Rhodium-Catalyzed Ring-Opening Reactions of *N*-Boc-Azabenzonorbornadienes with Amine Nucleophiles

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Supporting Information

General. All moisture and air sensitive manipulations were carried out under a dried nitrogen atmosphere. NMR spectra were recorded on Varian Mercury NMR spectrometer (300 MHz for ^1H , 75 MHz for ^{13}C , 121 MHz for ^{31}P , and 282 MHz for ^{19}F). Chemical shifts are reported in δ ppm referenced to SiMe_4 standard for ^1H NMR, chloroform-*d* (δ 77.0) for ^{13}C NMR, an external 85% H_3PO_4 standard for ^{31}P NMR and an external CFCl_3 standard for ^{19}F NMR. IR spectra were obtained using a Perkin-Elmer Spectrum 1000 FT-IR spectrometer as a neat film on a NaCl plate. High resolution mass spectra were obtained from a Micromass 70S-250 mass spectrometer (EI) or an ABI/Sciex Qstar mass spectrometer (ESI). Optical rotations were measured on a Perkin-Elmer Model 243 Polarimeter and melting points were taken on a Fisher-Johns melting point apparatus. HPLC analysis was performed on an Agilent 1100 Series HPLC with Chiralcel OD, OD-H, AD or Chiralpak AS columns.

Materials. Dioxane, Et_2O , THF, THP, and toluene were distilled from sodium benzophenone ketyl immediately prior to use. CH_2Cl_2 and CH_3CN were distilled from calcium hydride. DMF was dried over MgSO_4 and stored over activated molecular sieves. Azabenzonorbornadienes **1f**,¹ **1g**,² **1h**,³ **1l**,⁴ **1m**,⁴ and **4a**⁵ were prepared according to the reported procedure.

Preparation of 1,4-Dihydro-1,4-epiazano-naphthalene-9-carbamic acid *tert*-butyl ester (1a): To a stirred solution of anthranilic acid (8.0g, 58.3 mmol) and trichloroacetic acid (67 mg, 0.4 mmol) in dry THF (120 mL) was slowly added isoamyl nitrite (13 mL, 93.3 mmol) at 0 °C for 30 min and the mixture was stirred at room temperature for 1.5 h. The dark yellow precipitate of benzenediazonium-2-carboxylate was collected by filtration and washed with cold THF using minimal suction for draining so as to prevent

complete drying. The salt was immediately transferred to a flask and 1,2-dichloroethane (100 mL) and *N*-*tert*-butyl 1-pyrrolicarboxylate (7.8 mL, 46.7 mmol) were added. The mixture was heated at 60 °C for 45 min and the black mixture was cooled to room temperature. After concentration under reduced pressure, the residue was purified by flash column chromatography (hexane/ethyl acetate = 95/5) and recrystallization with hexane to give 7.8 g of **1a** (55% yield). mp 70-72 °C (lit.⁶ mp 72-73 °C for **1a**); IR (NaCl, cm⁻¹) 2976, 2931, 1708, 1455, 1367, 1332, 1252, 1167, 1074, 857, 830, 782, 748, 694, 643. ¹H NMR (CDCl₃) δ 1.37 (s, 9H), 5.48 (bs, 2H), 6.94-6.98 (m, 4H), 7.22-7.29 (m, 2H); ¹³C NMR (CDCl₃) δ 155.3, 148.5, 143.1 (d, *J* = 85.0 Hz), 125.1, 121.0 (d, *J* = 31.5 Hz), 80.7, 66.7 (d, *J* = 47.3 Hz), 28.3.

Preparation of 1,4-Dihydro-1,4-epiazano-naphthalene-9-carbamic acid methyl ester (1b): To a solution of 1,4-dihydro-1,4-epiazano-naphthalene⁷ (0.5 g, 3.5 mmol) and triethylamine (2.5 mL) in dry CH₂Cl₂ (10 mL) was added methyl chloroformate (0.8 mL, 10.5 mmol) dropwise at 0 °C over 10 min and the reaction was stirred at room temperature for 12 h. The mixture was quenched with saturated NaHCO₃ solution and extracted with CH₂Cl₂. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/ethyl acetate = 90/10) to give 0.6 g of **1b** (85% yield). mp 48-50 °C; IR (NaCl, cm⁻¹) 3027, 2953, 1717, 1441, 1333, 1250, 1190, 1091, 952, 856, 813, 742, 695. ¹H NMR (CDCl₃) δ 3.61 (s, 3H), 5.54 (s, 2H), 6.93-6.96 (m, 4H), 7.23 (bs, 2H); ¹³C NMR (CDCl₃) δ 155.7, 148.1, 143.1 (d, *J* = 86.5 Hz), 125.1, 120.1 (d, *J* = 25.0 Hz), 66.2, 52.7. HRMS calcd for C₁₂H₁₁NO₂ (M⁺): 201.0789. Found: 201.0791. The azabenzonorbornadienes **1c**, **1d**, and, **1e** were prepared in a similar manner.

1,4-Dihydro-1,4-epiazano-naphthalene-9-carbamic acid benzyl ester (1c): 80% yield. mp 85-87 °C; IR (NaCl, cm⁻¹) 3031, 1710, 1454, 1387, 1326, 1244, 1071, 805, 748, 694. ¹H NMR (CDCl₃) δ 5.05 (s, 2H), 5.57 (s, 2H), 6.92-6.96 (m, 4H), 7.20-7.32 (m, 7H); ¹³C NMR (CDCl₃) δ 155.3, 148.1, 143.1 (d, *J* = 93.3 Hz), 136.3, 128.5, 128.1, 127.8, 125.2, 121.1 (d, *J* = 35.7 Hz), 67.2, 66.3. HRMS calcd for C₁₈H₁₅NO₂ (M⁺): 277.1102. Found: 277.1102.

(1,4-Dihydro-1,4-epiazano-naphthalen-9-yl)-benzamide (1d): 90% yield. mp 94-97 °C; IR (NaCl, cm⁻¹) 3058, 1714, 1647, 1448, 1370, 1258, 1071, 784. ¹H NMR (CDCl₃) δ 5.52 (s, 1H), 6.00 (s, 1H), 6.88-6.89 (m, 1H), 6.94-7.00 (m, 2H), 7.16-7.17 (m, 2H), 7.34-7.54 (m, 6H); ¹³C NMR (CDCl₃) δ 167.5, 143.5 (d, *J* = 23.8 Hz), 134.5, 131.0,

128.5, 127.9, 125.3 (d, $J = 25.8$ Hz), 121.6, 120.4, 66.1 (d, $J = 43.2$ Hz). HRMS calcd for $C_{17}H_{13}NO$ (M^+): 247.0997. Found: 247.0997.

1-(1,4-Dihydro-1,4-epiazano-naphthalen-9-yl)-acetamide (1e): 85% yield, mp 63-64 °C; IR (NaCl, cm^{-1}) 3072, 1654, 1444, 1394, 1337, 1247, 1032, 795, 752. 1H NMR ($CDCl_3$) δ 1.95 (s, 3H), 5.50 (s, 1H), 5.87 (s, 1H), 6.95-6.98 (m, 3H), 7.05 (dd, $J = 5.6$ Hz, 2.4 Hz, 1H), 7.24-7.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 166.8, 148.4, 148.0, 144.3, 142.3, 125.3, 125.0, 121.4, 120.3, 66.2, 63.3, 21.4. HRMS calcd for $C_{12}H_{11}NO$ (M^+): 185.0840. Found: 185.0833.

Preparation of 1,4-dihydro-1,4-epiazano-5,8-dimethylnaphthalene-9-carbamic acid *tert*-butyl ester (1i): To a stirred solution of 3,6-dimethylantranilic acid⁸ (14.0 g, 84.7 mmol) and trichloroacetic acid (0.2 g, 0.9 mmol) in dry THF (100 mL) was slowly added isoamyl nitrite (14 mL, 101.7 mmol) at -20 °C for 40 min by syringe pump under nitrogen atmosphere. The mixture was allowed to stir at -20 °C for another 2 h. Then, *N-tert*-butyl 1-pyrrolicarboxylate (11 mL, 67.8 mmol) and 1,2-dichloroethane (100 mL) was added and the mixture was heated immediately at 80 °C for 30 min. The resulting mixture was then cooled to room temperature and all volatile substrates were removed under reduced pressure. The residue was purified by flash column chromatography (hexane/ethyl acetate = 95/5) and recrystallization with hexane to give 6.9 g (30% yield) of **1i**. mp 95-97 °C; IR (NaCl, cm^{-1}) 2974, 1709, 1490, 1455, 1366, 1329, 1253, 1167, 1073. 1H NMR ($CDCl_3$) δ 1.38 (s, 9H), 2.29 (s, 6H), 5.53-5.57 (m, 2H), 6.67 (s, 2H), 6.95-6.99 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 155.5, 146.3, 142.9 (d, $J = 97.9$ Hz), 127.9 (d, $J = 38.5$ Hz), 126.6, 80.6, 65.2 (d, $J = 42.9$ Hz), 28.3, 17.9. Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.19; H, 7.71; N, 5.19.

Preparation of 1,4-dihydro-1,4-epiazano-5,6,7,8-tetramethyl-naphthalene-9-carbamic acid *tert*-butyl ester (1j): To a solution of 1,2-dibromotetramethylbenzene⁹ (20.0 g, 68.5 mmol) prepared from commercially available tetramethylbenzene according to previously reported procedure¹⁰ in dry toluene (200 mL) was slowly added *n*-butyllithium solution in hexane (95 mL, 150.7 mmol) diluted with dry toluene (24 mL) and *N-tert*-butyl 1-pyrrolicarboxylate solution in dry toluene (14 mL, 82.2 mmol in 110 mL of toluene) at 0 °C by syringe pump for 3 h under nitrogen atmosphere. The mixture was allowed to stir at room temperature for 48 h and was quenched with water. The resulting mixture was extracted with ethyl acetate and the organic phase was dried over anhydrous $MgSO_4$. After removal of all volatile solvents under reduced pressure, flash column chromatography on silica gel (hexane/ethyl acetate = 95/5) and

recrystallization with hexane gave 7.0 g (34% yield) of **1j**. mp 125-127 °C; IR (NaCl, cm^{-1}) 2973, 1708, 1366, 1330, 1257, 1167, 1073. ^1H NMR (CDCl_3) δ 1.39 (s, 9H), 2.11 (s, 6H), 2.24 (s, 6H), 5.56-5.60 (m, 2H), 6.94-6.98 (m, 2H); ^{13}C NMR (CDCl_3) δ 155.3, 143.5, 143.1 (d, $J = 101.6$ Hz), 131.6, 127.2 (d, $J = 40.1$ Hz), 80.5, 65.8 (d, $J = 46.1$ Hz), 28.4, 16.5, 16.0. Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_2$: C, 76.32; H, 8.42; N, 4.68. Found: C, 76.71; H, 8.59; N, 4.65.

