

Supporting Information

Ligand-Free Ag(I)-Catalyzed Carboxylation of Terminal Alkynes with CO₂

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1. General Information

Methods. Unless otherwise statement, all manipulations were performed using standard Schlenk techniques under a dry nitrogen or CO₂ atmosphere. DMF was distilled from CaH₂ at 60 °C under reduced pressure and stored over 4A molecular sieves. NMR spectra were recorded on a Bruker AvanceII 400M type (¹H NMR, 400 MHz; ¹³C NMR, 100 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ¹H NMR and against the solvent (CDCl₃, 77.0 ppm) for ¹³C 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.

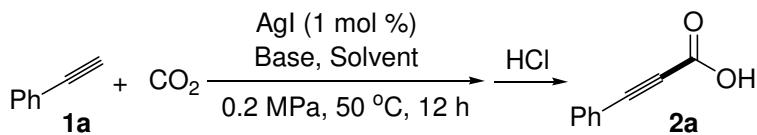
Materials. Unless otherwise noted, carbon dioxide (99.999%), ¹³C-labeled carbon dioxide (purity >99.9%, ¹³C 99%, ¹⁸O <1%), commercially available terminal alkynes, silver(I) salt and other all reagents were used without further purification. Silver phenylacetylide¹ and silver phenylpropiolate² were prepared 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), Cs₂CO₃ (978 mg, 3.0 mmol). Alkyne (2.0 mmol) and 20 mL dry DMF were added with syringe respectively after purging the autoclave with CO₂ three times. The sealed autoclave was pressurized to appropriate pressure with CO₂. The reaction mixture was stirred at 50 °C for 12 h, then the autoclave was cooled to room temperature and the remaining CO₂ was vented slowly. The reaction mixture was diluted with water (30 mL) and extracted with hexane or CH₂Cl₂ (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 Na₂SO₄ and filtered. The solvent was removed under vacuum to afford the acid product.

3. Optimization of Reaction Conditions

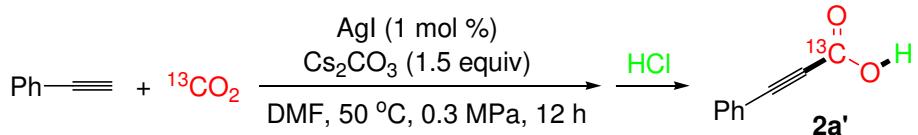
Table S1. Optimization of reaction conditions for AgI-catalyzed carboxylation of phenylacetylene (**1a**) with CO₂^a



| entry | base | solvent | yield (%) ^b |
|-----------------|--------------------------|--------------------------|------------------------|
| 1 ^c | Cs_2CO_3 | DMF | 86 |
| 2 ^d | Cs_2CO_3 | DMF | 82 |
| 3 ^e | Cs_2CO_3 | DMF | 71 |
| 4 ^f | Cs_2CO_3 | DMF | 57 |
| 5 | Cs_2CO_3 | DMSO | 80 |
| 6 | Cs_2CO_3 | DMAc | 61 |
| 7 | Cs_2CO_3 | THF | 33 |
| 8 | Cs_2CO_3 | CH_2Cl_2 | - |
| 9 | K_2CO_3 | DMF | 40 |
| 10 | NEt_3 | DMF | - |
| 11 | K_3PO_4 | DMF | - |
| 12 ^g | Cs_2CO_3 | DMF | 12 |
| 13 ^h | Cs_2CO_3 | DMF | 30 |

^a Reaction conditions: **1a** (2 mmol), base (3 mmol), CO_2 (0.2 MPa), 1 mol % AgI , 20 mL solvent, 50 °C, 12 h. ^b Isolated yield. ^c 5 mol% AgI . ^d 40 °C. ^e 60 °C. ^f 1 mol % (IPr)CuCl was used as catalyst. ^g In the absence of Ag catalyst, 80 °C. ^h In the absence of Ag catalyst, 100 °C. DMAc = *N,N*-dimethyl acetamide.

