Supplementary Information Material

Towards a Unified Fold-Cusp Model for Bond Polarity Scaling: Electron Rearrangements in the Pyrolytic Isomerization of Cubane to Cyclooctatetraene

Leandro Ayarde-Henríquez,[1*] Cristian Guerra,[2*] Patricia Pérez[3*], and Eduardo Chamorro[4*]

[1]Trinity College Dublin. School of Physics, Dublin 2, Ireland. AMBER, Advanced Materials and BioEngineering Research Centre, Dublin 2, D02 CP49, Ireland. Corresponding Author (L. Ayarde-Henríquez). E-mail: leandro.ayarde@tcd.ie ORCID ID: https://orcid.org/0000-0001-5963-6028.

[2]Universidad Autónoma de Chile. Facultad de Ingeniería. Avenida Pedro de Valdivia 425, 7500912, Santiago, Chile; Universidad de Córdoba. Grupo de Química Computacional. Facultad de Ciencias Básicas. Carrera 6 No. 77-305, Montería-Córdoba, Colombia. Corresponding Author (C. Guerra). E-mail: guerracbn@gmail.com. ORCID-ID: https://orcid.org/0000-0002-9664-2504.

[3]Universidad Andrés Bello. Facultad de Ciencias Exactas. Departamento de Ciencias Químicas. Avenida República 275, 8370146, Santiago, Chile. Corresponding Author (P. Pérez). E-mail: p.perez@unab.cl ORCID-ID: https://orcid.org/0000-0002-6920-703X.

[4] Departamento de Investigación y Desarrollo. ConsultoresAcademicos SpA. Santiago 1137, 8340457 Santiago, Chile. Corresponding Author (E. Chamorro). E-mail: ed.chamorro9@gmail.com. ORCID-ID: https://orcid.org/0000-0002-9200-9859.

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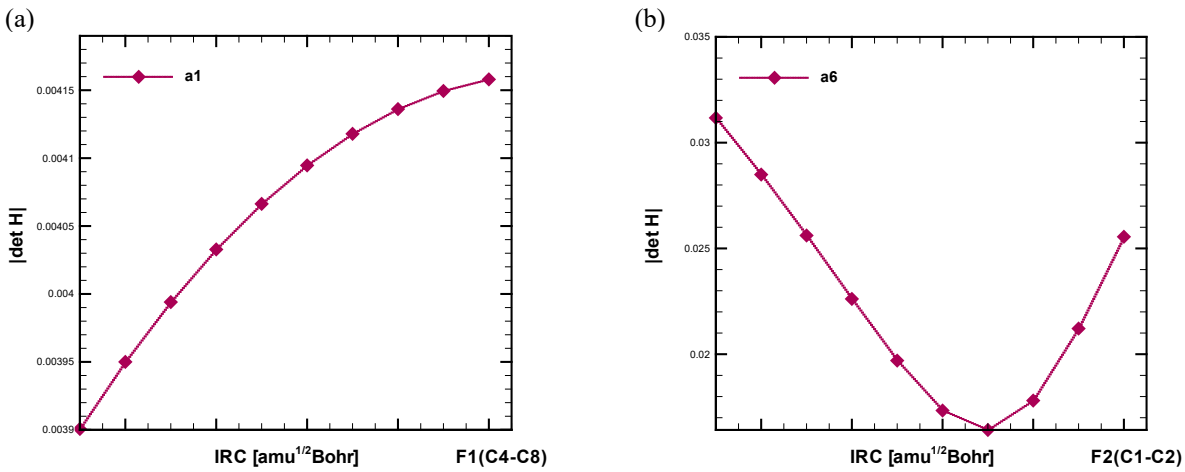


Figure S1. Variation in the modulus of the Hessian determinant, |det H|, at a1 (Panel a) and at a2 (Panel b) along the IRC for the process $CUB \rightarrow BOT$. Neither a1 nor a6 are degenerated CPs since the |det H| increases before the change in the ELF phase-space, indicating that C4-C8 and C1-C2 bond breakings must be described in terms of the fold polynomial. See Scheme 2 in the main text, namely $SSD\ I \rightarrow SSD\ II \rightarrow SSD\ III$.

(a) (b)

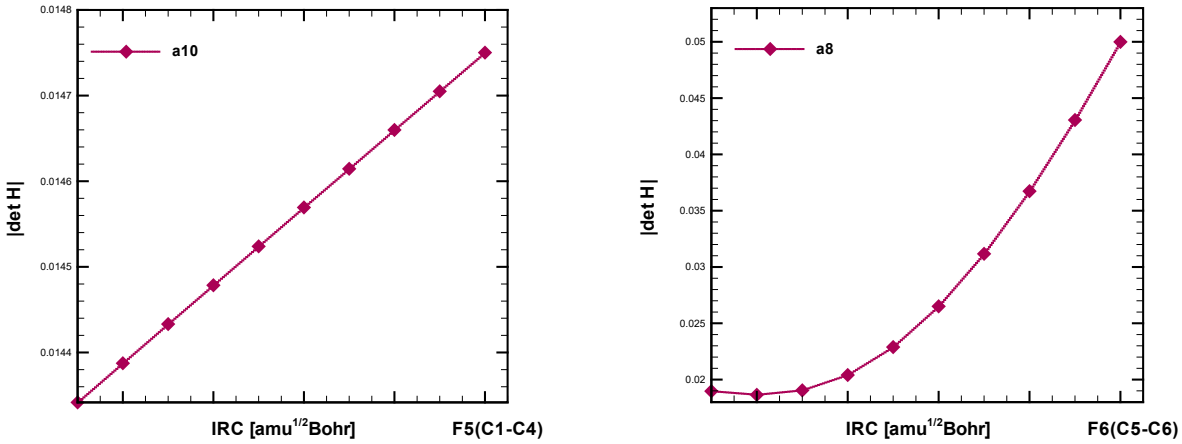
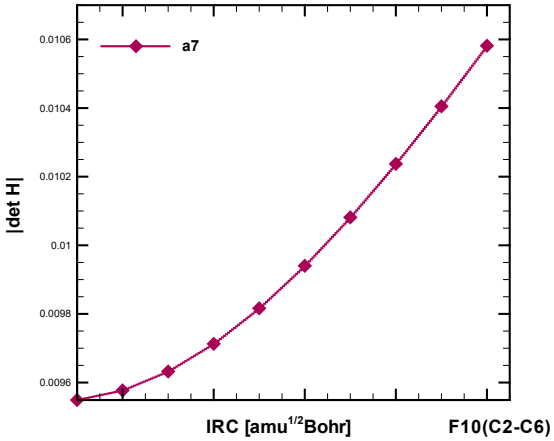


Figure S2. Variation in the modulus of the Hessian determinant, |det H|, at a10 (Panel a) and at a8 (Panel b) along the IRC for the process $CUB \rightarrow BOT$. Neither a10 nor a8 are degenerate CPs since the |det H| at them increases before the change in the ELF topography. This means that the double bond formation between C1 and C4 as well as the C5-C6 bond cleavage occurs through fold catastrophes. See Scheme 2 in the main text, namely $SSD\ VI \rightarrow SSD\ VII \rightarrow SSD\ VIII$.

