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# Supporting Information

# Manganese-Catalyzed Asymmetric Transfer Hydrogenation

## of Quinolines in Water using Ammonia Borane as a

## Hydrogen Source.

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## **Table of Contents**

1.	General experimental information	<b>S</b> 1
2.	General procedure for chiral benzimidazole ligands	<b>S</b> 1
3.	General procedure for the preparation of substrates	S2
4.	General procedure for the ATH of quinolines	<b>S</b> 3
5.	General procedure for gram-scale synthesis of (-)-cuspareine	S17
6.	Isotopic labelling experiments	S18
7.	References	S19
8.	Copies of NMR spectra	S21
9.	Copies of HPLC chart	S61

## 1. General experimental information

Anhydrous toluene was distilled from sodium. Mn(CO)<sub>5</sub>Br and other chemical reagents were purchased from commercial suppliers. <sup>1</sup>H NMR (600 MHz or 400MHz), <sup>13</sup>C NMR (150 MHz or 100 MHz), <sup>19</sup>F NMR (376 MHz) spectra were recorded on a Bruker ADVANCE III instruments in CDCl<sub>3</sub> with TMS as internal standard. <sup>1</sup>H NMR chemical shifts were referenced to Deuterium chloroform signal (7.26 ppm), <sup>13</sup>C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, CDCl<sub>3</sub>). Optical rotations were determined using an AUTOPOL V polarimeter. HPLC analysis were performed using Agilent 1100 or Waters e2695 equipped with OJ-H, OD-H, IC-H, IJ-H and IA-H. HRMS spectra were recorded on an Agilent 1200HPLC-6210TOFMS using ESI as ion source. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

## 2. General procedure for chiral benzimidazole ligands

The aminobenzimidazole ligands L1-L6 were prepared according to the reported method from the corresponding Boc-protected amino acids.<sup>1</sup>

(S)-3-methyl-1-(1-methyl-1H-benzo[d]imidazol-2-yl)butan-1-amine (L1) new Yellow oil, 65% yield,  $[\alpha]^{20}_{D} = +43.6$  (c = 0.51, CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 – 7.63 (m, 1H), 7.38 – 7.10 (m, 3H), 4.20 (t, *J* = 6.8 Hz, 1H), 3.75 (s, 3H), 1.97 (s, 2H), 1.81 (dt, *J* = 13.2, 6.8 Hz, 1H), 1.75 (dd, *J* = 6.8, 2.0 Hz, 2H), 0.96 (dd, *J* = 6.4, 4.0 Hz, 6H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  158.1, 142.0, 135.7, 122.1, 121.7, 119.1, 108.9, 46.8, 46.3, 29.6, 24.7, 23.0, 21.8. HRMS (ESI) calcd for C<sub>13</sub>H<sub>19</sub>N<sub>3</sub> [M+H]+: 217.1579, found: 217.1583.

(1S,2R)-2-methyl-1-(1-methyl-1H-benzo[d]imidazol-2-yl)butan-1-amine (L6) new Yellow oil, 58% yield,  $[\alpha]^{20}_{D} = +10.6$  (c = 0.35, CHCl<sub>3</sub>). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.84 – 7.65 (m, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.29 – 7.12 (m, 2H), 3.96 (dd, J = 7.2, 1.8 Hz, 1H), 3.78 (s, 3H), 2.03 – 1.86 (m, 3H), 1.80 – 1.65 (m, 1H), 1.29 – 1.23 (m, 1H), 0.92 (t, J = 7.2 Hz, 3H), 0.90 (d, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  157.8, 142.2, 135.7, 122.2, 122.0, 119.3, 109.1, 53.7, 40.8, 30.0, 24.5, 16.1, 11.1. HRMS (ESI) calcd for C<sub>13</sub>H<sub>19</sub>N<sub>3</sub> [M+H]+: 217.1579, found: 217.1575.

## **3.** General procedure for the preparation of substrates

The substrates **1a-1j** and **1af** were purchased from commercial sources. The substrates **1n-1ab** were prepared according to the reported procedures.<sup>2</sup>

#### General procedure for the synthesis of 1k-1m:



In a 50mL Schlenk flask, 2-methylquinoline-6-carboxylic acid (260 mg, 1.5 mmol) was dissolved in DCM (10 ml), HOBT (128 mg, 1.8 mmol) and EDCI (283 mg, 1.1 mmol) were added and the mixture was stirred 30 min at RT. Secondary amine (1.8 mmol) and Et<sub>3</sub>N (333 mg, 2.2 mmol) were added dropwise and stirring was continued overnight. DCM (25 mL) was added. The organic phase was washed with aqueous sodium hydrogencarbonate (25 mL), aqueous sodium hydrogensulfate (25 mL) and water (25 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacumm. Finally, the residue was purified by column chromatography (ethyl acetate : petroleum ether =1:10 to 1:20).



#### N,N-dibutyl-2-methylquinoline-6-carboxamide (1k):

Yellow oil, 62% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (t, *J* = 9.6 Hz, 2H), 7.79 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 3.39 (d, *J* = 180 Hz, 4H), 2.75 (s, 3H), 1.60 (d, *J* = 107.4 Hz, 4H), 1.47 – 1.06 (m, 4H), 0.87 (d, *J* = 153.6 Hz, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  170.9, 159.9, 147.6, 136.2, 134.5, 128.7, 127.5, 125.8, 125.6, 122.6, 48.7, 44.5, 30.7, 29.6, 25.3, 20.2, 19.6, 13.8, 13.4. HRMS (ESI) calcd for C<sub>19</sub>H<sub>26</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 298.2045, found: 298.2040.



## (2-methylquinolin-6-yl)(morpholino)methanone (11):

White solid, 65% yield, m.p. 94.6-96.7 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (dd, *J* = 13.8, 8.0 Hz, 2H), 7.85 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 3.71 (s, 8H), 2.74 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  169.8, 160.5, 148.0, 136.4, 132.5, 129.1, 127.7, 126.9, 125.9, 122.8, 66.8, 25.4. HRMS (ESI) calcd for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 256.1212, found: 256.1211.



## (2-methylquinolin-6-yl)(pyrrolidin-1-yl)methanone (1m):

White solid, 70% yield, m.p. 100.4-101.0 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.96 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 3.59 (d, J = 130.2 Hz, 4H), 2.76 (s, 3H), 2.34 – 1.47 (m, 4H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  169.0, 160.2, 148.0, 136.5, 134.4, 128.7, 127.9, 126.7, 125.7, 122.6, 49.6, 46.2, 26.4, 25.4, 24.4. HRMS (ESI) calcd for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 240.1263, found: 240.1268.

## 4. General procedure for the ATH of quinolines



Under argon atmosphere,  $Mn(CO)_5Br$  (0.02 mmol), L1 (0.022 mmol), degassed toluene (2 mL) was added into tube and the mixture was heated to reflux for 3 h. The mixture was cooled to room temperature and concentrated to dryness, affording the crude Mn-L1 complex. The Mn-L1 complex, TBAI (0.1 mmol), 1 (0.2 mmol) and H<sub>2</sub>O (1.0 mL) were added in a 10 mL Schlenk flask. The mixture was stirred for 10 min at 3 °C. (CH<sub>3</sub>)<sub>2</sub>NHBH<sub>3</sub> was added and the mixture was stirred at 3 °C for 30 h. The solvent was removed, and the mixture was purified by passing through a short column of silica gel to afford the corresponding product. The absolute configurations of 2a–2h, 2n-2r, 2u-2w, 2aa were determined by the comparison with the reported optical rotation.<sup>2-5</sup>

The absolute configurations of **2i-2m**, **2s-2t**, **2x-2z**, **2ab-2ae** were tentatively assigned by analogy. The absolute configurations of **2af** is still unclear.



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

Colorless oil, 85% yield, 89% *ee*;  $[\alpha]^{20}_{D} = -60.3$  (c = 1.23, CHCl<sub>3</sub>); lit.<sup>2</sup>  $[\alpha]^{25}_{D} = -84.3$  [c = 1.42, CHCl<sub>3</sub>, 97% ee (S)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 15.30 min (major), t<sub>R2</sub> = 16.87 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.09 – 6.93 (m, 2H), 6.64 (td, *J* = 7.2, 1.2 Hz, 1H), 6.50 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.62 – 3.24 (m, 1H), 3.05 – 2.82 (m, 1H), 2.80 – 2.73 (m, 1H), 2.05 – 1.88 (m, 1H), 1.68 – 1.56 (m, 1H), 1.24 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.7, 129.2, 126.6, 121.0, 116.9, 114.0, 47.1, 30.1, 26.5, 22.5. HRMS (ESI) calcd for C<sub>10</sub>H<sub>13</sub>N [M+H]<sup>+</sup>: 147.1048, found: 147.1052.



