Electronic Supplementary Information

HKUST-1 Derived Cu@CuO_x/Carbon Catalyst for Base-free Aerobic Oxidative Coupling of Benzophone Imine: High Catalytic Efficiency and Excellent Regeneration Performance

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Contents

A. General Information

X-ray photoelectron spectroscopic (XPS) experiments were carried out on a spectrometer (AXIS Supra, Kratos Analytical Ltd) with Al Ka radiation, The C1s peak (284.6 eV) was used for the calibration of binding energy values. Scanning electron microscopy (SEM) images were taken from a Hitachi 4800 microscope (20 kV). Scanning-transmission electron microscopy (STEM) images and energy dispersive X-ray spectroscopy (EDX) of catalysts were recorded on a JEOL JEM-2100 microscope (200 kV). The samples were dispersed in anhydrous alcohol using the ultrasonic technique, the suspension obtained was added dropwise to a micro-grid membrane and dried in air. ^{1}H, ^{13}C-NMR spectra were recorded with a Varian 700M spectrometer. Chemical shifts (in ppm) were referenced to CDCl3 (δ = 7.26 ppm) or TMS (δ = 0.00 ppm) as an internal standard.

B. Characterization of catalyst

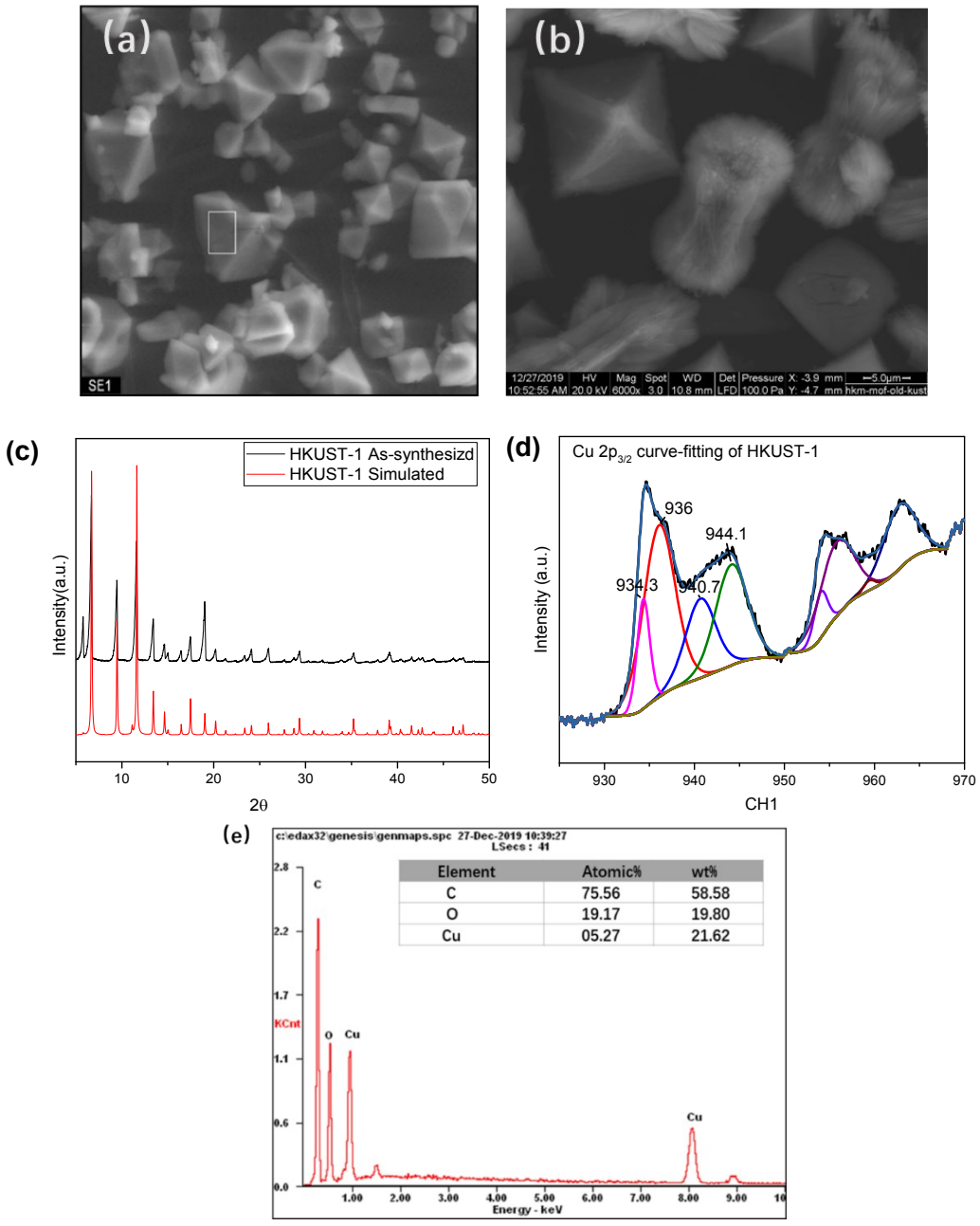


Fig. S1 (a-b) SEM of HKUST-1;(c) XRD of as-synthesized HKUST-1 and simulated XRD of HKUST-1; (d) Cu $2p_{3/2}$ curve-fitting of HKUST-1; (e) EDS of HKUST-1

