Supporting Information

A Formal (3+2) Annulation-Cannizzaro Cascade of Bifunctional Peroxides for the Synthesis of Dihydrofurans

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1. **General Information**

Unless otherwise stated, all reagents obtained from Adamas, Accela, or Acros were used without further purification. All solvents employed in the reactions were distilled from appropriate drying agents prior to use. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Visualization on TLC was achieved by use of UV light (254 nm). Flash column chromatography was performed using Tsingdao silica gel. $^1$H and $^{13}$C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) spectrometer or Agilent 600MR DD2 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and tetramethylsilane (TMS) or the residual solvent peak was used as an internal reference: $^1$H NMR (TMS, $\delta$ 0.00; CDCl$_3$, $\delta$ 7.26; CD$_3$OD, $\delta$ 3.31), $^{13}$C NMR (CDCl$_3$, $\delta$ 77.16; CD$_3$OD, $\delta$ 49.00). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) data were acquired on AB SCIEX TripleTOF 6600 mass spectrometer (AB SCIEX, USA) or Agilent 6546 Q-TOF mass spectrometer (Agilent Technologies, USA) with an ESI source.
2. Optimization of the reaction

Isolation and identification of the new products

\[
\begin{align*}
\text{1a (1.0 equiv) + 2a (1.0 equiv)} & \xrightarrow{\text{Cs}_2\text{CO}_3 (2.0 equiv), \text{EtOAc, rt}} \text{4a (8%)} + \text{5 (16%)} + \text{6 (5%)} \\
\text{3 (1.0 equiv) + 2a (1.0 equiv)} & \xrightarrow{\text{Cs}_2\text{CO}_3 (2.0 equiv), \text{EtOAc, rt}} \text{T (13%)}
\end{align*}
\]

Data of compound 5: \(^1\text{H NMR (600 MHz, CDCl}_3\text{)}\) \(\delta\) 7.79 - 7.70 (m, 2H), 7.47 - 7.34 (m, 3H), 4.36 (d, \(J = 11.7\) Hz, 1H), 4.31 (d, \(J = 11.8\) Hz, 1H), 4.13 (q, \(J = 7.2\) Hz, 2H), 3.75 (s, 2H), 3.05 (d, \(J = 15.5\) Hz, 1H), 2.96 (d, \(J = 15.5\) Hz, 1H), 2.26 (br, s, 1H), 2.11 (s, 3H), 1.21 (t, \(J = 7.1\) Hz, 3H). \(^{13}\text{C NMR (150 MHz, CDCl}_3\text{)}\) \(\delta\) 171.2, 165.0, 164.0, 130.6, 129.7, 129.4, 127.7, 102.6, 87.0, 64.8, 64.3, 60.0, 36.2, 20.9, 14.3. \text{HRMS (ESI) m/z: [M + H]\(^+\) Calcd for C}_{17}\text{H}_{21}\text{O}_6\text{: 321.1333; Found: 321.1335.}

\(^1\text{H-}^1\text{H COSY correlations of compound 5:}\)

![Figure S1. COSY spectrum of compound 5](image-url)
Figure S2. Enlarged view of COSY spectra of 5 (6.0 – 9.0 ppm)

Figure S3. Enlarged view of COSY spectra of 5 (2.5 – 5.0 ppm)
**Figure S4.** Enlarged view of COSY spectra of 5 (0.0 – 2.5 ppm)

$^1$H-$^{13}$C HSQC correlations of compound 5:

**Figure S5.** HSQC spectrum of compound 5
Figure S6. Enlarged view of HSQC spectra of 5 (6.0 – 9.0 and 85 – 175 ppm)

Figure S7. Enlarged view of HSQC spectra of 5 (2.5 – 5.0 and 0 – 100 ppm)
Figure S8. Enlarged view of HSQC spectra of 5 (0.0 – 2.5 and 0 – 55 ppm)

$^1$H-$^{13}$C HMBC correlations of compound 5:

Figure S9. HMBC spectrum of compound 5
Figure S10. Enlarged view of HMBC spectra of 5 (6.0 – 9.0 and 100 – 190 ppm)

Figure S11. Enlarged view of HMBC spectra of 5 (2.5 – 5.0 and 0 – 190 ppm)
Figure S12. Enlarged view of HMBC spectra of 5 (0.5 – 2.5 and 0 – 190 ppm)

Data of compound 6: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 (dd, $J = 8.2$, 1.7 Hz, 2H), 7.43 - 7.31 (m, 3H), 4.30 (d, $J = 11.7$ Hz, 2H), 4.26 (d, $J = 11.7$ Hz, 2H), 4.11 (q, $J = 7.1$ Hz, 2H), 3.02 (s, 2H), 2.10 (s, 6H), 1.18 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.8, 165.0, 164.2, 130.7, 129.4, 127.8, 102.2, 84.8, 64.9, 60.2, 36.7, 20.8, 14.2. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{19}$H$_{23}$O$_7$: 363.1439; Found: 363.1434.

Data of compound 7: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 8.5$ Hz, 2H), 4.34 (s, 2H), 3.76 (s, 2H), 3.04 (d, $J = 15.9$ Hz, 1H), 2.91 (d, $J = 15.9$ Hz, 1H), 2.13 (s, 3H), 1.40 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.3, 164.1, 161.2, 133.5, 131.9 (d, $J = 32.2$ Hz), 129.9, 124.7, 105.8, 87.1, 80.8, 64.7, 64.1, 36.5, 28.2, 20.9. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for C$_{20}$H$_{23}$F$_3$NaO$_6$: 439.1339; Found: 439.1346.

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Table S3. Bond Angles for 7

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<td>30 min</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>19</td>
<td>LiO₂Bu</td>
<td>2.0</td>
<td>DCM</td>
<td>rt</td>
<td>30 min</td>
<td>25</td>
<td>21</td>
</tr>
</tbody>
</table>

Conditions: 1 (0.1 mmol), 2 (0.1 mmol) and base in indicated solvent (1 mL) and temperature.

Table S5. Optimization of the epoxidation reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Equiv.</th>
<th>Sol.</th>
<th>Time</th>
<th>Yield of 12a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et₃N</td>
<td>2.0</td>
<td>DCM</td>
<td>6 h</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>DABCO</td>
<td>2.0</td>
<td>DCM</td>
<td>1 h</td>
<td>39</td>
</tr>
<tr>
<td>3</td>
<td>Na₂CO₃</td>
<td>2.0</td>
<td>DCM</td>
<td>24 h</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>K₂CO₃</td>
<td>2.0</td>
<td>DCM</td>
<td>30 min</td>
<td>81</td>
</tr>
<tr>
<td>5</td>
<td>K₂PO₄</td>
<td>2.0</td>
<td>DCM</td>
<td>20 min</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>K₂CO₃</td>
<td>2.0</td>
<td>PhMe</td>
<td>30 min</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>K₂CO₃</td>
<td>2.0</td>
<td>MeCN</td>
<td>20 min</td>
<td>63</td>
</tr>
<tr>
<td>8</td>
<td>K₂CO₃</td>
<td>2.0</td>
<td>DMF</td>
<td>30 min</td>
<td>55</td>
</tr>
<tr>
<td>9</td>
<td>K₂CO₃</td>
<td>1.0</td>
<td>DCM</td>
<td>45 min</td>
<td>77</td>
</tr>
<tr>
<td>10</td>
<td>K₂CO₃</td>
<td>3.0</td>
<td>DCM</td>
<td>20 min</td>
<td>69</td>
</tr>
</tbody>
</table>

Conditions: 1 (0.1 mmol), 2 (0.1 mmol) and base in indicated solvent (1 mL) and temperature; 12a was isolated as a pair of 1:1 diasteromers.
3. Preparation of the substrates

3.1 Preparation of β-keto esters

Note: Compounds 1a, 1i-k and 1q are commercial available. Other β-keto esters are known compounds and were prepared as following procedure.

**Method A: preparation of 1b.**

50 mL of the dried round bottom flask was taken, and dimethylhydroxylamine hydrochloride (1.02 g, 10.5 mmol, 1.05 equiv) in dry DCM (24 mL) was treated dropwise with triethylamine (2.9 mL, 21.0 mmol, 2.1 equiv) and S1 (1.2mL, 10.0 mmol, 1.0 equiv) at 0 °C. After the addition was completed, the system was returned to room temperature, stirred for 3 h, and the reaction progress was monitored by TLC plate. After the reaction was completed, the reaction was quenched with 10 mL sat. aq. NH₄Cl, the organic phase was separated and the aqueous phase was extracted with DCM (15 mL × 3). The organic phase was combined, washed with brine, dried over Na₂SO₄. The solvent was removed by vacuum and the mixture was purified by column chromatography on silica gel (petroleum ether / EtOAc = 5:1) to give product S2 in
85% yield.

\( n \)-Butyllithium (1.2 M in hexane, 3.1 equiv) was added at -78 °C to a THF solution (0.1 M) containing diisopropylamine (3.0 equiv) in a round-bottomed flask flushed with argon. After 30 min at 0 °C, the medium was recooled to -78 °C and freshly distilled tert-butyl acetate (3.0 equiv) was added. After 30 min at -78 °C, S2 (1.0 equiv) was added at this temperature. After 1 h, the reaction was quenched at room temperature with sat. aq. NaHCO\(_3\), and the mixture extracted with EtOAc (20 mL × 3). The combined organic layer was washed with sat. aq. NH\(_4\)Cl (20 mL) and brine (20 mL), dried over Na\(_2\)SO\(_4\), and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether / EtOAc = 50:1) to give product 1b in 92% yield.

**Method B: preparation of 1c.**

An aqueous sodium hydroxide solution (1.0 M, 50 mL) was added to ethylbenzoylacetate (8.7 mL, 50.0 mmol). This mixture was stirred overnight at room temperature then transferred to a separating funnel. It was washed with DCM (3 × 10 mL) and the aqueous layer acidified to pH 1 by the addition of 2.0 M HCl. The precipitate was collected by suction filtration and dried under vacuum to yield benzoylacetic acid S3 (6.3 g, 39.0 mmol, 78%), which was used without further purification.

