Electronic Supplementary Information for

C-H Oxidation by Hydroxo Manganese(V) Porphyrins. A DFT Study

David Balcells, Christophe Raynaud, Robert H. Crabtree and Odile Eisenstein

References for the theoretical methods

BP86 functional:

[1] J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822-8824.
[2] J. P. Perdew, *Phys. Rev. B*, 1986, **34**, 7406.
[3] A. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.

Basis sets:

Stuttgart-Bonn ECP

[4] D. Andrae, U. Haüssermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123-141.
[5] A. Bergner, M. Dolg, W. Küchle, H. Stoll and H. Preuss, *Mol. Phys.*, 1993, **30**, 1431-1441.

6-31g

[6] W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Phys. Chem.*, 1972, **56**, 2257-2261.

6-31g(d,p) basis set:

[7] A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Hollwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 111-114.
[8] A. Höllwarth, H. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **203**, 237-240.
[9] P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213-222.

Natural Population Analysis (NPA):

[10] A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899-926.

Continuum CPCM solvation model:

[11] V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995-2001.

Orbital diagrams

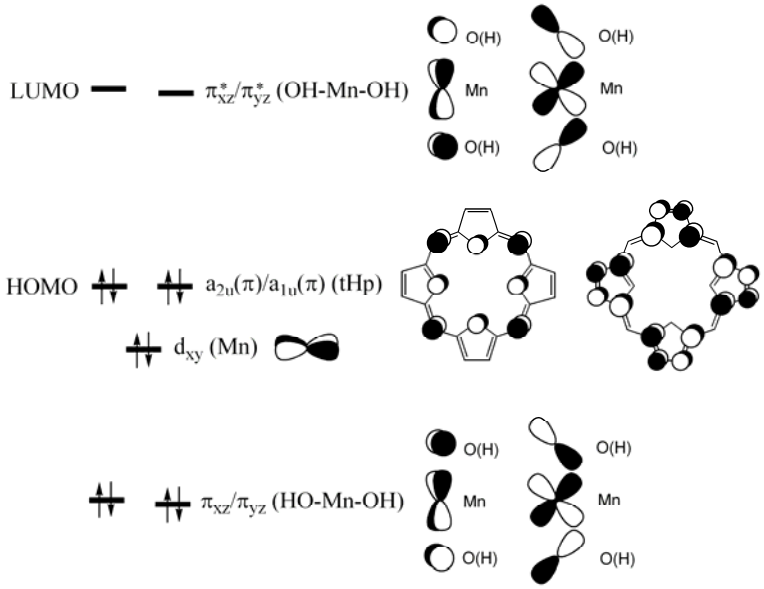

Figure 1. Molecular orbitals of interest in the singlet state of the $[Mn(OH)_2(tHp)]^+$ complex, **S-OH2**.

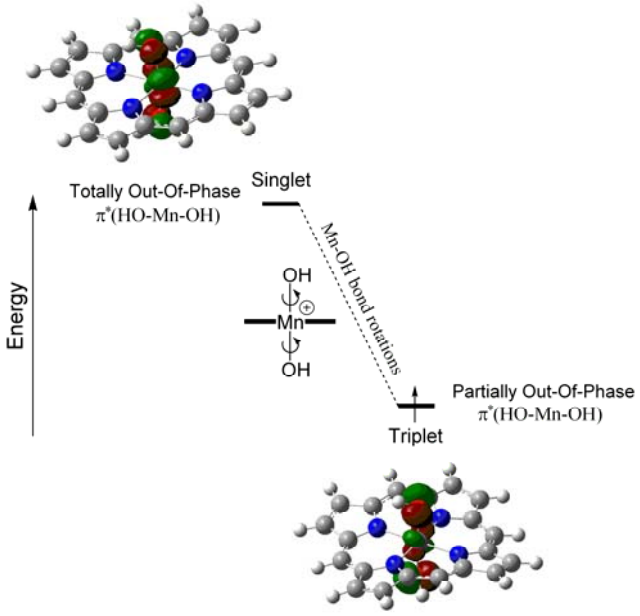

Figure 2. Stabilization of a π*(HO-Mn-OH) orbital from **S-OH2** to **T-OH2** by rotation of the Mn-OH bonds, which reduces the unfavorable overlap between the metal $d_{xz/yz}$ and oxygen $p_{x/y}$ orbitals.

Gas Phase and CPCM(Acetonitrile) Energy Profiles

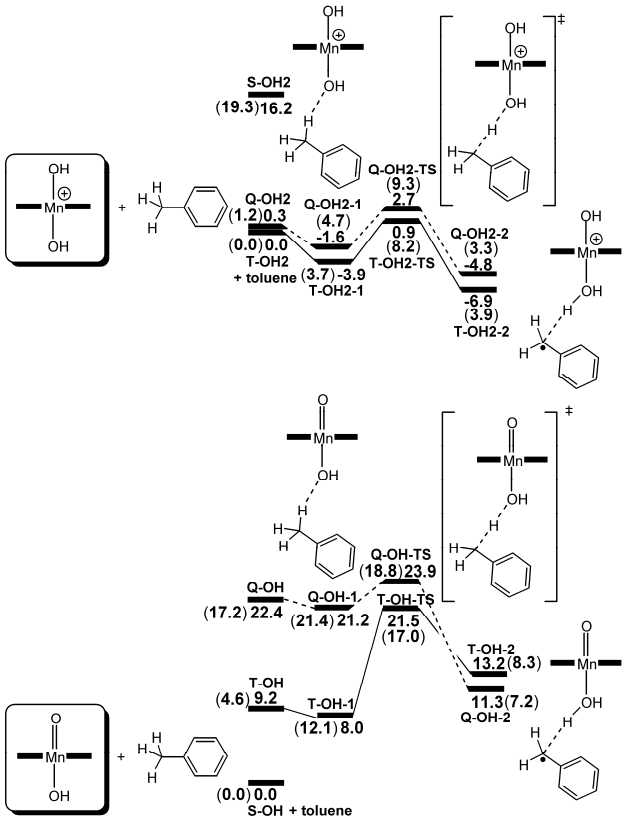

Figure 3. Energy profiles for H abstraction by $[Mn(OH)_2(tHp)]^+$ and MnO(tHp)(OH) with the relative CPCM(acetonitrile) energies given in parenthesis. All energies were computed with basis set II and are given in kcal mol^{-1}.

Mechanistic Details

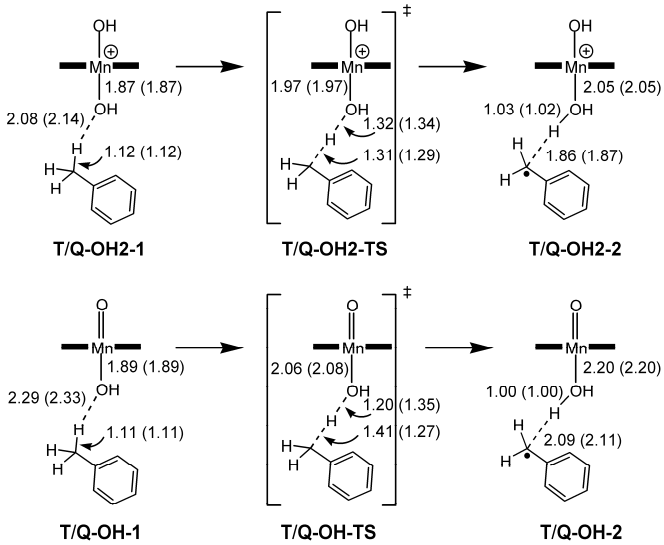

Figure 4. Relevant Mn-O and O-H bond distances, in Å, along the H abstraction pathways in the triplet state. The values for the quintet state are given in parentheses.

