Supporting Information

Self-hydrogen transfer hydrogenolysis of *β*-O-4 linkages in lignin catalyzed by MIL-100(Fe) supported Pd-Ni BMNPs

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1. General Considerations

All chemical reagents are obtained from commercial suppliers and used without further purification. GC-MS was performed on an ISQ Trace 1300 in the electron ionization (EI) mode. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H_2, FID detection. Transmission electron microscopy (TEM) images were taken using a PHILIPS Tecnai 12 microscope operating at 120kv. High Resolution Transmission electron microscopy (HRTEM) was performed on Philips-FEI Tecnai G2 F20 operating at 300kv. X-ray photoelectron spectroscopy (XPS) were performed on a ESCALAB 250Xi spectrometer, using a Al Kα X-ray source (1350 eV of photons) and calibrated by setting the C 1s peak to 284.80 eV. Inductively coupled plasma mass spectrometry (ICP-MS) was analyzed on Optima 7300 DV.

2. Catalysts Preparation

1). Preparation of the unsupported BMNPs

The unsupported BMNPs catalysts were prepared by chemical reduction, PVP was applied as stabilizer and the reductant was $NaBH_4$. In a typical preparation process for Pd_1Ni_4 BMNPs, $NiCl_2 \cdot 6H_2O$ (0.448 mg), $NaPdCl_4$ (0.112 mmol) and PVP (300 mg, average molecule weight = 40,000) were dissolved in DI water (30 mL) and charged into a 100mL reactor with a magnetic stirrer. Then a fresh prepared ethanol solution of $NaBH_4$ (2.24 mmol, in 5 mL DI water) was added into the reactor under vigorous stirring (1000 rpm) at 4 °C under argon atmosphere. The color of the colloid mixture would turn to black immediately which indicates that metal salts have been reduced to metal particles. The prepared BMNPs was separated by centrifugation, washed by water and redispersed in 10 mL deoxygenated DI water for further use. The prepared BMNPs should be kept under argon atmosphere because oxidation will happen when over-exposure to air.

2). Preparation of Pd-Ni/MIL-100(Fe) catalyst

a). Preparation of MIL-100(Fe) [1]

Ferric trichloride ($FeCl_3$) was chosen as the iron sources. Typically, $FeCl_3$ (0.1mol) was dissolved into 60 mL deionized water to form a solution, the solution was charged into a three-neck round bottom flask (100 ml) equipped with a magnetic stirrer and a reflux condenser. Then, 1, 3, 5-H_3BTC (0.9 mol) was added into above solution and the mixture was kept at 95 ^oC and a stirring speed of 300 rpm for 12 h. The reaction product was purified three times with a solvent extraction treatment with deionized water (350 ml) and ethanol (350 ml) at 70 ^oC for 24 h, finally dried in a vacuum desiccator at 150 ^oC for 10 h.

b). Preparation of Pd-Ni/MIL-100(Fe)

Nanoparticles immobilized on MIL-100(Fe) was prepared by impregnation-reduction method, and the composition of the bimetallic nanoparticles was controlled by adjusting the ratio of the metal precursors. In a typical procedure, Pd_1Ni_4/MIL-100(Fe) was prepared as following: 2.0 g MIL-100(Fe)

was dispersed into 50 mL aqueous solution of metal precursors (0.11 mmol $PdCl_2$ and 0.44 mmol $NiCl_2 \cdot 6H_2O$) under ultrasonic. Lysine aqueous solution (0.53 M) was then added into the mixture with vigorous stirring for 30 min at 4 °C. To this suspension, $NaBH_4$ aqueous solution (0.5 M) was added dropwise keeping the temperature below 10 °C, the color of the mixture would turn to black immediately indicating the formation of metal particles, the mixture was further stirred for 30 min and then aged for 24 h. Finally, the solid was separated, washed (water and ethanol) and dried at room temperature under *vacuum*.

3). Preparation of Pd-Ni@MIL-100(Fe) catalyst [2]

$FeCl_3 \cdot 6H_2O$ (22.2 mg), H_3BTC (11.4 mg) and PVP (0.367 g) were dissolved in 24 mL DMF-ethanol (v/v = 5:3) mixed solution, after dissolved thoroughly, the preformed Pd-Ni BMNPs was added in the mixture. Then the mixture was transferred into a Teflon-lined stainless steel autoclave (50 mL) and heated at 140 °C for 12 h. After cooling, the obtained catalyst was collected by centrifugation, washed with DMF and ethanol, and finally dried overnight at 120 °C under vacuum.

