Electronic Supplementary Information

Palladium-, ligand-, and solvent-free synthesis of ynones by coupling acid chlorides with terminal alkynes in the presence of a reusable copper nanocatalyst

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Experimental details

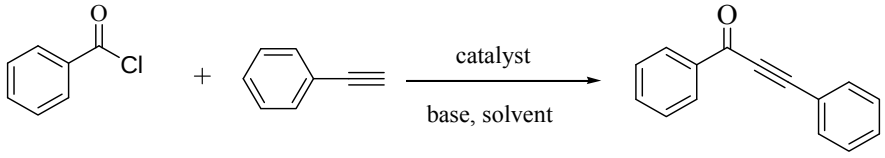
All materials were either purchased from commercial suppliers or synthesized using reported procedures. Amines and acid chlorides were used after redistillation while alkynes were used without purification. Nuclear magnetic resonance (NMR) spectra were recorded at 300 MHz in $CDCl_3$ at 25 °C and were recorded in ppm.

Synthesis of supported copper nanoparticles

$$4Cu(OAc)_2 \cdot H_2O + NaBH_4 + 8KOH \longrightarrow 4Cu + 8KOAc + NaBO_2 + 10H_2O$$

To a three-necked flask containing aqueous cupric acetate (0.025 M, 40 mL), polyvinylpyrrolidone (PVP, 200.0 mg), supporter (640 mg) and a stir-bar, 80 mL of aqueous solution containing sodium borohydride (151.5 mg, 4 mmol) and potassium hydroxide (224.4 mg, 4 mmol) was added dropwise over a period of 10 minutes. The reaction mixture was heated at 40 °C with vigorous stirring. The transparent solution was converted into the characteristic black color, which indicated the formation of copper nanoparticles. After about 5 hours, black precipitate was obtained. Then the precipitate was washed three times with distilled water (10 mL) and separated by centrifugation (11000 r•min^{-1}), and dried *in vacuo* at 80 °C for 12 h.

General procedure for screening reaction conditions

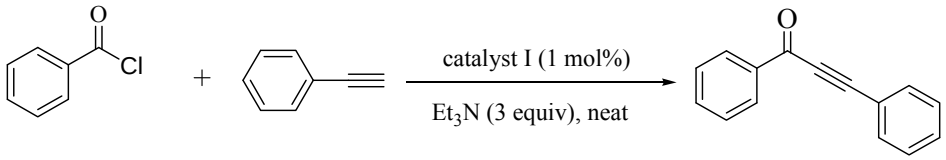


A oven-dried reaction tube was charged with catalyst, phenylacetylene (55 μL, 0.5 mmol), benzoyl chloride (87 μL, 0.75 mmol), base and solvent. The tube was sealed under nitrogen and was heated at 40 °C overnight. Then the reaction mixture was cooled and extracted with ethyl ether (3 × 10 mL). The yield of ynones were determined by GC analysis using dimethyl phthalate as an internal standard.

