*Supporting Information*

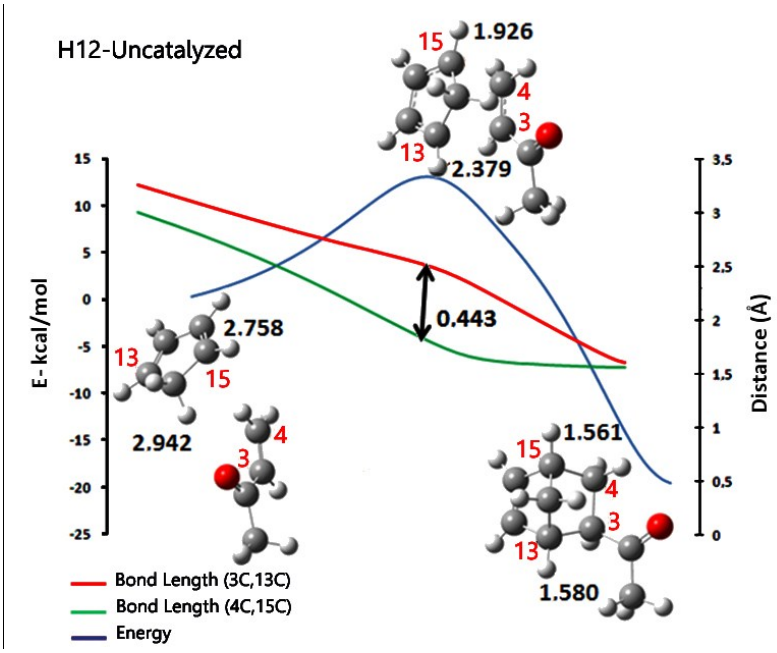
# Fluorine Substituent Effect on the Stereochemistry of Catalyzed and non-Catalyzed Diels-Alder Reactions. The Case of R-Butenone with Cyclopentadiene: A Computational Assessment of the Mechanism

**MERZOUD Lynda,[a,b] SAAL Amar,[a, b] MOUSSAOUI Ramdane,[c] OUAMERALI Ourida[a], MORELL Christophe[d], CHERMETTE Henry[d]**

[a]*Laboratory of Computational and Theoretical Chemistry and Photonics, USTHB University, 16111, Algeria;*
[b]*Département de Chimie, UMMTO University of Tizi–Ouzou, 15000, Algeria.*
[c]*Laboratoire de chimie Appliquée et de Génie Chimique, Université M. Mammeri, Tizi Ouzou, Algeria.*
[d] *Université de Lyon, Université Claude Bernard Lyon 1, ENS-Lyon, Institut des Sciences Analytiques, UMR CNRS 5280, 69622 Villeurbanne Cedex, France*

Corresponding author:

## 1. Geometry Evolution:



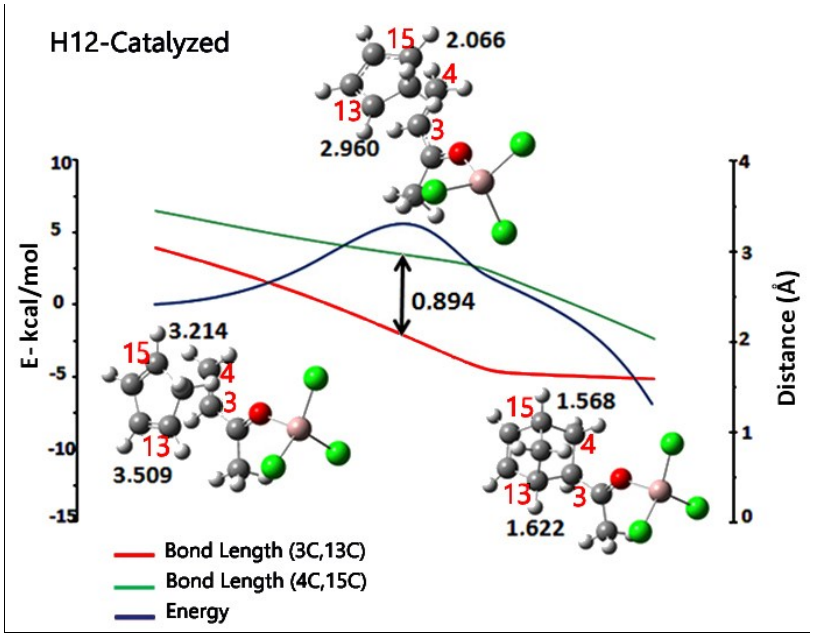
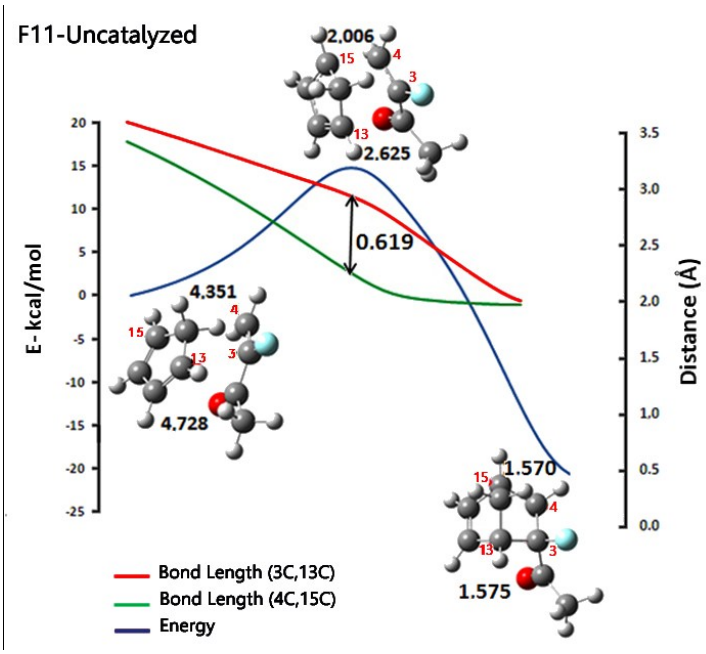



***Figure S.1.*** *IRC pathways of H12-Uncatalyzed and H12-Catalyzed reactions. The variation of the interatomic distances curves C4C15 (green) and C3C13 (red) along the reaction coordinate are plotted in the same graph as energies (blue).*



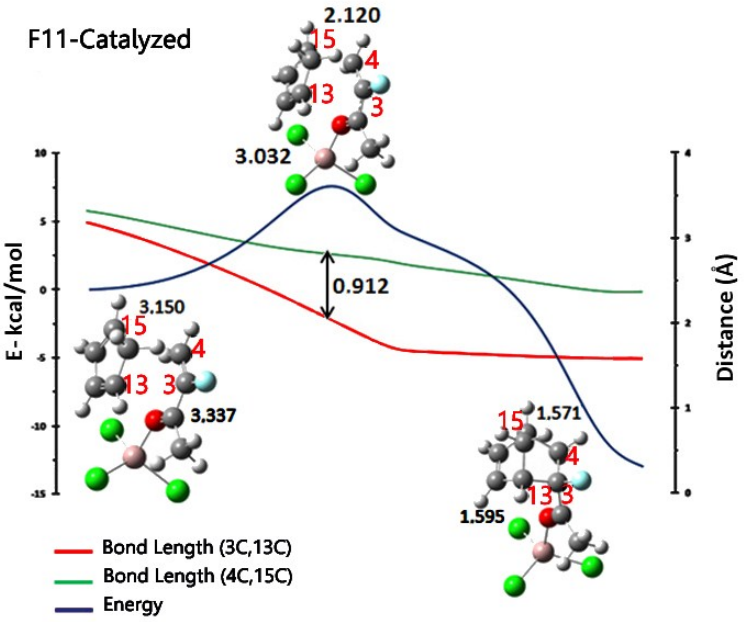
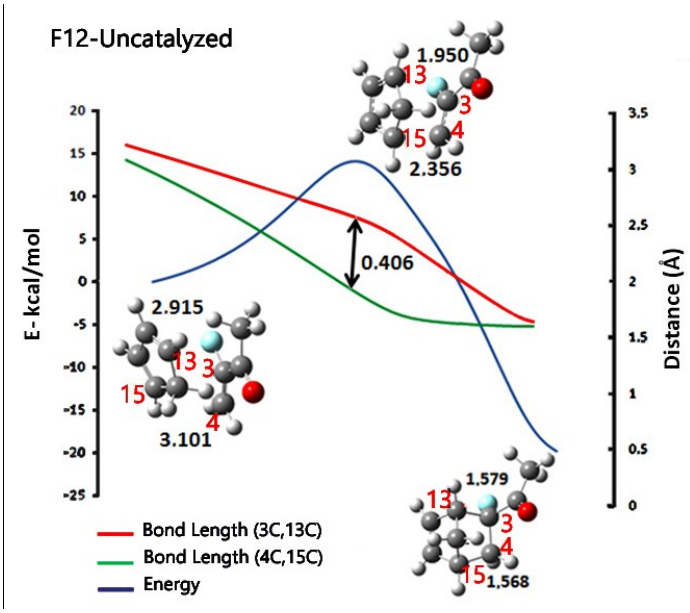



***Figure S.2.*** *IRC pathways of F11-Uncatalyzed and F11-Catalyzed reactions. The variation of the interatomic distances curves C4C15 (green) and C3C13 (red) along the reaction coordinate are plotted in the same graph as energies (blue).*



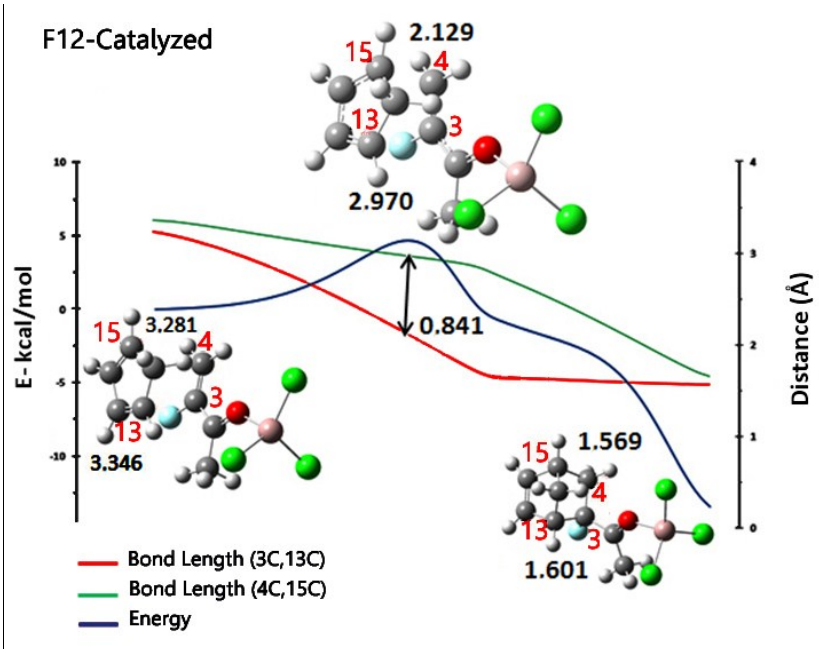



***Figure S.3.*** *IRC pathways of F12-Uncatalyzed and F12-Catalyzed reactions. The variation of the interatomic distances curves C4C15 (green) and C3C13 (red) along the reaction coordinate are plotted in the same graph as energies (blue).*

## 2. Energetics

***Table S.1.*** *The designation and the activation energy (kcal/mol) for the catalyzed and uncatalyzed studied reactions.*

| Reaction | R | structure | | Ea (kcal/mol) | |
|---|---|---|---|---|---|
| | | Dienophile | Adduct (endo/exo) | uncatalyzed | catalyzed |
| H11 | H | cis | endo | 18.3 | 5.1 |
| H12 | H | cis | exo | 18.7 | 7.1 |
| F11 | F | cis | endo | 19.3 | 9.1 |
| F12 | F | cis | exo | 17.9 | 6.0 |

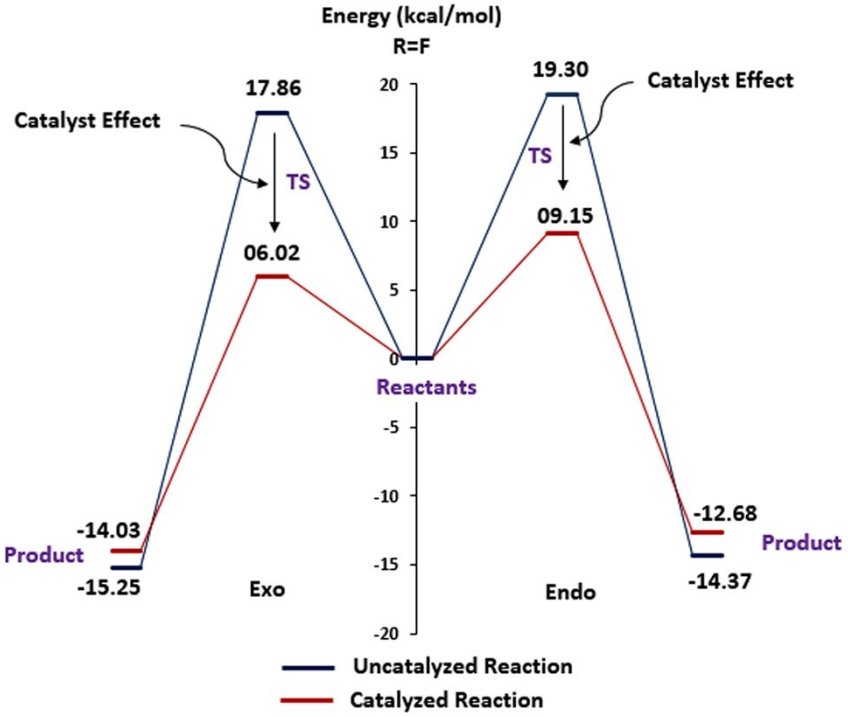



***Figure S.4.*** *Energy diagram corresponding to F11 and F12 reactions (with and without $AlCl_3$ catalyst). The calculations were performed at B3LYP/6-31G(d) level with ZPE correction.*

