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Supporting Information

A One-Pot Process for the Enantioselective Synthesis of Tetrahydroquinolines and Tetrahydroisoquinolines *via* Asymmetric Reductive Amination (ARA)

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1. General information

Unless otherwise mentioned, all experiments were carried out under an atmosphere of argon in a glovebox or using standard Schlenk techniques. Solvents were dried with standard procedures and degassed with N₂. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 300-400 mesh). NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz for ¹H NMR, 101 MHz for ¹³C NMR or a Bruker DPX 500 spectrometer at 500 MHz for ¹H NMR, 126 MHz for ¹³C NMR. Chemical shifts (δ) are reported in ppm and respectively referenced to internal standard Me₄Si and solvent signals (Me₄Si, 0 ppm for ¹H NMR in CDCl₃; 77.0 ppm in CDCl₃ for ¹³C NMR). HPLC and UPLC analysis was carried out on Angilent 1200 Series instrument using chiral columns.

2. General procedure for the preparation of substrates



Step 1:

S1 (10 mmol) and Et_3N (11 mmol) were dissolved in dichloromethane (30 mL) at 0 °C, followed by addition of $(Boc)_2O$ (12 mmol) and DMAP (0.5 mmol). The resulting solution was warmed to rt and stirred for 6 h. The reaction was quenched with saturated NH₄Cl aqueous solution (20 mL). The organic layer was extracted with dichloromethane (10 mL×2), combined, dried over anhydrous NaSO₄, and then concentrated under reduced pressure. The crude product was further purified by column chromatography to quantitatively provide pure **S2**. Step 2:

 R^2MgBr (1.3 equiv) was added dropwise to a solution of **S2** (3 mmol) in dried THF (10 mL) at -65 °C. The resulting mixture was then stirred overnight. After warming up to rt, the reaction was quenched with saturated NH₄Cl aqueous solution (15 mL) and extracted with EtOAc (10 mL×2). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography to give **1**.



tert-butyl (2-(3-oxobutyl)phenyl)carbamate (1a)¹: an oil, 500 mg, 63% yield ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, J = 5.9 Hz, 1H), 7.60 (s, 1H), 7.20 (m, 1H), 7.16-7.09 (m, 1H), 7.09-7.01 (m, 1H), 2.85 (m, 4H), 2.33-2.02 (m, 3H), 1.56 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 209.2, 153.8, 136.0, 131.9,

129.4, 126.9, 124.2, 123.2, 80.0, 44.6, 29.9, 28.4, 24.0 ppm.

tert-butyl (2-(3-oxopentyl)phenyl)carbamate (1b): an oil, 465 mg, 56% yield



¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.50 (s, 1H), 7.23-7.18 (m, 1H), 7.12 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.04 (td, *J* = 7.5, 1.2 Hz, 1H), 2.84 (m, 4H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.56 (s, 9H), 1.05 (t, *J* = 7.3 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 211.8, 153.8, 136.0, 132.0, 129.3, 126.9, 124.2, 123.3, 80.0, 43.1,

36.0, 28.4, 27.9, 24.1 ppm. HRMS Calculated for $C_{16}H_{24}NO_3$ [M+H]⁺ 278.1751; found 278.1741. *tert*-butyl (2-(3-oxohexyl)phenyl)carbamate (1c): an oil, 611 mg, 70% yield



¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, J = 7.7 Hz, 1H), 7.49 (s, 1H),

7.24-7.16 (m, 1H), 7.11 (dd, J = 7.6, 1.5 Hz, 1H), 7.04 (td, J = 7.5, 1.1 Hz, 1H), 2.91-2.72 (m, 4H), 2.37 (t, J = 7.4 Hz, 2H), 1.60 (dt, J = 7.4, 7.4 Hz, 2H), 1.56 (s, 9H), 0.88 (t, J = 7.4 Hz, 3 H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 211.4, 153.8, 136.0, 131.9, 129.3, 126.9, 124.2, 123.7, 80.0, 44.8, 43.5, 28.4, 24.1, 17.3, 13.6 ppm. HRMS Calculated for C₁₇H₂₆NO₃ [M+H]⁺292.1907; found 292.1896.

tert-butyl (2-(3-oxoheptyl)phenyl)carbamate (1d): an oil, 530 mg, 58% yield



¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, J = 7.6 Hz, 1H), 7.50 (s, 1H), 7.20 (t, J = 7.7 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 2.83 (s, 4H), 2.39 (t, J = 7.5 Hz, 2H), 1.56 (s, 9H), 1.54-1.49 (m, 2H), 1.34-1.20 (m, 2H), 0.89 (t, J = 7.5 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 211.6, 153.8, 136.0, 131.9, 129.3, 126.9, 124.2, 123.3, 80.0, 43.4, 42.7, 28.4, 25.9,

24.1, 22.2, 13.8 ppm. HRMS Calculated for $C_{18}H_{28}O_3N$ [M+H]⁺ 306.2064; found 306.2053.

tert-butyl (2-(3-oxooctyl)phenyl)carbamate (1e): an oil, 440 mg, 46% yield



¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, J = 7.7 Hz, 1H), 7.50 (s, 1H), 7.25-7.17 (m, 1H), 7.11 (dd, J = 7.6, 1.6 Hz, 1H), 7.04 (td, J = 7.5, 1.2 Hz, 1H), 2.83 (m, 4H), 2..38 (t, J = 7.6 Hz, 2H), 1.60-1.51 (m, 11H), 1.30 (m, 2H), 1.26-1.17 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H). ¹³C{¹H}

NMR (126 MHz, CDCl₃) δ 211.6, 153.8, 136.0, 131.9, 129.3, 126.9, 124.2, 123.3, 80.0, 43.4, 42.9, 31.3, 28.4, 24.1, 23.5, 22.4, 13.9 ppm. HRMS Calculated for C₁₉H₃₀O₃N [M+H]⁺ 320.2220; found 320.2210.

tert-butyl (2-(3-oxononyl)phenyl)carbamate (1f): an oil, 660 mg, 66% yield



¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, J = 7.6 Hz, 1H), 7.51 (s, 1H), 7.23 - 7.15 (m, 1H), 7.11 (dd, J = 7.6, 1.5 Hz, 1H), 7.04 (td, J = 7.5, 1.2 Hz, 1H), 2.83 (t, J = 3.7 Hz, 4H), 2.38 (t, J = 7.5 Hz, 2H), 1.56 (m, 11H), 1.35 - 1.11 (m,6 H), 0.88 (t, J = 7.0 Hz, 3H). ¹³C{¹H} NMR

 $(126 \text{ MHz}, \text{CDCl}_3) \delta 211.6, 153.8, 136.0, 132.0, 129.3, 126.9, 124.2, 123.3, 80.0, 43.4, 43.0, 31.5, 28.8, 28.4, 24.1, 23.8, 22.4, 14.0 ppm. HRMS Calculated for C₂₀H₃₂O₃N [M+H]⁺ 334.2377; found 334.2365.$ *tert*-butyl (2-(3-oxodecyl)phenyl)carbamate (1g): an oil, 560 mg, 54% yield



¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.50 (s, 1H), 7.23-7.16 (m, 1H), 7.11 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.04 (td, *J* = 7.5, 1.2 Hz, 1H), 2.83 (m, 4H), 2.38 (t, *J* = 7.5 Hz, 2H), 1.56 (m, 11H), 1.33 - 1.16 (m, 8H), 0.89 (t, *J* = 7.0 Hz, 3H). ¹³C{¹H} NMR

(126 MHz, CDCl₃) δ 211.6, 153.8, 136.0, 131.9 , 129.3, 126.9, 124.2, 123.3, 80.0, 43.4, 43.0, 31.6, 29.0, 29.0, 28.4, 24.1, 23.9, 22.5, 14.0 ppm. HRMS Calculated for C₂₁H₃₄O₃N [M+H]⁺ 348.2533; found 348.2522.

tert-butyl (2-(3-oxo-4-phenylbutyl)phenyl)carbamate (1h): a white solid, 750 mg, 74% yield



¹H NMR (500 MHz, CDCl₃) δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.38-7.22 (m, 4H), 7.22-7.15 (m, 1H), 7.15-7.10 (m, 2H), 7.06-6.96 (m, 2H), 3.65 (s, 2H), 2.83 (m, 2H), 2.79 (m, 2H), 1.52 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 208.7, 153.8, 135.9, 133.8, 131.7, 130.6, 129.3, 128.4, 127.1, 126.9, 124.2,

123.3, 80.1, 50.2, 42.7, 28.4, 24.2 ppm. HRMS Calculated for $C_{21}H_{26}O_3N$ [M+H]⁺ 340.1907; found 340.1896.

tert-butyl (5-methoxy-2-(3-oxobutyl)phenyl)carbamate (1i): an oil, 550 mg, 63% yield



¹H NMR (500 MHz, CDCl₃) δ 7.64 (s, 1H), 7.42 (s, 1H), 6.99 (d, J = 8.5 Hz, 1H), 6.60 (dd, J = 8.5, 2.7 Hz, 1H), 3.80 (s, 3H), 2.83 (t, J = 6.4 Hz,

2H), 2.76 (t, J = 6.4 Hz, 2H), 2.15 (s, 3H), 1.56 (s, 9H). ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 209.4, 158.5, 153.5, 137.0, 130.0, 123.1, 110.5, 107.2, 80.1, 55.3, 44.8, 30.0, 28.4, 23.3 ppm. HRMS Calculated for $C_{16}H_{24}O_4N \ [M+H]^+ 294.1700$; found 294.1692.

tert-butyl (2-methoxy-6-(3-oxobutyl)phenyl)carbamate (1j): an oil, 410 mg, 47% yield



¹H NMR (500 MHz, CDCl₃) δ 7.49 (s, 1H), 7.25 (s, 1H), 6.75 (dd, J = 8.8, 3.0 Hz, 1H), 6.67 (d, J = 2.9 Hz, 1H), 3.78 (s, 3H), 2.85 (m, 2H), 2.83-2.78 (m, 2H), 2.15 (s, 3H), 1.54 (s, 9H). ${}^{13}C{}^{1}H{}$ NMR (126 MHz, CDCl₃) δ 208.9, 156.7, 154.4, 134.9, 128.9, 125.9, 114.8, 111.8, 79.8, 55.4, 44.5, 30.0, 28.4, 24.4 ppm. HRMS Calculated for C₁₆H₂₄O₄N [M+H]⁺ 294.1700; found 294.1692.

tert-butyl (4-methyl-2-(3-oxobutyl)phenyl)carbamate (1k): an oil, 420 mg, 58% yield



¹H NMR (500 MHz, CDCl₃) δ 7.61-7.50 (m, 1H), 7.41 (s, 1H), 7.01 (dd, J = 8.2, 1.6 Hz, 1H), 6.92 (d, J = 1.5 Hz, 1H), 2.87-2.84 (m, 2H), 2.82-2.77 (m, 2H), 2.29 (s, 3H), 2.15 (s, 3H), 1.55 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) & 209.1, 154.0, 133.8, 133.3, 132.1, 130.0, 127.6, 123.6, 79.9, 44.6,

30.0, 28.4, 24.1, 20.8 ppm. HRMS Calculated for C₁₆H₂₄O₃N [M+H]⁺ 278.1751; found 278.1741. tert-butyl (5-(4-bromobutoxy)-2-(3-oxobutyl)phenyl)carbamate (11): an oil, 530 mg, 63% yield



¹H NMR (500 MHz, CDCl₃) δ 7.63 (s, 1H), 7.40 (s, 1H), 6.96 (d, J = 8.5 Hz, 1H), 6.56 (dd, J = 8.4, 2.6 Hz, 1H), 3.97 (t, J = 6.0Hz, 2H), 3.47 (t, J = 6.7 Hz, 2H), 2.81 (t, J = 6.4 Hz, 2H), 2.74 (t, J = 6.5 Hz, 2H), 2.13 (s, 3H), 2.05 (dt, J = 14.5, 6.7 Hz, 2H),

1.97-1.85 (m, 2H), 1.54 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 209.4, 157.8, 153.5, 137.0, 130.1, 123.1, 110.6, 107.9, 80.1, 66.8, 44.8, 33.6, 30.0, 29.5, 28.4, 27.9, 23.3 ppm. HRMS Calculated for C₁₉H₂₉O₄NBr [M+H]⁺414.1274; found 414.1260.

tert-butyl (2-fluoro-6-(3-oxobutyl)phenyl)carbamate (1m): an oil, 530 mg, 63% yield



¹H NMR (500 MHz, CDCl₃) δ 7.12 (m, 1H), 7.02-6.85 (m, 2H), 6.70 (s, 1H), 2.88 (dd, J = 10.5, 3.8 Hz, 2H), 2.81 (dd, J = 10.5, 3.8 Hz, 2H), 2.12 (s, 3H), 1.50 (s, 9H). ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 208.5, 158.24 (d, J = 248.4 Hz), 154.0, 140.0, 127.79 (d, J = 22.7 Hz), 127.47 (d, J = 8.7 Hz), 124.60 (d, J = 3.3

Hz), 113.86 (d, J = 20.9 Hz), 80.4, 44.3, 29.9, 28.2, 24.68 (d, J = 2.5 Hz) ppm. HRMS Calculated for C₁₅H₂₁O₃NF [M+H]⁺ 282.1500; found 282.1491.

tert-butyl (4-bromo-2-(3-oxobutyl)phenyl)carbamate (1n): a white solid, 798 mg, 78% yield



¹H NMR (500 MHz, CDCl₃) δ 7.74 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.30 (dd, J = 8.7, 2.4 Hz, 1H), 7.23 (d, J = 2.3 Hz, 1H), 2.88 (t, J = 6.2 Hz, 2H), 2.79 (t, J = 6.2 Hz, 2H), 2.17 (s, 3H), 1.55 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 209.0, 153.6, 135.3, 133.8, 132.1, 129.9, 124.7, 116.6, 80.3, 44.4, 29.9, 28.3,

23.7 ppm. HRMS Calculated for C₁₅H₂₁O₃NBr [M+H]⁺ 342.0699; found 342.0688. tert-butyl (2-(3-oxo-3-phenylpropyl)phenyl)carbamate (10)²: an oil, 690 mg, 71% yield



¹H NMR (500 MHz, CDCl₃) δ 7.99 (dd, J = 8.2, 1.1 Hz, 2H), 7.75 (d, J = 7.3Hz, 1H), 7.65-7.56 (m, 2H), 7.47 (t, J = 7.7 Hz, 2H), 7.25-7.16 (m, 2H), 7.07 (m, 1H), 3.41 (t, J = 6.7 Hz, 2H), 3.04 (t, J = 6.7 Hz, 2H), 1.56 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 199.9, 153.8, 136.5, 136.1, 133.4, 132.0,

129.5, 128.6, 128.1, 127.0, 124.2, 123.3, 80.1, 39.6, 28.4, 24.4 ppm.

tert-butyl (2-(3-(4-fluorophenyl)-3-oxopropyl)phenyl)carbamate (1p)²: a white solid, 500 mg, 49% yield



¹H NMR (500 MHz, CDCl₃) δ 8.09-7.91 (m, 2H), 7.73 (d, J = 7.6 Hz, 1H), 7.57 (s, 1H), 7.21 (m, 2H), 7.14 (t, J = 8.6 Hz, 2H), 7.06 (td, J = 7.6, 1.2 Hz, 1H), 3.37 (t, J = 6.7 Hz, 2H), 3.03 (t, J = 6.7 Hz, 2H), 1.56 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 198.3, 165.9 (d, J = 255.3 Hz), 153.8,

