

## Supporting Information

# Ligand-Free Ag(I)-Catalyzed Carboxylation of Terminal Alkynes with CO<sub>2</sub>

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## 1. General Information

**Methods.** Unless otherwise statement, all manipulations were performed using standard Schlenk techniques under a dry nitrogen or CO<sub>2</sub> atmosphere. DMF was distilled from CaH<sub>2</sub> at 60 °C under reduced pressure and stored over 4A molecular sieves. NMR spectra were recorded on a Bruker AvanceII 400M type (<sup>1</sup>H NMR, 400 MHz; <sup>13</sup>C NMR, 100 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for <sup>1</sup>H NMR and against the solvent (CDCl<sub>3</sub>, 77.0 ppm) for <sup>13</sup>C NMR, respectively. Multiplicity abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared spectra (IR) were measured using a Nicolet NEXUS FT-IR spectrophotometer.

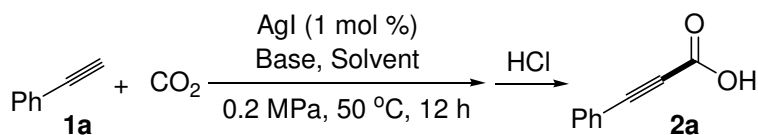
**Materials.** Unless otherwise noted, carbon dioxide (99.999%), <sup>13</sup>C-labeled carbon dioxide (purity >99.9%, <sup>13</sup>C 99%, <sup>18</sup>O <1%), commercially available terminal alkynes, silver(I) salt and other all reagents were used without further purification. Silver phenylacetylide<sup>1</sup> and silver phenylpropiolate<sup>2</sup> were prepared according to the literatures.

## 2. General Experimental Procedure for Carboxylation of Terminal Alkynes

A 70 mL oven dried autoclave containing a stir bar was charged the AgI (4.7 mg, 0.02 mmol), Cs<sub>2</sub>CO<sub>3</sub> (978 mg, 3.0 mmol). Alkyne (2.0 mmol) and 20 mL dry DMF were added with syringe respectively after purging the autoclave with CO<sub>2</sub> three times. The sealed autoclave was pressurized to appropriate pressure with CO<sub>2</sub>. The reaction mixture was stirred at 50 °C for 12 h, then the autoclave was cooled to room temperature and the remaining CO<sub>2</sub> was vented slowly. The reaction mixture was diluted with water (30 mL) and extracted with hexane or CH<sub>2</sub>Cl<sub>2</sub> (2 × 20 mL). The aqueous layer was acidified with aqueous HCl (6 N, 20 mL) at low temperature and then extracted with diethyl ether (4 × 30 mL). The combined organic layers were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed under vacuum to afford the acid product.

## 3. Optimization of Reaction Conditions

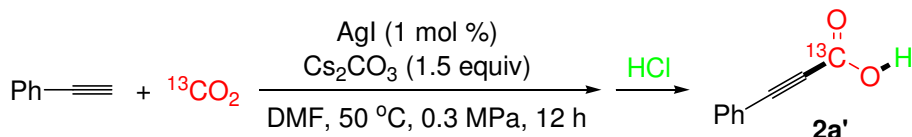
**Table S1.** Optimization of reaction conditions for AgI-catalyzed carboxylation of phenylacetylene (**1a**) with CO<sub>2</sub><sup>a</sup>



entry	base	solvent	yield (%) <sup>b</sup>
1 <sup>c</sup>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	86
2 <sup>d</sup>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	82
3 <sup>e</sup>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	71
4 <sup>f</sup>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	57
5	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	80
6	Cs <sub>2</sub> CO <sub>3</sub>	DMAc	61
7	Cs <sub>2</sub> CO <sub>3</sub>	THF	33
8	Cs <sub>2</sub> CO <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	-
9	K <sub>2</sub> CO <sub>3</sub>	DMF	40
10	NEt <sub>3</sub>	DMF	-
11	K <sub>3</sub> PO <sub>4</sub>	DMF	-
12 <sup>g</sup>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	12
13 <sup>h</sup>	Cs <sub>2</sub> CO <sub>3</sub>	DMF	30

