Optical Resolution of 2- and 3-Hydroxyalkyltriphenylphosphonium Salts. Stereoselective Synthesis of Enantiomerically Pure (*E*)- and (*Z*)-Homoallylic Alcohols

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Optically active 2- and 3-hydroxyalkyltriphenylphosphonium salts were prepared by the optical resolution of their 2,3-di-*O*-benzoyltartrates. The reaction of these salts with butyllithium afforded the corresponding ylides, which reacted with aldehydes to give optically active (*E*)-homoallylic alcohols in good yields. 3-Hydroxyalkyltriphenylphosphonium salts were converted into the corresponding diphenylphosphine oxides by the reaction with aq NaOH, which reacted with sodium hydride followed by the addition of benzaldehyde to afford optically active (*Z*)-homoallylic alcohols.

The synthesis of enantiomerically pure unsaturated alcohols is of current interest for their versatile utility in natural products.[1] One of these approaches is the reaction of hydroxyalkyltriphenylphosphonium ylides with carbonyl compounds.[2] Recently, we have reported the easy preparation and optical resolution of 2- (**1**) and 3-hydroxyalkyltriphenylphosphonium salts (**2**,**3**).[3,4] These results prompted us to investigate the possibility of the synthesis of optically active allylic (**4**) and homoallylic alcohols (**5**). In this paper, we would like to report a general synthesis and some reactions of enantiomerically pure **1** and **2**.

Results and Discussion

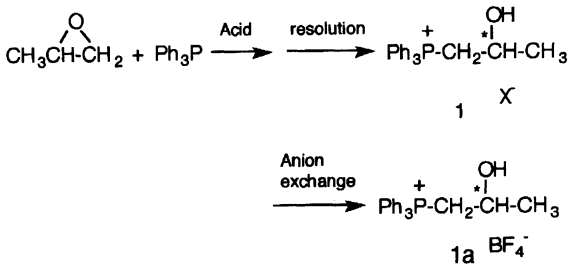
Synthesis of Optically Active 2-Hydroxypropyltriphenylphosphonium Salts (1). By using camphor-10-sulfonic acid (CSA) or 2,3-di-*O*-benzoyltartaric acid (DBTA), propene oxide reacted with triphenylphosphine to afford 2-hydroxypropyltriphenylphosphonium salts (**1**). Optical resolution by fractional recrystallization (MeOH–ether; three times) gave a pure diastereomer of salt **1a** (Scheme 1).

Their enantiomeric excess of **1a** and **1a′** was confirmed by their NMR spectra by tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium derivative (Table 1).

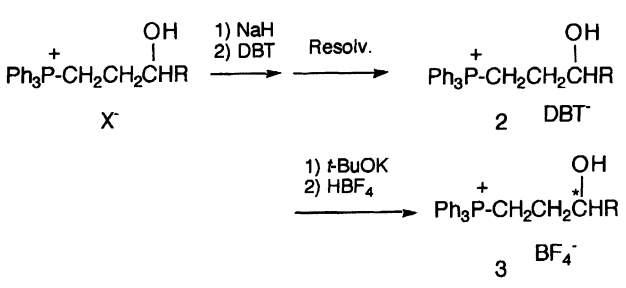
Synthesis of Optically Active 3-Hydroxyalkyltriphenylphosphonium Salts (2). Recemic 3-hydroxyalkyltriphenylphosphonium 2,3-di-*O*-benzoyl tartrates (DBT^-) were prepared by the reaction of methylenetriphenylphosphorane with epoxides followed by the addition of 2,3-di-*O*-benzoyl tartaric acid (DBTA). In a previous communication, these salts **2** were partially resolved by using acetone–ether.[3] After several trials for improving their enantiomeric excess, we found that good optical resolution was obtained by using methanol–ether as a resolving solvent.[4] By this method, the following phosphonium salts **2** were resolved into the corresponding pure diasteromers. These DBT salts were easily converted into their tetrafluoroborate (**3**) by adding potassium *t*-butoxide followed by the addition of HBF_4 solution or by elution with anion exchange resin (Amberlite IRA-400). In the case of cyclohexene oxide, the optical resolution of the corresponding phosphonium salt was unsuccesful. However, this method would provide a new synthesis of optically active 3-hydroxyalkyltriphenylphosphonium salts (Scheme 2, Table 2).

Since many simple epoxides could be transformed into the corresponding 3-hydroxyalkyltriphenylphosphonium salts by this method, we then tried the reaction of methylenetriphenylphosphorane with epichlorohydrin. However, the obtained product was not the ring-opened product but 3,4-epoxybutyltriphenylphosphonium iodide.[5]

Determination of the enantiomeric excess of 3-hydroxyalkyltriphenylphosphonium tetrafluoroborate **3** was carried out by their (*S*)-(−)-α-methoxy-α-(trifluo-



Scheme 1.



Scheme 2.

Table 1. Preparation of 2-Hydroxypropyltriphenylphosphonium Salts **1a**

Acid[a]			Chemical yield/%	After resolution/%	$[\alpha]_D$ °			$[\alpha]_D$ °	ee/%	Absolute configuration
(*R*)-CSA	**1a**	(*R*)-CS	65	23	−60.8	**1a**	BF_4^-	−61.3	>99	*R*
(*S*)-CSA	**1a′**	(*S*)-CS	68	31	+61.1	**1a′**	BF_4^-	+60.2	>99	*S*
(*R*,*R*)-DBTA	**1a**	(*R*,*R*)-DBT	90	47	+54.2	**1a**	BF_4^-	−12.3	22	*R*
(*S*,*S*)-DBTA	**1a′**	(*S*,*S*)-DBT	90	51	−58.2	**1a′**	BF_4^-	+19.5	32	*S*

a) CSA: Camphor-10-sulfonic acid. DBTA: 2,3-Di-*O*-benzoyltartaric acid. CS: Camphor-10-sulfonate. DBT: 2,3-Di-*O*-benzoyltartrate.

Table 2. Resolution of 3-Hydroxyalkylphosphonium Salts

R	Acid	Chemical yield/%		After resolution	$[\alpha]_D$ (MeOH)/° DBT	BF_4		ee/%[a]	Configuration
Me	(*S*,*S*)-DBT	**2a**	83	25	−68.1	**3a**	−2.4	>99	*R*
Me	(*R*,*R*)-DBT	**2a′**	72	11	+64.5	**3a′**	+2.2	>99	*S*[b]
Et	(*S*,*S*)-DBT	**2b**	63	36	−59.5	**3b**	−1.5	>99	
Et	(*R*,*R*)-DBT	**2b′**	49	27	+60.2	**3b′**	+1.3	>99	
4-ClC_6H_4	(*S*,*S*)-DBT	**2c**	86	13	−63.4	**3c**	−15.8	>98	
4-ClC_6H_4	(*R*,*R*)-DBT	**2c′**	94	21	+66.7	**3c′**	+14.1	>96	
$PhOCH_2$	(*S*,*S*)-DBT	**2d**	92	23	−58.1	**3d**	−5.2	>99	

a) Enantiomeric excess (ee) was determined by their MPTA esters. b) Determination of absolute configulation was carried out by its authentic sample derived from optically active (*S*)-(−)-propene oxide, which was purchased from Aldrich.

romethyl)phenylacetates [(*S*)-(−)-MTPA esters]. These MTPA esters were easily obtained by the reaction of **3** with (*S*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride in the presence of 4-dimethylaminopyridine. α-Methoxy signals of racemic ester were clearly separated (^1H NMR ($CDCl_3$) δ=3.38 and 3.58).

This procedure would provide a general synthesis of enantiomerically pure 3-hydroxyalkyltriphenylphosphonium salts **3**.

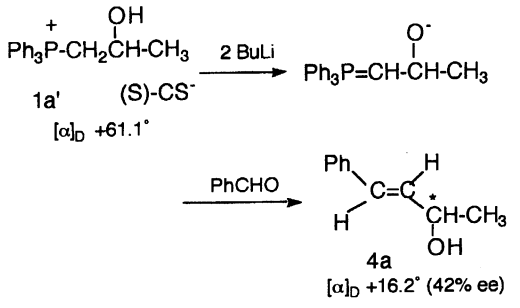
Reaction of 1 and 3 with Aldehydes in the Presence of Bases 2-Hydroxyalkyltriphenylphosphonium salts **1** form an important class of compounds for the preparation of allylic alcohols. Corey and Yamamoto reported that the reaction of Wittig reagents with aldehydes gave the corresponding adducts at low temperature, which further reacted with a base followed by the addition of aldehydes to give allylic alcohols.[2] Schlosser et al.[2] and Maryanoff et al.[2,6] also reported the stereoselective synthesis of allylic alcohols from 2-hydroxyalkyltriphenylphosphonium salts prepared from 2-hydroxyalkyl iodides and triphenylphosphine. The present method may afford a convenient approach for the synthesis of optically active allylic alcohols. To confirm this possibility, we investigated the reaction of salt **1a** with two molar amount of butyllithium followed by the addition of benzaldehyde. However, the obtained (*E*)-4-phenyl-3-buten-2-ol (**4a**) has only 42 % optical purity.

This result is quite different from that of Corey et al.[2,7] The racemization of **1a′** might partly occur before the formation of the olefin. Vedejs et al. reported that the intermediates from aliphatic aldehydes and nonstabilized ylides such as oxaphosphetanes obtained by the reaction of racemic **1** with an equimolar amount of the base did not revert to the starting materials under typical Wittig reaction conditions.[8] We also found that the reaction of **1a′** with an equimolar amount of butyllithium followed by the addition of aq HCl at low temperature recovered **1b′** without any racemization (Scheme 3).

Therefore, the racemization might occur in reversible retro Wittig reaction before the oxaphosphetane derived from β-oxide ylide and benzaldehyde decomposed to give **4** and triphenylphosphine oxide.

We then tried the reaction of **3** with bases followed by the addition of aldehydes. The corresponding (*E*)-homoallylic alcohols **5** were obtained in good yields (Scheme 4, Table 3).

In the case of butyraldehyde, (*E*) and (*Z*) isomers were obtained in only the 80 : 20 ratio. However, by using benzaldehyde as a substrate, the *E*: *Z* ratio was

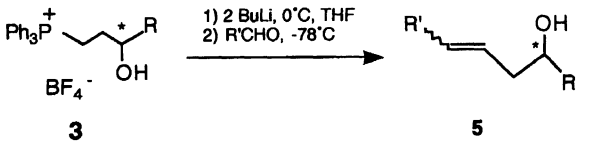


Scheme 3.

