Supplementary Materials

Mechanistic Analysis of the Photochemical Carboxylation of o-Alkylphenyl Ketones with Carbon Dioxide

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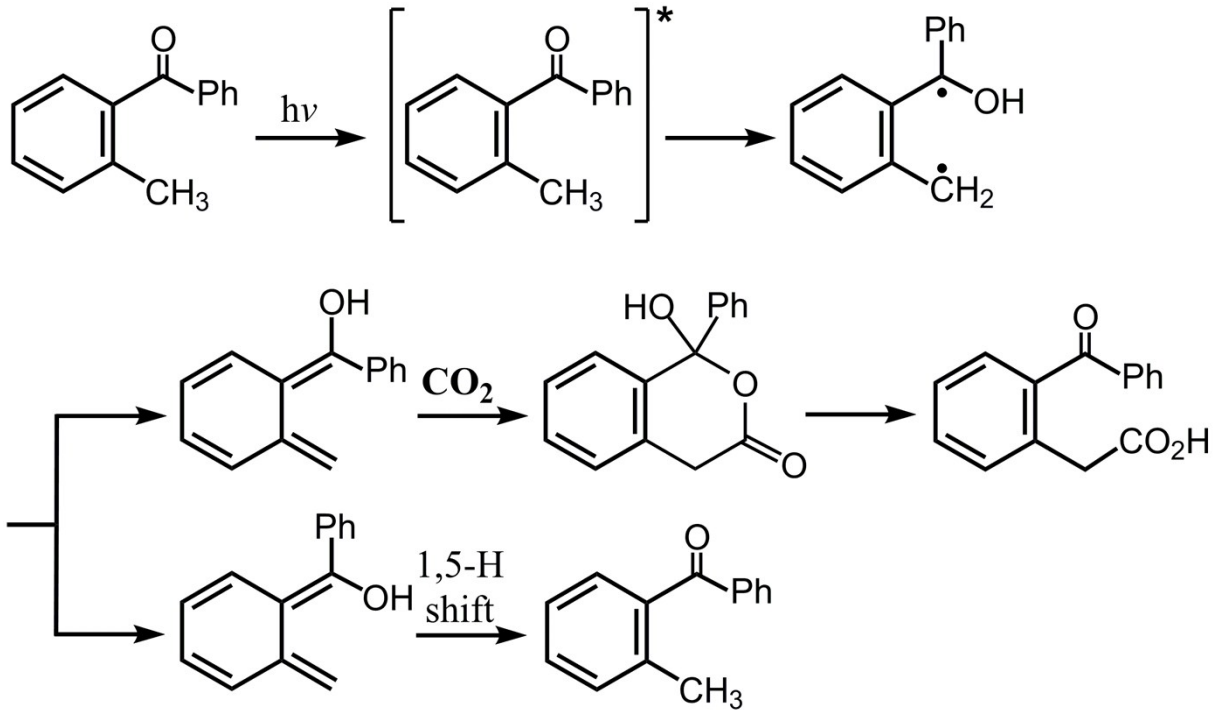

Scheme SA. Proposed mechanism by Murakami and co-workers. See ref. (1).

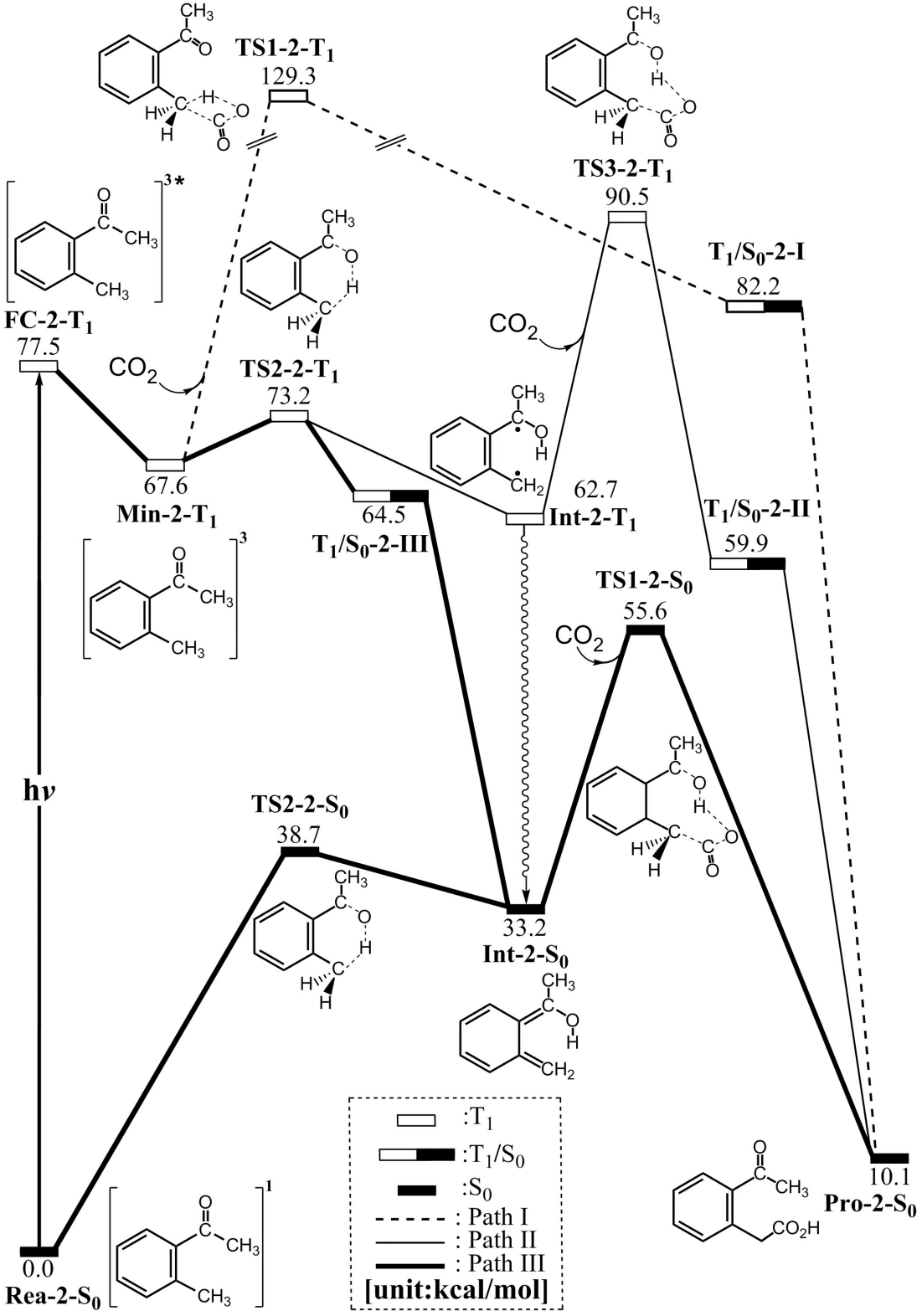

Figure SA Energy profiles for photocarboxylation of *o*-methylacetophenone (**Rea-2-S$_0$**) with CO_2 to produce carboxylic acid (**Pro-2-S$_0$**). The relative energies are obtained at the M06-L/6-311G(d,p) level of theory. All energies (in kcal/mol) are given with respect to the reactant (**Rea-2-S$_0$**). For the M06-L optimized structures for the crucial points, see Figure SB-SD. For more information, see the text.

