Mechanistic insights into β-oxygen atom transfer in olefin epoxidation mediated by W(VI) complexes and H_2O_2

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Supporting Information

Index:

1a.ESI Computational details.

Calculations were carried out using Gaussian 09[R0] package at the DFT level by means of the hybrid density functional B3PW91.[R1,R2] For the W,[R3,R4] and Cl[R5] atoms, the Stuttgart-Dresden pseudopotentials were used in combination with their associated basis sets augmented by a set of polarization functions (f-orbital polarization exponents of 0.823 for W,[R6] whereas a d-orbital polarization exponent of 0.643 for Cl[R7]). For the C, O and H atoms the all electron 6-311G(d,p)[R8] basis sets were used. The nature of the optimized stationary point, minima or transition state, has been verified by means of analytical frequency calculation at 298.15 K and 1 atm. The geometry optimizations have been achieved without any geometrical constraints. IRC calculations were carried out in order to confirm the connectivity between reactant(s), transition state and product(s). The energy data presented correspond to the free enthalpy of the computed compounds in gas phase. Compound **1**, **1_0$_2$**, **ts45a**, **ts45b**, **ts45e** and **ts45f** have been also optimised in water and acetonitrile by means of the PCM model implemented by default in Gaussian 09. The data presented in parenthesis and in brackets in Fig. 2, Fig.5, Fig. S3 and Fig. S8 therefore correspond to the free enthalpy of the computed compund in water and acetonitrile respectively.

The homolitic bond dissociation energies (BDE) have been computed for complexes 3 and 3_O2 without coordinated water and for complex 3_Cl.

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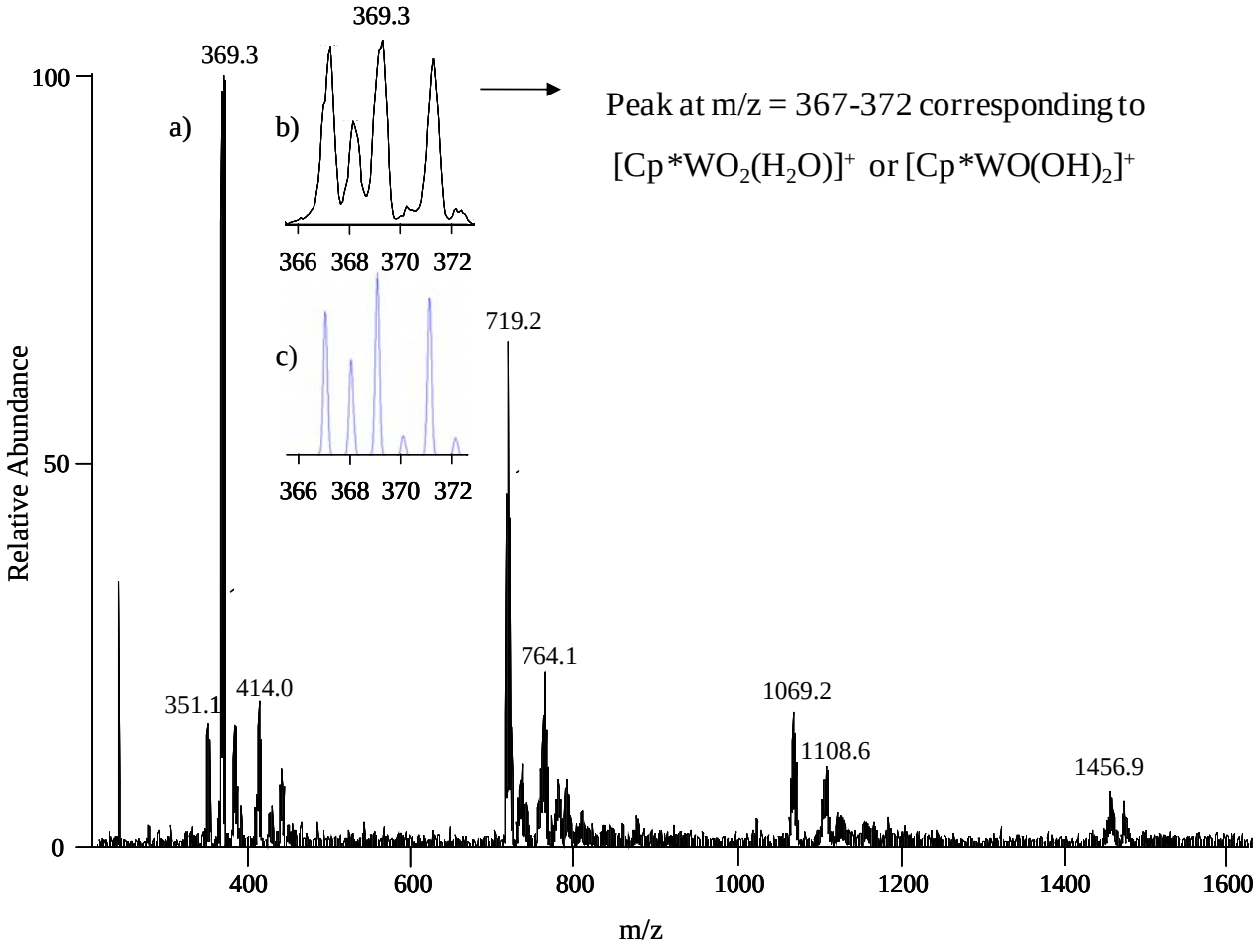
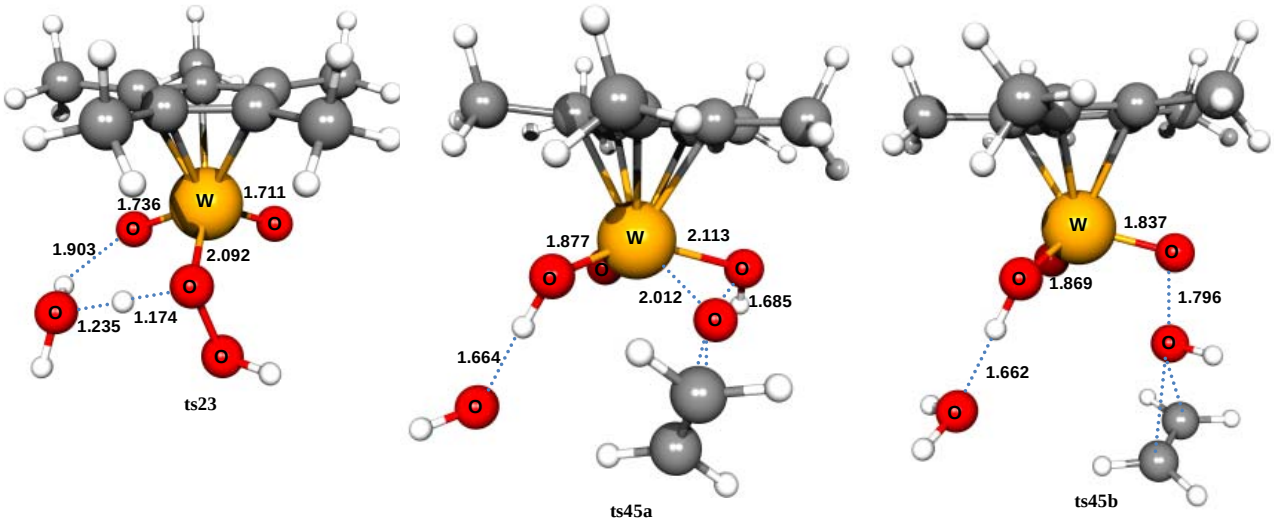
[R8] P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213.

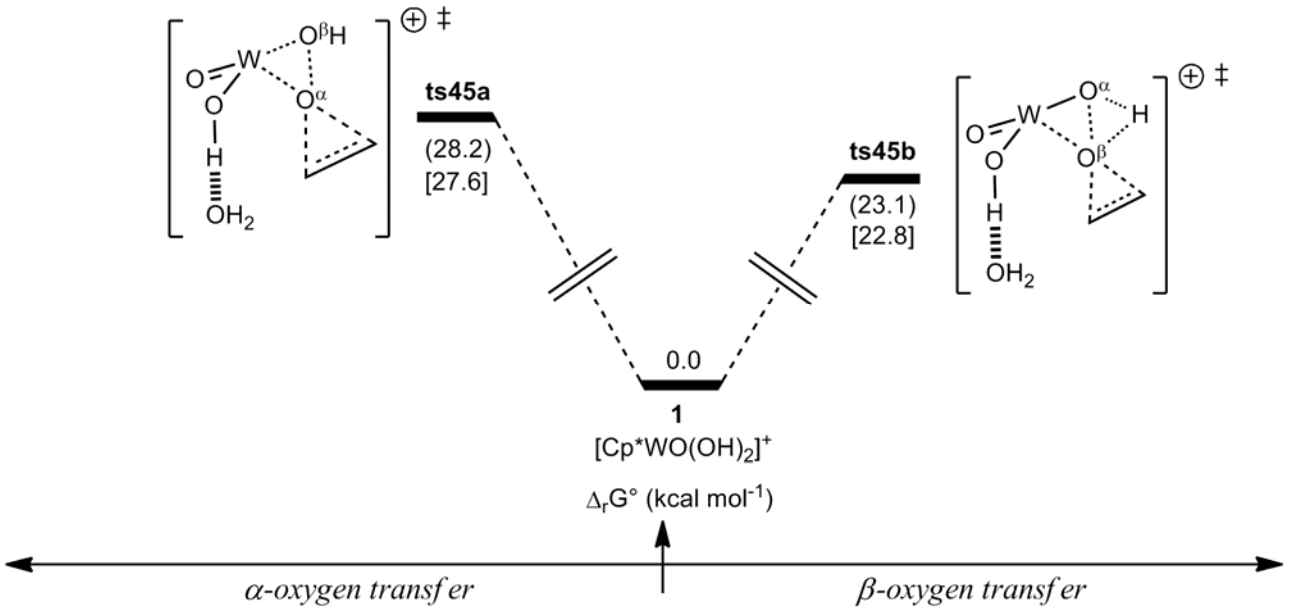
1b.Figure S1. ESI/MS spectrum of a solution of $[Cp^*_2W_2O_5]$ (0.1 mM) in H_2O/MeOH (1:1) at pH = 4; heated capillary temperature = 100 °C; (a) full spectrum in positive mode; (b) expansion of the main peaks: (c) simulation of the product ions.



2.Figure S2. Optimised geometries of the transition states computed in the Figure 1 and 2 of the text.



3.Figure S3. Free Enthalpy profile (kcal mol^{-1}) for the oxygen atom transfer from **1** to ethylene in water (values in parenthesis) and acetonitrile (values in brackets).



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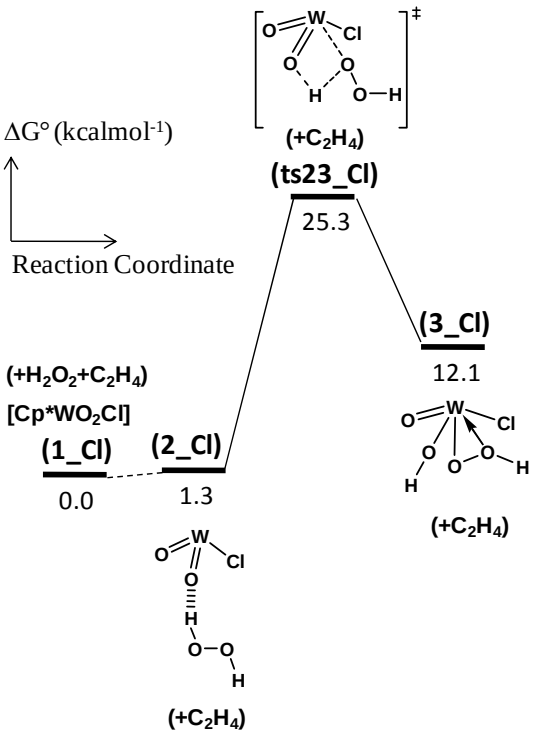
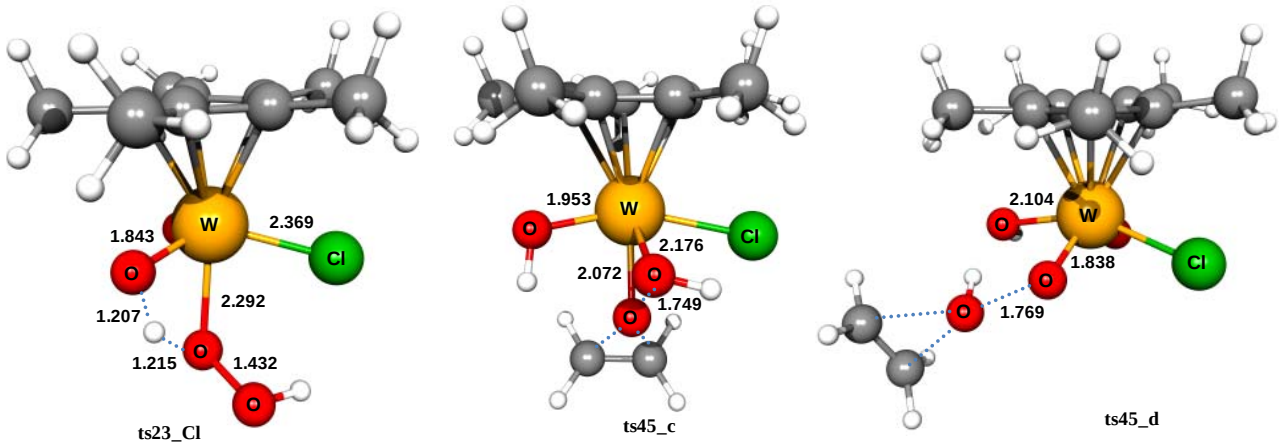
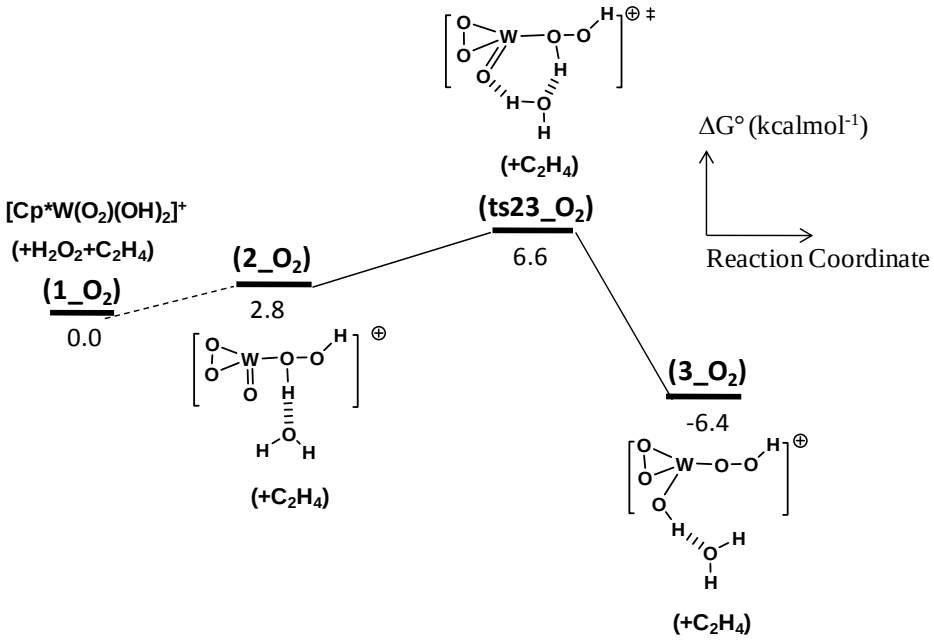
4.Figure S4. Free enthalpy profile in gas phase for the H_2O_2 activation by the neutral Cp^*WO_2Cl complex. Cp* omitted for clarity.



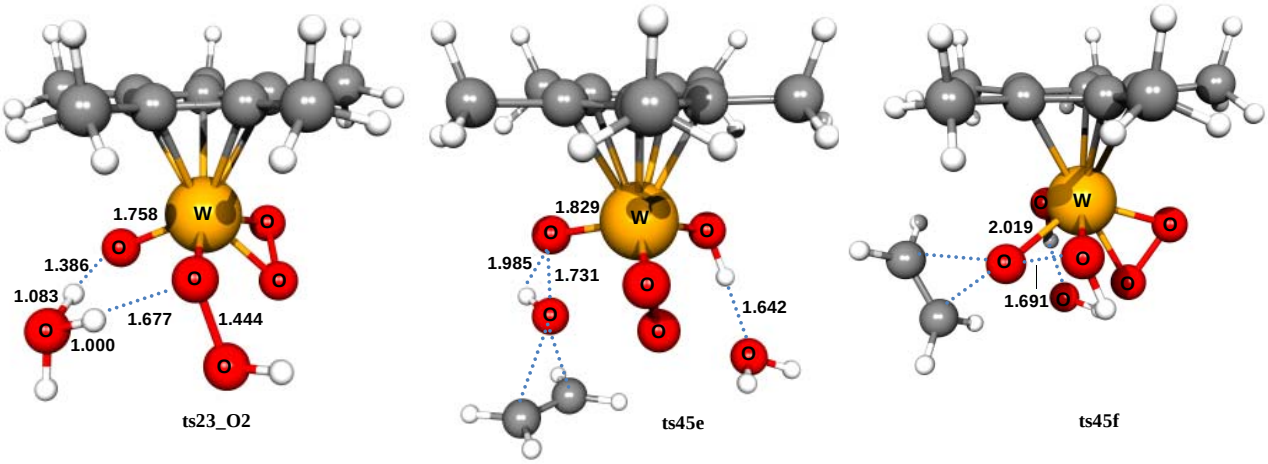
5.Figure S5. Optimised geometries of the transition states computed in the Figure S4 and 3 of the text.



