Heteroatom Chemistry
Volume 4, Number 5, 1993

Synthesis and Reactions of Optically Pure Cyclohexyl(*o*-methoxyphenyl)phosphine-Borane and *t*-Butyl-(*o*-methoxyphenyl)phosphine-Borane

Tsuneo Imamoto,* Masatoshi Matsuo, Taro Nonomura, Kuniyuki Kishikawa, and Masao Yanagawa

Department of Chemistry, Faculty of Science, Chiba University, Inage, Chiba 263, Japan

Received 1 May 1993

ABSTRACT

Cyclohexyl(o-methoxyphenyl)menthyloxyphosphine-borane and t-butyl(o-methoxyphenyl)menthyl-oxyphosphine-borane were prepared from dichloro-cyclohexylphosphine and t-butyldichlorophosphine by successive treatments with (−)-menthol, o-meth-oxyphenylmagnesium bromide, and borane-THF complex. The separated pure diastereomers of each of the compounds underwent reaction with lithium na-phthalenide to afford optically pure cyclohexyl(o-methoxyphenyl)phosphine-borane and t-butyl(o-methoxyphenyl)phosphine-borane, respectively. These secondary phosphine-boranes reacted readily with various electrophiles in the presence of bases with virtually net retention of configuration. A new chiral phosphine ligand, (S,S)-1,2-bis[cyclohexyl(o-meth-oxyphenyl)phosphino]ethane was synthesized via the optically pure phosphine-boranes.

INTRODUCTION

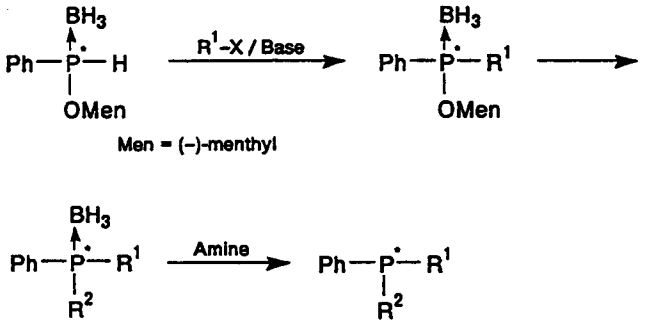
Recently, we studied the synthesis and reactions of optically active phosphine-boranes and found that diastereomerically pure menthyloxy(phenyl)-phosphine-boranes undergo stereospecific alkylation or arylation at chiral phosphorus [1–3]. These reactions, by combination with the further stereospecific transformations of the products, can be utilized for the synthesis of optically active tertiary phosphines (Scheme 1). It is noted that, in these reaction sequences, the boranato group acts both as an activating group and as a protecting group. That is, the boranato group in phosphine-boranes activates the adjacent hydrogen or methyl group to deprotonation with a strong base, and at the same time, it protects the phosphines which are generally sensitive toward electrophiles such as alkyl halides and oxygen. This approach is applicable to the synthesis of C_2-symmetric bidentate ligands with a homochiral phosphine center [1].

On the other hand, optically active tertiary phosphines having *o*-methoxyphenyl groups are known to be excellent ligands for use in catalytic asymmetric hydrogenation [4–6]. However, the previously existing methods for the synthesis of these ligands require laborious work, and these difficulties in synthesis have prevented their use in many kinds of catalytic asymmetric reactions. We envisioned that such phosphine ligands might be efficiently synthesized by the use of optically active secondary phosphine-boranes (that contain an *o*-methoxyphenyl group) as the intermediates. This idea led us to investigate the synthesis and reactions of new optically pure secondary phosphine-boranes, cyclohexyl(*o*-methoxyphenyl)phosphineborane (**1**) and *t*-butyl(*o*-methoxyphenyl)-phosphine-borane (**2**). In addition, we tried to prepare a new C_2-symmetric bidentate phosphine

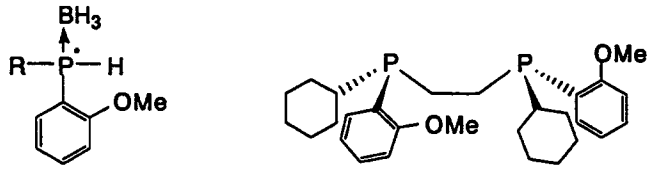
Dedicated to Prof. Antonino Fava on the occasion of his seventieth birthday.

*To whom correspondence should be addressed.

1042-7163/93/$5.00 + .25

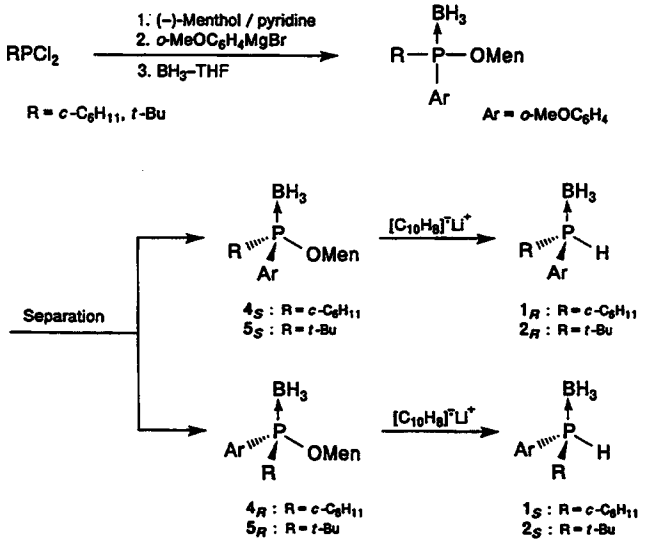


SCHEME 1



1 : R = Cyclohexyl
2 : R = *t*-Butyl

FIGURE 1



SCHEME 2

ligand, (*S,S*)-1,2-bis[cyclohexyl(*o*-methoxyphenyl)phosphino]ethane ($\mathbf{3}_{SS}$).

RESULTS AND DISCUSSION

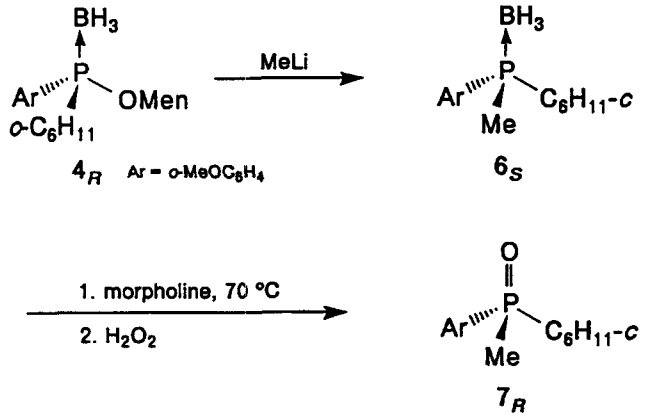
Preparation of Optically Pure Cyclohexyl(o-methoxyphenyl)phosphine-Borane and t-Butyl(o-methoxyphenyl)phosphine-Borane

Optically pure (*R*)- and (*S*)-cyclohexyl(*o*-methoxyphenyl)phosphine-boranes ($\mathbf{1}_R$ and $\mathbf{1}_S$) and (*R*)- and (*S*)-*t*-butyl(*o*-methoxyphenyl)phosphine-boranes ($\mathbf{2}_R$ and $\mathbf{2}_S$) were prepared from dichlorocyclohexylphosphine and *t*-butyldichlorophosphine, respectively. Thus, as shown in Scheme 2, the alkyldichlorophosphines were allowed to react successively with (−)-menthol, *o*-methoxyphenylmagnesium bromide, and borane-THF complex. The resulting products were chromatographed on silica gel to afford the corresponding pure diastereomers ($\mathbf{4}_S$, $\mathbf{4}_R$, $\mathbf{5}_S$, and $\mathbf{5}_R$). A recrystallization procedure was also effective for the separation of the diastereomers, particularly for compounds $\mathbf{5}_S$ and $\mathbf{5}_R$. Next, reductive removal of the menthyloxy group was examined. Previously, we found that the P–O bond of phosphinates and related substrates was stereospecifically cleaved by one electron reductants such as lithium naphthalenide [3,7,8]. This procedure was now applied to the reduction of compounds $\mathbf{4}_S$, $\mathbf{4}_R$, $\mathbf{5}_S$, and $\mathbf{5}_R$. The reduction with lithium naphthalenide occurred at −40°C to afford the corresponding secondary phosphine-boranes with almost 100% ee in excellent yields. The reaction at higher temperature resulted in a diminished optical purity of the product. For example, the reaction of $\mathbf{5}_R$ at 0°C afforded $\mathbf{2}_S$ with 86% ee.

Compounds $\mathbf{1}_R$ and $\mathbf{1}_S$, which were obtained as oils, were stereochemically more stable than a sterically less crowded secondary phosphine-borane, methylphenylphosphine-borane, but nevertheless, they gradually racemized at room temperature; the enantiomeric excess of compound $\mathbf{1}_R$ decreased from 100 to 57% after having been allowed to stand at room temperature for 10 days. On the other hand, compounds $\mathbf{2}_R$ and $\mathbf{2}_S$, which were crystalline solids, were stored without any loss of enantiomeric excess at room temperature for several weeks.

Determination of the Absolute Configurations of Menthyl Esters ($\mathbf{4}_S$, $\mathbf{4}_R$, $\mathbf{5}_S$, and $\mathbf{5}_R$) and Their Derivatives

Absolute configurations of compounds $\mathbf{4}_S$, $\mathbf{4}_R$, $\mathbf{5}_S$, and $\mathbf{5}_R$ were estimated on the basis of their ^{1}H NMR spectra. Mislow *et al.* reported that the protons of one of the methyls of the isopropyl group in (S_P)-menthyl alkylphenylphosphinates were subjected to a large upfield shift (ca. 0.5 ppm) due to the diamagnetic anisotropy of the phenyl ring [9]. Previously, we had also observed a similar large upfield shift in (S_P)-menthyloxy(methyl)phenylphosphine-boranes [1]. Compounds $\mathbf{4}_S$ and $\mathbf{5}_S$, which closely resemble the compounds mentioned previously, exhibited the signals of one of the methyls of the isopropyl groups at higher fields (0.14 and 0.43 ppm, respectively). On the other hand, compounds $\mathbf{4}_R$ and $\mathbf{5}_R$ showed the signals at around 0.8 ppm. These facts suggest that compounds $\mathbf{4}_S$ and $\mathbf{5}_S$ possess the *S* configuration at chiral phosphorus and compounds $\mathbf{4}_R$ and $\mathbf{5}_R$ possess the *R* configuration.



