Asymmetric hydrogenations of imines with chiral alkene-derived boron Lewis acids

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Supporting Information
**General consideration:** All air-sensitive compounds were handled under an atmosphere of argon or in a nitrogen-filled glovebox. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker AV 300/400/500 at ambient temperature with CDCl$_3$ as solvent and TMS as internal standard. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of TMS (0), to the carbon resonance of the CDCl$_3$ (77.23). Coupling constants (J) were given in Hertz (Hz). IR spectrums were recorded on Perkin-Elmer-983 spectrometer. Optical rotations were measured with PerkinElmer 341 polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). All solvents were purified by conventional methods, distilled before use. Commercially available reagents were used without further purification.

**General procedure for the synthesis of chiral alkenes 4**

![Chemical structure](image)

**Synthesis of compounds 3-2:** To a solution of compound 3-1 (0.2661 g, 0.5 mmol) and Pd(PPh$_3$)$_4$ (0.058 g, 0.05 mmol) in DME (3.0 mL), arylboronic acid (1.75 mmol) and aqueous Na$_2$CO$_3$ (5.2 mmol, 2 M, 2.6 mL) were added under argon atmosphere. The resulting mixture was stirred at room temperature for 15 min and then at 90 °C for another 12 h. After being cooled to room temperature, the reaction mixture was passed through a pad of Celite. After removal of the solvent, the residue was dissolved in DCM (20 mL). The organic phase was washed with saturated aqueous NH$_4$Cl (10 mL), water (10 mL), and brine (10 mL). The organic phase was dried over sodium sulfate, filtered, and concentrated. The crude residue was purified by column chromatography on silica gel using hexanes/DCM (2/1) to afford compounds 3-2.

**Synthesis of compounds 3:** To a flask containing a stir bar were charged with compound 3-2, conc. HCl (0.2 mL), and dioxane (3 mL). The resulting mixture was stirred at 60 °C for 12 h. After being cooled to the room temperature, the mixture was poured into a mixture of Et₂O (20 mL) and water (20 mL). The organic phase was separated, and the aqueous layer was extracted with Et₂O (2 x 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The residue was purified by column chromatography on silica gel with hexanes/ethyl acetate (10/1) to afford compound 3.

**Synthesis of compounds 4:** To a flask containing a stir bar were charged with compound 3, NaH (60% dispersion in mineral oil, 2.5 equiv), and in DMF (10 mL). The mixture was stirred for at room temperature1 h. Then 3-chloro-2-(chloromethyl)prop-1-ene (1.0 equiv) was added, the result mixture was stirred at 60 °C for 12 h. After being cooled to the room temperature, the reaction mixture was quenched by saturated aqueous NH₄Cl (10 mL). The aqueous phase was extracted with DCM (3 x 10 mL), and the combined organic layers were dried over sodium sulfate. After being filtered and concentrated, the residue was concentrated and purified by column chromatography on silica gel with petroleum ether/ethyl acetate (100/1) to afford compounds 4.


**General procedure for the asymmetric hydrogenation of imines (Scheme 3):** To a glass test tube (10 mL) in a nitrogen atmosphere glovebox, HB(C₆F₅)₂ (0.0104 g, 0.03 mmol), chiral alkene 4i (0.0104 g, 0.03 mmol), and dry p-xylene (0.75 mL) were added. The resulting mixture was stirred at room temperature for 5 min, followed by the addition of imine 6 (0.3 mmol). Then the tube was moved to a stainless-steel autoclave, and the autoclave was purged three times with H₂ and the final pressure of H₂ was adjusted to 30 bar. The reaction was stirred at 30 °C for 12 h. The solvent was removed under reduced pressure, and the crude residue was purified by flash chromatography on silica with petroleum ether/ethyl acetate (50/1) to afford amines 7.
Characterization of chiral alkenes 4

4a: Yellow solid, 0.196 g, 75% yield; m.p. 120-122 °C; \([\alpha]_D^{20} = +107.6\) (c 1.10, CHCl₃); IR (film): 1509, 1222, 1005, 837, 751 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃, ppm) δ 7.95-7.86 (m, 4H), 7.78-7.68 (m, 4H), 7.45-7.36 (m, 2H), 7.32-7.23 (m, 3H), 7.20-7.09 (m, 5H), 4.84 (s, 2H), 4.00 (d, \(J = 12.4\) Hz, 2H), 3.85 (d, \(J = 12.4\) Hz, 2H); \(^1^3\)C NMR (100 MHz, CDCl₃, ppm) δ 162.6 (d, \(J_{C-F} = 245.3\) Hz), 152.2, 141.5, 135.5 (d, \(J_{C-F} = 3.4\) Hz), 133.2, 131.0, 130.9, 130.8 (d, \(J_{C-F} = 20.3\) Hz), 128.3, 126.8, 126.7, 126.3, 125.4, 123.8, 115.9 (d, \(J_{C-F} = 21.2\) Hz), 77.4, 76.0; \(^1^9\)F NMR (377 MHz, CDCl₃, ppm) δ -114.8; HRMS (APCI) calcd. for C₃₆H₂₅O₂F₂ [M+H]^+: 527.1817, Found: 527.1811.

