

Supporting Information

Cu-catalysed sustainable synthesis of formamide with glycerol derivatives as carbonyl source via a radical-relay mechanism

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S11. General information and characterization methods

All solvents and chemicals were obtained commercially and were used as received. Zeolite 5A (Si/Al = 1) was received from Tianjin Komiou Chemical Reagent Co., Ltd and used as the support after being grinded into powder.

Mass spectra were in general recorded on an Agilent 5977A MSD GC-MS.

The contents of Cu in the catalysts were measured by a Varian 715-ES inductively coupled plasma-optical emission spectrometer (ICP-OES).

Nitrogen adsorption-desorption isotherms were measured at 77 K using an American Quantachrome iQ₂ automated gas sorption analyzer. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm.

XRD measurements were conducted by a STADI P automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator using CuK α 1 radiation and a 6° position sensitive detector (PSD).

The surface elemental composition of the catalysts was determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi).

STEM analysis was carried out on a JEOL JEM ARM200F probe aberration corrected scanning transmission electron microscope operating at 200 kV. The microscope is equipped with a JEOL DrySD60GV EDXS. The catalysts were dry deposited on carbon-coated nickel grids and investigated by using a low background specimen holder.

¹H NMR spectra were measured by using a Bruker ARX 400 or ARX 100 spectrometer at 400 MHz. All spectra were recorded in CD₃Cl, and chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks.

S12. Typical procedure for the preparation of CuZr/5A catalyst.

The catalyst was prepared an ion-exchange method our previously reported.¹ Cu(NO₃)₂·3H₂O (38 mg) and Zr(NO₃)₄·5H₂O (67.5 mg) with a molar ratio of Cu and Zr = 1:1, was dissolved in 60 mL deionized water and then 2g 5A molecular sieves (MS) were added as supports. The mixture was stirred at 60 °C for 12 h, then filtered and washed with 100 mL deionized water, and dried at 80 °C for 12 h. The obtained solid sample was calcined at 450 °C for 4 h in a muffle furnace in air with a heating ramp of 5 °C/min and the final catalyst sample is denoted as CuZr/5A. All other catalysts such as Cu/5A, CuNi/5A, CuAg/5A, CuPd/5A and CuRh/5A were prepared in the same way with the metal precursor of Cu(NO₃)₂·3H₂O, Ni(NO₃)₂·6H₂O, AgNO₃, H₂PdCl₄ (Pd, 5 mg/mL) and RhCl₃ (Rh, 5 mg/mL), respectively.

S13. Typical procedure for the N-formylation of aniline with DHA.

The N-formylation reaction was performed in a 38 mL pressure tube. 0.33 mmol 1,3-dihydroxyacetone (DHA), 3 mmol aniline, 6 mmol H₂O₂ (35wt%), 5 mg CuZr/5A catalyst, and 2 mL 1,4-dioxane were added to the reactor. Then, the reaction mixture was heated to 50 °C (oven temperature) and held at the reaction temperature for 24 h under magnetic stirring. After completion of the reaction, 50 mg biphenyl dissolved in 10 mL ethanol were added for quantitative analysis by GC-FID. The N-formylation of other amines with DHA and the N-formylation of aniline with glyceraldehyde and glycolic acid (0.5 mmol) were performed in the same way.

The recyclability test of the active catalyst CuZr/5A was performed with the model reaction between aniline and DHA under the optimized reaction conditions: 0.33 mmol DHA, 3 mmol aniline, 6 mmol H₂O₂ (35 wt.%), 5 mg CuZr/5A catalyst, 2 mL 1,4-dioxane, 50 °C, 24 h. After each run, the catalyst was recovered by simple centrifugation, washing by ethanol (3 × 8 mL) and drying at 60 °C for 4 h, and reused after calcination treatment at 450 °C for 4 h in a muffle furnace in air with a heating ramp of 5 °C/min.

S14. Typical procedure for the NH₃-TPD.

NH₃-TPD was performed on a chemisorption analyzer equipped with a thermal conductivity detector (TCD). The chemisorption analyzer was TP-5080D from Tianjin Xianquan Industrial and Trading Co., Ltd. The weighed sample (100 mg) was pretreated at 400 °C for 1 h under He (40 mL·min⁻¹) and cooled to 100 °C. Then NH₃ gas (30 mL·min⁻¹) was introduced at this temperature for 0.5 h to ensure the saturation adsorption of NH₃. The sample was then purged with He for 1 h (40 mL·min⁻¹) until the signal returned to the baseline as monitored by a thermal conductivity detector (TCD). The desorption curve of NH₃ was acquired by heating the sample from 100 °C to 700 °C at the ramp of 10 °C·min⁻¹ under He with the flow rate of 40 mL·min⁻¹.

S15. Typical procedure for the EPR spin-trapping experiments with DMPO.

The EPR spin-trapping experiments for the activation of H₂O₂ by catalysts were performed at room temperature. The mixture of 5 mg CuZr/5A catalyst and 50 μ L (about 2 mmol) H₂O₂ (35wt%) were directly mixed with 10 μ L DMPO. The mixed solution was transferred to a glass microcapillary tube (Hirschmann). Then, the capillary tube was placed into a quartz EPR tube (ϕ 4×250mm), and EPR

spectra were recorded immediately at room temperature. All spectra were obtained under the following conditions: central field = 3430 G; sweep width = 100 G; sweep time = 30 s; microwave frequency = 9.63729 GHz; microwave power = 0.3162 mW. Signal fitting was carried out by using the Spin Fit program (Bruker).

The EPR spin-trapping experiments for the reaction of aniline and DHA were performed at 50 °C (oven temperature) in a round bottom flask containing 5 mg CuZr/5A catalyst, and then the starting materials were added by the order of 6 mmol H₂O₂ (35wt%), 0.33 mmol DHA dissolved in 2 mL 1,4-dioxane, and 3 mmol aniline. The reaction mixture was held at the reaction temperature for 7 h under magnetic stirring. 50 µL reaction solutions were withdrawn and immediately mixed with 10 µL DMPO. The mixed solution was transferred to a glass microcapillary tube (Hirschmann). Then, the capillary tube was placed into a quartz EPR tube (φ4×250mm), and EPR spectra were recorded immediately at room temperature. All spectra were obtained under the following conditions: central field = 3430 G; sweep width = 100 G; sweep time = 30 s; microwave frequency = 9.63729 GHz; microwave power = 0.3162 mW. Signal fitting was carried out by using the Spin Fit program (Bruker).

SI6. Typical procedure for the operando ATR-FTIR experiments.

Operando ATR-FTIR spectra were recorded in the range from 650 to 1900 cm⁻¹ by a Mettler Toledo *ReactIR15* IR spectrometer equipped with a fiber-optical immersion probe using diamond as the ATR element. Operando ATR-IR experiments were carried out in a three-necked round bottom flask. The starting materials were added into the mixture of CuZr/5A catalyst (5 mg) and 1,4-dioxane (2 mL) by the order of 0.33 mmol DHA, 3 mmol aniline and 6 mmol H₂O₂ (35wt%).

