Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

S_N2 fluorination reactions in ionic liquids: A mechanistic study toward solvent engineering

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1. Calculational Methods

Density functional theory method (MPW1K)[1,2] is employed with the 6-311++G** basis set and the effective core potential for Cs (Hay-Wadt VDZ(n+1)),[3] as implemented in GAUSSIAN 03 set of programs.[4] Stationary structures are confirmed by ascertaining that all the harmonic frequencies are real. Structures of the transition state (TS) are obtained by verifying that one and only one of the harmonic frequencies is imaginary, and also by carrying out the intrinsic reaction coordinate (IRC) analysis along the reaction pathway. Zero point energies (ZPE) are taken into account, and default criteria are used for all optimizations.

1 B. J. Lynch, P. I. Fast, M. Harris, D. G. Truhlar, *J. Phys. Chem. A* **2000**, *104*, 4811.

2 B. J. Lynch, Y. Zhao, D. G. Truhlar, *J. Chem. Phys*. **1998**, *108*, 664.

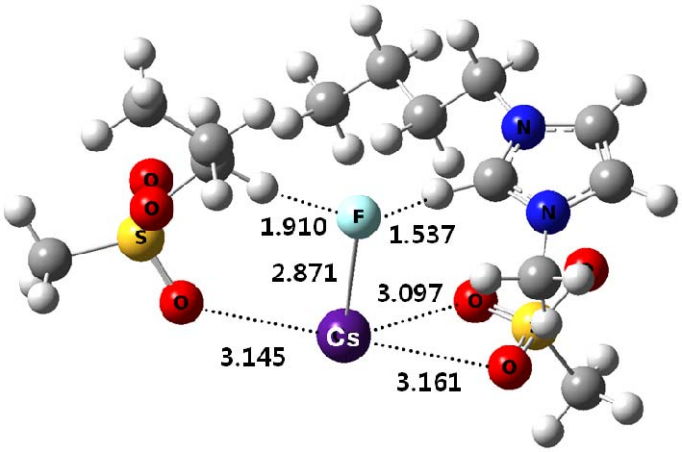
3 P. J. Hay, W. R. Wadt, *J. Chem. Phys*. **1985**, *82*, 299.

4 M. J. Frisch, et al., Gaussian, Inc., Wallingford CT, **2004**.

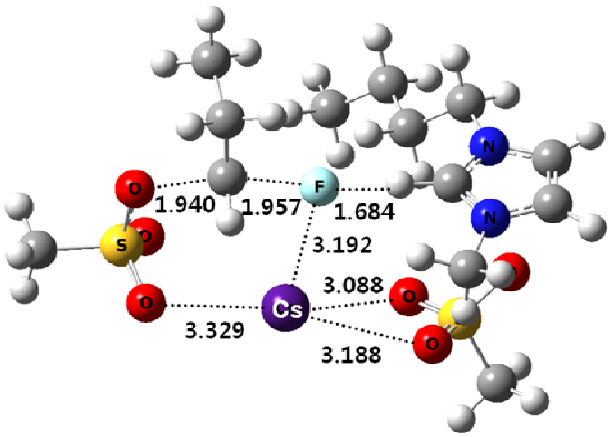
1. Figures and Tables

Fig. 1 (a) S_N2 Mechanism I in [bmim][OMs]

Pre-reaction complex



Transition state



Post-reaction complex

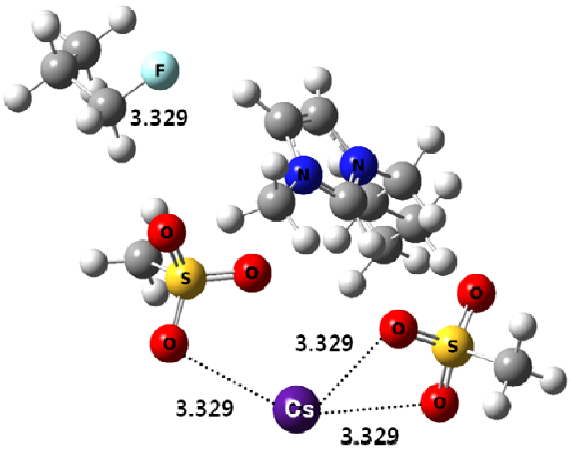
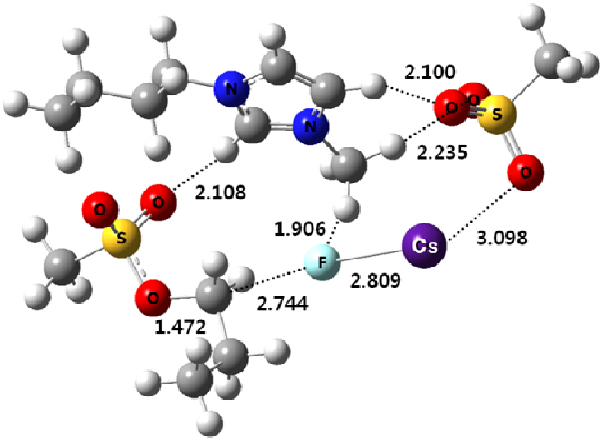
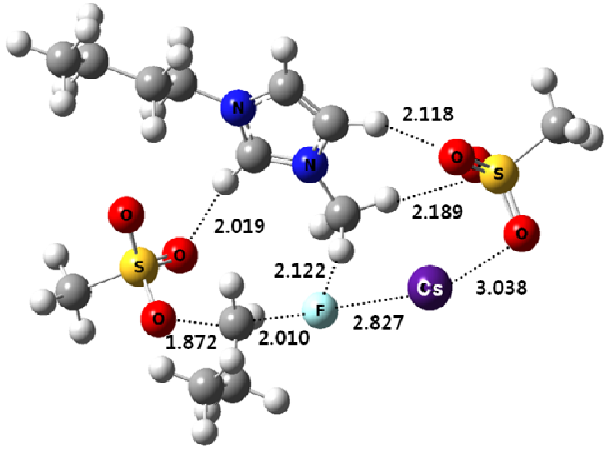


Fig. 1 (b) S_N2 Mechanism I in [bmim][OMs]

Pre-reaction complex



Transition state



Post-reaction complex

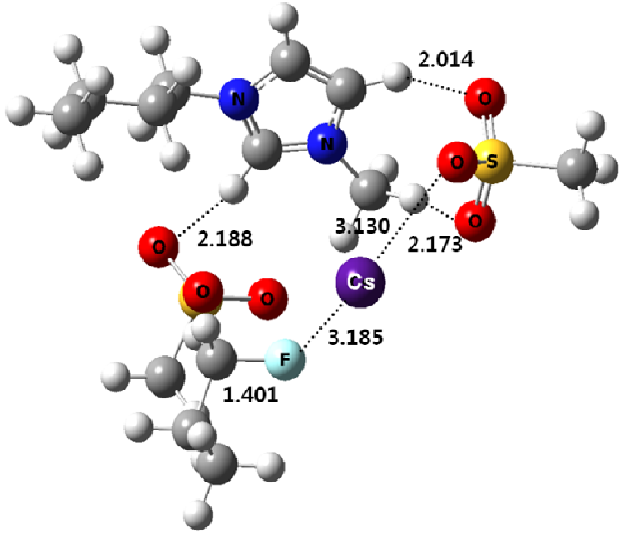
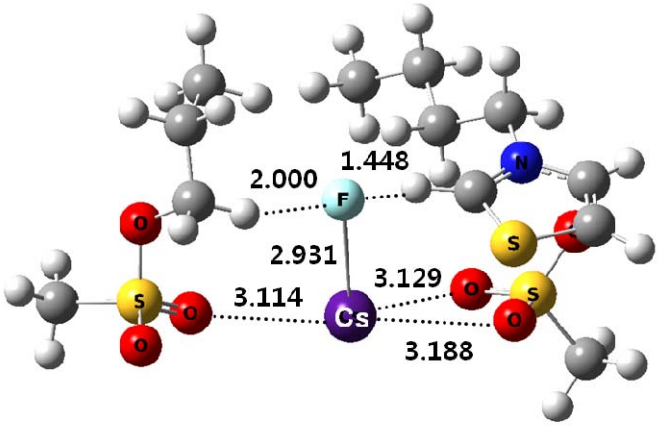
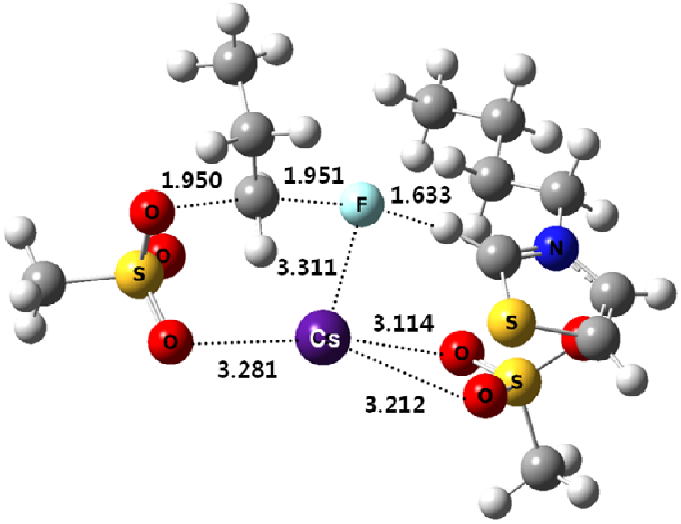


Fig. 2 (a) S_N2 Mechanism I in [*N*-butylthiazolium][OMs]

Pre-reaction complex



Transition state



Post-reaction complex

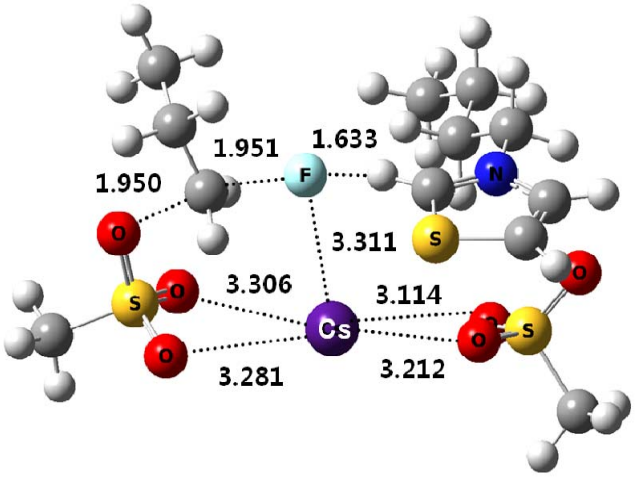
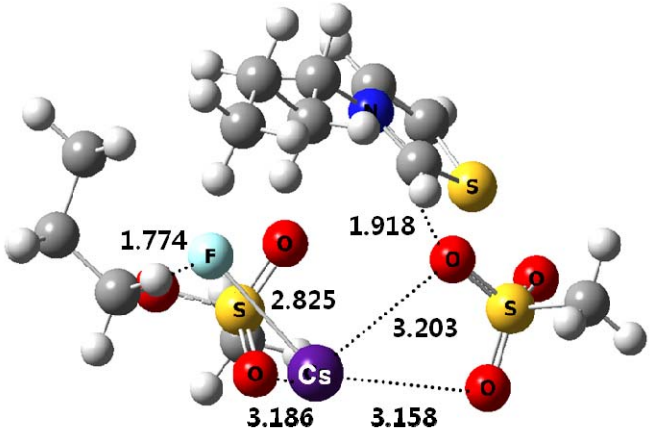
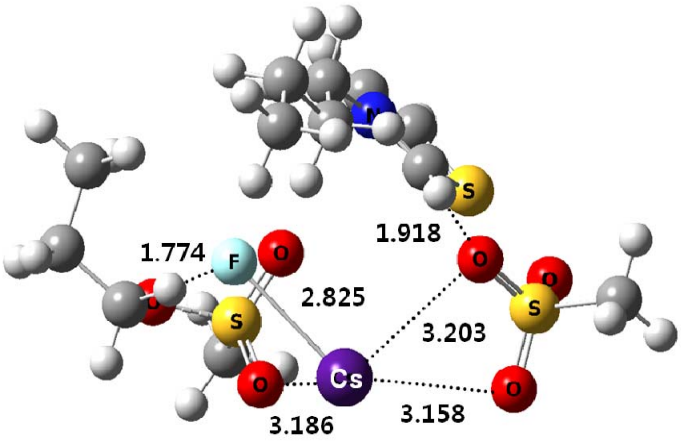


