Electronic Supplementary Information

~ Experimental Procedures and Spectral/Analytical Data ~

General Comments

Reactions were carried out under an CO_2 atmosphere (1 atm). Melting points (mp) were determined with a Yazawa micro melting point apparatus and uncorrected. Infrared (IR) data were recorded on SensIR ATR (Attenuated Total Reflectance) FT-IR and absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). NMR data were recorded on a JEOL AL400 spectrometer. Chemical shifts are expressed in δ (parts per million, ppm) values and coupling constants are expressed in herts (Hz). ^{1}H NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal ($CDCl_3$: 7.26 ppm). ^{13}C NMR spectra were referenced to tetramethylsilane as an internal standard or to a solvent signal ($CDCl_3$: 77.0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, dt = double triplet, ddd = double double doublet, ddt = double double triplet, br.s = broad singlet. Low and high resolution mass spectra (LRMS and HRMS) were obtained from Mass Spectrometry Resource, Graduate School of Pharmaceutical Sciences, Tohoku University, on a JEOL JMS-DX 303 and JMS-700/JMS-T 100 GC spectrometer respectively.

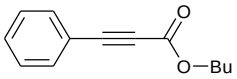
Materials

Commercially available materials were purchased from Tokyo Kasei Co., Aldrich Inc. and other suppliers and were used after appropriate purification (distillation or recrystallization). Flash column chromatography was performed with Kanto silica gel 60 N (spherical, neural, 70–230 mesh). A CO_2 gas cylinder was purchased from Taiyo Nissan Co. (G1 grade).

Representative Procedure for Carboxylation of Acetylenes in the Presence of an Alkyl Halide (Table 1, Entry 13)

A mixture of phenylacetylene (**1a**) (51.1 mg, 0.50 mmol), CuI (7.6 mg, 0.040 mmol), PEt_3 (20% toluene solution, 23.6 mg, 0.040 mmol), Cs_2CO_3 (0.52 g, 1.5 mmol) and BuI (**2a**) (92.0 mg, 0.5 mmol) in DMA (1.0 mL) was stirred at room temperature for 24 h under an atmosphere of CO_2. AcOEt was added to the reaction mixture and then filtered. The filtrate was extracted with AcOEt (30 mL × 3) and the combined organic phase was washed with brine (10 mL × 2), and then dried over $MgSO_4$. The organic phase was concentrated under a reduced pressure and the crude material was purified by silica gel column chromatography to give the coupling product **3aa** (0.066 g, 90%) as an yellow oil.

Butyl 3-Phenyl-2-propynoate (3aa)



Obtained as an yellow oil.

IR (neat): 2960, 2221, 1706, 1490, 1372, 1283, 1238, 1187, 1172, 1046, 756, 688 cm^{-1}.

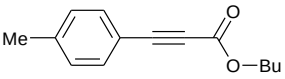
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.96 (t, *J* = 7.1 Hz, 3H), 1.43 (sext, *J* = 7.1 Hz, 2H), 1.71 (quint, *J* = 7.1 Hz, 2H), 4.24 (t, *J* = 7.1 Hz, 2H), 7.35–7.39 (m, 2H), 7.42–7.46 (m, 1H), 7.57–7.59 (m, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 13.6, 19.0, 30.4, 65.9, 80.6, 85.9, 119.5, 128.4, 130.4, 132.7, 153.9.

LRMS (EI) *m/z*: 202 (M^+).

HRMS: Calcd. for $C_{13}H_{14}O_2$: 202.0994, found: 202.0871.

Butyl 3-(4-Methylphenyl)-2-propynoate (3ba)



Obtained as an yellow oil.

IR (neat): 2960, 2933, 2874, 2216, 1701, 1508, 1286, 1188, 1167, 815, 743 cm^{-1}.

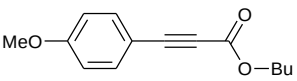
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.96 (t, *J* = 7.2 Hz, 3H), 1.43 (sext, *J* = 7.2 Hz, 2H), 1.69 (quint, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 4.23 (t, *J* = 7.2 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 13.5, 19.0, 21.5, 30.4, 65.7, 80.3, 86.4, 116.5, 129.2, 132.8, 141.1, 154.2.

LRMS (EI) *m/z*: 216 (M^+).

HRMS: Calcd. for $C_{14}H_{16}O_2$: 216.1150, found: 216.1136.

Butyl 3-(4-Methoxyphenyl)-2-propynoate (3ca)



Obtained as colorless prisms (recrystallized from AcOEt/hexane, mp 42–43 °C).

