

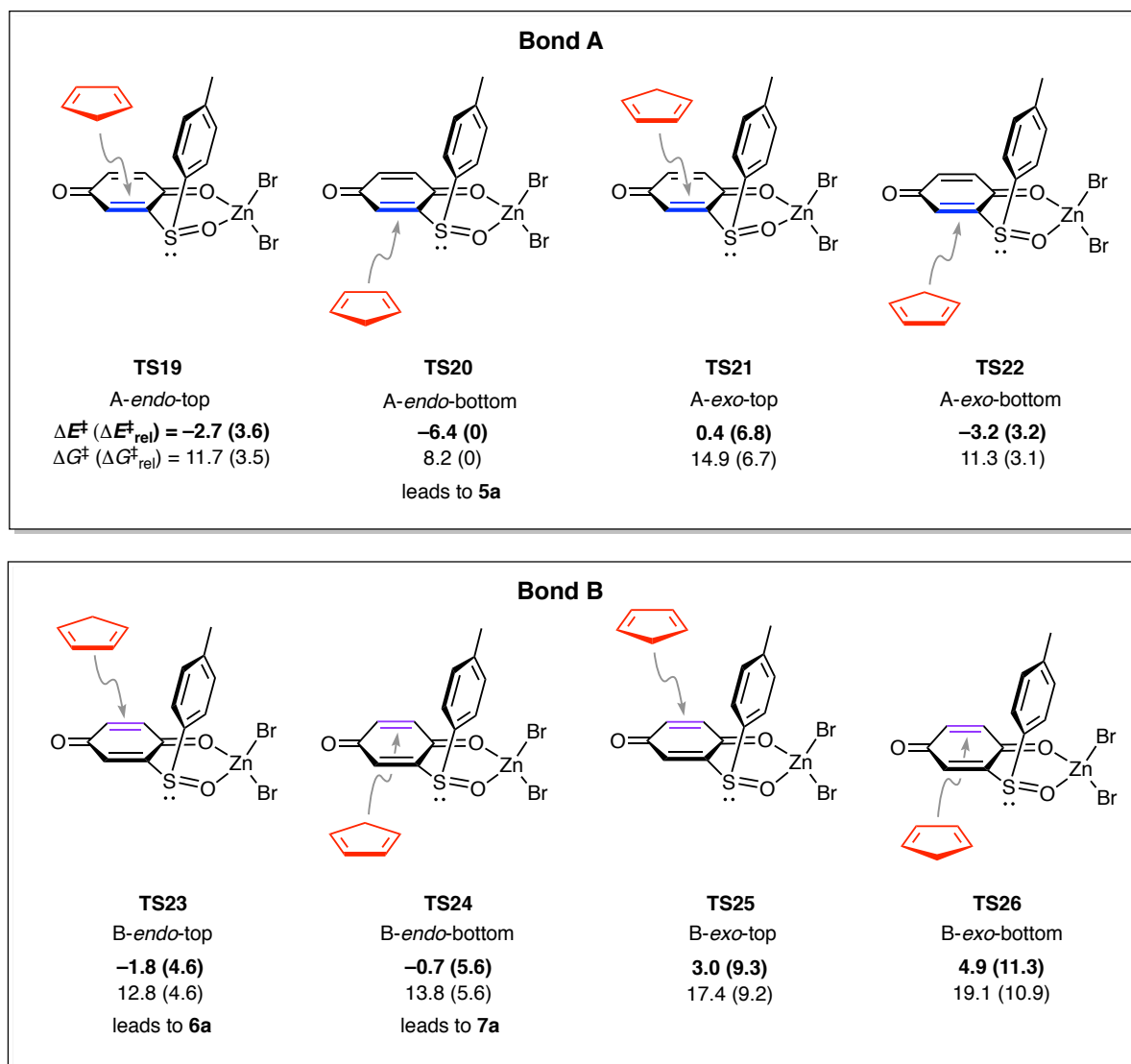
## SUPPLEMENTARY MATERIAL

### **Diels–Alder Reactions of Chiral Sulfinylquinones: From Sterically Directed to CH– $\pi$ Directed Stereoselectivity**

Ka Ho Chow,<sup>A</sup> Lawrence R. Gahan,<sup>A</sup> and Elizabeth H. Krenske<sup>A,B</sup>

<sup>A</sup>School of Chemistry and Molecular Biosciences, The University of Queensland, St Lucia,  
QLD 4072, Australia

<sup>B</sup>Corresponding author. Email: e.krenske@uq.edu.au



**Fig. S1.** Calculated activation energies for the eight different stereochemical modes of the  $\text{ZnBr}_2$ -catalyzed Diels–Alder reaction of sulfinylquinone **4a** with cyclopentadiene, modelling the dienophile as a mono-Zn complex. Calculations performed with M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-31G(d) in SMD implicit dichloromethane (kcal/mol, 25 °C). **TS20** is favoured by >3 kcal/mol relative to all other TSs involving the mono-Zn complex; this leads to the prediction that the A-endo-bottom cycloadduct (**5a**) would be effectively the sole product. In experiment, however, cycloadducts **5a**, **6a**, and **7a** were all obtained.

## Comparison of different DFT methods for predicting the selectivity of the Diels–Alder reaction of sulfinylquinone 4a with cyclopentadiene

The DFT calculations reported in Fig. 1 of the paper predict an over-stabilization of the A-*endo*-top transition state **TS1** relative to the B-*endo*-top transition state **TS5**. Experimentally, the reaction gave a 29:71 ratio of the B-*endo*-top and B-*endo*-bottom cycloadducts **6a** and **7a**. The computations reported in Fig. 1 correctly predicted that the B-*endo*-bottom transition state **TS6** leading to **7a** was lowest in energy, but incorrectly predicted that the A-*endo*-top transition state **TS1** was second-lowest in energy, lying 1.3 kcal/mol above **TS6** ( $\Delta\Delta G^\ddagger$ ). The B-*endo*-top transition state **TS5** was 2.0 kcal/mol higher in energy than **TS6**. Experimentally, no A-*endo*-top cycloadduct was detected.

As reported in the paper, a small improvement in the predicted selectivity was obtained when using structures that were optimized with B3LYP rather than with B3LYP-D3. This may indicate that the inaccurate selectivity prediction was due to basis set superposition error (BSSE) associated with the small 6-31G(d) basis set used for the geometry optimizations. To explore this possibility, the transition states were recomputed with the larger (triple-zeta) 6-311+G(d,p) basis set, both with B3LYP and B3LYP-D3. The results of these computations are shown in Table S1. The table reports various sets of energies for **TS1**, **TS5**, and **TS6**. These include the potential energy barriers ( $\Delta E_{\text{rel}}^\ddagger$ ) computed with the methods used for the geometry optimizations; the potential energy barriers ( $\Delta E_{\text{rel}}^\ddagger$ ) obtained from M06-2X-D3/6-311+G(d,p) single-point calculations on the optimized structures; and the Gibbs free energy barriers ( $\Delta G_{\text{rel}}^\ddagger$ ) obtained by adding to the M06-2X-D3 single-point energies the thermochemical corrections computed at the level of theory used for the corresponding optimization. All of the calculations included SMD implicit dichloromethane solvent.

For B3LYP-D3, the use of the triple-zeta basis set for the geometry optimizations led to small changes in the predicted selectivity (**TS1** vs **TS5**), generally in the direction of an improved agreement with experiment (raising **TS1** and lowering **TS5**) but falling short of achieving a qualitative match with experiment. For B3LYP without D3 dispersion, the triple-zeta basis set had only a minimal impact.

We also explored Grimme's geometrical counterpoise (gCP) correction<sup>[1]</sup> as an approach to addressing BSSE by calculating B3LYP-gCP-D3 energies for the three TSs (using the B3LYP/6-31G(d) geometries). These results are also shown in Table S1. The B3LYP-gCP-D3 methodology is one of the better-performing methods of those listed in the table. It predicts **TS5** to be lower in energy than **TS1**, albeit only by 0.1 kcal/mol. Out of all of the sets of numbers, the best agreement with experiment is in fact provided by the  $\Delta E_{\text{rel}}^\ddagger$  values computed with B3LYP/6-31G(d), which predicted **TS1** and **TS5** to lie 1.1 and 0.2 kcal/mol above **TS6**, respectively.

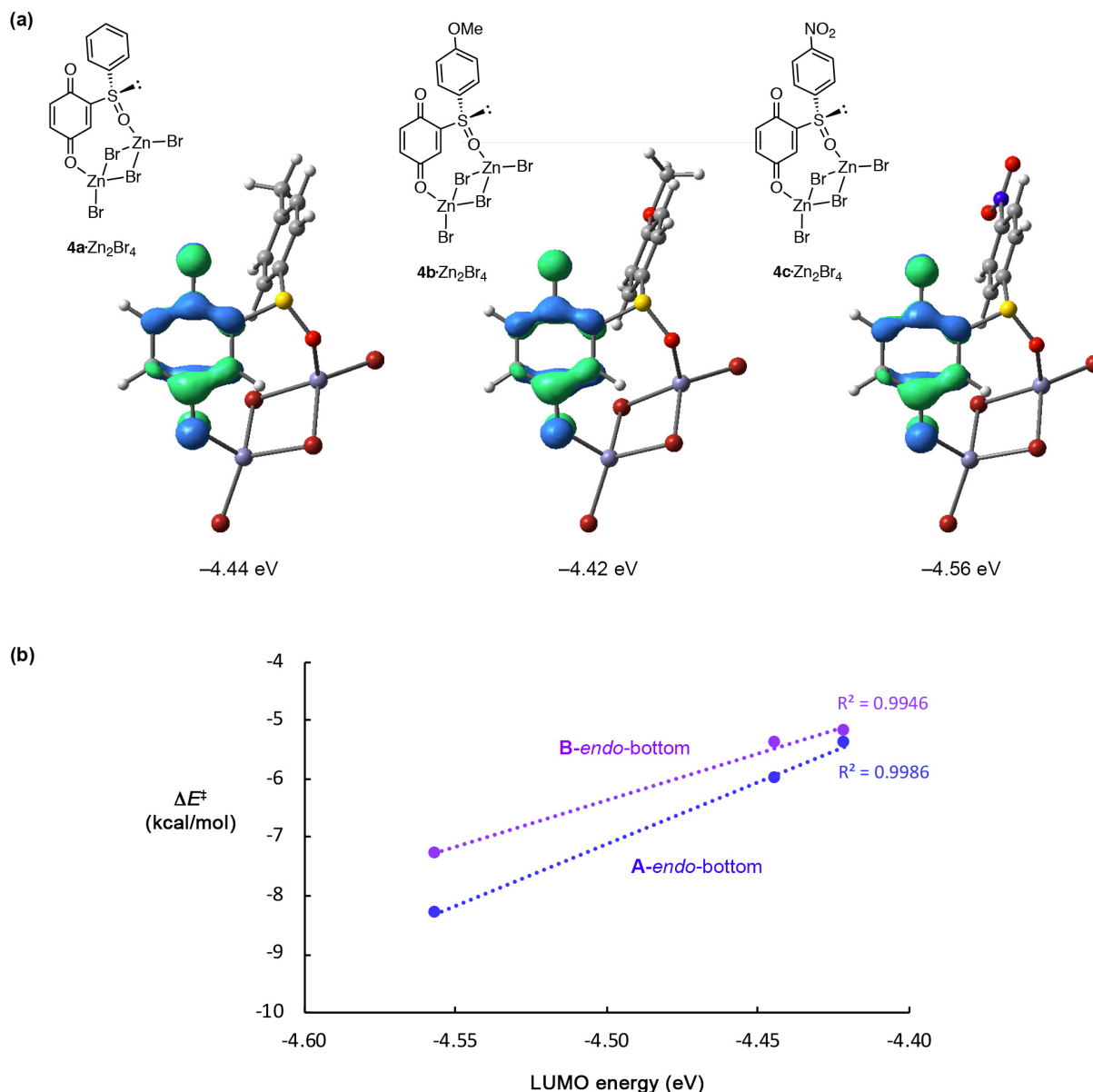
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[1] H. Kruse, S. Grimme, *J. Chem. Phys.* **2012**, *136*, 154101. Computations were performed using the gCP-D3 Webservice at <http://wwwtc.thch.uni-bonn.de>.