A solution of acid S3 (1.640 g, 10.0 mmol) and the benzyl alcohol (10.0 mmol) in acetonitrile (20 mL) was prepared. To this solution was added a solution of dicyclohexylcarbodiimide (2.1 g, 10.0 mmol) and 4-dimethylaminopyridine (61 mg, 0.5 mmol) in acetonitrile (10 mL) under rapid stirring. This mixture was stirred overnight at room temperature. Then the mixture was directly purified by column chromatography on silica gel (petroleum ether / EtOAc = 50:1) to give product 1c in 85% yield.
Method C: preparation of 1d-h and 1p.

\[
\text{O} \quad \text{O} \quad \overset{\text{NaH}}{\xrightarrow{\text{Tol, reflux}}} \quad \text{O} \quad \text{O} \\
S4 \quad \text{EtO} \quad \text{OEt} \quad \text{OEt} \quad 1d-h, 1p
\]

To a dried three-necked flask equipped with a dropping funnel, a condenser, and a magnetic stirrer was added NaH (1.1 g, 28.0 mmol, 2.8 equiv, 60% in mineral oil), diethyl carbonate (2.4 mL, 20.0 mmol, 2.0 equiv.), and toluene (10 mL). The mixture was heated to reflux. A solution of ketone S4 (10.0 mmol, 1.0 equiv.) in toluene (5 mL) was added dropwise from the dropping funnel over 1-2 h. After the addition, the mixture was heated to reflux until the evolution of hydrogen ceased (15-20 min). When the reaction was cooled to room temperature, glacial acetic acid (3 mL) was added dropwise and a heavy, pasty solid appeared. Ice-water was added until the solid was dissolved completely. The toluene layer was separated, and the aqueous layer was extracted with EtOAc (20 mL × 3). The combined organic layer was washed with water (20 mL) and brine (20 mL), then dried over Na\textsubscript{2}SO\textsubscript{4}. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether / EtOAc = 40:1 ~ 20:1) to give the corresponding \(\beta\)-keto esters 1d-h and 1p in 60-77% yields (Note: THF solvent was used in case of 1p).

Method D: preparation of 1l.

\[
\text{O} \quad \text{O} \quad \overset{\text{K}_2\text{CO}_3, \text{I}_2}{\xrightarrow{\text{THF, 60 }^\circ\text{C}}} \quad \text{O} \quad \text{O} \\
\text{S}5 \quad \text{Ph} \quad \text{SO} \quad \text{SO} \quad 1l \quad \text{Ph}
\]

To a round bottom flask charged with S5 (10.0 mmol, 1.0 equiv), sodium benzenesulfinate dihydrate (2.0 g, 12.0 mmol, 1.2 equiv), K\textsubscript{2}CO\textsubscript{3} (2.1 g, 15.0 mmol, 1.5 equiv), and iodine (5.0 g, 20.0 mmol, 2.0 equiv) was added THF (50 mL). This mixture was stirred at room temperature overnight until the complete consumption of the starting material as monitored by TLC. A solution of Na\textsubscript{2}SO\textsubscript{3} (5.0 g, 34.0 mmol) in H\textsubscript{2}O (50 mL) was added to the mixture and then the reaction was stirred at 60 °C for 4 h. Upon completion of the reaction, the solution was extracted with EtOAc (3 × 40 mL), and the organic layer was separated, dried and concentrated to give a residue, which
was purified by flash column chromatography on silica gel (petroleum ether / EtOAc = 9:1) to afford the desired β-keto sulfonate product 1I in 65% yield.

**Method E: preparation of 1m-n.**

![Chemical structure of S6 and 1m-n](image)

To a suspension of NaH (0.4 g, 10.0 mmol, 1.0 equiv, 60% in mineral oil) in dry THF (20 mL) was added dropwise S6 (10.0 mmol, 1.0 equiv). When the gas evolution stopped, alkyl halide (10.0 mmol, 1.0 equiv) was added slowly. The reaction mixture was stirred for a further 20 h at room temperature then quenched with sat. aq. NH₄Cl (30 mL). The phases were separated and the aqueous phase further extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether / EtOAc = 40:1 ~ 20:1) to give the corresponding β-keto esters 1m-n in 85-90% yields.

**Method F: preparation of 1o.**

![Chemical structure of S7 and 1o](image)

The mixture of S7 (30.0 mmol, 1.0 equiv), K₂CO₃ (45.0 mmol, 1.5 equiv) and methyl iodide (33.0 mmol, 1.1 equiv) in dry DMF (30 mL) was heated under an argon atmosphere at 60 °C for 4 h. The reaction mixture was then poured into water and the aqueous layer was extracted with EtOAc (3 × 50 mL). The organic layer was washed with water, brine and dried over anhydrous Na₂SO₄. Evaporation of solvent and purification by flash column chromatography on silica gel (petroleum ether / EtOAc = 20:1) afforded the product 1o in 77% yield.

Following the general method A, 1b was obtained as a yellow oil in 3:10 mixture of enol and keto form (10.0 mmol scale, 2.0 g, 92% yield). ^1H NMR (400 MHz, CDCl₃)
δ 12.72 (s, 0.3H), 7.94 (d, J = 7.4 Hz, 2H), 7.76 (d, J = 8.8 Hz, 0.6H), 7.59 (t, J = 7.4 Hz, 0.9H), 7.53 - 7.35 (m, 3H), 5.58 (s, 0.3H), 3.90 (s, 2H), 1.54 (s, 3H), 1.43 (s, 9H).

The spectral data of 1b was consistent with that reported in the literature.¹

Following the general method B, 1c was obtained as a yellow oil in 3:10 mixture of enol and keto form (10.0 mmol scale, 2.2 g, 85% yield).¹

**H NMR** (400 MHz, CDCl₃)

δ 12.48 (s, enol), 7.90 (d, J = 8.0 Hz, enol), 7.86 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 7.9 Hz, enol), 7.51 (t, J = 7.5 Hz, 1H), 7.44–7.24 (m, 7H), 5.68 (s, enol), 5.19 (s, enol), 5.13 (s, 2H), 3.98 (s, 2H). The spectral data of 1c was consistent with that reported in the literature.²

Following the general method C, 1d was obtained as a light yellow oil in 1:11 mixture of enol and keto form (10.0 mmol scale, 1.6 g, 73% yield).¹

**H NMR** (400 MHz, CDCl₃)

δ 12.63 (s, 0.09H), 7.93 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 5.58 (s, 0.09H), 4.21 (q, J = 7.1 Hz, 2H), 3.94 (s, 2H), 3.87 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). The spectral data of 1d was consistent with that reported in the literature.³

Following the general method C, 1e was obtained as a light yellow oil in 1:4 mixture of enol and keto form (10.0 mmol scale, 1.6 g, 75% yield).¹

**H NMR** (600 MHz, CDCl₃)

δ 12.61 (s, 0.25H), 7.98 (dd, J = 8.6, 5.4 Hz, 2H), 7.15 (t, J = 8.5 Hz, 2H), 5.59 (s, 0.25H), 4.21 (q, J = 7.1 Hz, 2H), 3.96 (s, 2H), 1.26 (t, J = 7.1 Hz, 3H). The spectral data of 1e was consistent with that reported in the literature.³
Following the general method C, 1f was obtained as a yellow oil in 1:2 mixture of enol and keto form (10.0 mmol scale, 1.6 g, 60% yield). \textbf{1H NMR (400 MHz, CDCl}_3) \( \delta \) 12.56 (s, 0.5H), 8.06 (d, \( J = 8.1 \) Hz, 2H), 7.88 (d, \( J = 8.1 \) Hz, 1H), 7.76 (d, \( J = 8.1 \) Hz, 2H), 7.68 (d, \( J = 8.1 \) Hz, 1H), 5.72 (s, 0.5H), 4.29 (q, \( J = 7.1 \) Hz, 1H), 4.22 (q, \( J = 7.1 \) Hz, 2H), 4.01 (s, 2H), 1.35 (t, \( J = 7.1 \) Hz, 1.5H), 1.26 (t, \( J = 7.1 \) Hz, 3H). The spectral data of 1f was consistent with that reported in the literature.\(^3\)

\begin{center}
\includegraphics[width=0.2\textwidth]{image1}
\end{center}

Following the general method C, 1g was obtained as a light yellow solid in 1:4 mixture of enol and keto form (10.0 mmol scale, 1.6 g, 62% yield). \textbf{1H NMR (600 MHz, CDCl}_3) \( \delta \) 12.67 (s, 0.25H), 8.46 (s, 1H), 8.02 (d, \( J = 8.6 \) Hz, 1H), 7.98 (d, \( J = 8.6 \) Hz, 1H), 7.90 (dd, \( J = 15.8, 8.3 \) Hz, 2H), 7.63 (t, \( J = 7.5 \) Hz, 1H), 7.57 (t, \( J = 7.5 \) Hz, 1H), 5.81 (s, 0.25H), 4.24 (q, \( J = 7.1 \) Hz, 2H), 4.12 (s, 2H), 1.27 (t, \( J = 7.1 \) Hz, 3H). The spectral data of 1g was consistent with that reported in the literature.\(^3\)

\begin{center}
\includegraphics[width=0.2\textwidth]{image2}
\end{center}

Following the general method C, 1h was obtained as a light yellow oil in keto form (10.0 mmol scale, 1.5 g, 76% yield). \textbf{1H NMR (600 MHz, CDCl}_3) \( \delta \) 7.72 (d, \( J = 3.8 \) Hz, 1H), 7.67 (d, \( J = 4.9 \) Hz, 1H), 7.13 (t, \( J = 4.4 \) Hz, 1H), 4.20 (q, \( J = 7.2 \) Hz, 2H), 3.90 (s, 2H), 1.25 (t, \( J = 7.1 \) Hz, 3H). The spectral data of 1h was consistent with that reported in the literature.\(^3\)

\begin{center}
\includegraphics[width=0.2\textwidth]{image3}
\end{center}

Following the general method D, 1l was obtained as a yellow solid (10.0 mmol scale, 1.7 g, 65% yield). \textbf{1H NMR (400 MHz, CDCl}_3) \( \delta \) 7.90 (d, \( J = 7.8 \) Hz, 4H), 7.67 - 7.59 (m, 2H), 7.54 (t, \( J = 7.7 \) Hz, 2H), 7.47 (t, \( J = 7.7 \) Hz, 2H), 4.74 (s, 2H). The spectral data of 1l was consistent with that reported in the literature.\(^3\)
Following the general method E, 1m was obtained as a yellow oil (10.0 mmol scale, 1.9 g, 90% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, $J = 7.1$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.49-7.45 (m, 2H), 4.37 (q, $J = 7.1$ Hz, 1H), 4.14 (q, $J = 7.1$ Hz, 2H), 1.49 (d, $J = 7.1$ Hz, 3H), 1.16 (t, $J = 7.1$ Hz, 3H). The spectral data of 1m was consistent with that reported in the literature.$^4$

Following the general method E, 1n was obtained as a colorless oil (10.0 mmol scale, 2.4 g, 85% yield). $^1$H NMR (600 MHz, CDCl$_3$). δ 7.96 (d, $J = 7.98$ Hz, 2H), 7.56 (t, $J = 7.26$ Hz, 1H), 7.45 (d, $J = 7.50$ Hz, 2H), 7.23 - 7.27 (m,5H), 7.19 (t, $J = 7.08$ Hz, 1H), 4.62 (t, $J = 7.26$ Hz, 1H), 4.11 (q, $J = 6.96$ Hz, 2H), 3.30 - 3.37 (m, 2H), 1.11 (t, $J = 7.02$ Hz, 3H). The spectral data of 1n was consistent with that reported in the literature.$^5$

