Electronic Supplementary Material (ESI) for RSC Advances

SUPPORTING INFORMATION

Understanding the Formation of [3+2] and [2+4] Cycloadducts in the Lewis Acid Catalysed Reaction between Methyl Glyoxylate Oxime and Cyclopentadiene. A Theoretical study.

Lydia Rhyman[a], Ponnadurai Ramasami[a*], John A. Joule[b], José A. Sáez[c] and Luis R. Domingo[d*]

[a] *Computational Chemistry Group, Department of Chemistry, University of Mauritius, Réduit, Mauritius*

[b] *The School of Chemistry, University of Manchester, Manchester M13 9PL, UK*

[c] *Instituto de Tecnología Química UPV-CSIC, Camino de Vera s/n, 46022 Valencia, Spain*

[d] *Departamento de Química Orgánica, Universidad de Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain*

Index

*ELF topological analysis of the 13DC and HDA reactions between Cp **1** and BF_3:nitrone complex **8b**.*

A topology analysis of the ELF of some selected points along the *endo* paths associated with the reaction between Cp **1** and BF_3:nitrone complex **8b** yielding the [3+2] CA **9n** and the [2+4] CA **10n** was performed in order to understand the bond formation in these reaction paths. The most relevant ELF valence basins and their corresponding *N* populations of these selected points are displayed in Table S1. A schematic representation of the bonding changes in these points is given in Figure 3, while the attractor positions are shown in Figure S1.

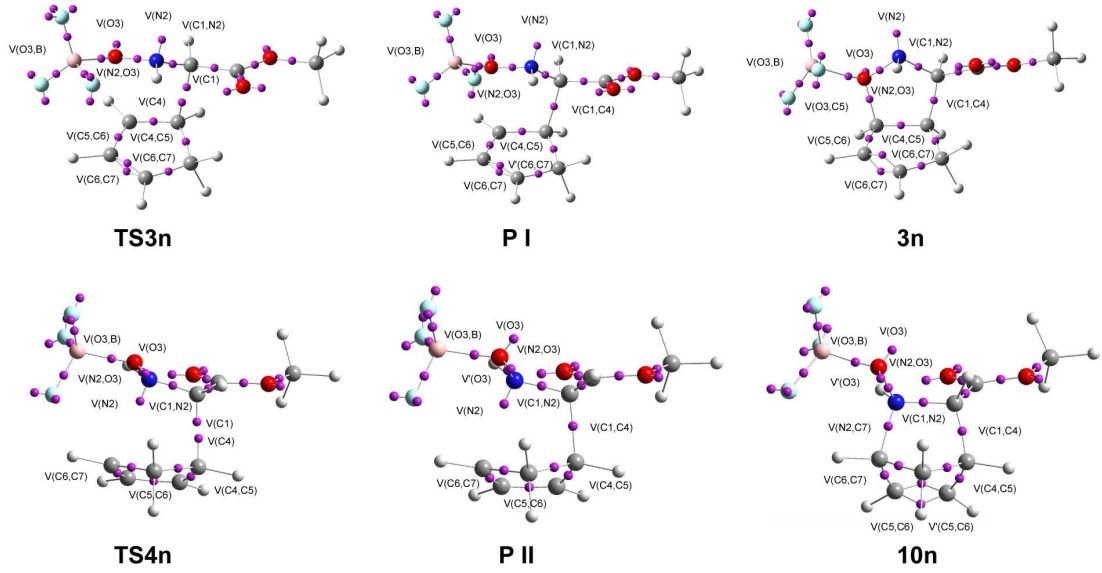


Figure S1. ELF attractors of some selected points involved in the formation of the *endo* [3+2] **9n** and [2+4] CAs **10n**.

ELF analysis of BF_3:nitrone complex **8b** shows one disynaptic basin V(N2,C3), whose electronic population integrates 3.54e, one disynaptic basin V(O1,N2) integrating 1.28e, and one disynaptic basin V(O1,B) integrating 2.14e. Finally, complex **8b** also shows one monosynaptic basin V(O1) integrating 4.14e, which is associated with the lone pairs present at the O1 oxygen atom. No monosynaptic basin at the N2 nitrogen is observed. On the other hand, Cp **1** presents one disynaptic basin V(C5,C6) integrating 2.23e, which is associated with the C5-C6 single bond, and two pairs of

Table S1. Valence basin populations *N* calculated from the ELF of some selected points involved in the formation of the *endo* [3+2] and [2+4] CAs **9n** and **10n**.

	Reagents	**TS3n**	**P I**	**9n**		**TS4n**	**P II**	**10n**
d(C3-C4) = d1		2.036	1.769	1.571	d(C1-C4)	1.961	1.722	1.568
d(O1-C5) = d2		2.454	2.323	1.495	d(N2-C7)	2.520	2.330	1.560
V(N2,C3)	3.54	2.35	2.02	1.73	V(N2,C3)	2.57	2.15	1.90
V(N2)		1.43	1.86	2.39	V(N2)	1.11	1.47	
V(O1,N2)	1.28	1.12	1.05	0.89	V(O1,N2)	1.08	1.04	1.05
V(O1)	4.14	4.11	4.00	2.65	V(O1)	4.57	2.66	2.54
V'(O1)					V'(O1)		1.99	2.38
V(O1,B)	2.14	2.03	2.17	2.53	V(O1,B)	1.74	1.72	1.57
V(C4,C5)	1.89	2.62	2.30	1.95	V(C4,C5)	2.52	2.19	1.99
V'(C4,C5)	1.61				V'(C4,C5)			
V(C5,C6)	2.23	2.38	2.46	2.07	V(C5,C6)	2.76	3.12	1.80
V'(C5,C6)					V'(C5,C6)			1.70
V(C6,C7)	1.58	1.66	1.63	1.71	V(C6,C7)	2.83	2.56	2.05
V'(C6,C7)	1.88	1.60	1.55	1.77	V'(C6,C7)			
V(C3)		0.54			V(C3)	0.62		
V(C4)		0.48			V(C4)	0.44		
V(C3,C4)			1.49	1.86	V(C3,C4)		1.55	1.85
V(O1,C5)				1.19	V(N2,C7)			1.83

disynaptic basins V(C4,C5) and V'(C4,C5), and V(C6,C7) and V'(C6,C7), integrating 1.89, 1.61, 1.58 and 1.88e, respectively, which are associated with the C4-C5 and C6-C7 double bonds.

