Supporting Information

Copper(II) Acetate Catalysed Ring-Opening Cross-Coupling of Cyclopropanols with Sulfonyl Azides
Mei-Hua Shen,* Xiao-Long Lu and Hua-Dong Xu*

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I General Information and Materials

NMR spectra were recorded using Bruker AV-300 / AV-400 spectrometers. The data are reported as follows: chemical shift in ppm on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were acquired on an agilent 6230 spectrometer and were obtained by peak matching. Gas Chromatography-Mass Spectra were acquired on a Agilent 7890A-5975C spectrometer. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator and/or by exposure to phosphormolybdic acid/cerium (IV) sulfate/ ninhydrine followed by brief heating with a heat gun. Liquid chromatography (flash chromatography) was performed on 60Å (40 – 60 µm) mesh silica gel (SiO₂). All reactions were carried out under nitrogen or argon with anhydrous solvents in oven-dried glassware, unless otherwise noted. All reagents were commercially obtained and, where appropriate, purified prior to use.

II Supporting Table

Conditions optimization for the reaction of cyclopropanols and Sulfonyl Azides.

To a solution of cyclopropanol 1a (0.5 mmol, 1eq.) in 2 mL solvent in a flame dried Schlenk tube was added dropwise Tosyl Azide (0.75 mmol, 1.5eq.) and catalyst. Then the solution was evacuated three times with N₂ and stirred for 12h at temperature indicated in the table below. After cooling to room temperature, solvent was removed in vacuum; the residue was purified by column chromatography to give the product.

Table 1. Catalyst screening and conditions optimizationa

<table>
<thead>
<tr>
<th>entry</th>
<th>cat</th>
<th>solvent</th>
<th>temp</th>
<th>products (yield)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Cu(OAc)₂ (0.2 eq)</td>
<td>DCM</td>
<td>30 °C (rt)</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>Cu(OAc)₂ (0.2 eq)</td>
<td>DCM</td>
<td>60 °C (reflux)</td>
<td>6a (51%) and 7aa (38%)</td>
</tr>
<tr>
<td>3</td>
<td>Mn(OAc)₃ (0.2 eq)</td>
<td>DCM</td>
<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>4</td>
<td>Cu(OTf)₂ (0.05 eq)</td>
<td>DCM</td>
<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>5</td>
<td>Ga(OTf)₃ (0.05 eq)</td>
<td>DCM</td>
<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>6</td>
<td>La(OTf)₃ (0.05 eq)</td>
<td>DCM</td>
<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>7</td>
<td>AgNO₃ (0.05 eq)</td>
<td>DCM</td>
<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>8</td>
<td>AgOAc (0.05 eq)</td>
<td>DCM</td>
<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>9</td>
<td>TsOH (0.2 eq)</td>
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<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>10</td>
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<td>DCE</td>
<td>100 °C reflux</td>
<td>6a only</td>
</tr>
<tr>
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<tr>
<td>11</td>
<td>CAN (0.2 eq)</td>
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<td>6a only</td>
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<tr>
<td>12</td>
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<td>6a only</td>
</tr>
<tr>
<td>13</td>
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<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>14</td>
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<td>6a only</td>
</tr>
<tr>
<td>15</td>
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<td>6a only</td>
</tr>
<tr>
<td>16</td>
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<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>17</td>
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<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>18</td>
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<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>19</td>
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<td>reflux</td>
<td>6a only</td>
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<tr>
<td>20</td>
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<td>6a only</td>
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<tr>
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<td>6a only</td>
</tr>
<tr>
<td>22</td>
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<td>THF</td>
<td>reflux</td>
<td>6a and 7aa (29%)</td>
</tr>
<tr>
<td>23</td>
<td>Cu(OAc)$_2$ (0.2 eq)</td>
<td>CH$_3$CN</td>
<td>reflux</td>
<td>NR</td>
</tr>
<tr>
<td>24</td>
<td>Cu(OAc)$_2$ (0.2 eq)</td>
<td>DMF</td>
<td>120 °C</td>
<td>NR</td>
</tr>
<tr>
<td>25</td>
<td>Cu(OAc)$_2$ (0.2 eq)</td>
<td>DMSO</td>
<td>120 °C</td>
<td>NR</td>
</tr>
<tr>
<td>26</td>
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<td>CHCl$_3$</td>
<td>reflux</td>
<td>6a and 7aa (27%)</td>
</tr>
<tr>
<td>27</td>
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<td>130 °C (reflux)</td>
<td>6a and 7aa (69%)</td>
</tr>
<tr>
<td>28</td>
<td>Pd(OAc)$_2$ (0.05 eq)</td>
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<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>29</td>
<td>Pd$_2$dba$_3$ (0.05 eq)</td>
<td>toluene</td>
<td>reflux</td>
<td>6a only</td>
</tr>
<tr>
<td>30</td>
<td>Cu(acac)$_2$ (0.2 eq)</td>
<td>toluene</td>
<td>reflux</td>
<td>6a and 7aa (51%)</td>
</tr>
<tr>
<td>31</td>
<td>Cu(hfacac)$_2$ (0.05 eq)</td>
<td>toluene</td>
<td>reflux</td>
<td>6a and 7aa (15%)</td>
</tr>
<tr>
<td>32</td>
<td>TcCu (0.05 eq)</td>
<td>toluene</td>
<td>reflux</td>
<td>6a and 7aa (11%)</td>
</tr>
<tr>
<td>33</td>
<td>FeCl$_3$.6H$_2$O (0.2 eq)</td>
<td>toluene</td>
<td>reflux</td>
<td>NR</td>
</tr>
</tbody>
</table>