Following the general method F, 1o was obtained as a yellow oil (10.0 mmol scale, 1.4 g, 77% yield). $^1$H NMR (400 MHz, CDCl$_3$). δ 4.17 (q, $J = 7.0$ Hz, 2H), 3.50 (q, $J = 7.2$ Hz, 1H), 2.64 - 2.39 (m, 2H), 1.63 - 1.50 (m, 2H), 1.37 - 1.21 (m, 8H), 0.89 (t, $J = 7.3$ Hz, 3H). The spectral data of 1o was consistent with that reported in the literature.$^6$

Following the general method C, 1p was obtained as a light brown oil (10.0 mmol scale, 1.7 g, 77% yield). $^1$H NMR (400 MHz, CDCl$_3$).δ12.49 (1H, s), 8.05 (dd, $J = 7.8$, 1.4 Hz, 1H), 7.80 (dd, $J = 7.6$, 1.5 Hz, 1H), 7.49 (td, $J = 7.5$, 1.5 Hz, 1H), 7.34 - 7.26 (m, 2H), 7.26 - 7.24 (m, 1H), 4.28 (q, 4H), 4.30 - 4.22 (m, 2H), 3.62 - 3.58 (dd, $J = 10.4$, 4.7 Hz, 1H), 3.10-2.94 (m, 2H), 2.83 - 2.79 ( m, 2H), 2.59 - 2.55 (m, 2H), 2.52 -
2.46 (m, 1H), 2.40 - 2.32 (m, 1H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H). The spectral data of 1p was consistent with that reported in the literature.9

3.2 Preparation of the peroxides

\[
\begin{align*}
\text{2a} & \quad \text{O} & \quad \text{O} & \quad \text{Bu} \\
\text{2b} & \quad \text{O} & \quad \text{O} & \quad \text{Bu} \\
\text{2c} & \quad \text{O} & \quad \text{O} & \quad \text{Bu} \\
\text{11} & \quad \text{O} & \quad \text{O} & \quad \text{Bu}
\end{align*}
\]


\[
\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad \text{Nal} & \quad \text{acetone, 50 °C} & \quad \text{S8} & \quad \text{S9} \\
\text{Cl} & \quad \text{Cl} & \quad \text{K}_2\text{CO}_3, \text{TFA} & \quad \text{DMF, 40 °C} & \quad \text{S10} & \quad \text{2a}
\end{align*}
\]

S8 and S9 were prepared according to literature report.3

To a solution of S9 (2.0 g, 7.4 mmol, 1.0 equiv) in DMF (74 mL) was added K$_2$CO$_3$ (2.6 g, 18.5 mmol, 2.5 equiv) and TFA (1.4 mL, 18.5 mmol, 2.5 equiv) at room temperature. The mixture was heated to 40 °C and stirred for 3.5 h. After completion, EtOAc (300 mL) was added and the mixture was washed with brine (100 mL × 3), dried over Na$_2$SO$_4$ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 10:1) to afford the compound S10 (889 mg, 75% yield) as a colorless oil.

To a solution of the S10 (889 mg, 5.5 mmol, 1.0 equiv) in DCM (55 mL) was added Dess-Martin reagent (3.5 g, 8.3 mmol, 1.5 equiv) at room temperature. The reaction mixture was stirred for 1 h. After completion, the solution was quenched with sat. aq. NaHCO$_3$ (100 mL). The organic layer was separated, the aqueous layer was extracted with DCM (20 mL × 3), dried over Na$_2$SO$_4$ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 30:1) to afford the product 2a (713 mg, 81% yield) as a colorless oil. $^1$H NMR (400
MHz, CDCl$_3$) $\delta$ 9.57 (d, $J$ = 1.0 Hz, 1H), 6.56 (s, 1H), 6.20 (s, 1H), 4.65 (s, 2H), 1.22 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.1, 144.9, 135.8, 80.7, 70.5, 26.2. HRMS (ESI) m/z: [M + K]$^+$ Calcd for C$_8$H$_{14}$KO$_3$: 197.0575; Found: 197.0507.

**Method B: preparation of 2b-c.**

Following a literature procedure$^8$, methyl acrylate (10.0 mmol, 1.0 equiv), aldehyde (12.0 mmol, 1.2 equiv), formamide (1.0 mmol, 0.1 equiv) and DABCO (3.0 mmol, 0.3 equiv) were stirred at room temperature for 1~3 days. After completion, the reaction was directly submitted to flash silica gel chromatography (petroleum ether / EtOAc = 2:1 - 1:1) to afford the MBH adduct $S_{11}$ in 85-92% yields.

LiBr (3.0 equiv) was added to a solution of the appropriate MBH adduct $S_{11}$ (1.0 equiv) in anhydrous DCM (1.0 M) at room temperature. After cooling to 0 °C, 98 % H$_2$SO$_4$ (1.5 equiv) was rapidly added. And then the reaction was allowed to warm to room temperature and stir for 15-20 h. After completion, the solution was quenched with sat. aq. Na$_2$CO$_3$. The organic layer was separated, the aqueous layer was extracted with DCM, dried over Na$_2$SO$_4$ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 70:1) to afford the product $S_{12}$ in 67-82% yields.$^8$

To a solution of the $S_{12}$ (1.0 equiv) in anhydrous DCM (0.1 M) was added DIBAL-H (3.0 equiv) dropwise under a N$_2$ atmosphere at 0 °C. After 1 h, added MeOH dropwise to quench the reaction. Then the mixture was added sat. aq. Rochelle's salt at room temperature and stir for 1 h. After completion, the solution was filtered through a pad of celite and washed with DCM. The filtrate was washed with brine, dried over
Na₂SO₄ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 10:1) to afford the compound S13 in 65-77% yields.

To a solution of the S13 (1.0 equiv), tert-butyl hydroperoxide (3.1 M solution in hexane, 1.0 equiv) and TBAB (0.1 equiv) in DCM (0.1 M) was added powder KOH (1.0 equiv). The resulting solution was stirred at room temperature for 2-4 h. After completion, the reaction was quenched by water. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 10:1) to afford the compound S14 in 85-89% yields.

To a solution of the S14 (1.0 equiv) in DCM (0.1 M) was added Dess-Martin reagent (1.5 equiv) at room temperature. The reaction mixture was stirred for 1 h. After completion, the solution was quenched with sat. aq. NaHCO₃. The organic layer was separated, the aqueous layer was extracted with DCM, dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 30:1) to afford the products 2b-c in 62-75% yields.

Following the above procedure, 2b was obtained as a light yellow oil (65 mg, 75% yield).¹H NMR (400 MHz, CDCl₃) δ 9.44 (s, 1H), 6.88 (q, J = 7.1 Hz, 1H), 4.68 (s, 2H), 2.13 (d, J = 7.0 Hz, 3H), 1.22 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 193.5, 155.6, 138.7, 80.6, 65.4, 26.4, 15.6. HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₉H₁₆NaO₅: 195.0992; Found: 195.1022.

Following the above procedure, 2c was obtained as a colorless oil (66 mg, 62% yield).
yield.\textsuperscript{1} \textbf{H NMR (400 MHz, CDCl\textsubscript{3})} \(\delta\) 9.44 (s, 0.8H), 9.41 (s, 0.2H), 6.78 (t, \(J = 7.6\) Hz, 0.8H), 6.71 (t, \(J = 7.6\) Hz, 0.2H), 4.65 (s, 1.5H), 4.09 (s, 0.5H), 2.40 (t, \(J = 7.2\) Hz, 2H), 1.84 (m, 1H), 0.97 (d, \(J = 6.7\) Hz, 6H). \textbf{13C NMR (100 MHz, CDCl\textsubscript{3})} \(\delta\) 193.5, 192.0, 159.5, 157.4, 140.5, 138.1, 80.6, 65.8, 38.3, 38.2, 28.4, 28.2, 26.4, 22.7, 22.6, 19.9. 
\textbf{HRMS (ESI)} m/z: [M + H]\textsuperscript{+} Calcd for C\textsubscript{12}H\textsubscript{23}O\textsubscript{3}: 215.1642; Found: 215.1648.

\textbf{Method C: preparation of 10.}

\[ \begin{array}{c}
\text{O} \quad \text{H} \quad \text{O} \quad \text{Bu} \\
\text{2a} \quad \text{MeLi} \quad \text{THF, -78 °C} \quad \text{HO} \quad \text{O} \quad \text{O} \quad \text{Bu} \\
\text{S15} \quad \text{Dess-Martin} \quad \text{DCM, rt} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{Bu} \\
\text{10}
\end{array} \]

To a solution of the 2a (158 mg, 1.0 mmol, 1.0 equiv) in anhydrous THF (10 mL) was added MeLi (2.5 equiv) dropwise under a N\textsubscript{2} atmosphere at -78 °C. After 1 h, quench the reaction by sat. aq. NH\textsubscript{4}Cl (10 mL). The mixture was extracted with EtOAc (5 mL × 3), dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuum to afford the crude product S15 (170 mg) without further purification.

To a solution of the crude compound S15 (170 mg, 1.0 mmol, 1.0 equiv) in DCM (10 mL) was added Dess-Martin reagent (636 mg, 1.5 mmol, 1.5 equiv) at room temperature. The reaction mixture was stirred for 1 h. After completion, the solution was quenched with sat. aq. NaHCO\textsubscript{3} (20 mL). The organic layer was separated, the aqueous layer was extracted with DCM (10 mL × 3), dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 30:1) to afford the product 10 (115 mg, 67% overall yield of two steps) as a light yellow oil. \textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} \(\delta\) 6.18 (s, 1H), 6.09 (s, 1H), 4.65 (s, 2H), 2.34 (s, 3H), 1.22 (s, 9H). \textbf{\textsuperscript{13C NMR (100 MHz, CDCl\textsubscript{3})} \(\delta\) 198.7, 143.9, 127.5, 80.7, 72.8, 26.4, 26.0. \textbf{HRMS (ESI)} m/z: [M + Na]\textsuperscript{+} Calcd for C\textsubscript{9}H\textsubscript{16}NaO\textsubscript{3}: 195.0992; Found: 195.0990.
4. General procedure for the synthesis of dihydrofurans

\[
\begin{align*}
&\text{O} \quad \text{EWG} + \quad \text{O} \quad \text{R}^2 \quad \text{H} \quad \text{O} \quad \text{O} \quad \text{Bu} \\
&\text{KOH} \quad \text{DCM}, \text{rt} \\
&\text{GWE} \quad \text{R}^1 \quad \text{OH} \quad \text{GWE} \quad \text{R}^2 \quad \text{OH} \\
&\text{OH} \\
&\text{OH}
\end{align*}
\]

To a solution of 1 (0.2 mmol, 1.0 equiv) and 2 (0.2 mmol, 1.0 equiv) in DCM (1 mL) was added powder KOH (22 mg, 0.4 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 10-60 min. After completion, the reaction was quenched by water (2 mL) and extracted with DCM (3 mL × 3). The separated aqueous layer was left for further acidification (see below). The separated organic layers were collected, dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 3:1 ~ 2:1) to afford the alcohol products 4 in 29-45% yields.

