

Competitive 1,2-C Atom Shifts in the Strained Carbene Spiro[3.3]hept-1-ylidene Explained by Distinct Ring-Puckered Conformers

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[‡] Some material taken from Ph.D. Dissertation, Ruhr-University Bochum, Bochum, Germany, December 21, 1989.

(S1) Relevant information from the spectra depicted herein is mentioned in the Experimental Section.

SUPPORTING INFORMATION

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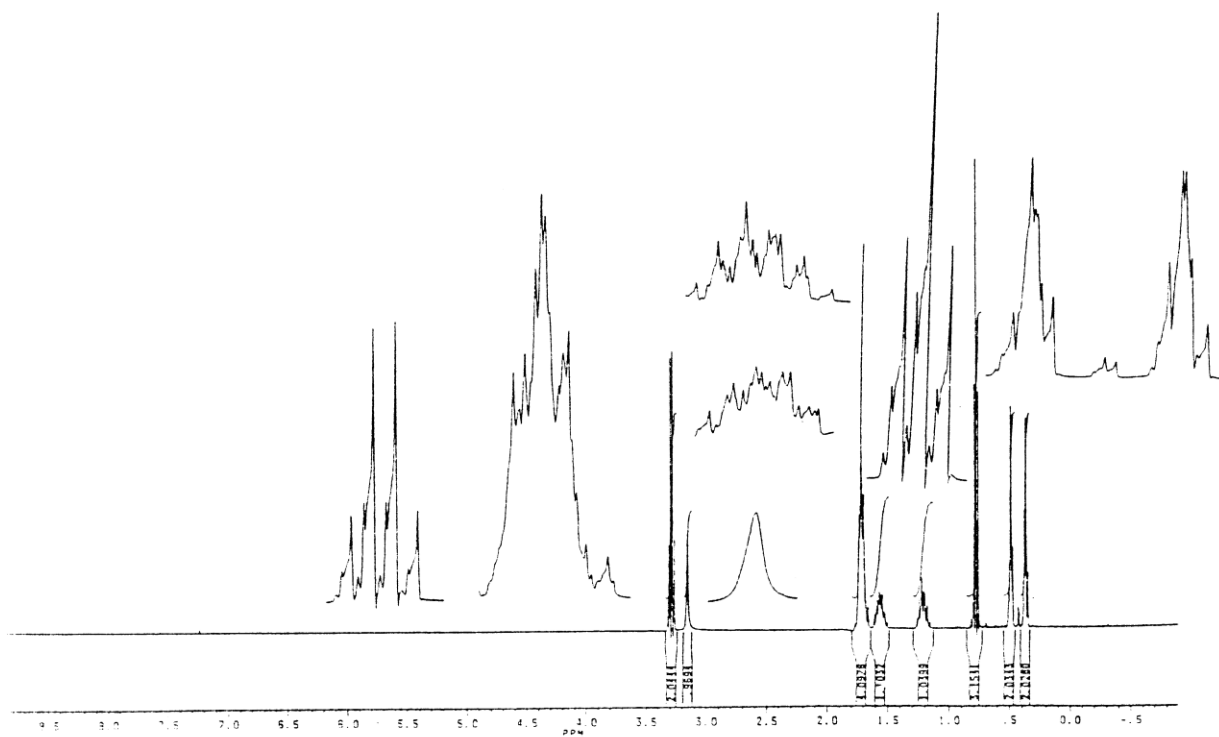
SPECTRAL DATA:**1-(1-Ethoxycyclopropyl)cyclobutanol (14):**

Figure S1. ¹H NMR spectrum (400.1 MHz, CDCl₃) of 1-(1-ethoxycyclopropyl)cyclobutanol (**14**) after workup.

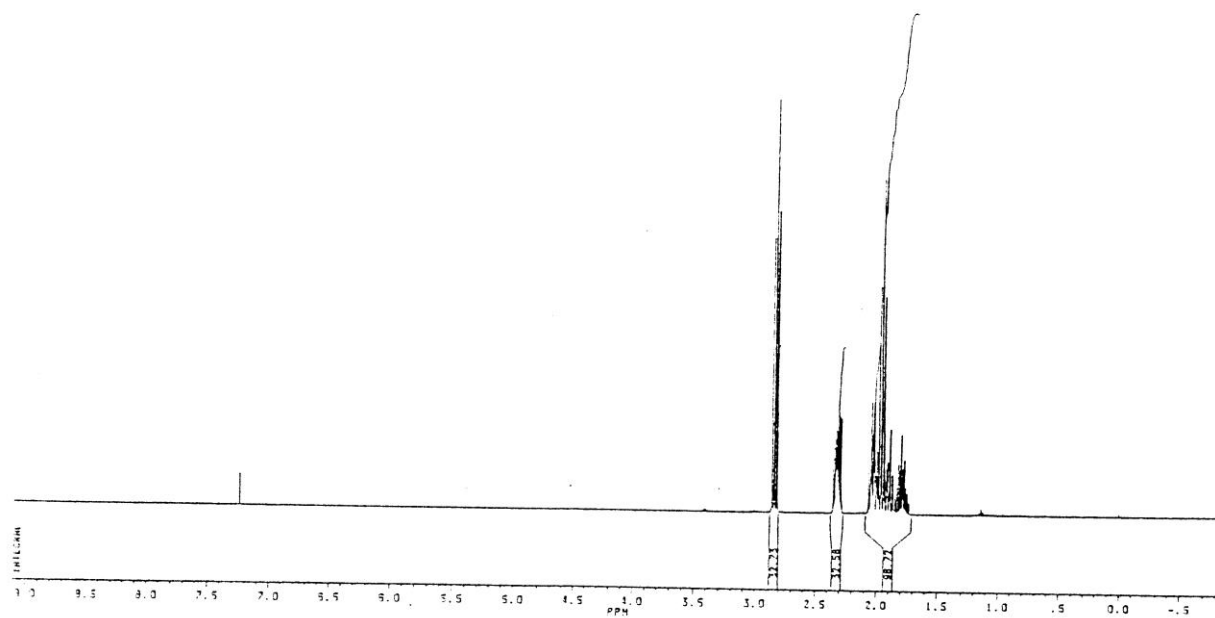
Spiro[3.3]heptan-1-one (**15**):

Figure S3. ^1H NMR spectrum (400.1 MHz, CDCl_3) of spiro[3.3]heptan-1-one (**15**) after workup.

Spiro[3.3]heptan-1-one (15): (cont'd)

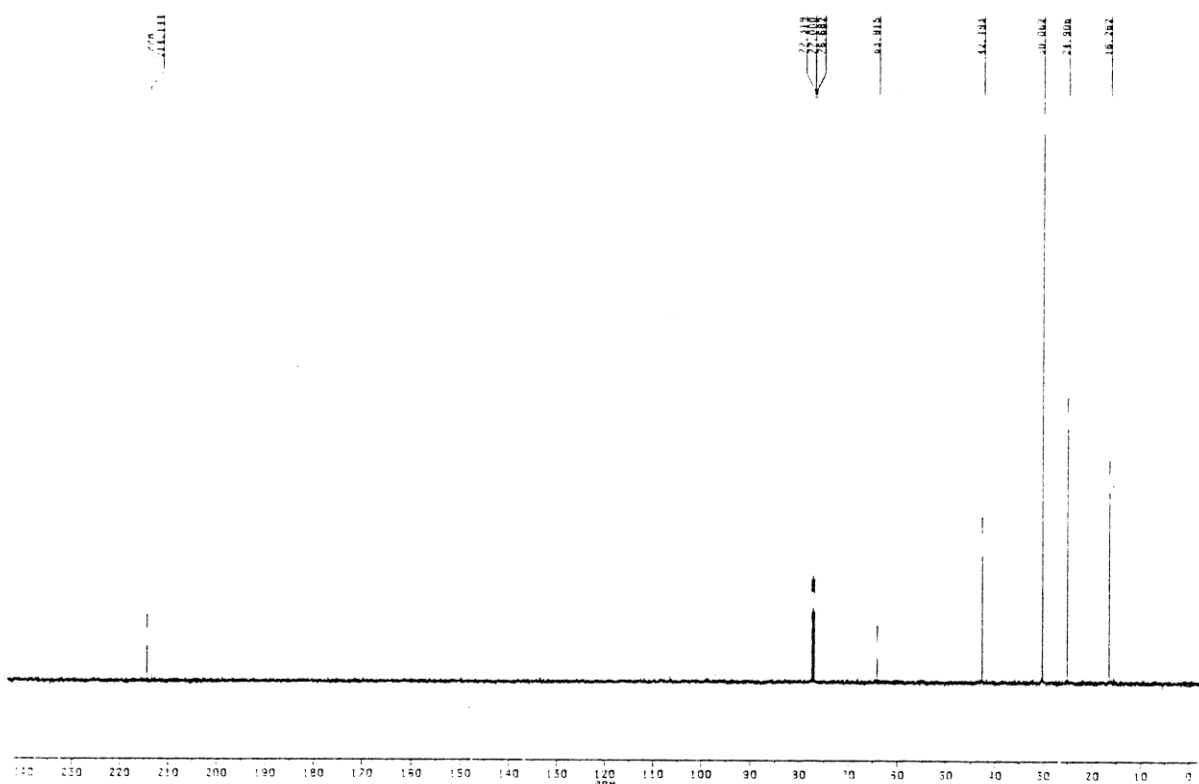


Figure S4. ^{13}C NMR spectrum (100.6 MHz, CDCl_3) of spiro[3.3]heptan-1-one (**15**) after workup.

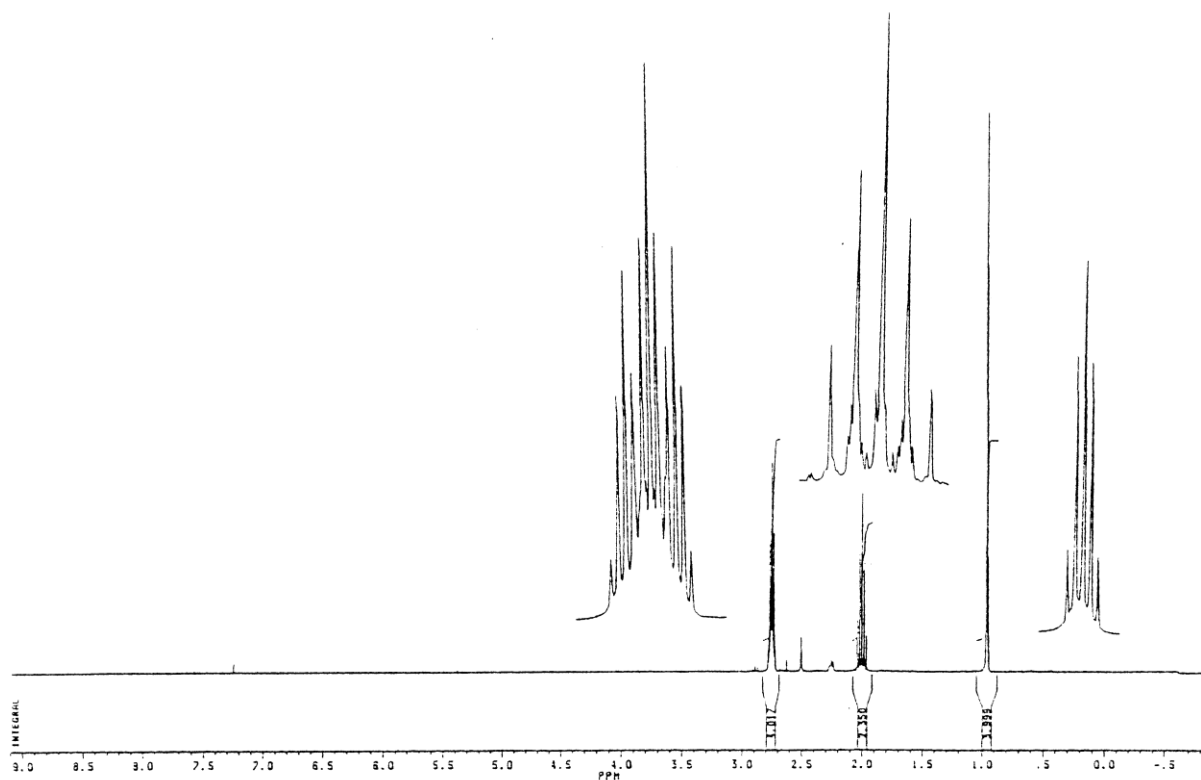
Cyclopropylidenecyclobutane (**18**):

Figure S6. ¹H NMR spectrum (400.1 MHz, CDCl₃) of cyclopropylidenecyclobutane (**18**) after workup.

Cyclopropylidenecyclobutane (**18**): (cont'd)

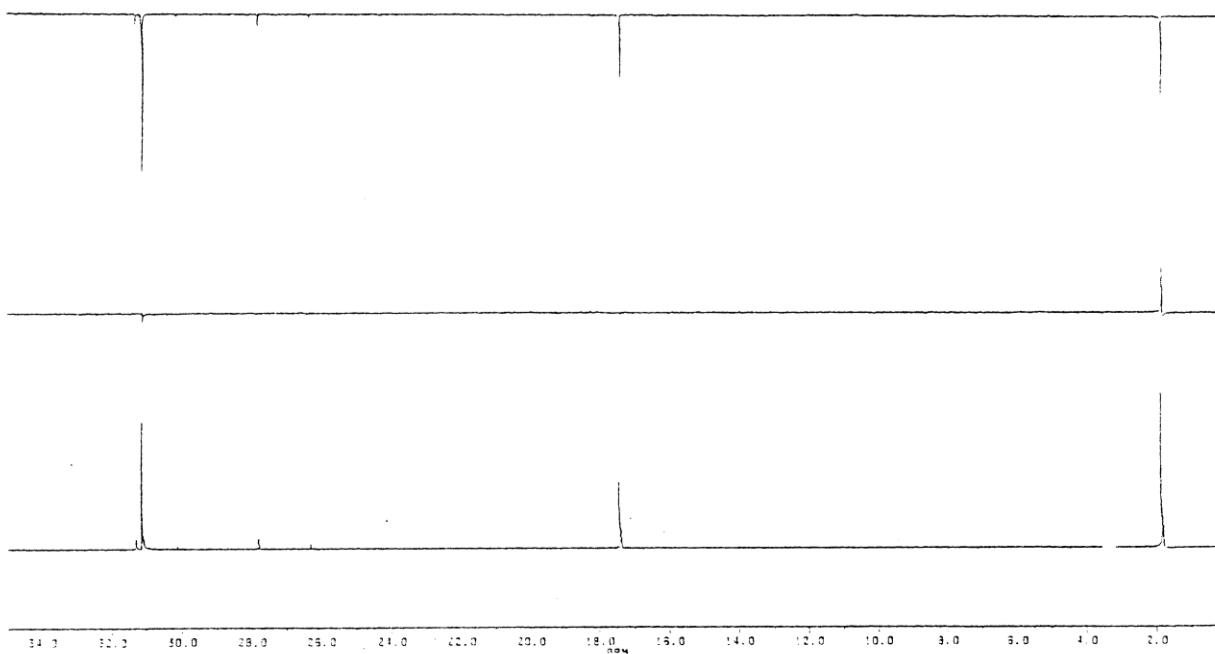


Figure S7. ¹³C NMR spectra (100.6 MHz, CDCl₃) of cyclopropylidenecyclobutane (**18**) after workup.

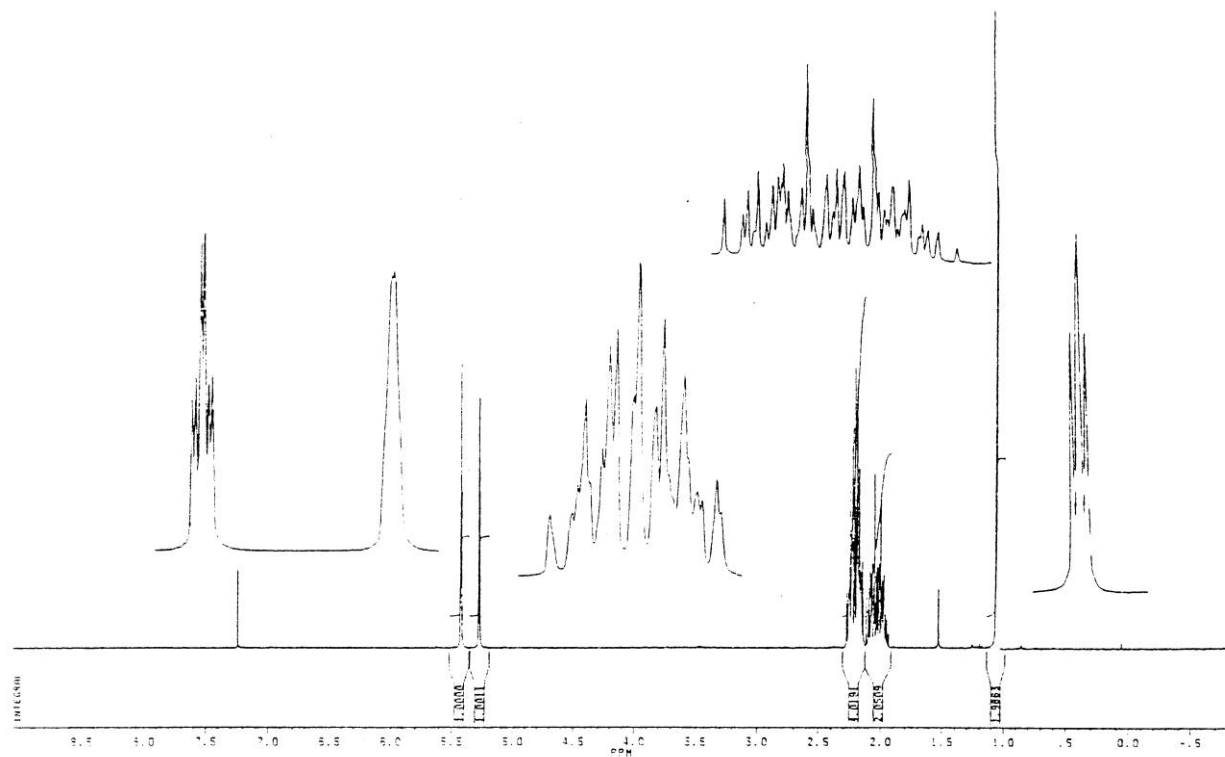
1-Methylenespiro[2.3]hexane (19):

Figure S8. ¹H NMR spectrum (400.1 MHz, CDCl₃) of 1-methylenespiro[2.3]hexane (**19**) after workup.

1-Methylenespiro[2.3]hexane (19): (cont'd)

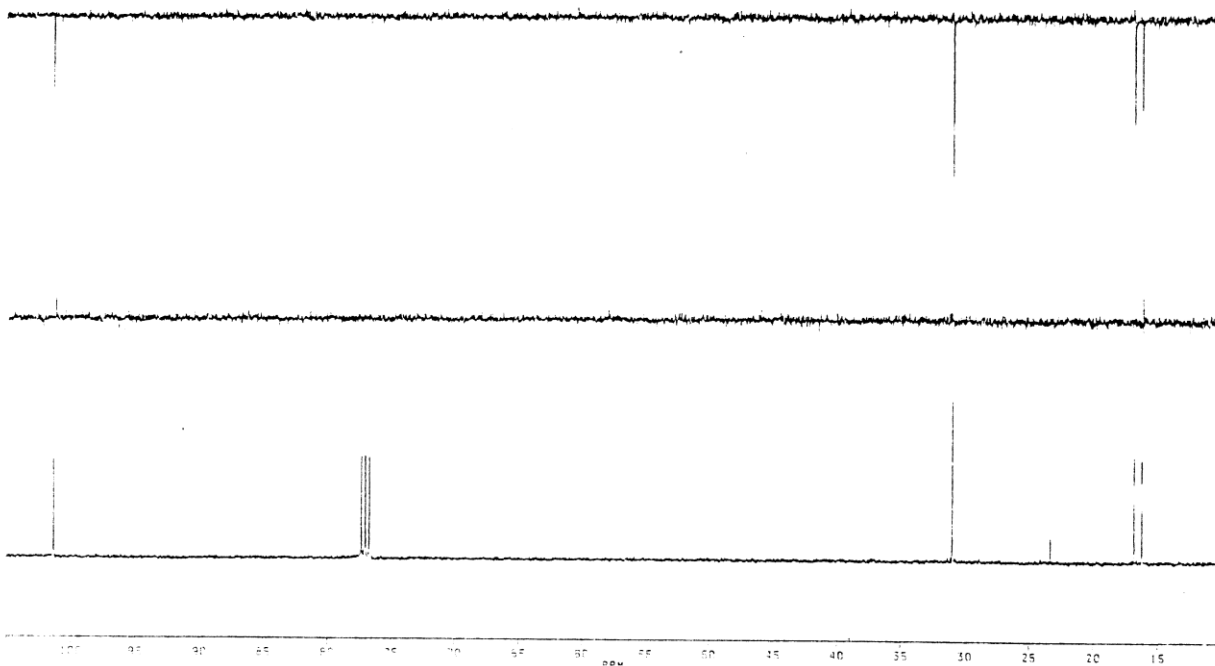


Figure S9. ^{13}C NMR spectra (100.6 MHz, CDCl_3) of 1-methylenespiro[2.3]hexane (**19**) after workup.

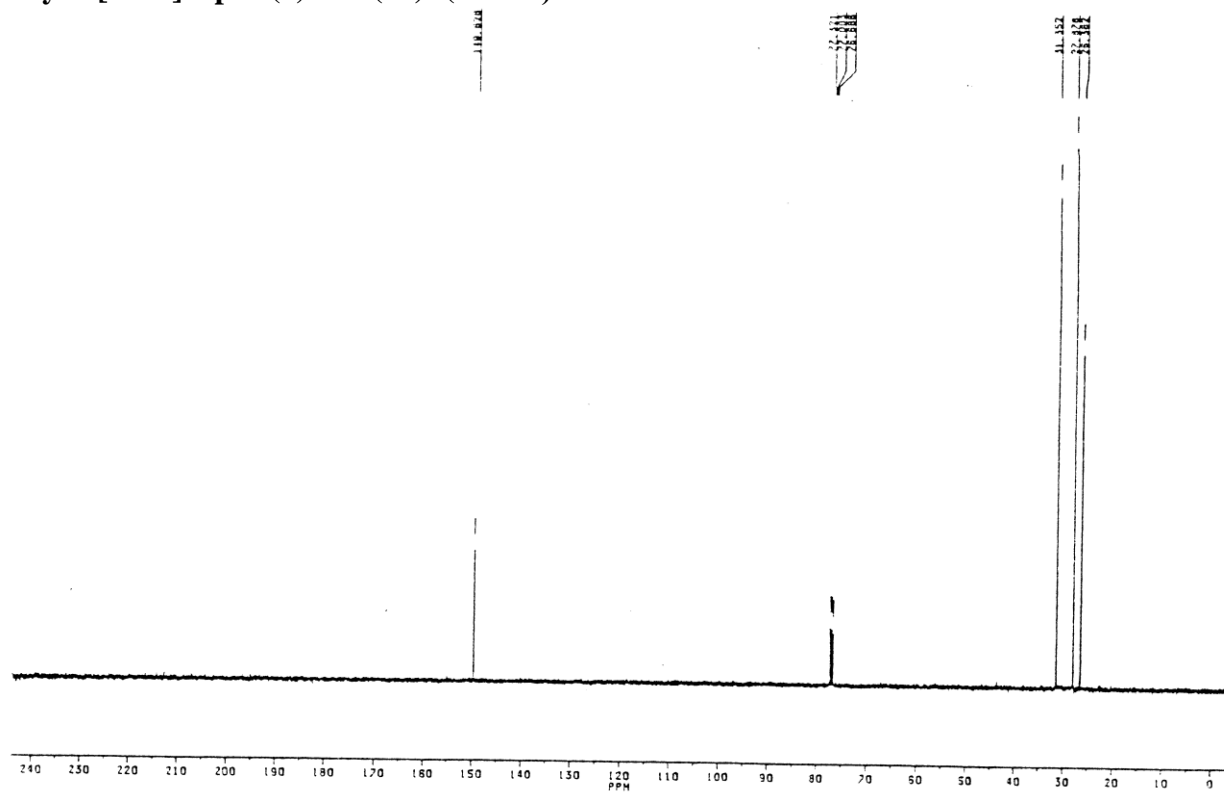
Bicyclo[3.2.0]hept-1(5)-ene (**20**): (cont'd)

Figure S11. ^{13}C NMR spectrum (100.6 MHz, CDCl_3) of bicyclo[3.2.0]hept-1(5)-ene (**20**) after workup.

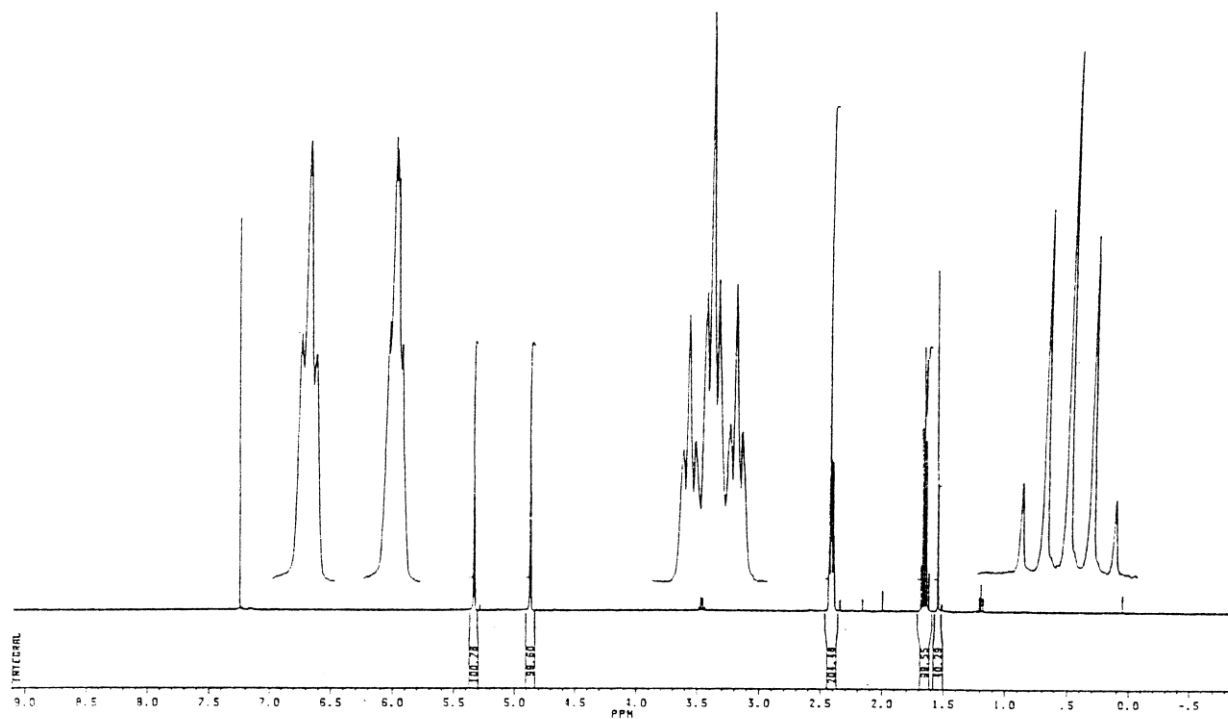
1,2-Dimethylenecyclopentane (21):

Figure S12. ¹H NMR spectrum (400.1 MHz, CDCl₃) of 1,2-dimethylenecyclopentane (**21**) after workup.

