

SUPPLEMENTARY MATERIAL TO  
**Environmentally benign copper nanoparticles supported on  
walnut shell as a highly durable nanocatalyst for the synthesis of  
propargylamines**

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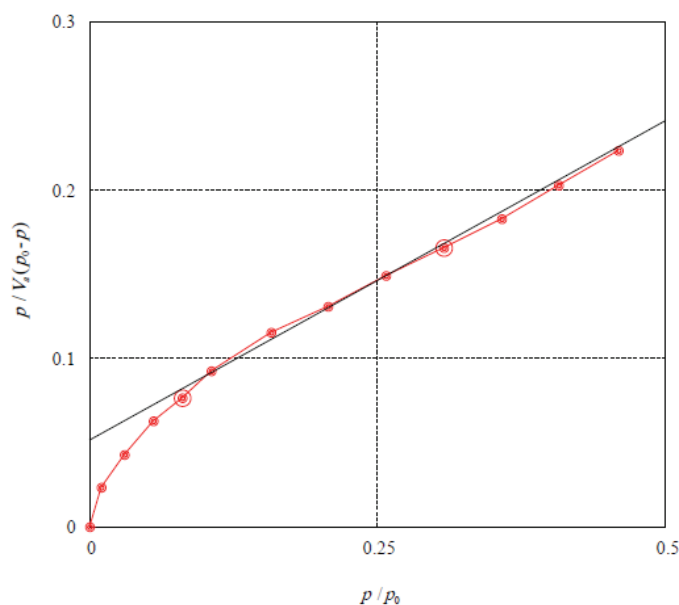


Fig. S-1. BET-Plot of walnut shell (WS).

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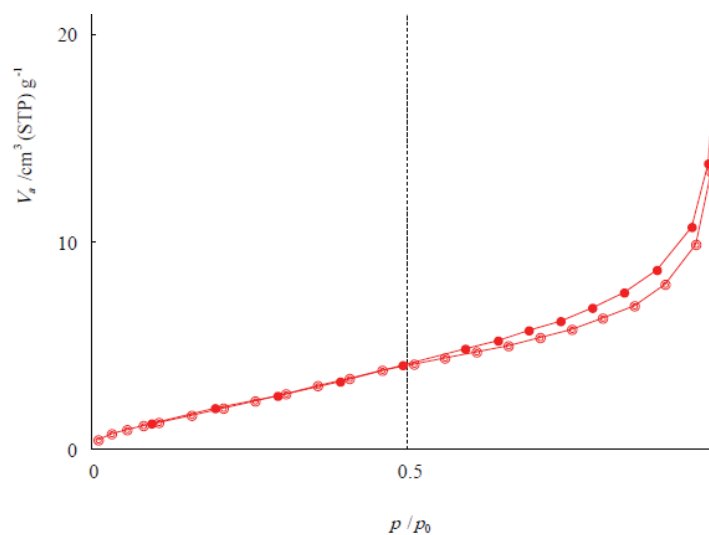


Fig. S-2. Adsorption / desorption isotherm of walnut shell (WS).

