

Catalytic self-transfer hydrogenolysis of lignin over Ni/C catalysts

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Materials

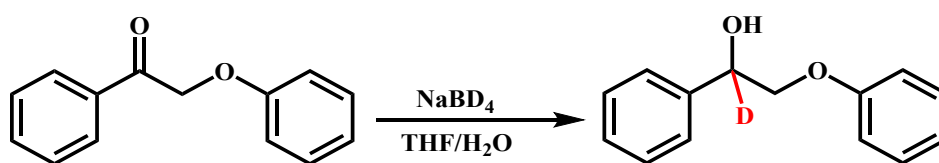
1,4-naphthalenedicarboxylic acid (95.0%), Phenethoxybenzene (98.0%), 1-Phenylethanol (99.0%), Ethyl acetate (99.9%), Phenylacetaldehyde (95.0%), Styrene (99.5%), 2-phenoxy-1-phenylethanol (99.0%), 3,4-Dimethoxyacetophenone (98.0%), 3,4-Dimethoxytoluene (98.0%) and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (95.0%), NaBD₄ (95.0%) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. 2-Phenoxy-1-phenylpropan-1-ol (99.24%) and 1-(3,4-Dimethoxyphenyl)propan-1-one (95%) was obtained from ARK. 2-(2-Methoxyphenoxy)-1-phenylethanol (99.0%) was purchased from Shanghai Achem-block Co. Ltd. 2-Phenoxyacetophenone (98.0%), Phenol (99.9%), Cesium carbonate (98.0%), CuI (98.0%) and 1-Methyl-2-pyrrolidone (99.0%) were provided by TCI (Shanghai) Development Co. Ltd. Ni(NO₃)₂ (99.0%), triethylamine (99.0%) and ethanol (99.9%) were obtained from Ourchem, Sinopharm Chemical Reagent Co. Ltd. Al₂O₃ (acid, 99.9%), SiO₂ (99.9%), DMF (99.0%), ethanol(99.0%) and Nickel sulfate (98.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd. 4-Ethyl-1,2-dimethoxybenzene (95.0%) were obtained from Macklin. Nickel powders(-325 mesh, typically 99.8% (metals basis)) were purchased from Alfa. (1-Methoxy-2-phenoxyethyl)benzene (95.0%) and 1,2-Diphenylethanol (97.0%) were obtained from Shanghai bidepharm. Poplar, eucalyptus, and sequoia wood powder were purchased from online sources.

Experiment Section

Lignin extraction process

Poplar, eucalyptus, and sequoia lignin were extracted followed a literature procedure^[1]. Each type of lignin (10 g) was air-dried overnight and then refluxed for 12h in 100 mL of methanol (99%) containing 3% hydrogen chloride by weight. The resulting residue was removed via suction filtration and washed with additional small portions of methanol. The methanol solution was concentrated to about 50 mL and then poured into 250 mL of ice-cold water with vigorous stirring, leading to the precipitation of a light brown solid as crude lignin. This lignin was filtered, dried under vacuum for 24 h, dissolved in 7 mL methanol, precipitated by adding 75 mL of water, and then dried. The resulting product was dissolved in 2.5 mL glacial acetic acid, and the insoluble fractions were discarded. The glacial acetic acid solution was poured into 150 mL water, and the extracted lignin was obtained via filtration, and dried at 35 °C under vacuum overnight. The yield of dried poplar, eucalyptus, and sequoia lignin was 0.83g (8.3 wt%), 1.41g (14.1%) and 4.1g (4.1 wt%), respectively. Furthermore, the number-average molecular weight (M_w) of the poplar, eucalyptus, and sequoia lignin were determined by gel permeation chromatography (Viscotek TDAmx, Malvern) as 5867, 4870 and 4400, respectively.

Lignin model compound preparation



2-phenoxy-1-phenylethan-1-d-1-ol (11a): The deuterated substrates were synthesized by literature procedure^[2]. A 50 mL pressure bottle was charged with 2-phenoxyacetophenone (0.42 g, 2 mmol) and THF/H₂O solvent (10 mL, 4:1 volume

ratio) was added. NaBD₄ (0.15 g, 4 mmol) was added in one portion and stirred at r.t. for 4 h. Then, an excess of saturated NH₄Cl aqueous solution (10 mL) was added. The crude product was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with brine (3×10 mL) and dried over anhydrous Na₂SO₄. The organic solvent was distilled under vacuum to deuterated 2-phenoxy-1-phenylethanol as a white solid. NMR results of 2-phenoxy-1-phenylethanol-1-d-1-ol are shown in **Figure S18**.

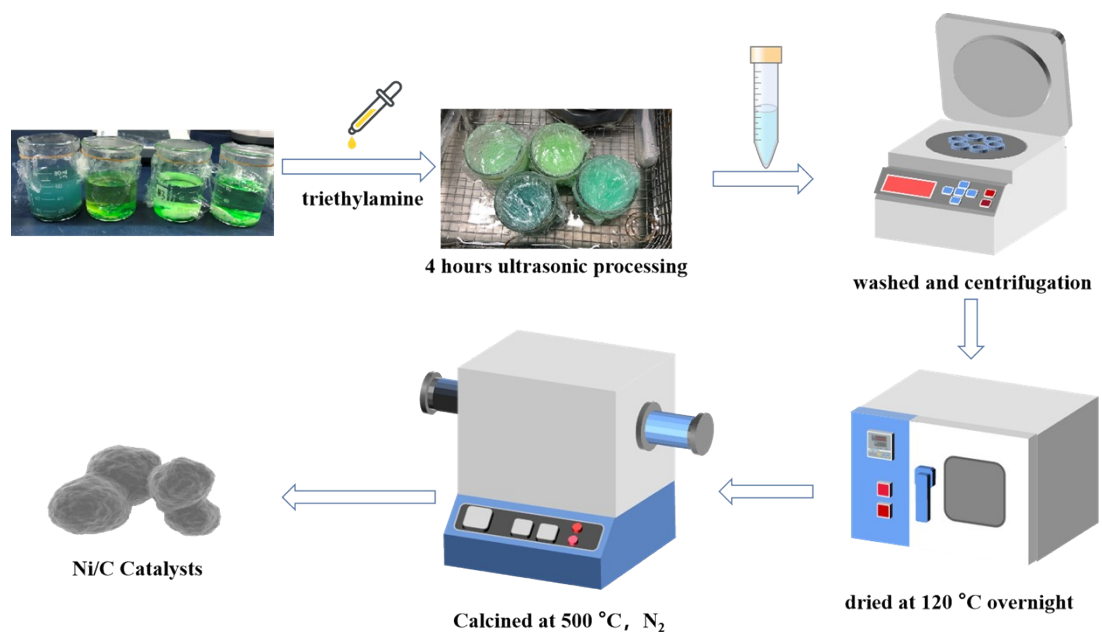


Figure S1 Schematic diagram of the preparation procedures of Ni-MOF derived catalysts.

Characterization

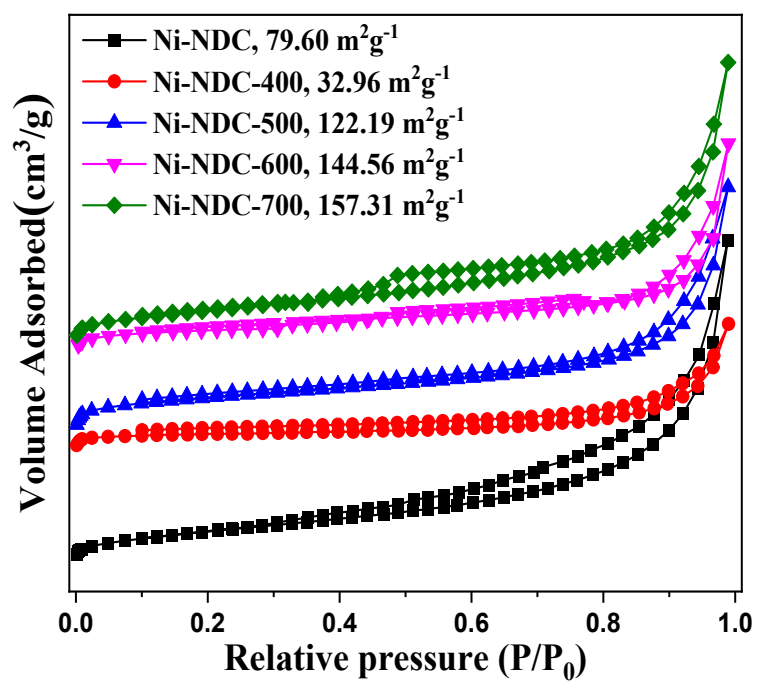


Figure S2 N₂ adsorption-desorption isotherms of the prepared catalysts. Surface areas were obtained by the BET method.

