

## Supporting Information

### Cu-Catalyzed Stereodefined Construction of Acrylic Acid Derivatives from Terminal Alkynes via CO<sub>2</sub> Insertion

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#### General procedures

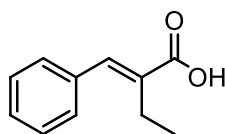
Reaction employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silicagel plates with UV indicator (Merck Silica gel 60F<sub>254</sub>). Flash chromatography columns were packed with 230-400 mesh silica gel as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL JNM-AL400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with JEOL JMS-700N. Distillation were carried out in a Kugelrohr apparatus (SIBATA glass tube oven GTO-350RG). Boiling points are meant to refer to the oven temperature ( $\pm 1$  °C). Melting points were measured by Stuart Scientific SMP3 melting point apparatus.

#### Solvents and Reagents

1,4-Dioxane, tetrahydrofuran, *N,N*-dimethylacetamide (DMA), toluene, and *n*-hexane (Wako) were purchased as anhydrous solvents and used without further purification. triethylborane, (1 M tetrahydrofuran, Aldrich), tributylborane (1 M diethyl ether, Aldrich), IPrCuCl (Aldrich), IMesCuCl (Tokyo Kasei Kogyo Co., Ltd), *t*-BuOK

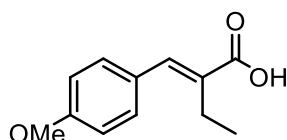
(Aldrich), *t*-BuONa (Tokyo Kasei Kogyo Co., Ltd), EtOK(Aldrich), MeOK (Merck) were purchased and used without further purification. *t*-BuOLi was prepared from *n*-BuLi and *t*-BuOH. <sup>Cl</sup>IPrCuCl, <sup>Me</sup>IPrCuCl and IPr<sup>\*</sup>CuCl were prepared by the reported procedures.<sup>1</sup> Tris(3,3-dimethylbutyl)borane was prepared by hydroboration of 3 equivalents of 3,3-dimethyl-1-butene with borane (1 M in tetrahydrofuran, Aldrich). Ethynylbenzene, 2-ethynylanisol, 4-ethynylanisol, 1-chloro-4-ethynylbenzene, 1-chloro-2-ethynylbenzene, 2-ethynylthiophene (Tokyo Kasei Kogyo Co., Ltd), and 1-ethynyl-2,4,5-trimethylbenzene, 1-ethynyl-4-pentylbenzene (Aldrich) were purchased and distilled via Kugelrohr apparatus under reduced pressure prior to use. 1-Benzyloxy-2-propyne was prepared by the known procedures.<sup>2</sup> NHC ligands employed in this study are as follows: IPrCuCl; chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] copper(I), <sup>Me</sup>IPrCuCl; chloro[1,3-bis(2,6-diisopropylphenyl)-4,5-methyl imidazol-2-ylidene]copper(I), <sup>Cl</sup>IPrCuCl; chloro[1,3-bis(2,6-diisopropylphenyl)-4,5-chloro imidazol-2-ylidene]copper(I), IPr<sup>\*</sup>CuCl; chloro[1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene] copper(I), IMesCuCl; chloro[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] copper(I).

**Typical procedure for three-component coupling reaction of terminal alkyne, organoborane, and carbon dioxide** (entry 6, Table 1): The reaction was undertaken as follows: Into a carbon dioxide-purged flask with IPrCuCl (24.4 mg, 0.05 mmol) and MeOK (140.2 mg, 2.0 mmol) were introduced successively 1,4-dioxane (3 mL), ethynylbenzene (45.9 mg, 0.45 mmol) and triethylborane (3 mL of 1 M tetrahydrofuran, 3.0 mmol) via syringe. The homogeneous mixture was stirred at room temperature for 24 h, during which the reaction was monitored by TLC. Then the mixture was quenched by adding 2N HCl (10 mL) and extracted with diethyl ether three times. The combined organic extracts were washed with brine, and then dried (MgSO<sub>4</sub>) and concentrated in vacuo and purified by column chromatography.