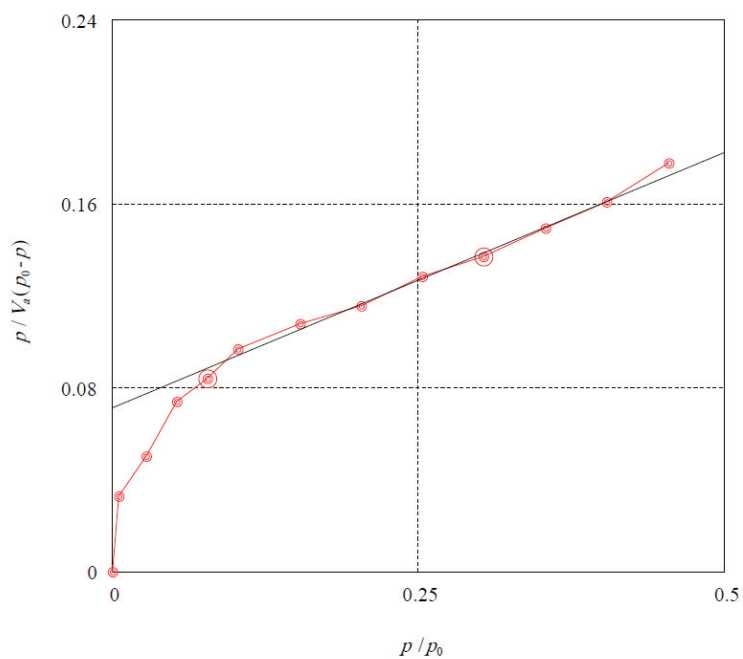


Fig. S-3. BET-Plot of Cu nanoparticles supported on walnut shell (CuNPs @WS).

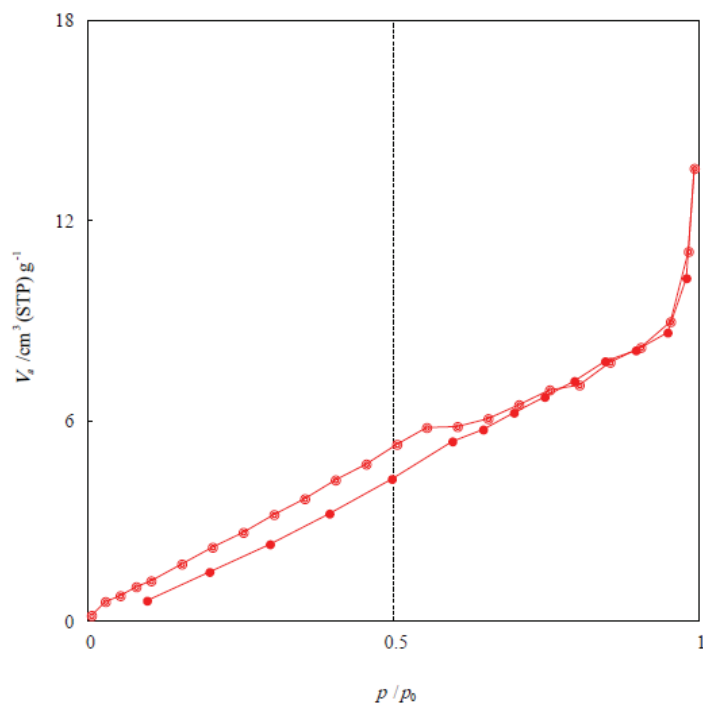
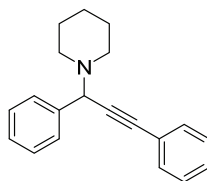


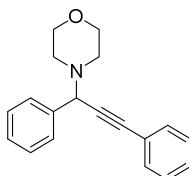
Fig. S-4. Adsorption / desorption isotherm of Cu nanoparticles supported on walnut shell (CuNPs @WS).

#### CHARACTERIZATION OF THE PRODUCTS

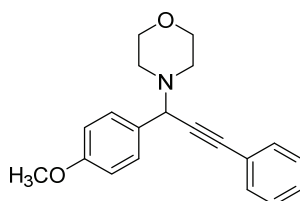
*1-(1,3-Diphenylprop-2-yn-1-yl)piperidine* (Table III, entry 1).<sup>1</sup>



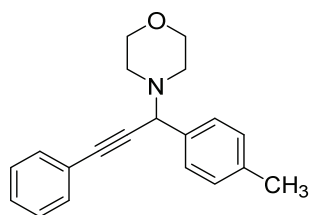
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.68–7.71 (2H, *m*), 7.55 (2H, *d*,  $J = 5$  Hz), 7.35–7.39 (6H, *m*), 4.89 (1H, *s*), 2.64 (4H, *br*), 1.48–1.67 (4H, *m*), 1.30–1.38 (2H, *m*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 138.02, 132.51, 131.84, 128.31, 128.15, 127.68, 123.18, 88.18, 85.64, 62.39, 50.68, 25.96, 24.31.

