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Enantioselective Synthesis of the Optically Active α-Methylene-β-hydroxy Esters, Equivalent Compounds to Morita−Baylis−Hillman Adducts, Using Successive Asymmetric Aldol Reaction and Oxidative Deselenization

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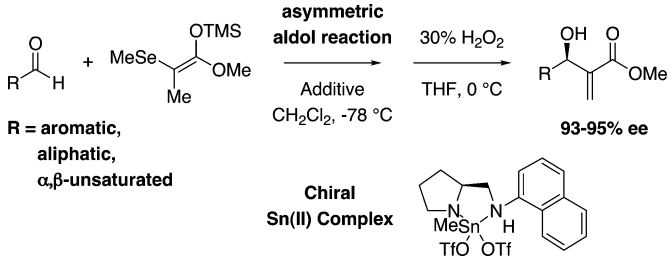

The asymmetric aldol reaction of a tetra-substituted ketene silyl acetal including an alkylseleno group with aldehydes has been developed by the promotion of $Sn(OTf)_2$ coordinated with a chiral diamine to afford the corresponding aldols having chiral quaternary centers at the α-positions. The facile oxidative deselenization of these aldol compounds produces optically active α-methylene-β-hydroxy esters which correspond to adducts prepared by the asymmetric Morita−Baylis−Hillman reaction.

Introduction

Optically active α-methylene-β-hydroxy esters are frequently employed for the synthesis of natural complicated molecules because these compounds simultaneously include both useful α,β-unsaturated ester moieties and asymmetric allylic alcohol systems. One of the most powerful methods for the synthesis of α-methylene-β-hydroxy esters is the reaction of α,β-unsaturated esters with aldehydes promoted by bases, the so-called Morita−Baylis−Hillman reaction;[1] however, there are limitations for the asymmetric version concerning chemical yields and generality of the substrates. On the other hand, several other approaches for the preparation of α-methylene-β-hydroxy esters have been developed, such as the nucleophilic addition of alkenylmetallic species to aldehydes[2] or an aldol reaction of a sulfur-substituted enolate with aldehydes followed by successive elimination of the α-alkylthio group in the intermediates.[3] Furthermore, an alternative method for the synthesis of optically active Morita−Baylis−Hillman adducts had been investigated via a sequential approach combining the Michael addition of chalcogens to α,β-unsaturated esters and consecutive diastereoselective aldol reactions of the generated enolates with aldehydes.[4]

Recently, an asymmetric aldol reaction of a tetra-substituted ketene silyl acetal with achiral aldehydes has been developed by our group and this method was applied to the synthesis of various optically active β-hydroxy

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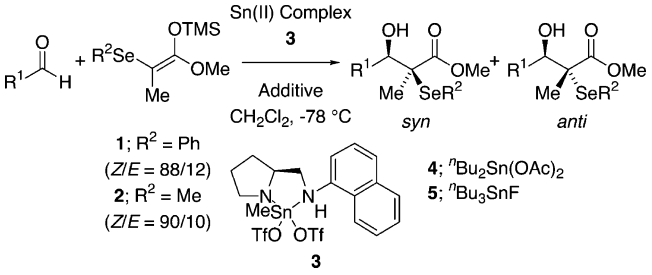
TABLE 1. Synthesis of the Optically Active α-Alkylseleno-β-hydroxy Esters Using Chiral Sn(II) Lewis Acid



entry	R^1	R^2	additive	yield[a]/%	*syn*/*anti*	ee/% (*syn*)
1	Ph	Ph	**4**	54	86/14	92
2	$Ph(CH_2)_2$	Ph	**4**	12	62/38	48
3	Ph	Me	**4**	86	92/8	93
4	Ph	Me	**5**	70	87/13	86
5	$Ph(CH_2)_2$	Me	**4**	55	77/23	75
6	$Ph(CH_2)_2$	Me	**5**	39	86/14	94

[a] Combined yield of the isolated *syn*- and *anti*-isomers.

esters having chiral quaternary centers at the α-positions.[5] This successful result prompted us to explore a new way to produce optically active α-methylene-β-hydroxy esters which correspond to adducts prepared by the asymmetric Morita−Baylis−Hillman reaction. Here, we report a new method for the synthesis of optically active α-methylene-β-hydroxy esters using the successive combination of the asymmetric aldol reaction[6] of tetrasubstituted ketene silyl acetal including alkylseleno group with aldehydes and facile oxidative deselenization.