136.0, 132.9 (d, *J* = 3.1 Hz), 132.0, 130.8 (d, *J* = 9.4 Hz), 129.5, 127.0, 124.3, 123.4, 115.7 (d, *J* = 21.9 Hz), 80.1, 39.5, 28.4, 24.4 ppm.

tert-butyl (2-(3-(4-fluorophenyl)-3-oxopropyl)-6-methoxyphenyl)carbamate (1q): a white solid, 650 mg, 58% yield



¹H NMR (500 MHz, CDCl₃) δ 7.98 (dd, J = 8.8, 5.4 Hz, 2H), 7.47 (s, 1H), 7.18 (s, 1H), 7.11 (t, J = 8.6 Hz, 2H), 6.82 - 6.69 (m, 2H), 3.76 (s, 3H), 3.33 (t, J = 6.8 Hz, 2H), 2.98 (t, J = 6.8 Hz, 2H), 1.51 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 198.1, 165.8 (d, J = 255.2 Hz), 156.8, 154.4, 133.0 (d,

J = 3.0 Hz), 130.7 (d, J = 9.3 Hz), 128.9, 127.7, 126.2, 115.7 (d, J = 21.9 Hz), 115.0, 111.8, 79.9, 55.4, 39.5, 28.4, 24.9 ppm. HRMS Calculated for C₂₁H₂₅O₄NF [M+H]⁺ 374.1762; found 374.1751.

tert-butyl (4-bromo-2-(3-(4-fluorophenyl)-3-oxopropyl)phenyl)carbamate (1r): a white solid, 860 mg, 68% yield



¹H NMR (500 MHz, CDCl₃) δ 8.07-7.95 (m, 2H), 7.73 (s, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.30-7.28 (m, 2H), 7.13 (t, J = 8.6 Hz, 2H), 3.36 (t, J = 6.5 Hz, 2H), 2.97 (t, J = 6.5 Hz, 2H), 1.54 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 198.0, 166.0 (d, J = 255.8 Hz), 153.6, 135.4,

134.0, 132.7 (d, J = 3.0 Hz), 132.2, 130.8 (d, J = 9.4 Hz), 129.9, 124.8, 116.8, 115.8 (d, J = 21.9 Hz), 80.4, 39.4, 28.4, 24.0 ppm. HRMS Calculated for C₂₀H₂₂BrFNO₃ [M+H]⁺ 422.0761; found 422.0746.



S3 were synthesized according to a known procedure³.

Step 1:

S3 (10 mmol) and Et_3N (11 mmol) were dissolved in dichloromethane (30 mL) at 0 °C, followed by addition of $(Boc)_2O$ (12 mmol) and DMAP (0.5 mmol). The resulting solution was warmed to rt and stirred for 6 h. The reaction was quenched with saturated NH₄Cl aqueous solution (20 mL). The organic layer was extracted with dichloromethane (10 mL×2), combined, dried over anhydrous NaSO₄, and then concentrated under reduced pressure. The crude product was further purified by column chromatography to quantitatively provide pure **S4**. Step 2:

 R^2MgBr (1.3 equiv) was added dropwise to a solution of **S4** (3 mmol) in dried THF (10 mL) at 0 °C. The resulting mixture was then stirred overnight at rt. The reaction was quenched with saturated NH₄Cl aqueous solution (15 mL) and extracted with EtOAc (10 mL×2). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography to give **3**.

tert-butyl (2-benzoylphenethyl)carbamate (3a)4: a white solid, 575 mg, 59% yield

¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, J = 7.4 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H),



7.48 (t, J = 7.5 Hz, 3H), 7.41 (d, J = 7.5 Hz, 1H), 7.32 (dd, J = 10.8, 6.9 Hz, 2H), 5.03 (s, 1H), 3.40 (m, 2H), 2.88 (t, J = 6.8 Hz, 2H), 1.42 (s, 9H). ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 198.5, 155.9, 138.6, 138.5, 137.6, 133.3, 130.9, 130.6, 130.4, 129.0, 128.4, 125.7, 79.0, 42.1, 33.1, 28.4 ppm.

tert-butyl (2-(4-methylbenzoyl)phenethyl)carbamate (3b)4: an oil, 488 mg, 48% yield



¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, J = 8.2 Hz, 2H), 7.51-7.43 (m, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.34-7.24 (m, 4H), 5.06 (s, 1H), 3.39 (m, 2H), 2.85 (t, J = 6.8 Hz, 2H), 2.44 (s, 3H), 1.41 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 198.2, 156.0, 144.3, 138.8, 138.3, 135.0, 130.8, 130.5, 130.4, 129.2, 128.8,

125.6, 78.9, 42.1, 33.0, 28.4, 21.7 ppm.

tert-butyl (2-(3-methylbenzoyl)phenethyl)carbamate (3c)4: an oil, 478 mg, 47% yield



¹H NMR (500 MHz, CDCl₃) δ 7.66 (s, 1H), 7.57 (d, J = 7.6 Hz, 1H), 7.47 (td, J = 7.6, 1.8 Hz, 1H), 7.42 (m, 2H), 7.36 (d, J = 7.6 Hz, 1H), 7.32 (m, 2H), 5.05 (s, 1H), 3.48-3.31 (m, 2H), 2.87 (t, J = 6.8 Hz, 2H), 2.42 (s, 3H), 1.42 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 198.7, 156.0, 138.7, 138.5, 138.3, 137.6,

134.2, 130.8, 130.6, 130.5, 129.0, 128.3, 127.8, 125.6, 78.9, 42.1, 33.1, 28.4, 21.3 ppm.

tert-butyl (2-(4-fluorobenzoyl)phenethyl)carbamate (3d)4: an oil, 576 mg, 56% yield



¹H NMR (400 MHz, CDCl₃) δ 7.90 - 7.81 (m, 2H), 7.53-7.45 (m, 1H), 7.41 (d, J = 7.7 Hz, 1H), 7.34-7.30 (m, 1H), 7.15 (t, J = 8.6 Hz, 2H), 5.00 (s, 1H), 3.40 (q, J = 6.6 Hz, 2H), 2.86 (t, J = 6.9 Hz, 2H), 1.42 (s, 9H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 196.8, 165.9 (d, J = 255.8 Hz), 155.9, 138.5, 138.2, 134.0 (d,

J = 2.9 Hz), 133.0 (d, *J* = 9.4 Hz), 130.9, 130.7, 128.8, 125.7, 115.6 (d, *J* = 22.0 Hz), 79.0, 42.1, 33.1, 28.4 ppm.

tert-butyl (2-(3-fluorobenzoyl)phenethyl)carbamate (3e)4: an oil, 545 mg, 53% yield



¹H NMR (500 MHz, CDCl₃) δ 7.55 (m, 2H), 7.51-7.39 (m, 3H), 7.31 (m, 3H), 4.99 (s, 1H), 3.40 (m, 2H), 2.88 (t, *J* = 6.8 Hz, 2H), 1.41 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 197.0, 162.6 (d, *J* = 248.4 Hz), 155.9, 139.8 (d, *J* = 6.2 Hz), 138.8, 137.8), 131.1, 131.0 (d, *J* = 11.5 Hz), 130.1 (d, *J* = 7.6 Hz), 129.1,

126.3 (d, J = 2.9 Hz), 125.8, 120.3 (d, J = 21.5 Hz), 116.8 (d, J = 22.3 Hz), 79.0, 42.1, 33.2, 28.3 ppm. *tert*-butyl (2-(4-chlorobenzoyl)phenethyl)carbamate (3f)⁴: an oil, 594 mg, 55% yield



¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, J = 8.5 Hz, 2H), 7.52-7.43 (m, 3H), 7.41 (d, J = 7.4 Hz, 1H), 7.30 (d, J = 4.0 Hz, 2H), 5.00 (s, 1H), 3.39 (m, 2H), 2.86 (t, J = 6.8 Hz, 2H), 1.41 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 197.1, 155.9, 139.9, 138.7, 138.0, 136.0, 131.7, 131.0, 130.9, 128.9, 128.8,

125.8, 79.0, 42.1, 33.2, 28.4 ppm.

tert-butyl (2-benzoyl-4-fluorophenethyl)carbamate (3g): an oil, 370 mg, 54% yield



¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, J = 7.3 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 7.40-7.31 (m, 1H), 7.16 (td, J = 8.4, 2.7 Hz, 1H), 7.01 (dd, J = 8.7, 2.7 Hz, 1H), 4.93 (s, 1 H), 3.35 (dd, J = 12.5, 6.3 Hz, 2H), 2.81 (t, J = 6.8 Hz, 2H), 1.40 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ

197.0, 160.4 (d, J = 247.4 Hz), 155.9, 140.0 (d, J = 5.9 Hz), 136.9, 134.1 (d, J = 2.6 Hz), 133.7, 132.6 (d, J = 7.6 Hz), 130.3, 128.6, 117.5 (d, J = 20.9 Hz), 115.6 (d, J = 22.6 Hz), 79.1, 42.0, 32.5, 28.3 ppm. HRMS Calculated for C₂₀H₂₃O₃NF [M+H]⁺ 344.1657; found 344.1646.

tert-butyl (2-benzoyl-6-chlorophenethyl)carbamate (3h): an oil, 396 mg, 55% yield

¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, J = 7.2 Hz, 2H), 7.65-7.56 (m, 1H), 7.53



(dd, J = 7.8, 1.2 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.24 (t, J = 7.7 Hz, 1H), 7.19 (dd, J = 7.6, 1.3 Hz, 1H), 5.07 (s, 1H), 3.42 (d, J = 6.1 Hz, 2H), 2.98 (t, J = 6.7 Hz, 2H), 1.38 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 197.4, 155.9, 140.9, 137.1, 136.1, 135.8, 133.7, 131.6, 130.4, 128.6, 127.0, 126.9, 78.9, 40.0, 30.8, 28.3 ppm. HRMS Calculated for C₂₀H₂₃O₃NCl [M+H]⁺ 360.1361; found 360.1348.

tert-butyl (2-benzoyl-4-bromophenethyl)carbamate (3i): an oil, 363 mg, 45% yield



¹H NMR (500 MHz, CDCl₃) δ 7.82-7.77 (m, 2H), 7.66-7.61 (m, 1H), 7.58 (dd, J = 8.3, 2.1 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.43 (d, J = 2.1 Hz, 1H), 7.27 (d, J = 6.4 Hz, 1H), 4.90 (s, 1H), 3.35 (dd, J = 12.5, 6.2 Hz, 2H), 2.79 (t, J = 6.8 Hz, 2H), 1.40 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 196.7,

155.9, 140.4, 137.3, 136.8, 133.7, 133.4, 132.5, 131.3, 130.3, 128.6, 119.5, 79.1, 41.8, 32.7, 28.3 ppm. HRMS Calculated for $C_{20}H_{23}O_3NBr$ [M+H]⁺ 404.0856; found 404.0842.

tert-butyl (2-(4-chlorobenzoyl)-4-fluorophenethyl)carbamate (3j): an oil, 430 mg, 47% yield



¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.42-7.34 (m, 1H), 7.19 (td, *J* = 8.3, 2.7 Hz, 1H), 7.01 (dd, *J* = 8.6, 2.7 Hz, 1H), 4.89 (s, 1H), 3.35 (dd, *J* = 12.5, 6.3 Hz, 2H), 2.81 (t, *J* = 6.8 Hz, 2H), 1.41 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 195.7, 160.4 (d, *J* = 4.5 Hz, 2H), 4.5 (dd, *J* = 4.5 Hz, 4.5 (dd, *J* = 4.5

247.6 Hz), 155.9, 140.4, 139.5 (d, J = 6.3 Hz), 135.2, 134.2 (d, J = 3.8 Hz), 132.7 (d, J = 7.6 Hz), 131.6, 129.0, 117.8 (d, J = 20.9 Hz), 115.5 (d, J = 22.6 Hz), 79.1, 42.0, 32.5, 28.3 ppm. HRMS Calculated for C₂₀H₂₂O₃NClF [M+H]⁺ 378.1267; found 378.1253.

tert-butyl (2-chloro-6-(4-chlorobenzoyl)phenethyl)carbamate (3k): an oil, 413 mg, 53% yield



¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, J = 8.5 H, 2H), 7.55 (dd, J = 8.0, 1.1 Hz, 1H), 7.46 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 9.3 Hz, 1H), 7.19 (dd, J = 7.6, 1.2 Hz, 1H), 5.02 (s, 1H), 3.43 (dd, J = 12.1, 5.9 Hz, 2H), 2.99 (t, J = 6.7 Hz, 2H), 1.40 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 196.1, 155.8, 140.4,

140.4, 136.3, 135.9, 135.4, 131.8, 131.8, 128.9, 127.0, 126.9, 78.9, 40.0, 30.8, 28.3 ppm. HRMS Calculated for $C_{20}H_{22}O_3NCl_2$ [M+H]⁺ 394.0971; found 394.0957.

tert-butyl (4-bromo-2-(4-chlorobenzoyl)phenethyl)carbamate (31): an oil, 360 mg, 41% yield



¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, J = 8.5 Hz, 2H), 7.58 (dd, J = 8.3, 2.1 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 2.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 4.87 (s, 1H), 3.34 (dd, J = 12.4, 6.2 Hz, 2H), 2.78 (t, J = 6.8 Hz, 2H), 1.40 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 195.5, 155.9,

140.4, 139.9, 137.5, 135.2, 133.7, 132.7, 131.7, 131.2, 129.0, 119.6, 79.2, 41.8, 32.8, 28.3 ppm. HRMS Calculated for $C_{20}H_{22}O_3NBrCl$ [M+H]⁺ 438.0466; found 438.0453.

3. General procedure for one-pot N-Boc deprotection and asymmetric reductive amination

Part 1: Asymmetric reductive amination for synthesizing tetrahydroquinolines



To a 2.5 mL vial was added the catalyst precursor $[Ir(COD)Cl]_2$ (3.4 mg, 0.005 mmol), ZhaoPhos (9.5 mg, 0.011 mmol) and anhydrous CH₂Cl₂ (0.3 mL) under argon atmosphere. The

mixture was stirred for 0.5 h at room temperature to give a clear solution.

A mixture of substrate 1 (0.2 mmol) and HCl (2 M in Et₂O) (4 equiv.) was dissolved in CH₂Cl₂ (1 mL) and then stirred at rt for 6 h. All volatiles were removed, and the crude intermediate was transferred to a nitrogen-filled glovebox. An aliquot of the above *in situ* prepared catalyst solution (60 μ L, 0.001mmol) was transferred to a vial containing crude intermediate via a syringe, followed by addition of 0.8 mL more DCM. The vial was placed in an autoclave which was then charged with 30 atm of H₂. The reaction was stirred at 25 °C for 24 h. After carefully releasing the hydrogen, the solution was neutralized with aqueous sodium bicarbonate solution (5 mL), and then extracted with DCM (5 mL×2). The combined organic phases were concentrated and passed through a short column of silica gel with EtOAc/Petroleum ether (1/20) as eluents to give the chiral tetrahydroquinoline products. The obtained products were pure enough for NMR analysis and determination of the enantiomeric excess.

