Supporting Information
for
Cyclization of alkynoic acids in water
in the presence of a vesicular self-assembled amphiphilic pincer
catalyst

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Experimental Section

**General.** When manipulations were performed under a nitrogen atmosphere, nitrogen gas was dried by passage through P$_2$O$_5$. Commercially available chemicals (purchased from Aldrich, TCI, Kanto, Wako, Nakalai, and AlfaAesar) are used without further purification unless otherwise noted. NMR spectra recorded on a JEOL JNM-A500 spectrometer (500 MHz for $^1$H, 125 MHz for $^{13}$C) or a JEOL ECS-400 spectrometer (396 MHz for $^1$H, 100 MHz for $^{13}$C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for $^1$H NMR. Chemical shifts of $^{13}$C NMR are given related to CDCl$_3$ as an internal standard (δ 77.0). $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ at 25 °C unless otherwise noted. HREI mass spectra were recorded on a JEOL AccuTOF GC JMS-T100GC equipped with Agilent 6890N GC. EI mass spectra were recorded on an Agilent 5973N equipped with Agilent 6890N GC. Melting points were determined using a Yanaco micro melting point apparatus MP-J3 and are uncorrected. IR spectra were obtained using a JASCO FT/IR-460plus spectrometer in ATR mode. Millipore water was obtained from a Millipore Milli-Q Biocel A10 purification unit.

**Preparation of alkynoic acids 2**

\[
\begin{align*}
\ce{C≡C-COOMe &<-> H2SO4 MeOH, reflux 24 h} \\
\ce{C≡C-COOH} &<-> \ce{PdCl2(PPh3)2 CuI CH3CN, Et3N 25 °C, 1 d} \\
\ce{C≡C-COOMe} &<-> \ce{LiOH·H2O THF-H2O 25 °C, overnight} \\
\end{align*}
\]

**Scheme S1.** Preparation of alkynoic acids 2.

**Methyl-4-pentynoate (S1)**

\[
\begin{align*}
\ce{C≡C-COOMe} \quad \text{CAS registry No.: 21565-82-2}
\end{align*}
\]

To a stirred MeOH (50 mL) solution of 4-pentynoic acid (5.00 g, 50.7 mmol) was added H$_2$SO$_4$ (1.63 mL, 30.6 mmol). After refluxing for 24 h, the reaction mixture was quenched by the addition of saturated sodium bicarbonate aqueous solution and the resulting solution was extracted with CH$_2$Cl$_2$ (30 mL × 3). The obtained organic layer was dried over magnesium sulfate. The solution was concentrated in vacuo to give
methyl-4-pentynoate (S1, 5.35 g, 47.7 mmol, 94.0%) as pale yellow oil.

\(^1\)H NMR (396 MHz, CDCl\(_3\)) \(\delta\) 1.97–1.99 (m, 1H, C\(\text{CH}\)), 2.48–1.60 (m, 4H, CH\(_2\)CH\(_2\)), 3.71 (s, 3H, COOCH\(_3\)); \(^{13}\)C\(^1\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 14.2, 33.0, 51.7, 68.9, 82.3, 172.1; MS (EI) \(m/z\) = 111 ([M+1]\(^+\)).

**General procedure for the Sonogashira coupling reaction of S1 with ArI.**

A typical procedure is given for the Sonogashira reaction of methyl-4-pentynoate with 4-trifluoromethyliodobenzene. To a suspension of PdCl\(_2\)(PPh\(_3\))\(_2\) (125 mg, 0.178 mmol) and copper iodide (68 mg, 0.357 mmol) in triethylamine (3 mL), methyl-4-pentynoate (S1, 1.00 g, 8.92 mmol) in anhydrous CH\(_3\)CN (1 mL) and 4-trifluoromethyliodobenzene (2.67 g, 9.81 mmol) were added. After being stirred for 1 day, saturated NH\(_4\)Cl aqueous solution (15 mL) was added to the reaction mixture and the resulting solution was extracted with AcOEt (15 mL, 4 times). The combined organic layer was dried over Na\(_2\)SO\(_4\). After evaporation of the solvent, the resulting residue was chromatographed on silica gel (eluent: 0-5% AcOEt/n-hexane) to give methyl 5-(4-trifluoromethylphenyl)-4-pentynoate (S2a, 1.85 g, 7.21 mmol, 81%) as pale yellow oil.

**Methyl 5-(4-trifluoromethylphenyl)-4-pentynoate (S2a)**

\[
\text{F}_3\text{C} = \text{C} \equiv \text{C} = \text{CH}_2 \quad \text{COOMe}
\]

81% yield; Pale yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.65 (t, \(J = 8\) Hz, 2H, CH\(_2\)), 2.75 (t, \(J = 8\) Hz, 2H, CH\(_2\)), 3.73 (s, 3H, CH\(_3\)), 7.26–7.30 (m, 3H, ArH), 7.37–7.40 (m, 2H, ArH); \(^{13}\)C\(^1\)H NMR (125 MHz, CDCl\(_3\)) \(\delta\) 15.3, 33.1, 51.8, 80.0, 90.7, 123.9 (q, \(J_{C-F} = 270\) Hz), 125.1 (q, \(J_{C-F} = 4\) Hz), 128.3 (q, \(J_{C-F} = 261\) Hz), 129.7, 131.8, 172.8; IR (ATR) 2999, 2955, 1738 (C=O), 1616, 1438, 1406, 1366, 1321 (CF\(_3\)), 1255, 1199, 1163, 1121, 1104, 1066, 1038, 1017, 989, 889, 840, 777, 738, 693, 597 cm\(^{-1}\); HR-EI-MS Calcd. for C\(_{13}\)H\(_{11}\)F\(_3\)O\(_2\) [M]\(^+\): \(m/z\) = 256.07111; Found 256.07061.

**Methyl 5-phenyl-4-pentynoate (S2b)**

\[
\text{H}_2\text{C} = \text{C} \equiv \text{C} \equiv \text{CH}_2 \quad \text{COOMe}
\]

68% yield; Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.62–2.67 (m, 2H, CH\(_2\)), 2.71–2.76 (m, 2H, CH\(_2\)), 3.72 (s, 3H, CH\(_3\)), 7.26–7.30 (m, 3H, ArH), 7.37–7.40 (m, 2H,
ArH; \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (125 MHz, CDCl\textsubscript{3})  \delta 15.3, 33.4, 51.8, 81.2, 87.9, 123.5, 127.8, 128.2, 131.6, 172.4; MS (EI) \textit{m/z} = 188 ([M\textsuperscript{+}]).

Methyl 5-(4-methylphenyl)-4-pentynoate (S2c)

Me-\equiv-COOMe CAS registry No. 1061175-65-2

75% yield; Color less oil; \textsuperscript{1}H NMR (395 MHz, CDCl\textsubscript{3})  \delta 2.32 (s, 3H, C\textsubscript{6}H\textsubscript{3}), 2.61−2.66 (m, 2H, CH\textsubscript{2}), 2.70−2.75 (m, 2H, CH\textsubscript{2}), 3.72 (s, 3H, CH\textsubscript{3}), 7.08 (d, J = 8 Hz, 2H, ArH), 7.27 (d, J = 8 Hz, 2H, ArH); \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3})  \delta 15.3, 21.4, 33.5, 51.8, 81.2, 87.1, 120.3, 128.9, 131.4, 137.8, 172.4; MS (EI) \textit{m/z} = 202 ([M\textsuperscript{+}]).

