Highly Efficient Asymmetric Construction of Novel Indolines and Tetrahydroquinoline Derivatives via aza-Barbier/C-N Coupling Reaction

Tao Guo,*ab Bin-Hua Yuan,b Wen-jie Liub

a College of Chemistry, Chemical and Environmental Engineering, Henan University of Technology, Zhengzhou, Henan 450001, PR China
b Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China.

Table of Contents

1 General Experimental .................................................................................................................... 2
2 General procedure for the synthesis of racemic compounds and sulfinylimines 1 .............. 2
3 General procedure for synthesis of chiral Indoline 4 .............................................................. 3
4 General procedure for synthesis of chiral tetrahydroquinoline 5 ........................................ 24
5 Preparation of tetrahydroquinolines 5r, 5s and 5t with quaternary stereocenters ............... 46
6 Determination of the Absolute Configuration of 6a, 6b and 3o ........................................ 49
7 Copies of 1H and 13C NMR spectra of products ................................................................... 50
1 General Experimental

THF was distilled from sodium, DMF, HMPA was distilled from CaH₂. Zinc dust was activated by stirring for 5 minutes with 1 M HCl, followed by washing successively with water, acetone and ether, and drying with a heat gun. Reactions were monitored by thin layer chromatography (TLC), on glass plates coated with silica gel with Fluorescent indicator (Huanghai, HSGF254). Flash chromatography was performed on silica gel (Huanghai, 300-400) using hexane-EtOAc as eluent. 

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM400 (400MHz) with chemical shift values in ppm relative to TMS (δH 0.00 and δC 0.0) or residual chloroform (δH 7.28 and δC 77.1) as standard. Mass spectra were recorded on a HP-5989A instrument.

2 General procedure for the synthesis of racemic compounds and sulfinylimines 1

(R)-tert-Butanesulfinamide (1 mmol) was stirred with benzaldehyde (2 mmol) in toluene (10 mL) in the presence of KHSO₄ (2 equiv.) for 24 h at 45 °C. KHSO₄ was then removed by filtration. The filtrate was concentrated to dryness. The residue was purified by flash chromatography to afford (R)-tert-butanesulfinyl imine (1a) as a colorless liquid.

(R)-tert-Butanesulfinamide (0.5 mmol) and (S)-tert-Butanesulfinamide (0.5 mmol) were stirred with benzaldehyde (2 mmol) in toluene (10 mL) in the presence of KHSO₄ (2 equiv.) for 24 h at 45 °C. KHSO₄ was then removed by filtration. The filtrate was concentrated to dryness. The residue was purified by flash chromatography to afford racemic tert-butanesulfinyl imine as a colorless liquid.
3 General procedure for synthesis of chiral Indoline 4

Under argon, to a Schlenk flask charged with activated zinc dust (32 mg, 0.5 mmol), 2-bromo-cinnamyl bromide 2 (0.5 mmol), and (R)-N-tertbutanesulfinyl imines 1a (0.25 mmol) was added THF (5 mL) distilled from Na. The resultant mixture was then stirred at rt for 12 hours, quenched with brine (5 mL), and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na2SO4. After concentrated, the residue was purified by flash column chromatography to afford the desired product 3a. The diastereomeric ratio (d.r.) was determined by 1H NMR spectroscopic analysis of the crude reaction mixture.

Then 3a was dissolved in HCl-dioxane (2M, 0.5 mL) and followed by stirring for two hour. After concentrated, Cs2CO3 (0.5 mmol), CuI (0.038 mmol), L-proline (0.075 mmol) and 2 mL dry DMF were added under argon then sirred at 70 °C for 3 hours. The reaction was quenched with brine (5 mL). Extraction with ethyl acetate, dried over anhydrous Na2SO4. After concentrated, the residue was purified by flash column chromatography to afford the desired product 4a.

Optimization of C-N coupling reaction conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>ligand</th>
<th>Time(h)</th>
<th>T (°C)</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1c</td>
<td>L-proline</td>
<td>12</td>
<td>50</td>
<td>74</td>
</tr>
<tr>
<td>2c</td>
<td>N,N-dimethylglycine</td>
<td>12</td>
<td>50</td>
<td>72</td>
</tr>
<tr>
<td>3c</td>
<td>dimethylglycine</td>
<td>12</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>4c</td>
<td>L-Hydroxyproline</td>
<td>12</td>
<td>50</td>
<td>28</td>
</tr>
</tbody>
</table>
The reaction was performed with 3a (0.25 mmol), CuI (0.15 equiv.), amino acid (0.3 equiv.), Cs2CO3 (2 equiv.) in dry solvent (2 mL) unless otherwise noted. b Isolated yield. c In the presence of CuI (0.2 equiv.) and amino acid (0.3 equiv.). d 2mL DMSO was used as solvent. e In the presence of K3PO4 (2 equiv.). f In the presence of CuI (0.05 equiv.) and amino acid (0.1 equiv.).

Characterization of the obtained product 4 and the enantioselectivities

(R)-N-((1S,2S)-2-(2-bromophenyl)-1-phenylbut-3-en-1-yl)-2-methylpropane-2-sulfinamide

Purified by flash chromatograph column (PE : EtOAc =2 : 1). colorless oil.

\[[\alpha]_D^16\] -59.9 (c 1.9, CHCl3)

1H NMR (400 MHz, CDCl3) δ 1.03 (s, 9H) , 3.44 (s, 1H), 4.35 (t, J = 8.4 Hz, 1H), 4.65 (dd, J = 2.0, 9.6 Hz, 1H), 4.82 (d, J = 17.2 Hz, 1H), 4.97 (d, J = 10.4 Hz, 1H), 5.69 - 5.78 (m, 1H), 7.12 - 7.16 (m, 1H), 7.28 - 7.35 (m, 7H), 7.63 (d, J = 7.6 Hz, 1H)

13C NMR (100 MHz, CDCl3) δ 22.4, 55.3, 55.5, 61.8, 118.6, 125.8, 128.1, 128.4, 128.5, 128.9, 129.1, 129.5, 133.4, 136.1, 139.1, 139.3

IR (film) 3414, 2958, 1632, 1470, 1455, 1070, 1023, 757, 701 cm⁻¹

HRMS for C20H24BrNNaOS⁺ (M⁺Na): calcd. 428.0660, found 428.0671.

(2S,3S)-2-phenyl-3-vinylindoline

Purified by flash chromatograph column (PE : EtOAc =25 : 1). colorless oil.

\[[\alpha]_D^16\] -6.6 (c 1.0, CHCl3)

1H NMR (400 MHz, CDCl3) δ 3.67 (t, J = 9.2 Hz, 1H), 3.82 (s, 1H), 4.53 (d, J = 9.6 Hz, 1H) , 4.99 (d,
$J = 16.8 \text{ Hz, 1H}$, 5.13 (d, $J = 10 \text{ Hz, 1H}$), 5.85 - 5.94 (m, 1H), 6.59 (d, $J = 8 \text{ Hz, 1H}$), 6.72 (t, $J = 8.0 \text{ Hz, 1H}$), 6.96 (d, $J = 7.6 \text{ Hz, 1H}$), 7.05 (t, $J = 7.2 \text{ Hz, 1H}$), 7.21 - 7.31 (m, 3H), 7.40 (d, $J = 8 \text{ Hz, 2H}$)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 57.1, 70.5, 109.1, 117.7, 119.0, 124.5, 126.9, 127.5, 128.1, 128.4, 130.4, 137.5, 142.7, 150.4

IR (film) 3417, 1632, 1601, 1447, 1242, 908, 747, 699 cm$^{-1}$

HRMS for C$_{16}$H$_{16}$N$^+$ (M$^+$+H): calcd. 222.1277, found 222.1267

HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; $n$-hexane /i-propanol = 80/20; flow = 1mL/min; Retention time: 7.9 min (2S, 3S), 12.6 min (2R, 3R).
(2S,3S)-2-(4-chlorophenyl)-3-vinylindoline

Purified by flash chromatograph column (PE : EtOAc =25 : 1). colorless oil.

