Supplementary Information-1

Stereoselective Synthesis of 4-Substituted-Cyclic Sulfamidate-5-Carboxylates By Asymmetric Transfer Hydrogenation Accompanying Dynamic Kinetic Resolution and Its Use in Concise Stereoselective Synthesis of (-)-epi-Cytoxazone and Taxotere Side-Chain.

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General

All commercial reagents were used as obtained commercially unless otherwise noted. Reactions were performed using oven dried glassware under an atmosphere of nitrogen. Dichloromethane (DCM), ether, THF were dried and purified using a solvent purification system. Flash column chromatography was carried out on Fuji Chromatorex silica gel (38-75 μm). Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates. Preparative thin layer chromatography (PLC) was performed on Merck silica gel 60 F_{254} 2mm plates. Visualization of the developed chromatogram was accomplished with UV light and by staining with ethanolic phosphomolybdic acid (PMA) solution or ninhydrin solution followed by heating.

Nuclear magnetic resonance (NMR) spectra were recorded using Bruker 500 MHz NMR instrument (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz) or Bruker 300 MHz NMR instrument (^{1}H NMR at 300 MHz and ^{13}C NMR at 75 MHz). ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constants (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High performance liquid chromatography (HPLC) was carried out on a Young Lin HPLC system (7725i Injector, SDV 30 Plus Solvent Degassor & Valve Module (Helium Sparging), SP930D Solvent Delivery Pump, UV 730D Absorbance Detector) equipped with a Chiralpak IB or Chiralpak AD-H column or an Agilent 1100 Series HPLC equipped with Chiralpak IB or Chiralpak IC column. Specific rotations were measured on a Rudolph Autopol IV (Automatic polarimeter). High-resolution mass spectra and elemental analysis were obtained from the Korea Research Institute of Chemical Technology (EI) or Korea Basic Science Institute (ESI). HR-MS were measured with electron impact (EI) ionization via double focusing mass analyzer (magnetic and electric fields) or electrospray ionization (ESI) via time of flight (TOF) analyzer. The formic acid/triethylamine mixtures (molar ratio = 5/2 or 1:1) are commercially available. (R,R)-1a^{1} and (R,R)-1b^{2} were prepared according to the literature procedures. Chiral catalysts, (R,R)-1c, (R,R)-1d, and (R,R)-1e are commercially available.

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1. Optimization of the ATH-DKR reaction of 6

1-1. Optimization of ATH-DKR reaction of 6a with various catalysts

Table S1. Optimization of chiral catalysts 1a-e in ATH-DKR of 6a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.1</th>
<th>Convn (%)</th>
<th>dr (syn:anti)</th>
<th>ee(%)</th>
<th>config</th>
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<tbody>
<tr>
<td>1</td>
<td>(R,R)-1a</td>
<td>&gt;99</td>
<td>&gt;25:1</td>
<td>98</td>
<td>S,S</td>
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<tr>
<td>2</td>
<td>(R,R)-1b</td>
<td>&gt;99</td>
<td>&gt;25:1</td>
<td>30</td>
<td>S,S</td>
</tr>
<tr>
<td>3</td>
<td>(R,R)-1c</td>
<td>13</td>
<td>-</td>
<td>95</td>
<td>S,S</td>
</tr>
<tr>
<td>4</td>
<td>(R,R)-1d</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>(R,R)-1e</td>
<td>17</td>
<td>-</td>
<td>83</td>
<td>S,S</td>
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</tbody>
</table>

*Reaction conditions: 6a (0.5 mmol), cat-1 (0.5 mol%), HCO₂H/Et₃N (5:2, 0.5 ml), EtOAc (5 mL), rt. *Determined by ¹H NMR analysis of the crude products. *Only 4,5-cis products were detected in ¹H NMR of crude products. *Determined by chiral HPLC. *See, Scheme S-1 below

1-2. Optimization of ATH-DKR reaction of 6a in various solvents

Table S2. Optimization of solvent effect in ATH-DKR of 3

4
### Table 1: Conversion and Enantiomeric Excess (ee) for Different Solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Convn (%)</th>
<th>ee (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>EtOAc</td>
<td>&gt;99</td>
<td>98.1</td>
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<tr>
<td>2</td>
<td>CH$_2$Cl$_2$</td>
<td>&gt;99</td>
<td>98.9</td>
</tr>
<tr>
<td>3</td>
<td>Cl(CH$_2$)$_2$Cl</td>
<td>&gt;99</td>
<td>98.1</td>
</tr>
<tr>
<td>4</td>
<td>CHCl$_3$</td>
<td>&gt;99</td>
<td>84.1</td>
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<td>5</td>
<td>Toluene</td>
<td>&gt;99</td>
<td>85.1</td>
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<tr>
<td>6</td>
<td>DMF</td>
<td>&gt;99</td>
<td>88.1</td>
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<tr>
<td>7</td>
<td>MeOH</td>
<td>&gt;99</td>
<td>97.1</td>
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<tr>
<td>8</td>
<td>THF</td>
<td>96</td>
<td>90.9</td>
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<tr>
<td>9</td>
<td>2-Propanol</td>
<td>&gt;99</td>
<td>96.8</td>
</tr>
</tbody>
</table>

*Reaction conditions: 6a (0.5 mmol), (R,R)-1a (0.5 mol%), HCO$_2$H/Et$_3$N (5:2, 0.5 ml), in 5.0 mL of solvent at rt. *Determined by $^1$H NMR analysis of the crude products. *Determined by chiral HPLC of the crude products.

### 2. General procedure for the synthesis of α-hydroxy-β-keto esters from β-keto-ester

**[Method A]**

\[
\begin{align*}
\text{R}_1\text{C} &= \text{CO} & \text{K}_2\text{CO}_3 &\text{TsN}_3 \\
\text{CH}_3\text{CN} &\rightarrow \text{R}_1\text{C} &= \text{CO} &\text{R}_1\text{C} &= \text{CO} \\
\text{THF/H}_2\text{O}(2:1) &\rightarrow \text{R}_1\text{OH} & \text{R}_2\text{OH}
\end{align*}
\]

4-4-1.\textsuperscript{3}

To a mixture of β-keto-ester (1.0 eq.) and potassium carbonate (1.25 eq.) in acetonitrile cooled in a water ice-bath, was added dropwise with stirring a solution of tosyl azide (1.25 eq) in acetonitrile. The reaction mixture was stirred at room temperature. The disappearance of

ester was monitored by TLC. Potassium carbonate was filtered off and the filterate was evaporated in vacuo to afford a residue which was purified by silica-gel chromatography to give the diazo compound.

**Step-2**
A solution of the diazo compound (1.0 eq) and Rh$_2$(OAc)$_4$ (0.03 eq) in THF- H$_2$O (2:1 ratio) was refluxed overnight and allowed to cool to room temperature. The mixture was concentrated in vacuo and the aqueous residue was extracted with EtOAc (x3). The combined organic layers were washed with water and brine, dried over anhydrous MgSO$_4$, filtered, and evaporated to dryness. The residue was purified by silica-gel chromatography to give the α-hydroxy β-ketocarbonates.

**[Method B]**

![Chemical structures](image)

**Step-1**
To a solution of 1 (4 g, 21.7 mmol) and PhI(OAc)$_2$ (7 g, 21.7 mmol) in dichloromethane (50 mL) was added BF$_3$·OEt$_2$ (1.4 mL, 10.85 mmol). The reaction mixture was stirred at room temperature for 20 min and then quenched by NaHCO$_3$. The layers were separated and the aqueous layer was extracted with dichloromethane (x3). The combined organic layers were washed with brine, dried over anhydrous MgSO$_4$, and evaporated. The residue was purified by silica-gel chromatography (Hexane/EtOAc=5:1) to give 2 (4.96 g, 94.4% yield).

**Step-2**

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A solution of 2 (1.3 g, 5.4 mmol) in anhydrous MeOH (10 mL) was added dropwise to a solution of KCN (175 mg, 2.7 mmol) in anhydrous MeOH (40 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 2 h. After removal of the solvent, the residue was dissolved in CH₂Cl₂ and then washed with brine. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated. The residue was purified by silica-gel chromatography (Hexane/EtOAc, 5:1) to give 3 (0.815 g, 75.4% yield).

[Method C]⁵

\[
\begin{align*}
\text{R}_1\text{CO}_2\text{H} + \text{Phl(OCOCF}_3\text{)}_2 & \xrightarrow{\text{H}_2\text{O}} \text{R}_1\text{CO}_2\text{OH} \\
\end{align*}
\]

To a suspension of β-keto-ester in H₂O was added PIFA (2.0 eq) portionwise for 10 minutes. The reaction mixture was stirred at room temperature until TLC indicated the total consumption of the β-keto-ester. Then the reaction mixture was treated with saturated NaHCO₃ (aq) and extracted with EtOAc (x3). The combined organic layers were washed with water and brine, dried over anhydrous MgSO₄, filtered, and concentrated. The residue was purified by silica-gel chromatography to give the α-hydroxy-β-keto ester.

3-Phenyl-2-hydroxy-3-oxo-propionic acid methyl ester⁶ [Method A]

yield: 89.3% (1.9 g as a yellow oil); ¹H NMR (500 MHz, CDCl₃) δ 8.04-8.05 (m, 2H), 7.59-7.62 (m, 1H), 7.45-7.48 (m, 2H), 5.60 (s, 1H), 4.42-4.49 (brs, 1H), 3.68 (s, 3H).; ¹³C NMR (75 MHz, CDCl₃) δ 193.8, 169.1, 134.7, 133.0, 129.5, 128.9, 74.3, 53.1.; HRMS (EI): m/z calcd for C₁₀H₁₀O₄ 194.0579, found 194.0542.

3-(2-Tolyl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method C]

The product was unstable in silica-gel chromatography and used next step without further purification. HRMS (EI): m/z calcd for C₁₁H₁₂O₄

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3-(3-Tolyl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method B]
yield: 82.1% (683.5 mg as a pale yellow oil); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.86-7.87 (m, 2H), 7.45 (d, 1H, $J$ = 7.6 Hz), 7.39 (t, 1H, $J$ = 7.6 Hz), 5.59 (s, 1H), 4.30 (brs, 1H), 3.71 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 193.8, 169.1, 138.8, 135.6, 133.0, 129.8, 128.7, 126.7, 74.3, 53.3, 21.3.; HRMS (EI): m/z calcd for C$_{11}$H$_{12}$O$_4$ 208.0736, found 208.0732.

