Catalytic Asymmetric Allylation Using a Chiral (Acyloxy)borane Complex as a Versatile Lewis Acid Catalyst

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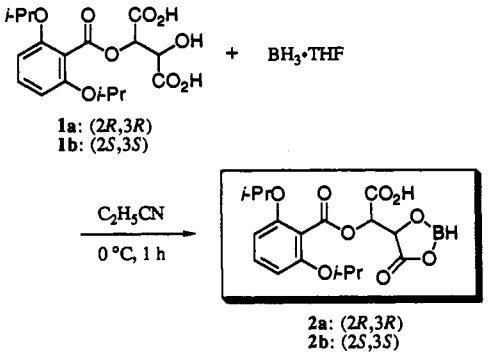
Abstract: In the presence of 20 mol % of a chiral (acyloxy)borane (CAB) complex prepared from (2*R*,3*R*)-2-*O*-(2,6-diisopropoxybenzoyl)tartaric acid and borane–tetrahydrofuran, various allyltrimethylsilanes react with achiral aldehydes to afford the corresponding homoallylic alcohols in good yields with high diastereo- and enantioselectivities. Furthermore, the reactivity of allylation can be improved without reducing the enantioselelctivity by using 10–20 mol % of the CAB complex prepared from 3,5-bis(trifluoromethyl)phenylboronic acid and chiral tartaric acid derivative. The observed selectivities and *re*-face attack of nucleophiles on the carbonyl carbons of aldehydes imply that the extended transition-state model is applicable.

Introduction

Reactions of γ-substituted allylmetallics with aldehydes leading to diastereomeric homoallylic alcohols have found increasingly widespread use in synthesis.[1] Asymmetric allylation is a valuable means of constructing chiral functionalized structures, and therefore many chiral allylmetal reagents directed toward a high level of asymmetric induction have been rationally designed and synthesized. Although some of them have exhibited good to excellent enantio- and diastereoselectivities in reactions with achiral aldehydes,[2] there is no method yet available for a catalytic (nonstoichiometric) process.

In our continuing efforts to develop catalytic asymmetric processes utilizing the chiral (acyloxy)borane (CAB) complex,[3] we have found that the CAB catalyst has a powerful activity for the Sakurai–Hosomi allylation reaction of aldehydes.[4] Herein we report *the catalytic asymmetric allylation of aldehydes with allyltrimethylsilanes using the CAB complex*, which makes it possible to furnish homoallylic alcohols in excellent diastereomeric and enantiomeric excess.[5]

Scheme I



Results and Discussion

CAB complex **2** was easily prepared *in situ* from reaction of tartaric acid derivative **1** and BH_3·THF in propionitrile solution at 0 °C (Scheme I). The allylations of allyltrimethylsilanes with achiral aldehydes were promoted by 20 mol % of this catalyst **2** 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 homoallylic alcohols) was treated with tetrabutylammonium fluoride (TBAF) to afford desilylated products. Diastereomeric and enantiomeric ratios of products were determined by analytical HPLC and ^{1}H NMR spectroscopy of the products and/or the corresponding (±)-MTPA esters. The stereochemical assignments (relative stereochemistries) were made from analyses of the ^{1}H NMR spectra, and the absolute configurations were established by measurement of optical rotation and comparison with literature values. Some of the results are summarized in Table I.

The reactions proceeded catalytically to afford homoallylic alcohols in modest to good yields. The relative stereochemistry of the major adducts was assigned as erythro, and predominant *re*-face attack of allyltrimethylsilanes at 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 slight reductions in both the enantio- and diastereoselectivities were observed in the reactions with saturated

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(1) (a) For a recent review of allylsilane and allylstannane additions, see: Fleming, I. In Comprephensive Organic Synthesis; Heathcock, C. H., Ed.; Pergamon Press: Oxford, 1991; Vol. 2, pp 595–628. (b) For a review of allylmetal chemistry, see: Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555.

(2) For example, see: (a) Brown, H. C.; Randad, R. S.; Bhat, K. S.; Zaidlewiez, M.; Racherla, U. S. *J. Am. Chem. Soc.* **1990**, *112*, 2389. (b) Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Park, J. C. *J. Org. Chem.* **1990**, *55*, 4109 and references cited therein.

(3) For precedent application of CAB catalysts to asymmetric reactions, see the following. Diels–Alder reaction: (a) Furuta, K.; Miwa, Y.; Iwanaga, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 6254. (b) Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 1481. (c) Furuta, K.; Kanematsu, A.; Yamamoto, H.; Takaoka, S. *Tetrahedron Lett.* **1989**, *30*, 7231. (d) Ishihara, K.; Gao, Q.; Yamamoto, H. *J. Org. Chem.*, in press. (e) Ishihara, K.; Gao, Q.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, in press. Aldol-type reaction: (f) Furuta, K.; Maruyama, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 1041. (g) Furuta, K.; Maruyama, T.; Yamamoto, H. *Synlett* **1991**, 439. (h) Ishihara, K.; Maruyama, T.; Mouri, M.; Gao, Q.; Furuta, K.; Yamamoto, H. *Bull. Chem. Soc. Jpn.*, in press. Hetero Diels–Alder reaction: (i) Gao, Q.; Maruyama, T.; Mouri, M.; Yamamoto, H. *J. Org. Chem.* **1992**, *57*, 1951.

(4) For example, see: (a) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. (b) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57.

(5) For a preliminary communication: Furuta, K.; Mouri, M.; Yamamoto, H. *Synlett* **1991**, 561. Asymmetric allylation of aldehydes with allylstannanes catalyzed by CAB complex was recently reported, see: Marshall, J. A.; Tang, Y. *Synlett* **1992**, 653. Very recently, the use of an (*S*)-binaphthol–titanium complex in catalytic asymmetric allylation of aldehydes with allylstannanes was reported, see: Costa, A. L.; Piazza, M. G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Am. Chem. Soc.* **1993**, *115*, 7001.