(a)



(b)

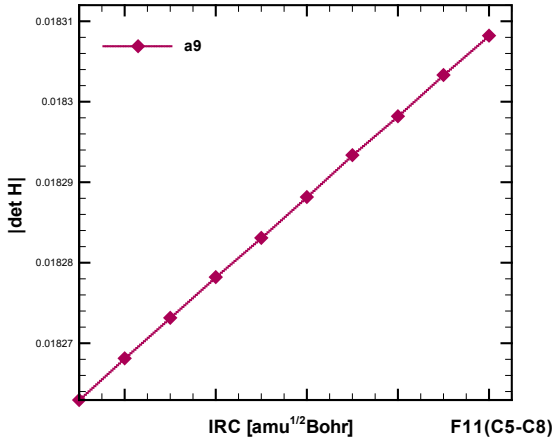


Figure S3. Variation in the modulus of the Hessian determinant, |det H|, at a7 (Panel a) and at a9 (Panel b) along the IRC for the process $CUB \rightarrow BOT$. Maxima a7 and a9 are not degenerate CPs since the |det H| at them increases before the change in the ELF topography. This means the double bond formation in the C2-C4 and C5-C8 regions occurs through fold catastrophes. See Scheme 2 in the main text, namely $SSD\ XI \rightarrow SSD\ XII \rightarrow SSD\ XIII$.

(a) (b)

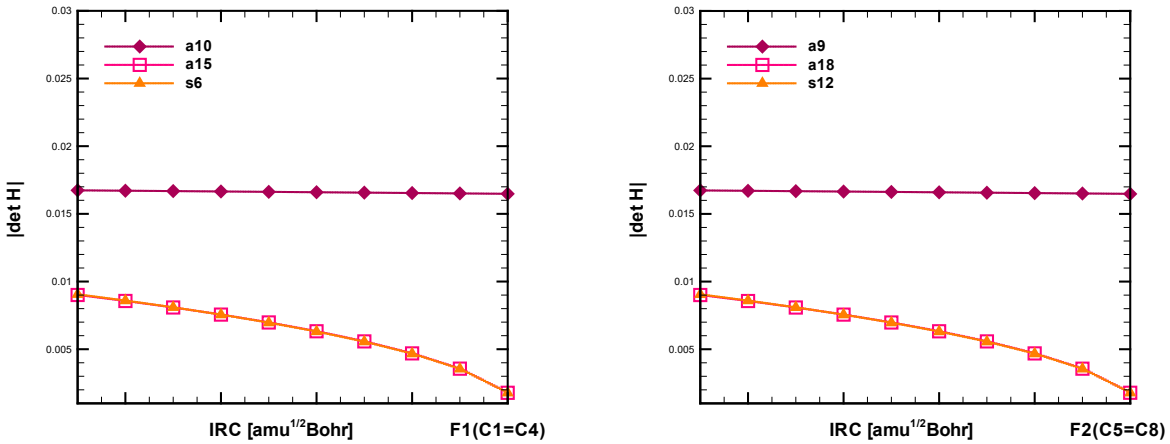


Figure S4. Variation in the modulus of the Hessian determinant, |det H|, at CPs a10, a15, and s6 (Panel a) and at points a9, a18, and s12 (Panel b) along the IRC for the process $BOT \rightarrow COT$. The remaining ELF maxima a9 and a10 are not degenerate CPs as the |det H| at them remains almost constant throughout the change in the phase space. However, the similar dropping ratio in |det H| at both (a15, s6) and (a18, s12) pairs constitutes a solid flag of a catastrophic bifurcation, as indicated by the degenerative process exhibited by these CPs. Thus, the double to single bond reductions co-occur through fold catastrophes. See Scheme 3 in the main text, namely $SSD\ I\ \rightarrow$ SSD II.

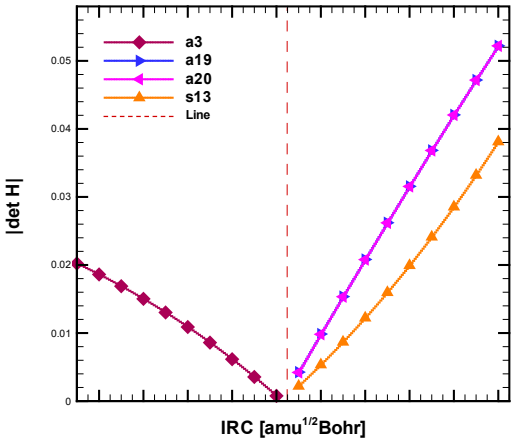
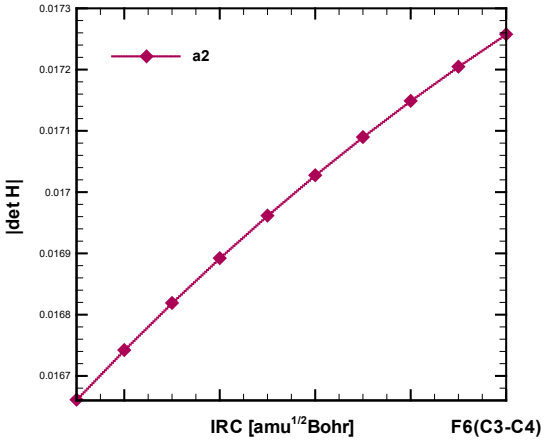
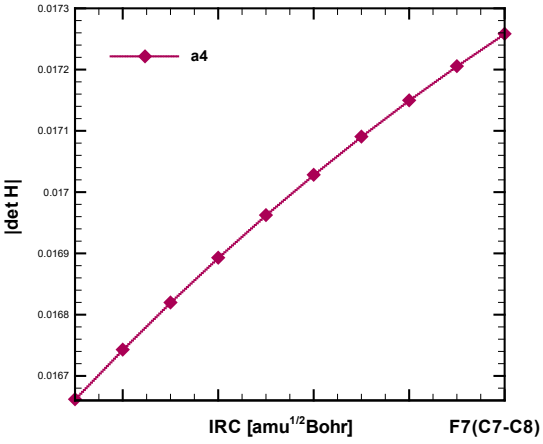


Figure S5. Variation in the modulus of the Hessian determinant, |det H|, at points a3, a19, a20, and s13 as we move along the IRC for the process $BOT \rightarrow COT$. The maximum a3 splits into three new CPs (a19, a20, and s13) through an abrupt change described by the cusp function, which is revealed by the symmetry in the |det H| at the new ELF maxima. The dashed red line indicates the C3-C7 homolysis via the discontinuous transformation in the ELF phase-space. See Scheme 3 in the main text, namely $SSD\ II \rightarrow$ SSD III.