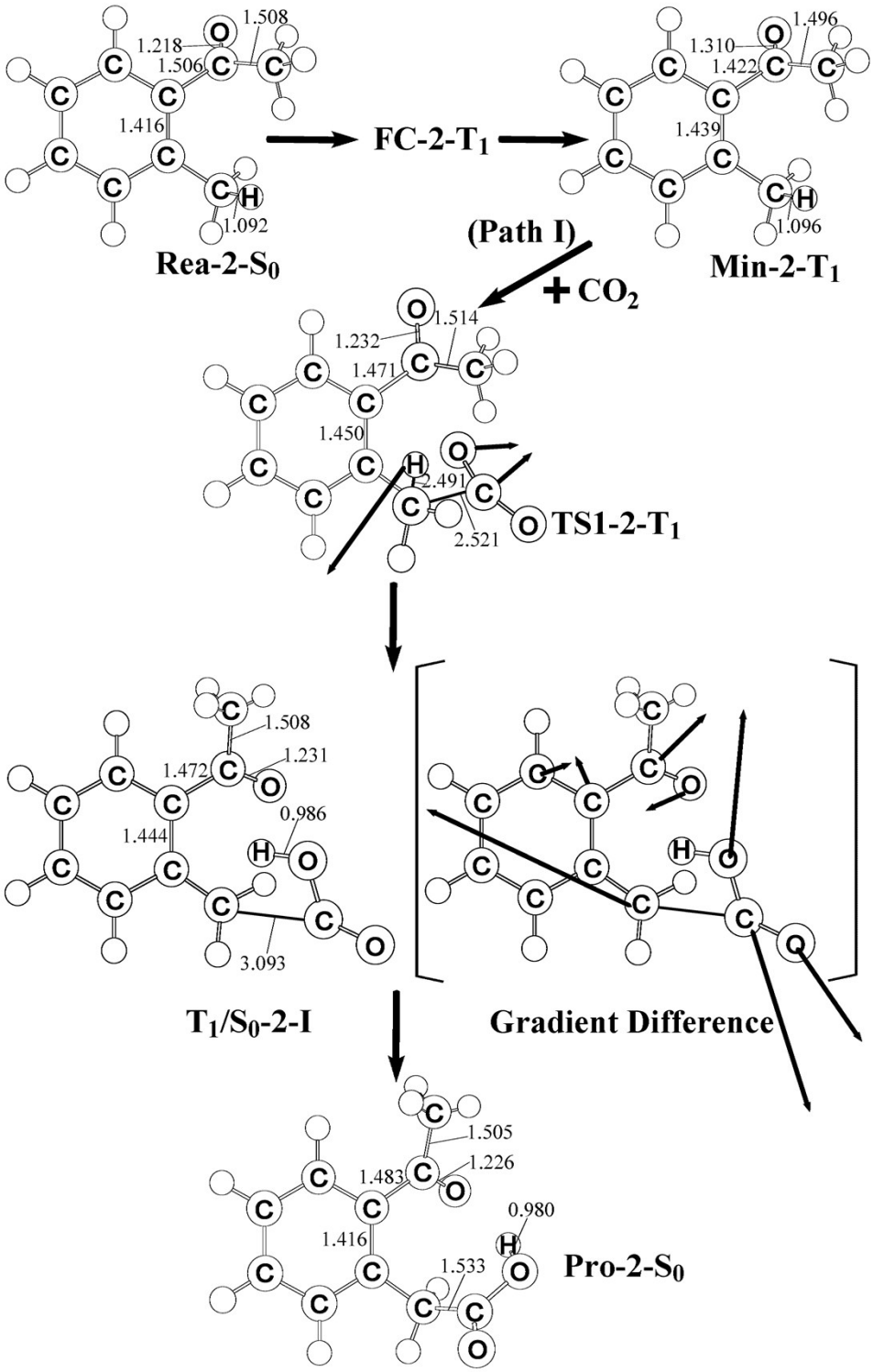

Figure SB The M06-L/6-311G(d,p) geometries (in Å and deg) for path I of 3- *o*-methylacetophenone (**Rea-2-S_0**), intermediate, transition state (**TS**), intersystem crossing (**T_1/S_0**), and insertion product (**Pro**). The heavy arrow in **TS** indicates the main atomic motions in the transition state eigenvector. The gradient difference vector of **T_1/S_0-I** computed with M06-L is shown in the square bracket. Hydrogen atoms are omitted for clarity. For more details see the Supporting Information.

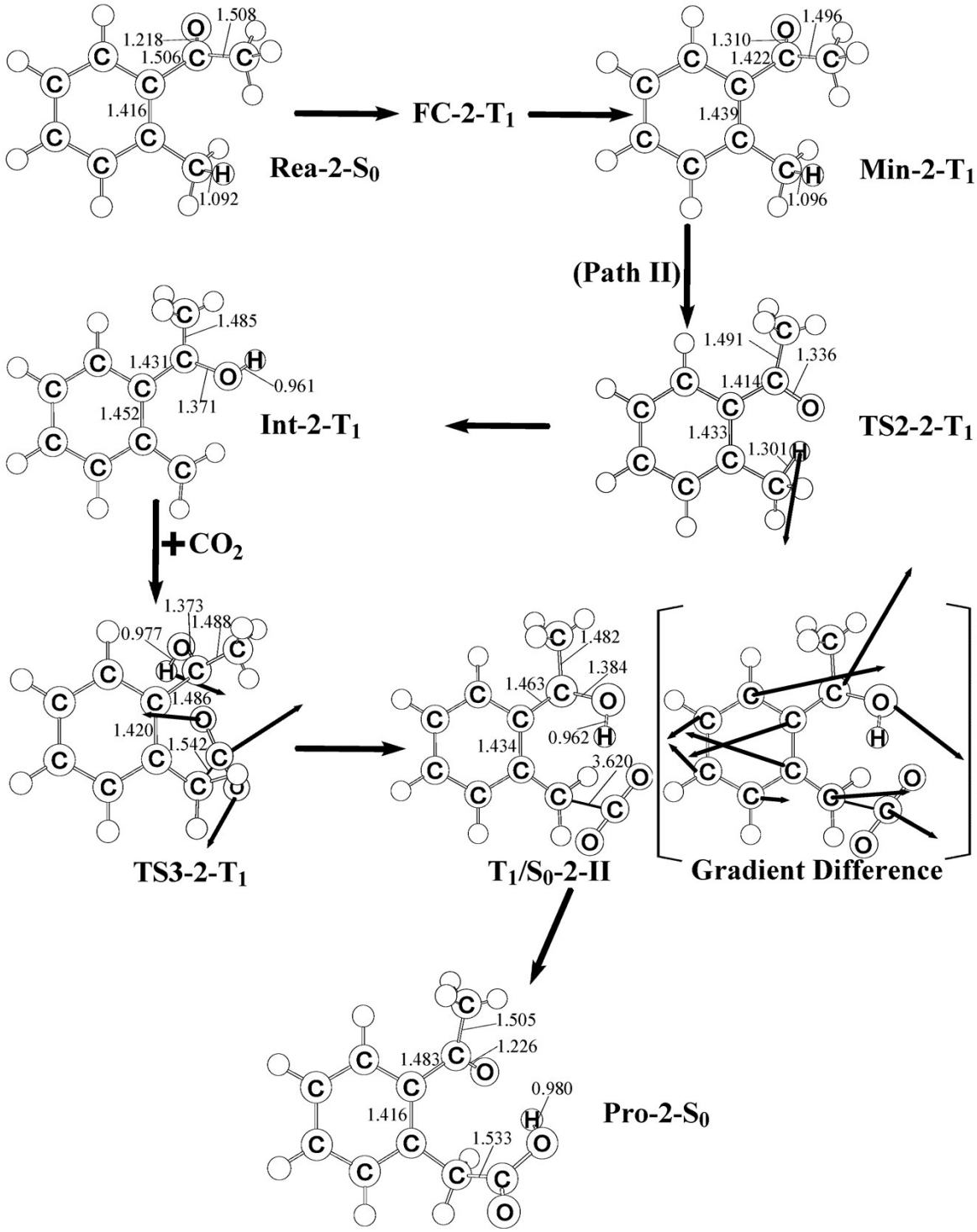

Figure SC The M06-L/6-311G(d,p) geometries (in Å and deg) for path II of 3-*o*-methylacetophenone (**Rea-2-S_0**), intermediate, transition state (**TS**), intersystem crossing (**T_1/S_0**), and insertion product (**Pro**). The heavy arrow in **TS** indicates the main atomic motions in the transition state eigenvector. The gradient difference vector of **T_1/S_0-II** computed with M06-L is shown in the square bracket. Hydrogen atoms are omitted for clarity. For more details see the Supporting Information.