$\left[\alpha\right]_{D}^{25}$ 12.3 (c 1.0, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.65 (t, $J = 9.2$ Hz, 1H), 4.11 (d, $J = 7.2$ Hz, 1H), 4.60 (d, $J = 10.4$ Hz, 1H), 5.03 (d, $J = 16.8$ Hz, 1H), 5.18 (d, $J = 10.4$ Hz, 1H), 5.87 - 5.96 (m, 1H), 6.68 (d, $J = 8.0$ Hz, 1H), 6.77 (t, $J = 7.6$ Hz, 1H), 6.98 (d, $J = 6.8$ Hz, 1H), 7.09 (t, $J = 7.6$ Hz, 1H), 7.30 (d, $J = 7.2$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 57.4, 69.9, 109.3, 118.2, 119.3, 124.6, 128.3, 128.3, 128.6, 130.3, 133.2, 137.2, 141.3, 150.2

IR (film) 3415, 1638, 1617, 1478, 1093, 913, 749 cm$^{-1}$

HRMS for C$_{16}$H$_{15}$ClN$^+$ (M$^+$+H) calcd. 256.0888, found 256.0880

HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; n-hexane /i-propanol = 90/10; flow = 1mL/min; Retention time: 6.6 min (2S, 3S), 12.4 min (2R, 3R).
N\textsubscript{H}
\begin{align*}
\text{4c} \\
(2S,3S)-2-(p\text{-tolyl})-3\text{-vinylindoline}
\end{align*}
Purified by flash chromatograph column (PE : EtOAc = 25 : 1). colorless oil.
\([\alpha]_D^{25}9.2\ (c\ 1.0,\ CHCl_3)\)

\begin{align*}
\text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3) & \delta 2.35\ (s,\ 3H),\ 3.72\ (t,\ J = 9.2\ Hz,\ 1H),\ 4.12\ (s,\ 1H),\ 4.63\ (d,\ J = 10.0\ Hz,\ 1H),\ 5.05\ (d,\ J = 16.8\ Hz,\ 1H),\ 5.17\ (d,\ J = 10.0\ Hz,\ 1H),\ 5.89\ - 5.98\ (m,\ 1H),\ 6.68\ (d,\ J = 8.0\ Hz,\ 1H),\ 6.76\ (t,\ J = 7.2\ Hz,\ 1H),\ 7.00\ (d,\ J = 7.2\ Hz,\ 1H),\ 7.10\ (t,\ J = 7.6\ Hz,\ 1H),\ 7.15\ (d,\ J = 7.6\ Hz,\ 2H),\ 7.34\ (d,\ J = 8.0\ Hz,\ 2H) \\
\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3) & \delta 21.2,\ 57.1,\ 70.3,\ 109.1,\ 117.6,\ 119.0,\ 124.6,\ 126.8,\ 128.2,\ 129.2,\ 130.6,\ 137.2,\ 137.6,\ 139.7,\ 150.4 \\
\text{IR (film)} & 3352,\ 2829,\ 1601,\ 1482,\ 1344,\ 1241,\ 1047,\ 920,\ 812,\ 740\ cm^{-1} \\
\text{HRMS for C}_{17}H_{18}N^+ (M^++H) & :\ \text{calcd. 236.1434, found 236.1433} \\
\text{HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; n-hexane /i-propanol = 90/10; flow = 1mL/min; Retention time: 9.5 min (2S, 3S), 17.1 min (2R, 3R).}
\end{align*}
(2S,3S)-2-(4-methoxyphenyl)-3-vinylindoline
Purified by flash chromatograph column (PE : EtOAc = 25 : 1). colorless oil.

$[\alpha]_D^{16}$ 4.1 (c 1.0, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.71 (t, $J = 9.2$ Hz, 1H), 3.80 (s, 3H), 4.61 (d, $J = 9.2$ Hz, 1H), 5.04 (d, $J = 17.6$ Hz, 1H), 5.16 (d, $J = 9.6$ Hz, 1H), 5.88 - 5.97 (m, 1H), 6.68 (d, $J = 7.2$ Hz, 1H), 6.76 (t, $J = 7.2$ Hz, 1H), 6.86 - 6.88 (m, 2H), 6.99 (d, $J = 6.8$ Hz, 1H), 7.09 (t, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 8.8$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 55.4, 57.2, 70.1, 109.1, 113.8, 117.7, 119.0, 124.6, 128.0, 128.2, 130.6, 134.7, 137.6, 150.4, 159.1
IR (film) 3378, 1637, 1607, 1513, 1482, 1244, 1170, 1026, 815, 754 cm\(^{-1}\)

HRMS for C\(_{17}\)H\(_{18}\)NO\(^+\) (M\(^+\)+H): calcd. 252.1383, found 252.1392

HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; n-hexane /i-propanol = 80/20; flow = 1mL/min; Retention time: 6.6 min (2S, 3S), 10.2 min (2R, 3R).

\[
\text{\begin{tabular}{|c|c|c|c|c|}
\hline
Peak No. & Peak ID & Ret Time & Height & Area \\
\hline
1 & 6.607 & 291554.983 & 2753724.900 & 51.7527 \\
2 & 10.237 & 160269.969 & 2569262.750 & 48.2673 \\
\hline
\textbf{Total} & & 651824.001 & 5525967.250 & 100.0000 \\
\hline
\end{tabular}}
\]

\[
\text{\begin{tabular}{|c|c|c|c|c|}
\hline
Peak No. & Peak ID & Ret Time & Height & Area \\
\hline
1 & 6.600 & 280641.844 & 2680406.000 & 98.2069 \\
2 & 10.223 & 3153.227 & 48993.551 & 1.7831 \\
\hline
\textbf{Total} & & 283735.071 & 272945.801 & 100.0000 \\
\hline
\end{tabular}}
\]

(2S,3S)-2-(4-fluorophenyl)-3-vinylindoline

Purified by flash chromatography column (PE : EtOAc = 25 : 1). colorless oil. 

\([\alpha]_D^{16} = -27.0 \text{ (c 1.1, CHCl}_3\text{)}\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 3.66 \text{ (t, } J = 9.2 \text{ Hz, } 1H\), 4.12 (s, 1H), 4.61 (d, \( J = 9.6 \text{ Hz, } 1H\) ), 5.02 (d,
$J = 16.4 \text{ Hz, } 1H)$, 5.18 (d, $J = 10.0 \text{ Hz, } 1H$), 5.87 - 5.96 (m, 1H), 6.67 (d, $J = 7.6 \text{ Hz, } 1H$), 6.76 (t, $J = 7.6 \text{ Hz, } 1H$), 6.98 - 7.03 (m, 3H), 7.09 (t, $J = 7.2 \text{ Hz, } 1H$), 7.42 (t, $J = 8.0 \text{ Hz, } 2H$)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 57.4, 70.0, 109.2, 115.3 (d, $J_{C-F} = 20.5 \text{ Hz}$), 118.1, 119.2, 124.6, 128.3, 128.4 (d, $J_{C-F} = 9.0 \text{ Hz}$), 130.4, 137.3, 138.4 (d, $J_{C-F} = 3.8 \text{ Hz}$), 150.3, 162.6 (d, $J_{C-F} = 244.1 \text{ Hz}$)

$^{19}$F NMR (400 MHz, CDCl$_3$) $\delta$ -115.7

IR (film) 3361, 1642, 1606, 1480,1462, 919, 751 cm$^{-1}$

HRMS for C$_{16}$H$_{16}$FN$^+$ (M$^+$H): calcd. 240.1183, found 240.1173

HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; n-hexane /i-propanol = 95/5; flow = 1mL/min; Retention time: 9.8 min (2S, 3S), 17.0 min (2R, 3R)
(2S,3S)-2-(napthalen-1-yl)-3-vinylindoline

Purified by flash chromatograph column (PE : EtOAc = 25 : 1). Colorless oil.

$[\alpha]_D^{25} -125.2$ (c 1.0, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.04 (t, $J = 7.6$ Hz, 1H), 4.25 (s, 1H), 5.03 - 5.13 (m, 2H), 5.41 (d, $J = 7.6$ Hz, 1H), 6.07 - 6.16 (m, 1H), 6.75 - 6.81 (m, 2H), 7.04 (d, $J = 7.2$ Hz, 1H), 7.15 (t, $J = 8.0$ Hz, 1H), 7.43 (t, $J = 8.0$ Hz, 1H), 7.48 - 7.51 (m, 2H), 7.64 (d, $J = 6.4$ Hz, 1H), 7.78 (d, $J = 8.8$ Hz, 1H), 7.87 - 7.90 (m, 1H), 8.22 - 8.24 (m, 1H)

$^1$C NMR (100 MHz, CDCl$_3$) $\delta$ 56.1, 67.0, 109.2, 116.8, 119.1, 124.1, 124.3, 125.2, 125.5, 125.7, 125.9, 128.2, 128.4, 129.1, 130.1, 131.3, 134.3, 138.7, 138.7, 150.4

IR (film) 3398, 1642, 1605, 1483, 1468, 918, 780 cm$^{-1}$

HRMS for C$_{20}$H$_{18}$N$^+$ (M$^+$+H$^-$): calcd. 272.1434, found 272.1442.

HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; n-hexane / i-propanol = 80/20; flow = 1mL/min; Retention time: 12.0 min (2S, 3S), 16.4 min (2R, 3R).
(2S,3S)-2-(thiophen-2-yl)-3-vinyllindoline

Purified by flash chromatograph column (PE : EtOAc = 25 : 1). colorless oil.

$[\alpha]_D^{16} 20.7$ (c 1.0, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.80 (t, $J = 9.2$ Hz, 1H), 4.34 (s, 1H), 4.90 (d, $J = 9.6$ Hz, 1H), 5.15 (d, $J = 17.2$ Hz, 1H), 5.24 (d, $J = 10.0$ Hz, 1H), 5.89 - 5.98 (m, 1H), 6.69 (d, $J = 7.2$ Hz, 1H), 6.79 (t, $J = 7.2$ Hz, 1H), 6.96 - 7.03 (m, 3H), 7.11 (t, $J = 7.6$ Hz, 1H), 7.22 - 7.23 (m, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 57.4, 66.3, 109.5, 118.4, 119.5, 124.1, 124.4, 124.5, 126.9, 128.2, 130.0, 136.9, 146.8, 149.7

IR (film) 3358, 1632, 1606, 1481, 1457, 1226, 913, 747, 703 cm$^{-1}$

HRMS for C$_{14}$H$_{14}$NS+ (M$^+$+H$^+$): calcd. 228.0841, found 228.0831

HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; n-hexane / i-propanol = 90/10; flow = 1mL/min; Retention time: 10.1 min (2S, 3S), 11.1 min (2R, 3R).
4h

(2R,3S)-2-isopropyl-3-vinylindoline
Purified by flash chromatograph column (PE : EtOAc = 25 : 1). colorless oil.
$[\alpha]_D^{16}$ 120.7 (c 1.0, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.99 (d, $J$ = 6.4 Hz, 6H), 1.81 - 1.90 (m, 1H), 3.34 - 3.41 (m, 1H), 3.65 (t, $J$ = 8.4 Hz, 1H), 5.11 - 5.20 (m, 2H), 5.81 - 5.90 (m, 1H), 6.62 (d, $J$ = 8.0 Hz, 1H), 6.70 (t, $J$ = 7.6 Hz, 1H), 6.97 (d, $J$ = 7.6 Hz, 1H), 7.03 (t, $J$ = 7.2 Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 18.9, 19.7, 32.7, 51.3, 72.0, 109.2, 115.9, 118.6, 124.7, 127.9, 131.4,
IR (film) 3413, 2959, 2921, 1638, 1484, 1465, 1252, 918, 748 cm\(^{-1}\)

HRMS for C\(_{13}\)H\(_{18}\)N\(^+\) (M\(^++\)H): calcd. 188.1434, found 188.1439

HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; \(n\)-hexane /\(i\)-propanol = 99/1; flow = 1mL/min; Retention time: 5.8 min (2\(R\), 3\(S\)), 7.0 min (2\(S\), 3\(R\)).

---

**Results**

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Ret Time</th>
<th>Height</th>
<th>Area</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.773</td>
<td>384672.750</td>
<td>3397721.250</td>
<td>50.9637</td>
</tr>
<tr>
<td>2</td>
<td>7.040</td>
<td>308141.719</td>
<td>3269220.500</td>
<td>49.0363</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>692811.469</td>
<td>666841.750</td>
<td>100.0000</td>
</tr>
</tbody>
</table>

---

**(2R,3S)-2-cyclohexyl-3-vinylindoline**

Purified by flash chromatograph column (PE : EtOAc =25 : 1). colorless oil.
\([\alpha]_D^{25}\) 128.9 (c 1.01, CHCl₃)

\(^1\)H NMR (400 MHz, CDCl₃)  δ 1.08 - 1.26 (m, 5H), 1.54 - 1.80 (m, 6H), 3.40 - 3.44 (m, 2H), 3.69 (t, \(J = 8.8\) Hz, 1H), 5.11 - 5.20 (m, 2H), 5.81 - 5.90 (m, 1H), 6.61 (d, \(J = 8.0\) Hz, 1H), 6.70 (t, \(J = 7.2\) Hz, 1H), 6.98 (d, \(J = 7.2\) Hz, 1H), 7.03 (t, \(J = 6.8\) Hz, 1H)

\(^13\)C NMR (100 MHz, CDCl₃)  δ 26.2, 26.3, 26.6, 29.5, 30.2, 42.9, 51.1, 71.1, 109.2, 115.8, 118.6, 124.7, 127.9, 131.4, 140.2, 150.2

IR (film) 3380, 2923, 2851, 1638, 1606, 1465, 1448, 1239, 980, 913, 747 cm\(^{-1}\)

HRMS for C₁₆H₂₂N\(^+\) (M\(^++\)H): calcld. 228.1747, found 228.1750

HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; \(n\)-hexane /i-propanol = 98/2; flow = 1mL/min; Retention time: 5.2 min (2\(^R\), 3\(^S\)), 6.5 min (2\(^S\), 3\(^R\)).
(2R,3S)-2-((E)-styryl)-3-vinylindoline

Purified by flash chromatograph column (PE : EtOAc =25 : 1). colorless oil.

$[\alpha]_{D}^{16} = 65.9$ (c 0.9, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.66 (t, $J = 8.8$ Hz, 1H), 4.21 (t, $J = 9.6$ Hz, 1H), 5.19 (d, $J = 14.0$ Hz, 2H), 5.85 - 5.95 (m, 1H), 6.36 (q, $J = 7.6$ Hz, 1H), 6.58 (d, $J = 16.0$ Hz, 1H), 6.65 (d, $J = 8.0$ Hz, 1H), 6.75 (t, $J = 7.6$ Hz, 1H), 7.01 (d, $J = 6.8$ Hz, 1H), 7.07 (t, $J = 8.4$ Hz, 1H), 7.22 (t, $J = 8.0$ Hz, 1H), 7.30 (t, $J = 7.2$ Hz, 2H), 7.38 (d, $J = 7.2$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 54.3, 69.2, 109.5, 117.7, 119.1, 124.7, 126.6, 127.8, 128.1, 128.7, 130.3, 130.9, 131.5, 136.9, 137.4, 150.2

IR (film) 3375, 3034, 1632, 1605, 1482, 1463, 1237, 965, 749, 692 cm$^{-1}$

HRMS for C$_{18}$H$_{18}$N$^+$ (M$^+$+H): calcd. 248.1434, found 248.1427

HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; n-hexane /i-propanol = 90/10; flow = 1mL/min; Retention time: 8.4 min (2R, 3S), 11.5 min (2S, 3R).
4k

(2S,3S)-5-methoxy-2-(p-toly)-3-vinylindoline

Purified by flash chromatograph column (PE : EtOAc = 25 : 1). colorless oil.

$[\alpha]_D^{25} 33.5$ (c 1.1, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.33 (s, 3H), 3.68 (t, $J = 9.2$ Hz, 1H), 3.73 (s, 3H), 4.57 (d, $J = 10.4$ Hz, 1H), 5.03 (d, $J = 17.2$ Hz, 1H), 5.15 (dd, $J = 1.6$, 10.4 Hz, 1H), 5.89 - 5.93 (m, 1H), 6.58 - 6.66 (m, 3H), 7.13 (d, $J = 7.6$ Hz, 2H), 7.33 (d, $J = 7.6$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.2, 56.1, 57.4, 70.9, 109.8, 111.3, 113.3, 117.9, 126.9, 129.2, 132.3, 137.2, 137.5, 139.7, 144.4, 153.8

IR (film) 3351, 2818, 1637, 1622, 1489, 1041, 908, 805, 749 cm$^{-1}$

HRMS for C$_{18}$H$_{20}$NO$^+$(M$^+$+H): calcd. 266.1545, found 266.1558

HPLC: Chiracel Lux Amylose-2 Column ; detected at 230 nm; $n$-hexane /$i$-propanol = 95/5; flow = 1mL/min; Retention time: 8.2 min (2S, 3S), 12.4 min (2R, 3R).
(2S,3S)-4-fluoro-2-(4-methoxyphenyl)-3-vinylindoline

Purified by flash chromatography column (PE : EtOAc = 25 : 1). Colorless oil.

