Asymmetric Addition of Allylic Stannanes to Aldehydes Catalyzed by BINAP•Ag(I) Complex

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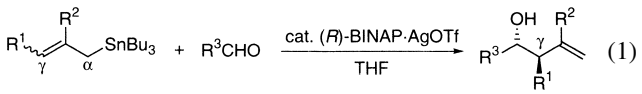
Catalytic asymmetric allylation of aldehydes with allylic trialkylstannanes was achieved with BINAP•AgOTf complex as catalyst. The chiral silver(I) catalyst was readily prepared by stirring an equimolar mixture of BINAP and silver(I) triflate in THF at room temperature. The allylation of a variety of aromatic and α,β-unsaturated aldehydes resulted in high yields and remarkable enantioselectivities. Addition of γ-substituted allylstannanes such as 2-butenyltributylstannane and trialkyl-2,4-pentadienylstannanes exclusively gave γ-adducts. High *anti*-selectivity was also obtained in the reaction with 2-butenyltributylstannane, irrespective of the configuration at the double bond.

Asymmetric allylation of carbonyl compounds to prepare optically active secondary homoallylic alcohols is a useful synthetic method, since the products are easily transformed into optically active β-hydroxy carbonyl compounds and various other chiral compounds.[1] Although many studies on the reaction employing a stoichiometric amount of chiral Lewis acids have been reported, there are few catalytic processes including chiral (acyloxy)borane (CAB) complex[2] or a binaphthol-derived chiral titanium complex[3] as a catalyst. Reported herein is a new catalytic enantioselective allylation reaction of aldehydes with allylic trialkylstannanes using BINAP•silver(I) complex as a catalyst (Eq. 1).[4] High γ-, *anti*-, and enantioselectivities are obtained by this method.



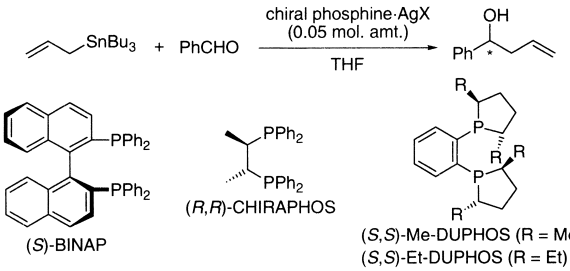
(1)

Results and Discussion

Enantioselective Allylation and Methallylation of Aldehydes. We have previously shown that highly chemoselective allylation of carbonyl compounds takes place with tetraallylstannane in acidic aqueous solution.[5] Our ongoing concern about selective allylation has guided us to attempt an investigation of allylation of aldehydes with allyltributylstannane catalyzed by various metal compounds under neutral reaction conditions. Among the metal catalysts tested, silver(I) compound showed remarkable reactivity. For example, treatment of benzaldehyde with allyltributylstannane under the influence of 0.05 molar amount of silver(I) trifluoroacetate in a 1:1 mixture of THF and H_2O at 20 °C for 4 h gave the homoallylic alcohol in 48% yield. Addition of 0.1 molar amount of triphenylphosphine raised the chemical yield to > 90%. This result led us to use chiral phosphine•silver(I) complex as a catalyst for asymmetric allylation of aldehydes with allylic stannanes.

The BINAP•silver(I) catalyst was readily prepared by stirring a 1:1 mixture of (*S*)-BINAP and silver(I) triflate in dry THF at room temperature for 10 min. Treatment of benzaldehyde with an equimolar amount of allyltributylstannane in dry THF in the presence of this catalyst (0.05 molar amount) at −20 °C for 8 h furnished the (*S*)-enriched homoallylic alcohol in 88% yield with 96% ee (Table 1, entry 4). Using a variety

Table 1. Allylation Reaction of Benzaldehyde with Allyltributylstannance in the Presence of Various Chiral Phosphine–Silver(I) Complex[a)]



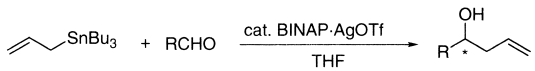
Entry	Chiral phosphine•AgX	Yield%[b)]	ee%[c)]	Configuration
1	(*S*)-BINAP•$AgOCOCF_3$	47	40	*S*
2	(*S*)-BINAP•$AgClO_4$	1	26	*S*
3	(*S*)-BINAP•$AgNO_3$	26	53	*S*
4	(*S*)-BINAP•AgOTf	88	96	*S*
5	(*R*,*R*)-CHIRAPHOS•AgOTf	97	2	*R*
6	(*S*,*S*)-Me-DUPHOS•AgOTf	4	48	*R*
7	(*S*,*S*)-Et-DUPHOS•AgOTf	13	3	*R*

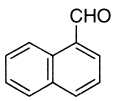
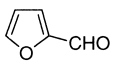
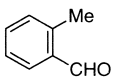
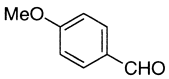
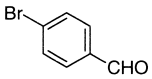
a) Unless otherwise specified, the reaction was carried out using chiral phophine•AgX (0.05 mol amt.), allyltributylstannane (1 mol amt.) and benzaldehyde (1 mol amt.) in THF at −20 °C for 8 h. b) Isolated yield. c) Determined by HPLC analysis (Chiralcel OD-H, Daicel Chemical Industries, Ltd.).

of chiral phosphine–silver(I) catalysts, we examined the enantioselectivity of this process; Table 1 shows enantiomeric excesses and yields of the products obtained by the reaction with 0.05 molar amount of other chiral phosphine–silver(I) complexes in THF at −20 °C. The allylation catalyzed by (*S*)-BINAP•AgOTf was also performed at various temperatures. The results are as follows (temperature, yield, enantioselectivity): 20 °C, 16% yield, 79% ee; 0 °C, 16% yield, 86% ee; −20 °C, 88% yield, 96% ee; −45 °C, 54% yield, 94% ee; −78 °C, < 1% yield. The catalyst was deactivated for prolonged periods above 0 °C. As a consequence, the reaction catalyzed by the BINAP•silver(I) triflate complex at −20 °C afforded the highest yield and ee.

Table 2 summarizes the data given by the reaction of diverse aldehydes with equimolar amounts of allyltributylstannane at −20 °C in THF. The chief features of the results are as follows: (1) all of the reactions were furnished in high yields and remarkable enantioselectivities not only with aromatic aldehydes but also with α,β-unsaturated aldehydes (entries 2 and 5), except one aliphatic aldehyde, which gave a lower chemical yield (entry 9); (2) In the reaction with α,β-unsaturated aldehydes, 1,2-addition reaction took place exclusively (entries 2 and 5); (3) the enantioselectivity was not affected by introduction of a methyl group into the *ortho*-position of benzaldehyde (compare entries 1 and 6); (4) an electron-withdrawing substituent at the *para*-position of benzaldehyde enhanced the allylation (compare entries 1, 7, and 8).

