ELECTRONIC SUPPLEMENTARY INFORMATION

Origins of stereoselectivity in uncatalyzed and $ZnBr_2$-catalyzed Diels–Alder reactions of a chiral sulfinylquinone

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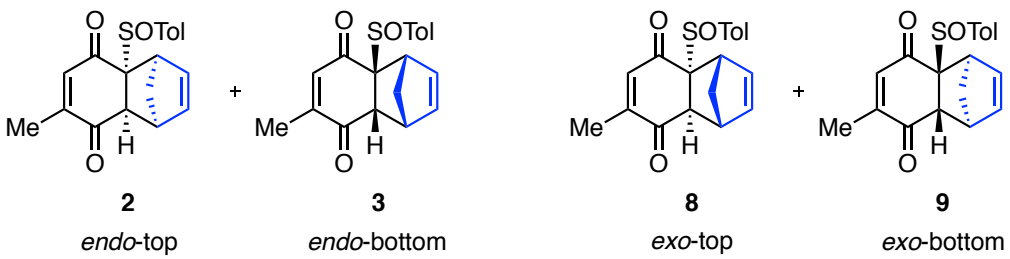
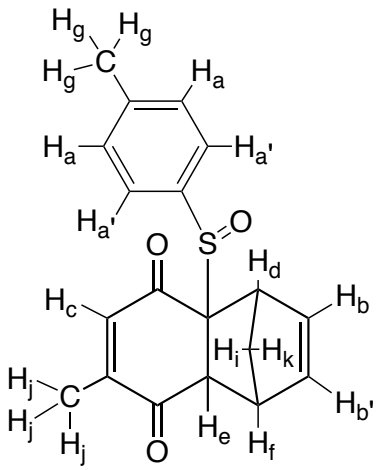
Computations of the NMR spectra of cyclopentadiene cycloadducts

The NMR chemical shifts of the cycloadducts derived from sulfinylquinone **1** and cyclopentadiene were computed using DFT and compared with the experimental spectra reported by Carreño.[1] The four diastereomeric cycloadducts are *endo*-top **2**, *endo*-bottom **3**, *exo*-top **8** and *exo*-bottom **9** (Scheme S1). A DP4 analysis[2] of the chemical shifts using a set of current best practice methodologies[3] was performed. The computations commenced with a conformational search of each cycloadduct with the MMFF forcefield[4] in MacroModel.[5] Conformers lying within 10 kJ/mol of the global minimum of each diastereomer were used for the analysis. Their potential energies were calculated with M06-2X/6-31G(d,p) and their NMR shielding constants were computed with mPW1PW91/6-311G(d). The PCM solvent model was used to simulate chloroform solvent in each of the DFT calculations.The Boltzmann-averaged chemical shifts for each diastereomer (reported relative to tetramethylsilane) are listed in Table S1, along with the experimental chemical shifts reported for **2** (*endo*-top) and **3** (*endo*-bottom) by Carreño. A common numbering system was used for all diastereomers, as shown in Scheme S1b.

(a)



(b)



Scheme S1. (a) Structures of cycloadducts **2**, **3**, **8**, and **9**, and (b) the numbering system used for the ^{1}H nuclei in the analysis of the NMR chemical shifts.

1. M. C. Carreño, J. L. García Ruano, C. Lafuente and M. A. Toledo, *Tet. Asymm.*, 1999, **10**, 1119.
2. S. G. Smith and J. M. Goodman, *J. Am. Chem. Soc.*, 2010, **132**, 12946.
3. K. Ermanis, K. E. B. Parkes, T. Agback and J. M. Goodman, *Org. Biomol. Chem.*, 2019, **17**, 5886.
4. (a) T. A. Halgren, *J. Comput. Chem.*, 1996, 17, 490; (b) T. A. Halgren, *J. Comput. Chem.*, 1996, **17**, 520; (c) T. A. Halgren, *J. Comput. Chem.* 1996, **17**, 553; (d) T. A. Halgren and R. B. Nachbar, *J. Comput. Chem.* 1996, **17**, 587; (e) T. A. Halgren, *J. Comput. Chem.* 1996, **17**, 616.
5. (a) MacroModel, Schrödinger, LLC, New York, NY, 2019; (b) Maestro, Schrödinger, LLC, New York, NY, 2019.

Table S1. Experimental chemical shifts for ^{1}H nuclei in cycloadducts **2** and **3**, as reported by Carreño, and theoretical chemical shifts for ^{1}H nuclei in **2**, **3**, **8**, and **9** computed with DFT.[a]

Nucleus	Experiment		Theory			
	Cycloadduct assigned as **2** (*endo*-top)	Cycloadduct assigned as **3** (*endo*-bottom)	**2** (*endo*-top)	**3** (*endo*-bottom)	**8** (*exo*-top)	**9** (*exo*-bottom)
H_a, $H_{a'}$	7.33, 7.21	7.39, 7.21	7.59, 7.56	7.62, 7.60	7.59, 7.49	7.62, 7.53
H_b, $H_{b'}$	6.18, 6.18	6.09, 6.09	6.58, 6.56	6.54, 6.47	6.89, 6.49	7.00, 6.76
H_c	5.94	5.94	6.14	6.04	6.23	6.17
H_d	3.80	3.61	3.60	3.74	3.56	3.20
H_e	3.75	3.17	4.02	3.47	3.46	2.74
H_f	3.55	3.58	3.44	3.56	3.12	3.78
H_g	2.35	2.33	2.51	2.53	2.52	2.53
H_i	2.29	2.0	2.37	2.09	1.38	1.29
H_j	1.57	1.52	1.55	1.60	1.64	1.59
H_k	1.48	1.60	1.82	1.97	1.77	1.92

[a] Chemical shifts (relative to tetramethylsilane) in chloroform computed with mPW1PW91/6-311G(d)//MMFF using M06-2X/6-31G(d,p) potential energies for Boltzmann averaging.

In the original experimental report, the NMR signals were not assigned to specific protons. An assignment was made by us in this work. Aromatic, vinyl and methyl protons were easily identified by chemical shift and integration. Among the methylene and methine protons, H_e was readily assigned to the signal reported as a 1H doublet at 5.94 ppm in each diastereomer, while H_d, H_f, H_i and H_k were all assigned to 1H multiplets. Within these groups of readily distinguishable types of protons, individual signals in the experimental spectra were assigned to the proton(s) with the closest NMR shift in the calculated spectrum.

DP4 probabilities were calculated to determine which of the four diastereomeric structures matched best with the experimental chemical shifts reported for **2** and **3**. The DP4 analysis was conducted using the ^{1}H chemical shifts only. This was because the experimental ^{13}C NMR spectrum of **2** contained one missing signal, which made a definite assignment of the ^{13}C peaks difficult. A DP4 analysis based on only the ^{1}H chemical shifts proved to allow structural assignments to be made with a high level of confidence. Table S2 shows the DP4 probabilities for the assignments of the two experimental NMR spectra.

Table S2. DP4 probabilities for assigning the spectra of the cycloadducts originally reported as **2** and **3**.

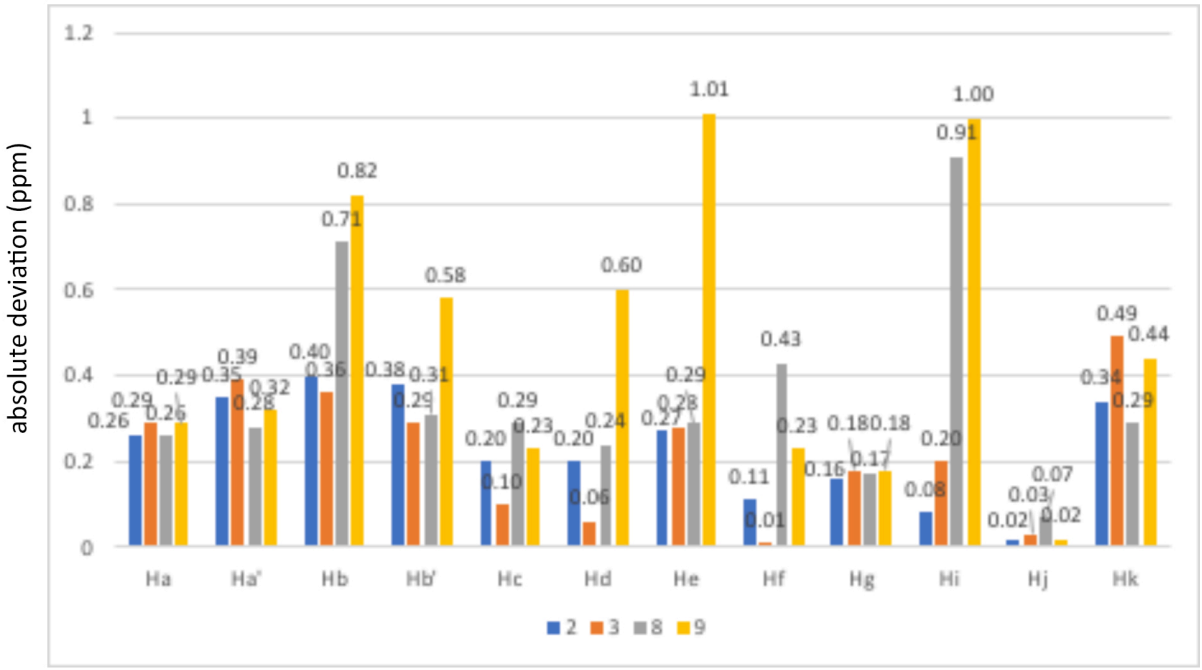
Candidate structure	DP4 probabilities	
	Cycloadduct originally assigned as **2**	Cycloadduct originally assigned as **3**
2	96.4%	0.1%
3	3.6%	99.9%
8	0.0%	0.0%
9	0.0%	0.0%

The DP4 probabilities support, with high confidence, the structural assignments originally made by Carreño et al. Diastereomer **2** is predicted to have a 96.4% probability of being the correct assignment for the spectrum originally assigned to **2**, while diastereomer **3** is predicted to have a 99.9% probability of being the correct assignment of the spectrum originally assigned to **3**.

Plots of the absolute errors showing the deviations between the calculated chemical shifts and the experimental values are shown in Figure S1. The mean absolute errors (MAEs) of **2** and **3** are both 0.23 ppm. These plots clearly show that there are large differences between the calculated chemical shifts of the *endo* and *exo* cycloadducts, which are the reason why the DP4 probabilities for the *exo* isomers are 0.0%.

Examining the experimental spectrum of **2** (Figure S1a), and focusing on the chemical shifts of just the *endo* cycloadducts (**2** and **3**), the nucleus displaying the largest deviation relative to experiment is H_k in **3** (deviation = 0.49 ppm). Conversely, when examining the experimental spectrum of **3** (Figure S1b) in the same way, the nucleus that displays the largest deviation from experiment is H_3 in **2** (deviation = 0.85 ppm). This large deviation is the strongest diagnostic indicator of an (in)correct assigment, and it explains why the DP4 probability of **3** (99.9%) is higher than that for **2** (96.4%).

(a)



(b)

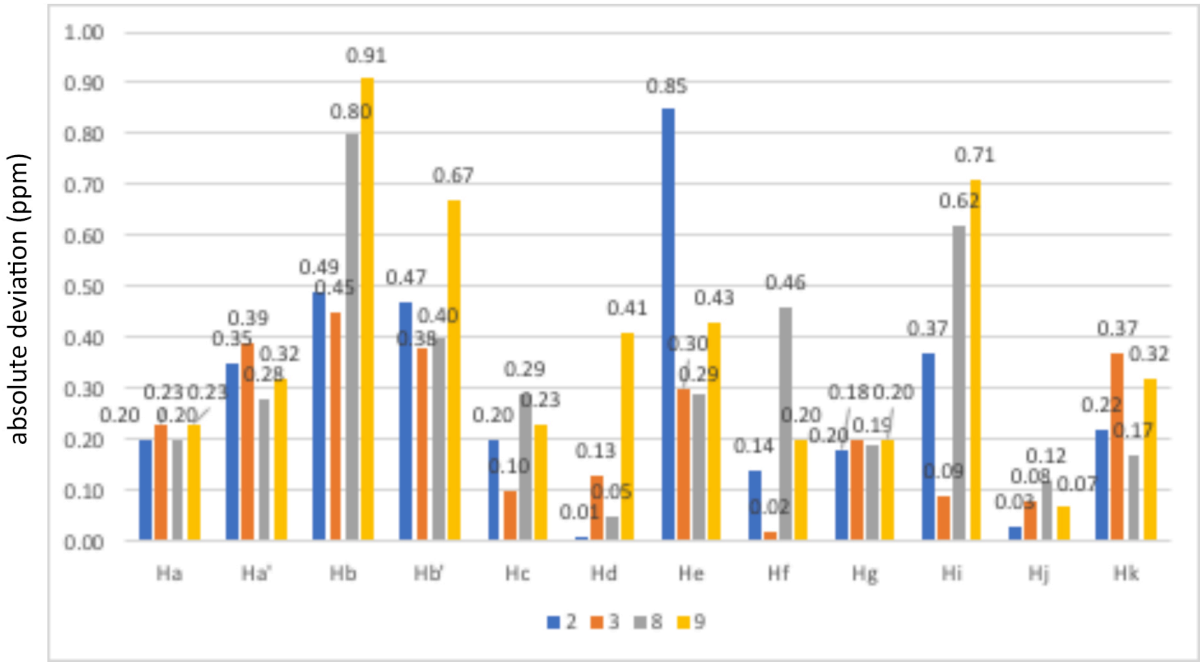


Figure S1. Absolute deviations between the calculated ^{1}H chemical shifts of **2**, **3**, **8**, and **9** and the experimental shifts of (a) **2** and (b) **3**.