Additionally, the above mentioned aqueous layer was treated with 2.0 M HCl to adjust the pH to 2~3 and extracted with DCM (3 mL × 3). The combined organic phase was dried and concentrated. The solid residue was triturated with petroleum ether / diethyl ether (10: 1) and filtered to afford the carboxylic acid products 8b-8e and 8g in 42-29% yields. While in case of slurry residue, the carboxylic acid products 8a, 8f, and 8h-n were purified by flash silica gel chromatography (DCM / MeOH = 15:1 ~ 5:1) in 43-27% yields.

Following the general procedure, 4a was obtained as a colorless oil (0.2 mmol scale, 25 mg, 45% yield). $^1$H NMR (400 MHz, CDCl₃) δ 7.80 - 7.70 (m, 2H), 7.45 - 7.33 (m, 3H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.85 - 3.79 (m, 4H), 2.95 (s, 2H), 2.38 (br, s, 2H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl₃) δ 165.1, 163.8, 130.5, 129.7, 129.3, 127.6, 102.8, 88.5, 65.1, 60.0, 35.8, 14.2. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{15}$H$_{19}$O$_5$: 279.1227; Found: 279.1217.
Following the general procedure, 8a was obtained as a colorless oil (0.2 mmol scale, 25 mg, 43% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.86 - 7.79 (m, 2H), 7.45 - 7.33 (m, 3H), 4.08 (q, $J = 7.1$ Hz, 2H), 3.93 (d, $J = 11.7$ Hz, 1H), 3.84 (d, $J = 11.7$ Hz, 1H), 3.28 (d, $J = 15.3$ Hz, 1H), 3.12 (d, $J = 15.3$ Hz, 1H), 1.17 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 178.7, 167.0, 166.9, 131.9, 131.2, 130.7, 128.5, 102.8, 92.0, 67.2, 60.9, 38.6, 14.5. HRMS (ESI) m/z: [M - H]$^-$ Calcd for C$_{15}$H$_{15}$O$_6$: 291.0863; Found: 291.0817.

Following the general procedure, 4b was obtained as a colorless oil (0.2 mmol scale, 24 mg, 39% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 - 7.67 (m, 2H), 7.41 - 7.34 (m, 3H), 3.88 - 3.82 (m, 4H), 2.93 (s, 2H), 1.64 (br, s, 2H), 1.39 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.6, 162.8, 130.3, 129.4, 127.8, 104.8, 88.2, 80.4, 65.4, 36.3, 28.3. HRMS (ESI) m/z: [M - H]$^-$ Calcd for C$_{17}$H$_{21}$O$_5$: 305.1383; Found: 305.1332.

Following the general procedure, 8b was obtained as a yellow solid (0.2 mmol scale, 27 mg, 42% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.78 - 7.71 (m, 2H), 7.44 - 7.34 (m, 3H), 3.92 (d, $J = 11.7$ Hz, 1H), 3.83 (d, $J = 11.7$ Hz, 1H), 3.24 (d, $J = 15.4$ Hz, 1H), 3.08 (d, $J = 15.4$ Hz, 1H), 1.35 (s, 9H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 178.8, 166.4, 165.7, 132.1, 131.0, 130.7, 128.5, 104.5, 90.8, 81.2, 66.7, 38.9, 28.5. HRMS (ESI) m/z: [M - H]$^-$ Calcd for C$_{17}$H$_{19}$O$_6$: 319.1176; Found: 319.1121. Melting point: 190.3 – 191.2 °C.
Following the general procedure, 4c was obtained as a white oil (0.2 mmol scale, 24 mg, 35% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 - 7.66 (m, 2H), 7.47 - 7.21 (m, 9H), 5.12 (s, 2H), 3.88 - 3.82 (m, 4H), 3.00 (s, 2H), 1.84 (br, s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.0, 164.7, 136.2, 130.6, 129.8, 129.4, 128.5, 128.2, 128.1, 128.1, 127.8, 102.6, 88.8, 65.9, 65.0, 35.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{20}$H$_{21}$O$_5$: 341.1384; Found: 341.1382.

Following the general procedure, 8c was obtained as a white solid (0.2 mmol scale, 28 mg, 39% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.79 (d, $J = 7.4$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.36 - 7.18 (m, 7H), 5.08 (s, 2H), 3.92 (d, $J = 11.8$ Hz, 1H), 3.83 (d, $J = 11.7$ Hz, 1H), 3.31 (d, $J = 15.3$ Hz, 1H), 3.17 (d, $J = 15.3$ Hz, 1H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 177.7, 167.1, 166.3, 137.7, 131.5, 131.3, 130.7, 130.5, 129.4, 129.0, 128.5, 102.6, 91.0, 66.6, 38.6. HRMS (ESI) m/z: [M - H]$^-$ Calcd for C$_{20}$H$_{17}$O$_6$: 353.1019; Found: 353.0958. Melting point: 132.1 – 133.4 ℃.

Following the general procedure, 4d was obtained as a colorless oil (0.2 mmol scale, 27 mg, 43% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 8.5$ Hz, 2H), 6.88 (d, $J = 8.5$ Hz, 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.90 - 3.73 (m, 7H), 2.92 (s, 2H), 2.32 (br, s, 2H), 1.22 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.5, 163.8, 161.5, 131.3, 122.1, 113.2, 101.5, 88.1, 65.3, 60.0, 55.5, 36.1, 14.4. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{16}$H$_{21}$O$_6$: 309.1333; Found: 309.1333.
Following the general procedure, 8d was obtained as a white solid (0.2 mmol scale, 26 mg, 41% yield). \(^1\)H NMR (400 MHz, CD\(_2\)OD) \(\delta\) 7.86 (d, \(J = 8.9\) Hz, 2H), 6.93 (d, \(J = 8.9\) Hz, 2H), 4.12 (q, \(J = 6.8\) Hz, 2H), 3.96 (d, \(J = 12.0\) Hz, 1H), 3.85 - 3.82 (m, 4H), 3.23 (d, \(J = 15.6\) Hz, 1H), 3.15 (d, \(J = 15.5\) Hz, 1H), 1.22 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CD\(_2\)OD) \(\delta\) 179.1, 167.0, 166.6, 162.9, 132.6, 123.9, 113.8, 101.3, 91.0, 66.9, 60.8, 55.8, 38.8, 14.6. HRMS (ESI) m/z: [M + H]\(^+\) Calcd for C\(_{16}\)H\(_{19}\)O\(_7\): 323.1125; Found: 323.1125. Melting point: 181.4 – 182.1 °C.

Following the general procedure, 4e was obtained as a colorless oil (0.2 mmol scale, 21 mg, 30% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90 (d, \(J = 8.4\) Hz, 2H), 7.63 (d, \(J = 8.4\) Hz, 2H), 4.14 (q, \(J = 7.1\) Hz, 2H), 3.88 - 3.82 (m, 4H), 2.99 (s, 2H), 2.23 (br, s, 2H), 1.21 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.0, 162.3, 133.4, 132.2 (d, \(J = 32.8\) Hz), 129.9, 124.7 (q, \(J = 3.8\) Hz), 124.0 (d, \(J = 271.9\) Hz), 104.6, 89.1, 65.2, 60.4, 36.0, 14.3. HRMS (ESI) m/z: [M + H]\(^+\) Calcd for C\(_{16}\)H\(_{18}\)F\(_3\)O\(_5\): 347.1100; Found: 347.1105.

Following the general procedure, 8e was obtained as a yellow solid (0.2 mmol scale, 24 mg, 33% yield). \(^1\)H NMR (400 MHz, CD\(_2\)OD) \(\delta\) 8.02 (d, \(J = 8.2\) Hz, 2H), 7.68 (d, \(J = 8.3\) Hz, 2H), 4.09 (q, \(J = 7.1\) Hz, 2H), 3.94 (d, \(J = 11.8\) Hz, 1H), 3.85 (d, \(J = 11.8\) Hz, 1H), 3.33 (d, \(J = 15.7\) Hz, 1H), 3.16 (d, \(J = 15.7\) Hz, 1H), 1.17 (t, \(J = 7.1\) Hz, 3H).
Figure 4

Following the general procedure, 4f was obtained as a colorless oil (0.2 mmol scale, 24 mg, 40% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (dd, $J = 8.1, 5.9$ Hz, 2H), 7.03 (t, $J = 8.6$ Hz, 2H), 4.11 (q, $J = 7.1$ Hz, 2H), 3.85 - 3.71 (m, 4H), 3.00 - 2.75 (m, 4H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.3, 164.0 (d, $J = 251.5$ Hz), 163.0, 131.8 (d, $J = 8.6$ Hz), 126.0 (d, $J = 3.3$ Hz), 114.8 (d, $J = 21.7$ Hz), 102.7, 88.6, 65.0, 60.2, 36.0, 14.3. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{15}$H$_{18}$FO: 297.1132; Found: 297.1126.

Following the general procedure, 8f was obtained as a colorless oil (0.2 mmol scale, 23 mg, 37% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.96 - 7.88 (m, 2H), 7.11 (t, $J = 8.8$ Hz, 2H), 4.11 (q, $J = 7.1$ Hz, 2H), 3.95 (d, $J = 11.9$ Hz, 1H), 3.84 (d, $J = 11.7$ Hz, 1H), 3.26 (d, $J = 15.6$ Hz, 1H), 3.16 (d, $J = 15.5$ Hz, 1H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 174.7, 166.3, 165.3 (d, $J = 249.0$ Hz), 165.1, 133.2 (d, $J = 8.6$ Hz), 127.4 (d, $J = 3.1$ Hz), 115.5 (d, $J = 22.0$ Hz), 102.9, 90.1, 66.2, 61.1, 38.4, 14.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{15}$H$_{16}$FO$_6$: 311.0925; Found: 311.0919.
Following the general procedure, 4g was obtained as a light yellow oil (0.2 mmol scale, 22 mg, 33% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.31 (s, 1H), 7.91 - 7.80 (m, 4H), 7.55 - 7.47 (m, 2H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.92 - 3.86 (m, 4H), 3.02 (s, 2H), 2.01 (br, s, 2H), 1.20 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.3, 163.8, 134.3, 132.5, 129.9, 128.9, 127.8, 127.5, 127.3, 126.5, 126.2, 103.3, 88.6, 65.4, 60.1, 36.2, 14.4. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{19}$H$_{21}$O$_5$: 329.1384; Found: 329.1381.

