Allylation of Carbonyl Compounds Bearing a Hydroxyl Group by Tetraallyltin: Highly Stereoselective Allylation in a Chelation-Controlled Manner

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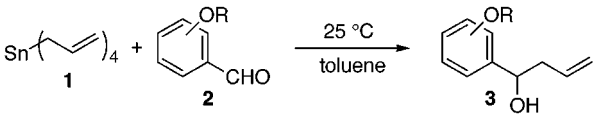
Introduction

Allylation of carbonyl compounds is an important method for forming carbon−carbon bonds. Many reagents have been developed for such allylations over the past few decades.[1] Allyltrialkyl or triaryltin compounds are widely used for stereoselective allylations.[2] However, they are limited from the viewpoint of a practical synthetic method: (i) They are inert to carbonyls such as simple aldehydes or ketones without activators. Proper activation is essential and has been widely studied; for example, the use of Lewis acids[1,2] for the activation of electrophiles. (ii) Three substituents other than the allylic one are disposed on the tin atom. They are considered to be dummy substituents and are not transferable. To overcome these problems, tetraallyl-substituted stannane could be used as a reagent. Young previously reported an effective allylation system using a quarter equivalent of tetraallyltin to carbonyls in methanol (eq 1).[3−6] In this paper, we report the reaction of tetraallyltin with carbonyls bearing a hydroxyl group (eq 2). The intramolecular hydroxyl groups in this system promote kinetic-controlled allylation via a chelation-model transition state with high stereoselectivity as well as high efficiency.

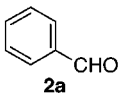
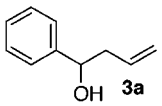
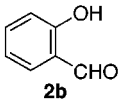
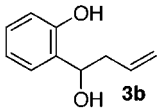
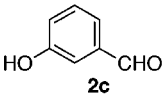
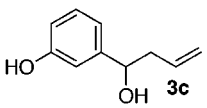
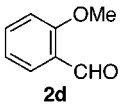
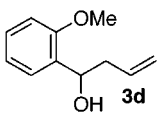
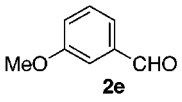
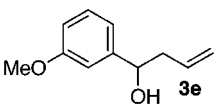
Results and Discussions

Reactions of Tetraallyltin with Hydroxy- or Methoxybenzaldehyde. Table 1 shows the results of allylation of the substituted benzaldehydes **2** with tetraallyltin (**1**). Salicylaldehyde (**2b**) was effectively allylated without any promoters in toluene, while the allylation of benzaldehyde (**2a**) did not proceed at all under the same conditions (entries 1 and 2). 3-Hydroxybenzaldehyde (**2c**) also gave the homoallylic alcohol **3c** in high yield (entry 3). The phenolic hydroxyl groups in aldehydes were indispensable for these allylations[7] because the corresponding methoxy-substituted aldehydes **2d** and **2e** were inert in this system (entries 4 and 5). We tried the allylation of a mixture of **2b** and **2d** (tetraallyltin:**2b**:**2d** = 0.25:1:1, 25 °C, 1 h). This reaction gave the products **3b** and **3d** in yields of 51 and 46%, respectively. This result suggests that the activation of carbonyl by an acidic hydroxyl group (phenolic OH) is not significant for this allylation, since even the aldehyde **2b**, which has an intramolecular hydrogen bond, had the same reactivity as **2d**. Therefore, we can conclude that the acidic

Table 1. Allylation of *O*-Substituted Benzaldehydes 2 by Tetraallyltin 1[a]



1 2 3

entry	aldehyde	time/h	product	yield/%
1	 **2a**	1	 **3a**	0
2	 **2b**	1	 **3b**	94
3	 **2c**	1	 **3c**	85
4	 **2d**	2	 **3d**	13
5	 **2e**	3	 **3e**	9

[a] All reactions were carried out in toluene (2 mL) using tetraallyltin **1** (0.5 mmol) and aldehyde **2** (2.0 mmol) at 25 °C.