**Table S1.** Relative energies of **TS1**, **TS5**, and **TS6** computed with different DFT methods.<sup>a</sup>

Method	TS1	TS5	TS6
		$\Delta E_{\text{rel}}^{\ddagger}$	
B3LYP/6-31G(d)	1.1	0.2	0
B3LYP-D3/6-31G(d)	1.3	2.5	0
B3LYP/6-311+G(d,p)	1.2	-0.1	0
B3LYP-D3/6-311+G(d,p)	1.1	2.1	0
		$\Delta E_{\text{rel}}^{\ddagger}$	
M06-2X-D3/6-311+G(d,p)//B3LYP/6-31G(d)	1.2	1.3	0
M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-31G(d)	1.6	2.3	0
M06-2X-D3/6-311+G(d,p)//B3LYP/6-311+G(d,p)	1.1	1.2	0
M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-311+G(d,p)	1.7	2.1	0
		$\Delta G_{\text{rel}}^{\ddagger}$	
M06-2X-D3/6-311+G(d,p)//B3LYP/6-31G(d)	1.1	1.2	0
M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-31G(d)	1.3	2.0	0
M06-2X-D3/6-311+G(d,p)//B3LYP/6-311+G(d,p)	1.0	1.2	0
M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-311+G(d,p)	1.4	1.8	0
		$\Delta E_{\text{rel}}^{\ddagger}$	
B3LYP-gCP-D3/6-31G(d)//B3LYP/6-31G(d)	1.3	1.2	0
		$\Delta G_{\text{rel}}^{\ddagger}$	
B3LYP-gCP-D3/6-31G(d)//B3LYP/6-31G(d)	1.2	1.1	0

<sup>a</sup> All calculations were performed in SMD implicit dichloromethane. Energies in kcal/mol.



**Fig. S2.** (a) LUMOs of the di-Zn complexes of **4a–c** as calculated with B3LYP-D3/6-31G(d) and plotted with an isovalue of 0.07. (b) Plot of  $\Delta E^\ddagger$  vs LUMO energy for the Diels–Alder reactions of cyclopentadiene with the complexes shown in part (a).

Figure S2(a) shows that the LUMO energies of the di-Zn complexes decrease as the substituent on the aryl ring is varied from OMe to H to NO<sub>2</sub>. A lower-lying LUMO corresponds to a lower activation energy for Diels–Alder cycloaddition. Figure S2(b) shows that there are strong correlations between the Diels–Alder activation energies ( $\Delta E^\ddagger$ ) and the LUMO energies. Separate correlations are observed for Bond A (blue) and Bond B (purple), with Bond A being the more reactive site. This is consistent with the fact that the LUMO coefficients on Bond A are larger than those on Bond B, as illustrated in part (a) of the figure.

## DFT Geometries and Energies used in the Calculations of Diels–Alder Reactions

The Cartesian coordinates of the B3LYP-D3/6-31G(d) optimized structures are listed below, along with their computed energies. All of the calculations were performed in SMD implicit dichloromethane. The data are divided into two sections. Part 1 gives the data for the uncatalyzed Diels–Alder reactions of **4a** and **1** with cyclopentadiene, where the thermochemical data is reported at a temperature of  $-20\text{ }^{\circ}\text{C}$ . Part 2 gives the data for ZnBr<sub>2</sub>-catalyzed Diels–Alder reactions, where the thermochemical data is reported at a temperature of  $25\text{ }^{\circ}\text{C}$ .

### Part 1 – Uncatalyzed Reactions, $-20\text{ }^{\circ}\text{C}$

Energies listed for each species in this part are as follows:

E: B3LYP-D3/6-31G(d) electronic potential energy excluding zero-point energy

G: B3LYP-D3/6-31G(d) Gibbs free energy at  $-20\text{ }^{\circ}\text{C}$  and 1 mol/L

E<sub>M06-2X-D3</sub>: M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-31G(d) single-point electronic potential energy

G<sub>tot</sub>: M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-31G(d) Gibbs free energy at  $-20\text{ }^{\circ}\text{C}$  and 1 mol/L

All energies are reported in Hartree.

#### Cyclopentadiene



C	0.000000	1.180823	0.282603
C	0.000000	0.735213	-0.992492
C	-0.000000	-0.735213	-0.992492
C	-0.000000	-1.180823	0.282603
H	0.000000	2.213737	0.613220
H	0.000000	1.347428	-1.889448
H	-0.000000	-1.347428	-1.889448
H	-0.000000	-2.213737	0.613220
C	-0.000000	0.000000	1.217475
H	0.877257	-0.000000	1.883134
H	-0.877257	0.000000	1.883134

0 imaginary frequencies

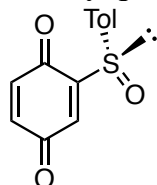
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G = -194.039994

E<sub>M06-2X-D3</sub> = -194.068288

G<sub>tot</sub> = -193.994557

#### Sulfinylquinone 4a

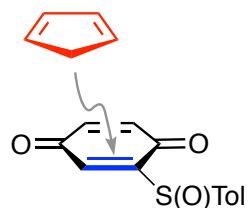


C	-3.249560	-0.118087	1.177954
C	-2.230073	0.751400	0.537625
C	-1.430979	0.267360	-0.423326
C	-1.562828	-1.118540	-0.944061
C	-2.570642	-1.984106	-0.287573
C	-3.359472	-1.518388	0.694610

O	-3.965586	0.304300	2.079433
H	-2.146750	1.778975	0.882514
O	-0.880461	-1.517714	-1.882988
H	-2.637533	-3.002126	-0.660307
S	-0.204414	1.372281	-1.214418
O	-0.393998	2.720351	-0.541183
C	1.267298	0.594851	-0.465373
C	1.952979	-0.411913	-1.145038
C	1.716580	1.078819	0.762398
C	3.097595	-0.956096	-0.561839
H	1.597348	-0.773454	-2.104285
C	2.864292	0.525345	1.327381
H	1.179762	1.885200	1.253594
C	3.568113	-0.501971	0.679618
H	3.638467	-1.741289	-1.084360
H	3.222087	0.898394	2.284002
C	4.791116	-1.118617	1.312572
H	5.501708	-1.467290	0.555543
H	5.305316	-0.407850	1.968094
H	4.514751	-1.987776	1.924922
H	-4.110687	-2.135135	1.179183

0 imaginary frequencies  
E = -1125.227786  
G = -1125.059666  
E<sub>M06-2X-D3</sub> = -1125.099147  
G<sub>tot</sub> = -1124.931027

### TS1

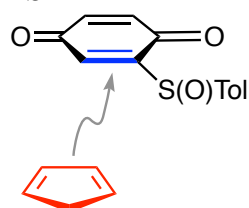


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C	-1.455854	2.513893	0.446256
H	-0.952451	-0.000148	-1.895936
H	-1.148842	2.284227	2.542465
O	-0.192213	-0.121804	2.510077
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C	-0.694697	0.408208	1.511886
S	0.232905	-1.759124	0.022781
O	-0.007486	-2.237005	-1.408960
C	1.839487	-0.894080	-0.012782
C	2.350307	-0.488358	-1.244772
C	2.554546	-0.683091	1.168607
C	3.584577	0.159412	-1.289833
H	1.787473	-0.689735	-2.151421
C	3.785774	-0.031203	1.105222
H	2.148771	-1.004431	2.121889
C	4.319500	0.399933	-0.119316
H	3.984880	0.481339	-2.248287
H	4.344044	0.142876	2.022224
C	5.667602	1.076337	-0.171343
H	6.477686	0.341058	-0.073922
H	5.815306	1.606536	-1.117785
H	5.785272	1.794988	0.647800
C	-3.867292	0.559804	-0.054623

C	-3.238758	-0.065635	-1.166266
C	-3.055364	-1.518116	-0.772664
C	-2.927212	-1.360931	0.716861
C	-3.637172	-0.211042	1.086669
H	-4.326703	1.541782	-0.069563
H	-3.421107	0.244117	-2.190679
H	-3.998966	-2.048067	-0.982631
H	-2.246532	-2.048970	-1.273424
H	-2.623041	-2.151247	1.393989
H	-3.869813	0.082690	2.104158
H	-1.717197	3.568313	0.476353

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## TS2

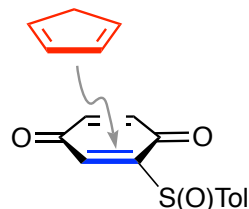


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C	2.651156	-1.496515	-1.410928
C	3.683858	-0.815665	-0.882338
H	2.035436	0.517020	1.858089
H	2.764112	-2.113081	-2.299178
O	0.501779	-2.421047	-1.101325
O	4.492506	0.378836	0.994981
C	1.313601	-1.546576	-0.762561
S	-0.243858	-1.068681	1.496369
O	-0.080164	-0.129284	2.690660
C	-1.800223	-0.559624	0.685735
C	-2.288360	-1.240733	-0.433186
C	-2.534329	0.469241	1.272341
C	-3.505831	-0.846801	-0.985773
H	-1.707555	-2.040159	-0.878888
C	-3.751935	0.850469	0.704679
H	-2.150122	0.964410	2.158521
C	-4.256115	0.203259	-0.431042
H	-3.882198	-1.364683	-1.865122
H	-4.319092	1.661881	1.154858
C	1.157219	1.414967	-1.984066
C	0.082316	1.315018	-1.105753
C	0.408820	2.090076	0.136563
C	1.925228	2.051923	0.086722
C	2.262812	1.922203	-1.289431
H	1.161456	1.077687	-3.014429
H	-0.906011	0.955627	-1.359205
H	0.089366	3.134383	-0.014775
H	-0.037781	1.734733	1.064438
H	2.540775	2.623491	0.774804
H	3.253914	2.070487	-1.703478
C	-5.585976	0.595224	-1.026729
H	-5.562342	0.550130	-2.121441
H	-6.379601	-0.086672	-0.692589
H	-5.876596	1.608402	-0.729976



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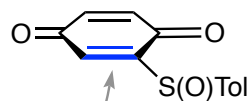
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C	-1.272944	2.000294	-0.970406
C	-1.277218	0.516122	-0.857007
C	-0.878628	-0.079676	0.360633
C	-0.806000	2.187239	1.450951
C	-1.102894	2.782079	0.283225
H	-1.025232	0.000179	-1.778654
H	-0.660985	2.750597	2.369090
O	-0.166647	0.227671	2.607394
O	-1.398414	2.571197	-2.050498
C	-0.600071	0.716560	1.558986
S	0.054422	-1.669190	0.258867
O	-0.301624	-2.252514	-1.103719
C	1.717212	-0.939860	0.068760
C	2.203783	-0.709497	-1.218310
C	2.496872	-0.657277	1.192009
C	3.476452	-0.164594	-1.378422
H	1.591212	-0.971247	-2.075995
C	3.767942	-0.108689	1.014040
H	2.115960	-0.850204	2.189618
C	4.275040	0.150919	-0.267599
H	3.859992	0.014876	-2.380284
H	4.378021	0.115132	1.885953
C	5.638392	0.771632	-0.451099
H	5.559328	1.862938	-0.549487
H	6.291738	0.566924	0.403638
H	6.129352	0.399789	-1.357160
C	-3.097529	-1.879265	0.003612
C	-2.968789	-0.933852	1.032303
C	-3.583514	0.346213	0.538793
C	-3.355932	0.186717	-0.949229
C	-3.350336	-1.206680	-1.194405
H	-2.903697	-2.940988	0.095880
H	-2.799094	-1.163562	2.078114
H	-4.668742	0.300765	0.722832
H	-3.217594	1.266671	0.990428
H	-3.681071	0.920705	-1.679319
H	-3.388235	-1.666394	-2.175424
H	-1.209246	3.859697	0.192481

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 E = -1319.332404  
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TS4



