Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

SUPPORTING INFORMATION

Understanding the Polar Mechanism of the Ene Reaction.

A DFT Study.

Luis R. Domingo[1]*, Maria J. Aurell[1] and Patricia Pérez[2]

[1] Universidad de Valencia, Departamento de Química Orgánica,

Dr. Moliner 50, E-46100 Burjassot, Valencia, Spain.

[2] Universidad Andrés Bello, Facultad de Ciencias Exactas,

Departamento de Ciencias Químicas, Laboratorio de Química Teórica,

Av. República 275, 8370146 Santiago, Chile.

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*ELF topological analysis along the N-ene reaction between propene **1** and ethylene **11**, the P-ene reaction between propene **1** and formaldehyde **16**, and the H-ene reaction between propene **1** and BF_3:formaldehyde complex **22**. A topological characterisation of the C−C bond formation and the hydrogen transfer process.*

A great deal of theoretical work has recently shown that the ELF topological analysis along a reaction path is a valuable tool to understand the bonding changes along the reaction path, and then to characterise the molecular mechanism. 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 basins and valence basins. The latter are characterised by the synaptic order, i.e. the number of atomic valence shells in which they participate. Thus, there are monosynaptic, disynaptic, trisynaptic basins and so on. Monosynaptic basins, labelled V(A), correspond to the lone pairs or non-bonding regions, while disynaptic basins connect the core of two nuclei A and B and, thus, correspond to a bonding region between A and B and are labelled V(A,B). This description recovers the Lewis bonding model, providing a very suggestive graphical representation of the molecular system.

A number of ELF topological analyses of bonding changes along the intrinsic reaction coordinates (IRC) associated with non-polar and polar organic reactions have shown that the C−C single bond formation begins in the short Cx-Cy 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. This behaviour indicates that C−C bond formation takes place *via* a C-to-C *pseudodiradical* coupling between the most nucleophilic and electrophilic centres of the reagents, which have monosynaptic basins with some electron density. Interestingly, the electron-density changes demanded for the C−C bond formation are facilitated by the global electron density transfer (GEDT) that takes place from the nucleophile to the electrophile along the polar process.

In the present work, a ELF topological analyses along the IRCs of the N-ene reaction between propene **1** and ethylene **11**, the P-ene reaction between propene **1** formaldehyde **16**, and the H-ene reaction between propene **1** and the BF_3:formaldehyde complex **22** are performed in order to characterise the bond breaking/ bond formation processes in these reactions, and then to establish the molecular mechanism of these ene reactions. The *N* populations of the most significant ELF valence basins at specific points along the two IRCs are displayed in Tables S1 and S2. The attractor positions and atom numbering for the most relevant points are shown in Figure S1 and S2, respectively.

Along the N-ene reaction between propene **1** and ethylene **11**, at **P11**, d(C1−C2) = 2.907 Å and d(C1−H) = 1.090 Å, ELF attractor schematic picture of the separated reagents of the reaction shown; two disynaptic basins associated with the C−C double bond of the ethylene fragment, V(C2,C3) and V'(C2,C3), integrating to 3.37e, and two disynaptic basins associated with the C−C double bond of the propene fragment, V(C1,C4) and V'(C1,C4), integrating 3.72e (see Figure S1a). Additionally, one disynaptic basin associated with the C−C single bond of propene, whose population integrates 2.0e, and other disynaptic ones can be associated with the C−H single bond of propene which integrates1.96e, can be observed.

At **P12**, d(C1−C2) = 2.068 Å and d(C1−H) = 1.295 Å, which corresponds to the TS of this ene reaction, some interesting bonding changes are found. Here, the two disynaptic basins present in **P11** and associated with the C2−C3 double bond of the ethylene moiety are merged into each other to become one (i.e. V(C2,C3)), with an electronic population of 2.63e. The propene fragment also shows that the two disynaptic basins found in the above phase have merged into one (i.e. V(C1,C4)), with a population of 3.17e. The most interesting change observed at this point is the formation of two monosynaptic basins in the ethylene moiety, i.e. V(C2) an V(C3) with an electronic population of 0.25e and 0.46e, respectively. According to previous results, the ethylenic fragment has acquired the *pseudodiradical* character needed to create the first C−C single bond in a further phase of the reaction. The electronic population of the V(C5,H) is 1.64e, indicating that hydrogen is still bonded to the terminal carbon of propene (see Figure S1b). Interestingly, the ELF picture of the ethylene framework is similar to that found in the TS associated with the non-polar Diels-Alder reactions between cyclopentadiene and ethylene.

At **P13,** d(C1−C2) = 2.043 Å and d(C1−H) = 1.419 Å, some relevant bonding changes are observed. The electronic population of the V(C2) monosynaptic basin on the ethylene fragment is progressing to reach 0.37e, while the propene fragment contains at this moment two monosynaptic basins in each one of the terminal carbon atoms, i.e V(C1) and V(C5) integrating 0.44e and 0.47e, respectively (see Figure S1c). An interesting change at this point of the IRC can be appreciated as the hydrogen atom has already been transferred from the C-propene to C-ethylenic moieties, i.e. a new V(C3,H) disynaptic basin, showing an electronic population of 1.64e, appears at **P13**.

At **P14**, d(C1−C2) = 2.015 Å and d(C1−H) = 1.542 Å, the second significant bonding change along the IRC is observed: V(C1) and V(C2) monosynaptic attractors are merged into one disynaptic attractor to form the new V(C1,C2) disynaptic basin, which is associated with the formation of the new C1−C2 single bond in the ene reaction, whose electronic population is 1.00e. The electronic population of the V(C2,C3) disynaptic basin has decreased to 2.23e, whereas the population of the V(C4,C5) one has increased to 3.25e. Finally, the electronic population associated with the V(C3,H) disynaptic basin has slightly increased to 1.74e (see Figure S1d).

Finally, in **P15**, d(C1−C2) = 1.580 Å and d(C1−H) = 2.105 Å, it may be observed that the population of the V(C2,C3) disynaptic basin has diminished to 1.87e in agreement with the formation of a C−C single bond in the ethylenic fragment, while two disynaptic basins appears, V(C4,C5) and V’(C4,C5), integrating a total electronic population of 3.69e, which is consistent with the C−C double bond character for the propene moiety. On the other hand, the population of the V(C1,C2) disynaptic basin has increased to 1.76e and the corresponding V(C3, H) disynaptic basin is 2.00e, in strong agreement with the C−H single bond formation for this entire processes (see Figure S1e). It is worth mentioning that along this N-ene reaction, the C1−C2 and C3−H bond formation processes occur without any appreciable GEDT.

Likewise, the schematic picture of the valence basins of selected points along the IRC of the P-ene reaction between propene **1** and formaldehyde **16** is displayed in Figure S2a-e and the electronic populations are shown in Table S2. At **P21**, d(C1-C2) = 2.460 Å and d(C1-H) = 1.419 Å, one V(C2,O3) disynaptic basin of the formaldehyde fragment which is associated with the C−O bond, whose electronic population is 2.36e, and two monosynaptic V(O3) and V´(O3) basins integrating 2.63e and 2.58e are observed. Thereafter, V(O3) will represent both basins. In this case the total population is 5.21e. This scenario indicates a very polarized C−O double bond, in which a significant electron-density population of the C−O double bond is located in the oxygen lone pairs. Similarly, two disynaptic basins, i.e. V(C1,C4) and V'(C1,C4), with a total integration of 3.33e, one V(C4,C5) disynaptic basin, which integrates 2.02e, and one V(C5,H) disynaptic basin integrating an electronic population of 1.94e and associated with the hydrogen atom that is being transferred in this processes can be observed (see Figure S2a).