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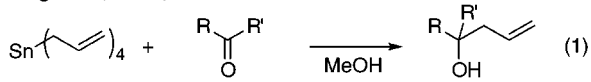
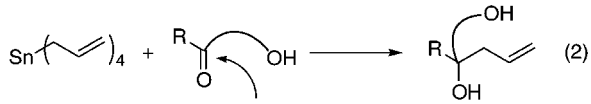


(1)

this work



(2)

selective addition

(1) (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207−2293. (b) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243−249.

(2) Nishigaichi, Y.; Takuwa, A.; Naruta, Y.; Maruyama K. *Tetrahedron* **1993**, *49*, 7395−7426.

(3) Cokley, T. M.; Harvey, P. J.; Marshall, R. L.; McCluskey, A.; Young, D. J. *J. Org. Chem.* **1997**, *62*, 1961−1964.

(4) Cokley, T. M.; Marshall, R. L.; McCluskey, A.; Young, D. J. *Tetrahedron Lett.* **1996**, *37*, 1905−1908.

(5) We independently investigated this type of acceleration system in alcohols. (a) Yasuda, M.; Fujibayashi, T.; Shibata, I.; Baba, A. 70th Annual Meeting of the Chemical Society of Japan, Abstr. No. 1J226 (March 1996). (b) Yasuda, M.; Fujibayashi, T.; Baba, A. 43rd Symposium on Organometallic Chemistry, Japan, 1996, Abstr. B207.

(6) Effective allylations with one-fourth the amount of tetraallyltin in the presence of Brönsted or Lewis acids under aqueous conditions have been reported. (a) Yanagisawa, A.; Inoue, H.; Morodome, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 10356−10357. (b) Hachiya, I.; Kobayashi, S. *J. Org. Chem.* **1993**, *58*, 6958−6960. (c) Kobayashi, S.; Nagayama, S. *J. Org. Chem.* **1996**, *61*, 2256−2257.

(7) We recently reported that phenol was effective for the allylation of simple ketones by tetraallyltin. Yasuda, M.; Kitahara, N.; Fujibayashi, T.; Baba, A. *Chem. Lett.* **1998**, 743−744. This system requires the premixing of phenol and tetraallyltin under heating to form a reactive aryloxyallyltin species with comsumption of some allyl groups of tetraallyltin. On the other hand, the reaction in this paper did not proceed via the activation manner because nearly quantitative formation of the product was obtained with one-fourth the amont of tetraallyltin.

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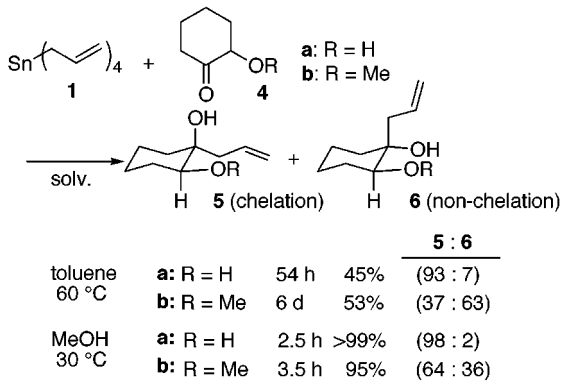
Scheme 1



				5 : 6
toluene 60 °C	**a:** R = H	54 h	45%	(93 : 7)
	b: R = Me	6 d	53%	(37 : 63)
MeOH 30 °C	**a:** R = H	2.5 h	>99%	(98 : 2)
	b: R = Me	3.5 h	95%	(64 : 36)

hydroxyl group acts by quenching the allylated stannoxide that is initially formed in either an intra- or intermolecular manner to form homoallylic alcohol. This protonolysis step is thermodynamically very important to complete the addition because of the reversibility of the allylstannation of carbonyls.[8,9]

Reactions of Tetraallyltin with α-Hydroxy- or α-Methoxyketones. Next, we investigated the reaction of carbonyls bearing an alcoholic hydroxyl group. The results of the allylation of 2-oxo-functionalized cyclohexanones **4** with tetraallyltin (**1**) are summarized in Scheme 1. High control of facial selectivity by the intramolecular hydroxyl group (R = H) was observed as was effective enhancement of the reaction rate in either toluene or MeOH, while methoxy-substituted ketone **4b** showed low selectivity. In particular, the reaction of **4a** in MeOH gave extremely high levels of selectivity and chemical yield (>99% yield, 96% de).