C	1.587015	2.239997	-0.404276
C	1.492889	0.803220	-0.763640
C	0.877150	-0.118706	0.118019
C	0.683263	1.734632	1.836181
C	1.214932	2.623168	0.980649
H	1.432569	0.638729	-1.834760
H	0.391621	2.007595	2.847100
O	-0.157442	-0.424759	2.251207
O	1.944670	3.091352	-1.216256
C	0.427484	0.314961	1.463395
S	-0.065338	-1.458261	-0.714168
O	-0.040868	-2.748380	0.084040
C	-1.722908	-0.729844	-0.495557
C	-2.077938	0.420437	-1.205220
C	-2.632653	-1.360957	0.347293
C	-3.358801	0.946200	-1.048229
H	-1.363273	0.911733	-1.861090
C	-3.913466	-0.823936	0.490791
H	-2.328511	-2.253200	0.884977
C	-4.296727	0.333203	-0.200964
H	-3.636728	1.846309	-1.591712
H	-4.624800	-1.309823	1.154604
C	-5.690636	0.896193	-0.066258
H	-5.679940	1.992061	-0.056930
H	-6.321199	0.586682	-0.910800
H	-6.176963	0.549483	0.851476
C	3.551461	-0.937337	-1.314594
C	3.600481	0.282529	-0.605134
C	3.488600	-0.074581	0.857424
C	2.693672	-1.348442	0.756795
C	2.997525	-1.921497	-0.490933
H	3.785338	-1.055124	-2.367227
H	4.096376	1.176465	-0.967692
H	4.497077	-0.333288	1.219008
H	3.097522	0.697830	1.517941
H	2.285518	-1.886355	1.603552
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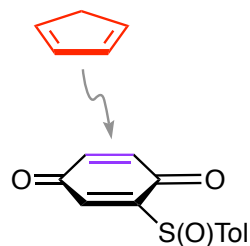
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**TS5**



C	-1.833242	1.360957	1.318847
C	-0.874421	1.387900	0.180986
C	-0.375937	0.248479	-0.321624
C	-0.789561	-1.102933	0.143460
C	-1.939881	-1.134116	1.049495
C	-2.465434	0.057876	1.609715
O	-2.070416	2.383117	1.958598
H	-0.546688	2.356592	-0.189749
O	-0.193845	-2.110752	-0.247083
H	-2.092924	-2.080827	1.558069
S	0.816382	0.328219	-1.709193
O	0.841248	1.787854	-2.136665
C	2.324901	0.049309	-0.714534
C	2.784835	-1.243282	-0.461908
C	3.030260	1.167856	-0.273619
C	3.963738	-1.406862	0.266087
H	2.221636	-2.104422	-0.804091
C	4.207126	0.984451	0.451094
H	2.660286	2.162428	-0.504696
C	4.692288	-0.301938	0.732017
H	4.324936	-2.411424	0.473143
H	4.758929	1.853079	0.802845
C	5.985167	-0.491375	1.486994
H	5.988740	-1.432585	2.047126
H	6.839184	-0.518967	0.796579
H	6.162117	0.329347	2.190517
H	-2.972410	0.009028	2.568849
C	-4.277046	0.334210	0.515493
C	-3.804012	0.641025	-0.783231
C	-3.324253	-0.527558	-1.374842
C	-3.498987	-1.596972	-0.473839
H	-4.813648	1.039813	1.141138
H	-3.705772	1.640891	-1.191363
H	-2.785804	-0.583188	-2.314701
H	-3.281304	-2.634106	-0.703968
C	-4.538573	-1.156966	0.528917
H	-4.500677	-1.642876	1.504880
H	-5.536406	-1.336406	0.096648

1 imaginary frequency

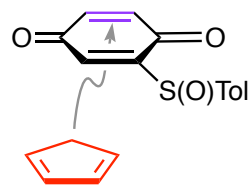
E = -1319.334082

G = -1319.073049

E<sub>M06-2X-D3</sub> = -1319.159766

G<sub>tot</sub> = -1318.898733

### TS6



C	2.948762	0.709105	-0.757279
C	1.670362	1.469946	-0.715751
C	0.836968	1.356297	0.329062
C	1.130612	0.510647	1.518805
C	2.234797	-0.436397	1.362329
C	3.110733	-0.360747	0.250210
O	3.802054	0.969303	-1.602533
H	1.457059	2.153274	-1.534385
O	0.471211	0.636682	2.554660
H	2.574944	-0.892403	2.286731
S	-0.661051	2.408287	0.393096
O	-0.640030	3.226032	-0.888667
C	-1.845956	1.043229	0.134402
C	-2.342434	0.319093	1.217409
C	-2.246348	0.762253	-1.171561
C	-3.238533	-0.723833	0.974413
H	-2.016216	0.543157	2.227336
C	-3.144581	-0.279434	-1.394375
H	-1.853289	1.354668	-1.992646
C	-3.652383	-1.039738	-0.327931
H	-3.623357	-1.299631	1.812450
H	-3.456435	-0.509271	-2.410577
C	-4.642578	-2.149474	-0.581901
H	-5.652140	-1.743919	-0.732011
H	-4.384646	-2.714863	-1.484503
H	-4.689424	-2.847026	0.260587
H	4.130337	-0.718055	0.360889
C	2.521689	-2.024603	-0.937340
C	1.228946	-1.652616	-1.378715
C	0.333953	-1.782310	-0.316273
C	1.034690	-2.252310	0.811011
H	3.372227	-2.137996	-1.601422
H	1.000849	-1.210338	-2.342325
H	-0.699546	-1.460722	-0.320574
H	0.571305	-2.509281	1.757203
C	2.316269	-2.868342	0.303762
H	2.100929	-3.901555	-0.014003
H	3.148513	-2.899367	1.008382

1 imaginary frequency

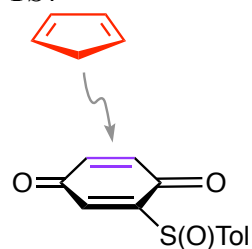
E = -1319.338038

G = -1319.076623

E<sub>M06-2X-D3</sub> = -1319.163409

G<sub>tot</sub> = -1318.901994

TS7



C	-1.798368	1.365066	1.292016
C	-0.751686	1.524388	0.243527
C	-0.260397	0.458119	-0.403015
C	-0.759920	-0.930003	-0.185753
C	-1.911486	-1.076275	0.711334
C	-2.430765	0.034283	1.421420
O	-2.091408	2.315326	2.015430
H	-0.376811	2.526402	0.047713
O	-0.211234	-1.880260	-0.750159
H	-2.038642	-2.078218	1.104152
S	1.019024	0.698679	-1.690911
O	1.152807	2.205238	-1.850271
C	2.441312	0.149741	-0.681842
C	2.818965	-1.193042	-0.651744
C	3.170371	1.122556	-0.000063
C	3.937395	-1.559756	0.097045
H	2.238702	-1.940351	-1.181650
C	4.286345	0.737075	0.741608
H	2.866382	2.163405	-0.060506
C	4.687325	-0.606129	0.802304
H	4.234448	-2.605226	0.131559
H	4.856025	1.490594	1.280422
C	5.916186	-1.012024	1.578372
H	5.817649	-2.024859	1.983789
H	6.804748	-1.004802	0.932467
H	6.111186	-0.325091	2.408821
H	-2.914623	-0.124204	2.378323
C	-3.494255	-1.343753	-0.871683
C	-4.509254	-1.792148	-0.003797
C	-4.990114	-0.704239	0.726965
C	-4.277641	0.454635	0.344755
H	-2.992900	-1.959802	-1.609910
H	-4.777011	-2.830460	0.160111
H	-5.694939	-0.758777	1.549786
H	-4.525753	1.458494	0.672583
C	-3.660934	0.147318	-0.998497
H	-2.771773	0.715356	-1.268267
H	-4.420852	0.341369	-1.772530

1 imaginary frequency

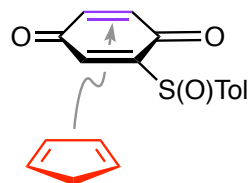
E = -1319.329082

G = -1319.068186

$E_{M06-2X-D3} = -1319.152420$

$G_{tot} = -1318.891524$

### TS8



C	2.724060	1.027989	-0.848799
C	1.443819	1.776957	-0.708176
C	0.648141	1.573303	0.350354
C	1.014892	0.676738	1.484618
C	2.148413	-0.220684	1.255773
C	2.973065	-0.071519	0.112091
O	3.515953	1.319548	-1.743027
H	1.172278	2.476187	-1.495428
O	0.382507	0.727981	2.543036
H	2.550298	-0.665014	2.158845
S	-0.950400	2.455033	0.464590
O	-1.028793	3.317879	-0.784154
C	-1.940804	0.950585	0.142892
C	-2.366466	0.140769	1.195457
C	-2.253010	0.642610	-1.180841
C	-3.096626	-1.012940	0.903475
H	-2.112281	0.387830	2.220709
C	-2.986182	-0.510949	-1.452790
H	-1.921471	1.301317	-1.978373
C	-3.415145	-1.357939	-0.418301
H	-3.425182	-1.654063	1.717824
H	-3.227464	-0.760948	-2.483274
C	-4.228900	-2.591581	-0.722348
H	-5.295534	-2.343328	-0.806939
H	-3.925919	-3.046150	-1.671989
H	-4.129268	-3.343078	0.067841
H	4.015234	-0.364301	0.170569
C	0.956769	-2.055121	0.680672
C	2.031637	-2.959971	0.787392
C	2.878620	-2.784660	-0.308125
C	2.364979	-1.749687	-1.123272
H	0.103832	-2.020579	1.349140
H	2.231826	-3.593912	1.644541
H	3.842781	-3.263213	-0.442856
H	2.762599	-1.490287	-2.098721
C	0.907253	-1.609756	-0.756268
H	0.338773	-2.363247	-1.325012
H	0.441473	-0.645866	-0.949991

1 imaginary frequency

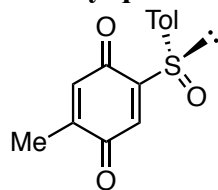
E = -1319.332555

G = -1319.071385

E<sub>M06-2X-D3</sub> = -1319.155867

G<sub>tot</sub> = -1318.894696

### Sulfinylquinone 1



C	3.015677	0.098215	-0.976569
C	1.868657	0.973645	-0.629818
C	1.075294	0.678031	0.407402
C	1.342522	-0.483783	1.295795
C	2.472367	-1.358114	0.930380
C	3.276568	-1.107550	-0.123239
O	3.725090	0.353774	-1.943298
H	1.691987	1.846697	-1.252984
O	0.657486	-0.688577	2.295667
H	2.629814	-2.215829	1.579092
S	-0.312626	1.791486	0.831401
O	-0.239287	2.921941	-0.180482
C	-1.640403	0.663309	0.284640
C	-2.230946	-0.220529	1.188010
C	-2.084671	0.759709	-1.033136
C	-3.270981	-1.037923	0.744837
H	-1.880516	-0.280439	2.213073
C	-3.127690	-0.062593	-1.456419
H	-1.626251	1.479241	-1.705285
C	-3.732182	-0.976122	-0.578965
H	-3.737034	-1.729988	1.441948
H	-3.481108	0.007895	-2.482306
C	-4.838872	-1.885833	-1.052575
H	-5.539997	-2.118503	-0.243872
H	-5.400706	-1.437622	-1.878840
H	-4.430091	-2.839282	-1.413942
C	4.440587	-1.964441	-0.511007
H	4.316313	-2.338160	-1.534458
H	5.366772	-1.377388	-0.504275
H	4.550965	-2.813621	0.168323

0 imaginary frequencies

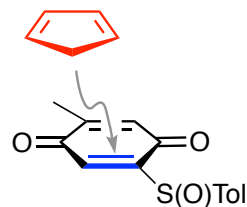
E = -1164.554175

G = -1164.359275

E<sub>M06-2X-D3</sub> = -1164.412163

G<sub>tot</sub> = -1164.217263

### TS9



C	-1.371856	1.529978	-1.038838
C	-1.166165	0.064567	-0.975748
C	-0.733670	-0.524276	0.233243
C	-1.154201	1.643487	1.414150
C	-1.492584	2.264099	0.263575
H	-0.832724	-0.390892	-1.905510
H	-1.192548	2.164577	2.368140
C	-1.945005	3.690058	0.189181
H	-2.935392	3.754146	-0.278472
H	-1.989607	4.148010	1.180976

H	-1.265846	4.272244	-0.444520
O	-0.124301	-0.182345	2.505068
O	-1.460303	2.130285	-2.106554
C	-0.634438	0.260647	1.470195
S	0.444690	-1.944833	0.133737
O	0.252537	-2.533033	-1.263080
C	1.977426	-0.959825	0.046296
C	2.455951	-0.580644	-1.208485
C	2.671111	-0.629725	1.211270
C	3.632860	0.159968	-1.291711
H	1.910996	-0.873923	-2.100899
C	3.847701	0.114858	1.109471
H	2.290893	-0.929633	2.182044
C	4.345728	0.520967	-0.136692
H	4.007407	0.462854	-2.266905
H	4.388450	0.381661	2.014332
C	5.634999	1.298079	-0.242807
H	6.476380	0.629285	-0.469572
H	5.587867	2.041285	-1.046678
H	5.870429	1.816491	0.692523
C	-3.800608	0.100998	-0.087260
C	-3.163504	-0.548742	-1.175375
C	-2.843480	-1.948988	-0.699763
C	-2.665197	-1.675713	0.771574
C	-3.478262	-0.572784	1.090605
H	-4.335233	1.042397	-0.148653
H	-3.365269	-0.307606	-2.214049
H	-3.745691	-2.569360	-0.827134
H	-2.012530	-2.444749	-1.200369
H	-2.307777	-2.405933	1.489538
H	-3.709137	-0.234849	2.094664

