Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 829–831

Synthesis of propargylamines catalyzed by *in situ* generated copper nanoparticles in water

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Contents

General Experimental

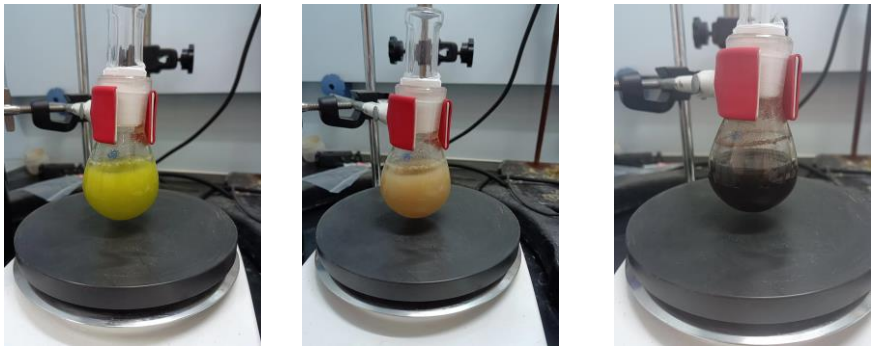
Unless otherwise noted, all chemicals were purchased from commercial suppliers (Aladdin) and used without further purification. ^{1}H NMR were recorded in $CDCl_3$ at ambient temperature on a 400 MHz NMR spectrometer. Liquid chromatography-mass spectrometry (LC-MS) was performed on a Shimadzu LCMS-2020 instrument with an electrospray ionization (ESI) source. X-ray diffraction (XRD) patterns were collected on a SHIMADZU XRD-6000 diffractometer with Cu Kα radiation at 40 kV and 30 mA in the range 5−80° at a scanning rate of 6 min^{-1}. Field-emission Scanning Electron Microscopy (SEM) images of the samples were taken at 30 kV with a ZEISS Supra 55 microscope. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

Experimental Procedure

*General procedure for the synthesis of **4a~l***

In an oven dried round bottom flask, aldehyde **1** (1.0 mmol), amine **2** (1.2 mmol) and alkyne **3** (1.5 mmol) were added to a mixture of $CuSO_4$•$5H_2O$ (25.0 mg, 0.1 mmol), rongalite (77 mg, 0.5 mmol), and *β*-CD (23 mg, 0.02 mmol) in H_2O (2 ml). The mixture was stirred at 80 °C for 6 h. After reaction, the mixture was extracted with ethyl acetate (3 x 10 ml). The organic layer was dried over Na_2SO_4 and concentrated

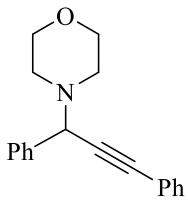
under reduced pressure. The crude products were purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1, *v*/*v*) as eluent. to afford product **4a~l**. **All the products are known compounds and were identified by comparing of their physical and spectra data with those reported in the literature.**



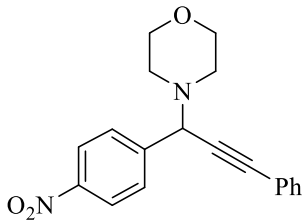
(a) 0 min (b) 10 mins (c) 30 mins

Figure S1. Color change.

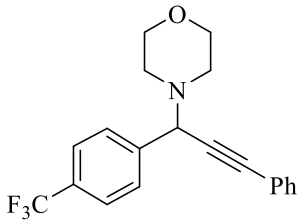
Characterization data



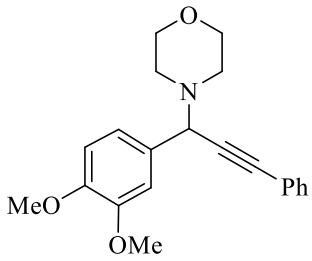
4-(1,3-Diphenylprop-2-yn-1-yl)morpholine **4a**.[S1] Yellow oil (274 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62 (d, J = 7.4 Hz, 2H), 7.55 (dd, J = 5.9, 3.0 Hz, 2H), 7.49-7.30 (m, 6H), 4.79 (s, 1H), 3.85-3.69 (m, 4H), 2.66-2.57 (m, 4H). MS (ESI): 278.4 $[M + H]^+$.



