Supporting Information


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S1
I. General information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. Yields referred to isolated compounds through flash column chromatography performed using 300-400 mesh silica gel. NMR spectra were recorded on Varian Brucker ARX 400 spectrometer in CDCl₃ solution and the chemical shifts were reported in parts per million (ppm) relative to internal standard TMS (0 ppm) for ¹H NMR and chloroform-d (77.0 ppm) for ¹³C NMR. Coupling constants were given in Hertz (Hz). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), brs (broad singlet) and m (multiplet). Infrared spectra (IR) spectra were recorded on a Perkin-Elmer 983G instrument. High resolution mass spectrometry (HRMS) were obtained on an IonSpec FT-ICR mass spectrometer with ESI or MALDI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected.

II. Preparation of the allenic esters

\[
\begin{align*}
\text{O} & \quad \text{Cl} & \quad \text{Ph₃P} & \quad \text{CO₂Bn} \\
\text{Et₃N} & & & \text{CH₂Cl₂} \\
\end{align*}
\]

Allenic esters is a known compound and synthesized according to a similar method developed by Hansen [1]. To a solution of benzyl (triphenylphosphoranylidene)acetate (0.1 mol) in CH₂Cl₂ (500 mL) was added 1.1 equivalent of Et₃N (0.11 mol). After stirred for about 15 minutes, 1.1 equivalent of acetyl chloride (0.11 mol) was added dropwise. Then the reaction mixture was stirred overnight at room temperature and was carefully evaporated to remove most of the solvent, and then the residue was extracted by petroleum ether (b.p. 30-60 °C, 5 × 200 mL). The combined extracting was concentrated and the residue was subjected to column chromatography (eluant: 5 % EtOAc in petroleum ether) to provide the allenic esters as light yellow oil.

III. Preparation of the α,β-unsaturated cyclic ketimines

\[
\begin{align*}
\text{O} & \quad \text{NH} & \quad \text{O} \\
\text{S} & \quad \text{O} & \quad \text{S} \\
\text{A} & \quad \text{MeLi} & \quad \text{B} & \quad \text{ArCHO} \\
\text{THF} & & & \text{EtOH} \\
\end{align*}
\]

The Synthesis of B: To a flame dried 500 mL round bottle flask with a magnetic
stirring bar under Argon atmosphere was added saccharin A (0.030 mol, 5.49 g) and anhydrous THF (250 mL). The flask was cooled to -78 °C and 2 equiv (0.060 mol) of the appropriate lithium reagent were carefully added by syringe or cannula. The reaction was stirred at -78 °C for an additional 4 h, then 100 mL of H₂O was added, and the reaction mixture was warmed to room temperature. The solution was transferred to a separatory funnel where 200 mL of ether was added and the aqueous layer was separated. The organic layer was washed successively with 10% HCl (2×100 mL), 10% NaHCO₃ (2×125 mL), and 100 mL of H₂O and dried over anhydrous MgSO₄. Removal of the solvent in vacuo gave a white solid, which was crystallized from absolute ethanol to give sulfonimine [2].

**The Synthesis of 1**: Piperidine (1 mmol) and acetic acid (1 mmol) were added to a solution of B (3-methyl-1,2-benzoisothiazole-1,1-dioxide) (10 mmol) and aldehyde (10 mmol) in EtOH and the mixture was refluxed for 3 hours. The mixture was cooled to 0 °C and the solid was collected by filtration, washed with cold EtOH, and dried to afford products 1 in 49-86% yield. They were generally used without further purification [3].

**IV. References**


**V. General procedure and spectroscopic data and HPLC chromatogram**

**Formal Synthesis processes for racemic systems:**

To a stirred solution of 1 (0.1 mmol) and 2 (0.12 mmol) in CH₂Cl₂ or CH₃CN (2.0 mL or 1 mL) at 40 °C or 60 °C, catalyst DMAP/DABCO was added in one portion. Then the reaction mixture was stirred at this temperature. After completion of the reaction (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give cycloadduct 3 and 4.

**Formal Synthesis processes for racemic systems:**
To a stirred solution of 1c (0.1 mmol) and 2a (0.12 mmol) in solvent (1 mL) at 25 °C, the chiral catalyst was added in one portion. Then the reaction mixture was stirred at this temperature. And the reaction was monitored by TLC, the reaction mixture was purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give cycloadduct 3c and 4c (for details see below).

\[
\text{Ar} = 4-\text{MeC}_{6}\text{H}_{4}
\]

\[
\begin{align*}
\text{Ar} &= 4-\text{MeC}_{6}\text{H}_{4} \\
1c &+ 2a \xrightarrow{\text{cat.}} 3c &+ 4c
\end{align*}
\]

\[
\begin{align*}
\text{Ar} &= 4-\text{MeC}_{6}\text{H}_{4} \\
\text{cat. 1} &\quad \beta-\text{ICD} \quad \text{cat. 2} \quad \text{cat. 3} \quad \text{Takemoto catalyst} \quad \text{cat. 4} \quad \text{cat. 5} \quad \text{cat. 6} \quad (\text{DHQD})_{2}\text{AQN}
\end{align*}
\]

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<th>Results</th>
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**Further transformations reactions:**

1) **Et\(_2\)O•BF\(_3\) reduction**: To a stirred solution of 4c (0.1 mmol) in CH\(_2\)Cl\(_2\) (1.0 mL), reducing agent Et\(_3\)SiH (1.0 mmol) and Et\(_2\)O•BF\(_3\) (1.0 mmol) was added in one portion. Then the reaction mixture was stirred at room temperature. After completion of the
reaction (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give 5 as white solid.

2) **LAH reduction**: To a stirred solution of 4c (0.1 mmol) in THF (1.0 mL), reducing agent LiAlH₄ (0.15 mmol) was added in one portion. Then the reaction mixture was stirred at room temperature. After completion of the reaction (monitored by TLC, about 10 min), the reaction mixture was purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give 6 as white solid.

