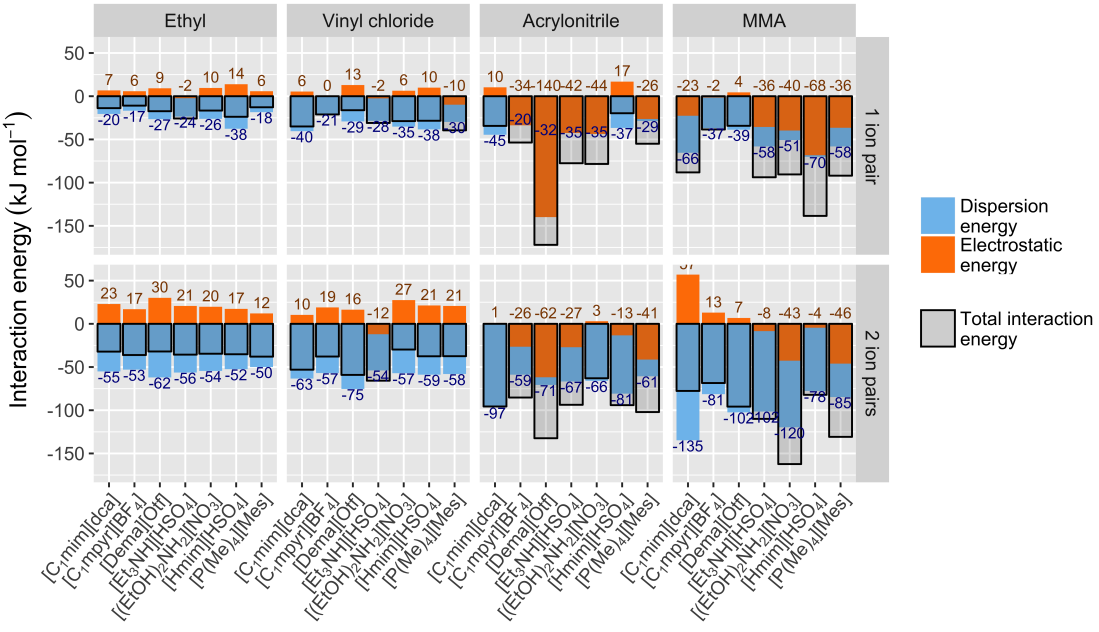


Figure 5 Average interaction energies (in $\mathrm{kJ\,mol^{-1}}$) across all system conformations for propagating radical interaction with 1 ion pair of ionic liquid. Contributions from dispersion forces are shown in blue, contributions from electrostatic forces in orange.

5 Figure S6

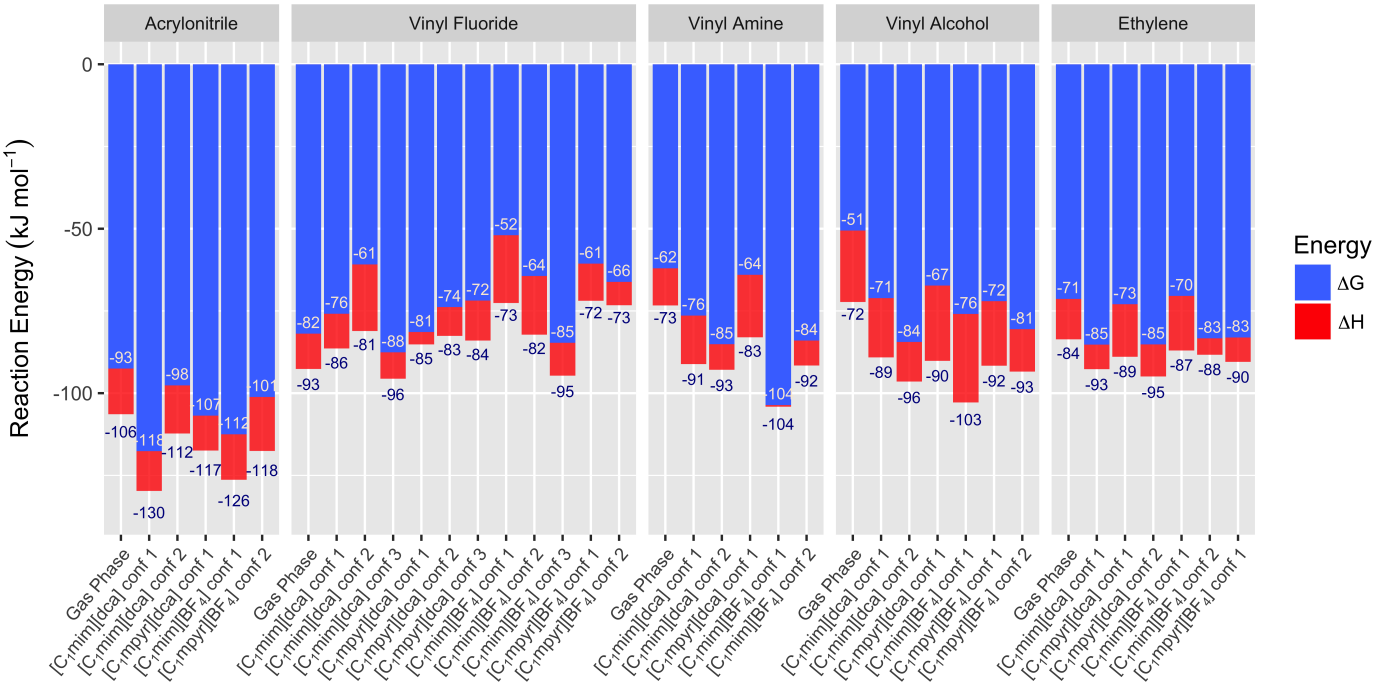


Figure 6 Reaction energies, ΔH and ΔG, in $\mathrm{kJ\,mol^{-1}}$ of the methyl radical addition to $CH_2{=}CHX$ in the presence of a single ion pair of ionic liquids. Enthalpies (ΔH) are presented in red, and Gibbs free energies (ΔG) in blue.

