Supporting Information
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Ligand-Promoted, Copper Nanoparticles-Catalyzed Oxidation of Propargylic Alcohols with TBHP or Air as Oxidant

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Supporting information

$^1$H and $^{13}$C NMR spectra were acquired by 300 and 75.5 MHz, respectively. Flash column chromatography was performed over silica gel 30-60μm. The reported yields are isolated yields and are the average of two runs. All commercially available reagents were used as received. All compounds described in the paper are known in literatures and were characterized by comparing their $^1$H and $^{13}$C NMR to the previously reported data.

Synthesis of Copper Nanoparticle (Cu Np) Catalyst

Under nitrogen atmosphere, 10 mL absolute alcohol was mixed with 25 mL aqueous solution of Cu(OAc)$_2$ (0.01 M) at 40°C. Then, 35 mL of aqueous solution containing sodium borohydride (NaBH$_4$, 0.4 mmol), potassium hydroxide (KOH, 0.4 mmol) and polyvinylpyrrolidone (PVP, average MW: 40,000, 100mg) was added to the solution above drop by drop with vigorous stirring in 30 minutes, and black precipitates were observed in the mixture. After 2 hours reaction, the particles were separated from the solution by centrifugation at 5000 ppm for 2 min. The precipitates were washed by distilled water and absolute alcohol for 3 times respectively. The final product was dried in vacuum at 50 °C overnight and stored under nitrogen atmosphere.

Typical Procedure for Cu Nps-Catalyzed Oxidation of Propargylic Alcohols with TBHP as Oxidant (entry 1, Table 2):

1,3-Diphenyl-2-propyn-1-ol (1a, 0.2 mmol), Cu NPs (1.3 mg, 10 mol%), bipyridine (3.2mg, 10 mol%), 55 μL of TBHP (2.0 equiv, 70% in water), and 1.5 mL of methylene chloride were added into a 20-mL Schlenk tube under air. The mixture was stirred at room temperature for 2 hours. Then, the reaction was stopped, and the reaction mixture was purified by flash column chromatography on silica gel (hexanes/EtOAc 30:1). Compound 2a was obtained in >98 % of yield.

Typical Procedure for Cu Nps-Catalyzed Aerobic Oxidation of Propargylic Alcohols (entry 1, Table 5)

1,3-Diphenyl-2-propyn-1-ol (1a, 0.2 mmol), Cu NPs (1.3 mg, 10 mol%), bipyridine
(3.2mg, 10 mol%) were mixed with 1.5 mL of toluene in a 20-mL Schlenk tube under air. The mixture was stirred at 80 ℃ for 8 hours. Then, the reaction was stopped, and the reaction mixture was purified by flash column chromatography on silica gel (hexanes/EtOAc 30:1). Compound 2a was obtained in 80 % of yield.

**TEM & XRD Images for Cu Nps**

The obtained copper nanoparticles were characterized by transmission electron microscope (TEM), X-ray power diffractometer (XRD). A typical TEM image of copper nanoparticles are shown in Fig. 1. The images (a and b) clearly shows the monodisperse Cu-NPs of different shapes, mainly sphere. The particles are of various sizes.

![TEM Images of Copper Nanoparticles](image1.png)

**Figure 1.** TEM Images of Copper Nanoparticles catalyst.

XRD patterns were shown in Fig.2, in which all of the peaks can be indexed to the phase of Cu (PDF#65-9026). Other diffraction peak 20 degree of 36.4° and 61.4° were indexed to the cubic phase of Cu₂O (PDF#34-1354), which was usually formed during preparation of the test sample.
Characterization for Compounds 2

1,3-Diphenylprop-2-yn-1-one (2a) \(^1\)H NMR (CDCl\(_3\), 300 MHz, ppm) \(\delta\) 8.26-8.22 (m, 2 H), 7.72-7.62 (m, 3 H), 7.56-7.43 (m, 5 H); \(^{13}\)C NMR (CDCl\(_3\), 75 Hz, ppm) \(\delta\) 178.2, 137.0, 134.3, 133.2, 130.9, 129.7, 128.8, 128.7, 120.2, 93.2, 87.0.

