Structural Effect on Eu(fod)$_3$-Catalyzed Rearrangement of Allylic Esters†

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A detail study on the Eu(fod)$_3$-catalyzed rearrangement of allylic esters was described. A significant effect of the substituents at the allylic backbone was observed. The migrating tendency of the alkoxyacetates was established in the order of *p*-$CF_3C_6H_4CH_2OCH_2CO_2$ > $MeOCH_2CO_2$ > $PhCH_2OCH_2CO_2$ > *p*-$MeOC_6H_4CH_2OCH_2CO_2$.

Keywords lanthanide, allylic ester, rearrangement

Introduction

In 1996, Koreeda and co-workers first reported rearrangement of allylic methoxyacetates in the presence of a catalytic amount of Eu(fod)$_3$ [europium tris-6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate] under mild reaction conditions.[1] The migrating potency of the ester group was established in the order of (−)-PhC(CF_3)(MeO)CO_2 [(−)-α-methoxy-α-(trifluoromethyl)phenylacetate] > $MeOCH_2CO_2$ > PhCH(MeO)CO_2. A chelating model of methoxyacetate with Eu(III) was proposed to account for the unique role of the α-methoxy group in the facile rearrangement of allylic methoxyacetates. In one example, Koreeda and co-workers demonstrated that Eu(fod)$_3$ promoted a selective rearrangement of allylic methoxyacetate over a propargylic methoxyacetate unit.[1] This was a remarkable advantage compared to the rearrangement of allylic esters promoted by Hg(II) or Pd(II).[2] The latter caused cleavage of the triple bond in the propargylic ester.[3] The other distinguished feature of Eu(III) catalysis was that the allylic substrates possessing a C(2) substituent underwent a smooth rearrangement,[1] which was failed by using Hg(II) or Pd(II) reagents.[3,4] Moreover, a complete 1,3-chirality transfer was observed for the chiral cyclic substrates in both the Pd(II)- and Eu(III)-catalyzed allylic rearrangement.[1,5]

We successfully applied the Eu(fod)$_3$-catalyzed rearrangement to the synthesis of acyclic and 10-membered ring enediynes starting from 1,2-dialkynyl-substituted allylic esters.[6] Beside Eu(III), it was found that other lanthanides such as Er(fod)$_3$, Pr(fod)$_3$ and Yb(fod)$_3$ catalyzed the rearrangements of 1,2-dialkynyl allylic[6b] and divinyl[7] alkoxyacetates with an equal efficiency. We also revealed that at elevated temperatures the allylic phenoxyacetate, acetate, benzoate and *o*-methoxybenzoate underwent the rearrangement to give the products in good yields.[6a] With the assistance of an internal nucleophilic group (OH), the rearrangement of the allylic acetate took place at room temperature.[6c] A chiral acyclic 1,2-dialkynyl allylic benzyloxyacetate of 92% *ee* was transformed into the chiral acyclic enediyne of 84% *ee*, demonstrating the 1,3-chirality transfer in an acyclic system and supporting for a concerted pathway.[6a] Here a detail study on the structural effects of both the substituents at the allylic backbone and the ester moiety on the rearrangement is reported. We expected that understanding of the structural effect on the allylic rearrangement would provide a basis for designing tandem reaction sequence under the catalysis of lanthanides.[7]

Results and discussion

Effect of alkoxyacetates on allylic rearrangement

In our previous study, it was noted that the ester unit significantly influenced the rate of the allylic rearrangement.[6a] A set of experiments were designed for examining the migrating ability of allylic alkoxyacetates. Two *para*-substituted benzyloxyacetic acids **3** and **4** (Scheme 1) were prepared for investigating the electronic effect on ester migration. Various substituted α, β-unsaturated aldehydes **5a—5d** were reacted with 1.2 equiv. of PhMgCl in THF at −78 ℃ to give the allyl alcohols **6a—6d** (55%—100%), which were condensed with *p*-$MeOC_6H_4CH_2CO_2H$

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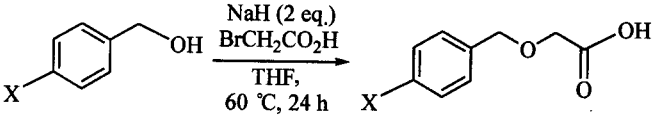
†Dedicated to Professor ZHOU Wei-Shan on the occasion of his 80th birthday.

Scheme 1

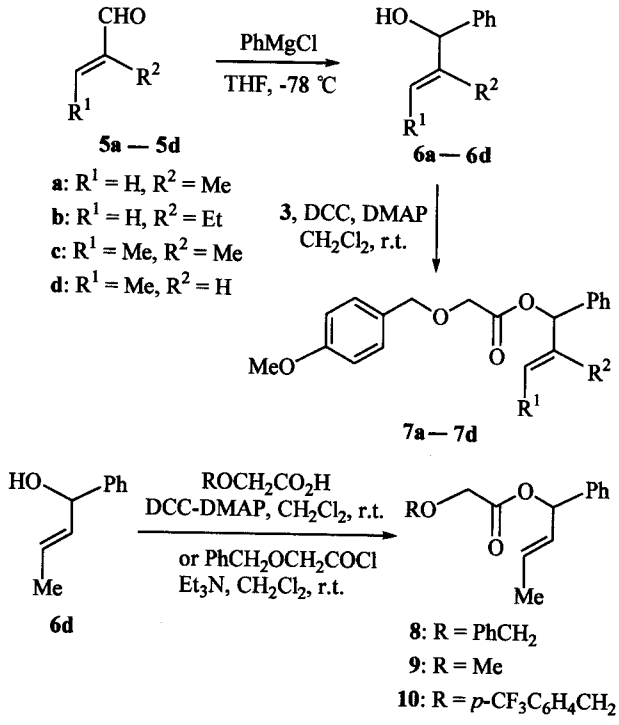


1: X = MeO
2: X = CF_3

3: X = MeO (79%)
4: X = CF_3 (72%)

(**3**) in the presence of DCC-DMAP at room temperature to furnish the esters **7a—7d** in 45%—87% yields (Scheme 2 and Table 1). The esters **9** (69%) and **10** (69%) were prepared from **6d** using the DCC-DMAP condensation whilst the benzyloxyacetate **8** was synthesized by treating **6d** with benzyloxyacetyl chloride in the presence of Et_3N (CH_2Cl_2, r.t., 4 h, 77%) (Scheme 2). Rearrangement of the allylic alkoxyacetates **7d** and **8—10** was examined and the relative reaction rate constants, k_{rel} were determined. Thus, a 0.1 mol/L solution of the ester in $CDCl_3$ containing 5 mmol/L $Eu(fod)_3$ at 20 ℃ was monitored by ^1H NMR on a 400 MHz instrument. The following equation was used to estimate the ratio of the starting materials [SM] at a given time t to the initially used starting materials $[SM]_{initio}$: $[SM]/[SM]_{initio} = [SM]/\{[SM] + [PDT]\}$, where [PDT] is the rearranged ester product at the given time. Assuming that both the starting materials and the ester product do not decompose or decompose at the same rate, the relationship of $[SM]_{initio} = [SM] + [PDT]$ should be applicable. The relative integrations of the characteristic signals for both the starting materials and the product were recorded at different time intervals and were used to calculate the ratio $[SM]/[SM]_{initio}$. The plots of $\ln[SM]/[SM]_{initio}$ vs. reaction time for the rearrangement of allylic alkoxyacetates **7d** and **8—10** in $CDCl_3$ at

Scheme 2



room temperature were illustrated in Fig. 1, showing the pseudo-first-order reactions. Table 2 lists the rate constants k calculated from the pseudo-first-order rate constants k_{obs}, which were obtained from the slopes of the plots in Fig. 1. The half-lives ($t_{1/2}$) of PMBO-, $PhCH_2O$-, MeO- and PTBO-substituted esters are 51.6, 46.5, 35.9 and 24.6 min, respectively. Compared to the known methoxyacetate **9**, the electron-withdrawing *p*-(trifluoromethyl)-benzyloxyacetate (**10**) showed an increased reactivity

Table 1 Synthesis and rearrangement of allylic esters[a]

Entry	R^1	R^2	Alcohol (%)	Ester (%)	Solvent, Temp., Time	Product (%)
1	H	Me	**6a**: 60	**7a**: 66	CH_2Cl_2, r.t., 24 h	no reaction
2					$CHCl_3$, 60 ℃, 24 h	no reaction
3					PhCl, 132 ℃, 72 h	**14a**: 21
4	H	Et	**6b**: 55	**7b**: 87	CH_2Cl_2, r.t., 24 h	no reaction
5					$CHCl_3$, 60 ℃, 24 h	no reaction
6					PhCl, 132 ℃, 96 h	**14b + 14b'**: 40[b]
7	Me	Me	**6c**: 100	**7c**: 60	$CDCl_3$, r.t., 276 h	**14c**: 95
8	Me	H	**6d**: 100	**7d**: 45	$CDCl_3$, r.t., 7 h	**14d**: 96
9	H	Me	**12a**: 74	**13a**: 63	CH_2Cl_2, r.t., 24 h	no reaction
10					$CHCl_3$, 60 ℃, 72 h	**15a**: 57[c]
11					$CHCl_3$, 60 ℃, 144 h	**15a**: 84[d]
12	H	Et	**12b**: 32	**13b**: 60	CH_2Cl_2, r.t., 24 h	no reaction
13					$CHCl_3$, 60 ℃, 144 h	**15b**: 59[e]
14	Me	Me	**12c**: 100	**13c**: 59	$CDCl_3$, r.t., 2.5 h	**15c**: 86
15	Me	H	**12d**: 99	**13d**: 68	$CDCl_3$, r.t., 26.5 h	**15d**: 80
16	Ph	Me	**12e**: 100	**13e**: 54	$CDCl_3$, r.t., < 10 min	**15e**: 70
17	Ph	H	**12f**: 100	**13f**: 78	$CDCl_3$, r.t., < 10 min	**15f + 15f'**: 91[f]

[a] Yields are referred to the isolated pure materials but not optimized. [b] A 84:16 mixture of (**14b + 14b'**):**7b**. The ratio of **14b**:**14b'** is 42:58. [c] Substrate **13a** was recovered in 17.8%. [d] Substrate **13a** was recovered in 15.5%. [e] A by-product **16** was obtained in 14% yield. [f] The ratio of **15f**:**15f'** is 87:13.