6 Table S1

C···C bond formation distance in the propagation transition state in ionic liquids and CPCM modelled solvent

Monomer	Solvent	R(C···C), Å	Ionic liquid	R(C···C), Å
Ethene	Gas	2.256	$[C_1mim][dca]$	2.258
	Ethanol	2.251	$[C_1mpyr][BF_4]$	2.245
	Toluene	2.253	[Dema][OTf]	2.247
			$[Et_3NH][HSO_4]$	2.258
			$[EtOH_2NH_2][NO_3]$	2.243
			$[Hmim][HSO_4]$	2.234
			$[PMe_4][Mes]$	2.239
VC	Gas	2.284	$[C_1mim][dca]$	2.282
	THF	2.278	$[C_1mpyr][BF_4]$	2.256
	Toluene	2.280	[Dema][OTf]	2.300
			$[Et_3NH][HSO_4]$	2.282
			$[EtOH_2NH_2][NO_3]$	2.268
			$[Hmim][HSO_4]$	2.264
			$[PMe_4][Mes]$	2.281
AN	Gas	2.272	$[C_1mim][dca]$	2.258
	DMF	2.263	$[C_1mpyr][BF_4]$	2.24
	Toluene	2.267	[Dema][OTf]	2.249
			$[Et_3NH][HSO_4]$	2.275
			$[EtOH_2NH_2][NO_3]$	2.269
			$[Hmim][HSO_4]$	2.245
			$[PMe_4][Mes]$	2.249
MMA	Gas	2.241	$[C_1mim][dca]$	2.201
	THF	2.240	$[C_1mpyr][BF_4]$	2.242
	Toluene	2.241	[Dema][OTf]	2.226
			$[Et_3NH][HSO_4]$	2.220
			$[EtOH_2NH_2][NO_3]$	2.229
			$[Hmim][HSO_4]$	2.190
			$[PMe_4][Mes]$	2.237

7 Table S2

Intermolecular separation (Å) between methyl radical and alkene CH_2=CHX in the reaction transition state, using M06-2X/cc-pvDZ optimised geometries.

X	Solvent	Conformation	Distance Å
C≡N	$[C_1mim][dca]$	1	2.356
	$[C_1mim][dca]$	2	2.335
	$[C_1mpyr][dca]$	1	2.356
	$[C_1mim][BF_4]$	1	2.345
	$[C_1mpyr][BF_4]$	2	2.345
	Gas phase		2.353
F	$[C_1mim][dca]$	1	2.258
	$[C_1mim][dca]$	2	2.258
	$[C_1mim][dca]$	3	2.255
	$[C_1mpyr][dca]$	1	2.254
	$[C_1mpyr][dca]$	2	2.255
	$[C_1mpyr][dca]$	3	2.254
	$[C_1mim][BF_4]$	1	2.250
	$[C_1mim][BF_4]$	2	2.258
	$[C_1mim][BF_4]$	3	2.246
	$[C_1mpyr][BF_4]$	1	2.251
	$[C_1mpyr][BF_4]$	2	2.255
	$[C_1mpyr][BF_4]$	3	2.266
	Gas phase		2.267
NH_2	$[C_1mim][dca]$	1	2.303
	$[C_1mim][dca]$	2	2.298
	$[C_1mpyr][dca]$	1	2.301
	$[C_1mpyr][dca]$	2	2.296
	$[C_1mim][BF_4]$	1	2.309
	$[C_1mim][BF_4]$	2	2.315
	Gas phase		2.309
OH	$[C_1mim][dca]$	1	2.284
	$[C_1mim][dca]$	2	2.284
	$[C_1mpyr][dca]$	1	2.285
	$[C_1mim][BF_4]$	1	2.284
	$[C_1mpyr][BF_4]$	1	2.280
	$[C_1mpyr][BF_4]$	2	2.282
	Gas phase		2.292
HC≡CH	$[C_1mim][dca]$	1	2.216
	$[C_1mpyr][dca]$	1	2.229
	$[C_1mpyr][dca]$	2	2.216
	$[C_1mim][BF_4]$	1	2.217
	$[C_1mim][BF_4]$	2	2.200
	$[C_1mpyr][BF_4]$	1	2.218
	Gas phase		2.229

8 Table S3

Intermolecular separation between the radical and monomer (in Å) in the transition state (TS) and pre-complex (PC), using M06-2X/cc-pvDZ optimised geometries.

Solvent	TS distance	PC distance	Solvent	TS distance	PC distance
	Ethene			*Vinyl chloride*	
Gas	2.256	3.256	Gas	2.284	3.411
Ethanol	2.251	3.270	THF	2.278	3.431
Toluene	2.253	3.269	Toluene	2.280	3.817
$[C_1mim][dca]$	2.258	3.344	$[C_1mim][dca]$	2.282	3.207
$[C_1mpyr][BF_4]$	2.245	3.628	$[C_1mpyr][BF_4]$	2.256	3.187
[Dema][OTf]	2.247	3.652	[Dema][OTf]	2.300	3.859
$[Et_3NH][HSO_4]$	2.258	3.273	$[Et_3NH][HSO_4]$	2.282	3.556
$[(EtOH)_2NH_2][NO_3]$	2.243	3.606	$[(EtOH)_2NH_2][NO_3]$	2.268	3.164
$[Hmim][HSO_4]$	2.234	3.183	$[Hmim][HSO_4]$	2.264	3.252
$[PMe_4][Mes]$	2.239	3.598	$[PMe_4][Mes]$	2.281	3.727
	onitrile			*Methyl methate*	
Gas	2.272	5.121	Gas	2.241	3.763
DMF	2.263	4.188	THF	2.240	3.383
Toluene	2.280	3.817	Toluene	2.267	5.854
$[C_1mim][dca]$	2.258	3.535	$[C_1mim][dca]$	2.201	3.537
$[C_1mpyr][BF_4]$	2.243	3.094	$[C_1mpyr][BF_4]$	2.242	3.328
[Dema][OTf]	2.244	3.115	[Dema][OTf]	2.226	3.888
$[Et_3NH][HSO_4]$	2.275	3.577	$[Et_3NH][HSO_4]$	2.220	3.603
$[(EtOH)_2NH_2][NO_3]$	2.269	3.684	$[(EtOH)_2NH_2][NO_3]$	2.229	2.947
$[Hmim][HSO_4]$	2.245	3.128	$[Hmim][HSO_4]$	2.190	3.454
$[PMe_4][Mes]$	2.249	3.328	$[PMe_4][Mes]$	2.237	3.245

9 Table S4

Total interaction energy E_{total} as the sum of dispersion $E_{dispersion}$ and electrostatic $E_{electrostatic}$ energies, in kJ mol^{-1} for model radicals in ionic liquids, calculated at the SRS-MP2/cc-pVTZ level of theory.

