Synthesis of New Captodative Alkenes: Alkyl 2-Aroyloxy Acrylates − Structure, and Reactivity in Diels−Alder Cycloadditions

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Novel captodative alkenes, namely the methyl and ethyl esters of 2-aroyloxyacrylic acids, **2** and **3**, have been prepared. Their reactivity and selectivity have been evaluated in Diels–Alder cycloadditions with unsymmetrical dienes, which generate the corresponding adducts with high regioselectivity. No significant stereoselectivity was observed in the reaction with cyclopentadiene (**9**), although Lewis acid catalysis improved the *exo*/*endo* isomeric ratio. Structural and electron spectroscopic studies of these alkenes are supported by MO calculations. FMO theory accounts for the regioselectivity observed with isoprene (**7**), and the reactivity seen in Diels–Alder additions correlates with the stabilization of the relevant vacant π^* MO in these alkenes, which is mainly due to the electron-withdrawing group.

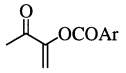
Introduction

The Diels−Alder cycloaddition reaction has been traditionally considered as a powerful method in the evaluation of the structural and electronic factors that control chemical reactivity and selectivity in pericyclic processes.[1] Alder's rule has demonstrated its effectiveness in predicting reactivity in Diels−Alder additions.[2] It establishes that the rate of cycloaddition increases when the diene bears electron-releasing groups and the dienophile bears electron-withdrawing groups, whereas it is retarded with dienophiles bearing electron-donating groups.[1a][2d] This behavior has been rationalized in terms of frontier molecular orbital (FMO) theory.[3]

Owing to the opposite electronic demands displayed by their geminally substituted functional groups, captodative alkenes have attracted particular interest in pericyclic cycloadditions.[4] The captodative alkenes 3-aroyloxy-3-buten-2-ones **1** have been shown to be highly reactive,[5] stereoselective,[6] and regioselective[7] in Diels−Alder and 1,3-dipolar cycloadditions.[8] Furthermore, they have also proved to be versatile synthons in natural product synthesis.[9]

As an extension of our ongoing interest in understanding the structural and electronic factors responsible for the high reactivity and selectivity of captodative alkenes in cycloaddition reactions, we present herein a new class of captodative alkenes, namely the methyl and ethyl esters of 2-aroyloxyacrylic acids, **2** and **3**,[10] as well as a study of their behavior in Diels−Alder additions to unsymmetrical and carbocyclic dienes.

In order to rationalize such behavior, a structural and theoretical study of these molecules has been undertaken, including gas-phase measurements by ultraviolet photoelectron spectroscopy (UPS) and electron transmission spectroscopy (ETS). The latter two techniques measure, respectively, the ionization energies (*IE*s) from the occupied MO′s, and the energies (vertical attachment energies, VAEs) of electron attachment to the vacant MO′s, in other words the negative of the vertical electron affinities (*VEA*s). The two complementary sets of data can be used to build a picture of the frontier orbital structure. The major limitation is that the formation of anion states stable with respect to the neutral molecule cannot be observed by ETS, i.e. positive *VEA*s cannot be measured. Hartree−Fock (HF) calculations using the 6−31G* basis set have been carried out to evaluate the localization properties of the occupied and vacant MO′s involved in reactivity and the relative energies of the vacant MO′s associated with stable anion states that are not accessible experimentally.



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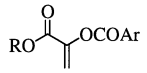

2, R = Me
3, R = Et

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Results

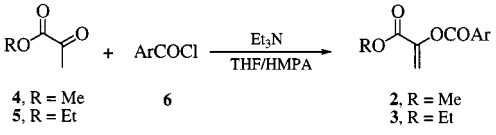
Preparation of the Captodative Alkenes, Alkyl 2-Aroyloxy Acrylates 2 and 3

The preparation of the captodative alkenes **2a**−**2e** and **3a**−**3d** involved the use of methyl and ethyl esters of pyruvic acid **4** and **5**, respectively, as starting materials [Equation (1)]. *O*-Acylation of the base-promoted enolates of **4** and **5**, under similar reaction conditions as those used for the preparation of compounds **1**,[5][9b] furnished the corresponding alkenes **2** and **3** (Table 1). In contrast to the procedure for the preparation of **1**, the pyruvic ester was added to the mixture of acyl chloride **6** and triethylamine at a lower temperature (−10 °C) to improve the yields. The stabilities of the new alkenes are comparable to that of the previously studied **1**, although most of them were obtained as colorless oils. Alkenes **2** and **3** have been fully characterized by spectroscopy and elemental analysis.

Table 1. Preparation of alkenes **2** and **3**

Entry[a]	Pyruvate	**6** (Ar)	Alkene	m.p. (°C)	Yield (%)[b]
1	4	**6a** (Ph)	**2a**	oil	65
2	4	**6b** (*m*-Me-C_6H_4)	**2b**	oil	55
3	4	**6c** (*p*-Cl-C_6H_4)	**2c**	42−43	71
4	4	**6d** (*p*-NO_2-C_6H_4)	**2d**	80−81	60
5	4	**6e** [3,5-$(NO_2)_2$-C_6H_3]	**2e**	91−92	60
6	4	**6f** (*p*-OMe-C_6H_4)	**2f**	oil	51
7	5	**6a** (Ph)	**3a**	oil	40
8	5	**6b** (*m*-Me-C_6H_4)	**3b**	oil	67
9	5	**6c** (*p*-Cl-C_6H_4)	**3c**	oil	40
10	5	**6d** (*p*-NO_2-C_6H_4)	**3d**	oil	50

[a] THF/HMPA (20:1) as solvent, containing Et_3N; stirring the reaction mixture at room temperature for 24 h. [b] After column chromatography and recrystallization.

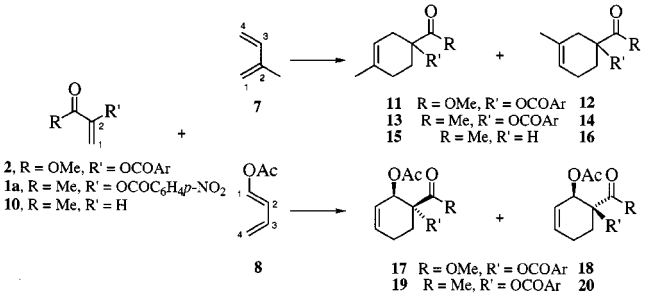


(1)

Diels−Alder Cycloadditions of Alkenes 2 to Unsymmetrical and Carbocyclic 1,3-Dienes

The reactivities and selectivities of these alkenes in Diels−Alder reactions were assessed under thermal and catalytic conditions. In order to evaluate representative alkenes, derivatives **2d** and **2f** were chosen, because of the opposite electron demands of their aryl substituents. Regioselectivity was studied with two dienes, isoprene (**7**) and 1-acetoxybutadiene (**8**), which contain distinct substituents at different positions within the conjugated system. Diene **8** was also useful for probing the stereoselectivity of the process, as was cyclopentadiene (**9**), a cyclic diene customarily employed for testing reactivity in these cycloadditions.

The thermal addition of dienophiles **2d** and **2f** to an excess of **7** gave mixtures of adducts **11** and **12** (Scheme 1). Table 2 shows that these alkenes were less reactive than alkene **1a** and methyl vinyl ketone (**10**) under comparable conditions, since their reactions required higher temperatures and longer times. Probably as a consequence of this lower reactivity, the regioselectivity was also lower, although the *para* isomer was still the major adduct. This behavior would seem to be readily rationalized, considering that the methoxycarbonyl group of the captodative alkenes **2** has a lesser electron-withdrawing effect than the acetyl group in alkene **1a**. This would support the hypothesis that the reactivity and regioselectivity of captodative alkenes of this kind is mainly controlled by the electronic effect of the electron-withdrawing group.[11] As expected,[4c,12] the regioselectivity was found to be substantially improved by adding aluminum chloride as a Lewis acid catalyst (Table 2, entries 5 and 6).



Scheme 1

Cycloaddition of diene **8** to alkenes **2d** and **2f** afforded exclusively the *ortho* regioisomers (Scheme 1). Interestingly, the process was also highly stereoselective since of two possible *endo*/*exo* isomers, **17**/**18**, the latter was not detected in the crude mixtures. These results are in agreement with those obtained for the addition of alkene **1a**,[7] in terms of both regio- and stereoselectivities (Table 2, entries 8−10). The structures of the major regioisomers **11** and **17** were established by NMR spectroscopy, and by comparison with the unambiguously established structures **13** and **19**.[7]

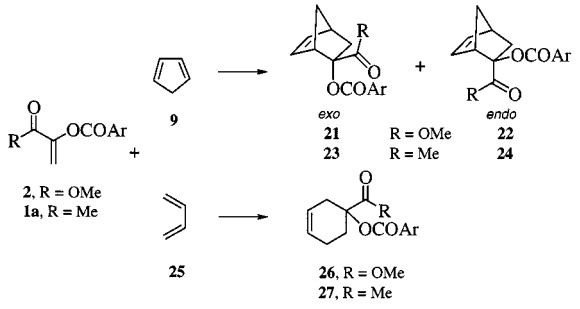
Alkenes **2d** and **2f** were found to react with the cyclic diene **9** under thermal conditions to give a mixture of the *exo*/*endo* stereoisomers, **21**/**22**, the former being the major adduct (Scheme 2). The stereoisomeric mixtures were produced with smaller ratios as compared to those obtained from **1a** (Table 2, entries 11, 15, and 18). The presence of $AlCl_3$ as a catalyst[13] did not greatly increase the stereoselectivity, but the excess of the *exo* isomer was maintained, in contrast to **1a**, for which the ratio was inverted (entries 12, 16, and 20). Although high stereoselectivity was obtained with **1a** using $TiCl_4$ as the Lewis acid,[6] the reaction of alkene **2d** with **9** in the presence of the same catalyst did not show any significant selectivity (entry 13). In contrast, under the same conditions, reaction of alkene **2f** led to a marked improvement in the *exo*/*endo* ratio (entry 17). It is noteworthy that captodative alkenes usually show a prefer-

Table 2. Diels–Alder cycloadditions of alkenes **1a**, **2d**, **2f**, and **10** with dienes **7**, **8**, **9**, and **25**

