The Development of Scalemic Multidentate Niobium Complexes as Catalysts for the Highly Stereoselective Ring-opening of *meso*-Epoxides and *meso*-Aziridines

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Determination of the Absolute Configuration of the (-)-Camphanic Ester of 14aa

Data for the absolute configuration and the optical rotation of β -amino alcohol **14aa** is recorded in the literature. However, as these represent estimated values arrived at by analogy with the cyclohexene oxide-derived compound we sought an unambiguous determination.

Thus the absolute configuration of **14aa** was determined by converting to the corresponding (-)-camphanic ester. Thus, **14aa** (91% ee) was treated with (-)-camphanic chloride, pyridine, and DMAP in CH_2Cl_2 at 0 °C, and desired product was purified by recrystallization (Et_2O -hexane). The obtained crystal was employed in X-ray crystal structural analysis (Figure 1). Data and crystallographic coordinates for this structure have been deposited at the Cambridge Crystallographic Database as

supplementary publication number CCDC 621150. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2J 1EZ, UK [fax: +44 1223 336033 or deposit@ccdc.cam.ac.uk].

Figure 1

Experimental

General. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECX400, JNM-ECX600 spectrometer in CDCl_3 , unless otherwise noted. Tetramethylsilane (TMS) served as internal standard (0 ppm) for ^1H NMR, and CDCl_3 was used as internal standard (77.0 ppm) for ^{13}C NMR. IR spectra were measured using a JASCO FT/IR-610 spectrometer. Optical rotations were measured with a JASCO P-1010 polarimeter. High-performance liquid chromatography was carried out using following apparatus: SHIMADZU LC-10AT (liquid chromatograph), SHIMADZU SPD-10A (UV detector), and SHIMADZU C-R6A Chromatopac. EI high-resolution mass spectra (EI-HRMS) were measured with JEOL JMX-SX-102 Mass Spectrometer. Column chromatography was conducted on Silica gel 60

(Merk) and preparative thin-layer chromatography was carried out using Wacogel B-5F. All solvents were distilled and dried over MS 4A. Niobium alkoxides were purchased from Kojundokagaku kenkyujo and Aldrich. MS 4A used in the reactions were dried under reduced pressure at 200 °C for 8 h for two times. Epoxides **3**, **12a**, **12e**, and **12h** and all amines were purchased from Wako, TCI, and Aldrich, and distilled or recrystallized from suitable solvents and stored in dark ampoules. Aziridines **18a-n** and **20a-e** were synthesized in accordance with literature protocol¹ and were purified twice by silica gel chromatography followed by recrystallization or distillation as appropriate, and stored under argon in dark ampoules. All reactions were carried out under argon atmosphere in well-dried glassware.

Synthesis of (*R*)-3,3'-bis(2-Hydroxy-3-isopropylbenzyl)-[1,1']binaphthalene-2,2'-diol (10c**):** A solution of (*R*)-2,2'-Bis(methoxy-methoxy)-1,1'-binaphthalene (5.33 g, 14.23 mmol) in THF (90 mL) was cooled to -78 °C, and to this was added *sec*-BuLi (0.99 M, in hexane, cyclohexane) slowly, and the mixture was stirred for 30 min. at the same temperature. The reaction mixture was then allowed to warm to 0 °C and stirred for 1.5 hr at that temperature, and subsequently cooled down to -78 °C. The solution of 3-isopropyl-2-methoxybenzaldehyde (11.85 g, 56.9 mmol) in THF (30 mL) was added, and warmed up to room temperature and stirred for over night. The reaction was quenched by the addition of saturated ammonium chloride aqueous solution, and extracted twice with diethyl ether. Combined organic layer was washed with water, and brine, and dried over anhydrous sodium sulfate. The solvent was removed *in vacuo*, and the residue was purified on silica gel column chromatography to afford (*R*)-(2,2'-Dimethoxy-methoxy-[1,1']binaphthyl-3-yl)- (3-isopropyl-2-methoxymethoxyphenyl) methanol as a mixture of diastereomers (11.28 g). The product was dissolved in dichloromethane (120 mL) and the mixture was cooled to 0 °C. A saturated solution of hydrogen chloride in methanol (45 mL) was added to the mixture and the whole was stirred for 30 min. At the end of this time the reaction mixture was neutralized by the addition of saturated aqueous NaHCO₃ solution and the whole was extracted twice with dichloromethane and the combined organic layers were washed with water and dried over anhydrous Na₂SO₄. Filtration and removal of solvent *in vacuo* gave a residue which was dissolved in

dichloromethane (70 mL) and cooled to 0 °C. To the solution, triethylsilane (8.62 g, 74.1 mmol) in dichloromethane (35 mL) and trifluoroborane diethyl ether complex (10.72 g, 75.5 mmol) in dichloromethane (35 mL) were added successively, and the mixture was stirred at the same temperature over night. The reaction was quenched with saturated aqueous NaHCO₃ solution, and extracted with two portions of dichloromethane. The combined organic layers were washed with water, and brine, and dried over anhydrous Na₂SO₄. Filtration and removal of solvent *in vacuo* to gave a residue that was purified by silica gel column chromatography to afford the title compound (5.76 g, 9.89 mmol, 69 % yield in 3 steps).

(R)-3,3'-Bis(2-hydroxy-3-isopropylbenzyl)-[1,1']binaphthalene-2,2'-diol (10c): $[\alpha]_D^{20} +38.9$ (*c* 1.01, CHCl₃). Mp 115-117 °C. IR (KBr) 3445, 2959, 1626, 1451, 1208, 1088, 753 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.22 (d, 12H, *J* = 8.0 Hz), 3.25 (sept, 2H, *J* = 6.8 Hz), 4.19 (d, 4H, *J* = 15.1 Hz), 5.67(s, 2H), 6.46 (s, 2H), 6.91 (dd, 2H, *J* = 7.5, 7.5 Hz), 7.05 (d, 2H, *J* = 8.1 Hz), 7.23 (m, 6H), 7.35 (dd, 2H, *J* = 8.0 Hz), 7.82 (d, 2H, *J* = 8.01 Hz), 7.93 (s, 2H). ¹³C NMR (CDCl₃): δ_C 22.6, 22.7, 27.1, 31.5, 111.4, 120.7, 124.0, 124.6, 124.9, 125.8, 127.2, 128.1, 128.1, 128.9, 129.9, 131.3, 132.0, 135.8, 149.9, 151.1. HPLC Daicel Chiralpak AD-H, hexane/ⁱPrOH = 19/1, flow rate = 1.0 mL/min: *t*_R = 13.1 min (*S*), *t*_R = 15.8 min (*R*). MS: Calcd for C₄₀H₃₈O₄ (M + Na⁺) 605, found 605. Anal. Calcd for C₄₀H₃₈O₄: C, 82.44; H, 6.57; N, 0.00. found: C, 82.38; H, 6.71; N, 0.00.

cis-1, 2-Epoxy-4-cyclohexene (3): Prepared according to literature procedure²

Bp 58 °C (20 mmHg). ¹H NMR (CDCl₃): δ_H 2.49 (dd, 4H, *J* = 18.0, 26.7 Hz), 3.22 (s, 2H), 5.42 (s, 2H). ¹³C NMR (CDCl₃): δ_C 24.8, 50.7, 121.3.

cis-3,4-Epoxyhexane (13b): Prepared according to literature procedure² Bp 90-95 °C. ¹H NMR (CDCl₃): δ_H 1.03 (m, 6H), 1.46-1.58 (m, 4H), 2.85-2.89 (m, 2H). ¹³C NMR (CDCl₃): δ_C 10.5, 20.9, 58.4.

cis-4,5-Epoxyoctane (13c): Prepared according to literature procedure² Bp 120-122 °C. ¹H NMR (CDCl₃): δ_H 0.99 (t, 6H, *J* = 6.9 Hz), 1.46-1.59 (m, 8H), 2.93 (m, 2H). ¹³C NMR (CDCl₃): δ_C 13.9, 19.8, 29.8, 56.8.

2,3-Epoxy-1,4-dihydronaphthalene (13f): Prepared according to literature procedure² ¹H NMR (CDCl₃): δ_{H} 3.32 (dd, 4H, $J = 17.4, 32.5$ Hz), 3.54 (s, 2H), 7.11 (m, 2H), 7.21 (m, 2H). ¹³C NMR (CDCl₃): δ_{C} 29.7, 51.7, 126.5, 129.2, 131.5.

***tert*-Butyl 6-oxa-3-aza-bicyclo[3.1.0]hexane-3-carboxylate (13i):** Prepared according to literature procedure² ¹H NMR (CDCl₃): δ_{H} 1.50 (s, 9H), 3.37 (dd, 2H, $J = 4.8, 12.4$ Hz), 3.72 (d, 2H, $J = 3.7$ Hz), 3.80 (d, 1H, $J = 12.8$ Hz), 3.87 (d, 1H, $J = 12.8$ Hz). ¹³C NMR (CDCl₃): δ_{C} 28.3, 46.7, 47.1, 54.9, 55.4, 79.6, 154.6.

Benzyl 6-oxa-3-aza-bicyclo[3.1.0]hexane-3-carboxylate (13j): ¹H NMR (CDCl₃): δ_{H} 3.30 (ddd, 2H, $J = 1.4, 9.3, 12.7$ Hz), 3.60 (dd, 2H, $J = 1.4, 6.2$ Hz), 3.78 (dd, 2H, $J = 12.7, 19.2$ Hz), 5.02 (d, 1H, $J = 8.8$ Hz), 5.04 (d, 1H, $J = 8.8$ Hz), 7.23 (m, 5H). ¹³C NMR (CDCl₃): δ_{C} 47.11, 47.39, 54.90, 55.46, 66.95, 127.89, 127.99, 128.44, 136.53, 155.20.

6-Oxa-3-oxa-bicyclo[3.1.0]hexane (13k): ¹H NMR (CDCl₃): δ_{H} 3.61 (dd, 2H, $J = 2.8, 10.4$ Hz), 3.55 (m, 2H), 3.98 (dd, 2H, $J = 3.2, 10.4$ Hz). ¹³C NMR (CDCl₃): δ_{C} 55.80, 67.24.

Typical Procedure for Asymmetric Epoxide Ring-opening with Amines. To a solution of ligand 1 (0.044 mmol) in toluene (0.4 mL) was added a solution of Nb(OMe)₅ (0.04 mmol) in toluene (0.60 mL) at 60 °C and the mixture was stirred at that temperature for 3 h. In a separate 2-necked flask under an Ar atmosphere were placed MS 4Å (100 mg) and the whole was maintained at 60 °C. To this was added the catalyst solution *via* cannular and the donor flask was rinsed with a further 0.5 mL of toluene and this was added to the flask containing the MS 4Å. After stirring for 30 min., the catalyst solution was cooled to the desired reaction temperature (see Table 1 in main text) and to this were added successively the epoxide (0.48 mmol) in CH₂Cl₂ (0.5 mL) and the amine (0.40 mmol) in CH₂Cl₂ (0.5 mL). The mixture was stirred for 18 h whereupon the reaction was stopped by the addition of saturated aqueous NaHCO₃, and the aqueous layers were extracted twice with CH₂Cl₂. The combined organic layers were washed with brine, and dried over anhydrous Na₂SO₄. The solvent was removed *in vacuo*, and the

residue was purified by preparative TLC (hexane : ethyl acetate = 3 : 1) The enantioselectivity of the reaction was determined by chiral column HPLC analysis.

(2*R*,3*R*)-2-*N*-phenylamino-3-butanol (14aa): $[\alpha]_{\text{D}}^{20}$ -88.0 (*c* 1.07, 90% ee, CH₂Cl₂) [lit.³ for (2*R*,3*R*), $[\alpha]_{\text{D}}^{20}$ -36.2 (*c* 1.5, 43% ee, CH₂Cl₂)]. IR (KBr) 3398, 3053, 2974, 2926, 1922, 1602, 1505, 1439, 1376, 1318, 1254, 1005, 902, 751, 692 cm⁻¹. ¹H NMR (CDCl₃): δ_{H} 1.14 (d, 1H, *J* = 6.8 Hz), 1.25 (d, 3H, *J* = 6.8 Hz), 2.61 (brs, 1H), 3.31 (m, 1H), 3.62 (m, 2H), 6.66-6.74 (m, 3H), 7.15-7.18 (m, 2H). ¹³C NMR (CDCl₃): δ_{C} 17.3, 19.5, 56.1, 71.4, 114.3, 118.2, 129.3, 147.7. HPLC Daicel Chiralcel OD, hexane/*i*PrOH = 40/1, flow rate = 1.0 mL/min: *t*_R = 27.1 min (2*S*, 3*S*), *t*_R = 32.4 min (2*R*, 3*R*). MS: Calcd for C₁₀H₁₅NO (*M* + *H*⁺) 166, found 166. Anal. Calcd for C₁₀H₁₅NO: C, 72.69; H, 9.15; N, 8.48. found: C, 72.63; H, 9.18; N, 8.36.

(2*R*,3*R*)-2-*N*-(2'-tolyl)amino-3-butanol (14ab): $[\alpha]_{\text{D}}^{20}$ -102.8 (*c* 1.04, 84% ee, CHCl₃). IR (KBr) 3414, 2972, 2923, 1601, 1511, 1448, 1378, 1313, 1256, 1056, 748, 512 cm⁻¹. ¹H NMR (CDCl₃): δ_{H} 1.18 (d, 3H, *J* = 6.2 Hz), 1.28 (d, 3H, *J* = 6.2 Hz), 2.16 (s, 3H), 3.40 (t, 1H, *J* = 6.2 Hz), 3.70 (t, 1H, *J* = 6.2 Hz), 6.68-6.73 (m, 2H), 7.07 (d, 1H), 7.11 (d, 1H). ¹³C NMR (CDCl₃): δ_{C} 17.5, 17.7, 19.6, 55.6, 71.4, 111.3, 117.6, 123.0, 127.2, 130.4, 145.6. HPLC Daicel Chiralcel OD, hexane/*i*PrOH = 40/1, flow rate = 0.8 mL/min: *t*_R = 21.3 min (2*R*, 3*R*), *t*_R = 26.4 min (2*S*, 3*S*). MS: Calcd for C₁₁H₁₇NO (*M* + *H*⁺) 180, found 180. Anal. Calcd for C₁₁H₁₇NO: C, 73.70; H, 9.56; N, 7.81. found: C, 73.49; H, 9.55; N, 7.68

(2*R*,3*R*)-2-*N*-(3'-tolyl)amino-3-butanol (14ac): $[\alpha]_{\text{D}}^{20}$ -77.2 (*c* 1.07, 93% ee, CHCl₃). IR (KBr) 3398, 2972, 2924, 1714, 1607, 1490, 1375, 1321, 1173, 771, 693, 527 cm⁻¹. ¹H NMR (CDCl₃): δ_{H} 1.13 (dd, 3H, *J* = 6.2, 6.9 Hz), 1.25 (dd, 3H, *J* = 6.2, 6.8 Hz), 2.28 (s, 3H), 3.32 (ddd, 1H, *J* = 6.2, 6.9, 13.2 Hz), 3.62 (ddd, 1H, *J* = 6.2, 6.9, 13.2 Hz), 6.49-6.51 (m, 2H), 6.57 (d, 1H), 7.07 (t, 1H). ¹³C NMR (CDCl₃): δ_{C} 17.1, 19.5, 21.6, 56.7, 71.3, 111.9, 115.5, 119.7, 129.2, 139.2, 147.1. HPLC Daicel Chiralpak AD-H, hexane/*i*PrOH = 40/1, flow rate = 0.8 mL/min: *t*_R = 20.7 min (2*S*, 3*S*), *t*_R = 22.2 min (2*R*, 3*R*). MS: Calcd for C₁₁H₁₇NO (*M* + *H*⁺) 180, found 180. Anal. Calcd for C₁₁H₁₇NO: C, 73.70; H, 9.56; N, 7.81. found: C, 73.42; H, 9.61; N, 7.94.