Rebound Mechanism Energy Profile

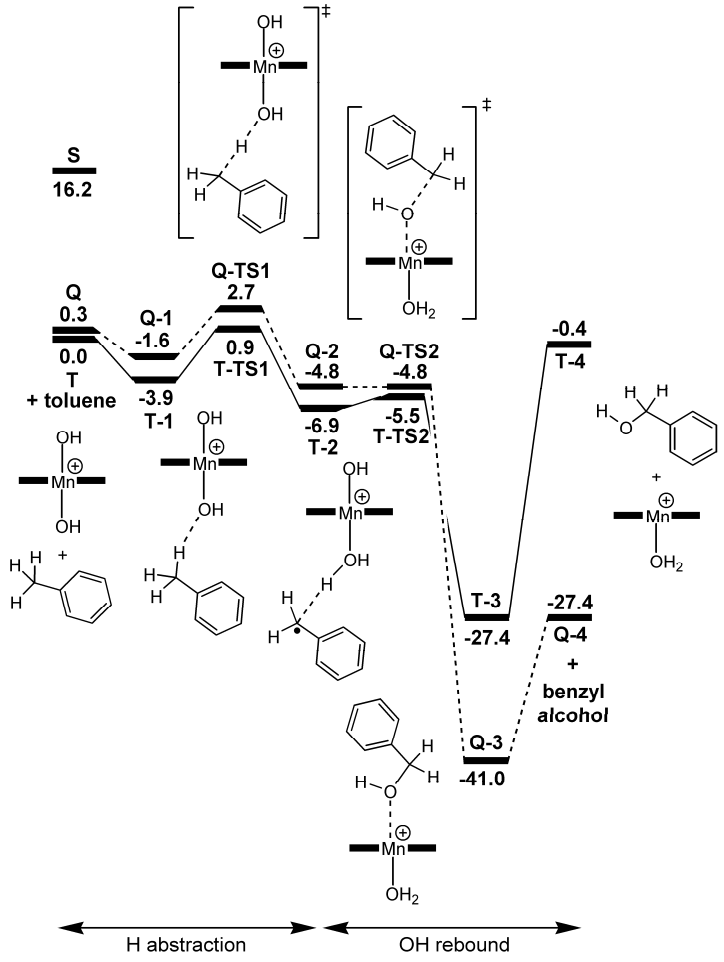

Figure 5. Energy profile for the full rebound mechanism, including the final OH rebound step. All values are gas phase energies at the basis set II level in kcal mol^{-1}.

Dependence of the results on the nature of the functional

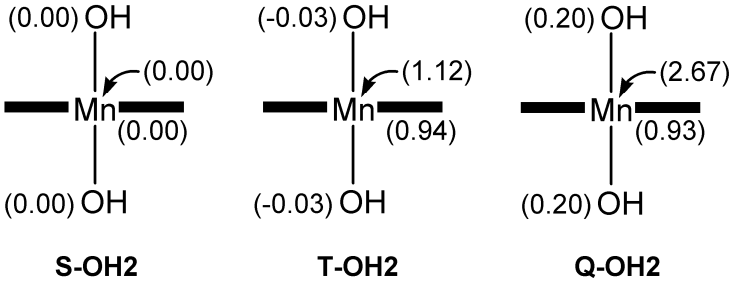

Figure 6. Spin densities of $[Mn(OH)_2(tHp)]^+$ recomputed at the DFT(B3LYP) level with basis set II. In the triplet state, two unpaired electrons, one in Mn and the other in tHp, are ferromagnetically coupled, in contrast with the antiferromagnetic coupling found at the DFT(BP86) level.

Spin density evolution along the reaction pathway

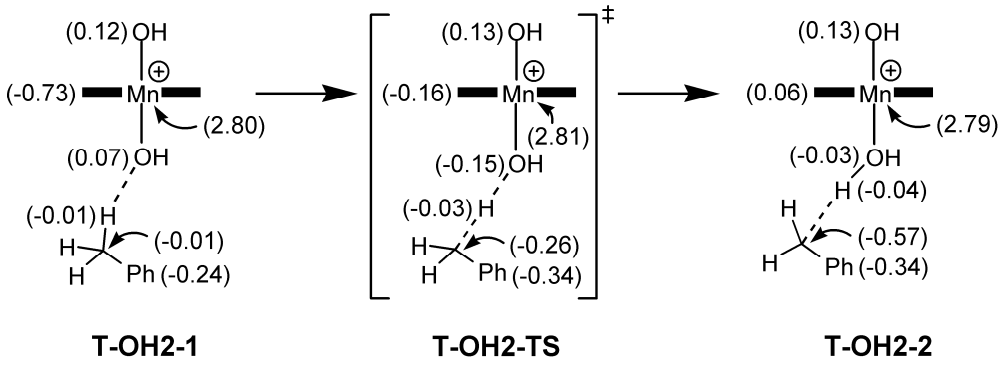

Figure 7. Evolution of the spin densities in toluene hydrogen abstraction by the triplet state of $[Mn(OH)_2(tHp)]^+$.

Full Gaussian03 reference

M. J. Frisch, G.W. Trucks, H.B. Schlegel, G. E. Scuseria, M.A.Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H.Nakatsuji,M.Hada,M. Ehara, K. Toyota,R.Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox,H. P.Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, GAUSSIAN 03 (Revision D.01), Gaussian, Inc., Wallingford, CT, 2004.

Geometries and energies

Optimized geometries with their absolute gas phase potential energies (E) and CPCM(acetonitrile) energies (E_{CPCM}) with basis set II:

S-OH2 E=-1244.29656239 E_{CPCM}=-1244.352657

Mn	0.109697	0.000000	0.000001
O	-0.119042	0.000000	1.747140
O	-0.119042	0.000000	-1.747139
C	2.868931	1.231508	0.000001
C	3.513648	2.524775	0.000000
C	2.518837	3.478430	-0.000001
C	1.247558	2.786225	-0.000001
N	1.470136	1.384360	0.000000
H	4.591121	2.678651	0.000000
H	2.629407	4.561418	-0.000002
C	0.011930	3.424583	-0.000001
C	-2.524914	3.501470	-0.000001
C	-3.506384	2.533539	0.000000
C	-2.835201	1.244161	0.000001
N	-1.445492	1.433915	0.000000
C	-1.248619	2.808113	-0.000001
H	-2.646799	4.583114	-0.000001
H	-4.586370	2.670726	0.000001
C	3.520445	0.000003	0.000001
N	1.470138	-1.384357	0.000000
C	1.247562	-2.786223	-0.000001
C	2.518843	-3.478426	-0.000001
C	3.513653	-2.524770	0.000000
C	2.868933	-1.231504	0.000001
H	2.629414	-4.561414	-0.000001
H	4.591125	-2.678644	0.000001
C	0.011935	-3.424583	-0.000001
N	-1.445490	-1.433917	0.000000
C	-2.835199	-1.244166	0.000001
C	-3.506380	-2.533545	0.000000
C	-2.524909	-3.501474	-0.000001
C	-1.248614	-2.808115	-0.000001
H	-4.586365	-2.670734	0.000001
H	-2.646791	-4.583118	-0.000002
C	-3.474963	-0.000003	0.000001
H	-4.568718	-0.000004	0.000002
H	0.026898	-4.518566	-0.000002
H	4.613587	0.000004	0.000002
H	0.026890	4.518567	-0.000002
H	-1.039385	-0.000006	2.119832
H	-1.039385	-0.000007	-2.119830