(S)-2-methyl-1,2,3,4-tetrahydroquinoline (2a)⁵:



an oil, 28.5 mg, 97% yield, 97% ee; $[\alpha]^{20}_{D}$ = -76.5 (*c* 0.15, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 6.95 (t, *J* = 6.7 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 8.2 Hz, 1H), 3.58-3.24 (m, 2H), 2.86-2.80 (m, 1H), 2.75-2.61 (m, 1H), 1.94-1.89 (m, 1H),

1.65-1.47 (m, 1H), 1.20 (d, J = 6.3 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 144.8, 129.3, 126.7, 121.1, 117.0, 114.0, 47.2, 30.1, 26.6, 22.6 ppm. Enantiomeric excess was determined by HPLC (OJ-H column, hexane/*i*PrOH 95/5, 0.80 mL/min, 254 nm): t₁ = 14.1 min (major), t₂ = 15.6 min (minor).

(S)-2-ethyl-1,2,3,4-tetrahydroquinoline (2b)⁵:



an oil, 30.6 mg, 95% yield; 97% ee; $[\alpha]^{20}_{D}$ = -68.9 (*c* 0.21, CHCl₃);¹H NMR (500 MHz, CDCl₃) δ 6.95 (t, *J* = 7.5 Hz, 2H), 6.59 (t, *J* = 7.6Hz, 1H), 6.47 (d, *J* = 7.7 Hz, 1H), 3.71 (brs, 1 H), 3.23 -3.11 (m, 1H), 2.84-2.77 (m, 1H), 2.72 (m, 1H), 2.01-1.92 (m, 1H), 1.64-1.55 (m, 1H), 1.55-1.48 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H).

 $^{13}C{^{1}H}$ NMR (126 MHz, CDCl₃) δ 144.7, 129.2, 126.7, 121.4, 116.9, 114.0, 53.0, 29.4, 27.6, 26.4, 10.1 ppm. Enantiomeric excess was determined by HPLC (OJ-H column, hexane/*i*PrOH 95/5, 0.80 mL/min, 254 nm): t₁ = 12.0 min (major), t₂ = 13.1 min (minor).

(S)-2-propyl-1,2,3,4-tetrahydroquinoline (2c)⁵:



an oil, 33.2 mg, 95% yield; 96% ee; $[\alpha]^{20}_{D} = -77.5$ (*c* 0.18, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.01 (t, *J* = 7.4 Hz, 2H), 6.76- 6.60 (m, 1H), 6.52 (d, *J* = 7.7 Hz, 1H), 3.78 (s, 1H), 3.30 (m, 1H), 2.86 (m 1H), 2.78 (dt, *J* = 16.3, 4.7 Hz,

1H), 2.11-1.92 (m, 1H), 1.65 (m 1H), 1.59 -1.42 (m, 4H), 1.02 (t, J = 7.0 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 144.7, 129.3, 126.7, 121.4, 116.9, 114.0, 51.3, 38.9, 28.1, 26.4, 18.9, 14.2 ppm. Enantiomeric excess was determined by HPLC (OJ-H column, hexane/*i*PrOH 95/5, 0.80 mL/min, 254 nm): t₁ = 10.8 min (major), t₂ = 13.3 min (minor).

(S)-2-butyl-1,2,3,4-tetrahydroquinoline (2d)⁵:



an oil, 36.6 mg, 97% yield; 97% ee; $[\alpha]^{20}_{D} = -70.4$ (*c* 0.15, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.01 (t, *J* = 7.5 Hz, 2H), 6.65 (t, *J* = 7.4, 1 H), 6.53 (d, *J* = 7.8 Hz, 1H), 3.81 (s, 1H), 3.37-3.23 (m, 1H), 2.87 (m 1H), 2.78

(m 1H), 2.11-1.95 (m, 1 H), 1.65 (m, 1H), 1.55 (m, 2H), 1.50-1.35 (m, 4H), 1.00 (t, J = 7.6, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 144.7, 129.3, 126.7, 121.4, 116.9, 114.0, 51.6, 36.4, 28.1, 27.9, 26.4, 22.9, 14.1 ppm. Enantiomeric excess was determined by HPLC (OJ-H column, hexane/*i*PrOH 95/5, 0.80 mL/min, 254 nm): t₁ = 9.3 min (major), t₂ = 10.8 min (minor).

(S)-2-pentyl-1,2,3,4-tetrahydroquinoline (2e)⁵:



an oil, 38.6 mg, 95% yield; 97% ee; $[\alpha]^{20}_{D}$ = -67.9 (*c* 0.12, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.01 (t, *J* = 7.5 Hz, 2H), 6.65 (td, *J* = 7.4, 0.9 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 3.80 (s, 1H), 3.36-3.23 (m, 1H), 2.86 (m,

1H), 2.78 (dt, J = 16.3, 4.7 Hz, 1H), 2.15-1.91 (m, 1H), 1.65 (m, 1H), 1.59-1.49 (m, 2H), 1.49-1.31 (m, 6H), 0.96 (t, J = 6.9 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 144.6, 129.2, 126.6, 121.3, 116.8, 113.9, 51.5, 36.6, 31.9, 28.0, 26.4, 25.3, 22.6, 14.0 ppm. Enantiomeric excess was determined by HPLC (OJ-H column, hexane/*i*PrOH 95/5, 0.80 mL/min, 254 nm): t₁ = 8.5 min (major), t₂ = 9.2 min (minor).

(S)-2-hexyl-1,2,3,4-tetrahydroquinoline (2f)⁵:



an oil, 41.6 mg, 96% yield; 94% ee; $[\alpha]^{20}_{D} = -78.3$ (*c* 0.14, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.02 (t, *J* = 7.5 Hz, 2H), 6.66 (td, *J* = 7.4, 0.9 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 3.82 (s, 1H), 3.38-3.22 (m, 1H),

2.87 (m, 1H), 2.79 (dt, J = 16.3, 4.7 Hz, 1H), 2.12-1.95 (m, 1H), 1.66 (m, 1H), 1.60-1.49 (m, 2H), 1.49-1.27 (m, 8H), 0.97 (t, J = 6.8 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 144.7, 129.3, 126.7, 121.4, 116.9, 114.0, 51.6, 36.7, 31.9, 29.5, 28.1, 26.5, 25.7, 22.7, 14.1 ppm. Enantiomeric excess was determined by HPLC (OJ-H column, hexane/*i*PrOH 95/5, 0.80 mL/min, 254 nm): t₁ = 8.8 min (major), t₂ = 9.5 min (minor).

(S)-2-heptyl-1,2,3,4-tetrahydroquinoline (2g):



an oil, 43.9 mg, 95% yield; 92% ee; $[\alpha]^{20}_{D}$ = -68.2 (*c* 0.21, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.00 (t, *J* = 7.5 Hz, 2H), 6.64 (t, *J* = 7.1 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 3.80 (s, 1H), 3.37-3.20 (m, 1H),

2.85 (m, 1H), 2.77 (dt, J = 16.3, 4.7 Hz, 1H), 2.12-1.82 (m, 1H), 1.76-1.58 (m, 1H), 1.58-1.49 (m, 2H), 1.49-1.27 (m, 10H), 0.94 (t, J = 6.9 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 144.7, 129.2, 126.7, 121.4, 116.9, 114.0, 51.6, 36.7, 31.8, 29.7, 29.3, 28.1, 26.4, 25.7, 22.7, 14.1 ppm. Enantiomeric excess was determined by HPLC (OJ-H column, hexane/*i*PrOH 95/5, 0.80 mL/min, 254 nm): t₁ = 9.3 min (major), t₂ = 9.9 min (minor). HRMS Calculated for C₁₆H₂₆N [M+H]⁺ 232.2060; found 232.2052

(*R*)-2-benzyl-1,2,3,4-tetrahydroquinoline (2h)⁶:



an oil, 43.8 mg, 94% yield; 97% ee; $[\alpha]^{20}_{D}$ = -79.9 (*c* 0.21, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.33 (dd, *J* = 10.2, 4.5 Hz, 2H), 7.29-7.20 (m, 3H), 6.93 (dd, *J* = 13.3, 7.0 Hz, 2H), 6.59 (td, *J* = 7.4, 1.0 Hz, 1H), 6.38 (d, *J* = 4.5Hz,

1H), 3.73 (s, 1H), 3.67-3.42 (m, 1H), 2.89-2.72 (m, 2H), 2.69 (dd, J = 13.3, 8.7 Hz, 1H), 2.03-1.98 (m, 1H), 1.75-1.68 (m, 1H). ${}^{13}C{}^{1}H{}$ NMR (126 MHz, CDCl₃) δ 144.4, 138.5, 129.3, 129.2 128.6, 126.7, 126.5, 121.3, 117.2, 114.2, 52.7, 43.0, 28.3, 26.2 ppm. Enantiomeric excess was determined by HPLC (OD-H column, hexane/*i*PrOH 85/15, 0.80 mL/min, 254 nm): t₁ = 6.4 min (minor), t₂ = 7.1 min (major).

(S)-7-methoxy-2-methyl-1,2,3,4-tetrahydroquinoline (2i):



an oil, 33.2 mg, 94% yield; 96% ee; $[\alpha]^{20}_{D}$ = -69.6 (*c* 0.17, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 6.89 (d, *J* = 8.2 Hz, 1H), 6.24 (dd, *J* = 8.2, 2.5 Hz, 1 H), 6.08 (d, *J* = 2.5 Hz, 1H), 3.76 (s, 4 H), 3.41 (m, 1H), 2.92-2.76 (m, 1H),

2.76-2.67 (m, 1H), 1.95 (m, 1H), 1.60 (m, 1H), 1.24 (d, J = 6.3 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 158.8, 145.6, 129.9, 113.7, 102.9, 99.2, 55.1, 47.1, 30.4, 25.9, 22.6 ppm. Enantiomeric excess was determined by HPLC (AD-3 column, hexane/*i*PrOH 95/5, 0.50 mL/min, 254 nm): t₁ =

12.2 min (minor), $t_2 = 13.5$ min (major). HRMS Calculated for $C_{11}H_{16}ON [M+H]^+ 178.1226$; found 178.1221.

(S)-8-methoxy-2-methyl-1,2,3,4-tetrahydroquinoline (2j)⁷:



an oil, 33.9 mg, 96% yield; 95% ee; $[\alpha]^{20}_{D}$ = -63.5 (*c* 0.16, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 6.62 (m, 2H), 6.48 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 3.43-3.30 (m, 1H), 2.91-2.84 (m, 1H), 2.76-2.71 (m, 1H), 1.97-1.91 (m, 1H), 1.73-1.53 (m, 1H), 1.23 (d, *J* = 6.3 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 151.8, 138.9, 122.5,

115.3, 114.6, 112.8, 55.8, 47.5, 30.3, 26.9, 22.5 ppm. Enantiomeric excess was determined by HPLC (OJ-H column, hexane/*i*PrOH 95/5, 0.80 mL/min, 254 nm): $t_1 = 25.4$ min (major), $t_2 = 30.1$ min (minor).

(S)-2,6-dimethyl-1,2,3,4-tetrahydroquinoline (2k)⁵:



an oil, 31.2 mg, 97% yield; 95% ee; $[\alpha]^{20}_{D}$ = -68.4 (*c* 0.15, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 6.81 (m, 2H), 6.44 (d, *J* = 7.7 Hz, 1H), 3.42-3.36 (m, 1H), 2.88-2.79 (m, 1H), 2.75-2.70 (m, 1H), 2.23 (s, 3H), 1.97-1.92 (m, 1H), 1.65-1.60 (m, 1H), 1.23 (d, *J* = 6.3 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃)

δ 142.4, 129.8, 127.2, 126.3, 121.2, 114.3, 47.3, 30.3, 26.6, 22.6, 20.4 ppm. Enantiomeric excess was determined by HPLC (OJ-H column, hexane/*i*PrOH 95/5, 0.80 mL/min, 254 nm): t₁ = 19.8 min (major), t₂ = 24.4 min (minor).

(S)-7-(4-bromobutoxy)-2-methyl-1,2,3,4-tetrahydroquinoline (2l):



an oil, 51.2 mg, 86% yield; 97% ee; $[\alpha]^{20}_{D}$ = -79.3 (*c* 0.16, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.87 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.21 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.05 (d, *J* = 2.5 Hz, 1H), 3.94 (t, *J* = 6.1

Hz, 2H), 3.50 (t, J = 6.7 Hz, 2H), 3.45 - 3.32 (m, 1H), 2.78 (m, 1H), 2.69 (m, 1H), 2.07 (m, 2H), 1.98 -1.84 (m, 2H), 1.58 (m, 1H), 1.22 (d, J = 6.3 Hz, 3H). ${}^{13}C{}^{1}H$ NMR (101 MHz, CDCl₃) δ 158.0, 145.5, 129.8, 113.8, 103.4, 99.8, 66.6, 47.1, 33.6, 30.3, 29.5, 27.9, 25.8, 22.5 ppm. Enantiomeric excess was determined by UPLC (OJ-3 column, hexane/*i*PrOH 65/35, 0.50 mL/min, 254 nm): t₁ = 7.1 min (major), t₂ = 8.8 min (minor). HRMS Calculated for C₁₄H₂₁ONBr [M+H]⁺298.0801; found 298.0793.

(S)-8-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (2m):



an oil, 31.0 mg, 94% yield; 98% ee; $[\alpha]^{20}_{D}$ = -67.9 (*c* 0.14, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 6.87 - 6.70 (m, 2H), 6.53 (td, *J* = 7.8, 5.4 Hz, 1H), 3.91 (s, 1H), 3.47-3.41 (m, 1H), 2.90-2.84 (m, 1H), 2.81-2.76 (m, 1H), 2.06 -1.94 (m, 1H), 1.74-1.60 (m, 1H), 1.29 (dd, *J* = 10.9, 6.3 Hz, 3H). ¹³C{¹H} NMR (126 MHz, 126 MHz, 126 MHz, 136).

CDCl₃) δ 150.7 (d, J = 237.3 Hz), 133.2 (d, J = 12.2 Hz), 124.2 (d, J = 2.8 Hz), 123.3 (d, J = 3.8 Hz), 115.6 (d, J = 7.4 Hz), 112.1 (d, J = 18.3 Hz), 46.6, 29.7, 26.2 (d, J = 2.9 Hz), 22.4 ppm. Enantiomeric excess was determined by HPLC (OJ-H column, hexane/*i*PrOH 95/5, 0.80 mL/min, 254 nm): t₁ = 6.2 min (major), t₂ = 6.6 min (minor). HRMS Calculated for C₁₀H₁₃ NF [M+H]⁺ 166.1027; found 166.1021.

(S)-6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline (2n)⁵:



an oil, 43.3 mg, 96% yield; 95% ee; $[\alpha]^{20}_{D}$ = -78.1 (*c* 0.18, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.07-7.04 (m, 1H), 7.01 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.32 (d, *J* = 8.4 Hz, 1H), 3.67 (s, 1H), 3.42-3.29 (m, 1H), 2.81-2.75 (m, 1H), 2.71-2.61

(m, 1H), 1.92-1.87 (m, 1H), 1.59-1.46 (m, 1H), 1.19 (d, J = 6.3 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 143.8, 131.6, 129.3, 123.1, 115.4, 108.2, 47.1, 29.6, 26.4, 22.5 ppm. Enantiomeric excess

was determined by HPLC (OJ-H column, hexane/*i*PrOH 95/5, 0.80 mL/min, 254 nm): $t_1 = 14.9$ min (major), $t_2 = 17.7$ min (minor).

