Supporting Information

Asymmetric Aza-Henry Reaction to Provide Oxindoles with Quaternary Carbon Stereocenter Catalyzed by a Metal-Templated Chiral Brønsted Base

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1. General Information

Solvents preparation: Acetonitrile (CH$_3$CN) and dichloromethane (CH$_2$Cl$_2$) were distilled under argon from calcium hydride while tetrahydrofuran (THF) and toluene from sodium/benzophenone; anhydrous 1-butoxybutane (nBu$_2$O, stored under argon), 2-methoxy-2-methyl-propane (MTBE, stored under argon) and 2-isopropoxypropane (iPr$_2$O, 99+% purity, stabilized with BHT) were purchased from Acros and used directly. All other reagents were purchased from commercial suppliers (Aldrich, Alfa and J&K) and used without further purification. Aryl nitromethanes$^{1,2}$ and N-alkoxycarbonyl ketimines$^3$ were prepared according to published procedures. Flash column chromatography was performed with silica gel (300-400 mesh). $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM (400 MHz) or Bruker AM (500 MHz) spectrometer at ambient temperature. NMR standards were used as follows: CDCl$_3$ = 7.26 ppm ($^1$H NMR) and 77.0 ppm ($^{13}$C NMR). IR spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer. Chiral HPLC chromatograms were obtained from an Agilent 1260 Series HPLC system. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0T FT-MS instrument using ESI technique. The optical rotations were measured on a Anton Paar MCP 500 polarimeter with [α]$_D^{20}$ values reported in degrees at concentrations of 1.0 g/100 mL. The ee and dr values of products were determined by chiral HPLC and absolute configurations were assigned based on a crystal structure of 3k'.
2. Synthesis of Substrates and Racemic References

2.1 Synthesis of N-BOC Ketimines

**General Procedure:** N-Alkoxy carbonyl ketimines (1a-o) were prepared by a published method with modifications. According to the general procedure, the mixture was heated at 110 °C until complete disappearance of the starting materials detected by TLC. Then, the reaction was cooled to room temperature. After an evaporation of the volatile organic solvents, the crude residue was purified by flash chromatography (silica gel, nhexane/ethyl acetate) and afforded the ketimines 1a-o, which have been reported except for 1m.3

*tert*-butyl (Z)-(1-benzyl-2-oxo-5-phenylindolin-3-ylidene)carbamate (1m)

Following the general procedure, the chromatography (eluent: EtOAc/nhexane = 1/10, v/v) afforded the title compound as a red foam (380 mg, 0.921 mmol, 92% yield).

**1H NMR** (500 MHz, CDCl₃) δ (ppm) 7.90 (s, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.51-7.39 (m, 4H), 7.38-7.28 (m, 6H), 6.79 (d, J = 7.8 Hz, 1H), 4.93 (s, 2H), 1.66 (s, 9H).

**13C NMR** (125 MHz, CDCl₃) δ (ppm) 160.35, 157.39, 153.10, 146.40, 139.42, 136.97, 134.58, 133.84, 128.95, 128.93, 128.05, 127.58, 127.39, 126.53, 122.86, 119.90, 110.58, 83.65, 44.05, 28.02.

IR (film): ν (cm⁻¹) 3064, 3033, 2979, 2931, 1739, 1680, 1621, 1597, 1478, 1369, 1340, 1268, 1251, 1150, 1127, 762, 698.
HRMS calcd for C_{26}H_{24}N_{2}NaO_{3} (M+Na)^{+} 435.1679, found: 435.1675.

2.2 Synthesis of Mixtures of Stereoisomers as HPLC References

**General Procedure**: To a stirred solution of aryl nitromethane (0.15 mmol) in iPr_{2}O (1.0 mL) was added the ketimine (0.10 mmol) in one portion, followed by Et_{3}N (0.030 mmol). The reaction mixture was stirred at room temperature until complete disappearance of the starting materials detected by TLC. After an evaporation of the volatile organic solvents, the crude residue was purified by flash chromatography (silica gel, nhexane/ethyl acetate). The samples were used as references to determine enantiomeric excess and diastereomer ratio in the asymmetric aza-Henry reactions.
3. Optimization of Reaction Conditions Providing the Kinetic Diastereomer

An oven-dried 3 mL vial was charged with ketimine 1a (13.0 mg, 0.050 mmol), iridium catalyst A-IrBB (0.5-3.0 mol%) and the indicated solvent (0.40 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene 2a (10.3 mg, 0.075 mmol) in the indicated solvent (50.0 μL) was added by syringe in one portion, then the same solvent (50.0 μL) used for rinsing was added in one portion as well. The reaction mixture was stirred at -30 °C for the indicated time. After evaporation of the solvent, the crude product was used directly for a determination of the conversion by $^1$H NMR as well as ee and dr values by chiral HPLC analysis.

Table S1. Optimization of reaction conditions.

<table>
<thead>
<tr>
<th>entry</th>
<th>conditions</th>
<th>t (h)</th>
<th>conv. (%)</th>
<th>ee</th>
<th>dr (3a:3a')</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>toluene (3 mol% cat)</td>
<td>9</td>
<td>99</td>
<td>90%</td>
<td>51:1</td>
</tr>
<tr>
<td>2</td>
<td>toluene (1 mol% cat)</td>
<td>23</td>
<td>&gt;99</td>
<td>89%</td>
<td>51:1</td>
</tr>
<tr>
<td>3</td>
<td>nBu₂O (1 mol% cat)</td>
<td>13</td>
<td>100</td>
<td>86%</td>
<td>60:1</td>
</tr>
<tr>
<td>4</td>
<td>MTBE (1 mol% cat)</td>
<td>13</td>
<td>100</td>
<td>91%</td>
<td>79:1</td>
</tr>
<tr>
<td>5</td>
<td>iPr₂O (1 mol% cat)</td>
<td>13</td>
<td>100</td>
<td>96%</td>
<td>90:1</td>
</tr>
<tr>
<td>6</td>
<td>iPr₂O (0.5 mol% cat)</td>
<td>24</td>
<td>100</td>
<td>96%</td>
<td>86:1</td>
</tr>
</tbody>
</table>
4. Optimization of the Conversion of Kinetic to Thermodynamic Diastereomer

An oven-dried 3 mL vial was charged with ketimine 1a (26.0 mg, 0.10 mmol), iridium catalyst Λ-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr₂O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr₂O (50.0 μL) was added by syringe in one portion and another indicated solvent (50.0 μL) used to rinse the vial was added in one portion. Then, the reaction was stirred at -30 °C for 24 hours. Upon completion, the precipitate was purified by centrifugation and washing with toluene/n-hexane (0.7 mL, 1/2, v/v) until the filtrate layer was almost colorless to afford a white solid (3a, 32.2 mg, 81% yield, >99% ee, 1:138 dr).

**tert-butyl ((S)-1-methyl-3-((S)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3a)**

\[
\begin{align*}
\text{H NMR (500 MHz, CDCl₃)} & \quad \delta (\text{ppm}) \quad 7.51 (s, 1H), \quad 7.37-7.31 (m, 3H), \quad 7.30-7.22 (m, 3H), \quad 7.03 (t, J = 7.6 Hz, 1H), \quad 6.65 (d, J = 7.7 Hz, 1H), \quad 6.15 (\text{brs}, 1H), \quad 5.75 (s, 1H), \quad 3.14 (s, 3H), \quad 1.33 (s, 9H). \\
\text{C NMR (125 MHz, CDCl₃)} & \quad \delta (\text{ppm}) \quad 171.87, \quad 154.00, \quad 143.35, \quad 130.20, \quad 130.08, \quad 129.44, \quad 128.24, \quad 127.89, \quad 126.51, \quad 125.10, \quad 123.02, \quad 108.31, \quad 91.39, \quad 81.14, \quad 63.28, \quad 28.03, \quad 26.53. \\
\text{HRMS calcd for C}_{21}H_{23}N_{3}NaO_{5} (M+Na)^{+} & \quad 420.1530, \quad \text{found: 420.1526.}
\end{align*}
\]

Subsequently, the product (8.0 mg, 0.020 mmol) was dissolved in THF, to which different organic bases (2 equiv.) as shown below were added. Then, the reaction was stirred at room temperature for
3 hours, at which point the reaction solution was diluted with dichloromethane and injected directly to chiral HPLC. The obtained ee and dr values are listed in Table S2.

