Electronic Supplementary Information

Lewis acid-promoted Cyclization/Halogenation of Allenyl Ethenetricarboxylates and the Amides: Stereoselective Synthesis of Haloalkenyl Five-membered Heterocycles

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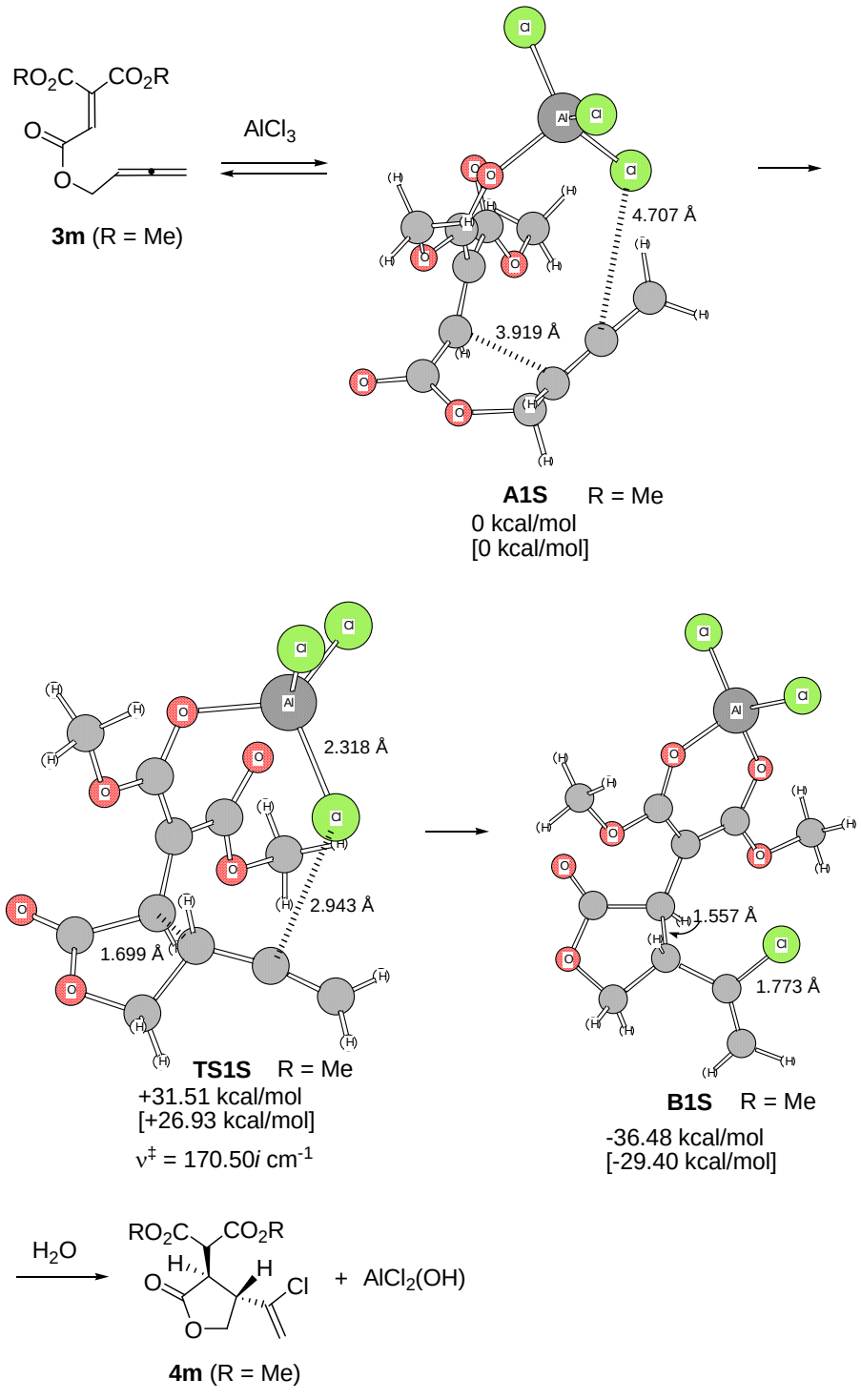
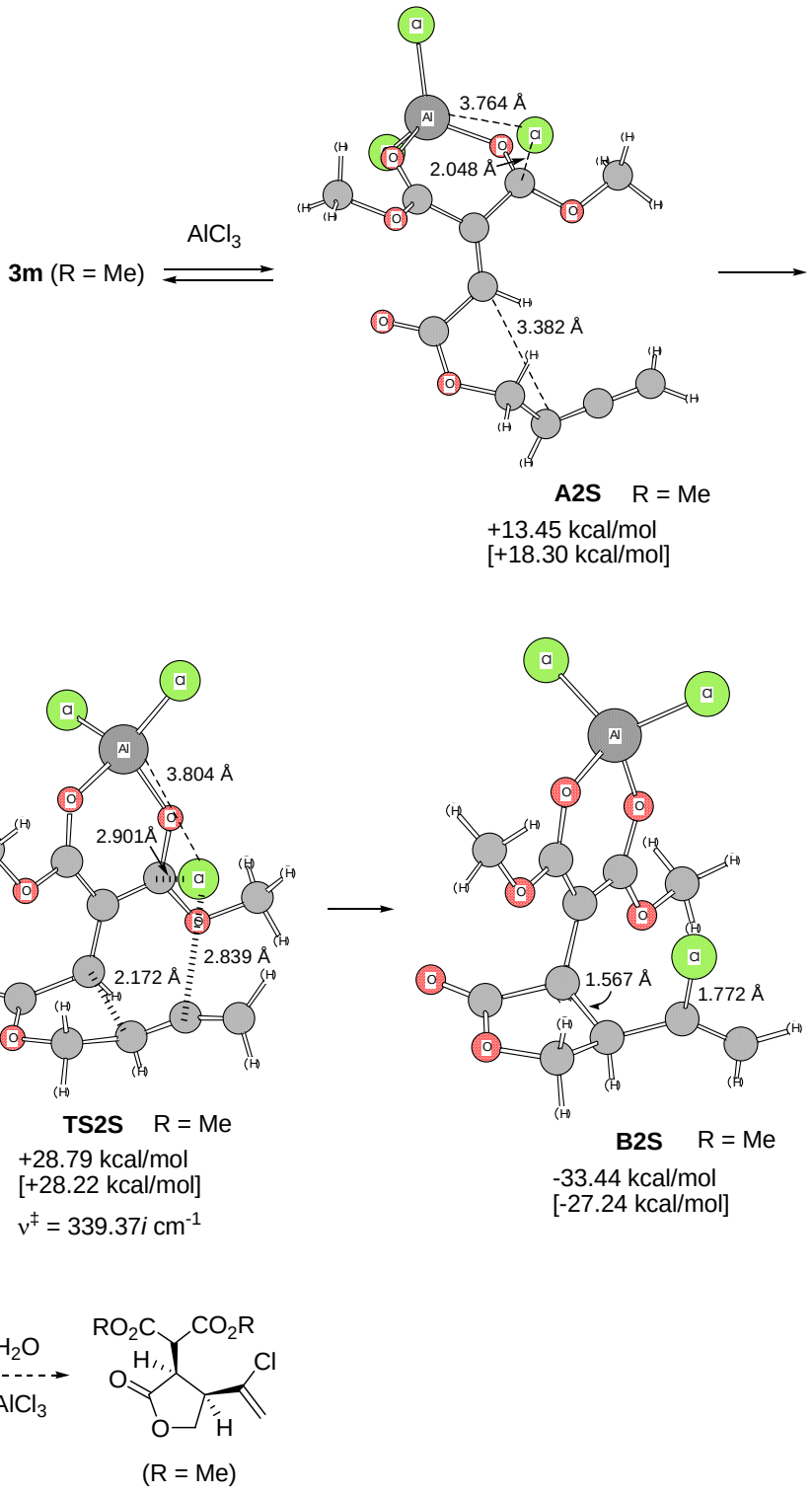
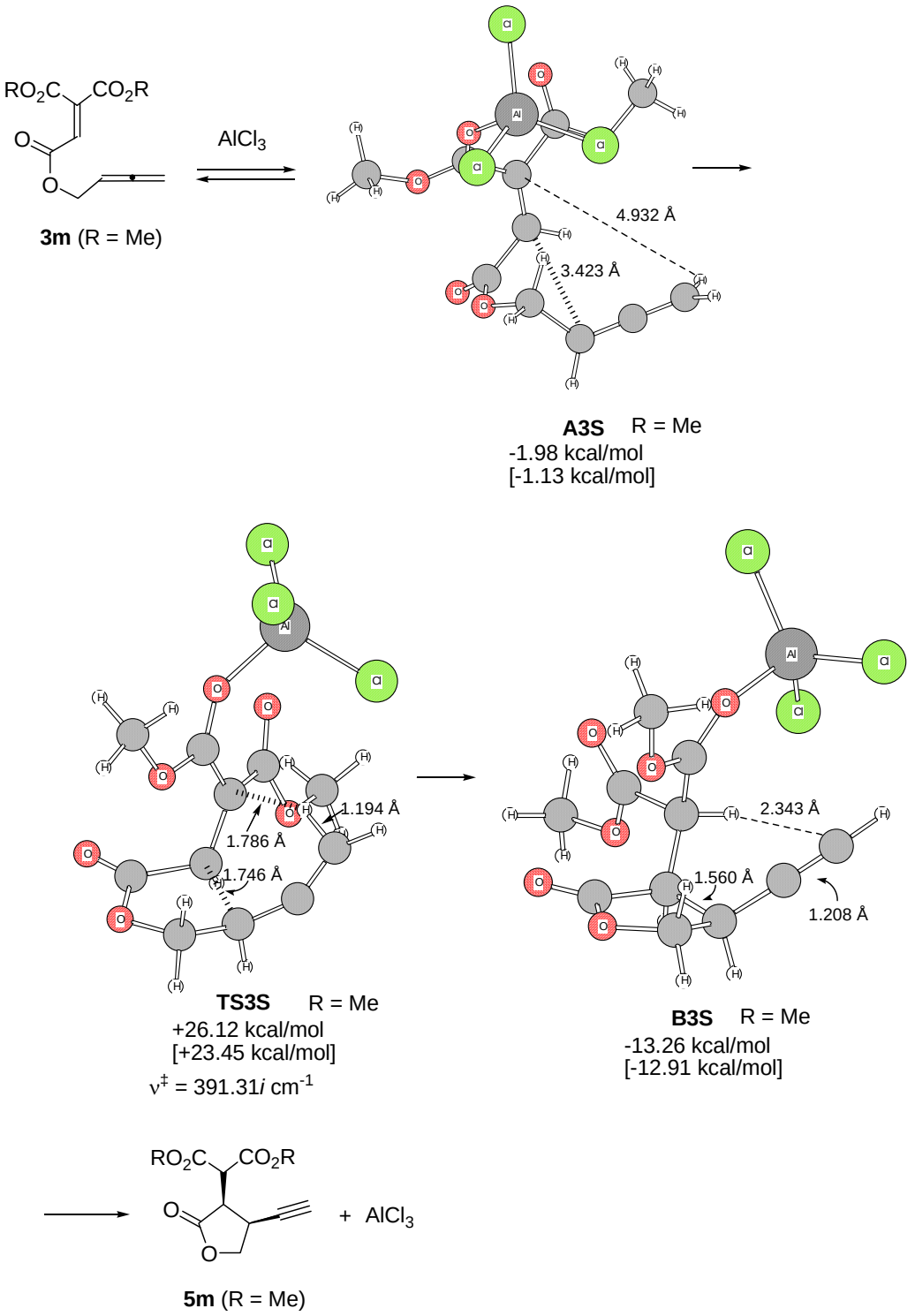
I. B3LYP/6-31G*-optimized structures of the model compounds, **3m** + $AlCl_3$



