Supplementary Information

Title: A Mechanistic study of S_N2 reaction in a diol solvent

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Supplementary Table 1. Electronic *E* (Hartree), zero-point energy (*ZPE*) (kcal/mol), Gibbs free energy G_{353K} (in Hartree) of the conformers of [Cs^+F^- …C_3H_7-OMs] system under the influence of two ethylene glycol molecules (MPW1K/6-311++G** ; ECP for Cs, Hay-Wadt VDZ(n+1))

(a)

	E	ZPE	G(353 K)
	-1362.65701	209.67	-1362.06641

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.280844	1.615125	-0.918534
2	1	0	-2.053178	1.447801	-1.967038
3	1	0	-1.391400	1.426883	-0.316384
4	6	0	-2.824106	2.993457	-0.673204
5	1	0	-2.082630	3.684514	-1.073581
6	1	0	-3.734019	3.137043	-1.256291

7	6	0	-3.069186	3.289227	0.792828
8	1	0	-2.147982	3.183342	1.361311
9	1	0	-3.435961	4.303884	0.928446
10	1	0	-3.805737	2.608748	1.213283
11	8	0	-3.344463	0.667865	-0.570201
12	16	0	-2.971844	-0.821037	-0.268814
13	8	0	-2.004132	-1.294739	-1.229966
14	8	0	-2.650587	-0.992394	1.126442
15	6	0	-4.538062	-1.554956	-0.578838
16	1	0	-4.433984	-2.611906	-0.360168
17	1	0	-5.263723	-1.097862	0.082816
18	1	0	-4.794281	-1.396226	-1.618847
19	55	0	1.188557	-1.334282	-0.714329
20	9	0	0.478104	1.467794	0.246600
21	1	0	1.450998	1.002339	1.298386
22	8	0	2.149323	0.523108	1.823165
23	6	0	1.668933	0.149765	3.079250
24	6	0	0.202388	-0.194645	3.078194
25	1	0	1.821116	0.950583	3.810066
26	1	0	2.245019	-0.712014	3.417077
27	1	0	-0.362859	0.661781	2.708356
28	1	0	-0.106818	-0.389957	4.108903
29	8	0	-0.040380	-1.320003	2.267407
30	1	0	-0.961501	-1.298909	2.007235
31	1	0	4.690606	0.597305	-1.847831
32	6	0	4.440995	0.997038	-0.865854
33	1	0	5.351377	1.444908	-0.453918
34	6	0	3.397130	2.080921	-1.014188
35	1	0	3.183223	2.509053	-0.031999
36	1	0	3.827342	2.879208	-1.625839
37	8	0	2.221568	1.608320	-1.602182
38	1	0	1.498443	1.693909	-0.945228
39	8	0	4.020062	-0.091138	-0.087592
40	1	0	3.587253	0.223805	0.716467

(b)

	E	ZPE	G(353 K)
	-1362.64948	209.3	-1362.06435

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.042014	2.113535	0.262786
2	1	0	-0.525539	2.338327	-0.665235
3	1	0	-0.570003	1.255706	0.740103
4	6	0	-1.085896	3.299617	1.182172
5	1	0	-0.051547	3.613797	1.317662
6	1	0	-1.598621	4.123641	0.686161
7	6	0	-1.720479	2.997904	2.524883
8	1	0	-1.180717	2.201998	3.033475
9	1	0	-1.707119	3.876137	3.165852
10	1	0	-2.755319	2.684176	2.410435
11	8	0	-2.427095	1.799660	-0.096842
12	16	0	-2.748759	0.416376	-0.753504
13	8	0	-1.728796	0.080374	-1.719413
14	8	0	-3.045807	-0.567193	0.257839
15	6	0	-4.239611	0.848283	-1.576310
16	1	0	-4.605057	-0.055147	-2.051750
17	1	0	-4.945549	1.201734	-0.834603
18	1	0	-4.019414	1.613161	-2.310442
19	55	0	0.931960	-1.641465	-1.164617
20	9	0	1.102760	0.192065	1.255649
21	1	0	1.447991	-1.275130	1.784749
22	8	0	1.580544	-2.248634	1.819163
23	6	0	0.602625	-2.823960	2.627726
24	6	0	-0.783970	-2.294854	2.365578

25	1	0	0.820194	-2.668041	3.690010
26	1	0	0.620013	-3.899255	2.449827
27	1	0	-0.788700	-1.216391	2.530608
28	1	0	-1.474329	-2.755676	3.077735
29	8	0	-1.172540	-2.583507	1.041449
30	1	0	-1.926243	-2.032099	0.830670
31	1	0	4.548590	1.471738	-0.935080
32	6	0	3.840488	1.533472	-0.108984
33	1	0	4.276387	1.022410	0.752636
34	6	0	3.585526	2.985271	0.225984
35	1	0	2.980188	3.046551	1.135223
36	1	0	4.522408	3.507866	0.409794
37	8	0	2.936799	3.624600	-0.840909
38	1	0	2.335534	2.970670	-1.193786
39	8	0	2.653969	0.918253	-0.524586
40	1	0	2.077748	0.719767	0.268489

(c)

	E	ZPE	G(353 K)
	-1362.64224	208.0	-1362.06396

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.423181	0.498786	1.137877
2	1	0	1.438764	0.104686	1.370422
3	1	0	2.341457	1.255456	0.360779
4	6	0	3.093741	1.045281	2.365360
5	1	0	2.392179	1.757452	2.797590