(a)



(b)



(c)

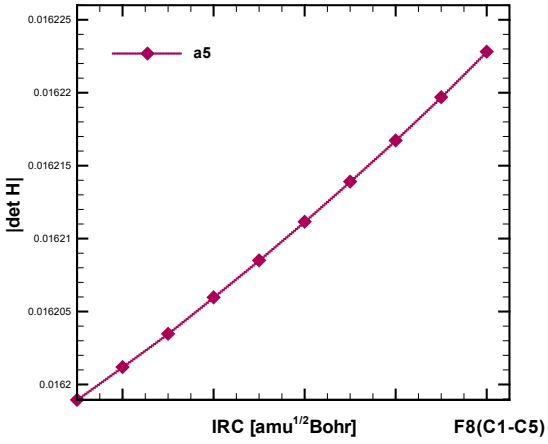


Figure S6. Variation in the modulus of the Hessian determinant, |det H|, at points a2 (Panel a), a4 (Panel b), and a5 (Panel c) when we traverse the IRC for the process $BOT \rightarrow COT$. The onset of forming double bonding at C3-C4 and C7-C8 regions are of the fold type since neither a2 nor a4 are degenerate. Similarly, the evolution of a double bond at C1-C5 can described via a fold catastrophe because the ELF maximum a5 is not involved in the topographical change. See Scheme 3 in the main text, namely $SSD\ IV$ → SSD V → SSD VI.

Optimized cartesian coordinates for minima and the first-order saddle point (TS) featuring the pyrolytic isomerization of cubane to bicyclo[4.2.0]octa-2,4,7-triene at the B3LYP/6-31G(d), and B3LYP/6-31+G(d,p) DFT levels.

B3LYP/6-31G(d)

cubane

C	0.21996400	-0.04121500	-1.34136500
C	-0.61575100	1.05762200	-0.59304000
C	0.50114900	1.15848100	0.50615800
C	1.33689500	0.05963400	-0.24218400
H	0.39656800	-0.07431200	-2.41834200
H	-1.11008800	1.90676200	-1.06922300
H	0.90350700	2.08859500	0.91255100
H	2.41023300	0.10749600	-0.43663000
C	-0.50114900	-1.15848100	-0.50615800
C	-1.33689500	-0.05963400	0.24218400
C	-0.21996400	0.04121500	1.34136500
C	0.61575100	-1.05762200	0.59304000
H	-0.90350700	-2.08859500	-0.91255100
H	-2.41023300	-0.10749500	0.43663200
H	-0.39656900	0.07431200	2.41834200
H	1.11008700	-1.90676200	1.06922300

bicyclo[4.2.0]octa-2,4,7-triene

C	1.70067900	-0.73240100	-0.26810900
C	-1.71169600	-0.66990200	-0.48700800
C	-1.71169600	0.66990200	-0.48700800
C	1.70067900	0.73240100	-0.26810900
H	2.60450300	-1.24098100	-0.59642500
H	-2.25066100	-1.42143300	-1.05925100
H	-2.25066100	1.42143300	-1.05925100
H	2.60450300	1.24098100	-0.59642500
C	0.64416300	-1.44637500	0.15439200
C	-0.64000000	-0.79566800	0.59199100
C	-0.64000000	0.79566800	0.59199100
C	0.64416300	1.44637500	0.15439200
H	0.68804000	-2.53417800	0.17654900
H	-1.00075700	-1.23866000	1.53152900
H	-1.00075700	1.23866000	1.53152900
H	0.68803900	2.53417800	0.17654900

TS

C	0.33215500	-0.36461400	-1.36300200
C	-0.75858900	1.13289600	-0.40144400
C	0.43282900	1.09081400	0.51073000
C	1.30899200	-0.04200000	-0.24213900
H	0.68209500	-0.51773300	-2.38570200
H	-1.20995900	1.88652300	-1.03457300
H	0.91395400	1.97039300	0.93592400
H	2.34336100	0.14168500	-0.55120000
C	-0.81244500	-1.01829900	-0.86854200
C	-1.32620700	-0.14514600	0.26295300
C	-0.17903400	-0.09753200	1.32732700
C	0.94197500	-1.04054300	0.85480200
H	-1.53626500	-1.43567200	-1.57095500

H	-2.37869300	-0.25339800	0.54193700
H	-0.45676300	-0.01937500	2.38102000
H	1.70259200	-1.28799700	1.60286500

B3LYP/6-31+G(d,p)

cubane

C	0.22014700	0.04126300	1.34247500
C	-0.61624400	-1.05852700	0.59354700
C	0.50157800	-1.15944500	-0.50657800
C	1.33795700	-0.05967900	0.24237100
H	0.39672700	0.07436200	2.41919100
H	-1.11050800	-1.90745000	1.06959500
H	0.90385000	-2.08932600	-0.91288800
H	2.41103800	-0.10756500	0.43678600
C	-0.50157800	1.15944500	0.50657800
C	-1.33795700	0.05967900	-0.24237100
C	-0.22014700	-0.04126300	-1.34247500
C	0.61624400	1.05852700	-0.59354700
H	-0.90385000	2.08932600	0.91288800
H	-2.41103800	0.10756500	-0.43678600
H	-0.39672700	-0.07436200	-2.41919100
H	1.11050800	1.90745000	-1.06959500

bicyclo[4.2.0]octa-2,4,7-triene

C	-0.26771300	-1.70464100	0.73284800
C	-0.48457200	1.71634300	0.67136700
C	-0.48457200	1.71634300	-0.67136700
C	-0.26771300	-1.70464100	-0.73284800
H	-0.59368800	-2.60779900	1.24274400
H	-1.05170500	2.26103700	1.42177400
H	-1.05170500	2.26103700	-1.42177400
H	-0.59368800	-2.60779900	-1.24274400
C	0.15197200	-0.64434200	1.44803100
C	0.59030300	0.63924100	0.79611700
C	0.59030300	0.63924100	-0.79611700
C	0.15197200	-0.64434200	-1.44803100
H	0.17553800	-0.69056200	2.53524000
H	1.52991600	0.99771500	1.23931900
H	1.52991600	0.99771500	-1.23931900
H	0.17553800	-0.69056200	-2.53524000

TS

C	0.33308900	-0.35927200	-1.35219400
C	-0.74623200	1.09141800	-0.42828300
C	0.44000400	1.07322900	0.50199100
C	1.31738100	-0.06083800	-0.23259600
H	0.66452300	-0.46601200	-2.38561400
H	-1.20612400	1.83990900	-1.06147800
H	0.90211000	1.96824700	0.91440000
H	2.35007700	0.11610900	-0.54749400
C	-0.83415500	-1.00118400	-0.88234600
C	-1.32647100	-0.16450000	0.27785300
C	-0.17772400	-0.10781600	1.33342200
C	0.95954400	-1.04582100	0.88304000

H	-1.56752600	-1.35630700	-1.60726400
H	-2.37640800	-0.26631200	0.56236400
H	-0.45886100	-0.02153200	2.38510800
H	1.72677000	-1.23931500	1.63909600

Optimized Cartesian coordinates for minima and the first-order saddle point (TS) featuring the pyrolytic isomerization of bicyclo[4.2.0]octa-2,4,7-triene to 1,3,5,7-cyclooctatetraene at the B3LYP/6-31+G(d,p), ωB97X-D/6-31+G(d,p), M06-2X/6-31+G(d,p), and MN15-L/6-31+G(d,p) DFT levels.