SI7. Fig. S1-S10.

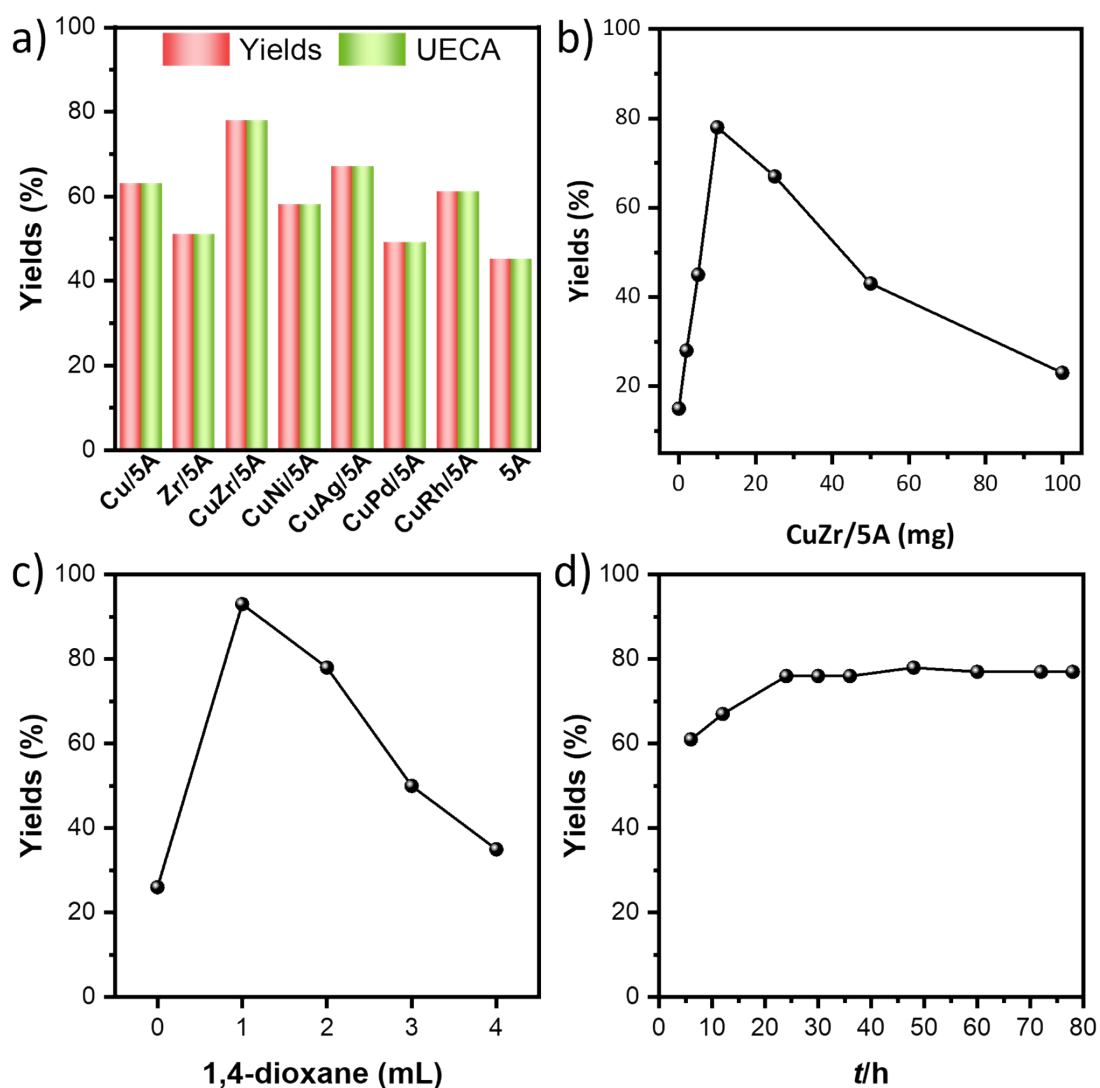


Fig. S1 a) Activity test of different catalysts. Reaction conditions: 0.33 mmol DHA (1 mmol carbon source), 3 mmol aniline, 4 mmol H₂O₂ (35wt%), 10 mg catalysts, 2 mL 1,4-dioxane, 50 °C, 24 h. Utilization efficiency of carbon atoms (UECA) in DHA = 100% × (n_{formamide product yields with DHA} - n_{formamide product yields without DHA}) / n_{carbon atoms in DHA} (mol/mol). Effect of b) catalyst (Reaction conditions: 0.33 mmol DHA, 3 mmol aniline, 4 mmol H₂O₂ (35wt%), 0-100 mg CuZr/5A, 2 mL 1,4-dioxane, 50 °C, 24 h.) and c) solvents (Reaction conditions: 0.33 mmol DHA, 3 mmol aniline, 4 mmol H₂O₂ (35wt%), 10 mg CuZr/5A, 0-4 mL 1,4-dioxane, 50 °C, 24 h.) amount on the catalytic performance. d) Activity test of CuZr/5A under continuous flow. Reaction conditions: CuZr/5A 0.2 g with a particle size of 350-833 μm, DHA 3 g, aniline 27.9 g and 35wt% H₂O₂ 58.2 g, 20 mL deionized water and 200 mL 1,4-dioxane, 0.005 mL/min, 50 °C). In the test, 0.3 g quartz sand particles with the same size as the catalyst particle was mixed with the catalyst to avoid the block of the reactor.

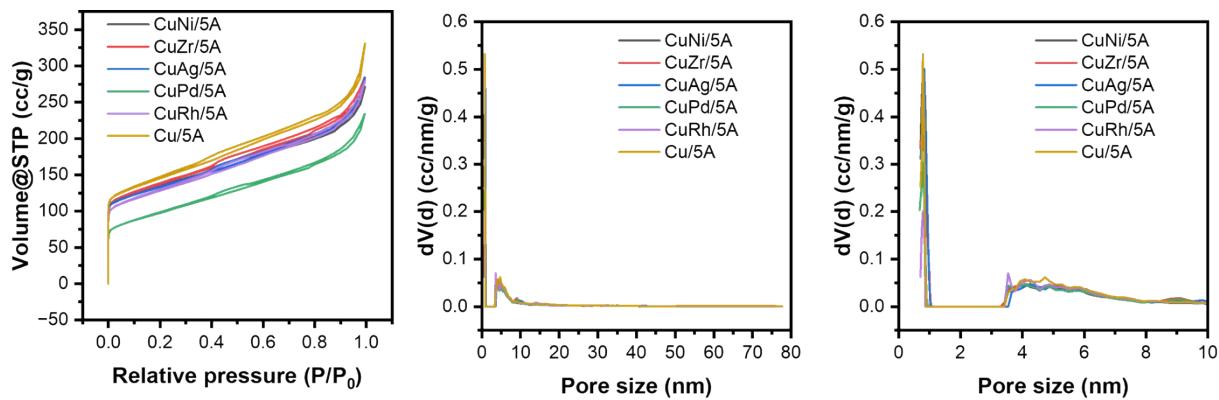


Fig. S2 N₂ adsorption-desorption analysis of the prepared catalysts.