Entry[a]	Alkene	Diene (mol equiv.)	Solvent	Catalyst (mol equiv.)	T (°C)	t (h)	Products (ratio)[b]	Yield (%)[c]
1	**2d**	**7** (15)	xylene	–	170	96	**11a/12a** (63:37)	58
2	**2f**	**7** (35)	xylene	–	170	96	**11b/12b** (67:33)	65
3	**1a**	**7** (7)	xylene	–	130	35	**13/14** (75:25)	77[d]
4	**10**	**7** (1.5)	toluene	–	120	15	**15/16** (71:29)	[e]
5	**2d**	**7** (15)	CH_2Cl_2	$AlCl_3$ (10)	25	48	**11a/12a** (96:4)	83
6	**2f**	**7** (35)	CH_2Cl_2	$AlCl_3$ (10)	25	48	**11b/12b** (88:12)	63
7	**1a**	**7** (4)	CH_2Cl_2	$ZnCl_2$ (5)	25	36	**13/14** (94:6)	98[d]
8	**2d**	**8** (1)	xylene	–	150	48	**17a/18a** (>98:<2)	52
9	**2f**	**8** (2)	xylene	–	150	48	**17b/18b** (>98:<2)	64
10	**1a**	**8** (3)	xylene	–	130	11	**19/20** (>95:<5)	79[d]
11	**2d**	**9** (19)	xylene	–	150	12	**21a/22a** (59:41)	79
12	**2d**	**9** (19)	CH_2Cl_2	$AlCl_3$ (10)	25	24	**21a/22a** (75:25)	70
13	**2d**	**9** (19)	CH_2Cl_2	$TiCl_4$ (5)	–50	8	**21a/22a** (55:45)	76
14	**2d**	**9** (19)	CH_2Cl_2	–	55	7	**21a/22a** (61:39)	38[f]
15	**2f**	**9** (24)	xylene	–	150	12	**21b/22b** (60:40)	76
16	**2f**	**9** (24)	CH_2Cl_2	$AlCl_3$ (10)	25	48	**21b/22b** (57:43)	73
17	**2f**	**9** (24)	CH_2Cl_2	$TiCl_4$ (5)	–50	8	**21b/22b** (84:16)	70
18	**1a**	**9** (5)	xylene	–	60	8.5	**23/24** (82:18)	70[g]
19	**1a**	**9** (5)	CH_2Cl_2	–	60	7	**23/24** (71:29)	70[g]
20	**1a**	**9** (5)	CH_2Cl_2	$AlCl_3$ (5)	25	0.3	**23/24** (36:64)	95[g]
21	**2d**	**25** (23)	xylene	–	150	48	**26a**	92
22	**2f**	**25** (29)	xylene	–	150	48	**26b**	93
23	**1a**	**25** (5)	toluene	–	110	12	**27**	91[h]

[a] All under N_2 atmosphere. Thermal trials in the presence of 1–2% hydroquinone. [b] Proportions as determined by ^{1}H NMR of the crude reaction mixtures. [c] As a mixture of isomers after purification by column chromatography. [d] See ref.[7] [e] See ref.[14] [f] Corresponding to the major isomer after column chromatography and recrystallization. [g] See ref.[6] [h] See ref.[9f]

ence for *exo* stereoselectivity, which is increased by the presence of Lewis acid catalysts.[4]



Scheme 2

Unexpectedly, and in contrast to the results with **1a**, for which the reactivity and *exo*/*endo* selectivity were scarcely modified by changing the polarity of the solvent (xylene, CH_2Cl_2) (Table 2, entries 18 and 19),[6] the reactivity of **2d** toward diene **9** was found to be significantly enhanced in the presence of dichloromethane, since the reaction took place at 55 °C and in a shorter time. This can probably be ascribed to an electrostatic effect.[15] An increase in the polarity of the solvent may enhance the solvophobic interactions with the reactants, facilitating their approach to the transition state,[16] without losing the concertedness of the mechanism. However, no significant solvent effect was found on the *exo*/*endo* ratios (Table 2, entries 11 and 14).

The *exo* configuration of adducts **21a** and **21b** was assigned by means of ^{1}H NMR spectroscopy. In the spectra of both the compounds, the signal of the vicinal proton *syn* to the alkoxycarbonyl group, 3-H_x, is shifted downfield with respect to that of the *anti* proton 3-H_n. This deshielding effect of the carbonyl group on the *syn* 3-H proton is characteristic of the skeleton of norbornene derivatives.[6,17] This assignment was confirmed by X-ray crystallographic analysis of the *endo* adduct **22a** (Figure 1).[18]

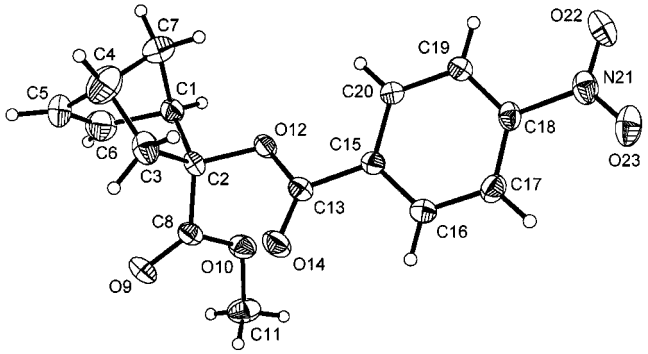


Figure 1. ORTEP view of the X-ray diffraction structure of **22a**; thermal ellipsoids are drawn at the 30% probability level

In order to further evaluate the reactivity of alkenes **2** with respect to **1a**, cycloadditions of **2d** and **2f** to butadiene (**25**) were also carried out. The reactions were performed in a nonpolar solvent at high temperature (150 °C) for 72 h (Table 2, entries 21 and 22), and led to the corresponding adducts **26a** and **26b** in good yields. Again, dienophiles **2** proved to be less reactive than **1a** (entry 23). No significant difference in reactivity was found between alkenes **2d** and **2f**. This analogous reactivity, along with the regio- and ste-

reoselectivities toward dienes **7**–**9**, suggests that the contribution of the substituent on the benzene ring of the electron-donating group to the polarizability of the double bond of the captodative alkene must be almost negligible.

Discussion

It is difficult to account for the slight *exo* stereoselectivity displayed by alkenes **2** with cyclopentadiene (**9**) and for the lack of significant changes on modification of the thermal and catalytic reaction conditions, due to the great number of possible stabilizing and destabilizing interactions at the transition state between the diene and dienophile.[19] However, the regioselectivity shown by dienes **7** and **8** seems to reflect electronic rather than steric control. This is much more evident with diene **8**, from which the most crowded adduct is obtained exclusively.

FMO theory has proved useful in the study of reactivity and regioselectivity of captodative alkenes **1**.[7,11] It predicts the correct orientation in the addition to dienes such as **7** and **8**, showing that the interaction is controlled by the energetically more favorable HOMO-diene/LUMO-dienophile gap. However, steric hindrance around the captodative center may be invoked to account for the more than twofold higher reactivity of alkene **10** with respect to **1a**,[5] since the LUMO of the latter is more stable than that of **10**.[11] The results of FMO calculations[20] were compared with the *IE*s and *VAE*s measured for these molecules and were found to reproduce the experimental energy trends.[11]

In order to correlate the structural and electronic factors with the high reactivity and selectivity shown by captodative alkenes in cycloaddition reactions, in particular the novel alkenes **2** and **3**, we undertook an extensive theoretical and spectroscopic study of these molecules. Figure 2 displays the UP spectra of compounds **2d** and **3d**, along with that of ethyl acrylate (**28**) for comparison purposes. A pronounced difference is seen compared to the UP spectrum of **1a**,[11] due to the additional oxygen lone pair [$n_{\pi(en)}$] cross-conjugated with the enone (en) π system. The relative intensity of the second band is appreciably higher and the valley between the first and second bands is occupied, in agreement with the appearance of an additional signal from the $n_{\pi(en)}$ MO in this region. Moreover, replacement of the methyl group (bonded to the carbonyl carbon atom, as in alkene **1a**) by an alkoxy group, as in alkenes **2** and **3**, causes a sizeable stabilization of the carbonyl oxygen lone pair [$n_{o(en)}$], such that the first two occupied MO′s of **2d** and **3d** are likely to be the benzene π_S and π_A MO′s (Figure 3). The stabilization of the carbonyl oxygen lone pair can be evaluated by comparing the UP spectra of **10**[11] and **28** (Figure 2). In the spectrum of the latter, the broad and intense first band seems to display a shoulder at about 10.2 eV and maxima at about 10.6 and 10.9 eV. In agreement, the (first) *IE* value determined by mass spectrometry is 10.3 eV.[21] We thus assign the first band in the UP spectrum of **28** to the unresolved contributions from the n_o, π_{CC}, and n_π MO′s, in order of increasing *IE*. The n_o σ lone pair orbital, associated with the shoulder, is thus stabilized by 0.6 eV with respect to **10** (9.60 eV). On going from **28** to **2b** and **3d**, all the corresponding MO′s in the latter two compounds are inductively stabilized by the nitrobenzoate group (Figure 3), so that the π_{CC} MO, having mainly ethene character, contributes to the second band of the UP spectrum, which shows a maximum at 11.2 eV.

