Supplementary Information

Synthesis of planar chiral [2.2]paracyclophane-based bisoxazoline ligands bearing no central chirality and application to Cu-catalyzed asymmetric O-H insertion reaction

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General Method. Melting points were measured with YANAGIMOTO micro melting point apparatus, and were uncorrected. Optical rotations were measured on a JASCO P-2200. IR spectra were measured with a SHIMADZU FTIR-8700 spectrometer for samples in CHCl₃. ¹H and ¹³C NMR spectra were measured with a JEOL JNM-ECS400 or JNM-ECA600 or BRUKER AVANCE-600 spectrometers for samples in CDCl₃. Tetramethyilsilane (0.00 ppm) for ¹H NMR and CDCl₃ (77.00 ppm) for ¹³C NMR were used as an internal standard, respectively. High resolution mass spectra were measured with a JEOL JMS-T100TD or JMS-SX102A or JMS-HX110. Commercially available reagents were used throughout without purification unless otherwise stated. CHCl₃, (CH₂Cl)₂, Et₃N and MeOH were distilled from calcium hydride under a nitrogen atmosphere. EtOH was distilled from CaO under a nitrogen atmosphere. DMF, DMSO and NMP were distilled from calcium sulfate under a nitrogen atmosphere. Silica gel (silica gel 60N, 40-50 µm, Kanto Chemical) was used for chromatography. All reactions were carried out under a nitrogen atmosphere unless otherwise stated. Organic extracts were dried over anhydrous Na₂SO₄. Bromocyclopheanyl triflate (Sₚ)-8, diazo compounds 16, 18 and 20, and NaBArF₅ were prepared according to the literature procedure.

2-(3-Bromophenyl)oxazoline (12a). To m-bromobenzoic acid (11) (3.36 g, 16.7 mmol) was added SOCl₂ (3.9 mL, 50 mmol) at room temperature. After stirring for 23 h at 50 °C, volatiles were evaporated. The residue was dissolved in CH₂Cl₂ (10 mL) and added in a dropwise manner to a solution of monoethanolamine (5.0 mL, 84 mmol) in CH₂Cl₂ (10 mL) at 0 °C. The mixture was stirred for 15 h at room temperature. The white precipitate was filtered and washed with water to afford 3-bromo-N-(2-hydroxyethyl)benzamide (3.86 g, 95%) as a colorless solid; Mp 105 °C; IR 3447, 1655 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.92 (t, 1H, J = 1.7 Hz), 7.70 (d, 1H, J = 7.9 Hz), 7.63 (dt, 1H, J = 8.1, 1.0 Hz), 7.31 (t, 1H, J = 7.9 Hz), 6.68 (brs, 1H), 3.84 (q, 2H, J = 5.2 Hz), 3.63 (t, 2H, J = 5.5, 4.8 Hz), 2.57 (t, 1H, J = 5.0 Hz); ¹³C NMR (150 MHz, CDCl₃): δ 170.0, 136.1, 134.6, 130.2, 130.2, 125.5, 122.8, 62.1, 42.8; MS (DART) m/z 246 (94.6, M⁺+1), 244 (100.0, M⁺+1); HRMS calcd for C₉H₁₁BrNO₂: 243.9973, found 243.9983.

To the above amide (3.86 g, 15.8 mmol) was added SOCl₂ (3.6 mL) at room temperature. The reaction mixture was stirred for 1 h at the same temperature and Et₂O (4 mL) was added. The mixture was neutralized with 50% NaOH aqueous solution and extracted with
AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was dissolved in THF (10 mL) and NaH (60% dispersion of mineral oil) was added until the chloride product disappeared (monitored by TLC). The mixture was quenched with water and extracted with Et$_2$O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane-AcOEt (2:1) to afford 12a (3.01 g, 84%) as a colorless solid; Mp 38 ºC; IR 1649 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$): δ 8.10 (t, 1H, $J = 1.7$ Hz), 7.87 (dt, 1H, $J = 7.8, 1.3$ Hz), 7.60 (dq, 1H, $J = 7.9, 1.0$ Hz), 7.28 (t, 1H, $J = 7.9$ Hz), 4.44 (t, 2H, $J = 9.6$ Hz), 4.07 (t, 2H, $J = 9.5$ Hz); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 163.3, 134.2, 131.2, 129.9, 129.7, 126.7, 122.3, 67.8, 54.9; MS (DART) $m$/z 228 (100.0, M$^+$+1), 226 (98.1, M$^+$+1); HRMS calcd for C$_9$H$_9$BrNO: 225.9868, found 225.9861.

2-(4-Bromobiphenyl-2-yl)oxazoline (12b).

To a solution of 12a (862 mg, 3.82 mmol) in NMP (7.6 mL) were added K$_2$CO$_3$ (1.06 g, 7.64 mmol), PPh$_3$ (100 mg, 0.382 mmol), PhI (0.55 mL, 5.0 mmol) and [RuCl$_2$(η-benzene)]$_2$ (47.8 mg, 0.0955 mmol) at room temperature. After stirring for 24 h at 120 ºC, the mixture was cooled to room temperature, and diluted with Et$_2$O. The mixture was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with CH$_2$Cl$_2$-AcOEt (40:1) to afford 12b (333 mg, 29%) as a colorless oil; IR 1653 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.93 (d, 1H, $J = 2.1$ Hz), 7.61 (dd, 1H, $J = 8.2, 2.1$ Hz), 7.40-7.32 (m, 5H), 7.25 (d, 1H, $J = 8.2$ Hz), 4.12 (t, 2H, $J = 9.6$ Hz), 3.91 (t, 2H, $J = 9.6$ Hz); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 164.7, 140.8, 140.1, 133.5, 132.9, 131.9, 129.2, 128.1, 128.1, 127.5, 121.0, 68.0, 55.0; MS (DART) $m$/z 304 (98.7, M$^+$+1), 302 (100.0, M$^+$+1); HRMS calcd for C$_{15}$H$_{13}$BrNO: 302.0181, found 302.0176.