Scheme S1. The reaction pathway leading to 3,4-*trans* intermediate **B1S** for model compounds (**3m** + $AlCl_3$). B3LYP/6-31G*-optimized structures of the model compounds are shown. The Gibbs free energies ΔG^o are relative to **A1S** (R = Me). ΔG^o values are obtained by B3LYP/6-31G* (without brackets) and [B3LYP/6-311+G(d,p) SCRF = (PCM, solvent = CH_2Cl_2) // B3LYP/6-31G*] (with square brackets [ ]).



Scheme S2. The reaction pathway leading to 3,4-*cis* intermediate **B2S** for model compounds (**3m** + $AlCl_3$). B3LYP/6-31G*-optimized structures of the model compounds are shown. The Gibbs free energies are relative to **A1S** (R = Me) in Scheme S1.



Scheme S3. The reaction pathway leading to 3,4-*cis* ethynyl-2-oxotetrahydrofuran **5m** for model compounds (**3m** + $AlCl_3$). B3LYP/6-31G*-optimized structures of the model compounds are shown. The Gibbs free energies are relative to **A1S** (R = Me) in Scheme S1.

II. Cartesian coordinates of the optimized geometries of Schemes 3-4, 6, S1-S3 and energies of B3LYP/6-31G* and B3LYP/6-311+G(d,p) SCRF = (PCM, solvent = CH_2Cl_2) // B3LYP/6-31G*.

