Asymmetric Allylation of Carbonyl Compounds with Tartrate-Modified Chiral Allylic Tin Reagents

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Chiral allylating reagents, readily generated in situ from tin(II) catecholate [$Sn^{II}(O_2C_6H_4)$], allyl halides, chiral dialkyl tartrates, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), reacted smoothly with aldehydes or reactive ketones at −78 °C in the presence of a catalytic amount of copper salts to afford the corresponding optically active homoallyl alcohols. Allylation of aromatic aldehydes and pyruvates by the present chiral tin reagents proceeded in high yields (81—99%) with high enantioselectivities (89—94%ee). In addition, both enantiomers of dimethyl citramalate were prepared from the allylation products of benzyl pyruvate.

Asymmetric allylation of carbonyl compounds by allylic metal reagents often has advantages over an aldol reaction, since the resulting homoallyl alcohols are converted not only to the aldol but also to other useful intermediates by simple modifications of reactive alkene parts which originated from allylic metals. Therefore, a number of allylic metal reagents have been developed and employed in the synthesis of complex molecules including natural products by controlling the stereochemistry of acyclic systems.[1)]

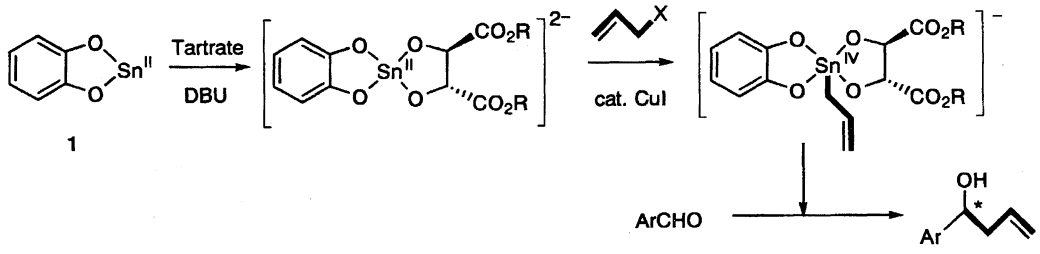
Allylic tin(IV) is one of the useful allylic metal reagents. Enantioselective allylation reactions of aldehydes using chiral sources such as (i) Lewis acids with chiral ligands[2)] or (ii) allylic metals directly combined with chiral ligands have been reported.[3,4)] On the other hand, there are few examples concerning the enantioselective allylation of ketones, which affords chiral tertiary carbon center in the resulting homoallyl alcohol.[5)]

Tartaric acid derivatives are often employed as useful chiral ligands of organometallics including allylic metal reagents. For example, Roush et al. reported on the utility of tartrate-modified allylboronates in asymmetric allylation of α-substituted aldehydes,[6)] while Trombini et al. prepared a pentacoordinated allylic tin complex containing diethyl tartrate ($H_2O_2R^*$) as a chiral auxiliary ligand and proposed Na-[CH_2=$CHCH_2$–$Sn^{IV}(O_2R^*)_2$] to be an active species which allylated several aldehydes in fairly good enantioselectivities without using Lewis acids.[3)]

Organosilicon compounds are also known as stable hypervalent allylic metal complexes.[7)] The allylation reaction of aldehydes with catechol-modified pentacoordinated allylsilicates is recognized to proceed via a six-membered cyclic transition state, which was supported by the enhanced nucleophilicity of the γ-carbon of allylsilicates as well as by their significant behavior as Lewis acids forming hexacoordinated silicates.

In 1980, a convenient method for generating active allylic tin reagents was reported from our laboratory.[8)] Namely, a divalent tin compound (SnF_2) undergoes oxidative addition with allyl iodide in dipolar solvent to generate an allylic tin(IV) compound which is highly reactive toward carbonyl compounds to form homoallyl alcohols in excellent yields, even in the absence of Lewis acids.

Based on these observations, we considered an incorporation of tartrate into divalent tin compound and an oxidative addition of thus generated stannate complex with allyl halides, which would be utilized in developing a facile procedure for the preparation of chiral allylating reagent. Then it was found, as shown in Scheme 1, that a divalent tin compound, tin(II) catecholate [$Sn^{II}(O_2C_6H_4)$],[9)] underwent oxidative addition with allyl bromide in the presence



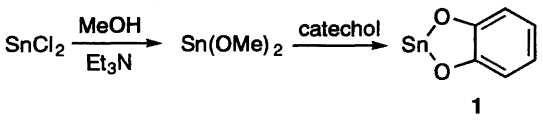
Scheme 1.

of chiral dialkyl tartrate, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and a catalytic amount of CuI. Recently we have reported preliminary results on the asymmetric reaction of the above-mentioned allylating reagents with aromatic aldehydes.[10] Now we would like to describe the full details of the present asymmetric allylation reaction of aromatic aldehydes and further application to other carbonyl compounds.

Preparation of Allylic Tin Reagent from Divalent Tin Compound via Oxidative Addition. Tin(II) catecholate (**1**) was prepared from commercially-available $SnCl_2$ via two steps according to the literature method (Scheme 2).[9] Since $Sn^{II}(O_2C_6H_4)$ (**1**) does not dissolve in nonpolar solvents such as CH_2Cl_2, combinations of several bases and solvents were screened for coordination of chiral diol with **1**. Thus, an oxidative addition of divalent tin complex to allyl halides and the subsequent allylation of carbonyl compounds proceeded smoothly in a clear CH_2Cl_2 solution at −78 °C after adding DBU to dissociate polymeric $Sn^{II}(O_2C_6H_4)$ (**1**). As shown in the following allylation reactions, the high enantioselectivities were successfully achieved at low temperature.

Asymmetric Allylation of Aldehydes with Chiral Allylating Reagents. In the first place, suitable reaction conditions were established using benzaldehyde as a model substrate; results are summarized in Table 1.

The asymmetric allylation of benzaldehyde was carried out as follows: a mixture of $Sn^{II}(O_2C_6H_4)$ (**1**), tartrate, DBU, and a catalytic amount of CuI in CH_2Cl_2 was stirred at room temperature for half an hour and then allyl bromide and benzaldehyde were allowed to react with the thus formed stannate complex at −78 °C for an additional 10—20 h.



Scheme 2.