P22, d(C1−C2) = 1.982 Å and d(C1−H) = 1.175 Å, shows a scenario very similar to that shown in Figure S2b for the N-ene reaction between propene **1** and ethylene **11**: only one V(C2) monosynaptic basin on the formaldehyde fragment is observed, integrating a population of 0.16e, and the corresponding V(O3) monosynaptic basins with a total population of 5.55e. At this point, the formaldehyde fragment shows a *pseudoradical* character to form subsequently the C−C single bond with the propene fragment. The population of the V(C1,C4) disynaptic basin is slightly decreased to 3.19e as well as the electronic population of the V(C5,H) one, reaching 1.73.e. The latter depopulation is indicative of a weakening of the electronic population in the C−H bond along the reaction progress (see Figure S2b).

At **P23**, d(C1−C2) = 1.959 Å and d(C1−H) = 1.218 Å, the population of the V(C2,O3) disynaptic basin has decreased to 1.89e, whereas the population of the V(O3) monosynaptic basins are narrowly increased to 5.60e. On the other hand, the population of the V(C1,C4) and V(C5,H) disynaptic basins has decreased to 2.76e and 1.66e, respectively. The population of de V(C4,C5) disynaptic basin has increased to 2.30e. One of most remarkable changes in **P23** is the disappearance of the V(C2) monosynaptic basin and the creation of the new V(C1,C2) disynaptic basin, whose population reaches 0.65e, which is associated with the formation of the new C−C single bond in this ene reaction (see Figure S2c). Interestingly, an elevate amount of electron density has been transferred at this point of the IRC, 0.31e.

At **P24**, d(C1−C2) = 1.946 Å and d(C1−H) = 1.260 Å, which corresponds to the TS of this P-ene reaction, the electronic population of the V(C1,C2) disynaptic basin associated with the new C−C single bond has increased to 0.76e whereas the electronic population of V(C2,O3), V(C1,C4) and V(O3) basins has moderately decreased to 1.82e, 2.67e and 5.59e, respectively. The electronic population of the V(C4,C5) disynaptic basin has increased to 2.34e, being associated to the new C−C double bond of the propene fragment. The electronic population of the V(C5,H) disynaptic basin associated to the hydrogen to be transferred has decreased to 1.60e. At this point, the system is preparing to transfer the hydrogen atom from the propene to the formaldehyde fragment (see Figure S2d). Note that at this point of the IRC the GEDT reaches its maximum value, 0.32e.

Finally, at **P25**, d(C1−C2) = 1.581 Å and d(C1−H) = 1.915 Å, a split of the V(C4,C5) disynaptic basin into two disynaptic basins, V(C4,C5) and V'(C4,C5), integrating 1.62 and 1.76e, respectively, is observed. The electronic population of the V(C2,O3) disynaptic basin has diminished to 1.33e, while the electronic population of the V(C1,C2) and V(O3,H) disynaptic basin has increased to 1.79e and 1.73e, respectively. These behaviours are consistent with the formation of the C2−O and C4−C5 double bonds, and the C1-C2 and O3−H single bonds at the corresponding ene adduct (see Figure 8e).

The present ELF topological analysis along the IRC of both N-ene and P-ene reactions shows that the bonding changes along these one-step reactions are non-concerted. Just as in other organic reactions, the formation of the new C−C bond is achieved by the C-to-C coupling of two *pseudodiradical* centres formed at the two interacting carbon atoms. Interestingly, while in the unfavourable N-ene reaction the hydrogen transfer takes place before the formation of the new C−C single bond, in the P-ene reaction, the new C−C single bond is formed in the first stage of the reaction, while the hydrogen transfer process occurs in the second stage of the reaction after the formation of the C−C single bond has practically been completed. Consequently, the ELF topological analysis of bonding changes along the IRC of P-ene reactions suggests that they take place trough a *two-stage one-step* mechanism.

A more asynchronous and advanced TS is expected in H-ene reactions. For verification, an ELF topological analysis of the TS associated with the H-ene reaction between propene **1** and the BF_3:formaldehyde complex **22**, was performed. The *N* electronic populations of the most important basins are shown in Table S2 and the corresponding attractors can be found in Figure S3. It can clearly be seen that the TS representation is similar to that found at the TS of the P-ene reaction between propene **1** and formaldehyde **16** (see Figure S2d and Table S3) but in this case the TS is more advanced being found at d(C1−C2) = 1.682 Å, in agreement with the high electrophilic character of BF_3:formaldehyde complex **22** (ω = 2.32 eV). At this TS, the presence of the V(C1,C2) disynaptic basin, integrating 1.30e, indicates that the formation of the new C−C single bond has already begun, while the presence of the V(C5,H) disynaptic basin, integrating 1.65e, indicates that the hydrogen atom remains bonded to the propene framework. The high GEDT that takes place at the TS associated with this H-ene reaction, 0.42e, is noteworthy.

This result confirms, once again, that in P-ene and H-ene reactions, while the new C−C single bond is being formed in the first stage of the reaction, the hydrogen transfer process has not begun yet at this stage. In H-ene reactions, for example, the reaction between propene **1** and BF_3:formaldehyde complex **22,** it is expected that once the C−C bond has practically formed, the reaction progresses to the expected products through the hydrogen atom transfer process occurring at the end of the second stage of the reaction.

Table S1 Valence basin populations N calculated from the ELF of some selected points associated with the formation of the C1-C2 and C3-H single bonds along the N-ene reaction between propene **1** and ethylene **11**. Distances are given in Å, while the GEDT is given in e.

	P11	**P12** (TS)	**P13**	**P14**	**P15**
d(C1-C2)	2.907	2.068	2.043	2.015	1.580
d(C1-H)	1.090	1.295	1.419	1.542	2.105
GEDT	0.02	0.03	0.02	0.04	0.01
V(C2,C3)	1.70	2.63	2.41	2.23	1.87
V'(C2,C3)	1.67				
V(C2)		0.25	0.37		
V(C3)		0.46			
V(C1,C2)				1.00	1.76
V(C1,C4)	1.69	3.17	2.61	2.43	2.02
V'(C1,C4)	1.72				
V(C4,C5)	2.00	2.40	2.70	3.25	2.02
V'(C4,C5)					1.67
V(C5,H)	1.96	1.64			
V(C3,H)			1.64	1.74	2.00
V(C1)			0.44		
V(C5)			0.47		

Table S2. Valence basin populations *N* calculated from the ELF of some selected points associated with the formation of the C1-C2 and C3-H single bonds along the P-ene reaction between propene **1** and formaldehyde **16**. Distances are given in Å, while the GEDT is given in e.

	P21	**P22**	**P23**	**P24** (TS)	**P25**
d(C1-C2)	2.460	1.982	1.959	1.946	1.581
d(C1-H)	1.419	1.175	1.218	1.260	1.915
GEDT	0.06	0.18	0.31	0.32	0.05
V(C2,O3)	2.36	1.97	1.89	1.82	1.33
V(C2)		0.16			
V(O3)	5.21	5.55	5.60	5.59	4.65
V(C1,C2)			0.65	0.76	1.79
V(C1,C4)	1.74	3.19	2.76	2.67	2.04
V'(C1,C4)	1.59				
V(C5,H)	1.94	1.73	1.66	1.60	
V(O3,H)					1.73
V(C4,C5)	2.02	2.24	2.30	2.34	1.62
V'(C4,C5)					1.76

Table S3. Valence basin populations *N* calculated from the ELF of the TS of H-ene reaction between propene **1** and BF_3:formaldehyde complex **22**. Distances are given in Å, while the GEDT is given in e.

	TS
d(C1-C2)	1.682
d(C1-H)	1.171
GEDT	0.42
V(C2,O3)	1.56
V(C1)	
V(O3)	5.99
V(C1,C2)	1.30
V(C1,C4)	2.33
V'(C1,C4)	
V(C5,H)	1.65
V(O3,H)	
V(C4,C5)	2.27
V'(C4,C5)	

Table S4. MPWB1K/6-311G(d,p) Total electronic energies, in au, of the stationary points involved in the ene reactions of isobutene **10** with the twelve enophiles **11 - 22**.