a, isolated yields; b, yields are reported for 7aa only

III Preparation of Cyclopropanols

Starting cyclopropanols 1a[1],1b[2],1c[2],1d[1],1e[3],[4],1f[3],1g[1],1i[4],1k[3],[4],1l[3] are prepared according to the previously reported procedures.

General method for the preparation of cyclopropanols

\[
\text{R-COOCH}_3 + \text{EtMgBr} \xrightarrow{\text{Ti(O-i-Pr)}_4} \text{THF, 0°C-rt} \xrightarrow{\text{reflux}} \text{R-CH(OH)}_3
\]

EtMgBr (2.8 eq., 3M in Et$_2$O) in THF was added dropwise over 30 minutes at 0 °C to a solution of ester (1equiv.) and Ti(O-i-Pr)$_4$ (1.4 eq.) in THF. The mixture was warmed to room temperature and stirred overnight. Then the mixture was quenched with water and the precipitated solid was removed by filtration. The filtrate was extracted with DCM, washed with water and dried over Na$_2$SO$_4$ followed by filtration
and concentration. The residue was subjected to column chromatography to afford the cyclopropanols 1h, 1j, 1m, 1n.

1h: Colorless oil (yield 55%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.94 (s, 1H), 1.66 – 1.62 (m, 1H), 1.56-1.0 (m, 2H), 1.46 – 1.32 (m, 4H), 1.20 – 1.00 (m, 3H), 0.97 (s, 3H), 0.65 – 0.62 (m, 2H), 0.55 – 0.52 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 63.7, 35.9, 33.0, 26.4, 21.9, 19.2, 10.1. GC-MS: \(m/z\) Calculated for C\(_{10}\)H\(_{18}\)O 154.1, found 154.1.

1j: Yellow oil (yield 54%): \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.44 (t, \(J\) = 6.7 Hz, 2H), 1.98-1.90 (m, 2H), 1.88 (s, 1H), 1.71 – 1.66 (m, 2H), 1.65 – 1.55 (m, 2H), 0.78 – 0.74 (m, 2H), 0.48 – 0.44 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 55.5, 37.4, 33.9, 32.7, 24.7, 13.7. GC-MS: \(m/z\) Calculated for C\(_7\)H\(_{13}\)BrO 192.0, found 192.0.