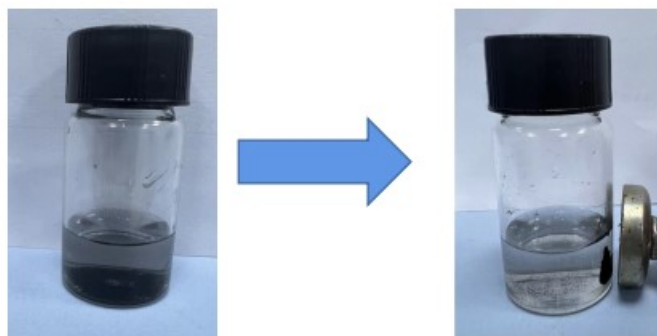


Figure S3 Magnetic separation of the catalyst after reaction.

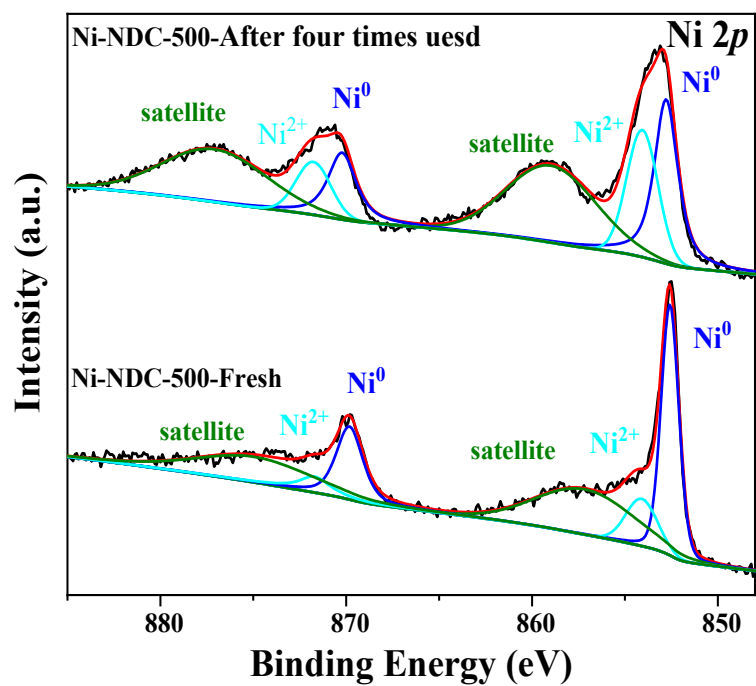


Figure S4 XPS spectra of the Ni-NDC-500 after four cycles and the fresh catalyst.

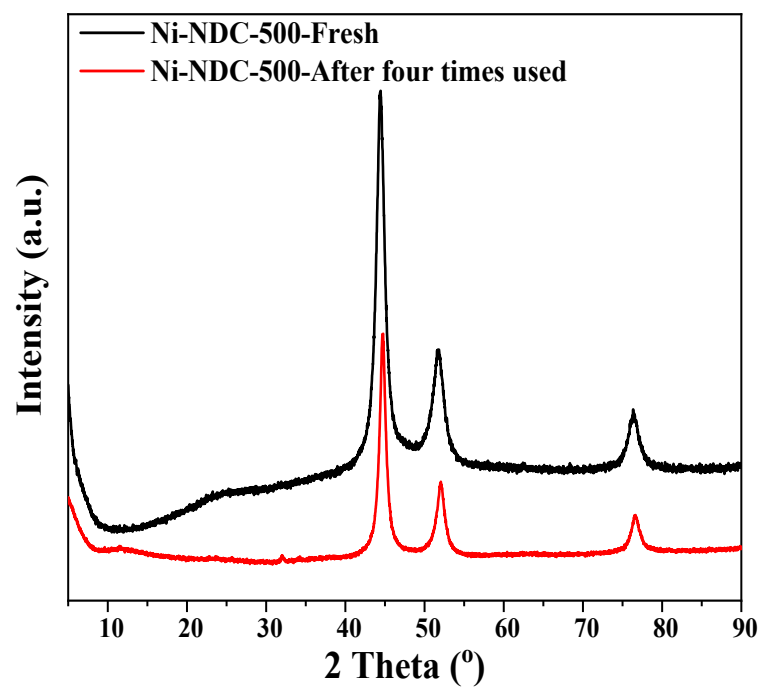


Figure S5 XRD patterns of the Ni-NDC-500 after four cycles and the fresh catalyst.

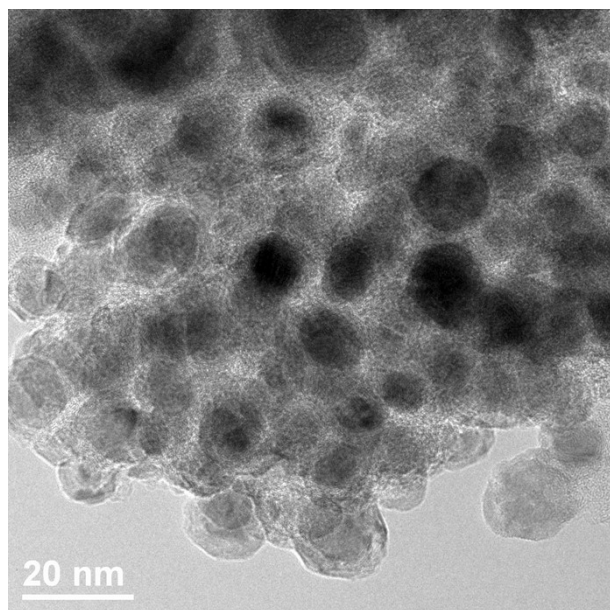


Figure S6 TEM images of the Ni-NDC-500 after four cycles.

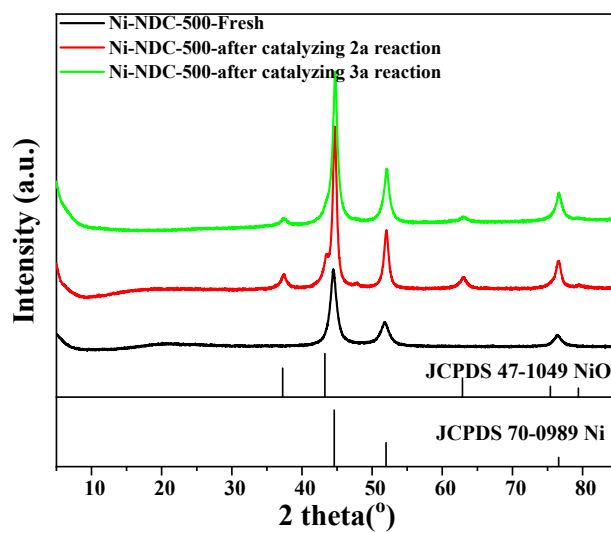


Figure S7 XRD pattern of Ni-NDC-500 after catalyzing the 2a and 3a.

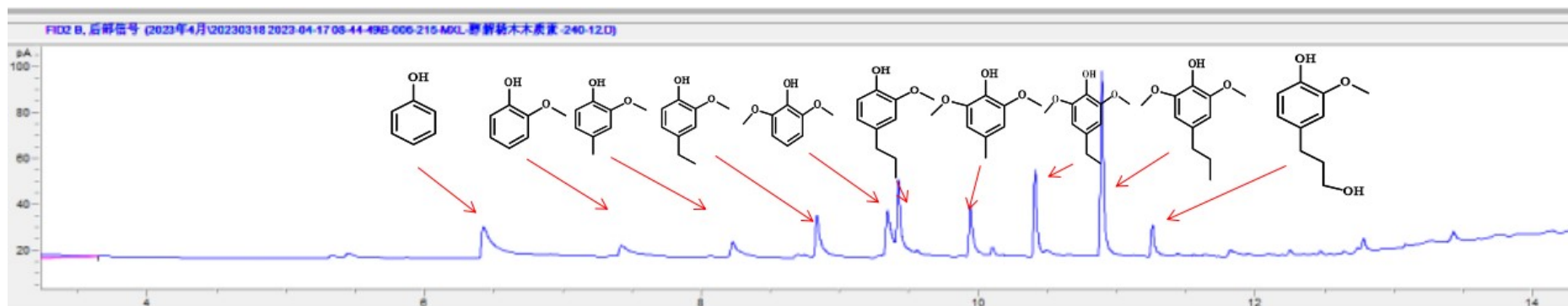


Figure S8 GC spectra of the reaction mixture after the STH process of poplar. Reaction conditions: 100 mg of lignin, 40 mg of Ni-NDC-500, 5 mL of distilled H₂O, initial pressure 2 MPa Nitrogen, 240 °C, 12 h, stirring at 800 rpm.

