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Hyperconjugative Aromaticity and Antiaromaticity Control the Reactivities and π-Facial Stereoselectivities of 5-Substituted Cyclopentadiene Diels–Alder Cycloadditions

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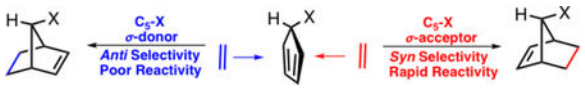
Abstract

The reactivities and π-facial stereoselectivities of Diels–Alder reactions of 5-substituted cyclopentadienes were studied using density functional theory. Burnell and co-workers previously showed that the π-facial selectivities result from the energies required to distort the reactants into the transition state geometries. We have discovered the origins of these distortions. C_5–X σ-donors predistort the cyclopentadiene into an envelope conformation that maximizes the stabilizing hyperconjugative interaction between the C5–X σ-bond and the diene π-system. This envelope conformation geometrically resembles the anti transition state. To minimize the destabilizing effect of negative hyperconjugation, C_5–X σ-acceptors predistort in the opposite direction toward an envelope geometry that resembles the syn transition state. We now show how hyperconjugative effects of the C_5–X substituent influence the stereoselectivities and have developed a unified model rationalizing the stereoselectivities and reactivities of 5-substituted cyclopentadiene Diels–Alder reactions.

Graphical Abstract



INTRODUCTION

Cyclopentadiene is generally more reactive than other cyclic dienes in the Diels–Alder reaction.[1] Substitution at the 5-position of the cyclopentadiene can alter the reactivity, and perhaps surprisingly, in the normal-electron demand Diels– Alder reaction, electron-withdrawing substituents increase the reactivity! We have shown how this arises by destabilization of the cyclopentadiene.[2] When the substituent at the 5-position is a σ-

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Notes

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ASSOCIATED CONTENT

Supporting Information

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Cartesian coordinates and energies of all optimized structures and transition structures (PDF)

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acceptor, negative hyperconjugation results in the cyclo-pentadiene having pseudo 4π electron antiaromatic character and accelerated reactivity.

5-Substituted cyclopentadienes (C_5–X) are facially asymmetric and, depending on the substituent, will react on either the *syn* or *anti* face of the cyclopentadiene with regard to the C_5–X substituent. As shown in Scheme 1, the π-facial stereoselectivity of the cycloaddition is considered *syn* when the dienophile (Y = Z) reacts on the same face of the C_5–X substituent, whereas addition to the face opposite of the C_5–X substituent is considered *anti*. Winstein and Woodward reported the first contrasteric (*syn*) Diels–Alder reaction of 5-acetoxycyclopentadiene (C_5–OAc) with ethylene (Scheme 2) during their seminal studies on 7-norbornenyl cations.[3]

Similar constrasteric cycloadditions have since been reported. Scheme 3 shows the π-facial selectivity in the Diels–Alder reactions of C_5–F, C_5–Cl, and C_5–Br with dimethyl acetylenedicarboxylate (DMAD).[4,5] C_5–F reacts with *syn* π-facial stereoselectivity; C_5–Cl forms a mixture of *syn* and *anti* adducts; and C_5–Br reacts with *anti* π-facial stereoselectivity.

Control of π-facial selectivity has been used in the synthesis of aconitine alkaloids. Scheme 4 shows how the reaction between 5-methoxycyclopentadiene 1 and cyclopropene 2 proceeds predominantly with *syn* selectivity to yield the desired intermediate 3a in the David Gin synthesis of neofinaconitine.[6] The late David Gin visited our group in early 2011, and he brought the subject of π-facial stereoselectivity in cyclo-pentadienes to our attention. We have worked on this problem since then and now offer a comprehensive explanation for the reactivities and stereoselectivities of Diels–Alder reactions involving 5-substituted cyclopentadienes.

Many explanations have been offered, and it seems that the origin of π-facial stereoselectivity in 5-substituted cyclo-pentadiene cycloadditions remains unsettled.[7] Cieplak proposed that the stereoselectivity of a number of nucleophilic reactions can be explained through the hyperconjugative stabilization of an incipient σ^*-bond by an antiperiplanar donor σ-bond in the transition state.[8] Fallis and Macaulay applied the Cieplak effect to Diels–Alder reactions of 5-substituted cyclopentadienes in order to rationalize the *syn* and *anti* π-facial stereoselectivity.[9] They proposed that the cycloaddition occurs *anti* to the C_5–X bond that is the better σ-donor. Scheme 5 shows the proposed $\sigma_{C5\text{-}X}$–σ^* hyperconjugative interaction of the antiperiplanar C_5–X bond with the incipient bonds. *Anti* stereoselectivity is predicted when the C_5–X substituent is a stronger σ-donor than the hydrogen atom of the C_5–H bond, while a C_5–X substituent that is a worse σ-donor is predicted to give *syn* selectivity. This explanation does not, however, explain why *anti* $C_{5\text{-}X}$ σ-donors slow down, instead of accelerate, reactivity.

Inagaki, Fujimoto, and Fukui explained the π-facial stereoselectivity of 5-substituted cyclopentadienes with orbital mixing.[10] They proposed that orbital mixing between the nonbonding orbital (n) of the C_5–X substituent, the diene π-HOMO, and the σ-orbitals of the diene carbon framework determines the π-facial selectivity. When the π-HOMO lies higher in energy than the nonbonding orbital of the C_5–X substituent, the mixing results in

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an increase in the amplitude of the C_1 and C_4 p-orbitals on the *syn* face of the 5-substituted cyclopentadiene (Scheme 6). Conversely, when the π-HOMO lies lower in energy than the nonbonding orbital of the C_5–X substituent, the mixing increases the amplitude of the C_1 and C_4 p-orbitals on the *anti* face of the 5-substituted cyclo-pentadiene. The dienophile then reacts on the face of the cyclopentadiene with the largest p-orbital amplitude at the C_1 and C_4 positions.

Burnell and co-workers studied computationally the π-facial selectivities of C_5–X cyclopentadienes.[11,12] They amassed extensive computational evidence to show that the π-facial stereoselectivity is controlled by the energy required to deform the diene into the transition state geometry. They associated the deformation with the change of the C_1–C_5–X angle between the ground and transition state geometries.

We have recently reported cyclopentadienes as potential bioorthogonal reactants[13] and showed how the C_5–X substituent has a very large effect on the Diels–Alder reactivity.[2] Understanding the reactivity and stereoselectivity trends in 5-substituted cyclopentadienes will be of further value in the development of new bioorthogonal cyclo-pentadienes. To better understand how the reactivity and the *syn* and *anti* π-facial stereoselectivity trends relate to the properties of the C_5–X substituent, we have investigated a wide scope of C_5–X cyclopentadienes (Scheme 7) with the distortion/interaction–activation strain model.[14]

COMPUTATIONAL METHODS

All calculations were performed with Gaussian 09.[15] Geometry optimizations and frequency calculations were calculated with the M06–2X[16] functional and the 6–31G(d) basis set. The M06–2X functional has been found to accurately reproduce experimental trends in the reactivity and selectivity of Diels–Alder reactions.[17] Normal mode analysis of each structure verified that each stationary point is either a first-order saddle point or an energy minimum. Single-point energies were computed using the 6–311++G(d,p) basis set. The distortion/interaction model was applied to the transition state structures to disect the activation energies into the distortion and interaction energy components. The procedure to carry out this analysis procedure has been reviewed recently.[14]

RESULTS AND DISCUSSION

The *anti* and *syn* transition structures and the activation free energies ($\Delta G^{\ddagger}$) for the Diels–Alder reactions of the 5-substituted cyclopentadienes with ethylene are shown in Figure 1. *Syn* π-facial stereoselectivity is favored when the C_5 substituent is F, OH, NH_2, or Cl. Poor π-facial selectivity is predicted when the substituent is Br, SH, or Me. *Anti* π-facial stereoselectivity is favored when the C_5–X substituent is SiH_3. The activation free energies of the *syn* and *anti* transition states range from 24 to 38 and from 29 to 33 kcal/mol, respectively. There is a correlation between the electronegativity of the C_5– X substituent and the activation barriers, as observed earlier by Burnell.[11,12] Electron-withdrawing substituents accelerate the reactivity, and electron-donating substituents decrease the reactivity, with a range in activation energies of 10 kcal/mol.