6	1	0	3.201318	0.241720	3.093127
7	6	0	4.429941	1.706959	2.094736
8	1	0	4.320857	2.536312	1.398013
9	1	0	4.864002	2.097589	3.012248
10	1	0	5.137641	1.002754	1.663962
11	8	0	3.258950	-0.590288	0.638823
12	16	0	3.049928	-1.067143	-0.843136
13	8	0	1.684492	-1.504271	-1.028310
14	8	0	3.565285	-0.096367	-1.765870
15	6	0	4.105135	-2.473082	-0.799244
16	1	0	4.067369	-2.915970	-1.788318
17	1	0	5.109376	-2.140215	-0.567912
18	1	0	3.732472	-3.162491	-0.052063
19	55	0	-1.247544	-0.453475	-0.932975
20	9	0	-0.630157	0.523072	1.883134
21	1	0	-0.355787	1.708108	1.013271
22	8	0	-0.209974	2.349365	0.266990
23	6	0	-1.249958	3.266171	0.227698
24	6	0	-1.554466	3.657959	-1.191157
25	1	0	-0.998970	4.182473	0.774172
26	1	0	-2.157597	2.860402	0.683897
27	1	0	-0.635213	3.996760	-1.671999
28	1	0	-2.272377	4.481027	-1.186838
29	8	0	-2.089606	2.545989	-1.888660
30	1	0	-2.329796	2.827523	-2.764090
31	1	0	-3.527859	-0.033497	1.963581
32	6	0	-3.394147	-1.094349	2.195432
33	1	0	-3.679317	-1.231388	3.244833
34	6	0	-4.350683	-1.897846	1.360258
35	1	0	-4.171300	-2.959967	1.535683
36	1	0	-5.373062	-1.660021	1.661658
37	8	0	-4.161811	-1.590939	-0.011206
38	1	0	-4.813220	-2.062805	-0.517385
39	8	0	-2.089328	-1.502079	1.962947
40	1	0	-1.483982	-0.728686	2.087495

(d)

	E	ZPE	G(353 K)
	-1362.64920	208.9	-1362.06260

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.737956	-1.683172	0.639312
2	1	0	1.050090	-2.183495	-0.034205
3	1	0	1.245121	-0.814692	1.072368
4	6	0	2.249258	-2.606685	1.706199
5	1	0	1.364256	-3.013494	2.193722
6	1	0	2.765949	-3.446155	1.240554
7	6	0	3.139386	-1.923430	2.724774
8	1	0	2.604182	-1.116880	3.221331
9	1	0	3.468224	-2.626574	3.486416
10	1	0	4.025171	-1.501608	2.255700
11	8	0	2.894224	-1.260409	-0.156511
12	16	0	2.720693	-0.045142	-1.126846
13	8	0	1.521354	-0.209050	-1.913510
14	8	0	2.873640	1.199763	-0.415155
15	6	0	4.139415	-0.304537	-2.130023
16	1	0	4.163181	0.508540	-2.847031
17	1	0	5.015107	-0.278101	-1.493095
18	1	0	4.039813	-1.260222	-2.629164
19	55	0	-1.443740	0.703472	-1.006221
20	9	0	-0.590878	-0.167537	1.838417
21	1	0	-1.315729	1.227720	1.975208
22	8	0	-1.745656	2.091087	1.773676
23	6	0	-0.882925	3.127651	2.120880
24	6	0	0.539411	2.907029	1.672837

25	1	0	-0.864521	3.285366	3.205172
26	1	0	-1.267216	4.042565	1.669060
27	1	0	0.905315	1.976508	2.109004
28	1	0	1.154405	3.730763	2.047053
29	8	0	0.603926	2.841624	0.265931
30	1	0	1.445627	2.453086	0.027866
31	1	0	-3.342523	-1.367112	1.443048
32	6	0	-2.918455	-2.261085	0.976668
33	1	0	-3.017966	-3.077707	1.700863
34	6	0	-3.748303	-2.622070	-0.223302
35	1	0	-3.294732	-3.476824	-0.728367
36	1	0	-4.749508	-2.902777	0.110259
37	8	0	-3.820055	-1.515495	-1.106686
38	1	0	-4.415435	-1.733035	-1.814830
39	8	0	-1.594203	-2.061588	0.612168
40	1	0	-1.186575	-1.376380	1.211631

(e)

	E	ZPE	G(353 K)
	-1362.65040	209.4	-1362.06165

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.350327	0.672942	1.112003
2	1	0	-2.002704	1.695618	1.196882
3	1	0	-1.484613	0.015121	1.167475
4	6	0	-3.391590	0.335370	2.138956
5	1	0	-2.947837	0.574814	3.104996

6	1	0	-4.245336	1.001880	2.016314
7	6	0	-3.836194	-1.112979	2.109299
8	1	0	-2.995132	-1.780714	2.284494
9	1	0	-4.581218	-1.306822	2.877266
10	1	0	-4.273347	-1.371479	1.147752
11	8	0	-2.984996	0.548616	-0.207440
12	16	0	-2.108382	0.163645	-1.440270
13	8	0	-0.936487	1.004941	-1.516632
14	8	0	-1.889331	-1.262403	-1.482375
15	6	0	-3.240181	0.601882	-2.710865
16	1	0	-2.767271	0.340094	-3.650791
17	1	0	-4.150197	0.032243	-2.567767
18	1	0	-3.425418	1.667248	-2.652980
19	55	0	2.071381	-0.175045	-0.878569
20	9	0	0.573572	-0.158547	1.686032
21	1	0	1.532764	-1.425653	1.787072
22	8	0	2.161682	-2.138001	1.531057
23	6	0	1.478674	-3.348222	1.431274
24	6	0	0.156229	-3.240428	0.715098
25	1	0	1.282701	-3.778473	2.419721
26	1	0	2.123073	-4.047624	0.898267
27	1	0	-0.466781	-2.515515	1.240117
28	1	0	-0.340450	-4.214334	0.749253
29	8	0	0.351742	-2.832412	-0.619931
30	1	0	-0.472973	-2.471535	-0.944819
31	1	0	2.222145	2.217179	1.988932
32	6	0	1.407639	2.943448	1.923073
33	1	0	1.520102	3.632343	2.765090
34	6	0	1.526012	3.723254	0.632841
35	1	0	0.803155	4.542237	0.633473
36	1	0	2.519944	4.154935	0.531598
37	8	0	1.315439	2.896216	-0.487225
38	1	0	0.428553	2.544419	-0.406730
39	8	0	0.174899	2.302447	1.976581
40	1	0	0.321681	1.323255	1.943356

