Supporting Information for

Photocatalytic reduction of CO_2 to CO and formate by a novel Co(II)-catalyst bearing a cis-oxygen atom: photocatalysis and DFT calculations

Cheng-Yi Zhu†[a], Ya-Qiong Zhang†[a], Rong-Zhen Liao*[a], Wu Xia[a], Jun-Chao Hu[a], Jin Wu[a], Hongfang Liu[a] and Feng Wang*[ab]

a. Key Laboratory of Materials Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology) of Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, 430074, P. R. China

b. Shenzhen Huazhong University of Science and Technology Research Institute, Shenzhen, 518057, P. R. China

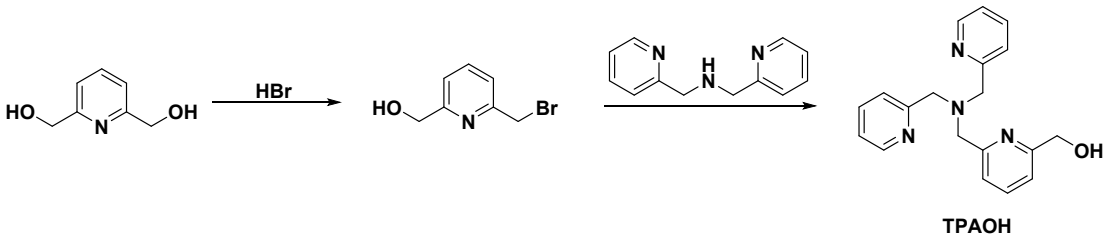
† These two authors contributed equally to this work.

Contents

1. **Synthesis**
2. **UV-Vis absorption of *C1***
3. **Photocatalysis**
4. **Stern-Volmer equation fitting**
5. **DFT calculations**

1. Synthesis

All chemicals, unless otherwise noted, were purchased from commercial sources. All solvents of analytical grade were purchased from commercial suppliers and used without further purification.



TPAOH

Scheme S1. The synthetic routes of **TPAOH** ligand

2. UV-Vis absorption of *C1*

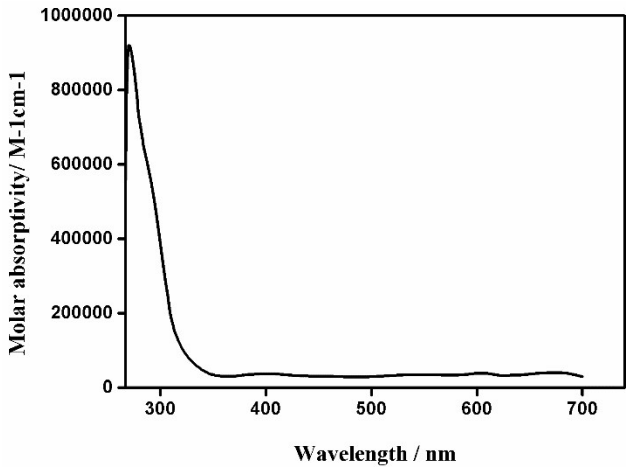


Figure S1. The Uv-vis absorption spectrum of ***C1*** (1.00×10^{-3} M) in DMF at room temperature

3. Photocatalysis

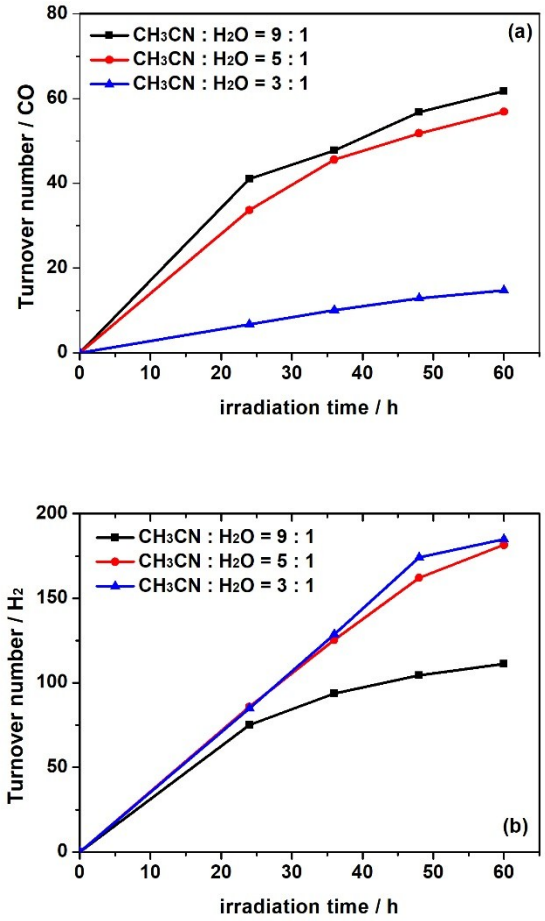


Figure S2. The photocatalytic CO_2 reduction in CH_3CN/H_2O mixture solution with different CH_3CN/H_2O ratio. The samples were irradiated under blue LED lamp (λ_{max} = 450 nm); the TON was calculated based on catalyst. Sample concentration: [***C1***] = 1.00 × 10^{-5} M, [$Ir(ppy)_3$] = 1.00 × 10^{-4} M, v(TEA) = 1.00 mL, total volume = 5.00 mL; sample A: v(CH_3CN):v(H_2O) = 9:1, sample B: v(CH_3CN):v(H_2O) = 5:1, v(CH_3CN):v(H_2O) = 3:1; irradiation time: 60 hours.

4. Stern-Volmer equation fitting

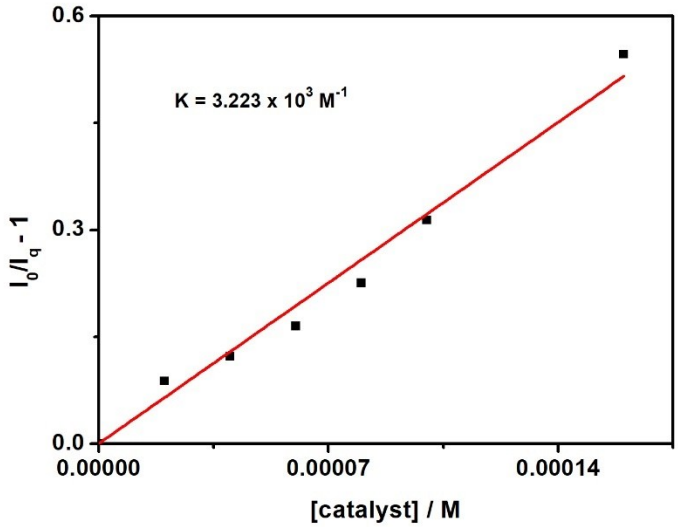
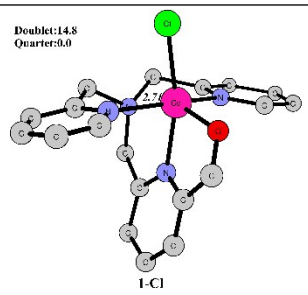
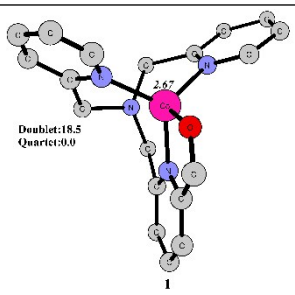
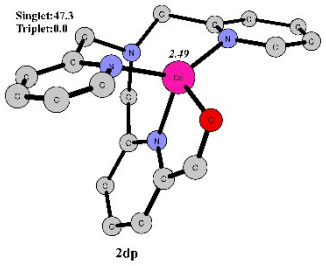
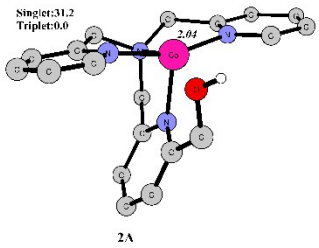
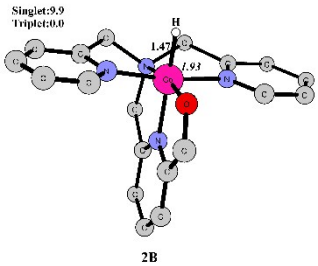
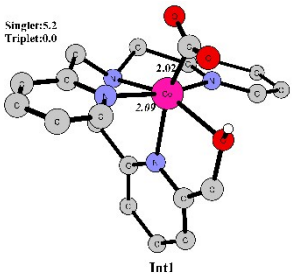
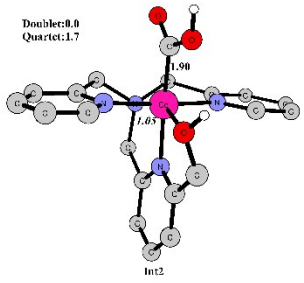
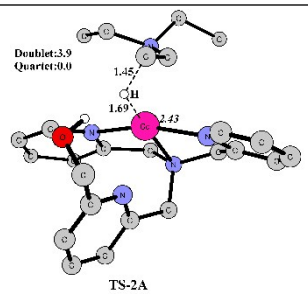
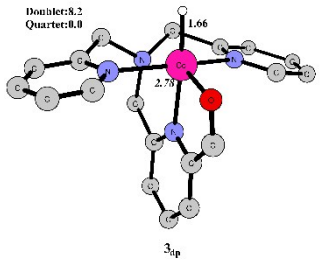
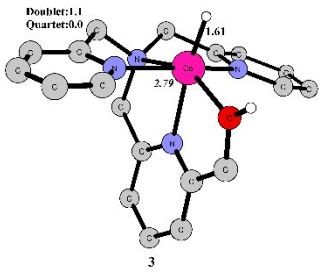
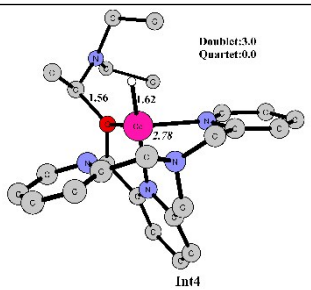
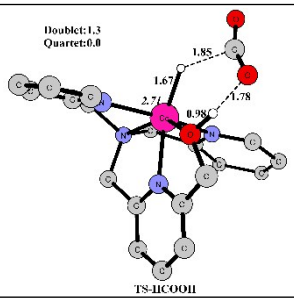
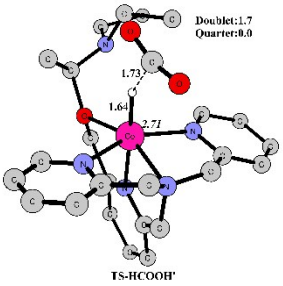