Radical	IL	Conformation	$E_{electrostatic}$	$E_{dispersion}$	E_{total}	% Dispersion
CH_2Cl	$[C_1mim][BF_4]$	1	-3.3	-26.4	-29.7	89
	$[C_1mim][BF_4]$	2	10.5	-22.8	-12.3	185
	$[C_1mim][BF_4]$	3	2.2	-22.1	-19.9	111
	$[C_1mim][BF_4]$	4	-7.7	-21.3	-29.0	73
	$[C_1mim][dca]$	1	6.3	-25.6	-19.3	133
	$[C_1mim][dca]$	2	-5.0	-26.3	-31.3	84
	$[C_1mim][dca]$	4	0.9	-27.8	-26.9	103
	$[P(Me)_4][BF_4]$	1	-0.7	-22.6	-23.3	97
	$[P(Me)_4][BF_4]$	2	-8.0	-21.0	-29.0	72
	$[P(Me)_4][dca]$	1	-7.9	-26.3	-34.2	77
	$[P(Me)_4][dca]$	2	-7.1	-26.4	-33.5	79
	$[P(Me)_4][dca]$	3	12.1	-30.3	-18.2	166
	$[P(Me)_4][Mes]$	1	-12.7	-22.5	-35.2	64
	$[C_1mpyr][BF_4]$	1	4.2	-20.0	-15.8	127
	$[C_1mpyr][BF_4]$	2	-4.1	-19.0	-23.1	82
	$[C_1mpyr][BF_4]$	3	-8.2	-14.9	-23.1	65
	$[C_1mpyr][dca]$	1	-6.1	-18.0	-24.1	75
	$[C_1mpyr][dca]$	2	0.1	-23.7	-23.6	100
	$[C_1mpyr][dca]$	3	-1.5	-24.9	-26.4	94
	$[C_1mpyr][dca]$	4	5.9	-25.0	-19.1	131
	$[C_1mpyr][dca]$	5	-4.8	-22.6	-27.4	82
CH_2CN	$[C_1mim][BF_4]$	1	-9.4	-23.3	-32.7	71
	$[C_1mim][BF_4]$	2	8.5	-26.1	-17.6	148
	$[C_1mim][BF_4]$	3	-7.7	-21.5	-29.2	74
	$[C_1mim][BF_4]$	4	-13.7	-17.6	-31.3	56
	$[C_1mim][dca]$	1	-11.6	-25.3	-36.9	69
	$[C_1mim][dca]$	2	-26.7	-24.9	-51.6	48
	$[C_1mim][dca]$	3	-23.1	-19.0	-42.1	45
	$[C_1mim][dca]$	4	-16.7	-26.6	-43.3	61
	$[P(Me)_4][BF_4]$	1	-29.9	-19.1	-49.0	39
	$[P(Me)_4][BF_4]$	2	-29.6	-20.8	-50.4	41
	$[P(Me)_4][dca]$	1	-32.6	-23.4	-56.0	42
	$[P(Me)_4][dca]$	2	-27.6	-24.7	-52.3	47
	$[P(Me)_4][dca]$	3	-25.4	-23.8	-49.2	48
	$[P(Me)_4][Mes]$	1	-36.6	-22.7	-59.3	38
	$[C_1mpyr][BF_4]$	1	-2.1	-20.3	-22.4	91
	$[C_1mpyr][BF_4]$	2	-18.5	-19.2	-37.7	51
	$[C_1mpyr][BF_4]$	3	-30.9	-13.7	-44.6	31
	$[C_1mpyr][dca]$	1	-19.9	-16.7	-36.6	46
	$[C_1mpyr][dca]$	2	-17.9	-24.4	-42.3	58
	$[C_1mpyr][dca]$	3	-15.9	-25.1	-41.0	61

	$[C_1mpyr][dca]$	4	-0.5	-26.0	-26.5	98
	$[C_1mpyr][dca]$	5	-22.7	-22.9	-45.6	50
CH_2F	$[C_1mim][BF_4]$	1	-10.2	-13.0	-23.2	56
	$[C_1mim][BF_4]$	2	8.2	-18.1	-9.9	183
	$[C_1mim][BF_4]$	3	0.1	-18.2	-18.1	101
	$[C_1mim][BF_4]$	4	-5.2	-15.7	-20.9	75
	$[C_1mim][dca]$	1	2.9	-20.4	-17.5	117
	$[C_1mim][dca]$	2	-6.1	-20.7	-26.8	77
	$[C_1mim][dca]$	3	1.1	-19.3	-18.2	106
	$[C_1mim][dca]$	4	-0.9	-21.7	-22.6	96
	$[P(Me)_4][BF_4]$	1	-0.8	-20.1	-20.9	96
	$[P(Me)_4][BF_4]$	2	-6.9	-18.4	-25.3	73
	$[P(Me)_4][dca]$	1	-8.9	-22.2	-31.1	71
	$[P(Me)_4][dca]$	2	-8.8	-21.3	-30.1	71
	$[P(Me)_4][dca]$	3	14.7	-24.4	-9.7	252
	$[P(Me)_4][Mes]$	1	-10.6	-20.0	-30.6	65
	$[C_1mpyr][BF_4]$	1	5.3	-17.0	-11.7	145
	$[C_1mpyr][BF_4]$	2	-2.9	-14.8	-17.7	84
	$[C_1mpyr][BF_4]$	3	-10.0	-12.9	-22.9	56
	$[C_1mpyr][dca]$	1	-7.1	-15.1	-22.2	68
	$[C_1mpyr][dca]$	2	8.4	-20.7	-12.3	168
	$[C_1mpyr][dca]$	3	-0.9	-19.5	-20.4	96
	$[C_1mpyr][dca]$	4	5.3	-20.9	-15.6	134
	$[C_1mpyr][dca]$	5	-5.5	-18.6	-24.1	77
CH_2NH_2	$[C_1mim][BF_4]$	1	-1.2	-21.2	-22.4	95
	$[C_1mim][BF_4]$	2	11.0	-21.5	-10.5	205
	$[C_1mim][BF_4]$	3	-9.4	-26.8	-36.2	74
	$[C_1mim][BF_4]$	4	0.9	-18.0	-17.1	105
	$[C_1mim][dca]$	1	-2.6	-18.8	-21.4	88
	$[C_1mim][dca]$	2	-5.2	-23.8	-29.0	82
	$[C_1mim][dca]$	3	-10.2	-33.0	-43.2	76
	$[C_1mim][dca]$	4	-24.7	-31.2	-55.9	56
	$[P(Me)_4][BF_4]$	1	-16.1	-26.2	-42.3	62
	$[P(Me)_4][BF_4]$	2	-1.9	-21.2	-23.1	92
	$[P(Me)_4][dca]$	1	-3.8	-23.7	-27.5	86
	$[P(Me)_4][dca]$	2	11.7	-25.1	-13.4	187
	$[P(Me)_4][dca]$	3	-2.2	-34.1	-36.3	94
	$[P(Me)_4][Mes]$	1	-15.6	-33.0	-48.6	68
	$[C_1mpyr][BF_4]$	1	1.3	-30.1	-28.8	105
	$[C_1mpyr][BF_4]$	2	6.3	-16.1	-9.8	164
	$[C_1mpyr][BF_4]$	3	-0.7	-15.9	-16.6	96
	$[C_1mpyr][dca]$	1	-1.3	-16.9	-18.2	93
	$[C_1mpyr][dca]$	2	-5.1	-29.1	-34.2	85
	$[C_1mpyr][dca]$	3	4.1	-24.2	-20.1	120
	$[C_1mpyr][dca]$	4	-11.5	-29.3	-40.8	72
	$[C_1mpyr][dca]$	5	-0.6	-21.6	-22.2	97