Fig. 2 (b) S_N2 Mechanism II in [*N*-butylthiazolium][OMs]

Pre-reaction complex



Transition state



Post-reaction complex

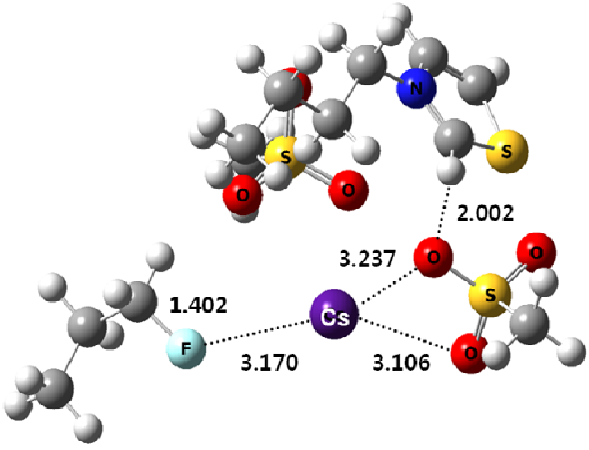
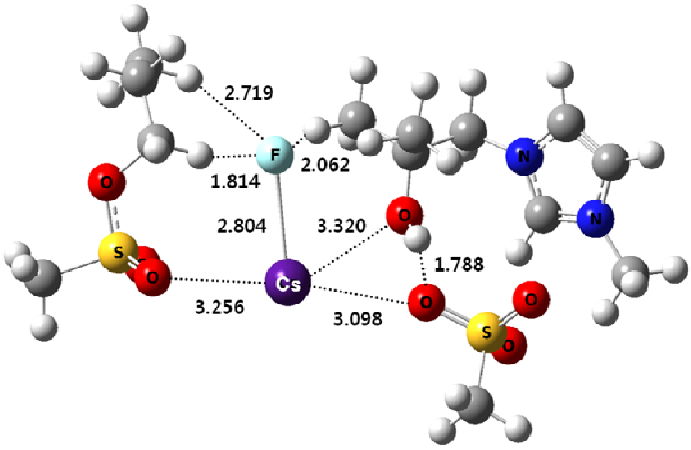
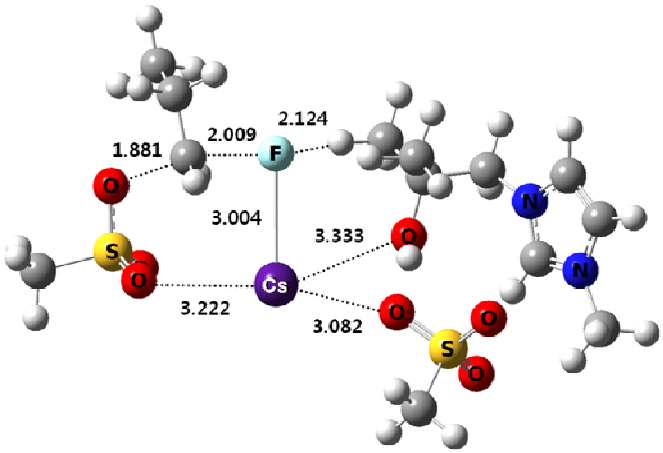


Fig. 3 (a) S_N2 Mechanism I in [mim-^{t}OH][OMs]

Pre-reaction complex



Transition state



Post-reaction complex

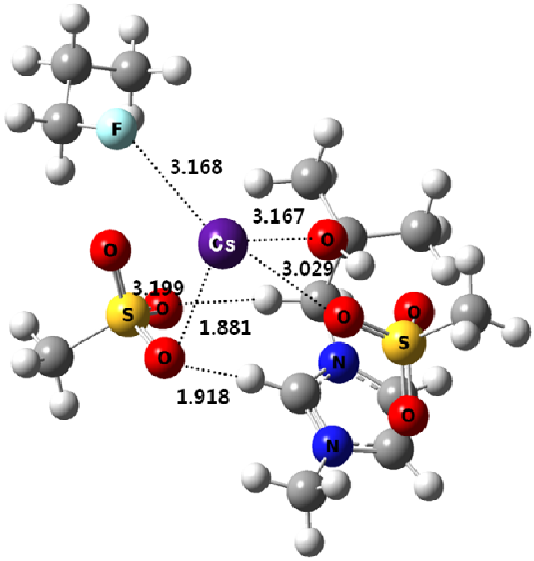
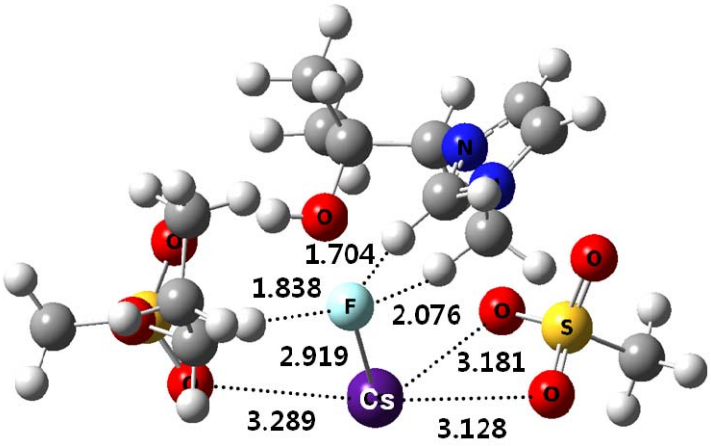
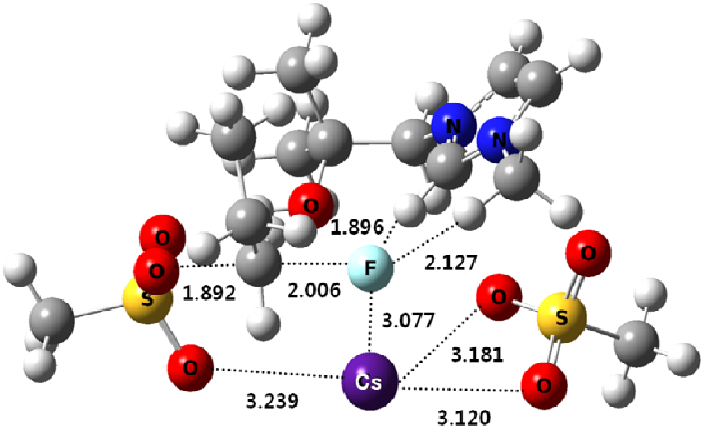


Fig. 3 (b) S_N2 Mechanism II in [mim-^{t}OH][OMs]

Pre-reaction complex



Transition state



Post-reaction complex

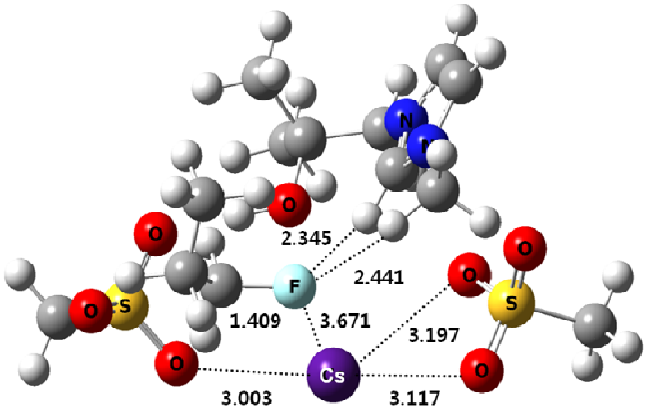
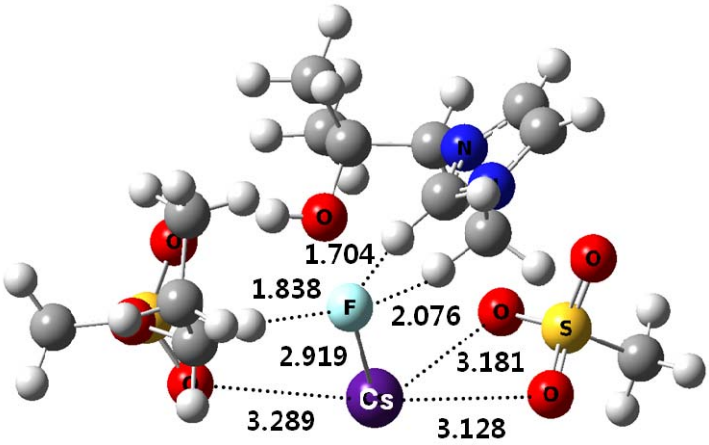
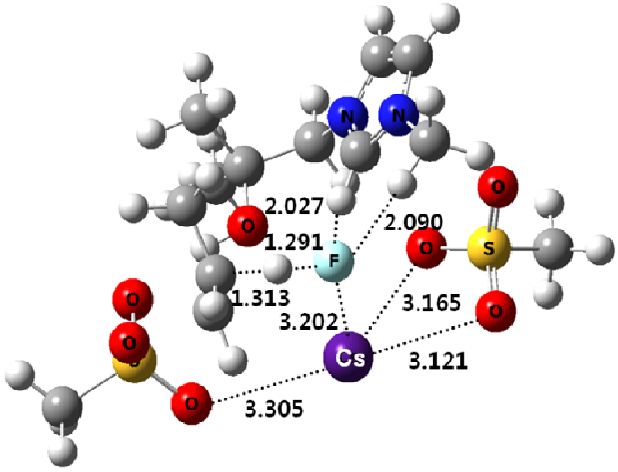


Fig. 3 (c) E2 mechanism in [mim-^{t}OH][OMs]

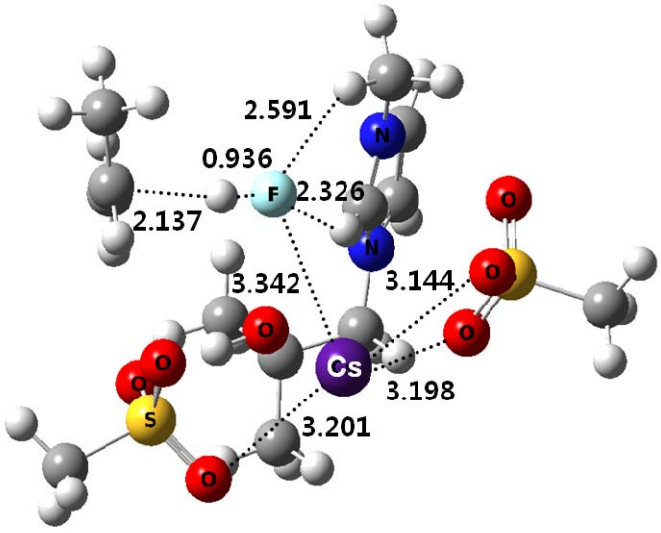
Pre-reaction complex



Transition state



Post-reaction complex



(1) Fig. 1 (a) : [Cs^+F^- + C_3H_7OMs → C_3H_7F + Cs^+OMs^-] in ionic liquid [bmim][OMs] (MPW1K/6-311++G**; ECP for Cs, Hay-Wadt VDZ(n+1)).

