Electronic Supplementary Information

Understanding the Domino Reaction between 3-Chloroindoles and Methyl Coumalate yielding Carbazoles. A DFT Study

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Index

*ELF topological analysis of the P-DA reaction between 3-chloroindole **10a** and methyl coumalate **11**.*

A great deal of work has emphasized that the ELF topological analysis of the bonding changes along a reaction path is a powerful tool to establish the molecular mechanism of a reaction.[1] After an analysis of the electron density, ELF provides basins which are the domains in which the probability of finding an electron pair is maximal. The basins are classified as core and valence basins. The latter are characterized by the synaptic order, *i.e.*, the number of atomic valence shells in which they participate.[2] Thus, there are monosynaptic, disynaptic, trisynaptic basins and so on. Monosynaptic basins, labelled as V(A), correspond to lone pairs or non-bonding regions, while disynaptic basins, labelled as V(A,B), connect the core of two nuclei A and B and, thus, correspond to a bonding region between A and B. This description recovers the Lewis bonding model, providing a very suggestive graphical representation of the molecular system.

The ELF topological analysis of significant organic reactions involving the formation of new C-C single bonds has shown that it begins in the short C-C distance range of 1.9 - 2.0 Å by merging two monosynaptic basins, V(Cx) and V(Cy), into a new disynaptic basin V(Cx,Cy) associated with the formation of the new Cx-Cy single bond.[3] The Cx and Cy carbons characterized by the presence of the monosynaptic basins, V(Cx) and V(Cy), have been called *pseudoradical* centers.[4]

ELF topological analysis of the IRC associated with the reaction between 3-chloroindole **10a** and methyl coumalate **11** *via* **TS1-xm** allows for the characterization of 15 relevant points between reagents and the formal [2+4] CA **21**. All electronic density changes are sequential, allowing us to portrait a detailed insight of the mechanism of this P-DA reaction. The *N* populations of the most significant ELF valence basins at specific points along the IRC together with the atomic numbering are displayed in Table S1. The attractor positions for the most relevant points associated with the formation of carbazole **12a** are shown in Figure S1.

Starting from **P1**, d(C3-C4) = 3.124 Å and d(C2-C7) = 3.473 Å, the most relevant basins are those corresponding to the interacting systems on both **10a** and **11**, *i.e.*, the C2=C3, C4=C5, and C6=C7 double bonds. In this way, while the C2-C3 bonding region of 3-chloroindole **10a** is represented by a unique V(C2,C3) disynaptic

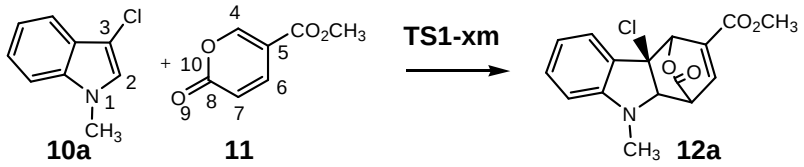
basin with a population of 3.54e, the C4-C5 and C6-C7 double bonds of methyl coumalate **11** are characterized by the presence of two disynaptic basins, V(C4,C5) and V'(C4,C5), and V(C6,C7) and V'(C6,C7), respectively. A distinguishing feature between the ELF representation of these double bonds is their different integration: 5.64e in the case of C4-C5 bonding region, and 3.21e in the case of C6-C7 one. This fact is due to the different environment of both unsaturated systems and will make the difference along the reaction.

At **P2**, d(C3-C4) = 2.254 Å and d(C2,C7) = 2.897 Å, the most remarkable change is the merging of V(C6,C7) and V'(C6,C7) disynaptic basins into a unique V(C6,C7) disynaptic basin, integrating 3.16e. Going toward **TS1-xm**, at **P3,** d(C3-C4) = 2.189 Å and d(C2-C7) = 2.877 Å, a V(C3) monosynaptic basin at the C3 carbon of indole appears, integrating 0.46e. As can be seen, the electronic density of this basin comes mainly from the V(C2,C3) disynaptic basin, which is depopulated to 3.00e. The V(C2,C3) disynaptic basin will provide most of the electronic density required for the C3-C4 bond formation, thus undergoing a continuously depopulation until the complete formation of this bond. At **P4**, d(C3-C4) = 2.123 Å and d(C2-C7) = 2.858 Å, one of the two monosynaptic basins present in N1 merges into the V(N1,C2) disynaptic basin, which increases its population to 3.04e.

This electronic density flow from N1 toward N1-C2 bonding region continues at **P5**, d(C3-C4) = 2.057 Å and d(C2-C7) = 2.839 Å, in which the V(N1) monosynaptic basin disappears and V(N1,C2) disynaptic basin increases its population in the same amount from 3.04 to 3.49e. At the same time, the V(C3) monosynaptic basin has increased its population to 0.69e. At **P6**, d(C3-C4) = 1.914 Å and d(C2-C7) = 2.820 Å, a new V(C4) monosynaptic basin appears over the C4 carbon with 0.12e. Therefore, at this point the two *pseudoradical* centers required for the C3-C4 formation are present.[3]

At **P7**, d(C3-C4) = 1.863 Å and d(C2-C7) = 2.714 Å, which corresponds with the TS of the reaction, **TS1-xm**, one of the most relevant bonding changes along this P-DA reaction takes place. The two V(C3) and V(C4) monosynaptic basins present at **P6** have merged into new V(C3,C4) disynaptic basin, with an initial integration of 1.19e. Consequently, at P7 the formation of the first C3-C4 single bond has begun.[3]

Table S1. Valence basin populations *N* calculated from the ELF of some selected points of the IRC curve of the P-DA reaction between 3-chloroindole **10a** and methyl coumalate **11**. Point **P7** is **TS1-xm**. d(Cx-Cy) distances are given in Å. The GEDT obtained by NPA analysis is given in e.