Results and Discussion

First, a stereoisomeric mixture of ketene silyl acetal **1** (KSA **1**) was prepared from methyl 2-phenylselenopropanoate by treatment with LDA and chlorotrimethylsilane according to a similar procedure reported by Guindon et al.[7] The asymmetric aldol reaction of **1** with benzaldehyde in the presence of di-*n*-butyltin diacetate (**4**) and a Sn(II) complex **3** generated in situ from Sn(OTf)$_2$ with chiral diamine gave the corresponding *syn*-aldol adduct with high diastereo- and enantioselectivities (see Table 1, entry 1). However, the reactivity of **1** is not sufficient and an unsatisfactory yield was attained in the reactions of **1** with an aliphatic aldehyde (entry 2). Therefore, the newly designed KSA **2** was prepared from methyl 2-methylselenopropanoate under conditions similar to those used for the preparation of **1**. Because the yield of the asymmetric aldol reaction of **2** with benzaldehyde increased without loss of the optical purity of the aldol adduct (entry 3), a further examination was carried out using **2** instead of **1**. Use of the additive **4** gave a fairly good yield and stereoselectivities as shown in entry 3, although it was found that the tri-*n*-butyltin fluoride (**5**) was not a suitable co-reagent for the reaction of the aromatic aldehyde (entry 4). On the other hand, better stereoselectivities were observed for the reaction of 3-phenylpropanal, an aliphatic aldehyde, by promotion of the Sn(II) complex **3** combined with the Sn(IV) compound **5** (entry 6).

SCHEME 1. Determination of the Relative Stereochemistry of the Aldol Adducts

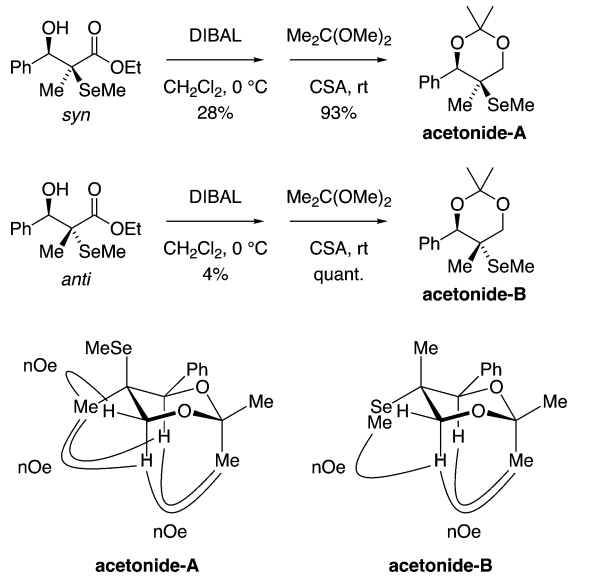
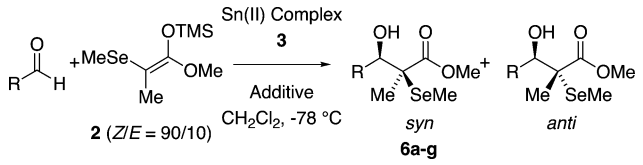


TABLE 2. Synthesis of a Variety of Optically Active α-Alkylseleno-β-hydroxy Esters Using Chiral Sn(II) Lewis Acid



entry	R	additive	yield[a]/%	*syn*/*anti*	adduct	ee/%
1	Ph	**4**	86	92/8	**6a**	93
2	4-MeC_6H_4	**4**	88	92/8	**6b**	93
3	4-$MeOC_6H_4$	**4**	80	96/4	**6c**	95
4	4-ClC_6H_4	**4**	94	93/7	**6d**	95
5	$PhCH_2CH_2$	**5**	39	86/14	**6e**	93
6	$CH_3(CH_2)_6$	**5**	66	89/11	**6f**	90
7	(*E*)-PhCH=CH	**4**	66	95/5	**6g**	94
8	(*E*)-CH_3CH=CH	**4**	85	94/6	**6h**	94

[a] Combined yield of the isolated *syn*- and *anti*-isomers.