## 3. Comparative ASM/EDA diagrams

***Table S.2.*** *Interaction energies given in kcal/mol for the uncatalyzed transition states*

| | Endo-cis | | Exo-cis | |
|---|---|---|---|---|
| | **H** | **F** | **H** | **F** |
| **Pauli Repulsion** | 111.93 | 118.24 | 112.58 | 123.39 |
| **Electrostatic Interaction** | -53.43 | -61.20 | -52.78 | -56.10 |
| **Orbital Interaction** | -63.62 | -64.99 | -62.96 | -66.03 |
| **Dispersion** | -9.31 | -8.81 | -5.66 | -8.94 |

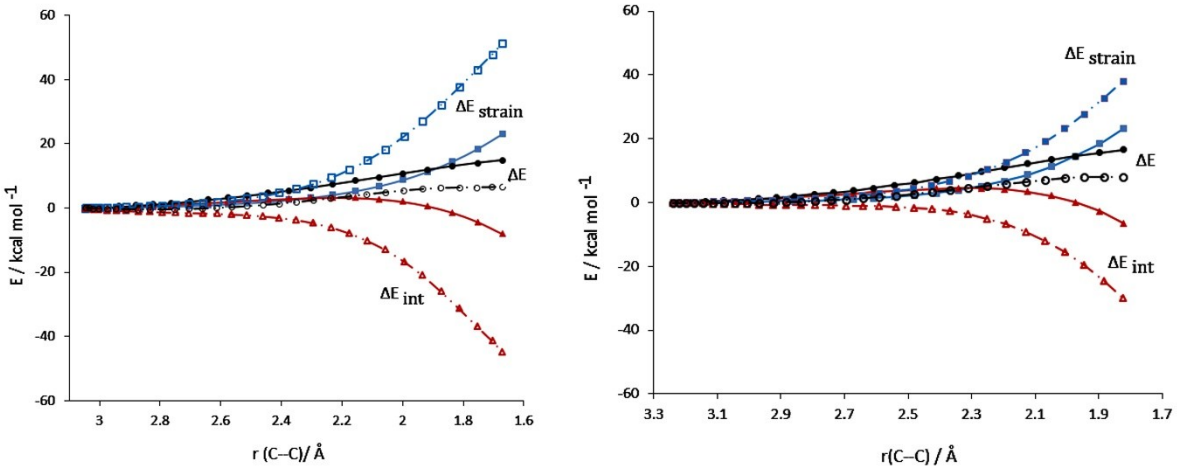



***Figure S.5.*** *Comparative activation-strain diagrams for the $AlCl_3$-catalyzed (dashed lines) and uncatalyzed (solid lines) Diels-Alder reactions between cyclopentadiene and butenone (left) and between the cyclopentadiene and 3-fluorobutenone (right) along the reaction coordinate projected onto the forming C--C bond distance, computed at BLYP-D3/TZ2P level.*

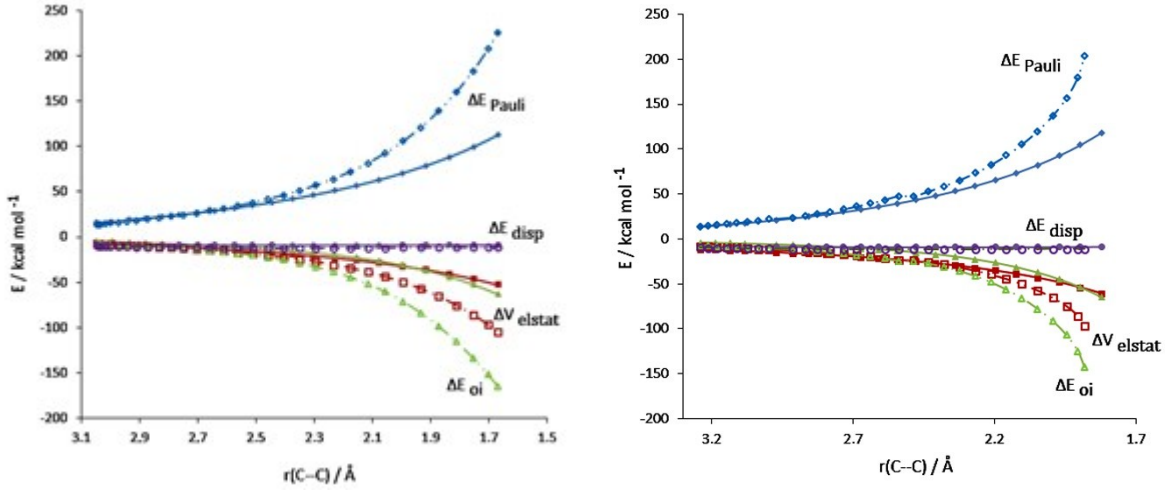
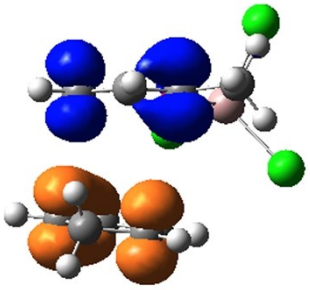
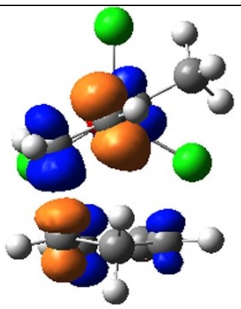
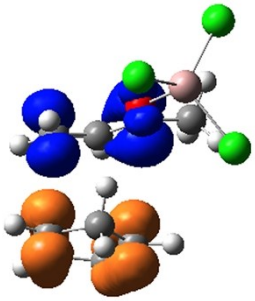
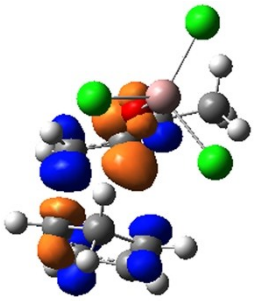
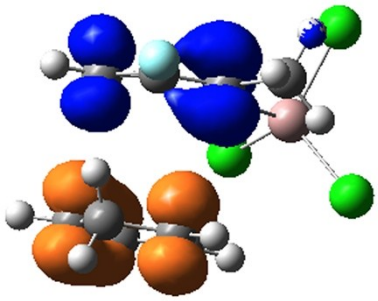
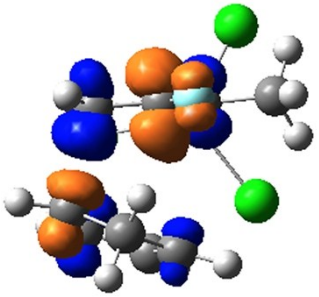
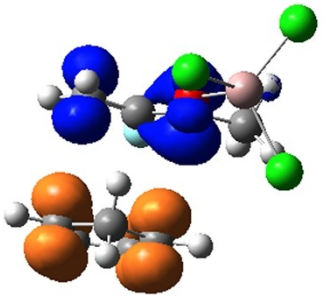
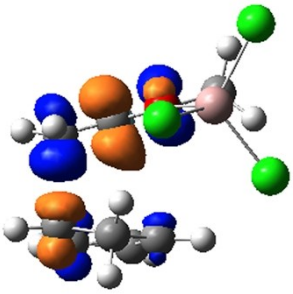


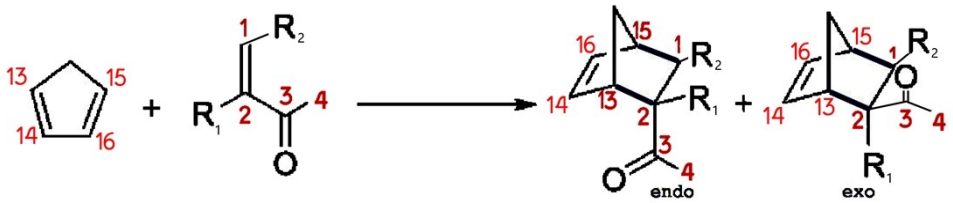

***Figure S.6.*** *Comparative energy decomposition analysis diagram for the $AlCl_3$-catalyzed (dashed lines) and uncatalyzed (solid lines) Diels-Alder reactions between cyclopentadiene and butenone (left) and between the cyclopentadiene and 3-fluorobutenone (right) along the reaction coordinate projected onto the forming C--C bond distance, computed at BLYP-D3/TZ2P level.*

## 4. Dual Descriptor

***Scheme S.1.*** *Dual descriptor of the interactions between cyclopentadiene and $AlCl_3$-catalyzed 3-R-butenone sites in its ground state. Blue lobes correspond to positive values of the dual descriptor, whereas orange lobes correspond to negative ones.*

| | **Reactants** | **Transition Structures** |
|---|---|---|
| **H-endo-cis** |  |  |
| **H-exo-cis** |  |  |
| **F-endo-cis** |  |  |
| **F-exo-cis** |  |  |

## 5. NBO analysis:




### ➢ *NBO_F_endo-cis (R1=F)*

***Table S.4.*** *Second–order perturbation theory analysis of Fock matrix in NBO basis of the F_endo_cis (R1=F) reactant: E(2) in kcal/mol is the hyperconjugative interaction energy, εj–εi is the energy difference between the donor NBO (i) and the acceptor NBO (j)and Fij is the Fock matrix element between the NBO orbitals i and j. εj–εi and Fij are given in atomic units.*

| NBO(i) | | NBO(j) | | $E^{(2)}$ | $\varepsilon_j - \varepsilon_i$ | $F_{i,j}$ |
|---|---|---|---|---|---|---|
| Donor | Occupation | Acceptor | Occupation | | | |
| π* $C_3$=$O_8$ | 0.144 | π* $C_1$=$C_2$ | 0.113 | 53.7 | 0.02 | 0.072 |
| lp2 $O_8$ | 1.883 | σ* $C_2$ - $C_3$ | 0.081 | 21.5 | 0.68 | 0.109 |
| lp3 $F_7$ | 1.924 | π* $C_1$=$C_2$ | 0.113 | 20.95 | 0.44 | 0.086 |
| lp2 $O_8$ | 1.883 | σ* $C_3$ - $C_4$ | 0.054 | 19.84 | 0.65 | 0.103 |
| lp1 $O_8$ | 1.978 | Ry*1 C3 | 0.018 | 15.75 | 1.47 | 0.136 |
| σ $C_1$ - $H_6$ | 1.973 | σ* $C_2$ - $F_7$ | 0.042 | 9.27 | 0.78 | 0.076 |
| lp1 $F_7$ | 1.988 | Ry*1 $C_2$ | 0.011 | 8.09 | 1.87 | 0.110 |
| lp2 $F_7$ | 1.965 | σ* $C_2$ - $C_3$ | 0.081 | 7.3 | 0.83 | 0.070 |
| cr 1 $O_8$ | 1.999 | Ry*1 $C_3$ | 0.018 | 6.08 | 19.66 | 0.310 |
| lp2 $F_7$ | 1.965 | σ* $C_1$ - $C_2$ | 0.017 | 5.34 | 1.05 | 0.067 |
| | | | | | | |
| π* $C_1$=$C_2$ | 0.113 | π* $C_{13}$=$C_{14}$ | 0.117 | 1.06 | 0.02 | 0.013 |
| lp3 $F_7$ | 1.924 | σ* $C_{12}$ - $H_{22}$ | 0.016 | 0.53 | 0.86 | 0.019 |
| π* $C_1$=$C_2$ | 0.113 | π* $C_{15}$=$C_{16}$ | 0.120 | 0.49 | 0.02 | 0.008 |
| **π $C_3$=$O_8$** | **1.974** | **π* $C_{15}$=$C_{16}$** | **0.120** | **0.26** | **0.42** | **0.010** |
| π $C_1$=$C_2$ | 1.906 | π* $C_{13}$=$C_{14}$ | 0.117 | 0.25 | 0.34 | 0.008 |
| π $C_1$=$C_2$ | 1.906 | σ* $C_{12}$ - $H_{21}$ | 0.014 | 0.19 | 0.73 | 0.011 |
| σ $C_1$ - $H_5$ | 1.982 | π* $C_{13}$=$C_{14}$ | 0.117 | 0.19 | 0.59 | 0.010 |
| lp2 $F_7$ | 1.965 | σ* $C_{12}$ - $H_{22}$ | 0.017 | 0.19 | 0.86 | 0.011 |
| σ $C_1$ - $H_5$ | 1.982 | Ry*2 $C_{13}$ | 0.002 | 0.14 | 1.31 | 0.012 |
| lp1 $F_7$ | 1.988 | σ* $C_{12}$ - $H_{22}$ | 0.016 | 0.14 | 1.49 | 0.013 |
| π $C_1$=$C_2$ | 1.906 | σ* $C_{12}$ - $H_{22}$ | 0.016 | 0.08 | 0.75 | 0.007 |
| π $C_1$=$C_2$ | 1.906 | π* $C_{15}$=$C_{16}$ | 0.120 | 0.08 | 0.34 | 0.005 |
| σ $C_2$ - $C_3$ | 1.984 | Ry*2 $C_{16}$ | 0.002 | 0.08 | 1.43 | 0.010 |
| lp3 $F_7$ | 1.924 | π* $C_{15}$=$C_{16}$ | 0.120 | 0.08 | 0.46 | 0.005 |
| σ $C_1$ - $C_2$ | 1.991 | Ry*1 $C_{13}$ | 0.003 | 0.06 | 2.08 | 0.010 |
| σ $C_1$ - $C_2$ | 1.991 | Ry*1 $H_{22}$ | 0.002 | 0.06 | 1.48 | 0.009 |
| σ $C_1$ - $H_5$ | 1.982 | Ry*4$C_{13}$ | 0.001 | 0.06 | 1.72 | 0.009 |

| | | | | | | |
|---|---|---|---|---|---|---|
| σ $C_1$ - $H_6$ | 1.974 | Ry*2 $C_{13}$ | 0.002 | 0.06 | 1.30 | 0.008 |
| σ $C_2$ - $C_3$ | 1.984 | Ry*3 $C_{16}$ | 0.002 | 0.06 | 1.37 | 0.008 |
| lp3 $F_7$ | 1.924 | Ry*2 $C_{16}$ | 0.002 | 0.06 | 1.15 | 0.008 |
| lp3 $F_7$ | 1.924 | Ry*1 $H_{22}$ | 0.002 | 0.06 | 1.12 | 0.008 |
| σ $C_1$ - $C_2$ | 1.991 | Ry*1 $C_{12}$ | 0.003 | 0.05 | 1.59 | 0.008 |
| σ C1 - $H_6$ | 1.974 | Ry*3 $C_{14}$ | 0.001 | 0.05 | 1.58 | 0.008 |