4. AgI-Catalyzed Carboxylation of Phenylacetylene with $^{13}\text{CO}_2$



A 20 mL oven dried autoclave containing a stir bar was charged the AgI (1.5 mg, 0.0063 mmol), Cs_2CO_3 (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 $^{13}\text{CO}_2$ (¹³C 99%). The reaction mixture was stirred at 50 °C for 12 h, then the autoclave was cooled to room temperature and the remaining $^{13}\text{CO}_2$ was vented slowly. The reaction mixture was diluted with water (10 mL) and extracted with hexane or CH_2Cl_2 (2 × 10 mL). The

aqueous layer was acidified with aqueous HCl (6 N, 8 mL) at low temperature and then extracted with diethyl ether (4×15 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4 and filtered. The solvent was removed under vacuum to afford the ^{13}C carbonyl-labeled phenylpropiolic acid (**2a'**) (83 mg, 90% yield). ^{13}C carbonyl-labeled phenylpropiolic acid (**2a'**): **1H NMR** (400 MHz, $\text{DMSO}-d_6$): δ = 13.83 (br s, 1H), 7.64-7.46 (m, 5H). **13C NMR** (100 MHz, CDCl_3): δ = 158.6. **IR** (cm^{-1}) (neat) 2233, 1661. **HRMS** (ESI, m/z) calcd. for $^{12}\text{C}_8^{13}\text{CH}_5\text{O}_2$ [M-H] $^-$: 146.0323, found: 146.0326.

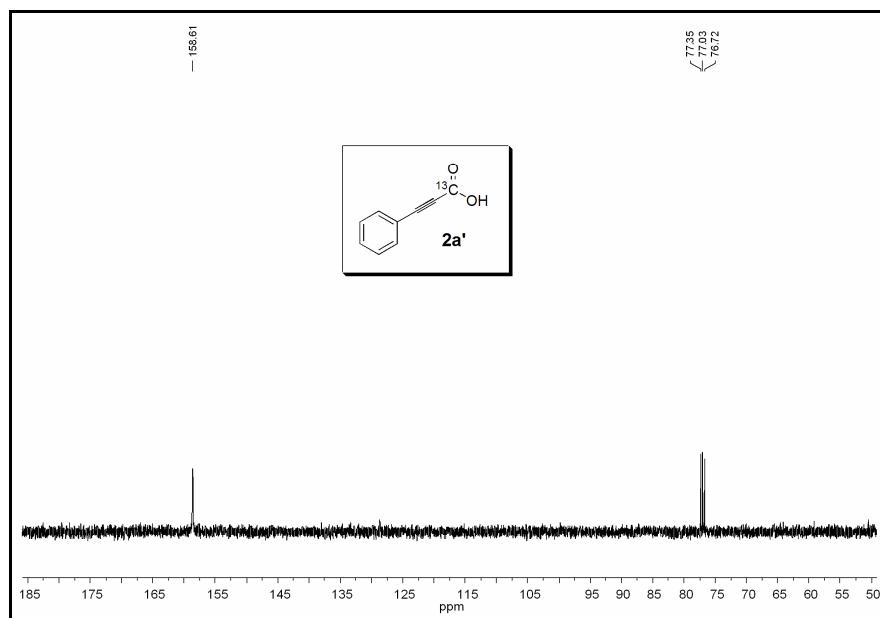


Figure S1. ^{13}C NMR spectrum of ^{13}C carbonyl-labeled phenylpropiolic acid (**2a'**)

