Electronic Supporting Information

A Molecular Electron Density Theory Study of the Mechanism, Chemo- and Stereoselectivity of the Epoxidation Reaction of R-Carvone with Peracetic Acid

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*1. BET study of the epoxidation reaction of R-carvone**8** with peracetic acid **9***

The so-called Bonding Evolution Theory[1] (BET) has proven to be a very useful methodological tool to achieve a better understanding of bonding changes in organic reactions. This approach allows characterising the bonding changes along the reaction path and, consequently, to establish the nature of the electronic rearrangement associated with a given molecular mechanism. Thus, in order to understand the C–O bond formation along in this epoxidation reaction, a BET study along the most favourable reaction path of the epoxidation reaction of R-carvone**8** with peracetic acid **9** was carried.The phases in whichIRC of the molecular mechanism of the epoxidation reaction is divided is giving in Figure S1. A representation of the bonding changes taking place along reaction path by Lewis-like structures arising from the topological analysis of the ELF is shown in Scheme S1. The populationsof the molecular regions directly involved in the reaction, among other relevant parameters, of the selected structures of the IRC, **Si**, defining the different topological phases are gathered in Table S1.

The topological analysis of Electron Localisation Function[2] (ELF) at the first structure **S1**of the reaction path reveals that theO12–O13single bond of the peracetic acid **9** presents a very low electron population of 0.64 e [V(O12,O13)], which could suggest some labile character. Accordingly, the first relevant bonding change occurring along the reaction path is the rupture of the O12–O13 bond at a relatively early stage of the reaction, 35 % (*PhaseII*),with a moderateenergy cost of 7.1 kcal·mol^{-1}, leading to the formation of a hydroxyl *pseudoradical*and an acyloxy*pseudoradical*. Note thatthe total population associated with the two O12 and O13 oxygen centersis 4.98 [V(O12)] and 5.31 e [V(O13)], respectively, after the rupture of the O12–O13 bond. However, it should be mentioned that the electron density of the broken O12–O13single bond is mostly gathered at the O13 oxygen, whose population increases by 0.50 e, while the O12 oxygen already has 4.86 e at the first structure **S1**. After that, the electron density at these two nuclei is redistributed, the total population belonging to the O13 oxygen remaining almost constant until the end of the reaction.It is interesting to emphasize that the bonding changes at the acyloxy system follow the expected behaviour associated with the formation of acetic acid **11**; the population of the C10–O12single bond, integrating 1.64 e at **S1**[V(C10,O12)], increases throughout the reaction path to 2.45 e,

while that of the C10–O11single bond decreases from 2.43 e to 1.65 e [V(C10,O11)]. Simultaneously to the early rupture of the O12–O13single bond, the depopoulation of the C7–C8 double bond of R-carvone **8** [V(C7,C8)] also takes place since the beginning of the reaction, but more gradually. Thus, the population of the C7–C8 bonding region, 3.47 e, decreases by approximately 0.10 e progressively along the reaction path. For instance, at the TS, found almost at half of reaction path (45 % of reaction progress, *Phase VI*), the C7–C8 bonding region, integrating 3.96 e, could already be considered a half-double bond. Once the TS is achieved, the bonding changes related to the rupture and formation of the H–O and O–C single bonds take place. At exactly 50 % of reaction progress (*Phase VIII*), a non-bonding population of 0.17 e, coming from the depopulation of the C7–C8 bonding region of the ethylene framework, appears at the C8 carbon and subsequently disappears [V(C8)]. The analysis of the population changes of the other regions suggests that this non-bonding electron density is redistributed into the hydroxyl O13 oxygen, whose population increases by 0.15 e, by means of the GEDT taking place from the ethylene framework towards the acyloxy one. At 54 % of reaction progress (*Phase XI*), the O13–H14single bond, which had even increased its population by 0.28 e [V(O13,H14)], breaks in an almost heterolytically fashion, approximately 75(O13):25(H14) relationship, releasing a hydrogen H14 free *pseudoradical* integrating 0.56 e and an anionic O13oxygenintegrating to 6.65 e. Subsequently, at 56 % of reaction progress (*Phase XII*), formation of the first C8–O13 single bond of the oxirane structure takes place with an initial population of 0.82 e [V(O8,C13)], by donation of some non-bonding electron density of the O13 oxygen anion, which decreases to 6.02 e, to the C8 carbon. Interestingly, after the C8–O13 single bond formation, the O13 oxygen should be still considered an anion. At 59 % of reaction progress (*Phase XIV*), similar to the formation pattern related to the first C8–O13 single bond, a small amount of non-bonding electron density of ca. 0.05 e is gathered at the C7 carbon [V(C7)]. Then, just before being redistributed in any other region, presumably at the O13 oxygen, which reaches 6.15 e, formation of the new O11-H14single bond [V(O13,H14)], whose population had been progressively increasing from 5.32 e to 5.70 e, takes place by donation of 1.33 e of the non-bonding electron density of the O11 oxygen to the hydrogen H14free *pseudoradical*. Formation of theC7–O13single bond [V(C7,O13)]takes place later, at 65 % of reaction progress (*Phase XVI*),with an initial population of 0.74 e by donation of some non-bonding

electron density of the anionic O13 oxygen to the C7 carbon. At this stage, with 35 % left to the end, all relevant bonding changes has practically occurred. At the last structure **S17** of the reaction path, the two new C7–O13 and C8–O13, single bonds integrating 1.02 and 0.98 e, respectively, are markedly polarised towards the O13 oxygen, 5.33 e, due to the high strain of the three-membered oxiranering.

References

1. X. Krokidis, S. Noury and B. Silvi, *J. Phys. Chem. A*1997, **101**, 7277-7282.
2. A. D. Becke and K. E. Edgecombe, *J. Chem. Phys.*1990, **92**, 5397-5403.