## (S)-6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (2b):

White solid, 88% yield, 89% *ee*, m.p. 46.8-48.3 °C;  $[\alpha]^{20}_{D} = -37.6$  (c = 0.62, CHCl<sub>3</sub>); lit.<sup>2</sup>  $[\alpha]^{25}_{D} = -80.9$  [c = 1.22, CHCl<sub>3</sub>, 93% ee (S)]. The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 0.5 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 16.95 min (minor), t<sub>R2</sub> = 22.95 min (major). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.89 – 6.62 (m, 2H), 6.48 – 6.33 (m, 1H), 3.38 – 3.31 (m, 1H), 2.87 – 2.78 (m, 1H), 2.73 – 2.67 (m, 1H), 1.95 – 1.89 (m, 1H), 1.61 – 1.51 (m, 1H), 1.21 (d, *J* = 6.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.4 (d, *J* = 233.2 Hz), 140.9 (d, *J* = 1.8 Hz), 122.4 (d, *J* = 6.8 Hz), 115.3 (d, *J* = 21.4 Hz), 114.7 (d, *J* = 7.5 Hz), 113.1 (d, *J* = 22.3 Hz), 47.3, 29.8, 26.7 (d, *J* = 1.4 Hz), 22.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -128.27. HRMS (ESI) calcd for C<sub>10</sub>H<sub>12</sub>FN [M+H]<sup>+</sup>: 165.0954, found: 165.0962.



### (S)-6-chloro-2-methyl-1,2,3,4-tetrahydroquinoline (2c):

Colorless oil, 92% yield, 90% *ee*;  $[\alpha]^{20}_{D}$  = -48.2 (c = 0.62, CHCl<sub>3</sub>); lit.<sup>3</sup>  $[\alpha]^{25}_{D}$  = +108.7 [c = 1.0, CHCl<sub>3</sub>, 72% ee (R)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 12.98 min (major), t<sub>R2</sub> = 15.39 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.84 (d, *J* = 8.0 Hz, 1H), 6.54 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.44 (d, *J* = 2.0 Hz, 1H), 3.42 – 3.36 (m, 1H), 2.84 – 2.56 (m, 2H), 1.96 – 1.88 (m, 1H), 1.60 – 1.49 (m, 1H), 1.20 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  145.7, 131.9, 130.1, 119.3, 116.6, 113.2, 47.0, 29.72, 26.0, 22.4. HRMS (ESI) calcd for C<sub>10</sub>H<sub>12</sub>CIN [M+H]<sup>+</sup>: 101.0658, found: 101.0666.

Br

## (S)-6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline (2d):

White solid, 89% yield, 91% *ee*, m.p. 52.0-54.6 °C;  $[\alpha]^{20}_{D} = -28.6$  (c = 0.51, CHCl<sub>3</sub>); lit.<sup>2</sup>  $[\alpha]^{25}_{D} = -61.6$  [c = 1.09, CHCl<sub>3</sub>, 97% ee (S)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 20.29 min (major), t<sub>R2</sub> = 32.96 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.09 – 6.98 (m, 2H), 6.34 (d, *J* = 8.4 Hz, 1H), 3.37 (td, *J* = 6.4, 3.2 Hz, 1H), 2.92 – 2.72 (m, 1H), 2.75 – 2.64 (m, 1H), 2.02 – 1.85 (m, 1H), 1.58 – 1.49 (m, 1H), 1.20 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 143.7, 131.7, 129.3, 123.2, 115.4, 108.4, 47.1, 29.6, 26.4, 22.4. HRMS (ESI) calcd for C<sub>10</sub>H<sub>12</sub>BrN [M+H]<sup>+</sup>: 225.0153, found: 225.0148.



### (S)-6-iodo-2-methyl-1,2,3,4-tetrahydroquinoline (2e):

White solid, 91% yield, 93% *ee*, m.p.55.6-57.9 °C;  $[\alpha]^{20}_{D} = -50.3$  (c = 1.13, CHCl<sub>3</sub>); lit.<sup>2</sup>  $[\alpha]^{25}_{D} = -56.2$  [c = 1.14, CHCl<sub>3</sub>, 94% ee (S)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 15.13 min (major), t<sub>R2</sub> = 18.90 min (minor). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 (s, 1H), 7.20 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.24 (d, *J* = 8.4 Hz, 1H), 3.73 (s, 1H), 3.40 – 3.36 (m, 1H), 2.88 – 2.74 (m, 1H), 2.70 – 2.65 (m, 1H), 1.93 - 1.88 (m, 1H), 1.57 - 1.50 (m, 1H), 1.20 (d, J = 6.0 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  144.3, 137.4, 135.1, 123.7, 115.9, 47.0, 29.5, 26.2, 22.4. HRMS (ESI) calcd for C<sub>10</sub>H<sub>12</sub>IN [M+H]<sup>+</sup>: 273.0014, found: 273.0016.



#### (S)-7-chloro-2-methyl-1,2,3,4-tetrahydroquinoline (2f):

White solid, 97% yield, 93% *ee*, m.p.51.3-52.7 °C;  $[\alpha]^{20}_{D} = -36.7$  (c = 0.68, CHCl<sub>3</sub>); lit.<sup>2</sup>  $[\alpha]^{25}_{D} = -74.4$  [c = 0.90, CHCl<sub>3</sub>, 92% ee (S)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 39.80 min (major), t<sub>R2</sub> = 45.27 min (minor). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  6.86 (d, *J* = 7.8 Hz, 1H), 6.55 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 3.76 (s, 1H), 3.41 – 3.37 (m, 1H), 2.79 – 2.73 (m, 1H), 2.72 – 2.51 (m, 1H), 1.98 – 1.85 (m, 1H), 1.59 – 1.51 (m, 1H), 1.21 (d, *J* = 6.0 Hz, 3H).<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  145.7, 131.8, 130.1, 119.2, 116.5, 113.2, 46.9, 29.7, 26.0, 22.4. HRMS (ESI) calcd for C<sub>10</sub>H<sub>12</sub>CIN [M+H]<sup>+</sup>: 181.0658, found: 181.0667.

### (S)-6-methoxy-2-methyl-1,2,3,4-tetrahydroquinoline (2g):

Yellow oil, 86% yield, 78% *ee*;  $[\alpha]^{20}_{D} = -28.1$  (c = 0.58, CHCl<sub>3</sub>); lit.<sup>2</sup>  $[\alpha]^{25}_{D} = -60.7$  [c = 1.21, CHCl<sub>3</sub>, 93% ee (S)]. The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 0.5 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 20.89 min (minor), t<sub>R2</sub> = 25.07 min (major). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.74 – 6.55 (m, 2H), 6.46 (d, *J* = 8.4 Hz, 1H), 3.74 (s, 3H), 3.38 – 3.30 (m, 1H), 3.17 (s, 1H), 2.91 – 2.80 (m, 1H), 2.76 – 2.69 (m, 1H), 1.96 – 1.88 (m, 1H), 1.64 – 1.53 (m, 1H), 1.21 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  151.7, 138.8, 122.4, 115.2, 114.5, 112.7, 55.7, 47.4, 30.2, 26.8, 22.4. HRMS (ESI) calcd for C<sub>11</sub>H<sub>15</sub>NO [M+H]<sup>+</sup>: 177.1154, found: 177.1159.



(S)-2-methyl-6-phenyl-1,2,3,4-tetrahydroquinoline (2h):

Yellow oil, 88% yield, 91% *ee*;  $[\alpha]^{20}_{D} = -60.3$  (c = 1.08, CHCl<sub>3</sub>); lit.<sup>4</sup>  $[\alpha]^{20}_{D} = -70.3$  [c = 1.26, CHCl<sub>3</sub>, 95% ee (S)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 53.89 min (minor), t<sub>R2</sub> = 55.87 min (major). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.33 – 7.27 (m, 3H), 6.58 (d, J = 9.6 Hz, 1H), 3.50 – 3.45 (m, 1H), 3.13 – 2.89 (m, 1H), 2.87 – 2.81 (m, 1H), 2.20 – 1.95 (m, 1H), 1.72 – 1.62 (m, 1H), 1.27 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.2, 141.4, 129.9, 128.5, 127.9, 126.2, 125.8, 125.4, 121.2, 114.2, 47.2, 30.0, 26.6, 22.5. HRMS (ESI) calcd for C<sub>16</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 223.1361, found:223.1366.