### ➢ *NBO_F_exo-cis (R1=F)*

***Table S.5.*** *Second–order perturbation theory analysis of Fock matrix in NBO basis of the F_exo_cis (R1=F) reactant: E(2) in kcal/mol is the hyperconjugative interaction energy, εj–εi is the energy difference between the donor NBO (i) and the acceptor NBO (j)and Fij is the Fock matrix element between the NBO orbitals i and j. εj–εi and Fij are given in atomic units.*

| NBO(i) | | NBO(j) | | $E^{(2)}$ | $\varepsilon_j$- $\varepsilon_i$ | $F_{i,j}$ |
|---|---|---|---|---|---|---|
| Donor | Occupation | Acceptor | Occupation | | | |
| π* $C_3$=$O_8$ | 0.145 | π* $C_1$=$C_2$ | 0.110 | 39.27 | 0.02 | 0.072 |
| lp3 $F_7$ | 1.921 | π* $C_1$=$C_2$ | 0.110 | 21.78 | 0.43 | 0.088 |
| lp2 $O_8$ | 1.885 | σ* $C_2$ - $C_3$ | 0.081 | 20.86 | 0.68 | 0.107 |
| lp2 $O_8$ | 1.885 | σ* $C_3$ - $C_4$ | 0.052 | 19.76 | 0.65 | 0.103 |
| π $C_1$=$C_2$ | 1.905 | π* $C_3$=$O_8$ | 0.145 | 17.53 | 0.30 | 0.066 |
| lp1 $O_8$ | 1.977 | Ry*1 $C_3$ | 0.018 | 15.49 | 1.46 | 0.134 |
| σ $C_1$ - $H_5$ | 1.974 | σ* $C_2$ - $F_7$ | 0.041 | 9.08 | 0.80 | 0.076 |
| lp1 $F_7$ | 1.989 | Ry*1 $C_2$ | 0.011 | 8.3 | 1.87 | 0.111 |
| lp2 $F_7$ | 1.965 | σ* $C_2$ - $C_3$ | 0.081 | 7.31 | 0.82 | 0.070 |
| cr1 $O_8$ | 1.999 | Ry*1 $C_3$ | 0.018 | 6.06 | 19.65 | 0.309 |
| σ $C_1$ - $H_6$ | 1.982 | σ* $C_2$ - $C_3$ | 0.081 | 6 | 0.95 | 0.069 |
| lp2 $F_7$ | 1.965 | σ* $C_1$ - $C_2$ | 0.017 | 5.71 | 1.05 | 0.069 |
| | | | | | | |
| π* $C_1$=$C_2$ | 0.110 | π* $C_{13}$=$C_{14}$ | 0.117 | 0.82 | 0.02 | 0.011 |
| π $C_3$=$O_8$ | 1.975 | σ* $C_{12}$ - $H_{22}$ | 0.018 | 0.54 | 0.84 | 0.019 |
| lp2 $O_8$ | 1.885 | σ* $C_{12}$ - $H_{22}$ | 0.018 | 0.53 | 0.73 | 0.018 |
| **π* $C_3$=$O_8$** | **0.145** | **π* $C_{15}$=$C_{16}$** | **0.122** | **0.48** | **0.04** | **0.011** |
| lp1 $O_8$ | 1.977 | σ* $C_{12}$ - $H_{22}$ | 0.018 | 0.29 | 1.16 | 0.016 |
| lp3 $F_7$ | 1.921 | π* $C_{15}$=$C_{16}$ | 0.122 | 0.28 | 0.46 | 0.010 |
| lp3 $F_7$ | 1.921 | Ry*3 $C_{15}$ | 0.001 | 0.15 | 1.26 | 0.013 |
| π $C_1$=$C_2$ | 1.905 | π* $C_{13}$=$C_{14}$ | 0.117 | 0.14 | 0.35 | 0.006 |
| **π $C_3$=$O_8$** | **1.976** | **π* $C_{15}$=$C_{16}$** | **0.122** | **0.13** | **0.43** | **0.007** |
| π $C_1$=$C_2$ | 1.905 | σ* $C_{12}$ - $H_{21}$ | 0.014 | 0.12 | 0.73 | 0.009 |
| σ $C_2$ - $C_3$ | 1.984 | Ry*2 $C_{16}$ | 0.002 | 0.11 | 1.42 | 0.011 |
| σ $C_1$ - $H_5$ | 1.974 | π* $C_{13}$=$C_{14}$ | 0.117 | 0.08 | 0.59 | 0.006 |
| σ $C_1$ - $H_5$ | 1.974 | Ry*2 $C_{13}$ | 0.002 | 0.07 | 1.29 | 0.008 |
| π $C_1$=$C_2$ | 1.905 | σ* $C_{12}$ - $H_{22}$ | 0.018 | 0.06 | 0.76 | 0.006 |
| σ $C_2$ - $C_3$ | 1.984 | Ry*3 $C_{16}$ | 0.002 | 0.06 | 1.40 | 0.008 |
| σ $C_2$ - $C_3$ | 1.984 | Ry*4 $C_{16}$ | 0.001 | 0.06 | 1.88 | 0.009 |

| | | | | | | |
|---|---|---|---|---|---|---|
| σ $C_2$ - $F_7$ | 1.995 | Ry*3 $C_{15}$ | 0.001 | 0.06 | 1.86 | 0.009 |
| σ $C_1$ - $H_5$ | 1.974 | σ* $C_{12}$ - $H_{22}$ | 0.018 | 0.05 | 1.00 | 0.007 |
| σ $C_1$ - $H_6$ | 1.982 | Ry*2 $C_{13}$ | 0.002 | 0.05 | 1.29 | 0.007 |

- ***NBO_H_endo-cis (R1=H)***

***Table S.6.*** *Second–order perturbation theory analysis of Fock matrix in NBO basis of the H_endo_cis (R1=H) reactant: E(2) in kcal/mol is the hyperconjugative interaction energy, εj–εi is the energy difference between the donor NBO (i) and the acceptor NBO (j)and Fij is the Fock matrix element between the NBO orbitals i and j. εj–εi and Fij are given in atomic units.*

| NBO(i) | | NBO(j) | | $E^{(2)}$ | $\varepsilon_j - \varepsilon_i$ | $F_{i,j}$ |
|---|---|---|---|---|---|---|
| Donor | Occupation | Acceptor | Occupation | | | |
| π* $C_3$=$O_8$ | 0.145 | π* $C_1$=$C_2$ | 0.046 | 41.89 | 0.01 | 0.071 |
| lp2 $O_8$ | 1.886 | σ* $C_3$ - $C_4$ | 0.054 | 20.61 | 0.64 | 0.104 |
| lp2 $O_8$ | 1.886 | σ* $C_2$ - $C_3$ | 0.065 | 20 | 0.69 | 0.106 |
| π $C_1$=$C_2$ | 1.899 | π* $C_3$=$O_8$ | 0.145 | 19.32 | 0.30 | 0.069 |
| lp1 $O_8$ | 1.977 | Ry*1 $C_3$ | 0.018 | 16.4 | 1.49 | 0.140 |
| cr1 $O_8$ | 1.999 | Ry*1 $C_3$ | 0.018 | 6.23 | 19.68 | 0.314 |
| σ $C_1$ - $H_6$ | 1.985 | σ* $C_2$ - $H_7$ | 0.016 | 5.25 | 0.99 | 0.064 |
| σ $C_1$ - $C_2$ | 1.989 | Ry*4 $C_{12}$ | 0.001 | 0.05 | 2.48 | 0.010 |
| σ $C_1$ - $C_2$ | 1.989 | Ry*1 $C_{13}$ | 0.003 | 0.06 | 2.06 | 0.010 |
| π $C_1$=$C_2$ | 1.899 | σ* $C_{12}$ - $H_{21}$ | 0.014 | 0.23 | 0.71 | 0.012 |
| π $C_1$=$C_2$ | 1.899 | σ* $C_{12}$ - $H_{22}$ | 0.015 | 0.19 | 0.72 | 0.011 |
| π $C_1$=$C_2$ | 1.899 | π* $C_{13}$=$C_{14}$ | 0.116 | 0.27 | 0.33 | 0.008 |
| π $C_1$=$C_2$ | 1.899 | π* $C_{15}$=$C_{16}$ | 0.120 | 0.15 | 0.32 | 0.006 |
| σ $C_1$ - $H_5$ | 1.987 | Ry*2 $C_{13}$ | 0.002 | 0.11 | 1.31 | 0.011 |
| σ $C_1$ - $H_5$ | 1.987 | π* $C_{13}$=$C_{14}$ | 0.116 | 0.15 | 0.59 | 0.009 |
| σ $C_1$ - $H_6$ | 1.985 | Ry*2 $C_{13}$ | 0.002 | 0.12 | 1.30 | 0.011 |
| σ $C_2$ - $C_3$ | 1.983 | Ry*2 $C_{16}$ | 0.002 | 0.08 | 1.40 | 0.009 |
| **π $C_3$=$O_8$** | **1.974** | **π* $C_{13}$=$C_{14}$** | **0.116** | **0.06** | **0.41** | **0.005** |
| **π $C_3$=$O_8$** | **1.974** | **π* $C_{15}$=$C_{16}$** | **0.120** | **0.5** | **0.41** | **0.013** |
| **lp2 $O_8$** | **1.886** | **π* $C_{13}$=$C_{14}$** | **0.116** | **0.12** | **0.30** | **0.005** |
| **π* $C_3$=$O_8$** | **0.145** | **π* $C_{13}$=$C_{14}$** | **0.116** | **0.05** | **0.03** | **0.003** |

- ***NBO_H_exo-cis (R1=H)***

***Table S.7.*** *Second–order perturbation theory analysis of Fock matrix in NBO basis of the H_exo_cis (R1=H) reactant: E(2) in kcal/mol is the hyperconjugative interaction energy, εj–εi is the energy difference between the donor NBO (i) and the acceptor NBO (j)and Fij is the Fock matrix element between the NBO orbitals i and j. εj–εi and Fij are given in atomic units.*

| NBO(i) | | NBO(j) | | $E^{(2)}$ | $\varepsilon_j - \varepsilon_i$ | $F_{i,j}$ |
|---|---|---|---|---|---|---|
| Donor | Occupation | Acceptor | Occupation | | | |
| π* $C_3$=$O_8$ | 0.149 | π* $C_1$=$C_2$ | 0.047 | 27.91 | 0.02 | 0.071 |
| lp2 $O_8$ | 1.887 | σ* $C_3$ - $C_4$ | 0.054 | 20.56 | 0.64 | 0.104 |
| π $C_1$=$C_2$ | 1.896 | π* $C_3$=$O_8$ | 0.149 | 19.92 | 0.29 | 0.069 |
| lp2 $O_8$ | 1.887 | σ* $C_2$ - $C_3$ | 0.063 | 18.99 | 0.70 | 0.104 |
| lp1 $O_8$ | 1.976 | Ry*1 $C_3$ | 0.017 | 15.86 | 1.48 | 0.137 |
| cr1 $O_8$ | 1.999 | Ry*1 $C_3$ | 0.017 | 6.17 | 19.67 | 0.312 |
| σ $C_1$ - $H_6$ | 1.987 | σ* $C_2$ - $C_3$ | 0.063 | 5.12 | 0.98 | 0.064 |
| σ $C_1$ - $H_5$ | 1.985 | σ* $C_2$ - $H_7$ | 0.016 | 5.08 | 0.99 | 0.063 |
| π $C_3$=$O_8$ | 1.974 | σ* $C_{12}$ - $H_{22}$ | 0.021 | 1.12 | 0.84 | 0.027 |
| lp2 $O_8$ | 1.887 | σ* $C_{12}$ - $H_{22}$ | 0.021 | 0.96 | 0.73 | 0.024 |
| lp1 $O_8$ | 1.976 | σ* $C_{12}$ - $H_{22}$ | 0.021 | 0.61 | 1.15 | 0.024 |
| **π* $C_3$=$O_8$** | **0.149** | **π* $C_{15}$=$C_{16}$** | **0.123** | **0.56** | **0.03** | **0.010** |
| σ $C_1$ - $H_5$ | 1.985 | π* $C_{13}$=$C_{14}$ | 0.122 | 0.2 | 0.58 | 0.010 |
| π $C_1$=$C_2$ | 1.896 | π* $C_{13}$=$C_{14}$ | 0.122 | 0.19 | 0.32 | 0.007 |
| π $C_1$=$C_2$ | 1.896 | σ* $C_{12}$ - $H_{21}$ | 0.013 | 0.17 | 0.71 | 0.010 |
| σ $C_1$ - $H_5$ | 1.985 | Ry*2 $C_{13}$ | 0.002 | 0.12 | 1.27 | 0.011 |
| σ $C_2$ - $C_3$ | 1.984 | Ry*3 $C_{16}$ | 0.002 | 0.09 | 1.40 | 0.010 |
| σ $C_1$ - $H_5$ | 1.985 | σ* $C_{12}$ - $H_{22}$ | 0.021 | 0.07 | 1.00 | 0.007 |
| **π $C_3$=$O_8$** | **1.975** | **π* $C_{15}$=$C_{16}$** | **0.123** | **0.07** | **0.42** | **0.005** |
| σ $C_1$ - $C_2$ | 1.989 | Ry*4 $C_{12}$ | 0.001 | 0.06 | 2.31 | 0.011 |
| σ $C_1$ - $H_5$ | 1.985 | Ry*4 $C_{13}$ | 0.001 | 0.06 | 1.70 | 0.009 |