SCHEME 3

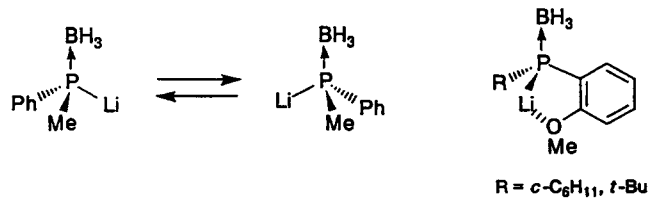


FIGURE 2

In order to confirm these assignments, we undertook chemical correlations. Compound $\mathbf{4}_R$ was converted to a known compound $\mathbf{7}_R$, as shown in Scheme 3. Thus, $\mathbf{4}_R$ was reacted with methyllithium to give compound $\mathbf{6}_S$, which was treated successively with morpholine and hydrogen peroxide to furnish phosphine oxide $\mathbf{7}_R$. The absolute configuration of compound $\mathbf{7}_R$ was determined to be *R* by comparison of the $[\alpha]_D$ value with that described in the literature [10]. These results clearly indicate that compound $\mathbf{4}_R$ possesses the *R* configuration, since the reaction of $\mathbf{4}_R$ with methyllithium proceeds with inversion of configuration [11] and the conversion of $\mathbf{6}_S$ to $\mathbf{7}_R$ occurs with retention of configuration [1].

Scheme 4 illustrates the chemical correlation for the determination of the configuration of compound $\mathbf{5}_R$. In order to correlate $\mathbf{5}_R$ with a known compound $\mathbf{11}_S$, *t*-butyl(menthyloxy)phenylphosphine-borane ($\mathbf{9}_S$) was prepared from dichlorophenylphosphine by successive treatments with (−)-menthol, *t*-butylmagnesium chloride, and borane-THF complex. This compound was converted into $\mathbf{11}_S$ by reduction with lithium naphthalenide and subsequent methylation with iodomethane. Comparison of the rotation of the product with the reported value [1] and HPLC analysis using a chiral column indicated that the product possessed the *S* configuration. Therefore, the configuration of compound $\mathbf{9}_S$ should be *S*, as shown. Next, $\mathbf{9}_S$ was converted to compound $\mathbf{8}_S$ via $\mathbf{10}_R$ by reduction with lithium naphthalenide, followed by palladium-catalyzed arylation. In a similar manner, the same compound $\mathbf{8}_S$ was synthesized from $\mathbf{5}_R$. All these transformations are known to proceed with retention of configuration, and hence, the configuration of compound $\mathbf{5}_R$ should be *R*, as shown.

Reactions of Optically Pure Secondary Phosphine-Boranes $\mathbf{1}_R$, $\mathbf{1}_S$, $\mathbf{2}_R$, *and* $\mathbf{2}_S$ *with Electrophiles*

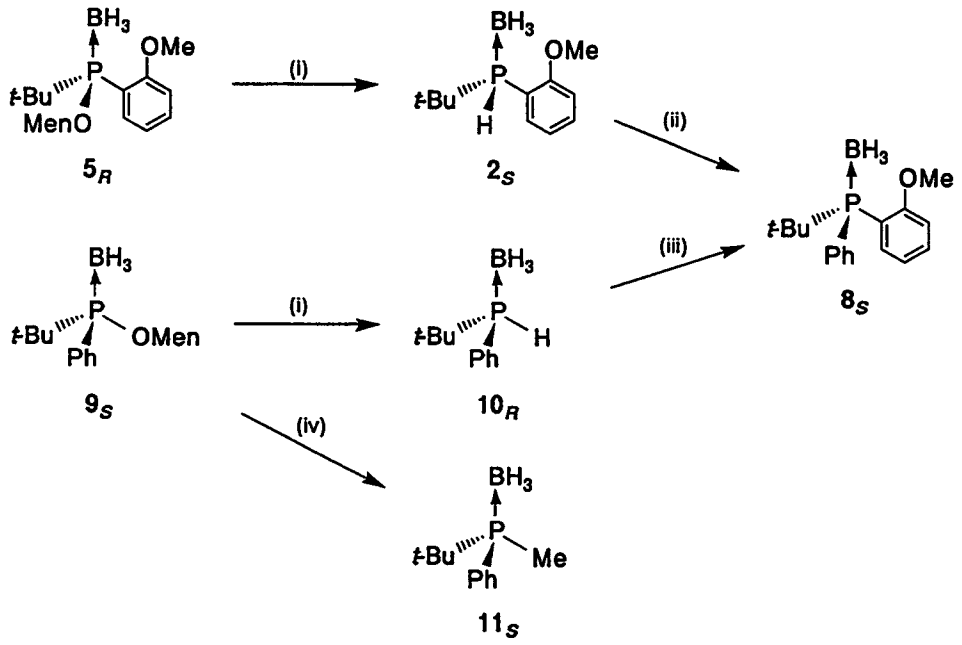
The optically pure secondary phosphine-boranes mentioned earlier were allowed to react with various electrophiles in the presence of bases. The results are summarized in Table 1. These secondary phosphine-boranes were readily subjected to deprotonation with butyllithium at −78°C, and the generated lithium derivatives underwent reaction with reactive alkyl halides without racemization (entries 2–6). Similar reactions were accomplished at around 0°C by the use of sodium hydride as the base (entries 1 and 8). The Michael addition also proceeded smoothly with ethyl acrylate in the presence of sodium ethoxide in ethanol to provide compound $\mathbf{17}_R$, with 100% ee (entry 7). An optically active bis-boranato-phosphino compound $\mathbf{18}_{SS}$ was also synthesized by the reaction of $\mathbf{2}_R$ with *o*-xylylene dibromide (entry 8).

Reactions of $\mathbf{1}_S$ and $\mathbf{2}_S$ with optically active, 1,2-epoxyoctane afforded $\mathbf{19}_R$ and $\mathbf{20}_R$, respectively (entries 9 and 10). The resulting stereochemical integrity is in sharp contrast to that obtained in the reaction of optically active methylphenylphosphine-borane with the same epoxide. As is shown in the Scheme 5, the latter reaction resulted in complete epimerization at chiral phosphorus.

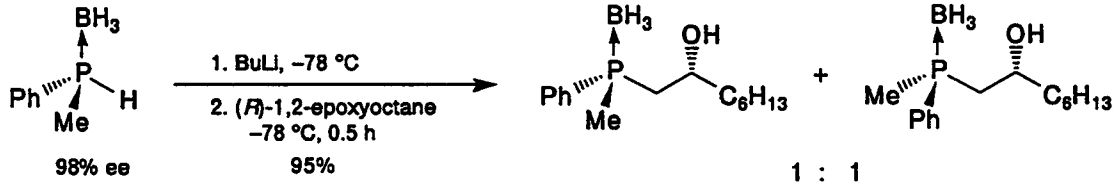
The formation of the epimerized products may be the result of the lithium derivative of methylphenylphosphine-borane being racemized prior to the reaction with the epoxide. On the other hand, the high stereochemical stability of the lithium derivatives derived from $\mathbf{1}_S$ and $\mathbf{2}_S$ may be ascribed to the coordination of the lithium ion with the *o*-methoxy group.

Reactions with acid chlorides were also examined. It was found that the results depended largely on the deprotonation agents employed. Use of NaH resulted in low yields of the acylation products with complete racemization (entries 11 and 13). On the other hand, the reactions involving the use of butyllithium provided the products with high enantiomeric excess in good to high yields (entries 12, 14, and 15). It should be noted that the products are a kind of mixed acid anhydride having a chiral, optically active component. These compounds may have potential utility as enantioselective acylation agents.

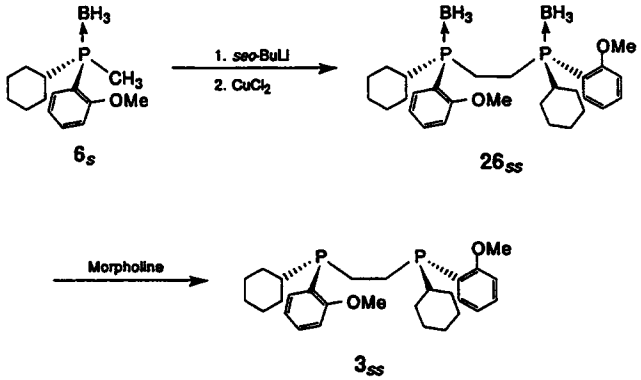
Reactions with benzyne are noteworthy. Recentry, Suzuki *et al.* reported that benzyne can be readily generated by the reaction of *o*-bromo-



SCHEME 4 Reagents and conditions: (**i**) lithium naphthalenide, THF, −40°C; (**ii**) PhI, Ag_2CO_3, $Pd(PPh_3)_4$ (5 mol%), MeCN, 50°C; (**iii**) *o*-$MeOC_6H_4I$, Ag_2CO_3, $Pd(PPh_3)_4$ (5 mol%), MeCN, 50°C; (**iv**) lithium naphthalenide, THF, −40°C, then MeI, THF, −40°C.