*4-(1,3-Diphenylprop-2-yn-1-yl)morpholine (Table III, entry 2).<sup>2</sup>*

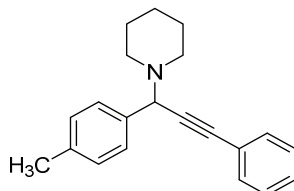
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.62–7.65 (2H, *m*), 7.505 (2H, *m*), 7.25–7.40 (6H, *m*), 4.80 (1H, *s*), 3.74 (4H, *br*), 2.64 (4H, *br*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 137.78, 131.79, 128.57, 128.21, 127.76, 122.97, 88.49, 85.03, 67.13, 62.03, 49.85.

*4-(1-(4-Methoxyphenyl)-3-phenylprop-2-yn-1-yl)morpholine (Table III, entry 3).<sup>2</sup>*

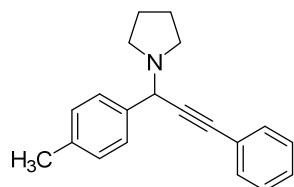
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.52–7.70 (4H, *m*), 7.31–7.34 (3H, *m*), 6.68–6.92 (2H, *d*, *J* = 8.7 Hz), 4.74 (1H, *s*), 3.82 (3H, *s*), 3.74 (4H, *br*), 2.62 (4H, *br*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 159.22, 131.77, 129.71, 128.27, 128.19, 123.01, 113.56, 88.25, 85.34, 67.13, 61.44, 55.27, 49.79.

*4-(3-Phenyl-1-p-tolylprop-2-yn-1-yl)morpholine (Table III, entry 4).<sup>2</sup>*

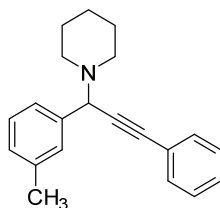
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.49–7.52 (2H, *m*), 7.25–7.34 (5H, *m*), 7.16–7.19 (2H, *m*), 4.75 (1H, *s*), 3.72 (4H, *br*), 2.63 (4H, *br*), 2.36 (3H, *s*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 137.48, 134.78, 131.78, 128.90, 128.50, 128.27, 128.18, 123.09, 88.23, 85.32, 67.15, 61.78, 49.86, 21.99.

*1-(3-Phenyl-1-p-tolylprop-2-yn-1-yl)piperidine (Table III, entry 5).*<sup>1</sup>

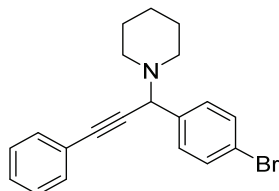
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, δ / ppm): 7.50–7.63 (4H, *m*), 7.31–7.41 (3H, *m*), 7.16–7.18 (2H, *m*), 4.71 (1H, *s*), 2.55–2.59 (4H, *m*), 2.36 (3H, *s*), 1.59–1.61 (4H, *m*), 1.44–1.46 (2H, *m*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>, δ / ppm): 137.08, 135.52, 131.79, 128.74, 128.47, 128.24, 127.98, 123.41, 87.59, 86.35, 62.22, 50.65, 26.15, 24.44, 21.11.

*1-(3-Phenyl-1-p-tolylprop-2-yn-1-yl)pyrrolidine (Table III, entry 6).*<sup>2</sup>

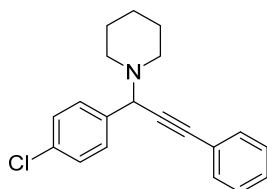
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, δ / ppm): 7.42–7.50 (4H, *br*), 7.30–7.32 (3H, *m*), 7.15–7.25 (2H, *m*), 4.93 (1H, *s*), 2.72 (4H, *br*), 2.39 (3H, *s*), 1.81 (4H, *br*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>, δ / ppm): 137.3, 131.77, 128.94, 128.19, 128.24, 128.06, 123.41, 88.01, 87.6, 58.80, 50.22, 23.46, 21.10.

