

Electronic Supplementary Information

Carboxylation of alkynylsilanes with carbon dioxide

mediated by cesium fluoride in DMSO

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Table of Contents

1. General comments	S2
2. Representative procedure for carboxylation of alkynylsilanes with CO ₂	S2
3. Representative procedure for syntheses of alkynoates	S2
4. Characterization data	S3
5. Copies of ¹ H NMR and ¹³ C NMR spectra of products	S10

1. General comments

All reactions were carried out under a CO₂ atmosphere unless otherwise noted. Anhydrous solvents were obtained from commercial suppliers and used without further purification. Commercially available materials were purchased from Tokyo Kasei Co., Aldrich Inc. and other suppliers and were used after appropriate purification (distillation or recrystallization). CsF was purchased from Aldrich and stored in a argon-filled glovebox after dried by a heat gun under vacuum. Flash column chromatography was performed with Kanto silica gel 60 N (spherical, neutral, 70–230 mesh). A CO₂ gas cylinder was purchased from Taiyo Nissan Co. (G1 grade).

Melting points were measured with a Yazawa micro melting point apparatus and uncorrected. IR spectra were recorded on a SHIMADZU IRAffinity. ¹H-NMR spectra were recorded on JEOL AL400 (400 MHz) or JEOL ECA600 (600MHz) spectrometer. ¹H NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal (CDCl₃: 7.26 ppm) or (acetone-d₆: 2.09 ppm) or (CD₃OD: 3.34 ppm). ¹³C NMR spectra were referenced to a solvent signal (CDCl₃: 77.0 ppm) or (acetone-d₆: 30.6 ppm) or (CD₃OD: 50.0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, dd = double doublet, dt = double triplet. Mass spectra and high resolution mass spectra were measured on JEOL JMS-DX303 and JMS-700/JMS-T 100 GC spectrometer respectively. Elemental analyses were performed by Yanaco CHN CORDER MT-6.

2. Representative procedure for carboxylation of alkynylsilanes with CO₂

Reaction of 1-phenyl-2-trimethylsilylacetylene (**1a**) with CO₂ (Table 1, entry 6)

A dried and CO₂ (balloon) infused Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with CsF (54.7 mg, 0.36 mmol) in DMSO (0.75 mL). 1-Phenyl-2-trimethylsilylacetylene (**1a**) (52.3 mg, 0.3 mmol) was added to a reaction mixture and the reaction was stirred at room temperature for 3 h. The reaction mixture was diluted with water (30 mL) and extracted with CH₂Cl₂ (2 × 10 mL). The aqueous layer was acidified (> pH 1) with aqueous HCl (6 M) at 0 °C and then extracted with diethyl ether (4 × 20 mL). The combined organic layers were dried over Na₂SO₄. The solvent was removed under vacuum to afford **2a** (42 mg, 96%).

3. Representative procedure for syntheses of alkynoates

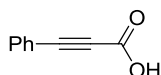
Reaction of 1-phenyl-2-trimethylsilylacetylene (**1a**) with CO₂ followed by addition of methyl iodide (Table 2, entry 1)

A dried and CO₂ (balloon) infused Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with CsF (54.7 mg, 0.36 mmol) in DMSO (0.75 mL). 1-Phenyl-2-trimethylsilylacetylene (**1a**) (52.3 mg, 0.3

mmol) was added to a reaction mixture and the reaction was stirred at room temperature for 3 h. Methyl iodide (0.36 mmol) was added to the reaction mixture and the reaction was stirred at room temperature for 1 h. Saturated aqueous NH₄Cl (5 mL) was added and the whole mixture was extracted with AcOEt (10 mL x 3). The combined organic layers were washed with brine (10 mL) and dried over MgSO₄. The organic phase was concentrated under reduced pressure and the crude material was purified by silica gel column chromatography to give **3aa** (39 mg, 81%).

4. Characterization data

3-Phenyl-2-propynoic acid (2a)



Yellow needles (recrystallized from AcOEt/hexane), mp 138–139 °C.

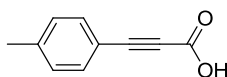
IR (neat): 2958, 2925, 2854, 2228, 2198, 1669, 1488, 1417, 1302, 1287, 1207, 1171, 918, 752, 738, 682 cm⁻¹.

¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 7.37–7.42 (m, 2H), 7.46–7.50 (m, 1H), 7.60–7.62 (m, 2H).

¹³C{¹H} NMR (150 MHz, CDCl₃) δ (ppm): 80.1, 89.1, 119.0, 128.6, 131.1, 133.2, 158.8.

