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# **1** Supporting Information

### 2 MOF-derived Ru@ZIF-8 catalyst with the extremely low metal Ru loading for selective

### 3 hydrogenolysis of C-O bonds in lignin model compounds under mild conditions

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#### **10** Experimental section

Materials. Ru(acac)<sub>3</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, 2-methylimidazole, benzene (>99.7% GC assay) and diphenyl ether (DPE) (>99% GC assay), methylcyclohexane (>99% GC assay), phenethyl phenyl ether (PPE) (> 98% GC assay) and toluene (>99% GC assay) were purchased from Aladdin Chemistry Co., Ltd. Cyclohexanol (>99% GC assay) and benzyl phenyl ether (BPE) (>98% GC assay) were gained from TCI Development Co., Ltd. Phenol (>99%), methanol (>99), cyclohexane (>99.7%) and isopropanol (>99.7%) were provided by Xilong Scientific Co., Ltd. H<sub>2</sub> (>99.999%) and Ar (>99.999%) were supplied by Xuzhou Specialty Gases Co., Ltd.

18 **Catalyst characterization.** The porous structure of catalysts was determined by a V-Sorb 19 4800TP N<sub>2</sub> adsorption-desorption instrument. The catalysts were degassed in N<sub>2</sub> atmosphere at 300 20 °C for 10 h in order to remove gas and moisture absorbed on the catalyst before adsorption. The 21 related information of total pore volume, specific surface area and average pore diameter were 22 analyzed by absorbed volume of nitrogen at a relative pressure  $P/P_0$  of 0.99 and the multipoint BET

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23 equation. The measurement accuracy of  $N_2$  adsorption-desorption instrument is that the repeatability 24 error is less than 1.5%.

X-ray diffractometer (XRD) was performed to test the crystalline structures of the samples on a
Bruker D8 Advance diffractometer using Cu-Kα radiation at 40 kV and 30 mA. The 2θ angel range
was scanned from 5° to 90° at a step size of 4 °/min. XRD diffractometer has high precision that the
reproducibility of the diffraction angle is up to 0.0001°.

29 Raman spectra were collected on a microscopic confocal Raman spectrometer (HORIBA30 EVOLUTION) with a 532 nm laser.

The inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 720ES)
measurement was conducted to analyze the metal elemental of the synthesized materials.

The morphologies of the catalysts were investigated by ZEISS Gemini SEM 500 scanning electron microscope (SEM) and FEI Talos S-FEG high-angle annular dark-field scanning transmission electron microscopic (HAADF-STEM).

FEI Tecnai G2 F20 transmission electron microscopy (TEM) was employed to investigate the morphologies of the catalysts. The sample was mixed with alcohol and deposited on a Cu grid covered with a perforated carbon membrane.

The reacted products were analyzed by Thermo Fisher Scientific Trace1300-ISQ7000 gas chromatograph/mass spectrometer (GC-MS). Liquid analysis was implemented on a Shimadzu GC-2014 gas chromatograph (GC) equipped with a flame ionization detector (FID) for isolating hydrocarbons on an alumina Bound/Na<sub>2</sub>SO<sub>4</sub> capillary column. Argon was used as the carrier gas and protective gas. The determined procedure of GC was as follows: The initial temperature value of column oven was set to 40. Ramp 1 was later adjusted at 1 °C /min to 60 °C. Ramp 2 was adjusted at 15 °C /min from 60 to 250 °C. The split ratio of chromatographic column was 39:1. The injector

- 46 temperature was 250 °C, and injected sample volume was 0.4  $\mu$ L. The external standard analysis was
- 47 used for quantification.





Fig. S1 XRD patterns of the ZIF-8 and Ru(acac)<sub>3</sub>@ZIF-8



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Fig. S2 XPS spectra for the survey scan of fresh Ru@ZIF-8



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Fig. S3 XRD patterns of the fresh and spent Ru@ZIF-8 (after four cycles)

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Fig. S4 XPS spectra for Zn 2p of the spent Ru@ZIF-8 (after four cycles)



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Fig. S5 TEM images of the spent Ru@ZIF-8 (after four cycles)

## 58 Table S1 The content of Zn or Ru metal in the samples <sup>a</sup>

sample	Zn metal content (wt.%)	Ru metal content (wt.%)
ZIF-8	25.5704	0
Ru(acac) <sub>3</sub> @ZIF-8	23.8695	0.0118

59 <sup>a</sup> detected by ICP-OES.