(*R*)-2-phenyl-1,2,3,4-tetrahydroquinoline (20)⁵:



an oil, 35.5 mg, 85% yield; 80% ee; $[\alpha]^{20}_{D}$ = +23.8 (*c* 0.25, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 1H), 7.06 (t, *J* = 7.7 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 4.49 (dd, *J* = 9.4, 3.2 Hz, 1H), 4.10 (s, 1H), 3.01-2.94 (m, 1H),

2.81-2.76 (m, 1H), 2.20-2.15 (m, 1H), 2.12-1.94 (m, 1H). ${}^{13}C{}^{1}H$ NMR (126 MHz, CDCl₃) δ 144.8, 144.7, 129.3, 128.6, 127.4, 126.9, 126.5, 120.9, 117.2, 114.0, 56.2, 31.0, 26.4 ppm. Enantiomeric excess was determined by HPLC (OD-H column, hexane/*i*PrOH 85/15, 0.80 mL/min, 250 nm): t₁ = 8.9 min (minor), t₂ = 10.8 min (major).

(*R*)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline (2p)⁵:



an oil, 39.0 mg, 86% yield; 84% ee; $[\alpha]^{20}_{D} = +25.2$ (*c* 0.16, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.34 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.01 (dd, *J* = 16.9, 8.3 Hz, 4H), 6.65 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 4.41 (dd, *J* = 9.4, 3.1 Hz, 1H), 3.99 (s, 1H), 2.94-2.88 (m, 1H), 2.74-2.69 (m, 1H),

2.11-2.05 (m, 1H), 2.02 -1.77 (m, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 162.1 (d, J = 245.2 Hz), 144.5, 140.5 (d, J = 3.0 Hz), 129.3, 128.1 (d, J = 7.9 Hz), 126.9, 120.8, 117.3, 115.3 (d, J = 21.2 Hz), 114.0, 55.6, 31.1, 26.3 ppm. Enantiomeric excess was determined by HPLC (OD-H column, hexane/*i*PrOH 85/15, 0.80 mL/min, 250 nm): t₁ = 8.4 min (minor), t₂ = 12.2 min (major).

(*R*)-2-(4-fluorophenyl)-8-methoxy-1,2,3,4-tetrahydroquinoline (2q):



an oil, 45.2 mg, 88% yield; 85% ee; $[\alpha]^{20}_{D} = +21.6$ (*c* 0.18, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.41- 7.30 (m, 2H), 7.02 (t, *J* =8.6 Hz, 2H), 6.68 - 6.55 (m, 1H), 6.50 (d, *J* = 8.5 Hz, 2H), 4.34 (dd, *J* = 9.7, 2.9 Hz, 1H), 3.74 (s, 4H), 2.96-2.89 (m, 1H), 2.71 (dt, *J* = 16.6, 4.6 Hz, 1H), 2.26-2.02 (m, 1H),

1.98-1.90 (m, 1H). ¹³C{1H} NMR (126 MHz, CDCl₃) δ 162.1 (d, J = 245.0 Hz), 152.0, 140.6 (d, J = 3.0 Hz), 138.7, 128.1 (d, J = 7.9 Hz), 122.1, 115.4, 115.2, 114.6, 113.1, 55.9, 55.8, 31.3, 26.8 ppm. Enantiomeric excess was determined by HPLC (OD-H column, hexane/*i*PrOH 85/15, 0.80 mL/min, 250 nm): t₁ = 6.3 min (minor), t₂ = 8.5 min (major). HRMS Calculated for C₁₆H₁₇ONF [M+H]⁺ 258.1289; found 258.1280.

(R)-6-bromo-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline (2r):



an oil, 55 mg, 90% yield; 90% ee; $[\alpha]^{20}_{D} = +25.6$ (*c* 0.24, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.34 (m, 2H), 7.16-7.09 (m, 2H), 7.09-7.03 (m, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 4.43 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.07 (s, 1H), 2.93-2.86 (m, 1H), 2.74-2.68 (m, 1H), 2.13-2.08 (m, 1H),

2.00 -1.85 (m, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 162.1 (d, J = 245.5 Hz), 143.5, 140.0 (d, J = 3.1 Hz), 131.7, 129.6, 128.0 (d, J = 8.0 Hz), 122.8, 115.5 (d, J = 8.0 Hz), 115.3, 108.7, 55.4, 30.5, 26.0 ppm. Enantiomeric excess was determined by HPLC (OD-H column, hexane/*i*PrOH 85/15, 0.80 mL/min, 254 nm): t₁ = 7.2 min (minor), t₂ = 13.6 min (major). HRMS Calculated for C₁₅H₁₄NBrF [M+H]⁺ 306.0288; found 306.0278.

Part 2: Asymmetric reductive amination for synthesizing tetrahydroisoquinolines **Table S1.** Optimization of reaction conditions for the synthesis of THIQs.

| I | | (1) HCI/Et ₂ O, DCM | | | |
|------------------------|--------------------|---|-------------------------|-----------------|--|
| | | (2)[Ir(COD)CI] ₂ /ZhaoPhos (0.5 mol%) additive, H ₂ (30 atm), solvent, rt, 24 h | | | |
| entry ^a | solvent | additive | conversion ^b | ee ^c | |
| 1 | DCM | Ti(O ⁱ Pr) ₄ | >95% | 75% | |
| 2 | toluene | Ti(O ⁱ Pr) ₄ | >95% | 78% | |
| 3 | THF | Ti(O ⁱ Pr) ₄ | >95% | 90% | |
| 4 | PhCF ₃ | Ti(O ⁱ Pr) ₄ | 90% | 85% | |
| 5 | dioxane | Ti(O ⁱ Pr) ₄ | >95% | 85% | |
| 6 | EtOH | Ti(O ⁱ Pr) ₄ | 90% | 60% | |
| 7 | ⁱ PrOH | Ti(O ⁱ Pr) ₄ | 92% | 55% | |
| 8 | ^t BuOMe | Ti(O ⁱ Pr) ₄ | 81% | 81% | |
| 9 | EtOAc | Ti(O ⁱ Pr) ₄ | >95% | 93% | |
| 10 ^d | EtOAc | Ti(O ⁱ Pr) ₄ | 95% | 93% | |
| 11 ^e | EtOAc | Ti(O [/] Pr) ₄ | 94% | 93% | |
| 12 | EtOAc | 1 | 0% | / | |
| 13 ^{<i>f</i>} | EtOAc | Ti(O [/] Pr) ₄ | 0% | / | |
| 14 ^g | EtOAc | Ti(O [/] Pr)₄ | 0% | / | |

^{*a*} Reaction conditions: **2a** (0.1 mmol), [Ir(cod)Cl]₂ (0.5 mol%), ligand (1.1 mol%), additive (1.0 equiv.), solvent (0.6 mL); ^{*b*} Determined by ¹H NMR analysis; ^{*c*} Determined by HPLC analysis of the corresponding benzamides. ^{*d*} 15 atm H₂; ^{*e*} 0.1 mol% [Ir(cod)Cl]₂ was used; ^{*f*} [Rh(cod)Cl]₂ was used; ^{*g*} [Rh(NBD)Cl]₂ was used.

Procedure for asymmetric reductive amination for the synthesis of tetrahydroisoquinolines



To a 2.5 mL vial was added the catalyst precursor $[Ir(COD)Cl]_2$ (3.4 mg, 0.005 mmol), ZhaoPhos (9.5 mg, 0.011 mmol) and anhydrous CH_2Cl_2 (0.3 mL) under argon atmosphere. The mixture was stirred for 0.5 h at room temperature to give a clear solution.

A mixture of substrate **3** (0.2 mmol) and HCl (2 M in Et₂O) (4 equiv.) was dissolved in CH₂Cl₂ (1 mL) and then stirred at rt for 6 h. All volatiles were removed, and the resulting crude intermediate was transferred to a nitrogen-filled glovebox. An aliquot of the above *in situ* prepared catalyst solution (60 μ L, 0.001mmol) was transferred to a vial containing crude intermediate via a syringe, followed by addition of EtOAc (0.8 mL) and Ti(^{*i*}OPr)₄ (1.0 equiv). The vial was placed in an autoclave which was then charged with 30 atm of H₂. The reaction was stirred at 25 °C for 24 h. After carefully releasing the hydrogen, the solution was neutralized with aqueous sodium bicarbonate solution (5 mL), extracted with DCM (5 mL×2). The combined organic phases were dried over anhydrous Na₂SO₄, concentrated and passed through a short column of silica gel with

petroleum/EtOAc (3:1) as eluents to give the chiral tetrahydroisoquinoline products. The obtained products were pure enough for NMR analysis. The enantiomeric excesses were determined by HPLC analysis of the corresponding benzamides.

(S)-1-phenyl-1,2,3,4-tetrahydroisoquinoline (4a)⁴:



a white solid, 39.2 mg, 94% yield; 93% ee; $[\alpha]^{20}_{D} = + 11.2$ (*c* 0.61, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.30 (m, 2H), 7.29-7.23 (m, 3H), 7.14 (d, *J* = 4.2 Hz, 2H), 7.04 (dd, *J* = 8.1, 4.7 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 5.10 (s, 1H), 3.27 (dt, *J* = 8.7, 4.6 Hz, 1H), 3.20-2.97 (m, 1H), 2.83 (dt, *J* = 8.6, 3.8 Hz, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 144.8, 138.2, 135.4, 129.0, 129.0, 128.45, 128.1, 127.4, 126.2, 125.6,

62.1, 42.2, 29.8 ppm. Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 70/30, 0.80 mL/min, 220 nm): $t_1 = 11.2$ min (major), $t_2 = 13.6$ min (minor).

(S)-1-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (4b)⁴:



a white solid, 41.0 mg, 92% yield; 90% ee; $[\alpha]^{20}_{D} = + 8.3$ (*c* 0.41, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.18-7.10 (m, 6H), 7.03 (dt, *J* = 8.3, 4.2 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.07 (s, 1H), 3.27 (dt, *J* = 8.8, 4.6 Hz, 1H), 3.17-2.96 (m, 2H), 2.83 (dt, *J* = 8.4, 3.7 Hz, 1H), 2.34 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 141.9, 138.4, 137.0, 135.4, 129.1, 129.0, 128.8, 128.1, 126.2, 125.6, 61.7, 42.2, 29.8, 21.1 ppm. Enantiomeric excess was determined by HPLC for the corresponding benzamide

(AD-3 column, hexane/*i*PrOH 70/30, 0.80 mL/min, 220 nm): $t_1 = 9.1$ min (major), $t_2 = 13.3$ min (minor).

(S)-1-(m-tolyl)-1,2,3,4-tetrahydroisoquinoline (4c)⁴:



a white solid, 41.4 mg, 93% yield; 90% ee; $[\alpha]^{20}_{D} = +7.6$ (*c* 0.22, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.23 (t, *J* = 10.3 Hz, 1H), 7.17 (d, *J* = 4.2 Hz, 2H), 7.12 (d, *J* = 6.1 Hz, 2H), 7.09-7.04 (m, 2H), 6.79 (d, *J* = 7.7 Hz, 1H), 5.09 (s, 1H), 3.38-3.27 (m, 1H), 3.21-3.02 (m, 2H), 2.86 (dt, *J* = 8.1, 7.5 Hz, 1H), 2.35 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 144.7, 138.3, 138.1, 135.4, 129.6, 129.0, 128.2, 128.2, 128.1,

126.2, 126.1, 125.6, 62.1, 42.4, 29.8, 21.4 ppm. Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 70/30, 1.0 mL/min, 220 nm): $t_1 = 8.1$ min, $t_2 = 8.6$ min (major).

$(S) \mbox{-}1\mbox{-}(4\mbox{-}fluorophenyl) \mbox{-}1\mbox{-}2\mbox{,}3\mbox{,}4\mbox{-}tetrahydroisoquinoline} \ (4d)^4\mbox{:}$



a white solid, 43.1 mg, 95% yield; 94% ee; $[\alpha]^{20}_{D} = +9.6$ (*c* 0.26, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.27-7.21 (m, 2H), 7.15 (d, *J* = 4.0 Hz, 2H), 7.08-6.97 (m, 3H), 6.72 (d, *J* = 7.7 Hz, 1H), 5.09 (s, 1H), 3.26 (dt, *J* = 8.8, 4.7 Hz, 1H), 3.07 (m, 2H), 2.82 (dt, *J* = 8.3, 3.9 Hz, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 162.1 (d, *J* = 245.5 Hz), 140.5, 138.0, 135.3, 130.5 (d, *J* = 8.0 Hz), 129.1, 128.0, 126.4, 125.7, 115.2 (d, *J* = 21.2 Hz), 61.3, 42.2, 29.6 ppm. Enantiomeric excess was determined by HPLC

for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 70/30, 0.80 mL/min, 220 nm): $t_1 = 11.0 \text{ min (major)}, t_2 = 11.7 \text{ min (minor)}.$

(S)-1-(3-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (4e)⁴:



a white solid, 42.2 mg, 94% yield; 88% ee; $[\alpha]^{20}_{D} = +13.3$ (*c* 0.22, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.31 (m, 1H), 7.23-7.16 (m, 2H), 7.13-7.05 (m, 2H), 7.00 m, 2H), 6.78 (d, J = 7.7 Hz, 1H), 5.13 (s, 1H), 3.28 (dt, J = 11.3, 4.9 Hz, 1H), 3.16-2.98 (m,

2H), 2.86 (dt, J = 16.1, 4.3 Hz, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 162.9 (d, J = 245.9 Hz), 147.4 (d, J = 6.6 Hz), 137.5, 135.4, 129.8 (d, J = 8.1 Hz), 129.1, 128.0, 126.5, 125.7, 124.6 (d, J = 2.8 Hz), 115.8 (d, J = 21.4 Hz), 114.3 (d, J = 21.2 Hz), 61.5 (d, J = 1.6 Hz), 42.0, 29.6 ppm. Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 70/30, 1.0 mL/min, 220 nm): t₁ = 10.4 min (minor), t₂ = 11.3 min (major).

(S)-1-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (4f)⁴:



a white solid, 45.2 mg, 93% yield; 93% ee; $[\alpha]^{20}_{D} = +17.8$ (*c* 0.21, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.29 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.15 (d, J =4.1 Hz, 2H), 7.04 (dt, J = 8.3, 4.2 Hz, 1H), 6.71 (d, J = 7.7 Hz, 1H), 5.08 (s, 1H), 3.25 (dt, J = 11.1, 4.8 Hz, 1H), 3.06 (m, 2H), 2.82 (dt, J = 8.5, 4.0 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 143.3, 137.7, 135.4, 133.1, 130.3, 129.1, 128.5, 127.9, 126.4, 125.7, 61.4, 42.2, 29.6 ppm. Enantiomeric excess was determined by HPLC for the

corresponding benzamide (AD-3 column, hexane/*i*PrOH 70/30, 0.80 mL/min, 210 nm): $t_1 = 10.3$ min (major), $t_2 = 12.9$ min (minor).

