Supporting Information

Water-mediated one-pot multi-step synthesis of chiral 1,3- diarylpropan-1-ols by asymmetric hydrofunctionalisation of simple alkynes

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1. General information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel. NMR spectra were recorded on Bruker AVANCE III (400 MHz) spectrometers. CDCl₃ was used for the NMR analysis with tetramethyl silane as the internal standard. Chemical shifts were reported upfield to TMS (0.00 ppm) for ¹H NMR and relative to CDCl₃ (77.0 ppm) for ¹³C NMR. HPLC analyses were performed on a Waters 2489 series instrument with chiral column OD-H, IA-H, AD-H, IC-H and OJ-H. Optical rotations were measured using an MCP-500. HRMS spectra were acquired on an Agilent 6210 ESI/TOF mass spectrometer.

2. General procedure for the synthesis of racemic 1,3-diarylpropan-1-ols



To a solution of chalcone derivative (0.25 mmol) in methanol (2 mL) was added NaBH₄ (38 mg, 1 mmol) at 0 °C. The mixture was stirred at 0 °C until the reaction was completed (monitored by TLC). Then Pd/C (26.5 mg, 0.25 mmol, 10%), AcOH (1 mL) and NaBH₄ (38 mg, 1 mmol) were added and stirred at 0 °C for 5 min. Pd/C was removed by filtration, the solvent was concentrated under reduced pressure. The residue was purified by thin layer chromatography to yield racemic 1,3-diphenylpropan-1-ol.

3. General procedure for the asymmetric hydrofunctionalisation of aryl alkynes



Under nitrogen atmosphere, alkyne (0.5 mmol), aldehyde (0.6 mmol) and 50% H₃PO₃ (82 mg, 0.5 mmol in H₂O) were added to a 10 mL Schlenk tube. The reaction mixture was stirred at 110 °C for 24 h. Then (*R*,*R*)-10 (1.9 mg, 0.5 mol%), CTAB (36.4 mg, 0.1 mol), HCOONa (170 mg, 2.5 mmol) and H₂O (1 mL) were added, the reaction mixture was stirred at 50 °C for 12 h. Then water (2 mL) was added and extracted with EtOAc, the combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was further purified by thin layer chromatography to afford desired product.

4. Gram-scale synthesis



S/C = 2 000: Under nitrogen atmosphere, phenylacetylene (1a, 1.02 g, 10 mmol), benzaldehyde (2a, 1.27 g, 12 mmol) and 50% H₃PO₃ (1.64 g, 10 mmol in H₂O) were added to a 50 mL Schlenk tube. The reaction mixture was stirred at 110 °C for 24 h. Then (*R*,*R*)-10 (3.8 mg, 0.05 mol%), CTAB (0.73 g, 2 mmol), HCOONa (3.40 g, 50 mmol) and H₂O (10 mL) were added. the reaction mixture was stirred at 50 °C for 12 h. Then water (10 mL) was added and extracted with EtOAc. the combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was further purified by silica gel column chromatography to afford chiral 4-phenyl-2-oxazolidanone **3a** with 74% yield and 98% ee.

S/C = 10~000: Under nitrogen atmosphere, phenylacetylene (1a, 2.04 g, 20 mmol), benzaldehyde (2a, 2.54 g, 24 mmol) and 50% H₃PO₃ (3.28 g, 20 mmol in H₂O) were added to a 50 mL Schlenk tube. The reaction mixture was stirred at 110 °C for 24 h. Then (*R*,*R*)-10 (1.5 mg, 0.01 mol%), CTAB (1.46 g, 4 mmol), HCOONa (6.80 g, 100 mmol) and H₂O (10 mL) were added, the reaction mixture was stirred at 50 °C for 24 h. Then water (20 mL) was added and extracted with EtOAc. the combined organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was further purified by silica gel column chromatography to afford chiral 4-phenyl-2-oxazolidanone **3a** with 68% yield and 98% ee.

5. Synthetic transformations of chiral secondary alcohol products



Synthesis of chiral chroman 6¹⁰

To a solution of **4d** (145 mg, 0.5 mmol, 97% ee) in anhydrous diglyme (2 mL) was added CuI (9.5 mg, 0.05 mmol), NaOMe (40.5 mg, 0.75 mmol) and 2-aminopyridine (9.4 mg, 0.1 mmol). The mixture was stirred at 100 °C for 24 h and then quenched with water, extracted with EtOAc.

The organic phase was dried over Na₂SO₄, evaporated under reduced pressure and the residue was purified by silica gel column chromatography to afford chiral chroman **6** as a yellow oil (57.8 mg, 55% yield, 93% ee); $[\alpha]_D^{25} = +30.4$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.46 – 7.27 (m, 5H), 7.14 – 7.06 (m, 2H), 6.92 – 6.84 (m, 2H), 5.06 – 5.02 (m, 1H), 3.02 – 2.93 (m, 1H), 2.81 – 2.74 (m, 1H), 2.22 – 2.15 (m, 1H), 2.12 – 2.02 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 155.1, 141.7, 129.5, 128.5, 127.8, 127.3, 126.0, 121.8, 120.3, 116.9, 77.7, 29.9, 25.0; HPLC (Chiralcel IA-H column, *n*-hexane, 0.4 mL/min; 220 nm): t_R = 27.0 min (minor), 28.9 min (major).