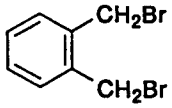
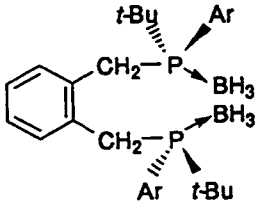
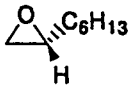
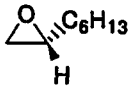
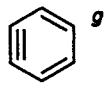
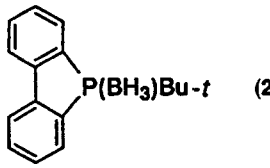


SCHEME 5



SCHEME 6

TABLE 1 Reactions of Optically Pure Secondary Phosphine-Boranes, $\mathbf{1}_R$, $\mathbf{1}_S$, $\mathbf{2}_R$, and $\mathbf{2}_S$, with Electrophiles

Entry	Substrate	Base	Eletrophile	Conditions[a]	Product	Yield[b] (%)	ee[c] (%)
1	$\mathbf{2}_S$	NaH	MeI	0°C	(*R*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)Me ($\mathbf{12}_R$)	97	100
2	$\mathbf{2}_R$	BuLi	CH_2=$CHCH_2Br$	−78–0°C	(*S*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)CH_2CH=CH_2 ($\mathbf{13}_S$)	84	100
3	$\mathbf{2}_R$	BuLi	CH_2=$CH(CH_2)_2OTs$	−78–0°C	(*S*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)$(CH_2)_2CH$=CH_2 ($\mathbf{14}_S$)	85	100
4	$\mathbf{2}_S$	BuLi	$I(CH_2)_3I$	−78–10°C	(*R*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)$(CH_2)_3I$ ($\mathbf{15}_R$)	67	100
5	$\mathbf{2}_S$	BuLi	$BrCH_2CO_2Me$	−78°C	(*R*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)CH_2CO_2Me ($\mathbf{16}_R$)	66	100
6	$\mathbf{2}_S$	BuLi	$Br(CH_2)_2CO_2Et$	−78°C	(*R*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)$(CH_2)_2CO_2Et$ ($\mathbf{17}_R$)	79	100
7	$\mathbf{2}_S$	EtONa	CH_2=$CHCO_2Et$	50°C[d]	(*R*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)$(CH_2)_2CO_2Et$ ($\mathbf{17}_R$)	92	100
8	$\mathbf{2}_R$	NaH		0°C[e]	 ($\mathbf{18}_{SS}$)	98	>98[f]
9	$\mathbf{1}_S$	BuLi		−78°C	(R_o, *R*)-*o*-C_6H_{11}(*o*-MeOC$_6$H$_4$)P(BH$_3$)$CH_2CH(OH)C_6H_{11}$ ($\mathbf{19}_R$)	61	>98%de[f]
10	$\mathbf{2}_S$	BuLi		−78°C	(R_o, *R*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)$CH_2CH(OH)C_6H_{11}$ ($\mathbf{20}_R$)	69	>98%de[f]
11	$\mathbf{2}_R$	NaH	MeCOCl	40°C	(*S*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)COMe ($\mathbf{21}_S$)	42	0
12	$\mathbf{2}_R$	BuLi	MeCOCl	−78°C	(*S*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)COMe ($\mathbf{21}_S$)	72	97
13	$\mathbf{2}_S$	NaH	PhCOCl	40°C	(*R*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)COPh ($\mathbf{22}_R$)	19	0
14	$\mathbf{2}_S$	BuLi	PhCOCl	−78°C	(*R*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)COPh ($\mathbf{22}_R$)	95	74
15	$\mathbf{2}_S$	BuLi	*p*-$MeOC_6H_4COCl$	−78°C	(*R*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)COC_6H_4OMe-*p* ($\mathbf{23}_R$)	71	94
16	$\mathbf{2}_S$	*t*-BuLi		−78°C	(*S*)-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)Ph ($\mathbf{8}_R$)	44	100
					 (**24**)	25	
17	$\mathbf{2}_S$	NaH	MeSSMe	0°C	(*R*-*t*-Bu(*o*-MeOC$_6$H$_4$)P(BH$_3$)SMe ($\mathbf{25}_R$)	89	98

[a]All reactions were carried out in THF unless otherwise stated.
[b]Isolated yield.
[c]Enantiomeric excess was determined by HPLC analysis using a chiral column.
[d]The reaction was carried out in EtOH.
[e]The reaction was carried out in DMF.
[f]Determined by ^{1}H NMR (500 MHz).
[g]This benzyne was generated by the reaction of *o*-bromophenyl triflate with 2 equivalents of *t*-BuLi in THF at −78°C.

phenyl triflate with butyllithium or *t*-butyllithium at −78°C [12]. Their protocol was applied to the phenylation of $\mathbf{2}_S$. Thus, a mixture of $\mathbf{2}_S$ (1 mmol) and *o*-bromophenyl triflate (2 mmol) in THF was treated with *t*-butyllithium (5 mmol) at −78°C. From the reaction mixture, optically pure *t*-butyl(*o*-methoxyphenyl)phenylphosphine-borane and compound **24** were isolated in 44 and 25% yields, respectively (entry 16). The formation of compound **24** is reasonably explained by the assump-

tion that the initially formed adduct, an aryllithium derivative, underwent an intramolecular displacement reaction.

Entry 17 shows the reaction of **2** with dimethyl disulfide. It should be noted that the methylthio group was introduced in high yields with exceedingly high stereochemical integrity.

Synthesis of (S,S)-1,2Bis[cyclohexyl(o-methoxyphenyl)phosphino]ethane

Based on the stereochemical studies described earlier, we devised a synthesis of (*S,S*)-1,2-bis[cyclohexyl(*o*-methoxyphenyl)phosphino]ethane ($\mathbf{3}_{SS}$), which is a C_2-symmetric bidentate ligand analogous to DIPAMP [5]. The synthetic route is shown in Scheme 6.

Compound $\mathbf{6}_S$, which was prepared by the reaction of $\mathbf{4}_R$ with methyllithium or by the reduction of $\mathbf{4}_S$ with lithium naphthalenide and subsequent methylation with iodomethane, was treated with *sec*-butyllithium at −78°C. The generated organolithium compound was oxidatively dimerized by copper(II) chloride to give the bis-phosphine-borane $\mathbf{26}_{SS}$ in 75% yield. The compound $\mathbf{26}_{SS}$ was warmed in morpholine at 70°C to provide the desired ligand $\mathbf{3}_{SS}$ in 98% yield. We believe that this protocol using phosphine-boranes as the intermediates will probably be useful for the preparation of analogous bidenate ligands containing a homochiral phosphine center.

EXPERIMENTAL SECTION

General

The NMR spectra were recorded on JEOL GX-270 (^{1}H NMR at 270 MHz, ^{13}C NMR at 68 MHz), JEOL JNM-GSX-400 (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz), and JEOL JNM-GSX-500 (^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz) spectrometers. Chemical shifts (δ) are expressed in parts per million relative to tetramethylsilane. The IR spectra were recorded on a Hitachi-IR 215 spectrometer. Optical rotations were measured with a JASCO DIP-370 digital polarimeter with a 10 cm cell. Analytical high performance liquid chromatography (HPLC) was performed with a Hitachi L-6000 pump and a Hitachi L-4000 UV detector. Mass spectra were obtained on JEOL JMS-HX 110 and JEOL JMS-DX-300 (FAB-Mass) instruments. Microanalyses were performed on a Perkin-Elmer 2400 instrument at the Chemical Analysis Center of Chiba University. Tetrahydrofuran was distilled from potassium benzophenone ketyl under argon prior to use. All experiments were carried out under an argon atmosphere. The products were isolated by column chromatography on silica gel (Wakogel C-200 or C-300) or preparative TLC on silica gel (Wakogel B-5F).

Materials

Dichlorocyclohexylphosphine and *t*-butyldichlorophosphine were prepared by the reactions of phosphorus trichloride with cyclohexylmagnesium chloride and *t*-butylmagnesium chloride, respectively, according to the literature procedures [13,14]. Tetrakis(triphenylphosphine)palladium(0) was prepared according to the reported procedure [15].

(Sp,1'R,2'S,5'R)-[(2'-Isopropyl-5'-methylcyclohexyl)oxy]cyclohexyl(o-methoxyphenyl)phosphine-Borane ($\mathbf{4}_S$) and (R_P,1'R,2'S,5'R)-[(2'-Isopropyl-5'-methylcyclohexyl)oxy]cyclohexyl(o-methoxyphenyl)phosphine-Borane ($\mathbf{4}_R$). A mixture of (−)-menthol (13.2 g, 85 mmol) and pyridine (6.8 mL, 84.6 mmol) in dry benzene (60 mL) was added dropwise during 4 hours into a stirred solution of cyclohexyldichlorophosphine (13.0 mL, 85 mmol) in dry benzene (60 mL) at room temperature under argon. The mixture was stirred for 15 hours, and it was filtered under nitrogen to remove the resulting pyridinium salt. *o*-Methoxyphenylmagnesium bromide (53.0 mL of 1.6 M/L THF solution) was added dropwise to the filtrate during 0.5 hour at 80°C under argon, and the mixture was stirred for an additional 6 hours at the same temperature. The flask was immersed in an ice bath, and borane-THF complex (127 mL of 1.0 M/L) was added. After the mixture had been stirred for 1 hour, the reaction was quenched by the addition of 1 M HCl (100 mL). The organic layer was separated, and the aqueous layer was extracted with hexane. The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel (chloroform/cyclohexane 1:3) to give $\mathbf{4}_S$ (5.9 g, 18%) and $\mathbf{4}_S$ (10.5 g, 32%), respectively. $\mathbf{4}_S$: colorless cubes (from hexane); mp 121–122°C; $[\alpha]_D^{27}$ −125.3° (*c* 1.1, $CHCl_3$). IR (KBr) 2895, 2330, 1580, 1440, 1245, 985, 760 cm^{-1}. ^{1}H NMR (500 MHz) ($CDCl_3$) δ 0.14 (d, J = 7.2 Hz, 3H), 0.64–1.07 (m, 10H), 1.15–1.42 (m, 7H), 1.51–1.69 (m, 6H), 1.87–1.89 (m, 1H), 1.99–2.02 (m, 1H), 2.28–2.30 (m, 1H), 2.65–2.69 (m, 1H), 3.86 (s, 3H), 3.83–3.92 (m, 1H), 6.87–6.89 (m, 1H), 6.98–7.01 (m, 1H), 7.26–7.49 (m, 1H), 7.94–7.98 (m, 1H); ^{13}C NMR (68 MHz) ($CDCl_3$) δ 14.6, 21.0, 22.2, 22.5, 24.7, 25.9 (d, J(CP) = 4.9 Hz), 26.1, 26.5, 26.7, 26.9, 31.4, 34.3, 36.4 (d, J(CP) = 50.9 Hz), 43.4, 48.9 (d, J(CP) = 4.9 Hz), 55.3, 78.6 (d, J(CP) = 4.9 Hz), 110.4 (d, J(CP) = 9.3 Hz), 118.8 (d, J(CP) = 48.9 Hz), 120.6 (d, J(CP) = 11.7 Hz), 133.9 (d, J(CP) = 2.0 Hz), 137.1 (d, J(CP) = 16.6 Hz), 161.3. Anal. calcd for $C_{23}H_{40}BO_2P$: C, 70.77; H, 10.33; found: C, 71.10; H, 10.37. $\mathbf{4}_R$: colorless cubes (from hexane); mp 118–119°C; $[\alpha]_D^{28}$ + 6.1° (*c* 1.1, $CHCl_3$). IR (KBr) 2895, 2320, 1570, 1440, 1250, 980, 770 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 0.68–1.02 (m, 12H), 1.15–1.39 (m, 6H), 1.48–1.71 (m, 4H), 1.81–1.91 (m, 2H), 2.22–

2.30 (m, 1H), 2.39–2.49 (m, 1H), 3.87 (s, 3H), 4.04–4.12 (m, 1H), 6.89–6.92 (m, 1H), 6.99–7.03 (m, 1H), 7.44–7.49 (m, 1H), 7.81–7.87 (m, 1H). ^{13}C NMR (68 MHz) ($CDCl_3$) δ 15.8, 21.2, 22.1, 25.2, 25.7 (d, J(CP) = 2.9 Hz), 26.0, 26.1, 26.7 (d, J(CP) = 12.7 Hz), 26.8 (d, J(CP) = 14.7 Hz), 31.2, 34.2, 37.3 (d, J(CP) = 48.9 Hz), 42.7, 49.3 (d, J(CP) = 6.8 Hz), 55.5, 78.4 (d, J(CP) = 4.9 Hz), 111.0 (d, J(CP) = 4.9 Hz), 120.6 (d, J(CP) = 11.7 Hz), 120.6 (d, J(CP) = 47.9 Hz), 133.5, 135.7 (d, J(CP) = 13.7 Hz), 161.3. Anal. calcd for $C_{23}H_{40}BO_2P$: C, 70.77; H, 10.33; found: C, 70.54; H, 10.44.

