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Hetero Diels−Alder Reaction of Vinyl Allenes and Aldehydes. An Experimental and Computational Study

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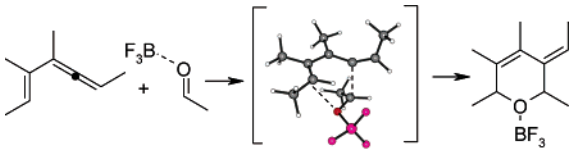

The hetero Diels−Alder reaction of vinyl allenes and aldehydes in the presence of a Lewis acid has been studied both experimentally and theoretically. Differently substituted vinyl allenes and aldehydes were used to obtain information on the structural requirements of the reaction. Theoretical calculations using the density functional theory indicate that the reaction proceeds through a highly asynchronous polar transition state.

Introduction

Vinyl allenes have been used as dienes in Diels−Alder reactions for many years in both the inter- and the intramolecular versions of the reaction.[1] The presence of the sp carbon, which implies out-of plane substituents on the extreme of the allene, introduces interesting differences with the cycloaddition reaction of standard dienes, especially in the regio- and facial selectivity of the reaction. For the parent system, 1,2,4-pentatriene, an 80:20 mixture of regioisomers, was obtained in the reaction with methyl vinyl ketone.[2] Depending on the position of the alkyl substituents on the allene, the ratio can change, favoring one of the two regioisomers. Theoretical calculations at the ab initio level have also been carried out for the Diels−Alder reaction of vinyl allenes and acrolein,[3] showing that, when the parent system is considered, no regioselectivity is expected. However, in the methyl substituted vinyl allenes, the electron-donating ability of the methyl group results in one of the regioisomers being favored. The same study concluded that the reaction is a concerted asynchronous process. In a study using cyclohexenyl-allenes, Krause and co-workers[4] concluded that the selectivity in this type of compound is due to the steric interaction of the incoming dienophile with the substituents on the vinyl allene, following a model first proposed by Reich and co-workers.[5] A recent study indicates that the presence of the allene causes the lowering of the activation energy of the reaction when compared to the nonallenic case,[6] making them more reactive than similarly substituted dienes.

Recently,[7] we found that 1-cyclohexenyl allenes, similar to those which were shown to display high selectivity in Diels−Alder reactions by Krause and co-workers,[4] can also act as dienes in hetero Diels−Alder reactions with aldehydes under Lewis acid catalysis. The reactivity was similar to that displayed by dienes activated by one silyloxy group,[8] that is, good facial and regioselectivity and moderate endo/exo selectivity, with the yields being moderate to good for this reaction (36−70%). Later, we found that the same reaction works with imines as heterodienophiles,[9] although some structural limitations to the reaction, as well as some selectivity problems arising from competing reactions, were observed. Furthermore, the intramolecular version of this reaction has also been explored with both aldehydes[10] and imines[11] as heterodienophiles.

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In this paper, we present the full account of our work using aldehydes as heterodienophiles, with different vinyl allenes as dienes, as well as a theoretical study of the reaction carried out using the density functional theory, intending to shed light on the mechanism of the process.

Computational Methods

All the calculations reported in this paper have been performed within the density functional theory,[12] using the hybrid functional B3LYP[13] and the standard basis set 6-31G-(d,p) as implemented in the Gaussian 98[14] suite of programs, which has been shown to be a satisfactory level for the study of the hetero Diels−Alder reaction.[15]

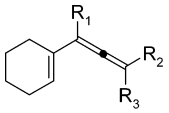
Activation energies and reaction energies were computed at the same level, including zero-point vibrational energy (ZPVE) corrections, which were not scaled. No basis-set superposition error corrections were applied.

The synchronicities[16] of the studied reactions were quantified using a previously described approach[17] using Wiberg bond indices[18] and evaluated using the natural bond orbital (NBO) method.[19] Donor−acceptor interactions have also been computed using the NBO method using second-order perturbation energy.

Results and Discussion

Experimental Studies. For this work, vinyl allenes with different substitution patterns were chosen following the general structure shown in Figure 1, the substituents being either hydrogen atoms or alkyl (Me, Et, *t*-Bu) or phenyl groups.[20]

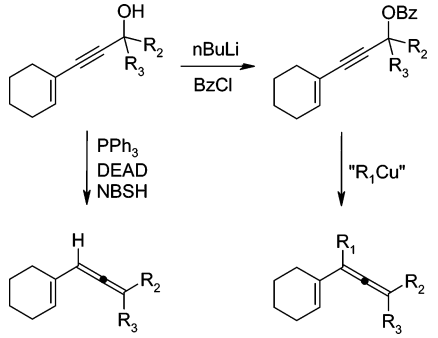
Those vinyl allenes were prepared either from the propargyl alcohols obtained from the addition of (cyclohexenylethynyl)-lithium to carbonyl compounds or from the corresponding benzoates as shown in Scheme 1.



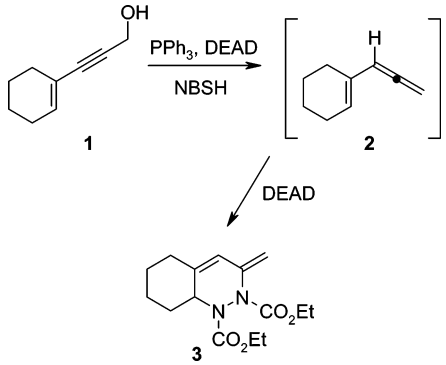
R_1, R_3 = H, alkyl
R_2 = H, alkyl, Ph

FIGURE 1. General structure of the vinyl allenes used in this work.

SCHEME 1



SCHEME 2



We started by attempting the synthesis of the vinyl allenes, unsubstituted at the inner position of the allene (R_1 = H), using Myers and Zheng's protocol.[21] Thus, when the known propargyl alcohol **1**[22] was treated with PPh_3, diethylazodicarboxylate (DEAD), and *o*-nitrobenzene sulfonylhydrazine (NBSH) in THF at −15 °C, a single compound was isolated in a 16% yield. Spectroscopic studies, however, indicated that the compound obtained was not the desired vinyl allene **2** but the diazine **3** resulting from the cycloaddition of **2** and DEAD (Scheme 2).

Reducing the amount of DEAD or lowering the temperature of the reaction did not allow us to isolate any allenic compound, since it apparently reacted as soon as it was formed. This behavior indicates that **2**, although not useful for our purposes, could act as a diene. The preparation of this vinyl allene has been reported previously using other procedures,[22] but in light of the results obtained with other vinyl allenes as described below, we decided not to pursue its preparation.

When Myers's protocol was applied to **4**,[7] the corresponding vinyl allene **5**[9] was obtained in a 55% yield as a nonpolar oily compound, without a trace of the cycloaddition products (Scheme 3). The vinyl allene **5**, after purification, reacted with DEAD in ether to give the diazine **6** (60%) as a 1:1 mixture of E and Z isomers on the exocyclic double bond.

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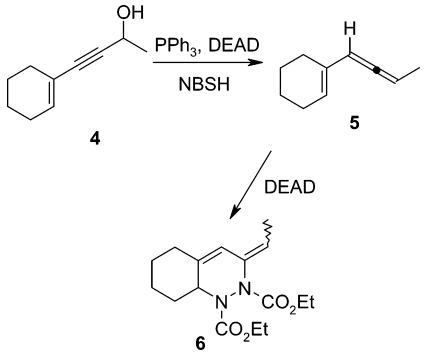
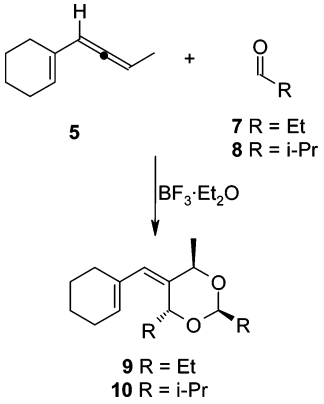
SCHEME 3



SCHEME 4



Those results indicate that this vinyl allene, although less reactive than **2** toward DEAD, was a good diene. However, when we assayed its reactivity toward aldehydes using $BF_3 \cdot Et_2O$ as a Lewis acid, the results were quite different. Thus, with propionaldehyde, a compound was isolated in a low yield (10%) showing a ^1H NMR spectrum consistent with the incorporation of two molecules of aldehyde and one molecule of vinyl allene. After further studies, the compound was identified as the dioxane **9**, the result of a Prins-type reaction between the terminal double bond of the allene and the aldehyde (Scheme 4). Increasing the amount of aldehyde allowed us to increase the yield, but only up to 15%.

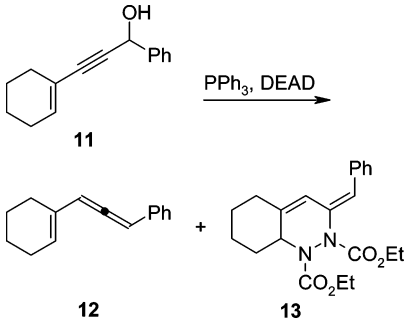
This type of Prins reaction has usually been carried out in aqueous media using protic acids, but examples of Lewis acid catalysis are known.[23]

Using isobutyraldehyde instead of propionaldehyde, a similar compound (**10**) was obtained in a 22% yield. No compound coming from a hetero Diels−Alder reaction was observed. The relative stereochemistry of **9** and **10** was established by GOESY experiments.[24]

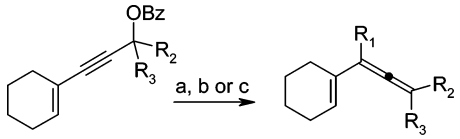
When we applied Myers's protocol to propargyl alcohol **11**,[9] a mixture of vinyl allene **12** (10%) and diazine **13** (15%) was obtained (Scheme 5). A slightly better yield of **12** (24%), without contamination with diazine, was obtained using $LiAlH_4/AlCl_3$ as the reagents.[25] However, its reaction with propionaldehyde gave only decomposition under all conditions tested.

From these results, it became clear that the vinyl allenes unsubstituted at the inner position of the allene ($R_1 = H$, Figure 1) were not reactive toward the hetero Diels−Alder reaction with aldehydes, and no further experiments with this type of compounds were made.

SCHEME 5



SCHEME 6 [a]



14 $R_2 = R_3 = H$
15 $R_2 = Me$; $R_3 = H$
16 $R_2 = Ph$, $R_3 = H$
17 $R_2 = R_3 = Me$
18 $R_1 = R_2 = Me$; $R_3 = H$ (64%)[a]
19 $R_1 = Me$; $R_2 = Ph$; $R_3 = H$ (67%)[a]
20 $R_1 = Et$; $R_2 = R_3 = H$ (61%)[b]
21 $R_1 = Et$; $R_2 = Me$; $R_3 = H$ (60%)[b]
22 $R_1 = Et$; $R_2 = Ph$; $R_3 = H$ (75%)[b]
23 $R_1 = t\text{-Bu}$; $R_2 = Me$; $R_3 = H$ (72%)[c]
24 $R_1 = Et$; $R_2 = R_3 = Me$ (64%)[b]

[a] (a) MeMgBr, CuI, LiBr, 0 °C; (b) EtMgBr, $CuBr \cdot Me_2S$, −60 °C; (c) *t*-BuLi, CuCN, −78 °C.

We then turned our attention to the alkyl substituted vinyl allenes, some of which had been prepared in our previous work from the S_N2' reaction of a suitable cuprate onto a propargyl benzoate.[9] The reagents and the yields are shown in Scheme 6.

All vinyl allenes prepared, with the exception of **20** which lacks substituents at the end of the allene moiety, showed good reactivity when maleic anhydride was used as the dienophile, indicating that they are at least as reactive in the Diels−Alder reaction as the vinyl allenes previously published.[4]

When we tried the hetero Diels−Alder reaction of those vinyl allenes with aldehydes and $BF_3 \cdot Et_2O$ as the Lewis acid, the reaction proceeded in all cases except for vinyl allenes **20** and **23**, which did not give any compounds under the conditions tried, and **24,** which only reacted with benzaldehyde. Table 1 shows the results obtained.

