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SYNTHESIS OF CHIRAL TETRAHYDROISOQUINOLINE-DERIVED β-AMINO ALCOHOLS AND THEIR APPLICATION TO ASYMMETRIC REACTION†

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† This paper is dedicated to Professor Dr. Ryoji Noyori on the occasion of his 70th birthday.

Abstract – Three chiral 1,2,3,4-tetrahydroisoquinoline-derived β-amino alcohols were synthesized by using the Ru-catalyzed asymmetric transfer hydrogenation of 6-methoxy-1-(2-methoxyphenyl)-3,4-dihydroisoquinoline as the key reaction. The ability of the synthesized β-amino alcohols as chiral ligands was evaluated in the addition of diethylzinc to benzaldehyde.

Chiral 1,2,3,4-tetrahydroisoquinolines are very promising as chiral bases,[1] chiral acids[2] and chiral ligands[3] in asymmetric reactions; however, there are not many reports on the application of chiral 1,2,3,4-tetrahydroisoquinolines to asymmetric reactions. On the other hand, a large number of chiral β-amino alcohols are well-known as quite useful ligands for various catalytic asymmetric reactions, especially, an asymmetric addition of organozinc to carbonyl compounds.[4] Under such a background, we were interested in β-amino alcohols bearing a 1,2,3,4-tetrahydroisoquinoline skeleton as chiral ligands. In this paper, we wish to describe our results on the synthesis of three chiral β-amino alcohols **1a**-**c** (Figure 1) and their evaluation as ligands in the asymmetric addition of diethylzinc to benzaldehyde.

Initially, the enantiopure tetrahydroisoquinoline **2**, a common intermediate for the synthesis of **1a**-**c**, was synthesized as shown in Scheme 1. 2-(3-Methoxyphenyl)ethanamine **3** was condensed with 2-methoxybenzoic acid using diethyl cyanophosphonate (DEPC)[5] and Et_3N to give the amide **4** in 99 % yield. The Bischler-Napieralski reaction[6] of **4** afforded the dihydroisoquinoline **5** in 82 % yield. Chiral

diamine-ruthenium(II) complexes is often used as catalysts for the asymmetric transfer hydrogenation of dihydroisoquinolines.[7] Thus, the asymmetric transfer hydrogenation of **5** using the complex, prepared from $[Ru(C_6H_6)Cl_2]_2$ and (1*R*,2*R*)-*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine [(1*R*,2*R*)-TsDPEN] in the presence of Et_3N, was examined. As expected, the tetrahydroisoquinoline **2** was obtained in 87 % yield with 84 % ee, which was recrystallized from EtOH containing D-tartaric acid to give the complex **6**. The X-ray crystallographic analysis of the complex **6** showed that **6** was the 1:1:1 complex of (*R*)-**2**, D-tartaric acid and EtOH (Figure 2). The enantiopure (*R*)-**2** was obtained by treatment of the complex **6** with sat. aqueous $NaHCO_3$ in 69 % yield from **5**.

