Catalytic Asymmetric Aldol-Type Reactions Using a Chiral (Acyloxy)borane Complex

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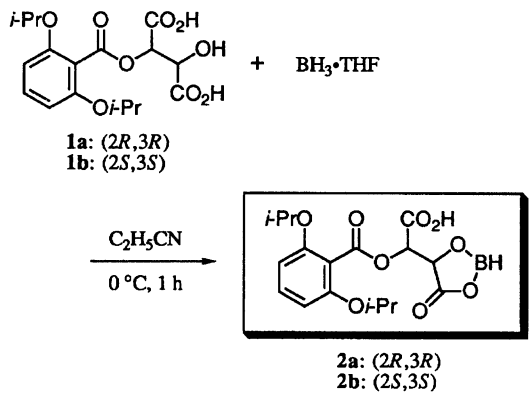
In the presence of 20 mol% of a chiral (acyloxy)borane (CAB) complex prepared from BH_3·THF and a chiral mono-*O*-acylated tartaric acid, achiral silyl enol ethers or ketene silyl acetals react with achiral aldehydes to afford the corresponding aldol-type adducts in good yields with high enantio- and diastereoselectivities. Furthermore, the reactivity of aldol-type reactions can be improved without reducing the enantioselectivity by use of 10—20 mol% of the CAB complex prepared from 3,5-bis(trifluoromethyl)phenylboronic acid and chiral tartaric acid derivative. The enantioselectivity can also be improved without reducing the chemical yield by use of 20 mol% of the CAB complex prepared from *o*-phenoxyphenylboronic acid and chiral tartaric acid derivative. The observed *erythro* selectivities and *re*-face attack of nucleophiles on carbonyl carbon of aldehydes imply that the extended transition state model is applicable.

The development of chiral catalysts that mediate the asymmetric aldol condensations in a highly stereocontrolled and truly catalytic manner has been a challenging goal in synthetic organic chemistry. Although much fascinating chemistry has been devoted to this problem, which provided excellent methods for chirality transfer from chiral substrates or auxiliaries to prochiral molecules, it has not led to an ultimate means of propagating chirality with a nonstoichiometric amount of a chiral source, except in a few special cases.[1] Recent research in our group has led to the development of a chiral (acyloxy)borane (CAB) complex as a Lewis acid catalyst for highly enantioselective Diels–Alder,[2a,2c] hetero-Diels–Alder,[2e] and Sakurai–Hosomi allylation reactions.[2d] These results led to investigation of catalytic asymmetric aldol-type reactions of achiral silyl enol ethers or ketene silyl acetals with achiral aldehydes. We now report a successful solution to this problem.[3]

Results and Discussion

Our method uses a CAB complex as a Lewis acid catalyst for the Mukaiyama condensation of simple chiral enol silyl ethers of ketones with various aldehydes.[4] This CAB-catalyzed aldol process allows the formation of adducts in a highly diastereo- and enantioselective manner (up to 96% ee)under mild reaction conditions. Furthermore, the reactions are catalytic, so that only 20 mol% of catalyst is needed for efficient conversions, and the chiral source is recoverable and reusable.

Chiral (acyloxy)borane complex **2** was easily prepared *in situ* from tartaric acid derivative **1** and BH_3·THF complex in propionitrile solution at 0 °C (Scheme 1). The aldol reactions of ketone enol silyl ethers with aldehydes were promoted by 20 mol% of this catalyst solution at low temperature. The use of 10 mol% catalyst for the reaction resulted in a significantly decreased reactivity. After the usual workup, the crude product mixture (mostly silylated β-hydroxy ketones) was treated with diluted hydrochloric acid to

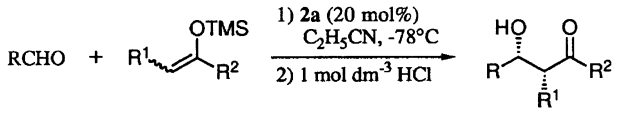


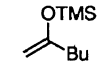
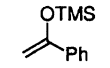
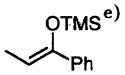
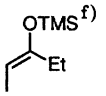
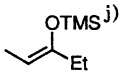
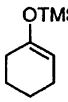
Scheme 1.

afford desilylated aldol adducts. Diastereomer ratios of product were determined by analytical HPLC and ^{1}H NMR spectroscopy of the adducts and/or the corresponding (+)/(−)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA) esters. The stereochemical assignments (relative stereochemistries) were made from analyses of the ^{1}H NMR spectra, and the absolute configurations were determined by comparison of the specific rotation values with those in the literature. Some results are summarized in Table 1.

The relative stereochemistry of the major adducts was assigned as *erythro*, and the selective approach of enol ethers from the *re*-face of the aldehyde carbonyl carbon was confirmed in cases where a natural tartaric acid derivative **1a** was used as a Lewis acid ligand. The use of an unnatural form of tartaric acid as a chiral source afforded the other enantiomer as expected (Entry 8). Almost perfect asymmetric inductions were achieved in the *erythro* adducts, reaching 96% ee, although a slight reduction in both the enantio- and diastereoselectivities was observed in the reactions with saturated aldehydes. It is noteworthy that, regardless of the stereochemistry (*E* or *Z*) of starting enol silyl ethers generated from ethyl ketones, *erythro* aldols were highly selectively obtained in the present reactions.[5]

Table 1. CAB-Catalyzed Asymmetric Aldol Reactions of Ketone Sily Ethers with Aldehydes[a)]



Entry	RCHO	Silyl ether	Yield[b)] (%)	*erythro* /*threo*	ee (%)[c)] (config)
1	PhCHO		81	—	85 (*R*)
2	C_4H_9CHO		70	—	80
3	PhCHO		98	—	85 (*R*)
4	PhCH=CHCHO[d)]		88	—	83
5	PhCHO		86	95/ 5	95
6	C_3H_7CHO		62	88/12	80
7	PhCHO		96	94 /6	96 (*R*)
8[g)]			99	94/6	96 (*S*)
9[h)]			95	88/12	90 (*R*)
10[i)]			55	82/18	77 (*R*)
11	$CH_3CH=CHCHO$[d)]		79	>94/ 6	93 (*R*)
12	C_3H_7CHO		61	80/20	88 (*S*)
13	PhCHO		97	93/ 7	94 (*R*)
14	PhCHO		57	>95/ 5	>95

a) Unless otherwise noted, the reaction was carried out in freshly distilled propionitrile using 20 mol% of catalyst **2a** and 1.2 equiv of the ketone silyl ether per aldehyde at −78 °C. b) Isolated yield by column chromatography for the *erythro*/*threo* mixture. c) The values correspond to the major diastereomers. Absolute configuration of the hydroxy group-attached carbon was indicated in parentheses. d) Trans isomer was used. e) Mixture of two isomers (E/Z=2/98). f) Mixture of two isomers (E/Z=4/1). g) **1b** was used as a ligand. h) Nitroethane was used as a solvent. i) Dichrolomethane was used as a solvent. j) Mixture of two isomers (E/Z=1/6).