(f)

	E	ZPE	G(353 K)
	-1362.64817	209.5	-1362.05758

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.065195	0.236063	-1.282005
2	1	0	-3.140002	-0.669814	-1.877168
3	1	0	-2.027297	0.579963	-1.251446
4	6	0	-3.993912	1.307495	-1.777512
5	1	0	-3.742739	1.461324	-2.827084
6	1	0	-5.021691	0.944164	-1.751812
7	6	0	-3.864734	2.613732	-1.019975
8	1	0	-2.846454	2.990450	-1.082294
9	1	0	-4.531462	3.368429	-1.430492
10	1	0	-4.113433	2.484591	0.030624
11	8	0	-3.516414	-0.122590	0.068269
12	16	0	-2.561376	-0.920053	1.015095
13	8	0	-1.853625	-1.932608	0.267452
14	8	0	-1.774346	-0.023035	1.823097
15	6	0	-3.770705	-1.672564	2.044852
16	1	0	-3.230515	-2.231391	2.800927
17	1	0	-4.363231	-0.888430	2.500270
18	1	0	-4.381865	-2.328857	1.437988
19	55	0	1.118497	-1.442059	-0.840560
20	9	0	-0.223170	1.023966	-1.476746
21	1	0	0.983990	1.681141	-1.083448
22	8	0	1.849085	2.032721	-0.683386
23	6	0	1.550610	2.993215	0.276611
24	6	0	0.382458	2.617099	1.153105

25	1	0	1.313929	3.957386	-0.186986
26	1	0	2.435750	3.152636	0.895847
27	1	0	-0.484932	2.443730	0.519829
28	1	0	0.167656	3.445576	1.832453
29	8	0	0.661056	1.448954	1.899731
30	1	0	-0.149131	0.943360	1.971717
31	1	0	5.554616	0.553770	0.034400
32	6	0	4.619585	-0.008220	0.130642
33	1	0	4.885770	-1.065581	0.164794
34	6	0	3.966533	0.386729	1.433935
35	1	0	4.665205	0.177107	2.248058
36	1	0	3.787149	1.462670	1.433070
37	8	0	2.764204	-0.303543	1.639960
38	1	0	2.063475	0.345413	1.789650
39	8	0	3.800948	0.174903	-0.986409
40	1	0	3.253326	0.971033	-0.876535

(g)

	E	ZPE	G(353 K)
	-1362.642918	209.8	-1362.05608

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.272821	0.115758	1.251912
2	1	0	-2.819260	1.098442	1.326396
3	1	0	-2.501036	-0.623984	1.047295
4	6	0	-4.045663	-0.233313	2.494857
5	1	0	-3.351277	-0.141036	3.330088

6	1	0	-4.821825	0.515387	2.648262
7	6	0	-4.648140	-1.624087	2.464799
8	1	0	-3.875686	-2.380150	2.333797
9	1	0	-5.174149	-1.840763	3.391694
10	1	0	-5.357543	-1.722047	1.647190
11	8	0	-4.218220	0.126195	0.157829
12	16	0	-3.720421	0.449561	-1.306915
13	8	0	-4.900956	0.687290	-2.076166
14	8	0	-2.702320	1.471859	-1.242351
15	6	0	-2.971518	-1.056449	-1.823753
16	1	0	-2.603356	-0.882210	-2.829261
17	1	0	-2.153859	-1.312260	-1.152110
18	1	0	-3.741025	-1.819721	-1.828548
19	9	0	1.293470	-0.334330	0.643197
20	1	0	1.477779	1.354808	0.574953
21	8	0	2.051942	2.125420	0.398483
22	6	0	1.396730	3.323985	0.701177
23	6	0	0.068937	3.459622	0.004841
24	1	0	2.051630	4.138069	0.392009
25	1	0	1.235402	3.415829	1.778757
26	1	0	0.210661	3.302629	-1.066539
27	1	0	-0.306027	4.478287	0.149480
28	8	0	-0.813108	2.519316	0.542631
29	1	0	-1.423498	2.216376	-0.130482
30	1	0	1.455905	-4.285655	-0.824817
31	6	0	1.058288	-3.270742	-0.795194
32	1	0	0.609641	-3.059596	-1.770830
33	6	0	-0.018251	-3.187365	0.265288
34	1	0	-0.763931	-3.957984	0.071002
35	1	0	0.426711	-3.396668	1.242632
36	8	0	-0.683009	-1.955591	0.276937
37	1	0	-0.041698	-1.250945	0.505340
38	8	0	2.122396	-2.392481	-0.545393
39	1	0	1.743572	-1.590713	-0.117786
40	55	0	4.097258	-0.041102	-0.055927

(h)

	E	ZPE	G(353 K)
	-1362.60473	208.7	-1362.02788

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.828369	-0.935484	1.627297
2	1	0	-1.370025	-0.114301	1.161226
3	1	0	-0.110682	-0.554889	2.349619
4	6	0	-1.765973	-1.942084	2.227202
5	1	0	-2.363947	-1.395700	2.956797
6	1	0	-2.461902	-2.268432	1.457395
7	6	0	-1.074976	-3.118922	2.887003
8	1	0	-0.408685	-2.790175	3.684519
9	1	0	-1.802102	-3.798707	3.324541
10	1	0	-0.485132	-3.681802	2.167613
11	8	0	-0.047109	-1.637060	0.599472
12	16	0	0.713044	-0.823503	-0.490586
13	8	0	1.347510	0.339666	0.108121
14	8	0	1.649379	-1.752837	-1.095126
15	6	0	-0.504026	-0.329707	-1.636438
16	1	0	0.013948	0.207311	-2.424254
17	1	0	-0.968313	-1.230561	-2.021825
18	1	0	-1.231275	0.315576	-1.110048
19	9	0	-2.336667	1.113957	-0.050793
20	1	0	-2.116601	2.400998	0.841188
21	8	0	-1.833287	3.172940	1.378976
22	6	0	-0.541113	3.521942	0.988573