Table 2. Asymmetric Allylation Reactions of Aldehydes Catalyzed by BINAP•AgOTf Complex[a)]

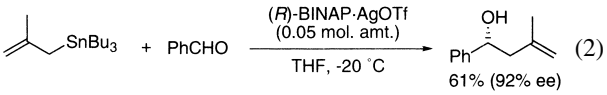


Entry	Aldehyde	Yield%[b)]	ee%[c)]	Configuration
1	PhCHO	88	96	*S*
2[d)]	(*E*)-PhCH=CHCHO	83	88	*S*
3[d)]		89	97	*S*
4[e)]		94	93	*S*
5[f)]	(*E*)-*n*-C_3H_7CH=CHCHO	72	93[g)]	
6		85	97	
7		59	97	*S*
8		95	96	
9[f)]	$PhCH_2CH_2CHO$	47	88	

a) Unless otherwise specified, the reaction was carried out using (*S*)-BINAP•AgOTf (0.05 mol amt.), allyltributylstannane (1 mol amt.) and aldehyde (1 mol amt.) in THF at −20 °C for 8 h. b) Isolated yield. c) Determined by HPLC analysis (Chiralcel OD-H, OJ, or Chiralpak AD, Daicel Chemical Industries, Ltd.). d) 3 mol amt. of allyltributylstannane and 0.15 mol amt. of (*S*)-BINAP•AgOTf was used. e) 4 mol amt. of allyltributylstannane and 0.2 mol amt. of (*S*)-BINAP•AgOTf was used. f) The reaction was started using 2 mol amt. of allyltributylstannane and 0.1 mol amt. of (*R*)-BINAP•AgOTf, and 0.1 mol amt. of the catalyst was added after 4 h. g) Determined by HPLC analysis (Chiralpak AD) of the benzoate of the product.

In order to elucidate the catalytic mechanism of the present allylation and to determine whether the BINAP•Ag(I) complex acts as a chiral Lewis acid catalyst or an allylsilver reagent, we undertook an experiment which had the following result: when (*S*)-BINAP•AgOTf complex was treated with an equimolar amount of allyltributylstannane in THF at 20 °C, followed by quenching half of the resulting reaction mixture with brine, 98% of the allylstannane compound was recovered. Exposure of another half of the mixture to an equimolar amount of benzaldehyde at −20 °C for 8 h gave the (*S*)-homoallylic alcohol in 35% yield with > 99% ee. In this reaction, allyltributylstannane was entirely consumed; however, ca. 50% of benzaldehyde remained unreacted, probably owing to unknown side reactions peculiar to this stoichiometric reaction system. This result shows that no transmetallation occurs prior to addition of benzaldehyde in this stoichiometric allylation.

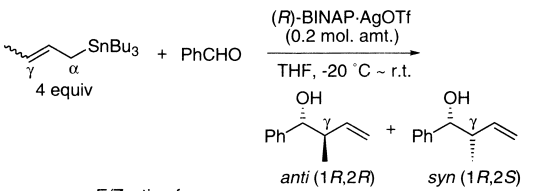
We found that additions of 2-methyl-2-propenylstannanes[6] to aldehydes also took place highly enantioselectively employing BINAP•AgOTf catalyst.[4a,8] For instance, the 2-methyl-2-propenylation of benzaldehyde by 0.05 molar amount of (*R*)-BINAP•silver(I) triflate in THF at −20 °C for 8 h gave the corresponding optically active homoallylic alcohol in 75% yield with 92% ee (Eq. 2). In general, reactivity of the 2-methyl-2-propenylstannane was relatively lower than that of allyltributylstannane, while use of an increased amount (up to 0.2 molar amount) of the catalyst resulted in satisfactory yields. The other features of this process were almost the same as those of the allyl addition process.[4a]



(2)

Asymmetric γ- and Antiselective 2-Butenylation of Aldehydes. Condensation of γ-substituted allylmetals with aldehydes is a fascinating subject with regard to the regioselectivities (α/γ) and stereoselectivities (*E*/*Z* or *anti*/*syn*). 2-Butenyltributylstannane is well known to react with aldehydes in CH_2Cl_2 γ- and *syn*(*erythro*)-selectively irrespective of the configuration of the 2-butenylstannane in the presence of 2 molar amounts of BF_3•OEt_2.[9] If the BINAP•silver(I) complex behaves as a chiral Lewis acid catalyst, optically active γ-allylated *syn*-homoallylic alcohols should be predominantly produced in the 2-butenylation. Accordingly, we investigated the BINAP•silver(I) catalyzed reaction of (*E*)- and (*Z*)-2-butenylstannane.[8] Addition of (*E*)-2-butenyltributylstannane (*E*/*Z* = 95/5) to benzaldehyde in the presence of 0.2 molar amount of (*R*)-BINAP•AgOTf in THF at −20 °C–r.t., however, exclusively gave the γ-adduct with an *anti*/*syn* ratio of 85/15, against our expectations.[10] The *anti*-isomer was obtained in 94% ee with

1*R*,2*R* configuration (Eq. 3). Use of (*Z*)-2-butenyltributylstannane (*E*/*Z* = 2/98) or a nearly 1:1 mixture of (*E*)- and (*Z*)-2-butenyltributylstannane resulted in a similar *anti*/*syn* ratio and enantioselectivity (Eq. 3).



(3)

E/*Z* ratio of 2-butenylstannane	Yield/%	*anti* (% ee)/*syn* (% ee)
95/5	56	85 (94)/15 (64)
2/98	72	85 (91)/15 (50)
53/47	45	85 (94)/15 (57)

Asymmetric γ-selective Pentadienylation of Aldehydes. Reaction of aldehydes with 2,4-pentadienylmetal compounds yields two regioisomeric dienols, ε-adduct and γ-adduct, which are both valuable synthetic intermediates of natural products, and various regioselective processes of introducing a pentadienyl group into organic compounds have been developed using diverse metal reagents (Fig. 1).[11] The ε-attacked conjugated dienols are selectively formed in the reaction of pentadienylsilanes or stannanes with aldehydes promoted by strong Lewis acid, such as BF_3•OEt_2 and $TiCl_4$, via an acyclic transition-state structure.[12] In contrast, predominant formation of the unconjugated γ-adducts via a cyclic transition-state structure has been accomplished employing more reactive pentadienylmetal compounds (M = Mg, Zn, B, etc.).[13] However, as far as we know, the asymmetric version of these reactions has still not been achieved, probably because the γ-pentadienylated products are not obtained by the Lewis acid-promoted reactions using silane and stannane reagents which are more suitable to asymmetric induction.[14] We achieved a novel catalytic enantioselective γ-pentadienylation reaction of aldehydes with pentadienylstannanes[15] using BINAP•silver(I) complex as a catalyst.[16]