Computation of the $[\alpha]_D$ value for *trans*-piperylene cycloadducts 4 and 5

The major enantiomer of the product formed in the reaction of sulfinylquinone **1** with *trans*-piperylene (either in the presence or in the absence of $ZnBr_2$) was assigned by Carreño et al.[1] as the *S* enantiomer **4**. This product, isolated in >97% ee, was reported to have an $[\alpha]_D$ value of +139.5 (*c* 0.94, $CHCl_3$) at 20 °C. We computed the $[\alpha]_D$ value of **4** using DFT. Stephens et al. previously showed[6] that the B3LYP functional in conjunction with the aug-cc-pVDZ or aug-cc-pVTZ basis sets in the gas phase gave a mean absolute deviation of approximately 20–25° for the $[\alpha]_D$ values of a set of rigid molecules. We computed the $[\alpha]_D$ value for **4** using three different B3LYP-based methods, as reported in Table S3. Each calculation used the geometry of **4** optimized with B3LYP-D3/6-31G(d) in SMD chloroform. The computed $[\alpha]_D$ values for **4** ranged from +80 to +168, in good agreement with the large positive reported $[\alpha]_D$. Best agreement was obtained with the larger aug-cc-pVTZ basis set in conjunction with the PCM[7] implicit solvent model. These results support the assignment of the absolute stereochemistry of **4** originally made by Carreño and coworkers.

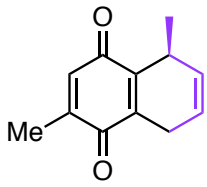


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Table S3. Calculated and experimental $[\alpha]_D$ values for **4**.

Method	$[\alpha]_D$
B3LYP/aug-cc-pVDZ (gas phase)	+168
B3LYP/aug-cc-pVDZ (PCM chloroform)	+80
B3LYP/aug-cc-pVTZ (PCM chloroform)	+124
Experiment (*c* 0.94, chloroform)	+139.5

6. P. J. Stephens, F. J. Devlin, J. R. Cheeseman and M. J. Frisch, *J. Phys. Chem. A*, 2001, **105**, 5356.
7. G. Scalmani and M. J. Frisch, *J. Chem. Phys.* 2010, **132**, 114110.

Interconversion of the sulfinylquinone conformers 1a–1c

The energy required for interconversion of the sulfinylquinone conformers **1a**–**1c** was evaluated by means of a relaxed torsional potential energy scan around the $C_{quinone}$–S bond in **1** (Figure S2). The maximum point between **1b** and **1c** on this scan was fully optimized to locate the TS for C–S bond rotation. The barrier ($\Delta G^{\ddagger}$) for bond rotation at the M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-31G(d) level of theory in SMD dichloromethane was estimated in this way to be 9.7 kcal/mol.

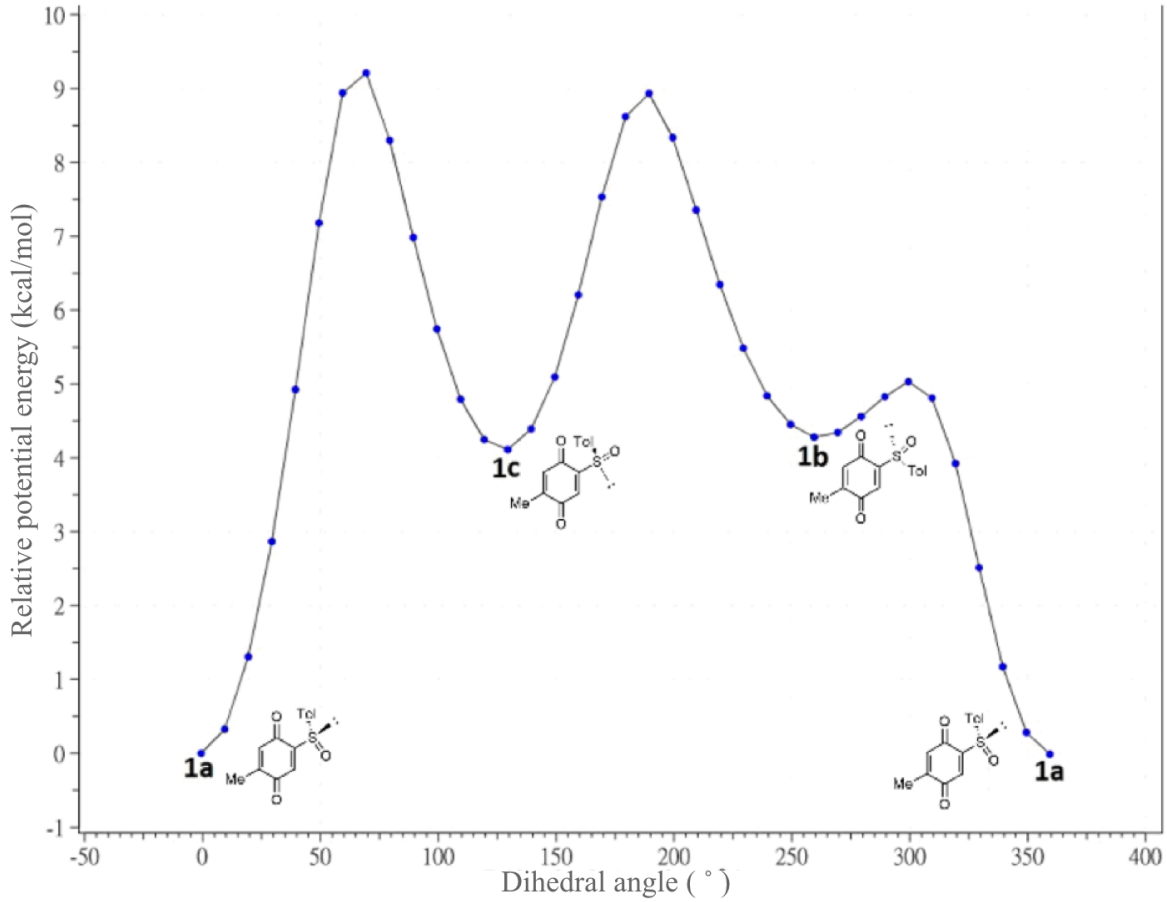

Figure S2. Torsional potential energy scan around the $C_{quinone}$–S bond (O=S–C=C dihedral) in sulfinylquinone **1**, calculated with B3LYP-D3/6-31G(d) in SMD dichloromethane.

Stepwise $ZnBr_2$-catalyzed reactions

The lowest-energy pathways for the Diels–Alder reactions of di-Zn complex **7** with cyclopentadiene and *trans*-piperylene are stepwise pathways. Bond formation to C-β precedes bond formation to C-α of the dienophile. The computed $\Delta G^{\ddagger}$ values for the first and second C–C bond-forming steps are shown in Figure S3. In each case, the second C–C bond-forming step has a lower barrier than the first.

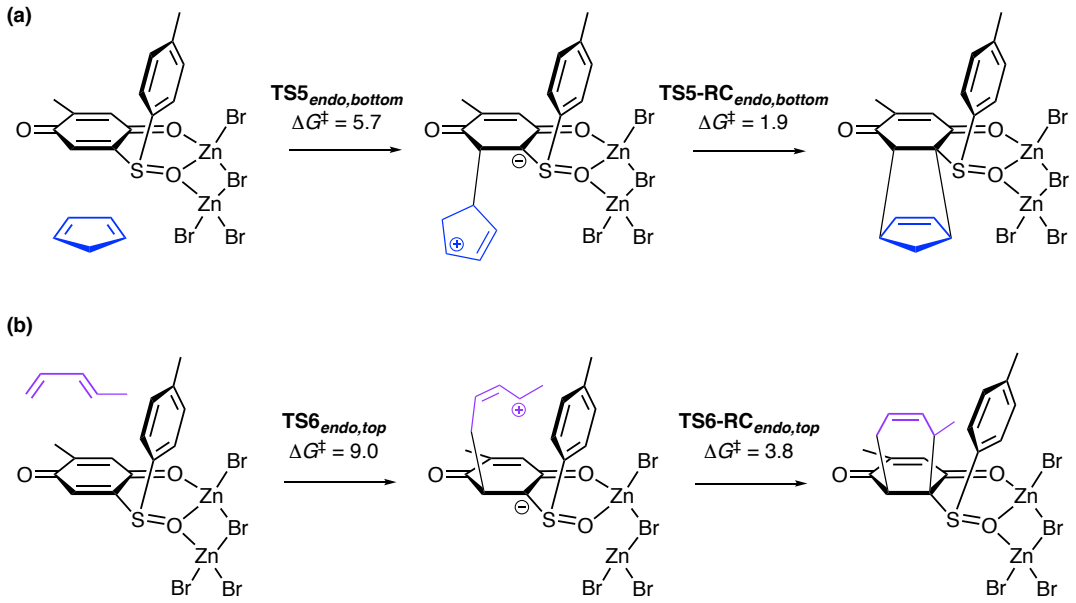

Figure S3. Computed barriers for the lowest-energy (stepwise) pathways for the Diels–Alder reactions of **7** with (a) cyclopentadiene and (b) *trans*-piperylene.

MMFF computed geometries used in NMR chemical shift calculations

Cartesian coordinates of cycloadduct conformers optimized with MMFF are listed below, together with the corresponding potential energy obtained from a M06-2X/6-31G(d,p) single-point calculation in PCM chloroform (in Hartree). Conformations listed are those found to lie within 10 kJ/mol of the global minimum by MMFF. The Boltzmann-weighted population of each conformer is given in parentheses.

Cycloadduct 2 (100% of total population)

C	-0.749749	1.679783	-0.874773
C	-1.317790	0.284419	-0.947671
C	-1.220858	-0.595366	0.327846
C	-0.187756	1.460122	1.513641
C	-0.169753	2.190445	0.394604
H	-0.825184	-0.197977	-1.800113
H	0.219306	1.841135	2.445311
C	0.411824	3.571384	0.347819
H	1.228467	3.618498	-0.380379
H	-0.353022	4.302103	0.064816
H	0.817783	3.877178	1.318105
O	-0.747050	-0.461036	2.692374
O	-0.770065	2.411431	-1.865229
C	-0.736942	0.092867	1.591807
S	-0.157108	-2.100117	0.078178
O	-0.431164	-2.648735	-1.291731
C	1.459300	-1.296322	-0.041065
C	1.971514	-0.877957	-1.271860
C	2.219841	-1.107136	1.117321
C	3.207514	-0.230940	-1.337557
H	1.419259	-1.059242	-2.191998
C	3.456889	-0.461519	1.050780
H	1.859995	-1.459770	2.082456
C	3.951066	-0.001284	-0.174637
H	3.589273	0.085270	-2.306524
H	4.035887	-0.326037	1.962182
C	5.295502	0.660470	-0.252346
H	6.074205	-0.091711	-0.411084
H	5.327518	1.383262	-1.074328
H	5.514516	1.208351	0.670164
C	-3.576489	0.996842	-0.099238
C	-2.843549	0.323747	-1.239169
C	-3.231963	-1.121715	-0.921707
C	-2.710252	-1.044007	0.521037
C	-3.522828	0.166318	0.951814
H	-4.048706	1.968161	-0.138928
H	-3.134024	0.669814	-2.232486
H	-4.312613	-1.308659	-0.985104
H	-2.725153	-1.855794	-1.552202
H	-2.887483	-1.940597	1.118377
H	-3.933206	0.333716	1.937706

E_{M06-2X} = -1358.226619

Cycloadduct 3a (92% of total population)

C	0.943995	1.906592	-0.555664
C	1.460605	0.539175	-0.926039
C	1.203943	-0.623615	0.076369
C	0.051732	1.121148	1.597151
C	0.183033	2.105696	0.703255
H	1.019480	0.310796	-1.905725
H	-0.482775	1.268767	2.530917

C	-0.400090	3.469160	0.919836
H	0.390012	4.227143	0.941185
H	-0.946448	3.534494	1.866946
H	-1.102072	3.716991	0.116761
O	0.590746	-0.983319	2.396606
O	1.128189	2.860933	-1.311682
C	0.622631	-0.230189	1.424097
S	0.142103	-1.914520	-0.737520
O	0.142418	-3.144212	0.119016
C	-1.478237	-1.146657	-0.529848
C	-2.293332	-1.479379	0.555982
C	-1.932465	-0.213843	-1.467030
C	-3.531000	-0.855659	0.726491
H	-1.965210	-2.222381	1.282471
C	-3.170844	0.410198	-1.295407
H	-1.342172	0.031883	-2.346120
C	-3.971286	0.107157	-0.188319
H	-4.149156	-1.131415	1.578685
H	-3.512218	1.130043	-2.037151
C	-5.316944	0.750123	-0.023863
H	-5.319171	1.762374	-0.441784
H	-6.081030	0.154782	-0.533046
H	-5.581718	0.836001	1.035307
C	3.477633	-0.181896	1.032932
C	2.648101	-1.198503	0.267248
C	3.278265	-0.969228	-1.115638
C	3.002852	0.537167	-1.094980
C	3.667529	0.866872	0.220678
H	3.800240	-0.281141	2.060019
H	2.733622	-2.220541	0.641135
H	4.347106	-1.218486	-1.155252
H	2.770891	-1.492784	-1.932419
H	3.393203	1.087277	-1.952724
H	4.186223	1.785396	0.456096

E_{M06-2X} = -1358.223004

Cycloadduct 3b (7% of total population)

C	-3.301258	0.129010	-0.404165
C	-1.964608	0.821813	-0.501940
C	-0.692209	0.041743	-0.022600
C	-2.293344	-1.947905	0.424020
C	-3.366927	-1.309519	-0.048760
H	-1.878348	1.121805	-1.553626
H	-2.343187	-2.988212	0.731595
C	-4.702142	-1.973943	-0.197683
H	-5.043995	-1.916971	-1.236411
H	-5.447317	-1.490950	0.443172
H	-4.664386	-3.032937	0.079429
O	-0.149226	-1.923272	1.287495
O	-4.344317	0.736842	-0.645628
C	-0.982280	-1.302998	0.626761
S	0.386027	-0.325250	-1.492594
O	0.331768	0.845857	-2.429940
C	2.041473	-0.293407	-0.774968
C	2.858518	0.833717	-0.923327
C	2.548798	-1.415921	-0.116831
C	4.146709	0.853462	-0.382645
H	2.500175	1.706162	-1.466334
C	3.836965	-1.395920	0.426278
H	1.956028	-2.321684	-0.017186
C	4.639493	-0.255686	0.312099
H	4.763192	1.740388	-0.512655