1,4-dihydro-1,4-epiazano-6,7-dimethyl-naphthalene-9-carbamic acid *tert*-butyl ester (1k): Prepared from 1,2-dibromo-4,5-dimethylbenzene¹¹ in a similar manner to **1j** in 35% yield. mp 93-95 °C; IR (NaCl, cm^{-1}) 2974, 1706, 1593, 1455, 1366, 1328, 1251, 1167, 1071. ^1H NMR (CDCl_3) δ 1.38 (s, 9H), 2.17 (s, 6H), 5.42 (m, 2H), 6.95 (m, 2H), 7.05 (s, 2H); ^{13}C NMR (CDCl_3) δ 155.2, 146.0, 143.3 (d, $J = 81.2$ Hz), 132.6, 122.9 (d, $J = 27.1$ Hz), 80.6, 66.4 (d, $J = 47.5$ Hz), 28.4, 19.9. Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.10; H, 7.89; N, 5.07.

Rhodium-Catalyzed Asymmetric Ring-Opening of 1a with Pyrrolidine (2a) in the presence of triethylamine hydrochloride in tetrahydropyran. The reaction conditions and results are summarized in Tables 2 and 6. A typical procedure is given for the reaction of **1a** with 5.0 eq. of pyrrolidine (**2a**) in the presence of 2.5 mol% of $[\text{Rh}(\text{cod})\text{Cl}]_2$ and 11.0 mol% of (*S,S'*)-(*R,R'*)- C_2 -Ferriphos (**4a**) (entry 14 in Table 2).

To a stirred solution of **1a** (80 mg, 0.33 mmol), triethylamine hydrochloride (45 mg, 0.33 mmol), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (4 mg, 8 μmol), and **4a** (26 mg, 36 μmol) in dry tetrahydropyran (1.6 mL) was added pyrrolidine (0.14 mL, 1.6 mmol) and the mixture was allowed to stir at 80 °C for 72 h under nitrogen atmosphere. The resulting mixture was quenched with 1N NaOH solution and was extracted with CH_2Cl_2 . The separated organic layer was dried over anhydrous MgSO_4 and was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/ethyl acetate = 70/30) to give 80 mg (78% yield) of **3aa**.

(1*S*,2*S*)-(2-Pyrrolidin-1-yl-1,2-dihydro-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3aa): >99% ee by HPLC analysis with a chiral column (Chiralcel OD-H, hexane/2-propanol = 90/10, 1.0 mL/min), t_{R} (*S*)-(+), 9.4 min (major); (*R*)-(−), 20.8 min (minor). $[\alpha]_{\text{D}}^{25} +282.4$ (c 1.10, CHCl_3) for **3aa** of >99% ee. mp 84-87 °C; IR (NaCl, cm^{-1}) 3450, 2809, 2360, 1716, 1653, 1557, 1251, 1169, 1005. ^1H NMR (CDCl_3) δ 1.42 (s, 9H), 1.68 (m, 4H), 2.59-2.69 (m, 4H), 3.34 (t, $J = 6.0$ Hz, 1H), 4.76 (d, $J = 6.0$ Hz, 1H), 4.93 (bs, 1H), 5.97 (dd, $J = 9.9, 3.0$ Hz, 1H), 6.60 (d, $J = 9.9$ Hz, 1H), 7.06-7.08 (m, 1H), 7.17-7.24 (m, 2H), 7.31-7.33 (m, 1H); ^{13}C NMR (CDCl_3) δ 155.2, 134.9, 132.2,

129.2, 128.4, 128.1, 126.8, 126.2, 61.2, 50.1, 28.4, 23.5. HRMS (EI) calcd for $C_{19}H_{26}N_2O_2$ (M^+): 314.1994. Found: 314.1991.

(1*S*,2*S*)-(2-(Pyrrolidin-1-yl)-1,2-dihydro-naphthalen-1-yl)-carbamic acid methyl ester (3ba): 63% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 90/10, 1.0 mL/min), t_R (*R*)-(-), 7.9 min (minor); (*S*)-(+), 15.2 min (major). $[\alpha]_D^{25} +229.0$ (*c* 0.82, $CHCl_3$) for **3ba** of 63% ee. IR (NaCl, cm^{-1}) 3317, 2962, 1718, 1528, 1451, 1351, 1256, 1192, 1119, 1040, 780. 1H NMR ($CDCl_3$) δ 1.67-1.71 (m, 4H), 2.58-2.68 (m, 4H), 3.36 (t, $J = 4.8$ Hz, 1H), 3.65 (s, 3H), 4.91-4.96 (m, 2H), 5.98 (dd, $J = 9.9, 4.8$ Hz, 1H), 6.63 (d, $J = 9.9$ Hz, 1H), 7.08-7.11 (m, 1H), 7.18-7.26 (m, 2H), 7.31 (d, $J = 6.9$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 156.5, 134.6, 132.2, 129.4, 128.5, 128.4, 128.4, 126.9, 126.2, 61.2, 52.2, 50.9, 50.2, 23.6. HRMS calcd for $C_{16}H_{20}N_2O_2$ (M^+): 272.1524. Found: 272.1517.

(1*S*,2*S*)-(2-Pyrrolidin-1-yl)-1,2-dihydro-naphthalen-1-yl)-carbamic acid benzyl ester (3ca): 68% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 90/10, 1.0 mL/min), t_R (*R*)-(-), 7.9 min (minor); (*S*)-(+), 9.7 min (major). $[\alpha]_D^{25} +200.6$ (*c* 0.80, $CHCl_3$) for **3ca** of 68% ee; mp 90-95 °C; IR (NaCl, cm^{-1}) 3318, 2963, 1711, 1498, 1453, 1251, 1118, 1038, 779, 746, 696. 1H NMR ($CDCl_3$) δ 1.70-1.88 (m, 4H), 2.59-2.68 (m, 4H), 3.37 (t, $J = 4.8$ Hz, 1H), 4.99 (bs, 2H), 5.05-5.12 (m, 2H), 5.97 (dd, $J = 9.9, 4.8$ Hz, 1H), 6.61 (d, $J = 9.9$ Hz, 1H), 7.07-7.32 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 155.8, 136.6, 134.6, 132.2, 129.3, 128.6, 128.5, 128.4, 128.3, 128.2, 126.9, 126.2, 66.8, 61.2, 50.9, 50.2, 23.6. HRMS calcd for $C_{22}H_{24}N_2O_2$ (M^+): 348.1837. Found: 348.1836.

(1*S*,2*S*)-*N*-(2-pyrrolidin-1-yl)-1,2-dihydro-naphthalen-1-yl)-benzamide (3da): 96% ee by HPLC analysis with a chiral column (Chiralcel OD-H, hexane/2-propanol = 90/10, 1.0 mL/min), t_R (*R*)-(-), 11.3 min (minor); (*S*)-(+), 19.1 min (major). $[\alpha]_D^{25} +372.4$ (*c* 1.00, $CHCl_3$) for **3da** of 96% ee. mp 114-116 °C; IR (NaCl, cm^{-1}) 3299, 3030, 2963, 2803, 1634, 1579, 1537, 1488, 1337, 1126, 779, 749, 706, 693. 1H NMR ($CDCl_3$) δ 1.69-1.73 (m, 4H), 2.63-2.66 (m, 2H), 2.76-2.79 (m, 2H), 3.49 (t, $J = 4.0$ Hz, 1H), 5.51 (dd, $J = 8.1, 3.3$ Hz, 1H), 6.05 (dd, $J = 9.6, 4.5$ Hz, 1H), 6.22 (d, $J = 8.1$ Hz, 1H), 6.69 (d, $J = 9.9$ Hz, 1H), 7.15 (dd, $J = 7.2, 1.5$ Hz, 1H), 7.19-7.30 (m, 2H), 7.35-7.41 (m, 3H), 7.47 (ddd, $J = 7.2, 6.0, 1.5$ Hz, 1H), 7.71 (dd, $J = 6.9, 1.5$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 166.7, 134.6, 134.4, 132.5, 131.6, 129.4, 128.8, 128.6, 128.5, 127.1, 126.6, 60.9, 50.3, 49.5, 23.7. HRMS calcd for $C_{21}H_{23}N_2O$ [$M+H^+$]: 319.1804. Found: 319.1813.

(1*S*,2*S*)-*N*-(2-pyrrolidin-1-yl-1,2-dihydro-naphthalen-1-yl)-acetamide (3ea): 99% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 90/10, 1.0 mL/min), *t_R* (*R*)-(-), 12.5 min (minor); (*S*)-(+), 14.6 min (major). $[\alpha]_D^{25} +313.0$ (*c* 1.00, CHCl₃) for **3ea** of 99% ee. IR (NaCl, cm⁻¹) 3279, 2966, 2236, 1650, 1537, 1451, 1371, 1293, 1128, 999, 923, 910, 781, 731. ¹H NMR (CDCl₃) δ 1.66-1.69 (m, 4H), 1.91 (s, 3H), 2.54-2.59 (m, 2H), 2.66-2.72 (m, 2H), 3.33 (t, *J* = 4.2 Hz, 1H), 5.29 (dd, *J* = 8.2, 3.2 Hz, 1H), 5.79 (d, *J* = 8.0 Hz, 1H), 5.98 (dd, *J* = 9.9, 4.8 Hz, 1H), 6.63 (d, *J* = 9.6 Hz, 1H), 7.09-7.11 (m, 1H), 7.19-7.28 (3H); ¹³C NMR (CDCl₃) δ 169.1, 134.5, 132.2, 129.2, 128.6, 128.3, 128.2, 126.8, 126.3, 60.6, 50.0, 48.9, 23.5, 23.4. HRMS calcd for C₁₆H₂₀N₂O (M⁺): 254.1419. Found: 254.1411.

(1*S*,2*S*)-*N*-Phenyl-(2-pyrrolidin-1-yl-1,2-dihydro-naphthalen-1-yl)amine (3fa): 25% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 95/5, 1.0 mL/min), *t_R* (*R*)-(-), 4.9 min (minor); (*S*)-(+), 5.4 min (major). $[\alpha]_D^{25} +58.6$ (*c* 1.22, CHCl₃) for **3fa** of 25% ee. IR (NaCl, cm⁻¹) 3332, 2963, 2361, 2343, 1722, 1600, 1501, 1451, 1430, 1314, 1261, 1123, 1056, 1032, 992, 908, 749, 693. ¹H NMR (CDCl₃) δ 1.72 (m, 4H), 2.60-2.65 (m, 4H), 3.73 (bs, 1H), 4.12 (bs, 1H), 4.58 (bs, 1H), 6.03 (dd, *J* = 9.9, 4.4 Hz, 1H), 6.68-6.74 (m, 4H), 7.11-7.29 (m, 6H); ¹³C NMR (CDCl₃) δ 147.9, 136.4, 132.5, 129.4, 128.1, 127.9, 126.7, 117.8, 113.8, 58.7, 55.5, 49.0, 23.7. HRMS calcd for C₂₀H₂₂N₂ (M⁺): 290.1782. Found: 290.1783.

