Supporting Information

Mechanistic outlook on thermal degradation of 1,3-dialkyl imidazolium ionic liquids and organoclays

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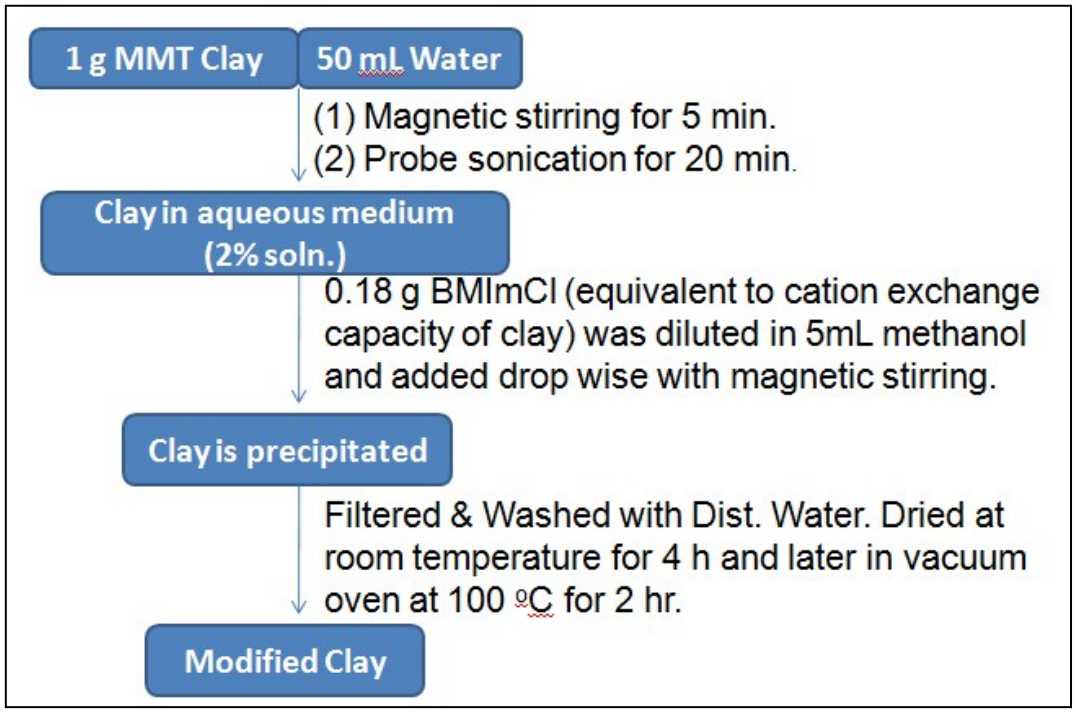
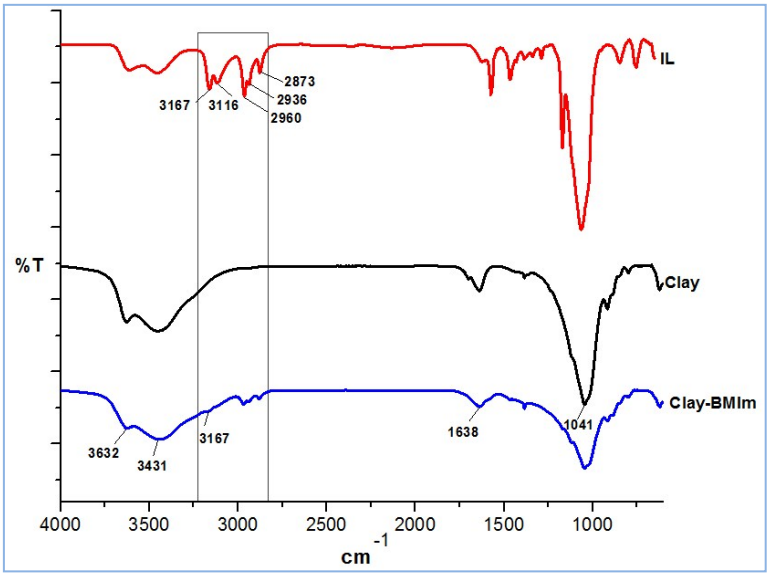
Captions

Part-I : Preparation of Clay-BMIm



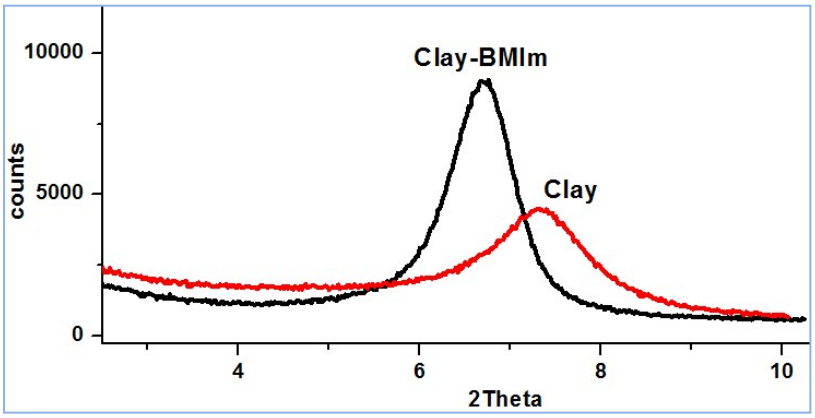
Part-II : Characterisation of Clay-BMIm

- **FT-IR spectra of BMImCl, clay and Clay-BMIm** (Fig. S1).



In IL, Carbon-hydrogen stretching peaks are shown in the range of 2840–3000 cm^{-1} with the band at 2873 and 2936 cm^{-1} representing methylene groups. The presence of peaks in the range of 2840–3000 cm^{-1} in Clay-BMIm was an indication of the exchanged cation, 1-butyl-3-methylimidazolium in the basal spacing of clay. The vibration bands of water gave two signals, a broad band at 3431 cm^{-1} and a peak at 1638 cm^{-1}. The peak at 3632 cm^{-1} was attributed to the hydroxyl groups of the clay. Signal near to 3167 and 3116 cm^{-1} observed in the spectra of clay-BMIm attributed to the aromatic C-H bonds in imidazolium ring.

- **XRD spectra of clay and clay-BMIm** (Fig. S2).

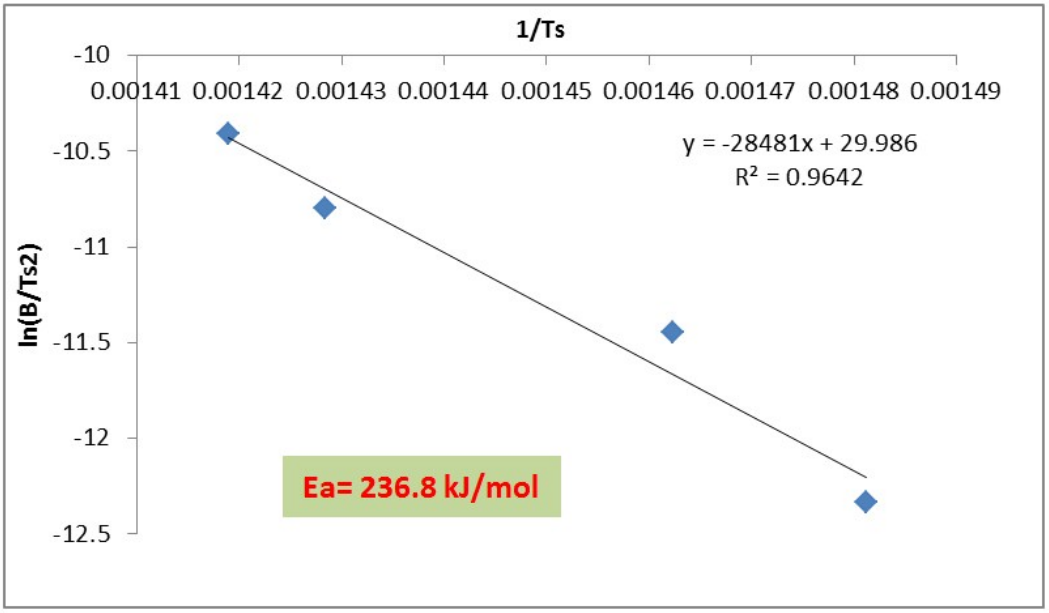


XRD analysis was performed to observe the basal spacing change between layers after exchanging sodium ions with the BMIm cation. X-ray diffraction pattern of clay exhibits 001 peak centred at 2θ = 7.306° corresponding to a basal d-spacing of 12.09 Å. For the clay-BMIm, the characteristic peak of the clay was shifted to lower 2θ value leading to an increase of the interlayer spacing (13.64 Å). This shift is a clear signature of the intercalation of the BMIm cation between the layers of MMT. The wide 001 peak of MMT became sharper and more symmetrical after intercalation of the BMIm cation.