H	4.209468	-2.280741	0.938493
C	6.033725	-0.248729	0.865390
H	6.102883	-0.880398	1.757196
H	6.736748	-0.619473	0.113168
H	6.331571	0.762935	1.160528
C	-0.997029	1.120931	2.210769
C	-0.077564	1.044942	1.001259
C	-0.434801	2.406680	0.390912
C	-1.935938	2.109392	0.363916
C	-2.115830	1.745304	1.819797
H	-0.789370	0.703945	3.186209
H	0.968759	0.930833	1.280401
H	-0.169921	3.255764	1.035261
H	-0.007234	2.583132	-0.599731
H	-2.562273	2.934502	0.021049
H	-2.995533	1.942680	2.415842

E_{M06-2X} = -1358.220610

Cycloadduct 3c (1% of total population)

C	-2.398473	-0.323615	-1.384231
C	-1.050423	0.165895	-0.917969
C	-0.775812	0.200585	0.608349
C	-3.216622	-0.635622	0.910306
C	-3.404346	-0.800387	-0.402213
H	-0.311044	-0.460694	-1.432000
H	-3.960627	-0.947238	1.636451
C	-4.642738	-1.426644	-0.967480
H	-4.386819	-2.303823	-1.570862
H	-5.182412	-0.712846	-1.598541
H	-5.329271	-1.756676	-0.180361
O	-2.024890	0.281290	2.682151
O	-2.676400	-0.326295	-2.584452
C	-2.011994	-0.006433	1.483198
S	0.327855	-1.159274	1.177555
O	-0.114313	-2.400501	0.456371
C	1.939787	-0.743639	0.513305
C	2.796369	0.082401	1.249192
C	2.390047	-1.292066	-0.691632
C	4.065852	0.399249	0.758509
H	2.491511	0.481170	2.214113
C	3.659227	-0.975029	-1.182013
H	1.760447	-1.978221	-1.255107
C	4.499598	-0.112331	-0.469615
H	4.718749	1.042214	1.345511
H	3.990020	-1.414631	-2.120910
C	5.876342	0.198086	-0.979059
H	6.196272	1.194354	-0.656223
H	6.589848	-0.542042	-0.604186
H	5.898531	0.189190	-2.073910
C	-1.397126	2.610397	0.655693
C	-0.226626	1.647074	0.809525
C	0.431577	1.974196	-0.542153
C	-0.823226	1.642368	-1.349632
C	-1.777988	2.567967	-0.629890
H	-1.869732	3.161146	1.457169
H	0.392349	1.835452	1.687566
H	0.746944	3.023207	-0.630983
H	1.279374	1.351523	-0.821593
H	-0.736997	1.822713	-2.422472
H	-2.608548	3.092929	-1.080237

E_{M06-2X} = -1358.218258

Cycloadduct 8a (96% of total population)

C	-0.656147	1.842995	-0.767082
C	-1.380768	0.517684	-0.798146
C	-1.254498	-0.389103	0.457161
C	0.141670	1.509393	1.534659
C	0.143471	2.241949	0.418217
H	-1.034064	0.014187	-1.709044
H	0.704207	1.810997	2.413018
C	0.920189	3.518641	0.297419
H	1.487270	3.739627	1.208168
H	1.636252	3.453942	-0.528572
H	0.248007	4.363282	0.113713
O	-0.635802	-0.275522	2.791755
O	-0.728461	2.614482	-1.724256
C	-0.603113	0.245286	1.676292
S	-0.367297	-1.982332	0.128014
O	-0.755337	-2.475609	-1.235895
C	1.314568	-1.345654	-0.067577
C	1.784367	-0.912833	-1.310330
C	2.165110	-1.299318	1.041629
C	3.074388	-0.392362	-1.433005
H	1.155430	-0.986885	-2.195721
C	3.455975	-0.780190	0.917783
H	1.833163	-1.665257	2.011751
C	3.913467	-0.304954	-0.316415
H	3.422628	-0.064359	-2.410661
H	4.105514	-0.755452	1.790643
C	5.312490	0.218569	-0.458502
H	5.994615	-0.599506	-0.709459
H	5.366348	0.979090	-1.244520
H	5.649438	0.688532	0.471377
C	-3.484010	-1.366135	-0.293535
C	-2.757527	-0.646257	0.823545
C	-3.347637	0.752133	0.572884
C	-2.914335	0.773937	-0.896384
C	-3.567298	-0.516229	-1.327269
H	-3.794780	-2.401026	-0.287045
H	-2.966092	-1.039613	1.820760
H	-4.436705	0.796951	0.708938
H	-2.896014	1.546822	1.174757
H	-3.241260	1.656724	-1.448126
H	-3.962585	-0.732856	-2.309104

E_{M06-2X} = -1358.222808

Cycloadduct 8b (4% of total population)

C	-3.149792	-0.644196	0.040792
C	-2.252300	0.514305	0.417614
C	-0.754747	0.401145	-0.022650
C	-1.292701	-2.006277	-0.771728
C	-2.546125	-1.954582	-0.311700
H	-2.356938	0.614528	1.507552
H	-0.830299	-2.927801	-1.106696
C	-3.427808	-3.158332	-0.199105
H	-4.290492	-3.070657	-0.867577
H	-2.895542	-4.078538	-0.463170
H	-3.791218	-3.269879	0.827684
O	0.362581	-0.769973	-1.826982
O	-4.374858	-0.532699	0.067639
C	-0.493433	-0.779761	-0.943999
S	0.294569	0.255069	1.483174
O	-0.062321	-1.049441	2.136558
C	1.931612	0.031825	0.761359

C	2.660857	1.142672	0.327576
C	2.514368	-1.237210	0.686747
C	3.939821	0.981498	-0.212635
H	2.253304	2.145886	0.411839
C	3.792822	-1.398417	0.146708
H	1.979558	-2.112170	1.049557
C	4.508609	-0.292043	-0.322823
H	4.491652	1.857943	-0.545706
H	4.224975	-2.395373	0.095648
C	5.892811	-0.461904	-0.875424
H	6.109781	0.304298	-1.627089
H	6.629182	-0.386131	-0.069532
H	6.001324	-1.435847	-1.364243
C	-0.741026	2.930912	0.123381
C	-0.544109	1.739015	-0.794521
C	-1.880521	1.838889	-1.550384
C	-2.719115	1.826018	-0.269512
C	-2.042040	2.974136	0.444003
H	0.030893	3.598886	0.476659
H	0.327755	1.810720	-1.447062
H	-1.983666	2.765176	-2.131352
H	-2.084576	0.991380	-2.213263
H	-3.789840	1.959263	-0.430481
H	-2.525265	3.677965	1.106522

E_{M06-2X} = -1358.219830

Cycloadduct 9a (99.8% of total population)

C	0.736038	2.038067	-0.393316
C	1.438363	0.746737	-0.742446
C	1.271047	-0.444035	0.246826
C	-0.207187	1.124073	1.678638
C	-0.169317	2.110339	0.779370
H	1.087555	0.488873	-1.750823
H	-0.836159	1.178993	2.562183
C	-0.995244	3.353587	0.912654
H	-0.353211	4.235790	1.003693
H	-1.641412	3.321797	1.796535
H	-1.640963	3.478751	0.037074
O	0.727614	-0.781463	2.591239
O	0.887680	3.035891	-1.098319
C	0.615437	-0.096598	1.575977
S	0.381630	-1.851757	-0.557666
O	0.417804	-3.029461	0.369548
C	-1.308798	-1.221857	-0.503209
C	-1.773641	-0.383783	-1.520878
C	-2.168716	-1.572235	0.542130
C	-3.069648	0.135814	-1.467622
H	-1.145197	-0.133782	-2.372074
C	-3.464175	-1.053472	0.594069
H	-1.833155	-2.249824	1.326813
C	-3.918148	-0.180297	-0.400486
H	-3.417592	0.782918	-2.270795
H	-4.117352	-1.342187	1.415265
C	-5.322227	0.347501	-0.363613
H	-5.668901	0.462421	0.668871
H	-5.380815	1.333268	-0.836952
H	-5.993882	-0.338438	-0.888674
C	3.580512	-0.192386	-1.528919
C	2.976845	0.970226	-0.776842
C	3.399561	0.563216	0.637536
C	2.762122	-0.831748	0.529774
C	3.460764	-1.272510	-0.744244

H	4.000975	-0.156906	-2.523450
H	3.336213	1.951621	-1.090211
H	4.488557	0.535086	0.777445
H	2.968515	1.195040	1.420836
H	2.954115	-1.474060	1.391664
H	3.760309	-2.284804	-0.976878

E_{M06-2X} = -1358.221846

Cycloadduct 9b (0.2% of total population)

C	3.354125	0.070904	0.200026
C	2.049726	0.831282	0.283235
C	0.744404	0.051778	-0.094498
C	2.245737	-2.042116	-0.319824
C	3.339059	-1.410136	0.113849
H	2.018594	1.224744	1.307808
H	2.220921	-3.116540	-0.469673
C	4.614989	-2.119515	0.447605
H	4.509951	-3.206578	0.364466
H	4.918548	-1.894776	1.475344
H	5.418298	-1.811435	-0.229710
O	0.272941	-1.864419	-1.513306
O	4.435968	0.654963	0.244830
C	1.031212	-1.308547	-0.720939
S	-0.267010	-0.294019	1.405844
O	-0.205999	0.889889	2.325112
C	-1.946104	-0.331801	0.743747
C	-2.837564	0.712560	1.013479
C	-2.402957	-1.436716	0.021246
C	-4.145393	0.679459	0.522673
H	-2.520347	1.563663	1.613633
C	-3.710938	-1.470722	-0.472460
H	-1.759274	-2.292077	-0.164725
C	-4.586730	-0.405180	-0.240880
H	-4.816771	1.505808	0.746346
H	-4.041593	-2.340258	-1.037046
C	-5.999465	-0.458212	-0.741970
H	-6.643454	-0.934613	0.003664
H	-6.379178	0.548272	-0.946913
H	-6.060887	-1.024772	-1.677080
C	0.956659	2.963510	-0.313978
C	2.053075	2.013756	-0.726676
C	1.360918	1.403861	-1.949360
C	0.104085	0.994596	-1.157980
C	-0.209701	2.359976	-0.581122
H	1.093463	3.928236	0.152267
H	3.009665	2.491452	-0.943603
H	1.156064	2.132521	-2.745352
H	1.910998	0.564338	-2.387298
H	-0.682524	0.577894	-1.789909
H	-1.194416	2.752553	-0.375844

E_{M06-2X} = -1358.215862

DFT computed geometry used in optical rotation calculation

The following geometry of **4** was computed with B3LYP-D3/6-31G(d) in SMD chloroform.

4

C	-2.313344	0.270230	0.020877
C	-1.454795	-0.954767	0.079370
C	0.026169	-0.816333	-0.017528
C	0.602456	0.399485	-0.146443
C	-0.255427	1.617254	-0.253226
C	-1.721121	1.467845	-0.137489
H	0.711285	-2.557712	1.019855
C	0.817413	-2.096576	0.025188
C	2.098862	0.603236	-0.201000
H	-2.291137	2.391107	-0.199308
C	2.831235	-0.693645	-0.437129
C	2.268851	-1.896743	-0.313511
H	2.309509	1.302183	-1.022104
H	3.889436	-0.606131	-0.677485
H	2.861869	-2.797010	-0.460985
O	0.239795	2.727449	-0.444589
O	-1.970086	-2.062802	0.209315
C	-3.793291	0.065905	0.136536
H	-4.151666	-0.598002	-0.658354
H	-4.038844	-0.426827	1.084270
H	-4.330241	1.016017	0.078086
C	2.610306	1.277550	1.098513
H	3.694363	1.427064	1.041848
H	2.133475	2.250803	1.241579
H	2.397545	0.643303	1.965828
H	0.352851	-2.822607	-0.655985

DFT computed geometries and energies used in calculations of reaction mechanisms and stereoselectivities

Cartesian coordinates of structures optimized with B3LYP-D3/6-31G(d) are listed below, together with the following energies. All of the below calculations were performed in SMD implicit dichloromethane.