1m: White solid, mp: 127 °C (yield 74%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (d, \(J\) = 8.4 Hz, 2H), 7.29 (d, \(J\) = 8.0 Hz, 2H), 3.84 (dd, \(J\) = 9.6, 2.0 Hz, 2H), 2.40 (s, 3H), 2.18 (s, 1H), 2.14 (dd, \(J\) = 11.6, 2.4 Hz, 2H), 1.77 – 1.58 (m, 4H), 0.90 – 0.82 (m, 1H), 0.70 – 0.67 (m, 2H), 0.37 – 0.34 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.5, 133.1, 129.6, 127.7, 58.0, 46.5, 42.5, 27.4, 21.5, 12.6. HRMS (ESI) \(m/z\) Calculated for C\(_{15}\)H\(_{22}\)NO\(_3\)S\(^+\) [M + H]\(^+\) 296.1315, found 296.1313.

1n: Yellow oil (yield 45%): \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.26 (m, 4H), 7.20 (t, \(J\) = 8.2 Hz, 1H), 6.41 (d, \(J\) = 16.0 Hz, 1H), 6.24 (dt, \(J\) = 15.6, 6.8 Hz, 1H), 2.32 – 2.26 (m, 2H), 1.97 (br, 1H), 1.76 – 1.68 (m, 2H), 1.66 – 1.55 (m, 2H), 0.77 – 0.71 (m, 2H), 0.48-0.41 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 137.8, 130.7, 130.1, 128.5, 126.9, 126.0, 55.7, 37.8, 32.9, 25.7, 13.6. HRMS (ESI) \(m/z\) Calculated for C\(_{14}\)H\(_{18}\)NaO\(^+\) [M + Na]\(^+\) 225.1250, found 225.1249.

IV Synthesis and Characterization of the \(^\beta\)-Tosylamidl ketone.
General Procedure for the synthesis of the $\beta$-Tosylamid ketone:

To a solution of cyclopropanol (0.5 mmol, 1 eq.) in 2mL toluene in a flame dried Schlenk tube was added dropwise sulfonyl azide (0.75 mmol, 1.5 eq.) and Cupric acetate (0.1 mmol, 0.2 eq.). Then the solution was evacuated and refilled with N$_2$ three times and stirred for 8 h at 120 $^\circ$C. After cooling to room temperature, solvent was removed in vacuum; the residue was purified by column chromatography to give the product of 7.

7aa: Brown solid, mp: 86 $^\circ$C (yield 69%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J$ = 7.6 Hz, 2H), 7.74 (d, $J$ = 7.6 Hz, 2H), 7.55 (t, $J$ = 7.4 Hz, 1H), 7.42 (t, $J$ = 7.4 Hz, 2H), 7.26 (d, $J$ = 8 Hz, 2H), 5.38 (br, 1H), 3.34 – 3.29 (m, 2H), 3.19 (t, $J$ = 5.8 Hz, 2H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.0, 143.5, 137.1, 136.1, 133.7, 129.8, 128.7, 128.0, 127.1, 38.4, 38.2, 21.6. HRMS (ESI) $m/z$ Calculated for C$_{16}$H$_{18}$NO$_3$S$^+$ [M + H]$^+$ 304.1002, found 304.1001.

7ba: Brown solid, mp: 96 $^\circ$C (yield 71%): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J$ = 2.1 Hz, 2H), 7.65 (d, $J$ = 2.1 Hz, 2H) 7.20 – 7.12 (m, 4H), 5.38 (t, $J$ = 3.3 Hz, 1H), 3.26 – 3.18 (m, 2H), 3.08 (t, $J$ = 5.7 Hz, 2H), 2.30 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.6, 144.6, 143.4, 137.1, 133.7, 129.8, 129.4, 128.1, 127.1, 38.5, 38.1, 21.7, 21.5. HRMS (ESI) $m/z$ Calculated for C$_{17}$H$_{20}$NO$_3$S$^+$ [M + H]$^+$ 318.1158, found 318.1158.