**Benzyl-7-methyl-9-phenyl-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3a)**

![Chemical Structure](image)

61% yield; white solid; mp 183-186°C; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 7.8 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.56 (d, J = 7.0 Hz, 2H), 7.32 – 7.23 (m, 6H), 7.20 (d, J = 7.3 Hz, 2H), 7.07 (s, 2H), 5.76 (d, J = 4.6 Hz, 1H), 5.00 (s, 2H), 4.73 (d, J = 4.2 Hz, 1H), 2.92 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.90, 144.77, 141.41, 135.76, 133.60, 131.89, 130.30, 128.43, 128.13, 128.11, 128.03, 127.24, 127.11, 126.85, 121.05, 120.88, 107.63, 105.67, 66.28, 41.31, 14.96: IR (neat): ν 3117, 3013, 2352, 2318, 1703, 1599, 1325, 1225, 1174, 1160, 1012, 984, 851, 755 cm⁻¹; HRMS (ESI) m/z calcd for C₂₆H₂₁NO₄S [M+H]⁺ = 444.1270, found = 444.1275.

**Benzyl-7-methyl-9-(p-tolyl)-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3c)**

![Chemical Structure](image)

66% yield; white solid; mp 132-133°C; ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 7.6 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.56 (t, J = 7.2 Hz, 2H), 7.28 (d, J = 4.8 Hz, 3H), 7.08 (s, 6H), 5.75 (d, J = 4.7 Hz, 1H), 5.01 (s, 2H), 4.70 (d, J = 4.6 Hz, 1H), 2.91 (s, 3H), 2.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.98, 141.84, 141.04, 136.80, 135.82, 133.58, 131.86, 130.25, 129.49, 128.39, 128.15, 128.03, 128.00, 127.30, 126.75, 121.03, 120.86, 107.88, 105.82, 66.24, 40.88, 21.12, 14.96: IR (neat): ν 2894, 2352, 2319, 1698, 1602, 1324, 1226, 1159, 1104, 1023, 983, 853, 755 cm⁻¹; HRMS (ESI) m/z calcd for C₂₇H₂₃NO₄S [M+H]⁺ = 458.1426, found = 458.1421.
Benzyl-9-(3,4-dimethylphenyl)-7-methyl-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3d)

95% yield; white solid; mp 146-148°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, J = 7.7 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.55 (t, J = 7.9 Hz, 2H), 7.27 (d, J = 7.9 Hz, 3H), 7.08 (d, J = 6.7 Hz, 2H), 7.04 (d, J = 8.1 Hz, 1H), 6.94 (s, 2H), 5.74 (d, J = 4.2 Hz, 1H), 5.08 – 4.94 (m, 2H), 4.67 (d, J = 4.2 Hz, 1H), 2.91 (s, 3H), 2.22 (s, 3H), 2.18 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.02, 142.26, 140.96, 136.98, 135.83, 135.45, 133.53, 131.87, 130.19, 130.08, 129.31, 128.35, 128.16, 127.97, 127.36, 126.64, 125.55, 121.01, 120.14. 

IR (neat): $\nu$ 2873, 2357, 2313, 1699, 1599, 1323, 1225, 1175, 1105, 1023, 983, 785, 744 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{28}$H$_{25}$NO$_4$S [M+H]$^+$ = 472.1583, found = 472.1592.

Benzyl-9-(4-methoxyphenyl)-7-methyl-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3e)

53% yield; white solid; mp 70-72°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, J = 7.8 Hz, 1H), 7.73 – 7.66 (m, 2H), 7.61 (t, J = 6.7 Hz, 1H), 7.43 – 7.29 (m, 5H), 7.16 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.33 (s, 1H), 5.99 (d, J = 3.7 Hz, 1H), 5.13 (q, J = 12.4 Hz, 2H), 3.79 (d, J = 6.7 Hz, 5H), 3.31 (dd, J = 16.6, 9.9 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.25, 165.79, 145.61, 134.13, 133.25, 131.92, 130.46, 129.09, 128.53, 128.42, 128.25, 128.12, 127.97, 121.37, 121.13, 114.31, 106.54, 110.65, 65.90, 55.34, 36.44, 31.74; IR (neat): $\nu$ 2916, 2848, 2352, 2312, 1700, 1325, 1317, 1248, 1160, 1105, 1023, 982, 785, 744 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{27}$H$_{23}$NO$_4$S [M+H]$^+$ = 474.1375, found = 474.1357.

Benzyl-7-methyl-9-(3,4,5-trimethoxyphenyl)-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3g)
43% yield; white solid; mp 135-138°C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.82 (d, \( J = 7.2 \) Hz, 1H), 7.69 – 7.62 (m, 1H), 7.63 – 7.55 (m, 2H), 7.28 (dd, \( J = 8.7, 2.6 \) Hz, 3H), 7.09 (d, \( J = 2.1 \) Hz, 2H), 6.38 (d, \( J = 2.2 \) Hz, 2H), 5.81 – 5.71 (m, 1H), 5.03 (dd, \( J = 28.9, 12.4 \) Hz, 2H), 4.69 (s, 1H), 3.83 (d, \( J = 2.3 \) Hz, 3H), 3.71 (d, \( J = 2.2 \) Hz, 6H), 2.93 (s, 3H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 166.93, 153.47, 141.32, 140.57, 136.90, 135.68, 133.65, 131.91, 130.35, 128.42, 128.14, 128.08, 127.25, 126.78, 121.07, 120.91, 107.50, 105.69, 104.73, 66.37, 60.84, 56.04, 41.66, 14.94. IR (neat): 2907, 2850, 2352, 1700, 1324, 1315, 1249, 1158, 1105, 1023, 982, 744 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{29}\)H\(_{27}\)NO\(_7\)S \([M+Na]^+\) = 556.1405, found = 556.1408.

**Benzyl-9-(2-fluorophenyl)-7-methyl-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3h)**

63% yield; white solid; mp 144-145°C; \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.80 (d, \( J = 7.6 \) Hz, 1H), 7.66 – 7.53 (m, 3H), 7.29 – 7.16 (m, 5H), 7.12 – 6.91 (m, 4H), 5.78 (d, \( J = 4.6 \) Hz, 1H), 5.14 (d, \( J = 4.3 \) Hz, 1H), 5.01 (q, \( J = 12.4 \) Hz, 2H), 2.98 (s, 3H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 166.57, 143.35, 135.73, 133.65, 131.80, 131.72, 131.58, 130.39, 129.76, 129.72, 128.59, 128.51, 128.38, 127.95, 127.46, 127.10, 124.81, 121.04, 120.93, 115.54, 115.32, 105.55, 104.14, 66.24, 33.98, 14.97; IR (neat): \( \nu \) 2895, 2352, 2318, 1698, 1324, 1252, 1158, 1105, 1022, 982, 893, 754 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{26}\)H\(_{20}\)FNO\(_4\)S \([M+H]^+\) = 462.1175, found = 462.1157.

