Supporting Information

Metallic Copper Wire-A Simple, Clear and Reusable Catalyst for the CuAAC Reaction in Supercritical Carbon Dioxide

Yuqin Jiang*, Xing He, Weiwei Zhang, Xingfeng Li, Niu Guo, Yaru Zhao, Guiqing Xu* and Wei Li

Henan Engineering Laboratory of Chemical Pharmaceuticals & Biomedical Materials, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Edu cation, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, P. R. China.

E-mail: jiangyuqin@htu.cn

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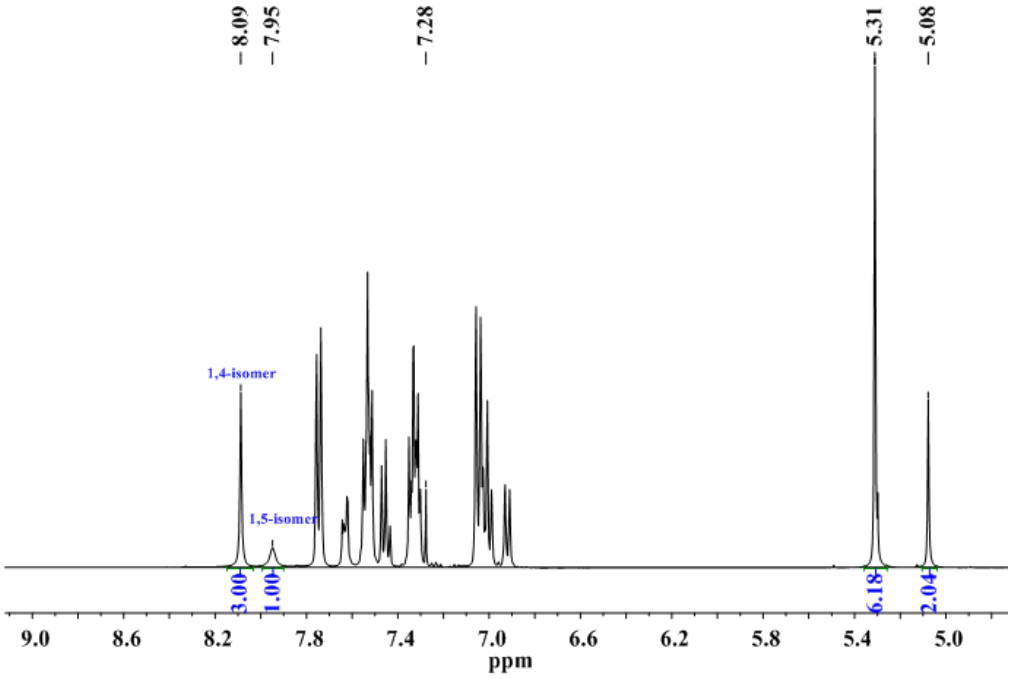
I. General Information

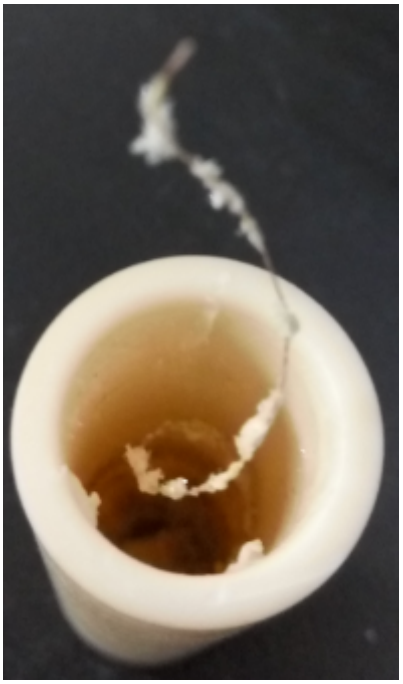
All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. The catalysts were characterized using X-ray powder diffraction (XRD) (Bruker D8 Advance) and scanning electron microscope (SEM) (Hitachi, TM3000). The products were characterized using energy dispersive X-ray spectrometer (EDS) and inductively coupled plasma massspectrometry (ICP-MS) (PerkinElme ELAN DRC-e). The products were characterized using ^{1}H NMR and ^{13}C NMR (Bruker Avance/400) which used $CDCl_3$ or DMSO-d_6 as the solvent and TMS as internal standard. Data is represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = double of doublets, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constants (J) in Hertz (Hz).