The observed unprecedentedly high *erythro* selectivities together with their independence of the stereochemistry of silyl ethers in the CAB-catalyzed reactions are fully consistent with Noyori's TMSOTf-catalyzed aldol reactions of acetals, and thus may reflect the acyclic extended transition state mechanism postulated in the latter reactions (Fig. 1).[6)] It was of considerable interest to us that the diastereoselectivities of these reactions showed significant solvent dependency; thus, in CH_2Cl_2 (standard solvent for this type of reaction) the ratio dropped to 82/18 (Entry 10). The polar solvent should be beneficial for the polarized extended transition state model.[7)] Judging from the product configurations, CAB catalyst (from natural tartaric acid) should effectively cover the *si*-face of carbonyl on its coordination and the selective approach of nucleophiles from the *re*-face should result. The behavior is totally systematic and in good agreement with the results of previously reported

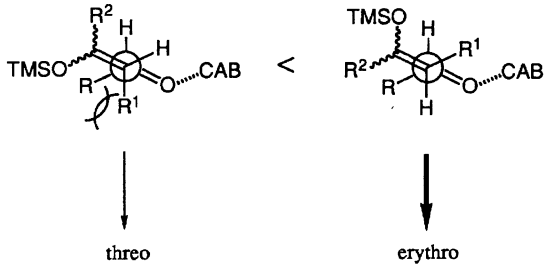


Fig. 1. Extended Transiton State Model.

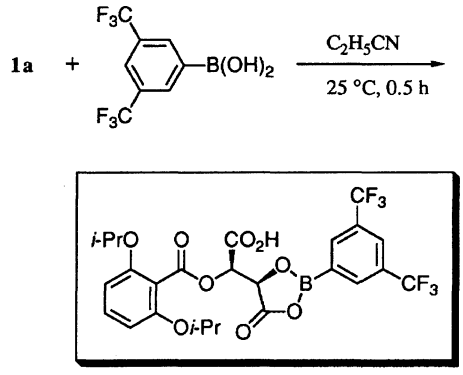
CAB-catalyzed Diels–Alder reactions.[2a—2c] It then follows that the sense of asymmetric induction of CAB-catalyzed reactions is the same for all aldehydes examined. Although the enol ethers derived from methyl ketones exhibited modest asymmetric induction (Entries 1—4), this reaction would be generally applicable to various ketone silyl ethers and aldehydes.

Next, several alkylboronic acids were exmined in place of BH_3·THF in order to improve the Lewis acidity of CAB and the stereoselectivity. The boron substituent of CAB was found to have strong influence on the chemical yield and the enantiomeric excess of aldol adduct, and 3,5-bis(trifluoromethyl)phenylboronic acid was most effective for the reactivity: when the complex which was easily prepared from tartaric acid derivative **1** and 3,5-bis(trifluoromethyl)phenylboronic acid in propionitrile at room temperature was employed, reactivity was improved without reducing the enantioselectivity (Scheme 2). For instance, the reaction of terminal trimethylsilyl enol ether derived from 2-hexanone with benzaldehyde in the presence of only 10 mol% CAB proceeded in 96% yield and enantiomeric excess of the product was 83%. Some of the results are listed in Table 2.

We also found that *o*-phenoxyphenylboronic acid was most effective for the asymmetric induction. Although lower levels of stereoregulation were exhibited in the reactions of terminal trimethylsilyl enol ethers with aldehydes catalyzed by the CAB **4a**, when the complex prepared from tartaric acid derivative **1** and *o*-phenoxyphenylboronic acid in propionitrile at room temperature was employed, enantioselectivity was improved without reducing chemical yield. Some results are listed in Table 3.

These arylboronic acids can be readily handled in air since they are air stable solid and do not react with oxygen. 3,5-Bis(trifluoromethyl)phenylboronic acid is commercially available and *o*-phenoxyphenylboronic acid can be easily prepared from trimethyl borate by reaction with *o*-phenoxyphenyllithium.

As an extension of this methodology, we next turned our attention to ketene silyl acetals derived from simple esters as nucleophile. The reactions of ketene silyl acetals with achiral aldehydes proceeded smoothly in propionitrile at low temperature promoted by 20 mol% of preformed CAB complex to afford *erythro* β-hydroxy esters in excellent chemical yields with modest to high diastereo- and enantioselectivities. Some results are listed in Table 4.



3a (2*R*, 3*R*)

Scheme 2.

One remarkable finding is the sensitivities of this reaction to the substituents on the starting ketene silyl acetals. Thus the reactions of silyl ketene acetals derived from ethyl esters were totally stereorandom giving a mixture of *erythro* and *threo* isomers in even ratios with moderate enantioselectivities. Benzyl esters also exhibited similar behaviors but somewhat improved chemical yields. In sharp contrast, the use of ketene silyl acetals generated from phenyl esters led to good diastero- and enantioselectivities with excellent chemical yields. The reason for this is not clear, but certain secondary interaction between electron rich ketene acetals derived from alkyl esters and Lewis acid may be responsible.[8]

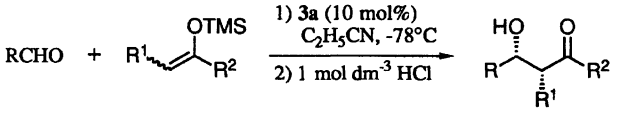
Analogous with the results of enol silyl ethers of ketones, unsubstituted ketene silyl acetals were found to exhibit lower levels of stereoregulation. On the other hand ketene silyl acetals derived from the propionate showed a high level of asymmetric induction. Reactions with aliphatic aldehydes, however, resulted in a slight reduction in optical and chemical yields. With ketene silyl acetals derived from phenyl ester *erythro* adducts predominated,[1a,9] but the selectivities were moderate in most cases in comparison with the reactions of silyl enol ethers. Exceptionally, α,β-unsaturated aldehydes revealed excellent diastereo- and enantioselectivities. The observed *erythro* selectivities and *re*-face attack of nucleophiles on carbonyl carbon of aldehydes are consistent with the aldol reactions of ketone enol silyl ethers, implying that the extended transition state model is also applicable to illustrate the stereochemistry of the present reactions.

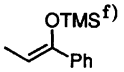
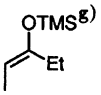
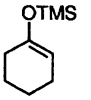
Experimental

General. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^{1}H NMR spectra were measured on a Varian Gemini-200 spectrometer and VXR 500. High performance liquid chromatography (HPLC) was done with Shimadzu 6A, 10A, and JASCO UVIDEC-100-II instruments using 4.6 mm×25 cm JASCO Finepak Sil column and Daicel chiral OD. Optical rotations were measured on a JASCO DIP-140 digital polarimeter. All experiments were carried out under an atmosphere of dry argon. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel E. Merck Art. 9385. Microanalyses were accomplished at the Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University.