2-(4-Br-3',5'-dimethylbiphenyl-2-yl)oxazoline (12c).

According to the procedure for preparation of 12b from 12a, 12c (526 mg, 36%) was obtained from 12a (997 mg, 4.41 mmol); A colorless oil; IR 1653, 1603 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.91 (d, 1H, $J = 2.1$ Hz), 7.60 (dd, 1H, $J = 8.2, 2.4$ Hz), 7.27 (s, 1H), 7.00-6.99 (m, 3H), 4.16 (t, 2H, $J = 9.5$ Hz), 3.94 (t, 2H, $J = 9.5$ Hz), 2.35 (s, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 164.9, 140.9, 139.8, 137.6, 133.4, 132.9, 131.9, 129.2, 129.2, 126.0, 120.8, 68.0, 55.0, 21.3; MS (DART) $m$/z 332 (96.1, M$^+$+1), 330 (100.0, M$^+$+1); HRMS calcd for C$_{17}$H$_{17}$BrNO: 330.0494, found 330.0479.
2-(4-Bromo-1,1’:4’,1”-terphenyl-2-yl)oxazoline (12d).
According to the procedure for preparation of 12b from 12a, 12d (38.4 mg, 23%) was obtained from 12a (100 mg, 0.442 mmol); A colorless solid; Mp 167-168 ºC; IR 1653 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.95 (d, 1H, \(J = 1.8\) Hz), 7.65-7.62 (m, 5H), 7.48-7.41 (m, 4H), 7.36 (t, 1H, \(J = 7.3\) Hz), 7.30 (d, 1H, \(J = 8.2\) Hz), 4.17 (t, 2H, \(J = 9.6\) Hz), 3.94 (t, 2H, \(J = 9.4\) Hz); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 164.7, 140.5, 140.3, 140.3, 139.1, 133.5, 133.0, 131.9, 129.2, 128.8, 128.6, 127.4, 127.0, 126.8, 121.1, 68.0, 55.1; MS (DART) \(m/z\) 380 (99.0, M\(^+\)+1), 378 (100.0, M\(^+\)+1); HRMS calcd for C\(_{21}\)H\(_{17}\)BrNO: 378.0494, found 378.0496.

2-Isopropylbenzoic acid (14).\(^7\)
To a solution of 13 (199 mg, 1.00 mmol) in THF (3.3 mL) was added \(n\)-BuLi (1.54 M in hexane, 0.97 mL, 1.5 mmol) at -78 ºC. After stirring for 0.5 h at the same temperature, anhydrous CO\(_2\) was bubbled through the mixture for 1 h. Then the mixture was stirred for an additional 20 min at room temperature, quenched with aqueous solution of saturated NaHCO\(_3\), and washed with Et\(_2\)O. Aqueous layer was acidified with aqueous solution of 10% HCl and extracted with Et\(_2\)O. The extract was dried and concentrated to dryness to afford 14 (168.8 mg, 100%) as a colorless solid; IR 2970, 1693 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.92 (d, 1H, \(J = 7.6\) Hz), 7.52 (m, 1H), 7.46 (d, 1H, \(J = 7.9\) Hz), 7.28-7.26 (m, 1H), 3.93 (sep, 1H, \(J = 6.9\) Hz), 1.28 (d, 6H, \(J = 6.9\) Hz); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 174.1, 151.0, 132.8, 130.9, 128.3, 126.5, 125.5, 29.3, 24.0; MS (DART) \(m/z\) 165 (M\(^+\)+1, 100.0); HRMS calcd for C\(_{10}\)H\(_{13}\)O\(_2\): 165.0916, found 165.0930.

5-Bromo-2-isopropylbenzoic acid (15).
To bromine (1.54 g, 9.62 mmol) in CH\(_2\)Cl\(_2\) (7 mL) was added Fe (26.9 mg, 0.481 mmol) at room temperature. After stirring for 40 min, a solution of 14 (1.17 g, 4.81 mmol) in CH\(_2\)Cl\(_2\) (7 mL) was added to the mixture. After stirring at refluxing temperature for 15 h, the mixture was cooled to room temperature and quenched with aqueous solution of saturated Na\(_2\)S\(_2\)O\(_3\). The mixture was filtered and filtrate was extracted with CH\(_2\)Cl\(_2\). The extract was washed with aqueous solution of saturated Na\(_2\)S\(_2\)O\(_3\), water and aqueous solution of 10% HCl, dried and concentrated to the dryness. The residue was chromatographed with hexane-AcOEt (5:1) to afford a mixture of 15 and starting material 14 (1.39 g) as a yellow
solid. 15: Mp 98-100 °C; IR 2970, 2635, 1697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, 1H, J = 2.3 Hz), 7.63 (dd, 1H, J = 8.2, 2.3 Hz), 7.34 (d, 1H, J = 8.2 Hz), 3.88 (sep, 1H, J = 6.9 Hz), 1.26 (d, 6H, J = 6.9 Hz); ¹³C NMR (150 MHz, CDCl₃): δ 171.9, 150.0, 135.7, 133.5, 129.8, 128.4, 119.0, 29.1, 23.8; MS (DART) m/z 245 (66.3, M⁺+1), 243 (100.0, M⁺+1); HRMS calcd for C₁₀H₁₂BrO₂: 243.0021, found 243.0017.

2-(5-Bromo-2-isopropylphenyl)oxazoline (12e).