	R	TS	P
10	-157.161850		
11	-78.552844	-235.659359	-235.759143
12	-193.098437	-350.205612	-350.301088
13	-153.787507	-310.901486	-310.970290
14	-169.750057	-326.864595	-326.946081
15	-306.401717	-463.519828	-463.519828
16	-114.472955	-271.596394	-271.665637
17	-451.513947	-608.648556	-608.709265
18	-901.841352	-1058.985527	-1059.048123
19	-788.540972	-945.689685	-945.749426
20	-141.088288	-298.239450	-298.290760
21	-173.554948	-330.715280	-330.764878
22	-439.042570	-596.206399	-596.250843

Table S5. MPWB1K/6-311G(d,p) Total electronic energies, in au, of the stationary points involved in the ene reactions of isobutene **10** with the p-substituted BF_3:benzaldehyde complexes **23** - **27**.

	X	R	TS	P
23	$N(CH_3)_2$	-803.992326	-961.125821	-961.164444
24	OCH_3	-784.560705	-941.699572	-941.738114
25	H	-670.055486	-827.199961	-827.238655
26	CO_2Me	-897.892822	-1055.040170	-1055.07874
27	NO_2	-874.518385	-1031.669329	-1031.70775

Table S6. MPWB1K/6-311G(d,p) Total electronic energies, in au, of the stationary points involved in the ene reactions of the propene derivatives **28-31** with trifluoroacetaldehyde **17**.

	ERG	R	TS	P
28	OAc	-345.699911	-797.184987	-797.25457
29	SCH_3	-555.408256	-1006.900248	-1006.965814
30	OCH_3	-232.355994	-683.856826	-683.920429
31	$N(CH_3)_2$	-251.786618	-703.296959	-703.342111

Table S7. MPWB1K/6-311G(d,p) Total electronic energies, in au, in DCM of the stationary points involved in the ene reactions of isobutene **10** with the p-substituted BF_3:benzaldehyde complexes **23** - **27**.

	X	R	TS	P
23	$N(CH_3)_2$	-804.013544	-961.147771	-961.176552
24	OCH_3	-784.578923	-941.721794	-941.750404
25	H	-670.070889	-827.220744	-827.249440
26	CO_2Me	-897.909756	-1055.064037	-1055.092365
27	NO_2	-874.536343	-1031.694434	-1031.722431

The total electronic energies of isobutene **10** is -157.163162 au.

Table S8. MPWB1K/6-311G(d,p) Lengths of the C−C and O−H forming bonds and the C−H breaking bond, in Angstroms, at the TSs associated with the ene reactions of isobutene **10** with the BF_3:p-substituted benzaldehyde complexes **23** - **27**, in gas phase and in DCM.

	X	C−C	C−H	O−H	C−C	C−H	O−H
			In gas phase			In DCM	
23	$N(CH_3)_2$	1.641	1.203	1.553	1.590	1.260	1.448
24	OCH_3	1.638	1.199	1.566	1.589	1.259	1.450
25	H	1.636	1.195	1.579	1.587	1.259	1.453
26	CO_2Me	1.633	1.195	1.581	1.586	1.260	1.452
27	NO_2	1.631	1.192	1.593	1.584	1.260	1.455

Figure S1. Attractor positions of the ELF for relevant points along the IRC for the N-ene reaction between propene **1** and ethylene **11**.

a. P11	b. P12	c. P13	d. P14	e. P15

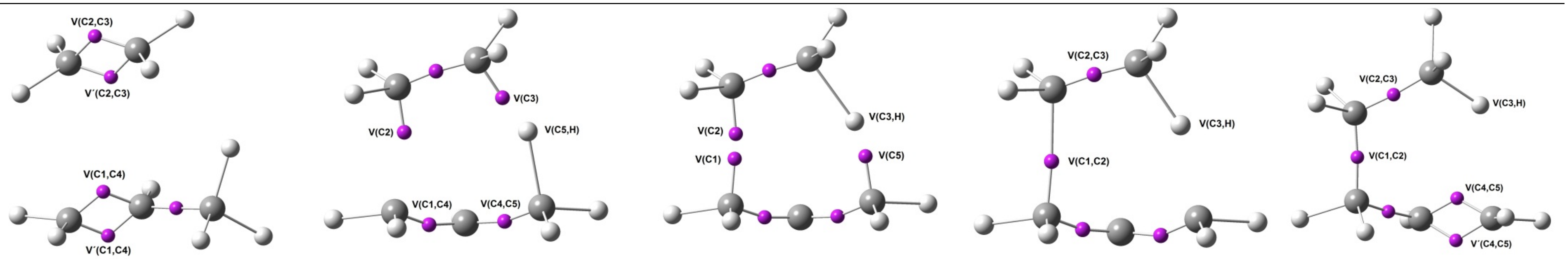


Figure S2. Attractor positions of the ELF for relevant points along the IRC for the P-ene reaction between propene **1** and formaldehyde **16**.

a. P21	b. P22	c. P23	d. P24	e. P25

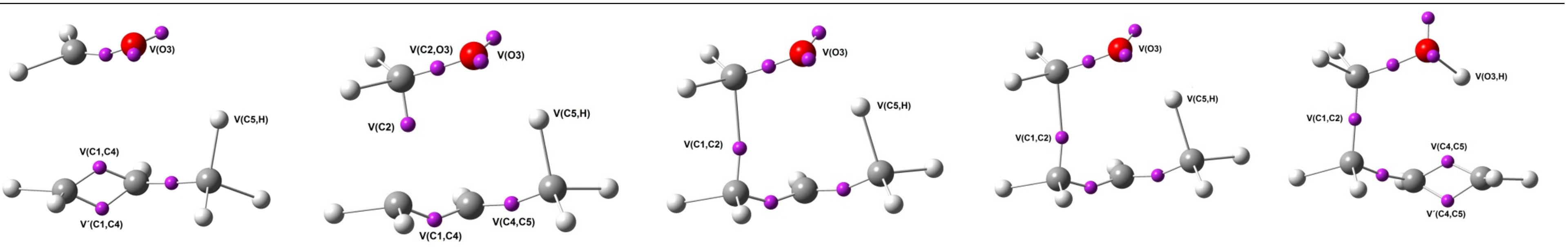
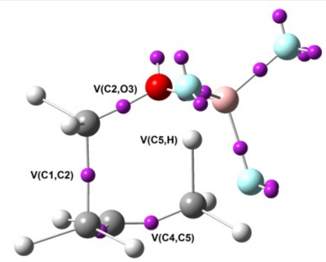


Figure S3. Attractor positions of the ELF for the TS associated with the H-ene reaction between propene **1** and BF_3:formaldehyde complex **22**.

TS


MPWB1K/6-311G(d,p) computed total energies, unique imaginary frequency, and cartesian coordinates of the transition state structures involved in the ene reactions.