Relative stereochemistry of the aldol adducts was determined as follows. The ester group of each stereoisomer was reduced by DIBAL to give the corresponding 1,3-diol, which was converted to **acetonide-A** or **-B**. As depicted in Scheme 1, the NOE experiment of **acetonide-A** and **-B** showed that major aldol product has syn configuration and the other has anti configuration.

Examples of the optically active *syn*-aldols prepared by the present protocol are listed in Table 2. The reaction of **2** with aromatic aldehydes (entries 1−4) and α,β-unsaturated aldehydes (entries 7 and 8) smoothly proceeded at −78 °C in the presence of the chiral Sn(II)

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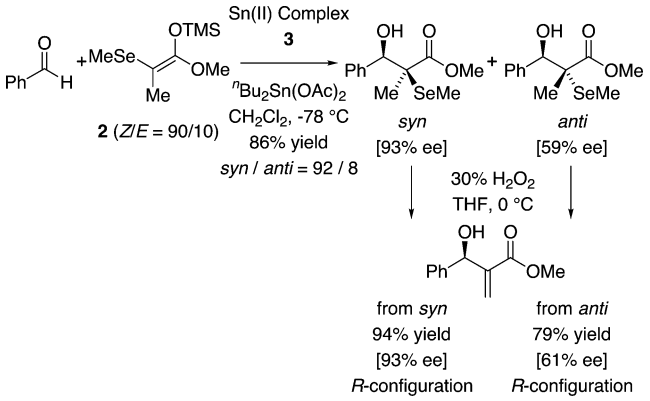
SCHEME 2. Synthesis of the Optically Active α-Methylene-β-hydroxy Esters via α-Alkylseleno-β-hydroxy Esters Using Oxidative Deselenization



Lewis acid to give the desired aldols in good yields with high stereoselectivities. Although the chemical yields were moderate when aliphatic aldehydes were used as shown in entries 5 and 6, the desired *syn*-aldols were obtained with satisfactorily high enantioselectivities.

Next, the conversion of the formed aldol adducts to the corresponding α-methylene-β-hydroxy esters was examined. When the *syn*- and *anti*-aldols derived from benzaldehyde with KSA **2** were treated with H_2O_2 in THF at 0 °C,[8] the desired deselenization rapidly proceeded to afford the eliminated compounds regioselectively as shown in Scheme 2. Since the HPLC analysis revealed that these α,β-unsaturated esters have an identical *R*-configuration at the C3 position, the same enantioface-selectivity of the benzaldehyde was observed for producing both diastereomers in this asymmetric aldol reaction. Based on the HPLC analysis for the other aldol adduct couples, it was found that all of the other C3 configurations of the *syn*- and *anti*-aldols are also identical.

The right column in Table 3 shows the yields and ee's of a variety of α-methylene-β-hydroxy esters formed by deselenization (method A). The yields and ee's of the corresponding *syn*-aldols generated by the asymmetric aldol reaction are listed in the left column as supplementary data. The optical purity of the aldol adducts remains in all cases to give the desired Morita−Baylis−Hillman type compounds. Recently, several asymmetric Morita−Baylis−Hillman reactions were developed to produce the optically active coupling products with good to excellent ees,[1f,g] however, a long period of reaction time is required for the synthesis of certain adducts, such as the ones derived from aromatic or α,β-unsaturated aldehydes. On the other hand, it is noted that our new protocol provides a wide generality to produce the optically active α-methylene-β-hydroxy esters from all types of aldehydes including aromatic, aliphatic, and α,β-unsaturated aldehydes.

Because both C3 configurations of the major enantiomers of *syn*- and *anti*-aldols are identical, shown in Scheme 2, a more convenient method for the preparation of α-methylene-β-hydroxy esters was investigated (Table 4, method B); that is, mixtures of diastereomeric isomers are directly converted to the desired olefins without separation of the intermediates, which have similar polarity after step **I**. This facile protocol could dispense chromatographic separation of the stereoisomers and the ee's of the final products, Morita−Baylis−Hillman-type adducts, are kept at a satisfactory level in all cases as listed in the right column (ca. 90%).

