Supporting Information

Asymmetric synthesis of some chiral aryl and hetero aryl substituted β -, γ -, δ -hydroxy esters

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General procedure for the asymmetric reduction of prochiral keto esters 1a-1s by (R)-(+)-2-methyl-CBS-oxazaborolidine [(R)-Me-CBS]

To a solution (R)-Me-CBS (0.1mmol, 0.1ml of 1M solution in toluen) was added $\text{BH}_3\cdot\text{SMe}_2$ (2M in THF, 1.5mmol, 0.75ml) and mixture was stirred under a nitrogen atmosphere at room temperature, then cooled to 0°C . After 10 min of stirring, the solution of prochiral keto ester **1a-1s** (1mmol) in 5 ml of THF was added dropwise within 30 min at 0°C . The reaction mixture was stirred for 15 min and then quenched with 2M HCl. The solution was extracted with ether (3x20ml). The organic layers were washed with water and dried over anhydrous Na_2SO_4 , concentrated under reduced pressure. The residue purified by column chromatography (hexane/ EtOAc 7:3,v/v).

Spectroscopic data of chiral hydroxy esters synthesized

(S)-(-)-Ethyl-β-hydroxy-β-phenylpropionate 2a

Yield: 85 %; Colorless oil; $[\alpha]_D^{25}$: -46.4 (0.01 g cm⁻³ in CHCl₃); lit.^[23] $[\alpha]_D^{25}$: -34.5 (0.01 g cm⁻³ in CHCl₃). Spectroscopic data identical to that reported in literature.^[17,23] HPLC analysis: Chiralcel OD-H chiral column, mobile phase hexane / iso-PrOH : 90:10, flow rate: 0.7 ml / min, wavelength: 230 nm; R_t (retention time): 10.9 min for (*S*)-isomer, 13.4 min for (*R*)-isomer; 94 % ee (*S*).

(S)-(-)-Ethyl-β-hydroxy-β-(p-methoxyphenyl) propionate 2b

Yield: 85 %; Colorless oil; $[\alpha]_D^{25}$: -27.2 (0.0103 g cm⁻³ in CHCl₃); lit.^[9] $[\alpha]_D^{25}$: -29.0 (c 0.01 g cm⁻³ in CHCl₃). Spectroscopic data identical to that reported in literature.^[9,17] HPLC analysis: Chiralcel OD-H chiral column, mobile phase hexane / iso-PrOH : 95:5, flow rate: 0.7 ml / min, wavelength: 230 nm; R_t (retention time): 24.1 min for (*S*)-isomer; >99 % ee (*S*).

(S)-(-)-Methyl-γ-hydroxy-γ-phenyl butanoate 2c

Yield: 87 %; Colorless oil; Anal. Calcd. for C₁₁H₁₄O: C, 68.02; H, 7.27. Found: C, 67.97; H, 7.25; IR (neat, cm⁻¹): 3446 (OH stretching), 3030 (CH stretching of aromatic rings), 2953 (-CH₂- stretching), 1738 (C=O stretching of COOCH₃ group), 1500, 1453 (C=C- stretching of aromatic rings), 1261 (CH stretching in aliphatic plane), 1076 (C-O stretching), 769 (out of plane bending CH of aromatic ring). ¹H NMR (500 MHz, CDCl₃, δ / ppm): 1.94 (2H, q, J= 8.33 Hz, -CH-CH₂-CH₂-), 2.30 (2H, t, J=7.5 Hz, CH₂-CH₂-), 2.71 (1H, br s, OH), 3.53 (3H, s, -OCH₃), 4.59 (1H, t, J= 7.5 Hz, -CH-), 7.31-7.14 (5H, m, -CH of aromatic ring). ¹³C NMR (125 MHz, CDCl₃, δ / ppm): 174.6 (C=O), 144.4 (C of aromatic ring), 128.7, 127.8, 126.0 (-

CH of aromatic ring), 73.5(-CH-), 51.9 (-OCH₃), 34.0, 30.4 (-CH₂-). MS m/z : 51, 56, 77, 91, 107, 117, 145, 162, 176, 194(M⁺); $[\alpha]_D^{25}$: -38.4 (0.01 g cm⁻³ in CHCl₃); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 90:10, flow rate: 0.8 ml / min, wavelength: 230 nm; R_t (retention time): 36.7 min for (*R*)-isomer, 39.0 min for (*S*)-isomer; 91 % ee (*S*).