	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	12a
d(C3-C4)	3.124	2.254	2.189	2.123	2.057	1.914	1.863	1.644	1.634	1.603	1.596	1.584	1.578	1.572	1.566	1.536
d(C2-C7)	3.473	2.897	2.877	2.858	2.839	2.820	2.714	2.606	2.561	2.365	2.311	2.197	2.139	2.079	2.019	1.561
GEDT	0.01	0.11	0.14	0.18	0.22	0.27	0.36	0.45	0.44	0.36	0.33	0.27	0.24	0.21	0.18	0.04
V(N1)	0.82	0.59	0.59	0.46						0.45	0.47	0.58	0.60	0.68	0.74	0.99
V'(N1)	0.53	0.52	0.48							0.84	0.91	1.04	1.12	1.18	1.22	1.35
V(N1,C2)	2.17	2.39	2.44	3.04	3.49	3.50	3.54	3.59	3.62	2.41	2.31	2.10	2.04	1.95	1.91	1.68
V(C2,C3)	3.54	3.45	3.00	2.90	2.77	2.66	2.48	2.29	2.29	2.24	2.21	2.17	2.16	2.15	2.15	2.02
V(C4,C5)	3.28	3.14	3.11	3.08	3.08	2.83	2.47	2.28	2.27	2.21	2.21	2.22	2.21	2.21	2.20	2.15
V'(C4,C5)	2.36	2.42	2.42	2.44	2.46	2.48	2.48	2.48	2.49	2.42	2.43	2.42	2.43	2.41	2.38	2.37
V(C5,C6)	2.40	2.54	2.59	2.64	2.69	2.75	3.04	3.20	3.17	3.27	3.25	3.28	1.71	1.76	1.75	1.71
V'(C5,C6)													1.60	1.56	1.58	1.67
V(C6,C7)	1.61	3.16	3.15	3.12	3.11	3.09	3.07	2.96	2.72	2.54	2.50	2.40	2.37	2.30	2.25	2.04
V'(C6,C7)	1.60															
V(C7,C8)	2.52	2.52	2.54	2.55	2.57	2.59	2.61	2.63	2.59	2.53	2.50	2.41	2.38	2.36	2.31	2.14
VC8, O9)	2.50	2.41	2.40	2.40	2.38	2.36	2.35	2.33	2.33	2.38	2.40	2.48	2.45	2.46	2.43	2.49
V(O9)	2.67	2.72	2.74	2.76	2.75	2.76	2.74	2.76	2.76	2.72	2.71	2.72	2.71	2.68	2.68	2.68
V'(O9)	2.62	2.62	2.63	2.62	2.65	2.68	2.66	2.68	2.70	2.71	2.71	2.63	2.65	2.65	2.65	2.66
VC8,O10)	1.80	1.78	1.76	1.75	1.71	1.73	1.69	1.64	1.65	1.66	1.66	1.66	1.69	1.68	1.70	1.70
V(O10)	3.98	4.15	4.18	4.28	4.35	4.35	4.46	4.51	4.48	4.41	4.45	4.56	4.54	4.54	4.52	4.51
V(C4,O10)	1.81	1.70	1.70	1.66	1.63	1.62	1.54	1.51	1.51	1.45	1.43	1.42	1.39	1.40	1.43	1.40
V(C3)			0.46	0.56	0.69	0.87										
V(C4)						0.12										
V(C3,C4)							1.34	1.74	1.77	1.83	1.85	1.88	1.89	1.91	1.92	1.96
V(C2)											0.23	0.38	0.43	0.51		
V(C7)									0.26	0.36	0.39	0.51	0.56	0.61		
V(C2,C7)															1.20	1.81

At **P8**, d(C3-C4) = 1.644 Å and d(C2-C7) = 2.606 Å, the V(C3,C4) disynaptic basin increases its population to 1.74e at the expenses of the V(C2,C3) one. It is worth to mention that the V(C2,C3) disynaptic basin has lost 1.25e from **P1** to **P8**, being the driving force of the C3-C4 bond formation.

At **P9**, d(C3-C4) = 1.634 Å and d(C2-C7) = 2.561 Å, a new V(C7) monosynaptic basin appears at C7 with an integration of 0.26e. This V(C7) monosynaptic basin will be involved in the formation of the second C2-C7 single bond. The maximum GEDT along this P-DA reaction is reached at **P8**-**P9** (0.44-0.45e) and it will decrease toward cycloadduct formation.

At **P10**, d(C3-C4) = 1.603 Å and d(C2-C7) = 2.365 Å, the two V(N1) and V'(N1) monosynaptic basins present at **P3** in the N1 nitrogen reappear with a population of 0.45 and 0.84e. This behaviour can be related to the depopulation of V(N1,C2) basin. In the

next structure along IRC, **P11**, d(C3-C4) = 1.596 Å and d(C2-C7) =2.311 Å, a V(C2) monosynaptic basin over C2 with an integration of 0.23e appears, while the V(C7) monosynaptic basin has reached 0.39e. Therefore, at this point, the two V(C2) and V(C7) monosynaptic basin required for the subsequent C-C single bond formation are present.