CH_2OH	$[C_1mim][BF_4]$	1	-9.0	-15.6	-24.6	63
	$[C_1mim][BF_4]$	2	3.0	-20.8	-17.8	117
	$[C_1mim][BF_4]$	3	-32.6	-29.2	-61.8	47
	$[C_1mim][BF_4]$	4	-1.5	-17.0	-18.5	92
	$[C_1mim][dca]$	1	-0.2	-21.6	-21.8	99
	$[C_1mim][dca]$	2	-2.8	-22.7	-25.5	89
	$[C_1mim][dca]$	3	-39.0	-35.8	-74.8	48
	$[C_1mim][dca]$	4	-43.5	-32.4	-75.9	43
	$[P(Me)_4][BF_4]$	1	-31.7	-27.3	-59.0	46
	$[P(Me)_4][BF_4]$	2	-31.7	-27.3	-59.0	46
	$[P(Me)_4][dca]$	1	-1.0	-23.8	-24.8	96
	$[P(Me)_4][dca]$	2	-3.9	-23.6	-27.5	86
	$[P(Me)_4][Mes]$	1	-46.0	-32.0	-78.0	41
	$[C_1mpyr][BF_4]$	1	10.3	-18.7	-8.4	223
	$[C_1mpyr][BF_4]$	2	1.4	-15.9	-14.5	110
	$[C_1mpyr][BF_4]$	3	-7.1	-16.2	-23.3	70
	$[C_1mpyr][dca]$	1	-32.8	-29.1	-61.9	47
	$[C_1mpyr][dca]$	2	18.6	-24.4	-5.8	421
	$[C_1mpyr][dca]$	3	1.3	-21.5	-20.2	106

10 Table S5

Total interaction energy E_{total} as the sum of dispersion (E_{disp}) and electrostatic (E_{elec}) energies, in kJ mol^{-1} for propagating radicals in various ionic liquids, calculated at the SRS-MP2/cc-pVTZ level of theory. Abbreviations for system conformation are as follows: aia = alternating ion arrangement, sia = same ion arrangement, p = planar.

Radical	Ionic liquid	IPs	Conformation	E_{elec}	E_{disp}	E_{total}	% Dispersion
$CH_3C^{\cdot}H_2$	$[C_1mim][dca]$	1	opt1	6.8	-20.5	-13.8	148
	$[C_1mim][dca]$	2	aia	26.6	-60.8	-34.1	178
	$[C_1mim][dca]$	2	sia	19.3	-49.5	-30.2	163
	$[C_1mpyr][BF_4]$	1	opt1	5.8	-16.7	-10.9	153
	$[C_1mpyr][BF_4]$	2	aia	25.0	-52.6	-27.6	190
	$[C_1mpyr][BF_4]$	2	sia	8.9	-53.5	-44.6	119
	[Dema][Otf]	1	in	9.4	-32.7	-23.3	140
	[Dema][Otf]	1	out	9.0	-20.5	-11.4	179
	[Dema][Otf]	2	aia	28.5	-54.0	-25.5	211
	[Dema][Otf]	2	sia	31.6	-70.1	-38.5	182
	$[Et_3NH][HSO_4]$	1	opt1	-2.3	-23.6	-25.8	91
	$[Et_3NH][HSO_4]$	2	aia	24.5	-58.0	-33.4	173
	$[Et_3NH][HSO_4]$	2	sia	16.9	-54.8	-37.9	144
	$[(EtOH)_2NH_2][NO_3]$	2	aia	24.5	-58.0	-33.4	173
	$[(EtOH)_2NH_2][NO_3]$	2	sia	15.1	-50.9	-35.8	142
	$[Hmim][HSO_4]$	1	p	13.8	-37.6	-23.8	157
	$[Hmim][HSO_4]$	2	aia	14.5	-54.2	-39.7	136
	$[Hmim][HSO_4]$	2	sia	20.0	-50.7	-30.7	165
	$[P(Me)_4][Mes]$	1	opt1	5.7	-18.4	-12.8	143
	$[P(Me)_4][Mes]$	2	aia	17.6	-47.6	-30.0	158
	$[P(Me)_4][Mes]$	2	sia	6.3	-52.2	-45.9	113
$CH_3C^{\cdot}HCl$	$[C_1mim][dca]$	1	opt1	5.5	-40.5	-35.0	115
	$[C_1mim][dca]$	2	aia	16.0	-64.8	-48.8	132
	$[C_1mim][dca]$	2	sia	4.6	-61.9	-57.3	108
	$[C_1mpyr][BF_4]$	1	opt1	0.0	-21.1	-21.1	100
	$[C_1mpyr][BF_4]$	2	aia	10.4	-53.4	-42.9	124
	$[C_1mpyr][BF_4]$	2	sia	27.7	-60.5	-32.8	184
	[Dema][Otf]	1	in	7.8	-33.2	-25.4	130
	[Dema][Otf]	1	out	18.1	-25.2	-7.0	360
	[Dema][Otf]	2	aia	43.3	-87.5	-44.2	197
	[Dema][Otf]	2	sia	-10.6	-63.3	-74.0	85
	$[Et_3NH][HSO_4]$	1	in	3.9	-30.5	-26.6	114
	$[Et_3NH][HSO_4]$	1	out	-8.9	-26.5	-35.3	75
	$[Et_3NH][HSO_4]$	2	aia	-2.9	-48.9	-51.7	94
	$[Et_3NH][HSO_4]$	2	sia	-21.1	-58.8	-79.9	73
	$[(EtOH)_2NH_2][NO_3]$	1	out	6.3	-35.1	-28.8	121
	$[(EtOH)_2NH_2][NO_3]$	2	aia	33.8	-60.8	-27.1	224
	$[(EtOH)_2NH_2][NO_3]$	2	sia	21.1	-53.5	-32.4	165
	$[Hmim][HSO_4]$	1	opt1	13.2	-38.1	-24.9	153
	$[Hmim][HSO_4]$	1	opt2	6.8	-38.8	-31.9	121
	$[Hmim][HSO_4]$	2	aia	24.3	-71.6	-47.3	151
	$[Hmim][HSO_4]$	2	sia	18.2	-46.0	-27.8	165
	$[P(Me)_4][Mes]$	1	opt1	-9.8	-29.7	-39.5	75
	$[P(Me)_4][Mes]$	2	aia	21.0	-61.5	-40.5	151

