Supplementary Material

Unveiling the Chemistry of Higher−Order Cycloaddition Reactions within Molecular Electron Density Theory

Luis R. Domingo,[1*] Mar Ríos-Gutiérrez,[1] and Patricia Pérez[2]

[1] Department of Organic Chemistry, University of Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain.

[2] Universidad Andres Bello, Facultad de Ciencias Exactas, Departamento de Ciencias Químicas, Centro de Química Teórica & Computacional. Av. República 275, 8370146, Chile.

E-mail: luisrdomingo@gmail.com

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*BET analysis of the most favorable reaction path associated with the higher-order cycloaddition reaction of tropone **1** with Cp **3**.*

To characterize the molecular mechanism of the higher-order cycloaddition reaction between tropone **1** with Cp **3**, the Bond Evolution Theory (BET) was applied along the most favourable [6+4] *exo* reaction path yielding the formal [6+4] CA **4** (See Scheme S1). This methodology comprehensively describes molecular mechanisms by topologically scanning the bonding changes along the corresponding reaction path. Complete BET analysis data are given in Table S1, while Table S2 gathers only the structures where significant chemical changes happen. Figure S1 shows the ELF attractor positions and populations of the ELF valence basins involved in the C2–C9 and C7–C12 bond formation. The resulting molecular mechanism is represented in Scheme S2 by Lewis-like structures.
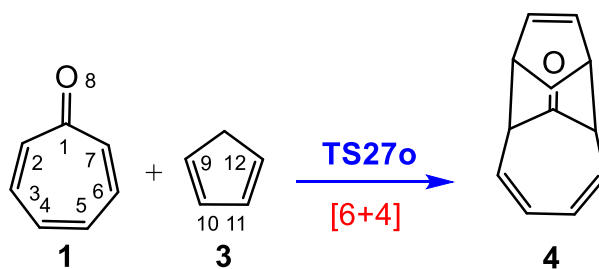
Scheme S1

The molecular mechanism of the cycloaddition reaction between tropone **1** and Cp **3** can be divided into three main groups of phases associated with a well-defined chemical event, namely: *Group A*, associated with the conjugation of the tropone multiple bond system; *Group B*, related to the formation of *pseudoradical* centers; and *Group C*, associated with the formation of the C2[7]–C9[12] single bonds. While *Group A* is independent of the others, *Group B* and *Group C* somewhat overlap each other due to the high asynchronicity of the bond formation (see later). Note that these groups are clearly defined in synchronous reactions such as the Diels-Alder reaction between butadiene and ethylene.

Group A, involving *Phases I – V*, begins at **S1** (d(C2–C9) = 3.266 Å and d(C7–C12) = 3.274 Å), which is the first point of the IRC. This structure resembles the molecular complex of the reaction path and thus, presents similar topological features to those of the separated reagents. Therefore, at **S1**, the C–C multiple bond regions of the Cp and

tropone frameworks, which integrate by between 3.14 and 3.35 e, are characterized as partial double bonds, while the C10−C11, C2(7)−C1, and C3(5)−C4(6) are characterized as single bonds integrating 2.22, 2.32 and 2.37 e, respectively. Note that the tropone carbonyl C−O group does not participate throughout the reaction, as can be observed from the insignificant variation of the population of the V(C1,O8) disynaptic basin along the IRC (see Table S1). Along *Group A*, the partial double bonds of tropone are depopulated, and their population is redistributed into the adjacent C3−C4 and C5−C6 single bonds to generate a large favorable 6-carbon conjugated system at the end of *Group A*; the C1−C2 region also gathers a small amount of this electron density, reaching 2.47e at **S6**. Interestingly, a slight asymmetry in the bonding changes can already be observed at this early stage of the reaction despite the symmetry of the reagents; note that **S5** shows an earlier conjugation of C3−C4 than C5−C6 (see Scheme S2). At the Cp framework, there are no significant bonding changes yet. The conjugation of the tropone framework along *Group A* has a high energy cost of ca. 20.4 kcal·mol^{-1}.

After the conjugation of the tropone system, the *pseudoradical* centers demanded for the C−C bond formation are created along *Group B*, which starts at **S6** (d(C2−C9) = 2.078 Å and d(C7−C12) = 2.631 Å) and involves *Phases VI – XIII*. According to the electrophilic Parr functions, the first *pseudoradical* center is formed at the C2 carbon, which is the most electrophilic center of tropone **1** (see section 3.2). This C2 *pseudoradical* center gathers an initial population of 0.20 e due to the depopulation of the contiguous C1−C2 region. Similarly, a C9 *pseudoradical* center at the Cp framework is created at **S7**, with a population of 0.29 e, at the most nucleophilic C9 carbon from the depopulation of the neighboring C9−C10 partial double bond. Note that at **S7**, no *pseudoradical* center is formed yet at the equivalent C7 and C12 carbons, emphasizing the asymmetry of the bonding changes. The formation of these two *pseudoradical* centers has an energy cost of only 0.5 kcal·mol^{-1}, confirming that this is a relatively easy chemical change. Indeed, the formation of *pseudoradical* centers and new bonds usually takes place after the corresponding TS, thus implying an energy release. As **TS27o** is found in *Phase VII*, its electronic structure is similar to **S7** (see ELF basin attractors of **T S27o** in Figure 7).

Group C, which begins at **S8** (d(C2−C9) = 1.933 Å and d(C7−C12) = 2.581 Å) and involves *Phases VIII – XIV*, overlaps with *Group B* almost entirely except for *Phase XIV*. At **S8**, the first C2−C9 single bond is formed with an initial population of 0.95 e through

the C-to-C coupling of both C2 and C9 *pseudoradical* centers, which had reached 0.41 and 0.50 e, respectively (see Scheme S2 and Figure S1). In addition, the continued depopulation of the C2–C3, C9–C10, and C11–C12 partial double bond regions since the beginning of the reaction while the electron population gathers at C10–C11, as well as the asymmetry of these changes, has led to an allylic conjugation of the electron density at the 5-membered ring. Both C2–C3 and C9–C10 regions can now be considered single bonds, and the conjugation at the tropone system involves five carbon atoms. Then, while the population of the recently formed C2–C9 single bond increases until the end of the reaction and the C4–C5 region keeps depopulating towards the two neighboring ones, the second pair of *pseudoradical* centers are formed in a similar way as the first one. At **S9**, C4–C5 can already be considered a single bond, and a new C7 *pseudoradical* center, integrating 0.20 e, is created from the depopulation of the C6–C7 region. At this point, the C6–C7 region reaches a maximum population of 2.59 e, contributing to the C7 *pseudoradical* center. Along *Phases IX* and *X*, the C6–C7 and C11–C12 regions keep depopulating to such an extent that they become single bonds, and a C12 *pseudoradical* center, integrating 0.21 e, is created at **S11** while the one at C7 has reached 0.39 e. Along *Phases XI – XIII*, there are only electron density adjustments with no relevant chemical meaning. The population of C7 and C12 *pseudoradical* centers increases to 0.60 and 0.43 e until they merge each other at **S14**, forming the new C7–C12 single bond when the first C2–C9 bond has already reached ca. 92% of its final population at a C2–C9 distance of 1.620 Å. From **S14** to the end of the reaction, the electron density rearrangements are mainly devoted to completing the C2–C9 and C7–C12 single bond formation by increasing their population.