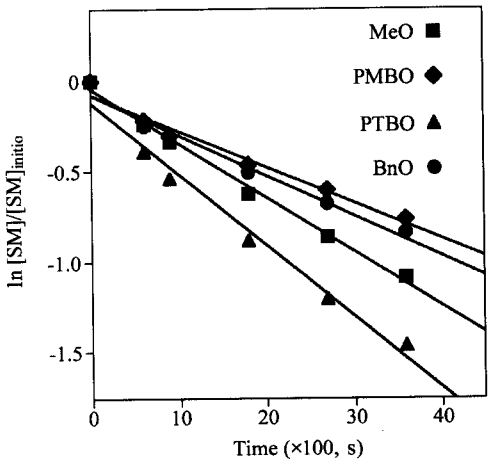


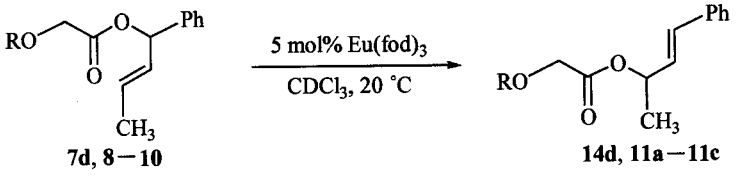
Fig. 1 Rearrangement of allylic alkoxyacetates **7d** and **8—10** (0.1 mol/L) in $CDCl_3$ at 20 ℃ in the presence of En(fod)$_3$ (5 mmol/L) as monitored by ^{1}H NMR on a 400 MHz instrument. The ratios $[SM]/[SM]_{initio}$ were obtained by the integrations of the starting [SM] and the rearranged [PDT] esters, respectively. At the given time t, $[SM]/[SM]_{initio} = [SM]/\{[SM] + [PDT]\}$.

toward rearrangement. On the other hand, the electron-rich *p*-methoxybenzyloxyacetate **7d** and the benzyloxyacetate **8** exhibited diminished reactivity. The relative reaction rate constants, k_{rel}, were established in the order of *p*-$CF_3C_6H_4CH_2OCH_2CO_2$ (1.95) > $MeOCH_2CO_2$ (1.50) > $PhCH_2OCH_2CO_2$(1.10) > *p*-$MeOC_6H_4CH_2OCH_2CO_2$(1.00) (Table 2). Indeed, these findings are quite similar to the Koreeda's results.[1] They observed that the CF_3 group greatly enhances the reactivity, whereas the phenyl group in α-methoxyphenylacetate is a detriment to the rate of the rearrangement.[1] It should be emphasized that the substituent at the α position of the methoxyacetate causes both electronic and steric effects. In the case of esters **7d** and **8—10**, the steric effect is not a concern. On the basis of our results, the electronic effect on the reactivity of the allylic alkoxyacetates is relatively weak. The migrating order may be varied for different types of the allylic systems. For example, the benzyloxyacetate rearranged faster than the methoxyacetate in the formation of acyclic enediyne.[6a]

Effect of backbone substituents on allylic rearrangement

In order to differentiate the reactivity among differently substituted allylic systems, the slow-migrating *p*-methoxybenzyloxyacetates were chosen as the substrates. Beside the esters **7a—7d** prepared in Scheme 2, another set of six *p*-methoxybenzyloxyacetates (**13a—13f**) were synthesized (Scheme 3). Thus, reactions of the aldehydes **5a—5f** with lithium phenylacetylide gave the allyl alcohols **12a—12f** (32—100%) which were condensed with *p*-methoxybenzyloxyacetic acid (**3**) under the DCC-DMAP conditions to provide **13a—13f** (54%—78%, Table 1). The rearrangement reactions were carried out in the given solvent with a 0.1 mol/L solution of the ester containing 5 mmol/L of Eu(fod)$_3$ (Scheme 4). Because the R_f values for the starting materials and product are very close, TLC is not suitable for monitoring the rearrangement reactions. Therefore, reaction times of the Eu(fod)$_3$-catalyzed rearrangement of **7c**, **7d** and **13c—13f** at room temperature were measured by ^{1}H NMR on a 400 MHz instrument

Table 2 Rate constants (k) and half-livies ($t_{1/2}$) of Eu(fod)$_3$-catalyzed rearrangement of allylic alkoxyacetates **7d**, and **8—10** in $CDCl_3$ at 20 ℃ as measured by ^{1}H NMR, $k = k_{obs}/[Eu(fod)_3]$

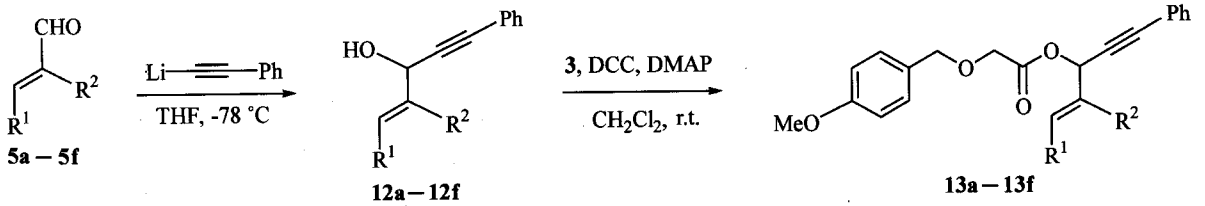


7d, 8—10 **14d, 11a—11c**

RO	Substrate	Product	k ($s^{-1}\cdot M^{-1}$)	Correlation coeff. (r^2)	$t_{1/2}$ (min)	k_{rel}
PMBO[a]	**7d**	**14d**	4.0×10^{-2}	0.972	51.6	1.00
$PhCH_2O$	**8**	**11a**	4.4×10^{-2}	0.975	46.5	1.10
MeO	**9**	**11b**	6.0×10^{-2}	0.994	35.9	1.50
PTBO[b]	**10**	**11c**	7.8×10^{-2}	0.980	24.6	1.95

[a] PMBO = *p*-$MeOC_6H_4CH_2O$. [b] PTBO = *p*-$CF_3C_6H_4CH_2O$.

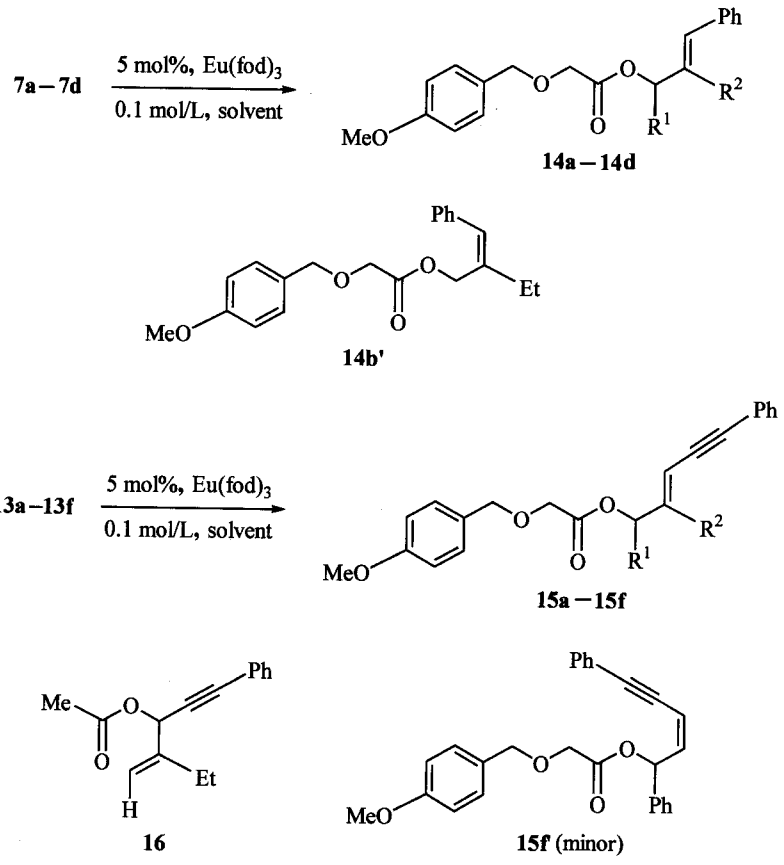
Scheme 3



5a—5f **12a—12f** **13a—13f**

a: R^1 = H, R^2 = Me; **b**: R^1 = H, R^2 = Et; **c**: R^1 = Me, R^2 = Me; **d**: R^1 = Me, R^2 = H; **e**: R^1 = Ph, R^2 = Me; **f**: R^1 = Ph, R^2 = H

Scheme 4



(Entries 7, 8, and 14—17, Table 1). In our previous study, it was found that the allylic methoxyacetates lacking a substituent at the C(3) position failed to undergo the $Eu(fod)_3$-catalyzed allylic rearrangement at 100—110 ℃.[6a] Similarly, the allylic esters **7a** and **7b** only rearranged in refluxing chlorobenzene (b.p. 132 ℃) to give **14a** and **14b** (with **14b'**) in 21% and 40% yield, respectively (Entries 3 and 6, Table 1). The low yields might be attributed to decomposition of both the starting materials and the products at high temperature. It was not surprising to note that a mixture of the rearranged esters (**14b** + **14b'**) with **7b** (84 : 16) was obtained. Koreeda and coworkers reported a similar phenomenon for non-terminal olefin.[1]

The different reactivity of the allylic acetates **7a** and **7d** could be explained by their molecular structures. The product ester **14a** possesses increased steric interaction between the *cis* configured phenyl group and R^2 (= Me) compared to **7a**. The repulsive interaction will be even severe if a larger group such as Et is placed at the C(2) position as in **14b**. Probably, the main driving force for the rearrangement is to acquire conjugation of the double bond with the benzene ring. Importantly, this factor is dominant in the allylic rearrangement and overcomes unfavourable steric repulsion. Since neither **7d** nor **14d** (R^2 = H) has such strong repulsive interaction, the rearrangement of **7d** occurred at room temperature in a relatively short time period to furnish **14d** in 96% yield.