1,2-Dimethylenecyclopentane (**21**): (cont'd)

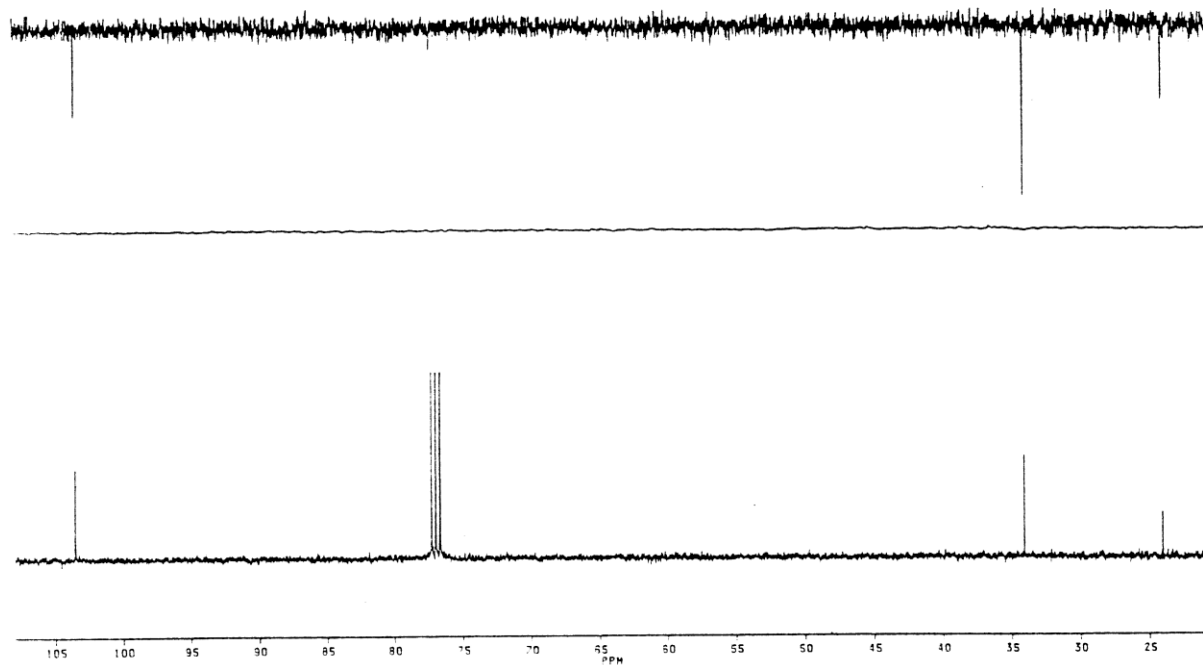


Figure S13. ^{13}C NMR spectra (100.6 MHz, CDCl_3) of 1,2-dimethylenecyclopentane (**21**) after workup.

Spiro[3.3]hept-1-ene (22c): (cont'd)

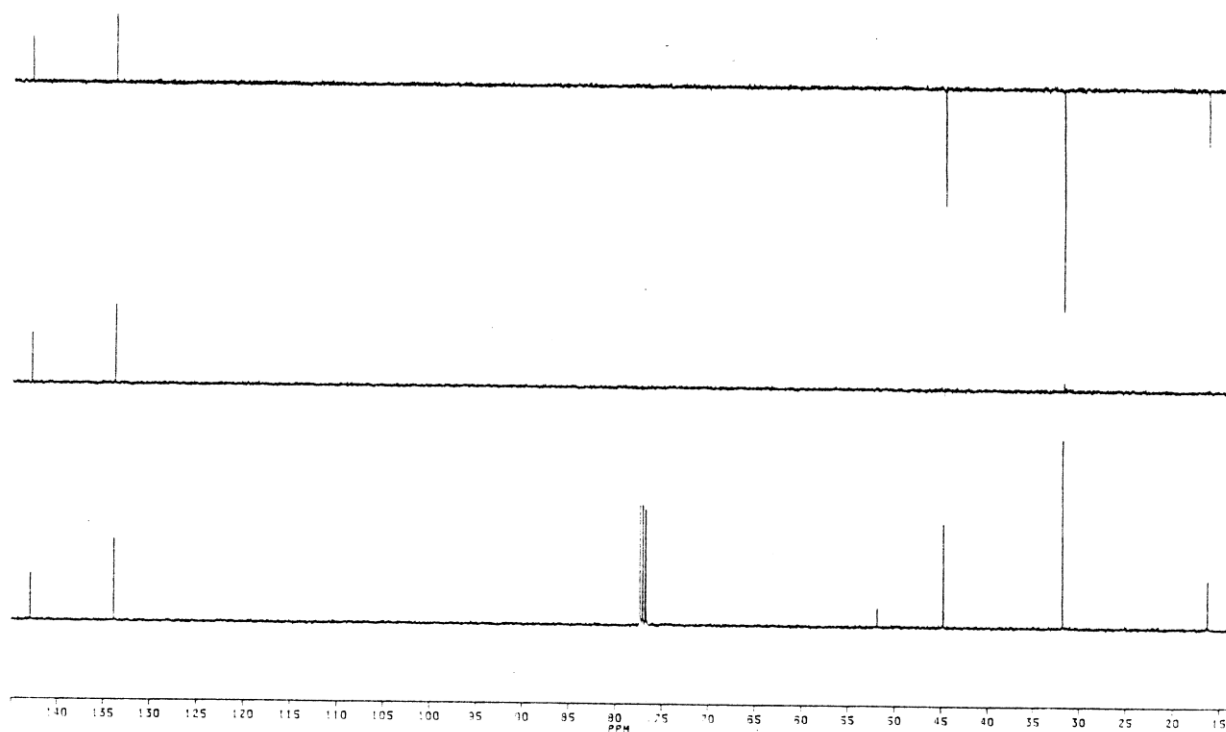


Figure S15. ^{13}C NMR spectra (100.6 MHz, CDCl_3) of spiro[3.3]hept-1-ene (22c) after workup.

(Prop-2-en-1-ylidene)cyclobutane (**22d**):

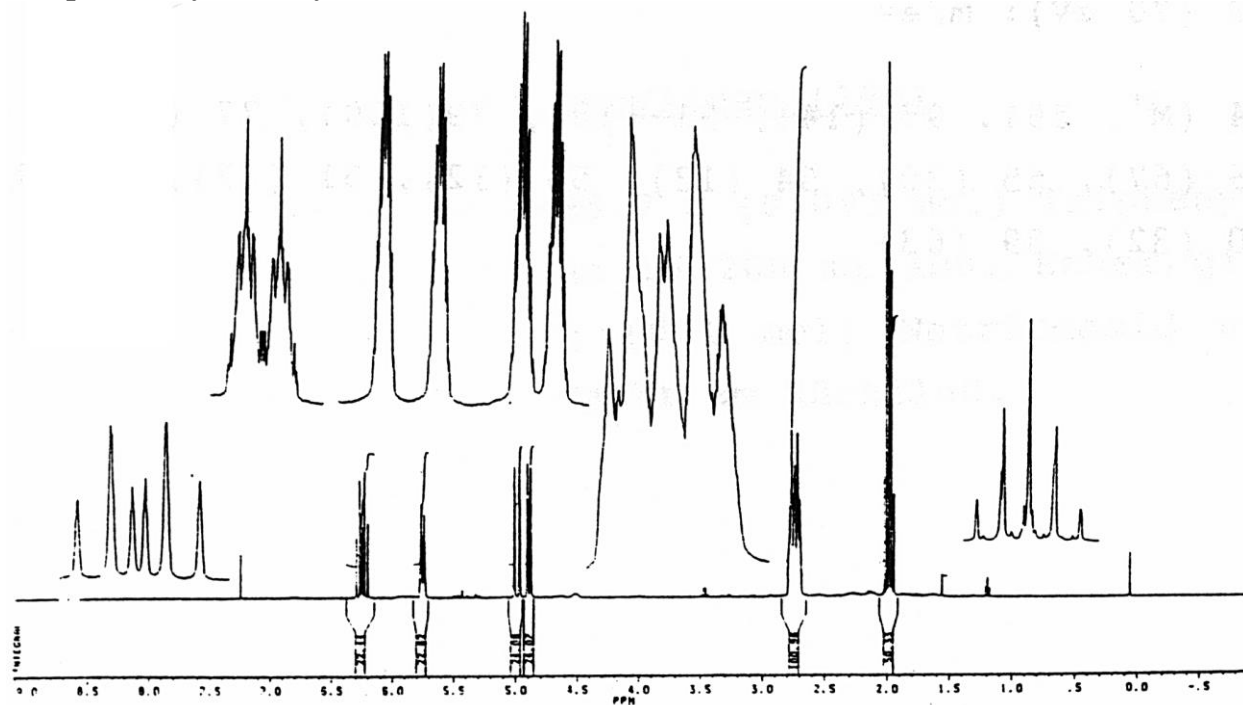


Figure S16. ^1H NMR spectrum (400.1 MHz, CDCl_3) of (prop-2-en-1-ylidene)cyclobutane (**22d**) after workup.

(Prop-2-en-1-ylidene)cyclobutane (22d): (cont'd)

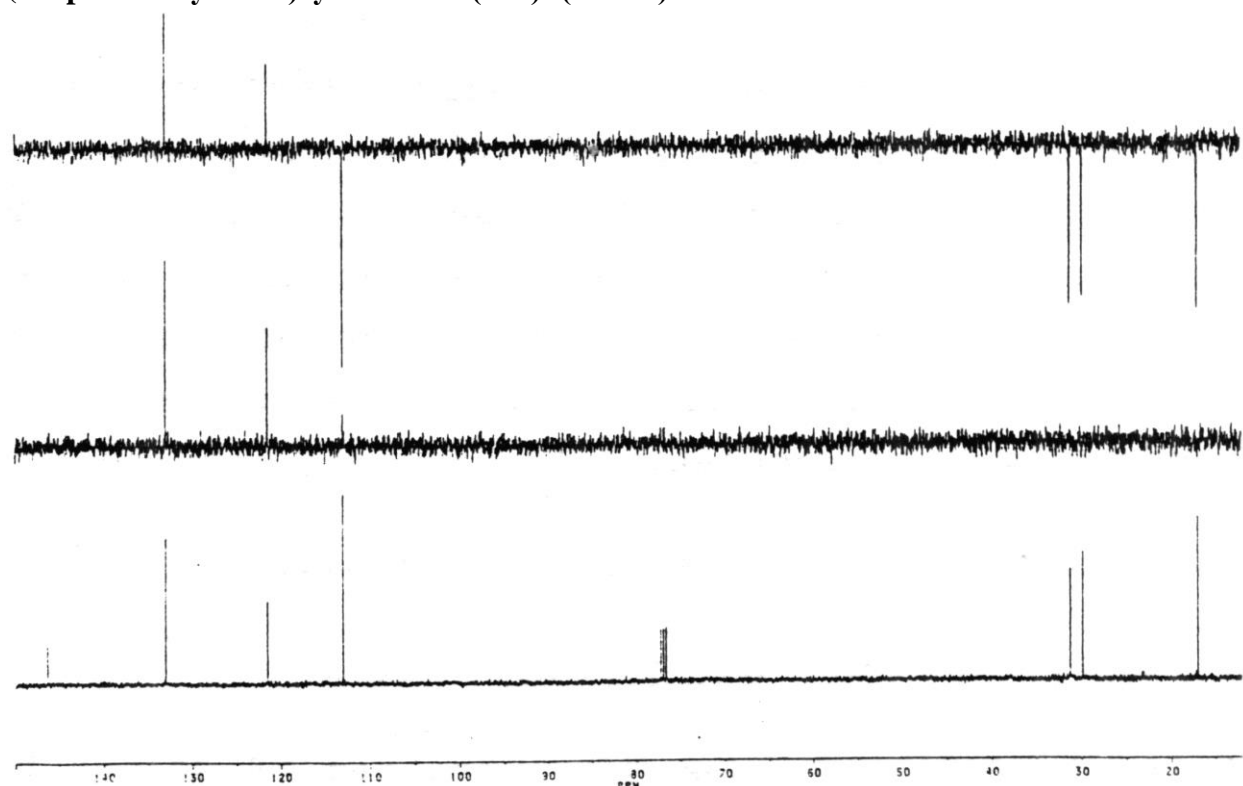


Figure S17. ^{13}C NMR spectra (100.6 MHz, CDCl_3) of (prop-2-en-1-ylidene)cyclobutane (22d) after workup.

Spiro[3.3]heptan-1-ol (**24**):

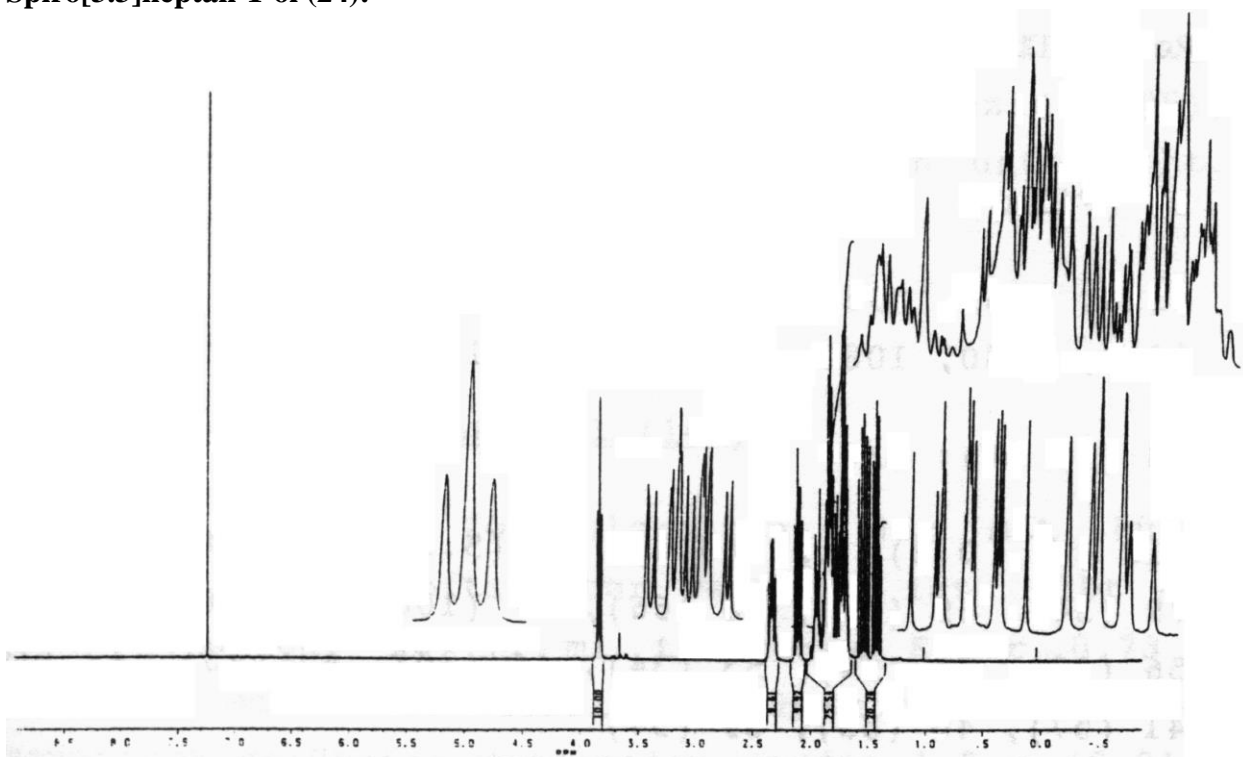


Figure S18. ¹H NMR spectrum (400.1 MHz, CDCl₃) of spiro[3.3]heptan-1-ol (**24**) after workup.

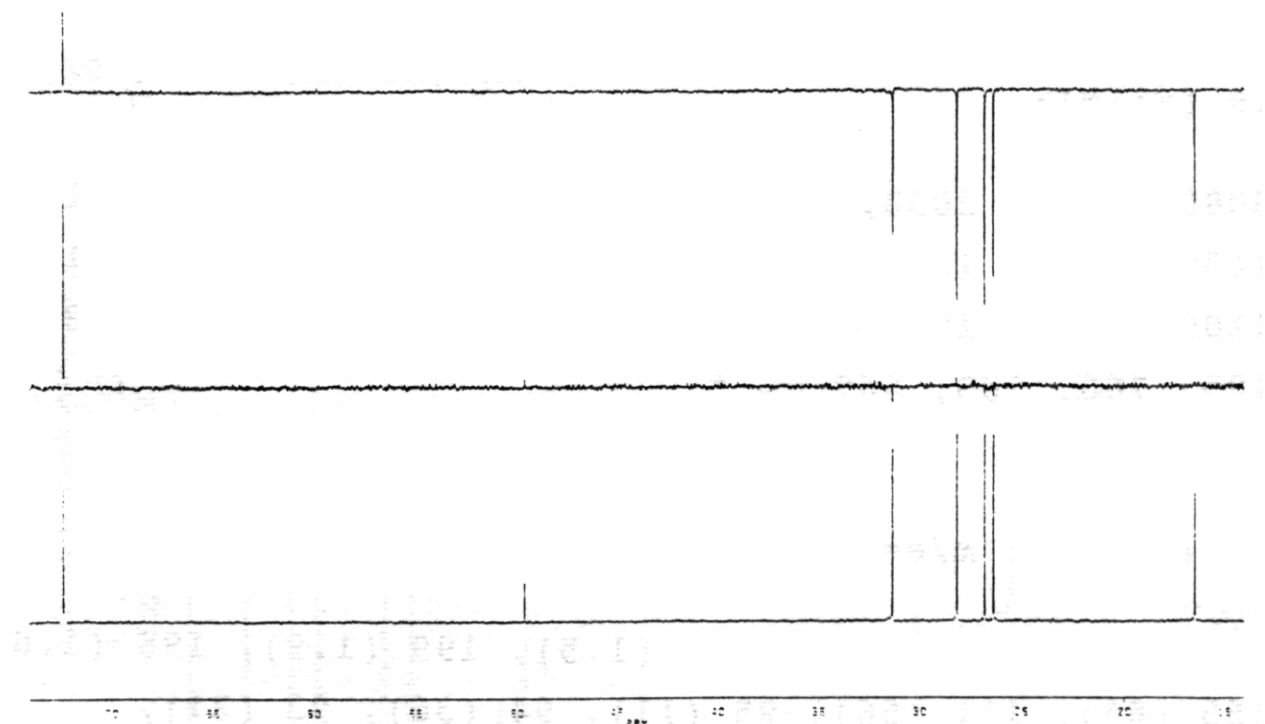
Spiro[3.3]heptan-1-ol (**24**): (cont'd)

Figure S19. ^{13}C NMR spectra (100.6 MHz, CDCl_3) of spiro[3.3]heptan-1-ol (**24**) after workup.

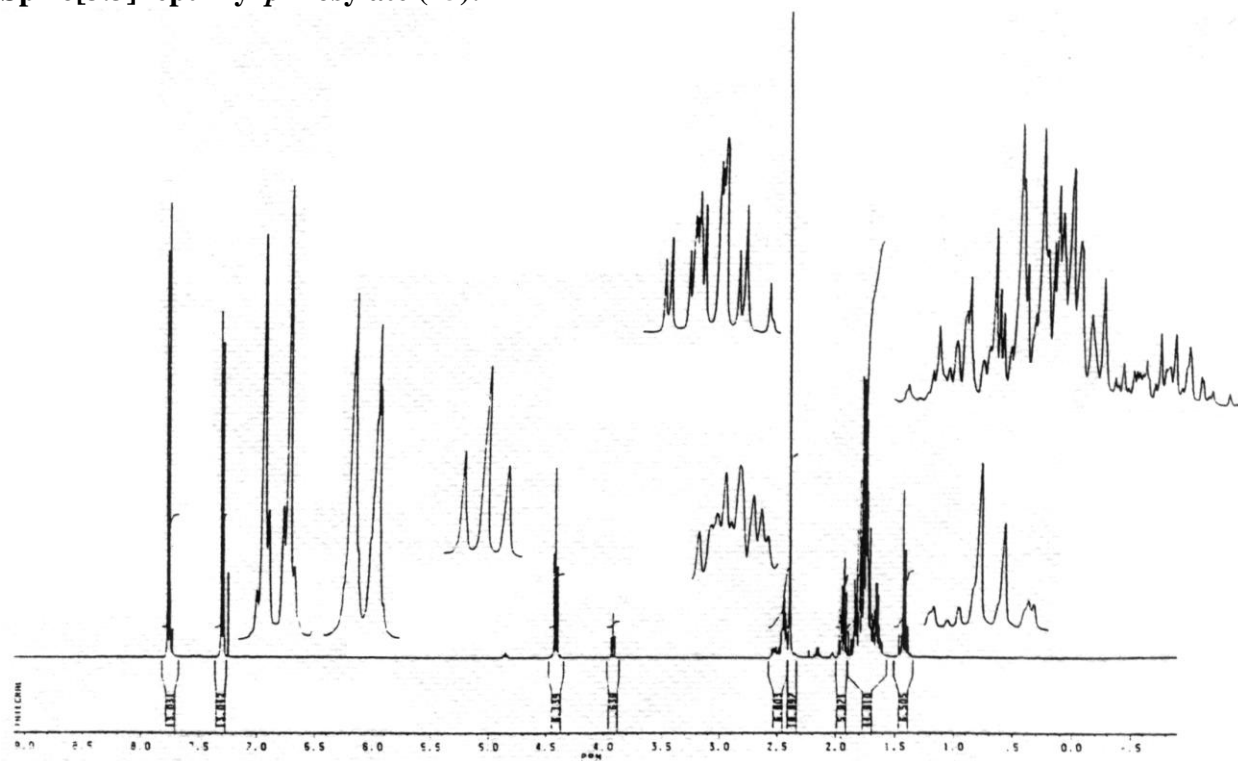
Spiro[3.3]hept-1-yl *p*-Tosylate (**25**):

Figure S20. ¹H NMR spectrum (400.1 MHz, CDCl₃) of spiro[3.3]hept-1-yl *p*-tosylate (**25**) after workup.

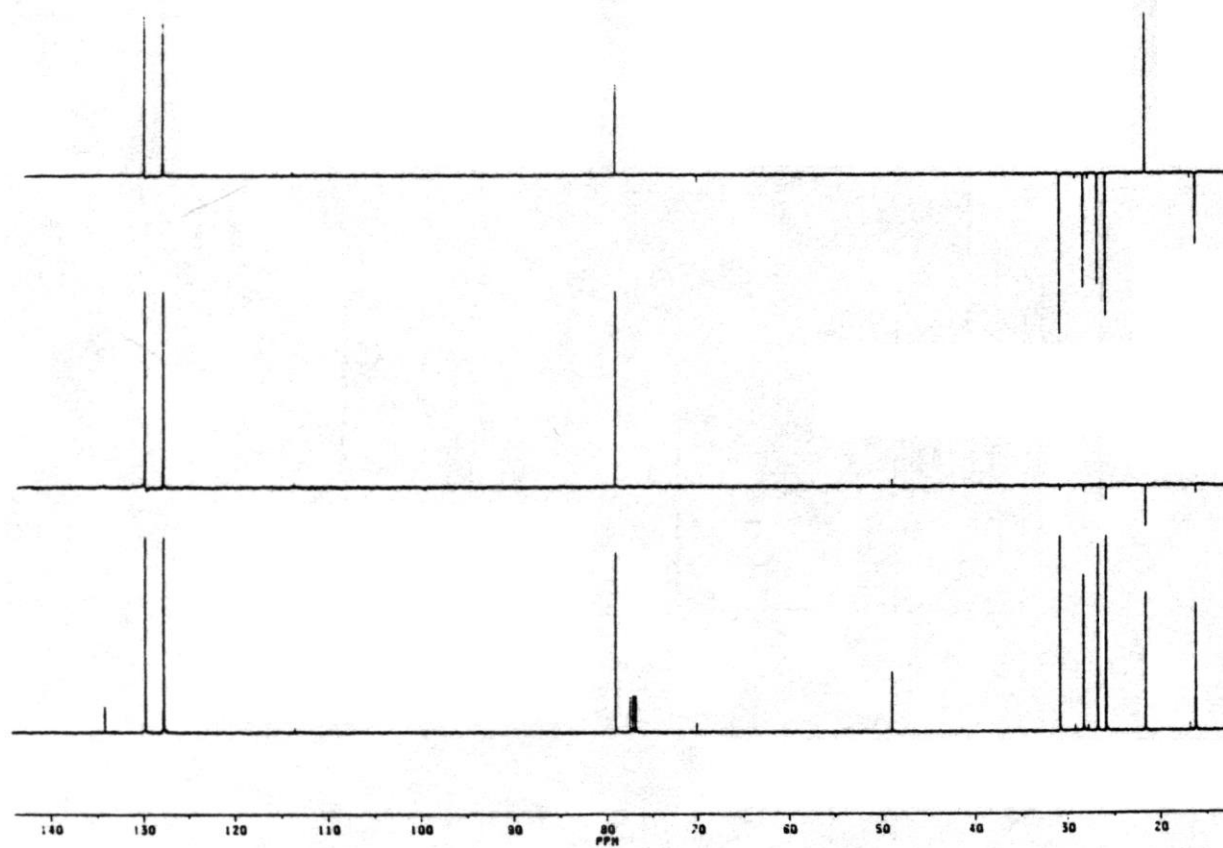
Spiro[3.3]hept-1-yl *p*-Tosylate (**25**): (cont'd)

Figure S21. ^{13}C NMR spectra (100.6 MHz, CDCl_3) of spiro[3.3]hept-1-yl *p*-tosylate (**25**) after workup.