(2R,3R)-2-N-(4'-tolyl)amino-3-butanol (14ad): $[\alpha]_D^{20}$ -73.8 (*c* 1.23, 91% ee, CHCl₃). IR (KBr) 3397, 2973, 2925, 2867, 1619, 1519, 1450, 1378, 1308, 1113, 807 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.13 (d, 3H, *J* = 6.4 Hz), 1.25 (d, 3H, *J* = 6.6 Hz), 2.24 (s, 3H), 3.26 (m, 1H), 3.59 (m, 1H), 6.60-6.63 (m, 2H), 6.95-7.01 (m, 2H). ¹³C NMR (CDCl₃): δ_C 17.2, 19.4, 20.4, 56.8, 71.4, 114.7, 127.7, 129.8, 145.3. HPLC Daicel Chiralpak AD, hexane/*i*PrOH = 40/1, flow rate = 1.0 mL/min: *t*_R = 19.2 min (2*R*, 3*R*), *t*_R = 21.0 min (2*S*, 3*S*). MS: Calcd for C₁₁H₁₇NO (*M* + *H*⁺) 180, found 180. Anal. Calcd for C₁₁H₁₇NO: C, 73.70; H, 9.56; N, 7.81. found: C, 73.51; H, 9.36; N, 7.77.

(2R,3R)-2-N-(2'-methoxyphenyl)amino-3-butanol (14ae): $[\alpha]_D^{20}$ -87.8 (*c* 1.28, 89% ee, CHCl₃). IR (KBr) 3414, 2970, 1602, 1510, 1456, 1249, 1220, 1110, 1025, 902, 737 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.21 (d, 3H, *J* = 8.3 Hz), 1.33 (d, 3H, *J* = 6.0 Hz), 2.78 (s, 1H), 3.40 (m, 1H), 3.74 (m, 1H), 3.91 (s, 3H), 4.13 (s, 1H), 6.75-6.80 (m, 2H), 6.85-6.87 (m, 1H), 6.91-6.96 (m, 1H). ¹³C NMR (CDCl₃): δ_C 17.2, 19.4, 55.4, 55.8, 71.4, 109.7, 111.4, 117.2, 121.2, 137.5, 147.5. HPLC Daicel Chiralcel OD, hexane/*i*PrOH = 19/1, flow rate = 1.0 mL/min: *t*_R = 15.0 min (2*R*, 3*R*), *t*_R = 21.8 min (2*S*, 3*S*). MS: Calcd for C₁₁H₁₇NO₂ (*M* + *H*⁺) 196, found 196. Anal. Calcd for C₁₁H₁₇NO₂: C, 67.66; H, 8.78; N, 7.17. found: C, 67.36; H, 8.85; N, 7.05.

(2R,3R)-2-N-(4'-methoxyphenyl)amino-3-butanol (14af): $[\alpha]_D^{20}$ -63.9 (*c* 1.32, 90% ee, CHCl₃). IR (KBr) 3394, 2970, 1617, 1512, 1455, 1377, 1236, 1037, 822 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.18 (d, 3H, *J* = 6.4 Hz), 1.32 (d, 3H, *J* = 6.0 Hz), 3.23 (t, 1H, *J* = 6.9 Hz), 3.63 (t, 1H, *J* = 6.6 Hz), 3.81 (s, 3H), 6.71-6.75 (m, 2H), 6.83-6.86 (m, 2H). ¹³C NMR (CDCl₃): δ_C 17.1, 19.4, 55.7, 58.0, 71.4, 114.9, 116.3, 141.0, 152.9. HPLC Daicel Chiralpak AD, hexane/*i*PrOH = 19/1, flow rate = 1.0 mL/min: *t*_R = 15.9 min (2*R*, 3*R*), *t*_R = 17.9 min (2*S*, 3*S*). MS: Calcd for C₁₁H₁₇NO₂ (*M* + *H*⁺) 196, found 196. Anal. Calcd for C₁₁H₁₇NO₂: C, 67.66; H, 8.78; N, 7.17. found: C, 67.45; H, 8.85; N, 7.20.

(2R,3R)-2-N-(3'-trifluoromethylphenyl)amino-3-butanol (14ag): $[\alpha]_D^{20}$ -61.5 (*c* 1.16, 96% ee, CHCl₃). IR (KBr) 3401, 2975, 2927, 2342, 1616, 1519, 1440, 1343, 1167, 1124, 1066, 1002, 866, 785, 698 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.18 (d, 3H, *J* = 6.4 Hz), 1.26 (d, 3H, *J* = 6.4 Hz), 2.25 (s, 1H), 3.38 (t,

1H, $J = 6.4$ Hz), 3.71 (t, 1H, $J = 6.4$ Hz), 6.78-6.95 (m, 3H), 7.23-7.27 (m, 1H). ^{13}C NMR (CDCl_3): δ_{C} 17.2, 19.7, 55.2, 71.1, 110.0, 114.2, 116.8, 124.4 (J (C-F) = 270 Hz), 129.7, 131.6 (J (C-F) = 31.5 Hz), 148.0 HPLC Daicel Chiralcel OD, hexane/ i PrOH = 40/1, flow rate = 0.8 mL/min: $t_{\text{R}} = 19.3$ min (2*R*, 3*R*), $t_{\text{R}} = 21.9$ min (2*S*, 3*S*). MS: Calcd for $\text{C}_{11}\text{H}_{14}\text{F}_3\text{NO}$ ($\text{M} + \text{H}^+$) 234, found 234. Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{F}_3\text{NO}$: C, 56.65; H, 6.05; N, 6.01. found: C, 56.63; H, 5.87; N, 6.06.

(2*R*, 3*R*)-2-*N*-(3', 5'-bistrifluoromethylphenyl)amino-3-butanol (14ah): $[\alpha]_{\text{D}}^{20} -48.7$ (c 1.63, 96% ee, CHCl_3). IR (KBr) 3410, 2979, 1622, 1521, 1475, 1434, 1396, 1278, 1172, 1126, 1016, 864, 701, 683 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.22 (d, 3H, $J = 6.4$ Hz), 1.28 (d, 3H, $J = 6.4$ Hz), 1.94 (s, 1H), 3.43 (m, 1H), 3.80 (m, 1H), 4.19 (s, 1H), 6.96 (s, 2H), 7.13 (s, 1H). ^{13}C NMR (CDCl_3): δ_{C} 17.2, 20.1, 54.5, 70.9, 110.3 (J (C-F) = 3.1 Hz), 112.6 (J (C-F) = 2.9 Hz), 122.2, 124.9, 127.6, 132.5 (J (C-F) = 33.3 Hz), 148.4. HPLC Daicel Chiralpak AD, hexane/ i PrOH = 40/1, flow rate = 1.0 mL/min: $t_{\text{R}} = 11.6$ min (2*R*, 3*R*), $t_{\text{R}} = 14.3$ min (2*S*, 3*S*). MS: Calcd for $\text{C}_{12}\text{H}_{13}\text{F}_6\text{NO}$ ($\text{M} + \text{H}^+$) 302, found 302. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{F}_6\text{NO}$: C, 47.85; H, 4.35; N, 4.65. found: C, 48.02; H, 4.67; N, 4.45.

(2*R*, 3*R*)-2-*N*-(4'-bromophenyl)amino-3-butanol (14ai): $[\alpha]_{\text{D}}^{20} -56.6$ (c 1.87, 95% ee, CHCl_3). IR (KBr) 3400, 2973, 1593, 1492, 1390, 1315, 1080, 1006, 813, 453 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.14 (dd, 1H, $J = 6.2$ Hz), 1.24 (d, 3H, $J = 6.2$ Hz), 2.45 (s, 1H), 3.27 (t, 1H, $J = 6.9$ Hz), 3.53 (s, 1H), 3.65 (t, 1H, $J = 6.2$ Hz), 6.53 (m, 2H), 7.23 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 17.2, 19.6, 55.8, 71.2, 109.5, 115.6, 132.0, 146.8. HPLC Daicel Chiralcel OD, hexane/ i PrOH = 40/1, flow rate = 1.0 mL/min: $t_{\text{R}} = 29.3$ min (2*S*, 3*S*), $t_{\text{R}} = 38.6$ min (2*R*, 3*R*). MS: Calcd for $\text{C}_{10}\text{H}_{14}\text{BrNO}$ ($\text{M} + \text{H}^+$) 244, found 244. Anal. Calcd for $\text{C}_{10}\text{H}_{14}\text{BrNO}$: C, 49.20; H, 5.78; N, 5.74. found: C, 49.26; H, 5.74; N, 5.70.

(3*R*,4*R*)-3-*N*-phenylamino-4-hexanol (14ba): $[\alpha]_{\text{D}}^{20} +2.1$ (c 0.97, 45% ee, CHCl_3). IR (KBr) 3128, 2966, 2931, 2872, 1602, 1505, 1458, 1378, 1318, 1271, 1147, 969, 866, 749, 691 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.00 (t, 3H, $J = 7.4$ Hz), 1.06 (t, 3H, $J = 7.3$ Hz), 1.55-1.77 (m, 4H), 3.29 (dt, 1H, $J = 5.0$, 7.3 Hz), 3.58-3.62 (m, 1H), 6.70-6.77 (m, 3H), 7.20-7.24 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 10.2, 10.6, 25.2, 26.9, 59.2, 74.5, 113.5, 117.4, 129.3, 148.6. HPLC Daicel Chiralcel OD, hexane/ i PrOH = 40/1,

flow rate = 1.0 mL/min: t_R = 13.8 min (3*R*, 4*R*), t_R = 15.9 min (3*S*, 4*S*). HRMS: Calcd for C₁₂H₁₉NO (M + H⁺) 194.1539, found 194.1530.

(4*R*,5*R*)-4-*N*-phenylamino-5-octanol (14ca): $[\alpha]_D^{20}$ +2.76 (*c* 1.32, 54% ee, CHCl₃). IR (KBr) 3402, 3052, 2961, 2866, 1601, 1504, 1458, 1317, 1259, 1146, 1020, 865, 747, 691 cm⁻¹. ¹H NMR (CDCl₃): δ_H 0.94-1.01 (m, 6H), 1.38-1.68 (m, 8H), 2.12 (m, 2H), 3.32-3.36 (m, 1H), 3.64-3.68 (m, 1H), 6.69-6.77 (m, 3H), 7.19-7.23 (m, 2H). ¹³C NMR (CDCl₃): δ_C 14.1, 14.2, 19.1, 19.4, 34.7, 36.2, 58.4, 73.2, 113.8, 117.8, 129.3, 148.2. HPLC Daicel Chiralcel OD, hexane/*i*PrOH = 19/1, flow rate = 1.0 mL/min: t_R = 6.1 min (4*R*, 5*R*), t_R = 7.2 min (4*S*, 5*S*). HRMS: Calcd for C₁₄H₂₃NO (M + H⁺) 222.1852, found 222.1859.

(4*R*,5*R*)-4-*N*-phenylamino-5-decanol (14da): $[\alpha]_D^{20}$ +1.91 (*c* 1.27, 31% ee, CHCl₃). IR (KBr) 2960, 2929, 2858, 1602, 1504, 1460, 1319, 1255, 1092, 746, 692 cm⁻¹. ¹H NMR (CDCl₃): δ_H 0.81 (m, 6H), 1.19-1.59 (m, 12H), 3.17-3.22 (m, 1H), 3.50-3.54 (m, 1H), 6.59 (d, 2H, *J* = 7.8 Hz), 6.64 (d, 1H, *J* = 7.3 Hz), 7.09 (t, 2H, *J* = 7.8 Hz). ¹³C NMR (CDCl₃): δ_C 14.0, 14.1, 22.7, 22.8, 28.1, 28.3, 32.1, 33.8, 58.4, 73.4, 113.7, 117.6, 129.3, 148.3. HPLC Daicel Chiralcel OD, hexane/*i*PrOH = 40/1, flow rate = 1.0 mL/min: t_R = 9.8 min (5*R*, 6*R*), t_R = 12.6 min (5*S*, 6*S*). HRMS: Calcd for C₁₆H₂₈NO (M + H⁺) 250.2165, found 250.2155.

(2*R*,3*R*)-1,2-diphenyl-2-(*N*-phenylamino)ethanol (14ea): $[\alpha]_D^{20}$ -67.2 (*c* 0.45, 85% ee, CHCl₃). IR (KBr) 3395, 2926, 1601, 1500, 1445, 1321, 1243, 1038, 753, 694 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.01 (d, 3H, *J* = 6.4 Hz), 3.12 (brs, 1H), 3.53 (brs, 1H), 3.71-3.77 (m, 1H), 4.59 (d, 2H, *J* = 7.3 Hz), 6.78-6.86 (m, 3H), 7.25-7.29 (m, 2H), 7.36-7.48 (m, 5H). ¹³C NMR (CDCl₃): δ_C 17.0, 56.2, 77.7, 114.5, 118.5, 127.0, 128.0, 128.3, 129.4, 141.0, 147.4. HPLC Daicel Chiralcel OD, hexane/*i*PrOH = 40/1, flow rate = 1.0 mL/min: t_R = 41.2 min (1*R*, 2*R*), t_R = 50.7 min (1*S*, 2*S*). HRMS: Calcd for C₁₅H₁₇NO (M⁺ + H⁺) 228.1383, found 228.1373.

