Supporting Information for

A porous metal-organic framework containing multiple active Cu^{2+} sites for highly efficient cross dehydrogenative coupling reaction

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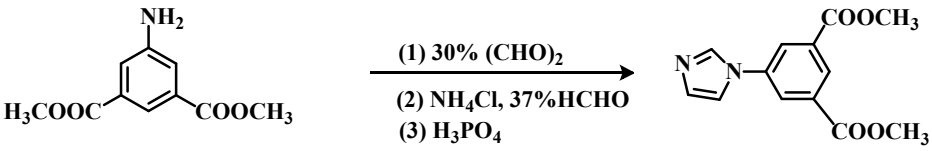
Experimental Section

Materials and methods. All reagents and solvents were obtained from commercial sources and used as received without further purification. FT-IR spectra were recorded from KBr pellets on a FTS-40 spectrophotometer. PXRD were recorded on a RIGAKU D/MAX 2550/PC for Cu-Kα radiation (λ = 1.5406 Å). TGA was carried out under N_2 atmosphere on a NETZSCH STA 409 PC/PG instrument at a heating rate of 10 ^oC min^{-1}. Elemental analysis was performed on a ThermoFinnigan Flash EA 1112 elementary analyzer. UV-Vis spectra were recorded on a UNICO 2802 spectraphotometer.

Single crystal X-ray data collection and structure determination. The determination of the unit cell and data collection for the crystal of **1** were performed on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector. The data were collected using graphite-monochromatic enhanced ultra Cu radiation (λ = 1.54178 Å) at 293 K. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[S1] The structure of compound **1** was solved by direct methods and refined by full-matrix least-square methods with the SHELX-97 program package.[S2] Because the solvent molecules and chlorine ions in compound **1** are highly disordered, it is impossible to reasonably map out these guest molecules based on the diffraction data. Therefore, the SQUEEZE subroutine of the PLATON software suits was used to remove the scattering from the highly disordered guest molecules. The resulting new

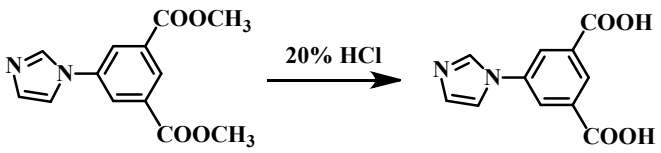
files were used to further refine the structure.[S3] All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. H atoms were generated geometrically.

Synthesis of dimethyl 5-(1*H*-imidazol-1-yl)isophthalate.



Scheme S1. Synthesis of dimethyl 5-(1*H*-imidazol-1-yl)isophthalate.

Dimethyl 5-aminoisophthalate (4.18 g, 0.02 mol), 30% oxalaldehyde aqueous solution (3.24 mL, 0.02 mol) in 250 mL MeOH were stirred at room temperature for 48 h. NH_4Cl (2.14 g, 0.04 mol) and 37% formaldehyde aqueous solution (3.2 mL, 0.04 mol) were stepwise added to the mixture under stirring. The mixture was diluted with 100 mL MeOH, which was refluxed for 1 h. 2.8 mL H_3PO_4 was dropwise added to the mixture, which was further refluxed for 72 h. The mixture was cooled down to room temperature, and filtered to remove insoluble solid. The filtrate was concentrated under reduced pressure, and poured into 100 mL water. The pH value of the mixture was adjusted to ~9 by 40% KOH aqueous solution, which resulted in large amount of light yellow precipitate. The solid was collected by filtration, and washed with water for several times. The product was purified by chromatography on silica gel with hexane/ethyl acetate (2/1). Yield: 2.3 g (44%). ^{1}H NMR (400 MHz, DMSO-d, ppm): δ = 8.26 (s, 2H), 7.97 (s, 1H), 7.39 (s, 1H), 7.27 (s, 1H), 4.00 (s, 6H).



Scheme S2. Synthesis of 5-(1*H*-imidazol-1-yl)isophthalic acid (H_2**L**).