4b: Yellow solid, 0.220 g, 73% yield; m.p. 170-172 °C; \([\alpha]_D^{20} = +88.1\) (c 1.21, CHCl₃); IR (film): 2961, 1258, 1194, 1005, 836, 749 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃, ppm) δ 7.93 (s, 2H), 7.89 (d, \(J = 8.2\) Hz, 2H), 7.72-7.65 (m, 4H), 7.50-7.44 (m, 4H), 7.42-7.34 (m, 2H), 7.26-7.20 (m, 4H), 4.85 (s, 2H), 4.01 (d, \(J = 12.4\) Hz, 2H), 3.89 (d, \(J = 12.4\) Hz, 2H), 1.37 (s, 18H); \(^1^3\)C NMR (100 MHz, CDCl₃, ppm) δ 152.5, 150.6, 141.8, 136.6, 134.1, 133.2, 131.1, 130.7, 128.8, 128.3, 126.6, 126.5, 126.4, 125.7, 125.1, 123.6, 76.0, 34.8, 31.6; HRMS (ESI) calcd. for C₄₄H₄₃O₂Na [M+Na]^+: 625.3077, Found: 625.3068.
4c:  White solid, 0.115 g, 55% yield; m.p. 119-122 °C; [α]D20 = +82.3 (c 0.83, CHCl3); IR (film): 1599, 1416, 1259, 1009, 911, 734 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.94 (s, 2H), 7.90 (d, J = 8.2 Hz, 2H), 7.45-7.35 (m, 4H), 7.35-7.28 (m, 4H), 7.28-7.20 (m, 4H), 6.97-6.90 (m, 2H), 4.87 (s, 2H), 4.04 (d, J = 12.4 Hz, 2H), 3.93 (d, J = 12.4 Hz, 2H), 3.84 (s, 6H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 160.1, 152.3, 141.7, 141.1, 134.1, 133.2, 131.0, 130.8, 129.9, 128.4, 126.7, 126.6, 126.4, 125.2, 123.6, 121.8, 114.4, 113.6, 76.0, 55.6; HRMS (ESI) calcd. for C₃₈H₃₀O₄Na [M+Na]+: 573.2036, Found:573.2029.

4d:  Yellow solid, 0.104 g, 38% yield; m.p. 146-147 °C; [α]D20 = +16.7 (c 0.91, CHCl₃); IR (film): 1494, 1462, 1421, 1248, 910, 751, 732 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.95-7.80 (m, 4H), 7.53-7.44 (m, 2H), 7.42-7.30 (m, 4H), 7.28-7.18 (m, 4H), 7.10-6.95 (m, 4H), 4.83 (s, 2H), 3.96-3.85 (m, 4H), 3.76 (s, 6H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 162.7, 157.2, 153.1, 142.0, 133.4, 131.5, 130.8, 129.2, 128.2, 126.4, 126.3, 126.0, 124.7, 122.8, 120.8, 111.3, 75.9, 55.9, 36.7, 31.6; HRMS (ESI) calcd. for C₃₈H₃₆O₄Na [M+Na]+: 573.2036, Found: 573.2032.
4e: Yellow solid, 0.211 g, 64% yield; m.p. 111-112 °C; [α]_D^{20} = +2.3 (c 1.24, CHCl₃); IR (film): 1492, 1448, 1421, 1005, 911, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 8.05-7.90 (m, 2H), 7.89-7.81 (m, 2H), 7.59-7.50 (m, 2H), 7.41-7.32 (m, 4H), 7.30-7.16 (m, 8H), 7.15-6.95 (m, 10H), 5.20-5.00 (m, 4H), 4.82 (s, 2H), 4.05-3.85 (m, 4H); ¹³C NMR (125 MHz, CDCl₃, ppm) δ 156.5, 153.2, 142.1, 137.3, 133.5, 131.9, 131.5, 130.7, 129.2, 128.5, 128.3, 128.2, 127.5, 127.0, 126.6, 126.4, 126.1, 124.6, 122.7, 121.3, 113.2, 75.9, 70.6, 29.9, 27.1; HRMS (ESI) calcd. for C₅₀H₄₈O₄Na [M+Na]⁺: 725.2662, Found: 725.2654.

4f: Yellow foam, 0.084 g, 86% yield; m.p. 110-112 °C; [α]_D^{20} = +6.8 (c 0.90, CHCl₃); IR (film): 1490, 1120, 1005, 749, 733 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.90 (s, 2H), 7.86 (d, J = 8.2 Hz, 2H), 7.54-7.46 (m, 2H), 7.40-7.28 (m, 4H), 7.24-7.18 (m, 4H), 7.06-6.96 (m, 4H), 4.85 (s, 2H), 4.58-4.39 (m, 2H), 3.95-3.84(m, 4H), 1.32-1.18 (m, 6H), 1.13 (d, J = 5.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃, ppm) δ 155.6, 153.3, 142.3, 133.4, 131.8, 131.3, 130.7, 128.9, 128.1, 126.4, 126.1(3), 126.0(8), 124.6, 122.9, 120.7, 114.7, 75.9, 70.7, 29.9, 22.5, 22.1; HRMS (ESI) calcd. for C₄₂H₃₈O₄Na [M+Na]⁺: 629.2662, Found: 629.2651.
4g: White solid, 0.169 g, 69% yield; m.p. 149-150 °C; $[\alpha]_{D}^{20} = -5.9$ (c 0.92, CHCl$_3$); IR (film): 1502, 1219, 1046, 1009, 730 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.95-7.80 (m, 4H), 7.41-7.31 (m, 2H), 7.25-7.20 (m, 4H), 7.10-7.05 (m, 2H), 7.00-6.87 (m, 4H), 4.87 (s, 2H), 4.02-3.92 (m, 4H), 3.79 (s, 6H), 3.72 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 153.8, 153.0, 151.7, 142.1, 133.4, 131.6, 130.7, 128.3, 126.5, 126.4, 126.0, 124.8, 122.9, 117.0, 114.3, 112.7, 77.4, 75.9, 56.6(1), 56.5(8), 56.1; HRMS (ESI) calcd. for C$_{40}$H$_{34}$O$_6$Na [M+Na]$^+$: 633.2248, Found: 633.2241.