TS-11

E(MPWB1K/6-311G(d,p)) = -235.659359 a.u.
unique imaginary frequency: -1223.3 cm^{-1}

C	-1.52308200	-0.75874400	-0.21286700
C	0.13530900	-0.89987600	0.95080600
H	-0.35285900	-0.62434700	1.87283500
H	0.35173700	-1.95315700	0.85554900
C	0.95897800	0.02753800	0.35248100
C	0.57158000	1.37287900	0.48573900
H	-0.56394600	1.25925400	-0.10439700
H	0.22293500	1.69088000	1.45975300
H	1.15137800	2.12814500	-0.02784600
H	-2.11914300	-1.24940100	0.53944000
H	-1.18461200	-1.41663100	-0.99822100
C	-1.81511200	0.56161900	-0.54060600
H	-1.72558300	0.88076700	-1.56766700
H	-2.54697400	1.10032400	0.04150600
C	1.79671500	-0.37090600	-0.81496900
H	2.09106600	-1.41383300	-0.76041600
H	1.23570500	-0.23286700	-1.74308000
H	2.69397300	0.23580000	-0.89095900

TS-12

E(MPWB1K/6-311G(d,p)) = -350.205612 a.u.
unique imaginary frequency: -956.9 cm^{-1}

C	1.10324200	0.00507400	-0.20346800
O	0.81990600	-0.89544700	-1.06226000
C	-0.26945900	-0.05797500	1.20119600
H	0.09398500	-0.96337200	1.66191500
H	-0.10673600	0.84322900	1.77284100
C	-1.39926300	-0.15792700	0.40938200
C	-1.57485200	-1.34666400	-0.32062400
H	-0.47053500	-1.18939900	-0.93830600
H	-1.34914900	-2.27412000	0.18796700
H	-2.41494800	-1.40457200	-0.99781100
C	1.03462300	1.43537200	-0.68895500
C	-2.18587300	1.05433100	0.05240400
H	-3.16902700	0.99307500	0.51533700
H	-1.70666300	1.96502700	0.39425200
H	-2.34444800	1.11662600	-1.02153400
C	2.29327600	-0.29281600	0.68092400
H	2.35072200	0.36247500	1.54501700
H	3.19536000	-0.15547900	0.08751900
H	1.10095500	2.15906200	0.11840600
H	2.26059200	-1.32671400	1.00440700
H	1.86942900	1.60187100	-1.36722100
H	0.12104100	1.59949800	-1.24986700

TS-13

E(MPWB1K/6-311G(d,p)) = -310.9014859 a.u.
unique imaginary frequency: -1249.7 cm^{-1}

C	-1.15224100	-0.06865700	-0.50112300
O	-0.92835200	1.17271300	-0.66380400
C	0.06853300	-0.79478300	0.80414000
H	-0.41362700	-0.39251400	1.68247900
H	-0.03382600	-1.86147800	0.67502100
C	1.22332800	-0.17211100	0.36623200
C	1.31769100	1.21955300	0.55671300
H	0.30252400	1.43118400	-0.15745100
H	0.97736200	1.60782300	1.50694400
H	2.18639000	1.72405000	0.15809500
C	2.10141600	-0.83615800	-0.63416600
H	3.11215600	-0.92229800	-0.24184100
H	1.74790500	-1.82846900	-0.89105700
H	2.16221900	-0.23750900	-1.54054100
C	-2.45405300	-0.44665300	0.15985200
H	-2.49215100	-1.49610400	0.43661800
H	-3.26125200	-0.24540400	-0.54043600
H	-2.61287500	0.17089400	1.03760100
H	-0.87604900	-0.73902900	-1.32488500

TS-14

E(MPWB1K/6-311G(d,p)) = -326.86459479 a.u.
unique imaginary frequency: -1032.8 cm^{-1}

O	0.80444800	0.76561600	1.05154800
C	-0.11516600	-1.03413100	-0.57406800
H	0.46218100	-0.96446300	-1.48287500
H	-0.24504300	-2.04132700	-0.21199700
C	-1.18048900	-0.14476300	-0.44113700
C	-0.91276200	1.19931200	-0.77944700
H	-0.10658700	1.37539300	0.13088500
H	-0.30466700	1.36348000	-1.66063200
H	-1.71471200	1.91621000	-0.67102800
C	-2.25597600	-0.44324200	0.53910700
H	-1.89133000	-0.18714400	1.53577100
H	-3.14939900	0.14298200	0.35119100
H	-2.51578500	-1.49655500	0.54293100
C	2.32510700	-0.15785500	-0.29471400
H	3.12761700	0.13820800	0.37202800
H	2.58508400	-1.08900800	-0.78703700
H	2.17734100	0.63616700	-1.02703500
N	1.13934800	-0.34782700	0.54242500

TS-15

E(MPWB1K/6-311G(d,p)) = -463.519828 a.u.
unique imaginary frequency: -795.3 cm^{-1}

C	-0.46765200	0.20303600	0.53124800
O	-0.21639700	-0.77973200	1.30530100
C	0.53522700	-0.02506400	-1.12041600
H	-0.00172800	-0.87615300	-1.51408200
H	0.36613300	0.90122100	-1.64667900

C	1.77428500	-0.27757400	-0.55048200
C	1.93157800	-1.49500500	0.13553500
H	1.00582800	-1.23410200	0.95639400
H	1.49983000	-2.37480900	-0.32269300
H	2.87165900	-1.67335900	0.63736500
C	-0.11733200	1.58923300	1.00461400
C	2.76223500	0.81857700	-0.36628900
H	3.61225500	0.64283700	-1.02321300
H	2.34297700	1.78852300	-0.60763800
H	3.14590100	0.83612900	0.65079200
H	0.89366200	1.60477400	1.39610500
H	-0.79124700	1.84752700	1.81765300
H	-0.23514700	2.33026800	0.22336700
C	-1.79294800	0.12316700	-0.20879100
O	-2.28839200	1.10468400	-0.68336900
C	-2.43902300	-1.22384500	-0.23927900
H	-1.72101300	-2.00344100	-0.46901900
H	-2.81200900	-1.44510600	0.75715800
H	-3.25701600	-1.21908200	-0.94781100

TS-16

E(MPWB1K/6-311G(d,p)) = -271.59639446 a.u.
unique imaginary frequency: -1140.0 cm^{-1}

C	-1.45605500	-0.65018700	-0.28162700
O	-1.70730000	0.56298300	-0.55565000
C	-0.04773600	-0.80708500	0.97140700
H	-0.56064900	-0.42312100	1.84003400
H	0.16046900	-1.86625600	0.99417600
C	0.84551700	0.03830000	0.33478000

C	0.53945500	1.41470500	0.33656600
H	-0.53752600	1.25002400	-0.26282400
H	0.18322500	1.83097700	1.26929000
H	1.19762400	2.07172300	-0.21436700
H	-2.15177400	-1.17377500	0.37807500
H	-1.06343200	-1.29805500	-1.07412200
C	1.81722400	-0.49941900	-0.65439100
H	1.72150800	-1.57249800	-0.77855200
H	1.68680600	-0.01771800	-1.62065200
H	2.83171600	-0.28305400	-0.32626600

TS-17

E(MPWB1K/6-311G(d,p)) = -608.648556 a.u.
unique imaginary frequency: -844.4 cm^{-1}

C	0.43777200	-0.96721200	0.53025200
O	0.06068300	-1.83934100	-0.30137200
C	-0.99111800	-0.11818000	1.33818200
H	-1.33276100	-0.98614000	1.88227500
H	-0.56940100	0.66256000	1.95143000
C	-1.74797800	0.24768900	0.22715700
C	-2.31430100	-0.81103300	-0.52368000
H	-1.26792500	-1.36167600	-0.75037000
H	-2.80480200	-1.58724900	0.04993700
H	-2.83876700	-0.54415700	-1.43003300
C	1.30045000	0.13913800	-0.05706300
F	0.82985100	0.54757100	-1.22685400
F	1.39165800	1.21261300	0.73373600
F	2.53518400	-0.29913300	-0.25130000
H	0.86368100	-1.30011400	1.48156700

C	-1.71179700	1.63007900	-0.30718200
H	-2.64874600	2.11883500	-0.04128500
H	-0.89578600	2.20746600	0.11105600
H	-1.63936300	1.63285900	-1.38983100

TS-18

E(MPWB1K/6-311G(d,p)) = -1058.985527 a.u.
unique imaginary frequency: -729.i cm^{-1}