These results are explained in Scheme 2. The allylic tin species **1** generally adds in an equatorial direction to the carbonyl groups in either form of cyclohexanone.[10] Homoallylic alcohol **5** is the product via the chelation-transition state **X**, where chelation contributes to a fast addition rate ($k_1 > k_2$).[11] The product distribution directly depends on the kinetics (k_1 vs k_2) in MeOH because of irreversible protonolysis into the products **5** and **6**. The reaction with hydroxyl ketone in toluene is also controlled kinetically due to intramolecular protonolysis (**7** → **8** or **10** → **11**) to predominantly give chelation-controlled product **5**, although the reaction rate is considerably slower than that in MeOH. On the other hand, the reaction with methoxy ketone in toluene gave the product under thermodynamic control, albeit in low efficiency due to lack of the protonolysis step. The stronger interaction between tin and the oxygen of OH compared to the interaction between tin and the oxygen of OMe is responsible for the higher selectivity of hydroxyketone **4a** compared to methoxyketone **4b**.

This allylation system was applicable to acyclic substrates as shown in Scheme 3. The hydroxyl ketone **12a** gave the allylated product **13a** selectively in either toluene or MeOH. In this case too, MeOH induced high efficiency (>99% yield), and did not impede the formation of a chelation intermediate, to give complete diastereoselectivity. On the other hand, the reactions of methoxyketone **12b** showed low efficiency and selectivity in both solvents. X-ray studies revealed the relative configurations of the products **13a** and **13b**, which are formed in a chelation-controlled manner as shown in Scheme 4. Kira and Sakurai reported an effective system for the chelation-controlled allylation of **12a** using trifluorosilane with Et_3N.[12] The base acts as a deprotonating reagent to form a covalent bond between the silicon center and the oxygen. In our present system, chelation control was attained via coordinative interaction between the tin center and the hydroxyl oxygen, where no deprotonation from the hydroxyl group was required.

Conclusion. In summary, the intramolecular hydroxyl group in carbonyl compounds acts as the reaction promoter and selectivity controller in allylation with tetraallyltin. The allylation of hydroxyl-substituted benzaldehydes proceeds smoothly to give homoallylic alcohols without a promoter or catalyst. The α-hydroxyl ketones are allylated in a highly chelation-controlled manner. This selective system shows unique features: (a) no Lewis acid capable of biligand for the chelation structure is needed and (b) a hydroxyl group can be directly used without protection for the chelation-controlled reaction.[11]

Experimental Section

General. IR spectra were recorded as thin films or as solids in KBr pellets. ^{1}H and ^{13}C NMR spectra were obtained with TMS as internal standard. Flash chromatography was performed on silica gel. Bulb-to-bulb distillation (Kugelrohr) was accomplished at the oven temperature and pressure indicated. Yields were determined by GLC or ^{1}H NMR using internal standards.

Materials. Tetraallyltin (**1**) was prepared by known methods from allyl Grignard reagent and tin tetrachloride.[13] All aldehydes and ketones are commercial available.

General Procedure for Allylation of Carbonyls by Tetraallyltin. Tetraallyltin **1** (0.5 mmol) and a carbonyl compound (2.0 mmol) were mixed in a solvent (2 mL) under the conditions in text. To the reaction mixture, diethyl ether (30 mL) and aqueous NH_4F (15%; 15 mL) were added, and the resulting Bu_3SnF was filtered off. The filtrate was washed with water (30 mL × 2), dried ($MgSO_4$), and evaporated. Flash chromatography and/or distillation gave pure products.

1-(2-Hydroxyphenyl)-3-buten-1-ol (3b): bp 80 °C/ 3 mmHg; IR (neat) 3200, 1600 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.20−6.81 (m, 4H), 5.90−5.73 (m, 1H), 5.25−5.19 (m, 2H), 4.90−4.85 (m, 1H), 2.77 (d, J = 2.93 Hz, 1H), 2.67−2.56 (m, 2H); ^{13}C NMR (22.6 MHz, $CDCl_3$) δ 155.15, 133.83, 128.80, 127.03, 119.78, 117.00, 126.52, 118.98, 74.44, 42.03; MS *m*/*z* 164 (M^+); HRMS calcd for $C_{10}H_{12}O_2$ 164.0837, found *m*/*z* 164.0844 (M^+). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.94; H, 7.50.