	Pre-reaction cplx	Transition state	Post-reaction cplx
E	-1989.24151	-1989.2082	-1989.272195
ZPE	0.438119	0.437122	0.439072
Gibbs(100℃)	0.334269	0.334151	0.33347

Pre-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.739445	2.956775	0.108872
2	6	0	-3.978224	2.562691	-1.156231
3	6	0	-1.924390	1.972572	-0.643175
4	7	0	-2.458944	2.578150	0.408650
5	1	0	-4.376613	3.435335	0.824309
6	1	0	-4.866729	2.620999	-1.750957
7	1	0	-0.884391	1.553552	-0.734062
8	7	0	-2.834892	1.963991	-1.604835
9	55	0	0.115233	-1.871519	-0.441135
10	9	0	0.512280	0.934588	-0.901859
11	1	0	5.384532	3.745457	-2.364301
12	6	0	5.182916	3.047409	-1.554945
13	1	0	5.297419	3.586734	-0.615603
14	1	0	5.944551	2.272100	-1.587941
15	6	0	3.792932	2.454866	-1.678295
16	1	0	3.039911	3.242387	-1.661983
17	1	0	3.675820	1.943655	-2.632705
18	6	0	3.424884	1.505266	-0.574370
19	1	0	3.566307	1.953289	0.406770
20	1	0	2.397426	1.151214	-0.684706
21	8	0	4.355268	0.379447	-0.663478
22	16	0	4.181051	-0.817478	0.338314
23	8	0	3.943639	-0.320826	1.665323
24	8	0	3.249508	-1.781645	-0.197388
25	6	0	5.803723	-1.487073	0.220873
26	1	0	5.819128	-2.372739	0.846350
27	1	0	5.995561	-1.745390	-0.813351
28	1	0	6.507514	-0.747960	0.582646
29	6	0	-1.797687	2.770106	1.691430
30	1	0	-1.175707	3.662336	1.632957
31	1	0	-2.584940	2.962895	2.415826
32	6	0	-0.980224	1.564626	2.105322
33	1	0	-0.190185	1.399427	1.372330
34	1	0	-1.620616	0.682138	2.089554
35	6	0	-0.373506	1.752072	3.484254
36	1	0	0.240880	2.654797	3.496748
37	1	0	-1.169004	1.912988	4.214604
38	6	0	0.468519	0.562973	3.906922
39	1	0	1.303463	0.409348	3.225817
40	1	0	0.878881	0.703631	4.904609
41	1	0	-0.127623	-0.347980	3.917839
42	16	0	-3.525313	-1.391885	0.048357
43	8	0	-2.919750	-1.601525	-1.281542
44	8	0	-2.547375	-1.629004	1.121194
45	8	0	-4.234243	-0.122226	0.163060
46	6	0	-4.754501	-2.659140	0.224786
47	1	0	-5.491984	-2.530848	-0.559210
48	1	0	-4.272806	-3.626350	0.138878

49	1	0	-5.214888	-2.549539	1.199967
50	6	0	-2.680788	1.246133	-2.852061
51	1	0	-3.051802	0.232650	-2.723534
52	1	0	-3.222892	1.768125	-3.633184
53	1	0	-1.626109	1.215412	-3.099587

Transition state

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.419880	2.006897	-0.756665
2	6	0	-4.344942	1.322565	-1.914660
3	6	0	-2.320909	1.487336	-1.094843
4	7	0	-3.148320	2.100980	-0.264250
5	1	0	-5.265575	2.401573	-0.231552
6	1	0	-5.112304	1.002821	-2.589696
7	1	0	-1.232460	1.400151	-0.996551
8	7	0	-3.027386	1.018479	-2.109562
9	55	0	0.836689	-1.688819	0.103169
10	9	0	0.447150	1.284934	-0.988639
11	1	0	2.933741	4.816487	-0.694649
12	6	0	2.809429	3.812560	-0.295517
13	1	0	1.967208	3.828830	0.393353
14	1	0	3.704836	3.557005	0.264834
15	6	0	2.576310	2.813482	-1.408758
16	1	0	1.673117	3.050370	-1.965875
17	1	0	3.403179	2.818538	-2.114978
18	6	0	2.398157	1.420792	-0.927978
19	1	0	2.234710	1.227551	0.111540
20	1	0	2.357615	0.622444	-1.639612
21	8	0	4.274252	1.022703	-0.638394
22	16	0	4.392916	-0.375888	-0.099678
23	8	0	3.741096	-0.505739	1.200010
24	8	0	3.934871	-1.364354	-1.071365
25	6	0	6.129049	-0.589021	0.128316
26	1	0	6.285073	-1.588342	0.518590
27	1	0	6.615719	-0.471475	-0.832275
28	1	0	6.473586	0.156760	0.834383
29	6	0	-2.773762	2.705596	1.007687
30	1	0	-2.455422	3.730937	0.825036
31	1	0	-3.680613	2.740251	1.605390
32	6	0	-1.699931	1.917163	1.726132
33	1	0	-0.790628	1.911304	1.124808
34	1	0	-2.026189	0.881795	1.821541
35	6	0	-1.401996	2.503531	3.094438
36	1	0	-1.097356	3.547185	2.992233
37	1	0	-2.314007	2.507896	3.694141
38	6	0	-0.322544	1.727845	3.824918
39	1	0	0.614342	1.740550	3.270378
40	1	0	-0.129219	2.149187	4.808815
41	1	0	-0.615193	0.688092	3.956700
42	16	0	-2.869146	-1.871832	0.364383
43	8	0	-2.156976	-2.113864	-0.906384
44	8	0	-1.925458	-1.725217	1.482351
45	8	0	-3.848300	-0.792973	0.275427
46	6	0	-3.791086	-3.350041	0.694292
47	1	0	-4.493014	-3.503233	-0.117302
48	1	0	-3.100464	-4.182679	0.761867
49	1	0	-4.318011	-3.216717	1.632042
50	6	0	-2.491208	0.156414	-3.142666
51	1	0	-2.544288	-0.873256	-2.799623
52	1	0	-3.060442	0.300727	-4.054112
53	1	0	-1.456561	0.428035	-3.315884

Post-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.687732	2.723588	-0.437322
2	6	0	2.280930	1.814090	-1.237643
3	6	0	0.124293	1.439377	-1.259733
4	7	0	0.340431	2.476378	-0.471405
5	1	0	2.106153	3.518592	0.146146
6	1	0	3.311662	1.643448	-1.481328
7	1	0	-0.833724	0.985246	-1.475597
8	7	0	1.281674	1.032163	-1.748849
9	55	0	-2.040928	-2.239439	0.477132
10	9	0	5.130889	0.519180	-2.044099
11	1	0	7.301289	0.732876	1.220340
12	6	0	6.420865	0.618416	0.592368
13	1	0	6.199136	1.587874	0.152802
14	1	0	5.584629	0.340820	1.231231
15	6	0	6.649577	-0.425737	-0.483367
16	1	0	7.497804	-0.147388	-1.108779
17	1	0	6.899504	-1.385178	-0.028257
18	6	0	5.447150	-0.655685	-1.354360
19	1	0	4.567821	-0.931129	-0.777916
20	1	0	5.641328	-1.412850	-2.110278
21	8	0	2.568979	-1.350218	0.117760
22	16	0	1.515116	-1.477486	1.124386
23	8	0	0.492918	-0.418665	1.026222
24	8	0	0.897451	-2.808309	1.174297
25	6	0	2.310858	-1.245733	2.692518
26	1	0	1.565376	-1.333302	3.474413
27	1	0	3.068516	-2.012711	2.804962
28	1	0	2.760378	-0.259467	2.705581
29	6	0	-0.685840	3.158499	0.304645
30	1	0	-0.579026	4.226979	0.127259
31	1	0	-1.644626	2.841808	-0.098858
32	6	0	-0.585586	2.829257	1.780730
33	1	0	0.362134	3.194165	2.182240
34	1	0	-0.569762	1.745963	1.892484
35	6	0	-1.739680	3.433596	2.559497
36	1	0	-1.752159	4.515803	2.415989
37	1	0	-2.678039	3.061815	2.147916
38	6	0	-1.667431	3.120967	4.041525
39	1	0	-0.751686	3.510846	4.483969
40	1	0	-2.506364	3.556635	4.579452
41	1	0	-1.684523	2.046327	4.215221
42	16	0	-3.584942	0.518924	-1.409111
43	8	0	-2.379209	-0.184585	-1.908112
44	8	0	-4.252386	-0.261747	-0.363649
45	8	0	-3.293312	1.901494	-1.039677
46	6	0	-4.709368	0.591625	-2.774564
47	1	0	-4.237396	1.148578	-3.575517
48	1	0	-4.933180	-0.420039	-3.092251
49	1	0	-5.609555	1.094409	-2.440632
50	6	0	1.462095	-0.130541	-2.592454
51	1	0	0.486614	-0.456562	-2.934194
52	1	0	2.076987	0.136061	-3.445258
53	1	0	1.937121	-0.909938	-2.004898

(2) Fig. 1 (b) : [Cs^+F^- + C_3H_7OMs → C_3H_7F + Cs^+OMs^-] in ionic liquid [bmim][OMs] (MPW1K/6-311++G**; ECP for Cs, Hay-Wadt VDZ(n+1)).

	Pre-reaction cplx	Transition state	Post-reaction cplx
E	-1989.226073	-1989.205291	-1989.274606
ZPE	0.438623	0.437756	0.438995
Gibbs(100℃)	0.332012	0.336881	0.333846

Pre-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.374729	-2.132874	-0.466612
2	1	0	-2.103943	-1.381607	0.266245
3	1	0	-1.832661	-1.943581	-1.383700
4	6	0	-2.125063	-3.514253	0.055809
5	1	0	-2.423264	-4.244884	-0.696459
6	1	0	-1.042390	-3.550871	0.158470
7	6	0	-2.808721	-3.798817	1.377823
8	1	0	-3.891139	-3.726523	1.295332
9	1	0	-2.569075	-4.799516	1.730971
10	1	0	-2.483174	-3.091901	2.139356
11	8	0	-3.812343	-2.022479	-0.764404
12	16	0	-4.371552	-0.611459	-1.138046
13	8	0	-4.559344	0.195002	0.041257
14	8	0	-3.579902	-0.029829	-2.199789
15	6	0	-5.934972	-1.107071	-1.769564
16	1	0	-6.455306	-0.200147	-2.056855
17	1	0	-5.772902	-1.748257	-2.626920
18	1	0	-6.470739	-1.624047	-0.982829
19	55	0	2.857047	-1.587000	1.165585
20	9	0	0.292180	-1.720297	0.028955
21	6	0	-2.481676	2.947696	0.106286
22	6	0	-0.996072	1.477268	-1.208369
23	6	0	0.034874	2.815257	0.175571
24	6	0	0.967705	2.063842	-0.451165
25	7	0	0.296784	1.244338	-1.314610
26	7	0	-1.187597	2.435501	-0.313143
27	6	0	-2.795994	2.611494	1.549208
28	6	0	-4.165862	3.123355	1.954147
29	1	0	-4.912022	2.683540	1.293183
30	1	0	-4.212024	4.204317	1.807783
31	1	0	6.653396	1.792275	0.240750
32	6	0	6.127706	1.965198	-0.691033
33	16	0	4.675846	0.951128	-0.715561
34	1	0	6.746453	1.684810	-1.535601
35	1	0	5.821776	3.001765	-0.771707
36	8	0	3.867823	1.355872	0.456355
37	8	0	5.138693	-0.434493	-0.584156
38	8	0	3.990759	1.237980	-1.973407
39	1	0	-1.779528	0.967802	-1.742751
40	1	0	2.039005	2.021845	-0.330929
41	1	0	0.141667	3.580616	0.917303
42	1	0	-3.225839	2.504826	-0.547731
43	1	0	-2.485768	4.023761	-0.057027
44	1	0	-2.032949	3.036299	2.203078
45	1	0	-2.760203	1.530279	1.670197
46	6	0	-4.504702	2.789634	3.393760
47	1	0	-3.783888	3.227982	4.082525
48	1	0	-5.489428	3.163581	3.664116

49	1	0	-4.503823	1.713024	3.552606
50	6	0	0.890073	0.179447	-2.113866
51	1	0	0.356504	0.118437	-3.056585
52	1	0	1.929224	0.436269	-2.293980
53	1	0	0.780934	-0.743451	-1.533430