All compounds obtained present the same geometry on the exocyclic double bond and are the result of a complete facial selectivity, with the approach of the dienophile through the less hindered face of the vinyl allene, the one opposite to the orthogonal group on the extreme of the allene. The regiochemistry of the approach is also high and the same in all examples studied, with the new bonds formed between the central bond of the allene and the carbonyl carbon atom and between the terminal carbon of the dienic system and the carbonyl oxygen. The endo/exo selectivity, however, is not very high, with mixtures of compounds with a cis (coming from the endo approach) and a trans (coming from the exo approach) relative

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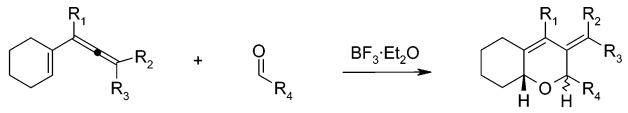
TABLE 1. Reaction of Vinyl Allenes with Aldehydes in the Presence of $BF_3{\cdot}Et_2O$[a]



18 $R_1 = R_2 = Me$; $R_3 = H$
19 $R_1 = Me$; $R_2 = Ph$; $R_3 = H$
21 $R_1 = Et$; $R_2 = Me$; $R_3 = H$
22 $R_1 = Et$; $R_2 = Ph$; $R_3 = H$
24 $R_1 = Et$; $R_2 = R_3 = Me$

7 $R_4 = Et$
8 $R_4 = i\text{-}Pr$
25 $R_4 = Ph$

26 - 38

entry	vinyl allene	aldehyde	compound (% yield)	cis:trans ratio
1	**18**	**7**	**26** (63)	46:54
2	**18**	**8**	**27** (26)	0:100
3	**18**	**25**	**28** (76)	49:51
4	**19**	**7**	**29** (49)	52:48
5	**19**	**8**	**30** (24)	57:43
6	**19**	**25**	**31** (74)	53:47
7	**21**	**7**	**32** (70)	70:30
8	**21**	**8**	**33** (60)	74:26
9	**21**	**25**	**34** (62)	64:36
10	**22**	**7**	**35** (54)	73:27
11	**22**	**8**	**36** (36)	66:34
12	**22**	**25**	**37** (40)	75:25
13	**24**	**25**	**38** (39)	0:100

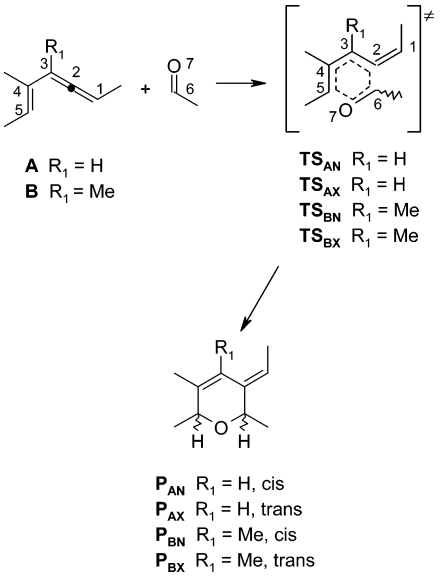
[a] The stereochemistry of the products was deduced from NMR data (GOESY experiments). The cis:trans ratio was obtained by integration of the ^1H NMR spectra of the crude reaction mixtures.

stereochemistry of the hydrogen atoms of the positions adjacent to the oxygen being obtained, in most cases. No explanation has been found for the lack of reactivity of **20**, which has two hydrogen atoms at the end of the allene moiety, although it may be due to decomposition under the reaction conditions since it resulted in the most acid-sensitive vinyl allene prepared, and no product could be isolated from any of the reactions tried. Compound **23**, substituted with a *tert*-butyl group on the allene, also presents low reactivity, which may be due to the difficulty in attaining the necessary s-cis conformation because of steric hindrance.[11]

Analyzing the results presented in Table 1, it can be observed that, with trisubstituted allenes, the endo/exo selectivity is higher for the ethyl substituted compounds, and thus the cis:trans ratio changes from endo isomers as a major compound when R_1 is Et (vinyl allenes **21**, **22**) to an almost 1:1 mixture of endo and exo isomers when R_1 is Me (using vinyl allene **19**) or even to exo isomers as the favored isomer with vinyl allene **18** and isobutyraldehyde. Since both alkyl groups exert a similar electronic and steric effect on the diene in Diels−Alder reactions,[26] we have attributed this behavior to the stability problems observed for the cycloadducts, stability being especially low for the cis compounds when R_1 is Me. When the allene is tetrasubstituted (**24**), only the trans compound is obtained, which may be explained by the slow reaction caused by the difficulties on the approach of the heterodienophile to either face of the diene because of the presence of the two orthogonal methyl groups. The longer reaction times may facilitate the decomposition mainly of the less stable cis cycloadduct.

If we compare the reactivity of the ethyl substituted vinyl allenes then it can be seen that the most reactive is **21**, which bears a methyl group and a hydrogen atom at the end of the allene. Next comes **22** in which the methyl group is replaced by a phenyl and gives slightly lower yields but similar selectivity (about 70:30 cis:trans). The least reactive is **20** which does not give any product under the conditions used in this work.

SCHEME 7



As a conclusion concerning the substitution patterns and the reactivity, it can be said that in order to react with aldehydes, the vinyl allenes need to have substituents at the R_1 position which must not exert too much steric hindrance. The allene terminus must be monosubstituted, and alkyl groups seem to be slightly more reactive than phenyl groups.

Computational Studies. These experimental results do not allow us to draw any conclusions regarding the mechanism of the Lewis acid-catalyzed reaction between vinyl allenes and aldehydes, which could range from a highly asynchronous pericyclic process to an ionic one. Also, a number of questions remain unanswered such as the role of the substituents on the inner carbon of the allene moiety or the difference in endo/exo selectivity when such a substituent changes from a methyl to an ethyl group.

For those reasons, it was decided to undertake a computational study of this reaction.

In order to better understand the reaction, we decided to first carry out the study of the uncatalyzed process in order to obtain information on the reactivity of the two systems, the vinyl allene and the aldehyde.

The computations were carried out using simplified models in order to reduce the computational cost. Thus, instead of cyclohexenyl allenes **5** or **18**, we chose as models vinyl allenes **A** and **B**, in which the cyclohexene ring is replaced by a 1,2-dimethylethene moiety, and the only difference between them is the substituent R_1 (Scheme 7). Acetaldehyde was selected as a model for the dienophile.

Only one regiochemistry was studied since preliminary calculations indicated that the one found experimentally was much lower in energy than the opposite one at any of the computational levels tried. Furthermore, the dienic system in the s-cis conformation of the vinyl allene presents two distinct faces because of the presence of the out-of-plane methyl group on the extreme of the allene moiety, and the published calculations[4] indicated, as mentioned before, that the approach of the dienophile is controlled by steric factors and should take place by the face opposite to the orthogonal alkyl group. Taking

(26) Robiette, R.; Marchand-Brynaert, J.; Peeters, D. *J. Org. Chem.* **2002**, *67*, 6823.

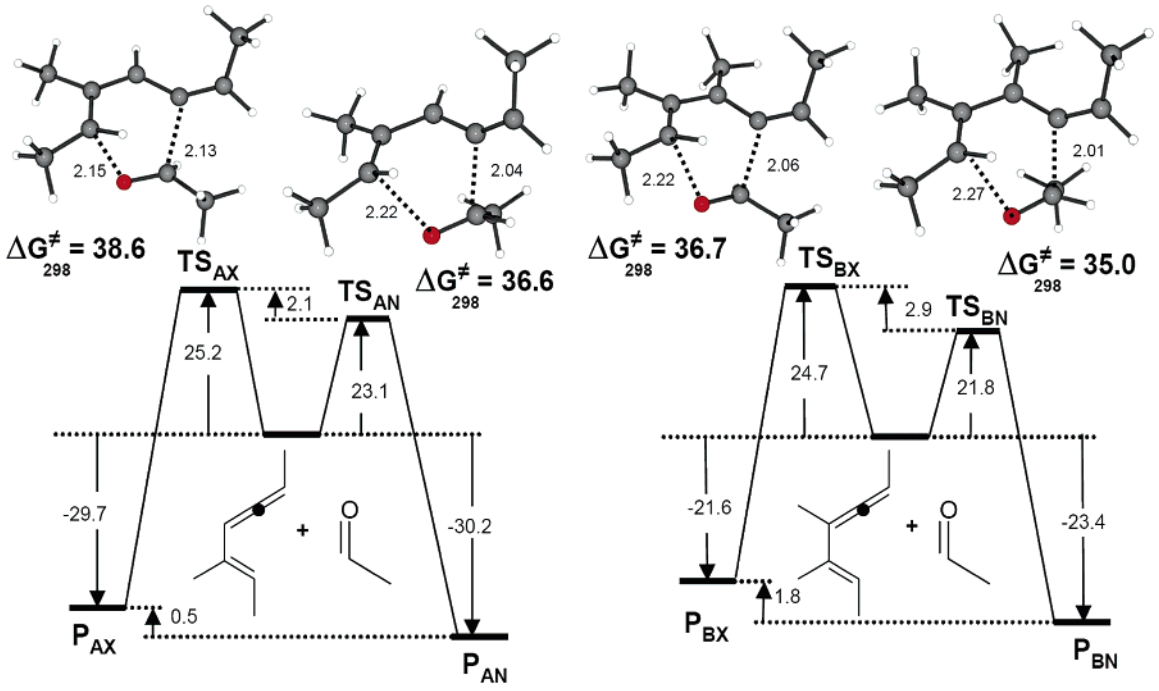


FIGURE 2. Calculated structures of the transition states and reaction profiles for the reactions of vinyl allenes **A** and **B** with acetaldehyde. Relevant distances are in Å, and activation energies, reaction energies, and Gibbs activation energies at 298 K are in kcal/mol.

all of this into account, we started by modeling the reaction coordinates and calculating all stationary points involved at the B3LYP/6-31G(d,p) level for the reactions depicted in Scheme 7. There are two possible transition states for each reaction which correspond to the endo (**TS$_{AN}$** and **TS$_{BN}$** for the reactions of **A** and **B**, respectively) and exo (**TS$_{AX}$** and **TS$_{BX}$**) approaches of the dienophile to the dienic part of the vinyl allene, and thus two cycloadducts are possible for each process. Scheme 7 shows the reactions studied, the naming convention, and the arbitrary numbering scheme used in this part of the discussion.

The transition states coming from the endo approach of the dienophile (**TS$_{AN}$** and **TS$_{BN}$**) lead to products in which the hydrogen atoms at the positions adjacent to the oxygen are cis (**P$_{AN}$** and **P$_{BN}$**), whereas those coming from the exo approach (**TS$_{AX}$** and **TS$_{BX}$**) produce trans compounds (**P$_{AX}$** and **P$_{BX}$**). Frontier molecular orbital analysis indicates that these reactions are controlled by the vinyl allenes HOMO aldehyde LUMO interactions and also indicates that the reaction of **B** should be favored.[27] Figure 2 depicts the profiles for the reactions of vinyl allenes **A** and **B** with acetaldehyde, calculated at the B3LYP/6-31G(d,p) level together with their activation energies, Gibbs activation energy at 298 K, reaction energies, and bond-forming distances. The reactions are calculated to be exothermic, with the cis product coming from the endo approach of the dienophile being the more stable in both cases.