IR (neat): 2963, 2935, 2202, 1694, 1602, 1510, 1286, 1254, 1197, 1163, 1025, 836, 743 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.95 (t, *J* = 7.5 Hz, 3H), 1.43 (sext, *J* = 7.5 Hz, 2H), 1.69 (quint, *J* = 7.5 Hz,

2H), 3.82 (s, 3H), 4.22 (t, *J* = 7.5 Hz, 2H), 6.86–6.89 (m, 2H), 7.52–7.54 (m, 2H).

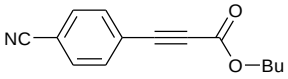
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 13.5, 19.0, 30.4, 55.2, 65.6, 80.1, 86.7, 111.3, 114.2, 134.8, 154.3, 161.4.

LRMS (EI) *m/z*: 232 (M^+).

HRMS: Calcd. for $C_{14}H_{16}O_3$: 232.1100, found: 232.1093.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.45; H, 6.93.

Butyl 3-(4-Cyanophenyl)-2-propynoate (3da)



Obtained as a colorless oil.

IR (neat): 2960, 2933, 2874, 2229, 1703, 1500, 1285, 1188, 1170, 839, 747 cm^{-1}.

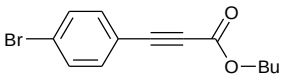
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.97 (t, *J* = 7.2 Hz, 3H), 1.44 (sext, *J* = 7.2 Hz, 2H), 1.71 (quint, *J* = 7.2 Hz, 2H), 4.26 (t, *J* = 7.2 Hz, 2H), 7.67 (br.s, 4H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 13.6, 19.0, 30.4, 66.3, 83.1, 83.7, 113.9, 117.8, 124.5, 132.2, 133.2, 153.4.

LRMS (EI) *m/z*: 227 (M^+).

HRMS: Calcd. for $C_{14}H_{13}NO_2$: 227.0946, found: 227.0931.

Butyl 3-(4-Bromophenyl)-2-propynoate (3ea)



Obtained as an yellow oil.

IR (neat): 2960, 2222, 1700, 1487, 1232, 1171, 1071, 1010, 822, 747 cm^{-1}.

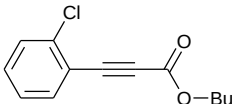
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.96 (t, *J* = 7.3 Hz, 3H), 1.44 (sext, *J* = 7.3 Hz, 2H), 1.70 (quint, *J* = 7.3 Hz, 2H), 4.24 (t, *J* = 7.3 Hz, 2H), 7.43–7.45 (m, 2H), 7.51–7.53 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 13.7, 19.1, 30.5, 66.1, 81.6, 84.7, 118.6, 125.3, 131.9, 134.2, 153.9.

LRMS (EI) *m/z*: 280 (M^+).

HRMS: Calcd. for $C_{13}H_{13}{}^{79}BrO_2$: 280.0099, found: 280.0068.

Butyl 3-(2-Chlorophenyl)-2-propynoate (3fa)



Obtained as an yellow oil.

IR (neat): 2960, 2225, 1705, 1472, 1294, 1250, 1186, 1062, 754, 687 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.96 (t, *J* = 7.3 Hz, 3H), 1.44 (sext, *J* = 7.3 Hz, 2H), 1.71 (quint, *J* = 7.3 Hz, 2H), 4.26 (t, *J* = 7.3 Hz, 2H), 7.27 (dt, *J* = 8.0, 1.4 Hz, 1H), 7.37 (dt, *J* = 8.0, 1.4 Hz, 1H), 7.44 (dd, *J* = 8.0, 1.4 Hz, 1H),

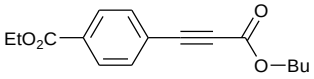
7.60 (dd, *J* = 8.0, 1.4 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 13.6, 19.0, 30.4, 66.1, 82.2, 85.0, 120.0, 126.6, 129.5, 131.5, 134.6, 137.3, 153.9.

LRMS (EI) *m/z*: 236 (M^+).

HRMS: Calcd. for $C_{13}H_{13}ClO_2$: 236.0604, found: 236.0597.

Butyl 3-(4-Ethoxycarbonylphenyl)-2-propynoate (3ga)



Obtained as colorless oil.

IR (neat): 2960, 2935, 2224, 1706, 1701, 1266, 1185, 1103, 1018, 859, 768 cm^{-1}.