At **P12**, d(C3-C4) = 1.584 Å and d(C2-C7) = 2.197 Å, both V(C2) and V(C7) monosynaptic basins have increased its population to 0.38 and 0.51e, respectively. Later on, at **P13**, d(C3-C4) = 1.578 Å and d(C2-C7) = 2.139 Å, the V(C5,C6) disynaptic basin splits up into two disynaptic basins, V(C5,C6) and V'(C5,C6), with an integration of 1.71 and 1.60e. Therefore, at **P13** the C4-C5 double bond present in carbazole **12a** has already been created.

At **P14**, d(C3-C4) = 1.572 Å and d(C2-C7) = 2.079 Å, the V(C2) and V(C7) monosynaptic basins have increased their population to 0.51 and 0.61e, respectively.

Finally, at **P15**, d(C3-C4) = 1.566 Å and d(C2-C7) = 2.019 Å, the second most relevant bonding changes along this P-DA reaction takes place. The two V(C2) and V(C7) monosynaptic basins present at **P14** have merged into the new V(C2,C7) disynaptic basin, with an initial integration of 1.20e. Consequently, at **P15** the formation of the second C2-C7 single bond has begun. It is worth to mention that in this P-DA reaction formation of the second single bond takes place before formation of the C4-C5 double bond.

From **P15** to final cycloadduct, only basin population changes take place, the most noticeable being the increase of V(C2,C7) integration from 1.20e to 1.81e. Taking a look at the final ELF picture of carbazole **12a** one can clearly see two C-C double bonds represented by the V(C4,C5) and V'(C4,C5) and the V(C5,C6) and V'(C5,C6) disynaptic basins.

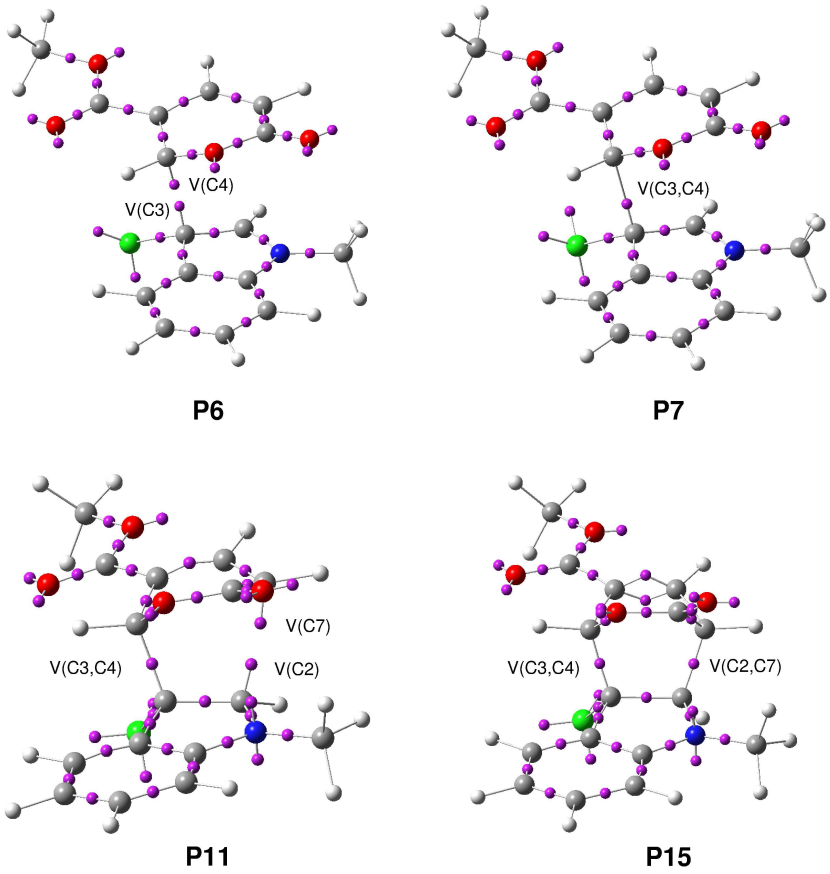


Figure S1. ELF attractor positions for the most relevant points associated with the formation the C3-C4 and C2-C7 single bonds along the P-DA reactions between 3-chloroindole **10a** and methyl coumalate **11**.

Some appealing conclusions can be drawn from this ELF topological analysis: i) ELF topological analysis along the one-step P-DA reaction between 3-chloroindole **11** and methyl coumalate **11** indicates that the bonding changes take place at least in 15 differentiated phases; each one of these phases corresponds to a bonding change with respect to the previous Lewis structure. Consequently, the bonding changes in this P-DA reaction are non-concerted; ii) as in most organic reactions, formation of the first C3-C4 single bond takes place at a distance of 1.927 Å, by coupling of two *pseudoradical* centers[4] created at the most nucleophilic center of 3-chloroindole **10a**, the C3 carbon, and the most electrophilic center of methyl coumalate **11**, the C4 carbon.[3] These relevant centers are clearly characterized when the electrophilic and nucleophilic Parr functions[5] at the ground state of the separated reagents (see later); iii) at the first TS of the reaction, with a C3-C4 distance of 1.863 Å, the formation of the