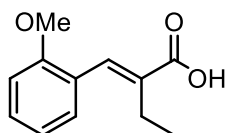
**(E)-2-Benzylidenebutanoic acid (1a).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to afford the title compound **1a** (61.8 mg, 0.35 mmol, 78%) as white solid.

TLC:  $R_f$  = 0.48 (hexane/ethyl acetate 2:1); Mp: 104.3-105.8 °C; IR (KBr): 3100 (w), 3061 (w), 2947 (w), 2619 (br), 1670 (s), 1623 (w), 1425 (s), 1261 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.22 (t,  $J$  = 7.3 Hz, 3 H), 2.58 (q,  $J$  = 7.3 Hz, 2 H), 7.26-7.42 (m, 5 H), 7.79 (s, 1 H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.8, 20.6, 128.6, 128.7, 129.4, 134.0, 135.5, 140.7, 173.3; HRMS:  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{11}\text{H}_{12}\text{O}_2$ : 176.0837; found 176.0842.



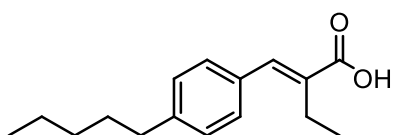
**(E)-2-(4-Methoxybenzylidene)butanoic acid (1b).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to afford the title compound **1b** (64.5 mg, 0.31 mmol, 62%) as white solid.

TLC:  $R_f$  = 0.49 (hexane/ethyl acetate = 2/1, v/v); Mp: 131.1-133.4 °C; IR (KBr): 3053 (w), 2976 (br), 2833 (w), 2633 (br), 1661 (s), 1605 (s), 1514 (s), 1427 (s), 1263 (s), 1180 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.22 (t,  $J$  = 7.3 Hz, 3 H), 2.60 (q,  $J$  = 7.3 Hz, 2 H), 3.85 (s, 3 H), 6.94 (d,  $J$  = 2.9 Hz, 2 H), 7.40 (d,  $J$  = 2.9 Hz, 2 H), 7.73 (s, 1 H).  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.6, 20.6, 55.3, 114.1, 128.1, 131.3, 131.6, 140.4, 160.2, 173.3; HRMS:  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_3$ : 206.0943; found 206.0944.



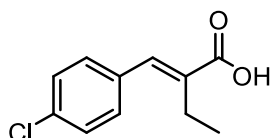
**(E)-2-(2-Methoxybenzylidene)butanoic acid (1c).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to afford the title compound **1c** (75.4 mg, 0.37 mmol, 73%) as white solid.

TLC:  $R_f$  = 0.51 (hexane/ethyl acetate = 2/1, v/v); Mp: 107.1-108.9 °C; IR (KBr): 2953 (m), 2867 (w), 2648 (br), 1676 (s), 1598 (w), 1487 (m), 1425 (m), 1248 (s), 1024 (m), 748 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.19 (t,  $J$  = 7.3 Hz, 3 H), 2.50 (q,  $J$  = 7.3 Hz, 2 H), 3.85 (s, 3 H), 6.91-7.00 (m, 2 H), 7.26-7.35 (m, 2 H), 7.95 (s, 1 H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 20.9, 55.5, 110.7, 120.3, 124.7, 129.6, 130.2, 133.8, 136.8, 157.7, 173.4; HRMS:  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_3$ : 206.0943; found 206.0946.



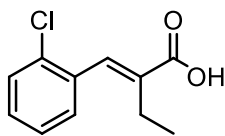
**(E)-2-(4-Pentylbenzylidene)butanoic acid (1d).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to afford the title compound **1d** (68.8 mg, 0.28 mmol, 56%) as white solid.