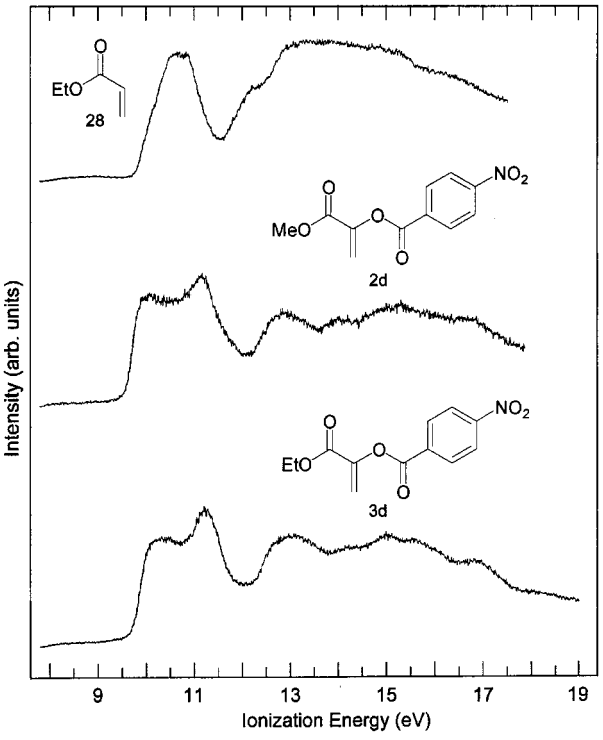


Figure 2. UP spectra of **2d**, **3d**, and **28**

The ET spectra of compounds **2d** and **3d**, along with that of the smaller reference molecule ethyl acrylate (**28**), are presented in Figure 4. The spectra of **2d** and **3d** show one additional resonance, at about 3.4 eV, as compared to the spectrum of **1a**[11] (see Figure 3). Moreover, the width of the first resonance is reduced from 1.0 to 0.65 eV. These findings fully confirm the previous assignment[11] of the first signal in the ET spectrum of **1a** to unresolved contributions from the π^*_{CO} MO of the OCOAr group and the highest-lying [$\pi^*_{2(en)}$] of the two vacant π* MO′s of the enone group. The latter is highly destabilized by mixing with the methoxy or ethoxy oxygen lone pair, in line with literature ETS data,[22] indicating considerable localization at the carbonyl carbon atom. Most importantly from the reactivity point of view, a similar destabilization should be experienced by the lowest-lying vacant π* MO [$\pi^*_{1(en)}$] localized at the enone group, i.e. the NLUMO (Figure 3). In this respect, it should be noted that the LUMO, with mainly NO_2 character, is not involved in the reactivity of the ethene double bond. The two enone vacant π* MO′s arise from a strong interaction between the (energetically close) $\pi^*_{CO(en)}$ and π^*_{CC} fragment orbitals. As a consequence, they possess similar localization properties, with nearly equal carbonyl

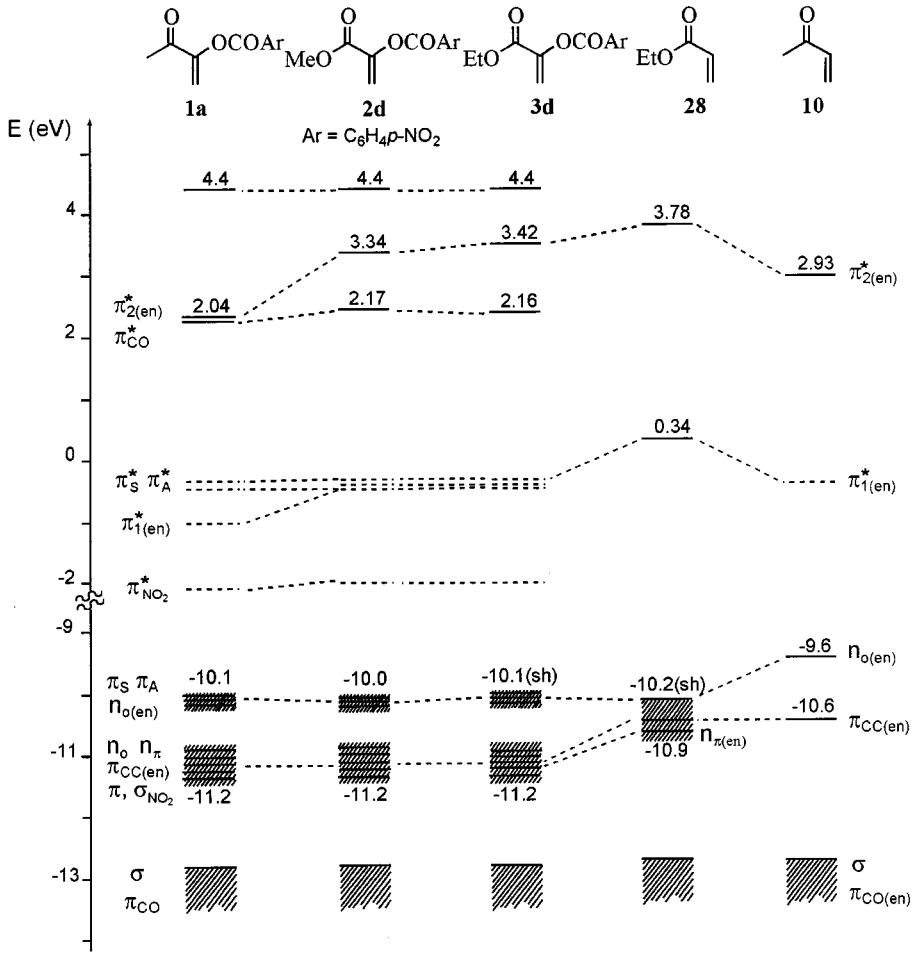


Figure 3. Correlation diagram for the FMO energies in **1a**, **2d**, **3d**, **10**, and **28**, as deduced from the UP and ET spectra; the energy positions of the vacant levels close to, or below, zero energy, as represented by dashed lines, are only tentative (see text); the UP and ET data of **1a** and **10** are taken from ref.[11]; n_o is the σ MO with mainly (carbonyl) oxygen lone pair character; n_π is the lone pair of the benzoyl oxygen atom bonded to the enone moiety; π_S and π_A are the symmetric and antisymmetric components of the benzene e_{1g} HOMO; π_S^* and π_A^* are the corresponding components of the benzene e_{1u} LUMO; π_{CO} and π_{CC} are the occupied π orbitals mainly localized at the carbonyl and the ethene groups, respectively; π^*_{CO} is the vacant MO with mainly carbonyl (OCOAr) character; $\pi^*_{1(en)}$ and $\pi^*_{2(en)}$ are the two vacant π* MO′s of the enone group; σ_{NO2} and π_{NO2} are the outermost occupied orbitals of the nitro group, and π^*_{NO2} is the vacant π* MO with mainly nitro group character; the MO′s with mainly enone character are labeled "en"

and alkene character, as confirmed by the wavefunction coefficients calculated for $\pi^*_{1(en)}$ (see Table 3). In order to confirm and to better evaluate the extent of the destabilizing effect caused by mixing with an adjacent oxygen lone pair on the enone vacant π* MO′s, we obtained the ET spectrum of **28** (Figure 4). Comparison with the ET spectrum of **10** (Figure 3) shows that the $\pi^*_{2(en)}$ VAE increases by 0.85 eV, while the $\pi^*_{1(en)}$ anion state, stable in **10**, increases to 0.34 eV above zero energy. According to the calculations (Table 3), the energy of the $\pi^*_{1(en)}$ MO increases by 0.4 eV on going from **1a** to **2d** and **3d**. These results are in qualitative agreement with experiment, but probably underestimate the destabilizing effect. On going from **28** to **2d** and **3d**, the inductive electron-withdrawing effect of the nitrobenzoate group stabilizes the $\pi^*_{2(en)}$ MO by 0.4 eV (Figure 3). Exactly the same energy shift is predicted by the calculations (Table 3) for the $\pi^*_{1(en)}$ MO′s. Therefore, if the VAE for **28** is 0.34 eV, the $\pi^*_{1(en)}$ MO′s for **2d** and **3d** should lie slightly below zero energy.

The geometries of alkenes **2a**−**2f**, **3a**, **3d**, and **28** were fully optimized at the ab initio 3−21G level, and then employed as the starting points for ab initio 6−31G* optimization (Table 4).[23] The nonplanar conformation of the aroyloxy group (with respect to the plane formed by the acrylate moiety) was found to be more stable than the planar form for all the derivatives. In contrast, the *s-cis*/*s-trans* conformers have almost the same energies, varying only over very small energy ranges (0.15−0.50 kcal mol^{-1}); for example, in **2a**, **2b**, **2f**, **3a**, and **28**, the *s-cis* conformer is more stable, while in **2d** and **3d** the *s-trans* conformer is more stable.

Since these energy differences are too insignificant to affirm that one of the two conformations is favored in the gas phase, and as we were unable to determine the equilibrium in solution by NMR, we carried out a crystallographic analysis of **2d** in order to establish the conformation of the ester conjugated system in the solid state. The X-ray structure is depicted in Figure 5.[18] The conformations of both conjug-

Table 3. Ab initio 6−31G* calculations of energies (eV) of the frontier molecular orbitals for alkenes **2a**−**2f**, **3a**, **3d**, **1a**, and **28**, and dienes **7** and **8**

Compd.[a]	HOMO[b]	LUMO[c]
2a	−10.6044	3.1770
2b	−10.5118	3.2333
2c	−10.7562	3.0322
2d	−10.9921	2.8080
2e	−11.2321	2.5261
2f	−10.5202	3.2689
3a	−10.5725	3.2140
3d	−10.9581	2.8485
1a	−11.0123	2.4588
28	−10.6103	3.1938
7[d]	−8.6193	3.5337
8[e]	−8.5695	3.2561

[a] Non-planar *s-trans* conformation for alkenes, and *s-cis* for dienes. [b] Energies of the corresponding π_{CC} MO of alkenes **1a**, **2**, **3**, and **28**. [c] Energies of the corresponding $\pi^*_{1(en)}$ MO of alkenes **1a**, **2**, **3**, and **28**. [d] See ref.[11] [e] Considered in its *s-cis* conformation.