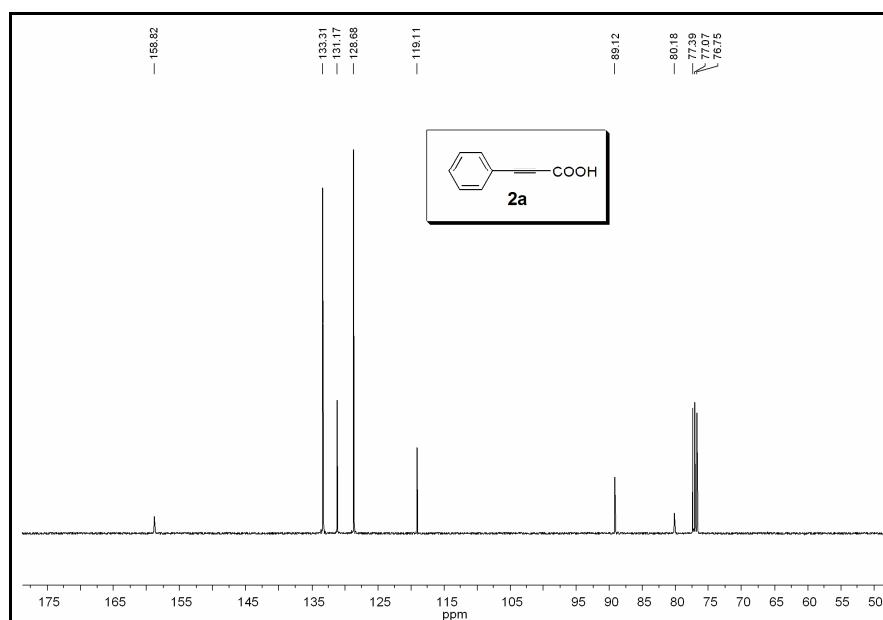


Figure S2. ^{13}C NMR spectrum of phenylpropiolic acid (**2a**)

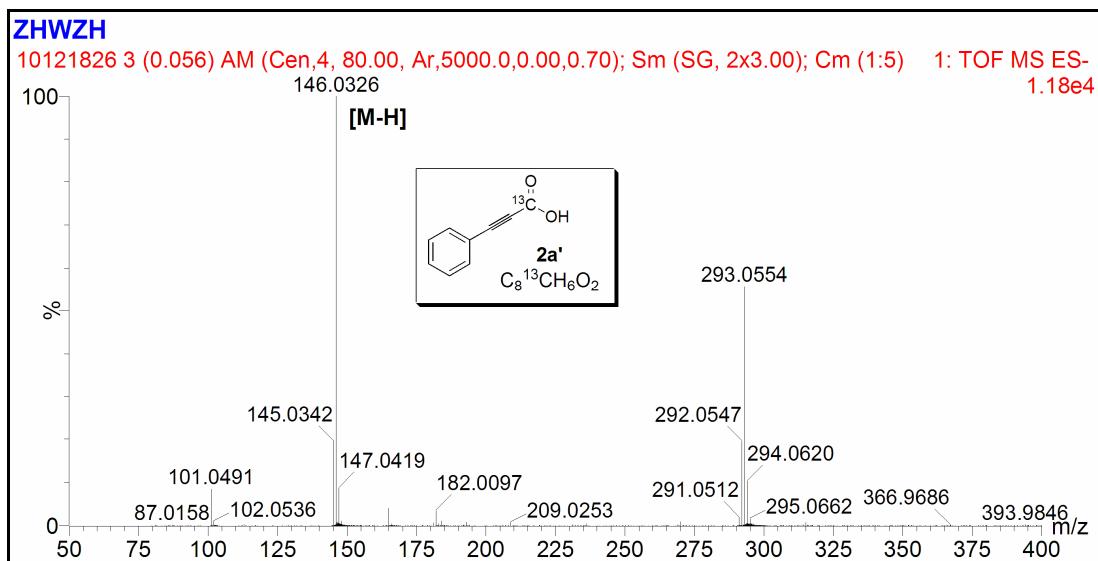
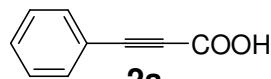


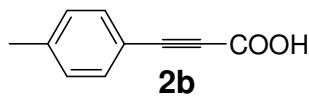
Figure S3. HRMS of ^{13}C carbonyl-labeled phenylpropiolic acid (**2a'**)

5. Characterization of Products



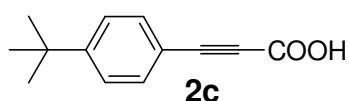
Phenylpropiolic acid (2a)

$^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$): δ = 13.84 (s, 1H), 7.64-7.46 (m, 5H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3): δ = 158.8, 133.3, 131.2, 128.7, 119.1, 89.1, 80.2. **IR** (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.



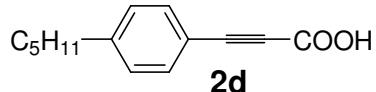
4-Methylphenylpropiolic acid (2b)

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ = 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, CDCl_3): δ = 158.9, 141.9, 133.3, 129.5, 116.0, 89.8, 79.8, 21.8. **IR** (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.