Part-III : KAS calculation

- **$BMImBF_4$** (Fig. S3).

Ts (°C)	Ts (K)	B	Ts2	B/Ts2	1/Ts	ln(B/Ts2)
402.12	675.12	2	455787.014	4.4E-06	0.00148	-12.3366
410.84	683.84	5	467637.146	1.1E-05	0.00146	-11.446
427.07	700.07	10	490098.005	2E-05	0.00143	-10.7998
431.73	704.73	15	496644.373	3E-05	0.00142	-10.4076



Slope = -Ea/R
Ea = 28481* 8.314 J/mol
= **236.8 kJ/mol**

BMImCl

Ts (°C)	Ts (K)	B	Ts2	B/Ts2	1/Ts	ln(B/Ts2)
257	530	2	280900	7.1E-06	0.00189	-11.8526
285.35	558.35	5	311755	1.6E-05	0.00179	-11.0405
296.64	569.64	10	324490	3.1E-05	0.00176	-10.3874
299.86	572.86	15	328169	4.6E-05	0.00175	-9.99323

***E*a = 101.5 kJ/mol**

Clay-BMIm

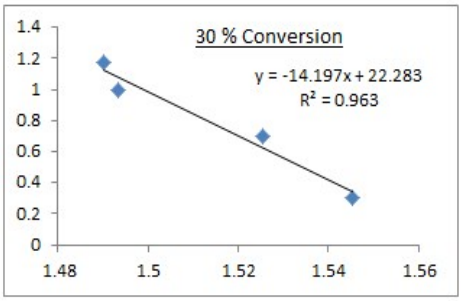
Ts (°C)	Ts (K)	B	Ts2	B/Ts2	1/Ts	ln(B/Ts2)
436.66	709.66	2	503617	4E-06	0.00141	-12.4364
442.25	715.25	5	511583	9.8E-06	0.0014	-11.5358
462.14	735.14	10	540431	1.9E-05	0.00136	-10.8975
468.55	741.55	15	549896	2.7E-05	0.00135	-10.5094

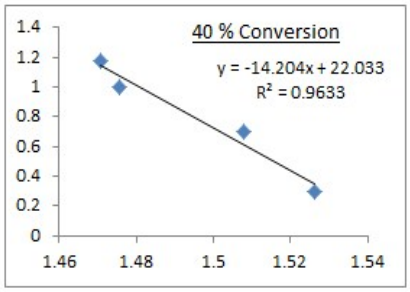
***E*a = 229.3 kJ/mol**

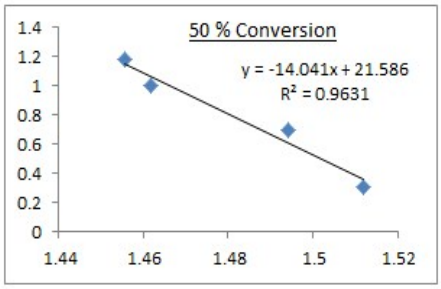
Part-IV : FWO calculation

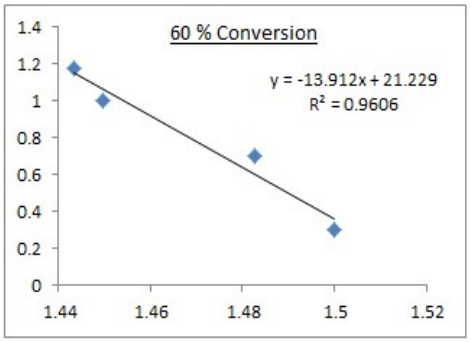
$BMImBF_4$ (Fig. S4).

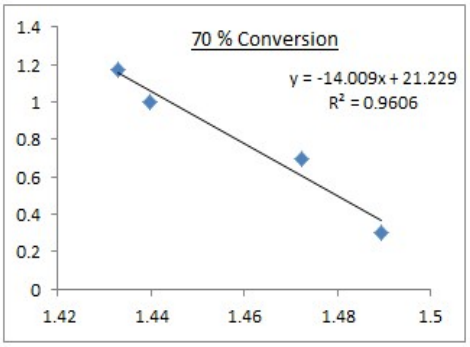
% Conv	B	Ts (K)	1000/Ts	log B	slope * 1000	Ea1 (J/mol)	Ea1/RTc	b	Ea2	Ea2/RTc	b	Ea3
30	2	647.1	1.545356205	0.30103	-14197	258279.7768	46.3964119	0.453	260560.3929	46.80609324	0.453	260560.4
	5	655.47	1.525622836	0.69897								
	10	669.57	1.493495826	1.00000								
	15	671.05	1.490201922	1.17609								
40	2	655.14	1.526391306	0.30103	-14204	258407.1247	45.86783566	0.453	260688.8653	46.27284966	0.453	260688.9
	5	663.16	1.507931721	0.69897								
	10	677.62	1.475753372	1.00000								
	15	679.85	1.470912701	1.17609								
50	2	661.41	1.511921501	0.30103	-14041	255441.7374	44.9054207	0.453	257697.2936	45.30193655	0.453	257697.3
	5	669.33	1.494031345	0.69897								
	10	684.2	1.461560947	1.00000								
	15	687.03	1.455540515	1.17609								
60	2	666.63	1.500082505	0.30103	-13912	253094.8972	44.12525457	0.454	254767.3304	44.41683114	0.454	254767.3
	5	674.51	1.482557709	0.69897								
	10	689.9	1.449485433	1.00000								
	15	692.81	1.44339718	1.17609								
70	2	671.41	1.489402898	0.30103	-14009	254859.5755	44.1379778	0.454	256543.6696	44.42963844	0.454	256543.7
	5	679.12	1.472493816	0.69897								
	10	694.51	1.439864077	1.00000								
	15	697.91	1.432849508	1.17609								
					Avg. Ea	256016.6223			258051.5104			258051.5











***E*a = <u>258.0 kJ/mol</u>**

<u>BMImCl</u>

% Conv	B	Ts (K)	1000/Ts	log B	slope * 1000	Ea1 (J/mol)	Ea1/RTc	b	Ea2	Ea2/RTc	b	Ea3
30	2	513.35	1.947989	0.30103	-5996	109082.5908	23.9112648	0.47	106065.4	23.24989	0.471	105840.2
	5	540.92	1.848702	0.69897								
	10	548.71	1.822456	1								
	15	549.72	1.819108	1.176091								
40	2	518.73	1.927785	0.30103	-6034.6	109783.0044	23.80278537	0.47	106746.5	23.14441	0.471	106519.8
	5	545.93	1.831737	0.69897								
	10	554.75	1.802614	1								
	15	556.74	1.796171	1.176091								
50	2	523.05	1.911863	0.30103	-6064.5	110328.7812	23.71337306	0.47	107277.1	23.05747	0.471	107049.4
	5	549.98	1.818248	0.69897								
	10	559.61	1.786959	1								
	15	562.06	1.779169	1.176091								
60	2	526.87	1.898001	0.30103	-6123.8	111407.6	23.77783693	0.47	108326.1	23.12015	0.471	108096.1
	5	553.67	1.80613	0.69897								
	10	563.55	1.774465	1								
	15	566.39	1.765568	1.176091								
70	2	530.41	1.885334	0.30103	-6213.4	113037.6534	23.97471569	0.47	109911.1	23.31159	0.471	109677.7
	5	556.9	1.795655	0.69897								
	10	567.1	1.763357	1								
	15	570	1.754386	1.176091								
					Avg. Ea	110727.926			107665.2			107436.7