Table 3. Preparation of Optically Active (*E*)-Homoallyl Alcohols **5**

Substrate	Aldehyde	Conditions		Products			
		Base	Temperature/°C		Yield/%	ee/%	*E*:*Z*
3a′	PhCHO	BuLi	−78	**5a′**[a]	60	>99	96:4
3a′	*trans*-PhCH=CHCHO	BuLi	−78	**5b′**	54	>99	87:13
3a′	$CH_3CH_2CH_2CHO$	BuLi	−78	**5c′**	53	>99	62:38
3b	PhCHO	BuLi	−78	**5d**	58	>99	94:6
3b′	PhCHO	BuLi	−78	**5d′**	40	>99	97:3
3b	*trans*-PhCH=CHCHO	BuLi	−78	**5e**	47	>99	85:15
3b	$CH_3CH_2CH_2CHO$	BuLi	−78	**5f**	77	>99	80:20
3d	PhCHO	BuLi	−78	**5g**	75	>99	91:9

a) Enantiomeric excess (ee) was determined by their MTPA esters.



3 **5**

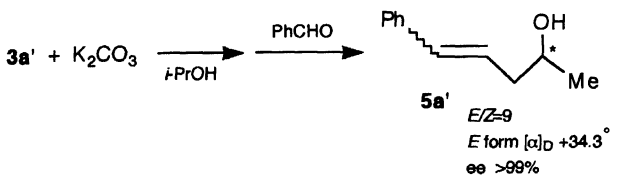
Scheme 4.

changed to 96:4. For example, Maryanoff et al. studied the reaction of hydroxyalkylphosphonium salts with bases followed by the addition of aldehydes.[2,6] They observed that the *E* selectivity increased by the reaction of 3-hydroxyalkyltriphenylphosphonium salts **3** with aromatic aldehydes, and it decreased by using aliphatic aldehydes. Their observation agrees with ours. α,β-Unsaturated aldehydes reacted with this ylide to give dienes in 54% yields. The obtained (*E*)-homoallylic alcohols **5** were easily separated by silica gel HPLC or by silver nitrate impregnated silica gel.

Cheik-Rouhou et al. reported a simplified Wittig synthesis using a solid–liquid transfer process.[9] We applied this method to the synthesis of optically active homallylic alcohols. The obtained (*E*)-homoallylic alcohols were easily separated by HPLC (Scheme 5).

Preparation of Optically Active *erythro* Phosphine Oxides. Recently, Warren and co-workers reported the preparation of (*E*)- and (*Z*)-olefins by the reaction of phosphine oxides with bases followed by the addition of aldehydes.[10] We also tried the preparation of 3-hydroxyalkyldiphenylphosphine oxides (**6**) (Table 4). As shown in Scheme 6, the corresponding optically active oxides were prepared easily, whose formation is applicable to the synthesis of homallylic alcohols.

Treatment of **6** with butyllithium followed by the addition of aldehydes resulted in the formation of a mixture of two *threo*- (minor) and two *erythro*-2-diphenylphosphinoyl-1,4-alkanediols (major) (**7**), which were easily separated into *erythro* forms in 37—75% yields (Table 5, Scheme 7). However, each *erythro* forms could not be isolated by silica gel chromatographic separation.

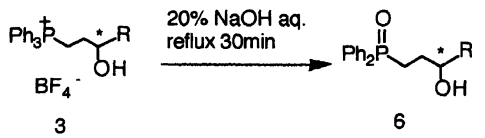


Scheme 5.

Table 4. Preparation of Optically Active 3-Hydroxyalkyldiphenylphosphine Oxides **6**

Substrate	Phosphine oxide			
3	**6**	Yield/%	ee/%	$[\alpha_D]$/°
3a′	**6a′**	96	>99	+9.9
3b	**6b**	95	>99	−9.3
3c	**6c**	93	>96	+21.9
3d	**6d**	95	>99	−10.6

a) Enantiomeric excess (ee) was determined by their MTPA esters.

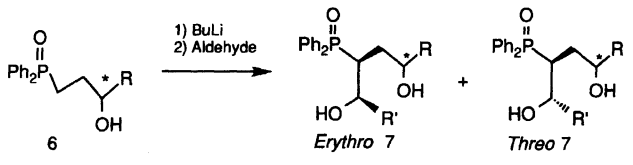


3 **6**

Scheme 6.

Structure determination of *erythro*-diols **7** was carried out by ^{1}H NMR spectroscopic analysis. According to Warren et al., the coupling constant of *erythro*-phosphinoyl α-hydrogens and β-hydrogens in 2-diphenylphosphinoyl-1-phenylalkan-1-ols are 1—2 Hz, whereas those of *threo*-isomers are 6—9 Hz.[10] The corresponding coupling constant s of **7a′**—**7g** are less than 1 Hz, which suggest that these compounds have *erythro* forms.

Preparation of Enantiomerically Pure (*Z*)-Homoallylic Alcohols. When *erythro* **7** were al-



Scheme 7.

Table 5. Synthesis of *erythro* 1,4-Alkanediol (**7**)

Phosphine oxide		Aldehyde R′CHO	*erythro* 1,4-Alkanediol		
6	R	R′	**7**	(Yield/%)	Ratio of two *erythro* **7**
6a′	Me	Ph	**7a′**	72	9:1
6a′	Me	*trans*-PhCH=CH	**7b′**	63	3:1
6a′	Me	Propyl	**7c′**	46	4:3
6b	Et	Ph	**7d**	48	8:1
6b′	Et	Ph	**7d′**	37	8:1
6b	Et	*trans*-PhCH=CH	**7e**	57	3:2
6b	Et	Propyl	**7f**	48	1:1
6d	$PhOCH_2$	Ph	**7g**	75	4:1

lowed to react with sodium hydride, (*Z*)-homoallylic ahcohols (**8**) were prepared in good yields and good stereoselectivity. The results are shown in Table 6 (Scheme 8).

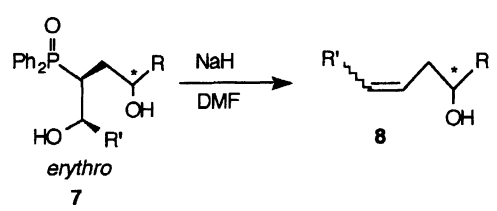
Recently, optically active homoallylic alcohols were prepared by the Wittig rearrangement of the corresponding allyl silyl ether[11] or by a diastereoselective addition of allyltrimethylsilane to *N*-(1,2-dioxoalkyl)-proline ketones.[12] The present results provide another method for the preparation of enantiomerically pure homoallylic alcohols.

Efforts to explore the chemistry of hydroxyalkylphosphonium salts and to expand it to the synthesis of natural products containing homoallylic alcohol moiety are in progress in our laboratories.

Experimental

General. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were obtained with a JEOL FX-90Q or a JEOL GSX-400 spectrometer. Chemical shifts are given in ppm units downfield from tetramethylsiane. TLC analyses were performed using Merck Silica gel 60 F254 aluminum plates. HPLC was performed on a Waters 510 by using Merck-Hiber column. Optical rotation was determined by using Jasco DIP-140 polarimeter.

Preparation of 2-Hydroxypropyltriphenylphosphonium Camphorsulfonate (1a CS). To a solution of triphenylphosphine (2.62 g, 10.0 mmol) and (*R*)-(−)-CSA (2.3 g, 10.0 mmol) in acetonitrile (50 mL) was added a solution of propene oxide (0.82 g, 14.0 mmol) in acetonitrile (10 mL) at room temperature. After refluxing for 15 h, the reaction mixture was evaporated to give a pale yellow oil as a diastereomeric mixture of the corresponding phosphonium salts. Optical resolution by fractional recrystallization (MeOH–ether; three times) gave a pure diastereomer of **1a** (−)-CS in 23 % yield. Mp 114—115 °C. $[\alpha]_D$ −60.8° (*c* 2.00, MeOH). ^1H NMR ($CDCl_3$) δ=0.83 (s, 3H), 1.14 (s, 3H), 1.30—1.35 (m, 1H), 1.49—1.51 (m, 3H), 1.59—1.66 (m, 2H), 2.25—2.32 (m, 1H), 2.80 (d, J=14.6 Hz, 1H), 3.03—3.10 (m, 1H), 3.36 (d, J=15.0 Hz, 1H), 4.11—4.17 (m, 1H), 4.20—4.26 (m, 1H), 7.64—7.81 (m, 15H, Ar). Found: C, 65.35; H, 6.96%. Calcd for $C_{31}H_{20}F_3O_3P \cdot H_2O$: C, 65.24; H, 6.89%. Optical yield was determined from its ^1H NMR spectra by using tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium.



Scheme 8.

When (*S*)-(+)-CS was used as an acid, another pure diastereomer of **1a′** CS was obtained in 31 % yield after fractional recrystallization (MeOH–ether, three times). **1a′** (+)-CS: Mp 114—115 °C. $[\alpha]_D$ +61.1° (*c* 2.00, MeOH). These salts were easily converted to their tetrafluoroborates by elution with anion exchange resin (Amberlite IRA-400). **1a** BF_4^-: Mp 144—145 °C. $[\alpha]_D$ −61.3° (*c* 2.00, MeOH). **1a′** BF_4^-: Mp 144—145 °C. $[\alpha]_D$ +60.2° (*c* 2.00, MeOH).

Preparation of 2-Hydroxypropyltriphenylphosphonium (*S,S*)-DBT (1a DBT). To a solution of triphenylphosphine (2.62 g, 10.0 mmol) and (*S,S*)-DBT (3.76 g, 10 mmol) in acetonitrile (50 ml) was added a solution of propene oxide (0.82 g, 14.0 mmol) via syringe. After refluxing for 15 h, the reaction mixture was evaporated to give a pale yellow oil as a diastereomeric mixture of the corresponding phosphonium salts. Optical resolution by fractional recrystallization (MeOH–ether; three times) gave a partically resolved diastereomer of **1a** (*S,S*)-DBT in 51% yield (3.28 g, 5.1 mmol). Mp 155—156 °C. $[\alpha]_D$ −58.2° (*c* 2.00, MeOH). ee 32%. ^1H NMR (CD_3CN) δ=1.39 (dd, 3H, Me), 3.1—3.65 (m, 2H, CH_2), 4.05 (m, CH), 5.85 (s, 2H, CH), 7.35—8.10 (m, 25H, Ar). Found: C, 69.02; H, 5.41%. Calcd for $C_{39}H_{35}O_9P$: C, 69.02; H, 5.20%.