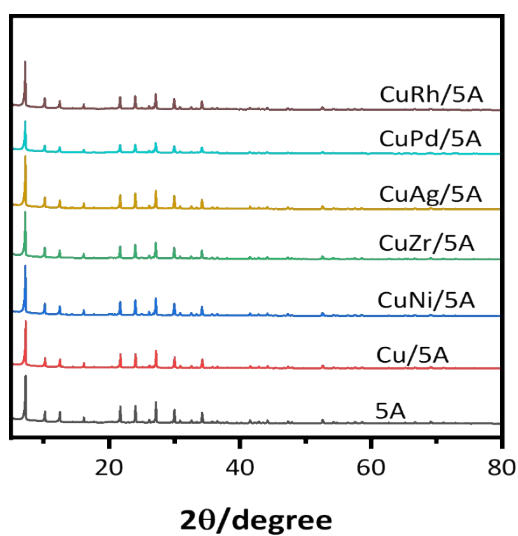


Fig. S3 XRD pattern of the 5A support and prepared catalysts.

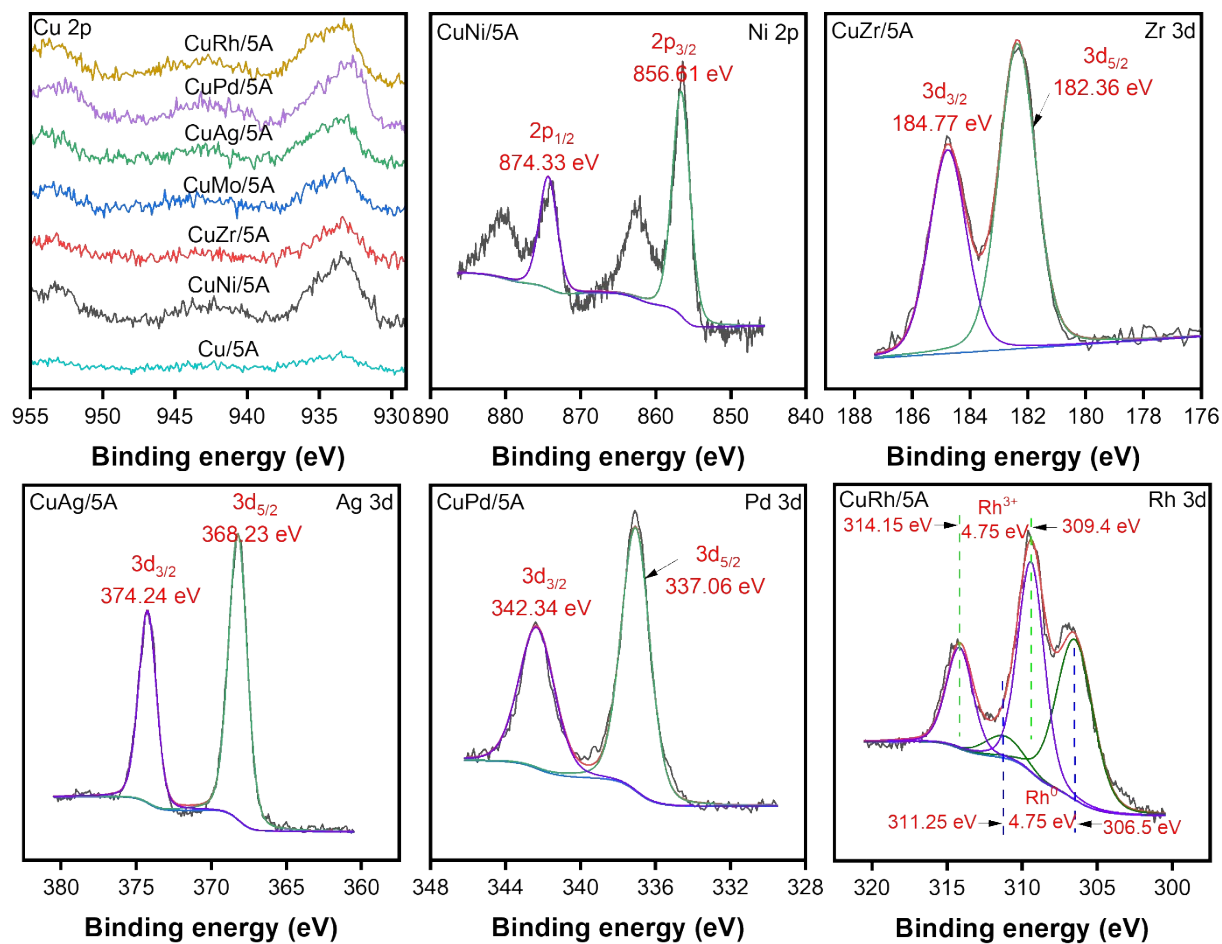


Fig. S4 XPS spectra of Cu 2p and the second metals of the prepared catalysts.