To the above mixture of 14 and 15 was added SOCl₂ (4 mL) at room temperature. After being stirred for 5 h at 50 °C, the volatiles were evaporated. The residue was dissolved in CH₂Cl₂ (4.1 mL) and added in a dropwise manner to a solution of monoethanolamine (1.7 mL) in CH₂Cl₂ (4.1 mL) at 0 °C. The reaction mixture was stirred for 10 h at room temperature and extracted with CH₂Cl₂. The extract was washed with water and brine, dried and concentrated to dryness to afford the crude amide (1.79 g) as a yellow solid: IR 3437, 1655 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.49 (dd, 1H, J = 8.6, 2.1 Hz), 7.40 (d, 1H, J = 2.1 Hz), 7.23 (d, 1H, J = 8.2 Hz), 6.43 (brs, 1H), 3.78 (q, 2H, J = 5.2 Hz), 3.54 (q, 2H, J = 5.4 Hz), 3.24 (sep, 1H, J = 6.9 Hz), 2.82 (t, 1H, J = 5.0 Hz), 1.22 (d, 6H, J = 6.9 Hz). ¹³C NMR (150 MHz, CDCl₃): δ 169.9, 145.6, 137.5, 133.0, 129.3, 128.0, 119.0, 61.9, 42.5, 29.7, 23.9; MS (DART) m/z 288 (93.2, M⁺+1), 286 (100.0, M⁺+1); HRMS calcd for C₁₂H₁₇BrNO: 286.0443, found 286.0438.

To the crude amide was added SOCl₂ (1.4 mL) at room temperature. The reaction mixture was stirred for 0.5 h, and Et₂O (3 mL) was added. The mixture was neutralized with aqueous solution of 20% NaOH and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was dissolved in THF (3 mL) and NaH (60% dispersion of mineral oil) was added to the mixture until chloro derivatives disappeared (monitored by TLC). The mixture was quenched with water and extracted with Et₂O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane-AcOEt (9:1) to afford 12e (929 mg, 72%) as a colorless oil; IR 1650 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ 7.82 (d, 1H, J = 2.4 Hz), 7.51 (dd, 1H, J = 8.6, 2.4 Hz), 7.25 (d, 1H, J = 8.6 Hz), 4.40 (t, 2H, J = 9.6 Hz), 4.09 (t, 2H, J = 9.6 Hz), 3.76 (sep, 1H, J = 6.9 Hz), 1.22 (d, 6H, J = 6.9 Hz). ¹³C NMR (150 MHz, CDCl₃): δ 164.0, 148.1, 133.6, 132.5, 128.7, 127.8, 118.9, 67.2, 55.5, 29.3, 23.8; MS (DART) m/z 270 (67.4, M⁺+1), 268 (69.0, M⁺+1); HRMS calcd for C₁₂H₁₅BrNO: 268.0337, found 268.0354.
Typical procedure for preparation of boronic acids 7.

**2-[4-(Dihydroxyboryl)biphenyl-2-yl]oxazoline (7b).**

To a solution of **12b** (84.7 mg, 0.280 mmol) in THF (1 mL) was added n-BuLi (1.43 M in hexane, 0.23 mL, 0.34 mmol) under an argon atmosphere at -78 ºC. After stirring for 20 min at the same temperature, B(OMe)_3 (0.13 mL, 1.1 mmol) was added to the mixture at -78 ºC, which was stirred for 30 min at the same temperature, and warmed to -15 ºC over 50 min. Aqueous solution of 5% HCl (1 mL) was added and the mixture was further stirred for 20 min at -15 ºC, basified with aqueous solution of 10% NaOH (1 mL), warmed to room temperature, and washed with Et₂O. Aqueous layer was neutralized with aqueous solution of 10% HCl, and extracted with Et₂O. The extract was washed with brine, dried and concentrated to dryness to afford the crude **7b** (38.4 mg, 51%) as a yellow solid, which was used without purification. Spectroscopic data of the boronic acid were not taken due to its instability.

Typical procedure for Suzuki-Miyaura coupling of boronic acid 7 and bromocyclophanyl triflate (**S_p**)-8.

**(S_p)-(-)-4,12-Bis[2-(2-oxazolinyl)biphenyl-4-yl][2.2]paracyclophane ((S_p)-6b).**

To a solution of (**S_p**)-8 (44.0 mg, 0.101 mmol) in DMSO (0.67 mL) and H₂O (67 µL) were added Na₂CO₃ (42.8 mg, 0.404 mmol), **7b** (108 mg, 0.404 mmol) and Pd(PPh₃)₄ (12.0 mg, 0.0104 mmol) at room temperature under an argon atmosphere. After stirring for 6 h at 100 ºC, the mixture was cooled to room temperature, diluted with water, and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane/AcOEt (1:1) to afford (**S_p**)-6b (51.2 mg, 78%) as a colorless solid; Mp 130-132 ºC; [α]_D^30 -204.9 (c 1.43, CHCl₃); IR 1651 cm⁻¹; ^1^H NMR (600 MHz, CDCl₃): δ 7.80 (s, 2H), 7.60 (d, 2H, J = 8.2 Hz), 7.46-7.32 (m, 12H), 6.77-6.74 (m, 4H), 6.66 (d, 2H, J = 7.9 Hz), 4.11-4.05 (m, 4H), 3.87-3.84 (m, 4H), 3.63-3.59 (m, 2H), 3.16-3.12 (m, 2H), 3.03-2.97 (m, 2H), 2.81-2.76 (m, 2H); ^13^C NMR (150 MHz, CDCl₃): δ 165.8, 140.9, 140.0, 139.8, 139.7, 139.8, 139.8, 139.7, 139.2, 137.1, 135.7, 132.5, 131.0, 131.0, 130.5, 129.9, 128.3, 128.0, 127.6, 127.1, 67.7, 55.1, 34.5, 34.5; MS (DART) m/z 651 (M⁺+1, 100.0); HRMS calcd for C₄₆H₃₉N₂O₂: 651.3012, found 651.3001.