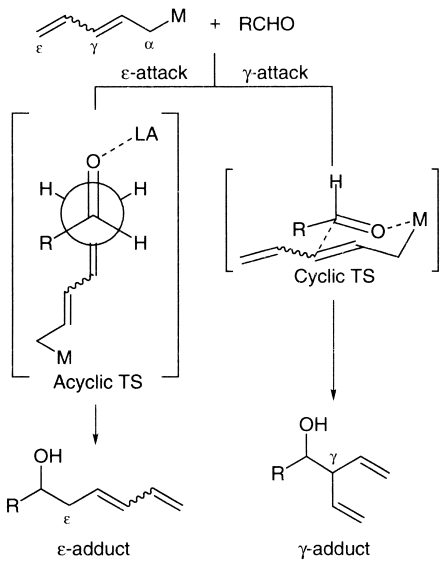
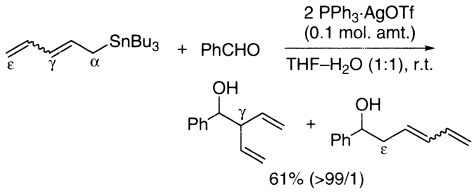


Fig. 1. Reaction of Pentadinylmetal reagents with aldehydes.

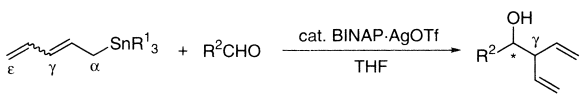
As described above, 2-butenyltributylstannane is proven to react selectively at the γ-position with an aldehyde in the presence of a catalytic amount of BINAP•silver(I) complex.[8] We first studied the condensation of pentadienylstannanes with aldehydes using achiral phosphine–silver(I) catalysts in aqueous media, with the expectation that such γ-substituted allylstannanes should also show similar high γ-selectivity. When tributylpentadienylstannane was added to a mixture of equimolar amount of benzaldehyde and 0.1 molar amount of bis(triphenylphosphine)–silver(I) triflate in a 1:1 mixture of THF and H_2O at 20 °C for 3 h, the γ-adduct was obtained nearly exclusively in 61% yield (Eq. 4).

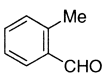
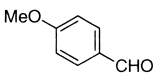
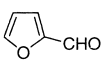


(4)

This γ-allylation preference encouraged us to investigate the BINAP•silver(I) complex-catalyzed pentadienylation under anhydrous reaction conditions. When benzaldehyde was treated with tributylpentadienylstannane in dry THF under the influence of 0.1 molar amount of (*S*)-BINAP•AgOTf at −20 °C for 8 h, the optically active γ-pentadienylated alcohol was produced in 61% yield with 90% ee (Table 3, entry 1). Table 3

Table 3. Enantioselective Addition of Pentadienylstannanes to Aldehydes Catalyzed by BINAP•AgOTf Complex[a)]



Entrry	$SnR^1{}_3$	Aldehyde	Yield%[b)]	ee%[c)]
1[d)]	$SnBu_3$	PhCHO	61	90
2	$SnMe_3$		68	89
3	$SnMe_3$		57	90
4	$SnMe_3$		41	87
5	$SnMe_3$		62	89
6	$SnBu_3$	(*E*)-PhCH=CHCHO	73	58
7	$SnMe_3$		68	58
8	$SnBu_3$	$PhCH_2CH_2CHO$	52	71
9	$SnBu_3$	$PhCOCH_3$	< 1	—

a) Unless otherwise specified, the reaction was carried out using (*R*)-BINAP•AgOTf (0.1 mol amt.), tributylpentadienylstannane (R^1 = *n*-Bu, *E*:*Z* = 97:3, 1 mol amt.) or trimethylpentadienylstannane (R^1 = Me, *E*:*Z* = 90:10, 1 mol amt.), and aldehyde (1 equiv) in THF at −20 °C for 8 h. b) Isolated yield. c) Determined by HPLC analysis (Chiralcel OD-H or Chiralpak AD, Daicel Chemical Industries, Ltd.). d) (*S*)-BINAP•AgOTf was used.

shows other results acquired in the reaction of various aldehydes and pentadienylstannanes catalyzed by (*R*)-BINAP•AgOTf. Several key findings are as follows: (1) no meaningful differences in chemical yield or enantioselectivity were seen between tributylpentadienylstannane and trimethylpentadienylstannane (compare entries 1, 2, 6, and 7); (2) substituted aromatic aldehydes and furfural exhibited comparable enantioselectivity to that of benzaldehyde (entries 3–5); (3) exclusive 1,2-selectivity was observed for the reaction of an α,β-unsaturated aldehyde (entries 6 and 7); (4) ketone showed no reactivity under the standard reaction conditions (entry 9).

It is not clear why *anti* selectivity is obtained for the 2-butenyl addition reaction (Eq. 3) regardless of the double-bond geometry of the stannane, although some transition-state models are conceivable (Fig. 2). (*E*)- and (*Z*)-2-Butenyltributylstannane have been reported to react with aldehydes in CH_2Cl_2 with γ- and *syn(erythro)*-selectivities in the presence of 2 molar amounts of BF_3•OEt_2. For the *syn*-selective reaction of 2-butenylstannane, Y. Yamamoto proposed an acyclic antiperiplanar transition-state structure **A**.[9] Subsequently, Keck et al. suggested a *syn*-synclinal alternative **B** to explain the higher *syn*-selectivity obtained with the *E*-stannane.[17] If the BINAP•Ag(I) complex acts as a Lewis acid in the *anti*-selective allylation, the reaction might proceed via an acyclic antiperiplanar **D**, which seems to have the least steric interaction between BINAP•Ag(I) and the stannyl methylene carbon and/or the R^1 group of the allylic stannane. A cyclic transition-state **E** is also a possible model for a Lewis acid mechanism, since pentadienylstannanes react selectively at the γ-carbon, as shown in Table 3. Nishigaichi and Takuwa proposed a similar cyclic model for $ZnCl_2$-promoted *anti*-selective γ-allylation of aldehydes with γ-substituted allylstannanes.[10a] In contrast, a cyclic transition-state model **G** containing a BINAP-coordinated silver atom instead of trialkylstannyl group is a probable alternative leading to the *anti*-product when transmetallation to an allylic silver occurs and *E*/*Z* isomerization of the silver compound is sufficiently rapid. The corresponding *syn*-homoallylic alcohol should be obtained from the (*Z*)-allylic silver via a cyclic transition-state model **F**. It is uncertain whether the BINAP•Ag(I) catalyzed allylation advances by the Lewis acid mechanism or the transmetallation mechanism. The result that almost no transmetallation took place at all before addition of aldehyde, as described above, supports the Lewis acid mechanism. However, the transmetallation pathway cannot be denied completely because the recovered 2-butenyltributylstannane was a little isomerized: for instance, reaction of equimolar amount of (*Z*)-2-butenyltributylstannane (*E*/*Z* = 7/93) with benzaldehyde in the presence of 0.2 molar amount of (*R*)-BINAP•AgOTf in THF at −20–20 °C for 24 h gave a 14/86 mixture of (*E*)- and (*Z*)-2-butenylstannane in 47% recovered yield and a mixture of homoallylic alcohols in 30% combined yield with an *anti*/*syn* ratio of 86/14. The enantioselectivities of the *anti*- and *syn*-isomers were 94% ee and 65% ee, respectively. Single electron transfer (SET) mechanism is also a conceivable alternative; however, at present we have no experimental evidence for the mechanism.