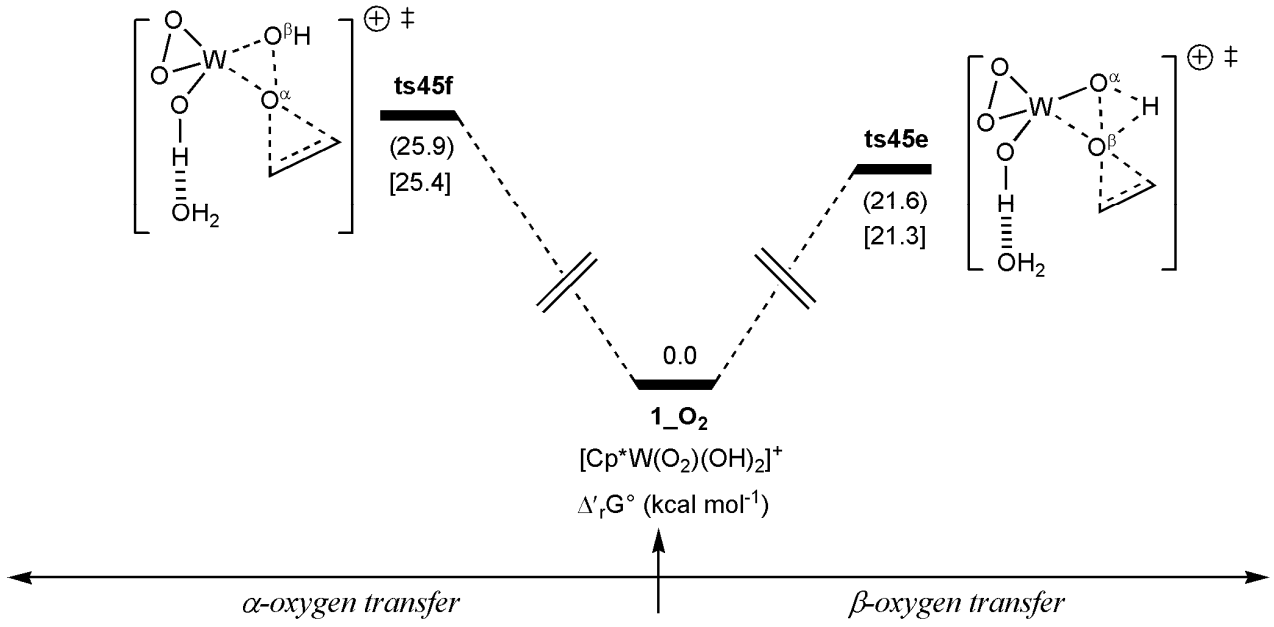
6.Figure S6. Free Enthalpy profile in gas phase for the H_2O_2 activation process with the cationic $[Cp^*W(O_2)(OH)_2]^+$ complex. Cp* omitted for clarity.



7.Figure S7. Optimised geometries of the transition states computed in the Figure S6 and 5 of the text.



8.Figure S8. Free Enthalpy profile (kcal mol^{-1}) for the oxygen atom transfer from **3_O₂** to ethylene in water (values in parenthesis) and acetonitrile (values in brackets).



9. Cartesian coordinates of all the computed compounds

A1) $[Cp^*WO(OH)_2]^+$ system

$Cp^*WO_2(H_2O)^+$

E= -683.966404 G= -683.759556

W	0.035923	-0.083002	0.990122
O	-0.483641	-1.540538	1.722552
C	-0.416648	-1.133416	-1.164006
C	-1.368468	-0.102369	-0.817761
C	0.835995	-0.507292	-1.324000
C	-0.703493	1.185210	-0.939658
C	0.654899	0.934359	-1.199454
O	-0.511243	1.216442	1.962661
O	2.140017	-0.075399	1.395468
H	2.816260	-0.496217	0.848350
H	2.456679	-0.002182	2.307080
C	-2.843689	-0.306097	-0.657855
H	-3.298717	0.468049	-0.038799
H	-3.318713	-0.265039	-1.644468
H	-3.072058	-1.276650	-0.216080
C	-1.377130	2.508194	-0.799809
H	-0.658068	3.322086	-0.710610
H	-1.995170	2.700881	-1.682814
H	-2.025741	2.539725	0.078045
C	1.722204	1.959150	-1.416876
H	1.812994	2.176922	-2.486567
H	1.497719	2.897119	-0.908077
H	2.704212	1.621512	-1.078257
C	2.118510	-1.177583	-1.708213
H	3.001352	-0.622686	-1.373126
H	2.181661	-2.203881	-1.341146
H	2.200595	-1.221458	-2.799652
C	-0.737042	-2.585918	-1.273027
H	0.160282	-3.192187	-1.399088
H	-1.265572	-2.946267	-0.386728
H	-1.379954	-2.759179	-2.141827

1

E= -684.000769 G= -683.793695

W	-0.768195	-0.178469	-0.329630
O	-1.115666	-1.718132	-0.947930
C	1.004950	-1.149691	0.838091
C	1.570085	-0.200296	-0.074359
C	0.243396	-0.411569	1.802760
C	1.214513	1.123685	0.379484
C	0.406998	0.993035	1.532146
O	-0.734113	0.915749	-1.834242
O	-2.277355	0.341866	0.676357
C	2.493426	-0.525075	-1.205170
H	2.454990	0.219787	-2.000751
H	3.522138	-0.552584	-0.828614
H	2.277316	-1.500181	-1.643207
C	1.672959	2.398519	-0.246512
H	0.964465	3.214525	-0.093977
H	2.623775	2.705576	0.202255
H	1.860978	2.288788	-1.317450
C	-0.204544	2.083250	2.344104
H	0.246900	2.100912	3.341195
H	-0.052598	3.064088	1.893688
H	-1.278749	1.924862	2.470687
H	-1.278749	1.924862	2.470687
C	-0.487077	-0.974838	2.976039
H	-1.385295	-0.398523	3.201391
H	-0.772778	-2.015820	2.822126
H	0.165228	-0.937579	3.855494
C	1.241071	-2.623597	0.830539
H	0.424237	-3.169968	1.302214
H	1.360185	-3.011991	-0.181291
H	2.158096	-2.841827	1.387971
H	-0.288974	1.725328	-2.103098
H	-3.157620	-0.000190	0.473381

2

E= -835.530017 G= -835.299908

W	-0.219834	-0.325703	-0.692041
O	0.260528	-1.687195	-1.610716
C	1.962123	-0.466794	0.362940
C	1.760516	0.771025	-0.366422
C	1.050298	-0.472618	1.433284
C	0.834007	1.590861	0.385830
C	0.353429	0.809357	1.452644
O	-1.059670	0.790572	-1.707302
O	-1.902777	-0.858019	0.489686
C	2.586707	1.239601	-1.525189
H	2.046705	1.956989	-2.144435
H	3.486383	1.736428	-1.145046
H	2.907200	0.412044	-2.159301
C	0.471447	2.996328	0.042577
H	-0.378160	3.349927	0.627147
H	1.317354	3.658821	0.252631
H	0.222357	3.099950	-1.016295
C	-0.590123	1.238721	2.529789
H	-0.017316	1.579475	3.399150
H	-1.230584	2.063166	2.215019
H	-1.226477	0.419179	2.870111
C	0.876325	-1.545099	2.459610
H	-0.167647	-1.655405	2.761173
H	1.234095	-2.512158	2.104656
H	1.445245	-1.292456	3.360965
C	2.942428	-1.526329	-0.011734
H	2.805499	-2.430404	0.581206
H	2.854572	-1.802581	-1.065054
H	3.960894	-1.163997	0.160612
O	-2.632206	-1.875387	-0.237923
H	-2.583858	-2.615980	0.387262
H	-3.030701	1.400151	-0.791269
O	-3.336992	1.076317	0.070216
H	-4.297677	1.002561	0.041021
H	-2.595551	-0.028863	0.403772

ts23

E= -835.529222 G= -835.298900

W	-0.243812	-0.330464	-0.662223
O	0.222597	-1.682741	-1.600831
C	1.950015	-0.465887	0.359151
C	1.739444	0.771077	-0.366364
C	1.049791	-0.471557	1.439802
C	0.822718	1.592353	0.398213
C	0.358871	0.813490	1.473166
O	-1.149119	0.787474	-1.634549
O	-1.879095	-0.826582	0.545372
C	2.547163	1.237766	-1.538814
H	1.998474	1.953854	-2.152015
H	3.451897	1.736386	-1.172092
H	2.859676	0.408979	-2.175321
C	0.459462	2.998775	0.058116
H	-0.375061	3.359146	0.659954
H	1.313148	3.657835	0.246998
H	0.187660	3.100674	-0.995090
C	-0.573367	1.235575	2.562316
H	0.005775	1.506253	3.451566
H	-1.169086	2.105674	2.282168
H	-1.252818	0.433069	2.857196
C	0.883159	-1.543408	2.467287
H	-0.160468	-1.657101	2.770347
H	1.244058	-2.510126	2.112978
H	1.452570	-1.287377	3.367076
C	2.924754	-1.526445	-0.026433
H	2.777082	-2.439394	0.549894
H	2.845054	-1.784303	-1.084796
H	3.944030	-1.174224	0.161806
O	-2.634545	-1.810920	-0.207975
H	-2.555700	-2.587615	0.368597
H	-2.788999	1.321395	-0.828282
O	-3.261105	1.048561	-0.012207
H	-4.180756	0.853937	-0.232400
H	-2.608196	0.079441	0.387015

3

E= -835.566251 G= -835.338674

W	-0.473623	-0.358102	-0.079571
O	-0.171211	-1.453172	-1.347728
C	1.848311	-0.408623	0.328263
C	1.449162	0.893292	-0.138431
C	1.253709	-0.597489	1.604909
C	0.721639	1.551532	0.927114
C	0.573664	0.628645	1.978913
O	-1.570097	0.993877	-0.690416
O	-1.346408	-1.376656	1.306987
C	1.905757	1.549450	-1.403391
H	1.190096	2.294630	-1.753361
H	2.856654	2.061541	-1.218437
H	2.070976	0.825575	-2.202513
C	0.213582	2.949936	0.860020
H	-0.284884	3.240605	1.784221
H	1.044411	3.641557	0.692683
H	-0.498684	3.070244	0.038695
C	-0.117793	0.846043	3.282946
H	0.624792	1.036083	4.065599
H	-0.793143	1.700822	3.248730
H	-0.695923	-0.029774	3.582540
C	1.411658	-1.783416	2.497219
H	0.491084	-2.010259	3.036804
H	1.713798	-2.673431	1.945172
H	2.188891	-1.572279	3.239810
C	2.746020	-1.353047	-0.398590
H	2.649054	-2.373093	-0.026895
H	2.536032	-1.367191	-1.469160
H	3.786758	-1.042012	-0.260216
O	-2.505475	-1.644252	0.480563
H	-2.421880	-2.597971	0.311913
H	-2.140517	1.040143	-1.521362
O	-3.017448	1.187056	-2.801665
H	-2.961221	0.594851	-3.556811
H	-3.935097	1.465453	-2.730361

4b

E= -914.152704 G= -913.880185

W	0.422719	0.220611	0.065952
O	1.981171	0.757073	-0.354773
C	-0.174622	2.501201	0.006006
C	-0.817567	1.803594	-1.069598
C	-0.721476	1.998649	1.221994
C	-1.859508	0.969860	-0.508117
C	-1.783858	1.070841	0.893635
O	-0.071989	-1.145720	-1.101145
O	0.481801	-0.380437	1.896000
C	-0.612620	2.056571	-2.529674
H	-0.851279	1.176457	-3.128311
H	-1.274547	2.868014	-2.851737
H	0.411825	2.358325	-2.751539
C	-2.809988	0.156364	-1.314940
H	-3.509297	-0.390760	-0.683175
H	-3.391213	0.807524	-1.974619
H	-2.274802	-0.566096	-1.937753
C	-2.655624	0.392363	1.897397
H	-3.426555	1.088447	2.245536

H	-3.160251	-0.478084	1.477611
H	-2.087608	0.069071	2.771356
C	-0.381340	2.450966	2.603578
H	-0.422926	1.630939	3.321578
H	0.612337	2.896096	2.655114
H	-1.104681	3.210422	2.920293
C	0.859445	3.565778	-0.141982
H	1.450862	3.687193	0.765483
H	1.546617	3.346774	-0.960340
H	0.367771	4.520645	-0.355527
O	1.453999	-1.370753	1.471571
H	0.977855	-2.226848	1.618321
H	0.617816	-1.679650	-1.594601
C	0.412288	-4.038549	2.773678
H	1.397459	-4.279136	3.162081
H	-0.308731	-3.648825	3.486150
C	0.092908	-4.247398	1.496574
H	-0.904073	-4.043161	1.117052
H	0.803613	-4.673477	0.794351
H	2.668127	-2.171517	-2.408119
O	1.776528	-2.522311	-2.324585
H	1.612208	-3.051039	-3.110528

ts45b

E= -914.127930 G= -913.853788

W	-0.040854	-0.002998	0.166329
O	1.665688	-0.013491	0.142447
C	-0.027907	2.328999	0.046490
C	-0.747816	1.854561	-1.105035
C	-0.822738	2.026920	1.194885
C	-2.004894	1.317442	-0.660822
C	-2.049733	1.419230	0.748675
O	-0.580473	-1.152652	-1.204983
O	-0.553661	-0.729813	1.773592
C	-0.337274	2.017166	-2.532567
H	-0.732182	1.214262	-3.156511
H	-0.733054	2.963820	-2.918025
H	0.747216	2.045171	-2.649016
C	-3.036342	0.737762	-1.567790
H	-3.892224	0.353986	-1.012950
H	-3.401154	1.499031	-2.263791
H	-2.616090	-0.084580	-2.154375
C	-3.152494	0.995878	1.658460
H	-3.654879	1.876571	2.071806
H	-3.900582	0.395969	1.140473
H	-2.765517	0.409427	2.495158
C	-0.509284	2.379752	2.611677
H	-0.840966	1.600465	3.299256
H	0.558434	2.538837	2.766026
H	-1.025262	3.308376	2.879479
C	1.249455	3.104267	0.028299
H	1.830521	2.950131	0.937966
H	1.879809	2.827070	-0.817053
H	1.024720	4.172926	-0.053246
O	0.468573	-2.203744	1.868931
H	-0.285547	-2.641861	2.294823
H	0.030524	-1.844493	-1.573979
C	1.944161	-3.519074	2.553193
H	2.767671	-2.868373	2.287089
H	1.720758	-3.618259	3.609851
C	1.318452	-4.282400	1.619929
H	0.544671	-4.991845	1.897502
H	1.584032	-4.224160	0.571161
H	1.923000	-2.732609	-2.475945
O	1.061178	-3.012338	-2.152704
H	0.716199	-3.624319	-2.809940

5b

E= -914.246959 G= -913.970835

W	0.046592	-0.009474	-0.150481
O	1.744460	0.075239	-0.162170
C	-0.046016	2.320040	0.028138
C	-0.819435	1.979496	-1.130101
C	-0.744422	1.804583	1.169070
C	-2.014710	1.312715	-0.694494
C	-1.970308	1.208002	0.715968
O	-0.405066	-0.870149	-1.733695
O	-0.393800	-1.143133	1.252793
C	-0.512613	2.352140	-2.544310
H	-0.855133	1.585509	-3.241025
H	-1.026284	3.286667	-2.795645
H	0.554742	2.510941	-2.704694
C	-3.077187	0.814795	-1.614130
H	-3.843140	0.250582	-1.082584
H	-3.565860	1.655535	-2.116292
H	-2.651105	0.165914	-2.384572
C	-2.972722	0.571387	1.616642
H	-3.379016	1.310606	2.313527
H	-3.805209	0.143316	1.058734
H	-2.510416	-0.227504	2.204098
C	-0.348364	1.968390	2.600899
H	-0.673501	1.119547	3.204151
H	0.730031	2.082966	2.720169
H	-0.821776	2.868546	3.008629
C	1.193959	3.153527	0.052171
H	1.837783	2.898824	0.894591
H	1.780484	3.035434	-0.859515
H	0.919990	4.209792	0.143017
O	1.149390	-3.076926	1.956258
H	0.204752	-1.894892	1.564196
H	0.229211	-1.464725	-2.231889
C	1.621904	-3.358178	3.287371
H	2.682984	-3.578339	3.338246
H	1.230026	-2.703028	4.059627
C	0.718141	-4.286134	2.610240
H	-0.331545	-4.305491	2.887491
H	1.112781	-5.191582	2.161520
H	2.131032	-2.171855	-3.233208
O	1.246037	-2.445145	-2.976511
H	0.941734	-3.067405	-3.642869