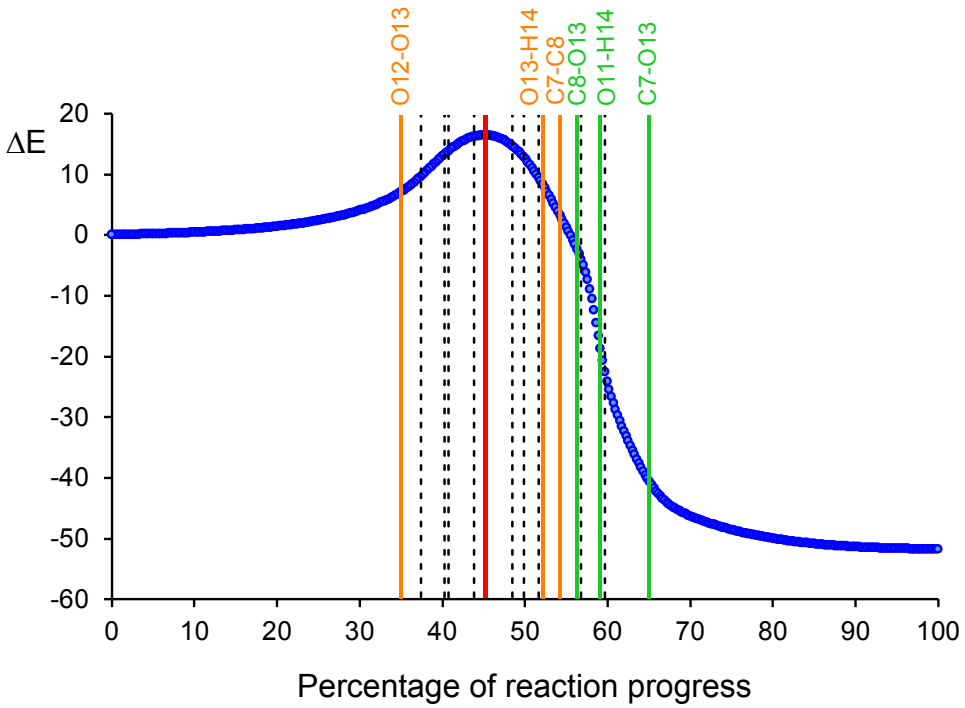
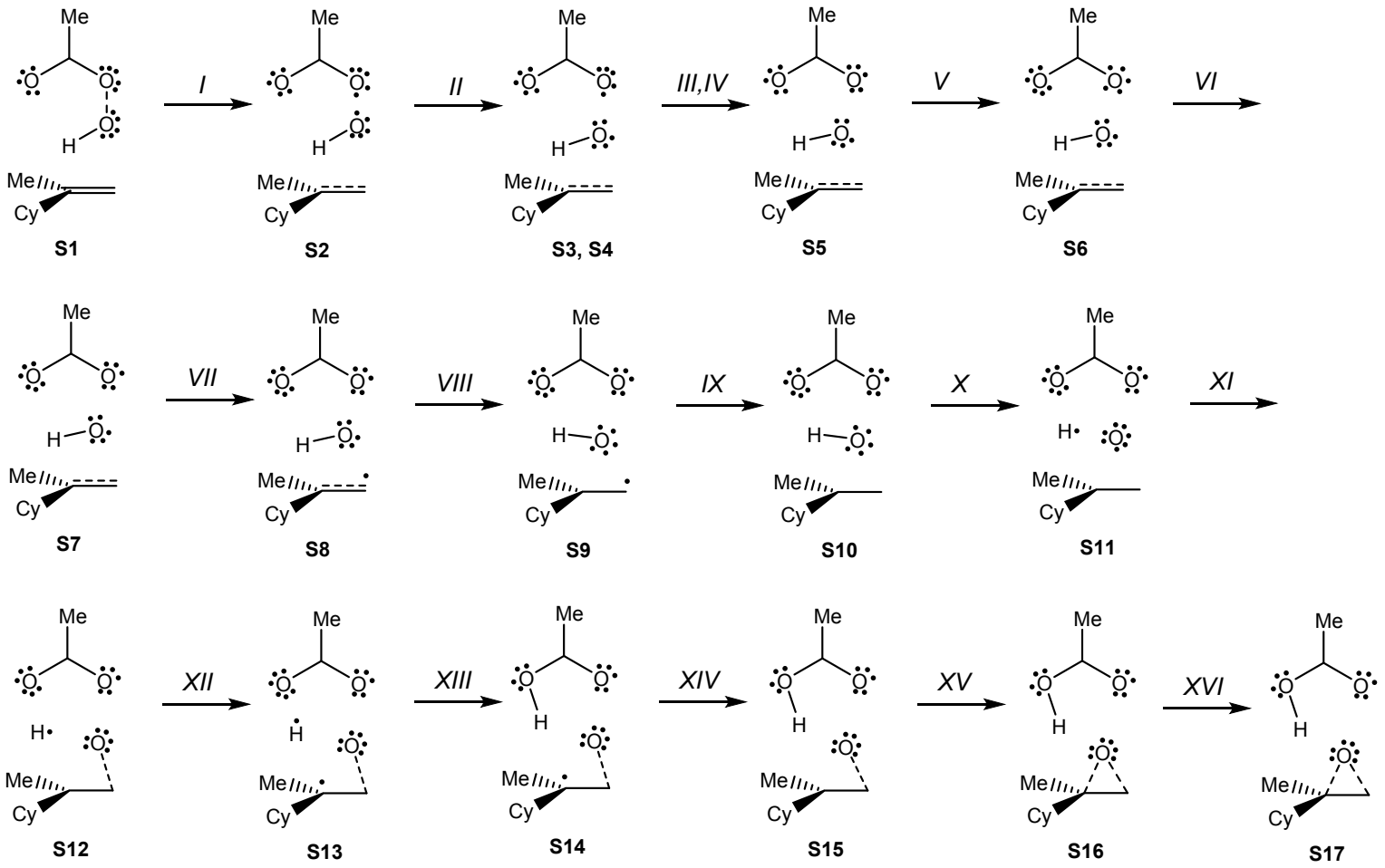


Figure S1. Phases in which the molecular mechanism of the most favourable reaction path associated with the monoepoxidation of R-carvone **8** with peracetic acid **9** is divided.



Scheme S1. Representation of the bonding changes taking place along the most favourable reaction path associated with the monoeoxidation of R-carvone**8** with peracetic acid **9**by Lewis-like structures arising from the topological analysis of the ELF.

Table S1. ELF valence basin populations, GEDT, relativeenergies, percentage of reaction progress and distances of the breaking and forming bonds, of the IRC structures **S1** – **S17** defining the sixteen topological phases along the most favourable reaction path associated with the monoepoxidation of R-carvone **8** with peracetic acid **9**. Electron populations are given in average number of electrons, e, relative energies in kcal·mol^{-1} and distances in angstroms, Å.