first C3-C4 single bond has already begun, with a population of 1.20e. Note that in most of the TSs associated with P-DA reactions showing a C-C distance larger than 2.1 Å,[6] the formation of the C-C single bond has not started; iv) at point **P8,** the maximum GEDT in this P-DA reaction, 0.45e, is reached. Beyond this point, there is a decrease of GEDT as a consequence of a retrodonation process associated with the formation of the second C-C single bond; v) formation of the second C2-C7 single bond takes place at a C-C distance of 2.019 Å at the last phase of the reaction. At this phase, the C3-C4 single bond, represented by the V(C3,C4) disynaptic basin with a population of 1.92e, is practically completed, in clear agreement with a *two-stage one-step* mechanism. vi) finally, the bonding changes associated with the formation of the first C3-C4 single bond are similar to those associated with the formation of C3-C4 single bond in the recently studied Friedel-Crafts reaction between *N*-methyl indole **19** and an electrophilically activated nitroolefin.[7] This similarity in the C-C bond formation found in these two different organic reactions, a DA reaction and an aromatic electrophilic substitution reaction, allows establishing that P-DA reactions begin through a nucleophilic/electrophilic two-center interaction as in most polar organic reactions. Formation of the different products occurs at the second part of the reaction when the first C-C single bond is already practically formed. These reactions can take place *via* a *one-step two-stage* mechanism as in most P-DA reactions or *via* a stepwise mechanism with formation of a zwitterionic intermediate as the aforementioned Friedel-Crafts reaction. Regardless of the *one-step* or stepwise nature of the reaction mechanism, the bonding changes at the first stage of the one step mechanism and those in the first step of the stepwise one are very similar. This quantum chemical topological similarity of both mechanisms supports Domingo's proposal that DA reactions are not a special type of organic reaction.[3]

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Table S2. MPWB1K/6-311G(d,p) gas phase total (E, in au) and relative (ΔE, in kcal/mol) electronic energies, for species involved in the domino reaction between 3-chloroindole **10a** and methyl coumalate **11**. Values of ΔE are relative to **10**+**11**.

	E	ΔE
10a	-862.686365	
11	-571.130177	
CO_2	-188.558279	
HCl	-460.873269	
TS1-no	-1433.779794	23.1
TS1-xo	-1433.784136	20.3
13	-1433.841537	-15.7
14	-1433.840888	-15.3
TS2-1	-1433.775362	25.8
17	-1245.281771	-14.8
TS2-2	-1245.246966	7.1
TS3-1	-1433.775394	25.8
18	-972.949187	-3.7
TS3-2	-972.924016	12.1
12a	-784.468430	-52.4

Table S3. MPWB1K/6-311G(d,p) enthalpies (H, in au), entropies (S, in cal/molK), and Gibbs free energies (G, in au) computed at 200 ºC and 1 atm in toluene, for species involved in the domino reaction between 3-chloroindole **10a** and methyl coumalate **11**.

	H	S	G
10a	-862.514738	116.1	-862.602252
11	-570.987281	113.0	-571.072450
CO_2	-188.541154	55.3	-188.582856
HCl	-460.862747	47.8	-460.898777
TS1-no	-1433.465391	179.6	-1433.600788
TS1-xo	-1433.467256	181.6	-1433.604174
13	-1433.520332	179.2	-1433.655447
14	-1433.519172	178.9	-1433.654062
TS2-1	-1433.457823	182.4	-1433.595374
17	-1244.979773	167.5	-1245.106047
TS2-2	-1244.959061	172.4	-1245.089063
TS3-1	-1433.469550	181.1	-1433.606124
18	-972.645475	170.5	-972.774022
TS3-2	-972.624068	170.4	-972.752515
12a	-784.183000	156.4	-784.300892

Complete citation for reference 25

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MPWB1K/6-311G(d,p) computed total electronic energies, unique imaginary frequency, and cartesian coordinates, in toluene, of the structures involved in the P-DA reaction between 3-chloroindole **10a** and methyl coumalate **11**.

10a E(RmPW+HF-B95) = -862.6896850400 au

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.40415194
N	1.29199770	0.00000000	1.83652050
C	2.11588811	0.00001229	0.75070373
C	1.36724242	0.00000928	-0.37850537
C	-1.20491775	-0.00000000	-0.69262107
C	-2.37334979	-0.00000000	0.02716658
C	-2.36083538	-0.00000000	1.42511647
C	-1.18254927	-0.00000000	2.13154381
C	1.70286535	0.00005642	3.21071723
Cl	1.96441703	0.00000579	-1.98412527
H	3.18240231	0.00001450	0.86276732
H	-1.21410479	-0.00000000	-1.77027618
H	-3.31884719	-0.00000000	-0.48946171
H	-3.29640653	-0.00000000	1.95983162
H	-1.17637929	-0.00000000	3.20930136
H	1.33366853	-0.88389664	3.72302824
H	2.78413662	0.00018560	3.25631312
H	1.33346089	0.88393436	3.72300713