LRMS (EI) *m/z*: 146 (M⁺). HRMS: Calcd. For C₉H₆O₂: 146.03678, found: 146.0391.

3-(4-Methylphenyl)-2-propynoic acid (2b)



Yellow needle (recrystallized from CH₃CN), mp 153–155 °C.

IR (neat): 2195, 1669, 1507, 1142, 1295, 1179, 819 cm⁻¹.

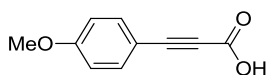
¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 2.39 (s, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ (ppm): 21.7, 79.8, 89.8, 115.9, 129.4, 133.3, 142.0, 158.9

LRMS (EI) *m/z*: 160 (M⁺). HRMS: Calcd. For C₁₀H₈O₂: 160.0524, found: 160.0511.

Anal. Calcd. for C₁₀H₈O₂: C, 74.99; H, 5.03; O, 19.98. Found: C, 75.01; H, 5.12.

3-(4-Methoxyphenyl)-2-propynoic acid (2c)



Colorless prism (recrystallized from CH₃CN), mp 146–147 °C.

IR (neat): 2198, 1666, 1599, 1509, 1316, 1295, 1252, 1214, 1167, 832 cm⁻¹.

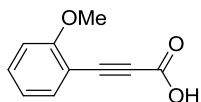
¹H NMR (400 MHz, CDCl₃/TMS) δ (ppm): 3.85 (s, 3H), 6.88–6.92 (m, 2H), 7.55–7.59 (d, 2H).

¹³C{¹H} NMR (100 MHz, acetone-d₆) δ (ppm): 56.7, 81.8, 87.6, 112.8, 116.2, 136.4, 155.5, 163.5.

LRMS (EI) m/z : 176 (M^+). HRMS: Calcd. For $C_{10}H_8O_3$: 176.0473, found: 176.0460.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.18; H, 4.58; O, 27.25, found: C, 68.31; H, 4.58.

3-(2-Methoxyphenyl)-2-propynoic acid (2d)



Colorless prism (recrystallized from AcOEt/petroleum ether), mp 132–133 °C.

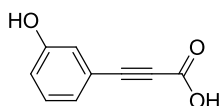
IR (neat): 2201, 1740, 1669, 1491, 1419, 1252, 1229, 1200 cm^{-1} .

1H NMR (600 MHz, $CDCl_3/TMS$) δ (ppm): 3.91 (s, 3H), 6.91–6.97 (m, 2H), 7.42–7.45 (m, 1H), 7.54–7.55 (m, 1H).

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ (ppm): 55.8, 84.0, 86.3, 108.3, 110.9, 120.6, 132.9, 135.2, 158.8, 161.9.

LRMS (EI) m/z : 176 (M^+). HRMS: Calcd. For $C_{10}H_8O_3$: 176.0473, found: 176.0462.

3-(3-Hydroxyphenyl)-2-propynoic acid (2e)



Colorless prism (recrystallized from acetone/hexane), mp 192–195 °C.

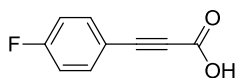
IR (neat): 3174, 2216, 1690, 1580, 1235, 980 cm^{-1} .

1H NMR (400 MHz, acetone- d_6) δ (ppm): 7.04–7.16 (m, 3H), 7.32–7.36 (m, 1H).

$^{13}C\{^1H\}$ NMR (1500 MHz, acetone- d_6) δ (ppm): 82.0, 86.8, 120.0, 120.6, 122.1, 125.7, 131.8, 155.3, 159.1.

LRMS (EI) m/z : 162 (M^+). HRMS: Calcd. For $C_9H_6O_3$: 162.0317, found: 162.0301.

3-(4-Fluorophenyl)-2-propynoic acid (2f)



Colorless needle (recrystallized from CH_3CN), mp 155–157 °C.

IR (neat): 2206, 1589, 1506, 1220, 1157, 834 cm^{-1} .

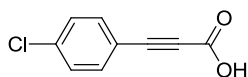
1H NMR (400 MHz, acetone- d_6) δ (ppm): 7.29–7.33 (m, 2H), 7.74–7.79 (m, 2H).

$^{13}C\{^1H\}$ NMR (150 MHz, acetone- d_6) δ (ppm): 82.3, 85.6, 117.9 (d, $J = 22.5$ Hz), 137.0 (d, $J = 10.5$ Hz), 155.2 (d, $J = 2.9$ Hz), 164.7, 166.4.

LRMS (EI) m/z : 164 (M^+). HRMS: Calcd. For $C_9H_5FO_2$: 164.0274, found: 164.0265.