Structures	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**TS**	**S7**	**S8**	**S9**	**S10**	**S11**	**S12**	**S13**	**S14**	**S15**	**S16**	**S17**
Phases	I	II	III	IV	V		VI	VI	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	
d(O13-H14)	0.984	0.985	0.987	0.990	0.991	0.998	1.002	1.018	1.026	1.043	1.049	1.081	1.155	1.193	1.466	1.531	1.728	1.805
d(O12-O13)	1.440	1.483	1.550	1.661	1.682	1.808	1.859	1.989	2.037	2.103	2.122	2.196	2.266	2.281	2.324	2.333	2.498	3.417
d(O11-H14)	1.936	1.793	1.761	1.729	1.723	1.692	1.680	1.645	1.631	1.607	1.599	1.556	1.464	1.421	1.135	1.072	0.986	0.982
d(C8-O13)	3.195	2.439	2.335	2.210	2.188	2.051	1.992	1.839	1.779	1.697	1.674	1.586	1.516	1.504	1.472	1.466	1.419	1.438
d(C7-O13)	3.350	2.554	2.472	2.372	2.355	2.250	2.207	2.099	2.059	2.003	1.987	1.921	1.853	1.837	1.786	1.775	1.549	1.449
Reaction progress	0	35	37	40	41	44	45	49	50	52	52	54	56	57	59	60	65	100
ΔE	0.0	7.1	9.6	13.3	13.8	16.2	16.4	14.6	12.8	9.4	8.3	3.2	-2.3	-4.0	-18.7	-22.6	-40.7	-51.8
GEDT	0.00	0.04	0.08	0.17	0.19	0.33	0.39	0.54	0.59	0.66	0.67	0.73	0.75	0.74	0.67	0.65	0.61	0.62
V(C7,C8)	1.77	1.75	1.75	3.20	3.18	3.03	2.96	2.83	2.62	2.50	2.47	2.36	2.30	2.25	2.21	2.20	2.05	1.98
V'(C7,C8)	1.70	1.64	1.58															
V(C10,O11)	2.43	2.39	2.36	2.32	2.31	2.24	2.21	2.12	2.09	2.03	2.02	1.96	1.89	1.87	1.76	1.72	1.62	1.65
V(O11)	2.55	2.52	2.52	2.52	2.51	2.50	2.48	2.41	2.36	2.27	2.24	2.04	1.69	1.56	4.37	4.35	4.35	4.30
V'(O11)	2.77	2.82	2.85	2.89	2.90	2.98	3.03	3.17	3.23	3.36	3.40	3.63	4.00	4.14				
V(C10,O12)	1.64	1.70	1.73	1.80	1.82	1.94	1.99	2.06	2.09	2.12	2.13	2.18	2.24	2.25	2.35	2.37	2.45	2.45
V(O12)	2.41	2.42	2.47	2.53	2.62	5.24	5.25	4.84	4.12	3.47	3.36	3.04	2.87	2.83	2.73	2.65	2.65	2.61
V'(O12)	2.40	2.43	2.46	2.52	2.61			0.48	1.22	1.90	2.03	2.39	2.57	2.60	2.65	2.71	2.65	2.69
V'"(O12)		0.46	0.34	0.18														
V(O13)	2.44	2.47	2.53	2.53	2.52	2.50	2.51	2.43	2.36	4.99	5.14	5.11	4.15	4.06	3.41	3.40	2.81	2.62

V'(O13)	2.42	2.45	2.50	2.53	2.53	2.54	2.54	2.57	2.61			1.54	1.87	1.98	2.66	2.75	2.68	2.71
V''(O13)		0.06																
V(O12,O13)	0.64																	
V(O13,H14)	1.73	1.75	1.75	1.77	1.77	1.81	1.82	1.89	1.91	1.99	2.01							
V(H14)												0.56	0.45	0.43				
V(O11,H14)															1.73	1.76	1.81	1.82
V(C8)									0.17	0.15								
V(C8,O13)													0.82	0.85	0.94	0.95	1.05	0.98
V(C7)														0.03	0.05			
V(C7,O13)																	0.74	1.02

Table S2. B3LYP/6-311G(d,p) enthalpies (H, in a.u.), entropies (S, in cal·mol^{-1}·K^{-1}) and Gibbs free energies (G, in a.u.), computed at 25 ºC and 1 atm in DCM, for the stationary points involved in the reaction of R-carvone **8** with peracetic acid **9**.

	H	S	G
8	-464.599661	98.3	-464.639325
9	-304.238030	71.4	-304.266847
TS1	-768.819029	133.3	-768.872806
TS2	-768.818858	132.5	-768.872317
TS3	-768.814118	132.5	-768.867587
TS4	-768.814703	132.7	-768.868232
10	-539.816996	100.2	-539.857433
13	-539.817054	99.9	-539.857356
14	-539.810492	101.0	-539.851234
15	-539.810931	99.9	-539.851217
TS5	-768.786988	128.8	-768.838955
IN1	-768.827312	123.7	-768.877234
TS6	-768.816568	125.6	-768.867246
16	-539.834406	102.2	-539.875634
TS7	-768.786197	129.3	-768.838369
IN2	-768.829953	128.9	-768.881934
TS8	-768.807237	126.6	-768.858307
17	-539.832970	100.4	-539.873480
TS9	-844.031328	134.5	-844.085573
TS10	-844.030072	134.9	-844.084486
12	-615.028861	102.9	-615.070381
18	-615.028554	102.6	-615.069957

B3LYP/6-311G(d,p) computed total energies, single imaginary frequencies and cartesian coordinates, in DCM, of the stationary points involved in the reaction of R-carvone**8**with peracetic acid **9**.

8

E(RB3LYP) = -464.824026 A.U.

C	3.06026400	1.17061100	0.67174900
H	4.13635000	1.16522600	0.49111200
C	2.39459300	-0.04044100	0.06205300
C	3.10371400	-0.95183000	-0.60766300
H	4.17423500	-0.83567700	-0.74055600
H	2.65965000	-1.83836000	-1.04335000
C	0.89401900	-0.14029200	0.28821900
C	0.11470000	0.92493700	-0.51182300
C	0.27441200	-1.51374700	0.00371100
H	0.72172000	0.07367300	1.35280800
C	-1.37921700	0.90066600	-0.22813400
H	0.24581400	0.73296400	-1.58562400
H	0.46851600	1.93884500	-0.32070100
C	-1.21866100	-1.50581100	0.16555900
H	0.50689700	-1.83301500	-1.02186500
H	0.70971600	-2.27422100	0.65888000
C	-1.99670000	-0.41158000	0.08653300
H	-1.68927200	-2.46856800	0.35181800
O	-2.05016900	1.92026800	-0.29679800
H	2.65523800	2.10332000	0.26662800
H	2.89308700	1.20003100	1.75432300
C	-3.48878900	-0.43712600	0.27608500
H	-3.78753000	0.21630800	1.10063400
H	-4.00262500	-0.06684300	-0.61573000
H	-3.84045400	-1.44815500	0.48827400

9

E(RB3LYP) = -304.307766 A.U.

O	1.85523800	-0.24063600	0.00006500
H	1.64698800	0.72057800	0.00026300
O	-0.12325600	1.34306200	-0.00001600
C	-0.42074000	0.17070900	-0.00014100
O	0.52745500	-0.79939900	-0.00009000
C	-1.79574300	-0.42156400	0.00007800
H	-2.32833900	-0.06479600	-0.88336800
H	-1.76744900	-1.50944000	-0.00029600
H	-2.32780300	-0.06542700	0.88410800

10

E(RB3LYP) = -540.047007 A.U.

