Supplementary Information (SI) for Green Chemistry.

Supplemental Information for

Insights into reductive catalytic deconstruction of lignin over ultralow-loading palladium-zinc catalysts derived from zinc imidazolate frameworks

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1. General information

Reagents and feedstocks

All commercially available chemical reagents were used without further purification unless especially noted. Methanol and 1,3,5-benzenetricarboxylic acid were purchased from Energy Chemical, China. Pine (*Pinus yunnanensis*, 5 years old), Birch (*Betula alnoides*, 6 years old), Beech (*Zelkova serrata,* 6 years old), Poplar (*Populus X Canadensis,* 5 years old), Fir (*Cunninghamia lanceolata,* 6 years old) and Eucalyptus (*Eucalyptus robusta*, 5 years old) were used as raw materials in this work, which was extracted, crushed and screened into powders in the size of 40 ~ 60 meshes (0.5 ~ 1.0 mm), and dried vacuum at 50 °C for 24 h before used. Double enzymatic lignin (DEL) were prepared from the ball-milled wood meal as previously descripted.[1]

Supplementary methods

GPC sample measurement method: GPC analyses were performed on a Water System (Sunnyvale, CA) equipped with an isocratic pump (Waters 1515), an automatic injector (Waters 717 plus), and a Dual Absorbance UV detector (Waters 2487) with an Agilent PLgel 3 μm 100 Å 300 × 7.5 mm column. THF was used as the mobile phase with a column flow rate and temperature of 0.5 mL/min and 30 °C, respectively.[1-2] GPC samples were prepared by dissolving 2 mg of lignin in 1 mL of THF and filtered with a 0.22 μm PTFE filter prior to injection. The filtered solution (20.0 μL) was injected into the GPC system and detected using an UV detector set at 280 nm.

Acetylation of lignin before GPC: The molecular weights of the lignin samples were determined after acetylation. Briefly, 20 mg lignin was dissolved in 0.5 mL pyridine. To this was added 0.5 mL of acetic anhydride and the mixture was heated at 80 °C for 4 h. The solution was then added dropwise to 100 mL of ice water. The mixture was then centrifuged and the water decanted. A small amount of water was added to the lignin precipitate to completely wash out the pyridine. The acetylated lignin samples were lyophilized and assayed as described above after repeated centrifugation and washing for 3 times.[1,2]

Standard curve of GPC:

1. Standard curve for lignin measurement: Eight GPC polystyrene standards (M_w, 620, 1230, 4720, 6660, 9830, 18000, 26520, 46400 g/mol) purchased from Agilent (Agilent Technologies, Inc., Santa Clara, CA) were used to fit the standard curves.

2. Standard curve for lignin oil measurement: Diphenylacetophenone (M_w, 182 g/mol), 2-bromoacetophenone (M_w, 199 g/mol) purchased from Aladdin and four GPC polystyrene standards (M_w, 620, 1230, 2790, and 6660 g/mol) purchased from Agilent were used to fit the standard curves.

GC measurement method: The injection temperature was 250 °C. The column temperature program was: 50 °C (3 min), 8 °C/min to 280 °C (5 min). The detection temperature was 200 °C for FID.

GC and GC-MS measurement conditions: GC and GC-MS analyses were carried out on a Shimadzu Model 2010 plus equipped with a HP-5 column (30 m × 0.25 mm × 0.25 mm) using a flame ionization detector (FID) and a Shimadzu GCMS-QP 2010pro equipped with a HP-5MS (30 m × 0.25 mm × 0.25 mm) column, respectively. The detection temperature was 60 °C, the velocity of the pump was 0.6 mL/min.

NMR measurement conditions: The NMR spectra were acquired on a Bruker Ascend-400 MHz spectrometer instrument (Bruker, Germany). Lignin, oily products and synthetic lignin polymer were dissolved in DMSO-d_6, whereas lignin models were dissolved in $CDCl_3$. As for 2D HSQC NMR experiment, the solvent peak (DMSO-d_6) at δ_C/δ_H 39.5/2.49 ppm was used as an internal reference. The standard Bruker implementations of 2D HSQC NMR experiments were used for structural characterization and the authentication were assigned according to previously reported papers.[1,2]

XPS analysis and fitting conditions: X-ray photoelectron spectroscopy (XPS) analysis was conducted using a Thermo Scientific K-alpha plus spectrometer with a monochromatic Al Kα X-ray source operated at a voltage of 1486.6 eV. All spectra were collected with a step of 0.1 eV and a pass energy of 50 eV using the C 1s binding energy of 284.8 eV for calibration.

XRD measurement conditions: X-ray diffraction (XRD) analysis was carried out using a Shimadzu Lab XRD-6100 diffractometer with a Kα radiation source operated at 15 mA and 40 kV. XRD patterns were collected in the 2θ range of 10° to 90° at a scan speed of 2 °/min.

2. Preparation of catalysts

2.1 Preparation of Pd-Zn@NC catalyst: The solubilization of 34 mg of potassium iodide (KI) and 100 mg of polyvinylpyrrolidone (M_w, 55000 g/mol) was achieved by heating a 10 mL solution of formamide to 120 °C. Next, 59 mg of sodium palladium chloride powder was added to the mixture while stirring for 15 min. Following this, the mixture was cooled to room temperature and 120 mL of acetone was added. The resulting dispersion was then collected through centrifugation at 10,000 revolutions per min for 10 min. The obtained palladium nanoparticles were dispersed in 21 mL of a mixed solvent consisting of a 4:1 volume ratio of N, N-dimethylformamide (DMF) to methanol. Additionally, 4,276 mg of zinc nitrate hexahydrate ($Zn(NO_3)_2$-$6H_2O$) was dissolved in 60 mL of the same mixed solvent in flask A. After that, 2 ml of the above solution of palladium nanoparticles was added to flask A with a dropper. In flask B, 4664 mg of 2-methylimidazole was made to dissolve in 80 mL of the same mixture under sonication for 5 min, resulting in a clear solution. Slowly poured the solution from flask B into flask A and set to room temperature for 12 h. The product obtained was separated through centrifugation at 10000 r/min, followed by three successive washes with methanol, and finally dried at 60 °C for 3 h. The white Pd-NPs@ZIF-8 powder, obtained after grinding, was transferred to a ceramic boat and placed in a tube furnace. The samples were then heated to 120 °C for 1 h to eliminate any moisture present, and subsequently heated to 900 °C at a rate of 5 °C/min, held at this temperature for 3 h, and cooled to room temperature at a rate of 5 °C/min. The collected black powder was the Pd-Zn@NC catalyst and could be used without any treatment.

2.2 Preparation of Zn@NC: 4276 mg of zinc nitrate hexahydrate ($Zn(NO_3)_2$-$6H_2O$) was dissolved in 60 mL of the same mixed solvent in flask A. In flask B, 4664 mg of 2-methylimidazole was made to dissolve in 80 mL of the same mixture under sonication for 5 min, resulting in a clear solution. Slowly poured the solution from flask B into flask A and set to room temperature for 12 h. The product obtained was separated through centrifugation at 10000 r/min, followed by three successive washes with methanol, and finally dried at 60 °C for 3 h. The white ZIF-8 powder, obtained after grinding, was transferred to a ceramic boat and placed in a tube furnace. The samples were then heated to 120 °C for 1 h to eliminate any moisture present, and subsequently heated to 900 °C at a rate of 5 °C/min, held at this temperature for 3 h, and cooled to room temperature at a rate of 5 °C/min. The resulting material was ready for use without any additional treatment. The black powder collected was the Zn@NC catalyst. It could be used without further treatment.

2.3 Preparation of Pd@NC: The procedure is the same as for the Pd-Zn@NC catalyst, except that the calcination temperature was set to be 1100 °C. Calcination was also carried out under nitrogen for 3 h. The black powder collected was the Pd@NC catalyst.

2.4 Recycling experiment of Pd-Zn@NC: The solid residue was rinsed with dichloromethane three times and drained after each reaction. Due to the finer and less dense nature of the catalyst particles, the upper portion of the solid residue in the funnel was separated and filtered through 100 mesh and 300 mesh sieves to isolate the fine black catalyst particles from the brown wood flour residue. Subsequently, 50 mg of the isolated black catalyst particles were taken under nitrogen protection and recalcined at 900 °C for 1 h in a tube furnace. It could be used without further treatment.

3. Determination of biomass composition

Biomass composition was determined according to the standard analytical procedure (NREL/TP-510-42618).[3] The biomass chips (40 ~ 60 mesh) were extracted with toluene/ethanol (2:1, v/v) in a Soxhlet apparatus for 12 h and then dried at 80 °C overnight. The mixture containing 300 mg of dried biomass and 3 mL of 72 wt% H_2SO_4 solution was stirred at 30 °C for 2 h, which was then diluted by adding 84 mL of deionized water and heated at 120 °C for 1 h in the high pressure autoclave. After cooling the reactor to room temperature, the solid residue and the solution were separated by filtration. The solid residue was dried at 110 °C to obtain Klason lignin (AIL). The acid soluble lignin (ASL) in the filtrate was analyzed using a UV-Vis spectrophotometer with high purity quartz cuvettes of pathlength1 cm by recording the absorbance of the soluble fraction at 205 nm. Finally, the monosaccharides were determined by high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD).

Table S1 The composition of softwood and hardwood sawdusts.[a]

Entry	Substrate	AIL[b] (wt%)	ASL[c] (wt%)	Lignin (wt%)	Cellulose (wt%)	Hemicellulose (wt%)
1	*Pinus yunnanensis*[d]	27.27	0.30	27.57	46.18	23.57
2	*Larix gmelinii*	26.55	0.72	27.27	44.31	28.35
3	*Pinus Koraiensis*	26.91	0.30	27.57	36.65	26.57
4	*Betula alnoides*[e]	27.36	1.70	29.06	44.20	26.42
5	*Eucalyptus robusta*[f]	26.63	1.89	28.52	40.32	22.70
6	*Zelkova serrata*[g]	21.33	2.81	23.13	42.03	26.81
7	*Populus X canadensis*[h]	27.27	0.30	27.57	38.54	15.48

[a] The compositions of biomass were analyzed according to the procedures of the NREL method.