(S)-7-fluoro-1-phenyl-1,2,3,4-tetrahydroisoquinoline (4g):



a white solid, 43.1 mg, 95% yield; 94% ee; $[\alpha]^{20}_{D} = +23.4$ (*c* 0.63, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.30 (m, 3H), 7.29 (dd, *J* = 5.9, 2.4 Hz, 2H), 7.12 (dd, *J* = 8.4, 5.8 Hz, 1H), 6.87 (td, *J* = 8.4, 2.6 Hz, 1H), 6.48 (dd, *J* = 9.9, 2.6 Hz, 1H), 5.08 (s, 1H), 3.37-3.19 (m, 1H), 3.10 (ddd, *J* = 11.8, 9.2, 4.3 Hz, 1H), 3.07-2.93 (m, 1H), 2.82 (dt, *J* = 16.0, 4.1 Hz, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 160.8

(d, J = 243.4 Hz), 144.0, 140.1 (d, J = 6.5 Hz), 130.9 (d, J = 3.0 Hz), 130.3 (d, J = 7.6 Hz), 128.9, 128.5, 127.6, 114.3 (d, J = 21.5 Hz), 113.5 (d, J = 21.4 Hz), 62.2 (d, J = 1.7 Hz), 42.3, 29.0 ppm. Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 1.0 mL/min, 210 nm): t₁ = 15.1 min (major), t₂ = 15.7 min (minor). HRMS Calculated for C₁₅H₁₅NF [M+H]⁺ 228.1183; found 228.1176.

(S)-5-chloro-1-phenyl-1,2,3,4-tetrahydroisoquinoline (4h):



a white solid, 44.7 mg, 92% yield; 86% ee; $[\alpha]^{20}_{D} = +72.9$ (*c* 0.96, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.30 (m, 3H), 7.28-7.20 (m, 2H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 5.11 (s, 1H), 3.33 (dt, *J* = 12.2, 5.3 Hz, 1H), 3.22-3.03 (m, 1H), 3.03-2.69 (m, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 144.2, 140.6, 134.4, 133.6, 128.9, 128.5, 127.6, 127.0, 126.6, 126.3, 62.1, 41.7, 27.7 ppm. Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column,

hexane/*i*PrOH 80/20, 1.0 mL/min, 210 nm): $t_1 = 13.3 \text{ min (major)}, t_2 = 20.6 \text{ min (minor)}.$ HRMS Calculated for $C_{15}H_{15}NCl [M+H]^+ 244.0888$; found 244.0881.

(S)-7-bromo-1-phenyl-1,2,3,4-tetrahydroisoquinoline (4i):



a white solid, 52.4 mg, 91% yield; 94% ee; $[\alpha]^{20}_{D} = -75.8$ (*c* 0.76, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.41-7.31 (m, 3H), 7.31 2 7.25 (m, 2H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 1.7 Hz, 1H), 5.07 (s, 1H), 3.53-3.16 (m, 1H), 3.11-3.06 (m, 1H), 3.02-2.96 (m, 1H), 2.82-2.77 (m, 1H), 2.01-1.47 (m, 1H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 143.9, 140.4, 134.4, 130.7, 130.7, 129.4, 128.9, 128.6, 127.7,

119.2, 61.8, 42.0, 29.3 ppm. Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 70/30, 1.0 mL/min, 210 nm): $t_1 = 8.1$ min (major), $t_2 = 8.6$ min (minor). HRMS Calculated for $C_{15}H_{15}NBr [M+H]^+ 288.0382$; found 288.0374.

(S)-1-(4-chlorophenyl)-7-fluoro-1,2,3,4-tetrahydroisoquinoline (4j):



a white solid, 49.0 mg, 94% yield; 93% ee; $[\alpha]^{20}_{D}$ = +43.3 (*c* 0.69, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.12 (dd, *J* = 8.5, 5.8 Hz, 1H), 6.91-6.85 (m, 1H), 6.45-6.42 (m, 1H), 5.05 (s, 1H), 3.35-3.21 (m, 1H), 3.12-3.06 (m, 1H), 3.05-2.97 (m, 1H), 2.83-2.77 (m, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 160.8 (d, *J* = 243.7 Hz), 142.5, 139.6 (d, *J* = 6.4 Hz), 133.4, 130.9 (d, *J* = 3.0 Hz), 130.5 (d, *J* = 7.7 Hz), 130.2, 128.7, 114.2 (d, *J* = 21.6

Hz), 113.7 (d, J = 21.3 Hz), 61.5 (d, J = 1.8 Hz), 42.3, 28.9 ppm. Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.5mL/min, 210 nm): t₁ = 24.8 min (major), t₂ =28.8 min (minor). HRMS Calculated for C₁₅H₁₄NFCl [M+H]⁺ 262.0793; found 262.0784.

(S)-5-chloro-1-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (4k):



a white solid, 50.6 mg, 91% yield; 85% ee; $[\alpha]^{20}_{D} = +85.4$ (*c* 0.85, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 5.08 (s, 1H), 3.33-3.27 (m, 1H), 3.15-3.08 (m, 1H), 2.94 (q, *J* = 5.6, 5.0 Hz, 2H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 142.71, 140.12, 134.56, 133.59, 133.38, 130.33, 128.65, 127.25, 126.45, 126.39, 61.42, 41.71, 27.67 ppm. Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 1.0

mL/min, 220 nm): $t_1 = 17.0$ min (major), $t_2 = 24.1$ min (minor). HRMS Calculated for $C_{15}H_{14}NCl_2$ [M+H]⁺ 278.0498; found 278.0489.

(S)-7-bromo-1-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (4l):



a white solid, 57.3 mg, 89% yield; 98% ee; $[\alpha]^{20}_{D} = -10.1$ (*c* 0.96, CHCl₃);¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.29-7.24 (m, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 2.1 Hz, 1H), 5.02 (s, 1H), 3.43-3.16 (m, 1H), 3.09-3.02 (m, 1H), 3.01-2.89 (m, 1H), 2.76 (dt, *J* = 16.2, 4.4 Hz, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 142.4, 139.9, 134.3, 133.5, 130.8, 130.6, 130.2, 129.6, 128.7, 119.3, 61.2, 42.0, 29.2 ppm. Enantiomeric excess was

determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.5 mL/min, 210 nm): $t_1 = 28.9$ min (major), $t_2 = 34.6$ min (minor). HRMS Calculated for C₁₅H₁₄NClBr [M+H]⁺ 321.9993; found 321.9966.

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5. NMR Spectra



17

¹H NMR for **1b** (500 MHz, CDCl₃)





¹H NMR for **1d** (500 MHz, CDCl₃)



¹H NMR for **1e** (500 MHz, CDCl₃)



¹H NMR for **1f** (500 MHz, CDCl₃)



¹H NMR for **1g** (500 MHz, CDCl₃)



¹H NMR for **1h** (500 MHz, CDCl₃)



¹H NMR for **1i** (500 MHz, CDCl₃)



¹H NMR for **1***j* (500 MHz, CDCl₃)



¹H NMR for 1k (500 MHz, CDCl₃)



¹H NMR for **11** (500 MHz, CDCl₃)













1 H NMR for 1q (500 MHz, CDCl₃)



33





¹H NMR for **3b** (500 MHz, CDCl₃)


































¹H NMR for **2f** (500 MHz, CDCl₃)





¹H NMR for **2h** (500 MHz, CDCl₃)



¹H NMR for 2i (500 MHz, CDCl₃)







¹H NMR for **2l** (400 MHz, CDCl₃)







¹H NMR for **2n** (500 MHz, CDCl₃)







¹H NMR for **2q** (500 MHz, CDCl₃)



¹H NMR for **2r** (500 MHz, CDCl₃)



¹H NMR for 4a (500 MHz, CDCl₃)



¹H NMR for **4b** (500 MHz, CDCl₃)



¹H NMR for 4c (500 MHz, CDCl₃)



¹H NMR for 4d (500 MHz, CDCl₃)



¹H NMR for 4e (500 MHz, CDCl₃)







¹H NMR for **4h** (500 MHz, CDCl₃)




¹H NMR for 4j (400 MHz, CDCl₃)



¹H NMR for 4k (400 MHz, CDCl₃)





6. HPLC spectra



6738.00513 339.06267

Totals :



Totals : 3337.36437 220.25550



Totals : 6410.85449 619.45602



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak | RetTime | Туре | Width | Area | Height | Area |
|------|---------|------|--------|------------|-----------|---------|
| # | [min] | | [min] | [mAU*s] | [mAU] | 8 |
| | | | | | | |
| 1 | 11.994 | BB | 0.1915 | 3206.67578 | 260.70264 | 98.6392 |
| 2 | 13.149 | BB | 0.3056 | 44.23962 | 2.17210 | 1.3608 |
| | | | | | | |
| | | | | | | |

Totals : 3250.91540 262.87473







| Acq. Instrument : Injection Date : Acq. Method : Last changed : Analysis Method : Last changed : DADIA_Sig=2 mail 1 | : 1260-DAD : 8/28/2017 : d:\Chem32' .M : 8/28/2017 : d:\Chem32' | 10:01:56 | PM | Location : Inj : | P2-A-0 | 08 | |
|--|---|---|--|-------------------------------------|-------------|------------------|------------|
| Injection Date : Acq. Method : Last changed : Analysis Method : Last changed : DADIA Sig-2 mAU 1 | <pre>8/28/2017 d:\Chem32' .M 8/28/2017 d:\Chem32' d:\Chem32'</pre> | 10:01:56 | PM | Inj : | | | |
| Acq. Method : Last changed : Analysis Method : Last changed : DADIA, Sig=2 mAU 1 | : d:\Chem32 .M : 8/28/2017 : d:\Chem32 | \1\Data\YA | | | 1 | | |
| Acq. Method : Last changed : Analysis Method : Last changed : DAD1 A Sig=21 mAU 1 | : d:\Chem32' .M : 8/28/2017 : d:\Chem32' | \1\Data\YA | | Inj Volume : | 1.000 µ1 | L | |
| Last changed : Analysis Method : Last changed : DAD1 A, Sig=2 mAU 1 | 8/28/2017 d:\Chem32 | | NGTAO\YT-95 | -2 2017-08-2 | 8 21-28-4 | 40\YT-OJ-H-95-5- | -0.8-25MIN |
| Analysis Method : Last changed : DAD1 A, Sig=21 mAU 1 | : d:\Chem32 | 9:31:36 PM | M by SYSTEM | | | | |
| Last changed : DAD1 A, Sig=2 | | \1\Data\YA | NGTAO\YT-95 | -2 2017-08-2 | 8 21-28-4 | 40\YT-OJ-H-95-5- | -0.8-25MIN |
| DAD1 A, Sig=2 mAII | .M (Sequer | nce Method) |) | | | | |
| mALI 1 | 54.4 Ref=360.100 | 9:45:19 P | 5-2 2017-08-28 21 | -28-40\003-P2-A8-Y | -95-D-CHIRA | _D) | |
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| | : | Signal | | | | | |
| Sorted By | | 1.0000 | | | | | |
| Sorted By Multiplier | : | | | | | | |
| Sorted By Multiplier Dilution | : | 1.0000 | | | | | |
| Sorted By Multiplier Dilution Use Multiplier & | : : Dilution Fa | 1.0000 actor with | ISTDs | | | | |
| Sorted By Multiplier Dilution Use Multiplier & | : : Dilution Fa | 1.0000 actor with | ISTDs | | | | |
| Sorted By Multiplier Dilution Use Multiplier & Signal 1: DAD1 A. | : Dilution Fa | 1.0000 actor with Ref=360.10 | ISTDs | | | | |
| Sorted By Multiplier Dilution Use Multiplier & Signal 1: DAD1 A, | : Dilution Fa | 1.0000 actor with Ref=360,10 | ISTDs | | | | |
| Sorted By Multiplier Dilution Use Multiplier & Signal 1: DAD1 A, Peak RetTime Type | : Dilution Fa Sig=254,4 Width | 1.0000 actor with Ref=360,10 Area | ISTDs 00 Height | Area | | | |
| Sorted By Multiplier Dilution Use Multiplier & Signal 1: DAD1 A, Peak RetTime Type # [min] | : Dilution Fa Sig=254,4 Width [min] | 1.0000 actor with Ref=360,10 Area [mAU*s] | ISTDs 00 Height [mAU] | ۸rea ۴ | | | |
| Sorted By Multiplier Dilution Use Multiplier & Signal 1: DADL A, Peak RetTime Type # [min] | : Dilution Fa Sig=254,4 Width [min] | 1.0000 actor with Ref=360,10 Area [mAU*s] | ISTDs 00 Height [mAU] | Area % | | | |
| Sorted By Multiplier Dilution Use Multiplier & Signal 1: DAD1 A, Peak RetTime Type # [min] | : Dilution Fa Sig=254,4 Width [min] - 0.1510 1 | 1.0000 actor with Ref=360,10 Area [mAU*s] | ISTDs 00 Height [mAU] 206.25394 | Area % 98.6379 | | | |
| Sorted By Multiplier Dilution Use Multiplier & Signal 1: DAD1 A, Peak RetTime Type # [min] | : Dilution F4 , Sig=254,4 Width [min] - 0.1510 19 0.1750 | 1.0000 actor with Ref=360,10 Area [mAU*s] | ISTDs 00 Height [mAU] 206.25394 2.45815 | Area % 98.6379 1.3621 | | | |
| Sorted By Multiplier Dilution Use Multiplier 6 Signal 1: DADL A, Peak RetTime Type # [min] | : : Dilution F: , Sig=254,4 Width [min] - | 1.0000 actor with Ref=360,10 Area [mAU*s] | ISTDs 00 Height [mAU] 206.25394 2.45815 | Area % 98.6379 1.3621 | | | |



| Acq. Operator | : SYS | TEM | S | eq. Line | : | 4 |
|-----------------|-------------|---------------------------|---------------------|----------------|------------|---------------------------------|
| Acq. Instrument | : 126 | 0-DAD | | Location | : | P2-A-09 |
| Injection Date | : 8/2 | 8/2017 10:17:45 PM | 1 | Inj | : | 1 |
| | | | In | j Volume | : 1 | .000 µl |
| Acq. Method | : d:\ .M | Chem32\1\Data\YANG | TAO\YT-95-2 | 2017-08 | -28 | 21-28-40\YT-OJ-H-95-5-0.8-25MIN |
| Last changed | : 8/2 | 8/2017 9:31:36 PM | by SYSTEM | | | |
| Analysis Method | : d:\ | Chem32\1\Data\YANG | TAO\YT-95-2 | 2017-08 | -28 | 21-28-40\YT-OJ-H-95-5-0.8-25MIN |
| | . M | (Sequence Method) | | | | |
| Last changed | : 8/2 | 8/2017 9:45:19 PM | by SYSTEM | | | |
| Additional Info | : Pea | k(s) manually inte | grated | | | |
| DAD1 A, Sig | =254,4 Re | f=360,100 (YANGTAO\YT-95- | 2 2017-08-28 21-28- | 40\004-P2-A9 | -YT-9 | 5-E-RACEMIC.D) |
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Area Percent Report -----

| Sorted By | | : | Signal | |
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| Multiplier | | : | 1.0000 | |
| Dilution | | : | 1.0000 | |
| Use Multiplier | & | Dilution | Factor with | ISTDs |