3-(4-Tolyl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method C]
yield: 84.8% (84.8 mg as a yellow oil); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.98 (d, 2H, $J$ = 8.3 Hz), 7.30 (d, 2H, $J$ = 8.2 Hz), 5.59 (s, 1H), 4.33-4.37 (brs, 1H), 3.71 (s, 3H), 2.43 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 193.1, 169.2, 146.1, 130.4, 129.6, 129.6, 74.2, 53.0, 21.9.; HRMS (EI): m/z calcd for C$_{11}$H$_{12}$O$_4$ 208.0736, found 208.0733.

3-(3-Chloro-phenyl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method B]
yield: 41.7% (0.11 g as a yellow oil); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.06 (s, 1H), 7.97 (d, 1H, $J$ = 7.8 Hz), 7.62 (m, 1H), 7.47 (m, 1H), 5.57 (s, 1H), 3.76 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 192.7, 168.8, 135.3, 134.6, 134.6, 130.2, 129.4, 127.6, 74.5, 53.3.; HRMS (EI): m/z calcd for C$_{10}$H$_9$ClO$_4$ 228.0189, found 228.0177.

3-(4-Chloro-phenyl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method A]
yield: 35.7% (0.24 g as a yellow oil); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.02 (d, 2H, $J$ = 8.3 Hz), 7.48 (d, 2H, $J$ = 8.3 Hz), 5.56 (s, 1H), 4.21 (brs, 1H), 3.73 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 192.6, 168.9, 141.4, 131.3, 130.9, 129.3, 74.4, 53.2.; HRMS (EI): m/z calcd for C$_{10}$H$_9$ClO$_4$ 228.0189, found 228.0183.

3-(4-Methoxy-phenyl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method A]
yield: 78% (5.6 g as a yellow oil); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.07 (d, 2H, $J = 8.5$ Hz), 6.97 (d, 2H, $J = 8.5$ Hz), 5.55 (d, 1H, $J = 5.6$ Hz), 4.35 (d, 1H, $J = 7.1$ Hz), 3.88 (s, 3H), 3.71 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 191.7, 169.3, 164.9, 132.0, 125.7, 114.2, 74.1, 55.6, 53.0; HRMS (EI): m/z calcd for C$_{11}$H$_{12}$O$_5$ 224.0685, found 224.0673.

3-(4-Fluoro-phenyl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method C]

yield: 66% (0.66 g as a pale yellow oil); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.13 (m, 2H), 7.13 (m, 2H), 5.38 (s, 1H), 3.88 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 196.5, 167.3, 166.3 (q, $J_{CF}$ = 248.7 Hz), 133.1 (d, $J_{CF}$ = 10.0 Hz), 130.2 (d, $J_{CF}$ = 3.4 Hz), 115.8 (d, $J_{CF}$ = 21.7 Hz), 85.3, 53.9; HRMS (EI): m/z calcd for C$_{10}$H$_3$F$_4$O$_4$ 212.0456, found 212.0456.

3-(4-Trifluoromethyl-phenyl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method A]

yield: 61% (0.77 g as a pale yellow oil); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.20 (d, 2H, $J = 7.9$ Hz), 7.78 (d, 2H, $J = 8.1$ Hz), 5.65 (s, 1H), 3.76 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 193.2, 168.9, 135.4 (q, $J_{CF}$ = 32.6 Hz), 130.5, 129.8, 125.9, 125.5 (q, $J_{CF}$ = 271.2 Hz), 74.7, 53.3; HRMS (EI): m/z calcd for C$_{11}$H$_3$F$_4$O$_4$ 262.0453, found 262.0441.

3-(4-Cyano-phenyl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method A]

yield: 49.6% (0.93 g as a yellow solid), mp = 100.4-102.6 °C, $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.17 (d, 2H, $J = 8.0$ Hz), 7.82 (d, 2H, $J = 8.0$ Hz), 5.59 (s, 1H), 4.09-4.17 (brs, 1H), 3.76 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 192.9, 168.7, 136.2, 132.6, 129.9, 117.7, 117.6, 74.7, 53.4; HRMS (EI): m/z calcd for C$_{11}$H$_3$NO$_4$ 219.0532, found 219.0528.

3-(4-Methoxycarbonyl-phenyl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method A]

yield: 42% (0.71 g as a yellow oil); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.06-8.11 (m, 4H), 5.60 (s, 1H), 3.91 (s, 3H), 3.68 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 193.6, 168.9, 165.9,
136.4, 135.0, 129.9, 129.3, 74.6, 53.2, 52.6.; HRMS (EI): m/z calcd for C$_{12}$H$_{12}$O$_{6}$ 252.0634, found 252.0632.

3-(Naphthalen-2-yl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method A]

yield: 59% (1.64 g as a yellow oil); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.68 (s, 1H), 8.11 (d, 1H, $J = 8.6$ Hz), 8.03 (d, 1H, $J = 8.2$ Hz), 7.90-7.95 (m, 2H), 7.67 (t, 1H, $J = 7.1$ Hz), 7.61 (t, 1H, $J = 7.4$ Hz), 5.81 (s, 1H), 4.46 (brs, 1H), 3.75 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 193.6, 169.2, 136.3, 132.3, 132.2, 130.3, 130.0, 129.5, 128.8, 127.9, 127.2, 124.2, 74.4, 53.1.; HRMS (EI): m/z calcd for C$_{14}$H$_{12}$O$_{6}$ 244.0736, found 244.0729.

3-(Furan-2-yl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method B]

yield: 69.3% (0.95 g as a yellow oil); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.71-7.72 (m, 1H), 7.49 (d, 1H, $J = 3.5$ Hz), 6.62-6.63 (m, 1H), 5.35 (d, 1H, $J = 8.3$ Hz), 4.01 (d, 1H, $J = 8.3$ Hz), 3.78 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 181.8, 169.1, 149.8, 148.5, 121.4, 113.1, 74.3, 53.3.; HRMS (EI): m/z calcd for C$_{8}$H$_{8}$O$_{5}$ 184.0372, found 184.0353.

3-(Thiophen-2-yl)-2-hydroxy-3-oxo-propionic acid methyl ester [Method B]

yield: 75.4% (0.81 g as a brown oil); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.01 (d, 1H, $J = 3.6$ Hz), 7.79 (d, 1H, $J = 4.9$ Hz), 7.19 (t, 1H, $J = 4.4$ Hz), 5.42 (s, 1H), 4.22 (brs, 1H), 3.76 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 186.1, 169.2, 139.4, 136.4, 135.3, 128.7, 75.1. 53.3.; HRMS (EI): m/z calcd for C$_{8}$H$_{8}$O$_{5}$S 200.0143, found 200.0139.

2-Hydroxy-3-oxo-hexanoic acid methyl ester [Method A]

yield: 80.1% (1.36 g as a coloress oil); $^1$H NMR (300 MHz, CDCl$_3$) δ 4.77 (s, 1H), 4.32 (brs, 1H), 3.80 (s, 3H), 2.05-2.78 (m, 2H), 1.57-1.69 (m, 2H), 0.90 (t, 3H, $J = 7.4$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 204.4, 169.0, 76.7, 53.2, 40.6, 17.0, 13.6.; HRMS (EI): m/z calcd for C$_{7}$H$_{12}$O$_{4}$ 160.0736, found 160.0728.
2-Hydroxy-3-oxo-5-phenyl-pentanoic acid methyl ester [Method A]

yield: 51.8% (1.14 g as a pale yellow oil); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26-7.30 (m, 2H), 7.16-7.22 (m, 3H), 4.76 (s, 1H), 3.85-3.89 (brs, 1H), 3.74 (s, 3H), 3.05-3.11 (m, 1H), 2.90-3.00 (m, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 203.7, 168.7, 140.2, 128.6, 128.3, 126.4, 77.9, 53.2, 40.4, 29.3.; HRMS (EI): m/z calcd for C$_{12}$H$_{14}$O$_4$ 222.0892, found 222.0888.

3-Cyclohexyl-2-hydroxy-3-oxo-propionic acid methyl ester$^7$ [Method A]

yield: 78.2% (2.18 g as a pale yellow oil); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 5.24 (s, 1H), 3.71 (s, 3H), 3.05-3.10 (m, 1H), 1.63-1.87 (m, 5H), 1.17-1.36 (m, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 212.1, 168.7, 84.0, 53.3, 46.5, 29.0, 28.6, 25.7.; HRMS (EI): m/z calcd for C$_{10}$H$_{16}$O$_4$ 200.1049, found 200.1040.

3. General procedure for the synthesis of cyclic imine 6 from $\alpha$-hydroxy-$\beta$-keto-ester.$^{8,9}$

To the solution of 3-phenyl-2-hydroxy-3-oxo-propionic acid methyl ester (1.85 g, 9.53 mmol) in DMA ($N,N$-dimethyl acetamide, 18 mL) was added sulfamoyl chloride (2.2 g, 19 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1.5 h and diluted with EtOAc (30 mL). The reaction mixture washed with brine and the organic layer was dried over anhydrous MgSO$_4$ and the solvent was evaporated under reduced pressure. The residue was re-dissolved in toluene (15 mL) and catalytic amount of PTSA ($p$-toluenesulfonic acid) was added. The reaction mixture was heated for 1 h at 110 °C and cooled to room temperature. The solvent was removed and the reaction mixture was diluted with EtOAc (30 mL) and

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washed brine. The organic layers were dried over anhydrous MgSO₄ and the solvent was evaporated under reduced pressure. The residue was recrystallized from EtOAc/Hexane, to give the desired imine, as white crystals 6a.

**Methyl 2,2-dioxo-4-phenyl-5H-1,2,3-oxathiazole-5-carboxylate, 6a**

Yield: 74.8% (1.81 g as a white solid), mp = 149.5-151.5 °C, ¹H NMR (300 MHz, CDCl₃) δ 8.09 (d, 2H, J = 7.6 Hz), 7.77 (t, 1H, J = 7.5 Hz), 7.58 (t, 2H, J = 7.8 Hz), 6.19 (s, 1H), 3.82 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.7, 163.5, 136.3, 130.3, 129.6, 126.3, 83.7, 54.4.; HRMS (EI): m/z calcd for C₁₀H₉NO₅S 255.0201, found 255.0233.