From Figure 2, it can be observed that the transition states arising from the reaction of vinyl allene **A** (**TS$_{AN}$** and **TS$_{AX}$**) present higher activation energy and Gibbs activation energy than those coming from the alkyl-substituted vinyl allene **B** (**TS$_{BN}$** and **TS$_{BX}$**). The endo approach is the more favorable one in both of these cases. The observed activation energies found are similar to those calculated for the reaction of butadiene and acetaldehyde.[28] The structure of the transition states studied and the transition vector motion along the reaction coordinates for all cases are consistent with a concerted Diels−Alder cycloaddition. In addition, no intermediate corresponding to a stepwise intermediate could be found after performing intrinsic reaction coordinate (IRC) calculations. Only the starting compounds and the cycloadducts were found on either side of the transition state along the reaction coordinate. Studying the geometry of the different transition states, we observed the expected changes in going from reactants to transition state, such as the shortening of the participating single bond of the vinyl allene and the lengthening of the carbonyl double bond and of the two double bonds of the dienic portion of the vinylallene. The difference in the bond-forming distances in the transition states indicates asynchronous processes, which were studied using the relative variation of the Wiberg bond index at the transition state ($\delta\beta_i$), which was calculated for each bond involved in the reaction using the NBO method. The results are presented in Table 2. The average variation of the bond orders at the transition state ($\delta\beta_{av}$) indicates that in all the reactions studied, the transition state occurs before the midpoint in the reaction coordinate; the transition states for the reaction of the alkyl-substituted vinyl allene **B** (0.41) were attained slightly earlier than the corresponding ones for the hydrogen-substituted vinyl allene **A** (0.42). The same values were found for the endo and exo approaches. Examination of the individual variation of the bond order for each bond involved in the reaction ($\delta\beta_i$) indicates that the bond between the carbonyl oxygen, O7, and the extreme of the diene, C5, presents the smaller change for each reaction, whereas the C2−C3 allenic double bond presents the larger one. This is consistent with the different bond-forming distances calculated at the transition

(27) The B3LYP/6-31.G(d,p) HOMO/LUMO energies (eV) are: s-trans **A** (−5.67/−0.16); s-trans **B** (−5.64/−0.13); s-trans **C**α (−5.70/0.16); s-trans **C**β (−5.65/0.10); acetaldehyde (−6.94/−0.60); BF_3−acetaldehyde complex (−9.22/−2.41); and s-trans **D** (−5.72/−0.18).

(28) (a) Park, Y. S.; Lee, B.-S.; Lee, I. *New J. Chem.* **1999**, *23*, 707. (b) McCarrick, M. A.; Wu, Y.-D.; Houk, K. N. *J. Org. Chem.* **1993**, *58*, 3330.

TABLE 2. Relative Wiberg Bond Index Variation at the Transition State for Each Bond Involved ($\delta\beta_i$), Average Bond Order Variation at the Transition State ($\delta\beta_{av}$), and Synchronicities (sy) for Each Transition State Calculated[a]

transition state	δB_i						$\delta\beta_{av}$	sy
	O_7-C_6	C_6-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-O_7		
TS_{AN}	0.44	0.44	0.57	0.39	0.40	0.26	0.42	0.91
TS_{AX}	0.43	0.41	0.54	0.41	0.44	0.29	0.42	0.93
TS_{BN}	0.45	0.46	0.57	0.35	0.37	0.24	0.41	0.87
TS_{BX}	0.45	0.43	0.56	0.37	0.40	0.26	0.41	0.90

[a] The arbitrary numbering presented in Scheme 7 is used.

TABLE 3. Second-Order Perturbation Energies for the Interaction between Donor and Acceptor π Orbitals at the Transition States of the Studied Reactions[a]

donor	acceptor	**TS_{AN}**	**TS_{AX}**	**TS_{BN}**	**TS_{BX}**
π_{2-3}	π^*_{6-7}	54.93	38.07	63.80	59.35
π_{6-7}	π^*_{2-3}	9.37	6.45	10.02	8.82
π_{4-5}	π^*_{2-3}	26.89	27.14	26.55	28.29
π_{2-3}	π^*_{4-5}	11.41	12.41	10.07	10.18
π_{6-7}	π^*_{4-5}	5.60	6.95	5.02	6.25
π_{4-5}	π^*_{6-7}	3.99	7.38	2.94	4.09
π_{1-2}	π^*_{6-7}	5.00	6.12	5.39	4.43
π_{6-7}	π^*_{1-2}	2.20	1.91	2.40	1.99

[a] Energies are in kcal/mol and are stabilizing (i.e., negative). The arbitrary numbering presented in Scheme 7 is used.

states and is consistent with the formation of the bond between C2−C6 being the more advanced of the two new bonds formed in the reaction. Those results give global asynchronicities of 0.91 for the endo and 0.93 for the exo approaches for the case of vinyl allene **A**, which may be described as slightly asynchronous, with smaller values for vinyl allene **B** (0.87 for the endo approach and 0.90 for the exo one), which indicates a higher degree of asynchronicity.

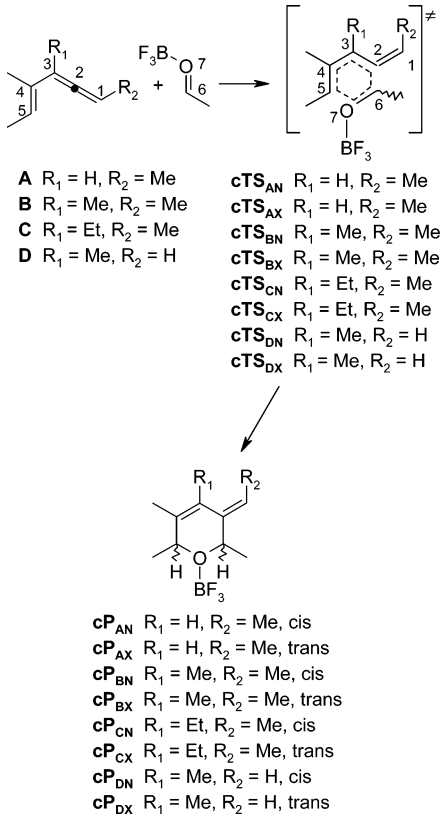
The NBO analysis also gives some insight into the electronic nature of the transition states of the reactions under study. Table 3 shows the interaction energy between the donor and the acceptor π orbitals for the systems involved in the reaction.

The expected interaction of π and π^* orbitals for a pericyclic process can be observed in Table 3, although in a nonsymmetrical distribution. Thus, the stronger donation goes from the allenic C2−C3 double bond (π_{2-3}) to the antibonding orbital of the carbonyl group (π^*_{6-7}) and is more important for the alkyl-substituted systems (**TS_{BN}** and **TS_{BX}**). The second one is the interaction between the two double bonds of the dienic system (π_{4-5} to π^*_{2-3}) which is similar in magnitude in all cases studied, whereas the interaction for the carbonyl double bond and the π^*_{4-5} is much smaller. As a result of these interactions, a charge transfer, calculated using a natural population analysis, from the vinyl allenes to the aldehyde takes place at the transition state which is larger for **TS_{BN}** and **TS_{BX}** (0.221 e for both) than for **TS_{AN}** (0.204 e) and **TS_{AX}** (0.183 e). Another interesting feature found is the interaction between the terminal allenic double bond π_{1-2}, orthogonal to the diene in the starting compounds, and the carbonyl group, which is of the same magnitude as those on the bond-forming interaction between the carbonyl group and the C4−C5 double bond. This is probably due to the distortion of the allene at the transition state, which allows for some overlap of the two orbitals.

All these data indicate that the studied reactions are pericyclic, slightly asynchronous processes.[29]

The next step in the calculations was to add a Lewis acid in order to compare them with the experimental results obtained.

SCHEME 8



BF_3 was selected as the model and included in the calculations. The Lewis acid−acetaldehyde complex was modeled as trans, since both the computational results and the experimental data[30] indicated that this is the preferred disposition. Scheme 8 shows the reaction under study and the naming convention used.

Figure 3 depicts the profiles for the reactions of vinyl allenes **A** and **B** with acetaldehyde catalyzed by boron trifluoride and calculated at the B3LYP/6-31G(d,p) level together with their activation energies, reaction energies, Gibbs activation energies at 298 K, and bond-forming distances. As with the uncatalyzed processes, no intermediate corresponding to a stepwise intermediate could be found after performing IRC calculations. The reactions are also calculated to be exothermic with the cis product, coming from the endo approach of the dienophile, being the more stable in both cases.

Also, the transition states arising from the reaction of vinyl allene **A** with the acetaldehyde−BF_3 complex (**cTS_{AN}** and **cTS_{AX}**) present activation energies similar to those calculated for butadiene and formaldehyde catalyzed by BH_3[27b] but are higher than those coming from the alkyl-substituted vinyl allene **B** (**cTS_{BN}** and **cTS_{BX}**). The difference between the two systems is now larger than in the uncatalyzed case. This is in agreement with the experimental observation that the alkyl-substituted vinyl allenes react with aldehydes in the presence of a Lewis acid, whereas the unsubstituted ones do not react under the same conditions. Looking at the difference in energy between the endo and the exo approaches in each case, it can be observed that the presence of the Lewis acid is especially significant for the

(29) The analysis of the Mulliken charges at the transition states also follows the same pattern. See Supporting Information for a discussion.

(30) Reetz, M. T.; Hüllmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405.

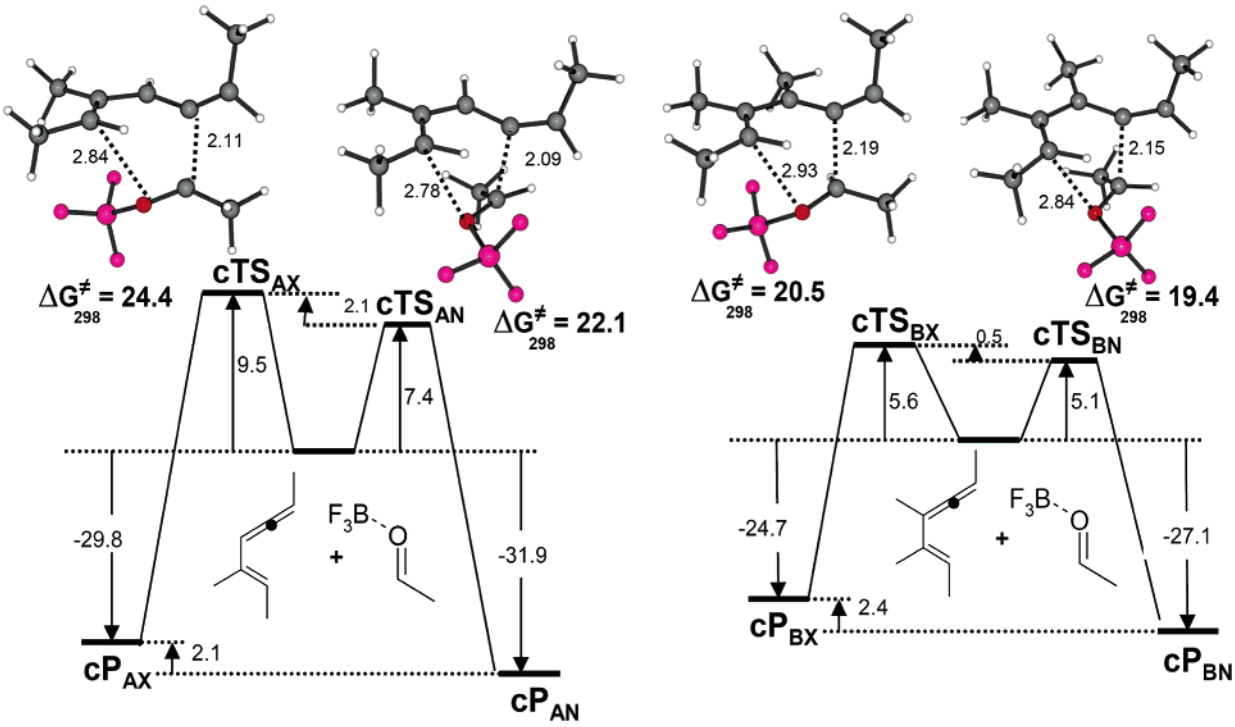


FIGURE 3. Calculated reaction profiles for the reactions of vinyl allenes **A** and **B** with BF_3-complexed acetaldehyde. Relevant distances are in Å, and activation energies, Gibbs activation energies at 298 K, and reaction energies are in kcal/mol.

reactions of **B**, since the endo−exo difference is only 0.5 kcal/mol, indicating that a mixture of cycloadducts should be expected in this case. The Gibbs activation energy differences also follow the same trend. This is in contrast with the experimental data since the methyl-substituted vinyl allenes gave either 1:1 ratios or even the cycloadduct coming from the exo approach as the only product.

