Supplementary Information


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1. General Information

Product Characterization

All reactions were carried out under nitrogen (99.95%) atmosphere. For TLC analyses precoated Kieselgel 60 F254 plates (Merck, 0.25 mm thick) were used; for column chromatography Silica Flash® P60 (SiliCycle, 40-63 μm) was used. Visualization was accomplished by UV light (254 nm), $^1$H and $^{13}$C NMR spectra were obtained using a JEOL 500 MHz NMR spectrometer. Chemical shifts for $^1$H NMR were described in parts per million (chloroform as an internal standard $\delta = 7.26$) in CDCl$_3$, unless otherwise noted. Chemical shifts for $^{13}$C NMR were expressed in parts per million in CDCl$_3$ as an internal standard ($\delta = 77.16$), unless otherwise noted. High resolution mass analyses were obtained using a ACQUITY UPLC/ TOF-MS for ESI. Purification was performed by SHIMADZU Gel Permeation Chromatography (GPC) System (Detector UV 254 nm). Anhydrous toluene and dichloromethane were purchased from Kanto Chemical Co., Ltd. Other chemicals were purchased from TCI, Aldrich and Wako and directly used from the bottles. $[\text{Cu(H}_2\text{O)}_6]\text{(BF}_4\text{)}_2$ (Lot. No. TLJ0500) was purchased from Wako.
2. Cyclopropanations

General Procedure

Cu salt (0.05 mmol) was added under air to a dram vial equipped with a stir bar and a screw cap. 2 (0.50 mmol), 1 (1.0 mmol), amine (0.60 mmol) and dried toluene (1.0 mL) were added by syringe and the resulting mixture vigorously stirred under nitrogen atmosphere (charged by general N$_2$ (99.95%) gas flow) for 20 h at the temperature shown in tables. After this time, the contents of the flask were filtered through the plug of silica gel, and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford the product 3.

Diethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate$^1$

\[
\text{\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.5\textwidth]{diethyl_2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate1}};
\end{tikzpicture}}
\]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 0.92 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H), 1.68 (dd, $J = 5.1$ and 9.3 Hz, 1H), 2.13 (dd, $J = 5.1$ and 7.9 Hz, 1H), 3.17 (t, $J = 8.6$ Hz, 1H), 3.77 (s, 3H), 3.80 – 3.97 (m, 2H), 4.12 – 4.35 (m, 2H), 6.80 (d, $J = 8.7$ Hz, 2H), 7.13 (d, $J = 8.7$ Hz, 2H),

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 13.7, 14.0, 18.8, 31.7, 37.2, 55.2, 61.0, 61.5, 113.5, 126.6, 129.7, 158.9, 166.8, 170.0.

Dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate$^2$

\[
\text{\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.5\textwidth]{dimethyl_2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate2}};
\end{tikzpicture}}
\]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.71 (dd, $J = 5.2$ and 9.3 Hz, 1H), 2.15 (dd, $J = 5.1$ and 8.0 Hz, 1H), 3.17 (t, $J = 8.6$ Hz, 1H), 3.38 (s, 3H), 3.77 (s, 3H), 3.78 (s, 3H), 6.77 – 6.82 (m, 2H), 7.08 – 7.14 (m, 2H),

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 19.2, 32.1, 37.0, 52.2, 52.7, 55.1, 113.5, 126.4, 129.5, 158.8, 167.1, 170.2.

Dibenzyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate

\[
\text{\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.5\textwidth]{dibenzyl_2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate}};
\end{tikzpicture}}
\]

IR (neat) $\nu$ 3009, 2931, 1719, 1441 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.73 (dd, $J = 5.1$ and 9.3 Hz, 1H), 2.18 (dd, $J = 5.1$ and 8.1 Hz, 1H), 3.22 (t, $J = 8.7$ Hz, 1H), 3.77 (s, 3H), 4.68 – 4.88 (m, 2H), 5.14 (d, $J = 12.4$, 1H), 5.25 (d, $J = 12.4$ Hz, 1H), 6.71 – 6.77 (m, 2H), 6.93- 6.99 (m, 2H), 7.07 – 7.12 (m, 2H), 7.17 – 7.27 (m, 3H), 7.28 – 7.35 (m, 5H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 19.3, 32.3, 37.3, 55.2, 67.1, 67.3, 113.6, 127.9, 128.0, 128.2, 128.3, 128.5, 129.7, 135.3,
135.5, 158.9, 166.6, 169.7. HRESIMS calcd. for C_{26}H_{24}O_{5}Na (M+Na\(^+\)): 439.1521; found 439.1530.

**Diallyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate**

![Chemical Structure]

**IR** (neat) \(\nu\): 3083, 2939, 1720, 1648, 1441 cm\(^{-1}\). **\(^1\)H NMR** (500 MHz, CDCl\(_3\)) \(\delta\): 1.73 (dd, \(J = 5.1\) and 9.3 Hz, 1H), 2.18 (dd, \(J = 5.2\) and 8.1 Hz, 1H), 3.22 (t, \(J = 8.6\) Hz, 1H), 3.78 (s, 3H), 4.20 \(\text{–} 4.38\) (m, 2H), 4.65 (ddt, \(J = 1.4, 5.5\) and 13.4 Hz, 1H), 4.73 (ddt, \(J = 1.5, 5.5\) and 13.4 Hz, 1H), 5.00 \(\text{–} 5.16\) (m, 2H), 5.25 (dt, \(J = 1.1\) and 10.4 Hz, 1H), 5.31 \(\text{–} 5.40\) (m, 1H), 5.46 \(\text{–} 5.59\) (m, 1H), 5.93 (ddt, \(J = 5.5, 10.7\) and 17.1 Hz, 1H), 6.77 \(\text{–} 6.83\) (m, 2H), 7.10 \(\text{–} 7.17\) (m, 2H). **\(^{13}\)C NMR** (126 MHz, CDCl\(_3\)) \(\delta\): 19.1, 32.1, 37.1, 55.1, 65.8, 66.0, 113.5, 118.1, 118.2, 126.3, 129.7, 131.6, 131.7, 159.0, 166.3, 169.5. HRESIMS calcd. for C\(_{18}\)H\(_{20}\)O\(_5\)Na (M+Na\(^+\)): 339.1208; found 339.1208.

**Diisopropyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate**

![Chemical Structure]

**IR** (neat) \(\nu\): 2980, 2936, 1714, 1463 cm\(^{-1}\). **\(^1\)H NMR** (500 MHz, CDCl\(_3\)) \(\delta\): 0.75 (d, \(J = 6.3\) Hz, 3H), 1.07 (d, \(J = 6.3\) Hz, 3H), 1.26 (d, \(J = 6.3\) Hz, 3H), 1.28 (d, \(J = 6.3\) Hz, 3H), 1.62 (dd, \(J = 5.1\) and 9.2 Hz, 1H), 2.07 (dd, \(J = 5.1\) and 7.9 Hz, 1H), 3.13 (t, \(J = 8.5\) Hz, 1H), 3.76 (s, 3H), 4.73 (hept, \(J = 6.3\) Hz, 1H), 5.08 (hept, \(J = 6.3\) Hz, 1H), 6.74 \(\text{–} 6.90\) (m, 2H), 6.98 (d, \(J = 7.2\) Hz, 1H), 7.18 \(\text{–} 7.25\) (m, 1H). **\(^{13}\)C NMR** (126 MHz, CDCl\(_3\)) \(\delta\): 18.5, 21.2, 21.3, 21.7, 21.7, 31.2, 37.6, 55.2, 68.4, 69.1, 113.4, 126.7, 129.7, 158.8, 166.3, 169.6. HRESIMS calcd. for C\(_{18}\)H\(_{24}\)O\(_5\)Na (M+Na\(^+\)): 343.1521; found 343.1524.

**Dimethyl 2-(2-methoxyphenyl)cyclopropane-1,1-dicarboxylate**

![Chemical Structure]

**\(^1\)H NMR** (500 MHz, CDCl\(_3\)) \(\delta\): 1.73 (dd, \(J = 5.1\) and 9.2 Hz, 1H), 2.20 (dd, \(J = 5.2\) and 8.5 Hz, 1H), 3.30 \(\text{–} 3.34\) (m, 1H), 3.33 (s, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 6.76 \(\text{–} 6.90\) (m, 2H), 6.98 (d, \(J = 7.2\) Hz, 1H), 7.18 \(\text{–} 7.25\) (m, 1H). **\(^{13}\)C NMR** (126 MHz, CDCl\(_3\)) \(\delta\): 18.7, 28.5, 36.2, 52.0, 52.6, 55.5, 110.1, 119.9, 123.2, 127.9, 128.6, 159.2, 167.4, 170.5.