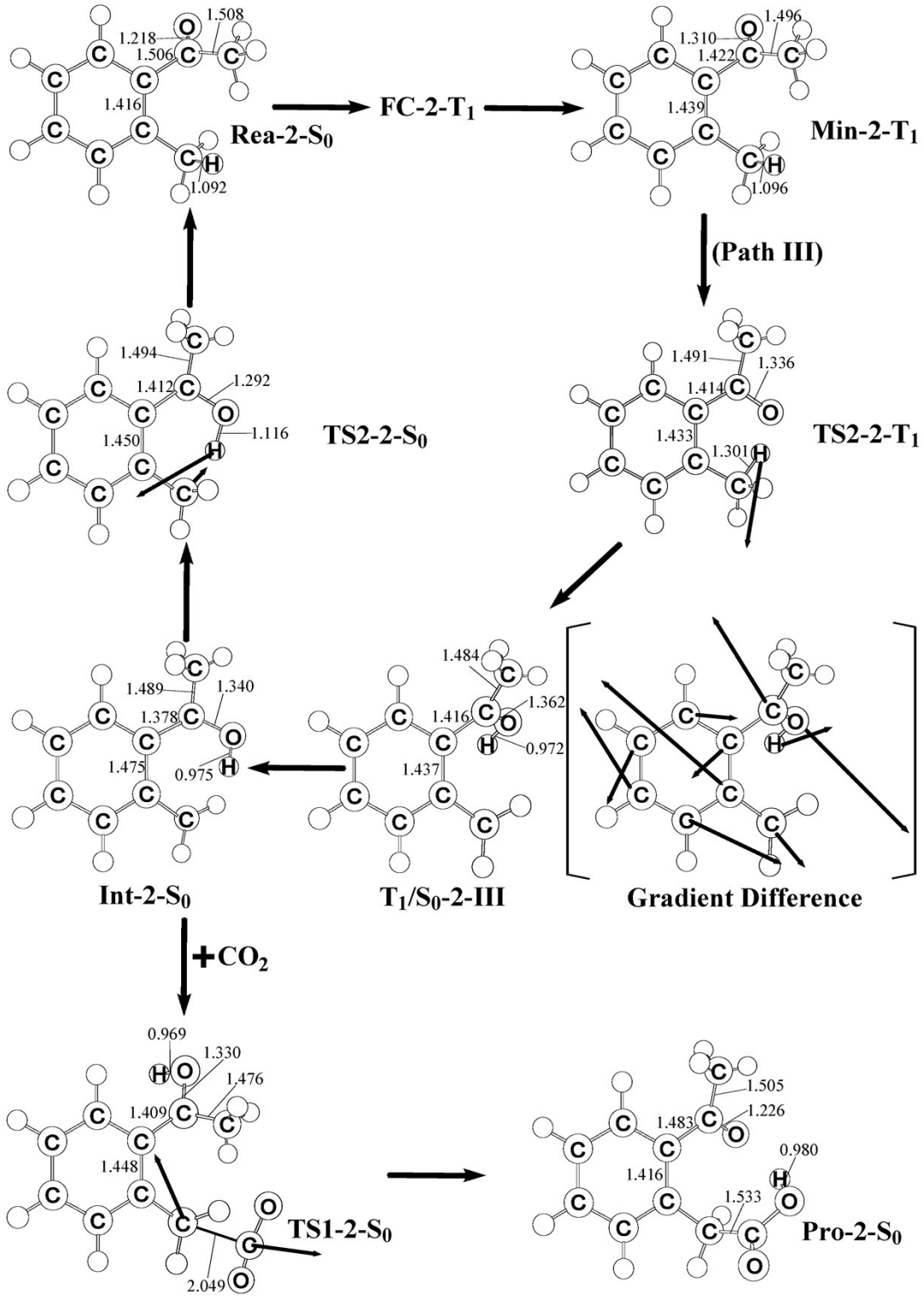

Figure SD The M06-L/6-311G(d,p) geometries (in Å and deg) for path III of 3-*o*-methylacetophenone (**Rea-2-S_0**), intermediate, transition state (**TS**), intersystem crossing (**T_1/S_0**), and insertion product (**Pro**). The heavy arrow in **TS** indicates the main atomic motions in the transition state eigenvector. The gradient difference vector of **T_1/S_0-III** computed with M06-L is shown in the square bracket. Hydrogen atoms are omitted for clarity. For more details see the Supporting Information.

(All geometries were calculated M06-L/6-311(d,p))

1. Rea-1-S_0

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-1.755215	2.005627	-1.383472
6	-2.074521	1.094544	-0.885880
6	-2.876115	-1.190966	0.450407
6	-1.216793	0.496361	0.038312
6	-3.313083	0.535326	-1.169155
6	-3.713357	-0.614397	-0.497695
6	-1.615768	-0.660020	0.730941
1	-3.966233	1.000698	-1.900743
1	-4.684079	-1.055352	-0.700925
1	-3.205543	-2.071656	0.996072
6	0.102577	1.162206	0.298359
8	0.143689	2.311235	0.702866
6	1.351654	0.407139	-0.000895
6	3.743313	-0.891020	-0.610844
6	2.571567	0.928250	0.443373
6	1.343910	-0.767950	-0.759845
6	2.536336	-1.410432	-1.068241
6	3.759360	0.278452	0.147978
1	2.555622	1.849910	1.017332
1	0.400056	-1.166826	-1.121263
1	2.526620	-2.314617	-1.669083
1	4.702506	0.682194	0.502482
1	4.674599	-1.395447	-0.849307
6	-0.743577	-1.300720	1.772032
1	-1.335268	-1.925783	2.444070
1	-0.221179	-0.559186	2.382829
1	0.025582	-1.940072	1.325994

M06L/6-311G** = -616.0124921

2. FC-1-T_1

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-1.755215	2.005627	-1.383472
6	-2.074521	1.094544	-0.885880
6	-2.876115	-1.190966	0.450407
6	-1.216793	0.496361	0.038312
6	-3.313083	0.535326	-1.169155
6	-3.713357	-0.614397	-0.497695
6	-1.615768	-0.660020	0.730941
1	-3.966233	1.000698	-1.900743
1	-4.684079	-1.055352	-0.700925
1	-3.205543	-2.071656	0.996072
6	0.102577	1.162206	0.298359
8	0.143689	2.311235	0.702866
6	1.351654	0.407139	-0.000895
6	3.743313	-0.891020	-0.610844
6	2.571567	0.928250	0.443373
6	1.343910	-0.767950	-0.759845
6	2.536336	-1.410432	-1.068241
6	3.759360	0.278452	0.147978
1	2.555622	1.849910	1.017332
1	0.400056	-1.166826	-1.121263
1	2.526620	-2.314617	-1.669083
1	4.702506	0.682194	0.502482
1	4.674599	-1.395447	-0.849307
6	-0.743577	-1.300720	1.772032
1	-1.335268	-1.925783	2.444070
1	-0.221179	-0.559186	2.382829
1	0.025582	-1.940072	1.325994

M06L/6-311G** = -615.8896255

3. **Min-1-T_1**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-1.813218	2.140942	-1.167740
6	-2.129586	1.188499	-0.756227

6	-2.875655	-1.257290	0.329382
6	-1.227017	0.473585	0.058221
6	-3.364065	0.654111	-1.071411
6	-3.735804	-0.580460	-0.534747
6	-1.630406	-0.740967	0.675754
1	-4.035101	1.187536	-1.737986
1	-4.705480	-1.006409	-0.771562
1	-3.189394	-2.199621	0.771048
6	0.115806	1.034627	0.288302
8	0.006863	2.252940	0.741853
6	1.359387	0.400462	0.021171
6	3.830567	-0.795223	-0.602673
6	2.578134	0.978946	0.459702
6	1.418302	-0.788344	-0.748443
6	2.635139	-1.371094	-1.045967
6	3.785713	0.381792	0.150001
1	2.544208	1.888117	1.054068
1	0.496636	-1.220844	-1.129458
1	2.660496	-2.276776	-1.646666
1	4.709493	0.834100	0.500239
1	4.782265	-1.254029	-0.849096
6	-0.754007	-1.447829	1.658710
1	-1.333590	-2.143553	2.268920
1	-0.249308	-0.738743	2.320657
1	0.039033	-2.019135	1.162100