Synthesis of (R)-BW683C¹⁰

To a solution of **5d** (89.5 mg, 0.25 mmol, 93% ee) in anhydrous diglyme (1 mL) was added CuI (4.8 mg, 0.025 mmol), NaOMe (20.3 mg, 0.375 mmol) and 2-aminopyridine(4.7 mg, 0.05 mmol). The mixture was stirred at 100 °C for 24 h and then quenched with water, extracted with EtOAc. The organic phase was dried over Na₂SO₄, evaporated under reduced pressure and the residue was purified by silica gel column chromatography to afford (*R*)-**BW683C** as a white solid (32.0 mg, 46% yield, 92% ee); $[\alpha]_D^{25} = +3.8$ (*c* = 1.0, CHCl₃); ¹**H** NMR (400 MHz, CDCl₃) δ 7.37 – 7.31 (m, 4H), 7.11 – 7.01 (m, 2H), 6.83 – 6.75 (m, 1H), 5.01 (dd, *J* = 10.1, 2.5 Hz, 1H), 2.99 – 2.90 (m, 1H), 2.78 – 2.71 (m, 1H), 2.21 – 2.15 (m, 1H), 2.06 – 1.96 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 153.4, 139.7, 133.7, 129.0, 128.7, 127.4, 127.3, 125.2, 123.2, 118.2, 77.1, 29.4, 24.8; **HPLC** (Chiralcel IA-H column, *n*-hexane : isopropanol = 99 : 1 (v/v); 1.0 mL/min; 220 nm): t_R = 6.3 min (minor), 7.1 min (major).

6. Analytical data of chiral alcohols

(*R*)-1,3-diphenylpropan-1-ol¹ (**3a**, known compound)



Colorless oil, 85.9 mg, 81% yield, 98% ee; $[\alpha]_D^{25} = +37.0 \ (c = 1.0, \text{CHCl}_3); {}^{1}\text{H} \text{ NMR} (400 \text{ MHz}, \text{CDCl}_3) \delta 7.35 - 7.16 \ (m, 10\text{H}), 4.67 \ (dd, J = 7.8, 5.4 \text{ Hz}, 1\text{H}), 2.78 - 2.62 \ (m, 2\text{H}), 2.17 - 1.97 \ (m, 3\text{H}); {}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, \text{CDCl}_3) \delta 144.5, 141.7, 128.5, 128.4, 128.4, 127.6, 125.9, 125.8, 73.8, 40.4, 32.0; \text{HPLC} (Chiralcel OD-H column,$ *n* $-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 17.0 min (minor), 20.1 min (major).$

(*R*)-3-phenyl-1-(*o*-tolyl)propan-1-ol³ (**3b**, known compound)



Colorless oil, 81.4 mg, 72% yield, 99% ee; $[\alpha]_D^{25} = +108.2$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz,

CDCl₃) δ 7.48 (d, J = 9.2 Hz, 1H), 7.30 – 7.07 (m, 8H), 4.91 (dd, J = 8.3, 4.4 Hz, 1H), 2.87 – 2.68 (m, 2H), 2.22 (s, 3H), 2.10 – 1.93 (m, 2H), 1.81 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.7, 141.8, 134.4, 130.4, 128.4, 128.4, 127.2, 126.3, 125.8, 125.1, 69.9, 39.4, 32.3, 18.9; HPLC (Chiralcel AD-H column, *n*-hexane : isopropanol = 99 : 1 (v/v); 1.0 mL/min; 220 nm): t_R = 29.6 min (minor), 32.5 min (major).

(R)-1-(2-methoxyphenyl)-3-phenylpropan-1-ol¹ (3c, known compound)



Colorless oil, 66.6 mg, 55% yield, 78% ee; $[\alpha]_D^{25} = +29.8$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.15 (m, 7H), 6.95 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 8.2 Hz, 1H), 4.88 (dd, J = 8.0, 5.1 Hz, 1H), 3.83 (s, 3H), 2.87 – 2.79 (m, 1H), 2.72 – 2.64 (m, 2H), 2.20 – 2.05 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 156.6, 142.1, 132.2, 128.4, 128.3, 128.3, 127.0, 125.7, 120.7, 110.5, 70.7, 55.2, 38.6, 32.3; HPLC (Chiralcel IB-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 10.3 min (minor), 12.6 min (major).