Methyl 5-(4-methoxyphenyl)-4-pentynoate (S2d)

MeO-\equiv-COOMe CAS No. 1061175-68-5

78% yield; Colorless oil; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3})  \delta 2.60−2.64 (m, 2H, CH\textsubscript{2}), 2.69−2.73 (t, 2H, CH\textsubscript{2}), 3.71 (s, 3H, CH\textsubscript{3}), 3.78 (s, 3H, CH\textsubscript{3}), 6.80 (d, J = 9 Hz, 2H, ArH), 7.31 (d, J = 9 Hz, 2H, ArH); \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (125 MHz, CDCl\textsubscript{3})  \delta 15.3, 33.5, 51.7, 55.1, 80.9, 86.3, 113.7, 115.5 132.9, 159.1, 172.4; MS (EI) \textit{m/z} = 218 ([M\textsuperscript{+}]).

Methyl 5-(4-tert-butylphenyl)-4-pentynoate (S2e)

Ph-\equiv-COOMe CAS registry No. none

47% yield (from 4-tert-butylbromobenzene: 5 mol\% PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} and 10 mol\% CuI were used. The reaction performed in a mixture of \textsuperscript{1}Pr\textsubscript{2}NH and toluene at 85 °C); Pale yellow oil; \textsuperscript{1}H NMR (396 MHz, CDCl\textsubscript{3})  \delta 1.29 (s, 9H, C(CH\textsubscript{3})\textsubscript{3}), 2.61−2.65 (m, 2H, CH\textsubscript{2}), 2.70−2.75 (m, 2H, CH\textsubscript{2}), 3.71 (s, 3H, CH\textsubscript{3}), 7.28–7.33 (m, 4H, ArH); \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CDCl\textsubscript{3})  \delta 15.3, 33.1, 33.5, 34.6, 51.8, 81.1, 87.1, 120.4, 125.1, 131.2, 150.9, 172.4; IR (ATR) 2959, 2905, 2869, 1737 (C=O), 1648, 1608, 1506, 1459, 1437, 1419, 1396, 1363, 1268, 1256, 1223, 1198, 1166, 1110, 1018, 991, 834, 779, 705, 562 cm\textsuperscript{-1}; HR-EI-MS Calcd. for C\textsubscript{16}H\textsubscript{20}O\textsubscript{2} [M\textsuperscript{+}]: \textit{m/z} = 244.14633; Found 244.14619.

Methyl 5-(4-phenylphenyl)-4-pentynoate (S2f)

Ph-\equiv-COOMe CAS registry No. 1061175-63-0
75% yield; Pale yellow oil; \(^1H\) NMR (500 MHz, CDCl$_3$) \(\delta\) 2.65 (t, \(J = 8\) Hz, 2H, CH$_2$), 2.76 (t, \(J = 8\) Hz, 2H, CH$_2$), 3.72 (s, 3H, CH$_3$), 7.32–7.36 (m, 1H, ArH), 7.41–7.46 (m, 4H, ArH), 7.52 (d, \(J = 8\) Hz, 2H, ArH), 7.57 (d, \(J = 8\) Hz, 2H, ArH); \(^1^3C\{^1H\}\) NMR (125 MHz, CDCl$_3$) \(\delta\) 15.4, 33.4, 51.8, 81.0, 88.6, 122.4, 126.8, 126.9, 127.4, 128.7, 131.9, 140.3, 140.5, 172.3; MS (EI) m/z = 264 ([M$^+$]).

**Methyl 5-(4-nitrophenyl)-4-pentynoate (S2g)**

85% yield; Yellow solids; Mp. 88.5–89.5 °C; \(^1H\) NMR (500 MHz, CDCl$_3$) \(\delta\) 2.66 (t, \(J = 7\) Hz, 2H, CH$_2$), 2.78 (t, \(J = 7\) Hz, 2H, CH$_2$), 3.74 (s, 3H, CH$_3$), 7.51 (d, \(J = 9\), 4 Hz, 2H, ArH), 8.15 (d, \(J = 9\) Hz, 2H, ArH); \(^1^3C\{^1H\}\) NMR (125 MHz, CDCl$_3$) \(\delta\) 15.3, 32.9, 51.8, 79.6, 94.0, 123.4, 130.4, 132.2, 146.7, 171.9; IR (ATR) 3113, 2951, 2844, 2219 (CC), 1730 (C=O), 1591, 1509 (NO$_2$), 1491, 1434, 1372, 1339, 1309, 1300, 1285, 1273, 1256, 1198, 1173, 1108, 1054, 1011, 986, 971, 887, 852, 831, 775, 749, 687, 591, 580 cm$^{-1}$; HR-EI-MS Calcd. for C$_{12}$H$_{11}$NO$_4$ [M$^+$]: m/z = 233.06881; Found 233.06890.

**Methyl 5-(4-fluorophenyl)-4-pentynoate (S2h)**

74% yield; Colorless oil; \(^1H\) NMR (500 MHz, CDCl$_3$) \(\delta\) 2.63 (t, \(J = 8\) Hz, 2H, CH$_2$), 2.72 (t, \(J = 8\) Hz, 2H, CH$_2$), 3.72 (s, 3H, CH$_3$), 6.94–6.99 (m, 2H, ArH), 7.33–7.37 (m, 2H, ArH); \(^1^3C\{^1H\}\) NMR (125 MHz, CDCl$_3$) \(\delta\) 15.2, 33.3, 51.8, 79.6, 94.0, 123.4, 130.4, 132.2, 146.7, 171.9; MS (EI) m/z = 206 ([M$^+$]).

**Methyl 5-(4-chlorophenyl)-4-pentynoate (S2i)**

79% yield; Colorless oil; \(^1H\) NMR (500 MHz, CDCl$_3$) \(\delta\) 2.62 (t, \(J = 8\) Hz, 2H, CH$_2$), 2.72 (t, \(J = 8\) Hz, 2H, CH$_2$), 3.71 (s, 3H, CH$_3$), 7.24 (d, \(J = 9\) Hz, 2H, ArH), 7.30 (d, \(J = 9\) Hz, 2H, ArH); \(^1^3C\{^1H\}\) NMR (125 MHz, CDCl$_3$) \(\delta\) 15.3, 33.2, 51.8, 80.1, 87.6, 115.3 (d, \(J_{C-F} = 22\) Hz), 119.5 (d, \(J_{C-F} = 4\) Hz), 133.3 (d, \(J_{C-F} = 8\) Hz), 162.1 (d, \(J_{C-F} = 248\) Hz), 172.3; MS (EI) m/z = 206 ([M$^+$]).
Methyl 5-(2-methylphenyl)-4-pentynoate (S2j)

\[
\text{Me} \quad \equiv \quad \text{COOMe} \quad \text{CAS registry No.} \quad 1369558-68-8
\]

74% yield; Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.39 (s, 3H, CH\(_3\)), 2.65 (t, \(J = 7\) Hz, 2H, CH\(_2\)), 2.77 (t, \(J = 7\) Hz, 2H, CH\(_2\)), 3.72 (s, 3H, CH\(_3\)), 7.07–7.12 (m, 1H, ArH), 7.15–7.18 (m, 2H, ArH); \(^{13}\)C\(^{\text{1}\text{H}}\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 15.5 (CH\(_2\)), 20.6 (CH\(_3\)), 33.6 (CH\(_2\)), 51.7 (CH\(_3\)), 80.1 (CC), 91.9 (CC), 123.2 (ArC), 125.3 (ArC), 127.8 (ArC), 129.3 (ArC), 131.8 (ArC), 140.0 (ArC), 172.4 (C=O); MS (EI) \(m/\text{z} = 202\) (\([\text{M}^+\]\)).