(1*R*,2*R*)-2-*N*-phenylamino-1,4-dihydronaphthalene (14fa): $[\alpha]_D^{20}$ -94.3 (*c* 1.54, 71% ee, CHCl₃). IR (KBr) 3384, 3021, 2920, 1602, 1500, 1434, 1314, 1059, 744, 697 cm⁻¹. ¹H NMR (CDCl₃): δ_H 2.91 (dd, 1H, *J* = 6.9, 9.7 Hz), 3.20 (m, 1H, *J* = 7.3, 9.2 Hz), 3.53-3.62 (m, 2H), 3.96 (dt, 1H, *J* = 4.0, 5.5

Hz) , 4.20 (dt, 1 H, $J = 3.7, 5.5$ Hz), 7.00-7.06 (m, 3H), 7.37-7.50 (m, 6H). ^{13}C NMR (CDCl_3): δ_{C} 35.3, 36.7, 56.2, 70.7, 114.3, 118.7, 126.2, 126.4, 128.7, 129.1, 129.3, 129.4, 133.9, 133.9, 147.5. HPLC Daicel Chiralcel OD, hexane/ i PrOH = 19/1, flow rate = 1.0 mL/min: $t_{\text{R}} = 28.5$ min (2*S*, 3*S*), $t_{\text{R}} = 41.6$ min (2*R*, 3*R*). MS: Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}$ ($\text{M} + \text{H}^+$) 240, found 240. Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}$: C, 80.30; H, 7.16; N, 5.85. found: C, 80.13; H, 7.43; N, 5.71.

(1*R*,2*R*)-2-*N*-phenylamino-1-cyclohex-2-en-ol (14ga): $[\alpha]_{\text{D}}^{20} -61.8$ (c 1.28, 82% ee, CHCl_3). IR (KBr) 3392, 3027, 2914, 2219, 1602, 1505, 1434, 1320, 1254, 1058, 868, 748, 695, 666 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.93-2.01 (m, 1H), 2.22-2.30 (m, 1H), 2.62-2.70 (m, 2H), 2.81 (s, 1H) , 3.46 (s, 1H), 3.58 (dt, 1H, $J = 3.7, 5.5$ Hz) , 3.83 (dt, 1H, $J = 3.2, 5.9$ Hz) , 5.66 (dt, 1H, $J = 3.2, 8.7$ Hz), 6.80-6.84 (m, 3H), 7.23-7.27 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 31.9, 33.1, 55.8, 70.4, 114.2, 118.5, 124.7, 124.8, 129.3, 147.7. HPLC Daicel Chiralcel OD, hexane/ i PrOH = 40/1, flow rate = 1.0 mL/min: $t_{\text{R}} = 37.0$ min (1*S*, 2*S*), $t_{\text{R}} = 52.1$ min (1*R*, 2*R*). MS: Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}$ ($\text{M} + \text{H}^+$) 190, found 190. Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}$: C, 76.16; H, 7.99; N, 7.40. found: C, 75.89; H, 8.10; N, 7.18.

(1*R*,2*R*)-2-*N*-phenylamino-cyclopentanol (14ha): ^1H NMR (CDCl_3): δ_{H} 1.44-1.51 (m, 1H), 1.68-2.37 (m, 4H), 2.30-2.37 (m, 1H), 3.68 (dd, 1H, $J = 6.4, 10.5$ Hz), 4.13 (q, 1H, $J = 4.9$ Hz), 6.72-6.79 (m, 3H), 7.22-7.26 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 20.9, 31.1, 32.8, 62.1, 78.1, 113.3, 117.6, 129.2, 147.6. HPLC Daicel Chiralpak AD, hexane/ i PrOH = 19/1, flow rate = 0.8 mL/min: $t_{\text{R}} = 22.1$ min (1*R*, 2*R*), $t_{\text{R}} = 24.2$ min (1*S*,2*S*).

(1*R*,2*R*)-*tert*-butyl 3-hydroxy-4-(phenylamino)pyrrolidine-1-carboxylate (4ia): $[\alpha]_{\text{D}}^{20} +19.3$ (c 1.72, 89% ee, CHCl_3). IR (KBr) 3361, 2977, 2930, 2878, 1685, 1601, 1506, 1424, 1324, 1256, 1171, 1118, 876, 844, 747, 695 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.51 (s, 9H), 3.33-3.48 (m, 2H), 3.70 (s, 1H), 3.91 (d, 1H, $J = 11.0$ Hz), 4.35 (s, 1H), 6.72-6.74 (m, 2H), 6.82-6.86 (m, 1H), 7.25-7.28 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 28.3, 46.8, 47.2, 55.0, 55.5, 79.9, 113.0, 117.8, 129.2, 146.5, 154.8. HPLC Daicel Chiralcel OD, hexane/ i PrOH = 9/1, flow rate = 1.0 mL/min: $t_{\text{R}} = 14.1$ min (1*S*, 2*S*), $t_{\text{R}} = 20.3$ min (1*R*,2*R*). HRMS: Calcd for $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_3$ ($\text{M} + \text{H}^+$) 279.1703, found 279.1700.

(1*R*,2*R*)-Benzyl 3-hydroxy-4-(phenylamino)pyrrolidine-1-carboxylate (14ja): $[\alpha]_{\text{D}}^{20} +16.9$ (*c* 1.67, 87% ee, CHCl₃). ¹H NMR (CDCl₃): δ 3.38 (dd, 2H, *J* = 4.6, 12.8 Hz), 3.67 (s, 2H), 3.86 (dd, 2H, *J* = 12.8, 16.9 Hz), 4.28 (d, 2H, *J* = 13.7 Hz), 5.10 (d, 2H, *J* = 4.1 Hz), 6.61-6.76 (m, 3H), 7.16-7.35 (m, 7H). ¹³C NMR (CDCl₃ rotamers): δ_C 47.1, 47.4, 50.3, 50.5, 51.9, 52.3, 54.9, 55.5, 58.7, 59.3, 67.1, 72.9, 73.7, 113.1, 118.2, 127.9, 128.0, 128.5, 129.4, 136.4, 136.5, 146.2, 155.3. HPLC Daicel Chiralcel OD, hexane/*i*PrOH = 4/1, flow rate = 1.0 mL/min: *t*_R = 17.3 min (3*S*, 4*S*), *t*_R = 23.7 min (3*R*, 4*R*). HRMS: Calcd for C₁₆H₂₁F₃N₂O₃ (M⁺ + H⁺) 313.1547, found 313.1559.

(1*R*,2*R*)-4-oxa-2-*N*-phenylamino-cyclopentanol (14ka): $[\alpha]_{\text{D}}^{20} +27.4$ (*c* 0.54, 75% ee, CHCl₃). IR (KBr) 3349, 2949, 2873, 1601, 1504, 1316, 1074, 903, 752, 692 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.98 (brs, 1H), 3.74-3.78 (m, 1H), 3.81-3.85 (m, 1H), 3.96 (s, 1H), 4.08-4.13 (m, 1H), 4.31-4.37 (m, 2H), 6.72-6.75 (m, 2H), 6.81-6.85 (m, 1H), 7.25-7.34 (m, 2H). ¹³C NMR (CDCl₃): δ_C 61.7, 72.5, 74.6, 76.0, 113.2, 118.2, 129.5, 146.4. HPLC Daicel Chiralcel OD, hexane/*i*PrOH = 19/1, flow rate = 1.0 mL/min: *t*_R = 53.5 min (1*S*, 2*S*), *t*_R = 59.3 min (1*R*, 2*R*). HRMS: Calcd for C₁₀H₁₃NO₂ (M + H⁺) 180.1019, found 180.1014.

(1*R*,6*R*)-6-(3-(trifluoromethyl)phenylamino)cyclohex-3-enol (14gg): $[\alpha]_{\text{D}}^{20} -38.7$ (*c* 1.18, 88% ee, CHCl₃). IR (KBr) 3402, 3034, 2919, 2845, 1614, 1520, 1441, 1344, 1277, 1249, 1164, 1122, 1066, 994, 916, 862, 785, 698, 664 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.91-1.97 (m, 1H), 2.18-2.24 (m, 1H), 2.59 (ddd, 2H, *J* = 6.2, 13.7, 22.4 Hz), 3.54 (td, 1H, *J* = 5.6, 9.2 Hz), 3.80 (td, 1H, *J* = 5.9, 8.9 Hz), 5.63 (s, 2H), 6.86-6.98 (m, 3H), 7.24-7.28 (m, 1H). ¹³C NMR (CDCl₃): δ_C 31.6, 33.0, 55.4, 70.2, 110.2, 114.7, 116.9, 124.4, 124.7, 129.8, 147.9. HPLC Daicel Chiralpak AD-H, hexane/*i*PrOH = 40/1, flow rate = 1.0 mL/min: *t*_R = 20.3 min (1*S*, 6*S*), *t*_R = 22.3 min (1*R*, 6*R*). HRMS: Calcd for C₁₃H₁₄F₃NO (M⁺ + H⁺) 258.11, found 258.1097.

(1*R*,2*R*)-2-(3'-(trifluoromethyl)phenylamino)cyclopentanol (14hg): $[\alpha]_{\text{D}}^{20} -13.8$ (*c* 1.44, 89% ee, CHCl₃). IR (KBr) 3360, 2963, 1614, 1440, 1346, 1163, 1120, 1069, 785, 698 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.42 (td, 1H, *J* = 7.0, 13.9 Hz), 1.66 (dq, 1H, *J* = 4.6, 18.0 Hz), 1.76 (tt, 1H, *J* = 4.4, 13.7 Hz), 1.84 (td,

1H, $J = 7.3, 14.3$ Hz), 2.00 (td, 1H, $J = 6.9, 13.7$ Hz), 2.29 (td, 1H, $J = 7.8, 13.3$ Hz), 4.07 (q, 1H, $J = 5.0$ Hz), 6.80-6.94 (m, 3H), 7.23-7.27 (m, 1H). ^{13}C NMR (CDCl_3): δ_{C} 20.9, 31.1, 33.1, 61.9, 78.1, 109.5, 113.9, 116.1, 129.7, 131.4, 131.6, 147.8. HPLC Daicel Chiralpak AD-H x2, hexane/ i PrOH = 39/1, flow rate = 1.0 mL/min: $t_{\text{R}} = 58.0$ min (1*R*, 2*R*), $t_{\text{R}} = 61.2$ min (1*S*, 2*S*). HRMS: Calcd for $\text{C}_{12}\text{H}_{14}\text{F}_3\text{NO}$ ($\text{M}^+ + \text{H}^+$) 246.11, found 246.1108.

(2*R*,3*R*)-2-*N*-phenylamino-3-pentanol (16aa): $[\alpha]_{\text{D}}^{20} -64.3$ (c 0.92, 95% ee, CHCl_3). IR (KBr) 3401, 3051, 2969, 2873, 1602, 1506, 1457, 1315, 1252, 1072, 975, 748, 693 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.07 (t, 3H, $J = 7.3$ Hz), 1.22 (d, 3H, $J = 6.0$ Hz), 1.53-1.62 (m, 1H), 1.70-1.76 (m, 1H), 2.47 (brs, 1H), 3.47-3.53 (m, 3H), 6.71-6.80 (m, 3H), 7.21-7.25 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 10.0, 17.5, 26.4, 53.8, 76.5, 114.2, 118.0, 129.3, 147.8. HPLC Daicel Chiralcel OD, hexane/ i PrOH = 40/1, flow rate = 1.0 mL/min: $t_{\text{R}} = 18.7$ min (2*R*, 3*R*), $t_{\text{R}} = 25.7$ min (2*S*, 3*S*). MS: Calcd for $\text{C}_{11}\text{H}_{17}\text{NO}$ ($\text{M} + \text{H}^+$) 180, found 180. Anal. Calcd for $\text{C}_{11}\text{H}_{17}\text{NO}$: C, 73.70; H, 9.56; N, 7.81. found: C, 73.58; H, 9.67; N, 7.85.

(2*R*,3*R*)-2-(2-tolylamino)pentan-3-ol (16ab): $[\alpha]_{\text{D}}^{23} -75.3$ (c 0.61, 88% ee, CHCl_3). IR (KBr) 3435, 2968, 2930, 2875, 1605, 1584, 1512, 1448, 1377, 1315, 1255, 1165, 1050, 976, 908, 746 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.02 (t, 3H, $J = 7.6$ Hz), 1.19 (d, 3H, $J = 6.2$ Hz), 1.54 (q, 1H, $J = 7.1$ Hz), 1.69 (dq, 1H, $J = 7.1, 13.9$ Hz), 2.16 (s, 3H), 3.47-3.50 (m, 2H), 6.67-6.71 (m, 2H), 7.06-7.13 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 10.0, 17.6, 17.6, 26.4, 53.6, 76.5, 111.4, 117.7, 123.1, 127.1, 130.4, 145.3. HPLC Daicel Chiralpak AD-H, hexane/ i PrOH = 9/1, flow rate = 0.5 mL/min: $t_{\text{R}} = 9.0$ min (2*R*, 3*R*), $t_{\text{R}} = 9.9$ min (2*S*, 3*S*). HRMS: Calcd for $\text{C}_{12}\text{H}_{19}\text{NO}$ ($\text{M} + \text{H}^+$) 194.1539, found 194.1533.

(2*R*,3*R*)-2-(2-methoxyphenylamino)pentan-3-ol (16ae): $[\alpha]_{\text{D}}^{23} -58.1$ (c 1.68, 89% ee, CHCl_3). IR (KBr) 3422, 3065, 2968, 2933, 2875, 2833, 1600, 1514, 1458, 1428, 1341, 1246, 1220, 1173, 1113, 1029, 977, 904, 866, 737 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.02 (t, 3H, $J = 7.6$ Hz), 1.15 (d, 3H, $J = 6.2$ Hz), 1.54 (q, 1H, $J = 7.1$ Hz), 1.64-1.72 (m, 1H), 2.16 (s, 3H), 3.34-3.47 (m, 2H), 3.83 (s, 3H), 6.67-6.71 (m, 2H), 6.77-6.87 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 10.0, 17.4, 26.3, 53.7, 55.4, 76.4, 109.7, 111.3, 117.1, 121.2, 137.4, 147.5. HPLC Daicel Chiralpak AD-H, hexane/ i PrOH = 9/1, flow rate = 0.5 mL/min: $t_{\text{R}} =$

11.7 min (2*R*, 3*R*), t_R = 12.8 min (2*S*, 3*S*). HRMS: Calcd for C₁₂H₁₉NO₂ (M + H⁺) 210.1489, found 210.1486.

(1*R*,2*R*)-1-phenyl-2-*N*-phenylamino-propanol (16ba): $[\alpha]_D^{20}$ -67.2 (*c* 0.45, 85% ee, CHCl₃). IR (KBr) 3395, 2926, 1601, 1500, 1445, 1321, 1243, 1038, 753, 694 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.01 (d, 3H, *J* = 6.4 Hz), 3.12 (brs, 1H), 3.53 (brs, 1H), 3.71-3.77 (m, 1H), 4.59 (d, 2H, *J* = 7.3 Hz), 6.78-6.86 (m, 3H), 7.25-7.29 (m, 2H), 7.36-7.48 (m, 5H). ¹³C NMR (CDCl₃): δ_C 17.0, 56.2, 77.7, 114.5, 118.5, 127.0, 128.0, 128.3, 129.4, 141.0, 147.4. HPLC Daicel Chiralcel OD, hexane/*i*PrOH = 40/1, flow rate = 1.0 mL/min: t_R = 41.2 min (1*R*, 2*R*), t_R = 50.7 min (1*S*, 2*S*). HRMS: Calcd for C₁₅H₁₇NO (M⁺ + H⁺) 228.1383, found 228.1373.