**Table S2.** Effect of the base and concentration on the epimerization.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>pK_a (in MeCN)</th>
<th>conc. (mM)</th>
<th>t (h)</th>
<th>ee of 3a'</th>
<th>dr (3a'/3a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pyrrolidine (2 eq)</td>
<td>19.56</td>
<td>50</td>
<td>3</td>
<td>&gt;99%</td>
<td>5.7:1</td>
</tr>
<tr>
<td>2</td>
<td>TEA (2 eq)</td>
<td>18.82</td>
<td>50</td>
<td>3.5</td>
<td>&gt;99%</td>
<td>7.5:1</td>
</tr>
<tr>
<td>3</td>
<td>DMAP (2 eq)</td>
<td>17.95</td>
<td>50</td>
<td>23</td>
<td>99%</td>
<td>7.6:1</td>
</tr>
<tr>
<td>4</td>
<td>benzylamine (2 eq)</td>
<td>16.91</td>
<td>50</td>
<td>5</td>
<td>&gt;99%</td>
<td>5.2:1</td>
</tr>
<tr>
<td>5</td>
<td>2,4,6-trimethylpyridine (2 eq)</td>
<td>14.98</td>
<td>50</td>
<td>3</td>
<td>&gt;99%</td>
<td>1:14.9</td>
</tr>
<tr>
<td>6</td>
<td>TEA (2 eq)</td>
<td><strong>18.82</strong></td>
<td><strong>200</strong></td>
<td>3</td>
<td>&gt;99%</td>
<td><strong>8.5:1</strong></td>
</tr>
<tr>
<td>7</td>
<td>TEA (2 eq)</td>
<td>18.82</td>
<td>500</td>
<td>3</td>
<td>&gt;99%</td>
<td>8.3:1</td>
</tr>
<tr>
<td>8</td>
<td>TEA (10 eq)</td>
<td>18.82</td>
<td>200</td>
<td>3</td>
<td>&gt;99%</td>
<td>8.4:1</td>
</tr>
</tbody>
</table>
5. Substrate Scope for the Formation of the Thermodynamic Diastereomer

![Chemical Structure]

3a' (R² = H, R³ = Me, R⁴ = H), 99% yield, 10:1 dr, 96% ee.  
3b' (R² = H, R³ = Et, R⁴ = H), 98% yield, 15:1 dr, 98% ee.  
3c' (R² = H, R³ = Allyl, R⁴ = H), 97% yield, 14:1 dr, 97% ee.  
3d' (R² = H, R³ = Bn, R⁴ = H), 99% yield, 14:1 dr, 96% ee.  
3e' (R² = H, R³ = Ac, R⁴ = H), 92% yield, 9:1 dr, 98% ee.  
3f' (R² = H, R³ = H, R⁴ = H), 96% yield, 8:1 dr, 92% ee.  
3g' (R² = 5-Me, R³ = Me, R⁴ = H), 99% yield, 9:1 dr, 98% ee.  
3h' (R² = 5-OMe, R³ = Me, R⁴ = H), 98% yield, 9:1 dr, 94% ee.  
3i' (R² = 5-F, R³ = Me, R⁴ = H), 99% yield, 19:1 dr, 92% ee.  
3j' (R² = 5-Cl, R³ = Me, R⁴ = H), 99% yield, 11:1 dr, 93% ee.  
3k' (R² = 5-Br, R³ = Me, R⁴ = H), 99% yield, 10:1 dr, 93% ee.  
3l' (R² = 5-Cl, R³ = Bn, R⁴ = H), 97% yield, 16:1 dr, 97% ee.  
3m' (R² = 5-Ph, R³ = Bn, R⁴ = H), 97% yield, 11:1 dr, 98% ee.  
3n' (R² = 6-Cl, R³ = Me, R⁴ = H), 98% yield, 10:1 dr, 92% ee.  
3o' (R² = 7-F, R³ = Me, R⁴ = H), 98% yield, 16:1 dr, 90% ee.  
3p' (R² = H, R³ = Bn, R⁴ = 3-ethyl), 98% yield, 23:1 dr, 98% ee.  
3q' (R² = H, R³ = Bn, R⁴ = 4-Me), 99% yield, 18:1 dr, 98% ee.  
3r' (R² = H, R³ = Bn, R⁴ = 4-OMe), 95% yield, 20:1 dr, 97% ee.  
3s' (R² = H, R³ = Bn, R⁴ = 4-Cl), 99% yield, 9:1 dr, 97% ee.  
3t' (R² = H, R³ = Bn, R⁴ = 4-Br), 98% yield, 10:1 dr, 96% ee.

tert-butyl ((S)-1-methyl-3-((R)-nitro(phenyl)methyl)-2-oxindolin-3-yl)carbamate (3a')

An oven-dried 3 mL vial was charged with ketimine 1a (26.0 mg, 0.10 mmol), iridium catalyst A-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and tPr₂O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in tPr₂O (50.0 μL) was added by syringe in one portion, then additional tPr₂O (50.0 μL) used for rinse was added in one portion. The reaction mixture was stirred at -30 °C for 24 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/5~1/3, v/v) to afford the title compound (39.2 mg, 0.099 mmol, 99%) as a white solid. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using...
a Chiralpak IC column, ee = 96%, dr = 10:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 75:25, flow rate = 0.90 mL/min, T = 25 °C; \( t_r(3a', \text{major}) = 9.2 \text{ min} \), \( t_r(3a', \text{minor}) = 15.7 \text{ min} \), \( t_r(3a, \text{major}) = 19.6 \text{ min} \), \( t_r(3a, \text{minor}) = 22.8 \text{ min} \). \([\alpha]D^{20} = 5.7^\circ (c 0.5, \text{CHCl}_3)\).

\[ \text{[\alpha]D}^{20} = 5.7^\circ (c 0.5, \text{CHCl}_3). \]

\[ {\text{H NMR (400 MHz, CDCl}}_3] \delta (\text{ppm}) 7.52 (d, J = 7.4 Hz, 1H), 7.39-7.29 (m, 2H), 7.21-7.11 (m, 3H), 6.99 (d, J = 7.5 Hz, 2H), 6.63 (d, J = 7.8 Hz, 1H), 6.01 (s, 1H), 5.92 (s, 1H), 2.83 (s, 3H), 1.29 (s, 9H). \]

\[ {\text{C NMR (100 MHz, CDCl}}_3] \delta (\text{ppm}) 172.38, 153.51, 144.21, 130.34, 130.30, 129.47, 128.25, 127.89, 125.41, 124.72, 122.99, 108.20, 92.77, 81.08, 64.18, 28.02, 26.17. \]

IR (film): \( \nu (\text{cm}^{-1}) 3438, 3361, 2978, 2928, 1716, 1615, 1558, 1495, 1471, 1456, 1366, 1255, 1168, 752, 728, 699, 624, 542. \]

HRMS calcd for C_{21}H_{23}N_3NaO_5 (M+Na)^+ 420.1530, found: 420.1532.

**tert-butyl ((S)-1-ethyl-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3b')**

An oven-dried 3 mL vial was charged with ketimine 1b (27.4 mg, 0.10 mmol), iridium catalyst \( \text{IrBB} (0.68 \text{ mg}, 0.50 \mu \text{mol}, 0.50 \text{ mol%}) \) and \( \text{iPr}_2\text{O} \) (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in \( \text{iPr}_2\text{O} \) (50.0 \mu L) was added by syringe in one portion, then additional \( \text{iPr}_2\text{O} \) (50.0 \mu L) used to rinse the vial was added in one portion. The reaction mixture was stirred at -30 °C for 25 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 \mu L, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel.
(eluent: EtOAc/nhexane = 1/5, v/v) to afford the title compound (40.2 mg, 0.098 mmol, 98%) as a yellowish foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 98%, dr = 15:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 75:25, flow rate = 0.90 mL/min, T = 25 °C; t_r (3b', major) = 8.7 min, t_r (3b, minor) = 13.4 min, t_r (3b, major) = 16.8 min, t_r (3b', minor) = 26.6 min). [α]_D^{20} = -7.1° (c 0.5, CHCl3).

1H NMR (400 MHz, CDCl3) δ (ppm) 7.52 (d, J = 7.4 Hz, 1H), 7.39-7.27 (m, 2H), 7.19-7.10 (m, 3H), 6.96 (d, J = 7.6 Hz, 2H), 6.65 (d, J = 7.8 Hz, 1H), 6.00 (s, 1H), 5.98 (s, 1H), 3.67 (dq, J = 14.6, 7.3 Hz, 1H), 3.20 (m, 1H), 1.27 (s, 9H), 0.60 (t, J = 7.2 Hz, 3H).