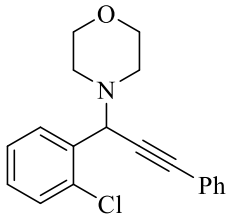
4-(1-(4-Nitrophenyl)-3-phenylprop-2-yn-1-yl)morpholine **4b**.[S3] Yellow oil (277 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21-8.17 (m, 2H), 7.87-7.85 (m, 2H), 7.54-7.53 (m, 2H), 7.36-7.34 (m, 3H), 4.88 (s, 1H), 3.71-3.64 (m, 4H), 2.66-2.61 (m, 4H). MS (ESI): 323.1 $[M + H]^+$.



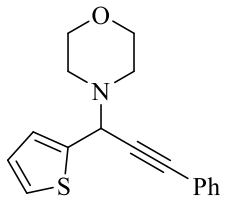
4-(3-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)morpholine **4c**.[S4] Yellow oil (289 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79-7.77 (m, 2H), 7.63-7.51 (m, 3H), 7.35-7.24 (m, 4H), 4.83 (s, 1H), 3.81-3.72 (m, 4H), 2.67 (t, J＝4.7 Hz, 4H). MS (ESI): 346.1 $[M + H]^+$.



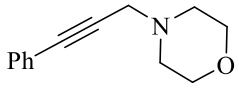
4-(1-(3,4-Dimethoxyphenyl)-3-phenylprop-2-yn-1-yl)morpholine **4d**.[S5] Yellow oil (273 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.49 (m, 2H), 7.45-7.40 (m, 3H), 7.30-7.22 (m, 2H), 6.94-6.83 (m, 1H), 4.72 (s, 1H), 3.94-3.84 (m, 6H), 3.76 (td, J＝5.2, 2.4 Hz, 4H), 2.67-2.58 (m, 4H). MS (ESI): 338.2 $[M + H]^+$.



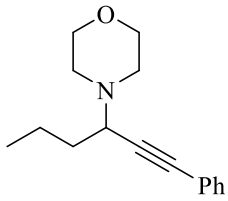
4-(1-(2-Chlorophenyl)-3-phenylprop-2-yn-1-yl)morpholine **4e**.[S6] Yellow oil (233 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67-7.66 (m, 1H), 7.41 (ddt, J = 5.6, 3.0, 1.6 Hz, 2H), 7.31-7.29 (m, 1H), 7.23 (ddt, J = 5.9, 4.2, 2.3 Hz, 3H), 7.20-7.13 (m, 2H), 5.03 (s, 1H), 3.64 (q, J = 4.6 Hz, 4H), 2.59 (t, J = 4.7 Hz, 4H). MS (ESI): 312.8 $[M + H]^+$.



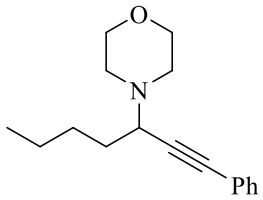
4-(3-Phenyl-1-(thiophen-2-yl)prop-2-yn-1-yl)morpholine **4f**.[S7] Yellow oil (232 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.53 (m, 2H), 7.38-7.37 (m, 3H), 7.10 (d, J = 4.8 Hz, 1H), 7.31-7.27 (m, 1H), 7.01 (d, J = 7.1 Hz, 1H), 5.03 (s, 1H), 3.83-3.77 (m, 4H), 2.67 (t, J = 6.8 Hz, 4H). MS (ESI): 284.4 $[M + H]^+$.



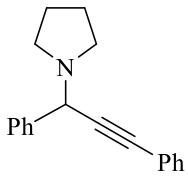
4-(3-Phenylprop-2-yn-1-yl)morpholine **4g**.[S5] Yellow oil (199 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (ddd, J = 6.7, 3.4, 1.6 Hz, 2H), 7.17 (dt, J = 5.0, 1.6 Hz, 3H), 3.68-3.66 (m, 4H), 3.41 (s, 2H), 2.55-2.53 (m, 4H). MS (ESI): 202.3 $[M + H]^+$.



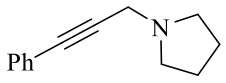
4-(1-Phenylhex-1-yn-3-yl)morpholine **4h**.[S6] Yellow oil (233 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43-7.42 (m, 2H), 7.28-7.27 (m, 3H), 3.79-3.70 (m, 4H), 3.45 (dd, J = 8.4, 6.3 Hz, 1H), 2.56 (dddd, J = 53.0, 11.3, 6.0, 3.7 Hz, 4H), 1.72-1.44 (m, 4H), 0.97 (t, J = 7.2 Hz, 3H). MS (ESI): 244.4 $[M + H]^+$.