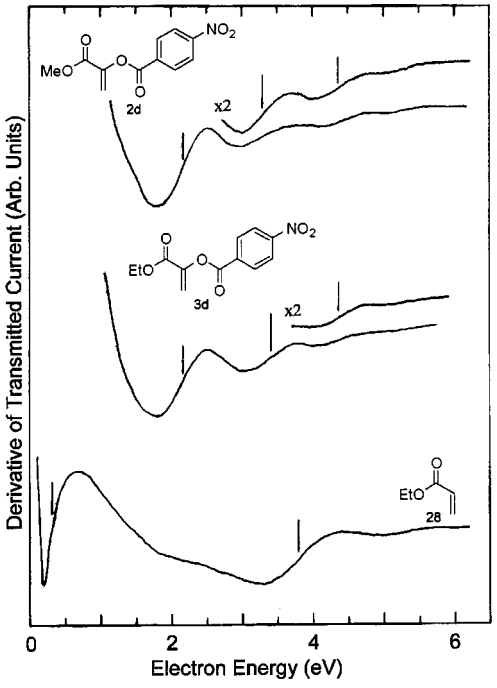


Figure 4. ET spectra of **2d**, **3d**, and **28**; vertical lines mark the most probable vertical AE values

ated moieties, the acrylate and *p*-nitrobenzoyl groups, show a good agreement with the calculated gas-phase structure, being almost identical to that of alkene **1a**.[11] Thus, the former is in a conjugated planar *s-trans* conformation, while the latter lies out of the plane formed by the acrylate π-system. Interestingly, the methyl group of the acrylate lies in the plane of the carbonyl double bond, as predicted by the calculations.

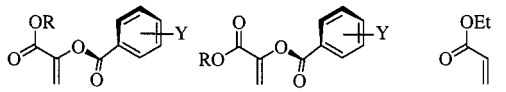
The FMO energies for the *s-trans* conformations of the same alkenes were calculated at the HF/6-31G* level. Table 3 lists the energies, of the highest occupied π MO (π_{CC}) and the lowest unoccupied π* MO [$\pi^*_{1(en)}$]. The atomic wavefunction coefficients were found to be largely localized at the ethene group and mostly involved in the Diels−Alder reaction. The same parameters for dienes **7** and **8** are also included.[12]

HF calculations neglect correlation and relaxation effects, which tend to cancel out when *IE*s, but not EAs, are evaluated. For this reason, π *IE*s are usually reproduced satisfactorily by this theoretical approach, whereas the VAEs are overestimated by several eV.[24] In agreement, the energies calculated for the occupied π_{CC} MO's in **1a**, **2d**, **3d** (−10.96 eV), and **28** (−10.6 eV) are close to the negatives of the energies (11.2 and 10.9 eV, respectively, see Figure 3) of the second bands in their UP spectra. For the vacant $\pi^*_{1(en)}$ MO, the only experimental value available is the VAE (0.34 eV) in **28**, the corresponding anion state in the other compounds being stable (and thus not observed in the ET spectra). As expected, the calculated orbital energy is much higher (3.19 − 0.34 = 2.85 eV). When the same shift is applied to the values calculated for **2d** and **3d**, the energy of the $\pi^*_{1(en)}$ MO is predicted to be slightly negative (Table 5), in perfect agreement with the conclusions drawn above from the VAE trends observed in the ET spectra.

The calculated FMO energies indicate that the HOMO(π_{CC})-diene/NLUMO[$\pi^*_{1(en)}$]-alkene interaction [i.e. normal electron demand (NED)] is preferred (Table 6). In this sense, considering a common diene, the reactivity of the analogous series **2a**−**2f** in Diels−Alder additions would be expected to be correlated with the stability of the vacant $\pi^*_{1(en)}$ MO. Thus, the lower the $\pi^*_{1(en)}$ energy, the more reactive the dienophile. This occurs when the alkene is substituted by electron-withdrawing groups on the aroyloxy group. Alkenes **2d** and **2e** should be more reactive than **2a**, and even more than **2f**, which bears an electron-donating group on the aromatic ring, since the latter two have the least energetically stable $\pi^*_{1(en)}$ MO's (Table 3). Even though there is a lack of kinetic data on this series, one could expect a correlation between $\pi^*_{1(en)}$ MO energies and reactivities, considering the antecedent of a similar reactivity trend found for the series of alkenes **1**.[5,7] Therefore, the reactivity of captodative alkenes of type **1**, or **2** and **3**, in Diels−Alder cycloaddition reactions, is most likely controlled, to a large extent, by the electron-withdrawing group (i.e. the acetyl and alkoxycarbonyl groups, respectively), and by the inductive effect of the aroyloxy group.[25] This is also supported by the fact that the $\pi^*_{1(en)}$ MO in alkene **28** is higher in energy than those in alkenes **2** and **3** (Figure 3).

In principle, the high reactivity and regioselectivity shown by these alkenes suggests that there is an additional factor that counterbalances or inhibits the expected deactivating effect of the electron-releasing group. As suggested previously for alkenes **1a**,[11] this inhibiting factor could be attributed to a conformational effect on the aroyloxy group.[26] This group is oriented in an almost orthogonal conformation (Figure 5), in which the lone pairs of the oxygen are restricted to be delocalized toward the double bond, favoring delocalization toward the carbonyl group of the aroyloxy ester.

Table 4. Ab initio (RHF/6-31G*) energies (au) of the minimum-energy conformations of alkenes **2a**−**2f**, **3a**, **3d**, and **28**



s-cis, nonplanar *s-trans*, nonplanar **28**, *s-cis*

Compound	R	Conformation	E	Relative stability (kcal/mol)[a]
2a	Me	*s-cis*	−721.836933	0.00
		s-trans	−721.836673	0.16
2b	Me	*s-cis*	−760.873767	0.00
		s-trans	−760.874068	0.19
2c	Me	*s-cis*	−1180.736084	0.00
		s-trans	−1180.736038	0.03
2d	Me	*s-cis*	−925.304619	0.19
		s-trans	−925.304917	0.00
2e	Me	*s-cis*	−1128.768845	0.50
		s-trans	−1128.769650	0.00
2f	Me	*s-cis*	−835.719713	0.00
		s-trans	−835.719380	0.21
3a	Et	*s-cis*	−760.876984	0.00
		s-trans	−760.876643	0.21
3d	Et	*s-cis*	−964.344686	0.17
		s-trans	−964.344958	0.00
28		*s-cis*	−343.720490	0.00
		s-trans	−343.719615	0.55

[a] Considered for each compound in its two conformations.

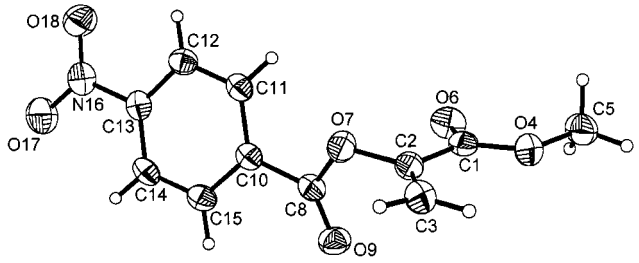


Figure 5. ORTEP view of the X-ray diffraction structure of **2d**; thermal ellipsoids are drawn at the 30% probability level

Table 5. Calculated ab initio (RHF/6-31G*) energies (eV) and corresponding values deduced from the UP and ET spectra of the highest occupied (π_{CC}) and lowest unoccupied [$\pi^*_{1(en)}$] π MO′s with mainly enone character in alkenes **2d**, **3d**, and **28**; the calculated $\pi^*_{1(en)}$ energies are shifted by 2.85 eV (see text)

Alkene	π_{CC} Exp. (−*IE*)	Calcd.	$\pi^*_{1(en)}$ Exp. (VAE)	Calcd.
2d[a]	−11.2	−10.99		−0.046
3d[a]	−11.2	−10.96		−0.005
28[b]	−10.9	−10.61	0.34	0.34

[a] Considered in its *s-trans* conformation. [b] Considered in its *s-cis* conformation.

From the viewpoint of the $\pi_{CC(en)}$ *IE* values (Figure 3), compounds **1**−**3** should resemble an electron-deficient alkene like **10** or **28** rather than an electron-rich alkene like methyl vinyl ether (*IE* = 8.93 eV),[20b] even though the *IE* value of an enol ester, such as vinyl acetate (*IE* = 10.76 eV),[20b] is much closer to those of our alkenes.

Table 6. Ab initio HF/6-31G* energy gaps (eV) between the relevant frontier orbitals for dienophiles **2** and **3**, and diene **7**

Alkene[a][b]	HOMO-$\pi^*_{1(en)}$	LUMO−HOMO	Difference
2a	11.7963	14.1381	2.3418
2b	11.8526	14.0455	2.1929
2c	11.6515	14.2899	2.6384
2d	11.4273	14.5258	3.0985
2e	11.1454	14.7658	3.6204
2f	11.8882	14.0539	2.1657
3a	11.8333	14.1062	2.2729
3d	11.4678	14.4918	3.0240

[a] HOMO-diene/$\pi^*_{1(en)}$-dienophile and LUMO-diene/π_{CC}-dienophile. [b] Of the nonplanar *s-trans* conformation.

On the other hand, it is noteworthy that a correlation is found between the energy of the $\pi^*_{1(en)}$ MO and experimental reactivity when alkenes **2d** and **1a** are compared, since the latter reacts faster than **2d** with **7** (Table 2, entries 1 and 3), in agreement with a lower vacant π* MO energy for **1a** (Table 3).[11]

On the basis of the atomic coefficient differences for the appropriate frontier orbital interaction [HOMO-diene/$\pi\delta_{1(en)}$-alkene] between dienophiles **2** and **3** and dienes **7** and **8** (Table 3), regioselectivity can be tentatively predicted.[3c] The calculations show that the relative value of the coefficient on the unsubstituted carbon C-1 is greater than that on the captodative carbon C-2 for the LUMO of both

2 and **3**. Therefore, the predicted main interaction is that between carbon C-1 of alkenes **2** and **3** and the terminal carbon C-1 of diene **7** (Scheme 1),[11] since the largest HOMO coefficient of the latter is located on this carbon. Although the reaction of dienophile **3d** was not examined experimentally, according to this analysis the regioselectivity can be expected to be comparable to that shown by its homologue **2d**. For diene **8**, several possible starting geometries, with *s-cis* and *s-trans* conformations, were analyzed. However, only a very small difference in the coefficients of carbons C-1 and C-4 of the HOMO was observed. Therefore, the reaction would not be expected to be regioselective. This is in contrast to the high *ortho* regioselectivity observed experimentally, hence there might be other factors involved in controlling the outcome of Diels−Alder reactions with **8**.