Transition state

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.375862	2.435150	-0.238121
2	1	0	1.480470	1.686134	0.519424
3	1	0	1.136580	2.123988	-1.234935
4	6	0	1.294352	3.877013	0.122444
5	1	0	1.895689	4.437356	-0.589455
6	1	0	0.256926	4.158571	-0.030774
7	6	0	1.730845	4.168909	1.542221
8	1	0	2.765006	3.871595	1.696251
9	1	0	1.647514	5.230486	1.764782
10	1	0	1.109402	3.627819	2.253111
11	8	0	3.215834	2.433210	-0.583258
12	16	0	3.835010	1.203374	-1.184917
13	8	0	4.123833	0.176935	-0.193063
14	8	0	3.056166	0.716144	-2.321422
15	6	0	5.373615	1.807474	-1.804361
16	1	0	5.892309	0.972557	-2.261719
17	1	0	5.167082	2.578475	-2.536575
18	1	0	5.942211	2.203656	-0.971639
19	55	0	-3.151260	1.463941	1.096695
20	9	0	-0.563399	2.045717	0.117330
21	6	0	3.156585	-2.879486	0.014153
22	6	0	1.424818	-1.543527	-1.118141
23	6	0	0.652402	-2.932460	0.381175
24	6	0	-0.400010	-2.267299	-0.146998
25	7	0	0.112108	-1.411307	-1.084038
26	7	0	1.783837	-2.464818	-0.238180
27	6	0	3.591714	-2.634821	1.443258
28	6	0	5.046302	-3.021939	1.644630
29	1	0	5.662551	-2.427243	0.970369
30	1	0	5.192035	-4.066045	1.360296
31	1	0	-6.135074	-2.461192	0.368878
32	6	0	-5.596770	-2.671979	-0.547849
33	16	0	-4.290611	-1.488433	-0.721691
34	1	0	-6.252320	-2.569119	-1.405006
35	1	0	-5.162539	-3.664323	-0.519110
36	8	0	-3.427799	-1.637795	0.473741
37	8	0	-4.940716	-0.172047	-0.733920
38	8	0	-3.586353	-1.825009	-1.953544
39	1	0	2.091467	-0.956518	-1.731962
40	1	0	-1.458772	-2.302437	0.063163
41	1	0	0.687675	-3.693707	1.133975
42	1	0	3.780561	-2.297408	-0.655656
43	1	0	3.245166	-3.931572	-0.251667
44	1	0	2.962277	-3.201276	2.131610
45	1	0	3.460031	-1.577630	1.664949
46	6	0	5.513837	-2.815786	3.072213
47	1	0	4.939075	-3.424155	3.769025
48	1	0	6.561420	-3.085005	3.186304
49	1	0	5.404767	-1.775265	3.371656
50	6	0	-0.650018	-0.448447	-1.867536
51	1	0	-0.098348	-0.241168	-2.777288
52	1	0	-1.615066	-0.885541	-2.105651
53	1	0	-0.759107	0.466272	-1.286103

Post-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.723649	-2.179926	-0.969905
2	1	0	3.902438	-2.125345	-2.042187
3	1	0	3.490935	-1.194718	-0.577530
4	6	0	4.872760	-2.823956	-0.249430
5	1	0	5.722720	-2.145483	-0.335113
6	1	0	4.631358	-2.880459	0.811833
7	6	0	5.235736	-4.194980	-0.785364
8	1	0	5.524275	-4.141960	-1.834021
9	1	0	6.068518	-4.623977	-0.233581
10	1	0	4.394940	-4.879362	-0.706888
11	8	0	2.242933	0.346921	0.503855
12	16	0	1.820431	1.063855	1.715363
13	8	0	1.790940	2.519950	1.555994
14	8	0	0.551847	0.529932	2.241549
15	6	0	3.049820	0.730822	2.945890
16	1	0	2.759294	1.233862	3.860768
17	1	0	3.102185	-0.340481	3.102145
18	1	0	3.999511	1.112610	2.589273
19	55	0	-0.220881	-1.730039	0.119642
20	9	0	2.569212	-2.955696	-0.805780
21	6	0	0.245686	4.044957	-0.711661
22	6	0	-1.077580	2.779932	0.936421
23	6	0	-1.980922	2.897564	-1.049162
24	6	0	-2.782573	2.131177	-0.278692
25	7	0	-2.194258	2.074367	0.958564
26	7	0	-0.922290	3.294240	-0.271174
27	6	0	1.095450	3.253146	-1.683627
28	6	0	2.333765	4.027789	-2.095468
29	1	0	2.903798	4.279984	-1.201134
30	1	0	2.042469	4.973836	-2.556324
31	1	0	-4.511207	-3.688818	-0.571062
32	6	0	-5.027261	-2.748636	-0.727419
33	16	0	-3.853400	-1.429243	-0.592093
34	1	0	-5.792163	-2.602549	0.026275
35	1	0	-5.459898	-2.712494	-1.720486
36	8	0	-2.827835	-1.680356	-1.611828
37	8	0	-3.280462	-1.524287	0.766152
38	8	0	-4.611846	-0.195620	-0.797226
39	1	0	-0.362127	2.869243	1.731765
40	1	0	-3.669528	1.561009	-0.511559
41	1	0	-2.068484	3.175186	-2.080092
42	1	0	0.823783	4.268068	0.178370
43	1	0	-0.103986	4.977321	-1.150587
44	1	0	0.510270	2.995163	-2.568056
45	1	0	1.392932	2.323101	-1.201397
46	6	0	3.211355	3.243479	-3.051402
47	1	0	2.675531	2.995368	-3.966508
48	1	0	4.096900	3.809976	-3.330307
49	1	0	3.540466	2.311485	-2.596131
50	6	0	-2.692630	1.341915	2.110639
51	1	0	-3.458179	1.926092	2.611733
52	1	0	-3.100814	0.393528	1.772075
53	1	0	-1.855211	1.157193	2.773511

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(3) Fig. 2 (a) : [Cs^+F^- + C_3H_7OMs → C_3H_7F + Cs^+OMs^-] in ionic liquid [*N*-butylthiazolium][OMs]. (MPW1K/6-311++G**; ECP for Cs, Hay-Wadt VDZ(n+1)).

	Pre-reaction cplx	Transition state	Post-reaction cplx
E	-2292.773957	-2292.739291	-2292.799273
ZPE	0.392128	0.391759	0.393405
Gibbs(100℃)	0.290543	0.292835	0.289975

Pre-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.991835	1.708672	-1.211864
2	6	0	-3.847899	1.404871	-2.508164
3	6	0	-1.732781	1.668283	-1.320098
4	7	0	-2.789268	1.868261	-0.566493
5	1	0	-4.901614	1.790533	-0.649930
6	1	0	-4.619453	1.208417	-3.226762
7	1	0	-0.630992	1.638756	-0.985013
8	55	0	0.321519	-1.547669	-0.005870
9	9	0	0.728240	1.286944	-0.629534
10	1	0	3.263785	4.125909	1.333509
11	6	0	3.223649	3.089257	1.006177
12	1	0	2.183503	2.774625	0.962623
13	1	0	3.733328	2.484184	1.752560
14	6	0	3.862627	2.924676	-0.358522
15	1	0	3.354788	3.562901	-1.081458
16	1	0	4.908678	3.231791	-0.345740
17	6	0	3.751471	1.524073	-0.891194
18	1	0	2.714002	1.191067	-0.848139
19	1	0	4.147007	1.436555	-1.899198
20	8	0	4.576644	0.677306	-0.032607
21	16	0	4.580967	-0.871325	-0.298615
22	8	0	3.419080	-1.482175	0.303956
23	8	0	4.825374	-1.135122	-1.688682
24	6	0	5.995507	-1.286800	0.659875
25	1	0	6.104746	-2.363809	0.596855
26	1	0	6.857330	-0.787089	0.235759
27	1	0	5.821237	-0.978313	1.683321
28	6	0	-2.742000	2.280093	0.843775
29	1	0	-2.678301	3.367660	0.854869
30	1	0	-3.690942	1.970691	1.267303
31	6	0	-1.612310	1.659822	1.630250
32	1	0	-0.657120	1.826235	1.133803
33	1	0	-1.784355	0.585772	1.680426
34	6	0	-1.570763	2.223692	3.040123
35	1	0	-1.398427	3.301094	3.000262
36	1	0	-2.541411	2.082704	3.517983
37	6	0	-0.495133	1.568043	3.884612
38	1	0	0.489440	1.706849	3.440759
39	1	0	-0.469324	1.986101	4.888602
40	1	0	-0.674524	0.498216	3.974548
41	16	0	-3.387451	-1.511068	0.469930
42	8	0	-2.747655	-1.387652	-0.851525
43	8	0	-2.400818	-1.850095	1.506052
44	8	0	-4.230177	-0.364861	0.812033
45	6	0	-4.482691	-2.900737	0.362909

46	1	0	-5.220384	-2.695313	-0.404190
47	1	0	-3.903441	-3.780448	0.107277
48	1	0	-4.962249	-3.028112	1.326514
49	16	0	-2.183814	1.287494	-2.895285

Transition state

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.072062	1.475224	-1.203947
2	6	0	-3.819565	1.284641	-2.506223
3	6	0	-1.840489	1.766882	-1.190896
4	7	0	-2.941449	1.763762	-0.481188
5	1	0	-5.010278	1.385000	-0.692710
6	1	0	-4.515797	1.027269	-3.280343
7	1	0	-0.816473	1.917880	-0.803984
8	55	0	0.644507	-1.483150	0.080042
9	9	0	0.759327	1.791622	-0.395595
10	1	0	3.911707	4.612944	0.481876
11	6	0	3.599580	3.585435	0.652845
12	1	0	2.800421	3.597556	1.391063
13	1	0	4.442324	3.039110	1.067794
14	6	0	3.132591	2.941940	-0.635344
15	1	0	2.278748	3.472027	-1.050393
16	1	0	3.919036	2.956864	-1.386180
17	6	0	2.691721	1.534950	-0.468869
18	1	0	2.535394	1.134643	0.511268
19	1	0	2.470687	0.944336	-1.333751
20	8	0	4.469679	0.734269	-0.435535
21	16	0	4.333159	-0.747982	-0.237356
22	8	0	3.770494	-1.067065	1.071423
23	8	0	3.600412	-1.368932	-1.338297
24	6	0	5.996654	-1.332459	-0.281586
25	1	0	5.967852	-2.407331	-0.143604
26	1	0	6.420549	-1.079882	-1.245893
27	1	0	6.545263	-0.856978	0.522423
28	6	0	-3.012449	2.061796	0.957591
29	1	0	-3.144307	3.138727	1.053066
30	1	0	-3.902381	1.553000	1.310211
31	6	0	-1.814086	1.582099	1.740842
32	1	0	-0.889738	1.993358	1.337088
33	1	0	-1.765475	0.497459	1.657264
34	6	0	-1.949872	1.961024	3.205889
35	1	0	-2.007348	3.047079	3.301377
36	1	0	-2.888173	1.564763	3.595777
37	6	0	-0.796832	1.436819	4.039519
38	1	0	0.155690	1.824513	3.681914
39	1	0	-0.901151	1.724182	5.083219
40	1	0	-0.752969	0.350203	3.998176
41	16	0	-3.096554	-1.699287	0.273845
42	8	0	-2.387146	-1.359771	-0.973616
43	8	0	-2.148911	-1.996002	1.356568
44	8	0	-4.117274	-0.714799	0.637112
45	6	0	-3.970743	-3.207101	-0.045313
46	1	0	-4.673739	-3.030442	-0.851126
47	1	0	-3.254910	-3.970849	-0.326431
48	1	0	-4.494194	-3.491865	0.859964
49	16	0	-2.142052	1.434122	-2.807738

Post-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.457094	2.220423	1.519913
2	6	0	0.277575	2.238756	2.160908
3	6	0	0.091814	1.568264	-0.138891
4	7	0	1.323373	1.850687	0.206838
5	1	0	2.438196	2.395700	1.917269
6	1	0	0.097125	2.466234	3.193790
7	1	0	-0.187938	1.196615	-1.115947
8	55	0	0.249953	-2.807097	-0.655512
9	9	0	-3.610155	1.370198	2.877029
10	1	0	-6.059549	3.126498	0.351733
11	6	0	-5.171638	2.614483	0.716318
12	1	0	-4.618721	3.313240	1.339785
13	1	0	-4.547536	2.356128	-0.136521
14	6	0	-5.543816	1.369863	1.499253
15	1	0	-6.174307	1.623577	2.351797
16	1	0	-6.124104	0.692447	0.871040
17	6	0	-4.347413	0.598846	1.981181
18	1	0	-3.688898	0.343114	1.155059
19	1	0	-4.638054	-0.304000	2.513618
20	8	0	-2.638229	0.650856	-1.035274
21	16	0	-2.226882	-0.401185	-1.969081
22	8	0	-0.797335	-0.273713	-2.332948
23	8	0	-2.544738	-1.757825	-1.519829
24	6	0	-3.143156	-0.134743	-3.459174
25	1	0	-2.845273	-0.884047	-4.183213
26	1	0	-4.197540	-0.228822	-3.226467
27	1	0	-2.920496	0.860658	-3.825136
28	6	0	2.456180	1.765670	-0.714816
29	1	0	3.212985	1.173720	-0.205988
30	1	0	2.108471	1.211464	-1.581622
31	6	0	2.963415	3.135643	-1.115340
32	1	0	3.270535	3.686559	-0.225406
33	1	0	2.155491	3.706837	-1.574847
34	6	0	4.135034	3.032545	-2.075330
35	1	0	4.928215	2.445582	-1.611659
36	1	0	3.825353	2.478944	-2.962904
37	6	0	4.673286	4.389584	-2.484624
38	1	0	5.026831	4.949492	-1.620450
39	1	0	5.506156	4.290533	-3.176530
40	1	0	3.905756	4.987044	-2.973950
41	16	0	2.654870	-1.252825	1.677259
42	8	0	1.207318	-0.972932	1.665105
43	8	0	2.993543	-2.320835	0.727889
44	8	0	3.467691	-0.043947	1.531701
45	6	0	3.025321	-1.889153	3.289430
46	1	0	2.767849	-1.133783	4.022758
47	1	0	2.442136	-2.788400	3.450406
48	1	0	4.085384	-2.111388	3.328834
49	16	0	-0.992730	1.750003	1.121224

(4) Fig. 2 (b) : [Cs^+F^- + C_3H_7OMs → C_3H_7F + Cs^+OMs^-] in ionic liquid [*N*-butylthiazolium][OMs]. (MPW1K/6-311++G**; ECP for Cs, Hay-Wadt VDZ(n+1)).