Anal. Calcd. for $C_9H_5FO_2$: C, 65.86; H, 3.07; F, 11.57; O, 19.50. Found: C, 65.92; H, 3.23.

3-(4-Chlorophenyl)-2-propynoic acid (2g)



Colorless plate (recrystallized from CH₃CN), mp 184–185 °C.

IR (neat): 2210, 1690, 1685, 1601, 1597, 1490, 1293, 1211, 1805, 1105 cm⁻¹.

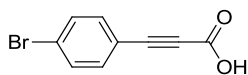
¹H NMR (400 MHz, acetone-d₆) δ (ppm): 7.56–7.58 (m, 2H), 7.69–7.72 (m, 2H).

¹³C{¹H} NMR (150 MHz, CD₃OD) δ (ppm): 83.9, 86.1, 120.8, 131.3, 136.4, 139.1, 157.4.

LRMS (EI) *m/z*: 180 (M⁺). HRMS: Calcd. For C₉H₅ClO₂: 179.9978, found: 179.9964.

Anal. Calcd. for C₉H₅ClO₂: C, 59.86; H, 2.79; Cl, 19.63; O, 17.72. Found: C, 59.66; H, 2.78.

3-(4-Bromophenyl)-2-propynoic acid (2h)



Colorless plate (recrystallized from CH₃CN), mp 193–195 °C.

IR (neat): 2208, 1696, 1616, 1596, 1577, 1488, 1379, 1292, 1211, 1010 cm⁻¹.

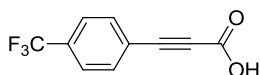
¹H NMR (400 MHz, acetone-d₆) δ (ppm): 7.61–7.65 (m, 2H), 7.71–7.74 (m, 2H).

¹³C{¹H} NMR (150 MHz, CD₃OD) δ (ppm): 83.8, 86.1, 121.1, 127.2, 134.2, 136.4, 157.3.

LRMS (EI) *m/z*: 224 (M⁺). HRMS: Calcd. For C₉H₅BrO₂: 223.9473, found: 223.9482.

Anal. Calcd. for C₉H₅BrO₂: C, 48.03; H, 2.24; Br, 35.51; O, 14.22. Found: C, 47.99; H, 2.39.

3-(4-Trifluoromethylphenyl)-2-propynoic acid (2i)



Colorless needle (recrystallized from hexane/acetone), mp 155–156 °C.

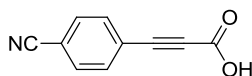
IR (neat): 2227, 1718, 1671, 1406, 1266, 1203, 1104, 857 cm⁻¹.

¹H NMR (400 MHz, acetone-d₆) δ (ppm): 7.87–7.93 (m, 4H).

¹³C{¹H} NMR (150 MHz, acetone-d₆) δ (ppm): 84.5, 84.8, 125.8, 125.9 (q, *J* = 271.5 Hz), 127.7 (d, *J* = 4.5 Hz), 133.5 (q, *J* = 33.0 Hz), 135.3, 155.2.

LRMS (EI) *m/z*: 214 (M⁺). HRMS: Calcd. For C₁₀H₅F₃O₂: 214.0242, found: 214.0217.

3-(4-Cyanophenyl)-2-propynoic acid (2j)



Yellow needle. Sublimation

IR (neat): 2230, 2203, 1684, 1593, 1373, 1329 cm⁻¹.

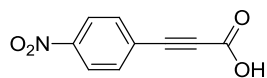
^1H NMR (600 MHz, acetone- d_6) δ (ppm): 7.88–7.90 (m, 2H), 7.94–7.96 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6) δ (ppm): 84.2, 85.1, 115.5, 119.3, 125.8, 134.2, 134.9, 154.8.

LRMS (EI) m/z : 171 (M^+). HRMS: Calcd. For $\text{C}_{10}\text{H}_5\text{NO}_2$: 171.0320, found: 171.0307.

Anal. Calcd. for $\text{C}_{10}\text{H}_5\text{NO}_2$: C, 70.18; H, 2.94; N, 8.18; O, 18.70. Found: C, 70.20; H, 3.06; N, 8.30.

3-(4-Nitrophenyl)-2-propynoic acid (2k)



Yellow needle (recrystallized from AcOEt/hexane), mp 195–196 °C.

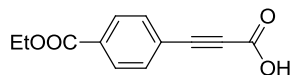
IR (neat): 2206, 1684, 1603, 1591, 1522, 1343, 1284, 1207, 858, 853, 748 cm^{-1} .

^1H NMR (400 MHz, acetone- d_6) δ (ppm): 7.96–7.99 (m, 2H), 8.36–8.40 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3OD) δ (ppm): 84.3, 86.3, 125.8 (d, $J = 17.0$ Hz), 128.5, 135.8 (d, $J = 17.0$ Hz), 151.0, 156.7.