(1*S*,2*S*)-(2-pyrrolidin-1-yl-1,2-dihydronaphthalen-1-yl)-*p*-toluenesulfonylamine (3ha): 10% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 90/10, 1.0 mL/min), *t_R* (*R*)-(-), 7.9 min (minor); (*S*)-(+), 9.7 min (major). $[\alpha]_D^{25} +31.3$ (*c* 1.22, CHCl₃) for **3ha** of 10% ee; mp 140-145 °C; IR (NaCl, cm⁻¹) 3496, 3035, 2967, 1454, 1193, 1117, 1048. ¹H NMR (CDCl₃) δ 1.58-1.63 (m, 4H), 2.29-2.36 (m, 2H), 2.45 (s, 3H), 2.49-2.58 (m, 2H), 3.89 (d, *J* = 4.2 Hz, 1H), 4.45 (d, *J* = 3.7 Hz, 1H), 4.70 (bs, 1H), 5.93 (dd, *J* = 9.9, 4.8 Hz, 1H), 6.61 (d, *J* = 9.9 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 7.02-7.08 (m, 2H), 7.17-7.22 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (CDCl₃) δ 143.4, 138.0, 133.6, 132.1, 129.7, 129.4, 128.5, 128.2, 128.1, 127.4, 126.9, 125.5, 61.2, 53.6, 49.9, 23.4, 21.6. Anal. Calcd for C₂₁H₂₄N₂O₂S: C, 68.45; H, 6.56; N, 7.60. Found: C, 68.51; H, 6.62; N, 7.55.

Rhodium-Catalyzed Asymmetric Ring-Opening of 1a with Piperidine (2b) under the neat reaction conditions. The reaction conditions and results are summarized in Tables, 3-6. A typical procedure is given for the reaction of **1a** with 5.0 eq. of piperidine

(**2b**) in the presence of 2.5 mol% of [Rh(cod)Cl]₂ and 11.0 mol% of **4a** (entry 1 in Table 3).

To a 10 mL round bottom flask were added **1a** (80 mg, 0.33 mmol), [Rh(cod)Cl]₂ (4 mg, 8 μmol), and **4a** (26 mg, 36 μmol) under nitrogen atmosphere. Then, piperidine (0.17 mL, 1.66 mmol) was added and the mixture was allowed to stir at 80 °C for 60 h. The resulting mixture was cooled to room temperature and diluted in CH₂Cl₂. The black solution was filtered through Celite and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/ethyl acetate = 70/30) to give 90 mg (83% yield) of **3ab** as a semisolid.

(1*S*,2*S*)-(2-Piperidin-1-yl-1,2-dihydro-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3ab**):** 97% ee by HPLC analysis with a chiral column (Chiralcel OD-H, hexane/2-propanol = 90/10, 1.0 mL/min), *t_R* (*S*)-(+), 9.8 min (major); (*R*)-(-), 25.1 min (minor). [α]_D²⁵ +261.0 (*c* 1.10, CHCl₃) for **3ab** of 97% ee. mp 118-122 °C; IR (NaCl, cm⁻¹) 3448, 2978, 2288, 1713, 1549, 1251, 1170, 1005, 760. ¹H NMR (CDCl₃) δ 1.45 (s, 9H), 1.37-1.50 (m, 6H), 2.42-2.44 (m, 2H), 2.56-2.61 (m, 2H), 3.37 (t, *J* = 6.0 Hz, 1H), 4.60 (bs, 1H), 5.03 (bs, 1H), 5.97 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.62 (d, *J* = 9.9 Hz, 1H), 7.06-7.09 (m, 1H), 7.19-7.23 (m, 2H), 7.34-7.36 (m, 1H); ¹³C NMR (CDCl₃) δ 155.3, 135.8, 132.6, 129.4, 128.2, 128.0, 127.8, 126.8, 126.4, 64.9, 50.1, 48.1, 29.8, 28.6, 26.6, 24.7. HRMS (EI) calcd for C₂₀H₂₈N₂O₂ (M⁺): 328.2150. Found: 328.2145.

(1*S*,2*S*)-[2-(4-Phenyl-piperazin-1-yl)-1,2-dihydro-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (3ac**):** 92% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 0.5 mL/min), *t_R* (*R*)-(-), 7.2 min (minor); (*S*)-(+), 8.5 min (major). [α]_D²⁵ +319.1 (*c* 1.00, CHCl₃) for **3ac** of 94% ee. mp 166-167 °C; IR (NaCl, cm⁻¹) 3453, 2979, 2328, 1711, 1562, 1483, 1367, 1169. ¹H NMR (CDCl₃) δ 1.44 (s, 9H), 2.68-2.70 (m, 2H), 2.76-2.82 (m, 2H), 3.10 (t, *J* = 4.8 Hz, 4H), 3.47 (t, *J* = 6.0 Hz, 1H), 4.60 (d, *J* = 6.0 Hz, 1H), 5.06 (bs, 1H), 6.00 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.66 (d, *J* = 9.9 Hz, 1H), 6.82 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 7.09-7.11 (m, 1H), 7.25 (m, 4H), 7.37 (m, 1H); ¹³C NMR (CDCl₃) δ 155.4, 151.6, 135.4, 132.5, 129.8, 129.2, 128.4, 128.3, 127.9, 126.9, 125.5, 119.7, 116.2, 79.6, 64.0, 49.8, 48.8, 48.6, 29.8, 28.6. HRMS (EI) calcd for C₂₅H₃₁N₃O₂ (M⁺): 405.2416. Found: 405.2411.

(1*S*,2*S*)-(2-Morpholin-4-yl-1,2-dihydro-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3ad**):** 97% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 0.5 mL/min), *t_R* (*S*)-(+), 15.3 min (major); (*R*)-(-), 16.7 min (minor). [α]_D²⁵ +337.7 (*c* 1.00, CHCl₃) for **3ad** of 97% ee. mp 167-168 °C; IR (NaCl,

cm⁻¹) 3448, 2978, 2281, 1714, 1550, 1367, 1250, 1170, 1005, 757. ¹H NMR (CDCl₃) δ 1.45 (s, 9H), 2.52-2.54 (m, 2H), 2.62-2.65 (m, 2H), 3.36 (t, *J* = 4.8 Hz, 1H), 3.61-3.62 (m, 4H), 4.59 (d, *J* = 6.0 Hz, 1H), 5.02 (bs, 1H), 5.97 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.65 (dd, *J* = 9.9, 1.2 Hz, 1H), 7.08-7.12 (m, 1H), 7.21-7.28 (m, 2H), 7.35-7.37 (m, 1H); ¹³C NMR (CDCl₃) δ 155.2, 135.1, 132.3, 129.7, 128.2, 128.1, 127.7, 126.7, 125.1, 79.5, 67.3, 64.2, 49.2, 48.6, 28.4. Anal. Calcd for C₁₉H₂₆N₂O₃: C, 69.06; H, 7.93; N, 8.48. Found: C, 68.86; H, 7.97; N, 8.39.

(1*S*,2*S*)-(2-Dibenzylamino-1,2-dihydro-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3ae): 97% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 99/1, 0.5 mL/min), *t_R* (*S*)-(+), 15.4 min (major); (*R*)-(-), 17.0 min (minor). [α]_D²⁵ +150.4 (*c* 1.00, CHCl₃) for **3ae** of 97% ee. ¹H NMR (CDCl₃) δ 1.53 (s, 9H), 3.43-3.50 (m, 1H), 3.55 (d, *J* = 13.5 Hz, 2H), 3.74 (d, *J* = 13.5 Hz, 2H), 4.48 (d, *J* = 9.0 Hz, 1H), 5.24 (t, *J* = 9.0 Hz, 1H), 6.05 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.59 (dd, *J* = 9.9, 1.8 Hz, 1H), 7.02-7.05 (m, 1H), 7.18-7.33 (m, 9H), 7.37 (d, *J* = 6.9 Hz, 4H); ¹³C NMR (CDCl₃) δ 155.7, 140.0, 135.8, 132.6, 129.5, 129.2, 129.1, 128.3, 128.1, 127.9, 127.4, 127.0, 126.9, 126.7, 79.5, 59.5, 54.0, 49.4, 28.6, 28.5. HRMS (EI) calcd for C₂₉H₃₂N₂O₂ (M⁺): 440.2463. Found: 440.2455.

(1*S*,2*S*)-[2-(*N*-Methyl-*N*-phenyl-amino)-1,2-dihydro-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (3af): 97% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 98/2, 1.0 mL/min), *t_R* (*R*)-(-), 11.5 min (minor); (*S*)-(+), 13.4 min (major). [α]_D²⁵ +35.6 (*c* 1.00, CHCl₃) for **3af** of 97% ee. mp 94-96 °C; IR (NaCl, cm⁻¹) 3404 2973, 1717, 1595, 1502, 1369, 1108, 1032, 991, 864, 811, 753. ¹H NMR (CDCl₃) δ 1.33 (s, 9H), 2.82 (s, 3H), 4.51 (d, *J* = 9.0 Hz, 1H), 4.77 (d, *J* = 9.0 Hz, 1H), 5.19 (t, *J* = 9.0 Hz, 1H), 5.90 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.58 (dd, *J* = 9.9, 3.0 Hz, 1H), 6.71 (t, *J* = 6.9 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.18-7.22 (m, 1H); ¹³C NMR (CDCl₃) δ 155.5, 150.2, 135.9, 132.8, 130.1, 129.9, 129.2, 128.0, 127.9, 126.7, 125.8, 117.1, 113.7, 79.4, 60.8, 52.4, 33.1, 28.3. HRMS (EI) calcd for C₂₂H₂₆N₂O₂ (M⁺): 350.1994. Found: 350.1999.