6

E= -760.450286 G= -760.224755

W	-0.066488	-0.533750	-0.810797
O	-0.061013	-2.222104	-0.627901
C	-0.031818	-0.341333	1.521080
C	1.122719	0.348707	1.008290
C	-1.182384	0.393774	1.103550
C	0.674981	1.542274	0.342879
C	-0.739167	1.563446	0.390845
O	1.339440	-0.173077	-1.942567
O	-1.666123	-0.113928	-1.734289
C	2.551122	-0.010890	1.265337
H	3.201039	0.311289	0.450775
H	2.888128	0.492542	2.178461
H	2.688168	-1.082994	1.414042
C	1.580674	2.539730	-0.295615
H	1.024706	3.301998	-0.840623
H	2.181284	3.043175	0.468335
H	2.266906	2.056046	-0.995971
C	-1.654840	2.589685	-0.181939
H	-2.166010	3.124877	0.624568
H	-1.120486	3.322865	-0.785365
H	-2.419154	2.123774	-0.809464
C	-2.605233	0.079254	1.429392
H	-3.274786	0.372546	0.619665
H	-2.755634	-0.981493	1.634181
H	-2.903388	0.633872	2.326056
C	-0.016066	-1.542349	2.408739
H	-0.927177	-2.132906	2.309268
H	0.829234	-2.196689	2.193159
H	0.064030	-1.219434	3.451969
H	-2.051235	-0.737524	-2.361875
H	1.964119	-0.802227	-2.427122
H	2.895066	-2.702037	-3.112330
O	2.967175	-1.743592	-3.139157
H	3.330623	-1.512079	-3.998916

3a

E= -835.555505 G= -835.325276

W	0.535490	-0.112826	-0.615570
O	0.887016	1.154288	-1.700048
C	-1.009037	1.290792	0.498920
C	-1.686531	0.055238	0.244068
C	0.048879	1.012056	1.416638
C	-1.089845	-0.967868	1.063720
C	-0.009307	-0.390922	1.767901
O	-0.276428	-1.396918	-1.679092
O	2.153640	-1.203463	-0.333509
C	-2.892892	-0.142901	-0.609826
H	-2.831500	-1.080046	-1.165623
H	-3.783941	-0.185674	0.025521
H	-3.030676	0.672180	-1.320630
C	-1.549364	-2.385131	1.104762
H	-0.839500	-3.030579	1.621735
H	-2.505926	-2.448790	1.634275
H	-1.702192	-2.777928	0.096759
C	0.877092	-1.065510	2.762412
H	0.496327	-0.885638	3.773496
H	0.915126	-2.143795	2.607214
H	1.898505	-0.684488	2.722329
C	0.957801	2.024105	2.033112
H	1.917259	1.592764	2.319771
H	1.138903	2.871215	1.370104
H	0.487559	2.413860	2.943076
C	-1.380924	2.636525	-0.032198
H	-0.504935	3.262868	-0.204979
H	-1.926959	2.563779	-0.972972
H	-2.025114	3.147598	0.690867
O	2.580643	0.067778	0.243256
H	3.224483	0.408255	-0.403873
H	-0.001538	-1.546105	-2.636751
H	0.669976	-2.659344	-4.448703
O	0.498416	-1.774055	-4.115120
H	0.174862	-1.253409	-4.855826

4a

E= -914.143235 G= -913.870566

W	0.185890	-0.566927	-0.259386
O	0.328519	-1.120421	-1.866066
C	2.442439	0.142183	-0.326932
C	1.671940	1.250094	0.153404
C	2.361967	-0.888412	0.657570
C	1.177863	0.924045	1.465639
C	1.576873	-0.397848	1.768393
O	-1.045602	0.802870	-0.375084
O	-1.036089	-1.750646	0.737521
C	1.508363	2.576237	-0.510043
H	0.497603	2.963624	-0.371667
H	2.208310	3.293489	-0.068293
H	1.714850	2.526370	-1.579503
C	0.362756	1.844027	2.308797
H	-0.064701	1.335153	3.172548
H	0.990494	2.661439	2.678985
H	-0.452406	2.287073	1.731530
C	1.315818	-1.148871	3.032587
H	2.189106	-1.078244	3.689705
H	0.458240	-0.747646	3.572431
H	1.128079	-2.207356	2.845373
C	3.088394	-2.192419	0.614889
H	2.590028	-2.957225	1.210622
H	3.205211	-2.564307	-0.404223
H	4.092904	-2.053128	1.030391
C	3.246936	0.095804	-1.584739
H	3.281803	-0.908878	-2.007672
H	2.845382	0.762468	-2.348379
H	4.274419	0.409136	-1.372180
O	0.047479	-2.684305	0.443072

H	-0.336103	-3.271806	-0.232411
H	-1.815694	0.798478	-1.049007
C	-5.710105	2.285581	-1.272120
H	-5.423345	2.576387	-0.265659
H	-5.663466	3.058561	-2.033812
C	-6.147030	1.057889	-1.547107
H	-6.471727	0.777819	-2.544973
H	-6.231128	0.296302	-0.777450
H	-2.805428	0.945450	-2.964294
O	-2.950267	0.722170	-2.040863
H	-3.849453	1.019787	-1.812815

ts45a
E= -914.125724 G= -913.846773

W	-0.203401	-0.218373	-0.621425
O	0.196986	-0.794519	-2.175019
C	2.127779	0.112561	-0.250281
C	1.475010	1.342505	0.069504
C	1.680329	-0.861759	0.690306
C	0.682869	1.140958	1.257794
C	0.791044	-0.214663	1.631156
O	-1.050664	1.403319	-1.040714
O	-1.937070	-1.006196	0.027317
C	1.671436	2.659151	-0.601015
H	0.722554	3.186630	-0.712052
H	2.337573	3.281932	0.005427
H	2.122555	2.552068	-1.587701
C	-0.097323	2.214901	1.936501
H	-0.795082	1.812302	2.670864
H	0.585049	2.890296	2.463661
H	-0.657367	2.812570	1.213746
C	0.175052	-0.884297	2.814679
H	0.934283	-1.035314	3.589362
H	-0.626459	-0.285687	3.247044
H	-0.233940	-1.862870	2.555975
C	2.173443	-2.265681	0.801199
H	1.410161	-2.933115	1.202519
H	2.512208	-2.658665	-0.158304
H	3.028017	-2.288925	1.487095
C	3.131877	-0.110389	-1.332622
H	3.036507	-1.103405	-1.774002
H	3.028972	0.619159	-2.135969
H	4.142090	-0.017712	-0.920706
O	-0.712277	-2.163520	0.030010
H	-1.024344	-2.722492	-0.698164
H	-1.579043	1.474208	-1.878678
C	-3.590785	0.547601	0.688842
H	-3.803966	0.060123	1.633348
H	-3.106138	1.516557	0.723482
C	-3.956839	-0.008825	-0.480319
H	-3.787511	0.489364	-1.428693
H	-4.479980	-0.957821	-0.508335
H	-2.129693	1.109574	-4.075064
O	-2.440525	1.583381	-3.297676
H	-2.753811	2.437495	-3.609909

5a
E= -914.246895 G= -913.971518

W	-0.101806	0.562404	-0.468174
O	-0.102746	0.155453	-2.118667
C	2.173769	0.027922	-0.364361
C	2.064156	1.366820	0.133005
C	1.511157	-0.828039	0.576618
C	1.392066	1.323953	1.401845
C	1.057168	-0.022988	1.676862
O	-0.640942	2.340644	-0.409465
O	-3.515308	-1.269245	-0.975313
C	2.646504	2.596617	-0.483926
H	2.005672	3.464548	-0.320870
H	3.619549	2.808205	-0.027069
H	2.805611	2.482459	-1.557012
C	1.101276	2.527487	2.232194
H	0.511191	2.280971	3.114604
H	2.034990	2.987913	2.569539
H	0.550734	3.273720	1.652310
C	0.335931	-0.561108	2.864684
H	0.975286	-1.262471	3.409143
H	0.042131	0.229900	3.554337
H	-0.567372	-1.096315	2.557607
C	1.423500	-2.318915	0.505869
H	0.515555	-2.689544	0.983632
H	1.444597	-2.682868	-0.522343
H	2.279499	-2.759647	1.029007
C	2.931514	-0.411827	-1.574361
H	2.497139	-1.306512	-2.021748
H	2.957128	0.362457	-2.341746
H	3.964308	-0.641859	-1.292466
O	-1.443319	-0.459379	0.305339
H	-2.257709	-0.802423	-0.185962
H	-1.181600	2.760949	-1.140431
C	-4.821305	-1.427793	-0.387341
H	-4.863360	-1.254828	0.683841
H	-5.622110	-0.992763	-0.975856
C	-4.092242	-2.586904	-0.898470
H	-4.354525	-3.006988	-1.863657
H	-3.605093	-3.259049	-0.198441
H	-1.825713	3.351867	-3.228619
O	-2.089334	3.378935	-2.304670
H	-2.573895	4.199213	-2.177252

A2) $[Cp^*WO(OH)_2]^+$ system in water

1_water
E= -684.077865 G= -683.869492

W	-0.796282	-0.183023	-0.326671
O	-1.161882	-1.757276	-0.866210
C	0.989938	-1.142681	0.824235
C	1.554842	-0.187912	-0.082582
C	0.238187	-0.411443	1.798778
C	1.205633	1.130283	0.382074
C	0.400053	0.992094	1.534124
O	-0.659999	0.787077	-1.923555
O	-2.273569	0.407838	0.703017
C	2.481598	-0.503833	-1.211147
H	2.449684	0.252071	-1.995565
H	3.505358	-0.538665	-0.823144
H	2.262366	-1.473018	-1.659642
C	1.660482	2.411748	-0.230197
H	0.936085	3.214785	-0.088959
H	2.598355	2.721794	0.242466
H	1.868744	2.311136	-1.297320
C	-0.201250	2.077993	2.355482
H	0.295794	2.117627	3.330052
H	-0.094903	3.052760	1.880505
H	-1.263166	1.890494	2.531675
C	-0.481124	-0.982982	2.973377
H	-1.371361	-0.401620	3.215460
H	-0.776398	-2.018952	2.806679
H	0.185564	-0.958497	3.842048
C	1.233313	-2.613905	0.814000
H	0.410168	-3.162602	1.271606
H	1.375487	-2.993482	-0.198043
H	2.142181	-2.825994	1.386179
H	-0.177920	1.595214	-2.132421
H	-3.153240	0.082612	0.467391

ts45a_water
E= -914.191042 G= -913.911935

W	-0.192967	-0.226828	-0.668281
O	0.247150	-0.773068	-2.227963
C	2.127364	0.091317	-0.247978
C	1.476331	1.329466	0.041895
C	1.663536	-0.864608	0.702089
C	0.667168	1.150891	1.220501
C	0.758663	-0.200178	1.612627
O	-1.051901	1.393098	-1.057906
O	-1.922342	-1.040138	0.005343
C	1.694698	2.633767	-0.645254
H	0.754603	3.175173	-0.762359
H	2.369958	3.250892	-0.043271
H	2.144454	2.504148	-1.629763
C	-0.119327	2.238500	1.866454
H	-0.800739	1.854115	2.624976
H	0.562090	2.944642	2.352435
H	-0.697993	2.795369	1.125640
C	0.114480	-0.851012	2.790826
H	0.853657	-0.979451	3.588462
H	-0.706213	-0.252249	3.184942
H	-0.273107	-1.839618	2.537383
C	2.152479	-2.265107	0.851507
H	1.371405	-2.927030	1.226017
H	2.532097	-2.668527	-0.087600
H	2.974606	-2.272993	1.575954
C	3.157108	-0.142892	-1.302220
H	3.130372	-1.169163	-1.669963
H	3.020958	0.524716	-2.153297
H	4.152159	0.040723	-0.884246
O	-0.657246	-2.183139	-0.043000
H	-0.970307	-2.736494	-0.775750
H	-1.624921	1.480293	-1.873592
C	-3.525125	0.466976	0.718329
H	-3.737479	-0.036722	1.654311
H	-3.024938	1.426666	0.770636
C	-3.900886	-0.061206	-0.463363
H	-3.727270	0.457490	-1.399645
H	-4.435180	-1.003218	-0.510174
H	-2.244295	1.289990	-3.988397
O	-2.571912	1.687161	-3.174614
H	-2.741614	2.610673	-3.388509

ts45b_water
E= -914.194294 G= -913.920157

W	-0.007871	-0.036171	0.195834
O	1.702081	-0.003338	0.299898
C	-0.009631	2.303920	-0.004667
C	-0.760140	1.795233	-1.123292
C	-0.768033	2.035449	1.171439
C	-1.995627	1.260908	-0.630126
C	-2.000709	1.403364	0.777772
O	-0.472385	-1.227213	-1.151879
O	-0.581532	-0.747087	1.793208
C	-0.384521	1.916887	-2.563334
H	-0.815092	1.110826	-3.158597
H	-0.768923	2.865111	-2.955797
H	0.696792	1.913550	-2.706333
C	-3.049422	0.645611	-1.487014
H	-3.852569	0.213590	-0.890297
H	-3.485997	1.400014	-2.148518
H	-2.626980	-0.145216	-2.112807
C	-3.076431	1.005820	1.728777
H	-3.567106	1.899967	2.126759
H	-3.835077	0.387397	1.249522
H	-2.663361	0.448491	2.572903
C	-0.419757	2.436948	2.566689
H	-0.751204	1.690658	3.290208
H	0.653404	2.584646	2.691423
H	-0.917779	3.382327	2.807902
C	1.257895	3.089244	-0.081527
H	1.875759	2.944634	0.805255
H	1.850056	2.817330	-0.955774
H	1.017473	4.154792	-0.156581
O	0.436823	-2.211518	1.980590
H	-0.379917	-2.724245	2.097909
H	0.155133	-1.804668	-1.692432
C	1.621389	-3.708825	2.951464
H	2.437359	-3.058437	3.241121
H	0.967932	-4.065172	3.739997

C	1.487416	-4.141667	1.671888
H	0.709744	-4.844174	1.391876
H	2.179359	-3.831285	0.898663
H	1.686830	-2.252388	-3.126525
O	1.119469	-2.727577	-2.510175
H	0.659288	-3.386729	-3.040659

A3) $[Cp^*WO(OH)_2]^+$ system in acetonitrile

1_acetonitrile

E= -684.076442 G= -683.867724

W	-0.782511	-0.180587	-0.345702
O	-1.080935	-1.729994	-0.988726
C	0.985065	-1.146375	0.831926
C	1.554710	-0.199493	-0.078968
C	0.237463	-0.405754	1.804305
C	1.203378	1.122920	0.374802
C	0.402426	0.993835	1.531833
O	-0.679651	0.895937	-1.874732
O	-2.284945	0.304581	0.695977
C	2.483259	-0.520813	-1.204689
H	2.427882	0.215465	-2.006626
H	3.509731	-0.522608	-0.822539
H	2.283736	-1.505000	-1.628891
C	1.668299	2.396392	-0.245392
H	0.953905	3.208625	-0.104826
H	2.610275	2.699408	0.223653
H	1.875084	2.286731	-1.312182
C	-0.194007	2.087794	2.347148
H	0.315986	2.141997	3.314421
H	-0.096957	3.057248	1.859399
H	-1.252601	1.900009	2.541246
C	-0.487208	-0.966819	2.979590
H	-1.382861	-0.387715	3.206846
H	-0.774839	-2.006545	2.824083
H	0.172213	-0.926924	3.853259
C	1.220137	-2.619416	0.825767
H	0.416914	-3.158790	1.327621
H	1.311092	-3.010197	-0.188098
H	2.153946	-2.831961	1.355946
H	-0.232518	1.737569	-2.021130
H	-3.153724	-0.039881	0.448366

ts45b_acetonitrile

E= -914.193057 G= -913.918597

W	-0.004654	-0.030914	0.194456
O	1.705493	0.000656	0.291341
C	-0.010406	2.308676	0.000359
C	-0.756839	1.801544	-1.121661
C	-0.772120	2.036134	1.173742
C	-1.993361	1.264663	-0.633177
C	-2.002950	1.403991	0.774869
O	-0.471971	-1.217847	-1.156327
O	-0.575705	-0.743768	1.791723
C	-0.377171	1.926813	-2.560393
H	-0.805218	1.121526	-3.158507
H	-0.761320	2.875445	-2.952098
H	0.704571	1.924911	-2.700339
C	-3.043711	0.650288	-1.494858
H	-3.850900	0.220685	-0.901872
H	-3.475329	1.404514	-2.159790
H	-2.619216	-0.142328	-2.117070
C	-3.080571	1.002426	1.722084
H	-3.572137	1.894789	2.122962
H	-3.838293	0.386012	1.238823
H	-2.669059	0.441619	2.564687
C	-0.428211	2.434260	2.571003
H	-0.758030	1.684149	3.291295
H	0.644116	2.585738	2.698333
H	-0.930370	3.376888	2.814419
C	1.255693	3.097057	-0.070294
H	1.874383	2.946168	0.814865
H	1.848049	2.833898	-0.947028
H	1.013103	4.162723	-0.136190
O	0.440349	-2.210082	1.973247
H	-0.377012	-2.720446	2.095998
H	0.153392	-1.807887	-1.684877
C	1.629577	-3.705444	2.936456
H	2.451111	-3.055696	3.211365
H	0.984404	-4.053216	3.735573
C	1.480057	-4.149208	1.662368
H	0.696878	-4.851450	1.397214
H	2.163692	-3.847278	0.878488
H	1.696126	-2.295615	-3.100893
O	1.111073	-2.753327	-2.487936
H	0.646622	-3.410057	-3.017596