toluene E=-271.559247897 E_{CPCM}=-271.553822

C	2.440570	0.000056	0.009313
H	2.828368	-0.008580	1.046883
H	2.851697	0.897557	-0.485430
H	2.851971	-0.889088	-0.500181
C	0.922670	0.000096	-0.011135
C	0.197121	-1.214109	-0.008989
C	-1.210208	-1.216423	0.002118
C	-1.919796	-0.000063	0.008522
C	-1.210381	1.216338	0.002120
C	0.196999	1.214156	-0.008991
H	0.742886	-2.164757	-0.018062
H	-1.752377	-2.167896	0.001458
H	-3.014455	-0.000142	0.014182
H	-1.752630	2.167764	0.001462
H	0.742699	2.164836	-0.018064

T-OH2 E=-1244.32243736 E_{CPCM}=-1244.383379

Mn	-0.018626	-0.000096	0.000009
O	0.019895	-0.058904	-1.849285
O	0.017698	0.057823	1.849351
C	-2.867042	-1.081573	0.220889
C	-4.254383	-0.654383	0.148444
C	-4.248753	0.690629	-0.146702
C	-2.857874	1.105958	-0.220154
N	-2.025767	0.008610	0.000120
H	-5.112642	-1.309325	0.285774
H	-5.101482	1.352874	-0.283467
C	-2.415024	2.425645	-0.365561
C	-0.667014	4.247331	-0.130061
C	0.680228	4.241028	0.161680
C	1.100802	2.852296	0.211415
N	0.003624	2.019465	-0.029360
C	-1.089516	2.861427	-0.226018
H	-1.325039	5.106137	-0.248138
H	1.338660	5.094216	0.313707
C	-2.435396	-2.405110	0.365423
N	-0.013617	-2.019482	0.028023
C	1.076487	-2.861444	-0.212664
C	0.644146	-4.246611	-0.163396
C	-0.703077	-4.241571	0.128406
C	-1.113798	-2.852145	0.224812
H	1.295333	-5.105312	-0.315578
H	-1.368349	-5.094791	0.246366
C	2.399945	-2.429724	-0.358433
N	2.014728	-0.008613	0.001212
C	2.858156	1.085146	0.217188
C	4.242350	0.656725	0.144548
C	4.236611	-0.692638	-0.143011
C	2.848846	-1.109335	-0.215513

H	5.102013	1.310928	0.277371
H	5.090682	-1.354060	-0.276166
C	2.420424	2.409453	0.358556
H	3.186113	3.171730	0.529386
H	3.159224	-3.198325	-0.529538
H	-3.204991	-3.166518	0.521614
H	-3.178163	3.193582	-0.521475
H	0.645958	0.574011	-2.286756
H	0.648104	-0.570585	2.287074

T-OH2-1 E=-1515.88790678 E_{CPCM}=-1515.931354

Mn	1.270040	0.053167	0.101178
O	3.083647	0.182965	0.417998
O	-0.553056	-0.124279	-0.287791
C	1.109222	-1.645576	2.637145
C	1.017090	-3.026231	3.077523
C	0.967128	-3.811872	1.946257
C	1.065389	-2.923424	0.801514
N	1.141086	-1.599308	1.242822
H	0.979595	-3.343038	4.118204
H	0.896191	-4.896276	1.883782
C	1.205381	-3.332057	-0.529014
C	1.867294	-2.938277	-2.944336
C	2.233547	-1.820108	-3.663355
C	2.085098	-0.675652	-2.783433
N	1.663783	-1.106634	-1.520784
C	1.523224	-2.496078	-1.605656
H	1.846325	-3.974031	-3.278484
H	2.555612	-1.764895	-4.701647
C	1.062199	-0.522307	3.470989
N	0.915899	1.206308	1.702836
C	0.643205	2.575305	1.709642
C	0.474348	3.032158	3.078880
C	0.678116	1.944277	3.898418
C	0.936313	0.801826	3.038545
H	0.254578	4.058830	3.365970
H	0.642529	1.904955	4.985581
C	0.654032	3.399142	0.579839
N	1.354584	1.696641	-1.078742
C	1.845220	1.768154	-2.387933
C	1.813716	3.145868	-2.844638
C	1.293526	3.904170	-1.818343
C	1.033646	3.003918	-0.708871
H	2.138065	3.479040	-3.828809
H	1.123998	4.979118	-1.796057
C	2.212260	0.665365	-3.165559
H	2.561574	0.864532	-4.182564
H	0.434674	4.459650	0.732323
H	1.049012	-0.699936	4.549976
H	1.135851	-4.404336	-0.732733

H	3.613601	-0.608581	0.139968
H	-0.799578	0.237732	-1.178471
C	-4.508401	-0.343817	0.255544
C	-4.994908	-1.390765	-0.580048
C	-6.054447	-1.168041	-1.469435
C	-6.656189	0.109814	-1.547747
C	-6.186706	1.161004	-0.725687
C	-5.126724	0.936242	0.163000
H	-4.533971	-2.381932	-0.513142
H	-6.422804	-1.983515	-2.098749
H	-7.486567	0.283239	-2.238412
H	-6.657831	2.146870	-0.779258
H	-4.769103	1.747118	0.806442
C	-3.356593	-0.579342	1.192156
H	-2.373705	-0.411252	0.679968
H	-3.387186	0.106487	2.056826
H	-3.339962	-1.619698	1.562878

T-OH2-TS E=-1515.88023957 E_{CPCM}=-1515.924185

Mn	1.135366	0.067574	0.340811
O	2.683545	0.196525	1.283735
O	-0.478979	-0.105876	-0.767877
C	0.463070	-2.296354	2.143048
C	0.470989	-3.746869	2.157620
C	0.856004	-4.168585	0.902536
C	1.132919	-2.982811	0.112653
N	0.865168	-1.842035	0.880589
H	0.201342	-4.357427	3.017674
H	0.976832	-5.189873	0.545382
C	1.727992	-2.976068	-1.151604
C	3.054050	-1.848699	-2.989589
C	3.477729	-0.554844	-3.207915
C	2.898107	0.271686	-2.166329
N	2.159938	-0.535328	-1.289074
C	2.243090	-1.843663	-1.786828
H	3.282011	-2.737133	-3.576012
H	4.104930	-0.181095	-4.015355
C	0.009038	-1.473756	3.177182
N	0.089508	0.670663	1.930483
C	-0.402064	1.957539	2.184248
C	-1.031898	1.983312	3.491238
C	-0.882953	0.729134	4.044510
C	-0.200169	-0.096948	3.067170
H	-1.495825	2.862283	3.935614
H	-1.217061	0.382287	5.020831
C	-0.195033	3.072105	1.367366
N	1.268205	1.974325	-0.309997
C	2.155523	2.463060	-1.282072
C	2.043561	3.907397	-1.354079
C	1.088049	4.293034	-0.438906