(1*S*,2*S*)-[2-(3,4-Dihydro-2*H*-quinolin-1-yl)-1,2-dihydronaphthalen-1-yl]-carbamic acid *tert*-butyl ester (3ag): 97% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 95/5, 1.0 mL/min), *t_R* (*S*)-(+), 7.5 min (major); (*R*)-(-), 8.4 min (minor). [α]_D²⁵ +269.3 (*c* 0.50, CHCl₃) for **3ag** of 97% ee. mp 155-160 °C; IR (NaCl, cm⁻¹) 3315, 2929, 1691, 1601, 1502, 1453, 1365, 1169, 1048, 877, 784. ¹H NMR (CDCl₃) δ 1.35 (s, 9H), 1.81-1.91 (m, 2H), 2.72 (t, *J* = 6.4 Hz, 2H), 3.21 (t, *J* =

5.2 Hz, 2H), 4.59 (d, $J = 9.0$ Hz, 1H), 4.79 (d, $J = 9.0$ Hz, 1H), 5.25 (t, $J = 9.0$ Hz, 1H), 5.89-5.92 (m, 1H), 6.56-6.63 (m, 2H), 6.77 (d, $J = 8.4$ Hz, 1H), 6.95 (d, $J = 7.2$ Hz, 1H), 7.00-7.04 (m, 1H), 7.09-7.11 (m, 1H), 7.20-7.24 (m, 2H), 7.35 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 155.6, 145.5, 136.1, 132.9, 130.3, 129.6, 129.6, 128.1, 127.9, 127.1, 126.8, 126.1, 123.8, 116.2, 111.3, 79.6, 58.5, 51.8, 43.7, 28.5, 28.4, 22.5. HRMS (EI) calcd for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_2$ (M^+): 376.2150. Found: 376.2159.

(1*S*,2*S*)-[2-Phenylamino-1,2-dihydronaphthalen-1-yl]-carbamic acid *tert*-butyl ester (3ah): 96% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 98/2, 1.0 mL/min), t_{R} (*R*)-(–), 16.2 min (minor); (*S*)-(+), 19.8 min (major). $[\alpha]_{\text{D}}^{25} +175.0$ (c 1.00, CHCl_3) for **3ah** of 96% ee. mp 91-96 °C; IR (NaCl, cm^{-1}) 3396, 2976, 1701, 1601, 1503, 1366, 1323, 1248, 1167, 1046, 781, 748, 692. ^1H NMR (CDCl_3) δ 1.45 (s, 9H), 3.82-3.97 (m, 1H), 4.22-4.30 (m, 1H), 4.69 (d, $J = 9.0$ Hz, 1H), 5.04 (t, $J = 9.0$ Hz, 1H), 6.09 (dd, $J = 9.9$, 6.0 Hz, 1H), 6.57 (d, $J = 9.9$ Hz, 1H), 6.71 (d, $J = 8.1$ Hz, 3H), 7.12-7.33 (m, 6H); ^{13}C NMR (CDCl_3) δ 156.1, 146.9, 134.2, 132.6, 129.6, 128.7, 128.6, 128.4, 128.1, 127.1, 117.7, 113.3, 80.0, 53.6, 52.5, 28.6. HRMS (EI) calcd for $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_4$ (M^+): 336.1837. Found: 336.1837.

(1*S*,2*S*)-[2-(Naphthalen-1-ylamino)-1,2-dihydro-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (3ai): 97% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 98/2, 1.0 mL/min), t_{R} (*R*)-(–), 20.5 min (minor); (*S*)-(+), 37.1 min (major). $[\alpha]_{\text{D}}^{25} +213.5$ (c 1.00, CHCl_3) for **3ai** of 97% ee. IR (NaCl, cm^{-1}) 3419, 2975, 1696, 1582, 1504, 1485, 1410, 1247, 1165, 1047, 909, 784, 733. ^1H NMR (CDCl_3) δ 1.43 (s, 9H), 4.40 (d, $J = 9.0$ Hz, 1H), 4.84 (d, $J = 9.0$ Hz, 1H), 4.97 (s, 1H), 5.29 (t, $J = 9.9$ Hz, 1H), 6.15 (dd, $J = 9.9$, 6.0 Hz, 1H), 6.54 (d, $J = 9.9$ Hz, 1H), 6.73 (d, $J = 7.6$ Hz, 1H), 7.12 (d, $J = 7.2$ Hz, 1H), 7.19-7.27 (m, 3H), 7.32-7.41 (m, 4H), 7.72-7.77 (m, 2H); ^{13}C NMR (CDCl_3) δ 156.8, 142.2, 134.6, 134.5, 133.1, 129.1, 128.6, 128.5, 128.2, 127.0, 126.8, 126.3, 125.8, 124.7, 123.5, 120.5, 117.3, 104.2, 80.3, 55.3, 52.9, 28.5. HRMS (EI) calcd for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_2$ (M^+): 386.1994. Found: 386.2002.

(1*S*,2*S*)-[2-(1*H*-Indol-3-yl)-1,2-dihydro-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (3aj): 96% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 1.0 mL/min), t_{R} (*S*)-(+), 13.0 min (major); (*R*)-(–), 15.5 min (minor). $[\alpha]_{\text{D}}^{25} +133.8$ (c 0.80, CHCl_3) for **3aj** of 96% ee. IR (NaCl, cm^{-1}) 3412, 3339, 2977, 1690, 1489, 1366, 1166, 1043, 1020, 908, 740. ^1H NMR (CDCl_3) δ 1.41 (s, 9H), 4.19 (s, 1H), 4.91 (d, $J = 8.4$ Hz, 1H), 5.08 (dd, $J = 8.8$, 4.8 Hz, 1H), 6.15 (dd, $J = 9.9$, 6.0 Hz, 1H), 6.64 (d, $J = 9.9$ Hz, 1H), 6.72 (s, 1H), 7.11-7.23 (m, 8H), 7.92 (m, 2H); ^{13}C

NMR (CDCl₃) δ 155.2, 136.7, 134.1, 132.8, 129.9, 128.8, 128.3, 127.9, 127.1, 126.9, 126.5, 122.1, 119.7, 119.5, 113.9, 111.2, 79.4, 53.5, 38.5, 28.5. HRMS calcd for C₂₃H₂₄N₂O₂ (M⁺): 302.1055. Found: 302.1062.

(1*S*,2*S*)-(2-Piperidin-1-yl-1,2-dihydro-5,8-dimethyl-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3ib): 94% ee by HPLC analysis with a chiral column (Chiralcel OD-H, hexane/2-propanol = 98/2, 1.0 mL/min), *t_R* (*R*)-(–), 11.5 min (minor); (*S*)-(+), 12.9 min (major). [α]_D²⁵ +206.4 (*c* 1.00, CHCl₃) for **3ib** of 94% ee. mp 143-145 °C; IR (NaCl, cm^{–1}) 3178, 2927, 2853, 1695, 1521, 1459, 1363, 1310, 1248, 1166, 1097, 1016, 992, 921, 859, 804, 732. ¹H NMR (CDCl₃) δ 1.33-1.57 (m, 15H), 2.14-2.38 (m, 8H), 2.52-2.70 (m, 2H), 3.35 (d, *J* = 6.0 Hz, 1H), 4.39 (d, *J* = 6.0 Hz, 1H), 5.15 (d, *J* = 8.1 Hz, 1H), 5.95 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.90 (d, *J* = 9.9 Hz, 1H), 6.98 (s, 2H); ¹³C NMR (CDCl₃) δ 155.1, 133.8, 133.1, 131.8, 130.5, 130.1, 129.7, 126.6, 125.1, 79.5, 64.0, 50.2, 43.5, 28.6, 28.4, 26.6, 24.8, 19.1, 18.7. HRMS (EI) calcd for C₂₂H₃₂N₂O₂ (M⁺): 356.2460. Found: 356.2463.

(1*S*,2*S*)-[2-(4-Phenyl-piperazin-1-yl)-1,2-dihydro-5,8-dimethyl-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (3ic): 94% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 0.5 mL/min), *t_R* (*R*)-(–), 10.1 min (minor); (*S*)-(+), 11.6 min (major). [α]_D²⁵ +325.4 (*c* 1.00, CHCl₃) for **3ic** of 94% ee. mp 147-149 °C; IR (NaCl, cm^{–1}) 3194, 2971, 1703, 1598, 1501, 1449, 1363, 1237, 1162, 998, 755. ¹H NMR (CDCl₃) δ 1.43 (s, 9H), 2.33 (s, 3H), 2.35 (s, 3H), 2.48-2.52 (m, 2H), 2.82-2.87 (m, 2H), 3.07 (t, *J* = 4.8 Hz, 4H), 3.46 (d, *J* = 6.0 Hz, 1H), 4.41 (d, *J* = 8.1 Hz, 1H), 5.17 (d, *J* = 8.1 Hz, 1H), 5.97 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.78-6.86 (m, 3H), 6.96 (d, *J* = 9.9 Hz, 1H), 7.00 (s, 2H), 7.21 (t, *J* = 8.6 Hz, 2H); ¹³C NMR (CDCl₃) δ 155.2, 151.6, 134.1, 132.7, 132.0, 130.4, 130.0, 129.2, 127.1, 124.5, 119.7, 116.2, 79.6, 62.8, 49.7, 48.9, 44.1, 28.6, 19.1, 18.7. HRMS (EI) calcd for C₂₇H₃₅N₃O₂ (M⁺): 443.2736. Found: 443.2729.

(1*S*,2*S*)-(2-Morpholin-4-yl-1,2-dihydro-5,8-dimethyl-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3id): 99% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 90/10, 0.5 mL/min), *t_R* (*R*)-(–), 19.3 min (minor); (*S*)-(+), 20.3 min (major). [α]_D²⁵ +327.0 (*c* 1.00, CHCl₃) for **3id** of 99% ee. mp 183-185 °C; IR (NaCl, cm^{–1}) 3195, 2972, 1701, 1522, 1448, 1362, 1247, 1163, 1114, 999, 862, 753. ¹H NMR (CDCl₃) δ 1.42 (s, 9H), 2.29-2.38 (m, 8H), 2.67-2.71 (m, 2H), 3.36 (d, *J* = 6.0 Hz, 1H), 3.58 (t, *J* = 4.8 Hz, 4H), 4.40 (d, *J* = 6.0 Hz, 1H), 5.15 (d, *J* = 6.0 Hz, 1H), 5.93 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.93 (d, *J* = 9.9 Hz, 1H), 6.99 (s, 2H); ¹³C NMR (CDCl₃) δ 155.4,

134.0, 132.7, 132.0, 130.4, 130.0, 127.2, 124.2, 79.6, 67.6, 63.1, 49.5, 44.2, 28.6, 19.1, 18.7. HRMS (EI) calcd for C₂₁H₃₀N₂O₃ (M⁺): 358.2257. Found: 358.2256.