When the phenyl group is replaced by the phenylethynyl group, the reactivity of the allylic esters **13a**—**13f** is generally enhanced, probably due to relieving of steric interaction between R^2 and the alkynyl group in the product such as **15b**. Although rearrangement of **13a** and **13b** did not occur at room temperature, the products **15a** and **15b** were obtained at 60 ℃ for 144 h in 84% and 59% yield, respectively. Surprisingly, decomposition of **13b** occurred during the prolonged heating to give the side product **16** (14% yield) whose formation remains unclear (Scheme 4 and Entry 13, Table 1). Overall, the C(2)-substituted allylic esters with R^1 being H exhibited a relatively low reactivity when compared with the C(2)-unsubstituted allylic esters with R^1 being an alkyl group.

Similarly, the substituent effect was observed on the reactivity of **7c** and **7d**. The ester **7c** possesses two *cis* methyl groups on the double bond, resulting in steric interaction. However, the product **14c** acquires much more severe steric interaction between the *cis* phenyl and methyl groups. On the other hand, such steric interaction does not exist in both **7d** and **14d**. Therefore, the $Eu(fod)_3$-catalyzed rearrangement of **7d** is much more fast than **7c** (Entries 7 and 8, Table 1).

There is no alkyl substituent at the C(2) position of **13d**. It was expected that **13d** would undergo facile rearrangement than **13c**. Actually, the reactivity of **13c** and **13d** was reversed compared to **7c** and **7d** (Entries 14 and 15 vs. Entries 7 and 8, Table 1). This phenomenon could be explained by the relative ground state energy difference between the starting materials and the product. The ground

state energy difference between **13d** and **15d** should be smaller than that of **13c** and **15c**. The *cis* methyl-methyl repulsive interaction in **13c** is stronger than the *cis* methyl-alkynyl interaction in **15c**. It provided the driving force for a rapid rearrangement of **13c** to **15c**.

In another pair of ester substrates **13e** and **13f**, we observed extremely accelerated reactivity due to a large difference in the ground state energy between the starting materials and the rearranged products (Entries 16 and 17, Table 1). The ester **13e** possesses a twisted phenyl ring on the double bond resulting from the *s-cis* butadiene-type interaction between the *ortho* phenyl proton and the C(2) methyl group. The twisted phenyl ring also weakens the conjugation with the double bond. Thus, it provided additional driving force for the rearrangement. The ester **13f** favors for a planar styrene-type conformation. But, the *s-cis* butadiene-type interaction between the *ortho* phenyl proton and the C(2) proton is still the main driving force for rearranging **13f** into **15f**. Both rearrangements of **13e** and **13f** were too rapid to observe their difference in reactivity. Purification of **13e** by column chromatography over silica gel resulted in formation of **15e** although in a trace amount. When **13e** was dissolved in CH_2Cl_2 in the presence of trace silica gel at room temperature for 3 days, **13e** was completely converted into **15e**. These observations indicated that protic acid also catalyzed the rearrangement of the allylic ester. However, it should proceed in a different mechanism under the Eu(fod)$_3$ catalysis.

In summary, a series of allylic *p*-methoxybenzyloxyacetates were prepared and their reactivity toward the Eu(fod)$_3$-catalyzed rearrangement were examined. A significant substituent effect on the allylic systems was observed. The C(3)-unsubstituted allylic esters **7a**, **7b** and **13a**, **13b** rearranged at elevated temperatures whereas the C(3)-substituted substrates **7c**, **7d** and **13c—13f** underwent the allylic migration at room temperature. By designing the allylic substrates possessing different substituents at C(3) and/or C(2) position(s), the reactivity of allylic *p*-methoxybenzyloxyacetates was systematically investigated. On the basis of the results, the main driving force for the Eu(fod)$_3$-catalyzed allylic rearrangement is the conjugation of the double bond with the π electron system such as a benzene ring or an alkynyl group. Moreover, torsional energy among the *cis* substituents on the double bond can significantly modify the easiness of the allylic rearrangement. A careful comparison on the relative reactivity of a series of allylic alkoxyacetates was carried out using (*E*)-1-phenyl-2-buten-1-ol as the allylic skeleton. Electronic effect on the alkoxyacetates was noted and the Eu(fod)$_3$-catalyzed allylic rearrangement exhibited the following reactivity order of *p*-(trifluoromethyl)benzyloxyacetate > methoxyacetate > benzyloxyacetate > *p*-methoxybenzyloxyacetate.

Experimental

^{1}H NMR and ^{13}C NMR spectra were recorded on either a JEOL EX-400 (^{1}H at 400 MHz, ^{13}C at 100 MHz) or a Bruker ARX-300 (^{1}H at 300 MHz, ^{13}C at 75 MHz) spectrometer. Infrared (IR) spectra were measured with a Perkin Elmer 16PC infrared spectrophotometer and the measured wavenumbers are uncorrected. Mass spectra (MS) were measured by Finnigan TSQ 7000 mass spectrometer. High-resolution mass spectra (HRMS) were measured by the EI method at the Kunming Institute of Botany, The Chinese Academy of Sciences. All reactions were carried out under a nitrogen atmosphere and monitored by thin-layer chromatography on 0.25-mm E. Merck silica gel plates (60 F-254) using UV light, or 7% ethanolic phosphomolybdic acid and heating as the visualizing methods. All reaction mixtures were stirred magnetically unless otherwise noted. Dichloromethane was distilled over calcium hydride prior to use. Tetrahydrofuran was distilled from Na-benzophenone ketyl immediately prior to use. Unless otherwise noted, all chemicals were commercial products and were used as received. E. Merck silica gel (60, particle size 0.040—0.063 mm) was used for flash column chromatography. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise noted. Room temperature is around 20 ℃.

General procedure for synthesis of compounds **3** and **4**

(p-Methoxybenzyloxy) acetic acid (**3**) To a stirred mixture of 4-methoxybenzyl alcohol (**1**, 1.93 g, 14.00 mmol) and 60% NaH (1.11 g, 27.75 mmol) in THF (100 mL) was added bromoacetic acid (1.99 g, 14.21 mmol) at 0 ℃. The resultant mixture was stirred for 1 h at 0 ℃ and for another 24 h at 60 ℃. The reaction was quenched by water (100 mL) and the mixture was extracted with EtOAc (2 × 50 mL). The organic layer was discarded. The aqueous layer was acidified to pH = 1 by using aqueous 10% HCl at 0 ℃ and extracted by EtOAc (3 × 50 mL). The combined organic layer was washed with brine (2 × 50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford **3** (1.98 g, 72%): pale yellow oil; R_f = 0.42 (40% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 10.19 (br s, 1H), 8.03 (d, J = 8.80 Hz, 2H), 7.28 (d, J = 8.80 Hz, 2H), 4.58 (s, 2H), 4.11 (s, 2H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 175.1, 159.6, 129.8 (×2), 128.6, 114.0 (×2), 73.1, 66.2, 55.3; IR (neat) ν: 2970, 1736, 1612, 1514, 1250, 1120, 1036 cm^{-1}; MS (+CI) m/z (%): 214 (M + NH_4^+, 100); HRMS (+EI) calcd for $C_{10}H_{12}O_4$ (M^+) 196.0736, found 196.0722.

(p-Trifluoromethyl) benzyloxyacetic acid (**4**) Prepared in 72% yield from 4-trifluorobenzyl alcohol (**2**) and bromoacetic acid; white solid; m.p. 47—49 ℃; R_f = 0.39 (40% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 9.80—8.90 (br s, 1H), 7.63 (d, J = 8.13 Hz, 2H), 7.48 (d, J = 8.13 Hz, 2H), 4.71 (s, 2H), 4.20 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 175.1, 140.7, 130.4 (q, J = 32.4 Hz), 127.9 (×2), 125.5

(q, J = 3.75 Hz, × 2), 72.7, 67.0 (CF_3 singal not observed); IR (nujol) ν: 3448, 2941, 1728, 1622, 1420, 1326, 1250, 1110, 1066, 1018 cm^{-1}; MS (+CI) m/z (%): 235 ($M+H^+$, 100); HRMS (+EI) calcd for $C_{10}H_9F_3O_3(M^+)$ 234.0504, found 234.0497.