Following the general procedure, 8g was obtained as a light yellow solid (0.2 mmol scale, 20 mg, 29% yield). $^1$H NMR (400 MHz, CD$_3$OD) δ 8.43 (s, 1H), 7.96 - 7.80 (m, 4H), 7.54 - 7.51 (m, 2H), 4.10 (q, $J = 7.1$ Hz, 2H), 3.97 (d, $J = 11.8$ Hz, 1H), 3.86 (d, $J = 11.8$ Hz, 1H), 3.33 (d, $J = 15.4$ Hz, 1H), 3.20 (d, $J = 15.4$ Hz, 1H), 1.16 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD) δ 178.2, 167.0, 166.7, 135.6, 133.8, 131.1, 129.7, 129.1, 128.6, 128.3, 127.8, 127.7, 127.3, 103.1, 91.8, 67.1, 61.0, 38.8, 14.6. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{19}$H$_{19}$O$_6$: 343.1176; Found: 343.1177. Melting point: 211.8 – 212.7 °C.

Following the general procedure, 4h was obtained as a yellow oil (0.2 mmol scale, 26 mg, 45% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.17 (d, $J = 3.8$ Hz, 1H), 7.49 (d, $J = 5.1$ Hz, 1H), 7.10 - 7.08 (m, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 3.82 (s, 4H), 2.98 (s, 2H), 2.09 (br, s, 2H), 1.31 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.3, 157.4, 132.4, 131.2, 130.3, 127.3, 101.3, 88.7, 65.2, 60.2, 36.0, 14.6. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{17}$O$_5$S: 285.0791; Found: 285.0790.
Following the general procedure, 8h was obtained as a yellow oil (0.2 mmol scale, 24 mg, 40% yield). ¹H NMR (400 MHz, CD₃OD) δ 8.19 (dd, J = 3.9, 1.3 Hz, 1H), 7.63 (dd, J = 5.0, 1.2 Hz, 1H), 7.11 (dd, J = 5.1, 3.8 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.94 (d, J = 11.8 Hz, 1H), 3.83 (d, J = 11.7 Hz, 1H), 3.27 (d, J = 15.7 Hz, 1H), 3.16 (d, J = 15.7 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CD₃OD) δ 177.4, 166.6, 159.7, 133.6, 132.3, 127.8, 101.0, 90.8, 66.7, 61.0, 38.7, 14.78. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₃H₁₅O₆S: 299.0584; Found: 299.0584.

Following the general procedure, 4i was obtained as a colorless oil (0.2 mmol scale, 13 mg, 30% yield). ¹H NMR (400 MHz, CDCl₃) δ 4.15 (q, J = 7.1 Hz, 2H), 3.75 (s, 4H), 2.69 (s, 2H), 2.27 (br, s, 2H), 2.20 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.8, 166.1, 102.5, 89.3, 65.4, 59.8, 34.4, 14.5, 14.3. HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₀H₁₆NaO₅: 239.0890; Found: 239.0898.

Following the general procedure, 8i was obtained as a colorless oil (0.2 mmol scale, 12 mg, 27% yield). ¹H NMR (400 MHz, CD₃OD) δ 4.14 (q, J = 7.1 Hz, 2H), 3.83 (d, J = 11.7 Hz, 1H), 3.72 (d, J = 11.7 Hz, 1H), 3.01 (d, J = 14.7 Hz, 1H), 2.89 (d, J = 14.8 Hz, 1H), 2.23 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CD₃OD) δ 179.4, 169.4, 167.7, 102.4, 91.8, 67.0, 60.7, 37.1, 14.8, 14.4. HRMS (ESI) m/z: [M - H]⁻ Calcd for C₁₀H₁₃O₆: 229.0707; Found: 229.0718.
Following the general procedure, 4j was obtained as a colorless oil (0.2 mmol scale, 22 mg, 43% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.14 (q, $J$ = 7.1 Hz, 2H), 3.75 - 3.69 (m, 4H), 2.75 - 2.37 (m, 6H), 1.56 - 1.49 (m, 2H), 1.39 - 1.24 (m, 6H), 0.90 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.5, 166.0, 101.7, 88.8, 65.0, 59.6, 34.3, 29.1, 27.5, 22.4, 14.3, 13.8. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{23}$O$_5$: 259.1540; Found: 259.1529.

![8j](image)

Following the general procedure, 8j was obtained as a colorless oil (0.2 mmol scale, 24 mg, 44% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 4.14 (q, $J$ = 7.1 Hz, 2H), 3.83 (d, $J$ = 11.6 Hz, 1H), 3.72 (d, $J$ = 11.6 Hz, 1H), 3.03 (d, $J$ = 14.9 Hz, 1H), 2.89 (d, $J$ = 14.9 Hz, 1H), 2.68 (t, $J$ = 7.6 Hz, 2H), 1.63 - 1.59 (m, 2H), 1.47 - 1.32 (m, 2H), 1.26 (t, $J$ = 7.1 Hz, 3H), 0.93 (t, $J$ = 7.3 Hz, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 177.4, 173.0, 167.4, 102.0, 91.0, 66.6, 60.7, 37.0, 30.0, 28.5, 23.4, 14.7, 14.1. HRMS (ESI) m/z: [M - H]$^-$ Calcd for C$_{13}$H$_{19}$O$_6$: 271.1176; Found: 271.1137.

![4k](image)

Following the general procedure, 4k was obtained as a colorless oil (0.2 mmol scale, 20 mg, 40% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.15 (q, $J$ = 7.1 Hz, 2H), 3.75 - 3.69 (s, 4H), 3.65 - 3.58 (m, 1H), 2.69 (s, 2H), 2.19 (br, s, 2H), 1.26 (t, $J$ = 7.1 Hz, 3H), 1.12 (d, $J$ = 6.9 Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 174.6, 166.0, 100.4, 88.7, 65.2, 59.7, 34.4, 27.0, 19.7, 14.5. HRMS (ESI) m/z: [M - H]$^-$ Calcd for C$_{12}$H$_{19}$O$_5$: 243.1227; Found: 243.1201.

![8k](image)
Following the general procedure, 8k was obtained as a colorless oil (0.2 mmol scale, 21 mg, 40% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 4.14 (q, $J = 7.1$ Hz, 2H), 3.81 (d, $J = 11.6$ Hz, 1H), 3.72 (d, $J = 11.7$ Hz, 1H), 3.63 - 3.53 (m, 1H), 3.09 - 2.98 (m, 1H), 2.90 - 2.81 (m, 1H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.17 (dd, $J = 9.2$, 6.9 Hz, 6H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 176.8, 176.4, 167.2, 100.3, 90.5, 66.3, 60.7, 36.9, 28.2, 19.8, 19.7, 14.7. HRMS (ESI) m/z: [M - H]$^-$ Calcd for C$_{12}$H$_7$O$_6$: 257.1019; Found: 257.0982.

Following the general procedure, 4l was obtained as a yellow oil (0.2 mmol scale, 24 mg, 35% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 - 7.68 (m, 2H), 7.69 - 7.63 (m, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.51 - 7.34 (m, 5H), 3.81 - 3.75 (m, 4H), 3.00 (s, 2H), 2.01 (br, s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.1, 141.8, 133.1, 131.3, 129.7, 129.2, 128.3, 128.0, 127.1, 111.1, 89.4, 64.9, 36.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{18}$H$_{19}$O$_5$S: 347.0948; Found: 347.0950.

Following the general procedure, 8l was obtained as a yellow oil (0.2 mmol scale, 20 mg, 28% yield). $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 7.75 - 7.69 (m, 4H), 7.62 - 7.55 (m, 1H), 7.52 - 7.43 (m, 3H), 7.40 - 7.36 (m, 2H), 3.86 (d, $J = 12.0$ Hz, 1H), 3.76 (d, $J = 11.9$ Hz, 1H), 3.32 (d, $J = 14.8$ Hz, 1H), 3.22 (d, $J = 14.8$ Hz, 1H). $^{13}$C NMR (100 MHz, CD$_3$OD) $\delta$ 177.9, 165.6, 143.2, 134.1, 131.8, 130.8, 130.2, 128.6, 127.8, 110.6, 92.0, 66.5, 39.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{18}$H$_{17}$O$_6$S: 361.0740; Found: 361.0743.
Following the general procedure, 4m was obtained as a colorless oil (0.2 mmol scale, 24 mg, 41% yield). 1H NMR (400 MHz, CDCl₃) δ 7.72 - 7.64 (m, 2H), 7.47 - 7.32 (m, 3H), 4.19 - 4.06 (m, 2H), 4.04 (d, J = 11.8 Hz, 1H), 3.95 (d, J = 11.8 Hz, 1H), 3.89 (d, J = 11.5 Hz, 1H), 3.73 (d, J = 11.5 Hz, 1H), 3.25 (q, J = 7.0 Hz, 1H), 2.51 (br, s, 1H), 1.80 (br, s, 1H), 1.28 (d, J = 6.9 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl₃) δ 165.2, 163.4, 130.6, 130.2, 129.5, 127.8, 109.1, 89.4, 64.7, 62.3, 60.0, 42.3, 14.4, 14.2. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₆H₂₁O₅: 293.1384; Found: 293.1387.

Following the general procedure, 8m was obtained as a colorless oil (0.2 mmol scale, 23 mg, 37% yield, dr = 2:1). 1H NMR (400 MHz, CD₃OD) δ 7.95 - 7.71 (m, 2H), 7.50 - 7.32 (m, 3H), 4.20 - 4.02 (m, 2.9H), 3.96 (d, J = 11.5 Hz, 0.7H), 3.89 - 3.78 (m, 0.4H), 3.62 (q, J = 5.8, 0.7H), 3.20 (q, J = 7.2 Hz, 0.3H), 1.31 - 1.26 (m, 3H), 1.14 (t, J = 7.3 Hz, 3H). 13C NMR (100 MHz, CD₃OD) δ 175.5, 166.7, 166.3, 166.2, 165.7, 131.6, 131.5, 131.4, 131.0, 130.8, 128.5, 128.5, 109.0, 108.8, 94.7, 92.5, 66.4, 63.4, 61.0, 45.7, 44.0, 16.3, 14.5, 14.4. HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₆H₁₈NaO₆: 329.0996; Found: 329.0987.