B3LYP/6-31+G(d,p)

bicyclo[4.2.0]octa-2,4,7-triene

C	-0.26771300	-1.70464100	0.73284800
C	-0.48457200	1.71634300	0.67136700
C	-0.48457200	1.71634300	-0.67136700
C	-0.26771300	-1.70464100	-0.73284800
H	-0.59368800	-2.60779900	1.24274400
H	-1.05170500	2.26103700	1.42177400
H	-1.05170500	2.26103700	-1.42177400
H	-0.59368800	-2.60779900	-1.24274400
C	0.15197200	-0.64434200	1.44803100
C	0.59030300	0.63924100	0.79611700
C	0.59030300	0.63924100	-0.79611700
C	0.15197200	-0.64434200	-1.44803100
H	0.17553800	-0.69056200	2.53524000
H	1.52991600	0.99771500	1.23931900
H	1.52991600	0.99771500	-1.23931900
H	0.17553800	-0.69056200	-2.53524000

1,3,5,7-cyclooctatetraene

C	1.68639000	-0.88173400	-0.57668600
C	-1.32856900	-0.86570700	0.30697600
C	-1.32175900	0.47893700	0.30581000
C	1.69319700	0.46291100	-0.57786100
H	2.29336800	-1.38625700	-1.32963600
H	-2.25086000	-1.36209000	0.00220900
H	-2.23897500	0.98411000	0.00017100
H	2.30524900	0.95994400	-1.33168400
C	1.02969900	-1.77615000	0.39388400
C	-0.26066300	-1.76929100	0.77208200
C	-0.24475400	1.37247100	0.76935600
C	1.04560600	1.36561900	0.39114600
H	1.66136800	-2.57580100	0.78305600
H	-0.59012500	-2.56383600	1.44294200
H	-0.56614500	2.17147700	1.43883200
H	1.68534600	2.15950600	0.77893000

TS

C	1.41012700	-0.68079300	-0.48620900
C	-1.71247800	-0.65820800	0.09962600
C	-1.71997300	0.66697100	0.11411800
C	1.40209400	0.73786500	-0.47063700
H	2.25616600	-1.14490100	-0.98947100
H	-2.34590000	-1.35875200	-0.44247500

H	-2.36133000	1.37199000	-0.41263400
H	2.24275500	1.22246200	-0.96348900
C	0.66398800	-1.46771100	0.38043000
C	-0.56349900	-1.06635900	0.97386900
C	-0.57561500	1.06887200	0.99726800
C	0.64717900	1.49706000	0.41296800
H	1.12606100	-2.39542400	0.72267400
H	-0.83432000	-1.59453800	1.89341100
H	-0.85234100	1.57362800	1.92813800
H	1.09873700	2.42222200	0.77554600

ωB97X-D/6-31+G(d,p)

bicyclo[4.2.0]octa-2,4,7-triene

C	-0.26673800	-1.69760900	0.73334400
C	-0.48641200	1.70581100	0.66905300
C	-0.48641200	1.70581100	-0.66905300
C	-0.26673800	-1.69760900	-0.73334400
H	-0.59495700	-2.59819700	1.24450600
H	-1.05645100	2.24461300	1.41968500
H	-1.05645100	2.24461300	-1.41968500
H	-0.59495700	-2.59819700	-1.24450600
C	0.15319400	-0.64089500	1.44256400
C	0.59148400	0.63905700	0.79045300
C	0.59148400	0.63905700	-0.79045300
C	0.15319400	-0.64089500	-1.44256400
H	0.17341600	-0.68312500	2.52916600
H	1.52882800	0.99852400	1.23314500
H	1.52882800	0.99852400	-1.23314500
H	0.17341600	-0.68312500	-2.52916600

1,3,5,7-cyclooctatetraene

C	1.66624100	-0.87873500	-0.58711500
C	-1.31717200	-0.86283700	0.28720600
C	-1.31041600	0.47596300	0.28604900
C	1.67296800	0.46005600	-0.58827700
H	2.24331300	-1.38904300	-1.35774500
H	-2.22390400	-1.36533900	-0.04839300
H	-2.21204200	0.98700300	-0.05041200
H	2.25512900	0.96320300	-1.35979300
C	1.03145700	-1.75986700	0.40986000
C	-0.25329100	-1.75293400	0.78639100
C	-0.23757700	1.35610900	0.78368600
C	1.04717500	1.34928400	0.40718300
H	1.67608500	-2.53597700	0.82146000
H	-0.58140700	-2.52386800	1.48303600
H	-0.55784700	2.13156600	1.47896000
H	1.69966000	2.11952500	0.81743100

TS

C	1.38727100	-0.67629800	-0.49595500
C	-1.69818200	-0.65575300	0.09443500
C	-1.70549600	0.66472900	0.10866300
C	1.37935500	0.73345600	-0.48045500
H	2.22743800	-1.13973000	-1.00825400

H	-2.32606600	-1.35350600	-0.45463900
H	-2.34108900	1.36715900	-0.42537000
H	2.21422200	1.21743300	-0.98232000
C	0.66212400	-1.45959300	0.39368500
C	-0.56298300	-1.07470700	0.97408000
C	-0.57513400	1.07719100	0.99754500
C	0.64547800	1.48876500	0.42607700
H	1.15174700	-2.36198900	0.76039800
H	-0.84184200	-1.60402100	1.88882700
H	-0.86006100	1.58291700	1.92369500
H	1.12487300	2.38832700	0.81271900

M06-2X/6-31+G(d,p)

bicyclo[4.2.0]octa-2,4,7-triene

C	-0.26894600	-1.69297500	0.73406400
C	-0.49246400	1.69678100	0.66896100
C	-0.49246400	1.69678100	-0.66896100
C	-0.26894600	-1.69297500	-0.73406400
H	-0.60067300	-2.59190800	1.24569300
H	-1.06940400	2.22672000	1.42109300
H	-1.06940400	2.22672000	-1.42109300
H	-0.60067300	-2.59190800	-1.24569300
C	0.15881300	-0.63877600	1.44238100
C	0.59569000	0.64143800	0.78941900
C	0.59569000	0.64143800	-0.78941900
C	0.15881300	-0.63877600	-1.44238100
H	0.18204600	-0.68168500	2.52907000
H	1.52947500	1.00806200	1.23272100
H	1.52947500	1.00806200	-1.23272100
H	0.18204600	-0.68168500	-2.52907000

1,3,5,7-cyclooctatetraene

C	1.65772500	-0.87866500	-0.59322400
C	-1.31328200	-0.86285000	0.27751500
C	-1.30652400	0.47589500	0.27633500
C	1.66449700	0.46008800	-0.59438400
H	2.22421800	-1.39094100	-1.37042200
H	-2.21474200	-1.36723500	-0.06936600
H	-2.20284600	0.98874900	-0.07143600
H	2.23614000	0.96524800	-1.37246500
C	1.03374300	-1.75322100	0.41765700
C	-0.25098700	-1.74637300	0.79418100
C	-0.23533700	1.34954600	0.79146600
C	1.04941000	1.34267600	0.41498200
H	1.68278900	-2.52102200	0.83784200
H	-0.57802500	-2.50893800	1.50050500
H	-0.55463700	2.11660300	1.49646500
H	1.70623000	2.10454800	0.83387500