13C NMR (100 MHz, CDCl3) δ (ppm) 171.81, 153.35, 143.46, 130.33, 130.29, 129.85, 127.97, 127.76, 125.5, 124.69, 122.77, 108.25, 92.82, 89.09, 63.93, 34.72, 27.98, 11.43.

IR (film): ν (cm⁻¹) 3427, 3315, 2979, 2934, 1725, 1613, 1559, 1489, 1468, 1456, 1368, 1349, 1253, 1162, 1134, 750, 699.

HRMS calcd for C_{22}H_{25}N_{3}NaO_{5} (M+Na)^+ 434.1686, found: 434.1691.

**tert-butyl ((S)-1-allyl-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3c')**

An oven-dried 3 mL vial was charged with ketimine 1c (28.6 mg, 0.10 mmol), iridium catalyst \(\Lambda\)-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr₂O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr₂O (50.0 μL) was added by syringe in one portion, then addition iPr₂O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 23 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which
TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/5, v/v) to afford the title compound (41.0 mg, 0.097 mmol, 97%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 97%, dr = 14:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; tₜ (3c', major) = 9.5 min, tₜ (3c, minor) = 15.2 min, tₜ (3c, major) = 16.9 min, tₜ (3c', minor) = 18.9 min). [α]D²⁰ = -20.9° (c 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.54 (d, J = 7.4 Hz, 1H), 7.36-7.30 (m, 2H), 7.21-7.11 (m, 3H), 6.99 (d, J = 7.4 Hz, 2H), 6.65 (d, J = 7.8 Hz, 1H), 6.02 (s, 1H), 5.92 (s, 1H), 5.14-5.00 (m, 1H), 4.96-4.91 (m, 1H), 4.83 (d, J = 17.1 Hz, 1H), 4.28-4.19 (m, 1H), 3.82 (dd, J = 16.1, 5.5 Hz, 1H), 1.30 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.15, 153.40, 143.65, 130.62, 130.38, 130.24, 129.84, 128.11, 127.83, 125.42, 124.59, 122.95, 117.75, 109.21, 92.89, 81.08, 64.05, 42.73, 28.06.

IR (film): ν (cm⁻¹) 3423, 3329, 2978, 2927, 1726, 1613, 1559, 1488, 1468, 1456, 1368, 1274, 1253, 1162, 753, 733, 699.

HRMS calcd for C₂₃H₂₅N₃NaO₅ (M+Na)⁺ 446.1686, found: 446.1692.

tert-butyl ((S)-1-benzyl-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3d')

An oven-dried 3 mL vial was charged with ketimine 1d (33.6 mg, 0.10 mmol), iridium catalyst Λ-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr₂O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr₂O (50.0 μL) was added by syringe in one
portion, then additional iPr₂O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 12 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/10~1/5, v/v) to afford the title compound (46.8 mg, 0.099 mmol, 99%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 98%, dr = 14:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 80/20, flow rate = 0.80 mL/min, T = 25 °C; tᵣ(3d', major) = 9.3 min, tᵣ(3d', minor) = 12.5 min, tᵣ(3d, minor) = 16.1 min, tᵣ(3d, major) = 19.8 min). [α]D²₀ = -36.7° (c 0.5, CHCl₃).

1H NMR (400 MHz, CDCl₃) δ (ppm) 7.55 (d, J = 7.4 Hz, 1H), 7.42-7.35 (m, 1H), 7.23 (dd, J = 7.8, 1.2 Hz, 1H), 7.21-7.09 (m, 6H), 7.07-7.02 (m, 2H), 6.70 (d, J = 7.0 Hz, 2H), 6.49 (d, J = 7.8 Hz, 1H), 6.08 (s, 1H), 5.97 (s, 1H), 4.83 (d, J = 16.0 Hz, 1H), 4.45 (d, J = 16.0 Hz, 1H), 1.32 (s, 9H).

13C NMR (100 MHz, CDCl₃) δ (ppm) 172.85, 153.44, 143.85, 134.81, 130.50, 130.29, 129.95, 128.60, 128.31, 127.83, 127.31, 126.76, 125.49, 124.66, 123.02, 109.52, 92.97, 81.12, 63.93, 44.43, 28.09.

IR (film): ν (cm⁻¹) 3422, 3323, 3062, 3033, 2978, 2929, 2855, 1717, 1613, 1559, 1487, 1468, 1456, 1368, 1270, 1253, 1163, 1081, 1002, 753, 737, 698.

HRMS calcd for C₂₇H₂₇N₃NaO₅ (M+Na)⁺ 496.1843, found: 496.1849.

**tert-butyl ((S)-1-acetyl-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3e')**

An oven-dried 3 mL vial was charged with ketimine 1e (28.8 mg, 0.10 mmol), iridium catalyst...
A-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr₂O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr₂O (50.0 μL) was added by syringe in one portion, then additional iPr₂O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 20 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/10, v/v) to afford the title compound (39.2 mg, 0.092 mmol, 92%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IA column, ee = 98%, dr = 9:1 (HPLC conditions: IA column, wavelength = 254 nm, eluents: nhexane/isopropanol = 85/15, flow rate = 1.0 mL/min, T = 25 °C; tᵣ (3e', major) = 9.2 min, tᵣ (3e', minor) = 16.8 min, tᵣ (3e, major) = 12.4 min, tᵣ (3e, minor) = 22.9 min). [α]D₂₀ = -26.4° (c 1.0, CHCl₃).

1H NMR (500 MHz, CDCl₃) δ (ppm) 8.05 (d, J = 8.2 Hz, 1H), 7.47-7.39 (m, 2H), 7.37-7.33 (m, 1H), 7.31-7.27 (m, 1H), 7.22-7.17 (m, 2H), 6.93-6.88 (m, 2H), 6.32 (s, 1H), 5.90 (s, 1H), 2.32 (s, 3H), 1.27 (s, 9H).

13C NMR (125 MHz, CDCl₃) δ (ppm) 173.64, 169.56, 140.91, 130.97, 130.80, 129.76, 128.29, 126.86, 125.55, 124.22, 116.48, 92.57, 81.82, 64.67, 27.91, 25.91.

IR (film): ν (cm⁻¹) 3417, 2977, 2926, 1770, 1716, 1605, 1562, 1477, 1466, 1371, 1337, 1310, 1270, 1173, 1016, 760, 700, 581.

HRMS calcd for C₂₇H₂₇N₃NaO₅ (M+Na)+ 448.1479, found: 448.1485.
tert-buty1 ((S)-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3f')

An oven-dried 3 mL vial was charged with ketimine 1f (24.6 mg, 0.10 mmol), iridium catalyst \( \Lambda\-\text{IrBB} \) (0.68 mg, 0.50 \( \mu \)mol, 0.50 mol%) and \( \text{iPr}_2\text{O} \) (0.90 mL). The resulting suspension was cooled to -10 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in \( \text{iPr}_2\text{O} \) (50.0 \( \mu \)L) was added by syringe in one portion, then additional \( \text{iPr}_2\text{O} \) (50.0 \( \mu \)L) used for rinse was added in one portion. Then the reaction was stirred at -10 °C for 30 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 \( \mu \)L, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/5~1/3, v/v) to afford the title compound (36.8 mg, 0.096 mmol, 96%) as a white solid. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 92%, dr = 8:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 70:30, flow rate = 0.20 mL/min, \( T = 25 \) °C; \( t_r \) (3f', major) = 27.3 min, \( t_r \) (3f', minor) = 29.6 min, \( t_r \) (3f, major) = 31.3 min, \( t_r \) (3f, minor) = 35.4 min). \([\alpha]_{D}^{20} = -33.4^\circ \) (c 0.5, CHCl3).

\(^1\text{H} \) NMR (500 MHz, CDCl3) \( \delta \) (ppm) 7.72 (brs, 1H), 7.44 (d, \( J = 7.5 \) Hz, 1H), 7.33 (t, \( J = 7.5 \) Hz, 1H), 7.30-7.25 (m, 1H), 7.19 (t, \( J = 7.7 \) Hz, 2H), 7.10 (t, \( J = 7.6 \) Hz, 1H), 7.03 (d, \( J = 7.7 \) Hz, 2H), 6.64 (d, \( J = 7.8 \) Hz, 1H), 6.10 (s, 1H), 5.96 (s, 1H), 1.31 (s, 9H).

\(^{13}\text{C} \) NMR (125 MHz, CDCl3) \( \delta \) (ppm) 173.99, 153.68, 141.41, 130.41, 130.35, 129.74, 128.13, 127.73, 125.62, 124.97, 122.97, 110.17, 92.61, 81.39, 64.23, 28.03.