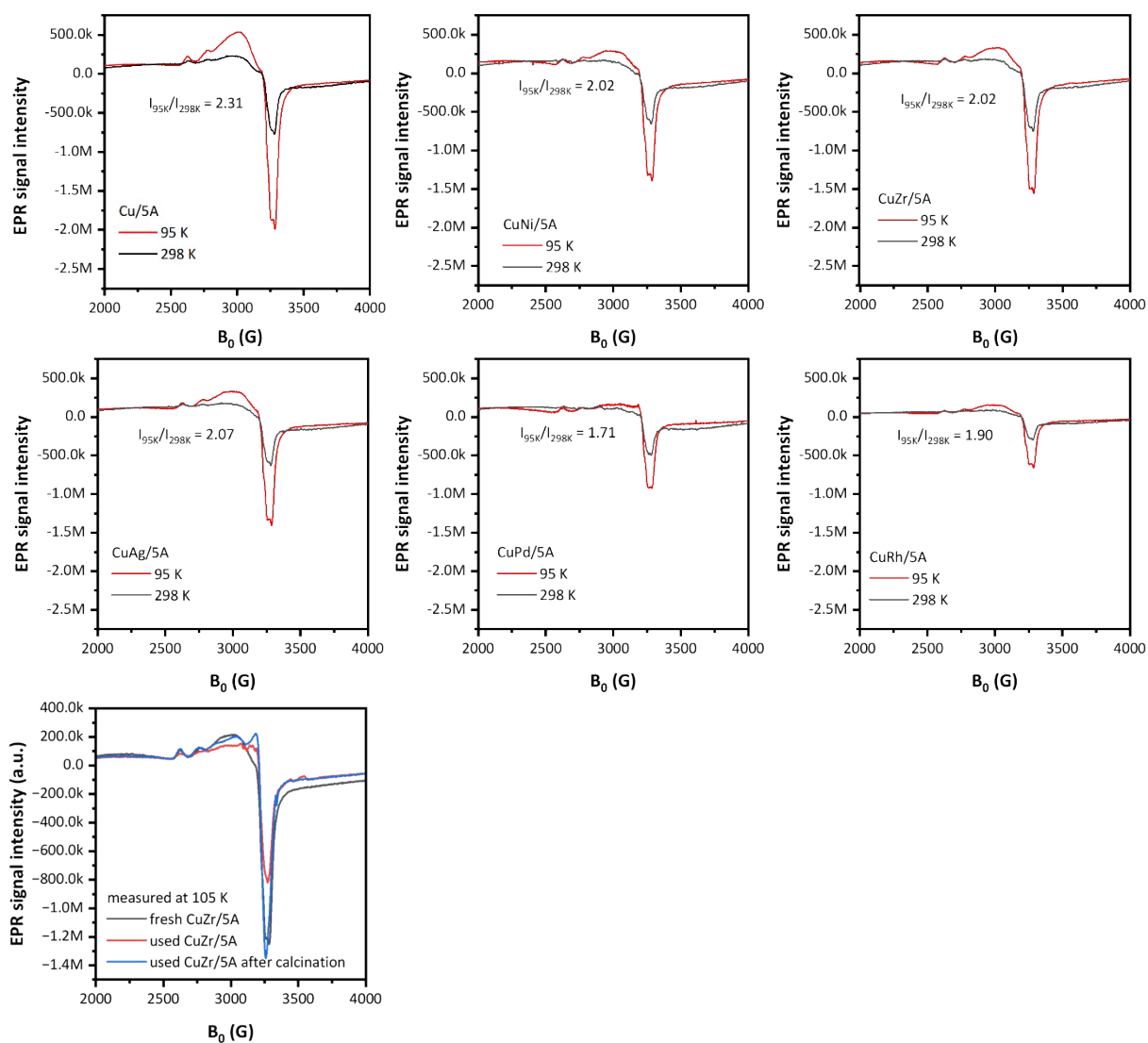


Fig. S5 EPR spectra of prepared catalysts measured at 95 K and 298 K, and EPR spectra of the fresh and used CuZr/5A catalyst measured at 105 K.

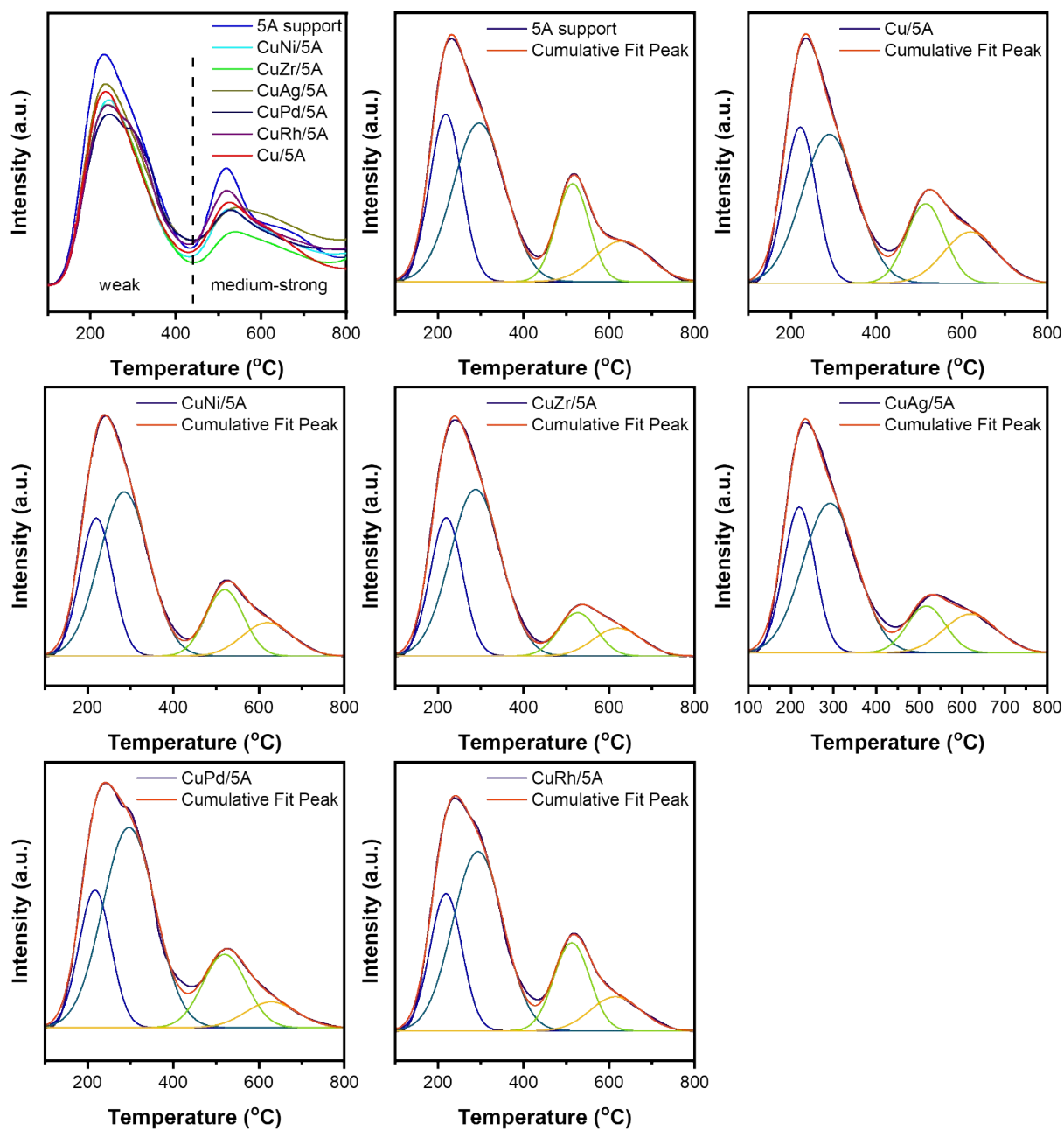


Fig. S6 NH₃-TPD pattern of catalysts.