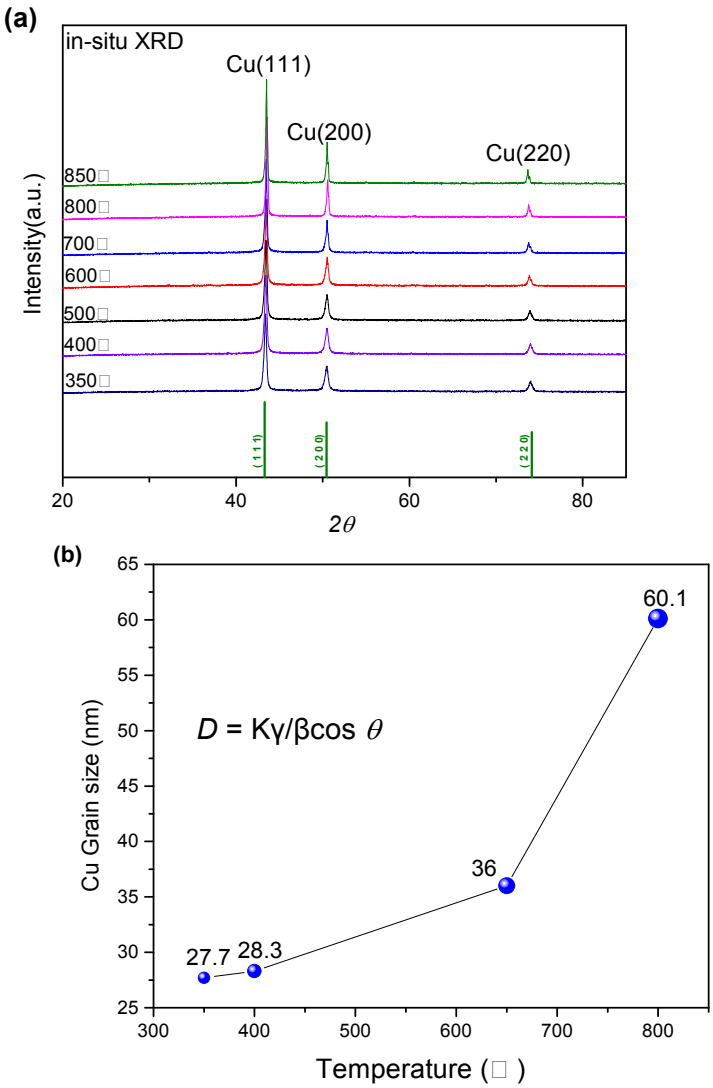


Fig. S2 (a) In-situ XRD characterization of MOF precursors in the N_2 atmosphere;(b) The crystallite size of metallic copper crystal according to the Scherrer formula

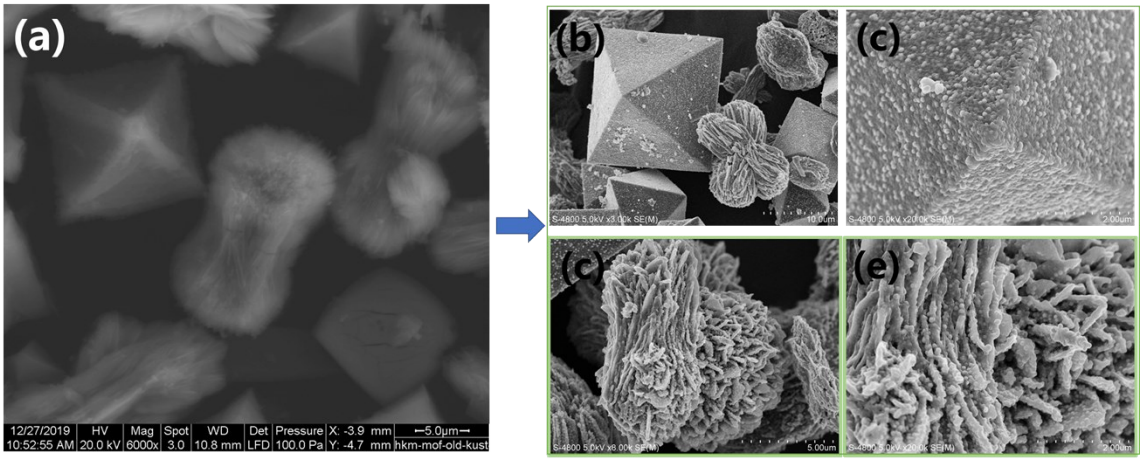
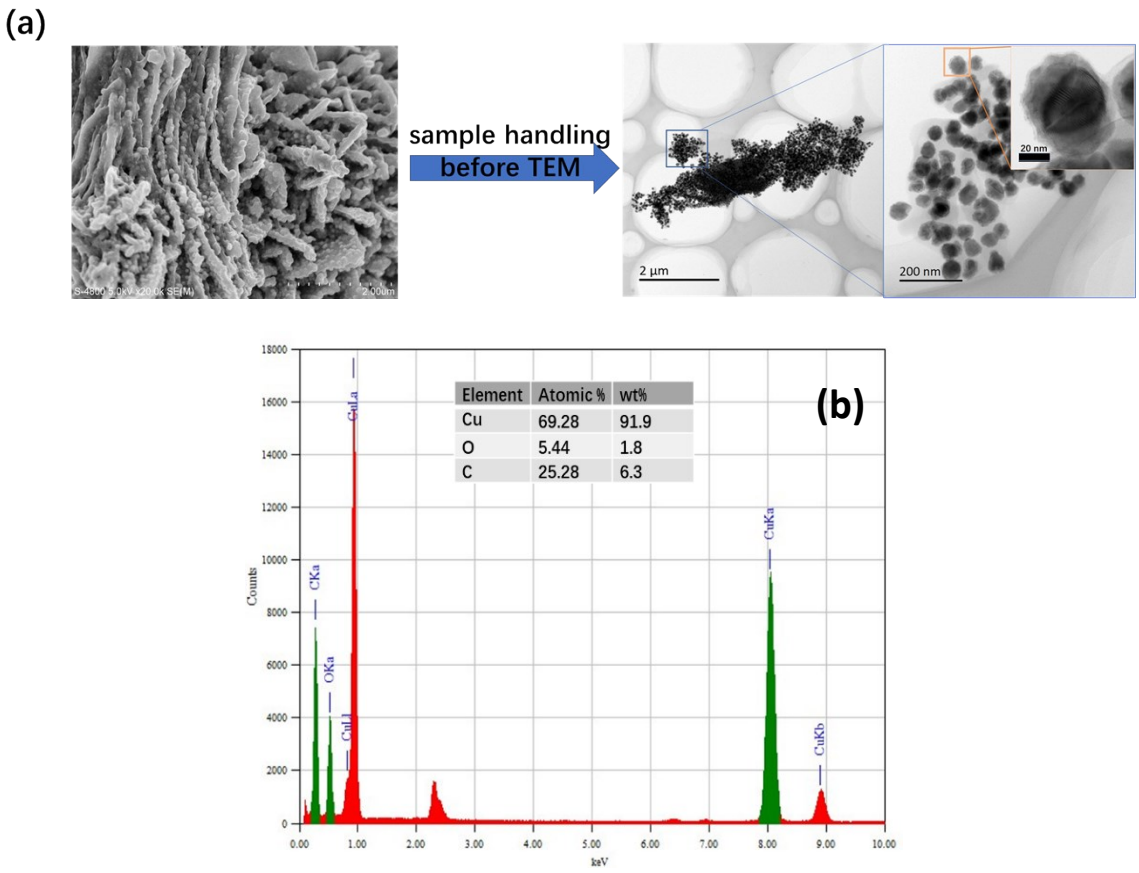