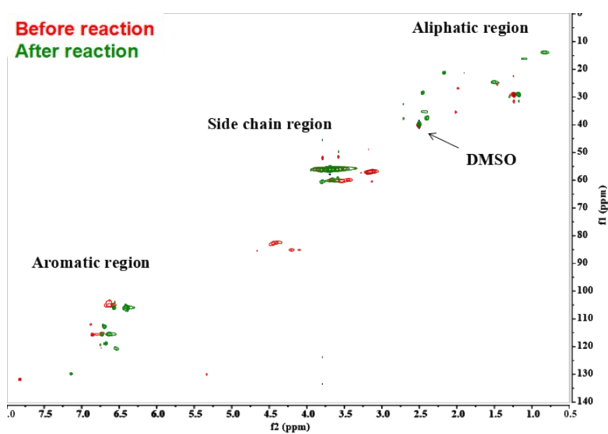


Figure S9 Total 2D HSQC NMR spectra (δ_C/δ_H 0–150/0–8 ppm) for eucalyptus lignin (labelled in red) and after STH process (labelled in green)) in DMSO- d_6 . Reaction conditions: 100 mg of eucalyptus lignin, 40 mg of Ni-NDC-500, 5 mL of distilled H₂O, 240 °C, 12 h, initial pressure 2 MPa Nitrogen, stirring at 800 rpm. ^{[3][4]}

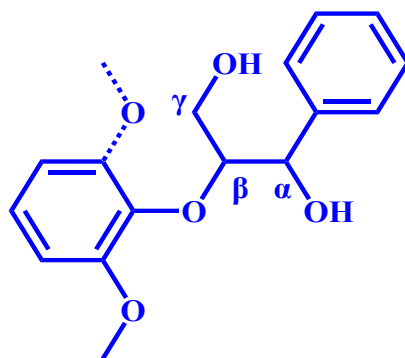
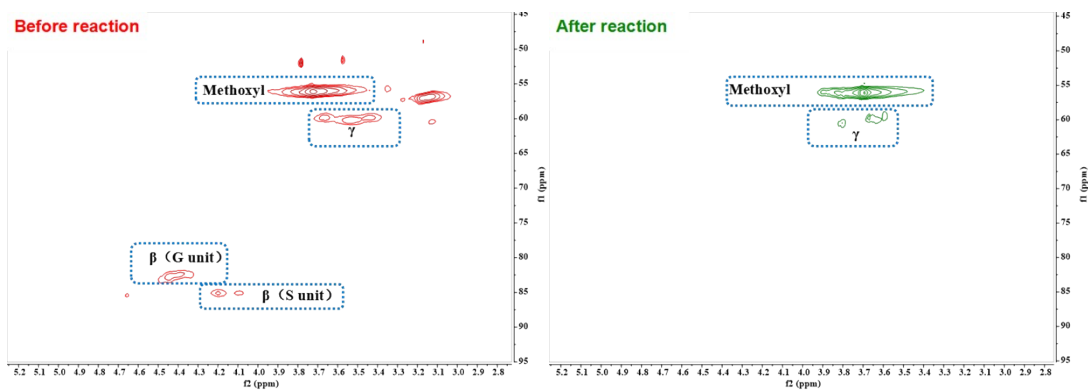


Figure S10 HSQC NMR spectra of lignin from eucalyptus before reaction and after the reaction. Reaction conditions: 100 mg of eucalyptus lignin, 40 mg of Ni-NDC-500, 5 mL of distilled H₂O, 240 °C, 12 h, initial pressure 2 MPa Nitrogen, stirring at 800 rpm. [3][4]