Scheme 3
A1 (Al2TS10.rev.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.433303	0.743621	-1.004863
2	6	0	-1.096676	1.259528	0.330352
3	6	0	-0.614109	2.526425	0.525093
4	1	0	-0.419494	2.830185	1.549007
5	6	0	-1.316461	0.381252	1.487275
6	6	0	-0.777106	3.664654	-0.459385
7	8	0	-1.914037	3.989549	-0.714744
8	8	0	0.272846	4.310507	-0.947815
9	6	0	1.625234	4.075630	-0.456395
10	1	0	1.807072	4.787685	0.353486
11	1	0	2.252086	4.344148	-1.310023
12	6	0	1.891406	2.663362	-0.016775
13	1	0	1.831791	1.868558	-0.762624
14	6	0	2.381944	2.390932	1.179337
15	6	0	2.877069	2.122236	2.351361
16	1	0	2.244835	1.830093	3.186383
17	1	0	3.952262	2.126378	2.517390
18	8	0	-1.970814	-0.695086	1.442586
19	8	0	-2.089941	-0.313915	-1.210009
20	8	0	-1.021697	1.465944	-1.997973
21	6	0	-1.282238	1.007194	-3.359695
22	1	0	-0.899192	1.806849	-3.989292
23	1	0	-2.355277	0.870169	-3.496697
24	1	0	-0.735702	0.077209	-3.517842
25	8	0	-0.845401	0.812465	2.621905
26	6	0	-0.992385	-0.043606	3.795825
27	1	0	-0.560766	0.535923	4.609086
28	1	0	-0.435673	-0.964986	3.622856
29	1	0	-2.049517	-0.246342	3.971054
30	13	0	-2.878903	-1.451577	0.017338
31	17	0	-2.374796	-3.448337	-0.305817
32	17	0	-4.901003	-0.877816	0.208584
33	17	0	1.566590	-0.548048	-1.901704
34	13	0	2.640803	-1.643575	-0.314727
35	17	0	1.362002	-1.435274	1.465362
36	17	0	4.508725	-0.634782	0.046770
37	17	0	2.864070	-3.698800	-0.845613

SCF Done: E(RB+HF-LYP) = -4124.20830839 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -4124.045838
Thermal correction to Gibbs Free Energy= 0.162470
After PCM corrections, the SCF energy is -4124.72302264 a.u.

TS1 (Al2TS10.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.479969	0.711270	-0.982539
2	6	0	-1.139983	1.169869	0.347562
3	6	0	-0.552228	2.431763	0.561889
4	1	0	-0.482435	2.727271	1.604630
5	6	0	-1.368838	0.280747	1.463538
6	6	0	-0.883414	3.618788	-0.343908
7	8	0	-2.033981	3.953738	-0.459597
8	8	0	0.128331	4.272446	-0.914706
9	6	0	1.467294	3.850134	-0.581086
10	1	0	1.886006	4.589703	0.106552
11	1	0	2.031352	3.866431	-1.516178
12	6	0	1.478457	2.457928	0.021634
13	1	0	1.419867	1.611795	-0.667813
14	6	0	2.051523	2.241753	1.216420

15	6	0	2.561595	2.040130	2.388014
16	1	0	1.941512	1.941239	3.276652
17	1	0	3.636197	1.902855	2.498521
18	8	0	-1.999414	-0.816104	1.395184
19	8	0	-2.137865	-0.339871	-1.242609
20	8	0	-1.067962	1.473894	-1.960146
21	6	0	-1.336002	1.057374	-3.330301
22	1	0	-0.947468	1.869873	-3.940574
23	1	0	-2.410300	0.934901	-3.472116
24	1	0	-0.802929	0.126063	-3.523564
25	8	0	-0.903237	0.679679	2.623050
26	6	0	-1.054593	-0.216750	3.761213
27	1	0	-0.641166	0.337074	4.602045
28	1	0	-0.486837	-1.127918	3.570296
29	1	0	-2.110567	-0.439039	3.919499
30	13	0	-2.896095	-1.525070	-0.051857
31	17	0	-2.355283	-3.506114	-0.446097
32	17	0	-4.939757	-1.029208	0.158751
33	17	0	1.542742	-0.637853	-1.895220
34	13	0	2.816418	-1.455797	-0.292231
35	17	0	1.548856	-1.487509	1.495161
36	17	0	4.409801	-0.014579	0.026596
37	17	0	3.537908	-3.397519	-0.789123

SCF Done: E(RB+HF-LYP) = -4124.20682332 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -4124.042317
Thermal correction to Gibbs Free Energy= 0.164507
After PCM corrections, the SCF energy is -4124.72023186 a.u.

B1 (Al2TS10.for.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.620897	0.354555	-1.050094
2	6	0	-1.409670	0.941827	0.219046
3	6	0	-0.454836	2.099840	0.373227
4	1	0	-0.562421	2.498608	1.388488
5	6	0	-2.190388	0.502057	1.302632
6	6	0	-0.778455	3.290529	-0.552817
7	8	0	-1.857477	3.652258	-0.931049
8	8	0	0.375969	3.933448	-0.882268
9	6	0	1.511114	3.307960	-0.264170
10	1	0	1.785388	3.873741	0.634698
11	1	0	2.338255	3.338502	-0.975338
12	6	0	1.048063	1.871817	0.084101
13	1	0	1.142753	1.252754	-0.813958
14	6	0	1.831077	1.228936	1.184292
15	6	0	1.478466	0.808244	2.391174
16	1	0	0.446357	0.907951	2.711653
17	1	0	2.179904	0.341895	3.072789
18	8	0	-3.087458	-0.418550	1.273153
19	8	0	-2.449568	-0.585930	-1.328152
20	8	0	-0.879067	0.828934	-2.040156
21	6	0	-1.077458	0.290937	-3.369187
22	1	0	-0.381304	0.845113	-3.996646
23	1	0	-2.106908	0.457948	-3.690493
24	1	0	-0.845366	-0.775342	-3.379989
25	8	0	-1.977937	1.093148	2.482112
26	6	0	-2.819661	0.705790	3.592383
27	1	0	-2.482382	1.323778	4.423775
28	1	0	-2.688898	-0.354106	3.818674
29	1	0	-3.866940	0.909198	3.361430
30	13	0	-3.618020	-1.383021	-0.179512
31	17	0	-3.137201	-3.425613	0.081848
32	17	0	-5.614050	-0.908266	-0.693557
33	17	0	2.365328	-1.285666	-1.731053
34	13	0	3.812090	-1.325395	-0.179795
35	17	0	3.337300	-2.467947	1.531014
36	17	0	3.586969	1.002804	0.725360
37	17	0	5.839231	-1.141902	-0.733418

SCF Done: E(RB+HF-LYP) = -4124.25611120 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -4124.085941
Thermal correction to Gibbs Free Energy= 0.170170
After PCM corrections, the SCF energy is -4124.75668199 a.u.

