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Catalytic enantioselective synthesis of secondary alcohols using C_2-symmetric diamino diol ligands

Biao Jiang,* Yan Feng and Jian-Feng Hang

Laboratory of Organometallic Chemistry, The Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, PR China

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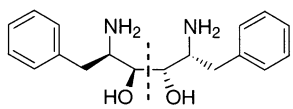
Abstract—A new class of diamino diols was evaluated as catalytic ligands in the enantioselective borane reduction of aromatic ketones and the enantioselective ethylation of arylaldehydes with diethylzinc. By variation of the substitution pattern on the ketone, e.e.s of up to 94% could be obtained by in situ borane reduction using 0.025 equiv. of the ligand at 35°C in THF. *N*,*N*,*N*′,*N*′-Tetramethyldiamino diol and *N*,*N*′-dialkyl diamino diol were used as promoters for the enantioselective addition of diethylzinc reagent to the arylaldehyde, where use of 0.1 equiv. of *N*,*N*,*N*′,*N*′-tetramethyl diamino diol as catalyst in the addition of diethylzinc to arylaldehyde achieved e.e.s of up to 98%.

1. Introduction

Enantioselective reactions on the carbonyl group, such as borane reduction and nucleophilic addition using modified catalysts with chelated metals, have received considerable attention.[1,2] Two-centered Lewis acid catalysts, as bidentate bisorganometals, are new in this area. Although other Lewis acids have been widely investigated in stereo- and regio-selective organic synthesis,[3] bisamino alcohols and bisoxazaborolidines are seldom used. A large number of chiral secondary and tertiary β-amino alcohols have been screened in the enantioselective catalytic borane reduction of aromatic ketones and the enantioselective addition of dialkylzinc reagents to aldehydes. However, apart from reactions in which sterically hindered β-amino alcohols were used, enantioselectivities were relatively low.[4–7] Compounds with C_2-symmetry have also received much attention for their utility as asymmetric ligands in stereoselective reactions.[8–15] The C_2-symmetric dibenzyldiamino diol, (2*R*,3*S*,4*S*,5*R*)-2,5-diamino-3,4-dihydroxy-1,6-diphenyl hexane **1**, which is the core C_2-symmetric unit of potent inhibitors of HIV protease, has been conveniently synthesized from natural L-tartaric acid or D-phenylalanine.[16–18] Our interest lies in the possibility of using the C_2-symmetric dibenzyldiamino diol **1** as a catalyst in the asymmetric borane reduction of prochiral carbonyl compounds and nucleophilic addition to aromatic aldehydes.



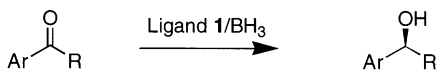
1

C_2 Symmetry

2. Results and discussion

Chiral amino alcohols are generally allowed to react with borane to form chiral oxazaborolidine complexes for asymmetric borane reduction of aromatic ketones. However, limited success has been achieved in the stereoselective synthesis, except when the rigid five-membered ring systems discovered by Itsuno et al.[19,20] and Corey et al.[21–23] were applied in the enantioselective reduction of ketones to obtain alcohol products with high e.e. Reduction of aromatic ketones with borane using stoichiometric ephedrine or benzyl amino alcohol as the ligand gives very poor enantioselectivity (37% e.e.).[24]

To investigate the ability of asymmetric borane reduction using C_2-symmetric diamino diol **1** as ligand, initially the in situ reduction of acetophenone was carried out as a model study using stoichiometric bisamino diol **1** as the ligand with 1.2 equiv. of borane (Scheme 1). It was found that the reaction temperature greatly affected the enantiomeric purity of the secondary alcohol product. At low temperature (–35°C) the reaction gave product with a



2 **3**

Scheme 1.