Along the *endo* pathway yielding the [3+2] CA **9n**, the ELF analysis of **TS3n**, d1 = 2.036 Å and d2 = 2.454 Å, shows that while the disynaptic basin V(N2,C3) present in complex **8b** is depopulated to 2.35e, a new monosynaptic basin V(N2) integrating 1.43e is created at the N2 nitrogen. Note that the population of V(N2) increases along the IRC to reach 2.39e at the formal [3+2] CA **9n**. On the other hand, while the population of the disynaptic basin V(C5,C6) increases to 2.38e at **TS3n**, the two disynaptic basins associated with the C4-C5 double bond present in Cp **1**, merge into a disynaptic basin

V(C4,C5), integrating 2.62e. The most significant behavior found in the electronic structure of **TS3n** is the formation of two new monosynaptic basins, V(C3) and V(C4), at the C3 and C4 carbons, each one integrating 0.54 and 0.48e, respectively (see Table S1). These monosynaptic basins are associated with the C3-C4 bond formation after passing **TS3n**. At this point of the IRC, a large CT takes place from Cp to BF_3:nitrone framework, 0.31e. ELF analysis of **TS3n** suggests that the electronic structure of this TS can be associated with a zwitterionic *pseudodiradical* species.[36]

ELF analysis of **P I**, d1 = 1.769 Å and d2 = 2.323 Å, shows some significant changes relative to the electronic structure of **TS3n**. While the disynaptic basin V(N2,C3) is depopulated to 2.02e, the population of the monosynaptic basin V(N2) increases to reach 1.86e. Similarly, while the disynaptic basin V(C4,C5) is depopulated to 2.30e, the disynaptic basin V(C5,C6) reaches 2.46e. On the other hand, the two monosynaptic basins V(C3) and V(C4) present in **TS3n** have merged into a new disynaptic basin V(C3,C4), integrating 1.49e. Conversely, no monosynaptic basin is observed at C5. Consequently, at this point of the IRC, while the C3–C4 bond formation is very advanced, O3-C5 bond formation has not yet begun. Thus, this point of the IRC divides the two stages of the one-step mechanism of this reaction path. At this point of the IRC, the CT that takes place from Cp to BF_3:nitrone framework reaches 0.38e.

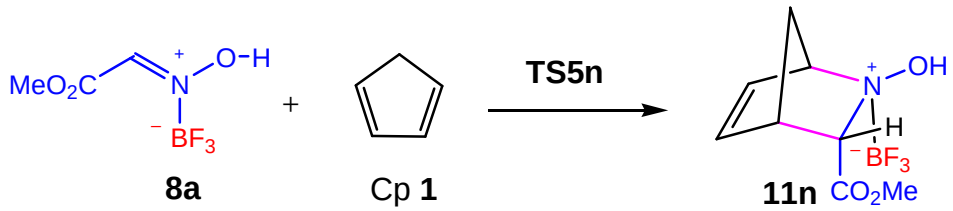
Finally, at the formal [3+2] CA **9n**, d1 = 1.571 Å and d2 = 1.495 Å, while the disynaptic basin V(N2,C3) is depopulated to 1.73e, the population of the monosynaptic basin V(N2) increases to reach 2.39e. Similarly, the disynaptic basins V(C4,C5) and V(C5,C6) are depopulated to 1.95e and 2.07e, respectively. On the other hand, while the monosynaptic basin V(O1) is depopulated to 2.65e, one new disynaptic basin V(O1,C5) is formed, integrating 1.19e and. Finally, the disynaptic basin V(C3,C4) reaches 1.86e at CA **9n**. These disynaptic basins account for the formation of the two new C3-C4 and O1-C5 σ bonds. The low populations of the disynaptic basins V(O1,N2) and V(O1,C5) point to very polarized O1–N2 and O1–C5 σ bonds.

Along the *endo* pathway yielding the [2+4] CA **10n**, the ELF analysis of **TS4n**, d1 = 1.961 Å and d2 = 2.520 Å, shows that while the disynaptic basin V(N2,C3) present in complex **8b** is depopulated to 2.57e, a new monosynaptic V(N2) integrating 1.11e is created at the N2 nitrogen. Note that this monosynaptic basin V(N2) will participate in

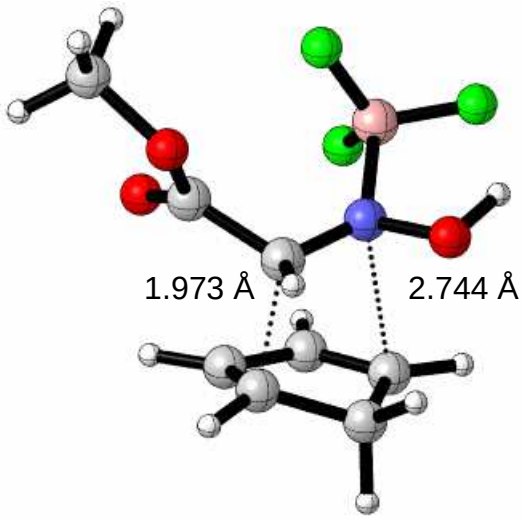
the formation of the new N2-C7 σ bond at the end of the reaction. On the other hand, while the disynaptic basin V(C5,C6) increases its population to reach 2.76e, the two pairs of disynaptic basins associated with the C4-C5 and C6-C7 double bonds present in Cp **1** merge into the disynaptic basins V(C4,C5) and V(C6,C7), each one integrating 2.52e and 2.83e, respectively. Together with this change at **TS4n**, the most significant behavior in the electronic structure of **TS4n** is the formation of two new monosynaptic basins at the C3 and C4 carbons, V(C3) and V(C4), each one integrating 0.62 and 0.44e. These monosynaptic basins are associated with the C3-C4 bond formation after passing **TS4n**. At this point of the IRC, a large CT takes place from Cp to the BF_3:nitrone framework, 0.38e. ELF analysis of **TS4n** indicates that the electronic structure of the TS can be associated with a zwitterionic *pseudodiradical* species.[36]