ts45a_acetonitrile

E= -914.189929 G= -913.910912

W	-0.192635	-0.227017	-0.668268
O	0.245996	-0.773548	-2.228143
C	2.127612	0.091637	-0.247881
C	1.476335	1.329736	0.041887
C	1.663708	-0.864373	0.702115
C	0.666958	1.150946	1.220370
C	0.758676	-0.200091	1.612599
O	-1.052356	1.392282	-1.058499
O	-1.921794	-1.040116	0.004518
C	1.694190	2.634263	-0.645066
H	0.753723	3.174927	-0.762641
H	2.368619	3.251969	-0.042748
H	2.144472	2.505137	-1.629402
C	-0.119457	2.238514	1.866470
H	-0.801004	1.854206	2.624898
H	0.562046	2.944341	2.352792
H	-0.697900	2.795849	1.125823
C	0.114014	-0.851094	2.790458
H	0.853274	-0.981556	3.587682
H	-0.705502	-0.251367	3.185517
H	-0.275420	-1.838776	2.536220
C	2.152907	-2.264808	0.851341
H	1.372045	-2.926943	1.225931
H	2.532562	-2.668004	-0.087864
H	2.975178	-2.272706	1.575629
C	3.157770	-0.142872	-1.301676
H	3.125752	-1.166917	-1.675221
H	3.027142	0.530138	-2.149266
H	4.153168	0.032615	-0.881041
O	-0.657304	-2.183202	-0.042698
H	-0.969876	-2.737023	-0.775284
H	-1.624001	1.479513	-1.874984
C	-3.524115	0.466789	0.720109
H	-3.734976	-0.038483	1.655566
H	-3.024068	1.426522	0.773030
C	-3.901970	-0.059372	-0.461750
H	-3.730060	0.460795	-1.397532
H	-4.436270	-1.001351	-0.509136
H	-2.242203	1.289726	-3.992424
O	-2.569498	1.684891	-3.177569
H	-2.746166	2.607246	-3.390680

b) Cp^*WO_2Cl system

1_Cl

E= -622.860200 G= -622.675894

W	0.104377	-0.680265	0.170905
C	0.169051	1.478270	1.496088
C	-0.298555	0.435765	2.318778
C	1.535224	1.182962	1.118238
C	0.741200	-0.562030	2.386869
C	1.903820	-0.040516	1.709848
O	-1.436798	-1.402599	0.407151
O	1.159366	-1.940728	-0.329357
Cl	-0.145471	0.678618	-1.705114
C	2.397811	2.096849	0.310621
H	2.697156	2.963261	0.910988
H	3.304853	1.599407	-0.034620
H	1.866899	2.469232	-0.568459
C	3.226037	-0.730288	1.644600
H	3.651406	-0.832137	2.648209
H	3.126680	-1.729429	1.210566
H	3.937979	-0.173423	1.034490
C	0.711086	-1.790641	3.244111
H	1.042473	-1.546939	4.260310
H	-0.295515	-2.206925	3.309843
H	1.370370	-2.567476	2.853324
C	-1.630078	0.317673	2.983149
H	-1.510678	0.274139	4.070455
H	-2.269311	1.170075	2.750946
H	-2.150653	-0.587627	2.657660
C	-0.550144	2.734241	1.126154
H	-0.165379	3.576805	1.711705
H	-0.411953	2.973138	0.069280
H	-1.622155	2.658729	1.312047

2_Cl

E= -774.407329 G= -774.201423

W	0.246143	-0.181023	-0.989657
O	-0.089386	-0.631110	-2.611881
C	-1.618056	1.311618	-0.168796
C	-2.177459	0.197558	-0.827896
C	-0.897178	0.839027	0.993351
C	-1.744529	-0.984218	-0.127762
C	-1.015466	-0.564972	1.045498
O	1.373014	-1.351829	-0.392858
O	2.998701	-1.345535	1.839502
C	-3.021223	0.186158	-2.059017
H	-3.996227	-0.264955	-1.849206
H	-3.193780	1.194824	-2.435754
H	-2.540745	-0.390920	-2.855095
C	-2.191507	-2.379851	-0.437151
H	-3.160615	-2.573976	0.036630
H	-2.304552	-2.532138	-1.511689
H	-1.484144	-3.122516	-0.065192
C	-0.504471	-1.465066	2.120626
H	0.367310	-1.044352	2.621658
H	-1.287365	-1.626209	2.870499
H	-0.216531	-2.439739	1.723496
C	-0.226365	1.705306	2.008941
H	0.640686	1.207986	2.446601
H	0.111502	2.645158	1.569510
H	-0.928730	1.948021	2.814873
C	-1.796430	2.751343	-0.523107
H	-0.851722	3.296153	-0.463445
H	-2.188313	2.875397	-1.533215
H	-2.499055	3.223499	0.172253
O	2.794696	0.055368	2.081626
H	3.591164	0.440269	1.696585
Cl	1.461174	1.792109	-1.185342
H	2.451915	-1.474057	1.037451

ts23_Cl

E= -774.369872 G= -774.163141

W	0.477584	-0.279328	-0.311092
O	0.457828	-0.657188	-1.976887
C	-1.387327	1.292845	-0.194477
C	-1.888198	0.131177	-0.831985
C	-1.100242	0.960031	1.189655
C	-1.779640	-0.945603	0.095180
C	-1.370980	-0.405485	1.369660
O	0.814349	-1.829386	0.628244
O	2.633787	-1.038753	-0.481195
C	-2.363301	0.015152	-2.238888
H	-3.273930	-0.587316	-2.286137
H	-2.583392	0.994763	-2.665170
H	-1.598826	-0.463218	-2.862534

C	-2.182087	-2.364412	-0.138577
H	-3.188621	-2.545805	0.255058
H	-2.183178	-2.607098	-1.202095
H	-1.489398	-3.043411	0.362352
C	-1.250486	-1.212705	2.613654
H	-0.877495	-0.620864	3.450143
H	-2.227233	-1.620364	2.894263
H	-0.563886	-2.047677	2.445187
C	-0.712268	1.947186	2.240113
H	-0.285321	1.458599	3.116912
H	0.021140	2.662779	1.865209
H	-1.595416	2.509276	2.564762
C	-1.380753	2.675787	-0.758994
H	-0.563043	3.269212	-0.349522
H	-1.276324	2.669655	-1.844764
H	-2.322662	3.178580	-0.510465
O	3.562178	-0.551971	0.493890
H	3.717718	0.344181	0.162733
Cl	1.715820	1.729259	-0.099744
H	1.930315	-1.784624	0.170239

3_Cl

E= -774.396203 G=-774.184186

W	0.621698	-0.303141	-0.376032
O	0.534664	-0.524191	-2.061468
C	-1.305965	1.268611	-0.237566
C	-1.856799	0.114073	-0.836879
C	-0.907602	0.932333	1.117727
C	-1.709482	-0.959635	0.075402
C	-1.170122	-0.434780	1.311370
O	0.637983	-2.141918	0.278379
O	2.577719	-0.722861	-0.273267
C	-2.368075	0.021673	-2.231574
H	-3.104105	-0.777879	-2.332225
H	-2.839375	0.956905	-2.540154
H	-1.538939	-0.187288	-2.920294
C	-2.202378	-2.354023	-0.107059
H	-3.152538	-2.484724	0.423643
H	-2.364790	-2.588482	-1.159699
H	-1.480344	-3.066454	0.293243
C	-1.014805	-1.221089	2.568853
H	-0.389475	-0.703570	3.297455
H	-1.996859	-1.386816	3.026552
H	-0.564109	-2.191943	2.358401
C	-0.465509	1.915266	2.151550
H	0.041588	1.426068	2.984803
H	0.211955	2.658066	1.727991
H	-1.337732	2.441799	2.555895
C	-1.378663	2.646806	-0.806304
H	-0.673426	3.321040	-0.324363
H	-1.168913	2.655825	-1.876960
H	-2.390879	3.041240	-0.654121
O	2.479155	-0.323189	1.125765
H	2.804677	0.595182	1.063092
Cl	1.675074	1.935229	-0.462580
H	1.525957	-2.499931	0.156013

4c

E= -852.977011 G= -852.723922

W	-0.162781	0.000160	-0.162397
O	-0.790992	-0.246029	1.401161
C	1.961425	1.059279	0.586557
C	1.961978	-0.190692	1.244958
C	2.058254	0.821636	-0.842425
C	1.947521	-1.202617	0.254110
C	2.065650	-0.569966	-1.041839
O	-0.328280	-1.772422	-0.961403
O	-1.970630	0.069549	-1.019645
C	1.848666	-0.398455	2.713986
H	2.333946	-1.326624	3.021475
H	2.308347	0.423843	3.265307
H	0.790292	-0.453003	3.001242
C	2.000539	-2.673855	0.485387
H	3.018703	-3.041103	0.313066
H	1.713248	-2.931106	1.505523
H	1.326126	-3.188664	-0.200147
C	2.248939	-1.302610	-2.327195
H	2.054400	-0.665602	-3.190949
H	3.280875	-1.664538	-2.402476
H	1.577243	-2.160439	-2.376945
C	2.284318	1.872291	-1.879869
H	2.022702	1.516088	-2.877811
H	1.697340	2.768308	-1.674015
H	3.343466	2.154287	-1.894598
C	2.107805	2.381763	1.263561
H	1.849770	3.206167	0.602038
H	1.474513	2.455954	2.148806
H	3.151181	2.506576	1.578000
O	-1.278945	0.440433	-2.247237
H	-1.392568	1.409656	-2.220630
Cl	-0.634927	2.426433	-0.264675
H	-1.249617	-1.911789	-1.213199
C	-4.817466	-1.103718	1.786562
H	-5.501726	-1.543249	2.507014
H	-3.805586	-0.906277	2.127132
C	-5.196066	-0.817128	0.547099
H	-4.505963	-0.376935	-0.166282
H	-6.207683	-1.010631	0.200891

ts45c

E= -852.956544 G= -852.695797

W	-0.384166	-0.150727	-0.003145
O	-0.949341	-0.331622	1.607766
C	1.709343	1.048489	0.595099
C	1.792856	-0.169861	1.306167
C	1.753498	0.752204	-0.823713
C	1.788223	-1.224186	0.359261
C	1.820682	-0.643901	-0.965858
O	-0.524452	-1.987377	-0.653388
O	-2.300865	-0.225687	-0.785860
C	1.756558	-0.312941	2.786820
H	2.263346	-1.223910	3.110658
H	2.238753	0.535768	3.275959
H	0.713298	-0.359073	3.126090
C	1.923534	-2.679570	0.648497
H	2.949128	-3.006360	0.442361
H	1.695165	-2.904447	1.690969
H	1.242275	-3.253029	0.018350
C	1.952015	-1.415911	-2.233873
H	1.597648	-0.843372	-3.091819
H	3.003307	-1.674170	-2.407446
H	1.372202	-2.337881	-2.182196
C	1.842094	1.769139	-1.912888
H	1.537240	1.353290	-2.874458
H	1.209975	2.632546	-1.698511
H	2.875333	2.121393	-2.012183
C	1.834290	2.404003	1.206145
H	1.496879	3.185575	0.528492
H	1.253454	2.488785	2.125428
H	2.888877	2.586554	1.447642
O	-1.130201	0.181288	-2.020595
H	-1.406287	1.108948	-2.076159
Cl	-1.030325	2.257621	-0.016649
H	-1.428353	-2.112766	-0.967021
C	-3.716459	-1.255313	0.651066
H	-4.294177	-1.864992	-0.035168
H	-3.056106	-1.758831	1.347487
C	-3.821934	0.090546	0.652027
H	-3.271451	0.694438	1.362315
H	-4.509084	0.603177	-0.010346

5c

E= -853.058505 G= -852.796383

W	-0.328074	-0.172624	0.110877
O	-0.972762	-1.065598	1.427331
C	1.829801	1.127669	0.454059
C	1.707592	-0.032556	1.286635
C	1.963986	0.705035	-0.898328
C	1.729666	-1.176407	0.431255
C	1.894128	-0.703643	-0.920856
O	-0.783819	-1.673793	-1.072471
O	-3.009345	-0.077960	-0.258600
C	1.677710	-0.044404	2.780695
H	2.698934	-0.037209	3.178402
H	1.148730	0.825970	3.171744
H	1.168154	-0.933041	3.154356
C	1.753734	-2.612100	0.847479
H	2.786650	-2.976711	0.887208
H	1.304765	-2.746472	1.831786
H	1.197241	-3.231356	0.141462
C	2.019216	-1.589206	-2.110327
H	1.905328	-1.034313	-3.042662
H	3.001763	-2.074358	-2.118591
H	1.259879	-2.375307	-2.078774
C	2.059263	1.610083	-2.076567
H	1.048302	1.862001	-2.419708
H	2.578746	2.536007	-1.820674
H	2.598790	1.138890	-2.900650
C	1.955554	2.537282	0.918751
H	1.385774	3.220791	0.287826
H	1.604445	2.659530	1.942124
H	3.011868	2.831706	0.881089
O	-0.783066	0.896921	-1.489641
H	-1.693192	1.207656	-1.520268
Cl	-1.102927	1.845701	1.265845
H	-0.880664	-1.346838	-1.973000
C	-3.680654	-1.322388	-0.011756
H	-4.470008	-1.549472	-0.722998
H	-3.007036	-2.132797	0.247859
C	-3.826189	-0.200553	0.913865
H	-3.258854	-0.213522	1.838831
H	-4.722224	0.412967	0.895191

6_Cl

E= -699.287738 G= -699.077436

W	0.624014	-0.591078	-0.193671
O	0.660178	-1.091289	-1.819694
C	-0.747212	1.427090	-0.564709
C	-1.559495	0.385146	-1.068996
C	-0.616312	1.251596	0.874651
C	-1.827510	-0.504208	-0.002259
C	-1.290746	0.070934	1.217739
O	0.056682	-2.232402	0.696847
C	-1.946558	0.201495	-2.496369
H	-2.879262	-0.358886	-2.582893
H	-2.085304	1.165454	-2.990129
H	-1.164864	-0.349297	-3.033342
C	-2.676277	-1.727658	-0.049086
H	-3.638566	-1.535628	0.438645
H	-2.869391	-2.043292	-1.074898
H	-2.179928	-2.547248	0.473773
C	-1.504082	-0.498758	2.578705
H	-0.846317	-0.042312	3.319796
H	-2.538508	-0.324717	2.896429
H	-1.323963	-1.575252	2.572171
C	-0.001700	2.244527	1.806252
H	0.232558	1.800268	2.774963
H	0.919028	2.658794	1.392772
H	-0.700657	3.071200	1.978056
C	-0.356932	2.649802	-1.327802
H	0.459378	3.184889	-0.846610
H	-0.043071	2.409009	-2.344451
H	-1.221701	3.322131	-1.386759
O	2.236921	-1.342586	0.614642
H	3.032827	-0.835702	0.421315
Cl	2.286448	1.190696	-0.475364
H	0.847439	-2.757268	0.876834

ts67_Cl

E= -699.257779 G= -699.051998

W	0.596468	-0.502079	-0.145584
O	0.639716	-1.046629	-1.776005
C	-0.780478	1.487823	-0.527131
C	-1.526760	0.406852	-1.051263
C	-0.729712	1.341752	0.916890
C	-1.791884	-0.490625	0.022916
C	-1.372467	0.141176	1.251527
O	0.360739	-1.913773	1.028853
C	-1.872775	0.179067	-2.480165
H	-2.834591	-0.330528	-2.569300
H	-1.936791	1.122825	-3.024284
H	-1.105124	-0.443423	-2.957605
C	-2.552897	-1.773145	-0.052306
H	-3.599202	-1.611944	0.231324
H	-2.533859	-2.190903	-1.059877
H	-2.122277	-2.510088	0.628310
C	-1.604591	-0.429456	2.606120
H	-1.135512	0.171523	3.385991
H	-2.678612	-0.478335	2.815443
H	-1.195813	-1.442529	2.655642
C	-0.214255	2.376678	1.859575
H	0.028058	1.954041	2.835611
H	0.683628	2.857897	1.470837
H	-0.977016	3.150318	2.006544
C	-0.323568	2.693090	-1.282063
H	0.614830	3.078818	-0.881446
H	-0.168202	2.470286	-2.338617
H	-1.075803	3.487047	-1.208114
O	2.388895	-1.757072	0.082556
H	2.601754	-2.171463	-0.759896
Cl	2.290112	1.109037	0.146737
H	1.475179	-2.249881	0.703623