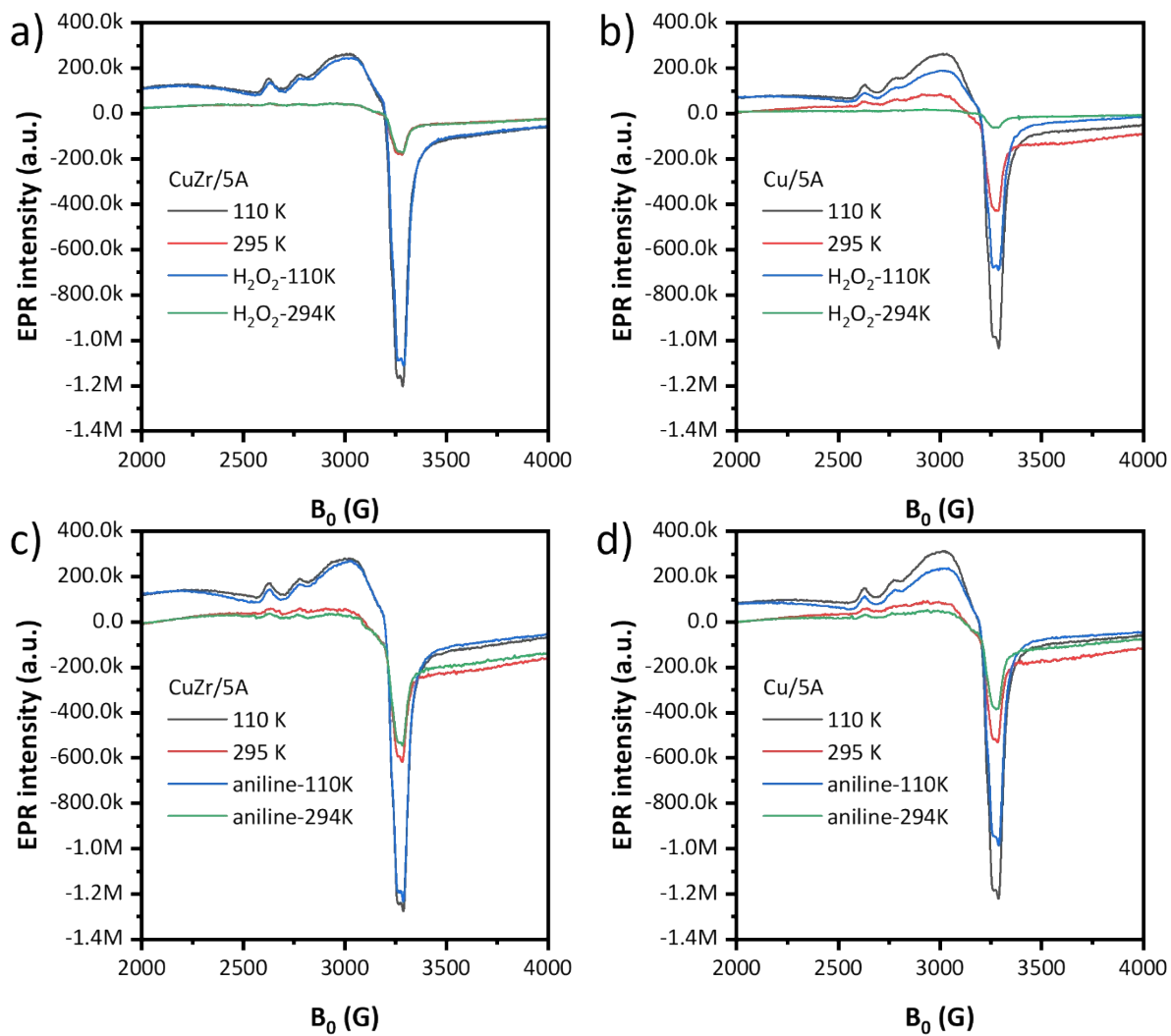


Fig. S7 EPR spectra of CuZr/5A and Cu/5A catalysts before and after being immersed in H_2O_2 and aniline.

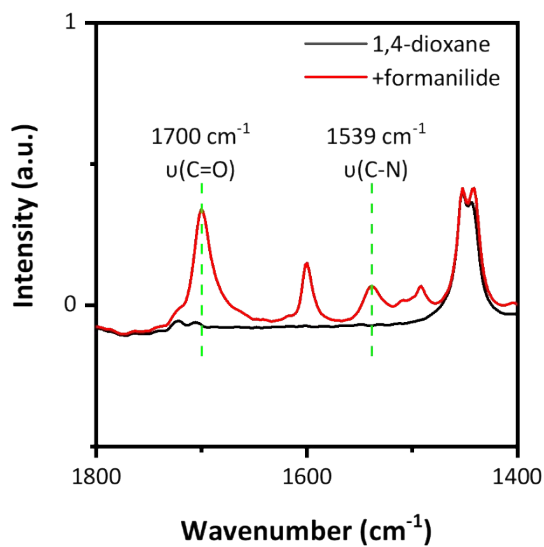


Fig. S8 ATR-FTIR spectra of the formanilide standard sample in 1,4-dioxane.

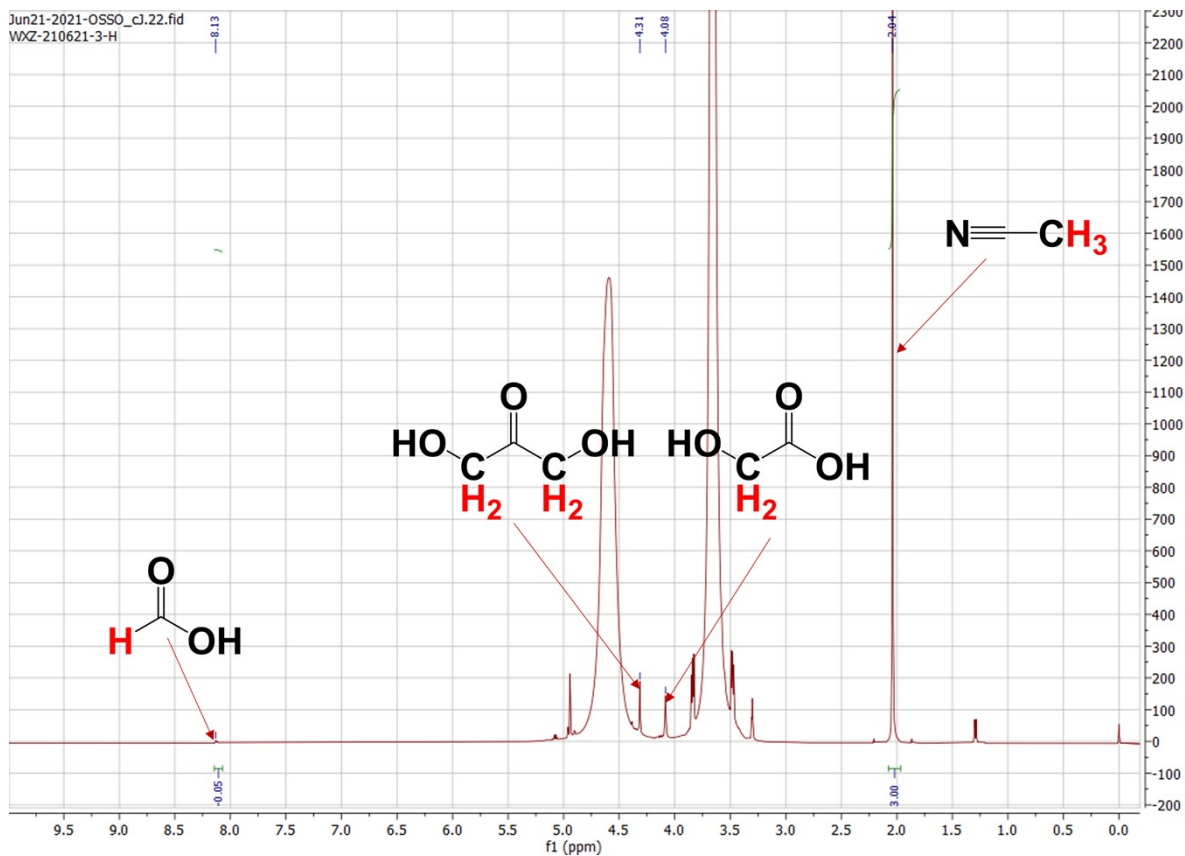


Fig. S9 ^1H NMR spectrum of the control reaction of DHA to GA and FA without aniline. Acetonitrile was used as the external standard sample.