ELF analysis of **P II**, d1 = 1.722 Å and d2 = 2.330 Å, shows some significant changes relative to the electronic structure of **TS4n**: While the disynaptic basin V(N2,C3) is depopulated to 2.15e, the population of the monosynaptic basin V(N2) increases to reach 1.47e. Similarly, while the disynaptic basins V(C4,C5) and V(C6,C7) are depopulated to 2.19e and 2.56e, the population of the disynaptic basin V(C5,C6) increases to reach 3.12e. On the other hand, the monosynaptic basin V(O1) present in BF_3:nitrone complex **8b** splits into two monosynaptic basins V(O1) and V'(O1), each one integrating 2.66e and 1.99e. Finally, the two monosynaptic basins V(C3) and V(C4) present at **TS4n** have merged into a new disynaptic basin V(C3,C4), integrating 1.55e. On the other hand, no monosynaptic basin is observed at C7. Consequently, while the C3–C4 bond formation is very advanced, the N2-C7 bond formation has not yet begun at this point of the IRC. Thus, this point of the IRC divides the two stages of the one-step mechanism of this reaction path.

Finally, at [2+4] CA **10n**, d1 = 1.568 Å and d2 = 1.560 Å, while the disynaptic basin V(N2,C3) is depopulated to 1.90e, the monosynaptic basin V(N2) has merged into the new disynaptic basin V(N2,C7) integrating 1.83e, and the disynaptic basin V(C3,C4) reaches 1.85e. These disynaptic basins account for the formation of the two new C3-C4 and N2-C7 σ bonds. Similarly, while the disynaptic basins V(C4,C5) and V(C6,C7) are depopulated to 1.99e and 2.05e, respectively, the disynaptic basin V(C5,C6) present in **P II** splits into two monosynaptic basins V(C5,C6) and V'(C5,C6), each one integrating 1.80e and 1.70e. Finally, the disynaptic basin V(C3,C4) reaches 1.85e at CA **10n**.



Scheme S1. *Endo* reactive channel associated with the nucleophilic attract of Cp **1** on BF_3:oxime complex **8a**.



TS5n

Figure S2. B3LYP6-31G*optimized geometries of **TS5n** involved in the cycloaddition reaction of Cp **1** with BF_3:oxime complex **8a**.

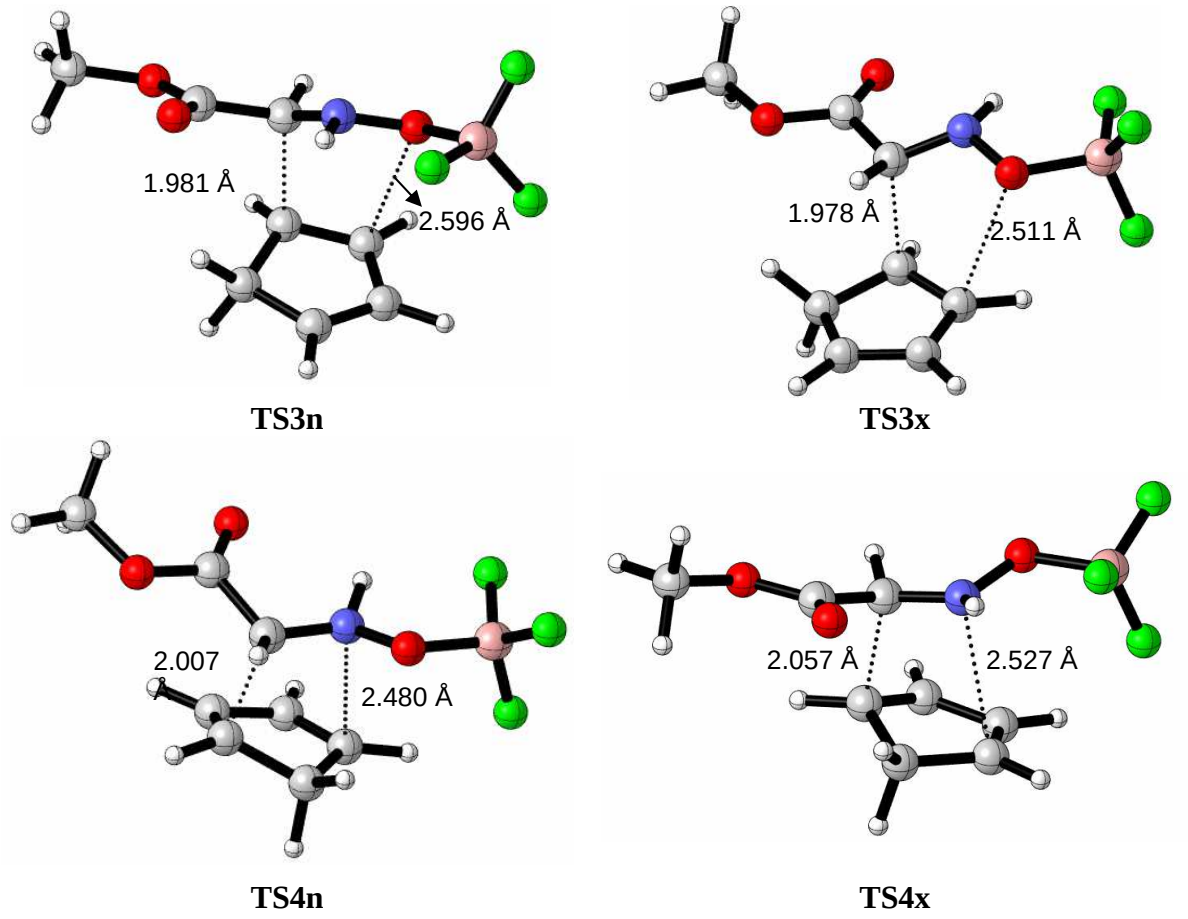


Figure S3. M06-2X/6-31G*optimized geometries in DCM of the TSs involved in the cycloaddition reactions of Cp **1** with BF_3:nitrone complex **8b**.