7_Cl

E= -699.293197 G= -699.088955

W	0.821117	-0.051214	0.082614
O	1.342194	-0.593406	-1.468230
C	-0.934952	1.635688	-0.463258
C	-1.293893	0.377748	-0.994213
C	-0.935692	1.533610	0.977183
C	-1.455654	-0.534703	0.112092
C	-1.289953	0.212430	1.328838
O	1.201756	-1.328206	1.175109
C	-1.493970	0.026132	-2.430749
H	-2.540489	0.187745	-2.712371
H	-0.867563	0.631730	-3.087029
H	-1.251992	-1.020933	-2.617628
C	-1.936870	-1.950347	0.015640
H	-2.993689	-1.962072	-0.273335
H	-1.370065	-2.536067	-0.711332
H	-1.844944	-2.456501	0.977449
C	-1.431336	-0.361857	2.700542
H	-1.136088	0.353993	3.468506
H	-2.471144	-0.646983	2.890660
H	-0.807259	-1.252267	2.816796
C	-0.698856	2.679710	1.903382
H	-0.489168	2.346047	2.920190
H	0.142554	3.292864	1.574479
H	-1.587434	3.320162	1.935780
C	-0.670613	2.889938	-1.232535
H	0.156765	3.458806	-0.802602
H	-0.425500	2.677998	-2.274298
H	-1.556842	3.534662	-1.223946
O	0.913650	-3.486666	-1.075963
H	1.265422	-2.723546	-1.549843
Cl	2.289140	1.665303	0.628714
H	1.166048	-3.299913	-0.16550

3d

E= -774.392836 G= -774.181126

W	0.212797	0.001641	1.659270
O	0.365062	-0.733031	3.198559
C	2.164698	1.089003	0.617765
C	2.545866	-0.127776	1.278830
C	1.329759	0.759406	-0.497188
C	1.919537	-1.201651	0.589270
C	1.188539	-0.642648	-0.527579
O	-0.879101	-1.572003	1.054499
O	-2.070003	0.333119	-0.145538
C	3.491937	-0.238642	2.431390
H	4.524216	-0.276048	2.065639
H	3.402712	0.612608	3.108041
H	3.304279	-1.141325	3.013721
C	2.090161	-2.661964	0.850734
H	2.867616	-3.071520	0.195977
H	2.381784	-2.854588	1.883706
H	1.161027	-3.198818	0.654138
C	0.460618	-1.448323	-1.545329
H	-0.141542	-0.818276	-2.199636
H	1.179212	-1.999608	-2.162159
H	-0.195987	-2.174276	-1.059239
C	0.701025	1.731558	-1.440669
H	-0.312648	1.419620	-1.697393
H	0.631512	2.723749	-0.994427
H	1.288050	1.813143	-2.361796
C	2.721050	2.439574	0.906288
H	1.998261	3.229635	0.705676
H	3.038364	2.535852	1.943941
H	3.595458	2.600611	0.263242
O	-1.386593	0.931962	0.959984
Cl	0.242142	2.132470	2.751937
H	-1.257247	-2.012842	1.821418
H	-1.997446	-0.617025	0.093742

4d

E= -852.973139 G= -852.720231

W	0.214787	0.000279	1.658374
O	0.365878	-0.744210	3.193045
C	2.168135	1.086902	0.619737
C	2.549129	-0.131043	1.278585
C	1.331153	0.759594	-0.494605
C	1.922365	-1.203253	0.586791
C	1.191838	-0.642736	-0.529066
O	-0.878161	-1.566576	1.041887
O	-2.113833	0.341116	-0.111073
C	3.495227	-0.245823	2.430430
H	4.527070	-0.291935	2.064214
H	3.412937	0.608165	3.104462
H	3.300712	-1.145135	3.015536
C	2.092307	-2.664382	0.845663
H	2.866394	-3.074017	0.187163
H	2.388784	-2.858514	1.877082
H	1.161908	-3.200712	0.652701
C	0.465906	-1.447349	-1.548855
H	-0.122804	-0.816773	-2.214402
H	1.185306	-2.010338	-2.154007
H	-0.203329	-2.163311	-1.065684
C	0.700113	1.734281	-1.433928
H	-0.307788	1.414958	-1.703690
H	0.614548	2.721085	-0.977657
H	1.294938	1.832566	-2.348750
C	2.726659	2.436595	0.909143
H	2.008907	3.228780	0.698848
H	3.034571	2.535221	1.949367
H	3.607512	2.591881	0.274034
O	-1.390172	0.932177	0.971927
Cl	0.249899	2.128247	2.754954
H	-1.266185	-2.008312	1.803577
C	-4.859612	-0.877766	-1.880360
H	-5.707570	-1.504877	-1.621771
H	-4.522968	-0.168805	-1.130427
C	-4.260762	-0.974436	-3.060826
H	-3.418037	-0.339013	-3.317632
H	-4.590193	-1.681428	-3.816361
H	-2.014782	-0.612472	0.105351

ts45d

E= -852.937588 G= -852.681162

W	-0.092641	0.260967	1.062955
O	-0.248502	-0.411279	2.641354
C	2.217638	1.077843	0.687483
C	2.339107	-0.230116	1.239051
C	1.594625	0.973973	-0.608489
C	1.742813	-1.132283	0.329056
C	1.295000	-0.383005	-0.829877
O	-1.037298	-1.519544	0.459163
O	-2.796778	-0.118685	-0.570480
C	2.955535	-0.592957	2.550857
H	3.916832	-1.096161	2.400670
H	3.131077	0.290611	3.165293
H	2.303306	-1.260505	3.119051
C	1.732091	-2.618916	0.444717
H	2.589271	-3.038911	-0.094571
H	1.803043	-2.939863	1.485610
H	0.820179	-3.034762	0.014893
C	0.691084	-0.996891	-2.048522
H	0.181714	-0.254708	-2.663907
H	1.470941	-1.467459	-2.658272
H	-0.032558	-1.765089	-1.768996
C	1.321632	2.125711	-1.520310
H	0.592452	1.862999	-2.287062
H	0.924007	2.979436	-0.966945
H	2.242320	2.445282	-2.021661
C	2.855318	2.311175	1.229198
H	2.357928	3.211450	0.871460
H	2.837390	2.337494	2.318667
H	3.901355	2.339011	0.899377
O	-1.531953	0.908180	0.119698
Cl	-0.132595	2.496566	1.985280
H	-1.191361	-2.034525	1.255627
C	-4.511573	-1.152136	-0.644331
H	-4.459421	-1.815307	0.211496
H	-5.198082	-0.318653	-0.574111
C	-3.856438	-1.435953	-1.803197
H	-3.974684	-0.814932	-2.681641
H	-3.231243	-2.316584	-1.896245
H	-2.231059	-0.883283	-0.186884

5d

E= -853.075378 G= -852.819920

W	0.382455	1.265119	1.077377
O	-0.991385	0.226932	1.208101
C	2.888419	1.207360	0.803842
C	2.491791	-0.083156	1.326383
C	2.291049	1.373934	-0.460380
C	1.646483	-0.703953	0.384503
C	1.444444	0.229237	-0.697667
O	-2.090405	-1.615320	-0.654026
O	-4.761841	-1.768117	-1.581142
C	2.996785	-0.669873	2.603660
H	4.035988	-0.995874	2.482129
H	2.969299	0.057936	3.417692
H	2.410174	-1.537665	2.907984
C	1.063901	-2.076596	0.458038
H	1.738051	-2.787616	-0.033634
H	0.929807	-2.403805	1.490578
H	0.095079	-2.132219	-0.040835
C	0.691530	-0.046803	-1.963272
H	0.391955	0.882154	-2.451740
H	1.331410	-0.601724	-2.659465
H	-0.206971	-0.640094	-1.776496
C	2.433297	2.529185	-1.394470
H	1.470944	3.026164	-1.551148
H	3.132597	3.271212	-1.007392
H	2.806660	2.189389	-2.365390

C	3.842387	2.135146	1.482994
H	3.796764	3.141336	1.064603
H	3.630922	2.210254	2.551790
H	4.869436	1.769661	1.371172
O	-0.152816	2.672476	0.251545
Cl	0.794846	1.978631	3.254739
H	-1.943273	-0.970572	0.053763
C	-5.261325	-2.480462	-0.446161
H	-4.644513	-2.405638	0.445283
H	-6.335079	-2.403077	-0.297194
C	-4.738113	-3.198609	-1.607011
H	-5.426150	-3.651146	-2.316307
H	-3.744781	-3.634950	-1.548867
H	-2.929387	-1.366868	-1.070183

C1) $[Cp^*W(O_2)(OH)_2]^+$ system

$[Cp^*WO(O_2)(H_2O)]^+$

E= -759.102197 G= -758.891530

W	-0.280644	-0.168143	-0.647538
O	-0.653933	-1.804177	-1.583654
C	1.961622	-0.470601	0.312670
C	1.834087	0.801393	-0.390080
C	1.044720	-0.464040	1.371636
C	0.960584	1.645743	0.368359
C	0.381338	0.844869	1.383359
O	-1.189803	1.100208	-1.318128
C	2.682580	1.217978	-1.548457
H	2.242208	2.052821	-2.094321
H	3.664195	1.537849	-1.182271
H	2.843273	0.396351	-2.248602
C	0.660648	3.075266	0.075332
H	-0.269298	3.400511	0.541306
H	1.469224	3.702199	0.465794
H	0.580238	3.261171	-0.996875
C	-0.557223	1.314126	2.451109
H	0.019417	1.736307	3.280909
H	-1.231122	2.095274	2.094452
H	-1.151899	0.497523	2.864264
C	0.829771	-1.535536	2.391065
H	-0.217003	-1.614723	2.690241
H	1.157578	-2.512254	2.034084
H	1.405527	-1.301048	3.293071
C	2.904587	-1.556784	-0.074069
H	2.714342	-2.478073	0.476142
H	2.848664	-1.777828	-1.141759
H	3.929637	-1.240589	0.147510
H	-2.682406	-0.352093	0.732734
O	-1.941312	-0.948238	0.556230
H	-2.301865	-1.785514	0.226933
O	0.543449	-1.162298	-2.059096

1_O2

E= -759.115948 G= -758.905098

W	-0.244957	-0.319963	-0.573633
O	-1.040498	-1.565290	-1.842249
C	1.924746	-0.435811	0.258301
C	1.805750	0.852645	-0.366059
C	1.062347	-0.435483	1.407044
C	0.889975	1.639898	0.402590
C	0.429955	0.845999	1.491970
O	-0.681235	1.089504	-1.748920
C	2.565176	1.326129	-1.559074
H	1.989661	2.045605	-2.141936
H	3.480947	1.824669	-1.220979
H	2.862424	0.505444	-2.213175
C	0.534632	3.053368	0.104580
H	-0.312305	3.396985	0.697205
H	1.390453	3.697445	0.332130
H	0.289264	3.180827	-0.951563
C	-0.509670	1.256604	2.570514
H	0.049438	1.408184	3.499770
H	-1.025332	2.186330	2.332700
H	-1.260170	0.484826	2.751864
C	0.910011	-1.542181	2.394506
H	-0.092987	-1.563476	2.820889
H	1.124702	-2.518783	1.959021
H	1.620431	-1.384779	3.214254
C	2.881730	-1.514579	-0.125079
H	2.526076	-2.501667	0.171016
H	3.071162	-1.532770	-1.198696
H	3.836282	-1.335418	0.381214
O	-1.644737	-0.716053	0.627815
H	-2.351550	-1.261672	0.249312
O	0.360910	-1.830356	-1.485824
H	-1.240852	0.824674	-2.495569

2_O2

E= -910.662081 G= -910.428220

W	-0.250035	-0.229805	-0.699518
O	-0.534620	-1.870029	-1.640705
C	1.971277	-0.471733	0.313201
C	1.841163	0.796843	-0.388470
C	1.027745	-0.480827	1.350534
C	0.928130	1.621827	0.343050
C	0.345517	0.815611	1.351495
O	-1.214942	1.011765	-1.374240
O	-1.893787	-0.909831	0.534319
C	2.703712	1.225902	-1.531271
H	2.260041	2.053527	-2.085500
H	3.674325	1.560756	-1.149421
H	2.888454	0.405933	-2.227732
C	0.606977	3.044455	0.036300
H	-0.329235	3.358244	0.497623
H	1.402821	3.689138	0.423682
H	0.527810	3.219162	-1.038054
C	-0.618793	1.266863	2.402748
H	-0.061593	1.643864	3.266921
H	-1.264947	2.071652	2.050345
H	-1.250972	0.451254	2.756441
C	0.809364	-1.555042	2.365996
H	-0.235458	-1.613156	2.676369
H	1.118861	-2.535268	2.001486
H	1.397877	-1.334222	3.263223
C	2.938186	-1.545032	-0.051593
H	2.744782	-2.469761	0.491944
H	2.910187	-1.764715	-1.120758
H	3.953493	-1.217504	0.196449
O	-2.542404	-2.103229	0.071909
H	-2.406013	-2.692075	0.829397
H	-3.306529	1.291117	-0.651800
O	-3.598376	0.827613	0.146281
H	-4.525313	0.591362	0.030763
H	-2.671770	-0.190598	0.428408
O	0.636861	-1.165714	-2.106517

ts23_O2

E= -910.657229 G= -910.422226

W	-0.294407	-0.274353	-0.642933
O	-0.561474	-1.920390	-1.572457
C	1.940946	-0.468792	0.311551
C	1.798158	0.795196	-0.385455
C	1.022411	-0.473429	1.375605
C	0.883235	1.614435	0.351918
C	0.335933	0.814480	1.384385
O	-1.361283	0.965180	-1.288715
O	-1.719863	-0.956452	0.640911
C	2.629957	1.221547	-1.551284
H	2.172539	2.047611	-2.096634
H	3.609794	1.558065	-1.195028
H	2.796600	0.399363	-2.249322
C	0.547523	3.031408	0.034777
H	-0.366624	3.355285	0.533864
H	1.357939	3.683940	0.372731
H	0.415975	3.188259	-1.037668
C	-0.611075	1.255689	2.454034
H	-0.043137	1.553814	3.342963
H	-1.208182	2.115257	2.146799
H	-1.284247	0.451988	2.754892
C	0.827785	-1.540265	2.401281
H	-0.221594	-1.637733	2.682533
H	1.184912	-2.511457	2.055321
H	1.390337	-1.282899	3.305337
C	2.905701	-1.540794	-0.065134
H	2.705806	-2.472754	0.463506
H	2.884439	-1.745189	-1.137240
H	3.920760	-1.220920	0.195787
O	-2.614886	-1.925954	0.053765
H	-2.393777	-2.727189	0.552959
H	-2.603312	1.092504	-0.687314
O	-3.397637	0.904873	0.024637
H	-4.196386	0.569848	-0.412956
H	-2.966667	0.160417	0.536092
O	0.568788	-1.172902	-2.083476

3_O2

E= -910.674642 G= -910.442885

W	-0.491507	-0.339859	-0.058809
O	-1.513513	-1.619979	-1.108071
C	1.822209	-0.458723	0.233409
C	1.542110	0.843508	-0.313911
C	1.260633	-0.499637	1.547296
C	0.857890	1.611011	0.679732
C	0.669997	0.784225	1.819424
O	-1.317621	1.085735	-0.879896
O	-1.441214	-0.870662	1.529097
C	1.978011	1.348079	-1.648437
H	1.301670	2.114853	-2.027302
H	2.974005	1.795723	-1.552164
H	2.048246	0.549318	-2.388103
C	0.427580	3.023674	0.505492
H	-0.079498	3.405737	1.390744
H	1.298336	3.657296	0.313469
H	-0.253207	3.113380	-0.346048
C	0.036303	1.175620	3.108248
H	0.820290	1.431383	3.829719
H	-0.614126	2.042809	2.997024
H	-0.552542	0.359095	3.526731
C	1.372950	-1.624913	2.522484
H	0.502202	-1.678303	3.176009
H	1.491130	-2.588708	2.025601
H	2.256483	-1.467150	3.150954
C	2.662948	-1.510749	-0.407729
H	2.431779	-2.506477	-0.029942
H	2.545199	-1.525482	-1.491907
H	3.715689	-1.302346	-0.188125
O	-2.818763	-1.115808	1.205501
H	-2.876769	-2.077737	1.313172
H	-2.052819	0.865544	-1.568647
O	-2.999518	0.424774	-2.643734
H	-2.994047	-0.537414	-2.709629
H	-3.916892	0.713167	-2.669534
O	-0.054840	-1.712155	-1.269454

4e

E= -989.261723 G= -988.986024

W	0.025292	-1.460888	0.229109
O	-1.153142	-0.754601	1.519047
C	1.176768	0.465659	0.875617
C	1.968080	-0.658993	1.300730
C	1.183249	0.476628	-0.553290
C	2.504366	-1.296141	0.137528
C	2.006884	-0.613537	-1.003223
O	0.594604	-3.164827	0.656361
O	-0.536712	-1.330098	-1.598874