This regioselectivity could find a better rationalization than that given by FMO theory by applying the novel DFT/HSAB theory.[8a,27] This has proved to be a reliable model in correlating the values of the condensed local softness for the terminal carbons of cycloaddends in Diels−Alder reactions with the regiochemistry observed for a wide range of dienes and dienophiles under NED conditions.[28]

Conclusion

Representatives of a new class of captodative alkenes, **2** and **3**, have been prepared from alkyl pyruvates **4** and **5** and the corresponding aroyl chlorides. Highly regio- and stereoselective cycloadditions are observed when alkenes **2** react with unsymmetrical and carbocyclic dienes. The electronic structures of these alkenes, as determined from experimental UPS and ETS data, as well as by FMO calculations, are consistent with the relative reactivity displayed by analogous captodative alkenes **1**. These results suggest a greater influence of the electron-withdrawing group than of its geminally substituted electron-donating group in controlling reactivity and selectivity in Diels−Alder cycloadditions.

The regioselectivity shown by the new alkenes **2** and diene **7** has been rationalized by considering the wavefunction coefficients of the appropriate (occupied π-diene and π*-alkene) FMOs of the cycloaddends. An unsatisfactory prediction was obtained by this theoretical approach in the case of diene **8**.

Interestingly, the structural features of these alkenes, such as the presence of hydroxyl and carboxylic groups, make them attractive potential synthons for the preparation of important synthetic targets such as functionalized α-hydroxy acids or α-hydroxy-β-amino acids.[29]

Experimental Section

General Remarks: Melting points (uncorrected) were determined on an Electrothermal capillary melting point apparatus. IR spectra were recorded on a Perkin−Elmer 1600 spectrophotometer. ^{1}H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded on a Varian Gemini-300 instrument, with samples in $CDCl_3$ solution containing TMS as an internal standard. Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained, in electron impact (EI) (70 eV) and fast-atom bombardment (FAB) modes, on a Hewlett−Packard 5971A or a Jeol JMS-AX 505 HA spectrometer. X-ray data were collected on a Siemens P-4 diffractometer. The UP spectra were obtained with a Perkin−Elmer PS18 photoelectron spectrometer. The ET spectroscopy apparatus was in the format devised by Sanche and Schulz,[30] as has been described previously.[31] Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ) and at the Centro de Investigaciones Químicas, Universidad Autónoma de Hidalgo (Pachuca, Hgo., Mexico). Analytical thin-layer chromatography was performed using E. Merck silica gel 60 F_{254} coated plates (0.25 mm), and spots were visualized using long- and short-wavelength UV lamps. Radial chromatography was performed on a "Chromatotron" from Harrison Research Instruments. All air- and moisture-sensitive reactions were carried out under nitrogen using oven-dried glassware. Dioxane, diethyl ether, THF, toluene, and xylene were freshly distilled from sodium, and dichloromethane from calcium hydride, prior to use. Li_2CO_3 was dried overnight at 120 °C prior to use. All other reagents were used without further purification.

General Method for the Preparation of Alkyl 2-Aroyloxyacrylates 2a−2f and 3a−3d: To a solution of triethylamine (6.0 mL, 4.3 mmol) in dry THF (20 mL) and HMPA (1.0 mL) at −10 °C under N_2 atmosphere, a solution of pyruvate **4** or **5** in dry THF (10 mL) was added dropwise. Then, at the same temperature, a solution of the acid chloride **6** in dry THF (10 mL) was slowly added. After stirring the mixture at room temperature for 24 h, the solvent was removed in vacuo, and the residue was redissolved in CH_2Cl_2 (50 mL). A saturated aqueous solution of NH_4Cl (100 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent was evaporated in vacuo. The residue was successively purified by flash column chromatography on silica gel (20 g; hexane/EtOAc, 95:5) and by radial chromatography (hexane/EtOAc, 90:10), to give the corresponding alkenes **2a−2f** and **3a−3d**.

Methyl 2-(Benzoyloxy)-2-propenoate (2a): Following the general procedure, reaction of **4** (1.0 g, 9.8 mmol) with **6a** (1.4 g, 10 mmol) afforded 1.31 g (65%) of **2a** as a colorless oil.[10] R_f = 0.7 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1736, 1649, 1452, 1439, 1321, 1317, 1267, 1196, 1152, 1088, 1067 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 3 H, CO_2CH_3), 5.59 (d, *J* = 1.7 Hz, 1 H, 3a-H), 6.12 (d, *J* = 1.7 Hz, 1 H, 3b-H), 7.44−7.52 (m, 2 H, 7-H), 7.57−7.65 (m, 1 H, 8-H), 8.09−8.16 (m, 2 H, 6-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 51.9 (CO_2CH_3), 114.0 (C-3), 127.8 (C-6), 128.5 (C-4), 129.8 (C-5), 134.2 (C-7), 144.3 (C-2), 161.6 (PhCO_2), 164.0 (CO_2CH_3). GC-MS (70 eV): *m*/*z* (%) = 206 (1) [M$^+$], 175 (3), 105 (100), 77 (38). $C_{11}H_{10}O_4$ (206.2): calcd. C 64.08, H 4.89; found C 64.11, H 4.82.

Methyl 2-(*m*-Methylbenzoyloxy)-2-propenoate (2b): Following the general procedure, reaction of **4** (1.0 g, 9.8 mol) with **6b** (1.54 g, 9.97 mmol) afforded 1.19 g (55%) of **2b** as a colorless oil. R_f = 0.8 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1736, 1650, 1314, 1275, 1189, 1151, 1093, 1072 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, Ar*Me*), 3.81 (s, 3 H, CO_2CH_3), 5.61 (d, *J* = 1.8 Hz, 1 H, 3a-H), 6.16 (d, *J* = 1.8 Hz, 1 H, 3b-H), 7.33−7.46 (m, 2 H, ArH), 7.90−7.97 (m, 2 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.1 (Ar*Me*), 52.6 (CO_2CH_3), 114.2 (C-3), 127.4 (C-9), 128.3 (C-4), 128.4 (C-8), 130.6 (C-5), 134.6 (C-7), 138.3 (C-6), 144.7 (C-2), 162.5

(Ar*C*O$_2$), 164.7 (*C*O$_2$CH$_3$). $C_{12}H_{12}O_4$ (220.2): calcd. C 65.45, H 5.49; found C 65.55, H 5.49.

Methyl 2-(*p*-Chlorobenzoyloxy)-2-propenoate (2c): Following the general procedure, reaction of **4** (1.0 g, 9.8 mmol) with **6c** (1.75 g, 10.0 mmol) afforded 1.67 g (71%) of **2c** as colorless crystals. R_f = 0.8 (hexane/EtOAc, 8:2). IR (KBr): $\tilde{\nu}$ = 1729, 1649, 1590, 1442, 1401, 1320, 1273, 1197, 1150, 1092, 1013, 935 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, CO_2CH_3), 5.63 (d, *J* = 1.9 Hz, 1 H, 3a-H), 6.18 (d, *J* = 1.9 Hz, 1 H, 3b-H), 7.45−7.52 (m, 2 H, ArH), 8.04−8.11 (m, 2 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 52.8 (CO_2CH_3), 114.6 (C-3), 127.0 (C-4), 128.8 (C-6), 131.8 (C-5), 140.4 (C-7), 144.6 (C-2), 161.9 (Ar*C*O$_2$), 163.8 (*C*O$_2$CH$_3$). GC-MS (70 eV): *m*/*z* (%) = 240 (1) [M$^+$], 139 (52), 111 (44), 75 (100). $C_{11}H_9ClO_4$ (240.6): calcd. C 54.90, H 3.77, Cl 14.73; found C 55.14, H 4.00, Cl 15.00.

Methyl 2-(*p*-Nitrobenzoyloxy)-2-propenoate (2d): Following the general procedure, reaction of **4** (1.0 g, 9.8 mmol) with **6d** (1.85 g, 9.97 mmol) afforded 1.47 g (60%) of **2d** as pale-yellow crystals. R_f = 0.6 (hexane/EtOAc, 8:2); m.p. 80−81 °C. IR (KBr): $\tilde{\nu}$ = 1744, 1727, 1648, 1607, 1526, 1439, 1346, 1324, 1272, 1197, 1152, 1094 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, CO_2CH_3), 5.70 (d, *J* = 2.0 Hz, 1 H, 3a-H), 6.23 (d, *J* = 2.0 Hz, 1 H, 3b-H), 8.28−8.37 (m, 4 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 52.8 (CO_2CH_3), 115.0 (C-3), 123.6 (C-6), 131.4 (C-5), 133.9 (C-4), 144.3 (C-2), 150.9 (C-7), 161.5 (Ar*C*O$_2$), 162.8 (*C*O$_2$CH$_3$). $C_{11}H_9NO_6$ (251.2): calcd. C 52.60, H 3.61, N 5.58; found C 52.69, H 3.75, N 5.48.

Methyl 2-(3,5-Dinitrobenzoyloxy)-2-propenoate (2e): Following the general procedure, reaction of **4** (1.0 g, 9.8 mol) with **6e** (2.19 g, 9.50 mmol) afforded 1.69 g (60%) of **2e** as colorless crystals. R_f = 0.5 (hexane/EtOAc, 8:2); m.p. 91−92 °C. IR (KBr): $\tilde{\nu}$ = 1749, 1651, 1631, 1552, 1349, 1318, 1284, 1199, 1160 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3 H, CO_2CH_3), 5.77 (d, *J* = 2.2 Hz, 1 H, 3a-H), 6.29 (d, *J* = 2.2 Hz, 1 H, 3b-H), 9.25−9.28 (m, 2 H, ArH), 9.29−9.32 (m, 1 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 53.0 (CO_2CH_3), 115.5 (C-3), 123.1 (C-7), 130.0 (C-5), 132.2 (C-4), 144.0 (C-2), 148.7 (C-6), 160.7 (Ar*C*O$_2$), 161.0 (*C*O$_2$CH$_3$). $C_{11}H_8N_2O_8$ (296.2): calcd. C 44.61, H 2.72, N 9.46; found C 44.74, H 3.00, N 9.36.