***E*a = <u>107.4 kJ/mol</u>**

Clay-BMIm

% Conv	B	Ts (K)	1000/Ts	log B	slope * 1000	Ea1 (J/mol)	Ea1/RTc	b	Ea2	Ea2/RTc	b	Ea3
30	2	657.16	1.5217	0.30103	-9034.74	164365.0511	29.09187088	0.463	162235.0505	28.71487039	0.463	162235.1
	5	660.14	1.5148	0.69897								
	10	679.56	1.4715	1.00000								
	15	695.35	1.4381	1.17609								
40	2	678.86	1.4731	0.30103	-11401.37	207420.1098	35.77431704	0.458	206967.2275	35.69620718	0.458	206967.2
	5	686.24	1.4572	0.69897								
	10	697.38	1.4339	1.00000								
	15	714.3	1.4000	1.17609								
50	2	695.47	1.4379	0.30103	-12624	229662.8796	38.80595694	0.456	230166.5263	38.89105772	0.456	230166.5
	5	705.87	1.4167	0.69897								
	10	711.84	1.4048	1.00000								
	15	730.09	1.3697	1.17609								
60	2	710.86	1.4067	0.30103	-13405.16	243874.18	40.47487864	0.456	244516.2357	40.58143822	0.455	244946.2
	5	723.86	1.3815	0.69897								
	10	724.72	1.3798	1.00000								
	15	744.39	1.3434	1.17609								
70	2	725.53	1.3783	0.30103	-11001.39	200143.4496	32.67954965	0.461	198406.847	32.39599608	0.461	198406.8
	5	728.62	1.3725	0.69897								
	10	736.64	1.3575	1.00000								
	15	760.06	1.3157	1.17609								
					Avg. Ea	209093.134			208458.3774			208544.4

$$Ea = \underline{\mathbf{208.5\ kJ/mol}}$$

Part-V: Calculation of *Ea* from Py-GC-MS and DFT study

Area ratio of standard solutions of 1-methylimidazole (MIm) to 1-butylimidazole (Bu-Im),

MIm: Bu-Im = **1 : 1.46**

1. BMImCl

Sample	Products	Avg. Area
BMImCl	MIm	26225477
	Bu-Im	340105531

Area ratio = **MIm: Bu-Im**
= 1 : 12.97

Comparing with Area ratio of standards **MIm: Bu-Im = 1 : 1.46**,

Actual area ratio = 1 : (12.97/1.46)
= **1 : 8.88**

When the ratio is converted for 100 % of the reaction,
= **10.12 : 89.88**

Ea of demethylation reaction = 122.7 kJ/mol
Ea of debutylation reaction = 130.8 kJ/mol
Ea of the reaction = (10.12*130.8)+(89.88*122.7)/100
= **123.5 kJ/mol**

2. $BMImBF_4$

Sample	Products	Avg. Area
$BMImBF_4$	MIm	51652142
	Bu-Im	79814872

Area ratio = **MIm: Bu-Im**
= 1 : 1.54

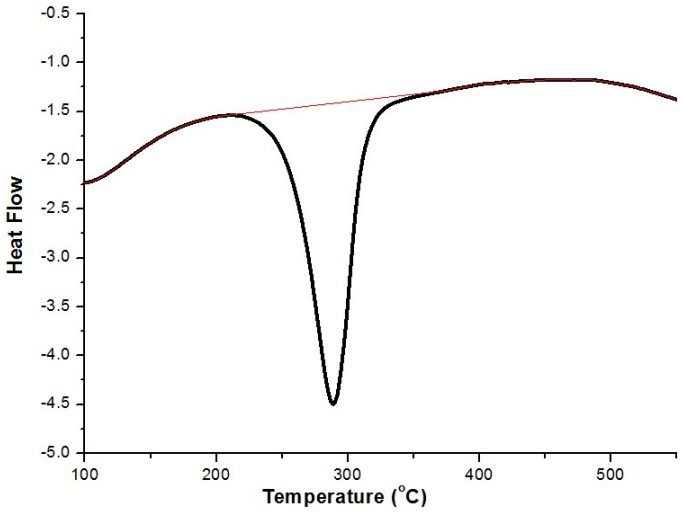
Comparing with Area ratio of standards **MIm: Bu-Im = 1 : 1.46**,
Actual area ratio = 1 : (1.54 /1.46)
= **1 : 1.05**

When the ratio is converted for 100 % of the reaction,
= **48.78 : 51.22**

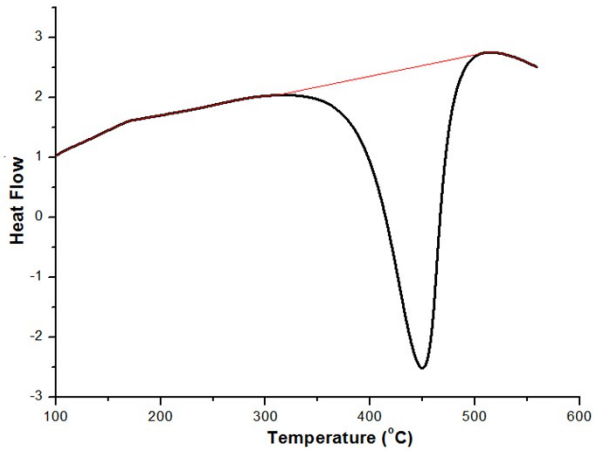
*E*a of demethylation reaction = 188.5 kJ/mol
*E*a of elimination reaction = 237.0 kJ/mol
*E*a of the reaction = (48.78*237.0)+(51.22*188.5)/100
= **212.1 kJ/mol**

Part-VI: DSC curves of ILs and Clay-BMIm

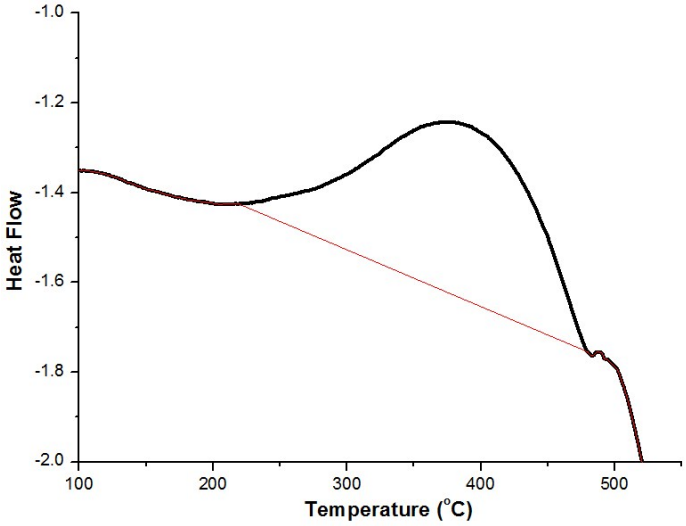
1. BMImCl (Fig. S5).



2. $BMImBF_4$ (Fig. S6).



3. Clay- BMIm (Fig. S7).



In modified clay, the concentration of $[BMIm]^+$ cation was less than 2 %.