* Corresponding author. E-mail: jiangb@pub.sioc.ac.cn

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Table 1. Enantioselective borane reduction of aryl ketone catalyzed by the C_2-symmetric diaminodiol **1**[a]

Entry	Ketone **2**	Temp. (°C)	Solvent	Ligand (equiv.)	E.e. (%) (config.)[b]	Yield (%)[c]
1	Acetophenone **2a**	−30	THF	1.00	34 (*S*)	55
2	Acetophenone **2a**	0	THF	1.00	55 (*S*)	90
3	Acetophenone **2a**	30	THF	1.00	61 (*S*)	95
4	Acetophenone **2a**	35	THF	1.00	66 (*S*)	95
5	Acetophenone **2a**	35	THF	0.10	81 (*S*)	99
6	Acetophenone **2a**	35	THF	0.05	81 (*S*)	99
7	Acetophenone **2a**	35	THF	0.025	81 (*S*)	99
8	Acetophenone **2a**	35	Et_2O	0.025	62 (*S*)	99
9	Acetophenone **2a**	35	PhMe	0.025	60 (*S*)	99
10	Acetophenone **2a**	35	CH_2Cl_2	0.025	60 (*S*)	99
11	Acetophenone **2a**	35	DME	0.025	73 (*S*)	99
12	$PhCOCH_2Cl$ **2b**	35	THF	0.025	87 (*R*)	92
13	$PhCOCH_2Br$ **2c**	35	THF	0.025	95 (*R*)	93
14	2-Acetonaphthone **2d**	35	THF	0.025	73 (*S*)	95
15	$PhCOCCl_3$ **2e**	35	THF	0.025	70 (*R*)	90
16	$PhCOCH_2CH_2Cl$ **2f**	35	THF	0.025	85 (*S*)	92

[a] The catalyst was generated in situ directly prior to use.
[b] The enantiomeric excesses were determined by HPLC with Chiralcel OD column. The configurations were determined by comparison rotation with the data given in the literature.
[c] Isolated yield.

poor e.e. of 34% (Table 1, entry 1). When the reaction was carried out at 35°C, 66% e.e. was achieved (Table 1, entry 4), while completing the reaction at 0°C gave 55% e.e. (Table 1, entry 2). These results prompted us to make efforts toward achieving the asymmetric borane reduction of ketones with catalytic amounts of bisamino diol **1** in a variety of solvents.

When C_2-symmetric diamino diol **1** (0.025 to 0.1 equiv.) was employed as a ligand in the borane reduction of acetophenone in THF at 35°C, a quantitative yield of secondary alcohol with 81% e.e. was obtained (Table 1, entries 5–7). The reactions attempted in ether, dichloromethane, toluene, or dimethoxyethane gave less enantiomeric excesses (e.e.s) of the corresponding secondary alcohols than that in THF (Table 1, entries 8–11). When applied to the reduction of α-chloroacetophenone and α-bromoacetophone, this system gave 87 and 95% e.e., respectively (Table 1, entries 12 and 13). Reduction of other arylketones also afforded alcohol products with good to excellent e.e.s of 70–95% (Table 1, entries 14–16).

To study the mechanism of the asymmetric borane reduction of arylketone catalyzed by C_2-symmetric diamino diol **1**, the configurations of each conceivable intermediate were optimized by calculating their minimum energies on an SGI O2 station with Universal 1.02 force field model. There are five possible intermediates due to the four active groups on the diamino diol **1** (Fig. 1). The results showed that the energies of the