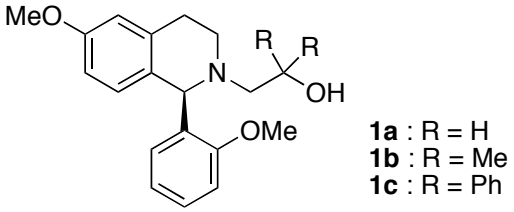
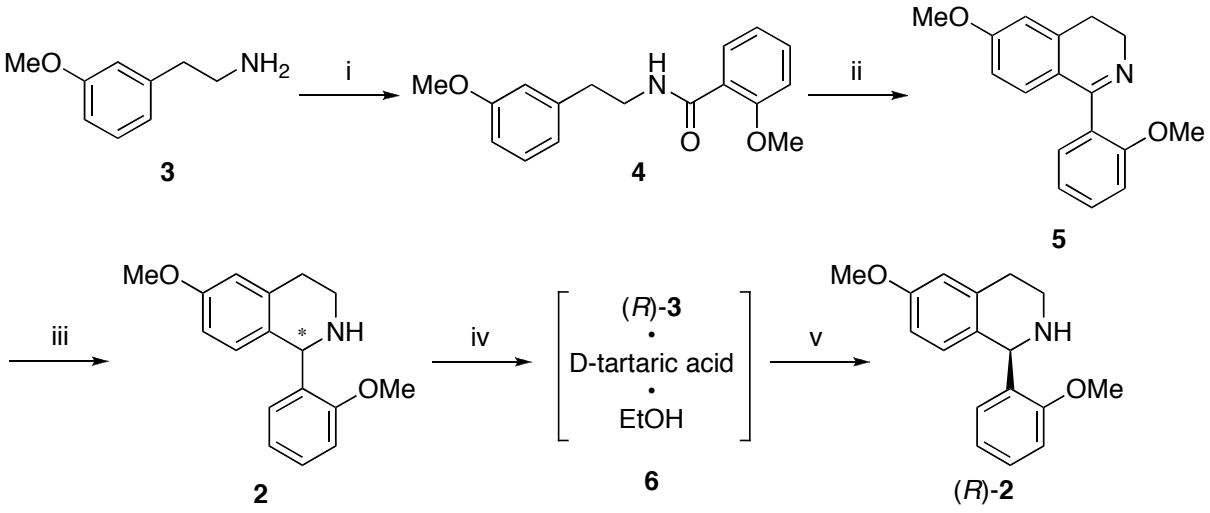
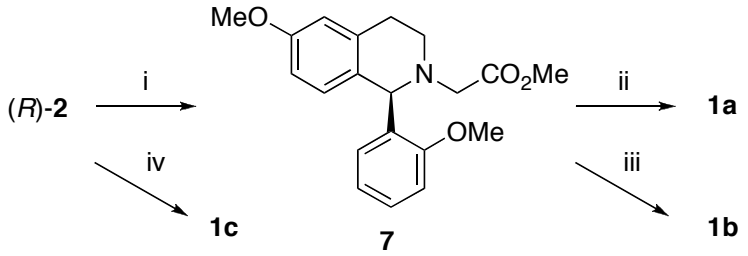


Figure 1. The structures of chiral tetrahydroisoquinoline-derived amino alcohols **1a**-**c**



Scheme 1. *Reagents and conditions*. i, 2-methoxybenzoic acid (1.1 eq.), DEPC (1.1 eq.), Et_3N (2.3 eq.), THF, 0 °C, 4 h, 99 %; ii, $POCl_3$ (2.0 eq.), MeCN, reflux, 2 h, 82 %; iii, $[Ru(C_6H_6)Cl_2]_2$ (2.5 mol %), (1*R*,2*R*)-TsDPEN (5.0 mol %), Et_3N (20 mol %), MeCN, HCO_2H-Et_3N (5:2) azeotrope, 30 °C, 24 h, 87 %, 84 % ee; iv, recrystalization from EtOH containing D-tartaric acid (1.0 eq.); v, wash with sat. aqueous $NaHCO_3$, 69 %, >99 % ee from **5**.



Scheme 2. *Reagents and conditions*. i, methyl bromoacetate (1.1 eq.), Et_3N (1.1 eq.), toluene, rt, 22 h, quant.; ii, $LiAlH_4$ (1.0 eq.), THF, rt, 3 h, 91 %; iii, MeMgBr (5 eq.), THF, rt, 7 h, 37 %; iv, *n*-BuLi (1.5 eq.), 1,1-diphenylethylene oxide (1.5 eq.), THF, reflux, 36 h, 40 %.

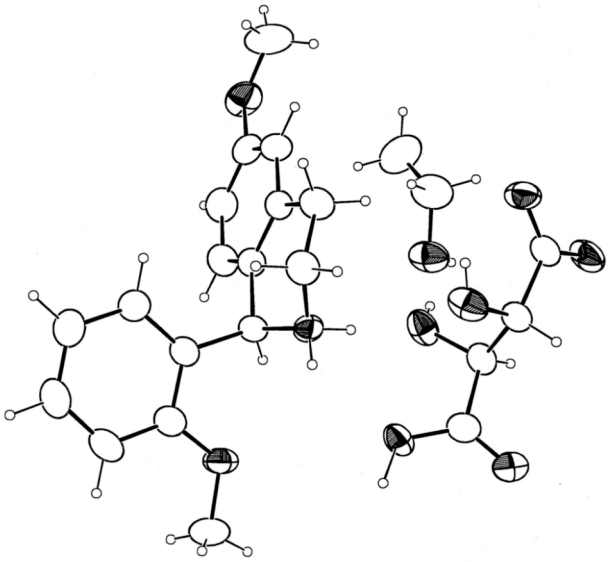
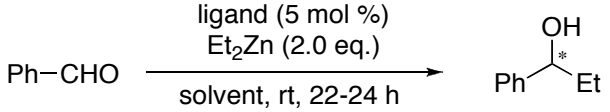


Figure 2. ORTEP drawing of the complex **6**.