(2*R*,3*R*)-2-(2-tolylamino)hexan-3-ol (16bb): $[\alpha]_D^{23}$ -32.3(*c* 1.11, 90% ee, CHCl₃). IR (KBr) 3419, 2928, 1714, 1604, 1511, 1451, 1321, 1261, 1092, 803, 7456 cm⁻¹. ¹H NMR (CDCl₃): δ_H 0.88 (t, 3H, *J* = 7.2 Hz), 1.13 (d, 3H, *J* = 6.9 Hz), 1.39-1.59 (m, 4H), 2.10 (s, 3H), 3.37-3.41 (m, 1H), 3.49, (t, 1H, *J* = 4.5 Hz), 6.62-6.67 (m, 2H), 7.05-7.11 (m, 2H). ¹³C NMR (CDCl₃): δ_C 14.3, 17.5, 19.0, 35.8, 54.4, 55.5, 75.0, 109.8, 111.6, 117.4, 121.3, 137.5, 147.6. HPLC Daicel Chiralcel AD-H, hexane/*i*PrOH = 9/1, flow rate = 0.5 mL/min: t_R = 8.9 min (2*R*, 3*R*), t_R = 10.4 min (2*S*, 3*S*). HRMS: Calcd for C₁₃H₂₁NO (M + H⁺) 208.1696, found 208.1690.

(2*R*,3*R*)-2-(2-methoxyphenylamino)hexan-3-ol (16be): $[\alpha]_D^{23}$ -58.6 (*c* 0.33, 86% ee, CHCl₃). IR (KBr) 3417, 2964, 2871, 1601, 1512, 1460, 1247, 1221, 1175, 1029, 909, 734, 649 cm⁻¹. ¹H NMR (CDCl₃): δ_H 0.95 (t, 3H, *J* = 6.9 Hz), 1.15 (d, 3H, *J* = 6.2 Hz), 1.43-1.59 (m, 4H), 3.39, (t, 1H, *J* = 6.8 Hz), 3.50-3.52 (m, 1H), 3.84 (s, 3H), 6.67-6.71 (m, 2H), 6.77-6.87 (m, 2H). ¹³C NMR (CDCl₃): δ_C 17.2, 20.4, 20.4, 35.4, 55.6, 74.4, 115.0, 125.8, 128.1, 128.4, 128.5, 130.0, 142.1, 144.8. HPLC Daicel Chiralpak AD-H, hexane/*i*PrOH = 9/1, flow rate = 0.5 mL/min: t_R = 11.7 min (2*R*, 3*R*), t_R = 13.1 min (2*S*, 3*S*). HRMS: Calcd for C₁₃H₂₁NO₂ (M + H⁺) 224.1640, found 224.1629.

(3*R*,4*R*)-1-phenyl-4-(phenylamino)pentan-3-ol (16ca): $[\alpha]_D^{24}$ -39.4 (*c* 1.49, 95% ee, CHCl₃). IR (KBr) 3405, 3056, 3026, 2926, 2863, 1944, 1602, 1502, 1452, 1430, 1375, 1318, 1523, 1178, 1152,

1061, 997, 920, 873, 750, 696 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.08 (d, 3H, $J = 6.9$ Hz), 1.73-1.87 (m, 2H), 2.63-2.84 (m, 2H), 3.35 (t, 1H, $J = 6.9$ Hz), 3.43-3.46 (m, 1H), 5.10 (d, 2H, $J = 4.1$ Hz), 6.66-6.73 (m, 3H), 7.09-7.23 (m, 7H). ^{13}C NMR (CDCl_3): δ_{C} 17.6, 32.3, 35.6, 54.6, 74.5, 114.4, 118.3, 126.1, 128.6, 128.7, 129.5, 142.2, 127.9. HPLC Daicel Chiralcel OJ-H x 2, hexane/ i PrOH = 9/1, flow rate = 0.5 mL/min: $t_{\text{R}} = 96.5$ min (3*R*, 4*R*), $t_{\text{R}} = 101.7$ min (3*S*, 4*S*). HRMS: Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}$ ($\text{M} + \text{H}^+$) 256.1696, found 256.1693.

(3*R*,4*R*)-1-phenyl-4-(4-tolylamino)pentan-3-ol (16cd): $[\alpha]_{\text{D}}^{24} -18.3$ (c 0.74, 86% ee, CHCl_3). IR (KBr) 3395, 2923, 2854, 2366, 1740, 1616, 1518, 1452, 1093, 1056, 810, 743, 699 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.11 (d, 3H, $J = 6.8$ Hz), 1.79-1.90 (m, 2H), 2.23 (s, 3H), 2.71-2.88 (m, 2H), 3.35 (t, 1H, $J = 6.5$ Hz), 3.43-3.46 (m, 1H), 6.62 (d, 2H, $J = 8.2$ Hz), 6.99 (d, 2H, $J = 7.6$ Hz), 7.17-7.29 (m, 5H). ^{13}C NMR (CDCl_3): δ_{C} 17.2, 20.4, 2.0, 35.4, 55.6, 74.4, 115.0, 125.8, 128.1, 128.4, 128.5, 130.0, 142.1, 144.8. HPLC Daicel Chiralcel OJ-H x 2, hexane/ i PrOH = 9/1, flow rate = 0.7 mL/min: $t_{\text{R}} = 55.0$ min (3*R*, 4*R*), $t_{\text{R}} = 58.5$ min (3*S*, 4*S*). HRMS: Calcd for $\text{C}_{18}\text{H}_{23}\text{NO}$ ($\text{M} + \text{H}^+$) 270.1852, found 270.1855.

(3*R*,4*R*)-4-(2-methoxyphenylamino)-1-phenylpentan-3-ol (16ce): $[\alpha]_{\text{D}}^{24} -30.2$ (c 0.50, 98% ee, CHCl_3). IR (KBr) 3413, 2926, 2852, 2363, 1600, 1513, 1455, 1430, 1247, 1220, 1028, 739, 700 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.13 (d, 3H, $J = 6.2$ Hz), 1.77-1.94 (m, 2H), 2.71-2.92 (m, 2H), 3.40 (t, 1H, $J = 6.5$ Hz), 3.52-3.56 (m, 1H), 3.84 (s, 3H), 6.71-6.80 (m, 4H), 7.17-7.29 (m, 5H). ^{13}C NMR (CDCl_3): δ_{C} 17.2, 32.0, 35.3, 54.8, 55.4, 74.4, 109.8, 112.1, 117.8, 121.2, 125.8, 128.4, 128.5, 136.8, 142.1, 147.7. HPLC Daicel Chiralcel OJ-H, hexane/ i PrOH = 9/1, flow rate = 0.7 mL/min: $t_{\text{R}} = 20.3$ min (3*R*, 4*R*), $t_{\text{R}} = 24.0$ min (3*S*, 4*S*). HRMS: Calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_2$ ($\text{M} + \text{H}^+$) 286.1802, found 286.1799.

(3*R*,4*R*)-1-phenyl-4-(3-trifluoromethylphenylamino)pentan-3-ol (16cg): $[\alpha]_{\text{D}}^{21} -29.6$ (c 2.08, >99% ee, CHCl_3). IR (KBr) 3410, 3062, 3029, 2974, 2929, 2861, 1612, 1495, 1439, 1343, 1281, 1247, 1166, 1121, 1067, 995, 929, 861, 785, 748, 699 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 1.21 (d, 3H, $J = 6.9$ Hz), 1.83-2.01 (m, 2H), 2.70 (q, 2H, $J = 7.1$ Hz), 3.25 (app. s, 1H), 3.95 (app. s, 1H), 6.81 (s, 2H), 7.09-7.27 (m, 7H). ^{13}C NMR (CDCl_3): δ_{C} 17.3, 32.0, 35.4, 53.8, 74.3, 110.0, 114.2, 116.8, 124.2, 126.0, 128.4, 128.4, 129.7,

131.6, 141.7, 147.8. HPLC Daicel Chiralpak AD-H, hexane/*i*PrOH = 9/1, flow rate = 0.5 mL/min: t_R = 11.8 min (3*R*, 4*R*), t_R = 12.5 min (3*S*, 4*S*). HRMS: Calcd for C₁₈H₂₀F₃NO (M + H⁺) 324.1570, found 324.1585.

(3*R*,4*R*)-4-(4-bromophenylamino)-1-phenylpentan-3-ol (16ci): $[\alpha]_D^{22}$ -23.6 (*c* 1.67, 94% ee, CHCl₃). IR (KBr) 3273, 1594, 1496, 1451, 1094, 815, 745, 699 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.13 (d, 3H, *J* = 6.2 Hz), 1.82-1.87 (m, 2H), 2.71-2.86 (m, 2H), 3.37 (t, 1H, *J* = 6.2 Hz), 3.47-3.51 (m, 1H), 6.52-6.53 (m, 2H), 7.18-7.30 (m, 7H). ¹³C NMR (CDCl₃): δ_C 17.3, 32.0, 35.4, 54.4, 74.3, 109.7, 114.9, 115.7, 125.9, 128.4, 132.0, 141.8, 146.4. HPLC Daicel Chiralpak AD-H, hexane/*i*PrOH = 9/1, flow rate = 0.5 mL/min: t_R = 20.1 min (3*R*, 4*R*), t_R = 21.5 min (3*S*, 4*S*). HRMS: Calcd for C₁₇H₂₀BrNO (M + H⁺) 334.0796, found 334.0805.

(3*R*,4*R*)-4-(2,6-dimethylphenylamino)-1-phenyl-pentan-3-ol (16cj): $[\alpha]_D^{21}$ +17.8 (*c* 0.54, 94% ee, CHCl₃). IR (KBr) 3389, 2926, 2854, 1623, 1477, 1440, 1267, 1222, 1094, 759, 699 cm⁻¹. ¹H NMR (CDCl₃): δ_H 0.99 (d, 3H, *J* = 6.9 Hz), 1.87-1.93 (m, 2H), 2.28 (s, 6H), 2.76-2.90 (m, 2H), 3.19 (t, 1H, *J* = 6.9 Hz), 3.48-3.50 (m, 1H), 6.84 (t, 1H, *J* = 7.6 Hz), 6.99 (d, 2H, *J* = 7.6 Hz), 7.19-7.24 (m, 5H). ¹³C NMR (CDCl₃): δ_C 14.2, 17.6, 19.1, 31.9, 35.4, 58.1, 60.4, 122.4, 125.8, 128.4, 128.5, 129.2, 129.6, 142.2, 143.6. HPLC Daicel Chiralpak AD-H, hexane/*i*PrOH = 40/1, flow rate = 1.0 mL/min: t_R = 19.1 min (3*R*, 4*R*), t_R = 22.9 min (3*S*, 4*S*). HRMS: Calcd for C₁₉H₂₅NO (M + H⁺) 284.2009, found 284.2004.

(3*R*,4*R*)-4-(2-chlorophenylamino)-1-phenyl pentan-3-ol (16ck): $[\alpha]_D^{22}$ -30.7 (*c* 0.51, 94% ee, CHCl₃). IR (KBr) 3408, 2946, 2363, 1596, 1506, 1455, 1322, 1123, 1034, 743, 699 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.17 (d, 3H, *J* = 6.2 Hz), 1.81-1.92 (m, 2H), 2.69-2.87 (m, 2H), 3.46 (t, 1H, *J* = 6.2 Hz), 3.60 (m, 1H), 6.67-6.80 (m, 3H), 7.02-7.29 (m, 6H). ¹³C NMR (CDCl₃): δ_C 17.2, 32.0, 35.3, 54.6, 74.2, 115.9, 119.0, 125.9, 127.6, 127.8, 128.4, 129.4, 141.8. HPLC Daicel Chiralcel OJ-H x 2, hexane/*i*PrOH = 9/1, flow rate = 0.7 mL/min: t_R = 36.1 min (3*S*, 4*S*), t_R = 39.4 min (3*R*, 4*R*). HRMS: Calcd for C₁₇H₂₀ClNO (M + H⁺) 290.1306, found 290.1317.

(3*R*,4*R*)-4-(3-chlorophenylamino)-1-phenyl-pentan-3-ol (16cl): $[\alpha]_D^{24}$ -25.3 (*c* 0.66, 99% ee, CHCl₃). IR (KBr) 3404, 3027, 2925, 2364, 1597, 1499, 1451, 1325, 1150, 1092, 988, 923, 760, 699 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.08 (d, 3H, *J* = 6.9 Hz), 1.73-1.85 (m, 2H), 2.63-2.84 (m, 2H), 3.35 (t, 1H, *J* = 6.5 Hz), 3.45 (dt, 1H, *J* = 4.0, 11.0 Hz), 6.66-6.73 (m, 3H), 7.08-7.23 (m, 6H). ¹³C NMR (CDCl₃): δ_C 17.3, 32.0, 35.4, 54.1, 74.2, 112.4, 113.7, 117.9, 125.9, 128.4, 130.3, 135.1, 141.8, 148.6. HPLC Daicel Chiralcel OJ-H, hexane/*i*PrOH = 9/1, flow rate = 0.7 mL/min: *t*_R = 28.7 min (3*R*, 4*R*), *t*_R = 32.0 min (3*S*, 4*S*). HRMS: Calcd for C₁₇H₂₀ClNO (*M* + *H*⁺) 290.1306, found 290.1306.

(3*R*,4*R*)-4-(4-fluorophenylamino)-1-phenylpentan-3-ol (16cm): $[\alpha]_D^{22}$ -24.3 (*c* 2.14, 97% ee, CHCl₃). IR (KBr) 3406, 3028, 2928, 2857, 1714, 1604, 1511, 1452, 1365, 1313, 1218, 1150, 1094, 919, 822, 743, 700 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.11 (d, 3H, *J* = 6.9 Hz), 1.79-2.02 (m, 2H), 2.70-2.87 (m, 2H), 3.30 (t, 1H, *J* = 6.5 Hz), 3.45-3.48 (m, 1H), 6.64 (dd, 2H, *J* = 4.1, 8.9 Hz), 6.88 (t, 2H, *J* = 8.8 Hz), 7.16-7.28 (m, 5H). ¹³C NMR (CDCl₃): δ_C 17.1, 32.0, 35.4, 56.1, 74.3, 115.9, 125.9, 128.4, 141.9, 143.2, 155.8, 157.4. HPLC Daicel Chiralcel OJ-H, hexane/*i*PrOH = 9/1, flow rate = 0.7 mL/min: *t*_R = 20.3 min (3*R*, 4*R*), *t*_R = 24.0 min (3*S*, 4*S*). HRMS: Calcd for C₁₇H₂₀FNO (*M* + *H*⁺) 274.1602, found 274.1607.