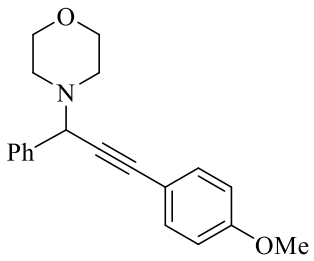
4-(1-Phenylhept-1-yn-3-yl)morpholine **4i**.[S5] Yellow oil (236 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.42 (m, 2H), 7.28 (d, J = 2.6 Hz, 3H), 3.79-3.70 (m, 4H), 3.51 (t, J = 7.4 Hz, 1H), 2.72 (dddd, J = 53.4, 11.4, 6.0, 3.6 Hz, 4H), 1.73-1.64 (m, 2H), 1.46-1.30 (m, 4H), 0.95 (d, J = 7.1 Hz, 3H). MS (ESI): 258.4 $[M + H]^+$.



1-(1,3-Diphenylprop-2-yn-1-yl)pyrrolidine **4j**.[S2] Yellow oil (248 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, J = 7.6 Hz, 2H), 7.51-7.45 (m, 2H), 7.45 (m, 2H), 7.37 (*t*, J = 7.4 Hz, 2H), 7.33-7.27 (m, 4H), 4.89 (s, 1H), 2.73-2.67 (m, 4H), 1.83-1.76 (m, 4H). MS (ESI): 262.2 $[M + H]^+$.



1-(3-Phenylprop-2-yn-1-yl)pyrrolidine **4k**.[S1] Yellow oil (177 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.32 (m, 2H), 7.20-7.18 (m, 3H), 3.54 (s, 2H), 2.61 (t, J = 6.8 Hz, 4H), 1.76-1.72 (m, 4H). MS (ESI): 186.3 $[M + H]^+$.



4-(3-(4-Methoxyphenyl)-1-phenylprop-2-ynyl)morpholine **4l**.[S8] Yellow oil (276 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64-7.61 (m, 2H), 7.46-7.43 (m, 2H), 7.37-7.32 (m, 3H) , 6.87-6.84 (m, 2H), 4.77 (s, 1H), 3.82 (s, 3H), 3.75-3.72 (m, 4H), 2.64-2.61 (m, 4H). MS (ESI): 308.4 $[M + H]^+$.

References

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Characterization of the CuNPs

