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Oxazaborolidine-Mediated Asymmetric Reduction of 1,2-Diaryl-2-benzyloxyiminoethanones and 1,2-Diarylethanediones

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Abstract: Highly enantioselective reduction of 1,2-diaryl-2-benzyloxyiminoethanones and 1,2-diarylethanediones was conducted using oxazaborolidine derived from L-threonine and borane complexes to give β-imino alcohols and 1,2-diaryl-1,2-ethanediols in high enantiomeric purity. Subsequent reduction of the imino functionality of the former products afforded either *syn*- or *anti*-2-amino-1,2-diarylethanols in high enantiomeric purity by choosing appropriate reduction methods. © 1998 Elsevier Science Ltd. All rights reserved.

Introduction

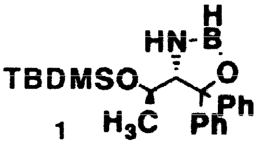
Widespread use of homochiral 2-amino-1,2-diarylethanols and 1,2-diaryl-1,2-ethanediols coupled with difficulties associated with their preparations prompted us to investigate new methodologies for their syntheses.[1] For the preparation of this highly useful class of compounds, the resolution of racemic amino alcohols with mandelic acid[2] or preferential crystallization[3] has been most often used for chiral 2-amino-1,2-diarylethanols. Transformation of chiral 1,2-diol,[4] enzyme-catalyzed cyanohydrin formation / arylation,[5] and asymmetric aminohydroxylation[6] are also used for their asymmetric synthesis. On the other hand, asymmetric dihydroxylation of *trans*-stylbene derivatives constitutes a rapid access to 1,2-diaryl-1,2-ethanediols.[7] A recent example using reduction of benzil with oxazaborolidine also offers another approach.[8,15]

Our previous investigation has revealed that the oxazaborolidine-mediated reduction of 1,2-diimine provides a short efficient route to homochiral (*R*,*R*)-1,2-diphenylethylenediamine in good overall yield.[9] Oxazaborolidine derived from L-threonine and borane has provided a convenient tool for the reduction of ketones and imines, and therefore, application to the multi-functionalized molecules has intrigued us, which leads to a rapid access to a useful class of compounds. This paper describes an efficient approach to both *syn*- and *anti*-2-amino-1,2-diarylethanols **3** and 1,2-diarylethyleneglycols in high enantiomeric excess.[10]

Results and Discussion

I. Reduction of 1,2-diaryl-2-benzyloxyiminoethanones

The starting α-imino ketones were prepared by simple imination of the corresponding diketones in good to excellent yields. The bis-reduction was conducted according to the published procedure[9] for the reduction of 1,2-diimines, and the results are shown in Table 1.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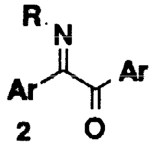
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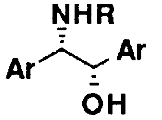
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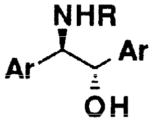
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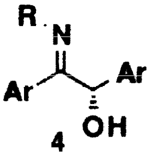
4

a: R = *p*-MeOC$_6$H$_4$, Ar = Ph
b: R = *p*-Ts, Ar = Ph
c: R = BnO, Ar = Ph
d: R = BnO, Ar = *p*-MeOC$_6$H$_4$
e: R = BnO, Ar = *p*-MeC$_6$H$_4$
f : R = BnO, Ar = *p*-BrC$_6$H$_4$
g: R = BnO, Ar = 2-Furyl

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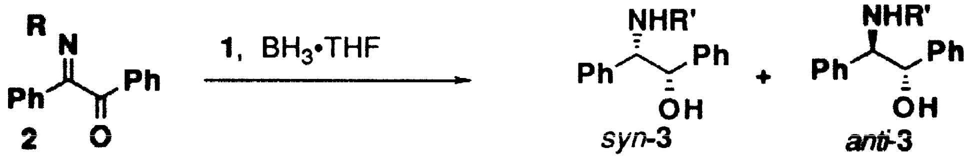


Table 1. Bis-reduction of Imino Ketone 2.[a]

Entry	R	R'	Ligand (mol%)	BH_3•THF (eq)	Solvent	%yield[b]	*syn* : *anti*[c]	% ee (*syn* / *anti*)[d]
1	An	An	20	3	THF	88	38 : 62	4 / 14
2	Ts	Ts	20	3	THF	56	22 : 78	38 / 8[e]
3	MeO	H	20	6	THF	66	72 : 28	38 / 32
4	BnO	H	20	3	THF	66	55 : 45	56 / 52
5	An	An	100	6	THF	34	48 : 52	0 / 4
6	An	An	100	5	DME	96	23 : 77	6 / 14
7	BnO	H	100	5	THF	46	77 : 23	80 / 74
8	BnO	H	100	5	DME	24	63 : 37	80 / 88

[a] The reaction was carried out according to the typical experimental procedure. [b] Isolated yield. [c] Determined by ^1H NMR (270MHz) analysis. [d] Determined by HPLC analysis of the corresponding MTPA ester. [e] Determined by HPLC analysis using a chiral stationary column (Daicel OJ).

As shown in Table 1, in contrast to the previous result on the stereoselective reduction of 1,2-bis(*p*-anisylimino)-1,2-diphenylethane,[9] initial examination into bis-reduction of *p*-anisylimino ketone **2a** in the presence of 20 mol% of the catalyst **1** with a stoichiometric amount of BH_3•THF in THF met with low enantio- and diasteoselectivity, and a mixture of *syn*-(1*S*,2*S*)-**3a** and *anti*-(1*S*,2*R*)-**3a** was obtained in 88% yield with a ratio of *syn* : *anti* = 38 : 62, where the enantiomeric purity of the product was less than 14% ee (entry 1). This may be due to the high coordination ability of the anisylimino functionality to borane to be reduced without influence of the oxazaborolidine catalyst. The produced imino alcohol **4a** or amino alcohols **3a** would act as precursors of oxazaborolidine to participate in the present reduction cycle as a ligand, which could also cause the low enantioselectivity. Although a more reactive derivative, *p*-tosylimino analogue **2b** was subjected to the same reduction conditions, only a slight increase in the enantiofacial selectivity was observed, *i.e.*, 38% ee for the *syn*-isomer **3b** (entry 2). Switching the substrate to oxime ether **2c** improved the enantioselectivity up to 56% ee (entry 4). Use of a stoichiometric amount of the oxazaborolidine increased the enantiomeric purity up to 88% ee (entry 8). The effects of certain additives were also examined using a stoichiometric amount of the ligand, and Table 2 summarizes the results.