	Pre-reaction cplx	Transition state	Post-reaction cplx
E	-2292.757755	-2292.73292	-2292.802589
ZPE	0.393305	0.392448	0.393691
Gibbs(100℃)	0.294117	0.296076	0.292021

Pre-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.741257	-1.210710	-0.328823
2	1	0	-2.819078	-1.297764	0.266127
3	1	0	-3.917676	-2.118284	-0.900045
4	6	0	-4.914514	-0.863924	0.543047
5	1	0	-5.807274	-0.716906	-0.066329
6	1	0	-5.099148	-1.740837	1.163978
7	6	0	-4.654899	0.341438	1.424752
8	1	0	-4.487219	1.232346	0.822955
9	1	0	-5.498063	0.535908	2.084318
10	1	0	-3.769231	0.167692	2.031626
11	8	0	-3.612713	-0.133300	-1.318984
12	16	0	-2.206960	0.198691	-1.926394
13	8	0	-1.564450	1.245776	-1.177298
14	8	0	-1.469364	-1.016868	-2.169545
15	6	0	-2.744175	0.862132	-3.466962
16	1	0	-1.852858	1.177621	-3.998009
17	1	0	-3.264399	0.086508	-4.014960
18	1	0	-3.392946	1.706734	-3.269383
19	55	0	0.682861	-2.420804	-0.286646
20	9	0	-1.429954	-1.505606	1.350280
21	6	0	-0.548307	2.170919	2.288034
22	6	0	1.075951	2.164637	0.421538
23	6	0	-0.465819	3.796993	0.426140
24	6	0	0.220185	4.130714	-0.676279
25	7	0	0.041822	2.679597	1.038933
26	6	0	-0.076226	0.799586	2.693338
27	6	0	-0.665128	0.419243	4.042908
28	1	0	-1.749071	0.539863	4.004786
29	1	0	-0.301741	1.094233	4.822183
30	1	0	5.440402	-1.193091	0.651911
31	6	0	5.303795	-0.237523	0.159280
32	16	0	3.631249	-0.134437	-0.411175
33	1	0	5.956777	-0.155823	-0.701915
34	1	0	5.480787	0.578089	0.850497
35	8	0	2.776249	-0.249316	0.792375
36	8	0	3.431409	-1.259948	-1.321848
37	8	0	3.492092	1.185620	-1.033051
38	1	0	1.615534	1.276429	0.742670
39	1	0	0.027000	4.954939	-1.336302
40	1	0	-1.327375	4.280490	0.847519
41	1	0	-1.622809	2.158178	2.124730
42	1	0	-0.326982	2.915088	3.053071
43	1	0	1.011909	0.766362	2.753793
44	1	0	-0.422177	0.055060	1.968610
45	6	0	-0.346935	-1.021754	4.390832
46	1	0	0.729303	-1.175532	4.467128
47	1	0	-0.791322	-1.306179	5.342860

48	1	0	-0.735868	-1.666836	3.605184
49	16	0	1.504535	3.029308	-0.953464

Transition state

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.158134	-1.122842	-0.321636
2	1	0	-2.546832	-0.762084	0.477031
3	1	0	-2.693443	-1.375234	-1.249838
4	6	0	-4.531265	-1.611495	-0.039116
5	1	0	-5.161063	-1.385723	-0.897516
6	1	0	-4.430470	-2.691627	0.026753
7	6	0	-5.126698	-1.045284	1.232564
8	1	0	-5.185838	0.039246	1.183975
9	1	0	-6.130026	-1.432153	1.395058
10	1	0	-4.522173	-1.322376	2.093792
11	8	0	-3.581512	0.562050	-0.912207
12	16	0	-2.423386	1.496548	-1.151313
13	8	0	-2.336844	2.528875	-0.131405
14	8	0	-1.185485	0.753781	-1.375243
15	6	0	-2.854867	2.294699	-2.666528
16	1	0	-2.065473	2.998273	-2.905633
17	1	0	-2.943525	1.540685	-3.439270
18	1	0	-3.796772	2.810107	-2.521057
19	55	0	0.437964	-2.234122	-0.881366
20	9	0	-2.156959	-2.807683	0.250875
21	6	0	-0.330060	1.997311	2.191794
22	6	0	1.620829	2.005086	0.687565
23	6	0	0.261919	3.792394	0.582277
24	6	0	1.192850	4.149272	-0.316307
25	7	0	0.532431	2.572650	1.148829
26	6	0	-0.297908	0.487961	2.229816
27	6	0	-1.258090	-0.056716	3.274176
28	1	0	-2.267107	0.297347	3.057158
29	1	0	-0.995629	0.351583	4.252182
30	1	0	4.988142	-2.343959	1.037439
31	6	0	5.177949	-1.316434	0.750176
32	16	0	3.734779	-0.682886	-0.053253
33	1	0	6.001374	-1.262930	0.047474
34	1	0	5.380764	-0.705645	1.621947
35	8	0	2.634906	-0.772615	0.939177
36	8	0	3.482837	-1.547040	-1.204576
37	8	0	4.027135	0.712784	-0.387442
38	1	0	1.980291	1.024258	0.985953
39	1	0	1.214845	5.046266	-0.905566
40	1	0	-0.637657	4.308820	0.856486
41	1	0	-1.331449	2.343382	1.958938
42	1	0	-0.013108	2.423721	3.142187
43	1	0	0.706496	0.120330	2.435215
44	1	0	-0.575401	0.119920	1.243302
45	6	0	-1.246176	-1.573839	3.330003
46	1	0	-0.250032	-1.942149	3.572801
47	1	0	-1.924691	-1.936409	4.099212
48	1	0	-1.551084	-2.020531	2.382816
49	16	0	2.395924	2.935765	-0.471093

Post-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.499892	-0.429872	0.638819
2	1	0	-4.675104	-0.613545	1.697283
3	1	0	-3.830120	0.415031	0.511069
4	6	0	-5.787970	-0.258969	-0.113231
5	1	0	-6.241616	0.667795	0.240683
6	1	0	-5.559167	-0.104520	-1.167499
7	6	0	-6.750983	-1.417438	0.057868
8	1	0	-7.023228	-1.549820	1.103907
9	1	0	-7.666670	-1.252921	-0.504732
10	1	0	-6.307730	-2.347105	-0.289652
11	8	0	-1.954923	1.450579	-0.134939
12	16	0	-1.019655	2.299944	-0.891870
13	8	0	-0.415423	3.363586	-0.090180
14	8	0	-0.033597	1.483503	-1.616777
15	6	0	-1.993478	3.118049	-2.126698
16	1	0	-1.335817	3.742353	-2.720418
17	1	0	-2.466904	2.367942	-2.749659
18	1	0	-2.738982	3.724210	-1.625073
19	55	0	-0.781665	-1.460436	-0.751092
20	9	0	-3.817941	-1.555821	0.156444
21	6	0	1.614423	2.387566	1.910018
22	6	0	2.728479	0.958507	0.246395
23	6	0	2.501639	3.127439	-0.288309
24	6	0	3.169417	2.686709	-1.365395
25	7	0	2.272578	2.128747	0.622487
26	6	0	0.716171	1.262840	2.369678
27	6	0	0.101355	1.587007	3.720244
28	1	0	-0.435205	2.534000	3.653276
29	1	0	0.891386	1.728605	4.460230
30	1	0	2.736548	-4.484855	1.379889
31	6	0	3.486356	-3.850135	0.922392
32	16	0	2.662454	-2.546397	0.055234
33	1	0	4.073103	-4.410302	0.203618
34	1	0	4.127800	-3.408703	1.676015
35	8	0	1.873337	-1.804958	1.067783
36	8	0	1.793664	-3.187010	-0.932490
37	8	0	3.711947	-1.701976	-0.518726
38	1	0	2.601644	0.041602	0.806359
39	1	0	3.451986	3.254631	-2.230789
40	1	0	2.106369	4.106366	-0.099861
41	1	0	1.021629	3.281831	1.755929
42	1	0	2.399503	2.589842	2.637285
43	1	0	1.260435	0.321423	2.434601
44	1	0	-0.079065	1.138125	1.636835
45	6	0	-0.846260	0.500410	4.190113
46	1	0	-0.333563	-0.455788	4.279983
47	1	0	-1.274583	0.741589	5.160342
48	1	0	-1.666579	0.373950	3.486023
49	16	0	3.480534	1.006511	-1.248348

(5) Fig. 3 (a) : [Cs^+F^- + C_3H_7OMs → C_3H_7F + Cs^+OMs^-] in ionic liquid [mim-^{t}OH][OMs]. (MPW1K/6-311++G**; ECP for Cs, Hay-Wadt VDZ(n+1)).

	Pre-reaction cplx	Transition state	Post-reaction cplx
E	-2064.445001	-2064.419177	-2064.506479
ZPE	0.443118	0.442107	0.444004
Gibbs(100℃)	0.339251	0.340936	0.342121

Pre-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.472620	1.278737	1.353327
2	1	0	-3.434541	1.172757	1.010244
3	1	0	-4.601707	0.852346	2.343809
4	6	0	-4.880829	2.722357	1.293613
5	1	0	-5.932080	2.829686	1.565336
6	1	0	-4.300835	3.226281	2.066898
7	6	0	-4.591490	3.353564	-0.053971
8	1	0	-5.177839	2.882814	-0.840082
9	1	0	-4.829849	4.415349	-0.049097
10	1	0	-3.538307	3.228297	-0.294695
11	8	0	-5.394582	0.542784	0.472547
12	16	0	-4.984082	-0.865783	-0.063281
13	8	0	-4.254718	-0.759124	-1.303143
14	8	0	-4.364900	-1.644673	0.981625
15	6	0	-6.593416	-1.489213	-0.406514
16	1	0	-6.460357	-2.476173	-0.835202
17	1	0	-7.148828	-1.542135	0.521475
18	1	0	-7.071944	-0.825455	-1.116234
19	55	0	-1.139299	-1.124827	-0.428486
20	9	0	-1.691882	1.433062	0.578153
21	1	0	1.705093	0.091963	-0.446410
22	8	0	1.500744	0.772263	-1.104105
23	6	0	1.336589	2.047715	0.947351
24	6	0	2.820641	2.727474	-0.989301
25	1	0	2.056327	1.382028	1.423364
26	1	0	1.461257	3.047958	1.362090
27	1	0	0.317761	1.723188	1.168493
28	6	0	4.514817	0.936175	-0.694128
29	6	0	4.744895	2.665969	0.620738
30	6	0	5.726979	1.788228	0.911560
31	7	0	5.569057	0.721142	0.074274
32	7	0	4.002854	2.120404	-0.390434
33	6	0	1.505237	2.072520	-0.559641
34	6	0	0.371400	2.849333	-1.202573
35	1	0	0.417847	2.758786	-2.286949
36	1	0	-0.569998	2.447800	-0.822606
37	1	0	0.422005	3.905062	-0.937780
38	1	0	2.427700	-3.941982	1.611346
39	6	0	2.956503	-3.833819	0.671384
40	16	0	3.202182	-2.106337	0.366311
41	1	0	2.383374	-4.252934	-0.147517
42	1	0	3.930466	-4.305758	0.729699
43	8	0	3.991571	-1.590499	1.479574
44	8	0	1.843714	-1.524160	0.305783
45	8	0	3.893033	-2.006678	-0.925949
46	1	0	4.118372	0.231488	-1.403211
47	1	0	6.510653	1.828129	1.640840