1 imaginary frequency

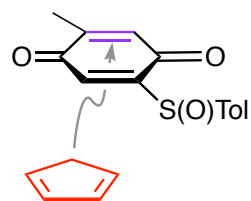
E = -1358.662176

G = -1358.374787

E<sub>M06-2X-D3</sub> = -1358.473937

G<sub>tot</sub> = -1358.186548

### TS10



C	2.677661	0.848259	-0.827702
C	1.358998	1.533066	-0.760081
C	0.558703	1.391217	0.305729
C	0.919793	0.551065	1.478183
C	2.056824	-0.348451	1.284701
C	2.958109	-0.206653	0.185357
O	3.491057	1.176012	-1.689473
H	1.099556	2.205941	-1.574011
O	0.281985	0.636645	2.531954
H	2.431350	-0.786479	2.206166
S	-0.972553	2.389595	0.415629
O	-1.010776	3.220822	-0.857063
C	-2.117404	0.988526	0.169398
C	-2.544232	0.219933	1.252570
C	-2.554431	0.721531	-1.126793
C	-3.405670	-0.852244	1.017025
H	-2.188989	0.434016	2.254798



C	-3.418546	-0.351384	-1.342076
H	-2.214484	1.346530	-1.947407
C	-3.855154	-1.155412	-0.277429
H	-3.735460	-1.462851	1.854100
H	-3.758067	-0.570217	-2.351701
C	-4.812003	-2.297812	-0.514101
H	-4.659594	-3.104911	0.210470
H	-5.852576	-1.960827	-0.412959
H	-4.699921	-2.711913	-1.521792
C	2.382255	-1.879271	-1.024780
C	1.079013	-1.537391	-1.468960
C	0.186529	-1.692070	-0.411692
C	0.903326	-2.144358	0.718911
H	3.234305	-1.971166	-1.690383
H	0.843904	-1.097017	-2.431879
H	-0.852892	-1.390601	-0.413964
H	0.442218	-2.421255	1.660918
C	2.184532	-2.749896	0.199197
H	1.973488	-3.777343	-0.139043
H	3.014032	-2.795810	0.903875
C	4.432523	-0.499120	0.392994
H	4.942783	-0.672611	-0.557390
H	4.915306	0.363110	0.871256
H	4.582803	-1.365158	1.042841

1 imaginary frequency  
E = -1358.657320  
G = -1358.368698  
E<sub>M06-2X-D3</sub> = -1358.469972  
G<sub>tot</sub> = -1358.181351

## Part 2 – ZnBr<sub>2</sub>-Catalyzed Reactions, 25 °C

Energies listed for each species in this part are as follows:

E: B3LYP-D3/6-31G(d) electronic potential energy excluding zero-point energy

G: B3LYP-D3/6-31G(d) Gibbs free energy at 25 °C and 1 mol/L

E<sub>M06-2X-D3</sub>: M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-31G(d) single-point electronic potential energy

G<sub>tot</sub>: M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-31G(d) Gibbs free energy at 25 °C and 1 mol/L

All energies are reported in Hartree.

### Cyclopentadiene

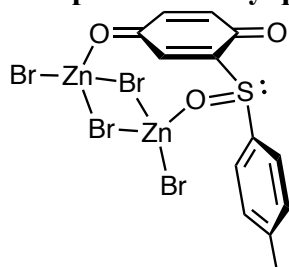


C	0.000000	1.180823	0.282603
C	0.000000	0.735213	-0.992492
C	-0.000000	-0.735213	-0.992492
C	-0.000000	-1.180823	0.282603
H	0.000000	2.213737	0.613220
H	0.000000	1.347428	-1.889448
H	-0.000000	-1.347428	-1.889448
H	-0.000000	-2.213737	0.613220
C	0.000000	0.000000	1.217475
H	0.877257	-0.000000	1.883134
H	-0.877257	0.000000	1.883134

0 imaginary frequencies  
E = -194.113725

G = -194.043998  
 E<sub>M06-2X-D3</sub> = -194.068288  
 G<sub>tot</sub> = -193.998561

### Complex of sulfinylquinone 4a with Zn<sub>2</sub>Br<sub>4</sub>



C	-0.685411	4.365320	-0.106356
C	0.620735	4.059819	0.014691
C	1.095868	2.738244	-0.405802
C	0.175637	1.853987	-1.134047
C	-1.137104	2.106593	-1.151079
C	-1.675479	3.419934	-0.694893
H	-1.090271	5.315170	0.228916
H	0.594856	0.948952	-1.554227
C	-3.376068	0.611899	-0.480849
C	-2.961519	0.504528	0.852806
C	-4.718429	0.467719	-0.838677
C	-3.912562	0.259829	1.833265
H	-1.917378	0.615762	1.122271
C	-5.658334	0.227472	0.163372
H	-5.030789	0.543442	-1.876308
C	-5.273828	0.117737	1.506071
H	-3.597956	0.176186	2.870097
H	-6.704927	0.117870	-0.105916
C	-6.285072	-0.145696	2.590658
H	-7.293725	-0.261490	2.183658
H	-6.030294	-1.056707	3.145779
H	-6.299853	0.678012	3.315342
S	-2.214942	0.809590	-1.822805
O	-2.854964	3.709346	-0.823779
O	2.219305	2.306684	-0.088185
O	-1.255988	-0.419213	-1.843430
Zn	-0.208812	-1.436663	-0.455347
Br	-1.337846	-3.372790	-0.023605
Br	0.640715	-0.194773	1.531483
Zn	2.681248	0.275629	0.255889
Br	2.026006	-1.256154	-1.551075
Br	4.819070	0.302882	1.028786
H	1.340813	4.730804	0.471570

0 imaginary frequencies

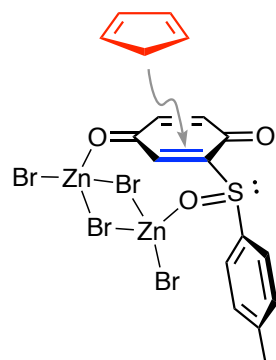
E = -14970.721572

G = -14970.569043

E<sub>M06-2X-D3</sub> = -14980.721905

G<sub>tot</sub> = -14980.569377

# TS11



C	-0.795273	3.771386	-1.970488
C	0.237496	2.876578	-2.624548
C	1.380221	3.078481	-1.665137
C	1.240455	4.371716	-1.115775
C	-0.068487	4.799969	-1.308991
C	0.219983	1.886746	-0.177149
C	-1.084939	2.400430	-0.342105
C	-1.646203	3.341471	0.658453
C	-0.678816	3.850563	1.669421
C	0.539431	3.297861	1.847999
C	0.993284	2.190297	0.995383
S	-2.286177	1.238468	-1.117169
O	-1.364249	0.153913	-1.774075
Zn	-0.378055	-1.418094	-1.038021
Br	0.238560	-1.336439	1.336053
Zn	2.404356	-0.361114	0.675341
O	2.022086	1.530002	1.299683
H	1.204917	3.617811	2.644092
O	-2.828071	3.666849	0.671503
C	-3.066324	0.434670	0.288156
C	-2.583465	0.452611	1.598945
C	-3.243498	-0.291223	2.572789
C	-4.366909	-1.069953	2.259545
C	-4.832395	-1.071846	0.935641
C	-4.196688	-0.322104	-0.049028
C	-5.042577	-1.908043	3.313486
Br	1.972446	-0.824788	-1.716955
Br	-1.419775	-3.307442	-1.813919
Br	4.423253	-0.976182	1.557267
H	-1.044763	4.646045	2.311937
H	-1.702976	1.020220	1.869717
H	-4.575042	-0.334055	-1.067724
H	-2.868810	-0.275203	3.592475
H	-5.706139	-1.662220	0.673832
H	-6.116553	-2.002418	3.121813
H	-4.620984	-2.922154	3.321000
H	-4.901217	-1.485950	4.313663
H	2.306843	2.516829	-1.700535
H	-0.502083	5.714175	-0.920351
H	1.997517	4.890401	-0.539131
H	0.482187	0.981116	-0.694911
H	-0.049973	1.842620	-2.814188
H	0.513066	3.331756	-3.588774
H	-1.803045	3.907807	-2.349882

1 imaginary frequency

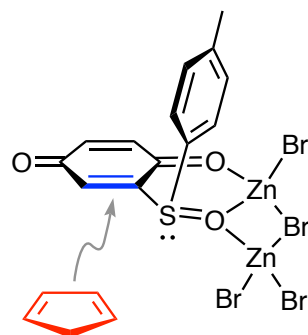
E = -15164.848230

G = -15164.603302

E<sub>M06-2X-D3</sub> = -15174.797467

G<sub>tot</sub> = -15174.552540

# TS12



C	-0.379224	5.017505	0.789127
C	-1.361089	4.049679	0.538867
C	-1.043651	2.833286	-0.062150
C	0.285116	2.573426	-0.395397
C	1.288015	3.521940	-0.175307
C	0.944525	4.733769	0.419004
S	0.657258	1.023188	-1.254331
O	-0.234536	-0.081946	-0.523839
Zn	-2.240903	-0.633023	-0.692136
Br	-3.515140	0.762130	-1.998006
C	-0.734506	6.343149	1.412574
C	2.305707	0.692328	-0.712145
C	3.345361	0.638565	-1.666289
C	4.747774	0.876661	-1.182260
C	4.982601	0.670494	0.266398
C	3.956825	0.552887	1.133100
C	2.555515	0.607222	0.698633
H	6.017143	0.667104	0.595781
O	5.643697	1.195875	-1.949826
O	1.648336	0.629003	1.581828
Zn	0.023970	-0.544976	1.467650
Br	0.827571	-2.463236	2.441064
Br	-2.283165	0.022694	1.792221
Br	-1.956372	-2.914404	-0.895760
C	3.628400	-1.309755	-2.319810
C	4.114042	-1.942001	-1.155595
C	3.030178	-2.427819	-0.386685
C	1.864608	-2.255499	-1.102997
H	4.114297	0.431404	2.200626
H	-1.820987	2.108705	-0.259265
H	2.321177	3.323531	-0.441064
H	-2.394026	4.243027	0.815428
H	1.723240	5.468550	0.605714
H	-0.864327	7.110849	0.637952
H	-1.670040	6.282928	1.977425
H	0.056251	6.691733	2.085731
H	3.157138	1.003278	-2.672922
H	4.264108	-1.080504	-3.168521
H	5.157731	-1.996293	-0.867114
H	3.094593	-2.847023	0.608536
H	0.863983	-2.520928	-0.780883
C	2.186494	-1.753327	-2.470708
H	1.481791	-1.032929	-2.892089
H	2.178420	-2.614449	-3.160110