General procedure for preparation of alcohols **6a—6d**

2-Methyl-1-phenylprop-2-en-1-ol (**6a**) To a stirred solution of methacrolein (**5a**, 0.6 mL, 7.25 mmol) in dry THF (150 mL) was added a THF solution of phenylmagnesium chloride (2.0 mol/L, 4.6 mL, 9.20 mmol) at −78 ℃. The resultant mixture was stirred at the same temperature for 1 h. Saturated aqueous NH_4Cl solution (50 mL) was added to quench the reaction. The reaction mixture was extracted with EtOAc (2 × 30 mL). The combined organic layer was washed with brine (2 × 50 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 30% EtOAc-hexane) to afford **6a** (0.64 g, 60%): colorless oil; R_f = 0.40 (30% EtOAc-hexane); ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.29—7.26 (m, 5H), 5.10 (s, 1H), 5.03 (s, 1H), 4.85 (s, 1H), 1.51 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 146.8, 141.9, 128.3 (×2), 127.6, 126.4 (×2), 111.1, 77.8, 18.2; IR (neat) ν: 3388 (br), 2974, 1724, 1492, 1452, 1242, 1046 cm^{-1}; MS (+CI) m/z (%): 148 (M^+, 98); HRMS (+EI) calcd for $C_{10}H_{12}O$ (M^+) 148.0888, found 148.0877.

2-Methylene-1-phenyl-1-butanol (**6b**) Prepared in 55% yield from 2-ethylacrolein (**5b**) and phenylmagnesium chloride after purification by flash column chromatography (silica gel, 30% EtOAc-hexane); colorless oil; R_f = 0.33 (30% EtOAc-hexane); ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.29—7.26 (m, 5 H), 5.17 (s, 1H), 5.07 (s, 1H), 4.89 (s, 1H), 1.93—1.74 (m, 2H), 0.90 (t, J = 7.32 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 152.6, 142.2, 128.3 (×2), 127.6, 126.6 (×2), 108.7, 77.4, 24.4, 12.0; IR (neat) ν: 3358 (br), 2966, 1648, 1492, 1452, 1024 cm^{-1}; MS (+CI) m/z (%): 162 (M^+, 100); HRMS (+EI) calcd for $C_{11}H_{14}O$ (M^+) 162.1045, found 162.1036.

(*E*)-*2-Methyl-1-phenylbut-2-en-1-ol* (**6c**) Prepared in 100% yield from *trans*-2-methyl-2-butenal (**5c**) and phenylmagnesium chloride after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); white solid; m.p. 38—40 ℃; R_f = 0.70 (30% EtOAc-hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.37—7.26 (m, 5H), 5.75—5.68 (m, 1H), 5.14 (s, 1H), 1.62 (dd, J = 6.81, 0.66 Hz, 3H), 1.50 (d, J = 0.93 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 142.5, 137.6, 128.2 (×2), 127.2, 126.2 (×2), 121.3, 79.3, 13.2, 11.7; IR (nujol) ν: 3422 (br), 2920, 1654, 1456, 1378 cm^{-1}; MS (+CI) m/z (%): 162 (M^+, 42), 145 (M^+ − OH, 100); HRMS (+EI) calcd for $C_{11}H_{14}O$ (M^+) 162.1045, found 162.1039.

(*E*)-*1-Phenylbut-2-en-1-ol* (**6d**) Prepared in 100% yield from crotonaldehyde (**5d**) and phenylmagnesium chloride after purification by flash column chromatography (silica gel, 20% EtOAc-hexane); colorless oil; R_f = 0.53 (40% EtOAc-hexane); ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.27—7.14 (m, 5H), 5.67—5.55 (m, 2H), 5.02 (d, J = 6.32 Hz, 1H), 2.11 (s, 1H), 1.62 (d, J = 5.36 Hz, 3H); IR (neat) ν: 3338 (br), 3028, 1492, 1450, 1068 cm^{-1}; MS (+CI) m/z (%): 296 (2 × M^+, 100), 148 (M^+, 5); HRMS (+EI) calcd for $C_{10}H_{12}O$ (M^+) 148.0888, found 148.0885.

General procedure for preparation of alcohols **12a—12f**

2-Methyl-5-phenylpent-1-en-4-yn-3-ol (**12a**) To a stirred solution of phenylacetylene (0.6 mL, 5.5 mmol) in dry THF (35 mL) was added 1.6 mol/L *n*-BuLi in hexanes (2.7 mL, 4.3 mmol) at −78 ℃ followed by stirring at the same temperature for 1 h. Methacrolein (**5a**, 0.3 mL, 3.6 mmol) was added to the above mixture followed by stirring at the same temperature for 2 h. Saturated aqueous NH_4Cl solution (10 mL) was added to quench the reaction. The reaction mixture was extracted with EtOAc (2 × 15 mL). The combined organic layer was washed with brine (2 × 15 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 10% EtOAc-hexane) to afford **12a** (0.46 g, 74%): pale yellow oil; R_f = 0.45 (20% EtOAc-hexane); ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.46—7.30 (m, 5H), 5.26 (s, 1H), 5.03 (s, 1H), 4.98 (s, 1H), 2.30 (s, 1H), 1.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 143.8, 131.6 (×2), 128.4, 128.2 (×2), 122.3, 112.5, 88.0, 85.8, 66.7, 18.3; IR (neat) ν: 3384 (br), 3000, 2918, 2229, 1654, 1490, 1444 cm^{-1}; MS (+CI) m/z (%): 173 ($M+H^+$, 98), 155 (M^+ − OH, 100); HRMS (+EI) calcd for $C_{12}H_{12}O$ (M^+) 172.0888, found 172.0886.

2-Ethyl-5-phenylpent-1-en-4-yn-3-ol (**12b**) Prepared in 32% yield from 2-ethylacrolein (**5b**) and lithium phenylacetylide after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); pale yellow oil; R_f = 0.47 (20% EtOAc-hexane); ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.46—7.30 (m, 5H), 5.35 (s, 1H), 5.08 (s, 1H), 5.00 (s, 1H), 2.38 (br s, 1H), 2.30 (q, J = 7.60 Hz, 2H), 1.15 (t, J = 7.60 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 149.5, 131.5 (×2), 128.3, 128.1 (×2), 122.4, 110.2, 88.2, 85.7, 66.1, 24.5, 12.2; IR (neat) ν: 3346 (br), 2966, 2229, 1490, 1442, 1030 cm^{-1}; MS (+CI) m/z (%): 186 (M^+, 100); HRMS (+EI) calcd for $C_{13}H_{14}O$ (M^+) 186.1045, found 186.1031.

(*E*)-*4-Methyl-1-phenylhex-4-en-1-yn-3-ol* (**12c**) Prepared in 100% yield from *trans*-2-methyl-2-butenal (**5c**) and lithium phenylacetylide after purification by flash column chromatography (silica gel, 20% EtOAc-hexane);

yellow oil; R_f = 0.35 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.45—7.26 (m, 5H), 5.77 (q, J = 6.80 Hz, 1H), 4.98 (s, 1H), 2.02 (s, 1H), 1.82 (s, 3H), 1.67 (d, J = 6.80 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 134.8, 131.6 (×2), 128.3, 128.2 (×2), 122.8, 122.5, 88.4, 85.9, 68.5, 13.4, 12.1; IR (neat) ν: 3352 (br), 2918, 2198, 1490, 1442 cm^{-1}; MS (+CI) m/z (%): 186 (M^+, 28), 169 (M^+ −OH, 100); HRMS (+EI) calcd for $C_{13}H_{14}O$ (M^+) 186.1045, found 186.1050.

(*E*)-1-*Phenylhex*-4-*en*-1-*yn*-3-*ol* (**12d**) Prepared in 99% yield from crotonaldehyde (**5d**) and lithium phenylacetylide after purification by flash column chromatography (silica gel, 20% EtOAc-hexane); white solid; m.p. 30—32 ℃; R_f = 0.29 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz,) δ: 7.46—7.26 (m, 5H), 6.00—5.95 (m, 1H), 5.71 (ddd, J = 11.40, 4.8, 1.2 Hz, 1H), 5.05 (t, J = 4.2 Hz, 1H), 2.15 (d, J = 4.2 Hz, 1H), 1.76 (d, J = 4.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 131.6 (×2), 130.1, 128.9, 128.4, 128.2 (×2), 122.4, 88.4, 85.8, 63.4, 17.5; IR (KBr) ν: 3202 (br), 2224, 1488, 1442, 1400, 1296 cm^{-1}; MS (+CI) m/z (%): 172 (M^+, 50), 155 (M^+ −OH, 100); HRMS (+EI) calcd for $C_{12}H_{12}O$ (M^+) 172.0888, found 172.0873.

(*E*)-2-*Methyl*-1,5-*diphenylpent*-1-*en*-4-*yn*-3-*ol* (**12e**) Prepared in 100% yield from α-methyl-*trans*-cinnamaldehyde (**5e**) and lithium phenylacetylide after purification by flash column chromatography (silica gel, 40% EtOAc-hexane); yellow oil; R_f = 0.58 (40% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.44—7.26 (m, 10H), 6.70 (s, 1H), 5.09 (d, J = 3.88 Hz, 1H), 2.18 (d, J = 4.40 Hz, 1H), 2.00 (d, J = 1.44 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 137.1, 136.7, 131.7 (×2), 129.0 (×2), 128.5, 128.3 (×2), 128.1 (×2), 127.2, 126.8, 122.4, 88.0, 86.3, 68.7, 14.1; IR (neat) ν: 3314 (br), 3056, 2916, 2228, 1598, 1490, 1442, 1264 cm^{-1}; MS (+CI) m/z (%): 248 (M^+, 16), 231 (M^+ − OH, 100); HRMS (+EI) calcd for $C_{18}H_{16}O$ (M^+) 248.1201, found 248.1190.