48	1	0	4.508494	3.620917	1.044438
49	6	0	6.394583	-0.471868	0.066494
50	1	0	7.413243	-0.198966	-0.191056
51	1	0	6.338261	-0.934936	1.044017
52	1	0	5.977687	-1.166444	-0.651936
53	1	0	2.914978	2.651608	-2.068371
54	1	0	2.839515	3.776987	-0.713607

Transition state

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.654506	1.339777	0.777978
2	1	0	-3.453148	1.279913	-0.270728
3	1	0	-3.318575	0.570220	1.440740
4	6	0	-4.166197	2.607908	1.353844
5	1	0	-4.891228	2.362459	2.126856
6	1	0	-3.306379	3.061886	1.840296
7	6	0	-4.764741	3.542563	0.324143
8	1	0	-5.606431	3.073405	-0.178792
9	1	0	-5.116335	4.460024	0.790759
10	1	0	-4.023862	3.812288	-0.425719
11	8	0	-5.295656	0.456065	0.527047
12	16	0	-5.043841	-0.889103	-0.105578
13	8	0	-4.489004	-0.756705	-1.447675
14	8	0	-4.246932	-1.747105	0.764651
15	6	0	-6.661081	-1.580493	-0.237453
16	1	0	-6.558274	-2.560698	-0.689094
17	1	0	-7.080499	-1.657983	0.758240
18	1	0	-7.259273	-0.929850	-0.863722
19	55	0	-1.251628	-0.960708	-0.436557
20	9	0	-1.690319	1.759505	0.759985
21	1	0	1.650554	0.146867	-0.380011
22	8	0	1.481870	0.853370	-1.023191
23	6	0	1.533483	2.093960	1.051364
24	6	0	2.981003	2.680173	-0.941049
25	1	0	2.223615	1.369253	1.481343
26	1	0	1.745844	3.074303	1.476565
27	1	0	0.512694	1.830826	1.324296
28	6	0	4.516373	0.733463	-0.805906
29	6	0	4.985094	2.388015	0.541893
30	6	0	5.901341	1.417868	0.737561
31	7	0	5.595417	0.400728	-0.119847
32	7	0	4.132081	1.945951	-0.432293
33	6	0	1.632384	2.135411	-0.461483
34	6	0	0.550655	3.028240	-1.040441
35	1	0	0.553579	2.969208	-2.127715
36	1	0	-0.412262	2.701760	-0.650040
37	1	0	0.700687	4.066523	-0.747083
38	1	0	2.159605	-3.757020	1.892076
39	6	0	2.634338	-3.777325	0.917970
40	16	0	2.990416	-2.111214	0.437141
41	1	0	1.979910	-4.220560	0.176412
42	1	0	3.571512	-4.319723	0.965052
43	8	0	3.884835	-1.559146	1.449220
44	8	0	1.677597	-1.426942	0.401481
45	8	0	3.598847	-2.179017	-0.896700
46	1	0	4.012784	0.096696	-1.510032
47	1	0	6.729799	1.361917	1.414358
48	1	0	4.864135	3.344064	1.009666
49	6	0	6.303512	-0.861685	-0.213728
50	1	0	7.304219	-0.684926	-0.595679
51	1	0	6.327570	-1.312226	0.770843

52	1	0	5.739904	-1.518304	-0.864767
53	1	0	3.009209	2.637126	-2.025666
54	1	0	3.112978	3.712853	-0.634540

Post-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.124617	-1.214294	-0.201983
2	1	0	-4.644677	-0.345444	-0.643884
3	1	0	-5.910730	-1.586837	-0.853899
4	6	0	-5.635568	-0.915348	1.177965
5	1	0	-6.428088	-0.174396	1.061411
6	1	0	-6.103002	-1.808507	1.592637
7	6	0	-4.563078	-0.384081	2.109947
8	1	0	-4.068493	0.481330	1.674359
9	1	0	-4.988918	-0.094102	3.067570
10	1	0	-3.807181	-1.141461	2.305970
11	8	0	-1.370557	2.990068	-0.116271
12	16	0	-1.879249	2.097427	-1.154314
13	8	0	-0.785121	1.398049	-1.866344
14	8	0	-2.899251	1.150724	-0.689911
15	6	0	-2.665855	3.125450	-2.362277
16	1	0	-3.036238	2.495569	-3.162654
17	1	0	-3.481798	3.649589	-1.878218
18	1	0	-1.933142	3.829974	-2.738134
19	55	0	-1.092684	-1.489227	-0.524870
20	9	0	-4.151862	-2.221729	-0.146627
21	1	0	1.447881	-0.441081	1.415449
22	8	0	0.615842	-0.013174	1.696262
23	6	0	2.073215	0.700444	3.461618
24	6	0	1.192666	2.315505	1.716772
25	1	0	2.947622	0.411359	2.883254
26	1	0	2.330661	1.531304	4.116743
27	1	0	1.801206	-0.149946	4.082107
28	6	0	1.889612	1.771703	-0.564867
29	6	0	3.552757	2.114066	0.811696
30	6	0	4.068830	1.787457	-0.390336
31	7	0	3.012523	1.588327	-1.235079
32	7	0	2.189240	2.098391	0.682347
33	6	0	0.907100	1.057826	2.554874
34	6	0	-0.341625	1.343855	3.365767
35	1	0	-1.179707	1.548919	2.704735
36	1	0	-0.582156	0.480593	3.980623
37	1	0	-0.198940	2.202756	4.018989
38	1	0	4.807989	-3.178520	0.724222
39	6	0	3.853385	-3.469041	0.301525
40	16	0	3.051294	-2.014447	-0.313474
41	1	0	3.220333	-3.918325	1.057833
42	1	0	3.997229	-4.149234	-0.530045
43	8	0	3.947390	-1.445333	-1.313847
44	8	0	2.877725	-1.134635	0.863164
45	8	0	1.758812	-2.456798	-0.849543
46	1	0	0.891871	1.685616	-0.981567
47	1	0	5.082846	1.651455	-0.706164
48	1	0	4.035185	2.340090	1.740332
49	6	0	3.094471	1.185476	-2.625100
50	1	0	3.710171	1.894489	-3.169057
51	1	0	3.512898	0.184921	-2.664320
52	1	0	2.092075	1.187502	-3.036806
53	1	0	0.281448	2.624497	1.210301
54	1	0	1.536490	3.130926	2.347781

(6) Fig. 3 (b) : [Cs^+F^- + C_3H_7OMs → C_3H_7F + Cs^+OMs^-] in ionic liquid [mim-^{t}OH][OMs]. (MPW1K/6-311++G**; ECP for Cs, Hay-Wadt VDZ(n+1)).

	Pre-reaction cplx	Transition state	Post-reaction cplx
E	-2064.463691	-2064.437759	-2064.491475
ZPE	0.442769	0.442363	0.44312
Gibbs(100℃)	0.340881	0.345407	0.336077

Pre-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.692108	0.084002	-1.757899
2	1	0	2.625459	0.221186	-1.544901
3	1	0	3.842965	-0.829111	-2.326479
4	6	0	4.260984	1.283557	-2.460465
5	1	0	5.329183	1.143687	-2.630026
6	1	0	3.787967	1.309128	-3.442241
7	6	0	3.996059	2.582044	-1.725053
8	1	0	4.467413	2.579460	-0.745050
9	1	0	4.384918	3.432482	-2.280700
10	1	0	2.926970	2.721945	-1.582919
11	8	0	4.458036	-0.088502	-0.516246
12	16	0	3.769875	-0.732851	0.730349
13	8	0	3.103063	0.276218	1.518918
14	8	0	3.000125	-1.888224	0.340915
15	6	0	5.215210	-1.241331	1.593107
16	1	0	4.880443	-1.682969	2.525115
17	1	0	5.741064	-1.968138	0.986719
18	1	0	5.825797	-0.366779	1.781413
19	55	0	-0.185335	-2.011959	-0.469107
20	9	0	0.806943	0.465796	-1.650512
21	6	0	-1.772769	1.492981	1.941133
22	6	0	-1.220731	1.808473	-0.463388
23	6	0	-2.881553	3.011844	0.300351
24	6	0	-2.779830	3.247093	-1.022136
25	7	0	-1.736101	2.488834	-1.473446
26	7	0	-1.896385	2.122438	0.633694
27	6	0	-0.347414	1.383099	2.463173
28	6	0	-0.418238	0.846604	3.885211
29	1	0	-0.958081	-0.096922	3.902565
30	1	0	-0.912849	1.546927	4.556088
31	1	0	-5.064421	-3.011026	0.204788
32	6	0	-5.282372	-1.958918	0.062360
33	16	0	-3.756973	-1.097120	-0.216059
34	1	0	-5.752946	-1.544142	0.946372
35	1	0	-5.913865	-1.815624	-0.806929
36	8	0	-3.154997	-1.711249	-1.405543
37	8	0	-2.932186	-1.338506	0.985973
38	8	0	-4.109830	0.310385	-0.383152
39	1	0	-0.350343	1.156869	-0.608244
40	1	0	-3.371622	3.858588	-1.672410
41	1	0	-3.589737	3.369232	1.019517
42	6	0	-1.268464	2.351711	-2.837740
43	1	0	-2.055541	1.911802	-3.442013
44	1	0	-0.998712	3.326860	-3.231922
45	1	0	-0.401485	1.692576	-2.809318
46	1	0	-2.211235	0.498046	1.867933

47	1	0	-2.366990	2.091071	2.625161
48	1	0	0.587826	0.671200	4.259445
49	8	0	0.287436	0.436986	1.633641
50	1	0	1.242350	0.533381	1.665612
51	6	0	0.389587	2.710433	2.425945
52	1	0	-0.117933	3.454707	3.036491
53	1	0	1.397764	2.586535	2.816869
54	1	0	0.468932	3.088849	1.410517

Transition state

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.319448	0.351681	-1.713088
2	1	0	1.902505	0.713239	-0.795950
3	1	0	2.298729	-0.695830	-1.926688
4	6	0	2.698963	1.300158	-2.789995
5	1	0	3.620142	0.943252	-3.245378
6	1	0	1.913453	1.214865	-3.536611
7	6	0	2.849416	2.729647	-2.315017
8	1	0	3.617001	2.800912	-1.548790
9	1	0	3.129115	3.384094	-3.137255
10	1	0	1.914405	3.098761	-1.898330
11	8	0	4.028591	0.169936	-0.922863
12	16	0	3.943137	-0.548888	0.394714
13	8	0	3.435270	0.326827	1.451019
14	8	0	3.214720	-1.805596	0.269025
15	6	0	5.623533	-0.915341	0.780042
16	1	0	5.632585	-1.430616	1.733765
17	1	0	6.020058	-1.548276	-0.004514
18	1	0	6.169389	0.018262	0.841230
19	55	0	0.023564	-2.150997	-0.164707
20	9	0	0.357449	0.213186	-2.105303
21	6	0	-1.321406	1.658034	2.037491
22	6	0	-1.450821	1.650296	-0.443022
23	6	0	-2.810635	3.030053	0.565394
24	6	0	-3.073157	3.080024	-0.755854
25	7	0	-2.202532	2.222441	-1.363429
26	7	0	-1.788321	2.135246	0.742896
27	6	0	0.185222	1.703795	2.242958
28	6	0	0.464005	1.283446	3.678016
29	1	0	0.024217	0.309729	3.880666
30	1	0	0.065346	2.003322	4.390252
31	1	0	-4.795256	-2.844127	1.242534
32	6	0	-5.035444	-1.922755	0.724837
33	16	0	-3.543350	-1.257610	0.035433
34	1	0	-5.449182	-1.194396	1.412726
35	1	0	-5.726107	-2.112380	-0.088743
36	8	0	-3.013434	-2.286415	-0.865278
37	8	0	-2.634071	-1.032604	1.179837
38	8	0	-3.923094	-0.014795	-0.633198
39	1	0	-0.671449	0.944741	-0.690645
40	1	0	-3.808741	3.633420	-1.303292
41	1	0	-3.269003	3.538113	1.389460
42	6	0	-2.225525	1.797688	-2.748748
43	1	0	-3.087078	1.152435	-2.887868
44	1	0	-2.283228	2.669178	-3.392582
45	1	0	-1.311937	1.238949	-2.933672
46	1	0	-1.682759	0.637209	2.140575
47	1	0	-1.804299	2.282162	2.782968
48	1	0	1.537801	1.210601	3.835178
49	8	0	0.730314	0.754631	1.354636
50	1	0	1.685459	0.681039	1.500781