(3*R*,4*R*)-4-(4-chlorophenylamino)-1-phenylpentan-3-ol (16cn): $[\alpha]_D^{24}$ -29.2 (*c* 2.73, 98% ee, CHCl₃). IR (KBr) 3405, 3027, 2928, 1599, 1497, 1451, 1401, 1316, 1249, 1177, 1092, 1003, 817, 746, 700 cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.13 (d, 3H, *J* = 6.2 Hz), 1.85 (tdd, 2H, *J* = 4.0, 7.3, 14.2 Hz), 2.71 (dt, 1H, *J* = 5.8, 17.9 Hz), 2.83-2.88 (m, 1H), 3.36 (t, 1H, *J* = 6.2 Hz), 3.47-3.50 (m, 1H), 6.57 (m, 2H), 7.09-7.11 (m, 2H), 7.17-7.29 (m, 5H). ¹³C NMR (CDCl₃): δ_C 17.3, 32.0, 35.4, 54.6, 74.3, 115.3, 122.7, 125.9, 128.4, 129.6, 141.8, 146.0. HPLC Daicel Chiralcel OD-H, hexane/*i*PrOH = 9/1, flow rate = 1.0 mL/min: *t*_R = 8.6 min (3*R*, 4*R*), *t*_R = 9.5 min (3*S*, 4*S*). HRMS: Calcd for C₁₇H₂₀ClNO (*M* + *H*⁺) 290.1306, found 290.1313.

7-Phenyl-7-aza-bicyclo[4.1.0]heptane (18a): Data consistent with literature.⁴

7-Benzyl-7-aza-bicyclo[4.1.0]heptane (18b): Data consistent with literature.⁵

7-Benzhydryl-7-aza-bicyclo[4.1.0]heptane (18c): white solid (76-77 °C), IR (KBr) 3081, 2930, 1447, 1193, 1069, 741, 702, 635 cm⁻¹. ¹H NMR (CDCl₃): δ_H 7.47-7.44 (m, 4H), 7.31-7.19 (m, 6H), 3.53 (s, 1H), 1.82-1.75 (m, 2H), 1.72-1.62 (m, 4H), 1.55-1.45 (m, 2H), 1.24-1.16 (m, 2H). ¹³C NMR (CDCl₃): δ_C 144.4, 128.3, 127.5, 126.8, 78.2, 38.5, 24.7, 20.8. HRMS: Calcd for C₁₉H₂₁N (M+H⁺) 264.1747, found 264.1753.

7-Tosyl-7-aza-bicyclo[4.1.0]heptane (18d): Data consistent with literature.⁶

7-Benzoyl-7-aza-bicyclo[4.1.0]heptane (18e): Data consistent with literature.⁷

7-(4-Fluorophenyl)-7-aza-bicyclo[4.1.0]heptane (18f): white solid (31-32 °C), IR (KBr) 3047, 2987, 2935, 2854, 1503, 1278, 1208, 1093, 835, 618 cm⁻¹. ¹H NMR (CDCl₃): δ_H 6.89-6.87(m,2H), 6.87-6.84 (m, 2H), 2.26-2.23 (m, 2H), 2.05-1.98 (m,2H), 1.92-1.85 (m, 2H), 1.51-1.43 (m, 2H), 1.31-1.22 (m, 2H). ¹³C NMR (CDCl₃): δ_C 158.2 (d, 1C, *J*_{CF} = 238 Hz), 151.8, 121.5 (d, 1C, *J*_{CF} = 8.5 Hz), 115.4 (d, 1C, *J*_{CF} = 22 Hz), 39.1, 24.6, 20.4. HRMS: Calcd for C₁₂H₁₄FN (M+H⁺) 192.1183, found 192.1180.

7-(4-Nitrophenyl)-7-aza-bicyclo[4.1.0]heptane (18g): Data consistent with literature.⁴

7-(4-Methoxyphenyl)-7-aza-bicyclo[4.1.0]heptane (18h): Data consistent with literature.⁸

7-(2-Methoxyphenyl)-7-aza-bicyclo[4.1.0]heptane (18i): Data consistent with literature.⁴

7-(3-Methoxyphenyl)-7-aza-bicyclo[4.1.0]heptane (18j): IR (film) 3066, 2992, 2934, 2854, 1599, 1482, 1200, 1151, 1048, 768, 690 cm⁻¹. ¹H NMR (CDCl₃): δ_H 7.11 (t,1H, *J* = 8.4 Hz), 6.58-6.47 (m, 3H), 3.77 (s, 3H), 2.32-2.30 (m, 2H), 2.07-2.00 (m,2H), 1.93-1.85 (m, 2H), 1.54-1.45 (m, 2H), 1.32-1.26 (m, 2H). ¹³C NMR (CDCl₃): δ_C 160.2, 157.2, 129.7, 113.0, 107.5, 106.4, 55.3, 38.8, 24.8, 20.5. HRMS: Calcd for C₁₃H₁₇NO (M+H⁺) 204.1383, found 204.1390.

7-(2-Hydroxyphenyl)-7-aza-bicyclo[4.1.0]heptane (18k): Data consistent with literature.⁹

7-(2-Ethoxyphenyl)-7-aza-bicyclo[4.1.0]heptane (18l): IR (film) 3065, 2978, 2932, 2854, 1592, 1496, 1230, 1121, 1047, 741 cm⁻¹. ¹H NMR (CDCl₃): δ_H 6.91-6.77 (m, 4H), 4.04 (q, 2H, *J* = 7.6 Hz), 2.25-2.23 (m, 2H), 2.15-2.09 (m, 2H), 1.94-1.85 (m, 2H), 1.56-1.46 (m, 2H), 1.48 (t, 3H, *J* = 7.6 Hz),

1.34-1.25 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 152.2, 144.1, 122.3, 120.4, 120.2, 111.6, 63.5, 39.4, 24.5, 20.6, 15.2. HRMS: Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}$ ($\text{M}+\text{H}^+$) 218.1539, found 218.1541.

7-(2-Phenoxyphenyl)-7-aza-bicyclo[4.1.0]heptane (18m): white solid (75-76 °C), IR (KBr) 3047, 3006, 2936, 2914, 2858, 1588, 1487, 1284, 1211, 749 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.30 (t, 2H, $J = 8.0$ Hz), 7.06-6.96 (m, 5H), 6.91-6.89 (m, 2H), 2.32-2.31 (m, 2H), 1.95-1.88 (m, 2H), 1.79-1.71 (m, 2H), 1.39-1.33 (m, 2H), 1.23-1.16 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 157.8, 148.3, 147.2, 129.6, 124.6, 122.4, 122.2, 121.6, 120.8, 117.1, 39.4, 24.3, 20.4. HRMS: Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}$ ($\text{M}+\text{H}^+$) 266.1539, found 266.1529.

7-(2,4-Dimethoxyphenyl)-7-aza-bicyclo[4.1.0]heptane (18n): white solid (79-80 °C), IR (KBr) 3001, 2934, 2854, 2826, 1505, 1208, 1156, 1141, 1039, 828 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 6.75 (d, 1H, $J = 8.4$ Hz), 6.41 (d, 1H, $J = 2.8$ Hz), 6.33 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 2.8$ Hz), 3.83 (s, 3H), 3.74 (s, 3H), 2.15-2.14 (m, 2H), 2.10-2.03 (m, 2H), 1.91-1.83 (m, 2H), 1.52-1.44 (m, 2H), 1.31-1.26 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 155.5, 153.6, 137.9, 120.0, 103.3, 99.4, 55.64, 55.60, 39.4, 24.5, 20.6. HRMS: Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}$ ($\text{M}+\text{H}^+$) 234.1489, found 234.1489.

Typical Procedure for Asymmetric Aziridine Ring-opening with Amines. To a solution of ligand **10c** (44.2 mg, 0.076 mmol) in toluene in a dry, 2-necked flask under an argon atmosphere was added $\text{Nb}(\text{O}^i\text{Pr})_5$ (27.0 mg, 0.070 mmol) as a solution in toluene (2.0 mL, and the reaction temperature was raised to 60 °C. The mixture was stirred for 3 h at the same temperature, and then allowed to cool to room temperature. The resulting yellow mixture was transferred via gas-tight syringe to another flask containing oven-dried MS3A (200 mg). The mixture was stirred for 30 minutes at room temperature after which time an aliquot (0.5 mL) of this mixture (0.017 ml, 5% catalyst loading) was filtered by gas type syringe fitted with a Puradisc 25 TF filter device (Whatman) to another dried 2-neck flask. The *meso*-aziridine (0.347 mmol) in toluene (0.60 mL) and aniline (39 mg, 0.416 mmol) in toluene (0.60 mL) were successively added to the resulting yellow clear solution. The reaction mixture was stirred for

3 h at room temperature, and then saturated aqueous NaHCO₃ was added to quench the reaction. The layers were separated and the aqueous layer was extracted with dichloromethane (3 times), and the organic layers were combined and dried over anhydrous Na₂SO₄. After filtration and concentration under reduced pressure, the crude product was purified by preparative thin layer chromatography (hexane-ethyl acetate = 9:1) to afford the product. The optical purity was determined by HPLC analysis using the appropriate Chiralcel column.

(1*S*,2*S*)-*N,N'*-Diphenylcyclohexane-1,2-diamine (19aa): Silica gel, CH₂Cl₂/methanol = 95 : 5. $[\alpha]_D^{25} = -38.3$ ($c = 0.94$, 62% ee, benzene, $[\alpha]_D^{25} = -61.9$ for >99.9% ee) [lit.¹⁰ value for (1*R*, 2*R*), $[\alpha]_D^{28} +64.1$ ($c = 0.95$, >99.9% ee, benzene)]. IR (film) 3383, 3051, 2855, 1600, 1497, 1315, 719, 693 cm⁻¹. ¹H NMR (CDCl₃): δ_H 7.17 (app. t, 4H, $J = 7.4$ Hz), 6.71 (app. t, 2H, $J = 7.4$ Hz), 6.61 (app. d, 4H, $J = 7.4$ Hz), 3.83 (bs, 2H), 3.24-3.17 (m, 2H), 2.37-2.33 (m, 2H), 1.80-1.75 (m, 2H), 1.45-1.38 (m, 2H), 1.30-1.18 (m, 2H). ¹³C NMR (CDCl₃): δ_C 147.8, 129.4, 117.7, 113.6, 57.4, 32.7, 24.7. HPLC: Daicel Chiralcel OD, hexane / ⁱPrOH = 100/1, flow rate = 1.0 ml / min: $t_R = 30.5$ min (1*R*, 2*R*), $t_R = 33.6$ min (1*S*, 2*S*). HRMS : Calcd for C₁₈H₂₂N₂ (M+1)⁺ 267.1856, found 267.1857.

(1*S*,2*S*)-*N*-phenyl-*N*-*p*-tolylcyclohexane-1,2-diamine (19ad): $[\alpha]_D^{20} -13.8$ (c 0.72, 48% ee, CHCl₃). IR (KBr) 3381, 2928, 2855, 1602, 1513, 1254, 808, 749, 692cm⁻¹. ¹H NMR (CDCl₃): δ_H 1.12-1.35 (m, 4H), 1.67-1.70 (m, 2H), 2.71-2.86 (m, 2H), 2.16 (s, 3H), 2.26 (dt, 2H, $J = 2.8, 9.7$ Hz), 3.07-3.11 (m, 2H), 6.46-6.55 (m, 4H), 6.63 (t, 1H, $J = 7.3$ Hz) , 6.91 (d, 2H, $J = 8.1$ Hz) , 7.09 (m, 2H). ¹³C NMR (CDCl₃): δ_C 20.3, 24.6, 24.6, 32.5, 32.6, 57.3, 57.6, 113.5, 113.8, 117.5, 126.9, 129.3, 129.8, 145.4, 147.8. HPLC Daicel Chiralcel OD, hexane/ⁱPrOH = 100/1, flow rate = 1.0 mL/min: $t_R = 18.9$ min (1*R*, 2*R*), $t_R = 25.0$ min (1*S*, 2*S*). HRMS: Calcd for C₁₉H₂₄N₂ (M + H⁺) 281.2012, found 281.2010.

(1*S*,2*S*)-*N*-Benzyl-*N'*-phenylcyclohexane-1,2-diamine (19ba):¹⁰ Silica gel, CH₂Cl₂/methanol = 95:5. $[\alpha]_D^{25} = -13.8.0$ ($c = 0.72$, 48% ee, chloroform). IR (KBr) 3388, 3055, 2850, 1599, 1498, 1316, 725, 690 cm⁻¹. ¹H NMR (CDCl₃): δ_H 7.35-7.22 (m, 5H), 7.16 (app. t, 2H, $J = 7.3$ Hz), 6.70 (td, 1H, $J_1 = 7.3$ Hz, $J_2 = 0.9$ Hz), 6.66 (dd, 2H, $J_1 = 7.3$ Hz, $J_2 = 0.9$ Hz), 3.81 (ABx, 2H, $J = 13.3$ Hz), 3.40 (brs, 1H), 3.18-

3.12 (m, 1H), 2.39-2.33 (m, 1H), 2.22-2.16 (m, 2H), 2.05 (brs, 1H), 1.78-1.70 (m, 2H), 1.36-1.22 (m, 3H), 1.07-1.02 (m, 1H). ^{13}C NMR (CDCl_3): δ_{C} 148.3, 140.7, 129.4, 128.5, 128.2, 127.0, 117.8, 114.2, 61.0, 57.6, 50.9, 32.6, 31.5, 25.1, 24.7, 22.1. HPLC: Daicel Chiralcel OD, hexane / i PrOH = 100/1, flow rate = 1.0 ml / min: t_{R} = 13.4 min (minor), t_{R} = 25.8 min (major). LRMS (ESI): Calcd for $\text{C}_{19}\text{H}_{24}\text{N}_2$ ($\text{M}+1$) $^+$ 281.2, found 281.3.

(1*S*,2*S*)-*N*-Benzhydryl-*N'*-*p*-tolylcyclohexane-1,2-diamine (19cd): Silica gel, hexane – ethyl acetate = 9 : 1). $[\alpha]_{\text{D}}^{25}$ = +1.6 (c = 0.40, 40% ee, chloroform). IR (KBr) 3360, 3062, 3024, 2926, 2855, 1616, 1516, 1451, 1298, 1115, 809, 700 cm^{-1} . ^1H NMR (CDCl_3): δ 7.36-7.32 (m, 5H), 7.26-7.22 (m, 5H), 6.99 (d, 2H, J = 8.0 Hz), 6.61 (d, 2H, J = 8.0 Hz), 5.02 (s, 1H), 3.19-3.15 (m, 1H), 2.34-2.30 (m, 1H), 2.24 (s, 3H), 2.22-2.13 (m, 2H), 1.72-1.63 (m, 2H), 1.34-1.13 (m, 3H), 1.02-0.93 (m, 1H). ^{13}C NMR (CDCl_3): δ 146.1, 144.9, 144.2, 129.9, 128.7, 128.4, 127.7, 127.2, 127.1, 126.9, 126.8, 114.2, 63.6, 58.9, 58.2, 32.5, 31.7, 24.9, 24.7, 20.5. HPLC: Daicel Chiralcel OD, hexane / i PrOH = 400/1, flow rate = 1.0 ml / min: t_{R} = 16.7 min (1*S*, 2*S*), t_{R} = 21.4 min. (1*R*, 2*R*) HRMS : Calcd for $\text{C}_{26}\text{H}_{30}\text{N}_2$ ($\text{M}+1$) $^+$ 371.2482, found 371.2483.