Methyl 2-(*p*-Methoxybenzoyloxy)-2-propenoate (2f): Following the general procedure, reaction of **4** (1.0 g, 9.8 mol) with **6f** (1.7 g, 10 mmol) afforded 1.18 g (51%) of **2f** as a colorless oil. R_f = 0.26 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1731, 1649, 1606, 1581, 1511, 1440, 1311, 1260, 1151, 1080, 1027, 846, 765 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, CO_2CH_3 or ArOMe), 3.88 (s, 3 H, ArOMe or CO_2CH_3), 5.59 (d, *J* = 1.7 Hz, 1 H, 3a-H), 6.14 (d, *J* = 1.7 Hz, 1 H, 3b-H), 6.93−6.98 (m, 2 H, 6-H), 8.05−8.10 (m, 2 H, 5-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 52.6 (CO_2CH_3), 55.5 ($ArOCH_3$), 113.8 (C-6), 114.1 (C-3), 120.7 (C-4), 132.4 (C-5), 144.7 (C-2), 162.2 (Ar*C*O$_2$), 164.1 (C-8 or *C*O$_2$CH$_3$), 164.4 (*C*O$_2$CH$_3$ or C-8). $C_{12}H_{12}O_5$ (236.2): calcd. C 61.02, H 5.12; found C 61.34, H 5.16.

Ethyl 2-(Benzoyloxy)-2-propenoate (3a): Following the general procedure, reaction of **5** (1.0 g, 8.6 mmol) with **6a** (1.24 g, 8.80 mmol) afforded 0.76 g (40%) of **3a** as a colorless oil. R_f = 0.8 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1735, 1650, 1452, 1373, 1302, 1266, 1151, 1087, 1067, 1024 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (t, 3 H, $CO_2CH_2CH_3$), 4.29 (q, 2 H, $CO_2CH_2CH_3$), 5.62 (d, *J* = 1.7 Hz, 1 H, 3a-H), 6.17 (d, *J* = 1.7 Hz, 1 H, 3b-H), 7.46−8.15 (m, 5 H, PhH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.0 ($CO_2CH_2CH_3$), 61.8 ($CO_2CH_2CH_3$), 113.8 (C-3), 128.1 (C-6), 128.4 (C-4), 130.7 (C-5), 134.5 (C-7), 145.0 (C-2), 161.5 (Ph*C*O$_2$), 164.9 (*C*O$_2$Et). GC-MS (70 eV): *m*/*z* (%) = 220 (1) [M$^+$], 191 (1), 175 (5), 105 (100), 77 (75). $C_{12}H_{12}O_4$ (220.2): calcd. C 65.45, H 5.49; found C 65.52, H 5.70.

Ethyl 2-(*m*-Methylbenzoyloxy)-2-propenoate (3b): Following the general procedure, reaction of **5** (1.50 g, 12.9 mol) with **6b** (2.0 g, 13 mmol) afforded 2.0 g (67%) of **3b** as a colorless oil. R_f = 0.6 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1734, 1650, 1274, 1192, 1150, 1093, 1071 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 2.40 (s, 3 H, Ar*Me*), 4.26 (q, *J* = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 5.58 (d, *J* = 1.7 Hz, 1 H, 3a-H), 6.13 (d, *J* = 1.7 Hz, 1 H, 3b-H), 7.34−7.45 (m, 2 H, 8-H, 7-H), 7.89−7.96 (m, 2 H, 5-H, 9-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.2 ($CO_2CH_2CH_3$), 21.6 (Ar*Me*), 61.4 ($CO_2CH_2CH_3$), 114.5 (C-3), 127.3 (C-9), 128.5 (C-8), 128.8 (C-4), 130.6 (C-5), 134.5 (C-7), 138.3 (C-6), 144.9 (C-2), 161.8 (Ar*C*O$_2$), 164.6 (*C*O$_2$Et). GC-MS (70 eV): *m*/*z* (%) = 234 (1) [M$^+$], 136 (75), 135 (100), 107 (20), 92 (30), 77 (50). $C_{13}H_{14}O_4$ (234.2): calcd. C 66.66, H 6.02; found C 66.82, H 5.83.

Ethyl 2-(*p*-Chlorobenzoyloxy)-2-propenoate (3c): Following the general procedure, reaction of **5** (2.0 g, 17 mmol) with **6c** (3.01 g, 17.2 mmol) afforded 1.75 g (40%) of **3c** as a colorless oil. R_f = 0.8 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1736, 1650, 1594, 1401, 1315, 1265, 1152, 1089, 1015, 754 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 4.28 (q, *J* = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 5.62 (d, *J* = 1.8 Hz, 1 H, 3a-H), 6.17 (d, *J* = 1.8 Hz, 1 H, 3b-H), 7.45−7.48 (m, 2 H, ArH), 8.05−8.08 (m, 2 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.0 ($CO_2CH_2CH_3$), 61.8 ($CO_2CH_2CH_3$), 114.2 (C-3), 127.0 (C-4), 128.9 (C-6), 131.6 (C-5), 140.3 (C-7), 144.8 (C-2), 161.3 (Ar*C*O$_2$), 163.9 (*C*O$_2$Et). GC-MS (70 eV): *m*/*z* (%) = 254 (1) [M$^+$], 209 (1), 141 (21), 139 (67), 111 (41), 75 (100). $C_{12}H_{11}ClO_4$ (254.7): calcd. C 56.60, H 4.35; found C 56.54, H 4.46.

Ethyl 2-(*p*-Nitrobenzoyloxy)-2-propenoate (3d): Following the general procedure, reaction of **5** (2.0 g, 17 mmol) with **6d** (3.19 g, 17.2 mmol) afforded 2.28 g (50%) of **3d** as a colorless oil. R_f = 0.7 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1735, 1650, 1530, 1348, 1317, 1267, 1151, 1088, 1015 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 4.23 (q, *J* = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 5.67 (d, *J* = 2.0 Hz, 1 H, 3a-H), 6.15 (d, *J* = 2.0 Hz, 1 H, 3b-H), 8.32 (m, 4 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 14.0 ($CO_2CH_2CH_3$), 62.0 ($CO_2CH_2CH_3$), 114.5 (C-3), 123.6 (C-6), 131.3 (C-5), 134.0 (C-4), 144.6 (C-2), 149.9 (C-7), 161.0 (Ar*C*O$_2$), 162.8 (*C*O$_2$Et). GC-MS (70 eV): *m*/*z* (%) = 265 (1) [M$^+$], 222 (3), 150 (100), 120 (47), 104 (26), 76 (17). $C_{12}H_{11}NO_6$ (265.2): calcd. C 54.34, H 4.18, N 5.28; found C 54.15, H 4.32, N 5.23.

1-Methoxycarbonyl-4-methyl-3-cyclohexen-1-yl *p*-Nitrobenzoate (11a) and 1-Methoxy-3-methyl-3-cyclohexen-1-yl *p*-Nitrobenzoate (12a) − Method A: In a screw-capped ACE pressure tube under N_2 atmosphere, a stirred mixture of **2d** (0.1 g, 0.4 mmol) and **7** (0.40 g, 5.9 mmol) in dry xylene (5 mL) was heated to 170 °C for 4 days. The solvent was then removed in vacuo, to leave 0.075 g (58%) of a mixture of **11a** and **12a** (63:37) as a greenish oily residue.

Method B: In a screw-capped ACE pressure tube under N_2 atmosphere, a mixture of **2d** (0.1 g, 0.4 mmol), $AlCl_3$ (0.53 g, 4.0 mmol), and **7** (0.40 g, 5.9 mmol) in dry CH_2Cl_2 (5 mL) was stirred at room temperature for 48 h. The mixture was then diluted with CH_2Cl_2 (50 mL) and washed with saturated aqueous $NaHCO_3$ solution (2 × 30 mL). The organic phase was dried (Na_2SO_4) and the solvent was removed in vacuo to leave 0.42 g (83%) of a mixture of **11a** and **12a** (96:4) as a greenish oily residue. This was purified by flash

column chromatography on silica gel (15 g; hexane/EtOAc, 100:2). **11a:** R_f = 0.57 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1747, 1728, 1529, 1349, 1292, 1251, 1103, 1078 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.71 (br. s, 3 H, 4-CH_3), 2.00−2.21 (m, 3 H, 5-H, 6-H), 2.40−2.56 (m, 1 H, 6-H), 2.63 (br. d, J = 18.1 Hz, 2-H), 2.77 (br. d, J = 18.1 Hz, 1 H, 2-H), 3.77 (s, 3 H, CO_2CH_3), 5.34 (br. s, 1 H, 3-H), 8.14−8.32 (m, 4 H, ArH). Signals attributed to **12a:** δ = 3.79 (s, CO_2CH_3), 5.50 (br. s, 4-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.1 (4-CH_3), 26.3 (C-5), 28.5 (C-6), 32.8 (C-2), 52.6 (CO_2CH_3), 79.9 (C-1), 116.2 (C-3), 123.5 (C-11), 130.8 (C-10), 133.2 (C-4), 135.3 (C-9), 150.6 (C-12), 163.6 (C-8), 172.3 (CO_2CH_3). Signals attributed to **12a:** δ = 21.5, 23.2, 28.1, 37.0, 80.5, 119.8. $C_{16}H_{17}NO_6$ (319.3): calcd. C 60.18, H 5.37, N 4.39; found C 60.43, H 5.23, N 4.24.

1-Methoxycarbonyl-4-methyl-3-cyclohexen-1-yl *p*-Methoxybenzoate (11b) and 1-Methoxycarbonyl-3-methyl-3-cyclohexen-1-yl *p*-Methoxybenzoate (12b): According to Method A for the preparation of **11a/12a**, a stirred mixture of **2f** (0.04 g, 0.17 mmol) and **7** (0.40 g, 5.9 mmol) was heated to 170 °C for 96 h. Workup gave 0.033 g (65%) of a mixture of **11b** and **12b** (67:33) as a greenish oily residue.