1-(3-Hydroxyphenyl)-3-buten-1-ol (3c): mp 119 °C; IR (KBr) 3330, 1640 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.19 (m, 1H), 6.92−6.86 (m, 2H), 6.76−6.73 (m, 1H), 5.86−5.75 (m, 1H), 5.20−5.13 (m, 2H), 5.02 (br, 1H), 4.70 (dd, J = 7.81, 4.89 Hz, 1H), 2.57−2.43 (m, 2H), 2.07 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.72, 145.80, 134.28, 129.68, 118.58, 118.20, 114.46, 112.65, 73.00, 43.72; MS *m*/*z* 164 (M^+); HRMS calcd for $C_{10}H_{12}O_2$ 164.0837, found *m*/*z* 164.0827 (M^+). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.06; H, 7.39.

(8) (a) Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1978**, *162*, 37−44. (b) Gambaro, A.; Marton, D.; Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1981**, *204*, 191−196.

(9) We previously reported the allylation of carbonyls with diallyldibutyltin in the presence of chlorotrimethylsilane. The formation of a stable Si−O bond from Sn−O caused the shift of equilibrium to the product, homoallyl silyl ethers, in excellent yields: Yasuda, M.; Fujibayashi, T.; Shibata, I.; Baba, A.; Matsuda, H.; Sonoda, N. *Chem. Lett.* **1995**, 167−168.

(10) Naruta, Y.; Ushida, S.; Maruyama, K. *Chem. Lett.* **1979**, 919−922 and references therein.

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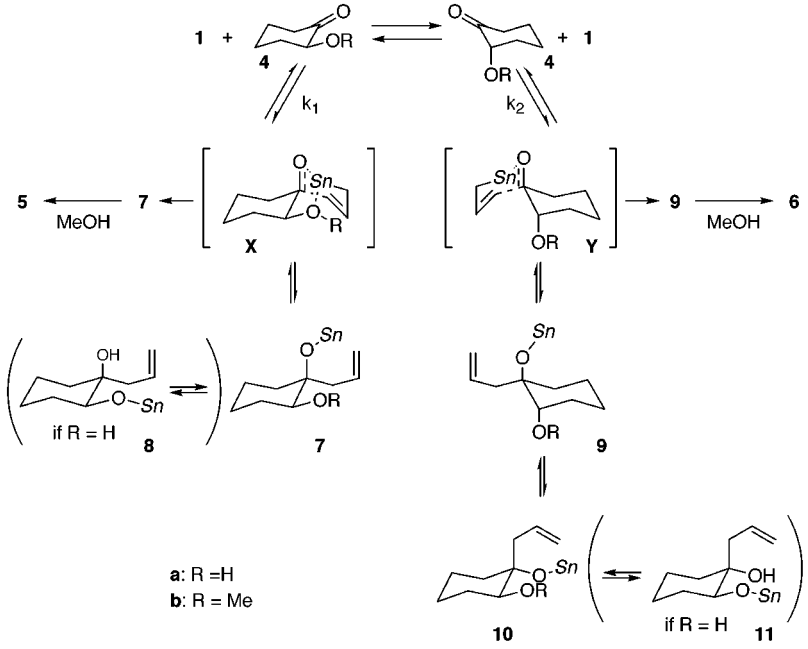
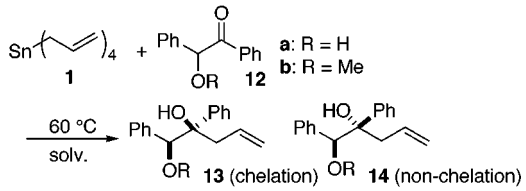
(12) Sato, K.; Kira, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 6429−6431.

(13) Fishwick, M.; Wallbridge, G. H. *J. Organomet. Chem.* **1970**, *25*, 69−79.