Scheme 4

A2 (Al2TS12.for.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.259689	-0.448599	-1.224475
2	6	0	0.570974	-1.019841	-0.038375
3	6	0	-0.436439	-1.915793	-0.123158
4	1	0	-0.909435	-2.244427	0.799106
5	6	0	1.059301	-0.566550	1.283687
6	6	0	-0.828682	-2.642124	-1.388736
7	8	0	0.039022	-3.180472	-2.040124
8	8	0	-2.113203	-2.729537	-1.707759
9	6	0	-3.160040	-2.164013	-0.849314
10	1	0	-3.939025	-1.882952	-1.560192
11	1	0	-2.812785	-1.254978	-0.353870
12	6	0	-3.644586	-3.208610	0.117767
13	1	0	-4.076237	-4.109938	-0.317934
14	6	0	-3.593043	-3.077206	1.421165
15	6	0	-3.566118	-2.945091	2.719907
16	1	0	-4.383860	-2.468772	3.256433
17	1	0	-2.728153	-3.303099	3.314865
18	8	0	2.225563	-0.128156	1.479595
19	8	0	2.466888	-0.080861	-1.211011
20	8	0	0.533190	-0.342253	-2.277651
21	6	0	1.087515	0.270176	-3.480696
22	1	0	1.874417	-0.374033	-3.875437
23	1	0	1.471342	1.258343	-3.226276
24	1	0	0.239698	0.336769	-4.157291
25	8	0	0.220164	-0.693764	2.257001
26	6	0	0.576527	-0.168885	3.571692
27	1	0	-0.312188	-0.336191	4.174945
28	1	0	0.790768	0.895732	3.474151
29	1	0	1.440071	-0.711451	3.959132
30	13	0	3.608035	0.003718	0.245431
31	17	0	4.565482	1.857615	0.359476
32	17	0	0.240346	2.261677	0.152167
33	17	0	4.714087	-1.786036	0.345570
34	13	0	-1.963995	2.243353	-0.065105
35	17	0	-2.733075	4.221221	0.122578
36	17	0	-2.694321	0.904920	1.490064
37	17	0	-2.383737	1.337228	-1.992740

SCF Done: E(RB+HF-LYP) = -4124.21623445 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -4124.054051
Thermal correction to Gibbs Free Energy= 0.162184
After PCM corrections, the SCF energy is -4124.72478315 a.u.

TS2 (Al2TS12.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.529381	0.423685	-1.051320
2	6	0	-1.662647	1.151669	0.196175
3	6	0	-1.101293	2.437633	0.388149
4	1	0	-1.475775	2.963743	1.259339
5	6	0	-2.425608	0.555148	1.262359
6	6	0	-0.847982	3.374604	-0.795000
7	8	0	-1.802952	3.911234	-1.296990
8	8	0	0.412421	3.587888	-1.156643
9	6	0	1.399607	2.805784	-0.437987
10	1	0	2.328229	3.373913	-0.496554
11	1	0	1.534187	1.837257	-0.920488
12	6	0	0.938812	2.670364	0.998872
13	1	0	0.836279	3.613511	1.540857
14	6	0	1.096183	1.552605	1.725020
15	6	0	1.139572	0.445615	2.386835
16	1	0	2.083179	0.020010	2.734687
17	1	0	0.242599	-0.152526	2.547767
18	8	0	-3.075422	-0.532576	1.184231
19	8	0	-2.091582	-0.685638	-1.303563
20	8	0	-0.792786	0.994062	-1.960334
21	6	0	-0.597484	0.329809	-3.247590
22	1	0	-1.568499	0.112703	-3.693283
23	1	0	-0.014352	-0.576741	-3.086377
24	1	0	-0.041493	1.054507	-3.838034
25	8	0	-2.434356	1.214090	2.403327

26	6	0	-3.234770	0.686520	3.497397
27	1	0	-3.085813	1.394396	4.310432
28	1	0	-2.878871	-0.307660	3.771961
29	1	0	-4.283850	0.643517	3.200713
30	13	0	-3.283663	-1.640877	-0.281920
31	17	0	-2.579686	-3.558783	0.177185
32	17	0	1.786765	-1.005973	-0.997314
33	17	0	-5.223748	-1.368904	-1.056217
34	13	0	3.769827	-0.969766	-0.030716
35	17	0	5.237549	-1.812768	-1.330463
36	17	0	3.594609	-2.006836	1.866936
37	17	0	4.198123	1.132596	0.412554

SCF Done: E(RB+HF-LYP) = -4124.19956852 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -4124.034410
Thermal correction to Gibbs Free Energy= 0.165158
After PCM corrections, the SCF energy is -4124.71607915 a.u.

B2 (Al2TS12.rev.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.542756	0.193251	-0.894828
2	6	0	-1.621113	0.997269	0.263998
3	6	0	-0.707861	2.193166	0.461953
4	1	0	-1.122537	2.748273	1.303510
5	6	0	-2.683081	0.775035	1.166804
6	6	0	-0.783878	3.154155	-0.747932
7	8	0	-1.775626	3.677201	-1.176869
8	8	0	0.449313	3.365865	-1.272310
9	6	0	1.433552	2.506140	-0.684957
10	1	0	2.351858	3.085029	-0.575360
11	1	0	1.611919	1.659439	-1.350694
12	6	0	0.838256	2.064015	0.678936
13	1	0	1.099824	2.851234	1.399864
14	6	0	1.410112	0.790297	1.227008
15	6	0	0.869946	-0.289605	1.771292
16	1	0	1.463193	-1.103946	2.170364
17	1	0	-0.208861	-0.379559	1.807002
18	8	0	-3.584971	-0.137215	1.066629
19	8	0	-2.307327	-0.793702	-1.196988
20	8	0	-0.573280	0.498045	-1.743893
21	6	0	-0.468125	-0.258968	-2.975298
22	1	0	-1.389283	-0.161161	-3.551937
23	1	0	-0.267797	-1.307956	-2.752980
24	1	0	0.371456	0.189333	-3.503129
25	8	0	-2.751623	1.574290	2.227091
26	6	0	-3.861188	1.404696	3.137458
27	1	0	-3.710533	2.166848	3.900924
28	1	0	-3.843144	0.406029	3.578129
29	1	0	-4.806666	1.563014	2.615215
30	13	0	-3.725163	-1.407408	-0.230969
31	17	0	-3.281832	-3.309741	0.587099
32	17	0	3.202112	-0.836617	-1.922306
33	17	0	-5.528071	-1.193409	-1.310053
34	13	0	4.234644	-1.020472	-0.079424
35	17	0	6.213886	-0.298583	0.012672
36	17	0	3.725783	-2.689303	1.113616
37	17	0	3.248842	0.868435	1.244756

SCF Done: E(RB+HF-LYP) = -4124.24632134 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -4124.076156
Thermal correction to Gibbs Free Energy= 0.170165
After PCM corrections, the SCF energy is -4124.74713666 a.u.