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Extensive computational and experimental studies by the Schleyer group on the aromaticity of cyclic π-systems with one saturated linkage (cyclopropene, cyclopentadiene, and cyclo-heptatriene) show that the substituents at the saturated linkage contribute to the π-electron count as pseudo π-donors or π-acceptors via hyperconjugative interactions with the π-system.[18] The effect of the C_5–X substituent on the stability on the cyclopentadiene was estimated here with the isodesmic equation shown in Figure 2. This isodesmic equation measures the aromatic stabilization enthalpy (H_{ASE}) of the cyclo-pentadiene relative to nonconjugated cyclopentadienes for which cyclic electron delocalization of the π-bonds is not possible. A positive reaction enthalpy in the isodesmic equation indicates that cyclic delocalization of the π-electrons via hyperconjugation is stabilizing. The weak hyperconjugative donors, C_5–H and C_5–Me, are stabilized by 2–3 kcal/mol, which arises mostly from the favorable π-conjugation. Silyl substitution further stabilizes the cyclopentadiene to 7.4 kcal/mol, whereas fluorine substitution destabilizes the cyclo-pentadiene to −3.4 kcal/mol in the isodesmic equation. When the C_5–X substituent is a σ-acceptor, the hyper-conjugative π–$\sigma^*_{C5\text{-}X}$ interaction destabilizes the cyclopenta-diene by giving it pseudo 4π electron antiaromatic character. When the C_5–X substituent is a σ-donor, positive hyperconjugation stabilizes the cyclopentadiene by giving it pseudo 6π electron aromatic character. The aromatic stabilization energies influence the activation and reaction energies.[2]

Figure 3a shows a plot of ΔH of reaction for the reactions of the C_5–X cyclopentadienes vs the aromatic stabilization energy (ΔH_{ASE}) of the diene. The linear correlation suggests that the exothermicities of these cycloadditions are related to the stabilities of the C_5–X cyclopentadienes. The norbornene π-bond donates into the $\sigma^*_{C5\text{-}X}$ bond of substituent *anti* to the norbornene π-bond.[20] The *syn* adducts are more stable than the *anti* adduct with the exception of C_5–SiH_3. The *syn* preference becomes increasingly favored as the C_5–X substituent becomes a stronger σ-acceptor, a result of a more stabilizing π–$\sigma^*_{C5\text{-}X}$ interaction.

Figure 3b shows a plot of the $\Delta H^{\ddagger}$ for the C_5–X cycloadditions with ethylene against the diene aromatic stabilization energies. Here the correlations are quite different for the *syn* and *anti* reactions with slopes of 1.1 and 0.33, respectively. The *syn* reactions are clearly favored for electron-withdrawing substituents, while the silyl-substituted cyclo-pentadiene reacts with a strong preference for the formation of the *anti* adduct.

We applied the distortion/interaction-activation strain analysis[14] in order to understand the origins of the *syn* and *anti* π-facial stereoselectivity in Diels–Alder reactions of 5-substituted cyclopentadienes. This analysis dissects the electronic activation energies in the distortion and interaction energies of the reaction. The distortion energy (ΔE_d) is the energy required to deform the reactants into the corresponding transition structures, and the interaction energy (ΔE_i) comprises of the interactions that occur between the diene and dienophile as they approach each other and adopt the geometries of the transition state. Figure 4 shows a plot of the stereoselectivity measured as the difference in the *anti* and *syn* electronic activation energies ($\Delta E^{\ddagger}(syn) - \Delta E^{\ddagger}(anti)$) with the difference in the distortion ($\Delta E^{\ddagger}(syn) - \Delta E^{\ddagger}(anti)$) required to achieve the *anti* and *syn* transition states.

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The excellent linear correlation suggests that the π-facial selectivity results from differences in the energies required to distort the reactants into the *syn* and *anti* geometries, as originally proposed by Burnell.[11,12] We also performed the distortion/interaction-activation strain analysis along the intrinsic reaction coordinate defined by the length of the forming C–C bonds. These plots are provided in the Supporting Information. When the forming bond lengths of the stereoisomers in the transition state are similar, as observed in these reactions, performing the distortion/interaction-activation strain analysis at the TS and along the IRC leads to the same conclusion, that the *syn* and *anti* stereoselectivity is distortion controlled.

As shown in Figure 5, the cyclopentadiene (C_5–H) ground state is planar. The electronic nature of the C_5–X substituent predistorts the cyclopentadiene into an envelope geometry. The angle θ_{env} is defined as the angle at which the C_5 atom of the cyclopentadiene puckers above or below the plane of the cyclopentadiene. The value of θ_{env} is negative when the C_5 atom extends below the plane and positive when it extends above the plane of the cyclopentadiene. When C_5–X is a σ-donor, the C_5 atom distorts above the plane of the cyclopentadiene. This distortion aligns the C_5–X bond with the cyclopentadiene π-system to maximize the stabilizing hyperconjugation interaction that induces hyperconjugative aromaticity.[2,18] The C_5 atom in C_5–SiH_3 is distorted 3° above the plane of the cyclopentadiene. When C_5–X is a σ-acceptor, the C_5 atom distorts below the plane of the cyclopentadiene to minimize the overlap of the diene π-system with the $\sigma^*_{C5\text{-}X}$ and reduce the destabilizing effect of the hyperconjugative aromaticity. For σ-acceptors, C_5–F, C_5–OH, and C_5–Cl, the C_5 atom is predistorted 2 to 4° below the plane of the cyclopentadiene ring. The poor σ-donors/acceptors, C_5–Br, C_5–CH_3, C_5–SH, and C_5–NH_2, are nearly planar with the C_5 atom predistorted less than 2° relative to the plane of the cyclopentadiene.

In the *syn* and *anti* transition structures θ_{env} ranges from −18° to −19° and from 16° to 19°, respectively. Figure 6 shows θ_{env} for the *syn* and *anti* Diels–Alder reactions of C_5–F, C_5–Br, and C_5–SiH_3 with ethylene. For the *syn* and *anti* reactions of C_5–F, the *syn* reactions require a −14° change about θ_{env} and a change of 21° to achieve the *anti* transitiond state geometry. To achieve the *syn* and *anti* transition state geometries, θ_{env} in C_5–Br distorts 17° and −18°, respectively. For C_5–SiH_3, the change about θ_{env} to achieve the *syn* and *anti* transition state geometries is 16° and −21° from the ground state geometry, respectively.

The stereoselectivity of C_5–X cyclopentadiene Diels–Alder reactions is determined by the distortion energies, which are related to how the C_5–X cyclopentadiene is predistorted in the ground state. Figure 7a shows a strong linear correlation when the difference in the diene distortion energies of the *syn* and *anti* transition states is plotted against the difference in the cyclopentadiene envelope angle, θ_{env}, required to achieve the *syn* and *anti* transition state geometries. The transition state that requires less of a change in θ_{env} is the stereoselectively favored reaction. When the substituent is a σ-donor, the ground state is predistorted into an envelope geometry that resembles and favors the *anti* transition state, whereas σ-acceptors predistort the cyclopentadiene ground state into an envelope geometry that resembles and favors the *syn* transition state.

We have also considered the contribution of the bending of the C_5–X bond to the distortion energy as proposed by Burnell.[12] The C_5–X ($\theta_{C5\text{-}X}$) bond angle is measured relative to the

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plane of the cyclopentadiene defined by the $C_1C_4C_5$ atoms. Figure 7b shows a plot of the differences in the diene distortion energies against the difference in the bending of the C_5–X ($\theta_{C5\text{-}X}$) bond from the plane of the cyclopentadiene between the *syn* and *anti* transition state. There is a strong linear correlation between the diene distortion and the bending of the C_5–X bond from the plane of the diene with the exception of C_5–SH, which is an outlier in the distribution.

The *x*-intercept shows that for diene distortion of the *syn* and *anti* transition states to be equal ($\Delta\Delta E_{\text{d-diene}}^{\ddagger} = 0$) an additional 5° distortion of the C_5–X bond toward the *anti* transition state is required about the C_5–X bond. Figure 7a shows the plot of the difference in the diene distortion energies against the difference in θ_{env} between the *syn* and *anti* transition states. From the *x*-intercept there is only a 1° difference between the envelope geometry of the *syn* and *anti* transition states when the distortion energy of the *syn* and *anti* transition states is equal ($\Delta\Delta E_{\text{d-diene}}^{\ddagger} = 0$).

The diffculty of distorting a bond is related to the strength of the bending force constants. Table 1 summarizes the computed force constants associated with the bending of the C_5–X bond and the C_5 carbon relative to the plane of the cyclopentadiene in the C_5–X cyclopentadiene ground states. The force constants for the bending of the C_5–X bonds range from 0.032 to 0.097 millidynes/Å and are significantly lower than the out-of-plane bending force constants associated with the out-of-plane bending of the C_5 carbon atom, which ranges from 0.56 to 1.20 millidynes/Å. The bending of the C_5–X alkyl bonds contributes less to the diene distortion energies of the *syn* and *anti* transition states than the distortion associated with the bending of the C_5 carbon from the plane of the cyclopentadiene and as a result has less influence on the stereoselectivity.