M06L/6-311G** = -615.9140807

4. **TS1-1-T_1**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.346455	-2.398631	1.072392
6	2.517738	-1.511216	0.473925
6	2.902336	0.788698	-1.030690
6	1.400267	-0.692648	0.171965
6	3.774233	-1.216500	-0.009187
6	3.973195	-0.059068	-0.768869
6	1.608847	0.508465	-0.586070

1	4.605455	-1.883356	0.197359
1	4.959758	0.184790	-1.148903
1	3.064043	1.700297	-1.599609
6	0.121462	-1.024021	0.773634
8	0.213625	-1.454166	2.003165
6	-1.184571	-0.945719	0.181053
6	-3.738814	-0.830447	-0.972242
6	-2.331886	-0.752454	0.988012
6	-1.352888	-1.121920	-1.210561
6	-2.612339	-1.050570	-1.774847
6	-3.586525	-0.684585	0.407671
1	-2.198628	-0.617375	2.056299
1	-0.479902	-1.320305	-1.827215
1	-2.728028	-1.182106	-2.846906
1	-4.457585	-0.506818	1.031422
1	-4.724299	-0.780923	-1.422818
6	0.521574	1.501812	-0.835344
1	0.889038	2.354996	-1.404046
1	-0.356510	1.073527	-1.314250
6	-0.586877	2.433414	0.502257
8	-0.008518	2.119969	1.574697
8	-1.465776	3.042990	0.015806
1	0.611037	1.646112	0.592689

M06L/6-311G** = -804.4077735

5. T_1/S_0-1-I

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.8269738	2.5660949	0.3067311
6	-0.2228348	2.3321161	0.1597076
6	-2.9117817	1.7621845	-0.2037833
6	-0.6664696	1.0411373	0.4501417
6	-1.0898960	3.3285083	-0.2731917
6	-2.4374226	3.0198680	-0.4926424
6	-2.0740380	0.7458890	0.3433457
1	-0.7217580	4.3336605	-0.4434449
1	-3.1151333	3.7793530	-0.8652835

1	-3.9631376	1.5278012	-0.3458168
6	0.3064160	0.0224933	0.9316178
8	0.0083554	-0.8100940	1.7774165
6	1.6818381	0.0088285	0.3428812
6	4.2730618	-0.1959480	-0.6862877
6	2.6985551	-0.6014304	1.0868352
6	1.9789132	0.4918241	-0.9377521
6	3.2665060	0.3858186	-1.4490712
6	3.9850949	-0.6922991	0.5835935
1	2.4474670	-0.9958556	2.0662875
1	1.1966763	0.9390045	-1.5443457
1	3.4884781	0.7609745	-2.4428781
1	4.7697835	-1.1493970	1.1765589
1	5.2828234	-0.2622255	-1.0787407
6	-2.6641150	-0.4503322	0.7667761
1	-3.7324644	-0.5844016	0.6440109
1	-2.1200254	-1.1956326	1.3253817
1	-0.9529618	-1.5416583	-1.2558606
6	-2.0693842	-2.9647774	-0.7727609
8	-0.8937605	-2.5061435	-1.2285522
8	-2.3584160	-4.0933672	-0.5794384

Gradient Difference:

-1	-0.00000951	-0.00009348	-0.00004351
-2	0.00133968	-0.00335698	0.00071023
-3	-0.00170473	0.00309337	-0.00291377
-4	0.00396471	0.00243199	-0.00106297
-5	0.00043928	0.00211695	-0.00020909
-6	-0.00246438	-0.00156337	-0.00123698
-7	-0.00677894	-0.00542328	0.01002403
-8	0.00009767	0.00040082	0.00015883
-9	-0.00008702	0.00009523	0.00005370
-10	-0.00016873	0.00018890	0.00015259
-11	0.00070145	-0.00195233	0.00128930
-12	-0.00007193	0.00143740	0.00033622
-13	-0.00009251	0.00005619	-0.00079408
-14	0.00000900	-0.00000355	-0.00000249
-15	-0.00029665	0.00022437	0.00008380
-16	0.00005762	0.00019542	0.00007768
-17	-0.00045505	0.00018684	-0.00000975
-18	0.00031350	-0.00004541	-0.00003299

-19	0.00000196	-0.00010054	0.00018455
-20	0.00029140	-0.00025848	0.00016699
-21	0.00000089	-0.00005257	0.00009582
-22	0.00003749	-0.00005270	0.00005241
-23	0.00010901	-0.00003715	-0.00002612
-24	0.00154547	0.04617277	0.02306381
-25	-0.00053407	-0.00202422	-0.00505983
-26	0.00432768	-0.00639823	-0.00844136
-27	0.00151952	0.00069169	-0.00206769
-28	-0.01285057	-0.02740803	-0.02998209
-29	0.00549251	0.00848585	0.00839451
-30	0.00526527	-0.01700748	0.00703828

M06L/6-311G** = -804.4929312920

6. **TS2-1-T_1**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-0.343566	-1.958645	-0.585242
6	-1.229093	-1.400111	-0.312923
6	-3.580977	0.029172	0.080859
6	-1.132729	-0.017992	-0.043622
6	-2.454773	-2.046766	-0.335127
6	-3.641829	-1.343774	-0.132241
6	-2.357302	0.691743	0.168051
1	-2.487298	-3.109442	-0.556886
1	-4.599281	-1.852314	-0.161701
1	-4.494301	0.599987	0.226614
6	0.102095	0.734834	-0.093134
8	0.038580	2.068551	-0.211236
6	1.456037	0.214673	-0.023697
6	4.135535	-0.688292	0.095470
6	2.535447	1.052595	-0.396011
6	1.777414	-1.074008	0.462645
6	3.090187	-1.515784	0.501994
6	3.844272	0.606317	-0.334775
1	2.322285	2.060805	-0.736334
1	1.002095	-1.717890	0.859262

1	3.301872	-2.515216	0.873752
1	4.650363	1.273899	-0.628288
1	5.161305	-1.040878	0.129085
6	-2.298219	2.123555	0.480207
1	-3.119196	2.737773	0.103099
1	-2.025732	2.384420	1.507091
1	-1.153582	2.392130	-0.046743

M06L/6-311G** = -615.8977823

7. **Int-1-T_1**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.287481	-1.658061	-1.027370
6	1.195753	-1.217166	-0.627459
6	3.543601	-0.077850	0.284902
6	1.143462	0.092854	-0.146837
6	2.378379	-1.958494	-0.644325
6	3.560452	-1.378622	-0.194399
6	2.359368	0.694342	0.345650
1	2.369978	-2.974472	-1.025850
1	4.490388	-1.937303	-0.214720
1	4.460760	0.374583	0.654649
6	-0.117603	0.815670	-0.204520
8	-0.012996	2.124727	-0.581621
6	-1.419392	0.249523	-0.045638
6	-4.032490	-0.781057	0.312664
6	-2.558239	0.907640	-0.579792
6	-1.647502	-0.948567	0.679601
6	-2.925502	-1.444646	0.850214
6	-3.832616	0.398890	-0.401759
1	-2.430617	1.792499	-1.198236
1	-0.803831	-1.461241	1.130495
1	-3.069262	-2.357880	1.419692
1	-4.679778	0.916800	-0.841138
1	-5.032237	-1.180449	0.447216
6	2.423112	1.975636	0.931661
1	1.555752	2.604204	1.063052