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Туре | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|-----------|------------------|------|----------------|-----------------|-----------------|-----------|
| | | | | | | |
| 1 | 8.533 | BB | 0.1371 | 3732.47144 | 422.28940 | 48.6869 |
| 2 | 9.137 | BB | 0.1496 | 3933.79907 | 411.10553 | 51.3131 |
| Total | .s : | | | 7666.27051 | 833.39493 | |

| : | 7666.27051 | 833.39 |
|---|------------|--------|
| | | |

| Acq. Operator | : SYSTEM Seq. Line : 5 |
|-----------------|---|
| Acq. Instrument | : 1260-DAD Location : P2-A-10 |
| Injection Date | : 8/28/2017 10:33:35 PM Inj : 1 |
| | Inj Volume : 1.000 µl |
| Acq. Method | : d:\Chem32\1\Data\YANGTAO\YT-95-2 2017-08-28 21-28-40\YT-0J-H-95-5-0.8-25MIN .M |
| Last changed | : 8/28/2017 9:31:36 PM by SYSTEM |
| Analysis Method | : d:\Chem32\1\Data\YANGTAO\YT-95-2 2017-08-28 21-28-40\YT-0J-H-95-5-0.8-25MIN .M (Sequence Method) |
| Last changed | : 8/28/2017 9:45:19 PM by SYSTEM |
| Additional Info | : Peak(s) manually integrated |
| DAD1 A, Sig | =254,4 Ref=360,100 (YANGTAO\YT-95-2 2017-08-28 21-28-40\005-P2-A10-YT-95-E-CHIRAL.D) |
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Area Percent Report ------Sorted By Multiplier Dilution : Signal : 1.0000 : 1.0000

| Dilution | | : | 1.0 | 000 | |
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| Use Multiplier | â | Dilution | Factor | with | ISTDs |

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Туре | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|-----------|------------------|------|----------------|-----------------|-----------------|-----------|
| | | | | | | |
| 1 | 8.532 | MM | 0.1482 | 1552.69312 | 174.59900 | 98.4167 |
| 2 | 9.154 | MF | 0.1747 | 24.98001 | 2.38271 | 1.5833 |
| | | | | | | |
| Total | s : | | | 1577.67313 | 176.98171 | |



| Acq. Instrument | : 1260-DAD | Location : P1-B-02 | |
|------------------|--|---|----|
| Injection Date | : 9/4/2017 4:18:50 PM | Inj : 1 | |
| | | Inj Volume : 1.000 µl | |
| Method | : d:\Chem32\1\Data\YANGTAO\YAN | <pre>NGTAO-2-95 2017-09-04 15-57-17\YTANT-0J-H-95-5</pre> | 5- |
| | 08-18MIN.M (Sequence Method) |) | |
| Last changed | : 7/26/2017 8:52:36 PM by SYST | ſEM | |
| Additional Info | : Peak(s) manually integrated | | |
| DAD1 B, Sig= | 254,4 Ref=360,100 (YANGTAO\YAAO-2-95 2017- | -09-04 15-57-17\002-P1-B2-YANGT-2-95-F-CHIRAL.D) | |
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| Sorted By | : Signal | | |
| Multiplier | : 1.0000 | | |
| Dilution | : 1.0000 | | |
| Use Multiplier a | Dilution Factor with ISTDs | | |
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| 0/ | 0/- 054 4 D-6 260 100 | | |
| Signal 1: DADI I | 3, Sig=254,4 Ref=360,100 | | |
| | | | |
| Peak RetTime Typ | pe Width Area Height | Area | |
| # [min] | [min] [mAU*s] [mAU] | 8 | |
| | | | |
| 1 8.822 BB | 0.1446 6252.17090 671.9231 | 10 90.4884 | |
| 2 9.503 BB | 0.1591 227.54153 22.2869 | 34 3.5110 | |
| | | | |
| Totals : | 6479.71243 694.2101 | 10 | |
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Seq. Line : 2

Acq. Operator : SYSTEM









Area

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Seq. Line : 7



| | • | SISTEM | Seq. Line | : | 3 | |
|----------------|----|--|------------------------------|-------|-------------------------|----------------|
| cq. Instrument | : | 1260-DAD | Location | : | P1-C-02 | |
| njection Date | : | 9/14/2017 11:30:04 AM | Inj | : | 1 | |
| | | | Inj Volume | : 1 | .000 µl | |
| .cq. Method | : | d:\Chem32\1\Data\YANGTA -30MIN.M | O\YANGTAO-2-99H-2 | 201 | 7-09-14 10-37-26\ | T-AD-3-95-0.5 |
| ast changed | : | 9/14/2017 11:25:08 AM b | y SYSTEM | | | |
| nalysis Method | : | d:\Chem32\1\Data\YANGTA -30MIN.M (Sequence Meth | O\YANGTAO-2-99H-2 | 201 | 7-09-14 10-37-26\ | (T-AD-3-95-0.5 |
| ast changed | : | 9/14/2017 11:29:16 AM b | V SYSTEM | | | |
| dditional Info | | Peak(s) manually integr | ated | | | |
| DAD1 A. Sig= | 25 | 4.4 Ref=360.100 (YANGTAO\YAO-2-9 | 9H-2 2017-09-14 10-37-26\003 | -P1-C | 2-YANGT-2-99H-CHIRAL.D) | |
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| Sorted By | : | Signal | | |
| Multiplier | : | 1.0000 | | |
| Dilution | : | 1.0000 | | |
| Use Multiplier & | Dilution | Factor with | ISTDs | |

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak | RetTime | Туре | Width | Area | Height | Area |
|------|---------|------|--------|------------|-----------|---------|
| # | [min] | | [min] | [mAU*s] | [mAU] | 8 |
| | | | | | | |
| 1 | 12.179 | BB | 0.1933 | 87.89921 | 6.86728 | 2.2018 |
| 2 | 13.458 | BB | 0.2144 | 3904.32129 | 273.75671 | 97.7982 |
| Tota | ls : | | | 3992.22050 | 280.62399 | |



| Acq. Operator : | : SYSTEM | Seq. Line : 2 | |
|-------------------|---|-----------------------------|-----------------------------|
| Acq. Instrument : | 1260-DAD | Location : P1-0 | C-02 |
| Injection Date : | : 9/10/2017 7:16:00 PM | Inj : 1 | |
| | | Inj Volume : 1.000 | μl |
| Acq. Method | : d:\Chem32\1\Data\YANGTAO-2-113 | 2017-09-10 18-41-3 | 33\YTANT-OJ-H-95-5-08-18MIN |
| | .M | | |
| Last changed : | : 9/10/2017 7:19:05 PM by SYSTEM | 1 | |
| | (modified after loading) | | |
| Analysis Method : | d:\Chem32\1\Data\YANGTAO-2-113 | 2017-09-10 18-41-3 | 33\YTANT-OJ-H-95-5-08-18MIN |
| | .M (Sequence Method) | | |
| Last changed | : 9/10/2017 7:51:03 PM by SYSTEM | I | |
| Additional Info : | : Peak(s) manually integrated | | |
| DAD1 B, Sig=2 | 54,4 Ref=360,100 (YANGTAO-2-113 2017-09-10 18-4 | 1-33\002-P1-C2-YANGT-2-113A | -CHIRAL.D) |
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| Sorted By | : Signal | | |
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| Dilution | : 1.0000 | | |
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Signal 1: DAD1 B, Sig=254,4 Ref=360,100

| Peak | RetTime | Type | Width | Area | Height | Area |
|-------|---------|------|--------|------------|-----------|---------|
| # | [min] | | [min] | [mAU*s] | [mAU] | 8 |
| | | | | | | |
| 1 | 25.366 | BB | 0.4300 | 3265.82690 | 118.31031 | 97.4480 |
| 2 | 30.089 | BB | 0.4753 | 85.52647 | 2.58967 | 2.5520 |
| | | | | | | |
| Total | s: | | | 3351.35337 | 120.89998 | |



| Acq. Operator | : SYSTEM | Seq. Line : 3 | |
|-----------------|--|--------------------------------------|-----------------------------|
| Acq. Instrument | : 1260-DAD | Location : P1- | C-02 |
| Injection Date | : 11/20/2017 19:12:44 | Inj : 1 | |
| | | Inj Volume : 1.000 | μl |
| Acq. Method | : d:\Chem32\1\Data\YANGTAC | VT-2-118-B-2-1 2017-11- | 20 18-00-10\YT-OJ-H-95-5-0. |
| Tast shanged | -2.5MIN.M | VOTEM | |
| Analucic Mothod | . d.\Chom32\1\Data\VANCTAC | Vm-2-119-p-2-1 2017-11- | 20 18-00-10\ 27-01-0-95-5-0 |
| Analysis Method | 8-25MTN M (Sequence Meth | (11-2-116-B-2-1 2017-11- | 20 18-00-10(11-03-h-95-5-0. |
| Tast changed | 11/20/2017 10:11:56 by 6 | VOTEM | |
| Additional Info | · Deck(a) manually integra | tod | |
| DADIA Sig | 254 4 Pd-260 100 (VANGTAOVT 118 P.2 | 1 2017 11 20 18 00 10/003 P1 C2 VT 2 | 119B.2.CHIPAL D) |
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| Multiplier | | : | 1.00 | 000 | |
| Dilution | | : | 1.00 | 000 | |
| Use Multiplier | & | Dilution | Factor | with | ISTDs |

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak | RetTime | Туре | Width | Area | Height | Area |
|-------|---------|------|--------|------------|------------|---------|
| # | [min] | | [min] | [mAU*s] | [mAU] | ę |
| | | | | | | |
| 1 | 19.818 | BB | 0.3346 | 1037.04272 | 48.27863 | 97.5628 |
| 2 | 24.372 | MM | 0.4406 | 25.90606 | 9.79966e-1 | 2.4372 |
| | | | | | | |
| Total | s : | | | 1062.94878 | 49.25860 | |

| 100010 . | 1001101010 | |
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| DAD 2017 5:32:41 FM In em32\1\Data\YANGTAO\YT-2-11 .M 2017 5:39:54 FM by SYSTEM fied after loading) em32\1\Data\YANGTAO\YT-2-11 .M (Sequence Method) | Location : P1-C-02 Inj : 1 ij Volume : 1.000 µ1 9 2017-09-13 17-05-10 .9 2017-09-13 17-05-10 | \YT-OJ-H-95-5-0.8- \YT-OJ-H-95-5-0.8- |
|---|--|--|
| 2017 5:32:41 PM In em32\1\Data\YANGTAO\YT-2-11 .M 2017 5:39:54 PM by SYSTEM fied after loading) m32\1\Data\YANGTAO\YT-2-11 .M (Sequence Method) | Inj : 1 nj Volume : 1.000 μl 19 2017-09-13 17-05-10 | \YT-OJ-H-95-5-0.8- \YT-OJ-H-95-5-0.8- |
| In em32\1\Data\YANGTAO\YT-2-11 .M 2017 5:39:54 PM by SYSTEM fied after loading) mm32\1\Data\YANGTAO\YT-2-11 .M (Sequence Method) | nj Volumë : 1.000 µl 19 2017-09-13 17-05-10 19 2017-09-13 17-05-10 | \YT-OJ-H-95-5-0.8- \YT-OJ-H-95-5-0.8- |
| em32\1\Data\YANGTAO\YT-2-11 .M 2017 5:39:54 PM by SYSTEM fied after loading) em32\1\Data\YANGTAO\YT-2-11 .M (Sequence Method) | 9 2017-09-13 17-05-10 | \YT-OJ-H-95-5-0.8- \YT-OJ-H-95-5-0.8- |
| .M 2017 5:39:54 PM by SYSTEM fied after loading) em32\1\Data\YANGTAO\YT-2-11 .M (Sequence Method) | 9 2017-09-13 17-05-10 | \YT-OJ-H-95-5-0.8- |
| 2017 5:39:54 PM by SYSTEM fied after loading) em32\1\Data\YANGTAO\YT-2-11 .M (Sequence Method) | 9 2017-09-13 17-05-10 | \YT-0J-H-95-5-0.8- |
| fied after loading) em32\1\Data\YANGTAO\YT-2-11 .M (Sequence Method) | 19 2017-09-13 17-05-10 | \YT-OJ-H-95-5-0.8- |
| em32\1\Data\YANGTAO\YT-2-11 .M (Sequence Method) | 19 2017-09-13 17-05-10 | \YT-OJ-H-95-5-0.8- |
| .M (Sequence Method) | | |
| | | |
| 2017 7:05:19 PM by SYSTEM | | |
| s) manually integrated | | |
| 30,100 (YANGTAO\YT-2-119 2017-09-13 17-0 | 05-10\002-P1-C2-YANGT-2-118-A-CH | IRAL.D) |
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| | 0,100 (YANGTAOYT-2-119 2017-08-13 17-0 | 0,100 (YANGTAOYT-2-119 2017-09-13 17-05-10002-P1-C2-YANGT-2-118-A-CF |

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak | RetTime | Туре | Width | Area | Height | Area |
|------|---------|------|--------|------------|-----------|---------|
| # | [min] | | [min] | [mAU*s] | [mAU] | 8 |
| | | | | | | |
| 1 | 6.160 | BB | 0.0954 | 1966.84399 | 321.26532 | 98.9761 |
| 2 | 6.556 | BB | 0.1006 | 20.34607 | 3.18360 | 1.0239 |
| | | | | | | |

Totals: 1987.19006 324.44892



| Acq. Operator | : | SYSTEM | Seq. Line : | | 2 | | | |
|-----------------|------|--|---------------------------------------|----------|-----------------|----------|------------|--|
| Acq. Instrument | : | 1260-DAD | Location : | | P1-D-02 | | | |
| Injection Date | : | 9/14/2017 11:00:59 AM | Inj : | | 1 | | | |
| | | | Inj Volume : | 1 | .000 µl | | | |
| Acg. Method | : | d:\Chem32\1\Data\YANGTAO\Y | т-2-113-в 2017-0 | 9-2 | 14 10-33-30 | YT-OJ-H- | -95-5-0.8- | |
| | | 25MIN.M | | | | | | |
| Last changed | : | 9/14/2017 11:19:27 AM by S | YSTEM | | | | | |
| | | (modified after loading) | | | | | | |
| Analysis Method | : | d:\Chem32\1\Data\YANGTAO\Y | т-2-113-в 2017-0 | 9-: | 14 10-33-30 | YT-OJ-H- | -95-5-0.8- | |
| | | 25MIN.M (Sequence Method) | | | | | | |
| Last changed | : | 9/14/2017 12:09:54 PM by S | YSTEM | | | | | |
| Additional Info | | Peak(s) manually integrate | d | | | | | |
| DAD1 A. Sig | =254 | 4 Ref=360.100 (YANGTAO\YT-2-113-B 2017 | | 2-YA | NGT-2-113-B-CHI | RAL.D) | | |
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| l | 2 | 4 <u>6</u> 8 | 10 1 | 2 | 14 | 16 | 18 | |
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| | | Area Percent Report | | | | | | |
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| Sorted By | | : Signal | | | | | | |
| Multiplier | | : 1.0000 | | | | | | |
| Dilution | | : 1.0000 | | | | | | |

| Signal | 1: | DAD1 | Α, | Sig=254,4 | Ref=360,100 |
|--------|----|------|----|-----------|-------------|