*(S_P,1'*R*,2'*S*,5'*R*)-[(2'-Isopropyl-5'-methylcyclohexyl)oxy](t-butyl)(o-methoxyphenyl)phosphine-Borane* (**5**$_S$) *and* (*R_P*,1'*R*,2'*S*,5'*R*)-[(2'-Isopropyl-5'-methylcyclohexyl)oxy](t-butyl)(o-methoxyphenyl)phosphine-Borane* (**5**$_R$). A mixture of (−)-menthol (26.4 g, 0.17 mol) and pyridine (13.7 mL, 0.17 mol) in dry benzene (130 mL) was added dropwise during 4 hours into a stirred solution of *t*-butyldichlorophosphine (26.8 g, 0.17 mol) in dry benzene (130 mL) at room temperature under argon. The mixture was stirred for 15 hours, and it was filtered to remove the resulting pyridinium salt. *o*-Methoxyphenylmagnesium bromide (110 mL of 1.8 M/L THF solution) was slowly added to the filtrate during 0.5 hours at 80°C under argon, and the mixture was stirred for an additional 6 hours at the same temperature. The flask was then immersed in an ice bath, and borane-THF complex (200 mL of 1.0 M/L) was added. After the mixture had been stirred for 1 hour, the reaction was quenched with 1 M HCl (200 mL). The organic layer was separated, and the aqueous layer was extracted with hexane. The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel (benzene/hexane 1:2) to give **5**$_S$ (7.3 g, 12%) and **5**$_R$ (15.9 g, 26%), respectively. **5**$_S$: colorless plates (from hexane); mp 90–92°C; $[\alpha]_D^{26}$ −105° (*c* 1.0, $CHCl_3$). IR (KBr) 2910, 2330, 1580, 1455, 1260, 990, 760 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 0.43 (d, J = 6.8 Hz, 3H), 0.73 (d, J = 7.0 Hz, 3H), 0.78–1.15 (m, 9H), 1.10 (d, J = 14.8 Hz, 9H), 1.27–1.33 (m, 1H), 1.42–1.46 (m, 1H), 1.56–1.65 (m, 2H), 1.77–1.82 (m, 1H), 2.19–2.25 (m, 1H), 3.79 (s, 3H), 4.22–4.25 (m, 1H), 6.87–6.90 (m, 1H), 6.96–7.01 (m, 1H), 7.41–7.46 (m, 1H), 7.76–7.81 (m, 1H). ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.4, 21.1, 22.2, 22.6, 25.0, 25.5 (d, J(CP) = 2.9 Hz), 31.5, 33.8 (d, J(CP) = 44.0 Hz), 34.1, 43.9, 48.9 (d, J(CP) = 4.4 Hz), 54.8, 79.8 (d, J(CP) = 5.9 Hz), 110.8 (d, J(CP) = 4.4 Hz), 119.1 (d, J(CP) = 49.9 Hz), 119.9 (d, J(CP) = 11.8 Hz), 133.1 (d, J(CP) = 2.9 Hz), 135.8 (d, J(CP) = 11.8 Hz), 161.0. Anal. calcd for $C_{21}H_{38}BO_2P$: C, 69.23; H, 10.51; found: C, 69.12; H, 10.85. **5**$_R$: colorless plates (from hexane); mp 107–110°C; $[\alpha]_D^{27}$ −6.7° (*c* 0.9, $CHCl_3$). IR (KBr) 2900, 2310, 1580, 1460, 1250, 990, 765 cm^{-1}. ^{1}H NMR (400 MHz) ($CDCl_3$) δ 0.72 (d, J = 6.4 Hz, 3H), 0.74–1.13 (m, 21H), 1.30–1.37 (m, 1H), 1.41–1.49 (m, 1H), 1.59–1.67 (m, 1H), 1.81–1.87 (m, 1H), 2.30–2.35 (m, 1H), 3.81 (s, 3H), 4.22–4.30 (m, 1H), 6.89–6.92 (m, 1H), 6.98–7.02 (m, 1H), 7.42–7.46 (m, 1H), 7.66–7.71 (m, 1H). ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.5, 21.1, 22.1, 22.6, 24.7 (d, J(CP) = 3.0 Hz), 25.4, 31.3, 33.8 (d, J(CP) = 45.5 Hz), 34.3, 42.7, 49.3 (d, J(CP) = 5.9 Hz), 55.0, 79.0 (d, J(CP) = 5.9 Hz), 111.3 (d, J(CP) = 5.9 Hz), 119.8 (d, J = 8.8 Hz), 120.0 (d, J = 45.5 Hz), 132.9 (d, J = 3.0 Hz), 134.6 (d, J(CP) = 7.3 Hz), 161.3 (d, J(CP) = 5.9 Hz). Anal. calcd for $C_{21}H_{38}BO_2P$: C, 69.23; H, 10.51; found: C, 69.07; H, 10.78.

Preparation of Compounds **1**$_R$, **1**$_S$, **2**$_R$, *and* **2**$_S$

A representative experimental procedure is described for the preparation of (*R*)-*t*-butyl(*o*-methoxyphenyl)phosphine-borane (**2**$_R$). A solution of phosphine-borane **5**$_S$ (1.17 g, 3.21 mmol) in dry THF (12 mL) was added dropwise into a large excess of lithium naphthalenide (32 mL of 1.0 M/L solution) at −40°C. After the mixture had been stirred for 1 hour at the same temperature, 1 M HCl (80 mL) was slowly added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and residue was subjected to column chromatography on silica gel (gradient elution, hexane, benzene/hexane 1:2) to give **2**$_R$ (0.63 g, 94%). Enantiomeric excess of this compound was determined to be 100% by HPLC analysis with "CHIRALCEL OJ" prepared by Daicel Chemical Industries, Ltd. **2**$_R$: colorless cubes (from hexane); mp 65–67°C; $[\alpha]_D^{26}$ +52.8° (*c* 1.0, benzene). IR (KBr) 2920, 2310, 1580, 1460, 1245, 1015, 760 cm^{-1}; ^{1}H NMR (500 MHz) ($CDCl_3$) δ 1.16 (d, J = 15.1 Hz, 9H), 3.86 (s, 3H), 5.60 (d, J(HP) = 383 Hz, 1H), 6.93–6.95 (m, 1H), 7.04–7.08 (m, 1H), 7.46–7.50 (m, 1H), 7.69–7.73 (m, 1H), ^{13}C NMR (68 MHz) ($CDCl_3$) δ 26.8 (d, J(CP) = 2.9 Hz), 29.1 (d, J(CP) = 34.2 Hz), 55.5, 110.6 (d, J(CP) = 3.9 Hz), 113.4 (d, J(CP) = 48.9 Hz), 121.0 (d, J(CP) = 11.7 Hz), 113.3 (d, J(CP) = 2.0 Hz), 135.7 (d, J(CP) = 12.7 Hz), 160.4. Anal. calcd for $C_{11}H_{20}BOP$: C, 62.90; H, 9.60; found: C, 62.67; H, 9.63.

(S)-t-Butyl(o-methoxyphenyl)phosphine-Borane (**2**$_S$). 93% yield; colorless cubes (from hexane); mp 64–66°C; $[\alpha]_D^{26}$ −49.9° (*c* 1.0, benzene).

(S)-Cyclohexyl(o-methoxyphenyl)phosphine-Borane (**1**$_S$). 98% yield; colorless oil; $[\alpha]_D^{26}$ −90.4° (*c* 1.6, $CHCl_3$). IR (neat) 2900, 2350, 1580, 1470, 1245, 1060, 905, 760 cm^{-1}. ^{1}H NMR (500 MHz) ($CDCl_3$) δ 1.17–1.43 (m, 5H), 1.66–1.82 (m, 5H), 2.04–2.16 (m, 1H), 3.90 (s, 3H), 5.51 (d, ^1J(HP) = 381 Hz, 1H), 6.92–6.95 (m, 1H), 7.03–7.07 (m, 1H), 7.47–7.51 (m,

1H), 7.69–7.74 (m, 1H). ^{13}C NMR (126 MHz) ($CDCl_3$) δ 25.7, 26.4, 26.5 (d, J(CP) = 8.6 Hz), 26.7, 27.2, 28.6, 31.7 (d, J(CP) = 36.5 Hz), 55.7, 110.5 (d, J(CP) = 4.3 Hz), 113.1 (d, J(CP) = 51.6 Hz), 121.1 (d, J(CP) = 10.7 Hz), 133.4, 135.7 (d, J(CP) = 12.9 Hz), 160.6. HRMS calcd for $C_{13}H_{21}BOP$ (M − H): 235.1423; found: 235.1425. Anal. calcd for $C_{13}H_{22}BOP$: C, 66.13; H, 9.39; found: C, 61.93; H, 8.67.