**Benzyl-9-(4-chlorophenyl)-7-methyl-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3i)**
58% yield; white solid; mp 174-175°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J = 7.7\) Hz, 1H), 7.68 – 7.61 (m, 1H), 7.58 (t, \(J = 7.6\) Hz, 2H), 7.29 (d, \(J = 5.0\) Hz, 3H), 7.20 (d, \(J = 7.3\) Hz, 2H), 7.09 (dd, \(J = 11.3, 6.3\) Hz, 4H), 5.70 (d, \(J = 4.0\) Hz, 1H), 5.02 (dd, \(J = 28.8, 12.2\) Hz, 2H), 4.70 (d, \(J = 4.3\) Hz, 1H), 2.92 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.68, 143.32, 141.68, 135.60, 133.70, 132.88, 131.90, 130.48, 129.43, 128.90, 128.46, 128.26, 128.18, 127.10, 127.06, 121.10, 120.88, 107.25, 104.96, 66.35, 40.78, 14.97; IR (neat): \(\nu\) 2895, 2352, 2318, 1700, 1324, 1252, 1159, 1104, 1022, 982, 893, 744 cm\(^{-1}\); HRMS (ESI) \(m/z\) calcd for C\(_{26}\)H\(_{20}\)ClNO\(_4\)S [M+H\(^+\)] = 478.0880, found = 478.0874.

**Benzyl-9-(4-bromophenyl)-7-methyl-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3k)**

74% yield; white solid; mp 171-172°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.81 (d, \(J = 7.6\) Hz, 1H), 7.67 – 7.61 (m, 1H), 7.58 (t, \(J = 8.0\) Hz, 2H), 7.35 (d, \(J = 7.5\) Hz, 2H), 7.32 – 7.26 (m, 3H), 7.05 (t, \(J = 7.1\) Hz, 4H), 5.70 (d, \(J = 4.4\) Hz, 1H), 5.02 (dd, \(J = 32.7, 12.2\) Hz, 2H), 4.69 (d, \(J = 4.1\) Hz, 1H), 2.92 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.66, 143.84, 141.76, 135.59, 133.72, 131.86, 130.49, 129.80, 129.69, 128.48, 128.26, 128.19, 127.11, 127.04, 121.10, 121.01, 120.88, 107.14, 104.88, 66.36, 40.87, 14.97; IR (neat): \(\nu\) 2895, 2352, 2318, 1699, 1324, 1252, 1159, 1104, 1023, 983, 893, 753 cm\(^{-1}\); HRMS (ESI) \(m/z\) calcd for C\(_{26}\)H\(_{20}\)BrNO\(_4\)S [M+H\(^+\)] = 522.0375, found = 522.0356.

**Benzyl-7-methyl-9-(naphthalen-1-yl)-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3n)**

62% yield; white solid; mp 146-148°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.19 – 8.09 (m, 1H), 7.95 – 7.86 (m, 1H), 7.80 (d, \(J = 7.3\) Hz, 1H), 7.74 (d, \(J = 6.4\) Hz, 1H), 7.62 – 7.37 (m, 7H), 7.10 (t, \(J = 7.2\) Hz, 1H), 6.97 (t, \(J = 7.3\) Hz, 2H), 6.62 (d, \(J = 7.3\) Hz, 2H), 5.86 (d, \(J = 4.4\) Hz, 1H), 5.65 (s, 1H), 4.95 – 4.73 (m, 2H), 3.04 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.86, 135.34, 133.96, 133.54, 131.80, 130.23, 129.03,
128.10, 127.70, 127.51, 127.28, 126.77, 126.48, 126.20, 125.79, 122.50, 121.01, 120.87, 107.06, 105.15, 66.18, 14.85; IR (neat): \( \nu \) 2895, 2352, 2313, 1703, 1324, 1249, 1160, 1105, 1022, 983, 893, 743 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{30}\)H\(_{23}\)NO\(_4\)S [M+H]\(^+\) = 494.1426, found = 494.1426.

**Benzyl-7-methyl-9-(naphthalen-2-yl)-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3o)**

\[
\begin{align*}
\text{S} & \quad \text{O}_2 \quad \text{N} \\
\text{S} & \quad \text{CO}_2 \quad \text{Bn}
\end{align*}
\]

55% yield; white solid; mp 168-170°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.80 (dd, J = 28.4, 8.7 Hz, 4H), 7.60 (t, J = 11.4 Hz, 4H), 7.47 (s, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.19 (d, J = 6.6 Hz, 1H), 7.11 (t, J = 6.7 Hz, 2H), 6.96 (d, J = 6.8 Hz, 2H), 5.80 (s, 1H), 4.96 (s, 2H), 4.91 (s, 1H), 2.97 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 166.90, 142.05, 141.50, 135.60, 133.62, 133.52, 132.62, 131.93, 130.34, 128.70, 128.29, 128.12, 127.98, 127.96, 127.65, 127.24, 126.93, 126.73, 126.27, 126.19, 125.86, 121.07, 120.87, 107.56, 105.46, 66.34, 41.54, 14.98. IR (neat): \( \nu \) 2896, 2352, 2313, 1700, 1324, 1250, 1160, 1105, 1022, 987, 893, 745 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{30}\)H\(_{23}\)NO\(_4\)S [M+H]\(^+\) = 494.1426, found = 494.1415.

**Benzyl-7-methyl-9-(thiophen-2-yl)-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3p)**

\[
\begin{align*}
\text{S} & \quad \text{O}_2 \quad \text{N} \\
\text{S} & \quad \text{CO}_2 \quad \text{Bn}
\end{align*}
\]

33% yield; white solid; mp 180-182°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.81 (d, J = 7.6 Hz, 1H), 7.70 – 7.54 (m, 3H), 7.31 (s, 3H), 7.23 – 7.08 (m, 3H), 6.90 (s, 1H), 6.82 (s, 1H), 5.84 (d, J = 4.8 Hz, 1H), 5.21 – 5.00 (m, 3H), 2.90 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 166.74, 148.80, 141.13, 135.81, 133.72, 131.94, 130.46, 128.50, 128.19, 128.12, 127.32, 127.12, 127.06, 124.82, 124.78, 121.10, 120.96, 107.43, 104.46, 66.40, 35.78, 14.94; IR (neat): \( \nu \) 2914, 2873, 2380, 2312, 1699, 1325, 1247, 1159, 1103, 1022, 982, 893, 744 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{24}\)H\(_{19}\)NO\(_4\)S\(_2\) [M+H]\(^+\) = 450.0834 , found = 450.0812.