The strength of the hyperconjugation interaction between the π-system and the C_5–X substituent determines the extent of the predistortion. The electronegativity of the C_5–X substituent correlates with the envelope angle θ_{env} in the ground state geometries of the C_5–X cyclopentadienes (Figure 8a) and is a useful way to predict the π-facial stereoselectivity in Diels–Alder reactions of C_5–X cyclopentadiene with ethylene (Figure 8b). As the C_5–X substituent becomes a stronger σ-acceptor it predistorts increasingly toward the envelope conformation of the *syn* transition state and becomes increasingly selective for the *syn* reaction.

The influence of the dienophile on the π-facial stereoselectivity was investigated by calculating the *syn* and *anti* Diels–Alder stereoselectivities for the concerted reactions with maleic anhydride (MA), tetracyanoethylene (TCNE), 1,2,4-triazoline-3,5-dione (TAD), and acetylene. Figure 9 summa-rizes the *syn* and *anti* π-facial stereoselectivity of the C_5–X cyclopentadienes with these dienophiles. For C_5–Br, C_5–SH, and C_5–Me, which are poor σ donor/acceptors, the π-facial stereoselectivity can be influenced by interactions between the C_5–X substituent and the dienophile. Steric interactions destabilize the *syn* transition state when TCNE is the dienophile, and *anti* π-facial selectivity becomes favored for C_5–Cl, C_5–Br, C_5–SH, and C_5–Me. Lone pair repulsions between the nitrogens of TAD with the halogen lone pair on the Cl and Br destabilize the *syn* transition states and result in poor stereoselectivity for the Diels–Alder reaction of C_5–Cl and *anti* stereoselectivity in the

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reaction of C–Br with TAD. The predistortion of the C–F, C – ground 5 OH, and C_{52} states toward the *syn* transition state geometry is significant enough that the destabilizing interactions between the C_5–X substituent and the dienophile in the *syn* transition state do not overrule the *syn* selectivity of these dienes. The Diels–Alder reaction of C_5–SiH_3 strongly favors the *anti* cycloaddition with all of the studied dienophiles.

CONCLUSION

The π-facial selectivity of C_5–X cyclopentadienes is distortion controlled. When the C_5–X substituent is a strong σ-acceptor (X = F, OH, and NH_2) the cyclopentadiene adopts an envelope geometry that minimizes the destabilizing π–$\sigma^*_{C5\text{-}X}$ hyperconjugative interaction that provides the cyclopentadiene with antiaromatic character. This distortion causes the cyclopentadiene to resemble the envelope geometry of the *syn* transition and lessens the distortion energy required of the *syn* cycloaddition. Conversely, when the C_5–X substituent is a σ-donor (X = SiH_3) the C_5 atom distorts to maximize the effect of the stabilizing hyperconjugative interaction that provides the cyclopentadiene with aromatic character. This distortion of the ground state causes the cyclopentadiene to resemble the envelope geometry of the *anti* transition state, and *anti* π-facial selectivity is favored. When the C_5–X substituent is a poor σ-acceptor/donor (X = Cl, Br, SH, and Me), the π-facial selectivity is sensitive to the nature of the dienophile.

Supplementary Material

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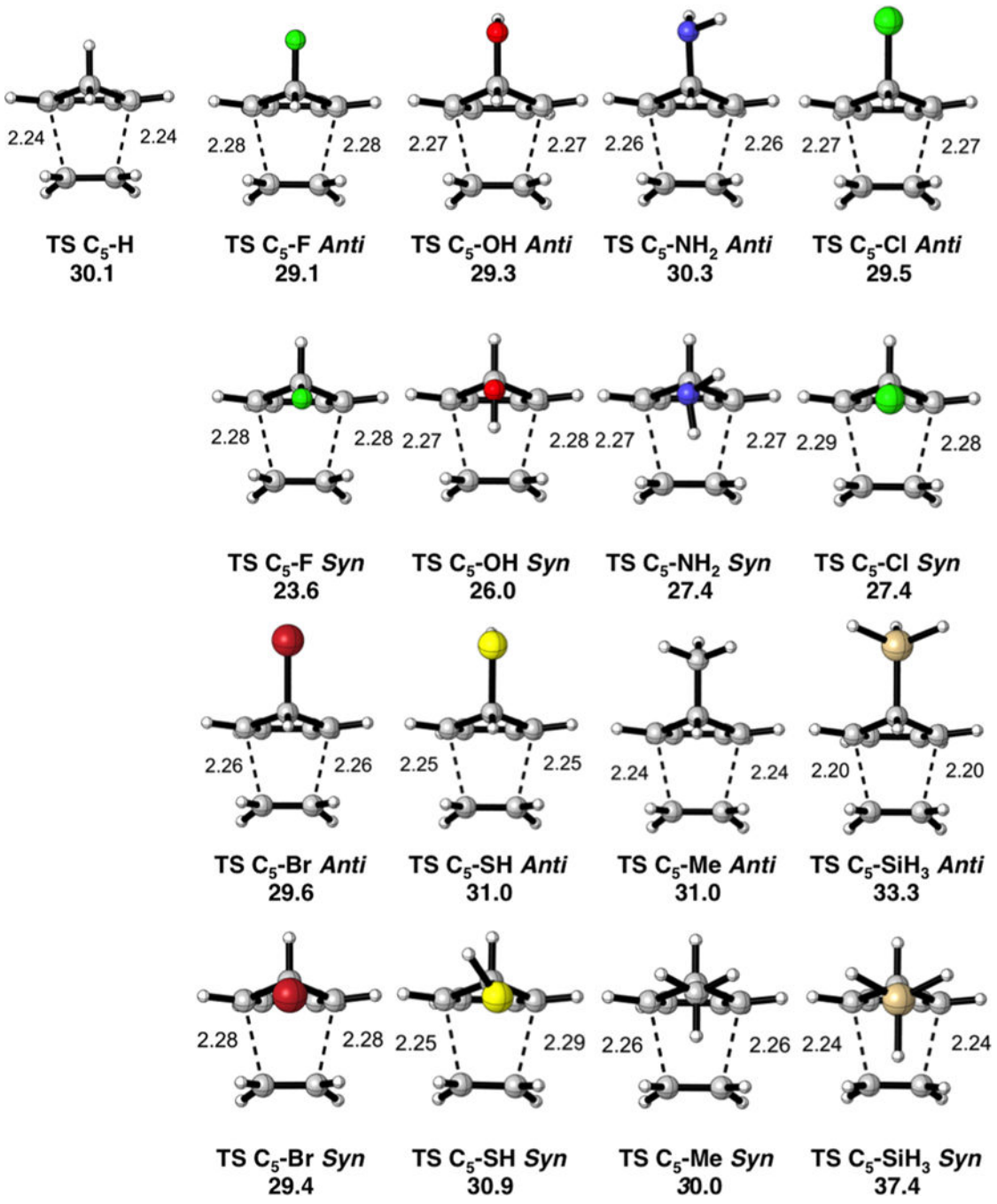

Figure 1.

Transition state structures with forming bond lengths reported in Å and activation free energies ($\Delta G^{\ddagger}$) in kcal/mol for the *syn* and *anti* Diels–Alder reactions of the 5-substituted cyclopentadienes with ethylene.