23	6	0	-0.581556	4.367976	-0.264763
24	1	0	0.085894	2.641904	0.822438
25	1	0	-0.102207	4.107724	1.798011
26	1	0	-0.911448	3.750909	-1.106148
27	1	0	0.407752	4.762298	-0.498284
28	8	0	-1.443001	5.458661	-0.090274
29	1	0	-2.192958	5.107306	0.389604
30	1	0	-5.303230	0.406959	-1.314226
31	6	0	-5.305304	-0.347143	-0.522530
32	1	0	-5.789605	0.088624	0.356864
33	6	0	-6.080711	-1.556050	-0.981573
34	1	0	-6.197592	-2.248884	-0.142618
35	1	0	-7.072732	-1.268975	-1.323817
36	8	0	-5.422254	-2.187255	-2.046404
37	1	0	-4.495279	-2.141991	-1.816250
38	8	0	-4.006084	-0.774527	-0.242999
39	1	0	-3.408387	0.005065	-0.159017
40	55	0	4.291577	-0.328540	-0.289628

Supplementary Table 2 Electronic *E* (Hartree), zero-point energy (*ZPE*) (kcal/mol), Gibbs free energy G_{353K} (in Hartree) of the conformers of [F^-…C_3H_7-OMs] system under the influence of two ethylene glycol molecules (MPW1K/6-311++G**)

(a)

	E	ZPE	G(353 K)
	-1342.74666	208.3	-1342.16571

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.632409	-0.750808	1.184357
2	1	0	0.709745	-0.305613	0.815437
3	1	0	2.206205	-0.009152	1.735841
4	6	0	1.346501	-1.968997	2.019138
5	1	0	0.676912	-1.650625	2.818254
6	1	0	0.784558	-2.679668	1.415424
7	6	0	2.588565	-2.620096	2.596165
8	1	0	3.133217	-1.926106	3.235785
9	1	0	2.332681	-3.493126	3.193931
10	1	0	3.261910	-2.938071	1.804240
11	8	0	2.437067	-1.186600	0.064834
12	16	0	2.791606	-0.132559	-1.066466
13	8	0	3.058354	1.142476	-0.453351
14	8	0	3.814826	-0.760439	-1.854883
15	6	0	1.304625	-0.034833	-1.998352
16	1	0	1.471539	0.722294	-2.757493
17	1	0	1.146820	-1.004256	-2.457064

18	1	0	0.466918	0.232865	-1.344589
19	9	0	-0.972000	0.377187	-0.140674
20	1	0	-1.246097	1.574304	0.786592
21	8	0	-1.329599	2.377839	1.358326
22	6	0	-0.398389	3.320528	0.922640
23	6	0	-0.986773	4.142093	-0.204560
24	1	0	0.534484	2.854264	0.598447
25	1	0	-0.174246	3.979531	1.763740
26	1	0	-1.070765	3.520534	-1.100480
27	1	0	-0.352123	4.996085	-0.439182
28	8	0	-2.249523	4.630671	0.169666
29	1	0	-2.640956	3.907432	0.661765
30	1	0	-4.004406	-0.475483	-0.433378
31	6	0	-3.683118	-1.338808	0.157463
32	1	0	-3.802391	-1.080223	1.215522
33	6	0	-4.553182	-2.526752	-0.173633
34	1	0	-4.334236	-3.338722	0.527506
35	1	0	-5.608114	-2.272899	-0.080130
36	8	0	-4.320899	-2.948308	-1.490569
37	1	0	-3.379958	-2.814605	-1.614262
38	8	0	-2.376144	-1.696139	-0.153737
39	1	0	-1.805880	-0.882467	-0.157978

(b)

	E	ZPE	G(353 K)
	-1342.74659	208.6	-1342.15985

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-1.199132	-1.228664	1.169551

2	1	0	-1.627366	-0.372740	1.680466
3	1	0	-0.278018	-0.914622	0.681574
4	6	0	-0.974270	-2.388063	2.100971
5	1	0	-0.342005	-2.018730	2.908600
6	1	0	-1.925530	-2.675715	2.549245
7	6	0	-0.321943	-3.582967	1.432472
8	1	0	0.639418	-3.307842	1.002396
9	1	0	-0.153368	-4.388675	2.144885
10	1	0	-0.949052	-3.966574	0.631577
11	8	0	-2.134767	-1.676493	0.158050
12	16	0	-2.700047	-0.621631	-0.878516
13	8	0	-3.752969	-1.307927	-1.572155
14	8	0	-3.006557	0.602759	-0.180574
15	6	0	-1.349613	-0.345246	-1.966803
16	1	0	-1.680334	0.413559	-2.668678
17	1	0	-0.472508	-0.004602	-1.401021
18	1	0	-1.153798	-1.278723	-2.482314
19	9	0	1.004621	0.430629	-0.373411
20	1	0	0.462775	1.254538	0.855697
21	8	0	0.050176	1.753473	1.596935
22	6	0	0.150550	3.112427	1.327062
23	6	0	-0.602525	3.531110	0.083463
24	1	0	1.197440	3.424690	1.211444
25	1	0	-0.260268	3.648897	2.183646
26	1	0	-0.201195	2.979525	-0.771310
27	1	0	-0.426893	4.593129	-0.095740
28	8	0	-1.988318	3.366630	0.185457
29	1	0	-2.190638	2.430871	0.217292
30	1	0	3.835261	0.201506	0.859005
31	6	0	4.183800	0.464162	-0.144611
32	1	0	4.257998	1.556907	-0.194114
33	6	0	5.545872	-0.142617	-0.379698
34	1	0	5.959207	0.252766	-1.313432
35	1	0	6.229547	0.112654	0.428864
36	8	0	5.450533	-1.539981	-0.446423
37	1	0	4.614372	-1.693373	-0.889613