SPECIAL EQUIPMENT:

High-Vacuum Flash Pyrolysis (HVFP) Apparatus

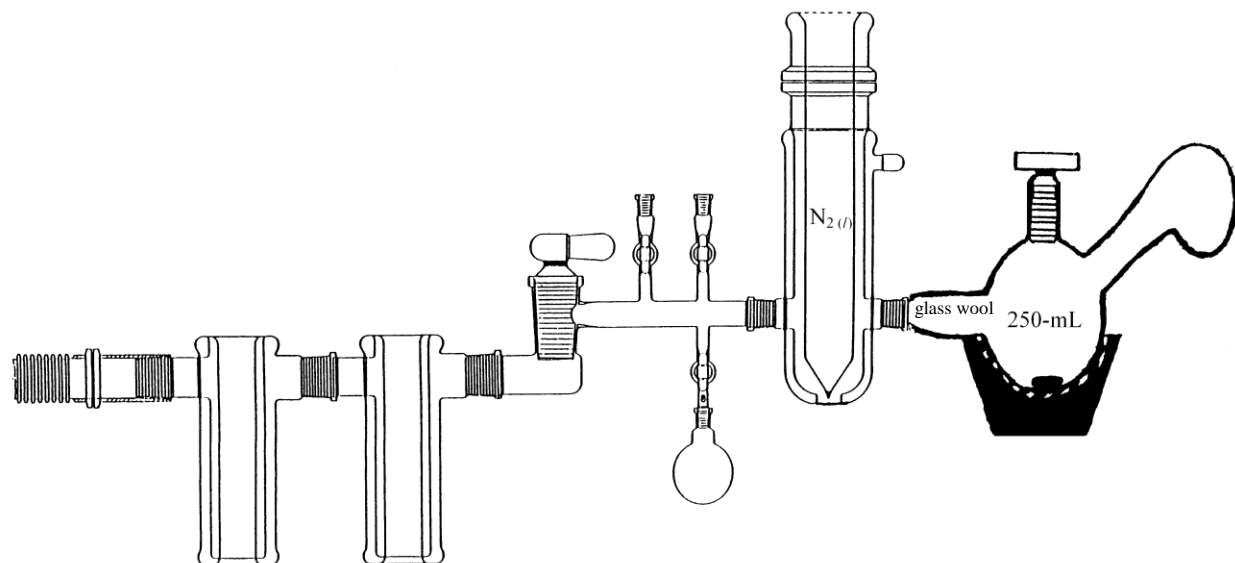


Figure S22. Schematic of the high-vacuum flash pyrolysis (HVFP) apparatus.

COMPUTATIONAL RESULTS:

Table S1. Values Used in Computations with Equation S1

$n = 1 \text{ mol}$	$T = 298.15 \text{ K}$ $= 25 \text{ }^\circ\text{C}$
$R = 1.9872 \times 10^{-3} \text{ (kcal/mol)/K}$ $= 8.2057 \times 10^{-2} \text{ (L}\cdot\text{atm/mol)/K}$	$3(1/2)RT = 0.889 \text{ kcal/mol}$ $RT = 0.592 \text{ kcal/mol}$
$1 \text{ au} = 1 \text{ hartree}$ $= 627.5095 \text{ kcal/mol}$	$V = nRT/p \text{ (} p = 1 \text{ atm)}$ $= 24.465 \text{ L}$
B3LYP/6-31G(d) scaling factors ^{S2} \rightarrow	$Z = 0.9826$ $H = 1.0004$

$$H = [E + Z(E_{\text{ZPVE}})] + H(H_{\text{vib}}) + (3(1/2)RT)_{\text{translational}} + (3(1/2)RT)_{\text{rotational}} + (RT)_{\text{ideal gas}} \quad (\text{S1})$$

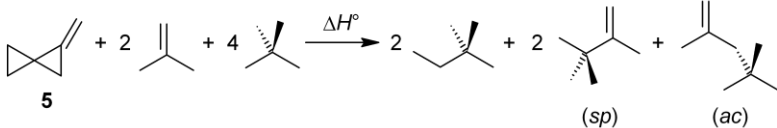
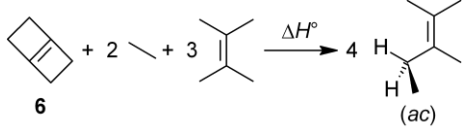
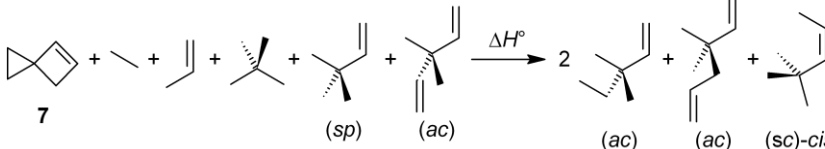
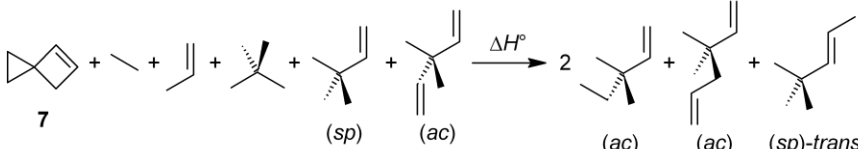
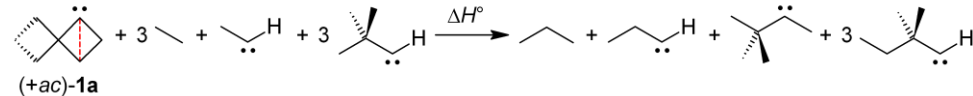
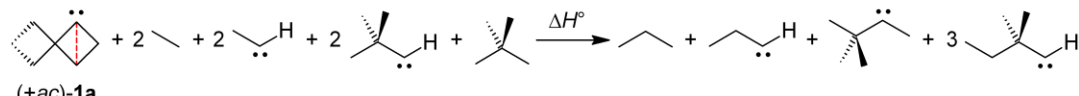
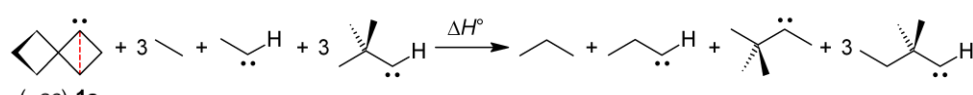
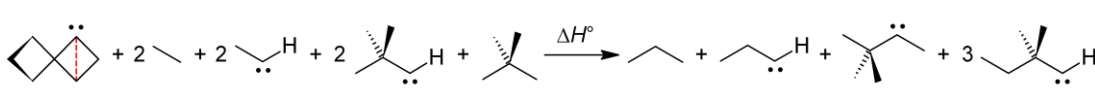
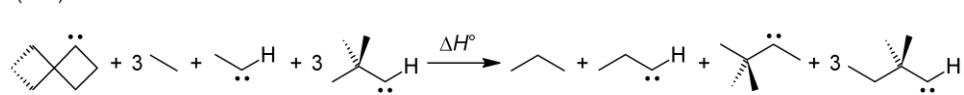
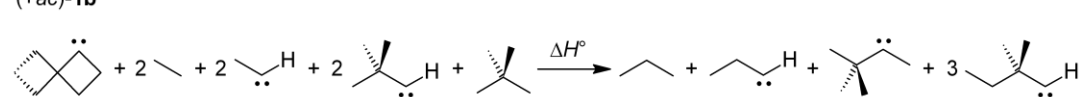
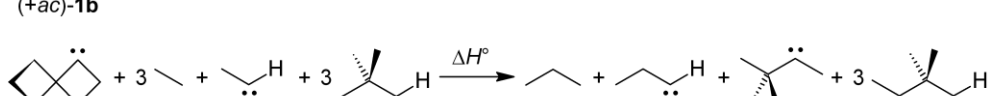
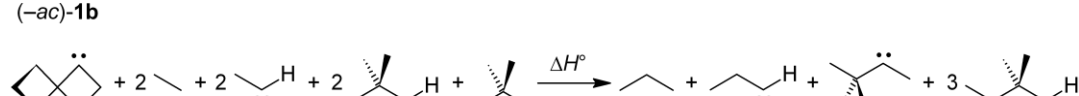
(S2) Frequency Scale Factors for E_{ZPVE} and $H_{\text{vib}}(T)$. Radom Group Scale Factors.
<http://groups.chem.usyd.edu.au/radom/More/ScaleFactor.html> (accessed Oct. 5, 2016).

SUPPORTING INFORMATION

Table S2. Homodesmotic Bond-Separation Reactions Used to Determine Ring-Strain Energy (E_s) Values

Homodesmotic Bond-Separation Reaction	$-\Delta H^{\circ a-c}$ (kcal/mol)
	(28.9)
	29.2
	(26.3)
	26.8
	52.0
	46.7
	26.8 ^e
	29.4 ^e
	29.5
	(30.9)
	39.9
	45.6 ^e
	77.2

SUPPORTING INFORMATION

Homodesmotic Bond-Separation Reaction		$-\Delta H^{\circ a-c}$ (kcal/mol)
 <p>5</p>	67.1	
 <p>6</p>	87.5	
 <p>7</p>	55.8	
 <p>7</p>	(60.1)	
 <p>(+ac)-1a</p>	44.7 ^e	
 <p>(+ac)-1a</p>	44.6 ^e	
 <p>(-ac)-1a</p>	45.3 ^e	
 <p>(-ac)-1a</p>	45.1 ^e	
 <p>(+ac)-1b</p>	45.8 ^e	
 <p>(+ac)-1b</p>	45.7 ^e	
 <p>(-ac)-1b</p>	47.1 ^e	
 <p>(-ac)-1b</p>	47.0 ^e	

SUPPORTING INFORMATION

Homodesmotic Bond-Separation Reaction		$-\Delta H^{\circ a-c}$ (kcal/mol)
<p>18</p>	ΔH°	61.0
<p>(+ac)-19</p>	ΔH°	63.9
<p>(-ac)-19</p>	ΔH°	63.9
<p>20</p>	ΔH°	40.8
<p>21</p>	ΔH°	3.7
<p>21</p>	ΔH°	(5.0)
<p>22a</p>	ΔH°	94.8
<p>22a</p>	ΔH°	(94.8)
<p>trans-22b</p>	ΔH°	83.8
<p>(+ac)-22c</p>	ΔH°	51.2
<p>(+ac)-22c</p>	ΔH°	(52.6)
<p>(-ac)-22c</p>	ΔH°	50.9

Homodesmotic Bond-Separation Reaction		$-\Delta H^{\circ a-c}$ (kcal/mol)
<p>(-ac)-22c</p>	(52.3)	
<p>s-cis-22d</p>	25.0	
<p>s-cis-22d</p>	(27.8)	
<p>s-trans-22d</p>	25.4	

^a The following IUPAC-recommended conformational stereodescriptors of Newman projections are used: (1) synperiplanar (*sp*), (2) synclinal (*sc*), (3) anticlinal (*ac*), and (4) antiperiplanar (*ap*).

^b Structures and energies were computed using the UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d) theoretical model. Standard-state H values are based on $T = 298.15$ K and $p = 1$ atm, according to eq S1, and ΔH° values were calculated using Hess's Law. ^c $E_s = -\Delta H^{\circ}$. ^d Values in parentheses do not appear elsewhere due to the following atom-environment reasons: (1) insufficient nearest-neighbor interactions, (2) conformational mismatches, (3) configurational mismatches, and (4) non-ring-related strain. ^e All carbenes were computed as spin-paired singlet electronic-states using restricted single-determinant wave functions.

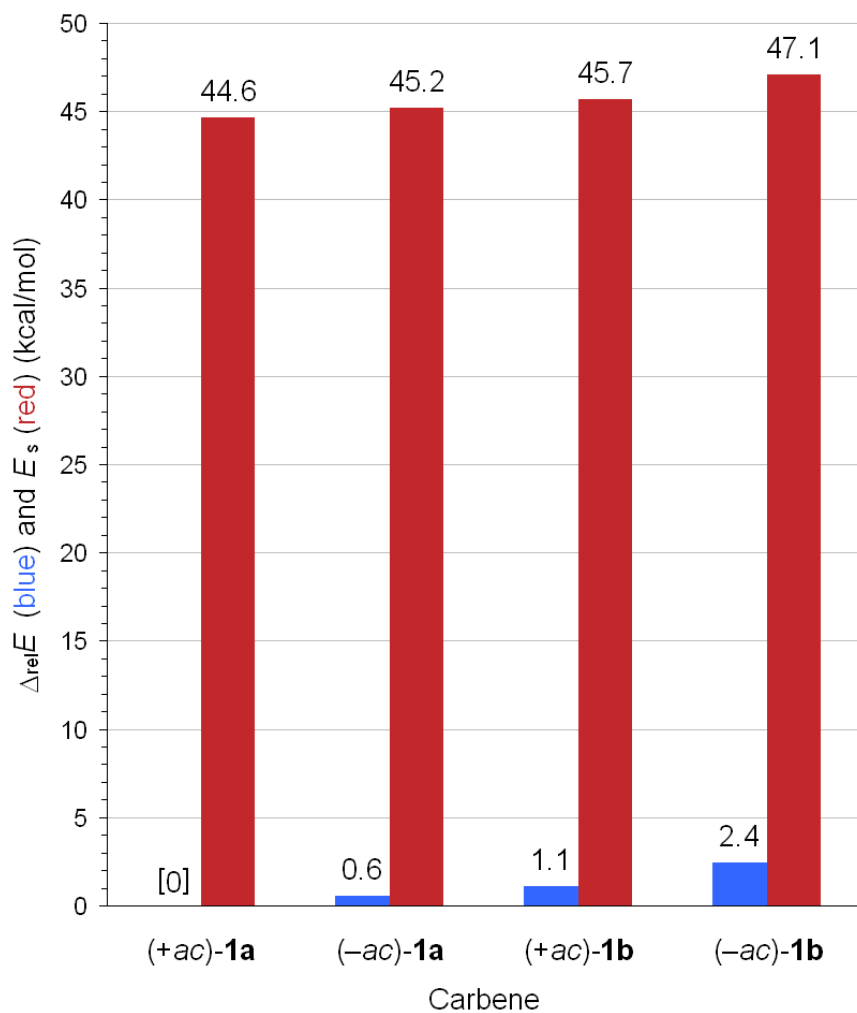
Relative ($\Delta_{\text{rel}}E$) and Ring-Strain Energies (E_s):

Figure S23. Energies relative to carbene (+ac)-1a ($\Delta_{\text{rel}}E$) ($T = 0$ K; $p = 0$ atm) and ring-strain energies (E_s) ($T = 298.15$ K; $p = 1$ atm) of carbene **1** conformers (Figure 2) were computed using the UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d) theoretical model and eq S1.

SUPPORTING INFORMATION

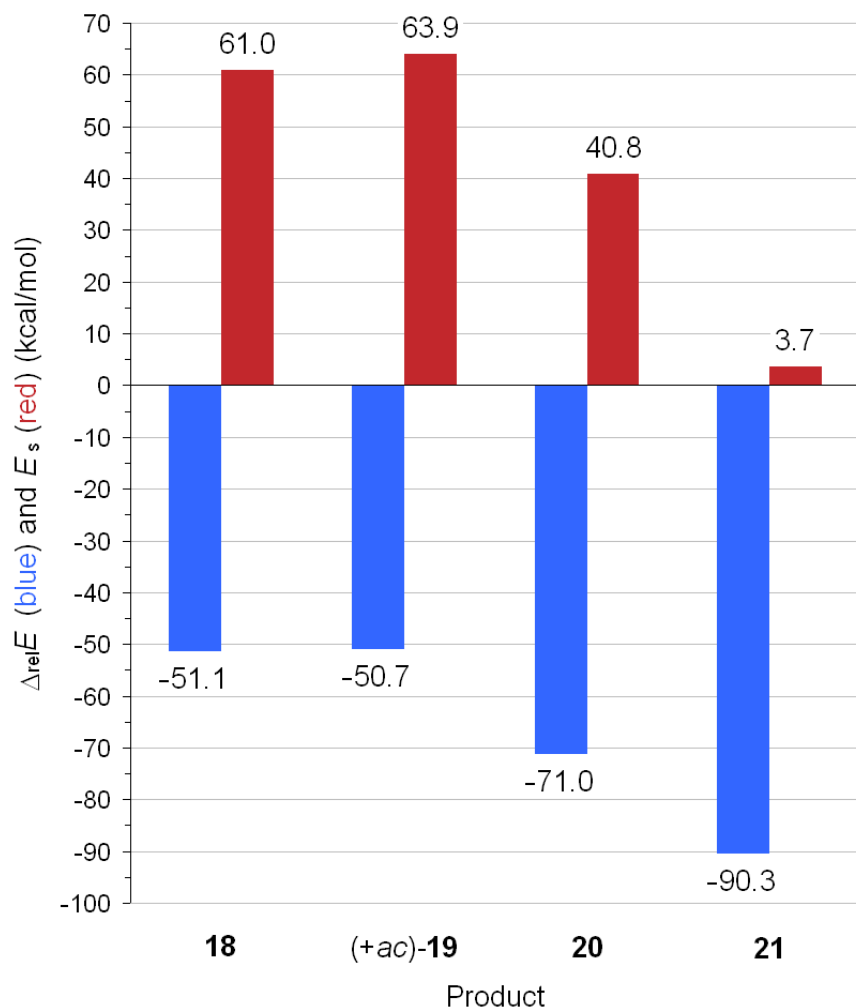


Figure S24. Energies relative to carbene (+ac)-**1a** ($\Delta_{\text{rel}}E$) ($T = 0 \text{ K}$; $p = 0 \text{ atm}$) and ring-strain energies (E_s) ($T = 298.15 \text{ K}$; $p = 1 \text{ atm}$) of products **18–21** (Table 1, Scheme 6a–d) were computed using the UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d) theoretical model and eq S1.

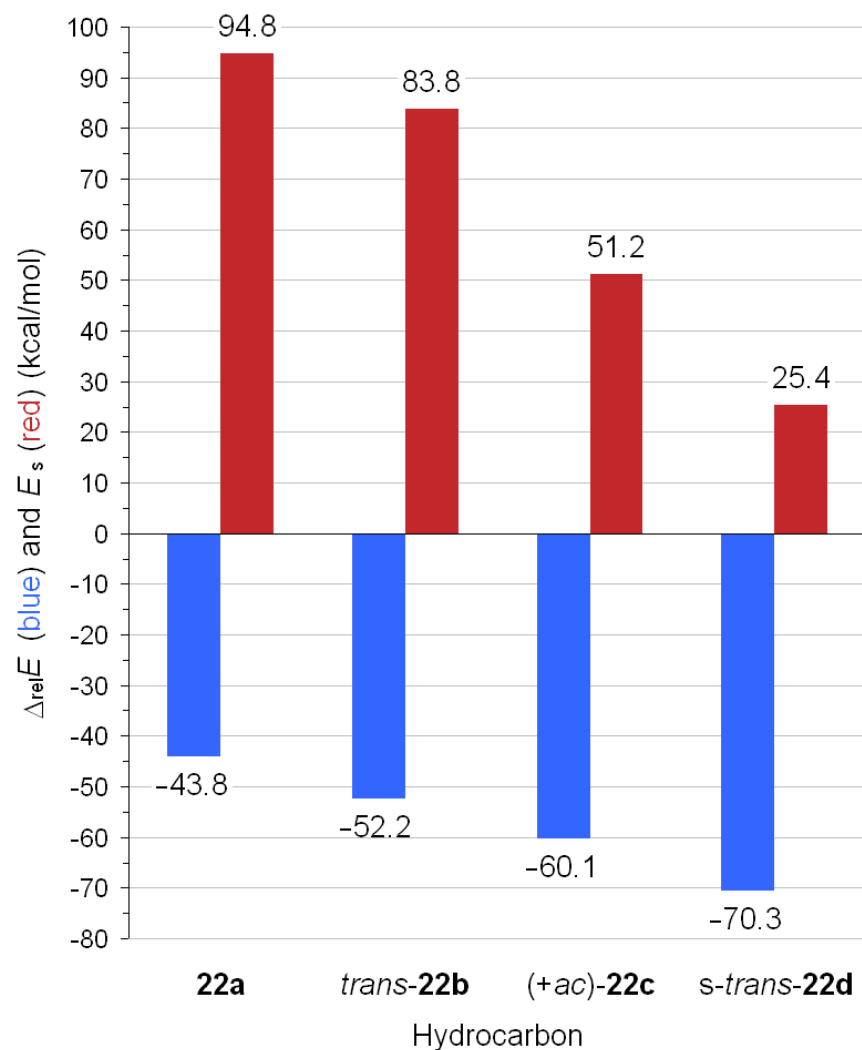


Figure S25. Energies relative to carbene (+ac)-**1a** ($\Delta_{\text{rel}}E$) ($T = 0 \text{ K}$; $p = 0 \text{ atm}$) and ring-strain energies (E_s) ($T = 298.15 \text{ K}$; $p = 1 \text{ atm}$) of product **22** (Table 1) candidates **22a–d** (Chart 1) were computed using the UQCISD(T)(fc)/6-311G(d,p)/B3LYP/6-31G(d) theoretical model and eq S1.

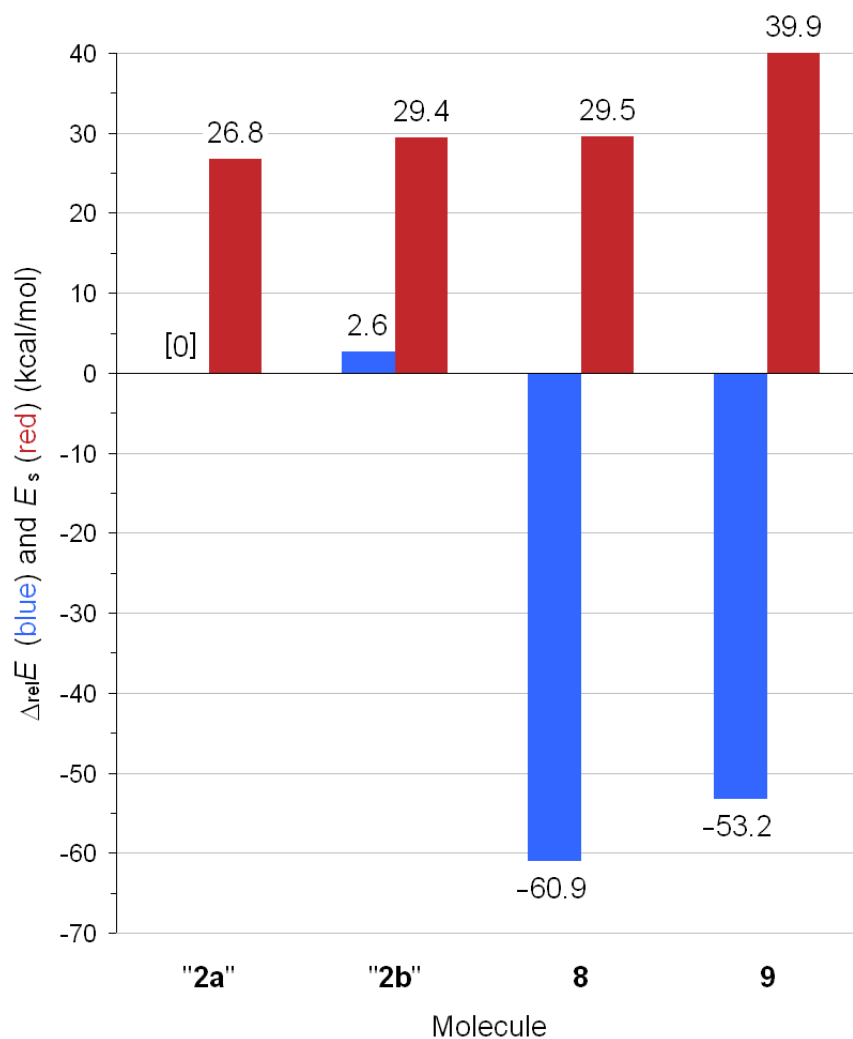


Figure S26. Energies relative to carbene “2a” ($\Delta_{\text{rel}}E$) ($T = 0 \text{ K}$; $p = 0 \text{ atm}$) and ring-strain energies (E_s) ($T = 298.15 \text{ K}$; $p = 1 \text{ atm}$) of **2**, **8**, and **9** (Scheme 2) were computed using the UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d) theoretical model and eq S1.

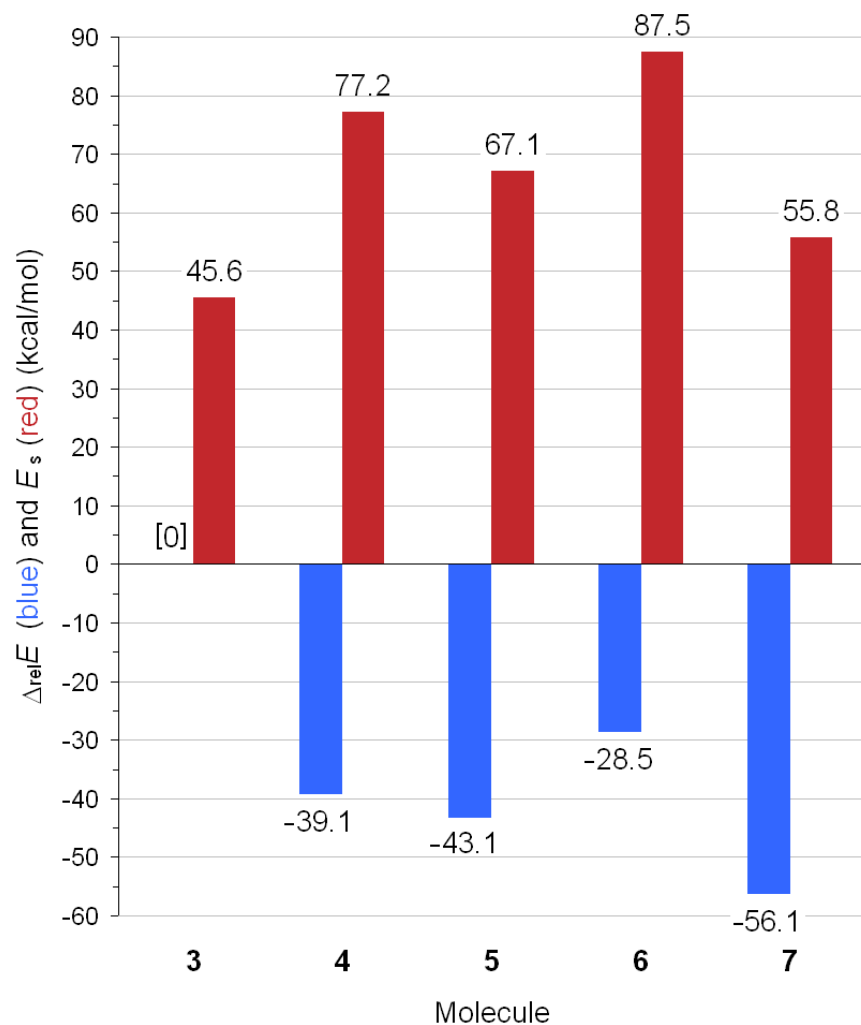


Figure S27. Energies relative to carbene **3** ($\Delta_{\text{rel}}E$) ($T = 0$ K; $p = 0$ atm) and ring-strain energies (E_s) ($T = 298.15$ K; $p = 1$ atm) of **3–7** (Scheme 1) were computed using the UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d) theoretical model and eq S1.