Table S1. Most relevant ELF valence basins and their total populations, C−C bond formation distances, IRC values, and relative energies for the structures of the IRC of the higher-order cycloaddition reaction between tropone **1** with Cp **3**, yielding the formal [6+4] CA **4**. Distances are given in angstroms, Å, IRC values in au, and relative energies concerning **S1** are shown in kcal·mol^{-1}.

Structures	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	P15
Phases	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	
d(C2−C9)	3.266	3.033	3.027	2.434	2.320	2.078	2.066	1.933	1.816	1.773	1.668	1.638	1.624	1.620	1.570
d(C7−C12)	3.274	3.093	3.087	2.746	2.707	2.631	2.627	2.581	2.529	2.503	2.383	2.275	2.164	2.126	1.569
IRC	-8.93	-6.73	-6.67	-2.39	-1.76	-0.50	-0.44	0.25	0.88	1.13	1.95	2.52	3.08	3.27	11.95
δE	0.0	1.0	1.0	11.5	14.6	20.4	20.5	20.9	19.2	18.2	14.8	12.2	8.9	7.6	-19.5
V(C1,C2)	2.32	2.34	2.34	2.38	2.39	2.47	2.47	2.51	2.52	2.51	2.44	2.39	2.33	2.32	2.11
V(C2,C3)	1.58	1.63	3.15	3.05	3.00	2.66	2.63	2.38	2.25	2.21	2.13	2.11	2.09	2.09	2.01
V'(C2,C3)	1.60	1.53													
V(C3,C4)	2.37	2.38	2.39	2.51	2.57	2.88	2.90	3.11	3.23	1.62	1.67	1.68	1.68	1.68	1.72
V'(C3,C4)										1.65	1.67	1.68	1.70	1.70	1.70
V(C4,C5)	3.14	3.12	3.12	3.04	3.00	2.76	2.74	2.56	2.45	2.41	2.34	2.31	2.28	2.28	2.22
V(C5,C6)	2.37	2.38	2.38	2.48	2.53	2.75	2.77	2.95	3.08	3.12	3.20	1.63	1.58	1.60	1.72
V'(C5,C6)												1.63	1.71	1.71	1.70
V(C6,C7)	1.57	3.16	3.15	3.08	3.04	2.93	2.92	2.83	2.59	2.55	2.41	2.34	2.27	2.25	2.01
V'(C6,C7)	1.60														
V(C1,C7)	2.33	2.34	2.34	2.36	2.36	2.33	2.32	2.25	2.2	2.18	2.15	2.13	2.13	2.13	2.05
V(C1,O8)	2.26	2.26	2.26	2.24	2.24	2.22	2.22	2.22	2.23	2.23	2.26	2.28	2.31	2.32	2.43
V(C9,C10)	1.65	1.63	1.63	3.21	3.17	3.08	2.79	2.51	2.32	2.26	2.15	2.11	2.08	2.07	1.99
V'(C9,C10)	1.70	1.71	1.71												
V(C10,C11)	2.22	2.23	2.23	2.31	2.34	2.51	2.52	2.69	2.87	2.93	3.06	3.15	1.62	1.69	1.77
V'(C10,C11)													1.61	1.56	1.69
V(C11,C12)	1.65	1.63	1.63	1.52	3.21	3.07	3.07	2.94	2.83	2.80	2.53	2.40	2.30	2.27	1.99
V'(C11,C12)	1.70	1.71	1.71	1.73											
V(C2)						0.20	0.22								
V(C7)										0.20	0.24	0.39	0.48	0.58	
V(C9)							0.29								
V(C12)												0.21	0.32	0.40	
V(C2,C9)								0.95	1.24	1.33	1.53	1.60	1.63	1.64	1.79
V(C7,C12)														1.04	1.79

Table S2. Most relevant ELF valence basins and their total populations, C−C bond formation distances, IRC values, and relative energies for the more relevant structures of the IRC of the higher-order cycloaddition reaction between tropone **1** with Cp **3**, associated with the formation of the C2−C9 and C7−C12 single bonds. Distances are given in angstroms, Å, IRC values in au, and relative energies with respect to **S1** are given in kcal·mol^{-1}. V(Ci,Cj)$_t$ is the sum of the populations of the V(Ci,Cj) and V'(Ci,Cj) disynaptic basins.