C	-2.98886100	-1.11353000	-0.81231800
H	-4.04435900	-0.93780000	-0.59902700
C	-2.13800200	-0.02432900	-0.19075500
C	-2.77531000	1.27115400	0.09434300
H	-3.82279000	1.40513000	-0.16392100
H	-2.19300700	2.18475900	0.14291400
O	-2.52549000	0.33016100	1.15696400
C	-0.62795600	-0.15618400	-0.40854200
C	0.17803500	1.07381900	0.02744300
C	-0.08206400	-1.40423200	0.31202700
H	-0.47405700	-0.29707100	-1.48597700
C	1.68040200	0.90140000	-0.12390700
H	-0.01937300	1.27762500	1.08844100
H	-0.09663700	1.96868400	-0.53267300
C	1.41555400	-1.48878900	0.29111300
H	-0.42498800	-1.39857600	1.35654400
H	-0.48974900	-2.31757400	-0.12970300
C	2.24597900	-0.45556200	0.06821300
H	1.84268400	-2.47185000	0.47647600
O	2.39910500	1.86359100	-0.35311800
H	-2.85341800	-1.13346200	-1.89749600
H	-2.72500000	-2.09806700	-0.41919500
C	3.74387200	-0.58702500	0.02539900
H	4.13598900	-0.25711500	-0.94078800
H	4.21391400	0.04556500	0.78382100
H	4.05197600	-1.62059900	0.19172100

11

E(RB3LYP) = -229.162261 A.U.

C	-0.09106600	0.12454700	-0.00001100
O	-0.63302700	1.20378600	-0.00010000
O	-0.78547600	-1.03564400	0.00004200
H	-1.72822500	-0.80848300	0.00000600
C	1.39290500	-0.11879400	0.00005000
H	1.67204600	-0.70123400	0.88073300
H	1.67207800	-0.70160700	-0.88037400
H	1.92108600	0.83166700	-0.00013100

12

E(RB3LYP) = -615.26384 A.U.

C	2.16696900	-0.25513000	0.01756200
C	1.32522300	-1.43780500	0.29777700
C	3.64859300	-0.24728600	0.28139900

C	-0.15213300	-1.32375300	0.59294700
H	1.83427800	-2.29788600	0.72783600
C	1.48311200	1.09852400	-0.05662300
H	4.16317300	0.35805000	-0.46691800
H	3.86252000	0.17932000	1.26466300
H	4.03993700	-1.26499400	0.24709300
C	-0.78113700	-0.14835700	-0.17080800
H	-0.27418300	-1.20406100	1.67529900
H	-0.64802300	-2.26045500	0.31808700
C	-0.02345800	1.15513700	0.12478700
O	2.14223000	2.10774800	-0.20149100
H	-0.67289300	-0.35609100	-1.23811200
H	-0.16039500	1.43951800	1.17742700
H	-0.40824300	1.98350900	-0.47369900
O	1.72683100	-1.14489500	-1.04860200
C	-2.75400300	0.27195600	1.49649000
H	-3.83869200	0.38856700	1.50464300
C	-2.27850500	-0.01037400	0.08774200
C	-3.20110300	-0.65084600	-0.86190800
H	-4.19820800	-0.93142400	-0.53253100
H	-2.80302300	-1.22773200	-1.69283400
O	-2.95546100	0.76617700	-0.92857500
H	-2.49263800	-0.54402300	2.17512000
H	-2.31376300	1.19306300	1.88706500

13

E(RB3LYP) = -540.047106 A.U.

C	-2.75390500	1.37881100	-0.73118700
H	-3.81687400	1.40926000	-0.48712100
C	-2.12678500	0.11018300	-0.18969900
C	-3.00331300	-1.05121900	0.03224200
H	-2.61137500	-2.06248400	0.01358400
H	-4.05907200	-0.96217100	-0.21124400
O	-2.56389100	-0.24508100	1.14274100
C	-0.62399400	-0.04675800	-0.43411500
C	0.17222800	0.99543600	0.37248800
C	-0.07624200	-1.44664700	-0.12446200
H	-0.45564600	0.14809700	-1.50092000
C	1.67409400	0.89704200	0.16759800
H	-0.02078600	0.83678200	1.44210100
H	-0.12065200	2.02016800	0.14129800
C	1.42298300	-1.50846400	-0.16175700
H	-0.41940800	-1.76499000	0.86996500
H	-0.47361300	-2.18030000	-0.83204100
C	2.24770800	-0.45190800	-0.05764200
H	1.85640400	-2.49874900	-0.28255300
O	2.38481100	1.88967600	0.23155700
H	-2.28436300	2.26915000	-0.30694400

H	-2.64646100	1.42437300	-1.81871600
C	3.74635700	-0.55626400	-0.13386500
H	4.13683600	0.05025500	-0.95583800
H	4.21170400	-0.17715700	0.78054800
H	4.06115900	-1.59026500	-0.28410900

14

E(RB3LYP) = -540.039899 A.U.

C	-1.09332300	-1.45565400	0.03331200
C	-1.91660000	-0.22829700	0.02575600
O	-1.49672600	-0.85347500	1.27251500
C	0.38587300	-1.43568100	-0.27266400
C	-1.20457500	1.08726500	-0.21915600
C	0.30879500	1.07814000	-0.35986000
H	0.49376900	1.11484500	-1.44298400
C	1.04577500	-0.14472500	0.22952100
H	0.90361900	-0.11391600	1.31521800
H	0.50582300	-1.54524500	-1.35634000
H	0.86236700	-2.30531300	0.18983700
H	-1.61609200	-2.38310000	-0.19142600
O	-1.84203500	2.11205500	-0.35568700
C	2.54377500	-0.05158700	-0.02270000
C	3.19147100	-0.80767800	-0.91159600
C	3.27673400	0.96331600	0.82176000
H	3.15719200	0.73644600	1.88708600
H	4.34323700	0.97790100	0.59129300
H	2.88531400	1.97469500	0.67149200
H	2.69497300	-1.55309200	-1.52079600
H	4.26134100	-0.70210900	-1.05761500
H	0.67910400	2.02120300	0.04607900
C	-3.39655600	-0.25639700	-0.24502200
H	-3.80604800	-1.23262300	0.01846000
H	-3.90386700	0.51255900	0.34044200
H	-3.59886000	-0.06309900	-1.30148100

15

E(RB3LYP) = -540.040556 A.U.

C	1.06361500	-1.39444100	-0.37346100
C	1.91132600	-0.21710700	-0.04285800
O	1.59927900	-1.23186000	0.94530400
C	-0.44615000	-1.32922800	-0.49419800
C	1.18304100	1.07980100	0.22116400
C	-0.26383700	0.94770200	0.64022900
H	-0.74665400	-1.78170300	-1.44278700
H	-0.85825700	-1.95966600	0.30023100
H	1.55385100	-2.18327200	-0.94041800

O	1.73518100	2.14992400	0.05752400
H	-0.30794300	0.46308500	1.61986800
C	-1.02760700	0.10190100	-0.41306400
H	-0.85457300	0.57558900	-1.38541100
C	-2.53007600	0.10364800	-0.18189400
C	-3.04100900	-0.32731800	1.17116300
H	-2.70759200	0.35737200	1.95791600
H	-4.13175000	-0.34997400	1.18635400
H	-2.67815700	-1.32240900	1.44689800
C	-3.36111800	0.47934800	-1.15657900
H	-0.68748600	1.94974000	0.72117100
H	-4.43730300	0.47665200	-1.01804500
H	-2.99250200	0.80192000	-2.12495600
C	3.35032300	-0.12441100	-0.47150200
H	3.94086100	0.39558000	0.28619400
H	3.76489000	-1.12263000	-0.61864200
H	3.43589300	0.43583300	-1.40498300

16

E(RB3LYP) = -540.064281 A.U.