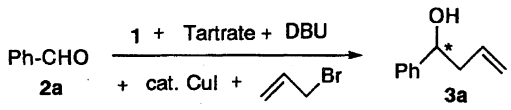


Table 1. Asymmetric Allylation[a] of Benzaldehyde (**2a**)

Entry	Tartrate	Molar ratio[b] Tartrate/DBU	Product (**3a**)[c] Yield (%)[d]	%Ee[e]
1	(+)-DIPT	2/4	70	49
2	(+)-DIPT	4/4	82	81
3	(+)-DIPT	6/4	82	80
4	(+)-DIPT	5/5	96	85
5	(+)-DMT	5/5	69	57
6	(+)-DET	5/5	88	72
7	(+)-DBT	5/5	90	73
8	(+)-DCHT	5/5	97	87
9	(+)-DTBT	5/5	98	91
10	(−)-DIPT	5/5	96	86[f]

a) All reactions were carried out using 0.2 mmol of benzaldehyde and the allylic tin reagents which were prepared from $Sn(O_2C_6H_4)$ (**1**) (2.0 molar amounts), allyl bromide (2.0 molar amounts), CuI (0.1 molar amount), tartrates (A molar amounts), and DBU (B molar amounts). b) Molar ratio of tartrates (A) and DBU (B). c) (*S*) Configuration except for Entry 10. d) Isolated yield based on benzaldehyde. e) Determined by HPLC analysis. f) (*R*) Configuration.

The ratio of tartrates to DBU was a significant factor in this reaction, as well as their amounts (Entries 1—4). For example, both yield and ee were moderate when (+)-diisopropyl tartrate (DIPT) and DBU were used in the minimum amounts required for the formation of stannate complex (Entry 1). Increased amounts of tartrate apparently improved yield along with ee (Entries 2 and 3). The use of more than 5.0 molar amounts each of (+)-DIPT and DBU gave the best result (Entry 4). Sufficient amounts of tartrate and DBU to $Sn^{II}(O_2C_6H_4)$ (**1**) were required for forming a preferable fixed structure of active allylic tin complex.

It is noted that the present allylation reaction proceeded smoothly even at −78 °C in the presence of CuI. Yields and ee's were not influenced by the amounts of the CuI. Compared to the result of using 0.1 molar amount of CuI (Entry 2), 0.02 molar amount was also effective (69% yield, 84%ee) and equimolar amount of CuI gave a similar result (86% yield, 80%ee) as well. Besides CuI, copper(II) salts ($CuCl_2$ and $CuSO_4$) were also effective like other copper(I) salts (CuBr, CuCl and CuCN) (54—75% yield, 75—82%ee). Other metal salts except for $PdCl_2$ (57% yield, 63%ee) did not catalyze this reaction. Copper salts, therefore, apparently have a key role in promoting the oxidative addition step to allyl halide to form an active allylic tin reagent, though the detailed mechanism has not yet been made clear.[11]

Concerning the structure of (+)-tartrate, the use of methyl ester (DMT, Entry 5), ethyl ester (DET, Entry 6) or benzyl ester[12] (DBT, Entry 7) did not afford better results than of isopropyl ester (Entry 4), whereas the use of bulky tartrates, *c*-hexyl ester[13] (DCHT, Entry 8) and *t*-butyl ester[14] (DTBT, Entry 9), gave satisfactory results. The homoallyl alcohol **3a** thus obtained had (*S*) configuration, which was determined by comparing its optical rotation with that reported in the literature.[15] It is noted that an enantiomer of the above product (*R*)-**3a** was readily obtained by employing commercially available (−)-DIPT in the same procedure (Entry 10).

The reactivity of the resulting coordinated complex was influenced by the structure of a ligand; that is, no allylating reagent having similar reactivity to that of the tartrate-modified one was formed at −78 °C when bis(dimethylamide) of tartaric acid (25% yield, 12%ee) or vicinal dihydroxy compound having no carbonyl functions such as (−)-2,3-butanediol (3% yield, 16%ee) and (−)-1,2-diphenyl-1,2-ethanediol (55% yield, 13%ee) was used. Coordination of the carbonyl function of the dialkyl tartrate to tin atom is thus expected to cause the formation of monomeric structure of the active stannate complex, which facilitates the addition of the complex to allyl halides.

Next, several aldehydes (**2a—k**) were allylated according to the optimized reaction procedure (Table 1, Entry 9); the results are summarized in Table 2. All of the examined aromatic aldehydes afforded the corresponding homoallylic alcohols in high chemical and optical yields (Entries 1—

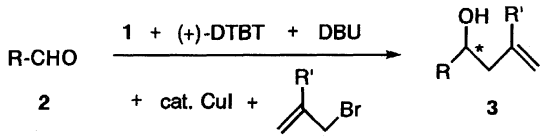


Table 2. Asymmetric Allylation[a] of Aldehydes **2**

Entry	Aldehydes **2**	Product (**3**)	/	R′	Yield (%)[b]	%Ee[c]		$[\alpha]_D$
1	C_6H_5CHO (**2a**)	**3a**		H	98	91	−48.8°	(*c* 1.00, benzene)
2	*p*-ClC_6H_4CHO (**2b**)	**3b**		H	99	89	−34.9°	(*c* 1.00, benzene)
3	*p*-$CH_3C_6H_4CHO$ (**2c**)	**3c**		H	96	92	−47.7°	(*c* 1.00, benzene)
4	*o*-$CH_3C_6H_4CHO$ (**2d**)	**3d**		H	99	94	−83.3°	(*c* 1.02, benzene)
5	*p*-$CH_3OC_6H_4CHO$ (**2e**)	**3e**		H	96	90	−34.2°	(*c* 1.03, benzene)
6	*p*-$CH_3O_2CC_6H_4CHO$ (**2f**)	**3f**		H	99	88	−25.0°	(*c* 1.00, benzene)
7	$C_{10}H_7CHO$ (**2g**)	**3g**		H	97	91	−99.0°	(*c* 1.00, benzene)
8	(*E*)-$C_6H_5CH{=}CHCHO$ (**2h**)	**3h**		H	96	62	+10.5°	(*c* 1.03, Et_2O)
9	$C_6H_5CH_2CH_2CHO$ (**2i**)	**3i**		H	83	55	+12.2°	(*c* 1.00, $CHCl_3$)
10	*c*-$C_6H_{11}CHO$ (**2j**)	**3j**		H	94	84[d]	−2.6°	(*c* 1.00, CH_2Cl_2)
11	*n*-$C_8H_{17}CHO$ (**2k**)	**3k**		H	98	58[d]	+8.7°	(*c* 1.02, benzene)
12	C_6H_5CHO (**2a**)	**3l**		Me	97	65	−41.3°	(*c* 1.04, benzene)
13	*c*-$C_6H_{11}CHO$ (**2j**)	**3m**		Me	89	86[d]	+2.7°	(*c* 1.49, benzene)

a) All reactions were carried out using 0.2 mmol of aldehydes under the conditions of Table 1 (Entry 9). b) Isolated yields based on aldehydes. c) Determined by HPLC analysis except for Entries 10, 11, and 13. d) Determined by NMR analysis of MTPA esters of **3**.

