Electronic Supporting Information

Enantioselective Three-component Reaction of Diazooacetates with Indoles and Enals by Iridium/Iminium Co-catalysis

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1. General Information and Materials

All $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) and $^{19}$F NMR (376 MHz) spectra were recorded on Brucker spectrometers in CDCl$_3$. Tetramethylsilane (TMS) served as an internal standard ($\delta = 0$) for $^1$H NMR, and CDCl$_3$ was used as internal standard ($\delta = 77.0$) for $^{13}$C NMR. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). High-resolution mass spectrometry (HRMS) was performed on IonSpec FT-ICR or Waters Micromass Q-TOF micro Synapt High Definition Mass Spectrometer. HPLC analysis was performed on Dalian Elite (UV230+ UV/Vis Detector and P230P High Pressure Pump). Chiralpak IC and AD-H column was purchased from Daicel Chemical Industries, LTD. Melting points were uncorrected. Single crystal X-ray diffraction data were recorded on Bruker-AXS SMART APEX II single crystal X-ray diffractometer. The racemic standards used in HPLC studies were prepared according to the general procedure by using racemic (S)-2-(diphenyl((trimethylsilyl)oxy)methyl)pyrrolidine catalysts. Yields for all compounds were total yield of isolated anti and syn products unless otherwise indicated.

All reactions and manipulations were carried out under an argon atmosphere in a flame-dried or oven-dried flask containing magnetic stir bar. Dichloromethane (DCM), 1, 2-dichloroethane (DCE), CHCl$_3$ and toluene was distilled over calcium hydride. Cinnamaldehydes 3 were prepared from palladium-catalyzed synthesis of cinnamaldehydes from acrolein diethyl acetal and aryl iodides according to the literature method.$^1$ Diarylprolinol silyl ethers 4a-d were prepared according to the literature procedure.$^2$ Indoles 2 were prepared according to the literature method.$^3$ Solvents for the column chromatography were distilled before use. 4 Å molecular sieves were dried in a Muffle furnace at 250 °C over 5 hrs.
2. General Procedure for Optimization of Reaction Conditions

General procedure for the preparation of racemic three-component products:

A mixture of Rh₂(OAc)₄ (5 mol%), substituted cinnamaldehydes 3 (0.1 mmol), 3, 5-(CF₃)₂C₆H₃COOH (40 mol%), rac-4a (20 mol%), and 4 Å MS (25 mg) in 0.35 mL of DCM under an argon atmosphere was cooled to 0 °C. The mixture of diazo compounds 1 (0.2 mmol) and indoles 2 (0.2 mmol) in 0.35 mL of DCM was then added over 0.35 h via a syringe pump. After completion of the addition, the reaction mixture was stirred for another 48 h under 0 °C. After the completion of the reaction (monitored by TLC, until diazo compounds 1 disappeared), the reaction mixture was filtrated and evaporated in vacuo to give the crude product. The crude products was purified by flash chromatography on silica gel (EtOAc/light petroleum ether = 1:50 ~ 1:20) to give the pure product.

General procedure for the preparation of enantioselective three-component products:

A mixture of [Ir(COD)Cl]₂ (10 mol%), substituted cinnamaldehydes 3 (0.1 mmol), 3, 5-(CF₃)₂C₆H₃COOH (40 mol%), (S)-4a (20 mol%), and 4 Å MS (25 mg) in 0.35 mL of DCM under an argon atmosphere was cooled to 0 °C. The mixture of diazo compounds 1 (0.2 mmol) and indoles 2 (0.2 mmol) in 0.35 mL of DCM was then added over 0.35 h via a syringe pump. After completion of the addition, the reaction mixture was stirred for another 48 h under 0 °C. After the completion of the reaction (monitored by TLC, until diazo compounds 1 disappeared), the reaction mixture was filtrated and evaporated in vacuo to give the crude product. The crude products was purified by flash chromatography on silica gel (EtOAc/light petroleum ether = 1:50 ~ 1:20) to give the pure product.

General procedure for the formation of iminium ion II:

A mixture of [Ir(COD)Cl]₂ (10 mol%), cinnamaldehyde 3a (0.1 mmol), 3, 5-(CF₃)₂C₆H₃COOH (40 mol%), (S)-4a (20 mol%), and 4 Å MS (25 mg) in 0.35 mL of DCM under an argon atmosphere was cooled to 0 °C. After stirring 1h, the mixture was monitored by LC-MS, iminium ion II (EM: 440.24) was detected, 440.34 was
found.

**Figure S1.** The formation of iminium ion II monitored by LC-MS.

**Table S1:** Screening of chiral diphenylprolinol cocatalysts

<table>
<thead>
<tr>
<th>entry</th>
<th>cocatalyst</th>
<th>Yield (%)</th>
<th>dr(anti/syn)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(S)-4a</td>
<td>67</td>
<td>61:39</td>
<td>78/95</td>
</tr>
<tr>
<td>2</td>
<td>(S)-4b</td>
<td>56</td>
<td>64:36</td>
<td>98/98</td>
</tr>
<tr>
<td>3</td>
<td>(S)-4c</td>
<td>62</td>
<td>64:36</td>
<td>92/94</td>
</tr>
<tr>
<td>4</td>
<td>(S)-4d</td>
<td>39</td>
<td>50:50</td>
<td>97/96</td>
</tr>
</tbody>
</table>

[a] General reaction conditions: [Ir(COD)Cl]$_2$: (S)-4: acid : 1a: 2a: 3a = 0.1:0.2:0.4:2:2:1. The mixture of 1a and 2a in CH$_2$Cl$_2$ was added to a suspension of
[Ir(COD)Cl]2, (S)-4, acid, 3a and 4Å M.S. in CH2Cl2 over 0.35 h by a syringe pump. [b] Total yield of isolated anti and syn products. [c] Determined by 1H NMR analysis of the crude mixture. [d] Determined by chiral HPLC analysis. M.S. = molecular sieves.

**Table S2: Screening of additive of acids**

<table>
<thead>
<tr>
<th>entry</th>
<th>acid</th>
<th>yield(%)</th>
<th>dr(anti/syn)</th>
<th>ee(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>p-NO2C6H4COOH</td>
<td>53</td>
<td>64:36</td>
<td>86/97</td>
</tr>
<tr>
<td>2</td>
<td>PhCOOH</td>
<td>43</td>
<td>50:50</td>
<td>89/93</td>
</tr>
<tr>
<td>3</td>
<td>p-ClC6H4COOH</td>
<td>44</td>
<td>52:48</td>
<td>89/94</td>
</tr>
<tr>
<td>4</td>
<td>p-CF3C6H4COOH</td>
<td>67</td>
<td>61:39</td>
<td>78/95</td>
</tr>
<tr>
<td>5</td>
<td>3,5-(CF3)2C6H3COOH</td>
<td>56</td>
<td>67:33</td>
<td>95/97</td>
</tr>
<tr>
<td>6[e]</td>
<td>3,5-(CF3)2C6H3COOH</td>
<td>45</td>
<td>66:34</td>
<td>94/96</td>
</tr>
<tr>
<td>7[f]</td>
<td>3,5-(CF3)2C6H3COOH</td>
<td>53</td>
<td>67:33</td>
<td>94/97</td>
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<td>TFA</td>
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<td>-</td>
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<td>9</td>
<td>TsOH·H2O</td>
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<td>-</td>
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<tr>
<td>10[g]</td>
<td>-</td>
<td>0</td>
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<td>-</td>
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</tbody>
</table>

[a], [b], [c], [d]: Reaction conditions as performed in Table 1. [e] The amount of 3,5-(CF3)2C6H3COOH is 20 mol%. [f] The amount of 3,5-(CF3)2C6H3COOH is 50 mol%. [g] No acid is added.

