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Synergy or Competition between Palladium-Catalysis and KF/Alumina-Mediation for the Allylic Substitution of the Acetates of Baylis–Hillman Adducts by Phenols

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Abstract—The addition of various substituted phenols [XC_6H_4OH, X=H, *o*-CHO, *o*-CO_2Me, *o*-CO_2CH_2Ph, *o*-CN, *m*-NHCOMe, *m*-OMe, *p*-OMe, *p*-CHO, *p*-Cl] to allylic acetates obtained from Baylis–Hillman adducts [$RCH(OAc)C(=CH_2)CO_2Et$, R=H, *n*-Pr] has been studied in the presence of a Pd(0) catalyst and/or KF/alumina. In some cases, the use of one of these two reagents was sufficient to promote the OAc/OAr exchange but in general, faster reactions and higher yields were achieved when both reagents were used together. Evidence for two routes, an η^3-allylpalladium intermediate and a Michael addition/elimination, was then obtained while a Heck type reaction could be involved under neutral conditions. © 2000 Published by Elsevier Science Ltd.

Introduction

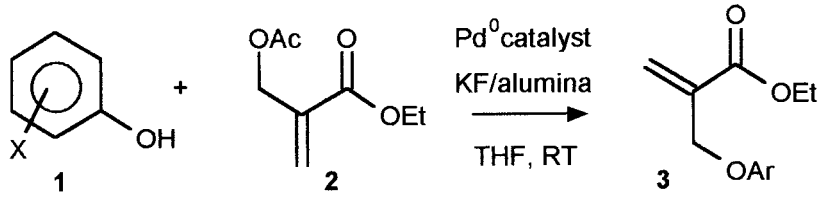
The formation of C–C bonds through palladium-catalyzed nucleophilic substitution reactions of allylic substrates has found widespread use in organic synthesis.[1] In contrast, the use of hydroxylated compounds as pronucleophiles[2] in Pd-catalyzed allylic substitutions is less common; some intra- and intermolecular substitutions using either alcohols[3,4] or phenols[4–6] have been reported. Previously, we have described the substitution of allylic acetates by phenol (**1a**) in the presence of KF-doped alumina and catalytic amounts of Pd(0) complexes.[5a]

For a synthetic project, the preparation of the arylether **3a** (Eq. (1)) was recently required. Thus, we envisaged to subject the Baylis–Hillman type product **2** to our experimental conditions.[5a] In fact, it has been extensively shown that Baylis–Hillman adducts and their derivatives are versatile compounds which can be subjected to a variety of organic transformations.[6–8]

In Eq. (1) X=H (**a**); *o*-CHO (**b**); *o*-CO_2Me (**c**); *o*-CO_2CH_2Ph (**d**); *o*-CN (**e**); *m*-NHCOMe (**f**); *m*-OMe (**g**); *p*-OMe (**h**); *p*-CHO (**i**); *p*-Cl (**j**).

Results and Discussion

The coupling of ethyl acrylate with formaldehyde in the presence of catalytic amounts of DABCO[9] followed by acetylation of the resulting hydroxy compound with acetyl chloride/pyridine afforded easily **2**. Then, the reaction of **2** with **1a** using home-made KF/alumina from an old batch[10] and catalytic amounts of a Pd(0) complex led effectively to **3a** at room temperature (Table 1, run 1). In the absence of KF/alumina, the reaction was sluggish and the yield dropped (run 2). Under these latter conditions, no evolution of **2** was observed when the Pd(0) catalyst was exchanged for $PdCl_2(MeCN)_2$. The use of a freshly prepared batch of KF/alumina had a notable consequence: the reaction was



(1)

Keywords: allylation; Baylis–Hillman reactions; palladium; phenols.

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Table 1. Synthesis of **3a** from **1a** (1.5 equiv.) and **2** in THF at room temperature

Run	Catalyst (equiv.)	Ligand (equiv.)	KF/alumina[a]	Time (h)	Conv.% of **2**	Yield%[b]
1	$Pd(dba)_2$ (0.05)	dppe (0.05)	A_1	19.5	100	74
2	$Pd(dba)_2$ (0.05)	dppe (0.05)	No	29	100	52
3	$Pd_2(dba)_3{\cdot}CHCl_3$ (0.025)	PPh_3 (0.1)	A_2	4.5	100	79
4	No	No	A_2	3	100	71

[a] KF/alumina (500 mg $mmol^{-1}$ of **2**) from either an old batch (A_1) or a batch freshly prepared (A_2) as described previously.[10]
[b] Yields are for isolated compounds and are calculated on the amount of **2** introduced.

faster (run 3) and furthermore, **3a** was isolated in a fair yield even in the absence of palladium-catalysis (run 4).

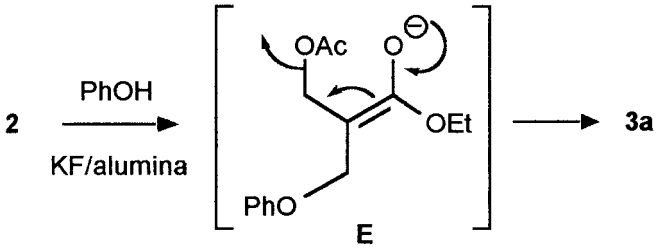
As we have shown previously that the OAc/OPh exchange between allyl acetate and phenol was not observed in the absence of palladium,[5a] the result of run 4 is due to the presence of the CO_2Et group which allows a base-catalyzed Michael addition of **1a**.[7a,11,12] This is followed by the elimination of the acetate group leading to **3a** (Scheme 1).