Synthesis of 5-(1*H*-imidazol-1-yl)isophthalic acid (H_2L).

In a 50 mL round bottomed flask, dimethyl 5-(1*H*-imidazol-1-yl)isophthalate (1.3 g, 5 mmol) in 10 mL 20% HCl aqueous solution was refluxed for 12 h. The mixture was cooled down to room temperature, and the solvent was removed under reduced pressure to result in light yellow powder. Yield: 0.8 g (73%). ^{1}H NMR (400 MHz, DMSO-d, ppm): δ = 9.9 (s, 1H), 8.57 (s, 2H), 8.54 (s, 1H), 8.47 (s, 1H), 7.94 (s, 1H), 3.54-3.57 (t, 2H), 2.96-2.99 (t, 2H). ^{13}C NMR (400 MHz, DMSO-d, ppm): δ = 164, 165, 136, 133, 131, 130, 127, 120. IR (KBr pellet. υ/cm^{-1}): 1729(s), 1600(m), 1574(m), 1539(m), 1448(m), 1402(m), 1346(m), 1293(m), 1255(s), 1205(s), 1146(m), 1121(m), 1072(s), 995(m), 963(m), 928(m), 893(m), 759(s), 671(m), 657(s), 636(m), 622(m), 573(m).

A typical procedure for the substrate and product adsorption experiments: Solid **1** (20 mg) was added to 2 mL 2-phenyl-1,2,3,4-tetrahydroisoquinoline nitromethane solution (200 mg·L^{-1}), which was stirred at room temperature for 24 h. The mixture was centrifugated, and the plasma was diluted to the appropriate concentrations and analyzed by UV-Vis absorption spectroscopy. The amount of adsorbed 2-phenyl-1,2,3,4-tetrahydroisoquinoline was calculated from the following mass balance equation:

$$Q_{ad} = \frac{(C_0 - C_{ad})}{m} V$$

where Q_{ad} (mmol/g) is the amount of adsorbed 2-phenyl-1,2,3,4-tetrahydroisoquinoline by adsorbent **1**, C_0 is the initial concentration of 2-phenyl-1,2,3,4-tetrahydroisoquinoline in CH_3NO_2 (mmol/L), C_{ad} is the concentration of 2-phenyl-1,2,3,4-tetrahydroisoquinoline after adsorption (mmol/L), V is the volume of the solution (L), and m is the mass of adsorbent **1** (g).

References

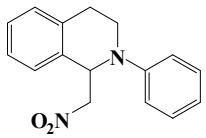
S1. Oxford Diffraction Ltd. CrysAlisPro, Version 1.171.33.56, **2010**.

S2. G. M. Sheldrick, Program for structure refinement, University of Göttingen,

Germany, **1997**.

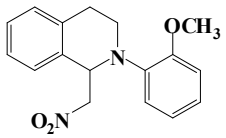
S3. A. L. Spek, Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.,* 2003, **36**, 7.

^{1}H NMR data for the CDC reaction products



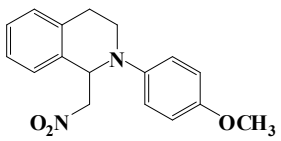
1,2,3,4-tetrahydro-1-(nitromethyl)-2-phenylisoquinoline (a).

^{1}H NMR (400 MHz, $CDCl_3$-d, ppm): δ = 7.13-7.22 (m, 2H), 7.05-7.13 (m, 4H), 6.90-6.92 (d, J = 8.0 Hz, 2H), 6.76-6.79 (t, 1H), 5.46-5.49 (t, 1H), 4.78-4.82 (m, 1H), 4.47-4.51 (m, 1H), 3.51-3.63 (m, 2H), 2.98-3.05 (m, 1H), 2.69-2.75 (m, 1H).