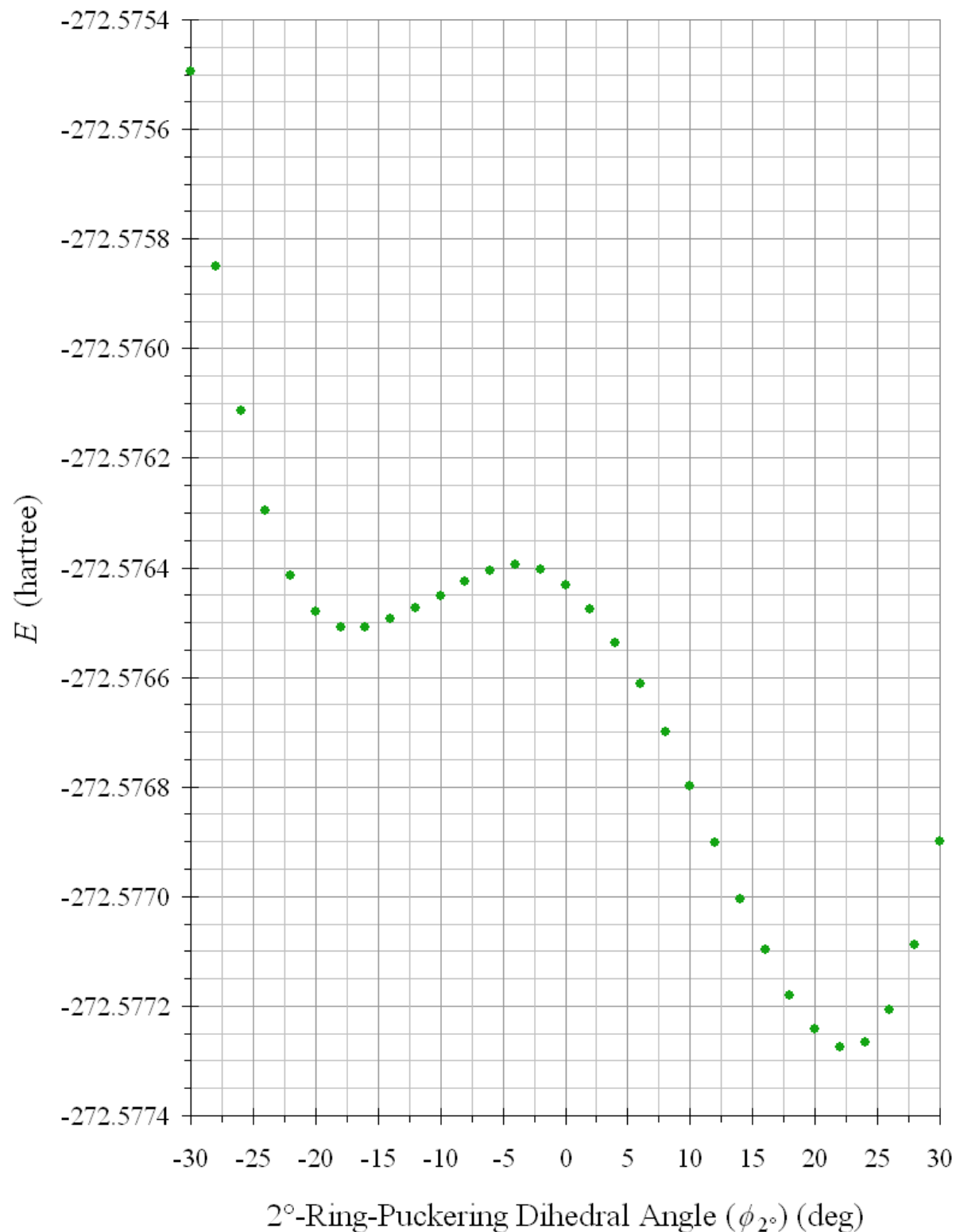


Figure S28. The energy profile of spiro[3.3]hept-1-ylidene **1a**, with unconstrained 1°-ring, was computed using the B3LYP/6-31G(d)//B3LYP/6-31G(d) theoretical model by varying $\phi_{2^\circ} = \pm(180^\circ - |\omega_2^\circ(\text{C4-C5-C7-C6})|)$ to reveal (+ac)-**1a** and (-ac)-**1a**.

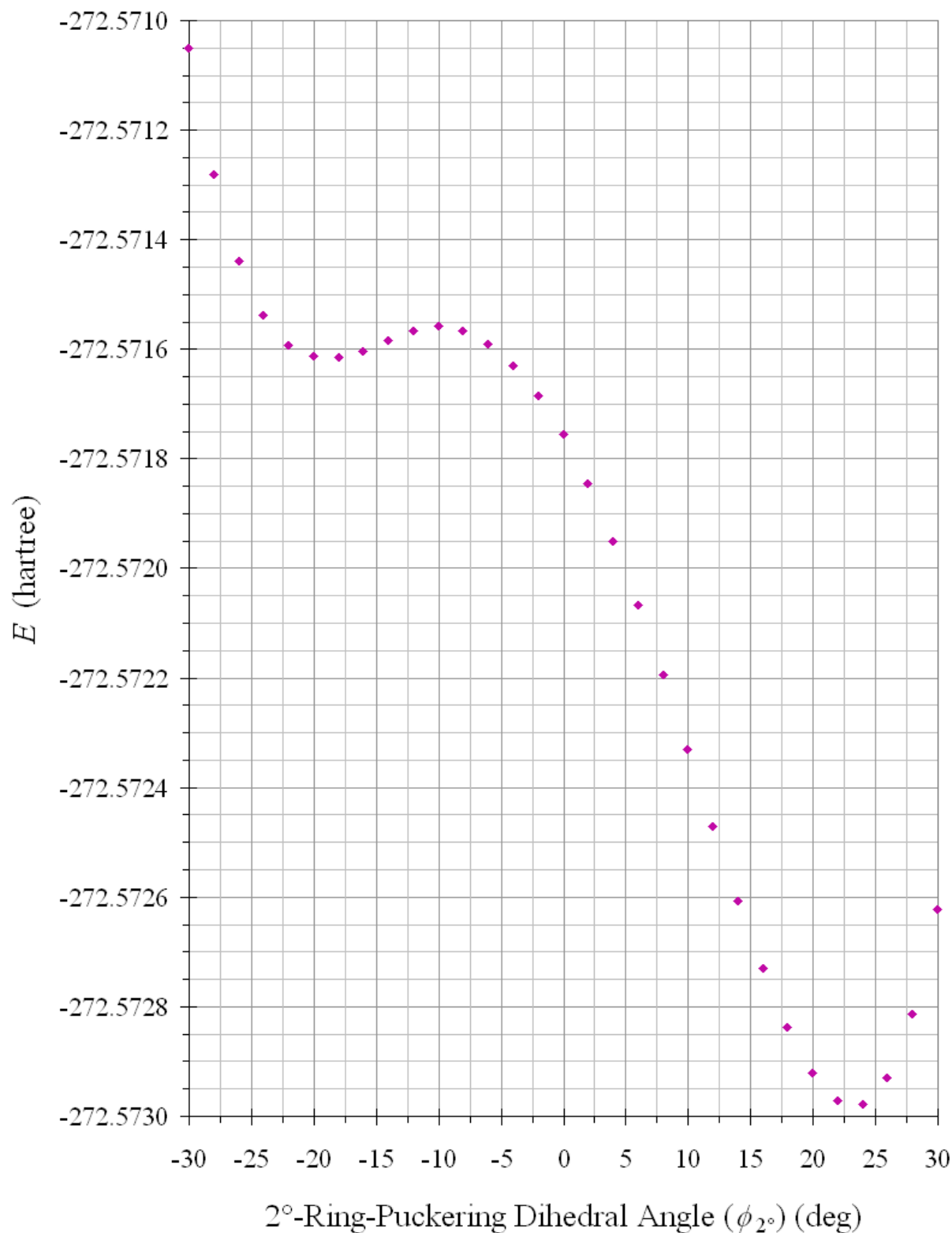


Figure S29. The energy profile of spiro[3.3]hept-1-ylidene **1b**, with unconstrained 1°-ring, was computed using the B3LYP/6-31G(d)//B3LYP/6-31G(d) theoretical model by varying $\phi_{2^\circ} = \pm(180^\circ - |\omega_{2^\circ}(\text{C4-C5-C7-C6})|)$ to reveal (+ac)-**1b** and (-ac)-**1b**.

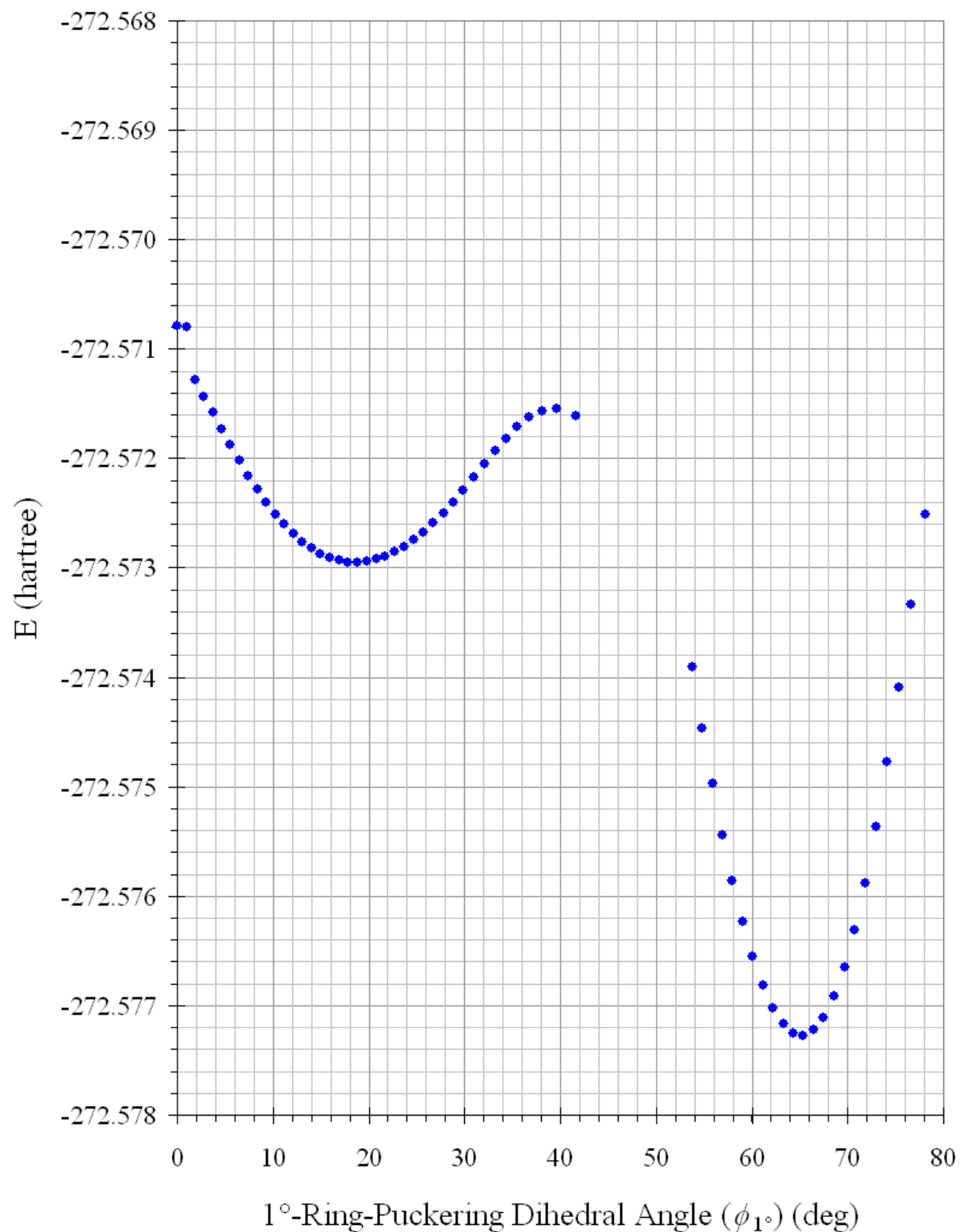


Figure S30. The energy profile of (+ac)-spiro[3.3]hept-1-ylidene ((+ac)-**1**), with unconstrained 2°-ring, was computed using the B3LYP/6-31G(d)//B3LYP/6-31G(d) theoretical model by varying $\phi_1^\circ = 180^\circ - |\omega_1^\circ(\text{C1-C2-C4-C3})|$ to reveal (+ac)-**1a** and (+ac)-**1b**.

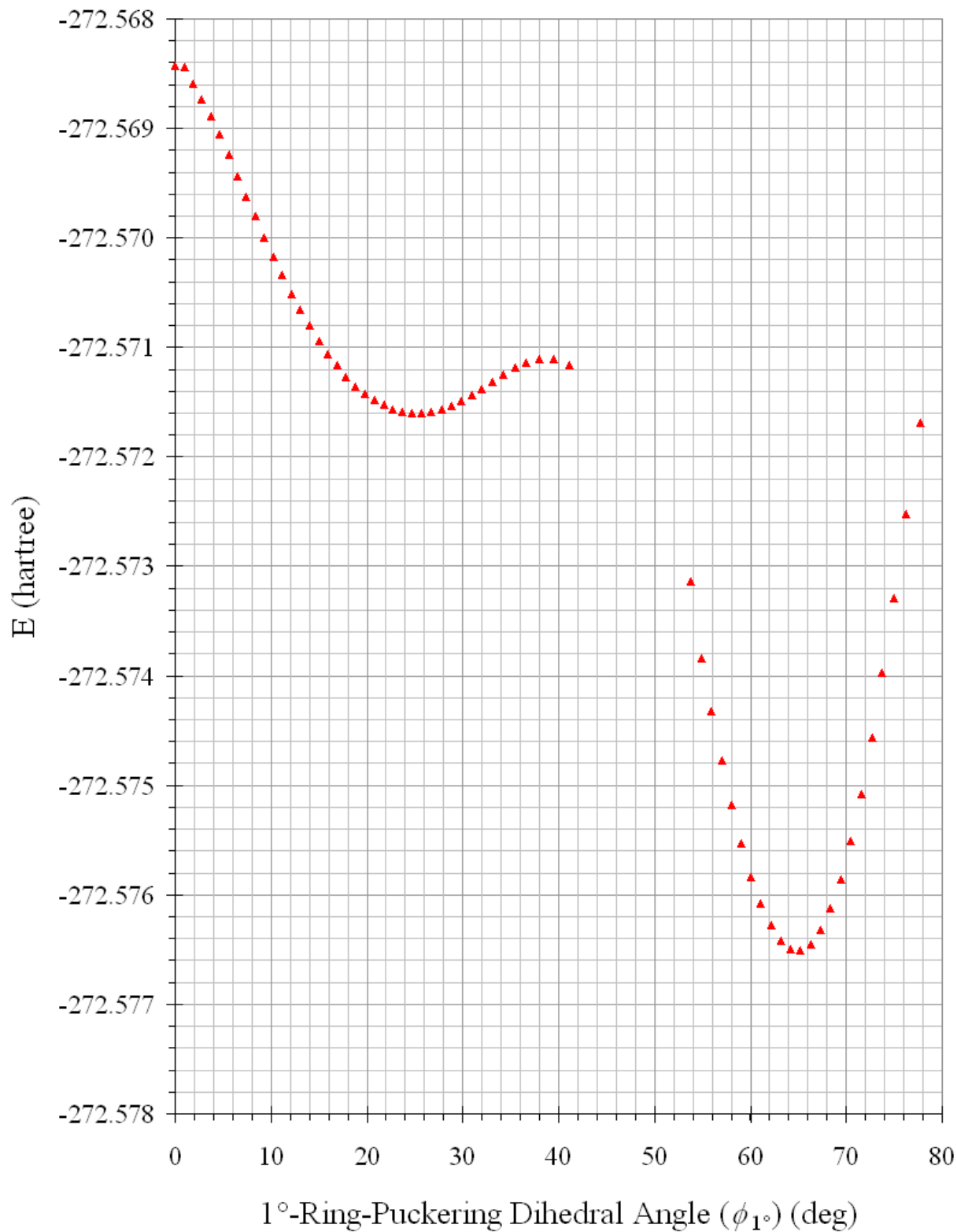


Figure S31. The energy profile of (*-ac*)-spiro[3.3]hept-1-ylidene ((*-ac*)-**1**), with unconstrained 2°-ring, was computed using the B3LYP/6-31G(d)//B3LYP/6-31G(d) theoretical model by varying $\phi_1^\circ = 180^\circ - |\omega_1^\circ(\text{C1-C2-C4-C3})|$ to reveal (*-ac*)-**1a** and (*-ac*)-**1b**.

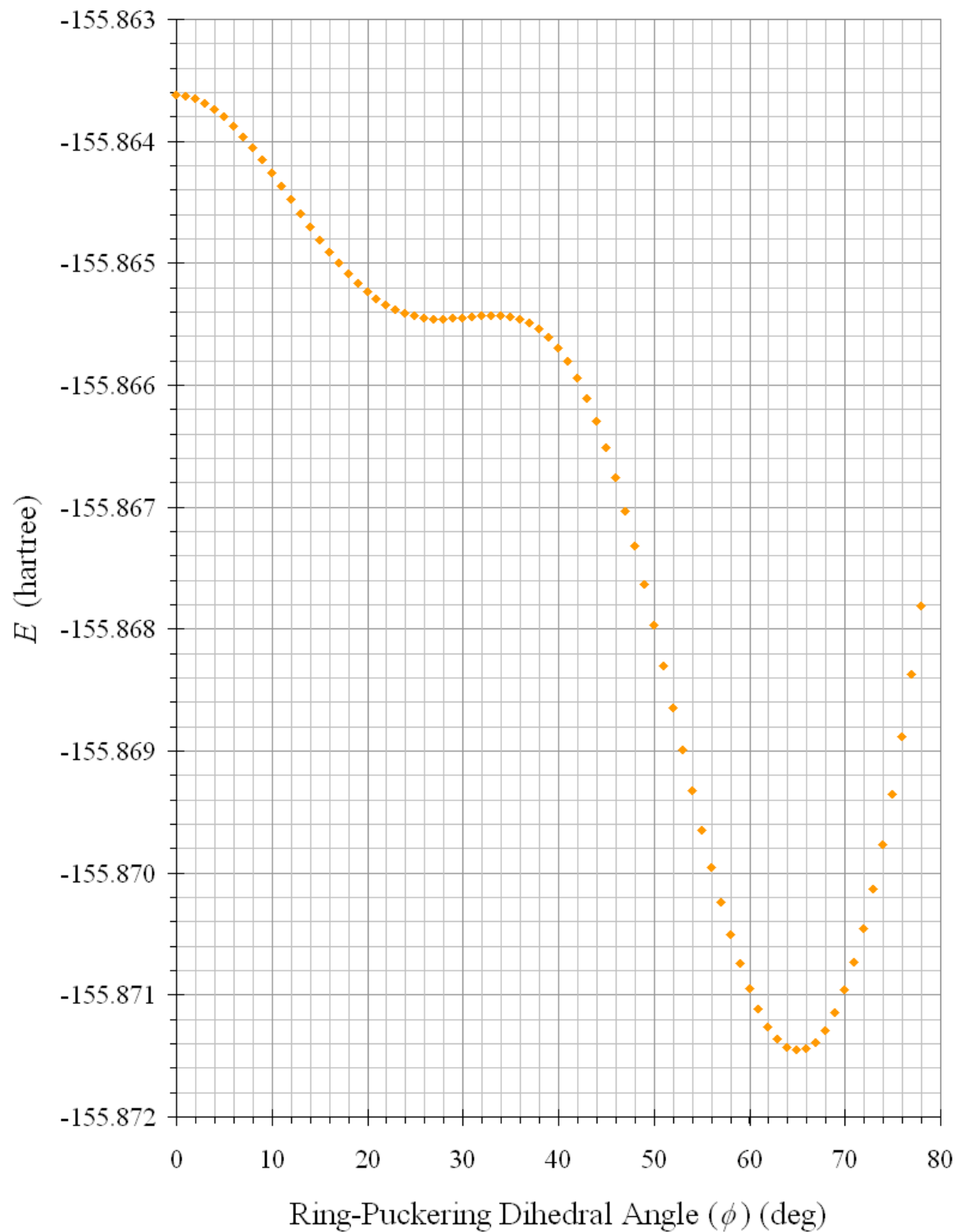


Figure S32. The energy profile of cyclobutylidene (**2**) was computed using the B3LYP/6-31G(d)//B3LYP/6-31G(d) theoretical model by varying $\phi = 180^\circ - |\omega(\text{C1-C2-C4-C3})|$ to reveal “**2a**” and “**2b**”.

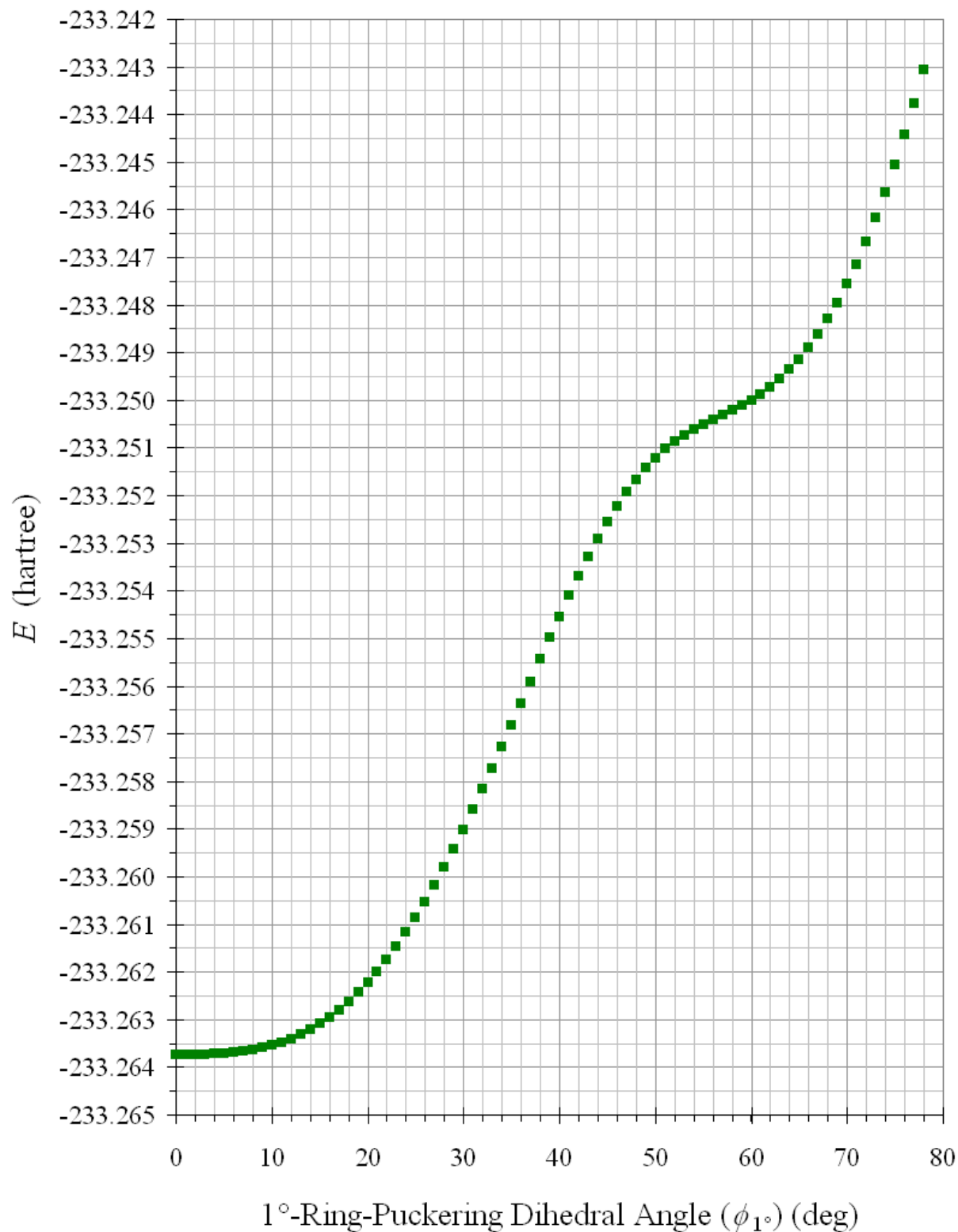


Figure S33. The energy profile of spiro[2.3]hex-4-ylidene (**3**) was computed using the B3LYP/6-31G(d)// B3LYP/6-31G(d) theoretical model by varying $\phi = 180^\circ - |\omega(\text{C4-C5-C3-C6})|$.