Next, the derivatization of (*R*)-**2** to β-chiral amino alcohols **1a**-**c** was performed (Scheme 2). After the reaction of (*R*)-**2** with methyl bromoacetate quantitatively giving **7**, whose reduction by $LiAlH_4$ and reaction with MeMgBr afforded **1a** and **1b** in 91 % and 37 % yields, respectively. The diphenyl derivative **1c** was obtained in 40 % yield by reaction of (*R*)-**2** with 1,1-diphenylethylene oxide[8].

Finally, the asymmetry-inducing ability of β-amino alcohols **1a**-**c** as catalysts was evaluated in the addition of diethylzinc to benzaldehyde and the results were summarized in Table 1. The reaction in the presence of 5 mol% of the ligand **1a** bearing a 2-hydroxyethyl group in hexane afforded (*S*)-1-phenylpropan-1-ol in 90 % yield with 21 % ee. On the other hand, in the cases of **1b** and **1c** bearing 2,2-dimethyl- and 2,2-diphenyl-2-hydroxyethyl groups, the enantiomer, (*R*)-1-phenylpropan-1-ol, was formed as a main product with 8 % ee and 27 % ee, respectively (entries 2 and 3). From these results, substituents at the 2-position of the 2-hydroxyethyl group were found to have a certain influence on the enantioselectivity and among **1a**-**c**, the ligand **1c** gave the best result as a chiral ligand in this reaction system though the enantioselectivity was not satisfactory. Additionally, replacement of hexane by toluene as a reaction solvent led to a significant decrease in the enantiomeric excess of 1-phenylpropan-1-ol

Table 1. Enantioselective addition of diethylzinc to benzaldehyde using chiral amino alcohols **1a**-**c**.



Entry	Ligand	Solvent	Yield (%)[a]	Ee (%)[b]	Configuration[c]
1	**1a**	hexane	90	21	*S*
2	**1b**	hexane	82	8	*R*
3	**1c**	hexane	82	27	*R*
4	**1a**	toluene	79	9	*S*
5	**1b**	toluene	82	3	*R*
6	**1c**	toluene	83	1	*R*

a, Isolated yield. b, The enantiomeric excess was determined by HPLC. c, The configuration was determined by optical rotation.

produced (entries 4-6).

In conclusion, the synthesis of new three chiral tetrahydroisoquinoline-derived β-amino alcohols were achieved and the evaluation of the synthesized β-amino alcohols as chiral ligands was performed in the addition of diethylzinc to benzaldehyde. Among them, the ligand bearing a 2,2-diphenyl-2-hydroxyethyl group was found to give the highest enantioselectivity though the selectivity was still not enough.

EXPERIMENTAL

IR spectra were recorded on a SHIMADZU FTIR-8400S spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer (^{1}H, 270 MHz; ^{13}C, 67.8 MHz). Mass spectra were recorded on a JEOL JMS-SX-102A spectrometer. Optical rotations were measured with a JASCO DIP 1000 digital polarimeter. A crystal was examined on a Nonius KappaCCD diffractometer using Mo-Kα radiation.

2-Methoxy-*N*-(3-methoxyphenethyl)benzamide (4). Under an argon atmosphere, DEPC (0.54 mL, 3.56 mmol) and Et_3N (1.05 mL, 7.53 mmol) were added to a solution of 2-(3-methoxyphenyl)ethanamine **3** (496 mg, 3.28 mmol) and 2-methoxybenzoic acid (548 mg, 3.60 mmol) in THF (5 mL) at 0 °C and the mixture was stirred at 0 °C for 4 h. After the dilution with EtOAc, the organic layer was washed with sat. aqueous $NaHCO_3$, H_2O and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane-EtOAc = 2:1) to give **4** (926 mg, 99 %) as a colorless oil. IR (neat): 3391, 1651, 1531 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.90 (t, *J* = 7 Hz, 2H), 3.72-3.79 (m, 2H), 3.77 (s, 3H), 3.79 (s, 3H), 6.78-6.93 (m, 4H), 7.06 (dd, *J* = 7, 8 Hz, 1H), 7.22-7.28 (m, 1H), 7.41 (dd, *J* = 7, 8 Hz, 1H), 7.90 (brs, 1H), 8.21 (d, *J* = 8 Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ: 35.7, 40.8, 55.1, 55.6, 111.1, 111.7, 114.5, 121.1, 121.4, 129.4, 132.5, 140.9, 157.3, 159.6, 164.9. MS *m*/*z*: 285 (M^+), 135 (bp). HR-MS calcd for $C_{17}H_{19}NO_3$: 285.1365, found: 285.1364.