1-(2-Bromophenyl)-3-phenylprop-2-yn-1-one (2b) \(^1\)H NMR (CDCl\(_3\), 300 MHz, ppm) \(\delta\) 8.08-8.05 (m, 1 H), 7.72-7.64 (m, 3 H), 7.51-7.36 (m, 5 H). \(^{13}\)C NMR (CDCl\(_3\), 75 MHz, ppm) \(\delta\) 177.7, 137.6, 135.1, 133.5, 133.3, 133.0, 131.2, 128.9, 127.6, 121.4, 120.1, 94.4, 88.1.
1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-one (2c) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 8.16 (d, $J = 8.4$ Hz, 2 H), 7.70-7.76 (m, 2 H), 7.53-7.40 (m, 5 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 176.8, 140.8, 135.4, 133.2, 131.1, 131.0, 129.1, 128.9, 120.0, 93.8, 86.7.

![1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-one (2c)](image)

1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one (2d) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 8.20(d, $J = 9.0$ Hz, 2 H), 7.68 (dd, $J = 1.5$, 8.1 Hz, 2 H), 7.48-7.39 (m, 3 H), 7.01-6.98 (m, 2 H), 3.91 (s, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 176.9, 164.6, 133.1, 132.1, 130.7, 130.4, 128.8, 120.5, 114.0, 92.5, 87.0, 55.8.

![1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-one (2d)](image)

1-(2,5-Dimethoxyphenyl)-3-phenylprop-2-yn-1-one (2e) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 7.65-7.58 (m, 3 H), 7.47-7.38 (m, 3 H), 7.12 (dd, $J = 3.0$, 9.0 Hz, 1 H), 6.98 (d, $J = 9.0$ Hz, 1 H), 3.94 (s, 3 H), 3.84 (s, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 176.4, 154.6, 153.3, 133.2, 130.6, 128.8, 127.1, 121.8, 120.8, 115.6, 114.2, 92.0, 89.5, 56.8, 56.0.

![1-(2,5-Dimethoxyphenyl)-3-phenylprop-2-yn-1-one (2e)](image)

1-(Naphthalen-1-yl)-3-phenylprop-2-yn-1-one (2f) $\delta$ 9.24 (d, $J = 8.7$ Hz, 1 H), 8.66 (d, $J = 6.6$ Hz, 1 H), 8.11 (d, $J = 8.4$ Hz, 1 H), 7.96-7.91 (m, 1 H), 7.72-7.56 (m, 5 H), 7.49-7.43 (m, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 179.9, 135.3, 134.7, 134.0, 133.1, 130.8, 130.0, 129.1, 128.8, 128.1, 126.9, 126.1, 124.6, 124.1, 120.4, 91.8, 88.6.
1-(Naphthalen-2-yl)-3-phenylprop-2-yn-1-one (2g) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 8.81 (s, 1 H), 8.22 (d, $J$ = 8.7 Hz, 1 H), 8.05 (d, $J$ = 8.1 Hz, 1 H), 7.96-7.91 (m, 2 H), 7.75 (d, $J$ = 7.5 Hz, 2 H), 7.67-7.57 (m, 2 H), 7.52-7.44 (m, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 178.1, 136.3, 134.5, 133.2, 132.8, 132.5, 130.9, 130.0, 129.2, 128.8, 128.7, 128.1, 127.1, 124.1, 120.3, 93.2, 87.2.

1-(Furan-2-yl)-3-phenylprop-2-yn-1-one (2h) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 7.70-7.65 (m, 3 H), 7.50-7.40 (m, 4 H), 6.62 (d, $J$ = 1.8 Hz, 1 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 164.9, 153.3, 148.2, 133.2, 131.0, 128.8, 121.1, 120.0, 112.8, 92.1, 86.3.