**Table S3: Screening of solvents**

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>yield(%)</th>
<th>dr(anti/syn)</th>
<th>ee(%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>CH2Cl2</td>
<td>56</td>
<td>67:33</td>
<td>95/97</td>
</tr>
<tr>
<td></td>
<td>solvent</td>
<td>53</td>
<td>65:35</td>
<td>92/94</td>
</tr>
<tr>
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<td>---------</td>
<td>-----</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>2</td>
<td>toluene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>39</td>
<td>69:31</td>
<td>94/90</td>
</tr>
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<td>4</td>
<td>CHCl3</td>
<td>43</td>
<td>69:31</td>
<td>94/98</td>
</tr>
<tr>
<td>5</td>
<td>DCE</td>
<td>54</td>
<td>64:36</td>
<td>93/97</td>
</tr>
<tr>
<td>6[a]</td>
<td>CH2Cl2</td>
<td>54</td>
<td>65:35</td>
<td>94/96</td>
</tr>
</tbody>
</table>

[a], [b], [c], [d]: Reaction conditions as performed in Table 1. [e] The amount of (S)-4a is 30 mol%.

The procedure for derivation of the three-component product

![Diagram](image)

To a flask charged with (2S, 3S)-anti-5a (0.03 mmol) in CH2Cl2 (4 mL) was stirred at 25 °C. BF3·Et2O (0.4 mmol%, 16 μL) was added. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched with saturated aqueous solution of NaHCO3. Then the product was extracted with CH2Cl2. The combined organic phases were washed by water and brine, and dried over Na2SO4. The product was then purified by flash chromatography (EtOAc/light petroleum ether = 1:50 ~ 1:10) to give the pure product anti-6.

![Diagram](image)

To a flask charged with (2S,3S)-anti-5a (0.2 mmol) in methanol (1 mL) was stirred at 25 °C. NaBH4 (0.3 mmol) was added in batches. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched with saturated aqueous solution of NH4Cl. Then the product was extracted with AcOEt. The
combined organic phases were washed by water and brine, and dried over Na$_2$SO$_4$. The product was then purified by flash chromatography (EtOAc/light petroleum ether = 1:50 ~ 1:10) to give the pure product 8.

To a flask charged with (2S,3S)-anti-8 (0.2 mmol) in CH$_2$Cl$_2$ (1 mL) was stirred at 25 °C. Then TsOH·H$_2$O (0.1 mmol) was added. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted with water. The combined organic phases were dried over Na$_2$SO$_4$ and the solvent was evaporated in vacuo. The product was then purified by flash chromatography (EtOAc/light petroleum ether = 1:50 ~ 1:10) to give the pure product 7.

**Several additional substrates used to test this reaction**

<table>
<thead>
<tr>
<th>entry</th>
<th>diazo</th>
<th>indole</th>
<th>enal</th>
<th>product</th>
<th>yield(%)</th>
<th>dr(anti/syn)</th>
<th>ee(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N$_2$</td>
<td></td>
<td></td>
<td>a trace amount</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td>a trace amount</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td>a trace amount</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td>no reaction</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td>no reaction</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
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<td></td>
<td></td>
<td>no reaction</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td>mess</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
3. Characterization Data of Compounds

(2S,3S)-methyl 2-(1-methyl-1H-indol-3-yl)-5-oxo-2,3-diphenylpentanoate (5a)

(2S,3S)-anti-5a: 97% ee. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.48 (s, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.25 (m, 5H), 7.17 – 7.07 (m, 4H), 6.84 (t, \(J = 7.5\) Hz, 1H), 6.77 (d, \(J = 7.3\) Hz, 2H), 6.57 (d, \(J = 8.2\) Hz, 1H), 5.09 – 4.97 (m, 1H), 3.77 (s, 3H), 3.56 (s, 3H), 3.17 (m, 1H), 2.90 – 2.60 (m, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 201.62, 173.68, 140.02, 139.04, 136.61, 132.70, 130.64, 129.28, 128.20, 127.66, 127.39, 127.37, 127.27, 122.38, 120.96, 118.90, 110.54, 109.35, 61.06, 52.18, 46.42, 44.59, 32.93.

HRMS(ESI) : Calcd. for C\(_{27}\)H\(_{26}\)NO\(_3\) [M+H]\(^+\): 412.1913, Found: 412.1902.

HPLC (Chiral IC, \(\lambda = 220\) nm, hexane/2-propanol = 15/1, Flow rate =0.8 mL/min), \(t_{\text{major}} = 18.83\) min, \(t_{\text{minor}} = 14.53\) min.

(2R,3S)-methyl 2-(1-methyl-1H-indol-3-yl)-5-oxo-2,3-diphenylpentanoate (5a)

(2R,3S)-syn-5a: 97%ee. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.55 (s, 1H), 7.34 – 7.26 (m, 3H), 7.22 (d, \(J = 7.1\) Hz, 2H), 7.18 – 7.07 (m, 6H), 6.95 – 6.82 (m, 4H), 5.02 (d, \(J = 10.9\) Hz, 1H), 3.81 (s, 3H), 3.47 (s, 3H), 3.22 (m, 1H), 2.70 (m, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 201.91, 173.06, 138.77, 137.27, 137.11, 131.45, 131.29, 128.86, 127.40, 127.25, 127.20, 126.72, 126.69, 122.35, 121.70, 119.20, 114.71, 109.21, 60.99, 51.91, 46.19, 43.86, 33.10. HRMS(ESI) : Calcd. for C\(_{27}\)H\(_{26}\)NO\(_3\) [M+H]\(^+\): 412.1913, Found: 412.1918.

HPLC (Chiral IC, \(\lambda = 220\) nm, hexane/2-propanol = 15/1, Flow rate =0.8 mL/min), \(t_{\text{major}} = 16.63\) min, \(t_{\text{minor}} = 13.81\) min.

(2S,3S)-methyl3-(4-bromophenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-2-phenylpentanoate (5b)
(2S,3S)-anti-5b: 96%ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.49 (s, 1H), 7.60 – 7.27 (m, 5H), 7.24 – 7.11 (m, 3H), 6.93 (s, 1H), 6.86 (t, $J = 7.5$ Hz, 1H), 6.69 – 6.49 (m, 2H), 5.23 – 4.74 (m, 1H), 3.79 (s, 2H), 3.56 (s, 2H), 3.26 – 2.88 (m, 1H), 2.81 – 2.40 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.91, 173.52, 139.63, 138.30, 136.68, 132.41, 132.36, 130.41, 129.18, 128.26, 127.50, 127.47, 122.33, 121.28, 121.17, 119.04, 110.45, 109.45, 60.90, 52.25, 46.45, 43.91, 32.96.

HRMS(ESI) : Calcd. for C$_{27}$H$_{24}$NO$_3$NaBr [M+Na]$^+$: 512.0837, Found: 512.0858.

HPLC (Chiral AD-H, $\lambda = 220$ nm, hexane/2-propanol = 15/1, Flow rate =1.0 mL/min), $t_{\text{major}} = 17.82$ min, $t_{\text{minor}} = 15.47$ min.

(2R,3S)-methyl3-(4-bromophenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-2-phenylpentanoate (5b)

(2R,3S)-syn-5b: 95%ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.56 (s, 1H), 7.40 – 7.29 (m, 2H), 7.29 – 7.25 (m, 3H), 7.23 (s, 1H), 7.22 – 7.13 (m, 2H), 7.08 (d, $J = 7.6$ Hz, 2H), 6.99 – 6.85 (m, 2H), 6.72 (d, $J = 8.4$ Hz, 2H), 5.01 (d, $J = 10.9$ Hz, 1H), 3.81 (s, 3H), 3.48 (s, 3H), 3.24 (d, $J = 17.6$ Hz, 1H), 2.74 – 2.57 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.17, 173.03, 138.00, 137.30, 136.91, 133.01, 131.26, 130.42, 128.87, 127.42, 126.88, 126.57, 122.29, 121.78, 121.24, 119.29, 114.31, 109.25, 77.34, 77.02, 76.71, 60.91, 51.97, 46.23, 43.18, 33.09.