(S)-Cyclohexyl(o-methoxyphenyl)phosphine-Borane ($\mathbf{1}_R$). 94% yield; colorless oil; $[\alpha]_D^{27}$ +87.7° (*c* 1.0, $CHCl_3$)

(S)-Cyclohexyl(o-methoxyphenyl)methylphosphine-Borane ($\mathbf{6}_S$). Methyllithium (2.7 mL, 1.5 M/L ether solution) was added to a solution of $\mathbf{4}_R$ (312 mg, 0.8 mmol) in dry benzene (2 mL) at 50°C under argon. After the mixture had been stirred for 5 hours, the reaction was quenched with 1 M HCl (5 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was subjected to preparative TLC on silica gel (benzene/hexane 1:1) to give $\mathbf{6}_S$ (198 mg, 98%). The enantiomeric excess of this compound was determined to be 100% by HPLC analysis with CHIRALCEL OJ. $\mathbf{6}_S$: colorless cubes (from hexane); mp 76–78°C; $[\alpha]_D^{26}$ +59.7° (*c* 1.0, $CHCl_3$). IR (KBr) 2890, 2320, 1580, 1570, 1450, 1245, 1065, 915, 770 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 1.12–1.34 (m, 5H), 1.40–1.51 (m, 1H), 1.57 (d, J = 10.6 Hz, 3H), 1.78–1.86 (m, 2H), 2.23–2.33 (m, 1H), 3.89 (s, 3H), 6.89–6.92 (m, 1H), 7.00–7.05 (m, 1H), 7.45–7.49 (m, 1H), 7.84–7.89 (m, 1H); ^{13}C NMR (68 MHz) ($CDCl_3$) δ 8.3 (d, J(CP) = 40.1 Hz), 25.9, 26.5, 26.6, 26.7, 26.8, 33.4 (d, J(CP) = 37.2 Hz), 55.4, 110.6 (d, J(CP) = 3.9 Hz), 116.2 (d, J(CP) = 50.9 Hz), 121.0 (d, J(CP) = 12.7 Hz), 113.2, 137.0 (d, J(CP) = 14.7 Hz), 161.5 (d, J(CP) = 2.9 Hz). Anal. calcd for $C_{14}H_{24}BOP$: C, 67.23; H, 9.67; found: C, 67.47; H, 9.40.

(R)-Cyclohexyl(o-methoxyphenyl)methylphosphine-Borane ($\mathbf{6}_R$). This compound was prepared from $\mathbf{4}_S$ in a similar manner as the preparation of $\mathbf{6}_S$. Colorless cubes (from hexane); mp 76–78°C; $[\alpha]_D^{26}$ −59.6° (*c* 1.2, $CHCl_3$). Anal. calcd for $C_{14}H_{24}BOP$: C, 67.23; H, 9.67; found: C, 67.45; H, 9.38.

(R)-Cyclohexyl(o-methoxyphenyl)methylphosphine Oxide ($\mathbf{7}_R$). Phosphine-borane $\mathbf{6}_S$ (35 mg, 0.14 mmol) was dissolved in 1 mL of degassed morpholine, and the solution was kept at 70°C for 3 hours under argon. Excess morpholine was removed in vacuo. The residue was dissolved in MeOH (1 mL), and hydrogen peroxide (0.5 mL of 30% solution) was added to the solution. The reaction mixture was treated with a $Na_2S_2O_3$ solution, and it was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was subjected to preparative TLC on silica gel (CH_2Cl_2/MeOH 10:1) to give $\mathbf{7}_R$ (22 mg, 62%). $[\alpha]_D^{27}$ +95.1° (*c* 1.2, MeOH) (Ref. [16] $[\alpha]_D$ +98.5° (*c* 1, MeOH)

Reaction of $\mathbf{2}_S$ with Iodobenzene in the Presence of $Pd(PPh_3)_4$. A mixture of silver carbonate (550 mg, 2 mmol), compound $\mathbf{2}_S$ (210 mg, 1 mmol), $Pd(PPh_3)_4$ (58 mg, 5 mol%), iodobenzene (170 μL, 1.5 mmol), and acetonitrile (3 mL) was stirred at 50°C under argon for 15 minutes. The reaction mixture was filtered by suction. Evaporation of the solvent in vacuo followed by purification of the residue by preparative TLC on silica gel (benzene/hexane 1:1) afforded *(S)-t-butyl(o-methoxyphenyl)phenylphosphine-borane* ($\mathbf{8}_S$) (160 mg, 56%): colorless plates (from hexane); mp 89–91°C; $[\alpha]_D^{27}$ +0.27° (*c* 1.0, $CHCl_3$) (100% ee by HPLC analysis using CHIRALCEL OJ). IR (KBr) 2870, 2310, 1420, 1240, 1060, 1020, 740 cm^{-1}. ^1H NMR (270 MHz) ($CDCl_3$) δ 1.33 (d, J = 14.6 Hz, 9H), 3.57 (s, 3H), 6.88–6.93 (m, 1H), 7.02–7.10 (m, 1H), 7.32–7.44 (m, 3H), 7.45–7.53 (m, 1H), 7.65–7.72 (m, 2H), 7.93–8.02 (m, 1H). ^{13}C NMR (126 MHz) ($CDCl_3$) δ 28.1, 31.6 (d, J = 32.3 Hz), 54.7, 111.4 (d, J(CP) = 4.3 Hz), 116.4 (d, J(CP) = 49.4 Hz), 120.9 (d, J(CP) = 10.8 Hz), 127.9 (d, J(CP) = 10.7 Hz), 129.9, 130.4 (d, J(CP) = 53.8 Hz), 132.5 (d, J(CP) = 8.6 Hz), 133.3, 137.5 (d, J(CP) = 10.8 Hz). Anal. calcd for $C_{17}H_{24}BOP$: C, 71.35; H, 8.45; found: C, 71.59; H, 8.37.

(S_P,1'R,2'S,5'R)-[(2'-Isopropyl-5'-methylcyclohexyl)oxy](t-butyl)phenylphosphine-Borane ($\mathbf{9}_S$). A mixture of (−)-menthol (7.8 g, 50 mmol) and pyridine (4.0 mL, 50 mmol) in dry benzene (50 mL) was added dropwise during 2 hours into a stirred solution of dichlorophenylphosphine (6.8 mL, 50 mmol) in dry benzene (50 mL) at room temperature under argon. The mixture was stirred for 15 hours, and it was filtered under nitrogen to remove the resulting pyridinium salt. t-Butylmagnesium chloride (46 mL of 1.3 M/L ether solution) was slowly added to the filtrate during 1 hour at 80°C under argon, and the mixture was stirred for an additional 4 hours at the same temperature. The flask was immersed in an ice bath, and borane-THF complex (75 mL of 1.0 M/L) was added to the mixture. After the mixture had been stirred for 1 hour, 1 M HCl (100 mL) was slowly added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with hexane. The combined extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel (benzene/hexane 1:2) to give a pasty oil (8.5 g). Trituration with hexane was carried out, and the resulting crystalline solid was recrystallized from hexane to give pure $\mathbf{9}_S$: colorless needles (from hexane); mp

81–82°C. IR (KBr) 2800, 2660, 1430, 1355, 980, 735 cm^{-1}. ^1H NMR (500 MHz) ($CDCl_3$) δ 0.40 (d, J = 6.9 Hz, 3H), 0.77 (d, J = 6.9 Hz, 3H), 0.79–0.97 (m, 7H), 0.94 (d, J = 6.6 Hz, 3H), 1.09 (d, J = 14.6 Hz, 9H), 1.09–1.13 (m, 1H), 1.31–1.37 (m, 1H), 1.41–1.46 (m, 1H), 1.59–1.65 (m, 1H), 4.11–4.15 (m, 1H), 7.40–7.49 (m, 2H), 7.75–7.79 (m, 2H). ^{13}C NMR (100 MHz) ($CDCl_3$) δ 15.2, 21.0, 22.2, 22.6, 24.5 (d, J(CP) = 3.0 Hz), 25.5, 31.5, 32.4 (d, J(CP) = 44.0 Hz), 34.1, 43.9, 48.9 (d, J(CP) = 4.4 Hz), 80.3 (d, J(CP) = 4.4 Hz), 127.6 (d, J(CP) = 10.3 Hz), 130.9 (d, J(CP) = 48.4 Hz), 131.2 (d, J(CP) = 5.8 Hz), 132.3 (d, J(CP) = 10.3 Hz). Anal. calcd for $C_{20}H_{36}BOP$: C, 71.86; H, 10.85; found: C, 72.03; H, 10.96.

(R)-t-Butylphenylphosphine-Borane (**10**$_R$). This compound was prepared in 93% yield from compound **9**$_S$ in a similar procedure for the preparation of **2**$_R$.

(S)-t-Butylmethylphenylphosphine-Borane (**11**$_S$). This compound was prepared in 83% yield from **9**$_S$ by reduction with lithium naphthalenide at −78 to −40°C, followed by reaction with iodomethane. $[\alpha]_D^{26}$ +8.0° (*c* 1.0, MeOH) (Ref. [1] $[\alpha]_D^{25}$ −8.2° (*c* 1.0, MeOH).

(S)-t-Butyl(o-methoxyphenyl)methylphosphine-Borane (**12**$_S$). A solution of phosphine-borane **5**$_S$ (328 mg, 0.9 mmol) in dry THF (6 mL) was added dropwise into a large excess of lithium naphthalenide (9 mL of 1.0 M/L solution) at −40°C under argon. Iodomethane (0.5 μL, 8 mmol) was added to the reaction mixture, and then the reaction mixture was treated with 1 M HCl (10 mL) at −40°C. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$). The solvent was evaporated under reduced pressure, and the residue was subjected to column chromatography on silica gel (gradient elution, hexane, benzene/hexane 1:1) to give **12**$_S$ (199 mg, 98%). Colorless needles (from hexane); mp 125–126°C; $[\alpha]_D^{28}$ +53.4° (*c* 1.0, $CHCl_3$). IR (KBr) 2920, 2320, 1460, 1255, 1080, 1025, 775 cm^{-1}. ^1H NMR (500 MHz) ($CDCl_3$) δ 1.12 (d, J = 14.3 Hz, 9H), 1.69 (d, J = 10.2 Hz, 3H), 3.83 (s, 3H), 6.89–6.92 (m, 1H), 7.02–7.05 (m, 1H), 7.45–7.48 (m, 1H), 7.88–7.93 (m, 1H). ^{13}C NMR (126 MHz) ($CDCl_3$) δ 7.0 (d, J(CP) = 38.7 Hz), 25.9 (d, J(CP) = 15.1 Hz), 29.9 (d, J(CP) = 34.4 Hz), 55.0, 110.9, 115.2 (d, J(CP) = 47.2 Hz), 120.8 (d, J(CP) = 12.9 Hz), 133.2, 137.8 (d, J(CP) = 12.9 Hz), 161.8. Anal. calcd for $C_{12}H_{22}BOP$: C, 64.32; H, 9.90; found: C, 64.51; H, 9.71.