C	2.273916	-1.032584	2.712773
H	3.166765	-0.489051	3.042501
H	1.460973	-0.769674	3.391284
H	2.475996	-2.099718	2.808630
C	3.411197	-2.474264	0.162473
H	4.290024	-2.256971	0.775732
H	2.898781	-3.339601	0.594027
H	3.753290	-2.742265	-0.836487
C	2.317296	-0.913898	-2.428030
H	1.435920	-0.792727	-3.058656
H	3.086213	-0.219264	-2.783822
H	2.692321	-1.928596	-2.558498
C	0.560595	1.508020	-1.434824
H	0.210108	1.075265	-2.371950
H	-0.278488	2.009361	-0.951106
H	1.308234	2.272065	-1.675110
C	0.579514	1.498558	1.770798
H	-0.259518	2.011448	1.301068
H	0.229966	1.072842	2.712257
H	1.344600	2.246680	2.005053
O	-1.475017	-2.385060	-1.850013
H	-2.302928	-1.888840	-2.040258
H	-0.137381	-3.832350	0.919785
O	-1.791299	-1.863250	0.794680
C	-4.472765	-1.217779	-2.010137
H	-4.464546	-0.432500	-1.260283
H	-4.898091	-2.170849	-1.709824
C	-4.024278	-1.012571	-3.247457
H	-4.064531	-1.789185	-4.005412
H	-3.632407	-0.048842	-3.559419
H	-2.068646	-4.128049	1.573742
O	-1.330163	-4.689436	1.312168
H	-1.297022	-5.436099	1.916805

ts45e
E= -989.242140 G= -988.963921

W	-0.074036	-1.159872	0.144972
O	-1.243502	-0.548416	1.505421
C	1.293764	0.370785	1.292058
C	1.975647	-0.895263	1.272127
C	1.262968	0.860494	-0.049714
C	2.391429	-1.158023	-0.073802
C	1.948160	-0.082183	-0.885776
O	0.336575	-2.983161	-0.008690
O	-0.638393	-0.531533	-1.477403
C	2.295112	-1.743482	2.458700
H	3.257835	-1.430877	2.879420
H	1.548223	-1.644962	3.248520
H	2.375179	-2.796130	2.185492
C	3.169454	-2.353809	-0.495685
H	4.127500	-2.380753	0.031655
H	2.619131	-3.268401	-0.256436
H	3.373111	-2.348526	-1.566012
C	2.167994	0.093154	-2.347605
H	1.257243	0.440429	-2.839200
H	2.946023	0.845460	-2.514927
H	2.486419	-0.831847	-2.827698
C	0.703425	2.166190	-0.504460
H	0.241707	2.079832	-1.488730
H	-0.041195	2.556154	0.190022
H	1.511245	2.903125	-0.573978
C	0.835839	1.098810	2.511075
H	-0.000919	1.764569	2.298699
H	0.527315	0.415265	3.302429
H	1.662809	1.706519	2.893866
O	-2.086237	-1.357023	-1.945274
H	-1.830395	-1.276480	-2.878468
H	-0.407751	-3.629757	0.160656
O	-1.820121	-1.697472	0.805185
C	-3.605606	-2.923174	-2.685851
H	-3.421608	-3.643868	-1.897823
H	-3.324264	-3.210956	-3.694512
C	-4.194923	-1.732374	-2.430258
H	-4.423198	-1.029371	-3.224743
H	-4.530359	-1.471614	-1.434204
H	-2.266414	-3.887327	1.113557
O	-1.768734	-4.472061	0.529188
H	-1.774897	-5.345343	0.931376

5e
E= -989.360359 G= -989.078711

W	-0.017815	-1.310453	0.231679
O	-1.177148	-0.721439	1.592934
C	1.274317	0.380650	1.210088
C	2.045677	-0.822893	1.321229
C	1.183728	0.703193	-0.184753
C	2.449710	-1.218293	0.007457
C	1.919120	-0.279343	-0.918973
O	0.495531	-3.073768	0.485157
O	-0.662854	-1.029896	-1.488263
C	2.439107	-1.506116	2.588395
H	3.406243	-1.116467	2.925689
H	1.718609	-1.332551	3.389013
H	2.543041	-2.581963	2.443980
C	3.287808	-2.411213	-0.289537
H	4.277506	-2.292266	0.161631
H	2.829282	-3.311440	0.128325
H	3.419497	-2.560313	-1.360651
C	2.086159	-0.272238	-2.397678
H	1.113727	-0.199234	-2.890845
H	2.686510	0.591912	-2.698599
H	2.584576	-1.172000	-2.757000
C	0.517843	1.902182	-0.773653
H	0.126487	1.688763	-1.768764
H	-0.301180	2.264823	-0.150820
H	1.247280	2.714736	-0.864964
C	0.783859	1.218996	2.343023
H	-0.095851	1.802172	2.069884
H	0.529937	0.617736	3.216573
H	1.574272	1.918922	2.634476
O	-2.888899	-2.118369	-2.186220
H	-1.562932	-1.423947	-1.738604
H	-0.254945	-3.737308	0.658954
O	-1.832702	-1.775427	0.807729
C	-3.497394	-1.982988	-3.485026
H	-3.827653	-2.923080	-3.914046
H	-2.988343	-1.300879	-4.159367
C	-4.160579	-1.453439	-2.294535
H	-4.136048	-0.385383	-2.100802
H	-4.982333	-2.001313	-1.845851
H	-2.175752	-3.988030	1.323303
O	-1.516530	-4.591049	0.959427
H	-1.517776	-5.385878	1.500054

6_O2
E= -835.565191 G= -835.333574

W	-0.014120	-1.298331	0.271795
O	-1.150136	-0.742410	1.658807
C	1.285968	0.396995	1.212864
C	2.064545	-0.803209	1.334569
C	1.174637	0.694147	-0.186308
C	2.451972	-1.221301	0.023791
C	1.900335	-0.304471	-0.914332
O	0.495352	-3.050104	0.554881
O	-0.676720	-1.051365	-1.486622
C	2.475883	-1.461394	2.608289
H	3.450867	-1.068075	2.917812
H	1.771342	-1.266145	3.417748
H	2.574028	-2.540480	2.485974
C	3.290061	-2.416437	-0.262614
H	4.291510	-2.274551	0.155065
H	2.854676	-3.307442	0.197244
H	3.392273	-2.597322	-1.331933
C	2.062086	-0.319018	-2.393833
H	1.097464	-0.200617	-2.891800
H	2.705168	0.512997	-2.698165
H	2.516690	-1.244189	-2.746328
C	0.497339	1.882322	-0.783846
H	0.119276	1.665961	-1.783115
H	-0.331834	2.236406	-0.169327
H	1.218907	2.703018	-0.866273
C	0.808824	1.253066	2.338080
H	-0.059541	1.850019	2.058966
H	0.545041	0.664789	3.217738
H	1.611857	1.941242	2.623015
H	-1.593844	-1.334525	-1.614117
H	-0.273231	-3.711283	0.682118
O	-1.846637	-1.715652	0.807193
H	-2.232652	-4.112596	1.298005
O	-1.526411	-4.578827	0.837565
H	-1.526635	-5.490659	1.142994

3f
E= -910.675455 G= -910.439436

W	-0.514591	-0.833910	0.195080
O	-1.554670	0.064863	1.484913
C	1.176227	0.421422	1.262152
C	1.669581	-0.922058	1.190027
C	1.070354	0.914356	-0.079664
C	1.855250	-1.258348	-0.188105
C	1.487764	-0.128520	-0.972941
O	-0.424198	-2.593249	0.737285
O	-1.109791	-1.040515	-1.684575
C	1.999518	-1.809336	2.338753
H	3.080816	-1.782425	2.512898
H	1.506091	-1.493171	3.257894
H	1.717556	-2.842230	2.130493
C	2.382361	-2.561840	-0.683815
H	3.465504	-2.601822	-0.527184
H	1.934945	-3.397916	-0.143404
H	2.195780	-2.700085	-1.748758
C	1.584020	-0.017274	-2.455329
H	0.849651	0.679369	-2.859556
H	2.580398	0.350547	-2.723349
H	1.435963	-0.980050	-2.943789
C	0.704438	2.309901	-0.459689
H	0.307213	2.367922	-1.472299
H	-0.025556	2.743400	0.225597
H	1.605184	2.932792	-0.417151
C	0.941521	1.217788	2.502455
H	0.123657	1.929400	2.380886
H	0.709599	0.583294	3.357750
H	1.847070	1.786013	2.740405
O	-1.434451	0.351974	-1.420685
H	-2.395913	0.321952	-1.242345
H	-1.312843	-3.068847	0.928743
O	-2.423021	-0.809570	0.703771
H	-2.879672	-4.418270	1.712539
O	-2.691037	-3.635307	1.187388
H	-3.292551	-2.936165	1.466630

4f
E= -989.256932 G= -988.981501

W	-0.513690	-0.836752	0.193160
O	-1.552996	0.052855	1.490586
C	1.174343	0.419463	1.260838
C	1.667827	-0.923979	1.189152
C	1.070220	0.912021	-0.081212
C	1.855870	-1.260528	-0.188937
C	1.488624	-0.130837	-0.974169
O	-0.422476	-2.599119	0.727186
O	-1.114912	-1.025737	-1.686488
C	1.996496	-1.811031	2.338502
H	3.077762	-1.785207	2.512900
H	1.502982	-1.494087	3.257352
H	1.713788	-2.843703	2.130239
C	2.385349	-2.562656	-0.684665
H	3.470529	-2.592672	-0.538509

H	1.950965	-3.397720	-0.132150
H	2.187071	-2.710510	-1.746597
C	1.586699	-0.019096	-2.456084
H	0.823434	0.643498	-2.864843
H	2.566513	0.395228	-2.718074
H	1.489111	-0.989269	-2.943037
C	0.706235	2.307604	-0.462766
H	0.313538	2.365002	-1.477160
H	-0.026176	2.742024	0.219402
H	1.607240	2.929923	-0.416759
C	0.938373	1.215957	2.500852
H	0.121630	1.928613	2.377901
H	0.704016	0.581594	3.355599
H	1.844218	1.782928	2.740652
O	-1.441713	0.363232	-1.407010
H	-2.401535	0.328584	-1.220414
H	-1.310586	-3.073656	0.919719
O	-2.423036	-0.816821	0.706461
C	2.136277	-3.564321	-4.939378
H	2.160853	-2.707902	-5.606737
H	3.086589	-4.050287	-4.739411
C	0.997808	-4.016668	-4.425430
H	0.970148	-4.893111	-3.784586
H	0.043829	-3.548533	-4.649236
H	-2.886134	-4.399837	1.731078
O	-2.694753	-3.632533	1.184267
H	-3.282659	-2.918691	1.456050

ts45f
E= -989.245558 G= -988.959916

W	-0.163538	-1.095324	-0.269816
O	-1.489661	-0.672398	0.996522
C	1.043733	0.338006	1.181278
C	1.768058	-0.896358	1.122818
C	1.105946	0.933988	-0.117180
C	2.277259	-1.055131	-0.205868
C	1.854188	0.062629	-0.977470
O	0.212141	-2.887675	0.062860
O	-0.471124	-1.290601	-2.256258
C	2.036212	-1.821439	2.259316
H	3.026568	-1.603782	2.674453
H	1.307057	-1.707392	3.061816
H	2.028491	-2.860798	1.929518
C	3.144540	-2.186083	-0.639929
H	4.136661	-2.076913	-0.189719
H	2.733675	-3.142491	-0.309130
H	3.273211	-2.214034	-1.721388
C	2.183833	0.360055	-2.400630
H	1.286623	0.601065	-2.974520
H	2.858261	1.220889	-2.447929
H	2.679907	-0.480066	-2.884500
C	0.598037	2.285648	-0.483427
H	0.353603	2.352398	-1.542679
H	-0.283223	2.566157	0.094835
H	1.381088	3.022500	-0.269249
C	0.448168	0.957036	2.401374
H	-0.413822	1.580539	2.161789
H	0.128342	0.206910	3.124769
H	1.198668	1.591791	2.884418
O	-1.012560	0.204788	-1.682921
H	-1.966667	0.011701	-1.705831
H	-0.565670	-3.528967	0.025650
O	-2.088628	-1.517121	-0.024425
C	0.608740	-3.207692	-3.214683
H	1.123962	-2.692369	-4.017448
H	1.213948	-3.668746	-2.442633
C	-0.732196	-3.323139	-3.208364
H	-1.252794	-3.881845	-2.437895
H	-1.333632	-2.911244	-4.010264
H	-2.134970	-5.119076	0.491917
O	-1.943194	-4.324110	-0.014123
H	-2.583220	-3.648805	0.247259

5f
E= -989.352223 G= -989.064222

W	-0.093455	-1.128748	-0.307942
O	-1.464035	-0.833581	0.946174
C	1.018321	0.320389	1.168305
C	1.854601	-0.844904	1.087425
C	1.057008	0.973565	-0.109547
C	2.325313	-0.956291	-0.250148
C	1.828861	0.164132	-0.992740
O	0.332165	-2.881835	0.267470
O	0.247620	-2.265042	-2.269885
C	2.206874	-1.762141	2.203559
H	3.227732	-1.544384	2.536531
H	1.542465	-1.640521	3.058830
H	2.166221	-2.802631	1.879142
C	3.235671	-2.026702	-0.747989
H	4.265895	-1.796105	-0.456496
H	2.973138	-2.994627	-0.317943
H	3.209778	-2.109148	-1.834499
C	2.125098	0.493508	-2.416312
H	1.255117	0.936593	-2.902745
H	2.945696	1.217319	-2.461809
H	2.427095	-0.388432	-2.981128
C	0.446064	2.287744	-0.444595
H	0.056239	2.294344	-1.462051
H	-0.365330	2.545914	0.235817
H	1.213358	3.066180	-0.363352
C	0.382493	0.858573	2.406255
H	-0.503750	1.452293	2.180899
H	0.085785	0.061898	3.089008
H	1.097568	1.503373	2.927954
O	-0.886888	0.009124	-1.652516
H	-1.812327	-0.217935	-1.813581
H	-0.384197	-3.567048	0.225910
O	-2.004375	-1.694587	-0.077438
C	-0.024987	-3.624028	-2.698282
H	0.855034	-4.136574	-3.070369
H	-0.675395	-4.181100	-2.031768
C	-0.572461	-2.483918	-3.439324
H	-1.619590	-2.231973	-3.310427
H	-0.108216	-2.152946	-4.361420
H	-2.073068	-5.191021	0.608902
O	-1.810200	-4.446142	0.060812
H	-2.400761	-3.708521	0.271963

C2) $[Cp^*W(O_2)(OH)_2]^+$ system in water

1_water
E= -759.190075 G= -758.978761

W	-0.261229	-0.360335	-0.553226
O	-1.094694	-1.658818	-1.744830
C	1.928517	-0.436027	0.247130
C	1.804786	0.850364	-0.368604
C	1.071682	-0.441394	1.402466
C	0.877065	1.624954	0.398802
C	0.433784	0.833084	1.493683
O	-0.552591	1.004936	-1.813955
C	2.565851	1.344290	-1.549520
H	1.955050	1.999936	-2.170527
H	3.424384	1.922820	-1.191148
H	2.944978	0.528350	-2.164229
C	0.507112	3.034692	0.105556
H	-0.389940	3.341322	0.642049
H	1.329507	3.689157	0.412546
H	0.342650	3.180869	-0.962899
C	-0.497908	1.238290	2.578274
H	0.066880	1.363936	3.507336
H	-0.999564	2.178152	2.352474
H	-1.257861	0.472288	2.744577
C	0.940328	-1.553196	2.386859
H	-0.023320	-1.527439	2.895014
H	1.064944	-2.531361	1.921002
H	1.726080	-1.442856	3.142421
C	2.896074	-1.506578	-0.128637
H	2.540704	-2.495281	0.161787
H	3.102578	-1.512925	-1.198853
H	3.839215	-1.320959	0.395401
O	-1.760840	-0.507313	0.590725
H	-2.482329	-1.056472	0.249830
O	0.349709	-1.844323	-1.537744
H	-1.189823	0.748690	-2.499822

ts45e_water
E= -989.309715 G= -989.031834

W	-0.122906	-1.105790	0.250640
O	-1.302267	-0.380448	1.567730
C	1.337152	0.410857	1.317613
C	1.991502	-0.868662	1.289629
C	1.269953	0.884708	-0.026851
C	2.335810	-1.165753	-0.068356
C	1.892508	-0.089111	-0.876412
O	0.194399	-2.926480	-0.101650
O	-0.723830	-0.430493	-1.330892
C	2.343110	-1.701687	2.476901
H	3.319866	-1.383356	2.858732
H	1.620866	-1.587542	3.286446
H	2.412615	-2.758584	2.217845
C	3.065342	-2.386662	-0.502558
H	4.034264	-2.438112	0.001874
H	2.494328	-3.282712	-0.242685
H	3.238201	-2.391747	-1.578107
C	2.057145	0.057869	-2.347566
H	1.136457	0.420646	-2.808447
H	2.845480	0.789118	-2.554087
H	2.333650	-0.882936	-2.822539
C	0.748518	2.205206	-0.480328
H	0.256663	2.125807	-1.450430
H	0.044560	2.634026	0.232978
H	1.586893	2.902444	-0.584501
C	0.949372	1.167107	2.543479
H	0.140887	1.871387	2.346385
H	0.635155	0.501807	3.348089
H	1.815213	1.737190	2.895808
O	-2.130003	-1.324915	-1.853011
H	-1.795595	-1.284668	-2.764312
H	-0.542400	-3.576920	0.084876
O	-1.829903	-1.627311	1.003860
C	-3.491823	-2.968681	-2.620757
H	-3.426988	-3.609419	-1.749326
H	-3.021315	-3.323047	-3.532376
C	-4.158446	-1.791079	-2.588014
H	-4.256122	-1.171742	-3.473167
H	-4.673708	-1.460799	-1.694350
H	-2.349177	-4.255597	1.077009
O	-1.810997	-4.575887	0.345019
H	-1.602873	-5.491305	0.558979

ts45f_water
E= -989.309024 G= -989.024935

W	-0.180240	-1.077437	-0.279804
O	-1.517237	-0.627849	0.973276
C	1.037308	0.334567	1.179678
C	1.755196	-0.903187	1.113069
C	1.103255	0.939309	-0.113146
C	2.262246	-1.056287	-0.215137
C	1.843699	0.067877	-0.979280
O	0.177870	-2.869985	0.056956
O	-0.461550	-1.317026	-2.274634
C	2.019426	-1.834314	2.243869
H	3.005999	-1.609629	2.663369
H	1.283023	-1.728974	3.040495
H	2.022946	-2.870599	1.905061
C	3.125702	-2.185871	-0.657059
H	4.118460	-2.072257	-0.210000
H	2.719557	-3.142920	-0.322929
H	3.247450	-2.211370	-1.739164