IR (film): \( \nu \) (cm\(^{-1}\)) 3401, 3347, 2921, 2850, 1746, 1712, 1558, 1471, 1455, 1368, 1252, 1165, 1048, 757, 744, 729, 698.
HRMS calcd for C_{20}H_{21}N_{3}NaO_{5} (M+Na)^+ 406.1373, found: 406.1381.

tert-butyl ((S)-1,5-dimethyl-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3g')

An oven-dried 3 mL vial was charged with ketimine 1g (27.4 mg, 0.10 mmol), iridium catalyst Λ-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr₂O (0.90 mL). The resulting suspension was cooled to -20 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr₂O (50.0 μL) was added by syringe in one portion, then additional iPr₂O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -20 °C for 16 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/5~1/3, v/v) to afford the title compound (40.6 mg, 0.099 mmol, 99%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IA column, ee = 98%, dr = 9:1 (HPLC conditions: IA column, wavelength = 254 nm, eluents: nhexane/isopropanol = 85:15, flow rate = 0.80 mL/min, T = 25°C; tᵣ (3g', major) = 10.2 min, tᵣ (3g, minor) = 20.3 min, tᵣ (3g', minor) = 22.1 min, tᵣ (3g, major) = 26.2 min). [α]D^{20} = -24.2° (c 1.0, CHCl₃).

^1H NMR (400 MHz, CDCl₃) δ (ppm) 7.35-7.28 (m, 2H), 7.22-7.12 (m, 3H), 6.99 (d, J = 7.6 Hz, 2H), 6.53 (d, J = 7.9 Hz, 1H), 6.00 (s, 1H), 5.93 (s, 1H), 2.80 (s, 3H), 2.38 (s, 3H), 1.30 (s, 9H).

^13C NMR (100 MHz, CDCl₃) δ (ppm) 172.25, 153.52, 141.84, 132.61, 130.63, 130.25, 129.56, 127.92, 127.84, 126.00, 124.65, 107.95, 92.75, 80.98, 64.21, 28.03, 26.16, 21.17.

IR (film): ν (cm⁻¹) 3417, 3314, 2977, 2928, 1726, 1622, 1605, 1559, 1500, 1456, 1367, 1253, 1164, 811, 746, 699, 553.
An oven-dried 3 mL vial was charged with ketimine 1h (29.0 mg, 0.10 mmol), iridium catalyst A-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr2O (0.90 mL). The resulting suspension was cooled to 0 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr2O (50.0 μL) was added by syringe in one portion, then additional iPr2O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at 0 °C for 22 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/5~1/3, v/v) to afford the title compound (41.9 mg, 0.098 mmol, 98%) as a yellowish foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IA column, ee = 94%, dr = 9:1 (HPLC conditions: IA column, wavelength = 254 nm, eluents: nhexane/isopropanol = 80:20, flow rate = 1.0 mL/min, T = 25 °C; t_r (3h', major) = 8.4 min, t_r (3h, minor) = 17.6 min, t_r (3h', minor) = 21.3 min, t_r (3h, major) = 23.8 min). [α]D20 = -20.3° (c 1.0, CHCl3).

1H NMR (400 MHz, CDCl3) δ (ppm) 7.35-7.28 (m, 1H), 7.22-7.11 (m, 3H), 7.01 (d, J = 7.5 Hz, 2H), 6.88 (dd, J = 8.5, 2.6 Hz, 1H), 6.54 (d, J = 8.5 Hz, 1H), 5.99 (s, 1H), 5.93 (s, 1H), 3.82 (s, 3H), 2.80 (s, 3H), 1.30 (s, 9H).

13C NMR (100 MHz, CDCl3) δ (ppm) 172.05, 156.15, 153.50, 137.63, 130.29, 129.49, 127.89, 127.85, 125.81, 115.18, 112.32, 108.67, 92.75, 81.10, 64.47, 55.90, 28.03, 26.24.
IR (film): ν (cm\(^{-1}\)) 3411, 3315, 2977, 2931, 1722, 1603, 1558, 1498, 1471, 1456, 1436, 1367, 1298, 1254, 1236, 1209, 1163, 1129, 1071, 1041, 739, 699.

HRMS calcd for C\(_{22}\)H\(_{25}\)N\(_3\)O\(_6\) (M+Na)\(^+\) 450.1636, found: 450.1639.

**tert-butyl ((S)-5-fluoro-1-methyl-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3i')**

![Chemical Structure](attachment:image.png)

An oven-dried 3 mL vial was charged with ketimine 1i (27.8 mg, 0.10 mmol), iridium catalyst \(\Lambda\text{-IrBB} \) (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr\(_2\)O (1.9 mL). The resulting suspension was cooled to -40 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr\(_2\)O (50.0 μL) was added by syringe in one portion, then additional iPr\(_2\)O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -40 °C for 17 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/5~1/3, v/v) to afford the title compound (41.1 mg, 0.099 mmol, 99%) as a yellowish foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 92%, dr = 19:1 ((HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; \(t_\tau \) (3i', major) = 8.8 min, \(t_\tau \) (3i', minor) = 11.0 min, \(t_\tau \) (3i, major) = 15.9 min, \(t_\tau \) (3i, minor) = 24.5 min; [\(\alpha\)]\(_{D}^{20}\) = 29.8° (c 0.5, CHCl\(_3\))).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ (ppm) 7.37 (dd, \(J = 8.0, 2.6 \text{ Hz}, \) 1H), 7.35-7.30 (m, 1H), 7.22-7.16 (m, 2H), 7.09-6.99 (m, 3H), 6.55 (dd, \(J = 8.5, 4.1 \text{ Hz}, \) 1H), 6.00 (s, 1H), 5.82 (s, 1H), 5.24 (s, 1H), 1.32 (s, 9H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)) δ (ppm) 172.19, 159.23 (d, \(J = 242.0 \text{ Hz})\), 153.49, 140.22, 130.44,
129.22, 128.04, 127.69, 116.63 (d, \( J = 23.5 \) Hz), 113.98 (d, \( J = 25.9 \) Hz), 108.72 (d, \( J = 7.9 \) Hz), 92.66, 81.38, 64.33, 28.04, 26.34.

IR (film): \( \nu \) (cm\(^{-1}\)) 3411, 3321, 2961, 2925, 2854, 1716, 1623, 1557, 1495, 1470, 1393, 1368, 1274, 1259, 1162, 1122, 1070, 1020, 974, 873, 812, 740, 699, 631, 559.

HRMS calcd for \( \text{C}_{21}\text{H}_{22}\text{FN}_{3}\text{NaO}_{5} \) (M+Na\(^+\)) 438.1436, found: 438.1435.

**tert-butyl ((S)-5-chloro-1-methyl-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3j')**

An oven-dried 3 mL vial was charged with ketimine \( 1j \) (29.5 mg, 0.10 mmol), iridium catalyst \( \Lambda\text{-IrBB} \) (0.68 mg, 0.50 \( \mu \)mol, 0.50 mol\%) and \( \text{iPr}_2\text{O} \) (1.9 mL). The resulting suspension was cooled to -40 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (\( 2a \)) (20.6 mg, 0.15 mmol) in \( \text{iPr}_2\text{O} \) (50.0 \( \mu \)L) was added by syringe in one portion, then additional \( \text{iPr}_2\text{O} \) (50.0 \( \mu \)L) used for rinse was added in one portion. Then the reaction was stirred at -40°C for 20 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 \( \mu \)L, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/\( n \)hexane = 1/5–1/3, v/v) to afford the title compound (42.8 mg, 0.099 mmol, 99%) as a yellowish foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 93\%, dr = 11:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: \( n \)hexane/isopropanol = 80:20, flow rate = 0.80 mL/min, \( T = 25 \) °C; \( t_r \) (3j', major) = 8.5 min, \( t_r \) (3j', minor) = 10.5 min, \( t_r \) (3j, major) = 14.8 min, \( t_r \) (3j, minor) = 24.7 min). \( [\alpha]_D^{20} = -19.3^\circ \) (c 1.0, \( \text{CHCl}_3 \)).

\(^{1}\text{H NMR (400 MHz, CDCl}_3\) \( \delta \) (ppm) 7.57 (d, \( J = 2.1 \) Hz, 1H), 7.36-7.29 (m, 2H), 7.23-7.17(m, 2H),
7.04-6.99 (m, 2H), 6.55 (d, J = 8.3 Hz, 1H), 5.98 (s, 1H), 5.88 (s, 1H), 2.82 (s, 3H), 1.32 (s, 9H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ (ppm) 172.05, 153.47, 142.80, 130.49, 130.27, 129.24, 128.47, 128.08, 127.63, 126.43, 126.04, 109.13, 92.61, 81.46, 64.20, 28.06, 26.31.