(R)-t-Butyl(o-methoxyphenyl)methylphosphine-Borane (**12**$_R$). This compound was prepared in 97% yield by the reaction of **2**$_S$ with iodomethane in the presence of sodium hydride. Colorless needles (from hexane); mp 124–126°C; $[\alpha]_D^{26}$ −51.6° (*c* 1.0, $CHCl_3$).

(S)-Allyl(t-butyl)(o-methoxyphenyl)phosphine-Borane (**13**$_S$). Mp 75–76°C; $[\alpha]_D^{27}$ −59.8° (*c* 0.97, $CHCl_3$). IR (KBr) 2900, 2330, 1460, 1250, 1060, 1020, 760 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.14 (d, ^3J(HP) = 14.2 Hz, 9H), 2.63–2.74 (m, 1H), 3.30–3.44 (m, 1H), 3.85 (s, 3H), 4.98–5.18 (m, 2H), 5.67–5.82 (m, 1H), 6.87–6.91 (m, 1H), 7.00–7.06 (m, 1H), 7.43–7.50 (m, 1H), 7.84–7.92 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 26.39, 26.43 (d, J(CP) = 35.2 Hz), 30.8 (d, J(CP) = 32.2 Hz), 54.8, 110.5 (d, J(CP) = 3 Hz), 113.4 (d, J(CP) = 45.5 Hz), 118.7 (d, J(CP) = 10.3 Hz), 120.9 (d, J(CP) = 11.8 Hz), 130.2 (d, J(CP) = 5.9 Hz), 133.3, 138.8 (d, J(CP) = 14.7 Hz), 161.3 (d, J(CP) = 2.9 Hz). HRMS (FAB) calcd for $C_{14}H_{23}BOP$ (M − H): 249.1580; found: 249.1582. Anal. calcd for $C_{14}H_{24}BOP$: C, 67.23; H, 9.67; found: C, 67.45; H, 9.75.

(S)-t-Butyl(3-butenyl)o-methoxyphenylphosphine-Borane (**14**$_S$). Colorless crystals; mp 118–119°C; $[\alpha]_D^{27}$ +4.7° (*c* 0.9, $CHCl_3$). IR (KBr) 2900, 2350, 1460, 1430, 1260, 780 cm^{-1}. ^1H NMR (270 MHz) ($CDCl_3$) δ 1.12 (d, ^3J(HP) = 13.8 Hz, 9H), 1.77–1.85 (m, 2H), 2.24–2.60 (m, 2H), 3.83 (s, 3H), 4.94–5.05 (m, 2H), 5.79–5.96 (m, 1H), 6.89–6.95 (m, 1H), 7.02–7.08 (m, 1H), 7.45–7.51 (m, 1H), 7.85–7.92 (m, 1H). ^{13}C NMR (125 MHz) ($CDCl_3$) δ 20.0 (d, J(CP) = 34.4 Hz), 26.2, 27.7, 30.4 (d, J(CP) = 32.3 Hz), 54.9, 110.6 (d, J(CP) = 4.3 Hz), 113.5 (d, J(CP) = 45.1 Hz), 114.4, 121.0 (d, J(CP) = 12.9 Hz), 138.73 (d, J(CP) = 15 Hz), 138.82 (d, J(CP) = 15 Hz), 161.5; HRMS (FAB) calcd for $C_{15}H_{25}BOP$ (M − H): 263.1736; found: 263.1731. Anal. calcd for $C_{15}H_{26}BOP$: C, 68.20; H, 9.92; found: C, 68.02; H, 9.94.

(R)-t-Butyl(3-iodopropyl)(o-methoxyphenyl)phosphine-Borane (**15**$_R$). Colorless crystals; mp 104–105°C; $[\alpha]_D^{28}$ +15.6° (*c* 1.1, $CHCl_3$). IR (KBr) 2920, 2340, 1460, 1250, 1235, 1070, 1020, 770 cm^{-1}. ^1H NMR (270 MHz) ($CDCl_3$) δ 1.13 (d, ^3J(HP) = 13.9 Hz, 9H), 1.66–1.80 (m, 2H), 2.04–2.24 (m, 1H), 2.72–2.88 (m, 1H), 3.14–3.38 (m, 2H), 3.88 (s, 3H), 6.88–6.96 (m, 1H), 7.02–7.10 (m, 1H), 7.46–7.54 (m, 1H), 7.83–7.91 (m, 1H). ^{13}C NMR (100 MHz) ($CDCl_3$) δ 9.9 (d, J(CP) = 16.1 Hz), 22.0 (d, J(CP) = 35.2 Hz), 26.2, 27.3, 30.5 (d, J(CP) = 33.7 Hz), 55.2, 110.5 (d, J(CP) = 3.0 Hz), 113.0 (d, J(CP) = 44.0 Hz), 121.0 (d, J(CP) = 13.3 Hz), 133.4 (d, J(CP) = 2.9 Hz), 138.8 (d, J(CP) = 51.6 Hz), 161.4 (d, J(CP) = 2.9 Hz); HRMS (FAB) calcd for $C_{14}H_{24}BIOP$ (M − H): 377.0703; found: 377.0695. Anal. calcd for $C_{14}H_{25}BIOP$: C, 44.48; H, 6.67; found: C, 45.02; H, 6.65.

(R)-t-Butyl(methoxycarbonylmethyl)(o-methoxyphenyl)phosphine-Borane (**16**$_R$). Colorless needles; mp 103.5–104.0°C; $[\alpha]_D^{27}$ +40.9° (*c* 0.34, $CHCl_3$). IR (KBr) 2910, 2320, 1730, 1420, 1280, 1135, 770 cm^{-1}. ^1H NMR (400 MHz, CDCl3) δ 1.16 (d, J = 14.6 Hz, 9H), 3.04 (dd, ^2J(HP) = 8.2 Hz, J = 13.7 Hz, 1H), 3.59 (s, 3H), 3.64, (dd, 1H), 3.84 (s, 3H), 6.91–6.94,

(m, 1H), 7.03–7.08 (m, 1H), 7.47–7.51 (m, 1H), 7.88–7.94 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3 (d, J(CP) = 2.9 Hz), 28.1 (d, J(CP) = 29.3 Hz), 31.1 (d, J(CP) = 32.3 Hz), 52.0, 55.0, 110.7 (d, J(CP) = 4.4 Hz), 113.6 (d, J(CP) = 47.0 Hz), 121.0 (d, J(CP) = 13.2 Hz), 133.5 (d, J(CP) = 2.9 Hz), 138.0 (d, J(CP) = 16.1 Hz), 161.3 (d, J(CP) = 3.0 Hz), 168.5. HRMS (FAB) calcd for $C_{14}H_{23}O_3BP$ (M − H): 281.1478; found: 281.1472. Anal. calcd for $C_{14}H_{24}O_3BP$: C, 59.60; H, 8.57; found: C, 59.45; H, 8.38. This compound was reduced by $LiAlH_4$ to afford (*R*)-*t*-butyl(2-hydroxyethyl)(*o*-methoxyphenyl)phosphine-borane: colorless needles; mp 73.5–74.5°C; $[\alpha]_D^{28}$ +10.5° (*c* 0.50, $CHCl_3$). IR (KBr) 3500, 2910, 2310, 1575, 1465, 1435, 1260, 1080, 1020, 775 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 1.13 (d, ^3J(HP) = 14.2 Hz, 9H), 2.08–2.18 (m, 2H), 2.81–3.02 (m, 1H), 3.75–3.93 (m, 2H), 3.84 (s, 3H), 6.91–6.95 (m, 1H), 7.03–7.10 (m, 1H), 7.46–7.53 (m, 1H), 7.87–7.94 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.0 (d, J(CP) = 34.4 Hz), 26.1, 30.5 (d, J(PC) = 34.4 Hz), 55.0, 58.5, 110.8 (d, J(PC) = 4.3 Hz), 113.2 (d, J(PC) = 45.1 Hz), 121.1 (d, J(CP) = 10.8 Hz), 133.5, 138.6 (d, J(CP) = 12.9 Hz), 161.5 (d, J(CP) = 4.3 Hz). HRMS (FAB) calcd for $C_{13}H_{23}O_2BP$: 253.1529; found: 253.1533.

*(R)-t-Butyl(2-ethoxycarbonylethyl)(o-methoxyphenyl)*phosphine-Borane (**17**$_R$). Colorless cubes; mp 108.5–109.0°C; $[\alpha]_D^{28}$ −28.6° (*c* 1.0, $CHCl_3$). IR (KBr) 2910, 2220, 1710, 1455, 1250, 1070, 1020, 805, 780 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, ^3J(HP) = 14.1 Hz, 9H), 1.23 (t, J = 7.2 Hz, 3H), 2.02–2.09 (m, 1H), 2.12–2.23 (m, 1H), 2.64–2.73 (m, 1H), 2.87–2.92 (m, 1H), 3.83 (s, 3H), 4.08–4.17 (m, 2H), 6.90–6.92 (m, 1H), 7.46–7.51 (m, 1H), 7.84–7.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 16.1 (d, J(CP) = 36.7 Hz), 26.1 (d, J(CP) = 2.9 Hz), 28.6 30.5 (d, J(CP) = 35.2 Hz), 55.0, 60.7, 110.9 (d, J(CP) = 3.0 Hz), 112.8 (d, J(CP) = 45.5 Hz), 121.1 (d, J(CP) = 11.7 Hz), 133.5 (d, J(CP) = 3.0 Hz), 138.8 (d, J(CP) = 14.7 Hz), 161.5 (d, J(CP) = 2.9 Hz), 173.26 (d, J(CP) = 17.6 Hz). HRMS (FAB) calcd for $C_{16}H_{27}O_3BP$ (M − H): 309.1791; found: 309.1794. Anal. calcd for $C_{16}H_{28}O_3BP$: C, 61.96; H, 9.10; found: C, 61.67; H, 9.14. This compound was reduced by $LiAlH_4$ to afford (*R*)-*t*-butyl(3-hydroxypropyl)(*o*-methoxyphenyl)phosphine-borane. Colorless needles; mp 136.5–137.5°C; $[\alpha]_D^{26}$ +3.6° (*c* 1.1, $CHCl_3$). IR (KBr) 3470, 2920, 2870, 2330, 1575, 1455, 1250, 1060, 1020, 775 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 1.13 (d, ^3J(HP) = 13.8 Hz, 9H), 1.39–1.60 (m, 2H), 1.73–1.97 (m 2H), 2.56–2.76 (m, 1H), 3.67 (dd, 2H), 3.84 (s, 3H), 6.88–6.92 (m, 1H), 7.02–7.08 (m, 1H), 7.44–7.50 (m, 1H), 7.85–7.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0 (d, J(CP) = 36.7 Hz), 26.2, 26.9, 30.5 (d, J(PC) = 33.8 Hz), 54.9, 63.6 (d, J(CP) = 14.7 Hz), 110.6 (d, J(CP) = 2.9 Hz), 113.4 (d, J(CP) = 44.0 Hz), 121.0 (d, J(CP) = 11.8 Hz), 133.3, 138.8 (d, J(CP) = 14.6 Hz), 161.5 (d, J(CP) = 2.9 Hz). HRMS (FAB) calcd for $C_{14}H_{25}O_2BP$ (M − H): 267.1685; found: 267.1683. Anal. calcd for $C_{14}H_{26}O_2BP$: C, 62.71; H, 9.77; found: C, 62.40; H, 9.73.