[b] AIL: acid insoluble lignin (Klason lignin).

[c] ASL: acid soluble lignin.

[d] In the following text, Pine refers to *Pinus yunnanensis*.

[e] In the following text, Birch refers to *Betula alnoides*.

[f] In the following text, Eucalyptus refers to *Eucalyptus robusta.*

[g] In the following text, Beech refers to *Zelkova serrata.*

[h] In the following text, Poplar refers to *Populus X Canadensis.*

4. Catalyst characterization

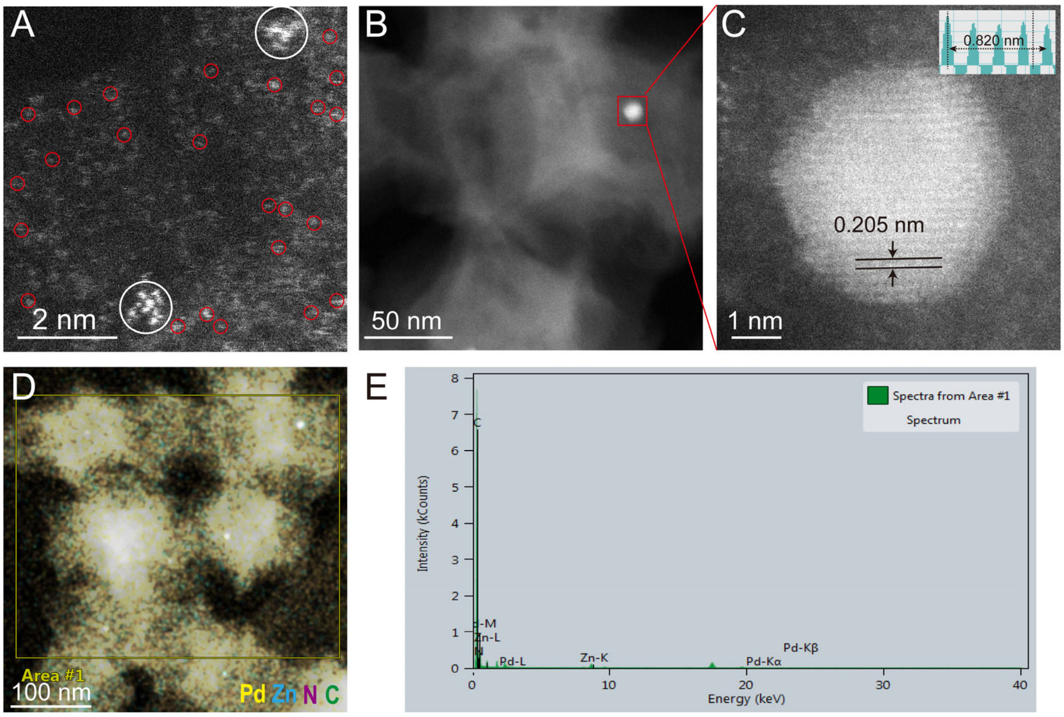


Figure S1. (A, B and C) High-resolution TEM of fresh Pd-Zn@NC catalyst. (D) The EDS elemental mapping of fresh Pd-Zn@NC. (E) The EDS spectra from fresh Pd-Zn@NC catalyst.

Note S1. TEM images showed a very small amount of nanoparticles. And these particles are concentrated in the centre of the MOF structure, which is due to the fact that there are more N-active sites exposed in the central part, so there is some aggregation of the metal target in there during sintering.

Table S2 Textural properties of Pd-Zn@NC, Zn@NC, and Pd @NC catalysts.

Sample	Specific surface area (m^2/g)[a]	Pore volume (cm^3/g)[b]	Pore diameter (nm)[c]
Pd-Zn@NC	992	1.01	9.16
Zn@NC	1113	0.78	11.60
Pd @NC	1492	1.37	9.06

[a] BET surface area.

[b] BJH Desorption cumulative volume of pores (d > 2 nm).

[c] BJH Adsorption average pore diameter.

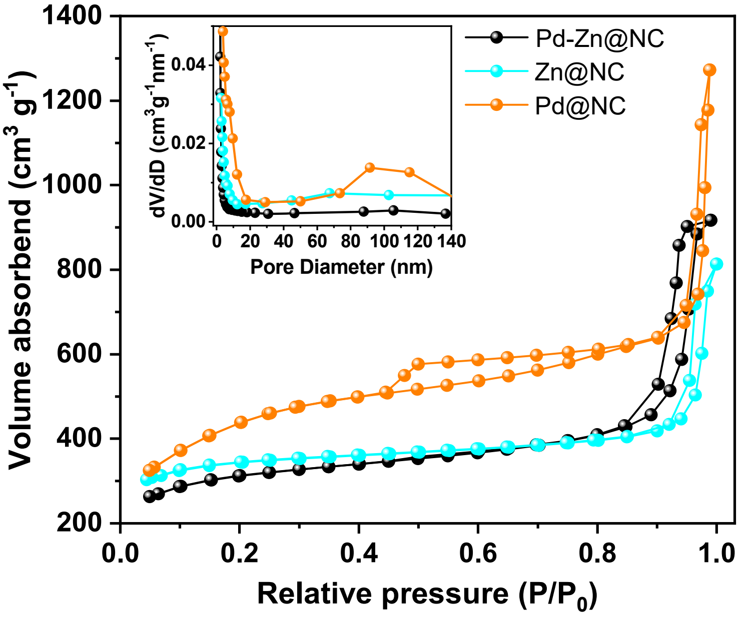


Figure S2. N_2 adsorption-desorption isotherms and pore diameter distribution of Pd-Zn@NC, Zn@NC, and Pd@NC catalysts.

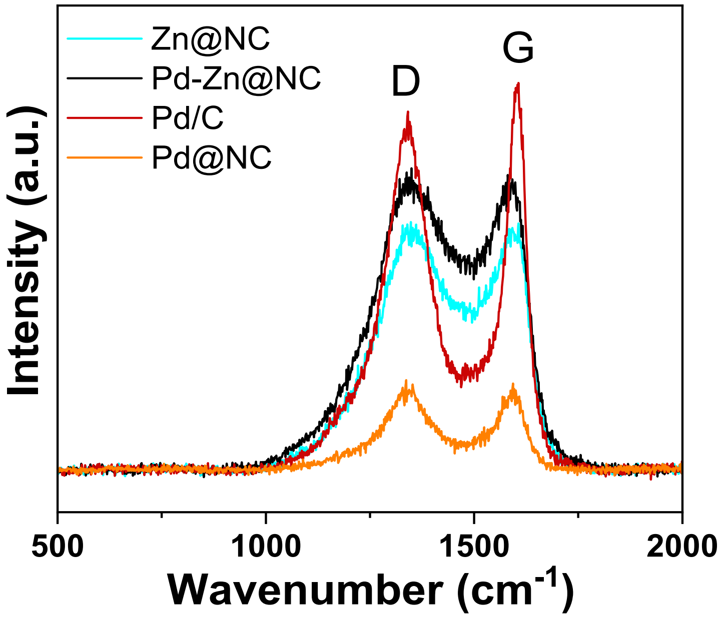


Figure S3. Roman spectra of the catalysts.

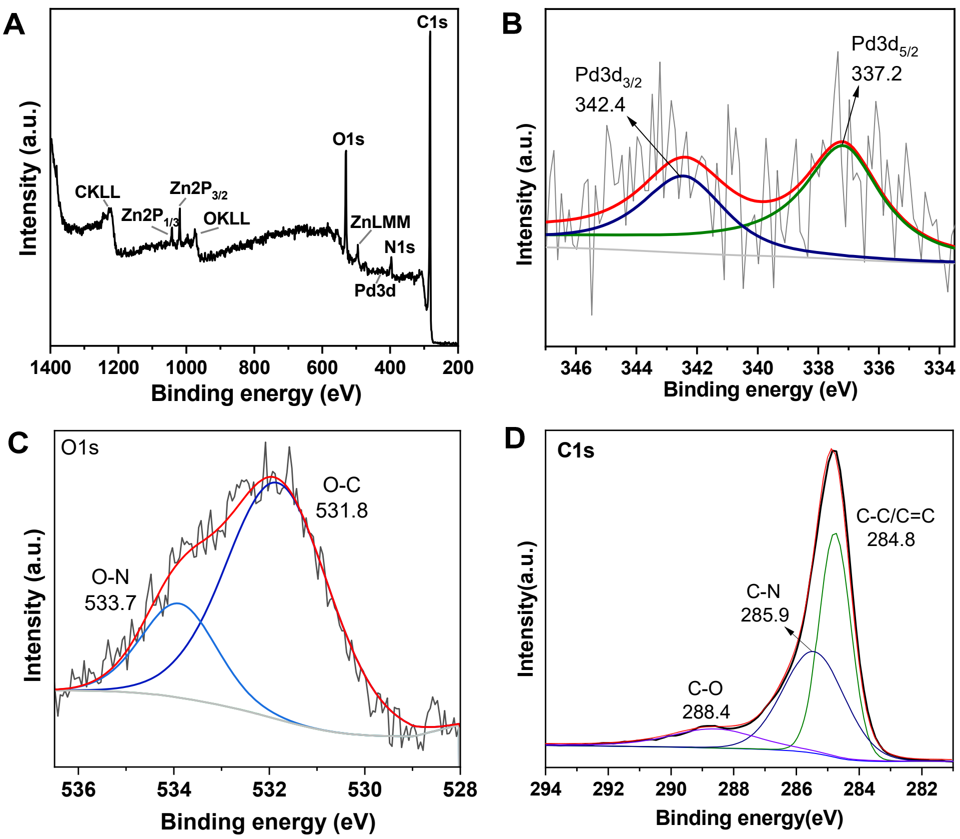


Figure S4. XPS spectra of fresh Pd-Zn@NC catalyst.

Note S2: The XPS spectra were further fitted to obtain the distribution of each element in the fresh Pd-Zn@NC catalyst as C 86.0%, N 5.7%, O 7.8%, Zn 0.6% and Pd 0.02%.86.0 % C, 5.7 % N, 7.8 % O, 0.6 % Zn and 0.02 % Pd.