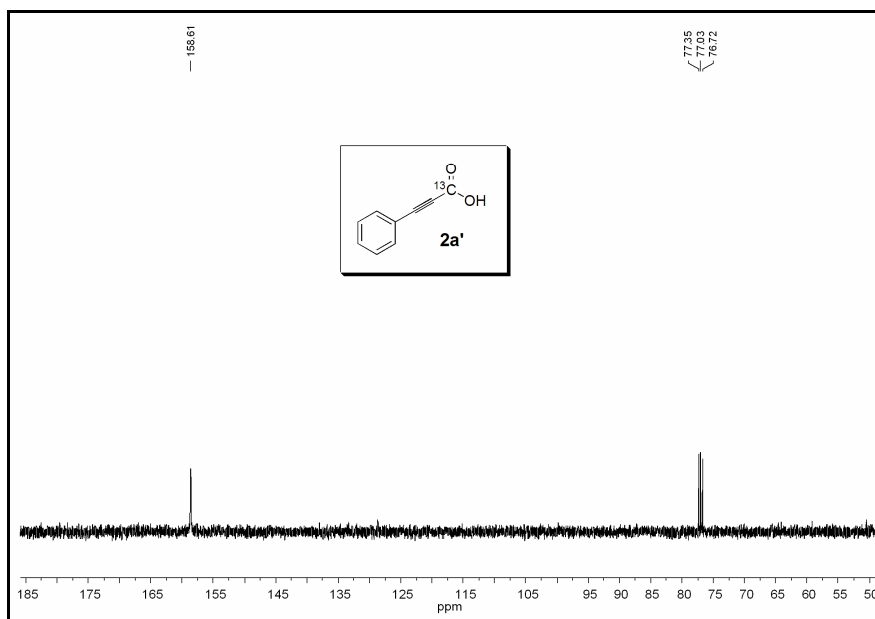
<sup>a</sup> Reaction conditions: **1a** (2 mmol), base (3 mmol), CO<sub>2</sub> (0.2 MPa), 1 mol % AgI, 20 mL solvent, 50 °C, 12 h. <sup>b</sup> Isolated yield. <sup>c</sup> 5 mol% AgI. <sup>d</sup> 40 °C. <sup>e</sup> 60 °C. <sup>f</sup> 1 mol % (IPr)CuCl was used as catalyst. <sup>g</sup> In the absence of Ag catalyst, 80 °C. <sup>h</sup> In the absence of Ag catalyst, 100 °C. DMAc = *N,N*-dimethyl acetamide.