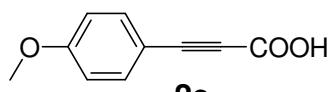
4-tert-Butylphenylpropiolic acid (2c)

¹H NMR (400 MHz, CDCl₃): δ = 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). **¹³C NMR** (100 MHz, CDCl₃): δ = 159.1, 155.0, 133.3, 125.8, 116.0, 89.8, 79.8, 35.1, 31.0. **IR** (cm⁻¹) (neat) 2230, 1673. **HRMS** (ESI, *m/z*) calcd. for C₁₃H₁₃O₂ [M-H]⁻: 201.0916, found: 201.0913.



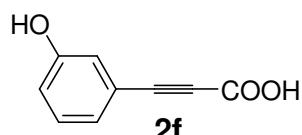
4-Pentylphenylpropiolic acid (2d)

¹H NMR (400 MHz, CDCl₃): δ = 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). **¹³C NMR** (100 MHz, CDCl₃): δ = 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⁻¹) (neat) 2202, 1674. **HRMS** (ESI, *m/z*) calcd. for C₁₄H₁₅O₂ [M-H]⁻: 215.1072, found: 215.1070.



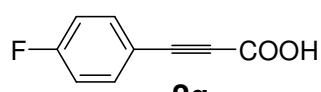
4-Methoxyphenylpropiolic acid (2e)

¹H NMR (400 MHz, CDCl₃): δ = 7.56 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H). **¹³C NMR** (100 MHz, CD₃OD): δ = 161.8, 155.7, 134.5, 114.2, 111.1, 86.3, 79.9, 54.6. **IR** (cm⁻¹) (neat) 2200, 1670. **HRMS** (ESI, *m/z*) calcd. for C₁₀H₇O₃ [M-H]⁻: 175.0395, found: 175.0391.



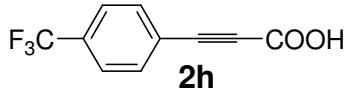
3-Hydroxyphenylpropiolic acid (2f)

¹H NMR (400 MHz, CD₃OD): δ = 7.24-6.90 (m, 4H). **¹³C NMR** (100 MHz, CD₃OD): δ = 157.4, 155.4, 129.7, 123.7, 120.3, 118.7, 118.0, 85.4, 79.9. **IR** (cm⁻¹) (neat) 3272, 2220, 1692. **HRMS** (ESI, *m/z*) calcd. for C₉H₅O₃ [M-H]⁻: 161.0239, found: 161.0236.



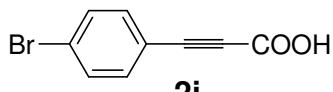
4-Fluorophenylpropiolic acid (2g)

¹H NMR (400 MHz, CD₃OD): δ = 7.64-7.60 (m, 2H), 7.19-7.14 (m, 2H). **¹³C NMR** (100 MHz, CD₃OD): δ = 165.2, 162.7, 155.3, 135.0, 115.9, 84.0, 80.5. **IR** (cm⁻¹) (neat) 2214, 1695. **HRMS** (ESI, *m/z*) calcd. for C₉H₄O₂F [M-H]⁻: 163.0195, found: 163.0198.



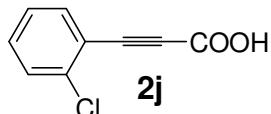
4-Trifluoromethylphenylpropiolic acid (2h)

¹H NMR (400 MHz, CD₃OD): δ = 7.77-7.71 (m, 4H). **¹³C NMR** (100 MHz, CD₃OD): δ = 157.0, 135.2, 134.1, 133.8, 127.6, 124.6, 84.9, 84.6. **IR** (cm⁻¹) (neat) 2235, 1694. **HRMS** (ESI, *m/z*) calcd. for C₁₀H₄O₂F₃ [M-H]⁻: 213.0163, found: 213.0166.