Following the general procedure, 4n was obtained as a colorless oil (0.2 mmol scale, 19 mg, 29% yield). 1H NMR (400 MHz, CDCl₃) δ 7.76 - 7.64 (m, 2H), 7.45 - 7.30 (m, 3H), 4.18 - 3.95 (m, 4H), 3.88 (d, J = 11.4 Hz, 1H), 3.70 (d, J = 11.5 Hz, 1H), 3.24 (dd, J = 8.3, 4.4 Hz, 1H), 2.64 (br, s, 2H), 1.59 (td, J = 10.5, 8.8, 5.2 Hz, 2H), 1.47 (dt, J = 9.8, 5.3 Hz, 1H), 1.18 (t, J = 7.1 Hz, 3H), 0.95 (dd, J = 12.2, 6.3 Hz, 6H). 13C NMR (100 MHz, CDCl₃) δ 165.4, 163.2, 130.6, 130.1, 129.7, 127.7, 108.8, 90.1, 64.7,
Following the general procedure, 8n was obtained as a yellow oil (0.2 mmol scale, 19 mg, 27% yield, dr > 20:1, relative configuration). \(^1\)H NMR (400 MHz, CD\(_3\)OD) \(\delta\) 7.84 (d, \(J = 7.2\) Hz, 2H), 7.43 - 7.35 (m, 3H), 4.19 (d, \(J = 11.7\) Hz, 1H), 4.12 - 3.97 (m, 3H), 3.55 (dd, \(J = 7.7, 5.0\) Hz, 1H), 1.76 - 1.56 (m, 1H), 1.46 - 1.24 (m, 2H), 1.16 (t, \(J = 7.1\) Hz, 3H), 0.98 (dd, \(J = 10.0, 6.5\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CD\(_3\)OD) \(\delta\) 175.7, 166.9, 166.3, 131.6, 131.2, 130.8, 128.4, 108.7, 93.4, 63.6, 61.0, 48.4, 40.4, 27.6, 23.6, 22.8, 14.4. HRMS (ESI) m/z: [M + Na]\(^+\) Calcd for C\(_{19}\)H\(_{26}\)NaO\(_5\): 371.1466; Found: 371.1468.

5. General procedure for the synthesis of epoxides

To a solution of 1 (0.2 mmol, 1.0 equiv) and 2a (31.6 mg, 0.2 mmol, 1.0 equiv) in DCM (1 mL) was added powder K\(_2\)CO\(_3\) (55.2 mg, 0.4 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 30 min. After completion, the solution was quenched with sat. aq. NH\(_4\)Cl (1 mL) and extracted with DCM (2 mL \(\times\) 3), dried over Na\(_2\)SO\(_4\) and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 10 : 1) to afford the epoxide products 12 in 52-81% yields.
Following the general procedure, 12a was obtained as a colorless oil (0.2 mmol scale, 45 mg, 81% yield, dr = 1:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.84 (d, $J = 3.5$ Hz, 1H), 8.03 - 7.97 (m, 2H), 7.62 - 7.57 (m, 1H), 7.51 - 7.45 (m, 2H), 4.65 (ddd, $J = 13.5, 8.1, 6.4$ Hz, 1H), 4.20 - 4.03 (m, 2H), 3.14 - 2.98 (m, 2H), 2.68 (ddd, $J = 41.9, 14.8, 7.3$ Hz, 1H), 2.57 - 2.38 (m, 1H), 1.16 (td, $J = 7.1, 5.3$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.5, 198.4, 194.3, 194.2, 169.3, 169.2, 135.8, 135.7, 133.9, 128.9, 128.8, 62.0, 61.9, 59.5, 59.4, 50.9, 50.3, 49.7, 49.6, 27.3, 27.0, 14.0, 14.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{15}$H$_{17}$O$_5$: 277.1071; Found: 277.1046.

Following the general procedure, 12b was obtained as a colorless oil (0.2 mmol scale, 46 mg, 75% yield, dr = 1:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.84 (s, 1H), 8.04 - 7.96 (m, 2H), 6.97 - 6.93 (m, 2H), 4.63 - 4.58 (m, 1H), 4.17 - 4.09 (m, 2H), 3.87 (d, $J = 2.2$ Hz, 3H), 3.11 - 3.01 (m, 2H), 2.64 (ddd, $J = 30.1, 14.8, 7.4$ Hz, 1H), 2.48 (ddd, $J = 22.5, 14.8, 7.1$ Hz, 1H), 1.17 (td, $J = 7.1, 4.9$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.5, 198.4, 192.7, 192.6, 169.5, 169.4, 164.2, 131.4, 131.3, 128.9, 128.8, 114.1, 61.9, 61.8, 59.5, 59.4, 55.7, 50.8, 50.4, 49.3, 27.4, 27.1, 14.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{16}$H$_{19}$O$_6$: 307.1176; Found: 307.1171.

Following the general procedure, 12c was obtained as a colorless oil (0.2 mmol scale, 49 mg, 71% yield, dr = 1:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.83 (d, $J = 9.8$ Hz, 1H), 8.11 (dd, $J = 11.9, 8.3$ Hz, 2H), 7.75 (dd, $J = 8.5, 4.5$ Hz, 2H), 4.63 (dt, $J = 18.1, 7.4$ Hz, 1H), 4.15 (q, $J = 6.7, 6.2$ Hz, 2H), 3.13 - 3.03 (m, 2H), 2.73 (ddd, $J = 46.9, 14.8, 7.2$ Hz, 1H), 2.47 (ddd, $J = 35.5, 14.8, 7.2$ Hz, 1H), 1.16 (td, $J = 7.1, 4.8$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.4, 198.3, 193.6, 193.3, 168.8, 168.7, 138.6, 135.2, 134.9, 129.3, 129.1, 126.0 (q, $J = 3.8$ Hz), 123.6 (q, $J = 273.1$ Hz), 62.2, 62.2, 59.4,
Following the general procedure, 12d was obtained as a colorless oil (0.2 mmol scale, 43 mg, 73% yield, dr = 1:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.82 (d, $J$ = 5.1 Hz, 1H), 8.07 - 8.00 (m, 2H), 7.17 - 7.11 (m, 2H), 4.59 (dt, $J$ = 14.9, 7.2 Hz, 1H), 4.16 - 4.09 (m, 2H), 3.06 (dt, $J$ = 13.9, 4.8 Hz, 2H), 2.67 (ddd, $J$ = 43.3, 14.8, 7.2 Hz, 1H), 2.45 (ddd, $J$ = 30.7, 14.8, 7.2 Hz, 1H), 1.15 (td, $J$ = 7.0, 4.8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.5, 198.4, 192.7, 192.5, 169.1, 169.0, 167.5, 165.0, 132.3, 131.7, 131.6, 131.5, 116.2, 116.0, 62.0, 62.0, 59.4, 59.3, 50.9, 50.3, 49.7, 49.6, 27.2, 27.0, 14.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{16}$H$_{16}$F$_3$O$_5$: 345.0944; Found: 345.0942.

Following the general procedure, 12e was obtained as a colorless oil (0.2 mmol scale, 48 mg, 79% yield, dr = 1:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.85 (s, 1H), 8.00 - 7.95 (m, 2H), 7.59 - 7.56 (m, 1H), 7.49 - 7.44 (m, 2H), 4.54 - 4.50 (m, 1H), 3.09 - 3.02 (m, 2H), 2.69 (dd, $J$ = 14.8, 6.7 Hz, 0.5H), 2.59 - 2.49 (m, 1H), 2.39 (dd, $J$ = 14.8, 8.0 Hz, 0.5H), 1.31 (d, $J$ = 7.7 Hz, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.6, 198.3, 194.6, 194.6, 168.3, 168.2, 136.2, 133.6, 128.8, 128.8, 82.6, 82.5, 59.5, 59.4, 50.9, 50.8, 50.8, 50.2, 27.8, 27.8, 27.1, 26.6. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for C$_{17}$H$_{20}$NaO$_5$: 327.1203; Found: 327.1212.

Following the general procedure, 12f was obtained as a colorless oil (0.2 mmol scale, 48 mg, 74% yield, dr = 1:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.86 (d, $J$ = 1.6 Hz, 1H), 8.58 (dd, $J$ = 19.8, 2.0 Hz, 1H), 8.09 - 7.96 (m, 2H), 7.93 - 7.87 (m, 2H), 7.65 - 7.55 (m, 2H), 4.85 - 4.79 (m, 1H), 4.14 (qt, $J$ = 7.0, 4.3 Hz, 2H), 3.16 - 3.02 (m, 2H),
2.74 (ddd, $J = 39.2$, 14.8, 7.3 Hz, 1H), 2.56 (ddd, $J = 32.1$, 14.7, 7.1 Hz, 1H), 1.16 (td, $J = 7.1$, 5.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.5, 198.4, 194.2, 194.1, 169.4, 169.3, 136.0, 133.2, 133.2, 132.6, 131.0, 130.9, 130.0, 129.1, 128.9, 127.9, 127.1, 124.3, 124.2, 62.0, 61.9, 59.5, 59.4, 50.9, 50.4, 49.8, 27.5, 27.2, 14.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{19}$H$_{19}$O$_5$: 327.1227; Found: 327.1214.

Following the general procedure, 12g was obtained as a colorless oil (0.2 mmol scale, 41 mg, 71% yield, dr = 1:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.84 (d, $J = 2.4$ Hz, 1H), 7.86 - 7.73 (m, 2H), 7.55 - 7.46 (m, 1H), 7.42 - 7.38 (m, 2H), 4.18 - 4.02 (m, 2H), 3.09 - 2.92 (m, 3H), 2.53 (d, $J = 15.0$ Hz, 0.5H), 2.41 (d, $J = 15.0$ Hz, 0.5H), 1.58 (d, $J = 3.7$ Hz, 3H), 1.07 (td, $J = 7.2$, 5.4 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.0, 197.9, 197.4, 197.3, 173.4, 173.3, 135.8, 135.8, 132.8, 132.6, 128.7, 128.6, 128.6, 77.4, 62.0, 61.9, 59.5, 59.4, 56.5, 56.2, 51.3, 51.0, 33.8, 33.8, 22.2, 22.1, 13.7. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{16}$H$_{19}$O$_5$: 291.1227; Found: 291.1218.

Following the general procedure, 12h was obtained as a colorless oil (0.2 mmol scale, 45 mg, 61% yield, dr = 1:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.81 (d, $J = 38.9$ Hz, 1H), 7.76 (dd, $J = 48.5$, 7.8 Hz, 2H), 7.50 - 7.36 (m, 3H), 7.31 - 6.85 (m, 5H), 4.34 - 3.88 (m, 2H), 3.70 - 3.33 (m, 2H), 3.15 - 2.85 (m, 3H), 2.46 (d, $J = 15.2$ Hz, 0.5H), 2.25 (d, $J = 15.4$ Hz, 0.5H), 0.96 (dt, $J = 22.7$, 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.4, 198.1, 197.9, 196.3, 172.6, 137.6, 135.8, 135.6, 132.9, 132.4, 130.7, 130.6, 128.9, 128.7, 128.4, 128.3, 127.2, 127.2, 62.1, 61.7, 61.5, 60.8, 59.7, 59.7, 50.8, 41.3, 40.8, 31.9, 31.6, 13.5, 13.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{22}$H$_{23}$O$_5$: 367.1540; Found: 367.1548.
Following the general procedure, 12i was obtained as a colorless oil (0.2 mmol scale, 33 mg, 65% yield, dr = 1:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.82 (d, $J = 3.4$ Hz, 1H), 4.22 - 4.15 (m, 2H), 3.71 (q, $J = 7.0$ Hz, 1H), 3.04 (d, $J = 3.4$ Hz, 2H), 2.67 - 2.44 (m, 3H), 2.28 (ddd, $J = 39.3$, 14.8, 7.2 Hz, 1H), 1.61 - 1.52 (m, 2H), 1.34 - 1.24 (m, 5H), 0.89 (td, $J = 7.3$, 2.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.2, 204.0, 198.3, 198.2, 169.2, 169.1, 61.9, 61.8, 59.5, 59.5, 54.4, 54.2, 50.6, 50.3, 42.1, 41.9, 26.0, 25.9, 25.7, 22.2, 14.1, 14.12, 13.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_{21}$O$_5$: 257.1384; Found: 257.1377.