Conclusion

We have described here a novel method for highly enantioselective allylation of aldehydes with allylic trialkylstannanes using a catalytic amount of BINAP•Ag(I) complex. The main features of the present process are as follows: (1) the procedure is operationally simple and can furnish a variety of optically active homoallylic alcohols with high enantioselectivity; (2) γ-adducts are exclusively formed in the reaction with 2-butenyl- and 2,4-pentadienylstannanes; (3) remarkable *anti*-selectivity is observed for the reaction with 2-butenyltributylstannanes, irrespective of the configuration at the double bond. The reaction represents a new class of asymmetric allylation catalyzed by chiral transition metal compounds and can be performed on a substantial scale using ordinary laboratory equipment, because no complex preparation of catalyst is required. The re-

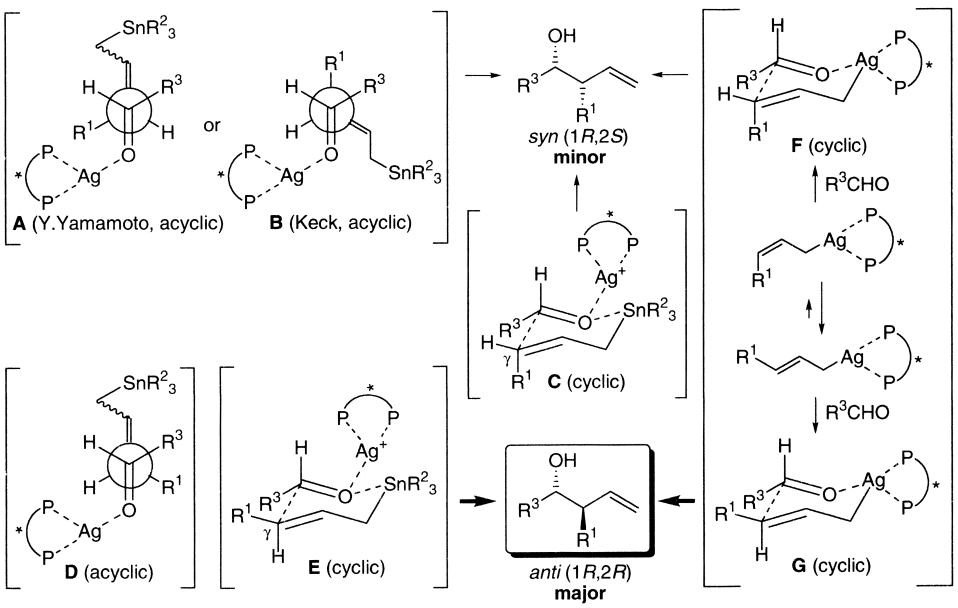


Fig. 2. Probable acyclic and cyclic transition state structures.

markable regio- and stereoselectivities of the allylation reaction provide an unprecedented route to homoallylic alcohols; the route is widely applicable to organic synthesis.

Experimental

General. Analytical TLC was done on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. Column chromatography was conducted using silica gel 60 (E. Merck 9385, 230–400 mesh). Infrared (IR) spectra were recorded on a Shimadzu FTIR-8100 spectrometer. ^{1}H NMR spectra were measured on a Varian Gemini-300 (300 MHz) spectrometer. Chemical shifts of ^{1}H NMR spectra were reported relative to tetramethylsilane (δ 0) or chloroform (δ 7.26). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were measured on a Varian Gemini-300 (75 MHz) spectrometer. Chemical shifts of ^{13}C NMR spectra were reported relative to $CDCl_3$ (δ 77.0). Analytical gas-liquid phase chromatography (GC) was performed on a Shimadzu GC-8A instrument equipped with a flame ionization detector and a capillary column of PEG-HT (0.25 × 25000 mm), using nitrogen as carrier gas. Analytical high-performance liquid chromatography (HPLC) was done with a Shimadzu 10A instrument using a chiral column (4.6 mm × 25 cm, Daicel CHIRALCEL OB-H, OD-H, OJ, or CHIRALPAK AD). Optical rotation was measured on a JASCO DIP-1000 polarimeter. Microanalyses were accomplished at the Faculty of Agriculture, Nagoya University.

All experiments were carried out under an atmosphere of standard grade argon gas (oxygen < 10 ppm) and exclusion of direct light. Dry THF was used as purchased from Wako Pure Chemical (dehydrated, > 99.5%, water: < 0.005%). Silver triflate (99+%) was used as purchased from Aldrich. (*R*)- and (*S*)-BINAP (guaranteed reagent) were used as purchased from Nacalai Tesque. Allyltributylstannane (Aldrich) and aldehydes were purified by distillation before use. Tributyl(2-methyl-2-propenyl)stannane, (*E*)-enriched 2-butenyltributylstannane (*E*/*Z* = 95/5), and (*Z*)-enriched 2-butenyltributylstannane (*E*/*Z* = 2/98) were synthesized from the corresponding allylic chlorides by reaction with tributylstannyllithium in dry THF[18] and were purified by distillation before use. (*E*)- and (*Z*)-enriched 2-butenyl chlorides were prepared by treatment of the corresponding allylic alcohols with a mixture of *N*-chlorosuccinimide, and dimethyl sulfide in CH_2Cl_2.[19] Pentadienylstannanes were prepared by reaction of a pentadienyl Grignard reagent, generated from 1-chloro-2,4-pentadiene and magnesium turnings, with R_3SnCl in ether, for R = *n*-Bu, *E*:*Z* = 97:3; for R = Me, *E*:*Z* = 90:10.[15] Other chemicals were used as purchased.