C	2.181577	0.373983	-2.397656
H	1.299289	0.694354	-2.954679
H	2.912542	1.188250	-2.424804
H	2.614620	-0.486157	-2.905580
C	0.606133	2.296387	-0.469018
H	0.371255	2.373980	-1.529500
H	-0.275772	2.576720	0.107698
H	1.396573	3.020873	-0.242244
C	0.452450	0.949953	2.405408
H	-0.398246	1.590427	2.170917
H	0.128215	0.196196	3.122870
H	1.216319	1.568420	2.887722
O	-0.983489	0.211734	-1.720722
H	-1.941172	0.042473	-1.763051
H	-0.605493	-3.511063	0.003724
O	-2.114816	-1.480739	-0.046325
C	0.611110	-3.221627	-3.181088
H	1.134355	-2.718552	-3.986174
H	1.209825	-3.665394	-2.394554
C	-0.731751	-3.332949	-3.179476
H	-1.255164	-3.876807	-2.400673
H	-1.328678	-2.936982	-3.992557
H	-1.973830	-5.101802	0.584866
O	-1.920819	-4.370973	-0.040237
H	-2.592120	-3.732254	0.232825

C3) $[Cp^*W(O_2)(OH)_2]^+$ system in acetonitrile

1_acetonitrile
E= -759.188664 G= -758.977166

W	-0.261690	-0.359021	-0.552730
O	-1.096556	-1.662272	-1.737705
C	1.927959	-0.435249	0.246770
C	1.804745	0.851765	-0.367910
C	1.070401	-0.441683	1.401729
C	0.877037	1.625994	0.399937
C	0.433411	0.833308	1.494235
O	-0.542909	1.000189	-1.822478
C	2.564967	1.345416	-1.549607
H	1.952908	1.999347	-2.171201
H	3.422864	1.925628	-1.192458
H	2.944895	0.529191	-2.163456
C	0.506593	3.035770	0.106979
H	-0.391031	3.341850	0.642848
H	1.328310	3.690776	0.414621
H	0.342782	3.182208	-0.961544
C	-0.497089	1.238122	2.579968
H	0.068166	1.359136	3.509393
H	-0.995688	2.180336	2.357275
H	-1.259517	0.474067	2.744024
C	0.939106	-1.553782	2.385934
H	-0.026771	-1.531825	2.890056
H	1.070191	-2.531669	1.921457
H	1.721001	-1.439681	3.144978
C	2.895078	-1.505750	-0.130349
H	2.540703	-2.494490	0.161112
H	3.099391	-1.512789	-1.200978
H	3.839310	-1.319649	0.391546
O	-1.762486	-0.504501	0.590268
H	-2.484268	-1.053066	0.249073
O	0.347003	-1.849797	-1.527009
H	-1.177040	0.742976	-2.510840

ts45e_acetonitrile
E= -989.308337 G= -989.030522

W	-0.121710	-1.104045	0.244013
O	-1.299956	-0.380334	1.562315
C	1.336715	0.410117	1.316825
C	1.989000	-0.870507	1.288648
C	1.272489	0.885650	-0.027264
C	2.337136	-1.165466	-0.069095
C	1.896413	-0.087467	-0.876689
O	0.195677	-2.925160	-0.104687
O	-0.719244	-0.428649	-1.339070
C	2.335616	-1.707184	2.474925
H	3.315011	-1.396246	2.856176
H	1.615479	-1.588742	3.285598
H	2.397794	-2.764281	2.214721
C	3.067038	-2.386076	-0.503497
H	4.032503	-2.441760	0.007051
H	2.492364	-3.281994	-0.251214
H	3.247052	-2.386929	-1.577888
C	2.064674	0.061197	-2.347337
H	1.146966	0.429877	-2.809406
H	2.857530	0.788301	-2.551238
H	2.336782	-0.880342	-2.823447
C	0.751691	2.206625	-0.480405
H	0.257652	2.127231	-1.449414
H	0.049539	2.636532	0.234007
H	1.590509	2.903006	-0.586770
C	0.946628	1.165050	2.542725
H	0.137353	1.868365	2.345511
H	0.632414	0.498903	3.346610
H	1.811424	1.735995	2.896274
O	-2.126982	-1.322308	-1.854768
H	-1.798835	-1.281996	-2.768384
H	-0.541974	-3.575121	0.079807
O	-1.828426	-1.625986	0.996841
C	-3.492961	-2.969162	-2.615024
H	-3.413836	-3.612987	-1.747027
H	-3.033842	-3.318437	-3.534418
C	-4.162209	-1.793639	-2.568229
H	-4.274254	-1.170959	-3.449316
H	-4.665938	-1.468513	-1.666155
H	-2.353462	-4.251950	1.067811
O	-1.811051	-4.573855	0.339690
H	-1.607214	-5.490027	0.554364

ts45f_acetonitrile
E= -989.307968 G= -989.023862

W	-0.179917	-1.077759	-0.278742
O	-1.515955	-0.628824	0.975449
C	1.038045	0.335096	1.179735
C	1.755604	-0.902833	1.113556
C	1.103633	0.939091	-0.113477
C	2.262576	-1.056580	-0.214694
C	1.844119	0.067337	-0.979268
O	0.178702	-2.870362	0.057681
O	-0.462349	-1.316168	-2.273258
C	2.019324	-1.833507	2.244892
H	3.005351	-1.608409	2.665487
H	1.282090	-1.728186	3.040763
H	2.023487	-2.869933	1.906547
C	3.125760	-2.186567	-0.656253
H	4.118986	-2.072582	-0.210315
H	2.719928	-3.143299	-0.320839
H	3.246507	-2.213241	-1.738457
C	2.181523	0.372850	-2.397915
H	1.298243	0.688917	-2.955864
H	2.909404	1.189845	-2.426067
H	2.618050	-0.486340	-2.904465
C	0.605893	2.295814	-0.469968
H	0.372879	2.373408	-1.530854
H	-0.277556	2.574925	0.105029
H	1.394906	3.021299	-0.241443
C	0.453862	0.951383	2.405343
H	-0.397695	1.590784	2.171087
H	0.130989	0.198304	3.124113
H	1.217618	1.571139	2.886203
O	-0.984703	0.211691	-1.718611
H	-1.942331	0.041980	-1.760462
H	-0.604516	-3.511386	0.003687
O	-2.114015	-1.481465	-0.043976
C	0.610671	-3.220377	-3.181452
H	1.134198	-2.716297	-3.985728
H	1.209056	-3.665113	-2.395205
C	-0.732113	-3.331925	-3.180627
H	-1.255896	-3.876730	-2.402722
H	-1.328656	-2.934883	-3.993463
H	-1.976875	-5.105223	0.577967
O	-1.920479	-4.370632	-0.042353
H	-2.592327	-3.732742	0.231253

d) Mimoun mechanism
- $[Cp^*WO_2Cl]$ TS insertion

E= -852.938676 G= -852.674414

W	-0.167395	0.036336	0.194433
O	0.516034	-0.676760	-1.470143
O	0.276258	-1.266787	1.225238
H	1.465150	-0.873964	-1.369410
C	0.526248	2.143203	-1.034986
C	1.880956	1.980553	-0.761541
H	0.006970	2.939940	-0.518456
H	0.187774	1.894384	-2.034019
H	2.548517	1.533934	-1.491607
H	2.368616	2.578158	-0.000866
O	1.973413	0.437878	0.403455
O	2.792807	-0.613985	-0.134032
C	-2.380144	-1.061061	0.598990
C	-2.059534	-1.133992	-0.780954
C	-2.116672	0.197377	-1.329093
C	-2.389454	1.088092	-0.272576
C	-2.526124	0.307280	0.934467
Cl	0.006357	1.674908	1.982155
H	2.760788	-1.245140	0.599380
C	-1.864745	-2.376391	-1.581082
H	-2.779416	-2.614432	-2.136338
H	-1.050164	-2.242994	-2.294810
H	-1.621462	-3.227432	-0.943537
C	-2.459967	-2.212161	1.537861
H	-3.059336	-1.965768	2.415754
H	-2.908292	-3.082190	1.053004
H	-1.451349	-2.484451	1.875559
C	-2.998341	0.830805	2.248727
H	-2.699979	1.867131	2.399135
H	-4.093751	0.778218	2.281312
H	-2.601642	0.250026	3.082044
C	-2.664942	2.552080	-0.358367
H	-2.320175	2.978795	-1.300663
H	-3.744094	2.730214	-0.285417
H	-2.183765	3.093388	0.459476
C	-1.980564	0.502281	-2.781926
H	-1.067282	0.053449	-3.180887
H	-2.830721	0.082053	-3.330768
H	-1.958087	1.575427	-2.974870

- $[Cp^*WO_2Cl]$ TS cycle opening

E= -852.917092 G= -852.654137

W	-0.510777	1.131744	0.619568
C	-2.651690	0.103348	2.291031
C	-3.450159	-0.046572	1.085558
O	-2.217433	-0.060852	0.317487
O	-2.089281	-0.778423	-1.419148
O	0.080295	-0.645628	0.199561
O	-0.312215	1.792089	-0.938474
H	-2.659937	1.038742	2.828265
H	-2.225878	-0.785759	2.738631
H	-3.942086	-1.002149	0.905710
H	-4.078047	0.804581	0.826742
H	-0.570986	-0.993415	-0.468090
C	1.655005	2.215158	0.985124
C	0.695461	2.854594	1.810144
C	0.280234	1.917902	2.833995

C	0.945397	0.699911	2.594030
C	1.791045	0.876860	1.439381
H	-2.066489	0.058164	-1.902621
Cl	-2.262196	2.848888	0.982146
C	2.368202	2.865070	-0.152329
H	2.975603	3.700992	0.208298
H	3.026814	2.164844	-0.666132
H	1.654384	3.248976	-0.886556
C	2.727283	-0.157973	0.927578
H	3.500088	-0.359052	1.677665
H	2.184255	-1.083105	0.722309
H	3.217704	0.158170	0.006923
C	0.862717	-0.566912	3.379332
H	1.796659	-0.733844	3.927507
H	0.051157	-0.541813	4.107574
H	0.707065	-1.421203	2.715918
C	-0.577070	2.277179	4.000547
H	0.006383	2.877580	4.707946
H	-1.437422	2.874375	3.689229
H	-0.937052	1.395965	4.532811
C	0.398317	4.316921	1.785435
H	-0.541019	4.548799	2.283633
H	1.207163	4.852837	2.297388
H	0.333213	4.693941	0.763754

- $[Cp^*WO(OH)_2]^+$ TS insertion

E= -914.105346 G= -913.822586

W	-0.101723	-0.284519	-0.550132
O	-0.511324	-0.690244	-2.358136
C	-2.180433	0.835709	-0.944897
C	-2.079832	0.727841	0.467781
C	-0.958672	1.497296	0.876257
C	-0.396313	2.154120	-0.296969
C	-1.173701	1.777649	-1.403425
O	1.770609	-0.688198	-1.257476
O	1.915770	-1.395384	-2.489640
H	0.180162	-1.259874	-2.758038
C	1.569144	-0.035403	1.240974
H	1.998464	0.958501	1.288487
H	0.799697	-0.281590	1.966893
C	2.350300	-1.070640	0.780117
H	3.349812	-0.915121	0.396008
H	2.029208	-2.101501	0.898981
H	2.554007	-0.816902	-2.983198
C	-3.241706	0.252972	-1.813030
H	-3.781703	-0.549811	-1.310849
H	-3.964705	1.032057	-2.077110
H	-2.813078	-0.142162	-2.735393
C	-2.985718	-0.056507	1.356439
H	-3.344611	-0.961114	0.864452
H	-2.488844	-0.360237	2.278387
H	-3.856173	0.550118	1.627346
C	-0.634597	1.845943	2.292493
H	0.397600	2.167352	2.429376
H	-1.274039	2.684932	2.589899
H	-0.840739	1.027343	2.983992
C	0.692978	3.178979	-0.287418
H	1.272983	3.169133	-1.211636
H	0.255939	4.178131	-0.182831
H	1.384221	3.043573	0.545378
C	-1.041605	2.247916	-2.809090
H	-1.856413	2.943907	-3.037688
H	-0.100259	2.771016	-2.980374
H	-1.112500	1.410811	-3.505910
O	-0.620688	-1.669988	0.288815
O	3.586230	0.169055	-3.868601
H	4.533800	0.088262	-3.726805
H	3.469870	0.210937	-4.822296

- $[Cp^*WO(OH)_2]^+$ TS cycle opening

E= -914.102418 G= -913.819745

W	-0.488621	0.982156	0.638016
C	-2.327842	0.387559	1.984034
C	-3.167029	-0.351534	0.989288
O	-1.932667	-0.603149	0.245628
O	-1.827649	-1.191008	-1.281039
O	0.235178	-0.060072	-0.622829
H	-2.679878	1.399249	2.183762
H	-2.055232	-0.193037	2.858216
H	-3.610530	-1.299176	1.286818
H	-3.841440	0.274448	0.405473
H	-0.802830	-0.856776	-1.231433
C	1.522668	2.112375	0.960060
C	0.572333	2.799088	1.787867
C	0.183490	1.909822	2.823751
C	0.919959	0.676917	2.658716
C	1.778815	0.823825	1.544391
H	-2.302464	-0.404624	-1.760521
C	2.264576	2.691138	-0.202134
H	3.198700	3.142736	0.149601
H	2.518686	1.923173	-0.934212
H	1.689536	3.469384	-0.705465
C	2.763286	-0.162373	1.018453
H	2.754225	-1.089498	1.591891
H	2.548404	-0.402934	-0.026875
H	3.773332	0.255250	1.071465
C	0.878642	-0.495849	3.586016
H	1.666675	-0.396975	4.340587
H	-0.068627	-0.565658	4.123097
H	1.043690	-1.439681	3.063336
C	-0.675774	2.257669	3.995215
H	-0.047919	2.694252	4.779837
H	-1.439532	2.996027	3.745794
H	-1.167723	1.386592	4.429790
C	0.128757	4.211900	1.598917
H	-0.738644	4.451101	2.214571
H	0.936388	4.894872	1.880795
H	-0.136331	4.412798	0.558768
O	-1.377955	2.201999	-0.207110
O	-2.895769	0.920680	-2.150553
H	-2.424268	1.654575	-1.715503
H	-3.102459	1.180251	-3.052998

-$[Cp^*W(O_2)(OH)_2]^+$ TS insertion

E= -989.201326 G= -988.914047

W	-0.160906	-0.179059	-0.701367
O	-1.207802	-1.761082	-0.328174
O	-0.414034	-0.167649	-2.542838
O	-0.402446	-1.429068	0.831332
C	-2.308936	0.948066	-0.847392
C	-2.123097	0.707257	0.550874
C	-0.988186	1.438587	0.976319
C	-0.501112	2.193687	-0.150843
C	-1.338529	1.904882	-1.265689
O	1.238933	-1.525575	-1.217533
O	0.771948	-2.721433	-1.825340
H	-0.122824	-0.854622	-3.233785
C	2.033196	0.595206	0.209043
H	2.488532	1.043852	-0.671736
H	1.652490	1.265582	0.966807
C	2.423044	-0.653048	0.605830
H	3.077569	-1.272934	0.009610
H	2.106407	-1.059267	1.561995
H	0.002503	-2.952212	-1.265782
C	-3.402207	0.382748	-1.684770
H	-3.702728	-0.604651	-1.330619
H	-4.279688	1.037297	-1.637555
H	-3.098592	0.300197	-2.728844
C	-2.986411	-0.162013	1.387322
H	-4.022847	0.184566	1.327093
H	-2.958369	-1.194133	1.024313
H	-2.679469	-0.158422	2.431780
C	-0.506747	1.496927	2.388723
H	0.427097	2.050814	2.496486
H	-1.250493	2.010131	3.006959
H	-0.374004	0.494791	2.804948
C	0.491793	3.310601	-0.116710
H	1.122270	3.343311	-1.007136
H	-0.061316	4.255661	-0.079333
H	1.134619	3.286788	0.763090
C	-1.286879	2.548362	-2.605038
H	-2.097267	3.281241	-2.684441
H	-0.345533	3.071055	-2.777076
H	-1.420742	1.808455	-3.395166
O	0.252517	-1.844943	-4.357884
H	0.683630	-2.539782	-3.842051
H	0.835435	-1.620156	-5.088064