(S)-(-)-Methyl-γ-hydroxy-γ-(p-methylphenyl) butanoate 2d

Yield: 85 %; Colorless oil; Anal. Calcd. for C₁₂H₁₆O₃: C, 69.21; H, 7.74. Found: C, 69.01; H, 7.90; IR (neat, cm⁻¹): 3462 (OH stretching), 3038 (CH stretching of aromatic rings), 2968 (-CH₂- stretching), 1742 (C=O stretching of COOCH₃ group), 1533, 1449 (C=C- stretching of aromatic rings), 1263 (CH stretching in aliphatic plane), 1171 (C-O stretching), 939, 824 (out of plane bending CH of aromatic ring); ¹H NMR (500 MHz, CDCl₃, δ / ppm): 1.18 (1H, br s, OH), 2.01-1.95 (2H, m, -CH-CH₂-CH₂-), 2.26 (3H, s, -CH₃), 2.34 (2H, t, J=7.5 Hz, CH₂-CH₂-), 3.58 (3H, s, -OCH₃), 4.61 (1H, t, J= 7.5 Hz, -CH-), 7.07 (2H, d, J=10 Hz, -CH of aromatic ring), 7.13 (2H, d, J=10 Hz, -CH of aromatic ring). ¹³C NMR (125 MHz, CDCl₃, δ / ppm): 173.3 (C=O), 140.1 (C of aromatic ring), 137.3, 128.1, 124.7 (-CH of aromatic ring), 80.4 (-CH-), 50.7 (-OCH₃), 32.8, 29.2 (-CH₂-), 19.8 (-CH₃); MS m/z : 51, 56, 77, 91, 107, 117, 145, 162, 176, 194(M⁺); $[\alpha]_D^{25}$: -22.5 (0.012 g cm⁻³ in CHCl₃); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 90:10, flow rate: 0.8 ml /min, wavelength:230 nm; R_t (retention time): 19.4 min for (*R*)-isomer, 20.9 min for (*S*)-isomer; 96 % ee (*S*).

(S)-(-)-Methyl-γ-hydroxy-γ-(p-chlorophenyl) butanoate 2e

Yield: 80 %; Colorless oil; Anal. Calcd. For $C_{11}H_{13}O_3Cl$: C, 57.75; H, 5.73. Found: C, 57.00; H, 6.05; IR (neat, cm^{-1}): 3447 (OH stretching), 3099 (CH stretching of aromatic rings), 2961 ($-CH_2-$ stretching), 1734 (C=O stretching of $COOCH_3$ group), 1503, 1456 (C=C- stretching of aromatic rings), 1263 (CH stretching in aliphatic plane), 1094 (C-O stretching), 939, 831 (out of plane bending CH of aromatic ring); ^1H NMR (500 MHz, $CDCl_3$, δ / ppm): 2.09-1.89 (2H, m, $-CH-CH_2-CH_2-$), 2.58 (2H, t, $J=7.5$ Hz, CH_2-CH_2-), 2.59 (1H, br s, OH), 3.37 (3H, s, $-OCH_3$), 5.39 (1H, t, $J=7.5$ Hz, $-CH-$), 7.19 (2H, d, 10Hz, $-CH$ of aromatic ring), 7.28 (2H, d, 10Hz, $-CH$ of aromatic ring); ^{13}C NMR (125 MHz, $CDCl_3$, δ / ppm): 175.8 (C=O), 136.9 (C of aromatic ring), 133.2, 127.9, 125.7 ($-CH$ of aromatic ring), 79.5 ($-CH-$), 49.6 ($-OCH_3$), 29.9, 27.9 ($-CH_2-$); MS m/z : 43, 56, 77, 88, 113, 125, 141, 151, 161, 196, 210, 228 (M^+). $[\alpha]_D^{25}$: -35.5 (0.0135 g cm^{-3} in $CHCl_3$); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 90:10, flow rate: 0.8 ml / min, wavelength: 230 nm; R_t (retention time): 35.6 min for (*S*)-isomer; >99 % ee (*S*).

(S)-(-)-Methyl- γ -hydroxy- γ -(p-bromophenyl) butanoate 2f

Yield: 80 %; Colorless oil; Anal. Calcd. for $C_{11}H_{13}O_3Br$: C, 48.37; H, 4.80. Found: C, 47.98; H, 5.30; IR (neat, cm^{-1}): 3447 (OH stretching), 3030 (CH stretching of aromatic rings), 2953, ($-CH_2-$ stretching), 1734 (C=O stretching of $COOCH_3$ group), 1503, 1449 (C=C- stretching of aromatic rings), 1263 (CH stretching in aliphatic plane), 1078 (C-O stretching), 939, 839 (out of plane bending CH of aromatic ring); ^1H (500 MHz, $CDCl_3$, δ / ppm): 1.94 (2H, q, $J=5$ Hz, $-CH-CH_2-CH_2-$), 2.33 (2H, t, $J=10$ Hz, CH_2-CH_2-), 2.48 (1H, br s, OH), 3.58 (3H, s, $-OCH_3$), 4.62 (1H, t, $J=5$ Hz, $-CH-$), 7.14 (2H, d, $J=10$ Hz, $-CH$ of aromatic ring), 7.39 (2H, d, $J=10$ Hz, $-CH$ of aromatic ring). ^{13}C NMR (125 MHz, $CDCl_3$, δ / ppm): 173.3 (C=O), 142.1 (C of aromatic ring), 130.5, 126.5, 120.3 ($-CH$ of aromatic ring), 71.7 ($-CH-$), 50.7 (-

OCH₃), 32.8, 29.1 (-CH₂-); MS m/z : 43, 56, 77, 88, 115, 161, 185, 196, 240, 255, 273(M⁺).