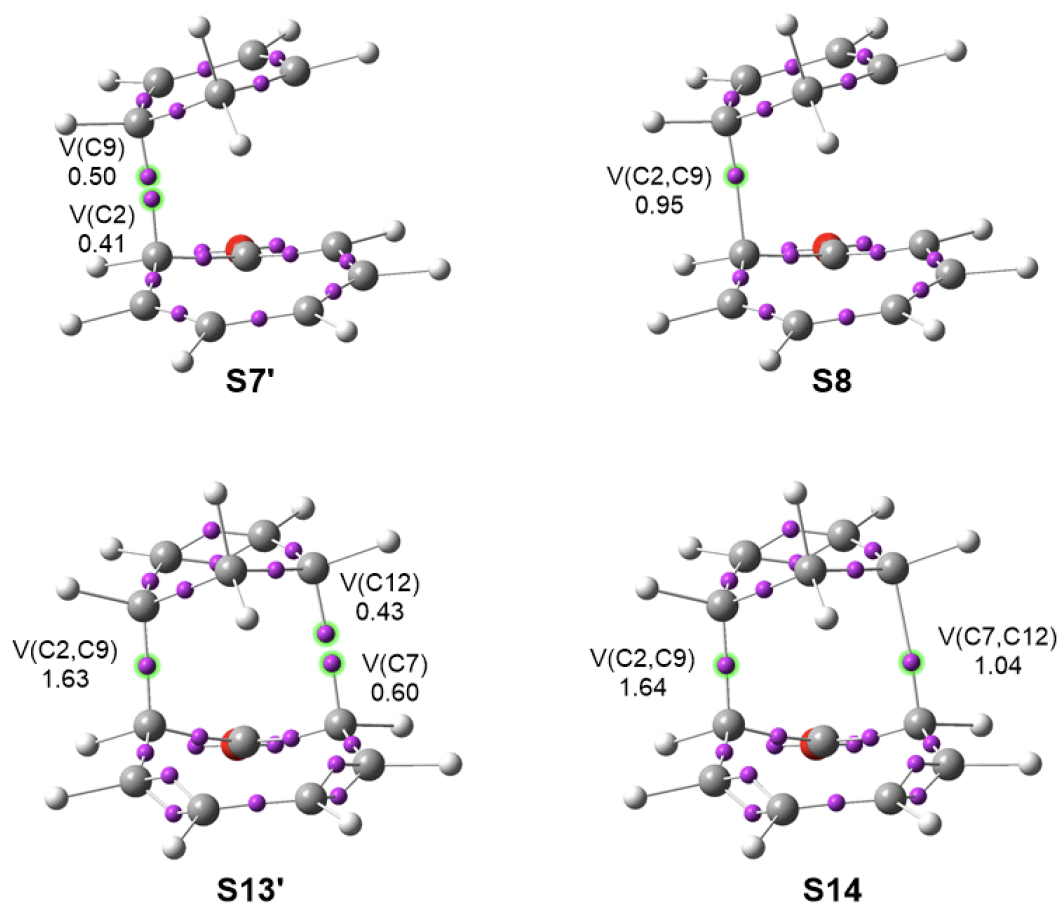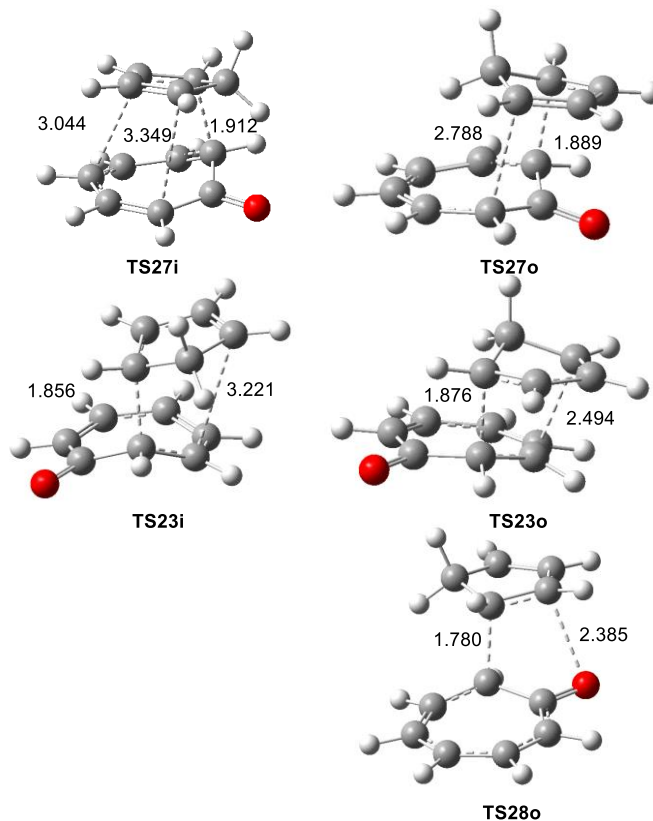| Structures	S1	S5	S6	S7	S8	S9	S11	S14	S15
d(C2−C9)	3.266	2.320	2.078	2.066	1.933	1.816	1.668	1.620	1.570
d(C7−C12)	3.274	2.707	2.631	2.627	2.581	2.529	2.383	2.126	1.569
IRC	-8.93	-1.76	-0.50	-0.44	0.25	0.88	1.95	3.27	11.95
ΔE	0.0	14.6	20.4	20.5	20.9	19.2	14.8	7.6	-19.5
V(C1,C2)	2.32	2.39	2.47	2.47	2.51	2.52	2.44	2.32	2.11
V(C2,C3)$_t$	3.18	3.00	2.66	2.63	2.38	2.25	2.13	2.09	2.01
V(C3,C4)$_t$	2.37	2.57	2.88	2.90	3.11	3.23	3.34	3.38	3.42
V(C4,C5)	3.14	3.00	2.76	2.74	2.56	2.45	2.34	2.28	2.22
V(C5,C6)	2.37	2.53	2.75	2.77	2.95	3.08	3.20	3.31	3.42
V(C6,C7)$_t$	3.17	3.04	2.93	2.92	2.83	2.59	2.41	2.25	2.01
V(C1,C7)	2.33	2.36	2.33	2.32	2.25	2.2	2.15	2.13	2.05
V(C9,C10)$_t$	3.35	3.17	3.08	2.79	2.51	2.32	2.15	2.07	1.99
V(C10,C11)	2.22	2.34	2.51	2.52	2.69	2.87	3.06	3.25	3.46
V(C11,C12)$_t$	3.35	3.21	3.07	3.07	2.94	2.83	2.53	2.27	1.99
V(C2)			0.20	0.22					
V(C9)				0.29					
V(C7)						0.20	0.39		
V(C12)							0.21		
V(C2,C9)					0.95	1.24	1.53	1.64	1.79
V(C7,C12)								1.04	1.79

Figure S1. ELF attractor positions and populations of the ELF valence basins involved in the C2–C9 and C7–C12 bond formation at **S8** and **S14**, respectively, and the structures immediately before. Populations are given in an average number of electrons, e.
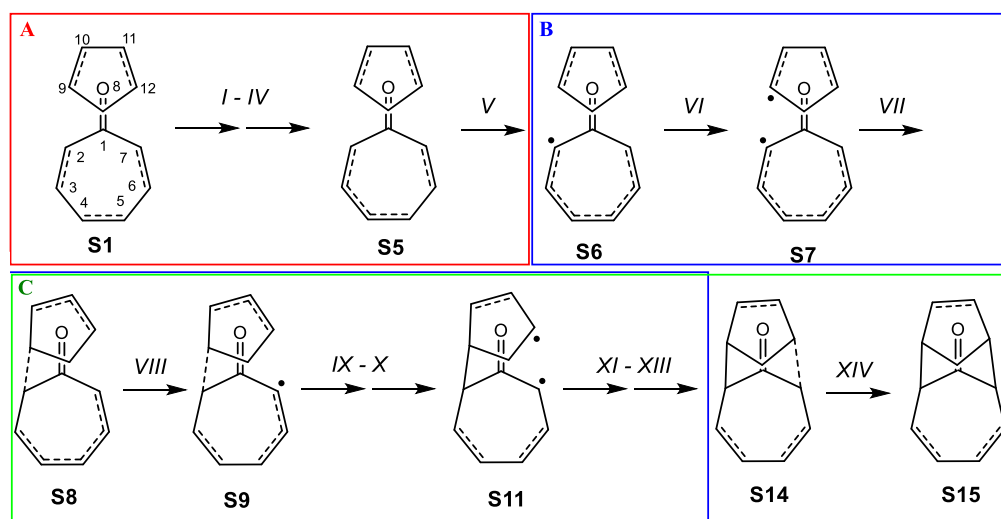
Scheme S2. Representation of the molecular mechanism of the cycloaddition reaction between tropone **1** and Cp **3** by Lewis-like structures based on the topological analysis of the ELF.

