Electronic Supplementary Information

A facile and rapid route for the synthesis of Cu/Cu$_2$O nanoparticles and its application in Sonogashira coupling reaction of acyl chlorides with terminal alkynes

Manohar A. Bhosale,$^a$ Takehiko Sasaki$^b$ and Bhalchandra M. Bhanage$^a$*

$^a$ Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai 400019, India.
$^b$ Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8561, Japan.

Table of contents

1. General Information 2
2. General reaction scheme and experimental procedure for the reaction 2
3. Characterization of Cu/Cu$_2$O nanocatalyst 3
4. GC-MS Data for Products 7

*Corresponding author Tel.: +91 22 3361 2601; fax: +91 22 3361 1020;
E-mail: bm.bhanage@ictmumbai.edu.in, bm.bhanage@gmail.com (Prof. B. M. Bhanage).
1) General information

All chemicals and reagents were purchased from commercial suppliers and used as received without further purification. The reaction progress was monitored by gas chromatograph (Perkin Elmer Clarus 400 GC) equipped with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). GC-MS analysis was performed with a Shimadzu GCMS-QP 2010 instrument (Rtx-17, 30 m × 25mmID, film thickness 0.25 μm df) (column flow- 2 mL/min, 80 °C to 240 °C at 10°/min rise.

2) General reaction scheme and experimental procedure for the reaction

\[
\text{R'OCl} + \text{H} \equiv \text{R'} \xrightarrow{\text{Nano Cu/Cu}_2\text{O}} \text{R'O} \equiv \text{R'}
\]

Typical experimental procedure for reaction:- In a 25 mL seal tube containing a magnetic stir bar was charged with alkynes (1 mmol) and acyl chlorides (1.2 mmol), Cu/Cu$_2$O NMPs (0.1 mmol, 10 mol%) as nanocatalyst, Et$_3$N (2 mmol) as base and toluene (2 mL) as solvent under N$_2$ atmosphere. The reaction mixture was stirred for 24 h at 90 °C. After completion of the reaction, the reaction mixture was poured into 15 ml water and the product was extracted with ethyl acetate (3 × 10 mL). The reaction solvent was dried over Na$_2$SO$_4$ and evaporated under vacuum. All products are well known in the literature and were confirmed by GC-MS analysis by the comparison with those of literature data.
3) Characterization of Cu/Cu$_2$O nanocatalyst

**Figure S1** The FEG-SEM images of Cu/Cu$_2$O nanoparticles.

**Figure S2** The TEM images of Cu/Cu$_2$O nanoparticles.
Fig. S3 FEG-SEM image shows the particle size of Cu/Cu$_2$O NPs is in range of 70 nm to 110 nm.
Fig. S4 FEG-SEM images and EDS spectrum of Cu/Cu$_2$O NPs by microwave irradiation for 4 min.
Fig. S5 FEG-SEM images and EDS spectrum of Cu/Cu$_2$O NPs by microwave irradiation for 6 min.
4) GC-MS data for products

1,3-diphenylprop-2-yn-1-one (Table 2, Entry 1)

The title compound was synthesized according to the general experimental procedure from phenylacetylene (102 mg, 1 mmol), Cu/Cu$_2$O NPs (14.3 mg, 10 mol%), Et$_3$N (202 mg, 2 mmol) and benzoyl chloride (168 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) $t_R = 13.0$ min; m/z (%) = 206 (78.1) [M$^+$], 178 (97.2), 152 (10.5), 129 (100), 101 (14.5), 89 (15.2), 77 (21), 75 (24.7), 63 (4.2), 51 (21.6).
1-phenyl-3-(p-tolyl)prop-2-yn-1-one (Table 2, Entry 2)

The title compound was synthesized according to the general experimental procedure from 4-Ethynyltoluene (116 mg, 1 mmol), Cu/Cu$_2$O NPs (14.3 mg, 10 mol%), Et$_3$N (202 mg, 2 mmol) and benzoyl chloride (168 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) $t_R = 14.3$ min; m/z (%) = 220 (85.3) [M$^+$], 192 (67), 165 (9.3), 143 (100), 115 (17.5), 94 (6.5), 89 (14.7), 77 (17.4), 63 (9.2), 51 (13).
1-phenyl-3-(m-tolyl)prop-2-yln-1-one (Table 2, Entry 3)