51	6	0	0.763883	3.080770	1.963739
52	1	0	0.340543	3.828989	2.631751
53	1	0	1.841147	3.064586	2.112933
54	1	0	0.572204	3.383256	0.937549

Post-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.716203	1.325546	-2.053656
2	1	0	1.888403	1.606406	-1.019985
3	1	0	2.244527	0.401288	-2.257039
4	6	0	2.115582	2.410585	-3.007115
5	1	0	3.199281	2.491472	-2.929084
6	1	0	1.895540	2.090106	-4.025416
7	6	0	1.463957	3.748684	-2.717560
8	1	0	1.710156	4.091990	-1.714063
9	1	0	1.800743	4.508008	-3.419374
10	1	0	0.380540	3.686462	-2.794770
11	8	0	4.464720	0.525127	-0.866905
12	16	0	4.007687	-0.280409	0.253397
13	8	0	3.226107	0.491961	1.248460
14	8	0	3.291564	-1.502605	-0.144988
15	6	0	5.453575	-0.818287	1.122750
16	1	0	5.145818	-1.422791	1.967904
17	1	0	6.058861	-1.399244	0.436479
18	1	0	5.994305	0.060096	1.455109
19	55	0	0.393871	-2.213248	-0.487192
20	9	0	0.339216	1.048602	-2.171077
21	6	0	-1.350048	0.936290	2.504215
22	6	0	-1.782901	1.588723	0.160744
23	6	0	-2.992705	2.638348	1.639554
24	6	0	-3.378684	3.053725	0.415626
25	7	0	-2.596302	2.396721	-0.491918
26	7	0	-1.988083	1.726021	1.458466
27	6	0	0.168508	1.046931	2.523020
28	6	0	0.680089	0.213998	3.688829
29	1	0	0.312061	-0.807274	3.618079
30	1	0	0.370935	0.630537	4.645921
31	1	0	-4.235880	-3.600526	0.193564
32	6	0	-4.627249	-2.611122	-0.012751
33	16	0	-3.267225	-1.524254	-0.342607
34	1	0	-5.168970	-2.228531	0.844460
35	1	0	-5.264555	-2.629248	-0.889259
36	8	0	-2.553686	-2.088602	-1.493544
37	8	0	-2.423183	-1.544326	0.869472
38	8	0	-3.853041	-0.207913	-0.597831
39	1	0	-1.050164	0.950047	-0.284798
40	1	0	-4.137302	3.749134	0.118520
41	1	0	-3.344844	2.909561	2.614115
42	6	0	-2.788366	2.367539	-1.926912
43	1	0	-3.532729	1.610831	-2.152924
44	1	0	-3.105572	3.348587	-2.261778
45	1	0	-1.848535	2.106385	-2.397797
46	1	0	-1.646122	-0.096259	2.334431
47	1	0	-1.761985	1.281510	3.447174
48	1	0	1.766283	0.188375	3.658430
49	8	0	0.608242	0.499313	1.305779
50	1	0	1.590807	0.522980	1.279719
51	6	0	0.636673	2.487570	2.651073
52	1	0	0.299494	2.932801	3.585863
53	1	0	1.723209	2.517793	2.628570
54	1	0	0.269558	3.091325	1.824308

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(7) Fig. 3 (c) : [Cs^+F^- + C_3H_7OMs → C_3H_6 + HF + Cs^+OMs^-] in ionic liquid [mim-^{t}OH][OMs]. (MPW1K/6-311++G**; ECP for Cs, Hay-Wadt VDZ(n+1)).

	Pre-reaction cplx	Transition state	Post-reaction cplx
E	-2064.463691	-2064.418242	-2064.47938
ZPE	0.442769	0.437175	0.438594
Gibbs(100℃)	0.340881	0.338942	0.333193

Pre-reaction complex

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.692108	0.084002	-1.757899
2	1	0	2.625459	0.221186	-1.544901
3	1	0	3.842965	-0.829111	-2.326479
4	6	0	4.260984	1.283557	-2.460465
5	1	0	5.329183	1.143687	-2.630026
6	1	0	3.787967	1.309128	-3.442241
7	6	0	3.996059	2.582044	-1.725053
8	1	0	4.467413	2.579460	-0.745050
9	1	0	4.384918	3.432482	-2.280700
10	1	0	2.926970	2.721945	-1.582919
11	8	0	4.458036	-0.088502	-0.516246
12	16	0	3.769875	-0.732851	0.730349
13	8	0	3.103063	0.276218	1.518918
14	8	0	3.000125	-1.888224	0.340915
15	6	0	5.215210	-1.241331	1.593107
16	1	0	4.880443	-1.682969	2.525115
17	1	0	5.741064	-1.968138	0.986719
18	1	0	5.825797	-0.366779	1.781413
19	55	0	-0.185335	-2.011959	-0.469107
20	9	0	0.806943	0.465796	-1.650512
21	6	0	-1.772769	1.492981	1.941133
22	6	0	-1.220731	1.808473	-0.463388
23	6	0	-2.881553	3.011844	0.300351
24	6	0	-2.779830	3.247093	-1.022136
25	7	0	-1.736101	2.488834	-1.473446
26	7	0	-1.896385	2.122438	0.633694
27	6	0	-0.347414	1.383099	2.463173
28	6	0	-0.418238	0.846604	3.885211
29	1	0	-0.958081	-0.096922	3.902565
30	1	0	-0.912849	1.546927	4.556088
31	1	0	-5.064421	-3.011026	0.204788
32	6	0	-5.282372	-1.958918	0.062360
33	16	0	-3.756973	-1.097120	-0.216059
34	1	0	-5.752946	-1.544142	0.946372
35	1	0	-5.913865	-1.815624	-0.806929
36	8	0	-3.154997	-1.711249	-1.405543
37	8	0	-2.932186	-1.338506	0.985973
38	8	0	-4.109830	0.310385	-0.383152
39	1	0	-0.350343	1.156869	-0.608244
40	1	0	-3.371622	3.858588	-1.672410
41	1	0	-3.589737	3.369232	1.019517
42	6	0	-1.268464	2.351711	-2.837740
43	1	0	-2.055541	1.911802	-3.442013
44	1	0	-0.998712	3.326860	-3.231922
45	1	0	-0.401485	1.692576	-2.809318
46	1	0	-2.211235	0.498046	1.867933

47	1	0	-2.366990	2.091071	2.625161
48	1	0	0.587826	0.671200	4.259445
49	8	0	0.287436	0.436986	1.633641
50	1	0	1.242350	0.533381	1.665612
51	6	0	0.389587	2.710433	2.425945
52	1	0	-0.117933	3.454707	3.036491
53	1	0	1.397764	2.586535	2.816869
54	1	0	0.468932	3.088849	1.410517

Transition state

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.575105	0.277715	1.765857
2	1	0	-2.065744	0.586216	0.866901
3	1	0	-2.622621	-0.781325	1.952937
4	6	0	-2.426366	1.118617	2.863725
5	1	0	-2.849570	0.762087	3.795405
6	1	0	-1.194890	0.673822	2.772149
7	6	0	-2.398001	2.611027	2.687189
8	1	0	-3.404580	3.025040	2.648144
9	1	0	-1.871896	3.092085	3.508598
10	1	0	-1.894811	2.882832	1.761385
11	8	0	-4.262889	0.228023	0.876551
12	16	0	-4.081797	-0.414962	-0.467691
13	8	0	-3.481169	0.511682	-1.429928
14	8	0	-3.367244	-1.683450	-0.358759
15	6	0	-5.724461	-0.747296	-1.014027
16	1	0	-5.655521	-1.208049	-1.992877
17	1	0	-6.186477	-1.420212	-0.301900
18	1	0	-6.261061	0.192230	-1.066250
19	55	0	-0.143576	-2.078683	0.251403
20	9	0	-0.019203	0.253906	2.442156
21	6	0	1.279162	1.682246	-2.000301
22	6	0	1.662047	1.616649	0.457469
23	6	0	2.989030	2.931948	-0.670191
24	6	0	3.394042	2.935884	0.615413
25	7	0	2.542652	2.119301	1.301137
26	7	0	1.899754	2.105531	-0.750805
27	6	0	-0.656861	1.480294	-3.489367
28	1	0	-0.298422	0.488796	-3.755963
29	1	0	-0.274512	2.197833	-4.212613
30	1	0	4.422543	-3.063174	-1.649409
31	6	0	4.792922	-2.186241	-1.131337
32	16	0	3.444098	-1.433785	-0.261329
33	1	0	5.190597	-1.465160	-1.836129
34	1	0	5.547940	-2.463920	-0.404907
35	8	0	2.927793	-2.452539	0.658223
36	8	0	2.438183	-1.091239	-1.290617
37	8	0	3.993439	-0.251770	0.399301
38	1	0	0.871746	0.953649	0.761140
39	1	0	4.216434	3.431839	1.089491
40	1	0	3.386573	3.430800	-1.530642
41	6	0	2.703764	1.665144	2.668790
42	1	0	3.521617	0.952022	2.688230
43	1	0	2.912921	2.517583	3.306366
44	1	0	1.781794	1.175520	2.967706
45	1	0	1.557489	0.640841	-2.145117
46	1	0	1.736273	2.283616	-2.779881
47	1	0	-1.742478	1.477139	-3.554144
48	8	0	-0.775515	0.901311	-1.166594
49	1	0	-1.729317	0.829062	-1.328003
50	6	0	-0.686647	3.240936	-1.712754

51	1	0	-0.264648	3.979423	-2.392470
52	1	0	-1.770501	3.303516	-1.775526
53	1	0	-0.393459	3.496652	-0.697783
54	6	0	-0.231923	1.836679	-2.072940