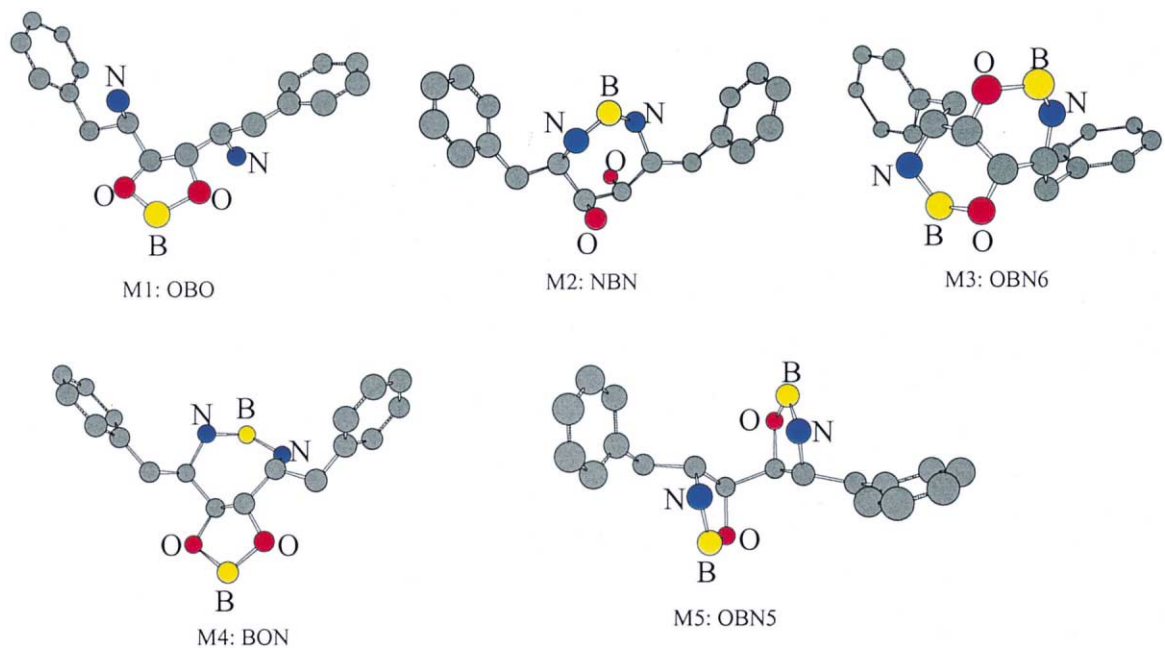


Figure 1. The possible intermediates in asymmetric borane reduction optimized by MM2.

one-centered catalysts (**M1**, **M2**) were higher than those of the two-centered (**M3**, **M4**, **M5**). Notably, the energy of the C_2-symmetric bisoxazaborolidine **M5** was the lowest. That indicated the conformation **M5** was the most stable and reasonable intermediate. To confirm the results simulated by the SGI workstation, in situ NMR was used to determine the structure of the oxazaborolidine B–H through ^{11}B, ^{1}H, ^{13}C NMR and DEPT 135 experiments.[25–27] However, as observed, the one-centered five-membered ring **M1** was formed at first as soon as the addition of borane to the solution of **1**. When borane was in excess and the mixture was stirred for 12–36 h at a suitable temperature, the intermediate **M1** slowly changed to the bisoxazaborolidine **M5**. The procedure depended on the reaction time, the temperature, and the quantity of borane. When 10 equiv. of borane was used, the transformation was fully complete after **1** was allowed to react with borane for more than 12 h at 35°C. Therefore, the structure of the catalyst affecting the enantioselectivity in the asymmetric borane reduction was determined as the C_2-symmetric bisoxazaboraolidine **M5**. Thus, the absolute stereochemistry and high enantioselectivity of this reaction can be easily understood in terms of the transition state (Fig. 2).

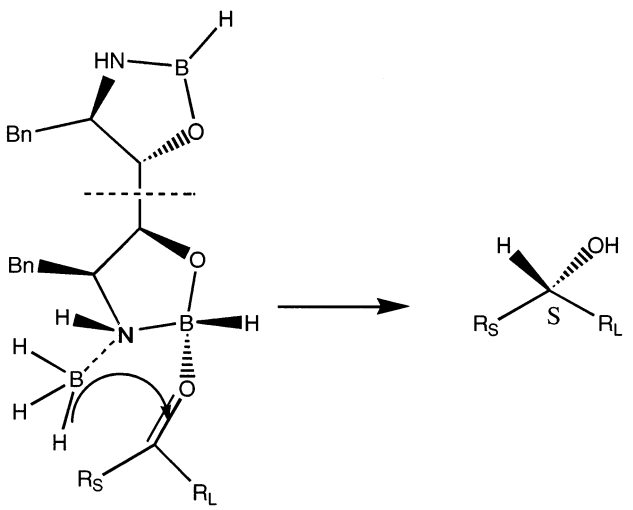


Figure 2. The transition state of catalytic asymmetric borane-reduction of ketone with **1** as catalyst (one side).