According to Method B for the preparation of **11a/12a**, a mixture of **2f** (0.04 g, 0.17 mmol), $AlCl_3$ (0.53 g, 4.0 mmol), and **7** (0.40 g, 5.9 mmol) was stirred at room temperature for 48 h. Workup gave 0.032 g (63%) of a mixture of **11b** and **12b** (88:12) as a greenish oily residue. **11b:** R_f = 0.65 (hexane/EtOAc, 8:2). IR (CH_2Cl_2): $\tilde{\nu}$ = 1746, 1712, 1606, 1291, 1257, 1167, 1101 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.70 (br. s, 3 H, 4-CH_3), 1.92−2.20 (m, 3 H, 5-H, 6-H), 2.36−2.64 (m, 2 H, 2-H, 6-H), 2.72 (br. d, J = 18.1 Hz, 1 H, 2-H), 3.75 (s, 3 H, CO_2CH_3), 3.86 (s, 3 H, $ArOCH_3$), 5.31 (br. s, 1 H, 3-H), 6.88−6.94 (m, 2 H, ArH), 7.92−7.98 (m, 2 H, ArH). Signals attributed to **12b:** δ = 3.76 (s, CO_2CH_3), 5.46 (br. s, 4-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 23.2 (4-CH_3), 26.5 (C-5), 28.6 (C-6), 33.0 (C-2), 52.4 (CO_2CH_3), 55.4 ($ArOCH_3$), 78.3 (C-1), 113.6 (C-11), 116.5 (C-3), 122.4 (C-9), 131.8 (C-10), 133.1 (C-4), 163.5 (C-8), 165.2 (C-12), 172.9 (CO_2CH_3). Signals attributed to **12b:** δ = 21.6, 23.3, 28.3, 37.1, 55.5, 79.1, 119.7, 122.3, 132.5, 173.1. FAB HRMS (*m*NBA): calcd. 305.1389 $[M + H]^+$; found 305.1399.

(1*R,2*R**)-2-Acetoxy-1-methoxycarbonyl-3-cyclohexen-1-yl *p*-Nitrobenzoate (17a):** In a screw-capped ACE pressure tube under N_2 atmosphere, a stirred mixture of **2d** (0.2 g, 0.8 mmol) and **8** (0.094 g, 0.84 mmol) in dry xylene (5 mL) was heated to 150 °C for 48 h. The solvent was then removed in vacuo to leave a greenish oily residue. This was purified by flash column chromatography on silica gel (20 g; hexane/EtOAc, 90:10) to yield 0.15 g (52%) of **17a** as colorless crystals. R_f = 0.34 (hexane/EtOAc, 8:2). IR (KBr): $\tilde{\nu}$ = 1751, 1724, 1607, 1534, 1438, 1347, 1296, 1232, 1104, 1026, 844, 719 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.90−2.30 (m, 1 H, 5-H), 2.06 (s, 3 H, AcO), 2.23−2.41 (m, 2 H, 5-H, 6-H), 2.63−2.72 (m, 1 H, 6-H), 3.76 (s, 3 H, CO_2CH_3), 5.46 (d, J = 4.9 Hz, 1 H, 2-H), 5.88−5.96 (m, 1 H, 3-H), 6.11−6.19 (m, 1 H, 4-H), 8.13−8.17 (m, 2 H, ArH), 8.27−8.32 (m, 2 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.8 (CH_3CO_2), 21.7 (C-5), 22.3 (C-6), 52.7 (CO_2CH_3), 68.2 (C-2), 80.5 (C-1), 121.6 (C-3), 123.7 (C-11), 131.0 (C-10), 133.4 (C-4), 134.4 (C-9), 150.8 (C-12), 162.9 (C-8), 169.4 ($MeCO_2$), 169.6 (CO_2CH_3). $C_{17}H_{17}NO_8$ (363.3): calcd. C 56.20, H 4.72, N 3.85; found C 56.50, H 4.52, N 3.71.

(1*R,2*R**)-2-Acetoxy-1-methoxycarbonyl-3-cyclohexen-1-yl *p*-Methoxybenzoate (17b):** According to the method used to prepare **17a**, reaction of **2f** (0.20 g, 0.85 mmol) with **8** (0.140 g, 1.25 mmol) gave 0.19 g (64%) of **17b** as a colorless oil. R_f = 0.40 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1750, 1718, 1606, 1286, 1259, 1228, 1168, 1100, 1024 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.96−2.12 (br. s, 1 H, 5-H), 2.04 (s, 3 H, AcO), 2.16−2.32 (m, 2 H, 5-H, 6-H), 2.63−2.78 (m, 1 H, 6-H), 3.74 (s, 3 H, CO_2CH_3), 3.86 (s, 3 H, $ArOCH_3$), 5.42 (d, J = 4.9 Hz, 1 H, 2-H), 5.87−5.93 (m, 1 H, 3-H), 6.10−6.15 (m, 1 H, 4-H), 6.89−6.94 (m, 2 H, ArH), 7.27−7.95 (m, 2 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.8 (CH_3CO_2), 21.8 (C-5), 22.4 (C-6), 52.3 (CO_2CH_3), 55.4 ($ArOCH_3$), 68.4 (C-2), 79.1 (C-1), 133.7 (C-11), 121.4 (C-9), 121.7 (C-3), 131.9 (C-10), 133.5 (C-4), 163.8 (C-8), 164.5 (C-12), 169.5 ($MeCO_2$), 170.3 (CO_2CH_3). $C_{18}H_{20}O_7$ (348.4): calcd. C 62.06, H 5.79; found C 62.19, H 5.82.

1-Methoxycarbonyl-3-cyclohexen-1-yl *p*-Nitrobenzoate (26a): According to the method used to prepare **17a**, reaction of **2d** (0.2 g, 0.8 mmol) with **25** (1.00 g, 18.5 mmol) for 72 h gave 0.22 g (92%) of **26a** as a colorless oil. R_f = 0.71 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1747, 1728, 1529, 1349, 1296, 1256, 1113, 1104 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.04−2.16 (m, 1 H, 6-H), 2.17−2.25 (m, 2 H, 5-H), 2.44−2.53 (m, 1 H, 6-H), 2.64 (dm, J = 18.3 Hz, 1 H, 2-H), 2.80 (dm, J = 18.3 Hz, 1 H, 2-H), 3.76 (s, 3 H, CO_2CH_3), 5.62−5.70 (m, 1 H, 3-H), 5.75−5.84 (m, 1 H, 4-H), 8.17−8.35 (m, 4 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.6 (C-5), 28.1 (C-6), 32.5 (C-2), 52.6 (CO_2CH_3), 79.9 (C-1), 122.3 (C-3), 123.5 (C-11), 126.0 (C-4), 130.8 (C-10), 135.3 (C-9), 150 (C-12), 163.6 (C-8), 172.9 (CO_2CH_3). $C_{15}H_{15}NO_6$ (305.3): calcd. C 59.02, H 4.95, N 4.59; found C 59.42, H 4.99, N 4.47.

1-Methoxycarbonyl-3-cyclohexen-1-yl *p*-Methoxybenzoate (26b): According to the method used to prepare **26a**, reaction of **2f** (0.15 g, 0.63 mmol) with **25** (1.00 g, 18.5 mmol) yielded 0.17 g (93%) of **26b** as a colorless oil. R_f = 0.63 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1746, 1712, 1606, 1295, 1254, 1168, 1102, 1069 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.02−2.10 (m, 1 H, 6-H), 2.17−2.22 (m, 2 H, 5-H), 2.44 (dm, J = 13.2 Hz, 1 H, 6-H), 2.63 (dm, J = 18.3 Hz, 1 H, 2-H), 2.75 (dm, J = 18.3 Hz, 1 H, 2-H), 3.76 (s, 3 H, CO_2CH_3), 3.85 (s, 3 H, $ArOCH_3$), 5.59−5.68 (m, 1 H, 3-H), 5.73−5.81 (m, 1 H, 4-H), 6.89−6.93 (m, 2 H, ArH), 7.95−7.98 (m, 2 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 21.6 (C-5), 28.2 (C-6), 32.6 (C-2), 52.3 (CO_2CH_3), 55.3 ($ArOCH_3$), 78.3 (C-1), 113.5 (C-11), 122.2 (C-9), 122.5 (C-3), 125.9 (C-4), 131.8 (C-10), 163.5 (C-8), 165.1 (C-12), 172.9 (CO_2CH_3). FAB HRMS (*m*NBA): calcd. 291.1232 $[M + H]^+$; found 291.1230.

(1*R,2*R**,4*R**)-2-Methoxycarbonyl-5-norbornen-2-yl *p*-Nitrobenzoate (21a) and (1*R**,2*S**,4*R**)-2-Methoxycarbonyl-5-norbornen-2-yl *p*-Nitrobenzoate (22a) − Method A:** According to Method A for the preparation of **17a**, a mixture of **2d** (0.2 g, 0.8 mmol) and **9** (1.0 g, 15 mmol) in dry xylene (2 mL) was stirred for 12 h. Column chromatographic workup on silica gel (15 g; hexane/EtOAc, 9:1) yielded 0.20 g (79%) of a mixture of **21a** and **22a** (59:41) as a colorless oil.

Method B: Under an N_2 atmosphere at −50 °C, a mixture of **2d** (0.2 g, 0.8 mmol), **9** (1.0 g, 15 mmol), and $TiCl_4$ (0.76 g, 4.0 mmol) in dry CH_2Cl_2 (5 mL) was stirred for 8 h. The mixture was then diluted with CH_2Cl_2 (50 mL) and washed with saturated aqueous $NaHCO_3$ solution (2 × 30 mL). The organic phase was dried (Na_2SO_4) and the solvent was removed in vacuo to leave a greenish oily residue. This was purified by flash column chromatography on silica gel (15 g; hexane/EtOAc, 9:1), giving 0.19 g (76%) of a mixture of **21a** and **22a** (55:45) as a colorless oil.