Typical Experimental Procedure for Asymmetric Allylation of Aldehydes with Allylic Tributylstannane Reagents Catalyzed by BINAP•AgOTf Complex: Synthesis of (*S*)-1-Phenyl-3-buten-1-ol (Entry 4 in Table 1 and Entry 1 in Table 2).[20] A mixture of AgOTf (26.4 mg, 0.103 mmol) and (*S*)-BINAP (66.5 mg, 0.107 mmol) was dissolved in dry THF (3 mL) under argon atmosphere and with direct light excluded, and stirred at 20 °C for 10 min. To the resulting solution was added dropwise a THF solution (3 mL) of benzaldehyde (208 mg, 1.96 mmol) and allyltributylstannane (663 mg, 2.00 mmol) successively at −20 °C. The mixture was stirred for 8 h at this temperature and treated with a mixture of 1 M (=1 mol dm^{-3}) HCl (10 mL) and solid KF (ca. 1 g) at ambient temperature for 30 min. The resulting precipitate was filtered off by a glass filter funnel filled with Celite® and silica gel. The filtrate was dried over $MgSO_4$ and concentrated in vacuo after filtration. The residual crude product was purified by column chromatography on silica gel (1:10 ethyl acetate/hexane as the eluant) to afford the homoallylic alcohol (258 mg, 88% yield) as a colorless oil. The enantioselectivity was determined to be 96% ee by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{minor} = 18.2 min (*R*), t_{major} = 19.9 min (*S*). The absolute configuration was determined to be *S* by comparison of the $[\alpha]_D$ value with reported data; (*R*)-enriched alcohol (90% ee): $[\alpha]_D$ +43.7° (*c* 6.7, benzene).[21] Observed $[\alpha]_D$ value of the product with 96% ee: $[\alpha]_D^{26}$ −50.5° (*c* 1.1, benzene). Spectral data of the product: TLC R_f 0.34 (1:3 ethyl acetate/hexane); IR (neat) 3700–3120, 3077, 3031, 2907, 1642, 1603, 1493, 1455, 1316, 1198, 1115, 1076, 1048, 916, 870, 758, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (d, 1 H, *J* = 2.5 Hz, OH), 2.52 (m, 2 H, CH_2), 4.75 (dt, 1 H, *J* = 6.9, 2.5 Hz, CH), 5.14–5.20 (m, 2 H, 2 vinyls), 5.82 (m, 1 H, vinyl), 7.25–7.37 (m, 5 H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.5, 73.2, 117.8, 125.7 (2 C), 127.2, 128.1 (2 C), 134.3, 143.8.

(*S*),(*E*)-1-Phenyl-1,5-hexadien-3-ol (Entry 2 in Table 2).[20] TLC R_f 0.28 (1:3 ethyl acetate/hexane); IR (neat) 3670–3120, 3079, 3026, 2979, 1642, 1599, 1579, 1493, 1449, 1130, 1071, 1030, 967, 916, 749, 693 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78 (br, 1 H, OH), 2.39 (m, 2 H, CH_2), 4.37 (dd, 1 H, *J* = 12.3, 6.1 Hz, CH_2), 5.16–5.22 (m, 2 H, 2 vinyls), 5.87 (m, 1 H, vinyl), 6.25 (dd, 1 H, *J* = 15.9, 6.3 Hz, vinyl), 6.62 (d, 1 H, *J* = 15.7 Hz, vinyl), 7.22–7.40 (m, 5 H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.9, 71.7, 118.4, 126.4 (2 C), 127.6, 128.5 (2 C), 130.3, 131.5, 134.0, 136.6; $[\alpha]_D^{24}$ +15.4° (*c* 1.1, Et_2O). The enantioselectivity was determined to be 88% ee by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 1.0 mL/min): t_{minor} = 13.3 min (*R*), t_{major} = 23.5 min (*S*).

(*S*)-1-(1-Naphthyl)-3-buten-1-ol (Entry 3 in Table 2).[21,22] TLC R_f 0.36 (1:3 ethyl acetate/hexane); IR (neat) 3650–3120, 3071, 2979, 2940, 2908, 1640, 1597, 1510, 1433, 1395, 1167, 1055, 916, 801, 777 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.16 (d, 1 H, *J* = 2.8 Hz, OH), 2.57–2.72 (m, 1 H, one proton of CH_2), 2.72–2.85 (m, 1 H, one proton of CH_2), 5.17–5.27 (m, 2 H, 2 vinyls), 5.54 (m, 1 H, CH), 5.94 (m, 1 H, vinyl), 7.46–7.55 (m, 3 H, aromatic), 7.67 (d, 1 H, *J* = 7.1 Hz, aromatic), 7.79 (d, 1 H, *J* = 8.2 Hz, aromatic), 7.87–7.90 (m, 1 H, aromatic), 8.08 (d, 1 H, *J* = 7.8 Hz, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.7, 69.8, 118.0, 122.7, 122.9, 125.3 (2 C), 125.9, 127.8, 128.8, 130.1, 133.6, 134.7, 139.4; $[\alpha]_D^{25}$ −96.0° (*c* 1.1, benzene). The enantioselectivity was determined to be 97% ee by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min): t_{major} = 7.8 min (*S*), t_{minor} = 12.8 min (*R*).

(*S*)-1-(2-Furyl)-3-buten-1-ol (Entry 4 in Table 2).[23] TLC R_f 0.30 (1:3 ethyl acetate/hexane); IR (neat) 3750–3040, 3079, 2980, 1644, 1505, 1436, 1341, 1229, 1150, 1057, 1011, 922, 885, 864, 812, 739 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (br, 1 H, OH), 2.61–2.66 (m, 2 H, CH_2), 4.76 (m, 1 H, CH), 5.14–5.23 (m, 2 H, 2 vinyls), 5.82 (m, 1 H, vinyl), 6.26 (d, 1 H, *J* = 3.2 Hz, vinyl), 6.34 (dd, 1 H, *J* = 3.1, 1.6 Hz, vinyl), 7.39 (d, 1 H, *J* = 1.8 Hz, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.0, 66.8, 106.0, 110.0, 118.4, 133.6, 141.9, 155.9; $[\alpha]_D^{23}$ −27.2° (*c* 1.1, Et_2O). The enantioselectivity was determined to be 93% ee by HPLC analysis using a chiral column (Chiralcel OB-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{minor} = 17.5 min (*R*), t_{major} = 18.7 min (*S*).

(*E*)-1,5-Nonadien-4-ol (Entry 5 in Table 2).[24] TLC R_f 0.40

(1:3 ethyl acetate/hexane); IR (neat) 3700–3110, 3079, 2961, 2930, 2874, 1671, 1642, 1457, 1437, 1379, 1315, 1032, 968, 914 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (s, 3 H, J = 7.3 Hz, CH_3), 1.40 (m, 2 H, CH_2), 1.61 (br, 1 H, OH), 2.02 (dd, 2 H, J = 14.0, 7.3 Hz, CH_2), 2.29 (m, 2 H, CH_2), 4.13 (m, 1 H, CH), 5.11–5.17 (m, 2 H, 2 vinyls), 5.45–5.53 (m, 1 H, vinyl), 5.63–5.80 (m, 2 H, 2 vinyls); $[\alpha]_D^{23}$ −1.2° (*c* 1.0, Et_2O). The enantioselectivity was determined to be 93% ee by HPLC analysis of the benzoate of the product using a chiral column (Chiralpak AD, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 400/1, flow rate = 0.5 mL/min): t_{major} = 13.3 min, t_{minor} = 15.5 min.