C	0.630105	3.094729	0.239945
H	2.617473	4.537687	-2.031151
H	0.742761	5.300441	-0.213099
C	2.936925	1.668260	-2.123237
H	3.563285	2.177941	-2.860098
H	-0.619897	4.023731	1.697822
H	-0.277899	-1.954312	4.116222
H	1.887774	-3.942052	-1.638022
H	3.420825	-0.362790	0.923038
H	-0.610658	0.679401	-1.361080
C	-3.872743	-0.558775	-0.693676
C	-4.236611	-1.335309	-1.843379
C	-5.287642	-0.934859	-2.673196
C	-6.000966	0.255057	-2.390815
C	-5.653281	1.042459	-1.266514
C	-4.602758	0.647856	-0.433278
H	-3.684815	-2.256525	-2.056700
H	-5.563783	-1.542288	-3.539573
H	-6.823006	0.566096	-3.041766
H	-6.212683	1.956572	-1.048646
H	-4.336909	1.249444	0.442166
C	-2.772041	-0.969186	0.167577
H	-1.645843	-0.510081	-0.305806
H	-2.770848	-0.538915	1.180791
H	-2.532363	-2.044728	0.154564

T-OH2-2 E=-1515.89275513 E_{CPCM}=-1515.931018

Mn	1.159102	0.053741	0.353717
O	2.672419	0.131080	1.331628
O	-0.549027	-0.050812	-0.775270
C	0.498644	-2.436244	1.977433
C	0.524331	-3.883008	1.886808
C	0.899727	-4.209505	0.600189
C	1.157852	-2.968526	-0.105255
N	0.883631	-1.886964	0.745314
H	0.269538	-4.557432	2.702575
H	1.026323	-5.201510	0.169885
C	1.748031	-2.863103	-1.366602
C	3.091617	-1.592537	-3.091956
C	3.524703	-0.286773	-3.197893
C	2.928160	0.457362	-2.107143
N	2.168024	-0.414386	-1.309901
C	2.260941	-1.681705	-1.907601
H	3.328269	-2.431861	-3.743675
H	4.168805	0.146389	-3.961167
C	0.033146	-1.695729	3.066428
N	0.062029	0.522980	1.954428
C	-0.464618	1.779567	2.284866
C	-1.100814	1.707028	3.586249
C	-0.917420	0.425866	4.064140

C	-0.209123	-0.320434	3.042917
H	-1.591933	2.543302	4.081016
H	-1.244600	0.012053	5.016484
C	-0.272819	2.949689	1.545623
N	1.248481	1.994466	-0.170481
C	2.154228	2.567812	-1.077716
C	2.018425	4.010948	-1.048439
C	1.028590	4.313544	-0.137877
C	0.574632	3.063080	0.441043
H	2.599720	4.698227	-1.660700
H	0.657713	5.296267	0.148234
C	2.963314	1.846136	-1.957536
H	3.601732	2.412897	-2.640091
H	-0.722836	3.868419	1.931003
H	-0.242575	-2.243400	3.971304
H	1.916305	-3.787802	-1.924772
H	3.412357	-0.409707	0.946936
H	-0.715168	0.724785	-1.359901
C	-3.949973	-0.628401	-0.680219
C	-4.242251	-1.246368	-1.948334
C	-5.170993	-0.679306	-2.823624
C	-5.838502	0.519968	-2.477044
C	-5.567721	1.148740	-1.237718
C	-4.640926	0.592630	-0.353325
H	-3.732428	-2.179166	-2.211634
H	-5.389371	-1.166548	-3.778217
H	-6.567742	0.958036	-3.164218
H	-6.093409	2.069805	-0.969709
H	-4.439468	1.071288	0.610922
C	-3.002596	-1.201619	0.214896
H	-1.420090	-0.446387	-0.403825
H	-2.889946	-0.805776	1.230460
H	-2.602539	-2.204893	0.025905

Q-OH2 E=-1244.32199225 E_{CPCM}=-1244.381419

Mn	0.000704	0.006102	0.000027
O	0.092104	0.039786	1.848851
O	-0.079709	0.062406	-1.848800
C	-0.878006	2.955070	-0.000735
C	-2.061820	3.797096	-0.035890
C	-3.152892	2.958056	-0.066318
C	-2.642650	1.597944	-0.044888
N	-1.248909	1.612491	-0.006333
H	-2.048124	4.885316	-0.038092
H	-4.207698	3.224314	-0.096114
C	-3.429001	0.441842	-0.035197
C	-3.792771	-2.058906	0.023287
C	-2.952374	-3.150959	0.053866
C	-1.594590	-2.642937	0.066292

N	-1.607275	-1.243248	0.068843
C	-2.955438	-0.875124	0.021945
H	-4.880795	-2.047520	-0.001644
H	-3.219289	-4.206077	0.056904
C	0.439899	3.425036	0.029864
N	1.616579	1.244864	0.008144
C	2.962032	0.878721	0.009067
C	3.799552	2.065680	0.040614
C	2.955197	3.152723	0.058190
C	1.596627	2.636849	0.036611
H	4.887797	2.056782	0.047003
H	3.216472	4.208943	0.081342
C	3.430592	-0.437782	-0.025435
N	1.241128	-1.609575	-0.070643
C	0.876083	-2.960687	-0.030277
C	2.062076	-3.794613	-0.028089
C	3.150783	-2.949706	-0.045820
C	2.638585	-1.593055	-0.058089
H	2.054445	-4.882755	-0.007584
H	4.206907	-3.212613	-0.042044
C	-0.439595	-3.432503	0.030678
H	-0.578509	-4.517399	0.046139
H	4.514974	-0.581038	-0.016314
H	0.579201	4.509909	0.043504
H	-4.513792	0.576929	-0.073511
H	-0.632322	-0.442142	2.325335
H	0.419570	-0.650939	-2.324136

Q-OH2-1 E=-1515.88427312 E_{CPCM}=-1515.929675

Mn	1.283132	0.052090	0.104968
O	3.089158	0.192833	0.466746
O	-0.558915	-0.034506	-0.222975
C	1.307657	-2.870957	1.093141
C	1.429319	-4.233770	0.611404
C	1.604997	-4.169138	-0.753761
C	1.604239	-2.765693	-1.119352
N	1.437837	-1.976792	0.025460
H	1.374876	-5.119297	1.242031
H	1.727197	-4.991176	-1.456690
C	1.758950	-2.273394	-2.418764
C	2.084348	-0.424372	-4.111692
C	2.126207	0.950336	-4.030176
C	1.847326	1.308131	-2.652605
N	1.626201	0.149899	-1.897386
C	1.793390	-0.923727	-2.781481
H	2.251017	-1.052378	-4.984949
H	2.328347	1.665775	-4.825184
C	1.041215	-2.510870	2.418694
N	0.858415	-0.062639	2.090480
C	0.586227	1.005174	2.943261