C	1.12928500	-1.60787900	-0.07805000
C	2.08826900	-0.68046000	-0.08615200
O	1.94198900	0.70376400	-0.25492200
C	0.90681500	1.49738300	0.15223100
C	-0.36727200	-1.52270200	-0.17721600
C	-0.32033900	0.84358100	0.72612700
H	-0.70108800	-2.13746400	-1.02137400
H	-0.77800900	-2.00920300	0.71611600
H	1.50353000	-2.62016300	0.04174800
O	1.02615700	2.68431800	-0.01587000
H	-0.06057200	0.29927100	1.63975000
C	-0.97163000	-0.11630000	-0.30975000
H	-0.74101200	0.26196400	-1.31041000
C	-2.48874300	-0.13407300	-0.18799300
C	-3.08983000	-0.51259300	1.14382300
H	-2.73887600	0.14796100	1.94351400
H	-4.17862700	-0.45150000	1.11036500
H	-2.81988900	-1.53209500	1.43664300
C	-3.25203800	0.18283600	-1.23578700
H	-0.99472200	1.65611500	0.99240800
H	-4.33513900	0.17402000	-1.17181600
H	-2.81945300	0.46114600	-2.19123100
C	3.55305100	-0.98381000	0.02408500
H	3.98034900	-0.49030800	0.90241400
H	3.72663700	-2.05663600	0.10264800
H	4.08629600	-0.60366500	-0.85234500

17

E(RB3LYP) = -540.063502 A.U.

C	-1.05239300	-1.46195300	-0.47289000
C	-1.97597300	-0.57031800	-0.08403800
O	-0.42559400	1.26439500	0.44476100
C	0.38145900	-1.13614000	-0.80877600
C	-1.64725500	0.88804900	-0.01427900
C	0.36836100	0.34913800	1.24253600
H	0.87561200	-2.01478000	-1.22568000
H	0.39846700	-0.36984100	-1.58896100
H	-1.36400800	-2.49667600	-0.58738000
O	-2.41739700	1.74821100	-0.37609800
H	1.00256700	0.99343300	1.85005800
C	1.20773800	-0.63063500	0.40592200
H	1.40165700	-1.48533600	1.06231400
C	2.55640400	-0.06787300	-0.01564300
C	2.57461600	1.19914200	-0.83606600
H	2.02693900	2.00527400	-0.33883000
H	3.59819900	1.53357000	-1.01251300
H	2.09493700	1.05557900	-1.80950100
C	3.68421100	-0.68504900	0.34396400
H	-0.29698900	-0.20253400	1.90708000
H	4.65764300	-0.30055600	0.05751400
H	3.67165600	-1.59471500	0.93565900
C	-3.42023400	-0.92045300	0.16065400
H	-3.72901100	-0.64469300	1.17394200
H	-4.06765900	-0.37294300	-0.52881600
H	-3.58769500	-1.99007600	0.02749900

18

E(RB3LYP) = -615.263728 A.U.

C	2.18154100	-0.18320700	-0.08073700
C	1.37292700	-1.39365700	-0.38888900
C	3.59137200	-0.01876700	-0.57887400
C	-0.14315100	-1.39822700	-0.43050700
H	1.86845400	-2.15057600	-0.99322100
C	1.41144000	1.07601100	0.24460100
H	3.60465000	0.55559300	-1.50763500
H	4.19450100	0.51915500	0.15594200
H	4.04306400	-0.99501700	-0.76026900
C	-0.77394600	0.00152300	-0.29658300
H	-0.48125300	-2.05513700	0.37732600
H	-0.47090900	-1.85673100	-1.36733300
C	-0.00745500	0.87120900	0.72762600
O	1.90963600	2.17162500	0.08096000
H	-0.68389100	0.50253900	-1.26690200

H	0.01920800	0.37757400	1.70361000
H	-0.47603900	1.85006500	0.83593300
O	1.96599900	-1.22635300	0.90398200
C	-2.72065100	-0.58814900	1.34244300
H	-3.80816400	-0.53999900	1.41408000
C	-2.26939300	-0.05164800	0.00167900
C	-3.19740900	-0.08693300	-1.13923300
H	-4.18437600	-0.52371600	-1.01160100
H	-2.80546900	-0.10524400	-2.15321700
O	-2.97260800	1.13956700	-0.41983900
H	-2.41477600	-1.62791800	1.48217000
H	-2.30086600	0.00177100	2.16113900

IN1

E(RB3LYP) = -769.123941 A.U.

C	-1.11339700	2.25005500	-0.13976900
C	0.12809200	1.76550700	-0.02441400
O	1.33254200	-0.22448900	-0.86958800
O	4.57098700	-0.59985200	0.27324300
C	3.45507000	-0.89215800	-0.06424400
O	2.66728600	0.17319700	-0.45117700
C	2.86789500	-2.26990600	-0.11216600
H	2.47882100	-2.49087000	-1.10652400
H	2.03579700	-2.33780700	0.58958000
H	3.64856000	-2.97794900	0.15749600
C	-2.37956900	1.44051600	-0.16089100
C	0.34123100	0.26140400	0.09960900
C	-0.88411700	-0.56004600	-0.30197800
H	-3.14095700	1.93675000	0.45010700
H	-2.77804100	1.43260100	-1.18411300
H	-1.23501800	3.32724800	-0.22823900
O	0.72520600	-0.12492500	1.39285000
H	-0.96580400	-0.54492000	-1.39203200
C	-2.15892300	0.00407000	0.34660500
H	-1.97166000	0.06179100	1.42335900
C	-3.36919000	-0.89233600	0.14475200
C	-3.76293100	-1.25613100	-1.26655800
H	-2.97106100	-1.82156500	-1.76872300
H	-4.66757900	-1.86627300	-1.27436500
H	-3.94958300	-0.36749000	-1.87784000
C	-4.05927500	-1.33890500	1.19674400
H	-0.70873500	-1.59149000	0.01086700
H	-4.93290300	-1.97147200	1.07706400
H	-3.77279400	-1.08554200	2.21235500
H	1.27938400	0.56265800	1.77993300
C	1.32771400	2.68266600	0.00421200
H	1.00019400	3.72345200	0.00873000

H	1.95301900	2.52693300	0.88957400
H	1.97458200	2.52408600	-0.86127200

IN2

E(RB3LYP) = -769.126466 A.U.