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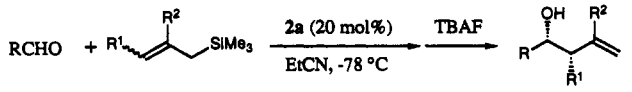
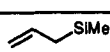
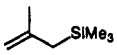
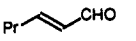
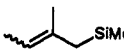
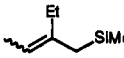
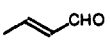
Table I. CAB-Catalyzed Asymmetric Allylation Reactions[a]



entry	aldehyde	allylsilane	yield[b] (%)	erythro/threo	ee (Config)[c] (%)
1[d]	PhCHO		46		55 (*R*)
2			68		82 (*R*)
3			50		80
4	PhCHO		63	(96/ 4)[f]	92
5[g]			64	(96/ 4)[f]	92
6	BuCHO		30	(94/ 6)[f]	85
7	PhCHO		74	97/ 3	96 (*R*)
8[i]			81	97/ 3	96 (*S*)
9[j]			55	80/20	57 (*R*)
10			21	(95/ 5)[f]	89
11	PrCHO		36	95/ 5	86 (*S*)

[a] Unless otherwise noted, the reaction was carried out in freshly distilled propionitrile with 20 mol % of catalyst **2a** and 1.2 equiv of allyltrimethylsilane per aldehyde at −78 °C. [b] Isolated yield by column chromatography for erythro/threo mixture. [c] Configuration given in parentheses corresponds to the alcohol carbon of the major isomer. [d] Reaction at −20 °C. [e] Mixture of two isomers (*E*/*Z* = 61/39). [f] Relative configurations were not determined. [g] A mixture of two isomers (*E*/*Z* = 36/64) was used. [h] Mixture of two isomers (*E*/*Z* = 65/35). [i] (2*S*,3*S*)-Tartaric acid derivative **1b** was used as a ligand. [j] Dichloromethane was used as solvent.

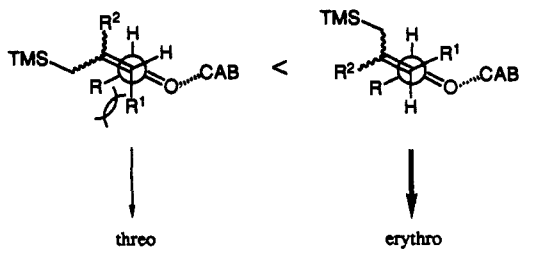
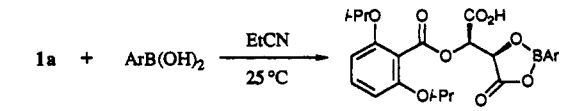
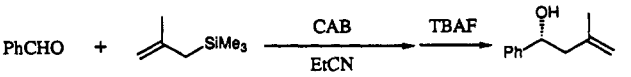


Figure 1. Extended transition-state model.

aldehydes. Unfortunately, simple allyltrimethylsilane was not reactive enough to give adducts efficiently under the conditions used (entry 1). Alkyl substitution at the olefin moiety of allyltrimethylsilanes, however, increased the reactivity, permitting a lower reaction temperature and improved asymmetric induction. Particularly, γ-alkylated allylsilanes exhibited excellent diastereo- and enantioselectivities, affording erythro homoallylic alcohols of higher optical purity.[6] It is noteworthy that, regardless of the stereochemistry (*E* or *Z*) of the starting γ-substituted allyltrimethylsilane, erythro homoallylic alcohols were highly selectively obtained in the present reactions.[7,8] The observed preference for relative and absolute configurations for the adduct alcohols obtained by the CAB-catalyzed allylation was predicted on the basis of an extended transition state model similar to that for the CAB catalyzed aldol reaction (Figure 1). All these behaviors are fully consistent with those of the previously reported CAB-catalyzed reactions.[3] It was of considerable interest to us that the enantio- and diastereoselectivities of these reactions showed significant solvent dependency; thus, propionitrile was found to be an appropriate choice of solvent. The ratio dropped to erythro/threo = 80/20 and 57% ee (erythro) in dichloromethane, which was a standard solvent for this type of reaction (entry 9). The polar solvent should be beneficial for the polarized extended transition-state model. 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 CAB-catalyzed reactions.[3] It is reasonable to speculate on the π-facial bias in the aldehyde–Lewis acid complex as a function of the chiral ligand environment.[3e] It then follows that the sense of asymmetric induction of CAB-catalyzed reactions is the same for all aldehydes examined.

Table II. CAB-Catalyzed Asymmetric Allylation Reactions[a]





entry	CAB (mol %) Ar	*t* (°C)	time (h)	yield[b] (%)	ee (config)[c] (%)
1[d]	H (20)	−78	4	68	82 (*R*)
2	Ph (20)	−40	5	94	75 (*R*)
3	4-$CF_3C_6H_4$ (20)	−78	6	92	81 (*R*)
4	2,4-$(CF_3)_2C_6H_3$ (20)	−78	20	83	89 (*R*)
5	3,5-$(CF_3)_2C_6H_3$ (20)	−78	2	99	88 (*R*)
6	(20)	−88	4.5	94	91 (*R*)
7	(10)	−78	24	96	86 (*R*)
8	(10)	−88	22	79	89 (*R*)

[a] Unless otherwise noted, the reaction was carried out in freshly distilled propionitrile with CAB catalyst and 1.2 equiv of methallyltrimethylsilane per aldehyde. [b] Isolated yield by column chromatography. [c] Configuration given in parentheses corresponds to the alcohol carbon of the major isomer. [d] The result of entry 2 in Table I.