C	0.358119	0.513645	4.291893
C	0.510597	-0.853927	4.255548
C	0.822702	-1.211430	2.882171
H	0.126909	1.143703	5.148814
H	0.423810	-1.564363	5.075598
C	0.586699	2.354233	2.573418
N	1.201366	2.078915	0.187785
C	1.479641	2.976016	-0.843614
C	1.342957	4.339527	-0.361225
C	0.971733	4.264627	0.962187
C	0.891226	2.854840	1.304949
H	1.506072	5.229211	-0.966599
H	0.777189	5.081385	1.654819
C	1.792763	2.614444	-2.156956
H	1.994187	3.424122	-2.863878
H	0.361443	3.084478	3.355806
H	0.976073	-3.320582	3.150918
H	1.894058	-3.008043	-3.217552
H	3.600996	-0.652212	0.372969
H	-0.793570	0.190794	-1.160912
C	-4.561949	-0.493223	0.133669
C	-5.065227	-1.308267	-0.920701
C	-6.107643	-0.859095	-1.742601
C	-6.674766	0.419772	-1.531524
C	-6.188062	1.242707	-0.488753
C	-5.145969	0.791469	0.332021
H	-4.632341	-2.301918	-1.077672
H	-6.489750	-1.499494	-2.542986
H	-7.491860	0.769033	-2.169480
H	-6.631873	2.228205	-0.319825
H	-4.774010	1.424722	1.144372
C	-3.427107	-0.965534	1.000948
H	-2.439477	-0.629667	0.597083
H	-3.502689	-0.558504	2.024930
H	-3.391099	-2.067504	1.059036

Q-OH2-TS E=-1515.87742892 E_{CPCM}=-1515.922357

Mn	1.159933	0.072760	0.319466
O	2.726013	0.168633	1.239982
O	-0.529156	0.012953	-0.697296
C	0.125455	-1.594128	2.677926
C	-0.097250	-2.968965	3.079487
C	0.221735	-3.769479	2.001764
C	0.682551	-2.899269	0.937368
N	0.613664	-1.565606	1.364098
H	-0.467998	-3.274981	4.056280
H	0.176710	-4.855279	1.935717
C	1.230378	-3.327008	-0.276347
C	2.677897	-2.958581	-2.318390
C	3.294733	-1.852564	-2.863761

C	2.852440	-0.694228	-2.112574
N	1.977145	-1.104113	-1.095683
C	1.879309	-2.501396	-1.197284
H	2.772831	-3.998983	-2.624505
H	3.978285	-1.814417	-3.710140
C	-0.214285	-0.464848	3.429678
N	0.219035	1.228456	1.670529
C	-0.036083	2.597216	1.561343
C	-0.659578	3.072758	2.784381
C	-0.740197	2.001319	3.646669
C	-0.204011	0.845902	2.949379
H	-0.962552	4.103149	2.962296
H	-1.136286	1.981883	4.660545
C	0.374284	3.411026	0.501348
N	1.638788	1.689090	-0.760576
C	2.555481	1.746031	-1.819449
C	2.681475	3.118075	-2.274677
C	1.825505	3.883849	-1.513839
C	1.192807	3.000890	-0.551047
H	3.331271	3.441669	-3.085825
H	1.651045	4.956675	-1.573847
C	3.152224	0.635783	-2.419347
H	3.847025	0.819264	-3.243002
H	0.115281	4.471901	0.552801
H	-0.583223	-0.628508	4.445691
H	1.236388	-4.402386	-0.473572
H	3.086753	-0.713602	1.518686
H	-0.399750	-0.150529	-1.666819
C	-3.927578	-0.525041	-0.672021
C	-4.367328	-1.356400	-1.755354
C	-5.424937	-0.959694	-2.577831
C	-6.069707	0.281664	-2.354942
C	-5.646011	1.123537	-1.297844
C	-4.588747	0.732470	-0.472269
H	-3.871918	-2.319049	-1.919478
H	-5.760796	-1.608827	-3.391280
H	-6.896912	0.590299	-3.000467
H	-6.150959	2.078417	-1.127402
H	-4.258691	1.378997	0.347090
C	-2.819579	-0.932298	0.182663
H	-1.715581	-0.455321	-0.280246
H	-2.799776	-0.473210	1.184848
H	-2.610663	-2.013368	0.205714

Q-OH2-2 E=-1515.88937321 E_{CPCM}=-1515.931919

Mn	-1.204232	0.015577	0.235816
O	-2.888680	0.010773	0.884012
O	0.698075	0.014154	-0.517930
C	-0.401388	1.318791	2.876575
C	-0.078431	2.613002	3.442522

C	-0.081613	3.528368	2.409747
C	-0.453854	2.820210	1.201000
N	-0.641743	1.461394	1.499966
H	0.144684	2.788896	4.493494
H	0.122284	4.596639	2.460582
C	-0.728207	3.414196	-0.033861
C	-1.901527	3.414338	-2.275248
C	-2.589392	2.456573	-2.991663
C	-2.414284	1.191863	-2.306662
N	-1.635310	1.391679	-1.154592
C	-1.333293	2.762808	-1.111389
H	-1.809698	4.476978	-2.493382
H	-3.152013	2.585622	-3.914677
C	-0.332904	0.096675	3.550651
N	-0.590856	-1.357993	1.558786
C	-0.444248	-2.733134	1.334535
C	-0.093863	-3.388392	2.581681
C	-0.085238	-2.423049	3.566107
C	-0.381905	-1.153571	2.930141
H	0.083191	-4.457273	2.688535
H	0.117840	-2.549407	4.628171
C	-0.749985	-3.389250	0.139610
N	-1.653609	-1.424048	-1.078374
C	-2.439121	-1.279008	-2.231125
C	-2.643004	-2.578937	-2.840699
C	-1.960735	-3.502887	-2.077670
C	-1.368975	-2.790745	-0.960309
H	-3.218604	-2.752098	-3.748292
H	-1.886728	-4.577821	-2.233187
C	-2.828449	-0.055423	-2.780136
H	-3.424724	-0.077124	-3.695889
H	-0.605378	-4.472396	0.108443
H	-0.137156	0.121840	4.625757
H	-0.560313	4.490554	-0.124447
H	-3.205377	0.913062	1.154916
H	0.832086	0.092046	-1.488367
C	4.119508	-0.243761	-0.159213
C	4.650360	1.072510	-0.405436
C	5.571031	1.292401	-1.432257
C	5.994511	0.219897	-2.253618
C	5.486306	-1.083114	-2.034277
C	4.564969	-1.316776	-1.010999
H	4.330941	1.899637	0.237462
H	5.973336	2.295871	-1.598680
H	6.718682	0.396802	-3.053728
H	5.823401	-1.911169	-2.664505
H	4.181071	-2.326988	-0.832941
C	3.179267	-0.475166	0.884809
H	1.564200	-0.163023	-0.003719
H	2.893599	-1.498172	1.155381