1	3.383078	2.356128	1.269081
1	-0.852444	2.558468	-0.383689

M06L/6-311G** = -615.9240618

8. **TS3-1-T_1**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-0.094241	-2.283191	1.557630
6	0.699160	-2.005382	0.870236
6	2.710797	-1.272305	-0.888527
6	0.690741	-0.710013	0.336956
6	1.672543	-2.925225	0.517006
6	2.687498	-2.554401	-0.370212
6	1.711658	-0.338786	-0.570556
1	1.638645	-3.932847	0.920829
1	3.447319	-3.273597	-0.657422
1	3.500887	-0.980985	-1.574662
6	-0.423611	0.155909	0.795745
8	-0.355831	0.551836	2.096562
6	-1.716225	0.106467	0.207736
6	-4.287085	-0.051715	-0.924484
6	-2.873103	0.311751	1.000654
6	-1.889409	-0.174763	-1.171232
6	-3.154161	-0.228128	-1.725014
6	-4.131789	0.208491	0.441061
1	-2.747968	0.511051	2.059339
1	-1.013923	-0.329339	-1.799542
1	-3.265004	-0.408911	-2.790540
1	-5.008812	0.323764	1.073140
1	-5.278672	-0.119254	-1.358771
6	1.748797	1.015306	-1.180632
1	2.496404	1.074196	-1.978867
1	0.782805	1.308295	-1.618763
1	0.537791	0.913976	2.212852
8	1.771015	1.981376	1.086114
8	2.588411	3.134324	-0.610338
6	2.050191	2.105553	-0.109388

M06L/6-311G** = -804.5067419

9. T_1/S_0-1-II

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-1.5859463	1.6622279	1.0323631
6	-0.8249830	1.2979480	1.7153404
6	0.9939025	0.3981754	3.5984344
6	-0.6478518	-0.0723263	1.8377781
6	-0.0759299	2.2227426	2.4581184
6	0.8260488	1.7734602	3.4085820
6	0.2920412	-0.5523045	2.8206114
1	-0.2243448	3.2838965	2.2672486
1	1.3822044	2.4957269	4.0019889
1	1.6984550	0.0346740	4.3449437
6	-1.5468528	-0.9799610	1.0819750
8	-2.3899635	-1.7699887	1.8340804
6	0.4291789	-1.9434371	3.0549816
8	-2.7926398	-0.8907514	4.7873289
8	-1.3590669	-0.4602167	6.5565828
6	-2.0720722	-0.6717288	5.6707977
1	1.0329038	-2.3294675	3.8687327
1	0.0574996	-2.6490809	2.3183497
6	-2.1212924	-0.6033083	-0.2078292
6	-3.2543493	0.2367896	-2.6322479
6	-1.3451886	-0.5347071	-1.3718483
6	-3.4901180	-0.2839951	-0.2902914
6	-4.0463436	0.1413294	-1.4887114
6	-1.9087523	-0.1290827	-2.5747838
1	-0.2963263	-0.8210437	-1.3273979
1	-4.0872168	-0.3225330	0.6142672
1	-5.1057807	0.3992312	-1.5252007
1	-1.2966736	-0.1130767	-3.4741789
1	-3.6802887	0.5834129	-3.5660988
1	-2.0008433	-1.8752679	2.7110914
Gradient Difference:			
-1	-0.00107582	-0.00195530	0.00084137

-2	-0.02637633	-0.04648652	0.01602923
-3	-0.00994216	-0.04844517	-0.01538158
-4	0.01128997	0.05080185	0.03889963
-5	0.03882759	0.00556447	0.03551981
-6	-0.02212168	0.04511898	-0.01853421
-7	0.00618478	0.07892863	-0.01766347
-8	0.00616304	0.00118517	-0.00348807
-9	-0.00108943	-0.00000904	-0.00019991
-10	0.00226057	-0.00014249	-0.00075936
-11	0.02661917	-0.05749645	-0.07148369
-12	-0.02142916	0.01298673	0.04202819
-13	-0.00106199	-0.04082742	0.00327137
-14	0.00171273	-0.00022724	0.00037662
-15	0.00172914	0.00023924	0.00067847
-16	-0.00332593	-0.00004382	-0.00065291
-17	-0.00068350	-0.00051378	0.00273981
-18	-0.00391750	0.00016699	-0.00158724
-19	0.00458896	0.00019982	0.00258687
-20	-0.00373515	0.00142287	-0.00091526
-21	-0.00387941	0.00040258	-0.00396852
-22	0.00276843	0.00280759	0.00048175
-23	0.00073199	-0.00065624	-0.00331301
-24	0.00198256	0.00043464	0.00213018
-25	0.00057446	-0.00049420	-0.00003142
-26	-0.00019940	-0.00035909	0.00009782
-27	-0.00054512	-0.00030636	-0.00043789
-28	0.00014259	-0.00008531	-0.00069243
-29	-0.00013902	-0.00011212	-0.00019144
-30	-0.00605440	-0.00209896	-0.00638070

M06L/6-311G** = -804.5423329040

10. T_1/S_0-1-III

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-0.4936343	-1.6837738	-1.4181055
6	-1.3258162	-1.2479617	-0.8730448
6	-3.4665869	-0.1245971	0.4919312

6	-1.1638321	0.0136855	-0.3127971
6	-2.5263822	-1.9534554	-0.7530213
6	-3.5994514	-1.3821010	-0.0745208
6	-2.2574696	0.6058127	0.4053930
1	-2.6189820	-2.9390233	-1.1972380
1	-4.5361233	-1.9220600	0.0183527
1	-4.2930589	0.3141712	1.0449546
6	0.0907465	0.7542688	-0.4875241
8	0.0095669	2.0114061	-1.0311824
6	1.3866049	0.2946435	-0.1586508
6	3.9789350	-0.5946739	0.5214010
6	2.5381178	1.0448988	-0.5157272
6	1.5847168	-0.9135075	0.5607790
6	2.8561396	-1.3407113	0.8893455
6	3.8020107	0.5993160	-0.1807911
1	2.4080370	1.9705435	-1.0632656
1	0.7212193	-1.4920786	0.8728968
1	2.9790157	-2.2637550	1.4481167
1	4.6674632	1.1869514	-0.4716682
1	4.9746246	-0.9379388	0.7812125
6	-2.1355197	1.8558766	1.0470403
1	-2.9770983	2.2683174	1.5921289
1	-1.2034976	2.4070734	1.0641920
1	-0.9001452	2.1580729	-1.3096074

Gradient Difference:

-1	0.00025277	0.00149895	0.00079850
-2	0.01295970	0.04721768	-0.01108139
-3	0.02780725	0.04063480	0.01037591
-4	-0.05701240	-0.02897148	0.00312750
-5	-0.04554706	0.00163735	0.01958003
-6	0.01346432	-0.04006481	-0.02815822
-7	-0.00498400	-0.08332145	-0.02682000
-8	0.00004810	-0.00256606	0.00422397
-9	0.00059983	-0.00011069	-0.00063182
-10	0.00027231	-0.00159394	0.00366557
-11	0.06318795	0.00557253	0.02700064
-12	-0.02276417	0.01446607	-0.02277334
-13	-0.01958286	0.00844620	0.00988744
-14	0.00584203	-0.00201569	0.00187250
-15	0.00554994	0.00183045	-0.00075900

-16	0.00500688	-0.00509391	0.00092364
-17	-0.00294028	0.00174765	0.00088213
-18	-0.00343986	-0.00038923	-0.00155913
-19	0.00010651	0.00038791	0.00030983
-20	0.00019569	-0.00170668	-0.00041272
-21	0.00017637	-0.00054253	0.00043569
-22	0.00036915	0.00032043	-0.00028798
-23	0.00025247	-0.00040428	-0.00033296
-24	0.01381356	0.04161453	0.01518791
-25	-0.00158783	0.00157600	-0.00036863
-26	0.00214198	-0.00070110	-0.00135096
-27	0.00581165	0.00053132	-0.00373510

M06L/6-311G** = -615.9272403460

11. **Int-1-S_0**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.223851	-1.839137	-0.618379
6	1.151297	-1.347555	-0.352484
6	3.601526	-0.068878	0.048846
6	1.113685	0.056364	-0.038848
6	2.311656	-2.048277	-0.444436
6	3.563489	-1.390636	-0.237971
6	2.404725	0.729440	0.232142
1	2.293997	-3.095273	-0.727563
1	4.487596	-1.954689	-0.325413
1	4.552624	0.432947	0.203370
6	-0.088558	0.755987	-0.115677
8	-0.100328	2.099835	-0.253575
6	-1.447463	0.218945	-0.052423
6	-4.110312	-0.670680	0.168363
6	-2.515874	0.983281	-0.563846
6	-1.757426	-0.982523	0.610917
6	-3.068360	-1.425576	0.704034
6	-3.825891	0.542835	-0.453300
1	-2.302420	1.933443	-1.040721