a) TSs associated with a two-center interaction process
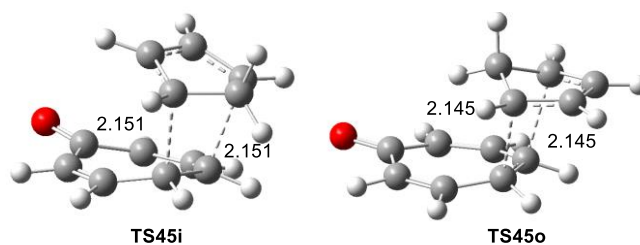

Figure S2. Gas-phase B3LYP/6-311G(d,p) geometries of the TSs involved in the higher-order cycloaddition reaction of tropone **1** with Cp **3**. Distances are given in Angstroms.

1.741 (1.787)

TS2o

1.655 (1.629)

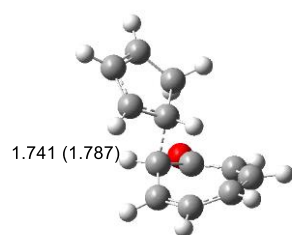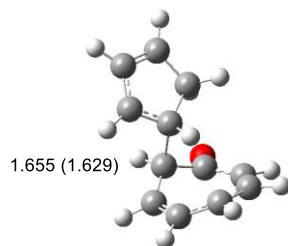**IN2o**

Figure S3. *ω*B97X-D/6-311G(d,p) geometries of **TS2o** and **IN2o**. Distances are given in Angstroms. Distance in benzene are given in parenthesis.
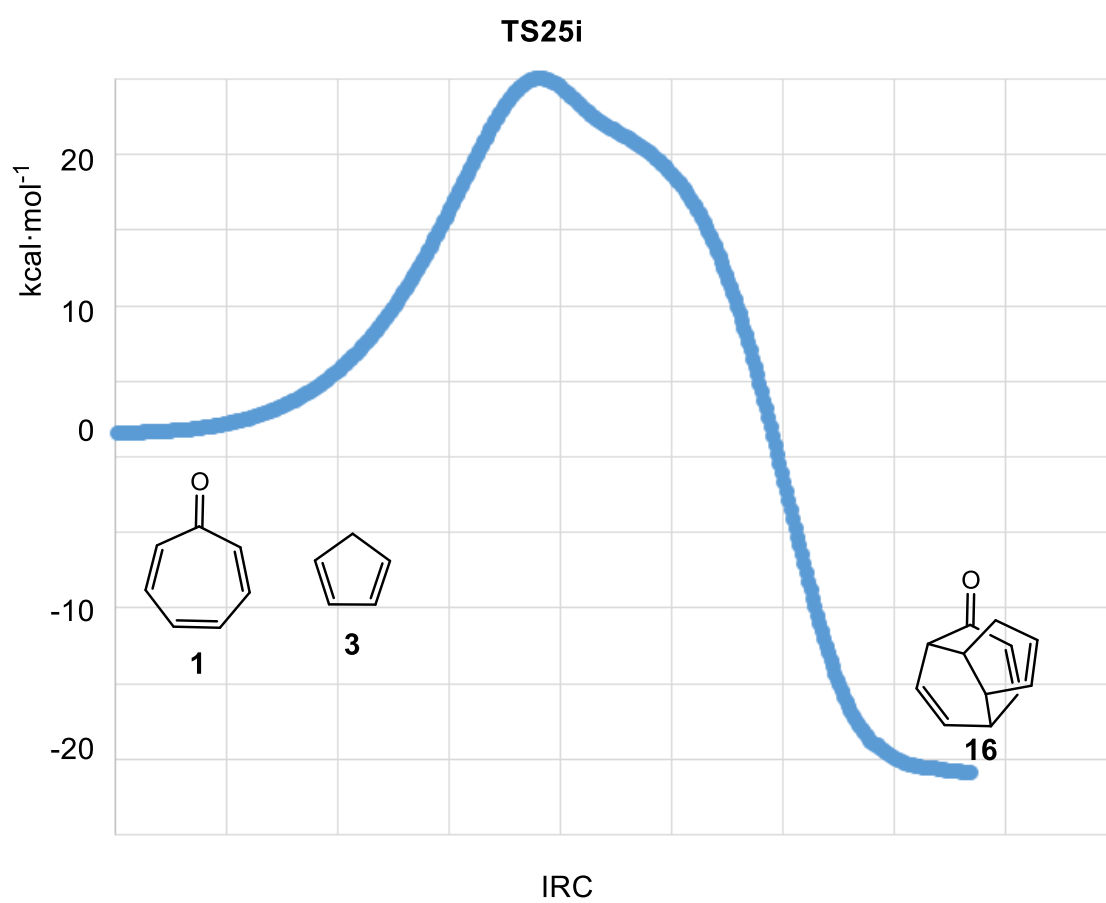
Figure S4. IRC connecting tropone **1** and Cp **3** with the formal [4+2] cycloadduct **16** *via* **TS25i**

Table S3. ωB97X-D/6-311G(d,p) total electronic energies, in a.u., in the gas phase and benzene, of the stationary points involved in the higher-order cycloaddition reaction of tropone **1** with Cp **3**.

	gas phase	benzene
1	-345.495830	-345.499902
3	-194.081297	-194.082370
TS25i	-539.549972	-539.554567
TS27o	-539.553489	-539.557822
TS23i	-539.550492	-539.555353
TS23o	-539.549180	-539.553419
TS28o	-539.537087	-539.541580
TS2o	-539.531437	-539.537066
TS45i	-539.546686	-539.551652
TS45o	-539.546326	-539.551118
CA25i	-539.623940	-539.627415
CA27o	-539.618242	-539.621695
CA23i	-539.603212	-539.606665
CA23o	-539.601904	-539.605257
CA28o	-539.611381	-539.614038
IN2o	-539.531552	-539.537847
CA45i	-539.602599	-539.606463
CA45o	-539.600812	-539.604541

Table S4. B3LYP/6-311G(d,p) gas phase total electronic energies, E in a.u., and relative energies, ΔE in kcal mol^{-1}, of the stationary points involved in the higher-order cycloaddition reaction of tropone **1** with Cp **3**.