Preparation of Optically Active 3-Hydroxyalkyltriphenylphosphonium DBT Salts (2). To a suspension of sodium hydride (1.44 g, 36.0 mmol, 60 % in mineral oil) in tetrahydrofuran (100 mL) was added a 3-hydroxybutyltriphenylphosphonium iodide (13.9 g, 30.1 mmol) in one portion. After refluxing for 5 h, the suspension was filtered off. The filtrate was added to a solution of (*S,S*)-2,3-di-*O*-benzoyltartaric acid (10.7 g, 29.8 mmol) in ether (100 mL). Colorless crystals were immediately precipitated, which were filtered off. The filtrate was evaporated to give colorless crystals (17.2 g, 24.9 mmol, 83 %), which were recrystallized from methanol–ether to give colorless crystals of **2a** (5.2 g, 7.5 mmol, 25 %). Mp 153—154 °C $[\alpha]_D$ −68.1° (*c* 2.00, MeOH). ^1H NMR ($CDCl_3$) δ=1.09 (d, 3H, J=5.9 Hz, Me), 1.60—1.70 (m, 2H, CH_2), 3.29—3.39 (m, 1H, PCHH), 3.63—3.74 (m, 1H, PCHH), 3.93—4.02 (m,

Table 6. Synthesis of Enantiomerically Pure (*Z*)-Homoallylic Alcohols (**8**)

erythro-Phosphinoylalkanediol			(*Z*)-Homoallylic alcohol				Absolute
7	R	R′	**8**	Yield/%	ee/%	*E*/*Z*	configuration
7a′	Me	Ph	**8a′**	55	>99	3:97	*S*
7b′	Me	*trans*-PhCH=CH	**8b′**	40	>99	22:78	*S*
7c′	Me	$CH_3CH_2CH_2$	**8c′**	70	>99	20:80	*S*
7d	Et	Ph	**8d**	61	>99	6:94	
7d′	Et	Ph	**8d′**	50	>99	4:96	
7e	Et	*trans*-PhCH=CH	**8e**	59	>99	21:79	
7f	Et	$CH_3CH_2CH_2$	**8f**	66	>99	19:89	
7g	$PhOCH_2$	Ph	**8g**	65	>99	17:83	

1H, CHOH), 5.86 (s, 2H, DBT-CH), 7.22—7.27 (m, 15H, Ar), 7.91—7.93 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ=18.99 (d, J=51.9 Hz, PCH_2), 23.07 (Me), 31.23 (d, J=65.6 Hz, CH_2), 65.91 (d, J=15.3 Hz, CHOH), 70.34 (DBT-CH), 117.85, 118.71, 127.99, 129.84, 130.42, 130.55, 132.72, 133.30, 133.39, 135.08, 135.11 (Ar), 165.54, 169.79, (C=O). Found: C, 69.33; H, 5.59%. Calcd for $C_{40}H_{37}O_9P$: C, 69.34; H, 5.39%.

(*R,R*)-DBT salt **2a′** was prepared in a similar manner by using sodium hydride (1.28 g, 32.0 mmol, 60% mineral oil dispersion), 3-hydroxybutyltriphenylphosphonium iodide (12.32 g, 26.7 mmol), and (*R, R*)-DBT (9.57 g, 26.7 mmol). **2a′** (2.0 g, 2.9 mmol, 11%). Mp 152—153 °C $[\alpha]_D$ +64.5° (*c* 2.00, MeOH).

(*S,S*)-DBT salt **2b** was prepared in a similar manner by using sodium hydride (1.06 g, 26.5 mmol, 60 % mineral oil dispersion), 3-hydroxypentyltriphenylphosphonium iodide (9.53 g, 20.0 mmol), and (*S,S*)-DBT (7.17 g, 20.0 mmol). **2b** (5.0 g, 7.2 mmol, 36 %). Mp 134—135 °C. $[\alpha]_D$ −59.5° (*c* 2.00, MeOH). ^{1}H NMR ($CDCl_3$) δ=0.79 (t, 3H, J=7.3 Hz, Me), 1.28—1.46 (m, 2H, CH_3CH_2), 1.57—1.73 (m, 2H, CH_2), 3.30—3.40 (m, 1H, CHOH), 3.65—3.74 (m, 2H, PCH_2), 5.85 (s, 2H, DBT-CH), 7.22—7.27 (m, 4H, Ar), 7.40 (m, 2H, Ar), 7.64—7.99 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$), δ=10.14 (Me), 19.00 (d, J_{P-C}=39.2 Hz, PCH_2), 29.72 (CH_2, J_{P-C}=38.7 Hz), 70.27 (DBT-CH), 71.22 (d, J_{P-C}=14.7 Hz, CHOH), 117.87, 118.73, 128.01, 129.83, 130.42, 130.42, 130.53, 132.74, 133.29, 133.38, 135.08 (Ar), 165.53, 169.78 (C=O). Found: C, 69.52; H, 5.97%. Calcd for $C_{41}H_{39}O_9P$: C, 69.34; H, 5.39%.

(*R,R*)-DBT salt **2b′** was prepared in a similar manner by using sodium hydride (0.80 g, 20.0 mmol, 60% mineral oil dispersion), 3-hydroxypentyltriphenylphosphonium iodide (8.56 g, 18.0 mmol), and (*R,R*)-DBT (6.34 g, 17.7 mmol). **2b′** (2.3 g, 3.3 mmol, 27%). Mp 133—134 °C $[\alpha]_D$ +60.2° (*c* 2.00, MeOH).

(*S,S*)-DBT salt **2c** was prepared in a similar manner by using sodium hydride (0.48 g, 12.0 mmol, 60 % mineral oil dispersion), 3-(4-chlorophenyl)-3-hydroxypropyltriphenylphosphonium iodide (5.58 g, 10.0 mmol), and (*S,S*)-DBT (3.58 g, 10.0 mmol). **2c** (1.03 g, 1.3 mmol, 13%). Mp 148—150 °C. $[\alpha]_D$ −63.4° (*c* 2.00, MeOH). ^{1}H NMR ($CDCl_3$) δ=1.73—1.84 (m, 1H, PCHH), 1.92—1.99 (m, 1H, PCHH), 3.51—3.60 (m, 2H, CH_2), 4.96—4.99 (m, 1H, CHOH), 5.86 (s, 2H, DBT-CH), 7.10—7.15 (m, 4H, Ar), 7.21—7.27 (m, 4H, Ar), 7.41 (t, J=7.3 Hz, 2H, Ar), 7.60—7.74 (m, 15H, Ar), 7.90 (d, J=6.6 Hz, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ=18.65 (d, J_{P-C}=51.4 Hz, PCH_2), 32.14 (CH_2), 70.72 (d, J_{P-C}=16.5 Hz, CHOH), 70.93 (DBT-CH), 117.67, 118.53, 127.11, 128.02, 128.24, 129.78, 129.85, 130.38, 130.51, 132.58, 132.78, 133.27, 133.36, 142.49 (Ar), 165.59, 169.90 (C=O). Found: C, 68.15; H, 5.02%. Calcd for $C_{45}H_{38}ClO_9P$: C, 68.51; H, 4.86%.

(*R,R*)-DBT salt **2c′** was prepared in a similar manner by using, sodium hydride (0.48 g, 12.0 mmol, 60% mineral oil despersion), 3-(4-chlorophenyl)-3-hydroxypropyltriphenylphosphonium iodide (5.58 g, 10.0 mmol), and (*R,R*)-DBT (3.58 g, 10.0 mmol). **2c′** (1.65 g, 2.1 mmol, 21%). Mp 147—149 °C. $[\alpha]_D$ +66.7° (*c* 2.00, MeOH).

(*S,S*)-DBT salt **2d** was prepared in a similar manner by using sodium hydride (0.48 g, 12.0 mmol, 60 % mineral oil dispersion), 3-hydroxy-4-phenoxybutyltriphenylphosphonium iodide (5.54 g, 10.0 mmol), and (*S,S*)-DBT (3.58 g, 10.0 mmol). **2d** (1.63 g, 2.3 mmol, 23 %). Mp 150—152 °C. $[\alpha]_D$ −58.1° (*c* 2.00, MeOH). ^{1}H NMR ($CDCl_3$) δ=1.78—1.88 (m, 1H, CHH), 1.92—2.04 (m, 1H, CHH), 3.37—3.49 (m, 1H, PCHH), 3.64—3.75 (m, 1H, PCHH), 3.76—3.81 (m, 1H, CHHOPh), 3.93—3.96 (m, 1H, CHHOPh), 4.18—4.23 (m, 1H, CHOH), 5.85 (s, 2H, DBT-CH), 6.73 (d, J=8.1 Hz, 2H, Ar), 6.88 (t, J=6.6 Hz, 1H, Ar), 7.16—7.27 (m, 6H, Ar), 7.39 (t, J=7.3 Hz, 2H, Ar), 7.64—7.75 (m, 15H, Ar), 7.91 (d, J=6.3 Hz, 4H, Ar).

^{13}C NMR ($CDCl_3$) δ=18.52 (d, J_{P-C}=53.3 Hz, PCH_2), 26.76 (CH_2), 68.04 (d, J_{P-C}=14.7 Hz, CHOH), 70.56 (CH_2OPh), 70.60 (DBT-CH), 114.40, 117.69, 118.55, 120.78, 128.01, 129.36, 129.76, 129.82, 130.38, 130.51, 132.74, 133.29, 133.40, 135.08, 158.40 (Ar), 165.51, 169.87 (C=O).

Preparation of Tetrafluoroborate Salt (3). By Using Anion Exchange Resin. The ion exchange resin (Organo IRA-400) was suspended in a solution of $NaBF_4$ (10 %, 200 mL) for 1 h and poured into a column (25×250 mm), which was eluted with a mixture of MeOH–water (5:1). A solution of DBT salt **2a** (0.51 g, 0.7 mmol) in MeOH–water (5:1) was charged into this column and eluted with MeOH:water (5:1). The eluant was evaporated to give colorless crystals, which were recrystallized from MeOH–ether to afford the corresponding salt **3a**. (0.25 g, 0.59 mmol, 84 %) Mp 159—160 °C. $[\alpha]_D$ −2.4° (*c* 2.00, MeOH). ^{1}H NMR ($CDCl_3$) δ=1.16 (d, 3H, J=6.6 Hz, Me), 1.60—1.73 (m, 2H, CH_2), 3.24—3.35 (m, 1H, PCHH), 3.45—3.55 (m, ^{1}H, PCHH), 3.99—4.04 (m, 1H, CHOH), 7.68—7.82 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) δ=18.73 (d, J_{P-C}=53.3 Hz, PCH_2), 23.05 (CH_3), 31.34 (d, J_{P-C}=3.7 Hz, CH_2), 66.47 (d, J_{P-C}=14.7 Hz, CHOH), 117.76, 118.62, 130.47, 130.60,

133.31, 133.40, 135.14 (Ar). Found: C, 62.54; H, 5.97%. Calcd for $C_{22}H_{24}BF_4OP$: C, 62.59; H, 5.73%.