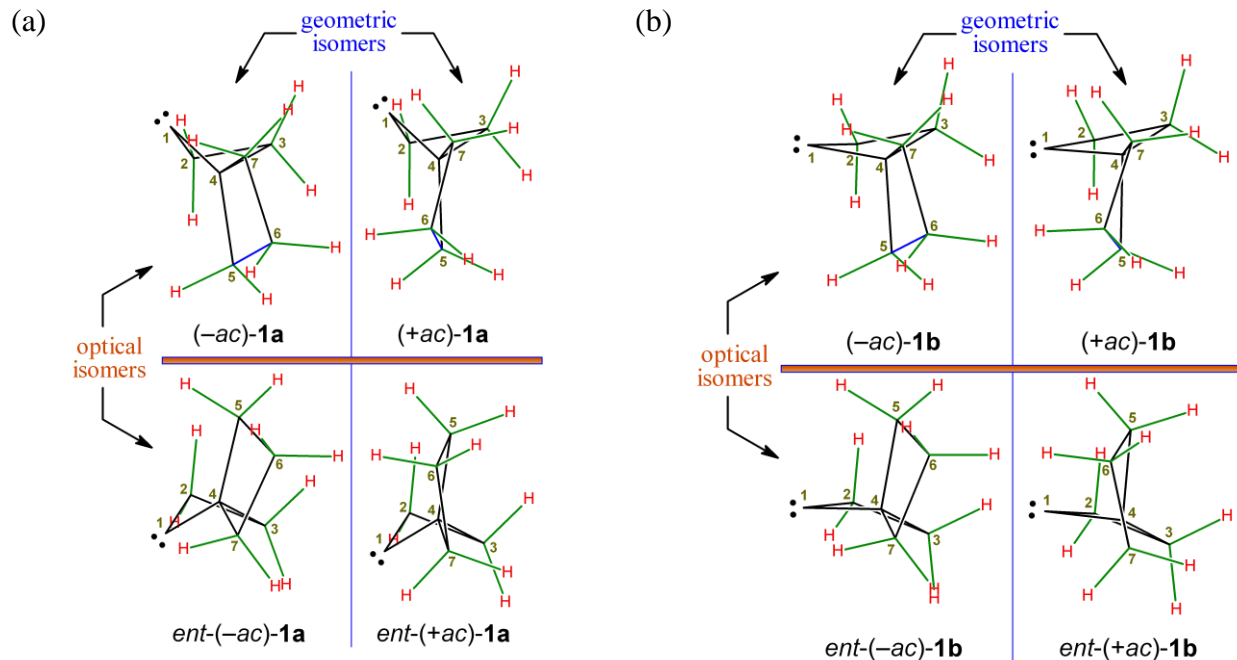
Eight Conformers of Spiro[3.3]hept-1-ylidene (**1**):

Figure S34. Dual 1°- and 2°-ring-puckering in carbene **1** affords (a) four conformational isomers of **1a** and (b) four conformational isomers of **1b**, which has an almost flat 1°-ring. The blue C6–C5 bond is used to classify the (+ac)-**1** and (–ac)-**1** geometric isomers. The 2-D renderings are of 3-D nuclear geometries optimized using the B3LYP/6-31G(d) model.

Definition of the Ring-Puckering Dihedral Angle (ϕ_n) within Cyclobutylidene(s):

Figure S35 shows that dihedral angles ϕ_n and ω_n are supplementary angles because their sum equals 180° . A modification of this relationship is plotted in Figure S36 wherein $\phi_+ = \omega + 180^\circ$ and $\phi_- = \omega - 180^\circ$. Ring-puckering dihedral angle ϕ_n can be calculated by measuring dihedral angle ω_n , using a graphical user interface, and by applying the appropriate relation plotted in Figure S36.

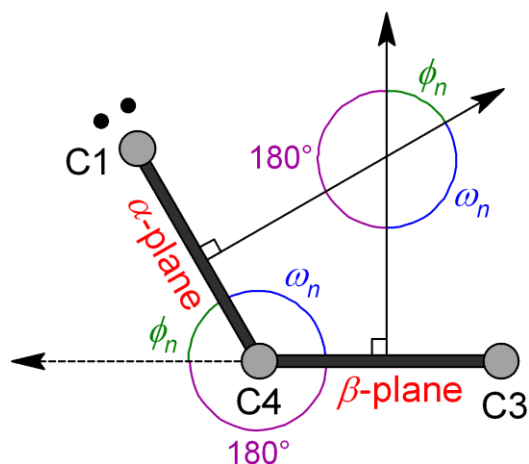


Figure S35. One sees that ϕ_n and ω_n are supplementary angles (i.e., their sum equals 180°) by viewing down the C4---C2 axis of cyclobutylidene(s), as depicted in Figure 3.

The amount of ring-puckering of a nonplanar four-membered ring also can be calculated directly from its 3-D Cartesian coordinates, because the value of ϕ_n also represents the acute angle between the normals of the α - and β -planes (Figure S35). First, the equations of the α - and β -planes must be obtained in determinant form.^{S3} Then the direction numbers of normals to the α -plane (i.e., A_α , B_α , and C_α) and β -plane (i.e., A_β , B_β , and C_β) are used in eq S2 to find the value of ϕ_n .^{S3}

$$\phi_n = \text{Arc cos} \left(\frac{|A_\alpha A_\beta + B_\alpha B_\beta + C_\alpha C_\beta|}{\sqrt{A_\alpha^2 + B_\alpha^2 + C_\alpha^2} \sqrt{A_\beta^2 + B_\beta^2 + C_\beta^2}} \right) \quad (\text{S2})$$

(S3) Oakley, C. O. *Analytic Geometry*; Harper & Row: New York, 1957; pp 179, 185.

Calculation of the Ring-Puckering Dihedral Angle (ϕ_n) Using 3-D Cartesian Coordinates:

Ring-Puckered Cyclobutylidene (2) ($\phi = 65^\circ$):

B3LYP/6-31G(d)//B3LYP/6-31G(d):

Atom	x	y	z
H	-0.293114	-0.203671	-2.088585
C	0.205945	-0.203057	-1.118265
C	-0.456426	-0.861858	0.000000
C	-0.192251	0.887134	0.000000
C	0.205945	-0.203057	1.118265
H	-0.293114	-0.203671	2.088585
H	1.301401	-0.136891	1.210861
H	1.301401	-0.136891	-1.210861
H	0.589551	1.643914	0.000000
H	-1.185403	1.322230	0.000000

C1(-0.456426, -0.861858, 0.000000)

C2(0.205945, -0.203057, -1.118265)

C3(-0.192251, 0.887134, 0.000000)

C4(0.205945, -0.203057, 1.118265)

Equation of the C2–C1–C4 α -plane:

$$\det \begin{vmatrix} x & y & z & 1 \\ 0.205945 & -0.203057 & -1.118265 & 1 \\ -0.456426 & -0.861858 & 0.000000 & 1 \\ 0.205945 & -0.203057 & 1.118265 & 1 \end{vmatrix} = 0$$

$$\det \begin{vmatrix} -0.203057 & -1.118265 & 1 \\ -0.861858 & 0.000000 & 1 \\ -0.203057 & 1.118265 & 1 \end{vmatrix} x - \det \begin{vmatrix} 0.205945 & -1.118265 & 1 \\ 0.205945 & 0.000000 & 1 \\ 0.205945 & 1.118265 & 1 \end{vmatrix} y + \det \begin{vmatrix} 0.205945 & -0.203057 & 1 \\ -0.456426 & -0.861858 & 1 \\ 0.205945 & -0.203057 & 1 \end{vmatrix} z - \det \begin{vmatrix} 0.205945 & -0.203057 & -1.118265 \\ -0.456426 & -0.861858 & 0.000000 \\ 0.205945 & -0.203057 & 1.118265 \end{vmatrix} = 0$$

$$-1.473428x + 1.481413y + 0.000000z + 0.604256 = 0$$

Equation of the C2–C3–C4 β -plane:

$$\det \begin{vmatrix} x & y & z & 1 \\ 0.205945 & -0.203057 & -1.118265 & 1 \\ -0.192251 & 0.887134 & 0.000000 & 1 \\ 0.205945 & -0.203057 & 1.118265 & 1 \end{vmatrix} = 0$$

$$\det \begin{vmatrix} -0.203057 & -1.118265 & 1 \\ 0.887134 & 0.000000 & 1 \\ -0.203057 & 1.118265 & 1 \end{vmatrix} x - \det \begin{vmatrix} 0.205945 & -1.118265 & 1 \\ -0.192251 & 0.000000 & 1 \\ 0.205945 & 1.118265 & 1 \end{vmatrix} y + \det \begin{vmatrix} 0.205945 & -0.203057 & 1 \\ -0.192251 & 0.887134 & 1 \\ 0.205945 & -0.203057 & 1 \end{vmatrix} z - \det \begin{vmatrix} 0.205945 & -0.203057 & -1.118265 \\ -0.192251 & 0.887134 & 0.000000 \\ 0.205945 & -0.203057 & 1.118265 \end{vmatrix} = 0$$

$$2.438245x + 0.890577y + 0.000000z - 0.321306 = 0$$

$$\cos \phi = \frac{(-0.1473428)(2.438245) + (1.481413)(0.890577) + (0.000000)(0.000000)}{\sqrt{(-0.1473428)^2 + 1.481413^2 + 0.000000^2} \sqrt{(2.438245)^2 + (0.890577)^2 + (0.000000)^2}} \quad \text{and} \quad \phi = \text{Arc cos}(0.419140)$$

$$= 0.419140 \quad \quad \quad = 1.13830 \text{ radians}$$

$$\quad \quad \quad = 65.2197 \text{ degrees}$$

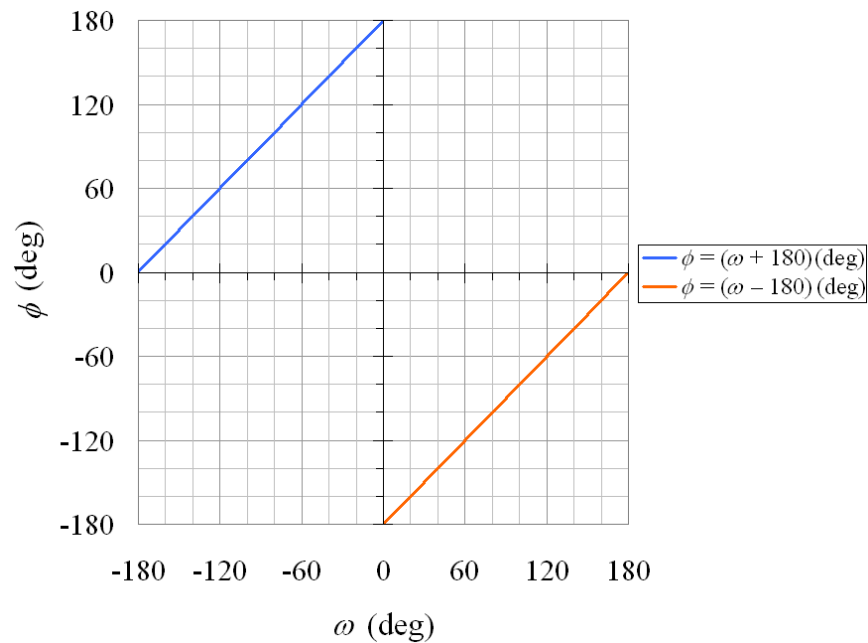
Calculation of the Ring-Puckering Dihedral Angle (ϕ_n) Using Measured ω_n Value:

Figure S36. Values of ϕ were found in this report by measuring those of dihedral angle ω , using a graphical user interface, and applying the $\omega \rightarrow \phi$ relation plotted above.

SUPPORTING INFORMATION

Molecular Energies and 3-D Cartesian Coordinates:

Cyclopropane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -73738.18 \text{ kcal/mol}$$

T = 298.15 K

$$H: -73735.48 \text{ kcal/mol}$$

Atom	x	y	z
H	1.463454	0.000000	-0.911006
C	0.871043	0.000000	0.000000
C	-0.435521	0.754345	0.000000
C	-0.435521	-0.754345	0.000000
H	1.463454	0.000000	0.911006
H	-0.731727	1.267388	-0.911006
H	-0.731727	1.267388	0.911006
H	-0.731727	-1.267388	-0.911006
H	-0.731727	-1.267388	0.911006

Cyclobutane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -98329.26 \text{ kcal/mol}$$

T = 298.15 K

$$H: -98326.14 \text{ kcal/mol}$$

Atom	x	y	z
H	-0.000080	1.963993	-0.529020
C	0.000000	1.084582	0.123437
C	1.084582	0.000000	-0.123437
C	-1.084582	0.000000	-0.123437
C	0.000000	-1.084582	0.123437
H	0.000080	-1.963993	-0.529020
H	0.000131	-1.426646	1.164322
H	-0.000131	1.426646	1.164322
H	-1.963993	-0.000080	0.529020
H	-1.426646	-0.000131	-1.164322
H	1.963993	0.000080	0.529020
H	1.426646	0.000131	-1.164322

Spiro[2.3]hexane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -146746.82 \text{ kcal/mol}$$

T = 298.15 K

$$H: -146742.73 \text{ kcal/mol}$$

Atom	x	y	z
H	-0.690185	-0.590407	-1.913901
C	-0.775672	0.134205	-1.096309
C	0.300472	0.077119	0.000000
C	-1.840912	-0.163947	0.000000
C	-0.775672	0.134205	1.096309
H	-0.690185	-0.590407	1.913901
H	-0.886674	1.135715	1.529055
H	-0.886674	1.135715	-1.529055
H	-2.735791	0.465529	0.000000
H	-2.153402	-1.212674	0.000000
C	1.498418	-0.832650	0.000000
H	1.732145	-1.376382	-0.913081
H	1.732145	-1.376382	0.913081
C	1.678467	0.671054	0.000000
H	2.034007	1.144689	-0.912803
H	2.034007	1.144689	0.912803

Spiro[3.3]heptane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -171340.64 \text{ kcal/mol}$$

T = 298.15 K

$$H: -171336.14 \text{ kcal/mol}$$

Atom	x	y	z
C	-0.962608	-0.901933	-0.658667
H	-1.082068	-1.889846	-0.197566
H	-0.740107	-1.039521	-1.723247
C	0.000000	0.000000	0.167290
C	-2.125479	0.052867	-0.277874
H	-3.083356	-0.402084	-0.006534
H	-2.307054	0.806268	-1.051589
C	-1.239569	0.604428	0.871443
H	-1.447959	0.101227	1.823670
H	-1.237057	1.687114	1.043983
C	1.239569	-0.604428	0.871443
H	1.237057	-1.687114	1.043983
H	1.447959	-0.101227	1.823670
C	0.962608	0.901933	-0.658667
H	1.082068	1.889846	-0.197566
H	0.740107	1.039521	-1.723247
C	2.125479	-0.052867	-0.277874
H	3.083356	0.402084	-0.006534
H	2.307054	-0.806268	-1.051589

SUPPORTING INFORMATION

Cyclobutylidene (“2a”; $\phi = 65^\circ$);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -97509.95 kcal/mol

$T = 298.15$ K

H : -97506.80 kcal/mol

Atom	x	y	z
H	-0.293114	-0.203671	-2.088585
C	0.205945	-0.203057	-1.118265
C	-0.456426	-0.861858	0.000000
C	-0.192251	0.887134	0.000000
C	0.205945	-0.203057	1.118265
H	-0.293114	-0.203671	2.088585
H	1.301401	-0.136891	1.210861
H	1.301401	-0.136891	-1.210861
H	0.589551	1.643914	0.000000
H	-1.185403	1.322230	0.000000

Cyclobutylidene (“2b”; $\phi = 28^\circ$);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -97507.31 kcal/mol

$T = 298.15$ K

H : -97504.12 kcal/mol

Atom	x	y	z
H	-0.461537	-0.144753	-1.992438
C	0.098439	-0.121406	-1.049409
C	-0.235645	-1.175795	0.000000
C	-0.104054	1.004827	0.000000
C	0.098439	-0.121406	1.049409
H	-0.461537	-0.144753	1.992438
H	1.165310	-0.233735	1.302209
H	1.165310	-0.233735	-1.302209
H	0.580305	1.860223	0.000000
H	-1.130921	1.379438	0.000000

Cyclobutene (8);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -97570.84 kcal/mol

$T = 298.15$ K

H : -97567.86 kcal/mol

Atom	x	y	z
H	1.246770	-0.889930	-1.146235
C	0.786221	0.000000	-0.699573
C	0.670206	0.000000	0.814722
C	-0.786221	0.000000	-0.699573
C	-0.670206	0.000000	0.814722
H	-1.420433	0.000000	1.601572
H	1.246770	0.889930	-1.146235
H	-1.246770	0.889930	-1.146235
H	-1.246770	-0.889930	-1.146235
H	1.420433	0.000000	1.601572

Methylenecyclopropane (9);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -97563.13 kcal/mol

$T = 298.15$ K

H : -97559.86 kcal/mol

Atom	x	y	z
C	0.000000	0.000000	0.318198
C	0.000000	0.000000	1.640489
H	0.927065	0.000000	2.209626
H	-0.927065	0.000000	2.209626
C	-0.769762	0.000000	-0.934102
H	-1.279603	0.912524	-1.240538
H	-1.279603	-0.912524	-1.240538
C	0.769762	0.000000	-0.934102
H	1.279603	-0.912524	-1.240538
H	1.279603	0.912524	-1.240538

SUPPORTING INFORMATION

Singlet Spiro[2.3]hex-4-ylidene (3);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -145932.04 kcal/mol

$T = 298.15$ K

H : -145927.89 kcal/mol

Atom	x	y	z
C	-0.911293	1.022886	-0.002004
H	-0.976685	1.661273	0.887268
H	-0.970569	1.659071	-0.893339
C	0.210063	-0.019683	0.005088
C	-0.648486	-1.206866	0.010212
C	-1.840370	-0.225979	-0.001860
H	-2.491481	-0.352850	0.874254
H	-2.477875	-0.360963	-0.886756
C	1.572995	0.003059	0.732194
H	1.792866	0.932352	1.250685
H	1.831891	-0.905944	1.265778
C	1.566012	-0.009442	-0.737755
H	1.818817	-0.927562	-1.258406
H	1.779517	0.910773	-1.274737

1,1'-Bi(cyclopropylidene) (4);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -145971.15 kcal/mol

$T = 298.15$ K

H : -145966.96 kcal/mol

Atom	x	y	z
C	0.655731	0.000000	0.000000
C	-0.655731	0.000000	0.000000
C	1.909854	0.769555	0.000000
H	2.216988	1.279658	0.912434
H	2.216988	1.279658	-0.912434
C	-1.909854	0.769555	0.000000
H	-2.216988	1.279658	0.912434
H	-2.216988	1.279658	-0.912434
C	-1.909854	-0.769555	0.000000
H	-2.216988	-1.279658	0.912434
H	-2.216988	-1.279658	-0.912434
C	1.909854	-0.769555	0.000000
H	2.216988	-1.279658	0.912434
H	2.216988	-1.279658	-0.912434

TS(Spiro[3.3]hept-1-ylidene (3))/1,1'-Bi(cyclopropylidene) (4);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -145914.49 kcal/mol

$T = 298.15$ K

H : -145910.22 kcal/mol

Atom	x	y	z
C	-0.428342	0.061899	-0.270071
C	0.798589	0.260018	-0.868129
C	1.838476	-0.515624	-0.163487
H	1.679403	-1.522354	0.246242
H	2.863312	-0.336608	-0.486728
C	-1.794281	0.592338	-0.146772
H	-2.355619	0.755426	-1.065435
H	-2.021625	1.307632	0.641316
C	-1.470523	-0.849864	0.290819
H	-1.494428	-1.063546	-1.357018
H	-1.797552	-1.679800	-0.332914
C	1.186796	0.584311	0.691552
H	1.606311	1.576518	0.842593
H	0.735910	0.164269	1.594433

1-Methylenespiro[2.2]pentane (5);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -145975.15 kcal/mol

$T = 298.15$ K

H : -145970.98 kcal/mol

Atom	x	y	z
C	0.381270	0.146708	0.000000
C	-0.499371	1.376414	0.000000
H	-0.569158	1.966757	-0.914734
H	-0.569158	1.966757	0.914734
C	1.564922	-0.355506	-0.760206
H	2.192214	0.373972	-1.267911
H	1.476238	-1.309562	-1.274716
C	1.564922	-0.355506	0.760206
H	1.476238	-1.309562	1.274716
H	2.192214	0.373972	1.267911
C	-1.052347	-0.007189	0.000000
C	-2.128739	-0.778640	0.000000
H	-2.051887	-1.863757	0.000000
H	-3.130642	-0.356271	0.000000

SUPPORTING INFORMATION

TS(Spiro[2.3]hex-4-ylidene (3)/1-Methylenespiro[2.2]pentane (5));
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -145911.55 kcal/mol

$T = 298.15$ K

H : -145907.21 kcal/mol

Atom	x	y	z
C	-0.922536	-0.199812	0.838772
C	-1.991805	-0.531102	0.016851
H	-2.980975	-0.676346	0.464993
H	-1.982488	-0.760021	-1.060106
C	-0.643492	1.048464	-0.458400
H	-0.873165	1.986260	0.036761
H	-0.951095	0.979774	-1.497845
C	0.336185	0.123881	0.071964
C	1.377308	-0.699731	-0.625044
H	1.702937	-0.415717	-1.624021
H	1.383608	-1.771054	-0.441428
C	1.744753	0.221162	0.540920
H	1.985796	-0.240816	1.495386
H	2.312900	1.120752	0.315887

TS(Spiro[2.3]hex-4-ylidene (3)/Bicyclo[2.2.0]hex-1(4)-ene (6));
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -145926.43 kcal/mol

$T = 298.15$ K

H : -145922.31 kcal/mol

Atom	x	y	z
C	1.023329	1.002253	-0.213168
H	1.474935	1.779822	0.414533
H	0.916249	1.404638	-1.228501
C	-0.200006	0.364617	0.412532
C	0.318939	-0.941992	0.637587
C	1.629093	-0.430447	-0.057652
H	2.511156	-0.507322	0.587292
H	1.855692	-0.932264	-1.004658
C	-1.120930	-0.700170	-0.562289
H	-1.562538	-1.662300	-0.343688
H	-0.870712	-0.541425	-1.609133
C	-1.655006	0.510476	0.203279
H	-1.987257	1.372935	-0.371742
H	-2.310037	0.257492	1.034160

Bicyclo[2.2.0]hex-1(4)-ene (6);
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -145960.49 kcal/mol

$T = 298.15$ K

H : -145956.65 kcal/mol

Atom	x	y	z
C	0.000000	-0.659689	0.000697
C	-1.524303	-0.802806	-0.000170
C	0.000000	0.659689	0.000697
C	-1.524303	0.802806	-0.000170
H	-1.977698	1.255511	-0.890472
H	-1.978867	1.255771	0.889403
H	-1.978867	-1.255771	0.889403
H	-1.977698	-1.255511	-0.890472
C	1.524303	-0.802806	-0.000170
H	1.977698	-1.255511	-0.890472
H	1.978867	-1.255771	0.889403
C	1.524303	0.802806	-0.000170
H	1.978867	1.255771	0.889403
H	1.977698	1.255511	-0.890472

Spiro[2.3]hex-4-ene (7);
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -145988.12 kcal/mol

$T = 298.15$ K

H : -145984.17 kcal/mol

Atom	x	y	z
C	-0.885563	1.059172	0.000000
H	-0.915020	1.696002	0.893119
H	-0.915020	1.696002	-0.893119
C	0.231742	-0.022218	0.000000
C	-0.861142	-1.046448	0.000000
C	-1.840934	-0.128385	0.000000
H	-2.925111	-0.187329	0.000000
C	1.534856	-0.015876	0.756387
H	1.823617	0.898995	1.268736
H	1.833959	-0.925668	1.271683
C	1.534856	-0.015876	-0.756387
H	1.833959	-0.925668	-1.271683
H	1.823617	0.898995	-1.268736
H	-0.842898	-2.133548	0.000000

SUPPORTING INFORMATION

TS(Spiro[2.3]hex-4-ylidene (3)/Spiro[2.3]hex-4-ene (7));

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -145921.00 kcal/mol

$T = 298.15$ K

H : -145916.81 kcal/mol

Atom	x	y	z
C	0.226814	-0.019137	0.006771
C	-0.885963	1.054457	0.032554
C	-0.775134	-1.162725	-0.141838
C	-1.790164	-0.163037	-0.047560
H	-2.875084	-0.254702	-0.140023
H	-0.943048	1.708555	-0.847109
H	-0.964140	1.670808	0.935715
C	1.533839	0.013267	-0.747795
H	1.818936	0.951067	-1.218471
H	1.800298	-0.877480	-1.309647
C	1.535459	-0.060159	0.753806
H	1.827793	0.827382	1.310140
H	1.806912	-1.001304	1.224274
H	-1.540779	-1.000324	0.909496

SUPPORTING INFORMATION

Singlet (+*ac*)-Spiro[3.3]hept-1-ylidene (¹(+*ac*)-**1a**; $\phi_1^\circ = 65^\circ$);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170521.47 kcal/mol

$T = 298.15$ K

H : -170516.89 kcal/mol

Atom	x	y	z
C	0.023711	-0.199495	-0.032812
C	-1.104639	-0.483811	-0.885613
C	-1.359880	-0.334084	0.839769
H	-1.701186	-1.299221	1.201242
H	-1.225078	0.386164	1.644566
C	-2.130466	0.406172	-0.344170
H	-1.981487	1.485705	-0.198145
H	-3.172385	0.157699	-0.550613
C	1.306221	-1.039085	0.022338
H	1.385976	-1.820071	-0.739946
H	1.482118	-1.484184	1.008610
C	2.120989	0.271515	-0.181573
H	2.999834	0.411663	0.454276
H	2.416920	0.413347	-1.225262
C	0.860964	1.103840	0.186958
H	0.881134	1.441929	1.229498
H	0.612752	1.956653	-0.453606

Singlet (+*ac*)-Spiro[3.3]hept-1-ylidene (¹(+*ac*)-**1b**; $\phi_1^\circ = 19^\circ$);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170520.41 kcal/mol

$T = 298.15$ K

H : -170515.82 kcal/mol

Atom	x	y	z
C	-0.065416	0.285855	0.060973
C	-0.787992	-0.568204	1.053670
C	-1.357910	0.777510	-0.615184
H	-1.669482	1.764630	-0.256873
H	-1.400453	0.777727	-1.712258
C	-2.038294	-0.375264	0.169870
H	-2.268776	-1.272445	-0.418974
H	-2.938656	-0.145909	0.755332
C	1.274187	0.991582	0.353295
H	1.384238	1.419665	1.354357
H	1.481208	1.766494	-0.393516
C	2.030366	-0.325629	0.049172
H	2.941561	-0.255992	-0.552058
H	2.244335	-0.889020	0.960794
C	0.774148	-0.877144	-0.660803
H	0.753370	-0.700042	-1.741350
H	0.498119	-1.917338	-0.461409