## (S)-2-methyl-6-(pyridin-4-yl)-1,2,3,4-tetrahydroquinoline (2i):

Yellow oil, 70% yield, 94% *ee*;  $[\alpha]^{20}_{D}$  = -73.2 (c = 1.21, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak IC-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 30.20 min (minor), t<sub>R2</sub> = 32.35 min (major). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.54 (d, *J* = 4.8 Hz, 2H), 7.43 (d, *J* = 4.8 Hz, 2H), 7.31 (d, *J* = 6.6 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 1H), 3.60 – 3.31 (m, 1H), 2.88 (td, *J* = 10.8, 5.4 Hz, 1H), 2.81 (dt, *J* = 16.2, 4.8 Hz, 1H), 2.00 – 1.96 (m, 1H), 1.69 – 1.53 (m, 1H), 1.25 (d, *J* = 6.4 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  149.9, 148.4, 145.9, 127.8, 125.8, 125.4, 121.2, 120.3, 114.1, 47.2, 29.8, 26.6, 22.5. HRMS (ESI) calcd for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 224.1313, found: 224.1305.



#### (S)-2-methyl-6-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline (2j):

Colorless oil, 86% yield, 92% *ee*;  $[\alpha]^{20}_{D} = -70.3$  (c = 1.06, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak IJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 64.52 min (minor), t<sub>R2</sub> = 78.21 min (major). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.25 (d, *J* = 7.8 Hz, 2H), 7.14 (dd, *J* = 9.0, 4.8 Hz, 2H), 7.05 – 7.00 (m, 1H), 6.48 (d, *J* = 7.2 Hz, 1H), 3.80 (s, 1H), 3.52 – 3.34 (m, 1H), 2.91 – 2.85 (m, 1H), 2.79 (dt, *J* = 16.2, 4.8 Hz, 1H), 2.06

- 1.86 (m, 1H), 1.73 - 1.51 (m, 1H), 1.24 (d, J = 6.6 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  145.5, 144.4, 127.7, 127.0, 124.7, 123.5, 122.5, 121.1, 120.7, 114.0, 47.2, 30.0, 26.5, 22.5. HRMS (ESI) calcd for C<sub>14</sub>H<sub>15</sub>NS [M+H]<sup>+</sup>: 229.0925, found: 229.0920.

(S)-N,N-dibutyl-2-methyl-1,2,3,4-tetrahydroquinoline-6-carboxamide (2k):

Colorless oil, 80% yield, 90% *ee*;  $[\alpha]^{20}_{D} = -56.2$  (c = 0.86, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5; flow rate = 0.6 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 71.48 min (minor), t<sub>R2</sub> = 75.53 min (major). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  6.95 (s, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.32 (d, J = 8.4 Hz, 1H), 4.08 (s, 1H), 3.44 – 3.09 (m, 5H), 2.71 (td, J = 11.4, 5.4 Hz, 1H), 2.65 – 2.58 (m, 1H), 1.83 (d, J = 3.6 Hz, 1H), 1.50 (d, J = 4.8 Hz, 5H), 1.21 (s, 4H), 1.12 (d, J = 6.0 Hz, 3H), 0.83 (s, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  172.1, 145.6, 128.2, 125.6, 124.6, 119.8, 112.6, 46.8, 30.0, 29.5, 26.1, 22.1, 19.8, 13.5. HRMS (ESI) calcd for C<sub>19</sub>H<sub>30</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 302.2358, found: 302.2354.



### (S)-(2-methyl-1,2,3,4-tetrahydroquinolin-6-yl)(morpholino)methanone (2l):

Colorless oil, 74% yield, 80% *ee*;  $[\alpha]^{20}_{D} = -42.6$  (c = 0.63, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak IA-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 67.62 min (minor), t<sub>R2</sub> = 76.05 min (major). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.08 (s, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.37 (d, J = 7.8 Hz, 1H), 4.03 (s, 1H), 3.75 – 3.55 (m, 8H), 3.44 – 3.39 (m, 1H), 2.81 – 2.75 (m, 1H), 2.73 – 2.68 (m, 1H), 1.97 – 1.81 (m, 1H), 1.58 – 1.50 (m, 1H), 1.19 (d, J = 6.0 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  171.2, 146.4, 129.3, 126.7, 122.4, 120.2, 112.6, 66.9, 47.0, 29.5, 26.3, 22.3. HRMS (ESI) calcd for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 260.1525, found: 260.1531.



## (S)-(2-methyl-1,2,3,4-tetrahydroquinolin-6-yl)(pyrrolidin-1-yl)methanone (2m):

Colorless oil, 83% yield, 87% *ee*;  $[\alpha]^{20}_{D} = -38.6$  (c = 0.74, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak IA-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 61.37 min (minor), t<sub>R2</sub> = 69.30 min (major). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.21 (s, 1H), 7.16 (d, J = 7.8 Hz, 1H), 6.36 (d, J = 8.4 Hz, 1H), 4.02 (s, 1H), 3.64 – 3.46 (m, 4H), 3.42 – 3.38 (m, 1H), 2.80 – 2.74 (m, 1H), 2.69 (dt, J = 16.2, 4.8 Hz, 1H), 2.02 – 1.71 (m, 5H), 1.61 – 1.44 (m, 1H), 1.18 (d, J = 6.0 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  170.0, 146.3, 129.2, 126.6, 124.6, 119.8, 112.4, 47.0, 29.6, 26.3, 22.3. HRMS (ESI) calcd for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 244.1576, found: 244.1581.



## (S)-2-ethyl-1,2,3,4-tetrahydroquinoline (2n):

Yellow oil, 85% yield, 94% *ee*;  $[\alpha]^{20}_{D} = -34.3$  (c = 0.64, CHCl<sub>3</sub>); lit.<sup>5</sup>  $[\alpha]^{25}_{D} = +75.9$  [c = 1.76 CHCl<sub>3</sub>, 96% ee (R)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 17.44 min (major), t<sub>R2</sub> = 19.03 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.03 (t, *J* = 7.2 Hz, 2H), 6.67 (td, *J* = 7.2, 1.2 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 3.26 – 3.18 (m, 1H), 3.02 – 2.60 (m, 2H), 2.07 – 2.00 (m, 1H), 1.72 – 1.63 (m, 1H), 1.63 – 1.53 (m, 2H), 1.06 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.6, 129.1, 126.6, 121.3, 116.8, 113.9, 52.9, 29.3, 27.5, 26.3, 10.0. HRMS (ESI) calcd for C<sub>11</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 161.1204, found: 161.1203.



#### (S)-2-propyl-1,2,3,4-tetrahydroquinoline (20):

Yellow oil, 83% yield, 80% *ee*;  $[\alpha]^{20}_{D} = -46.9$  (c = 0.81, CHCl<sub>3</sub>); lit.<sup>5</sup>  $[\alpha]^{25}_{D} = +72.7$  [c = 1.58 CHCl<sub>3</sub>, 93% ee (R)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 26.72 min (major), t<sub>R2</sub> = 33.33 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (d, *J* = 7.2 Hz, 2H), 6.65 (td, *J* = 7.2, 1.2 Hz, 1H), 6.52

(d, J = 8.0 Hz, 1H), 3.56 (s, 1H), 3.33 – 3.26 (m, 1H), 2.93 – 2.65 (m, 2H), 2.11 – 1.90 (m, 1H), 1.70 – 1.59 (m, 1H), 1.58 – 1.28 (m, 4H), 1.02 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.6, 129.2, 126.6, 121.3, 116.8, 114.0, 51.2, 38.8, 28.0, 26.4, 18.8, 14.1. HRMS (ESI) calcd for C<sub>12</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 175.1361, found: 175.1356.



#### (S)-2-butyl-1,2,3,4-tetrahydroquinoline (2p):

Yellow oil, 83% yield, 85% *ee*;  $[\alpha]^{20}_{D} = -49.3$  (c = 1.03, CHCl<sub>3</sub>); lit.<sup>5</sup>  $[\alpha]^{25}_{D} = +79.9$  [c = 1.0 CHCl<sub>3</sub>, 92% ee (R)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 23.36 min (major), t<sub>R2</sub> = 27.10 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (t, *J* = 7.6 Hz, 2H), 6.64 (td, *J* = 7.2, 1.2 Hz, 1H), 6.56 – 6.46 (m, 1H), 3.30 – 3.23 (m, 1H), 2.90 – 2.77 (m, 1H), 2.75 – 2.73 (m, 1H), 2.03 – 1.96 (m, 1H), 1.69 – 1.59 (m, 1H), 1.57 – 1.50 (m, 2H), 1.44 – 1.39 (m, 4H), 0.98 (t, *J* = 7.2, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.7, 129.2, 126.6, 121.3, 116.8, 114.0, 51.5, 36.4, 28.0, 27.9, 26.4, 22.8, 14.0. HRMS (ESI) calcd for C<sub>13</sub>H<sub>19</sub>N [M+H]<sup>+</sup>: 189.1517, found: 189.1510.