	E	ΔE
1	-345.626661	
3	-194.153723	
TS25i	-539.742084	24.0
TS27o	-539.746263	21.4
TS23i	-539.741946	24.1
TS23o	-539.740082	25.3
TS28o	-539.737497	26.9
TS2o	-539.723099	35.9
TS45i	-539.735564	28.1
TS45o	-539.736059	27.8
CA25i	-539.794566	-8.9
CA27o	-539.788537	-5.1
CA23i	-539.775824	2.9
CA23o	-539.774943	3.4
CA28o	-539.791101	-6.7
IN2o	-539.784950	-2.9
CA45i	-539.775291	3.2
CA45o	-539.774327	3.8

Table S5. ωB97X-D/6-311G(d,p) total enthalpies, H in a.u., entropies, S in kcal·mol^{-1}K^{-1}, and Gibbs free energies, G in a.u., and relative enthalpies, ΔH in kcal·mol^{-1}, entropies, ΔS in cal·mol^{-1}K^{-1}, and Gibbs free energies, ΔG in kcal·mol^{-1}, computed in benzene at 80 ºC , of the stationary points involved in the higher-order cycloaddition reaction of tropone **1** with Cp **3**.

	H	ΔH	S	ΔS	G	ΔG
1	-345.379230		85.5		-345.427326	
3	-193.982599		69.9		-194.021926	
TS25i	-539.333065	18.0	107.0	-48.4	-539.393270	35.1
TS27o	-539.335962	16.2	105.0	-50.4	-539.395027	34.0
TS23i	-539.333675	17.7	108.3	-47.1	-539.394602	34.3
TS23o	-539.331192	19.2	107.1	-48.2	-539.391473	36.3
TS28o	-539.319820	26.4	108.5	-46.8	-539.380881	42.9
TS45i	-539.329679	20.2	109.8	-45.5	-539.391497	36.2
TS45o	-539.333076	18.0	99.2	-56.1	-539.380215	43.3
CA25i	-539.401588	-24.9	103.3	-52.1	-539.459705	-6.6
CA27o	-539.395886	-21.4	101.0	-54.4	-539.452705	-2.2
CA23i	-539.381002	-12.0	104.1	-51.2	-539.439600	6.1
CA23o	-539.379537	-11.1	104.0	-51.4	-539.438038	7.0
CA28o	-539.392797	-19.4	96.6	-58.7	-539.438700	6.6
CA45i	-539.384924	-14.5	97.0	-58.4	-539.430999	11.5
CA45o	-539.382853	-13.2	96.6	-58.7	-539.428754	12.9

*ω*B97X-D /6-311G(d,p) gas phase computed total energies, unique imaginary frequency, and cartesian coordinates of the stationary points involved in the higher-order cycloaddition reaction of tropone **1** with Cp **3**.

1

E = -345.495829881 a.u.

C	1.84228500	0.67659800	-0.00009900
C	1.84301900	-0.67573800	-0.00012100
C	0.71353100	-1.56137500	-0.00002100
C	-0.60792600	-1.28510100	0.00003000
C	0.71220100	1.56146600	0.00005900
C	-0.60928300	1.28511100	0.00011900
C	-1.32591300	-0.00020800	0.00009100
H	2.81181900	1.16503700	-0.00020700
H	2.81303700	-1.16320300	-0.00023700
H	0.97125900	-2.61709800	-0.00000500
H	-1.29774800	-2.12390500	0.00006200
H	-1.29878000	2.12412000	0.00021000
O	-2.54708600	-0.00084500	-0.00003600
H	0.96961300	2.61729600	0.00012600

3

E = -194.081297195 a.u.

C	-0.00718900	-1.21268500	-0.00009600
H	-0.01100600	-1.87065900	-0.87834700
H	-0.01117800	-1.86990700	0.87869600
C	1.17337800	-0.28717600	0.00034800
H	2.20247100	-0.61939800	0.00007800
C	0.73938100	0.98211000	-0.00042700
H	1.35934600	1.86938700	-0.00050800
C	-1.17673000	-0.27332800	-0.00009400
H	-2.20969400	-0.59333600	-0.00068600
C	-0.72766300	0.99082400	0.00030500
H	-1.33700100	1.88543700	0.00054800

TS23i

E = -539.550492 a.u.
1 imaginary frequency   -376.8659   cm-1

C	1.77081500	-0.88920000	0.05806600
C	0.43266100	-0.88472400	0.75164000
C	2.25825200	0.30624400	-0.60343200

C	-0.02682500	0.15697600	1.60206200
C	1.68330800	1.53390700	-0.61124000
C	0.00734400	1.50438800	1.27943000
C	0.60192600	2.06057900	0.16154600
H	-0.55459000	-0.13366900	2.50346500
H	-0.56634200	2.17518100	1.91227100
H	0.37803600	3.10601800	-0.02912700
H	2.14947500	2.26456000	-1.26920100
H	3.15138800	0.14194800	-1.19665200
H	0.30444300	-1.87909300	1.17397200
O	2.38411800	-1.94418300	0.01175600
C	-2.06880200	-1.40855900	0.03293400
H	-1.94855100	-1.92858700	0.98336900
H	-2.64978500	-2.06688300	-0.62788800
C	-2.75255100	-0.08490700	0.12302900
H	-3.61868900	0.11064300	0.74070500
C	-2.19367500	0.77304400	-0.76840200
H	-2.54054700	1.77461000	-0.98513100
C	-0.77359100	-1.05444300	-0.69325000
H	-0.23746900	-1.83188300	-1.22919300
C	-1.02302100	0.18920500	-1.32302000
H	-0.43534600	0.60556100	-2.12680500