BF_4 salt **3a′** was prepared from **2a** in a similar manner by using the ion exchange resin (Organo IRA-400). **3a′** (0.17 g, 0.4 mmol, 57%). Mp 157—158 °C. $[\alpha]_D$ +2.2° (*c* 2.00, MeOH).

BF_4 salt **3b** was prepared in a similar manner by using *t*-butoxide (2.76 g, 20.0 mmol), **2b** (4.36 g, 10.0 mmol), and aqueous HBF_4 (2.09 g, 10.0 mmol, 42 %). **3b** (3.23 g, 7.4 mmol, 74 %). Mp 134—137 °C. $[\alpha]_D$ −1.5° (*c* 2.00, MeOH), optical purity: >99 %. ^{1}H NMR ($CDCl_3$) δ=0.85 (t, J=7.6 Hz, 3H, CH_3), 1.38—1.47 (m, 2H, C<u>H</u>$_2$CH$_3$), 1.56—1.79 (m, 2H, CH_2), 3.23—3.36 (m, 1H, PC<u>H</u>H), 3.46—3.60 (m, 1H, PCH<u>H</u>), 3.73 (br, 1H, C<u>H</u>OH), 7.68—7.82 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) δ=10.07, (CH_3), 18.69 (d, J_{P-C}=53.3 Hz, PCH_2), 29.51 (d, J_{P-C}=3.6 Hz, CH_2), 29.89 (C<u>H</u>$_2$CH$_3$), 71.67 (d, J_{P-C}=16.5 Hz, PCH_2), 117.82, 118.68, 130.47, 130.60, 133.29, 133.38, 135.10 (Ar). Found: C, 63.47; H, 6.40%. Calcd for $C_{23}H_{26}BF_4OP$: C, 63.33; H, 6.01%.

BF_4 salt **3b′** was prepared in a similar manner by using the ion exchange resin (Organo IRA-400), **2b′** (0.33 g, 0.5 mmol). **3b′** (0.16 g, 0.4 mmol, 80 %). Mp 134—135 °C. $[\alpha]_D$ +1.3° (*c* 2.00, MeOH).

BF_4 salt **3c** was prepared in a similar manner by using the ion exchange resin (Organo IRA-400), **3c** (0.5 g, 0.6 mmol). **3c** (0.25 g, 0.5 mmol, 75%). Mp 194—195 °C. $[\alpha]_D$ −15.8° (*c* 2.00, 1H, MeOH). ^{1}H NMR ($CDCl_3$) δ= 1.79—1.99 (m, 2H, PCH_2), 3.35—3.63 (m, 2H, CH_2), 4.98—5.01 (m, 1H, C<u>H</u>OH), 7.18—7.27 (m, 4H, Ar), 7.60—7.78 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) δ=18.67 (d, J_{P-C}=53.3 Hz, PCH_2), 32.06 (d, J_{P-C}=3.7 Hz, CH_2), 71.45 (d, J_{P-C}=16.6 Hz, CHOH), 117.53, 118.39, 127.15, 128.44, 130.46, 130.58, 132.94, 133.25, 133.53, 135.12, 142.00 (Ar). Found: C, 62.25; H, 4.96%. Calcd for $C_{27}H_{25}BF_4OPCl$: C, 62.52; H, 4.86%.

BF_4 salt **3c′** was prepared from **2c′** (0.50 g, 0.6 mmol) in a similar manner by using ion exchange resin (Organo IRA-400). **3c′** (0.23 g, 0.4 mmol, 69 %). Mp 194—195 °C. $[\alpha]_D$ +14.1° (*c* 2.00, MeOH).

BF_4 salt **3d** was prepared from **3c** (0.2 g, 0.3 mmol) in a similar manner by using the ion exchange resin (Organo IRA-400). **3d** (0.11 g, 0.2 mmol, 83 %). Mp 177—178 °C. $[\alpha]_D$ −5.2° (*c* 2.00, MeOH). ^{1}H NMR ($CDCl_3$) δ=1.79—2.05 (m, 2H, CH_2), 3.30—3.61 (m, 2H, PCH_2), 3.39 (dd, J=9.5 and 5.2 Hz, 1H, C<u>H</u>HOPh), 3.98 (dd, J=9.5 and 5.2 Hz, 1H, CH<u>H</u>OPh), 4.21—4.28 (m, 1H, C<u>H</u>OH), 6.80—6.82 (m, 2H, Ar), 6.90 (t, J=7.3 Hz, 1H, Ar), 7.19—7.23 (m, 2H, Ar), 7.66—7.81 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) δ=18.38 (d, J_{P-C}=53.4 Hz, PCH_2), 26.47 (CH_2), 68.62 (d, J_{P-C}=14.7 Hz, CHOH), 70.54 (CH_2), 114.49, 117.58, 118.44, 120.95, 129.43, 130.47, 130.60, 133.31, 133.40, 135.14, 135.17, 158.33, 158.33 (Ar). Found: C, 65.30; H, 5.67%. Calcd for $C_{28}H_{28}BF_4O_2P$: C, 65.39; H, 5.49%.

Ion exchange was also carried out by using potassium *t*-butoxide and aq HBF_4 solution.

To a solution of DBT salt **2a** (1.0 g, 1.4 mmol) in THF–DMF (9:1, 100 mL) was added potassium *t*-butoxide (0.4 g, 2.9 mmol) in one portion. After refluxing for 5 h, the reaction mixture was filtered. The filtrate was evaporated to give pale yellow oily crystals, which were extracted with ether (15 mL×3). Aqueous HBF_4 (0.30 g, 1.4 mmol, 42 %) was added to the combined extracts. Colorless crystals were precipitated and collected by filtration. The resulting crystals were recrystallized from MeOH–ether to give salt **3a**. (0.41 g, 0.96 g, 67 %). Mp 159—160 °C.

3b was prepared in a similar manner by using potassium *t*-butoxide (2.76 g, 20.0 mmol), **2b** (4.36 g, 10.0 mmol), and aqueous HBF_4 (2.09 g, 10.0 mmol, 42 %). **3b** (3.23 g, 7.4 mmol, 74%).

Synthesis of MTPA Ester of 3b. To a solution of 3-hydroxybutyltriphenylphosphonium tetrafluoroborate **3b** in DMF was added 4,4-dimethylaminopyridine and MTPA chloride. After stirring for 2 h at r. t. the reaction mixture was poured into water and extracted with dichloromethane (5 mL×3). The combined extracts were dried over magnesium sulfate and evaporated to give a pale yellow oil, which was chromatographed over silica gel by elution of dichloromethane. Colorless oil of MTPA ester (**3b**-MTPA) was obtained (85%). ^{1}H NMR ($CDCl_3$) δ=0.87 (t, J=7.6 Hz, CH_3), 1.67—1.82 (m, 3H, C<u>H</u>H and C<u>H</u>$_2$CH$_3$), 2.00—2.10 (m, 1H, CH<u>H</u>), 2.61—2.71 (m, 1H, PC<u>H</u>H), 3.02—3.40 (m, 1H, PCH<u>H</u>), 3.58 (s, 3H, OCH_3), 5.13—5.16 (m, 1H, CH), 7.10—7.21 (m, 3H, Ar), 7.48—7.53 (m, 8H, Ar), 7.67—7.71 (m, 6H, Ar), 7.80—7.84 (m, 3H, Ar).

3b′-MTPA: ^{1}H NMR ($CDCl_3$) δ=0.80 (t, J=7.2 Hz, 3H, CH_3), 1.70—1.85 (m, 3H, C<u>H</u>H and C<u>H</u>$_2$CH$_3$), 2.00—2.10 (m, 1H, CH<u>H</u>), 2.93—3.03 (m, 1H, PC<u>H</u>H), 3.38 (s, 3H, OCH_3), 3.38—3.49 (m, 1H, PCH<u>H</u>), 5.11—5.17 (m, 1H, CH), 7.25—7.34 (m, 3H, Ar), 7.47—7.71 (m, 14H, Ar), 7.79—7.83 (m, 3H, Ar). Other MTPA esters of **3** were prepared in a similar manner.

Reaction of 2-Hydroxypropyltriphenylphosphonium Camphor-10-sulfonate 1a′ with Butyllithium Followed by the Addition of Benzaldehyde To a suspension of **1a′** (1.14 g, 2.0 mmol) in THF (30 mL) was added a solution of two equimolar amounts of butyllithium (1.6 M in hexane (M=mol dm^{-3}), 2.7 mL, 4.2 mmol) at −78 °C. After stirring for 1 h, a solution of benzaldehyde (0.21 g, 2.0 mmol) in THF was added to the mixture at 0 °C. After stirring for 10 h at r. t. aq ammonium chloride (10 %, 20 mL) was added to this suspension and the solvent was concentrated. The resulting suspension was extracted with dichloromethane (10 mL×3). The combined extracts were dried over magnesium sulfate and evaporated to give a yellow oil, which was chromatographed over silica gel by elution with dichloromethane to give 4-phenyl-3-buten-2-ol (**4a**) (0.088 g, 0.6 mmol, 30%). However, its optical rotation was only +16.2° (*c* 0.25, MeOH), which has 42% enantiomeric excess compared with the reported one.[13]

Preparation Optically Active (*E*)-Homoallylic Alcohols. To a solution of salt **3a′** (0.42 g, 1.0 mmol) in THF (10 mL) was added a solution of butyllithium (1.6 M in hexane 3 mL, 2.1 mmol) by a syringe at 0 °C. After being stirred for 10 min, the solution was cooled to −78 °C and benzaldehyde (0.10 g, 1.0 mmol) in THF (5 mL) was added via syringe to this solution. After being stirred for 1 h at this temperature, the solution was warmed up to r. t. poured into saturated ammonium chloride, and extracted with dichloromethane (15 mL×3). The combined extracts were dried over magnesium sulfate and evaporated to give a pale orange oil. This oil was chromatographed over silica gel by elution with dichloromethane to afford homoallylic alcohol **5a′** (0.097 g, 60%, E/Z=96/4). Purification was performed on a silica gel HPLC using ethyl acetate–hexane

(15:85) as an eluant. (*E*)-**5a′** $[\alpha]_D$ +34.3° (*c* 0.80, CCl_4). Ee was determined by ^{1}H NMR spectrum of its MTPA ester. The reported specific rotation of (*E*)-**5a′** is +14.2° (*c* 1.6, CCl_4) having 64% ee, which should have +22.2° as 100% ee. The specific rotation of **5a′** obtained by us is much higher than the reported one.[11] ^{1}H NMR ($CDCl_3$) δ=1.25 (d, *J*=5.9 Hz, 3H, CH_3), 2.30—2.44 (m, 2H, CH_2), 3.92 (m, 1H, C<u>H</u>OH), 6.22 (dt, *J*=16.1 and 7.4 Hz, 1H, CH=), 6.48 (d, *J*=16.1 Hz, 1H, PhCH=), 7.20—7.38 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$) δ=22.87 (CH_3), 42.89 (CH_2), 67.38 (CHOH), 126.25 (CH=), 133.14 (PhCH=), 126.09, 127.26, 128.52, 137.22 (Ar).