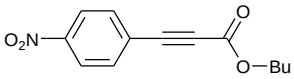
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.97 (t, *J* = 7.0 Hz, 3H), 1.43 (m, 5H), 1.71 (quint, *J* = 7.0 Hz, 2H), 4.25 (t, *J* = 7.0 Hz, 2H), 4.39 (q, *J* = 7.0 Hz, 2H), 7.64 (m, 2H), 8.04 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 13.6, 14.3, 19.0, 30.4, 61.4, 66.1, 82.6, 84.6, 124.0, 129.5, 132.0, 132.7, 153.8, 165.6.

LRMS (EI) *m/z*: 274(M^+).

HRMS: Calcd. for $C_{16}H_{18}O_4$: 274.1205, found: 274.1199.

Butyl 3-(4-nitrophenyl)-2-propynoate (3ha)



Obtained as colorless oil.

IR (neat): 3107, 2960, 2933, 2874, 2226, 1706, 1521, 1345, 1202, 1183, 834, 749 cm^{-1}.

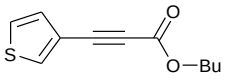
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.97 (t, *J* = 7.1 Hz, 3H), 1.44 (sext, *J* = 7.1 Hz, 2H), 1.71 (quint, *J* = 7.1 Hz, 2H), 4.27 (t, *J* = 7.1 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 8.25 (d, *J* = 8.3 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 13.6, 19.0, 30.4, 66.4, 82.7, 84.3, 123.7, 126.4, 133.6, 148.5, 153.4.

LRMS (EI) *m/z*: 174 (M^+–73).

HRMS: Calcd. for $C_9H_4NO_3$: 174.0191, found: 174.0165.

Butyl 3-(3-Thienyl)-2-propynoate (3ia)



Obtained as an yellow oil.

IR (neat): 3110, 2960, 2933, 2873, 2213, 1701, 1465, 1360, 1262, 1206, 1153, 784, 747, 677 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.96 (t, *J* = 7.3 Hz, 3H), 1.44 (sext, *J* = 7.3 Hz, 2H), 1.69 (quint, *J* = 7.3 Hz, 2H), 4.23 (t, *J* = 7.3 Hz, 2H), 7.22 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.31 (dd, *J* = 5.1, 3.1 Hz, 1H), 7.74 (dd, *J* = 3.1, 1.1 Hz,

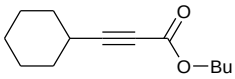
1H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm): 13.6, 19.0, 30.5, 65.9, 80.8, 81.5, 118.9, 126.0, 130.2, 133.7, 154.2.

LRMS (EI) *m/z*: 208 (M^+).

HRMS: Calcd. for $C_{11}H_{12}O_2S$: 208.0558, found: 208.0548.

Butyl 3-Cyclohexyl-2-propynoate (3ka)



Obtained as an yellow oil.

IR (neat): 2932, 2856, 2226, 1706, 1701, 1449, 1240, 1088, 752 cm^{-1}.

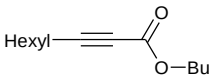
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.93 (t, *J* = 7.1 Hz, 3H), 1.30–1.43 (m, 6H), 1.50–1.54 (m, 2H), 1.62–1.73 (m, 4H), 1.82–1.85 (m, 2H), 2.49–2.54 (m, 1H), 4.16 (t, *J* = 7.1 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 13.6, 19.0, 24.6, 25.6, 28.9, 30.4, 31.4, 65.5, 73.1, 92.8, 154.2.

LRMS (EI) *m/z*: 153 (M^+–55).

HRMS: Calcd. for $C_9H_{13}O_2$: 153.0910, found: 153.0903.

Butyl 2-Nonynoate (3la)



Obtained as an yellow oil.

IR (neat): 2958, 2932, 2873, 2861, 2234, 1707, 1465, 1458, 1380, 1242, 1071, 752 cm^{-1}.

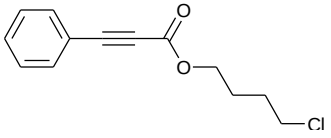
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 0.89 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H), 1.26–1.34 (m, 4H), 1.35–1.45 (m, 4H), 1.55–1.60 (m, 2H), 1.61–1.69 (m, 2H), 2.32 (t, *J* = 7.1 Hz, 2H), 4.16 (t, *J* = 7.1 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 13.6, 13.9, 18.6, 18.9, 22.4, 27.5, 28.5, 30.4, 31.2, 65.5, 73.1, 89.4, 154.0.

LRMS (EI) *m/z*: 155 (M^+–55).

HRMS: Calcd. for $C_9H_{15}O_2$: 155.1072, found: 155.1099.

4-Chlorobutyl 3-Phenyl-2-propynoate (3ae)



Obtained as an yellow oil (92.9 mg, 81%).

