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Supporting Information
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Thieme

Selective azidation of aryl halides to aryl azides Promoted by proline and $CuFeO_2$

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Supporting information

Experimental Section

All the starting materials and reagents are commercially available and used as received.

Preparation of the catalyst:

Micro-$CuFeO_2$ particles were synthesized according the method described by Hashimoto and co-workers with some modifications. In a typical synthesis, 5 mmol $Fe(NO_3)_3.9H_2O$ and 5 mmol $Cu(NO_3)_2.3H_2O$ were dissolved in 40 mL distilled water to form a clear solution, and then 0.1 mol NaOH was added into the solution with stirring to get a colloidal suspension. 0.8 mL of butyraldehyde was added into the suspension as a reducing agent. Then, this suspension was transferred to a 100 mL Teflon-lined stainless steel autoclave, which was closed and allowed to react at 180 ˚C for 24h. After the hydrothermal reaction, the autoclave was cooled naturally to room temperature. The solid products were collected by filtering and washed with distilled water several times, then dried in air at ambient conditions .

General procedure for the synthesis of aryl azides:

In a typical experiment, a flask equipped with a magnetic stirrer was charged with 1 mmol aryl halide, 2 mmol sodium azide, 2 ml mixtures of 9DMF/H_2O and 10 mol% $CuFeO_2$. This mixture was stirred at 115 ˚C (for aryl bromides) or 95 ˚C (for aryl iodides) and progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was filtered and product was extracted with 5 ml mixtures of hexane/ethyl acetate (for four times). The organic layer was dried with $CaCl_2$ and then the solvent removed under reduced-pressure to give the product. In order to examine the recyclability of the catalyst, spent $CuFeO_2$ was recovered from the reaction media and reused. The catalyst was separated from the reaction mixture by centrifuge, washed several times with water. Regenerated catalyst reused under the optimum reaction conditions. Spent $CuFeO_2$ gave a similar yield of products as the fresh catalyst till the 3th cycle. No significant changes in composition or in environment were observed after regeneration till the 3th cycle. All the products are known compounds and were characterized by comparison of their IR and ^1H NMR spectroscopic data with reported values.

XRD result: Structure of the $CuFeO_2$ particles was determined by powder X-ray diffraction (Figure S1). Diffraction patterns of all the peaks matched well with the standard XRD pattern. All of the peaks are highly crystallized as it is shown by sharp XRD patterns. Peak positions matched well with the obtained data for micro-$CuFeO_2$ with a rhombohedral structure. Impurities such as CuO, Cu_2O, $CuFe_2O_4$ and Fe_2O_3 were not observed that confirmed high purity of the produced $CuFeO_2$.

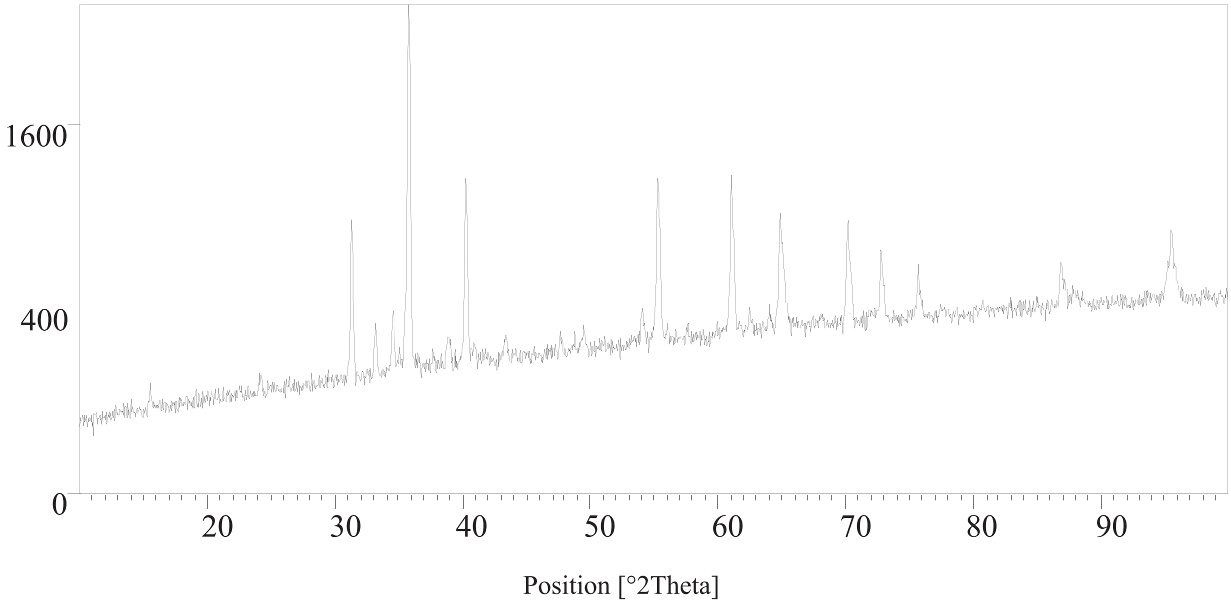
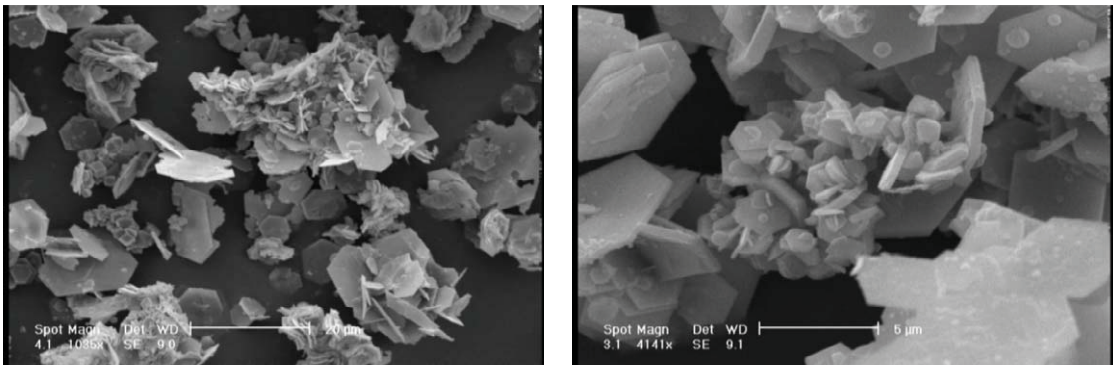