Scheme 2

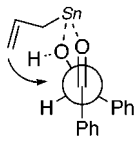


Scheme 3



				13 : 14
toluene	**a:** R = H	20 h	78 %	(90 : 10)
	b: R = Me	72 h	21 %	(80 : 20)
MeOH	**a:** R = H	1 h	>99 %	(>99 : < 1)
	b: R = Me	5 h	70 %	(74 : 26)

Scheme 4



1-(2-Methoxyphenyl)-3-buten-1-ol (3d): bp 75 °C/ 3 mmHg; IR (neat) 3300, 1600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−6.87 (m, 4H), 5.85 (ddt, J = 17.09, 10.26, 7.08 Hz, 1H), 5.14 (d, J = 17.09 Hz, 1H), 5.10 (d, J = 10.26 Hz, 1H), 4.96 (br, 1H), 3.86 (s, 3H), 2.63−2.47 (m, 3H); ^{13}C NMR (22.6 MHz, $CDCl_3$) δ 156.12, 135.05, 131.76, 128.04, 126.58, 120.51, 117.22, 110.29, 69.32, 55.14, 41.81; MS m/z 178 (M^+); HRMS calcd for $C_{11}H_{14}O_2$ 178.0994, found m/z 178.0977 (M^+).

1-(3-Methoxyphenyl)-3-buten-1-ol (3e): bp 90 °C/ 3 mmHg; IR (neat) 3400, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29−7.24 (m, 1H), 6.95−6.93 (m, 2H), 6.84−6.80 (m, 1H), 5.81 (ddt, J = 17.09, 10.25, 7.08 Hz, 1H), 5.20−5.13 (m, 2H), 4.72 (dd, J = 7.81, 4.88 Hz, 1H), 3.82 (s, 3H), 2.57−2.44 (m, 2H), 2.04 (br, 1H); ^{13}C NMR (22.6 MHz, $CDCl_3$) δ 159.51, 145.54, 134.35, 129.23, 118.01, 118.01, 112.86, 111.27, 73.19, 55.11, 43.64; MS m/z 178 (M^+); HRMS calcd for $C_{11}H_{14}O_2$ 178.0994, found m/z 178.1001 (M^+).

(1*S,2*S**)-1-Allylcyclohexane-1,2-diol (5a):** mp 75 °C; IR (KBr) 3420, 3300, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.90 (ddt, J = 16.85, 10.63, 7.70 Hz, 1H), 5.15 (d, J = 10.62 Hz, 1H), 5.14 (d, J = 16.85 Hz, 1H), 3.45 (dd, J = 9.35, 3.85 Hz, 1H), 2.40 (ddt, J = 13.56, 7.69, 1.10 Hz, 1H), 2.29 (ddt, J = 13.56, 7.69, 1.10 Hz, 1H), 1.94 (br, 2H), 1.77−1.23 (m, 8H); NOE was observed at allylmethylene protons when 2-H was irradiated.; ^{13}C NMR (22.6 MHz, $CDCl_3$) δ 133.77, 118.37, 73.19, 73.04, 43.58, 34.22, 30.32, 23.31, 21.08; MS m/z 156 (M^+); HRMS calcd for $C_9H_{16}O_2$ 156.1150, found m/z 156.1151 (M^+). Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.88; H, 10.31.

(1*R,2*S**)-1-Allylcyclohexane-1,2-diol (6a).** This minor product is analyzed by selected NMR signals. ^1H NMR (400 MHz, $CDCl_3$) δ 5.96−5.85 (m, 1H), 5.22−5.16 (m, 2H), 3.59 (dd, J = 9.77, 4.40 Hz, 1H).

(1*S,2*S**)-1-Allyl-2-methoxycyclohexan-1-ol (5b):** bp 100 °C/ 12 mmHg; IR (neat) 3450, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.96−5.82 (m, 1H), 5.16−5.08 (m, 2H), 3.37 (s, 3H), 3.01 (dd, J = 8.79, 3.91 Hz, 1H), 2.43−2.22 (m, 2H), 2.08 (br, 1H), 1.91−1.17 (m, 8H); ^{13}C NMR (22.6 MHz, $CDCl_3$) δ 134.05, 117.28, 81.85, 72.76, 56.30, 43.40, 34.22, 25.11, 22.73, 21.20; MS m/z 170 (M^+); HRMS calcd for $C_{10}H_{18}O_2$ 170.1307, found m/z 170.1297 (M^+). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.31; H, 10.69.