1-(2-Hydroxyphenyl)-3-phenylprop-2-yn-1-one (2i) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 11.76 (s, 1 H), 8.15-8.12 (m, 1 H), 7.72-7.42 (m, 6 H), 7.02-6.91 (m, 2 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 182.4, 162.9, 137.3, 133.3, 133.1, 131.3, 128.9, 120.9, 119.8, 119.5, 118.3, 96.1, 85.8.

1-(5-Chloro-2-hydroxyphenyl)-3-phenylprop-2-yn-1-one (2j) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 11.68 (s, 1 H), 8.07 (d, $J$ = 2.7 Hz, 1 H), 7.74-7.70 (m, 2 H), 7.55-7.42 (m, 4 H), 6.98 (d, $J$ = 9.0 Hz, 1 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$
181.3, 161.4, 137.1, 133.4, 131.9, 131.6, 129.0, 124.2, 121.4, 120.0, 119.4, 97.2, 85.4.

1-Phenylhept-2-yn-1-one (2k) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 8.15-8.12 (m, 2H), 7.63-7.57 (m, 1 H), 7.51-7.46 (m, 2 H), 2.51 (t, $J = 7.1$ Hz, 2 H), 1.72-1.63 (m, 2 H), 1.55-1.48 (m, 2 H), 0.97 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 178.4, 137.0, 134.0, 129.7, 128.6, 97.0, 79.7, 29.9, 22.2, 19.0, 13.7.

1-(4-Methoxyphenyl)hept-2-yn-1-one (2l) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 8.13-8.09 (m, 2 H), 6.97-6.93 (m, 2 H), 3.88 (s, 3 H), 2.49 (t, $J = 6.9$ Hz, 2 H), 1.70-1.61 (m, 2 H), 1.56-1.46 (m, 2 H), 0.96 (t, $J = 7.4$ Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 177.1, 164.3, 132.0, 130.4, 113.8, 96.1, 79.7, 55.7, 30.0, 22.2, 19.0, 13.6.

(E)-1-Phenylnon-1-en-4-yn-3-one (2m) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 7.82 (d, $J = 16.2$ Hz, 1 H), 7.60-7.56 (m, 2 H), 7.45-7.42 (m, 3 H), 6.78 (d, $J = 16.2$ Hz, 1 H), 2.49 (t, $J = 7.1$ Hz, 2 H), 1.69-1.51 (m, 4 H), 0.98 (t, $J = 7.4$ Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 178.8, 148.3, 134.2, 131.1, 129.1, 128.7, 128.6, 95.3, 79.4, 29.9, 22.2, 18.9, 13.7.

1-Cyclohexyl-3-phenylprop-2-yn-1-one (2n) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 7.60-7.57 (m, 2 H), 7.46-7.36 (m, 3 H), 2.56-2.46 (m, 1 H), 2.09-2.04 (m, 2 H), 1.53-1.44 (m, 3 H), 1.41-1.22 (m, 5 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 191.7,
133.2, 130.7, 128.7, 120.3, 91.5, 87.3, 52.4, 28.4, 25.9, 25.5.

1-Phenylyde-1-yn-3-one (2o) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 7.59-7.56 (m, 2 H), 7.49-7.36 (m, 3 H), 2.67 (t, $J = 7.4$ Hz, 2 H), 1.79-1.70 (m, 2 H), 1.33-1.29 (m, 8 H), 0.91-0.86 (m, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 188.4, 133.1, 130.8, 128.7, 120.2, 90.6, 88.0, 45.7, 31.8, 29.1 (d, $J = 3$ Hz), 24.3, 22.7, 14.2.

1-Cyclohexylhept-2-yn-1-one (2p) $^1$H NMR (CDCl$_3$, 300 MHz, ppm) $\delta$ 2.40-2.35 (m, 2 H), 1.98-1.94 (m, 2 H), 1.79-1.75 (m, 2 H), 1.68-1.25 (m, 11 H), 0.93 (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (CDCl$_3$, 75 MHz, ppm) $\delta$ 191.9, 95.1, 80.3, 52.4, 30.0, 28.4, 26.0, 28.4, 26.0, 25.5, 22.1, 18.8, 13.6.