**Isopropyl 2,2-dioxo-4-phenyl-5H-1,2,3-oxathiazole-5-carboxylate, 6b**

Yield: 53%; ¹H NMR (300 MHz, CDCl₃) δ 8.08 (d, 2H, J = 7.8), 7.77-7.72 (t, 1H, J = 7.4), 7.62-7.55 (t, 2H, J = 7.8), 6.13 (s, 1H), 5.05 (m, 1H), 1.18 (d, 6H, J = 6.21); ¹³C NMR (500 MHz, CDCl₃) δ 172.0, 162.3, 136.1, 130.3, 129.4, 126.5, 84.1, 72.6, 21.3, 21.2; HRMS (EI): m/z calcd for C₁₂H₁₃NO₅S 283.0514, found 283.0503.

**Benzyl 2,2-dioxo-4-phenyl-5H-1,2,3-oxathiazole-5-carboxylate, 6c**

Yield: 66%; ¹H NMR (300 MHz, CDCl₃) δ 7.97 (d, 2H, J = 7.4), 7.70 (t, 1H, J = 7.5), 7.49 (t, 2H, J = 7.8), 7.31-7.18 (m, 6H), 6.17 (s, 1H), 5.23 (q, 2H, J = 12.1); ¹³C NMR (500 MHz, CDCl₃) δ 171.7, 162.7, 136.1, 133.6, 130.3, 129.5, 128.9, 128.7, 128.4, 126.3, 83.8, 69.3.; HRMS (EI): m/z calcd for C₁₆H₁₃NO₅S 331.0514, found 331.0519.

**t-Butyl 2,2-dioxo-4-phenyl-5H-1,2,3-oxathiazole-5-carboxylate, 6d**

Yield: 48%; ¹H NMR (300 MHz, CDCl₃) δ 8.07 (d, 2H, J = 7.5), 7.73 (t, 1H, J = 7.5), 7.57 (t, 2H, J = 7.7), 6.06 (s, 1H), 1.36 (s, 9H); ¹³C NMR (500 MHz, CDCl₃) δ 172.3, 161.6, 136.0, 130.3, 129.4, 126.6, 86.2, 84.9, 27.5.; HRMS (EI): m/z calcd for C₁₃H₁₅NO₅S 297.0671, found 297.0680.
Methyl 4-(2-tolyl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6e

yield: 53.3% (0.93 g as a white solid), mp = 106.1-107.4 °C, ^1H NMR (300 MHz, CDCl₃) δ 7.68 (d, 1H, J = 7.9 Hz), 7.57 (t, 1H, J = 7.5 Hz), 7.37-7.43 (m, 2H), 6.24 (s, 1H), 3.75 (s, 3H), 2.69 (s, 3H); ^13C NMR (125 MHz, CDCl₃) δ 171.7, 163.4, 142.8, 134.8, 133.1, 130.9, 126.5, 125.2, 84.6, 54.2, 22.9.; HRMS (EI): m/z calcd for C₁₁H₁₁NO₅S 269.0358, found 269.0354.

Methyl 4-(3-tolyl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6f

yield: 71.4% (498.2 mg as a white solid), mp = 128.3-129.1 °C, ^1H NMR (300 MHz, CDCl₃) δ 7.90 (s, 1H), 7.82-7.84 (m, 1H), 7.45-7.53 (m, 2H), 6.17 (s, 1H), 3.81 (s, 3H), 2.45 (s, 3H); ^13C NMR (75 MHz, CDCl₃) δ 171.8, 163.7, 139.9, 137.3, 130.8, 129.5, 127.6, 126.4, 83.8, 54.5, 21.4.; HRMS (EI): m/z calcd for C₁₁H₁₁NO₅S 269.0358, found 269.0364.

Methyl 4-(4-tolyl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6g

yield: 53% (670 mg as a white solid), mp = 147.7-148.3 °C, ^1H NMR (500 MHz, CDCl₃) δ 7.96 (d, 2H, J = 8.3 Hz), 7.37 (d, 2H, J = 8.1 Hz), 6.16 (s, 1H), 3.81 (s, 3H), 2.48 (s, 3H); ^13C NMR (75 MHz, CDCl₃) δ 171.5, 163.8, 148.2, 130.5, 130.5, 123.8, 83.7, 54.4, 22.2.; HRMS (EI): m/z calcd for C₁₁H₁₁NO₅S 269.0358, found 269.0355.

Methyl 4-(3-chloro-phenyl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6h

yield: 50.7% (176 mg as a white solid), mp = 149.0-150.5 °C, ^1H NMR (500 MHz, CDCl₃) δ 8.10 (s, 1H), 7.93-7.95 (m, 1H), 7.70-7.72 (m, 1H), 7.52-7.55 (m, 1H), 6.15 (s, 1H), 3.84 (s, 3H); ^13C NMR (75 MHz, CDCl₃) δ 170.7, 163.3, 136.2, 136.1, 130.9, 130.2, 128.5, 128.1, 83.6, 54.7.; HRMS (EI): m/z calcd for C₁₀H₈ClNO₅S 288.9812, found 288.9818.

Methyl 4-(4-chloro-phenyl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6i

13
yield: 68\% (650 mg as a white solid), mp = 140.4-142.8 °C, $^1$H NMR (500 MHz, CDCl$_3$) δ 8.03 (d, 2H, $J = 8.7$ Hz), 7.57 (d, 2H, $J = 8.7$ Hz), 6.15 (s, 1H), 3.83 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 170.7, 163.5, 143.3, 131.7, 130.2, 124.8, 83.6, 54.6.; HRMS (EI): m/z calcd for C$_{10}$H$_8$ClNO$_5$S 288.9812, found 288.9817.

**Methyl 4-(4-methoxy-phenyl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6j**

yield: 63\% (0.5 g as a white solid), mp = 160.8-163.1 °C, $^1$H NMR (500 MHz, CDCl$_3$) δ 8.11 (d, 2H, $J = 8.4$ Hz), 7.17 (d, 2H, $J = 8.5$ Hz), 6.83 (s, 1H), 3.95 (s, 3H), 3.78 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 172.2, 172.2, 166.2, 164.0, 133.0, 119.0, 115.0, 83.9, 55.6, 53.5.; HRMS (EI): m/z calcd for C$_{11}$H$_{11}$NO$_6$S 285.0307, found 285.0308.

**Methyl 4-(4-fluoro-phenyl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6k**

yield: 69\% (750 mg as a white solid), mp = 130.6-133.5 °C, $^1$H NMR (500 MHz, CDCl$_3$) δ 8.15-8.18 (m, 2H), 7.29-7.32 (m, 2H), 6.18 (s, 1H), 3.86 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 170.5, 167.6 (d, $J_{CF} = 259.8$ Hz), 163.5, 133.4 (d, $J_{CF} = 9.9$ Hz), 122.8 (d, $J_{CF} = 3.1$ Hz), 117.3 (d, $J_{CF} = 22.3$ Hz), 83.6, 54.6.; HRMS (EI): m/z calcd for C$_{10}$H$_8$FNO$_5$S 273.0107, found 273.0107.

**Methyl 4-(4-trifluoromethyl-phenyl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6l**

yield: 44\% (0.37 g as a white solid), mp = 191.1-196.6 °C, $^1$H NMR (500 MHz, CDCl$_3$) δ 8.23 (d, 2H, $J = 8.1$ Hz), 7.86 (d, 2H, $J = 8.1$ Hz), 6.24 (s, 1H), 3.85 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 170.5, 163.0, 137.1 (q, $J_{CF} = 33.2$ Hz), 130.7, 129.4, 126.5, 123.0 (q, $J_{CF} = 271.4$ Hz), 83.6, 54.6.; HRMS (EI): m/z calcd for C$_{11}$H$_8$F$_3$NO$_5$S 323.0075, found 323.0077.

**Methyl 4-(4-cyano-phenyl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6m**
Methyl 4-(4-methoxycarbonyl-phenyl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6n

yield: 60.4% (1.13 g as a brown solid), mp = 118.2-123 °C, $^1$H NMR (500 MHz, CDCl$_3$) δ 8.21 (d, 2H, $J = 8.1$ Hz), 8.14 (d, 2H, $J = 8.2$ Hz), 6.23 (s, 1H), 3.97 (s, 3H), 3.81 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 171.0, 165.4, 163.1, 136.5, 130.4, 130.3, 129.8, 83.7, 54.5, 52.9.; HRMS (EI): m/z calcd for C$_{12}$H$_{11}$NO$_7$S 313.0256, found 313.0246.

Methyl 4-(naphthalen-2-yl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6o

yield: 59% (1.1 g as a white solid), mp = 151.5-155.7 °C, $^1$H NMR (500 MHz, CDCl$_3$) δ 8.60 (s, 1H), 8.11 (d, 1H, $J = 8.7$ Hz), 8.01(t, 2H, $J = 8.6$ Hz), 7.95 (d, 1H, $J = 8.2$ Hz), 7.65-7.75 (m, 2H), 6.35 (s, 1H), 3.83 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 171.5, 163.9, 136.9, 133.5, 132.4, 130.6, 130.1, 129.9, 128.3, 128.0, 124.6, 123.9, 83.9, 54.5.; HRMS (EI): m/z calcd for C$_{14}$H$_{11}$NO$_7$S 305.0358, found 305.0356.

Methyl 4-(furan-2-yl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6p

yield: 18% (0.14 g as an ivory solid), mp = 130.6-133.5 °C, $^1$H NMR (300 MHz, CDCl$_3$) δ 7.86-7.87 (m, 1H), 7.67-7.68 (m, 1H), 6.75-6.77 (m, 1H), 5.97 (s, 1H), 3.87 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 163.4, 159.8, 151.1, 143.3, 124.9, 114.6, 82.6, 54.5.; HRMS (EI): m/z calcd for C$_8$H$_7$NO$_6$S 244.9994, found 244.9997.

Methyl 4-(thiophen-2-yl)-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6q
yield: 88.7% (0.51g as a ivory solid), mp = 106.2-110.2 °C, \( ^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.07-8.08 (m, 1H), 7.98-7.99 (m, 1H), 7.29-7.31 (m, 1H), 6.09 (s, 1H), 3.90 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 164.7, 163.9, 139.1, 138.0, 130.2, 129.8, 83.3, 54.6.; HRMS (EI): m/z calcd for C\(_8\)H\(_7\)NO\(_5\)S\(_2\) 260.9766, found 260.9765.