7). Application of this allylating reagent to α,β-unsaturated aldehyde (Entry 8) and aliphatic aldehydes (Entries 9—11) afforded the adducts in high yields, although enantioselectivities were not always high as demonstrated in the case of aromatic aldehydes. For example, the allylated products were obtained respectively in 84%ee and 58%ee when cyclohexanecarbaldehyde (**2j**) and nonanal (**2k**) were treated with the present allylic tin reagent (Entries 9 and 10).

Allyl iodide gave the same results as allyl bromide did. 2-Methyl-2-propenyl bromide (R′ = Me) was also successfully employed in this reaction (Entries 12 and 13). However, allylation using 2-propynyl bromide or 3-methyl-2-butenyl bromide did not proceed smoothly.

2-Butenylation of benzaldehyde (Scheme 3) afforded a mixture of two isomers, **4a** (*anti*) and **4b** (*syn*), in 74% yield. Optical purity of an unseparable mixture of **4a** and **4b** was not determined. A ratio of **4a** to **4b** (80/20) corresponded to the *E*/*Z* ratio (88/12) of 2-butenyl bromide, which were determined by the ^1H NMR analysis.[16] This result was reasonably explained by considering the hexacoordinated stannate complex where a chair-like transition state was formed

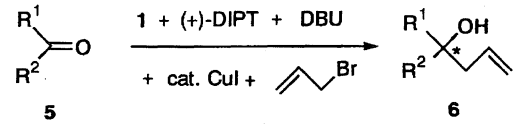
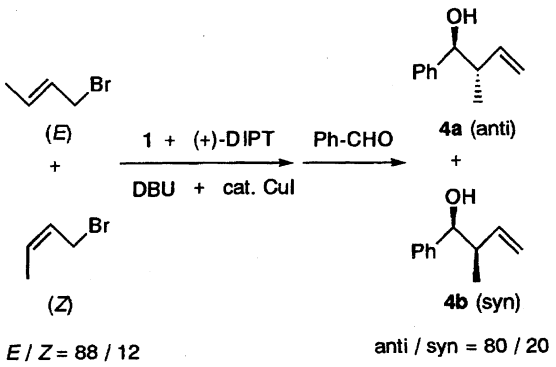


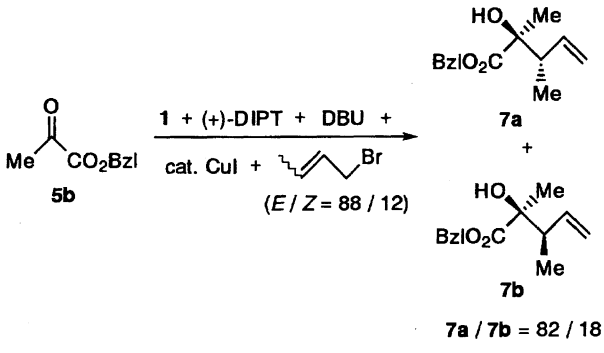
Table 3. Asymmetric Allylation of Ketones **5**[a]

Entry	Ketone	R^1	R^2	Product	Yield/%[b]	%Ee[c]
1	**5a**	Me	COPh	**6a**	81	—[f]
2	**5b**	Me	CO_2Bzl	**6b**	87	95
3	**5c**	Me	CO_2PCB[d]	**6c**	72	95
4	**5d**	Me	CO_2PMB[d]	**6d**	87	95
5	**5e**	*i*-Bu	CO_2Bzl	**6e**	52[e]	30

a) All reactions were carried out using 0.2 mmol of carbonyl compounds under the conditions of Table 1 (Entry 4). b) Isolated yields based on carbonyl compounds. c) Determined by HPLC analysis. d) PCB = 4-chlorobenzyl, PMB = 4-methoxybenzyl. e) Four days (reaction time). f) Adequate HPLC conditions were not found (ca. 60%ee).



Scheme 3.



Scheme 4.

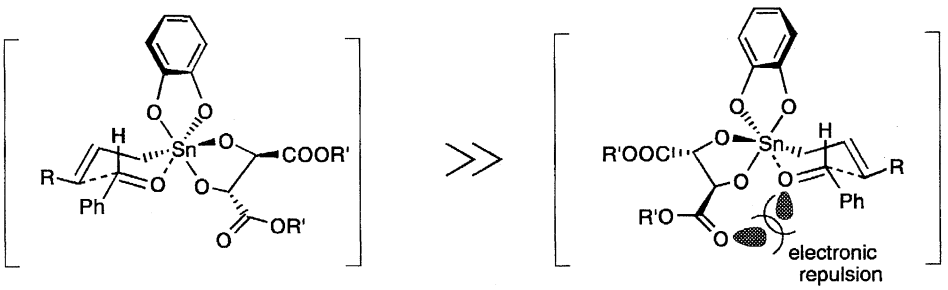
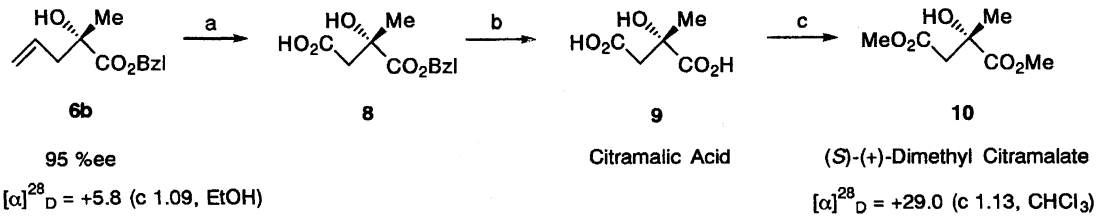


Fig. 1. Possible transition states. Allylation (R = H) and 2-butenylation (R = Me) of benzaldehyde.



a) $RuCl_3$, $NaIO_4$, 92 %. b) KOH. c) MeOH, HCl, 79 % (2 steps).