Scheme 6
3m s-cis (Enallene14.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.631565	1.084517	0.306173
2	6	0	1.364367	-0.393478	0.157450
3	6	0	0.159932	-0.957732	0.329129
4	1	0	0.066114	-2.036776	0.261582
5	6	0	2.530151	-1.291991	-0.130743

6	6	0	-1.064504	-0.170481	0.615855
7	8	0	-1.113693	1.039775	0.730522
8	8	0	-2.128532	-0.990104	0.737782
9	6	0	-3.397436	-0.348896	1.044223
10	1	0	-3.215826	0.412723	1.807810
11	1	0	-4.015765	-1.149458	1.450280
12	6	0	-4.028626	0.263220	-0.178985
13	1	0	-3.522179	1.125974	-0.608516
14	6	0	-5.135323	-0.189806	-0.712317
15	6	0	-6.246580	-0.641730	-1.229051
16	1	0	-7.217779	-0.272722	-0.904805
17	1	0	-6.243300	-1.402001	-2.007753
18	8	0	2.470914	-2.502057	-0.186189
19	8	0	2.051573	1.578874	1.325883
20	8	0	1.393669	1.740457	-0.838252
21	6	0	1.574401	3.166894	-0.769573
22	1	0	1.370504	3.533736	-1.775618
23	1	0	2.596229	3.409928	-0.467717
24	1	0	0.870881	3.595826	-0.051769
25	8	0	3.651475	-0.577520	-0.335742
26	6	0	4.833235	-1.347211	-0.617926
27	1	0	5.632006	-0.616580	-0.742888
28	1	0	4.696173	-1.932953	-1.530529
29	1	0	5.052586	-2.022928	0.212475

SCF Done: E(RB+HF-LYP) = -877.673032811 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -877.503361
Thermal correction to Gibbs Free Energy= 0.169672
After PCM corrections, the SCF energy is -877.959594148 a.u.

3m s-trans (Enallene15.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.665064	-1.037959	-0.265356
2	6	0	0.795984	0.196024	-0.232348
3	6	0	-0.539544	0.177331	-0.359527
4	1	0	-1.056194	1.130646	-0.364237
5	6	0	1.470837	1.530618	-0.121987
6	6	0	-1.306059	-1.099600	-0.444321
7	8	0	-0.831697	-2.171535	-0.140568
8	8	0	-2.592964	-1.055105	-0.874150
9	6	0	-3.190900	0.141349	-1.381368
10	1	0	-3.987081	-0.209678	-2.046673
11	1	0	-2.477884	0.699228	-2.002859
12	6	0	-3.776497	1.026128	-0.304854
13	1	0	-4.307661	1.907468	-0.667655
14	6	0	-3.696553	0.795955	0.980811
15	6	0	-3.613379	0.565385	2.263525
16	1	0	-2.790197	0.953203	2.860554
17	1	0	-4.362235	-0.028124	2.784444
18	8	0	0.894210	2.598399	-0.132646
19	8	0	2.080099	-1.527253	-1.289870
20	8	0	1.948714	-1.460280	0.973224
21	6	0	2.736486	-2.663397	1.040391
22	1	0	2.883095	-2.854485	2.103453
23	1	0	3.695572	-2.522103	0.535668
24	1	0	2.195151	-3.488210	0.570830
25	8	0	2.803463	1.390863	-0.007232
26	6	0	3.549495	2.616220	0.096603
27	1	0	4.593911	2.314271	0.170290
28	1	0	3.242870	3.173181	0.985643
29	1	0	3.386451	3.235560	-0.788937

SCF Done: E(RB+HF-LYP) = -877.658439823 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -877.489050
Thermal correction to Gibbs Free Energy= 0.169390
After PCM corrections, the SCF energy is -877.947095204 a.u.

11m s-cis (Nal4.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.758547	1.183998	0.289774
2	6	0	1.582961	-0.307297	0.153285

3	6	0	0.418880	-0.949231	0.337209
4	1	0	0.444578	-2.032844	0.288059
5	6	0	2.797882	-1.137630	-0.131856
6	6	0	-0.849056	-0.233451	0.669457
7	8	0	-0.831027	0.929766	1.077996
8	7	0	-2.022069	-0.936242	0.554204
9	6	0	-3.253677	-0.266876	0.990736
10	1	0	-2.984038	0.399654	1.812738
11	1	0	-3.943060	-1.031443	1.361880
12	6	0	-3.901555	0.532938	-0.122994
13	1	0	-3.320530	1.374053	-0.500251
14	6	0	-5.077127	0.263264	-0.631592
15	6	0	-6.261194	-0.003434	-1.118205
16	1	0	-7.162102	0.441164	-0.699103
17	1	0	-6.394818	-0.673196	-1.965707
18	8	0	2.816729	-2.351982	-0.138063
19	8	0	2.317447	1.696414	1.230783
20	8	0	1.279545	1.838522	-0.780581
21	6	0	1.329153	3.272411	-0.681607
22	1	0	0.946474	3.643477	-1.632803
23	1	0	2.354825	3.612389	-0.517689
24	1	0	0.698150	3.607062	0.145683
25	8	0	3.864106	-0.366893	-0.410270
26	6	0	5.081567	-1.074323	-0.698694
27	1	0	5.826005	-0.302563	-0.893302
28	1	0	4.951137	-1.717411	-1.573031
29	1	0	5.375703	-1.688042	0.156484
30	6	0	-2.199587	-2.194449	-0.160386
31	1	0	-2.442585	-3.013736	0.528978
32	1	0	-1.307122	-2.459902	-0.725603
33	1	0	-3.023305	-2.087111	-0.875435

SCF Done: E(RB+HF-LYP) = -897.114649212 A.U. after 2 cycles
Sum of electronic and thermal Free Energies= -896.906343
Thermal correction to Gibbs Free Energy= 0.208307
After PCM corrections, the SCF energy is -897.404540283 a.u.