(*E*)-1,5-*Diphenylpent*-1-*en*-4-*yn*-3-*ol* (**12f**) Prepared in 100% yield from *trans*-cinnamaldehyde (**5f**) and lithium phenylacetylide after purification by flash column chromatography (silica gel, 20% EtOAc-hexane); white solid; m.p. 62—64 ℃; R_f = 0.50 (40% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.50—7.28 (m, 10H), 6.84 (d, J = 16.00 Hz, 1H), 6.39 (dd, J = 15.60, 6.00 Hz, 1H), 5.31—5.27 (m, 1H), 2.09 (d, J = 6.00 Hz , 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 136.0, 132.0, 131.6, 128.5 (×4), 128.2 (×2), 128.0, 127.9, 126.7 (×2), 122.2, 87.8, 86.4, 63.5; IR (KBr) ν: 3384 (br), 2230, 1490, 1406, 1278 cm^{-1}; MS (+CI) m/z (%): 234 (M^+, 8), 217 (M^+ −OH, 100); HRMS (+EI) calcd for $C_{17}H_{14}O$ (M^+) 234.1045, found 234.1041.

General procedure for preparation of allylic 4-*methoxybenzyloxyacetates* **7a—7d** and **13a—13f**

3-(((*p*-*Methoxybenzyl*)*oxy*)*acetoxy*)-2-*methyl*-3-*phenyl*-1-*propene* (**7a**) To a solution of alcohol **6a** (0.21 g, 1.42 mmol), DCC (0.35 g, 1.70 mmol) and DMAP (35 mg, 0.30 mmol) in dry CH_2Cl_2 (14 mL) cooled in an ice-water bath (*ca*. 0 ℃) was added acid **3** (0.33 g, 1.68 mmol). The resultant mixture was stirred at room temperature for 4.5 h. The reaction mixture was filtered off through a short plug of Celite with rinsing by EtOAc (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 10% EtOAc-hexane) to afford **7a** (0.31 g, 66%): colorless oil; R_f = 0.50 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.26—7.17 (m, 7H), 6.79 (d, J = 7.84 Hz, 2H), 6.19 (s, 1H), 5.04 (s, 1H), 4.91 (s, 1H), 4.48 (s, 2H), 4.06 (s, 2H), 3.72 (s, 3H), 1.56 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.4, 159.4, 142.7, 138.0, 129.7 (×2), 129.1, 128.4 (×2), 128.2, 127.1 (×2), 113.8 (×2), 112.8, 78.6, 72.9, 66.9, 55.2, 18.8; IR (neat) ν: 2938, 1752, 1612, 1514, 1248, 1190, 1120, 1032 cm^{-1}; MS (+CI) m/z (%): 344 ($M + NH_4^+$, 100); HRMS (+EI) calcd for $C_{20}H_{22}O_4$ (M^+) 326.1518, found 326.1520.

2-[1′-(((*p*-*Methoxybenzyl*)*oxy*)*acetoxy*)-1′-*phenyl*]-*methyl*-1-*butene* (**7b**) Prepared in 87% yield from alcohol **6b** after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); colorless oil; R_f = 0.45 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.28—7.18 (m, 7H), 6.80 (dd, J = 6.84, 1.96 Hz, 2H), 6.24 (s, 1H), 5.08 (s, 1H), 4.93 (s, 1H), 4.48 (s, 2H), 4.05 (s, 2H), 3.72 (s, 3H), 1.86 (q, J = 7.32 Hz, 2H), 0.94 (t, J = 5.88 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.4, 159.4, 148.4, 138.2, 129.7 (×2), 129.2, 128.4 (×2), 128.2, 127.3 (×2), 113.8 (×2), 110.3, 78.2, 72.9, 66.9, 55.3, 25.0, 11.8; IR (neat) ν: 2966, 1756, 1614, 1514, 1248, 1190, 1120, 1036 cm^{-1}; MS (+CI) m/z (%): 358 ($M + NH_4^+$, 100); HRMS (+EI) calcd for $C_{21}H_{24}O_4$ (M^+) 340.1675, found 340.1682.

(*E*)-1-(((*p*-*Methoxybenzyl*)*oxy*)*acetoxy*)-2-*methyl*-1-*phenyl*-2-*butene* (**7c**) Prepared in 60% yield from alcohol **6c** after purification by flash column chromatography (silica gel, 5% EtOAc-hexane); colorless oil; R_f = 0.61 (30% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.36—7.26 (m, 7H), 6.90 (d, J = 8.55 Hz, 2H), 6.31 (s, 1H), 5.04 (q, J = 6.66 Hz, 1H), 4.58 (s, 2H), 4.16 (s, 2H), 3.81 (s, 3H), 1.66 (d, J = 6.51 Hz, 3H), 1.53 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 169.3, 138.6, 133.4, 129.7 (×2), 129.1, 128.2 (×2), 127.6, 126.5 (×2), 126.1, 123.4, 113.8 (×2), 80.4, 72.9, 66.9, 55.3, 13.3, 12.3; IR (neat) ν: 2918, 1760, 1614, 1456, 1250, 1192, 1122, 1034

cm^{-1}; MS (+CI) *m/z* (%): 358 ($M+NH_4^+$, 100); HRMS (+EI) calcd for $C_{21}H_{24}O_4$ (M^+) 340.1675, found 340.1687.

(*E*)-1-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-1-*phenyl*-2-*butene* (**7d**) Prepared in 45% yield from alcohol **6d** after purification by flash column chromatography (silica gel, 15% EtOAc-hexane); colorless oil; R_f = 0.68 (30% EtOAc-hexane); ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.30—7.17 (m, 7H), 6.78 (dd, *J* = 6.84, 2.92 Hz, 2H), 6.24 (d, *J* = 6.84 Hz, 1H), 5.73—5.57 (m, 2H), 4.48 (s, 2H), 4.02 (d, *J* = 3.40 Hz, 2H), 3.71 (s, 3H), 1.64 (d, *J* = 6.36 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.5, 159.4, 139.3, 130.2, 129.7 (×2), 129.2, 128.5 (×2), 128.0, 126.8 (×2), 126.6, 113.8 (×2), 76.6, 72.9, 67.0, 55.2, 17.7; IR (neat) ν: 2938, 1752, 1514, 1250, 1194, 1122 cm^{-1}; MS (+CI) *m/z* (%): 344 ($M+NH_4^+$, 43), 131 (M^+ – *p*-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{20}H_{22}O_4$ (M^+) 326.1518, found 326.1520.

3-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-2-*methyl*-5-*phenylpent*-4-*yn*-1-*ene* (**13a**) Prepared in 63% yield from alcohol **12a** after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); colorless oil; R_f = 0.38 (20% EtOAc-hexane); ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.46—7.30 (m, 7H), 6.88 (d, *J* = 8.80 Hz, 2H), 6.16 (s, 1H), 5.31 (s, 1H), 5.07 (s, 1H), 4.60 (s, 2H), 4.17 and 4.12 (ABq, *J* = 16.40 Hz, 2H), 3.80 (s, 3H), 1.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.1, 159.3, 139.9, 131.8 (×2), 129.7 (×2), 128.9, 128.7, 128.2 (×2), 121.9, 115.4, 113.8 (×2), 86.7, 84.3, 73.0, 68.0, 66.7, 55.3, 18.5; IR (neat) ν: 2950, 2239, 1736, 1512, 1230 cm^{-1}; MS (+CI) *m/z* (%): 351 ($M+H^+$, 7), 155 (M^+ – *p*-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{22}H_{22}O_4$ (M^+) 350.1518, found 350.1508.

3-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-2-*ethyl*-5-*phenylpent*-4-*yn*-1-*ene* (**13b**) Prepared in 60% yield from alcohol **12b** after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); pale yellow oil; R_f = 0.40 (20% EtOAc-hexane); ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.46—7.30 (m, 7H), 6.87 (d, *J* = 8.80 Hz, 2H), 6.21 (s, 1H), 5.39 (s, 1H), 5.08 (s, 1H), 4.60 (s, 2H), 4.17 and 4.12 (ABq, *J* = 16.40 Hz, 2H), 3.80 (s, 3H), 2.25 (q, *J* = 7.20 Hz, 2H), 1.13 (t, *J* = 7.20 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.2, 159.3, 145.5, 131.8 (×2), 129.7 (×2), 128.9, 128.7, 128.2 (×2), 121.9, 113.8 (×2), 113.3, 86.7, 84.5, 73.0, 67.6, 66.8, 55.3, 24.7, 12.1; IR (neat) ν: 2968, 2247, 1760, 1514, 1248, 1190, 1124 cm^{-1}; MS (+CI) *m/z* (%): 365 ($M+H^+$, 8), 169 (M^+ – *p*-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{23}H_{24}O_4$ (M^+) 364.1675, found 364.1715.