(R)-1-(2-fluorophenyl)-3-phenylpropan-1-ol¹ (3d, known compound)



Yellow oil, 74.8 mg, 65% yield, 75% ee; $[\alpha]_D^{25} = +21.0$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.46 (td, J = 7.5, 1.9 Hz, 1H), 7.28 – 7.12 (m, 7H), 7.04 – 6.99 (m, 1H), 5.02 (dd, J = 7.7, 5.3 Hz, 1H), 2.81 – 2.65 (m, 2H), 2.13 – 2.03 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.8 (d, J = 245.4 Hz), 141.6, 131.4 (d, J = 13.2 Hz), 128.9 (d, J = 8.3 Hz), 128.4, 128.4, 127.3 (d, J = 4.5 Hz), 125.9, 124.3 (d, J = 3.5 Hz), 115.3 (d, J = 21.9 Hz), 67.9 (d, J = 2.4 Hz), 39.4, 32.0; HPLC (Chiralcel IA-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 9.1 min (minor), 10.1 min (major).

(*R*)-1-(3-fluorophenyl)-3-phenylpropan-1-ol³ (3e, known compound)



Yellow oil, 64.4 mg, 56% yield, 96% ee; $[\alpha]_D^{25} = +12.0 \ (c = 1.0, \text{ CHCl}_3)$; ¹**H NMR** (400 MHz, CDCl₃) δ 7.32 – 7.25 (m, 3H), 7.21 – 7.17 (m, 3H), 7.10 – 7.05 (m, 2H), 6.96 (td, J = 8.4, 2.7 Hz, 1H), 4.68 (dd, J = 7.9, 5.2 Hz, 1H), 2.78 – 2.63 (m, 2H), 2.12 – 1.96 (m, 3H); ¹³**C NMR** (100 MHz,

CDCl₃) δ 162.9 (d, J = 246.0 Hz), 147.3 (d, J = 6.6 Hz), 141.5, 130.0 (d, J = 8.1 Hz), 128.4, 128.4, 125.9, 121.4 (d, J = 2.8 Hz), 114.4 (d, J = 21.2 Hz), 112.8 (d, J = 21.7 Hz), 73.2, 40.4, 31.9; **HPLC** (Chiralcel IA-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 10.5 min (minor), 12.4 min (major).

(*R*)-3-phenyl-1-(*p*-tolyl)propan-1-ol¹ (**3f**, known compound)



Colorless oil, 90.4 mg, 80% yield, 98% ee; $[\alpha]_D^{25} = +36.8 (c = 1.0, \text{CHCl}_3)$; ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.13 (m, 9H), 4.61 (dd, J = 7.7, 5.5 Hz, 1H), 2.75 – 2.59 (m, 2H), 2.33 (s, 3H), 2.15 – 1.95 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.8, 141.5, 137.3, 129.1, 128.4, 128.3, 125.9, 125.8, 73.7, 40.3, 32.0, 21.1; HPLC (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 15.0 min (minor), 18.2 min (major).

(*R*)-1-(4-ethylphenyl)-3-phenylpropan-1-ol (**3g**, unknown compound)



Yellow oil, 90.1 mg, 75% yield, 99% ee; $[\alpha]_D^{25} = +28.2$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.15 (m, 9H), 4.64 (dd, J = 7.8, 5.5 Hz, 1H), 2.77 – 2.61 (m, 4H), 2.15 – 1.95 (m, 3H), 1.23 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.7, 141.8, 141.8, 128.4, 128.3, 128.0, 125.9, 125.8, 73.7, 40.3 , 32.1, 28.5, 15.6; HRMS (ESI) Calculated for C₁₅H₂₀NO₂ [M+Na]⁺ 263.1406; found 263.1405; HPLC (Chiralcel OJ-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 12.0 min (major), 16.2 min (minor).

(*R*)-1-(4-isopropylphenyl)-3-phenylpropan-1-ol³ (**3h**, known compound)



Yellow oil, 101.7 mg, 80% yield, 99% ee; $[\alpha]_D^{25} = +40.0 \ (c = 1.0, \text{CHCl}_3); {}^{1}\text{H} \text{NMR}$ (400 MHz, CDCl₃) δ 7.29 – 7.15 (m, 9H), 4.64 (dd, J = 7.9, 5.4 Hz, 1H), 2.93 – 2.84 (m, 1H), 2.78 – 2.61 (m, 2H), 2.15 – 1.94 (m, 3H), 1.24 (d, J = 6.9 Hz, 6H); ${}^{13}\text{C}$ NMR (100 MHz, CDCl₃) δ 148.3, 141.9, 141.8, 128.4, 128.3, 126.5, 125.9, 125.7, 73.7, 40.3, 33.8, 32.1, 24.0; HPLC (Chiralcel IB-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 8.3 min (minor), 9.7 min (major).