**Methyl 4-propyl-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6r**

yield: 63.8% (2.79 g as a yellow oil); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.56 (s, 1H), 3.91 (s, 3H), 2.65-2.75 (m, 2H), 1.79-1.87 (m, 2H), 1.04 (t, 3H, \(J\) = 7.4 Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 179.9, 162.8, 85.1, 54.4, 33.2, 18.9, 13.9.; HRMS (EI): m/z calcd for C\(_7\)H\(_{11}\)NO\(_5\)S 221.0358, found 221.0365.

**Methyl 4-phenethyl-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6s**

yield: 45% (0.63 g as a ivory solid), mp = 83-87.1 °C, \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.20-7.37 (m, 5H), 5.54 (s, 1H), 3.86 (s, 3H), 3.05-3.13 (m, 4H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 179.6, 162.4, 138.7, 129.0, 128.4, 127.0, 85.2, 54.3, 33.1, 31.3.; HRMS (EI): m/z calcd for C\(_{12}\)H\(_{13}\)NO\(_5\)S 283.0514, found 283.0516.

**Methyl 4-cyclohexyl-5H-1,2,3-oxathiazole-5-carboxylate 2,2-dioxide, 6t**

yield: 79.4% (2.26g as a pale yellow oil); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 5.64 (s, 1H), 3.86 (s, 3H), 2.69-2.70 (m, 1H), 1.37-2.06 (m, 10H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 183.0, 162.9, 83.9, 54.2, 40.0, 30.8, 29.1, 25.7, 25.3, 24.9.; HRMS (EI): m/z calcd for C\(_{10}\)H\(_{15}\)NO\(_5\)S 261.0671, found 261.0683.

4. General procedure for the ATH-DKR reaction of 4,5-disubstituted cyclic imine 6 to 7
To the solution of 6a (255 mg, 1.0 mmol) in EtOA (10 mL) was added added (R,R)-Cp*RhCl(TsDPEN) (1a) catalyst (3.2 mg, 0.5 mol%), and then added slowly an azeotroic mixture of HCO$_2$H/Et$_3$N (molar ratio = 5:2, 1.0 mL) via a syringe. The reaction mixture was stirred for 0.5 h at room temperature and diluted with EtOAc. The reaction mixture was washed with water and brine. The organic layer was dried over anhydrous MgSO$_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane/EtOAc, 2:1) to give a white solid (234 mg, 91.6%).

**Methyl (4S,5S)-4-phenyl-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7a**

yield: 91.6% (234 mg as a white solid), mp = 101.9-104.7 °C, 97% ee: Chiralpak IB, 20% ethanol/n-hexane, 1.0 ml/min, 215 nm $t_R$(major) = 10.7 min, $t_R$(minor) = 12.5 min; [$\alpha$]$_D^{30}$ = +102.9 (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.41-7.42 (m, 3H), 7.29-7.32 (m, 2H), 5.39 (d, 1H, $J$ = 6.8 Hz), 5.28 (m, 1H), 5.07 (brs, 1H), 3.40 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.7, 132.0, 129.8, 129.9, 129.1, 126.6, 81.8, 61.4, 52.7.; HRMS (EI): m/z calcd for C$_{10}$H$_{11}$NO$_5$S 257.0358, found 257.0340.

**Methyl (4R,5R)-4-phenyl-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (R,R)-7a**

yield: 94% (24 mg as a white solid), mp = 103.2-105.4 °C, 98.1% ee: Chiralpak IB, 20% ethanol/n-hexane, 1.0 ml/min, 215 nm $t_R$(major) = 9.9 min, $t_R$(minor) = 13.7 min; [$\alpha$]$_D^{30}$ = -101.7 (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.41-7.42 (m, 3H), 7.30-7.31 (m, 2H), 5.38 (d, 1H, $J$ = 6.8 Hz), 5.28 (d, 1H, $J$ = 6.8 Hz), 5.02 (brs, 1H), 3.40 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.6, 131.9, 129.9, 129.2, 126.5, 81.6, 61.4, 52.7.; HRMS (EI): m/z calcd for C$_{10}$H$_{11}$NO$_5$S 257.0358, found 257.0343.
Isopropyl (4S,5S)-4-phenyl-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7b

yield: 85%; \([\alpha]_D^{23} = +76.8\) (c 0.3, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.39-7.34\) (m, 5H), 5.33 (m, 3H), 4.69 (s, 1H), 1.02 (s, 3H), 0.72 (s, 3H); \(^{13}\)C NMR (500 MHz, CDCl\(_3\)) \(\delta 164.8, 132.2, 129.7, 129.1, 126.9, 81.6, 70.8, 61.5, 21.4, 20.8\); HRMS (EI): m/z calcd for C\(_{12}\)H\(_{15}\)NO\(_3\)S 285.0671, found 285.0664.

Benzyl (4S,5S)-4-phenyl-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7c

yield: 87%; \([\alpha]_D^{21} = +71.5\) (c 0.3, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.39-7.29\) (m, 8H), 7.04 (d, 2H, \(J = 6.8\)), 5.44 (d, 1H, \(J = 6.7\)), 5.33 (d, 1H, \(J = 6.9\)), 4.93 (d, 1H, \(J = 12.0\)), 4.68 (d, 1H, \(J = 12.0\)); \(^{13}\)C NMR (500 MHz, CDCl\(_3\)) \(\delta 165.2, 133.7, 131.9, 129.8, 129.2, 128.8, 128.7, 128.6, 126.7, 81.8, 68.1, 61.5\); HRMS (EI): m/z calcd for C\(_{16}\)H\(_{15}\)NO\(_3\)S 333.0671, found 333.0662.

t-Butyl (4S,5S)-4-phenyl-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7d

yield: 87%; 99.9% ee (Chiralpak AD-H, 5% isopropanol/hexanes, 1.0 mL/min, 215 nm, \(t_r\)(minor) = 32.27 min, \(t_r\)(major) = 36.25 min); \([\alpha]_D^{20} = +89.3\) (c 0.3, CHCl\(_3\)); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.41-7.33\) (m, 5H), 5.27 (m, 3H), 1.08 (s, 9H); \(^{13}\)C NMR (500 MHz, CDCl\(_3\)) \(\delta 164.0, 132.6, 129.6, 129.1, 127.0, 84.5, 81.7, 61.5, 27.4\); HRMS (EI): m/z calcd for C\(_{13}\)H\(_{17}\)NO\(_3\)S 299.0827, found 299.0838.

Methyl (4S,5S)-4-(o-tolyl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7e

yield: 95.1% (25.7 mg as a white solid), mp = 119.8-120.4 °C, 92.1% ee: Chiralpak AD-H, 20% isopropanol/hexane, 1.0 mL/min, 215 nm \(t_r\)(major) = 8.4 min, \(t_r\)(minor) = 10.1 min; \([\alpha]_D^{30} = +91.3\) (c 0.15, MeOH); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.22-7.29\) (m, 3H), 7.18 (d, 1H, \(J = 7.6\) Hz), 5.52 (d, 1H, \(J = 7.0\) Hz), 5.36 (d, 1H, \(J = 7.0\) Hz), 3.31 (s, 3H), 2.41 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta 165.7, 136.1, 131.2, 129.7, 129.6, 126.8, 124.2, 80.6, 57.8, 52.5, 19.4\); HRMS (EI): m/z calcd for C\(_{11}\)H\(_{13}\)NO\(_3\)S 271.0514, found 271.0510.
Methyl (4S,5S)-4-(m-tolyl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7f

yield: 99.3% (31.4 mg as a white solid), mp = 97.1-99.4 °C, 98.7%
eee: Chiralpak AD-H, 10% isopropanol/n-hexane, 1.3 ml/min, 215 nm \( t_R(\text{major}) = 15.9 \text{ min}, t_R(\text{minor}) = 17.0 \text{ min}; [\alpha]_D^{20} = +54.2 \text{ (c 0.3, CHCl}_3) \); \(^1\text{H NMR} (500 \text{ MHz, CDCl}_3) \delta 7.29-7.33 (m, 1H), 7.23 (d, 1H, J = 7.6 Hz), 7.10-7.13 (m, 2H), 5.38 (d, 1H, J = 6.7 Hz), 5.28 (d, 1H, J = 6.5 Hz), 5.19 (brs, 1H), 3.44 (s, 3H), 2.39 (s, 3H); \(^13\text{C NMR} (75 \text{ MHz, CDCl}_3) \delta 165.9, 139.3, 131.8, 130.7, 129.2, 127.2, 123.6, 81.9, 61.5, 52.7, 21.5.; HRMS (EI): m/z calcd for C\(_{11}\)H\(_{13}\)NO\(_5\)S 271.0514, found 271.0507.

Methyl (4S,5S)-4-(p-tolyl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7g

yield: 98.6% (50.8 mg as a white solid), mp = 103.8-105.8 °C, 99.2%
eee: Chiralpak AD-H, 20% isopropanol/n-hexane, 1.0 ml/min, 215 nm \( t_R(\text{major}) = 10.1 \text{ min}, t_R(\text{minor}) = 12.4 \text{ min}; [\alpha]_D^{30} = +93.0 \text{ (c 0.3, CHCl}_3) \); \(^1\text{H NMR} (500 \text{ MHz, CDCl}_3) \delta 7.18-7.22 (m, 4H), 5.35 (d, 1H, J = 6.8 Hz), 5.25 (d, 1H, J = 6.9 Hz), 5.20 (brs, 1H), 3.42 (s, 3H), 2.36 (s, 3H); \(^13\text{C NMR} (75 \text{ MHz, CDCl}_3) \delta 165.8, 140.1, 130.0, 128.9, 126.5, 81.9, 61.4, 52.8, 21.3.; HRMS (EI): m/z calcd for C\(_{11}\)H\(_{13}\)NO\(_5\)S 271.0514, found 271.0515.