The title compound was synthesized according to the general experimental procedure from 3-Ethynyltoluene (116 mg, 1 mmol), Cu/Cu$_2$O NPs (14.3 mg, 10 mol%), Et$_3$N (202 mg, 2 mmol) and benzoyl chloride (168 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) $t_R = 14.3$ min; m/z (%) = 220 (31.6) [M$^+$], 105 (100), 89 (3.2), 77 (49.7), 51 (10.5), 44 (5).
3-(3-hydroxyphenyl)-1-phenylprop-2-yn-1-one (Table 2, Entry 4)

The title compound was synthesized according to the general experimental procedure from 3-ethynylphenol (118 mg, 1 mmol), Cu/Cu$_2$O NPs (14.3 mg, 10 mol%), Et$_3$N (202 mg, 2 mmol) and benzoyl chloride (168 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) \( t_R = 12.25 \) min; \( m/z \) (%) = 222 (8) [M$^+$], 105 (100), 89 (2.5), 77 (42.4), 63 (3.5), 51 (10.7).
3-(2-aminophenyl)-1-phenylprop-2-yn-1-one (Table 2, Entry 5)

The title compound was synthesized according to the general experimental procedure from 2-ethynylaniline (117 mg, 1 mmol), Cu/Cu$_2$O NPs (14.3 mg, 10 mol%), Et$_3$N (202 mg, 2 mmol) and benzoyl chloride (168 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) $t_R =$ 13.7 min; m/z (%) = 221 (8) [M$^+$], 193 (72.2), 165 (3.2), 152 (7), 118 (6.7), 105 (8.7), 89 (16.4), 77 (24), 50 (16.4), 44 (11.2).
3-(3-aminophenyl)-1-phenylprop-2-yn-1-one (Table 2, Entry 6)

The title compound was synthesized according to the general experimental procedure from 3-ethynylaniline (117 mg, 1 mmol), Cu/Cu₂O NPs (14.3 mg, 10 mol%), Et₃N (202 mg, 2 mmol) and 2-methoxybenzoyl chloride (204 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) \( t_R = 16.6 \text{ min} \); m/z (%) = 221 (31.4) [M⁺], 105 (100), 89 (4), 77 (51.6), 51 (11.2), 44 (9.6).
3-(4-aminophenyl)-1-phenylprop-2-yn-1-one (Table 2, Entry 7)

The title compound was synthesized according to the general experimental procedure from 4-ethynylaniline (117 mg, 1 mmol), Cu/Cu₂O NPs (14.3 mg, 10 mol%), Et₃N (202 mg, 2 mmol) and benzoyl chloride (168 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) tᵣ = 17.2 min; m/z (%) = 221 (30.4) [M⁺], 207 (32.8), 122 (7.1), 105 (100), 77 (58.6), 51 (14), 40 (5).
3-cyclohexyl-1-phenylprop-2-yn-1-one (Table 2, Entry 8)

The title compound was synthesized according to the general experimental procedure from cyclohexylacetylene (108 mg, 1 mmol), Cu/Cu$_2$O NPs (14.3 mg, 10 mol%), Et$_3$N (202 mg, 2 mmol) and benzoyl chloride (168 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) $t_R$ = 12.3 min; m/z (%) = 212 (3) [M$^+$], 183 (13.5), 165 (3.2), 144 (100), 141 (14.3), 128 (11.3), 115 (10), 105 (76.1), 91 (11.9), 77 (45.6), 51 (13.2), 40 (28.2).
3-cyclopropyl-1-phenylprop-2-yn-1-one (Table 2, Entry 9)

![Chemical Structure](image)