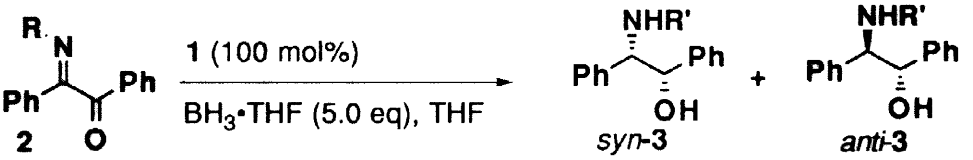


Table 2. Reduction of Imino Ketone 2 in the Presence of Additives.[a]

Entry	R	R'	Additive (1 eq)	%yield[b]	*syn* : *anti*[c]	% ee (*syn* / *anti*)[d]
1	BnO	H	BF_3•Et_2O	57	60 : 40	92 / 76
2	BnO	H	$Al(^iOPr)_3$	50	61 : 39	84 / 86
3	BnO	H	$MeAl(OPh)_2$	54	47 : 53	90 / 94
4	BnO	H	$ZnCl_2$	58	57 : 43	92 / 82
5	An	An	$MeAl(OPh)_2$	38	25 : 75	2 / 54
6	An	An	$ZnCl_2$	59	30 : 70	8 / 40

[a] The reaction was carried out according to the typical experimental procedure. [b] Isolated yield. [c] Determined by ^1H NMR (270MHz) analysis. [d] Determined by HPLC analysis of the corresponding MTPA ester.

In the presence of a Lewis acid, the enantiofacial selectivity was improved up to 94% ee (entry 3). However, the diastereoselectivity was not improved despite the addition of a variety of Lewis acids. These results indicated that, although the initial mono-reduction proceeded in a highly enantioselective fashion, the second step involved a non-stereoselective pathway without the influence of the oxazaborolidine **1**-BH_3•THF system. Among the reducing agents in the present reaction medium, BH_3•THF itself might effect the second reduction in a non-stereoselective fashion. In fact, the reduction of β-imino alcohol (*S*)-**4c** prepared as described below with BH_3•THF in THF gave a mixture of *syn*-**3** (Ar = Ph, R = H) and *anti*-**3** (Ar = Ph, R = H) with a 69 : 31 ratio in 54% yield. Therefore, sequential reduction was next investigated. Reduction using BH_3•THF as the stoichiometric reducing agent previously reported[9] gave only bis-reduction product **3** regardless of the amount of borane and the reaction time. However, the reduction of ketone was much faster than that of imine in the presence of a modifier such as *tert*-amine, and the β-imino alcohol **4** was obtained as the sole product. The results of mono-reduction are summarized in Table 3.

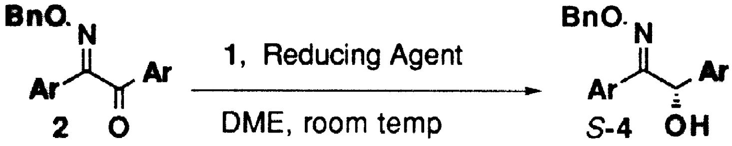


Table 3. Reduction of Imino Ketone 2.[a]

Entry	2	1 (mol%)	Reduction Agent (eq)	Time (h)	%yield of 4[b]	% ee[c]
1	**2c**	100	BH_3•THF (3.0)/DBU (1.0)	11	40	90
2	**2c**	100	Catecholborane (5.0)	22	66	90
3	**2c**	100	BH_3•SMe_2 (1.5)	24	78	98
4	**2c**	20	BH_3•SMe_2 (5.8)	40	25	56
5	**2c**	50	BH_3•SMe_2 (2.5)	75	43	90
6	**2d**	100	BH_3•SMe_2 (1.5)	3	80	98
7	**2e**	100	BH_3•SMe_2 (1.5)	25	83	98
8	**2f**	100	BH_3•SMe_2 (1.5)	14	71	98[d]
9	**2g**	100	BH_3•SMe_2 (1.5)	15	78	96

[a] The reaction was carried out according to the typical experimental procedure. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary column (Daicel OJ). [d] Determined by ^1H NMR (500MHz) analysis of the corresponding MTPA ester.

As shown in Table 3, the reduction in the presence of 1 eq of DBU gave the β-imino alcohol **4c** with 90% ee (entry 1), whereas the yield was improved using catecholborane as a stoichiometric reductant (entry 2). The best result was obtained when the reduction was conducted with 1.5 eq of BH_3•SMe_2 (78% yield, 98% ee). However, this reduction was sensitive to the amount of oxazaborolidine **1**, and the reaction in the presence of a catalytic amount of **1** gave β-imino alcohol **4c** in moderate yields (entries 4 & 5). Under the best conditions found for the reduction of **2c**, other benzil derivatives gave 71-83% yields of the mono-reduction products with 96-98% ee (entries 6~9). In all the cases examined in the present study, over-reduction producing amino alcohol **3** was not observed. The high enantioselectivity observed in the present reduction may be explained in terms of the six-membered cyclic transition state which is similar to the one proposed by Corey et al (Fig. 1).[11]

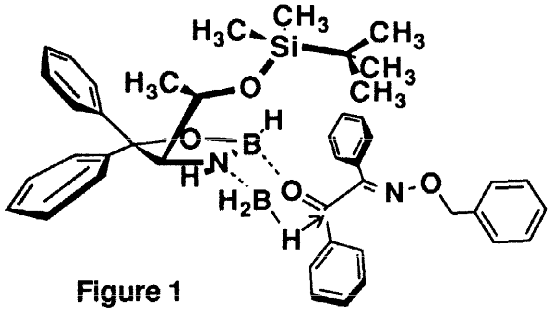
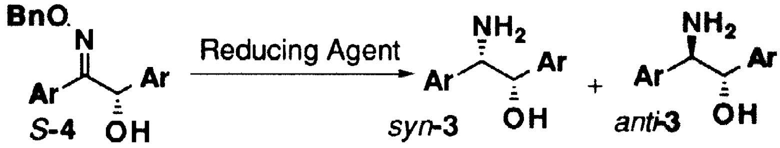


Figure 1

We next investigated the diastereoselective reduction of β-benzyloxyimino alcohols **4** into either *syn*- or *anti*-amino alcohol **3** under a variety of chelation or non-chelation conditions. In principle, the reduction which is explained in terms of a non-chelation or Felkin-Anh model produces *syn*-product *syn*-**3**, whereas a certain chelation between the hydroxy oxygen and the imino nitrogen effects the formation of *anti*-product *anti*-**3** (Fig. 2). Under the hydrogenation conditions the reduction of β-imino alcohol was reported to give *anti*-amino alcohol.[2,12] Using 10% Pd-C / H_2, β-imino alcohol **4** was transformed into *anti*-amino alcohol **3** in good yield with good diastereomeric excess, whereas reduction with $LiAlH_4$ or $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ afforded the *syn*-isomer as a major product. Representative examples are listed in Table 4.