Figure S3. Stern-Volmer equation fitting for the emission quenching of $Ir(ppy)_3$ (4.00×10^{-6} M) by ***C1*** (concentration range: 20 μM - 160 μM M) in degassed CH_3CN at room temperature, excited wavelength: 400 nm.

5. DFT calculations

		
^{4}1-Cl	^{4}1	$^{3}2_{dp}$
E_{opt}= -1635.9252798	E_{opt}= -1175.5210163	E_{opt}= -1175.6427842
Doublet is 14.8 kcal mol^{-1} higher	Doublet is 18.5 kcal mol^{-1} higher	Singlet is 47.3 kcal mol^{-1} higher
		
^{3}2A	^{1}2B	^{3}Int1
E_{opt}= -1176.0917896	E_{opt}= -1176.0760209	E_{opt}= -1364.683841
Singlet is 31.2 kcal mol^{-1} higher	Triplet is 9.9 kcal mol^{-1} higher	Singlet is 5.2 kcal mol^{-1} higher
		
^{2}Int2	^{2}TS-2A	$^{4}3_{dp}$
E_{opt}= -1365.2838613	E_{opt}= -1467.8910492	E_{opt}= -1176.2144031
Quartet is 1.7 kcal mol^{-1} higher	Quartet is 3.9 kcal mol^{-1} higher	Doublet is 8.2 kcal mol^{-1} higher
		
^{4}3	**^{4}Int3**	^{4}TS-HCOOH
E_{opt}= -1176.6669379	E_{opt}= -1467.9316799	E_{opt}= -1365.25932599
Doublet is 1.1 kcal mol^{-1} higher	Doublet is 3.0 kcal mol^{-1} higher	Doublet is 1.3 kcal mol^{-1} higher

		
^{4}TS-HCOOH’		
E_{opt}= -1656.51850825		
Doublet is 1.7 kcal mol^{-1} higher		
H_2	CO	H_2O
E_{opt}= -1.17853938133	E_{opt}= -113.3069132	E_{opt}= -76.418168
HCOOH	$HCOO^-$	CO_2
E_{opt}= -189.751402937	E_{opt}= -189.174974174	E_{opt}= -188.5777595
Et_3N	$Et_3N^{\cdot+}$	$Et_2N\dot{C}H_2CH_3$
E_{opt}= -292.4468438	E_{opt}= -292.1886762	E_{opt}= -291.7906207
Et_2N^+=$CHCH_3$	Et_2NCH=CH_2	
E_{opt}= -291.6205772	E_{opt}= -291.2191179	

(1) Cartesian coordinates for all optimized structures

1-Cl : E(opt)= -1635.9252798 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.195818	-0.422324	-0.953280
2	6	0	0.063155	0.355800	2.239301
3	1	0	-0.574347	0.186144	3.120110
4	1	0	1.038415	0.677950	2.623479
5	6	0	-0.494680	1.506528	1.410742
6	6	0	-1.084069	2.635657	1.975115
7	1	0	-1.223375	2.710252	3.049539
8	6	0	-1.486821	3.667618	1.119513
9	1	0	-1.948221	4.562024	1.529191
10	6	0	-1.297046	3.543403	-0.255084
11	1	0	-1.603327	4.330253	-0.938207
12	6	0	-0.710245	2.372383	-0.748243
13	6	0	-0.469988	2.043999	-2.223671
14	1	0	-1.474731	2.056200	-2.705232
15	1	0	0.060874	2.913026	-2.664514
16	6	0	-0.855879	-1.833339	1.573225
17	1	0	-0.524505	-2.761830	1.096372
18	1	0	-1.128840	-2.049182	2.619418
19	6	0	-2.085595	-1.383116	0.804298
20	6	0	-3.377170	-1.546376	1.306595
21	1	0	-3.522556	-1.941795	2.307145
22	6	0	-4.466415	-1.200539	0.505927
23	1	0	-5.479775	-1.320991	0.877487
24	6	0	-4.234720	-0.698428	-0.773759
25	1	0	-5.052094	-0.419585	-1.430001
26	6	0	-2.914392	-0.553192	-1.196876
27	1	0	-2.659115	-0.159869	-2.176844
28	6	0	1.591889	-1.476536	1.619444
29	1	0	1.564284	-2.449947	1.119109
30	1	0	1.882290	-1.625662	2.671950
31	6	0	2.639407	-0.647349	0.897136
32	6	0	3.926814	-0.453115	1.397947
33	1	0	4.201101	-0.861628	2.365920
34	6	0	4.846284	0.266937	0.632876
35	1	0	5.856068	0.427197	0.999528
36	6	0	4.449602	0.782799	-0.600505
37	1	0	5.133902	1.350494	-1.222033
38	6	0	3.139095	0.559124	-1.022714
39	1	0	2.736719	0.939449	-1.958293

40	7	0	0.256397	-0.883555	1.473125
41	7	0	-0.330165	1.403096	0.089931
42	7	0	-1.873095	-0.884713	-0.426685
43	7	0	2.267762	-0.141600	-0.289570
44	8	0	0.207969	0.861984	-2.415371
45	17	0	0.614398	-2.715398	-1.418694