The title compound was synthesized according to the general experimental procedure from cyclopropylacetylene (66 mg, 1 mmol), Cu/Cu₂O NPs (14.3 mg, 10 mol%), Et₃N (202 mg, 2 mmol) and benzoyl chloride (168 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) \( t_R = 9.5 \text{ min} \); m/z (%) = 170 (76.4) [M⁺], 141 (100), 122 (16.5), 115 (34.5), 105 (48.3), 93 (62.5), 77 (71.8), 65 (39), 51 (38.3).
3-phenyl-1-(p-tolyl)prop-2-yn-1-one (Table 2, Entry 10)

The title compound was synthesized according to the general experimental procedure from phenylacetylene (102 mg, 1 mmol), Cu/Cu$_2$O NPs (14.3 mg, 10 mol%), Et$_3$N (202 mg, 2 mmol) and 3-methyl benzoyl chloride (185 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) $t_R = 14.3$ min; $m/z$ (%) = 220 (78.8) [M$^+$], 205 (10.5), 192 (100), 165 (12.3), 129 (76.3), 101 (13), 91 (17.5), 75 (20), 65 (14.7), 51 (11).
1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one (Table 2, Entry 11)

The title compound was synthesized according to the general experimental procedure from phenylacetylene (102 mg, 1 mmol), Cu/Cu$_2$O NPs (14.3 mg, 10 mol%), Et$_3$N (202 mg, 2 mmol) and 2-methoxybenzoyl chloride (204 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) $t_R = 15.6$ min; m/z (%) = 236 (39.1) [M$^+$], 235 (100), 207 (58.3), 189 (8.6), 178 (19.3), 165 (20.8), 129 (67.6), 115 (34.4), 105 (36.1), 92 (14.7), 77 (35.5), 51 (18.2), 44 (16.5).
1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one (Table 2, Entry 12)

The title compound was synthesized according to the general experimental procedure from phenylacetylene (102 mg, 1 mmol), Cu/Cu\(_2\)O NPs (14.3 mg, 10 mol%), Et\(_3\)N (202 mg, 2 mmol) and 4-Chlorobenzoyl chloride (210 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) \(t_R = 14.6\) min; m/z (%) = 240 (54.2) [M\(^+\)], 212 (77.7), 176 (21.3), 129 (100), 101 (13.6), 88 (10.2), 75 (35.6), 51 (11.2).
1-(2-chlorophenyl)-3-phenylprop-2-yne-1-one (Table 2, Entry 13)

The title compound was synthesized according to the general experimental procedure from phenylacetylene (102 mg, 1 mmol), Cu/Cu₂O NPs (14.3 mg, 10 mol%), Et₃N (202 mg, 2 mmol) and 2-Chlorobenzoyl chloride (210 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) tᵣ = 14.8 min; m/z (%) = 240 (54.2) [M⁺], 212 (77.7), 176 (20), 151 (6.2), 129 (100), 101 (14.4), 88 (10.2), 75 (33), 51 (11.4).
The title compound was synthesized according to the general experimental procedure from phenylacetylene (102 mg, 1 mmol), Cu/Cu$_2$O NPs (14.3 mg, 10 mol%), Et$_3$N (202 mg, 2 mmol) and 2-naphthoyl chloride (228 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) $t_R = 22.0$ min; m/z (%) = 240 (54.2) [M$^+$/], 212 (77.7), 176 (20), 151 (6.2), 129 (100), 101 (14.4), 88 (10.2), 75 (33), 51 (11.4).
1-cyclopentyl-3-phenylprop-2-yn-1-one (Table 2, Entry 15)

The title compound was synthesized according to the general experimental procedure from phenylacetylene (102 mg, 1 mmol), Cu/Cu$_2$O NPs (14.3 mg, 10 mol%), Et$_3$N (202 mg, 2 mmol) and cyclopentanecarbonyl chloride (260.2 mg, 1.2 mmol) with toluene (2 ml) as solvent. The reaction product was confirmed by GC-MS analysis.

GC-MS (EI, 70 eV) $t_R = 14.6$ min; m/z (%) = 199 (33) [M$^+$], 170 (16.4), 143 (10), 129 (100), 102 (20.2), 75 (19.2), 70 (12), 51 (8.3).