$[\alpha]_D^{25}$ 10.3 (c 1.0, CHCl₃)

$^1$H NMR (400 MHz, CDCl₃) $\delta$ 3.68 (t, $J = 9.6$ Hz, 1H), 3.80 (s, 3H), 4.61 (d, $J = 10$ Hz, 1H), 5.05 (d, $J = 16.8$ Hz, 1H), 5.19 (d, $J = 10$ Hz, 1H), 5.86-5.95 (m, 1H), 6.56 (q, $J = 4.4$ Hz, 1H), 6.72-6.81 (m, 2H), 6.88 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl₃) 55.4 (d, $J_{CF} = 4.4$ Hz), 57.1, 70.8 (d, $J_{CF} = 2.0$ Hz), 109.3 (d, $J_{CF} = 8.3$ Hz), 112.0 (d, $J_{CF} = 23.0$ Hz), 113.9, 114.1 (d, $J_{CF} = 23.9$ Hz), 118.3, 128.1, 132.4 (d, $J_{CF} = 7.8$ Hz), 134.4, 136.9 (d, $J_{CF} = 2.6$ Hz), 146.3 (d, $J_{CF} = 1.8$ Hz), 157.3 (d, $J_{CF} = 233.9$ Hz), 159.2
$^{19}$F NMR (400 MHz, CDCl$_3$) $\delta$ -126.2

IR (film) 3363, 1611, 1510, 1484, 1026, 928, 800 cm$^{-1}$

HRMS for C$_{17}$H$_{18}$FNO$^+$ (M$^++$H$^+$): calcd. 270.1289, found 270.1292

HPLC: Chiracel Lux Amylose-2 Column; detected at 230 nm; n-hexane/i-propanol = 95/5; flow = 1mL/min; Retention time: 9.1 min (2S, 3S), 10.4 min (2R, 3R).

$\text{NH}$

4m

(2R,3S)-6-methyl-2-((E)-styryl)-3-vinylindoline

Purified by flash chromatograph column (PE : EtOAc = 25 : 1). colorless oil.

$[\alpha]_D^{25}$ 39.3 (c 1.0, CHCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.27 (s, 3H), 3.63 (t, $J = 9.2$ Hz, 1H), 4.19 (t, $J = 8.4$ Hz, 1H), 5.15 - 5.19 (m, 2H), 5.84 - 5.92 (m, 1H), 6.34 (q, $J = 8.0$ Hz, 1H), 6.48 (s, 1H), 6.55 - 6.58 (m, 2H), 6.89 (t, $J = 7.2$ Hz, 1H), 7.20 - 7.22 (m, 1H), 7.30 (t, $J = 7.2$ Hz, 2H), 7.38 (d, $J = 7.2$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.6, 54.0, 69.4, 110.4, 117.4, 119.9, 124.4, 126.6, 127.6, 128.2, 128.8, 130.3, 131.4, 136.9, 137.7, 138.1, 150.3

IR (film) 3416, 2918, 2849, 1617, 1607, 1492, 1237, 954, 750, 692 cm$^{-1}$

HRMS for : C$_{19}$H$_{20}$N$^+$ (M$^+$+H$^+$) : calcd. 262.1590, found 262.1594

HPLC: Chiracel Lux Amylose-2 Column; detected at 230 nm; n-hexane / i-propanol = 95/5; flow = 1mL/min; Retention time: 6.7 min (2R, 3S), 8.3 min (2S, 3R).
(2R,3S)-3-methyl-2-(p-tolyl)-3-vinylindoline

Purified by flash chromatograph column (PE : EtOAc = 25:1). Colorless oil.

$[\alpha]_D^{25} = 85.6 (c 0.9, \text{CHCl}_3)$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.82 (s, 3H), 2.35 (s, 3H), 4.06 (s, 1H), 4.77 (s, 1H), 5.07 (dd, $J = 1.2, 17.2$ Hz, 1H), 5.23 (dd, $J = 1.2, 10.4$ Hz, 1H), 6.15 (q, $J = 10.4$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 6.76 (td, $J = 1.2, 7.6$ Hz, 1H), 6.94 (dd, $J = 0.8, 7.2$ Hz, 1H), 7.08 (td, $J = 1.2, 7.6$ Hz, 1H), 7.13 (d, $J = 7.6$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.0, 21.3, 52.2, 73.2, 109.5, 114.4, 119.2, 124.1, 127.2, 127.9, 128.8, 136.1, 136.3, 137.1, 144.0, 149.6

HRMS for C$_{18}$H$_{20}$N$^+$ (M$^+$+H): calcd. 250.1590, found 250.1600

HPLC: Chiracel AD-H Column (250 mm); detected at 254 nm; n-hexane /i-propanol = 99/1; flow = 1mL/min; Retention time: 7.3 min (2S, 3R), 11.6 min (2R, 3S)

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Peak ID</th>
<th>Ret Time (min)</th>
<th>Height (arbitrary units)</th>
<th>Area (arbitrary units)</th>
<th>Conc. (mg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>7.30</td>
<td>96513.76</td>
<td>126883.375</td>
<td>49.8902</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>11.62</td>
<td>71822.98</td>
<td>125615.000</td>
<td>50.1918</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>104856.719</td>
<td>25505256.575</td>
<td>100.0000</td>
<td></td>
</tr>
</tbody>
</table>

21
NHO

(2R,3S)-2-(4-methoxyphenyl)-3-methyl-3-vinylindoline

Purified by flash chromatograph column (PE : EtOAc = 25:1). Colorless oil.

$[\alpha]_D^{25}$ 78.4 ($c$ 1.0, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.82 (s, 3H), 3.81 (s, 3H), 4.74 (s, 1H), 5.07 (dd, $J = 1.2$, 17.2 Hz, 1H), 5.23 (dd, $J = 1.2$, 10.4 Hz, 1H), 6.10 - 6.18 (m, 1H), 6.73 (d, $J = 8.0$ Hz, 1H), 6.75 (td, $J = 0.8$, 7.6 Hz, 1H), 6.84 - 6.88 (m, 2H), 6.95 (dd, $J = 0.8$, 7.2 Hz, 1H), 7.08 (td, $J = 1.2$, 7.6 Hz, 1H), 7.33 (d, $J = 8.4$ Hz, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.0, 52.2, 55.4, 72.9, 109.5, 113.4, 114.4, 119.2, 124.1, 127.9, 128.4, 131.1, 136.3, 144.0, 149.6, 159.1

HRMS for C$_{18}$H$_{20}$NO$^+$ (M$^+$+H): calcd. 266.1539, found 266.1556

HPLC: Chiralcel AD-H Column (250 mm); detected at 254 nm; n-hexane/i-propanol = 97/3; flow = 1mL/min; Retention time: 12.9min (2R, 3S), 23.2min (2S, 3R)
### Results

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Peak ID</th>
<th>Ret Time</th>
<th>Height</th>
<th>Area</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>12.857</td>
<td>170258.109</td>
<td>5560929.230</td>
<td>49.8386</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>23.240</td>
<td>91530.125</td>
<td>5535990.350</td>
<td>50.1614</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td>261788.234</td>
<td>7144919.500</td>
<td>100.0000</td>
</tr>
</tbody>
</table>

### Results

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Peak ID</th>
<th>Ret Time</th>
<th>Height</th>
<th>Area</th>
<th>Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>13.069</td>
<td>453861.083</td>
<td>9609355.090</td>
<td>95.0210</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>23.465</td>
<td>12169.260</td>
<td>459997.680</td>
<td>4.4790</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td>458030.325</td>
<td>10269312.680</td>
<td>100.0000</td>
</tr>
</tbody>
</table>
4 General procedure for synthesis of chiral tetrahydroquinoline 5

Under argon, to a Schlenk flask charged with activated zinc dust (48 mg, 0.75 mmol), 2-bromo-cinnamyl bromide 2 (0.75 mmol), LiCl (22 mg, 0.5 mmol) and (R)-N-tertbutanesulfinyl imines 1 (0.25 mmol) was added DMF (2 mL) distilled from CaH₂. The resultant mixture was then stirred at rt for 5 hours, quenched with brine (5 mL), and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄. After concentrated, the residue was purified by flash column chromatography to afford the desired product 3b. The diastereomeric ratio (d.r.) was determined by ¹H NMR spectroscopic analysis of the crude reaction mixture.

Then 3b was dissolved in HCl-dioxane (2M, 0.5 mL) and followed by stirring for two hour. After concentrated, K₃PO₄ (0.75 mmol), CuI (0.038 mmol), L-proline (0.075 mmol) and 1.5 mL dry DMF were added under argon then stirred at 90°C for 3 hours. The reaction was quenched with brine (5 mL). Extraction with ethyl acetate, dried over anhydrous Na₂SO₄. After concentrated, the residue was purified by flash column chromatography to afford the desired product 5.