(1*S*,2*S*)-(2-Dibenzylamino-1,2-dihydro-5,8-dimethyl-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3ie): 99% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 99/1, 0.5 mL/min), t_R (*S*)-(+), 13.3 min (major); (*R*)-(-), 15.3 min (minor). [α]²⁵_D +175.8 (*c* 1.00, CHCl₃) for **3ie** of 99% ee; IR (NaCl, cm⁻¹) 3408, 2974, 1707, 1493, 1365, 1228, 1163. ¹H NMR (CDCl₃) δ 1.40 (s, 9H), 2.29 (s, 3H), 2.38 (s, 3H), 3.39 (bs, 1H), 3.43 (d, *J* = 13.5 Hz, 2H), 3.53 (d, *J* = 13.5 Hz, 2H), 4.43 (d, *J* = 9.0 Hz, 1H), 5.32 (d, *J* = 9.0 Hz, 1H), 5.87 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.88 (d, *J* = 9.9 Hz, 1H), 6.95-7.01 (m, 2H), 7.15-7.27 (m, 6H), 7.35 (d, *J* = 6.9 Hz, 4H); ¹³C NMR (CDCl₃) δ 154.5, 140.4, 134.2, 132.3, 131.7, 130.1, 129.6, 129.0, 127.9, 126.6, 126.2, 125.8, 79.2, 58.5, 53.5, 43.9, 28.3, 18.9, 18.6. HRMS (ESI) calcd for C₃₁H₃₇N₂O₂ [M+H⁺]: 469.2849. Found: 469.2833.

(1*S*,2*S*)-[2-(*N*-Methyl-*N*-phenyl-amino)-1,2-dihydro-5,8-dimethyl-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (3if): 96% ee by HPLC analysis with a chiral column (Chiralcel OD-H, hexane/2-propanol = 99/1, 1.0 mL/min), t_R (*S*)-(+), 5.1 min (major); (*R*)-(-), 5.6 min (minor). [α]²⁵_D +292.6 (*c* 1.00, CHCl₃) for **3if** of 96% ee. mp 139-142 °C; IR (NaCl, cm⁻¹) 3402, 2975, 1715, 1597, 1504, 1365, 1165, 1107, 1034, 991, 900, 865, 812, 752, 693. ¹H NMR (CDCl₃) δ 1.44 (s, 9H), 2.26 (s, 3H), 2.37 (s, 3H), 2.39 (s, 3H), 4.45 (d, *J* = 9.0 Hz, 1H), 4.55 (d, *J* = 9.0 Hz, 1H), 5.06 (d, *J* = 9.0 Hz, 1H), 5.93 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.76 (t, *J* = 7.1 Hz, 1H), 6.97-7.58 (m, 5H), 7.23-7.29 (m, 2H); ¹³C NMR (CDCl₃) δ 155.2, 149.9, 134.6, 132.7, 132.1, 130.5, 130.1, 129.3, 127.6, 124.3, 117.6, 114.4, 79.6, 57.8, 48.6, 32.4, 28.5, 19.1, 18.7. Anal. Calcd for C₂₄H₃₀N₂O₂: C, 76.16; H, 7.99; N, 7.40. Found: C, 75.88; H, 8.04; N, 7.35.

(1*S*,2*S*)-[2-(4-Phenyl-piperazin-1-yl)-1,2-dihydro-5,6,7,8-tetramethyl-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (3jc): 89% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 0.5 mL/min), t_R (*S*)-(+), 11.2 min (major); (*R*)-(-), 12.7 min (minor). [α]²⁵_D +263.0 (*c* 1.00, CHCl₃) for **3jc** of 89% ee; IR (NaCl, cm⁻¹) 3242, 2973, 2842, 1700, 1598, 1494, 1449, 1364, 1233, 1167, 1046, 1002, 922, 871, 755, 692. ¹H NMR (CDCl₃) δ 1.42 (s, 9H), 2.24 (s, 6H), 2.28 (s, 3H), 2.30 (s, 3H), 2.43-2.57 (m, 2H), 2.78-2.90 (m, 2H), 3.07 (t, *J* = 4.8 Hz, 4H), 3.44 (d, *J* = 6.0 Hz, 1H), 4.42 (d, *J* = 8.1 Hz, 1H), 5.24 (d, *J* = 8.1 Hz, 1H), 5.92 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 9.9 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 155.1, 151.6, 135.9, 135.1,

132.2, 130.5, 130.3, 129.2, 128.1, 128.0, 123.3, 119.6, 116.1, 79.4, 62.8, 49.6, 49.0, 44.7, 28.6, 17.2, 17.0, 15.5, 15.2. HRMS (EI) calcd for $C_{29}H_{39}N_3O_2$ (M^+): 461.3032. Found: 461.3042.

(1*S*,2*S*)-(2-Morpholin-4-yl-1,2-dihydro-5,6,7,8-tetramethyl-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3jd): 94% ee by HPLC analysis with a chiral column (Chiralpak AS, hexane/2-propanol = 98/2, 0.5 mL/min), t_R (*S*)-(+), 17.5 min (major); (*R*)-(-), 21.6 min (minor). $[\alpha]_D^{25} +284.2$ (c 1.00, $CHCl_3$) for **3jd** of 94% ee; mp 198-202 °C; IR (NaCl, cm^{-1}) 3200, 2973, 2867, 1698, 1519, 1447, 1389, 1363, 1315, 1248, 1165, 1117, 1047, 999, 861, 754. 1H NMR ($CDCl_3$) δ 1.41 (s, 9H), 2.23 (s, 3H), 2.25 (s, 3H), 2.28 (s, 6H), 2.38-2.40 (m, 2H), 2.61-2.74 (m, 2H), 3.32 (d, J = 6.0 Hz, 1H), 3.57 (t, J = 4.8 Hz, 4H), 4.40 (d, J = 8.1 Hz, 1H), 5.20 (d, J = 8.1 Hz, 1H), 5.88 (dd, J = 9.9, 6.0 Hz, 1H), 7.04 (d, J = 9.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 155.1, 136.0, 135.2, 132.2, 130.5, 130.3, 128.2, 128.0, 123.1, 79.5, 67.6, 63.2, 49.7, 44.9, 28.6, 17.3, 17.0, 15.5, 15.2. HRMS (EI) calcd for $C_{23}H_{34}N_2O_3$ (M^+): 386.2573. Found: 386.2569.

(1*S*,2*S*)-(2-*N,N*-Dibenzylamino-1,2-dihydro-5,6,7,8-tetramethyl-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3je): 99% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 99/1, 0.5 mL/min), t_R (*S*)-(+), 9.6 min (major); (*R*)-(-), 12.0 min (minor). $[\alpha]_D^{25} +265.8$ (c 1.00, $CHCl_3$) for **3je** of 99% ee; IR (NaCl, cm^{-1}) 3418, 2925, 2358, 1705, 1489, 1365, 1165, 1047. 1H NMR ($CDCl_3$) δ 1.39 (s, 9H), 2.21 (s, 3H), 2.25 (s, 6H), 2.33 (s, 3H), 3.38 (d, J = 6.0 Hz, 1H), 3.44 (d, J = 13.5 Hz, 2H), 3.52 (d, J = 13.5 Hz, 2H), 4.42 (d, J = 9.0 Hz, 1H), 5.38 (d, J = 9.0 Hz, 1H), 5.83 (dd, J = 9.9, 6.0 Hz, 1H), 7.01 (d, J = 9.9 Hz, 1H), 7.14-7.25 (m, 6H), 7.35 (d, J = 7.2 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 154.7, 140.7, 135.8, 135.0, 132.5, 130.4, 130.2, 129.2, 128.1, 127.9, 127.3, 126.7, 124.8, 79.2, 58.6, 53.7, 44.9, 28.5, 17.2, 17.0, 15.4, 15.2. HRMS (ESI) calcd for $C_{33}H_{41}N_2O_2$ [$M+H^+$]: 497.3162. Found: 497.3174.

(1*S*,2*S*)-[2-(*N*-Phenyl-piperazin-1-yl)-1,2-dihydro-6,7-dimethyl-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (3kc): 94% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 0.5 mL/min), t_R (*S*)-(+), 17.9 min (major); (*R*)-(-), 19.6 min (minor). $[\alpha]_D^{25} +304.8$ (c 1.00, $CHCl_3$) for **3kc** of 94% ee. mp 178-181 °C; IR (NaCl, cm^{-1}) 3320, 2971, 2855, 1698, 1504, 1450, 1390, 1365, 1289, 1248, 1169, 1115, 1049, 1003, 882, 754. 1H NMR ($CDCl_3$) δ 1.45 (s, 9H), 2.24 (s, 3H), 2.25 (s, 3H), 2.62-2.69 (m, 2H), 2.77-2.84 (m, 2H), 3.10 (t, J = 4.8 Hz, 4H), 3.43 (t, J = 6.0 Hz, 1H), 4.44-4.58 (m, 1H), 4.92-5.05 (m, 1H), 5.91 (dd, J = 9.9, 6.0 Hz, 1H), 6.62 (d, J = 9.9 Hz, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 8.1 Hz, 2H), 6.89 (s, 1H), 7.11

(s, 1H), 7.21 (d, $J = 7.5$ Hz, 1H), 7.24 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 155.3, 151.6, 136.9, 136.4, 132.7, 130.2, 129.7, 129.5, 129.2, 128.3, 124.3, 119.6, 116.2, 79.5, 64.0, 49.7, 48.8, 48.1, 28.6, 19.8, 19.6. HRMS (EI) calcd for $\text{C}_{27}\text{H}_{35}\text{N}_3\text{O}_2$ (M^+): 443.2720. Found: 443.2729.

(1*S*,2*S*)-(2-Morpholin-4-yl-1,2-dihydro-6,7-dimethyl-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3kd): >99% ee by HPLC analysis with a chiral column (Chiralcel AS, hexane/2-propanol = 98/2, 0.5 mL/min), t_{R} (*S*)-(+), 29.4 min (major); (*R*)-(–), 34.9 min (minor). $[\alpha]_{\text{D}}^{25} +251.4$ (c 1.00, CHCl_3) for **3kd** of >99% ee; mp 57–60 °C; IR (NaCl, cm^{-1}) 3320, 2971, 2855, 1698, 1504, 1450, 1390, 1365, 1289, 1248, 1169, 1157, 1049, 1103, 883, 754. ^1H NMR (CDCl_3) δ 1.45 (s, 9H), 2.23 (s, 3H), 2.25 (s, 3H), 2.44–2.53 (m, 2H), 2.61–2.68 (m, 2H), 3.32 (t, $J = 6.0$ Hz, 1H), 3.61 (t, $J = 4.8$ Hz, 4H), 4.43–4.58 (m, 1H), 4.87–5.02 (m, 1H), 5.87 (dd, $J = 9.9, 6.0$ Hz, 1H), 6.60 (d, $J = 9.9$ Hz, 1H), 6.87 (s, 1H), 7.11 (s, 1H); ^{13}C NMR (CDCl_3) δ 155.4, 137.0, 136.6, 132.7, 130.2, 129.8, 129.5, 128.3, 124.1, 79.6, 67.6, 64.5, 49.4, 48.3, 28.7, 19.8, 19.6. Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{N}_2\text{O}_3$: C, 70.36; H, 8.44; N, 7.81. Found: C, 70.06; H, 8.79; N, 7.71.