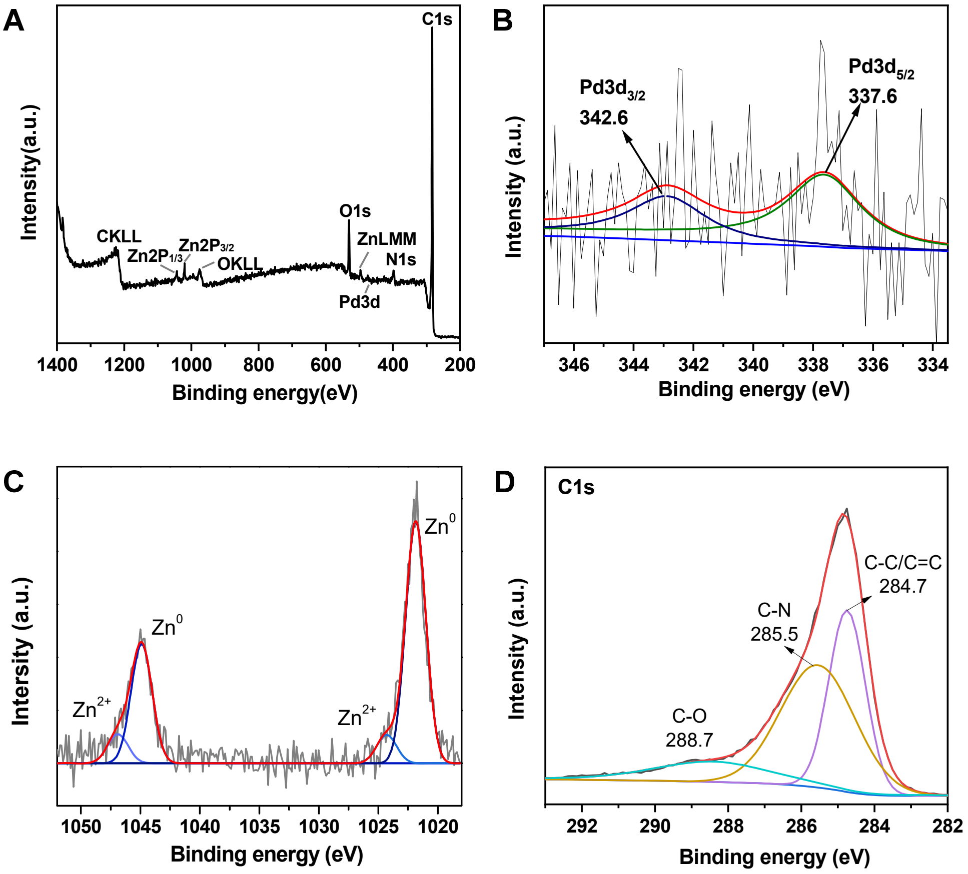


Figure S5. XPS spectra of the spent Pd-Zn@NC catalyst.

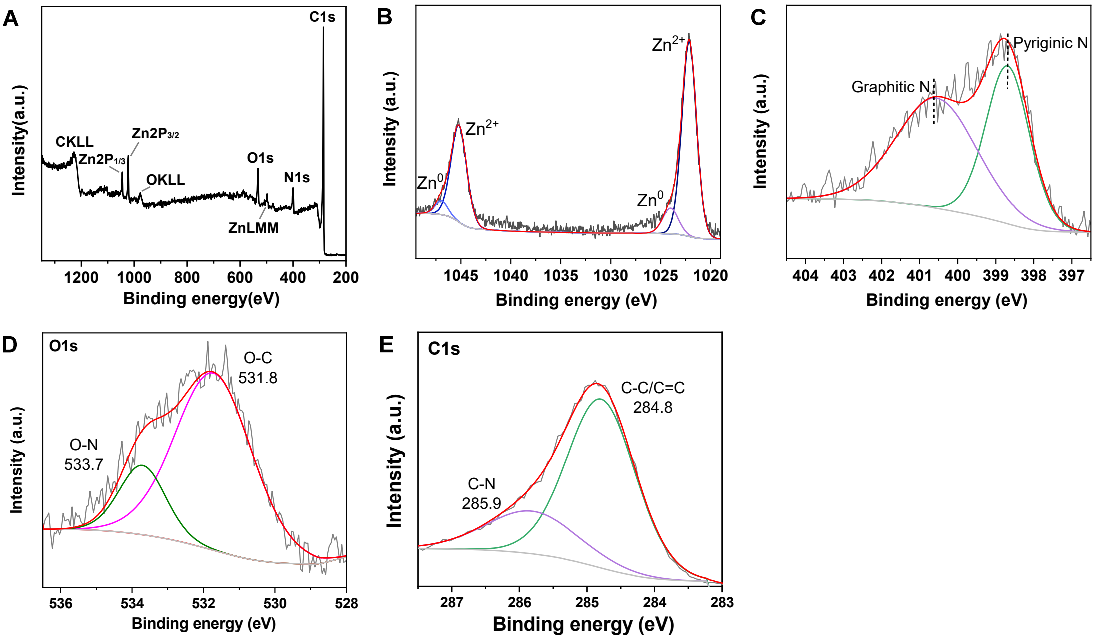


Figure S6. XPS spectra of the Zn@NC catalyst.

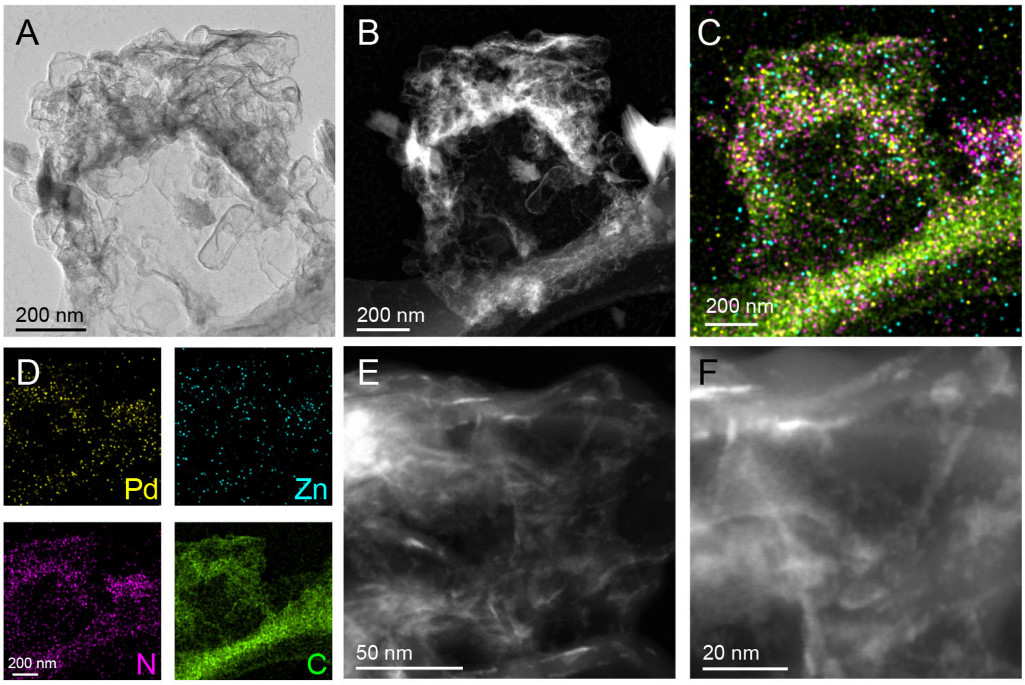


Figure S7. Characterizations of the spent Pd-Zn@NC catalyst. (A) TEM image. (B, E, and F) HAADF-TEM images. (C, D) HAADF-TEM-EDS elemental mapping results.

Table S3 ICP-OES analyses of the catalysts.

Sample	Pd content (%)	Zn content (%)
Fresh Pd-Zn@NC	0.10	3.72
Spent Pd-Zn@NC	0.05	2.03
Pd@NC	0.37	0.62
Pd/C + Zn@NC[a]	0.86	5.73

[a] Mixed in the contents of commercial 5 wt% Pd/C (1 mg) and the fabricated Zn@NC catalyst (5.5 mg).

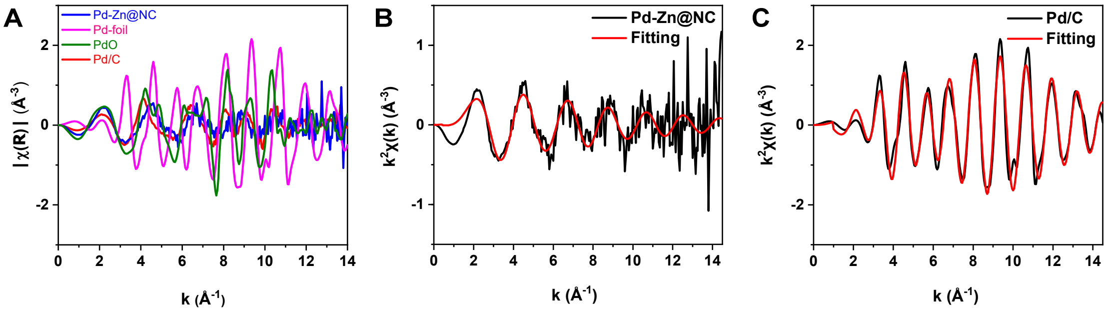


Figure S8. K space EXAFS.

(A) K space EXAFS of Pd-Zn@NC, Pd-foil, PdO and Pd/C.

(B) K space EXAFS of the Pd-Zn@NC catalyst and fitted curve.

(C) K space EXAFS of the commercial 5 wt% Pd/C catalysts and fitted curve.

Table S4 EXFS data fitting results of Pd-Zn@NC, Pd-foil, the coordination number for the absorber-back scatting pair.