$[\alpha]_D^{25}$: -28.0 (0.0107 g cm⁻³ in CHCl₃); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 90:10, flow rate: 0.8 ml / min, wavelength: 230 nm; R_t (retention time): 37.1 min for (*S*)-isomer; >99 % ee (*S*).

(S)-(-)-Methyl- γ -hydroxy- γ -(*p*-methoxyphenyl) butanoate **2g**

Yield: 75 %; Colorless oil; Anal. Calcd. for C₁₂H₁₆O₄: C, 64.27; H, 7.19. Found: C, 63.95; H, 7.79; IR (neat, cm⁻¹): 3470 (OH stretching), 3022 (CH stretching of aromatic rings), 2953 (-CH₂- stretching), 1734 (C=O stretching of COOCH₃ group), 1526, 1456 (C=C- stretching of aromatic rings), 1263 (CH stretching in aliphatic plane), 1032 (C-O stretching), 939, 847 (out of plane bending CH of aromatic ring); ¹H NMR (500 MHz, CDCl₃, δ / ppm): 1.18 (1H, br s, OH), 2.13-1.97 (2H, m, -CH-CH₂-CH₂-), 2.56 (2H, t, J=7.5 Hz, CH₂-CH₂-), 3.71 (3H, s, -OCH₃), 3.73 (3H, s, -OCH₃), 5.37 (1H, t, J= 7.5 Hz, -CH-), 6.83 (2H, d, J=10 Hz, -CH of aromatic ring), 7.18 (2H, d, J=10 Hz, -CH of aromatic ring). ¹³C NMR (125 MHz, CDCl₃, δ / ppm): 176.0 (C=O), 158.7 (C of aromatic ring), 130.2, 125.8, 113.1 (-CH of aromatic ring), 80.4 (-CH-), 54.4 (-OCH₃), 50.6 (-OCH₃), 32.8, 29.8 (-CH₂-); MS m/z : 43, 56, 77, 91, 109, 121, 137, 147, 192, 206, 224(M⁺). $[\alpha]_D^{25}$: -30.5 (0.0141 g cm⁻³ in CHCl₃); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 90:10, flow rate: 0.8 ml / min, wavelength: 230 nm; R_t (retention time): 36.7 min for (*R*)-isomer, 39.0 min for (*S*)-isomer; 91 % ee (*S*).

(S)-(-)-Methyl- δ -hydroxy- δ -phenyl pentanoate **2h**

Yield: 85 %; Colorless oil; Anal. Calcd. for C₁₂H₁₆O₃: C, 69.21; H, 7.74. Found: C, 68.87; H, 8.14; IR (neat, cm⁻¹): 3453 (OH stretching), 3023 (CH stretching of aromatic rings), 2946 (-CH₂- stretching), 1738 (C=O stretching of COOCH₃ group), 1500, 1453 (C=C- stretching of aromatic rings), 1246 (CH stretching in aliphatic plane), 1076 (C-O stretching), 769, 707 (out of plane bending CH of aromatic ring); ¹H NMR (500 MHz, CDCl₃, δ / ppm): 1.70-1.48 (4H, m, -CH-(CH₂)₂-CH₂-), 2.21-2.18 (2H, m, -(CH₂)₂-CH₂-C), 2.58 (1H, br s, OH), 3.52 (3H, s, -OCH₃), 4.53-4.50 (1H, m, -CH-), 7.24-7.13 (5H, m, -CH of aromatic ring). ¹³C NMR (125 MHz, CDCl₃, δ / ppm): 174.4 (C=O), 144.9 (C of aromatic ring), 128.7, 127.7, 126.1 (-CH of aromatic ring), 74.1 (-CH-), 51.8 (-OCH₃), 38.7, 34.0, 21.5 (-CH₂-); MS m/z : 42, 59, 74, 77, 91, 89, 107 (%100), 117, 130, 159, 176, 190, 208(M⁺). [α]_D²⁵: -31.5 (0.0104 g cm⁻³ in CHCl₃); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 95:5, flow rate: 1ml / min, wavelength: 230 nm; R_t (retention time): 33.4 min for (*S*)-isomer, 36.6 min for (*R*)-isomer; 95 % ee (*S*).