II. Catalyst Characterization



SI Figure 1. ^{1}H NMR of product obtained at 80 ºC in the absence of copper wire

Reaction conditions: A mixture of phenyl azide (1.0 mmol) and propargyl phenyl ether (1.0 mmol) in $scCO_2$ was stirred 80 ºC for 10 h at 100 bar.



SI Figure 2. The state of products obtained after CO_2 was vented

Reaction conditions: A mixture of phenyl azide (1.0 mmol), propargyl phenyl ether (1.0 mmol) and copper wire (30 mol%, 10 cm) in scCO_2 was stirred 50 ºC for 10 h at 100 bar.

III. General Procedure for the Synthesis of Triazoles

To an HF-50 autoclave containing copper wire (30 mol%, 10 cm), alkyne (1.0 mmol) and organic azide (1.0 mmol) were added. Liquid CO_2 was then transferred into the autoclave. The reaction mixture was stirred at 50 ºC for 10 h at 100 bar. After the reaction, the CO_2 was vented slowly and the metallic copper wire was picked up. The product could be obtained without further purification.

IV. ^{1}H and ^{13}C NMR Data of the Products

Compound 1 (**Table 3**, entry 1):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.05 (s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.54-7.42 (m, 3H), 7.31 (t, J = 8.0 Hz, 2H), 7.04-6.97 (m, 3H), 5.30 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 158.2, 145.1, 137.0, 129.8, 129.6, 128.9, 121.4, 120.9, 120.6, 114.8, 62.0.

Compound 2 (**Table 3**, entry 2):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.05 (s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.54-7.45 (m, 3H), 7.25 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 12.0 Hz, 2H), 5.26 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ:156.7, 144.5, 136.9, 129.8, 129.5, 129.0, 126.3, 121.0, 120.6, 116.1, 62.2.

Compound 3 (**Table 3**, entry 3):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.16 (s, 1H), 7.80 (dd, J = 8.0 Hz, 4.0 Hz, 4H), 7.55 (t, J = 4.0 Hz, 2H), 7.45 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.5, 138.3, 137.1, 129.8, 129.6, 128.7, 127.4, 125.8, 120.5, 117.3, 21.3.

Compound 4 (**Table 3**, entry 4):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.81 (s, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.33 (t, J = 8.0 Hz, 1H), 3.92 (t, J = 8.0 Hz, 2H), 3.26 (s, 1H), 2.96 (t, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 145.2, 136.0, 128.7, 127.6, 119.4, 119.1, 60.4, 27.8.

Compound 5 (**Table 3**, entry 5):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.53 (s, 1H), 7.37-7.26 (m, 7H), 6.96 (d, J = 8.0 Hz, 3H), 5.52 (s, 2H), 5.18 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 158.2, 144.7, 134.5, 129.5, 129.2, 128.8, 128.1, 122.6, 121.3, 114.8, 62.1, 54.3.

Compound 6 (**Table 3**, entry 6):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.16 (d, J = 12.0 Hz, 2H), 7.62 (s, 1H), 7.38-7.28 (m, 5H), 7.04 (d, J = 12.0 Hz, 2H), 5.55 (s, 2H), 5.26 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 163.2, 143.1, 141.8, 134.3, 129.2, 128.9, 128.2, 125.9, 123.2, 114.9, 62.4, 54.3.

Compound 7 (**Table 3**, entry 7):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.53 (s, 1H), 7.38-7.24 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 12.0 Hz, 2H), 5.50 (s, 2H), 5.12 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 156.8, 144.1, 134.4, 129.4, 129.2, 128.9, 128.1, 126.1, 122.8, 116.1, 62.3, 54.2.

Compound 8 (**Table 3**, entry 8):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.68 (d, J = 8.0 Hz, 2H), 7.62 (s, 1H), 7.37-7.25 (m, 5H), 7.20 (d, J = 8.0 Hz, 2H), 5.55 (s, 2H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.3, 138.0, 134.8, 129.5, 129.1, 128.8, 128.1, 127.7, 125.6, 119.2, 54.2, 21.3.

Compound 9 (**Table 3**, entry 9):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.74-7.72 (m, 2H), 7.59 (s, 1H), 7.34-7.30 (m, 5H), 7.25-7.23 (m, 3H), 5.50 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 147.2, 133.6, 129.4, 128.1, 127.8, 127.1, 127.0, 124.7, 118.5, 53.1.