C	-0.13239100	-0.18187200	0.25096400
O	-0.01985400	0.40998000	1.35856700
C	1.16594200	-0.50514200	-0.45810800
O	1.30327000	-1.34415800	-1.28330800
C	-1.11488900	-1.35908300	0.25345900
C	2.37513000	0.32740500	0.00779900
F	3.38984500	0.12856100	-0.80511800
F	2.09743600	1.62698400	0.00089800
F	2.73891000	-0.01834900	1.22330300
F	-1.56491100	-1.70406000	-0.94710900
F	-0.54285500	-2.42332400	0.78710300
F	-2.16748500	-1.04650200	0.99505200
C	-0.76792300	0.95437300	-1.11654600
H	0.11994900	1.56102200	-1.21708500
H	-0.97250800	0.30410800	-1.95210300
C	-1.83576000	1.55775100	-0.45105200
C	-1.50132400	2.41264900	0.62503200
H	-0.94504600	1.56564800	1.26996500
H	-0.66808900	3.08313200	0.45717100
H	-2.31784400	2.85332500	1.17828900
C	-3.23155900	1.11761500	-0.67686900

H	-3.77994400	1.04572300	0.25653700
H	-3.72434500	1.87562400	-1.28549900
H	-3.28131300	0.17287000	-1.20458000

TS-19

E(MPWB1K/6-311G(d,p)) = -945.689685 a.u.
unique imaginary frequency: -633.1 cm^{-1}

C	0.27416800	-0.16721000	-0.36817500
O	0.02151900	-0.56738400	-1.53154700
C	-0.79606300	-0.97558300	0.91761900
H	-0.33499900	-1.94989400	0.84985900
H	-0.60769400	-0.44793900	1.83856000
C	-2.06072200	-0.86651200	0.34081200
C	-2.28262600	-1.62087800	-0.84200100
H	-1.41349200	-1.12237800	-1.46815300
H	-1.93793800	-2.64690300	-0.81100900
H	-3.24208100	-1.50085200	-1.32443400
C	0.03789000	1.33649500	-0.15558000
F	-1.07740200	1.68973300	-0.77624000
F	-0.09149800	1.69407300	1.12116800
F	1.02827000	2.04520200	-0.66231000
C	-3.01907200	0.17538600	0.77019000
H	-3.81867700	-0.31311600	1.32698200
H	-2.55648800	0.91621500	1.41068300
H	-3.47342300	0.66495400	-0.08542600
C	1.63795100	-0.63957500	0.15922400
F	2.61327000	-0.06940800	-0.51964100
F	1.75285100	-1.94808400	0.01218300
F	1.82600800	-0.35748900	1.44514700

TS-20

E(MPWB1K/6-311G(d,p)) = -298,239450 a.u.
unique imaginary frequency: -368.2 cm^{-1}

C	-0.73353000	-1.10542100	-0.37502400
O	-1.41597000	-0.02525400	-0.74253000
C	0.33526400	-0.78701600	0.84545200
H	-0.32241400	-0.40726200	1.61963600
H	0.81529800	-1.72270900	1.10121700
C	1.18916700	0.19258600	0.27500200
C	0.63541300	1.47302200	0.05152300
H	-0.24693700	1.10981100	-0.62395000
H	0.01827300	1.85445900	0.86109300
H	1.26378500	2.20571300	-0.43289200
H	-1.35926000	-1.85441200	0.10678200
H	-0.17459500	-1.53799700	-1.20340900
B	-2.50082800	0.44578500	0.25507300
H	-3.12920000	1.30709700	-0.30228700
H	-1.92812100	0.89468600	1.24656000
H	-3.15378000	-0.52929900	0.55962300
C	2.49225000	-0.19123200	-0.29994300
H	2.74689700	0.40766200	-1.16761100
H	3.25290300	0.00160600	0.45874900
H	2.53766600	-1.24788500	-0.54069600

TS-21

E(MPWB1K/6-311G(d,p)) = -330.715280 a.u.

unique imaginary frequency: -248.cm^{-1}

C	-0.54627800	-0.80868000	-0.79072200
C	0.89314100	-1.30049000	0.23229200
H	0.38372600	-1.61261100	1.13302600
H	1.30606300	-2.10552800	-0.35753200
C	1.60212600	-0.11360400	0.27696800
C	1.22481900	0.88382300	1.28044400
H	0.13650300	1.00707000	1.21764900
H	1.40805300	0.49961800	2.28219100
H	1.72102100	1.83752400	1.15826900
H	-0.88184300	-1.83216000	-0.89278500
C	2.63036200	0.20870300	-0.72209700
H	3.58748100	0.28306000	-0.20155000
H	2.72321200	-0.54014400	-1.49890800
H	2.46084900	1.19210600	-1.15639100
N	-1.41978800	0.02394100	-0.19459300
H	-0.10264300	-0.43089300	-1.69966700
C	-1.60371700	1.36615400	-0.70078300
H	-1.89881800	2.03074500	0.10404700
H	-0.67613200	1.73180000	-1.12806000
H	-2.37384500	1.39420600	-1.46989400
C	-2.47124800	-0.51303900	0.63867200
H	-2.15659700	-1.45785300	1.06764100
H	-2.69064700	0.17410000	1.44873900
H	-3.38309800	-0.67583100	0.06672900

TS-22

E(MPWB1K/6-311G(d,p)) = -596.206399 a.u.

unique imaginary frequency: -272.2 cm^{-1}

C	0.26204100	-1.24932800	-0.44586700
O	-0.47577800	-0.20825800	-0.87048300
C	1.26109800	-0.86688000	0.78327600
H	0.59839700	-0.58129900	1.58814300
H	1.84324300	-1.75474100	0.99675900
C	2.02119700	0.21750000	0.24697400
C	1.38176000	1.46714000	0.12590500
H	0.55506000	1.05371200	-0.59487800
H	0.72921800	1.74334000	0.94505800
H	1.94587200	2.27154000	-0.32170000
H	-0.35126400	-2.03002700	-0.00348500
H	0.86573600	-1.65486500	-1.25452900
B	-1.70952400	0.10593900	-0.04172500
F	-2.37542300	1.08361700	-0.70612700
F	-1.24346100	0.55855500	1.20503300
F	-2.41383100	-1.05980900	0.12046600
C	3.31628700	-0.04281800	-0.40332800
H	4.08522900	0.11289900	0.35637700
H	3.40542100	-1.06916000	-0.74291200
H	3.51706700	0.65001900	-1.21245400

TS-23

E(MPWB1K/6-311G(d,p)) = -961.125821 a.u.
unique imaginary frequency: -961.1 cm^{-1}

C	1.22016700	-0.09336800	-0.69492500
O	1.93204500	-0.60104200	0.34064400
C	1.69050300	1.44486600	-1.01860700

H	2.70631500	1.33633100	-1.37340800
H	1.01748900	1.83001000	-1.77338200
C	1.60537000	2.12929900	0.24158100
H	2.24348300	0.66313800	1.18850800
C	2.57297400	1.82018500	1.20324700
H	3.57906500	1.64304200	0.84249900
H	2.48444100	2.27362600	2.17815600
H	1.49408200	-0.59239700	-1.62230200
C	-0.25452500	-0.15989800	-0.45666700
C	-1.15202900	0.20491400	-1.44617100
C	-0.76883800	-0.59035900	0.75162000
C	-2.51125400	0.17064200	-1.23761100
H	-0.78709000	0.51052000	-2.41625600
C	-2.12748900	-0.63113700	0.97813900
H	-0.08680100	-0.92503800	1.51519700
C	-3.03721400	-0.23574000	-0.00598400
H	-3.16697900	0.44682400	-2.04370200
H	-2.48129200	-0.99166400	1.92748300
B	3.28710400	-1.20172400	-0.00226600
F	4.07404500	-0.14746400	-0.49013100
F	3.78167800	-1.68803000	1.16638300
F	3.09607900	-2.13932100	-0.98025500
N	-4.38749600	-0.25160600	0.22043200
C	-4.88738900	-0.88279200	1.40798000
H	-5.96689400	-0.80196900	1.42344500
H	-4.62061700	-1.94061400	1.46726500
H	-4.51025600	-0.38985900	2.30118500
C	-5.28369400	-0.05957400	-0.88296400
H	-5.13858400	0.91699300	-1.33983900
H	-5.16529600	-0.81801500	-1.66078500
H	-6.30330800	-0.09991000	-0.52129800
C	0.38622500	2.88346700	0.57650500