1 imaginary frequency

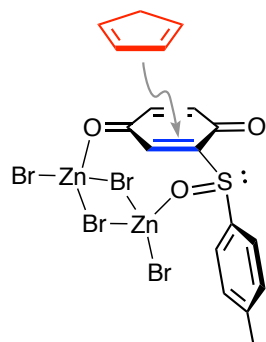
E = -15164.853580

G = -15164.609338

E<sub>M06-2X-D3</sub> = -15174.799679

G<sub>tot</sub> = -15174.555437

# TS13



C	-0.865784	3.891378	-1.859052
C	0.408907	4.414332	-1.243736
C	1.325105	3.253476	-1.513908
C	0.840321	2.605698	-2.671310
C	-0.477130	3.001939	-2.890737
C	0.199998	1.952417	-0.088328
C	-1.120950	2.425979	-0.221023
C	-1.704704	3.309263	0.815452
C	-0.782671	3.745243	1.905012
C	0.453256	3.228974	2.053536
C	0.954400	2.211949	1.113354
S	-2.288962	1.269654	-1.041157
O	-1.329656	0.238336	-1.727569
Zn	-0.346553	-1.348734	-1.028927
Br	0.290653	-1.326164	1.346824
Zn	2.431649	-0.301249	0.690683
O	1.998633	1.566141	1.383247
H	1.099233	3.500109	2.882955
O	-2.886281	3.639631	0.810222
C	-3.066067	0.395037	0.324678
C	-2.591835	0.363627	1.638817
C	-3.254903	-0.419988	2.579341
C	-4.373933	-1.189452	2.229854
C	-4.831660	-1.141461	0.904093
C	-4.192306	-0.352115	-0.046523
C	-5.055060	-2.069286	3.245805
Br	2.000873	-0.733390	-1.700291
Br	-1.376043	-3.226066	-1.849406
Br	4.481978	-0.849793	1.542160
H	-1.190913	4.470179	2.603016
H	-1.714867	0.922862	1.938383
H	-4.565399	-0.325218	-1.066936
H	-2.886762	-0.441769	3.601340
H	-5.702337	-1.723547	0.614687
H	-6.132404	-2.133821	3.059967
H	-4.653270	-3.090183	3.195874
H	-4.897525	-1.702798	4.265210
H	2.346350	3.187842	-1.154878
H	-1.134278	2.601738	-3.653751
H	1.365984	1.830845	-3.214302
H	0.479856	1.062652	-0.622015
H	0.356410	4.759045	-0.212325
H	0.747897	5.267216	-1.852667
H	-1.810086	4.424402	-1.832917

1 imaginary frequency

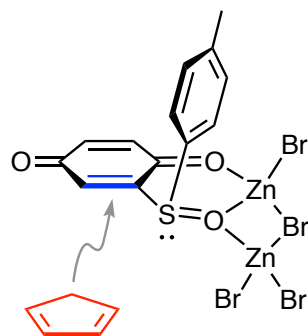
E = -15164.845089

G = -15164.600319

E<sub>M06-2X-D3</sub> = -15174.792264

G<sub>tot</sub> = -15174.547495

# TS14



C	-0.888014	5.042316	0.736719
C	-1.430797	3.825208	1.168869
C	-0.992892	2.608281	0.647154
C	0.012604	2.619726	-0.314417
C	0.569160	3.813706	-0.781039
C	0.118043	5.016015	-0.243025
S	0.593428	1.091970	-1.081760
O	-0.233658	-0.057710	-0.358989
Zn	-2.159140	-0.750237	-0.669050
Br	-3.504129	0.876470	-1.556493
C	-1.391839	6.354166	1.282695
C	2.235866	0.929139	-0.435091
C	3.323507	1.042243	-1.327100
C	4.692787	1.300443	-0.746258
C	4.858766	1.084010	0.706134
C	3.795723	0.874327	1.503996
C	2.421017	0.811494	0.979630
H	5.871548	1.140828	1.092961
O	5.613995	1.676854	-1.457409
O	1.470729	0.688473	1.809433
Zn	0.128140	-0.780024	1.522082
Br	1.354393	-2.630833	2.100196
Br	-2.223240	-0.699843	1.928483
Br	-1.688275	-2.904508	-1.343030
C	3.797769	-0.878149	-2.128867
C	2.785667	-0.885675	-3.107503
C	1.638745	-1.561748	-2.618263
C	1.930838	-2.080190	-1.378755
H	3.893371	0.734664	2.576347
H	-1.427383	1.679553	0.990091
H	1.346544	3.815170	-1.541011
H	-2.212165	3.820777	1.924185
H	0.551519	5.949252	-0.592620
H	-1.864182	6.225600	2.261750
H	-0.581007	7.084117	1.381094
H	-2.141698	6.789531	0.608663
H	3.183993	1.524467	-2.288182
H	4.835836	-0.677592	-2.367378
H	2.858481	-0.394980	-4.072424
H	0.680712	-1.632320	-3.118489
C	3.366956	-1.844784	-1.051600
H	3.924109	-2.785252	-1.197714
H	3.549630	-1.546462	-0.016762
H	1.237701	-2.620203	-0.747726

1 imaginary frequency

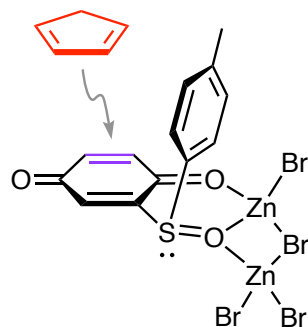
E = -15164.851464

G = -15164.607872

E<sub>M06-2X-D3</sub> = -15174.795316

G<sub>tot</sub> = -15174.551724

**TS15**



C	-6.172578	0.455794	0.242633
C	-5.681619	0.355806	1.552575
C	-4.311667	0.289840	1.805403
C	-3.430090	0.306817	0.723251
C	-3.884617	0.406084	-0.594406
C	-5.255069	0.482921	-0.821830
S	-1.675068	0.201279	1.058911
O	-0.997671	0.770114	-0.228284
Zn	0.428863	2.144310	-0.322386
Br	1.901072	2.011336	1.647247
Zn	2.395018	-0.133392	0.530634
Br	1.910163	0.752259	-1.721677
C	-7.652072	0.567473	-0.023767
O	0.815232	-0.978214	1.322339
C	0.041671	-1.921255	0.954013
C	-1.395346	-1.589093	0.874325
C	-2.355685	-2.511122	0.685295
C	-1.974883	-3.950575	0.595113
C	-0.529549	-4.230119	0.330597
C	0.429948	-3.245279	0.673218
O	-2.816882	-4.830150	0.693174
Br	4.251955	-1.472437	0.688770
Br	-0.458810	4.159641	-0.960177
C	0.966048	-2.668723	-1.941107
C	-0.282174	-2.099257	-2.131906
C	-1.254692	-3.113280	-2.050459
C	-0.634851	-4.333823	-1.664641
C	0.845864	-4.157038	-1.962178
H	-3.414166	-2.275159	0.653101
H	-3.944182	0.223529	2.826061
H	-3.174651	0.438854	-1.414429
H	-6.377668	0.338916	2.386757
H	-5.622363	0.565097	-1.841500
H	-8.242325	0.196869	0.820059
H	-7.937940	0.008202	-0.921383
H	-7.933923	1.615504	-0.191438
H	1.478674	-3.495266	0.786302
H	1.020108	-4.500853	-2.995265
H	1.544727	-4.694373	-1.319962
H	-1.137725	-5.289550	-1.775291
H	-0.253476	-5.272551	0.465961
H	1.909480	-2.138030	-1.918600
H	-2.322069	-2.971973	-2.178678
H	-0.478391	-1.040163	-2.242021

1 imaginary frequency

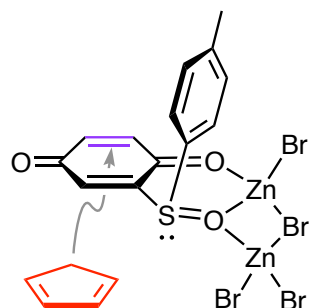
E = -15164.846767

G = -15164.602808

E<sub>M06-2X-D3</sub> = -15174.799574

G<sub>tot</sub> = -15174.555615

# TS16



C	-1.517448	-1.044025	-0.096272
C	-2.442462	-1.487621	-0.966510
C	-2.080248	-2.560085	-1.938287
C	-0.814404	-3.307707	-1.660840
C	0.157078	-2.714117	-0.818656
C	-0.162357	-1.613331	-0.000927
H	-3.428287	-1.045758	-1.067416
C	-3.452331	0.724533	0.814790
C	-4.342955	0.052060	1.654920
C	-3.894074	1.634801	-0.145949
C	-5.708093	0.289350	1.509191
H	-3.985247	-0.643741	2.409771
C	-5.263241	1.864837	-0.265916
H	-3.176612	2.157438	-0.770051
C	-6.188549	1.194721	0.549695
H	-6.410581	-0.226826	2.158046
H	-5.619335	2.577633	-1.004948
C	-7.669069	1.427811	0.385224
H	-8.207160	1.265208	1.324808
H	-8.087510	0.734623	-0.357030
H	-7.877465	2.444452	0.036322
H	1.187273	-3.053657	-0.818777
O	0.633781	-1.026119	0.804854
O	-2.800301	-2.803387	-2.894675
Br	4.072819	-2.078054	0.404239
Zn	2.457018	-0.462015	0.324237
Br	1.794098	0.614934	-1.798933
O	-1.023990	1.567573	0.236288
C	-1.606098	-4.857662	-0.674100
C	-0.362738	-4.384021	1.232559
C	-0.351131	-5.309120	0.057244
H	0.571959	-5.332723	-0.522185
H	-0.534945	-6.332235	0.425456
C	-2.434626	-4.258612	0.315455
C	-1.652533	-3.916168	1.432054
H	-2.025562	-5.416124	-1.505048
H	-0.461902	-3.901660	-2.499900
H	0.480560	-4.224787	1.894889
H	-3.485934	-4.026185	0.186262
H	-1.986438	-3.326781	2.278221
S	-1.699674	0.396748	1.011103
Zn	0.810657	2.189321	-0.156912
Br	0.530009	4.391379	-0.756327
Br	2.358716	1.582187	1.669890

1 imaginary frequency

E = -15164.840405

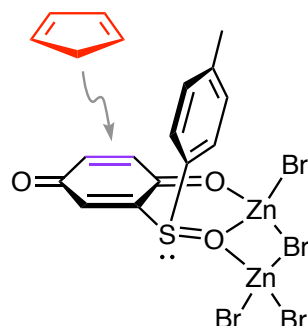
G = -15164.596980

E<sub>M06-2X-D3</sub> = -15174.798797

G<sub>tot</sub> = -15174.555372



TS17



C	-1.271862	-0.804081	-1.751875
C	-1.948699	-0.751163	-2.912821
C	-2.818610	0.421671	-3.216663
C	-3.009381	1.436985	-2.127534
C	-2.142864	1.397012	-1.009041
C	-1.312004	0.293039	-0.752177
H	-1.896604	-1.529402	-3.669407
C	-1.122242	-2.805284	0.102082
C	-2.321047	-3.507153	-0.037317
C	-0.580918	-2.518259	1.354251
C	-3.005964	-3.898980	1.113470
H	-2.725674	-3.740791	-1.019069
C	-1.274013	-2.931814	2.488322
H	0.336144	-1.949896	1.438401
C	-2.494438	-3.621242	2.389226
H	-3.945364	-4.436337	1.015755
H	-0.864441	-2.706876	3.469861
C	-3.217447	-4.074644	3.631926
H	-4.266240	-4.309804	3.425086
H	-3.180652	-3.308707	4.414623
H	-2.748807	-4.978725	4.042785
O	-0.549163	0.172820	0.257762
O	-3.347340	0.530130	-4.313478
Br	1.796351	1.731083	-1.238166
Zn	0.620058	1.588338	0.948565
Br	-0.339813	3.413450	1.930017
O	1.160579	-1.900218	-1.054701
C	-4.849976	0.847501	-1.473495
C	-4.054452	0.392270	0.667770
C	-4.472281	-0.316727	-0.575078
H	-3.761209	-1.044415	-0.963446
H	-5.399929	-0.872203	-0.359181
C	-4.605453	1.665715	0.670535
C	-5.149382	1.923789	-0.599275
H	-4.563855	2.370144	1.493134
H	-5.625152	2.850007	-0.902682
H	-5.363257	0.711770	-2.420186
H	-3.514928	-0.074881	1.483738
H	-3.316220	2.404512	-2.511742
S	-0.289674	-2.292778	-1.415637
H	-2.049432	2.243265	-0.338186
Zn	2.456225	-0.516402	-0.457014
Br	4.482841	-1.358795	-1.151759
Br	2.204207	0.030978	1.957442