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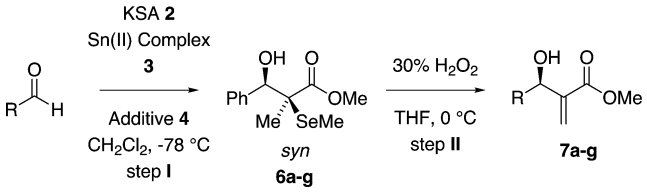
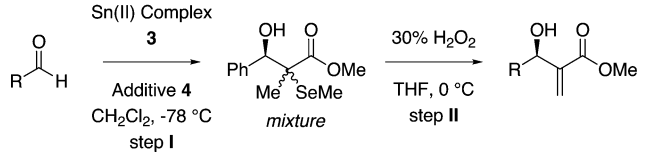
TABLE 3. Synthesis of a Variety of Optically Active α-Methylene-β-hydroxy Esters via α-Alkylseleno-β-hydroxy Esters Using Oxidative Deselenization (Method A)



		step **I**		step **II**		
entry	R	yield[a]/%	ee/%	yield[b]/%	olefin	ee/%
1	Ph	79	93	94	**7a**	93
2	4-MeC_6H_4	81	93	81	**7b**	94
3	4-$MeOC_6H_4$	77	95	69	**7c**	95
4	4-ClC_6H_4	87	95	83	**7d**	95
5[c]	$CH_3(CH_2)_6$	59	90	88	**7f**	95
6	(*E*)-PhCH=CH	63	94	86	**7g**	95
7	(*E*)-CH_3CH=CH	80	94	64	**7h**	95

[a] Isolated yield of *syn*-aldol. [b] Isolated yield. [c] Tri-*n*-butyltin fluoride (**5**) was used as an additive.

TABLE 4. Synthesis of a Variety of Optically Active α-Methylene-β-hydroxy Esters via α-Alkylseleno-β-hydroxy Esters Using Oxidative Deselenization without Separation of the Diastereomeric Aldol Isomers (Method B)



		step **I**		step **II**		
entry	R	yield[a]/%	*syn*/*anti*	yield[b]/%	olefin	ee/%
1	Ph	85	92/8	87	**7a**	90
2	4-MeC_6H_4	84	92/8	86	**7b**	86
3	4-$MeOC_6H_4$	83	97/3	86	**7c**	94
4	4-ClC_6H_4	89	90/10	76	**7d**	88
5[c]	$PhCH_2CH_2$	42	80/20	90	**7e**	82
6	(*E*)-PhCH=CH	78	95/5	81	**7g**	86
7	(*E*)-CH_3CH=CH	70	96/4	69	**7h**	92

[a] Combined yield of the mixture of *syn*- and *anti*-isomers. [b] Isolated yield. [c] Tri-*n*-butyltin fluoride (**5**) was used as an additive.

Conclusion

A new method for the synthesis of optically active α-methylene-β-hydroxy esters was established using the consecutive combination of the asymmetric aldol reaction of a tetra-substituted ketene silyl acetal including an alkylseleno group with aldehydes and the facile oxidative deselenization. This protocol provides another way for producing chiral Morita−Baylis−Hillman adducts with high ee's, and the wide range of the substrate generality

of this reaction could be applied to the synthesis of many kinds of α-methylene-β-hydroxy esters having aromatic, aliphatic and alkenyl substituents on the β-positions.

Experimental Section

General Information. ^{1}H and ^{13}C NMR spectra were recorded with chloroform (in chloroform-*d*) or benzene (in benzene-d_6) as an internal standard. Thin-layer chromatography was performed on Wakogel B5F. The asymmetric aldol reaction was carried out under argon atmosphere in dried glassware. Dichloromethane was distilled from diphosphorus pentoxide, then calcium hydride, and dried over MS 4 Å.