Figure 2



S-**4** *syn*-**3** *anti*-**3**

Table 4. Diastereoselective Reduction of β-Imino Alcohol 4.[a]

Entry	4	Reduction Agent	Solv.	Temp. (°C)	%yield[b]	*syn* : *anti* [c]	% ee[d]
1	**4c**	$Na[AlH_2(OCH_2CH_2OCH_3)_2]$	THF	-30~refl	59	98 : 2	98
2	**4c**	10% Pd-C / H_2	EtOH	rt	96	5 : 95	94
3	**4d**	$Na[AlH_2(OCH_2CH_2OCH_3)_2]$	THF	-30~refl	58[e]	>99 : <1	>99
4	**4d**	10% Pd-C / H_2	EtOH	rt	57	<1 : >99	98
5	**4e**	$LiAlH_4$	DME	0~refl	56[e]	88 : 12	82
6	**4e**	10% Pd-C / H_2	EtOH	rt	52	6 : 94	98
7	**4f**	$LiAlH_4$	DME	0~refl	49[e]	90 : 10	88
8	**4f**	10% Pd-C / H_2	EtOH	rt	56	<1 : >99	96

[a] The reaction was carried out according to the typical experimental procedure. [b] Isolated yield. [c] Determined by ^1H NMR (270 MHz) analysis. [d] The enantiomeric purity of the major isomer. Determined by HPLC analysis (Merk Hibar column) of the corresponding mono- or bis-MTPA derivative. [e] The product was isolated as acetamide after treatment with Ac_2O.

In all the cases examined, the diastereoselectiviy was good to excellent, giving either the *syn*- or *anti*-isomer with high diastereomeric excess, and the stereochemical integrity of the starting material was remained almost unaffected. The cases where $LiAlH_4$ was used as a reducing reagent were mainly due to the reaction rate; the use of $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ sometimes did not reach completion of the reduction, where the N-O bond remained intact. However, the use of $LiAlH_4$ caused racemization (entries 5 & 7) to some extent maybe due to the more forced reduction conditions. For isolation of the reduction product, in particular, from the $LiAlH_4$ or $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ mediated reduction of the substituted aryl derivatives, acetylation of the resulting amino moiety was found to be useful in terms of purity of the product.

II. Reduction of 1,2-diarylethanedione

The present oxazaborolidine-mediated reduction has offered an excellent environment for the discrimination of the enantioface of ketones, and therefore poly-ketones appear to be attractive substrates. As mentioned earlier, 1,2-diaryl-1,2-ethanediols **6** constitute an important class of chiral synthons.[14] The application of the present reduction to 1,2-diarylethanedione **5** is expected to lead to a facile approach to this useful class of compounds. Table 5 summarizes the results of bis-reduction of 1,2-diarylethanediones.

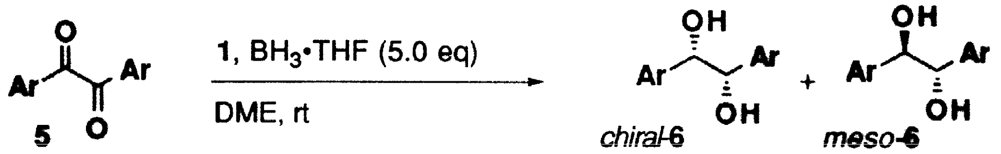


Table 5. **Reduction of Diketone 5 in the Presence of Additives.**[a]

Entry	Ar	1 (mol%)	Additive (eq)	%yield[b]	*chiral* : *meso*[c]	% ee[c]
1	Ph	20	none	99	50 : 50	>99
2	Ph	20	Al(^{i}OPr)$_3$ (1 eq)	78	51 : 49	98
3	Ph	20	TMSCl (2 eq)	57	50 : 50	95
4	3,5-Me$_2$C$_6$H$_3$	100	none	58	49 : 51	>99
5	3,5-Me$_2$C$_6$H$_3$	100	Al(^{i}OPr)$_3$ (1 eq)	59	53 : 47	98
6	2-MeOC$_6$H$_4$	100	none	70	22 : 78[d]	95[d]
7	2-MeOC$_6$H$_4$	100	Al(^{i}OPr)$_3$ (1 eq)	49	24 : 76[d]	90[d]

[a] The reaction was carried out according to the typical experimental procedure. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary column (Daicel OJ). [d] Determined by HPLC analysis (Mcrk Hibar column) of the corresponding bis-MTPA derivative.

Examination into Table 5 revealed that although the reduction proceeded well to give the diols in good yield with excellent enantiofacial selectivity, the diastereoselctivity was not sufficient. In order to improve the diastereoselecivity addition of certain additives was examined. As you can see, the selectivity was not improved despite the addition of additives. This may be due to the ability of the borane to coordinate to both carbonyls or the resulting alkoxyborane species to coordinate to the α-carbonyl function, resulting in the *syn*-type reduction. The reduction using a limited amount of BH$_3$•THF or other reducing reagents such as BH$_3$•Me$_2$S utilized successfully in the case of α-imino ketones did not stop the reaction at the mono-reduction stage, and the bis-reduction products were always obtained together with the starting materials. Recently Prasad and Joshi reported that the diastereoselectivity was improved by carrying out the reduction in THF-toluene at 45 °C, in which the selectivities were in the range of 76 to 84% de.[15]

Summary

Increasing needs for 1,2-amino alcohols in enantiomerically pure form have prompted the exploration into new efficient methodologies. In addition to the one-step procedure for 1,2-diphenylehtylenediamine disclosed recently, the present two-step procedure for (1*S*,2*S*)- or (1*S*,2*R*)-2-amino-1,2-diarylethanol realizes the power of oxazaborolidine-mediated reduction of poly-functionalized molecules, giving a rapid access to a highly useful class of compounds in a diastereo- and enantioselective manner. Since a variety of benzil derivatives are readily available and transformation into mono-imino compounds is straightforward in good overall yields, the present procedure may be applied to the preparation of a variety of 1,2-amino alcohols. Moreover, the benzyl ether protecting group at the nitrogen atom was removed during the second reduction step, eliminating an otherwise tedious deprotection sequence.