IR (film): ν (cm$^{-1}$) 3417, 3325, 2978, 2929, 1732, 1611, 1561, 1490, 1456, 1367, 1270, 1252, 1162, 1133, 1108, 1069, 816, 741, 699, 546.

HRMS calcd for C$_{21}$H$_{22}$ClN$_3$NaO$_5$ (M+Na)$^+$ 454.1140, found: 454.1141.

**tert-butyl (((S)-5-bromo-1-methyl-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3k')**

![Chemical Structure](image)

An oven-dried 3 mL vial was charged with ketimine 1k (33.9 mg, 0.10 mmol), iridium catalyst Λ-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr$_2$O (1.9 mL). The resulting suspension was cooled to -40 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr$_2$O (50.0 μL) was added by syringe in one portion, then additional iPr$_2$O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -40 °C for 24 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/5~1/3, v/v) to afford the title compound (47.6 mg, 0.100 mmol, 99%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 93%, dr = 10:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; t$_r$ (3k', major) = 8.8 min, t$_r$ (3k', major) = 11.1 min, t$_r$ (3k, major) = 15.4 min, t$_r$ (3k, minor) = 26.3 min). [α]$_D^{20}$ = -26.1° (c 1.0, CHCl$_3$).
$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.69 (d, $J = 1.9$ Hz, 1H), 7.48 (dd, $J = 8.3$, 2.0 Hz, 1H), 7.36-7.30 (m, 1H), 7.23-7.17 (m, 2H), 7.09-6.94 (m, 2H), 6.50 (d, $J = 8.3$ Hz, 1H), 5.97 (s, 1H), 5.86 (s, 1H), 2.82 (s, 3H), 1.32 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ (ppm) 171.94, 153.45, 143.26, 133.17, 130.48, 129.22, 128.69, 128.07, 127.59, 126.74, 115.63, 109.61, 92.59, 81.46, 64.14, 28.04, 26.28.

IR (film): ν (cm$^{-1}$) 3408, 3326, 2978, 2931, 1733, 1609, 1562, 1487, 1456, 1423, 1393, 1367, 1270, 1252, 1134, 1110, 1067, 813, 740, 699, 535.

HRMS calcd for C$_{21}$H$_{22}$BrN$_3$NaO$_5$ (M+Na)$^+$ 498.0635, found: 498.0634.

**tert-butyl ((S)-1-benzyl-5-iodo-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3l')**

![Chemical Structure](image)

An oven-dried 3 mL vial was charged with ketimine 1l (46.2 mg, 0.10 mmol), iridium catalyst A-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr$_2$O (1.9 mL). The resulting suspension was cooled to -40 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr$_2$O (50.0 μL) was added by syringe in one portion, then additional iPr$_2$O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -40 °C for 19 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/10~1/5, v/v) to afford the title compound (58.1 mg, 0.097 mmol, 97%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 97%, dr = 16:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 80:20, flow rate = 0.60 mL/min, T = 25 °C; t$_r$ (3l', major) = 9.2
An oven-dried 3 mL vial was charged with ketimine 1m (41.2 mg, 0.10 mmol), iridium catalyst Λ-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr₂O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr₂O (50.0 μL) was added by syringe in one portion, then additional iPr₂O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 22 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction
mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/10~1/5, v/v) to afford the title compound (53.3 mg, 0.097 mmol, 97%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 98%, dr = 11:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; t_r (3m', major) = 9.3 min, t_r (3m', minor) = 12.6 min, t_r (3m, major) = 16.5 min, t_r (3m, minor) = 18.8 min). [α]D^20 = -81.9° (c 1.0, CHCl3).

^1H NMR (400 MHz, CDCl3) δ (ppm) 7.77 (d, J = 1.7 Hz, 1H), 7.60-7.54 (m, 2H), 7.51-7.32 (m, 5H), 7.24-7.13 (m, 5H), 7.12-7.07 (m, 2H), 6.73 (d, J = 6.8 Hz, 2H), 6.56 (d, J = 8.2 Hz, 1H), 6.10 (s, 1H), 6.04 (s, 1H), 4.84 (d, J = 16.0 Hz, 1H), 4.51 (d, J = 15.9 Hz, 1H), 1.33 (s, 9H).

^13C NMR (100 MHz, CDCl3) δ (ppm) 172.89, 153.46, 143.07, 140.33, 136.29, 134.75, 130.56, 129.98, 129.01, 128.85, 128.64, 128.37, 127.75, 127.38, 127.21, 126.84, 126.79, 125.21, 124.15, 109.74, 92.92, 81.22, 64.05, 44.51, 28.10.

IR (film): ν (cm^-1) 3419, 3308, 2978, 2927, 1725, 1616, 1557, 1483, 1456, 1367, 1253, 1161, 764, 739, 698.

HRMS calcd for C_{33}H_{31}N_{3}NaO_{5} (M+Na)^+ 572.2156, found: 572.2167.

*tert*-butyl ((S)-6-chloro-1-methyl-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3n')

An oven-dried 3 mL vial was charged with ketimine 1n (29.5 mg, 0.10 mmol), iridium catalyst A-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr2O (0.90 mL). The resulting suspension was cooled to -20 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr2O (50.0 μL) was added by syringe in one
portion, then additional iPr$_2$O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -20 °C for 17 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane, 1/5, v/v) to afford the title compound (42.3 mg, 0.098 mmol, 98%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 92%, dr = 10:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; $t_r$ (3n', major) = 7.8 min, $t_r$ (3n', minor) = 10.5 min, $t_r$ (3n, major) = 15.4 min, $t_r$ (3n, minor) = 23.4 min). $[\alpha]_{D}^{20} = -9.3^\circ$ (c 1.0, CHCl$_3$).

$^1$H NMR (500 MHz, CDCl$_3$) δ (ppm) 7.48 (d, $J = 8.0$ Hz, 1H), 7.34 (t, $J = 7.4$ Hz, 1H), 7.21 (t, $J = 7.7$ Hz, 2H), 7.12 (d, $J = 7.9$ Hz, 1H), 7.02 (d, $J = 7.6$ Hz, 2H), 6.64 (s, 1H), 5.98 (s, 1H), 5.87 (s, 1H), 2.82 (s, 3H), 1.31 (s, 9H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ (ppm) 172.41, 153.48, 145.39, 136.25, 130.51, 129.27, 128.11, 127.58, 126.51, 123.09, 122.90, 109.01, 92.56, 81.38, 63.86, 28.04, 26.32.

IR (film): ν (cm$^{-1}$) 3414, 3331, 2978, 2918, 1731, 1610, 1560, 1495, 1456, 1369, 1248, 1162, 1076, 740, 699.

HRMS calcd for C$_{21}$H$_{22}$ClN$_3$NaO$_5$ (M+Na)$^+$ 454.1140, found: 454.1146.

**tert-butyl ((S)-7-fluoro-1-methyl-3-((R)-nitro(phenyl)methyl)-2-oxoindolin-3-yl)carbamate (3o')**

An oven-dried 3 mL vial was charged with ketimine 1o (27.8 mg, 0.10 mmol), iridium catalyst
**A-IrBB** (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr₂O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of (nitromethyl)benzene (2a) (20.6 mg, 0.15 mmol) in iPr₂O (50.0 μL) was added by syringe in one portion, then additional iPr₂O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 24 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/5, v/v) to afford the title compound (40.7 mg, 0.098 mmol, 98%) as a white solid. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 90%, dr = 16:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 80:20, flow rate = 0.70 mL/min, T = 25 °C; tᵣ (3o', major) = 8.9 min, tᵣ (3o', minor) = 13.6 min, tᵣ (3o, major) = 20.6 min, tᵣ (3o, minor) = 23.7 min). [α]D²⁰ = -16.1° (c 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.39-7.29 (m, 2H), 7.21 (t, J = 7.8 Hz, 2H), 7.12-7.04 (m, 2H), 6.97 (d, J = 7.5 Hz, 2H), 5.98 (s, 1H), 5.96 (s, 1H), 3.02 (d, J = 2.7 Hz, 3H), 1.31 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.16, 153.45, 148.81, 146.38, 131.01 (d, J = 8.0 Hz), 130.55, 129.38, 128.04, 127.54, 123.49 (d, J = 6.1 Hz), 121.19 (d, J = 3.3 Hz), 118.30 (d, J = 19.2 Hz), 92.65, 81.35, 64.32, 28.75 (d, J = 5.8 Hz), 28.03.