Scheme 5.

by aldehyde and allylic tin. (*E*)-2-Butenylstannate complex (Fig. 1, R = Me) affords anti adduct **4a**. According to the similar reaction modes of tartrate-modified allylboronates,[6] enantioselectivity of this allylation reaction is caused by a favorable transition state **A** (Fig. 1, R = H) which has smaller electronic repulsive interaction, compared with another possible transition state **B** (Fig. 1, R = H), between nonbonding lone pairs of the aldehyde and an ester carbonyl oxygen.

Asymmetric Allylation of Ketones with Chiral Allylating Reagents. Further, allylation of ketones using the present reagent employing (+)-DIPT was examined. Acetophenone gave no adduct, whereas hydroxyacetone was allylated with poor enantioselectivity (63% yield, 5%ee). As shown in Table 3, the desired homoallyl alcohols were obtained in good yields from ketones having a carbonyl group on α-position; namely, α-diketone (Entry 1) and pyruvate.

Allylation of pyruvates proceeded smoothly with good selectivities that reached 95%ee in the case of benzyl ester **5b** (Entry 2). The use of (+)-DTBT instead of (+)-DIPT did not improve enantioselectivity. Modification of the ester group of pyruvate did not give the increased ee (Entries 3 and 4). The reactivities of α-keto esters having a larger alkyl group decreased compared to that of pyruvate (Entry 5).

2-Butenylation of benzyl pyruvate (**5b**) was also examined as shown in Scheme 4. The relative configuration of the major product **7a**, which was confirmed by ^{1}H NMR analysis of a mixture of diastereomers,[17] supported the similar six-membered ring transition state as shown in Fig. 1 where the ester group of the pyruvate occupied a pseudo-equatorial position. Since the major product **7a** was not isolated cleanly, its optical purity was not determined.

Synthesis of Both Enantiomers of Citramalic Acid Dimethyl Ester.[18] 2-Hydroxy-2-methylbutanedioic acid (citramalic acid) has been isolated from various natural sources. In spite of their utility as a valuable chiral synthon for natural products such as isoprenoid,[19] only a few groups reported asymmetric syntheses of citramalic acids with acceptable enantiomeric purity.[20] Therefore, homoallylic tertiary alcohol **6b** with 95%ee (Table 3, Entry 2) was converted to dimethyl citramalate, as shown in Scheme 5. Alkene part of **6b** was oxidatively cleaved[21] to afford monobenzyl ester of citramalic acid **8** in good yield. Alkaline hydrolysis of the ester **8** gave crude citramalic acid **9**, which was purified after conversion to its dimethyl ester **10**.[18c] Optical rotation of thus obtained (+)-dimethyl citramalate **10** indicated (*S*) configuration of the starting material of homoallyl alcohol **6b**.

As mentioned above, enantiomerically enriched (+)-dimethyl citramalate **10** was prepared by four steps starting from benzyl pyruvate **5b**. Employing (−)-DIPT in the same procedure, an enantiomer, (−)-dimethyl citramalate, was also obtained.

Thus, a simple and effective procedure for preparing tartrate-modified allylic tin reagent and the subsequent asymmetric allylation of aromatic aldehydes or pyruvates has been successfully developed. Further, short-step synthesis of both enantiomers of dimethyl citramalate via asymmetric allylation of pyruvate was achieved.

Experimental

General Methods. Analytical TLC was done on precoated (0.25 mm) silica-gel 60 F_{254} plates (E. Merck). Preparative TLC was performed on silica-gel-coated plates (Wakogel, B-5F, 20 cm×20 cm). ^{1}H NMR spectra were recorded on a JEOL JNM-EX 270 (270 MHz) instrument. Chemical shifts were reported in δ units relative to internal tetramethylsilane. ^{13}C NMR spectra were

recorded on a JEOL JNM-EX 270 (67.8 MHz) instrument using the 77.0 ppm resonance of $CDCl_3$ as the internal standard. IR spectra were recorded on a Horiba FT-300 infrared spectrometer. Optical rotations were measured on a JASCO DIP-360 polarimeter using a 1-cm^3-capacity quartz cell (10-cm path length). High-resolution mass (HRMS) spectra were recorded on a JEOL JMS-SX102A instrument.

All reactions were conducted under an atmosphere of dry argon. Dichloromethane and acetonitrile were distilled successively from P_2O_5 and CaH_2.

The enantiomeric purity of the products was determined by HPLC analysis (detection: UV 220 nm) using 4.6 mm×25 cm Chiralcel column (OD, AD or AS; Daisel Chemical Industries, Ltd.) equipped with Hitachi L-6200 HPLC system or by ^1H NMR analysis of the (*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionates (MTPA esters) of the alcohols. The MTPA esters were prepared according to Mosher's procedure using the acid chloride supplied from Aldrich (99+%).[22]

Materials. Aldehydes **2a**—**k**, ketone **5a**, allyl bromide, 2-butenyl bromide, DBU, L-(+)-dimethyl tartrate, L-(+)-diethyl tartrate, L-(+)-diisopropyl tartrate, R-(−)-diisopropyl tartrate were purchased from TCI (Tokyo Chemical Industry Co., Ltd.) and were recrystallized or distilled immediately prior to use. Copper(I) iodide, sodium periodate and $RuCl_3 \cdot nH_2O$ were purchased from Wako Pure Chemical Industries, Ltd. and were used without any purification.