The ethyl-substituted vinyl allenes gave experimental endo/exo ratios close to 70:30, and it was also observed that these compounds were more stable than the methyl-substituted ones. The cis cycloadducts were also more prone to decomposition than the trans ones, and thus the difference in endo/exo ratios was attributed to the decomposition of the cis isomer. However, the possibility of other effects taking place could not be ruled out, and thus the reaction of the ethyl-substituted vinyl allene was studied using **C** as the model. For this vinyl allene the conformation of the ethyl group must be taken into account since two possible dispositions of the ethyl group can be described for the reacting s-cis conformation of vinyl allene **C**; one in which the terminal methyl of the ethyl group and the methyl on the extreme of the allene are syn relative to the plane defined by the diene, and another in which those two methyl groups are anti. Thus, there are two different starting points for this reaction, related by the rotation of the ethyl group. The more stable of the two conformers of the vinyl allene is the anti one, probably because of the nonbonded interaction of the two out-of-plane methyl groups in the syn conformer. However, in the transition states, the situation is reversed since the main interaction is that of the ethyl group with the incoming heterodienophile which is highly destabilizing. The results of this study are shown in Figure 4. The effect of the conformation of the ethyl group is clear from the comparison of the two reaction profiles. When the rotamer with the α disposition of the methyl group is considered, the transition states are higher in energy, and the bond-forming distances are also larger than when the disposition is β and the interaction with the incoming heterodienophile is minimized. Thus, the β disposition must be the reacting one. The reaction profile calculated for this more favorable approach is quite similar to that of the reaction of **B**. The main difference is the higher stability of the trans cycloadduct; however, the activation energies are of similar magnitude, and therefore, the expected endo/exo ratio should also be similar.

Thus, from these calculations, it can be concluded that the difference in selectivity of the reactions with the alkyl-substituted vinyl allenes is not due to structural reasons but to the experimentally observed lower stability of the cis compounds coming from the endo approach, especially those in which the substituent at the R_1 position is a methyl group.

The geometry of the transition states is also different from that of the uncatalyzed cases, the bond-forming distances now being larger and the differences among them greater, the largest being the one between the carbonyl oxygen and the end of the diene (O7−C5). This indicates a higher degree of asynchronicity for the catalyzed processes. The study of the synchronicity of the reactions is presented in Table 4. The average variation of the bond index at the transition state ($\delta\beta_{av}$) indicates that all reactions studied occur earlier in the reaction coordinate than in the uncatalyzed cases, with the transition states for the reaction of the alkyl-substituted vinyl allenes **B** and **C** (0.28−0.29) occurring earlier than the corresponding ones for the hydrogen-substituted vinyl allene **A** (0.32−0.33). Slightly larger values were found for the exo approaches. Examination of the individual variation of the bond index for each bond involved in the reaction ($\delta\beta_i$) shows values similar to those found for the uncatalyzed process for the bonds involved in the formation of the C2−C6 bond (C2−C3, C2−C6, and C6−O7), whereas the remainder of the bonds show smaller values. Those results give global asynchronicities of 0.78 for the endo and 0.77 for the exo approaches for the case of vinyl allene **A**, which may be described as highly asynchronous, and

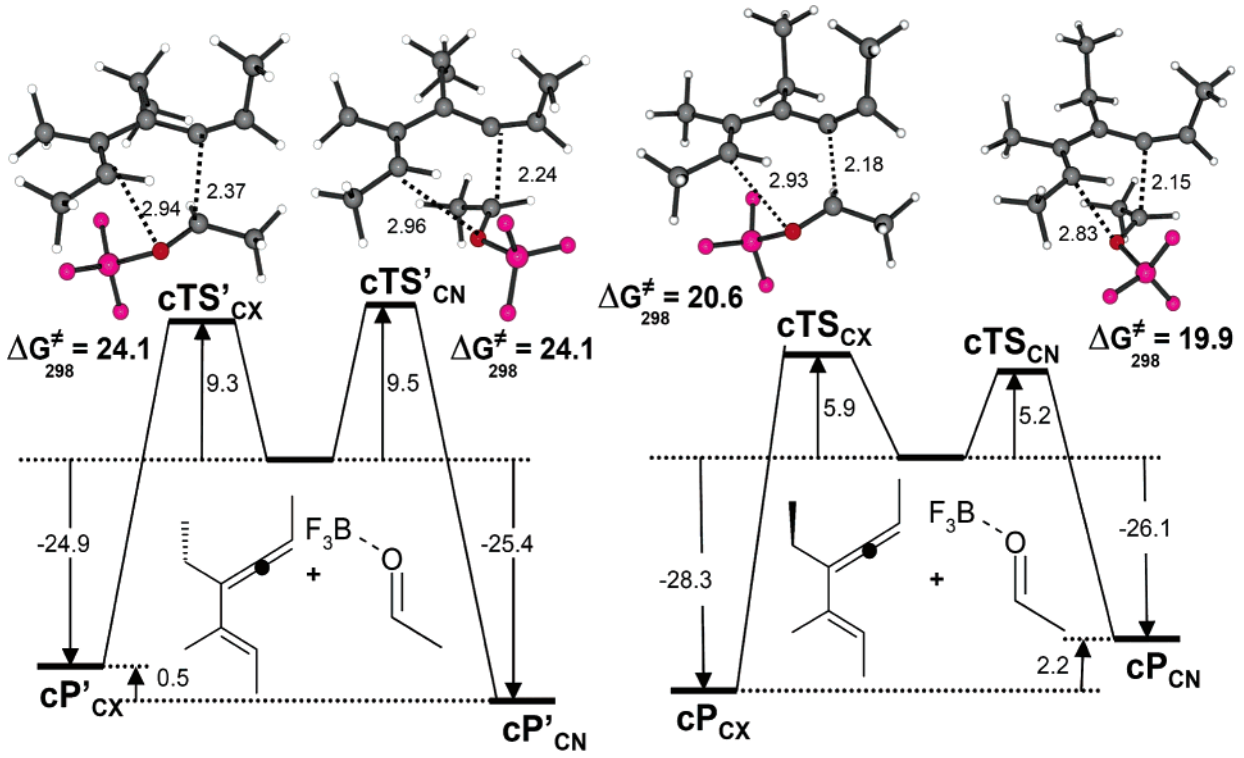


FIGURE 4. Calculated reaction profiles for the reactions of vinyl allene **C** with BF_3-complexed acetaldehyde in the two conformations of the ethyl group. Relevant distances are in Å, and activation energies, Gibbs activation energies, and reaction energies are in kcal/mol.

TABLE 4. Bond Order Variation at the Transition State for Each Bond Involved ($\delta\beta_i$), Average Bond Order Variation at the Transition State ($\delta\beta_{av}$), and Synchronicities (sy) for Each Transition State Calculated for the Catalyzed Reactions[a]

transition state	δB_i						$\delta\beta_{av}$	sy
	O_7-C_6	C_6-C_2	C_2-C_3	C_3-C_4	C_4-C_5	C_5-O_7		
cTS$_{AN}$	0.43	0.38	0.51	0.27	0.27	0.08	0.32	0.78
cTS$_{AX}$	0.46	0.39	0.54	0.28	0.27	0.07	0.33	0.77
cTS$_{BN}$	0.39	0.34	0.46	0.21	0.22	0.06	0.28	0.75
cTS$_{BX}$	0.42	0.35	0.49	0.21	0.22	0.05	0.28	0.74
cTS$_{CN}$	0.40	0.34	0.47	0.22	0.22	0.06	0.28	0.75
cTS$_{CX}$	0.42	0.35	0.47	0.21	0.22	0.05	0.29	0.74
cTS$_{DN}$	0.36	0.33	0.47	0.23	0.23	0.06	0.28	0.77
cTS$_{DX}$	0.39	0.35	0.49	0.22	0.23	0.05	0.29	0.75

[a] The arbitrary numbering presented in Scheme 8 is used.

even smaller values for vinyl allenes **B** and **C** (0.75 for the endo approach and 0.74 for the exo one).

The second-order perturbation analysis performed on the transition states is quite different from the one performed in the uncatalyzed reactions. Thus, the C2−C3 double bond (π_{2-3}) is not found in the NBO analysis. Instead, two p orbitals of similar energy are located on those atoms and labeled LP(C2) and LP*(C3), and the donation from LP(C2) to the antibonding orbital of the carbonyl double bond π^*_{6-7} is precisely the most important one in all catalyzed cases studied. The high value of this donation contrasts with the smaller ones found for the interactions of the carbonyl π orbitals and the C4−C5 double bond, and this difference agrees with the higher asynchronicity found in this catalyzed process. The interaction of the C1−C2 double bond of the allene and the carbonyl group is smaller than in the uncatalyzed process, probably because of the earlier transition state in which the distortion of the allene is not large enough to allow a good interaction between the corresponding orbitals.

The natural population analysis performed using the NBO method indicates that the net charge transfer in the transition state from the vinyl allene to the heterodienophile is quite similar in all cases, being 0.34 and 0.36 e for the endo and exo approaches of vinyl allene **A**, 0.32 and 0.33 e for **B**, and 0.32 and 0.34 e for the corresponding endo and exo approaches of the vinyl allene **C** to the aldehyde−BF_3 complex, which is much larger that those found for the uncatalyzed reactions. All these data also reinforce the idea that the reaction of vinyl allenes and aldehydes under BF_3 catalysis occurs through a highly polar transition state somewhat zwitterionic in character, similar to a nucleophilic attack by the central carbon of the allene on the carbonyl group in the early stages of the process.

Another observation made during the experimental work was the lack of reactivity of vinyl allene **20**, which bears no substituents at the terminal allene carbon, toward dienophiles. Only decomposition was obtained in all reactions assayed. This could be due to the high lability of the vinyl allene which decomposes under the reaction conditions as indicated above or be due to the importance of the substituents at the terminal carbon of the allene. Computational studies identical to those described above, using **D** as the model, were carried out, and it was found that the HOMO of **D** is lower in energy than any of the others calculated,[27] which does not correlate with the activation energies found (Figure 5).

The energies of activation are midway between those found for the reactions of **A** and **B**, and in this case, the endo transition state (**cTS$_{DN}$**) is slightly higher than the exo one (**cTS$_{DX}$**), although for Gibbs activation energies this situation is reversed, and the values are closer to those found for the reaction of **B**. Both approaches, endo and exo, present early transition states with bond-forming distances similar to those calculated for **cTS$_{BX}$** and **cTS$_{BN}$** and low synchronicities (Table 4). The net

TABLE 5. Second-Order Perturbation Energies for the Interaction between Donor and Acceptor π Orbitals at the Transition States of the Studied Catalyzed Reactions[a]

donor	acceptor	cTS_{AN}	cTS_{AX}	cTS_{BN}	cTS_{BX}	cTS_{CN}	cTS_{CX}	cTS_{DN}	cTS_{DX}
LP(C2)	π^*_{6-7}	195.08	194.49	159.05	152.93	163.14	154.82	145.83	151.29
π_{6-7}	LP(C2)[b]	11.01	10.63	8.30	6.71	8.51	6.68	8.03	6.95
π_{4-5}	LP*(C3)[b]			51.58	51.23	50.85	51.00	53.66	52.30
LP*(C3)[b]	π^*_{4-5}	29.30		27.81	27.77	27.97	28.25	27.80	28.01
π_{6-7}	π^*_{4-5}	0.35		0.29	0.20	0.29	0.20	0.28	0.20
π_{4-5}	π^*_{6-7}	0.59			0.54	0.50	0.56	0.50	0.55
π_{1-2}	π^*_{6-7}	1.13	0.47	0.96		1.07		0.74	0.35
π_{6-7}	π^*_{1-2}	0.59	0.37	0.52	0.28	0.58	0.25	0.41	0.30

[a] The arbitrary numbering presented in Scheme 8 is used. Energies are in kcal/mol and are stabilizing (i.e., negative). No entry indicates a value lower than the threshold of 0.5 kcal used by the program. [b] The orbitals denoted, LP(C2) and LP*(C3), are semi-occupied.