Following the general procedure, 12j was obtained as a colorless oil (0.2 mmol scale, 38 mg, 70% yield, dr = 1:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.80 (d, $J = 2.6$ Hz, 1H), 4.23 - 4.11 (m, 2H), 3.05 - 2.96 (m, 2H), 2.81 (d, $J = 14.8$ Hz, 1H), 2.54 - 2.41 (m, 2H), 2.33 (ddd, $J = 14.7$, 9.4 Hz, 1H), 1.53 (h, $J = 7.6$ Hz, 2H), 1.43 - 1.21 (m, 8H), 0.88 (td, $J = 7.3$, 3.3 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.1, 206.9, 198.2, 198.0, 172.6, 172.4, 61.8, 61.7, 59.6, 59.3, 58.4, 57.9, 52.0, 51.3, 38.1, 37.8, 31.6, 31.1, 26.1, 26.0, 22.3, 20.6, 20.4, 14.1, 14.0, 14.0, 13.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{14}$H$_{23}$O$_5$: 271.1540; Found: 271.1537.

Following the general procedure, 12k was obtained as a colorless oil (0.2 mmol scale, 26 mg, 52% yield, dr = 1:2). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.86 (d, $J = 17.3$ Hz, 1H), 4.18 (m, 2H), 3.10 - 2.90 (m, 2H), 2.76 (d, $J = 14.6$ Hz, 0.5H), 2.64 - 2.40 (m, 3H), 2.11 - 1.96 (m, 1.5H), 1.80 - 1.47 (m, 5H), 1.30 - 1.23 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 207.5, 207.3, 198.2, 198.1, 171.8, 171.3, 61.9, 61.8, 59.5, 59.4, 59.4, 51.6,
Following the general procedure, 12l was obtained as a colorless oil (0.2 mmol scale, 34 mg, 57% yield, dr = 1:2). 1H NMR (400 MHz, CDCl₃) δ 8.90 (d, J = 22.2 Hz, 1H), 8.02 (dd, J = 11.5, 8.2 Hz, 1H), 7.50 - 7.41 (m, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 4.19 - 4.06 (m, 2H), 3.27 - 2.82 (m, 5H), 2.76 - 2.58 (m, 1H), 2.51 - 2.43 (m, 1H), 2.40 (d, J = 14.4 Hz, 1H), 2.21 - 2.07 (m, 1H), 1.14 (dt, J = 20.7, 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl₃) δ 198.1, 198.0, 194.8, 171.9, 171.2, 143.1, 142.9, 133.8, 133.5, 132.3, 131.9, 128.8, 128.7, 128.3, 128.1, 126.9, 61.8, 59.7, 59.3, 56.4, 56.2, 52.7, 51.3, 33.3, 32.1, 31.1, 30.8, 26.3, 26.0, 14.0, 14.0. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₇H₁₉O₅: 303.1227; Found: 303.1225.

6. Mechanistic investigations

To a solution of 1a (19.2 mg, 0.1 mmol, 1.0 equiv) and 2a (15.8 mg, 0.1 mmol, 1.0 equiv), and TEMPO (15.6 mg, 0.1 mmol, 1.0 equiv) in DCM (1 mL) was added powder KOH (11.2 mg, 0.2 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 1 h. After completion, the reaction was quenched by water (2 mL) and extracted with DCM (3 mL × 3). Combined the organic phase, dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 3:1 ~ 2:1) to afford the alcohol product 4a in 38% yield. Additionally, the aqueous phase of step1 was added 2.0 M HCl to adjust pH to 2~3 and extracted with DCM (2 mL × 3). The combined organic phase was dried and concentrated to give a residue, which was purified by flash silica gel chromatography.
(DCM / MeOH = 15:1 ~ 5:1) to afford the carboxylic acid product \(8a\) in 35% yield.

To a solution of \(4a\) (27.8 mg, 0.1 mmol, 1.0 equiv) in EtOAc (1 mL) was added powder KOH (11.2 mg, 0.2 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 20 min. After completion, the solution was quenched with sat. aq. NH\(_4\)Cl (1 mL) and extracted with diethyl ether (2 mL \(\times\) 3), dried over Na\(_2\)SO\(_4\) and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 50:1 ~ 30:1) to afford the products \(5\) (17 mg, 53% yield) and \(6\) (4 mg, 10% yield).

To a solution of \(5\) (64 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) was added Dess-Martin reagent (127 mg, 0.3 mmol, 1.5 equiv) to at room temperature. The mixture was stirred for 1 h and quenched with sat. aq. NaHCO\(_3\) (5 mL). The organic layer was separated, and the aqueous layer was extracted with DCM (2 mL \(\times\) 3), dried over Na\(_2\)SO\(_4\) and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 20:1) to afford the aldehyde product \(9\) (39 mg, 62% yield) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 9.80 (s, 1H), 7.82 (dd, \(J = 8.3, 1.6\) Hz, 2H), 7.50 - 7.36 (m, 3H), 4.56 - 4.39 (m, 2H), 4.14 (q, \(J = 7.1\) Hz, 3H), 3.29 (d, \(J = 16.0\) Hz, 1H), 3.06 (d, \(J = 16.0\) Hz, 1H), 2.09 (s, 3H), 1.22 (t, \(J = 7.1\) Hz, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 198.5, 170.4, 164.0, 163.8, 130.9, 129.4, 128.8, 127.8, 102.2, 89.0, 64.6, 60.2, 36.1, 20.6, 14.1. HRMS (ESI) m/z: [M + H]\(^+\) Calcd for C\(_{17}\)H\(_{19}\)O\(_6\): 319.1177; Found: 319.1187.

To a solution of \(9\) (39 mg, 0.12 mmol, 1.0 equiv) in DCM (2 mL) was added powder KOH (14 mg, 0.24 mmol, 2.0 equiv) at room temperature. The reaction process
was monitored by TLC, and the products 4a, 5 and 8a could be detected at 20 min. When the reaction mixture was prolonged to 1 h, only the products 4a and 8a could be detected. Then, the reaction mixture was quenched by water (2 mL) and extracted with DCM (3 mL × 3). The combined organic phase was dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 2:1) to afford the alcohol product 4a (11 mg, 34% yield). Additionally, the aqueous phase was treated with 2.0 M HCl to adjust the pH to 2~3 and extracted with DCM (3 mL × 3). The combined organic phase was dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (DCM / MeOH = 15:1 ~ 5:1) to afford the carboxylic acid product 8a (13 mg, 37% yield).

To a solution of 1a (19.2 mg, 0.1 mmol, 1.0 equiv) and 10 (17.2 mg, 0.1 mmol, 1.0 equiv) in DCM (1 mL) was added powder KOH (11.2 mg, 0.2 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 30 min. After completion, the solution was quenched with sat. aq. NH₄Cl (1 mL) and extracted with DCM (2 mL × 3), dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 5:1) to afford the product 11 (20 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.90 - 7.79 (m, 2H), 7.47 - 7.40 (m, 3H), 4.14 (q, J = 7.1 Hz, 2H), 4.00 - 3.75 (m, 2H), 3.25 - 3.06 (m, 2H), 2.38 (s, 3H), 2.18 (br, s, 1H), 1.22 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 210.0, 164.5, 163.5, 131.0, 129.4, 129.3, 128.0 102.8, 92.6, 66.0, 60.3, 37.6, 27.0, 14.3. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₅H₁₇O₅: 291.1227; Found: 291.1241.

To a solution of 1a (38.4 mg, 0.2 mmol, 1.0 equiv) and 2a (31.6 mg, 0.2 mmol, 1.0 equiv) in DCM (1 mL) was added K₂CO₃ (55.2 mg, 0.4 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 30 min. After completion, the solution was quenched with sat. aq. NH₄Cl (1 mL) and extracted with DCM (2 mL × 3), dried over Na₂SO₄ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 5:1) to afford the product 12a (20 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.90 - 7.79 (m, 2H), 7.47 - 7.40 (m, 3H), 4.14 (q, J = 7.1 Hz, 2H), 4.00 - 3.75 (m, 2H), 3.25 - 3.06 (m, 2H), 2.38 (s, 3H), 2.18 (br, s, 1H), 1.22 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 210.0, 164.5, 163.5, 131.0, 129.4, 129.3, 128.0 102.8, 92.6, 66.0, 60.3, 37.6, 27.0, 14.3. HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₅H₁₇O₅: 291.1227; Found: 291.1241.
temperature. The reaction mixture was stirred for 30 min. After completion, the solution was quenched with sat. aq. NH$_4$Cl (1 mL) and extracted with DCM (2 mL × 3), dried over Na$_2$SO$_4$ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 10:1) to afford the epoxide product 12a (45 mg, 81% yield, dr = 1:1).

![Chemical structure](image)

To a solution of 12a (55 mg, 0.2 mmol, 1.0 equiv) in DCM (1 mL) was added powder KOH (22 mg, 0.4 mmol, 2.0 equiv) at room temperature. The reaction mixture was stirred for 30 min. After completion, the reaction was quenched by water (2 mL) and extracted with DCM (3 mL × 3). The combined organic phase was dried over Na$_2$SO$_4$ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether / EtOAc = 2:1) to afford the alcohol product 4a (18 mg, 33% yield). Additionally, the aqueous phase was treated with 2.0 M HCl to adjust the pH to 2~3 and extracted with DCM (3 mL × 3). The combined organic phase was dried over Na$_2$SO$_4$ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (DCM / MeOH = 15:1 ~ 5:1) to give carboxylic acid product 8a (17 mg, 30% yield).

7. Synthetic applications

![Chemical structure](image)

A 5 mL flask equipped with a stirrer bar was charged with 4a (56 mg, 0.2 mmol, 1.0 equiv) followed by the addition of dry DCM (2 mL). The resulting mixture was stirred at −40 °C for 20 min, and subsequently, triethylsilane (90 μL, 0.56 mmol, 2.8 equiv) and BF$_3$·OEt$_2$ (90 μL, 0.64 mmol, 3.2 equiv) were added. The mixture was stirred at −40 °C until the consumption of 4a and then the mixture was warmed up to room temperature. Finally, triethylamine (90 μL, 0.6 mmol, 3.0 equiv) and water (2
mL) were added. The mixture was extracted with DCM (3 × 2 mL), and the combined organic phase was dried with Na₂SO₄ and removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether / EtOAc = 3:1) to afford the tetrahydrofuran 17 (43 mg, 77% yield) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** δ 7.33 (m, 5H), 5.13 (d, J = 9.6 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.78 - 3.65 (m, 4H), 3.09 (q, J = 9.6 Hz, 1H), 2.53 - 1.68 (m, 4H), 1.18 (t, J = 7.1 Hz, 3H).