HRMS(ESI) : Calcd. for C$_{27}$H$_{24}$NO$_3$NaBr [M+Na]$^+$: 512.0837, Found: 512.0812.

HPLC (Chiral IC, $\lambda = 220$ nm, hexane/2-propanol = 15/1, Flow rate =1.0 mL/min), $t_{\text{major}} = 11.16$ min, $t_{\text{minor}} = 10.34$ min.

(2S,3S)-methyl 2-(1-methyl-1H-indol-3-yl)-5-oxo-2-phenyl-3-(p-tolyl)pentanoate (5c)
(2S,3S)-anti-5c: 96% ee. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.47 (dd, $J = 2.2$, 1.0 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.37 – 7.27 (m, 3H), 7.17 – 7.09 (m, 1H), 7.01 (s, 1H), 6.93 (dd, $J = 11.1$, 4.4 Hz, 2H), 6.86 – 6.78 (m, 1H), 6.68 – 6.61 (m, 2H), 6.54 (d, $J = 8.2$ Hz, 1H), 4.99 (dd, $J = 12.3$, 2.5 Hz, 1H), 3.79 (s, 2H), 3.56 (s, 2H), 3.13 (ddd, $J = 17.3$, 2.4, 1.0 Hz, 1H), 2.26 (s, 2H).

(2S,3S)-anti-5c: 96% ee. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.47 (dd, $J = 2.2$, 1.0 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.37 – 7.27 (m, 3H), 7.17 – 7.09 (m, 1H), 7.01 (s, 1H), 6.93 (dd, $J = 11.1$, 4.4 Hz, 2H), 6.86 – 6.78 (m, 1H), 6.68 – 6.61 (m, 2H), 6.54 (d, $J = 8.2$ Hz, 1H), 4.99 (dd, $J = 12.3$, 2.5 Hz, 1H), 3.79 (s, 2H), 3.56 (s, 2H), 3.13 (ddd, $J = 17.3$, 2.4, 1.0 Hz, 1H), 2.26 (s, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.74, 173.72, 140.08, 136.81, 136.60, 135.82, 132.75, 130.46, 129.29, 128.14, 127.69, 127.30, 122.39, 120.89, 118.84, 110.59, 109.27, 61.06, 52.11, 46.45, 44.24, 32.91, 21.02.


HPLC (Chiral IC, $\lambda = 220$ nm, hexane/2-propanol = 10/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 11.53$ min, $t_{\text{minor}} = 9.79$ min.

(2R,3S)-methyl 2-(1-methyl-1H-indol-3-yl)-5-oxo-2-phenyl-3-(p-tolyl)pentanoate (5c)

(2R,3S)-syn-5c: 82% ee. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.55 (d, $J = 1.0$ Hz, 1H), 7.37 – 7.27 (m, 2H), 7.25 – 7.20 (m, 3H), 7.17 – 7.13 (m, 1H), 7.11 – 7.07 (m, 2H), 6.94 (d, $J = 8.0$ Hz, 2H), 6.92 – 6.83 (m, 2H), 6.75 (d, $J = 8.0$ Hz, 2H), 4.96 (dd, $J = 12.2$, 2.1 Hz, 1H), 3.82 (s, 3H), 3.48 (s, 3H), 3.19 (dd, $J = 17.4$, 1.2 Hz, 1H), 2.78 – 2.49 (m, 1H), 2.28 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 202.08, 173.06, 137.06, 137.26, 137.12, 136.75, 135.57, 131.49, 131.09, 128.78, 128.14, 127.14, 126.72, 126.63, 122.37, 121.66, 119.14, 114.83, 109.14, 60.97, 51.83, 46.16, 43.57, 33.07, 21.02.


HPLC (Chiral IC, $\lambda = 220$ nm, hexane/2-propanol = 10/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 11.16$ min, $t_{\text{minor}} = 9.00$ min.

(2S,3S)-methyl 2-(1-methyl-1H-indol-3-yl)-5-oxo-2-phenyl-3-(m-tolyl)pentanoate (5d)
(2S,3S)-anti-5d: 98% ee. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 9.48 (s, 1H), 7.46 (d, \(J = 3.9\) Hz, 2H), 7.35 – 7.27 (m, 4H), 7.13 (t, \(J = 7.6\) Hz, 1H), 7.05 – 6.94 (m, 3H), 6.83 (t, \(J = 7.6\) Hz, 1H), 6.66 (d, \(J = 7.4\) Hz, 1H), 6.53 (d, \(J = 8.2\) Hz, 1H), 6.45 (s, 1H), 4.99 (d, \(J = 12.9\) Hz, 1H), 3.78 (s, 3H), 3.55 (s, 3H), 3.13 (d, \(J = 17.2\) Hz, 1H), 2.70 (dd, \(J = 17.2, 12.9\) Hz, 1H), 2.16 (s, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 201.71, 173.64, 140.13, 138.82, 136.65, 136.59, 132.80, 131.34, 129.31, 128.17, 127.96, 127.83, 127.76, 127.33, 127.24, 122.41, 120.93, 118.87, 110.62, 109.28, 61.09, 52.08, 46.34, 44.57, 32.86, 21.37.

HRMS(ESI): Calcd. for C\(_{28}\)H\(_{27}\)NO\(_3\)Na [M+Na]\(^+\): 448.1889, Found: 448.1875.

HPLC (Chiral IC, \(\lambda = 220\) nm, hexane/2-propanol = 15/1, Flow rate =1.0 mL/min),
\(t_{\text{major}} = 16.08\) min, \(t_{\text{minor}} = 11.96\) min.

(2R,3S)-methyl 2-(1-methyl-1H-indol-3-yl)-5-oxo-2-phenyl-3-(m-tolyl)pentanoate (5d)

(2R,3S)-syn-5d: 98% ee. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 9.56 (s, 1H), 7.33 – 7.27 (m, 2H), 7.22 (d, \(J = 9.1\) Hz, 2H), 7.18 – 6.95 (m, 6H), 6.92 – 6.83 (m, 2H), 6.75 (d, \(J = 7.3\) Hz, 1H), 6.55 (s, 1H), 4.97 (d, \(J = 11.8\) Hz, 1H), 3.82 (s, 3H), 3.48 (s, 3H), 3.19 (d, \(J = 16.8\) Hz, 1H), 2.68 (dd, \(J = 16.8, 11.8\) Hz, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 202.04, 172.99, 138.53, 137.25, 137.18, 136.66, 131.94, 131.50, 128.85, 128.38, 127.84, 127.22, 127.17, 126.73, 126.56, 122.34, 121.67, 119.16, 114.76, 109.14, 60.99, 51.81, 46.10, 43.87, 33.07, 21.36.


HPLC (Chiral IC, \(\lambda = 220\) nm, hexane/2-propanol = 15/1, Flow rate =1.0 mL/min),
\(t_{\text{major}} = 13.64\) min, \(t_{\text{minor}} = 11.57\) min.

(2S,3R)-methyl3-(furan-2-yl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-2-phenylpentanoate (5e)
(2S,3R)-anti-5e: 90% ee. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.60 (s, 1H), 7.49 – 7.28 (m, 6H), 7.18 – 7.10 (m, 2H), 7.03 (s, 1H), 6.91 – 6.79 (m, 1H), 6.70 – 6.60 (m, 1H), 6.18 (s, 1H), 5.72 (s, 1H), 5.11 (d, \(J = 11.2\) Hz, 1H), 3.76 (s, 3H), 3.65 (s, 3H), 2.98 (d, \(J = 16.7\) Hz, 1H), 2.78 – 2.59 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 200.89, 173.89, 153.48, 140.97, 138.78, 130.76, 129.47, 127.82, 127.79, 127.36, 127.20, 127.14, 122.00, 121.05, 118.91, 112.05, 110.34, 109.13, 60.41, 52.37, 44.95, 38.97, 32.89.