**(S_p)-(-)-4,12-Bis[3-(2-oxazolinyl)phenyl][2.2]paracyclophane ((S_p)-6a).**
According to the procedure for preparation of 6b from (S)-8 and 7b, (S)-6a (28.0 mg, 66%) was obtained from (S)-8 (38.3 mg, 0.0880 mmol) and 7a (108 mg, 0.352 mmol); A colorless solid; Mp 88-90 °C; [α]D 30 -164.4 (c 0.94, CHCl3); IR 1649 cm⁻¹; 1H NMR (400 MHz, CDCl3): δ 7.95-7.94 (m, 4H), 7.51 (d, 2H, J = 7.8 Hz), 7.45 (t, 2H, J = 7.8 Hz), 6.73 (d, 2H, J = 7.8 Hz), 6.69-6.64 (m, 2H), 4.38 (t, 4H, J = 9.6 Hz), 4.05 (t, 4H, J = 9.6 Hz), 3.58-3.52 (m, 2H), 3.12 (t, 2H, J = 11.7 Hz), 2.97 (dd, 2H, J = 12.8, 9.6, 6.4 Hz), 2.73 (ddd, 2H, J = 12.8, 9.6, 6.4 Hz); 13C NMR (150 MHz, CDCl3): δ 164.7, 141.1, 139.7, 139.6, 137.0, 135.7, 132.4, 131.9, 130.0, 128.9, 128.5, 127.9, 126.4, 67.6, 54.9, 34.4, 34.4; MS (DART) m/z 499 (M+1, 100.0); HRMS calcd for C34H31N2O2: 499.2386, found 499.2405.

(Sp)-(-)-4.12-Bis[3-(2-oxazolinyl)-4-(3,5-dimethylphenyl)phenyl][2.2]paracyclocphane ((Sp)-6c).

According to the procedure for preparation of 6b from (S)-8 and 7b, (S)-6c (80.7 mg, 88%) was obtained from (S)-8 (56.5 mg, 0.130 mmol) and 7c (126 mg, 0.428 mmol); A colorless solid; Mp 126-128 °C; [α]D 22 -212.9 (c 0.81, CHCl3); IR 1651 cm⁻¹; 1H NMR (600 MHz, CDCl3): δ 7.76 (s, 2H), 7.57 (d, 2H, J = 6.9 Hz), 7.46 (d, 2H, J = 7.9 Hz), 7.09 (s, 4H), 6.98 (s, 2H), 6.76 (s, 2H), 6.74 (d, 2H, J = 7.9 Hz), 6.66 (d, 2H, J = 7.6 Hz), 4.13-4.08 (m, 4H), 3.88 (t, 4H, J = 9.3 Hz), 3.60 (t, 2H, J = 11.3 Hz), 3.13 (t, 2H, J = 11.3 Hz), 3.01-2.96 (m, 2H), 2.80-2.75 (m, 2H), 2.36 (s, 12H); 13C NMR (150 MHz, CDCl3): δ 166.0, 140.6, 140.0, 139.7, 139.6, 139.2, 137.4, 137.0, 135.6, 132.4, 131.0, 130.9, 130.5, 129.9, 128.9, 127.5, 126.2, 67.8, 55.2, 34.5, 34.4, 21.4; MS (DART) m/z 707 (53.3, M+1); HRMS calcd for C58H47N2O2: 707.3638, found 707.3654.

(Sp)-(-)-4.12-Bis[2-(2-oxazolinyl)-1,1':4',1''-terphenyl-4-yl][2.2]paracyclophane ((Sp)-6d).

According to the procedure for preparation of 6b from (S)-8 and 7b, (S)-6d (37.1 mg, 57%) was obtained from (S)-8 (34.8 mg, 0.0805 mmol) and 7d (110 mg, 0.322 mmol); A colorless solid; Mp 159-161 °C; [α]D 21 -297.4 (c 1.70, CHCl3); IR 1653 cm⁻¹; 1H NMR (600 MHz, CDCl3): δ 7.82 (d, 2H, J = 2.1 Hz), 7.67-7.64 (m, 8H), 7.63 (dd, 2H, J = 7.9, 1.7 Hz), 7.54-7.51 (m, 6H), 7.47-7.44 (m, 4H), 7.37-7.34 (m, 2H), 6.79 (d, 2H, J = 1.7 Hz), 6.77 (d, 2H, J = 7.9 Hz), 6.68 (dd, 2H, J = 7.9, 1.7 Hz), 4.16-4.10 (m, 4H), 3.92-3.88 (m, 4H), 3.64-3.61 (m, 2H), 3.16 (t, 2H, J = 11.7 Hz), 3.01 (ddd, 2H, J = 13.3, 10.2, 6.6 Hz), 2.81 (ddd, 2H, J = 12.9, 9.8, 6.7 Hz); 13C NMR (600 MHz, CDCl3): δ 165.8, 140.7, 139.9,
139.9, 139.8, 139.5, 139.2, 137.1, 135.7, 131.1, 131.0, 130.5, 129.9, 128.8, 127.5, 127.3, 127.0, 126.8, 67.8, 55.2, 34.5, 34.5. HRMS (FAB+) calcd for C\textsubscript{58}H\textsubscript{47}N\textsubscript{2}O\textsubscript{2}: 803.3637, found 803.3626.

\((S_p)-(-)-4.12\text{-Bis[4-isopropyl-3-(2-oxazolinyl)phenyl][2.2]paracyclophane ((S_p)-6e)}.\)

According to the procedure for preparation of 6b from \((S_p)-8\) and 7b, \((S_p)-6e\) (86.8 mg, 89%) was obtained from \((S_p)-8\) (72.6 mg, 0.167 mmol) and 7e (136 mg, 0.584 mmol); A colorless solid; Mp 101-103 °C; \([\alpha]_D^{22} -210.5\) (c 1.03, CHCl\textsubscript{3}); IR 1647 cm\textsuperscript{-1}; \(^1\)H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta\) 7.73 (d, 2H, \(J = 1.7\) Hz), 7.47 (dd, 2H, \(J = 8.2, 2.1\) Hz), 7.42 (d, 2H, \(J = 8.2\) Hz), 6.71 (d, 2H, \(J = 7.9\) Hz), 6.67 (s, 2H), 6.61 (d, 2H, \(J = 6.5\) Hz), 4.33 (t, 4H, \(J = 9.6\) Hz), 4.08 (t, 4H, \(J = 9.6\) Hz), 3.90 (sep, 2H, \(J = 6.9\) Hz), 3.54-3.50 (m, 2H), 3.10-3.06 (m, 2H), 2.90 (ddd, 2H, \(J = 13.6, 10.1, 7.0\) Hz), 2.66 (ddd, 2H, \(J = 13.1, 9.6, 7.2\) Hz), 1.30 (d, 6H, \(J = 6.8\) Hz), 1.29 (d, 6H, \(J = 6.8\) Hz); \(^{13}\)C NMR (150 MHz, CDCl\textsubscript{3}): \(\delta\) 165.1, 147.3, 139.6, 139.6, 138.1, 137.0, 135.5, 132.0, 131.2, 130.6, 129.9, 126.7, 126.0, 66.9, 55.6, 34.6, 34.3, 29.2, 24.0, 23.9; MS (DART) \(m/z\) 583 (M\textsuperscript{+}+1, 100.0); HRMS calcd for C\textsubscript{40}H\textsubscript{43}N\textsubscript{2}O\textsubscript{2}: 583.3325, found 583.3306.