Sample	Scattering pair	CN	R (Å)	σ^2 (10^{-3} Å^2)	ΔE_0 (eV)	R factor
Pd-Zn@NC	Pd-N	2.95 ± 0.43	2.00 ± 0.10	2.0 ± 1.6	0.64 ± 2.08	0.0158
Pd-foil	Pd-Pd	12	2.74 ± 0.06	5.3 ± 0.3	3.51 ± 0.39	0.0027

5. Hydrogenolysis of Pine lignin

Sawdust (50 mg), catalyst (6.5 mg) and MeOH (10 mL) were placed in a 50 mL stainless steel autoclave. The autoclave was pressurized to 3 MPa H_2 at room temperature and then heated to the desired temperature with stirring at 800 rpm. Upon completion, the autoclave was cooled and depressurized. Reaction mixture was filtered and insoluble fraction washed with dichloromethane. The solution was extracted with dichloromethane (DCM) and the lignin oil product was obtained after removal of all volatiles under vacuum conditions. An external standard (1,3,5-trimethoxybenzene) was added to the lignin oil solution in dichloromethane. The solution was analyzed by GC and GC-MS. By comparison with authentic samples obtained from commercial purchase or independent synthesis, the identification and quantification of lignin monomers in the oily product was evaluated.

The lignin oil yields, monomer yields, conversion and turnover number were calculated using the following equations:

Lignin oil yield (wt%) = Mass (DCM soluble)/Mass (initial lignin) × 100%

Monomer yield (wt%) = Mass (total monomers)/Mass (initial lignin) × 100%

Monomer yield (wt%) = Mole (monomer)/Mole (β-*O*-4' lignin mimics) × 100%

Conversion (%) = Mass (total monomer)/Mass (β-*O*-4' lignin mimics) × 100%

(Hemi)cellulose residues yield (wt%) = Mass (residues)-Mass (catalyst)/Mass (raw material) × 100%

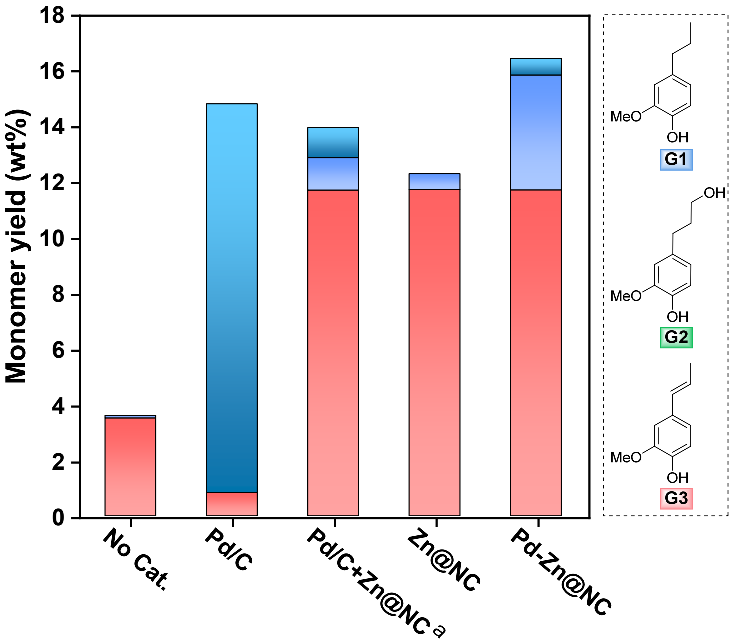
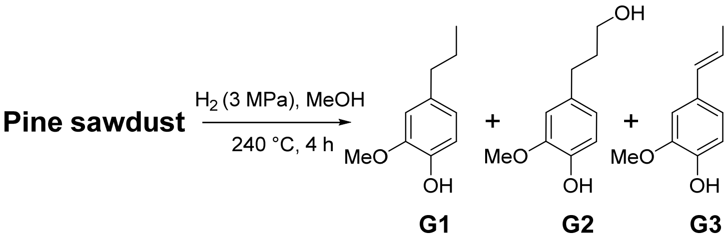


Figure S9. Hydrogenolysis of Pine sawdust over different catalysts. Reaction conditions: Pine sawdust (50 mg), catalyst (6.5 mg), MeOH (10 mL), H_2 (3 MPa), 240 °C, 4 h.

[a] Mixed in the contents of commercial 5 wt% Pd/C (1 mg) and the fabricated Zn@NC catalyst (5.5 mg).

Table S5 Hydrogenolysis of Pine lignin over different catalysts.[a]



Entry	Catalyst	Phenolic monomers yield (wt%)				Selectivity (%)[b]
		G1	G2	G3	Total monomers	
1	No cat.	0.1	0.0	3.5	3.6	98
2	Zn@NC	0.6	0.0	11.7	12.3	95
3	Pd-Zn@NC	4.1	0.6	11.7	16.5	71
4	Pd@NC[c]	10.1	0.5	5.6	16.2	34
5	Pd/C	0.0	14.0	0.8	14.8	94
6	Ru/C	12.5	2.4	ND	14.8	84
7	Pd/C + Zn@NC[d]	1.2	1.1	11.7	14.0	84
8	Pd-NPs@ZIF-8	0.3	0.3	1.9	2.4	78

[a] Reaction conditions: Softwood sawdust (50 mg), catalyst (6.5 mg), MeOH (10 mL), H_2 (3 MPa), 240 °C, 4 h.

[b] Contribution of G3 to total yield in phenolic monomer products, where for Pd/C and Ru/C are G2 and G1.

[c] Pd-NPs@ZIF-8 was calcined at 1100 °C under nitrogen for 3h

[d] Mixed in the contents of commercial 5 wt% Pd/C (1 mg) and the fabricated Zn@NC catalyst (5.5 mg).

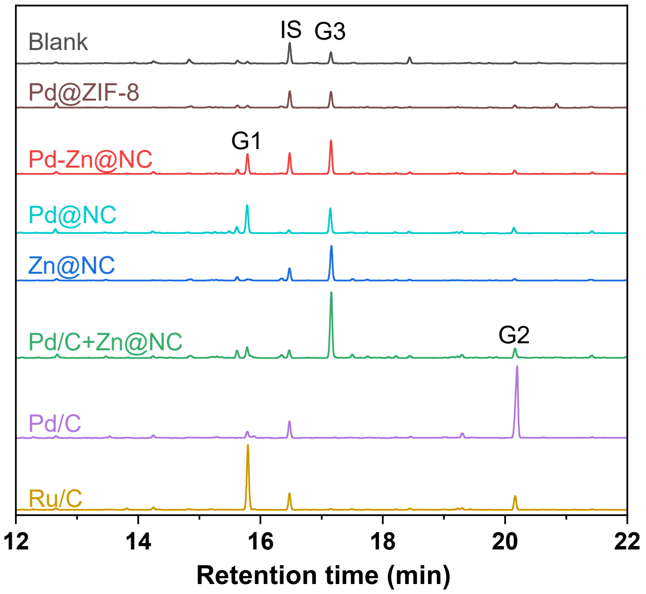


Figure S10. GC chromatogram of the monomers obtained from hydrogenolysis of Pine sawdust over different catalysts.

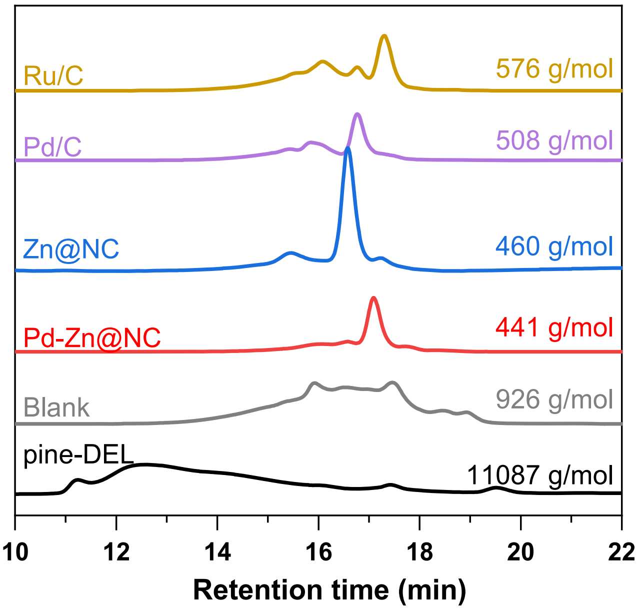
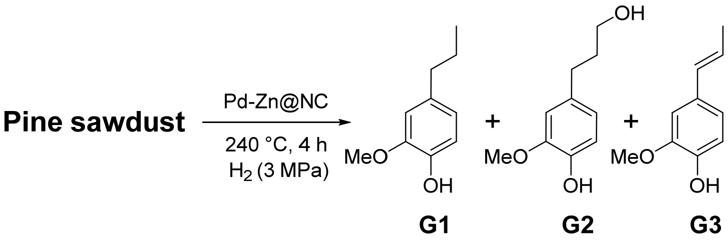


Figure S11. Molecular weight distribution of Pine lignin and oily products obtained from hydrogenolysis of Pine sawdust over different catalysts via GPC analysis.

Table S6 Pd-Zn@NC-catalyzed hydrogenolysis of Pine sawdust under different solvents.[a]



Entry	Solvent	Phenolic monomers yield (wt%)				Selectivity (%)[b]
		G1	G2	G3	Total monomers	
1	EtOH	7.3	0.8	5.3	13.4	39
2	THF	0.6	0.2	11.7	12.5	94
3	Dioxane	4.7	1.0	6.8	12.4	54
4	^{i}PrOH	8.2	1.2	2.5	11.9	21
5	EtOH+ H_2O	0.8	0.5	9.5	10.8	88
6	H_2O	1.4	0.3	0.6	2.3	27

[a] Reaction conditions: Pine sawdust (50 mg), Pd-Zn@NC (25 mg), solvent (10 mL), H_2 (3 MPa), 240 °C, 4 h.

[b] ND, not detectable.