	$[P(Me)_4][Mes]$	2	sia	20.2	-54.6	-34.4	158
$CH_3C^{\cdot}(CH_3)COOCH$	$[C_1mim][dca]$	1	in	-25.6	-83.1	-108.8	76
	$[C_1mim][dca]$	1	out	-19.6	-47.9	-67.5	70
	$[C_1mim][dca]$	2	aia	67.5	-144.7	-77.2	187
	$[C_1mim][dca]$	2	sia	46.6	-124.7	-78.1	159
	$[C_1mpyr][BF_4]$	1	opt1	-1.6	-36.9	-38.5	95
	$[C_1mpyr][BF_4]$	2	aia	6.3	-86.8	-80.5	107
	$[C_1mpyr][BF_4]$	2	sia	19.5	-76.0	-56.5	134
	[Dema][Otf]	1	in	8.5	-38.4	-29.9	128
	[Dema][Otf]	1	out	0.4	-39.0	-38.6	101
	[Dema][Otf]	2	aia	-14.3	-98.6	-112.9	87
	[Dema][Otf]	2	sia	27.8	-106.4	-78.7	135
	$[Et_3NH][HSO_4]$	1	opt1	-16.2	-60.9	-77.1	78
	$[Et_3NH][HSO_4]$	1	opt2	-55.1	-55.4	-110.5	50
	$[Et_3NH][HSO_4]$	2	aia	-21.4	-95.9	-117.3	81
	$[Et_3NH][HSO_4]$	2	sia	4.4	-107.2	-102.7	104
	$[(EtOH)_2NH_2][NO_3]$	1	in	-62.4	-53.3	-115.8	46
	$[(EtOH)_2NH_2][NO_3]$	1	out	-16.9	-48.3	-65.2	74
	$[(EtOH)_2NH_2][NO_3]$	2	aia	-42.6	-119.7	-162.3	73
	$[(EtOH)_2NH_2][NO_3]$	2	sia	-42.6	-119.7	-162.3	73
	[Hmim][HSO_4]	1	in	-68.3	-70.2	-138.5	50
	[Hmim][HSO_4]	2	aia	-6.7	-81.4	-88.1	92
	[Hmim][HSO_4]	2	sia	-2.3	-73.8	-76.2	96
	$[P(Me)_4][Mes]$	1	in	-68.8	-67.2	-130.6	51
	$[P(Me)_4][Mes]$	1	out	-4.1	-49.2	-53.3	92
	$[P(Me)_4][Mes]$	2	aia	-30.6	-81.8	-112.4	72
	$[P(Me)_4][Mes]$	2	sia	-61.4	-87.8	-149.2	58
$CH_3C^{\cdot}HCN$	$[C_1mim][dca]$	1	in	7.4	-57.0	-49.6	114
	$[C_1mim][dca]$	1	out	13.1	-32.2	-19.1	168
	$[C_1mim][dca]$	2	aia	41.8	-110.6	-68.8	160
	$[C_1mim][dca]$	2	sia	-39.4	-83.1	-122.5	67
	$[C_1mpyr][BF_4]$	1	out	-33.6	-19.9	-53.6	37
	$[C_1mpyr][BF_4]$	2	aia	-36.5	-54.1	-90.6	59
	$[C_1mpyr][BF_4]$	2	sia	-16.4	-63.6	-80.0	79
	[Dema][Otf]	1	in	-139.8	-32.2	-172.0	18
	[Dema][Otf]	2	aia	-31.2	-77.0	-108.2	71
	[Dema][Otf]	2	sia	-92.3	-64.3	-156.6	41
	$[Et_3NH][HSO_4]$	1	in	-62.8	-38.9	-101.7	38
	$[Et_3NH][HSO_4]$	1	out	-22.1	-31.3	-53.4	58
	$[Et_3NH][HSO_4]$	2	aia	-31.0	-68.3	-99.3	68
	$[Et_3NH][HSO_4]$	2	sia	-23.1	-65.0	-88.1	73
	$[(EtOH)_2NH_2][NO_3]$	1	in	-43.7	-34.7	-78.4	44
	$[(EtOH)_2NH_2][NO_3]$	2	aia	44.0	-69.9	-25.9	269
	$[(EtOH)_2NH_2][NO_3]$	2	sia	-38.0	-62.2	-100.1	62
	[Hmim][HSO_4]	1	ap	16.9	-36.6	-19.7	185
	[Hmim][HSO_4]	2	aia	-19.6	-85.9	-105.5	81
	[Hmim][HSO_4]	2	sia	-7.0	-75.6	-82.7	91
	$[P(Me)_4][Mes]$	1	opt1	-26.4	-28.6	-55.0	52
	$[P(Me)_4][Mes]$	2	aia	-36.7	-57.6	-94.3	61
	$[P(Me)_4][Mes]$	2	sia	-46.0	-63.9	-109.9	58

11 Table S6

Atomic charge (e) of each component in system, as calculated by the Geodesic partial charge scheme for methyl radical addition to selected alkenes CH_2=CHX using the MP2/KTZ2P level of theory.