7ca: Brown solid, mp: 123 $^\circ$C (yield 52%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J$ = 2.0 Hz, 1H), 7.72 (d, $J$ = 2.0 Hz, 1H), 7.71 (d, $J$ = 1.6 Hz, 1H), 7.69 (d, $J$ = 2.0 Hz, 1H), 7.57 (d, $J$ = 2.0 Hz, 1H), 7.55 (d, $J$ = 2.0 Hz, 1H), 7.26 (d, $J$ = 8.3 Hz, 2H), 5.32
(t, J = 6.6 Hz, 1H), 3.33 – 3.28 (m, 2H), 3.15 (t, J = 5.6 Hz, 2H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.9, 143.5, 137.1, 134.9, 132.0, 129.8, 129.5, 128.9, 127.0, 38.3, 38.2, 21.5. HRMS (ESI) m/z Calculated for C$_{16}$H$_{17}$BrNO$_3$S$^+$ [M + H]$^+$ 382.0107, found 382.0103.

7da: Brown solid, mp: 122 °C (yield 76%): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, J = 2.0 Hz, 1H), 7.83 (d, J = 2.0 Hz, 1H), 7.75 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 2.0 Hz, 1H), 7.29 – 7.25 (m, 2H), 6.91 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 2.4 Hz, 1H), 5.30 (t, J = 6.4 Hz, 1H), 3.85 (s, 3H), 3.33 – 3.28 (m, 2H), 3.16 (t, J = 5.6 Hz, 2H), 2.39 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 197.4, 163.9, 143.4, 137.1, 130.3, 129.8, 129.3, 127.0, 113.9, 55.5, 38.5, 37.7, 21.5. HRMS (ESI) m/z Calculated for C$_{17}$H$_{20}$NO$_3$S$^+$ [M + H]$^+$ 334.1108, found 334.1104.

7ea: Light yellow solid, mp: 82 °C (yield 64%): $^1$H NMR (300 MHz, CDCl$_3$) δ 7.71 (d, J = 2.1 Hz, 1H), 7.68 (d, J = 1.8 Hz, 1H), 7.34 – 7.22 (m, 5H), 7.13 (d, J = 1.8 Hz, 1H), 7.11 (d, J = 1.5 Hz, 1H), 5.25 (t, J = 6.6 Hz, 1H), 3.62 (s, 2H), 3.12 – 3.05 (m, 2H), 2.65 (t, J = 5.8 Hz, 2H), 2.40 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.8, 143.5, 136.9, 133.5, 129.8, 129.4, 128.9, 127.3, 127.0, 50.1, 41.4, 38.1, 21.6. HRMS (ESI) m/z Calculated for C$_{17}$H$_{20}$NO$_3$S$^+$ [M + H]$^+$ 318.1158, found 318.1157.

7fa: Light yellow solid, mp: 88 °C (yield 60%): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.30 – 7.25 (m, 4H), 7.19 (t, J = 7.2 Hz, 1H), 7.13 (d, J = 7.2 Hz, 2H), 5.19 (t, J = 6.4 Hz, 1H), 3.15 – 3.10 (m, 2H), 2.84 (t, J = 7.6 Hz, 2H), 2.67 (t, J = 7.4 Hz, 2H), 2.61 (t, J = 5.8 Hz, 2H), 2.41 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 209.2, 143.5, 140.6, 137.0, 129.8, 128.6, 128.3, 127.1, 126.3, 44.3, 42.2, 38.0, 29.5, 21.6. HRMS (ESI) m/z Calculated for C$_{18}$H$_{22}$NO$_3$S$^+$ [M + H]$^+$ 332.1315, found 332.1312.
7ga: White solid, mp: 87 °C (yield 98%): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 2.1$ Hz, 1H), 7.72 (d, $J = 2.1$ Hz, 1H), 7.32 (d, $J = 2.4$ Hz, 1H), 7.29 (d, $J = 2.4$ Hz, 1H), 5.21 (br, 1H), 3.16 – 3.09 (m, 2H), 2.70 – 2.65 (m, 2H), 2.42 (s, 3H), 2.29 – 2.20 (m, 1H), 1.77 – 1.62 (m, 5H), 1.32 – 1.12 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 213.5, 143.4, 137.1, 129.8, 127.0, 50.7, 39.8, 38.2, 28.3, 25.7, 25.5, 21.5. HRMS (ESI) $m/z$ Calculated for C$_{16}$H$_{24}$NO$_3$S$^+$ [M + H]$^+$ 310.1471, found 310.1470.