**Benzyl-9-(benzo[d][1,3]dioxol-5-yl)-7-methyl-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3r)**
71% yield; white solid; mp 161-163°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 7.7$ Hz, 1H), 7.69 – 7.50 (m, 3H), 7.30 (s, 3H), 7.14 (s, 2H), 6.66 (dd, $J = 18.0$, 9.3 Hz, 3H), 5.92 (s, 2H), 5.72 (d, $J = 4.6$ Hz, 1H), 5.04 (q, $J = 12.3$ Hz, 2H), 4.64 (d, $J = 4.3$ Hz, 1H), 2.90 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.92, 147.93, 146.64, 140.91, 138.86, 135.76, 133.62, 131.89, 130.31, 128.43, 128.28, 128.10, 127.25, 126.79, 121.31, 121.06, 120.85, 108.63, 108.40, 107.86, 105.54, 101.08, 66.31, 40.94, 14.92; IR (neat): $\nu$ 2917, 2849, 2352, 2318, 1698, 1323, 1247, 1159, 1104, 1023, 893, 744 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{27}$H$_{21}$NO$_6$S [M+H]$^+$ = 488.1168, found = 488.1155.

**Ethyl-7-methyl-9-(p-tolyl)-9H-benzo[4,5]isothiazolo[2,3-a]pyridine-8-carboxylate 5,5-dioxide (3t)**

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 8.1$ Hz, 1H), 7.67 – 7.61 (m, 1H), 7.60 – 7.52 (m, 2H), 7.13 (dd, $J = 17.5$, 7.9 Hz, 4H), 5.76 (d, $J = 4.7$ Hz, 1H), 4.69 (d, $J = 4.2$ Hz, 1H), 4.03 (q, $J = 7.1$ Hz, 2H), 2.89 (s, 3H), 2.31 (s, 3H), 1.11 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 167.16, 141.92, 140.20, 136.80, 133.54, 131.95, 130.21, 129.41, 128.06, 127.38, 126.86, 121.03, 120.84, 105.74, 60.33, 40.99, 21.09, 14.84, 14.00; IR (neat): $\nu$ 2946, 2912, 2352, 2319, 1698, 1350, 1247, 1159, 1104, 1023, 983, 893, 785, 744 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{22}$H$_{21}$NO$_4$S [M+H]$^+$ = 396.1270, found = 396.1239.

50% yield; white solid; mp 119-120°C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.86 (d, \(J = 7.7\) Hz, 1H), 7.75 – 7.66 (m, 2H), 7.61 (t, \(J = 6.3\) Hz, 1H), 7.35 (dd, \(J = 9.9, 5.8\) Hz, 6H), 7.27 (dd, \(J = 14.7, 7.1\) Hz, 4H), 6.34 (s, 1H), 6.01 (d, \(J = 3.7\) Hz, 1H), 5.13 (q, \(J = 12.4\) Hz, 2H), 3.87 (ddd, \(J = 12.6, 11.7, 4.9\) Hz, 2H), 3.27 (dd, \(J = 14.7, 8.3\) Hz, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 166.24, 146.01, 142.14, 136.13, 133.81, 131.47, 130.50, 129.28, 128.97, 128.53, 128.26, 128.12, 127.92, 127.42, 127.35, 121.39, 121.14, 106.18, 100.67, 65.93, 37.26, 31.59; IR (neat): \textnu\ 3029, 1708, 1672, 1620, 1494, 1471, 1453, 1394, 1327, 1248, 1183, 1162, 1130, 824, 754, 743 cm\textsuperscript{-1}; HRMS (ESI) m/z calcd for C\textsubscript{26}H\textsubscript{21}NO\textsubscript{4}S [M+H]\textsuperscript{+} = 444.1270, found = 444.1255.

**Benzyl-(E)-2-(5,5-dioxido-9-(o-tolyl)-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4b)**

![](image)

82% yield; white solid; mp 70-73°C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.85 (d, \(J = 7.8\) Hz, 1H), 7.69 (s, 2H), 7.60 (t, \(J = 6.5\) Hz, 1H), 7.39 – 7.29 (m, 5H), 7.14 (s, 4H), 6.33 (s, 1H), 5.99 (d, \(J = 3.7\) Hz, 1H), 5.13 (q, \(J = 12.4\) Hz, 2H), 3.93 – 3.71 (m, 2H), 3.27 (dd, \(J = 14.6, 8.1\) Hz, 1H), 2.34 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 166.24, 146.13, 139.10, 136.99, 136.17, 133.78, 131.46, 130.43, 129.70, 129.62, 129.13, 128.52, 128.35, 128.25, 128.10, 127.97, 127.27, 121.36, 121.13, 106.48, 100.63, 65.89, 36.84, 31.62, 21.09; IR (neat): \textnu\ 3065, 3030, 2952, 1708, 1620, 1492, 1470, 1455, 1394, 1326, 1244, 1183, 1162, 1130, 833, 754, 743 cm\textsuperscript{-1}; HRMS (ESI) m/z calcd for C\textsubscript{27}H\textsubscript{23}NO\textsubscript{4}S [M+H]\textsuperscript{+} = 458.1426, found = 458.1409.

**Benzyl-(E)-2-(5,5-dioxido-9-(p-tolyl)-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4c)**

![](image)

66% yield; white solid; mp 146-148°C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.85 (d, \(J = 7.8\) Hz, 1H), 7.75 – 7.64 (m, 2H), 7.64 – 7.55 (m, 1H), 7.50 – 7.27 (m, 5H), 7.14 (s, 4H), 6.33 (s, 1H), 5.99 (d, \(J = 2.8\) Hz, 1H), 5.13 (q, \(J = 12.5\) Hz, 2H), 3.97 – 3.68 (m, 2H), 3.27 (dd, \(J = 14.6, 8.0\) Hz, 1H), 2.34 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 166.24,
146.12, 139.09, 136.97, 136.15, 133.78, 130.43, 129.61, 129.13, 128.52, 128.25, 128.10, 127.97, 127.26, 121.36, 121.12, 106.48, 100.62, 65.89, 36.84, 31.61, 21.09; IR (neat): ν 3063, 3030, 2321, 1708, 1620, 1513, 1471, 1454, 1394, 1327, 1249, 1183, 1162, 1129, 834, 754 cm⁻¹; HRMS (ESI) m/z calcd for C₂₇H₂₃NO₄S [M+H]⁺ =458.1426, found =458.1403.