Part-VII: Coordinates of ILs

(Cartesian coordinates of all geometries in Å and SCF energies in a.u. Bond lengths in Å and bond angles in degrees)

[1] 1-butyl-3-methylimidazolium Cation

E(RB3LYP) = -423.287687637

7	0.492306000	0.207923000	0.472206000
6	1.414157000	-0.751450000	0.350814000
6	1.042379000	1.396263000	0.032359000
6	2.320397000	1.131331000	-0.353838000
7	2.534911000	-0.218155000	-0.148051000
1	1.278727000	-1.786909000	0.616051000
1	3.085137000	1.779848000	-0.746525000
1	0.489184000	2.319908000	0.035928000
6	-0.900027000	0.017272000	0.946919000
1	-0.914820000	-0.916702000	1.511257000
1	-1.108843000	0.827595000	1.647865000
6	3.786231000	-0.940288000	-0.423087000
1	4.028469000	-0.855739000	-1.481976000
1	4.589682000	-0.518051000	0.179658000
1	3.653274000	-1.988961000	-0.165128000
6	-1.914365000	-0.009291000	-0.198411000
1	-1.653891000	-0.815656000	-0.892979000
1	-1.853702000	0.927578000	-0.763056000
6	-3.345745000	-0.207868000	0.319323000
1	-3.399290000	-1.142345000	0.889603000
1	-3.593212000	0.596960000	1.020763000
6	-4.378225000	-0.238520000	-0.810901000
1	-4.177958000	-1.054398000	-1.511038000
1	-5.384069000	-0.383784000	-0.412198000
1	-4.378022000	0.697590000	-1.376376000

[2] 1-butyl-3-methylimidazolium chloride

E(RB3LYP) = -883.734683380

7	0.497582000	-0.765575000	-0.494834000
6	1.365374000	0.161724000	-0.077825000
6	1.097197000	-2.010615000	-0.429282000
6	2.361588000	-1.820559000	0.034805000
7	2.506964000	-0.458365000	0.248904000
1	1.103142000	1.250788000	-0.028079000
1	3.155704000	-2.522426000	0.223045000
1	0.585381000	-2.912089000	-0.718869000
6	-0.891144000	-0.458102000	-0.903496000
1	-0.896819000	0.602314000	-1.169311000
1	-1.106698000	-1.058607000	-1.790731000
6	-1.895924000	-0.721143000	0.218151000
1	-1.614774000	-0.108639000	1.080748000
1	-1.850334000	-1.772223000	0.530708000
6	-3.322890000	-0.365794000	-0.215415000
1	-3.344893000	0.684101000	-0.524658000
1	-3.597117000	-0.958768000	-1.096934000
6	-4.350980000	-0.595312000	0.895563000
1	-4.122947000	0.016374000	1.773154000
1	-4.369705000	-1.643036000	1.212857000
1	-5.357324000	-0.331572000	0.560528000
6	3.704839000	0.223143000	0.742061000
1	3.972877000	-0.163961000	1.725727000
1	4.531613000	0.072416000	0.046873000
1	3.484863000	1.286294000	0.818657000
17	-0.000774000	2.920385000	-0.147622000

[3] 1-butyl 3- methylimidazolium tetrafluoroborate

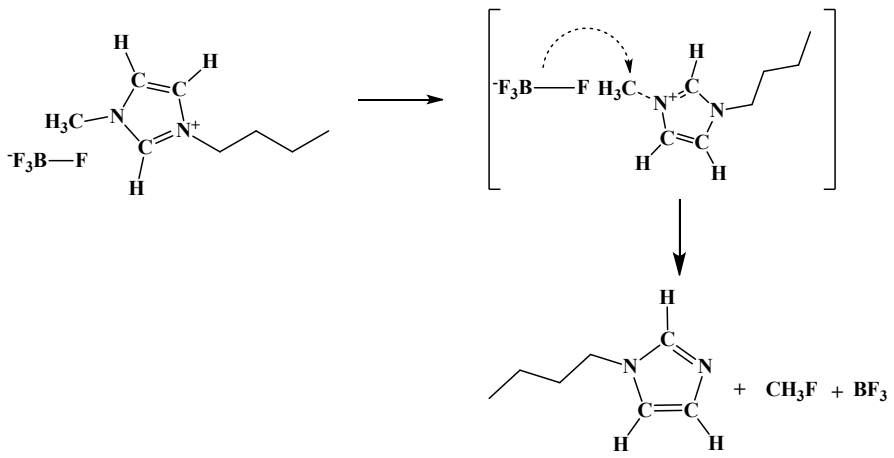
E(RB3LYP) = -848.099071499

7	0.683177000	1.044901000	-0.429318000
6	-0.352687000	0.861167000	0.391742000
6	0.602815000	2.320957000	-0.957702000
6	-0.511348000	2.900468000	-0.435033000
7	-1.091989000	1.971156000	0.408329000
1	-0.596821000	-0.050202000	0.914253000
1	-0.942477000	3.872404000	-0.600371000
1	1.326155000	2.695534000	-1.660730000
6	1.689594000	0.011852000	-0.749091000
1	1.165102000	-0.944375000	-0.713335000
1	1.999054000	0.187054000	-1.781439000
6	-2.377773000	2.100456000	1.105180000
1	-2.288622000	2.823762000	1.916691000
1	-3.132939000	2.423432000	0.389764000
1	-2.654280000	1.118854000	1.485525000
9	-0.796867000	-1.979368000	-0.298436000

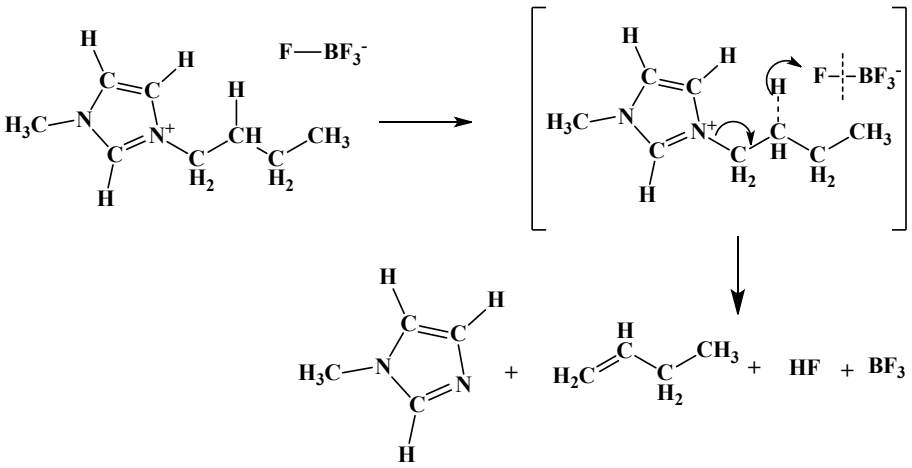
5	-2.170908000	-1.622959000	-0.120513000
9	-2.299714000	-1.153185000	1.234398000
9	-2.447235000	-0.519406000	-0.969602000
9	-3.007205000	-2.686583000	-0.362202000
6	2.888045000	0.042612000	0.200690000
1	2.534763000	-0.109001000	1.226793000
1	3.359811000	1.032123000	0.170684000
6	3.919530000	-1.036050000	-0.152227000
1	3.435182000	-2.018227000	-0.127636000
1	4.261909000	-0.887885000	-1.183431000
6	5.125062000	-1.033509000	0.791462000
1	4.818323000	-1.217724000	1.825299000
1	5.841404000	-1.810928000	0.515048000
1	5.649413000	-0.073268000	0.764832000

Part-VIII: Decomposition mechanism studied for $BMImBF_4$ (Fig. S8).