Methyl (4S,5S)-4-(3-chloro-phenyl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7h

yield: 99.6% (36.1 mg as a white solid), mp = 79.6-80.8 °C, 96.7%
eee: Chiralpak AD-H, 10% isopropanol/n-hexane, 1.2 ml/min, 215 nm \( t_R(\text{minor}) = 13.8 \text{ min}, t_R(\text{major}) = 15.0 \text{ min}; [\alpha]_D^{29} = +69.4 \text{ (c 0.3, CHCl}_3) \); \(^1\text{H NMR} (500 \text{ MHz, CDCl}_3) \delta 7.33-7.40 (m, 3H), 7.24-7.25 (m, 1H), 5.39 (d, 1H, J = 6.8 Hz), 5.25-5.26 (m, 2H), 3.47 (s, 3H); \(^13\text{C NMR} (75 \text{ MHz, CDCl}_3) \delta 165.4, 135.3, 134.4, 130.6, 130.2, 127.2, 124.9, 81.4, 60.9, 53.0.; HRMS (EI): m/z calcd for C\(_{10}\)H\(_{10}\)ClNO\(_5\)S 290.9968, found 290.9957.

Methyl (4S,5S)-4-(4-chloro-phenyl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7i
yield: 92.1% (28.3 mg as a white solid), mp = 123.2-125.8 ºC, 97.3% ee: Chiralpak AD-H, 20% isopropanol/n-hexane, 1.5 ml/min, 215 nm

$\tau_R$(minor) = 9.3 min, $\tau_R$(major) = 14.1 min; $[\alpha]_D^{29} = +69.9$ (c 0.3, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40 (d, 2H, $J = 8.5$ Hz), 7.28 (d, 2H, $J = 8.5$ Hz), 5.39 (d, 1H, $J = 6.8$ Hz), 5.25 (t, 1H, $J = 8.0$ Hz), 5.14 (d, 1H, $J = 7.5$ Hz), 3.46 (s, 3H), 3.45 (s, 3H);

$^1$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.4, 136.2, 130.9, 129.6, 128.2, 81.3, 61.0, 53.0.; HRMS (EI): m/z calcd for C$_{10}$H$_{10}$ClNO$_3$S 290.9968, found 290.9943.

**Methyl (45,5S)-4-(4-methoxy-phenyl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7j**

yield: 99.2% (28.5 mg as a white solid), mp = 120.8-123.7 ºC, 100% ee: Chiralpak AD-H, 20% isopropanol/n-hexane, 1.0 ml/min, 215 nm $\tau_R$(major) = 14.0 min, racemic: $\tau_R$(minor) = 18.7 min; $[\alpha]_D^{30} = +91.6$ (c 0.3, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.23 (d, 2H, $J = 8.1$ Hz), 7.13 (m, 2H), 5.38 (d, 1H, $J = 8.5$ Hz), 5.22 (d, 1H, $J = 6.8$ Hz), 3.81 (s, 3H), 3.45 (s, 3H); $^1$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.4, 160.8, 153.0, 130.9, 128.1, 123.9, 114.7, 81.8, 61.2, 55.5, 52.9.; HRMS (EI): m/z calcd for C$_{11}$H$_{13}$NO$_5$S 287.0464, found 287.0466.

**Methyl (45,5S)-4-(4-fluoro-phenyl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7k**

yield: 96.1% (45 mg as a white solid), mp = 142.5-146.4 ºC, 97.3% ee: Chiralpak IA, 20% ethanol/n-hexane, 1.0 ml/min, 215 nm $\tau_R$(minor) = 12.5 min, $\tau_R$(major) = 16.2 min; $[\alpha]_D^{29} = +78.3$ (c 0.3, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32-7.35 (m, 2H), 7.10-7.13 (m, 2H), 5.38 (d, 1H, $J = 6.7$ Hz), 5.22-5.28 (m, 2H), 3.45 (s, 3H); $^1$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.6, 163.5 (d, $J_{CF} = 248.8$ Hz), 128.9 (d, $J_{CF} = 8.5$ Hz), 128.4, 116.5 (d, $J_{CF} = 22.1$ Hz), 81.6, 61.0, 53.0.; HRMS (EI): m/z calcd for C$_{10}$H$_{10}$FNO$_5$S 275.0264, found 275.0234.
Methyl (4S,5S)-4-(4-trifluoromethyl-phenyl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7l

yield: 87.5% (28 mg as a white solid), mp = 146.2-150.6 °C, 98.5% ee: Chiralpak IA, 20% ethanol/n-hexane, 1.5 ml/min, 215 nm 
$t_R$(minor) = 6.5 min, $t_R$(major) = 10.83 min; $[\alpha]_D^{20} = +33.6$ (c 0.5, CHCl₃); $^1$H NMR (500 MHz, CDCl₃) δ 7.68 (d, 2H, $J = 7.9$ Hz), 7.50 (d, 2H, $J = 7.9$ Hz), 5.45 (d, 1H, $J = 6.9$ Hz), 5.36 (d, 1H, $J = 6.8$ Hz), 3.42 (s, 3H); $^{13}$C NMR (125 MHz, CDCl₃) δ 165.2, 136.4, 132.0, 113.8, 127.3, 126.1, 123.5 (q, $J_{CF} = 270.5$ Hz), 81.1, 60.9, 52.8.; HRMS (EI): m/z calcd for C₁₁H₁₀F₃NO₅S 325.0232, found 325.0232.

Methyl (4S,5S)-4-(4-cyano-phenyl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7m

yield: 95% (26.5 mg as a white solid), mp = 162.7-167 °C, 96.3% ee: Chiralpak IA, 30% ethanol/n-hexane, 1.3 ml/min, 215 nm 
$t_R$(minor) = 9.2 min, $t_R$(major) = 13.8 min; $[\alpha]_D^{20} = +22.7$ (c 0.5, MeOH); $^1$H NMR (500 MHz, acetone-d₆) δ 7.90 (d, 2H, $J = 7.5$ Hz), 7.78 (d, 2H, $J = 7.6$ Hz), 5.80 (d, 1H, $J = 7.2$ Hz), 5.71 (d, 1H, $J = 7.2$ Hz), 3.45 (s, 3H), 2.92 (brs, 1H); $^{13}$C NMR (125 MHz, acetone-d₆) δ 165.8, 141.0, 133.3, 129.5, 119.0, 113.8, 81.9, 61.5, 52.8.; HRMS (EI): m/z calcd for C₁₁H₁₀N₂O₅S 282.0310, found 282.0304.

Methyl (4S,5S)-4-(4-methoxycarbonyl-phenyl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7n

yield: 92% (29 mg as a white solid), mp = 145.6-147.1 °C, 96.7% ee: Chiralpak IA, 20% ethanol/n-hexane, 1.5 ml/min, 215 nm 
$t_R$(minor) = 12.0 min, $t_R$(major) = 14.0 min; $[\alpha]_D^{20} = +57.4$ (c 0.6, CHCl₃); $^1$H NMR (500 MHz, CDCl₃) δ 8.08 (d, 2H, $J = 7.9$ Hz), 7.44 (d, 2H, $J = 7.9$ Hz), 5.51-5.61 (brs, 1H), 5.45 (d, 1H, $J = 6.8$ Hz), 5.37 (d, 1H, $J = 6.9$ Hz), 3.94 (s, 3H), 3.41 (s, 3H); $^{13}$C NMR (125 MHz, CDCl₃) δ 166.2, 165.3, 137.1, 131.5, 130.3, 126.8, 81.2, 61.0, 52.8, 52.4.; HRMS (EI): m/z calcd for C₁₂H₁₃NO₇S 315.0413, found 315.0411.
Methyl (4S,5S)-4-(naphthalen-2-yl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7o

yield: 90.8% (27 mg as a white solid), mp = 134.9-137.4 °C, 96.7% ee: Chiralpak AD-H, 20% isopropanol /n-hexane, 1.0 ml/min, 215 nm τ_H(major) = 11.5 min, τ_H(minor) = 13.7 min; [α]D20 = +94.1 (c 0.4, CHCl3); 1H NMR (500 MHz, CDCl3) δ 7.80-7.90 (m, 4H), 7.53-7.56 (m, 2H), 7.37 (d, 1H, J = 8.6 Hz), 5.46 (s, 2H), 3.29 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 165.7, 133.5, 132.9, 129.2, 128.2, 127.8, 127.3, 127.1, 126.4, 123.3, 81.7, 61.6, 52.7.; HRMS (EI): m/z calcd for C14H13NO5S 307.0514, found 307.0513.

Methyl (4S,5S)-4-(furan-2-yl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7p

yield: 91.6% (22 mg as a white solid), mp = 97.9-110.2 °C, 94.9% ee: Chiralpak IA, 30% ethanol /n-hexane, 1.3 ml/min, 215 nm τ_H(major) = 8.7 min, τ_H(minor) = 14.3 min; [α]D28 = +95.8 (c 0.3, CDCl3); 1H NMR (500 MHz, CDCl3) δ 7.44 (s, 1H), 6.43-6.53 (m, 2H), 5.29-5.32 (m, 1H), 5.22-5.23 (m, 1H), 5.16-5.18 (m, 1H), 3.65 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 166.1, 144.3, 143.8, 111.5, 111.4, 80.8, 55.8, 53.5.; HRMS (EI): m/z calcd for C8H9NO5S 247.0151, found 247.0155.

Methyl (4S,5S)-4-(thiophen-2-yl)-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7q

yield: 93.8% (38.3 mg as a white solid), mp = 96-97 °C, 98.7% ee: Chiralpak IA, 20% ethanol /n-hexane, 1.5 ml/min, 215 nm τ_H(minor) = 12.5 min, τ_H(major) = 14.2 min; [α]D29 = +70.6 (c 0.3, CDCl3); 1H NMR (500 MHz, CDCl3) δ 7.37-7.38 (m, 1H), 7.14 (s, 1H), 7.04-7.05 (m, 1H), 5.49 (d, 1H, J = 5.9 Hz), 5.35 (d, 1H, J = 6.5 Hz), 5.13 (s, 1H), 3.59 (s, 3H); 13C NMR (125 MHz, CDCl3) δ 165.5, 133.5, 127.6, 127.4, 127.2, 81.7, 57.7, 53.0.; HRMS (EI): m/z calcd for C8H9NO5S2 262.9922, found 262.9918.