Typical procedure for the synthesis of ynone 3a

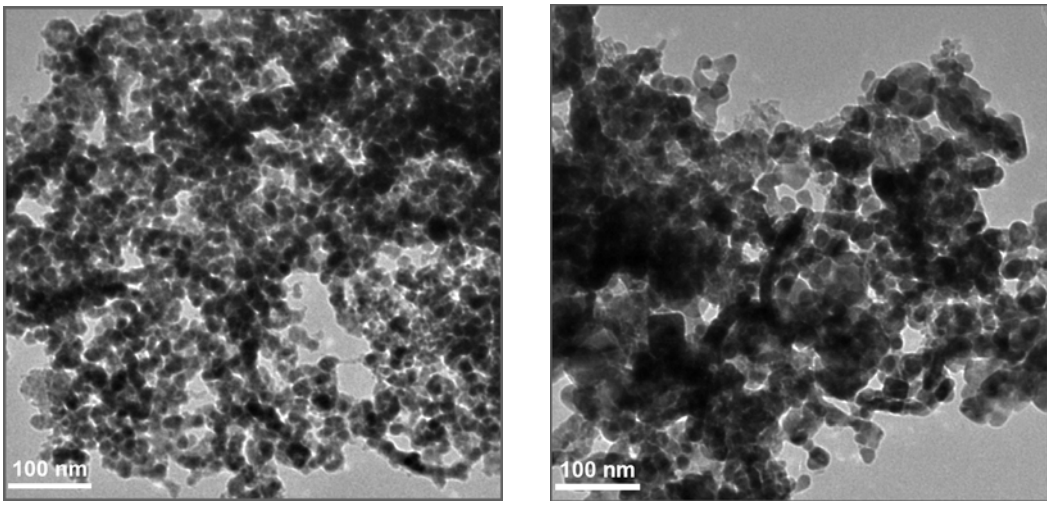
A oven-dried reaction tube was charged with catalyst I (silica gel supported copper nanoparticles) (3.2 mg, 1 mol%), phenylacetylene (55 μL, 0.5 mmol), benzoyl chloride (87 μL, 0.75 mmol), triethylamine (208 μL, 1.5 mmol). The tube was sealed under nitrogen and was heated at 40 °C overnight. Then the reaction mixture was cooled and extracted with ethyl ether (3 × 10 mL). and concentrated in *vacuo.* The residue was purified by flash column chromatography on silica gel (hexane : ethyl acetate = 15:1) to give the pure product. The product was characterized by ^{1}H NMR and ^{13}C NMR.

Typical procedure for the recycling of the catalyst I



The reaction procedure was conducted as described above. After completion, the catalyst was separated by filtration, and the filtrate was followed by centrifugation. The two parts of residue were combined, dried and reused in the same reaction under identical conditions.

Characterization for nanocatalysts

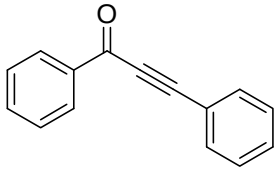


a) **b)**

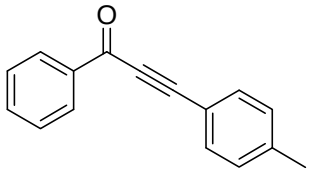
Figure 1 The TEM image of supported copper nanoparticles:

a) Cu-NPs/silica gel; b) Cu-NPs/γ-Al_2O_3

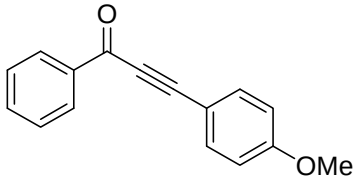
Characterization for ynones: (all of the ynones are known compounds)



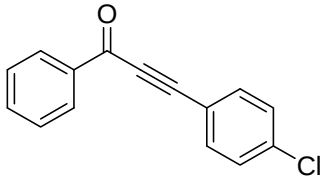
1,3-diphenylprop-2-yn-1-one (3a) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25-8.22 (m, 2 H), 7.70-7.61 (m, 3 H), 7.55-7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 178.2, 137.0, 134.3, 133.2, 130.9, 129.7, 128.8, 128.8, 120.2, 93.2, 87.0.



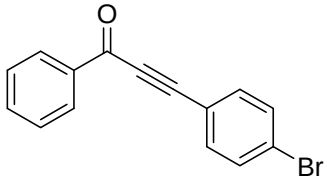
1-phenyl-3-p-tolylprop-2-yn-1-one (3b) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25-8.22 (m, 2 H), 7.66-7.50 (m, 5 H), 7.24 (d, *J* = 7.8 Hz, 2 H), 2.42 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 178.2, 141.7, 137.2, 134.2, 133.3, 129.7, 129.7, 128.8, 117.2, 94.0, 87.0, 21.9.