Methyl 5-(1-naphtyl)-4-pentynoate (S2k)

\[
\text{COOMe}
\]

CAS registry No. 1435518-72-1

71% yield; Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.73 (t, \(J = 8\) Hz, 2H, CH\(_2\)), 2.89 (t, \(J = 8\) Hz, 2H, CH\(_2\)), 3.74 (s, 3H, CH\(_3\)), 7.38 (dd, \(J = 8\), 8 Hz, 1H, ArH), 7.49 (ddd, \(J = 1, 8, 9\) Hz, 1H, ArH), 7.60 (ddd, \(J = 1, 7\) Hz, 1H, ArH), 7.77 (d, \(J = 8\) Hz, ArH), 7.82 (d, \(J = 8\) Hz, 1H, ArH), 8.30 (d, \(J = 9\) Hz, 1H, ArH); \(^{13}\)C\(^{\text{1}\text{H}}\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 15.7, 33.6, 51.8, 79.2, 92.9, 121.1, 125.1, 126.1, 126.2, 126.5, 128.1, 128.2, 130.1, 133.1, 133.4, 172.3; MS (EI) \(m/\text{z} = 238\) ([M\(^+\)]).

Methyl 5-(2-thienyl)-4-pentynoate (S2l)

\[
\text{COOMe}
\]

CAS registry No. none

67% yield; Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 2.63 (t, \(J = 8\) Hz, 2H, CH\(_2\)), 2.75 (t, \(J = 8\) Hz, 2H, CH\(_2\)), 3.72 (s, 3H, CH\(_3\)), 6.92–6.94 (dd, \(J = 4, 4\) Hz, 1H, ArH), 7.13 (d, \(J = 4\) Hz, 1H, ArH), 7.18 (d, \(J = 4\) Hz, 1H, ArH); \(^{13}\)C\(^{\text{1}\text{H}}\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 15.5, 33.1, 74.3, 91.9, 123.5, 126.2, 126.7, 131.3, 172.4; IR (ATR) 3107, 2996, 2952, 2844, 1735 (C=O), 1519, 1436, 1362, 1290, 1256, 1239, 1192, 1165, 1081, 1038, 1019, 980, 942, 880, 865, 832, 779, 698, 656, 592, 572 cm\(^{-1}\); HR-EI-MS Calcd. for C\(_{10}\)H\(_{10}\)O\(_2\)S \([\text{M}]^+\): \(m/\text{z} = 194.0401\); Found 194.0400.
General procedure for hydrolysis of methyl esters

A typical procedure is given for the reaction of methyl 5-(4-trifluoromethylphenyl)-4-pentyanoate (S2a). To a solution of methyl 5-(4-trifluoromethylphenyl)-4-pentyanoate (1.84 g, 7.19 mmol) in a mixture of THF (80 mL) and H₂O (20 mL), lithium hydroxide monohydrate (603 mg, 14.4 mmol) was added. After being stirred at 25 °C for overnight, the mixture was washed with tert-butyl methyl ether (20 mL, 3 times) and acidified with 4N HCl aqueous solution. The organic layer was extracted with tert-butyl methyl ether (20 mL, 3 times), dried over Na₂SO₄, and concentrated in vacuo to give 5-(4-trifluoromethylphenyl)-4-pentyanoic acid (2a, 1.64 g, 6.77 mmol, 94%) as white solids.

5-[(4-Trifluoromethyl)phenyl]pent-4-ynoic acid (2a)

\[
\begin{align*}
\text{F}_3\text{C} & \quad \equiv \\
& \quad \text{COOH}
\end{align*}
\]

CAS registry No. 876049-26-2

94% yield; White solids; \(^1\)H NMR (396 MHz, CDCl₃) \(\delta 2.69–2.79 \text{ (m, 4H, } \text{CH}_2\text{)}, 7.47 \text{ (d, } J = 8 \text{ Hz, 2H, ArH}))

13C\(^1\)H NMR (100 MHz, CDCl₃) \(\delta 15.0, 33.2, 80.2, 90.3, 123.2 \text{ (q, } J_{\text{C-F}} = 272 \text{ Hz}), 125.1 \text{ (q, } J_{\text{C-F}} = 4 \text{ Hz}), 127.2, 129.6 \text{ (q, } J_{\text{C-F}} = 32 \text{ Hz}), 131.8, 178.1\); MS (EI) \(m/z = 242 ([M^+]\)).

5-Phenylpent-4-ynoic acid (2b)

\[
\begin{align*}
\text{\textbf{C}} & \quad \equiv \\
& \quad \text{COOH}
\end{align*}
\]

CAS registry No. 3350-92-3

91% yield; White solids; \(^1\)H NMR (396 MHz, CDCl₃) \(\delta 2.66–2.76 \text{ (m, 4H, } \text{CH}_2\text{)}, 7.25–7.30 \text{ (m, 3H, ArH)), 7.36–7.42 \text{ (m, 2H, ArH)})

13C\(^1\)H NMR (100 MHz, CDCl₃) \(\delta 15.0, 33.4, 81.3, 87.5, 123.3, 127.9, 128.2, 131.6, 178.2\); EI (70eV) \(m/z = 174 ([M^+]\)).

5-[(4-Methyl)phenyl]pent-4-ynoic acid (2c)

\[
\begin{align*}
\text{Me} & \quad \equiv \\
& \quad \text{COOH}
\end{align*}
\]

CAS registry No. none

92% yield; White solids; Mp. 130.0–131.0 °C; \(^1\)H NMR (396 MHz, CDCl₃) \(\delta 2.33 \text{ (s, 3H, } \text{CH}_3\text{), 2.66–2.76 \text{ (m, 4H, } \text{CH}_2\text{)}, 7.08 \text{ (d, } J = 8 \text{ Hz, 2H, ArH}), 7.28 \text{ (d, } J = 8 \text{ Hz, 2H, ArH})\);

13C\(^1\)H NMR (100 MHz, CDCl₃) \(\delta 15.1, 21.4, 33.5, 81.4, 86.7, 120.2, 128.9, 131.4, 137.9, 178.2\); IR (ATR) 3097, 3042, 3031, 2988, 2935, 2918, 2859, 2653, 2629, 2604, 2557, 2504, 1922, 1704 (C=O), 1508, 1424, 1407, 1357, 1303, 1261, 1211, 1175, 1106,
1045, 1021, 930, 822, 767, 692, 634 cm$^{-1}$; **HR-EI-MS** Calcd. for C$_{12}$H$_{12}$O$_2$ [M]$^+$: m/z = 188.08373; Found 188.08348.

5-[(4-Methoxy)phenyl]pent-4-yonoic acid (2d)

\[
\text{MeO} \begin{array}{c} \\
\longrightarrow \\
\text{COOH}
\end{array} \text{CAS No. 137742-44-0}
\]

92% yield; White solids; **$^1$H NMR (396 MHz, CDCl$_3$)** $\delta$ 2.66–2.75 (m, 4H, CH$_2$), 3.80 (s, CH$_3$), 6.81 (d, $J = 9$ Hz, 2H, ArH), 7.32 (d, $J = 9$ Hz, 2H, ArH); **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** $\delta$ 15.1, 33.5, 55.3, 81.1, 86.0, 113.8, 115.5, 133.0, 159.2, 178.1; **MS (EI)** m/z = 204 ([M$^+$]).