(1*R,2*S**)-1-Allyl-2-methoxycyclohexan-1-ol (6b).** This minor product is analyzed by selected NMR signals: ^1H NMR (400 MHz, $CDCl_3$) δ 5.10−5.03 (m, 2H), 3.08 (dd, J = 8.30, 3.42 Hz, 1H); ^{13}C NMR (22.6 MHz, $CDCl_3$) δ 134.71, 117.98, 84.07, 73.19, 56.66, 39.31, 33.80, 25.11, 22.03, 21.63.

(1*S,2*R**)-1,2-Diphenyl-4-pentene-1,2-diol (13a):** mp 96−97 °C; IR (KBr) 3450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25−6.95 (m, 10H), 5.63−5.52 (m, 1H), 5.19−5.08 (m, 2H), 4.81 (d, J = 4.40 Hz, 1H), 2.96 (dd, J = 14.16, 5.86 Hz, 1H), 2.78 (dd, J = 14.16, 8.79 Hz, 1H), 2.71 (d, J = 4.40 Hz, 1H), 2.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.45, 139.34, 133.27, 127.74, 127.47, 127.32, 126.75, 126.49, 119.49, 80.29, 78.32, 42.44; MS m/z 237 (M^+ − 17). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 79.89; H, 7.16. The relative configuration was determined by X-ray analysis (see Supporting Information).

(1*S,2*S**)-1,2-Diphenyl-4-pentene-1,2-diol (14a).** This minor product is analyzed by selected NMR signals: ^1H NMR (400 MHz, $CDCl_3$) δ 5.73 (ddt, J = 17.09, 10.25, 7.32 Hz, 1H), 5.13−4.99 (m, 2H), 4.81 (d, J = 4.40 Hz, 1H), 3.13 (dd, J = 13.67, 7.32 Hz, 1H), 2.97 (dd, J = 13.67, 7.32 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.63, 138.73, 133.27, 120.19, 81.37, 78.43, 43.85.

(1*S,2*R**)-1-Methoxy-1,2-diphenyl-4-penten-2-ol (13b):** mp 47 °C; IR (KBr) 3500, 1640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25−6.95 (m, 10H), 5.63 (dddd, J = 17.09, 10.25, 7.57, 6.60 Hz, 1H), 5.10 (d, J = 17.09 Hz, 1H), 5.02 (d, J = 10.25 Hz, 1H), 4.29 (s, 1H), 3.25 (s, 3H), 2.91−2.81 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.99, 136.65, 133.67, 128.49, 128.37, 127.47, 127.27, 126.64, 126.40, 118.35, 89.51, 78.04, 57.24, 42.64; MS m/z 227 (M^+ − 41); HRMS calcd for $C_{18}H_{20}O_2$ 269.1533, found m/z 269.1541 (M^+ + 1). Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51.

Found: C, 80.30; H, 7.55. The relative configuration was determined by X-ray analysis (see Supporting Information).

(1*S,2*S**)-1-Methoxy-1,2-diphenyl-4-penten-2-ol (14b).** This minor product is analyzed by selected NMR signals: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (dddd, J = 17.09, 10.25, 7.56, 6.35 Hz, 1H), 5.01 (d, J = 17.09 Hz, 1H), 4.98 (d, J = 10.25 Hz, 1H), 4.28 (s, 1H), 3.22 (s, 3H), 2.91 (br, 1H), 2.68 (dd, J = 14.16, 6.35 Hz, 1H), 2.56 (dd, J = 14.16, 7.56 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.99, 136.65, 133.67, 128.49, 128.37, 127.47, 127.27, 126.64, 126.40, 118.35, 89.51, 78.04, 57.24, 42.64.

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Supporting Information Available: Details of X-ray sturcture analyses of compounds **13a** and **13b** (36 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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