IR (neat): 2960, 2221, 1710, 1444, 1287, 1190, 1173, 758, 689 cm^{-1}.

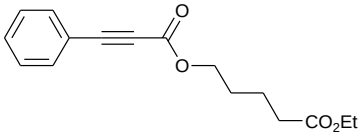
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.89–1.90 (m, 4H), 3.59 (t, *J* = 5.8 Hz, 2H), 4.27 (t, *J* = 5.8 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 25.8, 28.8, 44.2, 65.0, 80.4, 86.3, 119.4, 128.5, 130.6, 132.8, 153.9.

LRMS (EI) *m/z*: 236 (M^+).

HRMS: Calcd. for $C_{13}H_{13}{}^{35}ClO_2$: 236.0604, found: 236.0595.

4-Ethoxycarbonylbutyl 3-Phenyl-2-propynoate (3af)



Obtained as an yellow oil (114.8 mg, 91%).

IR (neat): 2961, 2221, 1733, 1444, 1376, 1287, 1189, 1174, 1032, 759, 690 cm^{-1}.

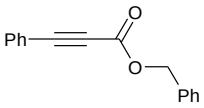
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 1.26 (t, *J* = 7.1 Hz, 3H), 1,74–1.77 (m, 4H), 2.36 (t, *J* = 6.2 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.24 (t, *J* = 6.2 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 14.1, 21.2, 27.7, 33.6, 60.2, 65.4, 80.5, 86.1, 119.4, 128.4, 130.5, 132.8, 153.9, 173.0.

LRMS (EI) *m/z*: 274 (M^+).

HRMS: Calcd. for $C_{16}H_{18}O_2$: 274.1205, found: 274.1192.

Benzyl 3-Phenyl-2-propynoate (3ag)



Obtained as an yellow oil.

IR (neat): 3065, 3035, 2960, 2219, 1705, 1489, 1279, 1164, 1045, 963, 755, 745, 689 cm^{-1}.

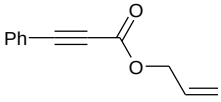
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 5.26 (s, 2H), 7.36–7.42 (m, 8H), 7.56–7.58 (m, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 67.6, 80.5, 86.7, 119.5, 128.4, 128.5, 128.6, 130.6, 132.9, 134.9, 153.8.

LRMS (EI) *m/z*: 236 (M^+).

HRMS: Calcd. for $C_{16}H_{12}O_2$: 236.0837, found: 236.0846.

Allyl 3-Phenyl-2-propynoate (3ah)



Obtained as an yellow oil.

IR (neat): 2224, 1705, 1490, 1294, 1278, 1184, 1168, 999, 920, 755, 746, 688 cm^{-1}.

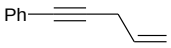
^1H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 4.73 (dt, *J* = 6.0, 1.3 Hz, 2H), 5.32 (ddd, *J* = 10.5, 2.7, 1.3 Hz, 1H), 5.41 (ddd, *J* = 17.3, 2.7, 1.3 Hz, 1H), 5.98 (ddt, *J* = 17.3, 10.5, 6.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 66.5, 80.4, 86.5, 119.3, 119.5, 128.5, 130.6, 131.2, 132.9, 153.6.

LRMS (EI) *m/z*: 186 (M^+).

HRMS: Calcd. for $C_{12}H_{10}O_2$: 186.0681, found: 186.0685.

1-Phenyl-4-penten-1-yne (4)



Obtained as an yellow oil.

IR (neat): 3059, 3032, 2922, 1641, 1489, 1442, 1070, 990, 914, 753, 689 cm^{-1}.

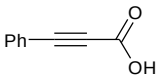
^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 3.17–3.19 (m, 2H), 5.14–5.17 (m, 1H), 5.37–5.43 (m, 1H), 5.84–5.93 (m, 1H), 7.26–7.28 (m, 3H), 7.41–7.43 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 23.7, 82.9, 86.5, 116.2, 123.7, 127.7, 128.2, 131.5, 132.4.

LRMS (EI) *m/z*: 142 (M^+).

HRMS: Calcd. for $C_{11}H_{10}$: 142.0783, found: 142.0760.

3-Phenyl-2-propynoic Acid (5)



Obtained as 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}

^{1}H NMR (400 MHz, $CDCl_3$/TMS) δ (ppm): 7.38–7.41 (m, 2H), 7.46–7.52 (m, 1H), 7.60–7.63 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm): 80.0, 88.7, 119.0, 128.5, 130.9, 133.1, 158.2.

LRMS (EI) *m/z*: 146 (M^+).

HRMS: Calcd. for $C_9H_6O_2$: 146.0368, found: 146.0379.