IR (film): ν (cm⁻¹) 3434, 3352, 2978, 2928, 1729, 1713, 1632, 1561, 1481, 1456, 1366, 1279, 1246, 1168, 1058, 768, 728, 701, 736, 564.

HRMS calcd for C₂₁H₂₂F₃NaO₆ (M+Na)⁺ 438.1436, found: 438.1441.
*tert*-butyl ((S)-1-benzyl-3-((R)-(3-ethylphenyl)(nitro)methyl)-2-oxoindolin-3-yl)carbamate (3p')

An oven-dried 3 mL vial was charged with ketimine 1d (33.6 mg, 0.10 mmol), iridium catalyst A-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr₂O (0.90 mL). The resulting suspension was cooled to -20 °C under an argon atmosphere and stirred for 10 min, at which point a solution of aryl nitromethane 2b (24.8 mg, 0.15 mmol) in iPr₂O (50.0 μL) was added by syringe in one portion, then additional iPr₂O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -20 °C for 15 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated *in vacuo*. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/10, v/v) to afford the title compound (49.4 mg, 0.098 mmol, 98%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak AD-H column, ee = 98%, dr = 23:1 (HPLC conditions: AD-H column, wavelength = 254 nm, eluents: nhexane/isopropanol = 75:25, flow rate = 0.90 mL/min, T = 25 °C; tᵣ (3p', major) = 7.1 min, tᵣ (3p', minor) = 16.5 min, tᵣ (3p, minor) = 22.1 min, tᵣ (3p, major) = 33.1 min). [α]D²⁰ = -40.5° (c 1.0, CHCl₃).

1H NMR (400 MHz, CDCl₃) δ (ppm) 7.57 (dd, J = 7.5, 0.9 Hz, 1H), 7.26-7.07 (m, 7H), 6.91 (d, J = 7.7 Hz, 1H), 6.78-6.75 (m, 1H), 6.60 (d, J = 7.4 Hz, 2H), 6.47 (d, J = 7.7 Hz, 1H), 6.03 (s, 1H), 5.99 (s, 1H), 4.89 (d, J = 16.0 Hz, 1H), 4.40 (d, J = 16.0 Hz, 1H), 2.41 (q, J = 7.6 Hz, 2H), 1.31 (s, 9H), 0.93 (t, J = 7.6 Hz, 3H).

13C NMR (100 MHz, CDCl₃) δ (ppm) 172.86, 153.38, 144.36, 143.95, 134.83, 130.20, 130.18, 129.14, 128.58, 128.25, 127.67, 127.57, 127.23, 126.64, 125.48, 124.75, 122.97, 109.50, 93.07, 81.08, 64.06, 44.42, 28.50, 28.08, 15.04.
IR (film): ν (cm⁻¹) 3424, 3329, 2970, 2931, 1727, 1613, 1560, 1487, 1468, 1456, 1368, 1271, 1253, 1163, 753, 733, 703.

HRMS calcd for C₂₉H₃₁N₃NaO₅ (M+Na)⁺ 524.2156, found: 524.2157.

tert-butyl (S)-1-benzyl-3-((R)-nitro(p-tolyl)methyl)-2-oxoindolin-3-yl)carbamate (3q′)

An oven-dried 3 mL vial was charged with ketimine 1d (33.6 mg, 0.10 mmol), iridium catalyst \( \Lambda\text{-IrBB} \) (0.68 mg, 0.50 μmol, 0.50 mol%) and {iPr}₂O (0.90 mL). The resulting suspension was cooled to -20 °C under an argon atmosphere and stirred for 10 min, at which point a solution of aryl nitromethane 2c (22.7 mg, 0.15 mmol) in {iPr}₂O (50.0 μL) was added by syringe in one portion, then additional {iPr}₂O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -20 °C for 14 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/10–1/5, v/v) to afford the title compound (48.1 mg, 0.099 mmol, 99%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IA column, ee = 98%, dr = 18:1 (HPLC conditions: IA column, wavelength = 254 nm, eluents: nhexane/isopropanol = 80:20, flow rate = 0.70 mL/min, T = 25 °C; \( t_r \) (3q′, major) = 9.3 min, \( t_r \) (3q, major) = 14.0 min, \( t_r \) (3q′, minor) = 23.2 min, \( t_r \) (3q, minor) = 26.4 min). [α]₅₀° = -53.2° (c 1.0, CHCl₃).

\(^{1}H\) NMR (400 MHz, CDCl₃) δ 7.53 (dd, \( J = 7.5, 0.8 \) Hz, 1H), 7.25-7.09 (m, 5H), 6.99-6.88 (m, 4H), 6.72 (d, \( J = 7.2 \) Hz, 2H), 6.50 (d, \( J = 7.7 \) Hz, 1H), 6.02 (s, 1H), 5.96 (s, 1H), 4.90 (d, \( J = 15.9 \) Hz,
1H), 4.42 (d, J = 15.9 Hz, 1H), 2.33 (s, 3H), 1.31 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl3) δ (ppm) 172.92, 153.41, 143.91, 140.67, 134.88, 130.22, 129.84, 129.01, 128.44, 127.27, 126.89, 125.44, 124.89, 124.78, 122.97, 109.46, 92.87, 81.05, 63.89, 44.47, 28.08, 21.34.

IR (film): ν (cm$^{-1}$) 3423, 3326, 2979, 2927, 1726, 1613, 1559, 1487, 1468, 1456, 1368, 1269, 1253, 1163, 1003, 878, 786, 753, 735, 697, 553.

HRMS calcd for C$_{28}$H$_{29}$N$_{3}$NaO$_{5}$ (M+Na)$^+$ 510.1999, found: 510.2003.

**tert-butyl ((S)-1-benzyl-3-((R)-(4-methoxyphenyl)(nitro)methyl)-2-oxoindolin-3-yl)carbamate (3r')**

An oven-dried 3 mL vial was charged with ketimine 1d (33.6 mg, 0.10 mmol), iridium catalyst $\Lambda$-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr$_2$O (0.90 mL). The resulting suspension was cooled to 0 °C under an argon atmosphere and stirred for 10 min, at which point a solution of aryl nitromethane 2d (25.1 mg, 0.15 mmol) in iPr$_2$O (50.0 μL) was added by syringe in one portion, then additional iPr$_2$O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at 0 °C for 24 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/10~1/5, v/v) to afford the title compound (47.8 mg, 0.095 mmol, 95%) as a yellow foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IA column, ee = 97%, dr = 20:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol =
80:20, flow rate = 0.75 mL/min, T = 25 °C; t_r (3r', major) = 9.7 min, t_r (3r, major) = 15.8 min, t_r (3r', minor) = 26.4 min, t_r (3r, minor) = 29.3 min). [α]_D^{20} = -75.4° (c 1.0, CHCl₃).

1H NMR (400 MHz, CDCl₃) δ (ppm) 7.50 (d, J = 7.1 Hz, 1H), 7.28-7.22 (m, 1H), 7.20-7.09 (m, 4H), 6.94-6.89 (m, 2H), 6.69-6.63 (m, 4H), 6.51 (d, J = 7.8 Hz, 1H), 6.00 (brs, 1H), 5.99 (s, 1H), 4.94 (d, J = 15.9 Hz, 1H), 4.39 (d, J = 15.9 Hz, 1H), 3.76 (s, 3H), 1.31 (s, 9H).

13C NMR (100 MHz, CDCl₃) δ (ppm) 172.96, 161.29, 153.37, 143.98, 134.84, 131.49, 130.28, 128.45, 127.33, 126.85, 125.31, 124.72, 122.98, 119.74, 113.69, 109.50, 92.63, 81.07, 64.01, 55.16, 44.45, 28.10.