\textbf{Preparation of \((S_p)-9a,b).}\n
\begin{align*}
\text{(S\textsubscript{p})-8} & \xrightarrow{\text{Pd(OAc)}_2 (10 \text{ mol\%}), \text{dppp} (10 \text{ mol\%}), \text{Et}_3\text{N}} \text{(S\textsubscript{p})-SI (80\%)} \\
\text{(S\textsubscript{p})-7a,b} & \xrightarrow{\text{Pd(PPh\textsubscript{3}})\textsubscript{4} (10 \text{ mol\%}) \text{Na}_2\text{CO}_3} \text{(S\textsubscript{p})-9a} \text{ R = H (76\%)} \\
& \quad \quad \quad \text{S9 (94\%)}
\end{align*}
To a solution of (S)<sub>p</sub>-8 (154 mg, 0.353 mmol) in MeOH (1.5 mL) and DMSO (1.5 mL) were added Pd(OAc)<sub>2</sub> (7.9 mg, 0.035 mmol), dppp (14.6 mg, 0.035 mmol) and Et<sub>3</sub>N (0.2 mL) at room temperature. After stirring for 2 h at 70 °C under a CO atmosphere, the reaction mixture was cooled to room temperature, diluted with water, and extracted with Et<sub>2</sub>O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane-AcOEt (30:1) to afford (S)<sub>p</sub>-SI1 (97.1 mg, 80%) as a colorless solid; Mp 106-108 ºC; [α]<sub>D</sub> +121.2 (c 1.15, CHCl<sub>3</sub>); IR 1711 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.76 (d, 1H, <i>J</i> = 1.8 Hz), 6.67-6.54 (m, 4H), 6.48 (d, 1H, <i>J</i> = 7.8 Hz), 4.06 (ddd, 1H, <i>J</i> = 12.6, 9.8, 1.1 Hz), 3.92 (s, 3H), 3.47 (ddd, 1H, <i>J</i> = 13.3, 10.1, 1.4 Hz), 3.26-3.18 (m, 1H), 3.15-2.97 (m, 3H), 2.87-2.76 (m, 2H); <sup>13</sup>C NMR (150 MHz, methanol-d4): δ 169.0, 143.4, 143.4, 140.9, 140.2, 138.2, 137.3, 136.5, 136.3, 132.7, 131.9, 131.5, 127.5, 52.2, 36.7, 36.4, 34.8, 33.5; MS (DART) <i>m</i>/<i>z</i> 347 (98.6, M<sup>+</sup>+1), 345 (100.0, M<sup>+</sup>); HRMS calcd for C<sub>18</sub>H<sub>18</sub>BrO<sub>2</sub>: 345.0490, found 345.0483.

To the above carboxylic acid (89.8 mg, 0.271 mmol) was added SOCl<sub>2</sub> (0.5 mL) at room temperature. After stirring for 16 h at 50 °C, the volatiles were evaporated. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) and added in dropwise manner to a solution of ethanolamine (0.1 mL) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) at 0 °C. The mixture was stirred for 2 h at room temperature, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extract was washed with water and brine,
dried and concentrated to dryness to afford the crude amide (96.7 mg, 95%) as a yellow solid; \([\alpha]_D^{20} +67.1\) (c 1.04, CHCl₃); IR 3420, 1647 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃): δ 7.24 (d, 1H, \(J = 1.8\) Hz), 6.81 (d, 1H, \(J = 1.9\) Hz), 6.63-6.59 (m, 3H), 6.53 (d, 1H, \(J = 7.8\) Hz), 6.45 (brs, 1H), 3.90-3.87 (m, 2H), 3.82-3.77 (m, 1H), 3.72-3.64 (m, 1H), 3.59-3.52 (m, 1H), 3.48-3.42 (m, 1H), 3.18-3.09 (m, 2H), 3.06-3.02 (m, 2H), 2.90-2.78 (m, 2H). \(^{13}\)C NMR (150 MHz, CDCl₃): δ 170.0, 142.2, 139.6, 139.6, 138.6, 135.9, 135.4, 135.1, 134.8, 134.7, 131.5, 126.8, 126.5, 62.6, 42.7, 35.6, 34.6, 34.4, 32.5. MS (DART) \(m/z\) 376 (100.0, M⁺+1), 374 (99.9, M⁺+1); HRMS calcd for C\(_{19}\)H\(_{21}\)BrN₂O: 374.0756, found 374.0769.