In experminents requiring dry solvents, propionitrile is freshly distilled from calcium hydride, and ether and tetrahydrofuran (THF) are freshly distilled from sodium metal using benzophenone ketyl as indicator. Benzene and toluene are dried over sodium metal. Dichloromethane and *N*, *N*-dimethylformamide (DMF) are stored over 4A molecular sieves. Pyridine and triethylamine are stored over potassium hydroxide pellets. BH_3·THF is obtained from Toso-Akzo Chem. Co., Ltd., Japan. 3,5-Bis(trifluoromethyl)phenylboronic acid is purchased from Lancaster. Other simple

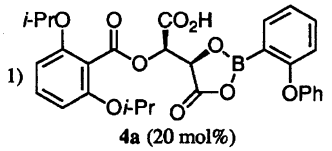
Table 2. CAB-Catalyzed Asymmetric Aldol Reactions of Ketone Silyl Ethers with Aldehydes[a]

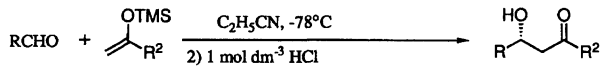


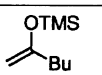
Entry	RCHO	Silyl ether	Yield[b] (%)	*erythro* /*threo*	ee (%)[c] (config)
1	PhCHO		96	—	83 (*R*)
2[d]	C_4H_9CHO		70	—	77
3	PhCHO		99	—	88 (*R*)
4	PhCH=CHCHO[e]		88	—	91
5	PhCHO		92	99/ 1	96
6[d]	C_3H_7CHO		55	94/ 6	80
7	PhCHO		81	91/ 9	95 (*R*)
8[d]	CH_3CH=CHCHO[e]		95	94/ 6	93 (*S*)
9[d]	PhCHO		83	>95/ 5	97

a) Unless otherwise noted, the reaction was carried out in freshly distilled propionitrile using 10 mol% of catalyst **3a** and 1.2 equiv of the ketone silyl ether per aldehyde at −78 °C. b) Isolated yield by column chromatography for the *erythro*/*threo* mixture. c) The values correspond to the major diastereomers. Absolute configuration of the hydroxy group-attached carbon was indicated in parentheses. d) 20 mol% of catalyst **3a** was used. e) Trans isomer was used. f) Mixture of two isomers (E/Z=2/98). g) Mixture of two isomers (E/Z=4/1).

Table 3. CAB-Catalyzed Asymmetric Aldol Reactions of Ketone Silyl Ethers with Aldehydes[a]





Entry	RCHO	Silyl ether	Yield[b] (%)	ee (%) (config)
1	PhCHO		91	88 (*R*)
2			93	91 (*R*)
3	PhCH=CHCHO[c]		93	94

a) Unless otherwise noted, the reaction was carried out in freshly distilled propionitrile using 20 mol% of catalyst **4a** and 1.2 equiv of the ketone silyl ether per aldehyde at −78 °C. b) Isolated yield by column chromatography. c) Trans isomer was used.

chemicals are purchased and used as such.

Preparation of Enol Silyl Ethers.[10] A solution of lithium diisopropylamide (LDA, 22 mmol) in THF (40 ml) was cooled to −78 °C and the corresponding ketone (20 mmol) was added dropwise over a few minutes. The solution was stirred for 30 min at that temperature and chlorotrimethylsilane (22 mmol) was added. This mixture was allowed to warm to room temparature over several hours. The white suspension was poured into saturated $NaHCO_3$ and extracted with hexane several times. The combined organic phase was dried over Na_2SO_4, concentrated with a rotary evaporator and the residue was distilled under reduced pressure.

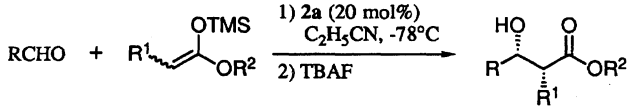
1-Phenyl-1-(trimethylsiloxy)ethylene: Obtained from Chisso Co., Ltd., Japan.

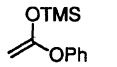
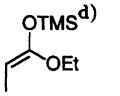
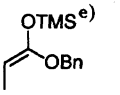
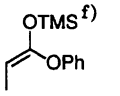
2-Trimethylsiloxy-1-hexene:[3f] (69% yield); ^{1}H NMR ($CDCl_3$) δ=0.17 (9H, s, $(CH_3)_3Si$), 0.87 (3H, t, J=7 Hz, CH_3), 1.19—1.49 (4H, m, $(CH_2)_2$), 1.98 (2H, t, J=7 Hz, CH_2CH_2C), 4.01 (2H, s, CH_2=CO).

(*Z*)-1-Phenyl-1-(trimethylsiloxy)propene:[11] (90% yield, E/Z=2/98); ^{1}H NMR ($CDCl_3$) δ=0.13 (9H, s, $(CH_3)_3Si$), 1.72 (3H, d, J=7 Hz, CH_3), 5.32 (1H, q, J=7 Hz, CH), 7.17—7.48 (m, 5H).

(*E*)-3-Trimethylsiloxy-2-pentene:[11] Lithium 2,2,6,6-tetramethylpiperidide (LTMP) was used instead of LDA (33% yield, E/Z=4/1). ^{1}H NMR ($CDCl_3$) δ=0.14 (9H, s, $(CH_3)_3Si$), 0.97 (3H, t, J=7 Hz, CH_3CH_2), 1.47 (3H, d,

Table 4. CAB-Catalyzed Asymmetric Aldol Reactions of Ketene Silyl Acetals with Aldehydes[a)]



Entry	RCHO	Silyl ether	Yield[b)] (%)	*erythro* /*threo*	ee (%)[c)] (config)
1	PhCHO		63	—	84(*R*)
2	C_3H_7CHO		49	—	76(*S*)
3	PhCHO		51	50/50	61/47
4			72	50/50	68(*R*)/57(*R*)
5			83	79/21	92(*R*)/ 6(*R*)
6[g)]			73	79/21	92(*S*)/ 3(*S*)
7	C_3H_7CHO		57	65/35	88/71
8	*i*-PrCHO		45	64/36	79/29
9	PrCH=CHCHO[h)]		97	96/ 4	97/—[i)]
10	MeCH=C(Me)CHO[h)]		86	>95/ 5	96/—[i)]

a) Unless otherwise noted, the reaction was carried out in freshly distilled propionitrile using 20 mol% of catalyst 2a and 1.2 equiv of the ketene silyl acetal per aldehyde at −78 °C. b) Isolated yield by column chromatography for the *erythro*/*threo* mixture. c) The values correspond to *erythro*/*threo*. Absolute configuration of the hydroxy group-attached carbon was indicated in parentheses. d) Mixture of two isomers (E/Z=82/18). e) Mixture of two isomers (E/Z=92/8). f) *E* isomer of >95% purity was used. g) **1b** was used as a ligand. h) Trans isomer was used. i) Not determined.

J=7 Hz, CH_3CH), 2.00 (2H, q, J=7 Hz,CH_2), 4.57 (1H, q, J=7 Hz, CH).