Methyl (4S,5S)-4-propyl-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7r
yield: 69% (98.5 mg as a colourless oil); \([\alpha]_D^{29} = +52.5\) (c 0.3, CHCl$_3$); \(^1\)H NMR (500 MHz, CDCl$_3$) \(\delta\) 5.06 (d, 1H, \(J = 5.3\) Hz), 4.48 (brs, 1H), 4.13 (brs, 1H), 3.86 (s, 3H), 1.48-1.61 (m, 4H), 0.97 (t, 3H, \(J = 6.9\) Hz); \(^{13}\)C NMR (75 MHz, CDCl$_3$) \(\delta\) 167.1, 82.3, 58.5, 53.2, 30.8, 19.8, 13.7; HRMS (EI): m/z calcd for C$_7$H$_{13}$NO$_5$S 223.0514, found 223.0537.

**Methyl (4S,5S)-4-phenethyl-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7s**

yield: 53.5% (14 mg as a ivory solid), mp = 90.6-92.3 °C, 76.1% ee:

Chiralpak IA, 20% ethanol / n-hexane, 1.5 ml/min, 215 nm \(t_R\) (minor) = 6.0 min, \(t_R\) (major) = 8.0 min; \([\alpha]_D^{20} = +41.3\) (c 0.3, CHCl$_3$); \(^1\)H NMR (500 MHz, CDCl$_3$) \(\delta\) 7.33-7.36 (m, 2H), 7.26-7.29 (m, 1H), 7.20 (d, 2H, \(J = 7.4\) Hz), 5.08 (d, 1H, \(J = 6.1\) Hz), 4.66 (d, 1H, \(J = 2.2\) Hz), 4.12-4.14 (m, 1H), 3.88 (s, 3H), 2.86-2.90 (m, 1H), 2.75-2.81 (m, 1H), 1.89-1.97 (m, 1H), \(^{13}\)C NMR (125 MHz, CDCl$_3$) \(\delta\) 166.9, 139.2, 128.9, 128.4, 126.8, 82.0, 57.7, 53.2, 32.3, 30.5; HRMS (EI): m/z calcd for C$_{12}$H$_{15}$NO$_5$S 285.0671, found 285.0666.

**Methyl (4S,5S)-4-cyclohexyl-1,2,3-oxathiazolidine-5-carboxylate 2,2-dioxide, (S,S)-7t**

yield: 66.7% (179 mg as a colourless oil); \([\alpha]_D^{30} = +41.4\) (c 0.68, CHCl$_3$); \(^1\)H NMR (300 MHz, CDCl$_3$) \(\delta\) 5.09 (d, 1H, \(J = 5.8\) Hz), 4.60 (bs, 1H), 3.87 (s, 3H), 3.84 (m, 1H), 1.02-1.88 (m, 11H); \(^{13}\)C NMR (75 MHz, CDCl$_3$) \(\delta\) 167.4, 82.5, 63.9, 53.1, 37.8, 30.7, 29.3, 25.7, 25.2, 25.1; HRMS (EI): m/z calcd for C$_{10}$H$_{17}$NO$_5$S 263.0827, found 263.0848.

5. Assignment of absolute stereochemistry of 7a via converting to the known 8a

In order to determine the absolute stereochemistry of the ATH-DKR product, 7a was converted to the known 2-azido-3-(Boc-amino)-3-phenyl propionic acid methyl ester 8a and it was compared with the stereochemically defined 8a which was derived from Sharpless asymmetric amino hydroxylation reaction.\(^{10}\) The spectroscopic data and specific rotation data of synthetic 8a were full agreement with those of the known ((2R,3S)-8a) in the

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literature. Additionally, the absolute stereochemistry of 7j was unambiguously assigned by using single-crystal X-ray crystallographic analysis (deposited, CCDC-1007235).

Scheme S1.

![Reaction scheme](image)

Reaction conditions: (a) (Boc)$_2$O, Et$_3$N, cat. DMAP, CH$_2$Cl$_2$, 100%; (b) i. NaN$_3$, DMF, 60 °C, 6 h; ii. 1N HCl, Et$_2$O, 12 h, rt, 92%.

5-1. Synthesis of (S,S)-N-Boc-7a

To a stirred mixture of (S,S)-7a (0.23 g, 0.92 mmol) and triethylamine (0.15 mL, 1.1 mmol) in dichloromethane (2.5 mL) was added successively di-tert-butyl dicarbonate (0.4 g, 1.83 mmol) and DMAP (catalytic amount). The reaction mixture was stirred at room temperature for 40 min. The reaction mixture was diluted with diethyl ether (20 mL) and washed successively with 1N HCl, saturated aqueous NaHCO$_3$ solution and brine. The organic layer was dried over anhydrous MgSO$_4$, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (Hexane/EtOAc=3:1) to give 0.33 g (99.7% yield) of (S,S)-N-Boc-7a.

yield: 99.7% (0.33 g as a white solid), mp=126.3-130.2 °C, 97.8% ee: Chiralpak AD-H, 10% isopropanol/n-hexane, 1.0 ml/min, 215 nm $t_R$ (minor) = 9.2 min, $t_R$ (major) = 13.4 min; $[\alpha]_D^{20} = -14.6$ (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.35-7.39 (m, 5H), 5.50 (d, 1H, $J = 6.35$ Hz), 5.45 (d, 1H, $J = 6.3$ Hz), 3.42 (s, 3H), 1.44 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 163.1, 147.8, 133.6, 129.8, 129.0, 127.5, 86.4, 62.9, 52.9, 28.0; HRMS (EI): m/z calcd for C$_{15}$H$_{19}$NO$_7$S 357.0882, found 357.0887.

5-2. 2-Azido-3-tert-butoxycarbonylamino-3-phenyl-propionic acid methyl ester, (2R,3S)-8a

yield: 99.7% (0.33 g as a white solid), mp=126.3-130.2 °C, 97.8% ee: Chiralpak AD-H, 10% isopropanol/n-hexane, 1.0 ml/min, 215 nm $t_R$ (minor) = 9.2 min, $t_R$ (major) = 13.4 min; $[\alpha]_D^{20} = -14.6$ (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.35-7.39 (m, 5H), 5.50 (d, 1H, $J = 6.35$ Hz), 5.45 (d, 1H, $J = 6.3$ Hz), 3.42 (s, 3H), 1.44 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 163.1, 147.8, 133.6, 129.8, 129.0, 127.5, 86.4, 62.9, 52.9, 28.0; HRMS (EI): m/z calcd for C$_{15}$H$_{19}$NO$_7$S 357.0882, found 357.0887.
NaN₃ (22.3 mg, 0.343 mol, 5.0 equiv) was added in a single portion to a solution of (S,S)-N-Boc-7a (24.5 mg, 68.6 mmol, 1.0 equiv) in DMF (2 mL) at 25 °C. The resulting mixture was warmed to 60 °C and stirred for 6 h. Upon completion, the reaction mixture was cooled to rt and the contents were diluted with Et₂O (3 mL), treated with 1N aqueous HCl (3 mL), and allowed to stir for an additional 12 h at 25 °C. Once this operation was complete, the reaction mixture was poured into saturated NaHCO₃ solution and extracted with Et₂O. The combined organic layers were then washed with water, dried (MgSO₄), and concentrated. The resultant light yellow solid was purified by flash column chromatography (silica gel, EtOAc/hexanes, 5:1).

White solid, yield: 92%; mp 133-134°C; [α]D²⁰ = +17.06 (c 0.8, CHCl₃);

$\text{H NMR (300 MHz, CDCl}_3\text{) } \delta$ 7.37 - 7.30 (m, 5H), 5.33 (brs, 2H), 4.38 (brs, 1H), 3.82 (s, 3H), 1.42 (s, 9H);

$\text{C NMR (500 MHz, CDCl}_3\text{) } \delta$ 168.8, 155.0, 138.4, 128.9, 128.3, 126.7, 80.4, 66.9, 55.3, 53.2, 28.4.

The spectroscopic and specific rotation data of synthetic 8a were full agreement with those of the known ((2R,3S)-8a) in the literature.¹¹

Lit.¹¹ mp 133–134°C; [α]D²⁰ = +16.5° (c 1, CHCl₃); $\text{H NMR (CDCl}_3\text{, 300 MHz) } \delta$ 7.25–7.50 (m, 5H), 5.34 (br s, 2H), 4.38 (br s, 1H), 3.81 (s, 3H), 1.42 (s, 9H); $\text{C NMR (CDCl}_3\text{, 75 MHz) } \delta$ 168.62, 154.78, 138.27, 128.71, 128.09, 126.51, 80.21, 66.71, 55.18, 52.95, 28.19.

6. Evaluation of ee’s of 7r and 7t by conversion to ring-opened derivatives

Because of difficulties in chiral separation of 7r and 7t themselves in various chiral columns and conditions, 7r and 7t were converted to the corresponding ring opened derivatives 8r and 8t and ee values were indirectly determined with these compounds.

Scheme S2.

Reaction conditions: (a) (Boc)$_2$O, Et$_3$N, cat. DMAP, CH$_2$Cl$_2$; (b) i. PhCO$_2$NH$_4$, DMF, 55 °C, 12 h; ii. 1N HCl, CH$_2$Cl$_2$, 6 h, rt.

6-1. Synthesis of N-Boc-7r and N-Boc-7t

6-1-1. N-Boc-7t

To a stirred mixture of (S,S)-7t (16.4 mg, 0.062 mmol) and triethylamine (0.01mL, 0.072 mmol) in dichloromethane (1 mL) at 0 °C was added successively di-tert-butyl dicarbonate (27.2 mg, 0.125 mmol) and DMAP (catalytic amount). The reaction mixture was stirred at room temperature for 2 h, diluted with CH$_2$Cl$_2$ (5 mL) and washed successively with 1 N HCl, saturated NaHCO$_3$ solution and brine. The organic layer was dried over anhydrous MgSO$_4$, and evaporated. The residue was purified by column chromatography (Hexane/EtOAc=10:1) to give 20 mg (87% yield) of (S,S)-N-Boc-7t.

Yield: 87% (20 mg); [α]$_D^{30}$ = -15.01 (c 0.92, CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$) δ 5.30 (d, $J$ = 4.7 Hz, 1H), 4.56 (m, 1H), 3.89 (s, 3H), 1.66-1.83 (m, 6H), 1.56 (s, 9H), 1.08-1.26 (m, 5H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 164.1, 149.1, 85.9, 77.2, 63.8, 53.2, 40.1, 30.7, 27.8, 27.0, 26.3, 25.9, 25.6.; HRMS (EI): m/z calcd for C$_{15}$H$_{25}$NO$_7$S 363.1352, found 363.1364.