**Dimethyl 2-(3-methoxyphenyl)cyclopropane-1,1-dicarboxylate**

![Chemical Structure]
IR (neat) ν 3002, 2952, 1721, 1434 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ: 1.73 (dd, J = 5.1 and 9.3 Hz, 1H), 2.17 (dd, J = dd, J = 5.0 and 8.0 Hz, 1H), 3.20 (t, J = 8.6 Hz, 1H), 3.40 (s, 3H), 3.78 (s, 3H), 3.79 (s, 3H), 6.72 – 6.83 (m, 3H), 7.18 (t, J = 7.9 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ: 19.4, 32.6, 37.3, 52.4, 52.9, 55.3, 113.3, 114.1, 120.7, 129.2, 136.3, 159.5, 167.1, 170.3. HRESIMS calcd. for C₁₄H₁₆O₅Na (M+Na⁺): 287.0895; found 287.0889.

Dimethyl 2-(p-tolyl)cyclopropane-1,1-dicarboxylate³

¹H NMR (500 MHz, CDCl₃) δ: 1.72 (dd, J = 5.1 and 9.3 Hz, 1H), 2.17 (dd, J = 5.3 and 8.0 Hz, 1H), 2.30 (s, 3H), 3.19 (t, J = 8.6 Hz, 1H), 3.38 (s, 3H), 3.78 (s, 3H), 7.07 (s, 4H). ¹³C NMR (126 MHz, CDCl₃) δ: 19.3, 21.2, 32.5, 37.2, 52.3, 52.9, 128.4, 129.0, 131.5, 137.1, 167.2, 170.4.

Dimethyl 2- (o-tolyl)cyclopropane-1,1-dicarboxylate⁴

¹H NMR (500 MHz, CDCl₃) δ: 1.72 (dd, J = 5.3 and 9.2 Hz, 1H), 2.31 (dd, J = 5.1 and 8.2 Hz, 1H), 2.36 (s, 3H), 3.18 (t, J = 8.7 Hz, 1H), 3.29 (s, 3H), 3.81 (s, 3H), 7.03 (d, J = 7.5 Hz, 1H), 7.08 – 7.19 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ: 18.6, 19.3, 31.4, 36.2, 52.0, 52.8, 125.5, 127.3, 127.6, 129.7, 132.7, 139.0, 167.1, 170.5.

Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate²

¹H NMR (500 MHz, CDCl₃) δ: 1.74 (dd, J = 5.3 and 9.3 Hz, 1H), 2.20 (dd, J = 5.3 and 8.1 Hz, 1H), 3.23 (t, J = 8.7 Hz, 1H), 3.36 (s, 3H), 3.79 (s, 3H), 7.15 – 7.31 (m, 5H). ¹³C NMR (126 MHz, CDCl₃) δ: 19.2, 32.7, 37.3, 52.3, 52.9, 127.5, 128.3, 128.5, 134.7, 167.1, 170.3.

Dimethyl 2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate³
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$: 1.74 (dd, $J = 5.2$ and 9.3 Hz, 1H), 2.15 (dd, $J = 5.2$ and 8.0 Hz, 1H), 3.18 (t, $J = 8.6$ Hz, 1H), 3.41 (s, 3H), 3.79 (s, 3H), 6.99 – 7.13 (m, 2H), 7.32 – 7.45 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$: 19.2, 31.9, 37.3, 52.5, 53.0, 121.5, 130.3, 131.4, 133.8, 166.9, 170.1.