(*E*)-3-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-4-*methyl*-1-*phenylhex*-1-*yn*-4-*ene* (**13c**) Prepared in 59% yield from alcohol **12c** after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); colorless oil; R_f = 0.54 (20% EtOAc-hexane); ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.45—7.26 (m, 7H), 6.87 (d, *J* = 8.40 Hz, 2H), 6.13 (s, 1H), 5.86 (q, *J* = 6.80 Hz, 1H), 4.59 (s, 2H), 4.14 and 4.09 (ABq, *J* = 16.40 Hz, 2H), 3.80 (s, 3H), 2.05 (s, 3H), 1.68 (d, *J* = 6.80 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.3, 159.4, 131.8 (×2), 131.1, 129.8 (×2), 129.1, 128.6, 128.2 (×2), 126.1, 122.1, 113.8 (×2), 86.7, 84.8, 73.0, 70.2, 66.8, 55.3, 13.5, 12.4; IR (neat) ν: 2936, 2228, 1756, 1614, 1514, 1490, 1444, 1248, 1182, 1120, 1036 cm^{-1}; MS (+CI) *m/z* (%): 382 ($M+NH_4^+$, 9), 365 ($M+H^+$, 3), 169 (M^+ – *p*-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{23}H_{24}O_4$ (M^+) 364.1675, found 364.1663.

(*E*)-3-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-1-*phenylhex*-1-*yn*-4-*ene* (**13d**) Prepared in 68% yield from alcohol **12d** after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); colorless oil; R_f = 0.58 (20% EtOAc-hexane); ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.47—7.26 (m, 7H), 6.87 (d, *J* = 6.60 Hz, 2H), 6.16 (d, *J* = 6.80 Hz, 1H), 6.16—6.08 (m, 1H), 6.66 (dd, *J* = 11.40, 5.10 Hz, 1H), 4.59 (s, 2H), 4.14 and 4.09 (ABq, *J* = 16.40 Hz, 2H), 3.78 (s, 3H) 1.78 (d, *J* = 4.50 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.2, 159.4, 132.2, 131.8 (×2), 129.8 (×2), 129.0, 128.7, 128.2 (×2), 125.8, 122.0, 113.8 (×2), 86.8, 84.6, 73.0, 66.8, 65.3, 55.3, 17.6; IR (neat) ν: 2936, 2226, 1752, 1612, 1508, 1248, 1201, 1124, 1036 cm^{-1}; MS (+CI) *m/z* (%): 368 ($M+NH_4^+$, 100), 351 ($M+H^+$, 4); HRMS (+EI) calcd for $C_{22}H_{22}O_4$ (M^+) 350.1518, found 350.1528.

(*E*)-3-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-2-*methyl*-1,5-*diphenylpent*-4-*yn*-1-*ene* (**13e**) Prepared in 54% yield from alcohol **12e** after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); pale yellow oil; R_f = 0.57 (20% EtOAc-hexane); ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.49—7.26 (m, 12H), 6.87 (d, *J* = 8.40 Hz, 2H), 6.83 (s, 1H), 6.30 (s, 1H), 4.61 (s, 2H), 4.19 and 4.14 (ABq, *J* = 16.40 Hz, 2H), 3.79 (s, 3H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.4, 159.5, 136.5, 132.8, 131.9 (×2), 130.3, 129.9 (×2), 129.1 (×4), 128.8, 128.3, 128.2 (×2), 127.2, 122.0, 113.9 (×2), 87.1, 84.5, 73.0, 70.3, 66.8, 55.3, 14.4; IR (neat) ν: 2927, 1756, 1614, 1514, 1250, 1190, 1120, 1034 cm^{-1}; MS (+CI) *m/z* (%): 427 ($M+H^+$, 4), 231 (M^+ – *p*-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{28}H_{26}O_4$ (M^+) 426.1831, found 426.1834.

(*E*)-3-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-1,5-*diphenylpent*-4-*yn*-1-*ene* (**13f**) Prepared in 78% yield from alcohol **12f** after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); yellow oil; R_f = 0.62 (20% EtOAc-hexane); ^1H NMR ($CDCl_3$, 300

MHz) δ: 7.51—7.26 (m, 12H), 6.94 (d, J = 15.60 Hz, 1H), 6.87 (d, J = 8.80 Hz, 2H), 6.39 (d, J = 15.60 Hz, 1H), 6.32 (dd, J = 15.60, 6.80 Hz, 1H), 4.60 (s, 2H), 4.18 and 4.13 (ABq, J = 16.40 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 169.4, 159.5, 135.6, 135.1, 131.9 (×2), 129.9 (×2), 129.0, 128.9 (×2), 129.1, 128.6 (×2), 128.2 (×2), 127.0 (×2), 123.5, 121.9, 113.9 (×2), 87.4, 84.2, 73.0, 66.8, 65.3, 55.2; IR (neat) ν: 2934, 2232, 1760, 1614, 1516, 1248, 1180, 1118, 1034 cm^{-1}; MS (+CI) m/z (%): 430 ($M + NH_4^+$, 1), 217 (M^+ – p-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{27}H_{24}O_4$ (M^+) 412.1675, found 412.1677.

General procedure for Eu(fod)$_3$*-catalyzed rearrangement of allylic p-methoxybenzyloxyacetates* **7a**, **7b** *and* **13a**, **13b** *under heating conditions*

(*E*)-3-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-2-*methyl*-1-*phenyl*-1-*propene* (**14a**) To a solution of **7a** (94.0 mg, 0.29 mmol) in chlorobenzene (3 mL) was added Eu(fod)$_3$ (15 mg, 1.40×10^{-2} mmol) followed by stirring at refluxing temperature (132 ℃) for 72 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 15% EtOAc-hexane) to afford **14a** (19.7 mg) in 21% yield. Chloroform was used as the solvent for rearrangement of **13a**, **13b** at refluxing temperature (60 ℃). The detailed reaction conditions are listed in Table 1. **14a**: white gum; R_f = 0.50 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.33—7.26 (m, 7H), 6.89 (d, J = 8.61Hz, 2H), 6.55 (s, 1H), 4.74 (s, 2H), 4.60 (s, 2H), 4.14 (s, 2H), 3.80 (s, 3H), 1.90 (d, J = 1.14 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 170.3, 159.5, 136.8, 132.2, 129.8 (×2), 129.1, 128.9 (×2), 128.8, 128.1 (×2), 126.8, 113.9 (×2), 73.0, 70.4, 66.8, 55.2, 15.5; IR (neat) ν: 2924, 1750, 1614, 1513, 1247, 1190, 1123, 1033 cm^{-1}; MS (+CI) m/z (%): 325 ($M - H^+$, 100); HRMS (+EI) calcd for $C_{20}H_{22}O_4$ (M^+) 326.1518, found 326.1521.

(*E*)-2-[1′-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*) *methyl*]-1-*phenyl*-1-*butene* (**14b**) *and* (*Z*)-*isomer* **14b′** Prepared as a 42:58 mixture of **14b** and **14b′** in 40% yield from **7b** in refluxing chlorobenzene (132 ℃) after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); colorless oil; R_f = 0.45 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.34—7.17 (m, 7H), 6.88 (d, J = 8.40 Hz, 2H), 6.57 (s, 0.42H for **14b**), 6.53 (s, 0.58H for **14b′**), 4.83 (s, 0.84H for **14b**), 4.78 (s, 1.16H for **14b′**), 4.60 (s, 1.16H for **14b′**), 4.57 (s, 0.84H for **14b**), 4.13 (s, 1.16H for **14b′**), 4.09 (s, 0.84H for **14b**) 3.80 (s, 3H), 2.32—2.25 (m, 2H), 1.16—1.09 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: assigned for **14b**: 170.3, 159.3, 137.9, 136.6, 129.7 (×2), 129.0, 128.5, 128.1 (×4), 126.8, 113.8 (×2), 73.0, 66.8, 63.1, 55.3, 28.3, 13.0; ^{13}C NMR ($CDCl_3$, 100 MHz) δ: assigned for **14b′**: 170.1, 159.3, 137.9, 136.7, 129.7 (×2), 129.0, 128.5, 128.2 (×4), 126.8, 113.8 (×2), 73.0, 68.1, 66.9, 55.3, 22.0, 12.7; IR (neat) ν: 2964, 1760, 1614, 1514, 1248, 1192, 1122, 1034 cm^{-1}; MS (+CI) m/z (%): 339 ($M - H^+$, 100); HRMS (+EI) calcd for $C_{21}H_{24}O_4$ (M^+) 340.1645, found 340.1674.

(*E*)-5-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-4-*methyl*-1-*phenylpent*-1-*yn*-3-*ene* (**15a**) Prepared in 84% yield from **13a** in refluxing chloroform (60 ℃) after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); white solid; m.p. 50—53 ℃; R_f = 0.42 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.45—7.31 (m, 7H), 6.90 (d, J = 8.58 Hz, 2H), 5.77 (d, J = 0.99 Hz, 1H), 4.70 (s, 2H), 4.64 (s, 2H), 4.18 (s, 2H), 3.81 (s, 3H), 2.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 170.1, 159.5, 144.2, 131.4 (×2), 129.8 (×2), 129.0, 128.3 (×2), 128.2, 123.3, 113.9 (×2), 108.3, 94.3, 85.9, 73.0, 67.9, 66.7, 55.3, 17.0; IR (KBr) ν: 2908, 1756, 1514, 1250, 1206, 1144, 1036 cm^{-1}; MS (+CI) m/z (%): 351 ($M + H^+$, 8), 155 (M^+ – p-$MeOC_6H_4CH_2OCH_2CO_2$, 96), 121 (100); HRMS (+EI) calcd for $C_{22}H_{22}O_4$ (M^+) 350.1518, found 326.1541.