(*Z*)-3-Trimethylsiloxy-2-pentene:[12)] To a solution of tetrabutylammonium fluoride (TBAF, 0.6 mmol) in THF (5 ml) was added ethyl (trimethylsilyl)acetate (24 mmol) drop by drop at −78 °C. After 10 min stirring, a solution of 3-pentanone (20 mmol) in THF (1.5 ml) was introduced during 10 min. This solution was stirred for 2 h, then at 0 °C for 2.5 h. The dark orange mixture was poured into precooled pentane (−78 °C, 40 ml) and the resulting suspension was removed by a celite filter. The filtarte was treated with saturated $NaHCO_3$ (50 ml), extracted with hexane, and dried over Na_2SO_4. After removal of the solvent, the residue was distilled under reduced pressure (55 Torr (1 Torr=133.322 Pa), 60 °C) to give a product (21% yield, E/Z=1/6). ^{1}H NMR ($CDCl_3$) δ=0.16 (9H, s, $(CH_3)_3Si$), 0.99 (3H, t, J=7 Hz, CH_3CH_2),1.48 (3H, d, J=7 Hz, CH_3CH), 2.00 (2H, q, J=7 Hz, CH_2), 4.50 (1H, q, J=7 Hz, CH).

1-Trimethylsiloxy-1-cyclohexene: Obtained from Aldrich Chemical Company, Inc.

Preparation of Ketene Silyl Acetals.[10)] A solution of LDA (20 mmol) in THF (40 ml) was cooled to −78 °C and the corresponding ketone (20 mmol) was added dropwise over a few minutes. The solution was stirred for 1 h at that temperature and then chlorotrimethylsilane (22 mmol) was added. This mixture was allowed to warm to room temperature over several hours. The resulting suspension was removed by a celite filter and the fitrate was concentrated. This operation was repeated for three times. The residue was distilled under reduced pressure.

1-Phenoxy-1-(trimethylsiloxy)ethylene:[3d)] (25% yield); ^{1}H NMR ($CDCl_3$) δ=0.26 (9H, s, $(CH_3)_3Si$), 3.27 (1H, d, J=2 Hz, C*H*H), 3.50 (1H, d, J=2 Hz, CH*H*), 7.03—7.37 (5H, m).

(*E*)-1-Ethoxy-1-(trimethylsiloxy)propene:[13)] (E/Z=82/18); ^{1}H NMR ($CDCl_3$) δ=0.23 (9H,s, $(CH_3)_3Si$), 1.23 (3H, t, J=7 Hz, CH_3CH_2), 1.52 (3H, d, J=7 Hz, CH_3CH), 3.74 (1H, q, J=7 Hz, CH; δ=3.47 for (*Z*)-CH), 3.83 (2H, q, J=7 Hz, CH_2; δ=3.69 for (*Z*)-CH_2).

(*E*)-1-Benzyloxy-1-(trimethylsiloxy)propene:[14)] (70% yield, E/Z=92/8); ^{1}H NMR ($CDCl_3$) δ=0.17 (9H, s, $(CH_3)_3Si$), 1.47 (3H, d, J=7 Hz, CH_3), 3.71 (1H, q, J=7 Hz,CH; δ=3.62 for (*Z*)-CH), 4.83 (2H, s, CH_2), 7.25—7.28 (5H, m).

(*E*)-1-Phenoxy-1-(trimethylsiloxy)propene:[3d)] (81% yield, E/Z=>95/5); ^{1}H NMR ($CDCl_3$) δ=0.12 (9H, s, $(CH_3)_3Si$), 1.48 (3H, d, J=7 Hz, CH_3), 4.27 (1H, q, J=7 Hz, CH), 6.95—7.31 (5H, m).

(2*R*,3*R*)-2-*O*-(2,6-Diisopropoxybenzoyl)tartaric Acid (1a). To a slightly suspended solution of 2,6-

diisopropoxybenzoic acid (4.77 g, 20 mmol) and dibenzyl tartrate (6.61 g, 20 mmol) in 100 ml of dry benzene was added trifluoroacetic anhydride (3.1 ml, 22 mol) dropwise over a period of 20 min at room temperature. After being stirred for 30 min, the pale yellow solution was poured into saturated $NaHCO_3$ and extracted with ether repeatedly. The combined organic layer was dried over Na_2SO_4, concentrated and the residue was purified by column chromatography on silica gel using a mixture (3 : 1 : 5) of hexane, ether, and dichloromethane as eluant to give 6.73 g (65% yield) of dibenzyl 2-*O*-(2,6-diisopropoxybenzoyl)tartrate as a colorless half solid. This tartrate was dissolved in 50 mL of ethyl acetate and to the solution was added 0.67 g of 10% Pd/C powder under argon atmosphere. The argon was then replaced by hydrogen and the reaction mixture was stirred at atmospheric pressure and room temperature for 15 h. The mixture was filtered through a pad of celite and the filtrate was concentrated in vacuo to afford 4.66 g (100% yield) of 2-*O*-(2,6-diisopropoxybenzoyl)tartaric acid as a colorless solid. Mp 81 °C; $[\alpha]_D$ −28.5° (*c* 1.1, EtOH); IR (KBr) 2982, 1744, 1547, 1466, 1255, 1113, 1070 cm^{-1}; ^1H NMR ($CDCl_3$–DMSO-d_6) δ=1.25 (6H, d, J=6 Hz, 2Me), 1.26 (6H, J=6 Hz, 2Me), 4.49 (2H, septet, J=6 Hz, 2C*H*(CH_3)$_2$), 4.73 (1H, d, J=1.4 Hz, HOC*H*CO_2), 5.70 (1H, d, J=1.4 Hz, CO_2CHCO_2), 6.46 (2H, d, J=8 Hz, ArH), 7.17 (1H, t, J=8 Hz, ArH). Found: C, 54.95; H, 6.24%. Calcd for $C_{17}H_{22}O_4$: C, 55.13; H, 5.94%.

***o*-Phenoxyphenylboronic Acid.** To a solution of diphenyl ether (2.6 g, 15 mmol) in 30 ml of THF was added *n*-BuLi (16 mmol) at 0 °C. To this yellow solution was added $B(OMe)_3$ (16 mmol) at the same temperature and the white suspension was stirred at room temperature for 1 h. Then the mixture was poured into diluted HCl (20 ml of 1 mol dm^{-3} HCl and 80 ml of water) and extracted with ether repeatedly. The combined ether layer was dried over Na_2SO_4, evaporated and the residue was purified by column chromatography on silica gel using EtOAc–hexane=1/3 as eluant. Recrystallization from ether/hexane afforded the correponding boronic acid as a white solid (29% yield). Mp 138—139 °C; IR ($CHCl_3$) 3550, 1447, 1348, 1323, 1225 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.7—5.8 (2H, br, OH), 6.71 (1H, d, J=8 Hz, CHCO), 7.04—7.43 (7H, m), 7.91 (1H, dd, J=2, 7 Hz, CHCB). Found: C, 67.40; H, 5.10%. Calcd for $C_{12}H_{11}O_3B$: C, 67.35; H, 5.14%.