H	-0.49568200	2.37097800	0.19967600
H	0.29343800	3.07779900	1.63776600
H	0.44203000	3.83869700	0.05210700

TS-24

E(MPWB1K/6-311G(d,p)) = -941,699572 a.u.
unique imaginary frequency: -494.8 cm^{-1}

C	-0.89699800	-0.20562800	0.66231600
O	-1.67906100	-0.53599200	-0.39270000
C	-1.24675500	1.30245800	1.19627800
H	-2.25039500	1.21365200	1.58873600
H	-0.51701100	1.54783700	1.95681400
C	-1.17323700	2.13815000	0.02923500
H	-1.95012800	0.85299700	-1.06364100
C	-2.20362900	2.01497700	-0.90907000
H	-3.20000200	1.85080100	-0.51643500
H	-2.13250800	2.58686500	-1.82112800
H	-1.15315700	-0.80691000	1.53195600
C	0.55995700	-0.31512000	0.32807100
C	1.52710600	-0.16418200	1.30206400
C	0.96740900	-0.54981500	-0.97651200
C	2.87433600	-0.22069400	0.99551500
H	1.23533100	-0.00799700	2.33032500
C	2.30279000	-0.60445000	-1.29721200
H	0.21846400	-0.71271900	-1.73276600
C	3.26772800	-0.43500000	-0.31566300
H	3.60021900	-0.10897900	1.78152500
H	2.62965800	-0.79339100	-2.30583300
B	-3.05536900	-1.09808300	-0.06132700

F	-3.75781600	-0.06820600	0.58191900
F	-3.62127400	-1.41380500	-1.25501000
F	-2.88056800	-2.15407000	0.79115900
O	4.54564800	-0.50252600	-0.72166000
C	5.55030900	-0.37861800	0.24285500
H	5.48492800	-1.16881500	0.98920000
H	6.48995800	-0.46566100	-0.28560300
H	5.50807200	0.58957500	0.74022700
C	0.06846400	2.86895500	-0.27176300
H	0.94149200	2.31726200	0.06428100
H	0.15520000	3.12682500	-1.32021600
H	0.03606800	3.79575800	0.30477300

TS-25

E(MPWB1K/6-311G(d,p)) = -827,199961 a.u.
unique imaginary frequency: -827.2 cm^{-1}

C	0.21808700	-0.25807800	-0.63087100
O	1.05404100	-0.48949500	0.40733300
C	0.40073800	1.26404900	-1.20198900
H	1.40084800	1.26903700	-1.61284100
H	-0.36464100	1.41965100	-1.95111800
C	0.26523400	2.11371800	-0.04967900
H	1.19135300	0.94343500	1.05733500
C	1.32060200	2.11661600	0.87011600
H	2.32128900	2.04439800	0.45995000
H	1.20865700	2.70201000	1.76936300
H	0.50914400	-0.84911200	-1.49697400
C	-1.21539300	-0.50500700	-0.26562200
C	-2.20300400	-0.44847500	-1.23712500
C	-1.56925300	-0.77374900	1.04337400

C	-3.52748800	-0.63572800	-0.90119900
H	-1.93322400	-0.26908300	-2.26745800
C	-2.89735300	-0.95818400	1.38006800
H	-0.79205600	-0.86063700	1.78336500
C	-3.87899500	-0.88321600	0.41306700
H	-4.28594500	-0.59756800	-1.66589800
H	-3.16335500	-1.17196000	2.40241800
B	2.47484600	-0.90314200	0.04820000
F	3.04573700	0.19012200	-0.62212500
F	3.09990400	-1.14014000	1.23009500
F	2.39642400	-1.98145600	-0.79039500
H	-4.91310200	-1.03150000	0.67707800
C	-1.03922900	2.72151900	0.25911100
H	-1.12350000	3.02311800	1.29585400
H	-1.12874400	3.61259900	-0.36540900
H	-1.85553800	2.05976700	-0.01902000

TS-26

E(MPWB1K/6-311G(d,p)) = -1055.040170 a.u.
unique imaginary frequency: -434.8 cm^{-1}

C	1.50895700	-0.15818400	-0.68576000
O	2.24262700	-0.58234200	0.36781200
C	1.91944700	1.36368600	-1.11385500
H	2.93694200	1.26786500	-1.46809800
H	1.23157900	1.67864700	-1.88772200
C	1.81859800	2.13185300	0.09906000
H	2.52607000	0.76643000	1.14298400
C	2.80735600	1.92569400	1.06787700

H	3.81504900	1.76466100	0.70363900
H	2.71243100	2.44420800	2.00917200
H	1.76932800	-0.71434100	-1.58444000
C	0.03598200	-0.24078500	-0.41552800
C	-0.87392800	0.01661000	-1.43062100
C	-0.42736600	-0.55935400	0.84852400
C	-2.22816300	-0.01928100	-1.18417700
H	-0.51969800	0.23413400	-2.42710200
C	-1.78316700	-0.59086600	1.09974100
H	0.28429700	-0.80372700	1.61808600
C	-2.68627100	-0.31378200	0.09026400
H	-2.93718800	0.17285000	-1.97062200
H	-2.16547900	-0.83678300	2.07645900
O	-4.55901200	-0.59917800	1.50672000
O	-4.89651900	-0.10393000	-0.63064000
B	3.61644500	-1.15795400	0.03991200
F	4.36712100	-0.09866300	-0.49136000
F	4.12846700	-1.58669200	1.22087900
F	3.44226800	-2.13291400	-0.90395100
C	-4.12569000	-0.36064700	0.41895600
C	-6.28827600	-0.14173300	-0.37627700
H	-6.76866400	0.09020600	-1.31617300
H	-6.58253900	-1.12619900	-0.03000200
H	-6.55459000	0.58809200	0.38020200
C	0.58682600	2.88177100	0.39215300
H	-0.28870700	2.38051400	-0.01059300
H	0.46421900	3.08298700	1.44931100
H	0.67141900	3.83835200	-0.12805600

TS-26

E(MPWB1K/6-311G(d,p)) = -1031.669329 a.u.
unique imaginary frequency: -400.92 cm^{-1}

C	-1.12767200	-0.13273000	0.68069400
O	-1.83995500	-0.57989200	-0.37673400
C	-1.55714700	1.38878800	1.08044600
H	-2.57715700	1.28601300	1.42582900
H	-0.88335500	1.72682200	1.85709700
C	-1.45550600	2.14372300	-0.14190400
H	-2.14053000	0.76383800	-1.17725500
C	-2.43639600	1.91738400	-1.11440900
H	-3.44445800	1.74906800	-0.75417700
H	-2.34173300	2.42773700	-2.06016500
H	-1.39656300	-0.67892400	1.58352300
C	0.35091300	-0.21882400	0.44101400
C	1.23926200	0.07466000	1.46643000
C	0.83748700	-0.59677000	-0.79767300
C	2.59797900	0.01841400	1.25718700
H	0.86669300	0.33487900	2.44508200
C	2.19762900	-0.65468500	-1.02328800
H	0.14002600	-0.86866900	-1.57057800
C	3.05306400	-0.33700200	0.00565500
H	3.30647100	0.23536700	2.03623900
H	2.60413000	-0.94730200	-1.97492400
N	4.49293200	-0.39013100	-0.22998800
O	4.86146400	-0.70354000	-1.32852300
O	5.21278300	-0.11131500	0.69019600
B	-3.21261600	-1.16910800	-0.05479100
F	-3.97547800	-0.11082900	0.45920400
F	-3.70700900	-1.61468200	-1.23570700
F	-3.03239100	-2.13045600	0.90079400
C	-0.22973400	2.90270600	-0.43512400