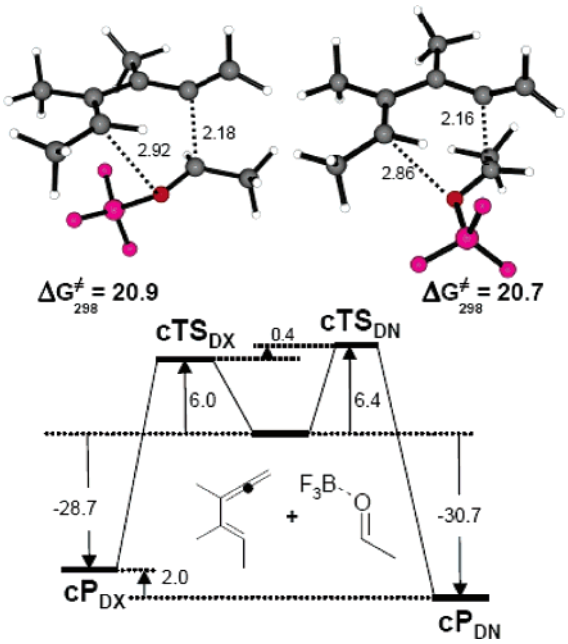


FIGURE 5. Calculated reaction profiles for the reactions of vinyl allene **D** with BF_3-complexed acetaldehyde. Relevant distances are in Å, and activation energies, Gibbs activation energies, and reaction energies are in kcal/mol.

charge transfers from the vinyl allene to the BF_3−acetaldehyde complex in both approaches (0.31 e for the endo and 0.34 e for the exo) are also similar to those found for **B**, and the second-order perturbation analysis is also quite similar in both cases (Table 5). All these data seem to indicate that **D** should be somewhat less reactive than vinyl allene **B** in a catalyzed reaction, but they do not clarify if the lack of results found experimentally is due to the higher activation energy or to its lability. These studies also indicate that the presence of the substituents at the terminal position of the allene is not as important for the success of the reaction as the ones at the inner carbon of the allene.

Conclusions

In conclusion, we have studied the reaction of vinyl allenes with aldehydes under Lewis acid catalysis and have found that the substitution pattern on the allene is important for its success. The regio- and facial selectivity are high, but an endo/exo mixture is obtained in most cases. The mechanism of the reaction was studied computationally using density functional theory, concluding that in the uncatalyzed case, the reaction is pericyclic, but when BF_3 is included as a Lewis acid, the reaction takes place through a highly polar transition state. Endo/exo mixtures are expected in all cases studied.

Experimental Section

(±)-Diethyl-3-methylene-6,7,8,8a-tetrahydrocinnoline-1,2-(3*H*,5*H*)-dicarboxylate (3). To a suspension of PPh_3 (5.6 g, 21.3 mmol) and DEAD (3.2 mL, 20.3 mmol) in THF (43 mL) at −15 °C was slowly added a solution of propargyl alcohol **1** (2.41 g, 17.7 mmol) in THF (7 mL). After 10 min, 2-nitrobenzenesulfonylhydrazine (4.6 g, 21.2 mmol) in THF (25 mL) was added via cannula. The reaction mixture was allowed to warm to rt and was stirred for 7 h. Then it was poured over pentane (50 mL), and the organic layer was washed with cold water (5 × 150 mL), dried (Na_2SO_4), and concentrated. Flash column chromatography (8:2 hexane/EtOAc) afforded 820 mg of compound **3** (2.8 mmol, 16%): amorphous orange solid; ^{1}H NMR (400 MHz, $CDCl_3$, 330 K) δ 5.80 (s, 1H), 5.21 (s, 1H), 4.88 (s, 1H), 4.51 (bs, 1H), 4.17 (m, 4H), 2.30 (m, 1H), 2.10 (m, 2H), 1.84 (m, 2H), 1.54−1.46 (m, 3H), 1.25 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 330 K) δ 154.2, 153.2, 141.6, 137.4, 116.3, 105.6, 62.1, 34.1, 31.9, 28.0, 25.0, 14.3, 14.2; IR ($CHCl_3$) 1700 cm^{-1}; MS (EI) *m*/*z* 294 (M$^+$, 17), 221 (39), 193 (11), 177 (8), 149 (100). HRMS (EI) *m*/*z*: calcd for $C_{15}H_{22}N_2O_4$, 294.1579; found, 294.1587.

(±)-(3-Cyclohexenylpropa-1,2-dienyl)benzene (12). To a stirred suspension of $LiAlH_4$ (815 mg, 21.4 mmol) and $AlCl_3$ (959 mg, 7.19 mmol) in diethyl ether (30 mL) at −15 °C under argon was slowly added a solution of propargyl alcohol **11** (2.28 g, 10.74 mmol) in diethyl ether (5 mL). The reaction mixture was allowed to warm to rt and stirred for 18 h. Then it was quenched by the successive addition of H_2O (1.8 mL), 10% NaOH (1.8 mL), and H_2O (5.3 mL) at 0 °C. The reaction mixture was diluted with ether, filtered through Celite, and concentrated. Purification of the residue by column chromatography (hexane) gave **12** (509 mg, 24%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4−7.17 (m, 5H), 6.39 (d, J = 6.2 Hz, 1H), 6.25 (d, J = 6.4 Hz, 1H), 5.77 (bs, 1H), 2.2−1.99 (m, 4H), 1.77−1.54 (m, 4H); IR ($CHCl_3$) 2900, 1940, 1585, 1488 cm^{-1}; MS (EI) *m*/*z* 196 (M$^+$, 89), 181 (21), 138 (98). HRMS (EI) *m*/*z*: calcd for $C_{15}H_{16}$, 196.1252; found, 196.1375.

(±)-(*E*)-Diethyl-3-benzylidene-6,7,8,8a-tetrahydrocinnoline-1,2(3*H*,5*H*)-dicarboxylate (13). We used a procedure identical to that described for the preparation of **3** from **1** to afford a mixture of vinyl allene **12** (241 mg, 10%) and the title compound **13** (690 mg, 15%) as an amorphous orange solid from the propargyl alcohol **11** (2.6 g, 12.3 mmol); ^{1}H NMR (400 MHz, $CDCl_3$, 330 K) δ 7.76 (m, 2H), 7.24−7.14 (m, 3H), 6.69 (s, 1H), 6.27 (bs, 1H), 6.18 (bs, 1H), 4.13 (m, 2H), 3.96 (m, 2H), 2.18 (m, 2H), 1.93 (m, 2H), 1.51−1.42 (m, 4H), 1.08 (t, J = 7.03 Hz, 3H), 0.97 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 330 K) δ 155.4, 137.4, 135.0, 128.4, 128.1, 127.6, 127.4, 120.6, 88.9, 82.2, 62.4, 61.2, 55.2, 29.1, 25.4, 22.2, 21.4, 14.0, 13.9; MS (EI) *m*/*z* 370 (M$^+$, 0.19), 341 (0.34), 282 (0.85), 196 (17), 195 (100). HRMS (EI) *m*/*z*: calcd for $C_{21}H_{26}N_2O_4$, 370.1892; found, 370.1892.

(±)-(*E*)-Diethyl-3-ethylidene-6,7,8,8a-tetrahydrocinnoline-1,2-(3*H*,5*H*)-dicarboxylate (6) and (*Z*)-Diethyl-3-ethylidene-6,7,8,-8a-tetrahydrocinnoline-1,2(3*H*,5*H*)-dicarboxylate (6). To a stirred solution of vinyl allene **5** (150 mg, 1.13 mmol) in diethyl ether (4 mL) at −78 °C was slowly added DEAD (0.18 mL, 1.13 mmol).

The reaction mixture was allowed to warm to rt and was stirred for 5 h. Then it was diluted with pentane (10 mL), poured over cold water, and extracted with diethyl ether (4 × 15 mL). After drying (Na_2SO_4), concentration, and flash chromatography (8:2 hexane/EtOAc), an *E*:*Z* mixture of (1:1) compound **6** was obtained (209 mg, 0.68 mmol, 60%) as an amorphous orange solid. (***E*-6**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.11 (s, 1H), 5.63 (bs, 1H), 4.48 (bs, 1H), 4.26−4.00 (m, 4H), 2.40−2.26 (m, 1H), 2.20−1.98 (m, 2H), 1.90−1.68 (m, 1H), 1.78 (d, J = 7.7 Hz, 3H), 1.67−1.36 (m, 4H), 1.25 (t, J = 7.0 Hz, 6H); IR ($CHCl_3$) 1700 cm^{-1}; MS (EI) *m*/*z* 308 (M^+, 19), 293 (49), 249 (8), 235 (78), 221 (36), 163 (100). HRMS (EI) *m*/*z*: calcd for $C_{16}H_{24}N_2O_4$, 308.1736; found, 308.1693. (***Z*-6**): ^{1}H NMR (400 MHz, $CDCl_3$, 328 K) δ 5.81 (s, 1H), 5.26 (q, J = 7.07 Hz, 1H), 4.43 (bs, 1H), 4.25−4.10 (m, 4H), 2.30−2.22 (m, 1H), 2.13−2.02 (m, 2H), 1.86−1.75 (m, 2H), 1.72 (d, J = 7.7 Hz, 3H), 1.55−1.40 (m, 3H), 1.25 (t, J = 7.0 Hz, 3H), 1.24 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 154.4, 138.5, 132.6, 119.3, 117.0, 62.3, 62.1, 57.9, 34.4, 32.7, 28.1, 25.4, 14.5, 13.5; IR ($CHCl_3$) 1700 cm^{-1}; MS (EI) *m*/*z* 308 (M^+, 21), 293 (36), 249 (6), 235 (51), 221 (32), 163 (100). HRMS (EI) *m*/*z*: calcd for $C_{16}H_{24}N_2O_4$, 308.1736; found, 308.1669.

3-Cyclohexenylprop-2-ynyl-benzoate (14). To a stirred solution of **1** (4.8 g, 35.0 mmol) in THF (200 mL) at −78 °C under argon was added dropwise *n*-BuLi (21.8 mL, 1.6 M in hexanes, 35 mmol). The reaction mixture was kept at this temperature for 40 min and was stirred further for 5 min at 0 °C. The reaction mixture was then cooled to −78 °C, benzoyl chloride (4.4 mL, 38.5 mmol) was added, and the reaction mixture was allowed to reach room temperature. The mixture was stirred for 3 h, and a saturated aqueous ammonium chloride solution was added. The mixture was then extracted with diethyl ether. The combined organic layers were washed with a saturated aqueous sodium chloride solution, dried ($MgSO_4$), and concentrated. Flash column chromatography (97:3 hexane/EtOAc) afforded 5.88 g of compound **14** (24.5 mmol, 70%): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.9 Hz, 2H), 7.57 (t, J = 7.0 Hz, 1H), 7.45−7.41 (m, 2H), 6.17 (bs, 1H), 5.04 (s, 2H), 2.12−2.08 (m, 4H), 1.63−1.56 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 136.3, 133.1, 129.7, 129.6, 128.3, 119.8, 88.4, 80.2, 53.4, 28.8, 25.5, 22.1, 21.3; IR ($CHCl_3$) 2900, 2200, 1700, 1590 cm^{-1}.