Singlet (-*ac*)-Spiro[3.3]hept-1-ylidene (¹(-*ac*)-**1a**; $\phi_1^\circ = 65^\circ$);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170520.92 kcal/mol

$T = 298.15$ K

H : -170516.33 kcal/mol

Atom	x	y	z
C	0.007239	-0.200648	-0.199608
C	-1.243623	-0.598950	-0.788794
C	-1.191139	-0.209917	0.919981
H	-1.438532	-1.119379	1.458858
H	-0.949147	0.613521	1.589245
C	-2.179680	0.356920	-0.200846
H	-2.035786	1.446079	-0.233112
H	-3.235353	0.081945	-0.177439
C	1.295418	-1.037581	-0.118019
H	1.540452	-1.480184	-1.089857
H	1.316250	-1.832622	0.634573
C	2.099512	0.255992	0.196831
H	2.346695	0.346506	1.259468
H	3.011168	0.421484	-0.384264
C	0.865433	1.113176	-0.197572
H	0.582098	1.924715	0.481041
H	0.943203	1.523987	-1.210354

Singlet (-*ac*)-Spiro[3.3]hept-1-ylidene (¹(-*ac*)-**1b**; $\phi_1^\circ = 25^\circ$);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170519.06 kcal/mol

$T = 298.15$ K

H : -170514.47 kcal/mol

Atom	x	y	z
C	-0.061139	0.233356	0.153098
C	-1.077022	-0.142439	1.190488
C	-1.158780	0.580633	-0.880455
H	-1.421908	1.643078	-0.857681
H	-1.012783	0.279309	-1.926054
C	-2.083578	-0.262734	0.035071
H	-2.164115	-1.312241	-0.282821
H	-3.101426	0.079864	0.260467
C	1.282322	0.959635	0.391949
H	1.476461	1.072636	1.463566
H	1.386675	1.935300	-0.093633
C	2.052340	-0.223509	-0.248300
H	2.350471	-0.023292	-1.282198
H	2.922741	-0.602003	0.295744
C	0.769561	-1.089282	-0.170531
H	0.446252	-1.614870	-1.074478
H	0.775407	-1.791744	0.669162

SUPPORTING INFORMATION

Triplet (+ac)-Spiro[3.3]hept-1-ylidene (³(+ac)-**1**; $\phi_1^\circ = 0^\circ$);

UQCISD(T)(fc)/6-311G(d,p)//UB3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -170516.30 \text{ kcal/mol}$$

T = 298.15 K

$$H: -170511.87 \text{ kcal/mol}$$

Atom	x	y	z
C	1.307274	0.000328	-0.925489
H	1.397775	0.897505	-1.546496
H	1.397752	-0.896344	-1.547233
C	0.015294	0.000048	-0.038956
C	2.261979	-0.000154	0.316599
H	2.899807	0.888794	0.415622
H	2.899542	-0.889351	0.415115
C	0.984472	-0.000241	1.104500
C	-1.102922	1.084398	-0.136550
H	-1.226927	1.429003	-1.170478
H	-1.003632	1.955185	0.518911
C	-1.102848	-1.084356	-0.137062
H	-1.003499	-1.955405	0.518041
H	-1.226842	-1.428553	-1.171127
C	-2.144161	-0.000098	0.242238
H	-2.354074	-0.000382	1.316494
H	-3.094435	0.000002	-0.300531

Triplet (-ac)-Spiro[3.3]hept-1-ylidene (³(-ac)-**1**; $\phi_1^\circ = 0^\circ$);

UQCISD(T)(fc)/6-311G(d,p)//UB3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -170516.33 \text{ kcal/mol}$$

T = 298.15 K

$$H: -170511.93 \text{ kcal/mol}$$

Atom	x	y	z
C	-1.091959	-0.000194	-0.962940
H	-1.050008	-0.897335	-1.588763
H	-1.049830	0.896652	-1.589179
C	-0.023640	-0.000074	0.193030
C	-2.292863	0.000105	0.043687
H	-2.936918	-0.888817	0.001730
H	-2.936496	0.889332	0.001632
C	-1.216631	-0.000025	1.089413
C	1.100668	-1.082688	0.189476
H	0.944821	-1.953486	-0.457650
H	1.306453	-1.434589	1.206067
C	1.100486	1.082750	0.189327
H	1.306207	1.434830	1.205869
H	0.944477	1.953427	-0.457922
C	2.111402	0.000086	-0.270125
H	3.097678	0.000205	0.203632
H	2.248839	0.000024	-1.356619

TS((+ac)-Spiro[3.3]hept-1-ylidene ((+ac)-**1a**; $\phi_1^\circ = 65^\circ$)/(+ac)-Spiro[3.3]hept-1-ylidene ((+ac)-**1b**; $\phi_1^\circ = 19^\circ$);

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -170519.96 \text{ kcal/mol}$$

T = 298.15 K

$$H: -170515.35 \text{ kcal/mol}$$

Atom	x	y	z
C	-1.258654	1.043043	-0.092202
H	-1.330961	1.712682	-0.954495
H	-1.460964	1.609727	0.823703
C	-2.058987	-0.283658	-0.154757
H	-2.296496	-0.568869	-1.183583
H	-2.968287	-0.352800	0.449792
C	-0.813843	-1.035572	0.369883
H	-0.554144	-1.985602	-0.108180
H	-0.819734	-1.176781	1.456705
C	0.062135	0.237836	0.017868
C	0.910628	-0.040533	-1.215969
C	1.331777	0.504232	0.859155
H	1.629497	1.557149	0.818010
H	1.353465	0.176698	1.907309
C	2.056908	-0.326534	-0.229724
H	2.033944	-1.404489	0.005819
H	3.077285	-0.089437	-0.557585

TS((-ac)-Spiro[3.3]hept-1-ylidene ((-ac)-**1a**; $\phi_1^\circ = 65^\circ$)/(-ac)-Spiro[3.3]hept-1-ylidene ((-ac)-**1b**; $\phi_1^\circ = 25^\circ$);

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -170519.42 \text{ kcal/mol}$$

T = 298.15 K

$$H: -170514.83 \text{ kcal/mol}$$

Atom	x	y	z
C	-1.273778	1.024641	-0.157047
H	-1.478803	1.386860	-1.170296
H	-1.349592	1.866327	0.539672
C	-0.804449	-1.102677	-0.144757
H	-0.855690	-1.540249	-1.147328
H	-0.493295	-1.877763	0.564036
C	0.049537	0.224066	-0.125154
C	1.176708	0.363690	-1.109031
C	1.136624	0.279800	0.989958
H	1.392554	1.303555	1.274296
H	0.965975	-0.312255	1.896983
C	2.096311	-0.295966	-0.092618
H	2.012528	-1.391443	-0.106680
H	3.158088	-0.027820	-0.126046
C	-2.060510	-0.262740	0.202591
H	-2.309555	-0.317336	1.267144
H	-2.964861	-0.474762	-0.375433

SUPPORTING INFORMATION

TS((+ac)-Spiro[3.3]hept-1-ylidene ((+ac)-**1b**; $\phi_1^\circ = 19^\circ$)/*ent*-(+ac)-Spiro[3.3]hept-1-ylidene (*ent*-(+ac)-**1b**; $\phi_1^\circ = -19^\circ$);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170519.09 kcal/mol

$T = 298.15$ K

H : -170514.49 kcal/mol

Atom	x	y	z
C	1.366761	0.023220	-0.970385
H	1.519096	0.925428	-1.574935
H	1.516094	-0.850970	-1.615459
C	0.071424	0.005067	-0.125833
C	2.113693	-0.009294	0.386570
H	2.733232	0.864418	0.640018
H	2.742253	-0.887387	0.598329
C	0.816912	-0.028929	1.196791
C	-1.065136	1.082428	-0.163846
H	-1.233163	1.402880	-1.198463
H	-0.938757	1.963623	0.472222
C	-1.061943	-1.073972	-0.212099
H	-0.932837	-1.982389	0.383857
H	-1.228405	-1.348100	-1.260185
C	-2.067145	-0.007811	0.281079
H	-2.160524	-0.032420	1.369607
H	-3.064386	0.000660	-0.168650

TS((+ac)-Spiro[3.3]hept-1-ylidene ((+ac)-**1a**; $\phi_1^\circ = 65^\circ$)/(-ac)-Spiro[3.3]hept-1-ylidene ((-ac)-**1a**; $\phi_1^\circ = 65^\circ$);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170520.47 kcal/mol

$T = 298.15$ K

H : -170515.88 kcal/mol

Atom	x	y	z
C	0.009868	-0.196396	-0.143945
C	-1.206528	-0.561447	-0.825473
C	-1.250011	-0.253702	0.900756
H	-1.530198	-1.187482	1.378762
H	-1.045594	0.533734	1.623835
C	-2.170380	0.372170	-0.245871
H	-2.017363	1.460315	-0.217839
H	-3.227298	0.106192	-0.297819
C	1.291983	-1.043163	-0.077679
H	1.466311	-1.603591	-1.002152
H	1.347836	-1.745650	0.760878
C	2.138217	0.254134	0.078995
H	2.615904	0.353736	1.058244
H	2.900392	0.410018	-0.689629
C	0.857871	1.123410	-0.078265
H	0.649887	1.811167	0.748238
H	0.814006	1.691529	-1.013629

TS((-ac)-Spiro[3.3]hept-1-ylidene ((-ac)-**1b**; $\phi_1^\circ = 25^\circ$)/*ent*-(-ac)-Spiro[3.3]hept-1-ylidene (*ent*-(-ac)-**1b**; $\phi_1^\circ = -25^\circ$);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170516.75 kcal/mol

$T = 298.15$ K

H : -170512.16 kcal/mol

Atom	x	y	z
C	-1.112335	0.000200	-1.044854
H	-1.099508	-0.887972	-1.687963
H	-1.099596	0.888649	-1.687585
C	-0.075110	0.000003	0.112221
C	-2.184380	-0.000062	0.071678
H	-2.847643	-0.876381	0.133522
H	-2.848450	0.875610	0.133656
C	-1.142946	0.000015	1.191099
C	1.063621	-1.077652	0.172420
H	0.932645	-1.938928	-0.490671
H	1.198555	-1.430315	1.199559
C	1.063742	1.077603	0.172627
H	1.198735	1.430102	1.199812
H	0.932863	1.938993	-0.490338
C	2.099883	-0.000049	-0.227086
H	3.056430	-0.000158	0.304713
H	2.301123	0.000050	-1.303331

TS((+ac)-Spiro[3.3]hept-1-ylidene ((+ac)-**1b**; $\phi_1^\circ = 19^\circ$)/(-ac)-Spiro[3.3]hept-1-ylidene ((-ac)-**1b**; $\phi_1^\circ = 25^\circ$);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170518.69 kcal/mol

$T = 298.15$ K

H : -170514.11 kcal/mol

Atom	x	y	z
C	-0.060843	0.256998	0.134756
C	-1.003140	-0.261319	1.174880
C	-1.210501	0.657120	-0.814994
H	-1.500971	1.705455	-0.690366
H	-1.101540	0.450658	-1.887960
C	-2.070631	-0.288654	0.063318
H	-2.181554	-1.301111	-0.348410
H	-3.068840	0.032454	0.387440
C	1.288469	0.963652	0.388940
H	1.461292	1.132897	1.456376
H	1.418227	1.910082	-0.145615
C	2.062587	-0.248366	-0.192631
H	2.511198	-0.052510	-1.171298
H	2.828644	-0.683200	0.455539
C	0.745057	-1.059982	-0.290452
H	0.458553	-1.437527	-1.276585
H	0.669007	-1.873889	0.437976

SUPPORTING INFORMATION

Cyclopropylidenecyclobutane (**18**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170572.59 kcal/mol

$T = 298.15$ K

H : -170568.00 kcal/mol

Atom	x	y	z
C	-1.347179	-0.091724	-1.099544
H	-1.478177	-1.067451	-1.585148
H	-1.230553	0.663258	-1.885348
C	-0.289879	-0.103020	0.000000
C	-2.417836	0.191951	0.000000
H	-3.296689	-0.459126	0.000000
H	-2.755022	1.232679	0.000000
C	-1.347179	-0.091724	1.099544
H	-1.478177	-1.067451	1.585148
H	-1.230553	0.663258	1.885348
C	1.027929	-0.030305	0.000000
C	2.279684	0.044263	0.769120
H	2.643372	-0.847460	1.279288
H	2.535540	0.973763	1.277483
C	2.279684	0.044263	-0.769120
H	2.535540	0.973763	-1.277483
H	2.643372	-0.847460	-1.279288

TS((+ac)-Spiro[3.3]hept-1-ylidene ((+ac)-**1a**; $\phi_1^\circ = 65^\circ$)/Cyclopropylidenecyclobutane (**18**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170517.49 kcal/mol

$T = 298.15$ K

H : -170512.86 kcal/mol

Atom	x	y	z
C	-0.096334	-0.161080	0.150717
C	1.100320	-0.407399	0.811594
C	2.149518	0.501557	0.309379
H	1.980536	1.558487	0.057628
H	3.161576	0.307888	0.663667
C	-1.332362	-1.049125	0.040823
H	-1.449416	-1.794475	0.832489
H	-1.407994	-1.548625	-0.932031
C	-2.195143	0.248708	0.092318
H	-3.020971	0.316759	-0.620838
H	-2.576647	0.450355	1.096855
C	-0.926828	1.092410	-0.232020
H	-0.866967	1.351856	-1.294404
H	-0.737377	1.992981	0.360212
C	1.582670	-0.449513	-0.757723
H	2.043138	-1.392822	-1.043704
H	1.183075	0.104241	-1.610407

TS((-ac)-Spiro[3.3]hept-1-ylidene ((-ac)-**1a**; $\phi_1^\circ = 65^\circ$)/Cyclopropylidenecyclobutane (**18**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170517.60 kcal/mol

$T = 298.15$ K

H : -170512.96 kcal/mol

Atom	x	y	z
C	-0.076592	-0.164893	0.354817
C	1.206494	-0.521355	0.746703
C	2.188719	0.421905	0.182307
H	2.039579	1.509381	0.124396
H	3.237245	0.146048	0.291832
C	-1.334822	-1.022562	0.201215
H	-1.690245	-1.354304	1.184605
H	-1.258250	-1.902696	-0.444540
C	-2.097012	0.226016	-0.331683
H	-2.196275	0.218739	-1.421649
H	-3.077686	0.429169	0.106648
C	-0.921898	1.123237	0.146609
H	-0.547352	1.896202	-0.531696
H	-1.114631	1.592337	1.119228
C	1.372380	-0.337185	-0.881667
H	0.869888	0.356114	-1.559670
H	1.714113	-1.241967	-1.378963

((+ac)-1-Methylenespiro[2.3]hexane ((+ac)-**19**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170572.19 kcal/mol

$T = 298.15$ K

H : -170567.57 kcal/mol

Atom	x	y	z
C	-1.110205	0.047130	-1.097379
H	-0.796915	-0.607135	-1.916971
H	-1.529217	0.967593	-1.520492
C	-0.063555	0.333283	-0.000001
C	-2.020691	-0.576449	0.000001
H	-1.977219	-1.669895	0.000006
H	-3.070743	-0.269692	-0.000001
C	-1.110206	0.047139	1.097378
H	-0.796918	-0.607120	1.916976
H	-1.529220	0.967605	1.520483
C	1.069789	1.362078	-0.000003
H	1.245264	1.931424	0.913916
H	1.245266	1.931419	-0.913926
C	1.338177	-0.088359	0.000001
C	2.227926	-1.068433	0.000003
H	3.297437	-0.868801	0.000002
H	1.924857	-2.113732	0.000006

SUPPORTING INFORMATION

TS((+ac)-Spiro[3.3]hept-1-ylidene ((+ac)-**1a**; $\phi_1^\circ = 65^\circ$)/(+ac)-1-Methylenespiro[2.3]hexane ((+ac)-**19**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170510.14 kcal/mol

$T = 298.15$ K

H : -170505.38 kcal/mol

Atom	x	y	z
C	1.186844	-0.310445	0.809264
C	2.252322	0.495654	0.443580
H	3.196989	0.413838	0.993240
H	2.278257	1.301788	-0.308135
C	1.099204	-0.614455	-0.941435
H	1.404134	-1.649029	-1.058784
H	1.431208	0.057622	-1.729026
C	-0.028435	-0.213117	-0.106079
C	-0.862708	1.075280	-0.372556
H	-0.981483	1.301662	-1.438583
H	-0.520682	1.979600	0.140048
C	-1.313508	-0.995424	0.239246
H	-1.267587	-1.541257	1.185632
H	-1.633466	-1.679116	-0.555051
C	-2.095073	0.351505	0.240562
H	-3.011649	0.380119	-0.355645
H	-2.327600	0.700791	1.250808

TS((-ac)-Spiro[3.3]hept-1-ylidene ((-ac)-**1a**; $\phi_1^\circ = 65^\circ$)/(-ac)-1-Methylenespiro[2.3]hexane ((-ac)-**19**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170512.34 kcal/mol

$T = 298.15$ K

H : -170507.65 kcal/mol

Atom	x	y	z
H	-2.422877	-0.129458	1.213613
C	-2.119492	-0.241307	0.167708
C	-1.296814	0.977333	-0.342016
C	-0.865102	-1.147535	0.014698
C	-0.012809	0.145823	-0.155851
H	-2.999082	-0.520249	-0.419830
H	-0.883499	-1.740923	-0.907013
H	-0.629436	-1.815860	0.850304
H	-1.476430	1.200668	-1.399048
H	-1.376927	1.910349	0.225514
C	1.303338	0.461138	-0.679854
C	2.267426	-0.452924	-0.291839
H	3.297375	-0.124175	-0.136541
H	2.126734	-1.544263	-0.188952
C	1.059631	0.519211	0.913422
H	1.166074	1.499616	1.380052
H	1.180996	-0.306145	1.624298

(-ac)-1-Methylenespiro[2.3]hexane ((-ac)-**19**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170572.20 kcal/mol

$T = 298.15$ K

H : -170567.58 kcal/mol

Atom	x	y	z
C	-1.078723	-0.219801	-1.095457
H	-0.924883	-1.220664	-1.514234
H	-1.172305	0.494398	-1.920630
C	-0.047364	0.121205	0.000000
C	-2.183670	-0.192500	0.000000
H	-2.898247	-1.020795	0.000000
H	-2.741230	0.749114	0.000000
C	-1.078723	-0.219801	1.095457
H	-0.924883	-1.220664	1.514234
H	-1.172305	0.494398	1.920630
C	0.865070	1.354878	0.000000
H	0.928349	1.946744	0.914352
H	0.928349	1.946744	-0.914352
C	1.406603	-0.017569	0.000000
C	2.470283	-0.805804	0.000000
H	3.480978	-0.402979	0.000000
H	2.375320	-1.889942	0.000000

Bicyclo[3.2.0]hept-1(5)-ene (**20**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170592.44 kcal/mol

$T = 298.15$ K

H : -170588.18 kcal/mol

Atom	x	y	z
H	1.267879	-0.699808	-2.032704
C	1.059964	0.071718	-1.280107
C	-0.306477	-0.009296	-0.665332
C	-0.306477	-0.009296	0.665332
C	1.059964	0.071718	1.280107
C	1.962428	-0.106134	0.000000
H	1.234096	1.039893	-1.772189
H	1.267879	-0.699808	2.032704
H	1.234096	1.039893	1.772189
H	2.386398	-1.115739	0.000000
H	2.804557	0.592957	0.000000
C	-1.825532	-0.017099	-0.792319
H	-2.273282	-0.905799	-1.254091
H	-2.279184	0.873575	-1.244759
C	-1.825532	-0.017099	0.792319
H	-2.279184	0.873575	1.244759
H	-2.273282	-0.905799	1.254091

SUPPORTING INFORMATION

TS((+ac)-Spiro[3.3]hept-1-ylidene ((+ac)-**1b**; ϕ_1^+ = 19°)/Bicyclo[3.2.0]hept-1(5)-ene (**20**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170517.67 kcal/mol

$T = 298.15$ K

H : -170513.08 kcal/mol

Atom	x	y	z
C	-0.673715	-0.961726	-0.566758
C	-1.302980	1.032658	0.246239
C	0.109422	0.456819	0.179197
H	-1.546792	1.533101	1.188975
H	-0.479700	-0.715867	-1.617976
C	0.589045	-0.688573	0.891316
C	1.944478	-0.466801	0.128498
H	2.199780	-1.235673	-0.608978
H	2.784837	-0.378280	0.825959
C	1.421635	0.880820	-0.455929
H	1.444876	1.037710	-1.541909
H	1.853569	1.767090	0.024280
H	-1.485505	1.730767	-0.578599
H	-0.479625	-2.020182	-0.403110
C	-1.960846	-0.342349	-0.008912
H	-2.240434	-0.835842	0.923847
H	-2.813239	-0.347912	-0.694389

1,2-Dimethylenecyclopentane (**21**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170611.80 kcal/mol

$T = 298.15$ K

H : -170607.29 kcal/mol

Atom	x	y	z
H	-1.173470	-0.386913	-2.129490
C	-0.975527	0.172400	-1.209357
C	-1.799089	-0.313747	0.000000
C	-0.975527	0.172400	1.209357
C	0.469378	0.051672	0.744407
C	0.469378	0.051672	-0.744407
H	-1.210620	1.227267	-1.416090
H	-1.845468	-1.409891	0.000000
H	-2.826860	0.062974	0.000000
H	-1.210620	1.227267	1.416090
H	-1.173470	-0.386913	2.129490
C	1.531146	-0.059373	-1.551467
H	1.423519	-0.070901	-2.632814
H	2.544020	-0.142944	-1.166242
C	1.531146	-0.059373	1.551467
H	2.544020	-0.142944	1.166242
H	1.423519	-0.070901	2.632814

TS(Bicyclo[3.2.0]hept-1(5)-ene (**20**)/1,2-Dimethylenecyclopentane (**21**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170559.85 kcal/mol

$T = 298.15$ K

H : -170555.28 kcal/mol

Atom	x	y	z
H	1.179088	1.937214	-0.927391
C	1.020109	1.275120	-0.066297
C	-0.363544	0.679946	0.013237
C	-0.353330	-0.681087	0.015198
C	1.023580	-1.241439	0.265977
C	1.909312	-0.015388	-0.157775
H	1.252968	1.869567	0.828685
H	1.265597	-2.139253	-0.314313
H	1.177872	-1.494016	1.325150
H	2.228601	-0.156541	-1.196258
H	2.817401	0.066204	0.447999
C	-1.734793	1.059198	0.194161
H	-2.178404	1.938282	-0.286796
H	-2.235444	0.774028	1.111683
C	-1.701814	-1.080688	-0.259525
H	-2.169715	-1.960856	0.195512
H	-2.135086	-0.808602	-1.214129

Spiro[bicyclo[1.1.0]butane-2,1'-cyclobutane] (**22a**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170565.26 kcal/mol

$T = 298.15$ K

H : -170560.90 kcal/mol

Atom	x	y	z
C	-1.262682	-1.034621	-0.087042
H	-1.468738	-1.474598	-1.069693
H	-1.283698	-1.835535	0.660446
C	-0.023211	-0.123236	-0.096845
C	-2.131088	0.225710	0.198226
H	-3.033674	0.344092	-0.408288
H	-2.408745	0.305095	1.253765
C	-0.920933	1.136179	-0.164853
H	-0.991324	1.545554	-1.178915
H	-0.690123	1.950170	0.529580
C	1.168163	-0.350383	0.778094
H	1.342640	-1.134941	1.503575
C	1.299596	-0.420722	-0.720701
H	1.595281	-1.267136	-1.327598
C	2.159983	0.520097	0.069517
H	1.988446	1.597530	0.003278
H	3.210970	0.251620	0.175467

SUPPORTING INFORMATION

TS((+ac)-Spiro[3.3]hept-1-ylidene ((+ac)-**1a**; $\phi_1^\circ = 65^\circ$)/Spiro[bicyclo[1.1.0]butane-2,1'-cyclobutane] (**22a**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -170506.35 \text{ kcal/mol}$$

T = 298.15 K

$$H: -170501.76 \text{ kcal/mol}$$

Atom	x	y	z
C	2.100462	-0.274494	0.140533
C	1.273979	1.036769	0.006860
C	0.838987	-1.104292	-0.240653
C	-0.000200	0.180906	-0.034268
H	2.966500	-0.377820	-0.519505
H	0.609324	-1.961046	0.401379
H	0.855718	-1.445321	-1.281767
H	1.336739	1.753064	0.832375
H	1.467752	1.564770	-0.934432
C	-1.132574	0.301969	1.018105
C	-2.044700	-0.552007	0.102031
H	-3.122337	-0.472464	0.246528
H	-1.710517	-1.567800	-0.102537
C	-1.318574	0.508133	-0.696002
H	-1.579142	1.412110	0.065096
H	-1.550463	0.972322	-1.656366
H	2.422144	-0.459724	1.169588

TS((-ac)-Spiro[3.3]hept-1-ylidene ((-ac)-**1a**; $\phi_1^\circ = 65^\circ$)/Spiro[bicyclo[1.1.0]butane-2,1'-cyclobutane] (**22a**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -170506.15 \text{ kcal/mol}$$

T = 298.15 K

$$H: -170501.56 \text{ kcal/mol}$$

Atom	x	y	z
H	-2.411675	-0.284702	1.237094
C	-2.094981	-0.258129	0.189863
C	-1.279264	1.020447	-0.156295
C	-0.831353	-1.130088	-0.070528
C	0.003597	0.174778	-0.115997
H	-2.964467	-0.467223	-0.439880
H	-0.864198	-1.639023	-1.040781
H	-0.580138	-1.866439	0.698992
H	-1.480449	1.407226	-1.161070
H	-1.345350	1.853133	0.553165
C	1.279853	0.421447	-0.949068
C	2.058082	-0.528056	-0.001251
H	3.143074	-0.428052	0.035484
H	1.718522	-1.562014	0.030372
C	1.193165	0.430703	0.785016
H	1.549652	1.416790	0.180356
H	1.260441	0.783686	1.815836

trans-Tricyclo[3.2.0.0^{1,4}]heptane (*trans*-**22b**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -170573.66 \text{ kcal/mol}$$