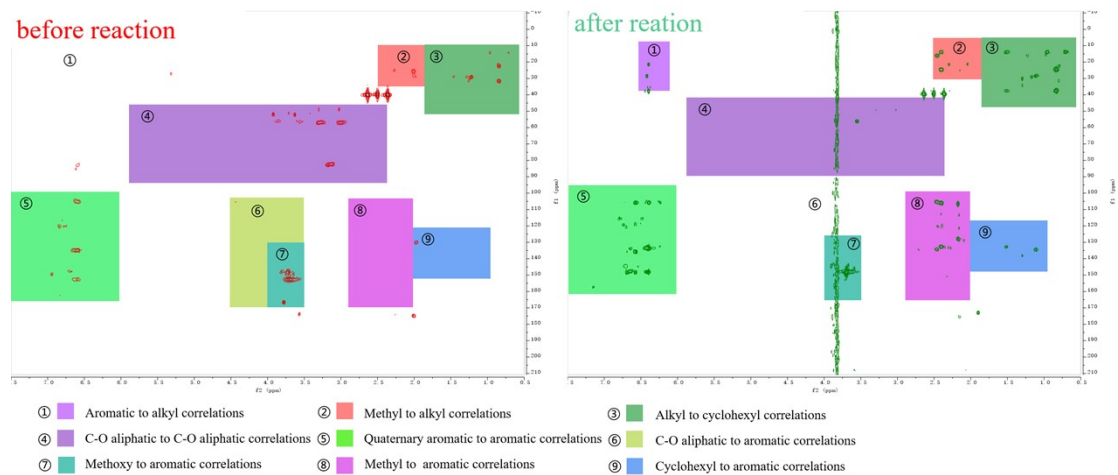
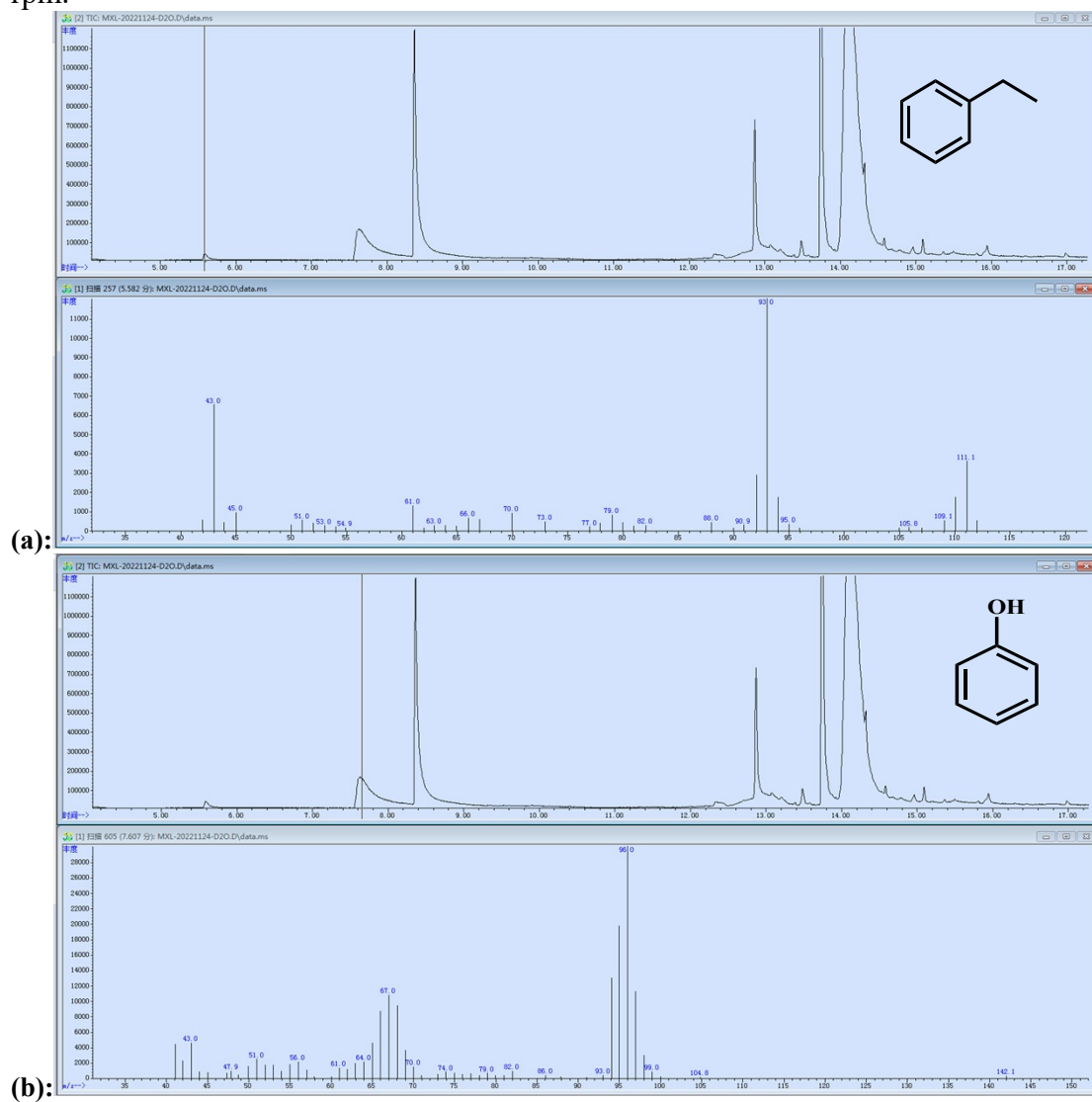
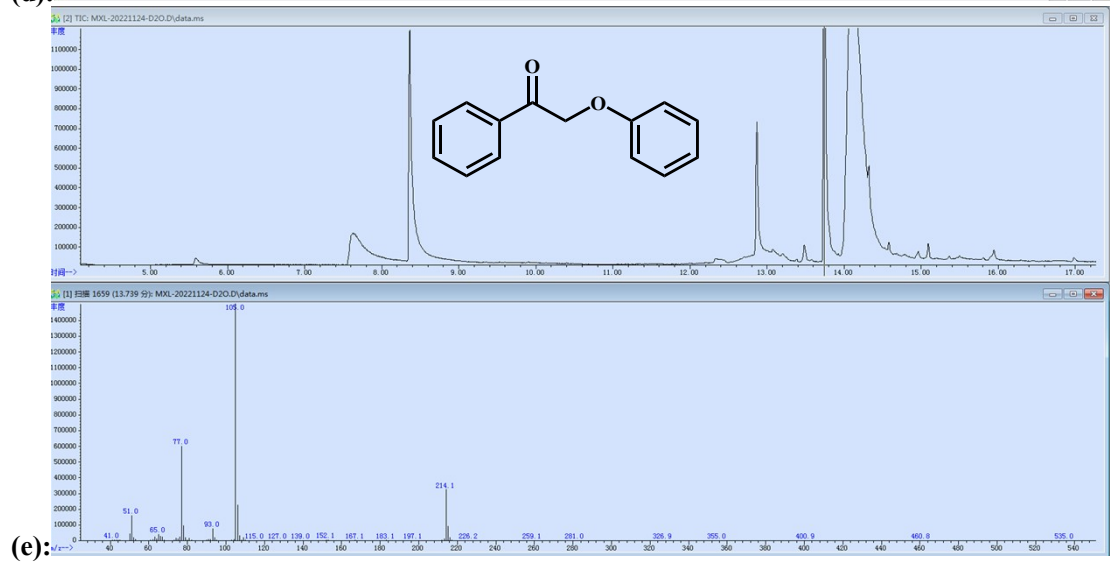
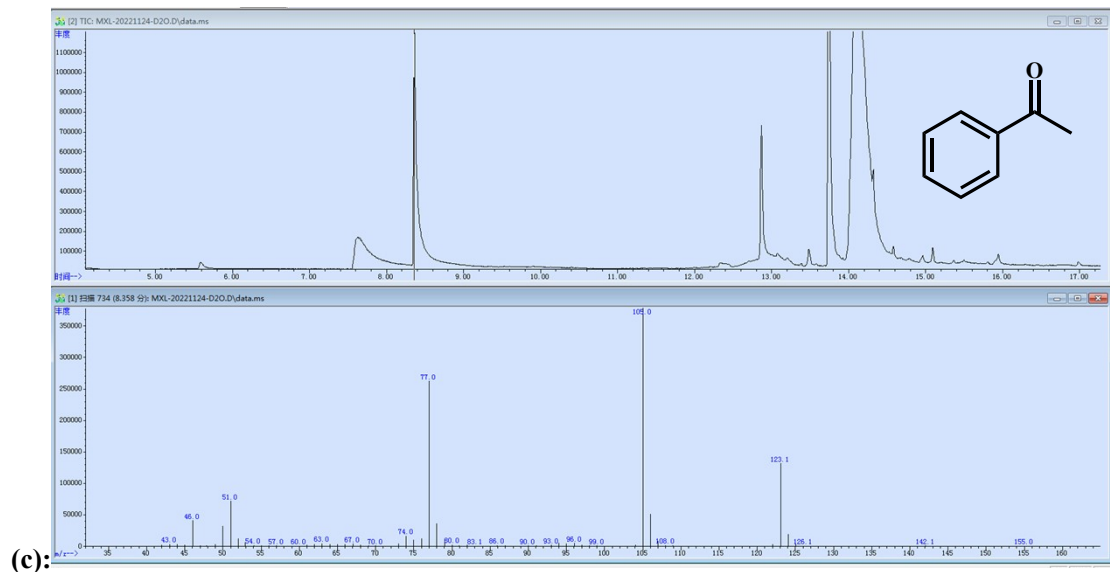
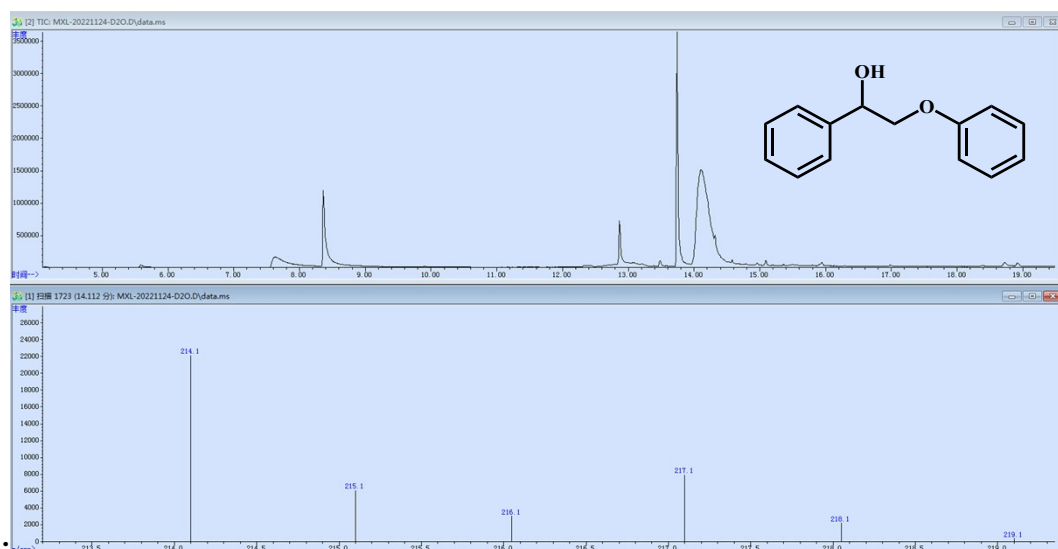