Fig. S3 (a) Morphology of HKUST-1 before calcination; (b-e) Morphology of Cu@CuOx/C after calcination.



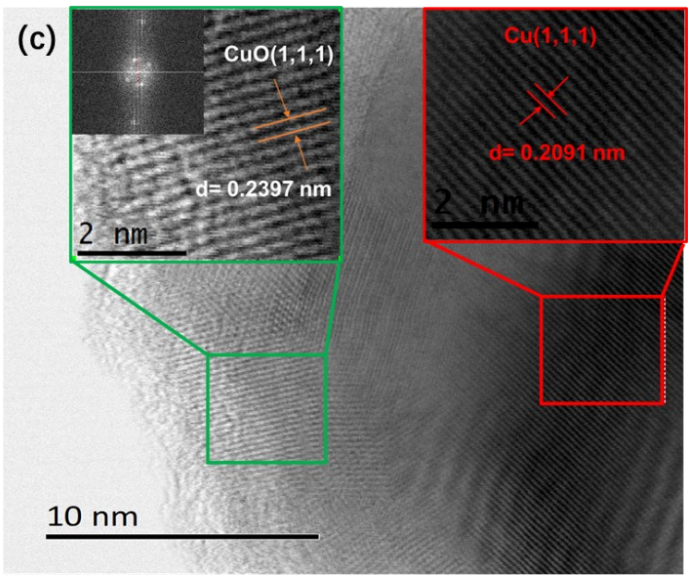
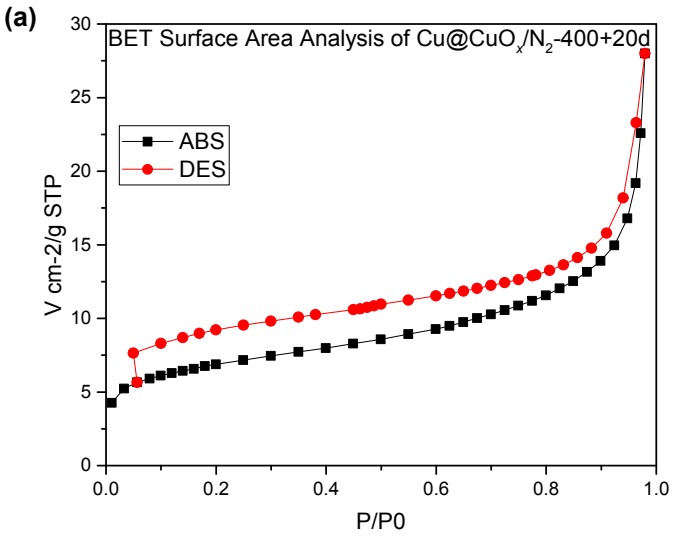


Fig S4 (a) TEM analysis of Cu@CuOx/C material (the samples were soaked in ethanol and treated with ultrasound); (b) STEM-EDS spectrum of Cu@CuO_x/C-N_2-400+20d (c)TEM of Cu@CuO_x/C-N_2-400+20d



(b)

Surface Area	BET Surface Area: 24.2 m^2/g
	t-Plot Micropore Area: 12.3 m^2/g
	t-Plot External Surface Area: 11.9 m^2/g
Pore Size	Adsorption average pore width (4V/A by BET): 71.6 nm

Fig. S5 BET surface area and pore size/volume analysis of Cu@CuO_x/C-N_2-400 +20d