38	8	0	3.336282	-0.051683	-1.116603
39	1	0	2.392644	0.127924	-0.853435

(c)

	E	ZPE	G(353 K)
	-1342.73975	208.1	-1342.15837

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	1.202736	-0.930950	-0.155742
2	1	0	1.084283	0.096349	-0.488978
3	1	0	0.967700	-0.987202	0.903282
4	6	0	0.352030	-1.861130	-0.969293
5	1	0	-0.656021	-1.445388	-0.924122
6	1	0	0.674126	-1.808808	-2.009715
7	6	0	0.386662	-3.294401	-0.477200
8	1	0	0.029033	-3.359338	0.549794
9	1	0	-0.256244	-3.926040	-1.086607
10	1	0	1.394183	-3.704609	-0.507494
11	8	0	2.590294	-1.321931	-0.327194
12	16	0	3.718308	-0.519940	0.433557
13	8	0	3.247737	-0.145021	1.739968
14	8	0	4.907406	-1.312845	0.306734
15	6	0	3.900220	0.933168	-0.546632
16	1	0	4.684415	1.519907	-0.080224
17	1	0	4.200734	0.624908	-1.541264
18	1	0	2.968995	1.495324	-0.568798
19	9	0	-2.077832	0.087438	-0.556107
20	1	0	-3.359210	-0.682043	-0.687731

21	8	0	-4.198669	-1.218791	-0.655685
22	6	0	-4.583441	-1.328394	0.676317
23	6	0	-5.444521	-0.144176	1.063807
24	1	0	-3.719540	-1.392471	1.343016
25	1	0	-5.168186	-2.244890	0.786410
26	1	0	-4.822694	0.753927	1.111124
27	1	0	-5.905533	-0.295295	2.040007
28	8	0	-6.472875	0.022670	0.121974
29	1	0	-6.048128	-0.166570	-0.716474
30	1	0	-0.438874	1.694771	0.996894
31	6	0	-0.684324	2.639300	0.506077
32	1	0	-1.311025	3.217489	1.194679
33	6	0	0.588007	3.409126	0.213348
34	1	0	0.344584	4.442526	-0.050766
35	1	0	1.250883	3.423180	1.076823
36	8	0	1.261169	2.792689	-0.856500
37	1	0	0.535348	2.492554	-1.415309
38	8	0	-1.316743	2.405621	-0.707712
39	1	0	-1.692031	1.469417	-0.693262

(d)

	E	ZPE	G(353 K)
	-1342.74441	208.8	-1342.15670

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	1.315299	-1.304126	-1.301216
2	1	0	1.621709	-0.641084	-2.105332
3	1	0	0.433076	-0.904253	-0.799960
4	6	0	1.063093	-2.702772	-1.794513

5	1	0	0.314283	-2.621181	-2.582795
6	1	0	1.971516	-3.093332	-2.255014
7	6	0	0.563540	-3.638483	-0.710875
8	1	0	-0.349540	-3.249550	-0.266966
9	1	0	0.351955	-4.625688	-1.117691
10	1	0	1.305728	-3.751201	0.076133
11	8	0	2.413065	-1.375251	-0.356471
12	16	0	2.713007	-0.113589	0.547562
13	8	0	3.994225	-0.365088	1.141995
14	8	0	2.544881	1.078753	-0.255917
15	6	0	1.453412	-0.165506	1.768187
16	1	0	1.560771	0.741193	2.354705
17	1	0	0.466625	-0.211551	1.285413
18	1	0	1.636867	-1.040661	2.381103
19	9	0	-1.108489	-0.420963	0.385843
20	1	0	-2.188317	-1.047320	-0.622601
21	8	0	-2.920360	-1.493001	-1.098946
22	6	0	-4.078702	-1.370597	-0.334154
23	6	0	-3.903462	-1.772683	1.116188
24	1	0	-4.833474	-2.018627	-0.785993
25	1	0	-4.467601	-0.345070	-0.358807
26	1	0	-3.444150	-2.769361	1.139218
27	1	0	-4.891593	-1.857980	1.574536
28	8	0	-3.176641	-0.859205	1.874830
29	1	0	-2.338110	-0.665021	1.406634
30	6	0	-0.560502	2.707516	-0.605060
31	1	0	-0.454284	2.606518	-1.689362
32	1	0	-0.854595	1.741716	-0.191729
33	6	0	-1.599102	3.751723	-0.303128
34	1	0	-2.535903	3.505249	-0.796848
35	1	0	-1.778956	3.778141	0.774745
36	8	0	0.644997	3.177088	-0.041541
37	1	0	1.323827	2.507909	-0.145394
38	8	0	-1.192604	5.019382	-0.760784
39	1	0	-0.263509	5.075397	-0.545478

(e)

	E	ZPE	G(353 K)
	-1342.74839	209.1	-1342.15494

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.565905	-0.592700	1.124979
2	1	0	-0.800530	0.454820	1.281489
3	1	0	0.177775	-0.697256	0.336085
4	6	0	-0.105810	-1.250275	2.396845
5	1	0	0.738912	-0.662342	2.755786
6	1	0	-0.891062	-1.161488	3.147907
7	6	0	0.302042	-2.699949	2.217501
8	1	0	1.094404	-2.789748	1.477237
9	1	0	0.662247	-3.123812	3.153511
10	1	0	-0.541069	-3.298750	1.880940
11	8	0	-1.781772	-1.278371	0.715410
12	16	0	-2.432600	-0.915593	-0.674767
13	8	0	-3.720267	-1.550063	-0.674567
14	8	0	-2.368038	0.516971	-0.868525
15	6	0	-1.384164	-1.694439	-1.848114
16	1	0	-1.750886	-1.392764	-2.823834
17	1	0	-0.339229	-1.387225	-1.701403
18	1	0	-1.498535	-2.764286	-1.714205
19	9	0	1.420191	-1.085276	-1.328995
20	1	0	2.870616	-1.639002	-0.875130
21	8	0	3.789332	-1.740568	-0.548598
22	6	0	4.108943	-0.608547	0.195419
23	6	0	3.918157	0.694226	-0.553702
24	1	0	5.160922	-0.692091	0.476908