IR (film): ν (cm⁻¹) 3422, 3332, 3061, 2978, 2932, 2840, 1716, 1612, 1583, 1557, 1514, 1489, 1368, 1308, 1255, 1181, 1031, 1002, 878, 836, 798, 754, 736, 698, 553, 539.


tert-butyl ((S)-3-((R)-(4-chlorophenyl)(nitro)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3s')

An oven-dried 3 mL vial was charged with ketimine 1a (26.0 mg, 0.10 mmol), iridium catalyst Λ-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr₂O (0.90 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of aryl nitromethane 2e (25.7 mg, 0.15 mmol) in iPr₂O (50.0 μL) was added by syringe in one portion, then additional iPr₂O (50.0 μL) used for rinse was added in one portion. Then the reaction was stirred at -30 °C for 5 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μL, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was
directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/nhexane = 1/5, v/v) to afford the title compound (42.8 mg, 0.099 mmol, 99%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 97%, dr = 9:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: nhexane/isopropanol = 80:20, flow rate = 0.90 mL/min, T = 25 °C; t₁ (3s', major) = 8.2 min, t₂ (3s, minor) = 15.7 min, t₃ (3s, major) = 19.0 min, t₄ (3s, minor) = 25.4 min). \([\alpha]_{D}^{20} = -31.1^\circ\) (c 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.54 (d, J = 7.4 Hz, 1H), 7.41-7.35 (m, 1H), 7.20-7.11 (m, 3H), 6.95 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 7.8 Hz, 1H), 6.04 (s, 1H), 5.87 (s, 1H), 2.89 (s, 3H), 1.29 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.24, 153.50, 144.15, 136.65, 130.90, 130.57, 128.18, 126.37, 125.44, 124.46, 123.18, 108.40, 91.90, 81.21, 63.92, 28.02, 26.29.

IR (film): ν (cm⁻¹) 3414, 3321, 2978, 2932, 1727, 1613, 1562, 1493, 1471, 1369, 1354, 1254, 1161, 1127, 1094, 1017, 791, 753, 539.

HRMS calcd for C₂₁H₂₂ClN₃NaO₅ (M+Na)⁺ 454.1140, found: 454.1145.

**tert-butyl ((S)-3-((R)-(4-bromophenyl)(nitro)methyl)-1-methyl-2-oxoindolin-3-yl)carbamate (3t')**

An oven-dried 3 mL vial was charged with ketimine 1a (26.0 mg, 0.10 mmol), iridium catalyst Λ-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr₂O (0.60 mL). The resulting suspension was cooled to -30 °C under an argon atmosphere and stirred for 10 min, at which point a solution of aryl nitromethane 2f (32.4 mg, 0.15 mmol) in iPr₂O (0.30 mL) was added by syringe in one portion, then additional iPr₂O (0.10 mL) used for rinse was added in one portion. Then the reaction was stirred at
-30 °C for 6 hours. Upon completion, the reaction mixture was warmed to room temperature and then concentrated in vacuo. The residue was dissolved in 0.50 mL of THF, to which TEA (28.0 μl, 0.20 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was directly subjected to a flash chromatography column packed by silica gel (eluent: EtOAc/n-hexane = 1/10~1/5, v/v) to afford the title compound (46.8 mg, 0.098 mmol, 98%) as a white foam. Enantiomeric excess and diastereomer ratio were established by HPLC analysis using a Chiralpak IC column, ee = 96%, dr = 10:1 (HPLC conditions: IC column, wavelength = 254 nm, eluents: n-hexane/isopropanol = 80:20, flow rate = 0.80 mL/min, T = 25 °C; t_r (3t', major) = 9.5 min, t_r (3t', minor) = 18.3 min, t_r (3t, major) = 21.9 min, t_r (3t, minor) = 27.7 min). [α]_D^{20} = -34.7° (c 1.0, CHCl₃).

1H NMR (400 MHz, CDCl₃) δ (ppm) 7.54 (d, J = 7.5 Hz, 1H), 7.41-7.30 (m, 3H), 7.18-7.12 (m, 1H), 6.92-6.86 (m, 2H), 6.69 (d, J = 7.8 Hz, 1H), 6.04 (s, 1H), 5.85 (s, 1H), 2.89 (s, 3H), 1.30 (s, 9H).

13C NMR (100 MHz, CDCl₃) δ (ppm) 172.20, 153.49, 144.12, 131.15, 131.09, 130.57, 126.85, 125.43, 124.97, 124.42, 123.19, 108.42, 91.92, 81.21, 63.83, 28.01, 26.30.

IR (film): ν (cm⁻¹) 3414, 3323, 2978, 2929, 1729, 1614, 1559, 1490, 1472, 1369, 1354, 1254, 1127, 1075, 1013, 790, 754, 736, 540.

HRMS calcd for C_{21}H_{22}BrN_{3}NaO_{5} (M+Na)^+ 498.0635, found: 498.0635.

Substrates which didn’t work:

Attempted reaction with substrate 2g: An oven-dried 3 mL vial was charged with ketimine 1d (33.6 mg, 0.10 mmol), iridium catalyst Λ-IrBB (0.68 mg, 0.50 μmol, 0.50 mol%) and iPr₂O (0.90 mL). Then, a solution of aryl nitromethane 2g (22.7 mg, 0.15 mmol) in iPr₂O (0.10 mL) was added by syringe in one portion. The reaction was stirred at 20 °C for 24 hours. No product could be
detected by TLC analysis.

**Attempted reaction with substrate 1p:** An oven-dried 3 mL vial was charged with ketimine 1p (13.7 mg, 0.050 mmol), iridium catalyst Λ-IrBB (0.68 mg, 0.50 μmol, 1.0 mol%) and iPr₂O (0.40 mL). Then, a solution of (nitromethyl)benzene (2a) (10.3 mg, 0.075 mmol) in iPr₂O (0.10 mL) was added by syringe in one portion. The reaction was stirred at 20 °C for 19 hours. No product could be detected by TLC analysis.
6. Control Experiments

An oven-dried 3 mL vial was charged with ketimine or isatin (0.050 mmol), iridium catalyst \( \Lambda\text{-IrBB} \) or \( \Lambda\text{-IrBB}' \) and \( iPr_2O \) (0.40 mL). The resulting suspension was stirred at 20 °C. A solution of (nitromethyl)benzene (2a) (0.075 mmol) in \( iPr_2O \) (50.0 μL) was added by syringe in one portion, then additional \( iPr_2O \) (50.0 μL) used for rinse was added in one portion. The stirring was kept for the indicated time shown in Table S3. Upon completion, the ee and dr values were directly determined by chiral HPLC analysis.

![Reaction Scheme](image)

Table S3. Control experiments.

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7. $^1$H NMR and $^{13}$C NMR Spectra

Figure S1. $^1$H and $^{13}$C NMR spectra of 3a.
Figure S2. $^1$H and $^{13}$C NMR spectra of 3a'.

$^1$H NMR, CDCl$_3$

$^{13}$C NMR, CDCl$_3$
Figure S3. $^1$H and $^{13}$C NMR spectra of 3b'.

S35
Figure S4. $^1$H and $^{13}$C NMR spectra of 3c'.

$^1$H NMR, CDCl$_3$
400 MHz

$^{13}$C NMR, CDCl$_3$
100 MHz
Figure S5. $^1$H and $^{13}$C NMR spectra of 3d'.

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\[ \text{S37} \]
Figure S6. $^1$H and $^{13}$C NMR spectra of 3e'.
Figure S7. $^1$H and $^{13}$C NMR spectra of 3f.
Figure S8. $^1$H and $^{13}$C NMR spectra of 3g'.
Figure S9. $^1$H and $^{13}$C NMR spectra of 3h'.
Figure S10. $^1$H and $^{13}$C NMR spectra of 3i'.
Figure S11. $^1$H and $^{13}$C NMR spectra of 3j'.
Figure S12. $^1$H and $^{13}$C NMR spectra of 3k'.
Figure S13. $^1$H and $^{13}$C NMR spectra of 3l'.

S45
Figure S14. $^1$H and $^{13}$C NMR spectra of 3m'.

$^1$H NMR, CDCl$_3$
400 MHz

$^{13}$C NMR, CDCl$_3$
100 MHz
Figure S15. $^1$H and $^{13}$C NMR spectra of 3n'.

$^1$H NMR, CDCl$_3$
500 MHz

$^{13}$C NMR, CDCl$_3$
100 MHz
Figure S16. $^1$H and $^{13}$C NMR spectra of 3o'.
Figure S17. $^1$H and $^{13}$C NMR spectra of 3p'.
Figure S18. $^1$H and $^{13}$C NMR spectra of 3q’.
Figure S19. $^1$H and $^{13}$C NMR spectra of 3r'.

S51
Figure S20. $^1$H and $^{13}$C NMR spectra of 3s'.
Figure S21. $^1$H and $^{13}$C NMR spectra of $3t'$. 
8. Chiral HPLC Traces

Stereoselectives of the asymmetric aza-Henry reactions were determined with a Daicel Chiralpak AD-H, IA or IC HPLC column (250 x 4.6 mm) on an Agilent 1260 Series HPLC System using nhexane/isopropanol as mobile phase. The column temperature was 25 °C and UV-absorption was measured at 254 nm.

![HPLC trace for the racemic reference rac-3a and 3a'].