11 E(RmPW+HF-B95) = -571.1354305340 au

O	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.38824973
C	1.30291928	0.00000000	1.99675476
C	2.41949697	0.00065888	1.25554850
C	2.33076860	0.00100821	-0.16683797
C	1.10515549	0.00050941	-0.71478887
O	-1.05706819	-0.00008349	1.93040778
C	3.48708632	0.00195521	-1.07037518
O	3.40962857	0.00096208	-2.26505216
O	4.63139304	0.00405536	-0.40689504
C	5.80149200	0.00545796	-1.20938325
H	1.32039520	-0.00034458	3.07134401
H	3.39177641	0.00089249	1.71816947
H	0.93285366	0.00062026	-1.77706430
H	6.63283127	0.01246403	-0.51981940
H	5.83021965	-0.88059530	-1.83283750
H	5.82203483	0.88553542	-1.84151979

CO_2
E(RmPW+HF-B95) = -188.5595759010 au

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.14701400
O	0.00000000	0.00000000	-1.14701400

HCl
E(RmPW+HF-B95) = -460.8749376880 au

Cl	0.00000000	0.00000000	0.00000000
H	0.00000000	0.00000000	1.27556400

TS1-no
E(RmPW+HF-B95) = -1433.7908485300 au
1 imaginary frequency: -195.5 cm^{-1}

O	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.36923041
C	1.29038147	0.00000000	1.98717709
C	2.42002961	0.23615342	1.24125985
C	2.38207441	0.09351531	-0.12643962
C	1.13655151	-0.39349800	-0.66703926
O	-1.06302312	0.03731369	1.92454608
C	3.50106673	0.30254693	-1.00912375
O	3.45487687	0.24597386	-2.21122689
O	4.64061837	0.55104462	-0.35224298
C	5.77395341	0.74855865	-1.17230388
H	1.29410631	0.05519417	3.06106726
H	3.34715048	0.50478966	1.72304951
H	1.00143564	-0.21490574	-1.72512337
H	6.58739380	0.99301051	-0.50293468
H	6.00223196	-0.15507669	-1.72917535
H	5.60574522	1.55853216	-1.87306824
C	2.24348831	-2.57530550	-1.43611391
C	3.25145780	-2.79009371	-0.51244918
N	2.68235441	-2.74938969	0.76947870
C	1.39495381	-2.51912177	0.69341506
C	1.06808700	-2.14879185	-0.66204100
C	2.50497916	-2.64702518	-2.78224690
C	3.79850818	-2.93607462	-3.17455275
C	4.80632424	-3.10855632	-2.23912710
C	4.55380721	-3.03754790	-0.88039122
C	3.42713158	-2.91995045	1.98823189
Cl	-0.51514849	-2.59088594	-1.24886842
H	0.73833957	-2.60513210	1.53603064
H	1.72569910	-2.48017111	-3.50673469
H	4.03246427	-3.00969506	-4.22276208

H	5.80925112	-3.31374464	-2.57463470
H	5.33663110	-3.17894932	-0.15481929
H	4.04137099	-3.81027693	1.91937378
H	4.05817679	-2.05080660	2.14780915
H	2.73588026	-3.01664959	2.81380245

TS1-xo

E(RmPW+HF-B95) = -1433.7927879900 au

1 imaginary frequency: -420.6 cm^{-1}

O	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.36965788
C	1.28600446	0.00000000	1.99039743
C	2.42254002	0.21881260	1.25307032
C	2.37125000	0.12175418	-0.12175012
C	1.14439858	-0.34099509	-0.65753530
O	-1.06902440	0.01524068	1.91909726
C	3.47463033	0.36998416	-1.02364011
O	3.41426326	0.29230411	-2.22292477
O	4.58978183	0.72249881	-0.38262927
C	5.69795494	1.00967329	-1.21173068
H	1.28951991	0.02155201	3.06543478
H	3.35681114	0.44448970	1.74093635
H	1.01672118	-0.23796374	-1.72414404
H	6.50048611	1.29688230	-0.54681085
H	5.98039148	0.13574402	-1.78859396
H	5.46467787	1.81925981	-1.89438062
C	-0.16479835	-2.52809582	-1.23225871
C	-1.08672258	-2.77534717	-0.22572522
N	-0.41178561	-2.80758817	0.98959877
C	0.86794773	-2.54730990	0.79819294
C	1.10278901	-2.21985597	-0.57386085
C	-0.57488072	-2.48717362	-2.54826147
C	-1.91023822	-2.70672689	-2.81878443
C	-2.82343115	-2.93573130	-1.79594859
C	-2.42801451	-2.96911671	-0.47550622
C	-1.04439834	-3.06369881	2.25902644
Cl	2.59629161	-2.76428390	-1.28864105
H	1.59366216	-2.65294164	1.57916876
H	0.13159827	-2.30101292	-3.34059061
H	-2.25411195	-2.69595317	-3.83937183
H	-3.86150914	-3.08849584	-2.03914782
H	-3.13400256	-3.13285861	0.32067432
H	-1.51498571	-4.04105149	2.24042065
H	-0.29156409	-3.03914083	3.03499181
H	-1.77838383	-2.29134513	2.45398914