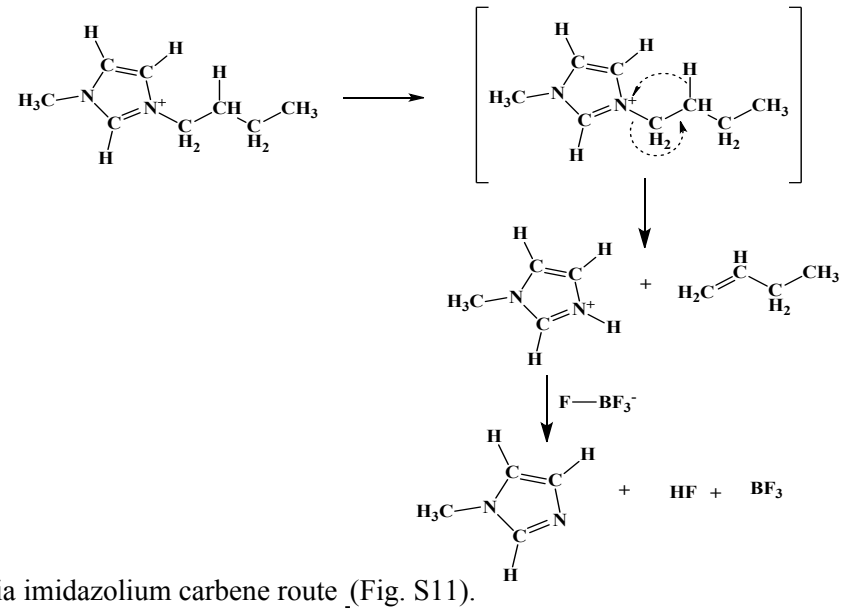
(1) Pathway-I (S_N2 Mechanism) for $BMImBF_4$



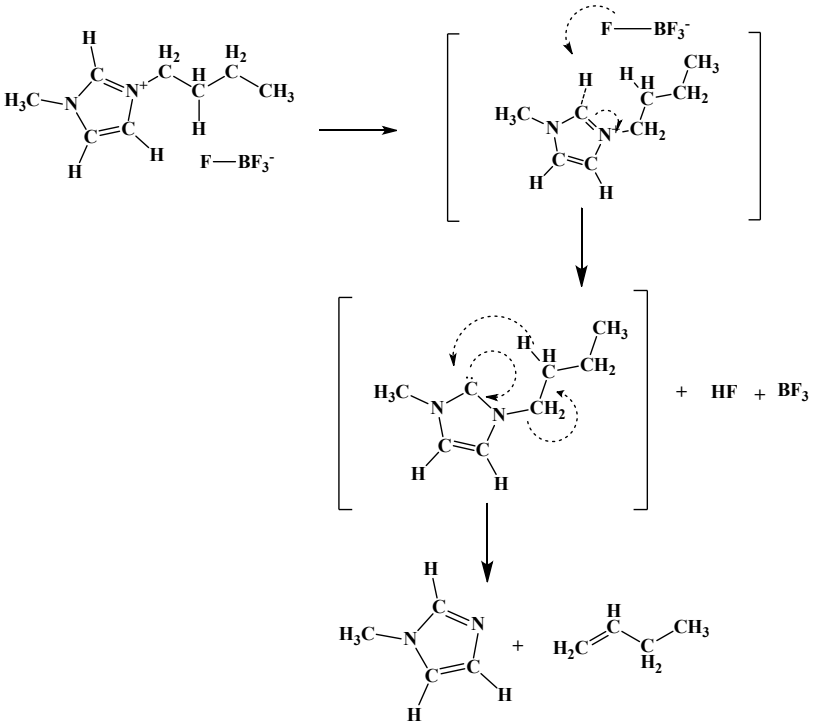
(2) Pathway-II (E2 Elimination) for $BMImBF_4$ (Fig. S9).



(3) Ei elimination pathway (Fig. S10).



(4) Elimination via imidazolium carbene route (Fig. S11).



Part-IX: Coordinates - Transition states

Cartesian coordinates of all geometries in Å and SCF energies in a.u. Bond lengths in Å and bond angles in degrees

[1] 1-butyl-3-methylimidazolium chloride - S_N2 mechanism (pathway-1)

E(RB3LYP) = -883.687938749

7	-0.837582000	0.660226000	0.437023000
6	0.290085000	-0.073234000	0.582557000
6	-0.500460000	1.788873000	-0.284198000

6	0.838477000	1.695403000	-0.547145000
7	1.310827000	0.528982000	0.000649000
1	0.331562000	-1.013430000	1.109409000
1	1.483526000	2.376583000	-1.077751000
1	-1.225981000	2.544214000	-0.535145000
6	-2.179759000	0.292020000	0.906632000
1	-2.049867000	-0.449203000	1.698222000
1	-2.625897000	1.178070000	1.365179000
6	-3.075558000	-0.257522000	-0.206973000
1	-2.588319000	-1.127549000	-0.660775000
1	-3.172510000	0.494015000	-0.998364000
6	-4.465581000	-0.647403000	0.309605000
1	-4.361199000	-1.396344000	1.103666000
1	-4.939776000	0.226037000	0.772882000
6	-5.374692000	-1.197086000	-0.792949000
1	-4.943456000	-2.090825000	-1.253311000
1	-5.530425000	-0.457515000	-1.583958000
1	-6.355143000	-1.468767000	-0.394747000
6	3.077745000	-0.094600000	-0.051743000
1	3.165106000	-0.121158000	-1.122374000
1	3.514290000	0.725646000	0.487935000
1	2.896711000	-1.016086000	0.471822000
17	5.378066000	-0.927462000	-0.114183000

[2] 1-butyl 3- methylimidazolium chloride - S_N2 Mechanism (pathway-II)

E(RB3LYP) = -883.684813158

7	-3.038336000	-0.150840000	-0.248220000
6	-1.774340000	-0.459485000	-0.621823000
6	-2.972943000	0.358040000	1.033905000
6	-1.652482000	0.336052000	1.389451000
7	-0.921887000	-0.171700000	0.343456000
1	-1.520210000	-0.885431000	-1.579638000
1	-1.190472000	0.645652000	2.312406000
1	-3.852335000	0.679480000	1.566408000
6	-4.245737000	-0.320317000	-1.051775000
1	-3.975517000	-0.777409000	-2.002455000
1	-4.952061000	-0.971401000	-0.534958000
6	0.951259000	-0.664171000	0.287746000
1	0.855218000	-1.396284000	1.071352000
1	0.868026000	-1.030624000	-0.720367000
17	3.080457000	-1.973434000	-0.089324000
1	-4.712020000	0.647411000	-1.242652000
6	1.625411000	0.655606000	0.567665000
1	2.571753000	0.429825000	1.060855000
1	1.025350000	1.229369000	1.285235000
6	1.882785000	1.488141000	-0.690650000
1	2.488381000	0.885239000	-1.373974000
1	0.930970000	1.693057000	-1.197569000
6	2.596970000	2.808058000	-0.390313000
1	3.566977000	2.627988000	0.082010000
1	2.775219000	3.379145000	-1.305478000
1	2.008987000	3.438606000	0.285438000

[3] 1-butyl-3-methylimidazolium tetrafluoroborate- S_N2 mechanism

E(RB3LYP) = -848.027197671

7	-2.052892000	0.951354000	0.441691000
6	-0.774292000	0.501413000	0.485508000
6	-2.028053000	2.172675000	-0.200685000
6	-0.717194000	2.412553000	-0.515646000
7	0.052763000	1.360795000	-0.080517000
1	-0.495057000	-0.439767000	0.934215000
1	-0.289704000	3.266932000	-1.015202000
1	-2.921893000	2.750638000	-0.365095000
6	-3.241204000	0.236429000	0.919877000
1	-2.906219000	-0.470848000	1.681968000
1	-3.889505000	0.961994000	1.417618000
6	2.170752000	0.971546000	-0.261973000
1	2.299954000	1.988849000	-0.587859000
1	2.148944000	0.752810000	0.790428000
1	1.898252000	0.213896000	-0.974121000
9	3.917208000	0.614817000	-0.398842000
5	4.282740000	-0.855437000	0.023379000
9	3.847632000	-0.943505000	1.333605000
9	3.534734000	-1.643409000	-0.831927000
9	5.629681000	-0.945784000	-0.141916000
6	-3.994850000	-0.492474000	-0.196818000
1	-3.309596000	-1.188543000	-0.692944000
1	-4.306798000	0.233108000	-0.956196000
6	-5.218327000	-1.251077000	0.330065000
1	-4.898406000	-1.967274000	1.096293000
1	-5.894843000	-0.548425000	0.831240000
6	-5.978161000	-1.992401000	-0.773528000
1	-5.337036000	-2.725872000	-1.271096000
1	-6.840311000	-2.526474000	-0.366846000
1	-6.345903000	-1.299930000	-1.536602000