TLC:  $R_f$  = 0.47 (hexane/ethyl acetate = 2/1, v/v); Mp: 76.7-77.5 °C; IR (KBr): 2960 (w), 2930 (w), 2862 (w), 1676 (s), 1609 (w), 1425 (s), 1256 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.90 (t,  $J$  = 6.8 Hz, 3 H), 1.23 (t,  $J$  = 7.3 Hz, 3 H), 1.32-1.37 (m, 4 H), 1.63 (quin,  $J$  = 7.3 Hz, 2 H), 2.57-2.65 (m, 4 H), 7.21-7.36 (m, 4 H), 7.76 (s, 1 H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.7, 14.0, 20.7, 22.5, 30.9, 31.5, 35.8, 128.7, 129.5, 132.7, 132.8, 140.7, 144.0, 171.7; HRMS:  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_2$ : 246.1620; found 246.1621.



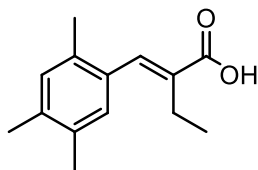
**(E)-2-(4-Chlorobenzylidene)butanoic acid (1e).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to afford the title compound **1e** (71.6 mg, 0.34 mmol, 68%) as white solid.

TLC:  $R_f$  = 0.49 (hexane/ethyl acetate = 2/1, v/v); Mp: 135.9-137.1 °C; IR (KBr): 3074 (m), 2961 (m), 2619 (w), 1676 (s), 1616 (w), 1421 (s), 1286 (w)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, acetone  $d_6$ ):  $\delta$  1.02 (t,  $J$  = 7.3 Hz, 3 H), 2.39 (q,  $J$  = 7.3 Hz, 2 H), 7.34 (s, 4 H), 7.50 (s, 1H), 10.70 (br, 1 H);  $^{13}\text{C}$  NMR: (100 MHz, acetone  $d_6$ )  $\delta$  13.4, 20.8, 129.0, 131.1, 134.0, 134.9, 136.0, 136.9, 168.4; HRMS:  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{11}\text{H}_{11}\text{ClO}_2$ : 210.0448; found 210.0444.



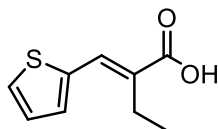
**(E)-2-(2-Chlorobenzylidene)butanoic acid (1f).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to afford the title compound **1f** (65.1 mg, 0.31 mmol, 59%) as white solid.

TLC:  $R_f$  = 0.49 (hexane/ethyl acetate = 2/1, v/v); Mp: 87.0-88.4 °C; IR (KBr): 3865 (w), 2982 (w), 2868 (w), 1690 (s), 1630 (s), 1418 (w), 1294 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.15 (t,  $J$  = 7.3 Hz, 3 H), 2.44 (q,  $J$  = 7.3 Hz, 2 H), 7.27-7.46 (m, 4 H), 7.86 (s, 1 H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.8, 20.8, 126.6, 129.7, 129.7, 129.9, 134.1, 134.3, 135.8, 137.9, 172.5; HRMS:  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{11}\text{H}_{11}\text{ClO}_2$ : 210.0448; found 210.0449.



**(E)-2-(2,4,5-Trimethylbenzylidene)butanoic acid (1g).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to afford the title compound **1g** (90.2 mg, 0.41 mmol, 83%) as white solid.

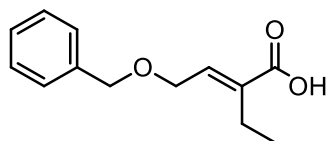
TLC:  $R_f$  = 0.47 (hexane/ethyl acetate = 2/1, v/v); Mp: 132.5-133.9 °C; IR (KBr): 2968 (w), 2363 (w), 1674 (s), 1616 (s), 1418 (w), 1258 (s)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.14 (t,  $J$  = 7.3 Hz, 3 H), 2.23 (s, 3 H), 2.25 (s, 6 H), 2.43 (q,  $J$  = 7.3 Hz, 2 H), 7.00 (s, 2 H), 7.82 (s, 1 H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 19.3, 19.4, 19.5, 20.6, 129.4, 131.5, 132.3, 133.6, 133.8, 134.1, 137.0, 140.5, 174.0; HRMS:  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{14}\text{H}_{18}\text{O}_2$ : 218.1307; found 218.1306.