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

H: B3LYP-D3/6-31G(d) enthalpy at 253.15 K

G: B3LYP-D3/6-31G(d) Gibbs free energy at 253.15 K and 1 mol/L

$\mathbf{E}_{\mathrm{M06\text{-}2X\text{-}D3}}$: M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-31G(d) single-point electronic potential energy

$\mathbf{H}_{\mathrm{tot}}$: Total M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-31G(d) enthalpy at 253.15 K

$\mathbf{G}_{\mathrm{tot}}$: Total M06-2X-D3/6-311+G(d,p)//B3LYP-D3/6-31G(d) Gibbs free energy at 253.15 K 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

H = -194.017129

G = -194.039994

$\mathrm{E_{M06\text{-}2X\text{-}D3}}$ = -194.068288

$\mathrm{H_{tot}}$ = -193.971692

$\mathrm{G_{tot}}$ = -193.994557

***Trans*-piperylene**

C	-2.420996	0.783323	0.000000
H	-2.236488	1.856525	0.000000
H	-3.460532	0.465972	0.000000
C	-1.412937	-0.103420	0.000000
H	-1.641610	-1.170578	0.000000
C	0.000000	0.253473	0.000000
H	0.235979	1.319547	0.000000
C	1.002672	-0.642541	0.000000
H	0.754223	-1.705749	0.000000
C	2.462305	-0.304780	0.000000
H	2.630519	0.778087	0.000000
H	2.965822	-0.730064	0.879935
H	2.965822	-0.730064	-0.879935

0 imaginary frequencies

E = -195.324499
H = -195.205328
G = -195.231890
$E_{M06-2X-D3}$ = -195.266787
H_{tot} = -195.147616
G_{tot} = -195.174178

p-Tolylsulfinylbenzoquinone 1a

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
H = -1164.311653
G = -1164.359275
$E_{M06-2X-D3}$ = -1164.412163
H_{tot} = -1164.169641
G_{tot} = -1164.217263

p-Tolylsulfinylbenzoquinone 1b

C	-2.077769	1.632037	-0.226471
C	-0.917220	0.700795	-0.170050
C	-1.084616	-0.603844	0.090239
C	-2.449549	-1.161798	0.330687
C	-3.592659	-0.232665	0.252975
C	-3.450773	1.083050	-0.005147
O	-1.896009	2.822607	-0.455809
H	0.054036	1.152067	-0.346792
O	-2.606867	-2.349944	0.597478
H	-4.568038	-0.680218	0.424411
S	0.238793	-1.880741	0.136582
O	0.204457	-2.593688	-1.205943
C	1.668625	-0.768032	0.122380
C	2.112960	-0.201791	1.319508
C	2.339697	-0.538485	-1.077010

C	3.234069	0.625849	1.300254
H	1.592713	-0.398261	2.254089
C	3.464523	0.286698	-1.077481
H	1.984651	-1.012133	-1.987561
C	3.924805	0.884562	0.104975
H	3.585150	1.071634	2.227615
H	3.994658	0.467538	-2.009424
C	5.122864	1.801501	0.093026
H	5.685483	1.737852	1.030718
H	5.800845	1.565128	-0.733712
H	4.809642	2.847387	-0.028312
C	-4.587787	2.052821	-0.086174
H	-4.456986	2.858752	0.645788
H	-4.613751	2.529276	-1.073591
H	-5.544763	1.556855	0.095385

0 imaginary frequencies
E = -1164.547321
H = -1164.304944
G = -1164.352795
$E_{M06-2X-D3}$ = -1164.406298
H_{tot} = -1164.163802
G_{tot} = -1164.211774

p-Tolylsulfinylbenzoquinone 1c

C	-3.207360	-0.291189	-0.850430
C	-2.039795	0.603800	-1.074639
C	-1.085028	0.760830	-0.144101
C	-1.185898	0.068197	1.180559
C	-2.362077	-0.802964	1.390638
C	-3.321672	-0.993924	0.462842
O	-4.047660	-0.436798	-1.731177
H	-2.008381	1.105769	-2.038558
O	-0.335578	0.203456	2.051109
H	-2.403609	-1.290724	2.361107
S	0.300200	1.891027	-0.525526
O	0.453039	2.897323	0.597510
C	1.628098	0.655851	-0.363248
C	2.526439	0.766734	0.694534
C	1.774388	-0.332169	-1.338304
C	3.579342	-0.142815	0.784956
H	2.391096	1.552848	1.430363
C	2.829060	-1.238298	-1.228364
H	1.076988	-0.403365	-2.169847
C	3.744149	-1.160561	-0.167186
H	4.284701	-0.062849	1.608804
H	2.946765	-2.013810	-1.981303
C	4.865622	-2.162212	-0.039172
H	5.747198	-1.718082	0.435537
H	4.556696	-3.014648	0.581121
H	5.162842	-2.559807	-1.015440
C	-4.516223	-1.875306	0.655742
H	-5.441081	-1.298176	0.537305
H	-4.539007	-2.661647	-0.108349
H	-4.510073	-2.339630	1.645184

0 imaginary frequencies
E = -1164.547615
H = -1164.305119
G = -1164.353091
$E_{M06-2X-D3}$ = -1164.405828
H_{tot} = -1164.163451
G_{tot} = -1164.211302

TS for $C_{quinone}$–S bond rotation in *p*-tolylsulfinylbenzoquinone 1

C	-2.322507	-1.467400	-0.562780
C	-1.208136	-0.559531	-0.929729
C	-1.078088	0.669738	-0.403888
C	-2.127411	1.196731	0.529309
C	-3.202847	0.257087	0.923957
C	-3.331138	-0.987919	0.426687
O	-2.392727	-2.588155	-1.058028
H	-0.490085	-0.978593	-1.630372
O	-2.131646	2.346545	0.949009
H	-3.916068	0.663186	1.636699
S	0.337252	1.729392	-0.983415
O	0.438952	2.995866	-0.165901
C	1.658248	0.618487	-0.406994
C	2.230430	-0.296122	-1.288912
C	2.117098	0.743465	0.906306
C	3.257005	-1.126665	-0.830512
H	1.889592	-0.365910	-2.318670
C	3.143678	-0.087369	1.344004
H	1.676664	1.488462	1.562857
C	3.725780	-1.037742	0.486202
H	3.705429	-1.844890	-1.512049
H	3.503476	-0.001373	2.366744
C	4.840517	-1.924595	0.982980
H	5.159182	-2.639389	0.218033
H	5.714730	-1.329153	1.275362
H	4.527743	-2.490133	1.869475
C	-4.429402	-1.936432	0.794300
H	-4.997296	-2.229386	-0.096840
H	-4.012964	-2.858943	1.216420
H	-5.112449	-1.488591	1.520755

1 imaginary frequency

E = -1164.539907

H = -1164.298352

G = -1164.345010

$E_{M06-2X-D3}$ = -1164.396768

H_{tot} = -1164.155213

G_{tot} = -1164.201871

TS1*$_{endo,top}$*

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

H = -1358.32112

G = -1358.374787

$E_{M06\text{-}2X\text{-}D3}$ = -1358.473937

H_{tot} = -1358.132881

G_{tot} = -1358.186548

TS1*endo,bottom*

C	3.248348	-0.463438	-0.424495
C	1.818583	-0.876644	-0.548726
C	0.816123	0.122065	-0.639400
C	2.514563	1.831444	0.028046
C	3.519234	0.930204	0.044962
H	1.673060	-1.769651	-1.152535
H	2.684558	2.868468	0.308980
C	4.927470	1.247918	0.446685
H	5.614412	1.057005	-0.386066
H	5.248615	0.597435	1.269680
H	5.027489	2.290930	0.759195
O	0.378409	2.456912	-0.750024
O	4.164471	-1.243514	-0.658723
C	1.150463	1.529067	-0.465056
S	-0.545815	-0.205286	-1.841809
O	-0.475020	-1.700871	-2.148151
C	-2.073963	0.020324	-0.866934
C	-2.485433	1.291662	-0.453945
C	-2.866697	-1.099529	-0.628202
C	-3.684752	1.419651	0.242994
H	-1.859118	2.154799	-0.648712
C	-4.066188	-0.951941	0.073031
H	-2.543485	-2.071848	-0.986222
C	-4.492338	0.303807	0.522624
H	-4.002695	2.404821	0.577289
H	-4.679745	-1.827983	0.269631
C	-5.790541	0.471388	1.273547
H	-6.260233	-0.494078	1.486883
H	-5.632360	0.991677	2.226269
H	-6.504261	1.072648	0.695641
C	0.983163	0.080682	2.361199
C	-0.127927	-0.346391	1.636020
C	0.103092	-1.769172	1.214233

C	1.619345	-1.799898	1.207758
C	2.031781	-0.823257	2.154856
H	1.051870	1.008216	2.918371
H	-1.089463	0.148317	1.613619
H	-0.249280	-2.430757	2.022705
H	-0.374400	-2.086689	0.287866
H	2.181814	-2.712899	1.038110
H	3.037434	-0.723714	2.548236

1 imaginary frequency
E = -1358.661971
H = -1358.320488
G = -1358.373882
$E_{M06-2X-D3}$ = -1358.472014
H_{tot} = -1358.130531
G_{tot} = -1358.183925

TS1*exo,top*

C	-1.303701	1.695052	-1.002778
C	-1.232208	0.221236	-0.867774
C	-0.814549	-0.348588	0.351956
C	-0.833664	1.939202	1.405852
C	-1.170842	2.528740	0.240065
H	-0.986525	-0.300300	-1.787420
H	-0.711211	2.516562	2.319310
C	-1.402312	4.000562	0.086912
H	-1.273422	4.526076	1.036991
H	-0.709686	4.420380	-0.651909
H	-2.413424	4.192001	-0.292980
O	-0.108916	0.029269	2.588719
O	-1.459522	2.236387	-2.095027
C	-0.560734	0.489311	1.535163
S	0.222248	-1.876925	0.257682
O	-0.095253	-2.487608	-1.102038
C	1.834222	-1.042726	0.067730
C	2.302141	-0.772032	-1.218258
C	2.597911	-0.722023	1.191762
C	3.538306	-0.147929	-1.376334
H	1.704651	-1.063633	-2.076935
C	3.832156	-0.094756	1.016073
H	2.231742	-0.946014	2.188479
C	4.318757	0.206675	-0.264501
H	3.907271	0.063693	-2.377360
H	4.429743	0.158634	1.888568
C	5.640428	0.912870	-0.443731
H	5.496932	2.001006	-0.491614
H	6.320725	0.710122	0.390322
H	6.134369	0.609533	-1.373245
C	-2.909010	-2.254230	0.024543
C	-2.785138	-1.295061	1.045355
C	-3.511636	-0.062060	0.576583
C	-3.345248	-0.216901	-0.917341
C	-3.254668	-1.604054	-1.162653
H	-2.647711	-3.301963	0.110548
H	-2.578360	-1.516181	2.086522
H	-4.580431	-0.181634	0.815556
H	-3.187985	0.885022	1.005306
H	-3.721118	0.502428	-1.637156
H	-3.303255	-2.069045	-2.140853

1 imaginary frequency
E = -1358.658434
H = -1358.317387
G = -1358.370976

$E_{M06\text{-}2X\text{-}D3}$ = -1358.468937
H_{tot} = -1358.127890
G_{tot} = -1358.181479

TS1*exo,bottom*

C	1.643048	1.843357	-0.755000
C	1.451296	0.384441	-0.913329
C	0.792103	-0.373715	0.081931
C	0.733599	1.708683	1.526298
C	1.315183	2.461230	0.570264
H	1.388168	0.077776	-1.952284
H	0.469688	2.128785	2.494190
C	1.641454	3.913987	0.733501
H	2.714426	4.085044	0.583043
H	1.123729	4.508912	-0.028080
H	1.358236	4.277819	1.724856
O	-0.230481	-0.312646	2.240989
O	2.047456	2.542762	-1.682599
C	0.384992	0.277619	1.355351
S	-0.261800	-1.733103	-0.569417
O	-0.314159	-2.915666	0.380010
C	-1.857825	-0.864022	-0.423155
C	-2.142295	0.218973	-1.259636
C	-2.795274	-1.325655	0.495236
C	-3.379675	0.850363	-1.154315
H	-1.405663	0.577307	-1.974590
C	-4.032652	-0.684563	0.585768
H	-2.545170	-2.168865	1.130958
C	-4.344396	0.409038	-0.232994
H	-3.603025	1.698992	-1.796855
H	-4.765455	-1.038105	1.307324
C	-5.689625	1.088643	-0.151699
H	-5.586549	2.179915	-0.170776
H	-6.321950	0.810432	-1.005513
H	-6.225583	0.810942	0.761704
C	3.405368	-1.549627	-1.215185
C	3.547266	-0.258740	-0.665442
C	3.389895	-0.411309	0.826819
C	2.492672	-1.620488	0.874147
C	2.768251	-2.373622	-0.282907
H	3.637432	-1.819741	-2.239766
H	4.102855	0.546905	-1.132714
H	4.368514	-0.700763	1.242965
H	3.055100	0.470192	1.371773
H	2.046288	-2.017518	1.777566
H	2.414922	-3.381548	-0.464242

1 imaginary frequency
E = -1358.654547
H = -1358.313566
G = -1358.367236
$E_{M06\text{-}2X\text{-}D3}$ = -1358.465924
H_{tot} = -1358.124943
G_{tot} = -1358.178613

TS2*endo,top*

C	-1.367161	1.958078	-0.669841
C	-0.833523	0.597660	-1.005334
C	-0.543191	-0.275600	0.057764
C	-1.792842	1.188940	1.617385
C	-2.006467	2.125469	0.667431
H	-0.161331	0.579982	-1.861519
H	-2.195022	1.306732	2.621302

C	-2.791677	3.383735	0.889259
H	-3.213372	3.417054	1.897594
H	-2.154148	4.263382	0.741478
H	-3.607204	3.464154	0.160033
O	-0.564313	-0.686799	2.393418
O	-1.307047	2.882358	-1.472543
C	-0.936397	-0.004963	1.418006
S	0.550101	-1.689206	-0.247206
O	0.374358	-2.014331	-1.732242
C	2.135629	-0.805090	-0.091181
C	2.888457	-0.561532	-1.235266
C	2.586347	-0.410935	1.173039
C	4.112097	0.102867	-1.112970
H	2.517176	-0.890367	-2.201417
C	3.806532	0.251980	1.274348
H	1.982918	-0.604011	2.055727
C	4.588326	0.519170	0.136602
H	4.704430	0.298889	-2.003625
H	4.162462	0.568314	2.252280
C	5.911420	1.232204	0.274925
H	5.786182	2.205233	0.766198
H	6.610056	0.650927	0.890220
H	6.381286	1.402117	-0.698982
C	-3.480976	-0.076429	-1.255570
C	-2.361386	-0.052478	-2.105078
C	-2.717442	-1.985549	0.080355
C	-3.615101	-0.972068	-0.180810
H	-4.186701	0.749357	-1.314468
H	-2.354624	0.681585	-2.907388
C	-2.709464	-2.791536	1.328926
H	-4.403841	-0.781804	0.545004
H	-1.839815	-0.975996	-2.342504
H	-2.040581	-2.303780	-0.707499
H	-3.578633	-2.579979	1.960495
H	-2.668758	-3.865400	1.107593
H	-1.805161	-2.552454	1.913778