TS

C	1.37932000	-0.67726300	-0.49947100
C	-1.69283000	-0.65581900	0.08890800
C	-1.70026800	0.66502200	0.10328500
C	1.37136000	0.73430800	-0.48395700

H	2.21715800	-1.13996800	-1.01583000
H	-2.31257400	-1.35733900	-0.46502400
H	-2.32794300	1.37141700	-0.43530500
H	2.20385600	1.21766600	-0.98992200
C	0.66179800	-1.45707500	0.39868500
C	-0.56235400	-1.06649400	0.98034600
C	-0.57448200	1.06887700	1.00370900
C	0.64512400	1.48602900	0.43100700
H	1.15154800	-2.35909500	0.76582800
H	-0.84237000	-1.58732400	1.89918600
H	-0.86035500	1.56620400	1.93369200
H	1.12466300	2.38523400	0.81799400

MN15-L/6-31+G(d,p)

bicyclo[4.2.0]octa-2,4,7-triene

C	-0.27652300	-1.69368200	0.73498600
C	-0.51062300	1.68505000	0.67628200
C	-0.51062300	1.68505000	-0.67628200
C	-0.27652300	-1.69368200	-0.73498600
H	-0.61927200	-2.59917000	1.25251500
H	-1.11496800	2.19535200	1.43872200
H	-1.11496800	2.19535200	-1.43872200
H	-0.61927200	-2.59917000	-1.25251500
C	0.17411500	-0.63589000	1.45287500
C	0.61003700	0.65247300	0.79633600
C	0.61003700	0.65247300	-0.79633600
C	0.17411500	-0.63589000	-1.45287500
H	0.20485800	-0.68212500	2.55070100
H	1.54734300	1.03823900	1.25029300
H	1.54734300	1.03823900	-1.25029300
H	0.20485800	-0.68212500	-2.55070100

1,3,5,7-cyclooctatetraene

C	1.66958600	-0.88608100	-0.59636600
C	-1.32507800	-0.87016200	0.28134400
C	-1.31823200	0.48330000	0.28019900
C	1.67643500	0.46739100	-0.59755300
H	2.25752300	-1.40162700	-1.37258000
H	-2.24401000	-1.37768100	-0.05325200
H	-2.23197100	0.99953900	-0.05527800
H	2.26956900	0.97558800	-1.37465900
C	1.04062400	-1.76558900	0.41528200
C	-0.25820800	-1.75868200	0.79594900
C	-0.24241100	1.36187500	0.79326000
C	1.05642000	1.35499100	0.41255600
H	1.69078100	-2.55362000	0.82792100
H	-0.59048000	-2.54151100	1.49648100
H	-0.56671300	2.14925800	1.49242000
H	1.71453400	2.13712200	0.82380300

TS

C	1.38690300	-0.68337100	-0.50567100
C	-1.70203300	-0.66256700	0.08838500
C	-1.70947700	0.67164600	0.10281400

C	1.37889700	0.74070900	-0.48998600
H	2.23486100	-1.14974000	-1.02702900
H	-2.32257200	-1.37533900	-0.47526800
H	-2.33791300	1.38948300	-0.44545400
H	2.22151300	1.22792200	-1.00083500
C	0.66426400	-1.47095200	0.39797100
C	-0.56800700	-1.07132200	0.99121700
C	-0.58017600	1.07338300	1.01465600
C	0.64744500	1.49996700	0.43067200
H	1.15770900	-2.38665800	0.76313700
H	-0.85102800	-1.60352400	1.91885500
H	-0.86926900	1.58181600	1.95368000
H	1.13053800	2.41293100	0.81598600

Optimized Cartesian coordinates for minima and the first-order saddle point (TS) of reactions R1-R9.

R1
MN15-L/6-31G(d)

bicyclo[4.2.0]octa-2,4,7-triene

C	-0.27821700	-1.68939500	0.73457800
C	-0.51003700	1.68184600	0.67485900
C	-0.51003700	1.68184600	-0.67485900
C	-0.27821700	-1.68939500	-0.73457800
H	-0.62411800	-2.59648000	1.25129100
H	-1.11972500	2.18759700	1.43913000
H	-1.11972500	2.18759700	-1.43913000
H	-0.62411800	-2.59648000	-1.25129100
C	0.17629500	-0.63591000	1.45149900
C	0.61281300	0.65280100	0.79640500
C	0.61281300	0.65280100	-0.79640500
C	0.17629500	-0.63591000	-1.45149900
H	0.20587100	-0.68015300	2.55117400
H	1.55208400	1.03994100	1.24960000
H	1.55208400	1.03994100	-1.24960000
H	0.20587100	-0.68015300	-2.55117400

1,3,5,7-cyclooctatetraene

C	1.67120100	-0.88487300	-0.59385800
C	-1.32506900	-0.86894500	0.28430900
C	-1.31823600	0.48209000	0.28316500
C	1.67803800	0.46617000	-0.59504300
H	2.26100700	-1.40186800	-1.37048700
H	-2.24582200	-1.37789100	-0.04959400
H	-2.23378300	0.99977400	-0.05162000
H	2.27305200	0.97579700	-1.37256700
C	1.03866000	-1.76642400	0.41290500
C	-0.25784800	-1.75953600	0.79287300
C	-0.24204200	1.36272100	0.79018100
C	1.05446400	1.35584100	0.41017700
H	1.69014000	-2.55640800	0.82497900
H	-0.59155400	-2.54430000	1.49365600
H	-0.56775900	2.15205300	1.48959000
H	1.71392200	2.13990900	0.82085900

TS

C	1.38148200	-0.68218400	-0.50475100
C	-1.69847500	-0.66149400	0.08945200
C	-1.70585900	0.67056900	0.10378900
C	1.37351600	0.73948700	-0.48908300
H	2.22921400	-1.14740100	-1.02769000
H	-2.31687500	-1.37201000	-0.47900500
H	-2.33207100	1.38626700	-0.44941200
H	2.21594500	1.22555600	-1.00151700
C	0.66291000	-1.47103200	0.39916400
C	-0.56743600	-1.07472500	0.99250100
C	-0.57962300	1.07675800	1.01597500
C	0.64611400	1.50004600	0.43187800
H	1.16052800	-2.38457400	0.76341000
H	-0.85139500	-1.60878200	1.91861400
H	-0.86972400	1.58701500	1.95352600
H	1.13340600	2.41088900	0.81627900

R2
MN15-L/LANL2DZ

2-iodobicyclo[4.2.0]octa-2,4,7-triene

C	-0.93279400	-0.18100100	-2.89877500
C	-2.25782200	2.36747900	-1.02352500
C	-1.37969100	2.11685800	-0.00670800
C	0.03995800	-0.43681200	-1.81599600
H	-0.64936500	-0.49254200	-3.90935600
H	-2.61087500	3.27870900	-1.51314900
H	-0.75060000	2.73810100	0.63539400
H	0.99355500	-0.90715100	-2.07116500
C	-2.15064100	0.38924500	-2.66894600
C	-2.56801400	0.87634300	-1.29568400
C	-1.52935400	0.58267400	-0.09553700
C	-0.26078300	-0.11891400	-0.52732800
H	-2.86056100	0.52925600	-3.49264100
H	-3.60548400	0.57263000	-1.05831200
H	-1.97655900	0.09666200	0.79152900
I	1.13834700	-0.50990100	1.06581500