Experimental

General. Infrared spectra were determined on a Jasco IR-810 spectrometer . ^{1}H NMR spectra were taken on a JEOL Alpha-500, JNM-EX270 or JNM-PMX60SI spectrometer using tetramethylsilane as an internal standard. High-performance liquid chromatography (HPLC) was carried out on a Hitachi L-4000 detector and a Hitachi L-6000 pump using a Finepak SIL column (Merck) or a chiral stationary column (Daicel OJ). Optical rotations were measured with a Union PM-101 polarimeter. Exact mass spectra were taken on a JEOL JMS-DX303-HF spectrometer. Tetrahydrofuran (THF) was freshly distilled from sodium diphenylketyl immediately before use. 1,2-Dimethoxyethane (DME) was distilled from LiAlH$_4$ and stored over sodium. Ethanol was distilled from sodium ethoxide and stored over molecular sieves 4A. TLC plates were prepared with Merck silica gel 60 PF$_{254}$. Flash column chromatography was carried out with Merck silica gel 60.

The ligand was prepared in five steps starting from L-threonine: methyl (2*S*,3*R*)-2-(benzyloxycarbonylamino)-3-hydroxybutyrate: To a solution of L-threonine (1.8 g, 15 mmol) in 1,4-dioxane (30 mL) and water (15 mL) was added an aqueous solution of NaOH (1N, 15 mL, 15 mmol) followed by benzyl chlororformate (2.4 mL, 17 mmol) at 0 °C, and the mixture was allowed to stand at room temperature for 5 h. After concentration of the crude reaction mixture in vacuo, it was acidified with aqueous potassium hydrogen sulfate, and the entire mixture was extracted with ethyl acetate (30 mL x 3). The combined extracts were dried and concentrated to leave white crystals, which were dissolved in THF (50 mL). Esterification with diazomethane followed by purification by silica gel column chromatography (*n*-hexane / ethyl acetate = 3 / 1 as eluent) gave the title compound (2.5 g, 61%). $[\alpha]^{23}{}_{D}$ = -16.0 (*c* 0.36, $CHCl_3$). ^1H NMR (270 MHz, $CDCl_3$): δ 1.24 (d, *J* = 6.60 Hz, 3H), 2.13 (brs, 1H), 3.76 (s, 3H), 4.15-4.37 (m, 2H), 5.13 (s, 2H), 5.59 (brs, 1H), 7.35 (s, 5H). IR (neat): 3410, 1720, 1340, 1310, 990, 540 cm^{-1}. Anal. Calcd for $C_{13}H_{17}O_5N$: C, 58.42; H, 6.41; N, 5.24. Found: C, 58.14; H, 6.41; N, 5.11.

Methyl (2*S*,3*R*)-2-(benzyloxycarbonylamino)-3-(*t*-butyldimethylsiloxy)-butyrate: To a solution of methyl (2*S*,3*R*)-2-(benzyloxycarbonylamino)-3-hydroxybutyrate (1.0 g, 3.8 mmol) in DMF (10 mL) was added imidazole (546 mg, 8.0 mmol) and *t*-butyldimethylchlorosilane (1.4 g, 9.6 mmol) at 0 °C, and the mixture was stirred at room temperature for 21 h. Sat. aqueous brine (20 mL) was added, and the entire mixture was extracted with ethyl acetate (10 mL x 3). After drying and concentration of the combined extracts the resulting crude oil was purified by silica gel column chromatography (*n*-hexane / ethyl acetate = 6 / 1 as eluent) to give the title compound (1.4 g, 98%). $[\alpha]^{23}{}_{D}$ = -14.0 (*c* 0.76, $CHCl_3$). ^1H NMR (270 MHz, $CDCl_3$): δ -0.05 (s, 3H), 0.00 (s, 3H), 0.80 (s, 9H), 1.17 (d, *J* = 6.27 Hz, 3H), 3.69 (s, 3H), 4.18-4.25 (m, 1H), 4.36-4.45 (m, 1H), 5.11 (s, 2H), 5.45 (brs, 1H), 7.35 (s, 5H). IR ($CHCl_3$): 3420, 2840, 1725, 1340, 1310, 960, 540, 470 cm^{-1}. Anal. Calcd for $C_{19}H_{31}O_5NSi$: C, 59.81; H, 8.19; N, 3.67. Found: C, 59.58; H, 8.23; N, 3.37.

(2*S*,3*R*)-2-(Benzyloxycarbonylamino)-3-(*t*-butyldimethylsiloxy)-1,1-diphenylbutanol: Under an argon atmosphere to a solution of methyl (2*S*,3*R*)-2-(benzyloxycarbonylamino)-3-(*t*-butyldimethylsiloxy)butyrate (1.3 g, 3.4 mmol) in THF (10 mL) was added phenylmagnesium bromide (0.44 N in THF, 27 mL, 12.0 mmol) at 0 °C, and the mixture was stirred at room temperature for 4 h. Sat aqueous NH_4Cl was added and the entire mixture was extracted with ethyl acetate (10 mL x 3), and the combined extracts were washed with saturated brine and dried (Na_2SO_4). Concentration of the extracts gave a crude oil, which was purified by silica gel column chromatography (*n*-hexane / ethyl acetate = 9 / 1 as eluent) to give the title compound (1.6 g, 93%). $[\alpha]^{23}{}_{D}$ = -40.0 (*c* 0.24, $CHCl_3$). ^1H NMR (270 MHz, $CDCl_3$): δ -0.01 (s, 3H), 0.01 (s, 3H), 0.89 (s, 9H), 1.23 (d, *J* = 6.27 Hz, 3H), 4.20-4.28 (m, 1H), 4.64 (unresolved d, *J* = 9.89 Hz, 1H), 4.95 (d, *J* = 12.54 Hz, 1H), 5.09 (d, *J* = 12.54 Hz, 1H), 5.57 (unresolved d, *J* = 9.89 Hz, 1H), 7.06-7.62 (m, 15H). IR ($CHCl_3$): 3425, 2880, 1710, 1370, 1330, 990, 550 cm^{-1}. Anal. Calcd for $C_{30}H_{39}O_4NSi$: C, 71.25; H, 7.77; N, 2.77. Found: C, 71.48; H, 7.82; N, 2.83.