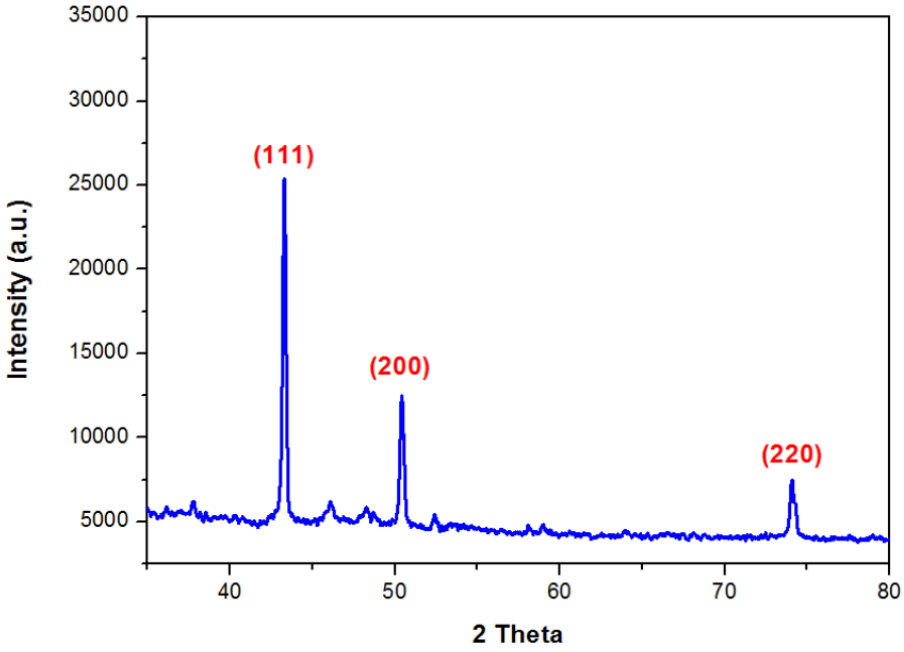


Figure S2. XRD pattern of synthesized CuNPs

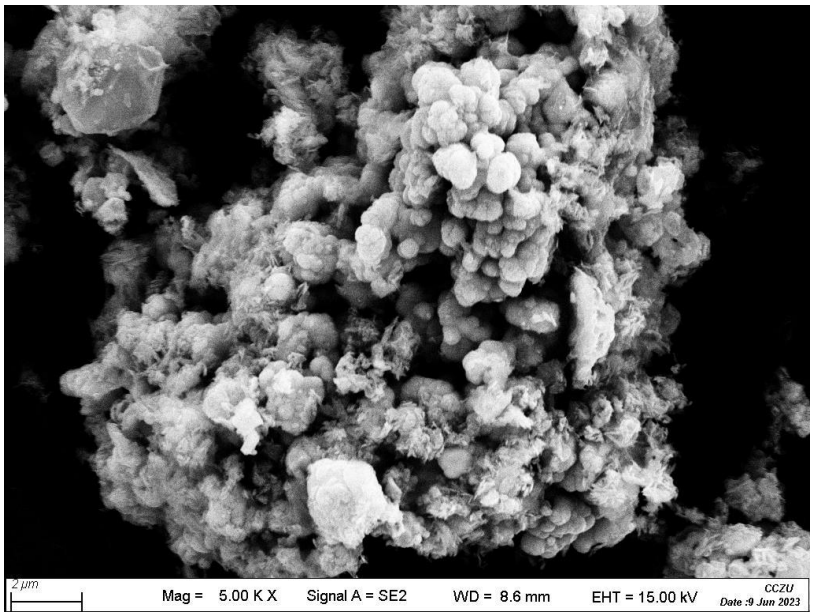


Figure S3. SEM image (2 µm scale)

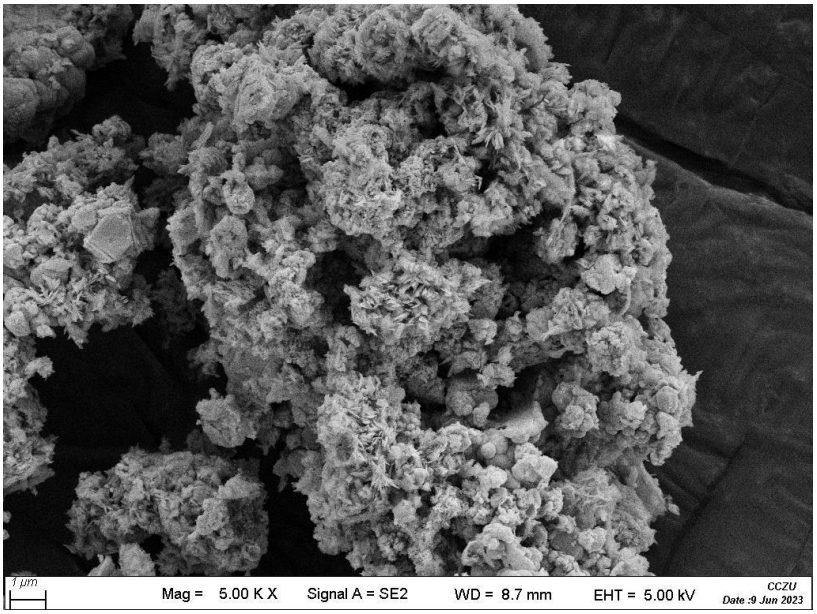


Figure S4. SEM image (1 µm scale)