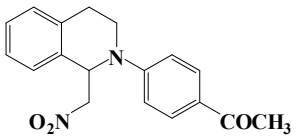
1,2,3,4-tetrahydro-2-(2-methoxyphenyl)-1-(nitromethyl)isoquinoline (b).

^{1}H NMR (400 MHz, $CDCl_3$-d, ppm): δ = 7.13-7.18 (m, 2H), 7.08-7.11 (m, 2H), 6.93-6.98 (m, 1H), 6.75-6.83 (m, 3H), 5.42-5.45 (m, 1H), 4.73-4.78 (m, 1H), 4.45-4.49 (m, 1H), 3.76 (s, 3H), 3.38-3.57 (m, 2H), 2.88-2.96 (m, 1H), 2.61-2.67 (m, 1H).



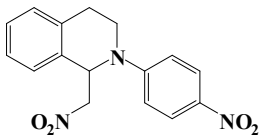
1,2,3,4-tetrahydro-2-(4-methoxyphenyl)-1-(nitromethyl)isoquinoline (c).

^{1}H NMR (400 MHz, $CDCl_3$-d, ppm): δ = 7.05-7.18 (m, 4H), 6.83-6.85 (d, J = 8.0 Hz, 2H), 6.73-6.75 (d, J = 8.0 Hz, 2H), 5.30-5.33 (m, 1H), 4.73-4.78 (m, 1H), 4.46-4.51 (m, 1H), 3.37 (s, 3H), 3.47-3.50 (m, 2H), 2.90-2.98 (m, 1H), 2.59-2.65 (m, 1H).



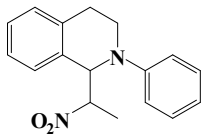
1-(4-(1-(nitromethyl)-3,4-dihydroisoquinolin-2(1H)-yl)phenyl)ethanone (d).

^{1}H NMR (400 MHz, $CDCl_3$-d, ppm): δ = 7.83-7.86 (d, J = 12.0 Hz, 2H), 7.19-7.24 (m, 2H), 7.15-7.18 (d, J = 12.0 Hz, 1H), 7.07-7.09 (d, J = 8.0 Hz, 1H), 6.89-6.91 (d, J = 8.0 Hz, 2H), 5.59-5.62 (t, 1H), 4.78-4.83 (m, 1H), 4.49-4.54 (m, 1H), 3.63-3.66 (t, 2H), 3.02-3.10 (m, 1H), 2.81-2.88 (m, 1H), 2.45 (s, 3H).



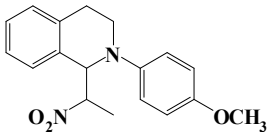
1-(nitromethyl)-2-(4-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (e).

^{1}H NMR (400 MHz, $CDCl_3$-d, ppm): δ = 8.09-8.14 (m, 2H), 7.12-7.27 (m, 2H), 7.10-7.11 (m, 1H), 7.09-7.10 (m, 1H), 6.89-6.91 (m, 2H), 5.62-5.66 (t, 1H), 4.79-4.83 (m, 1H), 4.53-4.58 (m, 1H), 3.66-3.70 (t, 2H), 3.06-3.13 (m, 1H), 2.87-2.93 (m, 1H).



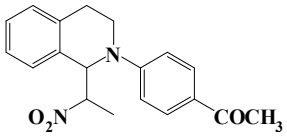
1,2,3,4-tetrahydro-1-(1-nitroethyl)-2-phenylisoquinoline (f).

The ratio of isolated diastereoisomers is 2.0. The major isomer: ^{1}H NMR (400 MHz, $CDCl_3$-d, ppm): δ = 5.17-5.19 (d, *J* = 8.0 Hz, 1H), 4.95-5.02 (m, 1H), 3.49-3.55 (m, 2H), 1.46-1.48 (d, *J* = 8.0 Hz, 3H); The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$-d, ppm): δ = 5.15 (s, 1H), 4.80-4.84 (m, 1H), 3.73-3.81 (m, 2H), 1.62-1.64 (d, *J* = 8.0 Hz, 3H); Other overlapped peaks: δ = 7.21-7.23 (m), 7.11-7.17 (m), 7.02-7.09 (m), 6.91-6.95 (m), 2.95-3.03 (m), 2.81-2.89 (m).