C	-1.43778900	2.09384000	-0.79882600
C	-0.21457600	2.13773400	-0.26367900
O	1.69952900	0.82145500	-0.12955700
O	2.62360000	-1.20450000	-1.52586200
C	2.84338700	-1.21404600	-0.34885800
O	2.39307300	-0.26767500	0.53935200
C	3.66205600	-2.22816800	0.40841900
H	3.57578700	-2.11061800	1.48696800
H	4.70814100	-2.10922700	0.11678600
H	3.33799300	-3.22583900	0.11066000
C	-2.35990300	0.90583000	-0.78436700
C	0.35625300	0.90756400	0.42717400
C	-0.42118300	-0.37807000	0.13008000
H	-3.38155400	1.24175200	-0.57846600
H	-2.38843600	0.46086500	-1.78774500
H	-1.82100000	2.99490400	-1.27215000
O	0.42431800	1.18925500	1.80443100
H	-0.16992200	-0.70030300	-0.88338000
C	-1.93529900	-0.14266900	0.26170200
H	-2.11078200	0.29324400	1.25038200
C	-2.74538400	-1.42544900	0.18114700
C	-2.57234900	-2.30475100	-1.03383000
H	-1.54480300	-2.67382900	-1.11638900
H	-3.23747800	-3.16871200	-0.98877400
H	-2.78498100	-1.76229400	-1.96049000
C	-3.58494600	-1.75584700	1.16539100
H	-0.09504900	-1.16246000	0.81922400
H	-4.18000300	-2.66254300	1.12572500
H	-3.70552600	-1.12832600	2.04264900
H	0.77675500	0.41035000	2.25333000
C	0.63248600	3.38421700	-0.24695300
H	0.08379100	4.22584300	-0.67321500
H	0.91911500	3.63802200	0.77747900
H	1.55726900	3.24978400	-0.81390700

TS1

E(RB3LYP) = -769.112953 A.U.
1 imaginary frequencies -428.6421 cm-1

C	0.81956900	2.40781600	1.45079800
H	1.69241500	3.02789100	1.24554200
C	0.21691000	1.86164300	0.18698700

C	0.79137000	2.13106300	-1.02581400
H	1.64669500	2.79233000	-1.09022100
H	0.32308200	1.85829600	-1.95911400
O	1.67050100	0.29744500	-0.70675100
H	2.40576200	0.67588500	-0.16018400
O	3.98488400	0.12012800	0.43389400
C	3.76954500	-0.95319100	-0.13589600
O	2.69398300	-1.20888300	-0.81600600
C	4.76276700	-2.09898900	-0.09145900
H	4.41734800	-2.96005100	-0.66044300
H	5.71625300	-1.74866700	-0.49180000
H	4.91884700	-2.38349200	0.95121900
C	-1.06837400	1.07591200	0.33181600
C	-1.70159600	0.62215800	-0.98803900
C	-0.91410800	-0.13933400	1.27419800
H	-1.77387000	1.76343600	0.82286600
C	-3.01089100	-0.12581700	-0.78905500
H	-1.01842400	-0.06158500	-1.50816200
H	-1.90421500	1.45788400	-1.65991400
C	-2.15472000	-0.98041800	1.33202900
H	-0.06958100	-0.75142600	0.93385100
H	-0.66501600	0.18618600	2.28761700
C	-3.14196400	-0.97495700	0.41976300
H	-2.23957900	-1.64302800	2.19032800
O	-3.89958100	-0.06405400	-1.62523100
H	0.07785300	3.01485500	1.98135600
H	1.11786100	1.60836200	2.13389800
C	-4.38596500	-1.81231600	0.53763000
H	-5.27957200	-1.18193800	0.54526200
H	-4.48695600	-2.48520400	-0.31871300
H	-4.37247200	-2.40823200	1.45161100

TS2

E(RB3LYP) = -769.112834 A.U.
1 imaginary frequencies -427.1433 cm-1

C	-0.69606500	2.21967900	1.66976600
H	-1.59178300	2.84106600	1.66548300
C	-0.22428700	1.91728300	0.27480800
C	-0.94078300	2.35509900	-0.80627000
H	-0.57580700	2.26422900	-1.81779600
H	-1.82100500	2.97014700	-0.66528600
O	-1.69344600	0.43614100	-0.69859000
H	-2.38728700	0.68283300	-0.03453000
O	-3.86230400	-0.05354700	0.61757100
C	-3.65315700	-1.01870000	-0.12263000
O	-2.64461600	-1.10185600	-0.93557600
C	-4.57231700	-2.22510200	-0.14751900
H	-5.58955300	-1.88469400	-0.35021200

H	-4.26834400	-2.95354900	-0.89681000
H	-4.56221700	-2.68896000	0.84120500
C	1.09658800	1.19065800	0.14262800
C	1.11329300	-0.15093100	0.90560400
C	1.57180000	0.96065300	-1.29716900
H	1.83489400	1.84431200	0.63228800
C	2.45778000	-0.85716800	0.83455400
H	0.35995300	-0.81442300	0.46436300
H	0.86625200	-0.03523400	1.96101300
C	2.83450900	0.15057600	-1.35749000
H	0.79253800	0.44040200	-1.86986000
H	1.73800800	1.91501000	-1.80575200
C	3.27573000	-0.66966900	-0.38810000
H	3.41835700	0.24294000	-2.27017600
O	2.82518100	-1.58853100	1.74196500
H	-0.91394000	1.30624400	2.22880200
H	0.09074700	2.74592900	2.22100900
C	4.55964100	-1.44787000	-0.47944400
H	5.22884000	-1.19207000	0.34681500
H	4.37094600	-2.52265700	-0.40580900
H	5.07449200	-1.24624600	-1.42014200

TS3

E(RB3LYP) = -769.107698 A.U.
1 imaginary frequencies -442.2501 cm-1

C	-0.11803700	0.82623800	1.38745800
C	0.04535000	1.77554800	0.39866800
O	1.15169300	-0.11543100	0.12323300
H	1.98677300	0.33210100	0.43387500
O	3.69223200	0.01057700	0.47606100
C	3.46992200	-1.05236200	-0.11298700
O	2.28418000	-1.45205900	-0.45170000
C	4.58635000	-2.00012900	-0.50657100
H	4.20474300	-2.90732400	-0.97099500
H	5.25070100	-1.48226900	-1.20162500
H	5.16108600	-2.25200800	0.38672500
C	-1.26451800	-0.13478000	1.44436400
C	-0.90026500	1.78666500	-0.76050300
C	-2.09883600	0.85877700	-0.70347900
H	-2.89864500	1.41599800	-0.19558800
C	-1.83927300	-0.45844300	0.06016600
H	-1.06023100	-0.99931400	-0.48772400
H	-2.02859400	0.32762000	2.08445600
H	-0.94600000	-1.04651800	1.95467300
H	0.49771000	0.90059700	2.27849400
O	-0.73613400	2.56913200	-1.67922700
C	-3.07225700	-1.34968800	0.07000200
C	-3.81771100	-1.57135200	1.15460400

C	-3.40164400	-2.00229000	-1.25138300
H	-2.56669000	-2.62409700	-1.59287500
H	-4.28922200	-2.63198100	-1.17299400
H	-3.58214600	-1.26120800	-2.03660100
H	-3.59893900	-1.13286900	2.12054100
H	-4.68823600	-2.21699800	1.10784300
H	-2.43101400	0.68961100	-1.72830100
C	1.06355700	2.87046200	0.46298400
H	1.75375200	2.73247200	1.29579100
H	1.62556000	2.93279400	-0.47051600
H	0.55781300	3.83377600	0.58795500