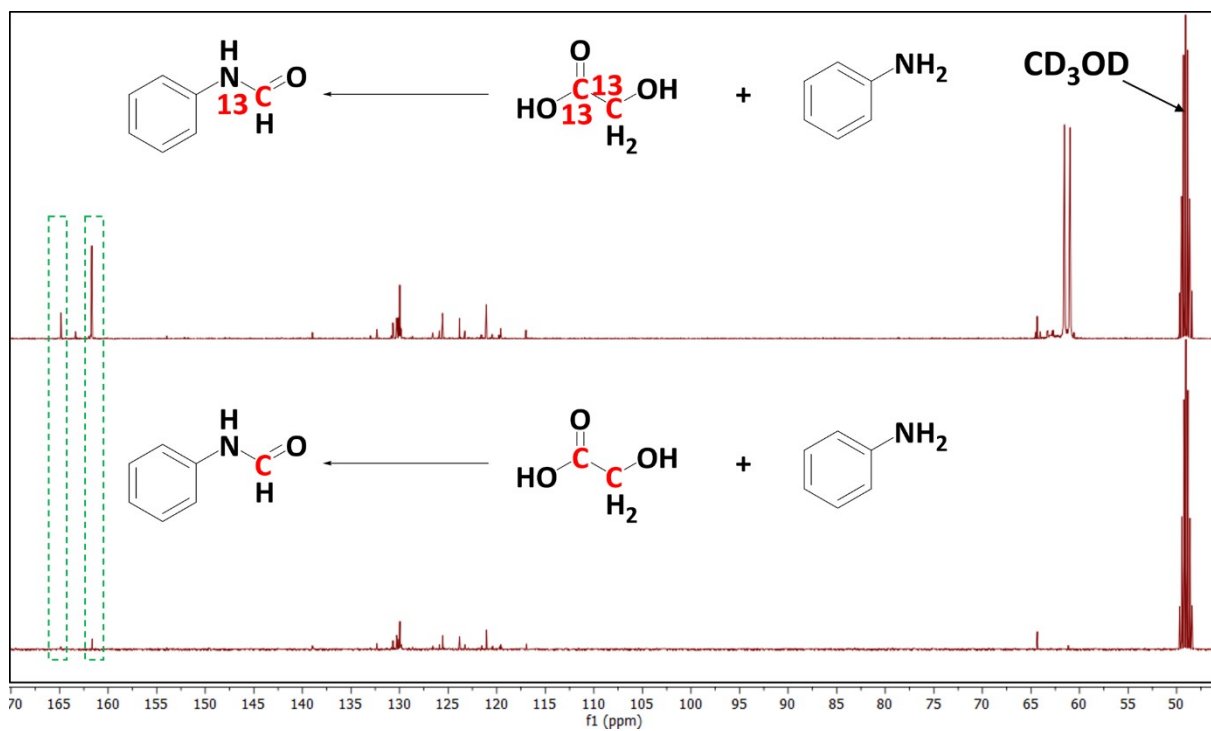


Fig. S10 Control experiments: the reaction of ^{13}C labeled GA with aniline.

S18. Tables S1-S2.

Table S1 Optimization of reaction conditions and catalyst screening

Entry	Catalysts		aniline /mmol	DHA /mmol	H ₂ O ₂ /mmol	T /°C	t /h	Yields ^a /%
1	5A	10mg	3	--	4	50	24	0
2	Cu/5A	10mg	3	--	4	50	24	0
3	Zr/5A	10mg	3	--	4	50	24	0
4	CuNi/5A	10mg	3	--	4	50	24	0
5	CuZr/5A	10mg	3	--	4	50	24	0
6	CuAg/5A	10mg	3	--	4	50	24	0
7	CuPd/5A	10mg	3	--	4	50	24	0
8	CuRh/5A	10mg	3	--	4	50	24	0
9	CuRh/5A	10mg	3	0.33	4	40	24	57
10	CuRh/5A	10mg	3	0.33	4	25	24	28

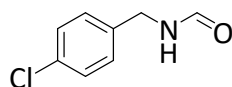
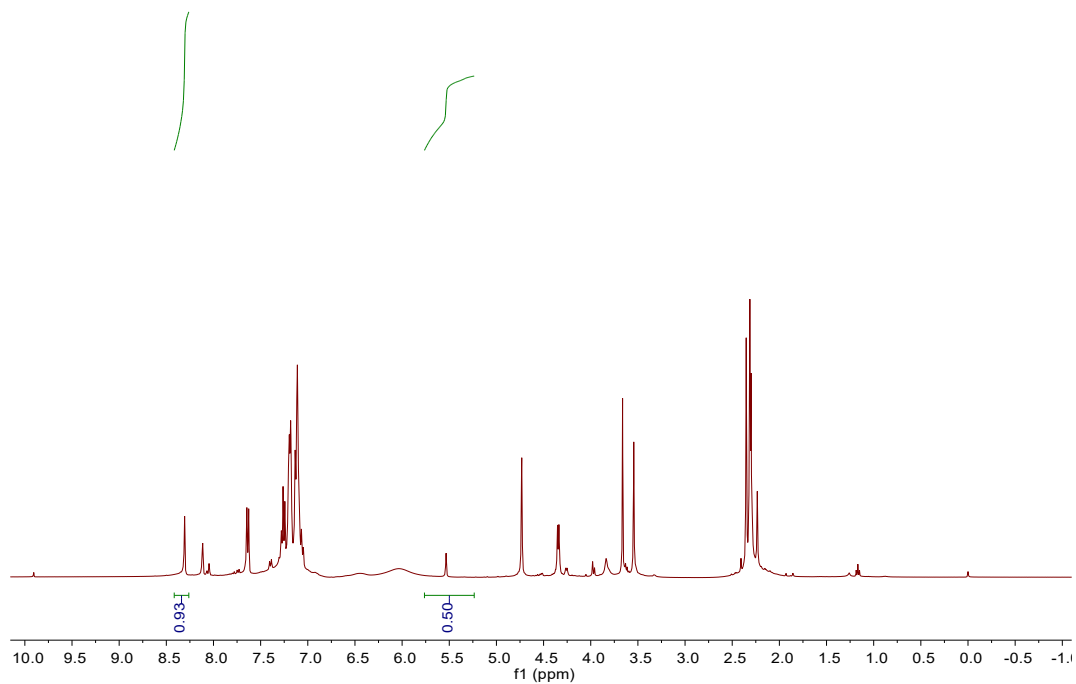
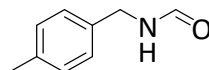
^aProduct yields were determined by GC-FID with biphenyl as the external standard.