1 imaginary frequency

E = -1359.875140

H = -1359.511580

G = -1359.567490

$E_{M06\text{-}2X\text{-}D3}$ = -1358.670749

H_{tot} = -1359.307189

G_{tot} = -1358.363099

TS2*endo,bottom*

C	-3.180855	0.636495	0.444401
C	-1.749124	1.103846	0.524400
C	-0.883195	0.760346	-0.535762
C	-2.529432	-0.899469	-1.347729
C	-3.469521	-0.511713	-0.457510
H	-1.647219	2.121597	0.899376
H	-2.727179	-1.707926	-2.048650
C	-4.834395	-1.127025	-0.355952
H	-4.950784	-1.954297	-1.061674
H	-5.017380	-1.499460	0.659515
H	-5.609578	-0.378246	-0.557352
O	-0.475725	-0.528383	-2.483741
O	-4.056720	1.165876	1.117797
C	-1.207255	-0.240652	-1.511977
S	0.449174	1.935725	-0.939576
O	0.311632	3.077868	0.064102
C	1.923817	0.995275	-0.433391

C	2.481015	1.238752	0.821570
C	2.500826	0.082972	-1.316602
C	3.617401	0.528453	1.208278
H	2.024993	1.977204	1.474406
C	3.641085	-0.614115	-0.915207
H	2.045526	-0.102431	-2.283996
C	4.214512	-0.407049	0.348700
H	4.051165	0.704753	2.189977
H	4.091510	-1.333614	-1.594812
C	5.463868	-1.145724	0.762109
H	6.361427	-0.560957	0.519095
H	5.480318	-1.331466	1.841631
H	5.551226	-2.107343	0.245327
C	-1.589450	-1.079908	2.094835
C	-1.214881	0.280728	2.170764
C	0.215637	-1.803471	0.595292
C	-0.934278	-2.044219	1.308507
H	-2.546315	-1.360136	2.530039
H	-1.767753	0.892294	2.880018
C	0.756639	-2.726949	-0.431851
H	-1.433916	-3.001917	1.172677
H	-0.160997	0.537588	2.102844
H	0.796479	-0.912497	0.803998
H	1.830685	-2.896891	-0.290802
H	0.226877	-3.685187	-0.447316
H	0.646164	-2.254999	-1.423604

1 imaginary frequency

E = -1359.872510

H = -1359.508886

G = -1359.564423

$E_{M06-2X-D3}$ = -1358.667957

H_{tot} = -1359.304333

G_{tot} = -1358.359870

TS2*exo,top*

C	-1.327622	2.043919	-0.815866
C	-1.098835	0.572865	-1.003382
C	-0.701472	-0.164388	0.129006
C	-1.410426	1.705274	1.610985
C	-1.655791	2.520303	0.564652
H	-0.636430	0.309148	-1.950763
H	-1.591060	2.027826	2.633888
C	-2.185922	3.917029	0.688373
H	-2.382158	4.176802	1.732227
H	-1.469608	4.634640	0.271369
H	-3.112777	4.031787	0.112761
O	-0.338481	-0.221353	2.471973
O	-1.284766	2.820583	-1.761877
C	-0.783341	0.366832	1.469270
S	0.289614	-1.672411	-0.131581
O	0.051666	-2.058126	-1.588992
C	1.935822	-0.881501	-0.082602
C	2.571671	-0.583752	-1.286104
C	2.552291	-0.614689	1.142961
C	3.835183	0.008320	-1.261048
H	2.077697	-0.821180	-2.223796
C	3.813341	-0.019810	1.149345
H	2.045392	-0.847119	2.074059
C	4.474641	0.299584	-0.047431
H	4.333473	0.246197	-2.198150
H	4.295241	0.197979	2.099823
C	5.854659	0.910561	-0.022849

H	6.076253	1.440262	-0.955370
H	5.964893	1.616132	0.808281
H	6.623118	0.136199	0.106020
C	-2.967791	-2.067466	-0.590490
C	-2.870031	-1.618398	0.711810
C	-2.990240	0.188779	-1.577194
C	-3.056778	-1.206656	-1.695186
H	-2.820591	-3.128412	-0.781441
H	-3.050985	0.784419	-2.484323
H	-2.969037	-1.646241	-2.685640
H	-3.451590	0.658897	-0.710589
H	-3.185780	-0.606303	0.948771
C	-2.554960	-2.490339	1.875169
H	-1.698868	-2.074957	2.428547
H	-3.396906	-2.510137	2.581677
H	-2.317839	-3.514995	1.572591

1 imaginary frequency

E = -1359.869980

H = -1359.506487

G = -1359.562205

$E_{M06-2X-D3}$ = -1358.665804

H_{tot} = -1359.302311

G_{tot} = -1358.358029

TS2*exo,bottom*

C	1.572515	2.138998	-0.554372
C	1.340092	0.724083	-0.994610
C	0.716139	-0.166313	-0.088924
C	1.150822	1.465048	1.758383
C	1.621624	2.404729	0.913659
H	1.069259	0.656834	-2.045293
H	1.129056	1.633781	2.832773
C	2.145405	3.742238	1.343155
H	1.545828	4.546207	0.900239
H	2.128712	3.844886	2.431657
H	3.172938	3.887733	0.987477
O	-0.099079	-0.499071	2.124787
O	1.749924	3.035397	-1.371389
C	0.537115	0.185488	1.312928
S	-0.283780	-1.465385	-0.878601
O	-0.268338	-2.779530	-0.119700
C	-1.907047	-0.693084	-0.554715
C	-2.300520	0.433875	-1.279227
C	-2.752727	-1.269526	0.388912
C	-3.554373	0.993694	-1.036918
H	-1.636425	0.881393	-2.014868
C	-4.005301	-0.698780	0.618551
H	-2.420128	-2.146843	0.933854
C	-4.426504	0.437025	-0.087889
H	-3.861936	1.875461	-1.594266
H	-4.665532	-1.141006	1.361252
C	-5.796557	1.027930	0.141016
H	-6.533269	0.585167	-0.543236
H	-6.147848	0.842225	1.161765
H	-5.801255	2.109535	-0.032949
C	3.337939	-1.065498	-1.592096
C	3.304409	0.304738	-1.295086
C	2.676340	-1.761916	0.658392
C	3.007362	-2.053422	-0.653163
H	3.433503	-1.366297	-2.633508
H	3.546152	1.011348	-2.084655
H	2.876096	-3.075781	-1.001764

H	2.971695	-0.799875	1.067760
H	3.614032	0.629313	-0.303587
C	2.164605	-2.751193	1.641694
H	1.196052	-2.409765	2.032809
H	2.023342	-3.739250	1.197698
H	2.852123	-2.821957	2.496740

1 imaginary frequency
E = -1359.864088
H = -1359.500625
G = -1359.556428
$E_{M06-2X-D3}$ = -1358.660569
H_{tot} = -1359.297106
G_{tot} = -1358.352909

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C	0.119496	3.380144	-0.229525
C	-1.076732	4.003925	-0.186532
C	-2.321597	3.179661	-0.279920
C	-2.191664	1.700206	-0.414864
C	-0.988115	1.109847	-0.444422
C	0.254619	1.928570	-0.350986
H	1.054531	3.928247	-0.160689
H	-3.124245	1.150349	-0.491745
C	-1.249295	5.480778	-0.047477
H	-0.283802	5.987916	0.016994
H	-1.838294	5.711245	0.848361
H	-1.809980	5.880195	-0.901154
C	-2.346961	-1.305239	-0.217857
C	-2.661550	-1.392215	1.142762
C	-3.245808	-1.700751	-1.209438
C	-3.910924	-1.881070	1.504043
H	-1.936698	-1.092373	1.892781
C	-4.498800	-2.177475	-0.822157
H	-2.981571	-1.638802	-2.261408
C	-4.848066	-2.276370	0.531562
H	-4.170043	-1.956532	2.556859
H	-5.209735	-2.484300	-1.584094
C	-6.189645	-2.820137	0.950184
H	-6.896760	-2.835654	0.115358
H	-6.088072	-3.847896	1.322918
H	-6.622058	-2.224412	1.761938
S	-0.754141	-0.679363	-0.726260
O	1.383383	1.416257	-0.374916
O	-3.432843	3.689607	-0.248372
O	0.233391	-1.112952	0.399424
Zn	2.146871	-0.530574	0.104944
Br	2.909487	-1.333473	-1.920457
Br	3.176960	-0.241198	2.137440

0 imaginary frequencies
E = -8087.294929
H = -8087.046982
G = -8087.103066
$E_{M06-2X-D3}$ = -8092.227818
H_{tot} = -8091.979871
G_{tot} = -8092.035955

6b

C	-0.404234	2.467070	1.636864
C	-0.854492	3.679656	1.245702
C	-1.265139	3.877346	-0.181328
C	-1.181615	2.716172	-1.114930
C	-0.742709	1.523694	-0.684619

C	-0.267219	1.345855	0.713978
H	-0.070866	2.279816	2.653382
H	-1.521546	2.893478	-2.131685
C	-0.957910	4.864666	2.147716
H	-0.645065	4.616905	3.164499
H	-1.988437	5.238995	2.167098
H	-0.335263	5.684187	1.768824
C	-2.101239	-0.829765	-0.932477
C	-1.749793	-1.940763	-0.167070
C	-3.430411	-0.423500	-1.072057
C	-2.760015	-2.645289	0.484203
H	-0.716022	-2.254881	-0.074634
C	-4.422512	-1.140931	-0.406376
H	-3.694924	0.440175	-1.677218
C	-4.105443	-2.260058	0.378583
H	-2.494926	-3.510130	1.086878
H	-5.458869	-0.828467	-0.502214
C	-5.185991	-3.052897	1.069035
H	-6.090042	-2.454456	1.220001
H	-5.465226	-3.928483	0.467760
H	-4.847207	-3.423432	2.042559
S	-0.833913	0.107533	-1.819413
O	0.247550	0.279279	1.087624
O	-1.675809	4.954718	-0.587119
O	0.481975	-0.697243	-1.704056
Zn	1.684041	-0.764542	-0.070795
Br	1.943364	-2.924646	0.662229
Br	3.207847	0.955516	-0.320107

0 imaginary frequencies
E = -8087.300307
H = -8087.052160
G = -8087.107618
$E_{M06-2X-D3}$ = -8092.227918
H_{tot} = -8091.979771
G_{tot} = -8092.035229

6c

C	4.778317	0.516101	-0.543432
C	5.070114	-0.630843	0.105670
C	3.980752	-1.626342	0.373113
C	2.601373	-1.322036	-0.101819
C	2.359993	-0.163978	-0.724717
C	3.421887	0.835027	-1.014029
H	5.538103	1.263078	-0.755567
H	1.827122	-2.059696	0.087216
C	6.438157	-0.991042	0.592104
H	7.159381	-0.202624	0.363328
H	6.772635	-1.927912	0.130489
H	6.425626	-1.163840	1.674787
C	0.284619	1.548123	-0.156128
C	0.159567	1.221223	1.198131
C	-0.017445	2.820826	-0.635409
C	-0.284127	2.198364	2.082033
H	0.393096	0.220651	1.551882
C	-0.444554	3.790154	0.271612
H	0.072669	3.055053	-1.691578
C	-0.593159	3.494893	1.633929
H	-0.387776	1.956222	3.136455
H	-0.681316	4.787130	-0.089482
C	-1.103543	4.531248	2.601609
H	-0.989037	5.544459	2.204376
H	-2.170948	4.371483	2.804219

H	-0.579466	4.471374	3.561834
S	0.711368	0.264653	-1.339281
O	3.147111	1.865878	-1.623478
O	4.204988	-2.668708	0.973981
O	-0.106471	-1.000272	-0.904908
Zn	-1.944176	-0.992872	-0.232475
Br	-3.213050	0.669300	-1.138470
Br	-2.338762	-2.888419	0.960299

0 imaginary frequencies
E = -8087.288945
H = -8087.041084
G = -8087.097256
$E_{M06-2X-D3}$ = -8092.222560
H_{tot} = -8091.974700
G_{tot} = -8092.030872

TS3*endo,top*

C	0.311542	2.910767	-1.338147
C	-0.847098	3.607589	-1.382761
C	-2.132005	2.892941	-1.110074
C	-2.035238	1.538047	-0.464605
C	-0.833675	0.812328	-0.652351
C	0.374781	1.477450	-1.045088
H	1.263579	3.386997	-1.557603
C	-0.940064	5.057227	-1.741556
H	0.048678	5.486131	-1.922970
H	-1.433673	5.620657	-0.940221
H	-1.557119	5.187201	-2.638479
C	-2.217578	-1.657520	-0.310497
C	-2.330831	-2.404788	0.861310
C	-3.288744	-1.535692	-1.202571
C	-3.553777	-3.006519	1.159768
H	-1.476122	-2.513690	1.520766
C	-4.502619	-2.136604	-0.879509
H	-3.182619	-0.985159	-2.133562
C	-4.656706	-2.876624	0.304538
H	-3.647986	-3.589895	2.071772
H	-5.341465	-2.039634	-1.563742
C	-5.984653	-3.504742	0.644860
H	-6.677187	-2.752507	1.045662
H	-6.458201	-3.939044	-0.242614
H	-5.876150	-4.290669	1.398781
S	-0.622259	-0.971185	-0.770381
O	1.478202	0.872736	-1.199970
O	-3.215903	3.407593	-1.343952
O	0.356995	-1.378926	0.382187
Zn	2.230432	-0.676649	-0.068220
Br	3.329473	-2.198958	-1.425371
Br	3.155123	0.402137	1.777723
C	-2.208259	2.156544	1.410769
C	-0.300020	1.051830	2.172749
C	-1.780091	0.889908	2.131217
H	-2.139357	-0.050382	1.718967
H	-2.161457	0.949057	3.164220
C	0.026224	2.378399	1.957588
C	-1.140952	3.077748	1.592890
H	1.026095	2.789117	2.022025
H	-1.201552	4.143968	1.405865
H	-3.242873	2.485795	1.394404
H	0.398469	0.265706	2.422714
H	-2.974521	0.992576	-0.482912

1 imaginary frequency

E = -8281.421250
H = -8281.074094
G = -8281.135240
$E_{M06-2X-D3}$ = -8286.299812
H_{tot} = -8285.952657
G_{tot} = -8286.013803