1-(*o*-Tolyl)-3-buten-1-ol (Entry 6 in Table 2).[20b,25] TLC R_f 0.40 (1:3 ethyl acetate/hexane); IR (neat) 3650–3125, 3075, 3025, 2979, 1640, 1489, 1462, 1051, 916, 870, 756, 725 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.94 (d, 1 H, J = 2.5 Hz, OH), 2.36 (s, 3 H, CH_3), 2.47 (m, 2 H, CH_2), 4.99 (m, 1 H, CH), 5.16–5.23 (m, 2 H, 2 vinyls), 5.88 (m, 1 H, vinyl), 7.13–7.27 (m, 3 H, aromatic), 7.50 (d, 1 H, J = 7.4 Hz, aromatic); $[\alpha]_D^{26}$ −83.8° (*c* 1.0, benzene). The enantioselectivity was determined to be 97% ee by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/i-PrOH = 20/1, flow rate = 0.5 mL/min): t_{minor} = 13.5 min, t_{major} = 15.2 min.

(*S*)-1-(*p*-Methoxyphenyl)-3-buten-1-ol (Entry 7 in Table 2).[20b,22] TLC R_f 0.27 (1:3 ethyl acetate/hexane); IR (neat) 3700–3120, 3075, 3002, 2936, 2900, 2838, 1642, 1613, 1586, 1514, 1464, 1443, 1302, 1248, 1175, 1036, 1003, 918, 872, 833, 812, 770 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.94 (d, 1 H, J = 0.9 Hz, OH), 2.50 (d, 2 H, J = 6.6 Hz, CH_2), 3.81 (s, 3 H, CH_3), 4.69 (t, 1 H, J = 6.3 Hz, CH), 5.11–5.18 (m, 2 H, 2 vinyls), 5.80 (m, 1 H, vinyl), 6.89 (d, 2 H, J = 8.8 Hz, aromatic), 7.29 (d, 2 H, J = 8.8 Hz, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.7, 55.2, 72.9, 113.7 (2 C), 118.1, 127.0 (2 C), 134.6, 136.0, 158.9; $[\alpha]_D^{25}$ −40.7° (*c* 1.1, benzene). The enantioselectivity was determined to be 97% ee by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{minor} = 11.1 min (*R*), t_{major} = 12.9 min (*S*).

1-(*p*-Bromophenyl)-3-buten-1-ol (Entry 8 in Table 2).[26] TLC R_f 0.39 (1:3 ethyl acetate/hexane); IR (neat) 3680–3120, 3079, 2979, 2934, 2905, 1642, 1593, 1489, 1431, 1406, 1297, 1194, 1071, 1011, 918, 870, 826, 777, 739, 718 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.03 (d, 1 H, J = 3.0 Hz, OH), 2.48 (m, 2 H, CH_2), 4.71 (m, 1 H, CH), 5.14–5.20 (m, 2 H, 2 vinyls), 5.80 (m, 1 H, vinyl), 7.24 (d, 2 H, J = 8.3 Hz, aromatic), 7.48 (d, 2 H, J = 8.3 Hz, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.6, 72.5, 118.6, 121.1, 127.5 (2 C), 131.3 (2 C), 133.9, 142.7; $[\alpha]_D^{23}$ −26.1° (*c* 1.1, benzene). The enantioselectivity was determined to be 96% ee by HPLC analysis using a chiral column (Chiralcel OJ, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 9/1, flow rate = 0.5 mL/min): t_{major} = 15.7 min, t_{minor} = 16.9 min.

1-Phenyl-5-hexen-3-ol (Entry 9 in Table 2).[22,25a,27] TLC R_f 0.33 (1:3 ethyl acetate/hexane); IR (neat) 3700–3120, 3027, 2930, 2863, 1642, 1603, 1497, 1455, 1075, 1049, 1040, 995, 916, 747, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.60 (d, 1 H, J = 1.9 Hz, OH), 1.80 (m, 2 H, CH_2), 2.16–2.23 (m, 1 H, one proton of CH_2), 2.29–2.36 (m, 1 H, one proton of CH_2), 2.64–2.84 (m, 2 H, CH_2), 3.68 (m, 1 H, CH), 5.15 (d, 2 H, J = 11.8 Hz, 2 vinyls), 5.75–5.86 (s, 1 H, vinyl), 7.16–7.31 (m, 5 H, aromatic); $[\alpha]_D^{23}$ +25.3° (*c* 1.0, benzene). The enantioselectivity was determined to be 88% ee by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{minor} = 17.3 min, t_{major} = 25.3 min.

(*R*)-3-Methy-1-phenyl-3-buten-1-ol (Eq. 2).[28] TLC R_f 0.33 (1:5 ethyl acetate/hexane); IR (neat) 3630–3130, 3031, 1647, 1602, 1495, 1455, 1375, 1200, 1055, 1026, 891, 756, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.81 (s, 3 H, CH_3), 2.11 (d, 1 H, J = 2.2 Hz, OH), 2.44 (d, 2 H, J = 6.9 Hz, CH_2), 4.83 (dt, 1 H, J = 6.9, 2.1 Hz, CH), 4.87 (s, 1 H, vinyl), 4.94 (s, 1 H, vinyl), 7.25–7.41 (m, 5 H, aromatic); $[\alpha]_D^{23}$ +55.3° (*c* 1.3, benzene). The enantioselectivity was determined to be 92% ee by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{minor} = 16.2 min (*S*), t_{major} = 17.9 min (*R*).