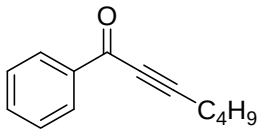
3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (3c) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24-8.21 (m, 2 H), 7.67-7.60 (m, 3 H), 7.52 (t, *J* = 7.5 Hz, 2 H), 6.95 (d, *J* = 8.7 Hz, 2 H), 3.87 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 178.2, 161.9, 137.2, 135.3, 134.0, 129.6, 128.7, 114.6, 112.1, 94.5, 87.0, 55.6.



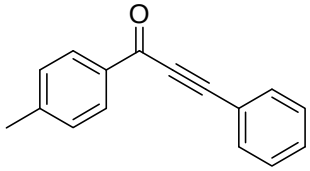
3-(4-chlorophenyl)-1-phenylprop-2-yn-1-one (3d) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (d, *J* = 7.2 Hz, 2 H), 7.66-7.51 (m, 7 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 178.0, 137.4, 136.9, 134.4, 129.7, 129.3, 128.8, 118.8, 91.8, 87.7.



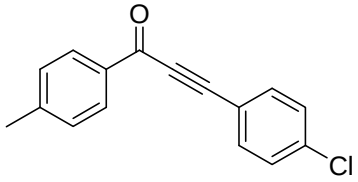
3-(4-bromophenyl)-1-phenylprop-2-yn-1-one (3e) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (m, 2 H), 7.66-7.51 (m, 7 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 177.9, 136.9, 134.4, 134.4, 132.3, 129.7, 128.8, 125.8, 119.2, 91.8, 87.8.



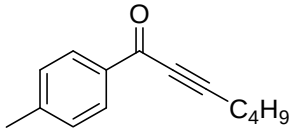
1-phenylhept-2-yn-1-one (3f) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16-8.13 (m, 2 H), 7.61-7.46 (m, 3 H), 2.52 (t, *J* = 7.2 Hz, 2 H), 1.71-1.48 (m, 4 H), 0.98 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 178.4, 137.0, 134.0, 129.7, 128.6, 97.0, 79.7, 29.9, 22.2, 19.0, 13.6



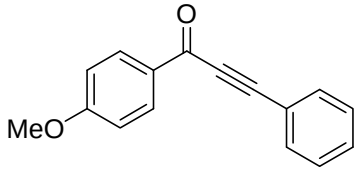
3-phenyl-1-p-tolylprop-2-yn-1-one (3g) ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 8.14 (d, *J* = 8.1 Hz, 2 H), 7.70 (d, *J* = 6.9 Hz, 2 H), 7.51-7.31 (m, 5 H), 2.46 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 177.9, 145.4, 134.8, 133.2, 130.8, 129.9, 129.5, 128.8, 120.4, 92.8, 87.1, 22.0.



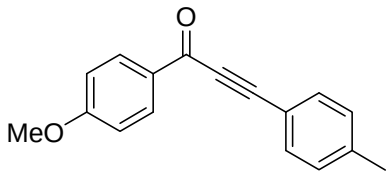
3-(4-chlorophenyl)-1-p-tolylprop-2-yn-1-one (3h) ^{1}H NMR ($CDCl_3$, 300 MHz, ppm) δ 8.11 (d, *J* = 8.1 Hz, 2 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.7 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 2.47 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 177.6, 145.6, 137.2, 134.6, 134.3, 129.9, 129.5, 129.3, 118.9, 91.2, 87.8, 22.0.



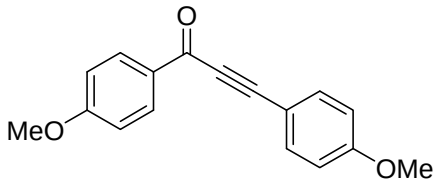
1-p-tolylhept-2-yn-1-one (3i) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 7.8 Hz, 2 H), 2.50 (t, *J* = 6.9 Hz, 2 H), 2.43 (s, 3 H), 1.70-1.47 (m, 4 H), 0.97 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 178.1, 145.0, 134.8, 129.8, 129.3, 96.4, 79.9, 30.0, 22.2, 21.9, 19.0, 13.6.