#### (S)-2-pentyl-1,2,3,4-tetrahydroquinoline (2q):

Yellow oil, 80% yield, 85% *ee*;  $[\alpha]^{20}_{D} = -50.3$  (c = 1.13, CHCl<sub>3</sub>); lit.<sup>5</sup>  $[\alpha]^{25}_{D} = +73.1$  [c = 1.02 CHCl<sub>3</sub>, 93% ee (R)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.5 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 13.73 min (major), t<sub>R2</sub> = 14.82 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.01 (t, *J* = 7.2 Hz, 2H), 6.65 (td, *J* = 7.2, 1.2 Hz, 1H), 6.52 (d, *J* = 7.2 Hz, 1H), 3.31 – 3.24 (m, 1H), 2.90 – 2.82 (m, 1H), 2.77 (dt, *J* = 16.4, 4.8 Hz, 1H), 2.04 – 1.96 (m, 2H), 1.70 – 1.60 (m, 1H), 1.59 – 1.49 (m, 2H), 1.48 – 1.23 (m, 6H), 0.97 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.7, 129.2, 126.6, 121.3, 116.8, 114.0, 51.5, 36.6, 31.9, 28.0, 26.4, 25.3, 22.6, 14.0. HRMS (ESI) calcd for C<sub>14</sub>H<sub>21</sub>N [M+H]<sup>+</sup>: 203.1674, found: 203.1668.



## (R)-2-isobutyl-1,2,3,4-tetrahydroquinoline (2r):

Yellow oil, 88% yield, 68% *ee*;  $[\alpha]^{20}_{D} = -19.3$  (c = 0.53, CHCl<sub>3</sub>); lit.<sup>3</sup>  $[\alpha]^{25}_{D} = +79.2$  [c = 1.0 CHCl<sub>3</sub>, 88% ee (R)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.5 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 13.59 min (major), t<sub>R2</sub> = 16.87 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (t, *J* = 7.2 Hz, 2H), 6.71 – 6.60 (m, 1H), 6.52 (d, J = 8.0 Hz, 1H), 3.48 – 3.20 (m, 1H), 2.91 – 2.82 (m, 1H), 2.77 (dt, *J* = 16.2, 4.8 Hz, 1H), 2.11 – 1.89 (m, 1H), 1.86 – 1.75 (m, 1H), 1.68 – 1.58 (m, 1H), 1.50 – 1.27 (m, 2H), 1.00 (d, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.6, 129.2, 126.6, 121.3, 116.9, 114.0, 49.2, 45.8, 28.5, 26.4, 24.4, 23.2, 22.4. HRMS (ESI) calcd for C<sub>13</sub>H<sub>19</sub>N [M+H]<sup>+</sup>: 189.1517, found: 189.1519.



## (R)-2-(cyclohexylmethyl)-1,2,3,4-tetrahydroquinoline (2s):

Yellow oil, 72% yield, 80% *ee*;  $[\alpha]^{20}_{D}$  = -20.1 (c = 0.62, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5; flow rate = 0.6 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 12.00 min (major), t<sub>R2</sub> = 13.03 min (minor). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (t, *J* = 7.6 Hz, 2H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 3.48 – 3.31 (m, 1H), 2.89 – 2.81 (m, 1H), 2.80 – 2.69 (m, 1H), 2.00 – 1.95 (m, 1H), 1.84 – 1.70 (m, 5H), 1.68 – 1.52 (m, 1H), 1.47 – 1.38 (m, 3H), 1.35 – 1.14 (m, 3H), 1.04 – 0.93 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.6, 129.2, 126.6, 121.3, 116.8, 114.0, 48.5, 44.4, 33.9, 33.9, 33.2, 28.5, 26.5, 26.4, 26.3, 26.2. HRMS (ESI) calcd for C<sub>16</sub>H<sub>23</sub>N [M+H]<sup>+</sup>: 229.1830, found: 229.1826.



## (S)-2-(2-cyclohexylethyl)-1,2,3,4-tetrahydroquinoline (2t):

Yellow oil, 70% yield, 76% *ee*;  $[\alpha]^{20}_{D} = -13.2$  (c = 0.43, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 98:2; flow rate = 1 mL/min; column temperature 25 °C; UV detection at 254 nm;  $t_{R1} = 6.27$  min (minor),  $t_{R2} = 7.04$  min (major). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (t, J = 7.8 Hz, 2H), 6.65 (td, J = 7.8, 1.2 Hz, 1H), 6.52 (d, J = 7.8 Hz, 1H), 3.37 (s, 1H), 3.27 – 3.22 (m, 1H), 2.89 – 2.82 (m, 1H), 2.77 (dt, J = 10.2, 4.2 Hz, 1H), 2.03 – 1.98 (m, 1H), 1.85 – 1.73 (m, 4H), 1.74 – 1.67 (m, 1H), 1.67 – 1.61 (m, 1H), 1.55 (td, J = 8.4, 6.0 Hz, 2H), 1.36 – 1.24 (m, 5H), 1.22 (dt, J = 12.0, 3.6 Hz, 1H), 1.02 – 0.90 (m, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  144.8, 129.3, 126.7, 121.4, 116.9, 114.1, 52.0, 37.9, 34.1, 33.5, 33.5, 28.2, 26.8, 26.5, 26.5. HRMS (ESI) calcd for C<sub>17</sub>H<sub>25</sub>N [M+H]<sup>+</sup>: 243.1987, found: 243.1995.



#### (S)-2-(4-methoxyphenethyl)-1,2,3,4-tetrahydroquinoline (2u):

Yellow oil, 86% yield, 87% *ee*;  $[\alpha]^{20}_{D} = -48.6$  (c = 1.11, CHCl<sub>3</sub>); lit.<sup>2</sup>  $[\alpha]^{25}_{D} = -91.0$  [c = 2.29, CHCl<sub>3</sub>, 89% ee (S)]. The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5; flow rate = 1 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 14.72 min (minor), t<sub>R2</sub> = 17.15 min (major). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18 (d, *J* = 9.2 Hz, 2H), 7.01 (d, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.66 (td, *J* = 7.2, 1.2 Hz, 1H), 6.51 (d, *J* = 7.2 Hz, 1H), 3.84 (s, 3H), 3.56 – 3.18 (m, 1H), 2.97 – 2.79 (m, 2H), 2.77 – 2.60 (m, 2H), 2.13 – 1.99 (m, 1H), 1.97 – 1.78 (m, 2H), 1.77 – 1.55 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  157.8, 144.5, 133.8, 129.2, 126.6, 121.2, 116.9, 114.1, 113.8, 55.2, 51.0, 38.4, 31.2, 27.9, 26.2. HRMS (ESI) calcd for C<sub>18</sub>H<sub>21</sub>NO [M+H]<sup>+</sup>: 267.1623, found: 267.1630.



#### (S)-2-phenethyl-1,2,3,4-tetrahydroquinoline (2v):

Yellow oil, 85% yield, 87% *ee*;  $[\alpha]^{20}{}_{D}$  = -31.6 (c = 0.69, CHCl<sub>3</sub>); lit.<sup>3</sup>  $[\alpha]^{25}{}_{D}$  = +73.4 [c = 1.0 CHCl<sub>3</sub>, 91% ee (R)]. The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 76.38 min (major), t<sub>R2</sub> = 82.72 min (minor). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.37 (dd, *J* = 8.4, 6.6 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 3H), 7.03 (t, *J* = 7.8 Hz, 2H), 6.68 (td, *J* = 7.8, 1.2 Hz, 1H), 6.51 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 1H), 3.38 – 3.33 (m, 1H), 2.90 – 2.84 (m, 1H), 2.80 (t, *J* = 7.8 Hz, 3H), 2.08 – 2.03 (m, 1H), 1.91 – 1.87 (m, 2H), 1.77 – 1.70 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  144.5, 141.8, 129.2,

128.4, 128.3, 126.7, 125.9, 121.2, 117.0, 114.1, 51.0, 38.2, 32.1, 27.9, 26.2. HRMS (ESI) calcd for C<sub>17</sub>H<sub>19</sub>N [M+H]<sup>+</sup>: 237.1517, found: 237.1510.