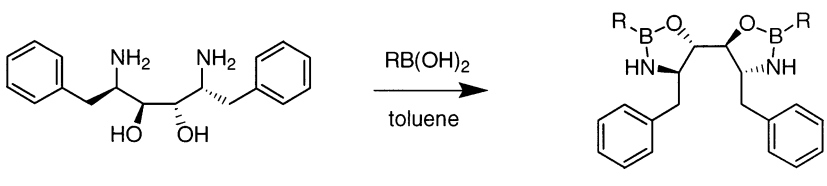
Corey reported that using *B*-alkyl oxazaborolidines as borane reduction ligands gave better enantioselectivities than those seen with B–H oxazaborolidines. Thus, the *B*-methyl oxazaborolidine **4a** and the *B*-Butyl oxazaborolidine **4b** were prepared by the reaction of diamino diol **1** with the appropriate alkylboronic acid in THF for 10 h (Scheme 2). After the solvent was removed the *B*-alkyl oxazaborolidine ligand was applied to the asymmetric borane reduction of aryl ketone. However, this reductive system gave less enantioselectivity than the diamino diol **1** due to the more hindered methyl and butyl groups on the bisoxazaborolidine **4**. Reduction of acetophenone with 0.025 equiv. of *B*-methyl oxaborolidine **4a** and *B*-Butyl oxaborolidine **4b**, afforded 2-phenylethan-1-ol with 74 and 70% e.e., respectively. Thus, reduction of aromatic ketones proceeded with moderate enantioselectivity. The results are summarized in Table 2.

The direct nucleophilic alkylation of a prochiral carbonyl group with total facial discrimination has been a long-standing goal in organic synthesis. Addition of an organozinc reagent to aldehydes is a powerful method for the generation of secondary alcohols[28] and a number of chiral catalysts have been devised for this pur-

Table 2. Enantioselective borane reduction of aryl ketone catalyzed by *B*-alkyl oxazaborolidine **4**[a]

Entry	Ketone **2**	Ligand **4**	E.e. (%) (config.)[b]	Yield (%)[c]
1	Acetophenone **2a**	**4a**	74 (*S*)	92
2	Acetophenone **2a**	**4b**	70 (*S*)	92
3	$PhCOCH_2CH_3$ **2g**	**4a**	69 (*S*)	92
4	$PhCOCH_2CH_3$ **2g**	**4b**	66 (*S*)	93
5	$PhCOCH_2Cl$ **2b**	**4a**	84 (*R*)	89
6	$PhCOCH_2Cl$ **2b**	**4b**	84 (*R*)	90
7	$PhCOCH_2Br$ **2c**	**4a**	88 (*R*)	85
8	$PhCOCH_2Br$ **2c**	**4b**	89 (*R*)	90
9	2-Acetonaphthone **2d**	**4a**	74 (*S*)	95
10	2-Acetonaphthone **2d**	**4b**	70 (*S*)	93

[a] The catalyst was generated in situ just prior to use.
[b] The enantiomeric excesses were determined by HPLC with Chiralcel OD column. The configurations were determined by comparison rotations with the data given in the literature.
[c] Isolated yield.



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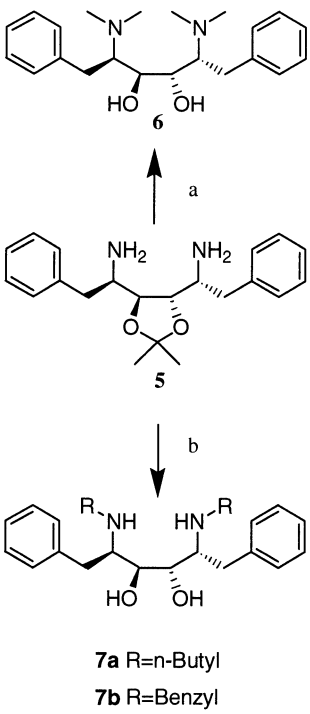
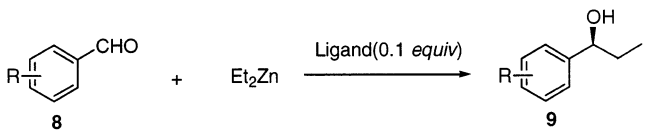
4a R = CH_3

4b R = *n*-Butyl

Scheme 2.



Scheme 3. *Reagents and conditions*: (a) $HCHO/HCO_2H$, reflux, 10 h; (b) 1. for **7a**, *n*-butyryl chloride; for **7b** benzoyl chloride, CH_2Cl_2, Et_3N; 2. borane–dimethyl sulfide/toluene, reflux.