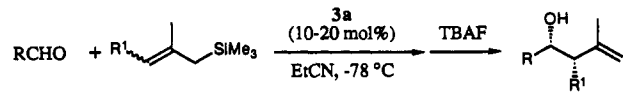
Next, several arylboronic acids were examined in place of BH_3·THF in order to improve the Lewis acidity of CAB and the stereoselectivity of the reaction. The boron substituent of CAB was found to have a strong influence on the chemical yield and the enantiomeric excess of allylation adduct, and 3,5-bis(trifluoromethyl)phenylboronic 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 reduction in the enantioselectivity (Table II). For instance, the reaction of 1-(trimethylsilyl)-2-methyl-2-propene with benzaldehyde in the presence of only 10 mol % CAB proceeded in 96% yield and 86% ee. The molecular weight of a new CAB catalyst prepared from arylboronic acid ($PhB(OH)_2$) in place of BH_3·THF, found cryoscopically in benzene, corresponds closely with the value calculated for a monomeric species. The IR spectrum of the product showed a new five-membered-ring carbonyl compound and differed from that of the six-membered-ring structure. The five-membered-ring carbonyl compound derived from lactic acid and phenylboric acid, 1811 cm^{-1}, while the six-membered-ring structure derived from β-hydroxybutyric acid and phenylboric acid, 1773 cm^{-1}.

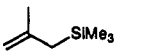
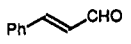
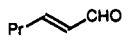
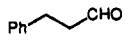
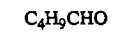
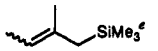
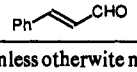
(6) For a definition of the relative stereochemistry (erythro/threo), see: Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1981**, *103*, 2106.

(7) Boron trifluoride catalyzed reaction of 2-methyl-1-(trimethylsilyl)-2-butene (*E*/*Z* = 36/64) with benzaldehyde at −20 °C gave a random mixture of allylation adducts (erythro/threo = 53/47).

(8) In sharp contrast, diastereoselectivities of the reaction of usual allylmetal reagents are known to be heavily dependent on their own stereochemistries. For example, it is reported that (*Z*)-crotylboranes condense with aldehydes to afford erythro homoallylic alcohols, while threo isomers are obtainable from (*E*)-crotylboranes. See ref 2.

Table III. CAB-Catalyzed Asymmetric Allylation Reactions[a]



entry	aldehyde	allylsilane	yield[b] (%)	erythro/threo	ee (Config)[c] (%)
1	PhCHO		99	-	88 (*R*)
2[d]			96	-	86 (*R*)
3			96	-	84
4[d]			95	-	85
5			88	-	77
6			81	-	73
7			71	-	48
8	$C_5H_{11}CHO$		65	-	63 (*S*)
9	C_4H_9CHO		70	-	63
10	C_3H_7CHO		55	-	54 (*S*)
11	PhCHO		82	(94/ 6)[f]	91
12			56	(92/ 8)[f]	89

[a] Unless otherwite noted, the reaction was carried out in freshly distilled propionitrile with 20 mol % of catalyst **3a** and 1.2 equiv of allyltrimethylsilane per aldehyde at −78 °C. [b] Isolated yield by column chromatography for erythro/threo mixture. [c] Configuration given in parentheses corresponds to the alcohol carbon of the major isomer. [d] 10 mol % of **3a** was used. [e] Mixture of two isomers (E/Z = 61/39). [f] Relative configurations were not determined.

The carbonyl peak at 1817 cm^{-1} was observed for the cyclic product derived from the cyclohexanol C-1-monoester of **1** and phenylboric acid.

3,5-Bis(trifluoromethyl)phenylboronic acid can be readily handled in air since it is an air stable solid and does not react with pure oxygen. It is commercially available and can be easily prepared from trimethyl borate by reaction with 3,5-bis(trifluoromethyl)phenyllithium or magnesium bromide.

To explore the generality and scope of the above allylation catalyzed by **3a**, the reactions of allyltrimethylsilanes with various aldehydes were examined. Several examples are demonstrated in Table III. Chemical yields were improved in all cases, but clearly the enantiomeric excesses are still not optimum. Nevertheless, the primary attractions of this method are that it appears to be experimentally straightforward and that the catalyst is easily prepared.

Conclusions

In summary, in this paper is described the successful application of the CAB complex as a catalyst for enantioselective and diastereoselective allylation of aldehydes with allyltrimethylsilanes. The effect of the change in the chiral ligand on boron and the structural change in the allyl side chain are matters of considerable interest, and further studies are in progress.

Experimental Section

General. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100 spectrometer. Analytical gas–liquid-phase chromatography (GC) was performed on Shimadzu Model 8A instrument with a flame-ionization detector and a capillary column of PEG-20M Bonded (25 m) with use of as carrier gas. ^1H and ^{13}C NMR spectra were measured on a Varian Gemini-200 spectrometer and VXR 500. High-performance liquid chromatography (HPLC) was done with Shimadzu 6A and 10A and JASCO UVIDEC-100-II instruments using a 4.6-mm × 25-cm Jasco Finepak Sil column and Daicel Chiralcel 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. High-resolution mass spectrometric molecular weights for the new compunds agreed to 5 ppm or better with the calculated mass.

In experiments requiring dry solvents, propionitrile was freshly distilled from calcium hydride. Ether and tetrahydrofuran (THF) were purchased from Aldrich Chemical Co., Inc., and used without further purification. Benzene and toluene were dried over sodium metal. Dichloroomethane and dimethylformamide (DMF) were stored over 4-Å molecular sieves. Pyridine and triethylamine were stored over potassium hydroxide pellets. BH_3·THF was obtained from Toso-Akzo Chem. Co., Ltd., Japan. Other simple chemicals were purchased and used without further purification.