To the above amide (96.7 mg, 0.258 mmol) was added SOCl₂ (0.5 mL) at room temperature. The reaction mixture was stirred for 10 min at the same temperature and Et₂O was added. The mixture was basified with aqueous solution of 20% NaOH at 0 ºC and extracted with Et₂O. The extract was washed with water and brine, dried and concentrated to dryness. The residue was dissolved in THF (2 mL) and NaH (60 % dispersion of mineral oil) was added to the mixture until chloro derivative disappeared (monitored by TLC). The precipitate was filtered and filtrate was concentrated to dryness. The residue was chromatographed with hexane-AcOEt (9:1) to afford (S\(_p\))-SI2 (81.0 mg, 88%) as a colorless solid; Mp 164-166 ºC; \([\alpha]_D^{19} +79.6\) (c 1.50, CHCl₃); IR 1636 cm⁻¹; \(^1\)H NMR (600 MHz, CDCl₃): δ 7.68 (d, 1H, \(J = 1.7\) Hz), 6.61-6.55 (m, 4H), 6.48 (d, 1H, \(J = 7.9\) Hz), 4.45-4.34 (m, 2H), 4.22-4.06 (m, 3H), 3.46 (ddd, 1H, \(J = 13.3, 10.1, 1.5\) Hz), 3.19 (ddd, 1H, \(J = 13.8, 10.1, 6.8\) Hz), 3.07 (dd, 2H, \(J = 12.9, 10.8\) Hz), 2.96 (ddd, 1H, \(J = 14.4, 10.1, 7.4\) Hz), 2.83-2.76 (m, 2H); \(^{13}\)C NMR (150 MHz, CDCl₃): δ 164.4, 142.0, 140.5, 139.2, 138.8, 135.6, 135.1, 135.0, 134.9, 131.2, 130.3, 128.0, 126.6, 66.6, 55.5, 36.0, 35.8, 33.8, 32.6; MS (DART) \(m/z\) 358 (98.4, M⁺+1), 356 (100.0, M⁺+1); HRMS calcd for C\(_{19}\)H\(_{19}\)BrNO: 356.0650, found 356.0643.

(\(S_p\))-(-)-4-(2-Oxazolinyl)-12-[2-(2-oxazolinyl)-1,1'-biphenyl-4-yl][2.2]paracyclophane (\(S_p\)-9b).

To a solution of (\(S_p\))-SI2 (30.9 mg, 0.0867 mmol) in DMSO (0.6 mL) and H₂O (58 µL) were added Na₂CO₃ (18.3 mg, 0.173 mmol), 7b (46.3 mg, 0.173 mmol) and Pd(PPh₃)₄ (10.0 mg, 0.00867 mmol) at room temperature under an argon atmosphere. After stirring for 10 h at 100 ºC, the reaction mixture was cooled to room temperature, diluted with water, and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with benzene-acetonitrile (7:1)
to afford \((S_p)-9b\) (40.6 mg, 94%) as a colorless solid; Mp 112-114 °C; \([\alpha]_D^{23}\) -90.7 (c 1.10, CHCl₃); IR 1639 cm⁻¹; \(^1\)H NMR (600 MHz, CDCl₃): \(\delta\) 8.07 (d, 1H, J = 1.7 Hz), 7.72 (dd, 1H, J = 7.9, 1.7 Hz), 7.47-7.40 (m, 5H), 7.37-7.34 (m, 1H), 6.70-6.64 (m, 5H), 6.61 (dd, 1H, J = 7.6, 1.7 Hz), 4.58 (dt, 1H, J = 9.6, 8.2 Hz), 4.43 (dt, 1H, J = 10.0, 8.6 Hz), 4.30-4.09 (m, 5H), 4.02-3.92 (m, 2H), 3.65-3.61 (m, 1H), 3.21 (dd, 1H, J = 13.1, 9.6 Hz), 3.01-2.93 (m, 2H), 2.89-2.82 (m, 2H), 2.50 (ddd, 1H, J = 13.5, 9.7, 7.5 Hz); \(^{13}\)C NMR (150 MHz, CDCl₃): \(\delta\) 166.3, 164.3, 141.1, 140.9, 140.3, 140.2, 140.1, 139.9, 139.5, 136.8, 135.9, 135.6, 134.9, 132.0, 131.9, 131.5, 130.9, 130.5, 128.2, 128.0, 127.7, 127.4, 127.1, 67.7, 66.6, 55.3, 55.0, 36.4, 34.9, 34.1, 33.8; MS (DART) \(m/z\) 499 (100.0, M⁺+1); HRMS calcd for C₃₄H₃₁N₂O₂: 499.2386, found 499.2384.

\((S_p)-(-)-4-(2-Oxazoliny)-12-[3-(2-oxazoliny)phenyl][2.2]paracyclophane ((S_p)-9a).

According to the procedure for preparation of \(9b\) from \((S_p)-SI2\) and \(7b\), \((S_p)-9a\) (15.0 mg, 76%) was obtained from \((S_p)-SI2\) (17.3 mg, 0.0486 mmol) and \(7a\) (18.5 mg, 0.0971 mmol); A colorless solid; Mp 57-59 °C; \([\alpha]_D^{18}\) -130.3 (c 0.34, CHCl₃); IR 1647 cm⁻¹; \(^1\)H NMR(600 MHz, CDCl₃): \(\delta\) 8.20 (t, 1H, J = 1.5 Hz), 7.93 (dt, 1H, J = 7.9, 1.4 Hz), 7.73 (dt, 1H, J = 7.7, 1.4 Hz), 7.49 (t, 1H, J = 7.7 Hz), 7.20 (d, 1H, J = 1.4 Hz), 6.69-6.60 (m, 5H), 4.64 (dt, 1H, J = 10.0, 8.2 Hz), 4.50-4.43 (m, 3H), 4.29-4.18 (m, 3H), 4.13-4.09 (m, 2H), 3.58 (ddd, 1H, J = 13.5, 9.7, 1.3 Hz), 3.21 (dd, 1H, J = 12.9, 9.8 Hz), 3.00 (dt, 1H, J = 12.5, 8.9 Hz), 2.94-2.79 (m, 3H), 2.40 (ddd, 1H, J = 13.1, 9.7, 7.6 Hz); \(^{13}\)C NMR (150 MHz, CDCl₃): \(\delta\) 164.9, 164.3, 141.1, 140.9, 140.7, 140.2, 139.5, 136.8, 136.0, 135.7, 134.8, 132.9, 131.9, 131.5, 130.9, 129.0, 128.5, 128.1, 127.4, 126.7, 67.6, 66.8, 55.4, 55.0, 36.4, 34.9, 34.1, 33.7; MS (DART) \(m/z\) 423 (100.0, M⁺+1); HRMS calcd for C₂₈H₂₇N₂O₂: 423.2073, found 423.2077.