3. Intramolecular hydrogen transfer of Lignin Model compounds

Model compounds were synthesized following a modified literature procedure.[3] In a typical reaction procedure, the catalyst (4%, based on metal Pd) and the substrate (0.5 mmol) was added into a reactor (10 mL) equipped with a magnetic stirrer, 1mL water was added as the solvent, and the reaction mixture was stirred under argon for 6h, the reaction system was sensitive to oxygen, argon atmosphere was essential in this system. After the reaction, the reaction mixture was allowed to cool to room temperature, the catalyst was collected by filtration and washed with water (2×3 mL) and ethyl acetate (2×3 mL), dried under vacuum and directly used in the next cycle. The filtrate was extracted using ethyl acetate (3×5 mL), the organic layer was analyzed by GC and GC-MS.

4. ICP-MS results of Pd_1Ni_4/MIL-100(Fe) catalyst

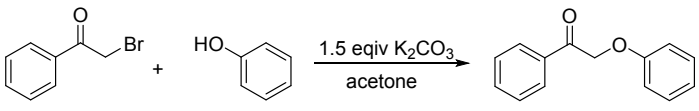
Table S1. ICP-MS analysis of the as prepared Pd_1Ni_4/MIL-100(Fe) catalyst.

Nanoparticles	Metal Content(mg/L)		wt%		Molar Ratio	
	Pd	Ni	Pd	Ni	Pd	Ni
Pd_1Ni_4	5.925	11.592	1.54	3.02	1	3.55

5. Synthesis of substrates

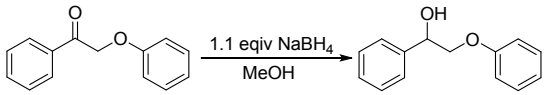
All substrates have been prepared according to literature procedures with minor modifications. [3,4]

Synthesis of 2-phenoxy-1-phenylethanol (1a)



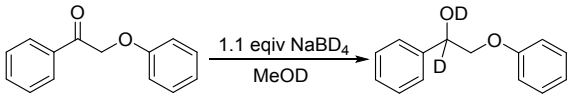
A 250 mL round bottom flask equipped with a reflux condenser and a dropping funnel was charged with phenol (0.520 g, 5.5 mmol) and K_2CO_3 (1.040 g, 7.6 mmol) in acetone (50 mL) and stirred at RT. To this solution, 2-bromoacetophenone (1.000 g, 5.0 mmol) in acetone (50 mL) was added dropwise over 30 min at RT. The resulting suspension was stirred at reflux for 4 h, after the

suspension was filtered and concentrated in *vacuo*. The crude product was purified by recrystallization from petroleum ether to give 2-phenoxy-1-phenylethanone as a white solid (1.050 g, 4.9 mmol) in 98% yield.



1a

A round bottom flask was charged with 2-phenoxy-1-phenylethanone (1.7 g, 8.0 mmol) and methanol (60 mL). Sodium borohydride (0.33 g, 8.8 mmol) was added to the solution in small portions at 25 ^{o}C. After stirring for 4 h, the suspension was quenched with saturated aqueous NH_4Cl (150 mL), followed by the addition of ethyl acetate (150 mL). After separation, the organic phase was washed with H_2O (2 x 100 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under vacuum. The crude product was purified by recrystallization from hexane to give a white crystalline in 96% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.41 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.38 – 7.33 (m, 1H), 7.33 – 7.27 (m, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.96 – 6.91 (m, 2H), 5.14 (dt, *J* = 8.8, 2.5 Hz, 1H), 4.14 – 4.00 (m, 2H), 2.89 (d, *J* = 2.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.54 (s), 139.82 (s), 129.73 (s), 128.73 (s), 128.35 (s), 126.45 (s), 121.47 (s), 114.80 (s), 77.33 (d, *J* = 31.9 Hz), 76.95 (s), 76.87 – 76.44 (m), 73.45 (s), 72.74 (s).

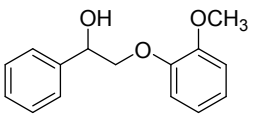


1a'

For the preparation of the isotope labeled compound **1a'**, sodium borodeuteride was used as the reductant and MeOD was chosen as the solvent, and other reaction parameter was the same as the synthesis process of **1a**. **1a' ^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.48 (dd, *J* = 10.4, 4.2 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.41 – 7.35 (m, 2H), 7.09 (dd, *J* = 5.1, 2.2 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 2H), 4.18 (d, *J* = 9.6 Hz, 1H), 4.11 (d, *J* = 9.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.53 (s), 138.86 (s), 128.68 (s), 127.75 (s), 127.47 (d, *J* = 50.5 Hz), 125.44 (s), 120.40 (s), 113.79 (s), 76.49 (s), 76.23 (s), 75.98 (s), 72.31 (s).