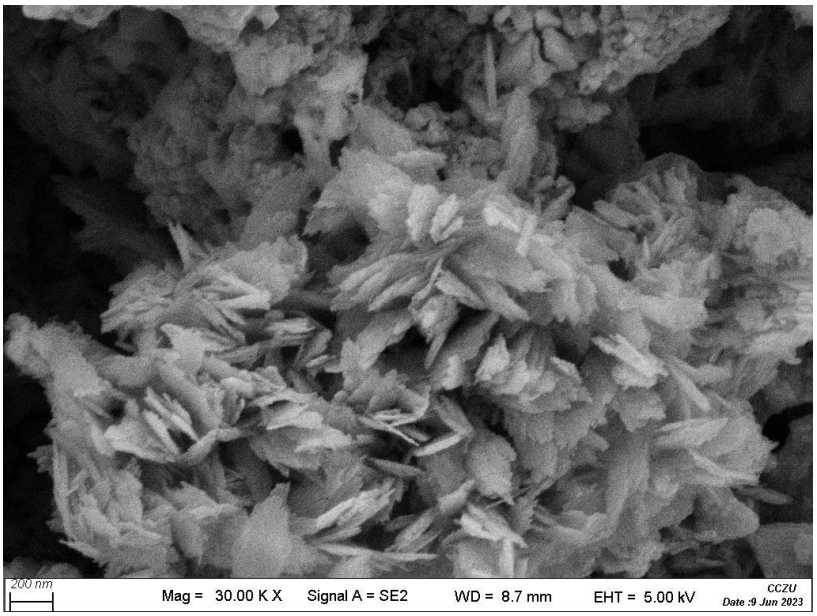
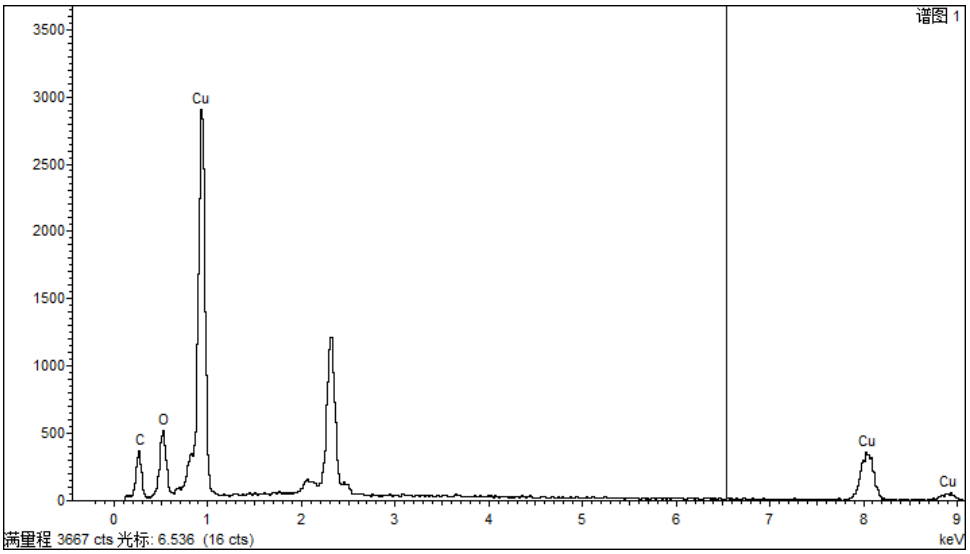
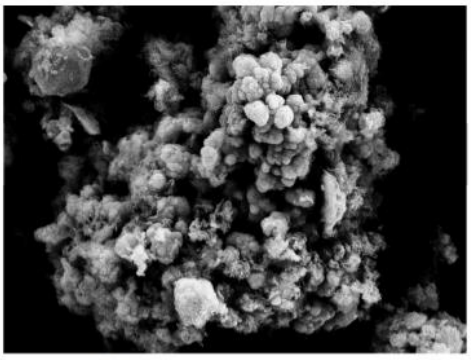
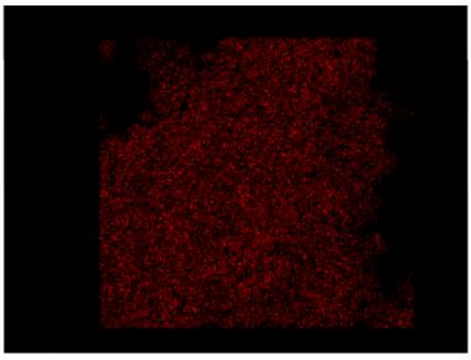


Figure S5. SEM image (200 nm scale)