#### 4. AgI-Catalyzed Carboxylation of Phenylacetylene with <sup>13</sup>CO<sub>2</sub>

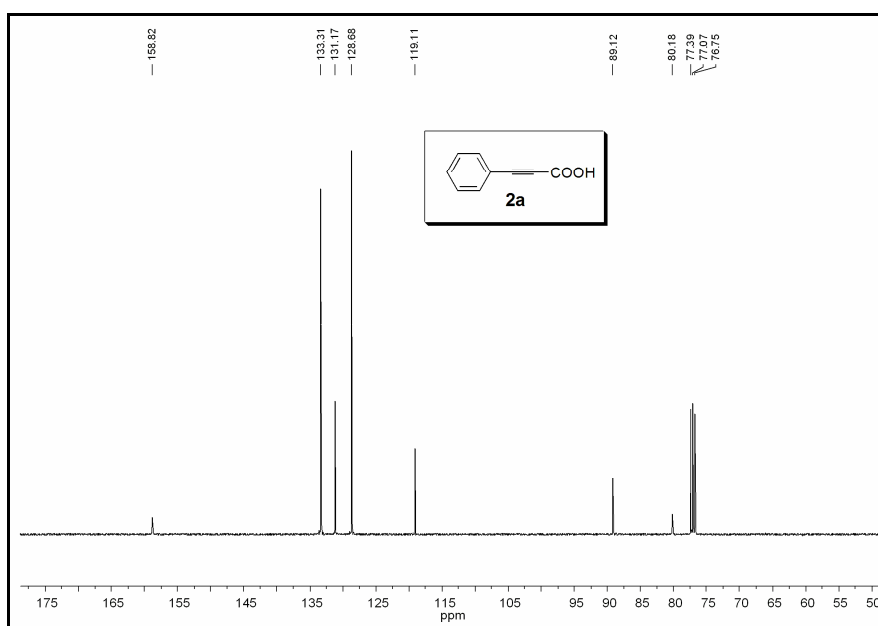


A 20 mL oven dried autoclave containing a stir bar was charged the AgI (1.5 mg, 0.0063 mmol), Cs<sub>2</sub>CO<sub>3</sub> (307 mg, 0.94 mmol). Phenylacetylene (64 mg, 0.63 mmol) and 6 mL dry DMF were added with syringe respectively after purging the autoclave with Ar gas three times. The sealed autoclave was pressurized to appropriate pressure with <sup>13</sup>CO<sub>2</sub> (<sup>13</sup>C 99%). The reaction mixture was stirred at 50 °C for 12 h, then the autoclave was cooled to room temperature and the remaining <sup>13</sup>CO<sub>2</sub> was vented slowly. The reaction mixture was diluted with water (10 mL) and extracted with hexane or CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The

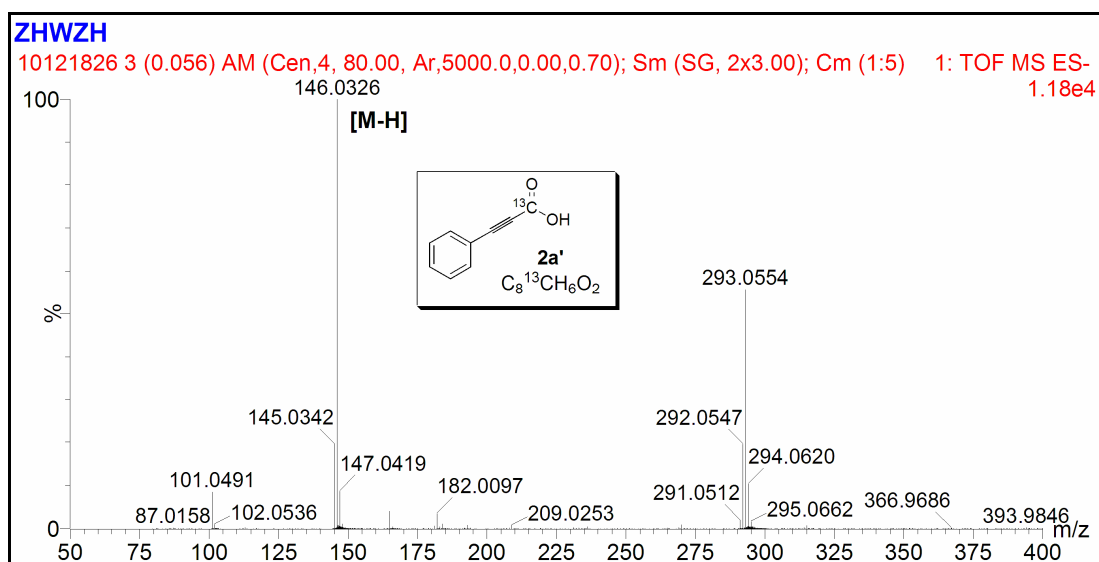
aqueous layer was acidified with aqueous HCl (6 N, 8 mL) at low temperature and then extracted with diethyl ether ( $4 \times 15$  mL). The combined organic layers were washed with water and brine, dried over  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was removed under vacuum to afford the  $^{13}\text{C}_{\text{carbonyl}}$ -labeled phenylpropionic acid (**2a'**) (83 mg, 90% yield).  $^{13}\text{C}_{\text{carbonyl}}$ -labeled phenylpropionic acid (**2a'**):  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 13.83 (br s, 1H), 7.64-7.46 (m, 5H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.6. IR ( $\text{cm}^{-1}$ ) (neat) 2233, 1661. HRMS (ESI,  $m/z$ ) calcd. for  $^{12}\text{C}_8^{13}\text{CH}_5\text{O}_2$   $[\text{M}-\text{H}]^-$ : 146.0323, found: 146.0326.