(2*S*,3*R*)-2-Amino-3-(*t*-butyldimethylsiloxy)-1,1-diphenylbutanol: Under an atmospheric pressure of hydrogen a suspension of 5 % Pd/C (1.2 g) in MeOH (4 mL) was added a solution of (2*S*,3*R*)-2-(benzyloxycarbonylamino)-3-(*t*-butyldimethylsiloxy)-1,1-diphenylbutanol (1.5 g, 3.0 mmol) in MeOH (6 mL) at room temperature, and the mixture was stirred at room temperature for 6 h. The mixture was filtered through a pad of celite with the aid of a small amount of ethyl acetate, and the filtrate was concentrated in vacuo to give a crude oil, which was purified by silica gel column chromatography (*n*-hexane / ethyl acetate = 4 / 1 as eluent) to give the title compound as a viscous oil (1.0 g, 91%). $[\alpha]^{23}{}_{D}$ = -37.0 (*c* 1.06, $CHCl_3$). ^1H NMR (270 MHz, $CDCl_3$): δ 0.00 (s, 3H), 0.10 (s, 3H), 0.99 (s, 9H), 1.34 (d, *J* = 6.60 Hz, 3H), 1.63 (brs, 1H), 3.63 (d, *J* = 1.65 Hz, 1H), 4.19 (dd, *J* = 1.65 and 6.60 Hz, 1H), 4.99 (brs, 1H), 7.20-7.42 (m, 6H), 7.65-7.72 (m, 4H). IR ($CHCl_3$): 3410, 2860, 1600, 1360, 950, 900, 550 cm^{-1}. Anal. Calcd for $C_{22}H_{33}O_2NSi$: C, 71.11; H, 8.88; N, 3.77. Found: C, 70.96; H, 8.95; N, 3.55.

2-Benzyloxyimino-1,2-diphenylethane-1-one (2c). General procedure for the preparation of 2: A mixture of benzil (5.0 g, 24 mmol), *O*-benzylhydroxylamine hydrochloride (2.1 g, 26 mmol), and sodium acetate (2.2 g, 11 mmol) in ethanol (31 mL) was heated at reflux for 12 h. After normal work-up recrystallization from absolute ethanol gave **2c** (3.4 g, 90%) as white powder. Mp 109-110 °C. ^1H NMR (270 MHz, $CDCl_3$): δ 5.16 (s, 2H), 7.17-7.61 (m, 13H), 7.85-7.88 (m, 2H). IR ($CHCl_3$): 3050, 2930, 1680, 1595, 1450, 1320, 1010, 910, 690 cm^{-1}. Anal. Calcd for $C_{21}H_{17}O_2N$: C, 79.98; H, 5.43; N, 4.44. Found: C, 80.21; H, 5.40; N, 4.72.

2-Benzyloxyimino-1,2-bis(*p*-methoxyphenyl)ethane-1-one (2d): Mp 90-91 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.87 (s, 3H), 3.94 (s, 3H), 5.26 (s, 2H), 6.95 (d, *J* = 8.91 Hz, 2H), 7.00 (d, *J* = 8.91 Hz, 2H), 7.32-7.43 (m, 5H), 7.63 (d, *J* = 8.91 Hz, 2H), 7.96 (d, *J* = 8.91 Hz, 2H). IR ($CHCl_3$): 2930, 2840, 1680, 1600, 1310, 1165, 1015, 835 cm^{-1}. Anal. Calcd for $C_{23}H_{21}O_4N$: C, 73.58; H, 5.64; N, 3.73. Found: C, 73.23; H, 5.91; N, 3.51.

2-Benzyloxyimino-1,2-bis(*p*-methylphenyl)ethane-1-one (2e): Mp 72-73 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.22 (s, 3H), 2.30 (s, 3H), 5.05 (s, 2H), 7.02 (d, *J* = 8.25, 2H), 7.10-7.18 (m, 7H), 7.35 (d, *J* = 8.25 Hz, 2H), 7.68 (d, *J* = 8.24 Hz, 2H). IR ($CHCl_3$): 3040, 2910, 2850, 1670, 1600, 1450, 1325, 1175, 1010, 915 cm^{-1}. Anal. Calcd for $C_{23}H_{21}O_2N$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.50; H, 6.06; N, 4.11.

2-Benzyloxyimino-1,2-bis(*p*-bromophenyl)ethane-1-one (2f): Mp 121-122 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.14 (s, 2H), 7.17-7.84 (m, 13H). IR ($CHCl_3$): 3050, 2940, 1680, 1590, 1400, 1175, 1070, 1010, 920, 840 cm^{-1}. Anal. Calcd for $C_{21}H_{15}O_2NBr_2$: C, 53.31; H, 3.20; N, 2.96. Found: C, 53.02; H, 3.50; N, 3.02.

2-Benzyloxyimino-1,2-bis(2-furyl)ethane-1-one (2g): Mp 84-85 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.19 (s, 2H), 6.42 (dd, *J* = 1.83 and 3.70 Hz, 1H), 6.52 (dd, *J* = 1.83 and 3.66 Hz, 1H), 6.53 (d, *J* = 3.70 Hz, 1H), 7.11 (d, *J* = 3.66 Hz, 1H), 7.22-7.30 (m, 5H), 7.49 (d, *J* = 1.83 Hz, 1H), 7.62 (d, 1.83 Hz, 1H). IR ($CHCl_3$): 3000, 2930, 1665, 1565, 1460, 1010, 950, 890 cm^{-1}. Anal. Calcd for $C_{17}H_{13}O_4N$: C, 69.15; H, 4.44; N, 4.74. Found: C, 68.99; H, 4.30; N, 4.48.