(S)-(-)-Methyl-δ-hydroxy-δ-(p-methylphenyl) pentanoate 2j

Yield: 90 %; Colorless oil; Anal. Calcd. for C₁₃H₁₈O₃: C, 70.24; H, 8.16. Found: C, 69.74; H, 8.96; IR (neat, cm⁻¹): 3454 (OH stretching), 3038 (CH stretching of aromatic rings), 2961 (-CH₂- stretching), 1734 (C=O stretching of COOCH₃ group), 1526, 1456 (C=C- stretching of aromatic rings), 1256 (CH stretching in aliphatic plane), 1078 (C-O stretching), 916, 831 (out of plane bending CH of aromatic ring); ¹H NMR (500 MHz, CDCl₃, δ / ppm): 1.79-1.61 (4H, m, -CH-(CH₂)₂-CH₂-), 2.23 (1H, br s, OH), 2.25 (3H, s, -CH₃), 2.27 (2H, t, J=7.5Hz, -CH₂-CH₂-C-), 3.55 (3H, s, -OCH₃), 4.53 (1H, t, J=7.5Hz, -CH-), 7.05 (2H, d, J=5Hz, -CH of aromatic ring), 7.11 (2H, d, J=10Hz, -CH of aromatic ring). ¹³C NMR (125 MHz, CDCl₃, δ / ppm): 173.0 (C=O), 140.6 (C of aromatic ring), 137.0, 128.2, 124.8 (-CH of aromatic ring),

72.8 (-CH-), 50.5 (-OCH₃), 37.2, 32.7, 20.2 (-CH₂-), 17.7 (-CH₃); MS m/z : 42, 59, 74, 77, 91, 89, 107 (%100), 117, 130, 159, 176, 190, 208(M⁺); $[\alpha]_D^{25}$: -29.9 (0.0102 g cm⁻³ in CHCl₃); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 95:5, flow rate: 0.8ml / min, wavelength: 230 nm; R_t (retention time): 46.0 min for (S)-isomer; >99 % ee (S).

(S)-(-)-Methyl-δ-hydroxy-δ-(p-chlorophenyl) pentanoate 2k

Yield: 85 %; Light yellow oil; Anal. Calcd. for C₁₂H₁₅O₃Cl: C, 59.39; H, 6.23. Found: C, 58.99; H, 7.01; IR (neat, cm⁻¹): 3454 (OH stretching), 3038 (CH stretching of aromatic rings), 2953 (-CH₂- stretching), 1734 (C=O stretching of COOCH₃ group), 1503, 1456 (C=C-stretching of aromatic rings), 1263 (CH stretching in aliphatic plane), 1094 (C-O stretching), 847, 762 (out of plane bending CH of aromatic ring); ¹H (500 MHz, CDCl₃, δ / ppm): 1.66-1.48 (4H, m, -CH-(CH₂)₂-CH₂-), 2.22 (2H, t, , J= 5.0 Hz, -CH₂-CH₂-C-), 2.81 (1H, br s, OH), 3.54 (3H, s, -OCH₃), 4.52 (1H, t, J= 5.0 Hz, -CH-), 7.15 (2H, d, J=10Hz, -CH of aromatic ring), 7.19 (2H, d, J=10Hz, -CH of aromatic ring). ¹³C NMR (125 MHz, CDCl₃, δ / ppm): 174.4 (C=O), 143.4 (C of aromatic ring), 133.0, 128.7, 127.6 (-CH of aromatic ring), 73.4 (-CH-), 51.6 (-OCH₃), 38.5, 34.0, 20.9 (-CH₂-); MS m/z : 42, 51, 77, 102, 113, 141, 151, 164, 193, 210, 224, 242(M⁺); $[\alpha]_D^{25}$: -26.6 (0.0105 g cm⁻³ in CHCl₃); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 95:5, flow rate: 0.8ml / min, wavelength: 230 nm; R_t (retention time): 49.2 min for (S)-isomer; >99 % ee (S).

(S)-(-)-Methyl-δ-hydroxy-δ-(p-bromophenyl) pentanoate 2l

Yield: 85 %; Colorless oil; Anal. Calcd. for C₁₂H₁₅O₃Br: C, 50.19; H, 5.27. Found: C, 49.79; H, 5.97; IR (neat, cm⁻¹): 3454 (OH stretching), 3038 (CH stretching of aromatic rings), 2961 (-CH₂- stretching), 1734 (C=O stretching of COOCH₃ group), 1503, 1456 (C=C- stretching of aromatic rings), 1256 (CH stretching in aliphatic plane), 1078 (C-O stretching), 839, 747 (out of plane bending CH of aromatic ring); ¹H NMR (500 MHz, CDCl₃, δ / ppm): 1.69-1.49 (4H, m, -CH-(CH₂)₂-CH₂-), 2.23 (2H, t, J= 5.0 Hz, -CH₂-CH₂-C-), 2.57 (1H, br s, OH), 3.56 (3H, s, -OCH₃), 4.52 (1H, t, J= 5.0 Hz, -CH-), 7.12 (2H, d, J=10.0 Hz, -CH of aromatic ring), 7.37 (2H, d, J= 5.0 Hz, -CH of aromatic ring). ¹³C NMR (125 MHz, CDCl₃, δ / ppm): 173.1 (C=O), 142.6 (C of aromatic ring), 130.4, 126.6, 120.1 (-CH of aromatic ring), 72.2 (-CH-), 50.5 (-OCH₃), 37.2, 32.5, 19.9 (-CH₂-); . MS m/z : 42, 51, 77, 102, 129, 157, 185, 195, 254, 268, 287(M⁺); [α]_D²⁵: -21.5 (0.0088 g cm⁻³ in CHCl₃); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane/iso-PrOH:95:5, flow rate:0.8ml/min, wavelength:230 nm; R_t (retention time):52.4 min for (S)-isomer;>99 % ee (S).