---

1 : E(opt)= -1175.52101632 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.009874	-0.065349	-0.787240
2	6	0	-1.063078	0.060064	2.155909
3	1	0	-1.020708	-0.252564	3.208524
4	1	0	-1.510446	1.060495	2.138459
5	6	0	-1.959678	-0.860223	1.341493
6	6	0	-3.054979	-1.556442	1.832081
7	1	0	-3.296878	-1.540762	2.889692
8	6	0	-3.845476	-2.271381	0.918102
9	1	0	-4.709610	-2.824484	1.273236
10	6	0	-3.529508	-2.270293	-0.438367
11	1	0	-4.137894	-2.811535	-1.155820
12	6	0	-2.401601	-1.559333	-0.864591
13	6	0	-1.893216	-1.440007	-2.299985
14	1	0	-1.721930	-2.466406	-2.672932
15	1	0	-2.726155	-1.039194	-2.905753
16	6	0	1.163057	-0.952902	1.912020
17	1	0	1.636149	-0.817571	2.895682
18	1	0	0.535728	-1.849637	1.978780
19	6	0	2.212242	-1.204294	0.845777
20	6	0	3.467681	-1.729450	1.141703
21	1	0	3.749917	-1.910108	2.173850
22	6	0	4.344402	-2.022249	0.095407
23	1	0	5.327274	-2.432495	0.304521
24	6	0	3.940564	-1.783422	-1.218152
25	1	0	4.588269	-2.004152	-2.058940
26	6	0	2.674912	-1.247379	-1.436387
27	1	0	2.295034	-1.046906	-2.433530
28	6	0	0.907548	1.486857	1.717562
29	1	0	1.979692	1.369953	1.520801
30	1	0	0.811920	1.874895	2.741737
31	6	0	0.358569	2.486950	0.716168
32	6	0	0.249364	3.845742	1.000726

33	1	0	0.514023	4.215839	1.985934
34	6	0	-0.200791	4.714568	0.004720
35	1	0	-0.291066	5.777226	0.206494
36	6	0	-0.540167	4.198902	-1.245844
37	1	0	-0.899411	4.838584	-2.043935
38	6	0	-0.420447	2.827816	-1.453258
39	1	0	-0.687984	2.356293	-2.394127
40	7	0	0.282185	0.166945	1.552923
41	7	0	-1.659941	-0.896164	0.033519
42	7	0	1.836015	-0.956331	-0.425993
43	7	0	0.023169	1.993920	-0.495162
44	8	0	-0.749467	-0.654098	-2.425589

2_{dp} : E(opt)= -1175.6427842 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.345252	0.059135	-0.904819
2	6	0	0.272343	-0.593411	2.143239
3	1	0	-0.093181	-1.155440	3.016911
4	1	0	1.264017	-0.197396	2.401566
5	6	0	-0.624964	0.595083	1.854724
6	6	0	-1.470938	1.208086	2.773893
7	1	0	-1.597159	0.795851	3.770322
8	6	0	-2.152622	2.365088	2.376073
9	1	0	-2.822431	2.862780	3.071829
10	6	0	-1.980163	2.873225	1.086804
11	1	0	-2.512150	3.760958	0.757895
12	6	0	-1.120997	2.202618	0.209968
13	6	0	-0.855075	2.567812	-1.256321
14	1	0	-1.858843	2.624866	-1.732363
15	1	0	-0.477059	3.610907	-1.260813
16	6	0	-0.632379	-2.419033	0.738350
17	1	0	-0.206647	-3.246074	0.152675
18	1	0	-1.015982	-2.849525	1.676295
19	6	0	-1.756014	-1.816257	-0.064307
20	6	0	-3.097578	-2.085957	0.190526
21	1	0	-3.364101	-2.688465	1.054696
22	6	0	-4.079313	-1.589620	-0.667090
23	1	0	-5.129828	-1.791570	-0.485083
24	6	0	-3.670716	-0.815527	-1.769288
25	1	0	-4.393247	-0.401409	-2.464778
26	6	0	-2.322489	-0.567088	-1.954005

27	1	0	-1.951912	0.070166	-2.750948
28	6	0	1.828284	-2.016324	0.842149
29	1	0	1.754777	-2.834077	0.112433
30	1	0	2.209614	-2.444465	1.781931
31	6	0	2.780232	-0.982608	0.304888
32	6	0	4.044449	-0.769565	0.842706
33	1	0	4.349599	-1.337752	1.717363
34	6	0	4.908052	0.156594	0.253210
35	1	0	5.899681	0.329345	0.657981
36	6	0	4.448013	0.866622	-0.871605
37	1	0	5.073299	1.602768	-1.366096
38	6	0	3.173682	0.623309	-1.349962
39	1	0	2.759779	1.171481	-2.190161
40	7	0	0.463333	-1.461928	0.968414
41	7	0	-0.476760	1.104861	0.621052
42	7	0	-1.362219	-1.049088	-1.123822
43	7	0	2.332254	-0.292212	-0.794731
44	8	0	-0.007142	1.698836	-1.911454

2A : E(opt)= -1176.0917896 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.347952	-0.021340	-0.853350
2	6	0	0.256608	-0.730605	2.029347
3	1	0	-0.153999	-1.353110	2.836598
4	1	0	1.240342	-0.381484	2.361982
5	6	0	-0.602247	0.503192	1.814236
6	6	0	-1.494258	0.994062	2.762199
7	1	0	-1.654555	0.457577	3.691910
8	6	0	-2.178816	2.182372	2.490430
9	1	0	-2.888691	2.583115	3.206442
10	6	0	-1.945045	2.842565	1.282825
11	1	0	-2.465754	3.763241	1.039586
12	6	0	-1.032554	2.292200	0.384837
13	6	0	-0.659509	2.961939	-0.918421
14	1	0	-1.474669	3.609975	-1.261146
15	1	0	0.230305	3.586507	-0.752936
16	6	0	-0.617947	-2.474217	0.511338
17	1	0	-0.217800	-3.240406	-0.161510
18	1	0	-0.957841	-2.993768	1.419097
19	6	0	-1.803384	-1.835382	-0.194164
20	6	0	-3.100108	-2.304213	0.002316

21	1	0	-3.285625	-3.089577	0.728392
22	6	0	-4.145105	-1.757787	-0.743678
23	1	0	-5.162190	-2.110983	-0.607381
24	6	0	-3.856087	-0.748344	-1.661578
25	1	0	-4.634424	-0.291696	-2.263105
26	6	0	-2.538697	-0.319598	-1.789361
27	1	0	-2.260100	0.484975	-2.460289
28	6	0	1.828258	-2.059200	0.677227
29	1	0	1.810044	-2.839662	-0.090842
30	1	0	2.179377	-2.533202	1.605597
31	6	0	2.825788	-1.000789	0.227419
32	6	0	4.157666	-1.048171	0.630293
33	1	0	4.481617	-1.814839	1.327076
34	6	0	5.061934	-0.110123	0.129158
35	1	0	6.104071	-0.133751	0.430643
36	6	0	4.597174	0.857798	-0.760184
37	1	0	5.259200	1.608743	-1.176958
38	6	0	3.249083	0.852522	-1.103047
39	1	0	2.835843	1.595531	-1.777131
40	7	0	0.464731	-1.517549	0.792719
41	7	0	-0.386857	1.143194	0.647452
42	7	0	-1.525404	-0.846601	-1.075330
43	7	0	2.369385	-0.049576	-0.625338
44	8	0	-0.368880	1.951756	-1.902437
45	1	0	0.101675	2.359333	-2.639745

2B : E(opt)= -1176.0760209 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.000135	-0.369041	-0.752519
2	6	0	-0.000016	-0.484654	2.164782
3	1	0	-0.877717	-0.695042	2.783875
4	1	0	0.877481	-0.695445	2.784030
5	6	0	0.000307	0.975044	1.752877
6	6	0	0.000634	2.069668	2.610804
7	1	0	0.000739	1.941433	3.688075
8	6	0	0.000817	3.348149	2.035071
9	1	0	0.001069	4.222935	2.677952
10	6	0	0.000674	3.508155	0.647771
11	1	0	0.000808	4.496184	0.199625
12	6	0	0.000359	2.363869	-0.153660
13	6	0	0.000161	2.258522	-1.669566