Table S2. M06-2X/6-31G* total (E, in au) and relative energies[a] (ΔE, in kcal mol^{-1}) in DCM of the stationary points involved in the reaction of Cp **1** and BF_3:nitrone complex **8b**.

	E	ΔE
Cp **1**	-194.006655	
8b	-722.014042	
TS3n	-916.019362	0.8
TS3x	-916.016141	2.9
9n	-916.068692	-30.1
9x	-916.067859	-29.6
TS4n	-916.021684	-0.6
TS4x	-916.020811	-0.1
10n	-916.076180	-34.8
10x	-916.075809	-34.6

[a] Relative to Cp **1** + **8b**.

[b] Relative to **8a**.

Table S3. Gas phase B3LYP/6-311+G** and M06-2X/6-311+G** total (E, in au) and relative[a] (ΔE, in kcal/mol) energies, and total (G, in au) and relative[a] (ΔG, in kcal/mol) free energies, computed[b] in DCM at -78 ºC, associated to the stereoisomeric TSs involved in the reaction of Cp **1** and BF_3:nitrone complex **8b**.

	B3LYP/6-311+G**				M06-2X/6-311+G**			
	Gas phase		DCM		Gas phase		DCM	
	E	ΔE	G	ΔG	E	ΔE	G	ΔG
TS3n	-916.636867	0.0	-916.506238	0.0	-916.291014	0.0	-916.155998	1.0
TS3x	-916.636196	0.4	-916.504018	1.4	-916.287673	2.1	-916.153485	2.6
TS4n	-916.632407	2.8	-916.503832	1.5	-916.290578	0.3	-916.157557	0.0
TS4x	-916.632001	3.1	-916.503859	1.5	-916.289461	1.0	-916.156994	0.4

a) relative to the most stable TS.
b) Frequency calculations were scaled by a factor of 0.90.

Complete citation for reference 22

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian 09; Gaussian, Inc., Wallingford CT, 2009.

B3LYP/6-31G* computed total energies, unique imaginary frequency, and cartesian coordinates of the stationary points involved uncatalysed and BF_3 catalysed reactions of Cp **1** with MGO **2a**.

1
E(RB3LYP) = -194.101058 au

C	1.16631000	-0.33692100	-0.00288100
C	-0.05748500	-1.21602800	0.00161100
C	-1.19293000	-0.22561500	-0.00268700
C	-0.68731200	1.02487200	0.00049700
C	0.78082800	0.95528900	0.00096900
H	-0.08888200	-1.86897100	0.88814600
H	-0.08874800	-1.89038200	-0.86808600
H	-2.24001500	-0.50631700	-0.00448700
H	-1.25670500	1.94887900	0.00183400
H	2.18264700	-0.71392800	-0.00442900
H	1.43523700	1.82113800	0.00196500

2a
E(RB3LYP) = -397.683410 au

C	-0.56873100	0.50189200	-0.00015200
O	-1.24767300	1.50950500	0.00044500
O	-1.05982300	-0.74928800	-0.00053800
C	0.91605300	0.56071200	-0.00052400
N	1.61911600	-0.50835100	0.00043500
O	2.97505400	-0.21422800	0.00005000
H	3.38573500	-1.09433800	0.00080000
C	-2.49417900	-0.83809500	0.00016800
H	-2.90951700	-0.35684200	-0.88932900
H	-2.71774100	-1.90498300	-0.00007800
H	-2.90861400	-0.35743600	0.89040500
H	1.35700100	1.55708600	-0.00144900

2b
E(RB3LYP) = -397.681243 au

C	-0.46182200	0.11081100	-0.00000900
O	-0.56683200	1.32862300	0.00000400
O	-1.50146100	-0.74469600	0.00000600
C	0.81510600	-0.59884600	-0.00000600
N	1.89373300	0.15576900	-0.00000700
O	3.09388600	-0.19642200	0.00001000
C	-2.80217000	-0.13061500	0.00000100
H	-2.93242200	0.49011100	-0.89024000
H	-3.51253400	-0.95721300	-0.00015900
H	-2.93254200	0.48987100	0.89039200
H	0.92480800	-1.67377400	-0.00000700
H	1.68512400	1.17248300	-0.00002100

TS1n
E(RB3LYP) = -591.760479 au
1 imaginary frequency -417.628 cm^{-1}

C	1.58128300	0.31373500	0.24347300
O	1.69328600	-0.00666900	1.41428600
O	2.51917700	0.08689400	-0.69733700
C	0.37801000	0.94421200	-0.33702400
N	-0.46435200	1.53119700	0.53786200
O	-1.58681100	1.95925900	0.07737000
C	3.70675300	-0.58067100	-0.23579600
H	4.20826100	0.01715900	0.52951100
H	3.45876200	-1.55969600	0.18264900
H	4.34046100	-0.68793200	-1.11613800
H	0.46205500	1.43624900	-1.29749600
C	-2.10385400	-1.46634500	0.77499300
C	-2.85570300	-0.48754800	0.22505000
C	-2.17513900	0.07553700	-0.92949700
C	-0.92683300	-0.56632600	-1.07709500
H	-2.33189000	-2.02288600	1.67763000
H	-3.80631600	-0.12323500	0.59964900
H	-2.65090100	0.69358900	-1.67866600
H	-0.43897100	-0.66441300	-2.04199600
C	-0.87724500	-1.70950600	-0.06575100
H	0.04019100	-1.76584500	0.53204500
H	-0.95711300	-2.67059600	-0.59832800
H	-0.44292600	1.17483100	1.50145200