TS23o

E = -539.549180 a.u.
1 imaginary frequency   -537.1475   cm-1

C	1.22805300	1.31578500	-0.26592700
C	0.02342600	0.65161500	-0.84876500
C	-1.27302600	1.03280300	0.65660800
C	2.26575900	0.58330700	0.46849400
C	-0.14925600	-0.72726200	-1.14166300
C	2.48920300	-0.74400800	0.58034700
C	0.68039800	-1.83590400	-0.76764900
C	1.78755000	-1.86175900	0.01200600
H	-0.81435500	-0.94140500	-1.96851700
H	0.35005100	-2.79287400	-1.16396900
H	2.23492500	-2.83300200	0.19611300
H	3.36710000	-1.01813600	1.16070400
H	2.98026600	1.25886800	0.92812300
H	-0.41798500	1.33039700	-1.56833200
O	1.33093100	2.52737500	-0.38171100
C	-1.08814400	-0.29253100	1.34944700
H	-1.63846000	-0.25288900	2.30051400
H	-0.06372900	-0.58917900	1.56396500
C	-1.84399700	-1.17979500	0.41148800
H	-1.87073900	-2.25826100	0.49564900
C	-2.82275000	-0.39993200	-0.20153700

H	-3.63492200	-0.77897300	-0.80823400
H	-0.89691300	1.96507200	1.06007800
C	-2.50151400	0.94316200	-0.02916400
H	-3.01691500	1.77848700	-0.48451700

TS25i

E = -539.549972 a.u.
1 imaginary frequency -436.3229 cm-1

C	0.12938900	1.49131600	0.39579500
C	0.44021400	0.98703200	-0.98200600
C	0.49480100	0.70838500	1.55765500
C	1.69752300	0.43782000	-1.34892600
C	1.23404500	-0.43698500	1.59540100
C	2.34815800	-0.55924900	-0.66342600
C	1.97866700	-1.07727300	0.57910900
H	2.07498800	0.70260900	-2.33173800
H	3.18547100	-1.04102000	-1.16062700
H	2.49312300	-1.98257800	0.88850900
H	1.27874000	-0.93131300	2.56321300
H	0.08482200	1.09489800	2.48445300
H	0.05280100	1.71490700	-1.69179500
O	-0.49682300	2.54048300	0.49705200
C	-2.18192400	0.16399900	-0.68282200
H	-3.01810200	-0.08145100	-1.35079000
H	-2.19561400	1.24504000	-0.52769200
C	-2.30372000	-0.62854200	0.57384200
H	-3.00073100	-0.39610700	1.36740100
C	-1.45139600	-1.68191000	0.53897600
H	-1.36465300	-2.44931300	1.29663500
C	-0.90925400	-0.39431900	-1.30872300
H	-0.79056900	-0.36037500	-2.38532000
C	-0.62428800	-1.59103800	-0.61750000
H	0.06100900	-2.35458400	-0.95291400

TS27o

E = -539.553489 a.u.
1 imaginary frequency -493.3301 cm-1

C	-0.07181900	-0.25478900	1.28403900
C	0.23033500	1.11818900	0.80250200
C	0.45998200	-1.41931200	0.60534700
C	1.50075100	1.54309200	0.31715500
C	1.64100000	-1.54824400	-0.12305400
C	2.49437400	0.80579400	-0.27967700
C	2.54662400	-0.57822100	-0.51501600

H	1.68205300	2.61242900	0.38711900
H	3.36113900	1.36830400	-0.61577900
H	3.42231100	-0.93303300	-1.04974100
H	1.88723700	-2.56420000	-0.42083000
H	-0.02515900	-2.33386600	0.92895300
H	-0.24947900	1.83933800	1.45729700
O	-0.92921400	-0.37818100	2.15226800
C	-0.64431000	0.24910400	-1.67690700
H	0.43374500	0.15127900	-1.80125800
H	-1.05587400	0.53728400	-2.65467800
C	-1.34697800	-0.98590300	-1.21282300
H	-1.19814000	-1.96377500	-1.64801100
C	-2.38794300	-0.61825400	-0.38865100
H	-3.12672000	-1.28708300	0.03012100
C	-1.10209700	1.27170800	-0.65581900
H	-0.99005600	2.33165200	-0.85005400
C	-2.28074700	0.74707100	-0.08398600
H	-2.94238100	1.28570800	0.58005600

TS28o

E = -539.537087 a.u.
1 imaginary frequency -417.2890 cm-1

C	-0.58629500	1.11949000	0.43400200
C	-0.09657900	-0.29184800	0.58166400
C	-1.86125400	1.47679600	-0.05413500
C	-0.95601300	-1.43791300	0.67329200
C	-2.93893000	0.68380300	-0.42717300
C	-2.22971800	-1.62505200	0.19540100
C	-3.11223600	-0.68968100	-0.35801500
H	-0.50140600	-2.31009100	1.13700400
H	-2.62312200	-2.63376400	0.29660400
H	-4.06539800	-1.07402700	-0.70616900
H	-3.78656200	1.23553600	-0.82646700
H	-1.98004300	2.55083000	-0.15961400
H	0.66721500	-0.29643300	1.36520600
O	0.28423200	1.98031700	0.67088600
C	2.10301000	-1.46163600	-0.36337100
H	2.49993500	-1.96173500	-1.25586000
H	1.71253600	-2.24309600	0.29124100
C	3.18147700	-0.63723800	0.26835900
H	3.99330700	-1.05427300	0.85031100
C	2.99887900	0.66983300	-0.01368200
H	3.64453700	1.48536500	0.28023800
C	1.08300200	-0.40943100	-0.79611700
H	0.44144600	-0.62289300	-1.64463600
C	1.78400600	0.82909900	-0.75775100
H	1.50760800	1.72471500	-1.28980000

TS45i

E = -539.546686 a.u.
1 imaginary frequency   -562.4246   cm-1

C	-0.50465900	0.79016700	-1.20286400
C	-0.51080000	-0.62295300	-1.30937800
C	-1.93883900	-1.15389500	0.31692000
C	-1.82829800	1.13864200	0.43505100
C	2.24992300	-0.03252200	0.25891400
C	1.77818800	1.28396700	-0.21257100
C	1.72762900	-1.28199000	-0.32177600
C	0.64221700	1.61035100	-0.84652900
C	0.59332500	-1.50707400	-1.00717500
H	0.51713200	2.66365200	-1.08842700
H	-1.18544100	1.29382000	-1.88133800
H	-1.20529700	-1.02874900	-2.03662100
H	0.43876100	-2.52992600	-1.34406300
H	2.38932100	-2.12253200	-0.13625500
H	2.47883500	2.07738900	0.02892900
O	3.16246900	-0.08322900	1.06823300
C	-2.75711200	0.05377100	-0.04248300
H	-3.07929200	0.12216100	-1.08094100
H	-3.65278500	0.06526500	0.59436400
H	-2.23891000	-2.16774300	0.08365600
C	-1.14835600	-0.79772200	1.41000600
H	-0.56248400	-1.48165500	2.00834500
H	-2.06302600	2.19290400	0.35028300
C	-1.08501500	0.59125200	1.48820000
H	-0.44579500	1.14928300	2.15831200