6-Methoxy-1-(2-methoxyphenyl)-3,4-dihydroisoquinoline (5). Under an argon atmosphere, $POCl_3$ (0.19 mL, 2.04 mmol) was added to a solution of **4** (285 mg, 1.00 mmol) in MeCN (5 mL) at rt and the mixture was refluxed for 4 h. After being cooled to rt, the reaction mixture was little by little poured into a mixture of $NaHCO_3$ powder and ice not to acidify. The whole was extracted with EtOAc. The organic extracts were washed with sat. aqueous $NaHCO_3$, H_2O and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane-EtOAc = 1:1 to 1:3) to give **5** (219 mg, 82 %) as a white powder. Mp 85-87 °C. IR (Nujol): 1601 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.83 (br, 2H), 3.63 (s, 3H), 3.82 (s, 3H), 3.87 (br, 2H), 6.65 (dd, *J* = 3, 8 Hz, 1H), 6.74 (d, *J* = 3 Hz, 1H), 6.89-6.95 (m, 2H), 7.02 (t, *J* = 7 Hz, 1H), 7.31-7.40 (m, 2H). ^{13}C-NMR (DMSO-d_6) δ: 25.6, 46.4, 54.7, 55.1, 111.0, 111.6, 112.1, 120.1, 122.2, 128.0, 128.0, 129.4, 129.6, 138.4, 156.2, 160.2, 164.1. MS *m*/*z*: 267 (M^+), 266 (bp). HR-MS calcd for $C_{17}H_{17}NO_2$: 267.1259, found: 267.1259.

(*R*)-6-Methoxy-1-(2-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline [(*R*)-2]. Under an argon atmosphere, $[Ru(C_6H_6)Cl_2]_2$ (177 mg, 0.35 mmol), (1*R*,2*R*)-TsDPEN (260 mg, 0.71 mmol) and Et_3N (0.39 mL, 2.80 mmol) in MeCN (10 mL) was stirred at 80 °C for 0.5 h. After the addition of a solution of **5** (3.79 g, 14.1 mmol) in MeCN (20 mL) and HCO_2H-Et_3N (5:2) azeotrope (15 mL) at 30 °C, the mixture was stirred at 30 °C for 24 h. Sat. aqueous $NaHCO_3$ was added and the mixture was extracted with EtOAc. The organic extracts were washed with H_2O and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc only) to give **2** (3.33 g, 87 %, 84 %ee), which was dissolved with EtOH (20 mL) and D-tartaric acid (0.5 M in EtOH, 25 mL) was added. The mixture was heated and recrystallized. The crystals obtained by filtration were recrystallized from EtOH again to give the complex **6** [(*R*)-**2**•(D-tartaric acid)•EtOH = 1:1:1](mp 111-112 °C). Then, after addition of sat. aqueous $NaHCO_3$, the mixture was extracted with EtOAc. The organic extracts were dried over Na_2SO_4 and concentrated *in vacuo* to give (*R*)-**2** (2.65 g, 69 %, >99 %ee from **5**) as a white powder. The enantiomeric excess was determined by HPLC using DAICEL chiral cel AD with 20 % propan-2-ol in hexane containing 0.1 % Et_3N (flow rate = 0.3 mL/min, retention time = 18 min for *R*-configuration and 27 min for *S*-configuration). Mp 78-80 °C. $[\alpha]_D$ -12.0 (*c* 1.62, $CHCl_3$, 21 °C). IR (Nujol): 3420 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.15 (s, 1H), 2.87 (t, *J* = 6 Hz, 2H), 3.79 (s, 3H), 3.86 (s, 3H), 5.50 (s, 1H), 6.61-6.74 (m, 3H), 6.82-6.84 (m, 2H), 6.91 (d, *J* = 8 Hz, 1H), 7.19-7.24 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 30.2, 40.7, 54.3, 55.2, 55.4, 110.3, 111.9, 113.2, 120.0, 128.0, 129.0, 129.8, 130.1, 132.9, 137.0, 157.1, 157.5. MS *m*/*z*: 269 (M^+), 162 (bp). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.52; H, 7.12; N, 5.22.