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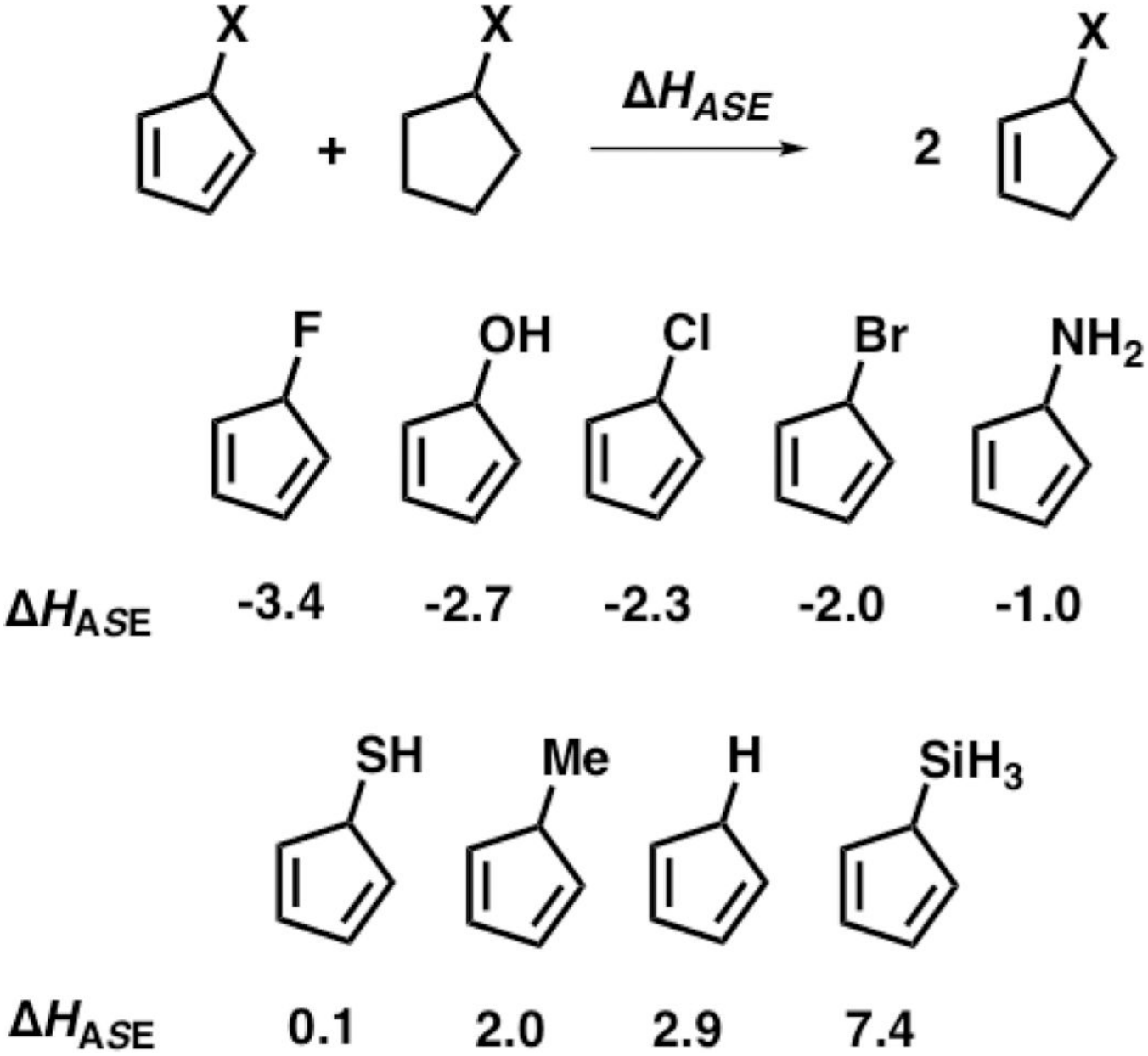

Figure 2.
Isodesmic equation (specifically hypohomodesmotic)[19] and calculated aromatic stabilization enthalpies of the cyclopentadienes.

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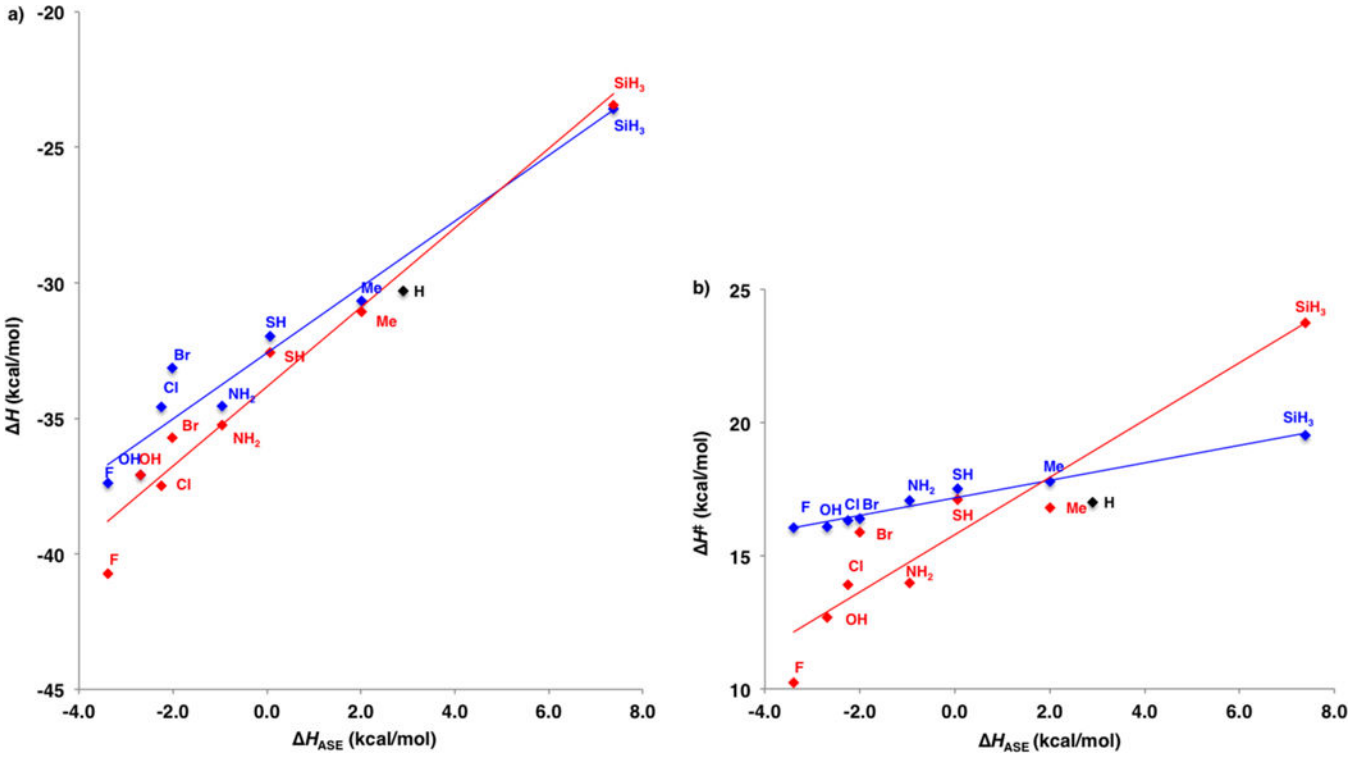

Figure 3.

Plots of the reaction enthalpies (a) and activation enthalpies (b) against the calculated aromatic stabilization enthalpies. *Syn*: red, (a) $\Delta H = 1.2\Delta H_{ASE} - 33$, $r2 = 0.95$; (b) $\Delta H^{\ddagger} = 1.1\Delta H_{ASE} + 16$, $r2 = 0.90$. *Anti*: blue, (a) $\Delta H = 1.5\Delta H_{ASE} - 34$, $r2 = 0.95$; (b) $\Delta H^{\ddagger} = 0.33\Delta H_{ASE} + 17$, $r2 = 0.98$.

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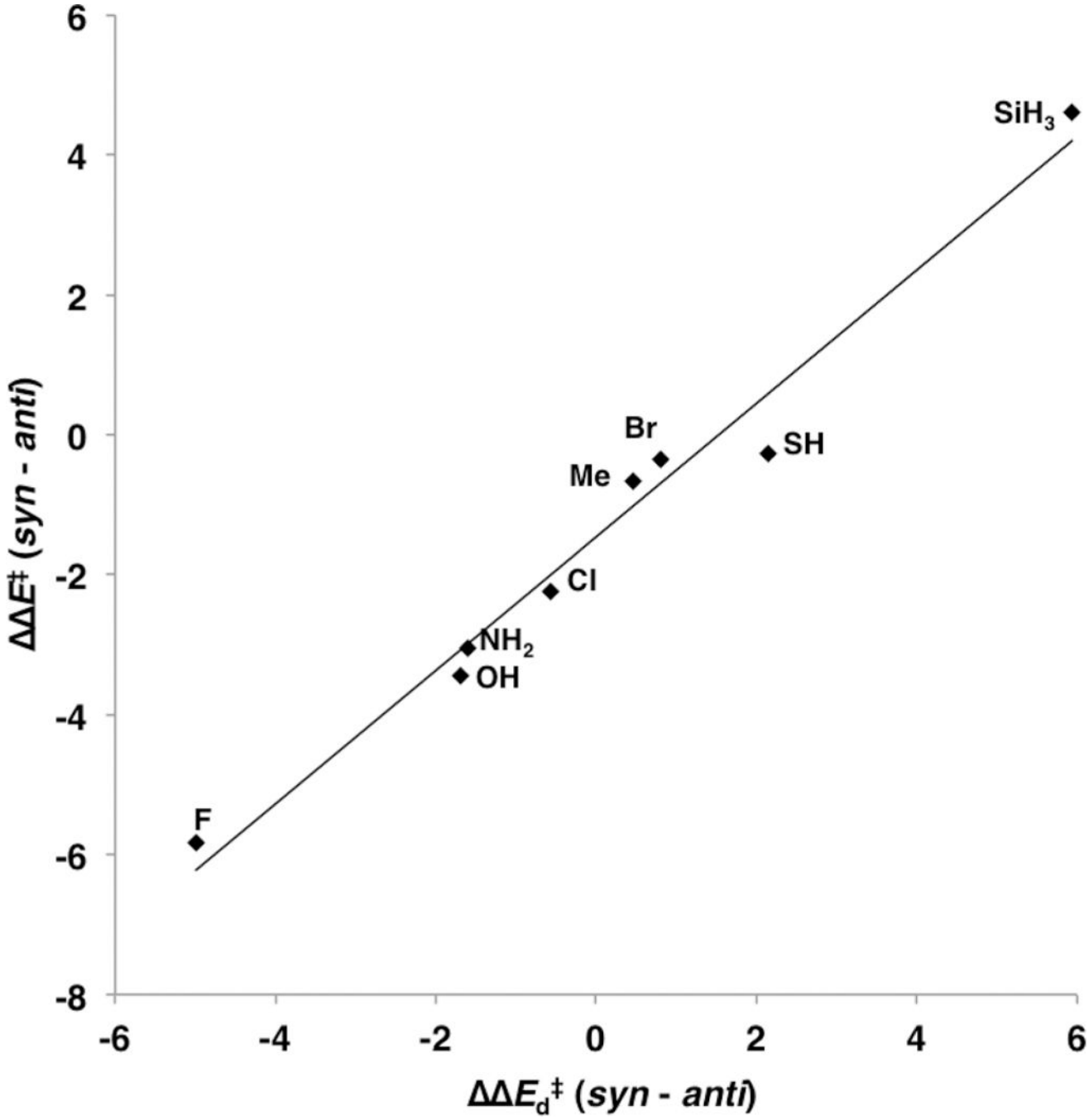