TS45o

E = -539.546326 a.u.
1 imaginary frequency   -581.3128   cm-1

C	-0.40795300	0.70980400	-1.10991300
C	-0.40793700	-0.70951200	-1.11015600
C	-1.67412700	1.14674600	0.60223300
C	-1.67440900	-1.14689100	0.60217400
C	2.46347400	-0.00007200	0.25553800
C	1.88895400	1.28758400	-0.17400700
C	1.88882100	-1.28761500	-0.17412700
C	0.71410400	1.56357200	-0.76712500
C	0.71398300	-1.56341200	-0.76738200
H	0.54611100	2.61142600	-1.00703400
H	-1.08548200	1.16851600	-1.81830700

H	-1.08555200	-1.16804800	-1.81858000
H	0.54592100	-2.61122000	-1.00744100
H	2.56056300	-2.11497700	0.03272900
H	2.56080800	2.11484700	0.03288300
O	3.48594100	-0.00014600	0.92362700
C	-1.07189400	-0.00018000	1.35744700
H	0.01258000	-0.00034200	1.44950400
H	-1.49251000	-0.00012700	2.37294700
H	-1.45707500	2.18212100	0.83302100
C	-2.90095200	0.69508700	0.09376700
H	-3.66055800	1.32408600	-0.35197800
H	-1.45740000	-2.18234100	0.83264000
C	-2.90108500	-0.69494900	0.09367300
H	-3.66081400	-1.32375100	-0.35213900

TS2o

E = -539.531437 a.u.
1 imaginary frequency -115.1251   cm-1

C	-0.81636000	1.28940800	0.59982800
C	-0.19303700	-0.04436500	0.99338800
C	0.86388500	-0.38814900	-0.34725600
C	1.81853400	-1.35275600	0.06453400
C	-1.75772900	1.33077300	-0.48142700
C	-1.06690100	-1.17170900	1.24105200
C	-2.30217100	0.27877700	-1.18082300
C	-1.94593200	-1.68849000	0.32308400
C	-2.33757000	-1.09486500	-0.88403400
H	-0.89112300	-1.73736400	2.15039400
H	-2.36782300	-2.66658200	0.54076400
H	-2.89693900	-1.71636900	-1.57557800
H	-2.85681700	0.56051800	-2.07356700
H	-1.99935400	2.33824900	-0.80338500
H	0.47340600	0.16419400	1.82861400
O	-0.38858900	2.29945700	1.15179200
C	1.68755100	0.82436400	-0.77348600
H	1.45636800	1.70949800	-0.16165600
H	1.48386500	1.12176100	-1.80848800
C	3.09300200	0.40920200	-0.54980700
H	3.94387900	1.06100100	-0.70064800
C	3.13906200	-0.85653800	-0.05110800
H	4.03191100	-1.39303900	0.24053400
H	0.08450700	-0.72983700	-1.04493000
H	1.55283000	-2.32160800	0.46993800

CA23i

E = -539.60321184 a.u.

C	-1.21100000	-1.24611600	-0.28010300
C	0.14849300	-0.77563100	-0.76801700
C	-2.14001100	-0.42465100	0.52110400
C	0.54612400	0.70694000	-1.04693800
C	-2.26368100	0.90798800	0.56394700
C	-0.38181300	1.85604600	-0.82765500
C	-1.51992200	1.94812900	-0.13496900
H	0.86036000	0.76468000	-2.09465900
H	-0.01948100	2.77974200	-1.27626200
H	-1.97438400	2.93322300	-0.07892000
H	-3.08000300	1.28651400	1.17443500
H	-2.85980200	-1.03131300	1.06148800
H	0.30874500	-1.35680800	-1.67865300
O	-1.50834800	-2.40516200	-0.49347400
C	2.47449700	-0.51521900	-0.32198600
H	2.68809300	-0.79165600	-1.35841100
H	3.36749100	-0.64233900	0.29216400
C	1.85039800	0.87923300	-0.17100100
H	2.45409600	1.73820500	-0.46270100
C	1.40141900	0.82666900	1.27562600
H	1.28830200	1.68541500	1.92326400
C	1.25015100	-1.23381500	0.26455800
H	1.29277600	-2.31595100	0.37090200
C	1.03998600	-0.43019100	1.53238400
H	0.57275900	-0.80470900	2.43344800

CA23o

E = -539.6019042 a.u.

C	1.18865800	1.30188700	-0.28235000
C	-0.17475800	0.71034900	-0.60176800
C	2.20506800	0.61973900	0.55088600
C	-0.42107600	-0.80918900	-0.86331700
C	2.48675500	-0.68783900	0.59194100
C	0.67478000	-1.82240800	-0.75169800
C	1.85081200	-1.79159700	-0.11826000
H	-0.83975100	-0.91972300	-1.86663400
H	0.41440500	-2.76848600	-1.22277200
H	2.43078800	-2.70999900	-0.12719100
H	3.34747500	-0.97693900	1.18979800
H	2.85288400	1.31429200	1.07587300
H	-0.50709600	1.29079200	-1.46218400
O	1.41507800	2.43886900	-0.64241200
C	-1.07524100	-0.31769900	1.38663200
H	-1.77288300	-0.34911500	2.22511700
H	-0.07059500	-0.57561300	1.72742700
C	-1.55344600	-1.15478300	0.19021600

H	-1.68482500	-2.22475600	0.34678900
C	-2.78374700	-0.37690500	-0.22563800
H	-3.64073700	-0.79848900	-0.73505400
C	-1.14980500	1.00583600	0.61069100
H	-0.91282800	1.92565700	1.14262300
C	-2.54427800	0.90956100	0.02652100
H	-3.15979500	1.75971200	-0.23764200

CA27o

E = -539.6182421 a.u.