(*R*)-1-(4-(tert-butyl)phenyl)-3-phenylpropan-1-ol¹ (**3i**, known compound)



Yellow oil, 111.3 mg, 83% yield, >99% ee; $[\alpha]_D^{25} = +27.6 \ (c = 1.0, \text{CHCl}_3); {}^{1}\text{H} \text{NMR}$ (400 MHz, CDCl₃) δ 7.38 – 7.15 (m, 9H), 4.64 (dd, J = 7.9, 5.4 Hz, 1H), 2.79 – 2.62 (m, 2H), 2.17 – 1.99 (m, 2H), 1.95 (s, 1H), 1.31 (s, 9H); {}^{13}\text{C} \text{NMR} (100 MHz, CDCl₃) δ 150.6, 141.8, 141.5, 128.4, 128.3, 125.8, 125.6, 125.4, 73.6, 40.2, 34.5, 32.1, 31.3; HPLC (Chiralcel OJ-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 10.2 min (major), 15.6 min (minor).

(R)-1-(4-methoxyphenyl)-3-phenylpropan-1-ol¹ (3j, known compound)



Colorless oil, 89.6 mg, 74% yield, 98% ee; $[\alpha]_D^{25} = +29.6$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.16 (m, 7H), 6.90 – 6.86 (m, 2H), 4.62 (dd, J = 7.7, 5.7 Hz, 1H), 3.80 (s, 3H), 2.75 – 2.59 (m, 2H), 2.16 – 1.96 (m, 2H), 1.91 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 159.0, 141.8, 136.6, 128.4, 128.3, 127.2, 125.8, 113.8, 73.4, 55.3, 40.3, 32.1; HPLC (Chiralcel AD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 19.6 min (major), 22.0 min (minor).

(*R*)-1-(4-fluorophenyl)-3-phenylpropan-1-ol¹ (3k, known compound)



Yellow oil, 78.2 mg, 68% yield, 92% ee; $[\alpha]_D^{25} = +16.6$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 6.99 (m, 9H), 4.65 (dd, J = 7.8, 5.4 Hz, 1H), 2.75 – 2.60 (m, 2H), 2.13 – 1.95 (m, 3H).; ¹³C NMR (100 MHz, CDCl₃) δ 162.1 (d, J = 245.4 Hz), 141.5, 140.2 (d, J = 3.2 Hz), 128.4, 128.4, 127.5 (d, J = 8.0 Hz), 125.9, 115.3 (d, J = 21.3 Hz), 73.1, 40.5, 31.9; HPLC (Chiralcel IA-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 10.6 min (minor), 12.0 min (major).

(R)-1-(4-chlorophenyl)-3-phenylpropan-1-ol¹ (**3**l, known compound)



Colorless oil, 96.0 mg, 78% yield, 95% ee; $[\alpha]_D^{25} = +17.0$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.16 (m, 9H), 4.64 (dd, J = 7.8, 5.3 Hz, 1H), 2.75 – 2.60 (m, 2H), 2.15 – 1.95 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.0, 141.4, 133.2, 128.6, 128.4, 128.4, 127.3, 125.9, 73.1, 40.4, 31.9; HPLC (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 17.9 min (minor), 22.1 min (major).

(R)-1-(4-bromophenyl)-3-phenylpropan-1-ol¹ (**3m**, known compound)



Colorless oil, 114.6 mg, 79% yield, 95% ee; $[\alpha]_D^{25} = +15.2$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.43 (m, 2H), 7.29 – 7.15 (m, 7H), 4.62 (dd, J = 7.9, 5.3 Hz, 1H), 2.73 – 2.60 (m, 2H), 2.12 – 1.93 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.5, 141.4, 131.5, 128.4, 128.4, 127.6, 125.9, 121.3, 73.1, 40.4, 31.8; HPLC (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 19.3 min (minor), 23.8 min (major).

(*R*)-3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-ol¹ (**3n**, known compound)



Yellow oil, 50.4 mg, 36% yield, 95% ee; $[\alpha]_D^{25} = +10.4$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.30 – 7.18 (m, 5H), 4.75 (dd, J = 8.0, 5.1 Hz, 1H), 2.79 – 2.65 (m, 2H), 2.15 – 1.97 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 148.5, 141.3, 129.7 (q, J = 32.3 Hz), 128.5, 128.4, 126.1, 126.0, 125.4 (q, J = 3.8 Hz), 124.3 (q, J = 272.0 Hz), 73.1, 40.5, 31.8; HPLC (Chiralcel IB-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 10.6 min (minor), 11.9 min (major).

(*R*)-3-phenyl-1-(thiophen-2-yl)propan-1-ol¹ (**30**, known compound)



Colorless oil, 89.4 mg, 82% yield, 99% ee; $[\alpha]_D^{25} = +18.0 (c = 1.0, \text{CHCl}_3)$; ¹**H NMR** (400 MHz, CDCl₃) δ 7.30 – 7.17 (m, 6H), 6.97 – 6.95 (m, 2H), 4.91 (dd, J = 7.6, 5.7 Hz, 1H), 2.79 – 2.66 (m, 2H), 2.24 – 2.08 (m, 3H); ¹³**C NMR** (100 MHz, CDCl₃) δ 148.5, 141.4, 128.5, 128.4, 126.6, 125.9, 124.6, 123.9, 69.5, 40.7, 32.0; **HPLC** (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 17.7 min (minor), 24.5 min (major).