TS1x
E(RB3LYP) = -591.758592 au
1 imaginary frequency -421.300 cm^{-1}

C	1.70961400	0.37631600	-0.05802700
O	2.34500000	1.16908200	0.61432800
O	2.18909700	-0.81073100	-0.48283200
C	0.29875900	0.56538300	-0.46063300
N	-0.16805500	1.82286300	-0.33719600
O	-1.43529800	2.01180900	-0.48194100
C	3.53723900	-1.10930700	-0.07900300
H	4.22991100	-0.36751300	-0.48459300
H	3.61906500	-1.11477300	1.01105100
H	3.75076600	-2.09740900	-0.48663700
H	-0.10093000	-0.00558100	-1.29264300
C	-2.42347200	-1.58615600	-0.50803200
C	-2.98809900	-0.40750700	-0.16627700
C	-2.12489600	0.31048300	0.76248300
C	-0.92981200	-0.42306800	0.91399200
H	-2.81950100	-2.30731800	-1.21497000
H	-3.93141900	-0.01975800	-0.53585200
H	-2.46270900	1.10384500	1.41464400
H	-0.30921500	-0.33081600	1.80100900
C	-1.13904200	-1.78313600	0.25594400
H	-1.27290300	-2.54557900	1.03937500
H	-0.30063400	-2.12620500	-0.36321300
H	0.34181700	2.43173000	0.31308200

3n
E(RB3LYP) = -591.815905 au

C	-1.51205800	-0.23744000	0.24616800
O	-1.60148100	0.14750100	1.39403500

O	-2.51073200	-0.16603900	-0.65312200
C	-0.25698600	-0.82024800	-0.36734600
N	0.50518800	-1.55305500	0.65042500
O	1.79656000	-1.67725800	0.05014500
C	-3.73642900	0.41575100	-0.17155400
H	-4.13641500	-0.17219400	0.65822100
H	-3.56667400	1.44119900	0.16691200
H	-4.41971100	0.39830400	-1.02058400
H	-0.53776900	-1.52771800	-1.15208600
C	2.01985800	1.67521400	0.47634300
C	2.75896000	0.57634500	0.30913700
C	2.10131100	-0.41936500	-0.60809700
C	0.73043100	0.23399600	-0.97633600
H	2.28759500	2.52000600	1.10590500
H	3.71624900	0.37300300	0.77944200
H	2.72049900	-0.69642700	-1.46799800
H	0.57604200	0.29609100	-2.05584300
C	0.74600300	1.65090200	-0.33191400
H	-0.12937700	1.85544200	0.29532400
H	0.75625200	2.42842200	-1.10798100
H	0.61567000	-0.92929800	1.45884600

3x
E(RB3LYP) = -591.814980 au

C	-1.68282500	-0.29423400	0.03797500
O	-2.16678500	-1.04635200	0.85853900
O	-2.35243100	0.70731000	-0.55962900
C	-0.23447700	-0.34560600	-0.40513500
N	0.19638600	-1.74180500	-0.51619100
O	1.62474200	-1.66509900	-0.43457100
C	-3.72757000	0.85704700	-0.15844500
H	-4.29532400	-0.04283000	-0.40759200
H	-3.79542000	1.03599100	0.91766100
H	-4.10147200	1.71502000	-0.71705600
H	-0.11568800	0.13901900	-1.37828000
C	2.56467500	1.57398800	-0.24077100
C	3.00834700	0.31857300	-0.13517300
C	1.98160800	-0.59245600	0.48052100
C	0.72263200	0.30442900	0.63687400
H	3.12928700	2.39993800	-0.66575000
H	3.98105600	-0.04135900	-0.45518600
H	2.31134000	-1.04436000	1.42699300
H	0.28520600	0.21708200	1.63549900
C	1.17116900	1.75151700	0.31418200
H	1.18025800	2.37641000	1.21750800
H	0.49491000	2.24963400	-0.39412000
H	-0.11443100	-2.21833000	0.33878000

TS2n
E(RB3LYP) = -591.743575 au
1 imaginary frequency -492.945 cm^{-1}

C	-1.35577500	0.27189500	-0.27588900
O	-1.52352200	-0.18518300	-1.38530900
O	-2.33932000	0.35750600	0.65884700
C	-0.07599300	0.77847200	0.29357300
N	0.84491600	1.19208900	-0.62097300

O	1.59651600	2.24097900	-0.00223100
C	-3.62381500	-0.11937800	0.23374500
H	-3.97936000	0.44762400	-0.63098500
H	-3.57450900	-1.17808700	-0.03675600
H	-4.28824900	0.02690700	1.08628700
H	-0.18222500	1.38771200	1.18925400
C	2.27424900	-0.44983400	-0.44948500
C	1.51007000	-1.54134500	-0.89046700
C	0.56576500	-1.84120400	0.08778800
C	0.68617100	-0.89728800	1.14606400
H	3.11737900	-0.02712900	-0.98436500
H	1.54892900	-1.97986300	-1.88102400
H	-0.24374800	-2.55391500	-0.02476300
H	0.17810900	-1.01775300	2.09902100
C	2.10118000	-0.35601100	1.04232600
H	2.78724200	-1.06354800	1.53317100
H	2.26966100	0.63748000	1.45802300
H	2.09185200	2.59768600	-0.75742800