C	0.06173700	0.00152500	1.22836000
C	0.02150400	1.29157000	0.41806500
C	0.02138800	-1.29054700	0.42129600
C	1.38397600	1.59985500	-0.14226900
C	1.38343700	-1.60038200	-0.13917800
C	2.34310000	0.73382400	-0.49434600
C	2.34267700	-0.73538000	-0.49340900
H	1.59849800	2.65705600	-0.27137400
H	3.26367800	1.16944000	-0.87246200
H	3.26260500	-1.17201100	-0.87194600
H	1.59704400	-2.65788900	-0.26735100
H	-0.25223300	-2.07926500	1.12638800
H	-0.25225900	2.08204000	1.12114600
O	0.13293000	0.00299600	2.42965700
C	-0.75804500	-0.00199400	-1.61198300
H	0.26511000	-0.00260600	-1.98524700
H	-1.44270200	-0.00302900	-2.46346900
C	-1.08717000	-1.17833000	-0.68380100
H	-1.19411600	-2.13460600	-1.19910000
C	-2.35769300	-0.66635000	-0.02859600
H	-3.08912200	-1.30135500	0.45609800
C	-1.08690600	1.17674800	-0.68681500
H	-1.19367700	2.13171800	-1.20457300
C	-2.35757700	0.66670100	-0.03034600
H	-3.08883900	1.30310100	0.45277300

CA28o

E = -539.6113812 a.u.

C	-0.42640900	-0.86564200	0.26109100
C	-0.18976000	0.59495500	-0.02140600
C	-1.50358300	-1.56861000	-0.13311100
C	-1.27777300	1.39439700	0.64379800
C	-2.66211900	-0.97355900	-0.74590300
C	-2.56862400	1.28789900	0.29614600

C	-3.12558000	0.29236400	-0.59237100
H	-0.98535300	2.09629600	1.42015700
H	-3.27653800	1.97920300	0.74661800
H	-4.07105900	0.53785900	-1.06674400
H	-3.27454700	-1.64910700	-1.33767000
H	-1.48385500	-2.64450300	-0.00098900
H	-0.23990000	0.74943200	-1.10705600
O	0.60694600	-1.42392900	0.92275800
C	2.20774100	1.42218800	-0.53892000
H	2.94338600	2.09328700	-0.08171400
H	1.69725100	1.99858100	-1.31597100
C	2.88722900	0.18847900	-1.07551200
H	3.52277000	0.20671000	-1.95337000
C	2.64454500	-0.88666600	-0.33525100
H	3.04155500	-1.88017700	-0.50130000
C	1.23245200	0.85798700	0.51243200
H	1.18964300	1.48041300	1.40738900
C	1.75062500	-0.56395900	0.83217200
H	2.26862200	-0.65556200	1.78960100

CA45i

E = -539.6025994 a.u.

C	-0.66754500	0.78047500	-0.95966700
C	-0.66749500	-0.78043300	-0.95968100
C	-1.75931300	-1.11965700	0.13175000
C	-1.75939100	1.11963000	0.13174900
C	2.34245700	-0.00000600	0.14882800
C	1.76537700	1.30268700	-0.25502900
C	1.76540800	-1.30272700	-0.25494800
C	0.55973300	1.59913100	-0.73696400
C	0.55979600	-1.59910600	-0.73700000
H	0.38925200	2.65290900	-0.95640400
H	-1.07827400	1.10813500	-1.92091000
H	-1.07821900	-1.10811200	-1.92092000
H	0.38925200	-2.65286500	-0.95647400
H	2.47278000	-2.11235400	-0.10252500
H	2.47278400	2.11229800	-0.10267200
O	3.38321500	0.00004300	0.77963300
C	-2.77422500	-0.00007800	-0.14024700
H	-3.16221200	-0.00007400	-1.16313900
H	-3.59998100	-0.00008900	0.57257200
H	-2.11542300	-2.14794000	0.07863900
C	-1.19259900	-0.66638800	1.46092400
H	-0.75869700	-1.31897300	2.20625600
H	-2.11561300	2.14787000	0.07858900
C	-1.19263700	0.66643900	1.46090100
H	-0.75875700	1.31904700	2.20622900

CA45o

E = -539.6008116 a.u.

C	0.55241700	-0.78064100	-0.75878600
C	0.55241700	0.78064200	-0.75878600
C	1.56941600	-1.11839800	0.40707200
C	1.56941600	1.11839800	0.40707300
C	-2.56109800	0.00000000	0.13595700
C	-1.92795300	-1.30134800	-0.17007500
C	-1.92795300	1.30134800	-0.17007500
C	-0.68775300	-1.59155500	-0.56116000
C	-0.68775400	1.59155600	-0.56115900
H	-0.49396000	-2.65078400	-0.72862000
H	0.98773800	-1.12749600	-1.70012600
H	0.98773800	1.12749700	-1.70012500
H	-0.49396000	2.65078500	-0.72862000
H	-2.62869800	2.12050900	-0.04012100
H	-2.62869700	-2.12051000	-0.04012100
O	-3.68036000	0.00000000	0.61446900
C	1.22403900	0.00000000	1.40132700
H	0.17598900	0.00000000	1.71197100
H	1.87204500	0.00000000	2.27886000
H	1.49657400	-2.14568300	0.76171400
C	2.93365900	-0.66609400	-0.06968600
H	3.70822900	-1.32417000	-0.44218800
H	1.49657500	2.14568300	0.76171500
C	2.93366000	0.66609300	-0.06968600
H	3.70822900	1.32417000	-0.44218800

IN2o

E = -539.531552086 a.u.

C	-0.86499700	1.30038000	0.58604200
C	-0.21220200	-0.01679900	1.01494000
C	0.83356500	-0.36443100	-0.21941400
C	1.82695900	-1.30225000	0.20021900
C	-1.73069900	1.29341800	-0.55609500
C	-1.10612700	-1.14636700	1.27245500
C	-2.17280000	0.20413600	-1.27585600
C	-1.89650800	-1.71171200	0.31474400
C	-2.17413200	-1.16282400	-0.95400900
H	-1.02928200	-1.63237800	2.23930900
H	-2.34775100	-2.67525600	0.53825200
H	-2.64325600	-1.82067600	-1.67859000
H	-2.65737000	0.44467700	-2.22020900

H	-1.99213600	2.28438500	-0.91183100
H	0.39567100	0.22746600	1.88573900
O	-0.50240000	2.32671400	1.15321600
C	1.63313800	0.83800800	-0.72528700
H	1.47087700	1.71066900	-0.07075500
H	1.33121700	1.17071700	-1.72457500
C	3.04497300	0.40626300	-0.63323100
H	3.88542200	1.02860900	-0.91343800
C	3.12896700	-0.83443400	-0.07048500
H	4.04249800	-1.36500400	0.16196900
H	0.11232900	-0.77402000	-0.95718900
H	1.59016000	-2.23323000	0.70144200