Scheme 4.

pose. Several *N*,*N*-dialkyl vicinal amino alcohols prepared from β-amino acids have been successfully used as catalysts for the enantioselective addition of dialkylzinc reagent to the aldehyde.[29–33] For investigation of C_2-symmetric diamino diol promoting enantioselective addition of dialkylzinc reagent to aldehyde, *N*,*N*,*N*′,*N*′-tetramethyldiamino diol **6** and *N*,*N*′-dialkyldiamino diol **7** ligand was required. The *N*,*N*,*N*′*N*′-tetramethyldiamino diol **6** was synthesized in 98% yield by heating **1** with formaldehyde in formic acid for 10 h. For preparation of *N*,*N*′-dialkyldiamino diol **7**, **1** was treated with *n*-butyryl chloride and benzoyl chloride, respectively, following reduction of the corresponding amide with borane–dimethyl sulfide to afford *N*,*N*′-dibutyl diamino diol **7a** in 87% yield and *N*,*N*′-dibenzyldiamino diol **7b** in 87% yield. (Scheme 3).

The ligands **6** and **7** were tested as promoters for the addition of dialkylzinc reagents to benzaldehyde. Toluene was chosen as the solvent in order to maximize the rate difference between the catalyzed and the uncatalyzed reaction. As a general procedure, the dialkylzinc reagent (1.2 equiv.) was added dropwise to the stirred solution of aromatic aldehyde and ligand (0.1 equiv.) in dry toluene, under argon over 10 min. After stirring at room temperature for 48 h, the mixture was quenched with saturated aqueous NH_4Cl and the secondary alcohol isolated by extraction (Scheme 4, Table 3).

The yields and e.e.s obtained are summarized in Table 3. With benzaldehyde as a model reaction, all of the alkyl diamino diols were shown to be good promoters for the addition reaction (Table 3, entries 1–3). An excellent e.e. of 98% was obtained when *N*,*N*,*N*′,*N*′-tetramethyldiamino diol **6** was used as promoter for addition of Et_2Zn to benzaldehyde. When the diamino diol **1** was used as promoter, the e.e. of the product dropped to 20%. Prompted by the excellent enantioselectivity obtained with ligand **6**, the addition of Et_2Zn to a variety of substituted arylaldehydes catalyzed by **6** was explored. In these reactions, all of the aldehyde substrates gave excellent e.e. (93–97% e.e.) with very high yields (Table 3, entries 4–7).

The solvent affected the enantioselective addition of benzaldehyde with diethylzinc. If the reaction was completed in hexane, 3 equiv. of diethylzinc were required for completion of the reaction, whereas if the reaction was carried out in toluene, only 1.2 equiv. of diethylzinc were required.

The secondary alcohol product had (*S*)-configuration, as established by comparison of the specific rotation with literature data. According to the reported mechanism for the enantioselective addition of Et_2Zn to benz-

Table 3. Addition reaction of Et_2Zn to arylaldehyde promoted by ligands **6** and **7**

Entry	Aldehyde **8**	Ligand (equiv.)	E.e. (%)[a] (config.)[b]	Yield (%)[c]
1	PhCHO **8a**	**6** (0.1)	98 (*S*)	95
2	PhCHO **8a**	**7a** (0.1)	95 (*S*)	92
3	PhCHO **8a**	**7b** (0.1)	94 (*S*)	93
4	4-MePhCHO **8b**	**6** (0.1)	93 (*S*)	94
5	2-MeOPhCHO **8c**	**6** (0.1)	97 (*S*)	96
6	4-ClPhCHO **8d**	**6** (0.1)	95 (*S*)	90
7	3-PhO-PhCHO **8e**	**6** (0.1)	95 (*S*)	95

[a] Determined by HPLC analysis on Chiralcel OD column.
[b] Determined by comparison rotation with the data given in the literature.
[c] Isolated yield.

aldehyde using *N*,*N*,*N*′,*N*′-tetramethyldiamino diol **6** as promoter, a transition state such as the one depicted in Fig. 3 could be used to explain the stereochemical outcome of the addition reaction.

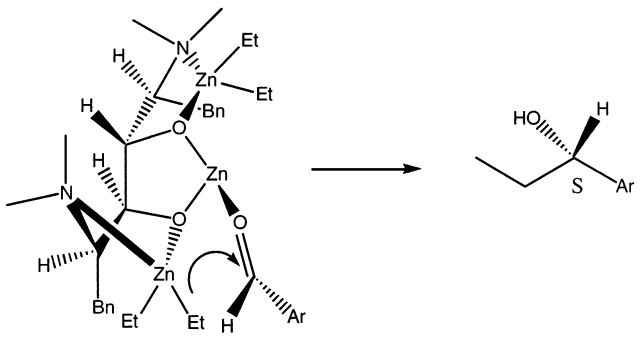


Figure 3. The transition state of catalytic asymmetric addition of diethylzinc to aldehyde (one side).