Dimethyl 2-(4-(methoxycarbonyl)phenyl)cyclopropane-1,1-dicarboxylate$^5$

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$: 1.78 (dd, $J = 5.2$ and 9.2 Hz, 1H), 2.22 (dd, $J = 5.2$ and 8.0 Hz, 1H), 3.25 (t, $J = 8.6$ Hz, 1H), 3.37 (s, 3H), 3.80 (s, 3H), 3.90 (s, 3H), 7.26 (d, $J = 8.2$ Hz, 2H), 7.95 (d, $J = 8.3$ Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$: 19.3, 32.2, 37.6, 52.2, 52.5, 53.0, 128.5, 129.3, 129.5, 140.1, 166.8, 170.0.
Dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate

\[
\text{MeO} \quad \text{O} \quad \text{O} \quad \text{OMe}
\]

\(3\r\)

**\(^1\text{H NMR}\)** (500 MHz, CDCl\(_3\)) \(\delta\): 1.52 (s, 3H), 1.70 (d, \(J = 5.1\) Hz, 1H), 2.22 (d, \(J = 5.2\) Hz, 1H), 3.33 (s, 3H), 3.83 (s, 3H), 7.19 – 7.24 (m, 1H), 7.25 – 7.30 (m, 4H).

**\(^{13}\text{C NMR}\)** (126 MHz, CDCl\(_3\)) \(\delta\): 24.4, 24.9, 38.2, 40.5, 52.2, 52.7, 127.2, 128.3, 141.2, 168.1, 168.9.

Ethyl 2-(4-methoxyphenyl)-1-(methylsulfonyl)cyclopropanecarboxylate

**IR** (neat) \(\nu\): 2934, 1722, 1440, 1303 cm\(^{-1}\).

**\(^1\text{H NMR}\)** (500 MHz, CDCl\(_3\), for major isomer) \(\delta\): 0.92 (t, \(J = 7.3\) Hz, 3H), 2.27 - 2.36 (m, 2H), 3.11 – 3.18 (m, 1H), 3.34 (s, 3H), 3.79 (s, 3H), 3.84 – 4.00 (m, 2H), 6.81 – 6.85 (m, 2H), 7.11 – 7.18 (m, 2H).

**\(^{13}\text{C NMR}\)** (126 MHz, CDCl\(_3\), for major isomer) \(\delta\): 13.5, 15.8, 32.1, 41.3, 50.6, 55.2, 62.1, 113.8, 124.6, 129.9, 159.4, 164.4.

**\(^1\text{H NMR}\)** (500 MHz, CDCl\(_3\), for minor isomer) \(\delta\): 1.36 (t, \(J = 7.1\) Hz, 3H), 2.23 (dd, \(J = 5.8\) and 9.6 Hz, 1H), 2.61 (dd, \(J = 5.8\) and 8.9 Hz, 1H), 2.79 (s, 3H), 3.07 (t, \(J = 9.3\) Hz, 1H), 3.80 (s, 3H), 4.33 (q, \(J = 7.1\) Hz, 2H), 6.85 – 6.89 (m, 2H), 7.23 – 7.28 (m, 2H).

**\(^{13}\text{C NMR}\)** (126 MHz, CDCl\(_3\), for minor isomer) \(\delta\): 13.9, 15.4, 35.0, 41.4, 49.6, 55.1, 62.5, 113.6, 122.7, 131.0, 159.5, 167.1.

**HRESIMS** calcd. for C\(_{14}\)H\(_{18}\)O\(_5\)SNa (M+Na\(^+\)): 321.0773; found 321.0771.

Ethyl 2-(4-methoxyphenyl)-1-(phenylsulfonyl)cyclopropanecarboxylate

**IR** (neat) \(\nu\): 2934, 1723, 1444, 1304 cm\(^{-1}\).

**\(^1\text{H NMR}\)** (500 MHz, CDCl\(_3\), for major isomer) \(\delta\): 0.79 (t, \(J = 7.2\) Hz, 3H), 2.36 (dd, \(J = 5.6\) and 8.5 Hz, 1H), 2.43 (dd, \(J = 5.6\) and 10.1 Hz, 1H), 3.37 – 3.45 (m, 1H), 3.74 (s, 3H), 3.76 (q, \(J = 7.1\) Hz, 2H), 6.72 – 6.78 (m, 2H), 6.95 – 7.02 (m, 2H), 7.59 – 7.63 (m, 2H), 7.66 – 7.71 (m, 1H), 8.03 – 8.10 (m, 2H).