Typical Experimental Procedure for Asymmetric 2-Butenylation of Benzaldehyde with 2-Butenyltributylstannane Catalyzed by BINAP•AgOTf Complex: Synthesis of (1*R*,2*R*)-2-Methyl-1-phenyl-3-buten-1-ol (Eq. 3).[29] A mixture of AgOTf (26 mg, 0.10 mmol) and (*R*)-BINAP (62 mg, 0.10 mmol) was dissolved in dry THF (3 mL) under argon atmosphere and exclusion of direct light, and stirred at 20 °C for 10 min. To the resulting solution was added a THF solution (3 mL) of benzaldehyde (53 mg, 0.50 mmol) and then (*E*)-2-butenyltributylstannane (*E*/*Z* = 95/5, 690 mg, 2.0 mmol) was added dropwise at −20 °C. The mixture was stirred for 8 h at this temperature and then for 16 h at 20 °C, and treated with a mixture of 1 M HCl (10 mL) and solid KF (ca. 1 g) at ambient temperature for 30 min. After the resulting precipitate was filtered off, the organic layer was separated, washed with a saturated aqueous $NaHCO_3$ solution and brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo after filtration. The residual crude product was purified by column chromatography on silica gel to afford a mixture of homoallylic alcohols (46 mg, 56% yield as a colorless oil): the α/γ and *anti*/*syn* ratios were determined to be < 1/99 and 85/15, respectively, by GC analysis. The enantioselectivities of the *anti*- and *syn*-isomers were determined to be 94% ee and 64% ee, respectively, by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 40/1, flow rate = 0.5 mL/min): $t_{anti\text{-}minor}$ = 15.0 min (1*S*,2*S*), $t_{syn\text{-}minor}$ = 15.5 min (1*S*,2*R*), $t_{anti\text{-}major\ +\ syn\text{-}major}$ = 17.8 min (1*R*,2*R* + 1*R*,2*S*). The absolute configuration of the major *anti*-isomer was determined to be 1*R*,2*R* by comparison of the $[\alpha]_D$ value with reported data. (1*S*,2*S*)-enriched alcohol (66% ee): $[\alpha]_D^{25}$ −73.4° (*c* 2.0, $CHCl_3$).[29] (1*S*,2*R*)-isomer (55% ee): $[\alpha]_D^{25}$ −15.0° (*c* 0.93, $CHCl_3$).[29] Observed $[\alpha]_D$ value of the product: $[\alpha]_D^{30}$ +77.5° (*c* 0.8, $CHCl_3$; data obtained on an 85:15 mixture of *anti*- and *syn*-isomers). The absolute configuration of the major *syn* isomer was determined to be 1*R*,2*S* by HPLC analysis.[30] Spectral data obtained on an 85:15 mixture of *anti* and *syn* isomers: TLC R_f 0.38 (1:5 ethyl acetate/hexane); IR (neat) 3630–3130, 3081, 3065, 3031, 2977, 2932, 2872, 1640, 1603, 1495, 1455, 1374, 1196, 1117, 1076, 1021, 914, 762, 702 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, *anti* isomer) δ 0.87 (d, 3 H, J = 6.9 Hz, CH_3), 2.16 (d, 1 H, J = 2.7 Hz, OH), 2.48 (m, 1 H, CH), 4.36 (dd, 1 H, J = 8.1, 2.4 Hz, CH), 5.17–5.24 (m, 2 H, 2 vinyls), 5.75–5.87 (m, 1 H, vinyl), 7.26–7.36 (m, 5 H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$, *anti* isomer) δ 16.5, 46.3, 77.8, 116.9, 126.8 (2 C), 127.6, 128.2 (2 C), 140.6, 142.4.

Typical Experimental Procedure for Asymmetric Pentadienylation of Aldehydes with (*E*)-Trialkyl-2,4-pentadienylstannanes Catalyzed by BINAP•AgOTf Complex: Synthesis of 1-Phenyl-2-vinyl-3-buten-1-ol (Entry 2 in Table 3).[13i] A mixture of AgOTf (26 mg, 0.10 mmol) and (*R*)-BINAP (62 mg, 0.10 mmol) was dissolved in dry THF (4 mL) under argon atmosphere and with exclusion of direct light, and stirred at 20 °C for 10 min. To the resulting solution was added benzaldehyde (100 μL, 0.98 mmol) and then trimethylpentadienylstannane (*E*/*Z* = 90/10, 229

mg, 0.99 mmol) was added over a period of 4 h with a syringe pump at −20 °C. After being stirred for 4 h at this temperature, the mixture was treated with a mixture of 1 M HCl (3 mL) and solid KF (ca. 1 g) at ambient temperature for 30 min. After the resulting precipitate was filtered off by a glass filter funnel filled with Celite® and silica gel, the filtrate was dried over anhydrous $MgSO_4$ and concentrated in vacuo after filtration. The residual crude product was purified by column chromatography on silica gel to afford the γ-pentadienylated alcohol (116.5 mg, 68% yield) as a colorless oil: TLC R_f 0.33 (1:5 ethyl acetate/hexane); IR (neat) 3625–3130, 3081, 3031, 2980, 2880, 1636, 1605, 1495, 1455, 1416, 1194, 1040, 999, 918 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.19 (d, 1 H, J = 3.2 Hz, OH), 3.11 (dt, 1 H, J = 7.1, 15.0 Hz, CH), 4.59 (dd, 1 H, J = 3.1, 7.0 Hz, CH), 5.01 (d, 1 H, J = 17.9 Hz, vinyl), 5.05 (d, 1 H, J = 10.4 Hz, vinyl), 5.19 (d, 1 H, J = 17.1 Hz, vinyl), 5.25 (d, 1 H, J = 10.4 Hz, vinyl), 5.68 (ddd, 1 H, J = 7.1, 10.4, 17.2 Hz, vinyl), 5.83 (ddd, 1 H, J = 8.2, 10.4, 18.2 Hz, vinyl), 7.25–7.38 (m, 5 H, aromatic); $[\alpha]_D^{29}$ +60.8° (*c* 1.1, $CHCl_3$). The IR and ^1H NMR spectral data indicated good agreement with reported data.[13i] The γ/ε ratio was determined to be > 99/1 by ^1H NMR analysis. The enantioselectivity of the γ-product was determined to be 89% ee by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{minor} = 18.7 min, t_{major} = 22.5 min.

1-(*o*-Tolyl)-2-vinyl-3-buten-1-ol (Entry 3 in Table 3). TLC R_f 0.26 (1:5 ethyl acetate/hexane); IR (neat) 3625–3125, 3079, 3023, 2979, 2921, 1636, 1607, 1489, 1462, 1414, 1379, 1302, 1200, 1181, 1038, 999, 918 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 1 H, OH), 2.32 (s, 3 H, CH_3), 3.10 (dd, 1 H, J = 7.0, 15.0 Hz, CH), 4.84 (d, 1 H, J = 6.9 Hz, CH), 5.01 (d, 1 H, J = 17.0 Hz, vinyl), 5.02 (d, 1 H, J = 10.2 Hz, vinyl), 5.16 (d, 1 H, J = 17.3 Hz, vinyl), 5.25 (d, 1 H, J = 10.4 Hz, vinyl), 5.71 (ddd, 1 H, J = 6.9, 10.7, 17.9 Hz, vinyl), 5.90 (ddd, 1 H, J = 8.5, 8.5, 16.8 Hz, vinyl), 7.10–7.24 (m, 3 H, aromatic), 7.41 (d, 1 H, J = 7.4 Hz, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5, 55.3, 71.9, 116.7, 118.5, 126.0, 126.4, 127.3, 130.2, 135.0, 136.6, 136.8, 140.1; $[\alpha]_D^{29}$ +69.7° (*c* 1.0, $CHCl_3$). Found: C, 82.76; H, 8.81%. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57%. The γ/ε ratio was determined to be > 99/1 by ^1H NMR analysis. The enantioselectivity of the γ-product was determined to be 90% ee by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{minor} = 14.7 min, t_{major} = 15.5 min.