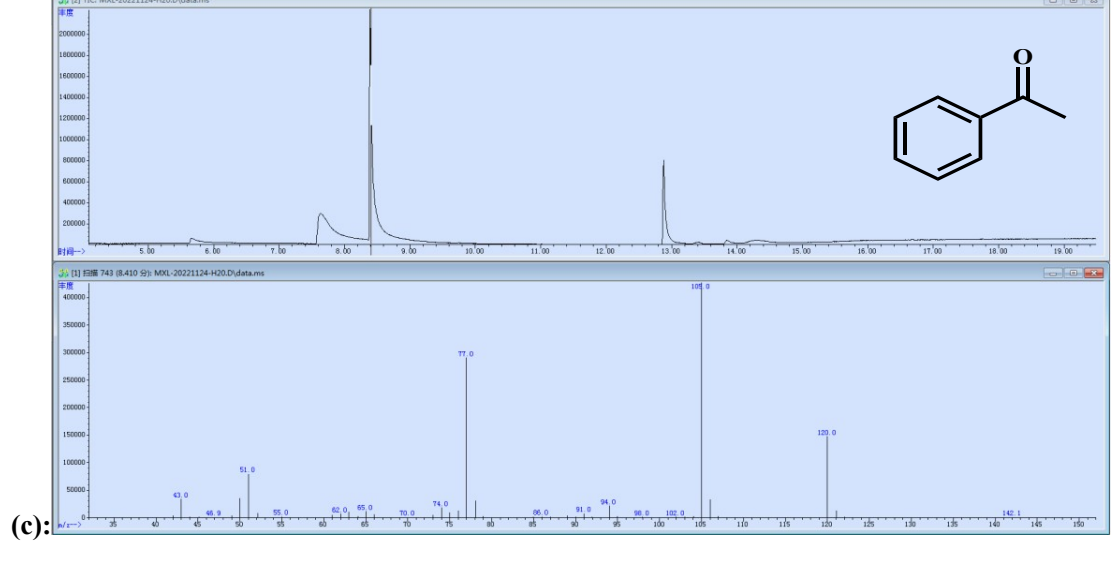
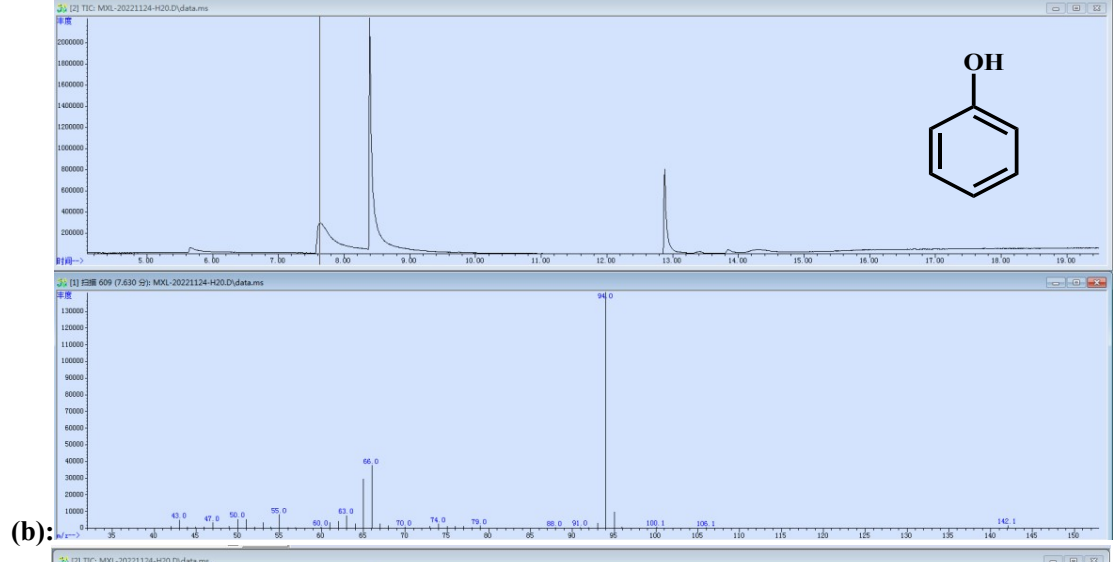
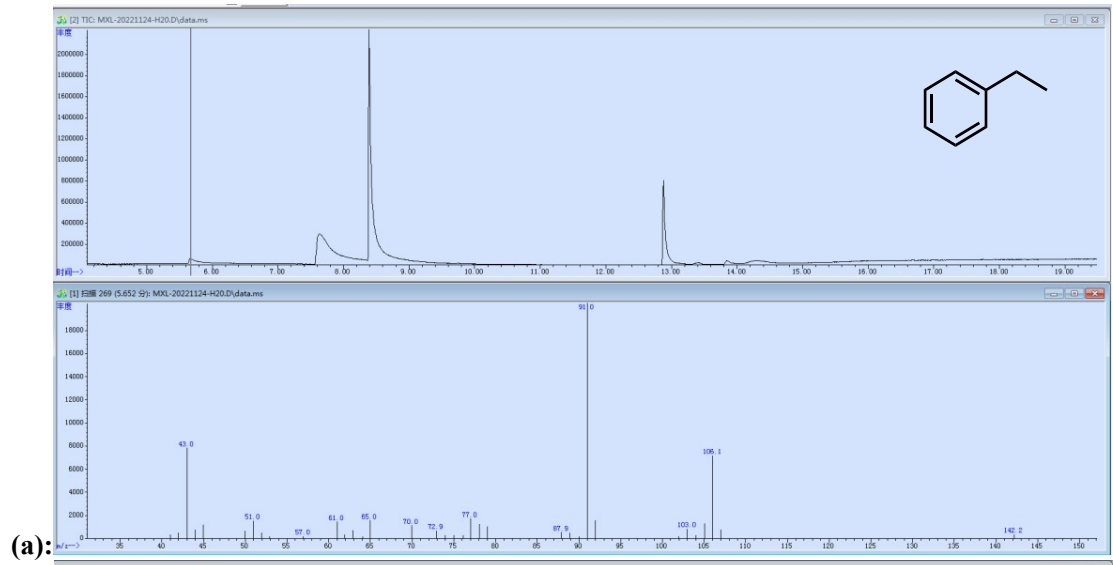
Figure S11 HMBC NMR spectra of lignin from eucalyptus before reaction and after the reaction. Reaction conditions: 100 mg of eucalyptus lignin, 40 mg of Ni-NDC-500, 5 mL of distilled H₂O, 240 °C, 12 h, initial pressure 2 MPa Nitrogen, stirring at 800 rpm. [5]







(f) **Figure S12** GC-MS profiles of product in D₂O solution. Reaction conditions: 0.3 mmol 2-phenoxy-1-phenylethanol, 40 mg catalysts, 5 mL of solvent, 150 °C, 12 h, initial pressure 2 MPa Nitrogen, stirring at 800 rpm.



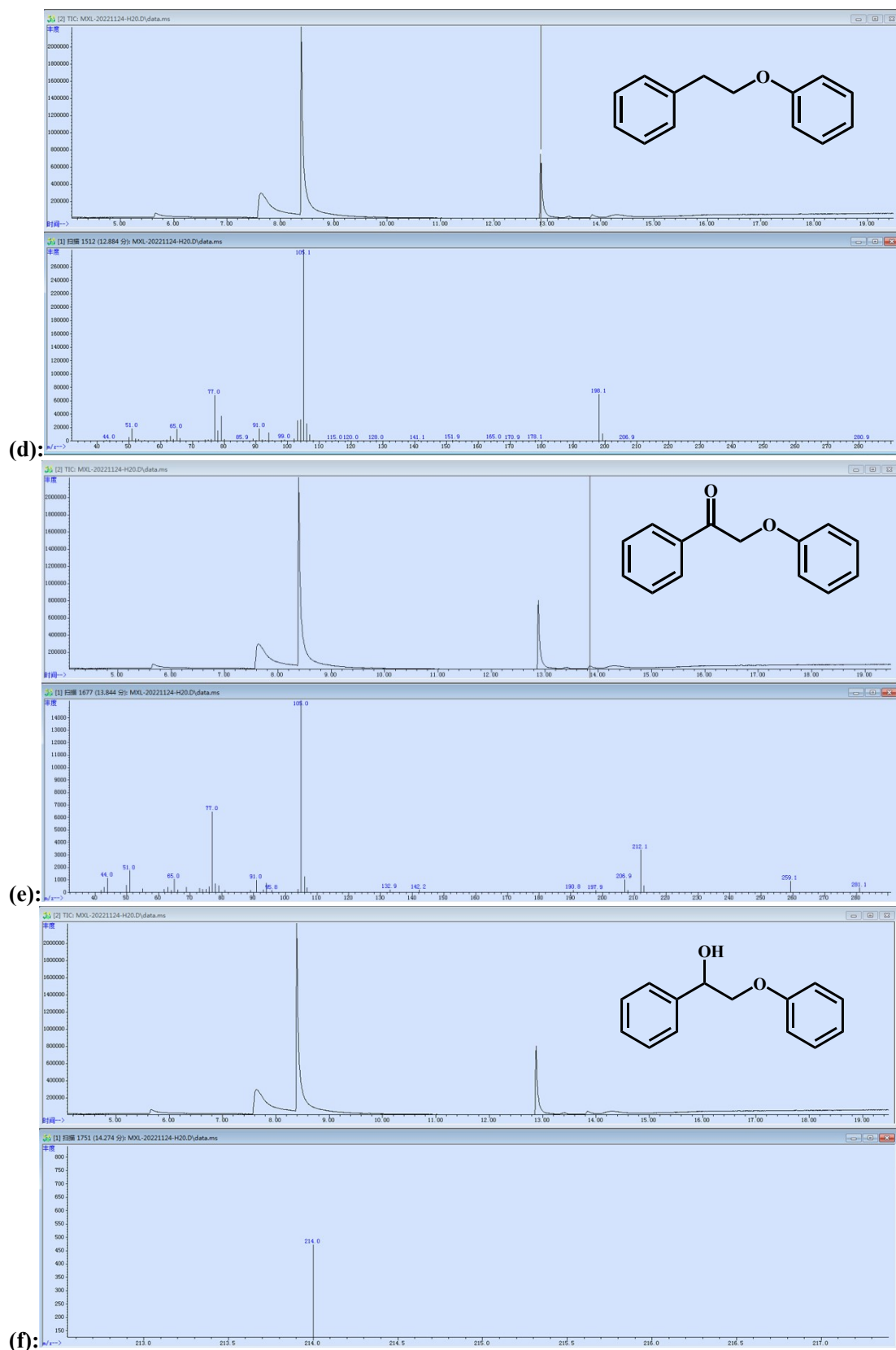


Figure S13 GC-MS profiles of product in H₂O solution. Reaction conditions: 0.3 mmol 2-phenoxy-1-phenylethanol, 40 mg catalysts, 5 mL of solvent, 150 °C, 12 h, initial pressure 2 MPa Nitrogen, stirring at 800 rpm.