(1*S*,2*S*)-*N*-Tosyl-*N'*-phenylcyclohexane-1,2-diamine (19da): Data consistent with published material.¹¹

(1*S*,2*S*)-*N*-(4-Fluorophenyl)-*N'*-phenylcyclohexane-1,2-diamine (19fa): Silica gel, hexane/ethyl acetate = 9 : 1. $[\alpha]_{\text{D}}^{23}$ = -6.8 (c = 0.80, 59% ee, chloroform). IR (KBr) 3385, 3052, 2932, 2856, 1602, 1507, 1316, 1217, 821, 749, 693 cm^{-1} . ^1H NMR (CDCl_3): δ 7.21-7.16 (m, 2H), 6.91-6.86 (m, 2H), 6.75-6.71 (m, 1H), 6.65-6.63 (m, 2H), 6.58-6.54 (m, 2H), 3.75 (brs, 2H), 3.21 (app. td, 1H, J_1 = 9.6 Hz, J_2 = 3.6 Hz), 3.11 (app. td, 1H, J_1 = 9.6 Hz, J_2 = 3.6 Hz), 2.36-2.30 (m, 2H), 1.80-1.76 (m, 2H), 1.45-1.37 (m, 2H), 1.27-1.18 (m, 2H). ^{13}C NMR (CDCl_3): δ 156.1 (d, 1C, J_{CF} = 235 Hz), 144.1, 138.4, 128.5, 127.9, 127.7, 115.8 (d, 1C, J_{CF} = 23 Hz), 114.7 (d, 1C, J_{CF} = 6.6 Hz), 58.3, 57.4, 32.7, 32.6, 24.8, 24.7. HPLC: Daicel Chiralcel OD, hexane / i PrOH = 9/1, flow rate = 1.0 ml / min: t_{R} = 7.6 min (1*R*, 2*R*), t_{R} = 10.9 min (1*S*, 2*S*). HRMS : Calcd for $\text{C}_{18}\text{H}_{21}\text{FN}_2$ ($\text{M}+1$) $^+$ 285.1762, found 285.1749.

(1*S*,2*S*)-*N*-(4-Nitrophenyl)-*N'*-phenylcyclohexane-1,2-diamine (19ga): Silica gel, hexane/ethyl acetate = 4 : 1). $[\alpha]_D^{24} = -106.2$ ($c = 0.36$, 53% ee, chloroform). IR (KBr) 3359, 3056, 2931, 2856, 1598, 1499, 1326, 828, 749, 693 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 8.05 (d, 2H, $J = 9.2$ Hz), 7.17 (dd, 2H, $J_1 = 8.0$ Hz, $J_2 = 7.4$ Hz), 6.73 (t, 1H, $J = 7.4$ Hz), 6.61 (d, 2H, $J = 8.0$ Hz), 6.49 (d, 2H, $J = 9.2$ Hz), 4.65 (brs, 1H), 3.65 (brs, 1H), 3.31-3.27 (m, 2H), 3.34-3.30 (m, 2H), 2.36-2.30 (m, 2H), 1.84-1.80 (m, 2H), 1.45-1.41 (m, 2H), 1.27-1.22 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 153.0, 138.1, 129.6, 128.5, 127.9, 126.5, 113.6, 111.6, 77.3, 57.4, 32.6, 32.3, 24.7, 24.5. HPLC: Daicel Chiralcel OD, hexane / i PrOH = 4/1, flow rate = 1.0 ml / min: $t_{\text{R}} = 14.1$ min (1*R*, 2*R*), $t_{\text{R}} = 25.7$ min (1*S*, 2*S*). HRMS : Calcd for $\text{C}_{18}\text{H}_{21}\text{N}_3\text{O}_2$ ($\text{M}+1$)⁺ 312.1707, found 312.1701.

(1*S*,2*S*)-*N*-(4-Methoxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (19ha)¹² Silica gel, hexane/ethyl acetate = 85 : 15. $[\alpha]_D^{23} = -26.4$ ($c = 1.33$, 70% ee, chloroform). IR (KBr) 3370, 3051, 2930, 2855, 1601, 1510, 1316, 1291, 1240, 1037, 821, 750, 693 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.19 (t, 2H, $J = 7.6$ Hz), 6.79 (d, 2H, $J = 8.9$ Hz), 6.73 (t, 1H, $J = 7.6$ Hz), 6.64 (d, 2H, $J = 7.6$ Hz), 6.61 (d, 2H, $J = 8.9$ Hz), 3.75 (s, 3H), 3.65 (brs, 2H), 3.19 (app. td, 1H, $J_1 = 9.8$ Hz, $J_2 = 3.7$ Hz), 3.10 (app. td, 1H, $J_1 = 9.8$ Hz, $J_2 = 3.7$ Hz), 2.36-2.31 (m, 2H), 1.79-1.76 (m, 2H), 1.44-1.38 (m, 2H), 1.26-1.18 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 152.5, 141.9, 138.4, 128.5, 127.9, 127.8, 115.4, 115.1, 58.5, 57.5, 55.9, 32.73, 32.68, 24.8. HPLC: Daicel Chiralcel OD-H, hexane / i PrOH = 19/1, flow rate = 1.0 ml / min: $t_{\text{R}} = 16.7$ min (1*R*, 2*R*), $t_{\text{R}} = 21.3$ min (1*S*, 2*S*). HRMS : Calcd for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}$ ($\text{M}+1$)⁺ 297.1961, found 297.1955.

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (19ia): Silica gel, hexane/ethyl acetate = 9 : 1 white solid. After a single crystallization using *n*-pentane, only one enantiomer was obtained in >99% (mpt 94-95 °C). $[\alpha]_D^{25} = -4.1$ ($c = 1.25$, > 99% ee, chloroform). IR (KBr) 3372, 3050, 2935, 2850, 1603, 1510, 1316, 1291, 1240, 1037, 821, 750, 693 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.18 (t, 2H, $J = 7.6$ Hz), 6.88 (t, 1H, $J = 7.6$ Hz), 6.77-6.66 (m, 4H), 6.63 (d, 2H, $J = 7.7$ Hz), 4.17 (brs, 2H), 3.76 (s, 3H), 3.28-3.25 (m, 2H), 2.40-2.30 (m, 2H), 1.79-1.76 (m, 2H), 1.46-1.41 (m, 2H), 1.29-1.25 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 148.0, 138.4, 137.6, 128.5, 127.9, 127.7, 121.2, 116.7, 110.3, 109.8, 57.2, 56.8,

55.4, 32.5, 32.4, 24.8, 24.6. HPLC: Daicel Chiralcel OD, hexane / ⁱPrOH = 100/1, flow rate = 1.0 ml / min: t_R = 13.9 min (1*R*, 2*R*), t_R = 17.8 min (1*S*, 2*S*). HRMS : Calcd for C₁₉H₂₄N₂O (M+1)⁺ 297.1961, found 297.1956.

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N'*-*o*-tolylcyclohexane-1,2-diamine (19ib): Silica gel, hexane/ethyl acetate = 9 : 1) (47% ee). After a single crystallization using *n*-pentane, enantioenriched compound was obtained in 85% ee (mpt = 95-96 °C). $[\alpha]_D^{23}$ = +6.2 (*c* = 1.62, 85 % ee, chloroform). IR (film) 3406, 3062, 2931, 2855, 1603, 1509, 1455, 1252, 1238, 1222, 1029, 738 cm⁻¹. ¹H NMR (CDCl₃): δ_H 7.14 (t, 1H, *J* = 7.7 Hz), 7.05 (d, 1H, *J* = 7.2 Hz), 6.89 (t, 1H, *J* = 7.7 Hz), 6.78-6.65 (m, 5H), 4.30 (brs, 1H), 3.87 (brs, 1H), 3.76 (s, 3H), 3.39-3.35 (m, 1H), 3.30 (app. td, 1H, *J*₁ = 9.4 Hz, *J*₂ = 3.4 Hz), 2.44-2.31 (m, 2H), 2.00 (s, 3H), 1.82-1.79 (m, 2H), 1.49-1.44 (m, 2H), 1.35-1.26 (m, 2H). ¹³C NMR (CDCl₃): δ_C 147.3, 146.1, 137.8, 130.3, 127.1, 123.1, 121.3, 116.9, 116.6, 110.3, 109.8, 57.8, 56.7, 55.4, 32.7, 32.6, 24.9, 24.6, 17.7. HPLC: Daicel Chiralcel AD-H, hexane / ⁱPrOH = 100/1, flow rate = 1.0 ml / min: t_R = 6.2 min (1*R*, 2*R*), t_R = 8.1 min (1*S*, 2*S*). HRMS : Calcd for C₂₀H₂₆N₂O (M+1)⁺ 311.2118, found 311.2126.

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N'*-*m*-tolylcyclohexane-1,2-diamine (19ic): Silica gel, hexane/ethyl acetate = 9 : 1 red solid (77% ee). After a single crystallization using *n*-pentane, only one enantiomer was obtained in >99% ee (mpt = 76-77 °C). $[\alpha]_D^{22}$ = -10.1 (*c* = 2.55, > 99% ee, chloroform). IR (KBr) 3394, 3043, 2931, 2855, 1602, 1510, 1455, 1254, 1238, 1222, 1029, 736 cm⁻¹. ¹H NMR (CDCl₃): δ_H 7.08 (t, 1H, *J* = 8.0 Hz), 6.89 (t, 1H, *J* = 7.4 Hz), 6.77 (d, 1H, *J* = 8.0 Hz), 6.71-6.67 (m, 2H), 6.55 (d, 1H, *J* = 7.4 Hz), 6.47-6.45 (m, 2H), 4.20 (brs, 2H), 3.77 (s, 3H), 3.29-3.25 (m, 2H), 2.41-2.31 (m, 2H), 2.30 (s, 3H), 1.80-1.78 (m, 2H), 1.49-1.42 (m, 2H), 1.29-1.25 (m, 2H). ¹³C NMR (CDCl₃): δ_C 148.1, 147.4, 139.1, 137.6, 129.2, 121.2, 118.4, 116.6, 114.5, 110.8, 110.3, 109.8, 57.1, 56.8, 55.4, 32.5, 32.4, 24.7, 24.6, 21.7. HPLC: Daicel Chiralcel OD, hexane / ⁱPrOH = 100/1, flow rate = 1.0 ml / min: t_R = 12.0 min (1*R*, 2*R*), t_R = 16.4 min (1*S*, 2*S*). HRMS : Calcd for C₂₀H₂₆N₂O (M+1)⁺ 311.2118, found 311.2107.

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N'*-*p*-tolylcyclohexane-1,2-diamine (19id): Silica gel, hexane/ethyl acetate = 9:1 red solid (76 % ee). After a single crystallization using *n*-pentane, enantioenriched

compound was obtained in 90% ee (mpt = 92-93 °C). $[\alpha]_D^{22} = -21.9$ ($c = 2.80$, 90 % ee, chloroform). IR (KBr) 3391, 3049, 3016, 2930, 2856, 1617, 1601, 1513, 1455, 1253, 1029, 808, 735 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.01-6.99 (m, 2H), 6.90-6.86 (m, 1H), 6.78-6.76 (m, 1H), 6.70-6.67 (m, 2H), 6.58-6.56 (m, 2H), 4.15 (brs, 2H), 3.77 (s, 3H), 3.26-3.22 (m, 2H), 2.39-2.30 (m, 2H), 2.26 (s, 3H), 1.82-1.78 (m, 2H), 1.46-1.41 (m, 2H), 1.29-1.25 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 147.4, 145.7, 137.7, 129.8, 126.8, 121.2, 116.6, 114.0, 110.4, 109.8, 57.5, 56.8, 55.4, 32.5, 32.4, 24.8, 24.6, 20.5. HPLC: Daicel Chiralcel OD, hexane / $i\text{PrOH} = 100/1$, flow rate = 1.0 ml / min: $t_{\text{R}} = 11.1$ min (1*R*, 2*R*), $t_{\text{R}} = 14.5$ min (1*S*, 2*S*). HRMS : Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}$ ($\text{M}+1$)⁺ 311.2118, found 311.2114.

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N'*-(4-methoxyphenyl)cyclohexane-1,2-diamine (19if): Silica gel, hexane/ethyl acetate = 9:1, white solid. After a single crystallization using methanol, enantioenriched product was obtained in 94% ee (mpt = 131-132 °C). $[\alpha]_D^{24} = -20.7$ ($c = 0.70$, 94 % ee, chloroform). IR (KBr) 3383, 3062, 2931, 2854, 2831, 1509, 1456, 1239, 1030, 820, 737 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 6.88 (td, 1H, $J_1 = 7.7$ Hz, $J_2 = 1.3$ Hz), 6.80-6.76 (m, 3H), 6.70-6.66 (m, 2H), 6.63-6.61 (m, 2H), 4.10 (brs, 2H), 3.77 (s, 3H), 3.75 (s, 3H), 3.24 (app. td, 1H, $J_1 = 9.5$ Hz, $J_2 = 3.6$ Hz), 3.16 (app. td, 1H, $J_1 = 9.5$ Hz, $J_2 = 3.6$ Hz), 2.36-2.28 (m, 2H), 1.78-1.76 (m, 2H), 1.44-1.39 (m, 2H), 1.28-1.21 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 152.4, 147.4, 142.1, 137.7, 121.2, 116.7, 115.6, 115.0, 110.5, 109.8, 58.4, 56.9, 55.9, 55.4, 32.6, 32.4, 24.8, 24.6. HPLC: Daicel Chiralcel OD, hexane / $i\text{PrOH} = 19/1$, flow rate = 1.0 ml / min: $t_{\text{R}} = 8.5$ min (1*R*, 2*R*), $t_{\text{R}} = 10.5$ min (1*S*, 2*S*). HRMS : Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2$ ($\text{M}+1$)⁺ 327.2067, found 327.2075.

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N'*-(3-trifluoromethylphenyl)cyclohexane-1,2-diamine (19ig): Silica gel, hexane/ethyl acetate = 9:1 yellowish solid (74% ee). After a single crystallization using *n*-pentane, only one enantiomer was obtained in >99% ee (m.p. 111-112 °C). $[\alpha]_D^{22} = -3.6$ ($c = 1.41$, >99 % ee, chloroform). IR (film) 3395, 3062, 2935, 2858, 1601, 1510, 1341, 1162, 1118, 738 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.22 (t, 1H, $J = 7.9$ Hz), 6.29-6.86 (m, 2H), 6.79-6.67 (m, 5H), 4.25 (brs, 2H), 3.74 (s, 3H), 3.28-3.26 (m, 2H), 2.35-2.28 (m, 2H), 1.81-1.78 (m, 2H), 1.48-1.40 (m, 2H), 1.29-1.24 (m, 2H).