- ***NBO_F_endo-cis (R2=F)***

***Table S.8.*** *Second–order perturbation theory analysis of Fock matrix in NBO basis of the F_endo_cis (R2=F) reactant: E(2) in kcal/mol is the hyperconjugative interaction energy, εj–εi is the energy difference between the donor NBO (i) and the acceptor NBO (j)and Fij is the Fock matrix element between the NBO orbitals i and j. εj–εi and Fij are given in atomic units.*

| NBO(i) | | NBO(j) | | $E^{(2)}$ | $\varepsilon_j - \varepsilon_i$ | $F_{i,j}$ |
|---|---|---|---|---|---|---|
| Donor | Occupation | Acceptor | Occupation | | | |
| lp3 $F_5$ | 1.897 | π* $C_1$=$C_2$ | 0.125 | 24.73 | 0.44 | 0.094 |
| lp2 $O_8$ | 1.887 | σ* $C_3$ - $C_4$ | 0.054 | 20.3 | 0.64 | 0.103 |
| lp2 $O_8$ | 1.887 | σ* $C_2$ - $C_3$ | 0.060 | 20.16 | 0.70 | 0.107 |
| π $C_1$=$C_2$ | 1.888 | π* $C_3$=$O_8$ | 0.164 | 20.07 | 0.31 | 0.072 |
| lp1 $O_8$ | 1.977 | Ry*1 $C_3$ | 0.018 | 16.37 | 1.50 | 0.140 |
| lp2 $F_5$ | 1.971 | σ* $C_1$ - $H_6$ | 0.026 | 6.85 | 0.89 | 0.070 |
| σ $C_4$ - $H_{10}$ | 1.968 | π* $C_3$=$O_8$ | 0.164 | 6.33 | 0.53 | 0.053 |
| cr1 $O_8$ | 1.999 | Ry*1 $C_3$ | 0.018 | 6.2 | 19.69 | 0.313 |
| lp2 $F_5$ | 1.971 | σ* $C_1$ - $C_2$ | 0.018 | 6 | 1.06 | 0.071 |
| lp1 $F_5$ | 1.991 | Ry*1 $C_1$ | 0.008 | 5.9 | 1.78 | 0.092 |

| | | | | | | |
|---|---|---|---|---|---|---|
| π* $C_1$=$C_2$ | 0.125 | π* $C_{13}$=$C_{14}$ | 0.117 | 0.95 | 0.03 | 0.014 |
| **π $C_3$=$O_8$** | **1.976** | **π* $C_{15}$=$C_{16}$** | **0.117** | **0.37** | **0.42** | **0.011** |
| lp3 $F_5$ | 1.897 | σ* $C_{12}$ - $H_{22}$ | 0.016 | 0.36 | 0.87 | 0.016 |
| π* $C_1$=$C_2$ | 0.125 | π* $C_{15}$=$C_{16}$ | 0.117 | 0.26 | 0.03 | 0.007 |
| π $C_1$=$C_2$ | 1.888 | π* $C_{13}$=$C_{14}$ | 0.117 | 0.22 | 0.35 | 0.008 |
| **π $C_3$=$O_8$** | **1.976** | **π* $C_{13}$=$C_{14}$** | **0.117** | **0.19** | **0.42** | **0.008** |
| π $C_1$=$C_2$ | 1.888 | σ* $C_{12}$ - $H_{21}$ | 0.014 | 0.16 | 0.74 | 0.010 |
| σ $C_1$ - $H_6$ | 1.984 | Ry*3 $C_{13}$ | 0.002 | 0.16 | 1.32 | 0.013 |
| **π* $C_3$=$O_8$** | **0.165** | **π* $C_{15}$=$C_{16}$** | **0.117** | **0.16** | **0.03** | **0.005** |
| **lp2 $O_8$** | **1.887** | **π* $C_{13}$=$C_{14}$** | **0.117** | **0.15** | **0.30** | **0.006** |
| π $C_1$=$C_2$ | 1.888 | π* $C_{15}$=$C_{16}$ | 0.117 | 0.12 | 0.35 | 0.006 |
| π $C_1$=$C_2$ | 1.888 | σ* $C_{12}$ - $H_{22}$ | 0.016 | 0.11 | 0.75 | 0.008 |
| lp2 $F_5$ | 1.971 | σ* $C_{12}$ - $H_{22}$ | 0.016 | 0.09 | 0.88 | 0.008 |
| **π* $C_3$=$O_8$** | **0.164** | **π* $C_{13}$=$C_{14}$** | **0.117** | **0.09** | **0.03** | **0.004** |
| σ $C_1$ - $H_6$ | 1.984 | Ry*4 $C_{13}$ | 0.001 | 0.08 | 1.74 | 0.010 |
| lp1 $F_5$ | 1.991 | σ* $C_{12}$ - $H_{22}$ | 0.016 | 0.08 | 1.50 | 0.010 |
| σ $C_1$ - $H_6$ | 1.984 | π* $C_{13}$=$C_{14}$ | 0.117 | 0.07 | 0.62 | 0.006 |
| π $C_1$=$C_2$ | 1.888 | Ry*3 $C_{13}$ | 0.002 | 0.06 | 1.05 | 0.007 |
| **lp1 $O_8$** | **1.977** | **π* $C_{13}$=$C_{14}$** | **0.117** | **0.06** | **0.73** | **0.006** |
| lp3 $F_5$ | 1.897 | Ry*2 $C_{13}$ | 0.002 | 0.05 | 1.11 | 0.007 |

### ➢ *NBO_F_exo-cis (R2=F)*

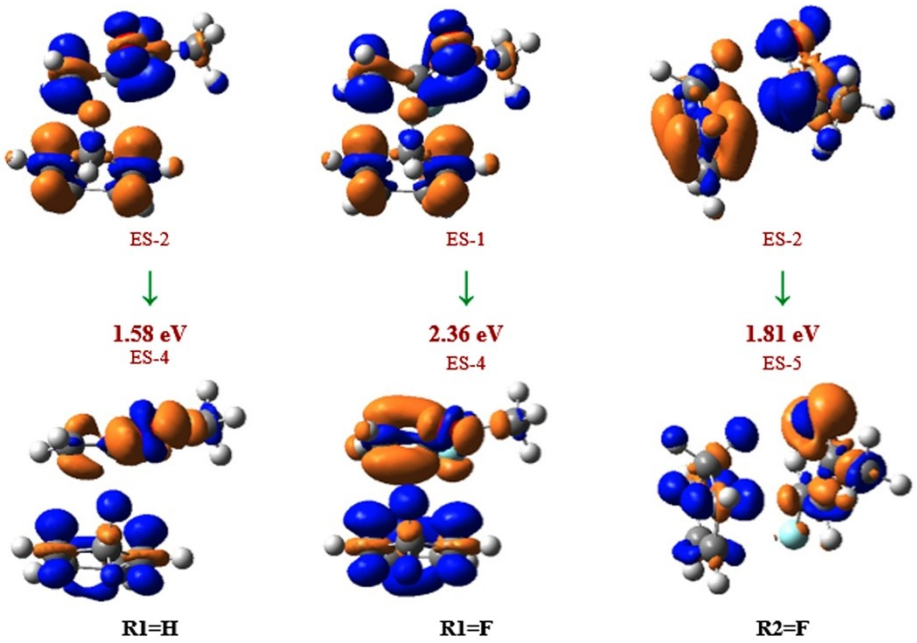
***Table S.9.*** *Second–order perturbation theory analysis of Fock matrix in NBO basis of the F_exo_cis (R2=F) reactant: E(2) in kcal/mol is the hyperconjugative interaction energy, εj–εi is the energy difference between the donor NBO (i) and the acceptor NBO(j) and Fij is the Fock matrix element between the NBO orbitals i and j. εj–εi and Fij are given in atomic units.*

| NBO(i) | | NBO(j) | | $E^{(2)}$ | $\varepsilon_j$- $\varepsilon_i$ | $F_{i,j}$ |
|---|---|---|---|---|---|---|
| Donor | Occupation | Acceptor | Occupation | | | |
| π* $C_3$=$O_8$ | 0.167 | π* $C_1$=$C_2$ | 0.129 | 86.69 | 0.01 | 0.071 |
| lp3 $F_5$ | 1.896 | π* $C_1$=$C_2$ | 0.129 | 25.05 | 0.44 | 0.094 |
| π $C_1$=$C_2$ | 1.883 | π* $C_3$=$O_8$ | 0.167 | 20.58 | 0.31 | 0.072 |
| lp2 $O_8$ | 1.889 | σ* $C_3$ - $C_4$ | 0.053 | 20.31 | 0.64 | 0.104 |
| lp2 $O_8$ | 1.889 | σ* $C_2$ - $C_3$ | 0.059 | 19.23 | 0.71 | 0.105 |
| lp1 $O_8$ | 1.975 | Ry*1 $C_3$ | 0.017 | 15.82 | 1.48 | 0.137 |
| lp2 $F_5$ | 1.970 | σ* $C_1$ - $H_6$ | 0.026 | 7.04 | 0.88 | 0.070 |
| lp2 $F_5$ | 1.970 | σ* $C_1$ - $C_2$ | 0.018 | 6.26 | 1.05 | 0.073 |
| cr1 $O_8$ | 1.999 | Ry*1 $C_3$ | 0.017 | 6.16 | 19.67 | 0.312 |
| lp1 $F_5$ | 1.991 | Ry*1 $C_1$ | 0.009 | 6.15 | 1.79 | 0.094 |
| | | | | | | |
| π $C_3$=$O_8$ | 1.976 | σ* $C_{12}$ - $H_{22}$ | 0.021 | 1.28 | 0.85 | 0.029 |
| lp2 $O_8$ | 1.889 | σ* $C_{12}$ - $H_{22}$ | 0.021 | 0.96 | 0.74 | 0.024 |
| π* $C_1$ - $C_2$ | 0.129 | π* $C_{13}$=$C_{14}$ | 0.126 | 0.86 | 0.03 | 0.012 |
| lp1 $O_8$ | 1.975 | σ* $C_{12}$ - $H_{22}$ | 0.021 | 0.71 | 1.16 | 0.026 |

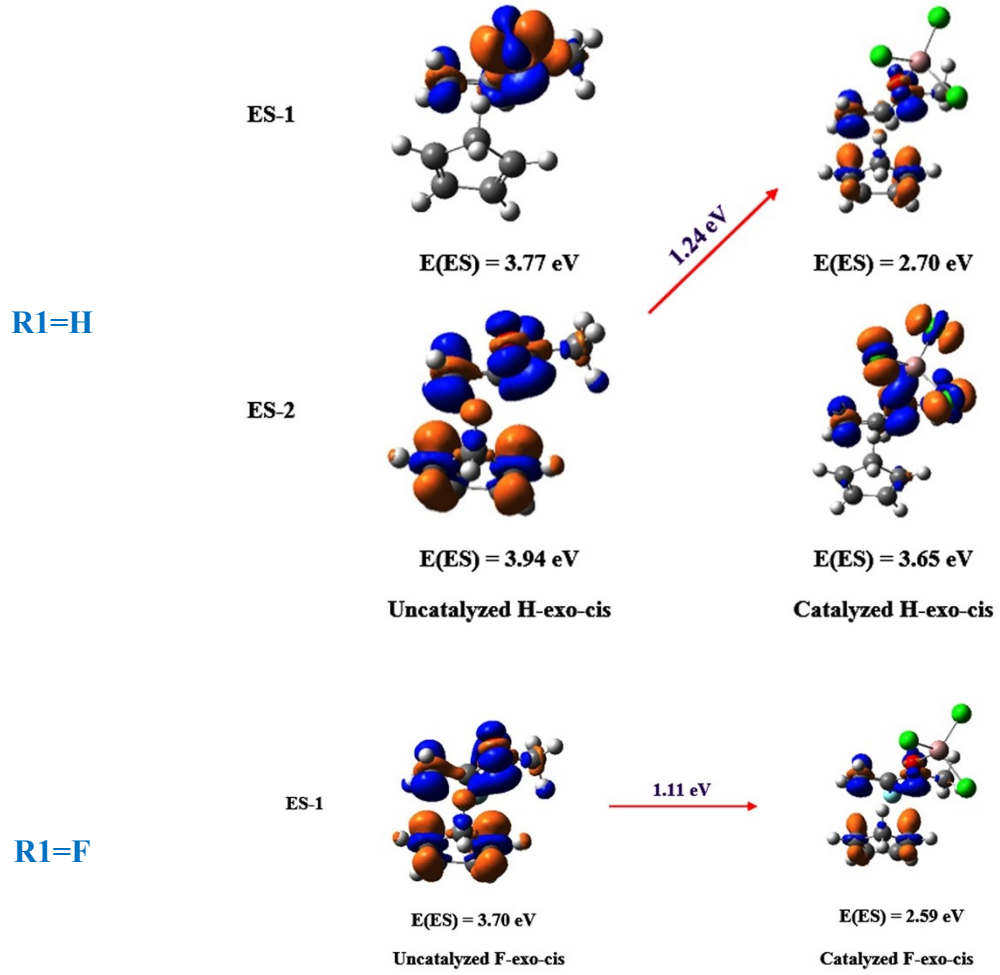
| | | | | | | |
|---|---|---|---|---|---|---|
| **π* $C_3$=$O_8$** | **1.976** | **π* $C_{15}$=$C_{16}$** | **0.123** | **0.43** | **0.04** | **0.009** |
| lp3 $F_5$ | 1.896 | π* $C_{13}$=$C_{14}$ | 0.126 | 0.22 | 0.47 | 0.009 |
| σ $C_1$ - $H_6$ | 1.985 | π* $C_{13}$=$C_{14}$ | 0.126 | 0.21 | 0.62 | 0.010 |
| π $C_1$=$C_2$ | 1.884 | π* $C_{13}$=$C_{14}$ | 0.126 | 0.19 | 0.35 | 0.007 |
| π $C_1$ - $C_2$ | 1.884 | σ* $C_{12}$ - $H_{21}$ | 0.014 | 0.15 | 0.74 | 0.010 |
| lp3 $F_5$ | 1.896 | Ry*3 $C_{14}$ | 0.001 | 0.15 | 1.22 | 0.012 |
| σ $C_1$ - $H_6$ | 1.985 | Ry*3 $C_{13}$ | 0.002 | 0.12 | 1.30 | 0.011 |
| σ $C_1$ - $H_6$ | 1.985 | Ry*4$C_{13}$ | 0.001 | 0.09 | 1.73 | 0.011 |
| π* $C_1$=$C_2$ | 0.129 | π* $C_{15}$=$C_{16}$ | 0.123 | 0.09 | 0.03 | 0.004 |
| σ $C_2$ - $C_3$ | 1.978 | Ry*2 $C_{16}$ | 0.002 | 0.08 | 1.40 | 0.010 |
| σ $C_1$ - $F_5$ | 1.996 | Ry*3 $C_{14}$ | 0.001 | 0.07 | 1.83 | 0.010 |
| σ $C_1$ - $H_6$ | 1.985 | Ry*2 $C_{13}$ | 0.002 | 0.07 | 1.33 | 0.009 |
| σ $C_1$ - $C_2$ | 1.990 | Ry*3 $C_{14}$ | 0.001 | 0.06 | 1.57 | 0.008 |
| π $C_1$=$C_2$ | 1.884 | Ry*2 $C_{13}$ | 0.002 | 0.06 | 1.06 | 0.007 |
| **π $C_3$=$O_8$** | **1.976** | **π* $C_{15}$=$C_{16}$** | **0.123** | **0.06** | **0.42** | **0.004** |
| lp3 $F_5$ | 1.897 | Ry*2 $C_{13}$ | 0.002 | 0.05 | 1.18 | 0.007 |