(S)-(-)-Methyl-δ-hydroxy-δ-(p-methoxyphenyl) pentanoate 2m

Yield: 80 %; Light yellow oil; Anal. Calcd. for C₁₃H₁₈O₄: C, 65.53; H, 7.61. Found: C, 64.93; H, 8.31; IR (neat, cm⁻¹): 3470 (OH stretching), 3015 (CH stretching of aromatic rings), 2961 (-CH₂- stretching), 1734 (C=O stretching of COOCH₃ group), 1526, 1456 (C=C- stretching of aromatic rings), 1256 (CH stretching in aliphatic plane), 1040 (C-O stretching), 847, 747 (out of plane bending CH of aromatic ring); ¹H NMR (500 MHz, CDCl₃, δ / ppm): 1.72-1.46 (4H, m, -CH-(CH₂)₂-CH₂-), 2.22 (2H, t, J= 10.0 Hz, -CH₂-CH₂-C-), 2.46 (1H br s, OH), 3.55 (3H, s, -OCH₃), 3.69 (3H, s, -OCH₃), 4.50 (1H, t, J= 7.5 Hz, -CH-), 6.78 (2H d, J=10.0 Hz, -CH of aromatic ring), 7.16 (2H d, J= 10.0 Hz, -CH of aromatic ring). ¹³C NMR (125 MHz, CDCl₃, δ / ppm): 174.3 (C=O), 159.1 (C of aromatic ring), 136.8, 127.4, 114.1 (-CH of

aromatic ring), 73.8 (-CH-), 55.5(-OCH₃), 51.8 (-OCH₃), 38.5, 34.0, 21.5 (-CH₂-); MS m/z : 41, 55, 77, 91, 109, 115, 121, 137, 147, 160, 189, 207, 220, 238(M⁺); $[\alpha]_D^{25}$: -24.8 (0.0131 g cm⁻³ in CHCl₃); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 95:5, flow rate: 0.8ml / min, wavelength: 230 nm; R_t (retention time): 57.7 min for (S)-isomer, 65.0 min for (R)-isomer, 94 % ee (S).

(S)-(-)-Methyl-γ-hydroxy-γ-(2-furanyl) butanoate 2n

Yield: 80 %; Yellow oil, Anal; Calcd. for C₉H₁₂O₄: C, 58.69; H, 6.57. Found: C, 58.00; H, 7.07; IR (neat, cm⁻¹): 3462 (OH stretching), 3138 (CH stretching of aromatic rings), 2953 (-CH₂- stretching), 1780 (C=O stretching of COOCH₃ group), 1510, 1456 (C=C- stretching of aromatic rings), 1248 (CH stretching in aliphatic plane), 1071 (C-O stretching), 824, 754 (out of plane bending CH of aromatic ring); ¹H NMR (500 MHz, CDCl₃, δ / ppm): 1.18 (1H, br s, OH), 2.34-2.11 (m, 2H, -CH-CH₂-CH₂-), 2.46 (2H, t, J=7.5 Hz, -CH₂-CH₂-C), 3.60 (3H, s, -OCH₃), 5.43 (1H, t, J= 7.5 Hz, -CH-), 6.25-6.35 (2H, m, -CH of aromatic ring), 7.25-7.38 (1H, m, -CH of aromatic ring). ¹³C NMR (125 MHz, CDCl₃, δ / ppm): 175.6 (C=O), 149.9 (C of aromatic ring), 142.5 (-CH of aromatic ring), 109.5 (-CH of aromatic ring), 108.3 (-CH of aromatic ring), 73.4 (-CH-), 50.7 (-OCH₃), 27.6, 25.5 (-CH₂-); MS m/z : 41, 55, 69, 79, 97, 107, 124, 152, 166, 184(M⁺); $[\alpha]_D^{25}$: -11.6 (0.0099 g cm⁻³ in CHCl₃); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 90:10, flow rate: 1 ml / min, wavelength: 230 nm; R_t (retention time): 16.0 min for (R)-isomer, 16.7 min for (S)-isomer; 83 % ee (S).