L-(+)-Dibenzyl tartrate,[12] L-(+)-dicyclohexyl tartrate,[13] L-(+)-di-*t*-butyl tartrate,[14] 2-methyl-2-propenyl bromide,[23] and benzyl pyruvates (**5b**, **5c**, and **5d**)[24] were prepared according to literature methods. Tin(II) catecholate (**1**) was prepared according to the method of Zuckerman.[9]

Racemic allylation products for determination of the enantiomeric purity were prepared by known methods using allylmagnesium bromide or allyltributylstannane.[25]

General Procedure for Asymmetric Allylation of Aldehydes with Chiral Allylating Reagents (Table 2). To a suspension of $Sn^{II}(O_2C_6H_4)$ (**1**) (0.4 mmol), (+)-DTBT (1.0 mmol) and CuI (0.02 mmol) in CH_2Cl_2 (0.6 ml) was added DBU (1.0 mmol) in CH_2Cl_2 (0.6 ml) at room temperature under an argon atmosphere. The reaction mixture turned to a clear solution immediately and stirring was continued for 30 min. Then aldehyde **2** (0.2 mmol) in CH_2Cl_2 (0.6 ml) and allyl bromide (0.4 mmol) in CH_2Cl_2 (0.6 ml) were successively introduced at −78 °C. After stirring for 10—20 h at this temperature (progress of the reaction was monitored by TLC), 1 M (1 M = 1 mol dm^{-3}) HCl (15 ml) and hexane (5 ml) were added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with hexane–CH_2Cl_2 (2 : 1) mixture. The combined organic layers were washed with water and brine, dried over sodium sulfate, and concentrated in vacuo. The crude product was purified by silica-gel TLC to afford the homoallyl alcohol **3**. The absolute configuration of chiral center of the product **3** was determined by comparison of the optical rotation with that reported in the literatures.

(*S*)-1-Phenyl-3-buten-1-ol (3a):[15,26] HPLC 91%ee, column: Chiralcel OD, eluent: hexane (Hex)/2-propanol (IPA) = 50/1, flow rate: 0.8 ml min^{-1}, retention time: 22.3 min (*S*) and 18.7 min (*R*); $[\alpha]_D^{29} = -48.8°$ (*c* 1.00, benzene); ^1H NMR ($CDCl_3$) δ = 7.36—7.24 (m, 5H), 5.81 (m, 1H), 5.16 (d, *J* = 17.1 Hz, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 4.74 (dd, *J* = 5.6, 7.6 Hz, 1H), 2.60—2.46 (m, 2H), 1.86 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 143.9, 134.5, 128.4, 127.5, 125.8, 118.4, 73.3, 43.8; IR (neat) 3386, 3072, 2908, 1641, 1446 cm^{-1}.

(*R*)-1-Phenyl-3-buten-1-ol (3a): HPLC 86%ee; $[\alpha]_D^{27} = +48.8°$ (*c* 1.03, benzene).

1-(4-Chlorophenyl)-3-buten-1-ol (3b):[26] HPLC 89%ee, column: Chiralcel AS, eluent: Hex/IPA = 300/1, flow rate: 0.5 ml min^{-1}, retention time: 55.8 min (major) and 53.6 min (minor); $[\alpha]_D^{21} = -34.9°$ (*c* 1.00, benzene); ^1H NMR ($CDCl_3$) δ = 7.34—7.28 (m, 4H), 5.78 (m, 1H), 5.18—5.13 (m, 2H), 4.72 (dd, *J* = 5.2, 7.6 Hz, 1H), 2.56—2.41 (m, 2H), 1.91 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 142.2, 133.9, 133.1, 128.5, 127.2, 118.8, 72.5, 43.8; IR (neat) 3419, 3076, 2914, 1641, 1491, 1410 cm^{-1}.

1-(4-Methylphenyl)-3-buten-1-ol (3c):[26] HPLC 92%ee, column: Chiralcel AS, eluent: Hex/IPA = 300/1, flow rate: 1.0 ml min^{-1}, retention time: 16.5 min (major) and 14.3 min (minor); $[\alpha]_D^{25} = -47.7°$ (*c* 1.00, benzene); ^1H NMR ($CDCl_3$) δ = 7.22 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 5.79 (m, 1H), 5.16—5.10 (m, 2H), 4.68 (t, *J* = 6.6 Hz, 1H), 2.49 (m, 2H), 2.33 (s, 3H), 2.04 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 140.9, 137.1, 134.6, 129.0, 125.7, 118.2, 73.1, 43.7, 21.1; IR (neat) 3371, 2922, 1641, 1514, 1431 cm^{-1}.

(*S*)-1-(2-Methylphenyl)-3-buten-1-ol (3d):[27] HPLC 94%ee, column: Chiralcel AS, eluent: Hex/IPA = 300/1, flow rate: 0.5 ml min^{-1}, retention time: 35.5 min (*S*) and 33.4 min (*R*); $[\alpha]_D^{23} = -83.3°$ (*c* 1.02, benzene); ^1H NMR ($CDCl_3$) δ = 7.50—7.10 (m, 4H), 5.86 (m, 1H), 5.20—5.14 (m, 2H), 4.96 (m, 1H), 2.56—2.36 (m, 2H), 2.33 (s, 3H), 1.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 141.9, 134.7, 134.3, 130.3, 127.2, 126.2, 125.1, 118.3, 69.6, 42.6, 19.0; IR (neat) 3377, 2925, 1639, 1458 cm^{-1}.

1-(4-Methoxylphenyl)-3-buten-1-ol (3e):[26,27] HPLC 90%ee, column: Chiralcel OD, eluent: Hex/IPA = 50/1, flow rate: 0.8 ml min^{-1}, retention time: 27.5 min (major) and 23.0 min (minor); $[\alpha]_D^{27} = -34.2°$ (*c* 1.03, benzene); ^1H NMR ($CDCl_3$) δ = 7.28 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.78 (m, 1H), 5.16—5.11 (m, 2H), 4.68 (t, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 2.50 (dd, *J* = 6.6, 6.9 Hz, 2H), 1.99 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 159.0, 136.0, 134.6, 127.1, 118.2, 113.8, 73.0, 55.3, 43.7; IR (neat) 3410, 2935, 1612, 1512, 1456 cm^{-1}.

Methyl 4-(1-Hydroxy-3-butenyl)benzoate (3f):[28] HPLC 88%ee, column: Chiralcel OD, eluent: Hex/IPA = 50/1, flow rate: 1.0 ml min^{-1}, retention time: 58.6 min (major) and 51.8 min (minor); $[\alpha]_D^{26} = -25.0°$ (*c* 1.00, benzene); ^1H NMR ($CDCl_3$) δ = 8.11 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 5.80 (m, 1H), 5.29—5.24 (m, 2H), 4.90 (dd, *J* = 5.3, 7.6 Hz, 1H), 4.01 (s, 3H), 2.70—2.51 (m, 2H), 2.46 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 166.9, 149.0, 133.8, 129.7, 129.2, 125.7, 118.9, 72.7, 52.0, 43.8; IR (neat) 3431, 2947, 1720, 1612, 1437, 1282 cm^{-1}.