H	2.962715	0.310927	1.617621

S-OH E=-1243.92218073 E_{CPCM}=-1243.925542

Mn	0.063897	0.025997	-0.090466
O	-0.049406	-0.009135	1.736544
O	-0.197481	-0.091534	-1.652646
C	2.638912	1.626355	-0.061179
C	3.112149	2.997353	-0.020032
C	2.003374	3.810989	0.047701
C	0.832454	2.952653	0.040673
N	1.238605	1.609512	-0.029253
H	4.161735	3.287785	-0.034412
H	1.967847	4.898521	0.095986
C	-0.481959	3.417528	0.072233
C	-3.003600	3.115809	0.023982
C	-3.825363	2.013226	-0.038647
C	-2.965925	0.835988	-0.053992
N	-1.630234	1.236277	-0.002756
C	-1.632666	2.623601	0.039381
H	-3.285882	4.167368	0.053797
H	-4.913907	1.984067	-0.067485
C	3.456994	0.497583	-0.098122
N	1.655437	-1.193589	-0.033610
C	1.636195	-2.592539	0.037925
C	3.001806	-3.094159	0.042717
C	3.839741	-2.004451	-0.025686
C	2.998215	-0.820308	-0.066278
H	3.269703	-4.148801	0.091801
H	4.928639	-1.989815	-0.039936
C	0.501425	-3.404145	0.078841
N	-1.222034	-1.633400	0.045026
C	-2.616001	-1.629923	-0.037311
C	-3.103578	-3.002237	-0.046564
C	-2.001670	-3.826431	0.016048
C	-0.827089	-2.966916	0.057689
H	-4.154408	-3.285001	-0.096228
H	-1.974061	-4.915285	0.025159
C	-3.419226	-0.486228	-0.079039
H	-4.501689	-0.639746	-0.125211
H	0.669148	-4.485085	0.109592
H	4.538540	0.657808	-0.122908
H	-0.622282	4.501882	0.112573
H	-0.863270	-0.392347	2.149843

T-OH E=-1243.90746198 E_{CPCM}=-1243.918213

Mn	-0.025738	0.021163	-0.067946
O	-0.002268	-0.143481	1.809459
O	0.108193	-0.130435	-1.721781
C	-2.654666	-1.563905	-0.183182
C	-3.166909	-2.925306	-0.118518

C	-2.091409	-3.750406	0.117196
C	-0.902991	-2.908547	0.170773
N	-1.276630	-1.577986	-0.006072
H	-4.216204	-3.196865	-0.223751
H	-2.083884	-4.833437	0.231251
C	0.406064	-3.384262	0.281213
C	2.923744	-3.147545	0.099884
C	3.768480	-2.084838	-0.132767
C	2.946262	-0.884987	-0.181470
N	1.611576	-1.233735	0.013072
C	1.569234	-2.617905	0.171123
H	3.179487	-4.201491	0.199593
H	4.851454	-2.096907	-0.247240
C	-3.427452	-0.406503	-0.305794
N	-1.600249	1.255959	-0.031065
C	-1.575568	2.639747	0.161761
C	-2.932693	3.156571	0.118113
C	-3.769430	2.090021	-0.120920
C	-2.941851	0.897667	-0.195711
H	-3.195862	4.206063	0.241141
H	-4.853953	2.092186	-0.219352
C	-0.423451	3.418115	0.285284
N	1.239876	1.601243	0.012119
C	2.626175	1.576024	-0.182773
C	3.142796	2.933418	-0.133194
C	2.076184	3.771352	0.105569
C	0.885281	2.942390	0.176442
H	4.192972	3.196659	-0.251406
H	2.079367	4.855678	0.206361
C	3.412324	0.426378	-0.301108
H	4.488174	0.569028	-0.436893
H	-0.557969	4.496408	0.408602
H	-4.507373	-0.531025	-0.425228
H	0.532747	-4.464816	0.396068
H	0.844354	0.187545	2.210189

T-OH-1 E=-1515.46864810 E_{CPCM}=-1515.460084

Mn	1.181784	0.026621	0.466180
O	2.512153	0.323038	1.421948
O	-0.344189	0.098408	-0.643573
C	0.739805	3.085828	0.414483
C	0.225207	4.181315	1.224277
C	-0.246848	3.637720	2.398541
C	-0.053333	2.198004	2.313674
N	0.540769	1.884638	1.093401
H	0.245485	5.229092	0.927884
H	-0.700615	4.151889	3.244547
C	-0.482902	1.252636	3.248212
C	-1.054185	-1.103191	3.960833
C	-0.895965	-2.345156	3.387592

C	-0.148035	-2.158214	2.156170
N	0.115693	-0.799323	1.971995
C	-0.434115	-0.133075	3.073671
H	-1.560224	-0.850107	4.891356
H	-1.233105	-3.309784	3.764012
C	1.417189	3.226853	-0.799607
N	2.138345	0.870125	-1.118618
C	3.001445	0.237744	-2.004467
C	3.509851	1.208073	-2.963994
C	2.931288	2.418601	-2.658510
C	2.084619	2.211738	-1.490248
H	4.203727	0.975460	-3.770386
H	3.068334	3.376813	-3.157639
C	3.253340	-1.136447	-2.019051
N	1.695438	-1.788131	-0.193795
C	1.211514	-3.015199	0.268886
C	1.843725	-4.092761	-0.472221
C	2.722295	-3.517191	-1.362440
C	2.617523	-2.076386	-1.205577
H	1.644256	-5.150975	-0.310154
H	3.373637	-4.011025	-2.082018
C	0.331494	-3.184450	1.339089
H	0.053028	-4.208736	1.602268
H	3.945369	-1.515717	-2.776136
H	1.493738	4.237958	-1.210289
H	-0.954537	1.624960	4.161980
H	-1.188149	0.271623	-0.149990
C	-3.776710	-0.519971	-2.226139
C	-4.224570	0.819388	-2.333113
C	-5.364873	1.261166	-1.636743
C	-6.084817	0.369723	-0.817178
C	-5.653412	-0.965592	-0.701986
C	-4.512484	-1.403500	-1.401057
H	-3.670666	1.517955	-2.970756
H	-5.694168	2.301056	-1.736914
H	-6.974255	0.711427	-0.277856
H	-6.208087	-1.668892	-0.071457
H	-4.184883	-2.445657	-1.310879
C	-2.524872	-0.981878	-2.946891
H	-1.616506	-0.713920	-2.368200
H	-2.522370	-2.077251	-3.087546
H	-2.433095	-0.509097	-3.941449

T-OH-TS E=-1515.44716726 E_{CPCM}=-1515.452336

Mn	1.169584	0.069433	0.420379
O	2.627461	0.216463	1.223358
O	-0.491220	-0.023332	-0.792867
C	0.605316	3.039079	1.060334
C	-0.072248	3.880095	2.033540
C	-0.734350	3.044898	2.904451