T = 298.15 K

$$H: -170569.50 \text{ kcal/mol}$$

Atom	x	y	z
C	0.000000	0.000000	-0.517286
C	0.471034	0.574846	0.820033
H	0.237860	1.544115	1.260407
C	-0.471034	-0.574846	0.820033
H	-0.237860	-1.544115	1.260407
C	1.414234	-0.323167	-0.969598
H	1.611408	-1.357833	-1.277638
H	1.788290	0.349582	-1.749598
C	1.902432	0.121729	0.452725
H	2.321331	-0.671913	1.082797
H	2.615031	0.949664	0.416931
C	-1.902432	-0.121729	0.452725
H	-2.321331	0.671913	1.082797
H	-2.615031	-0.949664	0.416931
C	-1.414234	0.323167	-0.969598
H	-1.788290	-0.349582	-1.749598
H	-1.611408	1.357833	-1.277638

TS((+ac)-Spiro[3.3]hept-1-ylidene ((+ac)-**1b**; $\phi_1^\circ = 19^\circ$)/*trans*-Tricyclo[3.2.0.0^{1,4}]heptane (*trans*-**22b**);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -170514.60 \text{ kcal/mol}$$

T = 298.15 K

$$H: -170510.11 \text{ kcal/mol}$$

Atom	x	y	z
H	-2.207033	-1.151762	0.661434
C	-1.942740	-0.409789	-0.099642
C	-1.362240	0.928894	0.441526
C	-0.625789	-0.682374	-0.913791
C	-0.017398	0.432887	-0.074041
H	-2.793972	-0.308667	-0.780452
H	-1.735768	1.788807	-0.123579
H	-1.443949	1.153919	1.512073
C	1.391264	0.969309	-0.332909
H	1.679312	1.786239	0.337111
H	1.602731	1.259547	-1.367177
C	0.526451	-0.871094	0.535708
H	0.221476	-1.209339	1.525536
H	0.143263	-1.689350	-0.286146
C	1.946886	-0.410420	0.138342
H	2.624064	-0.356906	0.994585
H	2.411274	-1.016958	-0.644537

SUPPORTING INFORMATION

(+ac)-Spiro[3.3]hept-1-ene ((+ac)-22c);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d);

$E + Z(E_{ZPVE})$: -170581.53 kcal/mol

$T = 298.15$ K

H : -170577.15 kcal/mol

Atom	x	y	z
C	-1.045373	0.171407	-1.083360
H	-0.934061	-0.470298	-1.963988
H	-1.205652	1.202443	-1.419999
C	0.069857	0.097971	0.000000
C	-2.075668	-0.244239	0.000000
H	-2.253742	-1.324876	0.000000
H	-3.044019	0.266045	0.000000
C	-1.045373	0.171407	1.083360
H	-0.934061	-0.470298	1.963988
H	-1.205652	1.202443	1.419999
C	1.039576	-1.072104	0.000000
H	0.878501	-2.148305	0.000000
C	1.351372	1.004654	0.000000
H	1.466047	1.635055	-0.891496
C	2.133377	-0.298833	0.000000
H	3.199980	-0.508842	0.000000
H	1.466047	1.635055	0.891496

TS((+ac)-Spiro[3.3]hept-1-ylidene ((+ac)-1b; $\phi_1 = 19^\circ$)/(+ac)-Spiro[3.3]hept-1-ene ((+ac)-22c));
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d);

$E + Z(E_{ZPVE})$: -170513.39 kcal/mol

$T = 298.15$ K

H : -170508.75 kcal/mol

Atom	x	y	z
H	-3.045937	-0.116192	0.139795
C	-2.053313	0.156713	-0.231013
C	-1.050831	0.776760	0.777515
C	-1.034950	-0.986654	-0.475850
C	0.066361	-0.059651	0.106568
H	-2.161417	0.785431	-1.118957
H	-0.896110	-1.343441	-1.501547
H	-1.215655	-1.844739	0.182306
H	-0.928823	1.865330	0.779319
H	-1.243170	0.437370	1.802543
C	0.916499	0.621786	-1.014786
C	2.065176	0.165516	-0.302711
H	1.720157	1.394079	-0.294222
H	3.124418	0.233177	-0.571077
C	1.358585	-0.588277	0.804416
H	1.541375	-0.251951	1.831905
H	1.500002	-1.676227	0.765105

(-ac)-Spiro[3.3]hept-1-ene ((-ac)-22c);
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d);

$E + Z(E_{ZPVE})$: -170581.80 kcal/mol

$T = 298.15$ K

H : -170577.45 kcal/mol

Atom	x	y	z
C	-1.042954	-0.201249	-1.081703
H	-1.224657	-1.231625	-1.409488
H	-0.919032	0.428555	-1.969574
C	0.073573	-0.142487	0.000000
C	-2.063965	0.241019	0.000000
H	-3.045041	-0.244075	0.000000
H	-2.213027	1.325961	0.000000
C	-1.042954	-0.201249	1.081703
H	-1.224657	-1.231625	1.409488
H	-0.919032	0.428555	1.969574
C	1.323147	-0.996373	0.000000
H	1.462032	-2.075612	0.000000
C	1.059689	1.088728	0.000000
H	1.002802	1.726403	-0.891476
C	2.165028	0.046554	0.000000
H	3.248415	0.137401	0.000000
H	1.002802	1.726403	0.891476

TS((-ac)-Spiro[3.3]hept-1-ylidene ((-ac)-1b; $\phi_1 = 25^\circ$)/(-ac)-Spiro[3.3]hept-1-ene ((-ac)-22c));
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d);

$E + Z(E_{ZPVE})$: -170512.05 kcal/mol

$T = 298.15$ K

H : -170507.44 kcal/mol

Atom	x	y	z
H	-2.276918	-0.417381	1.224559
C	-2.078241	-0.068872	0.205430
C	-1.042519	1.086088	0.174421
C	-1.037836	-0.959819	-0.523527
C	0.073211	0.048059	-0.112134
H	-3.036483	0.098843	-0.296099
H	-1.177301	-0.952434	-1.609543
H	-0.923103	-1.996886	-0.189881
H	-1.184737	1.743711	-0.689881
H	-0.933221	1.703401	1.073479
C	1.245238	0.289381	-1.110284
C	2.123787	-0.032661	-0.030954
H	1.981425	1.165729	-0.427741
H	3.213245	-0.141549	-0.024354
C	1.081622	-0.365294	1.015327
H	1.083734	0.240138	1.929442
H	1.061791	-1.424869	1.300343

SUPPORTING INFORMATION

s-cis-(Prop-2-en-1-ylidene)cyclobutane (*s-cis*-**22d**);
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170589.39 kcal/mol

$T = 298.15$ K

H : -170584.69 kcal/mol

Atom	x	y	z
C	0.358634	-0.385547	0.113142
C	-0.805193	-1.040433	-0.006903
H	-0.766106	-2.130304	-0.022888
C	-2.136665	-0.450819	-0.164264
H	-2.894837	-1.132943	-0.550808
C	-2.514657	0.806498	0.116931
H	-3.534727	1.135520	-0.059427
H	-1.836884	1.539007	0.544025
C	1.803686	-0.855628	0.173820
H	2.128340	-1.112136	1.191262
H	2.089610	-1.679822	-0.490021
C	0.777889	1.071941	0.024742
H	0.677743	1.611993	0.976106
H	0.289162	1.671476	-0.753256
C	2.235266	0.586395	-0.240087
H	3.024417	1.051331	0.357628
H	2.509520	0.651440	-1.296913

s-trans-(Prop-2-en-1-ylidene)cyclobutane (*s-trans*-**22d**);
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170591.77 kcal/mol

$T = 298.15$ K

H : -170587.05 kcal/mol

Atom	x	y	z
C	0.434194	0.239536	-0.102381
C	-0.857117	0.590079	-0.021711
H	-1.110917	1.649580	0.037518
C	-1.965404	-0.352347	-0.004478
H	-1.703155	-1.409159	-0.058026
C	-3.260071	-0.007022	0.069350
H	-4.050810	-0.751122	0.078265
H	-3.569542	1.034707	0.121419
C	1.734018	1.027229	-0.066311
H	1.999324	1.466108	-1.037481
H	1.816149	1.814338	0.692383
C	1.172972	-1.092850	-0.118102
H	1.196462	-1.562454	-1.110405
H	0.849852	-1.850302	0.605367
C	2.482516	-0.312606	0.214239
H	3.350421	-0.527293	-0.415530
H	2.775560	-0.416526	1.262860

TS((+ac)-Spiro[3.3]hept-1-ene ((+ac)-**22c**)/*s-cis*-(Prop-2-en-1-ylidene)cyclobutane (*s-cis*-**22d**);
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170546.73 kcal/mol

$T = 298.15$ K

H : -170542.04 kcal/mol

Atom	x	y	z
H	0.557229	1.260012	1.524168
C	0.841390	0.994969	0.500831
C	0.074765	-0.189446	-0.132513
C	2.149944	0.182346	0.279766
C	1.381956	-0.715996	-0.733448
H	1.535929	-1.801442	-0.697594
H	1.532491	-0.382486	-1.767720
H	0.833943	1.900867	-0.113318
H	3.019663	0.730615	-0.097202
H	2.441538	-0.376515	1.174518
C	-0.949945	-0.976129	0.475651
H	-0.838312	-2.003624	0.824077
C	-1.801863	0.710223	-0.680946
H	-2.167331	1.742914	-0.681903
H	-1.609007	0.318881	-1.673222
C	-2.085082	-0.203759	0.374281
H	-2.973136	-0.202470	1.006463

TS(*s-cis*-(Prop-2-en-1-ylidene)cyclobutane (*s-cis*-**22d**)/*s-trans*-(Prop-2-en-1-ylidene)cyclobutane (*s-trans*-**22d**);
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -170586.99 kcal/mol

$T = 298.15$ K

H : -170582.27 kcal/mol

Atom	x	y	z
H	-2.065975	1.741814	0.444840
C	-1.781021	0.919318	-0.221068
C	-2.384573	-0.487650	0.081794
C	-0.398041	0.312619	-0.019447
C	-0.955801	-1.103915	-0.030409
H	-0.630532	-1.771245	0.775839
H	-0.788479	-1.621767	-0.983488
H	-1.961135	1.241451	-1.254963
H	-3.135433	-0.859310	-0.621280
H	-2.789248	-0.556726	1.095826
C	0.809291	0.826994	0.213637
H	0.922035	1.913248	0.233328
C	2.025910	0.014306	0.480605
H	2.167763	-0.333595	1.507022
C	2.949518	-0.297284	-0.431198
H	2.861668	0.024472	-1.466412
H	3.827632	-0.884668	-0.174197

SUPPORTING INFORMATION

Ethane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{\text{ZPVE}}): -49913.35 \text{ kcal/mol}$$

T = 298.15 K

$$H: -49910.58 \text{ kcal/mol}$$

Atom	x	y	z
C	0.000000	0.000000	0.765284
H	1.020940	0.000000	1.164344
H	-0.510470	-0.884160	1.164344
H	-0.510470	0.884160	1.164344
C	0.000000	0.000000	-0.765284
H	0.510470	-0.884160	-1.164344
H	0.510470	0.884160	-1.164344
H	-1.020940	0.000000	-1.164344

Singlet Ethylidene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{\text{ZPVE}}): -49081.59 \text{ kcal/mol}$$

T = 298.15 K

$$H: -49078.92 \text{ kcal/mol}$$

Atom	x	y	z
C	0.593290	0.021152	-0.028476
H	1.038699	0.956653	-0.403637
H	0.658879	0.077924	1.089978
C	-0.857907	-0.190483	-0.034297
H	-1.305667	0.830952	0.001498
H	1.195787	-0.849538	-0.311198

Propane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{\text{ZPVE}}): -74502.09 \text{ kcal/mol}$$

T = 298.15 K

$$H: -74498.70 \text{ kcal/mol}$$

Atom	x	y	z
H	0.000000	-0.877610	-1.247143
C	0.000000	0.000000	-0.586434
H	0.000000	0.877610	-1.247143
C	-1.277198	0.000000	0.259894
H	-2.175928	0.000000	-0.367664
H	-1.322246	0.884616	0.907374
H	-1.322246	-0.884616	0.907374
C	1.277198	0.000000	0.259894
H	2.175928	0.000000	-0.367664
H	1.322246	-0.884616	0.907374
H	1.322246	0.884616	0.907374

Propene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{\text{ZPVE}}): -73746.17 \text{ kcal/mol}$$

T = 298.15 K

$$H: -73743.07 \text{ kcal/mol}$$

Atom	x	y	z
H	-0.164085	-1.546311	0.000000
C	-0.133802	-0.455569	0.000000
C	-1.283052	0.220414	0.000000
H	-2.245287	-0.284690	0.000000
H	-1.305533	1.308655	0.000000
C	1.234999	0.162892	0.000000
H	1.812286	-0.150430	0.880445
H	1.181469	1.256782	0.000000
H	1.812286	-0.150430	-0.880445

Singlet Prop-1-ylidene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{\text{ZPVE}}): -73671.57 \text{ kcal/mol}$$

T = 298.15 K

$$H: -73668.30 \text{ kcal/mol}$$

Atom	x	y	z
C	-1.220178	0.170028	-0.016058
H	-1.532669	0.363527	-1.048529
H	-1.227643	1.121748	0.523148
H	-1.955313	-0.507637	0.431971
C	0.185544	-0.427190	-0.005744
H	0.231436	-1.412335	-0.502240
H	0.502388	-0.631832	1.071464
C	1.329618	0.465765	-0.020724
H	2.211901	-0.185086	-0.220655

SUPPORTING INFORMATION

Singlet Prop-2-ylidene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -73677.60 \text{ kcal/mol}$$

T = 298.15 K

$$H: -73674.23 \text{ kcal/mol}$$

Atom	x	y	z
C	0.000000	0.000000	0.700203
C	-1.227589	0.000000	-0.147084
H	-2.160475	0.000000	0.425545
H	-1.231819	-0.875839	-0.821825
H	-1.231819	0.875839	-0.821825
C	1.227589	0.000000	-0.147084
H	2.160475	0.000000	0.425545
H	1.231819	0.875839	-0.821825
H	1.231819	-0.875839	-0.821825

(ap)-Butane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -99090.86 \text{ kcal/mol}$$

T = 298.15 K

$$H: -99086.83 \text{ kcal/mol}$$

Atom	x	y	z
H	2.750816	-0.640417	0.000000
C	1.962339	0.120957	0.000000
H	2.109914	0.752839	0.884647
H	2.109914	0.752839	-0.884647
C	0.568545	-0.514762	0.000000
H	0.463630	-1.168330	0.878036
H	0.463630	-1.168330	-0.878036
C	-0.568545	0.514762	0.000000
H	-0.463630	1.168330	0.878036
H	-0.463630	1.168330	-0.878036
C	-1.962339	-0.120957	0.000000
H	-2.109914	-0.752839	0.884647
H	-2.109914	-0.752839	-0.884647
H	-2.750816	0.640417	0.000000

2-Methylpropane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -99092.80 \text{ kcal/mol}$$

T = 298.15 K

$$H: -99088.68 \text{ kcal/mol}$$

Atom	x	y	z
C	0.000000	0.000000	0.372693
H	0.000000	0.000000	1.473259
C	1.462072	0.000000	-0.095845
H	1.997525	-0.886231	0.265477
H	1.997525	0.886231	0.265477
H	1.521183	0.000000	-1.192357
C	-0.731036	1.266191	-0.095845
H	-0.231264	2.173023	0.265477
H	-1.766262	1.286792	0.265477
H	-0.760591	1.317383	-1.192357
C	-0.731036	-1.266191	-0.095845
H	-0.231264	-2.173023	0.265477
H	-0.760591	-1.317383	-1.192357
H	-1.766262	-1.286792	0.265477

2-Methylpropene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -98338.15 \text{ kcal/mol}$$

T = 298.15 K

$$H: -98334.35 \text{ kcal/mol}$$

Atom	x	y	z
C	0.000000	0.000000	0.122852
C	-1.278150	0.000000	-0.678913
H	-1.332473	0.880014	-1.334900
H	-2.163161	0.000000	-0.035278
H	-1.332473	-0.880014	-1.334900
C	0.000000	0.000000	1.459474
H	-0.924660	0.000000	2.031579
H	0.924660	0.000000	2.031579
C	1.278150	0.000000	-0.678913
H	1.332473	0.880014	-1.334900
H	1.332473	-0.880014	-1.334900
H	2.163161	0.000000	-0.035278

SUPPORTING INFORMATION

(ac)-1-Butene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{\text{ZPVE}}): -98334.80 \text{ kcal/mol}$$

T = 298.15 K

$$H: -98331.08 \text{ kcal/mol}$$

Atom	x	y	z
H	0.800435	-0.826128	-1.332805
C	0.540117	-0.520621	-0.308163
H	0.366181	-1.444269	0.258337
C	1.729439	0.246377	0.294565
H	2.640981	-0.361615	0.273909
H	1.528527	0.525363	1.334827
H	1.930350	1.168560	-0.264150
C	-0.723376	0.296313	-0.339883
H	-0.672083	1.223870	-0.914154
C	-1.861819	-0.017896	0.279266
H	-1.959711	-0.929706	0.865735
H	-2.740853	0.618880	0.223591

trans-2-Butene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{\text{ZPVE}}): -98337.25 \text{ kcal/mol}$$

T = 298.15 K

$$H: -98333.34 \text{ kcal/mol}$$

Atom	x	y	z
H	-0.392482	-1.477731	0.000000
C	-0.538108	-0.395350	0.000000
C	-1.963510	0.079225	0.000000
H	-2.507861	-0.289084	-0.880436
H	-2.022821	1.173132	0.000000
H	-2.507861	-0.289084	0.880436
C	0.538108	0.395350	0.000000
H	0.392482	1.477731	0.000000
C	1.963510	-0.079225	0.000000
H	2.507861	0.289084	-0.880436
H	2.022821	-1.173132	0.000000
H	2.507861	0.289084	0.880436

cis-2-Butene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{\text{ZPVE}}): -98335.75 \text{ kcal/mol}$$

T = 298.15 K

$$H: -98331.95 \text{ kcal/mol}$$

Atom	x	y	z
C	0.669191	0.000000	-0.664154
H	1.169487	0.000000	-1.633414
C	-0.669191	0.000000	-0.664154
H	-1.169487	0.000000	-1.633414
C	-1.593081	0.000000	0.521801
H	-2.250470	-0.880071	0.505359
H	-2.250470	0.880071	0.505359
H	-1.060492	0.000000	1.476813
C	1.593081	0.000000	0.521801
H	2.250470	-0.880071	0.505359
H	1.060492	0.000000	1.476813
H	2.250470	0.880071	0.505359

Singlet But-2-ylidene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{\text{ZPVE}}): -98269.13 \text{ kcal/mol}$$

T = 298.15 K

$$H: -98265.12 \text{ kcal/mol}$$

Atom	x	y	z
C	-0.600534	-0.568479	-0.220368
C	0.496815	0.412843	-0.120394
H	0.297457	1.312915	0.496169
H	0.427367	0.779742	-1.172515
C	-1.914479	0.033208	0.101195
H	-2.039558	-0.309778	1.148781
H	-2.751542	-0.417874	-0.444267
H	-2.004090	1.136203	0.116655
C	1.902424	-0.147222	0.121069
H	2.001113	-0.500981	1.153449
H	2.672225	0.614647	-0.045783
H	2.091676	-0.996969	-0.541501

SUPPORTING INFORMATION

2,2-Dimethylpropane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -123684.41 \text{ kcal/mol}$$

T = 298.15 K

$$H: -123679.64 \text{ kcal/mol}$$

Atom	x	y	z
C	0.000000	0.000000	0.000000
C	0.889259	0.889259	-0.889259
H	1.535742	1.535742	-0.282760
H	1.535742	0.282760	-1.535742
H	0.282760	1.535742	-1.535742
C	-0.889259	-0.889259	-0.889259
H	-1.535742	-1.535742	-0.282760
H	-1.535742	-0.282760	-1.535742
H	-0.282760	-1.535742	-1.535742
C	-0.889259	0.889259	0.889259
H	-1.535742	0.282760	1.535742
H	-0.282760	1.535742	1.535742
H	-1.535742	1.535742	0.282760
C	0.889259	-0.889259	0.889259
H	0.282760	-1.535742	1.535742
H	1.535742	-1.535742	0.282760
H	1.535742	-0.282760	1.535742

(ap)-Pentane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -123679.69 \text{ kcal/mol}$$

T = 298.15 K

$$H: -123675.07 \text{ kcal/mol}$$

Atom	x	y	z
H	-2.606563	0.884605	0.971153
C	-2.560631	0.000000	0.323921
H	-2.606563	-0.884605	0.971153
H	-3.459038	0.000000	-0.303956
C	-1.283991	0.000000	-0.523250
H	-1.283427	0.878026	-1.184904
H	-1.283427	-0.878026	-1.184904
C	0.000000	0.000000	0.316140
H	0.000000	-0.878485	0.979008
H	0.000000	0.878485	0.979008
C	1.283991	0.000000	-0.523250
H	1.283427	0.878026	-1.184904
H	1.283427	-0.878026	-1.184904
C	2.560631	0.000000	0.323921
H	2.606563	-0.884605	0.971153
H	2.606563	0.884605	0.971153
H	3.459038	0.000000	-0.303956

(sc)-2-Methylbutane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -123680.98 \text{ kcal/mol}$$

T = 298.15 K

$$H: -123676.23 \text{ kcal/mol}$$

Atom	x	y	z
H	-0.774487	-1.724133	-0.007282
C	-0.765235	-0.662487	-0.291717
H	-0.668297	-0.643770	-1.387736
C	-2.102166	-0.032119	0.114776
H	-2.943896	-0.592267	-0.308460
H	-2.191628	1.003300	-0.231983
H	-2.222045	-0.028465	1.205601
C	0.482098	-0.002773	0.329532
H	0.347251	-0.003337	1.422825
C	1.740798	-0.823706	0.011636
H	1.921920	-0.859434	-1.070858
H	1.645334	-1.856928	0.366628
H	2.630645	-0.388132	0.481643
C	0.662596	1.454576	-0.121751
H	0.776409	1.513300	-1.212592
H	1.559782	1.896007	0.328430
H	-0.189532	2.082919	0.158930

(sc)-Pentane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -123679.06 \text{ kcal/mol}$$

T = 298.15 K

$$H: -123674.45 \text{ kcal/mol}$$

Atom	x	y	z
H	2.841767	-0.808286	-0.156051
C	2.449390	0.175687	0.129387
H	2.524016	0.255876	1.221057
H	3.108278	0.936074	-0.305457
C	1.001689	0.352427	-0.340853
H	0.964171	0.297914	-1.438637
H	0.657287	1.360304	-0.074149
C	0.049426	-0.698635	0.246889
H	0.062230	-0.624164	1.344998
H	0.439089	-1.698474	0.006902
C	-1.402734	-0.602300	-0.249522
H	-1.959744	-1.472100	0.124338
H	-1.415056	-0.683371	-1.346138
C	-2.136443	0.675755	0.174603
H	-1.665532	1.574270	-0.239613
H	-2.146661	0.780604	1.266965
H	-3.177814	0.663752	-0.167238

SUPPORTING INFORMATION

(ac)-2-Methylbut-1-ene;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -122926.43 kcal/mol

$T = 298.15$ K

H : -122922.03 kcal/mol

Atom	x	y	z
C	1.425970	1.108480	0.231886
H	1.130293	2.153367	0.171744
H	2.439538	0.910871	0.573034
C	0.587368	0.120351	-0.097225
C	1.002422	-1.329581	-0.022465
H	0.889854	-1.821581	-0.998751
H	0.380127	-1.893769	0.684371
H	2.045233	-1.434169	0.292361
C	-0.824040	0.403834	-0.569969
H	-0.979940	-0.074509	-1.548950
H	-0.941861	1.482528	-0.728018
C	-1.918275	-0.086011	0.395760
H	-1.884668	-1.172428	0.533386
H	-2.913148	0.166692	0.011959
H	-1.806092	0.380561	1.380938

Singlet 2,2-Dimethylprop-1-ylidene;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -122852.56 kcal/mol

$T = 298.15$ K

H : -122847.88 kcal/mol

Atom	x	y	z
C	1.071016	1.165771	-0.016145
H	1.893738	1.056387	0.700453
H	0.568136	2.113497	0.196833
H	1.508041	1.207208	-1.022068
C	0.088577	-0.004322	0.127519
C	-0.893460	0.140003	1.209462
H	-1.327593	-0.875266	1.360867
C	0.773507	-1.354713	-0.136749
H	0.054573	-2.180361	-0.088372
H	1.547803	-1.537822	0.617670
H	1.262204	-1.379883	-1.119189
C	-1.198494	0.190680	-0.792848
H	-2.112302	0.405501	-0.196288
H	-1.377919	-0.709690	-1.381580
H	-1.063554	1.075916	-1.415756

(sp)-3-Methylbut-1-ene;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -122925.53 kcal/mol

$T = 298.15$ K

H : -122921.05 kcal/mol

Atom	x	y	z
C	-0.371748	-0.309128	0.000000
H	-0.167737	-1.389220	0.000000
C	-1.178545	0.028128	1.268031
H	-0.627389	-0.248284	2.173345
H	-2.137737	-0.503458	1.274490
H	-1.393434	1.103233	1.321410
C	-1.178545	0.028128	-1.268031
H	-2.137737	-0.503458	-1.274490
H	-0.627389	-0.248284	-2.173345
H	-1.393434	1.103233	-1.321410
C	0.951883	0.415449	0.000000
H	0.886603	1.506439	0.000000
C	2.153600	-0.161997	0.000000
H	2.267384	-1.244607	0.000000
H	3.071009	0.420929	0.000000

2,2-Dimethylbutane;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -148272.17 kcal/mol

$T = 298.15$ K

H : -148266.68 kcal/mol

Atom	x	y	z
H	-0.865619	-1.486004	0.877399
C	-0.878686	-0.823271	0.000000
H	-0.865619	-1.486004	-0.877399
C	-2.194034	-0.033902	0.000000
H	-3.048415	-0.720608	0.000000
H	-2.290285	0.604815	-0.884994
H	-2.290285	0.604815	0.884994
C	0.436506	0.000669	0.000000
C	1.617722	-0.990332	0.000000
H	1.593035	-1.637205	-0.885958
H	1.593035	-1.637205	0.885958
H	2.578386	-0.460589	0.000000
C	0.529436	0.885125	1.258627
H	0.447509	0.283227	2.172571
H	-0.261455	1.643020	1.284069
H	1.490690	1.412502	1.292589
C	0.529436	0.885125	-1.258627
H	0.447509	0.283227	-2.172571
H	1.490690	1.412502	-1.292589
H	-0.261455	1.643020	-1.284069