X	Ionic liquid	Conformation	Reaction Stage	Anion charge	Cation charge	Methyl charge	Reactant charge	Radical+Reactant charge
F	$[C_1mim][BF_4]$	1	Intermediate	-0.89	0.90	-0.02	0.01	-0.01
	$[C_1mim][BF_4]$	1	Transition	-0.88	0.85	0.04	-0.01	0.03
	$[C_1mim][BF_4]$	1	Product	-0.87	0.88	-0.01		-0.01
	$[C_1mim][BF_4]$	3	Intermediate	-0.82	0.82	0.02	-0.02	-0.00
	$[C_1mim][dca]$	1	Intermediate	-0.84	0.85	-0.01	0.00	-0.00
	$[C_1mim][dca]$	1	Transition	-0.83	0.76	0.08	-0.02	0.08
	$[C_1mim][dca]$	1	Product	-0.84	0.83	0.01		0.01
	$[C_1mim][dca]$	2	Intermediate	-0.76	0.79	0.01	-0.04	-0.03
	$[C_1mim][dca]$	2	Transition	-0.78	0.76	0.03	-0.01	0.03
	$[C_1mim][dca]$	2	Product	-0.79	0.80	-0.01		-0.01
	$[C_1mpyr][BF_4]$	2	Intermediate	-0.82	0.84	-0.01	-0.01	-0.02
	$[C_1mpyr][BF_4]$	2	Transition	-0.82	0.77	0.06	-0.01	0.06
	$[C_1mpyr][BF_4]$	2	Product	-0.83	0.82	0.01		0.01
	$[C_1mpyr][BF_4]$	4	Intermediate	-0.86	0.82	0.04	-0.01	0.03
	$[C_1mpyr][BF_4]$	4	Transition	-0.86	0.82	0.03	0.01	0.03
	$[C_1mpyr][BF_4]$	4	Product	-0.85	0.82	0.03		0.03
	$[C_1mpyr][dca]$	1	Intermediate	-0.79	0.81	-0.01	-0.01	-0.02
	$[C_1mpyr][dca]$	1	Transition	-0.79	0.73	0.06	-0.01	0.06
	$[C_1mpyr][dca]$	1	Product	-0.78	0.81	-0.04		-0.04
NH_2	$[C_1mim][BF_4]$	1	Intermediate	-0.89	0.88	-0.04	0.06	0.01
	$[C_1mim][BF_4]$	1	Transition	-0.90	0.85	-0.05	0.09	-0.05
	$[C_1mim][BF_4]$	1	Product	-0.89	0.87	0.02		0.02
	$[C_1mim][BF_4]$	3	Intermediate	-0.89	0.85	0.00	0.03	0.04
	$[C_1mim][dca]$	1	Intermediate	-0.84	0.85	-0.03	0.02	-0.03
	$[C_1mim][dca]$	1	Product	-0.83	0.79	0.04		0.04
	$[C_1mim][dca]$	2	Intermediate	-0.82	0.82	-0.03	0.03	0.00
	$[C_1mim][dca]$	2	Transition	-0.84	0.76	0.03	0.05	0.03
	$[C_1mim][dca]$	2	Product	-0.82	0.80	0.02		0.02
	$[C_1mim][BF_4]$	2	Intermediate	-0.86	0.85	-0.01	0.01	0.01
	$[C_1mpyr][BF_4]$	2	Product	-0.82	0.81	0.01		0.01
	$[C_1mpyr][BF_4]$	4	Intermediate	-0.85	0.83	0.01	0.02	0.02
	$[C_1mpyr][BF_4]$	4	Transition	-0.86	0.77	0.02	0.07	0.09
	$[C_1mpyr][BF_4]$	4	Product	-0.85	0.78	0.07		0.07
	$[C_1mpyr][dca]$	1	Intermediate	-0.80	0.81	-0.03	0.02	-0.01
	$[C_1mpyr][dca]$	1	Transition	-0.78	0.74	-0.05	0.09	0.04
	$[C_1mpyr][dca]$	1	Product	-0.81	0.76	0.04		0.04
	$[C_1mpyr][dca]$	2	Intermediate	-0.85	0.85	-0.03	0.03	0.00
	$[C_1mpyr][dca]$	2	Transition	-0.83	0.78	0.02	0.04	0.06
	$[C_1mpyr][dca]$	2	Product	-0.79	0.78	0.01		0.01

12 Table S7

Atomic charge (e) of each component in system, as calculated by the Geodesic partial charge scheme for transition states in 2 ion pairs of ionic liquid (including gas-phase results for comparison), using the MP2/KTZ2P level of theory.

Monomer	Solvent	Transition state	Radical	Monomer	IL
Ethene	Gas	0.00	0.03	−0.03	
	$[C_1mim][dca]$	−0.05	−0.02	−0.03	0.05
	$[C_1mpyr][BF_4]$	0.16	0.26	−0.10	−0.16
	[Dema][OTf]	−0.08	0.09	−0.17	0.08
	$[Et_3NH][HSO_4]$	−0.04	−0.13	0.09	0.04
	$[(EtOH)_2NH_2][NO_3]$	0.04	−0.13	0.09	0.04
	$[Hmim][HSO_4]$	0.08	0.04	0.04	−0.08
	$[PMe_4][Mes]$	0.06	0.06	0.00	−0.06
VC	Gas	0.00	0.02	−0.02	
	$[C_1mim][dca]$	0.12	0.19	−0.07	−0.12
	$[C_1mpyr][BF_4]$	0.30	0.42	−0.12	−0.30
	[Dema][OTf]	−0.02	−0.04	0.03	0.02
	$[Et_3NH][HSO_4]$	−0.14	0.02	−0.16	0.14
	$[(EtOH)_2NH_2][NO_3]$	−0.31	−0.24	−0.07	0.31
	$[Hmim][HSO_4]$	0.07	0.00	0.07	−0.07
	$[PMe_4][Mes]$	0.07	−0.10	0.17	−0.07
AN	Gas	0.00	0.00	0.00	
	$[C_1mim][dca]$	−0.07	−0.10	0.04	0.07
	$[C_1mpyr][BF_4]$	0.06	−0.09	0.15	−0.06
	[Dema][OTf]	−0.35	−0.16	−0.20	0.35
	$[Et_3NH][HSO_4]$	0.18	0.15	0.02	−0.18
	$[(EtOH)_2NH_2][NO_3]$	0.02	0.02	0.00	−0.02
	$[Hmim][HSO_4]$	−0.14	−0.10	−0.04	0.14
	$[PMe_4][Mes]$	−0.08	0.02	−0.10	0.08
	Gas	0.00	0.02	−0.02	
	$[C_1mim][dca]$	0.04	0.05	−0.01	−0.04
	$[C_1mpyr][BF_4]$	0.24	0.23	0.01	−0.24
	[Dema][OTf]	−0.09	−0.05	−0.04	0.09
	$[Et_3NH][HSO_4]$	0.15	0.22	−0.07	−0.15
	$[(EtOH)_2NH_2][NO_3]$	0.31	0.49	−0.19	−0.31
	$[Hmim][HSO_4]$	0.13	0.30	−0.16	−0.13
	$[PMe_4][Mes]$	0.07	0.19	−0.12	−0.07

13 Table S8

Spin contamination results: $\mathbf{S}^2$ value for pre-complex and transition state optimised geometries before and after annihilation. As $\mathbf{S}^2$ after annihilation is not greater than the expectation value ($S = 0.75$) by 10%, spin contamination is not considered significant in these systems.