25	1	0	3.526021	-0.559105	1.123654
26	1	0	4.444998	0.621908	-1.511544
27	1	0	4.380142	1.501780	0.018307
28	8	0	2.578735	1.035714	-0.754792
29	1	0	2.075255	0.230910	-1.063431
30	1	0	-0.215126	2.361732	-1.008786
31	6	0	0.055824	3.135901	-0.285269
32	1	0	0.527395	3.951887	-0.849014
33	6	0	-1.202338	3.683521	0.341317
34	1	0	-0.929608	4.382518	1.130583
35	1	0	-1.744131	4.247467	-0.428137
36	8	0	-2.029896	2.722144	0.927357
37	1	0	-2.210773	2.033412	0.284477
38	8	0	0.916032	2.634437	0.689278
39	1	0	1.568637	2.069860	0.247456

(f)

	E	ZPE	G(353 K)
	-1342.74092	208.8	-1342.13882

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-1.062243	1.292228	-0.234122
2	1	0	-0.322754	1.051807	-0.988394
3	1	0	-0.800708	0.806150	0.705983
4	6	0	-1.202320	2.777723	-0.059699
5	1	0	-0.197177	3.142310	0.146195
6	1	0	-1.517088	3.223568	-1.004087
7	6	0	-2.153014	3.166291	1.056241
8	1	0	-1.837916	2.721445	1.998275

9	1	0	-2.187444	4.247235	1.184711
10	1	0	-3.163239	2.822143	0.844969
11	8	0	-2.353215	0.788000	-0.682780
12	16	0	-2.573269	-0.772300	-0.728252
13	8	0	-3.788434	-0.969230	-1.467895
14	8	0	-1.366716	-1.407738	-1.212251
15	6	0	-2.814666	-1.209417	0.954186
16	1	0	-2.956768	-2.285610	0.965176
17	1	0	-1.930081	-0.916339	1.547413
18	1	0	-3.715028	-0.706140	1.288777
19	9	0	-0.480494	-0.371660	2.398454
20	1	0	0.878304	-0.285625	2.093707
21	8	0	1.856001	-0.292517	1.781216
22	6	0	2.226363	-1.611723	1.561782
23	6	0	1.341960	-2.338568	0.574684
24	1	0	2.212288	-2.185724	2.497177
25	1	0	3.256153	-1.627359	1.197120
26	1	0	0.317834	-2.306284	0.940435
27	1	0	1.658177	-3.385098	0.523298
28	8	0	1.411501	-1.771301	-0.712456
29	1	0	0.524192	-1.528179	-0.980906
30	1	0	3.900977	2.429467	0.084449
31	6	0	3.335451	1.795744	-0.613860
32	1	0	3.266832	2.333108	-1.560476
33	6	0	4.130126	0.525512	-0.827152
34	1	0	5.130192	0.802295	-1.166888
35	1	0	4.249009	0.018585	0.135929
36	8	0	3.591844	-0.332525	-1.783449
37	1	0	2.803735	-0.756662	-1.421587
38	8	0	2.035653	1.582832	-0.170302
39	1	0	2.024236	0.919753	0.545654

Supplementary Table 3 Comparison of ion-pair reaction [Cs^+F^-…C_3H_7-OMs] and reaction of naked nucleophile [F^-…C_3H_7-OMs]. Electronic energy (*E*), Gibbs free energy G_{353K} (in Hartree) and zero-point energy (*ZPE*) (in kcal/mol) of pre-reaction complex, transition state and post-reaction complex.

Ion-pair	Pre-reaction cplx	Transition state	Post-reaction cplx
E (Hartree)	-1362.65701	-1362.62433	-1362.66352
ZPE (kcal/mol)	209.7	209.2	209.3
G (353 K) (Hartree)	-1362.06641	-1362.03216	-1362.07847

Pre-reaction cplx

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.280844	1.615125	-0.918534
2	1	0	-2.053178	1.447801	-1.967038
3	1	0	-1.391400	1.426883	-0.316384
4	6	0	-2.824106	2.993457	-0.673204
5	1	0	-2.082630	3.684514	-1.073581
6	1	0	-3.734019	3.137043	-1.256291
7	6	0	-3.069186	3.289227	0.792828
8	1	0	-2.147982	3.183342	1.361311
9	1	0	-3.435961	4.303884	0.928446
10	1	0	-3.805737	2.608748	1.213283
11	8	0	-3.344463	0.667865	-0.570201
12	16	0	-2.971844	-0.821037	-0.268814

13	8	0	-2.004132	-1.294739	-1.229966
14	8	0	-2.650587	-0.992394	1.126442
15	6	0	-4.538062	-1.554956	-0.578838
16	1	0	-4.433984	-2.611906	-0.360168
17	1	0	-5.263723	-1.097862	0.082816
18	1	0	-4.794281	-1.396226	-1.618847
19	55	0	1.188557	-1.334282	-0.714329
20	9	0	0.478104	1.467794	0.246600
21	1	0	1.450998	1.002339	1.298386
22	8	0	2.149323	0.523108	1.823165
23	6	0	1.668933	0.149765	3.079250
24	6	0	0.202388	-0.194645	3.078194
25	1	0	1.821116	0.950583	3.810066
26	1	0	2.245019	-0.712014	3.417077
27	1	0	-0.362859	0.661781	2.708356
28	1	0	-0.106818	-0.389957	4.108903
29	8	0	-0.040380	-1.320003	2.267407
30	1	0	-0.961501	-1.298909	2.007235
31	1	0	4.690606	0.597305	-1.847831
32	6	0	4.440995	0.997038	-0.865854
33	1	0	5.351377	1.444908	-0.453918
34	6	0	3.397130	2.080921	-1.014188
35	1	0	3.183223	2.509053	-0.031999
36	1	0	3.827342	2.879208	-1.625839
37	8	0	2.221568	1.608320	-1.602182
38	1	0	1.498443	1.693909	-0.945228
39	8	0	4.020062	-0.091138	-0.087592
40	1	0	3.587253	0.223805	0.716467