## (S)-2-(4-methylphenethyl)-1,2,3,4-tetrahydroquinoline (2w):

Yellow oil, 78% yield, 86% *ee*;  $[\alpha]^{20}_{D} = -46.9$  (c = 1.03, CHCl<sub>3</sub>); lit.<sup>3</sup>  $[\alpha]^{25}_{D} = +71.3$  [c = 1.0 CHCl<sub>3</sub>, 92% ee (R)]. The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 10.92 min (minor), t<sub>R2</sub> = 11.70 min (major). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.14 (s, 4H), 7.04 – 6.91 (m, 2H), 6.63 (td, *J* = 7.2, 1.2 Hz, 1H), 6.48 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.47 – 3.24 (m, 1H), 2.87 – 2.80 (m, 1H), 2.78 (t, *J* = 4.8 Hz, 1H), 2.75 – 2.71 (m, 2H), 2.36 (s, 3H), 2.05 – 1.99 (m, 1H), 1.90 – 1.77 (m, 2H), 1.73 – 1.66 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  144.6, 138.8, 135.5, 129.3, 129.2, 128.3, 126.8, 121.4, 117.0, 114.2, 51.1, 38.4, 31.7, 28.0, 26.3, 21.0. HRMS (ESI) calcd for C<sub>18</sub>H<sub>21</sub>N [M+H]<sup>+</sup>: 251.1674, found: 251.1680.



#### (S)-2-(3-fluorophenethyl)-1,2,3,4-tetrahydroquinoline (2x):

Yellow oil, 82% yield, 85% *ee*;  $[\alpha]^{20}_{D}$  = -63.4 (c = 1.21, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5; flow rate = 1 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 11.30 min (minor), t<sub>R2</sub> = 13.79 min (major). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (td, *J* = 7.6, 6.0 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 3H), 7.00 – 6.89 (m, 2H), 6.67 (td, *J* = 7.2, 1.2 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 3.38 – 3.30 (m, 1H), 2.97 – 2.62 (m, 4H), 2.11 – 1.97 (m, 1H), 1.90 – 1.83 (m, 2H), 1.78 – 1.67 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.9 (d, *J* = 245.4 Hz), 144.4, 144.4, 129.8 (d, *J* = 8.3 Hz), 129.2, 126.7, 123.9 (d, *J* = 2.8 Hz), 121.2, 117.1, 115.1 (d, *J* = 20.8 Hz), 114.1, 112.8 (d, *J* = 21.0 Hz), 50.9, 37.9, 31.7 (d, *J* = 1.8 Hz), 27.8 26.1. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -113.40. HRMS (ESI) calcd for C<sub>17</sub>H<sub>18</sub>FN [M+H]<sup>+</sup>: 255.1423, found: 255.1419.



## (S)-2-(3-chlorophenethyl)-1,2,3,4-tetrahydroquinoline (2y):

Yellow oil, 85% yield, 83% *ee*;  $[\alpha]^{20}_{D}$  = -36.3 (c = 1.08, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 16.46 min (minor), t<sub>R2</sub> = 17.91 min (major). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.23 – 7.12 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.95 (td, *J* = 7.2, 5.4 Hz, 2H), 6.60 (td, *J* = 7.2, 1.2 Hz, 1H), 6.45 (dd, *J* = 7.8, 1.2 Hz, 1H), 3.73 (s, 1H), 3.29 – 3.24 (m, 1H), 2.83 – 2.76 (m, 1H), 2.72 (dt, *J* = 16.8, 4.8 Hz, 1H), 2.68 (t, *J* = 8.4 Hz, 2H), 1.99 – 1.94 (m, 1H), 1.85 – 1.73 (m, 2H), 1.69 – 1.61 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  144.3, 143.8, 134.1, 129.6, 129.2, 128.4, 126.7, 126.5, 126.1, 121.1, 117.0, 114.1, 50.9, 37.9, 31.65, 27.7, 26.0. HRMS (ESI) calcd for C<sub>17</sub>H<sub>18</sub>CIN [M+H]<sup>+</sup>: 271.1128, found: 271.1130.



## (S)-2-(2-methylphenethyl)-1,2,3,4-tetrahydroquinoline (2z):

Yellow oil, 83% yield, 82% *ee*;  $[\alpha]^{20}{}_{D}$  = -39.2 (c = 1.16, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5; flow rate = 1 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 15.27 min (minor), t<sub>R2</sub> = 16.35 min (major). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.24 – 7.19 (m, 4H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.68 (td, *J* = 7.6, 1.2 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 3.44 – 3.55 (m, 1H), 3.02 – 2.82 (m, 2H), 2.81 – 2.73 (m, 2H), 2.40 (s, 3H), 2.18 – 2.01 (m, 1H), 1.94 – 1.80 (m, 2H), 1.80 – 1.62 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.5, 140.0, 135.7, 130.2, 129.2, 128.7, 126.7, 126.0, 126.0, 117.0 114.1, 51.4, 37.0, 29.4, 27.9, 26.2, 19.3. HRMS (ESI) calcd for C<sub>18</sub>H<sub>21</sub>N [M+H]<sup>+</sup>: 251.1674, found: 251.1676.



## (S)-2-(3,4-dimethoxyphenethyl)-1,2,3,4-tetrahydroquinoline (2aa):

Light yellow oil, 90% yield, 91% *ee*;  $[\alpha]^{20}_{D} = -30.2$  (c = 1.32, CHCl<sub>3</sub>); lit.<sup>2</sup>  $[\alpha]^{25}_{D} = -41.1$  [c = 3.17, CHCl<sub>3</sub>, 88% ee (S)]. The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5; flow rate = 1 mL/min; column temperature

25 °C; UV detection at 254 nm;  $t_{R1} = 61.48$  min (minor),  $t_{R2} = 73.16$  min (major). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.98 – 6.95(m, 2H), 6.84 – 6.73 (m, 3H), 6.61 (td, J = 7.6, 1.2 Hz, H), 6.46 (dd, J = 8.4, 1.2 Hz, 1H), 3.88 (d, J = 5.2 Hz, 6H), 3.52 – 3.20 (m, 1H), 2.95 – 2.49 (m, 4H), 2.04 – 1.97 (m, 2H), 1.90 – 1.77 (m, 1H), 1.75 – 1.63 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.9, 147.2, 144.4, 134.4, 129.2, 126.7, 121.2, 120.1, 117.0, 114.1, 111.6, 111.2, 55.9, 55.8, 51.2, 38.4, 31.8, 28.0, 26.2. HRMS (ESI) calcd for C<sub>19</sub>H<sub>23</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 297.1729, found: 297.1732.



## (S)-2-(2-(naphthalen-2-yl)ethyl)-1,2,3,4-tetrahydroquinoline (2ab):

Light yellow oil, 75% yield, 99% *ee*;  $[\alpha]^{20}_{D} = -78.3$  (c = 1.21, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 85:15; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 51.11 min (minor), t<sub>R2</sub> = 62.25 min (major). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.87 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.45 – 7.33 (m, 2H), 7.05 – 6.94 (m, 2H), 6.62 (td, *J* = 7.2, 1.2 Hz, 1H), 6.48 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.64 – 3.33 (m, 1H), 3.27 – 3.10 (m, 2H), 2.94 – 2.66 (m, 2H), 2.22 – 2.03 (m, 1H), 2.04 – 1.93 (m, 2H), 1.86 – 1.69 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.4, 137.9, 133.8, 131.6, 129.2, 128.8, 126.7, 126.7, 125.8, 125.8, 125.5, 123.5, 121.2, 117.0, 114.1, 51.3, 37.4, 29.1, 27.8, 26.2. HRMS (ESI) calcd for C<sub>21</sub>H<sub>21</sub>N [M+H]<sup>+</sup>: 287.1674, found: 287.1680.



### (S)-2-(but-3-en-1-yl)-1,2,3,4-tetrahydroquinoline (2ac):

Light yellow oil, 88% yield, 90% *ee*;  $[\alpha]^{20}_{D} = -39.2$  (c = 0.64, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 12.21 min (major), t<sub>R2</sub> = 13.36 min (minor). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (t, *J* = 8.4 Hz, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 5.93 – 5.85 (m, 1H), 5.18 – 4.99 (m, 2H), 3.34 – 3.28 (m, 1H), 2.88 – 2.80 (m, 1H), 2.77 (dt, *J* = 16.2, 4.8 Hz, 1H), 2.22

(q, J = 7.2 Hz, 2H), 2.03 – 1.97 (m, 1H), 1.73 – 1.55 (m, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  144.5, 138.2, 129.2, 126.7, 121.2, 116.9, 114.9, 114.1, 51.0, 35.6, 30.0, 27.9, 26.2. HRMS (ESI) calcd for C<sub>13</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 187.1361, found: 187.1353.