(1*S*,2*S*)-(2-Dibenzylamino-1,2-dihydro-6,7-dimethyl-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3ke): 97% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 99/1, 0.5 mL/min), t_{R} (*S*)-(+), 14.2 min (major); (*R*)-(–), 18.7 min (minor). $[\alpha]_{\text{D}}^{25} +135.8$ (c 1.00, CHCl_3) for **3ke** of 97% ee; IR (NaCl, cm^{-1}) 3415, 2973, 1713, 1494, 1364, 1245, 1166. ^1H NMR (CDCl_3) δ 1.51 (s, 9H), 2.19 (s, 3H), 2.23 (s, 3H), 3.41 (bs, 1H), 3.53 (d, $J = 13.5$ Hz, 2H), 3.70 (d, $J = 13.5$ Hz, 2H), 4.43–4.46 (m, 1H), 5.18 (m, 1H), 5.93–5.96 (m, 1H), 6.54 (dd, $J = 9.9, 1.8$ Hz, 1H), 6.82 (s, 1H), 7.08 (s, 1H), 7.15–7.28 (m, 6H), 7.37 (d, $J = 6.9$ Hz, 4H); ^{13}C NMR (CDCl_3) δ 155.6, 140.3, 136.6, 136.1, 133.1, 130.3, 129.4, 129.3, 128.9, 128.3, 128.1, 127.0, 125.8, 79.5, 59.5, 54.0, 48.9, 28.7, 19.9, 19.5. HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{37}\text{N}_2\text{O}_2$ [$\text{M}+\text{H}^+$]: 469.2849. Found: 469.2849.

(1*S*,2*S*)-(6,7-Dimethoxy-2-pyrrolidin-1-yl-1,2-dihydro-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3la): >99% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 90/10, 1.0 mL/min), t_{R} (*R*)-(–), 6.0 min (minor); (*S*)-(+), 7.9 min (major). $[\alpha]_{\text{D}}^{25} +152.7$ (c 1.00, CHCl_3) for **3la** of >99% ee. IR (NaCl, cm^{-1}) 3361, 2967, 2253, 1705, 1605, 1515, 1267, 1169, 732. ^1H NMR (CDCl_3) δ 1.43 (s, 9H), 1.69–1.71 (m, 4H), 2.58–2.60 (m, 2H), 2.70–2.72 (m, 2H), 3.26 (bs, 1H), 3.86 (s, 3H), 3.88 (s, 3H), 4.70 (d, $J = 8.0$ Hz, 1H), 4.86 (d, $J = 8.0$ Hz, 1H), 5.88 (dd, $J = 9.9, 6.0$ Hz, 1H), 6.54 (d, $J = 9.9$ Hz, 1H), 6.63 (s, 1H), 6.88 (s, 1H); ^{13}C NMR (CDCl_3) δ 155.2,

148.7, 148.6, 128.8, 127.3, 125.1, 123.9, 112.1, 110.2, 79.5, 61.5, 56.1, 56.0, 50.5, 28.5, 23.5. HRMS (EI) calcd for C₂₂H₂₆N₂O₂S (M⁺): 376.2362. Found: 376.2371.

(1*S*,2*S*)-(2-Morpholin-4-yl-1,2-dihydro-6,7-dimethoxynaphthalen-1-yl)-carbamic acid *tert*-butyl ester (3ld): 96% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 0.5 mL/min), *t_R* (*S*)-(+), 26.9 min (major); (*R*)-(-), 31.9 min (minor). [α]_D²⁵ +280.2 (*c* 1.00, CHCl₃) for **3ld** of 96% ee. IR (NaCl, cm⁻¹) 3348, 2961, 2855, 1698, 1604, 1514, 1463, 1365, 1316, 1266, 1170, 1115, 1001, 916, 869, 768, 731, 646. ¹H NMR (CDCl₃) δ 1.45 (s, 9H), 2.42-2.50 (m, 2H), 2.63-2.70 (m, 2H), 3.29-3.31 (m, 1H), 3.61 (t, *J* = 4.8 Hz, 4H), 3.88 (s, 3H), 3.90 (s, 3H), 4.56 (d, *J* = 8.1 Hz, 1H), 4.93 (d, *J* = 8.1 Hz, 1H), 5.84 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.59 (d, *J* = 9.9 Hz, 1H), 6.62 (s, 1H), 6.88 (s, 1H); ¹³C NMR (CDCl₃) δ 155.3, 149.0, 148.8, 129.5, 127.7, 125.4, 122.9, 111.5, 110.2, 79.7, 67.6, 64.1, 56.3, 56.1, 49.3, 48.2, 28.6. HRMS (EI) calcd for C₂₁H₃₀N₂O₅ (M⁺): 390.2165. Found: 390.2154.

(1*S*,2*S*)-[2-(*N*-Methyl-*N*-phenylamino)-1,2-dihydro-6,7-dimethoxy-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (3lf): 99% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 0.5 mL/min), *t_R* (*S*)-(+), 24.9 min (major); (*R*)-(-), 28.6 min (minor). [α]_D²⁵ +91.8 (*c* 1.00, CHCl₃) for **3lf** of 99% ee. mp 159-161 °C; IR (NaCl, cm⁻¹) 3363, 2975, 1711, 1598, 1505, 1364, 1273, 1228, 1164, 1108, 1013, 944, 868, 749, 692. ¹H NMR (CDCl₃) δ 1.37 (s, 9H), 2.75 (s, 3H), 3.87 (s, 3H), 3.89 (s, 3H), 4.52 (d, *J* = 9.0 Hz, 1H), 4.69 (d, *J* = 9.0 Hz, 1H), 5.06 (t, *J* = 9.0 Hz, 1H), 5.82 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.56 (dd, *J* = 9.9, 1.8 Hz, 1H), 6.66 (s, 3H), 6.86-6.89 (m, 3H), 7.23 (t, *J* = 7.2 Hz, 2H); ¹³C NMR (CDCl₃) δ 155.6, 150.1, 148.8, 148.6, 129.8, 129.4, 128.5, 126.9, 125.7, 117.3, 113.8, 110.5, 79.7, 60.4, 56.3, 56.2, 52.2, 33.1, 28.5. Anal. Calcd for C₂₄H₃₀N₂O₄: C, 70.22; H, 7.37; N, 6.82. Found: C, 69.82; H, 7.07; N, 6.73.

(1*S*,2*S*)-(6,7-Difluoro-2-pyrrolidin-1-yl-1,2-dihydro-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3ma): >99% ee by HPLC analysis with a chiral column (Chiralcel OD-H, hexane/2-propanol = 90/10, 1.0 mL/min), *t_R* (*S*)-(+), 7.5 min (major); (*R*)-(-), 9.6 min (minor). [α]_D²⁵ +272.6 (*c* 1.00, CHCl₃) for **3ma** of >99% ee. IR (NaCl, cm⁻¹) 3343, 2970, 1696, 1505, 1366, 1310, 1250, 1169, 1054, 1023, 912, 882, 742. ¹H NMR (CDCl₃) δ 1.44 (s, 9H), 1.69-1.72 (m, 4H), 2.58-2.68 (m, 4H), 3.29 (t, *J* = 6.0 Hz, 1H), 4.70 (bs, 1H), 4.86 (bs, 1H), 6.03 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.51 (d, *J* = 9.9 Hz, 1H), 6.90 (dd, *J* = 10.5, 7.8 Hz, 1H), 7.18 (dd, *J* = 10.5, 7.8, 1H); ¹³C NMR (CDCl₃) δ 155.3, 151.0 (q, *J* = 13.0 Hz), 148.6 (q, *J* = 13.0 Hz), 132.1 (dd, *J* = 4.0, 1.2 Hz), 129.1 (dd, *J* =

6.3, 4.0 Hz), 127.6, 127.3, 117.6 (d, $J = 18.2$ Hz), 115.5 (d, $J = 18.2$ Hz), 79.9, 61.1, 50.4, 49.9, 28.5, 23.6.; ^{19}F NMR (CDCl_3) δ -138.1 (t, $J = 9.0$ Hz), -139.5 (t, $J = 9.0$ Hz). HRMS (EI) calcd for $\text{C}_{19}\text{H}_{24}\text{N}_2\text{O}_2\text{F}_2$ (M^+): 351.1884. Found: 351.1887.

(1*S*,2*S*)-(2-Piperidin-1-yl-1,2-dihydro-5,8-dimethyl-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3mb): 97% ee by HPLC analysis with a chiral column (Chiralcel OD-H, hexane/2-propanol = 90/10, 0.5 mL/min), t_{R} (*S*)-(+), 15.0 min (minor); (*R*)-(-), 16.4 min (major). $[\alpha]_{\text{D}}^{25} +236.2$ (c 1.00, CHCl_3) for **3mb** of 97% ee. mp 112-115 °C; IR (NaCl, cm^{-1}) 3266, 2933, 1679, 1598, 1536, 1505, 1366, 1303, 1277, 1173, 1119, 880, 778. ^1H NMR (CDCl_3) δ 1.34-1.56 (m, 15H), 2.41-2.57 (m, 4H), 3.31-3.34 (m, 1H), 4.51-4.70 (m, 1H), 4.85-5.02 (m, 1H), 6.02 (dd, $J = 9.9$, 6.0 Hz, 1H), 6.50 (dd, $J = 9.9$, 1.5 Hz, 1H), 6.88 (dd, $J = 10.5$, 7.8 Hz, 1H), 7.20 (dd, $J = 10.5$, 7.8 Hz, 1H); ^{13}C NMR (CDCl_3) δ 155.17, 151.39 (q, $J = 13.4$ Hz), 148.10 (q, $J = 13.4$ Hz), 133.07 (t, $J = 4.5$ Hz), 129.46 (dd, $J = 6.3$, 4.5 Hz), 127.53 (d, $J = 4.5$ Hz), 127.50 (d, $J = 4.5$ Hz), 116.77 (d, $J = 18.0$ Hz), 115.33 (d, $J = 18.0$ Hz), 79.96, 64.80, 50.24, 48.19, 28.59, 26.61, 24.74.; ^{19}F NMR (CDCl_3) δ -138.2 (t, $J = 10.0$ Hz), -139.9 (t, $J = 10.0$ Hz). HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{27}\text{N}_2\text{O}_2\text{F}_2$ [$\text{M}+\text{H}^+$]: 365.2035. Found: 365.2052.