Optimization of C-N coupling reaction conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>ligand</th>
<th>base</th>
<th>Time(h)</th>
<th>T(°C)</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L-proline</td>
<td>Cs₂CO₃</td>
<td>12</td>
<td>70</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>L-proline</td>
<td>Cs₂CO₃</td>
<td>12</td>
<td>90</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>L-proline</td>
<td>Cs₂CO₃</td>
<td>12</td>
<td>110</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>dimethylglycine</td>
<td>K₃PO₄</td>
<td>3</td>
<td>90</td>
<td>trace</td>
</tr>
</tbody>
</table>
5  glycine    K$_3$PO$_4$    3    90    28
6  $L$-proline   K$_3$PO$_4$    3    90    75
7  $L$-proline   K$_3$PO$_4$    12    90    71
8  $L$-proline   K$_3$PO$_4$    3    110    72
9$^c$ $L$-proline   K$_3$PO$_4$    5    90    17
10$^d$ $L$-proline   K$_3$PO$_4$    3    90    73
11$^e$ $L$-proline   K$_3$PO$_4$    3    90    27

$^a$ In the presence of CuI (0.15 equiv.) and ligand (0.3 equiv.), base (3 equiv.), 1.5 mL DMF. $^b$ Isolated yield. $^c$ CuBr was used instead of CuI. $^d$ 1.5 mL DMSO was used as solvent. $^e$ In the presence of CuI (0.05 equiv.) and ligand (0.1 equiv.)

Characterization of the obtained product 5 and the enantioselectivities and the diastereoselectivities ($\text{trans:} \text{cis}$ ratios)

\[
\begin{align*}
\text{(R)-N-((R)-3-(2-bromophenyl)-1-phenylbut-3-en-1-yl)-2-methylpropane-2-sulfinamide} \\
\text{Purified by flash chromatograph column (PE : EtOAc = 2 : 1). colorless oil.} \\
[\alpha]_{D}^{16} & = -49.9 \left( c 1.94, \text{CHCl}_3 \right) \\
^1\text{H NMR (400 MHz, CDCl}_3\text{)} & \delta 1.17 (s, 9H), 2.90 - 2.96 (m, 1H), 3.24 - 3.29 (m, 1H), 3.46 (s, 1H), 4.32 - 4.37 (m, 1H), 5.00 (s, 1H), 5.18 (s, 1H), 6.88 (d, $J = 7.2$ Hz, 1H), 7.07 (t, $J = 8.0$ Hz, 1H), 7.15 (t, $J = 7.2$ Hz, 1H), 7.23 - 7.26 (m, 5H), 7.50 (d, $J = 8.0$ Hz, 1H) \\
^1\text{C NMR (100 MHz, CDCl}_3\text{)} & \delta 22.7, 43.8, 56.0, 58.1, 119.5, 121.9, 127.2, 127.7, 128.0, 128.6, 128.8, 130.7, 133.0, 141.5, 142.9, 145.6 \\
\text{IR (film)} & 3417, 2955, 1636, 1467, 1454, 1058, 1024, 760, 699 \text{ cm}^{-1} \\
\text{HRMS for C}_{20}\text{H}_{24}\text{BrNNaOS}^{+} (\text{M}^{+}\text{Na}) & \text{: calcd. 428.0654, found 428.0671.} \\
\end{align*}
\]

\[
\begin{align*}
\text{(R)-4-methylene-2-phenyl-1,2,3,4-tetrahydroquinoline} \\
\text{Purified by flash chromatograph column (PE : EtOAc = 30:1). colorless oil.} \\
[\alpha]_{D}^{16} & = -77.0 \left( c 1.03, \text{CHCl}_3 \right) \\
^1\text{H NMR (400 MHz, CDCl}_3\text{)} & \delta 2.62 - 2.71 (m, 2H), 4.04 (s, 1H), 4.33-4.37 (m, 1H), 4.71 (s, 1H), 5.36 (s, 1H), 6.48 (d, $J = 8.4$ Hz, 1H), 6.62 (t, $J = 8.0$ Hz, 1H), 6.99 (t, $J = 7.2$ Hz, 1H), 7.21 (t, $J = 7.2$ Hz,}
1H), 7.27 (t, J = 6.8 Hz, 2H), 7.32 (d, J = 7.6 Hz, 2H), 7.44 (d, J = 7.6 Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 41.0, 57.4, 106.9, 115.2, 118.0, 120.1, 124.8, 126.8, 127.9, 128.8, 129.3, 139.7, 143.6, 144.7.

IR (film) 3410, 1624, 1604, 1477, 1320, 1226, 877, 747, 699

HRMS for C$_{16}$H$_{16}$N+$^+$: calcd. 222.1277, found 222.1267

HPLC: Chiracel Lux Amylose-2 Column; detected at 230 nm; n-hexane /i-propanol = 95/5; flow = 1mL/min; Retention time: 5.024 min (S), 5.378 min (R).

(R)-4-methylene-2-(p-tolyl)-1,2,3,4-tetrahydroquinoline
Purified by flash chromatograph column (PE : EtOAc =30:1). colorless oil.

$\left[\alpha\right]_{D}^{16}$ -112.3 (c 0.98, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.26 (s, 3H), 2.59 - 2.65 (m, 2H), 4.00 (s, 1H), 4.28 - 4.32 (m, 1H), 4.70 (s, 1H), 5.35 (s, 1H), 6.46 (d, $J = 8.0$ Hz, 1H), 6.61 (t, $J = 8.0$ Hz, 1H), 6.98 (t, $J = 8.0$ Hz, 1H), 7.08 (d, $J = 7.6$ Hz, 2H), 7.20 (d, $J = 7.2$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.2, 41.0, 57.1, 106.8, 115.2, 117.9, 120.1, 124.8, 126.7, 129.3, 129.4, 137.6, 139.9, 140.7, 144.9.

IR (film) 3416, 1627, 1479, 1308, 1247, 872, 831, 750

HRMS for C$_{17}$H$_{18}$N$^+$ (M$^+$ +H$^+$): calcd. 236.1434, found 236.1433

HPLC: Chiracel Lux Amylose-2 Column ; detected at 230 nm; n-hexane /i-propanol = 95/5; flow = 1mL/min; Retention time:5.094min (S), 5.424min (R).
(R)-2-(4-fluorophenyl)-4-methylene-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc = 30:1). colorless oil. $[\alpha]_D^{16} -57.3 (c 1.01, CHCl_3)$

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.61 (d, $J = 6.4$ Hz, 2H), 4.01 (s, 1H), 4.33 (t, $J = 7.2$ Hz, 1H), 4.71 (s, 1H), 5.36 (s, 1H), 6.48 (d, $J = 8.0$ Hz, 1H), 6.62 (t, $J = 6.8$ Hz, 1H), 6.93 - 7.01 (m, 3H), 7.27 (t, $J = 6.4$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) 41.0, 56.7, 107.1, 115.3 (d, $J_{C-F} = 21.6$ Hz), 115.7, 118.2, 120.1, 124.8, 128.3 (d, $J_{C-F} = 8.1$ Hz), 129.3, 139.3 (d, $J_{C-F} = 2.5$ Hz), 139.5, 144.6, 161.4 (d, $J_{C-F} = 243.4$ Hz)

$^{19}$F NMR (400 MHz, CDCl$_3$) δ -115.1

IR (film) 3413, 1604, 1510, 1478, 1324, 1223, 1154, 836, 748 cm$^{-1}$

HRMS for C$_{16}$H$_{16}$FN$^+$ (M$^+$+H)$: \text{calcd.} 240.1183, \text{found} 240.1173$

HPLC: Chiracel Lux Amylose-2 Column; detected at 230 nm; n-hexane / i-propanol = 95/5; flow = 1mL/min; Retention time: 5.488min (S), 5.769min (R).
**NCl**

(R)-2-(4-chlorophenyl)-4-methylene-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc =30:1). colorless oil.

$[\alpha]_D^{16}$ -72.3 (c 1.00, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.60 - 2.61 (m, 2H), 4.01 (s, 1H), 4.30 - 4.34 (m, 1H), 4.70 (s, 1H), 5.35 (s, 1H), 6.48 (d, $J$ = 8.4 Hz, 1H), 6.62 (t, $J$ = 7.8 Hz, 1H), 6.99 (t, $J$ = 7.8 Hz, 1H), 7.23 (s, 4H), 7.42 (d, $J$ = 8.0 Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 40.8, 56.6, 107.2, 115.2, 118.2, 120.1, 124.8, 128.1, 128.9, 129.3, 133.4, 139.2, 142.1, 144.4.

IR (film) 3412, 1629, 1603, 1481, 1320, 1089, 1013, 822, 749 cm$^{-1}$

HRMS for C$_{16}$H$_{15}$ClN$^+$ (M$^+$+H$^-$): calcd. 256.0888, found 256.0880

HPLC: Chiracel Lux Amylose-2 Column; detected at 230 nm; $n$-hexane /i-propanol = 95/5; flow = 1mL/min; Retention time: 5.957 min (S), 6.251 min (R).
(R)-2-(4-methoxyphenyl)-4-methylene-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc =30:1). colorless oil.