TS4

E(RB3LYP) = -769.108316 A.U.
1 imaginary frequencies-434.4057 cm-1

C	-0.20004200	0.70560900	-1.36470500
C	0.02404700	1.65861500	-0.38971100
O	1.20930800	-0.10236800	-0.09802900
H	2.00822400	0.32111900	-0.52153800
O	3.70486400	0.05562100	-0.67140200
C	3.57694500	-0.94493900	0.04459800
O	2.44220100	-1.34236600	0.52417900
C	4.76371800	-1.80696000	0.42997400
H	5.24095600	-2.17061100	-0.48230800
H	4.46895600	-2.64859500	1.05378500
H	5.48574200	-1.18576800	0.96396900
C	-1.30524000	-0.30481700	-1.32480500
C	-0.77049400	1.59954200	0.88030500
C	-1.65958200	0.39121500	1.07324200
H	-1.77917800	-0.33877400	-2.31071500
H	-0.85127400	-1.28902500	-1.17095600
H	0.36053400	0.77924900	-2.29150700
O	-0.67731800	2.49052300	1.70426000
H	-1.01911600	-0.42735700	1.42106800
C	-2.36326200	-0.00264400	-0.24303700
H	-2.93055300	0.87101100	-0.58235600
C	-3.35762300	-1.13863500	-0.06893700
C	-2.86249500	-2.43396400	0.52607300
H	-2.50719400	-2.29163800	1.55183200
H	-3.65741300	-3.18094000	0.54686300
H	-2.02350300	-2.84898900	-0.04144700
C	-4.63079000	-0.97844100	-0.43644900
H	-2.37689300	0.61841400	1.86359700
H	-5.35723000	-1.77726200	-0.32993300
H	-4.98846500	-0.04327100	-0.85488600
C	0.94823900	2.82175500	-0.57028000
H	1.59715500	2.94352700	0.29857200
H	1.55632000	2.71831800	-1.46948900

H	0.35996900	3.74129900	-0.65421300

TS5

E(RB3LYP) = -769.080196 TS5 A.U.
1 imaginary frequencies -220.8243 cm-1

C	0.17906600	1.31034500	-0.63838200
O	-1.81544300	0.31460800	-1.24253100
O	-2.94116200	-0.09191800	-0.46641300
H	-1.29038000	1.82099200	-1.58664000
C	0.33099600	0.81765300	1.70019700
C	-0.27734300	1.52113000	0.71427500
O	-1.99184500	-2.14985000	-0.29164800
C	-2.89629800	-1.37859000	-0.07115800
C	-4.14954700	-1.72171800	0.70252100
H	-4.83023700	-0.87597900	0.78461000
H	-3.86606100	-2.06321200	1.70024200
H	-4.65449100	-2.54924500	0.19960100
C	1.43571100	-0.16476300	1.47911600
C	1.36519300	0.45833800	-0.94527500
H	2.05635600	-0.23863300	2.37548900
H	0.98739200	-1.15771300	1.32972400
H	-0.01432300	0.95841200	2.72044800
O	-0.29289900	2.00513500	-1.64424400
H	0.94010400	-0.48980700	-1.30005300
C	2.29382700	0.22756600	0.25945200
H	2.76321500	1.18804600	0.49677900
C	3.40868400	-0.75844200	-0.04131200
C	3.03467700	-2.17672400	-0.39436400
H	2.39826700	-2.21823400	-1.28417100
H	3.92507100	-2.77580400	-0.59048800
H	2.47430300	-2.65884600	0.41308500
C	4.68249000	-0.36229900	0.01110700
H	1.89287100	0.89823300	-1.79511700
H	5.49839900	-1.04580700	-0.19891200
H	4.95075000	0.65801800	0.26493400
C	-1.38769300	2.50424700	0.97512400
H	-1.49358500	2.68379600	2.04543100
H	-1.18920900	3.45996500	0.48324300
H	-2.33623500	2.12154100	0.59268800

TS6

E(RB3LYP) = -769.109979 A.U.
1 imaginary frequencies -327.6452 cm-1

C	-1.20291100	1.97155800	-1.02627900
C	-0.05851800	2.03325400	-0.30940200
O	0.89353900	0.41674100	-0.67101300

O	1.80896000	-1.27474600	-0.58483500
C	0.32643900	0.72779800	0.52106400
O	3.36130200	-0.18912400	0.64371200
C	2.97833500	-1.13006200	-0.06823600
C	3.94552600	-2.25535800	-0.41899400
H	3.41868500	-3.15940700	-0.71985400
H	4.59177400	-2.45440800	0.43594300
H	4.56758900	-1.91882900	-1.25308100
C	-1.99194200	0.71431600	-1.16250600
C	-0.85126700	-0.15440300	0.96185000
H	-2.95859700	0.91409700	-1.62658200
H	-1.45271600	0.00545200	-1.79857400
H	-1.59693100	2.89181200	-1.44955200
O	1.20024600	0.96373600	1.54310100
H	-0.49799400	-1.17472500	0.78908000
C	-2.19918100	0.10219500	0.25516300
H	-2.73314400	0.85883700	0.83710200
C	-3.07837900	-1.13848700	0.22044700
C	-2.66051400	-2.28063400	-0.67254200
H	-1.62991700	-2.59457500	-0.48096800
H	-3.31116100	-3.14467400	-0.52954900
H	-2.70847100	-1.99568100	-1.72889400
C	-4.18671900	-1.19623800	0.96199800
H	-0.97085400	-0.02683800	2.03741100
H	-4.82214700	-2.07572800	0.96498700
H	-4.49311600	-0.36790900	1.59245600
H	2.10592000	0.67514900	1.22234000
C	0.83884200	3.21930700	-0.15845500
H	1.83759900	2.99375800	-0.53833600
H	0.43983600	4.06643800	-0.71892600
H	0.94300300	3.49489200	0.89262100

TS7

E(RB3LYP) = -769.079460 A.U.
1 imaginary frequencies -267.9882 cm-1

C	-1.40510300	1.71423800	-1.37583900
C	-0.54390100	2.13679400	-0.41990800
O	1.89818000	0.51323700	0.78441900
O	3.91830000	-0.08983800	-0.82220500
C	3.35596500	-0.98566500	-0.24306100
O	2.31697300	-0.83765500	0.61051000
C	3.70529400	-2.45152400	-0.36714100
H	4.76673600	-2.57887600	-0.14657300
H	3.54085600	-2.76517000	-1.40058800
H	3.11373900	-3.07647600	0.29976200
C	-2.15783500	0.42344400	-1.33990400
C	-0.26612300	1.25154700	0.68721900
C	-0.81383100	-0.14466100	0.69666800