1,2,3,4-tetrahydro-2-(4-methoxyphenyl)-1-(1-nitroethyl)isoquinoline (g).

The ratio of isolated diastereoisomers is 2.0. The major isomer: ^{1}H NMR (400 MHz, $CDCl_3$-d, ppm): δ = 3.73 (s, 3H), 3.46-3.54 (m, 2H), 1.53-1.54 (d, *J* = 4.0 Hz, 3H); The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$-d, ppm): δ = 4.83-4.90 (m, 1H), 3.75 (s, 3H), 1.67-1.69 (d, *J* = 8.0 Hz, 3H); Other overlapped peaks: δ = 7.19-7.25 (m), 7.06-7.16 (m), 6.86-6.93 (m), 6.77-6.84 (m), 2.95-3.03 (m), 2.81-2.89 (m).



1-(1-nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (h).

The ratio of isolated diastereoisomers is 2.0. The major isomer: ^{1}H NMR (400 MHz, $CDCl_3$-d, ppm): δ = 4.93-4.99 (m, 1H), 4.02-4.08 (m, 1H), 3.49-3.63 (m, 2H), 2.43 (s, 3H), 1.48-1.50 (d, *J* = 8.0 Hz, 3H); The minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$-d, ppm): δ = 4.80-4.84 (m, 1H), 3.97-4.02 (m, 1H), 3.79-3.85 (m, 2H), 2.46 (s, 3H), 1.60-1.62 (d, *J* = 8.0 Hz, 3H); Other overlapped peaks: δ = 7.79-7.87 (m), 7.06-7.16 (m), 6.89-6.98 (m), 3.01-3.12 (m).

Figures

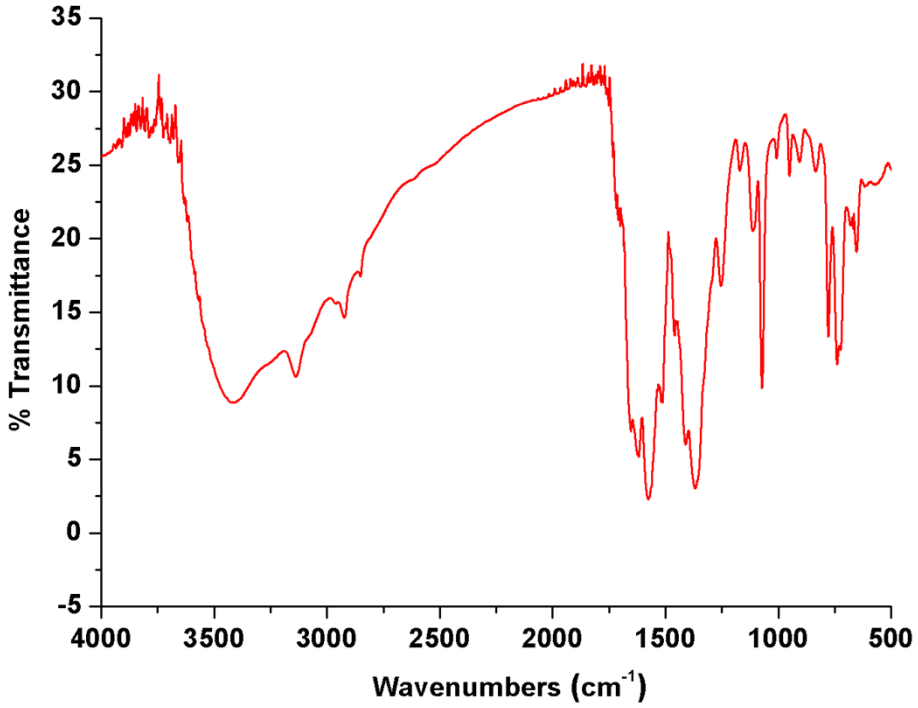


Fig. S1. FT-IR spectrum of **1**.