Use Multiplier & Dilution Factor with ISTDs

| Peak # | RetTime [min] | Туре | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|-----------|------------------|------|----------------|-----------------|-----------------|-----------|
| | | | | | | |
| 1 | 14.875 | BB | 0.2485 | 1.61275e4 | 1008.64667 | 97.6569 |
| 2 | 17.699 | BB | 0.2878 | 386.94376 | 20.91897 | 2.3431 |
| | | | | | | |
| m | | | | 1 65144-4 | 1000 55564 | |

| Totals | : | 1.65144e4 | 1029.56564 |
|--------|---|-----------|------------|
| | | | |

1583.03485 92.12502



| 2 | 10.858 MF | 0.2192 | 644.41962 | 49.00108 | 50.9 |
|--------|-----------|--------|------------|-----------|------|
| Totals | : | | 1265.02844 | 109.81207 | |



| == | == | ==: | == | == | ==: | | == | == | ==: | | | === | == | ==: | | == | ==: | | - | | === | = |
|--------|----|-----|----|----|-----|------|--------|----|-----|-----|-----|-----|----|-----|----|----|---------|------|---|------|-----|-------|
| | | | | | | | | A | rea | a I | Per | cen | t | Rej | or | t | | | | | | |

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| Sorted By | | : | Sig | nal | |
|----------------|---|----------|--------|------|-------|
| Multiplier | | : | 1.00 | 000 | |
| Dilution | | : | 1.00 | 000 | |
| Use Multiplier | æ | Dilution | Factor | with | ISTDs |

Signal 1: DAD1 A, Sig=250,4 Ref=360,100

| I | Peak | RetTime | Туре | Width | Area | Height | Area |
|---|------|---------|------|--------|------------|-----------|---------|
| | # | [min] | | [min] | [mAU*s] | [mAU] | ÷, |
| - | | | | | | | |
| | 1 | 8.852 | BB | 0.1574 | 274.36084 | 26.80852 | 9.9398 |
| | 2 | 10.840 | BB | 0.2036 | 2485.86548 | 188.87050 | 90.0602 |
| | | | | | | | |

Totals : 2760.22632 215.67901



| Signa | al 1: DAD | 01 A, S | Sig=250,4 | Ref=360,100 |) | |
|-----------|------------------|---------|----------------|-----------------|-----------------|-----------|
| Peak # | RetTime [min] | Туре | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
| | | | - | | - | |
| 1 | 8.359 | BB | 0.1479 | 904.66748 | 94.35817 | 49.9232 |
| 2 | 12.235 | BB | 0.2323 | 907.45160 | 60.73674 | 50.0768 |

1812.11908 155.09491 Totals :

| L | _ ~ ~ 0 | |
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| 60- | | |
| 80- | | |
| | | |
| 100 - | | |
| 120 - | | |
| | | |
| 140 | | |
| 160 | | |
| mAU 1 | =230,4 Ref=360,100 (TANGTAO/TA2-128-A 2017-09-21 18-35-43/00 | 9-P2-D2-TANG1-2-128-D-CHIKAL.D) |
| Additional Info | : Peak(s) manually integrated | |
| Last changed | : 9/21/2017 9:32:50 PM by SYSTEM | |
| Analysis Method | 0.8-15MIN.M (Sequence Method) | -A 2017-09-21 10-35-43(IT-OD-H-85-15- |
| Last changed | : 9/21/2017 8:36:09 PM by SYSTEM | 3 2017 00 21 19 25 42\Vm op # 85 15 |
| Acq. Method | 0.8-15MIN.M | -A 2017-09-21 18-35-43\IT-0D-H-85-15- |
| Non Mathad | Inj Volu | ne : 1.000 µl |
| Injection Date | : 9/21/2017 8:39:08 PM I | nj: 1 |
| Acq. Instrument | : 1260-DAD Locati | on : P2-D-02 |

| | i | Area Percent | Report |
|----------------|------------|--------------|--------|
| | | | |
| | | | |
| Sorted By | : | Signal | |
| Multiplier | : | 1.0000 | |
| Dilution | : | 1.0000 | |
| Use Multiplier | & Dilution | Factor with | ISTDs |

Signal 1: DAD1 A, Sig=250,4 Ref=360,100

| Peak | RetTime | Туре | Width | Area | Height | Area |
|------|---------|------|--------|------------|-----------|---------|
| # | [min] | | [min] | [mAU*s] | [mAU] | 8 |
| | | | | | | |
| 1 | 8.353 | BB | 0.1477 | 214.95056 | 22.44785 | 8.0959 |
| 2 | 12.202 | BB | 0.2326 | 2440.10107 | 163.06314 | 91.9041 |
| | | | | | | |

2655.05164 185.51099 Totals :

min



| Peak Re # | etTime [min] | Туре | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|--------------|-----------------|----------|----------------|------------------------|----------------------|--------------------|
| 1 2 | 6.360 8.679 | BB BB | 0.1223 | 215.52820 216.83179 | 27.23316 18.81563 | 49.8492 50.1508 |
| Totals | | | | 432.35999 | 46.04879 | |

| Acq. Method | Inj Volume : 1.000 µl : d:\Chem32\1\Data\YANGTAO\YANGTAO-2-128-A 2017-09-21 18-35-43\YT-OD-H-85-15- |
|--|---|
| | 0.8-15MIN.M |
| Last changed | (modified after loading) |
| Analysis Method | (modified after foading) : d:\Chem32\1\Data\YANGTAO\YANGTAO-2-128-A 2017-09-21 18-35-43\YT-OD-H-85-15- |
| | 0.8-15MIN.M (Sequence Method) |
| Last changed | : 3/27/2018 12:38:05 by SYSTEM |
| | (modified after loading) |
| Additional Info | : Peak(s) manually integrated |
| DAD1 A, Sig | •250,4 Ref=360,100 (YANGTAO\YA2-128-A 2017-09-21 18-35-43i011-P2-D4-YANGT-2-128-E-CHIRAL.D) |
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| Use Multiplier | E Dilution Factor with ISTDs |

| Peak | RetTime | Type | Width | Area | Height | Area |
|------|---------|------|--------|-----------|----------|---------|
| + | [min] | | [min] | [mAU*s] | [mAU] | 8 |
| | | | | | | |
| 1 | 6.255 | BB | 0.1211 | 72.06497 | 9.22822 | 7.4943 |
| 2 | 8.544 | FM | 0.1915 | 889.52808 | 77.41685 | 92.5057 |

961.59305 86.64508 Totals :



| Acq. Operator | : SYSTEM | Seq. Line : | 5 | |
|-----------------|---|---|--------------------------|--------------|
| Acq. Instrument | : 1260-DAD | Location : | P2-C-04 | |
| Injection Date | : 9/24/2017 8:12:05 PM | Inj : | 1 | |
| | | Inj Volume : 1 | 1.000 µl | |
| Acq. Method | : d:\Chem32\1\Data\YANGTAO\YA | NGTAO-2-134-A 201 | 17-09-24 19-07-54\YT | -OD-H-85-15- |
| | 0.8-15MIN.M | | | |
| Last changed | : 9/24/2017 7:08:18 PM by SYS | TEM | | |
| Analysis Method | : d:\Chem32\1\Data\YANGTAO\YA | NGTAO-2-134-A 201 | 17-09-24 19-07-54\YT | -OD-H-85-15- |
| | 0.8-15MIN.M (Sequence Metho | d) | | |
| Last changed | : 9/24/2017 8:53:46 PM by SYS | TEM | | |
| Additional Info | : Peak(s) manually integrated | | | |
| DAD1 A, Sig= | =254,4 Ref=360,100 (YANGTAO\YA2-134-A 201 | 7-09-24 19-07-54\005-P2-C4 | I-YANGT-2-134B-CHIRAL.D) | |
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| | Area Percent Report | | | |
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| Sorted By | : | Signal | |
|------------------|----------|-------------|-------|
| Multiplier | : | 1.0000 | |
| Dilution | : | 1.0000 | |
| Use Multiplier & | Dilution | Factor with | ISTDs |

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

| Peak # | RetTime [min] | Туре | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|-----------|------------------|------|----------------|-----------------|-----------------|-----------|
| | | | | | | |
| 1 | 7.206 | VB | 0.1345 | 55.48911 | 6.31725 | 4.7976 |
| 2 | 13.631 | BB | 0.2781 | 1101.10950 | 61.15631 | 95.2024 |
| | | | | | | |
| Total | ls : | | | 1156.59861 | 67.47356 | |





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|---|-----|
| Э | 5 |







| Acq. Operator | : SYSTEM | Seq. Line : | : 3 | | |
|-------------------------|----------------------------------|--|-------------------------|-----------------|------|
| Acq. Instrument | : 1260-DAD | Location : | P2-D-02 | | |
| Injection Date | : 10/6/2017 12:56:35 P | M Inj | 1 | | |
| log Mothod | . d.)Chom22\1\Data\VAN | Inj Volume : CTRO\VT-2-139DE 2017-1 | : 1.000 µl | ANCT-20-2-70-20 | 1 1 |
| kcų. Method | 20MIN .M | GIRO(II-2-155DE 2017-1 | 10-00 12-22-02(1 | ANG1-AD-3-70-30 |)-1- |
| last changed | : 10/6/2017 12:57:53 P | M by SYSTEM | | | |
| - | (modified after load | ing) | | | |
| analysis Method | : d:\Chem32\1\Data\YAN | GTAO\YT-2-139DE 2017-1 | 10-06 12-22-02\1 | ANGT-AD-3-70-30 |)-1- |
| | 20MIN .M (Sequence M | ethod) | | | |
| last changed | : 11/16/2017 9:44:21 P | M by SYSTEM | | | |
| Additional Info | (modified after load | ing) | | | |
| DAD1 C Sig | =220.4 Ref=360 100 (YANGTAO)YT 9 | egrated DE 2017-10-06 12-22-02\YT-2-139D- | CHIRAI 2017-10-0612-55- | 49 D) | |
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| Sorted By Multiplier | : Signal | | | | |
| Dilution | : 1.0000 | | | | |
| Use Multiplier | & Dilution Factor with | ISTDs | | | |
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| | | | | | |
| Signal 1: DAD1 | C, Sig=220,4 Ref=360,10 | 0 | | | |
| | | | | | |
| Peak RetTime Ty | pe Width Area | Height Area | | | |
| # [min] | [min] [mAU*s] | [mAU] % | | | |
| 1 8 118 ME | - 0 1644 1042 11769 | 105 62257 4 9216 | | | |
| 2 8.583 EM | 0.1855 2.0132464 1 | 809.22046 95.0784 | | | |
| 2 0.303 FM | 0.1000 2.0102404 1 | 000.22040 00.0784 | | | |

2.11745e4 1914.84303

97

Totals :

| Ph O F |
|--|
| Acg. Operator : SYSTEM Seg. Line : 2 |
| Acq. Instrument : 1260-DAD Location : P1-E-03 |
| Injection Date : 9/29/2017 11:27:09 AM Inj : 2 |
| Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-2-139B 2017-09-29 11-09-28\YANGT-AD-3-70-30-1- |
| 20MIN .M |
| Last changed : 9/29/2017 11:21:31 AM by SYSTEM Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-2-139B 2017-09-29 11-09-28\YANGT-AD-3-70-30-1- |
| 20MIN .M (Sequence Method) |
| Last changed : 11/17/2017 8:58:51 AM by SYSTEM (modified after loading) |
| Additional Info : Peak(s) manually integrated |
| DAD1 C, Sig=220,4 Ref=360,100 (YANGTACIYT9B 2017-09-29 11-09-28)YT-2-139B-RACEMIC2017-09-2911-26-20.D) |
| 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1 |
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| 100- |
| 50- |
| 7 8 9 10 11 12 13 14 |
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| Area Percent Report |
| |
| Sorted By . Signal |
| Multiplier : 1.0000 |
| Dilution : 1.0000 |
| use multiplier & bilution Factor With ISTUS |
| Signal 1: DADI C, Sig=220,4 Ref=360,100 |
| Peak RetTime Type Width Area Height Area |
| # [min] [min] [mAU*s] [mAU] % |
| 1 11.065 BV 0.2019 3065.04346 229.40308 49.7931 |
| 2 11.785 VB 0.2172 3090.51929 215.60413 50.2069 |

6155.56274 445.00720

Totals :

| Injection Date | : 9/29/2017 11:43:04 AM Inj : 1 Tni Volume : 1 000 ul |
|-----------------|--|
| Acq. Method | : d:\Chem32\1\Data\YANGTAO\YT-2-139B 2017-09-29 11-09-28\YANGT-AD-3-70-30-1- |
| Last changed | - 9/29/2017 11-21-31 AM by CYCTEM |
| Analysis Method | : d:\Chem32\1\Data\YANGTAO\YT-2-139B 2017-09-29 11-09-28\YANGT-AD-3-70-30-1- |
| Analysis Nechou | 20MIN .M (Sequence Method) |
| Last changed | : 11/16/2017 9:37:21 PM by SYSTEM |
| habe changed | (modified after loading) |
| Additional Info | · Peak(s) manually integrated |
| DAD1 C. Sig | 220.4 Ref=360.100 (YANGTAO\YT39B 2017-09-29 11-09-28\YT-2-139B-CHIRAL2017-09-2911-42-14.D) |
| mAU] | |
| 200 | and real |
| 175 | P ² |
| 150 | |
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| 3 | 10 11 12 13 14 |
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| | Area Percent Report |
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| Sorted By | : Signal |
| Multiplier | : 1.0000 |
| Dilution | : 1.0000 |
| Use Multiplier | Dilution Factor with ISTDs |
| | |
| Signal 1: DAD1 | 2, Sig=220,4 Ref=360,100 |

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Acq. Operator : SYSTEM

Acq. Instrument : 1260-DAD

Peak RetTime Type Width Area Height Area # [min] [min] [mAU*s] [mAU]

Totals : 2843.01088 215.18571

1 11.012 FM 0.2203 2762.76733 209.01520 97.1775 2 11.708 BB 0.1997 80.24355 6.17052 2.8225

Seq. Line : 3

Location : P1-E-04

98





2 11.338 BB 0.2161 3569.96777 250.79404 94.3107

3785.32784 267.64379

Totals :







| sorted By Multiplier Dilution Use Multiplier 6 | 7 7 11 12 12 13 14 15 15 16 17 18 19 Area Percent Report . |
|---|--|
| | 11 12 13 14 15 16 17 18 19 Area Percent Report |
| 600 500 400 300 100 0 10 10 | 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1 |
| 600 500 400 300 200 100 | 16714 |
| 600 500 400 200 | |
| 500 - 500 - 400 - 300 - | |
| 600 - 500 - 400 - | |
| 600 500 400 | |
| 600 - | |
| 600 - | |
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| 700 - | Ť. |
| Additional Info : DAD1 C, Sig=2 | : Peak(s) manually integrated 210,4 Ref=360,100 (YANGTAO/YT-2-163BC 2017-11-16 11-05-07/004-P1-A4-YT-2-163A-CHIRALD) |
| Last changed : | : 11/17/2017 9:14:05 AM by SYSTEM (modified after loading) |
| Analysis Method : | : d:\Chem32\1\Data\YANGTAO\YT-2-163BC 2017-11-16 11-05-07\YT-AD3-80-20-1 mL- 30Min.M (Sequence Method) |
| Last changed : | 30Min.M : 11/16/2017 11:58:32 AM by SYSTEM |
| Acq. Method : | Inj Volume : 1.000 µl : d:\Chem32\1\Data\YANGTAO\YT-2-163BC 2017-11-16 11-05-07\YT-AD3-80-20-1 mL- |
| Injection Date : | : 11/16/2017 12:15:34 PM Inj: 1 |
| Acq. Operator : | : SYSTEM Seq. Line : 4 |