Figure 4.

Plot of π-facial selectivity ($\Delta\Delta E^{\ddagger}$(*syn*–*anti*)) against the differences in the distortion energies ($\Delta\Delta E_d^{\ddagger}$(*syn*–*anti*)) ($\Delta\Delta E^{\ddagger} = 0.95\Delta\Delta E_d^{\ddagger} - 1.5$, $r2 = 0.98$).

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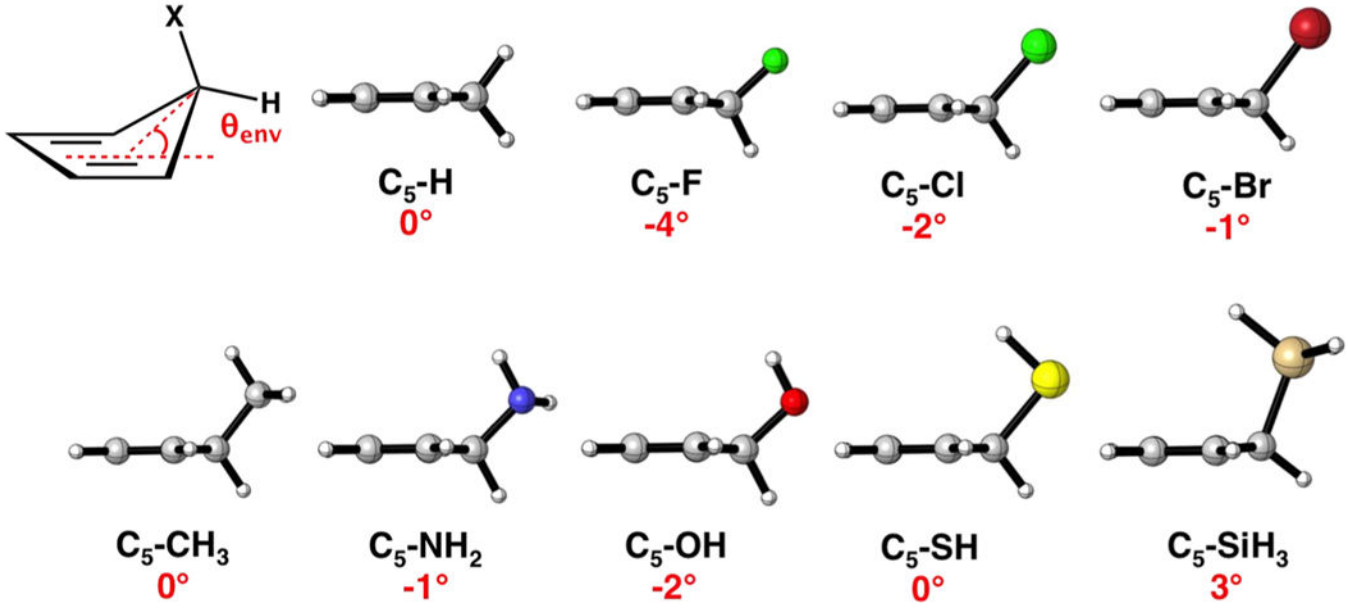

Figure 5.

Optimized M06–2X/6–31G(d) ground state geometries of the C_5–X cyclopentadienes with θ_{env}, the angle measuring the out-of-plane distortion of the C_5 atom, reported in degrees.

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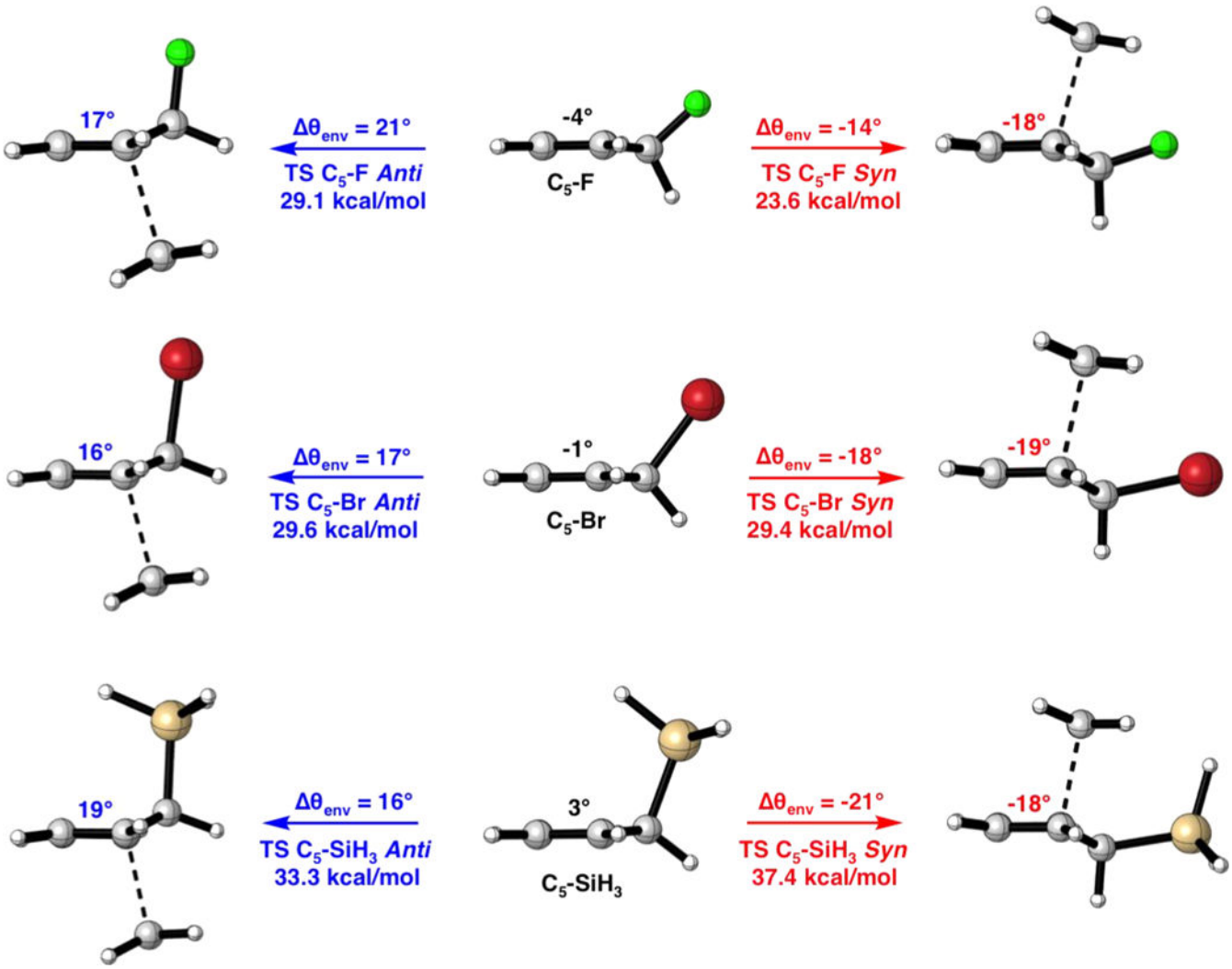

Figure 6.

Ground and *syn* and *anti* transition state structures of C_5–F, C_5–Br, and C_5–SiH_3 with θ_{env} shown in degrees.