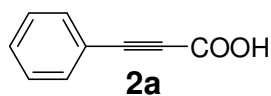
**Figure S1.**  $^{13}\text{C}$  NMR spectrum of  $^{13}\text{C}_{\text{carbonyl}}$ -labeled phenylpropionic acid (**2a'**)



**Figure S2.**  $^{13}\text{C}$  NMR spectrum of phenylpropionic acid (**2a**)

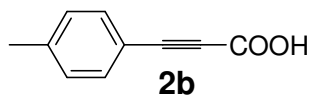


## 5. Characterization of Products



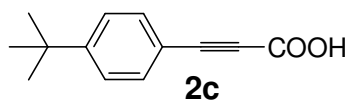
Phenylpropionic acid (**2a**)

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 13.84 (s, 1H), 7.64-7.46 (m, 5H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.8, 133.3, 131.2, 128.7, 119.1, 89.1, 80.2. IR ( $\text{cm}^{-1}$ ) (neat) 2202, 1674. HRMS (ESI,  $m/z$ ) calcd. for  $\text{C}_9\text{H}_5\text{O}_2$   $[\text{M}-\text{H}]^-$ : 145.0290, found: 145.0289.



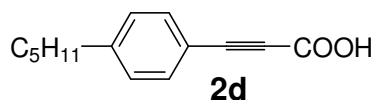
4-Methylphenylpropionic acid (**2b**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.55 (br s, 1H), 7.51 (d,  $J$  = 8.0 Hz, 2H), 7.20 (d,  $J$  = 8.0 Hz, 2H), 2.39 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.9, 141.9, 133.3, 129.5, 116.0, 89.8, 79.8, 21.8. IR ( $\text{cm}^{-1}$ ) (neat) 2199, 1673. HRMS (ESI,  $m/z$ ) calcd. for  $\text{C}_{10}\text{H}_7\text{O}_2$   $[\text{M}-\text{H}]^-$ : 159.0446, found: 159.0442.



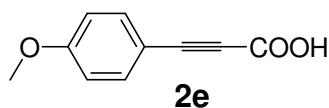
4-*tert*-Butylphenylpropionic acid (**2c**)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 11.19 (br s, 1H), 7.56 (d,  $J$  = 8.4 Hz, 2H), 7.41 (d,  $J$  = 8.4 Hz, 2H), 1.32 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 159.1, 155.0, 133.3, 125.8, 116.0, 89.8, 79.8, 35.1, 31.0. **IR** (cm<sup>-1</sup>) (neat) 2230, 1673. **HRMS** (ESI,  $m/z$ ) calcd. for C<sub>13</sub>H<sub>13</sub>O<sub>2</sub> [M-H]<sup>-</sup>: 201.0916, found: 201.0913.



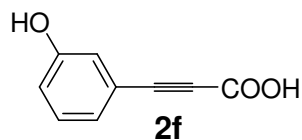
**4-Pentylphenylpropionic acid (2d)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 11.60 (s, 1H), 7.52 (d,  $J$  = 8.0 Hz, 2H), 7.19 (d,  $J$  = 8.0 Hz, 2H), 2.62 (t,  $J$  = 7.6 Hz, 2H), 1.61 (m, 2H), 1.32 (m, 4H), 0.89 (t,  $J$  = 6.8 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 159.2, 146.9, 133.4, 128.8, 116.2, 89.8, 80.0, 36.1, 31.4, 30.8, 22.5, 14.0. **IR** (cm<sup>-1</sup>) (neat) 2202, 1674. **HRMS** (ESI,  $m/z$ ) calcd. for C<sub>14</sub>H<sub>15</sub>O<sub>2</sub> [M-H]<sup>-</sup>: 215.1072, found: 215.1070.