1-(Penta-1,2-dien-3-yl)cyclohex-1-ene (20). Following the procedure previously described,[9] the propargyl benzoate **14** (2.0 g, 8.33 mmol) was converted into the title compound **20** (757 mg, 61%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72 (bs, 1H), 4.93 (bs, 2H), 2.20−2.11 (m, 6H), 1.70−1.56 (m, 4H), 1.06 (t, J = 9.8 Hz, 3H); IR ($CHCl_3$) 2900, 1925 cm^{-1}.

(±)-(3-Cyclohexenylpenta-1,2-dienyl)benzene (22). Following the procedure previously described,[9] the propargyl benzoate **16** (2.3 g, 7.27 mmol) was converted into the title compound **22** (1.23 g, 75%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.16 (m, 5H), 6.40 (bs, 1H), 5.85 (bs, 1H), 2.38−2.06 (m, 6H), 1.68−1.56 (m, 4H), 1.10 (t, J = 9.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 135.6, 132.6, 128.5, 126.6, 126.4, 122.8, 113.6, 98.0, 27.3, 26.0, 22.9, 22.5, 21.9, 12.5; IR ($CHCl_3$) 2900, 1915, 1585, 1480 cm^{-1}; MS (EI) *m*/*z* 224 (M^+, 90), 209 (17), 195 (53), 181 (20), 165 (98). HRMS (EI) *m*/*z*: calcd for $C_{17}H_{20}$, 224.1565; found, 224.1569.

1-(5-Methylhexa-3,4-dien-3-yl)cyclohex-1-ene (24). Following the procedure previously described,[9] the propargyl benzoate **17** (1.23 g, 4.6 mmol) was converted into the title compound **24** (522 mg, 64%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (bs, 1H), 2.13 (m, 4H), 2.04 (m, 2H), 1.71 (s, 6H), 1.65−1.55 (m, 4H), 0.99 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 134.2, 120.9, 107.1, 97.9, 27.3, 25.8, 23.0, 22.5, 21.8, 20.7, 12.4; IR ($CHCl_3$) 2900, 1940, 1600 cm^{-1}.

General Experimental Procedure for the Reaction of Vinyl Allenes and Aldehydes. To a stirred solution of the aldehyde (1.5 equiv) and boron trifluoride etherate (1.1 equiv) in diethyl ether (0.15 M) at 0 °C under N_2 atmosphere was added, after 15 min, the vinyl allene (1.0 equiv). The reaction mixture was stirred at room temperature (12−48 h), triethylamine (2.5 equiv) and water were added, and the reaction mixture was extracted with diethyl ether. Drying ($MgSO_4$) and concentration afforded crude products. Flash column chromatography on silica gel (98:2 hexane/EtOAc) gave the products in the yields indicated.

(2*R,4*R**,6*R**,*Z*)-5-(Cyclohexenylmethylene)-2,4-diethyl-6-methyl-1,3-dioxane (9).** We followed the general procedure for the reaction of vinyl allenes with aldehydes described above. Vinyl allene **5** (100 mg, 0.75 mmol), propionaldehyde **7** (0.08 mL, 1.12 mmol), and BF_3·Et_2O (1.1 equiv), after 12 h, provided compound **9** (28 mg, 15%) as an amorphous solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 (s, 1H), 5.50 (s, 1H), 4.93 (t, J = 5.3 Hz, 1H), 4.75 (dd, J = 10.8, 4.1 Hz, 1H), 4.46 (q, J = 6.2 Hz, 1H), 2.22 (m, 1H), 2.05 (m, 4H), 1.66−1.53 (m, 6H), 1.50−1.43 (m, 1H), 1.35 (d, J = 6.2 Hz, 3H), 1.02−0.92 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 133.7, 126.6, 125.6, 95.9, 74.8, 71.1, 29.1, 28.2, 25.5, 24.4, 22.7, 22.0, 17.6, 10.2, 8.7; IR ($CHCl_3$) 1590, 1445 cm^{-1}; MS (EI) *m*/*z* 250 (M^+, 1), 221 (3), 205 (2), 192 (39), 175 (22). HRMS (EI) *m*/*z*: calcd for $C_{16}H_{26}O_2$, 250.1932; found, 250.1943.

(2*R,4*R**,6*R**,Z)-5-(Cyclohexenylmethylene)-2,4-diisopropyl-6-methyl-1,3-dioxane (10).** We followed the general procedure for the reaction of vinyl allenes with aldehydes described above. Vinyl allene **5** (100 mg, 0.75 mmol), isobutyraldehyde **8** (0.10 mL, 1.12 mmol), and BF_3·Et_2O (1.1 equiv), after 20 h, provided compound **10** (46 mg, 22%) as an amorphous solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (s, 1H), 5.67 (bs, 1H), 4.65 (d, J = 6.0 Hz, 1H), 4.52 (d, J = 10.7 Hz, 1H), 4.38 (q, J = 6.1 Hz, 1H), 2.35 (m, 1H), 2.06 (m, 2H), 1.74−1.53 (m, 4H), 1.32 (d, J = 6.2 Hz, 3H), 1.02 (d, J = 6.4 Hz, 3H), 0.94 (m, 3H), 0.93 (m, 6H), 0.76 (d, J = 6.8 Hz, 3H); MS (EI) *m*/*z* 278 (M^+, 0.7), 277 (8), 251 (5), 199 (53), 127 (87), 98 (87), 98 (96), 83 (92), 57 (100). HRMS (EI) *m*/*z*: calcd for $C_{18}H_{30}O_2$, 278.2246; found, 278.2229.

Reaction of Vinyl Allene 18 and Propionaldehyde 7. Following the general procedure, vinyl allene **18** (100 mg, 0.68 mmol), propionaldehyde **7** (0.07 mL, 1.02 mmol), and BF_3·Et_2O (1.1 equiv), after 24 h, provided compounds **26** (88 mg, cis/trans 46:54, 63%), which were isolated after flash chromatography and HPLC as pale yellow oils. **(2*S**,8a*R**,*E*)-3-Ethylidene-4-methyl-2-phenyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*cis*-26).** ^{1}H NMR (400 MHz, C_6D_6) δ 5.41 (q, J = 7.2 Hz, 1H), 4.10 (m, 1H), 3.81 (bs, 1H), 2.66 (d, J = 14.4 Hz, 1H), 2.25−2.22 (m, 1H), 1.99 (s, 3H), 1.84−1.79 (m, 4H), 1.65−1.45 (m, 4H), 1.33−1.08 (m, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 138.5, 137.3, 123.3, 116.3, 77.6, 77.4, 35.3, 27.5, 27.2, 25.0, 24.6, 17.4, 15.4, 10.7; IR ($CHCl_3$) 1440, 1370 cm^{-1}. **(2*R**,8a*R**,*E*)-3-Ethylidene-4-methyl-2-phenyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*trans*-26).** ^{1}H NMR (400 MHz, C_6D_6) δ 5.22 (q, J = 7.3 Hz, 1H), 4.09 (d, J = 13.8 Hz, 2H), 2.68−2.65 (m, 1H), 2.21 (m, 1H), 1.97 (s, 3H), 1.88−1.82 (m, 1H), 1.78 (d, J = 7.3 Hz, 3H), 1.67−1.51 (m, 4H), 1.32−1.15 (m, 3H), 1.06 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 137.4, 137.0, 120.5, 119.3, 80.8, 71.5, 35.2, 27.5, 27.3, 24.8, 24.6, 17.0, 15.1, 10.7; IR ($CHCl_3$) 1450, 1370 cm^{-1}.

Reaction of Vinyl Allene 18 and Isobutyraldehyde 8. Following the general procedure, vinyl allene **18** (100 mg, 0.68 mmol), isobutyraldehyde **8** (0.09 mL, 1.02 mmol), and BF_3·Et_2O (1.1 equiv), after 48 h, provided compound **27** (38 mg, 26%) as a pale yellow oil. **(2*R**,8a*R**,*E*)-3-Ethylidene-2-isopropyl-4-methyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*trans*-27).** ^{1}H NMR (400 MHz, C_6D_6) δ 5.20 (q, J = 7.2 Hz, 1H), 4.05 (m, 1H), 3.67 (d, J = 10.0 Hz, 1H), 2.64 (d, J = 13.6 Hz, 1H), 2.21 (m, 1H), 2.04 (m, 1H), 1.96 (s, 3H), 1.78 (d, J = 7.2 Hz, 3H), 1.66−1.51 (m, 4H), 1.33−1.07 (m, 2H), 1.24 (d, J = 6.4 Hz, 3H), 0.87 (d, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 137.4, 136.5, 120.4, 86.2, 71.6, 35.5, 27.5, 27.5, 24.6, 20.0, 19.7, 17.1, 15.1; IR ($CHCl_3$) 1440, 1370 cm^{-1}; MS (EI) *m*/*z* 220 (M^+, 21), 205 (13), 177 (42), 159 (8), 149 (86). HRMS (EI) *m*/*z*: calcd for $C_{15}H_{24}O$, 220.1827; found, 220.1834.

Reaction of Vinyl Allene 18 and Benzaldehyde 25. Following the general procedure, vinyl allene **18** (100 mg, 0.68 mmol), benzaldehyde **25** (0.10 mL, 1.02 mmol), and $BF_3{\cdot}Et_2O$ (1.1 equiv), after 17 h, provided compounds **28** (131 mg, cis/trans 49:51, 76%), which were isolated after flash chromatography and HPLC as pale yellow oils. **(2*S**,8a*R**,*E*)-3-Ethylidene-4-methyl-2-phenyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*cis*-28).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.62−7.20 (5H), 5.10 (s, 1H), 5.02 (q, J = 7.3 Hz, 1H), 4.22 (m, 1H), 2.69 (d, J = 15.2 Hz, 1H), 2.31 (m, 1H), 2.01 (s, 3H), 1.70−1.58 (m, 3H), 1.64 (d, J = 7.1 Hz, 3H), 1.32−1.20 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 141.0, 139.7, 137.7, 128.3, 127.2, 123.6, 121.1, 79.9, 77.8, 35.2, 27.5, 27.2, 24.5, 17.4, 15.4. **(2*R**,8a*R**,*E*)-3-Ethylidene-4-methyl-2-phenyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*trans*-28).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.62−7.17 (m, 5H), 5.35 (s, 1H), 5.27 (q, J = 7.3 Hz, 1H), 3.97 (m, 1H), 2.50 (d, J = 13.3 Hz, 1H), 2.22 (m, 1H), 2.04 (s, 3H), 1.83 (d, J = 7.3 Hz, 3H), 1.67−1.50 (m, 3H), 1.24−1.12 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 141.2, 138.0, 135.4, 127.7, 127.5, 127.0, 122.4, 121.4, 80.0, 72.0, 34.9, 27.4, 27.1, 24.5, 17.0, 15.3; IR ($CHCl_3$) 1590, 1480, 1440 cm^{-1}; MS (EI) m/z 254 (M$^+$, 36), 239 (33), 225 (21), 211 (8), 197 (7). HRMS (EI) m/z: calcd for $C_{18}H_{22}O$, 254.1670; found, 254.1652.