Crystal data for the complex 6. Formula: $C_{23}H_{31}NO_9$: Crystal size: 0.42 mm x 0.32 mm x 0.18 mm; Crystal system: Orthorhombic; Space group: $P2_1P2_1P2_1$; Temperature: 293 K; Cell dimension: a = 5.910(1) Å, b = 13.389(1) Å, c = 29.229(1) Å; Cell volume: 2312.5(2) $Å^3$; Z = 4; F_{000} = 992; D_{calc} = 1.337 g•cm^{-3}; μ(Mo-Kα) = 0.96 cm^{-1}; Measured reflections: 5309; Observed reflections [$F_{obs} > 1.5\sigma(F_{obs})$]: 3306; R = 0.044; R_w = 0.045.

(*R*)-Methyl 2-(6-methoxy-1-(2-methoxyphenyl)-3,4-dihydroisoquinolin-2(1*H*)-yl)ethanoate (7). Under an argon atmosphere, methyl bromoacetate (80 μL, 0.85 mmol) and Et_3N (0.12 mL, 0.86 mmol) were added to a solution of (*R*)-**2** (207 mg, 0.77 mmol) in toluene (4 mL) at rt and the mixture was stirred at rt for 4 h. After the addition of H_2O, the mixture was extracted with EtOAc. The organic extracts were washed with H_2O and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane-EtOAc = 5:1) to give **7** (262 mg, quant.) as a white powder. Mp 109-110 °C. $[\alpha]_D$ +130.5 (*c* 1.87, $CHCl_3$, 23 °C). IR (Nujol): 1783 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.81-3.03 (m, 2H), 3.15-3.18 (m, 2H), 3.26 (s, 2H), 3.66 (s, 3H), 3.75 (s, 3H), 3.84 (s, 3H) 5.44 (s, 1H), 6.54-6.63 (m, 3H), 6.83-6.92 (m, 2H), 7.10 (d, *J* = 8 Hz, 1H), 7.20 (dd, *J* = 7, 7 Hz, 1H). ^{13}C-NMR

($CDCl_3$) δ: 48.6, 51.3, 55.1, 55.5, 55.7, 57.7, 110.4, 112.2, 112.4, 128.1, 129.3, 130.8, 131.0, 131.5, 135.6, 257.3, 157.8, 171.6. MS *m/z*: 341 (M^+), 234 (bp). HR-MS calcd for $C_{20}H_{23}NO_4$: 341.1627, found: 341.1634.

(*R*)-2-(6-Methoxy-1-(2-methoxyphenyl)-3,4-dihydroisoquinolin-2(1*H*)-yl)ethanol (1a). Under an argon atmosphere, $LiAlH_4$ (8.9 mg, 0.23 mmol) was added to a solution of **7** (80 mg, 0.23 mmol) in THF (2 mL) at 0 °C and the mixture was stirred at rt for 3 h. After the addition of Na_2SO_4•$10H_2O$, the mixture was filtered through a pad of Celite®. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (hexane-EtOAc = 1:1 to EtOAc only) to give **1a** (67 mg, 91 %) as a white powder. Mp 99-100 °C. $[\alpha]_D$ +86.0 (*c* 0.99, $CHCl_3$, 24 °C). IR (Nujol): 3487 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.66-2.99 (m, 6H), 3.14-3.23 (m, 1H), 3.62 (dd, *J* = 5, 5 Hz, 2H), 3.78 (s, 3H), 3.90 (s, 3H), 5.22 (s, 1H), 6.61-6.93 (m, 6H), 7.19-7.24 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 26.5, 45.2, 54.8, 55.2, 55.4, 58.5, 58.8, 110.4, 112.4, 112.7, 120.3, 128.1, 129.0, 129.8, 130.6, 132.3, 136.2, 157.2, 157.6. MS *m/z*: 313 (M^+), 282 (bp). HR-MS calcd for $C_{19}H_{23}NO_3$: 313.1678, found: 313.1678.