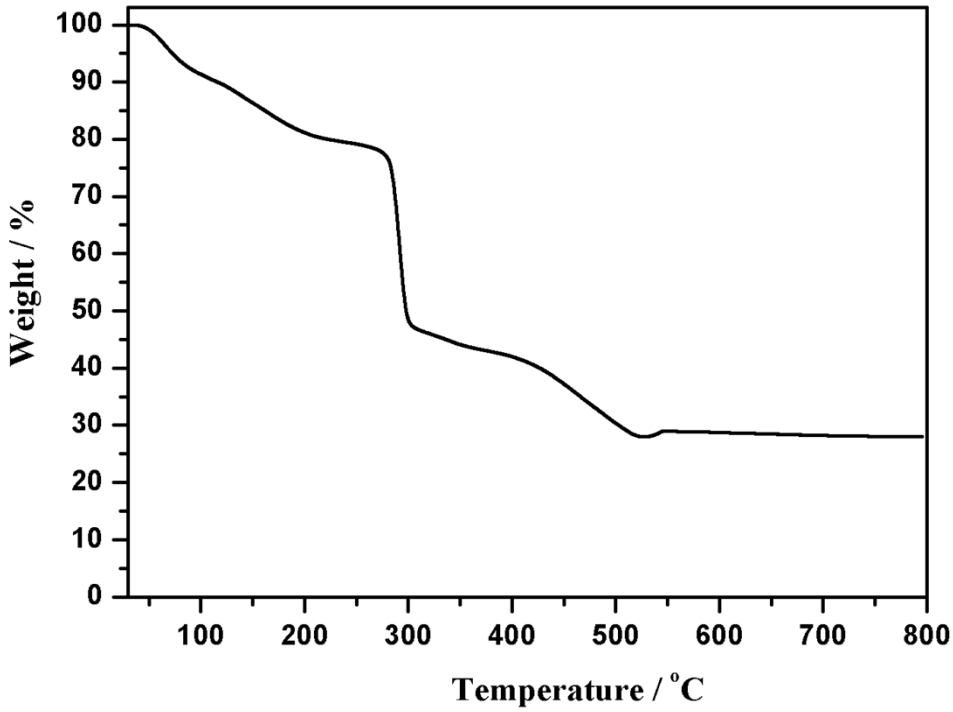


Fig. S2. TGA curve of **1**.