^{13}C NMR (CDCl_3): δ_{C} 148.2, 147.3, 137.4, 131.6 (*q*, 1C, $J_{\text{CF}}=31.2$ Hz), 129.6, 124.5 (*q*, 1C, $J_{\text{CF}}=271.0$ Hz), 121.2, 116.9, 116.6, 113.7 (*q*, 1C, $J_{\text{CF}}=3.8$ Hz), 110.4, 109.9, 109.5, (*q*, 1C, $J_{\text{CF}}=3.8$ Hz), 57.3, 57.0, 55.4, 32.5, 32.4, 24.8, 24.5. HPLC: Daicel Chiralcel OD, hexane / $^i\text{PrOH}$ = 100/1, flow rate = 1.0 ml / min: t_{R} = 15.9 min (1*S*, 2*S*), t_{R} = 19.7 min (1*R*, 2*R*). HRMS : Calcd for $\text{C}_{20}\text{H}_{23}\text{F}_3\text{N}_2\text{O}$ ($\text{M}+1$)⁺ 365.1835, found 365.1825.

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N'*-(4-bromophenyl)cyclohexane-1,2-diamine (19ii): Silica gel, hexane/ethyl acetate = 9:1. After a single crystallization using *n*-pentane, only one enantiomer was obtained in >99% ee (decomp. >350 °C). $[\alpha]_{\text{D}}^{24} = -40.6$ ($c = 0.48$, > 99% ee, chloroform). IR (KBr) 3386, 3069, 2931, 2856, 1595, 1502, 1455, 1301, 1235, 1028, 814, 730 cm^{-1} . ^1H NMR (CDCl_3): δ 7.24 (d, 2H, $J = 8.8$ Hz), 6.91-6.87 (m, 1H), 6.78-6.76 (m, 1H), 6.71-6.68 (m, 2H), 6.49 (d, 2H, $J = 8.8$ Hz), 4.10 (brs, 2H), 3.76 (s, 3H), 3.26-3.18 (m, 2H), 2.33-2.29 (m, 2H), 1.80-1.77 (m, 2H), 1.45-1.40 (m, 2H), 1.30-1.22 (m, 2H). ^{13}C NMR (CDCl_3): δ 147.3, 147.0, 137.5, 132.0, 121.3, 116.9, 115.2, 110.4, 109.9, 108.9, 57.5, 56.9, 55.4, 32.5, 32.4, 24.8, 24.6. HPLC: Daicel Chiralcel AD-H, hexane / $^i\text{PrOH}$ = 100/1, flow rate = 1.0 ml / min: t_{R} = 13.7 min (1*R*, 2*R*), t_{R} = 27.9 min (1*S*, 2*S*). HRMS : Calcd for $\text{C}_{19}\text{H}_{23}\text{BrN}_2\text{O}$ ($\text{M}+1$)⁺ 375.1067 (100 %), 377.1052 (97 %), found 375.1070 (100 %), 377.1046 (97 %).

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N'*-(3-chlorophenyl)cyclohexane-1,2-diamine (19il): Silica gel, hexane/ethyl acetate = 9:1) white solid. After a single crystallization using *n*-pentane, only one enantiomer was obtained in >99% ee (m.p.=124-125 °C). $[\alpha]_{\text{D}}^{22} = -22.9$ ($c = 1.52$, > 99.9 % ee, chloroform). IR (film) 3397, 3062, 2933, 2856, 1598, 1509, 1254, 1237, 1218, 1028, 737 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.05 (t, 1H, $J = 8.1$ Hz), 6.88 (app. td, 1H, $J_1 = 7.6$ Hz, $J_2 = 1.3$ Hz), 6.78-6.64 (m, 4H), 6.58 (app. t, 1H, $J = 2.0$ Hz), 6.47 (app. dd, 1H, $J_1 = 7.6$ Hz, $J_2 = 2.0$ Hz), 4.20 (brs, 2H), 3.76 (s, 3H), 3.25-3.21 (m, 2H), 2.35-2.27 (m, 2H), 1.80-1.77 (m, 2H), 1.45-1.39 (m, 2H), 1.29-1.24 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 149.2, 147.4, 137.1, 135.1, 130.2, 121.3, 117.2, 117.1, 113.1, 112.1, 110.7, 109.9, 57.3, 57.1, 55.5, 32.42, 32.37, 24.8, 24.5. HPLC: Daicel Chiralcel OD, hexane / $^i\text{PrOH}$ = 100/1, flow rate

=1.0 ml / min: t_R = 19.9 min (1*R*, 2*R*), t_R = 23.1 min (1*S*, 2*S*). HRMS : Calcd for $C_{19}H_{23}ClN_2O$ (M+1)⁺ 331.1572 (100%), 333.1542 (32%), found 331.1566 (100%), 333.1545 (32%).

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N'*-(4-fluorophenyl)cyclohexane-1,2-diamine (19im): Silica gel, hexane/ethyl acetate = 9:1 white solid (81 % ee). After a single crystallization using *n*-pentane, enantioenriched product was obtained in 97% ee (m.p. mpt = 110-111 °C) $[\alpha]_D^{22} = +3.0$ ($c = 1.21$, 97 % ee, chloroform). IR (KBr) 3394, 3062, 2933, 2855, 1601, 1507, 1456, 1221, 1028, 820, 737 cm⁻¹. ¹H NMR (CDCl₃): δ_H 6.90-85 (m, 3H), 6.77-6.66 (m, 3H), 6.57-6.54 (m, 2H), 4.10 (brs, 2H), 3.77 (s, 3H), 3.24 (app. td, 1H, $J_1 = 9.6$ Hz, $J_2 = 3.5$ Hz), 3.17 (app. td, 1H, $J_1 = 9.6$ Hz, $J_2 = 3.5$ Hz), 2.35-2.27 (m, 2H), 1.78-1.76 (m, 2H), 1.44-1.36 (m, 2H), 1.27-1.20 (m, 2H). ¹³C NMR (CDCl₃): δ_C 156.0 (d, 1C, $J_{CF} = 234$ Hz), 147.4, 144.3, 137.6, 121.3, 116.8, 115.7 (d, 1C, $J_{CF} = 22$ Hz), 114.8 (d, 1C, $J_{CF} = 7.6$ Hz), 110.5, 109.8, 58.2, 57.0, 55.4, 32.51, 32.48, 24.8, 24.6. HPLC: Daicel Chiralcel OD, hexane / ⁱPrOH = 100/1, flow rate =1.0 ml / min: t_R = 13.5 min (1*R*, 2*R*), t_R = 18.0 min (1*S*, 2*S*). HRMS : Calcd for $C_{19}H_{23}FN_2O$ (M+1)⁺ 315.1867, found 315.1851

(1*S*,2*S*)-*N*-(2-Methoxyphenyl)-*N'*-(4-chlorophenyl)cyclohexane-1,2-diamine (19in): Silica gel, hexane/ethyl acetate = 9:1, white solid. After a single crystallization using *n*-pentane, only one enantiomer was obtained in >99% ee (m.p.=122-123). $[\alpha]_D^{24} = -35.3$ ($c = 1.06$, > 99% ee, chloroform). IR (KBr) 3395, 3062, 2932, 2856, 1598, 1503, 1455, 1301, 1234, 1028, 816, 731 cm⁻¹. ¹H NMR (CDCl₃): δ_H 7.10 (d, 2H, $J = 8.8$ Hz), 6.89-6.86 (m, 1H), 6.77-6.75 (m, 1H), 6.70-6.67 (m, 2H), 6.52 (d, 2H, $J = 8.8$ Hz), 4.12 (brs, 2H), 3.76 (s, 3H), 3.27-3.17 (m, 2H), 2.34-2.27 (m, 2H), 1.79-1.77 (m, 2H), 1.44-1.39 (m, 2H), 1.27-1.22 (m, 2H). ¹³C NMR (CDCl₃): δ_C 147.4, 146.6, 137.5, 129.1, 121.9, 121.3, 116.9, 114.7, 110.4, 109.9, 57.6, 57.0, 55.4, 32.5, 24.8, 24.5. HPLC: Daicel Chiralcel AD-H, hexane / ⁱPrOH = 100/1, flow rate =1.0 ml / min: t_R = 13.7 min (1*R*, 2*R*), t_R = 27.9 min (1*S*, 2*S*). HRMS : Calcd for $C_{19}H_{23}ClN_2O$ (M+1)⁺ 331.1572 (100%), 333.1542 (32%), found 331.1559 (100%), 333.1555 (32%).

(1*S*,2*S*)-*N*-(3-Methoxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (19ja): Silica gel, hexane/ethyl acetate = 85 : 15. $[\alpha]_D^{21} = -14.4$ ($c = 1.19$, 56% ee, chloroform). IR (KBr) 3384, 3051, 2931, 2854, 1601,

1500, 1304, 1211, 1162, 1045, 828, 749, 691 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.18 (t, 2H, $J = 7.6$ Hz), 7.09 (t, 1H, $J = 8.0$ Hz), 6.72 (t, 1H, $J = 7.6$ Hz), 6.62 (d, 2H, $J = 7.6$ Hz), 6.27 (dd, 2H, $J_1 = 8.0$ Hz, $J_2 = 2.2$ Hz), 6.18 (t, 1H, $J = 2.2$ Hz), 3.85 (brs, 2H), 3.77 (s, 3H), 3.21-3.18 (m, 2H), 2.37-2.34 (m, 2H), 1.79-1.77 (m, 2H), 1.44-1.39 (m, 2H), 1.25-1.20 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 161.0, 149.2, 138.4, 130.2, 128.5, 127.9, 127.7, 106.7, 102.7, 99.6, 57.4, 57.3, 55.2, 32.7, 24.7. HPLC: Daicel Chiralcel OD, hexane / $^i\text{PrOH} = 4/1$, flow rate = 1.0 ml / min: $t_{\text{R}} = 17.5$ min (1*S*, 2*S*), $t_{\text{R}} = 24.0$ min (1*R*, 2*R*). HRMS : Calcd for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}$ ($\text{M}+1$)⁺ 297.1961, found 297.1955.

(1*S*,2*S*)-*N*-(2-Hydroxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (19ka):⁹ Silica gel, hexane/ethyl acetate = 7 : 3). $[\alpha]_{\text{D}}^{22} = -1.4$ ($c = 0.40$, 11% ee, chloroform). IR (KBr) 3384, 3251, 3050, 2937, 2853, 1600, 1501, 1302, 1211, 692 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.21-7.18 (m, 2H), 6.85-6.70 (m, 7H), 4.20 (brs, 2H), 3.20 (app. td, 1H, $J_1 = 10.0$ Hz, $J_2 = 3.6$ Hz), 3.00-2.96 (m, 2H), 2.29-2.21 (m, 2H), 1.77-1.75 (m, 2H), 1.39-1.30 (m, 2H), 1.27-1.20 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 148.0, 138.4, 137.6, 128.5, 127.9, 127.7, 121.2, 116.7, 110.3, 109.8, 56.8, 55.4, 32.5, 32.4, 24.8, 24.6. HPLC: Daicel Chiralcel OD, hexane / $^i\text{PrOH} = 9/1$, flow rate = 1.0 ml / min: $t_{\text{R}} = 16.0$ min (1*R*, 2*R*), $t_{\text{R}} = 21.9$ min (1*S*, 2*S*). HRMS : Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}$ ($\text{M}+1$)⁺ 283.1805, found 283.1800.

(1*S*,2*S*)-*N*-(2-Ethoxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (19la): Silica gel, hexane/ethyl acetate = 9:1. $[\alpha]_{\text{D}}^{23} = -2.2$ ($c = 1.28$, 72% ee, chloroform). IR (film) 3394, 3050, 2982, 2930, 2857, 1560, 1505, 1445, 1302, 1251, 1043, 741 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.18 (t, 2H, $J = 7.6$ Hz), 6.88 (td, 1H, $J_1 = 7.6$ Hz, $J_2 = 1.2$ Hz), 6.77-6.63 (m, 6H), 4.30 (brs, 2H), 4.06-3.93 (m, 2H), 3.31-3.22 (m, 2H), 2.38-2.29 (m, 2H), 1.80-1.77 (m, 2H), 1.47-1.39 (m, 2H), 1.31 (t, 3H, $J = 6.8$ Hz), 1.29-1.23 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 148.1, 138.4, 137.9, 128.5, 127.9, 127.7, 121.2, 116.8, 111.0, 110.7, 64.0, 57.4, 57.3, 32.7, 32.5, 24.8, 24.6, 15.0. HPLC: Daicel Chiralcel OD, hexane / $^i\text{PrOH} = 100/1$, flow rate = 1.0 ml / min: $t_{\text{R}} = 12.9$ min (1*R*, 2*R*), $t_{\text{R}} = 17.4$ min (1*S*, 2*S*). HRMS : Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}$ ($\text{M}+1$)⁺ 311.2118, found 311.2117.

(1*S*,2*S*)-*N*-(2-Phenoxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (19ma): Silica gel, hexane/ethyl acetate = 9 : 1. $[\alpha]_D^{24} = +27.5$ ($c = 1.33$, 70% ee, chloroform). IR (KBr) 3398, 3053, 2930, 2855, 1602, 1503, 1441, 1305, 1217, 745, 691 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.27-7.23 (m, 2H), 7.15-7.11 (m, 2H), 7.08-7.01 (m, 2H), 6.91-6.89 (m, 2H), 6.86-6.82 (m, 2H), 6.71-6.64 (m, 2H), 6.55-6.53 (m, 2H), 4.22 (brs, 1H), 3.85 (brs, 1H), 3.35-3.29 (m, 1H), 3.18 (app. td, 1H, $J_1 = 9.8$ Hz, $J_2 = 3.7$ Hz), 2.32-2.25 (m, 2H), 1.77-1.73 (m, 2H), 1.44-1.38 (m, 2H), 1.28-1.20 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 157.5, 143.9, 140.1, 138.4, 129.3, 128.5, 127.9, 127.8, 124.9, 122.8, 119.6, 117.5, 117.1, 112.2, 57.4, 56.8, 32.5, 32.4, 24.7, 24.4. HPLC: Daicel Chiralcel OD, hexane / $^i\text{PrOH} = 100/1$, flow rate = 1.0 ml / min: $t_{\text{R}} = 17.5$ min (1*S*, 2*S*), $t_{\text{R}} = 37.9$ min (1*R*, 2*R*). HRMS : Calcd for $\text{C}_{24}\text{H}_{26}\text{N}_2\text{O}$ ($\text{M}+1$)⁺ 359.2118, found 359.2123.