(S)-(-)-Methyl-γ-hydroxy-γ-(2-thienyl) butanoate 2p

Yield: 85 %; Yellow oil; Anal. Calcd. for C₉H₁₂O₃S: C, 53.98; H, 6.04; S, 16.01. Found: C, 53.18; H, 6.94; S, 15.85; IR (neat, cm⁻¹): 3377 (OH stretching), 3115 (CH stretching of aromatic rings), 2953 (-CH₂- stretching), 1780 (C=O stretching of COOCH₃ group), 1549, 1456 (C=C- stretching of aromatic rings), 1186 (CH stretching in aliphatic plane), 1032 (C-O stretching), 855, 716 (out of plane bending CH of aromatic ring); ¹H NMR (500 MHz, CDCl₃, δ / ppm): 1.18 (1H, br s, OH), 2.15-1.95 (2H, m, -CH-CH₂-CH₂-), 2.60 (2H, t, J=5 Hz, -CH₂-CH₂-C), 3.58 (3H, s, -OCH₃), 5.65 (1H, t, J= 5 Hz, -CH-), 6.93 (1H, t, J=5Hz, -CH of aromatic ring), 7.12-7.01 (1H, m, -CH of aromatic ring), 7.27-7.15 (1H, m, -CH of aromatic ring); ¹³C NMR (125 MHz, CDCl₃, δ / ppm): 175.2 (C=O), 140.7 (C of aromatic ring), 126.0 (-CH of aromatic ring), 125.2 (-CH of aromatic ring), 124.9 (-CH of aromatic ring), 76.3 (-CH-), 55.5 (-OCH₃), 29.8, 28.0 (-CH₂-); MS m/z : 45, 56, 69, 79, 85, 97, 113, 123, 126, 151, 168, 182, 200(M⁺). $[\alpha]_D^{25}$: -15.7 (0.0105 g cm⁻³ in CHCl₃); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 90:10, flow rate: 1 ml / min, wavelength: 230 nm; R_t (retention time): 37.0 min for (*S*)-isomer, 42.0 min for (*R*)-isomer; 81 % ee (*S*).

(S)-(-)-Methyl-δ-hydroxy-δ-(2-furanyl) pentanoate 2r

Yield: 80 %; Light yellow oil; Anal. Calcd. for C₁₀H₁₄O₄: C, 60.59; H, 7.12. Found: C, 59.89; H, 7.92; IR (neat, cm⁻¹): 3462 (OH stretching), 3138 (CH stretching of aromatic rings), 2953 (-CH₂- stretching), 1742 (C=O stretching of COOCH₃ group), 1456, 1387 (C=C- stretching of aromatic rings), 1256 (CH stretching in aliphatic plane), 1078 (C-O stretching), 932, 754 (out of plane bending CH of aromatic ring); ¹H NMR (500 MHz, CDCl₃, δ / ppm): 1.18 (1H, br s, OH), 1.74-1.56 (m, 4H, -CH-(CH₂)₂-CH₂-), 2.28 (2H, t, J=7.5 Hz, -CH₂-CH₂-C), 3.59 (3H, s, -OCH₃), 4.60 (t, 1H, J= 7.5 Hz, -CH-), 6.26-6.15 (m, 2H, -CH of aromatic ring),

7.34-7.22 (m, 1H, -CH of aromatic ring); ^{13}C NMR (125 MHz, CDCl_3 , δ / ppm): 173.2 (C=O), 155.6 (C of aromatic ring), 140.8 (-CH of aromatic ring), 109.0 (-CH of aromatic ring), 105.1 (-CH of aromatic ring), 66.3 (-CH-), 50.4 (-OCH₃), 33.8, 32.6, 19.8 (-CH₂-); MS m/z : 41, 55, 69, 79, 97 , 107, 120, 166, 180, 198(M⁺). $[\alpha]_D^{25}$: -9.2 (0.0146 g cm⁻³ in CHCl_3); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 90:10, flow rate: 1 ml / min, wavelength: 230 nm; R_t (retention time): 16.4 min for (*S*)-isomer, 17.2 min for (*R*)-isomer; 90 % ee (*S*).