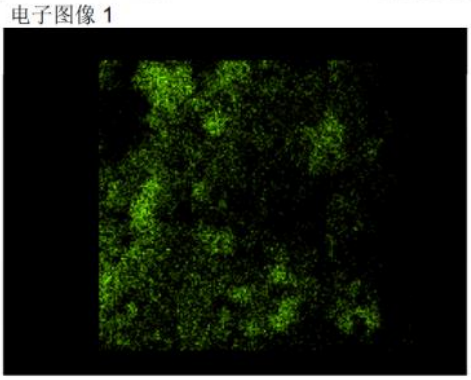




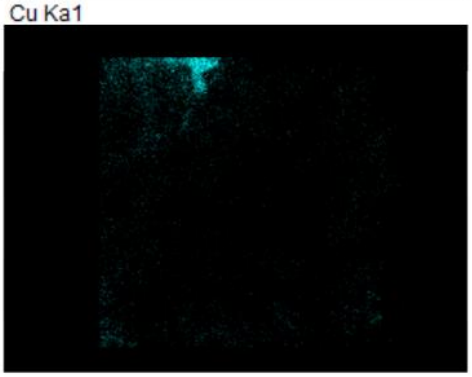
电子图像 1



Cu Ka1



O Ka1



C Ka1_2

Element	C	O	Cu
Weight Percentage (%)	31.75	17.04	51.21
Atomic Percentage (%)	58.56	23.59	17.85