HPLC (Chiral IC, \(\lambda = 254\) nm, hexane/2-propanol = 6/1, Flow rate = 0.8 mL/min), \(t_{\text{major}}\) = 16.44 min, \(t_{\text{minor}}\) = 11.86 min.

(2R,3R)-methyl3-(furan-2-yl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-2-phenylpentanoate (5e)

(2R,3R)-syn-5e: 94% ee. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 9.69 (s, 1H), 7.36 – 7.27 (m, 3H), 7.21 – 7.13 (m, 4H), 7.00 – 6.94 (m, 2H), 6.90 – 6.87 (m, 2H), 6.27 (dd, \(J = 3.2, 1.9\) Hz, 1H), 6.04 (d, \(J = 3.3\) Hz, 1H), 5.13 – 5.01 (m, 1H), 3.82 (s, 3H), 3.61 (s, 3H), 3.04 (dd, \(J = 17.9, 1.7\) Hz, 1H), 2.77 – 2.61 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 201.25, 173.30, 153.05, 141.20, 137.54, 137.20, 130.11, 128.56, 127.08, 126.95, 122.32, 121.71, 119.20, 113.41, 110.52, 110.15, 109.67, 109.16, 60.72, 52.17, 43.69, 38.67, 33.07.


HPLC (Chiral IC, \(\lambda = 254\) nm, hexane/2-propanol = 6/1, Flow rate = 0.8 mL/min), \(t_{\text{major}}\) = 13.86 min, \(t_{\text{minor}}\) = 10.95 min.

(2S,3S)-methyl2-(4-fluorophenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenylpentanoate (5f)

(2S,3S)-anti-5f: 97% ee. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.48 (s, 1H), 7.40 – 7.31 (m, 3H), 7.18 – 7.10 (m, 4H), 6.99 – 6.94 (m, 3H), 6.87 (t, \(J = 7.6\) Hz, 1H), 6.76 (d, \(J = 7.1\) Hz, 2H), 6.63 (d, \(J = 6.8\) Hz, 2H), 5.75 (s, 1H), 5.11 (d, \(J = 11.2\) Hz, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 2.98 (d, \(J = 16.7\) Hz, 1H), 2.78 – 2.59 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 200.89, 173.30, 153.05, 141.20, 137.54, 137.20, 130.11, 128.56, 127.08, 126.95, 122.32, 121.71, 119.20, 113.41, 110.52, 110.15, 109.67, 109.16, 60.72, 52.17, 43.69, 38.67, 33.07.
= 8.1 Hz, 1H), 4.95 (dd, J = 12.1, 2.2 Hz, 1H), 3.77 (s, 3H), 3.58 (s, 3H), 3.13 (d, J = 16.8 Hz, 1H), 2.85 – 2.73 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.37, 173.52, 161.93 (d, J = 247.2 Hz), 138.94, 136.72, 135.77 (d, J = 3.3 Hz), 132.35, 131.11 (d, J = 8.0 Hz), 130.57, 127.48, 127.40, 127.35, 122.19, 121.16, 119.08, 114.93 (d, J = 21.2 Hz), 110.66, 109.45, 60.54, 52.22, 46.53, 44.97, 32.93.

HRMS(ESI) : Calcd. for C$_{27}$H$_{24}$NO$_3$FNa [M+Na]$^+$: 452.1638, Found: 452.1616.

HPLC (Chiral IC, λ = 220 nm, hexane/2-propanol = 30/1, Flow rate =1.0 mL/min),
t$_{major}$ = 16.24 min, t$_{minor}$ = 12.30 min.

(2R,3S)-methyl2-(4-fluorophenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenylpentanoate (5f)

(2R,3S)-$^*$-5f: 97% ee. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.58 (s, 1H), 7.30 (d, J = 8.3 Hz, 1H), 7.24 – 7.12 (m, 5H), 7.09 – 7.02 (m, 2H), 6.99 – 6.80 (m, 6H), 4.99 (d, J = 11.8 Hz, 1H), 3.83 (s, 3H), 3.47 (s, 3H), 3.21 (d, J = 17.2 Hz, 1H), 2.73 – 2.56 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.58, 172.74, 161.99 (d, J = 246.7 Hz), 138.45, 137.30, 133.23 (d, J = 7.8 Hz), 132.72 (d, J = 3.2 Hz), 131.10, 128.61, 127.55, 127.39, 126.50, 122.19, 121.83, 119.31, 114.65, 113.46 (d, J = 21.1 Hz), 109.24, 60.38, 51.93, 45.90, 43.74, 33.10.

HRMS(ESI) : Calcd. for C$_{27}$H$_{25}$NO$_3$F [M+H]$^+$: 430.1818, Found: 430.1818.

HPLC (Chiral IC, λ = 220 nm, hexane/2-propanol = 30/1, Flow rate = 1.0 mL/min),
t$_{major}$ = 13.72 min, t$_{minor}$ = 11.63 min.

(2S,3S)-methyl2-(4-chlorophenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenylpentanoate (5g)

(2S,3S)-$^*$-5g: 94% ee. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.48 (s, 1H), 7.34 (t, J = 7.2 Hz, 3H), 7.27 – 7.24 (m, 2H), 7.20 – 7.07.
(m, 4H), 6.97 (s, 1H), 6.88 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 4.94 (d, J = 10.3 Hz, 1H), 3.78 (s, 3H), 3.58 (s, 3H), 3.11 (d, J = 16.3 Hz, 1H), 2.87 – 2.73 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.24, 173.29, 138.83, 138.58, 136.70, 133.29, 132.36, 130.83, 130.54, 128.22, 127.49, 127.38, 127.31, 122.15, 121.18, 119.13, 110.38, 109.46, 60.68, 52.27, 46.51, 44.85, 32.94. HRMS(ESI) : Calcd. for C$_{27}$H$_{24}$NO$_3$NaCl $[M+Na]^+$: 468.1342, Found: 468.1323.

HPLC (Chiral IC, $\lambda$ = 220 nm, hexane/2-propanol = 30/1, Flow rate = 1.0 mL/min), $t_{major}$ = 16.85 min, $t_{minor}$ = 12.54 min.

(2R,3S)-methyl2-(4-chlorophenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenylpentanoate (5g)

(2R,3S)-syn-5g: 99% ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.58 (s, 1H), 7.30 (d, J = 8.3 Hz, 1H), 7.24 – 7.11 (m, 7H), 7.03 (d, J = 8.7 Hz, 2H), 6.95 – 6.79 (m, 4H), 4.99 (dd, J = 12.1, 2.0 Hz, 1H), 3.83 (s, 3H), 3.47 (s, 3H), 3.25 – 3.14 (m, 1H), 2.73 – 2.59 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.47, 172.51, 138.32, 137.29, 135.51, 133.22, 133.01, 131.10, 128.58, 127.60, 127.45, 126.78, 126.42, 122.15, 121.87, 119.36, 114.38, 109.26, 60.46, 51.96, 45.85, 43.60, 33.12.

HRMS(ESI) : Calcd. for C$_{27}$H$_{25}$NO$_3$Cl $[M+H]^+$: 446.1523, Found: 446.1524.

HPLC (Chiral IC, $\lambda$ = 220 nm, hexane/2-propanol = 30/1, Flow rate = 1.0 mL/min), $t_{major}$ = 13.08 min, $t_{minor}$ = 11.23 min.