*1-(3-Phenyl-1-m-tolylprop-2-yn-1-yl)piperidine (Table III, entry 7).*<sup>1</sup>

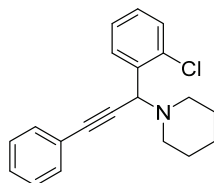
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, δ / ppm): 7.22–7.64 (8H, *m*), 7.09–7.12 (1H, *m*), 4.75 (1H, *s*), 2.56 (4H, *br*), 2.38 (3H, *s*), 1.44–1.59 (4H, *m*), 1.32–1.34 (2H, *m*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>, δ / ppm): 138.47, 137.63, 131.79, 129.20, 128.94, 128.43, 128.23, 127.97, 127.9, 125.66, 123.96, 87.65, 86.30, 62.45, 50.74, 31.18, 26.15, 24.43, 21.5.

*1-(1-(4-Bromophenyl)-3-phenylprop-2-yn-1-yl)piperidine (Table III, entry 8).<sup>2</sup>*

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, δ / ppm): 7.46–7.55 (6H, *m*), 7.33–7.35 (3H, *m*), 4.75 (1H, *s*), 2.52–2.54 (4H, *br*), 1.56–1.62 (4H, *m*), 1.44–1.46 (2H, *m*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>, δ / ppm): 145.41, 137.85, 131.8, 131.14, 130.18, 129.01, 128.51, 128.31, 123.05, 121.36, 88.27, 85.27, 61.77, 50.64, 26.14, 24.36.

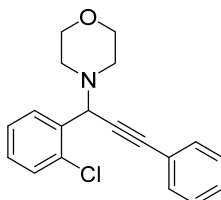
*1-(1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-yl)piperidine (Table III, entry 9).<sup>1</sup>*

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, δ / ppm): 7.47–7.85 (4H, *m*), 7.30–7.46 (5H, *m*), 4.70 (1H, *s*), 2.51 (4H, *br*), 1.44–1.59 (4H, *m*), 1.23–1.29 (2H, *m*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>, δ / ppm): 145.35, 131.79, 130.73, 129.79, 128.95, 128.50, 128.30, 128.17, 123.11, 87.54, 85.58, 61.69, 50.11, 26.13, 24.35.

*1-(1-(2-Chlorophenyl)-3-phenylprop-2-yn-1-yl)piperidine (Table III, entry 10).<sup>1</sup>*

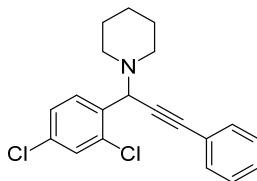
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, δ / ppm): 7.73–7.76 (2H, *d*, *J* = 9 Hz), 7.49 (2H, *br*), 7.20–7.41 (5H, *m*), 5.10 (1H, *s*), 2.58–2.61 (4H, *br*), 1.55–1.60 (4H, *m*), 1.42–1.46 (2H, *m*); <sup>13</sup>C-NMR (69.2 MHz, CDCl<sub>3</sub>, δ / ppm): 136.39, 134.63, 131.77, 130.56, 129.76, 128.74, 128.25, 128.1, 126.15, 123.17, 87.50, 85.8, 59.23, 50.73, 26.12, 24.43.

*4-(1-(2-Chlorophenyl)-3-phenylprop-2-yn-1-yl)morpholine* (Table III, entry 11).<sup>1</sup>



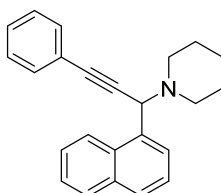
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.76 (1H, *br*), 7.50 (2H, *br*), 7.26–7.43 (6H, *m*), 5.14 (1H, *s*), 3.72 (4H, *br*), 2.68 (4H, *br*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 135.45, 134.63, 131.79, 130.57, 129.88, 129.67, 129.15, 128.31, 126.37, 122.75, 88.37, 84.56, 67.02, 58.92, 49.83.