**\(^{13}\text{C NMR}\)** (126 MHz, CDCl\(_3\), for major isomer) \(\delta\): 13.4, 17.6, 32.5, 52.1, 55.2, 61.7, 113.7, 124.8, 128.8, 129.3, 129.9, 133.7, 139.9, 159.2, 163.9.

**\(^1\text{H NMR}\)** (500 MHz, CDCl\(_3\), for minor isomer) \(\delta\): 1.23 (t, \(J = 7.1\) Hz, 3H), 2.28 (dd, \(J = 5.4\) and 9.7 Hz, 1H), 2.79 (dd, \(J = 5.5\) and 9.2 Hz, 1H), 3.13 (t, \(J = 9.4\) Hz, 1H), 3.84 (s, 3H), 4.12 – 4.25 (m, 2H), 6.84 – 6.89 (m, 2H), 7.20 – 7.25 (m, 2H), 7.31 – 7.37 (m, 2H), 7.25 (t, \(J = 7.5\) Hz, 1H).

**\(^{13}\text{C NMR}\)** (126 MHz, CDCl\(_3\), for minor isomer) \(\delta\): 13.8, 18.2, 36.2, 51.1, 55.3, 62.3, 113.4, 123.1, 128.1, 129.2, 131.5, 133.2, 140.1, 159.5, 167.0.

**HRESIMS**
calcd. for C$_{19}$H$_{21}$O$_5$ S$_1$Na (M+Na$^+$): 361.1110; found 361.1113.

Reference
3. Miscellaneous Reactions

4-1 Ring expand reaction with cyclopropane 3n

4-1-1 With imide

\[
\text{Sn(OTf)2, rt} \quad \begin{array}{c}
\text{MeO} \\
\text{O}
\end{array} \begin{array}{c}
\text{Ome} \\
\text{Ph}
\end{array} & \xrightarrow{(i-Pr)N=N=C=N(i-Pr)} \begin{array}{c}
\text{MeO} \\
\text{C} \\
\text{CO}_2\text{Me}
\end{array} \begin{array}{c}
\text{N(i-Pr)} \\
\text{Ph}
\end{array}
\]

Tin(II) trifluoromethanesulfonate (0.01 mmol) and dichloromethane (0.23 mL) were sequentially added under nitrogen atmosphere to a reaction tube equipped with a stir bar and a septum. The solution of 3n (0.25 mmol) and N,N-diisopropylcarbodiimide (0.28 mmol) in dichloromethane (0.62 mL) was added by syringe and vigorously stirred at room temperature for 20 h. After the reaction, the contents of the tube was diluted with dichloromethane (3.0 mL) and MeOH (1.0 mL). The solution obtained was filtered through the plug of celite, and concentrated by rotary evaporation. The residue was purified by flash chromatography eluting with dichloromethane/MeOH to afford the product 4 (94%).

\[\text{^1H NMR (500 MHz, CDCl}_3\text{)} \quad \delta: 0.87 (d, J = 6.9 Hz, 3H), 1.04 (d, J = 5.9 Hz, 3H), 1.10 (d, J = 5.9 Hz, 3H), 1.13 (d, J = 6.8 Hz, 3H), 2.31 (dd, J = 7.3 and 12.8 Hz, 1H), 2.94 (dd, J = 7.0 and 12.8 Hz, 1H), 3.48 (pent, J = 6.0 Hz, 1H), 3.70 (s, 3H), 3.79 (s, 3H), 4.00 (hept, J = 6.9 Hz, 1H), 4.52 (t, J = 7.1 Hz, 1H), 7.22 - 7.31 (m, 5H).\]

\[\text{^13C NMR (126 MHz, CDCl}_3\text{)} \quad \delta: 19.14, 19.72, 24.32, 24.66, 43.43, 47.31, 51.47, 59.85, 60.55, 127.09, 127.85, 128.61, 143.92, 151.55, 169.35, 169.83.\]

4-1-2 With Aldehyde

\[
\text{pClPhCHO} \quad \text{5 mol\% Sn(OTf)2, rt} \quad \begin{array}{c}
\text{MeO} \\
\text{O}
\end{array} \begin{array}{c}
\text{Ome} \\
\text{Ph}
\end{array} & \xrightarrow{\text{5 mol\% Sn(OTf)2, rt}} \begin{array}{c}
\text{MeO} \\
\text{C} \\
\text{CO}_2\text{Me}
\end{array} \begin{array}{c}
\text{pClPh} \\
\text{Ph}
\end{array}
\]