The reaction of phosphonium salt **3a′** (0.42 g, 1.0 mmol) with *trans* cinnamaldehyde (0.14 g, 1.0 mmol) and butyllithium (1.6 M in hexane, 1.3 mL, 2.1 mmol) was carried out in a similar manner. 0.10 g of homoallylic alcohol (**5b′**) was obtained (0.53 mmol, 53%,/*Z*=86/14]) (*E*)-**5b′**; ee >99% $[\alpha]_D$ +31.6° (*c* 0.62, CCl_4). Found: *m/z* 188.1162. Calcd for $C_{13}H_{16}O$: M, 188.1201. ^{1}H NMR ($CDCl_3$) δ=1.23 (d, *J*=5.9 Hz, 3H, CH_3), 2.24—2.38 (m, 2H, CH_2), 3.89 (m, 1H, C<u>H</u>OH), 5.82 (dt, *J*=14.7 and 7.3 Hz, 1H, CH=), 6.30 (dd, *J*=11.0 and 15.4 Hz, 1H, CH=), 6.50 (d, *J*=16.1 Hz, PhCH=), 6.77 (dd, *J*=16.1 and 11.0 Hz, 1H, CH=), 7.19—7.39 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$) δ=22.87 (CH_3), 42.73 (CH_2), 67.42 (CHOH), 128.76 (CH=), 130.64 (CH=), 131.24 (PhCH=), 133.75 (CH=), 126.21, 127.35, 128.57, 137.33 (Ar).

The reaction of phosphonium salt **3a′** (0.63 g, 1.5 mmol) with butyllithium (1.6 M in hexane, 1.9 mL, 3.1 mmol) and butyraldehyde (0.11 g, 1.5 mmol) was carried out in a similar manner. 0.10 g of 4-octene-2-ol (**5c′**) was obtained. (0.80 mmol, 53%, *E*/*Z*=62/38). ^{1}H NMR spectrum of the product (*E*-**5c′**) is identical with the reported one.[14] ee >99% $[\alpha]_D$ +11.2° (*c* 0.24, CCl_4). ^{1}H NMR ($CDCl_3$) δ=0.90 (t, *J*=7.6 Hz, 3H, CH_3), 1.19 (d, *J*=6.1 Hz, 3H, CH_3), 1.39 (sextet, *J*=7.3 Hz, 2H, CH_2), 2.01 (q, *J*=7.0 Hz, 2H, CH_2), 2.07—2.13 (m, 1H, C<u>H</u>H), 2.17—2.22 (m, 1H, CH<u>H</u>), 3.79 (sextet, *J*=6.1 Hz, 1H, C<u>H</u>OH), 5.37—5.45 (m, 1H, CH=), 5.51—5.58 (m, 1H, CH=). ^{13}C NMR ($CDCl_3$) δ=13.63 (CH_3), 22.56 (CH_2), 22.59 (CH_3), 34.72 (CH_2), 42.56 (CH_2), 67.18 (CHOH). 125.94 (CH=), 134.52 (CH=).

Homoallylic alcohol **5d** was prepared in a similar manner by using **3b** (0.65 g, 1.5 mmol), butyllithium (1.6 M in hexane, 1.9 mL, 3.1 mmol), and benzaldehyde (0.16 g, 1.5 mmol). **5d** (0.15 g, 0.87 mmol, 57 %; *E*/*Z*=94/6). (*E*)-**5d**: $[\alpha]_D$ −22.7° (*c* 2.00, CCl_4), ee>99 %. ^{1}H NMR ($CDCl_3$) δ=0.98 (t, *J*=7.3 Hz, 3H, CH_3), 1.48—1.61 (m, 2H, C<u>H</u>$_2$CH$_3$), 2.26—2.34 (m, 1H, C<u>H</u>H), 2.42—2.47 (m, 1H, CH<u>H</u>), 3.65 (quintet, *J*=6.1 Hz, 1H, C<u>H</u>OH), 6.23 (dt, *J*=15.4 and 7.3 Hz, 1H, CH=), 6.47 (d, *J*=15.4 Hz, 1H, PhCH=), 7.19—7.37 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$) δ= 9.92 (CH_3), 29.63 (C<u>H</u>$_2$CH$_3$), 40.59 (CH_2), 72.48 (CHOH), 126.40 (CH=), 132.98 (Ph<u>C</u>H=), 126.05, 127.18, 128.48 (Ar). Found: *m/z* 176.1204. Calcd for $C_{12}H_{16}O$: M, 176.1201.

Homoallylic alcohol **5d′** was prepared in a similar manner by using, **3b′** (0.42 g, 0.96 mmol), butyllithium (1.6 M in hexane, 1.3 mL, 2.0 mmol), and benzaldehyde (0.10 g, 0.96 mmol). **5d′** (0.068 g, 0.39 mmol, 40 %; *E*/*Z*=97/3). (*E*)-**5d′**: $[\alpha]_D$ +22.8° (*c* 1.22, CCl_4); ee>99 %.

(*E*)-**5d**-MTPA was obtained by the method described in the case of **3b**-MTPA. *E*-**5d**-MTPA: ^{1}H NMR ($CDCl_3$) δ= 0.97 (t, *J*=7.3 Hz, 3H, CH_3), 1.73 (quintet, *J*=7.3 Hz, 2H, C<u>H</u>$_2$CH$_3$), 2.45—2.58 (m, 2H, CH_2), 3.53 (s, 3H, OCH_3), 5.16 (quintet, *J*=5.9 Hz, 1H, CH), 6.01 (dt, *J*=16.1 Hz, 7.3 Hz, 1H, CH=), 6.35 (d, *J*=15.4 Hz, 1H, PhC<u>H</u>=), 7.19—7.37 (m, 8H, Ar), 7.51—7.53 (m, 2H, Ar).

(*E*)-**5d′**-MTPA: ^{1}H NMR ($CDCl_3$) δ=0.87 (t, *J*=7.3 Hz, 3H, CH_3), 1.66—1.73 (m, 2H, C<u>H</u>$_2$CH$_3$), 2.56—2.60 (m, 2H, CH_2), 3.53 (t, *J*=1.2 Hz, 3H, OCH_3), 5.18 (quintet, *J*=6.1 Hz, 1H, CH), 7.20—7.35 (m, 8H, Ar), 7.51—7.53 (m, 2H, Ar). Other MTPA esters of **5** were prepared in a similar manner.

Homoallylic alcohol **5e** was prepared in a similar manner by using **3b** (0.65 g, 1.5 mmol), butyllithium (1.6 M in hexane, 1.9 mL, 3.0 mmol), and *trans* cinnamaldehyde (0.20 g, 1.5 mmol). **5e** (0.14 g, 0.70 mmol, 47 %; *E*/*Z*=85/15). (*E*)-**5e**; $[\alpha]_D$ −28.9° (*c* 1.64, CCl_4), ee>99 %. ^{1}H NMR ($CDCl_3$) δ=1.23 (d, *J*=5.9 Hz, 3H, CH_3), 2.24—2.38 (m, 2H, CH_2), 3.89 (sextet, *J*=5.9 Hz, 1H, C<u>H</u>OH), 5.82 (dt, *J*=14.7 and 7.3 Hz, 1H, CH=), 6.30 (dd, *J*=15.4 and 11.0 Hz, 1H, CH=), 6.50 (d, *J*=16.1 Hz, 1H, PhC<u>H</u>=), 6.77 (dd, *J*=16.1 and 11.0 Hz, 1H, CH=), 7.19—7.39 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$) δ=22.87 (CH_3), 42.73 (CH_2), 67.42 (CHOH), 128.76 (CH=), 130.64 (CH=), 131.24 (Ph<u>C</u>H=), 133.75 (CH=), 126.21, 127.35, 128.57, 137.33 (Ar). Found: *m/z* 202.1370. Calcd for $C_{14}H_{18}O$: M, 202.1357.

Homoallylic alcohol **5f** was prepared in a similar manner by using **3b** (0.65 g, 1.5 mmol), butyllithium (1.6 M in hexane, 1.9 mL, 3.0 mmol), and butyraldehyde (0.11 g, 1.5 mmol). **5f** (0.16 g, 1.1 mmol, 76 %; *E*/*Z*=80/20). (*E*)-**5f**; $[\alpha]_D$ −4.3° (*c* 0.65, CCl_4), ee>99 %. ^{1}H NMR ($CDCl_3$) δ=0.90 (t, *J*=7.6 Hz, 3H, CH_3), 1.19 (d, *J*=6.1 Hz, 3H, CH_3), 1.39 (sextet, *J*=7.3 Hz, 2H, CH_2), 2.01 (q, *J*=7.0 Hz, 2H, CH_2), 2.07—2.13 (m, 1H, C<u>H</u>H), 2.17—2.22 (m, 1H, CH<u>H</u>), 3.79 (sextet, *J*=6.1 Hz, 1H, C<u>H</u>OH), 5.37—5.45 (m, 1H, CH=), 5.51—5.58 (m, 1H, CH=). ^{13}C NMR ($CDCl_3$) δ=13.63 (CH_3), 22.56 (CH_2), 22.59 (CH_3), 34.72 (CH_2), 42.56 (CH_2), 67.18 (CHOH), 125.94 (CH=), 134.52 (CH=). Found: *m/z* 142.1044. Calcd for $C_9H_{18}O$: M, 142.1357.