(*E*)-4-[1′-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*) *methyl*]-1-*phenylhex*-1-*yn*-3-*ene* (**15b**) Prepared in 59% yield from **13b** in refluxing chloroform (60 ℃) after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); pale yellow oil; R_f = 0.45 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.46—7.29 (m, 7H), 6.90 (d, J = 8.67 Hz, 2H), 5.75 (s, 1H), 4.73 (d, J = 1.20 Hz, 2H), 4.59 (s, 2H), 4.06 (s, 2H), 3.80 (s, 3H), 2.43 (q, J = 7.59 Hz, 2H), 1.13 (t, J = 7.59 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 170.0, 159.5, 149.7, 131.4 (×2), 129.7 (×2), 129.0, 128.3 (×2), 128.1, 123.4, 113.9 (×2), 107.7, 94.3, 85.7, 73.0, 66.7, 66.1, 55.2, 24.4, 12.4; IR (neat) ν: 2970, 2200, 1760, 1614, 1520, 1250, 1195, 1122, 1036 cm^{-1}; MS (+CI) m/z (%): 365 ($M + H^+$, 3), 169 (M^+ – p-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{23}H_{24}O_4$ (M^+) 364.1675, found 364.1601.

3-*Acetoxy*-2-*ethyl*-5-*phenylpent*-4-*yn*-1-*ene* (**16**) Obtained as a by product in 14% yield from the rearrangement of **13b** after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); pale yellow oil; R_f = 0.25 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.47—7.27 (m, 5H), 6.11 (s, 1H), 5.37 (t, J = 0.99 Hz, 1H), 5.06 (s, 1H), 2.26 (m, 2H), 2.14 (s, 3H), 1.14 (t, J = 7.44 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 169.8, 146.1, 131.9 (×2), 128.7, 128.2 (×2), 122.2, 112.8, 86.2, 85.0, 67.2, 24.7, 21.1, 12.0; MS (+CI) m/z (%): 229 ($M + H^+$, 8), 169 (M^+ – $MeCO_2$, 100); HRMS

(+EI) calcd for $C_{15}H_{16}O_2$ (M^+) 228.1150, found 228.1139.

General procedure for Eu(fod)$_3$*-catalyzed rearrangement of allylic p-methoxybenzyloxyacetates* **7c—7d** *and* **13c—13f**, *p-(trifluoromethyl) benzyloxyacetate* **8**, *methoxyacetate* **9**, *and benzyloxyacetate* **10** *at room temperature*

(*E*)-3-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-2-*methyl*-1-*phenyl*-1-*butene* (**14c**) Compound **7c** (32.3 mg, 9.5×10^{-2} mmol) was charged into an NMR tube and 1 mL of $CDCl_3$ solution containing Eu(fod)$_3$(30.3 mg, 2.9×10^{-2} mmol) was added. The NMR tube was shaken well and the reaction was monitored by ^{1}H NMR spectroscopy at room temperature. After 276 h, the characteristic signal of **7c** disappeared. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 5% EtOAc-hexane) to afford **14c** (30.6 mg, 95%): colorless oil; R_f = 0.61 (30% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.36—7.26 (m, 7H), 6.91 (d, J = 8.00 Hz, 2H), 6.58 (s, 1H), 5.04 (q, J = 6.00 Hz, 1H), 4.62 (s, 2H), 4.13 (s, 2H), 3.83 (s, 3H) 1.91 (d, J = 1.20 Hz, 3H), 1.47 (d, J = 6.40 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.6, 159.3, 136.9, 136.6, 129.7 (×2), 129.0 (×2), 128.0 (×2), 126.9, 126.6, 113.8 (×2), 76.1, 72.9, 67.0, 55.3, 19.3, 13.8; IR (neat) ν: 2924, 1752, 1612, 1508, 1248, 1205, 1123, 1032 cm^{-1}; MS (+CI) *m/z* (%): 341 ($M+H^+$, 4), 145 (M^+ − *p*-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{21}H_{24}O_4$ (M^+) 340.1675, found 340.1683.

The detailed reaction conditions for other allylic esters are listed in Table 1.

(*E*)-3-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-1-*phenyl*-1-*butene* (**14d**) Prepared in 96% yield from **7d** at room temperature after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); colorless oil; R_f = 0.43 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.39—7.26 (m, 7H), 6.90 (d, J = 8.76 Hz, 2H), 6.23 (d, J = 16.12 Hz, 1H), 6.19 (dd, J = 16.12, 6.84 Hz, 1H), 5.63 (quintet, J = 6.84 Hz, 1H), 4.58 (s, 2H), 4.08 (s, 2H), 3.80 (s, 3H) 1.44 (d, J = 6.84 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.7, 159.4, 136.1, 132.1, 129.8 (×2), 129.2, 128.6 (×2), 128.2, 128.0, 126.6 (×2), 113.8 (×2), 72.9, 71.7, 67.0, 55.2, 20.4; IR (neat) ν: 2934, 1748, 1614, 1516, 1456, 1248, 1201, 1132, 1036 cm^{-1}; MS (+CI) *m/z* (%): 344 ($M+NH_4^+$, 27), 131 (M^+ − *p*-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{20}H_{22}O_4$ (M^+) 326.1518, found 326.1536.

(*E*)-5-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-4-*methyl*-1-*phenylhex*-1-*yn*-3-*ene* (**15c**) Prepared in 86% yield from **13c** at room temperature after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); colorless oil; R_f = 0.54 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.42—7.26 (m, 7H), 6.89 (d, J = 8.00 Hz, 2H), 5.77 (s, 1H), 5.47 (q, J = 6.00 Hz, 1H), 4.58 (s, 2H), 4.09 (s, 2H), 3.81 (s, 3H) 1.98 (s, 3H), 1.38 (d, J = 6.00 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.4, 159.4, 148.9, 131.3 (×2), 129.7 (×2), 129.0, 128.2 (×2), 128.0, 123.4, 113.8 (×2), 106.8, 94.4, 86.1, 74.0, 73.0, 66.9, 55.3, 19.2, 15.7; IR (neat) ν: 2934, 1786, 1612, 1514, 1248, 1194, 1124, 1070, 1036 cm^{-1}; MS (+CI) *m/z* (%): 382 ($M+NH_4^+$, 10), 365 ($M+H^+$, 3), 169 (M^+ − *p*-$MeOC_6H_4CH_2O$-CH_2CO_2, 100); HRMS (+EI) calcd for $C_{23}H_{24}O_4$ (M^+) 364.1675, found 364.1664.

(*E*)-5-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-1-*phenyl*-*hex*-1-*yn*-3-*ene* (**15d**) Prepared in 80% yield from **13d** at room temperature after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); colorless oil; R_f = 0.58 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.42—7.26 (m, 7H), 6.90 (d, J = 8.40 Hz, 2H), 6.17 (dd, J = 16.00, 6.40 Hz, 1H), 5.94 (d, J = 15.60 Hz, 1H), 5.53 (quintet, J = 6.40 Hz, 1H), 4.58 (s, 2H), 4.07 (s, 2H), 3.80 (s, 3H) 1.39 (d, J = 6.40 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.4, 159.4, 141.0, 131.5 (×2), 129.7 (×2), 129.0, 128.3, 128.2 (×2), 122.9, 113.8 (×2), 112.0, 91.0, 86.7, 73.0, 70.7, 66.9, 55.3, 20.0; IR (neat) ν: 2934, 2202, 1754, 1614, 1514, 1248, 1198, 1124, 1036 cm^{-1}; MS (+CI) *m/z* (%): 368 ($M+NH_4^+$, 12), 351 ($M+H^+$, 5), 155 (M^+ − *p*-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{22}H_{22}O_4$ (M^+) 350.1518, found 350.1501.

(*E*)-5-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-4-*methyl*-1,5-*diphenylpent*-1-*yn*-3-*ene* (**15e**) Prepared in 70% yield from **13e** at room temperature after purification by flash column chromatography (silica gel, 10% EtOAc-hexane); white solid; m.p. 41—43 ℃; R_f = 0.57 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.44—7.28 (m, 12H), 6.90 (d, J = 8.80 Hz, 2H), 6.40 (s, 1H), 5.94 (s, 1H), 4.60 (s, 2H), 4.17 (d, J = 1.48 Hz, 2H), 3.83 (s, 3H), 1.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.3, 159.5, 147.5, 137.4, 131.4 (×2), 129.8 (×2), 129.0, 128.6 (×2), 128.5 (×2), 128.3, 128.2, 127.2 (×2), 123.3, 113.9 (×2), 107.6, 94.5, 86.1, 78.5, 73.0, 66.8, 55.3, 16.4; IR (KBr) ν: 2934, 1758, 1612, 1514, 1248, 1174, 1122, 1034 cm^{-1}; MS (+CI) *m/z* (%): 444 ($M+NH^+$, 7), 231 (M^+ − *p*-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{28}H_{26}O_4$ (M^+) 426.1831, found 426.1850.

(*E*)-5-(((*p-Methoxybenzyl*) *oxy*) *acetoxy*)-1,5-*diphenylpent*-1-*yn*-3-*ene* (**15f**) Prepared as a 87:13 mixture of **15f** and **15f′** in 91% yield from **13f** at room temperature after purification by flash column chromatography (silica gel, 10% EtOAc-hexane) **15f**: yellow oil; R_f = 0.62 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ:

7.51—7.26 (m, 12H), 6.88 (d, J = 8.40 Hz, 2H), 6.44 (d, J = 6.00 Hz, 1H), 6.34 (dd, J = 15.60, 6.00 Hz, 1H), 5.95 (d, J = 15.60 Hz, 1H), 4.57 (s, 2H), 4.14 and 4.04 (ABq, J = 15.00 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.2, 159.4, 139.5, 137.6, 131.4 (×2), 129.7 (×2), 128.7 (×2), 128.5, 128.3, 128.2 (×2), 127.1 (×2), 126.5, 122.8, 113.8 (×2), 112.9, 91.6, 86.6, 75.7, 73.0, 66.8, 55.3; IR (neat) ν: 2934, 2202, 1752, 1612, 1514, 1248, 1188, 1120, 1034 cm^{-1}; MS (+CI) m/z (%): 413 ($M+H^+$, 5), 217 (M^+ – p-$MeOC_6H_4CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{27}H_{24}O_4$ (M^+) 412.1675, found 412.1669.