11m s-trans (Nal1.log)
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.813308	1.092744	-0.208946
2	6	0	-1.067783	-0.219518	-0.197071
3	6	0	0.267786	-0.318690	-0.269518
4	1	0	0.691866	-1.317377	-0.288837
5	6	0	-1.865370	-1.485771	-0.169378
6	6	0	1.156589	0.884078	-0.252959
7	8	0	0.743471	1.963923	0.168842
8	7	0	2.442415	0.711945	-0.704399
9	6	0	2.945092	-0.512688	-1.310342
10	1	0	3.688717	-0.226509	-2.065685
11	1	0	2.142938	-1.009808	-1.867097
12	6	0	3.582352	-1.495521	-0.340375
13	1	0	4.068035	-2.358380	-0.799189
14	6	0	3.570684	-1.381595	0.963375
15	6	0	3.560631	-1.262726	2.264550
16	1	0	4.354076	-0.741446	2.797068
17	6	0	3.383733	1.819550	-0.586553
18	8	0	-1.392699	-2.604247	-0.182983
19	8	0	-2.095216	1.692422	-1.220608
20	8	0	-2.170888	1.453787	1.032194
21	6	0	-2.849155	2.718014	1.123623
22	1	0	-3.078177	2.849187	2.181498
23	1	0	-3.765546	2.707325	0.527690
24	1	0	-2.194399	3.517993	0.769125
25	8	0	-3.186951	-1.228397	-0.130219
26	6	0	-4.041571	-2.383545	-0.108795
27	1	0	-5.058466	-1.992140	-0.084615
28	1	0	-3.838967	-2.990534	0.777404
29	1	0	-3.882136	-2.991773	-1.002867
30	1	0	4.293335	1.484011	-0.076139
31	1	0	2.909367	2.613701	-0.012203
32	1	0	3.655623	2.205983	-1.577378
33	1	0	2.757012	-1.679748	2.868545

SCF Done: E(RB+HF-LYP) = -897.113080326 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -896.904877
Thermal correction to Gibbs Free Energy= 0.208203

After PCM corrections, the SCF energy is -897.404538646   a.u.

Scheme S1
A1S   (AlTS5.rev.log)
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.410271	0.117635	-1.107207
2	6	0	0.944589	1.285333	-0.370750
3	6	0	2.260552	1.453287	-0.127542
4	1	0	2.544775	2.336035	0.441410
5	6	0	-0.051644	2.339633	0.025402
6	6	0	3.426716	0.687794	-0.696953
7	8	0	3.918970	1.099246	-1.719536
8	8	0	3.953008	-0.346227	-0.033387
9	6	0	3.428802	-0.816458	1.239769
10	1	0	2.663225	-0.139498	1.628241
11	1	0	4.292639	-0.792361	1.912289
12	6	0	2.898313	-2.216200	1.091274
13	1	0	3.545606	-2.917391	0.564001
14	6	0	1.773316	-2.624828	1.627479
15	6	0	0.668733	-3.039032	2.186114
16	1	0	0.664235	-3.406106	3.211033
17	1	0	-0.284172	-3.030675	1.660189
18	8	0	-1.091837	2.515161	-0.567791
19	8	0	-0.761812	-0.293158	-1.041915
20	8	0	1.287712	-0.498965	-1.856658
21	6	0	0.872896	-1.716384	-2.540329
22	1	0	1.775546	-2.071564	-3.032803
23	1	0	0.094720	-1.473802	-3.265442
24	1	0	0.499964	-2.437443	-1.811876
25	8	0	0.381985	3.074889	1.057539
26	6	0	-0.521551	4.118546	1.486455
27	1	0	-0.019018	4.606304	2.320962
28	1	0	-1.467773	3.675814	1.803622
29	1	0	-0.699761	4.823330	0.671238
30	13	0	-2.362113	-0.520497	-0.060396
31	17	0	-1.943061	0.251881	1.895235
32	17	0	-2.449932	-2.668309	-0.060174
33	17	0	-3.905400	0.395857	-1.182472

SCF Done: E(RB+HF-LYP) = -2500.93736279   A.U. after   1 cycles
Sum of electronic and thermal Free Energies=   -2500.772050
Thermal correction to Gibbs Free Energy=   0.165313
After PCM corrections, the SCF energy is -2501.33648913   a.u.

TS1S   (AlTS5.log)
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.170937	-1.108660	-0.882808
2	6	0	0.765601	0.187070	-0.857595
3	6	0	2.117433	0.407168	-0.391141
4	1	0	2.371053	1.469709	-0.451789
5	6	0	-0.117207	1.299718	-1.085640
6	6	0	3.272373	-0.366276	-1.059776
7	8	0	3.363784	-0.623732	-2.223071
8	8	0	4.244864	-0.662055	-0.153203
9	6	0	3.936746	-0.166973	1.142306
10	1	0	4.416195	0.805948	1.296762
11	1	0	4.310464	-0.885980	1.873012
12	6	0	2.385072	-0.049739	1.223541
13	1	0	1.919031	-1.032497	1.339106
14	6	0	1.948276	0.859595	2.182407
15	6	0	1.772005	1.710014	3.138825
16	1	0	2.420162	1.692085	4.019183
17	1	0	0.956107	2.431312	3.135849
18	8	0	-1.363473	1.218534	-1.111851
19	8	0	-1.071111	-1.327264	-0.970918
20	8	0	1.010218	-2.136899	-0.775289
21	6	0	0.422663	-3.465015	-0.755830
22	1	0	1.252482	-4.131355	-0.523399
23	1	0	0.008704	-3.695575	-1.739393
24	1	0	-0.363573	-3.518770	-0.001222
25	8	0	0.486060	2.475110	-1.281524

26	6	0	-0.382155	3.618839	-1.451142
27	1	0	0.290336	4.471094	-1.545371
28	1	0	-1.038463	3.726543	-0.585386
29	1	0	-0.986785	3.500206	-2.352181
30	13	0	-2.278420	-0.212008	0.041866
31	17	0	-0.953595	0.653813	1.735965
32	17	0	-2.955741	-1.986775	1.159099
33	17	0	-4.152395	0.675280	-0.548092

SCF Done: E(RB+HF-LYP) = -2500.89514972 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -2500.721835
Thermal correction to Gibbs Free Energy= 0.173315
After PCM corrections, the SCF energy is -2501.30158004 a.u.

B1S (AlTS5.for.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.342140	1.082706	-0.508371
2	6	0	0.314097	0.223618	0.394153
3	6	0	1.786587	0.383527	0.674733
4	1	0	2.036089	-0.248758	1.534242
5	6	0	-0.437181	-0.763189	1.060646
6	6	0	2.179056	1.815710	1.081773
7	8	0	1.531681	2.609952	1.707486
8	8	0	3.439144	2.082210	0.637851
9	6	0	4.007194	0.931837	-0.012182
10	1	0	4.648414	0.416645	0.711233
11	1	0	4.620137	1.283543	-0.844422
12	6	0	2.810099	0.071113	-0.456404
13	1	0	2.417236	0.486646	-1.390241
14	6	0	3.121257	-1.384057	-0.682111
15	6	0	4.223717	-2.052292	-0.346733
16	1	0	5.049950	-1.558975	0.153850
17	1	0	4.337758	-3.107527	-0.566232
18	8	0	-1.699214	-0.981219	0.921780
19	8	0	-1.597187	1.085414	-0.794567
20	8	0	0.423823	1.973656	-1.129562
21	6	0	-0.213864	2.947502	-1.984124
22	1	0	0.600485	3.575250	-2.343637
23	1	0	-0.930871	3.538741	-1.411427
24	1	0	-0.718576	2.451242	-2.815447
25	8	0	0.219028	-1.545331	1.911738
26	6	0	-0.524805	-2.569376	2.604649
27	1	0	0.210127	-3.064555	3.238277
28	1	0	-0.955416	-3.274208	1.890579
29	1	0	-1.316944	-2.122909	3.208954
30	13	0	-2.852080	-0.053723	-0.134203
31	17	0	1.824666	-2.257599	-1.518497
32	17	0	-3.610648	-1.293778	-1.676671
33	17	0	-4.273055	0.986861	1.041340

SCF Done: E(RB+HF-LYP) = -2501.00692115 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -2500.830180
Thermal correction to Gibbs Free Energy= 0.176741
After PCM corrections, the SCF energy is -2501.39476329 a.u.