1	-0.970945	-1.551799	1.095052
1	-3.280430	-2.358857	1.218393
1	-4.633009	1.154165	-0.850023
1	-5.135626	-1.015439	0.253368
6	2.571320	1.999082	0.716334
1	1.770059	2.645323	1.050741
1	3.576007	2.350918	0.923807
1	0.798038	2.388871	-0.483947

M06L/6-311G** = -615.9554478

12. **TS1-1-S_0**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	1.671488	-2.334608	1.613257
6	2.003881	-1.670882	0.818717
6	2.806297	-0.061350	-1.298258
6	1.066958	-0.746924	0.268098
6	3.249785	-1.843576	0.278666
6	3.649066	-1.018558	-0.799379
6	1.477759	0.129934	-0.808069
1	3.910347	-2.620386	0.651171
1	4.635605	-1.149527	-1.234574
1	3.138610	0.583919	-2.106534
6	-0.200809	-0.667927	0.883947
8	-0.310129	-0.891506	2.194026
6	0.742867	1.252574	-1.234942
1	1.188732	1.837339	-2.034335
1	-0.340660	1.220958	-1.259399
1	0.562173	-0.773836	2.595999
8	0.122526	1.867522	1.209911
8	1.139815	3.536169	-0.012265
6	0.673694	2.496097	0.337425
6	-1.490891	-0.532867	0.229373
6	-4.012102	-0.445168	-0.957827
6	-1.679660	-1.028126	-1.069495
6	-2.583097	-0.002982	0.929423
6	-3.834271	0.045192	0.332440

6	-2.932881	-0.983907	-1.656858
1	-0.835826	-1.456278	-1.602408
1	-2.425674	0.387835	1.928331
1	-4.674282	0.468050	0.873319
1	-3.074503	-1.378383	-2.657532
1	-4.993284	-0.411742	-1.420233

M06L/6-311G** = -804.5584232

13. **Pro-1-S_0**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-0.710641	2.372107	-0.387220
6	0.326240	2.071811	-0.278409
6	2.967689	1.311098	-0.059467
6	0.663926	0.722889	-0.462622
6	1.287873	3.029093	0.007587
6	2.614468	2.640157	0.136777
6	2.023899	0.338784	-0.387361
1	1.001502	4.067541	0.133550
1	3.378962	3.370837	0.380343
1	4.006720	1.010913	0.036935
6	-0.410468	-0.246577	-0.812412
8	-0.184462	-1.224049	-1.524207
6	-1.786055	-0.043214	-0.281860
6	-4.388000	0.119428	0.714819
6	-2.858376	-0.569605	-1.010545
6	-2.031585	0.545271	0.964290
6	-3.325962	0.616645	1.462188
6	-4.152212	-0.473148	-0.524052
1	-2.648189	-1.051575	-1.959412
1	-1.201571	0.915487	1.556290
1	-3.506519	1.056011	2.437410
1	-4.980642	-0.866880	-1.103358
1	-5.400566	0.184067	1.100896
6	2.512697	-1.070641	-0.606771
1	3.602152	-1.048809	-0.674328
1	2.113824	-1.467276	-1.541925

6	2.183145	-1.986813	0.570624
8	2.849930	-2.031988	1.567849
8	1.078029	-2.749291	0.434536
1	0.633328	-2.530859	-0.401317

M06L/6-311G** = -804.6160143

14. **TS2-1-S_0**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-0.285093	-1.946719	-0.428090
6	-1.196943	-1.405560	-0.219398
6	-3.596016	-0.012573	-0.029863
6	-1.136903	-0.008997	0.060619
6	-2.386441	-2.079182	-0.307914
6	-3.602855	-1.369583	-0.197634
6	-2.389140	0.720851	0.170135
1	-2.396824	-3.146540	-0.500049
1	-4.548019	-1.904999	-0.250214
1	-4.531742	0.534776	0.042218
6	0.082012	0.737244	-0.009735
8	0.025649	2.031300	-0.049790
6	1.462764	0.200979	-0.046004
6	4.154674	-0.636098	0.055263
6	2.508974	1.050729	-0.458856
6	1.815141	-1.058900	0.470569
6	3.139054	-1.476530	0.499468
6	3.831792	0.637812	-0.407803
1	2.268363	2.052284	-0.798612
1	1.061721	-1.705449	0.901845
1	3.377934	-2.461048	0.891673
1	4.621302	1.318290	-0.716187
1	5.189943	-0.961196	0.093160
6	-2.445939	2.121929	0.387462
1	-3.435171	2.564568	0.277870
1	-1.912561	2.537281	1.245548
1	-1.056093	2.335624	-0.158686

M06L/6-311G** = -615.9410444

15. Rea-2-S_0

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.081596	-2.391904	0.018223
6	0.613710	-1.447036	0.013868
6	1.880595	0.987569	-0.005015
6	-0.169602	-0.282464	-0.004011
6	1.994843	-1.407940	0.027189
6	2.635711	-0.174463	0.017624
6	0.480871	0.975461	-0.013556
1	2.568471	-2.328844	0.044537
1	3.719587	-0.114703	0.027809
1	2.385433	1.949644	-0.015397
6	-0.194602	2.316858	-0.043924
1	0.556098	3.109002	-0.045160
1	-0.840800	2.486517	0.819901
1	-0.811804	2.457563	-0.934947
6	-1.651653	-0.548937	-0.011928
8	-2.051778	-1.696821	-0.082222
6	-2.665894	0.562292	0.086963
1	-2.530975	1.152718	0.996388
1	-3.657703	0.112843	0.098685
1	-2.599555	1.253696	-0.755527

M06L/6-311G** = -424.2544035

16. FC-2-T_1

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.081596	-2.391904	0.018223
6	0.613710	-1.447036	0.013868
6	1.880595	0.987569	-0.005015
6	-0.169602	-0.282464	-0.004011
6	1.994843	-1.407940	0.027189

6	2.635711	-0.174463	0.017624
6	0.480871	0.975461	-0.013556
1	2.568471	-2.328844	0.044537
1	3.719587	-0.114703	0.027809
1	2.385433	1.949644	-0.015397
6	-0.194602	2.316858	-0.043924
1	0.556098	3.109002	-0.045160
1	-0.840800	2.486517	0.819901
1	-0.811804	2.457563	-0.934947
6	-1.651653	-0.548937	-0.011928
8	-2.051778	-1.696821	-0.082222
6	-2.665894	0.562292	0.086963
1	-2.530975	1.152718	0.996388
1	-3.657703	0.112843	0.098685
1	-2.599555	1.253696	-0.755527

M06L/6-311G** = -424.1308738

17. **Min-2-T_1**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.149479	-2.412407	0.182927
6	0.647443	-1.453613	0.091376
6	1.855767	1.031423	-0.013685
6	-0.178213	-0.276610	0.054716
6	2.021401	-1.374783	0.076839
6	2.647894	-0.129138	0.032370
6	0.474283	1.003224	-0.031347
1	2.613169	-2.283574	0.123102
1	3.729128	-0.048362	0.033223
1	2.345605	2.001344	-0.056228
6	-0.276878	2.292787	-0.162867
1	0.404735	3.101251	-0.433893
1	-0.773614	2.593548	0.766286
1	-1.050923	2.239857	-0.933917
6	-1.583786	-0.491368	0.017366
8	-1.958927	-1.683845	-0.373928
6	-2.718988	0.442326	0.297787

1	-2.435464	1.196531	1.031893
1	-3.556922	-0.128804	0.707987
1	-3.087325	0.945886	-0.605301