**¹³C NMR (100 MHz, CDCl₃)** δ 172.3, 139.7, 128.7, 128.5, 126.4, 85.7, 83.6, 65.9, 65.6, 61.1, 52.6, 35.3, 14.2. **HRMS (ESI) m/z:** [M + Na]⁺ Calcd for C₁₅H₂₀NaO₅: 303.1203; Found: 303.1206.

A solution of 17 (43 mg, 0.15 mmol, 1.0 equiv) and PTSA (1.2 mg, 0.007 mmol, 0.05 equiv) in benzene (2 mL) was refluxed at 90 °C overnight. After completion, the reaction was quenched with solid Na₂CO₃ and filtered. Then the filtrate was concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether / EtOAc = 5 : 1) to afford 18 (25 mg, 72% yield) as a colorless oil. **¹H NMR (400 MHz, CDCl₃)** 7.42 - 7.28 (m, 5H), 5.43 (s, 1H), 4.47 (dd, J = 11.5, 2.1 Hz, 1H), 4.34 (d, J = 11.5 Hz, 1H), 3.97 (s, 2H), 3.19 (d, J = 4.1 Hz, 1H), 2.16 (m, 2H), 2.03 (d, J = 11.6 Hz, 1H). **¹³C NMR (100 MHz, CDCl₃)** δ 171.6, 140.6, 128.7, 128.2, 125.2, 82.6, 82.0, 76.8, 64.2, 50.3, 28.9. **HRMS (ESI) m/z:** [M + MeOH + Na]⁺ Calcd for C₁₄H₁₈NaO₅: 289.1047; Found: 289.1061.

A solution of 8a (58 mg, 0.2 mmol, 1.0 equiv), 19 (45 mg, 0.24 mmol, 1.2 equiv) and HBTU (91 mg, 0.24 mmol, 1.2 equiv) in CH₃CN (2 mL) was added TEA (83 μL, 0.6 mmol, 3.0 equiv) at room temperature. The reaction mixture was stirred for 30 min. After completion, the solution was added 2.0 M NaOH to adjust pH to 12~13 and extracted with EtOAc (3 mL × 3). The combined organic layer was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether / EtOAc = 2:1) to afford 20 (69 mg, 75% yield) as a yellow oil. **¹H NMR (400 MHz, CDCl₃)** 7.79 (d, J = 7.4 Hz, 2H), 7.49 - 7.36 (m, 3H), 5.18 (s, 1H), 4.47 (dd, J = 11.5, 2.1 Hz, 1H), 4.34 (d, J = 11.5 Hz, 1H), 3.97 (s, 2H), 3.19 (d, J = 4.1 Hz, 1H), 2.16 (m, 2H), 2.03 (d, J = 11.6 Hz, 1H). **¹³C NMR (100 MHz, CDCl₃)** δ 172.3, 139.7, 128.7, 128.5, 126.4, 85.7, 83.6, 65.9, 65.6, 61.1, 52.6, 35.3, 14.2. **HRMS (ESI) m/z:** [M + Na]⁺ Calcd for C₁₅H₂₀NaO₅: 303.1203; Found: 303.1206.
4.16 (qd, J = 7.1, 4.2 Hz, 2H), 3.92 (d, J = 11.5 Hz, 1H), 3.82 - 3.12 (m, 12H), 1.45 (s, 9H), 1.23 (t, J = 7.1 Hz, 3H). ^13^C NMR (100 MHz, CDCl₃) δ 170.3, 164.5, 162.7, 154.6, 131.1, 129.3, 129.0, 128.0, 103.1, 88.2, 80.6, 66.4, 60.4, 43.3, 38.7, 38.5, 28.5, 14.3. HRMS (ESI) m/z: [M + Na]^+ Caled for C₂₄H₃₂N₂NaO₇: 483.2102; Found: 483.2105.

To a suspension of [Ph₃PCH₃]Br (86 mg, 0.24 mmol, 1.2 equiv) in dry THF (1 mL) was added a solution of NaHMDS (2.0 M, 0.15 mL, 0.3 mmol, 1.5 equiv) at room temperature. The mixture was stirred for 1 h and a solution of aldehyde 12a (55 mg, 0.2 mmol, 1.0 equiv) in dry THF (1 ml) was added at -20 °C. The reaction mixture was stirred overnight at the same temperature and quenched with sat. aq. NH₄Cl. The mixture was extracted with diethyl ether (3 × 2 mL) and the extract was washed with brine, dried over Na₂SO₄ and concentrated in vacuum. Purification of the residue by column chromatography on silica gel (petroleum ether / EtOAc = 10:1) to afford 38 mg of the product 21 in 70% yield as a colorless oil. ^1^H NMR (400 MHz, CDCl₃) δ 7.80 (dd, J = 7.9, 1.9 Hz, 2H), 7.40 (m, 3H), 5.95 (dd, J = 17.3, 10.9 Hz, 1H), 5.46 (d, J = 17.3 Hz, 1H), 5.31 (d, J = 11.0 Hz, 1H), 4.12 (q, J = 7.0 Hz, 2H), 3.73 (t, J = 15.3 Hz, 2H), 3.22 (d, J = 15.3 Hz, 1H), 2.98 (d, J = 15.3 Hz, 1H), 1.92 (br, s, 1H), 1.20 (t, J = 7.0 Hz, 3H). ^1^C NMR (100 MHz, CDCl₃) δ 165.2, 163.8, 137.8, 130.6, 130.0, 129.5, 127.8, 115.8, 102.5, 88.9, 67.2, 60.0, 38.4, 14.3. HRMS (ESI) m/z: [M + H]^+ Caled for C₁₆H₁₉O₄: 275.1278; Found: 275.1273.

8. References

5. Gu, G; Lu, J; Yu, O; Wen, J; Yin, Q; Zhang X. Org. Lett. **2018**, *20*, 1888-1892.
9. NMR spectra for new compounds

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (150 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
**$^{1}H$ NMR (400 MHz, CDCl$_3$)**

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
(600 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$E : Z = 3:1$

$^{13}C$ NMR (100 MHz, CDCl$_3$)

$E : Z = 3:1$
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CD$_3$OD)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CD$_3$OD)

![NMR Spectrum]

$^{13}$C NMR (100 MHz, CD$_3$OD)

![NMR Spectrum]
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CD$_3$OD)

$^1$H NMR (400 MHz, CD$_3$OD)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
C NMR (100 MHz, CD$_3$OD)

8d

H NMR (400 MHz, CD$_3$OD)

13C NMR (100 MHz, CD$_3$OD)

8d
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$\text{C NMR (100 MHz, CD}_3\text{OD)}$

$\text{H NMR (400 MHz, CD}_3\text{OD)}$

$\text{13C NMR (100 MHz, CD}_3\text{OD)}$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CD$_3$OD)

$^{13}$C NMR (100 MHz, CD$_3$OD)
\textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})}

\textbf{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})}
$^{13}$C NMR (100 MHz, CD$_3$OD)

$^1$H NMR (400 MHz, CD$_3$OD)
**H NMR (400 MHz, CDCl₃)**

**13C NMR (100 MHz, CDCl₃)**
$^{13}$C NMR (100 MHz, CD$_3$OD)

$^1$H NMR (400 MHz, CD$_3$OD)

8h

O

S

OH

OH

O

O

8h

O

S

OH

OH

O

O

8h
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CD$_3$OD)

$^{13}$C NMR (100 MHz, CD$_3$OD)
**S73**

**H NMR (400 MHz, CDCl₃)**

![H NMR spectrum](image)

**13C NMR (100 MHz, CDCl₃)**

![13C NMR spectrum](image)
$\text{H NMR (400 MHz, CD}_3\text{OD)}$

$\text{C NMR (100 MHz, CD}_3\text{OD)}$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CD$_3$OD)

$^{13}$C NMR (100 MHz, CD$_3$OD)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
\[ \text{\textsuperscript{1}H NMR (400 MHz, CD\textsubscript{3}OD)} \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, CD\textsubscript{3}OD)} \]
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CD$_3$OD)
\[ \text{dr} = 2 : 1 \]

$^{13}C$ NMR (100 MHz, CD$_3$OD)
\[ \text{dr} = 2 : 1 \]
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CD$_3$OD)

$\text{dr} > 20 : 1$

$^{13}$C NMR (100 MHz, CD$_3$OD)

$\text{dr} > 20 : 1$
S83

1H NMR (400 MHz, CDCl₃)

13C NMR (100 MHz, CDCl₃)

dr = 1 : 1

12a

O

O

O

O

O

O

12a

O

O

O

O

O

12a
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

$dr = 1 : 1$
**\( ^1H \text{ NMR (400 MHz, CDCl}_3 \)**

\[
\text{dr} = 1 : 1
\]

**\( ^{13}C \text{ NMR (100 MHz, CDCl}_3 \)**

\[
\text{dr} = 1 : 1
\]
H NMR (400 MHz, CDCl$_3$)

\[ \text{dr} = 1 : 1 \]

\[ \text{F} \]

13C NMR (100 MHz, CDCl$_3$)

\[ \text{dr} = 1 : 1 \]
**H NMR** (400 MHz, CDCl$_3$)

$\text{dr} = 1 : 1$

**C NMR** (100 MHz, CDCl$_3$)

$\text{dr} = 1 : 1$
$\text{dr} = 1 : 1$

**$^1\text{H NMR (400 MHz, CDCl}_3$**

**$^{13}\text{C NMR (100 MHz, CDCl}_3$**

$\text{dr} = 1 : 1$
S89

H NMR (400 MHz, CDCl$_3$)

13C NMR (100 MHz, CDCl$_3$)

dr = 1 : 1
\[ \text{dr} = 1 : 1 \]

**1H NMR (400 MHz, CDCl}_3\)**

\[ \text{dr} = 1 : 1 \]

**13C NMR (100 MHz, CDCl}_3\)**
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

$\text{dr} = 1 : 1$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
\( ^1\text{H NMR} \quad (400 \text{ MHz, CDCl}_3) \)

\( ^{13}\text{C NMR} \quad (100 \text{ MHz, CDCl}_3) \)

\( \text{dr} = 1 : 2 \)

12k
H NMR (400 MHz, CDCl$_3$)  

$\text{dr} = 1 : 2$

$^{13}$C NMR (100 MHz, CDCl$_3$)  

$\text{dr} = 1 : 2$

$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$ NMR (100 MHz, CDCl$_3$)
$\text{H NMR (400 MHz, CDCl}_3\text{)}$

$\text{C NMR (100 MHz, CDCl}_3\text{)}$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
**1H NMR (400 MHz, CDCl$_3$)**

**13C NMR (100 MHz, CDCl$_3$)**
\[ \text{H NMR (400 MHz, CDCl}_3) \]

\[ \text{13C NMR (100 MHz, CDCl}_3) \]