3. Conclusions

We have demonstrated that C_2-symmetric diamino diols can be effectively used as catalytic ligands for the enantioselective reduction of prochiral ketones to secondary alcohols. High enantioselectivities were obtained in these catalytic processes.

N,*N*,*N*′,*N*′-Tetramethyldiamino diol and *N*,*N*′-dialkyl diamino diol were used as promoters for the enantioselective addition of diethylzinc to arylaldehydes. The use of 0.1 equiv. of *N*,*N*,*N*′*N*′-tetramethyldiamino diol as catalyst in the addition of the diethylzinc to arylaldehyde led to e.e.s of up to 98%. It should be noted that these ligands could also be easily recovered during the reaction work up.

4. Experimental

4.1. General procedure of asymmetric borane reduction of ketone using ligand 1 as catalyst

A solution of ligand (0.025 mmol) in THF (2.5 mL) was added to a solution of borane (2.3 M, 1 mL, 2.3 mmol) in THF. The resulting solution was warmed to 35°C and stirred at 35°C for 12 h. A solution of the ketone (1 mmol) in THF (2 mL) was added dropwise with a gas-tight syringe controlled by a pump at a rate of 0.5 mL/h and the resulting mixture was stirred for 5 h, then decomposed by the addition of aqueous HCl (2N, 2 mL). When gas emission ceased, the reaction mixture was extracted with ether. The aqueous layer was alkalized and filtered to obtain a white precipitate of the recycled catalyst. The combined ether extract was washed with brine and dried with $MgSO_4$. After the solvent was removed in vacuo, a colorless oil was obtained which was purified by flash chromatography.

4.2. *B*,*B*-Dimethyl bis(3-benzyloxazaborolidine) 4a

A solution of the diaminodiol **1** (300 mg, 1 mmol) and methylboronic acid (120 mg, 2 mmol) in toluene (20 mL) was heated under reflux with a Dean–Stark apparatus (containing 4 Å molecular sieves in the side arm) under argon for 12 h to give a deep red solution. The reaction solution was concentrated to ca. 2 mL, followed by removal of the remaining toluene under reduced pressure to give a red residue. Addition of freshly distilled air-free THF (10 mL) afforded a 0.1 M solution of the corresponding oxazaborolidine catalyst **4a**.

4.3. *B*,*B*-Di-*n*-butyl bis(3-benzyloxazaborolidine) 4b

This compound was prepared from the diaminodiol and *n*-butylboronic acid under similar conditions as described for **4a** and used as a 0.1 M solution in THF.

4.4. General procedure of asymmetric borane reduction of ketone using 4 as catalyst

To the prepared solution of the oxazaborolidine in THF was added the solution of the ketone (1 mmol) in THF (2 mL) dropwise with a gas-tight syringe controlled by a pump at a rate of 0.5 mL/h. The resulting solution was stirred for 1 h and quenched with aqueous HCl (2N), leading to a pure product.

4.5. (2*R*,3*S*,4*S*,5*R*)-*N*,*N*,*N*′,*N*′-Tetramethyl-2,5-diamino-3,4-dihydroxy-1,6-diphenylhexane 6

The acetalized diaminodiol **5** (1.36 g, 4.0 mmol) was dissolved in formic acid (6 mL) and treated with aqueous formaldehyde (3.2 mL, 37%) was added. The mixture was stirred under reflux for 8 h and the solvent was removed under vacuum to give yellow oil. After alkalization by addition of 3N NaOH, the resulting turbid mixture was extracted with ether. The combined extracts were washed with brine and then dried and evaporated to give a pale yellow solid. The product was recrystallized from ether to give the pure bisamino alcohol **6** (1.2 g, 84%). $[\alpha]_D^{20} = -4.2$ (*c*, 2.4, $CHCl_3$); IR: 3431, 2943, 2833, 1600, 1491, 1124, 1028, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.30–7.17 (m, 10H), 3.38 (d, 2H, *J* 2.2 Hz), 3.00 (dd, 2H, *J* 10.4 Hz, 12.9 Hz), 2.81 (dd, 2H, *J* 3.7 Hz, 12.9 Hz), 2.67 (m, 2H), 2.50 (s, 12H); MS(EI) *m*/*z*: 357, 209, 208, 178, 149, 148, 133, 91; E.A: calcd for $C_{22}H_{32}N_2O_2$: C, 74.1; H, 9.05; N, 7.85%; found: C, 74.32; H, 9.06; N, 7.91%.