-$[Cp^*W(O_2)(OH)_2]^+$ TS cycle opening

E= -989.220300 G= -988.933576

W	-0.610795	1.143609	0.604011
C	-2.380443	0.598680	2.045741
C	-3.069257	-0.450503	1.231592
O	-1.784211	-0.774654	0.597661
O	-1.680635	-1.586262	-0.768729
O	0.102477	0.105969	-0.637544
O	-1.127583	2.729210	-0.321313
H	-2.886542	1.564948	2.017027
H	-2.119155	0.263480	3.041774
H	-3.443938	-1.333749	1.745539
H	-3.768756	-0.069382	0.489213
H	-0.772646	-1.085139	-0.937566
C	1.489454	2.144080	0.913391
C	0.593913	2.833625	1.813173
C	0.173015	1.910311	2.794745
C	0.812942	0.639485	2.513070
C	1.693915	0.823669	1.418222
H	-2.347339	-1.029051	-1.390860
C	2.224993	2.756527	-0.233938
H	3.163827	3.194725	0.121761
H	2.466420	2.009742	-0.991400
H	1.647081	3.549419	-0.710384
C	2.615615	-0.178088	0.819813
H	2.611927	-1.117081	1.373336
H	2.333847	-0.384263	-0.217563
H	3.638015	0.210482	0.822667
C	0.721689	-0.584969	3.366379
H	1.477691	-0.537123	4.157415
H	-0.249886	-0.677929	3.853317
H	0.898248	-1.496060	2.793419
C	-0.605329	2.253849	4.022886
H	0.056188	2.778418	4.721177
H	-1.448192	2.916831	3.818062
H	-0.978757	1.371632	4.542083
C	0.262926	4.287064	1.759981
H	-0.662069	4.515937	2.290038
H	1.070428	4.854914	2.235574
H	0.162433	4.647378	0.735658
O	-2.198200	1.767321	-0.427416
O	-3.143668	-0.089305	-2.078419
H	-3.337177	-0.136498	-3.019395
H	-2.832983	0.811665	-1.849392

E1) Organics

C_2H_4

E= -78.579276 G= -78.550588

C	0.026843	-0.022798	0.056341
H	0.039513	0.296713	1.094038
H	0.992134	-0.145492	-0.425665
C	-1.108846	-0.250179	-0.589970

H	-2.074073	-0.127085	-0.108027
H	-1.121002	-0.568659	-1.627967

H_2O_2
E= -151.532090 G= -151.527613

O	0.431663	-0.878534	0.242374
H	1.258078	-0.770245	-0.242375
O	-0.049508	0.477250	0.242374
H	-0.875914	0.368964	-0.242390

C_2H_4O
E= -153.771659 G= -153.738396

C	0.240250	-0.101144	0.000000
C	1.703878	-0.101100	0.000000
H	-0.295942	-0.324423	-0.920301
H	-0.295942	-0.324423	0.920301
H	2.240084	-0.324346	-0.920301
H	2.240084	-0.324346	0.920301
O	0.972027	1.117435	0.000000

E2) Organics in water

C_2H_4_water
E= -78.580637 G= -78.552050

C	0.027602	-0.022409	0.056508
H	0.039733	0.296617	1.094741
H	0.993147	-0.145427	-0.425631
C	-1.109413	-0.250092	-0.590258
H	-2.074958	-0.127073	-0.108119
H	-1.121543	-0.569116	-1.628491

H_2O_2_water
E= -151.539896 G= -151.535413

O	0.457706	-0.867018	0.292506
H	1.220211	-0.769106	-0.292507
O	-0.075551	0.465734	0.292506
H	-0.838047	0.367825	-0.292522

C_2H_4O_water
E= -153.775827 G= -153.742583

C	0.240973	-0.103763	0.000000
C	1.703156	-0.103718	0.000000
H	-0.293609	-0.324653	-0.920719
H	-0.293609	-0.324653	0.920719
H	2.237750	-0.324576	-0.920719
H	2.237751	-0.324576	0.920719
O	0.972027	1.123593	0.000000

E3) Organics in acetonitrile

C_2H_4_acetonitrile
E= -78.580601 G= -78.552012

C	0.027585	-0.022414	0.056499
H	0.039727	0.296612	1.094722
H	0.993127	-0.145426	-0.425628
C	-1.109396	-0.250087	-0.590249
H	-2.074937	-0.127074	-0.108122
H	-1.121537	-0.569111	-1.628472

H_2O_2_acetonitrile
E= -151.539699 G= -151.535218

O	0.456862	-0.867402	0.291023
H	1.221540	-0.769189	-0.291024
O	-0.074707	0.466118	0.291023
H	-0.839375	0.367909	-0.291039

C_2H_4O_acetonitrile
E= -153.775724 G= -153.742480

C	0.240950	-0.103708	0.000000
C	1.703179	-0.103663	0.000000
H	-0.293682	-0.324637	-0.920707
H	-0.293682	-0.324637	0.920707
H	2.237824	-0.324560	-0.920707
H	2.237824	-0.324560	0.920707
O	0.972027	1.123419	0.000000

f) Radicals

Cp*WO(OH)_radical
E= -608.117977 G= -607.925972

W	0.033512	0.077213	-0.214552
O	1.719975	0.008381	-0.076168
C	0.246967	2.431984	-0.068259
C	-0.357476	2.081914	-1.312983
C	-0.615505	1.963241	0.970351
C	-1.698011	1.566340	-1.037540
C	-1.855914	1.496586	0.353642
O	-0.883708	-1.526985	-0.372711
C	0.175892	2.402533	-2.673282
H	-0.174386	1.697900	-3.429333
H	-0.167455	3.399438	-2.970836
H	1.266190	2.408407	-2.689931
C	-2.700373	1.202879	-2.082928
H	-3.468910	0.532724	-1.697794
H	-3.198051	2.111324	-2.439941
H	-2.238647	0.728250	-2.951252
C	-3.060798	1.040407	1.108270
H	-3.625483	1.913260	1.454174
H	-3.726576	0.438009	0.490336
H	-2.798124	0.457248	1.993490
C	-0.411233	2.144328	2.441288
H	-0.904196	1.363887	3.023338
H	0.645453	2.155483	2.709858
H	-0.842677	3.103432	2.748284
C	1.564494	3.108521	0.113074
H	2.028600	2.846857	1.064189
H	2.267269	2.852356	-0.680626
H	1.419278	4.193876	0.097761
H	-0.889435	-2.486690	-0.426989

Cp*WO(OH)Cl_radical
E= -623.447005 G= -623.254433

W	0.434128	-0.077599	1.792219
O	0.856029	-0.284286	3.431250
C	2.215668	1.029742	0.694487
C	2.692011	-0.198393	1.246045
C	1.336661	0.702068	-0.407213
C	2.018237	-1.274176	0.572885
C	1.230531	-0.697557	-0.488987
O	-1.028833	-1.274254	1.342324
C	3.726535	-0.346892	2.315609
H	4.717419	-0.462509	1.862565
H	3.753281	0.523551	2.972352
H	3.534454	-1.219238	2.941837
C	2.256310	-2.739798	0.765412
H	3.038867	-3.092258	0.083027
H	2.576794	-2.965004	1.783842
H	1.351565	-3.316733	0.565254
C	0.407010	-1.498254	-1.441457
H	-0.094074	-0.862414	-2.172169
H	1.035405	-2.207873	-1.988837
H	-0.358417	-2.063855	-0.901094
C	0.698908	1.712013	-1.304616
H	-0.096733	1.272070	-1.906686
H	0.262355	2.534040	-0.733514
H	1.445320	2.133718	-1.987188
C	2.685990	2.409658	1.033310
H	1.877670	3.137669	0.941853
H	3.069257	2.465387	2.053329
H	3.492133	2.716099	0.356307
Cl	-1.122288	1.701835	1.675203
H	-1.913476	-0.892623	1.377599

Cp*W(O_2)(OH)_radical
E= -683.235074 G= -683.039370

W	-0.067814	-1.174357	0.393647
O	-1.313630	-0.359201	1.504303
C	1.354549	0.470767	1.242914
C	1.983770	-0.811159	1.428520
C	1.228500	0.690857	-0.166475
C	2.317958	-1.333260	0.129331
C	1.838555	-0.423321	-0.848925
O	-0.040272	-2.673624	-0.754980
C	2.355891	-1.415416	2.743929
H	3.341156	-1.041749	3.043964
H	1.649902	-1.148327	3.531588
H	2.418258	-2.503057	2.693067
C	3.041038	-2.605836	-0.155029
H	4.080357	-2.380172	-0.416169
H	3.054804	-3.272269	0.707429
H	2.591889	-3.139534	-0.994043
C	1.983699	-0.576866	-2.325990
H	1.224359	-0.018344	-2.874656
H	2.961810	-0.192509	-2.634980
H	1.924880	-1.623359	-2.627239
C	0.665369	1.913105	-0.814842
H	0.245296	1.700297	-1.798889
H	-0.106866	2.382256	-0.204051
H	1.469108	2.645085	-0.952529
C	0.966661	1.425665	2.324008
H	0.113751	2.043367	2.039964
H	0.714088	0.913298	3.252920
H	1.808817	2.094701	2.530504
H	-0.782446	-3.272231	-0.909690
O	-1.898195	-1.539268	0.854669

Cp*WO(OH)O_radical
E= -683.342503 G= -683.150507

W	-0.734740	-0.240124	-0.622895
O	-0.961083	-1.666578	-1.519575
C	0.915517	-1.148009	0.764374
C	1.681888	-0.163134	-0.008142
C	0.191811	-0.413026	1.737306
C	1.292183	1.160644	0.409683
C	0.406390	1.026989	1.488861
O	-0.527939	1.159676	-1.875310
O	-2.163455	-0.003906	0.300676
C	2.738126	-0.479615	-0.993552
H	2.811943	0.283524	-1.770816
H	3.708124	-0.501417	-0.474482
H	2.600751	-1.459302	-1.453166
C	1.796412	2.417276	-0.206466
H	1.510670	3.292939	0.375005
H	2.887014	2.402785	-0.279031
H	1.388142	2.533714	-1.216309
C	-0.217721	2.097761	2.299370
H	0.186825	2.079108	3.319037
H	-0.034103	3.086777	1.882477
H	-1.298088	1.948900	2.381954
C	-0.556508	-0.958088	2.891282
H	-1.457213	-0.379597	3.101200
H	-0.828635	-2.003476	2.748195
H	0.086560	-0.902419	3.780306
C	1.165262	-2.625111	0.763684
H	0.316957	-3.173948	1.173816

H	1.343460	-3.004720	-0.242758
H	2.042256	-2.851328	1.379180
H	-0.996199	1.246754	-2.713123

Cp*WClO(OH)O_radical
E= -698.611458 G= -698.415704

W	0.584908	-0.292153	-0.394424
O	0.573854	-0.535288	-2.082927
C	-1.304196	1.257891	-0.257198
C	-1.878309	0.105285	-0.849599
C	-0.919307	0.931358	1.107081
C	-1.733744	-0.961955	0.068878
C	-1.186411	-0.432449	1.304812
O	0.693941	-2.165245	0.206621
O	2.333045	-0.452248	0.274395
C	-2.414299	0.023522	-2.239471
H	-3.084280	-0.829906	-2.354691
H	-2.975639	0.925918	-2.492652
H	-1.596819	-0.087077	-2.961082
C	-2.203601	-2.366152	-0.099549
H	-3.082002	-2.547437	0.529629
H	-2.472786	-2.579893	-1.134310
H	-1.418112	-3.063980	0.199377
C	-1.011077	-1.228082	2.554669
H	-0.389825	-0.706302	3.283668
H	-1.986290	-1.417769	3.017227
H	-0.544840	-2.189995	2.333553
C	-0.448203	1.920288	2.123285
H	-0.000621	1.428692	2.988166
H	0.293693	2.601815	1.703339
H	-1.295542	2.517971	2.478113
C	-1.342682	2.634687	-0.832938
H	-0.558443	3.267041	-0.417869
H	-1.225170	2.623075	-1.917514
H	-2.309746	3.096696	-0.599858
Cl	1.766773	1.837451	-0.520568
H	1.581487	-2.529549	0.108571

Cp*W(O_2)(OH)O_radical
E= -758.461887 G= -758.267445

W	-0.201211	-1.223058	0.160681
O	-1.322575	-0.624949	1.581871
C	1.221242	0.376168	1.272038
C	1.975020	-0.876295	1.269664
C	1.260980	0.882173	-0.045104
C	2.335388	-1.192878	-0.091669
C	1.953261	-0.099742	-0.897282
O	0.238314	-3.034238	-0.229305
O	-0.774268	-0.517801	-1.276516
C	2.361299	-1.651749	2.468357
H	3.307961	-1.249278	2.858757
H	1.628463	-1.565279	3.273114
H	2.530551	-2.703998	2.235673
C	3.111764	-2.393238	-0.501376
H	4.053324	-2.441211	0.053188
H	2.540675	-3.303825	-0.298533
H	3.346726	-2.376043	-1.564737
C	2.215531	0.100855	-2.338765
H	1.328166	0.476990	-2.853074
H	3.005935	0.852411	-2.463705
H	2.544229	-0.814823	-2.828011
C	0.777831	2.199893	-0.513990
H	0.296798	2.128083	-1.490958
H	0.084703	2.657282	0.191341
H	1.637336	2.875210	-0.619937
C	0.773282	1.101612	2.495768
H	-0.012104	1.823274	2.270505
H	0.385470	0.419167	3.252491
H	1.620493	1.646608	2.925894
H	-0.389175	-3.750598	-0.074005
O	-1.747218	-1.904403	1.047805

H_2O_2_radical
E= -150.890235 G= -150.898114

O	-0.587322	-0.199189	-1.721961
O	-1.793048	-0.705122	-1.564002
H	-1.875044	-1.406315	-2.235281

OH_radical
E= -75.724241 G= -75.732638

O	-0.797646	0.316456	0.000000
H	0.175368	0.316456	0.000000

3_without coordinated water
E= -759.116663 G= -758.906606

W	-0.653374	-0.177533	-0.517018
O	-0.747825	-1.703179	-1.264871
C	1.017356	-1.157403	0.814822
C	1.612002	-0.215560	-0.083761
C	0.181250	-0.422498	1.710365
C	1.233279	1.117544	0.349140
C	0.351042	0.989587	1.439120
O	-0.626067	1.122598	-1.855202
O	-2.233854	-0.044040	0.582539
C	2.612408	-0.545130	-1.146445
H	2.606510	0.177751	-1.963212
H	3.616094	-0.540674	-0.707470
H	2.438430	-1.534934	-1.569561
C	1.745663	2.387424	-0.240923
H	1.040821	3.213216	-0.127462
H	2.668535	2.678101	0.272666
H	2.002769	2.278931	-1.297424
C	-0.296241	2.088579	2.213268
H	0.213553	2.207993	3.175510
H	-0.241647	3.044438	1.691722
H	-1.345801	1.873323	2.422083
C	-0.603232	-0.978687	2.851145
H	-1.522822	-0.418540	3.024511
H	-0.863304	-2.025928	2.698414
H	0.003343	-0.913919	3.761249
C	1.252649	-2.629827	0.808016
H	0.497640	-3.164746	1.383652
H	1.248249	-3.032167	-0.206254
H	2.229246	-2.840938	1.255771
O	-3.017196	0.022434	-0.631557
H	-3.467227	-0.841086	-0.651945
H	-0.142066	1.929268	-2.053610

3_O2_without coordinated water
E= -834.225527 G= -834.012253

W	-0.523364	-0.162483	-0.053866
O	-1.037450	-0.143022	-1.906135
C	1.824044	-0.515685	0.285016
C	1.583603	0.742559	-0.374841
C	1.274829	-0.437597	1.596718
C	0.917877	1.606118	0.557855
C	0.679354	0.860048	1.754051
O	-1.801721	1.229410	0.181467
O	-1.171450	-1.404750	1.255842
C	2.073509	1.102840	-1.738698
H	1.512289	1.931137	-2.170943
H	3.124671	1.403597	-1.674460
H	2.005440	0.254780	-2.421224
C	0.578202	3.040925	0.353893
H	-0.388086	3.289435	0.793272
H	1.342405	3.652174	0.846907
H	0.564430	3.315423	-0.700782
C	0.018589	1.391862	2.982092
H	0.741031	1.976865	3.561558
H	-0.816167	2.048810	2.732369
H	-0.352441	0.592846	3.624104
C	1.350293	-1.492166	2.646129
H	0.493905	-1.464501	3.320097
H	1.414390	-2.492451	2.218277
H	2.251467	-1.325474	3.246757
C	2.567798	-1.658846	-0.314059
H	2.406721	-2.586956	0.233893
H	2.281225	-1.817409	-1.356137
H	3.640849	-1.439369	-0.296756
O	-2.262758	-1.671512	0.346141
H	-3.028366	-1.280119	0.804309
H	-2.441970	1.431925	-0.512102
O	-0.108698	-1.211375	-1.579656

Electronic Supplementary Material (ESI) for Dalton Transactions