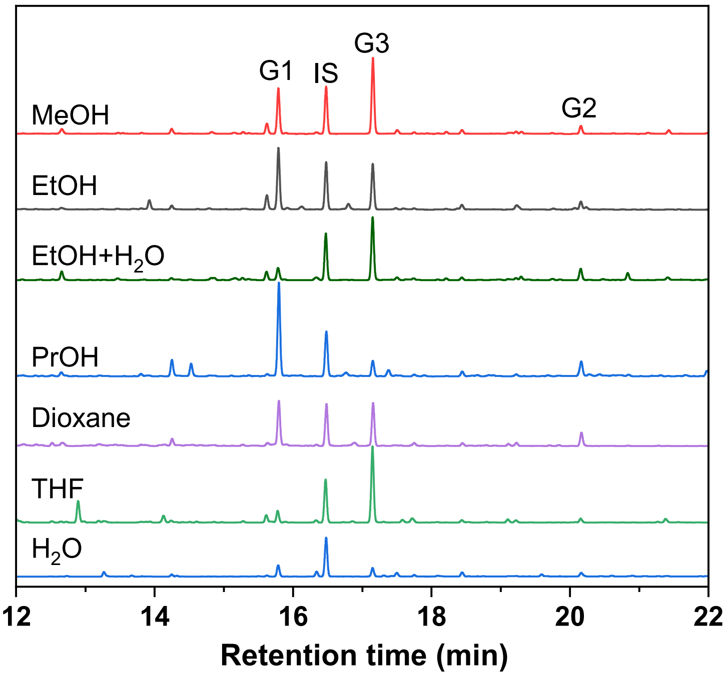


Figure S12. GC chromatogram of the monomers obtained from hydrogenolysis of Pine sawdust under different solvents.

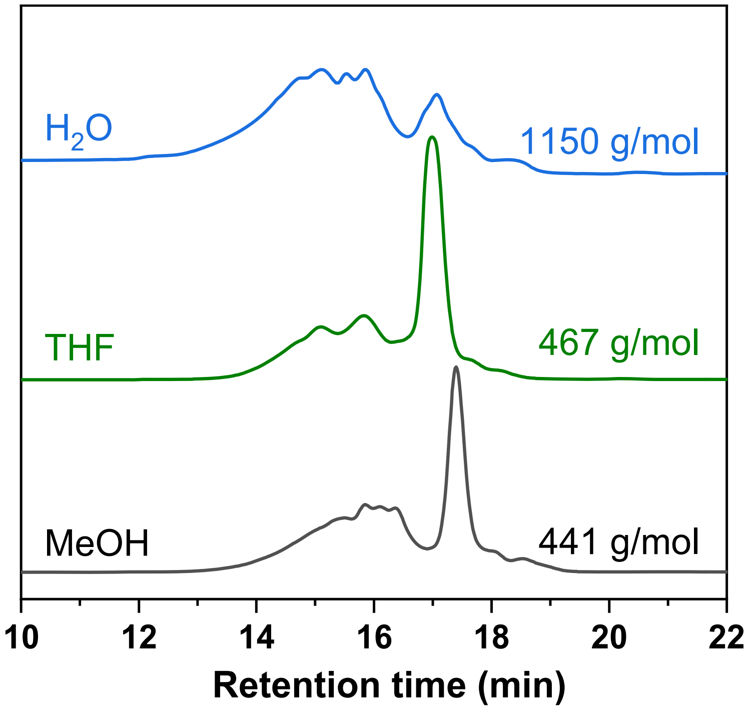
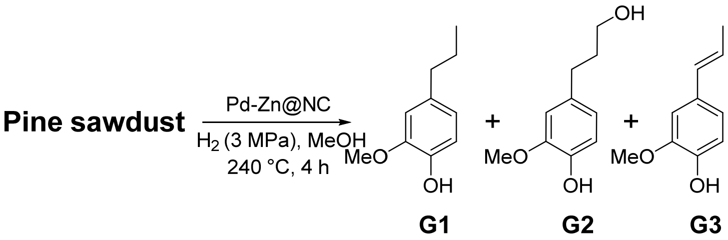


Figure S13. Molecular weight distribution of Pine lignin and oily products obtained from hydrogenolysis of Pine sawdust under different solvents via GPC analysis.

Table S7 Pd-Zn@NC-catalyzed hydrogenolysis of Pine sawdust with different catalyst dosages.[a]



Entry	Dosage (mg)	Phenolic monomers yield (wt%)				Selectivity (%)[b]
		G1	G2	G3	Total monomers	
1	3.5	2.0	0.2	6.6	8.8	75
2	5	2.2	0.6	11.0	13.8	80
3	6.5	4.1	0.6	11.7	16.5	71
4	8	3.6	1.3	11.5	16.4	70
5	10	7.4	1.1	7.1	15.6	45
6	50	13.2	0.6	ND[c]	13.8	0

[a] Reaction conditions: Pine sawdust (50 mg), Pd-Zn@NC, solvent (10 mL), H_2 (3 MPa), 240 °C, 4 h.

[b] Contribution of G3 to total yield in phenolic monomer products.

[c] ND, not detectable.

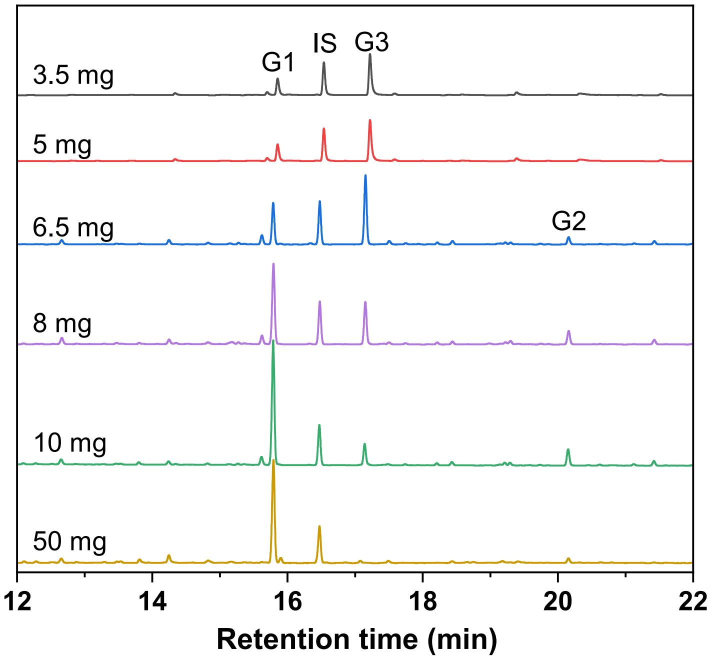
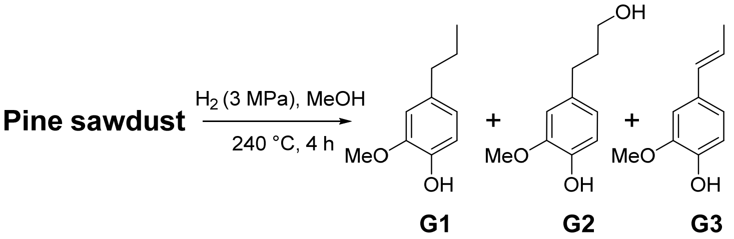


Figure S14. GC chromatogram of the monomers obtained from hydrogenolysis of Pine sawdust with different catalyst dosages.

Table S8 Pd-Zn@NC-catalyzed hydrogenolysis of Pine sawdust under different temperatures.[a]



Entry	Temperature (°C)	Phenolic monomers yield (wt%)				Selectivity (%)[b]
		G1	G2	G3	Total monomers	
1	200	3.3	0.6	7.7	11.6	66
2	220	2.1	0.5	10.1	12.7	80
3	240	4.1	0.6	11.7	16.5	71
4	260	1.1	0.8	8.9	10.8	82

[a] Reaction conditions: Pine sawdust (50 mg), Pd-Zn@NC (6.5 mg), solvent (10 mL), H_2 (3 MPa), 4 h.

[b] Contribution of G3 to total yield in phenolic monomer products.

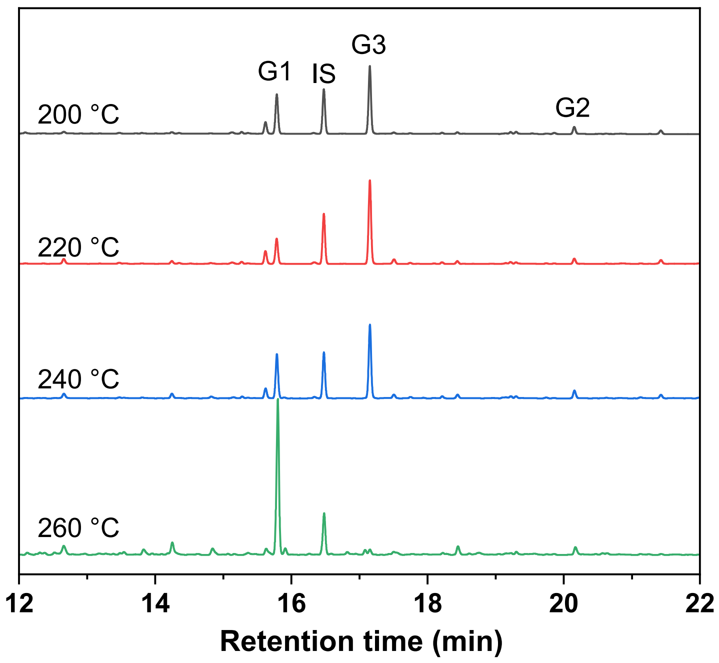


Figure S15. GC chromatogram of the monomers obtained from hydrogenolysis of Pine sawdust under different temperatures.