5-[(4-tert-Butyl)phenyl]pent-4-yonoic acid (2e)

\[
\text{Ph} \begin{array}{c} \\
\longrightarrow \\
\text{COOH}
\end{array} \text{CAS registry No. none}
\]

80% yield; White solids; **Mp.** 133.5–134.5 °C; **$^1$H NMR (396 MHz, CDCl$_3$)** $\delta$ 1.30 (s, 9H, C(CH$_3$)$_3$), 2.65–2.77 (m, 4H, CH$_2$), 7.27–7.36 (m, 4H, ArH); **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** $\delta$ 15.1, 31.2, 33.4, 34.7, 81.3, 86.8, 120.3, 125.2, 131.2, 151.0, 177.9; **IR (ATR)** 3037, 2952, 2901, 2865, 2633, 2596, 2552, 2503, 1703 (C=O), 1505, 1462, 1428, 1409, 1362, 1299, 1267, 1259, 1213, 1109, 1019, 936, 837, 775, 754, 682, 562 cm$^{-1}$; **HR-EI-MS** Calcd. for C$_{15}$H$_{18}$O$_2$ [M]$^+$: m/z = 230.13072; Found 230.13072.

5-[(4-Phenyl)phenyl]pent-4-yonoic acid (2f)

\[
\text{Ph} \begin{array}{c} \\
\longrightarrow \\
\text{COOH}
\end{array} \text{CAS registry No. 300663-09-6}
\]

74% yield; Pale yellow solids; **$^1$H NMR (396 MHz, CDCl$_3$)** $\delta$ 2.69–2.80 (m, 4H, CH$_2$), 7.32–7.37 (m, 1H, ArH), 7.40–7.48 (m, 4H, ArH), 7.50–7.54 (m, 2H, ArH), 7.55–7.59 (m, 2H, ArH); **$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$)** $\delta$ 15.2, 33.3, 81.2, 88.2, 122.3, 126.9, 127.0, 127.5, 128.76, 128.81, 132.0, 140.4, 140.6, 177.2; **EI (70eV)** m/z = 250 ([M$^+$]).

5-[(4-Nitro)phenyl]pent-4-yonoic acid (2g)

\[
\text{O}_2\text{N} \begin{array}{c} \\
\longrightarrow \\
\text{COOH}
\end{array} \text{CAS registry No. none}
\]

89% yield; Yellow solids; **Mp.** 157.0–158.0 °C; **NMR (396 MHz, CDCl$_3$)** $\delta$ 2.70–2.75 (m, 2H, CH$_2$), 2.77–2.82 (m, 2H, CH$_2$), 7.52 (d, $J = 9$ Hz, 1H, ArH), 8.15 (d, $J = 9$ Hz, 1H,
ArH; $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 15.1, 32.9, 79.9, 93.5, 123.5, 130.3, 132.4, 146.8, 177.3; IR (ATR) 3110, 3086, 3028, 2978, 2930, 2845, 2808, 2792, 2710, 2647, 2614, 2560, 2511, 2465, 2445, 1694 (C=O), 1592, 1510 (NO$_2$), 1432, 1407, 1339, 1317, 1305, 1286, 1275, 1261, 1212, 1172, 1103, 1096, 1011, 980, 922, 854, 776, 750, 689, 677 cm$^{-1}$; HR-EI-MS Calcd. for C$_{11}$H$_9$NO$_4$ [M$^+$]: m/z = 219.05316; Found 219.05341.

5-[(4-Fluoro)phenyl]pent-4-ynoic acid (2h)

\[
\begin{array}{c}
\text{F} \\
\text{C} \\
\text{O} \\
\text{H} \\
\text{COOH}
\end{array}
\]

CAS registry No. none

88% yield; White solids; Mp 112.5–113.5 °C; $^1$H NMR (396 MHz, CDCl$_3$) δ 2.65–2.76 (m, 4H, CH$_2$), 6.94–7.00 (m, 2H, ArH), 7.33–7.39 (m, 2H, ArH); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 15.0, 33.4, 80.3, 87.2, 115.4 (d, $J_{C-F} = 22$ Hz), 119.4 (d, $J_{C-F} = 4$ Hz), 133.4 (d, $J_{C-F} = 9$ Hz), 162.2 (d, $J_{C-F} = 249$ Hz), 178.4; IR (ATR) 3102, 3064, 3045, 3033, 2979, 2964, 2936, 2919, 2852, 2710, 2632, 2560, 2512, 1703 (C=O), 1597, 1504, 1432, 1409, 1360, 1308, 1259, 1214, 1161, 1095, 1014, 979, 918, 841, 829, 814, 776, 699, 634 cm$^{-1}$; HR-EI-MS Calcd. for C$_{11}$H$_9$FO$_2$ [M$^+$]: m/z = 192.05866; Found 192.05871.

5-[(4-Chloro)phenyl]pent-4-ynoic acid (2i)

\[
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{O} \\
\text{H} \\
\text{COOH}
\end{array}
\]

CAS registry No. 1172131-51-9

93% yield; White solids; $^1$H NMR (396 MHz, CDCl$_3$) δ 2.65–2.76 (m, 4H, CH$_2$), 7.24 (d, $J = 8$ Hz, 2H, ArH), 7.30 (d, $J = 8$ Hz, 1H, ArH); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 15.0, 33.3, 80.3, 88.6, 121.8, 128.5, 132.8, 133.8, 178.4; EI (70eV) m/z = 208 ([M$^+$]).

5-[(2-Methyl)phenyl]pent-4-ynoic acid (2j)

\[
\begin{array}{c}
\text{Me} \\
\text{C} \\
\text{O} \\
\text{H} \\
\text{COOH}
\end{array}
\]

CAS registry No. none

100% yield; White solids; Mp 61.0–62.0 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 2.38 (s, 3H, CH$_3$), 2.69–2.73 (m, 2H, CH$_2$), 2.77–2.81 (m, 2H, CH$_2$), 7.07–7.12 (m, 1H, ArH), 7.14–7.19 (m, 2H, ArH), 7.34–7.36 (m, 1H, ArH); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) δ 15.3, 20.6, 33.7, 80.3, 91.4, 123.1, 125.4, 127.8, 129.3, 131.8, 140.1, 178.1; IR (ATR) 3021, 2967, 2921, 2852, 2735, 2701, 2635, 2551, 2503, 1693 (C=O), 1487, 1432, 1411, 1351, 1302, 1289, 1253, 1212, 1176, 1161, 1114, 1044, 1017, 978, 918, 862, 803, 777, 748, 715,
664 cm$^{-1}$; **HR-EI-MS** Calcd. for C$_{12}$H$_{12}$O$_2$ [M$^+$]: $m/z = 188.08373$; Found 188.08375.

5-(1-Naphtyl)pent-4-ynoic acid (2k)

![Chemical structure](image)

CAS registry No. 928768-34-7

91% yield; White solids; $^1$H NMR (396 MHz, CDCl$_3$) $\delta$ 2.78–2.84 (m, 2H, CH$_2$), 2.88–2.93 (m, 2H, CH$_2$), 7.39 (t, $J = 8$ Hz, 1H, ArH), 7.49 (td, $J = 1, 7$ Hz, 1H, ArH), 7.54 (td, $J = 1, 7$ Hz, 1H, ArH), 7.61 (d, $J = 7$ Hz, 1H, ArH), 7.78 (d, $J = 8$ Hz, ArH), 7.82 (d, $J = 8$ Hz, 1H, ArH); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 15.4, 33.6, 79.5, 92.5, 121.0, 125.2, 126.1, 126.3, 126.6, 128.2, 128.3, 130.2, 133.1, 133.4, 178.1; EI (70eV) $m/z = 224$ ([M$^+$]).