Compounds 1b-1h were prepared under the same reaction condition with **1a**, expecting that 2-bromoacetophenone and phenols was changed into corresponding substituted 2-bromoacetophenone and phenols.

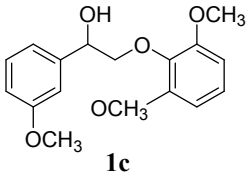
2-(2-methoxyphenoxy)-1-phenylethanol (1b) was prepared in 93% yield.



1b

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.39 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.34 (dt, *J* = 9.4, 4.3 Hz, 1H), 7.01 (ddd, *J* = 8.0, 7.0, 1.9 Hz, 1H), 6.98 – 6.87 (m, 3H), 5.14 (d, *J* = 9.3 Hz, 1H), 4.20 (dd, *J* = 10.0, 2.9 Hz, 1H), 4.02 (t, *J* = 9.7 Hz, 1H), 3.88 (s, 3H), 3.72 (d, *J* = 2.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.23 (s), 148.15 (s), 139.78 (s), 128.63 (s), 128.15 (s), 126.46 (s), 122.63 (s), 121.24 (s), 116.00 (s), 112.16 (s), 77.48 (s), 77.10 (d, *J* = 31.9 Hz), 76.36 (s), 72.48 (s), 55.99 (s).

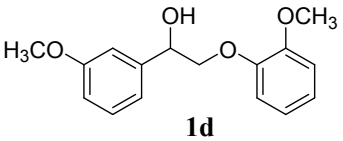
2-(2,6-dimethoxyphenoxy)-1-(3-methoxyphenyl)ethan-1-ol (1c) was prepared in 95% yield. ^{1}H



1c

NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 8.4 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.82 (dt, *J* = 12.3, 6.1 Hz, 1H), 6.62 (t, *J* = 8.3 Hz, 2H), 4.96 (dd, *J* = 9.9, 2.1 Hz, 1H), 4.57 (s, 1H), 4.44 (dd, *J* = 11.0, 2.5 Hz, 1H), 3.89 (s, 6H), 3.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.83 (s), 153.36 (s), 141.22 (s), 136.83 (s), 129.45 (s), 124.26 (s), 118.76 (s), 113.57 (s), 111.68 (s), 105.25 (s), 80.18 (s), 77.48 (s), 77.09 (d, *J* = 31.9 Hz), 72.46 (s), 56.23 (s), 55.37 (s).

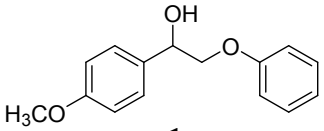
2-(2-methoxyphenoxy)-1-(3-methoxyphenyl) ethanol (1d) was prepared in 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.9 Hz, 1H), 6.98 (ddd, *J* = 10.0, 8.6, 1.9 Hz, 3H), 6.92 – 6.81 (m, 4H), 5.09 (dd, *J* = 9.2, 2.5 Hz, 1H), 4.14 (dd, *J* = 10.0, 2.9 Hz, 1H), 3.97 (t, *J* = 9.6 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.64 (d, *J* = 4.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.92 (s), 149.97 (s), 148.12 (s), 141.54 (s), 129.63 (s), 122.44 (s), 121.29 (s), 118.75 (s), 115.52 (s), 113.78 (s), 111.96 (d, *J* = 36.6 Hz), 78.04 – 76.98 (m), 76.98 – 76.74 (m), 76.11 (s), 72.36 (s), 55.99 (s), 55.39 (s).



1d

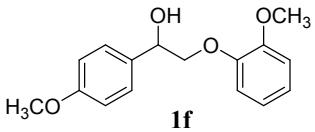
1-(4-methoxyphenyl)-2-phenoxyethanol (1e) was prepared in 95% yield.

^{1}H NMR(500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.31 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.97 – 6.89 (m, 4H), 5.11 – 5.06 (m, 1H), 4.09 (dd, *J* = 9.6, 3.3 Hz, 1H), 4.02 (t, *J* = 9.2 Hz, 1H), 3.84 (s, 3H), 2.90 (d, *J* = 2.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.67 (s), 158.58 (s), 132.00 (s), 129.71 (s), 127.73 (s), 121.41 (s), 114.80 (s), 114.13 (s), 77.47 (s), 77.09 (d, *J* = 31.9 Hz), 73.43 (s), 72.32 (s), 55.46 (s).