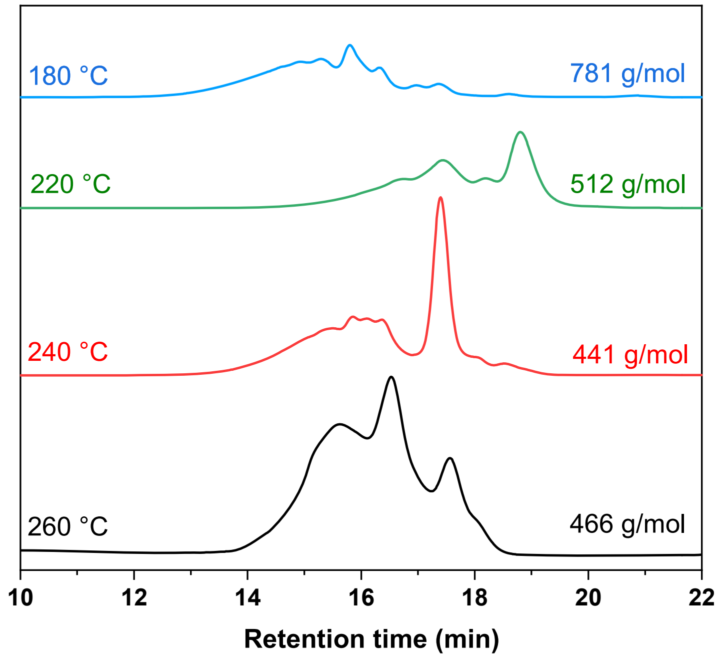
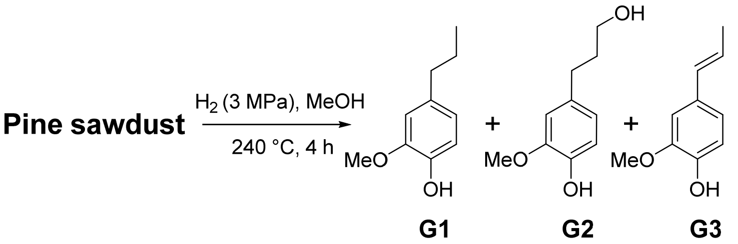


Figure S16. Molecular weight distribution of Pine lignin oil obtained from hydrogenolysis of Pine sawdust under different temperatures via GPC analysis.

Table S9 Pd-Zn@NC-catalyzed hydrogenolysis of Pine sawdust under different hydrogen pressure.[a]



Entry	Hydrogen pressure (MPa)	Phenolic monomers yield (wt%)				Selectivity (%)[b]
		G1	G2	G3	Total monomers	
1	0	0.8	0.2	3.1	4.0	77
2	1	2.1	0.4	7.5	10.0	75
3	2	3.6	0.4	7.8	11.8	66
4	3	4.1	0.6	11.7	16.5	71

[a] Reaction conditions: Pine sawdust (50 mg), Pd-Zn@NC (25 mg), solvent (10 mL), H_2, 240 °C, 4 h.

[b] Contribution of G3 to total yield in phenolic monomer products.

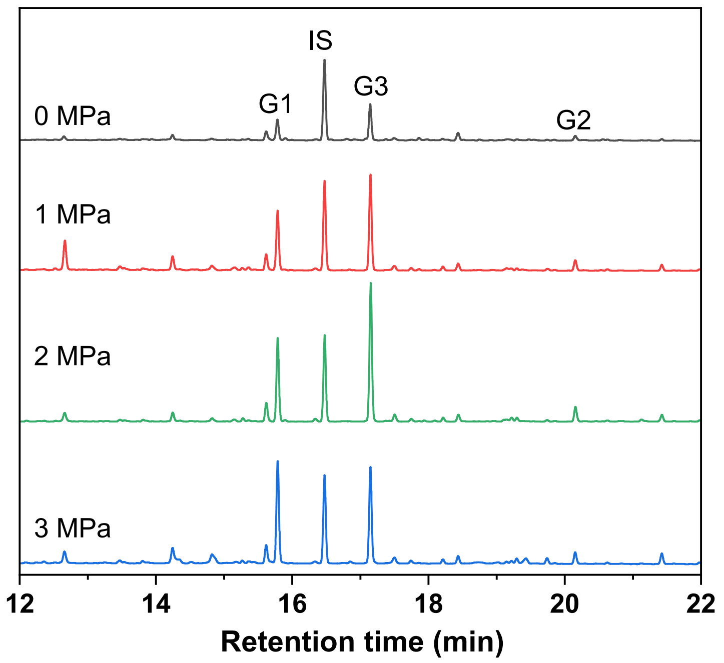
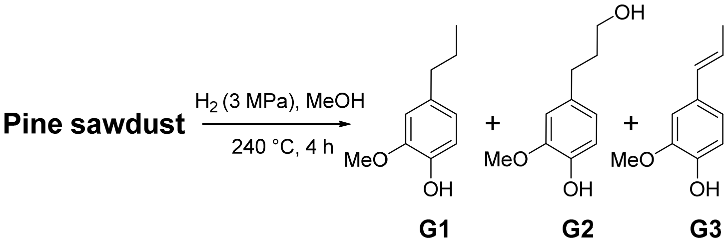


Figure S17. GC chromatogram of the monomers obtained from hydrogenolysis of Pine sawdust under different hydrogen pressure.

Table S10 Pd-Zn@NC-catalyzed hydrogenolysis of Pine sawdust with different reaction times.[a]



Entry	Time (h)	Phenolic monomers yield (wt%)				Selectivity (%)[b]
		G1	G2	G3	Total monomers	
1	1	0.9	0.7	10.7	12.3	87
2	2	0.8	0.5	12.9	14.2	91
3	4	4.1	0.6	11.7	16.5	71
4	8	6.6	0.7	8.2	15.6	53

[a] Reaction conditions: Pine sawdust (50 mg), Pd-Zn@NC (6.5 mg), solvent (10 mL), H_2 (3 MPa), 240 °C.

[b] Contribution of G3 to total yield in phenolic monomer products.

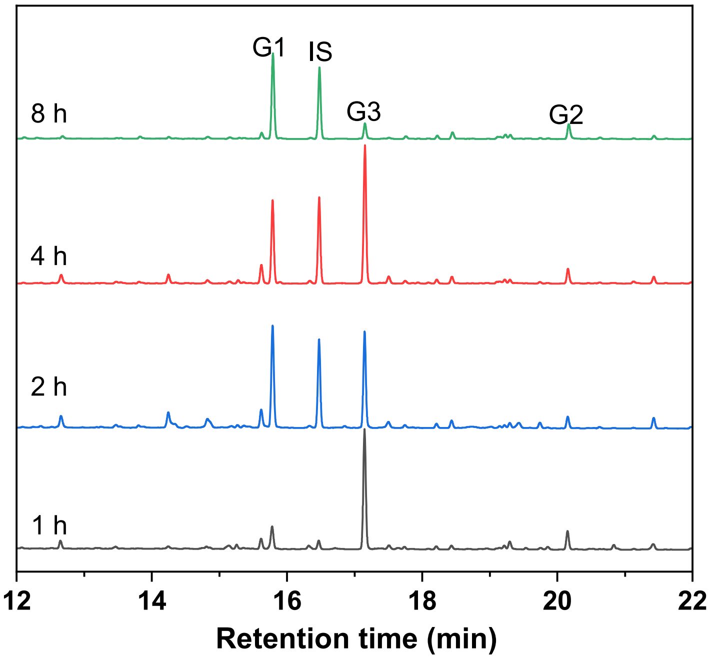


Figure S18. GC chromatogram of the monomers obtained from hydrogenolysis of Pine sawdust under different reaction times.

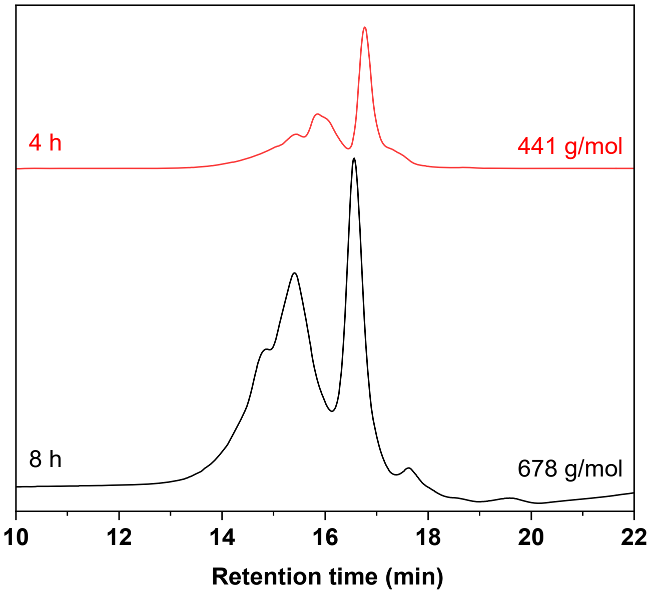


Figure S19. Molecular weight distribution of Pine lignin oil obtained from hydrogenolysis of Pine sawdust under different reaction time via GPC analysis.

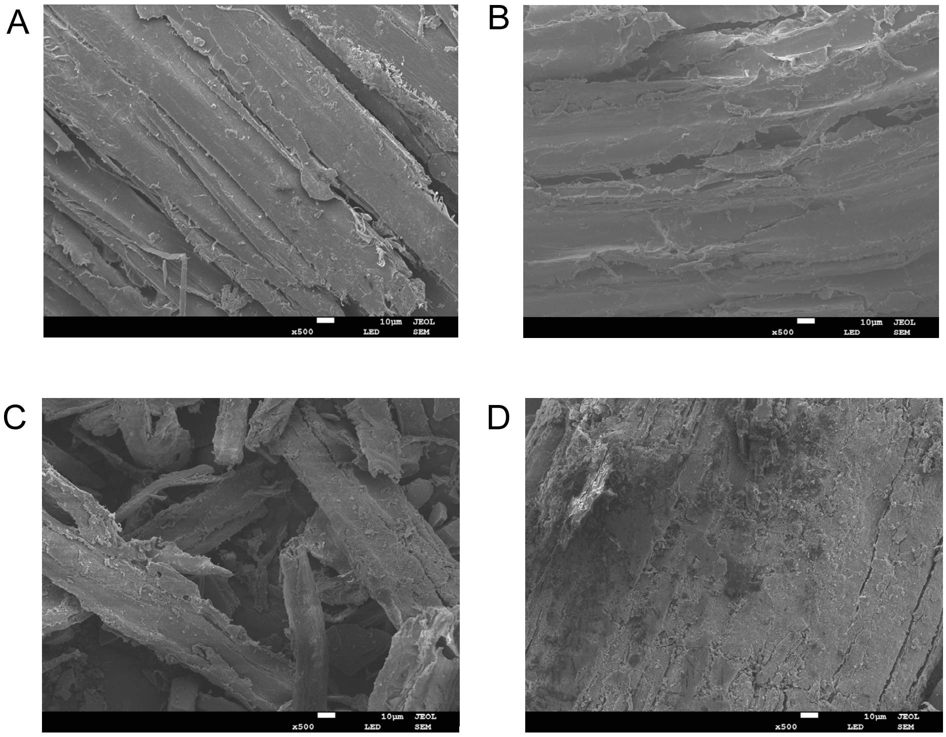


Figure S20. SEM of Pine sawdust.