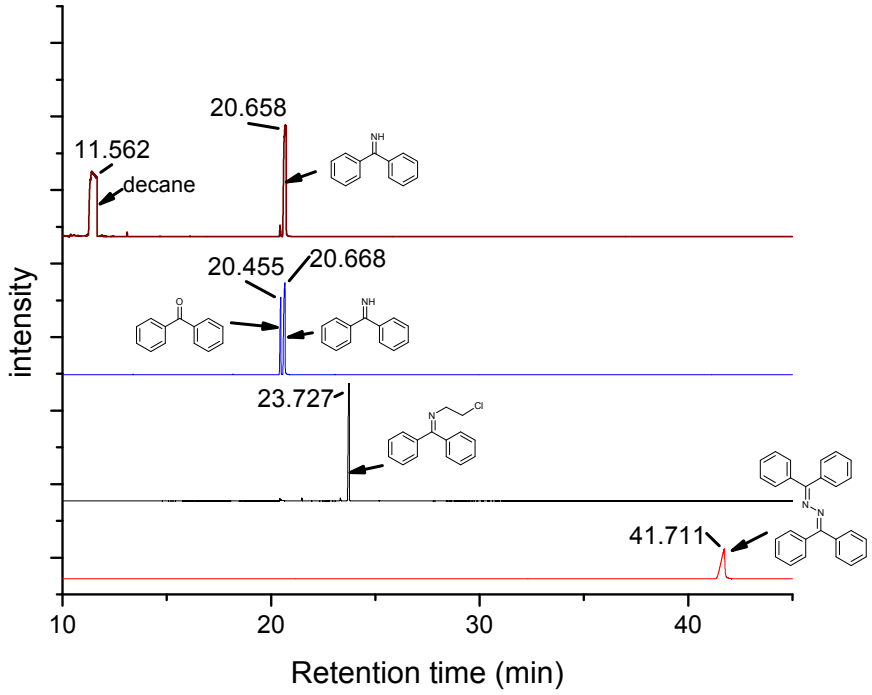


Fig. S6 GC-MS analysis of substrate and products

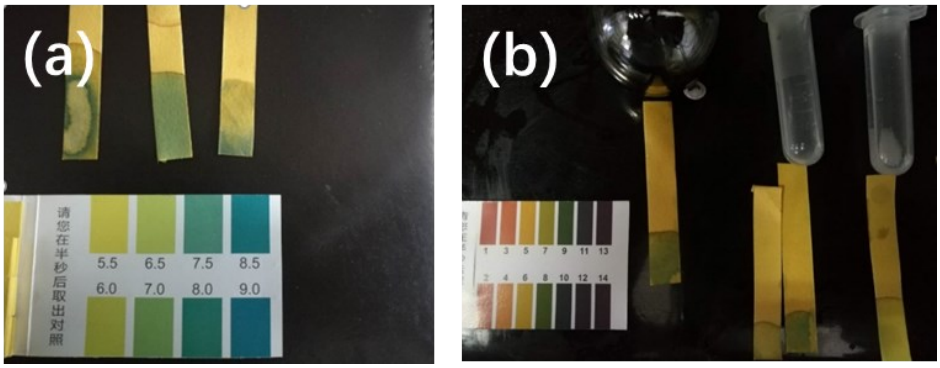


Fig. S7 (a) Left: BI substrate； Middle: the gas of BI；Right: a gas mixture of imine/DCE solution (b) Left: reaction system; Middle: with and without BI in DCE.

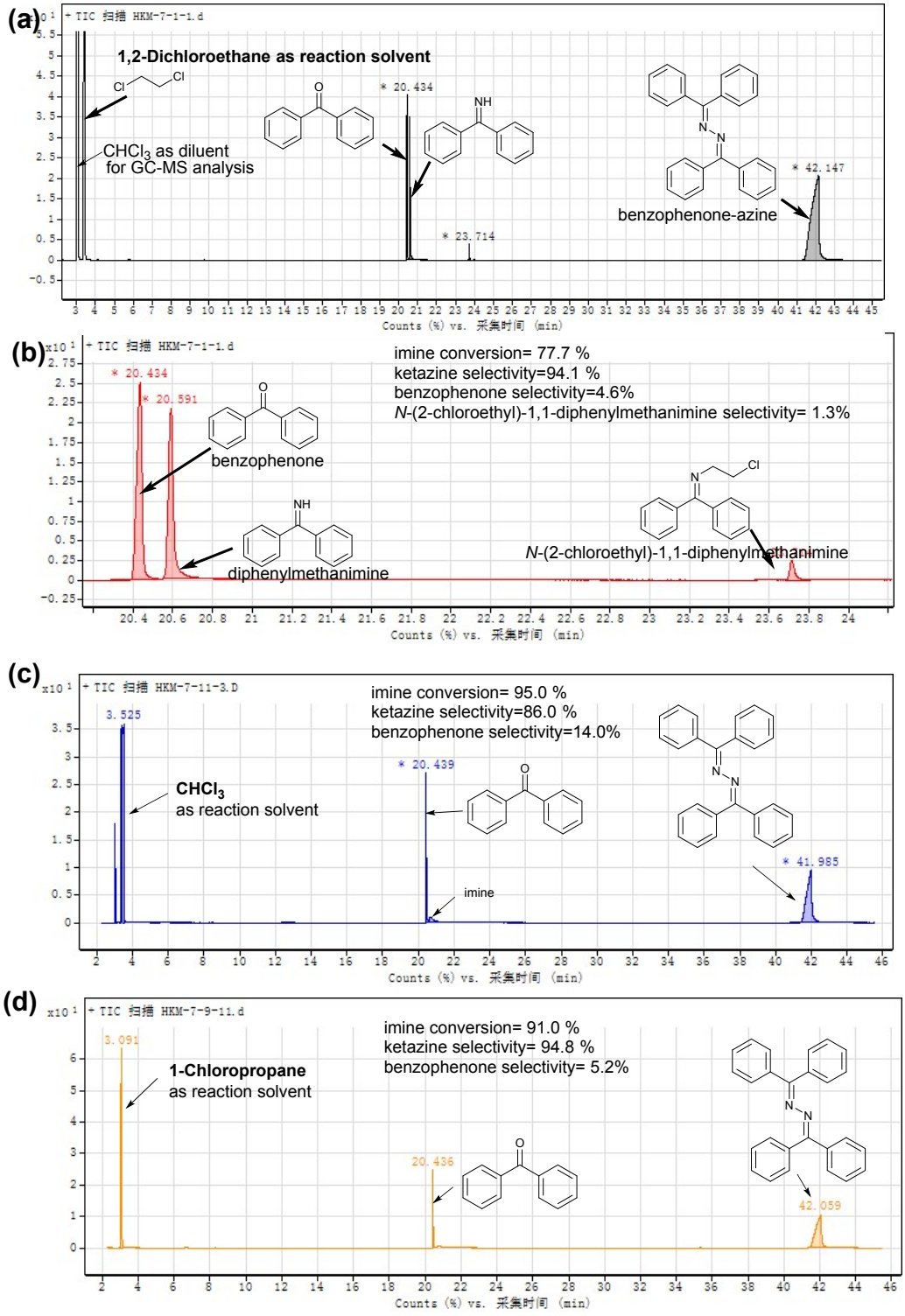
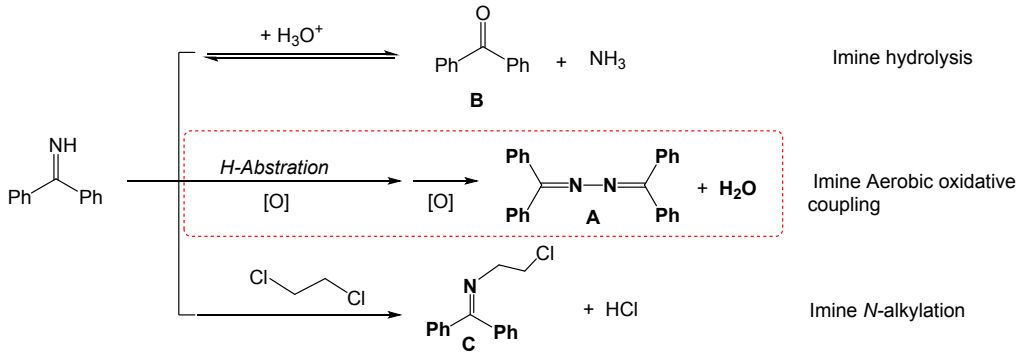