14	1	0	-0.878699	2.818001	-2.042709
15	1	0	0.879079	2.817770	-2.042919
16	6	0	-1.251947	-2.233983	0.906947
17	1	0	-1.053035	-3.080085	0.242363
18	1	0	-1.544785	-2.629430	1.886584
19	6	0	-2.351040	-1.410562	0.275090
20	6	0	-3.705177	-1.575739	0.542154
21	1	0	-4.028129	-2.271755	1.309261
22	6	0	-4.630806	-0.842695	-0.205091
23	1	0	-5.693980	-0.956173	-0.019345
24	6	0	-4.173210	0.026937	-1.194755
25	1	0	-4.862963	0.600086	-1.803864
26	6	0	-2.801398	0.157114	-1.396361
27	1	0	-2.353525	0.799230	-2.146320
28	6	0	1.251488	-2.234220	0.906831
29	1	0	1.052355	-3.080254	0.242226
30	1	0	1.544327	-2.629756	1.886432
31	6	0	2.350674	-1.410986	0.274906
32	6	0	3.704792	-1.576266	0.541986
33	1	0	4.027682	-2.272260	1.309138
34	6	0	4.630493	-0.843349	-0.205302
35	1	0	5.693655	-0.956908	-0.019539
36	6	0	4.172979	0.026260	-1.195021
37	1	0	4.862784	0.599312	-1.804162
38	6	0	2.801177	0.156550	-1.396638
39	1	0	2.353369	0.798669	-2.146633
40	7	0	-0.000151	-1.428034	0.976514
41	7	0	0.000192	1.162248	0.432163
42	7	0	-1.921249	-0.541519	-0.665531
43	7	0	1.920963	-0.541962	-0.665778
44	8	0	-0.000069	0.931281	-2.126384
45	1	0	-0.000359	-1.534674	-1.653505

Int1: E(opt)= -1364.683841 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.171775	-0.507158	-0.533025
2	6	0	0.080690	0.649172	2.268324
3	1	0	-0.875889	1.000384	2.671435
4	1	0	0.771632	0.589060	3.118315
5	6	0	0.564647	1.704179	1.283081
6	6	0	1.214574	2.869333	1.692037

7	1	0	1.445841	3.031702	2.739918
8	6	0	1.565386	3.812634	0.725477
9	1	0	2.078355	4.724463	1.014315
10	6	0	1.269125	3.569692	-0.617923
11	1	0	1.546848	4.278756	-1.390798
12	6	0	0.620384	2.381839	-0.945181
13	6	0	0.226874	1.993701	-2.355300
14	1	0	-0.801293	2.329857	-2.549586
15	1	0	0.887723	2.470559	-3.087632
16	6	0	-1.466373	-1.251402	1.977767
17	1	0	-1.457574	-2.299083	1.662118
18	1	0	-1.698016	-1.223925	3.051481
19	6	0	-2.547586	-0.546220	1.179888
20	6	0	-3.808982	-0.277734	1.706905
21	1	0	-4.027919	-0.525216	2.740605
22	6	0	-4.779191	0.301024	0.886708
23	1	0	-5.769197	0.515943	1.276080
24	6	0	-4.457295	0.595059	-0.437565
25	1	0	-5.182653	1.035861	-1.112198
26	6	0	-3.171220	0.306254	-0.886446
27	1	0	-2.869030	0.497920	-1.911141
28	6	0	0.982914	-1.631155	1.903601
29	1	0	0.619997	-2.631641	1.648397
30	1	0	1.296673	-1.646557	2.956672
31	6	0	2.168337	-1.341371	1.000551
32	6	0	3.484057	-1.500829	1.429671
33	1	0	3.690277	-1.779562	2.458089
34	6	0	4.522207	-1.304391	0.517208
35	1	0	5.555006	-1.427773	0.827444
36	6	0	4.212083	-0.944031	-0.793381
37	1	0	4.987702	-0.781977	-1.533619
38	6	0	2.872148	-0.786713	-1.140073
39	1	0	2.564739	-0.484482	-2.135580
40	7	0	-0.133548	-0.691900	1.669282
41	7	0	0.278710	1.488358	-0.006315
42	7	0	-2.234822	-0.241744	-0.098038
43	7	0	1.873607	-0.984518	-0.266605
44	8	0	0.312238	0.566366	-2.453174
45	6	0	-0.858808	-1.945432	-1.774921
46	8	0	-0.649111	-2.724812	-0.859223
47	8	0	-1.225700	-1.729288	-2.903285
48	1	0	-0.276180	0.207804	-3.138025

Int2: E(opt)= -1365.2838613 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.008765	-0.434143	0.478785
2	6	0	0.103398	0.725274	-2.316694
3	1	0	1.011905	0.827754	-2.922241
4	1	0	-0.737574	0.872109	-3.006006
5	6	0	0.080041	1.853855	-1.291264
6	6	0	0.142508	3.193715	-1.676919
7	1	0	0.217468	3.456446	-2.727388
8	6	0	0.113652	4.178628	-0.691686
9	1	0	0.171704	5.227526	-0.964320
10	6	0	0.010425	3.806152	0.650087
11	1	0	-0.014828	4.552239	1.437627
12	6	0	-0.062582	2.451510	0.961632
13	6	0	-0.267091	1.962717	2.384343
14	1	0	0.286732	2.600251	3.083899
15	1	0	-1.335415	2.043920	2.630112
16	6	0	1.275879	-1.416560	-1.905422
17	1	0	1.044295	-2.442291	-1.603054
18	1	0	1.630039	-1.425071	-2.945910
19	6	0	2.371727	-0.925995	-0.978337
20	6	0	3.718497	-0.958785	-1.331668
21	1	0	4.005844	-1.285266	-2.325884
22	6	0	4.679683	-0.579503	-0.394187
23	1	0	5.734378	-0.603438	-0.649150
24	6	0	4.262771	-0.168654	0.871208
25	1	0	4.974679	0.133279	1.631226
26	6	0	2.899395	-0.147185	1.149831
27	1	0	2.506917	0.168973	2.109122
28	6	0	-1.212446	-1.351290	-1.973221
29	1	0	-1.035056	-2.396688	-1.701956
30	1	0	-1.529613	-1.315000	-3.025066
31	6	0	-2.330216	-0.857482	-1.071377
32	6	0	-3.662390	-0.845256	-1.479400
33	1	0	-3.913833	-1.120030	-2.498626
34	6	0	-4.656266	-0.491983	-0.566524
35	1	0	-5.699115	-0.480810	-0.866652
36	6	0	-4.287645	-0.159099	0.736536
37	1	0	-5.025621	0.112118	1.483066
38	6	0	-2.937017	-0.180015	1.067903
39	1	0	-2.592125	0.061330	2.067036
40	7	0	0.044226	-0.627469	-1.732373

41	7	0	-0.013771	1.510398	0.001626
42	7	0	1.976213	-0.515201	0.247079
43	7	0	-1.979022	-0.509829	0.187675
44	8	0	0.173509	0.606994	2.474728
45	6	0	-0.050071	-2.249427	1.038023
46	8	0	0.035696	-3.272453	0.373552
47	8	0	-0.245757	-2.351428	2.404580
48	1	0	-0.271775	-3.304003	2.619200
49	1	0	-0.246969	0.124606	3.199666

Int3: E(opt)= -1467.931799 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.323260	-0.232520	-0.711548
2	6	0	-2.459557	1.768479	0.397945
3	1	0	-2.645865	2.849703	0.366587
4	1	0	-3.411981	1.301440	0.673072
5	6	0	-1.469792	1.456041	1.514516
6	6	0	-1.464048	2.165372	2.715027
7	1	0	-2.142289	2.999400	2.864757
8	6	0	-0.563427	1.785383	3.712119
9	1	0	-0.531014	2.326969	4.652356
10	6	0	0.301343	0.713736	3.490137
11	1	0	1.016740	0.404042	4.245191
12	6	0	0.232598	0.052131	2.263424
13	6	0	1.094085	-1.147771	1.930847
14	1	0	2.091340	-1.014389	2.370543
15	1	0	0.647777	-2.036225	2.408601
16	6	0	-1.466229	2.295328	-1.800473
17	1	0	-1.315740	1.837961	-2.784375
18	1	0	-2.128068	3.165702	-1.923459
19	6	0	-0.109814	2.731139	-1.286680
20	6	0	0.333170	4.051488	-1.356345
21	1	0	-0.317104	4.822193	-1.757612
22	6	0	1.617557	4.358256	-0.904863
23	1	0	1.986048	5.378178	-0.952547
24	6	0	2.414226	3.338614	-0.383902
25	1	0	3.414816	3.534621	-0.014519
26	6	0	1.891393	2.048703	-0.338916
27	1	0	2.455436	1.214798	0.062795
28	6	0	-3.100643	0.466209	-1.601084
29	1	0	-2.716969	0.213785	-2.595283