Transition state

Coordinates

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-1.386636	1.498873	-0.887317
2	1	0	-0.980775	0.873653	-1.656888
3	1	0	-1.279735	1.196711	0.133487
4	6	0	-2.001216	2.802019	-1.241846
5	1	0	-1.195828	3.408741	-1.648285
6	1	0	-2.709493	2.624109	-2.047483
7	6	0	-2.669633	3.495557	-0.074504
8	1	0	-1.946918	3.723088	0.706123
9	1	0	-3.120625	4.432927	-0.390516
10	1	0	-3.450833	2.868653	0.347362
11	8	0	-3.045317	0.470367	-0.973853
12	16	0	-2.974582	-0.847801	-0.267618
13	8	0	-1.911706	-1.690901	-0.809292
14	8	0	-2.908917	-0.681948	1.184200
15	6	0	-4.520213	-1.611595	-0.637285
16	1	0	-4.532388	-2.577150	-0.144655
17	1	0	-5.311127	-0.976621	-0.256999
18	1	0	-4.594221	-1.725352	-1.711996
19	55	0	1.114492	-1.646613	-0.114068
20	9	0	0.444610	2.137278	-0.611659
21	1	0	1.235594	1.699242	0.752301
22	8	0	1.777326	1.222341	1.413009
23	6	0	1.242449	1.320881	2.703548
24	6	0	-0.221239	0.964043	2.779820
25	1	0	1.373364	2.327721	3.109173
26	1	0	1.812825	0.638305	3.331284
27	1	0	-0.801892	1.686504	2.200393
28	1	0	-0.541134	1.056970	3.821714
29	8	0	-0.421100	-0.336299	2.300978
30	1	0	-1.352119	-0.466917	2.079199
31	1	0	4.633275	-0.443144	-1.562171
32	6	0	4.424596	0.377089	-0.875807
33	1	0	5.375404	0.876948	-0.668065
34	6	0	3.498364	1.368970	-1.536286

35	1	0	3.343190	2.217255	-0.866092
36	1	0	3.991201	1.752537	-2.433908
37	8	0	2.269175	0.782290	-1.861786
38	1	0	1.564042	1.362155	-1.525806
39	8	0	3.892634	-0.193384	0.290122
40	1	0	3.367352	0.461954	0.763416

Post-reaction cplx

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.082048	2.141512	-0.886708
2	1	0	-1.068921	1.435172	-1.708267
3	1	0	-1.453751	1.642679	0.001324
4	6	0	-1.861011	3.374904	-1.217583
5	1	0	-1.431438	3.845457	-2.101965
6	1	0	-2.853755	3.023162	-1.496206
7	6	0	-1.947599	4.364800	-0.072448
8	1	0	-0.961387	4.716208	0.222795
9	1	0	-2.537619	5.233874	-0.353008
10	1	0	-2.419701	3.910977	0.797159
11	8	0	-3.268210	0.132121	-1.272352
12	16	0	-2.992238	-0.881907	-0.265399
13	8	0	-1.996154	-1.880078	-0.683938
14	8	0	-2.644984	-0.301038	1.052012
15	6	0	-4.500168	-1.770996	-0.004241
16	1	0	-4.326398	-2.530769	0.748704
17	1	0	-5.254124	-1.067268	0.328354
18	1	0	-4.790332	-2.222961	-0.945650
19	55	0	0.961918	-1.830849	-0.283068
20	9	0	0.277715	2.479799	-0.621143

21	1	0	1.273425	1.808813	1.024327
22	8	0	1.873597	1.299541	1.568890
23	6	0	1.346086	1.150645	2.869483
24	6	0	-0.108441	0.762268	2.879340
25	1	0	1.475329	2.072582	3.440183
26	1	0	1.939123	0.375158	3.348376
27	1	0	-0.700562	1.551297	2.405491
28	1	0	-0.434158	0.707278	3.922935
29	8	0	-0.291836	-0.451442	2.220912
30	1	0	-1.202548	-0.477083	1.866999
31	1	0	4.535882	-0.552473	-1.503522
32	6	0	4.335353	0.227435	-0.770079
33	1	0	5.297275	0.665660	-0.490021
34	6	0	3.488744	1.306317	-1.393691
35	1	0	3.331540	2.104813	-0.666350
36	1	0	4.028112	1.732467	-2.242848
37	8	0	2.254353	0.770070	-1.804784
38	1	0	1.587474	1.446584	-1.713595
39	8	0	3.719732	-0.387911	0.326846
40	1	0	3.239940	0.275931	0.835083

Naked nucleophile	Pre-reaction cplx	Transition state	Post-reaction cplx
E (Hartree)	-1342.74666	-1342.70375	-1342.73812
ZPE (kcal/mol)	208.3	207.4	208.1
G (353 K) (Hartree)	-1342.16571	-1342.12412	-1342.15812