TS2x
E(RB3LYP) = -591.746089 au
1 imaginary frequency -470.825 cm^{-1}

C	1.49208100	0.19449500	0.23596400
O	1.75788400	-0.02906500	1.39818800
O	2.40445600	0.11526000	-0.76495000
C	0.15907200	0.56735100	-0.33404400
N	-0.67723900	1.23423700	0.50709600
O	-1.40801000	2.14327900	-0.31021100
C	3.73314900	-0.23914300	-0.35188900
H	4.13117600	0.50568500	0.34247000
H	3.73798800	-1.21660000	0.13837900
H	4.32637900	-0.26522700	-1.26659500
H	0.20994900	0.93118400	-1.35738700
C	-0.63687700	-1.25203100	-0.57071600
C	-1.83716400	-0.93660500	-1.26093800
C	-2.74290300	-0.38509300	-0.35339400
C	-2.15563000	-0.38434900	0.91794300
H	0.14117000	-1.86990200	-1.01275400
H	-1.96421400	-0.97011200	-2.33789100
H	-3.67745900	0.09644600	-0.61859400
H	-2.63072900	-0.03535000	1.82748800
C	-1.01960900	-1.36164100	0.89999100
H	-1.40177900	-2.37743900	1.08921600
H	-0.22156500	-1.15101100	1.61228900
H	-1.89759100	2.65897200	0.35198200

4n
E(RB3LYP) = -591.788015 au

C	1.26933100	-0.48759800	-0.15207600
O	1.44645900	-1.42066200	0.59826800
O	2.25245900	0.35407300	-0.54255400
C	-0.03917500	-0.13454100	-0.84317700
N	-0.61759000	1.19545100	-0.41216300
O	0.07866500	1.68601400	0.75747300
C	3.53400300	0.11817600	0.06334400
H	3.46904100	0.23119900	1.14888800

H	3.89022500	-0.88899400	-0.16838200
H	4.20175600	0.86818300	-0.36204300
H	0.18013500	-0.05121800	-1.91509900
C	-2.01989900	0.84851400	0.02719500
C	-1.95380800	-0.02894300	1.26977000
C	-1.46350500	-1.21451600	0.88240500
C	-1.21385900	-1.13614500	-0.61479100
H	-2.61843700	1.75854900	0.08412400
H	-2.14043400	0.31171800	2.28155500
H	-1.16749400	-2.04689800	1.50862100
H	-1.09874600	-2.08255000	-1.14651700
C	-2.37269400	-0.19655800	-1.04594200
H	-3.35849900	-0.63966200	-0.88836000
H	-2.28762200	0.18267300	-2.07054300
H	0.59017000	2.42311000	0.38703600

4x
E(RB3LYP) = -591.788324 au

C	-1.47238700	-0.38779400	0.09021400
O	-1.76438500	-1.41785800	-0.47964100
O	-2.36652700	0.55285400	0.44705800
C	-0.06152700	0.03156000	0.48844600
N	0.52810900	0.86461300	-0.61167900
O	0.71091800	2.21051500	-0.20554700
C	-3.72329100	0.29926600	0.04467300
H	-3.78853800	0.21428800	-1.04309500
H	-4.09141400	-0.62545900	0.49720900
H	-4.29735200	1.15600400	0.39814400
H	-0.11941200	0.62243300	1.40795500
C	0.94150500	-1.16010600	0.59597300
C	2.19902300	-0.55462900	1.20192200
C	2.74835700	0.24955200	0.27660000
C	1.83478700	0.19146100	-0.94552400
H	0.53610400	-2.05191200	1.07494200
H	2.51952800	-0.69642100	2.22948500
H	3.61546100	0.89212800	0.39150500
H	2.22147400	0.58787100	-1.88417200
C	1.37142400	-1.27283000	-0.89412900
H	2.19216200	-1.97884800	-1.04093300
H	0.54271800	-1.49686800	-1.56855300
H	1.30511700	2.18152400	0.57525300

8a
E(RB3LYP) = -722.257808 au

C	-1.55507000	0.75989000	0.02479800
O	-2.41885800	1.29059500	0.68734000
O	-1.61417300	-0.43599000	-0.55123400
C	-0.26679900	1.47435600	-0.24397900
N	0.86850500	0.88857800	-0.19200700
O	1.95259500	1.69802800	-0.37910900
H	2.69289600	1.09246100	-0.14088700
C	-2.77239600	-1.23381700	-0.22772700
H	-3.68653100	-0.69904200	-0.49513900
H	-2.66301600	-2.14386800	-0.81521300
H	-2.77479900	-1.46064100	0.84071700
H	-0.30584700	2.55155700	-0.38207600

B	1.29837700	-0.76524200	0.15443200
F	2.64346800	-0.57338400	0.46104400
F	0.52350100	-1.10039800	1.21809000
F	1.09691700	-1.45487800	-0.99136100

8b
E(RB3LYP) = -722.261154 au

C	2.12430600	0.04019000	-0.00047300
O	2.01348700	1.24981800	-0.00082500
O	3.26915600	-0.64806900	0.00045200
C	0.96190100	-0.88021400	-0.00050500
N	-0.20272000	-0.32089000	-0.00114700
O	-1.33476800	-0.94116500	-0.00145100
C	4.47386800	0.14998800	0.00088200
H	4.50589900	0.77982600	0.89277800
H	5.29274600	-0.56782900	0.00122800
H	4.50656600	0.77976800	-0.89102700
H	1.03819900	-1.95981100	0.00004000
B	-2.64235800	0.10833800	0.00045000
H	-0.28721200	0.71377900	-0.00175300
F	-2.01691800	1.35295000	-0.00455700
F	-3.28603300	-0.18384600	1.15388200
F	-3.29358500	-0.18973100	-1.14713700