Typical Procedure of an Asymmetric Aldol Reaction of Ketone Silyl Enol Ethers with Aldehydes. Method A: To a solution of mono-*O*-acylated tartaric acid (**1**, 0.2 mmol) in dry propionitrile (1 ml) was added BH_3·THF (0.2 mmol) at 0 °C under Ar. The reaction mixture was stirred for 1 h at that temperature, during which period the evolution of hydrogen gas ceased, and then the solution was cooled to −78 °C. To this were introduced enol silyl ether (1.2 mmol) and aldehyde (1.0 mmol) successively. After stirring for several hours, the solution was poured into diluted hydrochloric acid and the product was extracted with ether. The solvent was evaporated, and the residue was treated with 1 mol dm^{-3} HCl–THF solution (2 ml, 1/1 in vol.) Usual workup followed by chromatographic separation gave aldol adducts.

Method B: Mono-*O*-acylated tartaric acid (**1**, 0.2 mmol) and alkylboronic acid (0.2 mmol) were dissolved in dry propionitrile (1 mL), the resulting solution was stirred at 25 °C for 30 min, and the reaction system was cooled to −78 °C. Enol silyl ether (1.2 mmol) and aldehyde (1.0 mmol) were added successively and the reaction mixture was stirred for several hours at the low temperature. This cold solution was poured into water and the product was extracted with ether repeatedly. The combined ether layers were dried, concentrated and the residue was treated with 1 mol dm^{-3} HCl–THF solution (2 mL, 1/1 in vol.). Usual workup was followed by column chromatography to give aldol adducts.

The absolute configurations were determined by the comparison of optical rotation values with data in the literature, if it's necessarily, the adducts were converted to the known compounds. Product diastereo and enantio ratios were determined by analytical HPLC and ^1H NMR spectroscopy of the adduct/or the corresponding (+)/(−)-MTPA esters.

(*R*)-1-Hydroxy-1-phenyl-3-heptanone (Entry 1, Table 1):[3f,15] $[\alpha]_D$ +63.0° (*c* 1.13, PhH); IR (film) 3457, 2959, 1709, 1455, 1043, 758, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87 (3H, t, J=7 Hz, CH_3), 1.17—1.38 (2H, m, CH_2), 1.44—1.63 (2H, m, CH_2), 2.41 (2H, t, J=7 Hz, CH_2CO), 2.68—2.90 (3H, m, *H*OCHC*H*$_2$), 5.14 (1H, dd, J=5, 8 Hz, C*H*OH), 7.25—7.36 (5H, m, Ph). The ee was determined by ^1H NMR analysis of (+)-MTPA ester.

7-Hydroxy-5-undecanone (Entry 2, Table 1): $[\alpha]_D$ +29.6° (*c* 1.06, PhH); IR ($CHCl_3$) 3520, 2961, 2934, 1701 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (6H, t, J=7 Hz, 2CH_3), 1.15—1.65 (10H, m, $CH_3(CH_2)_3CH(OH)CH_2(C{=}O)$-$CH_2(CH_2)_2CH_3$), 2.10—2.50 (1H, br, OH), 2.42 (2H, t, J=7 Hz, CH_2CH_2CO), 2.40—2.67 (2H, m, O=CC*H*$_2$CHOH), 3.93—4.09 (1H, m, C*H*OH). Found: C, 71.30; H, 11.87%. Calcd for $C_{11}H_{22}O_2$: C, 70.97; H, 11.87%. HPLC analysis of (+)-MTPA ester (hexane/EtOAc=80/1, Flow rate=2 mL min^{-1}), t_R=29.8 min (minor isomer), t_R=32.0 min (major isomer).

(*R*)-1-Hydroxy-1,3-diphenyl-3-propanone (Entry 3, Table 1):[16a] $[\alpha]_D$ +69.5° (*c* 1.14, PhH); IR ($CHCl_3$) 3525, 3013, 1676, 1451, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.36 (2H, d, J=6 Hz, CH_2), 3.60 (1H, d, J=3 Hz, OH), 5.34 (1H, dt, J=3, 6 Hz, C*H*OH), 7.25—7.62 (8H, m, Ph), 7.95 (2H, d, J=7 Hz, Ph). HPLC analysis of (+)-MTPA ester (hexane/EtOAc=40/1), t_R=12.6 min ((*S*)-isomer), t_R=14.9 min ((*R*)-isomer).

(*E*)-3-Hydroxy-1,5-diphenyl-4-penten-1-one (Entry 4, Table 1):[17] $[\alpha]_D$ +31.1° (*c* 1.00, PhH); IR ($CHCl_3$) 3470, 1682, 1449, 968, 754, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50—2.50 (1H, br, OH), 3.23—3.32 (2H, m, CH_2), 4.93 (1H, ddd, J=<1, 7, 12 Hz, C*H*OH), 6.30 (1H, dd, J=7, 16 Hz, C*H*CHPh), 6.71 (1H, d, J=16 Hz, C*H*Ph), 7.17—7.63 (8H, m, Ph), 7.96 (2H, d, J=7 Hz, Ph). HPLC analysis of (+)-MTPA ester (hexane/EtOAc=40/1, Flow rate=2 mL min^{-1}), t_R=26.5 min (minor isomer), t_R=29.6 min (major isomer).

3-Hydroxy-2-methyl-1,3-diphenyl-1-propanone (Entry 5, Table 1):[11] $[\alpha]_D$ −17.4° (*erythro*, *c* 0.97, PhH); ^1H NMR ($CDCl_3$) for *erythro* isomer δ=1.18 (3H, d, J=6 Hz, CH_3), 3.40—3.80 (1H, br, OH), 3.69 (1H, dq, J=3, 6 Hz, C*H*CH_3), 5.23 (1H, d, J=3 Hz, C*H*OH), 7.20—7.62 (8H, m, Ph), 7.92 (2H, d, J=7 Hz, Ph); ^1H NMR ($CDCl_3$) for *threo* isomer δ=1.05 (3H, d, J=6 Hz, CH_3), 4.98 (1H, d, J=8 Hz, C*H*OH), other resonances could not be discerned for *threo* isomer. HPLC analysis of (+)-MTPA ester (hex-

ane/EtOAc=80/1, Flow rate=2 mL min^{-1}), t_R=31.8 min (*threo* major isomer), t_R=35.2 min (*erythro* major isomer), t_R=40.3 min (*erythro* minor isomer), t_R=42.0 min (*threo* minor isomer).