$[\alpha]_D^25 -77.6$ (c 0.97, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.58 - 2.67 (m, 2H), 3.71 (s, 3H), 4.00 (s, 1H), 4.27 - 4.29 (m, 1H), 4.70 (s, 1H), 5.35 (s, 1H), 6.46 (d, $J = 8.0$ Hz, 1H), 6.60 (t, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 2H), 6.96 - 6.99 (m, 1H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 7.2$ Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 41.1, 55.4, 56.8, 106.8, 114.1, 115.2, 117.9, 120.1, 124.8, 127.9, 129.3, 135.7, 139.9, 145.0, 159.3
IR (film) 3340, 2931, 1617, 1596, 1477, 1244, 1026, 882, 747 cm\(^{-1}\)

HRMS for C\(_{17}\)H\(_{18}\)NO\(^+\) (M\(^+\)+H\(^+\)): calcd. 252.1383, found 252.1392

HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; \(n\)-hexane /i-propanol = 95/5; flow = 1mL/min; Retention time: 12.232 min (R), 23.065 min (S).

\(\text{NH}^5f\) (\(R\))-4-methylene-2-(naphthalen-2-yl)-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc =30:1). colorless oil.

\([\alpha]_D^{16}\) 119.4(c 0.89, CHCl\(_3\))

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.75 - 2.86 (m, 2H), 4.10 (s, 1H), 4.71 (s, 1H), 5.15 - 5.17 (m, 1H), 5.38 (s, 1H), 6.52 (d, \(J = 8.4\) Hz, 1H), 6.65 (t, \(J = 8.0\) Hz, 1H), 7.01 (t, \(J = 8.0\) Hz, 1H), 7.36 - 7.48 (m, 4H), 7.61 (d, \(J = 6.4\) Hz, 1H), 7.70 (d, \(J = 8.0\) Hz, 1H), 7.79 (d, \(J = 7.6\) Hz, 1H), 8.03 (d, \(J = 7.6\) Hz, 1H)
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 39.7, 53.2, 107.0, 115.4, 118.1, 120.3, 122.8, 123.6, 125.0, 125.8, 126.4, 128.2, 129.2, 129.3, 130.7, 134.0, 138.9, 139.8, 145.0

IR (film) 3358, 1622, 1603, 1477, 1309, 1244, 882, 781, 749

HRMS for C$_{20}$H$_{18}$N$^+$ (M$^++$H$^+$): calcld. 272.1434, found 272.1442

HPLC: Chiralcel Lux Amylose-2 Column; detected at 230 nm; $n$-hexane /$i$-propanol = 95/5; flow = 1mL/min; Retention time: 6.153 min ($S$), 6.966 min ($R$).

N\H
\[ (R)-4\text{-methylene-2-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline} \]

Purified by flash chromatograph column (PE : EtOAc = 30:1). Colorless oil.
[α]_D^16 -96.5 (c 0.79, CHCl₃)

^1H NMR (400 MHz, CDCl₃) δ 2.74 - 2.76 (m, 2H), 4.19 (s, 1H), 4.66 - 4.68 (m, 1H), 4.76 (s, 1H), 5.39 (s, 1H), 6.49 (d, J = 7.6 Hz, 1H), 6.65 (t, J = 8.0 Hz, 1H), 6.88 - 6.90 (m, 1H), 6.94 - 7.02 (m, 2H), 7.15 - 7.16 (m, 1H), 7.44 (d, J = 8.0 Hz, 1H)

^13C NMR (100 MHz, CDCl₃) δ 41.6, 52.9, 107.4, 114.5, 118.5, 120.3, 124.2, 124.5, 124.8, 126.7, 129.3, 139.1, 143.9, 147.3

IR (film) 3416, 1617, 1476, 1252, 1154, 893, 745, 700 cm⁻¹

HRMS for C₄₁H₃₅NS⁺ (M⁺+H) calculated 228.0841, found 228.0831

HPLC: Chiracel Lux Amylose-2 Column; detected at 230 nm; n-hexane/i-propanol = 95/5; flow = 1mL/min; Retention time: 6.105 min (S), 6.980 min (R).
(R)-2-(furan-2-yl)-4-methylene-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc =30:1). colorless oil.

$[\alpha]_D^{16} = -229.8 (c 0.99, CHCl_3)$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.78 (d, $J = 6.4$ Hz, 2H), 4.18 (s, 1H), 4.44 (t, $J = 6.4$ Hz, 1H), 4.77 (s, 1H), 5.38 (s, 1H), 6.13 (s, 1H), 6.23 (s, 1H), 6.48 (d, $J = 8.0$ Hz, 1H), 6.61 (t, $J = 7.2$ Hz, 1H), 6.97 (t, $J = 7.6$ Hz, 1H), 7.27 (s, 1H), 7.42 (d, $J = 7.6$ Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 36.6, 50.2, 105.6, 107.4, 110.3, 115.5, 118.3, 120.2, 124.7, 129.3, 138.6, 141.9, 143.6, 155.3

IR (film) 3411, 1628, 1605, 1480, 1311, 872, 746 cm$^{-1}$

HRMS for C$_{14}$H$_{14}$NO$^+$ (M$^+$+H): calcd. 212.1070, found 212.1058

HPLC: Chiracel Lux Amylose-2 Column ; detected at 230 nm; n-hexane / i-propanol = 95/5; flow = 1mL/min; Retention time: 7.162 min (R), 7.903 min (S).
(R)-2-cyclohexyl-4-methylene-1,2,3,4-tetrahydroquinoline

$[\alpha]_D^{16} = -126.7 (c 0.98, CHCl_3)$

$^1H$ NMR (400 MHz, CDCl$_3$) δ 0.88 - 1.20 (m, 5H), 1.29 - 1.35 (m, 1H), 1.59 - 1.71 (m, 5H), 2.36 - 2.50 (m, 2H), 2.96 - 2.98 (m, 1H), 3.92 (s, 1H), 4.70 (s, 1H), 5.31 (s, 1H), 6.44 (d, $J = 8.0$ Hz, 1H), 6.55 (t, $J = 7.2$ Hz, 1H), 6.95 (t, $J = 7.8$ Hz, 1H), 7.39 (d, $J = 7.8$ Hz, 1H)

$^13C$ NMR (100 MHz, CDCl$_3$) δ 26.3, 26.4, 26.6, 28.6, 29.2, 34.7, 41.6, 57.1, 106.3, 115.1, 117.3, 120.4, 124.7, 129.1, 140.2, 144.7

IR (film) 3415, 2924, 2850, 1624, 1605, 1447, 1154, 867, 745 cm$^{-1}$

HRMS for C$_{16}$H$_{22}$N$^+$ (M$^+$+H): calcd. 228.1747, found 228.1750

HPLC: Chiracel Lux Amylose-2 Column; detected at 230 nm; $n$-hexane /i-propanol = 95/5; flow = 1mL/min; Retention time: 7.465 min (R), 8.798 min (S).
\( (R) \)-2-isopropyl-4-methylene-1,2,3,4-tetrahydroquinoline

Purified by flash chromatography column (PE : EtOAc = 30:1). Colorless oil.  
\([\alpha]_D^{16} -166.9 (c 1.00, CHCl_3)\)

\( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 0.90 (t, \( J = 7.2 \) Hz, 6H), 1.61 - 1.69 (m, 1H), 2.37 - 2.49 (m, 2H), 2.95 - 2.97 (m, 1H), 3.88 (s, 1H), 4.71 (s, 1H), 5.31 (s, 1H), 6.45 (d, \( J = 8.0 \) Hz, 1H), 6.56 (d, \( J = 7.6 \) Hz, 1H), 6.95 (t, \( J = 7.6 \) Hz, 1H), 7.39 (d, \( J = 7.6 \) Hz, 1H)

\( ^13C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 18.2, 18.7, 31.9, 34.6, 57.9, 106.3, 115.1, 117.4, 120.4, 124.7, 129.1, 140.2, 144.7

IR (film) 3416, 2959, 1628, 1606, 1483, 1318, 867, 745 cm\(^{-1}\)

HRMS for C\(_{13}\)H\(_{18}\)N\(^+\) (M\(^++\)H\(^+\)) calcd. 188.1434, found 188.1439

HPLC: Chiracel OD-H Column (250 mm); detected at 230 nm; \( n \)-hexane /i-propanol = 95/5; flow = 1mL/min; Retention time: 6.083 min \((R)\), 6.432 min \((S)\).
(R,E)-4-methylene-2-styryl-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc = 30:1). Colorless oil.