Scheme S2
A2S (AlTS8.rev.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.606994	-1.257366	-0.590672
2	6	0	-0.342514	-0.160121	-0.262886
3	6	0	-1.585875	-0.379098	0.187338
4	1	0	-2.204517	0.483245	0.410289
5	6	0	0.259178	1.228166	-0.374591
6	6	0	-2.116324	-1.744894	0.504676
7	8	0	-1.414965	-2.619729	0.962469
8	8	0	-3.428199	-1.980934	0.299955
9	6	0	-4.299744	-0.999233	-0.316242
10	1	0	-5.068054	-1.611798	-0.796589
11	1	0	-3.770959	-0.438754	-1.092443
12	6	0	-4.914127	-0.086002	0.713191
13	1	0	-5.424734	-0.573270	1.543894

14	6	0	-4.881545	1.221500	0.634837
15	6	0	-4.851240	2.523873	0.543248
16	1	0	-5.624141	3.075202	0.011441
17	1	0	-4.053738	3.107046	0.999221
18	8	0	1.393540	1.408181	0.277697
19	8	0	1.795581	-1.263686	-0.185443
20	8	0	0.147755	-2.203499	-1.347457
21	6	0	1.008053	-3.346436	-1.612568
22	1	0	1.210709	-3.861735	-0.672364
23	1	0	1.934815	-3.008213	-2.077514
24	1	0	0.429740	-3.973121	-2.287994
25	8	0	-0.684706	2.171557	-0.184573
26	6	0	-0.217882	3.530312	-0.117583
27	1	0	-1.118668	4.136983	-0.022173
28	1	0	0.314207	3.783191	-1.039088
29	1	0	0.435084	3.670947	0.746135
30	13	0	2.644418	0.193501	0.666885
31	17	0	4.500967	0.478733	-0.297333
32	17	0	2.691955	-0.232768	2.741643
33	17	0	0.695368	1.249060	-2.375251

SCF Done: E(RB+HF-LYP) = -2500.91876483 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -2500.750615
Thermal correction to Gibbs Free Energy= 0.168150
After PCM corrections, the SCF energy is -2501.31015631 a.u.

TS2S (AlTS8.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.023036	-1.028932	-0.465834
2	6	0	-0.474034	-0.273058	0.662042
3	6	0	-1.770637	-0.421932	1.155080
4	1	0	-1.951624	0.076204	2.100684
5	6	0	0.382278	0.766506	1.196593
6	6	0	-2.534591	-1.727533	1.025283
7	8	0	-2.213183	-2.693693	1.671674
8	8	0	-3.615043	-1.729371	0.231036
9	6	0	-3.846151	-0.541510	-0.550780
10	1	0	-4.930726	-0.511694	-0.692334
11	1	0	-3.359780	-0.653180	-1.523341
12	6	0	-3.342700	0.696731	0.157282
13	1	0	-3.769297	0.889730	1.142697
14	6	0	-3.024095	1.799953	-0.561308
15	6	0	-3.130389	2.924971	-1.210266
16	1	0	-4.125842	3.337011	-1.388238
17	1	0	-2.267899	3.452446	-1.604826
18	8	0	1.631989	0.864428	0.994904
19	8	0	1.237141	-1.099846	-0.825639
20	8	0	-0.872013	-1.741058	-1.107970
21	6	0	-0.436077	-2.509843	-2.258039
22	1	0	0.338881	-3.218115	-1.961440
23	1	0	-0.060466	-1.827565	-3.022436
24	1	0	-1.330805	-3.029344	-2.596206
25	8	0	-0.194369	1.606153	2.023857
26	6	0	0.593698	2.722566	2.506831
27	1	0	-0.082755	3.278077	3.154295
28	1	0	0.910750	3.328526	1.656255
29	1	0	1.459724	2.360540	3.063349
30	13	0	2.656906	-0.186223	-0.103235
31	17	0	3.789067	0.881084	-1.515837
32	17	0	3.720961	-1.542830	1.135186
33	17	0	-0.322271	1.769855	-1.432915

SCF Done: E(RB+HF-LYP) = -2500.89710798 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -2500.726175
Thermal correction to Gibbs Free Energy= 0.170933
After PCM corrections, the SCF energy is -2501.29714485 a.u.

B2S (AlTS8.for.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.096254	-1.058835	0.222691
2	6	0	0.400471	-0.069418	-0.649488

3	6	0	1.848566	-0.042859	-1.096826
4	1	0	1.860015	0.486824	-2.051060
5	6	0	-0.488884	0.908483	-1.135061
6	6	0	2.432363	-1.438964	-1.391148
7	8	0	2.050939	-2.223430	-2.217243
8	8	0	3.519906	-1.668537	-0.606379
9	6	0	3.675346	-0.644074	0.389204
10	1	0	4.745435	-0.474167	0.526727
11	1	0	3.239575	-0.996059	1.327456
12	6	0	2.940459	0.592085	-0.169982
13	1	0	3.640025	1.108085	-0.837525
14	6	0	2.514738	1.629558	0.834369
15	6	0	2.728238	2.938064	0.701089
16	1	0	3.245924	3.315659	-0.176025
17	1	0	2.399731	3.657393	1.442484
18	8	0	-1.745454	1.000666	-0.864701
19	8	0	-1.313495	-1.195813	0.617113
20	8	0	0.790044	-1.934249	0.677170
21	6	0	0.324613	-3.025134	1.500530
22	1	0	-0.417370	-3.615770	0.960034
23	1	0	-0.105581	-2.640846	2.427420
24	1	0	1.215764	-3.618144	1.701274
25	8	0	0.018168	1.828980	-1.951642
26	6	0	-0.878420	2.822158	-2.491589
27	1	0	-0.251344	3.444202	-3.129515
28	1	0	-1.319113	3.415165	-1.687571
29	1	0	-1.669123	2.346353	-3.075367
30	13	0	-2.716036	-0.122747	0.184299
31	17	0	-3.439136	0.893040	1.897424
32	17	0	-4.141969	-1.178740	-0.972398
33	17	0	1.684413	1.052741	2.290179

SCF Done: E(RB+HF-LYP) = -2501.00252569 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -2500.825339
Thermal correction to Gibbs Free Energy= 0.177187
After PCM corrections, the SCF energy is -2501.39176585 a.u.