1-Methoxy-2-methylseleno-1-(trimethylsiloxy)propene (2). To a solution of diisopropylamine (1.8 mL, 12.8 mmol) in THF (15 mL) at 0 °C was added *n*-butyllithium in hexane (1.66 M, 7.8 mL, 12.9 mmol). After the reaction mixture was stirred for 30 min at 0 °C, a solution of methyl 2-methylselenopropanoate (2.13 g, 11.8 mmol) in THF (10 mL) was added at −78 °C. The reaction mixture was stirred for 1 h at −78 °C and then chlorotrimethylsilane (3.0 mL, 23.7 mmol) was added. After the reaction mixture was stirred for 1 h at room temperature, it was concentrated by evaporation of the solvent. Petroleum ether was added to the residue, and the suspension was filtered through a small pad of Celite under argon atmosphere. After evaporation of the solvent, the crude product was purified by distillation to afford a mixture of KSA **2** (*Z*/*E* = 90/10, 2.22 g, 75%) as a pale yellow oil: bp 31 °C/0.4 mmHg. IR (neat): 1724, 1655, 1439, 1252, 1221, 1178, 1132, 1097, 901, 843 cm^{-1}. HR MS: calcd for $C_8H_{18}O_2SiSe$ (M + H$^+$) 254.0241, found 254.0240.

(*Z*)-1-Methoxy-2-methylseleno-1-(trimethylsiloxy)propene (*Z*-2). ^{1}H NMR (C_6D_6): δ 3.30 (s, 3H), 2.13 (s, 3H), 1.87 (s, 3H), 0.30 (s, 9H). ^{13}C NMR (C_6D_6): δ 152.8, 84.0, 56.0, 17.4, 4.5, 0.2.

Typical Procedure for the Synthesis of an Optically Active α-Methylene-β-hydroxy Ester Using Asymmetric Aldol Reaction and Successive Deselenization (Method A, Table 1, Entry 3; Table 2, Entry 1; Table 3, Entry 1; 86% combined yield, *syn*/*anti* = 92/8). Step I. To $Sn(OTf)_2$ (217.4 mg, 0.516 mmol) were added solutions of (*S*)-1-methyl-2-(1-naphthylaminomethyl)pyrrolidine (143.1 mg, 0.615 mmol) in CH_2Cl_2 (1.1 mL) and $^nBu_2Sn(OAc)_2$ (197.2 mg, 0.556 mmol) in CH_2Cl_2 (1.1 mL), respectively. The mixture was stirred for 5 min at room temperature, and then was cooled to −78 °C. To the reaction mixture were added solutions of KSA **2** (123.5 mg, 0.511 mmol) in CH_2Cl_2 (1.1 mL) and benzaldehyde (48.0 mg, 0.452 mmol) in CH_2Cl_2 (1.27 mL) at −78 °C, successively. The mixture was further stirred for 1 h, and then quenched with saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (three times). The combined organic layer was washed with water and brine, and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by preparative TLC on silica gel to afford methyl (2*S*,3*R*)-3-hydroxy-2-methyl-2-methylseleno-3-phenylpropanoate (**6a**) (102.8 mg, 79%, 93% ee) and its *anti*-(2*R*,3*R*)-isomer (9.0 mg, 7%, 59% ee).

Methyl (2*S*,3*R*)-3-Hydroxy-2-methyl-2-methylseleno-3-phenylpropanoate (6a). HPLC (CHIRALCEL AS, *i*-PrOH/hexane = 1/9, flow rate = 1.0 mL/min): t_R = 6.1 min (3.4%), t_R = 7.0 min (96.6%). IR (neat): 3479, 1716 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.40−7.23 (m, 5H), 5.16 (s, 1H), 3.70 (s, 3H), 3.28 (br s, 1H), 2.16 (s, 3H), 1.32 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 172.9, 137.8, 127.9, 127.9, 127.7, 73.2, 52.5, 52.2, 16.4, 4.6. HR MS: calcd for $C_{12}H_{16}O_3SeNa$ (M + Na$^+$) 311.0163, found 311.0160.