1-(*p*-Methoxyphenyl)-2-vinyl-3-buten-1-ol (Entry 4 in Table 3).[13d] TLC R_f 0.15 (1:5 ethyl acetate/hexane); IR (neat) 3710–3140, 3079, 3002, 2979, 2907, 2838, 1634, 1613, 1586, 1514, 1464, 1443, 1418, 1304, 1248, 1174, 1036, 1001, 918 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.23 (d, 1 H, J = 2.7 Hz, OH), 3.07 (dt, 1 H, J = 7.4, 15.4 Hz, CH), 3.79 (s, 3 H, CH_3), 4.51 (dd, 1 H, J = 2.7, 7.4 Hz, CH), 4.99 (d, 1 H, J = 14.3 Hz, vinyl), 5.03 (d, 1 H, J = 7.7 Hz, vinyl), 5.18 (d, 1 H, J = 17.9 Hz, vinyl), 5.23 (d, 1 H, J = 10.4 Hz, vinyl), 5.65 (ddd, 1 H, J = 7.1, 10.7, 17.6 Hz, vinyl), 5.84 (ddd, 1 H, J = 8.2, 10.4, 18.7 Hz, vinyl), 6.86 (d, 2 H, J = 8.8 Hz, aromatic), 7.22 (d, 2 H, J = 8.5 Hz, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 56.3. 75.9, 113.6 (2 C), 117.0, 118.3, 128.2 (2 C), 134.0, 136.9, 137.2, 159.1; $[\alpha]_D^{29}$ +59.9° (*c* 1.0, $CHCl_3$). The γ/ε ratio was determined to be > 99/1 by ^1H NMR analysis. The enantioselectivity of the γ-product was determined to be 87% ee by HPLC analysis using a chiral column (Chiralpak AD, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{major} = 23.9 min, t_{minor} = 25.6 min.

1-(2-Furyl)-2-vinyl-3-buten-1-ol (Entry 5 in Table 3). TLC R_f 0.21 (1:5 ethyl acetate/hexane); IR (neat) 3710–3170, 3081, 2980, 2890, 1636, 1505, 1150, 1011, 922 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.22 (d, 1 H, J = 5.2 Hz, OH), 3.31 (dd, 1 H, J = 7.4, 15.1 Hz, CH), 4.62 (dd, 1 H, J = 4.9, 7.1 Hz, CH), 5.10 (d, 1 H, J = 12.1 Hz, vinyl), 5.11 (d, 1 H, J = 15.9 Hz, vinyl), 5.22 (d, 1 H, J = 18.7 Hz, vinyl), 5.24 (d, 1 H, J = 9.3 Hz, vinyl), 5.68–5.90 (m, 2 H, J = 7.1, 10.4, 17.2 Hz, vinyl), 6.26 (d, 1 H, J = 3.3 Hz, vinyl), 6.33 (dd, 1 H, J = 1.9, 3.3 Hz, vinyl), 7.38 (dd, 1 H, J = 0.8, 1.9 Hz, vinyl); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.7, 69.9, 107.7, 110.2, 117.6, 118.5, 136.2, 136.6, 142.2, 154.5. Found: C, 73.00; H, 7.65%. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37%. The γ/ε ratio was determined to be > 99/1 by ^1H NMR analysis. The enantioselectivity of the γ-product was determined to be 89% ee by HPLC analysis using a chiral column (Chiralpak AD, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 100/1, flow rate = 0.5 mL/min): t_{minor} = 31.8 min, t_{major} = 33.3 min.

(*E*)-1-Phenyl-4-vinyl-1,5-hexadien-3-ol (Entry 6 in Table 3).[13h–k] TLC R_f 0.24 (1:5 ethyl acetate/hexane); IR (neat) 3640–3130, 3081, 3027, 2980, 2872, 1636, 1541, 1509, 1495, 1449, 997, 967, 920 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.03 (s, 1 H, OH), 2.99 (dd, 1 H, J = 7.7, 14.3 Hz, CH), 4.25 (t, 1 H, J = 6.0 Hz, CH), 5.12–5.25 (m, 4 H, vinyl), 5.79–5.93 (m, 2 H, vinyl), 6.22 (dd, 1 H, J = 6.3, 15.9 Hz, vinyl), 6.60 (dd, 1 H, J = 1.1, 15.9 Hz, vinyl), 7.20–7.39 (m, 5 H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.0, 74.5, 117.7, 118.1, 126.6 (2 C), 127.8, 128.6 (2 C), 130.0, 131.6, 136.7; $[\alpha]_D^{29}$ +11.9° (*c* 1.0, $CHCl_3$). The IR and ^1H NMR spectra data indicated good agreement with reported data.[13i] The γ/ε ratio was determined to be > 99/1 by ^1H NMR analysis. The enantioselectivity of the γ-product was determined to be 58% ee by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{major} = 23.8 min, t_{minor} = 37.7 min.

1-Phenyl-4-vinyl-5-hexen-3-ol (Entry 8 in Table 3).[13h–j] TLC R_f 0.26 (1:5 ethy acetate/hexane); IR (neat) 3700–3140, 3079, 3027, 2979, 2861, 1636, 1603, 1497, 1455, 1046, 999, 918 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.62–1.70 (m, 1 H, one proton of CH_2), 1.75 (d, 1 H, J = 4.4 Hz, OH), 1.80–1.92 (m, 1 H, one proton of CH_2), 2.61–2.71 (m, 1 H, CH), 2.78–2.90 (m, 2 H, CH_2), 3.56 (m, 1 H, CH), 5.09–5.21 (m, 4 H, vinyl), 5.72–5.87 (m, 2 H, vinyl), 7.15–7.30 (m, 5 H, aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.2, 36.1, 55.3, 72.5, 117.2, 117.9, 125.9, 128.5 (2 C), 128.6 (2 C), 137.0, 137.4, 142.3; $[\alpha]_D^{26}$ −9.4° (*c* 1.0, $CHCl_3$). The IR and ^1H NMR spectral data indicated good agreement with reported data.[13i] The γ/ε ratio was determined to be > 99/1 by ^1H NMR analysis. The enantioselectivity of the γ-product was determined to be 71% ee by HPLC analysis using a chiral column (Chiralcel OD-H, Daicel Chemical Industries, Ltd., hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min): t_{major} = 16.9 min, t_{minor} = 25.4 min.

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