(*R*)-1-phenyl-3-(*o*-tolyl)propan-1-ol³ (4a, known compound)



Colorless oil, 82.5 mg, 73% yield, 98% ee; $[\alpha]_D^{25} = +42.0 \ (c = 1.0, \text{CHCl}_3); {}^{1}\text{H} \text{NMR}$ (400 MHz, CDCl₃) δ 7.37 – 7.25 (m, 5H), 7.14 – 7.06 (m, 4H), 4.71 (dd, J = 7.8, 5.3 Hz, 1H), 2.78 - 2.57 (m, 2H), 2.25 (s, 3H), 2.11 – 1.92 (m, 3H); {}^{13}\text{C} \text{NMR} (100 MHz, CDCl₃) δ 144.5, 140.0, 135.9, 130.2, 128.7, 128.5, 127.6, 126.0, 125.9, 74.2, 39.2, 29.4, 19.2; **HPLC** (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 17.2 min (minor), 19.3 min (major).

(*R*)-3-(2-fluorophenyl)-1-phenylpropan-1-ol² (4b, known compound)



Yellow oil, 79.4 mg, 69% yield, 97% ee; $[\alpha]_D^{25} = +36.8 (c = 1.0, \text{CHCl}_3)$; ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.24 (m, 5H),7.20 – 7.13 (m, 2H), 7.04 – 6.95 (m, 2H), 4.68 (dd, J = 8.0, 5.2 Hz, 1H), 2.83 – 2.65 (m, 2H), 2.14 – 1.97 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.1 (d, J = 244.7 Hz), 144.4, 130.6 (d, J = 5.1 Hz), 128.6, 128.5, 127.6, 127.6, 127.5, 125.9, 115.2 (d, J = 22.3 Hz), 73.8, 39.1, 25.5 (d, J = 2.4 Hz); HPLC (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 12.5 min (minor), 13.1 min (major).

(R)-3-(2-chlorophenyl)-1-phenylpropan-1-ol⁶ (4c, known compound)



Colorless oil, 91.0 mg, 74% yield, 95% ee; $[\alpha]_D^{25} = +40.6$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.12 (m, 9H), 4.71 (dd, J = 7.8, 5.3 Hz, 1H), 2.93 – 2.85 (m, 1H), 2.80 – 2.73 (m, 1H), 2.14 – 1.99 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.3, 139.4, 133.9, 130.4, 129.5, 128.5, 127.6, 127.4, 126.8, 125.9, 73.9, 38.7, 30.0; HPLC (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 14.8 min (minor), 17.8 min (major).

(R)-3-(2-bromophenyl)-1-phenylpropan-1-ol⁵ (4d, known compound)



Colorless oil, 120.4 mg, 83% yield, 97% ee; $[\alpha]_D^{25} = +38.4$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.49 (m, 1H), 7.37 – 7.18 (m, 7H), 7.07 – 7.01 (m, 1H), 4.71 (dd, J = 7.7, 5.4 Hz, 1H), 2.92 – 2.72 (m, 2H), 2.12 – 1.98 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.3, 141.1, 132.8, 130.4, 128.5, 127.6, 127.6, 127.4, 125.9, 124.4, 73.9, 38.8, 32.5; HPLC (Chiralcel OJ-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 15.3 min (major), 16.9 min (minor).

(*R*)-1-phenyl-3-(*m*-tolyl)propan-1-ol³ (4e, known compound)



Colorless oil, 90.5 mg, 80% yield, 98% ee; $[\alpha]_D^{25} = +37.8$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.23 (m, 5H), 7.18 – 7.13 (m, 1H), 7.00 – 6.97 (m, 3H), 4.67 (dd, J = 7.8, 5.3 Hz, 1H), 2.74 – 2.58 (m, 2H), 2.31 (s, 3H), 2.17 – 1.96 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 141.7, 137.9, 129.2, 128.5, 128.3, 127.6, 126.6, 125.9, 125.4, 73.9, 40.5, 31.9, 21.4; HPLC (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 13.5 min (minor), 16.7 min (major).

(R)-3-(3-methoxyphenyl)-1-phenylpropan-1-ol² (4f, known compound)



Yellow oil, 61.7 mg, 51% yield, 98% ee; $[\alpha]_D^{25} = +31.4$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.17 (m, 6H), 6.79 – 6.71 (m, 3H), 4.67 (dd, J = 7.9, 5.3 Hz, 1H), 3.77 (s, 3H), 2.75 – 2.59 (m, 2H), 2.16 – 1.96 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 159.6, 144.5, 143.4, 129.3, 128.5, 127.6, 125.9, 120.8, 114.1, 111.1, 73.8, 55.1, 40.3, 32.1; HPLC (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 26.6 min (minor), 34.2 min (major).