(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 dry benzene (100 mL) was added trifluoroacetic anhydride (3.1 mL, 22 mmol) dropwise over a period of 20 min at room temperature.[9] After being stirred for 30 min, the pale yellow solution was poured into saturated $NaHCO_3$ and extracted with ether repeatedly. The combined organic layers were dried over Na_2SO_4 and concentrated, and the residue was purified by column chromatography on silica gel with use of a mixture of hexane, ether, and dichloromethane (6:1.5:2.5) as eluent to give 6.73 g (65%) of dibenzyl mono(2,6-diisopropoxybenzoyl) tartrate as a colorless semisolid. This tartrate was dissolved in ethyl acetate (50 mL), 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 Celite pad, and the filtrate was concentrated *in vacuo* to afford 4.66 g (100%) of mono(2,6-diisopropoxybenzoyl)tartaric acid as a colorless solid: $[\alpha]_D$ −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 (d, J = 6 Hz, 6H, $2CH_3$), 1.26 (d, J = 6 Hz, 6H, $2CH_3$), 4.49 (quint, J = 6 Hz, 2H, $CH(CH_3)_2$), 4.73 (d, J = 1.4 Hz, 1H, $HOCHCO_2$), 5.70 (d, J = 1.4 Hz, 1H, CO_2-$CHCO_2$), 6.46 (d, J = 8 Hz, 2H, *m*-C_6H_3), 7.17 (t, J = 8 Hz, 1H, *p*-C_6H_3); ^{13}C NMR ($CDCl_3$–DMSO-d_6) δ 21.49, 21.62, 70.31, 70.78, 73.04, 105.64, 114.59, 130.53, 155.81, 165.09, 168.58, 171.93. Anal. Calcd for $C_{17}H_{22}O_4$: C, 55.13; H, 5.94. Found: C, 54.95; H, 6.24.

1-(Trimethylsilyl)-2-methyl-2-propene.[10] To a mixture of magnesium turnings (14.6 g, 0.60 mol) in THF (160 mL) were added iodine and methalyl chloride (1 mL). When this mixture became colorless, a mixture of methalyl chloride (19.7 mL, 0.20 mol) and trimethylsilyl chloride (24.1 mL, 0.19 mol) in THF (60 mL) was added over 40 min at 0 °C. After being stirred for 30 min at 0 °C, the mixture was allowed to come to room temperature and was stirred for an additional 15 h. Saturated NH_4Cl was added to the mixture dropwise at −20 °C, and the mixture was extracted with ether. After the mixture was dried over Na_2SO_4, the solvent was removed by distillation at atmospheric pressure. The residue was purified by distillation (105–113 °C) to give 14.6 g (60%) of 1-(trimethylsilyl)-2-methyl-2-propene as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.01 (s, 9H, $Si(CH_3)_3$), 1.52 (s, 2H, CCH_2Si), 1.70 (s, 3H, CH_3), 4.45 and 4.58 (br, 2H, CH_2=C).

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1-(Trimethylsilyl)-2-methyl-2-butene.[11,12] To a solution of ((trimethylsilyl)methyl)magnesium chloride (240 mmol) in 240 mL of ether was added $Ni(acac)_2$ (3.1 g, 12 mmol) at 0 °C, followed by addition of 2-bromo-2-butene (20.4 mL, 200 mmol). The reaction mixture was allowed to come to room temperature and stirred for 15 h. The mixture was poured into saturated NH_4Cl and extracted with pentane. The organic layer was dried over $MgSO_4$. After filtration, the solvent was removed by distillation at atmospheric pressure. The residue was purified by distillation (128–138 °C) to give 1-(trimethylsilyl)-2-methyl-2-butene as a colorless oil: IR (film) 2955, 1250, 845, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.01 and 0.03 (s, 9H, $Si(CH_3)_3$), 1.45–1.67 (m, 8H, $SiCH_2C$, CH_3, CH_3), 5.00 and 5.10 (m, 1H, CCH=C).

1-(Trimethylsilyl)-2-ethyl-2-butene.[12] To a solution of lithium diisopropylamide (50 mmol) in THF (40 mL) was added diethyl ketone (5.05 mL, 50 mmol) at –78 °C, and the solution was stirred for 1 h at –78 °C. To this solution was added diethyl chlorophosphate (7.95 mL, 55 mmol), and the solution was allowed to come to room temperature and stirred for 1 h. The reaction mixture was poured into water and extracted with ethyl acetate. After the mixture was dried over Na_2SO_4 and concentrated, the residue was purified by column chromatography on silica gel with use of ethyl acetate to give 10.6 g of the enol phosphate. This enol phosphate was added to the mixture of ((trimethylsilyl)-methyl)magnesium chloride (60 mmol) and $NiBr_2$ (546 mg, 2.5 mmol) in ether (60 mL) at 0 °C. The reaction mixture was then stirred for 1.5 days at room temperature. The reaction mixture was poured into saturated NH_4Cl and extracted with pentane. After the mixture was dried over Na_2SO_4, solvent was removed by distillation at atmospheric pressure, and the residue was purified by distillation (50–53 °C, 17 Torr) to give 1-(trimethylsilyl)-2-ethyl-2-butene (E/Z = 65/35) as a colorless oil: IR (film) 2963, 1248, 846, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (E) and –0.02 (Z) (s, 9H, $Si(CH_3)_3$), 0.98 (E) and 0.94 (Z) (t, J = 8 Hz, 3H, CH_3CH_2), 1.43–1.58 (m, 5H, $SiCH_2C$, CH_3), 1.95 (m, 2H, CH_3CH_2), 5.08 (E) and 4.97 (Z) (q, J = 7 Hz, 1H, CH=C). Anal. Calcd for $C_9H_{20}Si$: C, 69.23; H, 12.82. Found: C, 69.41; H, 12.74.