(*E*)-3-((*Benzyloxy*)*acetoxy*)-1-*phenyl*-1-*butene* (**11a**) Prepared in 88% yield from **8** at room temperature after purification by flash column chromatography (silica gel, 5% EtOAc-hexane); colorless oil; R_f = 0.79 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.38—7.26 (m, 10 H), 6.63 (d, J = 16.00 Hz, 1H), 6.18 (dd, J = 16.00, 6.80 Hz, 1H), 4.65 (quintet, J = 6.40 Hz, 1H), 4.65 (s, 2H), 4.11 (s, 2H), 1.44 (d, J = 6.80 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.5, 137.1, 136.1, 132.1, 128.5 (×2), 128.4 (×4), 128.1, 128.0, 128.0, 127.9, 126.5 (×2), 73.4, 71.8, 67.4, 20.5; IR (neat) ν: 2932, 1748, 1496, 1456, 1270, 1200, 1128, 1038 cm^{-1}; MS (+CI) m/z (%): 314 ($M+NH_4^+$, 22), 131 (M^+ – $C_6H_5CH_2O$-CH_2CO_2, 100); HRMS (+EI) calcd for $C_{19}H_{20}O_3$ (M^+) 296.1412, found 296.1415.

(*E*)-3-*Methoxyacetoxy*-1-*phenyl*-1-*butene* (**11b**) Prepared in 96% yield from **9** at room temperature after purification by flash column chromatography (silica gel, 5% EtOAc-hexane); colorless oil; R_f = 0.46 (10% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.40—7.23 (m, 5H), 6.63 (d, J = 16.02 Hz, 1H), 6.19 (dd, J = 15.93, 6.99 Hz, 1H), 5.62 (quintet, J = 5.67 Hz, 1H), 4.04 (s, 2H), 3.46 (s, 3H), 1.45 (d, J = 6.48 Hz, 3H); ^{13}C NMR (acetone-d_6, 75 MHz) δ: 170.0, 137.4, 132.2 (×2), 129.7, 129.5 (×2), 128.8, 127.4, 71.9, 70.4, 59.2, 20.8; IR (neat) ν: 2934, 1756, 1450, 1260, 1192, 1128, 1038 cm^{-1}; MS (+CI) m/z (%): 238 ($M+NH_4^+$, 12), 131 (M^+ – $MeOCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{13}H_{16}O_3$ (M^+) 220.1099, found 220.1088.

(*E*)-3-(((*p*-(*Trifluoromethyl*)*benzyl*)*oxy*)*acetoxy*)-1-*phenyl*-1-*butene* (**11c**) Prepared in 94% yield from **10** at room temperature after purification by flash column chromatography (silica gel, 5% EtOAc-hexane); colorless oil; R_f = 0.52 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.61 (d, J = 8.00 Hz, 2H), 7.49 (d, J = 8.00 Hz, 2H), 7.39—7.23 (m, 5H), 6.04 (d, J = 16.00 Hz, 1H), 6.18 (dd, J = 16.00, 6.80 Hz, 1H), 5.65 (quintet, J = 6.80 Hz, 1H), 4.70 (s, 2H), 4.16 (s, 2H), 1.46 (d, J = 6.45 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.2, 141.2, 135.9, 132.2, 129.9 (q, J = 32.2 Hz), 128.5 (×2), 128.0, 127.9, 127.7 (×2), 126.5 (×2), 125.2 (q, J = 4.10 Hz, ×2), 72.5, 72.0, 67.7, 20.4 (CF_3 singal not observed); IR (neat) ν: 2927, 1754, 1326, 1200, 1170, 1124, 1066 cm^{-1}; MS (+CI) m/z (%): 382 ($M+NH_4^+$, 10), 131 (M^+ – p-$CF_3C_6H_4CH_2OCH_2CO_2$, 100). HRMS (+EI) calcd for $C_{20}H_{19}F_3O_3$ (M^+) 364.1286, found 364.1285.

Preparation of (*E*)-1-((*benzyloxy*)*acetoxy*)-1-*phenyl*-2-*butene* (**8**) To a solution of **6d** (0.30 g, 2.02 mmol) and benzyloxyacetyl chloride (0.48 mL, 3.04 mmol) in dry CH_2Cl_2 (15 mL) cooled in an ice-water bath (*ca*. 0 ℃) was added distillated triethylamine (0.57 mL, 4.09 mmol). The resultant mixture was stirred at room temperature for 4 h. The reaction mixture was quenched by saturated aqueous NH_4Cl solution (15 mL) and extracted with EtOAc (2×15 mL). The combined organic layer was washed with brine (2×20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 5% EtOAc-hexane) to afford **8** (0.46 g, 77%): colorless oil; R_f = 0.79 (20% EtOAc-hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.38—7.26 (m, 10H), 6.36 (d, J = 6.60 Hz, 1H), 5.84—5.68 (m, 2H), 4.65 (s, 2H), 4.18 and 4.12 (ABq, J = 13.20 Hz, 2H), 1.74 (d, J = 6.00 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.3, 139.1, 137.0, 130.1, 129.0, 128.4 (×2), 128.3 (×2), 127.9 (×2), 127.8, 126.7 (×2), 121.2, 76.8, 73.2, 67.3, 17.8; IR (neat) ν: 2916, 1760, 1496, 1456, 1194, 1128 cm^{-1}; MS (+CI) m/z (%): 314 ($M+NH_4^+$, 15), 131 (M^+ – $C_6H_5CH_2OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{19}H_{20}O_3$ (M^+) 296.1412, found 296.1424.

Preparation of (*E*)-1-*methoxyacetoxy*-1-*phenyl*-2-*butene* (**9**) To a solution of **6d** (0.12 g, 0.82 mmol), DCC (0.20 g, 0.97 mmol), and DMAP (20 mg, 0.16 mmol) in dry CH_2Cl_2 (8 mL) cooled in an ice-water bath (*ca*. 0 ℃) was added methoxyacetic acid (0.1 mL, 1.30 mmol). The resultant mixture was stirred at room temperature for 4.5 h. The reaction mixture was filtered off through a short plug of Celite with rinsing by EtOAc (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (alumina, 10% EtOAc-hexane) to afford **9** (0.12 g, 69%): colorless oil; R_f = 0.46 (10% EtOAc-hexane); ^{1}H NMR (acetone-d_6, 300 MHz) δ: 7.63—7.41 (m, 5H), 6.42 (d, J = 6.54 Hz, 1H), 6.01—5.73 (m, 2H), 4.22 (s, 2H), 3.51 (s, 3H), 1.84 (dd, J = 6.15, 0.75 Hz, 3H); ^{13}C NMR (acetone-d_6, 100 MHz) δ: 169.9, 130.6, 130.1, 129.3 (×2), 128.7, 127.6, 127.6 (×2), 77.1, 70.3, 59.3, 18.0; IR (neat) ν: 2918, 1762, 1258, 1190, 1128 cm^{-1}; MS (+CI) m/z (%): 238 ($M+NH_4^+$, 3), 220 (M^+, 2), 131 (M^+ – $CH_3OCH_2CO_2$, 100); HRMS (+EI) calcd for $C_{13}H_{16}O_3$ (M^+) 220.1099, found 220.1090.

Preparation of (*E*)-1-(((*p*-(*trifluoromethyl*)*benzyl*)*oxy*)*acetoxy*)-1-*phenyl*-2-*butene* (**10**) To a solu-

tion of **6d** (0.10 g, 0.69 mmol), DCC (0.16 g, 0.78 mmol), and DMAP (17 mg, 0.14 mmol) in dry CH_2Cl_2 (7 mL) cooled in an ice-water bath (*ca*. 0 ℃) was added *p*-trifluoromethylbenzyloxyacetic acid (**4**, 0.19 g, 0.82 mmol). The resultant mixture was stirred at room temperature for 4.5 h. The reaction mixture was filtered through a short plug of Celite with rinsing by EtOAc (10 mL). The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 5% EtOAc-hexane) to afford **10** (0.17 g, 69%), colorless oil; $R_f = 0.52$ (20% EtOAc-hexane); ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.60 (d, $J = 8.16$ Hz, 2H), 7.47 (d, $J = 8.07$ Hz, 2H), 7.39—7.27 (m, 5H), 6.32 (d, $J = 6.84$ Hz, 1H), 5.83—5.64 (m, 2H), 4.68 (s, 2H), 4.20 and 4.15 (ABq, $J = 16.80$ Hz, 2H), 1.72 (d, $J = 7.44$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 169.0, 141.2, 139.0, 130.3, 129.9 (q, $J = 33.0$ Hz), 128.9, 128.4 (×2), 128.0, 127.7 (×2), 126.8 (×2), 125.5 (q, $J = 3.30$ Hz), 72.5, 67.7, 17.9 (CF_3 signal not observed); IR (neat) ν: 2920, 1748, 1326, 1124, 1066 cm^{-1}; MS (+CI) *m/z* (%): 382 ($M + NH_4^+$, 7), 131 ($M^+ - p$-$CF_3C_6H_4CH_2O$-CH_2CO_2, 100); HRMS (+EI) calcd for $C_{20}H_{19}F_3O_3$ (M^+) 364.1286, found 364.1290.

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