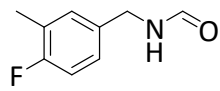
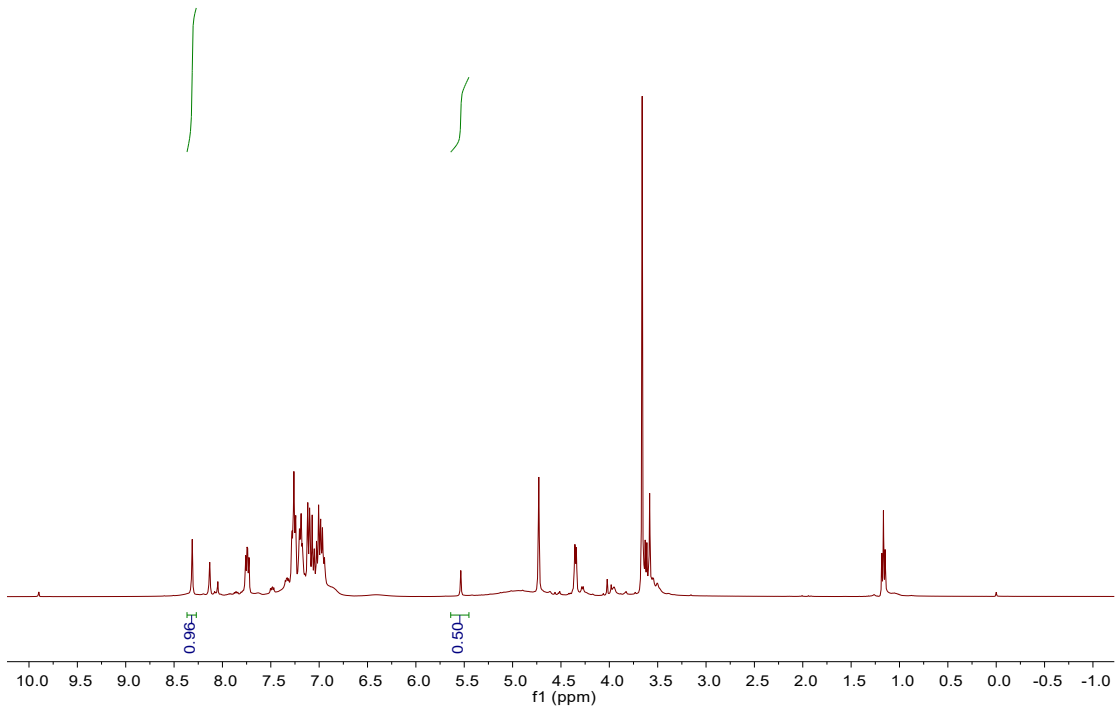
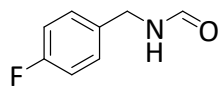
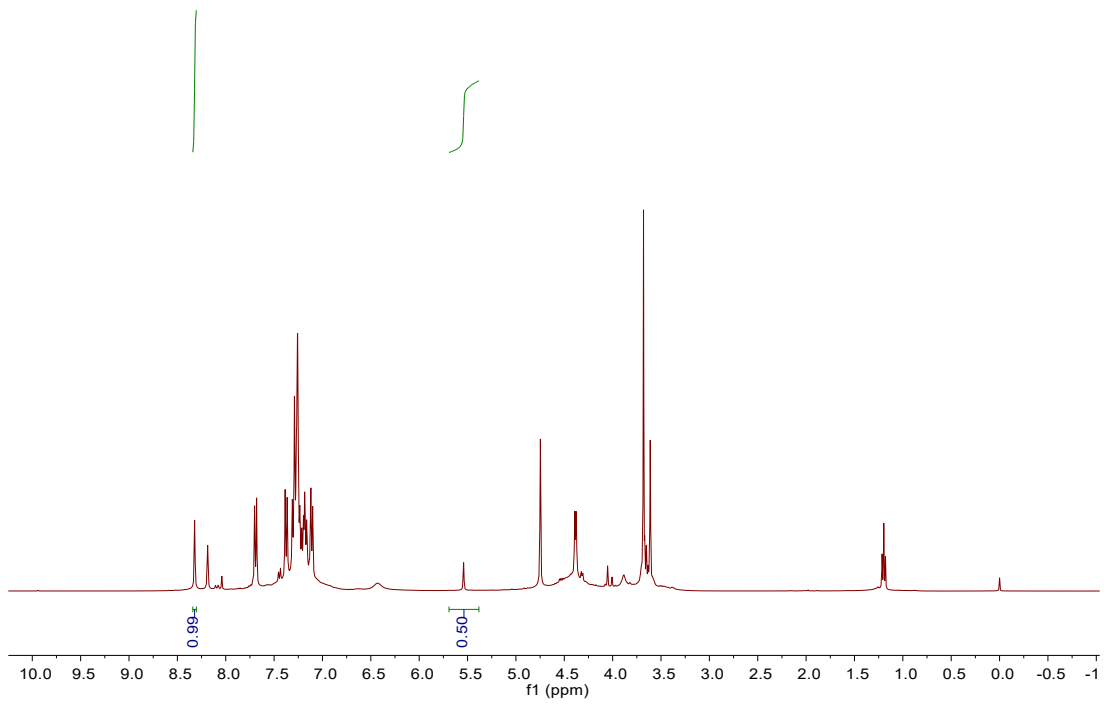
Table S2 The Cu content and basic physical property of catalysts