5-(2-Thienyl)pent-4-ynoic acid (2l)

![Chemical structure](image)

CAS No. 928768-35-8

86% yield; Pale brown solids; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.68–2.72 (m, 2H, CH$_2$), 2.74–2.78 (m, 2H, CH$_2$), 6.93–6.95 (m, 1H, ArH), 7.13–7.14 (m, 1H, ArH), 7.18–7.20 (m, 1H, ArH); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$) $\delta$ 15.3, 33.1, 74.6, 91.5, 123.4, 126.4, 126.8, 131.5, 177.9; EI (70eV) $m/z = 180$ ([M$^+$]).

**General procedure for cyclization of alkyenoic acids**

A typical procedure is given for the reaction with 5-(4-trifluoromethylphenyl)pentynoic acid (2a) in the presence of 1a$_{vscl}$ and Et$_3$N in water (Table 1, entry 2). 5-(4-Trifluoromethylphenyl)pentynoic acid (2a, 29.1 mg, 0.12 mmol) was placed in a vial, to which was added 1 mL aqueous suspension of 1a$_{vscl}$ (2.6 mg, 2.4 × 10$^{-3}$ mmol) and Et$_3$N (1 mL, 7.2 × 10$^{-3}$ mmol). The reaction mixture was agitated by shaking at 50 °C for 1 h, and then extracted with t-butyl methyl ether (MTBE) (1.5 mL, 4 times). The combined extract was dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was chromatographed on silica gel (eluent: CHCl$_3$) to give 3a (17.6 mg, 0.727 mmol, 61%).
(Z)-γ-(4-Trifluoromethylbenzyldiene)-γ-butyrolactone (3a)

CAS registry No. none

White solids; Mp 56.5–57.0 °C; $^1$H NMR (396 MHz, CDCl$_3$) $\delta$ 2.73–2.78 (m, 2H, CH$_2$), 3.05–3.11 (m, 2H, CH$_2$), 5.58–5.60 (m, 1H, C=CH), 7.56 (d, $J = 8$ Hz, 2H, ArH), 7.64 (d, $J = 8$ Hz, 2H, ArH); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 26.4, 26.7, 103.7, 124.2 (q, $J_{C-F} = 272$ Hz), 125.3 (q, $J_{C-F} = 4$ Hz), 128.3 (q, $J_{C-F} = 32$ Hz), 128.4, 137.5, 150.2, 174.5; IR (ATR) 2956, 2936, 1804 (C=O), 1680, 1614, 1443, 1415, 1323 (CF$_3$), 1290, 1227, 1165, 1093, 1064, 1015, 939, 853, 815, 755, 708, 652, 597 cm$^{-1}$; HR-EI-MS Calcd. for C$_{12}$H$_9$F$_3$O$_2$ [M]$^+$: m/z = 242.05546; Found 242.05518.

(Z)-γ-Benzylidene-γ-butyrolactone (3b)

CAS registry No. 69063-20-3

White solids; $^1$H NMR (396 MHz, CDCl$_3$) $\delta$ 2.69–2.74 (m, 2H, CH$_2$), 3.01–3.07 (m, 2H, CH$_2$), 5.54–5.56 (m, 1H, C=CH), 7.21 (t, $J = 7$ Hz, 1H, ArH), 7.33 (t, $J = 7$ Hz, 2H, ArH), 7.54 (d, $J = 7$ Hz, 2H, ArH); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 26.3, 26.9, 104.9, 126.7, 128.3, 128.4, 133.8, 148.1, 174.9; EIMS (70eV) m/z = 174 ([M$^+$]).

(Z)-γ-(4-Methylbenzyldiene)-γ-butyrolactone (3c)

CAS registry No. none

White solids; Mp 85.0–86.0 °C; $^1$H NMR (396 MHz, CDCl$_3$) $\delta$ 2.34 (s, 3H, CH$_3$), 2.68–2.73 (m, 2H, CH$_2$), 3.00–3.06 (m, 2H, CH$_2$), 5.51–5.53 (m, 1H, C=CH), 7.13 (d, $J = 8$ Hz, 2H, ArH), 7.44 (d, $J = 8$ Hz, 2H, ArH); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) $\delta$ 21.1, 26.2, 27.0, 104.7, 128.1, 129.1, 131.0, 136.4, 147.3, 175.1; IR (ATR) 3024, 2982, 2923, 2872, 1792 (C≡O), 1682, 1609, 1508, 1444, 1413, 1355, 1290, 1227, 1208, 1176, 1102,
(Z)-γ-(4-Methoxybenzylidene)-γ-butyrolactone (3d)

\[
\text{MeO}
\]

CAS registry No. none

Pale yellow oil; \textsuperscript{1}H NMR (396 MHz, CDCl\textsubscript{3}) \(\delta\) 2.68–2.73 (m, 2H, \(CH\textsubscript{2}\)), 2.99–3.05 (m, 2H, \(CH\textsubscript{2}\)), 3.81 (s, OCH\textsubscript{3}), 5.48–5.51 (m, 1H, C=CH), 6.86 (d, \(J = 9\) Hz, 2H, Ar\(H\)), 7.49 (d, \(J = 9\) Hz, 2H, Ar\(H\)); \textsuperscript{13}C\textsuperscript{1}H NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 26.2, 27.0, 55.2, 104.3, 113.80, 126.6, 129.5, 146.4, 158.2, 175.1; IR (ATR) 3003, 2958, 2934, 2838, 1792 (C=O), 1732, 1685, 1606, 1577, 1509, 1463, 1443, 1419, 1350, 1294, 1248, 1175, 1114, 1096, 1029, 941, 906, 848, 830, 815, 756, 722, 704, 657, 628, 597, 554 cm\textsuperscript{-1}; HR-EI-MS Calcd. for C\textsubscript{12}H\textsubscript{12}O\textsubscript{2} [M]\textsuperscript{+}: \(m/z\) = 204.07864 Found 204.07866.

(\textsc{Z})-γ-(\textsc{Z})-γ-(4-tert-Butylbenzylidene)-γ-butyrolactone (3e)

\[
\text{MeO}
\]

CAS registry No. none

White solids; Mp. 34.0–35.0 °C; \textsuperscript{1}H NMR (396 MHz, CDCl\textsubscript{3}) \(\delta\) 1.31 (s, 9H, C(CH\textsubscript{3}\textsubscript{3})), 2.68–2.73 (m, 2H, \(CH\textsubscript{2}\)), 3.00–3.05 (m, 2H, \(CH\textsubscript{2}\)), 5.53–5.54 (m, 1H, C=CH), 7.35 (d, \(J = 9\) Hz, 2H, Ar\(H\)), 7.48 (d, \(J = 9\) Hz, 2H, Ar\(H\)); \textsuperscript{13}C\textsuperscript{1}H NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 26.2, 27.1, 31.2, 34.5, 104.7, 125.3, 128.0, 131.0, 147.5, 149.7, 175.0; IR (ATR) 2959, 2928, 2868, 1799 (C=O), 1726, 1685, 1511, 1475, 1462, 1445, 1415, 1395, 1362, 1293, 1270, 1229, 1201, 1173, 1123, 1096, 1018, 941, 851, 836, 807, 705, 656, 575 cm\textsuperscript{-1}; HR-EI-MS Calcd. for C\textsubscript{15}H\textsubscript{18}O\textsubscript{2} [M]\textsuperscript{+}: \(m/z\) = 230.13068; Found 230.13070.
(Z)-γ-(4-Phenylbenzylidene)-γ-butyrolactone (3f)