TS3n
E(RB3LYP) = -916.350032 au
1 imaginary frequency -333.592 cm^{-1}

C	-2.19936200	-0.71317900	0.12673300
O	-2.22440700	-0.82682800	1.33527800
O	-3.27186100	-0.75727900	-0.67651800
C	-0.95300300	-0.47980100	-0.66512900
N	0.17207900	-0.90036700	-0.06907000
O	1.28375300	-0.65153100	-0.75971100
C	-4.53690900	-0.96051700	-0.01270900
H	-4.53495100	-1.91591900	0.51687000
H	-4.72572400	-0.15353500	0.69944900
H	-5.28257200	-0.95958200	-0.80686300
H	-0.99971600	-0.68067500	-1.72948500
C	0.34962800	2.40971900	1.01416100
C	1.28018600	2.16478800	0.05642800
C	0.62319000	1.68278900	-1.12848700
C	-0.76073600	1.53493300	-0.88383900
H	0.55087200	2.72445700	2.03215700
H	2.35449300	2.23864100	0.16032400
H	1.11062800	1.53719700	-2.08369100
H	-1.48651000	1.62678000	-1.68777500
C	-1.03132200	2.17485500	0.47727400
H	-1.65444500	1.58644300	1.15948100
H	-1.55673000	3.13033000	0.32440900
B	2.62546100	-0.92942700	0.07931600
F	2.22778200	-0.83375700	1.41122900
F	3.05513600	-2.17656400	-0.26468700
F	3.45840700	0.08740700	-0.31820200
H	0.29095400	-0.87462700	0.94798200

TS3x
E(RB3LYP) = -916.349882 au
1 imaginary frequency -331.163 cm^{-1}

C	-1.96429300	-1.13039100	-0.02612000
O	-1.85576700	-2.09355700	0.70250900
O	-3.11976700	-0.67043500	-0.53189900
C	-0.80787700	-0.27181300	-0.44231100
N	0.36872600	-0.91069000	-0.38498300
O	1.43959300	-0.15075000	-0.62044800
C	-4.29851000	-1.41297300	-0.15301300
H	-4.22162000	-2.44442400	-0.50408500
H	-4.41580700	-1.40925400	0.93326500
H	-5.12981900	-0.90068500	-0.63595600
H	-0.93774800	0.38975000	-1.29647700
C	-0.72930900	3.14502000	-0.50762600
C	0.55981200	2.83077600	-0.21977900
C	0.59292100	1.71870900	0.69854800
C	-0.72013300	1.22881300	0.87932900
H	-1.06267300	3.91660700	-1.19316200
H	1.44412700	3.32004600	-0.61133000
H	1.47977400	1.38591000	1.21947800
H	-0.99282800	0.68980700	1.78319400
C	-1.66277900	2.27248200	0.28139600
H	-2.11307600	2.84834000	1.10435900
H	-2.49697800	1.86836500	-0.30329300
B	2.80830500	-0.77821200	-0.04859100
F	2.41243300	-1.89702600	0.67952600
F	3.57805700	-1.07046800	-1.13151900
F	3.31662200	0.22338900	0.75113800
H	0.52856500	-1.66743500	0.28571100

9n
E(RB3LYP) = -916.386038 au

C	-2.27364600	-0.63020200	0.15936400
O	-2.29582700	-0.65623800	1.37148200
O	-3.35616600	-0.71763800	-0.62849200
C	-1.01180800	-0.45160500	-0.66397500
N	0.11816400	-1.02490000	0.06769300
O	1.23448900	-0.40769600	-0.59836300
C	-4.61640300	-0.85492400	0.05979700
H	-4.62400200	-1.77235200	0.65290500
H	-4.78681900	0.00045800	0.71812600
H	-5.37116100	-0.89590000	-0.72495400
H	-1.11680500	-0.99747200	-1.60469500
C	0.12847700	2.52310500	0.75922700
C	1.22760000	1.93706000	0.27846500
C	0.90687300	1.02631000	-0.86712200
C	-0.64208800	1.04102700	-0.98572200
H	0.11307100	3.23362300	1.58095400
H	2.24250100	2.07456600	0.62927100
H	1.45818200	1.23702400	-1.78445000
H	-0.97123500	1.27427500	-2.00012200
C	-1.12389700	2.12461500	0.02269600
H	-1.89865200	1.76927200	0.71151200
H	-1.55755600	2.98034200	-0.51160500
B	2.77938900	-0.81190800	0.12744200
F	2.51998000	-0.62003500	1.44975000

F	2.97078700	-2.08065000	-0.27077600
F	3.55690000	0.13846700	-0.46056900
H	0.12877100	-0.64977500	1.02295800

9x
E(RB3LYP) = -916.388934 au

C	-2.27860500	-0.75939600	0.01875500
O	-2.26656900	-1.65978700	0.83030600
O	-3.38078700	-0.25235100	-0.55153800
C	-1.02848900	-0.02483700	-0.43587200
N	0.07158900	-0.98361100	-0.51470000
O	1.23785900	-0.12978700	-0.41824000
C	-4.62591400	-0.85167400	-0.13548600
H	-4.63509700	-1.91452000	-0.38744500
H	-4.76172600	-0.73567000	0.94254400
H	-5.40112200	-0.31728900	-0.68373200
H	-1.18200100	0.42029700	-1.42226600
C	0.34506900	3.11311400	-0.26868400
C	1.38371300	2.29534000	-0.07321400
C	0.94734100	0.99798100	0.52805900
C	-0.59347600	1.07015400	0.58734200
H	0.41231000	4.11072600	-0.69364800
H	2.42412500	2.49673100	-0.30006200
H	1.43174700	0.73301100	1.46966200
H	-0.96069500	0.80344200	1.58171600
C	-0.96612700	2.52226700	0.19138800
H	-1.36861800	3.07456700	1.05045100
H	-1.74153200	2.55838500	-0.58550600
B	2.66750700	-1.03376600	-0.03986400
F	3.52845100	-0.01165400	0.21773900
F	2.25002900	-1.73266800	1.05947700
F	2.89175200	-1.75354200	-1.15251300
H	0.08675800	-1.53708600	0.35022200