When we replaced **1a** by salicylaldehyde (**1b**) as pronucleophile, we were surprised to observe strikingly different reactivities (Table 2). Indeed, no traces of **3b** were observed in using solely KF/alumina (run 5) while Pd(0)-catalysis in the absence of base induced a sluggish reaction affording a complex mixture which contained some **3b** as shown by thin-layer chromatography analysis (run 6). In contrast, the use of both Pd(0) and KF/alumina led to **3b** in good yields (runs 7 and 8). Interestingly, the Pd-catalyst loading can be decreased without strongly affecting the chemical yield (run 9).

The above intriguing results encouraged us to carry out the reactions of **2** with **1c**–**1j** using KF/alumina under both sets of conditions, i.e. either with or without Pd-catalysis and following the conversion of **2** by TLC (Table 3). Inspection of Table 3 reveals that the presence of a Pd-catalyst increased strongly both the rate and the yield of the reactions with the phenols having *o*-CO_2R or *o*-CN substituents (runs 10/12, 13/14 and 15/16). These increases were lower for *m*-OMe, *p*-OMe and *p*-Cl substituents (runs 19/20, 21/22 and 25/26), and not observed for a *m*-NHCOMe substituent (runs 17/18). As previously for an *o*-CHO substituent (Table 2), palladium-catalysis was required when the phenol carried a *p*-CHO group (run 23/24).

From the results shown in Tables 1–3, it appears that *m*-methoxyphenol and *p*-methoxyphenol are more reactive than the others phenols and, in particular, than PhOH. The reactions of aromatic compounds are often examined in reference to the Hammett equation; from the literature, *m*-OMe and *p*-OMe groups have respectively positive and negative σ values which correlate with strong differences of reactivity.[13] Therefore, the reactions of **2** with **1g** and **1h** do not correlate with these parameters (runs 19–22); similar conclusions can be drawn by comparing the reactivity of the other *m*- and *p*-substituted phenols.[14]

The most general observation from Tables 1–3 is that the yields of the C–O coupling reactions are always improved when both Pd(0) and KF/alumina are used except when **1f** is the pronucleophile. Under these conditions, two competitive



Scheme 1.

Table 2. Synthesis of **3b** from **1b** (1.5 equiv.) and **2** in THF at room temperature

Run	Catalyst (equiv.)	Ligand (equiv.)	KF/alumina[a]	Time (h)	Conv.% of **2**	Yield%[b]
5	No	No	A_2	72	0	0
6	$Pd_2(dba)_3{\cdot}CHCl_3$ (0.025)	dppe (0.05)	No	46.5	41	[c]
7	$Pd_2(dba)_3{\cdot}CHCl_3$ (0.025)	dppe (0.05)	A_2	5.5	100	81
8	$Pd_2(dba)_3{\cdot}CHCl_3$ (0.025)	PPh_3 (0.1)	A_2	6	100	88
9	$Pd(dba)_2$ (0.01)	dppe (0.01)	A_1	72	100	77

[a] See Table 1.
[b] See Table 1.
[c] Formation of many compounds with small amounts of **3b**.

Table 3. Reactions of **1c–1j** with **2**

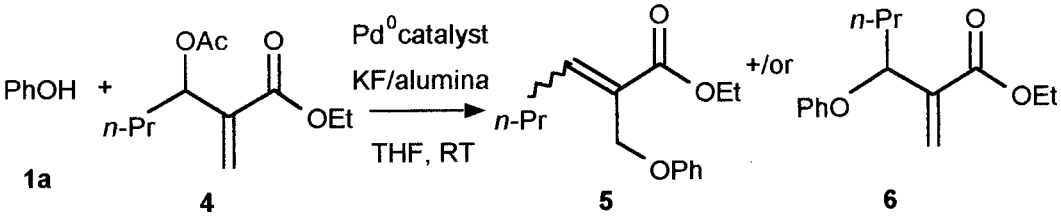
Run[a]	Phenol (1.5 equiv.)	$Pd_2(dba)_3{\cdot}CHCl_3$ (equiv.)	dppe (equiv.)	Time (h)	Conv.% of **2**	Yield%[b]
10	**1c**	0.025	0.05	4.5	100	**3c**: 95
11	**1c**	0	0	5	<9	**3c**: [c]
12	**1c**	0	0	168	66	**3c**: 52
13	**1d**	0.005	0.01	4	100	**3d**: 72
14	**1d**	0	0	170	100	**3d**: 59
15	**1e**	0.025	0.05	8.5	100	**3e**: 82
16	**1e**	0	0	168	100	**3e**: 71
17	**1f**	0.025	0.05	21	100	**3f**: 81
18	**1f**	0	0	21	100	**3f**: 82
19	**1g**	0.025	0.05	1.25	100	**3g**: 80
20	**1g**	0	0	2	100	**3g**: 72
21	**1h**	0.025	0.05	1.25	100	**3h**: 95
22	**1h**	0	0	2	100	**3h**: 91
23	**1i**	0.025	0.05	5.5	100	**3i**: 78
24	**1i**	0	0	120	0	**3i**: 0
25	**1j**	0.025	0.05	4	100	**3j**: 88
26	**1j**	0	0	12	100	**3j**: 83

[a] These runs have been carried out in THF at room temperature in the presence of KF/alumina freshly prepared (500 mg $mmol^{-1}$ of **2**).
[b] See Table 1.
[c] Not isolated.

mechanistic paths, which involve either a η^3-allylpalladium intermediate (Scheme 2) or an enolate such as **E** (Scheme 1), can be postulated.