Figure S1. XRD pattern of $CuFeO_2$ particles.

SEM result: Scanning electron microscopy (SEM) analysis of the catalyst showed that the average size of the $CuFeO_2$ particles was about 1–5 µm (Figure S2). Rhombohedral like $CuFeO_2$ crystals with specific corners and edges confirmed crystallinity of the $CuFeO_2$. It must be noted that agglomeration of the particles are low and by this way catalytic performance can also be increased.



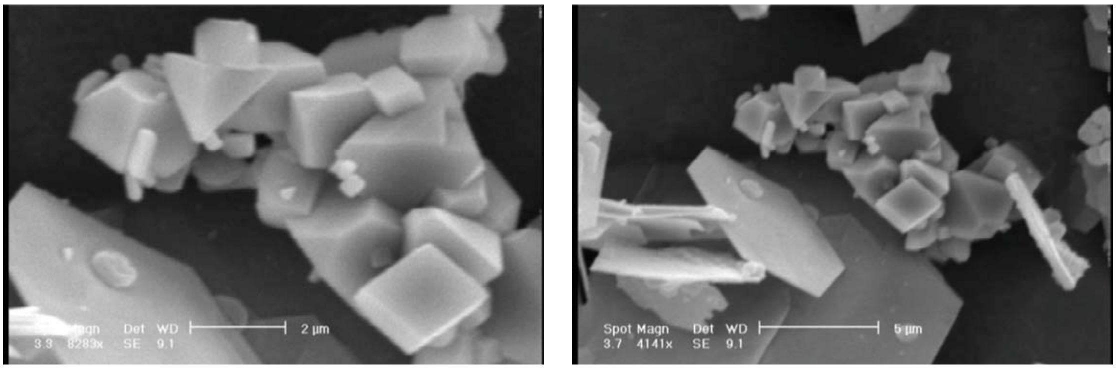


Figure S2. SEM images of $CuFeO_2$ particles.

IR result: A strong band associated with the Fe-O stretching vibrations at 532 cm^{-1} and 1100 cm^{-1} was detected in the FT-IR spectrum (Figure S3).

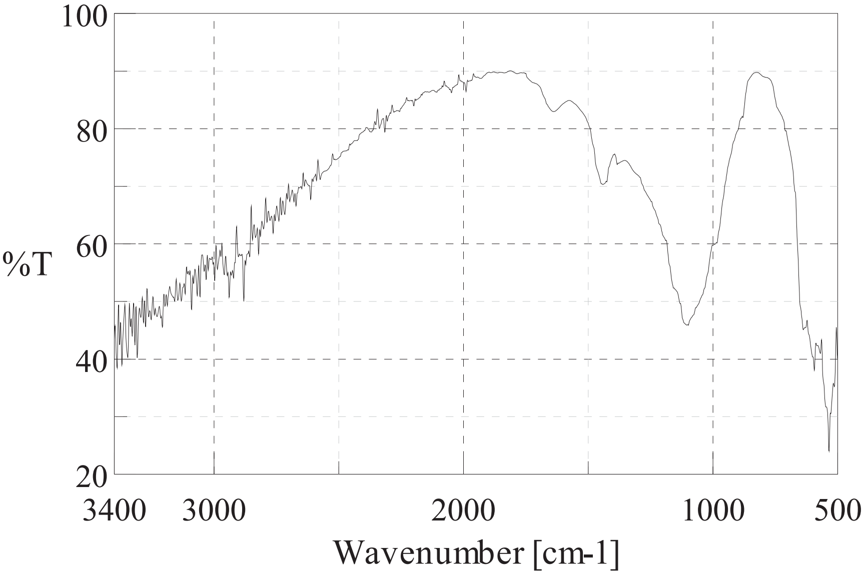


Figure S3. FT-IR spectrum of $CuFeO_2$ particles.