**Preparation of \((S_p)-10.**
(S_p)-(+)-4,12-Bis(carbomethoxy)[2.2]paracyclophane (S_p)-SI3). 9

To a solution of (S_p)-8 (37.4 mg, 0.0859 mmol) in MeOH (0.3 mL) and DMF (0.6 mL) were added dpff (9.5 mg, 0.017 mmol), Et$_3$N (0.05 mL) and Pd(OAc)$_2$ (3.9 mg, 0.017 mmol) at room temperature. After stirring for 47 h at 100 ºC under a CO atmosphere, the reaction mixture was cooled to room temperature, diluted with water, and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane-AcOEt (20:1) to afford (S_p)-SI3 (15.0 mg, 54%) as a colorless solid; Mp 176-178 ºC; [α]$_D$+$11.9$ (c 1.83, CHCl$_3$); IR 1713 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) δ 7.14 (d, 2H, J = 1.7 Hz), 6.71 (dd, 2H, J = 7.6, 1.7 Hz), 6.55 (d, 2H, J = 7.9 Hz), 4.12 (ddd, 2H, J = 12.7, 10.0, 1.5 Hz), 3.90 (s, 6H), 3.21-3.11 (m, 4H), 2.83 (ddd, 2H, J = 12.9, 10.1, 7.4 Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 167.1, 142.5, 140.3, 136.3, 136.0, 133.5, 130.4, 51.6, 35.8, 34.2; MS (DART) m/z 325 (100.0, M$^+$+1); HRMS calcd for C$_{20}$H$_{21}$O$_4$: 325.1440, found 325.1431.

(S_p)-(+)4,12-Bis(2-oxazolinyl)[2.2]paracyclophane (S_p)-10.

To a solution of (S_p)-SI3 (15.0 mg, 0.0463 mmol) in MeOH (0.25 mL) and THF (0.25 mL) was added aqueous solution of 40% NaOH (1 mL) at room temperature. After stirring for 6 h at 80 ºC, the reaction mixture was cooled to room temperature, acidified with aqueous solution of 10% HCl, and extracted with AcOEt-THF (10:1). The extract was washed with brine, dried and concentrated to dryness to afford the crude carboxylic acid (17.2 mg, quant.) as a colorless solid; $[α]$_D$^{20}$ -36.2 (c 0.1, EtOH); $^1$H NMR (400 MHz, methanol-d4): δ 7.20 (s, 2H), 6.75 (d, 2H, J = 6.9 Hz), 6.59 (d, 2H, J = 7.6 Hz), 4.09 (t, 2H, J = 10.7 Hz), 3.19-3.10 (m, 4H), 2.85-2.80 (m, 2H).

To the above carboxylic acid (17.2 mg, 0.0580 mmol) was added SOCl$_2$ (0.5 mL) at room temperature. After stirring for 15 h at 50 ºC, the volatiles were evaporated. The residue was dissolved in CH$_2$Cl$_2$ (0.4 mL) and added in dropwise manner to a solution of ethanolamine (0.1 mL) in CH$_2$Cl$_2$ (0.4 mL) at 0 ºC. The reaction mixture was stirred for 1 h at room temperature, diluted with water, and extracted with CH$_2$Cl$_2$-THF (5:1). The extract was washed with water and brine, dried and concentrated to dryness to afford the crude amide (25.3 mg, 0.0662 mmol) as an orange oil; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.88 (s, 2H), 6.84 (s, 2H), 6.64-6.58 (m, 4H), 3.85 (s, 4H), 3.75-3.50 (m, 8H), 3.14-3.09 (m, 2H), 2.90-2.77 (m, 4H).

To the above amide (25.3 mg, 0.0662 mmol) was added SOCl$_2$ (0.5 mL) at room
temperature. After stirring for 20 min at the same temperature, Et₂O was added to the mixture, which was basified with aqueous solution of 20% NaOH at 0 °C, and extracted with AcOEt. The extract was washed with water and brine, dried and concentrated to dryness. The residue was dissolved in THF (1 mL) and NaH (60% dispersion of mineral oil) was added to the mixture at room temperature until chloro derivative disappeared (monitored by TLC). The precipitate was filtered and filtrate was concentrated to dryness. The residue was chromatographed with AcOEt and treated with decolorizing charcoal to afford \( (S)_p \)-10 (7.8 mg, 34%) as a colorless solid; Mp 173-175 °C (decomp.); \([\alpha]_D^{20} +49.5\) (c 0.39, CHCl₃); IR 1636 cm⁻¹; \(^1\)H NMR (600 MHz, CDCl₃): \( \delta \) 7.12 (d, 2H, \( J = 2.1 \) Hz), 6.63 (dd, 2H, \( J = 7.9, 1.7 \) Hz), 6.54 (d, 2H, \( J = 7.9 \) Hz), 4.39-4.32 (m, 4H), 4.28-4.24 (m, 2H), 4.18 (dt, 2H, \( J = 13.7, 9.2 \) Hz), 4.08-4.03 (m, 2H), 3.16-3.10 (m, 4H), 2.84-2.79 (m, 2H); \(^1^3\)C NMR (150 MHz, CDCl₃) \( \delta \) 164.3, 140.8, 140.0, 135.7, 134.8, 132.6, 128.0, 66.4, 55.5, 35.8, 33.9; MS (DART) \( m/z \) 347 (100.0, M⁺+1); HRMS calcd for C₂₂H₂₃N₂O₂: 347.1760, found 347.1765.