13

E(RmPW+HF-B95) = -1433.8492153000 au

O	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.33456452
C	1.39884354	0.00000000	1.90034158
C	2.13435978	1.14940194	1.28710262
C	2.09508500	1.13535490	-0.03621184
C	1.29826835	-0.00212983	-0.58448653
O	-1.00785780	-0.01188066	1.96116878
C	2.78219767	2.05173182	-0.95055646
O	2.76163913	1.92848329	-2.14161547
O	3.43004320	3.01144817	-0.31607012
C	4.13608544	3.91959659	-1.14625208
H	1.35228088	0.02470997	2.97962177
H	2.65404412	1.88824370	1.87057156
H	1.16349338	0.05366154	-1.65459985
H	4.61399385	4.62061481	-0.47766737
H	4.87478683	3.39082649	-1.73746935
H	3.45059112	4.43365334	-1.81019552
C	3.42911517	-1.36399750	-0.58639078
C	4.23697601	-1.41070891	0.54052092
N	3.50219672	-1.26863983	1.69488214
C	2.09086724	-1.27918498	1.38234029
C	2.00939249	-1.28279848	-0.15721743
C	3.96014753	-1.39581352	-1.85346355
C	5.33143811	-1.50666795	-1.99583919
C	6.13429962	-1.59401491	-0.87087539
C	5.60805240	-1.55015217	0.40675420
C	3.93535084	-1.82052495	2.94636806
Cl	1.05661821	-2.68766560	-0.76003451
H	1.59940433	-2.15759011	1.79334377
H	3.31537360	-1.35220402	-2.71646109
H	5.77255512	-1.53766790	-2.97727485
H	7.20063905	-1.69862454	-0.99032413
H	6.25239175	-1.61645555	1.26682931
H	4.94728254	-1.49716190	3.16267803
H	3.30008061	-1.44764827	3.74285476
H	3.90493138	-2.91210080	2.95685734

14

E(RmPW+HF-B95) = -1433.8482384600 au

O	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.33426745
C	1.39605298	0.00000000	1.90041524
C	2.15015759	1.12033502	1.27153376
C	2.11574803	1.08825011	-0.05200963
C	1.30174269	-0.04216834	-0.58274794

O	-1.00653193	-0.02353535	1.96394896
C	2.78067819	2.01879432	-0.97007692
O	2.69534681	1.94405151	-2.16145283
O	3.48023651	2.94096435	-0.33330855
C	4.15149148	3.87661924	-1.16184244
H	1.35085602	0.04664243	2.97913054
H	2.67793115	1.86030726	1.84712912
H	1.16827133	-0.00383892	-1.65398147
H	4.67547755	4.54198588	-0.49136276
H	4.84936792	3.36683012	-1.81592493
H	3.43745325	4.42735005	-1.76335824
C	1.05876291	-2.54804181	-0.37346725
C	0.73110993	-3.12574603	0.84582902
N	1.38779368	-2.50579635	1.87497785
C	2.05370114	-1.32154135	1.41179476
C	1.92721015	-1.36788943	-0.12532339
C	0.56062816	-3.03994664	-1.55446703
C	-0.29017196	-4.13027424	-1.51593630
C	-0.63171083	-4.69195854	-0.29735787
C	-0.13727228	-4.20283092	0.89725409
C	1.05923741	-2.68171450	3.25652346
Cl	3.52620955	-1.52179902	-0.92889620
H	3.09272006	-1.30879266	1.72502161
H	0.83391388	-2.58518287	-2.49354471
H	-0.69198226	-4.53591887	-2.42849366
H	-1.30538704	-5.53332711	-0.27473929
H	-0.42279437	-4.64947765	1.83424722
H	0.94242850	-3.73783234	3.47510099
H	1.87633537	-2.31300768	3.86889478
H	0.14273080	-2.16068148	3.54051141

TS2-1
E(RmPW+HF-B95) = -1433.7828342800 au
1 imaginary frequency: -583.0 cm^{-1}

O	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.21596446
C	1.67998996	0.00000000	1.83071061
C	2.16225750	1.21974339	1.34157269
C	2.27759328	1.38688119	-0.02561389
C	1.97449279	0.28687556	-0.79451778
O	-0.77199605	-0.05771165	2.12284604
C	2.38004708	2.69989474	-0.67949456
O	2.26543401	2.86799943	-1.85831893
O	2.62307584	3.66845756	0.18629270
C	2.74819480	4.96848244	-0.36920204
H	1.57325963	-0.07319143	2.90136054
H	2.23070143	2.08003412	1.98737882
H	1.71994247	0.42011701	-1.83435457

H	2.94337831	5.62776519	0.46382034
H	3.56778083	4.99626722	-1.07779423
H	1.83135984	5.25118610	-0.87294823
C	1.61082668	-2.21342721	-0.96406315
C	0.98540264	-2.93428272	0.04349961
N	1.18182918	-2.34717193	1.26307191
C	2.14562508	-1.27848568	1.16129407
C	2.34630922	-1.08265778	-0.34677447
C	1.50244088	-2.57408734	-2.28382440
C	0.75711046	-3.69305867	-2.60793836
C	0.14823773	-4.42393317	-1.60181576
C	0.25327680	-4.06657201	-0.27058774
C	0.93206238	-2.97361760	2.52359834
Cl	4.11756244	-1.15854776	-0.77524803
H	3.09348167	-1.56963261	1.61438727
H	2.00810038	-2.00621371	-3.04906247
H	0.65909181	-4.00061588	-3.63475719
H	-0.42313635	-5.30119272	-1.85906522
H	-0.22881870	-4.65274116	0.49259359
H	0.68645393	-2.21715797	3.26272173
H	0.06885628	-3.62245446	2.43866885
H	1.78117974	-3.56203446	2.87697599