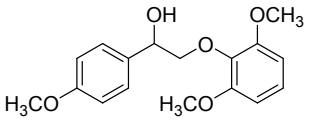
1e

2-(2-methoxyphenoxy)-1-(4-methoxyphenyl) ethanol (1f) was prepared in 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 5.7 Hz, 2H), 6.99 – 6.94 (m, 1H), 6.93 – 6.87 (m, 5H), 5.07 (dt, *J* = 9.2, 2.5 Hz, 1H), 4.13 – 4.10 (m, 1H), 3.98 (t, *J* = 9.6 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.04 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.51 (s), 150.11 (s), 148.21 (s), 132.05 (s), 127.73 (s), 127.00 (s), 122.42 (s), 121.22 (s), 115.67 (s), 114.02 (s), 112.14 (s), 78.11 (s), 76.92 (m), 77.04 (s), 77.04 (s), 76.14 (s), 72.05 (s), 55.95 (s), 55.41 (s), 21.17 (s), 14.35 (s).

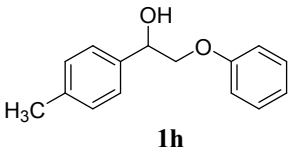


1f

2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-ol (1g) was prepared in 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.04 (t, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 4.93 (d, *J* = 9.8 Hz, 1H), 4.54 (s, 1H), 4.40 (dd, *J* = 10.9, 2.5 Hz, 1H), 3.88 (s, 6H), 3.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.33 (s), 153.38 (s), 136.84 (s), 131.68 (s), 127.70 (s), 124.24 (s), 113.89 (s), 105.26 (s), 80.17 (s), 77.57 (s), 77.32 (s), 77.06 (s), 72.14 (s), 56.29 (d, *J* = 19.6 Hz), 55.38 (s).



1g

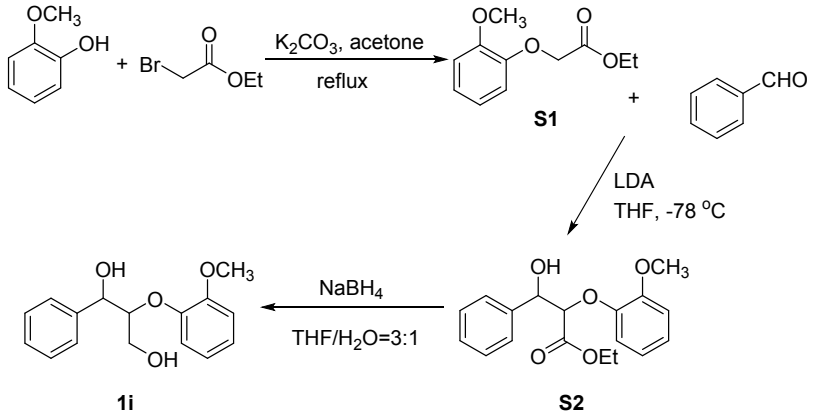


1h

2-phenoxy-1-(p-tolyl)ethan-1-ol (1h) was prepared in 97% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.36 (dt, *J* = 18.0, 9.0 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 7.9 Hz, 2H), 5.17 (dd, *J* = 8.8, 2.7 Hz, 1H), 4.16 (dd, *J* = 9.6, 3.2 Hz,

1H), 4.08 (t, *J* = 9.2 Hz, 1H), 2.86 (s, 1H), 2.44 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.55 (s), 138.09 (s), 136.82 (s), 129.70 (s), 129.40 (s), 126.37 (s), 121.40 (s), 114.77 (s), 77.43 (s), 77.05 (d, *J* = 31.9 Hz), 73.45 (s), 72.58 (s), 21.33 (s).