(S)-(-)-Methyl- δ -hydroxy- δ -(2-thienyl) pentanoate 2s

Yield: 85 %; Yellow oil; Anal. Calcd. for C₁₀H₁₄O₃S: C, 56.05; H, 6.59; S, 14.96. Found: C, 55.75; H, 7.19; S, 14.06; IR (neat, cm⁻¹): 3462 (OH stretching), 3115 (CH stretching of aromatic rings), 2953 (-CH₂- stretching), 1742 (C=O stretching of COOCH₃ group), 1456, 1387 (C=C- stretching of aromatic rings), 1256 (CH stretching in aliphatic plane), 1078 (C-O stretching), 847, 716 (out of plane bending CH of aromatic ring); ^1H NMR (500 MHz, CDCl_3 , δ / ppm): 1.80-1.59 (4H, m, -CH-(CH₂)₂-CH₂-), 2.25 (2H, t, J=5 Hz, -CH₂-CH₂-C), 2.95 (1H, br s, OH), 3.56 (3H, s, -OCH₃), 4.80 (1H, t, J= 5 Hz, -CH-), 6.86-6.85 (2H, m, -CH of aromatic ring), 7.14-7.12 (1H, m, -CH of aromatic ring). ^{13}C NMR (125 MHz, CDCl_3 , δ / ppm): 173.3 (C=O), 147.7 (C of aromatic ring), 125.6 (-CH of aromatic ring), 123.4 (-CH of aromatic ring), 122.6 (-CH of aromatic ring), 68.6 (-CH-), 50.7 (-OCH₃), 37.4, 32.7, 20.1 (-CH₂-); MS m/z : 45, 59, 79, 85, 97 , 113, 123, 136, 182, 196, 214(M⁺). $[\alpha]_D^{25}$: -11.0 (0.0132 g cm⁻³ in CHCl_3); HPLC analysis: Chiralcel OJ-H chiral column, mobile phase hexane / iso-PrOH : 90:10, flow rate: 1 ml / min, wavelength: 230 nm; R_t (retention time): 21.4 min for (*S*)-isomer, 23.4 min for (*R*)-isomer; 96 % ee (*S*).

Spectral Data

Figure S1. HPLC chromatogram of compound racemic **2a**

Figure S2. HPLC chromatogram of compound chiral **2a**

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	23.167	50210657	1278111	40.164	50.563	0.000
2	23.886	74803721	1248000	59.836	49.437	0.221
Total		125014378	2527780	100.000	100.000	

Figure S3. HPLC chromatogram of compound racemic **2b**

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	24.160	76391667	1295058	100.000	100.000	0.000
Total		76391667	1295058	100.000	100.000	

Figure S4. HPLC chromatogram of compound chiral **2b**

Figure S5. ^1H -NMR spectra of compound chiral **2c** (500 MHz, CDCl_3)

Figure S6. ^{13}C -NMR spectra of compound chiral **2c** (125 MHz, CDCl_3)

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	35.628	43590048	790980	49.644	53.192	0.000
2	39.360	44215355	696050	50.356	46.808	2.284
Total		87805403	1487030	100.000	100.000	

Figure S7. HPLC chromatogram of compound racemic **2c**

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	36.793	4324617	116562	4.325	9.902	0.000
2	39.093	95664068	1051465	95.675	90.098	1.349
Total		99988684	1167017	100.000	100.000	

Figure S8. HPLC chromatogram of compound chiral **2c**

Figure S9. ^1H -NMR spectra of compound chiral **2d** (500 MHz, CDCl_3)

Figure S10. ^{13}C -NMR spectra of compound chiral **2d** (125 MHz, CDCl_3)

<Results>

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	18.733	1706658	70212	50.840	52.039	0.000
2	20.716	1650255	64711	49.160	47.961	2.866
Total		3356913	134923	100.000	100.000	

Figure S11. HPLC chromatogram of compound racemic **2d**

<Results>

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	19.433	61846	3325	2.006	3.433	0.000
2	20.972	3021239	93531	97.994	96.567	2.146
Total		3083084	96857	100.000	100.000	

Figure S12. HPLC chromatogram of compound chiral **2d**

Figure S13. ^1H -NMR spectra of compound chiral **2e** (500 MHz, CDCl_3)

Figure S14. ^{13}C -NMR spectra of compound chiral **2e** (125 MHz, CDCl_3)

<Results>

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	32.153	8464694	207130	50.324	52.060	0.000
2	34.969	8355781	190738	49.676	47.940	2.443
Total		16820475	397868	100.000	100.000	

Figure S15. HPLC chromatogram of compound racemic **2e**

<Results>

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	35.671	4034513	101388	100.000	100.000	0.000
Total		4034513	101388	100.000	100.000	

Figure S16. HPLC chromatogram of compound chiral **2e**

Figure S17. ^1H -NMR spectra of compound chiral **2f** (500 MHz, CDCl_3)

Figure S18. ^{13}C -NMR spectra of compound chiral **2f** (125 MHz, CDCl_3)

Figure S19. HPLC chromatogram of compound racemic **2f**

Figure S20. HPLC chromatogram of compound chiral **2f**

Figure S21. ^1H -NMR spectra of compound chiral **2g** (500 MHz, CDCl_3)

Figure S22. ^{13}C -NMR spectra of compound chiral **2g** (125 MHz, CDCl_3)

Figure S23. HPLC chromatogram of compound racemic **2g**

Figure S24. HPLC chromatogram of compound chiral **2g**

Figure S25. ^1H -NMR spectra of compound chiral **2h** (500 MHz, CDCl_3)

Figure S26. ^{13}C -NMR spectra of compound chiral **2h** (125 MHz, CDCl_3)

Figure S27. HPLC chromatogram of compound racemic **2h**

Figure S28. HPLC chromatogram of compound chiral **2h**

Figure S29. ^1H -NMR spectra of compound chiral **2j** (500 MHz, CDCl_3)