(*R*)-1-(6-Methoxy-1-(2-methoxyphenyl)-3,4-dihydroisoquinolin-2(1*H*)-yl)-2-methylpropan-2-ol (1b). Under an argon atmosphere, MeMgBr (1.0 M in Et_2O, 1.45 mL, 1.45 mmol) was added to a solution of **7** (100 mg, 0.29 mmol) in THF (5 mL) at 0 °C and the mixture was stirred at rt for 7 h. After the addition of sat. aqueous NH_4Cl, the mixture was extracted with EtOAc. The organic extracts were washed with sat. aqueous NH_4Cl, H_2O and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane- EtOAc = 10:1) to give **1b** (69 mg, 40 %) as a white powder. Mp 108-109 °C. $[\alpha]_D$ +127.8 (*c* 2.55, $CHCl_3$, 23 °C). IR (Nujol): 3474 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.11 (s, 3H), 1.19 (s, 3H), 2.50-2.73 (m, 4H), 3.02-3.16 (m, 2H), 3.80 (s, 3H), 3.94 (s, 3H), 5.22 (s, 1H), 6.54-7.24 (m, 7H). ^{13}C-NMR ($CDCl_3$) δ: 24.2, 27.2, 27.8, 45.5, 55.1, 55.3, 61.9, 63.7, 70.4, 110.3, 112.2, 113.1, 119.9, 128.0, 128.5, 130.1, 131.2, 132.5, 136.8, 156.9, 157.8. Anal. Calcd for $C_{21}H_{27}NO_3$: C, 73.87; H, 7.97; N, 4.10. Found: C, 73.60; H, 7.88; N, 4.36.

(*R*)-2-(6-Methoxy-1-(2-methoxyphenyl)-3,4-dihydroisoquinolin-2(1*H*)-yl)-1,1-diphenylethanol (1c). Under an argon atmosphere, *n*-BuLi (1.6 M in hexane, 0.35 mL, 0.56 mmol) was added dropwise to a solution of (*R*)-**2** (100 mg, 0.37 mmol) in THF (2 ml) at -78 °C and the mixture was stirred at -78 °C for 0.5 h. A solution of 1,1-diphenylethylene oxide[8] (110 mg, 0.56 mmol) in THF (2 mL) was added dropwise at -78 °C and the mixture was refluxed for 36 h. After the addition of sat. aqueous NH_4Cl, the mixture was extracted with EtOAc. The organic extracts were washed with H_2O and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane-EtOAc = 5:1) to give **1c** (37 mg, 37 %) as a white powder. Mp 155-156 °C. $[\alpha]_D$ +23.2 (*c* 0.50, $CHCl_3$, 23 °C). IR (Nujol): 3416 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.14-2.20 (m, 1H), 2.42-2.49 (m, 1H), 2.68-2.78 (m, 1H), 2.84-2.92 (m, 1H), 3.30, 3.63 (ABq, *J* = 13 Hz, 2H), 3.80 (s, 3H), 4.00 (s, 3H), 5.16 (s,

1H), 6.52 (d, *J* = 8 Hz, 1H), 6.64-6.78 (m, 4H), 6.92 (d, *J* = 8 Hz, 1H), 7.11-7.30 (m, 7H), 7.39 (d, *J* = 8 Hz, 1H), 7.52 (d, *J* = 8 Hz, 1H). ^{13}C-NMR ($CDCl_3$) δ: 24.4, 43.8, 55.2, 55.3, 62.0, 62.7, 75.5, 110.3, 112.3, 113.1, 119.8, 126.0, 126.2, 126.5, 127.8, 127.8, 128.1, 128.2, 129.9, 131.1, 131.9, 136.6, 146.9, 147.2, 157.2, 157.9. Anal. Calcd for $C_{31}H_{31}NO_3$: C, 79.97; H, 6.71; N, 3.01. Found: C, 79.70; H, 6.69; N, 2.73.

Asymmetric addition of diethylzinc to benzaldehyde (General procedure). Diethylzinc (1.0 M in hexane, 2 mL, 2.0 mmol) was added to ligand **1** (0.050 mmol) in the solvent (2 mL) given in Table 1 under an argon atmosphere and the mixture was stirred for 0.5 h at rt. After addition of the aldehyde (1.0 mmol) at 0 °C, the mixture was stirred at rt and 1 N aqueous HCl was added at 0 °C. After extraction with EtOAc, the organic extracts were washed with H_2O and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane-EtOAc = 10:1) to give 1-phenylpropan-1-ol. The enantiomeric excess was determined by HPLC using DAICEL chiral cel OD with 2 % propan-2-ol in hexane (flow rate = 0.7 mL/min, retention time = 20 min for *R*-configuration and 25 min for *S*-configuration).

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