Benzyl-(E)-2-(9-(3,4-dimethylphenyl)-5,5-dioxido-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4d)

![Chemical structure of 4d]

66% yield; white solid; mp 152-154°C; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 7.8 Hz, 1H), 7.68 (d, J = 4.9 Hz, 2H), 7.60 (t, J = 6.8 Hz, 1H), 7.34 (dd, J = 15.6, 6.6 Hz, 5H), 7.10 (d, J = 7.6 Hz, 1H), 6.98 (t, 2H), 6.34 (s, 1H), 5.98 (d, J = 3.6 Hz, 1H), 5.21 – 5.06 (m, 2H), 3.93 (dd, J = 15.3, 5.7 Hz, 1H), 3.76 (dd, J = 8.8, 4.7 Hz, 1H), 3.18 (dd, J = 15.2, 9.2 Hz, 1H), 2.25 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 166.26, 146.30, 139.62, 137.16, 136.18, 135.64, 133.78, 131.43, 130.41, 130.16, 129.05, 128.69, 128.53, 128.27, 128.11, 128.00, 124.69, 121.35, 121.14, 106.76, 100.48, 65.89, 36.85, 31.67, 19.88, 19.44; IR (neat): ν 3064, 3032, 1708, 1673, 1620, 1501, 1471, 1453, 1394, 1327, 1291, 1255, 1183, 1163, 1130, 833, 755 cm⁻¹; HRMS (ESI) m/z calcd for C₂₈H₂₅NO₄S [M+H]⁺ =472.1583, found =472.1560.

Benzyl-(E)-2-(9-(4-methoxyphenyl)-5,5-dioxido-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4e)

![Chemical structure of 4e]

57% yield; white solid; mp 122-123°C; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 7.8 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.60 (t, J = 6.9 Hz, 1H), 7.45 – 7.27 (m, 5H), 7.15 (d, J = 7.6 Hz, 2H), 6.86 (d, J = 7.6 Hz, 2H), 6.34 (s, 1H), 5.98 (s, 1H), 5.20 – 5.02 (m, 2H), 3.79 (s, 5H), 3.31 (dd, J = 16.5, 10.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 166.24, 158.79, 146.12, 136.16, 134.13, 133.79, 131.46, 130.45, 129.09, 128.53, 128.41, 128.25, 128.11, 127.97, 121.36, 121.13, 114.31, 106.54, 100.66, 100.00, 65.89, 55.34, 36.43, 31.74; IR (neat): ν 3064, 3011, 1708, 1673, 1619, 1511, 1470, 1455, 1394,
1327, 1249, 1183, 1162, 1140, 832, 755 cm⁻¹; HRMS (ESI) m/z calcd for C₂₇H₂₃NO₅S [M+H]⁺ =474.1375, found =474.1356.

**Benzyl-(E)-2-(9-(2,4-dimethoxyphenyl)-5,5-dioxido-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4f)**

![Chemical Structure](image)

77% yield; white solid; mp 71-73°C; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 6.1 Hz, 1H), 7.69 (s, 2H), 7.59 (s, 1H), 7.36 (s, 5H), 7.03 (d, J = 7.2 Hz, 1H), 6.52 – 6.38 (m, 2H), 6.32 (s, 1H), 5.98 (s, 1H), 5.13 (s, 2H), 4.16 (s, 1H), 3.81 (d, J = 8.8 Hz, 6H), 3.65 – 3.41 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 166.32, 160.02, 157.78, 146.89, 136.27, 133.68, 131.29, 130.18, 128.93, 128.50, 128.26, 128.20, 128.16, 128.04, 122.28, 121.30, 121.05, 106.86, 104.17, 100.05, 98.85, 65.79, 55.45, 55.42, 30.26, 29.79; IR (neat): ν 2955, 2836, 2351, 2322, 1709, 1677, 1614, 1586, 1504, 1468, 1455, 1438, 1418, 1395, 1326, 1292, 1263, 1208, 1183, 1161, 1129, 833, 755 cm⁻¹; HRMS (ESI) m/z calcd for C₂₈H₂₅NO₆S [M+H]⁺ =504.1481, found =504.1462.

**Benzyl-(E)-2-(9-(2-fluorophenyl)-5,5-dioxido-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4h)**

![Chemical Structure](image)

70% yield; white solid; mp 132-133°C; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 7.8 Hz, 1H), 7.69 (q, J = 7.7 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.45 – 7.27 (m, 5H), 7.22 (dd, J = 17.2, 9.3 Hz, 2H), 7.08 (dd, J = 18.8, 8.6 Hz, 2H), 6.35 (s, 1H), 5.98 (d, J = 4.2 Hz, 1H), 5.22 – 5.04 (m, 2H), 4.18 (dd, J = 11.7, 6.2 Hz, 1H), 3.75 (dd, J = 15.4, 5.9 Hz, 1H), 3.48 (dd, J = 15.4, 8.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 166.20, 161.68, 159.24, 145.76, 136.10, 133.86, 131.39, 130.58, 129.60, 129.02, 128.94, 128.75, 128.55, 128.29, 128.15, 127.83, 124.64, 121.37, 115.86, 115.64, 104.84, 100.79, 65.98, 30.26, 29.70; IR (neat): ν 3065, 3032, 2892, 2351, 1709, 1679, 1621, 1584, 1490, 1472, 1454, 1395, 1328, 1229, 1183, 1162, 1140, 834, 754 cm⁻¹; HRMS (ESI) m/z calcd for C₂₈H₂₅NO₆S [M+H]⁺ =462.1175, found =462.1161.
Benzyl-(E)-2-(9-(4-chlorophenyl)-5,5-dioxido-8,9-dihydro-7H-
benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4i)

\[ \text{O} \quad \text{CO}_2 \text{Bn} \]

59% yield; white solid; mp 152-154°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 (d, \(J = 7.8\) Hz, 1H), 7.76 – 7.67 (m, 2H), 7.63 (dd, \(J = 9.5, 3.8\) Hz, 1H), 7.32 (dt, \(J = 21.8, 8.6\) Hz, 7H), 7.17 (d, \(J = 8.2\) Hz, 2H), 6.34 (s, 1H), 5.96 (d, \(J = 4.0\) Hz, 1H), 5.23 – 5.02 (m, 2H), 3.79 (dd, \(J = 20.8, 14.1\) Hz, 2H), 3.36 (dd, \(J = 15.0, 7.8\) Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.19, 145.49, 140.53, 136.05, 133.87, 133.12, 130.66, 129.57, 129.09, 128.78, 128.55, 128.26, 128.17, 127.75, 121.42, 121.18, 105.21, 101.06, 99.99, 65.99, 36.62, 31.40; IR (neat): \(\nu\) 3080, 2892, 2351, 2322, 1709, 1679, 1621, 1553, 1492, 1471, 1454, 1434, 1395, 1327, 1229, 1183, 1162, 1141, 832, 754 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{26}\)H\(_{20}\)ClNO\(_4\)S [M+H]\(^+\) = 478.0880, found = 478.0864.