[4] 1-butyl-3-methylimidazolium tetrafluoroborate - E2 Mechanism

E(RB3LYP) = -848.008716566

7	-1.387919000	-1.599021000	0.249327000
6	-1.726320000	-0.433611000	0.769583000
6	-2.393065000	-1.921333000	-0.635345000
6	-3.340253000	-0.932596000	-0.637687000
7	-2.904286000	0.011498000	0.268811000
1	-1.136595000	0.142180000	1.464493000
1	-4.260481000	-0.817139000	-1.185583000
1	-2.384044000	-2.836057000	-1.207479000
6	0.976459000	-2.512886000	0.137923000
1	0.722622000	-2.605760000	1.186322000
1	0.405302000	-3.128508000	-0.542784000
6	-3.506558000	1.314907000	0.524205000
1	-3.081560000	1.726899000	1.437908000
1	-3.288828000	1.998790000	-0.297249000
1	-4.584793000	1.205583000	0.648606000

9	0.741077000	0.427007000	-1.023852000
5	0.734973000	1.695050000	-0.159254000
9	1.787300000	2.461894000	-0.589299000
9	-0.502504000	2.272600000	-0.352360000
9	0.901473000	1.232195000	1.149515000
6	2.016701000	-1.720934000	-0.299559000
1	1.240989000	-0.731610000	-0.571043000
1	2.343766000	-1.904763000	-1.326351000
6	3.077052000	-1.164926000	0.655655000
1	2.581611000	-0.665463000	1.491754000
1	3.635844000	-2.012491000	1.068659000
6	4.048986000	-0.198223000	-0.026511000
1	3.538312000	0.691345000	-0.398353000
1	4.814286000	0.128599000	0.681373000
1	4.559998000	-0.679849000	-0.866584000

Part-X: Coordinates of clay-BMIm decomposition

[1] BMIm-Si(OH)$_3$O$^-$

E(RB3LYP) = -1016.00605327

7	2.090268000	-0.968766000	0.327792000
6	0.784118000	-1.263715000	0.218312000
6	2.847933000	-2.085440000	0.019589000
6	1.974235000	-3.081757000	-0.284188000
7	0.701609000	-2.549396000	-0.155624000
1	-0.090910000	-0.496703000	0.375286000
1	2.146075000	-4.102877000	-0.578073000
1	3.924048000	-2.076555000	0.041121000
6	2.601888000	0.360014000	0.720161000
1	2.261899000	0.559042000	1.739118000
1	3.691257000	0.280213000	0.739353000
6	-0.558811000	-3.265874000	-0.382718000
1	-0.543252000	-3.714365000	-1.377060000
1	-0.675635000	-4.047743000	0.369783000
1	-1.386700000	-2.557013000	-0.315522000
14	-2.584056000	0.536511000	0.088695000
6	2.136903000	1.470738000	-0.222606000
1	1.041851000	1.484138000	-0.230949000
1	2.477669000	1.244097000	-1.240048000
6	2.669210000	2.840576000	0.213741000
1	2.326891000	3.049217000	1.234097000
1	3.766230000	2.821983000	0.252120000
6	2.209146000	3.968687000	-0.714051000
1	1.117943000	4.027775000	-0.744355000
1	2.589966000	4.936957000	-0.378397000
1	2.562212000	3.808322000	-1.737488000
8	-2.973065000	-1.062801000	-0.301769000
1	-3.837239000	-1.172855000	-0.707731000
8	-3.076574000	1.367959000	-1.279776000
1	-3.369572000	2.267885000	-1.120555000
8	-3.646768000	1.103912000	1.261945000

1	-3.273184000	1.102625000	2.146253000
8	-1.064046000	0.596237000	0.529188000

[2] 1-butyl-3-methylimidazol-2-ylidene- $Si(OH)_4$

E(RB3LYP) = -1016.00952221

7	1.738345000	1.161742000	-0.481446000
6	0.392990000	1.262446000	-0.304255000
6	2.396643000	2.329772000	-0.120626000
6	1.437511000	3.195747000	0.290098000
7	0.227688000	2.524561000	0.172294000
1	-0.801214000	0.012675000	-0.636944000
1	1.512540000	4.210907000	0.642479000
1	3.465220000	2.447482000	-0.188589000
6	2.397597000	-0.062491000	-0.940183000
1	1.650268000	-0.627911000	-1.498242000
1	3.193191000	0.218910000	-1.637250000
6	-1.072467000	3.107958000	0.490861000
1	-1.063632000	3.504309000	1.508810000
1	-1.307024000	3.916229000	-0.206342000
1	-1.831114000	2.330935000	0.414810000
14	-2.837213000	-0.954539000	-0.037527000
6	2.958532000	-0.906784000	0.207432000
1	2.138644000	-1.153709000	0.890183000
1	3.678970000	-0.312167000	0.782180000
6	3.629433000	-2.192176000	-0.289299000
1	2.904780000	-2.774984000	-0.869940000
1	4.441520000	-1.936790000	-0.981293000
6	4.182064000	-3.055023000	0.848579000
1	3.386797000	-3.354036000	1.537943000
1	4.649721000	-3.965656000	0.464923000
1	4.936035000	-2.512631000	1.427654000
8	-3.392100000	0.527654000	0.473871000
1	-4.090515000	0.510493000	1.133437000
8	-2.759811000	-1.866748000	1.344628000
1	-2.783348000	-2.820116000	1.234846000
8	-3.911715000	-1.758830000	-1.013995000
1	-3.817066000	-1.606043000	-1.957264000
8	-1.466229000	-0.727722000	-0.862955000

[3] 1-butyl-3-methylimidazol-2-ylidene

E(RB3LYP) = -422.856392213

7	0.524256000	0.242436000	0.463058000
6	1.387864000	-0.816979000	0.456741000
6	1.082980000	1.392609000	-0.083700000
6	2.346120000	1.063245000	-0.447140000
7	2.506597000	-0.277102000	-0.112352000
1	3.123983000	1.658824000	-0.896101000
1	0.554538000	2.328601000	-0.161137000
6	-0.851192000	0.141568000	0.944178000

1	-0.876632000	-0.714471000	1.619660000
1	-1.081583000	1.038161000	1.529619000
6	3.731359000	-1.031878000	-0.327062000
1	3.991055000	-1.055071000	-1.388860000
1	4.561177000	-0.593737000	0.234126000
1	3.557269000	-2.047078000	0.023098000
6	-1.871471000	-0.038217000	-0.183955000
1	-1.601882000	-0.933764000	-0.754178000
1	-1.802522000	0.808032000	-0.878309000
6	-3.307468000	-0.160613000	0.336838000
1	-3.368327000	-1.006140000	1.032400000
1	-3.561878000	0.732962000	0.920377000
6	-4.336217000	-0.347409000	-0.782155000
1	-4.128968000	-1.252581000	-1.361003000
1	-5.349632000	-0.433919000	-0.380918000
1	-4.324411000	0.498888000	-1.476179000

[4] **Transition state of Clay-BMIm**

E(RB3LYP) = -422.781829528

7	-0.630129000	-1.060500000	0.030537000
6	-0.620042000	0.236914000	0.233178000
6	-1.892891000	-1.482644000	-0.303815000
6	-2.702193000	-0.379618000	-0.302907000
7	-1.885162000	0.691237000	0.037165000
1	-3.756712000	-0.267973000	-0.507601000
1	-2.138581000	-2.511499000	-0.515596000
6	1.101652000	-1.699267000	0.299640000
1	0.886790000	-2.382356000	1.114725000
1	1.211969000	-2.206192000	-0.655728000
6	-2.315501000	2.076817000	0.158101000
1	-1.456193000	2.675706000	0.453529000
1	-2.697663000	2.447595000	-0.796180000
1	-3.094995000	2.172664000	0.917799000
6	1.859881000	-0.524013000	0.561647000
1	0.682980000	0.375887000	0.540772000
6	2.781743000	0.028654000	-0.519355000
1	3.619413000	-0.653560000	-0.726129000
1	2.223132000	0.107169000	-1.462562000
6	3.352925000	1.405815000	-0.163327000
1	3.936216000	1.358218000	0.762214000
1	4.011565000	1.785005000	-0.950625000
1	2.553705000	2.137693000	-0.009520000
1	2.231968000	-0.429460000	1.582018000