4h: White solid, 0.265 g, 85% yield; m.p. 149-151 °C; $[\alpha]_{D}^{20} = +18.8$ (c 1.16, CHCl$_3$); IR (film): 2960, 1504, 1252, 1010, 750 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$, ppm) $\delta$ 7.95-7.84 (m, 4H), 7.55-7.49 (m, 2H), 7.42-7.33 (m, 4H), 7.29-7.18 (m, 4H), 6.95 (s, 1H), 6.94 (s, 1H), 4.82 (s, 2H), 3.94-3.88 (m, 4H), 3.74 (s, 6H), 1.32 (s, 18H); $^{13}$C NMR (125 MHz, CDCl$_3$, ppm) $\delta$ 155.0, 153.2, 143.6, 142.3, 133.3, 131.8, 130.7, 129.4, 129.0, 128.2, 126.7, 126.4, 126.2, 126.0, 125.6, 124.7, 122.4, 110.8, 75.8, 56.0, 34.4, 31.8; HRMS (ESI) calcd. for C$_{46}$H$_{46}$O$_{4}$Na [M+Na]$^+$: 685.3288, Found: 685.3278.
4i: Yellow solid, 1.227 g, 89% yield; m.p. 172-175 °C; [α]_D^{20} = +75.1 (c 1.11, CHCl₃); IR (film): 2963, 1594, 1014, 876, 750, 716 cm⁻¹; ^1H NMR (400 MHz, CDCl₃, ppm) δ 7.97-7.83 (m, 4H), 7.60-7.55 (m, 4H), 7.47-7.43 (m, 2H), 7.42-7.36 (m, 2H), 7.31-7.25 (m, 4H), 4.78 (s, 2H), 3.96 (d, J = 12.4 Hz, 2H), 3.84 (d, J = 12.4 Hz, 2H), 1.37 (s, 36H); ^13C NMR (100 MHz, CDCl₃, ppm) δ 152.6, 151.2, 142.1, 138.9, 135.2, 133.1, 131.0, 130.8, 128.3, 126.7, 126.5, 126.4, 125.0, 123.8, 122.9, 121.2, 75.7, 35.2, 31.8; HRMS (ESI) calcd. for C₅₂H₄₈O₂Na [M+Na]^+: 737.4340, Found: 737.4329.

4j: Yellow solid, 0.259 g, 68% yield; m.p. 170-172 °C; [α]_D^{20} = +74.9 (c 1.07, CHCl₃); IR (film): 2926, 1379, 1278, 1135 cm⁻¹; ^1H NMR (400 MHz, CDCl₃, ppm) δ 8.25 (s, 4H), 8.01 (s, 2H), 7.99 (s, 1H), 7.87 (s, 1H), 7.92 (s, 2H), 7.53-7.45 (m, 2H), 7.40-7.32 (m, 2H), 7.25-7.20 (m, 2H), 4.87 (s, 2H), 4.06 (d, J = 12.3 Hz, 2H), 3.76 (d, J = 12.3 Hz, 2H); ^13C NMR (100 MHz, CDCl₃, ppm) δ 151.5, 141.5, 140.5, 132.5 (q, J_C-F = 33.4 Hz), 132.4 (q, J_C-F = 277.7 Hz), 131.4, 129.3 (d, J_C-F = 2.9 Hz), 128.7, 127.9, 127.1, 126.2 (d, J_C-F = 20.0 Hz), 125.0, 124.9, 122.2, 121.5, 119.5, 76.4, 29.9; ^19F NMR (377 MHz, CDCl₃, ppm) δ -62.7; HRMS (ESI) calcd. for C₄₉H₂₃O₂F₁₂ [M+H]^+: 763.1501, Found: 763.1495.
4k: White solid, 0.198 g, 69% yield; m.p. 163-165 °C; [α]_D^{20} = -81.5 (c 0.82, CHCl₃); IR (film): 2920, 2851, 1258, 1007, 750 cm⁻¹; ^1H NMR (400 MHz, CDCl₃, ppm) δ 7.84 (d, J = 8.1 Hz, 2H), 7.71 (s, 2H), 7.40-7.33 (m, 2H), 7.23-7.16 (m, 2H), 7.12-7.06 (m, 2H), 7.03 (s, 2H), 6.97 (s, 2H), 4.87 (s, 2H), 3.99-3.86 (m, 4H), 2.34 (d, J = 11.4 Hz, 12H), 2.08 (s, 6H); ^13C NMR (100 MHz, CDCl₃, ppm) δ 153.3, 143.1, 137.8, 137.2, 135.8, 135.5, 133.3, 133.0, 131.3, 130.9, 128.7(3), 128.6(7), 128.1, 126.3(4), 126.2(9), 126.1, 124.7, 121.9, 77.4, 76.0, 21.8, 21.3, 20.5; HRMS (ESI) calcd. for C₄₂H₃₈O₂Na [M+Na]^+: 597.2775, Found: 597.2763.