3-Hydroxy-2-methyl-1-phenyl-1-hexanone (Entry 6, Table 1):[18] $[\alpha]_D$ −14.7° (*erythro*, *c* 1.06 PhH); ^{1}H NMR ($CDCl_3$) for *erythro* isomer δ=0.92 (3H, t, J=7 Hz, CH_3CH_2), 1.25 (3H, d, J=4, 7 Hz, $CHCH_3$), 1.30—1.65 (4H, m, $(CH_2)_2$), 3.04 (br, 1H, OH), 3.45 (1H, dq, J=4, 7 Hz, $CHCH_3$), 3.97—4.08 (1H, m, CHOH), 7.41—7.62 (3H, m, Ph), 7.92 (2H, d, J=7 Hz, Ph); ^{1}H NMR ($CDCl_3$) for *threo* isomer δ=3.79—3.91 (1H, m, CHOH), other resonances could not be discerned for *threo* isomer. HPLC analysis of (+)-MTPA ester (hexane/EtOAc=80/1, Flow rate=2 mL min^{-1}), t_R=26.0 min (*threo* minor isomer), t_R=27.2 min (*threo* major isomer), t_R=29.1 min (*erythro* major isomer), t_R=29.9 min (*erythro* minor isomer).

1-Hydroxy-2-methyl-1-phenyl-3-pentanone (Entry 7, Table 1):[16b] $[\alpha]_D$ +12.6° (*erythro*, *c* 0.95, PhH); ^{1}H NMR ($CDCl_3$) for *erythro* isomer δ=0.98 (3H, t, J=7 Hz, CH_3CH_2), 1.07 (3H, d, J=7 Hz, CH_3CH), 2.20—2.60 (2H, m, CH_2CO), 2.83 (1H, dq, J=4, 7 Hz, CH_3CH), 3.0—3.1 (1H, br, OH), 5.03 (1H, d, J=4 Hz, CHOH), 7.20—7.38 (5H, m, Ph); ^{1}H NMR ($CDCl_3$) for *threo* isomer δ=4.74 (1H, d, J=8 Hz, CHOH), other resonances could not be discerned for *threo* isomer. HPLC analysis of (+)-MTPA ester (hexane/EtOAc=40/1, Flow rate=2 mL min^{-1}), t_R=17.5 min (*threo* isomer), t_R=18.6 min (1*R*,2*R*) isomer), t_R=19.6 min (*threo* isomer), t_R=21.4 min (1*S*,2*S*) isomer).

(*E*)-5-Hydroxy-4-methyl-6-octen-3-one (Entry 11, Table 1):[1b] $[\alpha]_D$ −6.4° (*erythro*, *c* 1.17 $CHCl_3$); ^{1}H NMR ($CDCl_3$) for *erythro* isomer δ=1.04 (3H, t, J=7 Hz, CH_3CH_2), 1.13 (3H, d, J=7 Hz, CH_3CHCO), 1.72 (3H, d, J=7 Hz, CH_3CH=CH), 2.40—2.70 (4H, m, CH_2, CHCO and OH), 4.25—4.38 (1H, br, CHOH), 5.35—5.55 (1H, m, CH=CH), 5.60—5.78 (1H, m, CH=CH); ^{1}H NMR ($CDCl_3$) for *threo* isomer δ=4.05—4.24 (1H, br, CHOH), other resonances could not be discerned for *threo* isomer. HPLC analysis of (−)-MTPA ester (hexane/EtOAc=40/1, Flow rate=2 mL min^{-1}), t_R=16.5 min ((4*S*,5*S*) isomer), t_R=18.8 min (4*R*,5*R*) isomer)

5-Hydroxy-4-methyl-3-octanone (Entry 12, Table 1):[1b] $[\alpha]_D$ +7.8° (*erythro*, *c* 0.99, $CHCl_3$); ^{1}H NMR ($CDCl_3$) for *erythro* isomer δ=0.90 (3H, t, J=7 Hz, CH_3), 1.03 (3H, t, J=7 Hz, CH_3), 1.10 (3H, d, J=7 Hz, CH_3CH), 1.15—1.53 (4H, m, $CH_3(CH_2)_2$), 2.38—2.70 (4H, m, CH_2CO, $CHCH_3$, and OH), 3.83—3.94 (1H, m, CHOH); ^{1}H NMR ($CDCl_3$) for *threo* isomer δ=3.60—3.70 (1H, m, CHOH), other resonances could not be discerned for *threo* isomer. The ee was determined by ^{1}H NMR analysis of (+)-MTPA ester.

2-(α-Hydroxybenzyl)cyclohexanone (Entry 14, Table 1):[11] $[\alpha]_D$ +128.7° (*erythro*, *c* 1.05, PhH); ^{1}H NMR ($CDCl_3$) δ=1.35—1.90 (5H, m, *c*-C_6H_9), 1.95—2.15 (1H, m, *c*-C_6H_9), 2.25—2.50 (2H, m, CH_2CO), 2.50—2.65 (1H, m, CHCO), 2.99 (1H, d, J=4 Hz, OH), 5.34—5.42 (1H, m, CHOH), 7.20—7.40 (5H, m, Ph); ^{1}H NMR ($CDCl_3$) for *threo* isomer δ=4.73—4.80 (1H, m, CHOH), other resonances could not be discerned for *threo* isomer. The ee was determined by ^{1}H NMR analysis of (+)-MTPA ester.

Typical Procedure for an Asymmetric Aldol-Type Reaction of Silyl Ketene Acetals of Aldehydes. To a solution of mono-*O*-acylated tartaric acid (0.2 mmol) in dry propionitrile (1 ml) was added BH_3·THF (0.2 mmol) at 0 °C under Ar. After stirring for 1 h at that temperature, the solution was cooled to −78 °C. To this were added aldehyde (1.0 mmol) and then ketene silyl acetal (1.2 mmol) successively and the mixture was stirred for several hours. This solution was then poured into water and the product was extracted with ether. The solvent was evaporated, and the residue was treated with tetrabutylammonium fluoride (1 ml of 1 mol dm^{-3} solution in THF, 1 mmol) in THF (3 ml) to desilylate the containing siloxy ester. Usual workup followed by chromatographic separation gave aldol adducts.

The absolute configurations were determined by the comparison of optical rotation values with data in the literature, if it's necessarily, the adducts were converted to the known compounds. Product diastereo and enantio ratios were determined by analytical HPLC and ^{1}H NMR spectroscopy of the adduct/or the corresponding (+)/(−)-MTPA esters.

Phenyl (*R*)-3-Hydroxy-3-phenylpropanoate (Entry 1, Table 4):[3d] $[\alpha]_D$ +29.7° (*c* 1.01, $CHCl_3$); IR ($CHCl_3$) 3607, 3021, 1748, 1493, 1220, 1168, 700 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ=2.86—3.16 (3H, m, CH_2 and OH), 5.25 (1H, dd, J=5, 8 Hz, CHOH), 7.05 (2H, d, J=7 Hz, Ph), 7.15—7.48 (m, 8H, Ph). HPLC analysis of (+)-MPTA ester (hexane/EtOAc=40/1, Flow rate=2 mL min^{-1}), t_R=27.5 min ((*S*)-isomer), t_R=31.4 min ((*R*)-isomer).