30	1	0	-4.042179	1.021831	-1.724005
31	6	0	-3.348069	-0.831991	-0.858171
32	6	0	-4.615172	-1.412139	-0.784043
33	1	0	-5.467232	-0.916037	-1.238019
34	6	0	-4.763504	-2.630816	-0.121802
35	1	0	-5.737871	-3.104571	-0.055637
36	6	0	-3.644056	-3.222327	0.463917
37	1	0	-3.715746	-4.163270	0.998338
38	6	0	-2.419506	-2.567506	0.354866
39	1	0	-1.519330	-2.975380	0.805319
40	7	0	-2.057325	1.263193	-0.934007
41	7	0	-0.632243	0.429106	1.316809
42	7	0	0.665032	1.751296	-0.786808
43	7	0	-2.269064	-1.408199	-0.298218
44	8	0	1.175883	-1.334247	0.524541
45	1	0	-0.273439	-0.664310	-2.269102
46	7	0	3.320579	-2.246267	-0.294889
47	6	0	2.028966	-2.572407	0.113056
48	6	0	3.647969	-1.967898	-1.696812
49	6	0	4.347193	-1.984305	0.709346
50	6	0	1.174459	-3.301309	-0.909300
51	1	0	0.242552	-3.622979	-0.441678
52	1	0	1.702597	-4.186528	-1.273447
53	1	0	0.912508	-2.652545	-1.747347
54	6	0	3.183989	-0.614860	-2.248831
55	1	0	3.465728	-0.529822	-3.304014
56	1	0	3.645533	0.217641	-1.711872
57	1	0	2.096834	-0.509113	-2.186982
58	6	0	4.637310	-0.506830	1.009683
59	1	0	3.745480	0.008776	1.379950
60	1	0	4.985633	0.016880	0.115088
61	1	0	5.419745	-0.420883	1.770980
62	1	0	4.048335	-2.492682	1.634093
63	1	0	5.279123	-2.464890	0.383757
64	1	0	2.080564	-3.141053	1.048164
65	1	0	4.737001	-2.047387	-1.782813
66	1	0	3.240505	-2.768063	-2.323586

3_{dp} : E(opt)= -1176.2144031 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.000887	-0.201393	-1.311304

2	6	0	-0.000858	-0.814032	1.906689
3	1	0	-0.878080	-1.072497	2.513948
4	1	0	0.874643	-1.075143	2.515323
5	6	0	0.001428	0.695340	1.678171
6	6	0	0.003626	1.601562	2.736338
7	1	0	0.004071	1.252823	3.765207
8	6	0	0.005235	2.968657	2.436556
9	1	0	0.006960	3.700225	3.240171
10	6	0	0.004668	3.383870	1.107546
11	1	0	0.005936	4.438665	0.847460
12	6	0	0.002535	2.414244	0.097883
13	6	0	0.001935	2.704759	-1.406790
14	1	0	-0.876232	3.369870	-1.580073
15	1	0	0.881113	3.368270	-1.581067
16	6	0	-1.230985	-2.385780	0.454067
17	1	0	-1.060314	-3.002076	-0.435787
18	1	0	-1.464518	-3.049957	1.302532
19	6	0	-2.412929	-1.490644	0.141212
20	6	0	-3.680419	-1.677386	0.693448
21	1	0	-3.846747	-2.462792	1.424707
22	6	0	-4.720588	-0.838827	0.286953
23	1	0	-5.716917	-0.961696	0.701525
24	6	0	-4.461257	0.158861	-0.652805
25	1	0	-5.241869	0.832088	-0.991315
26	6	0	-3.162712	0.282262	-1.148361
27	1	0	-2.877855	1.040495	-1.873482
28	6	0	1.227646	-2.386950	0.453944
29	1	0	1.056167	-3.003401	-0.435642
30	1	0	1.460783	-3.051067	1.302567
31	6	0	2.410365	-1.493046	0.140470
32	6	0	3.677761	-1.680607	0.692641
33	1	0	3.843503	-2.465767	1.424297
34	6	0	4.718604	-0.843163	0.285567
35	1	0	5.714880	-0.966679	0.700075
36	6	0	4.460020	0.154261	-0.654677
37	1	0	5.241173	0.826637	-0.993630
38	6	0	3.161515	0.278538	-1.150125
39	1	0	2.877171	1.036682	-1.875541
40	7	0	-0.001284	-1.609334	0.665463
41	7	0	0.000948	1.112934	0.409622
42	7	0	-2.171388	-0.524197	-0.758717
43	7	0	2.169559	-0.526875	-0.759940
44	8	0	0.000482	1.592658	-2.200891
45	1	0	-0.002152	-1.417516	-2.446297

---

3 : E(opt)= -1176.6669379 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.000508	-0.294802	-1.201978
2	6	0	-0.000472	-0.763305	1.873297
3	1	0	-0.876628	-1.016803	2.481576
4	1	0	0.874674	-1.018319	2.482403
5	6	0	0.000818	0.742366	1.650261
6	6	0	0.002047	1.621458	2.733442
7	1	0	0.002287	1.239557	3.749515
8	6	0	0.002942	2.993320	2.483628
9	1	0	0.003905	3.699784	3.307637
10	6	0	0.002611	3.450181	1.166557
11	1	0	0.003305	4.511979	0.941206
12	6	0	0.001402	2.508886	0.138106
13	6	0	0.001025	2.937345	-1.317582
14	1	0	-0.886262	3.555038	-1.513799
15	1	0	0.888668	3.554310	-1.514465
16	6	0	-1.231450	-2.386794	0.483996
17	1	0	-1.068120	-3.061991	-0.362492
18	1	0	-1.433555	-3.000217	1.373395
19	6	0	-2.425335	-1.517896	0.146177
20	6	0	-3.699793	-1.761071	0.656131
21	1	0	-3.857478	-2.562169	1.371218
22	6	0	-4.761449	-0.963867	0.224449
23	1	0	-5.764134	-1.134274	0.603591
24	6	0	-4.514829	0.051621	-0.699138
25	1	0	-5.312122	0.690518	-1.062594
26	6	0	-3.208890	0.233006	-1.150601
27	1	0	-2.955531	1.007400	-1.869067
28	6	0	1.229634	-2.387418	0.483905
29	1	0	1.065831	-3.062649	-0.362465
30	1	0	1.431561	-3.000824	1.373356
31	6	0	2.423921	-1.519203	0.145764
32	6	0	3.698315	-1.762909	0.655625
33	1	0	3.855674	-2.563908	1.370894
34	6	0	4.760332	-0.966363	0.223610
35	1	0	5.762975	-1.137193	0.602672
36	6	0	4.514124	0.049013	-0.700209
37	1	0	5.311702	0.687400	-1.063933
38	6	0	3.208221	0.230960	-1.151553

39	1	0	2.955170	1.005308	-1.870179
40	7	0	-0.000693	-1.579023	0.634105
41	7	0	0.000529	1.191516	0.387597
42	7	0	-2.189820	-0.529857	-0.736805
43	7	0	2.188809	-0.531269	-0.737438
44	8	0	0.000233	1.769176	-2.132631
45	1	0	-0.001015	-1.160891	-2.556692
46	1	0	0.000120	1.978634	-3.074710

TS-2A：E(opt)= -1467.8910492 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.623683	0.272321	-0.675532
2	6	0	-1.085735	0.255089	2.298727
3	1	0	-0.861279	-0.258634	3.243969
4	1	0	-1.375554	1.279630	2.558792
5	6	0	-2.288840	-0.385070	1.623901
6	6	0	-3.267567	-1.081168	2.330147
7	1	0	-3.158664	-1.245532	3.397422
8	6	0	-4.380116	-1.563911	1.638654
9	1	0	-5.151930	-2.120500	2.160391
10	6	0	-4.485021	-1.328990	0.267260
11	1	0	-5.335791	-1.694085	-0.299080
12	6	0	-3.467333	-0.619713	-0.369002
13	6	0	-3.534877	-0.252358	-1.835700
14	1	0	-4.161603	-0.971366	-2.377116
15	1	0	-4.001075	0.739888	-1.925298
16	6	0	0.980810	-0.842877	1.496863
17	1	0	1.959735	-0.537607	1.106493
18	1	0	1.131021	-1.192511	2.529553
19	6	0	0.502242	-1.989773	0.626403
20	6	0	0.777571	-3.316327	0.953364
21	1	0	1.259244	-3.546767	1.898338
22	6	0	0.440333	-4.329476	0.055847
23	1	0	0.651553	-5.367623	0.291231
24	6	0	-0.176678	-3.979409	-1.145929
25	1	0	-0.457601	-4.730217	-1.876479
26	6	0	-0.442962	-2.637072	-1.394923
27	1	0	-0.945333	-2.306332	-2.296598
28	6	0	0.781231	1.632515	1.450166
29	1	0	1.747256	1.497113	0.957149
30	1	0	0.978577	1.997473	2.469663