4l: Yellow solid, 0.139 g, 47% yield; m.p. 103-105 °C; [α]_D^{20} = +74.6 (c 1.00, CHCl₃); IR (film): 2923, 1009, 913, 749 cm⁻¹; ^1H NMR (400 MHz, CDCl₃, ppm) δ 8.24 (s, 2H), 8.07 (s, 2H), 8.00-7.85 (m, 10H), 7.55-7.48 (m, 4H), 7.47-7.40 (m, 2H), 7.35-7.29 (m, 4H), 4.78 (s, 2H), 3.96 (d, J = 12.4 Hz, 2H), 3.86 (d, J = 12.4 Hz, 2H); ^13C NMR (125 MHz, CDCl₃, ppm) δ 152.5, 141.5, 137.1, 134.2, 133.9, 133.3, 132.8, 131.2, 131.1, 128.4(4), 128.3(9), 127.9(4), 127.9(1), 127.6, 126.9, 126.8, 126.5, 126.4(1), 126.3(7), 125.3, 123.7, 76.2, 29.9; HRMS (ESI) calcd. for C₄₄H₃₁O₂ [M+H]^+: 591.2319, Found: 591.2314.
(E)-N-(1-(4-fluoro-3-methylphenyl)ethylidene)aniline: Yellow solid, m.p. 46-47 °C; IR (film): 1630, 1447, 1114, 831, 708 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 7.90-7.82 (m, 1H), 7.78-7.69 (m, 1H), 7.39-7.30 (m, 2H), 7.12-7.01 (m, 2H), 6.82-6.74 (m, 2H), 2.33 (d, \(J = 1.7\) Hz, 3H), 2.20 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \(\delta\) 164.7, 163.1 (d, \(J_{C-F} = 249.8\) Hz), 151.8, 135.6 (d, \(J_{C-F} = 3.3\) Hz), 130.8 (d, \(J_{C-F} = 5.8\) Hz), 129.2, 126.8 (d, \(J_{C-F} = 8.6\) Hz), 125.1 (d, \(J_{C-F} = 17.5\) Hz), 123.5, 119.6, 115.0 (d, \(J_{C-F} = 22.6\) Hz), 17.5, 14.8 (d, \(J_{C-F} = 3.5\) Hz); \(^{19}\)F NMR (377 MHz, CDCl\(_3\), ppm) \(\delta\) -114.7; HRMS (APCI) calcd. for C\(_{15}\)H\(_{15}\)NF [M+H]\(^+\): 228.1183, Found: 228.1180.

\begin{figure}
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\caption{
(E)-N-(1-(4-ethylphenyl)ethylidene)-4-methoxyaniline: Yellow solid, m.p. 66-67 °C; IR (film): 2961, 1502, 1367, 1033, 845, 830 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 7.95-7.84 (m, 2H), 7.35-7.20 (m, 2H), 6.95-6.85 (m, 2H), 6.78-6.70 (m, 2H), 3.81 (s, 3H), 2.70 (q, \(J = 7.6\) Hz, 2H), 2.23 (s, 3H), 1.26 (t, \(J = 7.6\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \(\delta\) 165.8, 156.1, 147.1, 145.2, 137.5, 128.0, 127.4, 121.0, 114.4, 55.7, 28.9, 17.4, 15.7; HRMS (ESI) calcd. for C\(_{17}\)H\(_{20}\)ON [M+H]\(^+\): 254.1539, Found: 254.1540.
\end{figure}

\begin{figure}
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\caption{
(E)-N-(1-(3,4-dimethylphenyl)ethylidene)-4-methoxyaniline: Red solid, m.p. 72-73 °C; IR (film): 1627, 1502, 1240, 1034, 846, 755 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 7.78 (s, 1H), 7.68-7.62 (m, 1H), 7.18 (d, \(J = 7.9\) Hz, 1H), 6.94-6.85 (m, 2H), 6.79-6.70 (m, 2H), 3.79 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H), 2.21 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \(\delta\) 165.9, 156.0, 145.2, 139.4, 137.6, 136.7, 129.7, 128.3, 124.9, 120.9, 114.4, 55.6, 20.0, 19.9, 17.4; HRMS (ESI) calcd. for C\(_{17}\)H\(_{20}\)ON [M+H]\(^+\): 254.1539, Found: 254.1538.
\end{figure}
(E)-N-(1-[(1,1'-biphenyl]-4-yl)ethylidene)-2-methoxyaniline: Yellow solid, m.p. 141-143 °C; IR (film): 1630, 1487, 1240, 766, 756 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), ppm) \(\delta\) 8.14-8.04 (m, 2H), 7.72-7.60 (m, 4H), 7.52-7.41 (m, 2H), 7.40-7.33 (m, 1H), 7.12-7.03 (m, 1H), 7.01-6.90 (m, 2H), 6.85-6.75 (m, 1H), 3.79 (s, 3H), 2.20 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), ppm) \(\delta\) 166.8, 149.2, 143.3, 140.8, 140.7, 138.5, 129.0, 128.0, 127.9, 127.3, 127.2, 124.4, 121.1, 120.8, 111.8, 55.8, 17.9; HRMS (ESI) calcd. for C\(_{21}\)H\(_{20}\)ON [M+H]\(^+\): 302.1539, Found: 302.1538.

Characterization of amine products 7

(5)-N-(1-phenylethyl)aniline: Colorless liquid, 0.0573 g, 97% yield, 65% ee, \([\alpha]\)\(_D^{20}\) = +3.2 (c 1.33, CHCl\(_3\)); \(^1\)H NMR (300 MHz, CDCl\(_3\), ppm) \(\delta\) 7.42-7.25 (m, 4H), 7.25-7.16 (m, 1H), 7.08 (t, \(J = 8.3\) Hz, 2H), 6.63 (t, \(J = 7.3\) Hz, 1H), 6.50 (d, \(J = 7.8\) Hz, 2H), 4.48 (q, \(J = 6.7\) Hz, 1H), 4.00 (br s, 1H), 1.50 (d, \(J = 6.7\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\), ppm) \(\delta\) 147.5, 145.4, 129.3, 128.8, 127.0, 126.0, 117.4, 113.5, 53.6, 25.2.