TS3*endo,bottom*

C	2.006185	0.697434	1.940754
C	3.069705	1.513723	1.762577
C	3.263352	2.168450	0.432853
C	2.494334	1.597373	-0.722335
C	1.301926	0.888117	-0.433754
C	1.021323	0.413135	0.892702
H	1.807569	0.233223	2.903239
C	4.050326	1.859506	2.838035
H	3.821321	1.335133	3.769106
H	4.043286	2.940084	3.023403
H	5.069938	1.604338	2.523939
C	-1.229790	1.910812	-0.929361
C	-2.570576	1.553075	-1.056154
C	-0.856618	3.133426	-0.364181
C	-3.549005	2.424300	-0.576468
H	-2.846768	0.601028	-1.492760
C	-1.850141	3.990801	0.102526
H	0.188149	3.414204	-0.273324
C	-3.209153	3.650397	0.008980
H	-4.594332	2.137612	-0.655730
H	-1.564488	4.938724	0.551661
C	-4.271692	4.571292	0.554920
H	-3.988357	5.623142	0.439022
H	-5.233363	4.414560	0.055404
H	-4.425606	4.391388	1.627453
S	0.018659	0.819635	-1.667952
O	-0.037362	-0.192509	1.217167
O	4.044839	3.096117	0.279521
O	-0.622770	-0.604480	-1.662370
Zn	-1.075254	-1.528322	0.089747
Br	-3.349739	-1.547082	0.542348
Br	0.216187	-3.465415	0.344723
C	3.920269	0.355108	-1.395445
C	2.485933	-1.482064	-1.453652
C	3.070700	-0.452474	-2.361033
H	2.361098	0.103894	-2.976197
H	3.754859	-0.962125	-3.059588
C	4.171780	-0.500442	-0.293411
C	3.237759	-1.555743	-0.295298
H	4.649118	1.084338	-1.735370
H	2.514123	2.234835	-1.603753
H	1.660033	-2.132734	-1.708134
H	4.913765	-0.319013	0.476053
H	3.085664	-2.280123	0.494859

1 imaginary frequency
E = -8281.429313
H = -8281.082298
G = -8281.143150
$E_{M06-2X-D3}$ = -8286.305744
H_{tot} = -8285.958729
G_{tot} = -8286.019581

TS3*exo,top*

C	0.286179	3.096945	-1.179989
C	-0.899825	3.738326	-1.246704
C	-2.153356	2.970444	-0.982091
C	-2.031643	1.556749	-0.461877
C	-0.782247	0.914444	-0.604262
C	0.407500	1.656528	-0.900856
H	1.222723	3.616343	-1.364821
C	-1.053306	5.187987	-1.586478
H	-0.083004	5.656857	-1.769279
H	-1.560614	5.721513	-0.773404
H	-1.681668	5.305974	-2.477060
C	-2.104125	-1.604429	-0.468024
C	-2.209446	-2.462331	0.625740
C	-3.172906	-1.422604	-1.352252
C	-3.425046	-3.101408	0.866641
H	-1.351309	-2.631352	1.266099
C	-4.382390	-2.061496	-1.086409
H	-3.070826	-0.797686	-2.235400
C	-4.531683	-2.901859	0.028182
H	-3.512007	-3.770378	1.718828
H	-5.219186	-1.914738	-1.764039
C	-5.853355	-3.566564	0.319623
H	-6.398261	-3.795480	-0.602351
H	-5.718506	-4.495757	0.882653
H	-6.493205	-2.907298	0.921708
S	-0.514936	-0.852580	-0.850129
O	1.550182	1.123056	-1.005937
O	-3.255310	3.470495	-1.161826
O	0.455180	-1.335714	0.277729
Zn	2.309517	-0.556006	-0.058086
Br	3.439582	-1.838096	-1.624776
Br	3.194467	0.232949	1.944073
C	-2.401984	1.969832	1.495006
C	-0.368560	1.159516	2.312963
C	-1.041913	2.442613	1.974751
H	-0.480479	3.101822	1.313108
H	-1.201334	3.006182	2.909179
C	-1.317212	0.163933	2.442493
C	-2.563083	0.664026	2.014926
H	-1.121996	-0.847418	2.771737
H	-3.489186	0.100552	1.992136
H	-3.243626	2.643679	1.371819
H	0.694868	1.050589	2.494185
H	-2.940641	0.991605	-0.633893

1 imaginary frequency
E = -8281.417506
H = -8281.070222
G = -8281.131508
$E_{M06-2X-D3}$ = -8286.294492
H_{tot} = -8285.947209
G_{tot} = -8286.008495

TS3*exo,bottom*

C	1.963794	0.591171	2.153662
C	3.082578	1.334111	2.015310
C	3.433933	1.869461	0.666960
C	2.655508	1.364609	-0.522239
C	1.425911	0.707507	-0.278066
C	1.046847	0.291038	1.041063
H	1.662760	0.196107	3.120228
C	3.998514	1.689829	3.144050

H	3.648865	1.263247	4.087470
H	4.069966	2.778928	3.246968
H	5.014069	1.327755	2.942319
C	-0.962350	1.943538	-0.968461
C	-2.319988	1.718360	-1.189687
C	-0.511872	3.138140	-0.399315
C	-3.238641	2.694359	-0.802811
H	-2.657578	0.786978	-1.627683
C	-1.445797	4.101241	-0.024538
H	0.545930	3.318004	-0.234566
C	-2.821494	3.895061	-0.214784
H	-4.298843	2.510792	-0.956107
H	-1.099787	5.027005	0.428326
C	-3.823901	4.929026	0.233899
H	-4.749421	4.869548	-0.348266
H	-4.089855	4.777452	1.288763
H	-3.421591	5.943770	0.142232
S	0.217645	0.708486	-1.589093
O	-0.049659	-0.265444	1.320430
O	4.332897	2.685831	0.519215
O	-0.570757	-0.637170	-1.585528
Zn	-1.207845	-1.465763	0.146747
Br	-3.462643	-1.145241	0.589422
Br	-0.212377	-3.572570	0.374537
C	4.048035	0.017656	-1.194195
C	2.584433	-1.803067	-1.189777
C	3.687589	-1.210750	-0.383353
H	3.460689	-1.060183	0.672684
H	4.551130	-1.895784	-0.421183
C	3.539251	-0.209118	-2.493612
C	2.607478	-1.267421	-2.464137
H	4.954416	0.588999	-1.023564
H	2.730585	2.044835	-1.365204
H	1.918531	-2.580844	-0.832908
H	3.765923	0.403481	-3.359781
H	1.974114	-1.573806	-3.287979

1 imaginary frequency

E = -8281.425724

H = -8281.078602

G = -8281.139781

$E_{M06\text{-}2X\text{-}D3}$ = -8286.300322

H_{tot} = -8285.953200

G_{tot} = -8286.014379

TS4*endo,top*

C	-2.038838	-2.446767	0.599156
C	-1.937526	-1.751378	-0.607820
C	-2.964000	-1.784772	-1.554670
C	-4.135884	-2.478147	-1.251470
C	-4.281540	-3.161038	-0.035383
C	-3.213135	-3.142473	0.876151
S	-0.427271	-0.845137	-0.987661
O	0.593074	-1.345401	0.080524
Zn	2.392476	-0.394627	-0.101082
Br	3.747806	-0.883278	1.703297
C	-5.537009	-3.936216	0.274039
C	-0.855356	0.857660	-0.495194
C	-2.131476	1.379486	-0.776717
C	-2.295545	2.861972	-0.956660
C	-1.258919	3.727989	-0.338104
C	-0.105568	3.155569	0.070689
C	0.211911	1.724987	-0.078082

O	1.410655	1.380922	0.139842
C	-1.538412	5.197777	-0.275416
O	-3.259267	3.319925	-1.556378
Br	3.011236	-0.398483	-2.348434
C	-3.383549	1.197543	0.824362
C	-2.841642	2.032104	1.812318
C	-1.671751	1.745895	2.545421
C	-0.952118	0.581910	2.413847
C	0.375648	0.350346	3.025833
H	0.698944	3.753927	0.490251
H	-0.719636	5.738236	0.206647
H	-2.467415	5.390753	0.274585
H	-1.683662	5.599781	-1.285168
H	-1.206108	-2.454382	1.294650
H	-2.861134	-1.284024	-2.513409
H	-3.301424	-3.683152	1.814973
H	-4.943919	-2.497182	-1.977725
H	-6.380612	-3.594607	-0.333876
H	-5.390584	-5.004901	0.068299
H	-5.809998	-3.844905	1.331123
H	-3.265256	3.028048	1.922135
H	-1.267717	2.534999	3.176191
H	-4.310685	1.507736	0.349879
H	-2.801920	0.805098	-1.408917
H	0.626046	1.107613	3.775371
H	1.150767	0.380686	2.246922
H	0.441516	-0.651589	3.465745
H	-3.246829	0.123041	0.894034
H	-1.392220	-0.250810	1.877397

1 imaginary frequency

E = -8282.632062

H = -8282.262397

G = -8282.325944

$E_{M06\text{-}2X\text{-}D3}$ = -8287.497847

H_{tot} = -8287.128183

G_{tot} = -8287.191730

TS4*endo,bottom*

C	0.054962	2.919112	-0.852011
C	1.254688	3.304263	-1.341446
C	2.385148	2.338623	-1.297136
C	2.214882	1.127228	-0.420178
C	0.909972	0.718103	-0.088618
C	-0.210814	1.588995	-0.285266
H	-0.810537	3.574204	-0.907879
C	1.508673	4.624763	-2.000080
H	0.618885	5.259147	-1.974630
H	1.810176	4.476478	-3.043794
H	2.336633	5.148360	-1.506875
C	2.013996	-1.817275	0.211507
C	2.262823	-2.301080	-1.076832
C	2.919807	-2.011742	1.254433
C	3.451610	-2.981636	-1.314532
H	1.532336	-2.149978	-1.865351
C	4.113445	-2.685834	0.990134
H	2.704794	-1.649009	2.256298
C	4.395802	-3.179567	-0.290290
H	3.656882	-3.365669	-2.310565
H	4.828120	-2.838482	1.794074
C	5.674966	-3.924393	-0.575661
H	6.342241	-3.927898	0.291424
H	5.465111	-4.966739	-0.846999

H	6.210263	-3.474862	-1.420732
S	0.503219	-0.925326	0.560409
O	-1.414605	1.274916	-0.042172
O	3.424636	2.523291	-1.915528
O	-0.552993	-1.486830	-0.444724
Zn	-2.346083	-0.541328	-0.219472
Br	-3.171646	-1.060804	1.895517
Br	-3.479117	-0.601155	-2.232541
C	0.549257	1.926003	2.585344
C	3.198054	1.834660	1.195388
C	2.513320	3.003796	1.562407
C	1.243497	3.038768	2.175620
H	0.742609	4.003070	2.229310
H	2.914285	3.950521	1.207047
H	2.968323	0.365144	-0.596621
H	4.188150	1.947961	0.761442
C	-0.865281	1.935097	3.022275
H	-1.298623	2.939378	3.008880
H	-0.960420	1.503526	4.028062
H	-1.463397	1.284321	2.363900
H	1.064298	0.972684	2.663400
H	3.068429	0.923154	1.772150

1 imaginary frequency

E = -8282.630098

H = -8282.260730

G = -8282.324420

$E_{M06\text{-}2X\text{-}D3}$ = -8287.497630

H_{tot} = -8287.128261

G_{tot} = -8287.191951

TS4*exo,bottom* (2.9 kcal/mol higher in energy than **TS4*endo,top***)

C	0.621012	4.776534	-0.484996
C	0.682233	4.307103	-1.803796
C	0.695913	2.939669	-2.077048
C	0.641596	2.028668	-1.017417
C	0.574107	2.473656	0.308029
C	0.569570	3.839718	0.561273
S	0.646407	0.291761	-1.484617
O	-0.811081	-0.254147	-1.463642
Zn	-1.942453	-0.478907	0.190253
Br	-3.485559	-2.172778	-0.206916
C	0.612405	6.252485	-0.178567
C	1.559529	-0.428236	-0.117291
C	2.955610	-0.271596	-0.196076
C	3.767132	-0.477829	1.051956
C	3.151975	-1.297550	2.136152
C	1.828684	-1.554897	2.078578
C	0.938006	-1.041154	1.019178
C	4.047846	-1.734837	3.252975
O	4.894210	-0.013771	1.151909
O	-0.304514	-1.155934	1.209942
Br	-2.589845	1.492542	1.243182
C	3.895211	-1.831781	-1.225269
C	3.109380	-2.003453	-2.366315
C	1.822787	-2.586551	-2.359749
C	1.216300	-3.082202	-1.229114
C	-0.194779	-3.520808	-1.153386
H	1.327177	-2.111335	2.865943
H	3.497371	-2.312306	4.000153
H	4.502493	-0.863196	3.738244
H	4.874259	-2.344457	2.867437
H	0.753026	2.590753	-3.104934

H	0.523927	1.768469	1.128650
H	0.725397	5.016471	-2.625843
H	0.515899	4.189200	1.589105
H	0.643587	6.855468	-1.091009
H	-0.288967	6.527958	0.382817
H	1.473508	6.528232	0.443057
H	4.881048	-1.388497	-1.329981
H	3.359099	0.501264	-0.844478
H	3.438040	-1.532065	-3.290259
H	1.240619	-2.540404	-3.277706
H	-0.749213	-3.327653	-2.074108
H	-0.705830	-3.003188	-0.331405
H	-0.246462	-4.591685	-0.907392
H	1.809731	-3.241357	-0.331651
H	3.799465	-2.545200	-0.410063

1 imaginary frequency
E = -8282.629995
H = -8282.260836
G = -8282.324507
$E_{M06-2X-D3}$ = -8287.492595
H_{tot} = -8287.123436
G_{tot} = -8287.187107