## 6. State Specific Dual Descriptors

***Scheme S.2.*** *State-specific dual descriptor of the interactions between cyclopentadiene and R-butenone for* ***exo*** *orientation. Blue lobes correspond to positive values of the dual descriptor, whereas orange lobes correspond to negative ones calculated at the TD-B3LYP/6-31G(d,p) level.*



***Scheme S.3.*** *State-specific dual descriptor of the interactions of catalyzed and uncatalyzed Diels-Alder reaction between cyclopentadiene and 3-R-butenone for* ***exo*** *orientation. Blue lobes correspond to positive values of the dual descriptor, whereas orange lobes correspond to negative ones calculated at the TD-B3LYP/6-31G(d,p) level.*




## 7. Domains

***Table S.10.*** *Electrostatic interaction energy of the excited states in u.a and activation energy in kcal/mol and numerical values from the condensation of the nucleophilic domains for oxygen atom in u.a. are given for the* ***exo*** *reactions between the cyclopentadiene and R-butenone.* $\Delta s(D_O^-)$ *is the integrated value of the domain volume.*

| | $E_{PSCube}$ | Ea | $\Delta s(D_O^-)$ |
|---|---|---|---|
| R1=H | 0.115 | 18.7 | -0.016 |
| R1=F | 0.121 | 17.9 | -0.015 |
| R2=F | 0.062 | 16.9 | -0.272 |

## 8. Geometric Structures

### Uncatalyzed Reactant_H_endo-cis (R1=H)

| | | | |
|---|---|---|---|
| H | -1.07240400 | 1.47439100 | -1.45250300 |
| C | -0.95563100 | 1.77783600 | -0.41667000 |
| C | 0.22668200 | 1.63351400 | 0.19308800 |
| C | 1.39431000 | 1.05054100 | -0.52432700 |
| C | 2.72678800 | 1.10548200 | 0.20251300 |
| H | -1.81687800 | 2.21241200 | 0.08232800 |
| H | 0.37434100 | 1.95090100 | 1.22362900 |
| O | 1.29539200 | 0.57251100 | -1.64524900 |
| H | 3.49484900 | 0.60252700 | -0.38812100 |
| H | 3.02191400 | 2.15027700 | 0.36719800 |
| H | 2.64877300 | 0.63433500 | 1.18997400 |
| C | -2.12827600 | -0.94999400 | 0.07834800 |
| C | -1.17951400 | -1.50386500 | -0.70876900 |
| C | 0.01454700 | -1.77588400 | 0.09266400 |
| C | -0.20184600 | -1.38280300 | 1.36713500 |
| C | -1.60858800 | -0.85785700 | 1.48987400 |
| H | -3.12606700 | -0.64846000 | -0.22011100 |
| H | -1.26039700 | -1.70799800 | -1.77085800 |
| H | 0.92659900 | -2.20930400 | -0.30281500 |
| H | 0.48782900 | -1.46572200 | 2.19981600 |
| H | -2.20549000 | -1.48275700 | 2.17392900 |
| H | -1.65014100 | 0.16148700 | 1.89516000 |

### Uncatalyzed Product_H_endo-cis (R1=H)

| | | | |
|---|---|---|---|
| H | -1.03554600 | 1.23264100 | -1.32319700 |
| C | -1.20010600 | 1.01272200 | -0.26645300 |
| C | 0.14182900 | 0.80757600 | 0.48655400 |
| C | 1.35322100 | 0.84188400 | -0.42971100 |
| C | 2.69942700 | 1.15528300 | 0.20184900 |
| H | -1.77921000 | 1.83132600 | 0.17720400 |
| H | 0.27366700 | 1.52464300 | 1.30578900 |
| O | 1.26216400 | 0.58131600 | -1.61626400 |
| H | 3.49863500 | 0.69546900 | -0.38438200 |
| H | 2.85559700 | 2.24259600 | 0.19622600 |
| H | 2.75488700 | 0.82361200 | 1.24443900 |
| C | -1.93512300 | -0.35196000 | -0.04727200 |
| C | -1.12391500 | -1.43813300 | -0.73873700 |
| C | -0.01615800 | -1.65419100 | -0.01646400 |
| C | -0.03796800 | -0.66000800 | 1.13189600 |
| C | -1.55366900 | -0.62359000 | 1.42760500 |
| H | -3.00064200 | -0.32535400 | -0.29010200 |
| H | -1.36837000 | -1.86904600 | -1.70423400 |
| H | 0.82489100 | -2.28716000 | -0.27924300 |
| H | 0.63654400 | -0.85276600 | 1.96951500 |
| H | -1.92835100 | -1.58174800 | 1.80009900 |
| H | -1.84925200 | 0.18115300 | 2.11186400 |

### Uncatalyzed TS_H_endo-cis (R1=H)

| | | | |
|---|---|---|---|
| H | -1.10928072 | 1.28521897 | -1.39879287 |
| C | -1.10928072 | 1.28521897 | -0.31359687 |
| C | 0.14194028 | 1.28521897 | 0.31251313 |

| | | | |
|---|---|---|---|
| C | 1.33118928 | 0.94540097 | -0.46227787 |
| C | 2.69072028 | 1.13904297 | 0.19851113 |
| H | -1.91911772 | 1.84673597 | 0.14646713 |
| H | 0.26265928 | 1.65538997 | 1.32633713 |
| O | 1.24772628 | 0.52394397 | -1.61862987 |
| H | 3.45256428 | 0.59489397 | -0.36445487 |
| H | 2.95538628 | 2.20484197 | 0.19632513 |
| H | 2.68952528 | 0.80584697 | 1.24253913 |
| C | -1.94432072 | -0.53067303 | -0.01533387 |
| C | -1.11344872 | -1.40771303 | -0.73956987 |
| C | 0.01011028 | -1.73547703 | 0.04458213 |
| C | -0.11544572 | -1.14016703 | 1.28594513 |
| C | -1.53547172 | -0.67304503 | 1.44266713 |
| H | -2.97568772 | -0.34178003 | -0.30163387 |
| H | -1.24405172 | -1.67666503 | -1.78159487 |
| H | 0.87899628 | -2.27507303 | -0.31433187 |
| H | 0.58743328 | -1.22917903 | 2.10672713 |
| H | -2.12834972 | -1.48992803 | 1.88842113 |
| H | -1.67748272 | 0.21310897 | 2.06491113 |

**Uncatalyzed Reactant_H_exo-cis (R1=H)**

| | | | |
|---|---|---|---|
| C | 2.54614400 | 0.18037300 | -0.46662900 |
| C | 1.81232800 | 1.42133800 | -0.21683200 |
| C | 0.99540500 | 1.24990500 | 0.84757600 |
| C | -0.94087100 | -0.33101600 | -1.20959600 |
| C | -0.20268600 | -1.44219800 | -1.31560900 |
| C | 2.17424300 | -0.74790000 | 0.44400800 |
| H | 3.26523100 | 0.04283000 | -1.26817900 |
| H | 1.91996900 | 2.32702400 | -0.80566800 |
| H | 0.33803000 | 1.99116600 | 1.28830200 |
| C | -1.94822800 | -0.16155200 | -0.12822500 |
| H | 0.51605400 | -1.58252300 | -2.11554800 |
| H | -0.32361100 | -2.25202000 | -0.60075000 |
| H | 2.54748200 | -1.76257800 | 0.52656000 |
| O | -2.02253100 | -0.92744200 | 0.82467100 |
| C | 1.17591100 | -0.14030400 | 1.39218100 |
| H | 0.23425500 | -0.70131800 | 1.45120900 |
| H | 1.57637600 | -0.11059000 | 2.41861800 |
| H | -0.84536600 | 0.47457800 | -1.93373200 |
| C | -2.90098100 | 1.01110200 | -0.27619500 |
| H | -2.34069100 | 1.95072700 | -0.35969000 |
| H | -3.48880400 | 0.90742500 | -1.19748400 |
| H | -3.57394100 | 1.05655500 | 0.58202000 |

**Uncatalyzed Product_H_exo-cis (R1=H)**

| | | | |
|---|---|---|---|
| C | 2.45031100 | 0.18242100 | -0.54582600 |
| C | 1.75786000 | 1.31168200 | -0.34011000 |
| C | 0.49418400 | 0.93484600 | 0.41648200 |
| C | -0.42018500 | 0.13248300 | -0.61964000 |
| C | 0.39109200 | -1.18042500 | -0.82238300 |
| C | 1.65975400 | -0.96204200 | 0.07276200 |
| H | 3.35504100 | 0.06543500 | -1.13471600 |
| H | 1.97498300 | 2.30237200 | -0.72729000 |

| | | | |
|---|---|---|---|
| H | -0.02412900 | 1.74831900 | 0.93082900 |
| C | -1.79326300 | -0.06379400 | 0.01058400 |
| H | 0.64670700 | -1.34968500 | -1.87171200 |
| H | -0.18495700 | -2.03720900 | -0.45959000 |
| H | 2.21905100 | -1.87758200 | 0.28044200 |
| O | -2.03104100 | -0.97439900 | 0.78542500 |
| C | 1.01805900 | -0.23618500 | 1.27900800 |
| H | 0.22450200 | -0.81270400 | 1.76192700 |
| H | 1.75394200 | 0.09226200 | 2.01902200 |
| H | -0.52584800 | 0.71192300 | -1.54252700 |
| C | -2.85518900 | 0.97072400 | -0.32725100 |
| H | -2.42691300 | 1.96874600 | -0.46969300 |
| H | -3.33899400 | 0.68851600 | -1.27234000 |
| H | -3.61670800 | 0.99228400 | 0.45552600 |

**Uncatalyzed TS_H_exo-cis (R1=H)**

| | | | |
|---|---|---|---|
| C | 2.44793610 | 0.16628144 | -0.52543088 |
| C | 1.79557310 | 1.38149044 | -0.25251988 |
| C | 0.79676610 | 1.15769044 | 0.68724612 |
| C | -0.66474990 | -0.15345356 | -0.94536888 |
| C | 0.17973210 | -1.26840656 | -1.00558488 |
| C | 1.80494310 | -0.86806556 | 0.18355312 |
| H | 3.22099310 | 0.02533844 | -1.27415188 |
| H | 1.98523710 | 2.32224244 | -0.75924888 |
| H | 0.16005610 | 1.91888644 | 1.12430612 |
| C | -1.83177090 | -0.12285556 | -0.05967188 |
| H | 0.71159110 | -1.47553456 | -1.92830388 |
| H | -0.13769490 | -2.14972856 | -0.45366188 |
| H | 2.24180610 | -1.85520956 | 0.30692312 |
| O | -2.01315790 | -0.95050056 | 0.83571212 |
| C | 1.01062610 | -0.19943656 | 1.28821912 |
| H | 0.10379910 | -0.71828356 | 1.60555512 |
| H | 1.66984010 | -0.09186956 | 2.16683312 |
| H | -0.59898490 | 0.61639944 | -1.70768088 |
| C | -2.85591290 | 0.97816344 | -0.31043788 |
| H | -2.37506190 | 1.94777744 | -0.48296488 |
| H | -3.44155390 | 0.74262844 | -1.20893188 |
| H | -3.53747290 | 1.04541644 | 0.54033912 |