7ha: Colorless viscous oil (yield 88%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (d, $J = 1.6$ Hz, 1H), 7.74 (d, $J = 2.0$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 5.22 (t, $J = 6.6$ Hz, 1H), 3.17 – 3.12 (m, 2H), 2.70 (t, $J = 5.6$ Hz, 2H), 2.42 (s, 3H), 1.87 – 1.80 (m, 2H), 1.56 – 1.46 (m, 2H), 1.45 – 1.19 (m, 6H), 1.01 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 215.7, 143.4, 137.1, 129.8, 127.0, 48.1, 38.5, 36.3, 34.4, 25.7, 24.8, 22.8, 21.5. HRMS (ESI) $m/z$ Calculated for C$_{17}$H$_{26}$NO$_3$S$^+$ [M + H]$^+$ 324.1628, found 324.1629.

7ia: Light yellow solid, mp: 70 °C (yield 69%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (d, $J = 1.6$ Hz, 1H), 7.71 (d, $J = 2.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 5.16 (t, $J = 6.6$ Hz, 1H), 3.39 (t, $J = 6.4$ Hz, 2H), 3.16 – 3.11 (m, 2H), 2.67 (t, $J = 5.6$ Hz, 2H), 2.55 (t, $J = 7.0$ Hz, 2H), 2.42 (s, 3H), 2.10 – 2.03 (m, 2H) $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.7, 143.6, 136.9, 129.8, 127.0, 42.2, 40.8, 38.0, 33.1, 26.1, 21.6. HRMS (ESI) $m/z$ Calculated for C$_{13}$H$_{19}$BrNO$_3$S$^+$ [M + H]$^+$ 348.0264, found 348.0263.
7ja: Light yellow solid, mp: 69 °C (yield 71%): ¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, J = 1.8 Hz, 1H), 7.73 (d, J = 1.8 Hz, 1H), 7.33 (d, J = 0.9 Hz, 1H), 7.30 (d, J = 0.9 Hz, 1H), 5.17 (t, J = 5.5 Hz, 1H), 3.38 (t, J = 6.5 Hz, 2H), 3.17 – 3.11 (m, 2H), 2.66 (t, J = 5.8 Hz, 2H), 2.43 (s, 3H), 2.40 (t, J = 7.2 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.73 – 1.65 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 209.4, 143.5, 137.0, 129.8, 127.0, 42.0, 41.7, 38.0, 33.2, 31.9, 22.0, 21.6. HRMS (ESI) m/z Calculated for C₁₄H₂₁BrNO₃S⁺ [M + H]⁺ 362.0420, found 362.0416.

7ka: Yellow viscous oil (yield 81%): ¹H NMR (300 MHz, CDCl₃) δ 7.91 (d, J = 1.8 Hz, 1H), 7.89 (d, J = 1.8 Hz, 1H), 7.48 (d, J = 0.9 Hz, 1H), 7.45 (d, J = 0.6 Hz, 1H), 5.31 (t, J = 6.8 Hz, 1H), 3.76 (t, J = 6.1 Hz, 2H), 3.22 – 3.26 (m, 2H), 2.54 (t, J = 7.2 Hz, 2H), 1.78 – 1.67 (m, 2H), 1.66 – 1.57 (m, 2H), 1.05 (s, 9H), 0.20 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 210.2, 143.4, 137.0, 129.8, 127.0, 62.7, 42.6, 41.8, 38.1, 32.1, 26.0, 21.5, 20.1, 18.3. HRMS (ESI) m/z Calculated for C₂₀H₃₆NO₄SSi⁺ [M + H]⁺ 414.2129, found 414.2129.