H	0.64858800	2.41646200	-0.02009600
H	-0.10177000	3.09495700	-1.49327500
H	-0.32748300	3.86390100	0.07427100

TS-28

E(MPWB1K/6-311G(d,p)) = -2797.184987a.u.
unique imaginary frequency: -656.3 cm^{-1}

C	-1.77396300	0.76981100	0.15653700
O	-1.71661900	1.48517300	-0.88285900
C	-0.49849700	1.21172300	1.38483900
H	-0.85155000	2.20637400	1.60314300
H	-0.57947800	0.49941900	2.18956000
C	0.65770500	1.15800200	0.60509800
H	-0.23651700	1.87612700	-0.96547100
C	0.79700000	2.11631700	-0.43512000
H	0.61200000	3.12423900	-0.08744800
H	1.64585500	2.03429600	-1.08786000
C	-1.60007200	-0.72362900	-0.09825200
F	-0.63899500	-0.95169900	-0.98934000
F	-1.29848900	-1.42198400	0.99740100
F	-2.72048400	-1.23492300	-0.58525200
H	-2.60695700	0.92212200	0.85229500
O	1.31213500	-0.00147000	0.69491900
C	2.38614600	-0.38918700	-0.07344000
C	2.54132900	-1.85841500	0.04465100
H	1.65763100	-2.33206400	-0.37242200
H	3.42796000	-2.17316500	-0.48637000
H	2.59793300	-2.14006600	1.09049000
O	3.05410200	0.36035100	-0.69294400

TS-29

E(MPWB1K/6-311G(d,p)) = -1006.900248 a.u.
unique imaginary frequency: -530.3 cm^{-1}

C	-1.39894500	0.91461600	0.29506600
O	-1.35514000	1.69560300	-0.70530000
C	0.01774700	1.05618500	1.34619700
H	-0.10828200	2.09505200	1.61703200
H	-0.11041800	0.37179000	2.17253700
C	1.10247600	0.81280300	0.47662700
H	0.17947900	1.73909300	-1.01779100
C	1.27164100	1.74564200	-0.59567400
H	1.33988900	2.76902700	-0.24355200
H	2.02461400	1.52074000	-1.33499000
C	-1.52172300	-0.55496700	-0.08122200
F	-0.67506700	-0.87229400	-1.05927300
F	-1.28267700	-1.37899900	0.94066400
F	-2.74322900	-0.82243700	-0.51669200
H	-2.13064000	1.13338700	1.08424900
S	1.88539200	-0.69410400	0.61993300
C	2.71739800	-0.89609800	-0.95214500
H	1.98886900	-0.88914900	-1.75402400
H	3.47442000	-0.13672600	-1.10509000
H	3.19411600	-1.86787900	-0.91027200

TS-30

E(MPWB1K/6-311G(d,p)) = -683.856826 a.u.

unique imaginary frequency: -401.1 cm^{-1}

C	-1.05887100	1.02155000	0.30597400
O	-0.91478800	1.77349400	-0.70456000
C	0.37745800	0.96153000	1.34507000
H	0.43840200	2.01322400	1.57707200
H	0.17379200	0.31947600	2.18763300
C	1.37186900	0.50294000	0.46452400
H	0.65955200	1.56978100	-1.04068200
C	1.72376600	1.35492800	-0.63632100
H	2.04051000	2.33543200	-0.30293900
H	2.39084500	0.94648100	-1.37982300
C	-1.35576800	-0.43010200	-0.04609400
F	-0.52492800	-0.85905200	-1.00082200
F	-1.22881200	-1.26561000	0.98563300
F	-2.58739800	-0.56501300	-0.50846600
H	-1.75058400	1.33801900	1.09880400
O	1.70213300	-0.75215400	0.56672400
C	2.43700800	-1.38106400	-0.46591800
H	1.86972000	-1.36089300	-1.38945200
H	3.40207600	-0.90187800	-0.59707000
H	2.57439900	-2.40197200	-0.14137000

TS-31

E(MPWB1K/6-311G(d,p)) = -703.296959 a.u.
unique imaginary frequency: -220.2 cm^{-1}

C	-1.38138100	0.91382500	0.48174600
O	-1.36631000	1.88745200	-0.29444800
C	0.21256200	0.69317600	1.45519000

H	0.13029400	1.62903900	1.98450600
H	0.06114600	-0.17280000	2.07728900
C	1.24060100	0.68261800	0.49227600
H	0.44269600	2.15455200	-0.67778000
C	1.43123500	1.95445500	-0.21793900
H	1.58079000	2.75791300	0.49421100
H	2.22095900	1.96208600	-0.95414600
C	-1.54821300	-0.44892400	-0.17584100
F	-0.64150000	-0.66099500	-1.13251700
F	-1.44140900	-1.46661100	0.69051100
F	-2.74070700	-0.55543600	-0.73872400
H	-2.00032000	0.93741700	1.39368800
N	1.87659000	-0.40784200	0.09589900
C	1.69873300	-1.68369200	0.74705100
H	2.62380300	-2.24418100	0.67031600
H	1.47647700	-1.54120400	1.79565200
H	0.89691700	-2.25374600	0.28789500
C	2.58897100	-0.43632500	-1.16433700
H	3.45038600	0.22435600	-1.15048000
H	2.93747500	-1.44546000	-1.33762400
H	1.93121300	-0.15611400	-1.98154200

MPWB1K/6-311G(d,p) computed total energies, unique imaginary frequency, and cartesian coordinates of the transition state structures involved in the ene reactions of isobutene **10** with the p-substituted BF_3:benzaldehyde complexes **23** - **27** in DCM.

TS-23 DCM

E(MPWB1K/6-311G(d,p)) = -961.147771 a.u.
unique imaginary frequency: -873.6 cm^{-1}

C	1.21902400	-0.02059100	-0.72348900
O	1.94603000	-0.52763000	0.34083600
C	1.68671600	1.46793900	-1.02997900
H	2.68836100	1.39156500	-1.43272700
H	1.00309100	1.89554500	-1.75172700
C	1.67314400	2.16235200	0.25212900
H	2.27871000	0.67860000	1.06888400
C	2.69619700	1.86612500	1.13269900
H	3.66610400	1.62631500	0.71727700
H	2.67607700	2.28317000	2.12618000
H	1.47947300	-0.56613600	-1.62648600
C	-0.25423600	-0.10907800	-0.46468300
C	-1.16055100	0.25499800	-1.44794300
C	-0.76029000	-0.55271700	0.74240000
C	-2.51834400	0.20072400	-1.23534900
H	-0.80373300	0.58164500	-2.41373800
C	-2.11831000	-0.61431900	0.97397900
H	-0.07785500	-0.87100700	1.51239400
C	-3.03758300	-0.22344000	-0.00475500
H	-3.17964400	0.48175900	-2.03528100
H	-2.46344300	-0.97872900	1.92511700
B	3.20771200	-1.24812300	0.00056200

F	4.06832600	-0.34850300	-0.63478000
F	3.74425800	-1.67476600	1.19037800
F	2.91348500	-2.29215100	-0.85060100
N	-4.38353000	-0.25633800	0.22523300
C	-4.87505800	-0.89883300	1.41236400
H	-5.95471700	-0.82846000	1.42988000
H	-4.59800000	-1.95407300	1.46292300
H	-4.49933000	-0.40911200	2.30767500
C	-5.28896100	-0.05311200	-0.87143400
H	-5.15400800	0.93085400	-1.31449700
H	-5.16744300	-0.79869600	-1.66030700
H	-6.30518900	-0.10911600	-0.50393800
C	0.47541500	2.91218700	0.65742700
H	-0.42949900	2.41407200	0.32195900
H	0.44358600	3.10473600	1.72204600
H	0.51777900	3.86845000	0.13306300