1-(1-Naphthyl)-3-buten-1-ol (3g):[26] HPLC 91%ee, column: Chiralcel AD, eluent: Hex/IPA = 50/1, flow rate: 0.8 ml min^{-1}, retention time: 22.3 min (major) and 25.7 min (minor); $[\alpha]_D^{22} = -99.0°$ (*c* 1.00, benzene); ^1H NMR ($CDCl_3$) δ = 8.07—7.42 (m, 7H), 5.90 (m, 1H), 5.48 (m, 1H), 5.19—5.16 (m, 2H), 2.79—2.51 (m, 2H), 2.18 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 139.4, 134.7, 133.7, 130.2, 128.9, 127.9, 126.0, 125.5, 122.9, 122.8, 118.3, 69.6, 42.8; IR (neat) 3381, 3068, 2912, 1639, 1510, 1431 cm^{-1}.

(*S*)-1-Phenyl-1,5-hexadien-3-ol (3h):[26] HPLC 62%ee, column: Chiralcel OD, eluent: Hex/IPA = 50/1, flow rate: 1.0 ml min^{-1}, retention time: 13.2 min (*S*) and 8.4 min (*R*); $[\alpha]_D^{26} = +10.5°$ (*c* 1.03, Et_2O); ^1H NMR ($CDCl_3$) δ = 7.39—7.20 (m, 5H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.24 (dd, *J* = 6.3, 15.8 Hz, 1H), 5.86 (m, 1H), 5.19—5.14 (m, 2H), 4.35 (m, 1H), 2.49—2.31 (m, 2H), 1.91 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 136.6, 134.0, 131.5, 130.3, 128.5, 127.6, 126.4, 118.5, 71.7, 42.0; IR (neat) 3431, 2922, 1705, 1643, 1603, 1495, 1444 cm^{-1}.

(*R*)-1-Phenyl-5-hexen-3-ol (3i):[26] HPLC 55%ee, column:

Chiralcel OD, eluent: Hex/IPA = 50/1, flow rate: 1.0 ml min^{-1}, retention time: 30.5 min (*R*) and 18.0 min (*S*); $[\alpha]_D^{24} = +12.2°$ (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 7.34—7.15 (m, 5H), 5.89—5.73 (m, 1H), 5.18—5.09 (m, 2H), 3.71—3.62 (m, 1H), 2.86—2.62 (m, 2H), 2.37—2.12 (m, 2H), 1.86—1.69 (m, 3H); ^{13}C NMR ($CDCl_3$) δ = 142.0, 134.6, 128.4, 128.3, 125.8, 118.3, 69.9, 42.0, 38.4, 32.0; IR (neat) 3373, 2925, 1641, 1495, 1448 cm^{-1}.

1-Cyclohexyl-3-buten-1-ol (3j):[3b,26] 84%ee, (MTPA ester); $[\alpha]_D^{27} = -2.6°$ (*c* 1.00, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ = 5.92—5.77 (m, 1H), 5.17—5.12 (m, 2H), 3.43—3.36 (m, 1H), 2.07—2.39 (m, 2H), 1.88—0.94 (m, 11H); ^{13}C NMR ($CDCl_3$) δ = 135.5, 118.0, 74.7, 43.1, 38.8, 29.1, 28.1, 26.5, 26.3, 26.1; IR (neat) 3371, 2920, 2854, 1641, 1446 cm^{-1}.

1-Dodecen-4-ol (3k):[3b,26] 58%ee (MTPA ester); $[\alpha]_D^{27} = +8.7°$ (*c* 1.02, benzene); ^1H NMR ($CDCl_3$) δ = 5.91—5.76 (m, 1H), 5.16—5.11 (m, 2H), 3.69—3.60 (m, 1H), 2.35—2.08 (m, 2H), 1.68 (s, 1H), 1.52—1.28 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ = 134.9, 118.0, 70.7, 41.9, 36.8, 31.9, 29.6, 29.5, 29.2, 25.6, 22.6, 14.1; IR (neat) 3365, 2927, 2856, 1641, 1460 cm^{-1}.

(*S*)-3-Methyl-1-phenyl-3-buten-1-ol (3l):[3b,26] HPLC 65%ee, column: Chiralcel OD, eluent: Hex/IPA = 300/1, flow rate: 0.8 ml min^{-1}, retention time: 46.5 min (*S*) and 53.4 min (*R*); $[\alpha]_D^{27} = -41.3°$ (*c* 1.04, benzene); ^1H NMR ($CDCl_3$) δ = 7.40—7.23 (m, 5H), 4.92 (br s, 1H), 4.86 (br s, 1H), 4.81 (t, *J* = 6.9 Hz, 1H), 2.42 (d, *J* = 6.9 Hz, 2H), 2.02 (s, 1H), 1.80 (s, 3H); ^{13}C NMR ($CDCl_3$) δ = 144.0, 142.4, 128.4, 127.4, 125.7, 114.0, 71.4, 48.3, 22.3; IR (neat) 3409, 2914, 1647, 1448, 1379 cm^{-1}.

1-Cyclohexyl-3-methyl-3-buten-1-ol (3m):[3b] 86%ee (MTPA ester); $[\alpha]_D^{27} = +2.7°$ (*c* 1.49, benzene), $[\alpha]_D^{29} = +0.75°$ (*c* 2.00, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ = 4.89 (br s, 1H), 4.80 (br s, 1H), 3.51—3.44 (m, 1H), 2.28—2.02 (m, 2H), 1.89—1.01 (m, 11H); ^{13}C NMR ($CDCl_3$) δ = 143.3, 113.5, 72.4, 43.4, 43.0, 29.0, 28.1, 26.6, 26.3, 26.2, 22.2; IR (neat) 3417, 2912, 2852, 1647, 1448, 1377 cm^{-1}.

2-Butenylation of Benzaldehyde (Scheme 3). 2-Butenyl bromide (*E*/*Z* = 88/12) was employed in the same procedure of Table 1, Entry 4.