Preparation of Boronic Acids. A solution of the corresponding Grignard reagent in ether was added to the solution of $B(OMe)_3$ in ether at 0 °C. The reaction mixture was allowed to come to room temperature and stirred for 1 h. The reaction mixture was poured into saturated NH_4Cl and extracted with ether. The organic layer was dried over Na_2SO_4. After concentration, the residue was purified by column chromatography and/or recrystallization to give a boronic acid as a colorless solid.

Phenylboronic Acid: Obtained from Aldrich Chemical Co., Inc.

4-(Trifluoromethyl)phenylboronic acid: (39%) mp > 200 °C; IR (KBr) 3300, 1520, 1408, 1159, 1018, 844, 696, 401 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.70 (s, 2H, $B(OH)_2$), 7.60–8.38 (m, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$ + DMSO-d_6) δ 123.98, 124.31 (q, J = 273.5 Hz), 131.40 (q, J = 32.4 Hz), 133.90, 134.97. Anal. Calcd for $C_7H_6O_2BF_3$: C, 44.21; H, 3.16. Found: C, 44.33; H, 2.91.

2,4-Bis(trifluoromethyl)phenylboronic acid: (82%) mp > 200 °C; IR (KBr) 3350, 1510, 1344, 1190, 914, 850, 677 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.02 (br, 2H, $B(OH)_2$), 7.76–7.92 (m, 3H, C_6H_3); ^{13}C NMR ($CDCl_3$ + DMSO-d_6) δ 121.98 (septet, J = 4.3 Hz), 123.50 (q, J = 272.4 Hz), 124.01 (q, J = 273.5 Hz), 127.41 (q, J = 3.0 Hz), 131.11 (q, J = 33.2 Hz), 133.28 (q, J = 32.0 Hz), 134.03, 135.66 (q, J = 1.5 Hz). Anal. Calcd for $C_8H_5O_2BF_6$: C, 37.21; H, 1.94. Found: C, 37.35; H, 1.71.

3,5-Bis(trifluoromethyl)phenylboronic acid: Obtained from Lancaster Synthesis Ltd., U.K.

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(12) Schlosser, M.; Rachel, D.; Sylvain, C. *Helv. Chim. Acta.* **1984**, *67*, 284.

Typical Procedure for Asymmetric Allylation Reaction. Method A: To a solution of mono(2,6-diisopropoxybenzoyl) tartrate (**1**) (74 mg, 0.2 mmol) in dry propionitrile (1 mL) was added BH_3·THF (0.189 mL of 1.06 M solution in THF, 0.2 mmol) at 0 °C under argon. The reaction mixture was stirred for 1 h at 0 °C and cooled to –78 °C. To this solution were added aldehyde (1 mmol) and allyltrimethylsilane (1.2 mmol). After being stirred for several hours, the reaction mixture was poured into brine and extracted with ether. After drying and concentration, the residue was treated with tetrabutylammonium fluoride (1.5 mL of 1 M solution in THF, 1.5 mmol) in THF (3 mL). Usual workup followed by chromatographic separation gave products.

Method B: A solution of mono(2,6-diisopropoxybenzoyl) tartrate (**1**) (74 mg, 0.2 mmol) and arylboronic acid (0.2 mmol) in dry propionitrile (1 mL) was stirred for 30 min at room temperature under argon. After the reaction mixture cooled to –78 °C, to this solution were added aldehyde (1 mmol) and allyltrimethylsilane (1.2 mmol). After being stirred for several hours, the reaction mixture was poured into brine and extracted with ether. After drying and concentration, the residue was purified by column chromatography on silica gel to give products.

The absolute configurations were determined by comparison of optical rotation values with literature data; if necessary, the products were converted to known compounds. Diastereomeric and enantiomeric ratios were determined by analytical HPLC and ^1H NMR spectroscopy of the products and/or the corresponding (+)-MTPA esters.

(*R*)-1-Phenyl-3-buten-1-ol:[13] (entry 1, Table I; 46 %, 55% ee) $[\alpha]_D$ +31.8° (c 1.05, C_6H_6); IR (film) 3400, 2850, 1660, 1500, 1460, 1060, 920, 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10 (br, 1H, OH), 2.50 (m, 2H, CH_2), 4.71 (dd, J = 7, 6 Hz, 1H, C*H*OH), 5.15 (m, 2H, CH=CH_2), 5.82 (m, 1H, C*H*=CH_2), 7.32 (m, 5H, C_6H_5). HPLC (Daicel Chiralcel OD, hexane/*i*-PrOH = 20:1, flow rate = 0.5 mL/min): t_R = 17.5 min ((*R*)-isomer), t_R = 20.7 min ((*S*)-isomer).

(*R*)-3-Methyl-1-phenyl-3-buten-1-ol:[14] (entry 7, Table II; 96%, 86% ee) $[\alpha]_D$ +50.2° (c 1.19, C_6H_6); IR (film) 3400, 2850, 1660, 1470, 1060, 890, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.78 (s, 3H, CH_3), 2.09 (d, J = 2.5 Hz, 1H, OH), 2.41 (d, J = 7.5 Hz, 2H, CH_2), 4.80 (m, 1H, C*H*OH), 4.83 (br s, 1H, C=CH_2), 4.91 (br s, 1H, C=CH_2), 7.20–7.40 (m, 5H, C_6H_5). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.41; H, 8.74. HPLC (Daicel Chiralcel OD, hexane/*i*-PrOH = 20:1, flow rate = 0.5 mL/min): t_R = 16.5 min ((*S*)-isomer), t_R = 18.4 min ((*R*)-isomer).