(5)-N-(1-(4-ethylphenyl)ethyl)aniline: Colorless liquid, 0.0650 g, 96% yield, 78% ee, \([\alpha]\)\(_D^{20}\)
= +0.6 (c 1.09, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.26 (d, J = 8.0 Hz, 2H), 7.17-7.02 (m, 4H), 6.67-6.57 (m, 1H), 6.54-6.45 (m, 2H), 4.44 (q, J = 6.7 Hz, 1H), 3.96 (br s, 1H), 2.60 (q, J = 7.6 Hz, 2H), 1.47 (d, J = 6.7 Hz, 3H), 1.21 (t, J = 7.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ 147.6, 142.9, 142.6, 129.3, 128.3, 126.0, 117.3, 113.4, 53.3, 28.6, 25.1, 15.7.


(5)-N-(4-(tert-butyl)phenyl)ethyl)aniline: Colorless liquid, 0.0697 g, 92% yield, 79% ee, [α]D²⁰ = -9.1 (c 0.86, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.36-7.24 (m, 4H), 7.13-7.03 (m, 2H), 6.68-6.58 (m, 1H), 6.57-6.46 (m, 2H), 4.47 (q, J = 6.7 Hz, 1H), 3.97 (br s, 1H), 1.49 (d, J = 6.7 Hz, 3H), 1.30 (s, 9H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ 149.8, 147.6, 142.2, 129.3, 125.7(1), 125.6(6), 117.3, 113.4, 53.1, 34.6, 31.6, 24.9.


(5)-N-(1-(4-methoxyphenyl)ethyl)aniline: Colorless liquid, 0.0570 g, 84% yield, 67% ee, [α]D²⁰ = +8.2 (c 1.01, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.26 (d, J = 8.5 Hz, 2H), 7.08 (t, J = 7.7 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.62 (t, J = 7.3 Hz, 1H), 6.50 (d, J = 7.9 Hz, 2H), 4.43 (q, J = 6.7 Hz, 1H), 3.96 (br s, 1H), 3.75 (s, 3H), 1.47 (d, J = 6.7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃, ppm) δ 158.7, 147.5, 137.4, 129.3, 127.1, 117.3, 114.2, 113.5, 55.4, 53.0, 25.1.

(S)-N-(1-(4-ethoxyphenyl)ethyl)aniline: Colorless liquid, 0.0609 g, 84% yield, 65% ee, 
\([\alpha]_D^{20} = +5.4 \ (c \ 0.88, \text{CH}_2\text{Cl}_2); \ ^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3, \text{ppm}) \ \delta \ 7.31-7.20 \ (m, 2\text{H}), 
7.13-7.03 \ (m, 2\text{H}), 6.87-6.79 \ (m, 2\text{H}), 6.67-6.59 \ (m, 1\text{H}), 6.55-6.46 \ (m, 2\text{H}), 4.43 \ (q, J = 6.6 
Hz, 1\text{H}), 4.00 \ (q, J = 7.0 \text{ Hz, 2H}), 3.95 \ (\text{br s, 1H}), 1.48 \ (d, J = 6.7 \text{ Hz, 3H}), 1.38 \ (t, J = 7.0 \text{ Hz, 
3H}); \ ^{13}\text{C} \text{NMR} \ (75 \text{ MHz, CDCl}_3, \text{ppm}) \ \delta \ 158.0, 147.6, 137.3, 129.2, 127.0, 117.3, 114.7,
113.5, 63.5, 53.0, 25.1, 15.1.


(S)-N-(1-(1,1'-biphenyl)-4-yl)ethyl)aniline: White solid, 0.0781 g, 95% yield, 66% ee, 
\([\alpha]_D^{20} = -20.5 \ (c \ 0.89, \text{CH}_2\text{Cl}_2); \ ^1\text{H} \text{NMR} \ (300 \text{ MHz, CDCl}_3, \text{ppm}) \ \delta \ 7.62-7.49 \ (m, 4\text{H}), 
7.48-7.36 \ (m, 4\text{H}), 7.35-7.27 \ (m, 1\text{H}), 7.16-7.03 \ (m, 2\text{H}), 6.65 \ (t, J = 7.3 \text{ Hz, 1H}), 6.54 \ (d, J = 
8.0 \text{ Hz, 2H}), 4.53 \ (q, J = 6.6 \text{ Hz, 1H}), 4.03 \ (\text{br s, 1H}), 1.54 \ (d, J = 6.7 \text{ Hz, 3H}); \ ^{13}\text{C} \text{NMR} \ (75 
MHz, \text{CDCl}_3, \text{ppm}) \ \delta \ 147.5, 144.5, 141.1, 140.0, 129.3, 128.9, 127.6, 127.3, 127.2, 126.5,
117.5, 113.5, 53.4, 25.2.

(S)-N-(1-(4-fluorophenyl)ethyl)aniline: Colorless liquid, 0.0656 g, 99% yield, 60% ee, $[\alpha]_D^{20} = +27.9$ (c 0.99, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.37-7.25 (m, 2H), 7.13-7.03 (m, 2H), 7.02-6.92 (m, 2H), 6.64 (t, $J$ = 7.3 Hz, 1H), 6.47 (d, $J$ = 7.8 Hz, 2H), 4.44 (q, $J$ = 6.7 Hz, 1H), 3.97 (br s, 1H), 1.46 (d, $J$ = 6.7 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 161.9 (d, $J_{C-F}$ = 242.8 Hz), 147.3, 141.1 (d, $J_{C-F}$ = 3.0 Hz), 129.3, 127.5 (d, $J_{C-F}$ = 8.0 Hz), 117.6, 115.6 (d, $J_{C-F}$ = 21.2 Hz), 113.5, 53.1, 25.3; $^{19}$F NMR (377 MHz, CDCl$_3$, ppm) $\delta$ -116.9.