7la: Light yellow solid, mp: 67 °C (yield 57%): ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 1.6 Hz, 1H), 7.75 (d, J = 2.0 Hz, 1H), 7.71 (d, J = 1.6 Hz, 1H), 7.69 (d, J = 2.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.08 (br, 1H), 3.98 (t, J = 5.8 Hz, 2H), 3.10 (t, J = 5.8 Hz, 2H), 2.60 (t, J = 5.8 Hz, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 2.32 (t, J = 6.8 Hz, 2H), 1.64 – 1.50 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 209.3, 144.9, 143.5, 136.9, 132.9, 129.9, 129.8, 127.9, 127.0, 70.0, 42.0, 41.7, 38.0, 28.1, 21.7, 21.5, 19.4. HRMS (ESI) m/z Calculated for C₂₁H₂₈NO₆S₂⁺ [M + H]⁺ 454.1353, found 454.1351.
**7ma:** White solid, mp: 170 °C (yield 64%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J$ = 2.0 Hz, 1H), 7.70 (d, $J$ = 2.0 Hz, 1H), 7.64 (d, $J$ = 1.6 Hz, 1H), 7.62 (d, $J$ = 1.6 Hz, 1H), 7.33 (d, $J$ = 8.4 Hz, 2H), 7.30 (d, $J$ = 8.0 Hz, 2H), 4.97 (t, $J$ = 6.6 Hz, 1H), 3.75 – 3.70 (m, 2H), 3.14 – 3.09 (m, 2H), 2.66 (t, $J$ = 5.8 Hz, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 2.34 (td, $J$ = 11.6, 2.8 Hz, 2H), 2.18 (tt, $J$ = 11.2, 4.0 Hz, 1H), 1.87 – 1.81 (m, 2H), 1.70 – 1.62 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 210.7, 143.8, 143.6, 136.9, 133.0, 129.8, 129.7, 127.7, 127.0, 47.5, 45.5, 40.1, 37.9, 26.8, 21.6, 21.5. HRMS (ESI) m/z Calculated for C$_{22}$H$_{29}$N$_2$O$_2$S$_2^+$ [M + H]$^+$ 465.1512, found 465.1512.

**7na:** Light yellow viscous oil (yield:57%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J$ = 2.0 Hz, 1H), 7.74 (d, $J$ = 2.4 Hz, 1H), 7.36 – 7.28 (m, 6H), 7.24 – 7.19 (m, 1H), 6.40 – 6.35 (m, 1H), 6.18 – 6.10 (m, 1H), 5.22 (t, $J$ = 6.8 Hz, 1H), 3.16 – 3.08 (m, 2H), 2.65 (t, $J$ = 5.8 Hz, 2H), 2.43 (s, 3H), 2.40 (t, $J$ = 6.8 Hz, 2H), 2.24 – 2.17 (m, 2H), 1.78 – 1.68 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 210.1, 143.5, 137.5, 137.0, 130.9, 129.8, 129.6, 128.6, 127.1, 127.0, 126.0, 42.1, 38.1, 32.3, 23.0, 21.5. HRMS (ESI) m/z Calculated for C$_{21}$H$_{25}$NNaO$_3$S$^+$ [M + Na]$^+$ 394.1447, found 394.1452.

**7ab:** Yellow solid, mp: 77 °C (yield 56%): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J$ = 1.2 Hz, 1H), 7.85 (d, $J$ = 1.5 Hz, 1H), 7.82 (d, $J$ = 0.3 Hz, 1H), 7.79 (d, $J$ = 2.1 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.47 – 7.41 (m, 2H), 6.96 (d, $J$ = 2.1 Hz, 1H), 6.93 (d, $J$ = 2.1 Hz, 1H), 5.32 (t, $J$ = 6.6 Hz, 1H), 3.83 (s, 3H), 3.36 – 3.30 (m, 2H), 3.23 – 3.18 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 198.9, 162.9, 136.2, 133.7, 131.7, 129.1, 128.7, 128.0, 114.3, 55.6, 38.3, 38.2. HRMS (ESI) m/z Calculated for C$_{16}$H$_{18}$NO$_4$S$^+$ [M + H]$^+$ 320.0951, found 320.0948.
**7ac:** Yellow solid, mp: 106°C (yield 61%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J$ = 7.6 Hz, 2H), 7.59 (t, $J$ = 7.2 Hz, 1H), 7.47 (t, $J$ = 7.6 Hz, 2H), 5.17 (t, $J$ = 6.8 Hz, 1H), 3.55 – 3.50 (m, 2H), 3.31 (t, $J$ = 5.4 Hz, 2H), 2.98 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.9, 136.2, 133.8, 128.8, 128.1, 40.2, 38.9, 38.3. HRMS (ESI) m/z Calculated for C$_{10}$H$_{14}$NO$_3$S$^+$ [M + H]$^+$ 280.0689, found 228.0687.