Methyl (2*R*,3*R*)-3-Hydroxy-2-methyl-2-methylseleno-3-phenylpropanoate. HPLC (CHIRALCEL AS, *i*-PrOH/hexane = 1/9, flow rate = 1.0 mL/min): t_R = 8.8 min (20.6%), t_R = 10.4 min (79.4%). ^{1}H NMR ($CDCl_3$): δ 7.40−7.25 (m, 5H), 5.13 (s, 1H), 3.74 (s, 3H), 3.47 (br s, 1H), 1.96 (s, 3H), 1.43 (s, 3H).

Step II. To a solution of pure *syn*-α-methyl-α-methylseleno-β-hydroxy ester (18.5 mg, 64.4 μmol) in THF (0.64 mL) at 0 °C was added a 30% aqueous solution of hydrogen peroxide (6.0 μL, 77 μmol). The mixture was stirred for 2 h at room temperature, and then quenched with saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with diethyl ether (three times). The combined organic layer was washed with water and brine, and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by preparative TLC on silica gel to afford methyl (*R*)-3-hydroxy-2-methylene-3-phenylpropanoate (**7a**) (11.6 mg, 94%, 93% ee).

Methyl (*R*)-3-Hydroxy-2-methylene-3-phenylpropanoate (7a).[1f,9] HPLC (CHIRALCEL AS, *i*-PrOH/hexane = 1/9, flow rate = 0.5 mL/min): t_R(*R*) = 14.5 min (96.7%), t_R(*S*) = 23.4 min (3.3%). $[\alpha]^{20}_D$ = −110 (*c* 0.947, MeOH). ^{1}H NMR ($CDCl_3$): δ 7.40−7.25 (m, 5H), 6.34 (dd, *J* = 1.0, 0.7 Hz, 1H), 5.84 (dd, *J* = 1.3, 1.0 Hz, 1H), 5.53 (dd, *J* = 1.3, 0.7 Hz, 1H), 3.72 (s, 1H), 3.00 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 166.7, 141.9, 141.2, 128.4, 127.8, 126.5, 126.1, 73.2, 51.9.

Typical Procedure for the Synthesis of an Optically Active α-Methylene-β-hydroxy Ester Using Asymmetric Aldol Reaction and Successive Deselenization (Method B, Table 4, Entry 1; 85% combined yield, *syn*/*anti* = 92/8). Step I. To $Sn(OTf)_2$ (100.5 mg, 0.241 mmol) were added solutions of (*S*)-1-methyl-2-(1-naphthylaminomethyl)pyrrolidine (74.0 mg, 0.308 mmol) in CH_2Cl_2 (0.5 mL) and $^nBu_2Sn(OAc)_2$ (92.0 mg, 0.262 mmol) in CH_2Cl_2 (0.5 mL), respectively. The mixture was stirred for 5 min at room temperature, and then was cooled to −78 °C. To the reaction mixture were added solutions of KSA **2** (65.0 mg, 0.257 mmol) in CH_2Cl_2 (0.5 mL) and benzaldehyde (22.8 mg, 0.215 mmol) in CH_2Cl_2 (0.5 mL) at −78 °C, successively. The mixture was further stirred for 1 h, and then quenched with saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (three times). The combined organic layer was washed with water and brine, and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by preparative TLC on silica gel to afford a mixture of methyl (2*S*,3*R*)-3-hydroxy-2-methyl-2-methylseleno-3-phenylpropanoate (**6a**) and its *anti*-(2*R*,3*R*)-isomer (52.4 mg, 85%, syn/anti = 92/8).

Step II. To a solution of the mixture of *syn*-α-methyl-α-methylseleno-β-hydroxy ester (**6a**) and its *anti*-(2*R*,3*R*)-isomer (26.5 mg, 92.3 μmol) in THF (1.85 mL) at 0 °C was added a 30% aqueous solution of hydrogen peroxide (10.0 μL, 129 μmol). The mixture was stirred for 3 h at room temperature, and then quenched with saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with diethyl ether (three times). The combined organic layer was washed with water and brine, and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by preparative TLC on silica gel to afford methyl (*R*)-3-hydroxy-2-methylene-3-phenylpropanoate (**7a**) (15.4 mg, 87%, 90% ee).

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Supporting Information Available: Spectra for products **6b**−**6h** and **7b**−**7h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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