(1*S*)-2-Benzyloxyimino-1,2-diphenylethane-1-ol (4c). General procedure for the reduction of 2-benzyloxyimino-1,2-diarylethane-1-one: To a solution of (2*S*,3*R*)-2-amino-3-(*t*-butyldimethylsiloxy)-1,1-diphenylbutanol (371.7 mg, 1.0 mmol) in 15.0 mL of DME was added $BH_3 \cdot SMe_2$ complex (0.24 mL, 2.5 mmol), and the mixture was stirred for 20 min at room temperature. A solution of 2-benzyloxyimino-1,2-diphenylethanone **2c** (315.4 mg, 1.0 mmol) in DME (2.5 mL) was added dropwise during 30 min. After stirring for 24 h at rt, the reaction mixture was quenched by adding MeOH (2 mL) and concentrated to leave a crude oil, which was purified on preparative TLC (eluent: *n*-Hex / AcOEt = 5 / 1) to give β-imino alcohol **4c** as a colorless oil (246.2 mg, 78 %). $[\alpha]^{23}_D$ = -35.3 (*c* 1.11, $CHCl_3$). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.65 (d, *J* = 9.40, 1H), 5.19 (d, *J* = 12.2, 1H), 5.24 (d, *J* = 12.2 Hz, 1H), 6.15 (d, *J* = 9.40 Hz, 1H), 7.23-7.41 (m, 13H), 7.52-7.56 (m, 2H). IR (neat): 3430, 3050, 2930, 1490, 1440, 1020, 700 cm^{-1}. The enantiomeric purity was determined to be 98% ee by HPLC analysis using a chiral stationary column (Daicel OJ). The absolute configuration was assigned to be *S* by transforming into amino alcohol **3c** (R = H) and comparison with the reported data.[2]

(1*S*)-2-Benzyloxyimino-1,2-bis(*p*-methoxyphenyl)ethane-1-ol (4d): $[\alpha]^{23}_D$ = -2.24 (*c* 3.03, $CHCl_3$). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.71 (s, 3H), 3.73 (s, 3H), 3.85 (d, *J* = 6.93 Hz, 1H), 5.16 (s, 2H), 6.11 (d, *J* = 6.93 Hz, 1H), 6.78-6.82 (m, 4H), 7.23-7.30 (m, 7H), 7.47 (d, *J* = 8.58 Hz, 2H). IR ($CHCl_3$): 3510, 3000, 2925, 2820, 1605, 1505, 1250, 1170, 1030 cm^{-1}. The absolute stereochemistry was determined to be *S* by comparison with an authentic sample prepared by transforming the known (1*S*,2*S*)-diol[15] into the corresponding *anti*-(1*S*,2*R*)-**3d** (R = H) *via* carbonate formation, azidation, reduction,[4b] and formation of bis-MTPA derivative.

(1*S*)-2-Benzyloxyimino-1,2-bis(*p*-methylphenyl)ethane-1-ol (4e): $[\alpha]^{23}_D$ = -80.7 (*c* 1.73, $CHCl_3$). ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.25 (s, 3H), 3.68 (brs, 1H), 5.09 (d, *J* = 12.2 Hz, 1H), 5.14 (d, *J* = 12.2 Hz, 1H), 6.63 (s, 1H), 7.02-7.05 (m, 4H), 7.14-7.28 (m, 7H), 7.36 (d, *J* = 7.92 Hz, 2H). IR ($CHCl_3$): 3510, 3050, 2920, 1615, 1520, 1450, 1360, 1080, 1000, 900, 820 cm^{-1}. The absolute stereochemistry was determined to be *S* by comparison with an authentic sample prepared by transforming the known (1*S*,2*S*)-diol[15] into the corresponding *anti*-(1*S*,2*R*)-3e (R = H) *via* carbonate formation, azidation, and reduction,[4b] and formation of bis-MTPA derivative.

(1*S*)-2-Benzyloxyimino-1,2-bis(*p*-bromophenyl)ethane-1-ol (4f): $[\alpha]^{23}_{D}$ = -53.9 (*c* 1.27, $CHCl_3$). ^1H NMR (270 MHz, $CDCl_3$): δ 3.51 (d, *J* = 8.25 Hz, 1H), 5.16 (d, *J* = 11.9 Hz, 1H), 5.21 (d, *J* = 11.9 Hz, 1H), 6.13 (d, *J* = 8.25, 1H), 7.18-7.45 (m, 13H). IR ($CHCl_3$): 3500, 3050, 2930, 1590, 1490, 1360, 1075, 1010, 910, 830 cm^{-1}. The absolute stereochemistry was determined to be *S* by transforming into *syn*-3c (R = H) *via* reduction into *anti*-(1*S*,2*R*)-2-amino-1,2-bis(*p*-bromophenyl)ethane-1-ol (*vide infra*) followed by debromination with *n*-BuLi, and analyzed by its specific rotation.

(1*S*)-2-Benzyloxyimino-1,2-bis(2-furyl)ethane-1-ol (4g): $[\alpha]^{23}_{D}$ = +55.7 (*c* 6.34, $CHCl_3$). ^1H NMR (270 MHz, $CDCl_3$): δ 3.96 (brs, 1H), 5.24 (s, 2H), 6.04 (s, 1H), 6.25 (dd, *J* = 0.66 and 3.30 Hz, 1H), 6.30 (dd, *J* = 1.98 and 3.30 Hz, 1H), 6.45 (dd, *J* = 1.71 and 3.30 Hz, 1H), 6.79 (dd, *J* = 0.66 and 1.98 Hz, 1H), 7.31 (s, 5H), 7.35 (dd, *J* = 1.71 and 3.30 Hz, 1H), 7.46 (dd, *J* = 0.66 and 3.30 Hz, 1H);. IR ($CHCl_3$): 3520, 3050, 2930, 1660, 1560, 1460, 1010, 950, 880 cm^{-1}. The absolute configuration was determined to be *S* by comparison with the authentic sample prepared as follows. The 2-furyl derivative **2g** was mono-reduced with **1** and BH_3•THF to give the known β-keto alcohol,[15] which was benzyloxyiminated to afford **4g** and compared using HPLC.