(*E*)-5-Methyl-1-phenyl-1,5-hexadien-3-ol:[15] (entry 3, Table III; 96%, 84% ee) $[\alpha]_D$ +19.0° (c 1.44, C_6H_6); IR (film) 3400, 2950, 1650, 1500, 1450, 970, 890, 750, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.78 (s, 3H, CH_3), 1.84 (br s, 1H, OH), 2.32 (d, J = 7 Hz, 2H, CH_2), 4.42 (m, 1H, C*H*OH), 4.84 (br s, 1H, C=CH_2), 4.92 (br s, 1H, C=CH_2), 6.21 (dd, J = 7, 16 Hz, 1H, PhCH=C*H*), 6.62 (d, J = 16 Hz, 1H, PhC*H*=CH), 7.15–7.40 (m, 5H, C_6H_6). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.91; H, 8.68. ^1H NMR ($CDCl_3$) of (+)-MTPA ester: δ 3.51 (major isomer) and 3.55 (minor isomer) (s, 3H, CH_3O).

(*E*)-2-Methyl-1,5-nonadien-4-ol: (entry 5, Table III; 88%, 77% ee) $[\alpha]_D$ +4.04° (c 1.93, C_6H_6); IR (film) 3400, 2920, 1650, 1380, 1280, 1050, 970, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80–1.00 (m, 3H, CH_3CH_2), 1.35–1.50 (m, 2H, CH_3CH_2), 1.72 (br, 1H, OH), 1.78 (s, 3H, CCH_3), 2.02 (q, J = 7 Hz, 2H, $EtCH_2$), 2.24 (d, J = 7 Hz, 2H, CCH_2CHOH), 4.22 (m, 1H, C*H*OH), 4.88 (m, 2H, C=CH_2), 5.50 (m, 1H, PrCH=C*H*), 5.72 (m, 1H, PrC*H*=CH); ^{13}C NMR ($CDCl_3$) δ 13.74, 22.36, 22.54, 34.36,

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46.41, 70.13, 113.73, 131.99, 132.37, 142.37, 142.42. Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.79; H, 11.98. HPLC analysis of (+)-MTPA ester (JASCO Finepak Sil, hexane/Et_2O = 500:1, flow rate = 2 mL/min): t_R = 39.0 min (major isomer), t_R = 40.6 min (minor isomer).

(*E*)-2-Methyl-1,5-heptadien-4-ol:[16] (entry 6, Table III; 81%, 73% ee) $[\alpha]_D$ +1.55° (*c* 2.28, C_6H_6); IR (film) 3400, 2960, 1650, 1450, 1050, 1000, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56 (br, 1H, OH), 1.67 (d, *J* = 6 Hz, 3H, C*H*$_3$CH), 1.74 (s, 3H, C*H*$_3$C=CH_2), 2.19 (d, *J* = 7 Hz, 2H, CH_2), 4.17 (m, 1H, C*H*OH), 4.78 (s, 1H, C=CH_2), 4.85 (s, 1H, C=CH_2), 5.41–5.50 (m, 1H, CH_3-CH=C*H*), 5.52–5.75 (m, 1H, CH_3C*H*=CH). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.11; H, 11.17. ^1H NMR ($CDCl_3$) of (+)-MTPA ester δ 4.64 (major isomer) and 4.77 (minor isomer) (s, 1H, C*H*H=C): δ 4.72 (major isomer) and 4.83 (minor isomer) (s, 1H, CH*H*=C).

5-Methyl-1-phenyl-5-hexen-3-ol:[15] (entry 7, Table III; 71%, 48% ee) $[\alpha]_D$ −11.4° (*c* 1.50, C_6H_6); IR (film) 3350, 2940, 1650, 1500, 1450, 890, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56 (br, 1H, OH), 1.72 (s, 3H, CH_3), 1.77 (m, 2H, C*H*$_2$C=CH_2), 2.17 (m, 2H, PhCH_2C*H*$_2$), 2.60–2.82 (m, 2H, PhCH_2), 4.79 (m, 1H, C*H*OH), 4.78 (br s, 1H, C=CH_2), 4.86 (br s, 1H, C=CH_2), 7.16–7.27 (m, 5H, C_6H_5). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.00; H, 9.60. ^1H NMR ($CDCl_3$) of (+)-MTPA ester: δ 2.87 (major isomer) and 2.89 (minor isomer) (s, 3H, CH_3O).

(*S*)-2-Methyl-1-nonen-4-ol:[17] (entry 8, Table III; 65%, 63% ee) $[\alpha]_D$ −9.36° (*c* 1.56, C_6H_6); IR (film) 3370, 2960, 1650, 1450, 1380, 1130, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7 Hz, 3H, CH_3), 1.25–1.50 (m, 8H, CH_3(CH_2)$_4$), 1.60 (br, 1H, OH), 1.68 (s, 3H, C*H*$_3$C=CH_2), 2.08–2.22 (m, 2H, CH_2=CCH_2), 4.80 (s, 1H, C=CH_2), 4.88 (s, 1H, C=CH_2). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.81; H, 12.85. ^1H NMR ($CDCl_3$) of (+)-MTPA ester: δ 4.65 (major isomer) and 4.76 (minor isomer) (s, 1H, C*H*H=C), 4.72 (major isomer) and 4.83 (minor isomer) (s, 1H, CH*H*=C).

2-Methyl-1-octen-4-ol: (entry 9, Table III; 70%, 63% ee) $[\alpha]_D$ −8.56° (*c* 1.48, C_6H_6); IR (film) 3400, 2930, 1650, 1450, 1380, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7 Hz, 3H, C*H*$_3$-(CH_2)$_3$), 1.20–1.55 (m, 6H, CH_3(CH_2)$_3$), 1.64 (br, 1H, OH), 1.75 (s, 3H, C*H*$_3$C=CH_2), 2.01–2.18 (m, 2H, C*H*$_2$C=CH_2), 3.72 (m, 1H, C*H*OH), 4.79 (br s, 1H, C=CH_2), 4.88 (br s, 1H, C=CH_2); ^{13}C NMR ($CDCl_3$) δ 14.16, 22.49, 22.84, 28.00, 36.90, 46.30, 68.75, 113.52, 142.99. Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.75. Found: C, 75.85; H, 12.95. ^1H NMR ($CDCl_3$) of (+)-MTPA ester: δ 4.65 (major isomer) and 4.76 (minor isomer) (s, 1H, C*H*H=C), 4.72 (major isomer) and 4.82 (minor isomer) (s, 1H, CH*H*=C).