LRMS (EI) m/z : 191 (M^+). HRMS: Calcd. For $\text{C}_9\text{H}_5\text{NO}_4$: 191.0219, found: 191.0217.

3-(4-Ethoxycarbonylphenyl)-2-propynoic acid (2l)



Colorless plate (recrystallized from CH_3CN), mp 131–134 °C.

IR (neat): 2231, 1689, 1318, 1279, 1125, 1106, 1065, 845, 834 cm^{-1} .

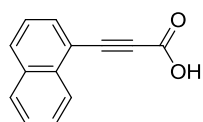
^1H NMR (600 MHz, acetone- d_6) δ (ppm): 1.42 (t, $J = 7.2$ Hz, 3H), 4.42 (d, $J = 7.2$ Hz, 2H), 7.81 (d, $J = 8.4$ Hz, 2H), 8.13 (d, $J = 8.4$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, acetone- d_6) δ (ppm): 15.3, 62.7, 84.4, 85.2, 125.6, 131.2, 133.9, 134.4, 154.9, 166.6.

LRMS (EI) m/z : 218 (M^+). HRMS: Calcd. For $\text{C}_{12}\text{H}_{10}\text{O}_4$: 218.0579, found: 218.0563.

Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_4$: C, 66.05; H, 4.62; O, 29.33. Found: C, 66.05; H, 4.62.

3-(1-naphthyl)-2-propynoic acid (2c)



Colorless prism (recrystallized from AcOEt/petroleum ether), mp 140–142 °C.

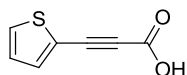
IR (neat): 2197, 1669, 1414, 1297, 1262, 1221, 1210 cm^{-1} .

^1H NMR (600 MHz, CDCl_3/TMS) δ (ppm): 7.48–7.51 (m, 1H), 7.57–7.60 (m, 1H), 7.64–7.67 (m, 1H), 7.89–7.91 (m, 2H), 7.99 (d, $J = 8.2$ Hz, 1H), 8.35 (d, $J = 8.3$ Hz, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ (ppm): 84.7, 87.6, 116.6, 125.1, 125.6, 127.0, 127.9, 128.5, 131.9, 133.0, 133.6, 133.7, 158.8.

LRMS (EI) m/z : 196 (M^+). HRMS: Calcd. For $\text{C}_{13}\text{H}_8\text{O}_3$: 196.0524, found: 196.0508.

3-(2-Thienyl)-2-propynoic acid (2n)



Colorless prism (recrystallized from hexane/AcOEt), mp 138–140 °C.

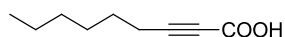
IR (neat): 2198, 1663, 1399, 1276, 1222, 1176, 884, 854, 839, 711 cm^{-1} .

^1H NMR (600 MHz, CDCl_3/TMS) δ (ppm): 7.07–7.09 (m, 1H), 7.51–7.55 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, acetone- d_6) δ (ppm): 80.5, 86.7, 120.6, 129.6, 133.5, 138.3, 155.1..

LRMS (EI) m/z : 151 (M^+). HRMS: Calcd. For $\text{C}_7\text{H}_4\text{O}_2\text{S}$: 151.9932, found: 151.9920.

2-nonynoic acid (2p)



Colorless oil

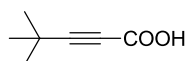
IR (neat): 2237, 1684, 1277 cm^{-1} .

^1H NMR (400 MHz, CDCl_3/TMS) δ (ppm): 0.89 (t, $J = 6.8$ Hz, 3H), 1.26–1.44 (m, 6H), 1.55–1.62 (m, 2H), 2.36 (t, $J = 6.8$ Hz, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ (ppm): 13.9, 18.7, 22.4, 27.3, 28.5, 31.1, 72.6, 92.8, 158.6.

LRMS (EI) m/z : 153 ($\text{M}^+ - 1$). HRMS: Calcd. For $\text{C}_9\text{H}_{13}\text{O}_2$: 153.0916, found: 153.0913.

4,4-Dimethyl-2-pentynoic acid (2q)



Yellow oil.

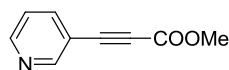
IR (neat): 2216, 1696, 1684, 1261, 1220, 1101, 947, 818 cm^{-1} .

^1H NMR (400 MHz, CDCl_3/TMS) δ (ppm): 1.30 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ (ppm): 29.8, 39.7, 71.6, 98.5, 157.5.