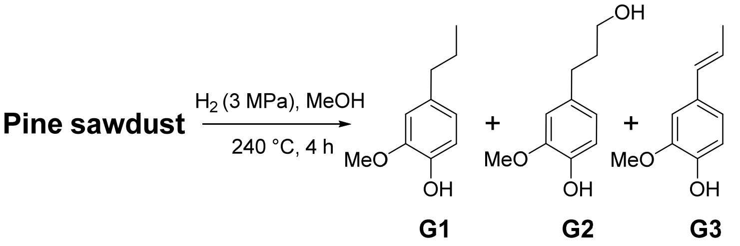
(A) Raw materials.

(B) Residues after hydrogenolysis with the Pd-Zn@NC catalyst at 240 °C and (C) 260 °C.

(D) Residues after hydrogenolysis with the Zn@NC catalyst at 240 °C.

6. Analysis of the lignin oil for the Pd-Zn@NC catalyst cycling performance

Table S11 Recycled Pd-Zn@NC-catalyzed hydrogenolysis of Pine sawdust.[a]



Entry	Times	Phenolic monomers yield (wt%)				Selectivity (%)[b]
		G1	G2	G3	Total monomers	
1	1	2.2	0.4	11.6	14.3	82
2	2	0.7	0.3	11.0	12.1	91
3	3	0.4	0.3	8.0	8.7	92
4	4	2.8	0.3	11.2	14.4	78
5	5	2.5	ND[c]	11.5	13.9	82

[a] Reaction conditions: Pine sawdust (500 mg), Pd-Zn@NC (50 mg), solvent (20 mL), H_2 (3 MPa), 240 °C.

[b] Contribution of G3 to total yield in phenolic monomer products.

[c] ND, not detectable.

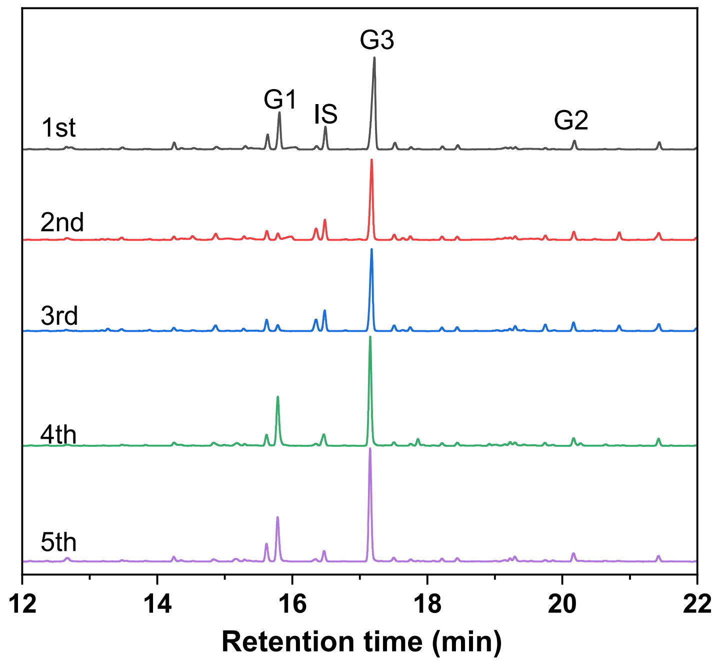


Figure S21. GC chromatograms of the monomers obtained from hydrogenolysis of Pine sawdust with five cycles.

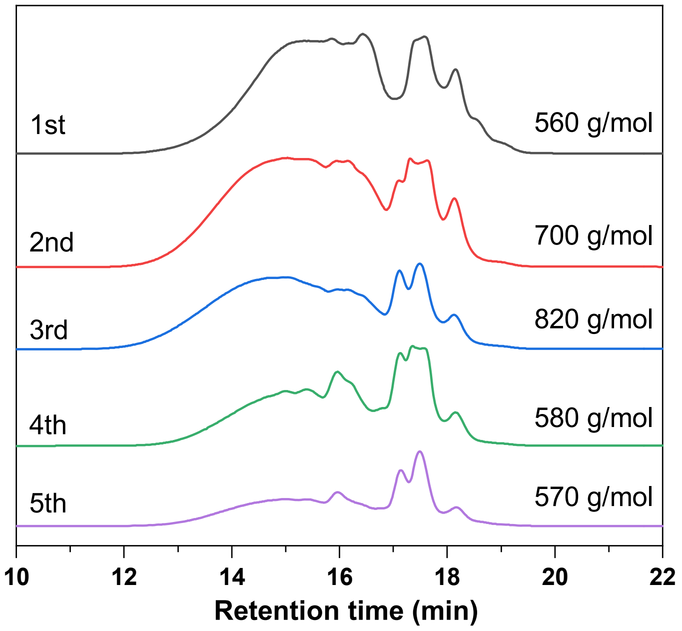
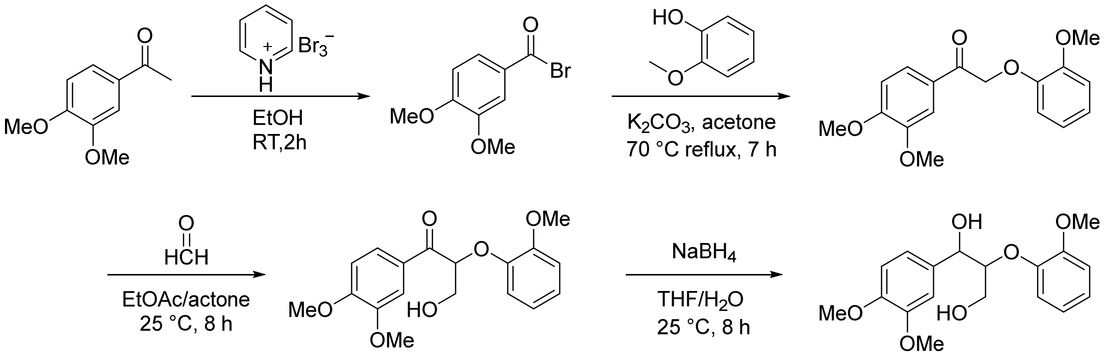


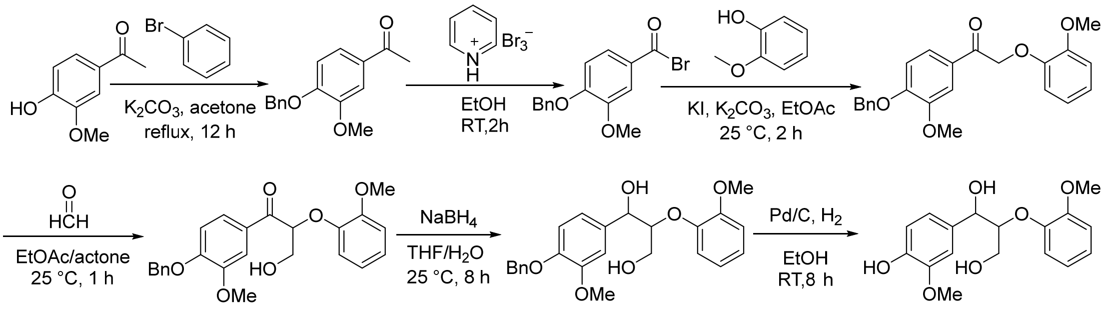
Figure S22. GPC spectra of Pine lignin oil after hydrogenolysis with five cycles of the Pd-Zn@NC catalyst.

7. Preparation of lignin model compounds

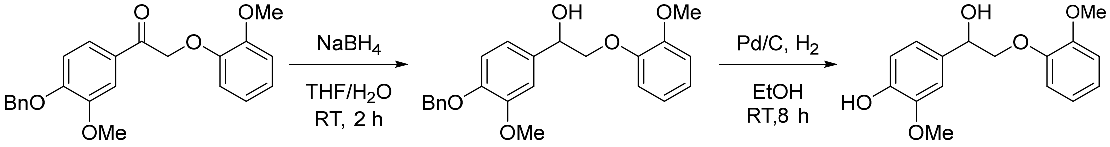
A diastereomeric mixture of dimeric lignin model compounds were prepared following previously reported procedures with minor modifications.



Scheme S1. Synthesis of dimeric lignin model compounds **1**. ^1H NMR and ^{13}C NMR spectra were recored in accordance with previous literatures.[4] ^1H NMR ($CDCl_3$, 400 MHz): δ 7.05 ~ 6.82 (m, 7H, aromatic H), 4.56 (d, 1H, $C_\alpha H$), 4.27 (m, 2H, $C_\beta H$), 3.83 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.80 ~ 3.70 (m, 2H, $C_\gamma H$), 3.42 (d, 1H, $C_\alpha OH$), 3.09 (bs, 1H, $C_\gamma OH$); ^{13}C NMR (DMSO-d_6): δ 150.3, 149.1, 148.0, 132.4, 121.6, 121.3, 120.8, 120.3, 116.7, 115.8, 112.6, 111.4, 82.3 (threo C_β),80.6 (erythro C_β), 72.3 (threo C_α), 72.2 (erythro C_α), 58.9 (threo C_γ), 57.0 (erythro C_γ), 56.1 (threo $ArOCH_3$).