**Figure S22.** HPLC trace for the racemic reference *rac*-3a and 3a'.

![HPLC trace for (3S,8S)-3a.]

**Figure S23.** HPLC trace for (3S,8S)-3a.
Figure S24. HPLC trace for (3S,8R)-3a'.

Figure S25. HPLC trace for the racemic reference rac-3b and 3b'.

Figure S26. HPLC trace for (3S,8S)-3b.
Figure S27. HPLC trace for (3S,8R)-3b'.

Figure S28. HPLC trace for the racemic reference rac-3c and 3c'.

Figure S29. HPLC trace for (3S,8S)-3c.
**Figure S30.** HPLC trace for (3S,8R)-3c'.

![HPLC trace for (3S,8R)-3c'](image)

**Figure S31.** HPLC trace for the racemic reference rac-3d and 3d'.

![HPLC trace for rac-3d and 3d'](image)

**Figure S32.** HPLC trace for (3S,8S)-3d.

![HPLC trace for (3S,8S)-3d](image)
Figure S33. HPLC trace for (3S,8R)-3d'.

<table>
<thead>
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<th>[min]</th>
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<th>[mAU]</th>
<th>%</th>
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Figure S34. HPLC trace for the racemic reference rac-3e and 3e'.

Figure S35. HPLC trace for (3S,8S)-3e.
Figure S36. HPLC trace for (3S,8R)-3e'.

Figure S37. HPLC trace for the racemic reference rac-3f and 3f'.

Figure S38. HPLC trace for (3S,8S)-3f.
Figure S39. HPLC trace for (3S,8R)-3f'.

Figure S40. HPLC trace for the racemic reference rac-3g and 3g'.

Figure S41. HPLC trace for (3S,8S)-3g.
**Figure S42.** HPLC trace for (3S,8R)-3g'.

**Figure S43.** HPLC trace for the racemic reference rac-3h and 3h'.

**Figure S44.** HPLC trace for (3S,8S)-3h.
Figure S45. HPLC trace for (3S,8R)-3h'.

Figure S46. HPLC trace for the racemic reference rac-3i and 3i'.

Figure S47. HPLC trace for (3S,8S)-3i.
Figure S48. HPLC trace for (3S,8R)-3i'.

Figure S49. HPLC trace for the racemic reference rac-3j and 3j'.

Figure S50. HPLC trace for (3S,8S)-3j.
Figure S51. HPLC trace for (3S,8R)-3j'.

Figure S52. HPLC trace for the racemic reference rac-3k and 3k'.

Figure S53. HPLC trace for (3S,8S)-3k.
Figure S54. HPLC trace for \((3S,8R)-3k'\).

Figure S55. HPLC trace for the racemic reference \textit{rac-3l} and \(3l'\).

Figure S56. HPLC trace for \((3S,8S)-3l\).
Figure S57. HPLC trace for \((3S,8R)-3l'\).

Figure S58. HPLC trace for the racemic reference \(rac-3m\) and \(3m'\).

Figure S59. HPLC trace for \((3S,8S)-3m\).
Figure S60. HPLC trace for (3S,8R)-3m'.

Figure S61. HPLC trace for the racemic reference rac-3n and 3n'.

Figure S62. HPLC trace for (3S,8S)-3n.
Figure S63. HPLC trace for (3S,8R)-3n'.

Figure S64. HPLC trace for the racemic reference rac-3o and 3o'.

Figure S65. HPLC trace for (3S,8S)-3o.
Figure S66. HPLC trace for (3S,8R)-3o'.

Figure S67. HPLC trace for the racemic reference rac-3p and 3p'.

Figure S68. HPLC trace for (3S,8S)-3p.
Figure S69. HPLC trace for (3S,8R)-3p'.

Figure S70. HPLC trace for the racemic reference rac-3q and 3q'.

Figure S71. HPLC trace for (3S,8S)-3q.
Figure S72. HPLC trace for (3S,8R)-3q'.

Figure S73. HPLC trace for the racemic reference rac-3r and 3r'.

Figure S74. HPLC trace for (3S,8S)-3r.
Figure S75. HPLC trace for (3S,8R)-3r'.

Figure S76. HPLC trace for the racemic reference rac-3s and 3s'.

Figure S77. HPLC trace for (3S,8S)-3s.
Figure S78. HPLC trace for (3S,8R)-3s'.

Figure S79. HPLC trace for the racemic reference rac-3t and 3t'.

Figure S80. HPLC trace for (3S,8S)-3t.
Figure S81. HPLC trace for (3S,8R)-3t'.

<table>
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<th>[min]</th>
<th>[mAU*s]</th>
<th>[mAU]</th>
<th>%</th>
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<td>BB</td>
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9. Single Crystal X-Ray Diffraction

9.1 Substrate (Z)-1k

Crystals of (Z)-1k were obtained by slow diffusion from a solution in CH$_2$Cl$_2$ layered with nhexane. Data were collected on an Oxford Xcalibur, Sapphire3, Gemini ultra detector employing graphite-monochromated Mo-Kα radiation (= 0.71073 Å). The crystal was kept at 173 K during data collection. The structure was solved by SHELXL-97$^4$. Refinement was done by full-matrix least squares based on F$^2$ data of one twin domain using SHELXL-97. The absolute configuration was determined. The structure is shown in Figure S82. Crystallographic information is listed in the Table S4.

Figure S82. Ortep drawing of ketimine (Z)-1k with 50% probability thermal ellipsoids. Coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1060112).
Table S4. Crystal data and structure refinement for (Z)-1k.

Identification code (Z)-1k
Empirical formula C14 H15 Br N2 O3
Formula weight 339.19
Temperature 173(2) K
Wavelength 0.71073 Å
Crystal system Orthorhombic
Space group Pna2(1)
Unit cell dimensions
a = 7.1573(4) Å, α = 90°
b = 21.4898(9) Å, β = 90°
c = 9.4975(4) Å, γ = 90°
Volume 1460.80(12) Å³
Z 4
Density (calculated) 1.542 Mg/m³
Absorption coefficient 2.822 mm⁻¹
F(000) 688
Crystal size 0.20 x 0.15 x 0.12 mm³
Theta range for data collection 3.42 to 25.98°.
Index ranges -8<=h<=7, -26<=k<=24, -8<=l<=11
Reflections collected 3518
Independent reflections 2200 [R(int) = 0.0289]
Completeness to theta = 25.98° 99.8 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7282 and 0.6022
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 2200 / 1 / 181
Goodness-of-fit on F² 0.999
Final R indices [I>2sigma(I)] R1 = 0.0344, wR2 = 0.0787
R indices (all data) R1 = 0.0376, wR2 = 0.0811
Absolute structure parameter 0.002(13)
Largest diff. peak and hole 0.647 and -0.744 e.Å⁻³
9.2 Compound (3S,8R)-3k' 

Crystals of product 3k' were obtained by slow diffusion from the solution in CH₂Cl₂ layered with n-hexane. Data were collected on an Oxford Xcalibur, Sapphire3, Gemini ultra detector employing graphite-monochromated Mo-Kα radiation (= 0.71073 Å). The crystal was kept at 173 K during data collection. The structure was solved by SHELXL-97. Refinement was done by full-matrix least squares based on F² data of one twin domain using SHELXL-97⁴. The absolute configuration was determined. The structure is shown in Figure S83. Crystallographic information is listed in the Table S5.

![Ortep drawing of product 3k' with 50% probability thermal ellipsoids](image-url)

**Figure S83.** Ortep drawing of product 3k' with 50% probability thermal ellipsoids, the absolute configuration was identified as 3S, 8R. Coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC number 1060102).
Table S5. Crystal data and structure refinement for (3S,8R)-3k'.

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<tr>
<th>Property</th>
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<td>Identification code</td>
<td>(3S,8R)-3k'</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C21 H22 Br N3 O5</td>
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<tr>
<td>Formula weight</td>
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<tr>
<td>Temperature</td>
<td>153(2) K</td>
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<tr>
<td>Wavelength</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
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<tr>
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</tr>
<tr>
<td>Volume</td>
<td>1095.31(8) Å³</td>
</tr>
<tr>
<td>Z</td>
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<tr>
<td>Density (calculated)</td>
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<td>Crystal size</td>
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<td>Index ranges</td>
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<td>Reflections collected</td>
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<tr>
<td>Independent reflections</td>
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<tr>
<td>Completeness to theta = 26.00°</td>
<td>99.6 %</td>
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<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<td>Max. and min. transmission</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
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<tr>
<td>Absolute structure parameter</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.375 and -0.237 e.Å⁻³</td>
</tr>
</tbody>
</table>
10. References