4.6. (2*R*,3*S*,4*S*,5*R*)-*N*,*N*′-Di-*n*-butyl-2,5-diamino-3,4-dihydroxy-1,6-diphenylhexane 7a

The acetalized diaminodiol **5** (680 mg, 2.0 mmol) and triethylamine (0.7 mL, 5 mmol) was dissolved in CH_2Cl_2 (15 mL) and cooled to 0°C with an ice-water bath. Then, *n*-butyryl chloride (0.5 mL, 4.8 mmol) was added dropwise while the temperature of the reaction mixture was kept between 0 and 5°C. After the addition was complete, the resulting mixture was warmed to

room temperature and stirred for 5 h, followed by addition of CH_2Cl_2 (30 mL). The organic phase was washed with brine and then dried and concentrated. The amide was obtained as a white solid which was used without further purification.

To the solution of the amide in freshly-distilled toluene (10 mL) was added a solution of borane–dimethyl sulfide (10 M, 1 mL, 10 mmol) in THF. The mixture was refluxed for 6 h under argon. Then aqueous HCl (2N, 10 mL) was added and the resulting mixture was stirred for 24 h. After neutralization with 2N NaOH, the reaction mixture was extracted with ether. The combined ethereal extract was washed with brine, dried and then concentrated. The residue was purified by silica gel column (CH_2Cl_2/MeOH, 9/1) to give compound **7a** as a pale yellow oil (717 mg, 87%). $[\alpha]_D^{20} = -89.3$ (*c*, 2.5, $CHCl_3$); IR: 3061, 2955, 2926, 2856, 1732, 1601, 1454, 1126 cm^{-1}; ^1H NMR (300 Hz, $CDCl_3$) δ: 7.28–7.16 (m 10H), 3.38 (s, 2H), 2.99–2.47 (m, 10H), 1.54–1.22 (m, 8H), 0.92 (t, 6H, $J=7.2$ Hz); MS (EI) *m*/*z*: 413, 248, 236, 230, 206, 176, 120, 91; HRMS (EI): calcd for $C_{26}H_{40}N_2O_2$: 412.3125, found: 412.3160.

4.7. (2*R*,3*S*,4*S*,5*R*)-*N*,*N*′-Dibenzyl-2,5-diamino-3,4-dihydroxy-1,6-diphenylhexane 7b

Compound **7b** was prepared by the same procedure as **7a** using benzoyl chloride instead of *n*-butylryl chloride in 87% yield as a foam. $[\alpha]_D^{20} = -75.3$ (*c*, 3.1, $CHCl_3$); IR: 3063, 2921, 2854, 1603 cm^{-1}; ^1H NMR (300 Hz, $CDCl_3$) δ: 7.36–7.13 (m 10H), 3.97 (d, 2H, *J* 12.5 Hz), 3.74 (d, 2H, *J* 12.5 Hz), 3.34 (s, 2H), 3.06 (dd, 2H, *J* 3.4 Hz, 12.1 Hz), 2.87–2.74 (m, 4H); MS (EI) *m*/*z*: 481, 282, 270, 264, 240, 210. HRMS (EI): calcd for $C_{30}H_{36}N_2O_2$: 480.2754, found: 480.2731.

4.8. General procedure of asymmetric addition of diethylzinc to aldehyde

To a solution of the ligand (0.1 mmol) in freshly distilled toluene (1.5 mL) was added aldehyde (1 mmol), followed by addition of diethylzinc (1.1 M in toluene, 1 mL, 1.1 mmol). The mixture was then maintained at room temperature for 48 h and quenched with aqueous NH_4Cl (2N, 1 mL). Ether was added to dilute the mixture. The organic layer was washed with brine and then dried. After the solvent was removed the product was purified on a silica gel column.

Acknowledgements

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