#### (S,E)-2-(4-phenylbut-3-en-1-yl)-1,2,3,4-tetrahydroquinoline (2ad):

Light yellow oil, 86% yield, 90% *ee*;  $[\alpha]^{20}_{D} = -41.6$  (c = 0.71, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 18.68 min (minor), t<sub>R2</sub> = 21.36 min (major). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.54 – 6.45 (m, 2H), 6.25 (dt, *J* = 16.2, 7.2 Hz, 1H), 3.84 (s, 1H), 3.36 – 3.32(m, 1H), 2.85 – 2.79 (m, 1H), 2.75 (dt, *J* = 16.2, 4.8 Hz, 1H), 2.36 (q, *J* = 6.6 Hz, 2H), 2.03 – 1.97 (m, 1H), 1.72 – 1.63 (m, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  144.5, 137.5, 130.4, 130.1, 129.2, 128.5, 127.0, 126.7, 125.9, 121.3, 117.0, 114.1, 51.1, 36.1, 29.3, 27.9, 26.2. HRMS (ESI) calcd for C<sub>19</sub>H<sub>21</sub>N [M+H]<sup>+</sup>: 263.1674, found: 263.1680.



### (S)-2-(pent-4-yn-1-yl)-1,2,3,4-tetrahydroquinoline (2ae):

Light yellow oil, 80% yield, 87% *ee*;  $[\alpha]^{20}_{D} = -29.4$  (c = 0.52, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 32.89 min (major), t<sub>R2</sub> = 40.87 min (minor). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  6.98 (t, *J* = 7.8 Hz, 2H), 6.63 (td, *J* = 7.2, 1.2 Hz, 1H), 6.50 (dd, *J* = 7.8, 1.2 Hz, 1H), 3.43 – 3.15 (m, 1H), 2.87 – 2.80 (m, 1H), 2.76 (dt, *J* = 16.2, 4.8 Hz, 1H), 2.27 (dt, *J* = 6.6, 3.0 Hz, 2H), 2.07 – 1.92 (m, 2H), 1.75 – 1.58 (m, 5H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  144.5, 129.2, 126.7, 121.2, 117.0, 114.0, 84.1, 68.7, 51.0, 35.6, 27.8, 26.2, 24.5, 18.5. HRMS (ESI) calcd for C<sub>14</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 199.1361, found: 199.1354.



#### 2,3-dimethyl-1,2,3,4-tetrahydro-quinoline (2af):

Light yellow oil, 93% yield, dr = 1.28:1, 97% *ee*, 89% *ee*;  $[\alpha]^{20}_{D} = -8.6$  (c = 0.32, CHCl<sub>3</sub>). The *dr* and *ee* were determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 0.8 mL/min; column temperature 25 °C; UV detection at 254 nm; t<sub>R1</sub> = 19.71 min (minor), t<sub>R2</sub> = 23.25 min (major), t<sub>R3</sub> = 25.15 min (major), t<sub>R4</sub> = 29.00 min (minor). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 – 6.91 (m, 2H), 6.63 – 6.57 (m, 1H), 6.47 (dd, *J* = 7.8, 1.2 Hz, 1H), 3.68 (s, 1H), 3.03 – 2.99 (m, 1H), 2.73 (dd, *J* = 16.2, 4.8 Hz, 1H), 2.57 – 2.42 (m, 1H), 1.66 - 1.60 (m, 1H), 1.20 (d, *J* = 6.0 Hz, 3H), 1.02 (d, *J* = 6.6 Hz, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  144.5, 129.0, 126.7, 121.3, 116.8, 113.4, 53.3, 35.5, 33.5, 20.8, 18.3. HRMS (ESI) calcd for C<sub>11</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 161.1204, found: 161.1210.

## 5. General procedure for gram-scale synthesis of (-)-cuspareine



Under argon atmosphere, Mn(CO)<sub>5</sub>Br (0.1 mmol), L1 (0.11 mmol), degassed toluene (10 mL) was added into a tube and the mixture was heated to reflux for 4 h. The mixture was cooled to room temperature and concentrated to dryness, affording the crude Mn-L1 complex. The Mn-L1 complex, TBAI (2 mmol), **1aa** (5 mmol) and H<sub>2</sub>O (15 mL) were added in a 50mL Schlenk flask. The mixture was stirred for 60 min at 3 °C. (CH<sub>3</sub>)<sub>2</sub>NHBH<sub>3</sub> (20 mmol) was added and the mixture was stirred at 3 °C for 50 h. The solvent was removed, and the mixture was purified by passing through a short column of silica gel to afford the corresponding product **2aa** with 1.37 g, 92% yield in 91.5% *ee*.



Under  $N_2$  atmosphere, a solution of **2aa** (4.6 mmol) and 1M HCHO-AcOH solution (9.2 mL) was stirred at RT. The NaBH<sub>3</sub>CN (9.2 mmol) was added and the mixture was stirred at RT for 2h. Then, the solvent was removed under vacuum and 20 mL water

and 35 mL DCM were added. The organic phase was washed with aqueous sodium hydrogencarbonate (25 mL), aqueous sodium hydrogensulfate (25 mL) and water (25 mL). The organic phase was dried over  $Na_2SO_4$  and evaporated under vacumm. Finally, the crude product (-)-cuspareine was purified by column chromatography (ethyl acetate: petroleum ether = 1:15 to 1:20) on silica gel with 1.38g, 96% yield, 89% *ee*.



#### (S)-2-(3,4-dimethoxyphenethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (3aa):

Light yellow oil, 96% yield, 89% *ee*;  $[\alpha]^{20}_{D} = -62.6$  (c = 1.51, CHCl<sub>3</sub>). The *ee* was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10; flow rate = 1 mL/min; column temperature 25 °C; UV detection at 210 nm; t<sub>R1</sub> = 21.42 min (minor), t<sub>R2</sub> = 45.66 min (major). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.17 – 7.08 (m, 1H), 7.02 (dd, *J* = 7.2, 1.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.78 – 6.71 (m, 2H), 6.63 (td, *J* = 7.2, 1.2 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 3.90 (d, *J* = 10.2 Hz, 6H), 3.32 (dd, *J* = 9.0, 4.2 Hz, 1H), 2.95 (s, 3H), 2.94 – 2.85 (m, 1H), 2.78 – 2.65 (m, 2H), 2.60 – 2.53 (m, 1H), 2.04 – 1.89 (m, 3H), 1.81 – 1.73 (m, *J* = 13.9, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  148.8, 147.1, 145.2, 134.6, 128.6, 127.0, 121.6, 120.0, 115.3, 111.5, 111.2, 110.5, 58.3, 55.8, 55.8, 38.0, 33.0, 31.8, 24.3, 23.5. HRMS (ESI) calcd for C<sub>20</sub>H<sub>25</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 311.1815, found: 311.1810.

## 6. Isotopic labelling experiments



To gain further mechanistic insights, the ATH of 1a using (CH<sub>3</sub>)<sub>2</sub>NHBD<sub>3</sub> instead of (CH<sub>3</sub>)<sub>2</sub>NHBH<sub>3</sub> as the hydrogen source was examined.

Under argon atmosphere,  $Mn(CO)_5Br$  (0.02 mmol), L1 (0.022 mmol), degassed toluene (2 mL) was added into tube and the mixture was heated to reflux for 3 h. The mixture was cooled to room temperature and concentrated to dryness, affording the crude Mn-L1 complex. The Mn-L1 complex, TBAI (0.1 mmol), 1 (0.2 mmol) and H<sub>2</sub>O (1.0 mL) were added in a 10 mL Schlenk flask. The mixture was stirred for 10 min at

3 °C. (CH<sub>3</sub>)<sub>2</sub>NHBD<sub>3</sub> was added and the mixture was stirred at 3 °C for 30 h. The solvent was removed, and the mixture was purified by passing through a short column of silica gel to afford the corresponding product. The product was dissolved in CDCl<sub>3</sub> and analyzed through <sup>2</sup>H NMR spectroscopy.

The result indicated that the hydrogen atoms added at N and C2 positions were from the (CH<sub>3</sub>)<sub>2</sub>NH motif in ammonia borane, and the hydrogen atoms at C1 and C3 positions were from the BH<sub>3</sub> motif in ammonia borane.