Method C: According to Method B for the preparation of **11a/12a**, a mixture of **2d** (0.2 g, 0.8 mmol), **9** (1.0 g, 15 mmol), and $AlCl_3$ (1.08 g, 8.01 mmol) was stirred for 24 h. The mixture was then

worked-up by flash column chromatography on silica gel (15 g; hexane/EtOAc, 9:1), giving 0.177 g (70%) of a mixture of **21a** and **22a** (75:25) as a colorless oil. The isomers were separated by radial chromatography (hexane/EtOAc, 100:2), giving 0.06 g (24%) of **21a** as a colorless oil and 0.025 g (10%) of **22a** as colorless crystals. **21a:** R_f = 0.46 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1742, 1728, 1530, 1349, 1290, 1250, 1164, 1117, 1102 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.47 (dd, J = 13.2, 3.6 Hz, 1 H, 3-H_n), 1.60 (dm, J = 9.1 Hz, 1 H, 7-H_s), 1.90 (br. d, J = 9.1 Hz, 1 H, 7-H_a), 2.82 (dd, J = 13.2, 3.6 Hz, 1 H, 3-H_x), 3.03 (br. s, 1 H, 4-H), 3.45 (br. s, 1 H, 1-H), 3.77 (s, 3 H, CO_2CH_3), 6.20 (dd, J = 5.6, 3.0 Hz, 1 H, 6-H), 6.46 (dd, J = 5.6, 3.0 Hz, 1 H, 5-H), 8.11−8.18 (m, 2 H, ArH), 8.26−8.32 (m, 2 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 40.1 (C-3), 42.1 (C-4), 47.5 (C-7), 51.0 (C-1), 52.8 (CO_2CH_3), 88.0 (C-2), 123.5 (C-12), 130.8 (C-11), 132.6 (C-6), 135.1 (C-10), 140.5 (C-5), 150.6 (C-13), 164.2 (C-9), 172.5 (C-8). $C_{16}H_{15}NO_6$ (317.3): calcd. C 60.57, H 4.77, N 4.41; found C 60.63, H 4.80, N 4.11. Data for **22a:** R_f = 0.43 (hexane/EtOAc, 8:2); m.p. 139−140 °C. IR (KBr): $\tilde{\nu}$ = 1749, 1727, 1528, 1288, 1102, 1053 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.77 (dm, J = 8.8 Hz, 1 H, 7-H_s), 1.86 (dd, J = 13.3, 3.8 Hz, 1 H, 3-H_x), 1.98 (br. d, J = 8.8 Hz, 1 H, 7-H_a), 2.48 (dd, J = 13.3, 2.9 Hz, 1 H, 3-H_n), 3.03 (br. s, 1 H, 4-H), 3.30 (br. s, 1 H, 1-H), 3.69 (s, 3 H, CO_2CH_3), 5.92 (dd, J = 5.6, 3.2 Hz, 1 H, 6-H), 6.46 (dd, J = 5.6, 2.9 Hz, 1 H, 5-H), 8.21−8.33 (m, 4 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 39.2 (C-3), 42.0 (C-4), 49.1 (C-7), 51.8 (C-1), 52.5 (CO_2CH_3), 87.7 (C-2), 123.6 (C-12), 130.1 (C-6), 130.9 (C-11), 135.1 (C-10), 142.0 (C-5), 150.6 (C-13), 164.3 (C-9), 170.9 (C-8). $C_{16}H_{15}NO_6$ (317.3): calcd. C 60.57, H 4.77, N 4.41; found C 60.29, H 5.01, N 4.68.

(1*R,2*R**,4*R**)-2-Methoxycarbonyl-5-norbornen-2-yl *p*-Methoxybenzoate (21b) and (1*R**,2*S**,4*R**)-2-Methoxycarbonyl-5-norbornen-2-yl *p*-Methoxybenzoate (22b) − Method A:** According to Method A for the preparation of **21a/22a**, a mixture of **2f** (0.15 g, 0.63 mmol) and **9** (1.0 g, 15 mmol) in dry xylene (2 mL) was allowed to react to give 0.14 g (76%) of a mixture of **21b** and **22b** (60:40) as a colorless oil.

Method B: According to Method B for the preparation of **11a/11b**, a mixture of **2f** (0.15 g, 0.63 mmol), **9** (1.0 g, 15 mmol), and $AlCl_3$ (0.84 g, 6.3 mmol) was allowed to react to give 0.14 g (73%) of a mixture of **21b** and **22b** (57:43) as a colorless oil.

Method C: According to Method B for the preparation of **21a/22a**, a mixture of **2f** (0.15 g, 0.63 mmol), **9** (1.0 g, 15 mmol), and $TiCl_4$ (0.57 g, 3.0 mmol) was allowed to react to give 0.134 g (70%) of **21b** and **22b** (84:16). The mixture was purified by flash column chromatography on silica gel (15 g; hexane/EtOAc, 9:1). The isomers were separated by radial chromatography (hexane/EtOAc, 100:2), giving 0.04 g (21%) of **21b** and 0.021 g (11%) of **22b** as colorless oils. Data for **21b:** R_f = 0.43 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1742, 1712, 1607, 1511, 1291, 1257, 1162, 1102 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.43 (dd, J = 13.0, 3.7 Hz, 1 H, 3-H_n), 1.60 (dm, J = 9.1 Hz, 1 H, 7-H_s), 1.86 (br. d, J = 9.1 Hz, 1 H, 7-H_a), 2.79 (dd, J = 13.0, 3.6 Hz, 1 H, 3-H_x), 2.98 (br. s, 1 H, 4-H), 3.41 (br. s, 1 H, 1-H), 3.75 (s, 3 H, CO_2CH_3), 3.85 (s, 3 H, ArOMe), 6.19 (dd, J = 5.7, 3.1 Hz, 1 H, 6-H), 6.41 (dd, J = 5.7, 3.0 Hz, 1 H, 5-H), 6.89−6.92 (m, 2 H, ArH), 7.90−7.93 (m, 2 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 39.9 (C-3), 42.1 (C-4), 47.3 (C-7), 51.0 (C-1), 52.6 (CO_2CH_3), 55.4 (ArOCH_3), 86.7 (C-2), 133.5 (C-12), 122.0 (C-10), 131.8 (C-11), 132.8 (C-6), 140.1 (C-5), 163.5 (C-9), 165.8 (C-13), 173.2 (C-8). $C_{17}H_{18}O_5$ (302.3): calcd. C 67.54, H 6.00; found C 67.28, H 6.07. − Data for **22b:** R_f = 0.40 (hexane/EtOAc, 8:2). IR (film): $\tilde{\nu}$ = 1745, 1712, 1606, 1511, 1288, 1259, 1167, 1101, 1032 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.73 (dm, J = 8.7 Hz, 1 H, 7-H_s), 1.83 (dd, J = 13.2, 3.3 Hz, 1 H, 3-H_x), 1.99 (br. d, J = 8.7 Hz, 1 H, 7-H_a), 2.44 (dd, J = 13.2, 3.0 Hz, 1 H, 3-H_n), 2.98 (br. s, 1 H, 4-H), 3.25 (br. s, 1 H, 1-H), 3.68 (s, 3 H, CO_2CH_3), 3.87 (s, 3 H, ArOMe), 5.91 (dd, J = 5.8, 3.0 Hz, 1 H, 6-H), 6.43 (dd, J = 5.8, 3.0 Hz, 1 H, 5-H), 6.91−6.95 (m, 2 H, ArH), 7.99−8.03 (m, 2 H, ArH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 39.1 (C-3), 41.9 (C-4), 49.0 (C-7), 51.7 (C-1), 55.2 (CO_2CH_3), 55.4 (ArOCH_3), 86.3 (C-2), 113.6 (C-12), 122.1 (C-10), 130.2 (C-6), 131.9 (C-11), 141.8 (C-5), 163.6 (C-9), 165.9 (C-13), 171.6 (C-8). $C_{17}H_{18}O_5$ (302.3): calcd. C 67.54, H 6.00; found C 67.85, H 6.14.

X-ray Crystallographic Study: Alkene **2d** (hexane/CH_2Cl_2, 30:5) and adduct **22a** (hexane/EtOAc, 100:2) were obtained as pale-yellow and colorless crystals, respectively. The selected specimens were mounted on glass fibers. Crystallographic measurements were performed at room temperature on a Siemens P4 diffractometer using Mo-K_α radiation (graphite crystal monochromator, λ = 0.71073 Å). Two standard reflections were monitored periodically; they showed no change during data collection. Unit cell parameters were obtained from a least-squares refinement of 26 reflections in the range $2 < 2\Theta < 20°$. Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions and their atomic coordinates were refined. Unit weights were used in the refinement. The structures were solved using SHELXTL[32] on a personal computer. Data for **2d:** Formula: $C_{11}H_9NO_6$; molecular weight: 251.19; crystal system: monoclinic; space group: $C2/c$; unit cell parameters: a = 24.087(4), b = 7.0305(5), c = 13.6270(9) Å; α = 90°, β = 100.533(12)°, γ = 90°; V = 2268.7(5) $Å^3$; T = 293(2) K; Z = 8; θ scan range: 1.72−27.00°; no. of reflections collected: 3056; no. of observed reflections: 2443; R = 0.0597; GoF = 1.025. Data for **22a:** Formula: $C_{16}H_{15}NO_6$; molecular weight: 317.29; crystal system: monoclinic; space group: $C2/c$; unit cell parameters: a = 23.926(3), b = 7.9688(9), c = 16.659(2) Å; α = 90°, β = 109.541(13)°, γ = 90°; V = 2993.4(6) $Å^3$; T = 293(2) K; Z = 8; θ scan range: 1.81−26.99°; no. of reflections collected: 4028; no. of observed reflections: 3273; R = 0.0775; GoF = 1.052.

UP and ET Spectroscopy: The UP spectra were obtained with a He^I source in conjunction with a Datalab DL400 signal analysis system. The bands, calibrated against rare-gas lines, were located using the positions of their maxima, which were taken as corresponding to the vertical ionization energies. The accuracy of the *IE* values was estimated to be better than ±0.05 eV. The ET spectra were obtained by operating the instrument in such a mode as to obtain a signal related to the nearly total scattering cross section. The energy scales were calibrated using the $(1s^1-2s^2)$ ^2S anion state of helium and the estimated accuracy of the measured VAE values was ±0.05 eV.

Theoretical Calculations: The ab initio SCF/RHF calculations were carried out with the 3−21G and 6−31G* basis sets using GAUSSIAN-94[23a] (PC-Linux) and GAMESS[23b] for Windows 95/98/NT (v. 6.0). Geometries were optimized using the 3−21G level basis set, and these were employed as starting points for optimization at the 6−31G* level.

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