Reaction of Vinyl Allene 19 and Propionaldehyde 7. Following the general procedure, vinyl allene **19** (100 mg, 0.48 mmol), propionaldehyde **7** (0.05 mL, 0.72 mmol), and $BF_3{\cdot}Et_2O$ (1.1 equiv), after 26 h, provided compounds **29** (63 mg, cis/trans 52:48, 49%), which were isolated after flash chromatography and HPLC as pale yellow oils. **(2*S**,8a*R**,*E*)-3-Benzylidene-2-ethyl-4-methyl-3,5,6,7,8,-8a-hexahydro-2*H*-chromene (*cis*-29).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.39−7.12 (m, 5H), 6.52 (s, 1H), 4.13 (m, 1H), 3.90 (dd, J = 5.4, 7.2 Hz, 1H), 2.57 (m, 1H), 2.28 (m, 1H), 1.88 (m, 2H), 1.69 (s, 3H), 1.62−1.53 (m, 3H), 1.32−1.17 (m, 3H), 1.24 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 139.8, 139.5, 129.5, 127.7, 126.4, 121.1, 77.7, 77.5, 35.5, 27.6, 27.2, 24.9, 24.5, 17.2, 10.6; IR ($CHCl_3$) 1590, 1440 cm^{-1}; MS (EI) m/z 268 (M$^+$, 55.5), 253 (10), 239 (45), 225 (10), 211 (17). HRMS (EI) m/z: calcd for $C_{19}H_{24}O$, 268.1827; found, 268.1807. **(2*R**,8a*R**,*E*)-3-Benzylidene-2-ethyl-4-methyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*trans*-29).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.33−7.12 (m, 5H), 6.32 (s, 1H), 4.21 (t, J = 7.2 Hz, 1H), 4.12 (m, 1H), 2.58 (d, J = 13.8 Hz, 1H), 2.23 (m, 1H), 1.86 (m, 1H), 1.65 (m, 4H), 1.67 (s, 3H), 1.52 (m, 1H), 1.33−1.17 (m, 2H), 1.10 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 139.7, 139.1, 138.6, 129.3, 127.7, 126.4, 124.0, 120.3, 79.8, 72.1, 35.2, 27.7, 27.3, 24.6, 24.5, 16.9, 10.6; IR ($CHCl_3$) 1630, 1585, 1480, 1440 cm^{-1}; MS (EI) m/z 268 (M$^+$, 49), 253 (13), 239 (50), 225 (10.5), 211 (36). HRMS (EI) m/z: calcd for $C_{19}H_{24}O$, 268.1827; found, 268.1818.

Reaction of Vinyl Allene 19 and Isobutyraldehyde 8. Following the general procedure, vinyl allene **19** (100 mg, 0.48 mmol), isobutyraldehyde **8** (0.06 mL, 0.72 mmol), and $BF_3{\cdot}Et_2O$ (1.1 equiv), after 26 h, provided compounds **30** (32 mg, cis/trans 57:43, 24%), which were isolated after flash chromatography and HPLC as pale yellow oils. **(2*S**,8a*R**,*E*)-3-Benzylidene-2-isopropyl-4-methyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*cis*-30).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.37−7.11 (m, 5H), 6.49 (s, 1H), 4.15 (m, 1H), 3.81 (d, J = 6.3 Hz, 1H), 2.58 (d, J = 15.6 Hz, 1H), 2.24 (m, 2H), 1.68 (s, 3H), 1.65−1.57 (m, 3H), 1.31 (d, J = 6.6 Hz, 3H), 1.29−1.19 (m, 3H), 1.16 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 139.5, 139.3, 138.4, 129.4, 127.7, 126.4, 123.4, 122.4, 82.1, 76.7, 35.4, 29.1, 27.6, 26.7, 24.4, 20.8, 17.8, 17.2; IR ($CHCl_3$) 1590, 1440 cm^{-1}; MS (EI) m/z 282 (M$^+$, 32), 253 (11), 239 (89), 225 (16), 211 (88). HRMS (EI) m/z: calcd for $C_{20}H_{26}O$, 282.1983; found, 282.1960. **(2*R**,8a*R**,*E*)-3-Benzylidene-2-isopropyl-4-methyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*trans*-30).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.35−7.11 (m, 5H), 6.30 (s, 1H), 4.09 (m, 1H), 3.82 (d, J = 10.1 Hz, 1H), 2.57 (d, J = 135.6 Hz, 1H), 2.27 (m, 1H), 2.07 (m, 1H), 1.70−1.60 (m, 3H), 1.66 (s, 3H), 1.52 (m, 1H), 1.34−1.17 (m, 2H), 1.26 (d, J = 6.5 Hz, 3H), 0.93 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 140.1, 139.0, 137.7, 129.3, 127.7, 126.4, 125.2, 120.2, 85.5, 72.1, 35.7, 27.7, 27.5, 27.4, 24.6, 19.8, 19.5, 16.8; IR ($CHCl_3$) 1630, 1480, 1440 cm^{-1}; MS (EI) m/z 282 (M$^+$, 37), 239 (100), 211 (95), 184 (29), 169 (24). HRMS (EI) m/z: calcd for $C_{20}H_{26}O$, 282.1983; found, 282.1960.

Reaction of Vinyl Allene 19 and Benzaldehyde 25. Following the general procedure, vinyl allene **19** (100 mg, 0.48 mmol), benzaldehyde **25** (0.07 mL, 0.72 mmol), and $BF_3{\cdot}Et_2O$ (1.1 equiv), after 24 h, provided compounds **31** (112 mg, cis/trans 53:47, 74%), which were isolated after flash chromatography and HPLC as pale yellow oils. **(2*S**,8a*R**,*E*)-3-Benzylidene-4-methyl-2-phenyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*cis*-31).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.66−7.64 (m, 2H), 7.34−7.03 (m, 8H), 6.10 (s, 1H), 5.20 (s, 1H), 4.26 (m, 1H), 2.62 (d, J = 13.8 Hz, 1H), 2.33 (m, 1H), 1.77−1.49 (m, 4H), 1.74 (s, 3H), 1.34−1.22 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 140.9, 140.3, 140.2, 139.0, 129.4, 128.4, 127.7, 127.6, 126.4, 125.2, 123.3, 79.9, 78.1, 35.5, 27.8, 27.3, 24.5, 17.4; IR ($CHCl_3$) 1720, 1590, 1480, 1440 cm^{-1}; MS (EI) m/z 316 (M$^+$, 28), 225 (19), 220 (13), 219 (75), 218 (100). HRMS (EI) m/z: calcd for $C_{23}H_{24}O$, 316.1827; found, 316.1788. **(2*R**,8a*R**,*E*)-3-Benzylidene-4-methyl-2-phenyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*trans*-31).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.65−7.63 (m, 2H), 7.34−7.11 (m, 8H), 6.35 (s, 1H), 5.48 (s, 1H), 4.06 (m, 1H), 2.44 (d, J = 11.6 Hz, 1H), 2.27 (m, 1H), 1.78−1.62 (m, 2H), 1.76 (s, 3H), 1.50 (m, 1H), 1.24−1.15 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 140.6, 138.7, 136.7, 130.2, 129.4, 128.1, 128.0, 127.7, 127.5, 127.2, 126.7, 121.2, 79.3, 72.6, 35.0, 27.7, 27.1, 24.5, 16.9; IR ($CHCl_3$) 1720, 1670, 1590, 1440 cm^{-1}; MS (EI) m/z 316 (M$^+$, 30), 225 (24), 220 (14), 219 (75), 218 (100). HRMS (EI) m/z: calcd for $C_{23}H_{24}O$, 316.1827; found, 316.1791.

Reaction of Vinyl Allene 21 and Propionaldehyde 7. Following the general procedure, vinyl allene **21** (100 mg, 0.62 mmol), propionaldehyde **7** (0.07 mL, 0.93 mmol), and $BF_3{\cdot}Et_2O$ (1.1 equiv), after 48 h, provided compounds **32** (96 mg, cis/trans 70:30, 70%), which were isolated after flash chromatography and HPLC as pale yellow oils. **(2*S**,8a*R**,*E*)-2,4-Diethyl-3-ethylidene-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*cis*-32).** ^{1}H NMR (400 MHz, C_6D_6) δ 5.41 (q, J = 7.4 Hz, 1H), 4.10 (dd, J = 4.9, 11.3 Hz, 1H), 3.79 (t, J = 6.3 Hz, 1H), 2.67 (m, 1H), 2.49−2.45 (m, 2H), 2.22 (m, 1H), 1.81 (d, J = 7.5 Hz, 3H), 1.65−1.54 (m, 4H), 1.38−1.19 (m, 4H), 1.20 (t, J = 7.5 Hz, 3H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 137.4, 136.6, 129.9, 116.0, 78.3, 77.3, 35.5, 27.5, 27.3, 25.1, 24.6, 22.3, 14.8, 14.2, 10.7. **(2*R**,8a*R**,*E*)-2,4-Diethyl-3-ethylidene-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*trans*-32).** ^{1}H NMR (400 MHz, C_6D_6) δ 5.21 (q, J = 7.4 Hz, 1H), 4.08 (m, 2H), 2.66 (d, J = 13.9 Hz, 1H), 2.45 (c, J = 7.4 Hz, 2H), 1.85−1.77 (m, 3H), 1.78 (d, J = 7.4 Hz, 3H), 1.67−1.51 (m, 4H), 1.33−1.08 (m, 2H), 1.05 (t, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 137.1, 135.5, 119.0, 81.5, 71.6, 35.3, 27.7, 27.2, 24.7, 21.8, 14.6, 14.2, 10.7; IR ($CHCl_3$) 2900, 1500, 1425 cm^{-1}; MS (EI) m/z 220 (M$^+$, 15), 191 (100), 177 (5), 163 (16). HRMS (EI) m/z: calcd for $C_{15}H_{24}O$, 220.1827; found, 220.1833.

Reaction of Vinyl Allene 21 and Isobutyraldehyde 8. Following the general procedure, vinyl allene **21** (100 mg, 0.62 mmol), isobutyraldehyde **8** (0.08 mL, 0.93 mmol), and $BF_3{\cdot}Et_2O$ (1.1 equiv), after 22 h, provided compounds **33** (87 mg, cis/trans 74:26, 60%), which were isolated after flash chromatography and HPLC as pale yellow oils. **(2*S**,8a*R**,*E*)-4-Ethyl-3-ethylidene-2-isopropyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*cis*-33).** ^{1}H NMR (400 MHz, C_6D_6) δ 5.38 (q, J = 7.3 Hz, 1H), 4.10 (dd, J = 5.1, 11.2 Hz, 1H), 3.66 (d, J = 7.07 Hz, 1H), 2.67 (d, J = 15.8 Hz, 1H), 2.48−2.44 (m, 2H), 2.16−2.11 (m, 2H), 1.80 (d, J = 7.3 Hz, 3H), 1.62−1.54 (m, 4H), 1.30 (d, J = 6.56 Hz, 3H), 1.27−0.97 (m, 2H), 1.08 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 137.1, 135.6, 130.0, 117.6, 83.4, 76.3, 35.5, 29.2, 27.4, 27.0, 24.6, 22.4, 20.7, 18.3, 14.9, 14.3; IR ($CHCl_3$) 1585, 1440 cm^{-1}. **(2*R**,8a*R**,*E*)-4-Ethyl-3-ethylidene-2-isopropyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*trans*-33).** ^{1}H NMR (400 MHz, C_6D_6) δ 5.21 (q, J = 7.4 Hz, 1H), 4.05 (dd, J = 4.7, 11.2 Hz, 1H), 3.66 (d, J =

10.2 Hz, 1H), 2.65 (d, J = 13.7 Hz, 1H), 2.45 (q, J = 7.4 Hz, 2H), 2.23 (m, 1H), 2.01 (m, 1H), 1.78 (d, J = 7.4 Hz, 3H), 1.66−1.58 (m, 3H), 1.33−1.16 (m, 3H), 1.25 (d, J = 6.5 Hz, 3H), 1.05 (t, J = 7.4 Hz, 3H), 0.88 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 137.5, 134.7, 120.2, 86.7, 71.7, 35.6, 27.7, 27.4, 27.3, 24.7, 21.9, 19.8, 19.6, 14.7, 14.1; IR ($CHCl_3$) 2900, 1440 cm^{-1}; MS (EI) m/z 234 (M^+, 45), 205 (71), 191 (80), 163 (100). HRMS (EI) m/z: calcd for $C_{16}H_{26}O$, 234.1983; found, 234.2033.