7a

C	-0.473551	4.258010	-0.263313
C	0.823848	3.901037	-0.126394
C	1.199606	2.526899	-0.522780
C	0.227612	1.678312	-1.222222
C	-1.068105	2.003663	-1.236359
C	-1.518288	3.361968	-0.814314
H	-0.824598	5.239317	0.042420
H	0.594407	0.739675	-1.616876
C	1.890657	4.767188	0.463631
H	1.488485	5.738533	0.759864
H	2.702471	4.919369	-0.257899
H	2.333033	4.276908	1.339000
C	-3.382952	0.665119	-0.506003
C	-2.964856	0.598376	0.829090
C	-4.732674	0.564781	-0.850731
C	-3.919509	0.439605	1.823792
H	-1.915198	0.674630	1.089191
C	-5.675903	0.411515	0.165036
H	-5.048206	0.607639	-1.889189
C	-5.287971	0.345388	1.509615
H	-3.602361	0.387898	2.861910
H	-6.728069	0.336938	-0.094412
C	-6.304143	0.183325	2.609484
H	-7.314373	0.054566	2.210304
H	-6.065960	-0.685378	3.234891
H	-6.305813	1.061843	3.267116
S	-2.223559	0.753243	-1.860768
O	-2.681610	3.714967	-0.947477
O	2.297313	2.034818	-0.203764
O	-1.337409	-0.530060	-1.847952
Zn	-0.348234	-1.551819	-0.422057
Br	-1.594775	-3.394279	0.091093
Br	0.587553	-0.297002	1.516469
Zn	2.643987	0.001953	0.218274
Br	1.892733	-1.555034	-1.525661
Br	4.779677	-0.036451	0.997580

0 imaginary frequencies
E = -15010.049187

H = -15009.792784
G = -15009.858312
$E_{M06-2X-D3}$ = -15020.035682
H_{tot} = -15019.779278
G_{tot} = -15019.844806

7b

C	4.159756	-0.221139	0.779415
C	5.136328	-0.170499	-0.155084
C	4.763266	0.102473	-1.580553
C	3.326841	0.354467	-1.908170
C	2.392108	0.307706	-0.946318
C	2.752441	-0.057780	0.451487
H	4.373587	-0.448483	1.819572
H	3.107639	0.599085	-2.944170
C	6.582249	-0.392680	0.135167
H	6.747834	-0.580734	1.198247
H	7.168595	0.481086	-0.174376
H	6.958546	-1.243117	-0.446279
C	0.595813	2.327230	-0.404102
C	0.105126	2.321445	0.902025
C	0.989263	3.506633	-1.041229
C	0.034355	3.528780	1.587181
H	-0.242458	1.408803	1.366566
C	0.917321	4.702207	-0.329578
H	1.347042	3.502894	-2.067402
C	0.439477	4.733289	0.988981
H	-0.354764	3.536354	2.601570
H	1.225112	5.625614	-0.812039
C	0.320817	6.035001	1.737817
H	0.994774	6.795771	1.331772
H	-0.703109	6.425076	1.663933
H	0.541513	5.903326	2.802522
S	0.711458	0.820659	-1.370463
O	1.877417	-0.245100	1.318023
O	5.599652	0.138314	-2.469228
O	-0.220153	-0.240274	-0.662775
Zn	0.209861	-1.425999	0.959540
Br	-1.810210	-0.790239	1.990512
Br	1.204293	-3.453095	0.697523
Zn	-2.349130	-0.206000	-0.485999
Br	-2.870128	-2.140086	-1.599533
Br	-3.138693	1.930204	-0.671621

0 imaginary frequencies
E = -15010.041349
H = -15009.785535
G = -15009.851337
$E_{M06-2X-D3}$ = -15020.032332
H_{tot} = -15019.776518
G_{tot} = -15019.842320

TS5*endo,top*

C	-0.414527	3.547847	-2.356632
C	0.472017	2.483048	-2.973664
C	1.690280	2.640937	-2.106993
C	1.726441	3.975644	-1.662528
C	0.463794	4.537705	-1.832024
C	0.419667	1.723218	-0.427782
C	-0.797378	2.407532	-0.615485
C	-1.168555	3.509556	0.313876
C	-0.094254	3.960989	1.227913
C	1.054440	3.271159	1.437463

C	1.290648	2.027430	0.665405
S	-2.186423	1.359465	-1.228296
O	-1.455846	0.096969	-1.802899
Zn	-0.672944	-1.519626	-0.928529
Br	0.056615	-1.287745	1.404449
Zn	2.307513	-0.717368	0.573846
O	2.238181	1.258641	0.986622
C	2.092355	3.662907	2.441163
O	-2.290524	4.005193	0.324608
C	-3.001772	0.808800	0.276071
C	-2.465679	0.891153	1.563503
C	-3.171191	0.335812	2.626907
C	-4.394509	-0.320371	2.428037
C	-4.912583	-0.389872	1.125876
C	-4.230956	0.174071	0.051864
C	-5.121399	-0.962044	3.581169
Br	1.702425	-1.362864	-1.737570
Br	-2.012142	-3.301815	-1.466985
Br	4.256039	-1.524052	1.462179
H	-0.318126	4.858850	1.797590
H	1.809729	4.576026	2.970414
H	3.060223	3.817243	1.948333
H	2.238151	2.854252	3.166950
H	-1.509325	1.361396	1.748837
H	-4.651194	0.111288	-0.948281
H	-2.753732	0.401557	3.627862
H	-5.862529	-0.887291	0.950630
H	-4.909300	-0.448995	4.524834
H	-6.204361	-0.965193	3.420046
H	-4.803791	-2.007104	3.696336
H	2.536209	1.963047	-2.116447
H	0.161458	5.528317	-1.512501
H	2.568327	4.449300	-1.170996
H	0.546948	0.756533	-0.881888
H	0.061684	1.475626	-3.042535
H	0.729024	2.810873	-3.993313
H	-1.412004	3.779806	-2.716716

1 imaginary frequency

E = -15204.175656

H = -15203.820333

G = -15203.891376

$E_{M06-2X-D3}$ = -15214.110799

H_{tot} = -15213.755476

G_{tot} = -15213.826519

TS5*endo,bottom*

C	-0.264606	5.028118	0.757318
C	-1.298269	4.104513	0.543017
C	-1.055406	2.870597	-0.053969
C	0.250421	2.547480	-0.425228
C	1.300024	3.451321	-0.247622
C	1.030648	4.683939	0.345484
S	0.527870	0.978887	-1.287214
O	-0.400624	-0.078834	-0.532649
Zn	-2.431300	-0.537294	-0.648823
Br	-3.682675	0.916382	-1.913853
C	-0.542665	6.347492	1.431211
C	2.167760	0.570596	-0.781441
C	3.186677	0.477331	-1.753660
C	4.603756	0.670320	-1.297352
C	4.886366	0.439242	0.153765
C	3.852071	0.361286	1.024330

C	2.452147	0.480807	0.623553
C	6.323413	0.356841	0.557390
O	5.487310	0.966992	-2.087400
O	1.564518	0.544964	1.527021
Zn	-0.105455	-0.556628	1.450891
Br	0.619071	-2.518413	2.402344
Br	-2.378137	0.113907	1.835342
Br	-2.248384	-2.827960	-0.873685
C	3.388932	-1.466537	-2.403926
C	3.871028	-2.117615	-1.247200
C	2.782969	-2.558027	-0.458339
C	1.611574	-2.336032	-1.152087
H	4.020758	0.220404	2.088358
H	6.425414	0.187954	1.632055
H	6.845911	1.282130	0.287110
H	6.826730	-0.453846	0.016382
H	-1.870823	2.182100	-0.225175
H	2.312945	3.205535	-0.549073
H	-2.313307	4.350661	0.843631
H	1.846038	5.386646	0.494596
H	-1.483398	6.783679	1.077356
H	-0.636613	6.213252	2.516998
H	0.262282	7.067584	1.253803
H	2.995714	0.855750	-2.754704
H	4.017867	-1.268399	-3.265566
H	4.917227	-2.212771	-0.978261
H	2.848381	-2.976196	0.537275
H	0.606753	-2.555789	-0.808997
C	1.929047	-1.857798	-2.529646
H	1.245355	-1.114595	-2.946106
H	1.878932	-2.723952	-3.210802

1 imaginary frequency

E = -15204.180949

H = -15203.826172

G = -15203.897222

$E_{M06\text{-}2X\text{-}D3}$ = -15214.114001

H_{tot} = -15213.759224

G_{tot} = -15213.830274

TS5-RC*$_{endo,bottom}$* (TS for formation of second C–C bond)

C	0.506827	4.940205	0.944289
C	-0.437876	3.959078	1.270684
C	-0.426733	2.706586	0.655764
C	0.555904	2.439651	-0.291949
C	1.509201	3.396576	-0.652834
C	1.479295	4.637757	-0.024075
S	0.592284	0.864595	-1.173391
O	-0.502720	-0.030516	-0.450369
Zn	-2.556991	-0.154769	-0.677209
Br	-3.442639	1.795295	-1.488630
C	0.474102	6.301302	1.592008
C	2.128680	0.136728	-0.654994
C	3.258933	0.193375	-1.618646
C	4.605663	0.527333	-1.000190
C	4.821461	0.145857	0.428975
C	3.744835	-0.066126	1.222604
C	2.365082	0.056728	0.758808
C	6.235052	0.097667	0.911863
O	5.499236	1.014946	-1.671645
O	1.448157	0.101387	1.636518
Zn	-0.277408	-0.878467	1.406355
Br	0.307659	-3.039092	1.924961

Br	-2.502665	-0.144711	1.911821
Br	-2.622149	-2.337188	-1.418757
C	3.457003	-1.270443	-2.376355
C	3.866319	-2.269862	-1.367854
C	2.752264	-2.733309	-0.707675
C	1.610334	-2.172815	-1.327151
H	3.862046	-0.291787	2.279240
H	6.287848	-0.179703	1.967240
H	6.712096	1.074765	0.770890
H	6.816762	-0.620141	0.320556
H	-1.159948	1.958722	0.924833
H	2.268878	3.182194	-1.399878
H	-1.198715	4.169446	2.017406
H	2.221911	5.385364	-0.290156
H	0.048404	7.045386	0.905825
H	-0.136126	6.299757	2.500474
H	1.482664	6.641776	1.852391
H	3.079963	0.886186	-2.444327
H	4.136601	-1.115064	-3.213287
H	4.896195	-2.504150	-1.121560
H	2.728999	-3.341449	0.187237
H	0.584463	-2.311191	-1.004021
C	2.005975	-1.684471	-2.681321
H	1.371745	-0.912479	-3.120393
H	2.013122	-2.542163	-3.369181

1 imaginary frequency
E = -15204.184132
H = -15203.828474
G = -15203.898711
$E_{M06-2X-D3}$ = -15214.121684
G_{tot} = -15213.836263

TS5*exo,top*

C	-0.640071	3.531156	-2.413628
C	0.700898	4.052181	-1.947210
C	1.536396	2.817616	-2.111060
C	0.945413	2.036341	-3.119723
C	-0.359164	2.483480	-3.328796
C	0.318276	1.797382	-0.416084
C	-0.943531	2.385998	-0.609993
C	-1.395586	3.467215	0.310708
C	-0.400465	3.950896	1.298805
C	0.792953	3.349171	1.514210
C	1.144328	2.155068	0.699023
S	-2.253498	1.237317	-1.208421
O	-1.425753	0.031679	-1.769088
Zn	-0.553119	-1.523925	-0.874594
Br	0.177315	-1.235117	1.455914
Zn	2.371829	-0.513561	0.602263
O	2.141086	1.456413	1.023828
C	1.771418	3.776216	2.562118
O	-2.536062	3.918355	0.267815
C	-3.037394	0.641132	0.295729
C	-2.512696	0.764399	1.583331
C	-3.190977	0.180726	2.651300
C	-4.375379	-0.541090	2.455188
C	-4.882600	-0.654059	1.150208
C	-4.229402	-0.064423	0.074145
C	-5.095952	-1.190646	3.608161
Br	1.807354	-1.234930	-1.692188
Br	-1.787341	-3.386468	-1.392604
Br	4.398293	-1.123153	1.472230

H	-0.713183	4.808218	1.888371
H	1.404600	4.641924	3.118421
H	2.736924	4.025145	2.104935
H	1.960307	2.951831	3.259698
H	-1.583811	1.287042	1.767340
H	-4.639812	-0.161031	-0.927527
H	-2.780429	0.277517	3.652450
H	-5.801992	-1.207186	0.977409
H	-6.133566	-0.840365	3.669436
H	-5.131538	-2.279431	3.477635
H	-4.604725	-0.978346	4.562411
H	2.560645	2.721049	-1.769119
H	-1.079671	2.025094	-3.995928
H	1.391274	1.157544	-3.567515
H	0.514899	0.836153	-0.853818
H	0.733437	4.529116	-0.968783
H	1.040230	4.798952	-2.682355
H	-1.538638	4.138522	-2.444762

1 imaginary frequency

E = -15204.172375

H = -15203.817109

G = -15203.888219

$E_{M06-2X-D3}$ = -15214.105306

H_{tot} = -15213.750040

G_{tot} = -15213.821150

TS5*exo,bottom*

C	0.501669	5.094747	-0.700557
C	1.159979	3.941880	-1.148762
C	0.867315	2.685533	-0.619128
C	-0.110330	2.589515	0.366419
C	-0.780455	3.717331	0.847163
C	-0.472485	4.961248	0.302008
S	-0.503978	1.006592	1.144422
O	0.399298	-0.050318	0.371224
Zn	2.391229	-0.555258	0.590172
Br	3.624994	1.177190	1.441069
C	0.852413	6.452156	-1.255380
C	-2.146996	0.688312	0.573316
C	-3.201374	0.684146	1.512363
C	-4.610222	0.823771	0.989114
C	-4.843531	0.592055	-0.466315
C	-3.779646	0.494406	-1.293822
C	-2.390379	0.570845	-0.833446
C	-6.266985	0.521283	-0.919076
O	-5.525469	1.112618	1.746318
O	-1.467965	0.557469	-1.706107
Zn	0.016351	-0.775704	-1.504591
Br	-1.037771	-2.734515	-2.074339
Br	2.337431	-0.480550	-2.002955
Br	2.147170	-2.744938	1.274289
C	-3.452412	-1.253508	2.299623
C	-2.395121	-1.199462	3.231090
C	-1.222689	-1.764427	2.671863
C	-1.531530	-2.279090	1.433672
H	-3.903910	0.344767	-2.362593
H	-6.332303	0.361903	-1.998060
H	-6.794580	1.446423	-0.658651
H	-6.791363	-0.292852	-0.403835
H	1.387271	1.807826	-0.977008
H	-1.538067	3.636043	1.622356
H	1.917742	4.020512	-1.923823