31	6	0	0.009937	2.681958	0.665762
32	6	0	0.032186	4.027034	1.025495
33	1	0	0.563242	4.333575	1.921337
34	6	0	-0.625929	4.964798	0.227915
35	1	0	-0.615793	6.017417	0.491283
36	6	0	-1.300615	4.518726	-0.908158
37	1	0	-1.829082	5.206422	-1.559289
38	6	0	-1.292222	3.157504	-1.195181
39	1	0	-1.809338	2.757487	-2.061383
40	7	0	0.100691	0.329824	1.428498
41	7	0	-2.391812	-0.173030	0.299493
42	7	0	-0.112923	-1.655403	-0.533342
43	7	0	-0.655162	2.249288	-0.433833
44	8	0	-2.206942	-0.224660	-2.376802
45	1	0	-2.205478	0.277744	-3.200440
46	7	0	3.774813	-0.009302	-0.440041
47	6	0	3.153893	0.948569	-1.234734
48	6	0	5.014030	0.441075	0.222286
49	6	0	3.696300	-1.405705	-0.897318
50	6	0	2.132266	0.726458	-2.145295
51	1	0	1.830877	1.584881	-2.737583
52	1	0	0.788824	0.526228	-1.432938
53	1	0	2.052222	-0.223224	-2.664091
54	6	0	4.737008	1.361712	1.413355
55	1	0	5.676895	1.668136	1.882321
56	1	0	4.129486	0.844858	2.163309
57	1	0	4.207671	2.271877	1.113733
58	6	0	4.124181	-2.439574	0.144961
59	1	0	3.640568	-2.255806	1.109453
60	1	0	5.204936	-2.463306	0.305092
61	1	0	3.825050	-3.434419	-0.196856
62	1	0	2.649832	-1.594295	-1.149902
63	1	0	4.275982	-1.544130	-1.824580
64	1	0	3.391656	1.970772	-0.955745
65	1	0	5.551728	-0.437118	0.578770
66	1	0	5.673339	0.940842	-0.501765

TS-CO : E(opt)= -1365.2645845 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.289067	-0.603106	0.198091
2	6	0	0.219964	2.174189	-1.153489

3	1	0	1.215911	2.543808	-0.885300
4	1	0	-0.168093	2.839677	-1.935828
5	6	0	-0.632246	2.253065	0.097070
6	6	0	-1.405805	3.351980	0.450901
7	1	0	-1.494351	4.204802	-0.213880
8	6	0	-2.057734	3.330359	1.690225
9	1	0	-2.665432	4.175857	1.997260
10	6	0	-1.924942	2.225253	2.528026
11	1	0	-2.418772	2.190946	3.493779
12	6	0	-1.146483	1.148533	2.094412
13	6	0	-0.966763	-0.140672	2.880687
14	1	0	-0.729346	0.104049	3.924843
15	1	0	-1.927657	-0.679125	2.886327
16	6	0	1.726609	0.564278	-2.227291
17	1	0	1.706579	-0.396211	-2.752877
18	1	0	2.005095	1.335506	-2.959127
19	6	0	2.767996	0.468803	-1.129653
20	6	0	4.080135	0.905811	-1.295449
21	1	0	4.381890	1.383833	-2.221787
22	6	0	4.991640	0.712083	-0.255646
23	1	0	6.020626	1.040313	-0.362848
24	6	0	4.562471	0.097701	0.920772
25	1	0	5.239086	-0.067811	1.751529
26	6	0	3.231891	-0.301684	1.014313
27	1	0	2.827814	-0.775035	1.903972
28	6	0	-0.714614	0.385535	-2.569123
29	1	0	-0.334030	-0.412628	-3.215279
30	1	0	-1.018511	1.211086	-3.226591
31	6	0	-1.914013	-0.182833	-1.836195
32	6	0	-3.217555	-0.012971	-2.295334
33	1	0	-3.415791	0.622114	-3.152817
34	6	0	-4.254555	-0.682979	-1.641690
35	1	0	-5.279290	-0.565994	-1.980207
36	6	0	-3.954035	-1.511132	-0.561267
37	1	0	-4.728206	-2.064167	-0.041064
38	6	0	-2.625454	-1.623046	-0.154888
39	1	0	-2.309249	-2.268251	0.661167
40	7	0	0.378915	0.785674	-1.657820
41	7	0	-0.525030	1.191717	0.910041
42	7	0	2.360031	-0.119786	0.010654
43	7	0	-1.634739	-0.958340	-0.772124
44	8	0	0.050893	-0.934291	2.306905
45	6	0	0.667883	-2.679499	0.115210
46	8	0	1.217036	-3.604088	-0.343400

47	8	0	-0.400572	-3.130229	1.477792
48	1	0	-0.117657	-3.994607	1.813345
49	1	0	-0.194869	-1.986950	2.171750

TS-H_2 : E(opt)= -1467.91559838 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.171268	-0.039911	-0.262181
2	6	0	-2.296671	2.024333	-0.253391
3	1	0	-1.891910	3.029038	-0.092609
4	1	0	-3.324931	2.154345	-0.611294
5	6	0	-2.280988	1.298146	1.076764
6	6	0	-3.180998	1.522974	2.111806
7	1	0	-3.999035	2.225623	1.991788
8	6	0	-3.002735	0.818712	3.309192
9	1	0	-3.689877	0.976295	4.134802
10	6	0	-1.952975	-0.089719	3.437727
11	1	0	-1.808495	-0.652325	4.354388
12	6	0	-1.092194	-0.281651	2.354587
13	6	0	0.068286	-1.257391	2.261141
14	1	0	0.781663	-0.999154	3.071500
15	1	0	-0.329355	-2.255143	2.538783
16	6	0	-0.561130	2.303552	-1.978892
17	1	0	-0.102397	1.768751	-2.816711
18	1	0	-1.107464	3.165911	-2.386763
19	6	0	0.545797	2.759803	-1.046729
20	6	0	1.107139	4.034538	-1.112096
21	1	0	0.728480	4.763424	-1.821935
22	6	0	2.159828	4.348785	-0.250693
23	1	0	2.617494	5.332591	-0.281232
24	6	0	2.606127	3.385351	0.654394
25	1	0	3.415717	3.593047	1.345686
26	6	0	1.980174	2.139932	0.660717
27	1	0	2.275633	1.347750	1.341055
28	6	0	-2.272556	0.548214	-2.242850
29	1	0	-1.617695	0.284199	-3.079275
30	1	0	-3.113677	1.130235	-2.644421
31	6	0	-2.758027	-0.743272	-1.613200
32	6	0	-4.042459	-1.249575	-1.801659
33	1	0	-4.771256	-0.696116	-2.385641
34	6	0	-4.366427	-2.481032	-1.226019
35	1	0	-5.358689	-2.901488	-1.356433

36	6	0	-3.402434	-3.157271	-0.478463
37	1	0	-3.618292	-4.113552	-0.014271
38	6	0	-2.145759	-2.569526	-0.329792
39	1	0	-1.351018	-3.024289	0.255351
40	7	0	-1.458141	1.344855	-1.294077
41	7	0	-1.275755	0.422220	1.225678
42	7	0	0.978963	1.834720	-0.173442
43	7	0	-1.834588	-1.396275	-0.888962
44	8	0	0.669849	-1.256154	1.006989
45	1	0	0.695494	-0.435262	-1.589569
46	7	0	3.669862	-2.276937	-0.186800
47	6	0	2.478412	-2.742662	-0.554354
48	6	0	4.524046	-1.529935	-1.121239
49	6	0	4.088886	-2.372932	1.221445
50	6	0	1.838808	-2.557713	-1.786121
51	1	0	1.016662	-3.238794	-1.989925
52	1	0	2.422642	-2.275214	-2.659370
53	1	0	1.122490	-1.337232	-1.541034
54	6	0	4.085279	-0.076906	-1.346226
55	1	0	4.733513	0.388253	-2.095639
56	1	0	4.154959	0.506988	-0.426355
57	1	0	3.052186	-0.020889	-1.695052
58	6	0	3.835603	-1.084971	2.008918
59	1	0	2.787723	-0.801048	1.876935
60	1	0	4.481647	-0.271366	1.666531
61	1	0	4.043320	-1.250505	3.070669
62	1	0	3.530888	-3.197792	1.672175
63	1	0	5.147858	-2.651506	1.241817
64	1	0	1.920318	-3.223163	0.240414
65	1	0	5.542635	-1.561702	-0.725088
66	1	0	4.537641	-2.071847	-2.072856