(S,S)-α,α'-Bis[boranato(t-butyl)(o-methoxyphenyl)phosphino]xylene (**18**$_{SS}$). Colorless needles (from AcOEt); mp 210–213°C; $[\alpha]_D^{26}$ −522° (*c* 1.0, benzene). IR (KBr) 2900, 2320, 1565, 1450, 1240, 1160, 1060, 1010, 755 cm^{-1}. ^1H NMR (400 MHz) ($CDCl_3$) δ 1.26 (d, J = 13.7 Hz, 18H), 3.73–3.78 (m, 2H), 3.96 (s, 6H), 4.01–4.29 (m, 2H), 6.68–6.73 (m, 4H), 6.93–6.99 (m, 4H), 7.44–7.49 (m, 2H), 7.78–7.84 (m, 2H). ^{13}C NMR (68 MHz) ($CDCl_3$) δ 23.4 (d, J(CP) = 30.3 Hz), 27.2 (d, J(CP) = 2.0 Hz), 31.4 (d, J(CP) = 31.3 Hz), 54.8, 110.5 (d, J(CP) = 3.9 Hz), 113.6 (d, J(CP) = 44.0 Hz), 121.0 (d, J(CP) = 2.9 Hz), 121.1 (d, J(CP) = 11.7 Hz), 129.5 (d, J(CP) = 2.0 Hz), 133.4 (d, J(CP) = 2.0 Hz) 134.1 (t, J(CP) = 4.9 Hz), 139.3 (d, J(CP) = 13.7 Hz) 161.5 (d, J = 2.9 Hz). Anal. calcd for $C_{30}H_{46}B_2O_2P_2$: C, 68.99; H, 8.88; found: C, 69.13; H, 8.95.

(R$_P$,2R)-Cyclohexyl(2-hydroxyoctyl)(o-methoxyphenyl)phosphine-Borane (**19**$_R$). Colorless oil; $[\alpha]_D^{26}$ −16.2° (*c* 0.76, $CHCl_3$). IR (neat) 3400, 2880, 2325, 1440, 1240, 1015, 760 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 0.84–1.78 (m, 23H), 2.08–2.18 (m, 1H), 2.23 (br, 1H), 2.31–2.41 (m, 2H), 3.90 (s, 3H), 3.92–4.07 (m, 1H), 6.89–6.93 (m, 1H), 7.01–7.06 (m, 1H), 7.45–7.51 (m, 1H), 7.83–7.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 31.2 (d, J(CP) = 35.3 Hz), 31.8, 33.6 (d, J(CP) = 38.1 Hz), 38.7 (d, J(CP) = 10.3 Hz), 55.5, 68.3, 110.6 (d, J(CP) = 4.4 Hz), 115.6 (d, J(CP) = 51.3 Hz), 121.3 (d, J(CP) = 11.8 Hz), 133.5, 137.1 (d, J(CP) = 14.7 Hz), 161.2. HRMS (FAB) calcd for $C_{21}H_{37}O_2BP$ (M − H): 363.2624; found: 363.2618. Anal. calcd for $C_{21}H_{38}O_2BP$: C, 69.23; H, 10.51; found: C, 69.37; H, 10.70.

(R$_P$,2R)-t-Butyl(2-hydroxyoctyl)(o-methoxyphenyl)phosphine-Borane (**20**$_R$). Colorless oil; $[\alpha]_D^{27}$ −17.8° (*c* 1.8, $CHCl_3$). IR (neat) 3450, 2900, 2300, 1455, 1245, 1020, 760 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$) δ 0.85–1.57 (m, 22H), 1.12 (d, ^3J(HP) = 14.2 Hz, 9H), 3.86 (s, 3H), 3.11–3.22 (m, 1H), 3.43 (br, 1H), 3.62–3.77 (m, 1H), 4.04–4.17 (m, 1H), 6.89–6.93 (m, 1H), 7.00–7.07 (m, 1H), 7.43–7.50 (m, 1H), 7.87–7.95 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 25.7, 26.4, 28.6 (d, J(CP) = 34.4 Hz), 29.2, 30.8 (d, J(CP) = 34.4 Hz), 31.8, 38.9, (d, J(CP) = 10.8 Hz), 55.0, 68.2, 110.0 (d, J(CP) = 4.3 Hz), 115.0 (d, J(CP) = 47.3 Hz), 121.0 (d, J(CP) = 12.9 Hz), 133.29, 137.89 (d, J(CP) = 15.1 Hz), 161.4. HRMS (FAB) calcd for $C_{19}H_{35}O_2BP$: 337.2468 (M − H); found: 337.2477. Anal. calcd for $C_{19}H_{36}O_2BP$: C, 67.46; H, 10.73; found: C, 67.00; H, 10.81.

(S)-Acetyl(t-butyl)(o-methoxyphenyl)phosphine-Borane (**21**$_S$). Colorless needles; mp 74–75°C; $[\alpha]_D^{27}$ −29.2° (*c* 1.1, $CHCl_3$)(97% ee). IR (KBr) 2910, 2340, 1690, 1455, 1250, 1100, 765 cm^{-1}. ^1H NMR

(500 MHz, $CDCl_3$) δ 1.20 (d, ^3J(HP) = 14.6 Hz, 9H), 2.28 (s, 3H), 3.78 (s, 3H), 6.94–6.96 (m, 1H), 7.13–7.16 (m, 1H), 7.54–7.57 (m, 1H), 7.88–7.92 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.9, 31.9 (d, J(CP) = 30.1 Hz), 54.8, 110.7 (d, J(CP) = 4.3 Hz), 113.8 (d, J(CP) = 43.0 Hz), 121.6 (d, J(CP) = 12.9 Hz), 134.2, 137.8 (d, J(CP) = 12.8 Hz), 159.7, 212.0 (d, J(CP) = 23.6 Hz). HRMS (FAB) calcd for $C_{13}H_{21}O_2BP$ (M − H); 251.1372; found: 251.1373. Anal. calcd for $C_{13}H_{22}O_2BP$: C, 61.94; H, 8.80; found: C, 62.18; H, 8.67.

(R)-Benzoyl(t-butyl)(o-methoxyphenyl)phosphine-Borane (**22**$_R$). Colorless needles; mp 135°C (decomp); $[\alpha]_D^{27}$ −59.8° (*c* 1.0, $CHCl_3$) (74% ee). IR (KBr) 2900, 2320, 1645, 1430, 1250, 1180, 1060, 775 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (d, ^3J(HP) = 14.8 Hz, 9H), 3.27 (s, 3H), 6.68–6.71 (m, 1H), 7.13–7.17 (m, 1H), 7.23–7.30, (m, 2H), 7.40–7.50, (m, 2H), 7.81–7.84 (m, 2H), 7.98–8.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 33.1 (d, J(CP) = 32.3 Hz), 54.4, 110.9 (d, J(CP) = 4.4 Hz), 115.9 (d, J(CP) = 41.1 Hz), 121.5 (d, J(CP) = 11.8 Hz), 127.9 (d, J(CP) = 20.5 Hz), 128.5 (d, J(CP) = 22.0 Hz), 133.3, 134.0 (d, J(CP) = 3.0 Hz), 136.5 (d, J(CP) = 13.2 Hz), 136.9 (d, J(CP) = 39.6 Hz), 159.8, 204.0 (d, J(CP) = 27.9 Hz). HRMS (FAB) calcd for $C_{18}H_{23}O_2BP$ (M − H): 313.1529; found: 313.1530. Anal. calcd for $C_{18}H_{24}O_2BP$: C, 68.82; H, 7.70; found: C, 68.30; H, 7.44.

(R)-Butyl(p-methoxybenzoyl)(o-methoxyphenyl)phosphine-borane (**23**$_R$). Colorless needles; mp 135°C (decomp); $[\alpha]_D^{28}$ −122° (*c* 1.04, $CHCl_3$) (94% ee). IR (KBr) 2900, 2380, 1630, 1580, 1250, 1170 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (d, ^3J(HP) = 16.2 Hz, 9H), 3.30 (s, 3H), 3.75 (s, 1H), 6.67–6.72 (m, 3H), 7.10–7.16 (m, 1H), 7.43–7.49 (m, 1H), 7.77–7.80 (m, 2H), 7.93–8.02 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.1, 33.0 (d, J(CP) = 32.3 Hz), 54.6, 55.4, 111.1 (d, J(CP) = 4.3 Hz), 116.2 (d, J(CP) = 40.8 Hz), 121.4 (d, J(CP) = 10.8 Hz), 130.1, 133.9, 136.4 (d, J(CP) = 10.8 Hz), 160.0, 163.6, 201.6 (d, J(CP) = 30.1 Hz). HRMS (FAB) calcd for $C_{19}H_{25}O_3BP$ (M − H): 343.1634; found: 343.1649. Anal. calcd for $C_{19}H_{26}O_3BP$: C, 66.30; H, 7.61; found: C, 66.64; H, 7.55.

Reaction of **2**$_S$ *with Benzyne.* To a mixture of **2**$_S$ (210 mg, 1 mmol) and *o*-bromophenyltriflate (610 mg, 2 mmol) in dry THF (10 mL) was added *t*-butyllithium (3.5 mL, 1.4 M/L pentane solution) at −78°C under argon. After the mixture had been stirred for 10 minutes the reaction was quenched with 1 M HCl. The organic layer was separated, and the aqueous layer was extracted with ether. The combined extracts were dried over $MgSO_4$. Evaporation of the solvent followed by preparative TLC on silica gel (benzene/hexane 1:1) afforded **8**$_S$ (127 mg, 44%) (100% ee) and compound **24** (65 mg, 25%).