TS4n
E(RB3LYP) = -916.346132 au
1 imaginary frequency -396.415 cm^{-1}

C	-1.99266500	-0.79687300	0.09330800
O	-1.96890700	-0.95841200	1.29554100
O	-3.06008300	-0.99990000	-0.69415500
C	-0.82864200	-0.30050200	-0.70280600
N	0.36632400	-0.45520400	-0.08122800
O	1.44752200	-0.75173300	-0.83187500
C	-4.24432700	-1.47775000	-0.02253900
H	-4.04346300	-2.43709800	0.45972600
H	-4.57115200	-0.75724200	0.73128000
H	-4.99483100	-1.58768900	-0.80458000
H	-0.81009800	-0.56063700	-1.75610200
C	0.73040000	1.98863900	0.41325500
C	-0.39816300	2.16085800	1.20526100
C	-1.53893100	2.02530800	0.40284600
C	-1.14419600	1.62396600	-0.90425100
H	1.76206200	1.96179800	0.73899100
H	-0.39995400	2.30123400	2.28018200
H	-2.56226700	2.06204900	0.76064000
H	-1.82693900	1.68498300	-1.74787400

C	0.32582200	2.00964600	-1.02417900
H	0.38295900	3.04203600	-1.40389600
H	0.95131100	1.38351500	-1.66368100
B	2.75286000	-0.77943300	0.03460500
F	3.57319600	-1.66433400	-0.59694700
F	3.25671200	0.51751100	0.06290100
F	2.34199100	-1.18279300	1.31046000
H	0.43265200	-0.76220200	0.89170500

TS4x
E(RB3LYP) = -916.345627 au
1 imaginary frequency -370.803 cm^{-1}

C	-2.12581200	-0.70122600	0.07274500
O	-2.12211200	-1.09274300	1.22234200
O	-3.20012400	-0.68324100	-0.72967000
C	-0.92654200	-0.14756400	-0.63450300
N	0.25171900	-0.49803600	-0.07302100
O	1.31579200	-0.64900700	-0.87789300
C	-4.41622300	-1.20284100	-0.15088800
H	-4.27892100	-2.24672400	0.13982600
H	-4.69847100	-0.61723900	0.72730800
H	-5.16801500	-1.11494900	-0.93438400
H	-0.94259600	-0.21122600	-1.71619000
C	-1.14770300	1.79224600	-0.38184900
C	-0.01416300	2.29590300	-1.07132000
C	1.10761400	2.24354200	-0.22783300
C	0.70138700	1.82369100	1.02622900
H	-2.15992500	1.97019200	-0.73688600
H	0.00668800	2.55026000	-2.12583200
H	2.13547400	2.38369100	-0.53262000
H	1.36138100	1.61953900	1.86004600
C	-0.79076200	1.85303100	1.09983200
H	-1.12272900	2.82930000	1.48864700
H	-1.23752300	1.08424800	1.73375700
B	2.61340500	-0.94465500	-0.04547600
F	3.39451800	-1.69460500	-0.87250400
F	3.17915700	0.27592200	0.29793700
F	2.16880600	-1.62421100	1.09710000
H	0.31802000	-0.99228900	0.81936300

10n
E(RB3LYP) = -916.387325 au

C	-1.85425800	-0.78201500	0.04476700
O	-1.62701500	-1.23269100	1.14597400
O	-2.97131600	-0.98796800	-0.66288100
C	-0.90754700	0.12666000	-0.71645700
N	0.43929800	0.15579700	-0.03391000
O	1.40507500	-0.40092300	-0.87050400
C	-3.95705900	-1.84099800	-0.03878900
H	-3.52954900	-2.82672700	0.15686400
H	-4.29752300	-1.40026400	0.90106000
H	-4.77479700	-1.90737500	-0.75536200
H	-0.73043400	-0.25935900	-1.72064500
C	0.70812600	1.66628300	0.24937600
C	-0.30579500	2.07454900	1.29688500
C	-1.50642900	2.07526100	0.70106700

C	-1.30180800	1.64438200	-0.74764700
H	1.77139300	1.76280000	0.44934900
H	-0.07912500	2.23982700	2.34351500
H	-2.47183200	2.24740300	1.16452500
H	-2.10775600	1.85292100	-1.45134700
C	0.09755000	2.25177300	-1.03129000
H	0.09011400	3.34318800	-1.02074100
H	0.57696900	1.88028000	-1.94089500
B	2.62662900	-0.84845200	-0.01646900
F	3.28886100	-1.74980400	-0.79309500
F	3.37532100	0.28521600	0.29250800
F	2.07139600	-1.39067600	1.15708300
H	0.43347500	-0.40634900	0.83675000

10x

E(RB3LYP) = -916.385274 au

C	-2.00564900	-0.65478900	0.05457700
O	-1.84158900	-1.27444400	1.08519600
O	-3.10321200	-0.69663000	-0.70567200
C	-0.99047500	0.31361700	-0.52814800
N	0.35747700	0.05436300	0.10045800
O	1.26913200	-0.39372500	-0.84661400
C	-4.15739800	-1.56844400	-0.23813000
H	-3.79643500	-2.59787500	-0.18719000
H	-4.49771600	-1.25283900	0.75075200
H	-4.95565500	-1.47274300	-0.97297900
H	-0.88318600	0.16555100	-1.60126900
C	-1.25574100	1.81438600	-0.13229300
C	-0.21923200	2.62273100	-0.89954500
C	0.97979800	2.35997500	-0.36361500
C	0.74799900	1.40100700	0.78261000
H	-2.30089700	2.10546300	-0.24252000
H	-0.43211600	3.19839000	-1.79368900
H	1.95920500	2.65806300	-0.71350700
H	1.56717000	1.20512700	1.46734800
C	-0.63626500	1.82451300	1.29012500
H	-0.62065200	2.82175000	1.73354300
H	-1.09213200	1.11391900	1.98717400
B	2.47746700	-1.03767500	-0.11427900
F	3.10122600	-1.80240900	-1.05248000
F	3.26654700	-0.00617700	0.39040100
F	1.91071700	-1.77003000	0.94700600
H	0.28344700	-0.68901600	0.81941500