To discriminate between these two mechanistic paths, one extremity of the allyl part of the substrate has to be substituted. Therefore, we studied the regioselectivity of the reaction of **1a** with **4** (Eq. (2)). We presumed that the allylpalladium pathway could lead to the two isomeric compounds **5** and **6**[5a] while the enolate pathway would afford exclusively **5**.[11]

The formation of a small quantity of **6** in run 27 led us to envisage a subsequent process similar to the one depicted in Scheme 1 starting from **5** with phenate as leaving group instead of acetate. In fact, the addition of KF/alumina to a stirred THF solution of **1a** and **5** ([**1a**]/[**5**]: 1.5/1) provided a 60/40 mixture of **5** and **6** in 171 h. Consequently, it appeared that the KF/alumina mediated-reaction of **1a** was more effective with **4** than with **5**. This is in agreement with the greater leaving group properties of AcO^- compared to those of PhO^-.[15] These observations imply that the high proportions of **6** observed in runs 30 and 31 are not

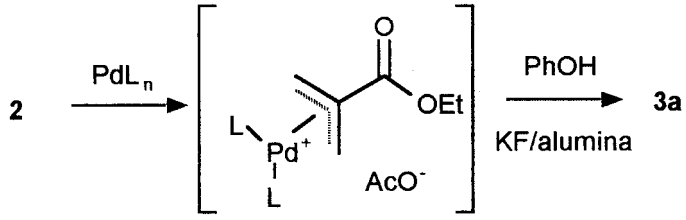


(2)

The results are assembled in Table 4. In the absence of a Pd-catalyst, the KF/alumina-mediated addition/elimination led mainly to **5**, a small amount of **6** being however obtained (run 27). In the absence of base, no evolution of **4** was detected under palladium-catalysis (runs 28 and 29). When both Pd(0) and KF/alumina were used, a mixture of **5** and **6** was obtained and the yield was improved as in Table 1, runs 3/4; moreover, the ratio between these two compounds was highly dependent on the nature of the ligand (runs 30 and 31).

mainly due to a KF/alumina-mediated Michael addition of **1a** on **5**.

The influence of the nature of the phosphine ligands on the regioselectivity of nucleophilic additions on η^3-allylpalladium complexes has been often exemplified.[5g,16] Therefore, the strong dependence under Pd(0)-catalysis of the **5/6** ratio on the nature of the ancillary ligand (runs 30 and 31) is highly indicative of a η^3-allylpalladium intermediate followed by the



Scheme 2.

Table 4. Reactivity of **1a** towards **4**

Run[a]	Equiv. of the Pd-catalyst	Ligand (equiv.)	KF/alumina	Time (h)	Conv.% of **4**	Yield% of **5**[b]+**6**	**5**[b]/**6** ratio
27	0	No	Yes	52	100	71	95/5
28	0.025	dppe (0.05)	No	168	0	–	–
29	0.025	PPh_3 (0.1)	No	192	0	–	–
30	0.025	dppe (0.05)	Yes	52	100	85	32/68
31	0.025	PPh_3 (0.1)	Yes	45	100	77	55/45

[a] These runs have been carried out using 1.5 equiv. of **1a** in THF at room temperature, the reagents were KF/alumina freshly prepared (500 mg $mmol^{-1}$ of **4**) and $Pd_2(dba)_3{\cdot}CHCl_3$.
[b] The *E* isomer of **5** was exclusively obtained except in run 27 where 3% of the *Z*-isomer was detected from the study of the ^1H NMR spectra (see Experimental).

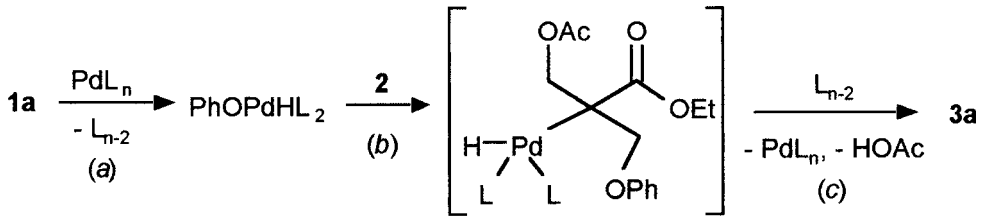
addition of phenate to either one allylic terminus or the other.