6-1-2. N-Boc-7r

Yield: 97% (270 mg); [α]$_D^{29}$ = -26.77 (c 1.48, CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$) δ 5.28 (d, $J$ = 5.4 Hz, 1H), 4.61-4.67 (m, 1H), 3.89 (s, 3H), 1.62-1.77 (m, 2H), 1.55 (s, 9H), 1.35-1.43 (m, 2H), 0.90-0.95 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 163.9, 148.4, 86.0, 77.0, 59.2, 53.3, 31.9, 27.9, 18.1, 13.9.; HRMS (EI): m/z calcd for C$_{12}$H$_{21}$NO$_7$S 323.1039, found 323.1014.

6-2. Synthesis of 8r and 8t
6-2-1. (2R,3S)-8t
Ammonium benzoate (65.24 mg, 0.47 mmol) was added to a solution of (4S,5S)-N-Boc-7t (85.2 mg, 0.23 mmol) in dry DMF (10 mL). The solution was heated to 60 °C under inert atmosphere (N₂) and stirred for 14 h at that temperature. The solvent was evaporated under reduced pressure and the residue was re-dissolved in dichloromethane (10 mL) and 1N HCl (10 mL) was added. The reaction mixture was stirred at room temperature for 6 h before the pH was adjusted to 8 with saturated aqueous NaHCO₃ solution. The layers were separated and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were washed with water and brine, dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica-gel (Hexane/EtOAc, 4:1) to give 66 mg of 8t.

yield: 70.8% (66 mg); 47% ee, dr = 31:1.; Chiralpak IC, 10% isopropanol/n-hexane, 0.7 ml/min, 254 nm \( t_R \) (minor) = 8.35 min, \( t_R \) (major) = 9.55 min; \([\alpha]_D^{20} = -35.44 \) (c 0.35, CHCl₃); \(^1\)H NMR (300 MHz, CDCl₃) \( \delta \) 8.07 (d, \( J = 7.3 \) Hz, 2H), 7.61 (m, 1H), 7.48 (m, 2H), 5.44 (d, \( J = 2.25 \) Hz, 1H), 4.78 (d, \( J = 10.5 \) Hz, 1H), 4.09 (m, 1H), 3.75 (s, 3H), 1.61-1.92 (m, 6H), 1.43 (s, 9H), 1.06-1.15 (m, 5H); \(^13\)C NMR (125 MHz, CDCl₃) \( \delta \) 169.2, 165.7, 155.5, 133.6, 129.9, 129.2, 128.5, 79.6, 72.4, 56.0, 52.5, 39.8, 29.7, 29.6, 28.3, 26.0, 25.9.; HRMS (EI): m/z calcd for C₂₂H₃₁NO₆ 405.2151, found 405.2158.

6-2-2. (2R,3S)-8r

yield: 72.3% (220 mg); 91% ee, dr = 100:0.; Chiralpak IC, 10% isopropanol/n-hexane, 0.7 ml/min, 254 nm \( t_R \) (minor) = 9.27 min, \( t_R \) (major) = 11.15 min; \([\alpha]_D^{29} = -70.5 \) (c 0.99, CHCl₃); \(^1\)H NMR (300 MHz, CDCl₃) \( \delta \) 8.07 (d, \( J = 8.4 \) Hz, 2H), 7.61 (m, 1H), 7.47 (m, 2H), 5.27 (d, \( J = 2.3 \) Hz, 1H), 4.77(d, \( J = 9.9 \) Hz, 1H), 4.32 (m, 1H), 3.77 (s, 3H), 1.53-1.62 (m, 2H), 1.46 (s, 9H), 1.36-1.48 (m, 2H), 0.93-0.97 (t, \( J = 7.3 \) Hz, 3H); \(^13\)C NMR (125 MHz, CDCl₃) \( \delta \) 168.8, 165.7, 155.3, 133.6, 129.9, 129.1, 128.5, 79.7, 74.2, 52.5, 51.1, 34.4, 28.3, 19.2, 13.7.; HRMS (EI): m/z calcd for C₁₀H₂₇NO₆ 365.1838, found 365.1856.

7. Synthesis of Taxotere side chain, (2R,3S)-10

Scheme S3.
7-1. Synthesis of (4S,5S)-N-Boc-7a
To a stirred mixture of (S,S)-7a (0.23 g, 0.92 mmol) and triethylamine (0.15 mL, 1.1 mmol) in dichloromethane (2.5 mL) was added successively di-tert-butyl dicarbonate (0.4 g, 1.83 mmol) and DMAP (cat) and the mixture was stirred at room temperature for 40 min. It was then diluted with diethyl ether (20 mL) and washed successively with 1 N HCl, NaHCO₃ and brine. The organic layer was dried over anhydrous MgSO₄, and evaporated under reduced pressure. The residue was purified by column chromatography on silicagel (Hexane/EtOAc = 3:1) to give 0.33 g (99.7% yield) of (4S,5S)-N-Boc-7a.

yield: 99.7% (0.33 g as a white solid), mp=126.3-130.2 °C, 97.8% ee: Chiralpak AD-H, 10% isopropanol/n-hexane, 1.0 ml/min, 215 nm 
\[ t_R(\text{minor}) = 9.2 \text{ min}, \ t_R(\text{major}) = 13.4 \text{ min}; \ [\alpha]_D^{20} = -14.6 \text{ (c 1.0, CHCl}_3); \]
\[ ^1\text{H NMR (500 MHz, CDCl}_3) \ \delta 7.35-7.39 (m, 5H), 5.50 (d, 1H, J = 6.35 Hz), 5.45 (d, 1H, J = 6.3 Hz), 3.42 (s, 3H), 1.44 (s, 9H); \]
\[ ^{13}\text{C NMR (75 MHz, CDCl}_3) \ \delta 163.1, 147.8, 133.6, 129.8, 129.0, 127.5, 86.4, 62.9, 52.9, 28.0.; \]
HRMS (EI): m/z calcd for C₁₅H₁₉NO₇S 357.0882, found 357.0887.

7-2. Synthesis of (4R,5R)-N-Boc-7a
yield: 94.2% (109 mg as a white solid), mp=127.2-129.4 °C, 98.1% ee: Chiralpak AD-H, 10% isopropanol/n-hexane, 1.0 ml/min, 215 nm 
\[ t_R(\text{major}) = 9.3 \text{ min}, \ t_R(\text{minor}) = 13.8 \text{ min}; \ [\alpha]_D^{20} = +12.3 \text{ (c 1.0, CHCl}_3); \]
\[ ^1\text{H NMR (500 MHz, CDCl}_3) \ \delta 7.35-7.38 (m, 5H), 5.49 (d, 1H, J = 6.35 Hz), 5.44 (d, 1H, J = 6.3 Hz), 3.42 (s, 3H), 1.43 (s, 9H); \]
\[ ^{13}\text{C NMR (125 MHz, CDCl}_3) \ \delta 163.0, 147.7, 133.4, 129.6, 128.8, 127.3, 86.2, 62.8, 52.8, 27.8. \]

7-3. Synthesis of (2R,3S)-8a
Ammonium benzoate (0.16 g, 1.17 mmol) was added to a solution of (4S,5S)-N-Boc-7a (0.21 g, 0.58 mmol) in dry DMF (2 mL). The solution was heated to 60 °C and stirred for 12 h at that temperature. The solvent was evaporated under reduced pressure and the residue was redissolved in dichloromethane (3 mL) and 1N HCl (3 mL) was added. The reaction mixture was stirred at room temperature for 6 h before the pH was adjusted to 8 with saturated aqueous NaHCO₃ solution. The layers were separated and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were washed with water and brine, dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica-gel (Hexane/EtOAc, 3:1) to give (2R,3S)-8a (0.23 g, 82.1% yield).

yield: 82.1% (0.23 g as a colorless oil), [α]D²² = +11.49 (c 1.0, CHCl₃), (lit.¹² [α]D²¹ = -9.1 (c 0.86, CHCl₃)). ¹H NMR (500 MHz, CDCl₃) δ 7.96-7.98 (m, 2H), 7.55-7.58 (m, 1H), 7.41-7.45 (m, 2H), 7.31-7.37 (m, 4H), 7.25-7.27 (m, 1H), 5.49 (s, 2H), 3.76 (s, 3H), 1.42 (s, 9H), 1.23-1.29 (brs, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 168.3, 165.5, 155.0, 138.0, 133.6, 130.0, 129.9, 129.8, 128.9, 128.7, 128.5, 128.0, 127.2, 126.5, 80.3, 75.3, 54.9, 52.7, 31.6, 28.3, 22.7, 14.1.; HRMS (EI): m/z calcd for C₂₂H₂₅NO₆ 399.1682, found 399.1690.

7-4. Synthesis of (2R,3S)-9a
KCN (14 mg, 0.22 mmol) was added to a stirred solution of (2R,3S)-8a (0.17 g, 0.44 mmol) in MeOH (2 mL). The resulting mixture was stirred at 65 °C for 2 h. After removal of the solvent, the residue was dissolved in CH₂Cl₂ and then washed with brine. The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica-gel (Hexane/EtOAc, 3:1) to give (2R,3S)-9a (0.11 g, 84.5% yield). yield: 84.5% (0.11 g as a white solid), mp=113.2-116.2 °C, [α]D²³ = -5.49 (c 1.0, CHCl₃), (lit.¹³ [α]D²³ = -6.7 (c 0.85, CHCl₃)). ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.39 (m, 4H), 7.30-7.33 (m, 1H), 5.41 (d, 1H, J = 8.6 Hz),

5.24 (d, 1H, J = 9.2 Hz), 4.50 (s, 1H), 3.87 (s, 3H), 3.15 (d, 1H, J = 3.7 Hz), 1.45 (s, 9H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta \) 173.4, 155.1, 139.1, 128.6, 127.8, 126.7, 80.0, 73.5, 56.1, 28.3; HRMS (ESI): m/z calcd for C\(_{14}\)H\(_{21}\)NO\(_3\)Na 318.1317, found 318.1313.