(*R*)-1-phenyl-3-(*p*-tolyl)propan-1-ol³ (4g, known compound)



Colorless oil, 75.8 mg, 67% yield, 98% ee; $[\alpha]_D^{25} = +18.6$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.25 (m, 1H), 7.08 (s, 4H), 4.67 (dd, J = 7.8, 5.4 Hz, 1H), 2.73 – 2.58 (m, 2H), 2.31 (s, 3H), 2.19 – 1.93 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 138.6, 135.3, 129.0, 128.5, 128.3, 127.6, 125.9, 73.9, 40.5, 31.6, 21.0; HPLC (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 12.7 min (major), 15.4 min (minor).

(R)-3-(4-(tert-butyl)phenyl)-1-phenylpropan-1-ol⁸ (4h, known compound)



Colorless oil, 93.9 mg, 70% yield, 96% ee; $[\alpha]_D^{25} = +25.8 (c = 1.0, \text{CHCl}_3)$; ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.24 (m, 7H), 7.14 – 7.09 (m, 2H), 4.68 (dd, J = 7.8, 5.4 Hz, 1H), 2.75 – 2.58 (m, 2H), 2.16 – 1.96 (m, 3H), 1.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 148.6, 144.6, 138.6, 128.5, 128.0, 127.6, 125.9, 125.2, 73.9, 40.4, 34.3, 31.5, 31.4; HPLC (Chiralcel IB-H column, *n*-hexane : isopropanol = 98 : 2 (v/v); 1.0 mL/min; 220 nm): t_R = 12.1 min (major), 12.9 min (minor).

(R)-3-(4-chlorophenyl)-1-phenylpropan-1-ol³ (4i, known compound)



Colorless oil, 99.7 mg, 81% yield, 98% ee; $[\alpha]_D^{25} = +19.2$ (c = 1.0, CHCl₃); ¹**H NMR** (400 MHz, CDCl₃) δ 7.36 – 7.25 (m, 7H), 7.13 – 7.08 (m, 2H), 4.65 (dd, J = 7.9, 5.3 Hz, 1H), 2.75 – 2.59 (m, 2H), 2.14 – 1.93 (m, 3H); ¹³**C NMR** (100 MHz, CDCl₃) δ 144.4, 140.2, 131.5, 129.8, 128.6, 128.4, 127.7, 125.9, 73.7, 40.3, 31.3; **HPLC** (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 12.9 min (major), 14.5 min (minor).

(R)-3-(4-bromophenyl)-1-phenylpropan-1-ol³ (4j, known compound)



Colorless oil, 116.0 mg, 80% yield, 99% ee; $[\alpha]_D^{25} = +17.2$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.26 (m, 7H), 7.07 – 7.03 (m, 2H), 4.65 (dd, J = 7.9, 5.3 Hz, 1H), 2.73 – 2.57 (m, 2H), 2.13 – 1.93 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.3, 140.7, 131.4, 130.2, 128.5, 127.7, 125.8, 119.5, 73.6, 40.2, 31.4; HPLC (Chiralcel OJ-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); flow

rate = 1.0 mL/min; 220 nm): t_R = 19.2 min (major), 21.6 min (minor).

(*R*)-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-ol² (4k, known compound)



Colorless oil, 82.6 mg, 59% yield, 96% ee; $[\alpha]_D^{25} = +23.8$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.0 Hz, 2H), 7.36 – 7.25 (m, 7H), 4.67 (dd, J = 7.9, 5.3 Hz, 1H), 2.84 – 2.68 (m, 2H), 2.17 – 1.97 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.9, 144.3, 128.7, 128.6, 128.1, 127.8, 125.8, 125.3 (q, J = 4.0 Hz), 124.3 (q, J = 270 Hz), 73.7, 40.0, 31.8; HPLC (Chiralcel FLM-H column, *n*-hexane : isopropanol = 98 : 2 (v/v); 1.0 mL/min; 220 nm): t_R = 19.1 min (major), 22.8 min (minor).

(*R*)-3-(naphthalen-2-yl)-1-phenylpropan-1-ol³ (4l, known compound)



Yellow oil, 85.2 mg, 65% yield, 96% ee; $[\alpha]_D^{25} = +3.6$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.76 (dd, J = 14.6, 7.9 Hz, 3H), 7.61 (s, 1H), 7.45 – 7.38 (m, 2H), 7.34 – 7.23 (m, 6H), 4.68 (dd, J = 7.9, 5.3 Hz, 1H), 2.92 – 2.77 (m, 2H), 2.24 – 2.02 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.5, 139.2, 133.6, 132.0, 128.5, 127.9, 127.6, 127.6, 127.4, 127.3, 126.4, 125.9, 125.9, 125.1, 73.8, 40.3, 32.1; HPLC (Chiralcel OJ-H column, *n*-hexane : isopropanol = 85 : 15 (v/v); 1.0 mL/min; 220 nm): t_R = 18.5 min (major), 22.5 min (minor).