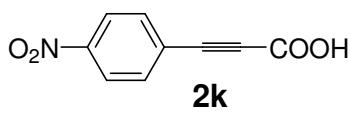
4-Bromophenylpropiolic acid (2i)

¹H NMR (400 MHz, CD₃OD): δ = 7.61 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H). **¹³C NMR** (100 MHz, CD₃OD): δ = 154.9, 134.0, 131.9, 124.9, 118.7, 83.7, 81.4. **IR** (cm⁻¹) (neat) 2232, 1695. **HRMS** (ESI, *m/z*) calcd. for C₉H₄O₂Br [M-H]⁻: 222.9395, found: 222.9397.



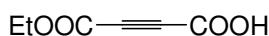
2-Chlorophenylpropiolic acid (2j)

¹H NMR (400 MHz, CD₃OD): δ = 7.67-7.36 (m, 4H). **¹³C NMR** (100 MHz, CD₃OD): δ = 154.8, 136.6, 134.4, 131.7, 129.4, 126.8, 119.7, 85.0, 81.1. **IR** (cm⁻¹) (neat) 2230, 1699. **HRMS** (ESI, *m/z*) calcd. for C₉H₄O₂Cl [M-H]⁻: 178.9900, found: 178.9901.

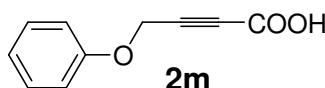


4-Nitrophenylpropiolic acid (2k)

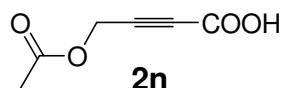
¹H NMR (400 MHz, CD₃OD): δ = 8.27 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H). **¹³C NMR** (100 MHz, DMSO-*d*₆): δ = 154.3, 146.0, 131.9, 129.3, 123.2, 94.8, 72.7. **IR** (cm⁻¹) (neat) 2229, 1690. **HRMS** (ESI, *m/z*) calcd. for C₉H₄NO₄ [M-H]⁻: 190.0140, found: 190.0142.

**2l****Monoethyl acetylenedicarboxylate (2l)**

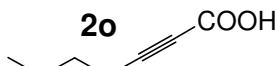
¹H NMR (400 MHz, CDCl₃): δ = 10.37 (s, 1H), 4.29 (t, J = 7.2 Hz, 2H), 1.31 (q, J = 7.2 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ = 154.7, 152.0, 76.3, 74.2, 63.6, 13.8. **IR** (cm⁻¹) (neat) 1722. **HRMS** (ESI, *m/z*) calcd. for C₆H₅O₄ [M-H]⁻: 141.0188, found: 141.0183.

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

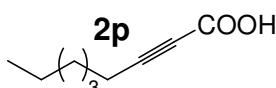
¹H NMR (400 MHz, CDCl₃): δ = 10.23 (br s, 1H), 7.34-6.94 (m, 5H), 4.83 (s, 2H). **¹³C NMR** (100 MHz, CDCl₃): δ = 157.2, 129.7, 122.2, 114.9, 84.9, 77.8, 55.5. **IR** (cm⁻¹) (neat) 2249, 1674. **HRMS** (ESI, *m/z*) calcd. for C₁₀H₇O₃ [M-H]⁻: 175.0395, found: 175.0398.

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

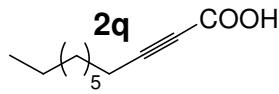
¹H NMR (400 MHz, CDCl₃): δ = 9.69 (s, 1H), 4.78 (s, 2H), 2.10 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ = 170.8, 155.9, 83.0, 77.5, 51.5, 20.5. **IR** (cm⁻¹) (neat) 2239, 1740, 1685. **HRMS** (ESI, *m/z*) calcd. for C₆H₅O₄ [M-H]⁻: 140.0188, found: 140.0186.

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

¹H NMR (400 MHz, CDCl₃): δ = 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). **¹³C NMR** (100 MHz, CDCl₃): δ = 158.7, 92.8, 72.6, 29.3, 21.9, 18.4, 13.4. **IR** (cm⁻¹) (neat) 2238, 1686. **HRMS** (ESI, *m/z*) calcd. for C₇H₉O₂ [M-H]⁻: 125.0603, found: 125.0603.