(2S,3S)-methyl2-(4-bromophenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenylpentanoate (5h)

(2S,3S)-anti-5h: 94% ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.48 (s, 1H), 7.41 (d, J = 8.6 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.18 – 7.09 (m, 4H), 6.97 (s, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.76 (d, J = 7.1 Hz, 2H), 2.87 – 2.73 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.24, 173.29, 138.83, 138.58, 136.70, 133.29, 132.36, 130.83, 130.54, 128.22, 127.49, 127.38, 127.31, 122.15, 121.18, 119.13, 110.38, 109.46, 60.68, 52.27, 46.51, 44.85, 32.94. HRMS(ESI) : Calcd. for C$_{27}$H$_{24}$NO$_3$NaCl $[M+Na]^+$: 468.1342, Found: 468.1323.
Hz, 2H), 6.65 (d, J = 8.2 Hz, 1H), 4.94 (m, 1H), 3.78 (s, 3H), 3.58 (s, 3H), 3.11 (m, 1H), 2.86 – 2.73 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.22, 173.21, 139.12, 138.81, 136.70, 132.37, 131.18, 130.53, 127.50, 127.38, 127.29, 122.15, 121.54, 121.19, 119.14, 110.30, 109.46, 60.76, 52.28, 46.50, 44.78, 32.94.

HRMS(ESI) : Calcd. for C$_{27}$H$_{24}$NO$_3$NaBr [M+Na]$^+$: 512.0837, Found: 512.0812

HPLC (Chiral IC, $\lambda$ = 220 nm, hexane/2-propanol = 30/1, Flow rate =1.0 mL/min),
t$_{major}$ = 18.43 min, t$_{minor}$ = 13.44 min.

$(2R,3S)$-methyl2-(4-bromophenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenylpentanoate (5h)

$(2R,3S)$-syn-5h: 97%ee. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.58 (s, 1H), 7.36 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.2 Hz, 1H), 7.25 – 7.09 (m, 5H), 7.08 – 6.36 (m, 6H), 4.99 (d, J = 11.3 Hz, 1H), 3.83 (s, 3H), 3.47 (s, 3H), 3.19 (d, J = 17.4 Hz, 1H), 2.74 – 2.51 (m, 1H).

$(2R,3S)$-syn-5h

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.44, 172.44, 138.29, 137.29, 136.04, 133.37, 131.09, 129.74, 128.58, 127.61, 127.46, 126.40, 122.14, 121.88, 121.51, 119.37, 114.31, 109.26, 60.52, 51.97, 45.84, 43.53, 33.12.

HRMS(ESI) : Calcd. for C$_{27}$H$_{25}$NO$_3$Br [M+H]$^+$: 490.1018, Found: 490.1013

HPLC (Chiral IC, $\lambda$ = 220 nm, hexane/2-propanol = 30/1, Flow rate =1.0 mL/min),
t$_{major}$ = 13.69 min, t$_{minor}$ = 11.89 min.

$(2S,3S)$-methyl 2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenyl-2-(p-tolyl)pentanoate (5i)

$(2S,3S)$-anti-5i: 96%ee. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.48 (s, 1H), 7.38 – 7.30 (m, 3H), 7.18 – 7.06 (m, 6H), 6.92 (s, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.75 (d, J = 7.2 Hz, 2H), 6.65 – 6.58 (m, 1H), 6.09 – 5.88 (m, 1H).
5.03 (d, $J = 12.2$ Hz, 1H), 3.77 (s, 3H), 3.56 (s, 3H), 3.15 (d, $J = 17.4$ Hz, 1H), 2.77 – 2.63 (m, 1H), 2.36 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.70, 173.83, 139.11, 137.04, 136.88, 136.58, 132.69, 130.66, 129.14, 128.92, 127.70, 127.32, 127.18, 122.49, 120.89, 118.81, 110.58, 109.29, 60.76, 52.13, 46.36, 44.57, 32.89, 21.06.

HRMS(ESI) : Calcd. for C$_{28}$H$_{28}$NO$_3$ [M+H]$^+$: 426.2069, Found: 426.2079.

HPLC (Chiral IC, $\lambda = 220$ nm, hexane/2-propanol = 15/1, Flow rate =1.0 mL/min), $t_{\text{major}} = 14.30$ min, $t_{\text{minor}} = 10.69$ min.

(2R,3S)-methyl2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenyl-2-(p-tolyl)pentanoate (5i)

$\begin{align*}
\text{MeO} & \quad \text{O} \\
\text{MeO}_2\text{C} & \quad \text{O}
\end{align*}$

(2R,3S)-syn-5i: 98% ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.56 (s, 1H), 7.43 – 7.26 (m, 2H), 7.24 – 7.08 (m, 5H), 7.07 – 6.81 (m, 7H), 4.97 (d, $J = 11.8$ Hz, 1H), 3.82 (s, 3H), 3.47 (s, 3H), 3.20 (d, $J = 17.3$ Hz, 1H), 2.79 – 2.63 (m, 1H), 2.38 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 202.00, 173.18, 138.86, 137.23, 136.80, 134.03, 131.31, 131.28, 128.78, 127.41, 127.35, 127.12, 126.75, 122.39, 121.62, 119.10, 114.90, 109.12, 60.64, 51.84, 46.28, 43.96, 33.07, 21.10.


HPLC (Chiral IC, $\lambda = 220$ nm, hexane/2-propanol = 15/1, Flow rate =0.8 mL/min), $t_{\text{major}} = 14.50$ min, $t_{\text{minor}} = 12.73$ min.

(2S,3S)-methyl2-(4-methoxyphenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenylpentanoate (5j)

$\begin{align*}
\text{MeO} & \quad \text{O} \\
\text{MeO}_2\text{C}_m & \quad \text{O}
\end{align*}$

(2S,3S)-anti-5j: 94% ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.48 (s, 1H), 7.44 – 7.29 (m, 3H), 7.22 – 7.04 (m, 4H), 7.00 – 6.81 (m, 4H), 6.75 (d, $J = 7.4$ Hz, 2H), 6.68 – 6.51 (m, 1H), 5.22 – 4.72 (m, 1H), 3.82 (s, 3H), 3.77 (s, 2H), 3.56 (s, 2H), 3.19 – 3.02 (m, 1H), 2.83 – 2.61 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.67, 173.87, 158.69, 139.14,
136.63, 132.59, 131.91, 130.65, 127.67, 127.34, 127.19, 122.50, 120.94, 118.88, 113.47, 110.72, 109.31, 60.42, 55.24, 52.10, 46.39, 44.75, 32.88.


HPLC (Chiral IC, \(\lambda = 220\) nm, hexane/2-propanol = 30/1, Flow rate =1.0 mL/min),

\(t_{\text{major}} = 33.41\) min, \(t_{\text{minor}} = 23.44\) min.

\((2R,3S)\)-methyl2-(4-methoxyphenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenylpentanoate (5j)

\((2R,3S)\)-syn-5j: 99%ee. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 9.56\) (s, 1H), 7.29 (d, \(J = 8.2\) Hz, 1H), 7.22 – 7.12 (m, 5H), 7.01 (d, \(J = 8.8\) Hz, 2H), 6.94 – 6.84 (m, 4H), 6.77 (d, \(J = 8.8\) Hz, 2H), 4.96 (d, \(J = 11.0\) Hz, 1H), 3.83 (d, \(J = 4.7\) Hz, 6H), 3.47 (s, 3H), 3.20 (d, \(J = 17.3\) Hz, 1H), 2.75 – 2.62 (m, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 201.95, 173.16, 158.61, 138.84, 137.27, 132.58, 131.26, 129.16, 128.70, 127.40, 127.16, 126.74, 122.40, 121.66, 119.15, 115.02, 111.98, 109.12, 60.30, 55.21, 51.82, 46.20, 44.07, 33.06.


HPLC (Chiral IC, \(\lambda = 220\) nm, hexane/2-propanol = 30/1, Flow rate =1.0 mL/min),

\(t_{\text{major}} = 24.84\) min, \(t_{\text{minor}} = 22.35\) min.