17

E(RmPW+HF-B95) = -1245.2866019500 au

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.32455926
C	1.24941258	0.00000000	2.06881156
C	2.41529951	-0.21620538	1.46556925
C	1.26808532	0.19097370	3.53595795
O	2.25554590	0.18073371	4.21150359
O	0.05300503	0.37898911	4.02774903
C	-0.01306258	0.57168948	5.43026298
H	-0.92675542	-0.02963623	-0.54925305
H	-0.91900294	-0.01724264	1.88389347
H	3.32602864	-0.25711730	2.04073870
H	-1.05805233	0.72008998	5.66082268
H	0.37179706	-0.29927333	5.94837891
H	0.56882661	1.43982654	5.71780316
C	3.59875973	0.39879090	-0.61127124
C	3.00915905	1.47529325	-1.25916778
N	1.63779997	1.43814950	-1.13176542
C	1.27294048	0.06872004	-0.76976074
C	2.50678549	-0.41799250	-0.00095987
C	4.96175450	0.25425034	-0.55344478
C	5.75687906	1.19854928	-1.18228991
C	5.16988844	2.26005217	-1.84665066
C	3.79517063	2.41281389	-1.90379764

C	0.80901251	2.11049678	-2.08926819
Cl	2.75221317	-2.19262482	-0.25753307
H	1.19277999	-0.53581415	-1.67776903
H	5.39943598	-0.59325683	-0.05024501
H	6.82893199	1.10063543	-1.16320756
H	5.79556306	2.98478409	-2.34218939
H	3.35793117	3.24096033	-2.43516280
H	-0.22440606	2.06963241	-1.76353701
H	1.08936625	3.15647895	-2.14576384
H	0.88239412	1.67354719	-3.08952375

TS2-2
E(RmPW+HF-B95) = -1245.2640598600 au
1 imaginary frequency: -85.1 cm^{-1}

O	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.34280382
C	1.39456413	0.00000000	1.93207524
C	2.12240081	1.14541154	1.28973751
C	2.12369849	1.08828303	-0.03141215
C	1.32288455	-0.04285445	-0.58495527
O	-1.01119088	0.01026119	1.96091928
C	2.83009668	1.98779754	-0.95378849
O	2.72649076	1.90937869	-2.14312120
O	3.56264695	2.87641539	-0.31966545
C	4.33443231	3.73295706	-1.14695381
H	1.34602357	0.04907741	3.00965578
H	2.64296544	1.89011289	1.86410336
H	1.20271686	-0.00984768	-1.65591865
H	4.87461437	4.38291866	-0.47451858
H	5.02274994	3.14688878	-1.74398807
H	3.68879822	4.30930799	-1.79983151
C	1.63019812	-2.63122088	-0.36368348
C	1.73507822	-3.37777078	0.85569478
N	1.91511989	-2.56417059	1.88902562
C	2.14180725	-1.23931123	1.39263780
C	1.82247874	-1.32858166	-0.02627342
C	1.33252282	-3.28441407	-1.58342209
C	1.20260016	-4.62795605	-1.56717533
C	1.35976923	-5.35882480	-0.35693778
C	1.62530015	-4.77679157	0.84191397
C	2.27963038	-2.97356367	3.22120011
Cl	4.90360468	-0.77552062	-0.08834180
H	3.23290579	-1.03698481	1.41095884
H	1.24428204	-2.71431282	-2.49208326
H	0.99325670	-5.16842634	-2.47356759
H	1.26398537	-6.43168063	-0.39918744
H	1.74462273	-5.36332877	1.73518287
H	1.63663091	-3.78521784	3.53948800

H	3.31854386	-3.28728984	3.26515430
H	2.13089349	-2.14011340	3.89533831

TS3-1
E(RmPW+HF-B95) = -1433.7966340900 au
1 imaginary frequency: -140.3 cm^{-1}

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.32922161
C	1.23603969	0.00000000	2.08338262
C	2.43942244	0.04618954	1.48412373
C	1.22262111	0.00676371	3.56518640
O	2.20269871	0.09371422	4.24411815
O	-0.00180586	-0.09165624	4.05306559
C	-0.09333246	-0.10378680	5.46881496
H	-0.92092720	-0.03418011	-0.55807334
H	-0.92411434	0.00667407	1.87892296
H	3.33670433	0.12150820	2.07241463
H	-1.14583386	-0.18727095	5.69669249
H	0.45328973	-0.94871699	5.87118010
H	0.31627402	0.81220504	5.87882002
C	3.37049638	0.86481506	-0.72915471
C	2.73473043	1.07550727	-1.97447065
N	1.49242592	0.57615689	-1.97156204
C	1.28005144	-0.14532066	-0.73817166
C	2.48955982	0.13463103	0.06670908
C	4.65381978	1.36835915	-0.48214953
C	5.28734132	2.04203901	-1.47915039
C	4.66075643	2.21239801	-2.72988654
C	3.40930067	1.73855568	-3.00471045
C	0.69671521	0.34869212	-3.14478351
Cl	3.49259901	-2.30691294	-0.06264489
H	1.35595666	-1.21766980	-0.97077293
H	5.12940223	1.19469038	0.46810037
H	6.27880115	2.43279819	-1.33062247
H	5.19626048	2.73658093	-3.50498198
H	2.96322713	1.87755461	-3.97357332
H	-0.32755317	0.15539215	-2.85024294
H	0.69926530	1.23767746	-3.76514903
H	1.06171116	-0.49547234	-3.72633805