H	-3.16233100	0.57669100	-1.74610300
H	-1.66296300	-0.27717400	-2.02761000
H	-1.58007600	2.35875200	-2.23309600
O	0.25433900	1.78208000	1.76543700
H	-0.14421900	-0.78438200	0.11673100
C	-2.23311700	-0.16839900	0.08138600
H	-2.86830000	0.49899200	0.67347100
C	-2.86236500	-1.54896600	0.12832200
C	-2.14102400	-2.68964500	-0.54671300
H	-1.15744100	-2.86399500	-0.09874600
H	-2.71486300	-3.61388000	-0.46527700
H	-1.97128800	-2.49065400	-1.60975800
C	-4.02635300	-1.73113600	0.75652300
H	-0.82050000	-0.51696000	1.72265300
H	-4.50207100	-2.70530500	0.79833300
H	-4.54123300	-0.91250500	1.24850400
H	0.99665400	1.11796700	1.98341100
C	0.15389200	3.47089000	-0.46109800
H	-0.09947700	4.01041600	-1.37418800
H	-0.12552600	4.08703900	0.39680400
H	1.23698600	3.33142300	-0.42174300

TS8

E(RB3LYP) = -769.100177 TS8 A.U.
1 imaginary frequencies -383.2685 cm-1

C	1.17964900	2.22742500	-0.14561600
C	-0.05683400	1.73210700	-0.18455000
O	-0.94110900	-0.24673800	0.93634200
O	-2.90704000	-1.41345300	-0.80115700
C	-3.46338600	-0.77284900	0.11417300
O	-2.91408900	0.07959700	0.89136000
C	-4.94864900	-1.00567400	0.37090400
H	-5.36073700	-0.26812800	1.05687900
H	-5.06691000	-2.00339600	0.80183000
H	-5.48320400	-0.98171400	-0.57973700
C	2.44454100	1.42631700	-0.03595400
C	-0.35593700	0.24475000	-0.11840200
C	1.08607500	-0.62712700	0.54768800
H	3.18777300	1.81732300	-0.73875000
H	2.87281300	1.56922500	0.96352900
H	1.30042700	3.30643100	-0.19509600
O	-0.67539400	-0.29019900	-1.30968500
H	1.20612300	-0.42925500	1.60767000
C	2.21730700	-0.05974400	-0.31767400
H	1.92972900	-0.18495000	-1.36321800
C	3.43115300	-0.95236700	-0.05611600
C	4.22125400	-0.75419100	1.21349900
H	3.58446800	-0.78788200	2.10262900

H	4.98260500	-1.52865300	1.31550600
H	4.72578200	0.21687600	1.22110300
C	3.75489600	-1.88858400	-0.95307700
H	0.84480200	-1.66131200	0.33344700
H	4.61128700	-2.53789800	-0.80566200
H	3.18324500	-2.02809300	-1.86416700
H	-1.49896400	-0.87743200	-1.15253800
C	-1.29154300	2.58764800	-0.32467800
H	-1.81761600	2.34842300	-1.25395900
H	-1.99137100	2.40613100	0.49357700
H	-1.02035800	3.64438900	-0.33910600

TS9

E(RB3LYP) = -844.330531 A.U.
1 imaginary frequencies -445.4464 cm-1

C	-0.32026600	2.20782900	-0.29991000
C	-0.10515000	1.39827100	-1.40186400
C	-1.23545900	3.38758700	-0.32234100
C	0.95068200	0.33633700	-1.46460600
H	-0.54492300	1.69551400	-2.34687400
C	0.46299000	1.96493600	0.95371300
H	-1.88562900	3.38504700	0.55412200
H	-0.64988300	4.31275500	-0.27710800
H	-1.84302100	3.40055000	-1.22649200
C	1.34848800	-0.19709200	-0.08049900
H	1.81622500	0.78566600	-1.97029700
H	0.60705900	-0.47471800	-2.11168100
C	1.60694600	0.97070900	0.88493300
O	0.22756100	2.61085900	1.95927900
H	0.50572200	-0.77263000	0.31539000
H	2.48223700	1.54749100	0.55647700
H	1.81460900	0.61677500	1.89592900
O	-1.76189700	0.54953300	-0.75178500
H	-1.44633000	0.05189000	0.04993000
O	-3.15165600	-0.67289000	-0.77330000
O	-1.91562900	-1.36983500	0.95168700
C	-2.89678700	-1.47912600	0.20669900
C	-3.91382500	-2.59065500	0.38491400
H	-3.39856300	-3.54933400	0.29678700
H	-4.32897200	-2.52120000	1.39226800
H	-4.71418000	-2.53223600	-0.35001300
C	3.86355100	-0.67632600	-0.62337900
H	4.59814700	-1.48048800	-0.56328300
C	2.51940500	-1.17464300	-0.13937300
C	2.20693400	-2.60899500	-0.23793900
H	2.93612400	-3.28475800	-0.67692700
H	1.17066200	-2.93120400	-0.29941300
O	2.59147500	-2.03011100	1.02289800

H	3.81436000	-0.33665200	-1.66113100
H	4.22246900	0.15409600	-0.01000700

TS10

E(RB3LYP) = -844.32928 A.U.
1 imaginary frequencies -442.6929 cm-1

C	0.36312900	2.07210400	-0.31586500
C	0.10088400	1.26665400	-1.40942100
C	1.14838900	3.33945000	-0.40833000
C	-0.88888400	0.13570600	-1.41131400
H	0.49939700	1.56784700	-2.37083800
C	-0.25742600	1.73462200	1.00764000
H	0.47555500	4.19763800	-0.30748700
H	1.87219300	3.40528000	0.40511700
H	1.66644000	3.41283300	-1.36420800
C	-1.83472700	0.17291900	-0.19844200
H	-0.33754600	-0.80914000	-1.45874200
H	-1.46471100	0.18802100	-2.34030500
C	-1.04762600	0.44322900	1.09583000
O	-0.11574900	2.48153800	1.95787900
H	-2.51942500	1.01623900	-0.34139800
H	-0.33628900	-0.36754200	1.29522300
H	-1.71257900	0.51440300	1.95794400
O	1.88818300	0.59391400	-0.69941500
H	1.52285700	-0.07665800	-0.05819500
O	3.39944000	-0.48725300	-0.62915900
O	1.95576000	-1.55544000	0.69497200
C	3.06454900	-1.46352500	0.15032300
C	4.14468000	-2.50574500	0.36240900
H	4.39575200	-2.53298200	1.42486600
H	3.74604000	-3.48334700	0.08436800
H	5.03743500	-2.28883200	-0.22084200
C	-2.05340000	-2.40246500	0.17911100
H	-2.81191000	-3.18324000	0.24966600
C	-2.71375300	-1.07002700	-0.09926000
C	-4.02410200	-1.03951700	-0.76739300
H	-4.48843600	-1.97328600	-1.07302000
H	-4.32029000	-0.16139100	-1.33575900
O	-3.92510500	-0.84153800	0.65507700
H	-1.35382600	-2.67617700	-0.61465100
H	-1.50117200	-2.37985200	1.12170200