The Pd(0)-catalyzed isomerisation of allyl acetates is well known.[17] With simple allyl phenyl ethers, we have previously shown that the corresponding Pd(0)-catalyzed 1,3-transposition of the PhO group required heating;[5a] this is in agreement with the subsequent report of Sinou's team.[5e] Nevertheless, we had to investigate whether **6** could be obtained through a Pd(0)-catalyzed rearrangement of **5**. To examine this possibility, a solution of **5** in THF containing $Pd_2(dba)_3{\cdot}CHCl_3$ (0.025 equiv.) and PPh_3 (0.1 equiv.) was stirred at room temperature for 45 h: no traces of **6** were detected. With these results in hand, we propose that in runs 28 and 29, the main following reactive steps are: (i) the formation of PhO^- or strongly polarized $PhO^{-\delta}{-}H^{+\delta}$ from **1a** and KF/alumina; (ii) the formation of a η^3-allylpalladium complex from **3** and Pd(0); (iii) the non-regioselective nucleophilic addition of the phenolic species to the allylpalladium complex which provides **5** or **6** and the active Pd(0) catalyst. For these two runs, the KF/alumina-mediated Michael addition of **1a** to **4** would be a very limited pathway. Although assistance by KF/alumina was thus required, its role was mainly restricted to the activation of **1a**.

As exemplified in Tables 1 and 4, the experimental conditions for an effective Pd(0)-catalyzed addition of **1a** to Baylis–Hillman type compounds are very dependent on the substitution of the allyl part since the reaction with **2** worked in the absence of base (run 2) while this latter was required when using **4** (runs 28 and 29). Recently, Poli and Giambastiani have reported the formation of C–C bonds through $Pd(PPh_3)_n$-catalyzed alkylation of allylic acetates by active methylenes under neutral conditions; they have proposed a mechanism involving formation of the η^3-allylpalladium complex followed by coordination of the soft pronucleophile to palladium and its deprotonation by the acetate anion.[18] However, their reactions were carried out under reflux of THF, CH_2Cl_2 or $Cl(CH_2)_2Cl$, and the process was seriously or totally inhibited when a bis-coordinating phosphine such as dppe was used instead of PPh_3.[18] In contrast, dppe was effective as a Pd-ligand for the phenoxylation of **2** in the absence of base even at room temperature (run 2). These remarks led us to envisage a Heck type mechanism (Scheme 3) rather than an η^3-allylpalladium intermediate for phenoxylation under neutral conditions. Examples of the each three steps of Scheme 3—oxidative addition, insertion and β-elimination—have been described in the literature; Step *a*: a phenoxopalladium(II) hydride complex has been characterized unambiguously from the oxidative insertion of $Pd(PCy_3)_2$ into the O–H bond of phenol,[19] Step *b*: recently, such complexes have been postulated as reactive intermediates for the hydrophenoxylation of double bonds,[20] and Step *c*: β-acetoxy eliminations have been exemplified in various Heck reactions using vinyl acetate as substrate.[21] For Heck reactions, the alkenes bearing electron-withdrawing groups are the most reactive;[1b] this could explain the low reactivity[5a] of simple allyl acetates. The high difference of reactivity between **2** and **4** can be explained in considering Step *c* which requires a *syn* relationship between OAc and Pd. In contrast to **2**, a Heck-type reaction using **4** as substrate would lead to an intermediate where this relationship will develop strong steric interactions between the propyl substituent and either the ester group or the CH_2OPh group.

Conclusion

We have shown that the efficiency and the required experimental conditions for the OAc/OAr exchanges between allylic acetates derived from Baylis–Hillman adducts and ArOH's induced by Pd(0) and KF/alumina depend strongly upon the substitution of both the Ar group and the allylic termini. In general, there is a noticeable synergy between Pd(0) and KF/alumina. The use of these reagents together



Scheme 3.

has a significant beneficial effect on reaction rates and yields in most cases.

Experimental

^{1}H and ^{13}C NMR (250 and 63 MHz) spectra were obtained on a Bruker AC 250 spectrometer using TMS as internal standard and $CDCl_3$ as solvent. IR spectra were recorded on a Spectra file Plus Midac using film for oil and KBr for solid. Mass spectra were recorded on a Jeol D 300 at 'UFR Pharmacie' of Reims. Microanalyses were performed by the Service of Microanalyses of UMR 6519. THF was distilled over Na/benzophenone. $Pd_2dba_3{\cdot}CHCl_3$,[22] ethyl 2-(hydroxymethyl)acrylate[9] and KF-doped alumina[10] were prepared according to literature methods.

Ethyl 3-hydroxy-2-methylenehexanoate. A mixture of butanal (20 ml, 227 mmol), ethyl acrylate (50 ml, 454 mmol) and DABCO (7.6 g, 68 mmol) was sonicated in an ultrasound bath[23] for 21 days. The excess of ethyl acrylate was evaporated and the residue was taken up in ether (200 ml). The organic layer was washed with 2N aqueous HCl (2×50 ml), water (2×50 ml) and brine (2×50 ml) and dried over $MgSO_4$. The solvent was removed under vacuo to give ethyl 3-hydroxy-2-methylenehexanoate (38.82 g, 94%) as colorless oil; IR (cm^{-1}) 3437, 2872, 1705, 1466; ^{1}H NMR 0.92 (t, 3H, J=7.2 Hz, $CH_2CH_2CH_3$), 1.31 (t, 3H, J=7.1 Hz, OCH_2CH_3), 1.40 (m, 2H, $CH_2CH_2CH_3$), 1.62 (m, 2H, $CH_2CH_2CH_3$), 2.67 (bs, 1H, OH), 4.22 (q, 2H, J=7.1 Hz, OCH_2CH_3), 4.39 (t, 1H, J=6.6 Hz, CHOH), 5.72 (bs, 1H, C=CHH), 6.21 (bs, 1H, C=CHH); ^{13}C NMR 13.8 ($CH_2CH_2CH_3$), 14.1 (OCH_2CH_3), 19.0 ($CH_2CH_2CH_3$), 38.3 ($CH_2CH_2CH_3$), 60.7 (OCH_2CH_3), 71.4 (CHOH), 124.6 (C=CH_2), 142.7 (C=CH_2), 166.6 (C=O).