## 7. References

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## 8. Copies of NMR spectra







## N,N-dibutyl-2-methylquinoline-6-carboxamide (1k)



## (2-methylquinolin-6-yl)(morpholino)methanone (11)



## (2-methylquinolin-6-yl)(pyrrolidin-1-yl)methanone (1m):





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## (S)-2-methyl-6-(pyridin-4-yl)-1,2,3,4-tetrahydroquinoline (2i):




# (S)-N,N-dibutyl-2-methyl-1,2,3,4-tetrahydroquinoline-6-carboxamide (2k):



(S)-(2-methyl-1,2,3,4-tetrahydroquinolin-6-yl)(morpholino)methanone (2l):



# (S)-(2-methyl-1,2,3,4-tetrahydroquinolin-6-yl)(pyrrolidin-1-yl)methanone (2m):























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# (S)-2-(3,4-dimethoxyphenethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (3aa):

# 9. Copies of HPLC charts

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



	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	15.365	19408778	49.99	814896
2	W2489 ChA 254nm	16.888	19418582	50.01	747283







Processed	Channel	Descr.:	W2489	ChA 254n	m

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	16.884	65880038	48.33	2026759
2	W2489 ChA 254nm	22.717	70444454	51.67	1706753



# (S)-6-chloro-2-methyl-1,2,3,4-tetrahydroquinoline (2c):

	Processed Channel Descr.: W2489 ChA 254nm								
	Processed Channel Descr.	RT	Area	% Area	Height				
1	W2489 ChA 254nm	12.975	20017619	95.05	930351				
2	W2489 ChA 254nm	15.390	1041614	4.95	54767				





Processed Channel Descr.:	W2489	ChA 254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.166	10728039	49.86	608236
2	W2489 ChA 254nm	14.468	10787741	50.14	560942



# (S)-6-bromo-2-methyl-1,2,3,4-tetrahydroquinoline (2d):

	Processed Channel Descr.: W2489 ChA 254nm							
	Processed Channel Descr.	RT	Area	% Area	Height			
1	W2489 ChA 254nm	29.285	6675876	95.65	191778			
2	W2489 ChA 254nm	32.962	303475	4.35	7992			



<ul> <li>Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3893; Processir</li> </ul>	g Method: (	0
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Processed	Channel	Descr.:	W2489	ChA 254nm	

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	27.447	63823325	49.69	1872216
2	W2489 ChA 254nm	33.581	64608655	50.31	1531591



#### (S)-6-iodo-2-methyl-1,2,3,4-tetrahydroquinoline (2e):



	Processed Channel Descr.: W2489 ChA 254nm								
	Processed Channel Descr.	RT	Area	% Area	Height				
1	W2489 ChA 254nm	15.127	13271183	96.63	702775				
2	W2489 ChA 254nm	18.897	463506	3.37	21329				



#### Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3958; Processing Method: 0

#### Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	15.096	4553854	49.99	233844
2	W2489 ChA 254nm	18.797	4555823	50.01	191229



#### (S)-7-chloro-2-methyl-1,2,3,4-tetrahydroquinoline (2f):

	riocesseu onan	HEI Des			2041111
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	39.221	83281109	49.65	1638085
2	W2489 ChA 254nm	44.057	84440657	50.35	1337321







Processed	Channel	Descr.:	W2489	ChA	254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	20.840	25638673	49.60	574214
2	W2489 ChA 254nm	25.141	26052337	50.40	522244



(S)-2-methyl-6-phenyl-1,2,3,4-tetrahydroquinoline (2h):



	Processed	Channel	Descr.:	W2489	ChA 254nn
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	52.859	6442693	50.15	98914
2	W2489 ChA 254nm	56.440	6403107	49.85	90557



## (S)-2-methyl-6-(pyridin-4-yl)-1,2,3,4-tetrahydroquinoline (2i):



F	Processed Channel Descr.: W2489 ChA 254nm									
	Processed Channel Descr.	RT	Area	% Area	Height					
1	W2489 ChA 254nm	30.203	72393	2.89	1431					
2	W2489 ChA 254nm	32.346	2436388	97.11	38007					



Processed	Channel	Descr.:	W2489	ChA 254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	29.432	2656884	49.37	48654
2	W2489 ChA 254nm	32.398	2724850	50.63	44796



## (S)-2-methyl-6-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline (2j):

	Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	64.516	199061	3.62	2605
2	W2489 ChA 254nm	78.205	5299517	96.38	43968





Processed	Channel	Descr.:	W2489	ChA	254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	64.116	7737979	49.95	78187
2	W2489 ChA 254nm	79.465	7754212	50.05	59085



(S)-N,N-dibutyl-2-methyl-1,2,3,4-tetrahydroquinoline-6-carboxamide (2k):

- Channel: W2489 ChB; Processed Channel: W2489 ChB 254nm; Result Id: 4498; Processing Method: 0

	Processed	Channel	Descr.:	W2489	ChB	254nm
-						_

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 254nm	71.484	603202	<mark>4.94</mark>	4518
2	W2489 ChB 254nm	75.526	11611863	95.06	48158



Channel: W2489 ChB; Processed Channel: W2489 ChB 254nm; Result Id: 4495; Processing Method: 0

Processed	Channel	Descr.:	W2489	ChB	254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 254nm	72.342	15267594	49.11	93510
2	W2489 ChB 254nm	76.737	15818215	50.89	62594


(S)-(2-methyl-1,2,3,4-tetrahydroquinolin-6-yl)(morpholino)methanone (2l):



F	Processed Channel Descr.: W2489 ChA 254nm						
	Processed Channel Descr.	RT	Area	% Area	Height		
1	W2489 ChA 254nm	67.623	391013	9.75	2963		
2	W2489 ChA 254nm	76.051	3620806	90.25	30029		





Processed Ch	annel Descr.	: W2489	ChA	254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	66.888	8410373	50.71	76480
2	W2489 ChA 254nm	76.258	8176399	49.29	67438





- Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4510; Processing Method: 0

	Processed Channel Descr.: W2489 ChA 254nm						
	Processed Channel Descr.	RT	Area	% Area	Height		
1	W2489 ChA 254nm	61.368	686299	6.33	6858		
2	W2489 ChA 254nm	69.298	10156993	93.67	81736		





Processed Channel Desc	cr.: W2489 ChA 254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	61.321	3251687	50.25	31271
2	W2489 ChA 254nm	70.812	3219175	49.75	27735



### (S)-2-ethyl-1,2,3,4-tetrahydroquinoline (2n):



	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	17.655	947167	49.27	26477
2	W2489 ChA 254nm	19.533	975220	50.73	32161

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



Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height		
1	W2489 ChA 254nm	26.724	36517447	89.86	1047470		
2	W2489 ChA 254nm	33.334	4120452	10.14	101325		





	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	26.807	37447334	49.83	1092756
2	W2489 ChA 254nm	33.299	37704742	50.17	883333



# (S)-2-butyl-1,2,3,4-tetrahydroquinoline (2p):

	Processed Channel Descr.: W2489 ChA 254nm							
	Processed Channel Descr.	RT	Area	% Area	Height			
1	W2489 ChA 254nm	23.364	56428601	92.57	1693205			
2	W2489 ChA 254nm	27.100	4530511	7.43	135193			





	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	22.738	55727498	49.70	1809188
2	W2489 ChA 254nm	26.651	56400013	50.30	1543517



## (S)-2-pentyl-1,2,3,4-tetrahydroquinoline (2q):



	Processed Channel Descr.: W2489 ChA 254nm						
	Processed Channel Descr.	RT	Area	% Area	Height		
1	W2489 ChA 254nm	13.733	10432770	92.52	523869		
2	W2489 ChA 254nm	14.816	843816	7.48	39956		





Processed Channel Descr.: V	N2489 ChA	254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.587	11818787	49.19	614671
2	W2489 ChA 254nm	14.565	12209976	50.81	578648



# (R)-2-isobutyl-1,2,3,4-tetrahydroquinoline (2r):

	Processed Channel Descr.: W2489 ChA 254nm								
	Processed Channel Descr.	RT	Area	% Area	Height				
1	W2489 ChA 254nm	13.594	28241160	84.04	1348305				
2	W2489 ChA 254nm	16.872	5364803	15.96	276522				



<ul> <li>Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3996; Processing Method</li> </ul>	d:	0
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Processed	Channel	Descr.:	W2489	ChA	254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.665	1536300	50.04	74510
2	W2489 ChA 254nm	16.903	1533768	49.96	85744



# (R)-2-(cyclohexylmethyl)-1,2,3,4-tetrahydroquinoline (2s):



	Processed Channel Descr.: W2489 ChB 254nm								
	Processed Channel Descr.	RT	Area	% Area	Height				
1	W2489 ChB 254nm	11.996	15563213	90.09	848729				
2	W2489 ChB 254nm	13.033	1711807	9.91	98757				