LRMS (EI) m/z : 125 ($\text{M}^+ - 1$). HRMS: Calcd. For $\text{C}_7\text{H}_9\text{O}_2$: 125.0603, found: 126.0590.

Methyl 3-(3-pyridinyl)-2-propynoate (3o)



Yellow plate (recrystallized from petroleum ether), mp 52–53 °C.

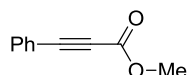
IR (neat): 2228, 1696, 1474, 1438, 1296, 1207, 1176 cm^{-1} .

^1H NMR (400 MHz, CDCl_3/TMS) δ (ppm): 3.86 (s, 3H), 7.31–7.35 (m, 1H), 7.86–7.88 (m, 1H), 8.65–8.67 (m, 1H), 8.81–8.81 (m, 1H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3) δ (ppm): 53.0, 82.7, 83.2, 116.9, 123.2, 139.8, 150.7, 153.3, 153.9.

LRMS (EI) m/z : 161 (M^+). HRMS: Calcd. For $\text{C}_9\text{H}_7\text{NO}_2$: 161.0477, found: 161.0465.

Methyl 3-phenyl-2-propynoate (3aa)



yellow oil

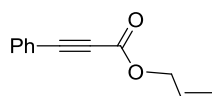
IR (neat): 2224, 1707, 1490, 1434, 1285, 1199, 1169, 756 cm^{-1} .

^1H NMR (400 MHz, CDCl_3/TMS) δ (ppm): 3.84 (s, 3H), 7.35–7.40 (m, 2H), 7.43–7.48 (m, 1H), 7.56–7.60 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ (ppm): 52.7, 80.3, 86.5, 119.5, 128.6, 130.7, 133.0, 154.4.

LRMS (EI) m/z : 160 (M^+). HRMS: Calcd. For $\text{C}_{10}\text{H}_8\text{O}_2$: 160.0524, found: 160.0535.

Allyl 3-phenyl-2-propynoate (3ab)



yellow oil

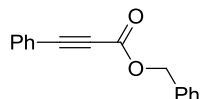
IR (neat): 2220, 1704, 1281, 1184, 1165, 755 cm^{-1} .

^1H NMR (400 MHz, CDCl_3/TMS) δ (ppm): 4.74 (dt, $J = 1.2, 5.8$ Hz, 2H), 5.32 (dd, $J = 1.0, 10.2$ Hz, 2H), 5.41 (dd, $J = 1.5, 17.1$ Hz, 2H), 5.93–6.03 (m, 1H), 7.36–7.40 (m, 2H), 7.43–7.46 (m, 1H), 7.58–7.60 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ (ppm): 66.5, 80.4, 86.5, 119.4, 119.5, 128.6, 130.7, 131.2, 133.0, 153.7.

LRMS (EI) m/z : 186 (M^+). HRMS: Calcd. For $\text{C}_{12}\text{H}_{10}\text{O}_2$: 186.0681, found: 186.0688.

Benzyl 3-phenyl-2-propynoate (3ac)



yellow oil

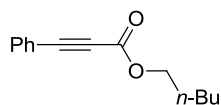
IR (neat): 2225, 1706, 1490, 1293, 1279, 1183, 1169, 756, 746 cm^{-1} .

^1H NMR (400 MHz, CDCl_3/TMS) δ (ppm): 5.27 (s, 2H), 7.35–7.47 (m, 8H), 7.55–7.59 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ (ppm): 67.7, 80.5, 86.7, 119.5, 128.5, 128.6, 128.7, 130.7, 133.0, 134.9, 153.9.

LRMS (EI) m/z : 236 (M^+). HRMS: Calcd. For. $C_{16}H_{12}O_2$: 236.0837, found: 236.0829.

Butyl 3-phenyl-2-propynoate (3ad)



yellow oil

IR (neat): 2960, 2221, 1705, 1283, 1185, 1172, 756, 748 cm^{-1}

1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.97 (t, $J = 7.2$ Hz, 3H), 1.44 (sext, $J = 7.2$ Hz, 2H), 1.71 (quint, $J = 7.2$ Hz, 2H), 4.24 (t, $J = 7.2$ Hz, 2H), 7.35–7.39 (m, 2H), 7.42–7.47 (m, 1H), 7.57–7.60 (m, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 13.6, 19.0, 30.5, 65.9, 80.7, 86.0, 119.7, 128.5, 130.5, 132.9, 154.2.

LRMS (EI) m/z : 202 (M^+). HRMS: Calcd. For. $C_{13}H_{14}O_2$: 202.0994, found: 202.0990.

5. Copies of ^1H NMR and ^{13}C NMR spectra of products