Compound 10 (**Table 3**, entry 10):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.61 (s, 1H), 7.38-7.28 (m, 5H), 7.23 (s, 1H), 7.16 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 5.55 (s, 2H), 3.37 (br s, 2H, NH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.3, 146.8, 134.7, 131.4, 129.7, 129.1, 128.8, 128.1, 119.6, 116.1, 115.0, 112.3, 54.2.

Compound 11 (**Table 3**, entry 11):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.38-7.23 (m, 5H), 7.16 (s, 1H), 5.45 (s, 2H), 1.94-1.88 (m, 1H), 0.94-0.79 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 150.7, 134.9, 129.0, 128.6, 128.0, 119.6, 54.0, 7.7, 6.7.

Compound 12 (**Table 3**, entry 12):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.32-7.27 (m, 3H), 7.26 (s, 1H), 7.20-7.17 (m, 2H), 5.41 (s, 2H), 3.83 (t, J = 4.0 Hz, 2H), 3.09 (brs, 1H), 2.83 (t, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 144.9, 133.6, 128.1, 127.7, 127.1, 120.6, 60.4, 53.1, 27.2.

Compound 13 (**Table 3**, entry 13):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.22 (d, J = 8.0 Hz, 2H), 7.63 (s, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 5.66 (s, 2H), 5.18 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 156.7, 148.1, 144.8, 141.5, 129.5, 128.6, 126.3, 124.3, 123.0, 116.1, 62.2, 53.2.

Compound 14 (**Table 3**, entry 14):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.18 (d, J = 8.0 Hz, 2H), 7.75 (s, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 5.66 (s, 2H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.7, 148.0, 141.9, 138.4, 129.6, 128.6, 127.3, 125.6, 124.3, 119.6, 53.1, 21.3.

Compound 15 (**Table 3**, entry 15):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.77 (s, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 3.92 (s, 2H), 3.10 (brs, 1H), 2.95 (t, J = 4.0 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 137.7, 133.8, 129.2, 119.3, 119.0, 60.5, 27.8, 20.1.

Compound 16 (**Table 3**, entry 16):

^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.85 (s, 1H), 8.37 (d, J = 8.0 Hz, 2H), 8.25 (d, J = 12.0 Hz, 2H), 7.81 (d, J = 12.0 Hz, 1H), 7.33 (d, J = 12.0 Hz, 2H), 5.46 (s, 2H), 2.32

(s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 163.6, 146.5, 142.7, 141.8, 141.5, 136.8, 133.2, 127.3, 126.3, 124.8, 121.5, 115.8, 62.2, 18.4.

Compound 17 (**Table 3**, entry 17):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.29 (d, J = 8.0 Hz, 2H), 8.02 (s, 1H), 7.80 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 9.2 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 148.2, 146.4, 141.6, 138.6, 136.8, 132.6, 129.6, 126.9, 125.7, 124.2, 121.1, 120.7, 21.3, 18.6.

Compound 18 (**Table 3**, entry 18):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.75 (s, 1H), 7.29 (t, J = 12.0 Hz, 2H), 6.98 (d, J = 8.0 Hz, 3H), 5.22 (s, 2H), 5.14 (s, 2H), 4.25 (q, J = 8.0 Hz, 2H), 1.28 (t, J = 16.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.3, 158.2, 144.6, 129.6, 124.3, 121.3, 114.8, 62.4, 61.8, 50.9, 14.0.

Compound 19 (**Table 3**, entry 19):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.76 (s, 1H), 7.23 (d, J = 12.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 5.19 (s, 2H), 5.16 (s, 2H), 4.25 (q, J = 8.0 Hz, 2H), 1.28 (t, J = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.2, 156.8, 144.2, 129.4, 126.2, 124.2, 116.2, 62.5, 62.2, 50.9, 14.0.

Compound 20 (**Table 3**, entry 20):

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.85 (s, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.36 (t, J = 4.0 Hz, 2H), 7.27 (t, J = 8.0 Hz, 1H), 5.13 (s, 2H), 4.20 (q, J = 8.0 Hz, 2H), 1.23 (t, J = 8.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 165.0, 146.9, 129.3, 127.8, 127.3, 124.8, 120.0, 61.3, 49.9, 13.0.