Homoallylic alcohol **5g** was prepared in a similar manner by using **3d** (0.47 g, 0.90 mmol), butyllithium (1.6 M in hexane, 1.8 mL, 1.8 mmol), and benzaldehyde (0.096 g, 0.90 mmol). **5g** (0.17 g, 0.68 mmol, 75 %; *E*/*Z*=91/9). Pure (*E*)-**5g** was obtained by recrystallization from hexane. (*E*)-**5g**; Mp 97—98 °C. $[\alpha]_D$ +25.7° (*c* 2.00, $CHCl_3$), ee>99 %. ^{1}H NMR ($CDCl_3$) δ=2.50—2.59 (m, 2H, CH_2), 3.91—3.95 (m, 1H, C<u>H</u>HOPh), 4.01—4.04 (m, 1H, CH<u>H</u>OPh), 4.11—4.17 (m, 1H, C<u>H</u>OH), 6.28 (dt, *J*=16.1 and 7.3 Hz, 1H, CH=), 6.51 (d, *J*=16.1 Hz, 1H, PhC<u>H</u>=), 6.91—6.98 (m, 3H, Ar), 7.20—7.38 (m, 7H, Ar). ^{13}C NMR ($CDCl_3$) δ=37.08 (CH_2), 69.74 (CHOH), 71.39 (<u>C</u>H$_2$OPh), 125.26 (CH=), 133.20 (Ph<u>C</u>H=), 114.58, 121.17, 126.12, 127.33, 128.54, 129.51, 137.11, 158.53 (Ar). Found: C, 80.57; H, 7.26%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%.

Reaction of Phosphonium Salts with Potassium Carbonate Followed by the Addition of Benzaldehyde. To a solution of salt **3a′** (0.82 g, 2.0 mmol) in isopropyl alcohol (10 mL) was added potassium carbonate (1.38 g, 10 mmol). After being stirred for 2 h, benzaldehyde (0.21 g, 2.0 mmol) was added to this suspension at r. t. After refluxing for 15 h, the reaction mixture was poured into water. Benzene (20 mL) was added to the reaction mixture. The benzene layer was dried over magnesium sulfate, filtered, and evaporated to give a pale yellow oil, which,

on being chromatographed over silica gel by elution with dichloromethane afforded the corresponding homoallylic alcohol **5a′**. 0.087 g (1.06 mmol, 53%, $E/Z=9/1$). Pure (*E*)-**5a′** was obtained by HPLC (silica gel) separation by elution ethyl acetate–hexane (15:85). $[\alpha]_D$ +34.3° (*c* 2.00, CCl_4)

Preparation of Enantiomerically Pure 3-Hydroxybutyldiphenylphosphine Oxide (6a′). To a solution of **3a′** (6.93 g, 10 mmol) in water (20 mL) was added a solution of 20 % aq NaOH (80 mL). After refluxing for 30 min, the reaction mixture was cooled to r.t. and extracted with dichloromethane (20 mL×3). The combined extracts were dried over magnesium sulfate and evaporated to give colorless crystals, which on recrystallization from MeOH gave the corresponding phosphine oxide **6a′** (2.6 g, 9.6 mmol, 96%). Mp 135—136 °C. $[\alpha]_D$ +9.9° (*c* 2.00, MeOH). ^{1}H NMR ($CDCl_3$) δ=1.17 (d, J=6.6 Hz, 3H, Me), 1.62—1.74 (m, 1H, PCHH), 1.7—1.89 (m, 1H, PCHH), 2.33—2.54 (m, 2H, CH_2), 3.83—3.90 (m, 1H, CH–O), 7.43—7.53 (m, 6H, Ar), 7.66—7.76 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ=23.22 (Me), 26.26 (d, J_{P-C}=71.7 Hz, PCH_2), 31.06 (d, J_{P-C}=3.7 Hz, CH_2), 67.34 (d, J_{P-C}=11.0 Hz, CH–O), 128.55, 128.68, 130.66, 130.69, 130.75, 130.79, 131.72, 131.96, 132.03, 132.94, 133.02. Found: C, 69.67; H, 6.79%. Calcd for $C_{16}H_{19}O_2P$: C, 70.06; H, 6.98%.

3-Hydroxypentyldiphenylphosphine oxide **6b** was obtained in a similar manner by using **3b** (10.60 g, 15.0 mmol). **6b** (4.11 g, 14.3 mmol, 95%): $[\alpha]_D$ −9.3° (*c* 2.00, MeOH). Mp 108—109 °C. ^{1}H NMR ($CDCl_3$) δ=0.91 (t, J=7.6 Hz, 3H, Me), 1.43—1.52 (m, 2H, CH_2), 1.61—1.72 (m, 1H, PCHH), 1.82—1.94 (m, 1H, PCHH), 2.34—2.52 (m, 2H, CH_2), 3.56—3.63 (m, 1H, CH–OH), 7.45—7.54 (m, 6H, Ar), 7.2—7.78 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ=10.03 (Me), 26.10 (d, J_{P-C}=71.7 Hz, PCH_2), 28.81 (CH_2), 29.96 (CH_2), 72.57 (d, J_{P-C}=11.1 Hz, CH–O), 128.52, 128.63, 130.68, 130.77, 131.65, 132.03, 132.23, 133.02, 133.22 (Ar). Found: C, 70.58; H, 7.33%. Calcd for $C_{17}H_{21}O_2P$: C, 70.82; H, 7.34%. **6b**-MTPA was obtained according to a procedure described before. **6b**-MTPA (90%): ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=7.6 Hz, 3H, CH_3), 1.59—1.74 (m, 3H, PCHH and CH_2CH_3), 1.98—2.07 (m, 3H, PCHH and CH_2), 3.56 (d, J=1.2 Hz, 3H, OCH_3), 5.02—5.06 (m, 1H, CH), 7.30—7.61 (m, 15H, Ar). Other MTPA esters of **6** were prepared in a similar manner.

3-(4-Chlorophenyl)-3-hydroxypropyldiphenylphosphine oxide **6c** was prepared in a similar manner by using **3c** (2.79 g, 5.0 mmol). **6c** (1.72 g, 4.7 mmol, 93 %): Mp 171—172 °C. $[\alpha]_D$ +21.9° (*c* 0.80, MeOH), ee>96%. ^{1}H NMR ($CDCl_3$) δ=1.96—2.08 (m, 2H, CH_2), 2.33—2.38 (m, 2H, PCH_2), 4.79—4.83 (m, 1H, CHOH), 7.24 (s, 4H, Ar), 7.44—7.52 (m, 6H, Ar), 7.65—7.71 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ=25.83 (d, J_{P-C}=71.7 Hz, PCH_2), 31.39 (d, J_{P-C}=3.7 Hz, CH_2), 72.66 (d, J=9.2 Hz, CHOH), 127.20, 128.41, 128.68, 128.79, 130.69, 130.73, 130.78, 130.82, 131.55, 131.74, 131.92, 132.54, 132.72, 132.82, 142.69 (Ar). Found: C, 67.90; H, 5.63%. Calcd for $C_{21}H_{20}O_2PCl$: C, 68.02; H, 5.44%.

3-Hydroxy-4-phenoxybutyltriphenylphosphphine oxide **6d** was obtained in a similar manner by using **3d** (7.06 g, 9.0 mmol). **6d** (3.14 g, 8.6 mmol, 95%): $[\alpha]_D$ −10.6° (*c* 2.00, MeOH). Mp 141—142 °C. ^{1}H NMR ($CDCl_3$) δ=1.79—1.89 (m, 1H, CHH), 2.02—2.12 (m, 1H, CHH), 2.39—2.62 (m, 2H, PCH_2), 3.84 (dd, J=5.2 and 9.5 Hz, 1H, CHH), 3.92 (dd, J=6.0 and 9.5 Hz, 1H, CHH), 4.03—4.12 (m, 1H, CH–OH), 6.83 (d, J=7.6 Hz, Ar), 6.92 (t, J=7.3 Hz, 1H, Ar), 7.21—7.26 (m, 2H, Ar), 7.42—7.52 (m, 4H, Ar), 7.71—7.76 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ=25.87 (d, J_{P-C}=73.5 Hz, PCH_2), 25.92 (d, J_{P-C}=3.7 Hz, CH_2), 69.48 (d, J_{P-C}=11.0 Hz, CH–OH), 71.18 (CH_2), 114.42, 120.80, 128.57, 128.68, 129.30, 130.66, 130.75, 131.75, 132.67, 132.82, 158.44 (Ar). Found: C, 71.91; H, 6.29%. Calcd for $C_{22}H_{33}O_3P$: C, 72.12; H, 6.33%.

Preparation of *erythro*-Phosphinoyl Diol 7a′. To a solution of phosphine oxide **6a′** (1.10 g, 4.0 mmol) in THF (30 mL) was added butyllithium (1.6 M in hexane, 5.5 mL, 8.8 mmol) at 0 °C and stirred for 2 h. A solution of benzaldehyde (0.42 g, 4.0 mmol) in THF (2 mL) was added to this solution at −78 °C. After being stirred for 4 h, the reaction mixture was warmed up to r. t. and stirred for additional 2 h. The reaction mixture was poured into aq ammonium chloride (10 %, 100 mL) and extracted with dichloromethane (20 mL×3). The combined extracts were dried over magnesium sulfate, filtered, and evaporated to affored a pale yellow oil, which was chromatographed over silica gel by elution with dichloromethane/pentane to give a mixture of *erythro* forms (1.09 g, 2.8 mmol, 72%) of phosphinoyl diol **7a′** (9:1). This crystals were recrystallized from dichloromethane–hexane to afford the pure crystals of *erythro* **7a′**. Mp 179—180 °C. ^{1}H NMR ($CDCl_3$) δ=0.75 (d, J=5.9 Hz, 3H, Me), 1.38 (s, 1H, CHOH), 1.66—1.93 (m, 2H, CH_2), 2.81—2.88 (m, 1H, PCH), 3.02—3.11 (br m, 1H, CH_3CHOH), 4.73 (s, 1H, PhCHOH), 5.26 (br d, J_{HP}=9.5 Hz, 1H, PhCHOH), 7.20—7.32, 7.45—7.59, 7.80—7.85, 8.00—8.05 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) δ=23.78 (Me), 31.19 (CH_2), 41.52 (d, J_{P-C}=68.0 Hz, PCH), 65.81 (CH_3CHOH), 71.22 (PhCHOH), 125.61—141.85 (Ar). Found: *m/z* 380.1453. Calcd for $C_{23}H_{25}O_3P$: M, 380.1541.