1 imaginary frequency

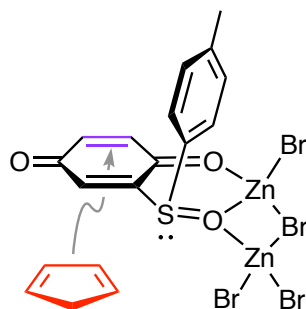
E = -15164.838047

G = -15164.594480

E<sub>M06-2X-D3</sub> = -15174.789388

G<sub>tot</sub> = -15174.545821

# TS18



C	-1.329803	-1.407303	-0.017251
C	-2.132847	-2.157836	-0.786835
C	-1.534561	-3.190196	-1.681979
C	-0.056193	-3.437205	-1.574503
C	0.732962	-2.536978	-0.820027
C	0.141548	-1.577213	0.017309
H	-3.208999	-2.030037	-0.838698
C	-3.620272	-0.071611	0.821251
C	-4.334824	-0.797727	1.776365
C	-4.258259	0.572434	-0.241058
C	-5.719339	-0.892257	1.646245
H	-3.827525	-1.284484	2.605449
C	-5.643357	0.473143	-0.344561
H	-3.677926	1.144636	-0.957476
C	-6.393052	-0.259561	0.590446
H	-6.285345	-1.458349	2.381068
H	-6.152422	0.970692	-1.165879
C	-7.894740	-0.332840	0.479090
H	-8.216041	-0.360264	-0.567642
H	-8.357886	0.550743	0.938340
H	-8.293056	-1.215931	0.988868
H	1.812932	-2.524944	-0.905945
O	0.760240	-0.775747	0.791581
O	-2.236990	-3.788286	-2.484620
Br	4.378040	-0.963441	0.502828
Zn	2.413892	0.193126	0.342108
Br	1.566549	1.052589	-1.808399
O	-1.453653	1.249326	0.114734
C	-0.128422	-5.194307	-0.520593
C	1.100054	-4.299259	1.243976
C	-0.302653	-4.663434	0.890564
H	-1.048855	-3.883683	1.042079
H	-0.606998	-5.516173	1.519875
C	1.229943	-5.585792	-0.620108
C	1.971619	-4.985895	0.413050
H	-0.920613	-5.710248	-1.053540
H	0.358953	-3.860838	-2.482926
H	1.379323	-3.688545	2.094878
H	1.645460	-6.167188	-1.435982
H	3.051309	-5.000464	0.504404
S	-1.839530	0.023016	0.996735
Zn	0.165283	2.336866	-0.211417
Br	-0.660689	4.385517	-0.852157
Br	1.769853	2.163841	1.656665

1 imaginary frequency

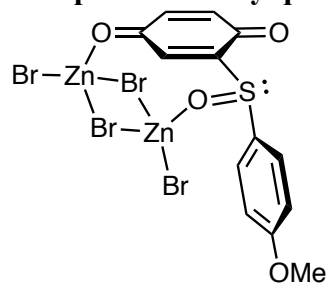
E = -15164.834532

G = -15164.591412

E<sub>M06-2X-D3</sub> = -15174.790720

G<sub>tot</sub> = -15174.547600

### Complex of sulfinylquinone 4b with Zn<sub>2</sub>Br<sub>4</sub>



C	-0.421212	4.391911	-0.131053
C	0.870703	4.058014	0.050712
C	1.339574	2.731756	-0.361627
C	0.437198	1.872796	-1.140065
C	-0.868578	2.150374	-1.216741
C	-1.401059	3.471883	-0.775721
H	-0.822773	5.346877	0.193437
H	0.858277	0.964431	-1.550741
C	-3.151618	0.680677	-0.664282
C	-2.805780	0.564660	0.692779
C	-4.477412	0.529870	-1.081552
C	-3.792656	0.306953	1.624260
H	-1.777161	0.676840	1.016097
C	-5.474126	0.276033	-0.143559
H	-4.740535	0.612663	-2.132153
C	-5.134634	0.157315	1.214721
H	-3.553290	0.211696	2.678367
H	-6.498585	0.165717	-0.476711
S	-1.939300	0.878901	-1.945928
O	-2.565834	3.789362	-0.959911
O	2.440084	2.276491	0.000666
O	-0.990535	-0.360721	-1.949891
Zn	-0.036843	-1.411562	-0.523151
Br	-1.221862	-3.329325	-0.162658
Br	0.747102	-0.211639	1.520001
Zn	2.849971	0.234178	0.341066
Br	2.251825	-1.266397	-1.511137
Br	4.952103	0.214957	1.208086
O	-6.013390	-0.096104	2.202788
C	-7.395773	-0.285227	1.871732
H	-7.526494	-1.141103	1.199466
H	-7.897960	-0.484699	2.819607
H	-7.819279	0.616699	1.414652
H	1.581471	4.709817	0.548270

0 imaginary frequencies

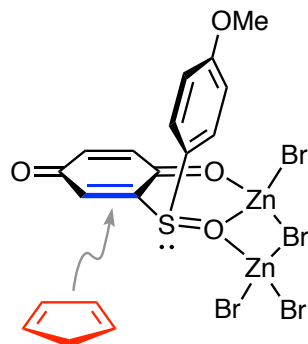
E = -15045.930062

G = -15045.772741

E<sub>M06-2X-D3</sub> = -15055.930006

G<sub>tot</sub> = -15055.772686

### A-endo-bottom TS for the 4b-Zn<sub>2</sub>Br<sub>4</sub> complex



C	-2.455376	4.230209	0.386700
C	-2.943048	2.958383	0.049471
C	-2.074552	1.998439	-0.462916
C	-0.720802	2.297077	-0.618477
C	-0.226562	3.571065	-0.306105
C	-1.093558	4.528866	0.196062
S	0.328329	1.028474	-1.356544
O	-0.021233	-0.317951	-0.564283
Zn	-1.606862	-1.668759	-0.683443
Br	-3.307232	-1.132309	-2.135594
C	1.934846	1.472964	-0.771403
C	2.941539	1.789457	-1.710332
C	4.099301	2.623921	-1.238820
C	4.333408	2.646424	0.224073
C	3.418038	2.166781	1.089592
C	2.143393	1.590860	0.642975
H	5.257931	3.105255	0.561056
O	4.820939	3.221019	-2.024294
O	1.279815	1.284238	1.516940
Zn	0.293856	-0.461761	1.468607
Br	1.765012	-1.798102	2.619589
Br	-2.063460	-0.837820	1.698212
Br	-0.376373	-3.622179	-0.648624
C	4.034014	0.098859	-2.197790
C	4.701938	-0.179001	-0.985521
C	3.900802	-1.021128	-0.178704
C	2.799641	-1.417691	-0.907588
H	3.568354	2.199860	2.164537
H	-2.468065	1.029034	-0.740249
H	0.820849	3.817487	-0.442852
H	-3.987336	2.701809	0.178524
H	-0.734120	5.519475	0.455392
H	2.656468	1.969090	-2.743971
H	4.543558	0.510155	-3.062883
H	5.660476	0.236569	-0.695796
H	4.102252	-1.298263	0.847603
H	1.996869	-2.060513	-0.564888
C	2.923916	-0.928162	-2.311304
H	1.993604	-0.613274	-2.789140
H	3.308262	-1.758127	-2.927937
O	-3.208129	5.232400	0.891729
C	-4.601997	4.995404	1.119717
H	-5.122582	4.756971	0.184478
H	-4.753419	4.186544	1.844497
H	-4.995090	5.928238	1.527517

1 imaginary frequency

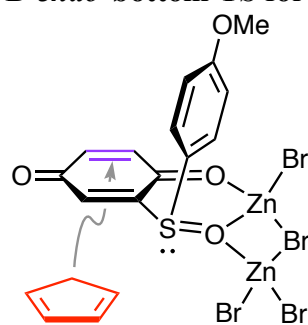
E = -15240.061425

G = -15239.812389

E<sub>M06-2X-D3</sub> = -15250.006844

G<sub>tot</sub> = -15249.757808

### B-endo-bottom TS for the 4b-Zn<sub>2</sub>Br<sub>4</sub> complex



C	-1.202703	-1.270203	-0.072382
C	-2.078408	-1.854004	-0.910451
C	-1.595737	-2.882680	-1.876694
C	-0.232106	-3.443439	-1.623926
C	0.667515	-2.710226	-0.812655
C	0.218273	-1.650858	-0.000674
H	-3.118591	-1.555521	-0.989948
C	-3.334786	0.255762	0.853850
C	-4.136879	-0.463809	1.750124
C	-3.896866	1.043825	-0.150680
C	-5.515426	-0.405575	1.617375
H	-3.693118	-1.062929	2.541162
C	-5.282644	1.112622	-0.275542
H	-3.254329	1.608296	-0.818703
C	-6.098126	0.380666	0.604527
H	-6.165922	-0.951287	2.293167
H	-5.713238	1.731994	-1.052742
H	1.734250	-2.905910	-0.832539
O	0.943435	-0.953162	0.783303
O	-2.299519	-3.242340	-2.808304
Br	4.477707	-1.574659	0.295778
Zn	2.674501	-0.168008	0.277146
Br	1.846678	0.843953	-1.818954
O	-1.040611	1.381928	0.239256
C	-0.783871	-5.070731	-0.600408
C	0.421405	-4.399131	1.270779
C	0.535140	-5.334824	0.109207
H	1.441160	-5.244385	-0.490238
H	0.498929	-6.366559	0.496822
C	-1.666491	-4.573874	0.398957
C	-0.916026	-4.108810	1.492739
H	-1.139839	-5.693673	-1.415012
H	0.178412	-3.996196	-2.464721
H	1.248438	-4.114404	1.911208
H	-2.742017	-4.489532	0.290511
H	-1.310216	-3.555686	2.337423
S	-1.561046	0.142394	1.029071
Zn	0.693922	2.249662	-0.132637
Br	0.126926	4.411910	-0.676169
Br	2.341093	1.826296	1.660271
O	-7.448941	0.369833	0.566438
C	-8.116964	1.148654	-0.432859
H	-7.894391	2.216224	-0.318944
H	-9.183002	0.980063	-0.271274
H	-7.843286	0.818816	-1.442255

1 imaginary frequency

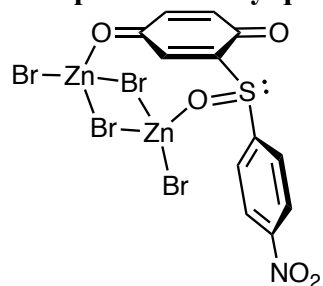
E = -15240.048250

G = -15239.800369

E<sub>M06-2X-D3</sub> = -15250.006529

G<sub>tot</sub> = -15249.758648

**Complex of sulfinylquinone 4c with Zn<sub>2</sub>Br<sub>4</sub>**



C	-0.418483	4.363641	-0.203821
C	0.871726	4.059857	0.036513
C	1.391409	2.744370	-0.348357
C	0.547291	1.861922	-1.168212
C	-0.757638	2.113665	-1.305282
C	-1.346296	3.416606	-0.883251
H	-0.855856	5.309509	0.100499
H	1.010093	0.965643	-1.560657
C	-3.061434	0.630030	-0.870311
C	-2.760877	0.404069	0.475986
C	-4.371046	0.618687	-1.353685
C	-3.800009	0.170336	1.368237
H	-1.738828	0.424986	0.835058
C	-5.414780	0.389722	-0.459408
H	-4.584588	0.786561	-2.404433
C	-5.106997	0.167919	0.880110
H	-3.603077	-0.007670	2.417913
H	-6.443526	0.376991	-0.796016
S	-1.757822	0.824743	-2.101710
O	-2.515857	3.688569	-1.107133
O	2.482803	2.314224	0.065600
O	-0.826862	-0.412967	-2.012069
Zn	0.148913	-1.449356	-0.563436
Br	-1.055059	-3.360811	-0.261449
Br	0.804288	-0.222876	1.500969
Zn	2.941796	0.282311	0.406951
Br	2.443189	-1.226342	-1.477887
Br	5.010020	0.302568	1.344153
N	-6.212464	-0.080015	1.825783
O	-7.357530	-0.106509	1.376798
O	-5.927478	-0.245199	3.011007
H	1.543769	4.730734	0.561798