\((2S,3S)\)-methyl2-(3-methoxyphenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenylpentanoate (5k)

\((2S,3S)\)-anti-5k: 98%ee. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 9.48\) (s, 1H), 7.31 (d, \(J = 8.0\) Hz, 1H), 7.25 – 7.21 (m, 1H), 7.16 – 7.00 (m, 6H), 6.95 (s, 1H), 6.89 – 6.82 (m, 2H), 6.77 (d, \(J = 6.9\) Hz, 2H), 6.65 (d, \(J = 7.9\) Hz, 1H), 4.99 (d, \(J = 11.7\) Hz, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 3.57 (s, 3H), 3.19 (d, \(J = 17.3\) Hz, 1H), 2.81 – 2.65 (m, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 201.52, 173.56, 159.35, 141.66, 139.09, 136.61, 132.56, 130.65, 129.03, 127.69, 127.36, 127.25, 122.38, 121.70, 120.97, 118.94, 115.40, 112.78, 110.52, 109.29, 61.08, 55.25, 52.16, 46.49, 44.79, 32.90.

HPLC (Chiral IC, λ = 220 nm, hexane/2-propanol = 30/1, Flow rate = 0.8 mL/min),
t_major = 30.76 min, t_minor = 27.30 min.

(2R,3S)-methyl2-(3-methoxyphenyl)-2-(1-methyl-1H-indol-3-yl)-5-oxo-3-phenylpentanoate (5k)

(2R,3S)-syn-5k: 99%ee. 1H NMR (400 MHz, CDCl_3) δ 9.55 (s, 1H), 7.28 (s, 1H), 7.22 – 7.09 (m, 6H), 6.98 – 6.83 (m, 5H), 6.71 (d, J = 7.6 Hz, 1H), 6.65 (s, 1H), 5.00 (d, J = 11.6 Hz, 1H), 3.80 (s, 3H), 3.65 (s, 3H), 3.48 (s, 3H), 3.21 (d, J = 17.5 Hz, 1H), 2.86 – 2.64 (m, 1H).

13C NMR (100 MHz, CDCl_3) δ 201.82, 172.99, 158.09, 138.84, 138.78, 137.24, 131.23, 128.85, 127.57, 127.38, 127.21, 126.73, 123.82, 122.28, 121.67, 119.21, 117.62, 114.62, 112.75, 109.16, 61.07, 51.89, 46.22, 44.01, 33.06.


HPLC (Chiral IC, λ = 220 nm, hexane/2-propanol = 30/1, Flow rate = 0.8 mL/min),
t_major = 32.66 min, t_minor = 29.69 min.

(2S,3S)-methyl2-(5-fluoro-1-methyl-1H-indol-3-yl)-5-oxo-2,3-diphenylpentanoate (5l)

(2S,3S)-anti-5l: 97%ee. 1H NMR (400 MHz, CDCl_3) δ 9.50 (d, J = 1.3 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.37 – 7.26 (m, 3H), 7.25 – 7.07 (m, 4H), 7.01 (s, 1H), 6.88 (m, 1H), 6.77 (d, J = 7.1 Hz, 2H), 6.15 (dd, J = 10.8, 2.3 Hz, 1H), 5.01 (dd, J = 12.2, 2.2 Hz, 1H), 3.77 (s, 3H), 3.56 (s, 3H), 3.13 (dd, J = 17.4, 1.8 Hz, 1H), 2.81 – 2.59 (m, 1H).

13C NMR (100 MHz, CDCl_3) δ 201.29, 173.48, 157.17 (d, J = 233.6 Hz), 139.53, 138.85, 134.19, 133.23, 130.56, 129.17, 128.33, 127.98 (d, J = 10.1 Hz), 127.56, 127.45, 127.35, 110.68 (d, J = 4.7 Hz), 109.89 (d, J = 10.0 Hz), 109.49 (d, J = 26.5 Hz), 107.13 (d, J = 24.7 Hz), 60.89, 52.19, 46.28, 44.42, 33.19.

19F NMR (376 MHz, CDCl_3) δ -124.62.

HPLC (Chiral IC, $\lambda$= 220 nm, hexane/2-propanol = 15/1, Flow rate =0.8 mL/min),

t$_{major}$ = 18.17 min, t$_{minor}$ = 13.72 min.

(2R,3S)-methyl2-(5-fluoro-1-methyl-1H-indol-3-yl)-5-oxo-2,3-diphenylpentanoate

(5l)

(2R,3S)-syn-5l: 98%ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.56 (s, 1H), 7.36 – 7.29 (m, 1H), 7.27 – 7.22 (m, 3H), 7.20 – 7.10 (m, 4H), 7.08 – 7.04 (m, 2H), 6.95 – 6.80 (m, 3H), 6.46 (d, $J$ = 10.5 Hz, 1H), 4.93 (d, $J$ = 10.5 Hz, 1H), 3.80 (s, 3H), 3.51 (s, 3H), 3.18 (d, $J$ = 17.0 Hz, 1H), 2.80 – 2.67 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.74, 172.96, 157.26 (d, $J$ = 234.2 Hz), 138.67, 136.78, 133.87, 131.24, 131.20, 130.26, 127.41, 127.24, 127.11 (d, $J$ = 10.3 Hz), 126.88, 114.80 (d, $J$ = 4.8 Hz), 110.25 (d, $J$ = 26.7 Hz), 109.76 (d, $J$ = 9.9 Hz), 107.26 (d, $J$ = 24.6 Hz), 60.86, 51.92, 46.22, 43.95, 33.35.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -124.34.


HPLC (Chiral IC, $\lambda$= 220 nm, hexane/2-propanol = 15/1, Flow rate =0.8 mL/min),

t$_{major}$ = 16.55 min, t$_{minor}$ = 14.83 min.

(2S,3S)-methyl2-(5-chloro-1-methyl-1H-indol-3-yl)-5-oxo-2,3-diphenylpentanoate

(5m)

(2S,3S)-anti-5m: 98%ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$

9.51 (s, 1H), 7.49 – 7.39 (m, 2H), 7.38 – 7.28 (m, 3H), 7.22 (d, $J$ = 8.7 Hz, 1H), 7.19 – 7.04 (m, 4H), 6.98 (s, 1H), 6.77 (d, $J$ = 7.3 Hz, 2H), 6.43 (s, 1H), 5.01 (d, $J$ = 10.8 Hz, 1H), 3.76 (s, 3H), 3.57 (s, 3H), 3.13 (d, $J$ = 16.6 Hz, 1H), 2.78 – 2.62 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.25, 173.43, 139.56, 138.78, 134.98, 133.86,
130.55, 129.14, 128.70, 128.35, 127.62, 127.46, 127.39, 124.86, 121.49, 121.41, 110.54, 110.34, 60.88, 52.22, 46.19, 44.33, 33.11.


HPLC (Chiral IC, \lambda = 220 nm, hexane/2-propanol = 15/1, Flow rate = 1.0 mL/min),
t_{major} = 14.23 min, t_{minor} = 10.90 min.

(2R,3S)-methyl2-(5-chloro-1-methyl-1H-indol-3-yl)-5-oxo-2,3-diphenylpentanoate (5m)

(2R,3S)-syn-5m: 99%ee. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 9.55 (s, 1H), 7.37 – 7.31 (m, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.24 – 6.99 (m, 8H), 6.87 (d, J = 7.3 Hz, 2H), 6.73 (s, 1H), 4.91 (d, J = 11.8 Hz, 1H), 3.79 (s, 3H), 3.52 (s, 3H), 3.16 (d, J = 17.5 Hz, 1H), 2.85 – 2.67 (m, 1H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 201.70, 172.97, 138.64, 136.95, 135.62, 131.20, 131.03, 130.09, 127.73, 127.47, 127.44, 127.30, 126.99, 125.07, 122.12, 121.57, 114.69, 110.18, 60.85, 51.98, 46.28, 44.14, 33.25.

HRMS(ESI): Calcd. for C_{27}H_{24}NO_{3}Cl [M+Na]^+ : 468.1342, Found: 468.1342.