(*S*)-2-Methyl-1-hepten-4-ol:[18] (entry 10, Table III; 55%, 54% ee) $[\alpha]_D$ −8.22° (*c* 1.22, C_6H_6); IR (film) 3350, 2970, 1650, 1460, 1380, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7 Hz, 3H, C*H*$_3$(CH_2)$_2$), 1.37–1.47 (m, 4H, CH_3(CH_2)$_2$), 1.60 (br, 1H, OH), 1.73 (s, 3H, C*H*$_3$C=CH_2), 2.04–2.16 (m, 2H, C*H*$_2$C=CH_2), 3.73 (m, 1H, C*H*OH), 4.77 (br s, 1H, C=CH_2), 4.85 (br s, 1H, C=CH_2). Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.89; H, 12.46. ^1H NMR ($CDCl_3$) of (+)-MTPA ester: δ 4.65 (major isomer) and 4.76 (minor isomer) (s, 1H, C*H*H=C), 4.72 (major isomer) and 4.82 (minor isomer) (s, 1H, CH*H*=C).

2,3-Dimethyl-1-phenyl-3-buten-1-ol: (entry 4, Table I; 63%, diastereoselectivity = 96/4, 92% ee) $[\alpha]_D$ +1.0° (*c* 5.0, C_6H_6); IR (film) 3350, 2970, 1650, 1452, 1010, 890, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (d, *J* = 7 Hz, 3H, CHC*H*$_3$), 1.74 (s, 3H, C*H*$_3$C=CH_2), 1.88 (br, 1H, OH), 2.47 (m, 3H, CHC*H*$_3$), 4.70-4.84 (m, 3H, C=CH_2 and C*H*OH) 7.20–7.38 (m, 5H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 13.09, 21.93, 48.01, 74.96, 112.02, 126.16, 127.15, 128.13, 143.08, 147.53. Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.70; H, 9.34. ^1H NMR ($CDCl_3$) of (+)-MTPA ester: δ 5.80 (minor enantiomer of minor diastereomer), 5.87 (major enantiomer of minor diastereomer), 5.88 (minor enantiomer of major diastereomer), 5.93 (major enantiomer of major diastereomer).

2,3-Dimethyl-1-octen-4-ol: (entry 6, Table I; 30%, diastereoselectivity = 94/6, 85% ee) $[\alpha]_D$ −24.3° (*c* 1.14, C_6H_6); IR (film) 3300, 2960, 1650, 1460, 1380, 890 cm^{-1}; ^1H NMR δ 0.89 (t, 3H, $CH_3(CH_2)_3$, *J* = 7 Hz), 1.01 (d, 3H, CHC*H*$_3$), 1.20–1.52 (m, 7H, $CH_3(CH_2)_3$ and OH), 1.70 (s, 3H, C*H*$_3$C=CH_2), 2.22 (m, 1H, CH_3C*H*), 3.55 (m, 1H, C*H*OH), 4.75 (br s, 1H, C=CH_2), 4.82 (br s, 1H, C=CH_2); ^{13}C NMR ($CDCl_3$) δ 13.22, 14.10, 21.30, 22.75, 28.38, 34.41, 46.20, 72.37, 111.24, 148.30. Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.80; H, 12.80. Allylation products were converted to aldol derivatives by ozonolysis, and diastereomeric and enantiomeric ratios were determined by ^1H NMR spectroscopy of the corresponding (+)-MTPA esters. 4-Hydroxy-3-methyl-2-octanone: ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7 Hz, 3H, C*H*$_3$(CH_2)$_3$), 1:12 (d, *J* = 8 Hz, 3H, C*H*$_3$CH), 1.18-1.52 (m, 6H, CH_3(CH_2)$_3$), 2.15 (s, 3H, CH_3C=O), 2.25 (br, 1H, OH), 2.54 (dq, *J* = 2, 8 Hz, 1H, CH_3C*H*), 3.90 (m, 1H, C*H*OH). ^1H NMR ($CDCl_3$) of (+)-MTPA ester: δ 2.00 (major enantiomer of minor diastereomer), 2.04 (major enantiomer of major diastereomer), 2.08 (minor enantiomer of minor diastereomer), and 2.14 (minor enantiomer of major diastereomer) (s, 3H, CH_3C=O).

4,5-Dimethyl-3-hydroxy-1-phenyl-1,5-hexadiene: (entry 12, Table III; diastereoselectivity = 92/8, 89% ee) IR (film) 3400, 2968, 1645, 1448, 1375, 964, 891, 748, 642 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (d, 3H, *J* = 7 Hz, threo CH_3), 1.12 (d, *J* = 7 Hz, 3H, erythro CH_3), 1.75 (s, 3H, C*H*$_3$C=CH_2), 1.90 (br, 1H, OH), 2.35 (quint, 1H, *J* = 6 Hz, CH_3C*H*), 4.05 (t, *J* = 9 Hz, 1H, threo C*H*OH), 4.30 (t, *J* = 6 Hz, 1H, erythro C*H*OH), 4.80–5.00 (m, 2H, C=CH_2), 6.20 (m, 1H, PhCH=C*H*), 6.60 (dd, *J* = 2, 16 Hz, 1H, PhC*H*=CH); ^{13}C NMR ($CDCl_3$) δ 13.92, 21.48, 47.13, 73.84, 112.27, 126.49, 127.56, 128.61, 130.27, 130.96, 136.99, 147.19. Anal. Calcd for $C_{14}H_{18}O$: C, 83.17; H, 8.91. Found: C, 83.35; H, 8.89. ^1H NMR ($CDCl_3$) of (+)-MTPA ester: δ 0.30 (major enantiomer of minor diastereomer), 0.33 (major enantiomer of major diastereomer), 0.35 (minor enantiomer of minor diastereomer), and 0.455 (minor enantiomer of major diastereomer) (d, *J* = 7 Hz, 3H, C*H*$_3$CH).