(R)-3-(naphthalen-1-yl)-1-phenylpropan-1-ol⁹ (4m, known compound)



Yellow oil, 89.1 mg, 68% yield, 96% ee; $[\alpha]_D^{25} = +48.0 \ (c = 1.0, \text{CHCl}_3); ^1\text{H} \text{NMR}$ (400 MHz, CDCl₃) δ 7.97 – 7.91 (m, 1H), 7.84 – 7.80 (m, 1H), 7.69 (d, J = 6.8 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.36 – 7.24 (m, 7H), 4.74 (dd, J = 7.8, 5.2 Hz, 1H), 3.25 – 3.18 (m, 1H), 3.11 – 3.03 (m, 1H), 2.26 – 2.08 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.5, 138.0, 133.9, 131.8, 128.7, 128.5, 127.6, 126.6, 125.9, 125.9, 125.8, 125.5, 125.4, 123.7, 74.1, 39.8, 29.1; **HPLC** (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 32.2 min (minor), 36.9 min (major).

(R)-1,3-di-*p*-tolylpropan-1-ol⁴ (5a, known compound)



Colorless oil, 90.1 mg, 75% yield, 97% ee; $[\alpha]_D^{25} = +15.2$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.21 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.07 (s, 4H), 4.62 (dd, J = 7.7, 5.5 Hz, 1H), 2.70 – 2.56 (m, 2H), 2.33 (s, 3H), 2.30 (s, 3H), 2.12 – 1.93 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.6, 138.7, 137.2, 135.2, 129.1, 129.0, 128.3, 125.9, 73.7, 40.4, 31.6, 21.1, 21.0; HPLC (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 12.1 min (major), 13.7 min (minor).

(R)-3-(4-fluorophenyl)-1-(p-tolyl)propan-1-ol¹ (5b, known compound)



Yellow oil, 90.3 mg, 74% yield, 98% ee; $[\alpha]_D^{25} = +27.4$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.08 (m, 6H), 6.97 – 6.91 (m, 2H), 4.59 (dd, J = 7.8, 5.5 Hz, 1H), 2.72 – 2.56 (m, 2H), 2.33 (s, 3H), 2.12 – 1.90 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 161.2 (d, J = 243.2 Hz), 141.5, 137.4 (d, J = 3.2 Hz), 137.3, 129.7 (d, J = 7.8 Hz), 129.2, 125.8, 115.0 (d, J = 21.1 Hz), 73.5, 40.4, 31.2, 21.1; HPLC (Chiralcel OJ-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 15.1 min (major), 18.2 min (minor).

(*R*)-3-(4-chlorophenyl)-1-(*p*-tolyl)propan-1-ol⁷ (5c, known compound)



Colorless oil, 100.1 mg, 77% yield, 98% ee; $[\alpha]_D^{25} = +18.8 (c = 1.0, \text{CHCl}_3)$; ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.08 (m, 8H), 4.60 (dd, J = 7.8, 5.5 Hz, 1H), 2.72 – 2.56 (m, 2H), 2.34 (s, 3H), 2.12 – 2.03 (m, 1H), 1.99 – 1.90 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 141.4, 140.2, 137.4, 131.4, 129.8, 129.2, 128.4, 125.8, 73.5, 40.2, 31.4, 21.1; HPLC (Chiralcel OD-H column, *n*-hexane : isopropanol = 97 : 3 (v/v); 1.0 mL/min; 220 nm): t_R = 17.1 min (major), 18.5 min (minor).

(*R*)-3-(2-bromo-5-chlorophenyl)-1-(4-chlorophenyl)propan-1-ol (**5d**, unknown compound)



Colorless oil, 136.0 mg, 76% yield, 93% ee; $[\alpha]_D^{25} = +21.4$ (c = 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.40 (m, 1H), 7.35 – 7.26 (m, 4H), 7.19 (d, J = 2.6 Hz, 1H), 7.03 (dd, J = 8.4, 2.6 Hz, 1H), 4.69 (dd, J = 7.8, 5.1 Hz, 1H), 2.87 – 2.67 (m, 2H), 2.12 – 1.92 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.7, 142.6, 133.8, 133.4, 133.3, 130.2, 128.7, 127.8, 127.2, 122.2, 73.0, 38.5, 32.3; HPLC (Chiralcel OD-H column, *n*-hexane : isopropanol = 95 : 5 (v/v); 1.0 mL/min; 220 nm): t_R = 11.1 min (minor), 11.7 min (major).