Monomer	Ionic liquid	Pre-complex		Transition state	
		Before	*After*	*Before*	*After*
Ethene	$[C_1mim][dca]$	0.7548	0.7500	0.7791	0.7502
	$[C_1mpyr][BF_4]$	0.7549	0.7500	0.7794	0.7502
	[Dema][OTf]	0.7545	0.7500	0.7797	0.7502
	$[Et_3NH][HSO_4]$	0.7552	0.7500	0.7788	0.7502
	$[EtOH_2NH_2][NO_3]$	0.7548	0.7500	0.7782	0.7502
	$[Hmim][HSO_4]$	0.7551	0.7500	0.7782	0.7502
	$[PMe_4][Mes]$	0.7551	0.7500	0.7781	0.7502
VC	$[C_1mim][dca]$	0.7556	0.7500	0.7750	0.7502
	$[C_1mpyr][BF_4]$	0.7549	0.7500	0.7794	0.7502
	[Dema][OTf]	0.7553	0.7500	0.7755	0.7502
	$[Et_3NH][HSO_4]$	0.7550	0.7500	0.7758	0.7502
	$[EtOH_2NH_2][NO_3]$	0.7555	0.7500	0.7757	0.7502
	$[Hmim][HSO_4]$	0.7554	0.7500	0.7757	0.7502
	$[PMe_4][Mes]$	0.7551	0.7500	0.7748	0.7502
AN	$[C_1mim][dca]$	0.7642	0.7501	0.7849	0.7506
	$[C_1mpyr][BF_4]$	0.7648	0.7501	0.7835	0.7505
	[Dema][OTf]	0.7545	0.7500	0.7797	0.7502
	$[Et_3NH][HSO_4]$	0.7631	0.7501	0.7823	0.7505
	$[EtOH_2NH_2][NO_3]$	0.7636	0.7501	0.7825	0.7505
	$[Hmim][HSO_4]$	0.7635	0.7501	0.7841	0.7505
	$[PMe_4][Mes]$	0.7634	0.7501	0.7833	0.7505
	$[C_1mim][dca]$	0.7574	0.7500	0.7783	0.7503
	$[C_1mpyr][BF_4]$	0.7572	0.7500	0.7787	0.7503
	[Dema][OTf]	0.7576	0.7500	0.7781	0.7503
	$[Et_3NH][HSO_4]$	0.7570	0.7500	0.7788	0.7502
	$[EtOH_2NH_2][NO_3]$	0.7568	0.7500	0.7789	0.7503
	$[Hmim][HSO_4]$	0.7564	0.7500	0.7790	0.7502
	$[PMe_4][Mes]$	0.7577	0.7500	0.7779	0.7503

14 Table S9

Activation and reaction energies in kJ mol^{-1} of the addition of a methyl radical to an ethane derivative monomer using CCSD(T)/CBS ONIOM, with SRS-MP2/cc-pVTZ to model the solvent effect.

Monomer	Ionic liquid	Conf	$\Delta H^{\ddagger}$	ΔH	$\Delta G^{\ddagger}$	ΔG	Average $\Delta\Delta S$	Average $\Delta\Delta H$	Average $\Delta\Delta G$	Average $\Delta\Delta S^{\ddagger}$	Average $\Delta\Delta H^{\ddagger}$	Average $\Delta\Delta G^{\ddagger}$
CH2=CH2	Gas		34.4		60.3							
CH_2=CHCN	[C_1mim][dca]	2	28.2	-112.2	40.6	-97.6						
	Gas		37.5	-106.4	48.8	-92.5						
	[C_1mim][dca]	1	15.7	-129.7	28.1	-117.6						
	[C_1mpyr][dca]	1	12.2	-117.4	13.3	-106.8	1.3	-14.2	-14.6	9.9	-17.6	-17.4
	[C_1mim][BF_4]	1	14.6	-126.3	27.9	-112.5						
	[C_1mpyr][BF_4]	2	29.0	-117.5	47.0	-101.1	-4.0	-15.5	-14.3	22.1	-15.7	-11.4
CH_2=CHF	[C_1mim][dca]	2	26.8	-81.1	37.0	-60.8						
	[C_1mpyr][BF_4]	3	28.5		43.8		5.0	20.0	18.5	-10.2	13.9	17.0
	[C_1mpyr][BF_4]	2	30.6	-73.3	35.2	-66.2						
	[C_1mpyr][BF_4]	1	30.5	-71.9	39.2	-60.6						
	[C_1mim][BF_4]	3	22.0	-94.7	27.2	-84.7	-18.2	9.4	14.9	-16.0	14.3	19.1
	[C_1mim][BF_4]	1	42.3	-72.6	61.5	-52.0						
	[C_1mim][dca]	3	25.5	-95.6	30.8	-87.6	-7.6	4.9	7.2	-2.9	9.9	10.8
	[C_1mpyr][dca]	1	27.0	-85.2	33.2	-81.4						
	[C_1mpyr][dca]	2	35.1	-82.6	44.6	-73.8						
	[C_1mpyr][dca]	3	32.5	-84.0	39.1	-71.9	8.3	8.7	6.2	-0.2	12.5	12.6
	Gas		16.4	-92.6	24.6	-81.9						
	[C_1mim][BF_4]	2	27.9	-82.2	42.4	-64.4						
	[C_1mim][dca]	1	26.7	-86.4	38.4	-75.8						
CH_2=CHNH$_2$	[C_1mpyr][dca]	1	35.2	-83.0	51.2	-64.0						
	[C_1mpyr][dca]	2	19.2		21.6		-8.5	-15.7	-13.2	3.8	-10.1	-11.2
	[C_1mim][dca]	1	25.8	-91.1	35.6	-76.4						
	Gas		35.4	-73.3	43.4	-62.0						
	[C_1mim][BF_4]	2	28.1	-91.6	39.4	-84.0	24.3	-24.6	-31.8	3.9	-10.3	-11.5
	[C_1mim][dca]	2	21.2	-92.9	20.5	-85.1						
	[C_1mim][BF_4]	1	22.1	-104.1	24.5	-103.6						
CH_2=CHOH	[C_1mim][dca]	1	25.9	-89.1	37.7	-71.1						
	[C_1mim][dca]	2	19.6	-96.5	31.2	-84.4						
	[C_1mim][BF_4]	1	27.7	-102.8	46.7	-75.9						
	[C_1mpyr][BF_4]	1	24.0	-91.6	35.7	-72.0						
	[C_1mpyr][BF_4]	2	24.0	-93.4	37.1	-80.6	6.8	-23.6	-25.7	13.4	-10.3	-14.3
	[C_1mpyr][dca]	1	25.5	-90.2	45.2	-67.3	13.9	-19.6	-23.8	14.2	-11.8	-16.1
	Gas		35.5	-72.3	54.1	-50.5						
HC≡CH	[C_1mpyr][dca]	2	30.7	-94.9	37.0	-85.1	4.1	-8.6	-9.8	-0.6	-15.1	-14.9
	[C_1mpyr][BF_4]	1	33.5	-90.5	35.1	-83.0	8.7	-5.0	-7.6	7.6	-12.3	-14.6
	[C_1mim][BF_4]	2	33.3	-88.3	38.4	-83.3			-8.7			
	[C_1mim][BF_4]	1	33.9	-87.0	45.9	-70.4						
	[C_1mim][dca]	1	31.5	-92.7	34.6	-85.2						
	[C_1mpyr][dca]	1	30.2	-88.9	46.8	-73.0						
	Gas		45.9	-83.6	54.4	-71.3						