Figure S6.The EDS element analysis

Copies of ^{1}H and LC-MS Spectra for compund 4a

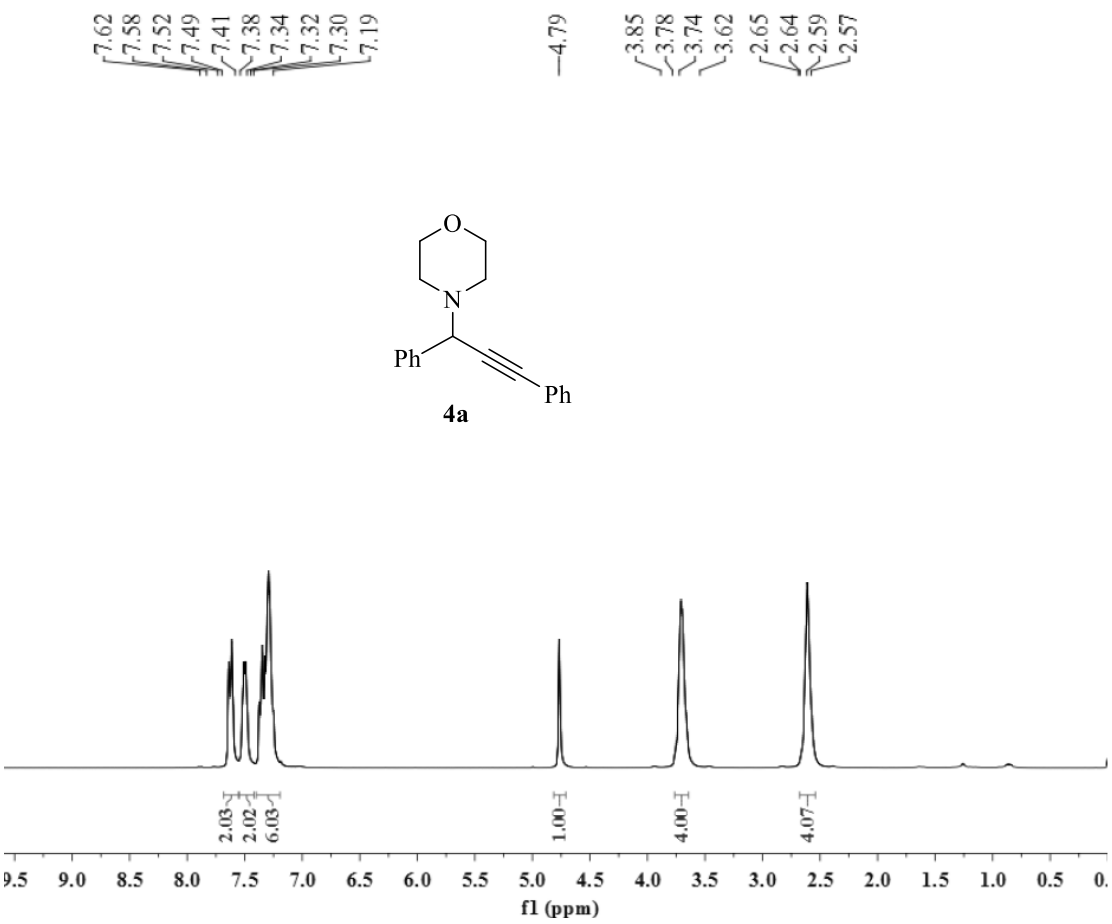


Figure S7.The ^{1}H NMR for compound **4a**

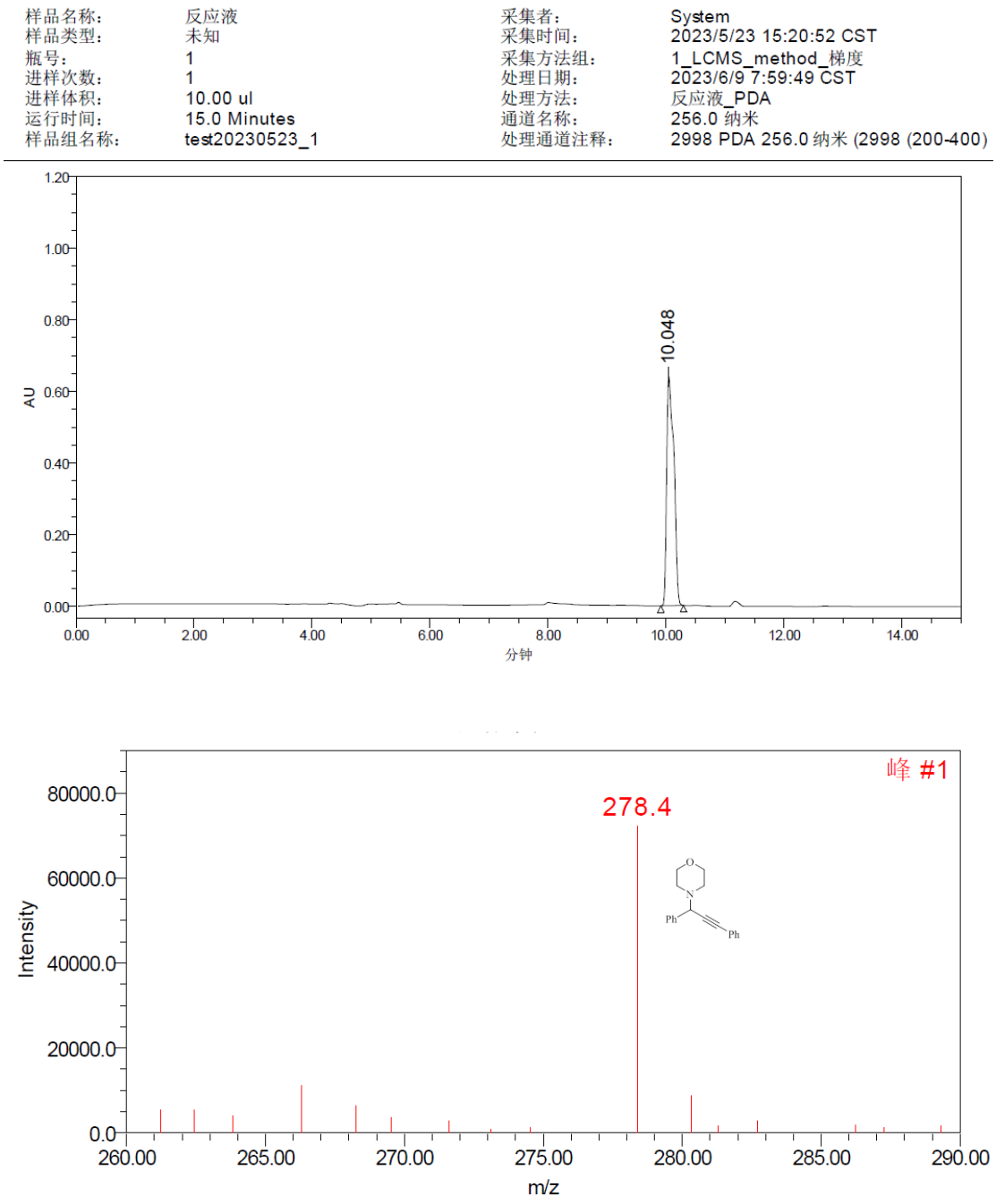


Figure S8. LC-MS spectrum for the compound **4a**