Synthesis of 2-(2-methoxyphenoxy)-1-phenylpropane-1,3-diol (1i) [5,6]



1) Preparation of ethyl 2-(2-methoxyphenoxy)acetate (S1)

A 100 mL three-necked flask equipped with magnetic stir bar and reflux condenser was charged with anhydrous K_2CO_3 (2.76 g, 20 mmol, 1 equiv), 2-methoxyphenol (2.48 g, 20 mmol, 1 equiv) and anhydrous acetone (30 mL). The mixture was stirred at room temperature during 15 min, and Ethyl bromoacetate (4.0 g, 24 mmol, 1.2 equiv) dissolved in 10 mL acetone was added dropwise using a syringe in 10 min. The reaction mixture was subsequently warmed to 65 °C (reflux), and the reaction process was tracked by TLC. Upon the completion of the reaction, the reaction mixture was allowed to cool to room temperature and filtered over a pad of celite (the celite was washed with acetone before use). The filtrate was concentrated under reduced pressure until almost dryness, and diluted with ethyl acetate (30 mL). The organic layer was consecutively washed with an aqueous NaOH solution (5% w/w, 3x10 mL), H_2O (10 mL) and brine (10 mL). The organic layer was dried using anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, yielding S1 as a colorless oil (3.8 g, 90%).

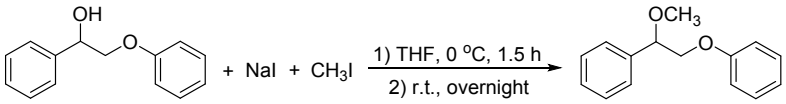
2) Preparation of ethyl 3-hydroxy-2-(2-methoxyphenoxy)-3-phenylpropanoate (S2)

A dried and Ar-flushed 100 mL flask equipped with magnetic stir bar was charged with 5.5 mL Lithium diisopropylamide (2M in THF), the solution was cooled to -78 °C and a solution of S1 (2.1 g, 10 mmol, 1 equiv) in anhydrous THF (10 mL) was added dropwise over a period of 2 h. After stirring for an additional 30 min, a solution of benzaldehyde (1.17 g, 11 mmol, 1.1 equiv) in anhydrous THF (5 mL) was added in 30 min at -78 °C, the reaction was kept under -78 °C for another 2h, and 20 mL saturated NH_4Cl solution was added to quench the reaction. The aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic layers were washed brine (20 mL), and dried using anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (EtOAc / petroleum ether = 1:10 to 1:1) yielded a mixture of erythro and threo diastereomers (2.7 g, 85%, slightly yellow syrup) of S2.

3) Preparation of 2-(2-methoxyphenoxy)-1-phenylpropane-1,3-diol (1i)

To a solution of S2 (1.58 g, 5 mmol) in THF/H_2O (3:1, 15 mL) was added $NaBH_4$ (0.95 g, 25 mmol) portionwise. The reaction mixture was stirred at room temperature overnight then quenched by addition of H_2O (10 mL). The mixture was extracted with EtOAc (20 mL x 3), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The resulting oil was purified by flash column chromatography with EtOAc / petroleum ether = 3:7. Yield 95%.

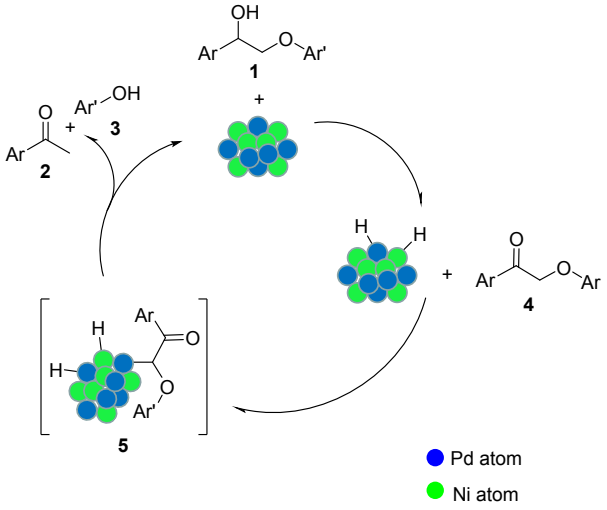
Synthesis of (1-methoxy-2-phenoxyethyl)benzene (1j) [7]