**Catalyzed Reactant_H_endo-cis (R1=H)**

| | | | |
|---|---|---|---|
| C | -4.32496400 | -0.20537500 | 0.40612200 |
| C | -3.30355700 | -0.00572300 | 1.49400300 |
| C | -2.26118700 | -0.84442900 | 1.28817800 |
| C | -2.49221900 | -1.60848000 | 0.06198200 |
| C | -3.67662800 | -1.23604100 | -0.48220400 |
| C | -2.17970000 | 0.88898500 | -2.07324200 |
| C | -1.80170000 | 1.75835300 | -1.11325100 |
| C | -0.57363500 | 1.56643600 | -0.36399200 |
| C | -0.12939800 | 2.57261300 | 0.65040500 |
| H | -4.57361700 | 0.72551400 | -0.12322500 |
| H | -5.27562300 | -0.57796500 | 0.81846600 |
| H | -3.43294000 | 0.67556500 | 2.32749300 |
| H | -1.38364300 | -0.95038300 | 1.91694500 |

| | | | |
|---|---|---|---|
| H | -1.80630200 | -2.35169600 | -0.33067600 |
| H | -4.14033800 | -1.64884600 | -1.37106600 |
| H | -1.55773300 | 0.03953400 | -2.33201000 |
| H | -3.09171400 | 1.03679800 | -2.64254600 |
| H | -2.40234500 | 2.62764100 | -0.86580400 |
| O | 0.13321700 | 0.55041900 | -0.60715600 |
| H | -0.85874700 | 3.37225200 | 0.79058700 |
| H | 0.06846200 | 2.06918100 | 1.60316100 |
| H | 0.82696000 | 3.00007200 | 0.32133500 |
| Al | 1.74288600 | -0.22403300 | -0.04190100 |
| Cl | 1.69146300 | -2.12447100 | -1.00396600 |
| Cl | 1.59012200 | -0.32784900 | 2.09877700 |
| Cl | 3.22431600 | 1.14926400 | -0.74136900 |

**Catalyzed Product_H_endo-cis (R1=H)**

| | | | |
|---|---|---|---|
| C | -4.06688200 | -0.06314400 | 0.16632800 |
| C | -2.81089900 | 0.48887900 | 0.87546600 |
| C | -2.01293500 | -0.78238100 | 1.05084300 |
| C | -2.25089100 | -1.54654100 | -0.02728900 |
| C | -3.25608500 | -0.82364600 | -0.90812700 |
| C | -2.53448800 | 0.38581300 | -1.59697400 |
| C | -2.17006500 | 1.30993100 | -0.40217300 |
| C | -0.72042000 | 1.47004100 | -0.15449400 |
| C | -0.16820900 | 2.62897800 | 0.61095700 |
| H | -4.72496400 | 0.71314600 | -0.24175900 |
| H | -4.63822200 | -0.72482600 | 0.82285300 |
| H | -2.94770200 | 1.12958600 | 1.74802300 |
| H | -1.27912100 | -0.95447800 | 1.82994400 |
| H | -1.74832300 | -2.47034100 | -0.29145100 |
| H | -3.81394400 | -1.44790600 | -1.60873300 |
| H | -1.65624000 | 0.07830500 | -2.16622300 |
| H | -3.22244000 | 0.90113300 | -2.27372800 |
| H | -2.66012800 | 2.28615800 | -0.44167900 |
| O | 0.03131400 | 0.53458400 | -0.51252800 |
| H | -0.90409700 | 3.42045900 | 0.76127800 |
| H | 0.18303500 | 2.26107700 | 1.58530200 |
| H | 0.71552400 | 3.01975700 | 0.09391300 |
| Al | 1.67277700 | -0.23960500 | -0.02582200 |
| Cl | 1.61769200 | -2.14836900 | -0.96228700 |
| Cl | 1.57574900 | -0.32882000 | 2.12065300 |
| Cl | 3.13135500 | 1.12843200 | -0.76667900 |

**Catalyzed TS_H_endo-cis (R1=H)**

| | | | |
|---|---|---|---|
| C | -3.98735400 | -0.14545200 | 0.26571900 |
| C | -3.02155200 | -0.00082100 | 1.40328200 |
| C | -1.98161500 | -0.87354900 | 1.24061800 |
| C | -2.09862500 | -1.50007000 | -0.03784200 |
| C | -3.18100700 | -0.95797300 | -0.73177500 |
| C | -2.24835700 | 0.60085400 | -1.81862400 |
| C | -1.82274400 | 1.58835400 | -0.92671900 |
| C | -0.55828600 | 1.50014700 | -0.30864600 |
| C | -0.02936900 | 2.57921100 | 0.58886800 |
| H | -4.40068500 | 0.79625300 | -0.10572400 |

| | | | |
|---|---|---|---|
| H | -4.84441000 | -0.75396900 | 0.59901700 |
| H | -3.18940000 | 0.63930800 | 2.26229500 |
| H | -1.16150100 | -1.03222500 | 1.93126400 |
| H | -1.40095600 | -2.23365600 | -0.42763500 |
| H | -3.63406500 | -1.44369200 | -1.59015000 |
| H | -1.50039700 | -0.03312600 | -2.28033600 |
| H | -3.13515300 | 0.78713600 | -2.41750900 |
| H | -2.45680400 | 2.43369800 | -0.68335800 |
| O | 0.16007600 | 0.45951800 | -0.54218600 |
| H | -0.74838200 | 3.39062400 | 0.72213100 |
| H | 0.23746400 | 2.15580500 | 1.56369400 |
| H | 0.89610100 | 2.98090900 | 0.15799300 |
| Al | 1.77854100 | -0.24953900 | -0.03022700 |
| Cl | 1.74924200 | -2.18260400 | -0.95691100 |
| Cl | 1.70433000 | -0.36820800 | 2.12425700 |
| Cl | 3.28231100 | 1.08825800 | -0.75855300 |

**Catalyzed Reactant_H_exo-cis (R1=H)**

| | | | |
|---|---|---|---|
| C | 4.45976000 | -0.40030900 | -0.06493200 |
| C | 3.93713700 | 0.36580800 | 1.06429200 |
| C | 2.76155700 | -0.17515800 | 1.46629000 |
| C | 1.74189800 | 1.50725400 | -1.36421500 |
| C | 2.13670900 | 0.52703400 | -2.20286500 |
| C | 3.60095600 | -1.40739300 | -0.35881200 |
| H | 5.39364300 | -0.18501300 | -0.57445200 |
| H | 4.43282600 | 1.22467900 | 1.50496900 |
| H | 2.13970100 | 0.14913100 | 2.29275500 |
| C | 0.49941500 | 1.43485300 | -0.62062200 |
| H | 3.05804300 | 0.60724000 | -2.76837300 |
| H | 1.51984000 | -0.35032100 | -2.36989700 |
| H | 3.72593700 | -2.16513800 | -1.12401100 |
| O | -0.22685800 | 0.40597400 | -0.73039200 |
| Al | -1.81817600 | -0.23792000 | 0.03600400 |
| Cl | -1.37629100 | -0.23722700 | 2.13859000 |
| Cl | -1.99841200 | -2.17757200 | -0.82062800 |
| Cl | -3.31054200 | 1.17676900 | -0.55066000 |
| C | 2.45876700 | -1.38043000 | 0.62123800 |
| H | 1.47306000 | -1.33760200 | 0.14019700 |
| H | 2.44174900 | -2.29469100 | 1.23528300 |
| H | 2.35023300 | 2.39261100 | -1.21296100 |
| C | 0.06414300 | 2.57813700 | 0.24085400 |
| H | 0.79425200 | 3.38880900 | 0.25467900 |
| H | -0.90025100 | 2.95075700 | -0.12862400 |
| H | -0.11571600 | 2.21672000 | 1.26059500 |

**Catalyzed Product_H_exo-cis (R1=H)**

| | | | |
|---|---|---|---|
| C | 4.42783200 | -0.33912100 | -0.11264800 |
| C | 3.97637400 | 0.37506300 | 0.94392700 |
| C | 2.52277300 | 0.17745400 | 1.01508300 |
| C | 2.00302500 | 1.13592200 | -0.69442500 |
| C | 2.50088900 | 0.07969000 | -1.65822000 |
| C | 3.25858500 | -1.00871900 | -0.78344200 |
| H | 5.44148400 | -0.34175900 | -0.50063600 |

| | | | |
|---|---|---|---|
| H | 4.54208400 | 1.06667900 | 1.55880900 |
| H | 1.92541600 | 0.54630600 | 1.84485200 |
| C | 0.59588400 | 1.32017800 | -0.46861700 |
| H | 3.16263100 | 0.50821000 | -2.41493800 |
| H | 1.66524800 | -0.40968300 | -2.16640200 |
| H | 3.49388700 | -1.90150200 | -1.36592100 |
| O | -0.20701400 | 0.36711600 | -0.72622600 |
| Al | -1.80609300 | -0.23228900 | 0.01088500 |
| Cl | -1.36034900 | -0.23555600 | 2.12537900 |
| Cl | -2.01555400 | -2.18989100 | -0.80471600 |
| Cl | -3.32744600 | 1.16402000 | -0.54170300 |
| C | 2.28881800 | -1.18635300 | 0.40546500 |
| H | 1.25589000 | -1.38807500 | 0.12076100 |
| H | 2.63103500 | -1.97365300 | 1.08807100 |
| H | 2.57747700 | 2.05561600 | -0.63602200 |
| C | 0.07548700 | 2.58202200 | 0.15441300 |
| H | 0.84378000 | 3.35357500 | 0.23105800 |
| H | -0.77007000 | 2.95156600 | -0.43597200 |
| H | -0.31893700 | 2.35745000 | 1.15373500 |

**Catalyzed TS_H_exo-cis (R1=H)**

| | | | |
|---|---|---|---|
| C | 4.26934700 | -0.36157700 | -0.11706800 |
| C | 3.85582300 | 0.30980100 | 1.06159200 |
| C | 2.58301900 | -0.10427800 | 1.38661800 |
| C | 1.75836300 | 1.29585900 | -1.08800000 |
| C | 2.25249400 | 0.22736500 | -1.85202000 |
| C | 3.20893100 | -1.12892300 | -0.62010300 |
| H | 5.22987700 | -0.22742500 | -0.60457200 |
| H | 4.43917400 | 1.05132800 | 1.59591800 |
| H | 1.98784000 | 0.23388300 | 2.22738700 |
| C | 0.45332000 | 1.33250400 | -0.55579700 |
| H | 3.08746000 | 0.41407500 | -2.51915100 |
| H | 1.53611100 | -0.50570200 | -2.21253500 |
| H | 3.35113100 | -1.92192500 | -1.34781200 |
| O | -0.33398200 | 0.32579300 | -0.71590200 |
| Al | -1.91909000 | -0.25625300 | 0.02169100 |
| Cl | -1.49038600 | -0.26979300 | 2.14169200 |
| Cl | -2.13764200 | -2.21842400 | -0.79739000 |
| Cl | -3.44927200 | 1.13434500 | -0.53468000 |
| C | 2.18019800 | -1.22421400 | 0.48845400 |
| H | 1.13314800 | -1.21960300 | 0.18301400 |
| H | 2.34077000 | -2.17509900 | 1.02485700 |
| H | 2.38301400 | 2.16502900 | -0.91432900 |
| C | -0.05206800 | 2.55046300 | 0.16371000 |
| H | 0.69781100 | 3.34318000 | 0.20668500 |
| H | -0.95056300 | 2.92116100 | -0.34324100 |
| H | -0.35821800 | 2.27987800 | 1.18111400 |

**Uncatalyzed Reactant_F_endo-cis (R1=F)**

| | | | |
|---|---|---|---|
| H | -1.07241700 | 1.33638300 | -1.65985800 |
| C | -1.01371900 | 1.54648300 | -0.60079000 |
| C | 0.14593400 | 1.35554800 | 0.02553900 |
| C | 1.39755800 | 0.87787600 | -0.62890200 |

| | | | |
|---|---|---|---|
| C | 2.67104600 | 0.97830600 | 0.18399300 |
| H | -1.88841900 | 1.92097000 | -0.08194000 |
| F | 0.26594200 | 1.60912400 | 1.35861100 |
| O | 1.37262500 | 0.46203100 | -1.77586200 |
| H | 3.50972000 | 0.62573700 | -0.41865200 |
| H | 2.84474100 | 2.01636800 | 0.49275000 |
| H | 2.59276500 | 0.38491200 | 1.10159000 |
| C | -2.21301800 | -1.16835300 | -0.02418300 |
| C | -1.37943200 | -1.71865300 | -0.93528400 |
| C | -0.10073100 | -2.02942500 | -0.29411400 |
| C | -0.15416000 | -1.67085600 | 1.00789300 |
| C | -1.52146700 | -1.12001400 | 1.31422500 |
| H | -3.23402100 | -0.84357500 | -0.19027400 |
| H | -1.59683700 | -1.89617600 | -1.98324400 |
| H | 0.74986700 | -2.46300900 | -0.80872800 |
| H | 0.62991200 | -1.78531600 | 1.74795500 |
| H | -2.04580000 | -1.74684500 | 2.05435000 |
| H | -1.47942700 | -0.11241600 | 1.74763800 |

**Uncatalyzed Product_F_endo-cis (R1=F)**

| | | | |
|---|---|---|---|
| H | -1.11039900 | 0.99838700 | -1.49292400 |
| C | -1.23815800 | 0.79493200 | -0.42854500 |
| C | 0.11346600 | 0.56600300 | 0.28152100 |
| C | 1.36608700 | 0.69677500 | -0.57379600 |
| C | 2.64940500 | 1.06252200 | 0.14494700 |
| H | -1.73670400 | 1.64633200 | 0.04383800 |
| F | 0.22125100 | 1.47825100 | 1.35519100 |
| O | 1.32867200 | 0.42290000 | -1.75836700 |
| H | 3.50095000 | 0.82842600 | -0.49696500 |
| H | 2.65544600 | 2.13323400 | 0.38095900 |
| H | 2.73304500 | 0.53215300 | 1.09948600 |
| C | -2.00473600 | -0.54442700 | -0.15734700 |
| C | -1.29404000 | -1.62467900 | -0.96095700 |
| C | -0.12001800 | -1.87062200 | -0.36570700 |
| C | -0.02038500 | -0.93203400 | 0.83604400 |
| C | -1.50126800 | -0.88471900 | 1.26774000 |
| H | -3.08506800 | -0.47043700 | -0.29971500 |
| H | -1.64691300 | -2.02529200 | -1.90529400 |
| H | 0.67875100 | -2.51131600 | -0.72236600 |
| H | 0.72997100 | -1.16922000 | 1.59361800 |
| H | -1.86380400 | -1.85032500 | 1.63108200 |
| H | -1.70741700 | -0.10360900 | 2.00679500 |