Light brown solids; \( \text{Mp} \, 116.5–117.5 \, ^\circ\text{C} \); \(^1\)H NMR (396 MHz, CDCl\(_3\)) \( \delta \) 2.71–2.76 (m, 2H, CH\(_2\)), 3.04–3.10 (m, 2H, CH\(_2\)), 5.59–5.60 (m, 1H, C=CH), 7.33–7.36 (m, 1H, ArH), 7.41–7.44 (m, 2H, ArH), 7.56–7.65 (m, 6H, ArH); \(^{13}\)C\(^{1}\)H NMR (100 MHz, CDCl\(_3\)) \( \delta \) 26.3, 26.9, 104.5, 126.9, 127.1, 127.2, 128.7, 128.8, 132.9, 139.3, 140.7, 148.3, 174.9; IR (ATR) 3 031, 2932, 1793 (C=O), 1678, 1604, 1593, 1554, 1486, 1449, 1414, 1294, 1234, 1218, 1208, 1181, 1097, 1103, 940, 913, 876, 852, 838, 809, 762, 723, 688, 659, 607, 570 cm\(^{-1}\); HR-EI-MS Calcd. for C\(_{17}\)H\(_{14}\)O\(_2\) [M]: m/z = 250.09938 Found 250.09936.

(Y)-γ-(4-Nitrobenzylidene)-γ-butyrolactone (3g)

Yellow solids; \( \text{Mp.} \, 120.0–121.0 \, ^\circ\text{C} \); \(^1\)H NMR (396 MHz, CDCl\(_3\)) \( \delta \) 2.75–2.80 (m, 2H, CH\(_2\)), 3.08–3.14 (m, 2H, CH\(_2\)), 5.63–5.64 (m, 1H, C=CH), 7.68 (d, \( J = 9 \, \text{Hz} \), 2H, ArH), 8.17 (d, \( J = 9 \, \text{Hz} \), 2H, ArH); \(^{13}\)C\(^{1}\)H NMR (100 MHz, CDCl\(_3\)) \( \delta \) 26.5, 26.6, 103.2, 123.8, 128.6, 140.6, 145.9, 151.9, 174.0; IR (ATR) 3361, 2955, 2923, 2852, 1821 (C=O), 1666, 1587, 1504, 1469, 1437, 1414, 1335, 1289, 1224, 1180, 1085, 1009, 933, 863, 820, 801, 751, 705, 691, 654, 637, 626, 559 cm\(^{-1}\); HR-EI-MS Calcd. for C\(_{11}\)H\(_{9}\)NO\(_4\) [M]: m/z = 219.05316 Found 219.05319.

(Z)-γ-(4-Fluorobenzylidene)-γ-butyrolactone (3h)

CAS registry No. none
White solids; Mp 78.0–79.0 °C; $^1$H NMR (396 MHz, CDCl$_3$) δ 2.70–2.74 (m, 2H, CH$_2$), 3.00–3.06 (m, 2H, CH$_2$), 5.51–5.53 (m, 1H, C=CH), 6.98–7.04 (m, 2H, ArH), 7.50–7.54 (m, 2H, ArH); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 26.2, 26.9, 103.7, 115.3 (d, $J_{C-F}$ = 22 Hz), 129.8 (d, $J_{C-F}$ = 8 Hz), 130.0 (d, $J_{C-F}$ = 4 Hz), 147.7 (d, $J_{C-F}$ = 3 Hz), 161.4 (d, $J_{C-F}$ = 247 Hz), 174.8; IR (ATR) 3006, 2936, 2852, 1788 (C=O), 1687, 1601, 1504, 1443, 1416, 1352, 1297, 1226, 1173, 1159, 1101, 1091, 1013, 1002, 935, 855, 833, 818, 769, 706, 658, 626, 562 cm$^{-1}$; HR-EI-MS Calcd. for C$_{11}$H$_9$FO$_2$ [M]$^+$: m/z = 192.05866; Found 192.05866.

(Z)-γ-(4-Chlorobenzylidene)-γ-butyrolactone (3i)

White solids; Mp 81.5–82.5 °C; $^1$H NMR (396 MHz, CDCl$_3$) δ 2.70–2.75 (m, 2H, CH$_2$), 3.01–3.07 (m, 2H, CH$_2$), 5.50–5.52 (m, 1H, C=CH), 7.28 (d, $J$ = 8 Hz, 2H, ArH), 7.48 (d, $J$ = 8 Hz, 2H, ArH); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 26.3, 26.8, 103.8, 128.6, 129.5, 132.2, 132.4, 148.6, 174.7; IR (ATR) 2956, 2925, 2851, 1793 (C=O), 1680, 1657, 1486, 1438, 1411, 1353, 1294, 1227, 1176, 1109, 1096, 1010, 944, 851, 833, 804, 714, 708, 679, 653, 625, 559 cm$^{-1}$; HR-EI-MS Calcd. for C$_{11}$H$_9$ClO$_2$ [M]$^+$: m/z = 208.02911; Found 208.02920.

(Z)-γ-(2-Methylbenzylidene)-γ-butyrolactone (3j)

White solids; Mp 90.0–91.0 °C; $^1$H NMR (396 MHz, CDCl$_3$) δ 2.32 (s, 3H, CH$_3$), 2.70–2.75 (m, 2H, CH$_2$), 3.04–3.10 (m, 2H, CH$_2$), 5.68–5.70 (m, 1H, C=CH), 7.11–7.22 (m, 3H, ArH), 7.76 (d, $J$ = 8 Hz, 2H, ArH); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) δ 20.2, 26.3, 27.1, 102.1, 126.0, 126.8, 129.0, 129.9, 132.3, 135.0, 148.2, 175.0; IR (ATR) 3069, 2956, 2930, 2862, 1793 (C=O), 1679, 1597, 1489, 1480, 1461, 1437, 1409, 1377, 1362, 1292, 1226, 1202, 1174, 1151, 1110, 1096, 1053, 1038, 1002, 945, 836, 769, 718, 650, 610, 568 cm$^{-1}$; HR-EI-MS Calcd. for C$_{12}$H$_{12}$O$_2$ [M]$^+$: m/z = 188.08373; Found 188.08370.
(Z)-γ-(1-Naphthalenylmethylene)-γ-butyrolactone (3k)

\[ \begin{array}{c}
\text{O} \\
\text{CAS registry No. none} \\
\text{White solids; } M_p 91.0-92.0 \degree C; \text{ } ^1H \text{ NMR (396 MHz, CDCl}_3) \delta 2.76-2.81 (m, 2H, CH}_2), 3.16-3.21 (m, 2H, CH}_2), 6.24-6.25 (m, 1H, C=CH), 7.46-7.54 (m, 3H, ArH), 7.75 (d, J = 8 Hz, 1H, ArH), 7.85 (dd, J = 3, 7 Hz, 1H, ArH), 7.89 (d, J = 7 Hz, 1H, ArH), 8.03 (dd, J = 2, 8 Hz, 1H, ArH); \text{ } ^13C{^1H} \text{ NMR (100 MHz, CDCl}_3) \delta 26.3, 27.2, 101.1, 123.6, 125.5, 125.6, 125.9, 127.1, 127.3, 128.7, 129.8, 131.0, 133.6, 149.4, 174.9; \text{ IR (ATR) } 3048, 2929, 2868, 1789 (C=O), 1686, 1589, 1579, 1506, 1443, 1414, 1397, 1353, 1293, 1222, 1194, 1166, 1105, 1038, 1017, 959, 941, 910, 866, 832, 801, 775, 748, 740, 693, 650, 640, 612 cm^{-1}; \text{ HR-EI-MS Calcd. for C}_{15}H_{12}O_2 [M]^+: m/z = 224.08373; Found 224.08369.
\end{array} 