M06L/6-311G** = -424.1466776

18. **TS1-2-T_1**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-3.070505	1.172026	0.050266
6	-2.464642	0.272122	0.017518
6	-0.951723	-2.051814	0.026434
6	-1.094770	0.388156	-0.220360
6	-3.083087	-0.955078	0.226713
6	-2.302528	-2.121011	0.266680
6	-0.299197	-0.821350	-0.308500
1	-4.155681	-1.006703	0.382052
1	-2.770675	-3.080878	0.461332
1	-0.356961	-2.960896	0.007015
6	0.952696	-0.928856	-0.948272
1	1.409920	-1.914414	-1.027056
6	-0.446425	1.708161	-0.234204
8	0.764005	1.818760	-0.433705
6	-1.265369	2.926627	0.136969
1	-0.596064	3.783104	0.214508
1	-1.764428	2.780839	1.101006
1	-2.044022	3.151672	-0.600395
1	1.358473	-0.133264	-1.556153
6	3.057076	-0.357891	0.317260
8	2.561593	0.092951	1.329932
8	3.936312	-0.690363	-0.398411
1	1.282477	0.083335	1.303470

M06L/6-311G** = -612.6760442

19. **T_1/S_0-2-I**

Atomic Coordinates (Angstroms)

Number	X	Y	Z
1	2.7681275	1.4023566	0.8636410
6	2.3642808	0.4611080	0.5055802
6	1.3667491	-1.9817478	-0.3497104
6	1.0553218	0.4191277	0.0151455
6	3.1546515	-0.6761639	0.5912938
6	2.6374222	-1.9075520	0.1698012
6	0.5346177	-0.8319497	-0.4843020
1	4.1617240	-0.6153081	0.9901882
1	3.2458681	-2.8035122	0.2414115
1	0.9755345	-2.9348862	-0.6919827
6	0.2255945	1.6325569	0.0937801
8	-1.0044015	1.5938580	0.1148090
6	-0.6750316	-0.9601293	-1.1676867
1	-0.9840314	-1.9323211	-1.5347066
1	-1.2932189	-0.1118258	-1.4210538
1	-2.2081845	0.5447732	0.8111136
6	-3.2447067	-1.0175013	0.5564412
8	-2.9298617	0.0507841	1.2663612
8	-4.0702145	-1.8387638	0.7912684
6	0.9032855	2.9777497	0.1635858
1	0.1549749	3.7488509	-0.0105736
1	1.7119972	3.0721112	-0.5638743
1	1.3382099	3.1499840	1.1532638
Gradient Difference:			
-1	-0.00026696	-0.00003456	-0.00000343
-2	-0.00470449	0.00330383	-0.00002461
-3	-0.00043332	-0.00199894	0.00088444
-4	0.00354995	-0.00114981	0.00095488
-5	0.00021790	-0.00288776	-0.00064635
-6	0.00083828	-0.00208582	0.00090114
-7	0.00076994	-0.00101539	-0.00858706
-8	0.00024312	0.00004405	-0.00007001
-9	-0.00008650	0.00027635	-0.00013731
-10	0.00013773	-0.00021354	-0.00010149
-11	-0.00854398	0.00731182	-0.00000162
-12	0.00886487	-0.00096790	-0.00260607
-13	0.04414476	0.00738227	-0.01976404
-14	-0.00408390	-0.00264018	0.00560317

-15	-0.00412522	-0.00106769	0.00728481
-16	-0.00828787	-0.00412608	0.00347851
-17	-0.01557034	0.00361290	-0.03025525
-18	0.00777851	0.01272473	0.02073870
-19	-0.02095314	-0.01578326	0.02241371
-20	0.00035954	-0.00042437	-0.00001831
-21	0.00004561	-0.00026312	0.00006278
-22	0.00010430	0.00002694	-0.00008848
-23	0.00000121	-0.00002448	-0.00001812

M06L/6-311G** = -612.7511308600

20. **TS2-2-T_1**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-0.017507	-2.426687	0.095438
6	-0.552054	-1.482090	0.072300
6	-1.941147	0.935201	-0.072245
6	0.179130	-0.267971	0.048754
6	-1.933310	-1.474409	0.012741
6	-2.641678	-0.273195	-0.075956
6	-0.557096	0.961671	0.027316
1	-2.470445	-2.417960	0.009434
1	-3.723539	-0.275270	-0.146129
1	-2.483160	1.876413	-0.109761
6	0.198366	2.219672	0.153376
1	-0.093511	3.055855	-0.494429
1	0.424965	2.545023	1.173628
6	1.590888	-0.228860	-0.025104
8	2.251268	0.919778	-0.192976
6	2.467817	-1.433284	0.032675
1	2.213413	-2.072663	0.891473
1	3.515789	-1.126258	0.121787
1	2.371822	-2.051384	-0.878285
1	1.386532	1.794294	-0.162497

M06L/6-311G** = -424.1377556

21. **Int-2-T_1**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.151369	-2.325136	0.090696
6	-0.450586	-1.423768	0.043365
6	-2.039656	0.829013	-0.000067
6	0.191410	-0.176086	-0.003525
6	-1.845355	-1.556286	0.068824
6	-2.644461	-0.429405	0.060817
6	-0.645730	1.008692	-0.052146
1	-2.285763	-2.547457	0.106735
1	-3.725419	-0.512821	0.089499
1	-2.660580	1.720185	-0.040680
6	1.622599	-0.153255	-0.017528
8	2.274992	0.976978	0.401438
6	-0.149577	2.322442	-0.219954
1	0.898214	2.546245	-0.329542
1	-0.855354	3.145297	-0.252271
1	3.218184	0.838634	0.276278
6	2.457826	-1.358845	-0.247988
1	2.048072	-1.989350	-1.041245
1	2.559345	-1.991956	0.648380
1	3.473184	-1.074475	-0.550146

M06L/6-311G** = -424.1545192

22. **TS3-2-T_1**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.736961	1.133301	-0.536397
6	2.179422	0.226476	-0.322103
6	0.762054	-2.092880	0.202193
6	0.836978	0.341215	0.058860
6	2.802376	-1.007300	-0.446146
6	2.086040	-2.178523	-0.186163
6	0.127156	-0.851534	0.360942

1	3.843624	-1.061644	-0.749267
1	2.570558	-3.145832	-0.268215
1	0.208786	-2.998191	0.435040
6	0.258712	1.703258	0.191369
8	-0.387459	2.239626	-0.894261
6	0.992066	2.730239	0.978964
6	-1.242977	-0.819260	0.946770
1	-1.492246	-1.770777	1.426971
1	-1.325056	-0.029342	1.707874
1	-0.948907	1.534243	-1.270128
8	-2.141439	0.219967	-1.094307
8	-3.465713	-0.972949	0.181177
6	-2.331715	-0.484081	-0.092647
1	0.362673	3.617722	1.084645
1	1.249047	2.360949	1.977287
1	1.930787	3.060779	0.499094

M06L/6-311G** = -612.7378198

23. T_1/S_0-2-II

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-1.1379846	1.6129820	0.8679359
6	-0.5334211	1.3105177	1.7179035
6	0.9507217	0.5725228	3.9326625
6	-0.3054562	-0.0408704	1.9381852
6	-0.0185640	2.2970392	2.5734006
6	0.7114492	1.9243893	3.6875271
6	0.4728774	-0.4348288	3.0761039
1	-0.1999320	3.3447949	2.3575159
1	1.1061409	2.6759753	4.3633301
1	1.5464232	0.2751801	4.7912012
6	-0.8373364	-1.0393223	1.0112668
8	-1.5450217	-2.0599010	1.6210172
6	0.7916169	-1.7947954	3.3310168
8	-3.1551127	-0.1023880	3.5066550
8	-2.0977270	-1.6819594	4.8399372
6	-2.6153271	-0.8948643	4.1612284

1	1.3705837	-2.0542655	4.2109512
1	0.4305544	-2.5947403	2.7029561
6	-1.1972696	-0.7235217	-0.3910491
1	-0.4658867	-0.0510270	-0.8429383
1	-2.1866772	-0.2445887	-0.4812376
1	-1.2316612	-1.6321691	-1.0044125
1	-1.8607999	-2.6558750	0.9347253

Gradient Difference:

-1	-0.00056908	-0.00155547	-0.00015432
-2	-0.02653110	-0.06573820	0.00303128
-3	-0.00790916	-0.06467072	-0.01881384
-4	0.01924372	0.07544015	0.06110924
-5	0.03926471	0.01737826	0.05994376
-6	-0.03128023	0.05480458	-0.03780560
-7	-0.01192002	0.10768276	-0.02163196
-8	0.00586797	0.00126639	-0.00190292
-9	-0.00048229	0.00078530	-0.00064968
-10	0.00280104	-0.00035916	-0.00094984
-11	0.03405453	-0.06824565	-0.06305460
-12	-0.02864618	0.00255788	0.02412218
-13	0.00635544	-0.06486902	-0.00353611
-14	0.00043340	-0.00159136	0.00221592
-15	0.00300528	-0.00176832	0.00119506
-16	-0.00241949	0.00333436	-0.00470913
-17	-0.00052349	-0.00103760	0.00163371
-18	-0.00327344	0.00012262	-0.00073750
-19	0.00200732	-0.00091865	0.00222924
-20	0.00055925	0.00090033	-0.00075234
-21	-0.00023910	0.00286489	-0.00078641
-22	-0.00039718	-0.00024257	-0.00054377
-23	0.00059810	0.00385919	0.00054762

M06L/6-311G** = -612.7866275920

24. T_1/S_0-2-III

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.0465642	-2.3572677	-0.1095711

6	-0.5198121	-1.4342670	-0.0477562
6	-1.9884578	0.9082039	0.0341400
6	0.1864024	-0.2015231	-0.0059201
6	-1.9009733	-1.4885983	-0.0499074
6	-2.6552321	-0.3191423	-0.0138304
6	-0.6031866	0.9986438	0.0427829
1	-2.3963260	-2.4537695	-0.0954963
1	-3.7384586	-0.3509007	-0.0347910
1	-2.5639029	1.8292141	0.0769448
6	-0.0025400	2.3357758	0.1598341
1	-0.2330720	3.1120432	-0.5654241
1	0.4426476	2.6669688	1.0966081
6	1.6024177	-0.2215444	-0.0213861
8	2.3715536	0.8928581	-0.1688582
6	2.4184194	-1.4548329	0.1014730
1	2.0989490	-2.0823490	0.9393668
1	3.4638086	-1.1833336	0.2516981
1	2.3677282	-2.0774770	-0.8016220
1	1.7900705	1.6589979	-0.3067850

Gradient Difference:

-1	0.00136578	0.00223292	-0.00421056
-2	0.01442650	0.01312523	-0.00280092
-3	0.04578112	0.02764868	0.03630916
-4	-0.00722634	0.00355476	-0.02677907
-5	-0.02721779	0.02273146	0.00423745
-6	-0.01066802	-0.04153612	0.00195803
-7	-0.04168880	-0.06649221	-0.00812185
-8	-0.00103940	0.00004625	-0.00009067
-9	0.00105393	0.00072084	-0.00672117
-10	-0.00274700	0.00064335	-0.00002753
-11	-0.00639047	0.02982990	0.01271637
-12	0.03056986	-0.00384711	-0.01618615
-13	-0.02135032	0.01048440	0.01028884
-14	-0.01074456	-0.04901677	0.00320757
-15	0.00004347	0.08048075	-0.01301081
-16	-0.00533061	0.00381663	0.01213985
-17	0.00205409	-0.00403714	0.00201228
-18	0.00153626	-0.00029525	0.00066378
-19	0.00082330	-0.00063152	-0.00168916
-20	0.03674899	-0.02945906	-0.00389542

M06L/6-311G** = -424.1515702130

25. **Int-2-S_0**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	-0.201012	-2.345758	0.416747
6	0.414562	-1.467362	0.250168
6	2.013646	0.780420	-0.239901
6	-0.230799	-0.181473	0.162453
6	1.750067	-1.610979	0.067961
6	2.552546	-0.461318	-0.233845
6	0.623667	1.019295	0.095973
1	2.209967	-2.591780	0.117394
1	3.611794	-0.591321	-0.436561
1	2.637070	1.651080	-0.423636
6	0.217842	2.298956	0.348373
1	-0.721953	2.552317	0.827921
1	0.923290	3.114781	0.236471
6	-1.595239	-0.137203	-0.026832
8	-2.264507	0.986248	-0.320113
6	-2.498327	-1.321482	-0.024264
1	-2.384368	-1.914610	-0.938037
1	-3.533742	-0.986493	0.031555
1	-2.299225	-1.983451	0.820548
1	-1.613554	1.692133	-0.492020

M06L/6-311G** = -424.2014757

26. **TS1-2-S_0**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	2.145326	1.867123	-0.756602
6	1.950840	0.835396	-0.473324
6	1.483760	-1.753932	0.405125
6	0.679716	0.522685	0.100838

6	2.975986	-0.068547	-0.485352
6	2.720889	-1.392376	-0.056733
6	0.413119	-0.820017	0.572882
1	3.976669	0.238645	-0.775766
1	3.523264	-2.123697	-0.077895
1	1.302150	-2.780167	0.710184
6	-0.239201	1.588511	0.161010
8	-0.261251	2.489050	-0.816807
6	-0.996187	2.046237	1.342881
6	-0.839937	-1.285162	1.013945
1	-0.887306	-2.342575	1.262612
1	-1.472065	-0.657546	1.632797
1	0.159352	2.101816	-1.599767
8	-2.221813	0.203477	-0.628770
8	-2.639472	-2.062749	-0.788212
6	-2.198384	-0.997419	-0.492402
1	-1.997976	2.397071	1.081839
1	-1.037641	1.296432	2.127452
1	-0.435102	2.912426	1.732237

M06L/6-311G** = -612.7935296

27. **Pro-2-S_0**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	3.035597	0.019781	-0.655120
6	2.153870	0.580122	-0.363372
6	-0.083037	2.014355	0.377307
6	1.017250	-0.114307	0.083438
6	2.166028	1.959286	-0.471763
6	1.035101	2.679389	-0.100525
6	-0.126082	0.621301	0.477531
1	3.049080	2.469497	-0.840509
1	1.027696	3.761723	-0.176335
1	-0.961759	2.578420	0.676381
6	-1.397575	0.019331	1.012814
1	-1.222305	-0.949831	1.481875
1	-1.825476	0.695414	1.754684

6	1.057127	-1.596527	0.094521
8	0.044784	-2.285129	0.022070
6	2.393578	-2.284605	0.168908
1	2.241033	-3.322521	0.464709
1	3.086253	-1.792779	0.854168
1	2.858412	-2.289264	-0.823363
6	-2.439724	-0.110471	-0.103565
8	-2.285017	-1.170901	-0.901554
1	-1.497216	-1.673179	-0.604241
8	-3.316082	0.692966	-0.268516

M06L/6-311G** = -612.8659005

28. **TS2-2-S_0**

Atomic Number	Coordinates (Angstroms) X	Y	Z
1	0.071399	-2.389358	0.373675
6	-0.496538	-1.471843	0.240863
6	-1.942902	0.878416	-0.211976
6	0.194683	-0.226573	0.224703
6	-1.851550	-1.531005	0.066161
6	-2.573071	-0.335504	-0.190405
6	-0.554721	1.008176	0.095491
1	-2.371208	-2.481999	0.096715
1	-3.650468	-0.383880	-0.345240
1	-2.514908	1.789140	-0.376785
6	0.075189	2.268965	0.164438
1	-0.527837	3.127707	-0.122673
1	0.715607	2.476049	1.023228
6	1.590120	-0.188353	0.010930
8	2.215526	0.929735	-0.159659
6	2.425043	-1.416651	-0.152602
1	2.290322	-2.092679	0.695903
1	3.476378	-1.140155	-0.215649
1	2.153711	-1.974262	-1.054525
1	1.435276	1.717786	-0.282992

M06L/6-311G** = -424.1926985

29. CO_2

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	0.000000	0.000000	0.000000
8	0.000000	0.000000	1.160311
8	0.000000	0.000000	-1.160311

M06L/6-311G** = -188.6276614