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7. NMR spectra of chiral alcohols










































































8. HRMS spectra of 3g







9. HPLC spectra of chiral alcohols



2

20.232

Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C 20.232 6.982 0.30 0.20 AU 0.10 0.00 5.00 10.00 15.00 0.00 20.00 25.00 Peak Ret Time[min] % Area Height Area 49.78 1 16.982 7961334 313551



8032529

50.22

Peak	Ret Time[min]	Area	% Area	Height
1	17.008	179694	0.97	9973
2	20.087	18403209	99.03	277064



Chiralcel AD-H column, n-hexane/isopropanol = 99 : 1 (v/v), 1.0 mL/min, 220 nm, 30 °C







Chiralcel IB-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C







Chiralcel IA-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C 0.60 9.129 10.121 0.50 0.40 ₹ 0.30 0.20 0.10 0.00 200 4.00 6.00 8.00 10.00 12,00 0.00 % Area Peak Ret Time[min] Area Height 1 9.129 5879751 50.15 455500 2 10.121 5843772 49.85 415329





Chiralcel IA-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C







18.204

Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C







Chiralcel OJ-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





Chiralcel IB-H column, *n*-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





Chiralcel OJ-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





Chiralcel AD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





Peak	Ret Time[min]	Area	% Area	Height
1	19.616	38417128	99.02	934913
2	21.955	381332	0.98	11271



Chiralcel IA-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





Peak	Ret Time[min]	Area	% Area	Height
1	10.573	280492	4.13	19414
2	11.985	6506196	95.87	399576



Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C



Peak	Ret Time[min]	Area	% Area	Height
1	17.998	23076013	50.17	854289
2	22.080	22920351	49.83	648719



Peak	Ret Time[min]	Area	% Area	Height
1	17.947	1341968	2.52	54977
2	22.071	51894151	97.48	1401879



Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C



U	.00 5.00		20.00	25.00	30.00
Peak	Ret Time[min]	Area	% Area	Height	
1	19.322	670677	2.43	31225	
2	23.792	26875930	97.57	691488	



Chiralcel IB-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C







0.35 0.30 7.576 24.766 0.25 0.20 AU 0.15 0.10 0.05 0.00 30.00 5.00 10.00 15.00 20.00 25.00 0.00 Peak Ret Time[min] Area % Area Height 1 17.576 6513370 49.72 289001 2 24.766 6586665 50.28 182714 1.00 24.53 0.80 0.60 ٩U 0.40 17.685 0.20 0.00 15.00 10.00 20.00 25.00 30.00 5.00 0.00 Height Peak Ret Time[min] Area % Area 1 17.685 165790 0.58 8907 2 24.539 28237388 99.42 754469

Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C



Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





13.081

Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C



Peak	Ret Time[min]	Area	% Area	Height
1	12.797	2019330	49.57	109553
2	13.501	2054432	50.43	108669



98.45

473172



Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C







Chiralcel OJ-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C







Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





Peak	Ret Time[min]	Area	% Area	Height
1	12.740	22039388	99.20	1200956
2	15.416	177932	0.80	11491



Chiralcel IB-H column, n-hexane/isopropanol = 98 : 2 (v/v), 1.0 mL/min, 220 nm, 30 °C




14.714

Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C



49.85

235474





Chiralcel OJ-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





Chiralcel FLM-H column, n-hexane/isopropanol = 98 : 2 (v/v), 1.0 mL/min, 220 nm, 30 °C





22.518

18.493 1.20 1.00-0.80 ٩U 0.60 0.40 0.20 0.00 5.00 10.00 15.00 20.00 25.00 0.00 Peak Ret Time[min] Area % Area Height 49.90 1237118 18.493 66124859 1 2 22.339 66377080 50.10 1031649 200-8.495 1.50-٩ 1.00-22.518 0.50-0.00 15.00 20.00 0.00 5.00 10.00 25.00 Peak Ret Time[min] Area % Area Height 103751321 98.00 1880633 1 18.495

Chiralcel OJ-H column, n-hexane/isopropanol = 85 : 15 (v/v), 1.0 mL/min, 220 nm, 30 °C

2117634

2.00





Peak	Ret Time[min]	Area	% Area	Height
1	32.173	2718747	2.05	54422
2	36.870	130042178	97.95	1915640



Chiralcel OD-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





Реак	Ret Time[min]	Area	% Area	Height
1	12.103	72492981	98.68	2881945
2	13.727	970543	1.32	55216



Chiralcel OJ-H column, n-hexane/isopropanol = 95 : 5 (v/v), 1.0 mL/min, 220 nm, 30 °C





18.782

Chiralcel OD-H column, n-hexane/isopropanol = 97 : 3 (v/v), 1.0 mL/min, 220 nm, 30 °C



49.91

1699877









Peak	Ret Time[min]	Area	% Area	Height
1	11.036	31509684	49.77	1672826
2	11.706	31804260	50.23	1627204





29.285

Chiralcel IA-H column, n-hexane, 0.4 mL/min, 220 nm, 30 °C



50.39

530588





Chiralcel IA-H column, n-hexane/isopropanol = 99 : 1 (v/v), 1.0 mL/min, 220 nm, 30 °C



I Cak	Ket Thile[hill]	Inca	70 7 fied	meight
1	6.326	31673110	49.75	2674662
2	7.109	31989169	50.25	2439120