TS-HCOOH：E(opt)= -1365.25932599 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.252487	0.679316	0.067294
2	6	0	-0.530992	-2.124852	-1.178444
3	1	0	-1.579417	-2.401819	-1.022812
4	1	0	-0.126531	-2.824515	-1.921174
5	6	0	0.171389	-2.298133	0.155184
6	6	0	0.689634	-3.513589	0.593406
7	1	0	0.678645	-4.384418	-0.053801

8	6	0	1.211116	-3.585016	1.888659
9	1	0	1.614806	-4.521135	2.261362
10	6	0	1.207209	-2.452057	2.701160
11	1	0	1.598911	-2.485517	3.712678
12	6	0	0.694487	-1.263484	2.179168
13	6	0	0.702522	0.047972	2.943192
14	1	0	0.375559	-0.119002	3.976522
15	1	0	1.730344	0.434930	2.978200
16	6	0	-1.800867	-0.334858	-2.282735
17	1	0	-1.647764	0.625632	-2.785965
18	1	0	-2.151866	-1.054259	-3.035447
19	6	0	-2.844624	-0.132147	-1.201542
20	6	0	-4.195819	-0.408416	-1.398177
21	1	0	-4.534586	-0.834418	-2.337157
22	6	0	-5.097076	-0.121678	-0.371026
23	1	0	-6.155736	-0.323219	-0.500029
24	6	0	-4.618156	0.421718	0.820933
25	1	0	-5.285440	0.656621	1.642641
26	6	0	-3.250628	0.657788	0.942573
27	1	0	-2.810874	1.071841	1.844489
28	6	0	0.649649	-0.468790	-2.578016
29	1	0	0.423316	0.438471	-3.148194
30	1	0	0.796278	-1.280837	-3.303116
31	6	0	1.932078	-0.199041	-1.813175
32	6	0	3.175829	-0.626038	-2.273898
33	1	0	3.244781	-1.244035	-3.163353
34	6	0	4.323380	-0.235441	-1.580770
35	1	0	5.303446	-0.554353	-1.921192
36	6	0	4.192635	0.575277	-0.453867
37	1	0	5.058980	0.912979	0.103916
38	6	0	2.912508	0.951611	-0.053040
39	1	0	2.747035	1.594197	0.806952
40	7	0	-0.502669	-0.729875	-1.688164
41	7	0	0.192225	-1.212180	0.940331
42	7	0	-2.387734	0.387214	-0.046909
43	7	0	1.809718	0.564774	-0.710754
44	8	0	-0.160699	0.980094	2.293448
45	1	0	-0.404686	2.329110	-0.129216
46	1	0	0.226386	1.882349	2.302615
47	6	0	0.711517	3.673181	0.478105
48	8	0	1.034562	3.287024	1.569988
49	8	0	0.691141	4.393666	-0.450003

TS-HCOOH' : E(opt)= -1656.51850825 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.375441	-0.232141	0.145115
2	6	0	2.394687	2.082291	0.167360
3	1	0	2.612056	3.030922	0.674937
4	1	0	3.341874	1.730318	-0.255607
5	6	0	1.445843	2.318742	-0.996611
6	6	0	1.480436	3.467977	-1.783277
7	1	0	2.165942	4.276161	-1.549818
8	6	0	0.617431	3.550666	-2.879295
9	1	0	0.628838	4.430659	-3.514693
10	6	0	-0.261247	2.502419	-3.152701
11	1	0	-0.942627	2.546758	-3.996153
12	6	0	-0.252975	1.395423	-2.303341
13	6	0	-1.224443	0.243044	-2.440105
14	1	0	-2.217268	0.572971	-2.100968
15	1	0	-1.313095	-0.051938	-3.495146
16	6	0	1.202840	1.643126	2.293925
17	1	0	1.081735	0.839927	3.027379
18	1	0	1.782177	2.451828	2.760310
19	6	0	-0.183398	2.126326	1.919665
20	6	0	-0.723652	3.314355	2.409547
21	1	0	-0.128770	3.959163	3.048244
22	6	0	-2.034929	3.651814	2.069690
23	1	0	-2.477358	4.570902	2.440966
24	6	0	-2.765075	2.793150	1.248469
25	1	0	-3.787578	3.015984	0.963893
26	6	0	-2.151662	1.627176	0.796970
27	1	0	-2.668588	0.907649	0.170150
28	6	0	2.981618	0.116716	1.533060
29	1	0	2.579891	-0.493824	2.347107
30	1	0	3.877457	0.635594	1.901670
31	6	0	3.331697	-0.803368	0.381832
32	6	0	4.620033	-1.299204	0.186689
33	1	0	5.423857	-0.998859	0.851211
34	6	0	4.851521	-2.182561	-0.868353
35	1	0	5.844646	-2.586723	-1.037060
36	6	0	3.791961	-2.527244	-1.707291
37	1	0	3.930304	-3.201744	-2.545009
38	6	0	2.537884	-1.978769	-1.450210
39	1	0	1.678044	-2.198487	-2.073184
40	7	0	1.914371	1.061625	1.132305

41	7	0	0.593339	1.323291	-1.271628
42	7	0	-0.893373	1.302614	1.124681
43	7	0	2.309577	-1.145958	-0.425391
44	8	0	-0.787116	-0.861267	-1.654027
45	1	0	0.085961	-1.487586	1.164030
46	7	0	-2.896707	-1.676703	-0.785966
47	6	0	-1.774538	-1.990553	-1.621539
48	6	0	-3.031702	-2.360808	0.523723
49	6	0	-4.172561	-1.556433	-1.518997
50	6	0	-0.939209	-3.219158	-1.293582
51	1	0	-0.222234	-3.387325	-2.100110
52	1	0	-1.582477	-4.100142	-1.224112
53	1	0	-0.393753	-3.098754	-0.355333
54	6	0	-3.119972	-1.431434	1.735092
55	1	0	-3.274545	-2.031523	2.637533
56	1	0	-3.940435	-0.713647	1.660062
57	1	0	-2.184525	-0.883018	1.856293
58	6	0	-5.220456	-0.693013	-0.819059
59	1	0	-4.836201	0.313570	-0.621080
60	1	0	-5.542803	-1.127976	0.129709
61	1	0	-6.105412	-0.601147	-1.456127
62	1	0	-3.957887	-1.115200	-2.498092
63	1	0	-4.603768	-2.554548	-1.710207
64	1	0	-2.120004	-2.069134	-2.658626
65	1	0	-3.918401	-3.009868	0.484932
66	1	0	-2.178595	-3.014730	0.691175
67	6	0	0.171140	-2.286991	2.690645
68	8	0	-0.379030	-3.305069	2.428808
69	8	0	0.742215	-1.504242	3.389191

H_2：E(opt)= -1.1785394 hartree

Center Number	Atomic Number	Forces (Hartrees/Bohr) X	Y	Z
1	1	0.000000000	0.000000000	-0.000000256
2	1	0.000000000	0.000000000	0.000000256

H_2O：E(opt)= -76.418168 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.118840

2	1	0	0.000000	0.760114	-0.475358
3	1	0	0.000000	-0.760114	-0.475358

CO：E(opt)= -113.3069132 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	-0.650135
2	8	0	0.000000	0.000000	0.487601

CO_2：E(opt)= -188.5777595 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.169716
3	8	0	0.000000	0.000000	-1.169716

HCOOH：E(opt)= -189.751402937 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.130942	0.362442	-0.000002
2	8	0	1.178812	-0.219748	0.000000
3	1	0	0.037621	1.467566	0.000005
4	8	0	-1.059257	-0.281248	0.000001
5	1	0	-1.779714	0.365755	-0.000002