2-Methyl-1-phenyl-3-buten-1-ol (4a, 4b):[16] A mixture of diastereomers (**4a**/**4b** = 80/20). ^1H NMR ($CDCl_3$), **4a** (*anti*, major isomer) δ = 7.38—7.23 (m, 5H), 5.81 (m, 1H), 5.23—5.17 (m, 2H), 4.37 (d, *J* = 7.6 Hz, 1H), 2.55—2.41 (m, 1H), 2.14 (s, 1H, OH), 0.88 (d, *J* = 6.9 Hz, 3H); **4b** (*syn*, minor isomer) δ = 7.38—7.23 (m, 5H), 5.77 (m, 1H), 5.10—5.02 (m, 2H), 4.62 (d, *J* = 5.3 Hz, 1H), 2.62—2.55 (m, 1H), 1.92 (s, 1H), 1.01 (d, *J* = 6.9 Hz, 3H).

General Procedure for Asymmetric Allylation of Ketones with Chiral Allylating Reagent (Table 3). Substituted-benzyl pyruvates (**5c**, **5d**) were prepared by a method similar to the synthesis of benzyl pyruvate.[17a]

4-Chlorobenzyl Pyruvate (5c): Bp = 112 °C (0.5 mmHg, 1 mmHg = 133.322 Pa); ^1H NMR ($CDCl_3$) δ = 7.35 (m, 4H), 5.24 (s, 2H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$) δ = 191.3, 160.3, 134.8, 132.8, 130.0, 128.9, 67.1, 26.7; IR (neat) 1747, 1730, 1294, 1144 cm^{-1}. HR EIMS Calcd for $C_{10}H_9ClO_3$: $[M]^+$, 212.0240. Found: *m*/*z* 212.0242.

4-Methoxybenzyl Pyruvate (5d): Bp = 108 °C (1.0 mmHg); ^1H NMR ($CDCl_3$) δ = 7.35 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.22 (s, 2H), 3.81 (s, 3H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$) δ = 191.7, 160.5, 160.0, 130.6, 126.5, 114.0, 67.9, 55.2, 26.7; IR (neat) 1734, 1516, 1296, 1252, 1138 cm^{-1}. EI HRMS Calcd for $C_{11}H_{12}O_4$: $[M]^+$, 208.0736. Found: *m*/*z* 208.0735. The same procedure as the asymmetric allylation of aldehydes (Table 1, Entry 4) was used.

2-Hydroxy-2-methyl-1-phenyl-4-penten-1-one (6a): $[\alpha]_D^{29} = +12.4°$ (*c* 1.02, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 8.10—8.07 (m, 2H), 7.67—7.51 (m, 3H), 5.83 (m, 1H), 5.14—5.09 (m, 2H), 4.12 (s, 1H), 2.88 (dd, *J* = 7.3, 14.2 Hz, 1H), 2.71 (dd, *J* = 7.3, 14.2 Hz, 1H), 1.70 (s, 3H); ^{13}C NMR ($CDCl_3$) δ = 204.1, 134.3, 132.9, 132.2, 129.5, 128.4, 119.3, 78.7, 45.4, 26.8; IR (neat) 3467, 2979, 1674, 1595, 1448, 1371 cm^{-1}.

Benzyl (*S*)-2-Hydroxy-2-methyl-4-pentenoate (6b):[29] HPLC 95%ee, column: Chiralcel AS, eluent: Hex/IPA = 500/1, flow rate: 0.6 ml min^{-1}, retention time: 32.9 min (*S*) and 35.1 min (*R*); $[\alpha]_D^{28} = +5.8°$ (*c* 1.09, EtOH), $[\alpha]_D^{24} = -6.9°$ (*c* 1.04, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 7.36 (m, 5H), 5.73 (m, 1H), 5.18 (s, 2H), 5.10—5.00 (m, 2H), 3.18 (s, 1H), 2.52 (dd, *J* = 7.3, 13.9 Hz, 1H), 2.40 (dd, *J* = 7.3, 13.9 Hz, 1H), 1.44 (s, 3H); ^{13}C NMR ($CDCl_3$) δ = 176.3, 135.2, 132.1, 128.6, 128.5, 128.2, 119.2, 74.4, 67.5, 44.6, 25.4; IR (neat) 3479, 2979, 1732, 1454, 1377, 1219, 1165 cm^{-1}. EI HRMS Calcd for $C_{13}H_{17}O_3$: $[M+H]^+$, 221.1178. Found: *m*/*z* 221.1176. The absolute configuration was determined to be (*S*) by conversion to (*S*)-(+)-dimethyl citramalate (**10**) as described below.

4-Chlorobenzyl 2-Hydroxy-2-methyl-4-pentenoate (6c): HPLC 95%ee, column: Chiralcel AS, eluent: Hex/IPA = 500/1, flow rate: 0.6 ml min^{-1}, retention time: 29.8 min (major) and 28.1 min (minor); $[\alpha]_D^{27} = -7.2°$ (*c* 1.01, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 7.37—7.26 (m, 4H), 5.72 (m, 1H), 5.15 (s, 2H), 5.10—5.01 (m, 2H), 3.10 (s, 1H), 2.49 (dd, *J* = 7.3, 13.9 Hz, 1H), 2.39 (dd, *J* = 7.3, 13.9 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR ($CDCl_3$) δ = 176.2, 134.4, 133.7, 132.1, 129.7, 128.8, 119.3, 74.4, 66.6, 44.6, 25.4; IR (neat) 3458, 2979, 1734, 1493, 1454, 1219, 1163 cm^{-1}. EI HRMS Calcd for $C_{13}H_{15}ClO_3$: $[M]^+$, 254.0710. Found: *m*/*z* 254.0705.