$[\alpha]_D^{16} - 229.1 (c 1.08, CHCl_3)$

$^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 2.48 - 2.65 (m, 2H), 3.94 (s, 2H), 4.75 (s, 1H), 5.36 (s, 1H), 6.14 - 6.20 (m, 1H), 6.46 - 6.52 (m, 2H), 6.61 (t, $J = 6.8$ Hz, 1H), 6.98 (t, $J = 7.6$ Hz, 1H), 7.14 - 7.17 (m, 1H), 7.22 (t, $J = 7.6$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 1H)

$^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 38.4, 55.2, 107.2, 115.3, 118.0, 120.3, 124.8, 126.6, 127.9, 128.7, 129.3, 131.1, 131.1, 136.7, 139.1, 143.9

IR (film) 3414, 3378, 1623, 1476, 1314, 1247, 966, 749, 692 cm$^{-1}$
HRMS for C_{18}H_{18}N^{+} (M'+H): calcd. 248.1434, found 248.1427

HPLC: Chiracel Lux Amylose-2 Column; detected at 230 nm; n-hexane /i-propanol = 95/5; flow = 1mL/min; Retention time: 7.962 min (S), 8.642 min (R).

\[
\begin{align*}
\text{Peak} & \quad \text{Ret Time} & \quad \text{Width} & \quad \text{Area} & \quad \text{Height} & \quad \text{Area} \\
1 & \quad 7.962 \text{ min} & \quad 0.2244 & \quad 6539.52100 & \quad 442.72687 & \quad 49.1057 \\
2 & \quad 8.642 \text{ min} & \quad 0.2006 & \quad 6321.69043 & \quad 294.28690 & \quad 55.8943 \\
\end{align*}
\]

Totals: 1.2421264 707.02979

\[
\begin{align*}
\text{Peak} & \quad \text{Ret Time} & \quad \text{Width} & \quad \text{Area} & \quad \text{Height} & \quad \text{Area} \\
1 & \quad 7.835 \text{ min} & \quad 0.2005 & \quad 170.63319 & \quad 11.43131 & \quad 0.3905 \\
2 & \quad 6.465 \text{ min} & \quad 0.3335 & \quad 1.9246244 & \quad 611.20191 & \quad 99.1095 \\
\end{align*}
\]

Totals: 1.9721881 862.82034

(2R,3R)-2-(4-methoxyphenyl)-3-methyl-4-methylene-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc = 20:1), colorless oil.

\([\alpha]_D^{25} -146.7 \ (c\ 1.09, \ CHCl_3)\)

\(\text{H NMR (400 MHz, CDCl}_3\) \delta 1.01 (d, \ J = 6.0 Hz, 3H), 2.62 - 2.68 (m, 1H), 3.78 (s, 3H), 4.01 (d, \ J = 8.0 Hz, 1H), 4.15 (s, 1H), 4.84 (s, 1H), 5.40 (s, 1H), 6.50 (d, \ J = 8.0 Hz, 1H), 6.66 (t, \ J = 6.8 Hz, 1H),
6.84 (d, $J = 8.4$ Hz, 2H), 7.05 (t, $J = 6.8$ Hz, 1H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 7.6$ Hz, 1H)

$^1$H NMR (100 MHz, CDCl$_3$) δ 16.6, 40.4, 55.4, 62.4, 105.7, 113.9, 114.3, 117.5, 120.4, 125.4, 128.4, 129.1, 135.9, 143.7, 144.7, 159.1

IR (film) 3352, 2967, 1610, 1512, 1481, 1243, 1021, 891, 826, 744

HRMS for C$_{18}$H$_{20}$NO$^+$ (M$^+$+H): calcd. 266.1545, found 266.1565

HPLC: Chiracel Lux Amylose-2 Column; detected at 230 nm; n-hexane /i-propanol = 95/5; flow = 1mL/min; Retention time: (trans) 7.335 min (2S, 3S), 7.812 min (2R, 3R). (cis) 6.635 min, 6.851 min
(2R,3R)-2-(4-chlorophenyl)-3-methyl-4-methylene-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc = 20:1). colorless oil.

\[ \alpha \] \text{D} \text{16} -131.7 (c 0.99, CHCl3)  

\textbf{1H NMR (400 MHz, CDCl3)} \delta 1.07 (d, \textit{J} = 6.8 Hz, 3H), 2.61 - 2.68 (m, 1H), 4.09 (d, \textit{J} = 7.6 Hz, 1H), 4.20 (s, 1H), 4.81 (s, 1H), 5.39 (s, 1H), 6.55 (d, \textit{J} = 8.0 Hz, 1H), 6.70 (t, \textit{J} = 7.6 Hz, 1H), 7.08 (t, \textit{J} = 7.2 Hz, 1H), 7.21 - 7.29 (m, 4H), 7.47 (d, \textit{J} = 7.6 Hz, 1H)  

\textbf{13C NMR (100 MHz, CDCl3)} \delta 17.2, 40.6, 62.1, 106.4, 114.2, 117.7, 120.2, 125.5, 128.5, 128.7, 129.2, 133.2, 142.5, 143.1, 143.8  

\textbf{IR (film)} 3413, 2957, 1615, 1480, 1308, 1083, 1011, 872, 745 cm\(^{-1}\)  

\textbf{HRMS for C\textsubscript{17}H\textsubscript{17}ClN\textsuperscript{+} (M\textsuperscript{+}+H)}: calcd. 270.1044, found 270.1037  

\textbf{HPLC}: Chiracel Lux Amylose-2 Column; detected at 230 nm; \textit{n}-hexane /\textit{i}-propanol = 99/1; flow = 0.5 mL/min; Retention time: \textbf{(trans)} 15.242 min (2S, 3S), 15.774 min (2R, 3R). \textbf{(cis)} 13.126 min, 14.616 min. Several chiral column (AD-H, OD-H, AS-H, OB-H, Lux Amylose-2) have been tried, and Lux Amylose-2 column led to the best result of separation.
(2R,3R)-3-methyl-4-methylene-2-(p-tolyl)-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc =20:1). colorless oil.

[α]D16 -128.8 (c 0.63, CHCl3)

1H NMR (400 MHz, CDCl3) δ 1.04 (d, J = 6.8 Hz, 3H), 2.33 (s, 3H), 2.66 - 2.71 (m, 1H), 4.05 (d, J = 8.0 Hz, 1H), 4.18 (s, 1H), 4.84 (s, 1H), 5.40 (s, 1H), 6.52 (d, J = 7.2 Hz, 1H), 6.67 (t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 7.05 - 7.20 (m, 4H), 7.47 (d, J = 8.0 Hz, 1H)

13C NMR (100 MHz, CDCl3) δ 16.8, 21.2, 40.3, 62.6, 105.7, 114.2, 117.4, 120.4, 125.4, 127.2, 129.1, 129.3, 137.3, 140.8, 143.6, 144.5

IR (film) 3414, 2916, 1617, 1482, 1303, 749 cm⁻¹

HRMS for C18H20N⁺ (M⁺+H): calcd. 250.1590, found 250.1598

HPLC: Chiralcel Lux Amylose-2 Column ; detected at 230 nm; n-hexane /i-propanol = 99/1; flow = 1mL/min; Retention time:7.327 min (2S, 3S), 7.756 min (2R, 3R).
(2R,3R)-2-(β-naphthyl)-3-methyl-4-methylene-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc =20:1). colorless oil.