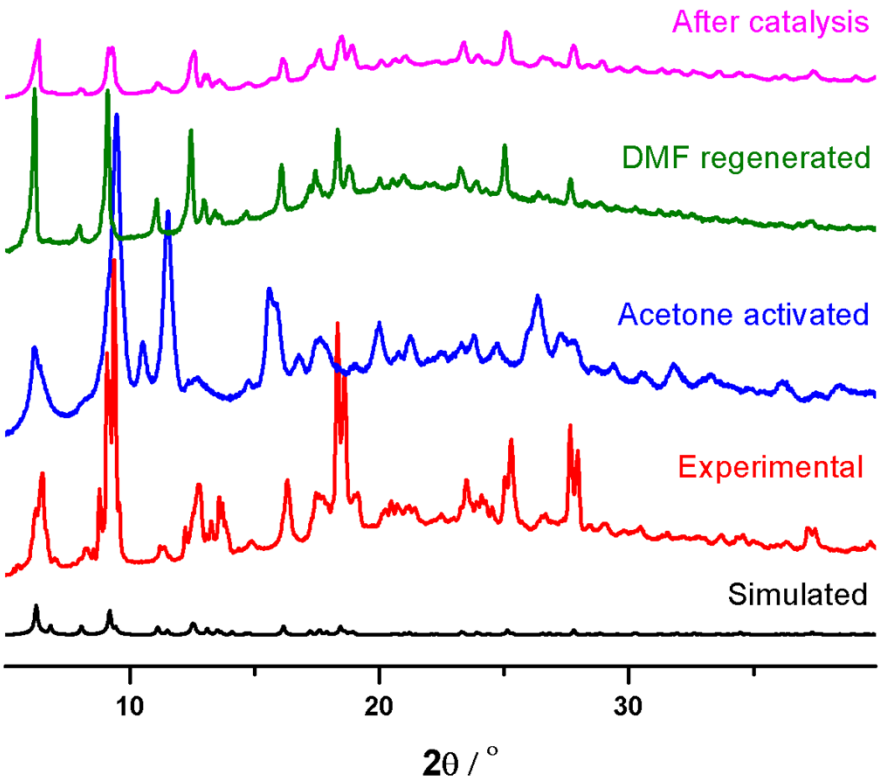


Fig. S3. PXRD patterns for **1**.

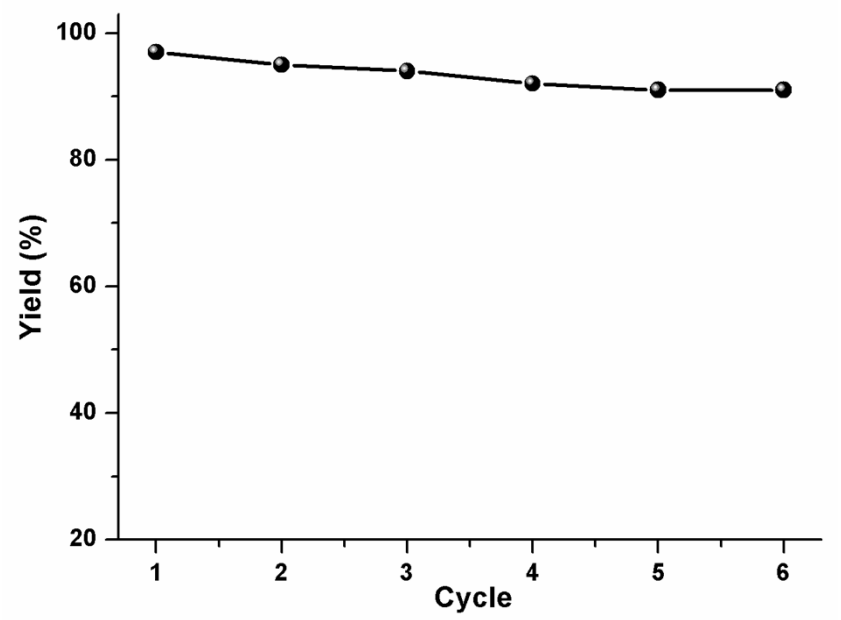


Fig. S4. 1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline yield versus catalytic cycle in the CDC reaction between 2-phenyl-1,2,3,4-tetrahydroisoquinoline and nitromethane catalyzed by **1**.

Table S1. Crystal data and structural refinement for compound **1**

Formula	$C_{22}H_{14}Cu_2N_4O_9$
Formula weight	605.45
Crystal size/mm	0.25 × 0.23 × 0.13
Crystal color	Blue
Crystal system	Monoclinic
Space group	*C*2/m
a (Å)	17.2044(9)
b (Å)	25.9374(14)
c (Å)	14.6116(8)
β (°)	100.672(6)
Volume (Å^3)	6407.5(6)
Z	4
ρ (g.cm^{-3})	0.628
F(000)	1216
μ (mm^{-1})	1.021
θ for data collection (°)	3.08 to 58.92
Reflection collected	9195 (R_{int} = 0.0553)
Data/parameters	4705 / 172
Goodness-of fit on F^2	1.048
R_1 (wR_2) [$I > 2\sigma(I)$]	0.0881 (0.2086)
R_1 (wR_2) (all data)	0.1055 (0.2199)

$R1 = \sum(|F_o| - |F_c|) / \sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.