(1*R*,2*S*)-3-Ethyl-2-methyl-1-phenyl-3-buten-1-ol: (entry 7, Table I; 74%, erythro/threo = 97/3, 96% ee) $[\alpha]_D$ −13.0° (*c* 6.50, C_6H_6); IR (film) 3350, 2970, 1640, 1450, 1010, 890, 760, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (d, *J* = 6 Hz, 3H, CHC*H*$_3$), 1.01 (t, *J* = 7 Hz, 3H, C*H*$_3$CH$_2$), 1.84 (br s, 1H, OH), 2.02 (m, *J* = 7.4 Hz, 2H, CH_3C*H*$_2$), 2.47 (m, 1H, CH_3C*H*), 4.42 (d, *J* = 9.5 Hz, 1H, C*H*OH (threo isomer)), 4.72 (d, *J* = 5 Hz, 1H, C*H*OH (erythro isomer)), 4.88 (d, *J* = 2 Hz, 1H, C=CH_2), 4.92 (d, *J* = 2 Hz, 1H, C=CH_2). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.00; H, 9.72. Allylation products were converted to aldol derivatives by ozonolysis, and diastereomeric and enantiomeric ratios were determined by analytical HPLC of the corresponding (+)-MTPA esters. 1-Hydroxy-2-methyl-1-phenyl-3-pentanone:[19] ^1H NMR ($CDCl_3$) δ 0.98 (t, *J* = 7 Hz, 3H, C*H*$_3$CH$_2$), 1.05 (d, *J* = 7 Hz, 3H, C*H*$_3$CH), 2.20–2.70 (m, 2H, CH_3C*H*$_2$), 2.82 (m, 1H, CH_3C*H*), 3.10 (br, 1H, OH), 5.05 (d, *J* = 3 Hz, 1H, C*H*OH), 7.15–7.38 (m, 5H, C_6H_5). HPLC of (+)-MTPA ester (JASCO Finepak Sil, hexane/*i*-PrOH = 40:1, flow rate = 2 mL/min): t_R = 21.7 min (threo major isomer), t_R = 22.5 (erythro major isomer), t_R = 23.8 min (threo minor isomer), t_R = 26.1 min (erythro minor isomer).

2-Ethyl-3-methyl-1,5-heptadien-4-ol: (entry 10, Table I; 21%, diastereoselectivity = 95/5, 89% ee) $[\alpha]_D$ −30° (*c* 0.79, C_6H_6);

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IR (film) 3350, 2966, 1650, 1541, 1458, 966, 891 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (m, 6H, CH_3CH_2 and CH_3), 1.58 (br, 1H, OH), 1.67 (d, J = 6 Hz, 3H, CH_3CH=CH), 1.90–2.28 (m, 3H, CH_3CH_2 and CH), 4.02 (m, 1H, CHOH), 4.79 (br s, 1H, C=CH_2), 4.84 (br s, 1H, C=CH_2), 5.45 (dd, J = 7, 15 Hz, 1H, CH_3CH=CH), 5.65 (dq, J = 6, 15 Hz, 1H, CH_3CH=CH); ^{13}C NMR ($CDCl_3$) δ 12.89, 13.88, 17.76, 28.21, 38.11, 74.00, 109.19, 126.66, 132.30, 153.53. GC (130 °C) of (+)-MTPA ester: t_R = 73.7 min (major enantiomer of minor diastereomer), t_R = 76.8 min (minor enantiomer of minor diastereomer), t_R = 79.7 min (major enantiomer of major diastereomer), t_R = 83.7 min (minor enantiomer of major diastereomer).

(2*S*,3*S*)-2-Ethyl-3-methyl-1-hepten-4-ol: (entry 11, Table I; 36%, erythro/threo = 95/5, 86% ee) $[\alpha]_D$ −39° (*c* 2.4, C_6H_6); IR (film) 3350, 2963, 1641, 1460, 970, 891 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, J = 8 Hz, 3H, $CH_3(CH_2)_2$), 1.02 (m, 6H, CH_3CH_2 and CH_3CH), 1.20–1.50 (m, 4H, $CH_3(CH_2)_2$), 1.52 (br, 1H, OH), 1.88–2.20 (m, 3H, CH_3CH_2 and CH), 3.52 (m, 1H, CHOH), 4.78 (s, 1H, C=CH_2), 4.88 (s, 1H, C=CH_2); ^{13}C NMR ($CDCl_3$) δ 13.04, 13.95, 17.00, 19.58, 28.28, 36.74, 44.76, 72.25, 108.85, 154.27. Allylation products were converted to aldol derivatives by ozonolysis, and diastereomeric and enantiomeric ratios were determined by ^1H NMR spectroscopy of the corresponding (+)-MTPA esters. 5-Hydroxy-4-methyl-3-octanone:[20] ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7 Hz, 3H, $CH_3(CH_2)_2$), 1.02 (t, J = 7 Hz, 3H, CH_3CH_2), 1.08 (d, J = 7 Hz, 3H, CH_3-CH), 1.12–1.55 (m, 4H, $CH_3(CH_2)_2$), 2.50 (m, 3H, CH_3CH_2 and CH_3CH), 2.78 (br 1H, OH), 3.85 (m, 1H, CHOH). ^1H NMR ($CDCl_3$) of (+)-MTPA ester: δ 3.48 (threo minor isomer), 3.51 ((2*R*,4*R*)-isomer), 3.53 (threo major isomer), 3.55 ((2*S*,4*S*)-isomer) (s, 3H, CH_3O).

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