Reaction of Vinyl Allene 21 and Benzaldehyde 25. Following the general procedure, vinyl allene **21** (100 mg, 0.62 mmol), benzaldehyde **25** (0.09 mL, 0.93 mmol), and BF_3·Et_2O (1.1 equiv), after 24 h, provided compounds **34** (103 mg, cis/trans 64 :36, 62%), which were isolated after flash chromatography and HPLC as pale yellow oils. **(2*S**,8a*R**,*E*)-4-Ethyl-3-ethylidene-2-phenyl-3,5,6,7,8,-8a-hexahydro-2*H*-chromene (*cis*-34).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.61−7.14 (m, 5H), 5.07 (s, 1H), 5.03 (q, J = 7.6 Hz, 1H), 4.22 (dd, J = 4.8, 11.1 Hz, 1H), 2.70 (d, J = 14 Hz, 1H), 2.51−2.43 (m, 2H), 2.33 (m, 1H), 1.68−1.55 (m, 2H), 1.65 (d, J = 7.4 Hz, 3H), 1.34−0.86 (m, 4H), 1.12 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 141.0, 138.0, 130.2, 128.3, 127.8, 127.2, 120.7, 80.5, 77.9, 35.3, 27.6, 27.4, 24.6, 22.4, 14.7, 14.4; IR ($CHCl_3$) 1670, 1440 cm^{-1}; MS (EI) m/z 268 (M^+, 23), 253 (100), 239 (45), 225 (65). HRMS (EI) m/z: calcd for $C_{19}H_{24}O$, 268.1827; found, 268.1829. **(2*R**,8a*R**,*E*)-4-Ethyl-3-ethylidene-2-phenyl-3,5,6,7,8,-8a-hexahydro-2*H*-chromene (*trans*-34).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.68−7.07 (m, 5H), 5.37 (s, 1H), 5.27 (q, J = 7.4 Hz, 1H), 4.02 (dd, J = 11.3, 4.8 Hz, 1H), 2.56−2.48 (m, 2H), 2.27 (m, 1H), 1.87 (d, J = 7.4 Hz, 3H), 1.70−1.52 (m, 3H), 1.24−0.96 (m, 4H), 1.16 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 141.2, 138.3, 133.6, 128.0, 127.3, 127.0, 122.0, 80.4, 71.9, 35.1, 27.4, 27.2, 24.5, 22.0, 14.7, 14.4; IR ($CHCl_3$) 1590, 1480, 1440 cm^{-1}; MS (EI) m/z 268 (M^+, 36), 253 (22), 239 (66), 225 (10), 211 (17). HRMS (EI) m/z: calcd for $C_{19}H_{24}O$, 268.1827; found, 268.1790.

Reaction of Vinyl Allene 22 and Propionaldehyde 7. Following the general procedure, vinyl allene **22** (100 mg, 0.45 mmol), propionaldehyde **7** (0.05 mL, 0.67 mmol), and BF_3·Et_2O (1.1 equiv), after 24 h, provided compounds **35** (69 mg, cis/trans 73:27, 54%), which were isolated after flash chromatography and HPLC as pale yellow oils. **(2*S**,8a*R**,*E*)-3-Benzylidene-2,4-diethyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*cis*-35).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.43−7.11 (m, 5H), 6.51 (s, 1H), 4.16 (dd, J = 4.9, 11.1 Hz, 1H), 3.91 (t, J = 6.4 Hz, 1H), 2.63 (d, J = 15.6 Hz, 1H), 2.59−2.21 (m, 3H), 1.91−1.84 (m, 2H), 1.69−1.58 (m, 4H), 1.33−1.20 (m, 2H), 1.23 (t, J = 7.3 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 139.3, 138.9, 137.9, 130.6, 129.2, 127.9, 126.4, 121.0, 78.4, 77.7, 35.7, 27.6, 27.4, 25.0, 24.6, 22.0, 14.3, 10.6; IR ($CHCl_3$) 1590, 1440 cm^{-1}; MS (EI) m/z 282 (M^+, 21), 267 (14), 253 (74), 239 (19), 225 (23). HRMS (EI) m/z: calcd for $C_{20}H_{26}O$, 282.1983; found, 282.2031. **(2*R**,8a*R**,*E*)-3-Benzylidene-2,4-diethyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*trans*-35).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.38−7.10 (m, 5H), 6.33 (s, 1H), 4.20 (t, J = 7.2 Hz, 1H), 4.10 (dd, J = 4.9, 11.1 Hz, 1H), 2.58 (d, J = 13.8 Hz, 1H), 2.26−2.23 (m, 3H), 1.85 (m, 1H), 1.70−1.59 (m, 4H), 1.50−1.18 (m, 3H), 1.10 (t, J = 7.4 Hz, 3H), 0.78 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 139.0, 138.9, 136.9, 129.1, 127.8, 126.5, 124.1, 80.4, 72.3, 35.4, 27.6, 27.5, 24.7, 24.2, 21.4, 14.1, 10.5; MS (EI) m/z 282 (M^+, 28), 267 (6), 253 (100), 235 (11), 225 (33). HRMS (EI) m/z: calcd for $C_{20}H_{26}O$, 282.1983; found, 282.1986.

Reaction of Vinyl Allene 22 and Isobutyraldehyde 8. Following the general procedure, vinyl allene **22** (100 mg, 0.45 mmol), isobutyraldehyde **8** (0.06 mL, 0.67 mmol), and BF_3·Et_2O (1.1 equiv), after 26 h, provided compounds **36** (48 mg, cis/trans 66: 34, 36%), which were isolated after flash chromatography and HPLC as a pale yellow oil. **(2*S**,8a*R**,*E*)-3-Benzylidene-4-ethyl-2-isopropyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*cis*-36).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.46−7.07 (m, 5H), 6.46 (s, 1H), 4.18 (dd, J = 4.9, 11.1 Hz, 1H), 3.76 (d, J = 7.7 Hz, 1H), 2.64−2.60 (m, 1H), 2.37−2.19 (m, 4H), 1.63−1.58 (m, 4H), 1.32 (d, J = 6.5 Hz, 3H), 1.26−0.93 (m, 2H), 1.12 (d, J = 6.5 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); MS (EI) m/z 296 (M^+, 16), 295 (59), 285 (19), 267 (18), 251 (100). HRMS (EI) m/z: calcd for $C_{21}H_{28}O$, 296.2140; found, 296.2135. **(2*R**,8a*R**,*E*)-3-Benzylidene-4-ethyl-2-isopropyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*trans*-36).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.39−7.10 (m, 5H), 6.31 (s, 1H), 4.09 (dd, J = 4.9, 11.2 Hz, 1H), 3.79 (d, J = 10.3 Hz, 1H), 2.57 (d, J = 13.6 Hz, 1H), 2.29−2.21 (m, 2H), 2.05 (m, 1H), 1.69−1.62 (m, 3H), 1.50−1.49 (m, 1H), 1.28−1.19 (m, 3H), 1.25 (d, J = 6.5 Hz, 3H), 0.97 (d, J = 6.6 Hz, 3H), 0.79 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 139.4, 139.0, 136.2, 129.1, 128.0, 127.8, 126.4, 125.3, 85.8, 72.3, 35.8, 27.7, 27.6, 27.2, 24.7, 21.5, 19.5, 19.3, 14.0; IR ($CHCl_3$) 1590, 1440 cm^{-1}; MS (EI) m/z 296 (M^+, 51), 267 (16), 253 (100), 235 (10), 225 (74). HRMS (EI) m/z: calcd for $C_{21}H_{28}O$, 296.2140; found, 296.2112.

Reaction of Vinyl Allene 22 and Benzaldehyde 25. Following the general procedure, vinyl allene **22** (100 mg, 0.45 mmol), benzaldehyde **25** (0.07 mL, 0.67 mmol), and BF_3·Et_2O (1.1 equiv), after 24 h, provided compounds **37** (59 mg, cis/trans 75:25, 40%), which were isolated after flash chromatography and HPLC as pale yellow oils. **(2*S**,8a*R**,*E*)-3-Benzylidene-4-ethyl-2-phenyl-3,5,6,7,8,-8a-hexahydro-2*H*-chromene (*cis*-37).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.67−7.02 (m, 10H), 6.11 (s, 1H), 5.19 (s, 1H), 4.29 (dd, J = 4.8, 11.5 Hz, 1H), 2.64 (d, J = 14.6 Hz, 1H), 2.39−2.35 (m, 1H), 2.28 (q, J = 7.3 Hz, 2H), 1.79−1.57 (m, 3H), 1.63−1.20 (m, 3H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 140.1, 139.4, 139.2, 139.0, 130.8, 129.1, 128.3, 127.9, 127.7, 127.5, 126.5, 124.9, 80.5, 78.4, 35.6, 27.6, 27.5, 24.6, 22.1, 14.2; MS (EI) m/z 330 (M^+, 21), 301 (6), 239 (34), 232 (100). HRMS (EI) m/z: calcd for $C_{24}H_{26}O$, 330.1983; found, 330.1959. **(2*R**,8a*R**,*E*)-3-Benzylidene-4-ethyl-2-phenyl-3,5,6,7,8,8a-hexahydro-2*H*-chromene (*trans*-37).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.73−7.10 (m, 10H), 6.34 (s, 1H), 5.47 (s, 1H), 4.19 (dd, J = 4.9, 11.4 Hz, 1H), 2.46 (d, J = 14.3 Hz, 1H), 2.34−2.25 (m, 3H), 1.75 (m, 1H), 1.63 (m, 1H), 1.50 (m, 1H), 1.26−1.12 (m, 3H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 140.5, 140.0, 138.9, 135.5, 129.1, 128.0, 127.8, 127.3, 127.2, 126.7, 126.6, 79.4, 72.9, 35.2, 27.7, 27.4, 24.6, 21.7, 14.0; IR ($CHCl_3$) 1590, 1440 cm^{-1}; MS (EI) m/z 330 (M^+, 25), 312 (9), 253 (17), 239 (39), 232 (100). HRMS (EI) m/z: calcd for $C_{24}H_{26}O$, 330.1983; found, 330.1973.

Reaction of Vinyl Allene 24 and Benzaldehyde 25. Following the general procedure, vinyl allene **24** (100 mg, 0.57 mmol), benzaldehyde **25** (0.08 mL, 0.85 mmol), and BF_3·Et_2O (1.1 equiv), after 48 h, provided compound **38** (64 mg, 39%) as a pale yellow oil. **(2*R**,8a*R**)-4-Ethyl-2-phenyl-3-(propan-2-ylidene)-3,5,6,7,8,-8a-hexahydro-2*H*-chromene (*trans*-38).** ^{1}H NMR (400 MHz, C_6D_6) δ 7.43−7.11 (m, 5H), 6.61 (s, 1H), 4.06 (m, 1H), 2.59 (d, J = 13.6 Hz, 1H), 2.26 (m, 2H), 2.17 (m, 1H), 1.71−1.51 (m, 4H), 1.64 (s, 3H), 1.42 (s, 3H), 1.42−1.21 (m, 2H), 0.67 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 142.0, 139.7, 138.8, 129.3, 127.5, 126.9, 126.5, 120.2, 75.6, 35.6, 26.8, 26.0, 24.8, 24.0, 22.5, 13.9; IR ($CHCl_3$) 1590, 1480, 1440, 1370 cm^{-1}; MS (EI) m/z 282 (M^+, 64), 267 (31), 253 (30). HRMS (EI) m/z: calcd for $C_{20}H_{26}O$, 282.1983; found, 282.1940.

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Supporting Information Available: General methods, NMR spectra for all new compounds, and tables including total energies and Cartesian coordinates for all stationary points discussed in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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