Determination of the Absolute Configuration: A mixture of the phyenyl ester and NaOH in MeOH–H_2O (4/1) solution was stirred at room temperature for 30 min. The solution was basified to pH=9 by 1 mol dm^{-3} HCl and extracted with ethyl acetate repeatedly. The combined organic layer was dried over Na_2SO_4 and concentrated to furnish (*R*)-3-hydroxy-3-phenylpropanoic acid as a white crystalline solid.[19a] (89% yield); $[\alpha]_D$ +56.0° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.74—2.86 (2H, m, CH_2), 5.15 (1H, dd, J=5, 10 Hz, CH), 7.25—7.45 (5H, m), other resonances (OH and CO_2H) could not be discerned.

Phenyl (*S*)-3-Hydroxyhexanoate (Entry 2, Table 4): $[\alpha]_D$ +15.6° (*c* 0.95, $CHCl_3$): ^{1}H NMR ($CDCl_3$) δ=0.93 (3H, t, J=7 Hz, CH_3), 1.3—1.7 (4H, m, $(CH_2)_2$), 2.65—2.85 (3H, m, CH_2CO and OH), 4.05—4.22 (1H, m, CHOH), 7.05—7.45 (5H, m, Ph). HPLC analysis (+)-MTPA ester (hexane/EtOAc=40/1, Flow rate=2 mL min^{-1}), t_R=20.6 ((*R*)-isomer), t_R=23.4 min ((*S*)-isomer).

Determination of the Absolute Configuration: A mixture of the phenyl ester and NaOH in MeOH–H_2O (4/1) solution was stirred at room temperature for 30 min. The solution was basified to pH=9 by 1 mol dm^{-3} HCl and extracted with ethyl acetate repeatedly. The combined organic layer was dried over Na_2SO_4 and concentrated to furnish (*S*)-3-hydroxyhexanoic acid as a white crystalline solid.[19a] (100% yield); $[\alpha]_D$ +18.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, t, J=7 Hz, CH_3), 1.25—1.65 (4H, m, $((CH_2)_2)$, 2.34—2.67 (2H, m, CH_2CO), 3.94—4.13 (1H, m, CH), 6.00—7.05 (2H, br, CO_2H and OH).

Ethyl 3-Hydroxy-2-methyl-3-phenylpropanoate (Entry 3, Table 4):[20] $[\alpha]_D$ +14.2° (*erythro*, *c* 1.0, $CHCl_3$), +24.1° (*threo*, *c* 2.0, $CHCl_3$); IR (film) 3475, 2982, 2732, 1186, 702 cm^{-1};^{1}H NMR ($CDCl_3$) for *erythro* isomer δ=1.02 (3H, d, J=8 Hz, CH_3CH), 1.25 (3H, t, J=8 Hz, CH_3CH_2), 2.67—2.89 (1H, m, $CHCH_3$), 2.97 (1H, br, OH), 5.08 (1H, dd, J=3, 4 Hz, CHOH), 7.22—7.43 (5H, m); ^{1}H NMR

($CDCl_3$) for *threo* isomer δ=1.12 (3H, d, J=8 Hz, CH_3CH), 1.20 (3H, t, J=8 Hz, CH_3CH_2), 4.73 (1H, dd, J=4, 9 Hz, CHOH), other resonances could not be discerned for *threo* isomer. HPLC analysis of (+)-MTPA ester (hexane/EtOAc=40/1, Flow rate=2 mL min^{-1}), t_R=31.8 min (*threo* minor isomer), t_R=33.8 min (*erythro* major isomer), t_R=35.2 min (*erythro* minor isomer), t_R=38.6 min (*threo* major isomer).

Benzyl 3-Hydroxy-2-methyl-3-phenylpropanoate (Entry 4, Table 4): IR (film) 3458, 1732, 1456, 1169, 1026, 700 cm^{-1}; ^1H NMR ($CDCl_3$) for *erythro* isomer δ=1.14 (3H, d, J=7 Hz, CH_3), 2.75—3.92 (2H, m, CHCH$_3$ and OH), 5.05—5.11 (1H, m, CHOH), 5.14 (2H, s, CH_2Ph), 7.19—7.36 (m, 5H, Ph); ^1H NMR ($CDCl_3$) for *threo* isomer δ=1.02 (3H, d, J=7 Hz, CH_3), 4.75 (1H, dd, J=4, 8 Hz, CHOH), other resonances could not be discerned for *threo* isomer. Found: C, 75,43; H, 6.86%. Calcd for $C_{17}H_{18}O_3$: C, 75.56, H, 6.66%. HPLC analysis of (+)-MTPA ester (hexane/EtOAc=40/1), Flow rate=2 mL min^{-1}), t_R=19.1 min ((2*R*,3*S*) isomer), t_R=20.0 min ((2*R*,3*R*) isomer), t_R=21.1 min ((2*S*,3*S*) isomer), t_R=22.7 min ((2*S*,3*R*) isomer).

Determination of the Absolute Configuration: The benzyl ester was hydrolyzed as above procedure. This carboxylic acid was stirred with K_2CO_3 and MeI in DMF at room temperature and then the mixtures were poured into 1 mol dm^{-3} HCl. The methyl ether extract was dried, concentrated and the residue was purified by column chromatography to separate pure two isomers.

Methyl *erythro*-3-hydroxy-2-methyl-3-phenylpropanoate:[19b] $[\alpha]_D$ +17.2° (from benzyl ester, *c* 1.5, $CHCl_3$), +22.5° (from phenyl ester, *c* 1.5); ^1H NMR ($CDCl_3$) δ=1.10 (3H, J=7 Hz, CH_3CH), 2.77 (1H, dq, J=4, 7 Hz, CH_3CH), 2.93 (1H, d, J=3 Hz, OH), 3.66 (3H, s, CH_3CO), 5.09 (1H, dd, J=3, 4 Hz, CHOH), 7.25—7.35 (5H, m).

Methyl *threo*-3-hydroxy-2-methyl-3-phenylpropanoate:[15b] $[\alpha]_D$ +31.2° (from benzyl ester, *c* 1.7, $CHCl_3$), 8.5° (from phenyl ester, *c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$) δ=0.97 (3H, d, J=7 Hz, CH_3CH), 2.79 (1H, dq, J=9, 7 Hz, $CHCH_3$), 2.97 (1H, d, J=4 Hz, OH), 3.70 (3H, s, CH_3O), 4.72 (1H, dd, J=4, 9 Hz, CHOH), 7.25—7.35 (5H, m, Ph).

Phenyl 3-Hydroxy-2-methyl-3-phenylpropanoate (Entry 5, Table 4)[3d] $[\alpha]_D$ −7.2° (*c* 0.98, $CHCl_3$); IR (film) 3470, 1755, 1493, 1456, 1196, 1163, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.32 (3H, d, J=7 Hz, CH_3), 2.50—3.00 (1H, br, OH), 3.04 (1H, dq, J=5, 7 Hz, MeCH), 5.16 (1H, d, J=5 Hz, CHOH), 6.85—7.45 (10H, m, Ph); ^1H NMR ($CDCl_3$) for *threo* isomer δ=1.17 (3H, d, J=7 Hz, CH_3), 4.87 (1H, d, J=8 Hz, CHOH), other resonances could not be discerned for *threo* isomer. HPLC analysis of (+)-MTPA ester (hexane/EtOAc=40/1, Flow rate=2 mL min^{-1}), t_R=27.8 min ((2*S*,3*R*) isomer), t_R=29.4 min ((2*R*,3*R*) isomer), t_R=31.4 min ((2*S*,3*S*) isomer), t_R=35.6 min ((2*R*,3*S*) isomer).