$[\alpha]_D^{16} 43.7 \text{ (c 1.03, CHCl}_3$)

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.20 (d, $J = 6.8$ Hz, 3H), 2.96 - 3.02 (m, 1H), 4.33 (s, 1H), 4.69 (s, 1H), 5.00 (d, $J = 6.4$ Hz, 1H), 5.35 (s, 1H), 6.60 (d, $J = 7.6$ Hz, 1H), 6.72 (t, $J = 7.2$ Hz, 1H), 7.11-7.15 (m, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.49 - 7.54 (m, 4H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.89 (t, $J = 7.2$ Hz, 1H), 8.13 (d, $J = 8.0$ Hz, 1H)
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 18.3, 40.2, 58.3, 106.8, 114.0, 117.4, 119.7, 123.1, 124.5, 125.5, 125.6, 126.1, 128.0, 129.3, 130.8, 134.0, 139.4, 143.5, 143.9

IR (film) 3423, 1632, 1605, 1487, 1308, 1252, 882, 774 cm$^{-1}$

HRMS for C$_{21}$H$_{20}$N$^+$ (M$^+$+H$^+$): calcd. 286.1590, found 286.1586

HPLC: Chiracel Lux Amylose-2 Column; detected at 230 nm; $n$-hexane /i-propanol = 99/1; flow = 0.5 mL/min; Retention time: (trans) 6.679 min (2S, 3S), 7.585 min (2R, 3R).

\[
\text{\begin{tabular}{|c|c|c|c|c|c|}
\hline
Peak & Retime (min) & Width (s) & Max Height & Area & Area% \\
\hline
1 & 4.670 & 0.0794 & 0.355 & 473 & 3.0854 \\
2 & 7.585 & 0.1807 & 19.559 & 90.5746 \\
\hline
Total & & & 94.553 & & 99.987 \\
\end{tabular}}
\]

\[
\text{\begin{tabular}{|c|c|c|c|c|c|}
\hline
Peak & Retime (min) & Width (s) & Max Height & Area & Area% \\
\hline
1 & 6.670 & 0.0224 & 50.14 & 5.014 & 1.000 \\
2 & 7.581 & 0.0421 & 4.082 & 4.082 & 0.844 \\
\hline
Total & & & 13.382 & & 2.850 \\
\end{tabular}}
\]

$\text{(2R,3R)-3-ethyl-2-(4-methoxyphenyl)-4-methylene-1,2,3,4-tetrahydroquinoline}$

Purified by flash chromatograph column (PE : EtOAc =20:1). colorless oil.
$[\alpha]_D^{16} = -115.4$ (c 0.62, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.93 (t, $J = 7.6$ Hz, 3H), 1.53 - 1.62 (m, 2H), 2.31 - 2.35 (m, 1H), 3.75 (s, 3H), 4.35 - 4.35 (m, 2H), 4.58 (s, 1H), 5.29 (d, $J = 11.6$ Hz, 1H), 6.54 (d, $J = 8.4$ Hz, 1H), 6.64 (t, $J = 7.2$ Hz, 1H), 6.77 (d, $J = 8.8$ Hz, 2H), 7.06 - 7.10 (m, 3H), 7.43 (d, $J = 8.0$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 12.0, 26.2, 49.7, 55.3, 59.0, 109.0, 113.7, 117.0, 119.5, 125.7, 127.2, 129.2, 137.7, 140.6, 142.6, 158.5

IR (film) 3414, 2957, 1617, 1519, 1484, 1247, 749 cm$^{-1}$

HRMS for C$_{19}$H$_{22}$NO$^+$(M$^+$+H): calcd. 280.1701, found 280.1717

HPLC: Chiracel Lux Amylose-2 Column; detected at 230 nm; n-hexane /i-propanol = 99/1; flow = 1mL/min; Retention time: (trans) 9.396 min (2S, 3S), 10.07 min (2R, 3R). (cis) 7.674 min, 8.268 min
(2R,3R)-3-ethyl-4-methylene-2-(p-tolyl)-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc = 20:1). colorless oil.

$[\alpha]_D^{16} -138.3$ (c 0.79, CHCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.94 (t, $J = 7.2$ Hz, 3H), 1.51-1.67 (m, 2H), 2.29 (s, 3H), 2.35 - 2.36 (m, 1H), 4.37 (s, 2H), 4.57 (s, 1H), 5.31 (s, 1H), 6.56 (d, $J = 8.0$ Hz, 1H), 6.65 (t, $J = 7.6$ Hz, 1H), 7.03 - 7.11 (m, 5H), 7.41 (t, $J = 7.6$ Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 12.0, 21.1, 26.3, 49.6, 59.3, 108.9, 113.7, 116.9, 119.5, 125.7, 126.0, 129.1, 129.2, 136.4, 140.4, 142.6, 142.6

IR (film) 3413, 2957, 1627, 1605, 1490, 1319, 1247, 867, 745 cm$^{-1}$

HRMS for C$_{19}$H$_{22}$N$^+$ (M$^+$+H$^+$): calcd. 264.1747, found 264.1755

HPLC: Chiracel AD-H Column; detected at 230 nm; $n$-hexane / i-propanol = 99/1; flow = 1mL/min;
Retention time: (trans) 7.848 min (2R, 3R), 11.623min (2S, 3S).
5 Preparation of tetrahydroquinolines 5r, 5s and 5t with quaternary stereocenters

(2S,3S)-2-(4-chlorophenyl)-2,3-dimethyl-4-methylene-1,2,3,4-tetrahydroquinoline
Purified by flash chromatograph column (PE : EtOAc =20:1). colorless oil.
$[\alpha]_D^{16}$ -126.5 (c 0.9, CHCl3)

$^1$H NMR (400 MHz, CDCl3) $\delta$ 1.04 (d, $J$ = 6.8 Hz, 3H), 1.43 (s, 3H), 2.77 (q, $J$ = 6.8 Hz, 1H), 4.16 (s, 1H), 4.67 (s, 1H), 5.23 (s, 1H), 6.59 - 6.67(m, 2H), 7.09 (td, $J$ = 1.6, 8.4 Hz, 1H), 7.20 - 7.23 (m, 2H), 7.29 - 7.32 (m, 2H), 7.38 (dd, $J$ = 1.2, 7.6 Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl3) $\delta$ 14.9, 24.7, 44.4, 59.1, 106.5, 114.2, 117.5, 119.7, 125.5, 127.4, 128.4, 129.2, 132.3, 142.5, 144.3, 146.8

HRMS for C18H19ClN+(M++H): calcd. 284.1201, found 284.1209

HPLC: Chiracel OD-H Column ; detected at 254 nm; $n$-hexane /$i$-propanol = 97/3; flow = 1 mL/min;
Retention time: 7.2 min (2S, 3S), 8.3 min (2R, 3R)
(2R,3S)-2,3-dimethyl-4-methylene-2-pentyl-1,2,3,4-tetrahydroquinoline

Purified by flash chromatograph column (PE : EtOAc = 20:1). colorless oil.

$[\alpha]_D^{16} -133.6 \ (c \ 1.1, \ \text{CHCl}_3)$

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.84 (t, $J = 7.2$ Hz, 3H), 1.02 (d, $J = 6.8$ Hz, 3H), 1.07 (s, 3H), 1.20 - 1.44 (m, 8H), 2.35 (q, $J = 6.8$ Hz, 1H), 3.75 (s, 1H), 4.80 (s, 1H), 5.37 (s, 1H), 6.46 (d, $J = 8.0$ Hz, 1H), 6.61 (t, $J = 7.6$ Hz, 1H), 7.02 (t, $J = 6.4$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.1, 14.9, 22.8, 22.9, 32.4, 40.3, 42.2, 54.6, 105.8, 114.7, 116.9, 119.0, 125.3, 129.0, 142.7, 145.5

HRMS for C$_{17}$H$_{26}$N$^+$ (M$^+$+H$^+$): calcd. 244.2060, found 244.2055

HPLC: Chiracel AD-H Column; detected at 230 nm; n-hexane /i-propanol = 99/1; flow = 1 mL/min;
Retention time: (trans) 4.540 min (2S, 3R), 4.905 min (2R, 3S).
(3S,4S)-3-phenyl-4-vinyl-3,4-dihydroisoquinolin-1(2H)-one

Purified by flash chromatograph column (PE : EtOAc =5:1). colorless oil.

$\alpha_{D}^{16} \ 6.4 \ (c \ 0.62, \ CHCl_{3})$

$^1$H NMR (400 MHz, CDCl$_3$)  $\delta$ 3.78 (t, $J = 8.0$ Hz, 1H), 4.65 (d, $J = 8.4$ Hz, 1H), 4.91 (d, $J = 17.2$ Hz, 1H), 5.15 (d, $J = 10.0$ Hz, 1H), 5.81 - 5.90 (m, 1H), 6.30 (s, 1H), 7.18 (d, $J = 8.0$ Hz, 1H), 7.26-7.31 (m, 5H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 8.13 (d, $J = 7.6$ Hz, 1H)

$^{13}$C NMR (100 MHz, CDCl$_3$)  $\delta$ 50.8, 60.5, 119.6, 127.2, 127.5, 127.6, 128.1, 128.2, 128.3, 128.8, 132.8, 136.6, 139.2, 140.4, 165.8

HRMS for C$_{17}$H$_{16}$NO$^+$ (M$^+$+H): calcd. 250.1226, found 250.1227
6 Determination of the Absolute Configuration of 6a, 6b and 3o

[Chemical structures and diagrams with atomic labels and CCDC numbers]
7 Copies of $^1$H and $^{13}$C NMR spectra of products
The image contains a chemical structure and a graph谱. The chemical structure is labeled as 68, and the graph谱 shows peaks at various PPM values, indicating a spectral analysis or NMR spectrum.