**Typical procedure for asymmetric EtOH insertion reaction of 16 (Table 1, entry 5). (S)-(−)-Methyl 2-ethoxy-2-phenylacetate (17).**

To a suspension of \( (S)_p \)-6b (7.8 mg, 0.012 mmol) and MS5A (300 mg) in CH₂Cl₂ (1 mL) were added NaBARF (10.6 mg, 0.0120 mmol) and Cu(OTf)₂ (3.6 mg, 0.010 mmol) at room temperature under an argon atmosphere. After being stirred for 4 h at the same temperature, EtOH (56 µL, 1.0 mmol) and then a solution of 16 (35 mg, 0.20 mmol) in CH₂Cl₂ (1 mL) were added to the reaction mixture at 40 °C. The mixture was stirred at the same temperature for 1.5 h and filtered, and filtrate was concentrated to dryness. The residue was chromatographed with hexane-Et₂O (20:1) to afford 17 (34.1 mg, 86%) as a colorless oil; \([\alpha]_D^{23} +65.6\) (c 0.86, CH₂Cl₂) \{lit.\[10\] \([\alpha]_D^{20} -85.7\) (c 1.60, CH₂Cl₂) for -95% ee\}; \(^1\)H NMR (600 MHz, CDCl₃): \( \delta \) 7.45 (d, 2H, \( J = 7.6 \) Hz), 7.37-7.31 (m, 3H), 4.89 (s, 1H), 3.71 (s, 3H), 3.62-3.57 (m, 1H), 3.53-3.48 (m, 1H), 1.27 (t, 3H, \( J = 7.0 \) Hz); \(^1^3\)C NMR (150 MHz, CDCl₃) \( \delta \) 171.4, 136.6, 128.6, 128.6, 127.1, 80.8, 65.3, 52.2, 15.1; 76% ee; HPLC: OD-H column; \( \lambda \) = 254 nm; eluent: hexane/isopropanol = 99.5/0.5; Flow rate: 1.0 mL/min; \( t_R \) = 11.6 min for (R)-enantiomer, \( t_R \) = 9.9 min for (S)-enantiomer.

**Typical procedure for asymmetric intramolecular insertion reaction of 18 (Table 2, entry 1). (−)-Benzyl tetrahydro-2H-pyran-2-carboxylate (19).**
To a suspension of \((S)_6\)-6b (7.7 mg, 0.012 mmol) and MS5A (300 mg) in CH\(_2\)Cl\(_2\) (1 mL) were added NaBAr\(_F\) (10.6 mg, 0.012 mmol) and Cu(OTf)\(_2\) (3.56 mg, 0.00987 mmol) at room temperature under an argon atmosphere. After stirring for 4 h at the same temperature, a solution of 18 (44.5 mg, 0.179 mmol) in CH\(_2\)Cl\(_2\) (1 mL) was added to the mixture at -78 °C. The reaction mixture was warmed to room temperature and stirred for 4.5 h. The mixture was filtered and filtrate was concentrated to dryness. The residue was chromatographed with hexane-CH\(_2\)Cl\(_2\) (1:4) to afford 19 (25.0 mg, 63%) as a colorless oil; \([\alpha]_D^{27} -11.9 \text{ (c 0.90, CH}_2\text{Cl}_2)\) \{lit., \(^3 [\alpha]_D^{20} +17.1 \text{ (c 1.73, CH}_2\text{Cl}_2)\} \text{ for -93% ee}\}; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.36–7.31 (m, 5H), 5.20 (s, 2H), 4.11–4.08 (m, 1H), 4.04 (dd, 1H, \(J = 10.7, 2.7 \text{ Hz}\)), 3.50 (td, 1H, \(J = 11.4, 2.3 \text{Hz}\)), 1.97–1.94 (m, 1H), 1.89–1.84 (m, 1H), 1.68–1.52 (m, 4H); \(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta\) 171.5, 135.6, 128.5, 128.3, 128.3, 76.2, 68.1, 66.5, 28.8, 25.2, 22.8; 61% ee; HPLC: AS-H column; \(\lambda = 254 \text{ nm}\); eluent: hexane/isopropanol = 97/3; Flow rate: 1.0 mL/min; \(t_R = 11.8 \text{ min for major isomer, } t_R = 15.3 \text{ min for minor isomer.}\)

**Typical procedure for asymmetric PhOH insertion reaction of 20 (Table 3, entry 3).**

**\((S)\)-(-)-Ethyl 2-phenoxypropionate (21).**

To a suspension of \((S)_p\)-6e (7.3 mg, 0.013 mmol) and MS5A (315 mg) in CH\(_2\)Cl\(_2\) (1 mL) were added NaBAr\(_F\) (11.2 mg, 0.0126 mmol) and CuCl (1.0 mg, 0.010 mmol) at room temperature under an argon atmosphere. After stirring for 4 h at the same temperature, a solution of PhOH (98.8 mg, 1.05 mmol) in CH\(_2\)Cl\(_2\) (0.5 mL) was added to the mixture. After 20 min, a solution of 20 (28.0 mg, 0.210 mmol) in CH\(_2\)Cl\(_2\) (0.6 mL) was added to the mixture, which was stirred at room temperature for 1 h. The mixture was filtered and filtrate was concentrated to dryness. The residue was chromatographed with hexane-AcOEt (30:1) to afford 21 (28.0 mg, 66%) as a colorless oil; \([\alpha]_D^{23} -37.5 \text{ (c 0.43, MeOH)}\) \{lit., \(^{12} [\alpha]_D^{18} +47.2 \text{ (c 0.5, MeOH) for -99% ee}\}; \(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.29–7.25 (m, 2H), 6.98-6.95 (m, 1H), 6.89-6.87 (m, 2H), 4.74 (q, 1H, \(J = 6.9 \text{ Hz}\)), 4.22 (q, 2H, \(J = 7.1 \text{ Hz}\)), 1.62 (d, 3H, \(J = 6.9 \text{ Hz}\)), 1.25 (t, 3H, \(J = 7.2 \text{ Hz}\)); \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 172.3, 157.6, 129.5, 121.5, 115.1, 72.6, 61.2, 18.6, 14.1; 80% ee; HPLC: OD-H column; \(\lambda = 254 \text{ nm}\); eluent: hexane/isopropanol = 9/1; Flow rate: 1.0 mL/min; \(t_R = 8.8 \text{ min for (R)-enantiomer, } t_R = 4.9 \text{ min for (S)-enantiomer.}\)
References