Fig. S8. GC-MS analysis of the oxidation reaction in various solvent. (a) 1,2-Dichloroethane as reaction solvent;(b) N-(2-chloroethyl)-1,1-diphenylmethanimine was detected by GC-MS when 1,2-dichloroethane was used as solvent;(c) GC-MS spectra of oxidation reaction in chloroform as solvent;(d) GC-MS spectra of oxidation reaction of 1-chloropropane as solvent.

Table S1. Effect of free radical inhibitor



Entry	Catalyst	Free radical inhibitor 1 mmo	Convertion (%)	Selectivity (%)		
				A	B	C
1	Cu@CuO_x/C-N_2-400-20d	TEMPO	42.5	82.3	12.7	5
2	Cu@CuO_x/C-N_2-400-20d	NHPI	96	59	36.4	4.6
3	Cu@CuO_x/C-N_2-400-20d	benzoquinone	65.1	59.4	38.7	1.7

Reaction conditions: 2 ml solvent, 50 mg Cu@CuO_x/C-N_2-400+20d as catalyst, 1 mmol substrate, 1 mmol additive, 80°C, 24 h, 1 O_2 balloon. Yields are determined by GC spectroscopy.

C. Characterization of recycled and regenerated catalyst

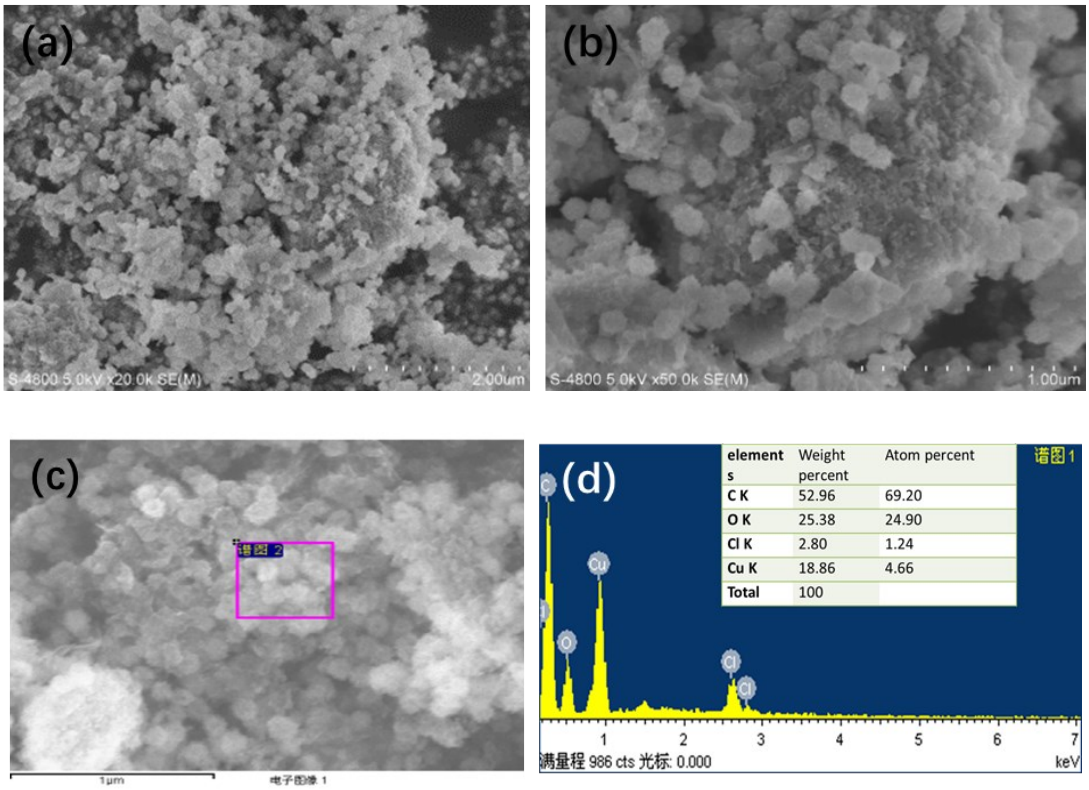


Fig S9. (a-b) SEM of recycled catalyst;(c-d) SEM-EDX of recycled catalyst

D. Recycled Experiments

Catalytic stability and regeneration method: Add 220 mg of Cu@CuO_x/C-N_2-400+20d catalyst, 6 ml of dichloromethane, and 800 mg (5 mmol) of diphenylketimine to the reaction flask and keep the reaction temperature to 80 ° C under the oxygen balloon. After 72 h, dichloromethane adds into the reaction to quench. After the catalyst was centrifuged twice, it was separated and dried at room temperature for 2 hours, followed by the next cycle experiment.