Part-XI: IRC Results

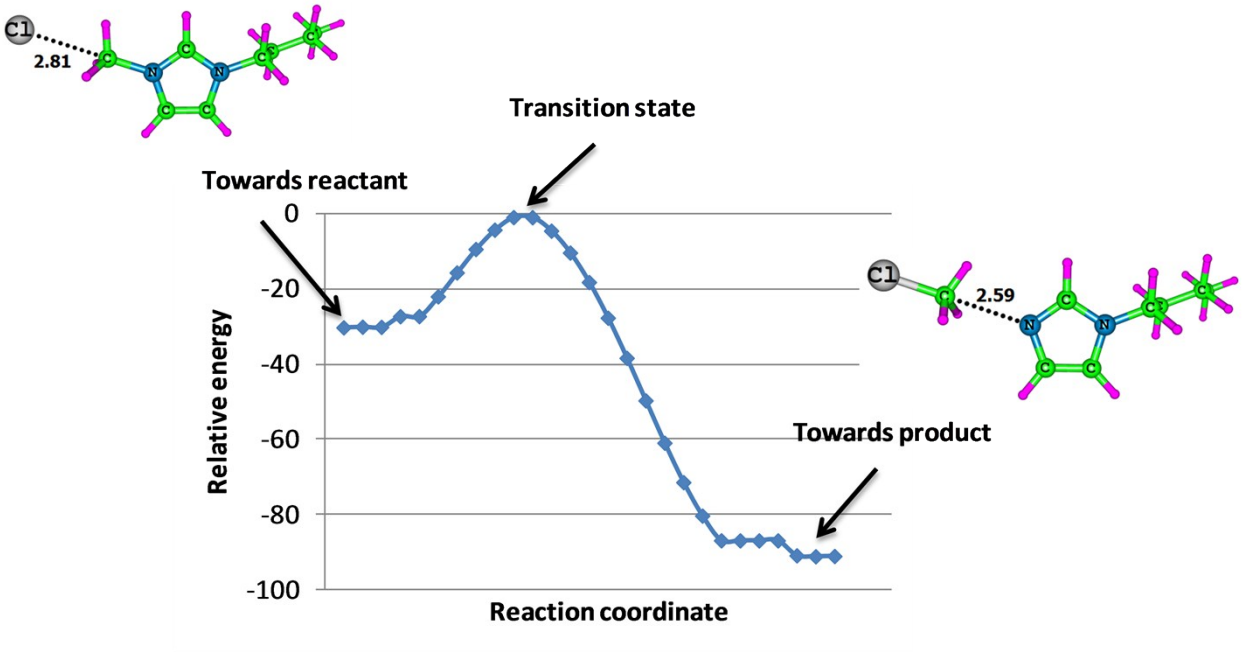


Fig. S12.IRC energy profile (in kJ/mol) for transition state given in Fig. 4a. Intermediate structures on the IRC profile are also shown (bond lengths in Å). These structures converge to the respective reactant (BMImCl) and products (Methylchloride and BIm).

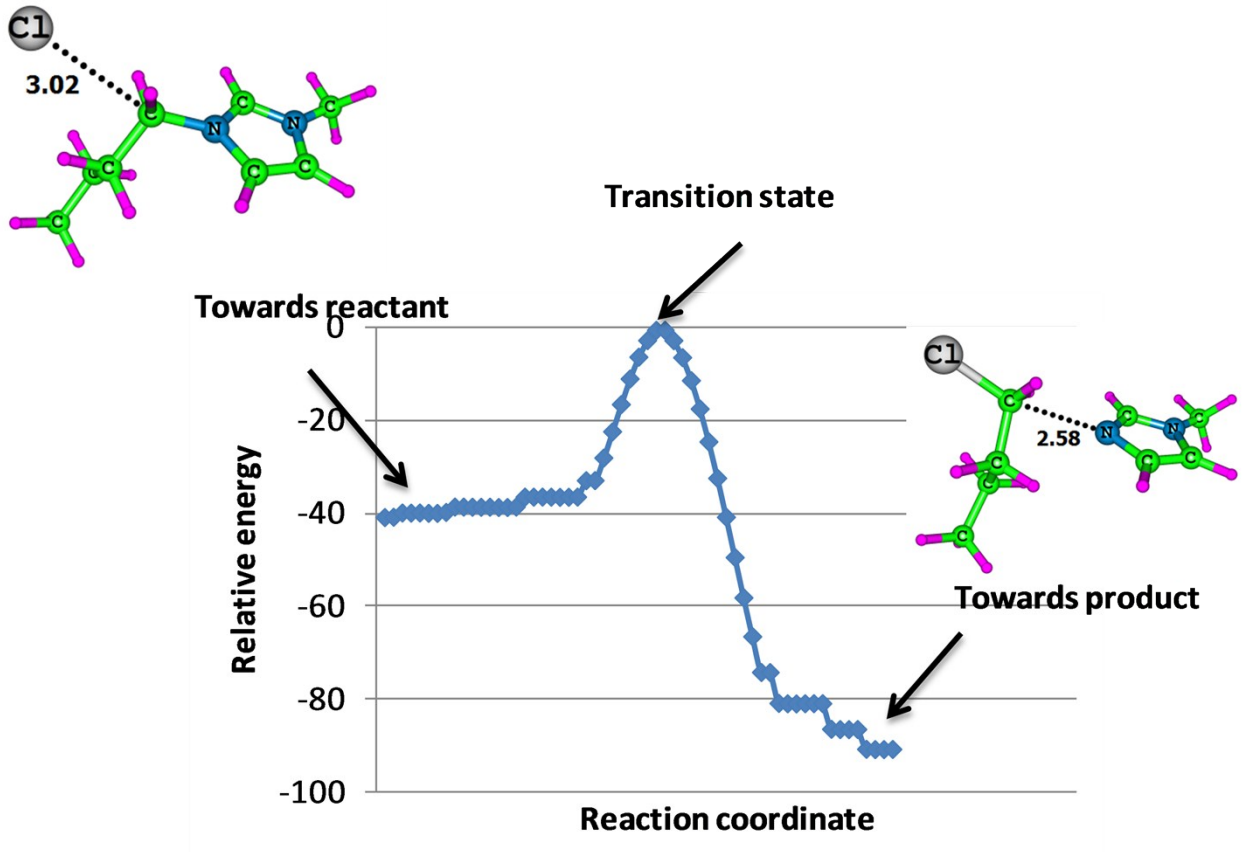


Fig. S13.IRC energy profile (in kJ/mol) for transition state given in Fig. 4b. Intermediate structures on the IRC profile are also shown (bond lengths in Å). These structures converge to the respective reactants (BMImCl) and products (Butylchloride and MIm).