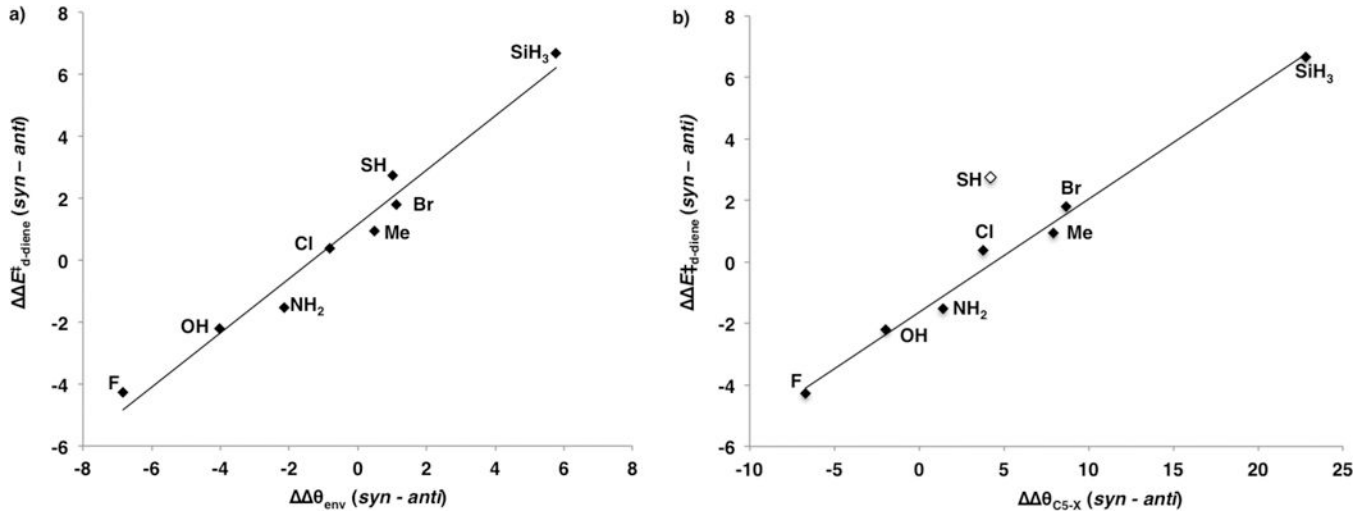

Figure 7.

(a) Plot of differences in the diene distortion energies ($\Delta\Delta E_{\text{d-diene}}^{\ddagger}$(*syn*–*anti*)) against the change in the envelope angle required to achieve the *syn* and *anti* transition state geometries $\Delta\Delta\theta_{\text{env}}$(*syn*–*anti*) ($\Delta\Delta E_{\text{d-diene}}^{\ddagger} = 0.88\Delta\Delta\theta_{\text{env}} + 1.2$, $r2 = 0.97$). (b) Plot of differences in the diene distortion energies ($\Delta\Delta E_{\text{d-diene}}^{\ddagger}$(*syn*–*anti*)) against the change in the bending of the $C_{5\text{-}X}$ bond required to achieve the *syn* and *anti* transition state geometries ($\Delta\Delta E_{\text{d-diene}}^{\ddagger} = 0.37\Delta\Delta\theta_{\text{C5-X}} - 1.6$, $r2 = 0.99$).

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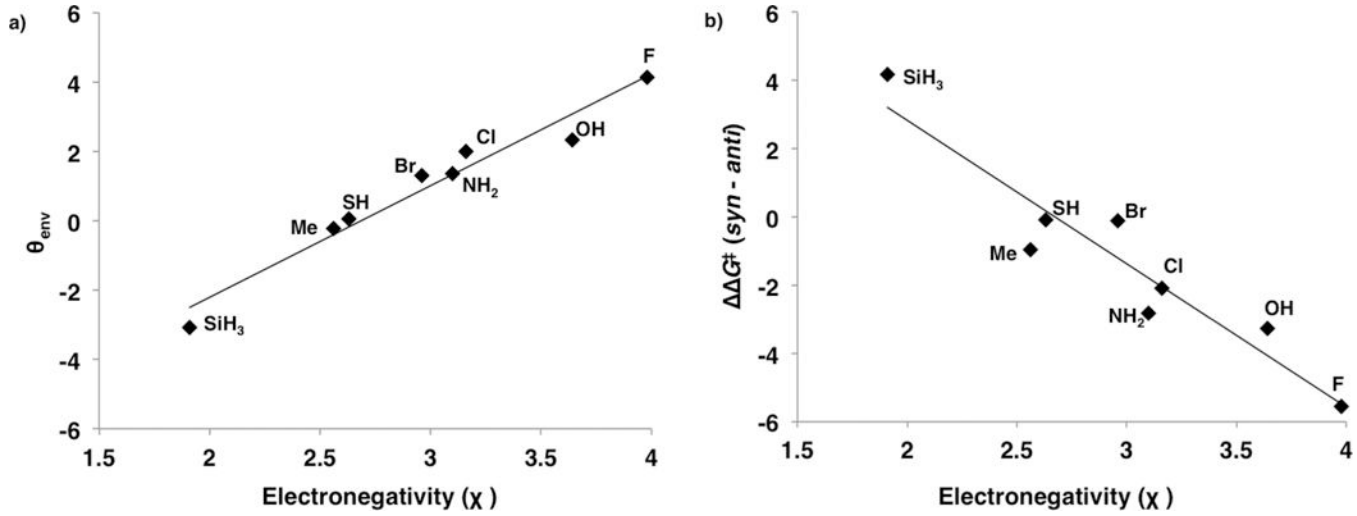

Figure 8.

(a) Plot of θ_{env} in the ground state of the C_5–X cyclopentadienes against the electronegativity of the C_5–X substituent ($\theta_{env} = 3.2\chi - 8.7$, $r_2 = 0.96$). (b) Plot of π-facial selectivity against the electronegativity of the C_5–X substituent ($\Delta\Delta G^{\ddagger} = -4.2\chi + 11.2$, $r_2 = 0.90$).

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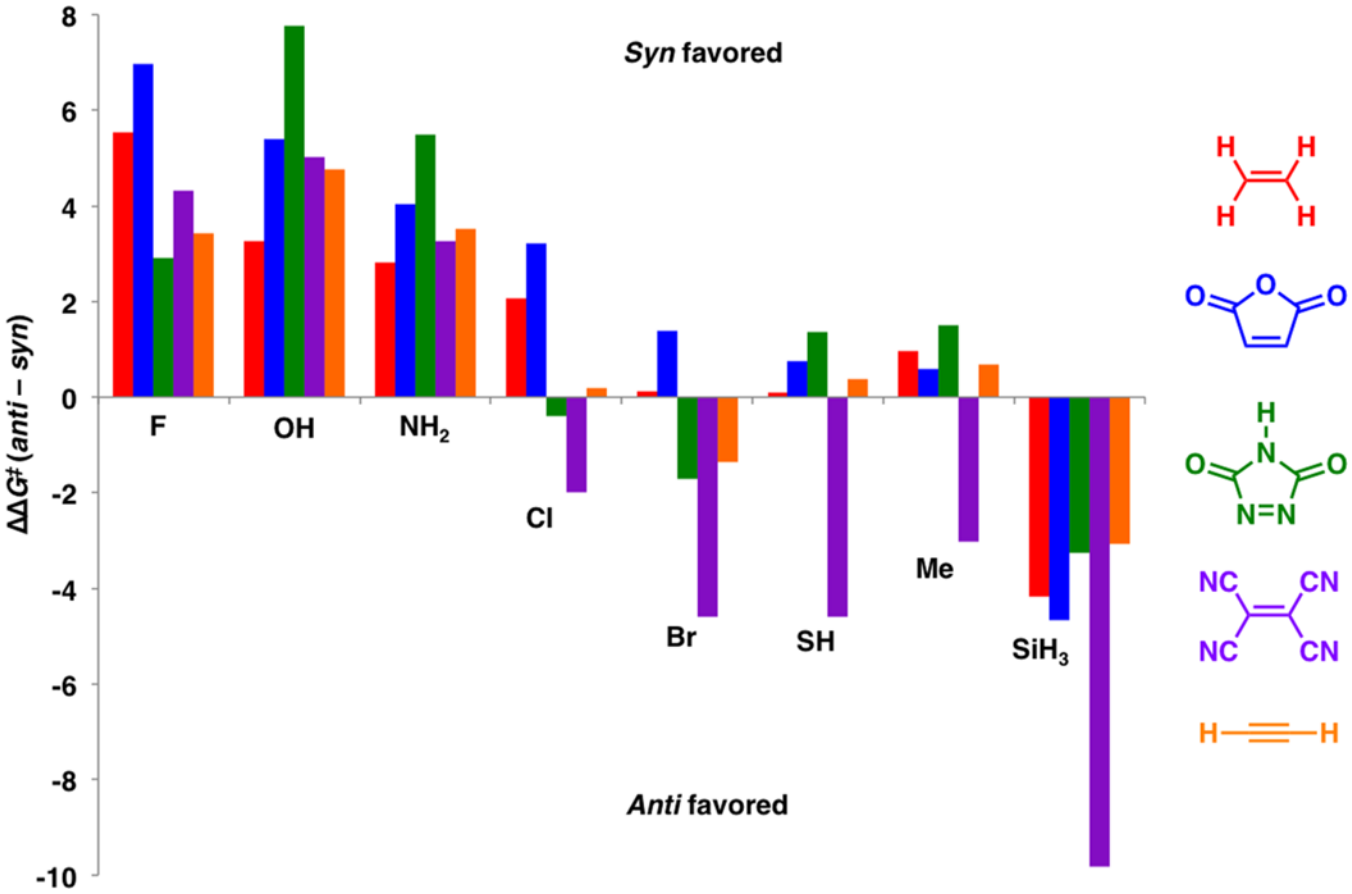
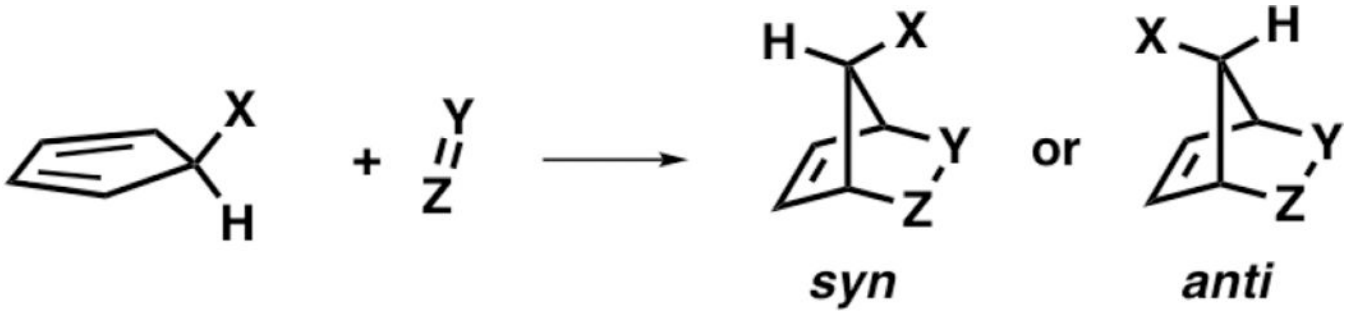