erythro Form **7b′** was prepared in a similar manner by using phosphine oxide **6a′** (0.55 g, 2.0 mmol), butyllithium (1.6 M in hexane, 2.5 mL, 4.0 mmol), and *trans* cinnamaldehyde (0.26 g, 2.0 mmol). After chromatographic separation, a mixture of two *erythro* isomers (**7b′**) was obtained 0.51 g (ratio; 3:1, 1.3 mmol, 63%). Mp 174—179 °C. ^{1}H NMR ($CDCl_3$) δ=0.96 and 0.98 (d, J=6.1 Hz, 3H, CH_3), 1.68—2.05 (m, 2H, CH_2), 2.80—3.05 (m, 1H, PCH), 3.35—3.45 and 3.93—4.00 (m, 1H, CH_3CHOH), 4.76—4.88 (m, 1H, CHOH), 6.11 and 6.15 (dd, J=15.9 and 4.9 Hz), 1H, CH=) 6.56 and 6.59 (d, J=15.9 Hz, 1H, PhCH=), 7.15—7.26, 7.43—7.52, 7.80—7.94 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) δ=23.97 and 24.13 (CH_3), 32.38 and 32.65 (CH_2), 40.12 and 40.69 (d, J_{P-C}=68.0 Hz, PCH), 65.76 (d, J_{P-C}=9.2 Hz, CH_3CHOH), 66.11 (d, J_{P-C}=5.5 Hz, CH_3CHOH), 69.59 and 60.53 (CHOH), 126.36—136.56 (Ar and olefin). Found: *m/z* 406.1692. Calcd for $C_{25}H_{27}PO$: M, 406.1697.

erythro Form **7c′** was prepared in a similar manner by using phosphine oxide **6a′** (0.82 g, 3.0 mmol), butyllithium (1.6 M in hexane, 3.8 mL, 6.0 mmol), and butyraldehyde (0.22 g, 3.0 mmol). After chromatographic separation, a mixture of two *erythro* isomers (**7c′**) was obtained 0.48 (ratio; 4:3, 1.4 mmol, 46%). Mp 132—135 °C. ^{1}H NMR ($CDCl_3$) δ=0.80 (t, J=7.3 Hz, 3H, CH_3), 0.98 and 1.01 (d, J=6.1 Hz, 3H, CH_3), 1.35—2.01 (m, 6H, CH_2×3), 2.65—2.75 (m, 1H, PCH), 3.25—3.35 and 3.98—4.15 (m, 2H, MeCHOH and PrCHOH), 7.45—7.55 (m, 6H, Ar), 7.77—7.94 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$) δ=13.65 (CH_3), 18.90 and 19.08

(CH_2), 24.04 (CH_3), 31.72 and 32.12 (CH_2), 37.25 and 37.54 (d, $J_{P-C}=12.8$ Hz, CH_2), 38.83 and 38.91 (d, $J_{P-C}=69.8$ Hz, PCH), 65.79 and 65.88 (MeCHOH), 68.92 and 69.52 (d, $J_{P-C}=3.7$ Hz, PrCHOH). Found: m/z 346.1613. Calcd for $C_{20}H_{27}O_3P$: M, 346.1697.

erythro Form **7d** was obtained in a similar manner by using phosphine oxide **6b** (0.58 g, 2.0 mmol), butyllithium (1.6 M in hexane, 2.5 mL, 4.0 mmol), and benzaldehyde. **7d** 0.38 g, (ratio; 8:1, 0.96 g, 48%). Mp 184—189 °C. ^{1}H NMR ($CDCl_3$) $\delta=0.50$ and 0.55 (t, $J=7.3$ Hz, 3H, CH_3), 0.97—1.07 (m, 2H, CH_2CH_3), 1.59—1.98 (m, 2H, CH_2), 2.65—2.73 (br s, 1H, EtCHOH), 2.86—2.90 and 3.00—3.06 (m, 1H, PCH), 4.79 (s, 1H, PhCHOH), 5.29 (br d, $J_{HP}=8.8$ Hz, 1H, PhCHOH), 7.22—7.33, 7.44—7.54, 7.80—7.85, 8.01—8.06 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) $\delta=9.63$ (CH_3), 28.79 (CH_2CH_3), 30.77 (CH_2), 41.26 (d, $J_{P-C}=68.0$ Hz, PCH), 71.28 (PhCHOH), 71.33 (EtCHOH), 125.35—142.36 (Ar). Found: m/z 394.1755. Calcd for $C_{24}H_{27}O_3P$: M, 394.1697.

erythro Form **7e** was obtained from phosphine oxide **6b** (0.58 g, 2.0 mmol), butyllithium (1.6 M in hexane, 2.5 mL, 4.0 mmol), and *trans* cinnamaldehyde (0.26 g, 2.0 mmol). Two *erythro* isomers of **7e** were obtained after chromatographic separation (ratio; 3:2). 0.48 g, (1.1 mmol, 57%). Mp 188—193 °C. ^{1}H NMR ($CDCl_3$) $\delta=0.61$ and 0.67 (t, $J=7.3$ Hz, 3H, CH_3), 1.17—1.39 (m, 2H, CH_2CH_3), 1.73—2.05 (m, 2H, CH_2), 2.77—2.82 and 2.90—2.98 (m, 1H, PCH), 2.90—3.00 and 3.22—3.28 (m, 1H, EtCHOH), 4.70—4.86 (m, 1H, CHOH), 6.11 and 6.36 (dd, $J=15.9$ and 4.9 Hz, 1H, CH=), 6.03 and 6.40 (dd, $J=15.9$ and 1.5 Hz, 1H, PhCH=), 7.18—7.29, 7.42—7.55, 7.78—7.97 (m, 15H, Ar). ^{13}C NMR ($CDCl_3$) $\delta=9.76$ (CH_3), 29.69 (CH_2), 29.96 (CH_2), 30.66 (CH_2), 30.95 (CH_2), 31.46 (CH_2), 40.05 (d, $J_{P-C}=69.0$ Hz, PCH), 43.06 (d, $J_{P-C}=66.0$ Hz, PCH), 70.44 (CHOH), 71.48 (CHOH), 71.79 (d, $J_{P-C}=9.2$ Hz, EtCHOH), 73.37 (d, $J_{P-C}=9.2$ Hz, EtCHOH), 126.41—136.64 (Ar and olefin). Found: m/z 420.1744. Calcd for $C_{26}H_{29}O_3P$: M, 420.1854.

erythro Form **7f** was prepared in a similar manner by using phosphine oxide **6b** (0.87 g, 3.0 mmol), butyllithium (1.6 M in hexane, 3.8 mL, 6.0 mmol), and butyraldehyde (0.22 g, 3.0 mmol). Two *erythro* isomers were obtained as a mixture after chromatographic separation (ratio; 5:5). **7f**: 0.52 g, (1.4 mmol, 48%). Mp 143—146 °C. ^{1}H NMR ($CDCl_3$) $\delta=$ 0.65 and 0.71 (t, $J=7.3$ Hz, CH_3), 0.81 and 0.83 (d, $J=6.6$ Hz, CH_3), 1.19—1.48 (m, 4H, CH_2 and CH_2), 1.62—2.06 (m, 4H, CH_2 and CH_2), 2.61—2.74 (m, 1H, PCH), 2.87—2.95 and 3.67—3.74 (br m, 1H, EtCHOH), 4.04—4.23 (m, 2H, PrCHOH and PrCHOH), 7.45—7.56 (m, 9H, Ar), 7.77—7.94 (m, 6H, Ar). ^{13}C NMR ($CDCl_3$) $\delta=9.76$ and 9.83 (CH_3), 13.72 and 13.82 (CH_3), 18.97 and 19.14 (CH_2), 29.42 and 30.06 (CH_2), 30.90 and 31.08 (CH_2), 37.09 (d, $J_{P-C}=12.9$ Hz, CH_2), 37.39 (d, $J_{P-C}=11.1$ Hz, CH_2), 38.52 and 38.78 (d, $J_{P-C}=69.9$ Hz, PCH), 69.06 and 69.76 (EtCHOH), 71.15 and 71.46 (d, $J_{P-C}=7.3$ Hz, PrCHOH), 128.55—131.97 (Ar). Found: m/z 360.1867. Calcd for $C_{21}H_{29}O_3P$: M, 360.1850.

erythro Form **7g** was obtained in a similar manner by using phosphine oxide **6d** (0.92 g, 2.5 mmol), butyllithium (1.6 M in hexane, 3.2 mL, 5.1 mmol), and benzaldehyde (0.27 g, 2.5 mmol). A mixture of the *erythro* isomers was obtained after chromatographic separation (ratio; 4:1). **7g**: 0.89 g (1.9 mmol, 75%). Mp 131—133 °C. ^{1}H NMR ($CDCl_3$) $\delta=1.98$—2.10 (m, 2H, CH_2), 2.95—3.08 (m, 1H, PCH), 3.24—3.30 (m, 1H, CH_2CHOH), 3.38—3.49 (m, 2H, CH_2OPh), 5.32 (d, $J=9.2$ Hz, PhCHOH), 6.61—8.02 (m, 20H, Ar). ^{13}C NMR ($CDCl_3$) $\delta=25.76$ (CH_2), 40.80 (d, $J=$ 68.0 Hz, PCH), 67.55 (CH_2CHOH), 71.17 (CH_2OPh), 71.20 (PhCHOH), 114.29—158.22 (Ar). Found: m/z 472.1782. Calcd for $C_{29}H_{29}O_4P$: M, 472.1803.

Preparation of Optically Active (*Z*)-Homoallylic Alcohols. A solution of *erythro* phosphine oxide **7a′** (0.42 g, 1.0 mmol) in DMF (10 mL) was added to a suspension of sodium hydride (0.088 g, 2.2 mmol, 60% mineral oil dispersion) in DMF (15 mL) at r. t. After being stirred for 30 min at 50 °C, the resulting suspension was poured into aq ammonium chloride (100 mL) and extracted with dichloromethane (20 mL×3). The combined extracts were dried over magnesium sulfate, filtered, and evaporated to give a pale yellow oil, which was chromatographed over silica gel by elution with hexane/dichloromethane (4:1) to afford *Z*-riched homoallylic alcohol of **8a′** ($E/Z=3/9$, 0.13 g, 0.8 mmol, 75%). Pure (*Z*)-alcohol was obtained by HPLC using a silica gel column (Merck) or by using silver nitrate impregnated silica gel by elution with dichloromethane–ethyl acetate. (*Z*)-**8a′**: $[\alpha]_D$ −39.7° (*c* 2.20, CCl_4), ee>99%. ^{1}H NMR ($CDCl_3$) $\delta=1.23$ (d, $J=8.8$ Hz, 3H, CH_3), 2.43—2.58 (m, 2H, CH_2), 3.93 (sextet, $J=5.9$ Hz, 1H, CHOH), 5.72 (dt, $J=11.7$ Hz, 7.3 Hz, CH=), 6.58 (d, $J=11.7$ Hz, 1H, PhCH=), 7.21—7.35 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$) $\delta=23.23$ (CH_3), 38.25 (CH_2), 67.95 (CHOH), 126.82 (CH=), 131.66 (PhCH=), 126.16, 128.23, 128.79, 137.24 (Ar). Found: m/z 162.1069. Calcd for $C_{11}H_{14}O$: M, 162.1045.