Post-reaction complex

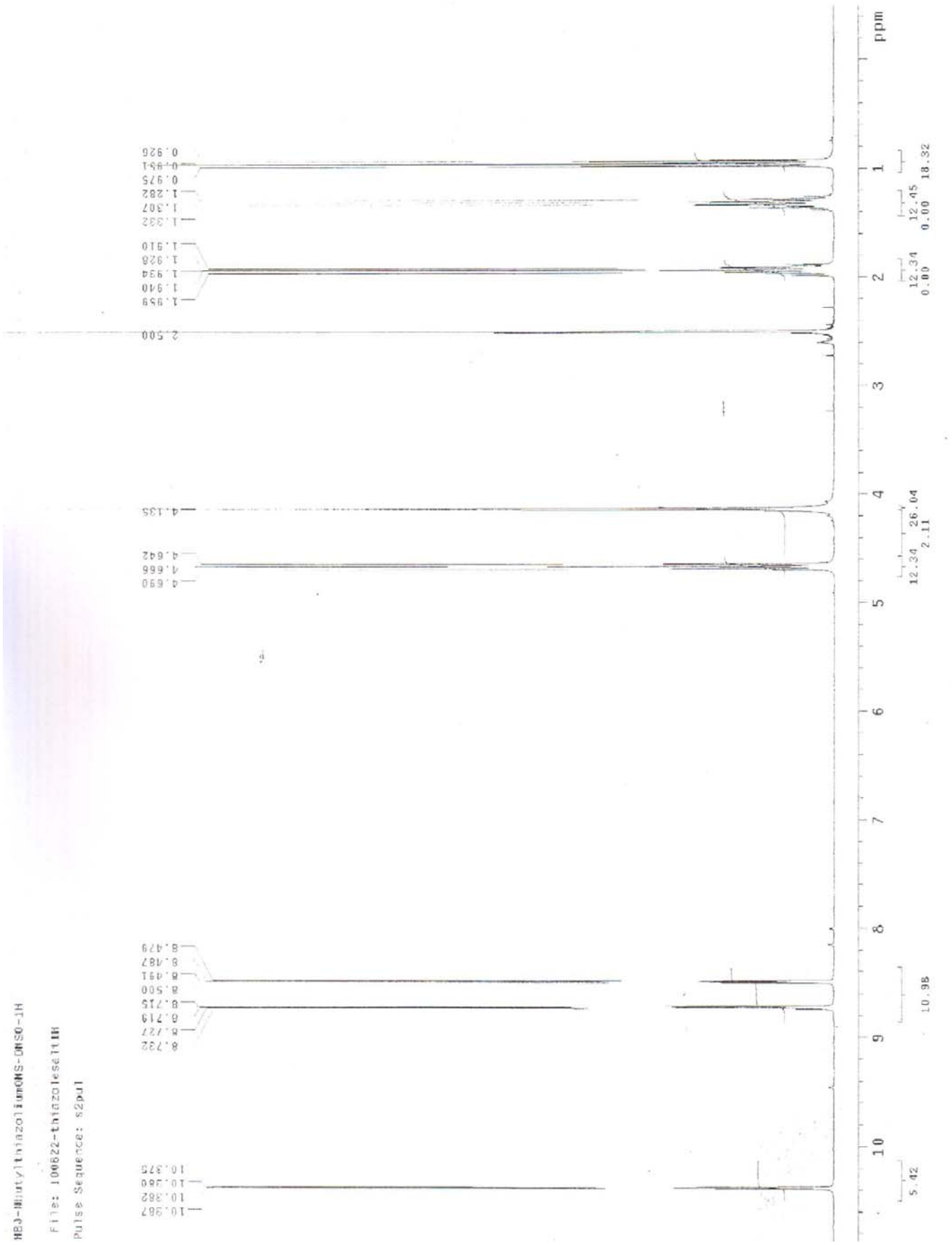
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.687322	2.316333	2.105952
2	1	0	-2.266732	3.260310	2.429186
3	1	0	-2.796744	2.144348	1.043901
4	6	0	-3.099132	1.408812	2.985212
5	1	0	-3.521392	0.491581	2.591097
6	1	0	-1.160421	0.943020	2.217185
7	6	0	-3.036507	1.557151	4.464702
8	1	0	-4.038557	1.511392	4.890089
9	1	0	-2.469996	0.743261	4.915693
10	1	0	-2.582951	2.500289	4.759157
11	8	0	-3.435519	-0.695485	0.569831
12	16	0	-3.592083	-0.302051	-0.836507
13	8	0	-3.080344	1.062282	-1.088829
14	8	0	-3.032106	-1.291594	-1.756935
15	6	0	-5.329792	-0.217711	-1.154949
16	1	0	-5.471644	0.073971	-2.188905
17	1	0	-5.751788	-1.199517	-0.974423
18	1	0	-5.764858	0.515385	-0.485870
19	55	0	-0.552339	-2.110978	0.093196
20	9	0	-0.341777	0.490025	2.181393
21	6	0	1.629347	1.460104	-2.190156
22	6	0	1.989894	1.570186	0.244154
23	6	0	3.283209	2.885349	-0.920703
24	6	0	3.618522	3.017095	0.379373
25	7	0	2.785164	2.197185	1.089541
26	7	0	2.257981	1.979601	-0.983122
27	6	0	-0.404334	1.099985	-3.530023
28	1	0	-0.188128	0.034786	-3.533763
29	1	0	0.024602	1.550736	-4.423603
30	1	0	4.039084	-3.571416	-0.859733
31	6	0	4.473732	-2.721238	-0.346944
32	16	0	3.160566	-1.703685	0.270174
33	1	0	5.073436	-2.129525	-1.028796
34	1	0	5.069495	-3.049956	0.496750
35	8	0	2.369573	-2.548304	1.169271
36	8	0	2.371659	-1.293345	-0.910044
37	8	0	3.805810	-0.567785	0.930195
38	1	0	1.228055	0.868654	0.507437
39	1	0	4.371317	3.614838	0.852081
40	1	0	3.683322	3.352195	-1.797856
41	6	0	2.888578	1.873442	2.497516
42	1	0	3.580483	1.045020	2.607705
43	1	0	3.225644	2.751143	3.037278
44	1	0	1.911254	1.575381	2.857716
45	1	0	1.803294	0.387500	-2.186880
46	1	0	2.146047	1.908346	-3.032855
47	1	0	-1.484024	1.218634	-3.566585
48	8	0	-0.417075	1.147319	-1.124757
49	1	0	-1.391732	1.208864	-1.148132
50	6	0	-0.153468	3.242081	-2.261300
51	1	0	0.285006	3.736280	-3.127049
52	1	0	-1.228381	3.404152	-2.287946
53	1	0	0.231776	3.709289	-1.357616
54	6	0	0.134845	1.749102	-2.265669

3. Preparation and Characterization of [*N*-butylthiazolium][OMs]

A solution of [*N*-butylthiazolium][Br] (1 g, 4.52 mmol) in methaol (15 mL) was prepared. To this was added slowly potassium methanesulfonate (5.33 g, 45.2 mmol) with stiring. After addition, the mixture was heated at reflux for 120 h, and then the organic phase was filtered. The filtrate was concentrated *in vacuo* to afford 1.0 g (93%) of [*N*-butylthiazolium][OMs] as a yellow thick liquid.

^{1}H NMR (300 MHz, DMSO-d_6) δ 0.95 (t, J = 7.5 Hz, 3H), 0.97-1.33 (m, 2H) 1.91-1.96 (m, 2H), 4.13 (s, 3H) 4.67 (t, J = 7.2 Hz, 2H) 8.49 (dd, 3.6, 2.1 Hz, 1H) 8.73 (dd, 3.6, 1.2 Hz, 1H) 10.38 (dd, 2.1, 1.2 Hz 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 13.4, 18.9, 31.7, 39.8, 54.4, 127.0, 137.3, 159.4; Anal. Calcd for $C_8H_{15}NO_3S_2$: C, 40.48; H, 6.37; N, 5.90; O, 20.22; S, 27.02. Found: C, 40.52; H, 6.38; N, 5.87.

^{1}H and ^{13}C NMR spectra of [*N*-butylthiazolium][OMs]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0.975
1.282
1.307
1.332
1.910
1.926
1.934
1.940
1.959
2.500
4.135
4.642
4.666
4.690
8.479
8.487
8.491
8.500
8.715
8.719
8.727
8.732
10.367
10.382
10.386
10.387
18.32
12.45
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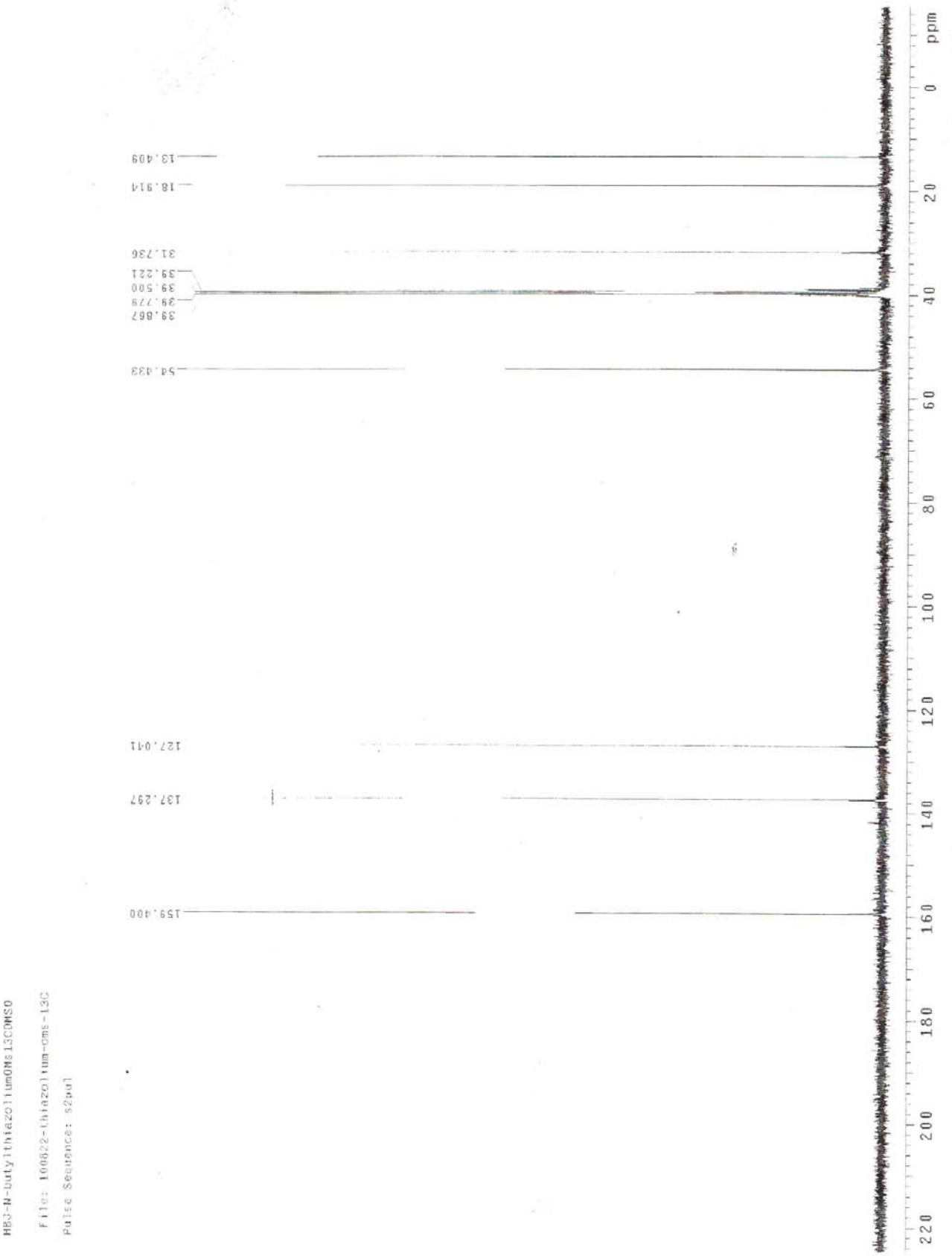
12.34
0.00
26.04
2.11
12.34
10.98
5.42


NBJ-N-butylthiazoliumOMs13CDMSO
File: 100822-thiazolium-oms-13C
Pulse Sequence: s2pul
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31.736
39.221
39.500
39.779
39.867
54.033
127.041
137.297
159.400
ppm
0
20
40
60
80
100
120
140
160
180
200
220

4. General Procedure for Fluorination in Table 1

CsF (151 mg, 1.0 mmol) was added to the mixture of 2-(3-methanesulfonyloxypropoxy)naphthalene (56 mg, 0.2 mmol) and each ionic liquid (1.6 mmol) in 0.6 mL CH_3CN. The mixture was stirred for 50 min at 100 °C. The reaction mixture was extracted with diethyl ether (10 mL × 3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The conversion was determined by ^{1}H NMR and the crude product was purified by flash column chromatography (5% EtOAc/hexane) to obtain 2-(3-fluoro-*n*-propoxy)naphthalene as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.14-2.39 (m, 2H), 4.24 (t, *J* = 6.2 Hz, 2H), 4.72 (dt, *J* = 46.8, 5.8 Hz, 2H), 7.16-7.22 (m, 2H), 7.34-7.53 (m, 2H), 7.76-7.83 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.4, 63.6, 80.8, 106.8, 118.8, 123.7, 126.4, 126.7, 127.6, 129.1, 129.4, 134.6, 156.7; see D. W. Kim, C. E. Song, D. Y. Chi, *J. Am. Chem. Soc.* **2002**, *124,* 10278-10279.