0 imaginary frequencies

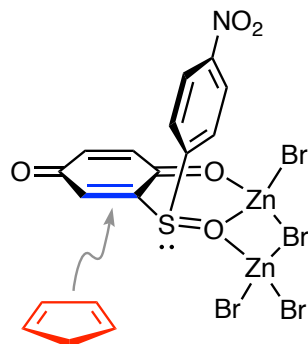
E = -15135.898065

G = -15135.771479

E<sub>M06-2X-D3</sub> = -15145.896197

G<sub>tot</sub> = -15145.769611

### A-endo-bottom TS for the 4c-Zn<sub>2</sub>Br<sub>4</sub> complex



C	-4.747559	0.860492	0.373633
C	-3.913508	-0.193777	0.736134
C	-2.603439	-0.205603	0.263274
C	-2.172842	0.844698	-0.541528
C	-3.013210	1.897826	-0.913574
C	-4.322294	1.907577	-0.444282
S	-0.503741	0.828327	-1.253230
O	0.276384	-0.308324	-0.473022
Zn	0.304146	-2.376370	-0.779507
Br	-1.580564	-2.997066	-1.922777
C	0.150016	2.345297	-0.620695
C	0.428260	3.394378	-1.521698
C	0.497811	4.788971	-0.967258
C	0.719654	4.902354	0.493450
C	0.595365	3.835670	1.308452
C	0.248425	2.503033	0.802283
H	0.942268	5.894051	0.875237
O	0.404237	5.768870	-1.691503
O	0.009263	1.577516	1.635107
Zn	0.874237	-0.229468	1.499335
Br	2.948756	0.107511	2.410836
Br	-0.082317	-2.418623	1.767555
Br	2.554490	-2.613172	-1.201644
C	2.403299	3.285077	-2.190081
C	3.117575	3.567471	-1.008227
C	3.356549	2.368177	-0.295550
C	2.935512	1.302750	-1.062849
H	0.727099	3.912235	2.383597
H	-1.936779	-1.009282	0.540346
H	-2.663204	2.706838	-1.547515
H	-4.276299	-0.990167	1.373679
H	-5.000505	2.709937	-0.705335
H	0.046263	3.337539	-2.537627
H	2.307964	3.996521	-3.003397
H	3.393379	4.560443	-0.671096
H	3.780097	2.295719	0.696930
H	2.974199	0.253868	-0.789667
C	2.519729	1.790921	-2.410751
H	1.664503	1.283262	-2.862885
H	3.360484	1.626189	-3.105669
N	-6.132913	0.871281	0.871139
O	-6.854658	1.814685	0.546015
O	-6.496417	-0.062606	1.585768

1 imaginary frequency

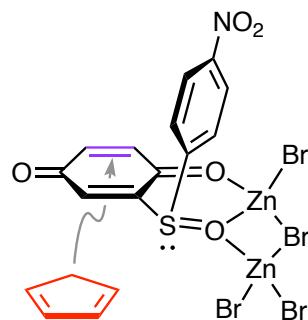
E = -15330.032974

G = -15329.814838

E<sub>M06-2X-D3</sub> = -15339.977661

G<sub>tot</sub> = -15339.759525

### B-*endo*-bottom TS for the 4c-Zn<sub>2</sub>Br<sub>4</sub> complex



C	-1.105257	-1.235089	-0.158895
C	-1.974558	-1.761148	-1.040054
C	-1.501727	-2.803648	-1.998785
C	-0.171097	-3.420874	-1.704988
C	0.732234	-2.730397	-0.860404
C	0.298588	-1.667623	-0.047643
H	-2.995483	-1.413835	-1.158961
C	-3.201892	0.332735	0.739364
C	-4.016186	-0.504516	1.506961
C	-3.721092	1.279377	-0.142744
C	-5.397005	-0.405865	1.370455
H	-3.591568	-1.224532	2.200371
C	-5.103970	1.385149	-0.272922
H	-3.055888	1.922128	-0.708713
C	-5.913285	0.537785	0.481789
H	-6.062060	-1.039335	1.943720
H	-5.546252	2.106735	-0.948344
H	1.789942	-2.970168	-0.851252
O	1.019013	-0.998477	0.766003
O	-2.189882	-3.127274	-2.954141
Br	4.566989	-1.669447	0.475560
Zn	2.786813	-0.242085	0.347559
Br	2.076797	0.787969	-1.782099
O	-0.870752	1.419763	0.164075
C	-0.822555	-5.030994	-0.710692
C	0.342109	-4.434194	1.211711
C	0.458762	-5.356815	0.040759
H	1.388232	-5.294802	-0.525007
H	0.367958	-6.391491	0.411411
C	-1.717801	-4.505658	0.262643
C	-0.988044	-4.085645	1.388357
H	-1.176185	-5.631270	-1.543069
H	0.243567	-3.985413	-2.535788
H	1.157044	-4.192511	1.884494
H	-2.784158	-4.373831	0.115713
H	-1.387501	-3.528208	2.227598
S	-1.413948	0.189552	0.941865
Zn	0.907502	2.250137	-0.165370
Br	0.393406	4.410616	-0.749171
Br	2.431197	1.767381	1.709301
N	-7.375660	0.644020	0.338586
O	-7.819677	1.497113	-0.429427
O	-8.076362	-0.128584	0.993121

1 imaginary frequency

E = -15330.019535

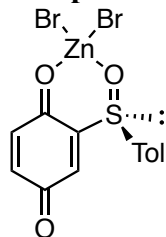
G = -15329.802135

E<sub>M06-2X-D3</sub> = -15339.976184

G<sub>tot</sub> = -15339.758784



### Complex of sulfinylquinone 4a with ZnBr<sub>2</sub>



C	0.293229	3.572227	-0.383936
C	-0.870746	4.239276	-0.319734
C	-2.162006	3.514466	-0.314607
C	-2.125592	2.024570	-0.400570
C	-0.958516	1.364080	-0.461839
C	0.335504	2.102006	-0.437599
H	1.257915	4.069815	-0.380098
H	-3.090016	1.527265	-0.421819
C	-2.453337	-0.973846	-0.197995
C	-2.778805	-1.036210	1.161432
C	-3.366691	-1.327324	-1.192506
C	-4.053712	-1.458005	1.518399
H	-2.043223	-0.770579	1.913894
C	-4.644215	-1.736795	-0.809418
H	-3.094453	-1.284905	-2.243424
C	-5.004847	-1.810431	0.542977
H	-4.321675	-1.514283	2.570176
H	-5.366174	-2.010528	-1.573542
C	-6.374752	-2.282609	0.956611
H	-7.073395	-2.278947	0.114529
H	-6.325676	-3.307333	1.347742
H	-6.786176	-1.652960	1.753592
S	-0.827893	-0.441371	-0.705911
O	1.427828	1.521387	-0.460700
O	-3.234396	4.099392	-0.247301
O	0.132950	-0.905790	0.431197
Zn	2.078255	-0.459176	0.116591
Br	2.801081	-1.375306	-1.871915
Br	3.114268	-0.114147	2.135553
H	-0.919838	5.322197	-0.264361

0 imaginary frequencies

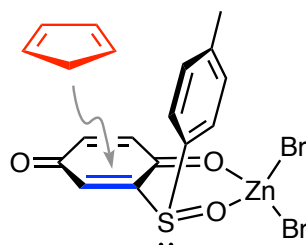
E = -8047.967320

G = -8047.811756

E<sub>M06-2X-D3</sub> = -8052.913671

G<sub>tot</sub> = -8052.758107

### TS19

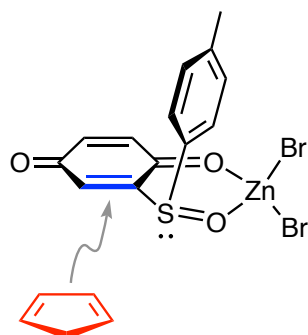


C	0.422412	2.845934	-1.789459
C	-0.715964	3.555121	-1.918302
C	-2.027754	2.964514	-1.563569
C	-1.987189	1.695522	-0.754753
C	-0.814086	0.906663	-0.841878
C	0.426244	1.459656	-1.299908
H	1.388918	3.250959	-2.075295

H	-0.727894	4.559709	-2.330323
C	-2.305917	-1.436394	-0.196778
C	-2.464225	-2.017620	1.060991
C	-3.360736	-1.387930	-1.114848
C	-3.715800	-2.521405	1.416026
H	-1.621545	-2.076173	1.742087
C	-4.603794	-1.887644	-0.734837
H	-3.220896	-0.968487	-2.107692
C	-4.803201	-2.457151	0.533551
H	-3.845731	-2.975518	2.394767
H	-5.430501	-1.845173	-1.439083
C	-6.161745	-2.974094	0.934546
H	-6.805331	-2.149522	1.269507
H	-6.668153	-3.458334	0.092474
H	-6.091151	-3.693159	1.756752
S	-0.677234	-0.884893	-0.717023
O	1.503708	0.797098	-1.361025
O	-3.085462	3.498454	-1.865723
O	0.272219	-1.171332	0.495423
Zn	2.179903	-0.625910	-0.024603
Br	3.202808	-2.364635	-1.161287
Br	3.148981	0.658879	1.657438
C	-2.143039	2.554970	1.038052
C	-0.272158	1.504671	1.957751
C	-1.755205	1.379080	1.917014
H	-2.136498	0.403013	1.624867
H	-2.144346	1.578514	2.929475
C	0.095954	2.778579	1.567335
C	-1.049046	3.458269	1.104136
H	1.106910	3.166187	1.587485
H	-1.076600	4.491599	0.777692
H	-3.167319	2.908258	0.968300
H	0.399885	0.739478	2.320311
H	-2.945922	1.187469	-0.705971

1 imaginary frequency  
E = -8242.094583  
G = -8241.846277  
E<sub>M06-2X-D3</sub> = -8246.986315  
G<sub>tot</sub> = -8246.738009

## TS20



C	1.806895	1.023715	2.230080
C	2.718696	2.010934	2.139981
C	2.928689	2.744231	0.870660
C	2.335605	2.119670	-0.360055
C	1.261896	1.210431	-0.187668
C	0.971443	0.618242	1.087300
H	1.613595	0.501485	3.162822
H	3.297048	2.343201	2.996960
C	-1.372123	1.788071	-0.829530
C	-2.613606	1.217572	-1.102841

C	-1.267083	3.001758	-0.143964
C	-3.765518	1.860377	-0.648417
H	-2.681434	0.274333	-1.631139
C	-2.430279	3.629652	0.294381
H	-0.298774	3.448045	0.060943
C	-3.695504	3.068826	0.055465
H	-4.733468	1.405334	-0.840728
H	-2.353677	4.568584	0.836981
C	-4.942526	3.740548	0.573654
H	-5.101830	3.496290	1.632524
H	-4.869353	4.831326	0.500233
H	-5.831546	3.415391	0.023744
S	0.101474	0.987434	-1.522545
O	0.018249	-0.178491	1.301179
O	3.578585	3.778813	0.816061
O	-0.266409	-0.526914	-1.632987
Zn	-0.687372	-1.611262	0.032434
Br	-2.951124	-2.041818	0.282230
Br	0.903024	-3.301480	0.340660
C	3.996149	1.161690	-0.987720
C	2.910382	-0.888955	-1.228432
C	3.358745	0.276416	-2.043803
H	2.601505	0.735428	-2.682353
H	4.162361	-0.068115	-2.715799
C	4.318153	0.304320	0.093024
C	3.582329	-0.893181	-0.020451
H	4.606216	2.022718	-1.242133
H	2.308529	2.792443	-1.214423
H	2.229546	-1.656620	-1.570949
H	4.967074	0.566181	0.920993
H	3.507803	-1.674821	0.724900

1 imaginary frequency

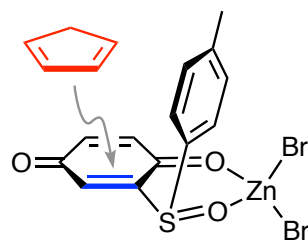
E = -8242.102450

G = -8241.853999

E<sub>M06-2X-D3</sub> = -8246.992092

G<sub>tot</sub> = -8246.743641

## TS21



C	0.402894	3.014733	-1.730699
C	-0.762681	3.666245	-1.890404
C	-2.047624	3.033059	-1.520621
C	-1.986283	1.705846	-0.797918
C	-0.764412	0.997870	-0.834127
C	0.461506	1.627893	-1.221634
H	1.357024	3.461080	-1.995757
H	-0.816695	4.668437	-2.304473
C	-2.198437	-1.411289	-0.319432
C	-2.352550	-2.075502	0.896184
C	-3.251416	-1.324164	-1.237412
C	-3.599737	-2.610241	1.218592
H	-1.510663	-2.173268	1.572002
C	-4.491609	-1.854594	-0.890180
H	-3.114548	-0.847761	-2.204524
C	-4.687836	-2.501058	0.340973

H	-3.726958	-3.122534	2.168645
H	-5.318197	-1.774183	-1.591294
C	-6.028257	-3.099261	0.686173
H	-6.152888	-4.075336	0.198660
H	-6.133563	-3.253085	1.764779
H	-6.849887	-2.460064	0.344639
S	-0.574774	-0.797646	-0.792110
O	1.580486	1.039143	-1.226333
O	-3.122637	3.559985	-1.774021
O	0.365318	-1.135802	0.411184
Zn	2.257243	-0.506310	-0.014034
Br	3.342899	-2.053472	-1.355118
Br	3.160729	0.543700	1.854634
C	-2.342139	2.431167	1.082123
C	-0.341605	1.695013	2.041743
C	-0.969457	2.928156	1.495147
H	-0.380833	3.454333	0.743992
H	-1.113834	3.640466	2.324660
C	-1.320184	0.757556	2.303914
C	-2.546983	1.223721	1.788090
H	-1.158808	-0.197155	2.785201
H	-3.490122	0.691246	1.839398
H	-3.160589	3.103121	0.845599
H	0.716012	1.582606	2.252247
H	-2.917809	1.158228	-0.881780