Figure S30. ^{13}C -NMR spectra of compound chiral **2j** (125 MHz, CDCl_3)

Figure S31. HPLC chromatogram of compound racemic **2j**

Figure S32. HPLC chromatogram of compound chiral **2j**

Figure S33. ^1H -NMR spectra of compound chiral **2k** (500 MHz, CDCl_3)

Figure S34. ^{13}C -NMR spectra of compound chiral **2k** (125 MHz, CDCl_3)

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	49.330	4729223	84315	49.999	51.016	0.000
2	51.545	4729360	80956	50.001	48.984	1.448
Total		9458583	165271	100.000	100.000	

Figure S35. HPLC chromatogram of compound racemic **2k**

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	49.261	16332405	238088	100.000	100.000	0.000
Total		16332405	238088	100.000	100.000	

Figure S36. HPLC chromatogram of compound chiral **2k**

Figure S37. ^1H -NMR spectra of compound chiral **2I** (500 MHz, CDCl_3)

Figure S38. ^{13}C -NMR spectra of compound chiral **2I** (125 MHz, CDCl_3)

<Results>

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	51.624	20430728	296200	49.651	52.867	0.000
2	55.332	20718358	264072	50.349	47.133	1.828
Total		41149085	560272	100.000	100.000	

Figure S39. HPLC chromatogram of compound racemic **21**

<Results>

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	52.462	9893476	154097	100.000	100.000	0.000
Total		9893476	154097	100.000	100.000	

Figure S40. HPLC chromatogram of compound chiral **21**

Figure S41. ^1H -NMR spectra of compound chiral **2m** (500 MHz, CDCl_3)

Figure S42. ^{13}C -NMR spectra of compound chiral **2m** (125 MHz, CDCl_3)

<Results>

PDA Ch1 224nm 4nm

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	66.563	2651019	36807	49.756	51.510	0.000
2	67.906	2677071	34649	50.244	48.490	0.217
Total		5328091	71456	100.000	100.000	

Figure S43. HPLC chromatogram of compound racemic **2m**

<Results>

PDA Ch1 230nm 4nm

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	57.707	72359525	631143	97.064	95.706	0.000
2	65.061	2188851	28320	2.936	4.294	3.025
Total		74547176	659463	100.000	100.000	

Figure S44. HPLC chromatogram of compound chiral **2m**

Figure S45. ^1H -NMR spectra of compound chiral **2n** (500 MHz, CDCl_3)

Figure S46. ^{13}C -NMR spectra of compound chiral **2n** (125 MHz, CDCl_3)

Figure S47. HPLC chromatogram of compound racemic **2n**

Figure S48. HPLC chromatogram of compound chiral **2n**

Figure S49. ^1H -NMR spectra of compound chiral **2p** (500 MHz, CDCl_3)

Figure S50. ^{13}C -NMR spectra of compound chiral **2p** (125 MHz, CDCl_3)

<Results>

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	36.839	11361297	280623	50.692	53.917	0.000
2	41.585	11051005	239848	49.308	46.083	4.097
Total		22412302	520471	100.000	100.000	

Figure S51. HPLC chromatogram of compound racemic **2p**

<Results>

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	37.073	10829866	264166	90.570	91.049	0.000
2	42.097	1127647	25970	9.430	8.951	4.441
Total		11957513	290137	100.000	100.000	

Figure S52. HPLC chromatogram of compound chiral **2p**

Figure S53. ^1H -NMR spectra of compound chiral **2r** (500 MHz, CDCl_3)

Figure S54. ^{13}C -NMR spectra of compound chiral **2r** (125 MHz, CDCl_3)

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	16.424	8143691	414097	40.230	53.351	0.000
2	17.039	8398567	362074	50.770	46.649	1.055
Total		16542258	776171	100.000	100.000	

Figure S55. HPLC chromatogram of compound racemic **2r**

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	16.482	7090596	348095	95.200	95.027	0.000
2	17.204	357502	18216	4.800	4.973	1.244
Total		7448098	366311	100.000	100.000	

Figure S56. HPLC chromatogram of compound chiral **2r**

Figure S57. ^1H -NMR spectra of compound chiral **2s** (500 MHz, CDCl_3)

Figure S58. ^{13}C -NMR spectra of compound chiral **2s** (125 MHz, CDCl_3)

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	21.699	21074821	804879	50.051	52.624	0.000
2	23.269	21031888	724436	49.949	47.376	2.255
Total		42106709	1529114	100.000	100.000	

Figure S59. HPLC chromatogram of compound racemic **2s**

Peak #	Ret. Time	Area	Height	Area %	Height %	Resolution
1	21.410	47491197	1591163	97.964	97.540	0.000
2	23.471	987039	40134	2.036	2.460	2.769
Total		48478236	1631297	100.000	100.000	

Figure S60. HPLC chromatogram of compound chiral **2s**