HCOO'：E(opt)= -189.174974174 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000047	0.310939	0.000095
2	8	0	-1.142138	-0.208219	-0.000037
3	1	0	-0.000400	1.465409	-0.000005
4	8	0	1.142152	-0.208162	-0.000033

Et_3N：E(opt)= -292.446843802 hartree

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	7	0	0.000018	-0.000076	0.028323
2	6	0	-1.117780	-0.851224	0.452735
3	6	0	1.296005	-0.542433	0.452855
4	6	0	-0.178290	1.393521	0.452733
5	6	0	-2.347100	-0.701783	-0.445755
6	1	0	-3.147713	-1.373142	-0.116908
7	1	0	-2.086942	-0.944041	-1.480308
8	1	0	-2.745811	0.317626	-0.431376
9	6	0	1.781461	-1.681502	-0.445808
10	1	0	2.763473	-2.038744	-0.117381
11	1	0	1.860618	-1.334920	-1.480358
12	1	0	1.098387	-2.536796	-0.431174
13	6	0	0.565713	2.383418	-0.445712
14	1	0	0.225881	2.279236	-1.480279
15	1	0	1.647919	2.219146	-0.431322
16	1	0	0.384472	3.412432	-0.116846
17	1	0	-1.246258	1.628636	0.410730
18	1	0	0.122666	1.534131	1.509531
19	1	0	-0.787535	-1.893704	0.410873
20	1	0	-1.390050	-0.660736	1.509508
21	1	0	2.033519	0.264961	0.411161
22	1	0	1.267194	-0.873527	1.509604

$Et_3N^{\cdot+}$: E(opt)= -292.188676170 hartree

1	7	0	-0.000175	-0.000045	-0.632887
2	6	0	-1.456029	-0.079211	-0.613512
3	6	0	0.659192	1.300398	-0.613765
4	6	0	0.796294	-1.221279	-0.613510
5	6	0	-1.987896	-0.654460	0.716108
6	1	0	-3.078524	-0.684810	0.656097
7	1	0	-1.701700	-0.022192	1.559105
8	1	0	-1.628923	-1.671333	0.890205
9	6	0	0.427319	2.048704	0.715888
10	1	0	0.946378	3.008360	0.655680
11	1	0	0.831954	1.484782	1.558836
12	1	0	-0.632748	2.246318	0.890245
13	6	0	1.561182	-1.394113	0.715705
14	1	0	0.871095	-1.462879	1.559118
15	1	0	2.262062	-0.574522	0.889549
16	1	0	2.133184	-2.323165	0.655172
17	1	0	0.129978	-2.066268	-0.795861

18	1	0	1.508947	-1.150465	-1.445579
19	1	0	-1.854711	0.920199	-0.796400
20	1	0	-1.751068	-0.732258	-1.445200
21	1	0	1.724002	1.145918	-0.796890
22	1	0	0.240932	1.882396	-1.445351

$Et_2N^{\zeta}HCH_3$: E(opt)= -291.790620717 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.055750	-0.103434	-0.239181
2	6	0	1.115240	-1.014564	-0.261417
3	6	0	-1.258161	-0.624074	-0.617716
4	6	0	0.290222	1.314833	-0.497216
5	6	0	2.433512	-0.674163	0.363136
6	1	0	3.072691	-1.561831	0.376905
7	1	0	2.336268	-0.318627	1.404336
8	1	0	2.988238	0.103166	-0.181621
9	6	0	-1.985657	-1.285315	0.556538
10	1	0	-2.951662	-1.692955	0.238340
11	1	0	-2.157867	-0.561225	1.358819
12	1	0	-1.388602	-2.104997	0.968017
13	6	0	-0.493373	2.219858	0.457968
14	1	0	-0.205058	2.018788	1.494180
15	1	0	-1.573039	2.058045	0.372693
16	1	0	-0.297018	3.274661	0.236690
17	1	0	1.357279	1.514679	-0.382622
18	1	0	0.039006	1.564666	-1.542602
19	1	0	0.791595	-2.050949	-0.226015
20	1	0	-1.863040	0.202534	-1.004794
21	1	0	-1.149751	-1.341370	-1.445814

$Et_2N^{+}=CHCH_3$: E(opt)= -291.620577211 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.001888	-0.383097	0.308686
2	6	0	0.986775	-1.086670	-0.138057
3	6	0	0.156396	1.029719	0.777115
4	6	0	-1.374719	-0.959440	0.380488
5	6	0	2.404655	-0.672822	-0.254058
6	1	0	3.029386	-1.433432	0.229354

7	1	0	2.632015	0.306807	0.161994
8	1	0	2.683630	-0.685297	-1.316221
9	6	0	0.280061	2.021255	-0.381048
10	1	0	0.367776	3.029941	0.030828
11	1	0	-0.597586	1.993126	-1.029587
12	1	0	1.166434	1.827161	-0.989796
13	6	0	-2.364994	-0.239438	-0.531988
14	1	0	-2.039985	-0.272346	-1.575257
15	1	0	-2.518921	0.801380	-0.237894
16	1	0	-3.330088	-0.747506	-0.459121
17	1	0	-1.298474	-2.017134	0.119382
18	1	0	-1.678959	-0.892899	1.429560
19	1	0	0.738462	-2.096888	-0.461507
20	1	0	-0.722189	1.245853	1.386417
21	1	0	1.026240	1.067289	1.436328

$Et_2NCH{=}CH_3$: E(opt)= -291.219117936 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.020874	-0.262683	0.545426
2	6	0	0.769293	-1.251005	-0.011590
3	6	0	0.522135	1.073402	0.742125
4	6	0	-1.462948	-0.467783	0.595196
5	6	0	2.062361	-1.182949	-0.380515
6	1	0	2.560272	-2.076268	-0.736666
7	1	0	2.653205	-0.276259	-0.325409
8	6	0	0.642586	1.928425	-0.530315
9	1	0	1.173414	2.862097	-0.313840
10	1	0	-0.341384	2.185825	-0.932161
11	1	0	1.194468	1.390435	-1.305317
12	6	0	-2.206190	-0.228655	-0.727864
13	1	0	-1.785043	-0.855719	-1.520270
14	1	0	-2.130147	0.814047	-1.048222
15	1	0	-3.268900	-0.474921	-0.622738
16	1	0	-1.647299	-1.497478	0.928282
17	1	0	-1.871037	0.185565	1.375428
18	1	0	0.241652	-2.197926	-0.119497
19	1	0	-0.108505	1.587209	1.477035
20	1	0	1.511996	0.963562	1.203180

---

(2) References

1. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

2. G. W. T. M. J. Frisch, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox,Gaussian, Inc., and Wallingford CT, *Gaussian 09, Revision D.01,*, 2013
3. D. Andrae, U. H/iuBermann, H. S. M. Dolg and H. PreuB, *Theor. Chim. Acta*, 1990, **77**, 123.
4. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378.
5. R.-Z. Liao, M. Wang, L. Sun and P. E. M. Siegbahn, *Dalton Trans.*, 2015, **44**, 9736.
6. K. Ye, Y.-Y. Li and R.-Z. Liao, *RSC Adv.*, 2016, **6**, 90035.
7. J. K. Nganga, C. R. Samanamu, J. M. Tanski, C. Pacheco, C. Saucedo, V. S. Batista, K. A. Grice, M. Z. Ertem and A. M. Angeles-Boza, *Inorg Chem*, 2017, **56**, 3214.
8. G. J. Tawa, I. A. Topol, S. K. Burt, R. A. Caldwell and A. A. Rashin, *The Journal of Chemical Physics*, 1998, **109**, 4852.
9. R.-Z. Liao and P. E. M. Siegbahn, *Journal of Catalysis*, 2017, **354**, 169.
10. L. B. Flamigni, A.; Sabatini, C.; Ventura, B.; Barigelletti, F. , *Top. Curr. Chem.* , 2007, **281**.
11. H.-W. Shih, M. N. V. Wal, R. L. Grange and D. W. C. MacMillan, *J. AM. CHEM. SOC.*, 2010, **132**, 13600.
12. J. J. Devery Iii, J. J. Douglas, J. D. Nguyen, K. P. Cole, R. A. Flowers Ii and C. R. J. Stephenson, *Chem Sci*, 2015, **6**, 537.