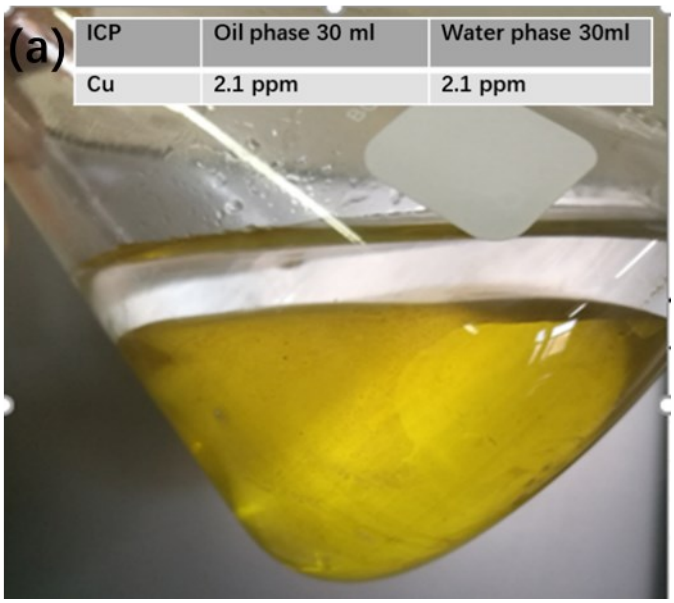


Fig. S10 ICP-AES analysis of the content of copper in water phase and organic phase

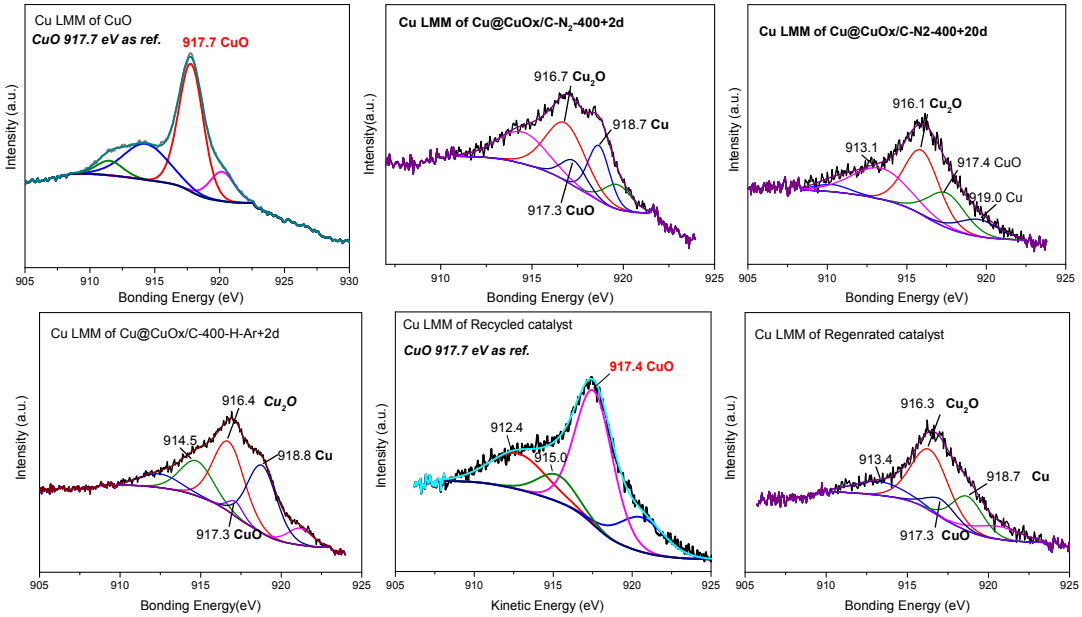


Fig. S11 Cu $L_3M_{4,5}M_{4,5}$ curve-fitting of Cu catalysts

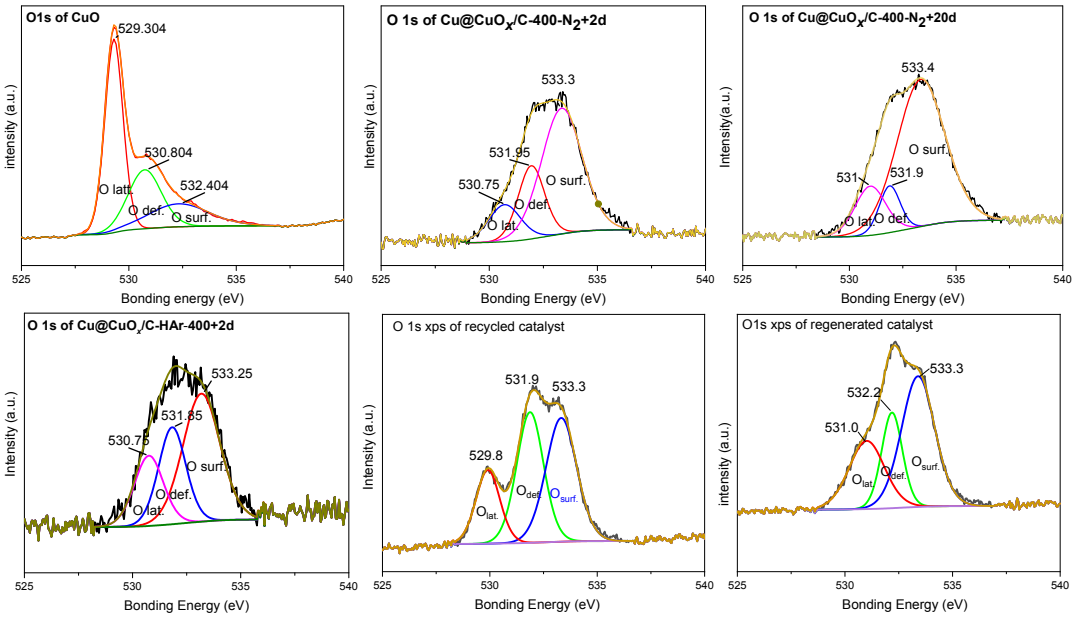
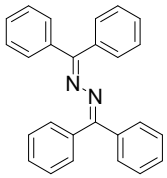