Scheme S3
A3S (AlTS10.for.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.266317	-0.701022	-1.382620
2	6	0	0.742732	0.385598	-1.267098
3	6	0	2.042240	0.126971	-1.036755
4	1	0	2.722592	0.968547	-0.944807
5	6	0	0.204870	1.771908	-1.459391
6	6	0	2.680875	-1.235706	-1.003984
7	8	0	3.315933	-1.603221	-1.962016
8	8	0	2.510338	-2.021790	0.072409
9	6	0	2.140816	-1.455959	1.369000
10	1	0	1.830391	-2.334710	1.938543
11	1	0	1.290345	-0.776972	1.279047
12	6	0	3.318556	-0.772304	2.008870
13	1	0	4.212513	-1.378334	2.156390
14	6	0	3.295439	0.478019	2.402363
15	6	0	3.258153	1.718032	2.807836
16	1	0	2.915639	1.976581	3.807591
17	1	0	3.559239	2.539727	2.161340
18	8	0	-0.902909	1.986180	-1.902420
19	8	0	-1.367628	-0.713982	-0.803545
20	8	0	0.096267	-1.691307	-2.151774
21	6	0	-0.786535	-2.848398	-2.244318
22	1	0	-1.717542	-2.550059	-2.728686
23	1	0	-0.986815	-3.237915	-1.245279
24	1	0	-0.234077	-3.562982	-2.850467
25	8	0	1.099529	2.711632	-1.130428
26	6	0	0.647332	4.072775	-1.296873
27	1	0	1.491488	4.693727	-0.998949
28	1	0	-0.217715	4.256468	-0.656195
29	1	0	0.376766	4.256797	-2.339028
30	13	0	-2.288827	-0.133350	0.748173
31	17	0	-0.967979	1.271858	1.687347
32	17	0	-4.140622	0.618265	0.051378
33	17	0	-2.371945	-1.989941	1.810349

SCF Done: E(RB+HF-LYP) = -2500.93843102 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -2500.775213

Thermal correction to Gibbs Free Energy= 0.163218
After PCM corrections, the SCF energy is -2501.33618851 a.u.

TS3S (AlTS10.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.258378	-0.641345	-0.541928
2	6	0	1.046963	0.534160	-0.250290
3	6	0	2.506357	0.446158	-0.172190
4	1	0	2.916893	1.443850	-0.316748
5	6	0	0.421243	1.866956	-0.491531
6	6	0	3.226750	-0.512829	-1.146533
7	8	0	3.202328	-0.391393	-2.338550
8	8	0	3.973782	-1.454077	-0.521068
9	6	0	3.773616	-1.476137	0.893343
10	1	0	4.730414	-1.730244	1.353329
11	1	0	3.028901	-2.236639	1.143714
12	6	0	3.292718	-0.072942	1.297828
13	1	0	4.122237	0.632938	1.391988
14	6	0	2.339817	0.020304	2.316223
15	6	0	1.119517	0.222540	2.586080
16	1	0	0.417312	0.205881	3.404764
17	1	0	0.699660	0.490210	1.501016
18	8	0	-0.674414	2.054941	-0.971578
19	8	0	-0.982233	-0.685313	-0.715480
20	8	0	0.955735	-1.770627	-0.588747
21	6	0	0.239865	-3.000078	-0.892753
22	1	0	-0.155831	-2.945517	-1.908411
23	1	0	-0.574802	-3.148726	-0.182926
24	1	0	0.992910	-3.782457	-0.813285
25	8	0	1.243846	2.870864	-0.098639
26	6	0	0.719304	4.197592	-0.306228
27	1	0	1.487858	4.873423	0.069178
28	1	0	-0.214962	4.324111	0.245085
29	1	0	0.535800	4.371553	-1.369060
30	13	0	-2.639839	-0.283563	0.039621
31	17	0	-2.219733	0.924991	1.780389
32	17	0	-3.896466	0.546764	-1.450417
33	17	0	-3.241919	-2.254902	0.675125

SCF Done: E(RB+HF-LYP) = -2500.89893875 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -2500.730431
Thermal correction to Gibbs Free Energy= 0.168508
After PCM corrections, the SCF energy is -2501.30230741 a.u.

B3S (AlTS10.rev.log)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.190345	-0.329139	0.656649
2	6	0	-0.931006	0.394411	-0.447607
3	6	0	-2.323306	-0.164575	-0.820056
4	1	0	-2.666278	0.471055	-1.640535
5	6	0	-1.004058	1.871783	-0.009728
6	6	0	-3.365773	-0.023289	0.297685
7	8	0	-3.680610	0.993843	0.857173
8	8	0	-3.944203	-1.220813	0.560287
9	6	0	-3.270207	-2.300450	-0.102449
10	1	0	-4.029380	-2.983786	-0.486964
11	1	0	-2.648576	-2.824648	0.627826
12	6	0	-2.410017	-1.665280	-1.235605
13	1	0	-2.979542	-1.718554	-2.170585
14	6	0	-1.131097	-2.339436	-1.426568
15	6	0	-0.056121	-2.870420	-1.575897
16	1	0	0.909446	-3.312522	-1.695081
17	1	0	-0.292666	0.356185	-1.335377
18	8	0	-0.555305	2.277041	1.037640
19	8	0	1.046708	-0.386170	0.750824
20	8	0	-0.951520	-0.866158	1.569518
21	6	0	-0.308999	-1.483171	2.722910
22	1	0	0.305728	-0.739179	3.230598
23	1	0	0.303103	-2.322871	2.390281
24	1	0	-1.133016	-1.813290	3.351997
25	8	0	-1.588106	2.611791	-0.951773

26	6	0	-1.756728	4.009844	-0.624219
27	1	0	-2.204778	4.458994	-1.509659
28	1	0	-0.788143	4.462438	-0.403638
29	1	0	-2.418339	4.105082	0.239329
30	13	0	2.705259	0.003708	-0.072117
31	17	0	2.255193	1.223599	-1.774404
32	17	0	3.786443	0.967692	1.478009
33	17	0	3.390381	-1.959825	-0.577763

SCF Done: E(RB+HF-LYP) = -2500.96525170 A.U. after 1 cycles
Sum of electronic and thermal Free Energies= -2500.793180
Thermal correction to Gibbs Free Energy= 0.172071
After PCM corrections, the SCF energy is -2501.36382493 a.u.