C	-0.456779	1.680469	2.485986
N	0.352260	1.692875	1.346925
H	-0.041612	4.968823	2.034045
H	-1.345840	3.314031	3.764665
C	-0.886136	0.533457	3.156577
C	-0.889717	-1.951940	3.606674
C	-0.282969	-3.035500	3.011914
C	0.445632	-2.542175	1.856246
N	0.280833	-1.155798	1.755548
C	-0.526611	-0.776321	2.833595
H	-1.516466	-1.934096	4.497261
H	-0.321818	-4.080892	3.314965
C	1.346463	3.509785	-0.025407
N	1.866756	1.316549	-1.050483
C	2.530097	0.921286	-2.212908
C	2.984446	2.099361	-2.936398
C	2.620927	3.199951	-2.193881
C	1.923784	2.710784	-1.014655
H	3.524443	2.071665	-3.881841
H	2.796976	4.251783	-2.414957
C	2.780256	-0.398351	-2.594636
N	1.816920	-1.552665	-0.618009
C	1.778682	-2.882448	-0.204824
C	2.423963	-3.723761	-1.202174
C	2.839810	-2.897223	-2.219986
C	2.470620	-1.537808	-1.849803
H	2.528615	-4.804986	-1.123564
H	3.360154	-3.165825	-3.138306
C	1.155974	-3.340193	0.957860
H	1.196818	-4.413625	1.163559
H	3.311646	-0.550874	-3.538683
H	1.458737	4.593249	-0.124435
H	-1.515106	0.675409	4.040270
H	-0.808041	0.885555	-1.027893
C	-3.745884	-0.791605	-1.000199
C	-4.047873	-1.053456	-2.373601
C	-5.094393	-0.386828	-3.024447
C	-5.872550	0.567047	-2.332161
C	-5.590530	0.844803	-0.976479
C	-4.545766	0.180312	-0.320432
H	-3.444452	-1.790648	-2.914481
H	-5.310214	-0.608254	-4.074818
H	-6.689014	1.087091	-2.842652
H	-6.192989	1.580680	-0.433755
H	-4.330451	0.396604	0.731861
C	-2.629478	-1.448167	-0.333618
H	-1.464679	-0.687735	-0.562129
H	-2.646678	-1.454723	0.765811
H	-2.281076	-2.394135	-0.775594

T-OH-2 E=-1515.46046785 E_{CPCM}=-1515.466188

Mn	-1.245029	0.021353	0.401269
O	-2.641875	0.062280	1.340139
O	0.549825	0.007038	-0.866313
C	0.495692	-0.204263	2.940165
C	1.172922	0.614354	3.932916
C	1.044417	1.926287	3.534516
C	0.276858	1.927394	2.299257
N	-0.037616	0.613197	1.938020
H	1.674626	0.223323	4.817243
H	1.415944	2.821902	4.031012
C	-0.115725	3.073901	1.604988
C	-1.401196	4.302349	-0.191092
C	-2.208419	3.905111	-1.233674
C	-2.222588	2.452422	-1.238577
N	-1.411544	1.968539	-0.204020
C	-0.918464	3.097829	0.462837
H	-1.158024	5.315819	0.125620
H	-2.752140	4.529630	-1.941377
C	0.423989	-1.598560	2.964978
N	-0.823322	-1.913193	0.843674
C	-1.264504	-3.038829	0.143102
C	-0.864297	-4.244683	0.851134
C	-0.202061	-3.847322	1.990193
C	-0.179344	-2.393041	1.988130
H	-1.080387	-5.257684	0.514102
H	0.235203	-4.470243	2.769475
C	-2.012667	-3.016865	-1.035151
N	-2.238313	-0.558208	-1.272167
C	-2.916854	0.262575	-2.174693
C	-3.590320	-0.555764	-3.172637
C	-3.313869	-1.869085	-2.872815
C	-2.476913	-1.870674	-1.681613
H	-4.188748	-0.160682	-3.992475
H	-3.644519	-2.765802	-3.395244
C	-2.919395	1.658398	-2.151171
H	-3.505310	2.172557	-2.918609
H	-2.287094	-3.982225	-1.470647
H	0.889391	-2.110572	3.812324
H	0.197144	4.038439	2.015909
H	0.611576	0.906131	-1.269777
C	4.109514	-0.354386	-0.605882
C	4.746897	0.932822	-0.708006
C	5.582129	1.238927	-1.785845
C	5.816738	0.284789	-2.803658
C	5.202094	-0.987127	-2.727854
C	4.365224	-1.306355	-1.655333
H	4.568975	1.671304	0.081356
H	6.059318	2.222556	-1.841812
H	6.470804	0.529516	-3.645858

H	5.383115	-1.726312	-3.514599
H	3.888131	-2.290597	-1.599979
C	3.253458	-0.668255	0.483945
H	1.410236	-0.218118	-0.403562
H	2.838084	-1.674340	0.604964
H	3.111452	0.032988	1.312102

Q-OH E=-1243.88653478 E_{CPCM}=-1243.898096

Mn	0.008181	-0.004030	0.042956
O	0.081013	0.092482	1.916352
O	-0.032669	-0.173291	-1.783559
C	2.868239	-1.132014	-0.032878
C	4.261517	-0.714281	0.027017
C	4.268696	0.656271	0.136650
C	2.880088	1.093885	0.131272
N	2.039992	-0.016881	0.052398
H	5.111088	-1.394221	-0.014798
H	5.125563	1.325734	0.195242
C	2.461897	2.422829	0.103872
C	0.721708	4.238850	-0.103915
C	-0.651212	4.247171	-0.224876
C	-1.091705	2.864305	-0.208832
N	0.017826	2.021606	-0.109935
C	1.138724	2.850940	-0.028292
H	1.401142	5.088934	-0.064046
H	-1.317763	5.105274	-0.296831
C	2.431618	-2.451809	-0.160760
N	-0.014780	-2.013003	-0.063909
C	-1.141683	-2.846779	0.002118
C	-0.720269	-4.230720	-0.085774
C	0.653238	-4.238150	-0.204634
C	1.099774	-2.860085	-0.175546
H	-1.398061	-5.082433	-0.053277
H	1.317461	-5.097445	-0.283195
C	-2.460954	-2.419045	0.140554
N	-2.034346	0.022896	0.102808
C	-2.865614	1.140897	-0.033710
C	-4.256657	0.720509	-0.001900
C	-4.265602	-0.649466	0.128623
C	-2.879502	-1.086964	0.161332
H	-5.106397	1.397014	-0.081289
H	-5.123882	-1.318347	0.171919
C	-2.427684	2.454899	-0.191966
H	-3.191314	3.232472	-0.282460
H	-3.235115	-3.190141	0.184380
H	3.195555	-3.231148	-0.229449
H	3.234363	3.195127	0.156785
H	-0.812483	0.246602	2.321121