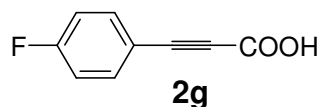
**4-Methoxyphenylpropionic acid (2e)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.56 (d,  $J$  = 8.7 Hz, 2H), 6.89 (d,  $J$  = 8.7 Hz, 2H), 3.84 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD):  $\delta$  = 161.8, 155.7, 134.5, 114.2, 111.1, 86.3, 79.9, 54.6. **IR** (cm<sup>-1</sup>) (neat) 2200, 1670. **HRMS** (ESI,  $m/z$ ) calcd. for C<sub>10</sub>H<sub>7</sub>O<sub>3</sub> [M-H]<sup>-</sup>: 175.0395, found: 175.0391.



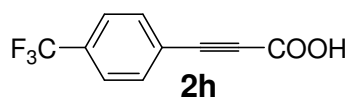
**3-Hydroxyphenylpropionic acid (2f)**

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD):  $\delta$  = 7.24-6.90 (m, 4H). **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD):  $\delta$  = 157.4, 155.4, 129.7, 123.7, 120.3, 118.7, 118.0, 85.4, 79.9. **IR** (cm<sup>-1</sup>) (neat) 3272, 2220, 1692. **HRMS** (ESI,  $m/z$ ) calcd. for C<sub>9</sub>H<sub>5</sub>O<sub>3</sub> [M-H]<sup>-</sup>: 161.0239, found: 161.0236.



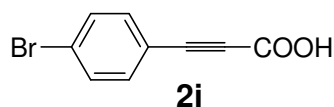
**4-Fluorophenylpropionic acid (2g)**

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD):  $\delta$  = 7.64-7.60 (m, 2H), 7.19-7.14 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD):  $\delta$  = 165.2, 162.7, 155.3, 135.0, 115.9, 84.0, 80.5. **IR** (cm<sup>-1</sup>) (neat) 2214, 1695. **HRMS** (ESI, *m/z*) calcd. for C<sub>9</sub>H<sub>4</sub>O<sub>2</sub>F [M-H]<sup>-</sup>: 163.0195, found: 163.0198.



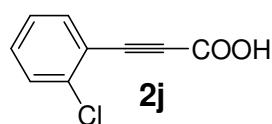
**4-Trifluoromethylphenylpropionic acid (2h)**

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD):  $\delta$  = 7.77-7.71 (m, 4H). **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD):  $\delta$  = 157.0, 135.2, 134.1, 133.8, 127.6, 124.6, 84.9, 84.6. **IR** (cm<sup>-1</sup>) (neat) 2235, 1694. **HRMS** (ESI, *m/z*) calcd. for C<sub>10</sub>H<sub>4</sub>O<sub>2</sub>F<sub>3</sub> [M-H]<sup>-</sup>: 213.0163, found: 213.0166.



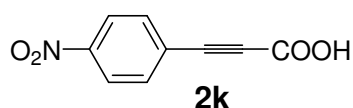
**4-Bromophenylpropionic acid (2i)**

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD):  $\delta$  = 7.61 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H). **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD):  $\delta$  = 154.9, 134.0, 131.9, 124.9, 118.7, 83.7, 81.4. **IR** (cm<sup>-1</sup>) (neat) 2232, 1695. **HRMS** (ESI, *m/z*) calcd. for C<sub>9</sub>H<sub>4</sub>O<sub>2</sub>Br [M-H]<sup>-</sup>: 222.9395, found: 222.9397.



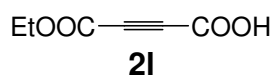
**2-Chlorophenylpropionic acid (2j)**

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD):  $\delta$  = 7.67-7.36 (m, 4H). **<sup>13</sup>C NMR** (100 MHz, CD<sub>3</sub>OD):  $\delta$  = 154.8, 136.6, 134.4, 131.7, 129.4, 126.8, 119.7, 85.0, 81.1. **IR** (cm<sup>-1</sup>) (neat) 2230, 1699. **HRMS** (ESI, *m/z*) calcd. for C<sub>9</sub>H<sub>4</sub>O<sub>2</sub>Cl [M-H]<sup>-</sup>: 178.9900, found: 178.9901.