Benzyl-(E)-2-(9-(2,4-dichlorophenyl)-5,5-dioxido-8,9-dihydro-7H-
benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4j)

\[ \text{O} \quad \text{CO}_2 \text{Bn} \]

68% yield; white solid; mp 82-84°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 (d, \(J = 7.6\) Hz, 1H), 7.77 – 7.68 (m, 2H), 7.67 – 7.59 (m, 1H), 7.43 (s, 1H), 7.36 (s, 5H), 7.21 (d, \(J = 8.1\) Hz, 1H), 7.14 (d, \(J = 8.3\) Hz, 1H), 6.35 (s, 1H), 5.94 (d, \(J = 4.0\) Hz, 1H), 5.22 – 5.04 (m, 2H), 4.31 (d, \(J = 5.0\) Hz, 1H), 3.59 (ddd, \(J = 32.5, 15.4, 6.5\) Hz, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.05, 145.06, 137.64, 135.99, 134.14, 133.92, 133.66, 131.44, 130.76, 130.13, 129.74, 129.22, 128.54, 128.31, 128.18, 127.72, 127.64, 121.43, 121.23, 103.82, 101.35, 66.04, 33.24, 29.42; IR (neat): \(\nu\) 3080, 2892, 2352, 2321, 1710, 1679, 1621, 1554, 1471, 1380, 1329, 1264, 1184, 1162, 1141, 833, 754 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{26}\)H\(_{19}\)Cl\(_2\)NO\(_4\)S [M+H]\(^+\) = 512.0466, found = 512.0476.

Benzyl-(E)-2-(9-(4-bromophenyl)-5,5-dioxido-8,9-dihydro-7H-
benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4k)

\[ \text{O} \quad \text{CO}_2 \text{Bn} \]
53% yield; white solid; mp 139-141°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 (d, \(J = 7.8\) Hz, 1H), 7.75 – 7.66 (m, 2H), 7.63 (dd, \(J = 9.5, 4.0\) Hz, 1H), 7.45 (d, \(J = 8.3\) Hz, 2H), 7.31 (d, \(J = 39.2\) Hz, 5H), 7.12 (d, \(J = 8.3\) Hz, 2H), 6.34 (s, 1H), 5.95 (d, \(J = 3.7\) Hz, 1H), 5.22 – 5.01 (m, 2H), 3.77 (dd, \(J = 23.7, 8.7\) Hz, 2H), 3.36 (dd, \(J = 14.7, 7.6\) Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.17, 145.45, 141.06, 136.05, 133.87, 132.04, 131.51, 130.67, 129.60, 129.14, 128.55, 128.26, 128.16, 127.73, 121.41, 121.18, 105.09, 101.08, 100.00, 65.99, 36.68, 31.32; IR (neat): \(\nu\) 3080, 3031, 2890, 2321, 1708, 1674, 1621, 1487, 1472, 1454, 1398, 1264, 1184, 1162, 1140, 824, 754 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{26}\)H\(_{20}\)BrNO\(_4\)S \([M+H]^+\) =522.0375, found =522.0365.

**Benzyl-(E)-2-(9-(4-cyanophenyl)-5,5-dioxido-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4l)**

41% yield; white solid; mp 70-72°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.87 (d, \(J = 7.7\) Hz, 1H), 7.73 (d, \(J = 2.7\) Hz, 2H), 7.65 (dd, \(J = 14.5, 5.3\) Hz, 3H), 7.36 (s, 7H), 6.35 (s, 1H), 5.95 (d, \(J = 4.0\) Hz, 1H), 5.20 – 5.06 (m, 2H), 3.91 (d, \(J = 5.5\) Hz, 1H), 3.72 (dd, \(J = 15.2, 5.6\) Hz, 1H), 3.48 (dd, \(J = 15.3, 7.6\) Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.11, 147.40, 144.84, 135.94, 133.96, 132.79, 131.58, 130.91, 130.11, 128.56, 128.28, 128.24, 127.52, 121.48, 121.24, 118.63, 111.34, 103.68, 101.47, 66.07, 37.18, 30.93; IR (neat): \(\nu\) 2352, 2312, 2228, 1842, 1731, 1699, 1553, 1329, 1264, 1183, 1162, 1141, 821, 744 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{27}\)H\(_{20}\)N\(_2\)O\(_4\)S \([M+H]^+\) =469.1222, found =469.1205.

**Benzyl-(E)-2-(5,5-dioxido-9-((E)-styryl)-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4m)**
60% yield; white solid; mp 72-75°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 7.4$ Hz, 1H), 7.77 – 7.67 (m, 2H), 7.64 – 7.58 (m, 1H), 7.49 – 7.27 (m, 10H), 6.53 (d, $J = 15.9$ Hz, 1H), 6.36 (s, 1H), 6.15 (dd, $J = 15.9$, 6.8 Hz, 1H), 5.92 (s, 1H), 5.34 – 5.06 (m, 2H), 3.60 – 3.51 (m, 1H), 3.51 – 3.38 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.37, 145.99, 136.66, 136.15, 133.77, 131.41, 130.46, 129.08, 129.02, 128.61, 128.53, 128.29, 128.12, 127.93, 127.71, 127.08, 126.39, 121.37, 121.10, 104.95, 100.97, 65.97, 34.44, 29.33; IR (neat): $\nu$ 3080, 3030, 2943, 2321, 1708, 1619, 1495, 1471, 1453, 1394, 1264, 1183, 1163, 1141, 842, 753 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{28}$H$_{23}$NO$_4$S [M+H]$^+$ = 470.1426, found = 470.1428.