Compound **24**: Colorless oil. ^1H NMR (270 MHz) ($CDCl_3$) δ 1.12 (d, J = 14.6 Hz, 9H), 7.39–7.47 (m, 1H), 7.56–7.62 (m, 1H), 7.75–7.81 (m, 1H), 7.89 (d, J = 7.9 Hz, 1H). ^{13}C NMR (126 MHz) ($CDCl_3$) δ 25.1, 30.8, 121.5 (d, J(CP) = 6.5 Hz), 128.4 (d, J(CP) = 10.8 Hz), 130.8 (d, J(CP) = 10.7 Hz), 131.6 (d, J(CP) = 53.8 Hz), 131.7, 144.0 (d, J(CP) = 8.6 Hz). Anal. calcd for $C_{16}H_{20}BOP$: C, 75.62; H, 7.93; found: C, 75.46; H, 7.99.

(R)-t-Butyl(o-methoxyphenyl)methylthiophosphine-Borane (**25**$_R$). Colorless needles; mp 89–91°C; $[\alpha]_D^{25}$ +102° (*c* 0.93, $CHCl_3$) (98% ee). IR (KBr) 2910, 2320, 1455, 1065, 1020, 810, 765 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.18 (d, ^3J(HP) = 15.8 Hz, 9H), 2.34 (d, ^3J(HP) = 11.9 Hz, 3H), 3.84 (s, 3H), 6.90–6.94 (m, 1H), 7.02–7.08 (m, 1H), 7.44–7.51 (m, 1H), 7.97–8.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 25.9 (d, J(CP) = 4.4 Hz), 35.5 (d, J(CP) = 26.4 Hz), 55.1, 111.5 (d, J(CP) = 4.4 Hz), 115.9 (d, J(CP) = 42.6 Hz), 120.7 (d, J(CP) = 10.2 Hz), 133.4 (d, J(CP) = 2.9 Hz), 136.1 (d, J(CP) = 13.2 Hz), 161.3. HRMS (FAB) calcd for $C_{12}H_{21}OBPS$ (M − H): 255.1140; found: 255.1145.

(S,S)-1,2-Bis[boranato(cyclohexyl)(o-methoxyphenyl)phosphino]ethane (**26**$_{SS}$). Phosphine-borane **6**$_S$ (225 mg, 0.90 mmol) was dissolved in dry THF (2 mL) under argon, and the solution was cooled to −78°C. To this solution, *s*-butyllithium (0.90 mL of 1.2 M/L cyclohexane solution) was added, and stirring was continued for 1.5 hours. Anhydrous copper (II) chloride (180 mg, 1.3 mmol) was added with vigorous stirring. The temperature was elevated during 0.5 hours to 0°C and kept at this level for 0.5 hours. The reaction was quenched with 1 M HCl (2 mL), and the mixture was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. The residue was subjected to preparative TLC on silica gel (benzene/hexane 1:4) to afford **26**$_{SS}$ (168 mg, 75%). Colorless needles (from ether); mp 207–208°C; $[\alpha]_D^{26}$ − 92.1° (*c* 1.0, $CHCl_3$). IR (KBr) 2900, 2325, 1580, 1470, 1240, 1060, 760 cm^{-1}. ^1H NMR (500 MHz) ($CDCl_3$) δ 1.03–1.27 (m, 10H), 1.42–1.49 (m, 2H), 1.62–1.64 (m, 4H), 1.80–1.82 (m, 4H), 1.99–2.07 (m, 2H), 2.10–2.16 (m, 2H), 2.19–2.27 (m, 2H), 3.43 (s, 6H), 6.71–6.72 (m, 2H), 6.99–7.02 (m, 2H), 7.42–7.45 (m, 2H), 7.81–7.85 (m, 2H). ^{13}C NMR (126 MHz) ($CDCl_3$) δ 16.0 (d, J = 36.6 Hz), 25.8, 26.6, 26.7, 26.7 (d, J(CP) = 8.6 Hz), 26.9 (d, J(CP) = 8.6 Hz), 33.0 (d, J(CP) = 36.5 Hz) 54.8, 110.1, 114.1 (d, J(CP) = 47.3 Hz), 120.8–120.9 (m), 133.2, 138.1–138.2 (m), 161.3. Anal. calcd for $C_{28}H_{46}B_2O_2P_2$: C, 67.50; H, 9.31; found: C, 67.73; H, 9.03.

In a similar manner, (*R,R*)-1,2-bis(boranato-(*t*-butyl)(*o*-methoxyphenyl)phosphino)ethane was prepared from **12**$_R$ in 72% yield. Colorless needles (from hexane); mp 179–180°C; $[\alpha]_D^{27}$ +49.9° (*c* 1.0, benzene). IR (KBr) 2930, 2325, 1475, 1250, 1070,

760 cm^{-1}. ^1H NMR (500 MHz) ($CDCl_3$) δ 1.11–1.14 (m, 18H), 2.38–2.41 (m, 4H), 2.49–2.53 (m, 4H), 3.50 (s, 6H), 6.77 (d, J = 8.3 Hz, 2H), 7.01 (t, J = 7.43 Hz, 2H), 7.42 (t, J = 7.2 Hz, 2H), 7.89–7.92 (m, 2H). ^{13}C NMR (126 MHz) ($CDCl_3$) δ 15.5 (d, J = 34.3 Hz), 26.6, 31.0 (d, J = 34.4 Hz) 54.6, 110.5, 114.1 (d, J = 45.1 Hz), 120.6–120.8 (m), 133.1, 138.4–138.5 (m), 161.6. Anal. calcd for $C_{24}H_{42}B_2O_2P_2$: C, 64.31; H, 9.49; found: C, 64.57; H, 9.35.

(S,S)-1,2-Bis(cyclohexyl(o-methoxyphenyl)phosphino)ethane ($\mathbf{3}_{SS}$). Compound $\mathbf{26}_{SS}$ (120 mg, 0.24 mmol) was dissolved in degassed morpholine (1.5 mL) under argon, and the solution was kept at 70°C for 2 hours. The solvent was removed in vacuo, and the residue was dissolved in degassed benzene. The solution was passed through a short column packed with silica gel using degassed benzene as the eluent. Evaporation of the filtrate under reduced pressure afforded $\mathbf{3}_{SS}$ (110 mg, 98%). Colorless crystals; mp 69–74°C; $[\alpha]_D^{27}$ −130° (c 1.1, benzene). IR (KBr) 2880, 1565, 1420, 1240, 1025, 765 cm^{-1}. ^1H NMR (500 MHz) (C_6D_6) δ 1.07–1.21 (m, 12H), 1.24–1.67 (m, 6H), 1.74–1.76 (m, 2H), 1.97–2.04 (m, 4H), 2.13–2.19 (m, 2H), 3.26 (s, 6H), 6.48–6.50 (m, 2H), 6.83–6.86 (m, 2H), 7.11–7.16 (m, 2H), 7.46–7.49 (m, 2H). ^{13}C NMR (68 MHz) (C_6D_6) δ 19.1, 25.4, 25.9–26.1 (m), 28.5–28.8 (m), 28.9–29.2 (m), 34.8–34.9 (m), 53.6, 109.3, 119.4, 124.1–124.4 (m), 128.9, 133.8–134.0 (m), 161.6 (t, J(CP) = 3.9 Hz). HRMS calcd for $C_{28}H_{41}O_2P_2$ (M + H): 471.2582; found: 471.2582.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-aid for Scientific Research on a Priority Area of Organic Unusual Valency No. 02247104 from the Ministry of Education, Science and Culture, Japan. We are grateful to Prof. K. Ogata, Mrs. H. Seki, Mr. T. Kuramochi, Mrs. R. Hara, Miss S. Osanai, and Mrs. S. Imamoto (Chemical Analysis Center, Chiba University) for the measurements of ^1H NMR (500 MHz), ^{13}C NMR, mass spectra, and elemental analyses. We thank Prof. K. Suzuki, Keio University, for sending us a detailed experimental procedure for the generation of benzyne from *o*-bromophenyl triflate.

REFERENCES

[1] T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, *J. Am. Chem. Soc., 112*, 1990, 5244.
[2] T. Oshiki, T. Imamoto, *J. Am. Chem. Soc., 114*, 1992, 3975.
[3] T. Imamoto, T. Oshiki, T. Onozawa, M. Matsuo, T. Hikosaka, M. Yanagawa, *Heteroatom Chem., 3*, 1992, 563.
[4] W. S. Knowles, M. J. Sabacky, B. D. Vineyard, *J. Chem. Soc., Chem. Commun.*, 1972, 10.
[5] B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, D. J. Weikauff, *J. Am. Chem. Soc., 99*, 1977, 5946.
[6] C. R. Johnson, T. Imamoto, *J. Org. Chem., 52*, 1987, 2170.
[7] T. Oshiki, T. Hikosaka, T. Imamoto, *Tetrahedron Lett., 32*, 1991, 3371.
[8] Y. Koide, A. Sakamoto, T. Imamoto, *Tetrahedron Lett., 32*, 1991, 3375.
[9] (a) R. A. Lewis, O. Korpiun, K. Mislow, *J. Am. Chem. Soc., 89*, 1967, 4786; (b) R. A. Lewis, O. Korpiun, K. Mislow, *J. Am. Chem. Soc., 90*, 1968, 4847; (c) G. Zon, K. Mislow, *Fortsch. Chem. Forsch., 19*, 1971, 61.
[10] W. S. Knowles, M. J. Sabacky, B. D. Vineyard, *Adv. Chem. Ser., 132*, 1974, 274.
[11] T. Oshiki, T. Imamoto, *Bull. Chem. Soc. Jpn., 63*, 1990, 3719.
[12] T. Matsumoto, T. Hosoya, M. Katsuki, K. Suzuki, *Tetrahedron Lett., 32*, 1991, 6735.
[13] T. Weil, B. Prijs, H. Erlenmeyer, *Helv. Chim. Acta., 36*, 1953, 1314.
[14] M. Fild, O. Stelzer, R. Schmutzler, *Inorg. Synth., 14*, 1972, 5.
[15] D. R. Coulson, *Inorg. Synth., 13*, 1972, 121.
[16] W. S. Knowles, M. J. Sabacky, B. D. Vineyard, *Adv. Chem. Ser., 132*, 1974, 274.