Figure 9.

Histogram showing the *syn* and *anti* π-facial stereoselectivity in the Diels–Alder reactions of the C_5–X cyclopentadienes with ethylene (red), maleic anhydride (blue), 1,2,4-triazoline-3,5-dione (green), tetracyanoethylene (purple), and acetylene (orange).



scheme 1.

Syn and *Anti* Diels–Alder π-Facial Selectivity to a C_5–X Cyclopentadiene with the X═Y Dienophile

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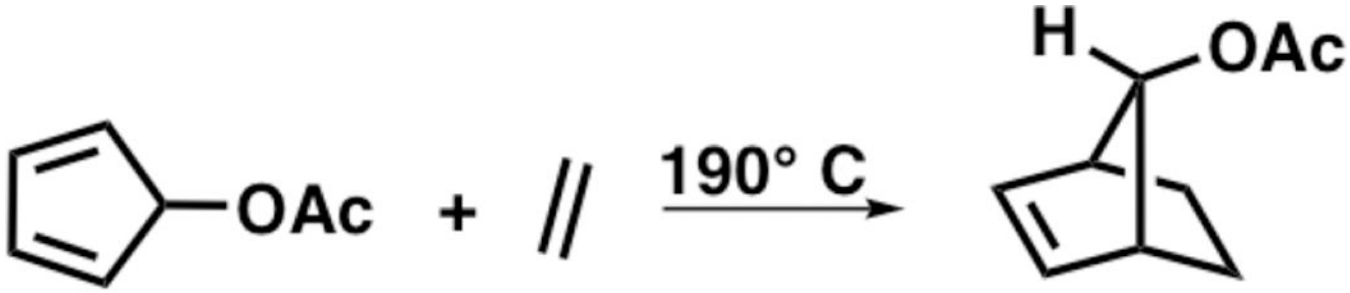
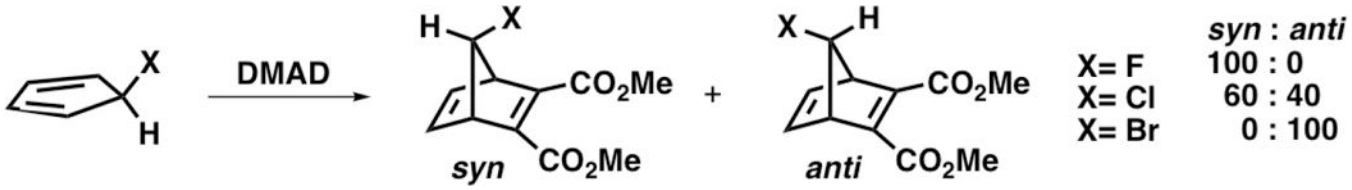


Scheme 2.
Reaction of C_5–OAc with Ethylene Exclusively Forms the *Syn* Adduct[3]



Scheme 3.

Syn and *Anti* π-Facial Stereoselectivity in the Diels–Alder Reactions of C_5–F, C_5–Cl, and C_5–Br with DMAD[4,5]

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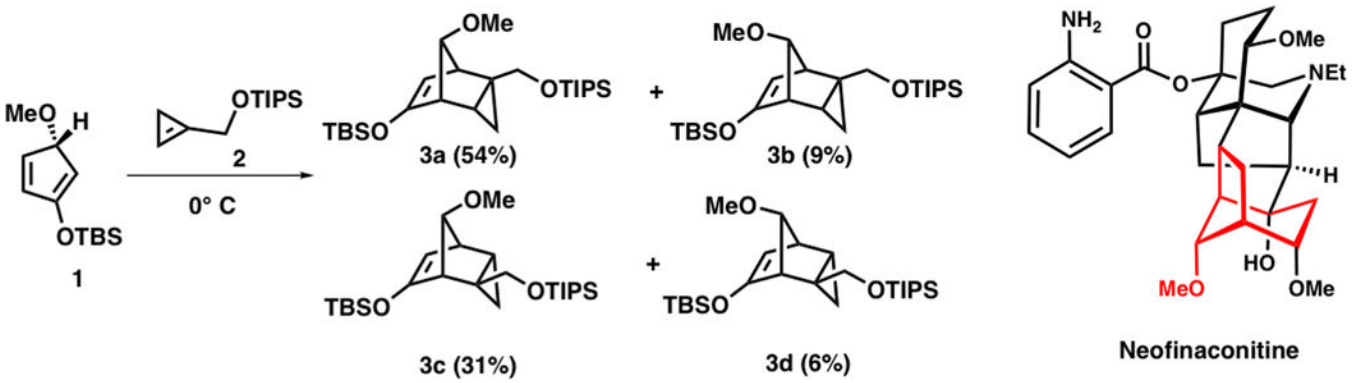

Scheme 4.

Gin's Exploitation of π-Facial Stereoselectivity in the Total Synthesis of Neofinaconitine[6]