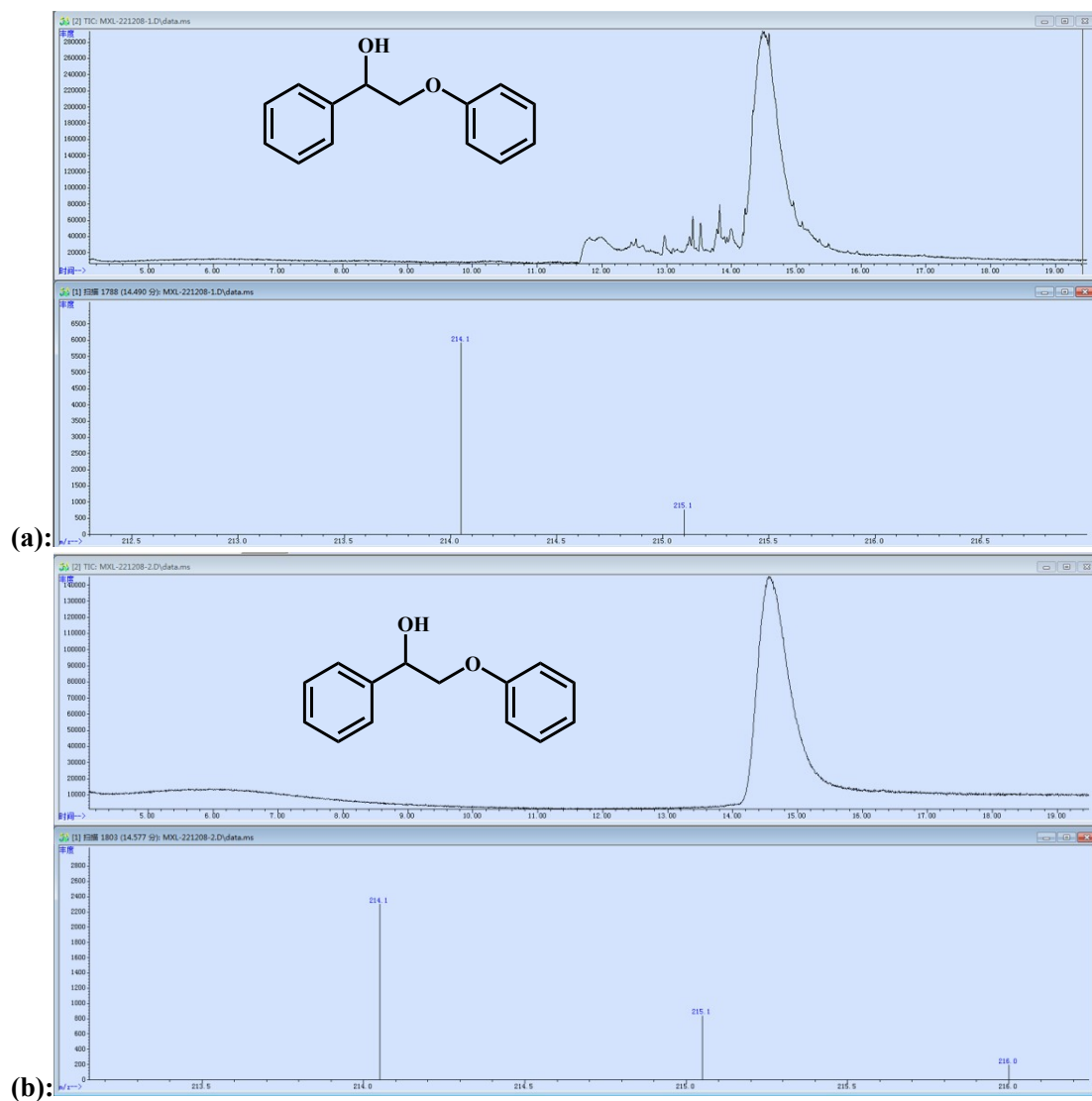
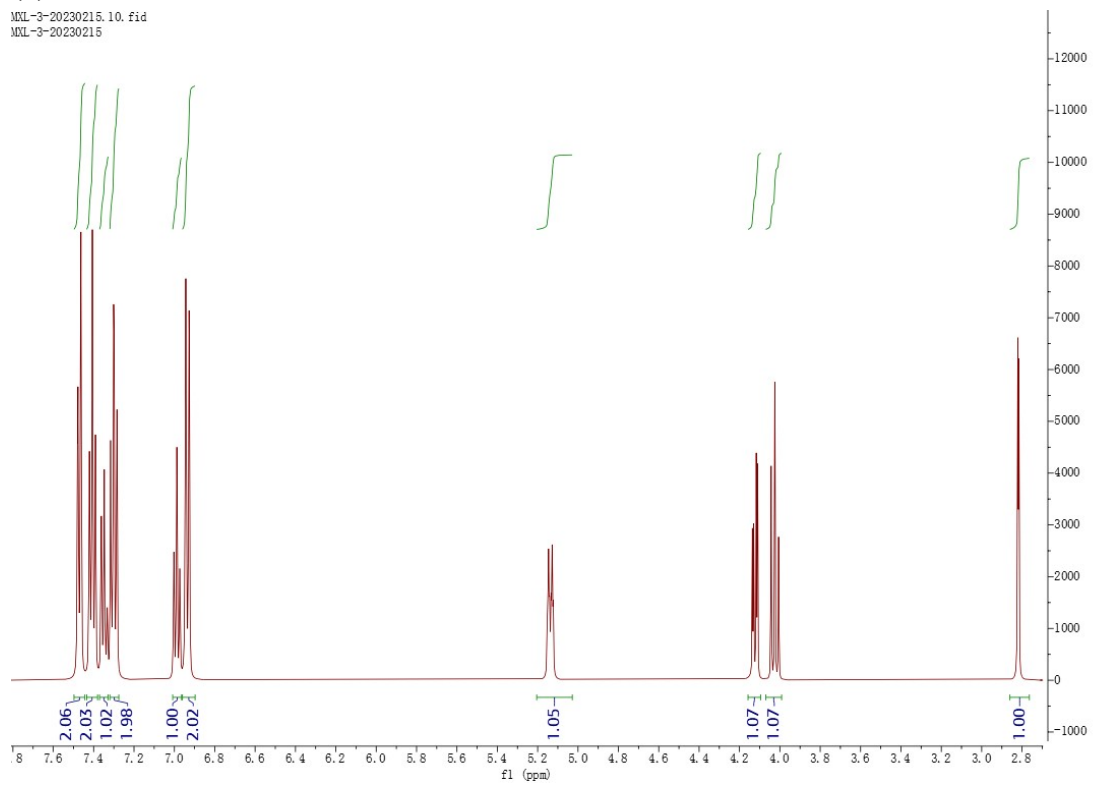