Benzyl-(E)-2-(9-(naphthalen-1-yl)-5,5-dioxido-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4n)

88% yield; white solid; mp 82-85°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (d, $J = 8.2$ Hz, 1H), 7.90 (dd, $J = 14.8$, 7.9 Hz, 2H), 7.80 (d, $J = 7.9$ Hz, 1H), 7.70 (q, $J = 8.0$ Hz, 2H), 7.58 (ddd, $J = 19.5$, 14.6, 7.1 Hz, 3H), 7.48 – 7.37 (m, 2H), 7.29 (d, $J = 27.9$ Hz, 5H), 6.37 (s, 1H), 6.11 (d, $J = 3.7$ Hz, 1H), 5.09 (q, $J = 12.4$ Hz, 2H), 4.80 – 4.51 (m, 1H), 4.13 (dd, $J = 15.2$, 5.6 Hz, 1H), 3.42 (dd, $J = 15.1$, 9.1 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.14, 146.17, 137.50, 136.09, 134.12, 133.82, 131.46, 130.95, 130.49, 129.50, 129.26, 128.50, 128.27, 128.10, 128.06, 127.94, 126.66, 125.88, 125.63, 124.51, 122.77, 121.41, 121.19, 106.48, 100.73, 65.93, 33.05, 30.51; IR (neat): $\nu$ 3079, 2974, 2352, 2313, 1708, 1620, 1515, 1471, 1454, 1395, 1264, 1183, 1161, 1141, 833, 754 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{30}$H$_{23}$ClNO$_4$S [M+H]$^+$ = 494.1426, found = 494.1420.

Benzyl-(E)-2-(9-(naphthalen-2-yl)-5,5-dioxido-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4o)
81% yield; white solid; mp 155-147°C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.76 (m, 4H), 7.72 (dd, J = 14.0, 8.0 Hz, 3H), 7.61 (t, J = 7.4 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.42 – 7.21 (m, 6H), 6.36 (s, 1H), 6.07 (d, J = 3.0 Hz, 1H), 5.11 (q, J = 12.4 Hz, 2H), 4.09 – 3.84 (m, 2H), 3.41 (dd, J = 14.8, 8.2 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.23, 145.95, 139.46, 136.11, 133.84, 133.51, 132.65, 131.52, 130.55, 129.45, 128.85, 128.51, 128.25, 128.11, 127.92, 127.81, 127.70, 126.37, 126.00, 125.96, 125.59, 121.40, 121.22, 105.94, 100.84, 65.93, 37.37, 31.51; IR (neat): ν 3079, 2352, 2320, 1708, 1620, 1537, 1471, 1454, 1395, 1265, 1183, 1162, 1141, 841, 752 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{30}$H$_{23}$NO$_4$S [M+H]$^+$ =494.1426, found =494.1419.


57% yield; white solid; mp 53-56°C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, J = 7.7 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.62 (t, J = 6.8 Hz, 1H), 7.36 (d, J = 12.3 Hz, 5H), 7.20 (d, J = 4.4 Hz, 1H), 6.95 (d, J = 8.1 Hz, 2H), 6.36 (s, 1H), 6.05 (d, J = 3.6 Hz, 1H), 5.16 (q, J = 12.4 Hz, 2H), 4.14 (d, J = 5.1 Hz, 1H), 3.74 (dd, J = 15.1, 5.3 Hz, 1H), 3.62 (dd, J = 15.0, 7.6 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.21, 145.39, 145.03, 136.10, 133.86, 131.54, 130.66, 129.05, 128.55, 128.28, 128.14, 127.77, 127.08, 124.51, 124.38, 121.38, 121.26, 105.41, 101.30, 65.99, 32.43, 31.63; IR (neat): ν 2920, 2850, 2352, 2320, 1710, 1622, 1537, 1470, 1454, 1395, 1265, 1184, 1162, 1142, 745 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{24}$H$_{19}$NO$_4$S$_2$ [M+H]$^+$ =450.0834, found =450.0832.

**Benzyl-(E)-2-(9-(furan-2-yl)-5,5-dioxido-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4q)**
49% yield; white solid; mp 63-65°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, J = 7.7 Hz, 1H), 7.71 (t, J = 8.3 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.43 – 7.32 (m, 6H), 6.40 – 6.27 (m, 2H), 6.15 (s, 1H), 6.03 (d, J = 4.0 Hz, 1H), 5.24 – 5.10 (m, 2H), 3.94 (dd, J = 11.4, 5.7 Hz, 1H), 3.76 (dd, J = 15.3, 5.5 Hz, 1H), 3.56 (dd, J = 15.3, 8.1 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.27, 154.05, 145.58, 142.07, 136.12, 133.81, 131.47, 130.60, 129.35, 128.55, 128.29, 128.15, 127.81, 121.35, 121.23, 110.41, 105.65, 102.93, 100.99, 66.00, 30.86, 28.09; IR (neat): $\nu$ 2962, 2894, 2352, 2320, 1711, 1622, 1537, 1471, 1454, 1395, 1263, 1184, 1162, 1141, 744 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{24}$H$_{19}$NO$_5$S [M+H]$^+$ =434.1062, found =434.1068.

Benzyl-(E)-2-(9-(benzo[d][1,3]dioxol-5-yl)-5,5-dioxido-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4r)

82% yield; white solid; mp 72-74°C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 13.4 Hz, 2H), 7.61 (t, J = 6.3 Hz, 1H), 7.45 – 7.28 (m, 5H), 6.88 – 6.60 (m, 3H), 6.34 (s, 1H), 5.95 (s, 3H), 5.14 (q, J = 12.5 Hz, 2H), 3.79 (dd, J = 22.9, 8.4 Hz, 2H), 3.28 (dd, J = 13.9, 7.1 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.24, 148.04, 146.77, 145.92, 136.13, 135.94, 133.82, 131.47, 130.52, 129.23, 128.53, 128.27, 128.13, 127.88, 121.38, 121.14, 120.53, 108.56, 107.81, 106.12, 101.14, 100.75, 65.93, 36.95, 31.80; IR (neat): $\nu$ 2918, 2849, 2352, 2319, 1711, 1621, 1537, 1471, 1453, 1396, 1264, 1183, 1161, 1142, 745 cm$^{-1}$; HRMS (ESI) m/z calcd for C$_{27}$H$_{21}$NO$_6$S [M+H]$^+$ =488.1168, found =488.1171.