(5)-N-(1-(4-chlorophenyl)ethyl)aniline: Colorless liquid, 0.0645 g, 93% yield, 58% ee, $[\alpha]_D^{20} = +5.8$ (c 0.86, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.32-7.21 (m, 4H), 7.13-7.02 (m, 2H), 6.64 (t, $J$ = 7.3 Hz, 1H), 6.46 (d, $J$ = 7.8 Hz, 2H), 4.43 (q, $J$ = 6.7 Hz, 1H), 3.97 (br s, 1H), 1.46 (d, $J$ = 6.7 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 147.2, 144.0, 132.6, 129.3, 129.0, 127.4, 117.7, 113.5, 53.1, 25.2.


(5)-N-(1-(3-chlorophenyl)ethyl)aniline: Colorless liquid, 0.0662 g, 95% yield, 45% ee, $[\alpha]_D^{20} = +10.6$ (c 1.02, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.46 (s, 1H), 7.38-7.26 (m, 3H), 7.25-7.13 (m, 2H), 6.77 (t, $J$ = 7.3 Hz, 1H), 6.59 (d, $J$ = 7.9 Hz, 2H), 4.53 (q, $J$ = 6.7 Hz, 1H), 4.08 (br s, 1H), 1.58 (d, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 147.8, 147.1, 134.7, 130.1, 129.3, 127.3, 126.2, 124.2, 117.7, 113.5, 53.4, 25.2.
(S)-N-(1-(3,4-dimethylphenyl)ethyl)aniline: Colorless liquid, 0.0659 g, 97% yield, 83% ee, \([\alpha]_D^{20} = +7.3 \text{ (c 0.87, CH}_2\text{Cl}_2); \) \(^1\text{H NMR (300 MHz, CDCl}_3, \text{ ppm}) \delta 7.15-7.02 (m, 5H), 6.62 (t, \(J = 7.3 \text{ Hz, 1H}), 6.51 (d, J = 7.9 \text{ Hz, 2H}), 4.41 (q, J = 6.7 \text{ Hz, 1H}), 3.96 (br s, 1H), 2.23 (s, 3H), 2.22 (s, 3H), 1.48 (d, \(J = 6.7 \text{ Hz, 3H}); \) \(^{13}\text{C NMR (75 MHz, CDCl}_3, \text{ ppm}) \delta 147.7, 142.9, 136.9, 135.2, 130.0, 129.3, 127.3, 123.4, 117.3, 113.5, 53.4, 25.2, 20.1, 19.6.

(S)-N-(1-(4-fluoro-3-methylphenyl)ethyl)aniline: Yellow liquid, 0.0664 g, 96% yield, 89% ee, \([\alpha]_D^{20} = +23.6 \text{ (c 0.56, CH}_2\text{Cl}_2); \) \(^1\text{H NMR (400 MHz, CDCl}_3, \text{ ppm}) \delta 7.19-7.04 (m, 4H), 6.91 (t, \(J = 9.0 \text{ Hz, 1H}), 6.69-6.60 (m, \text{ 1H}), 6.55-6.45 (m, \text{ 2H}), 4.40 (q, J = 6.6 \text{ Hz, 1H}), 3.96 (brs, \text{ 1H}, 2.23 (s, \text{ 3H}), 1.46 (d, \text{ J = 6.7 Hz, 3H}; \) \(^{13}\text{C NMR (100 MHz, CDCl}_3, \text{ ppm}) \delta 160.3 (d, J_{C:F} = 241.6 \text{ Hz}), 147.4, 140.8 (d, J_{C:F} = 3.4 \text{ Hz}), 129.3, 129.0 (d, J_{C:F} = 5.1 \text{ Hz}), 125.0 (d, J_{C:F} = 17.4 \text{ Hz}), 124.7 (d, J_{C:F} = 8.0 \text{ Hz}), 117.5, 115.2 (d, J_{C:F} = 22.3 \text{ Hz}), 113.5, 53.1, 25.4, 14.9 (d, J_{C:F} = 3.5 \text{ Hz}); \) \(^{19}\text{F NMR (377 MHz, CDCl}_3, \text{ ppm}) \delta -120.5; \) HRMS (ESI) calcd. for C\(_{15}\)H\(_{15}\)NF [M-H]: 228.1194, Found: 228.1187.
**(S)-N-(1-(benzo[d][1,3]dioxol-5-yl)ethyl)aniline:** Colorless liquid, 0.0659 g, 91% yield, 72% ee, $[\alpha]_D^{20} = +0.8$ (c 0.77, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.08 (t, $J = 7.8$ Hz, 2H), 6.90-6.77 (m, 2H), 6.76-6.69 (m, 1H), 6.63 (t, $J = 7.3$ Hz, 1H), 6.49 (d, $J = 7.8$ Hz, 2H), 5.93-5.82 (m, 2H), 4.37 (q, $J = 6.7$ Hz, 1H), 3.95 (br s, 1H), 1.45 (d, $J = 6.7$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 148.1, 147.4, 146.5, 139.7, 129.3, 119.0, 117.5, 113.5, 108.5, 106.4, 101.1, 53.5, 25.4; HRMS (ESI) calcd. for C$_{15}$H$_{14}$O$_2$N [M-H]: 240.1030, Found: 240.1024.