H	-0.995676	5.842781	0.663073
H	-0.019904	7.114196	-1.275087
H	1.616483	6.937008	-0.632962
H	1.255442	6.377699	-2.270574
H	-3.071160	1.177819	2.469481
H	-4.489707	-1.158465	2.600470
H	-2.461013	-0.736459	4.210121
H	-0.237809	-1.766296	3.122332
C	-2.997060	-2.167236	1.184293
H	-3.461356	-3.154545	1.345075
H	-3.258811	-1.873839	0.165285
H	-0.826801	-2.741936	0.755882

1 imaginary frequency

E = -15204.178611

H = -15203.823968

G = -15203.895307

$E_{M06-2X-D3}$ = -15214.109276

H_{tot} = -15213.754633

G_{tot} = -15213.825972

TS6*endo,top*

C	-3.470701	-1.491996	-0.649234
C	-4.346858	-1.823651	0.327784
C	-4.105545	-1.328799	1.710067
C	-3.031918	-0.286456	1.880500
C	-2.057623	-0.152399	0.877757
C	-2.259705	-0.695690	-0.426993
H	-3.590639	-1.864542	-1.662604
C	-5.525629	-2.722514	0.122359
H	-5.620626	-3.019098	-0.925178
H	-6.449890	-2.225149	0.440465
H	-5.426883	-3.623452	0.739459
C	-0.432691	2.152430	0.502546
C	-0.043045	2.256675	-0.833984
C	-0.787239	3.276905	1.253034
C	-0.039265	3.512746	-1.428149
H	0.266433	1.383661	-1.390676
C	-0.793767	4.524432	0.629425
H	-1.052552	3.189513	2.303286
C	-0.419493	4.662210	-0.714511
H	0.270009	3.604667	-2.465936
H	-1.074995	5.403817	1.202143
C	-0.386071	6.014684	-1.378295
H	0.645728	6.384527	-1.442653
H	-0.774540	5.963793	-2.401609
H	-0.970220	6.752827	-0.820157
S	-0.497176	0.586175	1.362169
O	-1.409040	-0.589074	-1.372431
O	-4.743057	-1.730646	2.672412
O	0.594798	-0.338916	0.674682
Zn	0.342085	-1.493603	-1.027211
Br	2.264454	-0.474198	-1.989336
Br	-0.104118	-3.728868	-0.872683
Zn	2.668341	0.018414	0.514416
Br	3.507420	-1.863984	1.536427
Br	3.216531	2.219059	0.859075
C	-4.278422	1.391153	1.848819
C	-3.552906	1.970347	-1.030798
H	-2.752618	-0.110389	2.916786
C	-4.745659	1.439958	-0.618420
C	-5.097360	1.194928	0.732386
H	-3.457364	2.100299	1.803923

H	-4.718061	1.247591	2.831853
C	-3.108389	2.008696	-2.442821
H	-2.871978	2.392458	-0.298471
H	-3.892641	1.692967	-3.137014
H	-2.245012	1.331690	-2.555335
H	-2.744376	3.007601	-2.713468
H	-6.051184	0.699270	0.902082
H	-5.444489	1.091679	-1.375794

1 imaginary frequency

E = -15205.380803

H = -15205.004006

G = -15205.077899

$E_{M06-2X-D3}$ = -15215.307478

H_{tot} = -15214.930681

G_{tot} = -15215.004574

TS6-RC*endo,top* (TS for formation of second C–C bond)

C	-3.575785	-0.696814	-0.941894
C	-4.446866	-1.085611	0.016779
C	-4.141568	-0.778544	1.440030
C	-3.063936	0.264367	1.752065
C	-2.129202	0.558628	0.625395
C	-2.313264	-0.011514	-0.657372
H	-3.726951	-0.967373	-1.982992
C	-5.670418	-1.903212	-0.252968
H	-5.826849	-2.044750	-1.325254
H	-6.555558	-1.424983	0.183093
H	-5.577340	-2.885671	0.225255
C	0.140063	2.344230	0.296384
C	0.692376	2.280770	-0.984214
C	0.074636	3.548768	1.002033
C	1.152668	3.453362	-1.571321
H	0.776150	1.338343	-1.505029
C	0.525857	4.715662	0.386687
H	-0.318516	3.583635	2.015081
C	1.073121	4.686595	-0.903840
H	1.589254	3.408869	-2.565512
H	0.470119	5.656889	0.926519
C	1.604621	5.939737	-1.550469
H	2.697637	5.985071	-1.455505
H	1.372261	5.964216	-2.620834
H	1.193402	6.840067	-1.083384
S	-0.439312	0.894909	1.171542
O	-1.413061	0.021321	-1.568256
O	-4.773703	-1.287689	2.352294
O	0.405808	-0.323222	0.589842
Zn	-0.030035	-1.382468	-1.140431
Br	2.187705	-1.012280	-1.914303
Br	-1.107995	-3.397680	-1.076291
Zn	2.492722	-0.582289	0.619025
Br	2.664420	-2.602594	1.708022
Br	3.637485	1.369897	0.997115
C	-3.850556	1.565586	2.293343
C	-3.113666	2.701134	-0.290934
H	-2.513747	-0.097873	2.626889
C	-4.459345	2.433401	0.034223
C	-4.831257	1.977577	1.269641
H	-3.091360	2.326472	2.493975
H	-4.333104	1.282558	3.229267
C	-2.667164	2.933684	-1.683861
H	-2.451140	3.045242	0.493844
H	-3.432260	2.660762	-2.414882

H	-1.746030	2.382273	-1.903630
H	-2.412620	3.998271	-1.795449
H	-5.876673	1.730274	1.439267
H	-5.199043	2.484753	-0.761470

1 imaginary frequency
E = -15205.387478
H = -15205.009629
G = -15205.081841
$E_{M06-2X-D3}$ = -15215.318557
G_{tot} = -15215.012920

TS6*endo,bottom*

C	-0.637751	4.908839	1.081638
C	-0.936269	3.668527	1.666479
C	-0.643798	2.472392	1.019196
C	-0.035609	2.521970	-0.233233
C	0.260027	3.736553	-0.854526
C	-0.036516	4.922757	-0.184861
S	0.415491	1.045745	-1.164221
O	-0.348755	-0.180414	-0.482476
Zn	-2.442991	-0.403606	-0.597072
Br	-3.443333	1.620176	-1.041028
C	-0.995258	6.192358	1.787065
C	2.113555	0.833523	-0.700363
C	3.111741	1.123464	-1.645216
C	4.511909	1.356977	-1.146217
C	4.858963	0.800839	0.193471
C	3.853520	0.438569	1.023086
C	2.440662	0.525806	0.657340
C	6.307902	0.760690	0.560995
O	5.328445	1.960850	-1.826834
O	1.568514	0.361531	1.566733
Zn	0.148513	-1.013570	1.365395
Br	1.282785	-2.854738	2.145877
Br	-2.185017	-0.858834	1.893201
Br	-2.849022	-2.367063	-1.735968
C	3.622683	-0.485986	-2.902311
C	3.909260	-1.520615	-2.016251
C	2.953102	-2.382950	-1.411380
C	1.623706	-2.413333	-1.735581
C	0.655522	-3.419004	-1.240758
H	4.049735	0.084524	2.031316
H	6.451848	0.348707	1.562812
H	6.735280	1.769641	0.521677
H	6.870212	0.155214	-0.160441
H	-0.917884	1.530912	1.471937
H	0.714169	3.770784	-1.841577
H	-1.416794	3.634685	2.640708
H	0.193687	5.871897	-0.661185
H	-0.436002	7.042826	1.384601
H	-2.064752	6.411640	1.668757
H	-0.796755	6.123354	2.862371
H	2.858659	1.704746	-2.528441
H	2.673277	-0.467341	-3.428862
H	4.443044	0.008751	-3.413025
H	4.943642	-1.642612	-1.701661
H	3.320240	-3.096251	-0.678043
H	1.234642	-1.716084	-2.475178
H	0.261077	-3.976859	-2.103081
H	-0.222900	-2.934240	-0.799764
H	1.092870	-4.108813	-0.518807

1 imaginary frequency

E = -15205.381636
H = -15205.004069
G = -15205.077327
$E_{M06-2X-D3}$ = -15215.299776
H_{tot} = -15214.922210
G_{tot} = -15214.995468

TS6*exo,top*

C	-0.832389	3.916723	1.568536
C	0.478514	3.577894	1.567199
C	0.873956	2.390067	0.781133
C	-0.063331	1.872304	-0.225065
C	-1.429821	2.093795	-0.010951
C	-1.897381	3.114700	0.897365
H	-1.190981	4.756761	2.157455
C	1.542668	4.275561	2.358193
H	1.129497	5.122204	2.911751
H	2.341925	4.634807	1.698668
H	2.006567	3.578396	3.065861
C	-2.851428	-0.233020	0.819626
C	-2.598281	0.129889	2.141532
C	-3.323366	-1.513079	0.502079
C	-2.818443	-0.806252	3.150806
H	-2.208859	1.106194	2.398233
C	-3.521305	-2.436603	1.523962
H	-3.503780	-1.800783	-0.528990
C	-3.276690	-2.098935	2.863463
H	-2.608851	-0.528965	4.180443
H	-3.863745	-3.437202	1.273958
C	-3.515577	-3.103166	3.961844
H	-4.585989	-3.171862	4.197734
H	-3.185467	-4.103933	3.662055
H	-2.990148	-2.825946	4.881135
S	-2.564917	0.833192	-0.618637
O	-3.093352	3.300224	1.164957
O	1.983168	1.842179	0.945564
O	-1.655280	-0.054452	-1.546818
Zn	-0.346127	-1.468939	-1.018357
Br	-1.027707	-3.521108	-1.783252
Br	0.515158	-1.246818	1.279694
Zn	2.474036	-0.081997	0.360791
Br	1.842948	-0.585267	-1.958525
Br	4.612449	-0.391633	1.102834
C	0.734830	2.923146	-1.781379
C	-2.068853	3.696247	-2.074518
C	-3.536359	3.913335	-2.031239
H	-3.902707	3.771790	-1.002774
H	-4.079140	3.242261	-2.702885
H	-3.769294	4.955518	-2.292771
C	-0.074420	2.505079	-2.847665
H	0.576098	3.905913	-1.344951
C	-1.427450	2.856010	-2.966690
H	-2.026613	2.335643	-3.710525
H	0.304761	1.717982	-3.493614
H	0.221523	0.927163	-0.644030
H	-1.473543	4.356225	-1.448916
H	1.764962	2.578007	-1.758039

1 imaginary frequency
E = -15205.382770
H = -15205.005413
G = -15205.079006
$E_{M06-2X-D3}$ = -15215.301118

H_{tot} = −15214.923761
G_{tot} = −15214.997354

TS6*exo,bottom*

C	−0.423855	4.914219	−0.715926
C	0.086926	3.809523	−1.413418
C	0.038927	2.526770	−0.876002
C	−0.535554	2.350103	0.381301
C	−1.033767	3.429389	1.114965
C	−0.978244	4.704266	0.555679
S	−0.703005	0.736055	1.163118
O	0.367097	−0.209031	0.445671
Zn	2.477832	0.050145	0.457132
Br	2.988956	2.218320	1.019592
C	−0.388508	6.293658	−1.323015
C	−2.301311	0.245618	0.552236
C	−3.381898	0.310452	1.442024
C	−4.759011	0.550567	0.881224
C	−4.982907	0.196540	−0.551090
C	−3.906267	−0.024944	−1.336725
C	−2.526477	0.063868	−0.854695
C	−6.398059	0.169326	−1.031233
O	−5.642881	1.021954	1.580504
O	−1.593066	0.007590	−1.709831
Zn	0.041072	−1.087041	−1.386250
Br	−0.740501	−3.210786	−1.747458
Br	2.189288	−0.342021	−2.070024
Br	3.562738	−1.809743	1.280821
C	−3.957728	−1.703617	2.020025
C	−3.053226	−1.817036	3.064915
C	−1.688154	−2.214436	2.966020
C	−1.109117	−2.730795	1.843882
C	0.305318	−3.164442	1.763962
H	−4.011783	−0.255211	−2.393188
H	−6.451995	−0.066398	−2.096756
H	−6.876238	1.139393	−0.851490
H	−6.977697	−0.573908	−0.469608
H	0.477979	1.698010	−1.412249
H	−1.454412	3.289331	2.107620
H	0.547064	3.953729	−2.387279
H	−1.359488	5.549634	1.122212
H	−1.314344	6.494574	−1.879026
H	−0.295627	7.067216	−0.553429
H	0.444762	6.400303	−2.025156
H	−3.248987	0.723907	2.436164
H	−3.751810	−2.131697	1.043735
H	−5.004461	−1.552420	2.263971
H	−3.392809	−1.494462	4.047574
H	−1.080507	−2.109870	3.862584
H	−1.707647	−2.896113	0.950962
H	0.867852	−2.939164	2.672750
H	0.814466	−2.691688	0.920284
H	0.348079	−4.245375	1.565903

1 imaginary frequency
E = −15205.381179
H = −15205.004343
G = −15205.078522
$E_{M06-2X-D3}$ = −15215.298554
H_{tot} = −15214.921718
G_{tot} = −15214.995898