Methyl-(E)-2-(5,5-dioxido-9-(p-tolyl)-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4s)
53% yield; white solid; mp 149-150°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 7.7\) Hz, 1H), 7.68 (d, \(J = 12.9\) Hz, 2H), 7.60 (t, \(J = 6.8\) Hz, 1H), 7.14 (s, 4H), 6.30 (s, 1H), 5.98 (s, 1H), 3.85 – 3.75 (m, 2H), 3.68 (s, 3H), 3.28 (dd, \(J = 17.1, 10.2\) Hz, 1H), 2.33 (s, 3H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.85, 145.79, 139.11, 136.97, 133.79, 131.45, 130.45, 129.61, 129.12, 127.98, 127.92, 121.34, 121.14, 106.41, 100.61, 51.22, 36.84, 31.56, 21.09; IR (neat): \(\nu\) 2948, 2352, 2314, 1710, 1622, 1533, 1471, 1454, 1385, 1266, 1187, 1162, 1145, 755 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{19}\)NO\(_4\)S [M+H]\(^+\) = 382.1113, found = 382.1116.

Ethyl-(E)-2-(5,5-dioxido-9-(p-tolyl)-8,9-dihydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-ylidene)acetate (4t)

59% yield; white solid; mp 108-110°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (d, \(J = 6.5\) Hz, 1H), 7.69 (s, 2H), 7.60 (s, 1H), 7.14 (s, 4H), 6.29 (s, 1H), 5.98 (s, 1H), 4.13 (s, 2H), 3.82 (d, \(J = 14.8\) Hz, 2H), 3.27 (s, 1H), 2.33 (s, 3H), 1.26 (s, 3H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.44, 145.55, 139.17, 136.93, 133.78, 131.46, 130.43, 129.60, 129.14, 128.00, 127.27, 121.33, 121.15, 106.41, 101.12, 59.99, 36.86, 31.53, 21.09, 14.29; IR (neat): \(\nu\) 2953, 2873, 2352, 2313, 1703, 1622, 1571, 1471, 1454, 1383, 1266, 1185, 1162, 1144, 754 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{21}\)NO\(_4\)S [M+H]\(^+\) = 396.1270, found = 396.1277.

Benzyl-2-(5,5-dioxido-9-(p-tolyl)-8,9,10,10a-tetrahydro-7H-benzo[4,5]isothiazolo[2,3-a]pyridin-7-yl)acetate (5)

92% yield; white solid; mp 64-66°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.77 (d, \(J = 7.2\) Hz, 1H), 7.54 (dt, \(J = 27.8, 7.1\) Hz, 2H), 7.34 (s, 6H), 7.11 (d, \(J = 8.6\) Hz, 4H), 5.14 (q, \(J = 12.1\) Hz, 2H), 4.39 (d, \(J = 11.0\) Hz, 1H), 3.96 (s, 1H), 3.67 (d, \(J = 15.8\) Hz, 1H), 3.07 – 2.82 (m, 2H), 2.42 (d, \(J = 12.2\) Hz, 1H), 2.32 (s, 3H), 2.09 (d, \(J = 12.3\) Hz, 1H), 1.75 (dt, \(J = 23.3, 11.8\) Hz, 2H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.30, 140.85, 137.61, 136.59, 135.61, 132.87, 129.63, 129.43, 129.29, 128.60, 128.34, 127.29,
(E)-7-(2-hydroxyethylidene)-9-(p-tolyl)-8,9-dihydro-7H-
benzo[4,5]isothiazolo[2,3-a]pyridine 5,5-dioxide (6)

53% yield; white solid; mp 125-128°C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (d, J = 7.7 Hz, 1H), 7.66 (q, J = 7.8 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.19 – 7.07 (m, 4H), 6.23 (t, J = 7.2 Hz, 1H), 5.83 (d, J = 3.4 Hz, 1H), 4.12 (dd, J = 17.6, 7.2 Hz, 2H), 3.79 (d, J = 4.8 Hz, 1H), 2.89 (dd, J = 13.8, 4.9 Hz, 1H), 2.64 (dd, J = 13.8, 7.1 Hz, 1H), 2.33 (s, 3H), 1.13 (s, 1H). \(^1^3\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 139.72, 137.01, 133.31, 132.01, 131.95, 130.25, 130.21, 129.54, 128.45, 127.37, 121.21, 121.06, 112.37, 103.68, 57.68, 38.06, 32.07, 21.06; IR (neat): v 3059, 3021, 2922, 2860, 2378, 2319, 1711, 1672, 1513, 1470, 1316, 1275, 1175, 1158, 1132, 817, 751 cm\(^{-1}\); HRMS (ESI) m/z calcd for C\(_{27}\)H\(_{28}\)NO\(_4\)S [M+H]\(^+\) = 462.1739, found = 462.1735.
S31
The racemic system of 3c, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 99/1; flow rate 1.0 mL/min; 25°C; \( \lambda = 210 \text{ nm} \))

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The asymmetric system of 3c with the chiral cat.1 (\( \beta \)-ICD) in CH\(_2\)Cl\(_2\), enantiomeric excess: 25%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 99/1; flow rate 1.0 mL/min; 25°C; \( \lambda = 210 \text{ nm} \))

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The asymmetric system of 3c with the chiral cat.1 (β-ICD) in toluene, enantiomeric excess: 1%, determined by HPLC (Chiralpak OD-H, hexane/2-propanol = 99/1; flow rate 1.0 mL/min; 25°C; λ = 210 nm)

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The racemic system of 4c, determined by HPLC (Chiralpak IA, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; λ = 210 nm)

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The asymmetric system of 4c with the chiral cat.1 (β-ICD) in CH$_2$Cl$_2$, enantiomeric excess: 17%, determined by HPLC (Chiralpak IA, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; $\lambda = 210$ nm) (The impurity substance peak in HPLC chromatogram could be detected in the $^1$H NMR, but we could not know the structure of the impurity substance).

The asymmetric system of 4c with the chiral cat.1 (β-ICD) in toluene, enantiomeric excess: (-)23%, determined by HPLC (Chiralpak IA, hexane/2-propanol = 80/20; flow rate 1.0 mL/min; 25°C; $\lambda = 210$ nm) (The impurity substance peak in HPLC chromatogram could be detected in the $^1$H NMR, but we could not know the structure of the impurity substance).
VI. X-Ray crystal structure of 3k and 4k

X-ray structure of 3k (The H-atoms are omitted for clarity)  CCDC NO.1438835

X-ray structure of 4k (The H-atoms are omitted for clarity)  CCDC NO. 1438830