Q-OH-1 E=-1515.44771199 E_{CPCM}=-1515.445283

Mn	1.290707	-0.003049	0.110735
O	3.057450	-0.235772	0.527240
O	-0.546090	0.159629	-0.284083
C	1.034098	-2.334523	2.083605
C	1.024065	-3.782774	2.118318
C	1.159941	-4.229420	0.820766
C	1.274964	-3.063004	-0.031698
N	1.203610	-1.903670	0.756986
H	0.903486	-4.374847	3.024242
H	1.177518	-5.257242	0.461451
C	1.432188	-3.093523	-1.416254
C	1.985734	-2.028853	-3.640980
C	2.264125	-0.740820	-4.037935
C	2.063489	0.118352	-2.882747
N	1.639847	-0.651852	-1.793416
C	1.630079	-1.976903	-2.232104
H	2.040160	-2.943593	-4.229367
H	2.585534	-0.390614	-5.017735
C	0.801972	-1.505024	3.178029
N	0.871331	0.662639	1.982712
C	0.714594	1.991181	2.380017
C	0.394964	2.041661	3.799311
C	0.396133	0.746341	4.260801
C	0.700919	-0.112752	3.126048
H	0.218916	2.958926	4.359227
H	0.212432	0.388824	5.272842
C	0.942567	3.103719	1.573330
N	1.625656	1.906221	-0.494689
C	2.044895	2.327629	-1.758409
C	2.104258	3.777323	-1.792182
C	1.689089	4.230668	-0.558464
C	1.388718	3.063463	0.249816
H	2.403736	4.361854	-2.660747
H	1.588888	5.259501	-0.216040
C	2.268155	1.496719	-2.860040
H	2.597335	1.972199	-3.788184
H	0.801518	4.090170	2.023789
H	0.656614	-1.985026	4.149689
H	1.462176	-4.076523	-1.894426
H	-0.730403	0.048342	-1.253021
C	-4.719047	-0.272452	0.123530
C	-5.444993	-1.204313	-0.654029
C	-6.472064	-0.785100	-1.521641
C	-6.794772	0.580759	-1.627395
C	-6.081014	1.522003	-0.858859
C	-5.055941	1.098493	0.006216
H	-5.200850	-2.270033	-0.573882
H	-7.021889	-1.526329	-2.111789
H	-7.594463	0.909259	-2.299276

H	-6.325181	2.587336	-0.932672
H	-4.503763	1.836203	0.599811
C	-3.599117	-0.718725	1.043644
H	-2.605560	-0.422213	0.648766
H	-3.695774	-0.259606	2.045389
H	-3.600083	-1.815348	1.173006

Q-OH-TS E=-1515.44333507 E_{CPCM}=-1515.449468

Mn	1.199059	0.045703	0.381982
O	2.641444	0.062266	1.298914
O	-0.515174	0.126813	-0.788796
C	-0.155284	-1.524571	2.657444
C	-0.381063	-2.883930	3.122502
C	0.138344	-3.730994	2.170686
C	0.698910	-2.900602	1.116028
N	0.502691	-1.550731	1.424365
H	-0.876711	-3.141745	4.057440
H	0.157540	-4.819996	2.174095
C	1.358293	-3.383123	-0.015585
C	2.749839	-3.124096	-2.111228
C	3.252156	-2.042188	-2.798549
C	2.779567	-0.845966	-2.121769
N	1.983270	-1.205443	-1.028141
C	1.974392	-2.602775	-0.997494
H	2.896067	-4.183166	-2.319310
H	3.886181	-2.040393	-3.684143
C	-0.573395	-0.369384	3.320562
N	0.237561	1.287746	1.666591
C	0.172601	2.679932	1.583941
C	-0.537318	3.207530	2.739590
C	-0.885451	2.134448	3.527042
C	-0.400707	0.937182	2.857028
H	-0.726770	4.265372	2.916747
H	-1.420970	2.137413	4.475461
C	0.737447	3.458726	0.572212
N	1.768963	1.641094	-0.759365
C	2.572225	1.618763	-1.899606
C	2.793797	2.978081	-2.371317
C	2.117767	3.817457	-1.516917
C	1.484651	2.982051	-0.506367
H	3.386342	3.238816	-3.247144
H	2.049917	4.903940	-1.550056
C	3.056875	0.464170	-2.517965
H	3.689796	0.596396	-3.400469
H	0.606017	4.542441	0.646667
H	-1.088269	-0.498773	4.277094
H	1.436701	-4.469392	-0.121027
H	-0.345841	-0.312247	-1.664722
C	-3.908508	-0.423372	-0.738076
C	-4.391018	-1.344895	-1.714613

C	-5.441393	-1.000164	-2.577092
C	-6.036981	0.277136	-2.495421
C	-5.570030	1.206590	-1.540472
C	-4.520485	0.864333	-0.676828
H	-3.932630	-2.338209	-1.777313
H	-5.802347	-1.725166	-3.313763
H	-6.856128	0.545822	-3.169647
H	-6.029358	2.198044	-1.473720
H	-4.155210	1.587588	0.060026
C	-2.789379	-0.771413	0.149622
H	-1.695636	-0.330291	-0.333565
H	-2.778401	-0.242838	1.117633
H	-2.609420	-1.851047	0.270932

Q-OH-2 E=-1515.46335608 E_{CPCM}=-1515.467967

Mn	-1.246620	0.021388	0.402375
O	-2.637129	0.060970	1.352949
O	0.546735	0.010078	-0.874519
C	0.506073	-0.208773	2.932818
C	1.188419	0.608019	3.923716
C	1.059616	1.920606	3.527481
C	0.286664	1.924075	2.295612
N	-0.030694	0.610515	1.934028
H	1.693502	0.215373	4.805423
H	1.434207	2.815173	4.023611
C	-0.107997	3.071783	1.604198
C	-1.400978	4.303535	-0.184212
C	-2.214340	3.908327	-1.222755
C	-2.230334	2.455683	-1.228841
N	-1.414230	1.969667	-0.199245
C	-0.916296	3.097702	0.466074
H	-1.154817	5.316425	0.132121
H	-2.761096	4.534196	-1.926924
C	0.433423	-1.603103	2.955997
N	-0.822952	-1.914317	0.839606
C	-1.268453	-3.038553	0.139882
C	-0.865901	-4.245761	0.844336
C	-0.198203	-3.850421	1.981021
C	-0.174453	-2.396092	1.980677
H	-1.084432	-5.258187	0.507078
H	0.242014	-4.474651	2.757633
C	-2.023189	-3.014369	-1.034041
N	-2.249303	-0.555104	-1.265270
C	-2.932307	0.267429	-2.162924
C	-3.612012	-0.548950	-3.158228
C	-3.334543	-1.862888	-2.862162
C	-2.490772	-1.866900	-1.675850
H	-4.214881	-0.152258	-3.974060
H	-3.668627	-2.758565	-3.384173
C	-2.933318	1.663227	-2.138051

H	-3.523157	2.178595	-2.901712
H	-2.300617	-3.978928	-1.469434
H	0.901906	-2.116458	3.800878
H	0.207884	4.035569	2.014597
H	0.605748	0.911635	-1.273020
C	4.116602	-0.358393	-0.611512
C	4.757606	0.927557	-0.706064
C	5.592415	1.238109	-1.782874
C	5.822479	0.289608	-2.806994
C	5.203889	-0.980903	-2.738857
C	4.367539	-1.304592	-1.667288
H	4.582631	1.661417	0.088170
H	6.072564	2.220550	-1.833250
H	6.476172	0.537586	-3.648528
H	5.381560	-1.715346	-3.530759
H	3.887510	-2.287690	-1.617649
C	3.261899	-0.676633	0.477524
H	1.405408	-0.217643	-0.414077
H	2.842208	-1.681605	0.591772
H	3.122044	0.020444	1.309541