1-iodocycloocta-1,3,5,7-tetraene

C	1.69404800	-0.88672700	-0.58679000
C	-1.32567900	-0.86957000	0.28003600
C	-1.34359000	0.49325400	0.26312100
C	1.65316700	0.47538200	-0.63313500
H	2.28719500	-1.40399300	-1.35456600
H	-2.23089300	-1.39453700	-0.05846100
H	-2.25212400	0.99956600	-0.09218500
H	2.20227500	0.99935300	-1.42623700
C	1.06426900	-1.75675200	0.43572500
C	-0.24869700	-1.74542300	0.80921400
C	-0.27709900	1.38533300	0.79670300
C	1.01426200	1.34245500	0.38339300

H	1.70837500	-2.54438500	0.85112400
H	-0.58450600	-2.52664300	1.50639700
H	-0.58794400	2.14806900	1.52159500
I	2.41639100	2.79385500	1.23025000

TS

C	1.40776100	-0.68723300	-0.49288700
C	-1.71917000	-0.66646700	0.09303100
C	-1.70978000	0.68029900	0.07801000
C	1.40578500	0.74712300	-0.49054200
H	2.23584900	-1.15595700	-1.03833400
H	-2.35661400	-1.38023700	-0.43960200
H	-2.31787900	1.39668500	-0.48257100
H	2.22573300	1.24030400	-1.02247100
C	0.67019700	-1.47912700	0.40192100
C	-0.57425400	-1.07819400	1.00146500
C	-0.58304100	1.06950700	1.02116500
C	0.64125000	1.49334900	0.41788000
H	1.14022000	-2.41160900	0.74612400
H	-0.85491200	-1.61275900	1.92635500
H	-0.86648600	1.53959500	1.97602500
I	1.57414000	3.32523400	1.18622800

R3
MN15-L/LANL2DZ

2,5-diiodobicyclo[4.2.0]octa-2,4,7-triene

C	0.33999600	-0.48384900	-1.37109300
C	-1.21877700	2.25548900	0.02548800
C	-0.23554200	2.36216700	0.96882700
C	1.40390300	-0.36857800	-0.35025600
H	0.59275600	-0.97216700	-2.31602300
H	-1.75049300	2.96644800	-0.61095600
H	0.33519200	3.19282000	1.39016300
H	2.38813100	-0.77770000	-0.59332300
C	-0.91420000	-0.01121800	-1.13441000
C	-1.32352000	0.71849000	0.12573400
C	-0.15881100	0.84480300	1.24316100
C	1.15999600	0.21352200	0.85560900
H	-2.28159200	0.33278700	0.52066800
H	-0.47419300	0.52883700	2.25477300
I	2.70505400	0.37123300	2.34208500
I	-2.46234900	-0.18648900	-2.61569900

1,6-diiodocycloocta-1,3,5,7-tetraene

C	1.66233400	-0.89090900	-0.61899100
C	-1.34043100	-0.87508100	0.26108600
C	-1.33355800	0.48832700	0.25994600
C	1.66920300	0.47228800	-0.62016400
H	2.21175300	-1.42340700	-1.40611700
H	-2.24657400	-1.38826800	-0.09025500
H	-2.23447100	1.01005300	-0.09227000
H	2.22397200	0.99786600	-1.40818900
C	1.02144400	-1.73771900	0.41047500

C	-0.27810300	-1.76129800	0.80786300
C	-0.26231600	1.36472200	0.80520300
C	1.03692700	1.32731300	0.40785500
H	-0.60275700	-2.52346700	1.52750700
H	-0.57922600	2.13139600	1.52351300
I	2.42762600	2.77345900	1.25566100
I	2.39730800	-3.19650300	1.26088300

TS

C	1.42217700	-0.68829600	-0.49110100
C	-1.70671600	-0.66895700	0.07477200
C	-1.71453200	0.67838500	0.08976900
C	1.41395900	0.74547000	-0.47531300
H	2.23581600	-1.16076200	-1.05065000
H	-2.32815100	-1.38093200	-0.47688400
H	-2.34427200	1.39521200	-0.44595900
H	2.22205500	1.23939400	-1.02424300
C	0.66125600	-1.46568100	0.39314300
C	-0.57405300	-1.07624500	1.00197500
C	-0.58641200	1.07801200	1.02577400
C	0.64433200	1.49451300	0.42572000
H	-0.85028500	-1.58200800	1.94101600
H	-0.86809400	1.56016100	1.97552800
I	1.55025300	3.34291100	1.16081800
I	1.58797400	-3.31927600	1.08786200

R4
B3LYP/6-31G(d)

Cubane

C	0.21998600	0.04123100	1.34150000
C	-0.61579900	-1.05776200	0.59311600
C	0.50121200	-1.15860600	-0.50621300
C	1.33698200	-0.05963600	0.24219400
H	0.39662200	0.07434000	2.41851500
H	-1.11020500	-1.90691800	1.06930100
H	0.90360200	-2.08874600	-0.91263400
H	2.41036200	-0.10753000	0.43666700
C	-0.50121200	1.15860600	0.50621300
C	-1.33698200	0.05963600	-0.24219400
C	-0.21998600	-0.04123100	-1.34150000
C	0.61579900	1.05776200	-0.59311600
H	-0.90360200	2.08874600	0.91263400
H	-2.41036200	0.10753000	-0.43666700
H	-0.39662200	-0.07434000	-2.41851500
H	1.11020500	1.90691800	-1.06930100

bicyclo[4.2.0]octa-2,4,7-triene

C	1.70067900	-0.73240100	-0.26810900
C	-1.71169600	-0.66990200	-0.48700800
C	-1.71169600	0.66990200	-0.48700800
C	1.70067900	0.73240100	-0.26810900
H	2.60450300	-1.24098100	-0.59642500
H	-2.25066100	-1.42143300	-1.05925100

H	-2.25066100	1.42143300	-1.05925100
H	2.60450300	1.24098100	-0.59642500
C	0.64416300	-1.44637500	0.15439200
C	-0.64000000	-0.79566800	0.59199100
C	-0.64000000	0.79566800	0.59199100
C	0.64416300	1.44637500	0.15439200
H	0.68804000	-2.53417800	0.17654900
H	-1.00075700	-1.23866000	1.53152900
H	-1.00075700	1.23866000	1.53152900
H	0.68803900	2.53417800	0.17654900