**(E)-2-[(Thiophen-2-yl)methylene]butanoic acid (1h).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to afford the title compound **1h** (50.0 mg, 0.27 mmol, 53%) as white solid.

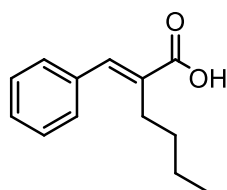
TLC:  $R_f$  = 0.51 (hexane/ethyl acetate = 2/1, v/v); Mp: 109.9-111.2 °C; IR (KBr): 2976 (w), 2606 (br), 2355 (w), 1665 (s), 1605 (m), 1418 (m), 1286 (m), 1256 (m), 1057 (w), 860 (w), 706 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.20 (t,  $J$  = 7.3 Hz, 3 H), 2.74 (q,  $J$  = 7.3 Hz, 2 H), 7.11 (dd,  $J$  = 5.4, 3.4 Hz, 1 H), 7.31 (d,  $J$  = 3.4 Hz, 1 H), 7.51 (d,  $J$  = 5.4 Hz, 1 H), 7.92 (s, 1 H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  12.7, 21.2, 127.4, 129.7, 130.2, 132.7, 133.1, 138.3, 173.2.

HRMS:  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_9\text{H}_{10}\text{O}_2\text{S}$ : 182.0402; found 182.0400.



**(E)-4-(Benzyloxy)-2-ethylbut-2-enoic acid (1i).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to afford the title compound **1i** (27.3 mg, 0.12 mmol, 24%) as colorless oil.

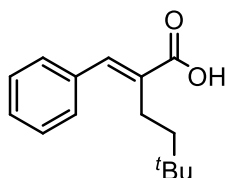
TLC:  $R_f$  = 0.41 (hexane/ethyl acetate = 2/1, v/v); IR (KBr): 3031 (w), 2976 (w), 2648 (w), 1693 (s), 1671 (w), 1454 (w), 1258 (w)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.02 (t,  $J$  = 7.3 Hz, 3 H), 2.28 (q,  $J$  = 7.3 Hz, 2 H), 4.24 (d,  $J$  = 5.9 Hz, 2 H), 4.56 (s, 2 H), 7.00 (t,  $J$  = 5.9 Hz, 1 H), 7.26-7.39 (m, 5 H);  $^{13}\text{C}$  NMR: (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.6, 20.3, 66.3, 72.7, 127.7, 127.8, 128.4, 134.8, 137.6, 140.4, 172.7; HRMS:  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{13}\text{H}_{16}\text{O}_3$ : 220.1099; found 220.1102.



**(E)-2-Benzylidenehexanoic acid (1j).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to afford the title compound **1j** (43.5 mg, 0.21 mmol, 43%) as white solid.

TLC:  $R_f$  = 0.40 (hexane/ethyl acetate = 2/1, v/v); Mp: 80.1-82.2 °C; IR (KBr): 2947(m), 2868(w), 2633(Br), 2363(w), 1674(s), 1618(w), 1421(w), 1275(m), 1223(w), 928(w), 772(w)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, acetone  $d_6$ ):  $\delta$  0.91 (t,  $J$  = 7.3 Hz, 3 H), 1.38 (sext,  $J$  = 7.3 Hz, 2 H), 1.52-1.59 (m, 2 H), 2.53 (t,  $J$  = 8.1 Hz, 2 H), 7.35-7.45 (m, 5 H), 7.69 (s, 1 H);  $^{13}\text{C}$  NMR: (100 MHz, acetone  $d_6$ )  $\delta$  14.1, 23.5, 27.9, 32.2, 129.2, 129.4, 130.0,

134.8, 136.9, 139.1, 169.5; HRMS:  $m/z$  ( $M^+$ ) calcd for  $C_{13}H_{16}O_2$ : 204.1150; found 204.1154.