![Image of 7m](image.png)


**[(S)-N-(1-phenylpropyl)aniline]:** Colorless liquid, 0.0645 g, 99% yield, 66% ee, $[\alpha]_D^{20} = +3.3$ (c 0.95, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.38-7.24 (m, 4H), 7.23-7.15 (m, 1H), 7.06 (t, $J = 7.8$ Hz, 2H), 6.61 (t, $J = 7.3$ Hz, 1H), 6.50 (d, $J = 7.9$ Hz, 2H), 4.21 (t, $J = 6.7$ Hz, 1H), 4.03 (br s, 1H), 1.90-1.72 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 147.7, 144.1, 129.3, 128.7, 127.1, 126.7, 117.3, 113.4, 59.9, 31.8, 11.0.

![Image of 7n](image.png)


**[(S)-N-(1-(3,4-dimethylphenyl)ethyl)-4-methoxyaniline]:** Yellow liquid, 0.0618 g, 91% yield, 65% ee, $[\alpha]_D^{20} = -0.9$ (c 0.78, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$7.40-7.25 (m, 4H), 7.24-7.15 (m, 1H), 7.11-7.02 (m, 2H), 6.66-6.57 (m, 1H), 6.55-6.45(m, 2H), 4.29 (t, $J = 6.8$ Hz, 1H), 4.03 (br s, 1H), 1.85-1.66 (m, 2H), 1.50-1.28 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 147.7, 144.5, 129.3, 128.7, 127.0, 126.6, 117.3, 113.4, 58.2, 41.3, 19.7, 14.2.

**17**

(S)-4-methoxy-N-(1-phenylethyl)aniline: Colorless liquid, 0.0725 g, 99% yield, 73% ee, $[\alpha]_D^{20} = +7.5$ (c 1.01, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.39-7.23 (m, 4H), 7.23-7.13 (m, 1H), 6.72-6.62 (m, 2H), 6.50-6.39 (m,2H), 4.38 (q, $J = 6.7$ Hz, 1H), 3.73 (br s, 1H), 3.65 (s, 3H), 1.46 (d, $J = 6.7$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) $\delta$ 152.0, 145.7, 141.7, 128.7, 126.9, 126.0, 114.9, 114.7, 55.8, 54.4, 25.2.


![](image1.png)

(S)-N-(1-(4-ethylphenyl)ethyl)-4-methoxyaniline: Yellow liquid, 0.0775 g, 99% yield, 70% ee, $[\alpha]_D^{20} = -3.7$ (c 1.14, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta$ 7.26 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 7.9$ Hz, 2H), 6.72-6.65(m, 2H), 6.52-6.43 (m, 2H), 4.38 (q, $J = 5.8$ Hz, 1H), 3.72 (br s, 1H), 3.67 (s, 3H), 2.61 (q, $J = 7.6$ Hz, 2H), 1.47 (d, $J = 6.7$ Hz, 3H), 1.21 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 152.0, 142.8, 141.9, 128.2, 126.0, 114.9, 114.7, 55.9, 54.1, 28.6, 25.2, 15.7.


![](image2.png)

(S)-4-methoxy-N-(1-(4-methoxyphenyl)ethyl)aniline: Colorless liquid, 0.0770 g, 99% yield, 73% ee, $[\alpha]_D^{20} = -5.1$ (c1.01, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.31-7.21 (m, 2H), 6.90-6.79 (m, 2H), 6.76-6.61(m, 2H), 6.52-6.40 (m, 2H), 4.36 (q, $J = 6.7$ Hz, 1H), 3.75(s, 3H),
3.72 (br s, 1H), 3.67 (s, 3H), 1.45 (d, J = 6.7 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) δ 158.6, 152.0, 141.8, 137.7, 127.1, 114.9, 114.7, 114.1, 55.9, 55.4, 53.8, 25.2.


![Chemical structure](image)

(S)-N-(1-(3,4-dimethylphenyl)ethyl)-4-methoxyaniline: Yellow liquid, 0.0777 g, 99% yield, 71% ee, $[\alpha]_D^{20} = -0.9$ (c 0.78, CH$_2$Cl$_2$); $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ 7.18-7.02 (m, 3H), 6.80-6.64 (m, 2H), 6.55-6.43 (m, 2H), 4.34 (q, J = 6.6 Hz, 1H), 3.72 (br s, 1H), 3.67 (s, 3H), 2.23 (s, 3H), 2.21 (s, 3H), 1.46 (d, J = 6.7 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) δ 152.0, 143.2, 142.0, 136.9, 135.2, 130.0, 127.4, 123.4, 114.9, 114.7, 55.9, 54.2, 25.3, 20.1, 19.6.


![Chemical structure](image)

(S)-4-methyl-N-(1-phenylethyl)aniline: Colorless liquid, 0.0636 g, 99% yield, 63% ee, $[\alpha]_D^{20} = +11.7$ (c 1.14, CH$_2$Cl$_2$); $^1$H NMR (300 MHz, CDCl$_3$, ppm) δ 7.40-7.24 (m, 4H), 7.23-7.14 (m, 1H), 6.88 (d, J = 8.1 Hz, 2H), 6.48-6.36 (m, 2H), 4.43 (q, J = 6.7 Hz, 1H), 3.86 (br s, 1H), 2.17 (s, 3H), 1.47 (d, J = 6.7 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$, ppm) δ 145.6, 145.2, 129.8, 128.8, 127.0, 126.5, 126.0, 113.6, 53.8, 25.2, 20.5.