1a **1j**

A round bottom flask was charged with **1a** (1.01 g, 4.7 mmol) and tetrahydrofuran (12 mL). The resulting solution was cooled to 0 °C and sodium hydride (188 mg, 60 wt% in mineral oil, 4.7 mmol) was added in one portion. The resulting suspension was stirred at 0 °C for 1.5 h after which iodomethane (0.3 mL, 5 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature, stirred overnight, and the reaction was quenched with bicarbonate solution. The aqueous layer was extracted EtOAc (20 mL x 3). The combined organic extracts were washed with brine, dried over Na_2SO4, filtered, concentrated in vacuo, and purified by silica gel chromatography with EtOAc / petroleum ether = 5:95, yield 92%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.5–7.4 (m, 5H), 7.35–7.30 (m, 2H), 7.05–6.95 (m, 3H), 4.67 (dd, J = 7.9, 3.7 Hz, 1H), 4.25 (dd, J = 10.3, 7.9 Hz, 1H), 4.08 (dd, J = 10.3, 3.7 Hz, 1H), 3.43 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.79 (s), 137.63 (s), 128.47 (s), 127.51 (d, J = 42.9 Hz), 126.91 (s), 126.11 (s), 120.02 (s), 113.86 (s), 81.34 (s), 76.37 (s), 76.12 (s), 75.87 (s), 71.38 (s), 56.26 (s).

6. Proposed mechanism for the cleavage of *β*-O-4 linkages in lignin



Scheme S1. Proposed mechanism for the transformation of **1** to **2** and **3.**

7. Extraction of Lignin[4]

The birch sawdust (10 g) was added extracted in soxhlet extracter with toluene and EtOH (2:1) for 24h. The solid was dried under air and then put into a 250 mL round bottom flask with a reflux condenser charged with 100 mL 0.7wt% HCl solution (dioxann:water = 9:1). The mixture was heated to a gentle reflux under a N_2 atmosphere for 6 hours. The mixture was allowed to cool to room temperature and the lignin containing liquor was collected by filtration, the liquor was neutralized by $NaHCO_3$ and the solvent was removed by evaporation at reduced pressure, the obtained residue was dissolve by 10 mL dioxane. Then, the solution was added in 100 mL 1wt% Na_2SO_4 solution and stirred in a low speed for 1h. The precipitated lignin was collect by filtration and wash with water to remove SO_4^{2-}, finally, the lignin was dried under vacuum at 60 ^oC overnight. This lignin was used in subsequent experiments without further processing.

8. GS-MS spectrum of the lignin depolymerization product

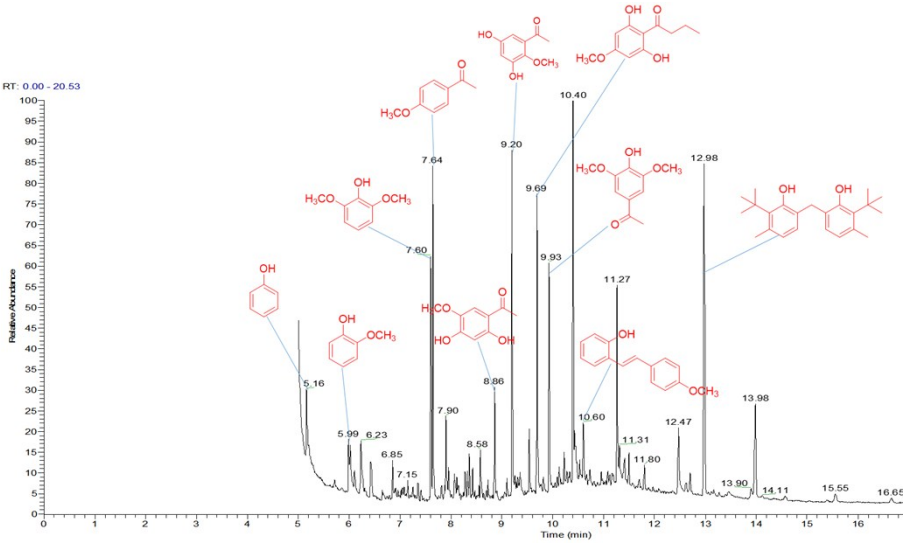


Figure S1. GC-MS spectrum of the soluble crude product mixture from depolymerization of organosolv lignin.

9. TEM imagines for Pd_1Ni_4/MIL-100(Fe) catalyst after the recycle experiment.

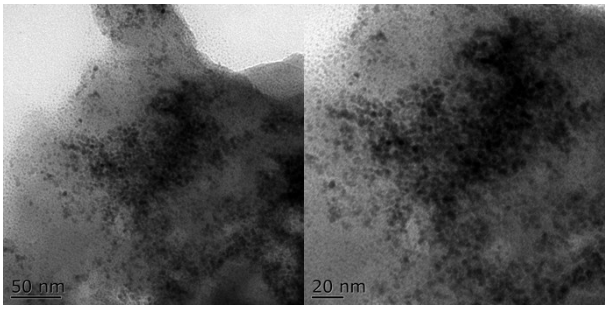


Figure S2. TEM imagines for catalyst after five cycles.

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