1 15.118 BV R 0.2336 1.12653e4 740.16235 96.8749

2 15.714 VB E 0.2379 363.41055 23.04964 3.1251

1.16287e4 763.21199

Totals :



C

| reak | recrime | Type | width | Area | Height | Area | |
|-------|---------|------|--------|-----------|------------|---------|--|
| | [min] | | [min] | [mAU*s] | [mAU] | £ | |
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| 1 | 13.308 | BB | 0.2026 | 1.19905e4 | 904.56006 | 50.0625 | |
| 2 | 20.610 | BB | 0.3421 | 1.19606e4 | 536.40411 | 49.9375 | |
| | | | | | | | |
| Total | s : | | | 2.39512e4 | 1440.96417 | | |

| Acq. Operator | : SYSTEM | | | Seq. Line : | 6 | | |
|----------------|--------------------|-----------------|--------------------|-----------------------|-----------------|--------------|-----------|
| Acq. Instrumen | t : 1260-DA | D | | Location : | P1-A-06 | | |
| Injection Date | : 11/16/2 | 017 1:17:16 | PM | Inj : | 1 | | |
| - | | | | Inj Volume : | 1.000 µl | | |
| Acq. Method | : d:\Chem | 32\1\Data\Y | ANGTAO\YT-2- | 163BC 2017-11 | -16 11-05-0 | 7\YT-AD3-80- | -20-1 mL- |
| | 30Min.M | | | | | | |
| Last changed | : 11/16/2 | 017 11:58:3 | 2 AM by SYST | EM | | | |
| nalysis Metho | d : d:\Chem | 32\1\Data\Y | ANGTAO\YT-2- | 163BC 2017-11 | -16 11-05-0 | 7\YT-AD3-80- | -20-1 mL- |
| | 30Min.M | (Sequence | Method) | | | | |
| Last changed | : 11/17/2 | 017 9:17:13 | AM by SYSTE | M | | | |
| | (modifi | ed after lo | ading) | | | | |
| Additional Inf | o : Peak(s) | manually i | ntegrated | | | | |
| DAD1 C, S | ig=210,4 Ref=360,1 | 100 (YANGTAO\YT | -2-163BC 2017-11-1 | 6 11-05-07\006-P1-A6- | YT-2-163B-CHIRA | L.D) | |
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| | | Area Percen | t Report | | | | |
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| and a first | | <i>a</i> / | | | | | |
| Sorted By | : | Signal | | | | | |
| Multipiler | : | 1.0000 | | | | | |
| Jiiution | : C Dilution | I.UUUU | L TOWDA | | | | |
| /se Muitipilêr | & Dilution | ractor wit | n istus | | | | |
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| 0/1 1. F3-54 | a ai - ai a | 1 8-6 363 | 1.0.0 | | | | |
| Signai 1: DAD1 | C, Sig=210 | ,4 Ref=360, | 100 | | | | |

| Peak Re | tTime | Type | Width | Area | Height | Area |
|---------|-------|----------|------------------|------------------------|-----------------------|-------------------|
| # | min] | | [min] | [mAU*s] | [mAU] | % |
| 1 1 2 2 | 3.307 | BB BB | 0.2024 0.3380 | 1.00749e4 775.06598 | 761.04272 35.31589 | 92.8565 7.1435 |

Totals : 1.08499e4 796.35862





Totals : 2608.46026 252.53815



| Acg. Operator | : SYSTEM | | | Seg. Line | : | 3 | | | |
|-----------------|-------------------|------------------|------------------------|---------------------|-------|-------------------|-----------|----------|-----|
| Acq. Instrument | : 1260-D | AD | | Location | : | P1-C-02 | | | |
| Injection Date | : 11/27/ | 2017 21:06:3 | 4 | Inj | : | 1 | | | |
| | | | | Inj Volume | : 1 | .000 µl | | | |
| Acq. Method | : d:\Che | m32\1\Data\Y | ANGTAO\YT-2 | 2-175 2017-11 | 1-27 | 19-57-43\Y | ANGT-AD-3 | -80-20-0 | .5- |
| | 30MIN | .M | | | | | | | |
| Last changed | : 11/27/ | 2017 20:30:4 | 5 by SYSTEM | М | | | | | _ |
| Analysis Method | : d:\Che 30MIN | .M (Sequence | ANGTAO\YT-2 Method) | 2-175 2017-11 | 1-27 | 19-57-43\Y | ANGT-AD-3 | -80-20-0 | .5- |
| Last changed | : 12/9/2 | 017 17:51:28 | by SYSTEM | | | | | | |
| Additional Info | : Peak(s |) manually i | ntegrated | | | | | | |
| DAD1 C, Sig | =210,4 Ref=36 | ,100 (YANGTAO\YT | 5 2017-11-27 19 | 9-57-43\YT-2-175A-C | HIRAL | -2017-11-27-21-05 | i-47.D) | | |
| mAU | | | 87 | | | | | | |
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| 15 1 | 7.5 | 20 22.5 | 25 | 27.5 | 30 | 32.5 | 35 | 37.5 | min |
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| | | Area Percen | t Report | | | | | | |
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| Sorted By | : | Signal | | | | | | | |
| Dilution | : | 1 0000 | | | | | | | |
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Height Area

8

Totals :

Use Multiplier & Dilution Factor with ISTDs

[min] [min] [mAU*s] [mAU]

1 24.787 BB 0.4297 3767.78003 132.51323 96.4970

2 28.848 BB 0.5366 136.77548 3.52586 3.5030

3904.55551 136.03909

Signal 1: DAD1 C, Sig=210,4 Ref=360,100

Peak RetTime Type Width Area



| Acq. Operator | : SYSTEM | | Seq. Line | : 2 | | |
|----------------------------|---------------------------------|-------------------------------|-------------------|---------------------|----------------|---------|
| Acq. Instrument | : 1260-DAD | | Location | : P1-D-02 | | |
| Injection Date | : 11/20/2017 16:3 | 16:08 | Inj | : 1 | | |
| | | I | nj Volume | : 1.000 µl | | |
| Acq. Method | : d:\Chem32\1\Dat | a\YANGTAO\YANGTA | 0-2-169-A | 2017-11-20 16 | -06-25\YT-AD3- | 80-20-1 |
| | mL-30Min.M | | | | | |
| Last changed | : 11/20/2017 16:3 | 3:19 by SYSTEM | | | | |
| Analysis Method | : d:\Chem32\1\Dat | a\YANGTAO\YANGTA | 0-2-169-A | 2017-11-20 16 | -06-25\YT-AD3- | 80-20-1 |
| | mL-30Min.M (Sec | [uence Method) | | | | |
| Last changed | : 12/9/2017 17:45 | :15 by SYSTEM | | | | |
| | (modified after | loading) | | | | |
| Additional Info | : Peak(s) manual: | y integrated. | | | | |
| DAD1 A, Sig | 220,4 Ref=360,100 (YANGT/ | OIYANGTAO-2-169-A 201 | -11-20 16-06-25 | 002-P1-D2-YT-2-169A | -CHIRAL.D) | |
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| | Area Per | cent Report | | | | |
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| Sorted By | : Sign | ai | | | | |
| Multiplier | : 1.00 | 00 | | | | |
| Dilution | : 1.00 | 00 | | | | |
| Jse Multiplier | Dilution Factor | with ISTDs | | | | |
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| | | | | | | |
| Signal 1: DAD1 2 | A, Sig=220,4 Ref=3 | 60,100 | | | | |
| | | | | | | |
| Peak RetTime Typ | pe Width Area | . Height | Area | | | |
| # [min] | [min] [mAU*s | [mAU] | 윢 | | | |
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| | | | | | | |
| 1 16.994 BB | 0.3106 1408.07 | '959 70.02197 | 92.4680 | | | |
| 1 16.994 BB 2 24.071 BB | 0.3106 1408.07 0.4522 114.69 | 1959 70.02197 1593 3.77794 | 92.4680 7.5320 | | | |
| 1 16.994 BB 2 24.071 BB | 0.3106 1408.0 0.4522 114.69 | 7959 70.02197 9593 3.77794 | 92.4680 7.5320 | | | |



| 1260-DAD 11/28/2017 d:\Chem32\ 5-30MIN .h 11/28/2017 d:\Chem32\ 5-30MIN .h 12/9/2017 (modified Peak(s) ma | 7 09:50:49 (1)Data\YANG M 7 09:10:06 b (1)Data\YANG M (Sequence 17:55:34 by after loadi anually inte (YANGTAO\YTB) | TAO\YT-2 Y SYSTEM TAO\YT-2 Method) SYSTEM ng) grated 2017-11-28 06 | Locati I Inj Volu -175-B 20 -175-B 20 | on : nj : me : 1 17-11 17-11 | P1-C-04 1 1.000 µl -28 09-09- -28 09-09- | 06\YANGT-AD- 06\YANGT-AD- 9-50-01.D) | -3-80-20- |
|--|---|---|---|--|---|--|----------------------------|
| 11/28/2017 d:\Chem32\ 5-30MIN .N 11/28/2017 d:\Chem32\ 5-30MIN .N 12/9/2017 (modified Peak(s) ma 10,4 Ref=360,100 (| 7 09:50:49 (1)Data\YANG 7 09:10:06 b (1)Data\YANG 4 (Sequence 17:55:34 by after loadi anually inte (YANGTAOVYTB) | TAO\YT-2 y SYSTEM TAO\YT-2 Method) 'SYSTEM ng) grated 2017-11-28 05 | I Inj Volu -175-B 20 4 -09-06/YT-2-175 8 | nj : me : 1 17-11 | 1 1.000 µ1 -28 09-09- -28 09-09- | 06\YANGT-AD- 06\YANGT-AD- 9-50-01.D) | -3-80-20- -3-80-20- |
| d:\Chem32\ 5-30MIN . 11/28/2017 d:\Chem32\ 5-30MIN . 12/9/2017 (modified Peak(s) mm 0.4 Ref=360,100 (| <pre>\1\Data\YANG M 7 09:10:06 b 1\Data\YANG M (Sequence 17:55:34 by after loadi anually inte (YANGTAOVYT_B)</pre> | TAO\YT-2 y SYSTEM TAO\YT-2 Method) · SYSTEM ng) grated 2017-11-28 05 | Inj Volu -175-B 20 4 -175-B 20 | me : : : 17-11- 17-11- | 1.000 μ1 -28 09-09- -28 09-09- AL-2017-11-28-0 | 06\YANGT-AD- 06\YANGT-AD- 9-50-01.D) | -3-80-20- -3-80-20- |
| d:\Chem32\ 5-30MIN .h 11/28/2017 d:\Chem32\ 5-30MIN .h 12/9/2017 (modified Peak(s) mm 10.4 Ref=360,100 (| <pre>\\\Data\YANG 4 7 09:10:06 h \\\Data\YANG 4 (Sequence 17:55:34 by after loadi anually inte anually inte (YANGTAOLYTB)</pre> | TAO\YT-2 y SYSTEM TAO\YT-2 Method) · SYSTEM ng) grated 2017-11-28 06 | I-175-В 20 I I-175-В 20 | 17-11- 17-11- | -28 09-09- -28 09-09- AL-2017-11-28-0 | 06\YANGT-AD- 06\YANGT-AD- 9-50-01.D) | -3-80-20- |
| 5-30MIN .N 11/28/2017 d:\Chem32 5-30MIN .N 12/9/2017 (modified Peak(s) ma 0.4 Ref=360,000 | M 7 09:10:06 b 1\Data\YANG M (Sequence 17:55:34 by after loadi anually inte anually inte (YANGTAOVYT_B) | y SYSTEM TAO\YT-2 Method) SYSTEM ng) grated 2017-11-28 05 | t -175-B 20 ⊷09-06\YT-2-174 | 17–11 | -28 09-09- AL-2017-11-28-0 | 06\YANGT-AD- 3-50-01.D) | -3-80-20- |
| 11/28/2017 d:\Chem32' 5-30MTN .N 12/9/2017 (modified Peak(s) ma 10,4 Ref=360,100 (| 7 09:10:06 b (1\Data\YANG (Sequence 17:55:34 by after loadi anually inte (YANGTAOVYT_B: | y SYSTEM TAO\YT-2 Method) · SYSTEM ng) grated 2017-11-28 06 | I -175-B 20 | 17-11 | -28 09-09- AL-2017-11-28-0 | 06\YANGT-AD- 9-50-01.D) | -3-80-20- |
| d:\Chem32 5-30MIN.h 12/9/2017 (modified Peak(s) ma 10,4 Ref=360,100 (| <pre>\\\Data\YANG 4 (Sequence 17:55:34 by after loadi anually inte (YANGTAONYT_B)</pre> | TAO\YT-2 Method) · SYSTEM ng) grated 2017-11-28 09 | -175-в 20 | 17–11 | -28 09-09- | 06\YANGT-AD- 9-50-01.D) | -3-80-20- |
| 5-30MIN .N 12/9/2017 (modified Peak(s) ma 10,4 Ref=360,100 (| M (Sequence 17:55:34 by after loadi anually inte (YANGTAO(YTB) | Method) SYSTEM ng) grated 2017-11-28 05 | -09-06\YT-2-17: | 5B-CHIR | AL-2017-11-28-0 | 9-50-01.D) | |
| 12/9/2017 (modified Peak(s) ma 10.4 Ref=360,100 (| 17:55:34 by after loadi anually inte (YANGTAOYYT_B: | SYSTEM ng) grated 2017-11-28 05 | -09-06\YT-2-17 | B-CHIR | AL-2017-11-28-0 | 9-50-01.D) | |
| (modified Peak(s) ma 10,4 Ref=360,100 (| after loadi anually inte (YANGTAO(YT.B: | ng) grated 2017-11-28 09 | ⊢09-06\YT-2-179 | B-CHIR | AL-2017-11-28-0 | 9-50-01.D) | |
| Peak(s) ma 10,4 Ref=360,100 (| anually inte | grated 2017-11-28 09 | -09-06\YT-2-175 | B-CHIR | AL-2017-11-28-0 | 9-50-01.D) | |
| 0,4 Ref=360,100 (| (YANGTAOIYTB : | 2017-11-28 05 | -09-06(YT-2-175 | B-CHIR | AL-2017-11-28-0 | 9-50-01.D) | |
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| 5 20 | 22.5 | 25 | 27.5 | 30 | 32.5 | 35 | 37.5 |
| | 20 | 20 22.5 | 20 22.5 25 | 20 22.5 25 27.5 | 20 22.5 25 27.5 30 | 20 225 25 27.5 30 32.5 | 20 22.5 25 27.5 30 32.5 35 |

| 1 | Peak # | RetTime [min] | Туре | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|-----------|------------------|------|----------------|-----------------|-----------------|-----------|
| | | | | | | | |
| | 1 | 28.879 | BB | 0.5211 | 5574.14453 | 162.12366 | 98.9920 |
| | 2 | 34.576 | FM | 0.5711 | 56.75779 | 1.65625 | 1.0080 |
| | | | | | | | |
| | [ota] | s: | | | 5630.90232 | 163.77991 | |