Ethyl 2-(acetoxymethyl)acrylate (2)[24]. A stirred mixture of ethyl 2-(hydroxy-methyl)acrylate (20.00 g, 154 mmol) and pyridine (13.38 g, 169 mmol) in dichloromethane (150 ml) was cooled to 0°C, then acetyl chloride (15.7 g, 200 mmol) was added dropwise. The cold bath was removed after 5 min. The mixture was stirred at room temperature for 24 h, hydrolysed and extracted with ether (100 ml). The etheral solution was washed with water (3×50 ml), aqueous saturated solution of NH_4Cl (3×50 ml), brine (50 ml) and dried over $MgSO_4$. The solvent was evaporated giving **2** as a colorless oil (23.6 g, 89%). The IR and ^{1}H NMR spectroscopy data are in agreement with literature.[24]

Ethyl 3-acetoxy-2-methylenehexanoate (4). Prepared by adapting a literature procedure.[25] Acetyl chloride (0.85 ml, 12 mmol) was added dropwise to a mixture of ethyl 3-hydroxy-2-methylenehexanoate (1.72 g, 10 mmol) and pyridine (0.9 ml, 11 mmol) in dichloromethane (30 ml) cooled at 0°C. Then the mixture was warmed to room temperature and the stirring was continued for 8.5 h. The mixture was hydrolysed then extracted with ether (3×50 ml). The organic layer was washed with brine (50 ml) and dried over $MgSO_4$. The solvent was evaporated. Flash chromatography gave **4** as a colorless oil (1.9 g, 89%); IR (cm^{-1}) 2961, 2872, 1743, 1718; ^{1}H NMR 0.92 (t, 3H, J=7.2 Hz, 3H, $CH_2CH_2CH_3$), 1.30 (t, 3H, J=7.2 Hz, OCH_2CH_3), 1.35 (m, 2H, $CH_2CH_2CH_3$), 1.69 (m, 2H, $CH_2CH_2CH_3$), 2.17 (s, 3H, O=CCH_3), 4.23 (q, 2H, J=7.2 Hz, OCH_2CH_3), 5.64 (dd, 1H, J=7.1 and 5.0 Hz, CHOAc), 5.73 (bs, 1H, C=CHH), 6.21 (bs, 1H, C=CHH); ^{13}C NMR 13.7 ($CH_2CH_2CH_3$), 14.1 (OCH_2CH_3), 18.6 ($CH_2CH_2CH_3$), 21.1 (O=CCH_3), 36.4 ($CH_2CH_2CH_3$), 60.8 (OCH_2CH_3), 71.6 (CHOAc), 124.6 (C=CH_2), 140.5 (C=CH_2), 165.3 (CO_2Et), 170.0 (CH_3CO_2).

General procedure for the reaction of 2 and 4 with various phenols. To a solution of **2** or **4** (1 mmol) in THF (5 ml) under argon was added **1** (1.5 mmol), palladium (0–0.05 mmol), phosphine (0–0.1 mmol), and then KF/Alumina (0 or 500 mg). After stirring for the times indicated in the tables, ethyl acetate (20 ml) was added. After stirring for 30 min, the mixture was filtered over Celite. The solvent was evaporated and the residue was purified by flash chromatography (ethyl acetate/ petroleum ether).

Ethyl 2-methylene-3-phenoxypropanoate (3a)[26]. Colorless oil; IR (cm^{-1}) 2982, 1713,1645, 1601, 1496; ^{1}H NMR 1.31 (t, 3H, J=7.2 Hz, OCH_2CH_3), 4.26 (q, 2H, J=7.2 Hz, OCH_2CH_3), 4.76 (t, 2H, J=1.5 Hz, CH_2OPh), 5.99 (q, 1H, J=1.5 Hz, C=CHH), 6.39 (q, 1H, J=1.5 Hz, C=CHH), 6.95 (m, 3H), 7.29 (m, 2H); ^{13}C NMR 14.2 (OCH_2CH_3), 60.9 (OCH_2CH_3), 65.9 (CH_2OPh), 114.7, 121.1, 126.1 (C=CH_2), 129.5, 136.0, 158.3 (C=CH_2), 165.5 (CO_2Et); EIMS m/z 206 (M^+, 35), 161 (78), 131 (100), 113 (48), 105 (98); Anal. calcd for $C_{12}H_{14}O_3$: C: 69.88%, H: 6.84%; found: C: 69.56%, H: 6.98%.