7-5. Synthesis of (2\(R\),3\(S\))-10, Toxotere side chain

To a solution of compound (2\(R\),3\(S\))-9\(a\) (100 mg, 0.34 mmol) in methanol (2 mL) and THF (2 mL) was added 1N NaOH (1 mL). After being stirred at room temperature for 0.5 h, the solution was concentrated and H\(_2\)O (10 mL) was added. The aqueous solution was extracted with dichloromethane (3x10 mL). The remaining aqueous layer was acidified to pH 3~4 with 1N HCl and extracted with ethyl acetate (6x10 mL). The combined ethyl acetate fractions were dried over anhydrous MgSO\(_4\), filtered, and concentrated under reduced pressure. The resulting residue was washed with H\(_2\)O and collected via filtration affording (2\(R\),3\(S\))-10 (83.5 mg, 88%).

yield: 88% (83.5 mg as a white solid), mp = 122.5-123.9 °C; [\(\alpha\)]\(_D\)\(^{23}\) = +26.58 (c 1.0, MeOH), (lit.\(^{14}\) mp = 123.7-124.9 °C, [\(\alpha\)]\(_D\)\(^{25}\) = +24.9 (c 1.0, MeOH)); \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta \) 7.27-7.31 (m, 4H), 7.20-7.23 (m, 1H), 7.06 (d, 1H, J = 9.4 Hz), 4.91-4.94 (dd, 1H, J = 3.5, 9.4 Hz), 4.17 (d, 1H, J = 3.5 Hz), 1.34 (s, 9H), 1.21-1.22 (brs, 1H); \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta \) 173.9, 155.4, 141.3, 128.4, 127.3, 127.3, 78.6, 74.2, 57.3, 28.6; HRMS (ESI): m/z calcd for C\(_{14}\)H\(_{19}\)NO\(_3\)Na 304.1161, found 304.1159.

8. Synthesis of (-)-epi-Cytoxazole, (2\(R\),3\(S\))-12

Scheme S4.

---

8-1. Synthesis of (4S,5S)-N-Boc-7j

The (4S,5S)-N-Boc-7j was prepared by using the procedure for the synthesis of (4S,5S)-N-Boc-7a as depicted in 7-1.

\[
\text{yield: } 94.2\% (109 \text{ mg as a white oil}), [\alpha]_{D}^{22} = -17.4 (c \text{ 1.07, CHCl}_3);
\]

\[
\text{H NMR (500 MHz, CDCl}_3 \delta 7.32 (d, 2H, } J = 8.0 \text{ Hz), 6.88 (d, 2H, } J = 8.0 \text{ Hz), 5.48 (d, 1H, } J = 6.2 \text{ Hz), 5.41 (d, 1H, } J = 5.9 \text{ Hz), 3.79 (s, 3H, } J = 3H), 3.47 (s, 3H), 1.45 (s, 9H);} \]

\[
\text{C NMR (125 MHz, CDCl}_3 \delta 163.1, 160.4, 147.7, 128.8, 125.4, 114.2, 86.1, 62.4, 55.3, 52.8, 27.8; HRMS (EI): m/z calcd for C}_{16}H_{21}NO_8S 387.0988, \text{ found 387.0991.}
\]

8-2. Synthesis of (2R,3S)-8j

The (2R,3S)-8j was prepared by using the procedure for the synthesis of (2R,3S)-8a as depicted in 7-3.

\[
\text{yield: } 100\% (96.6 \text{ mg as a colorless oil}), [\alpha]_{D}^{20} = +20.4 (c \text{ 1.0, CHCl}_3); \]

\[
\text{H NMR (500 MHz, CDCl}_3 \delta 8.00 (d, 2H, } J = 7.6 \text{ Hz), 7.58 (t, 1H, } J = 7.5 \text{ Hz), 7.45 (t, 2H, } J = 7.6 \text{ Hz), 7.29 (d, 2H, } J = 8.0 \text{ Hz), 6.86 (d, 2H, } J = 8.2 \text{ Hz), 5.44-5.47 (m, 3H), 3.77 (s, 6H), 1.43 (s, 9H);}
\]

\[
\text{C NMR (125 MHz, CDCl}_3 \delta 159.2, 133.6, 129.9, 128.5, 127.7, 114.1, 55.3, 52.7, 28.3; HRMS (EI): m/z calcd for C}_{23}H_{27}NO_7 429.1788, \text{ found 429.1781.}
\]

8-3. Synthesis of (2R,3S)-9j

The (2R,3S)-9j was prepared by using the procedure for the synthesis of (2R,3S)-9a as depicted in 7-4.

\[
\text{yield: } 86.3\% (63 \text{ mg as a white solid), mp = 127.1-129.2 }^\circ\text{C, [\alpha]_{D}^{20} = +3.9 (c \text{ 0.5, CHCl}_3), (lit.}^{15} \text{ mp = 110-112 }^\circ\text{C, [\alpha]_{D}^{23} = -3.8 (c \text{ 0.5, CHCl}_3);}
\]

\[
\text{H NMR (500 MHz, CDCl}_3 \delta 7.29 (d, 2H, } J = 7.9 \text{ Hz), 6.88 (t, 1H, } J = 8.3 \text{ Hz), 5.35 (d, 1H, } J = 9.3 \text{ Hz), 5.15 (d, 1H, } J = 8.8 \text{ Hz), 4.43 (brs, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.20 (brs, 1H), 1.41 (s, 9H);}
\]

\footnote{15 For enantiomeric (2S,3R)-9j. Mishra, R. K.; Coates, C. M.; Revell, K. D.; Turos, E., \textit{Org. Lett.}, 2007, 9, 575.}
\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 173.4, 159.1, 155.1, 131.3, 127.9, 114.0, 79.9, 73.6, 55.6, 55.3, 53.0, 28.3.; HRMS (ESI): m/z calcd for C\(_{16}\)H\(_{23}\)NO\(_6\)Na 348.1423, found 348.1417.

8-4. Synthesis of (2R,3S)-11

The (2R,3S)-9j (63mg, 0.19 mmol) was dissolved in ethanol (2 mL) and cooled to 0 °C. To this was added dropwise NaBH\(_4\) (24 mg, 0.63 mmol) as a solution in ethanol (1 mL). After the addition was complete the ice bath was removed and the reaction mixture was stirred at room temperature for 4 h before the addition of a saturated aqueous NH\(_4\)Cl solution (5 mL). The ethanol was evaporated under reduced pressure. The remaining aqueous solution was extracted with ethyl acetate (3 x 5 mL) and the combined organic layers were washed with brine and dried over MgSO\(_4\). Solvents were removed under reduced pressure and the residue was purified by silicagel chromatography eluting with CH\(_2\)Cl\(_2\)/MeOH (20/1), affording (2R,3S)-11 as a white solid (51.7 mg, 91.7%).

yield: 91.7% (51.7 mg as a white solid), mp = 125.7-127.9 °C, \([\alpha]^{D}_{20} = +36.9\) (c 0.4, CHCl\(_3\)), (lit.\(^{16}\) \([\alpha]^{D}_{23} = -36.1\) (c 1.0, CHCl\(_3\)));

\(^1\)H NMR (500 MHz, CD\(_3\)OD) \(\delta\) 7.23 (d, 2H, \(J = 7.8\) Hz), 6.86 (d, 2H, \(J = 7.6\) Hz), 6.72 (brs, 1H), 4.62 (brs, 1H), 3.76 (s, 3H), 3.73 (brs, 1H), 3.43-3.46 (m, 1H), 3.35-3.39(m, 1H), 3.30 (s, 1H), 1.41 (s, 9H).

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 159.1, 156.9, 128.6, 127.9, 114.3, 114.2, 80.4, 75.3, 63.7, 55.3, 28.3.; HRMS (EI): m/z calcd for C\(_{15}\)H\(_{23}\)NO\(_5\) 297.1576, found 297.1556.

8-5. Synthesis of (2R,3S)-12, (-)-epi-Cytoxzone.

To a stirred solution of (2R,3S)-11 (41 mg, 0.14 mmol) in dry THF (2 mL) at 0 °C was added sodium hydride (20 mg, 60% w/w in mineral oil, 0.45 mmol) at room temperature, and the reaction mixture was refluxed for 1 h. The reaction mixture was cooled to room temperature and quenched with a saturated aqueous NH\(_4\)Cl (10 mL), then extracted with ethyl acetate (2x10 mL). The organic layer was washed with water and brine, dried over anhydrous MgSO\(_4\), and concentrated under reduced pressure. The residue was purified by column chromatography on silica-gel (Hexane/EtOAc = 2:1) to give (2R,3S)-12 as a white solid (29 mg, 95.1%).

yield: 95.1% (29 mg as a white solid), mp = 141-142 °C, [α]_D^{19} = -28.2
(c 0.5, MeOH), lit.\textsuperscript{17} [α]_D^{25} = -27.2 (c 1.1, MeOH), lit.\textsuperscript{18} [α]_D^{28} = -
22.8 (c 0.5, MeOH); \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}OD-d\textsubscript{4}) δ 7.36 (d, 2H, J = 8.2 Hz), 7.02 (d, 2H, J = 8.1 Hz), 4.81 (d, 1H, J = 6.5 Hz), 4.38-4.39
(m, 1H), 3.88 (m, 1H), 3.86 (s, 3H), 3.73-3.76 (dd, 1H, J = 4.2, 12.5 Hz); \textsuperscript{13}C NMR (125 MHz, CD\textsubscript{3}OD-d\textsubscript{4}) δ 160.1, 160.0, 132.2, 127.2, 114.0, 85.4, 61.1, 57.2,
54.4.; HRMS (EI): m/z calcd for C\textsubscript{11}H\textsubscript{13}NO\textsubscript{4} 223.0845, found 223.0829.

9. X-ray crystallography analysis data of (S,S)-7j

CCDC-1007235 contains the supplementary crystallographic data for (S,S)-7j. These data can
be obtained free of charge from The Cambridge Crystallographic Data Centre via
www.ccdc.cam.ac.uk/data_request/cif.

\textsuperscript{17} Matsunaga, S.; Yoshida, T.; Morimoto, H.; Kumagai, N.; Shibasaki, M., J. Am. Chem. Soc.,
2004, 126, 8777.
Crystal data and structure refinement for (S,S)-7j

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