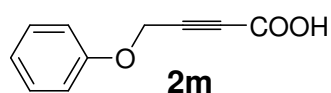
**4-Nitrophenylpropionic acid (2k)**

**<sup>1</sup>H NMR** (400 MHz, CD<sub>3</sub>OD):  $\delta$  = 8.27 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H). **<sup>13</sup>C NMR** (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 154.3, 146.0, 131.9, 129.3, 123.2, 94.8, 72.7. **IR** (cm<sup>-1</sup>) (neat) 2229, 1690. **HRMS** (ESI, *m/z*) calcd. for C<sub>9</sub>H<sub>4</sub>NO<sub>4</sub> [M-H]<sup>-</sup>: 190.0140, found: 190.0142.



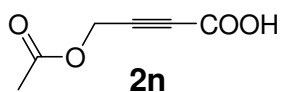
**Monoethyl acetylenedicarboxylate (2l)**

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.37 (s, 1H), 4.29 (t,  $J$  = 7.2 Hz, 2H), 1.31 (q,  $J$  = 7.2 Hz, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 154.7, 152.0, 76.3, 74.2, 63.6, 13.8. **IR** ( $\text{cm}^{-1}$ ) (neat) 1722. **HRMS** (ESI,  $m/z$ ) calcd. for  $\text{C}_6\text{H}_5\text{O}_4$   $[\text{M}-\text{H}]^-$ : 141.0188, found: 141.0183.



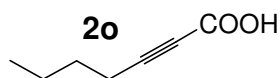
**4-Phenoxy-2-butynoic acid (2m)**

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.23 (br s, 1H), 7.34-6.94 (m, 5H), 4.83 (s, 2H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 157.2, 129.7, 122.2, 114.9, 84.9, 77.8, 55.5. **IR** ( $\text{cm}^{-1}$ ) (neat) 2249, 1674. **HRMS** (ESI,  $m/z$ ) calcd. for  $\text{C}_{10}\text{H}_7\text{O}_3$   $[\text{M}-\text{H}]^-$ : 175.0395, found: 175.0398.



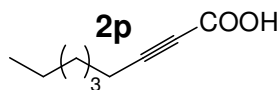
**4-Acetyloxy-2-butynoic acid (2n)**

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.69 (s, 1H), 4.78 (s, 2H), 2.10 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 170.8, 155.9, 83.0, 77.5, 51.5, 20.5. **IR** ( $\text{cm}^{-1}$ ) (neat) 2239, 1740, 1685. **HRMS** (ESI,  $m/z$ ) calcd. for  $\text{C}_6\text{H}_5\text{O}_4$   $[\text{M}-\text{H}]^-$ : 140.0188, found: 140.0186.



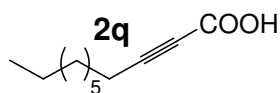
**2-Heptynoic acid (2o)**

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 11.32 (s, 1H), 2.37 (t,  $J$  = 7.0 Hz, 2H), 1.58 (m, 2H), 1.44 (m, 2H), 0.93 (t,  $J$  = 6.8 Hz, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.7, 92.8, 72.6, 29.3, 21.9, 18.4, 13.4. **IR** ( $\text{cm}^{-1}$ ) (neat) 2238, 1686. **HRMS** (ESI,  $m/z$ ) calcd. for  $\text{C}_7\text{H}_9\text{O}_2$   $[\text{M}-\text{H}]^-$ : 125.0603, found: 125.0603.



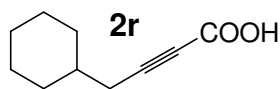
**2-Nonynoic acid (2p)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.05 (s, 1H), 2.35 (t,  $J$  = 7.2 Hz, 2H), 1.59 (m, 2H), 1.41 (m, 2H), 1.29 (m, 4H), 0.89 (t,  $J$  = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.3, 92.5, 72.7, 31.2, 28.5, 27.4, 22.4, 18.7, 14.0. **IR** (cm<sup>-1</sup>) (neat) 2238, 1686. **HRMS** (ESI,  $m/z$ ) calcd. for C<sub>9</sub>H<sub>13</sub>O<sub>2</sub> [M-H]<sup>-</sup>: 153.0916, found: 153.0918.