(1*S*,2*S*)-2-Amino-1,2-diphenylethane-1-ol (*syn*-3c, R = H). **General procedure for the preparation of *syn*-3:** To a solution of $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ (481 mg, 70% in toluene, 1.7 mmol) in THF (5 mL) was added a solution of *S*-**4c** (98% ee, 122.4 mg, 0.39 mmol) in THF (2 mL) at -30 °C for 10 min, and the mixture was allowed to stand at -30 °C for 2 h and then heated at reflux for 3 h. Usual work-up followed by purification on TLC gave **3c** (R = H) (49.0 mg, 59%) as white powder: $[\alpha]^{23}_{D}$ = -106.7 (*c* 0.72, EtOH). ^1H NMR (270 MHz, $CDCl_3$) δ 2.55 (brs, 3H), 3.95 (d, *J* = 6.60 Hz, 1H), 4.61 (d, *J* = 6.60 Hz, 1H), 7.11-7.30 (m, 10H). IR (nujol): 3320, 3050, 1580, 1020, 750, 690 cm^{-1}. The spectral data was identical with that reported.[2,3,13] The diastereomeric ratio was determined by ^1H NMR (500 MHz) to be *syn* : *anti* = 92 : 8, and the enantiomeric purity of *syn*-**3c** (R = H) by HPLC of the corresponding bis-MTPA derivative to be 98% ee.

(1*S*,2*R*)-2-Amino-1,2-diphenylethane-1-ol (*anti*-3c, R = H). **General procedure for the preparation of *anti*-3:** A solution of *S*-**4c** (98% ee, 41.0 mg, 0.13 mmol) in EtOH (3 mL) was stirred under an atmospheric pressure of hydrogen in the presence of 10% Pd-C (13.8 mg) at rt for 25 h. Filtration of the crude mixture through a celite pad followed by concentration gave a crude oil, which was purified by Florisil® column chromatography to give **3c** (R = H) (26.9 mg, 96%) as a colorless oil. $[\alpha]^{23}_{D}$ = -5.6 (*c* 0.54, EtOH). ^1H NMR (270 MHz, $CDCl_3$): δ 1.65 (brs, 3H), 4.13 (d, *J* = 6.30 Hz, 1H), 4.71 (d, *J* = 6.30 Hz, 1H), 7.15-7.27 (m, 10H). IR (nujol): 3320, 3050, 1580, 1020, 750, 690 cm^{-1}. The spectral data was identical with that reported.[2,3,13] The diastereomeric ratio was determined by ^1H NMR (500 MHz) to be *syn* : *anti* = 5 : 95, and the enantiomeric purity of *anti*-**3c** (R = H) by HPLC of the corresponding bis-MTPA derivative to be 94% ee.

(1*S*,2*S*)-2-Acetamido-1,2-bis(*p*-methoxyphenyl)ethane-1-ol (*syn*-3d, R = Ac): $[\alpha]^{23}_{D}$ = +74.0 (*c* 0.65, EtOH). ^1H NMR (270 MHz, $CDCl_3$): δ 1.99 (s, 3H), 3.79 (s, 3H), 3.84 (s, 3H), 3.89 (dd, *J* = 3.96 and 13.9 Hz, 1H), 4.17 (dd, *J* = 9.24 and 13.9 Hz, 1H), 5.95 (dd, *J* = 3.96 and 9.24 Hz, 1H), 6.83-7.03 (m, 6H), 7.24-7.28 (m, 2H). IR ($CHCl_3$): 3410, 3000, 2810, 1731, 1650, 1510, 1300, 1170, 1030, 835 cm^{-1}. HRMS Found: *m/z* 295.1345. Calcd for $C_{18}H_{19}O_3N$: $[M-H_2O]^+$, 297.1365. The diastereomeric ratio was determined by ^1H NMR (270 MHz) to be *syn* : *anti* = >99 : <1, and the enantiomeric purity of *syn*-**3d** (R = Ac) by HPLC of the corresponding MTPA ester to be >99% ee.

(1*S*,2*R*)-2-Amino-1,2-bis(*p*-methoxyphenyl)ethane-1-ol (*anti*-3d: R = H): $[\alpha]^{23}_{D}$ = -1.7 (*c* 0.24, EtOH). ^1H NMR (500 MHz, $CDCl_3$): δ 1.15 (brs, 3H), 3.79 (s, 3H), 3.80 (s, 3H), 4.06 (d, *J* = 6.41 Hz, 1H), 4.63 (d, *J* = 6.41, 1H), 6.82-6.86 (m, 4H), 7.15-7.20 (m, 4H). IR ($CHCl_3$): 3590, 3550, 3360, 3000, 2940, 2830, 1610, 1515, 1250, 1175, 1035, 835 cm^{-1}. HRMS Found: *m/z* 255.1265. Calcd for $C_{16}H_{17}O_2N$: $[M-H_2O]^+$, 255.1260. The diastereomeric ratio was determined by ^1H NMR (500 MHz) to be *syn* : *anti* = <1 : >99, and the enantiomeric purity of *anti*-**3d** (R = H) by HPLC of the corresponding bis-MTPA derivative to be 98% ee.

(1*S*,2*S*)-2-Acetamide-1,2-bis(*p*-methylphenyl)ethane-1-ol (*syn*-3e: R = Ac): $[\alpha]^{23}_{D}$ = -4.0 (c 0.30, EtOH). ^1H NMR (270 MHz, $CDCl_3$): δ 1.96 (s, 3H), 2.72 (s, 6H), 2.76 (d, *J* = 3.96 Hz, 1H), 4.93

(dd, *J* = 3.96 and 4.62 Hz, 1H), 5.18 (dd, *J* = 4.62 and 7.92 Hz, 1H), 6.25 (d, *J* = 7.92 Hz, 1H), 7.08-7.26 (m, 8H). IR (CHCl$_3$): 3550, 3410, 3000, 1670, 1520, 1370, 1260, 1070, 820 cm^{-1}. HRMS Found: *m/z* 265.1473. Calcd for $C_{18}H_{19}ON$: [M-H$_2$O]$^+$, 265.1467. The diastereomeric ratio was determined by ^{1}H NMR (270 MHz) to be *syn* : *anti* = 88 : 12, and the enantiomeric purity of *syn*-3e (R = Ac) by HPLC of the corresponding MTPA ester to be 82% ee.