(1*S*,2*S*)-[2-(*N*-Methyl-*N*-phenylamino)-1,2-dihydro-6,7-difluoro-naphthalen-1-yl]-carbamic acid *tert*-butyl ester (3mf): 98% ee by HPLC analysis with a chiral column (Chiralcel OD-H, hexane/2-propanol = 99/1, 1.0 mL/min), t_{R} (*R*)-(-), 10.0 min (minor); (*S*)-(+), 13.7 min (major). $[\alpha]_{\text{D}}^{25} +16.8$ (c 1.00, CHCl_3) for **3mf** of 98% ee. mp 148-151 °C; IR (NaCl, cm^{-1}) 3342, 2976, 1680, 1598, 1503, 1367, 1305, 1169, 1104, 940, 885, 779, 745. ^1H NMR (CDCl_3) δ 1.34 (s, 9H), 2.84 (s, 3H), 4.46 (d, $J = 9.9$ Hz, 1H), 4.78 (d, $J = 10.5$ Hz, 1H), 5.14 (d, $J = 9.9$ Hz, 1H), 5.97 (dd, $J = 9.9$, 2.4 Hz, 1H), 6.49 (dd, $J = 9.9$, 2.4 Hz, 1H), 6.75 (t, $J = 7.2$ Hz, 1H), 6.83 (d, $J = 8.5$ Hz, 2H), 6.92 (dd, $J = 10.5$, 7.8 Hz, 1H), 7.16 (dd, $J = 10.5$, 7.8 Hz, 1H), 7.23 (dd, $J = 8.5$, 7.2 Hz, 2H); ^{13}C NMR (CDCl_3) δ 155.51, 151.40 (t, $J = 13.0$ Hz), 150.18, 148.10 (t, $J = 13.0$ Hz), 133.34, 131.33, 129.76, 129.45, 128.45, 117.67, 115.65 (d, $J = 18.0$ Hz), 113.99, 80.14, 60.81, 52.09, 33.40, 28.40.; ^{19}F NMR (CDCl_3) δ -138.0 (t, $J = 11.1$ Hz), -140.2 (t, $J = 11.1$ Hz). HRMS (EI) calcd for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2\text{F}_2$ (M^+): 386.1806. Found: 386.1805.

Preparation of dialkylammonium iodide from the corresponding chloride. Ammonium chloride was dissolved in appropriate solvent (EtOH in the case of diethylammonium chloride and MeOH in dimethylammonium chloride) (0.5-1.0 M). NaI (1 equiv.) solution (0.5-1.0 M) in the same solvent was added dropwise to the chloride solution at room temperature. White precipitate was immediately formed. After

addition was completed, the mixture was stirred for 0.5-1h. After filtration to remove NaCl, the solution was evaporated. The residue was dissolved in CH₂Cl₂ and insoluble precipitate was filtered off again. Evaporation of the solvent gave the corresponding iodide (quantitative yield at this stage). If product had yellow color, the solid was carefully washed with the cold solvent in which the reaction was carried out.

Catalytic Ring-Opening of 1a with Et₂NH₂I in the presence of *i*-Pr₂NEt in dioxane. To a stirred solution of **1a** (100 mg, 0.41 mmol), [Rh(cod)Cl]₂ (2 mg, 4 μmol), dppf (7 mg, 12 μmol), and Et₂NH₂I (165 mg, 0.82 mmol) in dry 1,4-dioxane (2.0 mL) was added *i*-Pr₂NEt (0.2 mL, 1.23 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir at 110 °C for 14 h. The resulting mixture was cooled to room temperature and quenched with 1N NaOH solution. The mixture was extracted with CH₂Cl₂ and the separated organic layer was dried over anhydrous MgSO₄. After evaporation under reduced pressure, the residue was purified by flash column chromatography (hexane/ethyl acetate = 70/30) to give 115 mg (90% yield) of **3ak**. Similarly, the ring-opening product **3al** (89% yield) was prepared under the same condition.

(1*S*,2*S*)-(2-Diethylamino-1,2-dihydro-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3ak**):** 85% ee by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 0.5 mL/min), *t_R* (*S*)-(+), 10.4 min (major); (*R*)-(–), 11.4 min (minor). [α]_D²⁵ +145.4 (*c* 1.00, CHCl₃) for **3ak** of 85% ee; mp 85-87 °C; IR (NaCl, cm^{–1}) 3346, 1701, 1524, 1488, 1452, 1390, 1305, 1250, 1171, 1113, 1045, 1023, 979, 903, 858, 780. ¹H NMR (CDCl₃) δ 1.01 (t, *J* = 6.6 Hz, 6H), 1.46 (s, 9H), 2.47-2.60 (m, 4H), 3.51-3.55 (m, 1H), 4.63 (bs, 1H), 4.93 (t, *J* = 6.6 Hz, 1H), 5.97 (dd, *J* = 9.9, 4.8 Hz, 1H), 6.58 (dd, *J* = 9.9, 1.5 Hz, 1H), 7.05-7.08 (m, 1H), 7.19-7.24 (m, 2H), 7.32-7.35 (m, 1H); ¹³C NMR (CDCl₃) δ 155.4, 135.7, 132.5, 129.0, 127.9, 127.8, 127.7, 127.4, 126.4, 79.2, 60.5, 49.6, 43.8, 23.4, 14.2. Anal. Calcd for C₁₉H₂₉N₂O₂: C, 72.12; H, 8.92; N, 8.85. Found: C, 71.90; H, 8.90; N, 8.80.

Asymmetric Ring-Opening of 1a with Me₂NH₂Cl in the presence of Et₃N in tetrahydropyran. To a stirred solution of **1a** (100 mg, 0.41 mmol), [Rh(cod)Cl]₂ (5 mg, 10 μmol), **4a** (32 mg, 45 μmol), and Me₂NH₂Cl (168 mg, 2.06 mmol) in dry tetrahydropyran (2.0 mL) was added triethylamine (0.43 mL, 3.08 mmol) under nitrogen atmosphere. The reaction mixture was allowed to stir at 80 °C for 144 h. The resulting mixture was cooled to room temperature and quenched with 1N NaOH solution. The mixture was extracted with CH₂Cl₂ and the separated organic layer was

dried over anhydrous MgSO_4 . After evaporation under reduced pressure, the residue was purified by flash column chromatography (hexane/ethyl acetate = 70/30) to give 75 mg (60% yield) of **3al**. Similarly, the ring-opening product **3ak** (9% yield) was prepared under the same condition.

(1*S*,2*S*)-(2-Dimethylamino-1,2-dihydro-naphthalen-1-yl)-carbamic acid *tert*-butyl ester (3al): 99% ee by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 90/10, 0.5 mL/min), t_R (*S*)-(+), 10.6 min (major); (*R*)-(–), 13.7 min (minor). $[\alpha]_D^{25} +266.0$ (c 1.00, CHCl_3) for **3al** of 99% ee; IR (NaCl, cm^{-1}) 3340, 3188, 1704, 1513, 1487, 1454, 1390, 1365, 1250, 1173, 1044, 1019. ^1H NMR (CDCl_3) δ 1.45 (s, 9H), 2.28 (s, 6H), 3.30 (t, $J = 4.5$ Hz, 1H), 4.76 (bs, 1H), 4.97 (bs, 1H), 5.94 (dd, $J = 9.6, 4.8$ Hz, 1H), 6.63 (d, $J = 9.6$ Hz, 1H), 7.07–7.10 (m, 1H), 7.21–7.23 (m, 2H), 7.32–7.34 (m, 1H); ^{13}C NMR (CDCl_3) δ 155.0, 135.1, 132.1, 129.3, 128.1, 127.9, 127.8, 126.6, 125.9, 79.3, 63.5, 48.1, 41.3, 28.3. HRMS (EI) calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_2$ (M^+): 288.1838. Found: 288.1841.

Preparation of (α *S*, α *S'*)-2,2'-Bis(α -*N,N*-dimethylaminoethyl)-(*R,R*)-1,1'-bis{di(4-methylphenyl)-phosphino}ferrocene (4b): To a solution of (*S,S'*)-1,1'-bis(α -*N,N*-dimethylaminoethyl)ferrocene (1.2 g, 3.6 mmol) prepared according to the reported procedure by Knochel⁵ in dry ether was slowly added *n*-butyllithium solution in hexane (6.9 mL, 10.9 mmol) by syringe pump at room temperature for 45 min under nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature for 2.5 h and di(4-methylphenyl)chlorophosphine¹² (2.9 g, 11.7 mmol) was slowly added at room temperature. The mixture was refluxed for another 15 h. The resulting mixture was quenched with saturated NaHCO_3 solution and was extracted with benzene. The separated organic layer was dried over anhydrous MgSO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 50/50) to give 0.9 g (33% yield) of **4b**. $[\alpha]_D^{25} +460.2$ (c 1.00, CHCl_3); mp 174–176 °C; IR (NaCl, cm^{-1}) 2966, 2929, 2812, 2796, 1596, 1496, 1447, 1271, 1242, 1184, 1093, 1019, 929, 804, 756, 623. ^1H NMR (CDCl_3) δ 1.27 (d, $J = 6.3$ Hz, 6H), 1.73 (s, 12 H), 2.25 (s, 6H), 2.34 (s, 6H), 3.03 (s, 2H), 4.00–4.09 (m, 2H), 4.13 (s, 2H), 4.34 (s, 2H), 6.93–6.97 (m, 12H), 7.19 (t, $J = 7.7$ Hz, 4H); ^{31}P NMR (CDCl_3) δ –25.5. Anal. Calcd for $\text{C}_{46}\text{H}_{54}\text{FeN}_2\text{P}_2$: C, 73.40; H, 7.23; N, 3.72. Found: C, 73.53; H, 7.31; N, 3.72.

Preparation of (1*S*,2*S*)-2-(4-Phenyl-piperazin-1-yl)-1,2-dihydro-naphthalen-1-yl-amine (5): To a stirred solution of **3ac** (300 mg, 0.91 mmol) in dry CH_2Cl_2 , was added

dropwise trifluoroacetic acid (dropwise addition, 1 mL) at 0 °C. The mixture was stirred at room temperature for 45 min. The reaction was quenched with 10% KOH and the mixture was extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give 274 mg of **5** (99% yield) as a white solid. mp 120-123 °C; [α]_D²⁵ +404.0 (*c* 1.10, CHCl₃); IR (NaCl, cm⁻¹) 3620, 3022, 2400, 1599, 1522, 1423, 1333, 1233, 1046, 928, 720. ¹H NMR (CDCl₃) δ 1.66 (s, 2H), 2.63-2.78 (m, 4H), 3.07-3.19 (m, 4H), 3.29-3.33 (m, 1H), 4.12 (d, *J* = 10.0 Hz, 1H), 6.03 (dd, *J* = 13.0, 6.0 Hz, 1H), 6.59 (dd, *J* = 13.0, 2.0 Hz, 1H), 6.78-6.88 (m, 3H), 7.05-7.08 (m, 1H), 7.24 (m, 4H), 7.37-7.40 (m, 1H); ¹³C NMR (CDCl₃) δ 151.1, 138.9, 131.7, 129.2, 128.9, 127.8, 127.1, 126.5, 125.7, 124.7, 119.6, 116.0, 66.9, 50.1, 49.9, 48.8. HRMS calcd for C₂₀H₂₃N₃ (M⁺): 305.1891. Found: 305.1899.