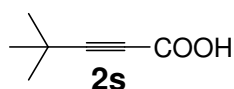
**2-Decynoic acid (2q)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.81 (s, 1H), 2.36 (t,  $J$  = 7.2 Hz, 2H), 1.58 (m, 2H), 1.41-1.28 (m, 10H), 0.88 (t,  $J$  = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 157.8, 91.8, 71.7, 30.8, 28.1, 28.0, 27.8, 26.4, 21.6, 17.8, 13.1. **IR** (cm<sup>-1</sup>) (neat) 2239, 1687. **HRMS** (ESI,  $m/z$ ) calcd. for C<sub>11</sub>H<sub>17</sub>O<sub>2</sub> [M-H]<sup>-</sup>: 181.1229, found: 181.1227.



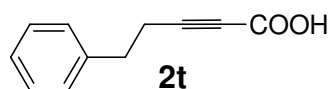
**4-Cyclohexyl-2-butynoic acid (2r)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.68 (s, 1H), 2.26 (d,  $J$  = 6.8 Hz, 2H), 1.83-1.54 (m, 6H), 1.31-0.97 (m, 5H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.6, 91.9, 73.6, 36.6, 32.6, 26.5, 26.0, 25.9. **IR** (cm<sup>-1</sup>) (neat) 2238, 1675. **HRMS** (ESI,  $m/z$ ) calcd. for C<sub>10</sub>H<sub>13</sub>O<sub>2</sub> [M-H]<sup>-</sup>: 165.0916, found: 165.0913.



**4,4-Dimethyl-2-pentynoic acid (2s)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 11.59 (s, 1H), 1.30 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.9, 99.7, 71.3, 29.8, 27.6. **IR** (cm<sup>-1</sup>) (neat) 2219, 1687. **HRMS** (ESI,  $m/z$ ) calcd. for C<sub>7</sub>H<sub>9</sub>O<sub>2</sub> [M-H]<sup>-</sup>: 125.0603, found: 125.0605.



**5-Phenyl-2-pentynoic acid (2t)**

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 11.50 (s, 1H), 7.42-7.29 (m, 5H), 2.97 (d,  $J$  = 7.4 Hz, 2H), 2.70 (d,  $J$  = 7.4 Hz, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.7, 139.5, 128.7, 128.5, 126.9, 91.9, 73.4, 33.7, 21.0. **IR** (cm<sup>-1</sup>) (neat) 2239, 1680. **HRMS** (ESI,  $m/z$ ) calcd. for C<sub>11</sub>H<sub>9</sub>O<sub>2</sub> [M-H]<sup>-</sup>: 173.0603, found: 173.0607.



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 11.29 (br s, 1H), 1.44-1.38 (m, 1H), 1.02-0.94 (m, 4H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.7, 96.8, 68.1, 9.6, -0.5. **IR** (cm<sup>-1</sup>) (neat) 2229, 1674. **HRMS** (ESI,  $m/z$ ) calcd. for C<sub>6</sub>H<sub>5</sub>O<sub>2</sub> [M-H]<sup>-</sup>: 109.0290, found: 109.0288.



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 11.18 (br s, 1H), 2.81-2.74 (m, 1H), 2.00-1.59 (m, 8H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.0, 95.8, 71.1, 31.9, 28.7, 24.2. **IR** (cm<sup>-1</sup>) (neat) 2235, 1679. **HRMS** (ESI,  $m/z$ ) calcd. for C<sub>8</sub>H<sub>9</sub>O<sub>2</sub> [M-H]<sup>-</sup>: 137.0603, found: 137.0601.

## 6. References

- (1) Teo, B. K.; Xu, Y.-H.; Zhong, B.-Y.; He, Y.-K.; Chen, H.-Y.; Qian, W.; Deng, Y.-J.; Zou, Y. H. *Inorg. Chem.* **2001**, *40*, 6794.
- (2) Hiroyuki, H.; Kozo, S.; Hiroshi, H. EP 0143424A2, **1984**.

## 7. Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra of Products