(1*S*,2*R*)-2-Amino-1,2-bis(*p*-methylphenyl)ethane-1-ol (*anti*-3e: **R = H**): $[\alpha]^{23}_D$ = -7.1 (*c* 0.14, EtOH). ^{1}H NMR (270 MHz, CDCl$_3$): δ 1.54 (s, 3H), 2.33 (s, 3H), 2.34 (s, 3H), 4.08 (d, *J* = 6.71 Hz, 1H), 4.80 (d, *J* = 6.71 Hz, 1H), 7.10-7.19 (m, 8H). IR (CHCl$_3$): 3550, 3360, 2910, 1510, 1380, 1110, 1020, 890, 820 cm^{-1}. HRMS Found: *m/z* 223.1314. Calcd for $C_{16}H_{17}N$: [M-H$_2$O]$^+$, 223.1361. The diastereomeric ratio was determined by ^{1}H NMR (270 MHz) to be *syn* : *anti* = 6 : 94, and the enantiomeric purity of *anti*-3e (R = H) by HPLC of the corresponding bis-MTPA derivative to be 98% ee.

(1*S*,2*S*)-2-Acetamido-1,2-bis(*p*-bromophenyl)ethane-1-ol (*syn*-3f: **R = Ac**): $[\alpha]^{23}_D$ = -9.4 (*c* 0.25, EtOH). ^{1}H NMR (270 MHz, CDCl$_3$): δ 1.946 (s, 3H), 2.92 (d, *J* = 3.96 Hz, 1H), 5.00 (dd, *J* = 3.96 and 4.62 Hz, 1H), 5.22 (dd, *J* = 4.62 and 7.59 Hz, 1H), 6.28 (d, *J* = 7.59 Hz, 1H), 7.25-7.36 (m, 8H). IR (CHCl$_3$): 3550, 3410, 3070, 2990, 1660, 1490, 1370, 1260, 1060 cm^{-1}. HRMS Found: *m/z* 392.9659. Calcd for $C_{16}H_{13}ONBr_2$: [M-H$_2$O]$^+$, 392.9643. The diastereomeric ratio was determined by ^{1}H NMR (270 MHz) to be *syn* : *anti* = 90 : 10, and the enantiomeric purity of *syn*-3f (R = H) by HPLC of the corresponding MTPA ester to be 88% ee.

(1*S*,2*R*)-2-Amino-1,2-bis(*p*-bromophenyl)ethane-1-ol (*anti*-3f: **R = H**): $[\alpha]^{23}_D$ = +15.4 (*c* 0.23, EtOH). ^{1}H NMR (270 MHz, CDCl$_3$): δ 1.86 (brs, 3H), 4.12 (d, *J* = 5.61 Hz, 1H), 4.73 (d, *J* = 5.61 Hz, 1H), 7.00-7.06 (m, 4H), 7.35-7.42 (m, 4H). IR (CHCl$_3$): 3580, 3380, 2980, 2850, 1590, 1490, 1400, 1070, 1010, 830 cm^{-1}. HRMS Found: *m/z* 350.9261. Calcd for $C_{14}H_{11}NBr_2$: [M-H$_2$O]$^+$, 350.9258. The diastereomeric ratio was determined by ^{1}H NMR (270 MHz) to be *syn* : *anti* = <1 : >99, and the enantiomeric purity of *anti*-3f (R = H) by HPLC of the corresponding bis-MTPA derivative to be 96% ee.

(1*S*,2*S*)-1,2-diphenylethane-1,2-diol (6: Ar = Ph). General procedure for the reduction of 1,2-diarylethane-1,2-dione: To a solution of (2*S*,3*R*)-2-amino-3-(*t*-butyldimethylsiloxy)-1,1-diphenylbutanol (22.3 mg, 0.06 mmol) in 0.3 mL of DME were added dropwise BH$_3$•THF complex (1.5 mL, 1.5 mmol) and a solution of benzil (63.1 mg, 0.3 mmol) in DME (2.0 mL) during 3 hr. After stirring for 1 h at rt, the reaction mixture was quenched by adding 2N HCl (2 mL) and extracted with AcOEt (5 mL x 3). The combined extracts were dried and concentrated in vacuo to give a crude oil, which was purified on preparative TLC (eluent: *n*-Hex / AcOEt = 5 / 1) to afford the title compound **6** as a colorless oil (63.9 mg, 99 %) as a mixture of (1*S*,2*S*)- and (1*S*,2*R*)-isomers. $[\alpha]^{23}_D$ = -13.0 (*c* 1.20, EtOH). ^{1}H NMR (270 MHz, CDCl$_3$): δ 2.29 (brs, 2H), 4.66 (s, 1H), 4.79 (s, 1H), 7.07-7.29 (m, 10H). IR (neat): 3350, 2920, 2850, 1450, 1190, 750, 695 cm^{-1}. The spectral data was identical with that reported.[14,15] The ratio of *chiral*- and *meso*-isomers and the enantiomeric purity were determined by HPLC analysis using a chiral stationary column (Daicel OJ) to be 50 : 50 and >99% ee, respectively. The absolute configuration was assigned to be (1*S*,2*S*) by comparison of the optical rotation with the reported data.[15]

(1*S*,2*S*)-1,2-bis(3,5-dimethylphenyl)ethane-1,2-diol (6: Ar = 3,5-Me$_2$C$_6$H$_3$): $[\alpha]^{23}_D$ = -39.0 (*c* 0.94, EtOH). ^{1}H NMR (270 MHz, CDCl$_3$): δ 2.30 (s, 6H), 2.39 (s, 6H), 2,63 (brs, 2H), 4.60 (s, 1H), 4.62 (s, 1H), 6.79-6.97 (m, 6H). IR (neat): 3400, 3000, 2900, 1460, 1400, 850 cm^{-1}. Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.99; H, 8.39. The ratio of *chiral*- and *meso*-isomers and the enantiomeric purity were determined by HPLC analysis using a chiral stationary column (Daicel OJ) to be 49 : 51 and >99% ee, respectively.

(1*S*,2*S*)-1,2-bis(2-methoxylphenyl)ethane-1,2-diol (6: Ar = 2-MeOC$_6$H$_4$): $[\alpha]^{23}_D$ = -0.87 (*c* 0.46, EtOH). ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.69 (s, 2H), 5.23 (s, 2H), 5.24 (s, 2H), 6.70-6.90 (m, 4H), 7.10-7.25 (m, 4H). IR (neat): 3500, 2950, 1450, 1220,1010, 750 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 70.30; H, 6.49. The ratio of *chiral*- and *meso*-isomers and the enantiomeric purity were determined by HPLC analysis (Merck Hibar column) of the corresponding bis-MTPA ester to be 22 : 78 and 95% ee, respectively.

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