(Z)-γ-(2-Thienylmethylene)-γ-butyrolactone (3l)

\[ \begin{array}{c}
\text{CAS registry No. none} \\
\text{White solids; } M_p 96.5-97.5 \degree C; \text{ } ^1H \text{ NMR (396 MHz, CDCl}_3) \delta 2.73-2.78 (m, 2H, CH}_2), 3.00-3.05 (m, 2H, CH}_2), 5.84-5.86 (m, 1H, C=CH), 6.99 (dd, J = 4, 5 Hz, 1H, ArH), 7.08 (d, J = 4 Hz, 1H, ArH), 7.24 (d, J = 5 Hz, 1H, ArH); \text{ } ^13C{^1H} \text{ NMR (100 MHz, CDCl}_3) \delta 25.5, 27.3, 99.0, 125.1, 125.7, 126.8, 136.5, 146.6, 174.2; \text{ IR (ATR) } 3093, 3069, 2961, 2928, 2852, 1786 (C=O), 1683, 1610, 1442, 1425, 1364, 1297, 1242, 1202, 1167, 1142, 1091, 1045, 1023, 939, 903, 846, 824, 819, 806, 780, 752, 698, 673, 653, 611, 588 cm^{-1}; \text{ HR-EI-MS Calcd. for C}_{9}H_{8}O_2S [M]^+: m/z = 180.02450; Found 180.02446.
\end{array} 

Preparation of 2-Phenylpropargyloxyphenol (4)

Under a nitrogen atmosphere, a mixture of pyrocatechol (2.00 g, 18.2 mmol) and K$_2$CO$_3$ (1.38 g, 9.99 mmol) in anhydrous acetone (90 mL) was stirred for 1 h at 25 °C. Propargyl bromide (2.16 g, 18.2 mmol) in dry acetone (1.5 mL) was slowly added at 25 °C during 1 h. The mixture was refluxed at 65 °C for 16 h. After being cooled to 25 °C, acetone was evaporated from the mixture. To the resulting residue was added water (50 mL). The suspension was extracted with CHCl$_3$ (15 mL, 4 times). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated in vacuo. The resulting crude material was chromatographed on silica gel (eluent: 5-20% AcOEt/n-hexane) to give 2-propargyloxyphenol (1.90 g, 12.8 mmol, 71%) as white solids.

$^1$H NMR (396 MHz) δ 2.56 (t, J = 2.3 Hz, 1H, H-C毒性C-), 4.75 (d, J = 2.3 Hz, 2H, CH毒性C-CH$_2$), 5.64 (s, 1H, -OH), 6.83–6.88 (m, 1H, ArH), 6.90–7.00 (m, 3H, ArH); $^{13}$C($^1$H) NMR (100 MHz) δ 56.9, 76.1, 78.1, 112.8, 115.2, 120.1, 122.6, 144.6, 146.0; MS (EI) m/z = 148 ([M$^+$]).

1-Methoxymethoxy-2-propargyloxybenzene (S4)

Under a nitrogen atmosphere, to a mixture of 2-propargyloxyphenol (700 mg, 4.72 mmol)
and K₂CO₃ (979 mg, 7.09 mmol) was added acetone (20 mL) at 25 °C. After being stirred at 25 °C for 1 h, methoxymethyl chloride (0.53 mL, 7.09 mmol) was slowly added to the resulting suspension at 25 °C. The reaction mixture stirred at 65 °C for 24 h. After being cooled to 25 °C, saturated NH₄Cl aqueous solution (15 mL) was added to the reaction mixture and then the resulting mixture was evaporated. The solution was extracted with MTBE (15 mL, 3 times). The combined organic layer was dried over Na₂SO₄, and concentrated in vacuo. The resulting crude mixture was chromatographed on silica gel (eluent: 5-10% AcOEt/n-hexane) to give 1-methoxymethoxy-2-propargyloxybenzene (720 mg, 3.75 mmol, 79%) as pale yellow oil.

**¹H NMR (396 MHz, CDCl₃)** δ 2.51 (t, J = 2 Hz, 1H, CCH), 3.52 (d, J = 0.9 Hz, 3H, OCH₂OCH₃), 4.77 (d, J = 2 Hz, 2H, CH₂CCH), 5.22 (d, J = 0.9 Hz, 2H, OCH₂OCH₃), 6.93–7.02 (m, 2H, ArH), 7.07 (dd, J = 2 Hz, 1H, ArH), 7.17 (dd, J = 2 Hz, 1H, ArH);

**¹³C{¹H} NMR (100 MHz, CDCl₃)** δ 56.2, 56.7, 75.7, 78.6, 95.5, 114.7, 117.0, 122.3, 122.4, 147.2, 147.6; **IR (ATR)** 3284 (CCH), 3071, 2993, 2956, 2934, 2827, 2120 (CC), 1594, 1499, 1456, 1374, 1324, 1302, 1242 (Ar-O-CH₂), 1216, 1188, 1153, 1119, 1078, 994, 922, 835, 745, 682, 671, 646, 639 cm⁻¹; **HR-EI-MS** Calcd. for C₁₁H₁₂O₃ [M]+: m/z = 192.07864; Found 192.07883.

**1-Methoxymethoxy-2-phenylpropargyloxybenzene (S5)**

Under a nitrogen atmosphere, to a suspension of PdCl₂(PPh₃)₂ (64 mg, 0.091 mmol) and copper iodide (35 mg, 0.182 mmol) in triethylamine (2 mL), 1-methoxymethoxy-2-propargyloxybenzene (350 mg, 1.82 mmol) in CH₃CN (2 mL) and iodobenzene (0.22 mL, 2.00 mmol) were added at 25 °C. After being stirred at 25 °C for 24 h, saturated NH₄Cl aqueous solution (20 mL) was added to the reaction mixture and the resulting solution was extracted with AcOEt (20 mL, 3 times). The combined organic layer was dried over Na₂SO₄. After evaporation of the solvent, the resulting mixture was chromatographed on silica gel to give 1-methoxymethoxy-2-phenylpropargyloxybenzene (255.6 mg, 0.953 mmol, 52%) as pale yellow oil.
\[ ^1\text{H NMR (396 MHz, CDCl}_3 \] \delta 3.53 (s, 3H, OCH\textsubscript{3}), 4.98 (s, 2H, CH\textsubscript{2}), 5.24 (s, 2H, OCH\textsubscript{2}OCH\textsubscript{3}), 6.93−7.02 (m, 2H, ArH), 7.13−7.20 (m, 2H, ArH), 7.28−7.32 (m, 3H, ArH), 7.39−7.43 (m, 2H, ArH); \[ ^{13}\text{C}[^1\text{H}] \text{ NMR (100 MHz, CDCl}_3 \] \delta 56.2, 56.6, 84.0, 87.3, 95.6, 114.9, 117.0, 122.1, 122.3, 122.4, 128.2, 128.6, 131.7, 147.2, 147.9; \[ \text{IR (ATR)} \] 3063, 2993, 2953, 2930, 2898, 2848, 2825, 2237 (CC), 1592, 1498, 1490, 1455, 1441, 1403, 1371, 1322, 1300, 1240 (Ar-O-CH\textsubscript{2}), 1214, 1187, 1152, 1118, 1076, 1051, 1030, 991, 920, 837, 817, 742, 690, 648, 607 cm\textsuperscript{-1}; \[ \text{HR-EI-MS} \] Calcd. for C\textsubscript{17}H\textsubscript{16}O\textsubscript{3} [M]: \textit{m/z} = 268.10994; Found 268.10991.