EDX result: Catalyst was subjected to the composition analysis at one area by an energy dispersive X-ray analyzer (EDX). The EDX spectrum for that area consisted of Cu, Fe and O elements (Figure S4). The spectrum shows the presence of these elements in the catalytic system as their proportions shown in Table S1.

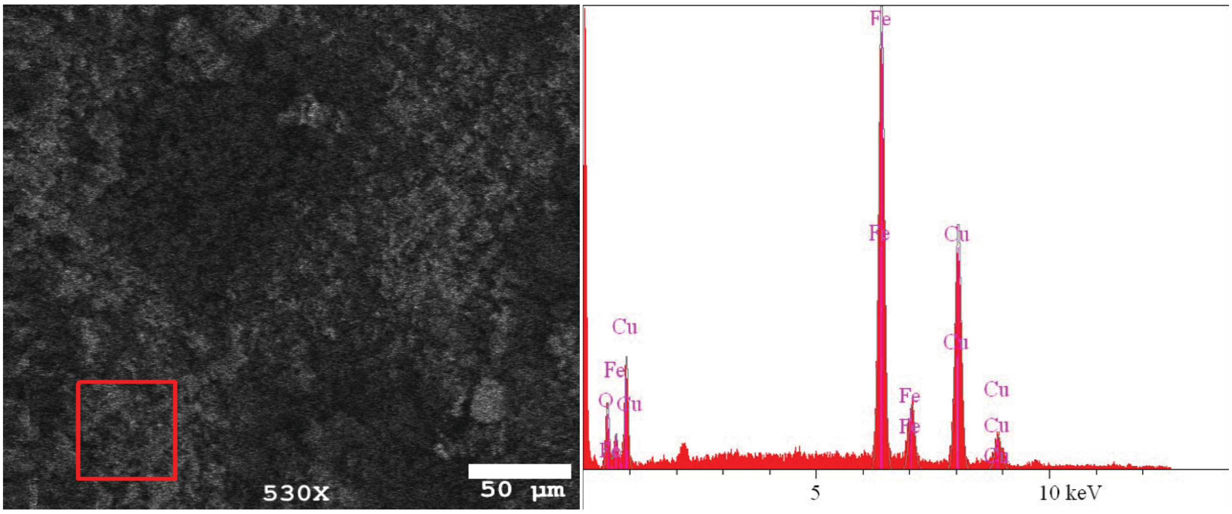


Figure 4S. EDX spectra of $CuFeO_2$ particles.

Elt.	Line	Intensity (c/s)	Atomic %	Conc	Units	
O	Ka	26.41	19.65	6.16	wt.%	
Fe	Ka	342.25	41.35	45.26	wt.%	
Cu	Ka	196.56	39.00	48.58	wt.%	
			100.00	100.00	wt.%	Total

Table S1. EDX data of $CuFeO_2$ particles.

Selected ^{1}H and ^{13}C NMR data for the synthesized compounds:

1-azido-3-methoxybenzene
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (t, *J*=8.3, 1H), 6.68 (d, *J*= 8.3 Hz, 2H), 6.62 (d, *J*= 8.3 Hz, 2H), 6.52 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 141.2, 130.3, 111.2, 110.5, 104.8, 55.3.

1-Azido-4-iodobenzene

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (d, *J* = 7.4 Hz, 2H), 7.70 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 140.1, 122.2, 89.0.

4′-Azidoacetophenone
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53 (s, 3 H), 7.13 (d, J = 8.4 Hz, 2 H), 8.00 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8, 146.5, 135.0, 131.5, 120.0, 26.5.

Azidobenzene
IR (KBr, cm-1): 2100; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.37 (m, 2H), 7.14-7.18 (m, 1H), 6.98-7.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 129.6, 124.7, 118.8.

1-azido-4-methoxybenzene

IR (KBr, cm^{-1}): 2260, 2105; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (d, *J*=8.8, 2H), 6.90 (d, *J*=8.0, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 132.1, 119.8, 114.9, 55.3.

1-azido-4-methylbenzene

IR (KBr, cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J*=6.8, 2H), 6.95 (d, *J*=6.4, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 134.4, 130.2, 118.7, 20.7

1-azido-4-bromobenzene

IR (KBr, cm^{-1}): 2106, 2270; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J*=9.2, 2H), 7.16 (d, *J*=9.2, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 132.6, 120.4, 117.6

1-azido-3-nitrobenzene

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J=8.3, 1H), 7.88 (s, 1H), 7.53 (t, J=8.3, 1H), 7.33 (d, J=8.3, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 141.8, 130.4, 124.7, 119.5, 113.9.

1-azido-4-chlorobenzene

IR (KBr, cm^{-1}): 2088, 2130; ^{1}H NMR (400 MHz, CDCl3): 7.32 (d, J=8.4, 2H), 6.94 (d, J=6.8, 2H). ^{13}C NMR (100 MHz, CDCl3): δ 138.8, 130.3, 130.0, 120.4.