(*Z*)-Homoallylic alcohol **8b′** was prepared in a similar manner by using, **7b′** (0.27 g, 0.64 mmol), sodium hydride (60 % dispersion oil, 0.051 g, 1.3 mmol). **8b′** (0.047 g, 0.25 mmol, 40 %; $E/Z=22/78$): (*Z*)-**8b′**: $[\alpha]_D$ −17.3° (*c* 3.77, CCl_4), ee>99%. ^{1}H NMR ($CDCl_3$) $\delta=1.23$ (d, $J=8.8$ Hz, 3H, CH_3), 2.43—2.58 (m, 2H, CH_2), 3.93 (sextet $J=5.9$ Hz, 1H, CH–O), 5.72 (dt, $J=11.7$ and 7.3 Hz, CH=), 6.58 (d, $J=11.7$ Hz, 1H, PhCH=), 7.21—7.35 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) $\delta=23.23$ (CH_3), 38.25 (CH_2), 67.95 (CHOH), 126.82 (CH=), 131.66 (PhCH=), 126.16, 128.79, 137.24 (Ph). Found: m/z 188.1201. Calcd for $C_{13}H_{16}O$: M, 188.1201.

(*Z*)-4-Octen-2-ol **8c′** was obtained by using **7c′** (0.48 g, 1.4 mmol) and sodium hydride (60% mineral oil dispersion, 0.11 g, 2.8 mmol). **8c′**: 0.13 g (0.98 mmol, 70%, $E/Z=$ 20/80). The *Z*-isomer was isolated by silver nitrate impregnated preparative TLC (ethyl acetate:benzene=1:4). (*Z*)-**8c′**: $[\alpha]_D$ +5.6° (*c* 0.40, CCl_4). ^{1}H NMR ($CDCl_3$) $\delta=0.91$ (t, $J=7.3$ Hz, 3H, CH_3), 1.21 (d, $J=6.1$ Hz, 3H, CH_3), 1.38 (sextet, $J=7.3$ Hz, 2H, CH_2), 2.04 (q, $J=7.3$ Hz, 2H, CH_2), 2.17—2.29 (m, 2H, CH_2), 3.80—3.85 (m, 1H, CHOH), 5.38—5.44 (m, 1H, CH=), 5.54—5.61 (m, 1H, CH=). ^{13}C NMR ($CDCl_3$) $\delta=13.78$ (CH_3), 22.76 (CH_3), 22.76 (CH_2), 29.43 (CH_2), 37.13 (CH_2), 67.73 (CHOH), 125.17 (CH=), 133.33 (CH=). Found: m/z 128.1205. Calcd for $C_8H_{16}O$: 128.1201.

The reaction of **7d** (0.080 g, 0.20 mmol) with sodium hydride (60% mineral oil dispersion, 0.016 g, 0.40 mmol) was carried out in a similar manner. **8d**: 0.032 g (0.18 mmol, 90%, $E/Z=6/94$). (*Z*)-**8d**: $[\alpha]_D$ +35.8° (*c* 1.19, CCl_4) ee> 99%. ^{1}H NMR ($CDCl_3$) $\delta=0.94$ (t, $J=7.6$ Hz, 3H, CH_3), 1.45—1.58 (m, 2H, CH_2), 2.49—2.52 (m, 2H, CH_2), 3.66 (quintet, $J=6.4$ Hz, 1H, CHOH), 5.75 (dt, $J=11.6$ and 7.3 Hz, 1H, CH=), 6.57 (d, $J=11.6$ Hz, 1H, PhCH=), 7.20—7.35 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) $\delta=9.88$ (CH_3), 29.80

(CH_2), 35.93 (CH_2), 73.15 (CHOH), 128.41 (CH=), 131.43 (PhCH=), 126.71, 128.15, 128.72, 137.24 (Ph). Found: m/z 176.1210. Calcd for $C_{12}H_{16}O$: M, 176.1201.

Another enantiomer was obtained by using **7d'** (0.22 g, 0.56 g) and sodium hydride (60% mineral oil dispersion, 0.045 g, 1.1 mmol). **8d'**: 0.060 g (0.34 mmol, 61%, E/Z=4/96). (*Z*)-**8d'**: $[\alpha]_D$ −35.0° (*c* 0.99, CCl_4), ee>99%.

(*Z*)-**8d**-MTPA was obtained according to a procedure described before. (*Z*)-**8d**-MTPA; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, J=7.6 Hz, 3H, CH_3), 1.66—1.73 (m, 2H, $C\underline{H}_2CH_3$), 2.59—2.66 (m, 2H, CH_2), 3.54 (dd, J=8.2, 1.2 Hz, 3H, OCH_3), 5.15 (quintet, J=6.4 Hz, 1H, CH), 5.52 (dt, J=11.6 and 7.3 Hz, 1H, CH=), 6.47 (d, J=11.6 Hz, 1H, PhC$\underline{H}$=), 7.17—7.55 (m, 5H, Ar).

(*Z*)-**8d'**-MTPA: ^{1}H NMR ($CDCl_3$) δ=0.78 (t, J=7.6 Hz, 3H, CH_3), 1.60—1.67 (m, 2H, $C\underline{H}_2CH_3$), 2.60—2.67 (m, 1H, C$\underline{H}$H), 2.71—2.79 (m, 1H, CH$\underline{H}$), 3.52 (t, J=1.2 Hz, 3H, OCH_3), 5.15—5.21 (m, 1H, CH), 5.62—5.69 (m, 1H, CH=), 6.55 (d, J=11.6 Hz, 1H, PhC$\underline{H}$=), 7.21—7.25 (m, 3H, Ar), 7.31—7.40 (m, 5H, Ar), 7.53—7.55 (m, 2H, Ar). Other MTPA esters of *Z*-homoallylic alcohols were prepared in a similar manner.

The reaction of **7e** (0.36 g, 0.86 mmol) with sodium hydride (60% mineral oil dispersion, 0.068 g, 1.7 mmol) was carried out in a similar manner. 0.10 g of (*Z*)-homoallylic alcohol (**8e**) was obtained (0.50 g, 59%, E/Z=21/79). (*Z*)-**8e**: $[\alpha]_D$ +23.8° (*c* 1.58, CCl_4), ee>99%. ^{1}H NMR ($CDCl_3$) δ=0.99 (t, J=7.6 Hz, 3H, CH_3), 1.49—1.62 (m, 2H, CH_2), 2.45—2.49 (m, 2H, CH_2), 3.64 (quintet, J=6.1 Hz, 1H, C$\underline{H}$OH), 5.57 (dt, J=11.0 and 7.6 Hz, 1H, CH=), 6.32 (t, J=11.0 Hz, 1H, CH=), 6.57 (d, J=15.6 Hz, 1H, PhCH=), 8.02—7.09 (m, 1H, CH=), 7.20—7.25 (m, 1H, Ph), 7.29—7.33 (m, 2H, Ph), 7.40—7.42 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$) δ=9.99 (CH_3), 29.65 (CH_2), 35.52 (CH_2), 72.89 (CHOH), 124.00 (CH=), 128.10 (CH=), 131.16 (PhCH=), 133.55 (CH=), 126.41, 127.55, 128.55, 137.33 (Ph). Found: m/z 202.1352. Calcd for $C_{14}H_8O$: M, 202.1358.

The reaction of **7f** (0.52 g, 1.4 mmol) with sodium hydride (60% mineral oil dispersion, 0.12 g, 1.9 mmol) was carried out in a similar manner. (*Z*)-5-nonen-3-ol (**8f**) was obtained. **8f**: 0.14 g (0.97 mmol, 66%, E/Z=19/81). (*Z*)-**8f**; $[\alpha]_D$ +6.9° (*c* 0.64, CCl_4), ee>99%. ^{1}H NMR ($CDCl_3$) δ=0.91 (t, J=7.3 Hz, 3H, CH_3), 0.96 (t, J=7.3 Hz, 3H, CH_3), 1.38 (m, 2H, CH_2), 1.45—1.58 (m, 2H, CH_2), 2.04 (q, J=7.3 Hz, 2H, CH_2), 2.22 (t, J=7.3 Hz, 2H, CH_2), 3.52—3.59 (m, 1H, C$\underline{H}$OH), 5.39—5.45 (m, 1H, CH=), 5.54—5.61 (m, 1H, CH=). ^{13}C NMR ($CDCl_3$) δ=10.01 (CH_3), 13.78 (CH_3), 22.79 (CH_2), 29.43 (CH_2), 29.56 (CH_2), 34.88 (CH_2), 72.87 (CHOH), 125.28 (CH=), 133.27 (CH=). Found: m/z 142.1366. Calcd for $C_9H_{18}O$: M, 142.1358.

The reaction of **7g** (0.47 g, 1.0 mmol) with sodium hydride (60 % mineral oil dispersion, 0.080 g, 2.0 mmol) was carried out in a similar manner. 0.17 g of homoallylic alcohol (**8g**) was obtained. (0.65 mmol, 65%, E/Z=17/83). (*Z*)-**8g**: $[\alpha]_D$ +29.5° (*c* 2.18, CCl_4), ee>99%. ^{1}H NMR ($CDCl_3$) δ=2.63—2.67 (m, 2H, CH_2), 3.84 (dd, J=9.5 and 7.3 Hz, 1H, C$\underline{H}$H), 3.95 (dd, J=9.5 and 7.3 Hz, 1H, CH$\underline{H}$), 4.08—4.13 (m, 1H, C$\underline{H}$OH), 5.58 (d, J=11.7 Hz, 1H, PhCH=), 5.78 (dt, J=11.7 and 7.3 Hz, 1H, CH=), 6.87 (2H, Ph), 6.93—6.96 (m, 1H, Ph), 7.20—7.34 (m, 7H, Ph). ^{13}C NMR ($CDCl_3$) δ=32.34 (CH_2), 70.07 (CHOH), 71.42 (CH_2O), 127.16 (CH=), 131.55 (PhCH=), 114.49, 121.09, 126.80, 128.19, 128.68, 129.45, 137.04, 158.40 (Ar). Found: m/z 254.1276. Calcd for $C_{17}H_{18}O_2$: M, 254.1307.

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