**Uncatalyzed TS_F_endo-cis (R1=F)**

| | | | |
|---|---|---|---|
| H | -1.15844369 | 1.04896912 | -1.56498778 |
| C | -1.15844369 | 1.04896912 | -0.48207478 |
| C | 0.09996431 | 1.04896912 | 0.11887522 |
| C | 1.34588431 | 0.78018712 | -0.58942078 |
| C | 2.64514531 | 1.02669412 | 0.15866422 |
| H | -1.92361269 | 1.66144712 | -0.01317978 |
| F | 0.21232631 | 1.55765712 | 1.38631322 |
| O | 1.32048831 | 0.38781812 | -1.75671278 |
| H | 3.48066731 | 0.71611412 | -0.47151778 |

| | | | |
|---|---|---|---|
| H | 2.74921231 | 2.09151912 | 0.40087222 |
| H | 2.67048531 | 0.48195112 | 1.10858322 |
| C | -2.01678169 | -0.72882088 | -0.12146278 |
| C | -1.30771669 | -1.61240988 | -0.96509878 |
| C | -0.10906669 | -1.98951288 | -0.33115978 |
| C | -0.07419469 | -1.43925788 | 0.93760922 |
| C | -1.44674969 | -0.93032888 | 1.27404122 |
| H | -3.06777469 | -0.49996088 | -0.27836678 |
| H | -1.56478169 | -1.83406188 | -1.99509278 |
| H | 0.69691431 | -2.53832988 | -0.80467078 |
| H | 0.71832031 | -1.56789988 | 1.66618822 |
| H | -2.01708569 | -1.73410188 | 1.76949422 |
| H | -1.46842769 | -0.05816188 | 1.93006222 |

**Uncatalyzed Reactant_F_exo-cis (R1=F)**

| | | | |
|---|---|---|---|
| C | 2.51898200 | -0.53579300 | 0.00500500 |
| C | 1.68393900 | -0.88681500 | -1.14625200 |
| C | 1.05436100 | 0.22174500 | -1.59571300 |
| C | -0.85798600 | -0.40476300 | 0.94965200 |
| C | -0.16642400 | 0.12711300 | 1.95535700 |
| C | 2.39428800 | 0.78567700 | 0.25916800 |
| H | 3.12810400 | -1.24314500 | 0.55877500 |
| H | 1.59505900 | -1.88790000 | -1.55524400 |
| H | 0.38204200 | 0.29016600 | -2.44360300 |
| C | -1.82526400 | 0.33931000 | 0.09166400 |
| H | 0.50387900 | -0.47088100 | 2.55948900 |
| H | -0.28797500 | 1.17992600 | 2.17700100 |
| H | 2.89085300 | 1.34657700 | 1.04305400 |
| O | -1.87159100 | 1.55990800 | 0.12499500 |
| C | 1.46493600 | 1.40009200 | -0.75434400 |
| H | 0.60355100 | 1.90675300 | -0.29774100 |
| H | 1.98087100 | 2.16373500 | -1.35846700 |
| C | -2.74550800 | -0.49404200 | -0.77402100 |
| H | -3.33485800 | -1.17977800 | -0.15313700 |
| H | -3.41132500 | 0.16679400 | -1.33143000 |
| H | -2.16478300 | -1.11512800 | -1.46456100 |
| F | -0.74918800 | -1.72374200 | 0.65250400 |

**Uncatalyzed Product_F_exo-cis (R1=F)**

| | | | |
|---|---|---|---|
| C | 2.44459300 | -0.58065800 | 0.10236300 |
| C | 1.68261600 | -0.97580600 | -0.92657000 |
| C | 0.53236300 | 0.00607300 | -1.02907500 |
| C | -0.37328700 | -0.26157000 | 0.25029000 |
| C | 0.48747000 | 0.28953400 | 1.40790900 |
| C | 1.82539200 | 0.68292700 | 0.68762800 |
| H | 3.29815900 | -1.10338300 | 0.52212100 |
| H | 1.77246300 | -1.88522200 | -1.50996100 |
| H | -0.02216500 | 0.01706000 | -1.97045500 |
| C | -1.71839700 | 0.40217900 | -0.02502700 |
| H | 0.60739300 | -0.47810900 | 2.17624500 |
| H | 0.01949200 | 1.17294300 | 1.85148700 |
| H | 2.48603600 | 1.30507800 | 1.29521800 |
| O | -1.87778100 | 1.59534700 | 0.15546700 |

| | | | |
|---|---|---|---|
| C | 1.22860400 | 1.31771000 | -0.59125700 |
| H | 0.53361800 | 2.13831100 | -0.39002800 |
| H | 1.98821100 | 1.63275300 | -1.31347700 |
| C | -2.78210700 | -0.48182400 | -0.64850000 |
| H | -3.23046100 | -1.11982200 | 0.12245000 |
| H | -3.55698000 | 0.14545000 | -1.09344000 |
| H | -2.35338600 | -1.15422300 | -1.39804300 |
| F | -0.60298400 | -1.63085500 | 0.44786100 |

**Uncatalyzed TS_F_exo-cis (R1=F)**

| | | | |
|---|---|---|---|
| C | 2.39555955 | -0.57898254 | 0.07912646 |
| C | 1.67063455 | -0.90901754 | -1.08181254 |
| C | 0.85021855 | 0.15404946 | -1.42391654 |
| C | -0.62512445 | -0.33152654 | 0.68408446 |
| C | 0.28099355 | 0.22956046 | 1.58134646 |
| C | 1.95682455 | 0.67801646 | 0.54907446 |
| H | 3.06466655 | -1.24747554 | 0.61067646 |
| H | 1.69405155 | -1.87320054 | -1.57813554 |
| H | 0.19981555 | 0.20062546 | -2.29005154 |
| C | -1.72670045 | 0.36814046 | 0.02942446 |
| H | 0.70318855 | -0.42714654 | 2.33429346 |
| H | 0.04681955 | 1.23521146 | 1.91475246 |
| H | 2.51189755 | 1.25081246 | 1.28746946 |
| O | -1.83563945 | 1.59410946 | 0.10287046 |
| C | 1.25456055 | 1.35088346 | -0.61830454 |
| H | 0.43273455 | 2.02328446 | -0.36120654 |
| H | 2.00371455 | 1.93088646 | -1.18376754 |
| C | -2.74462245 | -0.48815054 | -0.70658754 |
| H | -3.30148045 | -1.11001754 | 0.00531546 |
| H | -3.44135745 | 0.16664746 | -1.23328654 |
| H | -2.26061745 | -1.17095554 | -1.41216654 |
| F | -0.63445345 | -1.69275554 | 0.58775446 |

**Catalyzed Reactant_F_endo-cis (R1=F)**

| | | | |
|---|---|---|---|
| C | -2.20955900 | -2.09845900 | -0.12736800 |
| C | -1.84945500 | -1.47768200 | 1.14519700 |
| C | -2.85026300 | -0.65296500 | 1.53949900 |
| C | -1.85082600 | 1.40603500 | -0.87999400 |
| C | -2.14038100 | 0.67157700 | -1.96469000 |
| C | -3.43327000 | -1.65628900 | -0.51128900 |
| H | -1.57829400 | -2.79838400 | -0.66425100 |
| H | -0.91924100 | -1.65710900 | 1.67325900 |
| H | -2.88729100 | -0.07010800 | 2.45287900 |
| C | -0.60783000 | 1.30377100 | -0.12584600 |
| H | -1.41148300 | -0.02832200 | -2.34881800 |
| H | -3.07774900 | 0.80436400 | -2.49179800 |
| H | -3.98599300 | -1.96382400 | -1.39178200 |
| O | 0.23296100 | 0.45564900 | -0.52368700 |
| Al | 1.94625900 | -0.16840400 | -0.05752200 |
| Cl | 3.21120200 | 1.46779300 | -0.58355500 |
| Cl | 2.11496800 | -1.92516700 | -1.24865000 |
| Cl | 1.83781800 | -0.55378800 | 2.05211800 |
| C | -3.97571400 | -0.72521500 | 0.54307900 |

| | | | |
|---|---|---|---|
| H | -4.26212500 | 0.26056000 | 0.15221500 |
| H | -4.88504100 | -1.13970600 | 1.00563600 |
| C | -0.32487300 | 2.22690100 | 1.01292100 |
| H | -1.21037300 | 2.77924400 | 1.32364900 |
| H | 0.09808900 | 1.66109500 | 1.84872700 |
| H | 0.44952500 | 2.93573300 | 0.68652600 |
| F | -2.74091900 | 2.30444800 | -0.39858400 |

**Catalyzed Product_F_endo-cis (R1=F)**

| | | | |
|---|---|---|---|
| C | -1.96550900 | -1.91327500 | -0.22505300 |
| C | -1.69502400 | -1.38823400 | 1.00558500 |
| C | -2.59712500 | -0.29629200 | 1.21204100 |
| C | -2.01452800 | 1.11478300 | -0.48190500 |
| C | -2.43886700 | 0.17498700 | -1.55543800 |
| C | -3.06554600 | -1.13583100 | -0.87099400 |
| H | -1.38251100 | -2.67872400 | -0.72661000 |
| H | -0.85596600 | -1.64148000 | 1.64255700 |
| H | -2.61092600 | 0.33043800 | 2.09802000 |
| C | -0.67767900 | 1.26015400 | -0.05045900 |
| H | -1.60408600 | -0.09767600 | -2.20246400 |
| H | -3.21930800 | 0.64859900 | -2.15634100 |
| H | -3.66257100 | -1.68729100 | -1.59974600 |
| O | 0.14224500 | 0.35830300 | -0.44874500 |
| Al | 1.85839500 | -0.18991300 | -0.04749000 |
| Cl | 3.15345700 | 1.42738800 | -0.58047400 |
| Cl | 2.08027100 | -1.95806800 | -1.23001100 |
| Cl | 1.81615800 | -0.58863900 | 2.07372200 |
| C | -3.80700700 | -0.55377300 | 0.35403800 |
| H | -4.41312400 | 0.33058000 | 0.14382200 |
| H | -4.44409600 | -1.31627500 | 0.82427700 |
| C | -0.24683500 | 2.36158300 | 0.86715500 |
| H | -1.07173900 | 3.03129000 | 1.11147300 |
| H | 0.17218600 | 1.92973700 | 1.78378700 |
| H | 0.56024400 | 2.92827000 | 0.38832100 |
| F | -2.84812600 | 2.17318800 | -0.27127900 |

**Catalyzed TS_F_endo-cis (R1=F)**

| | | | |
|---|---|---|---|
| C | -1.92691200 | -1.92459600 | -0.21884300 |
| C | -1.66565900 | -1.45569700 | 1.10157500 |
| C | -2.66378500 | -0.59448800 | 1.47304900 |
| C | -1.82009900 | 1.29165000 | -0.74636300 |
| C | -2.20841900 | 0.37828700 | -1.71780500 |
| C | -3.06375100 | -1.29061800 | -0.72869600 |
| H | -1.28803600 | -2.60916600 | -0.76635700 |
| H | -0.78417900 | -1.69989900 | 1.68282100 |
| H | -2.72714800 | -0.05982900 | 2.41413900 |
| C | -0.55725800 | 1.28954900 | -0.11431000 |
| H | -1.42611500 | -0.15134300 | -2.24446400 |
| H | -3.10945700 | 0.59776600 | -2.28119100 |
| H | -3.61405000 | -1.66520800 | -1.58594600 |
| O | 0.27060900 | 0.38266600 | -0.49158700 |
| Al | 1.97410500 | -0.17703300 | -0.06251500 |
| Cl | 3.27880400 | 1.43515800 | -0.58755600 |

| | | | |
|---|---|---|---|
| Cl | 2.18424500 | -1.95118400 | -1.24202500 |
| Cl | 1.91659200 | -0.58278800 | 2.05604400 |
| C | -3.74174900 | -0.58526300 | 0.43286300 |
| H | -4.14919200 | 0.40635500 | 0.21916300 |
| H | -4.58565400 | -1.20508100 | 0.77777900 |
| C | -0.17189300 | 2.32052000 | 0.90065400 |
| H | -1.00779200 | 2.97176600 | 1.15653400 |
| H | 0.21229400 | 1.82620400 | 1.79934700 |
| H | 0.65066700 | 2.92340200 | 0.49535200 |
| F | -2.72625700 | 2.22321200 | -0.34049200 |

**Catalyzed Reactant_F_exo-cis (R1=F)**

| | | | |
|---|---|---|---|
| C | 4.19632900 | -0.73221100 | 0.18110600 |
| C | 3.43656700 | -0.18961100 | 1.30580900 |
| C | 2.27060800 | -0.87088000 | 1.43213000 |
| C | 1.75208000 | 1.28013600 | -1.09052900 |
| C | 2.00103800 | 0.51242200 | -2.15989200 |
| C | 3.49593200 | -1.74614000 | -0.38243600 |
| H | 5.16752900 | -0.36719800 | -0.13646000 |
| H | 3.77543500 | 0.62528900 | 1.93652300 |
| H | 1.50659800 | -0.73229100 | 2.18836900 |
| C | 0.53403300 | 1.21928900 | -0.28569400 |
| H | 2.92588700 | 0.61985800 | -2.71312400 |
| H | 1.26096600 | -0.20313100 | -2.49496700 |
| H | 3.80367000 | -2.35994600 | -1.22129700 |
| O | -0.32947800 | 0.36284600 | -0.61196000 |
| Al | -2.01734000 | -0.21238500 | 0.00668500 |
| Cl | -1.66604600 | -0.66276600 | 2.07550300 |
| Cl | -2.37209500 | -1.91455100 | -1.21798800 |
| Cl | -3.28034800 | 1.47604900 | -0.32543400 |
| C | 2.21770800 | -1.95094500 | 0.38687900 |
| H | 1.31805400 | -1.90058300 | -0.24241100 |
| H | 2.18865600 | -2.94733300 | 0.85525500 |
| C | 0.29869300 | 2.20328000 | 0.81221400 |
| H | 1.20463300 | 2.74528900 | 1.07801600 |
| H | -0.46306500 | 2.91579600 | 0.46450400 |
| H | -0.12163400 | 1.69247900 | 1.68367200 |
| F | 2.65702400 | 2.18815900 | -0.67252100 |