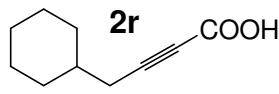
**2p****2-Nonynoic acid (2p)**

¹H NMR (400 MHz, CDCl₃): δ = 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). **¹³C NMR** (100 MHz, CDCl₃): δ = 158.3, 92.5, 72.7, 31.2, 28.5, 27.4, 22.4, 18.7, 14.0. **IR** (cm⁻¹) (neat) 2238, 1686. **HRMS** (ESI, *m/z*) calcd. for C₉H₁₃O₂ [M-H]⁻: 153.0916, found: 153.0918.



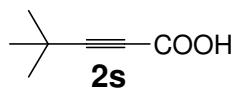
2-Decynoic acid (2q)

¹H NMR (400 MHz, CDCl₃): δ = 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). **¹³C NMR** (100 MHz, CDCl₃): δ = 157.8, 91.8, 71.7, 30.8, 28.1, 28.0, 27.8, 26.4, 21.6, 17.8, 13.1. **IR** (cm⁻¹) (neat) 2239, 1687. **HRMS** (ESI, *m/z*) calcd. for C₁₁H₁₇O₂ [M-H]⁻: 181.1229, found: 181.1227.



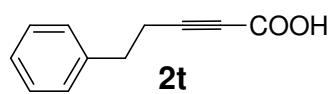
4-Cyclohexyl-2-butynoic acid (2r)

¹H NMR (400 MHz, CDCl₃): δ = 10.68 (s, 1H), 2.26 (d, J = 6.8 Hz, 2H), 1.83-1.54 (m, 6H), 1.31-0.97 (m, 5H). **¹³C NMR** (100 MHz, CDCl₃): δ = 158.6, 91.9, 73.6, 36.6, 32.6, 26.5, 26.0, 25.9. **IR** (cm⁻¹) (neat) 2238, 1675. **HRMS** (ESI, *m/z*) calcd. for C₁₀H₁₃O₂ [M-H]⁻: 165.0916, found: 165.0913.



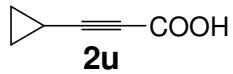
4,4-Dimethyl-2-pentynoic acid (2s)

¹H NMR (400 MHz, CDCl₃): δ = 11.59 (s, 1H), 1.30 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃): δ = 158.9, 99.7, 71.3, 29.8, 27.6. **IR** (cm⁻¹) (neat) 2219, 1687. **HRMS** (ESI, *m/z*) calcd. for C₇H₉O₂ [M-H]⁻: 125.0603, found: 125.0605.



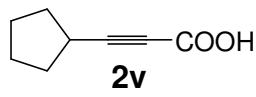
5-Phenyl-2-pentyneoic acid (2t)

¹H NMR (400 MHz, CDCl₃): δ = 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). **¹³C NMR** (100 MHz, CDCl₃): δ = 158.7, 139.5, 128.7, 128.5, 126.9, 91.9, 73.4, 33.7, 21.0. **IR** (cm⁻¹) (neat) 2239, 1680. **HRMS** (ESI, *m/z*) calcd. for C₁₁H₉O₂ [M-H]⁻: 173.0603, found: 173.0607.



3-Cyclopropyl-2-propynoic acid (2u)

¹H NMR (400 MHz, CDCl₃): δ = 11.29 (br s, 1H), 1.44-1.38 (m, 1H), 1.02-0.94 (m, 4H). **¹³C NMR** (100 MHz, CDCl₃): δ = 158.7, 96.8, 68.1, 9.6, -0.5. **IR** (cm⁻¹) (neat) 2229, 1674. **HRMS** (ESI, *m/z*) calcd. for C₆H₅O₂ [M-H]⁻: 109.0290, found: 109.0288.



3-Cyclopentyl-2-propynoic acid (2v)

¹H NMR (400 MHz, CDCl₃): δ = 11.18 (br s, 1H), 2.81-2.74 (m, 1H), 2.00-1.59 (m, 8H). **¹³C NMR** (100 MHz, CDCl₃): δ = 158.0, 95.8, 71.1, 31.9, 28.7, 24.2. **IR** (cm⁻¹) (neat) 2235, 1679. **HRMS** (ESI, *m/z*) calcd. for C₈H₉O₂ [M-H]⁻: 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 ^1H NMR and ^{13}C NMR Spectra of Products