![7ac](image)

**7ad:** Brown viscous oil (yield 31%): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J$ = 1.2 Hz, 1H), 7.84 (d, $J$ = 1.5 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.48 – 7.42 (m, 2H), 6.92 (d, $J$ = 0.9 Hz, 2H), 5.44 (t, $J$ = 6.6 Hz, 1H), 3.32 – 3.26 (m, 2H), 3.20 – 3.15 (m, 2H), 2.67 (s, 6H), 2.26 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 199.1, 142.1, 138.9, 136.1, 134.0, 133.7, 132.0, 128.7, 128.0, 37.9, 37.8, 22.8, 20.9. HRMS (ESI) m/z Calculated for C$_{18}$H$_{21}$NNaO$_3$S$^+$ [M + Na]$^+$ 354.1134, found 354.1136.

![7ad](image)

**7ae:** Brown viscous oil (yield 18%): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J$ = 1.2 Hz, 1H), 7.94 (d, $J$ = 1.5 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.52 – 7.47 (m, 2H), 5.70 (t, $J$ = 6.3 Hz, 1H), 4.63 (s, 2H), 3.69 – 3.63 (m, 2H)不是 t, 3.38 (t, $J$ = 5.4 Hz, 2H) $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 199.1, 136.0, 134.0, 128.9, 128.1, 93.5, 78.2, 39.3, 37.6. HRMS (ESI) m/z Calculated for C$_{11}$H$_{12}$Cl$_3$NNaO$_4$S$^+$ [M + Na]$^+$ 381.9445, found 381.9447.

![7ae](image)

**7af:** Brown viscous oil (yield 44%): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.96 – 7.92 (m, 2H), 7.60 – 7.54 (m, 1H), 7.48 – 7.26 (m, 2H), 5.66 (t, $J$ = 5.5 Hz, 1H), 3.60 – 3.51 (m, 2H), 3.47 (d, $J$ = 15.0 Hz, 1H), 3.35 – 3.30 (m, 2H), 2.94 (d, $J$ = 15.0 Hz, 1H), 2.43 – 2.22 (m, 2H), 2.12 – 1.83 (m, 4H), 1.47 – 1.38 (m, 1H), 1.03 (s, 3H), 0.89 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 216.4, 198.7, 136.3, 133.6, 128.7, 128.1, 59.0, 49.4, 48.6, 42.9, 42.8, 39.1, 38.6, 27.0, 26.1, 19.9, 19.6. HRMS (ESI) m/z Calculated for C$_{19}$H$_{23}$NNaO$_4$S$^+$ [M + Na]$^+$ 386.1397, found 386.1399.

V References.
VI NMR Spectra of Compounds

$^1$H NMR (400 MHz, CDCl₃)

$^13$C NMR (100 MHz, CDCl₃)
$^1$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 (500 MHz, CDCl$_3$)

$^1$C NMR (100 MHz, CDCl$_3$)
7ca

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

$^1$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl₃)

$^{13}$C NMR (100 MHz, CDCl₃)
7ea

$^1$H NMR (300 MHz, CDCl$_3$)

788

$^{13}$C NMR (100 MHz, CDCl$_3$)
7fa
$^1$H NMR (400 MHz, CDCl$_3$)

7fa
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

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

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

$^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}$
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)