HPLC (Chiral IC, \lambda = 220 nm, hexane/2-propanol = 15/1, Flow rate = 1.0 mL/min),
t_{major} = 12.64 min, t_{minor} = 11.43 min.

(2S,3S)-methyl2-(5-bromo-1-methyl-1H-indol-3-yl)-5-oxo-2,3-diphenylpentanoate (5n)

(2S,3S)-anti-5n: 95%ee. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 9.51 (s, 1H), 7.42 (d, J = 3.0 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.24 – 7.14 (m, 3H), 7.11 (t, J = 7.4 Hz, 2H), 6.96 (s, 1H), 6.77 (d, J = 7.4 Hz, 2H), 6.57 (s, 1H), 5.01 (d, J = 10.5 Hz, 1H), 3.76 (s, 3H), 3.57 (s, 3H), 3.12 (d, J = 16.0 Hz, 1H), 2.76 – 2.61 (m, 1H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 201.24, 173.41, 139.57, 138.75, 135.22, 133.68, 132.57, 131.57, 128.73, 128.47, 128.30, 127.30, 126.99, 125.07, 122.12, 121.57, 114.69, 110.18, 60.85, 51.98, 46.28, 44.14, 33.25.
130.54, 129.38, 129.12, 128.35, 127.62, 127.46, 127.40, 124.56, 123.96, 123.96, 112.54, 110.79, 110.52, 60.88, 52.22, 46.15, 44.29, 33.09.

HRMS(ESI) : Calcd. for C$_{27}$H$_{25}$NO$_3$ Br [M+H]$^+$: 490.1018, Found: 490.0997.

HPLC (Chiral IC, $\lambda$= 220 nm, hexane/2-propanol = 15/1, Flow rate =1.0 mL/min),
$t_{\text{major}}$ = 14.28 min, $t_{\text{minor}}$ = 11.06 min.

(2R,3S)-methyl2-(5-bromo-1-methyl-1H-indol-3-yl)-5-oxo-2,3-diphenylpentanoate (5n)

(2R,3S)-syn-5n: 73% ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.55 (s, 1H), 7.36 – 7.31 (m, 1H), 7.27 (d, $J$ = 10.0 Hz, 2H), 7.23 – 7.03 (m, 8H), 6.88 (s, 3H), 4.90 (d, $J$ = 11.1 Hz, 1H), 3.78 (s, 3H), 3.53 (s, 3H), 3.15 (d, $J$ = 17.3 Hz, 1H), 2.84 – 2.69 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.67, 172.98, 138.64, 137.02, 135.85, 131.18, 130.95, 129.98, 128.37, 127.49, 127.45, 127.32, 127.02, 124.66, 124.64, 114.67, 112.74, 110.62, 60.86, 51.99, 46.32, 44.21, 33.22.


HPLC (Chiral IC, $\lambda$= 220 nm, hexane/2-propanol = 15/1, Flow rate =1.0 mL/min),
$t_{\text{major}}$ = 12.58 min, $t_{\text{minor}}$ = 11.55 min.

(2S,3S)-methyl2-(7-bromo-1-methyl-1H-indol-3-yl)-5-oxo-2,3-diphenylpentanoate (5o)

(2S,3S)-anti-5o: 98% ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.49 (s, 1H), 7.44 – 7.39 (m, 2H), 7.34 – 7.29 (m, 3H), 7.20 – 7.07 (m, 3H), 6.94 (s, 1H), 6.77 (d, $J$ = 7.1 Hz, 2H), 6.61 (t, $J$ = 7.8 Hz, 1H), 6.45 (d, $J$ = 8.1 Hz, 1H), 5.01 (d, $J$ = 10.6 Hz, 1H), 4.15 (s, 3H), 3.56 (s, 3H), 3.12 (d, $J$ = 16.6 Hz, 1H), 2.83 – 2.56 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.28, 173.36, 139.63, 138.75, 135.82, 133.00, 130.75, 130.57, 129.18, 128.26, 127.49, 127.40, 126.18, 121.73, 119.97, 110.61, 103.99, 60.84, 52.23, 46.29, 44.43, 37.21.


HPLC (Chiral IC, $\lambda$= 220 nm, hexane/2-propanol = 30/1, Flow rate =1.0 mL/min),
$t_{\text{major}} = 14.73 \text{ min}, t_{\text{minor}} = 11.15 \text{ min}.$

$(2R,3S)$-methyl2-(7-bromo-1-methyl-1H-indol-3-yl)-5-oxo-2,3-diphenylpentanoate (5o)

$(2R,3S)$-syn-5o: 94% ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.56 (s, 1H), 7.40 – 7.29 (m, 1H), 7.27 – 7.20 (m, 3H), 7.19 – 7.11 (m, 4H), 7.07 (d, $J = 7.8$ Hz, 2H), 6.88 (d, $J = 7.1$ Hz, 2H), 6.76 (d, $J = 8.1$ Hz, 1H), 6.62 (t, $J = 7.8$ Hz, 1H), 4.93 (d, $J = 11.5$ Hz, 1H), 4.20 (s, 3H), 3.49 (s, 3H), 3.16 (d, $J = 17.4$ Hz, 1H), 2.81 – 2.49 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.62, 172.65, 138.54, 136.76, 133.64, 131.72, 131.34, 131.16, 129.79, 127.49, 127.34, 126.85, 126.80, 121.74, 120.28, 114.79, 103.68, 60.59, 51.94, 46.15, 43.93, 37.36.


HPLC (Chiral IC, $\lambda = 220$ nm, hexane/2-propanol = 30/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 11.83$ min, $t_{\text{minor}} = 10.75$ min.

(3R,4S)-methyl9-methyl-3,4-diphenyl-4,9-dihydro-3H-carbazole-4-carboxylate (6)

$(2S,3S)$-anti-6: 96% ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (d, $J = 8.3$ Hz, 1H), 7.26 – 7.03 (m, 12H), 7.00-6.90 (m, 1H), 6.70 (dd, $J = 9.9$, 2.3 Hz, 1H), 6.33 (dd, $J = 9.9$, 4.0 Hz, 1H), 4.35 (dd, $J = 4.0$, 2.3 Hz, 1H), 3.79 (s, 3H), 3.32 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.54, 143.04, 138.97, 137.95, 135.56, 132.22, 130.66, 128.51, 127.49, 126.99, 126.88, 126.05, 121.70, 121.34, 119.71, 115.53, 109.70, 109.08, 59.76, 54.85, 51.30, 29.40.


HPLC (Chiral IC, $\lambda = 254$ nm, hexane/2-propanol = 10/1, Flow rate = 1.0 mL/min), $t_{\text{major}} = 6.48$ min, $t_{\text{minor}} = 17.74$ min.

(3S,4S)-3-(1-methyl-1H-indol-3-yl)-3,4-diphenyltetrahydro-2H-pyran-2-one (7)

$(2S,3S)$-anti-7: 96% ee. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51 (d, $J =$
8.1 Hz, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.23 (d, J = 7.3 Hz, 1H), 7.17 – 7.11 (m, 1H), 7.09 – 7.01 (m, 2H), 6.88 – 6.79 (m, 1H), 6.68 (d, J = 7.3 Hz, 1H), 4.70 – 4.55 (m, 1H), 4.43 – 4.29 (m, 1H), 3.77 (s, 1H), 2.52 – 2.34 (m, 1H), 2.31 – 2.10 (m, 1H).

13C NMR (100 MHz, CDCl3) δ 173.08, 140.97, 138.39, 137.77, 130.14, 129.48, 129.12, 127.66, 126.82, 126.80, 126.38, 121.97, 121.20, 119.62, 115.09, 109.61, 58.97, 46.49, 33.02, 26.79.


HPLC (Chiral IA, λ = 254 nm, hexane/2-propanol = 4/1, Flow rate = 1.0 mL/min), tmajor = 10.23 min, tminor = 14.64 min.