18
E(RmPW+HF-B95) = -972.9571669000 au

O	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.32752365
C	1.41504268	0.00000000	1.92483402
C	2.07713716	1.19309604	1.27768725

C	2.05615578	1.14166385	-0.04440594
C	1.33530524	-0.06809349	-0.57991726
O	-0.99962822	0.01288455	1.96973804
C	2.60148517	2.13973091	-0.96722176
O	2.51347093	2.05320222	-2.15858190
O	3.20171681	3.13878042	-0.34276170
C	3.74744405	4.14112712	-1.18455234
H	1.35721589	0.04097941	3.00160929
H	2.47911624	2.00702434	1.85398052
H	1.20159542	-0.03868789	-1.64959451
H	4.17720031	4.87986309	-0.52385061
H	4.50950560	3.71803170	-1.82909342
H	2.97029986	4.58356811	-1.79712209
C	2.53144953	-2.53356543	-0.40383419
C	2.85413109	-3.18414834	0.80637089
N	2.51826904	-2.36959525	1.85964086
C	2.01703749	-1.22863028	1.33106035
C	1.99439326	-1.27723881	-0.01937134
C	2.78720410	-3.18791281	-1.60571012
C	3.34795615	-4.44163775	-1.57364329
C	3.66475289	-5.06492803	-0.36549052
C	3.42384308	-4.44591272	0.83817574
C	2.70454123	-2.69482874	3.24455748
H	2.55041162	-2.71744375	-2.54593166
H	3.54884914	-4.95674496	-2.49857111
H	4.10450078	-6.04847692	-0.37693880
H	3.66650742	-4.92555143	1.77248710
H	3.75549498	-2.86286604	3.46138792
H	2.35271289	-1.87429421	3.85583819
H	2.14190564	-3.58596644	3.50605722

TS3-2
E(RmPW+HF-B95) = -972.9331623170 au
1 imaginary frequency: -506.3 cm^{-1}

O	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.24372511
C	1.54307462	0.00000000	1.92489606
C	2.11558553	1.19958460	1.31484153
C	2.24009908	1.16226252	-0.01582605
C	1.83604167	-0.07790592	-0.64769788
O	-0.88385343	-0.00533062	2.05633066
C	2.58110789	2.30637116	-0.86709469
O	2.54152885	2.27711997	-2.06381937
O	2.93813772	3.36928200	-0.16685876
C	3.27259105	4.51703258	-0.92964380
H	1.40364022	0.03280134	2.99292781
H	2.26912542	2.09798624	1.88615212
H	1.64114431	-0.04837211	-1.70647050

H	4.09730810	4.29804280	-1.59805274
H	2.41929070	4.84343793	-1.51298051
H	3.55460091	5.27533112	-0.21383095
C	2.42241994	-2.63677054	-0.36738893
C	2.42484372	-3.34220952	0.84467880
N	2.19530786	-2.45622443	1.88133492
C	2.09180370	-1.22228633	1.36000829
C	2.23496698	-1.26563388	-0.01019697
C	2.62148625	-3.32544342	-1.55478454
C	2.81052761	-4.68764648	-1.50380584
C	2.81952058	-5.36929739	-0.28928200
C	2.63198302	-4.70739653	0.90389165
C	2.04823243	-2.83729858	3.25879583
H	2.62625746	-2.80509883	-2.49827394
H	2.95659776	-5.23899497	-2.41772889
H	2.97292463	-6.43562918	-0.28261651
H	2.63384827	-5.23658213	1.84228074
H	2.02106050	-1.94970183	3.87606757
H	1.12959935	-3.39673207	3.40653723
H	2.89217645	-3.44612895	3.56650785

12a

E(RmPW+HF-B95) = -784.4734955360 au

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.37323980
C	1.19232473	0.00000000	2.09969527
C	2.41176332	-0.00239407	1.44855869
C	1.20266634	-0.00087970	3.56912887
O	2.19496587	-0.00281884	4.24304843
O	-0.01897529	0.00110579	4.09240757
C	-0.07688985	0.00053891	5.50578334
H	-0.92812121	-0.00801836	-0.54547918
H	-0.93325421	-0.00295276	1.90834692
H	3.31635456	-0.00586792	2.03428360
H	-1.12742173	0.00127676	5.75996705
H	0.40890978	-0.88239795	5.90588022
H	0.41023931	0.88240859	5.90664369
C	3.49076858	-0.00956127	-0.90519373
C	2.86402010	-0.00587317	-2.15733932
N	1.50141064	0.01516177	-1.98535521
C	1.22697481	0.00440019	-0.64897607
C	2.43665188	-0.00231711	0.07001815
C	4.87423328	-0.02085996	-0.83155754
C	5.60279598	-0.03268914	-2.00040871
C	4.96361911	-0.03488558	-3.23660913
C	3.58935417	-0.02313138	-3.33616507
C	0.54651588	-0.00950002	-3.05279399
H	5.37044687	-0.02246683	0.12551326

H	6.67921708	-0.04293132	-1.96032653
H	5.55582635	-0.04885866	-4.13695311
H	3.10353290	-0.03236400	-4.29758959
H	-0.41920246	0.30887093	-2.68223449
H	0.84852051	0.68080298	-3.83375952
H	0.44881212	-1.00493591	-3.47987216