*1-(1-(2,4-Dichlorophenyl)-3-phenylprop-2-yn-1-yl)piperidine* (Table III, entry 12).<sup>2</sup>



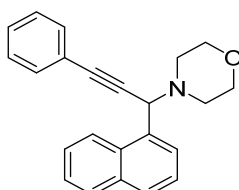
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.71 (1H, *d*, *J* = 10 Hz), 7.28–7.48 (7H, *m*), 5.05 (1H, *s*), 2.60 (4H, *br*), 1.43–1.57 (6H, *br*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 135.28, 133.96, 131.79, 131.44, 129.55, 128.31, 126.56, 122.80, 88.14, 84.97, 58.83, 50.75, 25.95, 24.30.

*1-(1-(Naphthalen-1-yl)-3-phenylprop-2-yn-1-yl)piperidine* (Table III, entry 13).<sup>1</sup>



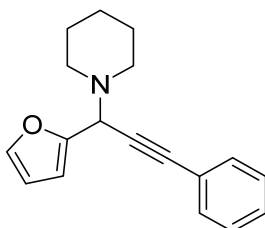
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 8.475 (1H, *d*, *J* = 7.5 Hz), 8.01 (1H, *d*, *J* = 7 Hz), 7.84–7.91 (2H, *m*), 7.48–7.62 (2H, *m*), 7.38–7.39 (2H, *m*), 5.51 (1H, *s*), 2.72 (4H, *br*), 1.51–1.60 (6H, *m*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 134.08, 131.88, 128.63, 128.44, 128.35, 128.10, 126.96, 125.81, 125.60, 125.04, 124.82, 123.47, 88.64, 85.2, 60.52, 50.76, 26.28, 24.62.

*4-(1-(Naphthalen-1-yl)-3-phenylprop-2-yn-1-yl)morpholine* (Table III, entry 14).<sup>3</sup>



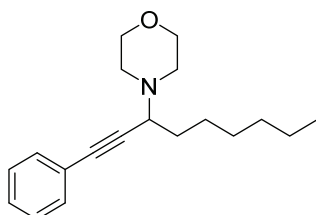
<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 8.34 (1H, *d*, *J* = 7.5 Hz), 7.82–7.94 (3H, *m*), 7.43–7.59 (4H, *m*), 7.34–7.36 (3H, *m*), 5.45 (1H, *s*), 3.68–3.76 (4H, *br*), 2.71–2.73 (4H, *br*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 134.06, 133.19, 131.82, 131.6, 128.90, 128.51, 128.33, 128.25, 127.11, 125.90, 125.69, 124.79, 123.05, 88.02, 84.98, 67.21, 60.17, 49.84.

*1-(1-(Furan-2-yl)-3-phenylprop-2-yn-1-yl)piperidine* (Table III, entry 15).<sup>1</sup>



<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.42–7.52 (3H, *m*), 7.31–7.34 (3H, *m*), 6.485 (1H, *d*, *J* = 2.5 Hz), 6.35 (1H, *d*, *J* = 2.5 Hz), 4.87 (1H, *s*), 2.59 (4H, *br*), 1.61–1.70 (4H, *m*), 1.42–1.49 (2H, *m*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 151.62, 142.53, 131.83, 128.25, 122.93, 109.94, 109.21, 86.37, 83.83, 56.55, 50.51, 25.95, 24.90.

*4-[1-2-(Phenylethynyl)heptyl]morpholine* (Table III, entry 16).<sup>1</sup>



<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 7.42 (2H, *br*), 7.29 (3H, *br*), 3.75 (4H, *br*), 3.48 (1H, *t*, *J* = 7.2 Hz), 2.73 (2H, *br*), 2.57 (2H, *br*), 1.67–1.72 (2H, *m*), 1.31–1.55 (8H, *m*), 0.89 (3H, *br*); <sup>13</sup>C-NMR (62.9 MHz, CDCl<sub>3</sub>,  $\delta$  / ppm): 131.70, 129.07, 128.19, 127.89, 123.26, 87.21, 86.12, 67.13, 58.13, 49.73, 32.93, 31.72, 29.65, 29.01, 26.53, 22.57, 14.02.