(2S,3S)-methyl 5-hydroxy-2-(1-methyl-1H-indol-3-yl)-2,3-diphenylpentanoate (8)

(2S,3S)-anti-6: 96%ee. 1H NMR (400 MHz, CDCl3) δ 7.65 – 7.49 (m, 1H), 7.42 – 7.27 (m, 2H), 7.21 – 7.00 (m, 3H), 6.87 – 6.70 (m, 1H), 6.56 (d, J = 8.1 Hz, 1H), 5.34 (s, 1H), 4.59 (d, J = 12.1 Hz, 1H), 3.78 (s, 1H), 3.53 (s, 1H), 3.44 – 3.37 (m, 1H), 3.31 – 3.17 (m, 1H), 2.56 – 2.38 (m, 1H), 2.09 – 1.92 (m, 1H). 13C NMR (100 MHz, CDCl3) δ 174.16, 140.65, 139.71, 136.50, 132.62, 130.84, 129.61, 128.04, 127.91, 127.26, 126.98, 126.94, 122.82, 120.70, 118.53, 111.21, 109.02, 61.23, 61.09, 51.99, 46.89, 34.55, 32.88.


HPLC (Chiral IA, λ = 254 nm, hexane/2-propanol = 10/1, Flow rate = 1.0 mL/min), tmajor = 13.54 min, tminor = 11.05 min.

methyl 2-(1-methyl-1H-indol-3-yl)-2-phenylacetate (9)

1H NMR (400 MHz, CDCl3) δ 7.36 – 7.32 (m, 3H), 7.22 – 7.09 (m, 5H), 6.98 – 6.94 (m, 2H), 5.17 (s, 1H), 3.63 (s, 3H), 3.60 (s, 3H).

References


4. X-ray Diffraction Parameters and Data

Single Crystal X-ray Diffraction Data of *anti*-5m (CCDC NO.: 1030110)

![Diagram of molecule](image)

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Single Crystal X-ray Diffraction Data of syn-5b (CDCC NO.: 1030118)

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5. NMR Spectra of Compounds

(2S,3S)-anti-5a

(2S,3S)-anti-5a
(2R,3S)-syn-5c
(2S,3S)-anti-5d
(2R,3S)-syn-5n
(2S,3S)-anti-6

(2S,3S)-anti-6
(2S,3S)-anti-7

(2S,3S)-anti-7
(2S,3S)-anti-8
6. HPLC spectra of compounds

**Condition:** hexane/2-propanol = 15/1
Flow rate = 0.8 mL/min
\( \lambda = 220 \) nm
Chiral IC
**Condition:** hexane/2-propanol = 15/1
Flow rate = 0.8 mL/min
$\lambda$ = 220 nm
Chiral IC
**Condition:** \( \text{hexane/2-propanol = 15/1} \)

Flow rate = 1.0 mL/min

\( \lambda = 220 \text{ nm} \)

Chiral AD-H
**Condition:** hexane/2-propanol = 15/1  
Flow rate = 1.0 mL/min  
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Chiral IC
**Condition:** hexane/2-propanol = 10/1  
Flow rate = 1.0 mL/min  
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Chiral IC
**Condition:** hexane/2-propanol = 10/1
Flow rate = 1.0 mL/min
\( \lambda = 220 \text{ nm} \)
Chiral IC
Condition: hexane/2-propanol = 15/1
Flow rate = 1.0 mL/min
$\lambda = 220$ nm
Chiral IC
**Condition:** hexane/2-propanol = 15/1
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\( \lambda = 220 \text{ nm} \)
Chiral IC
**Condition:** hexane/2-propanol = 6/1
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Chiral IC

![Chiral IC graph with peaks labeled race-anti-5e and (2S,3R)-anti-5e]
**Condition:** hexane/2-propanol = 6/1  
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Chiral IC

![Graph showing retention times and peak areas for race-syn-5e](image1)

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![Graph showing retention times and peak areas for (2R,3R)-syn-5e](image2)

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Flow rate = 1.0 mL/min
$\lambda = 220$ nm
Chiral IC
**Condition:** hexane/2-propanol = 30/1
Flow rate = 1.0 mL/min
\( \lambda = 220 \text{ nm} \)
Chiral IC
**Condition:** hexane/2-propanol = 30/1
Flow rate = 1.0 mL/min
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Chiral IC
**Condition:** hexane/2-propanol = 30/1

Flow rate = 1.0 mL/min

\[ \lambda = 220 \text{ nm} \]

Chiral IC
**Condition:** hexane/2-propanol = 30/1  
Flow rate = 1.0 mL/min  
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Chiral IC
**Condition:** hexane/2-propanol = 30/1  
Flow rate = 1.0 mL/min  
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Chiral IC
**Condition:** hexane/2-propanol = 15/1
Flow rate = 1.0 mL/min
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Chiral IC
**Condition:** hexane/2-propanol = 15/1  
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Chiral IC
Condition: hexane/2-propanol = 30/1
Flow rate = 1.0 mL/min
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**Condition:** hexane/2-propanol = 30/1
Flow rate = 1.0 mL/min
\( \lambda = 220 \text{ nm} \)
Chiral IC
**Condition:** hexane/2-propanol = 30/1

Flow rate = 0.8 mL/min

$\lambda = 220$ nm

Chiral IC

---

**Graph 1:**

Chemical structure: rac-anti-5k

---

**Table:**

<table>
<thead>
<tr>
<th>#</th>
<th>保留时间(min)</th>
<th>同位素(mv.sec)</th>
<th>面积百分比(%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>11853.08</td>
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<tr>
<td>2</td>
<td>31.35</td>
<td>11088.40</td>
<td>49.6053</td>
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<tr>
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<td>23541.48</td>
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</tr>
</tbody>
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**Graph 2:**

Chemical structure: (2S,3S)-anti-5k

---

**Table:**

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<tr>
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</table>
**Condition:** hexane/2-propanol = 30/1  
Flow rate = 0.8 mL/min  
$\lambda = 220$ nm  
Chiral IC
**Condition:** hexane/2-propanol = 15/1

Flow rate = 0.8 mL/min

$\lambda = 220$ nm

Chiral IC
**Condition:** hexane/2-propanol = 15/1  
Flow rate = 0.8 mL/min  
$\lambda = 220$ nm  
Chiral IC
**Condition:** hexane/2-propanol = 15/1

Flow rate = 1.0 mL/min

$\lambda = 220$ nm

Chiral IC
**Condition:** hexane/2-propanol = 15/1
Flow rate = 1.0 mL/min
\( \lambda = 220 \text{ nm} \)
Chiral IC
**Condition:** hexane/2-propanol = 15/1
Flow rate = 1.0 mL/min
$\lambda = 220$ nm
Chiral IC
**Condition:** hexane/2-propanol = 15/1  
Flow rate = 1.0 mL/min  
$\lambda = 220$ nm  
Chiral IC

![Chiral IC diagram](image1)

<table>
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<tr>
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<th>峰面积(mv.sec)</th>
<th>面积百分比(%)</th>
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<td>2</td>
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</table>

![Chiral IC diagram](image2)

<table>
<thead>
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<th>峰面积(mv.sec)</th>
<th>面积百分比(%)</th>
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</thead>
<tbody>
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</table>
**Condition:** hexane/2-propanol = 30/1
Flow rate = 1.0 mL/min
$\lambda = 220$ nm
Chiral IC
**Condition:** hexane/2-propanol = 30/1

Flow rate = 1.0 mL/min

$\lambda = 220$ nm

Chiral IC
**Condition**: hexane/2-propanol = 10/1
Flow rate = 1.0 mL/min
\( \lambda = 254 \text{ nm} \)
Chiral IC
**Condition:** hexane/2-propanol = 4/1  
Flow rate = 1.0 mL/min  
$\lambda = 254$ nm  
Chiral IA
**Condition:** hexane/2-propanol = 10/1  
Flow rate = 1.0 mL/min  
$\lambda = 254$ nm  
Chiral IA