Ethyl 3-(*o*-formylphenyl)-oxy-2-methylenepropanoate (3b). Mp 39–40°C; IR (cm^{-1}) 2982, 1713, 1689, 1599, 1483; ^{1}H NMR 1.32 (t, 3H, J=7.2 Hz, OCH_2CH_3), 4.28 (q, 2H, J=7.2 Hz, OCH_2CH_3), 4.88 (s, 2H, $OCH_2C{=}CH_2$), 6.04 (d, 1H, J=1.5 Hz, C=CHH), 6.46 (d, 1H, J=1.5 Hz, C=CHH), 7.04 (m, 2H), 7.55 (m, 1H), 7.86 (dd, 1H, J=7.6 and 1.9 Hz), 10.53 (1H, s, CHO); ^{13}C NMR 14.1 (OCH_2CH_3), 61.0 (OCH_2CH_3), 66.5 ($OCH_2C{=}CH_2$), 112.8, 121.1, 125.0, 126.6 (C=CH_2), 128.6, 135.3, 135.9, 160.4 (C=CH_2), 165.1 (CO_2Et), 189.4 (CHO); EIMS m/z 234 (M^+, 16), 205 (13), 188 (50), 161 (67), 131 (41), 121 (100); Anal. calcd for $C_{13}H_{14}O_4$: C: 66.66%, H: 6.02%; found: C: 66.92%, H: 5.95%.

Ethyl 3-(*o*-methoxycarbonylphenyl)-oxy-2-methylenepropanoate (3c). Colorless oil; IR (cm^{-1}) 2984, 1726, 1713, 1601, 1493, 1450; ^{1}H NMR 1.33 (t, 3H, J=7.2 Hz, OCH_2CH_3), 3.89 (s, 3H, OCH_3), 4.28 (q, 2H, J=7.2 Hz, OCH_2CH_3), 4.82 (t, 2H, J=1.9 Hz, $OCH_2C{=}CH_2$), 6.27 (dd, 1H, J=1.9 and 1.5 Hz, C=CHH), 6.45 (dd, 1H, J=1.9 and 1.5 Hz, C=CHH), 7.02 (m, 2H), 7.46 (m, 1H), 7.86 (dd, 1H, J=7.7 and 1.9 Hz); ^{13}C NMR 14.0 (OCH_2CH_3), 51.8 (OCH_3), 60.7 (OCH_2CH_3), 66.4 ($OCH_2C{=}CH_2$), 113.3, 120.0, 120.5, 126.0 (C=CH_2), 131.8, 133.5, 135.3, 157.7 (C=CH_2), 165.2 (CO_2Et), 166.4 (CO_2Me); EIMS m/z 264 (M^+, 36), 232 (21), 219 (20), 190 (44), 186 (74), 158 (36), 120 (100); Anal. calcd for $C_{14}H_{16}O_5$: C: 63.63%, H: 6.10%; found: C: 63.76%, H: 6.23%.

Ethyl 3-(*o*-benzoxycarbonylphenyl)-oxy-2-methylenepropanoate (3d). Mp 61–62°C; IR (cm^{-1}) 3079, 2994, 1715,

1686, 1603, 1454; ^{1}H NMR 1.31 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 4.22 (q, 2H, J=7.2 Hz, OC*H*$_2$CH$_3$), 4.80 (s, 2H, OC*H*$_2$C=CH$_2$), 5.35 (s, 2H, OC*H*$_2$Ph), 6.15 (s, 1H, C=CH*H*), 6.33 (s, 1H, C=C*H*H), 7.0 (m, 2H), 7.40 (m, 6H), 7.87 (dd, 1H, J=8.0 and 1.9 Hz); ^{13}C NMR 14.0 (OCH$_2$*C*H$_3$), 60.7 (O*C*H$_2$CH$_3$), 66.5 (O*C*H$_2$C=CH$_2$, O*C*H$_2$Ph), 113.2, 120.0, 120.5, 126.3 (C=*C*H$_2$), 128.0, 128.4, 133.6, 135.1, 135.9, 157.8 (*C*=CH$_2$), 165.2 and 165.7 (*C*O$_2$Et and *C*O$_2$Bn); EIMS m/z 341 (M$^+$, 16), 233 (58), 203 (13), 181 (8), 161 (15), 131 (15), 121 (100); Anal. calcd for $C_{20}H_{20}O_5$: C: 70.28%, H: 5.90%; found: C: 70.53%, H: 5.72%.

Ethyl 3-(*o*-cyanophenyl)-oxy-2-methylenepropanoate (3e). Mp 41–42°C; IR (cm^{-1}) 2991, 2222, 1707, 1599, 1493; ^{1}H NMR 1.33 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 4.27 (q, 2H, J=7.2 Hz, OC*H*$_2$CH$_3$), 4.85 (s, 2H, OC*H*$_2$C=CH$_2$), 6.15 (bs, 1H, C=CH*H*), 6.45 (bs, 1H, C=C*H*H), 7.02 (m, 2H), 7.55 (m, 2H); ^{13}C NMR 14.1 (OCH$_2$*C*H$_3$), 61.0 (O*C*H$_2$CH$_3$), 66.5 (O*C*H$_2$C=CH$_2$), 102.2, 112.5, 116.2, 121.2, 126.6 (C=*C*H$_2$), 133.7, 134.3, 134.6, 159.8 (*C*=CH$_2$), 165.0 (*C*O$_2$Et); EIMS m/z 231 (M$^+$, 69), 186 (55), 157 (11), 129 (18), 119 (93), 113 (100); Anal. calcd for $C_{13}H_{13}O_3N$: C: 67.52%, H: 5.67%, N: 6.06%; found: C: 67.49%, H: 5.38%, N: 5.76%.