1 imaginary frequency

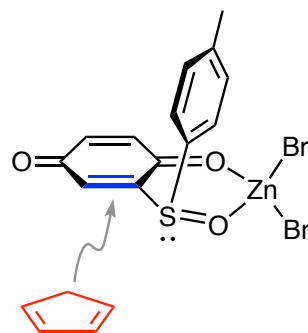
E = -8242.091122

G = -8241.842731

E<sub>M06-2X-D3</sub> = -8246.981327

G<sub>tot</sub> = -8246.732937

## TS22

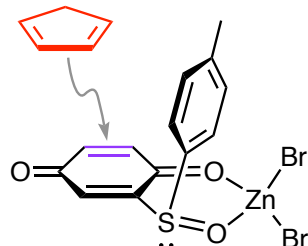


C	1.737632	0.895883	2.466044
C	2.695801	1.838735	2.431863
C	3.058801	2.515475	1.168270
C	2.468484	1.959496	-0.105484
C	1.374567	1.067306	0.005519
C	0.984535	0.492450	1.258590
H	1.446723	0.399701	3.387470
H	3.223989	2.161510	3.323929
C	-1.150215	1.853869	-0.833082
C	-2.414464	1.383495	-1.183296
C	-0.991413	3.072292	-0.166129
C	-3.536295	2.133073	-0.827959
H	-2.525366	0.435919	-1.696197
C	-2.124559	3.807111	0.174232
H	-0.006256	3.442762	0.099991
C	-3.413080	3.349434	-0.145304
H	-4.523729	1.756743	-1.081762
H	-2.005923	4.750107	0.702040
C	-4.632104	4.136325	0.266727

H	-5.492679	3.904739	-0.369297
H	-4.914397	3.898609	1.301222
H	-4.446901	5.215123	0.220439
S	0.295828	0.915677	-1.408417
O	0.004019	-0.283101	1.414425
O	3.805380	3.484725	1.146180
O	-0.204226	-0.555294	-1.539768
Zn	-0.798600	-1.609132	0.081026
Br	-3.100353	-1.766567	0.317214
Br	0.581855	-3.484690	0.308829
C	4.145208	0.941074	-0.746913
C	3.087210	-1.134024	-0.941776
C	3.988286	-0.381769	-0.025298
H	3.664319	-0.344588	1.015520
H	4.974430	-0.875610	-0.024522
C	3.767529	0.703920	-2.087242
C	3.072174	-0.521041	-2.179761
H	4.904323	1.669548	-0.482890
H	2.469972	2.692951	-0.906226
H	2.573931	-2.050839	-0.674332
H	3.914746	1.404754	-2.902155
H	2.565017	-0.893564	-3.061569

1 imaginary frequency  
E = -8242.099161  
G = -8241.850856  
E<sub>M06-2X-D3</sub> = -8246.987012  
G<sub>tot</sub> = -8246.738708

### TS23



C	0.770153	1.048172	0.949965
C	1.578339	1.953331	1.535697
C	2.125356	3.097838	0.754306
C	2.017891	2.987044	-0.729504
C	1.065190	2.091904	-1.275604
C	0.400628	1.115555	-0.491389
H	1.817978	1.928945	2.595653
C	1.054170	-1.667130	1.288072
C	2.280053	-1.998134	1.870830
C	0.546091	-2.378862	0.199216
C	3.027679	-3.039573	1.322010
H	2.656075	-1.449881	2.730964
C	1.307892	-3.417228	-0.329429
H	-0.425494	-2.141655	-0.217868
C	2.557285	-3.760329	0.214012
H	3.985677	-3.298990	1.764544
H	0.923059	-3.974467	-1.179700
C	3.352726	-4.904610	-0.360592
H	2.992175	-5.862359	0.037813
H	4.415173	-4.821783	-0.110342
H	3.253694	-4.949980	-1.450558
O	-0.483036	0.342376	-0.964112
O	2.646026	4.048648	1.319020
Br	-3.216714	-1.920313	-0.985252
Zn	-2.252795	-0.032792	-0.060424

Br	-3.165921	2.080811	0.261184
O	-1.352061	-0.504136	1.715307
C	3.829651	2.272789	-1.125790
C	2.904271	0.420815	-2.177973
C	3.521947	1.740992	-2.517617
H	2.936906	2.390131	-3.169815
H	4.485181	1.548783	-3.018928
C	3.337926	0.029477	-0.918772
C	3.960312	1.123170	-0.296360
H	3.166546	-0.939725	-0.469047
H	4.386765	1.122015	0.700650
H	4.433887	3.160716	-0.966922
H	2.353916	-0.198043	-2.877142
H	2.174080	3.929737	-1.247789
S	0.149462	-0.291996	2.018798
H	0.716270	2.208383	-2.295357

1 imaginary frequency

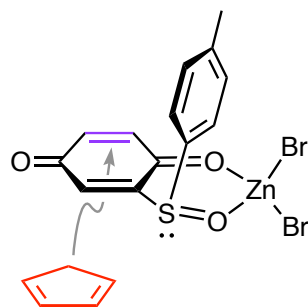
E = -8242.093127

G = -8241.844702

E<sub>M06-2X-D3</sub> = -8246.984755

G<sub>tot</sub> = -8246.736330

## TS24



C	-0.524238	1.511883	0.525759
C	-1.104699	2.686803	0.845778
C	-1.914693	3.421785	-0.164334
C	-2.397587	2.607452	-1.316955
C	-1.714700	1.406452	-1.631691
C	-0.761033	0.817860	-0.766771
H	-0.919996	3.198593	1.786986
C	2.180951	1.423955	0.870983
C	2.540343	2.768157	1.010094
C	2.961545	0.531741	0.142247
C	3.695419	3.221805	0.379745
H	1.932765	3.455264	1.593483
C	4.118617	1.007795	-0.475668
H	2.688169	-0.512979	0.053489
C	4.500762	2.351969	-0.374538
H	3.981298	4.265701	0.480614
H	4.732434	0.315690	-1.046311
C	5.737705	2.865668	-1.067371
H	5.469413	3.434397	-1.967652
H	6.306585	3.540287	-0.417430
H	6.394889	2.046503	-1.375284
O	-0.088437	-0.212235	-1.082183
O	-2.172137	4.608093	-0.021531
Br	-1.816096	-2.846967	0.516546
Zn	0.236214	-1.841982	0.046387
Br	2.077740	-3.059581	-0.666541
O	0.662896	-0.680388	1.678985
C	-4.183057	2.149089	-0.572448
C	-3.743014	-0.131095	-0.680273

C	-4.474318	0.931847	-1.436415
H	-4.231813	1.016387	-2.496229
H	-5.554805	0.724718	-1.361500
C	-3.565621	0.279858	0.631402
C	-3.904439	1.639507	0.728425
H	-3.163792	-0.339493	1.423389
H	-3.878241	2.235057	1.634132
H	-4.697265	3.094912	-0.713653
H	-3.517904	-1.122072	-1.053231
H	-2.788098	3.196174	-2.143176
S	0.683606	0.863893	1.723257
H	-1.841537	0.938285	-2.601520

1 imaginary frequency

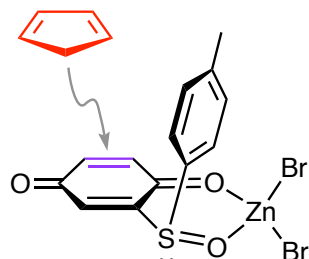
E = -8242.094759

G = -8241.846378

E<sub>M06-2X-D3</sub> = -8246.983108

G<sub>tot</sub> = -8246.734727

### TS25



C	0.726524	0.981993	1.095659
C	1.535672	1.853070	1.722843
C	2.321160	2.848515	0.938920
C	2.340586	2.680610	-0.550667
C	1.370223	1.836261	-1.146393
C	0.526616	0.993301	-0.387407
H	1.668061	1.868599	2.801506
C	0.798364	-1.720961	1.380670
C	2.095272	-1.998465	1.819734
C	0.166418	-2.511324	0.421508
C	2.779766	-3.074971	1.258031
H	2.573964	-1.382869	2.577258
C	0.866801	-3.587929	-0.119839
H	-0.846103	-2.296222	0.098529
C	2.178669	-3.884804	0.282112
H	3.792593	-3.292089	1.586969
H	0.383646	-4.206867	-0.871544
C	2.911748	-5.068103	-0.297125
H	2.617824	-5.250446	-1.336215
H	2.682530	-5.979567	0.271162
H	3.996651	-4.924309	-0.262439
O	-0.389665	0.289099	-0.903774
O	2.933206	3.740970	1.508594
Br	-3.385695	-1.662058	-1.055496
Zn	-2.254150	0.125076	-0.123966
Br	-2.932643	2.335859	0.106867
O	-1.545167	-0.420709	1.719862
C	4.143040	1.782459	-0.756414
C	3.159805	-0.077435	-1.749389
C	3.757586	0.346438	-0.450254
H	3.142345	0.169872	0.429733
H	4.691995	-0.218537	-0.299046
C	3.640009	0.751425	-2.755848
C	4.293744	1.844776	-2.166227
H	3.477112	0.613313	-3.818570

H	4.740603	2.674679	-2.702748
H	4.754859	2.376834	-0.084990
H	2.579000	-0.981616	-1.888101
H	2.596199	3.602907	-1.062916
S	-0.054925	-0.304864	2.115342
H	1.134817	1.924821	-2.199972

1 imaginary frequency

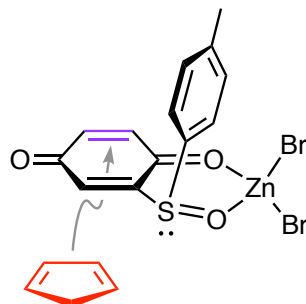
E = -8242.087763

G = -8241.839529

E<sub>M06-2X-D3</sub> = -8246.977212

G<sub>tot</sub> = -8246.728978

## TS26



C	0.439352	1.381588	-0.830996
C	1.125767	2.421818	-1.337637
C	2.089013	3.166466	-0.485118
C	2.416362	2.576907	0.855838
C	1.619312	1.511046	1.345961
C	0.672799	0.841329	0.545184
H	0.955962	2.816181	-2.336227
C	-2.283887	1.437723	-0.822190
C	-2.571301	2.800977	-0.923363
C	-3.028994	0.592110	-0.002932
C	-3.617242	3.324082	-0.166037
H	-1.991199	3.450452	-1.574155
C	-4.074666	1.136630	0.740838
H	-2.805168	-0.466815	0.060359
C	-4.382353	2.503691	0.677818
H	-3.846766	4.384064	-0.237032
H	-4.661150	0.483454	1.381907
C	-5.494839	3.082792	1.515036
H	-5.115081	3.398596	2.496174
H	-5.940052	3.962473	1.038417
H	-6.285851	2.346860	1.693167
O	-0.027903	-0.136258	0.957905
O	2.565535	4.225720	-0.869583
Br	1.740562	-2.548745	-0.849777
Zn	-0.350630	-1.810760	-0.118935
Br	-2.032376	-3.104040	0.796463
O	-1.024882	-0.767271	-1.743312
C	4.236289	1.846434	0.385104
C	3.750804	-0.331502	1.061247
C	3.892595	0.480772	-0.180356
H	3.052197	0.413553	-0.870843
H	4.779748	0.122681	-0.728896
C	4.379975	0.316077	2.110773
C	4.742445	1.607526	1.689542
H	4.524986	-0.084350	3.107457
H	5.240937	2.352502	2.300694
H	4.620286	2.652302	-0.232377
H	3.309542	-1.319729	1.076837
H	2.760754	3.330188	1.557188



S -0.944610 0.772519 -1.844769  
H 1.676409 1.211255 2.385345  
1 imaginary frequency  
E = -8242.088326  
G = -8241.840370  
E<sub>M06-2X-D3</sub> = -8246.974151  
G<sub>tot</sub> = -8246.726195