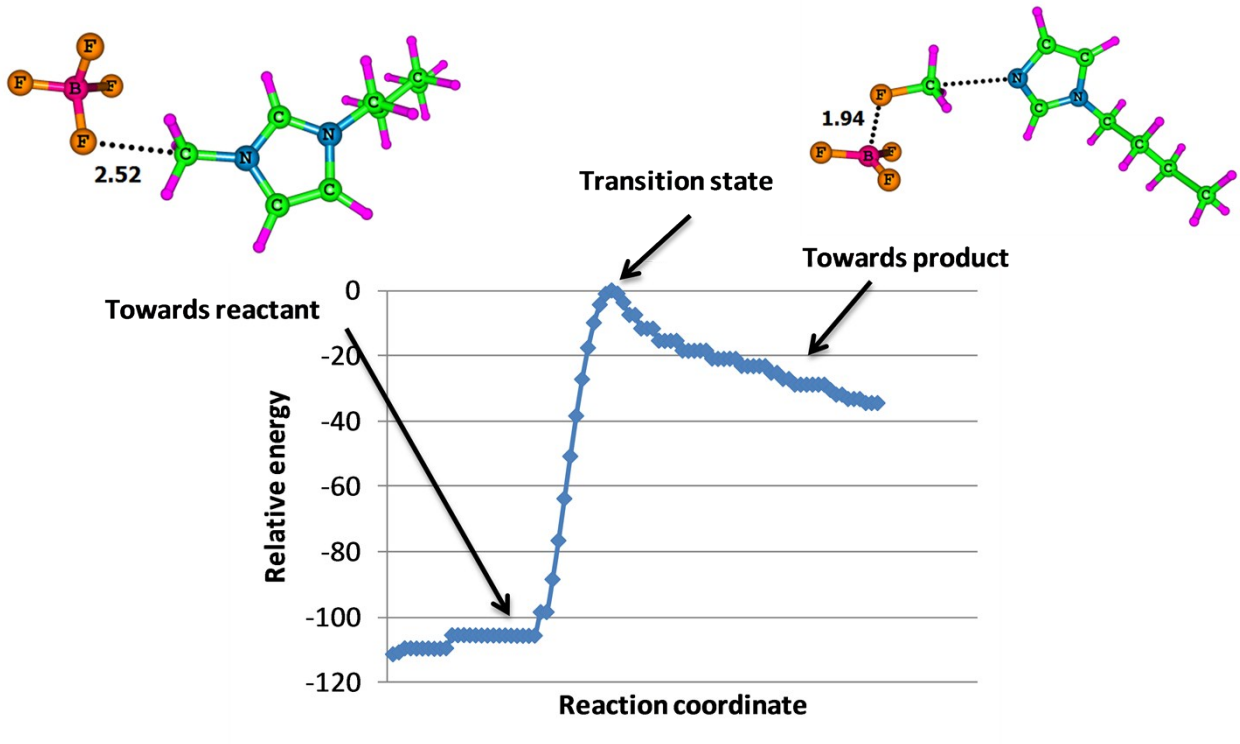


Fig. S14.IRC energy profile (in kJ/mol) for transition state Fig.6a. Intermediate structures on the IRC profile are also shown (bond lengths in Å). These structures converge to the respective reactants ($BMImBF_4$) and products (BF_3, Methylfluoride and BIm).

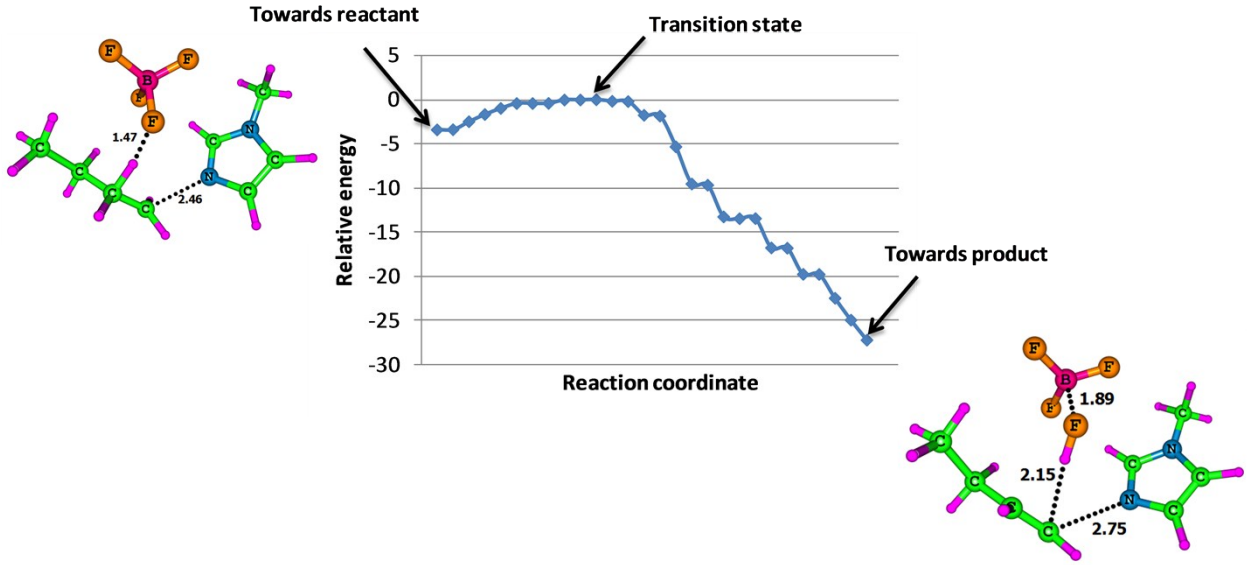


Fig. S15.IRC energy profile (in kJ/mol) for transition state Fig. 6b. Intermediate structures on the IRC profile are also shown (bond lengths in Å). These structures converge to the respective reactants ($BMImBF_4$) and products (Butene, HF, BF_3 and MIm).

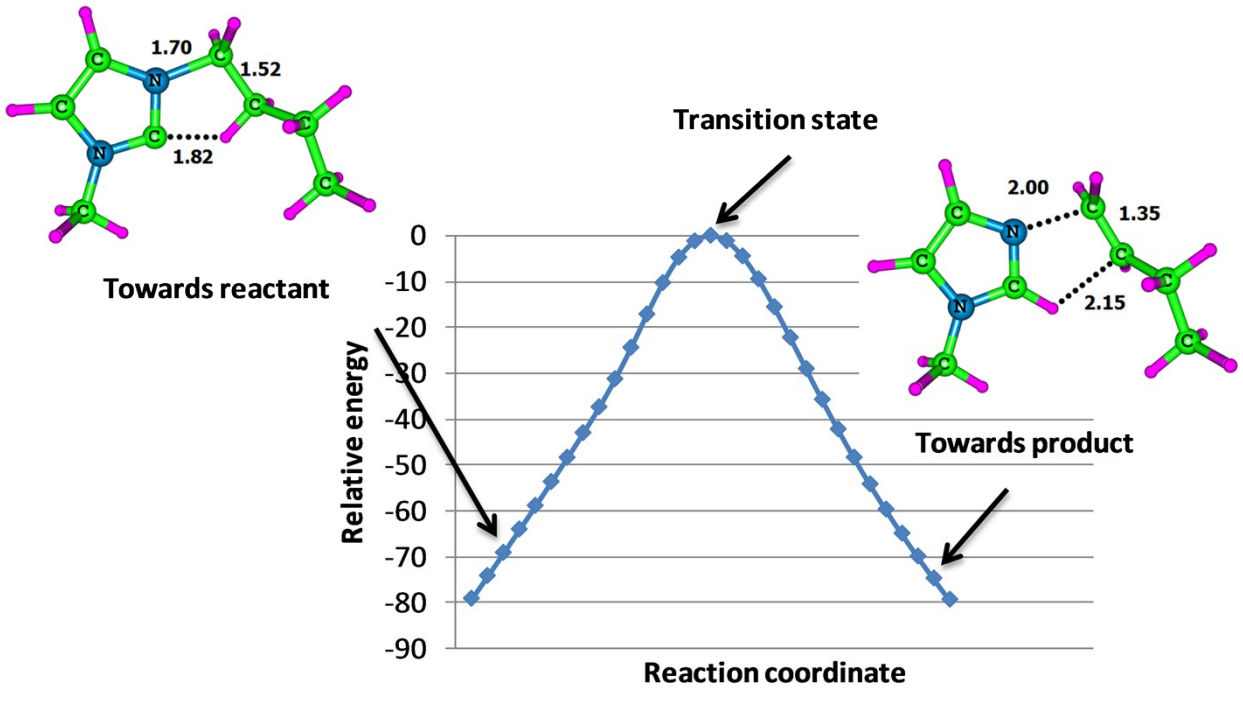


Fig. S16.IRC energy profile (in kJ/mol) for transition state given in Fig. 8g. Intermediate structures on the IRC profile are also shown (bond lengths in Å). These structures converge to the respective reactants (BMIm) and products (Butene and MIm).