TS

C	0.33215500	-0.36461400	-1.36300200
C	-0.75858900	1.13289600	-0.40144400
C	0.43282900	1.09081400	0.51073000
C	1.30899200	-0.04200000	-0.24213900
H	0.68209500	-0.51773300	-2.38570200
H	-1.20995900	1.88652300	-1.03457300
H	0.91395400	1.97039300	0.93592400
H	2.34336100	0.14168500	-0.55120000
C	-0.81244500	-1.01829900	-0.86854200
C	-1.32620700	-0.14514600	0.26295300
C	-0.17903400	-0.09753200	1.32732700
C	0.94197500	-1.04054300	0.85480200
H	-1.53626500	-1.43567200	-1.57095500
H	-2.37869300	-0.25339800	0.54193700
H	-0.45676300	-0.01937500	2.38102000
H	1.70259200	-1.28799700	1.60286500

R5
M06-2X/6-311G(2df,p)

$CH_3F + OH^-$

C	0.05059800	0.40269700	0.06257200
H	0.73132800	0.62735800	-0.76541000
H	-0.90225500	0.90844000	-0.12350300
H	-0.12195900	-0.70983200	0.10112100
F	0.60534300	0.96716800	1.22671000
O	-0.53852000	-2.22255200	-0.69322700
H	0.37742900	-2.30106500	-0.98821100

$CH_3OH + F^-$

C	0.03025500	-0.66300900	-0.35331600
H	1.05290600	-0.35226900	-0.59491100
H	-0.56038200	0.26621500	-0.28852600
H	0.02886000	-1.09019500	0.65574200
F	-0.41580800	1.74866900	0.70587800
O	-0.46469600	-1.61003100	-1.31719800
H	0.12056800	-2.36811300	-1.28923000

TS

C	-0.09211700	-0.02453700	-0.00009800
H	-0.02367900	0.50308000	0.93348500
H	-0.02370100	0.50297900	-0.93374500

H	-0.04647200	-1.09819800	0.00013600
F	-1.80577600	0.01993800	0.00004400
O	1.85491300	-0.09780400	0.00001400
H	2.05923200	0.84235700	0.00020900

R6
ωB97X-D/6-31G(d)

1,3,5-hexatriene

C	-0.37574800	0.96811000	-0.81160800
C	0.90889200	0.58438200	-0.75318200
H	1.59631400	1.09270000	-1.42960000
C	1.55062300	-0.42482600	0.10777800
C	-1.55221600	0.42410600	-0.11050500
H	-0.60226000	1.79818500	-1.48105600
H	-2.28382000	1.16698900	0.20833300
H	2.33929500	-1.00556700	-0.37130400
C	-1.82668300	-0.86620500	0.08252900
C	1.31282000	-0.61955800	1.40511100
H	-1.14648900	-1.64788900	-0.24231700
H	-2.74067800	-1.17838500	0.57883700
H	0.55916800	-0.04776400	1.93823500
H	1.86340500	-1.36445100	1.97181400

1,3-cyclohexadiene

C	-0.39909200	0.86855900	-1.05250600
C	1.00016000	0.80382900	-0.61344700
H	1.71262900	1.50665700	-1.03701900
C	1.39233600	-0.11782700	0.27435600
C	-1.35464500	0.21974000	-0.37622500
H	-0.64458800	1.46763500	-1.92534400
H	-2.39624000	0.29092400	-0.67873400
H	2.43353200	-0.19014500	0.57798100
C	-1.01261300	-0.55731400	0.87141000
C	0.40856500	-1.12998300	0.80846200
H	-1.73436800	-1.36385100	1.03786200
H	-1.09913300	0.11930800	1.73668700
H	0.42234800	-2.01068100	0.14649500
H	0.71348300	-1.48433400	1.79871700

TS

C	0.69919400	1.23279800	0.16225900
C	-0.69968300	1.23264200	0.16189100
H	-1.17233800	2.21220200	0.11517800
C	-1.47374500	0.12345300	-0.19348200
C	1.47367200	0.12396500	-0.19332700
H	1.17166100	2.21248100	0.11633900
H	2.31242200	0.32639800	-0.86072600
H	-2.31222900	0.32542900	-0.86134900
C	1.13686600	-1.20083600	0.06166800
C	-1.13645200	-1.20110000	0.06218500
H	0.92986300	-1.49101700	1.07869700
H	1.63166800	-1.97970000	-0.51762700
H	-0.92948100	-1.49089200	1.07931600

H	-1.63067700	-1.98042800	-0.51698900

R7
ωB97X-D/6-31G(d)

cyclobutene

C	-0.63496300	0.80690400	0.10979300
C	0.68531900	0.71418200	0.29435000
H	1.45094500	1.42116300	0.59961200
C	0.75015300	-0.75307600	-0.07747200
C	-0.79641400	-0.64436300	-0.29382300
H	-1.35068100	1.61766900	0.20784900
H	-1.39857200	-1.26353900	0.38035900
H	-1.12901500	-0.81977800	-1.32295600
H	1.05452600	-1.43557700	0.72380800
H	1.32409900	-0.99221900	-0.97962100

1,3-butadiene

C	-0.67896200	0.60351500	-0.08684600
C	0.71221700	0.43960400	0.36373000
H	1.10780700	1.23517200	0.99425400
C	1.50657400	-0.58250100	0.03998700
C	-1.53773900	-0.39537600	-0.29956500
H	-1.01652300	1.62888900	-0.23405200
H	-1.26286000	-1.43085500	-0.11501700
H	-2.54758600	-0.20902800	-0.65185900
H	2.52003600	-0.65564200	0.42231400
H	1.17347500	-1.37207800	-0.62892600

TS

C	-0.68377500	0.72846400	-0.08722000
C	0.68407400	0.72821600	0.08740600
H	1.33779600	1.53055800	0.42115800
C	1.06097600	-0.62079900	-0.12497700
C	-1.06131500	-0.62041200	0.12501700
H	-1.33703400	1.53085000	-0.42180600
H	-0.83974400	-1.08487900	1.07838700
H	-1.88999900	-1.09220100	-0.41252800
H	1.88997400	-1.09256700	0.41210100
H	0.83923900	-1.08457400	-1.07866800

R8
MPW1K/6-31G(d,p)

norbonene + diazomethane

C	0.65686200	-0.12256500	2.88184300
C	1.40785700	0.15461600	1.49514600
C	-0.81774000	0.17482000	0.88658800
C	-0.88188500	-0.10797700	2.46100000
H	0.97625500	-1.09919500	3.34402100
H	0.88527300	0.69773300	3.62278400
H	-1.40930400	-1.07622400	2.69250000
H	-1.44077300	0.72027500	2.98590300
C	0.40419500	1.17487200	0.82625800