Determination of the Absolute Configuration: The phenyl ester was converted to the corresponding methyl ester as above procedure.[15b,19b]

Phenyl 3-Hydroxy-2-methylhexanoate (Entry 7, Table 4):[3e] IR (film) 3450, 2961, 1755, 1493, 1196, 1163, 750 cm^{-1}; ^1H NMR ($CDCl_3$) for *erythro* isomer δ=0.95 (3H, t, J=7 Hz, CH_3), 1.34 (3H, d, J=7 Hz, CH_3CH), 1.3—1.7 (m, 4H, $(CH_2)_2$), 2.30—2.45 (1H, br, OH), 2.68—2.83 (1H, m, $CHCH_3$), 3.98—4.11 (1H, br, CHOH), 7.02—7.44 (5H, m, Ph); ^1H NMR ($CDCl_3$) for *threo* isomer δ=1.36 (3H, d, J=7 Hz, CH_3CH), 3.72—3.86 (1H, br, CHOH), other resonances could not be discerned for *threo* isomer. Found: C, 70.17; H, 8.26%. Calcd for $C_{13}H_{18}O_3$: C, 70.25, 8.16%. The phenyl ester was hydrolyzed as above procedure. The carboxylic acid was stirred with K_2CO_3 and BnBr in DMF at room temperature and then the mixtures were poured into 1 mol dm^{-3} HCl. The benzyl ether extract was dried, concentrated and the residue was purified by column chromatography: HPLC analysis of (+)-MTPA ester (hexane/EtOAc=60/1, Flow rate=2 mL min^{-1}), t_R=22.3 min (*erythro* major isomer), t_R=24.6 min (*erythro* minor isomer), t_R=25.6 min (*threo* minor isomer), t_R=26.7 min (*threo* major isomer).

Phenyl 3-Hydroxy-2,4-dimethylpentanoate (Entry 8, Table 4):[3e] ^1H NMR ($CDCl_3$) for *erythro* isomer δ=0.89—1.11 (6H, m, $(CH_3)_2CH$), 1.32 (3H, d, J=7 Hz, CH_3CH), 1.78 (1H, sept, J=7 Hz, $CH(CH_3)_2$), 2.25—2.45 (1H, br, OH), 2.81—2.98 (1H, m, $CHCH_3$), 3.66—3.78 (1H, m, CHOH), 7.02—7.44 (5H, m); ^1H NMR ($CDCl_3$) for *threo* isomer δ=1.36 (3H, d, J=7 Hz, CH_3CH), 3.45—3.57 (1H, m, CHOH), other resonances could not be discerned for *threo* isomer. HPLC analysis of (+)-MTPA ester (hexane/EtOAc=40/1, Flow rate=2 mL min^{-1}), t_R=20.0 min (*erythro* minor isomer), t_R=22.4 min (*erythro* major isomer), t_R=25.7 min (*threo* minor isomer), t_R=31.1 min (*threo* major isomer).

Phenyl (*E*)-3-Hydroxy-2-methyl-4-octenoate (Entry 9, Table 4): IR (film) 3456, 1755, 1593, 1493, 1196, 748, 690 cm^{-1}; ^1H NMR ($CDCl_3$) for *erythro* isomer δ=0.91 (3H, t, J=7 Hz, CH_3CH_2), 1.32 (3H, d, J=7 Hz, CH_3), 1.3—1.5 (2H, m, CH_2CH_3), 2.00—2.10 (2H, m, CH_2CH), 2.20—2.40 (1H, br, OH), 2.77—2.92 (1H, m, $CHCH_3$), 4.40—4.45 (1H, m, CHOH), 5.55 (1H, dd, J=6, 16 Hz, CH=$CHCH_2$), 5.77 (1H, dt, J=16, 6 Hz, $CHCH_2$), 7.00—7.44 (5H, m, Ph); ^1H NMR ($CDCl_3$) for *threo* isomer δ=4.20—4.40 (1H, m, CHOH), other resonances could not be discerned for *threo* isomer. Found: C, 72.61; H, 8.33%. Calcd for $C_{15}H_{20}O_3$: C, 72.58; H, 8.06%. The phenyl ester was converted to methyl *erythro*-(*E*)-3-hydroxy-2-methyl-4-octenoate as above procedure. $[\alpha]_D$ −8.6° (*c* 1.06, $CHCl_3$); ^1H NMR ($CDCl_3$) δ=0.86 (3H, t, J=7 Hz, CH_3CH_2), 1.15 (3H, d, J=8 Hz, CH_3CH), 1.37 (2H, sext, J=7 Hz, CH_2CH_3), 2.00 (2H, q, J=7 Hz, CH_2CH), 2.47 (1H, d, J=8 Hz, OH), 2.62 (1H, dq, J=5, 8 Hz, $CHCH_3$), 3.68 (3H, s, CH_3O), 4.23—4.35 (1H, br, CHOH), 5.42 (1H, dd, J=7, 15 Hz, 1H, CHCHOH), 5.69 (1H, dt, J=15, 7 Hz, $CHCH_2$); HPLC analysis of (+)-MTPA ester (hexane/EtOAc=60/1, Flow rate=2 mL min^{-1}), t_R=25.6 min (*erythro* major isomer), t_R=27.1 min (*threo* minor isomer).

Phenyl (E)-3-Hydroxy-2,4-dimethyl-4-hexenoate (Entry 10, Table 4): $[\alpha]_D$ +15.4° (*erythro*, *c*, 1.10, $CHCl_3$); IR (film) 3450, 2979, 1757, 1493, 1196, 1163 cm^{-1}; ^1H NMR ($CDCl_3$) for *erythro* isomer δ=1.31 (3H, d, J=6 Hz, CH_3CHCO_2), 1.65 (3H, d, J=8 Hz, CH_3CH=C), 1.68 (3H, s, CH_3C), 2.0—2.1 (1H, br, OH), 2.92 (1H, quint, J=6 Hz, $CHCO_2$), 4.35 (1H, d, J=6 Hz, CHOH), 5.62 (1H, q, J=8 Hz, CH=C), 6.97—7.42 (5H, m, Ph); ^1H NMR ($CDCl_3$) for *threo* isomer δ=4.21 (1H, d, J=8 Hz, CHOH), other resonances could not be discerned for *threo* isomer. Found: C, 71.70; H, 7.88%. Calcd for $C_{14}H_{18}O_3$: C, 71.79, H, 7.69%; HPLC analysis of (+)-MTPA ester (hexane/EtOAc=60/1, Flow rate=2 mL min^{-1}), t_R=20.4 min (*erythro* major iso-

mer), t_R=27.7 min (*erythro* minor isomer).

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