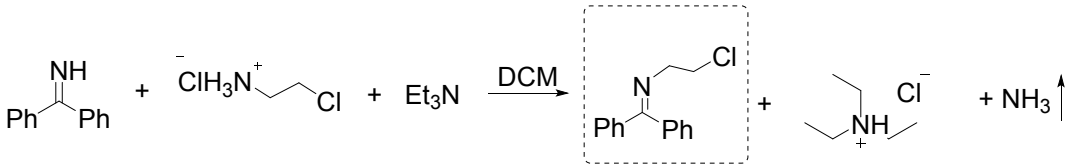
Fig. S12 O1s XPS curve-fitting of Cu catalysts

E. ^{1}H,^{13}C-NMR spectrum

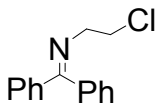


1,2-bis(diphenylmethylene)hydrazine (Benzophone-imine)

^{1}H NMR (700 MHz, Chloroform-d) δ 7.54 (d, J = 7.8 Hz, 4H), 7.45 (t, J = 7.3 Hz, 4H), 7.42 (d, J = 6.8 Hz, 2H), 7.38 (dd, J = 14.3, 7.3 Hz, 6H), 7.33 (t, J = 7.6 Hz, 4H). ^{13}C NMR (176 MHz, Chloroform-d) δ 158.9, 138.1, 135.4, 129.6, 129.3, 128.6, 128.0, 127.8. MS (70 eV): m/z (%) =360.1. Spectroscopic data were identical to literature values [1]



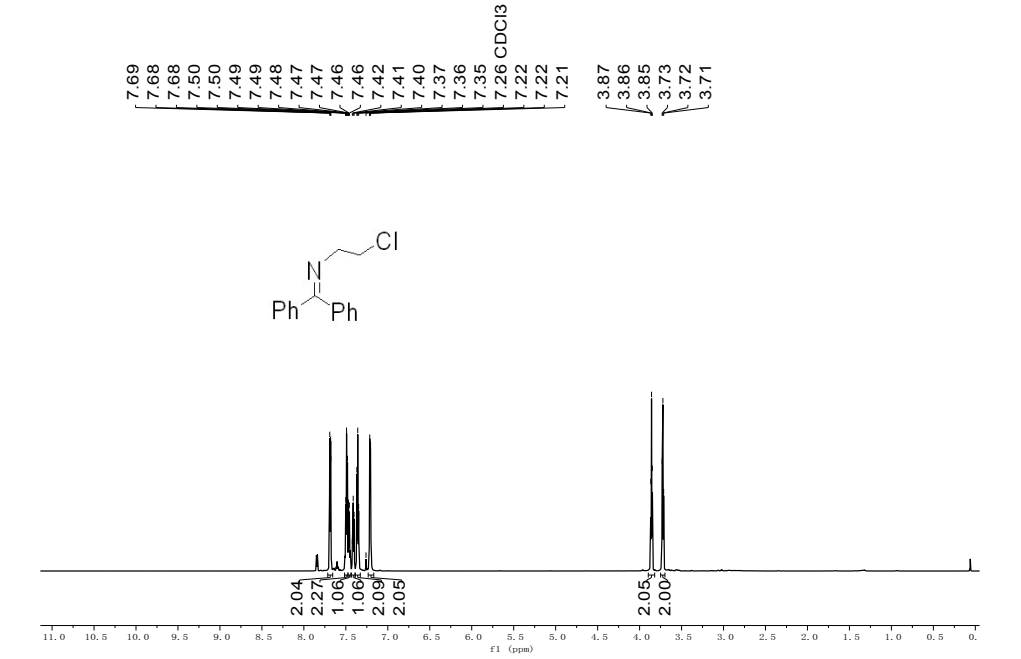
The synthesis route of N-(2-chloroethyl)-1,1-diphenylmethanimine is based on the reference. [2]