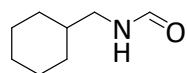
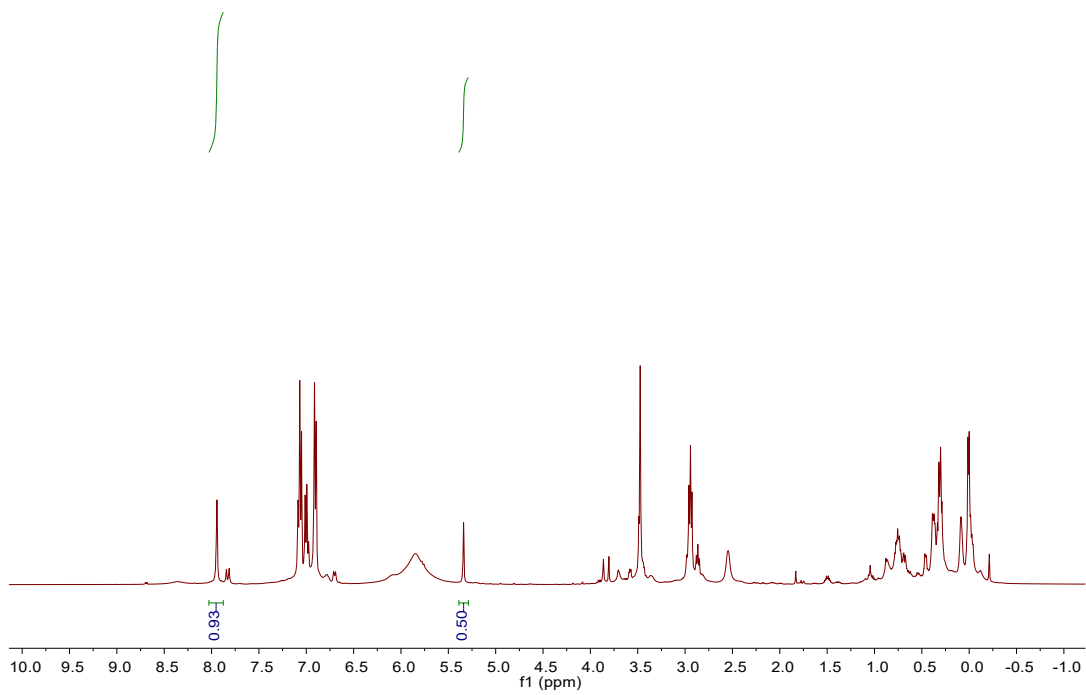
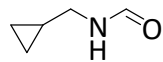
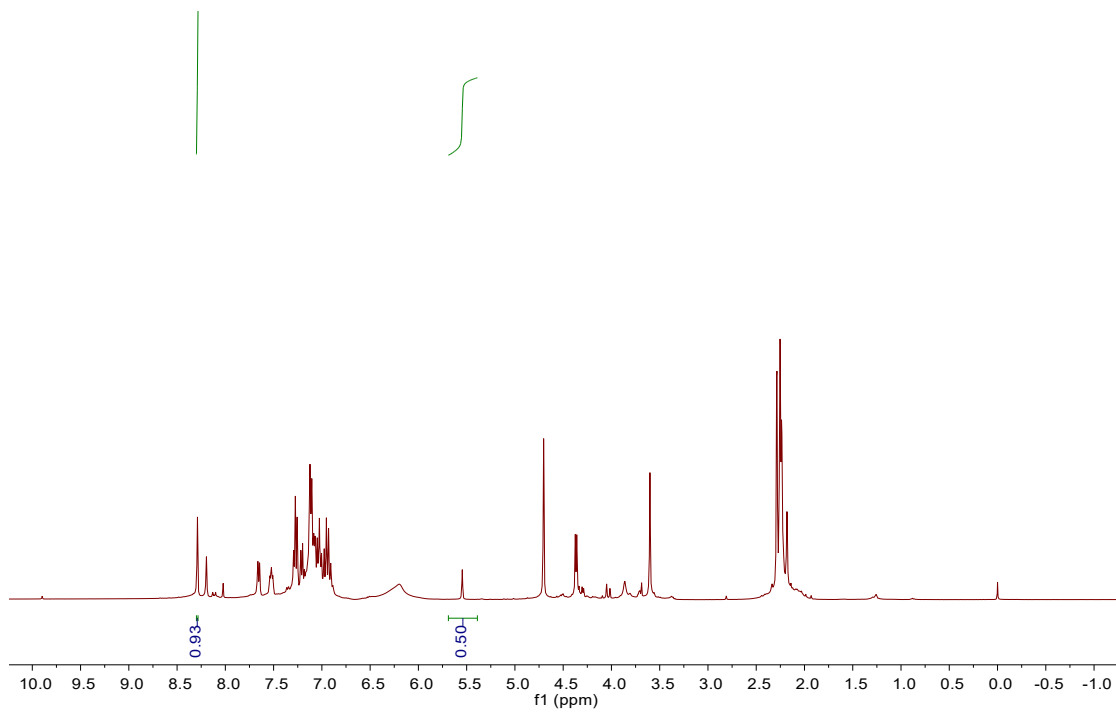
Entry	Catalysts	Cu content ^a /wt%	BET surface area /m ² g ⁻¹	Total pore volume /cm ³ g ⁻¹	Average pore size /nm
1	Cu/5A	0.51	521.6	0.512	3.9
2	CuNi/5A	0.51	491.0	0.421	3.4
3	CuZr/5A	0.51	496.1	0.441	3.6
4	CuAg/5A	0.56	484.3	0.439	3.6
5	CuPd/5A	0.51	344.4	0.362	4.2
6	CuRh/5A	0.53	459.2	0.432	3.8

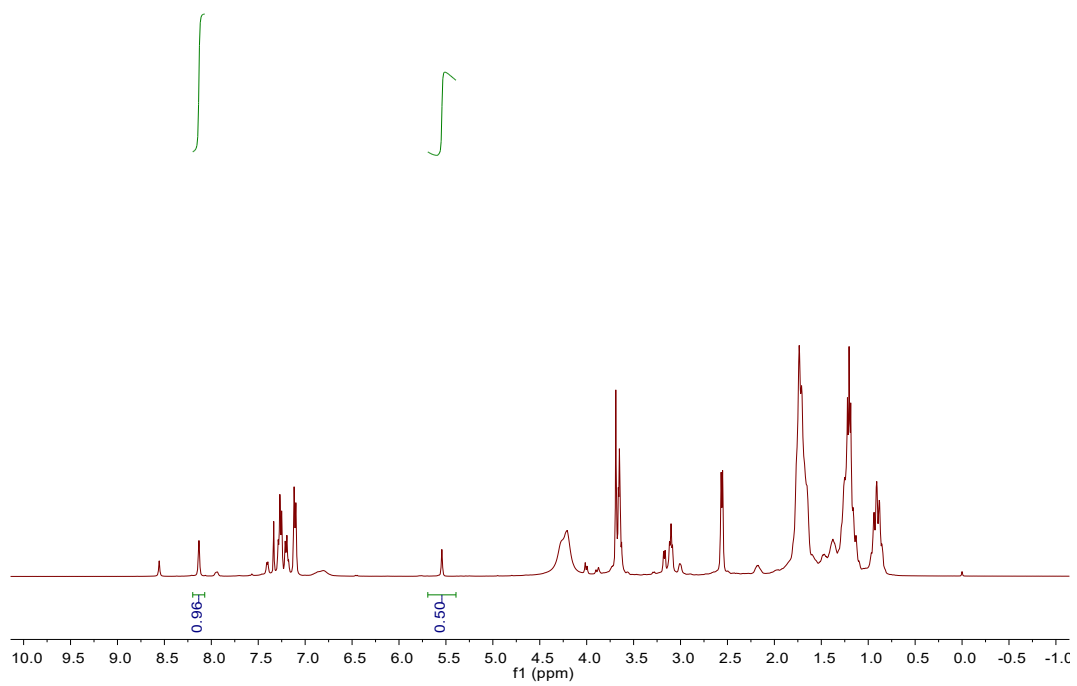
S19. NMR.

^1H NMR yields: After the reaction finished, the press tube was cooled to room temperature and 0.5 mmol triphenylmethane was added. Subsequently, the reaction mixture was diluted with 10 mL ethanol and centrifuged. Then, 1 mL of the supernatant liquid was taken and concentrated by a rotary evaporator. Finally, 0.5 mL CDCl_3 was added for quantitative analysis by ^1H NMR.









1. X. Dai, X. Wang, J. Rabeah, C. Kreyenschulte, A. Brückner and F. Shi, *Chem. Eur. J.*, 2021, **27**, 16889–16895.