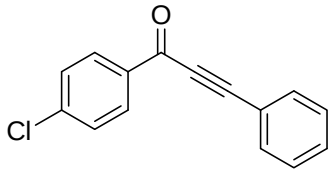
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (3j) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, *J* = 9.0 Hz, 2 H), 7.68 (d, *J* = 6.6 Hz, 2 H), 7.49-7.40 (m, 3 H), 7.00 (d, *J* = 8.7 Hz, 2 H), 3.91 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 176.9, 164.6, 133.1, 132.1, 130.7, 130.4, 128.8, 120.5, 114.0, 92.5, 87.0, 55.8.



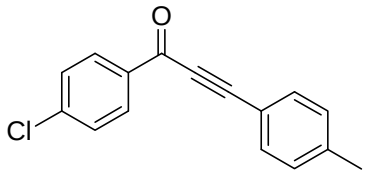
1-(4-methoxyphenyl)-3-p-tolylprop-2-yn-1-one (3k) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.7 Hz, 2 H), 7.57 (d, *J* = 8.1 Hz, 2 H), 7.22 (d, *J* = 8.1 Hz, 2 H), 6.99 (d, *J* = 9.0 Hz, 2 H), 3.90 (s, 3 H), 2.41 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 176.9, 164.6, 141.4, 133.1, 132.1, 130.6, 129.6, 117.4, 114.0, 93.1, 86.9, 55.7, 21.9.



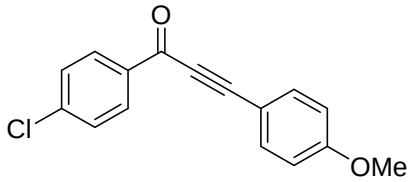
1,3-bis(4-methoxyphenyl)prop-2-yn-1-one (3l) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.7 Hz, 2 H), 7.64 (d, *J* = 8.7 Hz, 2 H), 6.99 (d, *J* = 8.7 Hz, 2 H), 6.94 (d, *J* = 8.7 Hz, 2 H), 3.91 (s, 3 H), 3.87 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 176.9, 164.5, 161.7, 135.1, 132.0, 130.6, 114.5, 114.3, 114.0, 93.6, 86.9, 55.7, 55.6.



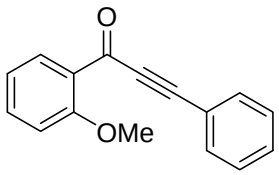
1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one (3m) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 2 H), 7.71-7.67 (m, 2 H), 7.53-7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 176.8, 140.8, 135.4, 133.2, 131.1, 131.0, 129.1, 128.9, 120.0, 93.8, 86.7.



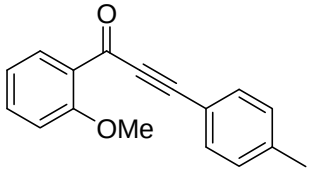
1-(4-chlorophenyl)-3-p-tolylprop-2-yn-1-one (3n) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18-8.12 (m, 2 H), 7.58 (d, *J* = 8.1 Hz, 2 H), 7.51-7.46 (m, 2 H), 7.24 (d, *J* = 7.8 Hz, 2 H), 2.40 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 176.9, 142.0, 140.7, 135.6, 133.3, 131.0, 129.7, 129.1, 116.9, 94.5, 86.7, 21.9.



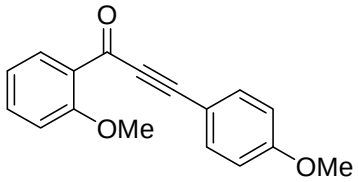
1-(4-chlorophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one (3o) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.7 Hz, 2 H), 7.65 (d, *J* = 8.7 Hz, 2 H), 7.50 (d, *J* = 8.7 Hz, 2 H), 6.95 (d, *J* = 8.7 Hz, 2 H), 3.88 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 172.4, 162.0, 140.6, 135.6, 135.4, 130.9, 129.1, 114.6, 111.8, 95.0, 86.8, 55.6.