4-Methoxybenzyl 2-Hydroxy-2-methyl-4-pentenoate (6d): HPLC 95%ee, column: Chiralcel AS, eluent: Hex/IPA = 100/1, flow rate: 0.8 ml min^{-1}, retention time: 44.1 min (major) and 32.8 min (minor); $[\alpha]_D^{26} = -9.2°$ (*c* 1.04, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 7.28 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.71 (m, 1H), 5.11 (s, 2H), 5.08—4.98 (m, 2H), 3.80 (s, 3H), 3.17 (s, 1H, OH), 2.48 (dd, *J* = 7.3, 13.9 Hz, 1H), 2.36 (dd, *J* = 7.3, 13.9 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR ($CDCl_3$) δ = 176.3, 159.7, 132.2, 130.2, 127.3, 119.1, 113.9, 74.3, 67.3, 55.2, 44.6, 25.4; IR (neat) 3483, 2983, 1732, 1614, 1516, 1458, 1250, 1171 cm^{-1}. EI HRMS Calcd for $C_{14}H_{18}O_4$: $[M]^+$, 250.1205. Found: *m*/*z* 250.1213.

Benzyl 2-Hydroxy-2-(2-methylpropyl)-4-pentenoate (6e): HPLC 30%ee, column: Chiralcel AD, eluent: Hex/IPA = 50/1, flow rate: 0.4 ml min^{-1}, retention time: 15.2 min (major) and 16.8 min (minor); $[\alpha]_D^{27} = -4.0°$ (*c* 1.01, $CHCl_3$), 95%ee (Chiralcel AD); ^1H NMR ($CDCl_3$) δ = 7.37 (s, 5H), 5.70 (m, 1H), 5.16 (dd, *J* = 11.9, 17.2 Hz, 2H), 5.07—4.99 (m, 2H), 3.20 (s, 1H), 2.45 (dd, *J* = 7.3, 13.9 Hz, 1H), 2.36 (dd, *J* = 7.3, 13.9 Hz, 1H), 1.83—1.59 (m, 3H), 0.93 (d, *J* = 6.3 Hz, 3H), 0.78 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ = 176.5, 135.0, 132.1, 128.6, 119.0, 77.1, 67.5, 47.0, 45.2, 24.2, 24.1, 23.0; IR (neat) 3521, 2956, 1734, 1460, 1215, 1161 cm^{-1}.

2-Butenylation of Benzyl Pyruvate (Scheme 4). 2-Butenylation products were obtained in 72% yield using 2-butenyl bromide (*E*/*Z* = 88/12) in the procedure of Entry 4 in Table 1.

Benzyl 2,3-Dimethyl-2-hydroxy-4-pentenoate (7a, 7b):[17] A mixture of diastereomers (**7a**/**7b** = 82/18); ^1H NMR ($CDCl_3$) **7a** (*anti*) δ = 7.36 (s, 5H), 5.82—5.62 (m, 1H), 5.17 (s, 2H), 4.98—4.90 (m, 2H), 3.09 (s, 1H), 2.54—2.41 (m, 1H), 1.39 (s, 3H), 1.05 (d, *J* = 6.9 Hz, 3H); **7b** (*syn*) δ = 7.36 (s, 5H), 5.82—5.62 (m, 1H), 5.21 (s, 2H), 5.12—5.03 (m, 2H), 3.11 (s, 1H), 2.54—2.41 (m, 1H), 1.37 (s, 3H), 0.91 (d, *J* = 6.9 Hz, 3H).

Synthesis of Both Enantiomers of Citramalic Acid Dimethyl Ester (10) (Scheme 5). Step a.[21] A solution of benzyl 2-hy-

droxy-2-methyl-4-pentenoate (**6b**) (100 mg, 0.454 mmol), sodium periodate (437 mg, 2.04 mmol), and $RuCl_3 \cdot nH_2O$ (5.1 mg) in carbon tetrachloride (4 ml), acetonitrile (4 ml), and water (6 ml) was stirred at room temperature for 4 h. The reaction mixture was extracted five times with CH_2Cl_2 and then the combined organic layers were dried over sodium sulfate and concentrated in vacuo. The crude product was purified by silica-gel TLC (hexane : acetone = 2 : 1, containing 5% acetic acid) to afford 100 mg (92%) of 1-benzyl hydrogen 2-hydroxy-2-methylbutanedioate (**8**): $[\alpha]_D^{27} = +12.3°$ (*c* 1.24, Et_2O); ^{1}H NMR ($CDCl_3$) $\delta = 7.33$ (s, 5H), 5.20 (s, 2H), 3.03 (d, $J = 16.8$ Hz, 1H), 2.73 (d, $J = 16.8$ Hz, 1H), 1.45 (s, 3H); ^{13}C NMR ($CDCl_3$) $\delta = 176.2$, 175.2, 135.1, 128.6, 128.4, 128.2, 72.4, 67.8, 43.8, 26.2, 20.7; IR (neat) 3510—2885, 1738, 1454, 1398, 1282, 1203, 1119 cm^{-1}; EI HRMS Calcd for $C_{12}H_{14}O_5$: $[M]^+$, 238.0841. Found: *m/z* 238.0859.

Step b and c. According to the literature method,[18c] alkaline hydrolysis of 1-benzyl hydrogen 2-hydroxy-2-methylbutanedioate (**8**) (100 mg, 0.420 mmol) to citramalic acid (**9**) and following esterification of **9** were performed to give (+)-dimethyl citramalate (**10**) in 79% yield (58.7 mg). The absolute configuration of thus obtained (+)-dimethyl citramalate (**10**) was determined to be (*S*) by comparison of its optical rotation, $[\alpha]_D^{28} = +29.0°$ (*c* 1.13, $CHCl_3$), with that reported in the literature, $[\alpha]_D^{21} = -30.1°$ (*c* 2.10, $CHCl_3$) for (*R*) configuration (> 96.7%ee).[18a] (−)-Dimethyl citramalate (**10**), $[\alpha]_D^{28} = -27.5°$ (*c* 2.71, $CHCl_3$), was prepared by the same procedure using benzyl (*R*)-2-hydroxy-2-methyl-4-pentenoate (**6b**, 92%ee), $[\alpha]_D^{27} = +7.0°$ (*c* 1.03, $CHCl_3$). Data of **10**: ^{1}H NMR ($CDCl_3$) $\delta = 3.81$ (s, 3H), 3.69 (s, 3H), 2.99 (d, $J = 16.5$ Hz, 1H), 2.68 (d, $J = 16.5$ Hz, 1H), 1.45 (s, 3H); ^{13}C NMR ($CDCl_3$) $\delta = 175.9$, 171.4, 72.5, 52.9, 43.9, 26.2; IR (neat) 3504, 2956, 1739, 1444, 1207 cm^{-1}.

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