H	0.69302800	1.45104700	-0.22772800
H	0.24436700	2.10997600	1.44018800
C	1.15202900	-1.10405900	0.61474800
H	1.89008600	-1.92637300	0.44535100
C	-0.17032900	-1.09292800	0.25518300
H	-0.73390500	-1.90307400	-0.26982400
H	2.47988200	0.47871300	1.60288300
H	-1.78719900	0.51711200	0.43074200
C	0.57950800	0.25887500	-3.11916000
H	1.17373200	-0.21415400	-2.30824500
H	0.99290100	0.69943700	-4.05059500
N	-1.88305500	0.30608600	-2.80180200
N	-0.73146700	0.28754500	-2.95583200

hexahydro-4,7-methanoindazole

C	0.85042000	-0.32142200	2.17425000
C	1.18367600	0.37135300	0.79377900
C	-1.13542800	0.33730800	0.81914900
C	-0.74823100	-0.36116600	2.18373200
H	1.31331500	-1.34724600	2.25634400
H	1.24571900	0.29426800	3.03306800
H	-1.15943000	-1.40956400	2.25488000
H	-1.16474600	0.22060200	3.05562700
C	0.00598800	1.41653900	0.67663400
H	-0.02250000	1.96975800	-0.30628600
H	0.00406100	2.17087400	1.51586200
C	0.83184100	-0.65426900	-0.35915100
H	1.28475100	-1.66841600	-0.16998700
C	-0.76027400	-0.66336900	-0.34181100
H	-1.25005000	-1.67202100	-0.21347300
H	2.22974900	0.78602800	0.72720600
H	-2.19627600	0.70774000	0.76122300
C	1.12349500	-0.15267000	-1.81753200
H	1.73907800	0.79347600	-1.86282700
H	1.63629500	-0.91467700	-2.47346600
N	-1.19667900	-0.11715500	-1.69321200
N	-0.22869600	0.15356300	-2.45416600

TS

C	2.27940300	0.85524100	-0.24165900
C	0.80338300	1.14655800	0.29317300
C	0.89750900	-1.16117900	0.26587700
C	2.35016300	-0.74106900	-0.24912600
H	2.45117200	1.30659500	-1.26047100
H	3.04989400	1.29362900	0.45816200
H	2.57108900	-1.16483800	-1.26996000
H	3.14934300	-1.11555100	0.45627800
C	0.64069600	-0.02830500	1.33309100
H	-0.38280500	-0.08155100	1.80272600
H	1.42247600	-0.00458500	2.14803200
C	-0.16696500	0.67288900	-0.83608100
H	-0.37604500	1.30418500	-1.73502600
C	-0.09339600	-0.73607100	-0.85764600
H	-0.31311400	-1.37786100	-1.74502800
H	0.64783300	2.19440900	0.67586600

H	0.81786200	-2.22546200	0.62276100
C	-2.30884700	1.14009600	0.00351800
H	-2.21234900	1.68474500	0.97772100
H	-2.91925500	1.65588800	-0.78140500
N	-2.27205400	-1.29543100	0.04348600
N	-2.63048600	-0.18436200	0.15415300

R9
ωB97X-D/6-31G(d)

1,3-butadiene + ethylene

C	-0.46382000	0.18898500	-1.27614900
C	0.97471500	-0.03098900	-1.05739700
H	1.63980600	0.74928200	-1.42573100
C	1.50482900	-1.10814500	-0.47298200
C	-1.43521100	-0.22745500	-0.46071500
H	-0.73017400	0.74952700	-2.17153800
H	-1.21739800	-0.73571700	0.47491400
H	-2.48121400	-0.05030400	-0.69186200
H	0.88490400	-1.93559800	-0.13725200
H	2.57624100	-1.20276400	-0.32538700
C	-0.79991200	1.75250700	2.46535000
C	0.25669200	0.97039600	2.65809000
H	-1.18488800	1.94388100	1.46730500
H	-1.32000800	2.22864100	3.29285900
H	0.64706700	0.77304900	3.65346200
H	0.77437400	0.50048400	1.82535600

cyclohexene

C	-0.45589400	0.07112100	-1.37195600
C	0.82626700	-0.23035400	-1.16609800
H	1.56074100	-0.16840200	-1.96519900
C	1.25433400	-0.66796300	0.20963300
C	-1.41896400	-0.04013100	-0.21974700
H	-0.81592700	0.39029400	-2.34681100
H	-1.62344000	-1.10326000	-0.02276600
H	-2.38379900	0.41868900	-0.45805500
H	0.90681600	-1.69723300	0.38488000
H	2.34483700	-0.69257200	0.30123900
C	-0.83340600	0.60283000	1.05602000
C	0.65767700	0.25466100	1.29418100
H	-0.93888900	1.68899600	0.96557100
H	-1.44034300	0.30369300	1.91745300
H	0.79096500	-0.21418000	2.27517300
H	1.24449800	1.17901900	1.31074400

TS

C	1.31220200	-0.70343000	-0.29283200
C	1.31213400	0.70354400	-0.29281500
H	1.84878400	1.21485900	-1.08926700
C	0.44736500	1.42917800	0.49434500
C	0.44751800	-1.42916500	0.49432400
H	1.84889500	-1.21467500	-1.08930000
H	0.12436500	-1.05277600	1.45840600

H	0.38797400	-2.50879100	0.38534400
H	0.12424900	1.05274000	1.45842100
H	0.38773400	2.50880200	0.38539500
C	-1.56693400	-0.68965700	-0.22886000
C	-1.56696400	0.68954500	-0.22889300
H	-1.45290700	-1.23269800	-1.15987400
H	-2.06398400	-1.23253900	0.56963200
H	-2.06406300	1.23244300	0.56955900
H	-1.45296400	1.23254300	-1.15993700

Optimized Cartesian coordinates of reference species used for computing the bond polarity index (BPI).

ethane
ωB97X-D/6-31G(d)

C	-0.76355800	-0.00002600	-0.00024600
C	0.76355800	0.00002600	0.00024600
H	-1.16071000	0.96405800	0.33457100
H	-1.16015500	-0.77173000	0.66783200
H	-1.16057400	-0.19200500	-1.00255600
H	1.16057400	0.19200500	1.00255600
H	1.16015500	0.77173000	-0.66783200
H	1.16071000	-0.96405800	-0.33457100

F2
ωB97X-D/6-311G(d)

F	0.00000000	0.00000000	0.69376700
F	0.00000000	0.00000000	-0.69376700

diazane
ωB97X-D/6-31G(d)

H	1.13494600	0.31282800	-0.78671800
H	1.05275500	-0.84305700	0.37106000
H	-1.13496100	0.31344400	0.78646000
H	-1.05275200	-0.84333400	-0.37042200
N	0.70581100	0.07576500	0.10166800
N	-0.70581000	0.07568100	-0.10172200

Table S1. Performance of DFT levels in predicting the activation enthalpy of the thermal isomerization of bicyclo[4.2.0]octa-2,4,7-triene to 1,3,5,7-cyclooctatetraene at 533 K.

Level	$\Delta H^{\ddagger}_{533K}$[kcal/mol]	Absolute Error [kcal/mol][a]
B3LYP/6-31+G(d,p)	18.56	1.62
ωB97X-D/6-31+G(d,p)	24.26	7.32
M06-2X/6-31+G(d,p)	22.58	5.64
MN15-L/6-31+G(d,p)	21.08	4.14

$\Delta H^{\ddagger}_{533K}(\text{exp.}) = E_a(exp.) - RT = 16.94\ kcal/mol$ where $E_a(exp.) = 18.0\ kcal/mol$. R stands as the universal constant of gases, and $\mathrm{T} = 533\mathrm{K}$ See H. D. Martin, T. Urbanek, P. Pfohler and R. Walsh, J Chem Soc, Chem Commun, 1985, 964-965.