SUPPORTING INFORMATION

(ap)-2,3-Dimethylbutane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -148270.20 kcal/mol

$T = 298.15$ K

H : -148264.79 kcal/mol

Atom	x	y	z
C	-0.708726	-0.318177	0.000000
H	-0.573359	-1.412145	0.000000
C	-1.517405	0.054087	-1.254710
H	-2.524947	-0.375523	-1.206406
H	-1.051274	-0.308416	-2.175886
H	-1.627682	1.143531	-1.340423
C	-1.517405	0.054087	1.254710
H	-1.051274	-0.308416	2.175886
H	-2.524947	-0.375523	1.206406
H	-1.627682	1.143531	1.340423
C	0.708726	0.318177	0.000000
H	0.573359	1.412145	0.000000
C	1.517405	-0.054087	1.254710
H	1.627682	-1.143531	1.340423
H	1.051274	0.308416	2.175886
H	2.524947	0.375523	1.206406
C	1.517405	-0.054087	-1.254710
H	1.627682	-1.143531	-1.340423
H	2.524947	0.375523	-1.206406
H	1.051274	0.308416	-2.175886

(sc)-2,3-Dimethylbutane;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -148270.26 kcal/mol

$T = 298.15$ K

H : -148264.76 kcal/mol

Atom	x	y	z
C	-0.711283	0.314139	-0.377199
C	0.711283	-0.314139	-0.377199
H	0.753826	-0.962947	-1.265832
C	1.810360	0.747469	-0.544685
H	2.792988	0.275895	-0.664935
H	1.871731	1.408956	0.327822
H	1.630128	1.373577	-1.427085
C	1.003560	-1.199193	0.845937
H	0.253965	-1.987519	0.975556
H	1.034610	-0.610930	1.770927
H	1.978899	-1.688742	0.739230
C	-1.810360	-0.747469	-0.544685
H	-1.871731	-1.408956	0.327822
H	-1.630128	-1.373577	-1.427085
H	-2.792988	-0.275895	-0.664935
H	-0.753826	0.962947	-1.265832
C	-1.003560	1.199193	0.845937
H	-1.034610	0.610930	1.770927
H	-1.978899	1.688742	0.739230
H	-0.253965	1.987519	0.975556

(sp)-3,3-Dimethylbut-1-ene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -147516.59 kcal/mol

$T = 298.15$ K

H : -147511.37 kcal/mol

Atom	x	y	z
H	-0.967866	-1.758171	0.000000
C	-1.010024	-0.666345	0.000000
C	-2.208560	-0.081587	0.000000
H	-3.121627	-0.671239	0.000000
H	-2.335386	0.997514	0.000000
C	0.353492	0.001378	0.000000
C	1.121199	-0.465302	-1.258678
H	0.609999	-0.143323	-2.172990
H	1.207402	-1.558304	-1.289202
H	2.136333	-0.049354	-1.269836
C	1.121199	-0.465302	1.258678
H	1.207402	-1.558304	1.289202
H	0.609999	-0.143323	2.172990
H	2.136333	-0.049354	1.269836
C	0.256506	1.535207	0.000000
H	-0.271975	1.902818	-0.887002
H	1.258487	1.979927	0.000000
H	-0.271975	1.902818	0.887002

(sp)-2,3-Dimethylbut-1-ene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -147516.68 kcal/mol

$T = 298.15$ K

H : -147511.49 kcal/mol

Atom	x	y	z
C	0.666976	0.470960	-0.012388
H	0.733481	1.566904	-0.041661
C	1.384276	-0.066453	-1.266258
H	2.423512	0.282237	-1.291911
H	0.889067	0.274320	-2.182353
H	1.406268	-1.162671	-1.281493
C	1.383875	0.001104	1.268556
H	0.888849	0.391103	2.164887
H	2.423394	0.349824	1.275414
H	1.404877	-1.092749	1.342751
C	-0.815902	0.120356	-0.003166
C	-1.201853	-1.340469	0.033401
H	-0.806045	-1.885814	-0.833026
H	-2.289399	-1.460962	-0.036014
H	-0.806942	-1.842102	0.926300
C	-1.746741	1.080377	-0.026928
H	-1.481233	2.134871	-0.053436
H	-2.809614	0.849791	-0.020785

SUPPORTING INFORMATION

(ac)-2,3-Dimethylbut-1-ene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -147516.05 \text{ kcal/mol}$$

T = 298.15 K

$$H: -147510.92 \text{ kcal/mol}$$

Atom	x	y	z
C	-1.069687	-1.397622	-0.525539
H	-2.097782	-1.664465	-0.758343
H	-0.317441	-2.142219	-0.766389
C	-0.768953	-0.216660	0.025610
C	0.653774	0.217495	0.362255
C	1.676400	-0.926142	0.380246
H	1.362219	-1.735757	1.047580
H	2.649566	-0.558543	0.724851
H	1.822801	-1.349914	-0.620561
C	1.131999	1.341702	-0.582896
H	0.463858	2.208987	-0.566334
H	1.184778	0.977104	-1.615649
H	2.131239	1.688192	-0.293922
H	0.619973	0.644647	1.377530
C	-1.856598	0.779496	0.359004
H	-1.844322	1.030903	1.428696
H	-2.848467	0.386969	0.114914
H	-1.728033	1.724479	-0.184448

2,3-Dimethylbut-2-ene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -147516.59 \text{ kcal/mol}$$

T = 298.15 K

$$H: -147511.32 \text{ kcal/mol}$$

Atom	x	y	z
C	0.674768	0.000000	0.000000
C	1.529678	1.249480	-0.000017
H	2.190201	1.262001	0.878757
H	0.964711	2.182386	-0.000098
H	2.190283	1.261905	-0.878730
C	1.529678	-1.249480	0.000017
H	0.964711	-2.182386	0.000098
H	2.190283	-1.261905	0.878730
H	2.190201	-1.262001	-0.878757
C	-0.674768	0.000000	0.000000
C	-1.529678	-1.249480	-0.000017
H	-2.190201	-1.262001	0.878757
H	-0.964711	-2.182386	-0.000098
H	-2.190283	-1.261905	-0.878730
C	-1.529678	1.249480	0.000017
H	-2.190283	1.261905	0.878730
H	-2.190201	1.262001	-0.878757
H	-0.964711	2.182386	0.000098

s-cis-2,3-Dimethylbuta-1,3-diene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -146762.93 \text{ kcal/mol}$$

T = 298.15 K

$$H: -146758.07 \text{ kcal/mol}$$

Atom	x	y	z
C	0.745142	-0.026891	-0.125014
C	1.426389	-0.475252	-1.189244
H	2.513466	-0.493617	-1.200584
H	0.919824	-0.847702	-2.074628
C	1.459846	0.427128	1.129215
H	1.169869	1.449404	1.405691
H	2.545107	0.404990	0.992997
H	1.216858	-0.213323	1.986782
C	-0.745142	0.026891	-0.125014
C	-1.459846	-0.427128	1.129215
H	-1.169869	-1.449404	1.405691
H	-2.545107	-0.404990	0.992997
H	-1.216858	0.213323	1.986782
C	-1.426389	0.475252	-1.189244
H	-0.919824	0.847702	-2.074628
H	-2.513466	0.493617	-1.200584

s-trans-2,3-Dimethylbuta-1,3-diene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$$E + Z(E_{ZPVE}): -146764.16 \text{ kcal/mol}$$

T = 298.15 K

$$H: -146759.38 \text{ kcal/mol}$$

Atom	x	y	z
C	0.705729	0.227064	0.000022
C	1.027880	1.532213	0.000512
H	2.065874	1.853140	0.000510
H	0.284618	2.322263	0.001026
C	1.798589	-0.818862	-0.000483
H	1.733598	-1.468276	0.881404
H	2.786387	-0.349555	-0.001195
H	1.732427	-1.468576	-0.882052
C	-0.705729	-0.227064	0.000022
C	-1.798589	0.818862	-0.000483
H	-1.733598	1.468276	0.881404
H	-2.786387	0.349555	-0.001195
H	-1.732427	1.468576	-0.882052
C	-1.027880	-1.532213	0.000512
H	-0.284618	-2.322263	0.001026
H	-2.065874	-1.853140	0.000510

SUPPORTING INFORMATION

s-cis-4-Methylpenta-1,3-diene;
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -146761.66 kcal/mol

$T = 298.15$ K

H : -146756.78 kcal/mol

Atom	x	y	z
H	0.073808	-1.970925	0.023212
C	-0.190429	-0.914445	-0.047244
C	0.829968	-0.032182	-0.023061
C	2.248248	-0.511429	0.165123
H	2.707876	-0.043070	1.047298
H	2.876326	-0.233692	-0.693281
H	2.302786	-1.597074	0.292690
C	0.679180	1.457295	-0.201982
H	0.752463	1.985611	0.759652
H	-0.279133	1.724089	-0.654927
H	1.486943	1.849989	-0.833512
C	-1.627167	-0.664733	-0.204269
H	-2.163364	-1.441105	-0.753732
C	-2.345824	0.358580	0.281233
H	-1.907036	1.138625	0.896023
H	-3.414523	0.429038	0.097780

s-trans-4-Methylpenta-1,3-diene;
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -146764.49 kcal/mol

$T = 298.15$ K

H : -146759.58 kcal/mol

Atom	x	y	z
H	-0.524369	-1.568965	-0.000337
C	-0.364221	-0.489861	-0.000254
C	0.912408	-0.050726	-0.000140
C	2.061029	-1.028000	0.000146
H	2.704299	-0.881926	0.879804
H	2.704257	-0.882703	-0.879669
H	1.715973	-2.066545	0.000627
C	1.323065	1.400011	-0.000014
H	1.941290	1.625599	0.880269
H	0.479074	2.092890	-0.001544
H	1.943958	1.624987	-0.878560
C	-1.581487	0.308084	-0.000062
H	-1.479365	1.391764	0.000214
C	-2.817488	-0.215438	0.000119
H	-2.980992	-1.291100	-0.000080
H	-3.703963	0.411580	0.000504

Singlet 2,2-Dimethylbut-1-ylidene;
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -147440.65 kcal/mol

$T = 298.15$ K

H : -147435.37 kcal/mol

Atom	x	y	z
C	-0.963670	0.324836	-0.717108
H	-1.159850	-0.246812	-1.634908
H	-0.899969	1.374416	-1.026607
C	0.431269	-0.089992	-0.201954
C	1.542710	0.513988	-0.950859
H	2.447180	-0.079864	-0.685428
C	0.500892	-1.565877	0.222078
H	1.503952	-1.820989	0.581780
H	0.277057	-2.213688	-0.634224
H	-0.216452	-1.810384	1.014199
C	0.966538	0.879643	0.940627
H	1.808040	1.515248	0.579764
H	1.318270	0.301251	1.795676
H	0.188888	1.594619	1.210772
C	-2.133207	0.127972	0.254839
H	-1.976822	0.664516	1.199180
H	-2.294219	-0.928163	0.498060
H	-3.063266	0.506428	-0.184000

Singlet 3,3-Dimethylbut-2-ylidene;
 UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -147448.29 kcal/mol

$T = 298.15$ K

H : -147442.78 kcal/mol

Atom	x	y	z
C	-1.582491	0.065767	-1.007506
H	-1.481230	-0.665967	-1.817869
H	-1.640390	1.058859	-1.462213
H	-2.522423	-0.145404	-0.480988
C	-0.375270	-0.016295	-0.049914
C	0.840588	0.552820	-0.705227
C	2.137758	0.020170	-0.233615
H	2.960771	0.735224	-0.348021
H	2.321211	-0.753808	-1.008695
H	2.209535	-0.491867	0.741175
C	-0.316073	-1.418214	0.598316
H	0.457063	-1.495330	1.369472
H	-0.117363	-2.188066	-0.157394
H	-1.274703	-1.663178	1.071227
C	-0.550679	1.068899	1.071824
H	0.242153	1.008350	1.824700
H	-1.510345	0.880761	1.567223
H	-0.567281	2.081544	0.658117

SUPPORTING INFORMATION

(sp)-2,3,3-Trimethylbut-1-ene;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -172106.68 kcal/mol

$T = 298.15$ K

H : -172100.84 kcal/mol

Atom	x	y	z
C	1.482950	-1.430705	0.006726
C	0.931312	-0.211190	0.003049
C	-0.588257	0.026663	0.001372
C	-1.002617	0.725160	-1.317066
H	-0.730315	0.114648	-2.185602
H	-0.529924	1.706377	-1.431203
H	-2.088181	0.880469	-1.338484
C	1.829405	1.009450	-0.000134
H	1.608832	1.683306	-0.836929
H	2.880929	0.717288	-0.076988
H	1.715913	1.600156	0.917406
H	2.563312	-1.554707	-0.001324
H	0.901969	-2.346262	0.018583
C	-1.382896	-1.287568	0.114199
H	-1.185398	-1.954101	-0.732585
H	-2.457786	-1.073377	0.122804
H	-1.142231	-1.827474	1.036857
C	-0.981258	0.931061	1.194263
H	-0.521590	1.922621	1.127880
H	-0.679120	0.480061	2.146865
H	-2.068248	1.073767	1.218266

(sc)-2,4-Dimethylpentane;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -172860.23 kcal/mol

$T = 298.15$ K

H : -172854.16 kcal/mol

Atom	x	y	z
H	-0.156141	-0.864494	-1.335848
C	0.000000	0.000000	-0.671911
H	0.156141	0.864494	-1.335848
C	-1.297250	0.228886	0.131123
H	-1.153469	1.105655	0.779214
C	1.297250	-0.228886	0.131123
H	1.153469	-1.105655	0.779214
C	2.458333	-0.550439	-0.822635
H	2.656599	0.291824	-1.498758
H	2.235566	-1.427613	-1.441969
H	3.382594	-0.755853	-0.269406
C	1.653393	0.967139	1.027170
H	1.782408	1.878694	0.428293
H	2.592611	0.788242	1.564240
H	0.879492	1.168063	1.776022
C	-1.653393	-0.967139	1.027170
H	-1.782408	-1.878694	0.428293
H	-2.592611	-0.788242	1.564240
H	-0.879492	-1.168063	1.776022
C	-2.458333	0.550439	-0.822635
H	-2.656599	-0.291824	-1.498758
H	-2.235566	1.427613	-1.441969
H	-3.382594	0.755853	-0.269406

SUPPORTING INFORMATION

(ac)-3,3-Dimethylpent-1-ene;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -172104.98 kcal/mol

$T = 298.15$ K

H : -172099.13 kcal/mol

Atom	x	y	z
H	0.895880	-0.615330	1.757849
C	0.960172	-0.620261	0.666799
C	1.742042	-1.532265	0.086901
H	2.302574	-2.251047	0.679068
H	1.860727	-1.602996	-0.990796
C	0.127880	0.458597	-0.001506
C	0.251611	0.435204	-1.534003
H	-0.055332	-0.525834	-1.958794
H	1.284419	0.623815	-1.848164
H	-0.379409	1.214485	-1.977766
C	0.626827	1.828110	0.518609
H	0.556789	1.887879	1.611554
H	0.025641	2.644511	0.099412
H	1.673044	1.996405	0.239676
C	-1.357875	0.294624	0.435559
H	-1.924395	1.150385	0.041656
H	-1.402993	0.380555	1.530771
C	-2.043745	-1.008712	0.011344
H	-3.060041	-1.057075	0.418914
H	-1.494116	-1.884853	0.372455
H	-2.124269	-1.092684	-1.078051

(ac)-2,3-Dimethylpent-2-ene;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -172105.71 kcal/mol

$T = 298.15$ K

H : -172099.82 kcal/mol

Atom	x	y	z
H	2.536007	-0.238098	1.265245
C	2.326634	0.627222	0.625532
H	1.804890	1.371107	1.237853
H	3.288349	1.054097	0.316718
C	1.478897	0.229568	-0.597096
H	2.066010	-0.457455	-1.222170
H	1.304158	1.115715	-1.215685
C	0.170861	-0.455401	-0.224845
C	-0.986521	0.212413	-0.039725
C	-2.305198	-0.437428	0.318135
H	-2.670982	-0.069674	1.287753
H	-2.267992	-1.526628	0.368544
H	-3.074166	-0.168421	-0.420125
C	-1.116254	1.715596	-0.166799
H	-1.522107	2.142723	0.761267
H	-1.828677	1.980169	-0.961628
H	-0.175493	2.227053	-0.376912
C	0.325730	-1.953456	-0.070427
H	1.196119	-2.185199	0.558403
H	0.516522	-2.427134	-1.044414
H	-0.537529	-2.449340	0.376502

SUPPORTING INFORMATION

(sc)-cis-4,4-Dimethylpent-2-ene;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -172103.54 kcal/mol

$T = 298.15$ K

H : -172097.60 kcal/mol

Atom	x	y	z
C	1.687062	0.844922	0.000000
C	0.358259	1.015424	0.000000
C	-0.776272	-0.013243	0.000000
C	-2.115706	0.754961	0.000000
H	-2.203982	1.395276	0.886276
H	-2.203982	1.395276	-0.886276
H	2.289967	1.754730	0.000000
C	2.502000	-0.419961	0.000000
H	1.899386	-1.329727	0.000000
H	3.159735	-0.453880	0.879507
H	3.159735	-0.453880	-0.879507
H	0.017888	2.051982	0.000000
H	-2.965030	0.061716	0.000000
C	-0.728809	-0.898069	-1.266773
H	-0.776679	-0.283742	-2.173074
H	-1.580273	-1.590554	-1.281976
H	0.186917	-1.494347	-1.318923
C	-0.728809	-0.898069	1.266773
H	-0.776679	-0.283742	2.173074
H	0.186917	-1.494347	1.318923
H	-1.580273	-1.590554	1.281976

(sp)-trans-4,4-Dimethylpent-2-ene;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -172107.90 kcal/mol

$T = 298.15$ K

H : -172101.94 kcal/mol

Atom	x	y	z
C	1.654178	0.328863	0.000000
H	1.544727	1.413093	0.000000
C	0.566267	-0.445942	0.000000
H	0.709535	-1.530249	0.000000
C	3.068456	-0.181445	0.000000
H	3.621442	0.174222	0.880295
H	3.621442	0.174222	-0.880295
H	3.101922	-1.276409	0.000000
C	-0.890668	-0.017555	0.000000
C	-1.570272	-0.606814	-1.258150
H	-1.464598	-1.698109	-1.291033
H	-1.124266	-0.199528	-2.172651
H	-2.642451	-0.373943	-1.266992
C	-1.570272	-0.606814	1.258150
H	-1.464598	-1.698109	1.291033
H	-2.642451	-0.373943	1.266992
H	-1.124266	-0.199528	2.172651
C	-1.059186	1.510389	0.000000
H	-0.602301	1.964007	0.887062
H	-2.122854	1.776179	0.000000
H	-0.602301	1.964007	-0.887062

SUPPORTING INFORMATION

(ac)-3,3-Dimethylpenta-1,4-diene;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{\text{ZPVE}})$: -171348.54 kcal/mol

$T = 298.15 \text{ K}$

H : -171342.98 kcal/mol

Atom	x	y	z
H	3.040328	0.574002	1.478095
C	2.345931	0.102674	0.787488
H	2.733860	-0.734567	0.214070
C	1.093597	0.544459	0.663944
H	0.772948	1.387721	1.277957
C	0.000000	0.000000	-0.247320
C	-1.093597	-0.544459	0.663944
H	-0.772948	-1.387721	1.277957
C	-2.345931	-0.102674	0.787488
H	-3.040328	-0.574002	1.478095
H	-2.733860	0.734567	0.214070
C	0.503673	-1.152879	-1.138932
H	1.332771	-0.823675	-1.775777
H	-0.304720	-1.508377	-1.786578
H	0.851402	-2.002713	-0.540806
C	-0.503673	1.152879	-1.138932
H	0.304720	1.508377	-1.786578
H	-0.851402	2.002713	-0.540806
H	-1.332771	0.823675	-1.775777

(ac)-3,3-Dimethylhexa-1,5-diene;
UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{\text{ZPVE}})$: -195937.91 kcal/mol

$T = 298.15 \text{ K}$

H : -195931.73 kcal/mol

Atom	x	y	z
H	3.665856	-1.165939	0.628641
C	2.865216	-0.437964	0.526837
H	3.090171	0.570962	0.860959
C	1.682263	-0.783094	0.016754
H	1.537873	-1.820212	-0.295259
C	0.463243	0.096952	-0.194249
C	-0.690505	-0.517918	0.669637
H	-0.354334	-0.516888	1.716758
H	-0.818571	-1.570379	0.383279
C	-2.020426	0.181026	0.577589
H	-2.059122	1.202047	0.958452
C	-3.137461	-0.361437	0.089178
H	-4.076098	0.185969	0.060226
H	-3.158006	-1.379701	-0.295020
C	0.083386	0.038840	-1.690845
H	0.883958	0.460340	-2.309044
H	-0.836998	0.600133	-1.883668
H	-0.082856	-0.995216	-2.017383
C	0.725814	1.555814	0.213712
H	1.572687	1.970563	-0.344188
H	0.951733	1.641151	1.283224
H	-0.145480	2.183853	0.001349

SUPPORTING INFORMATION

(*ac*)-2,4,4-Trimethylpent-1-ene;

UQCISD(T)(fc)/6-311G(d,p)//B3LYP/6-31G(d):

$E + Z(E_{ZPVE})$: -196696.78 kcal/mol

$T = 298.15$ K

H : -196690.27 kcal/mol

Atom	x	y	z
H	2.402729	-0.582973	1.631709
C	2.316007	0.221745	0.891055
H	2.255690	1.172516	1.435425
H	3.240618	0.232887	0.301016
C	1.086425	0.017107	-0.016069
C	-0.173152	-0.033602	0.908246
H	-0.155177	0.861636	1.546360
C	-1.535956	-0.130427	0.241962
C	-2.096243	-1.311999	-0.043430
H	-1.601961	-2.252258	0.188162
H	-3.074474	-1.383013	-0.513191
H	-0.045897	-0.892240	1.580532
C	-2.268180	1.164306	-0.026770
H	-2.461425	1.698190	0.914413
H	-3.230317	0.988743	-0.518455
H	-1.683981	1.846950	-0.654866
C	1.008430	1.180817	-1.021383
H	0.858937	2.141709	-0.513262
H	0.190144	1.041284	-1.736183
H	1.939237	1.252449	-1.597467
C	1.245081	-1.306470	-0.786191
H	1.351123	-2.155531	-0.099006
H	2.139698	-1.278572	-1.420425
H	0.380584	-1.500650	-1.429286

MISCELLANEOUS FIGURES:

General Energy Profile for Chemical Activation

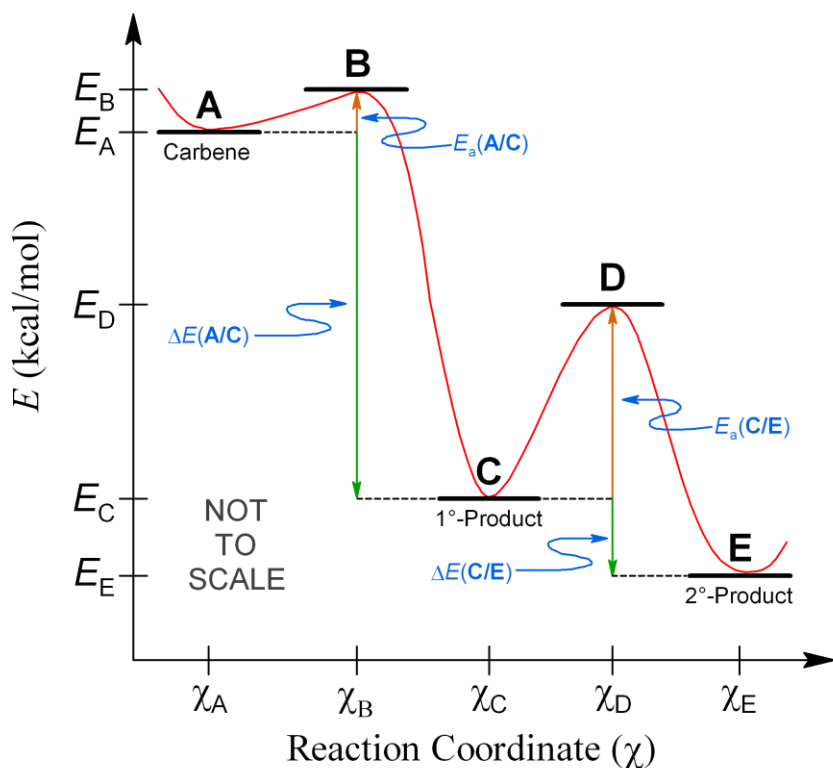


Figure S37. This generic energy profile outlines chemical activation. Under HVFP conditions, a high-energy carbene (**A**) can produce “hot” product **C***. Some **C*** molecules have enough energy to overcome $E_a(C/E)$ and form secondary product **E**, while the rest of **C*** relaxes to **C**.

General Energy Profile for Elementary Steps

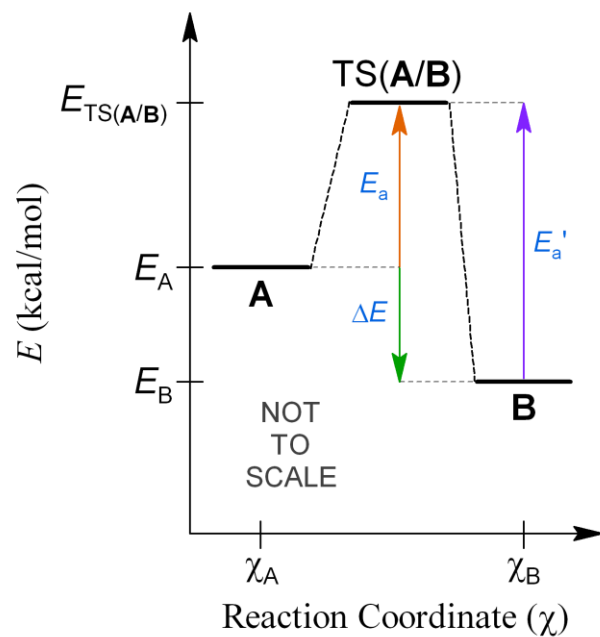


Figure S38. The general energy profile above is used for Table 4 and Table 6.