**Catalyzed Product_F_exo-cis (R1=F)**

| | | | |
|---|---|---|---|
| C | 4.20795000 | -0.74866600 | 0.06004100 |
| C | 3.62933800 | -0.15851400 | 1.11739500 |
| C | 2.14425700 | -0.23586600 | 0.89170800 |
| C | 1.93891600 | 0.79379900 | -0.39927100 |
| C | 2.42987800 | -0.05778300 | -1.58101400 |
| C | 3.11298300 | -1.27357300 | -0.85991900 |
| H | 5.27006400 | -0.79039400 | -0.16038800 |
| H | 4.10556800 | 0.40085600 | 1.91372300 |
| H | 1.48376900 | -0.03540400 | 1.73583500 |
| C | 0.51645700 | 1.16484000 | -0.23364500 |
| H | 3.10824200 | 0.53976200 | -2.19369100 |
| H | 1.59865900 | -0.40388200 | -2.20139500 |
| H | 3.40621900 | -2.07050200 | -1.54590800 |

| | | | |
|---|---|---|---|
| O | -0.34061200 | 0.34811000 | -0.64518700 |
| Al | -2.02685200 | -0.22171600 | -0.01913500 |
| Cl | -1.59764200 | -0.64112400 | 2.04726300 |
| Cl | -2.38442800 | -1.94926900 | -1.19809900 |
| Cl | -3.33696400 | 1.43171700 | -0.31465600 |
| C | 2.00816600 | -1.59331500 | 0.17168100 |
| H | 1.02805800 | -1.78187800 | -0.27225500 |
| H | 2.26696000 | -2.41599900 | 0.84141800 |
| C | 0.15178200 | 2.35068900 | 0.59898700 |
| H | 1.02031000 | 2.96270100 | 0.83358100 |
| H | -0.60803400 | 2.94257300 | 0.07726100 |
| H | -0.31901000 | 1.98592700 | 1.52191500 |
| F | 2.73012700 | 1.93195700 | -0.29543100 |

**Catalyzed TS_F_exo-cis (R1=F)**

| | | | |
|---|---|---|---|
| C | 4.01559200 | -0.65701100 | 0.08446300 |
| C | 3.41420000 | -0.22754000 | 1.29887300 |
| C | 2.14182400 | -0.74244400 | 1.37838200 |
| C | 1.73830300 | 1.12517100 | -0.89616100 |
| C | 2.17321300 | 0.17459000 | -1.80751700 |
| C | 3.08390500 | -1.37788900 | -0.66957900 |
| H | 5.01673400 | -0.39390600 | -0.24030100 |
| H | 3.87983700 | 0.43178200 | 2.02238000 |
| H | 1.42828600 | -0.59297300 | 2.18068200 |
| C | 0.46234700 | 1.19660600 | -0.28765600 |
| H | 3.04758500 | 0.40920300 | -2.40307700 |
| H | 1.42343300 | -0.45520000 | -2.27211100 |
| H | 3.35350400 | -2.00769800 | -1.51140400 |
| O | -0.42576200 | 0.34183900 | -0.65192700 |
| Al | -2.07709100 | -0.20106300 | -0.02842700 |
| Cl | -1.70008200 | -0.65346300 | 2.05137700 |
| Cl | -2.46978400 | -1.94150300 | -1.20302600 |
| Cl | -3.42437900 | 1.43392800 | -0.31962400 |
| C | 1.91990300 | -1.69401600 | 0.24816900 |
| H | 0.92329700 | -1.65274000 | -0.19645800 |
| H | 2.04488400 | -2.72346800 | 0.62433600 |
| C | 0.12307600 | 2.29437000 | 0.67516900 |
| H | 0.99163000 | 2.90387300 | 0.92248600 |
| H | -0.65448000 | 2.92587900 | 0.22780200 |
| H | -0.30651600 | 1.86322000 | 1.58562500 |
| F | 2.65867600 | 2.03974900 | -0.49869000 |

**Uncatalyzed Reactant_F_endo-cis (R2=F)**

| | | | |
|---|---|---|---|
| C | 0.23311400 | 1.70137200 | 0.29536100 |
| C | -0.75777100 | 1.24603100 | -0.47534400 |
| C | -1.83218600 | 0.43145900 | 0.13585500 |
| C | -2.96965000 | 0.00188300 | -0.77394600 |
| O | -1.81877000 | 0.12292900 | 1.32109900 |
| H | -3.71402000 | 0.80767500 | -0.82008500 |
| H | -2.63090800 | -0.19368400 | -1.79596400 |
| H | -3.45232900 | -0.88460100 | -0.35989100 |
| C | 1.98504300 | -0.75440900 | 0.63198600 |
| C | 0.96631800 | -1.48924200 | 1.12923300 |

| | | | |
|---|---|---|---|
| C | 0.21802700 | -2.08821200 | 0.02115000 |
| C | 0.77538400 | -1.71243000 | -1.15052400 |
| C | 1.97609300 | -0.84764200 | -0.87081300 |
| H | 2.72275800 | -0.19762300 | 1.19732400 |
| H | 0.71445100 | -1.61842500 | 2.17518700 |
| H | -0.65170100 | -2.72311900 | 0.14611700 |
| H | 0.45526300 | -2.00059400 | -2.14482400 |
| H | 2.89920700 | -1.31351000 | -1.24781600 |
| H | 1.91997300 | 0.13773100 | -1.35086500 |
| H | -0.75293700 | 1.43328500 | -1.54390300 |
| H | 0.28459300 | 1.56762200 | 1.36796300 |
| F | 1.27550800 | 2.37530200 | -0.21319800 |

**Uncatalyzed Product_F_endo-cis (R2=F)**

| | | | |
|---|---|---|---|
| C | 0.63427400 | 1.06785800 | 0.36216500 |
| C | -0.37989700 | 0.46489600 | -0.64196000 |
| C | -1.70131000 | 0.19710400 | 0.05289500 |
| C | -2.96633000 | 0.02279500 | -0.76694100 |
| O | -1.72543900 | 0.02028300 | 1.26027000 |
| H | -3.76304100 | 0.63515600 | -0.33478600 |
| H | -2.84040300 | 0.27689400 | -1.82178900 |
| H | -3.28907300 | -1.02117600 | -0.68827300 |
| C | 1.61297700 | -0.11011200 | 0.60850800 |
| C | 0.86031000 | -1.31926700 | 1.15028800 |
| C | 0.16630000 | -1.87029000 | 0.14629700 |
| C | 0.33294000 | -0.94571300 | -1.04760000 |
| C | 1.81402100 | -0.54832800 | -0.86533600 |
| H | 2.49601700 | 0.19657100 | 1.17220900 |
| H | 0.85173200 | -1.61872000 | 2.19138100 |
| H | -0.53102900 | -2.69801300 | 0.20964400 |
| H | 0.02093200 | -1.32130400 | -2.02347100 |
| H | 2.48955200 | -1.40112900 | -0.96532000 |
| H | 2.13833400 | 0.26999900 | -1.51301900 |
| H | -0.49001200 | 1.10215000 | -1.52513800 |
| H | 0.15612000 | 1.45376000 | 1.26317000 |
| F | 1.36295100 | 2.12339300 | -0.21394200 |

**Uncatalyzed TS_F_endo-cis (R2=F)**

| | | | |
|---|---|---|---|
| C | 0.50221800 | 1.36165600 | 0.35007000 |
| C | -0.57826600 | 1.04276800 | -0.48714000 |
| C | -1.68265700 | 0.35409800 | 0.11164500 |
| C | -2.91721700 | 0.04141700 | -0.71980700 |
| O | -1.62526000 | -0.00226300 | 1.30487200 |
| H | -3.74855600 | 0.66773200 | -0.37730200 |
| H | -2.76814200 | 0.21833600 | -1.78828800 |
| H | -3.21271400 | -0.99896800 | -0.55859100 |
| C | 1.60429300 | -0.21018300 | 0.60766000 |
| C | 0.79979900 | -1.23980100 | 1.14975100 |
| C | 0.20633800 | -1.97281700 | 0.09535700 |
| C | 0.66549400 | -1.48875700 | -1.10607000 |
| C | 1.82836900 | -0.57687800 | -0.85540200 |
| H | 2.39987600 | 0.24730800 | 1.19023100 |
| H | 0.60429400 | -1.39794000 | 2.20202300 |

| | | | |
|---|---|---|---|
| H | -0.55889600 | -2.72847100 | 0.22547600 |
| H | 0.35708300 | -1.82663600 | -2.08845600 |
| H | 2.76172600 | -1.15807400 | -0.92821200 |
| H | 1.92294800 | 0.27307900 | -1.53237400 |
| H | -0.56288300 | 1.32250300 | -1.53353800 |
| H | 0.30693200 | 1.56184200 | 1.39950300 |
| F | 1.43668700 | 2.21870800 | -0.16953700 |

**Uncatalyzed Reactant_F_exo-cis (R2=F)**

| | | | |
|---|---|---|---|
| C | -2.41954800 | -0.34273000 | -0.29640200 |
| C | -1.63554200 | -1.31670600 | -1.05628000 |
| C | -0.73713100 | -1.90513000 | -0.23388500 |
| C | 0.92251700 | 0.85045600 | -0.61168800 |
| C | 0.08264300 | 1.60246600 | 0.10580200 |
| C | -1.99835400 | -0.33758200 | 0.98843200 |
| H | -3.19827300 | 0.28255800 | -0.71825000 |
| H | -1.76747300 | -1.52014700 | -2.11365400 |
| H | -0.02420100 | -2.67759600 | -0.49715300 |
| C | 2.03188200 | 0.12816900 | 0.04556500 |
| H | 0.15020700 | 1.74465100 | 1.17735300 |
| H | -2.38900700 | 0.27141300 | 1.79507300 |
| O | 2.12079100 | 0.02080500 | 1.26447600 |
| C | -0.90556000 | -1.35677900 | 1.15594400 |
| H | 0.02207600 | -0.93501100 | 1.56407000 |
| H | -1.20781300 | -2.15063100 | 1.85662200 |
| C | 3.07320400 | -0.47308100 | -0.87865700 |
| H | 3.56491300 | 0.31727400 | -1.45808500 |
| H | 3.81753600 | -1.01455100 | -0.29415900 |
| H | 2.59954600 | -1.15010200 | -1.59864100 |
| H | 0.80285900 | 0.78623900 | -1.68764600 |
| F | -0.91005800 | 2.29250700 | -0.46600600 |

**Uncatalyzed Product_F_exo-cis (R2=F)**

| | | | |
|---|---|---|---|
| C | -2.35330300 | -0.26965000 | -0.38480000 |
| C | -1.60016800 | -1.13717200 | -1.07381100 |
| C | -0.28435300 | -1.28816200 | -0.32811400 |
| C | 0.49034100 | 0.10013600 | -0.49603300 |
| C | -0.41028500 | 1.06615100 | 0.32893200 |
| C | -1.55945900 | 0.15570600 | 0.84297500 |
| H | -3.30844700 | 0.14919000 | -0.67769300 |
| H | -1.81344800 | -1.57122600 | -2.04443200 |
| H | 0.31828800 | -2.16476500 | -0.57514400 |
| C | 1.89832300 | -0.05123300 | 0.07036700 |
| H | 0.15248400 | 1.50567400 | 1.15680500 |
| H | -2.13076000 | 0.59548400 | 1.66225300 |
| O | 2.12180200 | 0.06276600 | 1.26438300 |
| C | -0.76665100 | -1.13891300 | 1.13486800 |
| H | 0.04744400 | -1.00434500 | 1.85077900 |
| H | -1.41374700 | -1.96098900 | 1.44866400 |
| C | 3.01160000 | -0.40752400 | -0.89744700 |
| H | 3.37090400 | 0.51008200 | -1.38028800 |
| H | 3.84141300 | -0.85992000 | -0.35229000 |
| H | 2.66602600 | -1.07560800 | -1.69229400 |

| | | | |
|---|---|---|---|
| H | 0.52571600 | 0.40517200 | -1.54521100 |
| F | -0.91221600 | 2.11396100 | -0.44339600 |

**Uncatalyzed TS_F_exo-cis (R2=F)**

| | | | |
|---|---|---|---|
| C | -2.35247400 | -0.21528900 | -0.34097800 |
| C | -1.65350500 | -1.20714500 | -1.05105100 |
| C | -0.59220800 | -1.65237100 | -0.27449100 |
| C | 0.68180100 | 0.57281400 | -0.52240900 |
| C | -0.23942400 | 1.30704500 | 0.23287000 |
| C | -1.67736200 | 0.04165000 | 0.86986200 |
| H | -3.17776100 | 0.36841600 | -0.73068200 |
| H | -1.85803100 | -1.50973400 | -2.07184100 |
| H | 0.10681800 | -2.43349500 | -0.54978900 |
| C | 1.91635300 | 0.08437400 | 0.08076800 |
| H | 0.05197500 | 1.64655600 | 1.22340700 |
| H | -2.13349700 | 0.60436000 | 1.67903900 |
| O | 2.09607700 | 0.05907700 | 1.30202400 |
| C | -0.77886900 | -1.14955400 | 1.12518700 |
| H | 0.14251900 | -0.94080600 | 1.67317000 |
| H | -1.34949400 | -1.90217200 | 1.69382000 |
| C | 3.00970600 | -0.38116600 | -0.87069600 |
| H | 3.47003800 | 0.48628400 | -1.35885600 |
| H | 3.77742300 | -0.91507600 | -0.30879600 |
| H | 2.60882400 | -1.02265400 | -1.66222700 |
| H | 0.58832600 | 0.58282000 | -1.60192400 |
| F | -0.98665100 | 2.24008200 | -0.43287600 |