Pre-reaction cplx

Coordinates

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	1.632409	-0.750808	1.184357
2	1	0	0.709745	-0.305613	0.815437
3	1	0	2.206205	-0.009152	1.735841
4	6	0	1.346501	-1.968997	2.019138
5	1	0	0.676912	-1.650625	2.818254
6	1	0	0.784558	-2.679668	1.415424
7	6	0	2.588565	-2.620096	2.596165
8	1	0	3.133217	-1.926106	3.235785
9	1	0	2.332681	-3.493126	3.193931
10	1	0	3.261910	-2.938071	1.804240
11	8	0	2.437067	-1.186600	0.064834
12	16	0	2.791606	-0.132559	-1.066466
13	8	0	3.058354	1.142476	-0.453351
14	8	0	3.814826	-0.760439	-1.854883
15	6	0	1.304625	-0.034833	-1.998352
16	1	0	1.471539	0.722294	-2.757493
17	1	0	1.146820	-1.004256	-2.457064
18	1	0	0.466918	0.232865	-1.344589
19	9	0	-0.972000	0.377187	-0.140674
20	1	0	-1.246097	1.574304	0.786592
21	8	0	-1.329599	2.377839	1.358326
22	6	0	-0.398389	3.320528	0.922640
23	6	0	-0.986773	4.142093	-0.204560
24	1	0	0.534484	2.854264	0.598447
25	1	0	-0.174246	3.979531	1.763740
26	1	0	-1.070765	3.520534	-1.100480
27	1	0	-0.352123	4.996085	-0.439182
28	8	0	-2.249523	4.630671	0.169666
29	1	0	-2.640956	3.907432	0.661765
30	1	0	-4.004406	-0.475483	-0.433378
31	6	0	-3.683118	-1.338808	0.157463
32	1	0	-3.802391	-1.080223	1.215522
33	6	0	-4.553182	-2.526752	-0.173633
34	1	0	-4.334236	-3.338722	0.527506

35	1	0	-5.608114	-2.272899	-0.080130
36	8	0	-4.320899	-2.948308	-1.490569
37	1	0	-3.379958	-2.814605	-1.614262
38	8	0	-2.376144	-1.696139	-0.153737
39	1	0	-1.805880	-0.882467	-0.157978

Transition state

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.849400	-0.417222	0.909273
2	1	0	0.463835	-1.390323	0.681866
3	1	0	0.965333	0.285425	0.107766
4	6	0	1.166853	-0.059236	2.318899
5	1	0	0.241219	-0.160717	2.879887
6	1	0	1.862618	-0.804919	2.694846
7	6	0	1.739127	1.334523	2.469788
8	1	0	1.024874	2.082391	2.133072
9	1	0	1.976254	1.542035	3.511711
10	1	0	2.651524	1.440444	1.887971
11	8	0	2.632274	-1.115034	0.494871
12	16	0	3.461998	-0.569978	-0.634333
13	8	0	2.838857	0.609146	-1.218333
14	8	0	4.857150	-0.448250	-0.265197
15	6	0	3.382106	-1.842956	-1.871181
16	1	0	3.964676	-1.514016	-2.724550
17	1	0	3.799411	-2.752332	-1.454278
18	1	0	2.345482	-1.988267	-2.153278
19	9	0	-0.993857	0.178217	0.957223
20	1	0	-1.351654	1.763728	0.896540
21	8	0	-1.505360	2.721254	0.781447
22	6	0	-0.975521	3.109996	-0.453576

23	6	0	-1.949452	2.782806	-1.563218
24	1	0	-0.009311	2.641498	-0.651271
25	1	0	-0.825402	4.189051	-0.413313
26	1	0	-1.999320	1.698426	-1.695056
27	1	0	-1.625092	3.223714	-2.504610
28	8	0	-3.220098	3.298591	-1.259603
29	1	0	-3.319955	3.155278	-0.318332
30	1	0	-2.858541	-1.399332	-1.133500
31	6	0	-3.580537	-1.350134	-0.313003
32	1	0	-4.108420	-0.394532	-0.386843
33	6	0	-4.565162	-2.483956	-0.442227
34	1	0	-5.359737	-2.353900	0.298967
35	1	0	-5.020043	-2.485936	-1.431022
36	8	0	-3.926365	-3.718899	-0.259029
37	1	0	-3.301168	-3.566891	0.449181
38	8	0	-2.946534	-1.505141	0.919414
39	1	0	-2.204117	-0.871390	0.981487

Post-reaction cplx

Coordinates

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.184119	-1.678347	0.461932
2	1	0	-0.247679	-2.265555	-0.343161
3	1	0	0.708614	-0.818227	0.059335
4	6	0	1.053196	-2.503417	1.358712
5	1	0	0.489508	-3.361903	1.728453
6	1	0	1.850840	-2.871984	0.714849
7	6	0	1.654845	-1.715380	2.506520
8	1	0	0.885251	-1.304608	3.157258
9	1	0	2.298469	-2.349916	3.112636
10	1	0	2.260399	-0.894896	2.129018

11	8	0	3.000036	-1.437110	-0.987622
12	16	0	3.270713	0.001178	-0.885918
13	8	0	2.053389	0.780275	-0.598352
14	8	0	4.399218	0.339967	-0.026184
15	6	0	3.754587	0.503485	-2.526822
16	1	0	3.951645	1.569842	-2.514064
17	1	0	4.650325	-0.043573	-2.799980
18	1	0	2.945512	0.274054	-3.211393
19	9	0	-0.927090	-1.166784	1.198319
20	1	0	-0.709202	0.698826	1.927826
21	8	0	-0.759959	1.611828	2.205531
22	6	0	0.002339	2.403692	1.313569
23	6	0	-0.789620	2.658179	0.055103
24	1	0	0.952679	1.938693	1.059750
25	1	0	0.184130	3.343093	1.832609
26	1	0	-0.850067	1.736568	-0.528884
27	1	0	-0.290803	3.401928	-0.561730
28	8	0	-2.078882	3.135093	0.364394
29	1	0	-2.324902	2.680381	1.169030
30	1	0	-2.908397	-0.495372	-1.575038
31	6	0	-3.621846	-0.162877	-0.817359
32	1	0	-3.365171	0.856061	-0.522532
33	6	0	-5.013708	-0.196674	-1.387879
34	1	0	-5.709378	0.224985	-0.656902
35	1	0	-5.063594	0.407169	-2.290808
36	8	0	-5.392034	-1.504250	-1.727251
37	1	0	-5.095537	-2.053272	-1.004105
38	8	0	-3.622841	-1.040976	0.281519
39	1	0	-2.735110	-1.120677	0.628717