2-[(3-phenylprop-2-yn-1-yl)oxy]phenol (4)

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\text{O} \\
\text{OH}
\end{array}
\]

CAS registry No. 73222-90-9

HCl aqueous solution (4 mol/L, 6 mL) was added to a solution of 1-methoxymethoxy-2-phenylpropargyloxybenzene (225 mg, 0.839 mmol) in THF (6 mL) at 25 °C and the reaction mixture was stirred for 20 h at 25 °C. The resulting solution was extracted with t-butyl methyl ether (10 mL, 3 times). The combined organic layer was dried over Na\textsubscript{2}SO\textsubscript{4}. The organic layer was concentrated under reduced pressure to give 2-phenylpropargyloxyphenol (175.5 mg, 0.783 mmol, 93%) as brown oil.

\[ ^1\text{H NMR (396 MHz, CDCl}_3 \] \delta 4.97 (s, 2H, CH\textsubscript{2}), 5.70 (s, 1H, OH), 6.84−6.99 (m, 3H, ArH), 7.04−7.08 (m, 1H, ArH), 7.29−7.35 (m, 3H, ArH), 7.42−7.45 (m, 2H, ArH); \[ ^{13}\text{C}[^1\text{H}] \text{ NMR (100 MHz, CDCl}_3 \] \delta 57.9, 83.3, 87.7, 113.0, 115.1, 120.1, 121.9, 122.5, 128.3, 128.8, 131.8, 144.9, 146.1; \[ \text{MS (EI)} \textit{m/z} = 224 ([M^+]).\]

Cyclization reaction of 2-phenylpropargyloxyphenol (4) (Scheme 1)

2,3-Dihydro-2-(Z)-phenylmethene-1,4-benzodioxin (5)

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\begin{array}{c}
\text{O} \\
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CAS registry No. 73249-12-4

2-Phenylpropargyloxyphenol (4, 13.5 mg, 0.060 mmol) was placed in a vial, to which was
added 0.5 mL aqueous suspension of 1a (1.3 mg, 1.2 × 10^{-3} mmol) and Et₃N (0.5 µL, 3.6 × 10^{-3} mmol). The reaction mixture was agitated by shaking at 50 °C for 4 h, and then extracted with t-butyl methyl ether (1.5 mL, 4 times). The combined extract was dried over Na₂SO₄ and concentrated in vacuo. The residue was chromatographed on silica gel (eluent: 5-15% AcOEt/n-hexane) to give 5 (5.6 mg, 0.025 mmol, 42%) as colorless oil.

^1H NMR (396 MHz, CDCl₃) δ 4.62 (s, 2H, CH₂), 5.59 (s, 1H, C=CH), 6.93–6.99 (m, 3H, ArH), 7.12–7.15 (m, 1H, ArH), 7.21–7.25 (m, 1H, ArH), 7.34–7.38 (m, 2H, ArH), 7.68–7.71 (m, 2H, ArH); ^13C\(^{1}H\) NMR (100 MHz, CDCl₃) δ 66.1, 107.0, 116.8, 117.4, 122.3, 122.6, 126.9, 128.4, 128.9, 134.2, 142.5, 143.4, 144.1; MS (EI) m/z = 224 ([M⁺]).
$^1$H and $^{13}$C NMR spectra

Methyl-4-pentynoate (S1)
Methyl 5-(4-trifluoromethylphenyl)-4-pentyanoate (S2a)
Methyl 5-phenyl-4-pentynoate (S2b)
Methyl 5-(4-methylphenyl)-4-pentynoate (S2c)
Methyl 5-(4-methoxyphenyl)-4-pentynoate (S2d)
Methyl 5-(4-tert-butylphenyl)-4-pentyanoate (S2e)
Methyl 5-(4-phenylphenyl)-4-pentynoate (S2f)
Methyl 5-(4-nitrophenyl)-4-pentylnoate (S2g)
Methyl 5-(4-fluorophenyl)-4-pentyanoate (S2h)
Methyl 5-(4-chlorophenyl)-4-pentynoate (S2i)
Methyl 5-(2-Methylphenyl)-4-pentynoate (S2j)
Methyl 5-(1-naphthyl)-4-pentyanoate (S2k)
Methyl 5-(2-thienyl)-4-pentyanoate (S21)
5-(4-trifluoromethylphenyl)-4-pentynoic acid (2a)
5-Phenyl-4-pentynoic acid (2b)
5-(4-methylphenyl)-4-pentynoic acid (2c)
5-(4-methoxyphenyl)-4-pentyonoic acid (2d)
5-(4-tert-butylphenyl)-4-pentyne acid (2e)
5-(4-phenylphenyl)-4-pentynoic acid (2f)
5-(4-nitrophenyl)-4-pentynoic acid (2g)
5-(4-fluorophenyl)-4-pentynoic acid (2h)
5-(4-chlorophenyl)-4-pentyloic acid (2i)
5-(2-methylphenyl)-4-pentynoic acid (2j)
5-(1-naphtyl)-4-pentyonic acid (2k)
5-(2-thienyl)-4-pentynoic acid (2l)
(Z)-"\(\gamma\)-(4-Trifluoromethylbenzylidene)-\(\gamma\)-butyrolactone (3a)"
(Z)-γ-Phenylbenzylidene-γ-butyrolactone (3b)
(Z)-\(\gamma\)-(4-Methylbenzylidene)-\(\gamma\)-butyrolactone (3c)
(Z)-γ-(4-Methoxybenzylidene)-γ-butyrolactone (3d)
(Z)-γ-(4-tert-Butylbenzylidene)-γ-butyrolactone (3e)
(Z)-γ-(4-Phenylbenzylidene)-γ-butyrolactone (3f)
(Z)-γ-(4-Nitrobenzylidene)-γ-butyrolactone (3g)
(Z)-γ-(4-Fluorobenzylidene)-γ-butyrolactone (3h)
(Z)-γ-(4-Chlorobenzylidene)-γ-butyrolactone (3i)
(Z)-γ-(2-Methylbenzylidene)-γ-butyrolactone (3j)
(Z)-γ-(1-Naphthalenylmethylene)-γ-butyrolactone (3k)
(Z)-γ-(2-Thienylmethylene)-γ-butyrolactone (3l)
2-Propargyloxyphenol (S3)
1-Methoxymethoxy-2-propargyloxybenzene (S4)

![S58]
1-Methoxymethoxy-2-phenylpropargyloxybenzene (S5)
2-Phenylpropargyloxyphenol (4)
2,3-Dihydro-2-(Z)-phenylmethylene-1,4-benzodioxin (5)