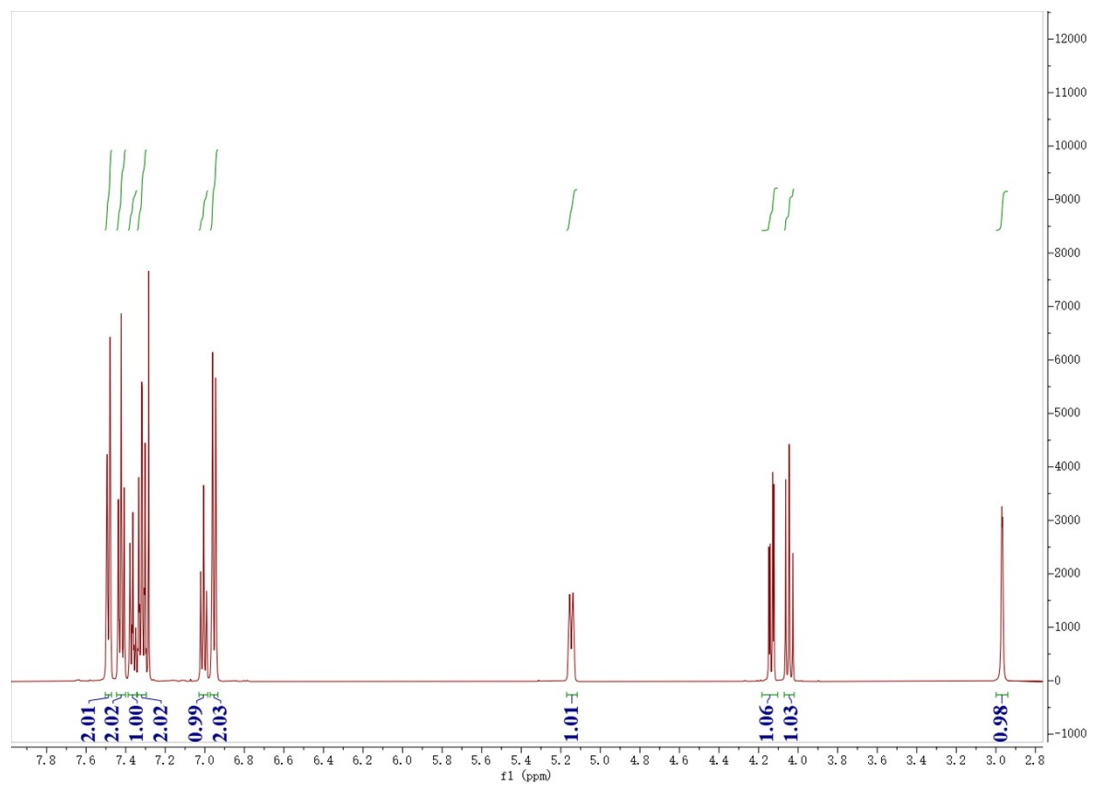
Figure S14 GC-MS profiles of 2-phenoxy-1-phenylethanol in H₂O and D₂O after 12 h at 150°C without catalysts. Reaction conditions: 0.3 mmol substrate, 5 mL of solvent, 150 °C, 12 h, initial pressure 2 MPa Nitrogen, stirring at 800 rpm.

(a):

MXI-3-20230215.10.fid
MXI-3-20230215



(b):



(c):

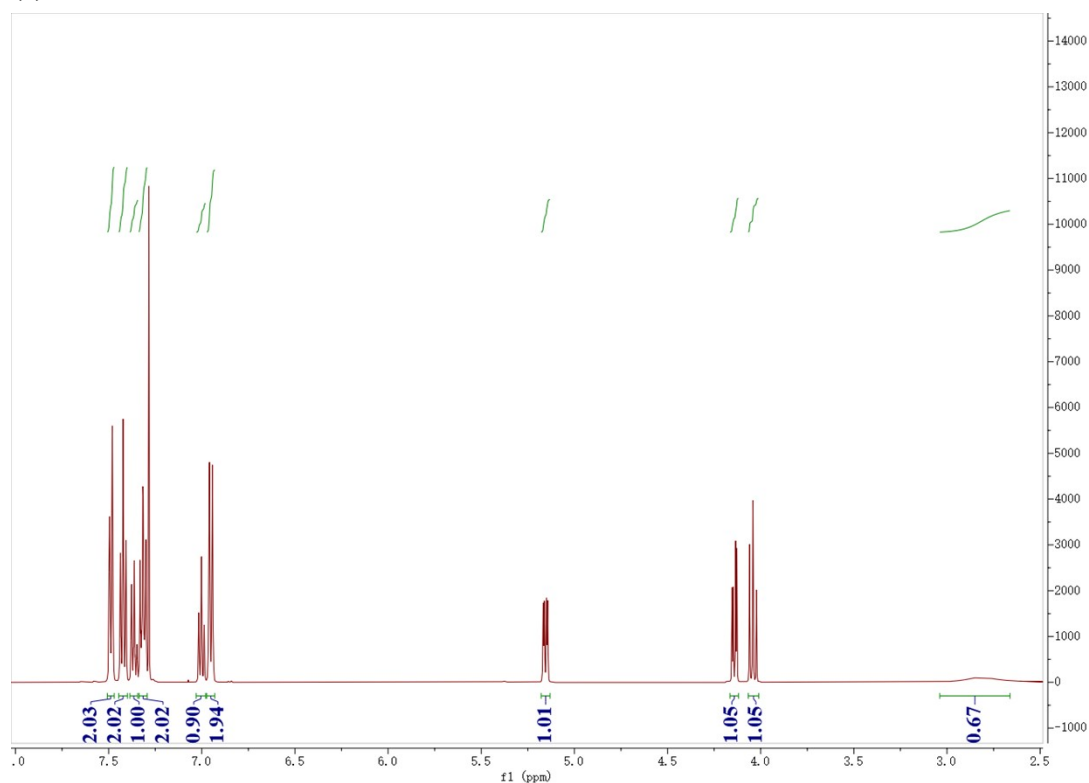
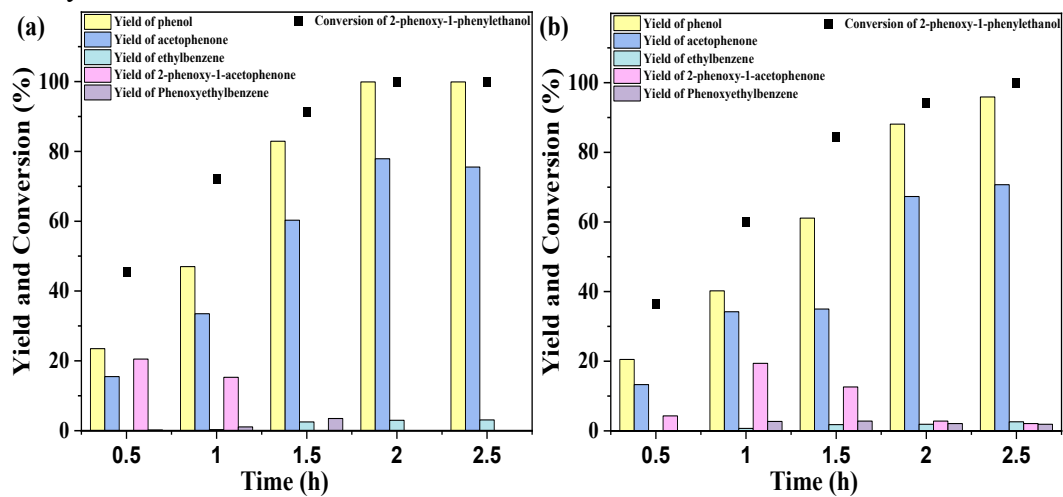


Figure S15 ^1H NMR (400 MHz, CDCl_3) of 2-phenoxy-1-phenylethanol (a), and 2-phenoxy-1-phenylethanol in H_2O (b), D_2O (c) solutions at 150°C after 12 h without catalysts.



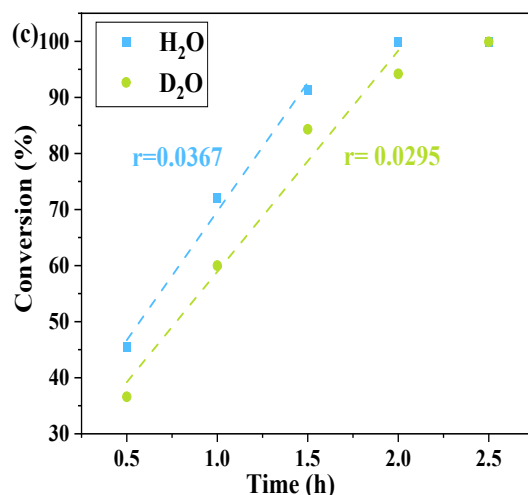


Figure S16 The conversion and yield of hydrogenolysis of 2-Phenoxy-1-phenylethanol over Ni-NDC-500 in (a) H₂O and (b) D₂O, and reaction rate comparison (c). Reaction conditions: 40 mg catalysts, 0.3 mmol 2-phenoxy-1-phenylethanol, 5 mL of solvent, 220 °C, initial pressure 2 MPa nitrogen, stirring at 800 rpm. Yields and conversions were determined by GC relative to an internal standard.