![Chemical structure](image)

(S)-N-(1-([1,1'-biphenyl]-4-yl)ethyl)-2-methoxyaniline: White solid, 0.0904 g, 99% yield, 55% ee, $[\alpha]_D^{20} = +16.8$ (c 1.20, CH$_2$Cl$_2$); IR (film): 1602, 1511, 1224, 734 cm$^{-1}$; $^1$H NMR
(400 MHz, CDCl$_3$, ppm) $\delta$7.61-7.50 (m, 4H), 7.47-7.37 (m, 4H), 7.35-7.28 (m, 1H), 6.82-6.75 (m, 1H), 6.75-6.68 (m, 1H), 6.66-6.57 (m, 1H), 6.43-6.35 (m, 1H), 4.65 (br s, 1H), 4.57-4.46 (m, 1H), 3.89 (s, 3H), 1.58 (d, $J = 6.7$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, ppm) $\delta$ 146.8, 144.8, 141.2, 139.9, 137.4, 128.9, 127.6, 127.3, 127.2, 126.5, 121.4, 116.6, 111.3, 109.5, 55.7, 53.3, 25.4; HRMS (ESI) calcd. for C$_{21}$H$_{22}$ON [M+H]$^+$: 304.1696, Found: 304.1697.

**Computational Details:** All calculations were performed with the Gaussian 09 program.$^1$ Geometry optimizations of all stationary points were performed with the M06-2X functional,$^2$ which has been proven to be suitable to describe the dispersion effects. The 6-31G(d) basis set was applied for all elements in the catalyst. Frequency calculations at the same level were performed to confirm each stationary point to be either a minimum structure. All figures of structures were prepared using CYLView.$^3$


**Coordinates of All Stationary Points**
The chromatography for the determination of enantiomeric excess

**HPLC Conditions:**
- **Column:** Chiralcel OD-H, Daicel Chemical Industries, Ltd.
- **Eluent:** Hexanes/IPA (98/2)
- **Flow rate:** 0.5 mL/min
- **Detection:** UV 254 nm

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HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., Eluent: Hexanes/IPA (99/1); Flow rate: 0.5 mL/min; Detection: UV 254 nm

Racemic

Chiral
HPLC Conditions: **Column:** Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (98/2); **Flow rate:** 1.0 mL/min; **Detection:** UV 254 nm

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**Racemic**

**Chiral**

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HPLC Conditions: **Column:** Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (98/2); **Flow rate:** 0.5 mL/min; **Detection:** UV 254 nm

**Racemic**

**Chiral**
HPLC Conditions: **Column:** Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (98/2); **Flow rate:** 0.5 mL/min; **Detection:** UV 254 nm

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<tr>
<td>2</td>
<td>14.151</td>
<td>48.839</td>
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**Chiral**

<table>
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<th>Peak</th>
<th>RT [min]</th>
<th>Area</th>
<th>Area %</th>
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<tr>
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<tr>
<td>2</td>
<td>14.226</td>
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</table>
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., Eluent: Hexanes/IPA (98/2); Flow rate: 0.6 mL/min; Detection: UV 254 nm

Racemic

Chiral

HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., Eluent: Hexanes/IPA (98/2); Flow rate: 0.5 mL/min; Detection: UV 254 nm

Racemic

Chiral
HPLC Conditions: **Column:** Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA (98/2); **Flow rate:** 0.5 mL/min; **Detection:** UV 254 nm

**Racemic**

<table>
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<td>2</td>
<td>17.707</td>
<td>49.957</td>
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**Chiral**

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<tr>
<td>2</td>
<td>17.632</td>
<td>16.604</td>
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HPLC Conditions: **Column:** Chiralcel OD-H, Daicel Chemical Industries, Ltd., **Eluent:** Hexanes/IPA(98/2); **Flow rate:** 0.5 mL/min; **Detection:** UV 254 nm

**Racemic**

<table>
<thead>
<tr>
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<th>Area %</th>
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<tbody>
<tr>
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<tr>
<td>2</td>
<td>28.781</td>
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**Chiral**

<table>
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<tr>
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<td>82.661</td>
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<tr>
<td>2</td>
<td>21.633</td>
<td>17.333</td>
<td>0.816</td>
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</table>
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., Eluent: Hexanes/IPA(98/2); Flow rate: 0.5 mL/min; Detection: UV 254 nm

**Racemic**

**Chiral**

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**HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., Eluent: Hexanes/IPA(98/2); Flow rate: 0.5 mL/min; Detection: UV 254 nm**

**Racemic**

**Chiral**
HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., Eluent: Hexanes/IPA(98/2); Flow rate: 0.5 mL/min; Detection: UV 254 nm

Racemic

Chiral

HPLC Conditions: Column: Chiralcel OD-H, Daicel Chemical Industries, Ltd., Eluent: Hexanes/IPA(98/2); Flow rate: 0.5 mL/min; Detection: UV 254 nm

Racemic

Chiral
**HPLC Conditions:**

**Column:** Chiralcel OD-H, Daicel Chemical Industries, Ltd.,

**Eluent:** Hexanes/IPA (99/1); **Flow rate:** 1.0 mL/min; **Detection:** UV 254 nm

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**Racemic**

**Chiral**

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**HPLC Conditions:**

**Column:** Chiralcel OD-H, Daicel Chemical Industries, Ltd.,

**Eluent:** Hexanes/IPA (98/2); **Flow rate:** 0.5 mL/min; **Detection:** UV 254 nm

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**Racemic**

**Chiral**