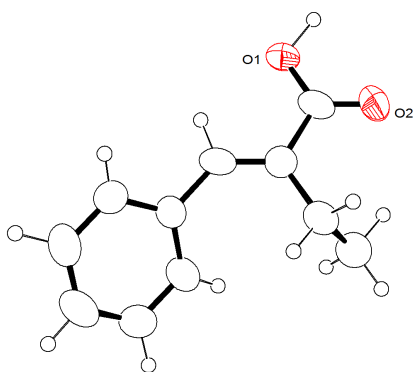


**(*E*)-2-Benzylidene-5,5-dimethylhexanoic acid (1k).** The product was isolated by column chromatography over silica gel (hexane/ethyl acetate = 2/1, v/v) to afford the title compound **1k** (28.3 mg, 0.12 mmol, 23%) as white solid.

TLC:  $R_f$  = 0.43 (hexane/ethyl acetate = 2/1, v/v); Mp: 112.3-114.4 °C; IR (KBr): 2961 (s), 2862 (w), 1678 (s), 1624 (w), 1418 (w), 1252(w)  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  0.95 (s, 9 H), 1.48-1.52 (m, 2 H), 2.51-2.55 (m, 2 H), 7.34-7.41 (m, 5 H), 7.79 (s, 1 H);  $^{13}C$  NMR: (100 MHz,  $CDCl_3$ )  $\delta$  22.9, 29.2, 30.8, 42.8, 128.5, 128.7, 129.4, 133.2, 135.6, 140.8, 173.4; HRMS:  $m/z$  ( $M^+$ ) calcd for  $C_{15}H_{20}O_2$ : 232.1463; found 232.1467.

### X-ray Crystallographic Study of **1a**

The colorless crystal of **1a** was obtained in chloroform solvent by slow evaporation at room temperature. The crystal was mounted using Perfluoropolyether RS 3000 (Riedel-de Haën) on a MicroMount (MiTeGen) and used for data collection. All measurements were made on a Rigaku MicroMax-007HF diffractometer equipped with a Rigaku Saturn 724+ CCD area detector using graphite monochromated Mo-K $\alpha$  radiation. The structure was solved by direct methods with SIR2008<sup>3</sup> and refined by full-matrix least-squares against  $F^2$  using SHELXL-97 software.<sup>4</sup> All calculations were performed using the CrystalStructure<sup>5</sup> crystallographic software package except for refinement, which was performed using SHELXL97<sup>4</sup>. The program ORTEP3<sup>6</sup> was used to generate X-ray structural diagrams. An ORTEP drawing is shown in Figure S1. The details of the crystal and data collection parameters are summarized in Table S1. CCDC-1517933 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Figure S1.** ORTEP drawing of **1a**. Thermal ellipsoids are drawn at 50% probability.



**Table S1.** Crystal data and data refinement for **1a**

formula	C <sub>11</sub> H <sub>12</sub> O <sub>2</sub>
formula weight	176.21
crystal size (mm <sup>3</sup> )	0.10 x 0.04 x 0.02
crystal system	triclinic
space group	<i>P</i> -1
crystal color	colorless
<i>a</i> (Å)	8.584(4)
<i>b</i> (Å)	9.914(5)
<i>c</i> (Å)	11.987(6)
$\alpha$ (°)	86.06(2)
$\beta$ (°)	77.29(2)
$\gamma$ (°)	75.91(2)
<i>V</i> (Å <sup>3</sup> )	965.1(8)
<i>Z</i>	4
<i>d</i> <sub>calc</sub> (gcm <sup>-3</sup> )	1.213
<i>F</i> (000)	376
$\mu$ <sub>calc</sub> (cm <sup>-1</sup> )	0.823
no. of data collected	6806
no. of unique data	3358 ( <i>R</i> <sub>int</sub> = 0.0901)
<i>R</i> <sub>1</sub> <sup>a</sup> (all reflections)	0.2659
<i>wR</i> <sub>2</sub> <sup>b</sup> (all reflections)	0.1221
goodness of fit indicator	0.986

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$$

$$^b wR_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma wF_o^2]^{1/2}.$$

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