<ul> <li>Channel: W2489 ChB;</li> </ul>	Processed Channel:	W2489 ChB 254nm;	Result Id: 3990;	Processing Method:	0
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Processed	Channel	Descr.:	W2489	ChB	254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 254nm	12.070	3320809	49.86	184645
2	W2489 ChB 254nm	13.109	3339712	50.14	170031



## (S)-2-(2-cyclohexylethyl)-1,2,3,4-tetrahydroquinoline (2t):

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 254nm	6.270	1295440	11.92	76746
2	W2489 ChB 254nm	7.040	9571215	88.08	557802





Processed	Channel	Descr.:	W2489	ChB	254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 254nm	6.358	2732621	50.51	180069
2	W2489 ChB 254nm	7.138	2677074	49.49	177109



## (S)-2-(4-methoxyphenethyl)-1,2,3,4-tetrahydroquinoline (2u):



	Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 254nm	14.721	1904095	6.27	71237
2	W2489 ChB 254nm	17.153	28488331	93.73	875177



Channel. W2403 Chb, Trocessed Channel. W2403 Chb 254nn, Tresult M. 5500, Trocessing Metho	nel: w	nel: wz	489 ChB;	Processed	Channel:	W2489 ChB 2	54nm;	Result Id:	3966;	Processing	Metho
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Processed	Channel	Descr.:	W2489	ChB	254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 254nm	14.500	51942568	49.57	1684058
2	W2489 ChB 254nm	17.081	52854007	50.43	1533517



### (S)-2-phenethyl-1,2,3,4-tetrahydroquinoline (2v):

1 W2489 ChA 254nm 76.379 25840465 93.69 250850	1         W2489 ChA 254nm         76.379         25840465         93.69         250850           2         W2489 ChA 254nm         82.718         1739053         6.31         18602
2 W0400 Ch4 054mm 00 740 4720052 6 24 40600	2 W2489 ChA 254nm 82.718 1739053 6.31 18602
2 W2489 ChA 254nm 82.718 1739053 6.31 18602	



<ul> <li>Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3859; Processing Metho</li> </ul>	d:	C
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	76.300	33678329	50.12	323721
2	W2489 ChA 254nm	81.940	33516640	49.88	310305



### (S)-2-(4-methylphenethyl)-1,2,3,4-tetrahydroquinoline (2w):



	Processed Channel Descr.: W2489 ChA 254nm								
	Processed Channel Descr.	RT	Area	% Area	Height				
1	W2489 ChA 254nm	10.918	465624	6.90	28924				
2	W2489 ChA 254nm	11.702	6278668	93.10	344229				





	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	10.838	6190757	54.91	344269
2	W2489 ChA 254nm	11.702	5083955	45.09	286725



### (S)-2-(3-fluorophenethyl)-1,2,3,4-tetrahydroquinoline (2x):



	Processed Channel Descr.: W2489 ChB 254nm								
	Processed Channel Descr.	RT	Area	% Area	Height				
1	W2489 ChB 254nm	11.302	1699536	7.15	79903				
2	W2489 ChB 254nm	13.790	22056558	92.85	781607				





	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 254nm	11.276	59375946	47.75	2173735
2	W2489 ChB 254nm	13.832	64974645	52.25	1948485



## (S)-2-(3-chlorophenethyl)-1,2,3,4-tetrahydroquinoline (2y):

Processed Channel Descr.: W2489 ChA 254nm								
	Processed Channel Descr.	RT	Area	% Area	Height			
1	W2489 ChA 254nm	16.462	3896081	8.74	209686			
2	W2489 ChA 254nm	17.905	40659348	91.26	1073762			





Processed Channel Descr.: V	N2489 ChA	254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	16.234	5461019	50.11	396822
2	W2489 ChA 254nm	18.180	5436178	49.89	161027



### (S)-2-(2-methylphenethyl)-1,2,3,4-tetrahydroquinoline (2z):

Processed Channel Descr.: W2489 ChB 254nm							
Processed Channel Descr.		RT	Area	% Area	Height		
1	W2489 ChB 254nm	15.270	1012265	8.99	39733		
2	W2489 ChB 254nm	16.347	10247460	91.01	348643		





Processed Channel Descr.: W248	9 ChB	254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 254nm	15.317	20805752	49.49	700908
2	W2489 ChB 254nm	16.380	21232479	50.51	655803



(S)-2-(3,4-dimethoxyphenethyl)-1,2,3,4-tetrahydroquinoline (2aa):

	Frocessed Channel Desch. W2409 ChD 234hhh						
	Processed Channel Descr.	RT	Area	% Area	Height		
1	W2489 ChB 254nm	61.481	646280	4.33	5052		
2	W2489 ChB 254nm	73.161	14291265	95.67	86766		



Channel: W2489 ChB; Processed Channel: W2489 ChB 254nm; Result Id: 3888; Processing Method: 0

Processed Channel Descr.: W2489 ChB 254nm							
Processed Channel Descr	. RT	Area	% Area	Height			

	Channel Descr.		Alca	<i>in a</i> ca	rieigitt
1	W2489 ChB 254nm	61.372	24696468	49.96	172228
2	W2489 ChB 254nm	73.787	24738601	50.04	148647



(S)-2-(2-(naphthalen-2-yl)ethyl)-1,2,3,4-tetrahydroquinoline (2ab):



Processed Channel Descr.: W2489 ChA 254nm							
	Processed Channel Descr.	RT	Area	% Area	Height		
1	W2489 ChA 254nm	51.113	15745	0.17	305		
2	W2489 ChA 254nm	62.251	9345323	99.83	79613		





Processed	Channel	Descr.:	W2489	ChA	254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	51.846	81586997	48.86	404708
2	W2489 ChA 254nm	63.955	85378506	51.14	686612



## (S)-2-(but-3-en-1-yl)-1,2,3,4-tetrahydroquinoline (2ac):



	Processed Channel Descr.: W2489 ChA 254nm							
	Processed Channel Descr.	RT	Area	% Area	Height			
1	W2489 ChA 254nm	12.205	16218217	95.03	880197			
2	W2489 ChA 254nm	13.364	848145	4.97	50766			



- Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3955; Processing Method: 0

Processed	Channel	Descr.:	W2489	ChA 254nm
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	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	12.125	55903168	47.78	2014052
2	W2489 ChA 254nm	13.224	61103724	52.22	2011327





Processed Channel Descr.: W2489 ChA 254nm						
Processed Channel Descr.	RT	Area	% Area	Height		

1	W2489 ChA 254nm	18.683	2119116	4.99	43620
2	W2489 ChA 254nm	21.356	40374471	95.01	731663



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Ρ	rocessed	Channel	Descr.:	W2489	ChA 254nn	n

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	18.718	3432753	49.45	68348
2	W2489 ChA 254nm	22.231	3509801	50.55	80467



(S)-2-(pent-4-yn-1-yl)-1,2,3,4-tetrahydroquinoline (2ae):



	Processed Channel Descr.: W2489 ChA 254nm							
	Processed Channel Descr.	RT	Area	% Area	Height			
1	W2489 ChA 254nm	32.891	22958347	93.50	438248			
2	W2489 ChA 254nm	40.869	1595273	6.50	32954			





	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	33.234	12322293	49.82	267131
2	W2489 ChA 254nm	40.556	12413644	50.18	221678



### 2,3-dimethyl-1,2,3,4-tetrahydro-quinoline (2af):



	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	19.708	155456	1.28	6958
2	W2489 ChA 254nm	23.250	6097192	50.18	225350
3	W2489 ChA 254nm	25.150	5158348	42.45	176185
4	W2489 ChA 254nm	29.004	739403	6.09	22527

Processed Channel Descr.: W2489 ChA 254nm



#### - Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 3914; Processing Method: 0

Processed	Channe	Descr.:	W2489	ChA 2	54nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	20.141	9785191	33.33	409613
2	W2489 ChA 254nm	23.779	4990549	17.00	181812
3	W2489 ChA 254nm	25.702	9634002	32.81	321502
4	W2489 ChA 254nm	29.630	4949149	16.86	146274



(S)-2-(3,4-dimethoxyphenethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (3aa):

	Frocessed channel Desch. W2409 CHA 2341111						
	Processed Channel Descr.	RT	Area	% Area	Height		
1	W2489 ChA 254nm	13.214	1757459	5.35	62760		
2	W2489 ChA 254nm	15.650	31079505	94.65	853699		





Processed	Channel	Descr.:	W2489	ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	12.971	41144753	49.74	1380611
2	W2489 ChA 254nm	15.571	41580684	50.26	1125968