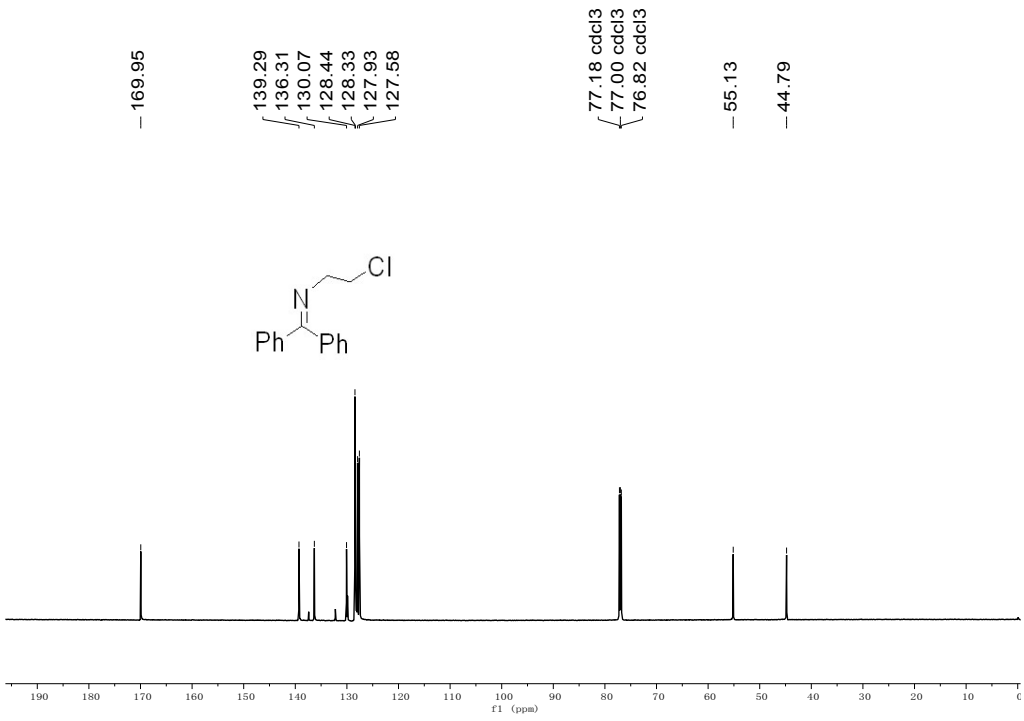


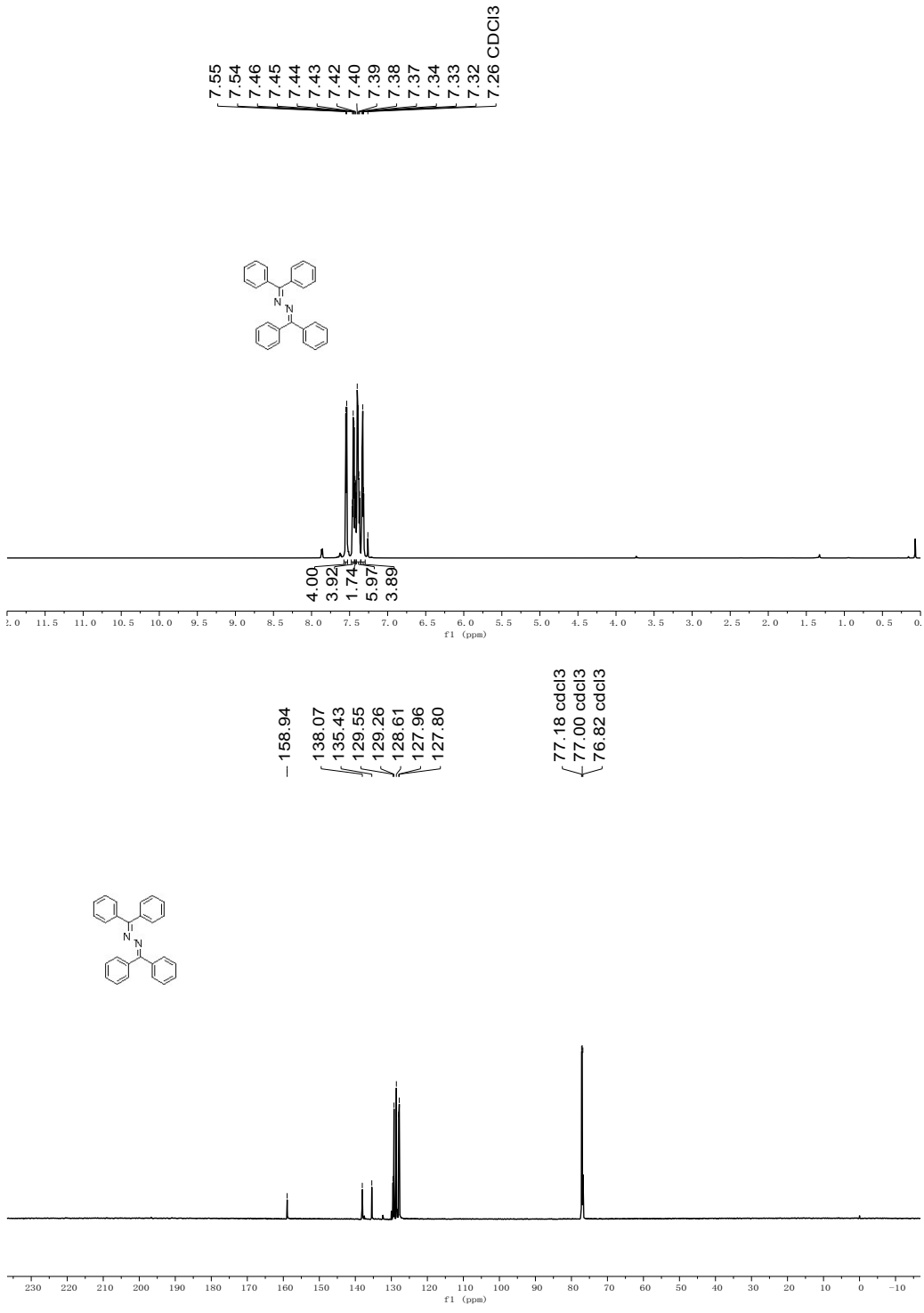
N-(2-chloroethyl)-1,1-diphenylmethanimine

^{1}H NMR (700 MHz, Chloroform-d) δ 7.72 – 7.66 (m, 2H), 7.49 (dd, J = 8.0, 6.3 Hz, 2H), 7.47 – 7.44 (m, 1H), 7.41 (t, J = 7.3 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.23 – 7.17 (m, 2H),

3.86 (t, J = 6.4 Hz, 2H), 3.72 (t, J = 6.4 Hz, 2H). ^{13}C NMR (176 MHz, Chloroform-d) δ 170.0, 139.3, 136.3, 130.1, 128.4, 128.3, 127.9, 127.6, 55.1, 44.8.







F. References

[1]A. Laouiti, M.M. Rammah, M.B. Rammah, J. Marrot, F. Couty, G. Evano, Org. Lett. 14 (2012) 6-9.
[2]K. Li, X. Shao, L. Tseng, S.J. Malcolmson, *J. Am. Chem. Soc.*, 140 (2018) 598-601.