(1*S*,2*S*)-*N*-(2,4-Dimethoxyphenyl)-*N'*-phenylcyclohexane-1,2-diamine (19na): Silica gel, hexane/ethyl acetate = 9 : 1. $[\alpha]_D^{22} = -18.7$ ($c = 1.17$, 69% ee, chloroform). IR (KBr) 3384, 3049, 2931, 2855, 1601, 1512, 1459, 1288, 1204, 1153, 1036, 749 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.18 (t, 2H, $J = 7.4$ Hz), 6.71 (t, 1H, $J = 7.4$ Hz), 6.65-6.61 (m, 3H), 6.45 (t, 1H, $J = 2.7$ Hz), 6.43 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 2.7$ Hz), 4.02 (brs, 2H), 3.77 (s, 3H), 3.75 (s, 3H), 3.25 (app. td, 1H, $J_1 = 9.6$ Hz, $J_2 = 3.7$ Hz), 3.16 (app. td, 1H, $J_1 = 9.6$ Hz, $J_2 = 3.7$ Hz), 2.39-2.27 (m, 2H), 1.78-1.76 (m, 2H), 1.46-1.38 (m, 2H), 1.28-1.20 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 152.3, 148.8, 138.4, 131.7, 128.5, 127.9, 127.7, 111.5, 103.9, 99.4, 64.0, 57.8, 57.3, 55.9, 55.5, 32.5, 32.4, 24.8, 24.6. HPLC: Daicel Chiralcel OD-H, hexane / $^i\text{PrOH} = 30/1$, flow rate = 1.0 ml / min: $t_{\text{R}} = 11.9$ min (1*R*, 2*R*), $t_{\text{R}} = 22.0$ min (1*S*, 2*S*). HRMS : Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2$ ($\text{M}+1$)⁺ 327.2067, found 327.2061.

***cis*-1-(2-Methoxyphenyl)-2,3-dimethylaziridine (20a):** IR (film) 3065, 2992, 2926, 2833, 1591, 1496, 1456, 1237, 1124, 1029, 743 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 6.93-6.83 (m, 2H), 6.81 (t, 2H, $J = 7.6$ Hz), 3.86 (s, 3H), 2.11 (dq, 2H, $J_1 = 6.0$ Hz, $J_2 = 4.0$ Hz), 1.35 (d, 6H, $J = 6.0$ Hz). ^{13}C NMR (CDCl_3): δ_{C} 152.8, 144.2, 122.4, 120.6, 119.9, 110.8, 55.6, 39.9, 13.2. HRMS: Calcd for $\text{C}_{11}\text{H}_{15}\text{NO}$ ($\text{M}+\text{H}^+$) 178.1226, found 178.1229.

cis-1-(2-Methoxyphenyl)-2,3-dipropylaziridine (20b): IR (film) 3070, 2958, 2870, 2831, 1592, 1497, 1456, 1235, 1124, 1031 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 6.93-6.78 (m, 4H), 3.84 (s, 3H), 2.05-2.02 (m, 2H), 1.73-1.49 (m, 8H), 1.01 (t, 6H, $J = 7.0$ Hz). ^{13}C NMR (CDCl_3): δ_{C} 152.8, 144.1, 122.5, 120.5, 120.1, 110.6, 55.2, 44.8, 30.7, 21.2, 14.4. HRMS: Calcd for $\text{C}_{15}\text{H}_{23}\text{NO}$ ($\text{M}+\text{H}^+$) 234.1852, found 234.1856.

6-(2-Methoxyphenyl)-6-aza-bicyclo[3.1.0]hexane (20c): IR (KBr) 3023, 2949, 2852, 1592, 1496, 1379, 1259, 1228, 1119, 1030, 870, 744 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 6.88 (t, 2H, $J = 7.7$ Hz), 6.82-6.77 (m, 2H), 3.85 (s, 3H), 2.68-2.67 (m, 2H), 2.14-2.09 (m, 2H), 1.65-1.50 (m, 4H). ^{13}C NMR (CDCl_3): δ_{C} 152.5, 142.7, 122.1, 120.8, 120.6, 111.0, 55.5, 46.1, 27.5, 20.8. HRMS: Calcd for $\text{C}_{12}\text{H}_{15}\text{NO}$ ($\text{M}+\text{H}^+$) 190.1226, found 190.1222.

3-Carbo-tert-butoxy-6-(2-methoxyphenyl)-3,6-diaza-bicyclo[3.1.0]hexane (20d): IR (KBr) 3062, 2974, 2873, 1695, 1592, 1498, 1381, 1260, 1174, 1110, 1029, 865, 748 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 6.93-6.90 (m, 1H), 6.83-6.78 (m, 3H), 3.86-3.78 (m, 2H), 3.82 (s, 3H), 3.41-3.34 (m, 2H), 2.90-2.87 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (CDCl_3): δ_{C} 154.6, 152.4, 140.2, 123.3, 120.6, 120.2, 111.1, 79.4, 55.6, 48.1, 47.8, 44.1, 43.4, 28.5. HRMS: Calcd for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_3$ ($\text{M}+\text{H}^+$) 291.1703, found 291.1692.

N-(2-Methoxyphenyl)-2,3-iminotetralin (20e): IR (KBr) 3062, 3001, 2906, 2830, 1592, 1496, 1454, 1264, 1230, 1122, 1028, 743 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.12-7.07 (m, 4H), 6.96-6.88 (m, 2H), 6.84-6.77 (m, 2H), 3.85 (s, 3H), 3.32 (m, 4H, $J = 16.8$ Hz), 2.63-2.61 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 152.6, 143.4, 133.1, 129.3, 126.2, 122.3, 120.42, 120.40, 110.8, 55.5, 39.4, 29.7. HRMS: Calcd $\text{C}_{17}\text{H}_{17}\text{NO}$ ($\text{M}+\text{H}^+$) 252.1383, found 252.1383.

(1S,2S)-N-(2-Methoxyphenyl)-N'-(4-bromophenyl)butane-2,3-diamine (21ai): Silica gel, hexane/ethyl acetate = 85:15). $[\alpha]_{\text{D}}^{23} = +17.7$ ($c = 2.00$, 53 % ee, chloroform). IR (film) 3402, 3056, 2929, 1595, 1499, 1456, 1246, 1221, 1027, 813, 738 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.26 (m, 2H, $J = 8.7$ Hz), 6.91-6.87 (m, 1H), 6.80-6.78 (m, 1H), 6.72-6.68 (m, 2H), 6.52 (d, 2H, $J = 8.7$ Hz), 4.05 (brs, 2H), 3.83 (s, 3H), 3.62-3.56 (m, 2H), 1.24-1.20 (m, 6H). ^{13}C NMR (CDCl_3): δ_{C} 147.2, 146.7, 137.2, 132.1, 121.4, 116.9, 115.2, 110.7, 109.8, 109.0, 55.5, 52.6, 52.2, 16.9, 16.8. HPLC: Daicel Chiralcel OD,

hexane / ⁱPrOH = 100/1, flow rate = 1.0 ml / min: t_R = 19.8 min (minor), t_R = 26.4 min (major). HRMS : Calcd for C₁₇H₂₁BrN₂O (M+1)⁺ 349.0910 (100 %), 351.0895 (97 %), found 349.0902 (100 %), 351.0898 (97 %).

(1S,2S)-N-(2-Methoxyphenyl)-N'-phenyloctane-4,5-diamine (21ba): Silica gel, hexane/ethyl acetate = 10 : 1. $[\alpha]_D^{21}$ = -5.0 (c = 1.49, 61% ee, chloroform). IR (film) 3406, 3050, 2956, 2869, 1600, 1506, 1458, 1250, 1222, 1030, 739, 692 cm⁻¹. ¹H NMR (CDCl₃): δ_H 7.17 (app. t, 2H, J = 7.4 Hz), 6.88 (app. t, 1H, J = 7.4 Hz), 6.78 (app. d, 1H, J = 8.1 Hz), 6.70-6.63 (m, 5H), 4.15 (brs, 2H), 3.85 (s, 3H), 3.55-3.51 (m, 2H), 1.63-1.58 (m, 2H), 1.50-1.41 (m, 4H), 1.38-1.32 (m, 2H), 0.88 (t, 6H, J = 7.0 Hz). ¹³C NMR (CDCl₃): δ_C 148.7, 146.8, 138.6, 129.4, 121.4, 117.0, 116.0, 113.1, 110.2, 109.8, 56.1, 55.9, 55.6, 35.1, 35.0, 20.0, 19.9, 14.3. HPLC: Daicel Chiralcel OD, hexane / ⁱPrOH = 500/1, flow rate = 1.0 ml / min: t_R = 17.2 min (major), t_R = 22.4 min (minor). HRMS : Calcd for C₂₁H₃₀N₂O (M+1)⁺ 327.2431, found 327.2422.

(1S,2S)-N-(2-Methoxyphenyl)-N'-(4-bromophenyl)octane-4,5-diamine (21bi): Silica gel, hexane/ethyl acetate = 9:1. $[\alpha]_D^{21}$ = -4.0 (c = 1.96, 62% ee, chloroform). IR (film) 3406, 3056, 2956, 2869, 1596, 1502, 1316, 1249, 1029, 812, 737 cm⁻¹. ¹H NMR (CDCl₃): δ_H 7.23 (d, 2H, J = 8.6 Hz), 6.87 (app. t, 1H, J = 7.8 Hz), 6.78 (app. d, 1H, J = 7.8 Hz), 6.68-6.64 (m, 2H), 6.50 (d, 2H, J = 8.6 Hz), 4.05 (brs, 2H), 3.84 (s, 3H), 3.50-3.46 (m, 2H), 1.62-1.58 (m, 2H), 1.50-1.43 (m, 4H), 1.36-1.32 (m, 2H), 0.87 (t, 6H, J = 6.7 Hz). ¹³C NMR (CDCl₃): δ_C 147.7, 146.9, 138.3, 132.1, 121.4, 116.4, 114.7, 110.3, 109.8, 108.3, 56.4, 56.1, 55.6, 35.2, 35.0, 19.95, 19.90, 14.3, 14.2. HPLC: Daicel Chiralcel OD, hexane / ⁱPrOH = 100/1, flow rate = 1.0 ml / min: t_R = 8.7 min (major), t_R = 11.1 min (minor). HRMS : Calcd for C₂₁H₂₉BrN₂O (M+1)⁺ 405.1536 (100 %), 407.1516 (97 %), found 405.1541 (100 %), 407.1522 (97 %).

(1S,2S)-N-(2-Methoxyphenyl)-N'-phenylcyclopentane-1,2-diamine (21ca): Silica gel, hexane/ethyl acetate = 9:1. $[\alpha]_D^{24}$ = +27.2 (c = 1.50, 50% ee, chloroform). IR (film) 3400, 3051, 2955, 2870, 2834, 1601, 1508, 1310, 1243, 1222, 1028, 742 cm⁻¹. ¹H NMR (CDCl₃): δ_H 7.19 (app. t, 2H, J = 7.4 Hz), 6.87 (td, 1H, J_1 = 7.7 Hz, J_2 = 1.3 Hz), 6.80-6.65 (m, 5H), 4.10 (brs, 2H), 3.84 (s, 3H), 3.71-3.61 (m, 2H),

2.32-2.22 (m, 2H), 1.87-1.80 (m, 2H), 1.63-1.54 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 147.0, 138.4, 137.7, 128.5, 127.9, 127.7, 121.4, 116.7, 110.7, 109.5, 60.8, 60.5, 55.4, 31.5, 31.4, 21.7. HPLC: Daicel Chiralcel OD, hexane / i PrOH = 40/1, flow rate = 1.0 ml / min: t_{R} = 21.1 min (minor), t_{R} = 29.3 min (major). HRMS : Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}$ ($\text{M}+1$) $^{+}$ 283.1805, found 283.1810.

(1S,2S)-1-Carbo-*tert*-butoxy-3-(2-methoxyphenylamino)-4-(phenylamino)pyrrolidine (21da) : Silica gel, hexane/ethyl acetate = 75:25. white solid. After a single crystallization using ethanol, enantioenriched product was obtained in 95% ee (mp. 183-184 °C). $[\alpha]_{\text{D}}^{23} = +22.4$ ($c = 1.66$, 95% ee, chloroform). IR (KBr) 3355, 3057, 2974, 2936, 2890, 2830, 1687, 1602, 1513, 1408, 1171, 1136, 747 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.23-7.17 (m, 2H), 6.88-6.84 (m, 1H), 6.81-6.70 (m, 3H), 6.68-6.61 (m, 3H), 4.25 (brs, 2H), 3.96-3.90 (m, 2H), 3.89-3.80 (m, 2H), 3.84 (s, 3H), 3.36-3.32 (m, 2H), 1.47 (s, 9H). ^{13}C NMR (CDCl_3): δ_{C} 154.8, 147.1, 146.7, 136.5, 129.6, 121.3, 118.4, 117.7, 113.5, 110.6, 109.8, 80.0, 57.4, 55.5, 50.4, 28.6. HPLC: Daicel Chiralcel AD-H, hexane / i PrOH = 19/1, flow rate = 1.0 ml / min: t_{R} = 28.3 min (minor), t_{R} = 33.6 min (major). HRMS : Calcd for $\text{C}_{22}\text{H}_{29}\text{N}_3\text{O}_3$ ($\text{M}+1$) $^{+}$ 384.2282, found 384.2264.

(1S,2S)-*N*-(2-methoxyphenyl)-*N'*-phenyltetralin-2,3-diamine (21ea) : Silica gel, hexane/ethyl acetate = 9 : 1) white solid. After a single crystallization using methanol, only one enantiomer was obtained. (m.p.=152-153 °C). $[\alpha]_{\text{D}}^{25} = +120.4$ ($c = 1.12$, > 99% ee, chloroform). IR (KBr) 3396, 3051, 3016, 2930, 2835, 1600, 1506, 1307, 1245, 1223, 1124, 1028, 742 cm^{-1} . ^1H NMR (CDCl_3): δ_{H} 7.24-7.11 (m, 6H), 6.92 (app. td, 1H, $J_1 = 7.7$ Hz, $J_2 = 1.4$ Hz), 6.82-6.69 (m, 6H), 4.45 (brs, 1H), 3.96 (brs, 1H), 3.95-3.91 (m, 2H), 3.78 (s, 3H), 3.50-3.42 (m, 2H), 2.84-2.80 (m, 2H). ^{13}C NMR (CDCl_3): δ_{C} 147.5, 147.3, 137.2, 134.0, 133.9, 129.5, 129.4, 129.3, 126.51, 126.49, 121.4, 117.8, 117.1, 113.7, 110.6, 109.9, 55.5, 52.3, 51.9, 34.6, 34.5. HPLC: Daicel Chiralcel AD-H, hexane / i PrOH = 19/1, flow rate = 1.0 ml / min: t_{R} = 10.6 min (major), t_{R} = 12.4 min (minor). HRMS : Calcd for $\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}$ ($\text{M}+1$) $^{+}$ 345.1961, found 345.1968.

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