Tin(II) trifluoromethanesulfonate (0.017 mmol) and dichloromethane (0.25 mL) were sequentially added under nitrogen atmosphere to a reaction tube equipped with a stir bar and a septum. The solution of 3n (0.34 mmol) and p-chlorobenzaldehyde (1.0 mmol) in dichloromethane (0.25 mL) was added by syringe and vigorously stirred at room temperature for 20 h. After the reaction, the contents of the tube was diluted with EtOAc. The solution obtained was filtered through the plug of celite, and concentrated by rotary evaporation. The residue was purified by flash chromatography eluting with Hexan/EtOAc to afford the product 5 (0.28 mmol, 82%).

\[\text{^1H NMR (500 MHz, CDCl}_3\text{)} \quad \delta: 2.75 (dd, J = 6.2 and 13.5 Hz, 1H), 2.99 (dd, J = 10.5 and 13.5 Hz, 1H), 3.18 (s, 3H), 3.84 (s, 3H), 4.95 (dd, J = 6.2 and 10.5 Hz, 1H), 5.74 (s, 1H), 7.28 - 7.33 (m, 2H), 7.33 - 7.38 (m, 1H), 7.39 - 7.47 (m, 4H), 7.52 - 7.57 (m, 2H).\]

\[\text{^13C NMR (126 MHz, CDCl}_3\text{)} \quad \delta: 42.6, 52.3, 53.0, 66.1, 79.9, 83.8, 126.5, 128.0, 128.2, 128.4, 128.6, 133.9, \]
3n (0.43 mmol), and NaOH (0.52 mmol) were sequentially added under nitrogen atmosphere to a reaction tube equipped with a stir bar and a septum. MeOH (0.3 mL) was added by syringe and vigorously stirred at room temperature for 20 h. After the reaction, dil. HCl was added and the mixture was extracted with EtOAc. The solution obtained was filtered through a plug of silica gel and anhydrous MgSO₄ and concentrated by rotary evaporation. The residue was purified by flash chromatography eluting with Hexan/EtOAc to afford the product cis-6 (0.42 mmol, 98%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 2.34 (dd, $J = 4.8$ and 9.3 Hz, 1H), 2.42 (dd, $J = 4.8$ and 8.6 Hz, 1H), 3.26 (s, 3H), 3.43 (t, $J = 9.0$ Hz, 1H), 7.21 – 7.36 (m, 5H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 21.2, 33.6, 40.6, 52.5, 127.9, 128.3, 129.2, 134.0, 170.7, 173.4.

4-3. The synthesis of the core 8 of Borreverine derivatives.

[Cu(H$_2$O)$_6$](BF$_4$)$_2$ (0.050 mmol) and TPMA (0.025 mmol) were added under air to a dram vial equipped with a stir bar and a screw cap. 7 (0.50 mmol), 1c (1.0 mmol), PMDETA (0.60 mmol) and dried toluene (1.0 mL) were added by syringe and the resulting mixture vigorously stirred under nitrogen atmosphere (charged by general N$_2$ (99.95%) gas flow) for 20 h at room temperature. After this time, the contents of the flask were filtered through the plug of silica gel, and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford the product 8 (0.25 mmol, 50%).

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 1.93 (dd, $J = 4.9$ and 9.6 Hz, 1H), 2.32 (s, 3H), 2.52 (dd, $J = 4.9$ and 8.3 Hz, 1H), 3.15 (t, $J = 8.8$ Hz, 1H), 3.33 (s, 3H), 3.69 (s, 3H), 3.85 (s, 3H), 7.06 (ddd, $J = 1.1$, 6.8 and 7.8 Hz, 1H), 7.15 – 7.24 (m, 2H), 7.49 (d, $J = 7.9$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 9.0, 20.0, 25.0, 29.8, 34.9, 52.3, 53.0, 108.6, 110.0, 118.7, 121.7, 128.2, 128.5, 136.9, 167.0, 170.2.
4. Spectral Data for New Compounds