Preparation of (1*S*,2*S*)-4-Bromo-*N*-[2-(4-phenyl-piperazin-1-yl)-1,2-dihydro-naphthalen-1-yl]-benzenesulfonamide (6**):** To a solution of **5** (300 mg, 0.98 mmol) and triethylamine (0.27 mL, 1.96 mmol) in dry CH₂Cl₂ (10 mL) was added 4-bromobenzenesulfonyl chloride (301 mg, 1.18 mmol) and the mixture was allowed to stir at room temperature for 16 h. The resulting mixture was quenched with 10% KOH solution and was extracted with CH₂Cl₂. After concentration under reduced pressure, the crude residue was purified by flash column chromatography (hexane/ethyl acetate = 80/20) to give 274 mg of **6** (95% yield); mp 188-190 °C; [α]_D²⁵ +224.2 (*c* 0.85, CHCl₃); IR (NaCl, cm⁻¹) 3387, 3014, 2400, 2046, 1968, 1912, 1600, 1522, 1422, 1331, 1202, 1045, 929, 795. ¹H NMR (CDCl₃) δ 2.42-2.47 (m, 2H), 2.63-2.68 (m, 2H), 2.97-3.04 (m, 4H), 3.53-3.55 (m, 1H), 4.62 (s, 1H), 4.66-4.68 (m, 1H), 5.95 (dd, *J* = 9.9, 6.0 Hz, 1H), 6.69 (d, *J* = 9.9 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.82-6.85 (m, 3H), 7.07-7.11 (m, 2H), 7.21-7.26 (m, 4H), 7.72-7.74 (m, 4H); ¹³C NMR (CDCl₃) δ 151.4, 140.1, 133.4, 132.6, 132.3, 130.1, 129.2, 128.9, 128.6, 127.9, 122.8, 127.8, 127.2, 124.5, 120.0, 116.4, 63.8, 51.4, 49.7, 48.6. HRMS calcd for C₂₅H₂₆N₃O₂SBr (M⁺): 523.0929. Found: 523.0918.

Preparation of (1*S*,2*S*)-1,2,3,4-Tetrahydronaphthalen-1,2-diamine (*R,R*)-tartrate (7**):** To a solution of **3ae** (1.0 g, 2.27 mmol, 97% ee) in ethyl acetate (15 mL) and methanol (30 mL) was added ammonium formate (1.4 g, 22.70 mmol) and 30 mol% of Pd/C (10 wt %, 0.7 g, 0.68 mmol). The mixture was refluxed for 25 min and was cooled to room temperature. The resulting black suspension was filtered through Celite and the Celite cake was washed with triethylamine/methanol (1/1 = v/v) several times. The filtrate was concentrated under reduced pressure. The residue was treated with 50% hydrochloric acid (80 mL) at 100 °C for 24 h. The reaction mixture was cooled to room temperature and the acidic solution was washed with ether several times. Then, to

the separated aqueous solution was slowly added 4N NaOH solution at 0 °C for 30 min and its pH was adjusted around pH 11. The resulting basic solution was extracted with CH₂Cl₂ and dried over anhydrous MgSO₄. After removal of all volatile solvents under reduced pressure, the crude solid was dissolved with ethanol (40 mL) and H₂O (5 mL) and L-(+)-tartaric acid (0.3 g, 1.82 mmol) solution in ethanol (10 mL) was slowly added. The resulting suspension was refluxed for 18 h and was slowly cooled to room temperature. The precipitate was collected by filtration and the collected solid was washed with cold methanol. After drying under vacuum, 0.4 g (52% yield, 3 step) of (*S,S*)-diamine (*R,R*)-tartrate **7** was obtained. $[\alpha]_D^{25} +27.2$ (*c* 1.00, H₂O); mp 238-240 °C (decomp); ¹H NMR (*d*⁶-DMSO) δ 1.71-1.85 (m, 1H), 2.08-2.16 (m, 1H), 2.80-2.84 (m, 2H), 3.02-3.10 (m, 1H), 3.80 (d, *J* = 9.0 Hz, 1H), 5.18 (bs, 10H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.15-7.24 (m, 2H), 7.60 (d, *J* = 6.9 Hz, 1H); ¹³C NMR (*d*⁶-DMSO) δ 174.5, 138.1, 135.3, 128.1, 127.6, 126.8, 126.1, 71.4, 53.5, 53.4, 27.0, 26.4.; Anal. Calcd for C₁₄H₂₂N₂O₇: C, 50.90; H, 6.71; N, 8.48. Found: C, 51.13; H, 6.70; N, 8.44.

Rhodium-Catalyzed CO Insertion of Azabenzonorbornadiene: The mixture of **1a** (100 mg, 0.41 mmol) and [Rh(CO)₂Cl]₂ (8 mg, 0.02 mmol) in dry toluene (3.0 mL) was flushed with CO for 5-10 minutes and then place under a CO atmosphere (a balloon with CO is attached to the top of the reflux condenser). The mixture was allowed to stir at 110 °C for 20 h. The solvent was removed under high vacuum and the residue was purified by flash column chromatography (hexane/ethyl acetate = 90/10) to give 100 mg (99% yield) of **Naphthalen-1-yl-carbamic acid *tert*-butyl ester (8)**:¹³ mp 95 °C; IR (NaCl, cm⁻¹) 3329, 3051, 2978, 1694, 1531, 1494, 1392, 1367, 1345, 1234, 1157, 1102, 1069, 996, 862. ¹H NMR (CDCl₃) δ 1.56 (s, 9H), 6.87 (bs, 1H), 7.42-7.54 (m, 3H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.83-7.90 (m, 3H); ¹³C NMR (CDCl₃) δ 28.3, 80.6, 118.6, 120.4, 124.4, 125.8, 125.2, 125.9, 126.4, 128.7, 132.9, 134.0, 153.4.

Preparation of 1-Methyl-9-*N*-(4-methylbenzenesulfonyl)-1,4-dihydro-1,4-epiazano-naphthalene (10): To a stirred solution of anthranilic acid (1.0 g, 7.57 mmol) and isoamyl nitrite (1.0 mL, 7.57 mmol) in dry DME (5.0 mL) was slowly added a solution of 2-methyl-1-(4-methylbenzenesulfonyl)-*1H*-pyrrole¹⁴ (0.9 g, 3.78 mmol) in dry DME (3.0 mL) at 50 °C for 30 min. The reaction was allowed to stir at 50 °C for 2 h until no further gas was evolved. The resulting mixture was then concentrated and purified by flash column chromatography (hexane/diethyl ether = 90/10) to give 0.3 g of **10** in 27% yield. mp 165-170 °C; IR (NaCl, cm⁻¹) 3384, 2360, 1596, 1453, 1339, 1157, 1087, 1022, 815, 677. ¹H NMR (CDCl₃) δ 2.03 (s, 3H), 2.31 (s, 3H), 5.48 (d, *J* = 2.4 Hz, 1H), 6.47 (dd, *J* = 5.5, 0.9 Hz, 1H), 6.77-6.80 (m, 2H), 6.81-6.85 (m, 1H), 6.89-6.92 (m,

1H), 7.02-7.05 (m, 1H), 7.06 (d, $J = 8.1$ Hz, 2H), 7.44 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 150.2, 148.1, 146.6, 143.0, 135.9, 129.2, 128.3, 124.9, 124.9, 120.9, 119.2, 75.2, 68.4, 48.2, 42.8, 21.5, 13.6. HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2\text{S}$ (M^+): 311.0980. Found: 311.0988.

Preparation of *trans*-4-Methyl-*N*-[4-methyl-2-(*N*-methyl-*N*-phenylamino)-1,2-dihydronaphthalen-1-yl]-benzenesulfonamide (11): To a solution of **10** (100 mg, 0.32 mmol), $[\text{Rh}(\text{cod})\text{Cl}]_2$ (6.0 mg, 0.01 mmol), and dppf (17.0 mg, 0.03 mmol) in dry THF (2.5 mL) was added *N*-methylaniline (104 mg, 0.96 mmol) and the mixture was allowed to stir at 80 °C for 15 h under N_2 atmosphere. The resulting mixture was then concentrated and purified by flash column chromatography (hexane/ethyl acetate = 70/30) to give 60 mg of **11** (45% yield) and 30 mg of **12** (30% yield) as a byproduct. mp 143-147 °C; IR (NaCl, cm^{-1}) 3274, 3060, 2921, 1598, 1503, 1450, 1323, 1094, 1034, 909, 813, 749, 665. ^1H NMR (CDCl_3) δ 2.14 (s, 3H) 2.30 (s, 3H), 2.42 (s, 3H), 4.50 (dd, $J = 7.6, 5.6$ Hz, 1H), 4.61-4.65 (m, 2H), 5.69 (d, $J = 4.4$ Hz, 1H), 6.72-6.77 (m, 2H), 6.93 (d, $J = 7.2$ Hz, 1H), 7.09-7.14 (m, 1H), 7.18-7.22 (m, 2H), 7.25-7.32 (m, 2H), 7.62 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 149.2, 143.5, 137.8, 135.9, 134.4, 134.0, 129.7, 129.3, 128.7, 128.4, 127.9, 127.4, 123.9, 123.1, 117.5, 113.8, 58.7, 54.8, 32.4, 21.7, 19.2. HRMS calcd for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_2\text{S}$ (M^+): 418.1715. Found: 418.1710.

***N*-(4-Methylbenzenesulfonyl)-4-methyl-1-amino-naphthalene (12):** mp 152-156 °C; IR (NaCl, cm^{-1}) 3267, 2924, 1598, 1431, 1337, 1161, 1092, 813, 754; ^1H NMR (CDCl_3) δ 2.34 (s, 3H), 2.64 (s, 3H), 6.66 (s, 1H), 7.15 (d, $J = 8.0$ Hz, 2H), 7.19 (s, 2H), 7.40-7.45 (m, 2H), 7.47-7.51 (m, 2H), 7.61 (dd, $J = 6.8, 1.6$ Hz, 4H), 7.86 (d, $J = 8.4$ Hz, 2H), 7.95 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 143.8, 136.6, 134.3, 133.4, 129.7, 129.6, 127.5, 126.4, 126.2, 124.8, 123.6, 122.4, 21.6, 19.5. HRMS calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2\text{S}$ (M^+): 311.0980. Found: 311.0989.

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