15 Table S10

Activation Gibbs free energy ($\Delta G^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$), entropy ($T\Delta S^{\ddagger}$), and energy (E_a) in kJ mol^{-1}; and propagation constant (k_p) in L mol^{-1} s^{-1} for T = 298 K and molecularity = 2.
ONIOM results using SRS-MP2 to treat the ionic liquid, and CCSD(T)/cc-pVTZ for ethene and vinyl chloride; CCSD(T)/CBS for acrylonitrile; and CCSD/CBS for methyl methacrylate.

Monomer	Solvent	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	k_p	$T\Delta S^{\ddagger}$	E_a
Ethene	Gas	50.5	25.9	8.99×10^{3}	-24.6	28.3
	Ethanol	46.3	25.8	4.78×10^{4}	-19.6	28.3
	Toluene	46.5	25.8	4.42×10^{4}	-20.1	28.3
	$[C_1mim][dca]$	45.2	40.0	7.58×10^{4}	-13.2	34.5
	$[C_1mpyr][BF_4]$	50.7	34.2	8.19×10^{3}	-16.5	36.6
	[Dema][OTf]	44.2	37.0	1.12×10^{5}	-7.2	39.5
	$[Et_3NH][HSO_4]$	36.5	23.1	2.46×10^{6}	-13.5	25.5
	$[(EtOH)_2NH_2][NO_3]$	46.1	31.5	5.26×10^{4}	-14.6	34.0
	$[Hmim][HSO_4]$	30.6	20.7	2.72×10^{7}	-9.9	23.2
	$[PMe_4][Mes]$	49.6	36.3	1.28×10^{4}	-13.3	38.8
VC	Gas	34.0	21.4	6.88×10^{6}	-12.6	23.9
	THF	34.0	21.4	1.31×10^{7}	-12.9	23.9
	Toluene	36.9	24.9	2.54×10^{6}	-12.0	27.4
	$[C_1mim][dca]$	21.1	13.4	1.23×10^{9}	-7.7	15.9
	$[C_1mpyr][BF_4]$	37.2	28.0	1.86×10^{6}	-9.2	30.5
	[Dema][OTf]	41.1	32.4	3.92×10^{5}	-8.7	34.9
	$[Et_3NH][HSO_4]$	34.4	22.1	5.88×10^{6}	-12.3	24.6
	$[(EtOH)_2NH_2][NO_3]$	43.3	26.9	1.60×10^{5}	-16.4	29.4
	$[Hmim][HSO_4]$	18.8	17.8	3.12×10^{9}	-1.1	20.2
	$[PMe_4][Mes]$	68.7	76.3	5.75	7.6	78.8
AN	Gas	50.2	40.6	1.00×10^{4}	-9.5	43.1
	DMF	46.1	32.7	5.17×10^{4}	-15.9	35.1
	Toluene	56.6	46.4	7.43×10^{2}	-11.2	48.9
	$[C_1mim][dca]$	46.6	46.4	4.33×10^{4}	-0.1	48.9
	$[C_1mpyr][BF_4]$	27.2	17.8	1.05×10^{8}	-9.5	20.2
	[Dema][OTf]	34.7	18.1	5.27×10^{6}	-16.6	20.5
	$[Et_3NH][HSO_4]$	26.9	27.7	1.19×10^{8}	0.8	30.2
	$[(EtOH)_2NH_2][NO_3]$	35.4	23.4	3.90×10^{6}	-12.0	25.8
	$[Hmim][HSO_4]$	31.6	24.3	1.80×10^{7}	-7.3	26.8
	$[PMe_4][Mes]$	33.5	25.7	8.24×10^{6}	-7.9	28.2
MMA	Gas	45.0	34.6	8.00×10^{4}	-10.4	37.1
	THF	47.6	35.2	2.90×10^{4}	-9.6	37.7
	Toluene	45.0	34.3	8.01×10^{4}	-9.5	36.8
	$[C_1mim][dca]$	32.0	28.7	1.56×10^{7}	-3.3	31.2
	$[C_1mpyr][BF_4]$	62.0	54.5	8.62×10^{1}	-7.5	57.0
	[Dema][OTf]	45.0	41.0	8.15×10^{4}	-4.0	43.4
	$[Et_3NH][HSO_4]$	37.6	30.5	1.64×10^{6}	-7.1	32.9
	$[(EtOH)_2NH_2][NO_3]$	43.3	32.4	1.62×10^{5}	-10.9	34.8
	$[Hmim][HSO_4]$	61.2	55.7	1.16×10^{2}	-5.5	58.2
	$[PMe_4][Mes]$	52.5	35.1	3.98×10^{3}	-17.4	37.6