Ethyl 3-(*m*-acetamidophenyl)-oxy-2-methylenepropanoate (3f). Mp 87–88°C; IR (cm^{-1}) 3267, 3150, 2978, 1720, 1666, 1614, 1564, 1495; ^{1}H NMR 1.30 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 2.13 (s, 3H, O=CC*H*$_3$), 4.24 (q, 2H, J=7.2 Hz, OC*H*$_2$CH$_3$), 4.71 (s, 2H, OC*H*$_2$C=CH$_2$), 5.95 (d, 1H, J=1.1 Hz, C=CH*H*), 6.37 (d, 1H, J=1.1 Hz, C=C*H*H), 6.63 (d, 1H, J=8.3 Hz), 7.01 (d, 1H, J=8.3 Hz), 7.18 (t, 1H, J=8.3 Hz), 7.3 (bs, 1H), 8.0 (bs, 1H, N*H*); ^{13}C NMR 14.0 (OCH$_2$*C*H$_3$), 24.3 (O=C*C*H$_3$), 60.8 (O*C*H$_2$CH$_3$), 66.0 (O*C*H$_2$C=CH$_2$), 106.7, 110.3, 112.6, 126.4 (C=*C*H$_2$), 129.5, 135.7, 139.3, 158.6 (*C*=CH$_2$), 165.4 (*C*O$_2$Et), 168.9 (O=*C*CH$_3$); EIMS m/z 263 (M$^+$, 32), 217 (20), 190 (15), 175 (100), 147 (66), 131 (10), 122 (32), 109 (41); Anal. calcd for $C_{14}H_{17}O_4N$: C: 63.87%, H: 6.51%, N: 5.32%; found: C: 63.44%, H: 6.41%, N: 5.10%.

Ethyl 3-(*m*-methoxyphenyl)-oxy-2-methylenepropanoate (3g). Colorless oil; IR (cm^{-1}) 2937, 1715, 1595, 1493; ^{1}H NMR 1.33 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 3.79 (s, 3H, OC*H*$_3$), 4.27 (q, 2H, J=7.2 Hz, OC*H*$_2$CH$_3$), 4.75 (s, 2H, OC*H*$_2$C=CH$_2$), 6.00 (s, 1H, C=CH*H*), 6.40 (s, 1H, C=C*H*H), 6.52–6.57 (m, 3H), 7.20 (t, 1H, J=8.0 Hz); ^{13}C NMR 14.1 (OCH$_2$*C*H$_3$), 55.2 (O*C*H$_3$), 60.9 (O*C*H$_2$CH$_3$), 66.0 (O*C*H$_2$C=CH$_2$), 101.2, 106.6, 106.8, 126.2 (C=*C*H$_2$), 129.9, 135.9, 159.5 (*C*=CH$_2$), 160.8, 165.4 (*C*O$_2$Et); EIMS m/z 236 (M+, 70), 190 (100), 162 (60), 147 (34); Anal. calcd for $C_{13}H_{16}O_4$: C:66.09%, H: 6.82%; found: C: 66.09%, H: 6.82%.

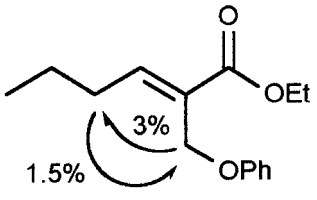
Ethyl 3-(*p*-methoxyphenyl)-oxy-2-methylenepropanoate (3h). Colorless oil; IR (cm^{-1}) 2909, 1714, 1510; ^{1}H NMR 1.33 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 3.78 (s, 3H, OC*H*$_3$), 4.27 (q, 2H, J=7.2 Hz, OC*H*$_2$CH$_3$), 4.71 (s, 2H, OC*H*$_2$C=CH$_2$), 5.99 (s, 1H, C=CH*H*), 6.40 (s, 1H, C=C*H*H), 6.80–6.92 (m, 4H); ^{13}C NMR 14.1 (OCH$_2$*C*H$_3$), 55.6 (O*C*H$_3$), 60.8 (O*C*H$_2$CH$_3$), 66.8 (O*C*H$_2$C=CH$_2$), 114.5 (2 CH), 115.7 (2 CH), 126.0 (C=*C*H$_2$), 136.2, 152.4, 154.0 (*C*=CH$_2$), 165.0 (*C*O$_2$Et); EIMS m/z 236 (M+,85), 191 (27), 123 (100); Anal. calcd for $C_{13}H_{16}O_4$: C: 66.09%, H: 6.82%; found: C: 66.10%, H: 6.83%.

Ethyl 3-(*p*-formylphenyl)-oxy-2-methylenepropanoate (3i). Colorless oil; IR (cm^{-1}) 2990, 1692, 1645, 1603, 1580, 1510; ^{1}H NMR 1.24 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 4.18 (q, 2H, J=7.2 Hz, OC*H*$_2$CH$_3$), 4.75 (s, 2H, OC*H*$_2$C=CH$_2$), 5.91 (s, 1H, C=C*H*H), 6.35 (s, 1H, C=CH*H*), 6.96 (d, 2H, J=8.8 Hz), 7.75 (d, 2H, J=8.8 Hz), 9.79 (s, 1H, C*H*O); ^{13}C NMR 13.9 (OCH$_2$*C*H$_3$), 60.8 (O*C*H$_2$CH$_3$), 66.0 (O*C*H$_2$C=CH$_2$), 114.8 (2 CH), 126.4 (C=*C*H$_2$), 130.0, 131.7, 135.0, 162.9 (*C*=CH$_2$), 164.9 (*C*O$_2$Et), 190.4 (*C*HO); EIMS m/z 234 (M$^+$, 49), 205 (8), 188 (100), 161 (54), 131 (39), 121 (80); Anal. calcd for $C_{13}H_{14}O_4$: C: 66.66%, H: 6.02%; found: C: 66.62%, H: 6.10%.