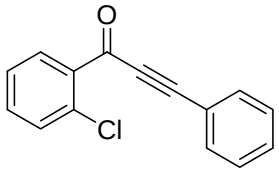
1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one (3p) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (dd, *J* = 8.4, 1.5 Hz, 1 H), 7.66-7.52 (m, 3 H), 7.47-7.37 (m, 3 H), 7.10-7.02 (m, 2 H), 3.96 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 176.9, 160.0, 135.2, 133.1, 132.8, 130.6, 128.7, 126.9, 120.9, 120.5, 112.4, 91.7, 89.4, 56.1.



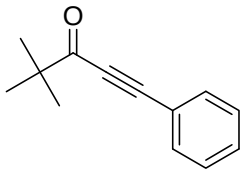
1-(2-methoxyphenyl)-3-p-tolylprop-2-yn-1-one (3r) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (dd, *J* = 7.8, 1.8 Hz, 1 H), 7.56-7.49 (m, 3 H), 7.19 (d, *J* = 7.8 Hz, 2 H), 7.07-6.99 (m, 2 H), 3.95 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 177.0, 159.9, 141.3, 135.0, 133.2, 132.7, 129.6, 127.0, 120.5, 117.7, 112.4, 92.4, 89.3, 56.1, 21.9.



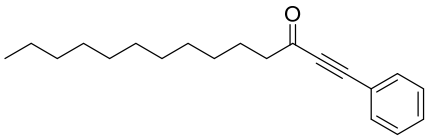
1-(2-methoxyphenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one (3r) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 7.5, 1.5 Hz, 1 H), 7.61-7.49 (m, 3 H), 7.07-6.99 (m, 2 H), 6.93-6.86 (m, 2 H), 3.96 (s, 3 H), 3.83 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 176.9, 161.6, 159.8, 135.1, 134.9, 132.6, 127.1, 120.4, 114.5, 112.6, 112.4, 92.9, 89.3, 56.1, 55.5.



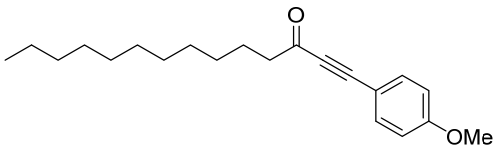
1-(2-chlorophenyl)-3-phenylprop-2-yn-1-one (3s) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.2 Hz, 1 H), 7.67-7.63 (m, 2 H), 7.52-7.38 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 176.9, 136.0, 133.7, 133.6, 133.2, 132.7, 131.7, 131.1, 128.8, 127.0, 120.2, 94.1, 88.5.



4,4-dimethyl-1-phenylpent-1-yn-3-one (3t) ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61-7.57 (m, 2 H), 7.50-7.36 (m, 3 H), 1.30 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 194.4, 133.1, 130.7, 128.7, 120.4, 92.4, 86.1, 45.0, 26.3.



1-phenyltetradec-1-yn-3-one (3u) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.45 (m, 2H), 7.42-7.29 (m, 3H), 2.38 (t, *J* =7.4 Hz, 2H), 1.57-1.54 (m, 2H), 1.25 (w, 16H), 0.88 (t, *J* =6.7 Hz, 3H). ^{13}CNMR(100MHz, $CDCl_3$): δ 211.80, 132.51, 129.21, 128.44, 121.82, 81.54, 73.81, 42.83, 31.91, 29.61, 29.49, 29.43, 29.34, 29.29, 22.69, 14.11.



1-(4-methoxyphenyl)tetradec-1-yn-3-one (3v) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35(d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.73 (s,3H), 2.39-1.98 (m,2H), 1.18 (w, 16H), 0.80 (t, *J* =6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.95, 133.59 ,133.19, 114.19, 113.94, 83.67, 75.78, 55.27, 34.12, 31.93, 29.63, 29.51, 29.35, 29.29, 29.12, 22.70, 14.12.