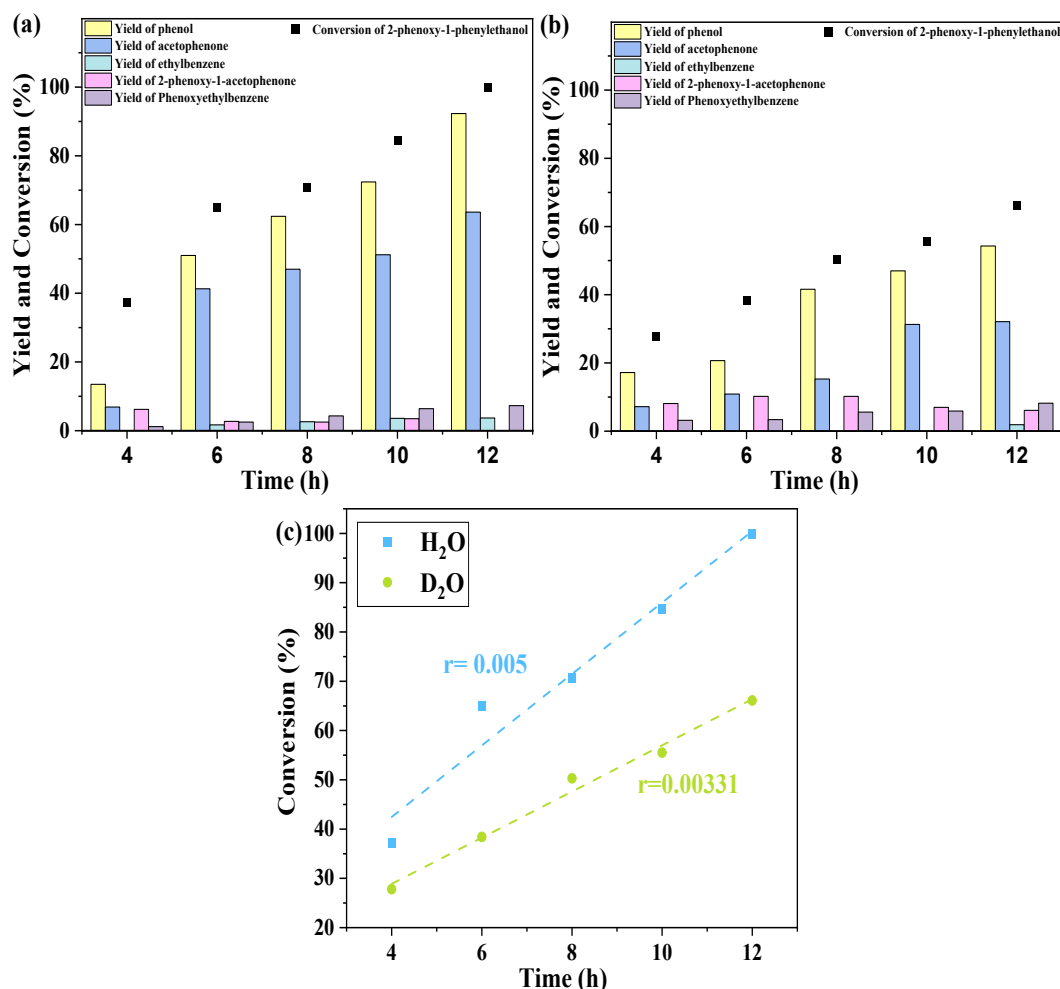


Figure S17 The conversion and yield of hydrogenolysis of 2-Phenoxy-1-phenylethanol over Ni-NDC-500 in (a) H₂O and (b) D₂O, and reaction rate

comparison (c). Reaction conditions: 40 mg catalysts, 0.3 mmol 2-phenoxy-1-phenylethanol, 5 mL of solvent, 150 °C, initial pressure 2 MPa nitrogen, stirring at 800 rpm. Yields and conversions were determined by GC relative to an internal standard.

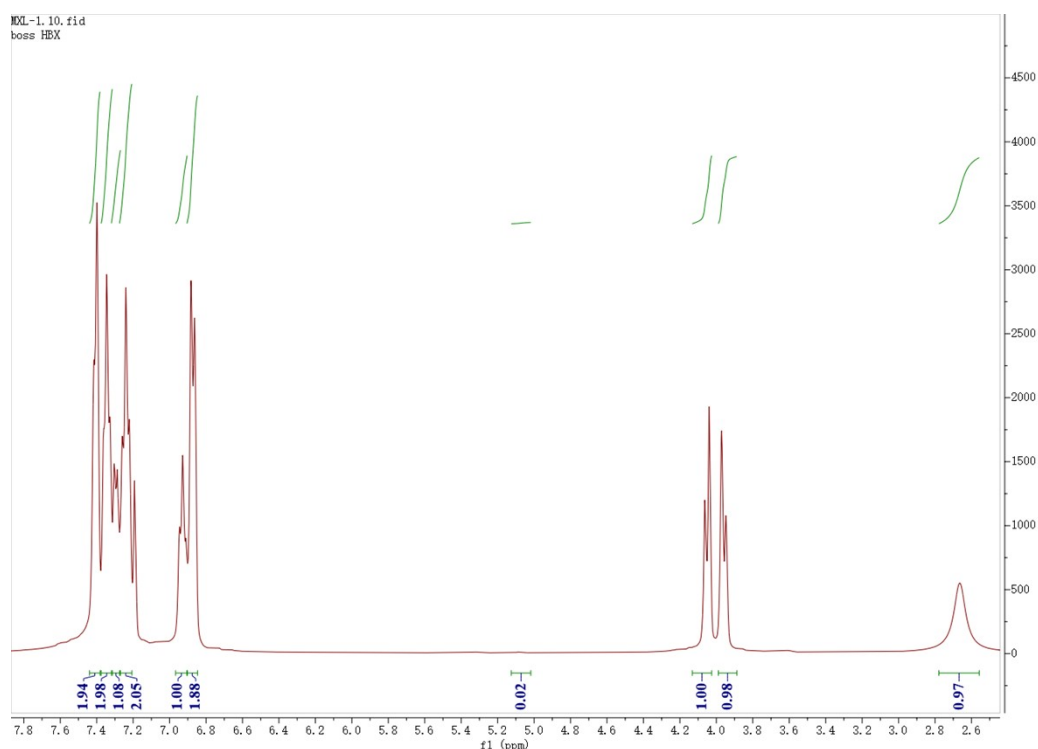
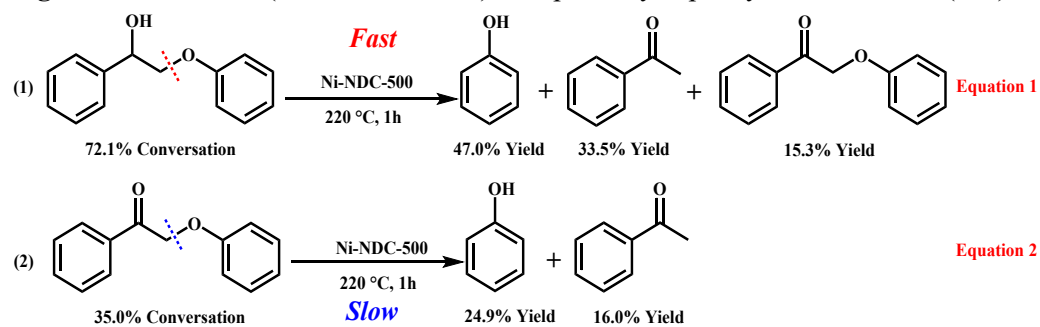


Figure S18 ^1H NMR (400 MHz, CDCl_3) of 2-phenoxy-1-phenylethan-1-d-1-ol (11a).



Scheme S1 The conversion of β -O-4 model compounds with $\text{C}_\alpha\text{-OH}$ and $\text{C}_\alpha\text{=O}$. Reaction conditions: 40 mg catalysts, 0.3 mmol 2-phenoxy-1-phenylethanol, 5 ml distilled water, 220 °C, 1h, initial pressure 2 Mpa Nitrogen, stirring at 800rpm. Yields and conversions were determined by GC relative to an internal standard.

Reference:

- [1] L. Dong, L. Lin, X. Han, X. Si, X. Liu, Y. Guo, F. Lu, S. Rudić, S. F. Parker, S. Yang and Y. Wang, *Chem*, 2019, 5, 1521-1536.
- [2] Z. Dou, Z. Zhang and M. Wang, *Appl. Catal., B*, 2022, 301, 120767.
- [3] L. Li, L. Dong, D. Li, Y. Guo, X. Liu and Y. Wang, *ACS Catal.*, 2020, **10**, 15197-15206.
- [4] L.-P. Xiao, S. Wang, H. Li, Z. Li, Z.-J. Shi, L. Xiao, R.-C. Sun, Y. Fang and G. Song, *ACS Catal.*, 2017, **7**, 7535-7542.
- [5] X. Kong, C. Liu, Y. Fan, W. Xu and R. Xiao, *ACS Sustainable Chem. Eng.*, 2021, **10**, 495-507.