Ethyl 3-(*p*-chlorophenyl)-oxy-2-methylenepropanoate (3j). Colorless oil; IR (cm^{-1}) 2984, 1713, 1493; ^{1}H NMR 1.31 (t, 3H, J=7.1 Hz, OCH$_2$C*H*$_3$), 4.26 (q, 2H, J=7.1 Hz, OC*H*$_2$CH$_3$), 4.72 (t, 2H, J=1.5 Hz, OC*H*$_2$C=CH$_2$), 5.96 (q, 1H, J=1.5 Hz, C=CH*H*), 6.40 (q, 1H, J=1.5 Hz, C=C*H*H), 6.90 (m, 2H), 7.22 (m, 2H); ^{13}C NMR 14.0 (OCH$_2$*C*H$_3$), 60.8 (O*C*H$_2$CH$_3$), 66.2 (O*C*H$_2$C=CH$_2$), 115.9, 125.8, 126.1 (C=*C*H$_2$), 129.2, 135.6, 156.7 (*C*=CH$_2$), 165.2 (*C*O$_2$Et); EIMS m/z 240, 242 (M$^+$,100, 33), 194 (54), 166 (23), 159 (72), 128 (87), 113 (92); Anal. calcd for $C_{12}H_{14}O_3Cl$: C: 59.88%, H: 5.44%; found: C: 60.09%, H: 5.42%.

Ethyl 2-phenoxymethylhex-2-enoate (5). Colorless oil; IR (cm^{-1}) 2961, 2874, 1713, 1599, 1497; ^{1}H NMR 0.95 (t, 3H, J=7.4 Hz, CH$_3$CH$_2$C*H*$_3$), 1.39 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 1.51 (sext, 2H, J=7.4 Hz, CH$_2$C*H*$_2$CH$_3$), 2.40 (q, 2H, J=7.4 Hz, C*H*$_2$CH$_2$CH$_3$), 4.23 (q, 2H, J=7.4 Hz, OC*H*$_2$CH$_3$), 4.77 (s, 2H, C*H*$_2$OPh), 6.95 (m, 3H), 7.12 (t, 1H, J=7.4 Hz, C=C*H*), 7.29 (m, 2H); ^{13}C NMR 13.8 (CH$_2$CH$_2$*C*H$_3$), 14.1 (OCH$_2$*C*H$_3$), 21.9 (CH$_2$*C*H$_2$CH$_3$), 30.9 (*C*H$_2$CH$_2$CH$_3$), 60.8 (O*C*H$_2$CH$_3$), 61.8 (*C*H$_2$OPh), 114.9, 120.9, 128.1, 129.4, 149.4 (C=*C*HCH$_2$), 158.8 (*C*=CHCH$_2$), 166.7 (*C*O$_2$Et); EIMS m/z 248 (M$^+$, 83), 203 (68), 155 (93), 139 (19), 127 (49), 109 (100); Anal. calcd for $C_{15}H_{20}O_3$: C: 72.55%, H: 8.12%; found: C:72.77%, H: 8.42%.

The *E*-stereochemistry of the double bond of **5** was determined by NOE experiments (Scheme 4).



Scheme 4.

Ethyl 2-methylene-3-phenoxyhexanoate (6). Colorless oil; IR (cm^{-1}) 2961, 2874, 1713, 1599, 1495; ^{1}H NMR 0.94 (t, 3H, J=7.4 Hz, CH$_2$CH$_2$C*H*$_3$), 1.33 (t, 3H, J=7.2 Hz, OCH$_2$C*H*$_3$), 1.48 (m, 2H, CH$_2$C*H*$_2$CH$_3$), 1.76 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 4.27 (q, 2H, J=7.2 Hz, OC*H*$_2$CH$_3$),

5.10 (dd, 1H, J=7.2 and 4.2 Hz, C*H*OPh), 5.72 (s, 1H, C=C*H*H), 6.25 (s, 1H, C=CH*H*), 6.88 (m, 3H), 7,24 (m, 2H); ^{13}C NMR 13.9 ($CH_2CH_2CH_3$), 14.2 (OCH_2CH_3), 18.9 ($CH_2CH_2CH_3$), 38.3 ($CH_2CH_2CH_3$), 60.8 (OCH_2CH_3), 74.9 (*C*HOPh), 115.4, 120.7, 125.3 (C=*C*H_2), 129.4, 140.6, 157.8 (*C*=CH_2),166.0 (CO_2Et); EIMS *m/z* 248 (M^+, 83), 203 (33), 155 (100), 139 (16), 127 (50), 109 (95); Anal. calcd for $C_{15}H_{20}O_3$: C: 72.55%, H: 8.12%; found: C: 72.86%, H: 8.00%.

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