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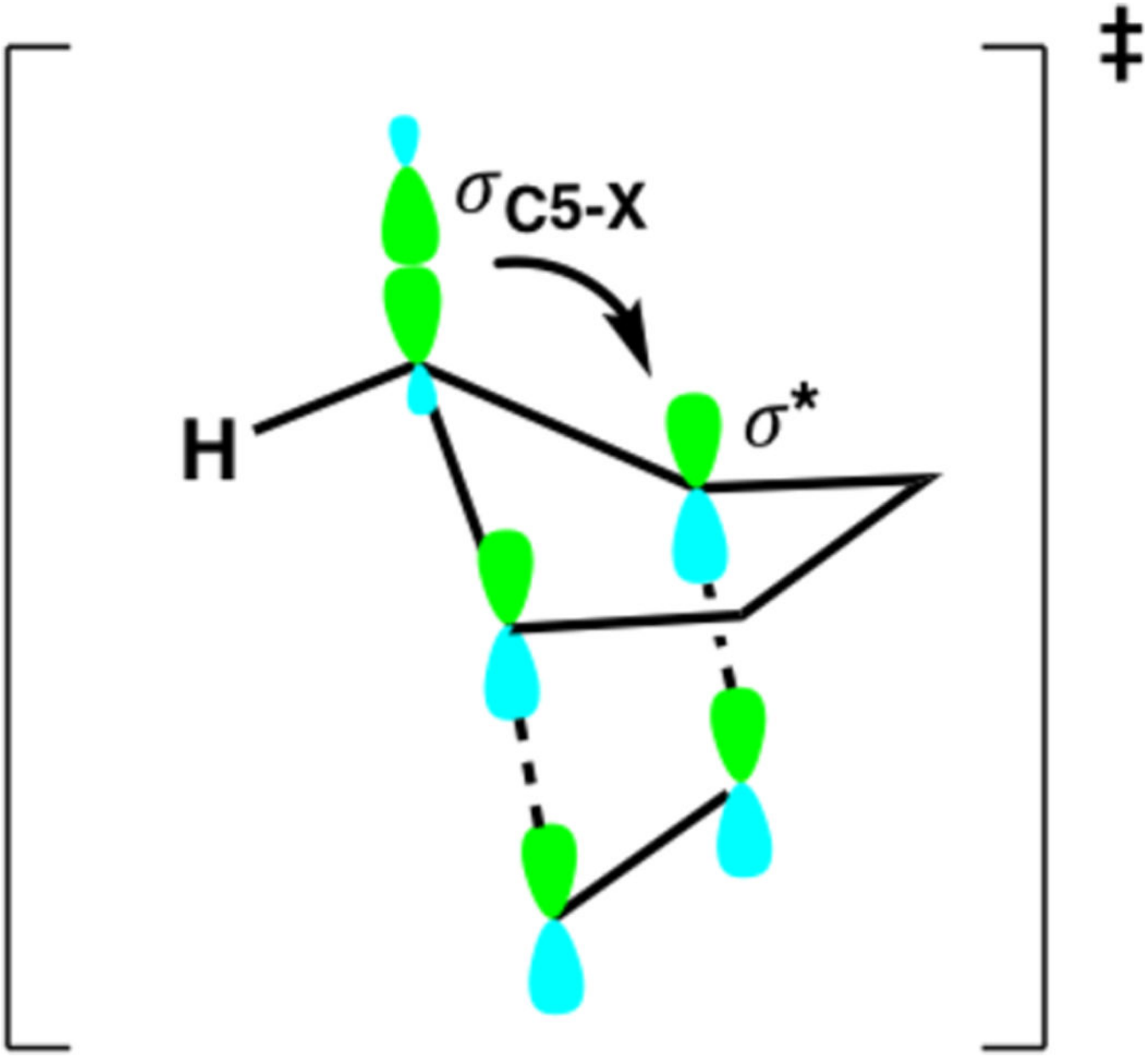

Scheme 5.

Hyperconjugative Stabilization of the Incipient σ^* Bonds by the Antiperiplanar C_5–X σ-Bond (Cieplak Effect)

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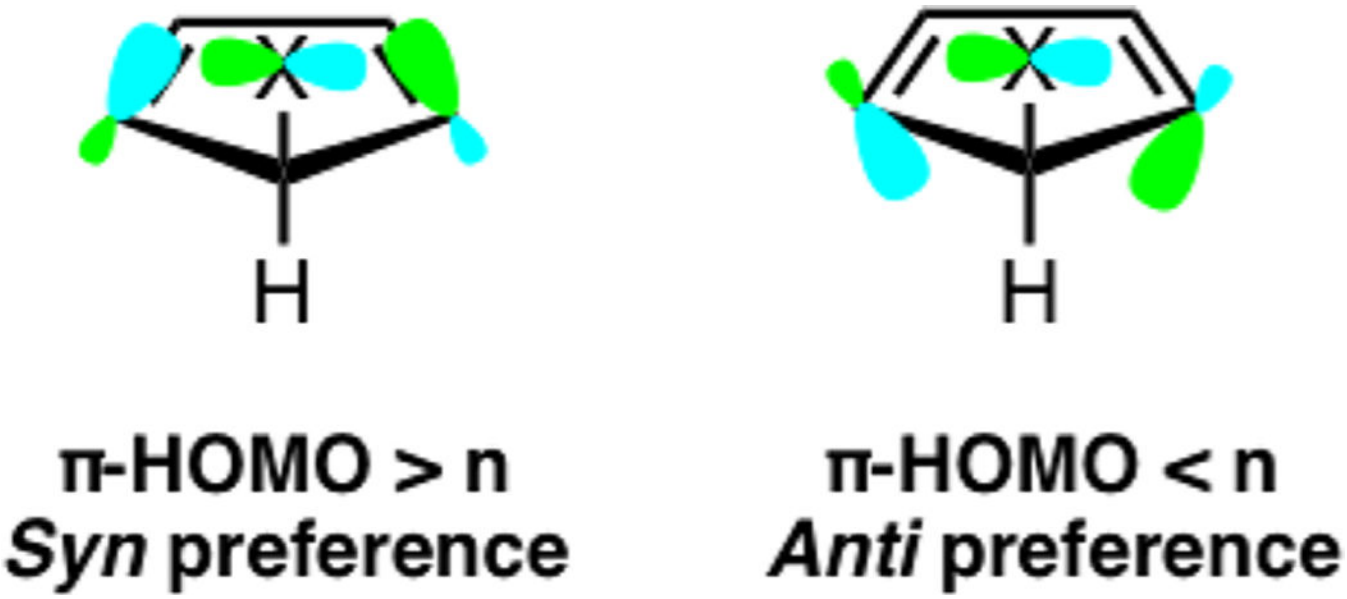

Scheme 6.

Deformation of the π-HOMO from Orbital Mixing Proposed by Inagaki, Fujimoto, and Fukui

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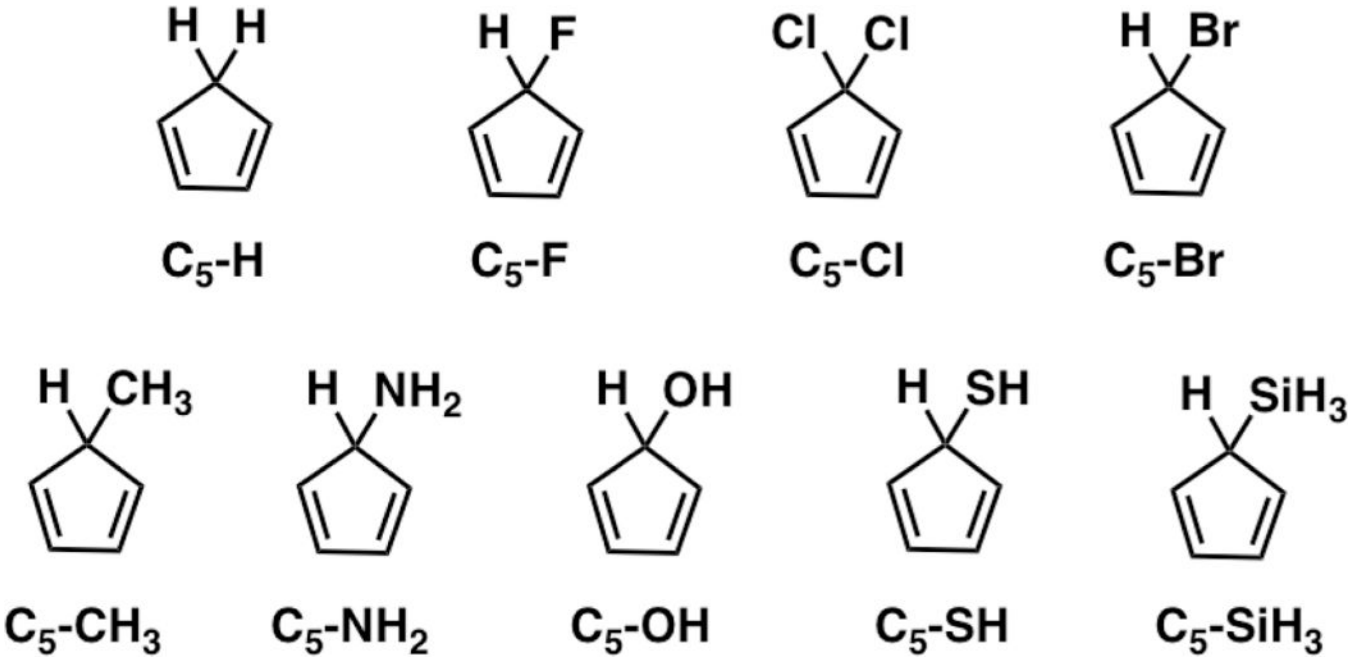

Scheme 7.
C_5–X Cyclopentadienes Studied in This Work

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Table 1.

Force Constants Computed at the M06–2X/6–31G(d) Level of Theory for Bending of the C_5–X Bonds and for the out-of-Plane Motion of the C_5 Atom from the Plane of the Cyclopentadiene

C_5–X	bending of C_5–X bond (mDyne/Å)	out-of-plane bending of C_5 atom (mDyne/Å)
C_5–F	0.097	1.20
C_5–Cl	0.064	1.12
C_5–Br	0.047	0.80
C_5–CH_3	0.047	0.56
C_5–NH_2	0.049	0.79
C_5–OH	0.066	0.97
C_5–SH	0.048	1.20
C –SiH	0.032	0.84