TS-24 DCM

E(MPWB1K/6-311G(d,p)) = -941.721794 a.u.
unique imaginary frequency: -882.0 cm^{-1}

C	-0.88338700	-0.13328600	0.69142500
O	-1.69048000	-0.46327400	-0.38325500
C	-1.24501100	1.32497800	1.20822900
H	-2.22653700	1.25207400	1.65787500
H	-0.50065100	1.62248900	1.93523700
C	-1.25989800	2.17792000	0.02458700
H	-1.99057800	0.84385800	-0.93532500
C	-2.34306700	2.04703300	-0.82344200
H	-3.30112900	1.79941500	-0.38463300

H	-2.35368500	2.58774400	-1.75557100
H	-1.11983200	-0.77953100	1.53195800
C	0.56785500	-0.25690600	0.33034500
C	1.54040500	-0.12667300	1.30362300
C	0.96876000	-0.48604300	-0.97657000
C	2.88501500	-0.20618600	0.99448100
H	1.25519400	0.03636400	2.33210700
C	2.30369100	-0.56323200	-1.30032400
H	0.22301100	-0.61480300	-1.74221800
C	3.27323500	-0.42068600	-0.31887600
H	3.61287700	-0.10641600	1.78003300
H	2.62081300	-0.74214400	-2.31413700
B	-2.97613200	-1.15454600	-0.06726300
F	-3.74865500	-0.29913600	0.72277800
F	-3.59127100	-1.39378600	-1.27082100
F	-2.70238700	-2.31321500	0.62711800
O	4.55000600	-0.51006900	-0.72490600
C	5.55991200	-0.38770200	0.24255200
H	5.48780700	-1.17416600	0.99074500
H	6.49817200	-0.48329400	-0.28618500
H	5.52148500	0.58245700	0.73362200
C	-0.05022800	2.92518400	-0.34857600
H	0.85050800	2.37253700	-0.10028900
H	-0.04987200	3.22689900	-1.38810700
H	-0.04600800	3.82483700	0.27009200

TS-25 DCM

E(MPWB1K/6-311G(d,p)) =-827.220744 a.u.
unique imaginary frequency: -863.1 cm^{-1}

C	0.19703200	-0.17626500	-0.66549800
O	1.05878600	-0.40140600	0.39247700
C	0.38341500	1.30280600	-1.20966700
H	1.35464200	1.33005900	-1.68647500
H	-0.40739700	1.50876200	-1.91928000
C	0.33576400	2.17040800	-0.03626600
H	1.23007800	0.94225400	0.91818500
C	1.44856200	2.17423700	0.78234800
H	2.41652400	2.02541800	0.32143400
H	1.42287700	2.72568800	1.70784600
H	0.48003900	-0.80763000	-1.50300200
C	-1.22638900	-0.45124000	-0.27342300
C	-2.22149800	-0.40513500	-1.23848900
C	-1.56624100	-0.74073300	1.03494900
C	-3.53865300	-0.63029300	-0.89683700
H	-1.96442900	-0.19852000	-2.26647700
C	-2.88778100	-0.96362400	1.37759600
H	-0.79048700	-0.80159400	1.77870000
C	-3.87643800	-0.90513800	0.41625700
H	-4.30246000	-0.59588300	-1.65621300
H	-3.14224200	-1.18819900	2.40053300
B	2.40236700	-0.95800400	0.05120100
F	3.06527300	-0.02799000	-0.75360300
F	3.06328200	-1.13148800	1.24115100
F	2.23502600	-2.13941300	-0.63908900
H	-4.90512900	-1.08068800	0.68467500
C	-0.94053100	2.78189600	0.36143100
H	-0.94724500	3.09850500	1.39649300
H	-1.06343400	3.66493100	-0.26877300
H	-1.77914500	2.12666700	0.14600200

TS-26 DCM

E(MPWB1K/6-311G(d,p)) = -1055.064037 a.u.
unique imaginary frequency: -849.9 cm^{-1}

C	1.50137700	-0.08450600	-0.71696800
O	2.25664200	-0.49951000	0.36332700
C	1.91099000	1.39053200	-1.13076400
H	2.90706500	1.32011500	-1.54757200
H	1.20314300	1.75235000	-1.86519200
C	1.90142600	2.17126900	0.10423400
H	2.56884300	0.76734300	1.00098200
C	2.95215800	1.96707000	0.97682200
H	3.91913300	1.72349500	0.55610700
H	2.94131600	2.44813300	1.94098500
H	1.74549900	-0.68842900	-1.58648000
C	0.03276000	-0.18703700	-0.42242600
C	-0.88388200	0.05324600	-1.43579300
C	-0.42209500	-0.50230500	0.84553500
C	-2.23607600	-0.00071800	-1.18416800
H	-0.53719600	0.27968000	-2.43216000
C	-1.77667400	-0.55297500	1.10127600
H	0.28836600	-0.71527000	1.62485600
C	-2.68739500	-0.29743900	0.09287300
H	-2.94592400	0.18365500	-1.97145400
H	-2.14509900	-0.79250500	2.08460000
O	-4.55490700	-0.60622700	1.51397400
O	-4.89842400	-0.10643900	-0.62046200
B	3.53392700	-1.21292900	0.04653200
F	4.36307500	-0.32682800	-0.64468800
F	4.08842000	-1.56415700	1.25039500
F	3.24790600	-2.30288000	-0.74617800

C	-4.12565500	-0.35856800	0.42216900
C	-6.29511600	-0.14509500	-0.37668700
H	-6.76697200	0.06700600	-1.32486500
H	-6.58804300	-1.12478100	-0.01751800
H	-6.56999600	0.60199200	0.35903800
C	0.69483000	2.92217800	0.47982500
H	-0.20977600	2.41458700	0.15973700
H	0.65980800	3.15459600	1.53635400
H	0.73922100	3.86095600	-0.07613400

TS-27 DCM

E(MPWB1K/6-311G(d,p)) = -1031.694434a.u.
unique imaginary frequency: -835.3 cm^{-1}

C	-1.12176100	-0.06317200	0.71402100
O	-1.85340400	-0.49159300	-0.37615600
C	-1.54395800	1.41165900	1.10783600
H	-2.54171100	1.33642100	1.51985000
H	-0.84564800	1.79005000	1.84303000
C	-1.53621500	2.18222700	-0.13491000
H	-2.18100800	0.76998700	-1.02216300
C	-2.58302000	1.96420100	-1.00788800
H	-3.54828700	1.71114900	-0.58921100
H	-2.57367100	2.43739200	-1.97588000
H	-1.37658400	-0.66221600	1.58403800
C	0.35292700	-0.16916000	0.45047400
C	1.24775500	0.09322200	1.47874200
C	0.83007300	-0.52428500	-0.79874600
C	2.60404800	0.02202200	1.26341000
H	0.88302300	0.34860600	2.46073700

C	2.18770700	-0.59657600	-1.03126800
H	0.13438800	-0.75408000	-1.58582300
C	3.05045400	-0.31632900	0.00311800
H	3.31099100	0.21955800	2.04838500
H	2.57880000	-0.86769600	-1.99508600
N	4.48363200	-0.38699400	-0.23826800
O	4.85252500	-0.67916600	-1.34509500
O	5.21974200	-0.14655300	0.68231000
B	-3.12593500	-1.22277500	-0.06945700
F	-3.96775800	-0.34569200	0.61671700
F	-3.66573000	-1.57902800	-1.27746200
F	-2.82958900	-2.30811100	0.72479800
C	-0.33345700	2.93743200	-0.51376900
H	0.57432600	2.43570900	-0.19329800
H	-0.30024400	3.16737100	-1.57081000
H	-0.38066400	3.87711600	0.04033300