Scheme S2. Synthesis of dimeric lignin model compounds **2**. ^{1}H NMR and ^{13}C NMR spectra were recorded in accordance with previous literatures.[1] ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.27 ~ 6.76 (m, 7H, aromatic H), 5.80 (d, 1H, Ar-OH), 4.41 (d, 1H, C$_\alpha$H), 4.38 (m, 1H, C$_\beta$H), 4.12 (s, 3H, OCH$_3$), 3.98 (s, 3H, OCH$_3$), 3.88 ~ 3.76 (m, 2H, C$_\gamma$H), 3.48 (d, 1H, C$_\alpha$OH), 2.82 (bs, 1H, C$_\gamma$OH); ^{13}C NMR (DMSO-*d*$_6$): δ 151.3, 147.7, 146.7, 145.6, 145.1, 131.8, 131.5, 124.3, 121.7, 121.1, 120.3, 119.1, 114.3, 112.2, 109.4, 108.7, 89.5 (threo C$_\beta$), 87.4 (erythro C$_\beta$), 74.0 (threo C$_\alpha$), 72.8 (erythro C$_\alpha$), 61.0 (threo C$_\gamma$), 60.8 (erythro C$_\gamma$), 56.0 (threo ArOCH$_3$).



Scheme S3. Synthesis of dimeric lignin model compounds **3.**[5]

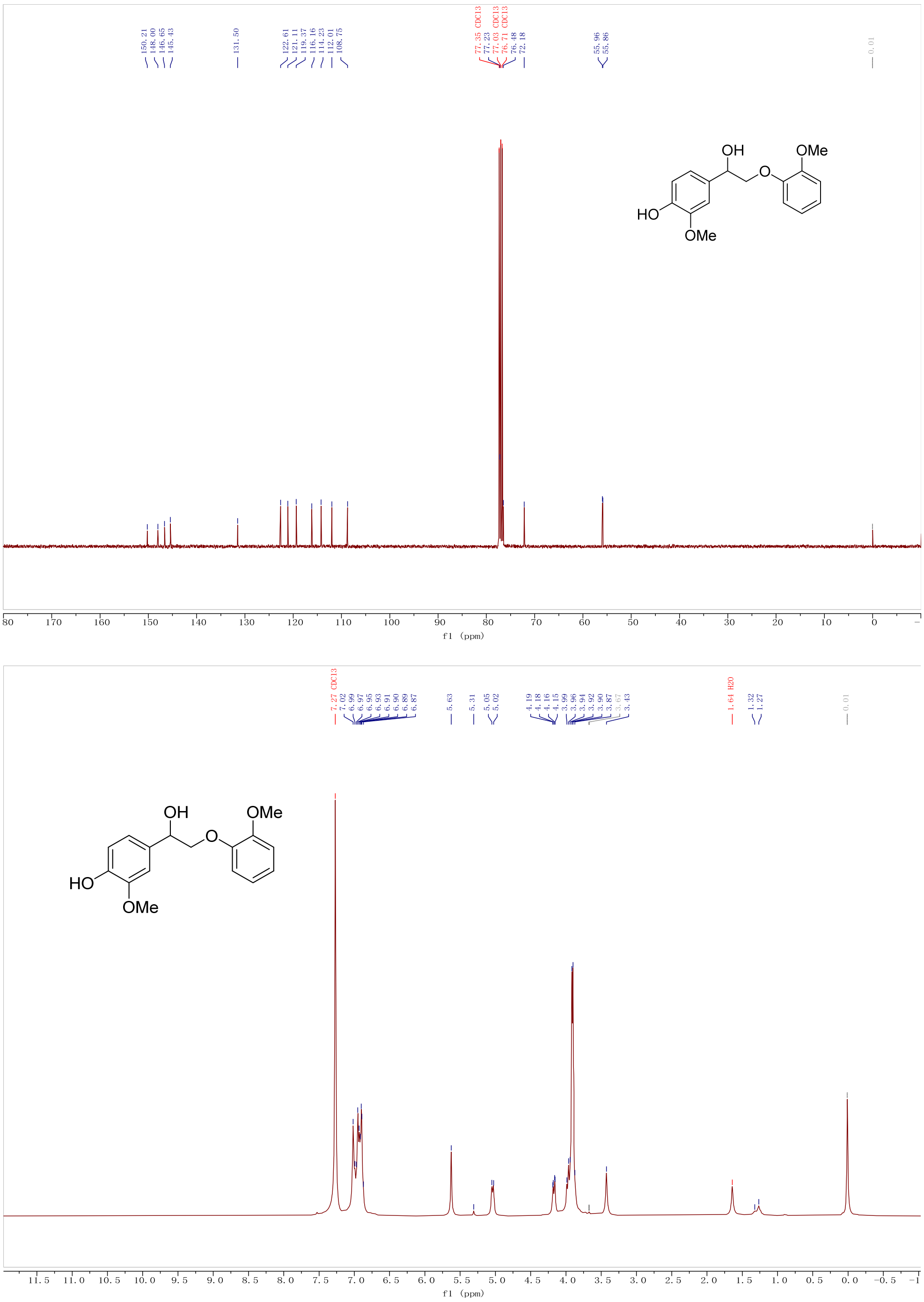
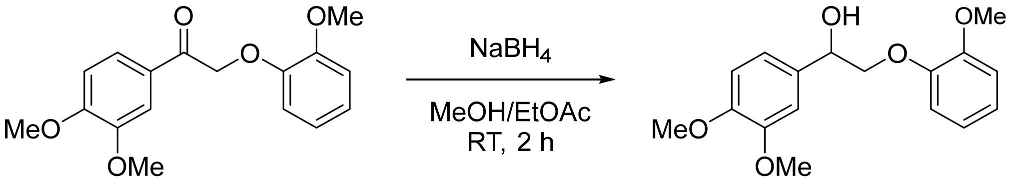


Figure S23. ^{1}H and ^{13}C NMR spectra of lignin model compound **3**.



Scheme S4. Synthesis of dimeric lignin model compounds **4.**[6]

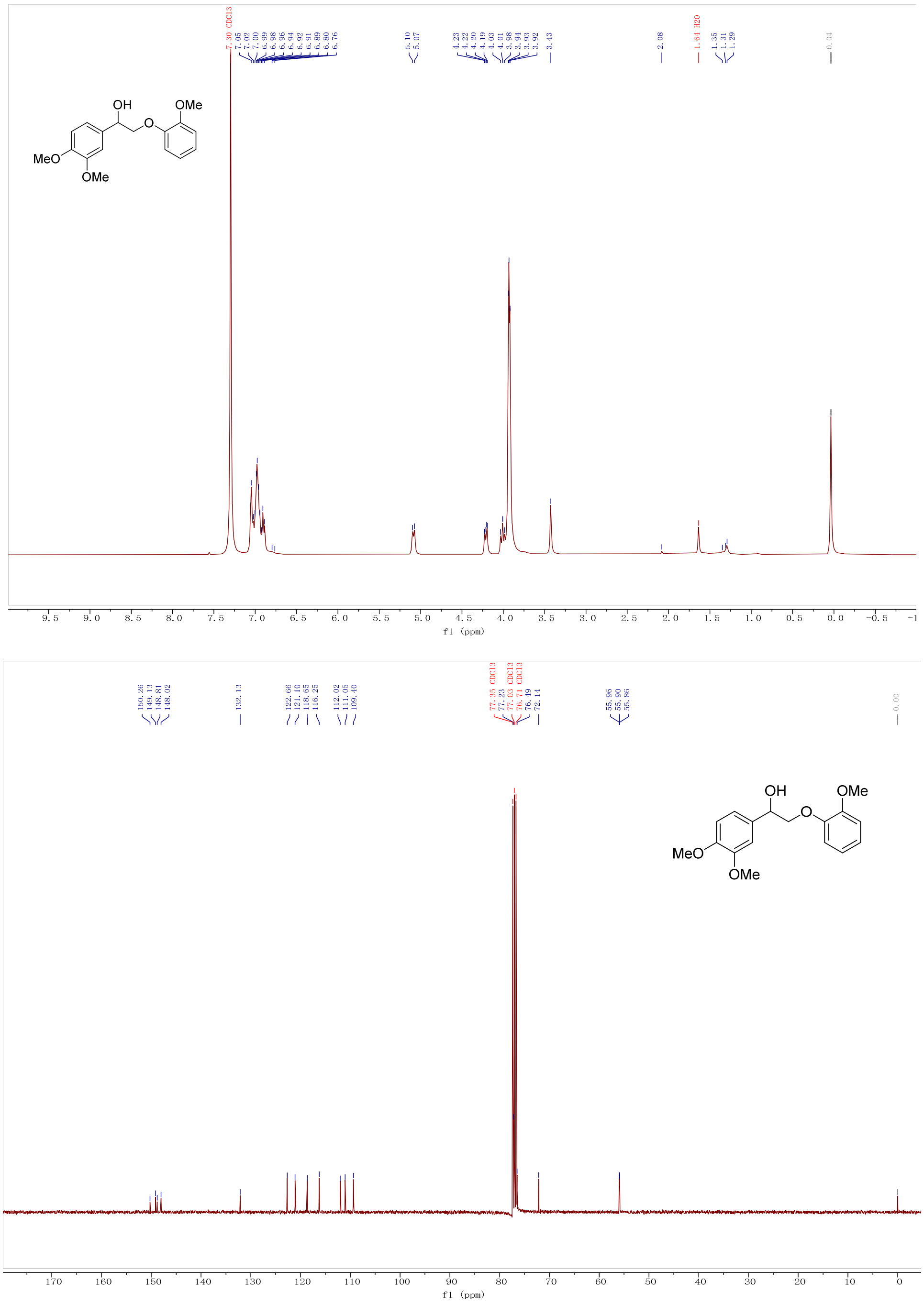
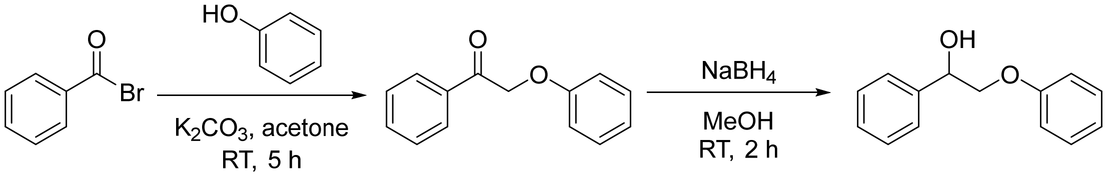


Figure S24. ^{1}H and ^{13}C NMR spectra of lignin model compound **4**.



Scheme S5. Synthesis of dimeric lignin model compounds **5.**[5]

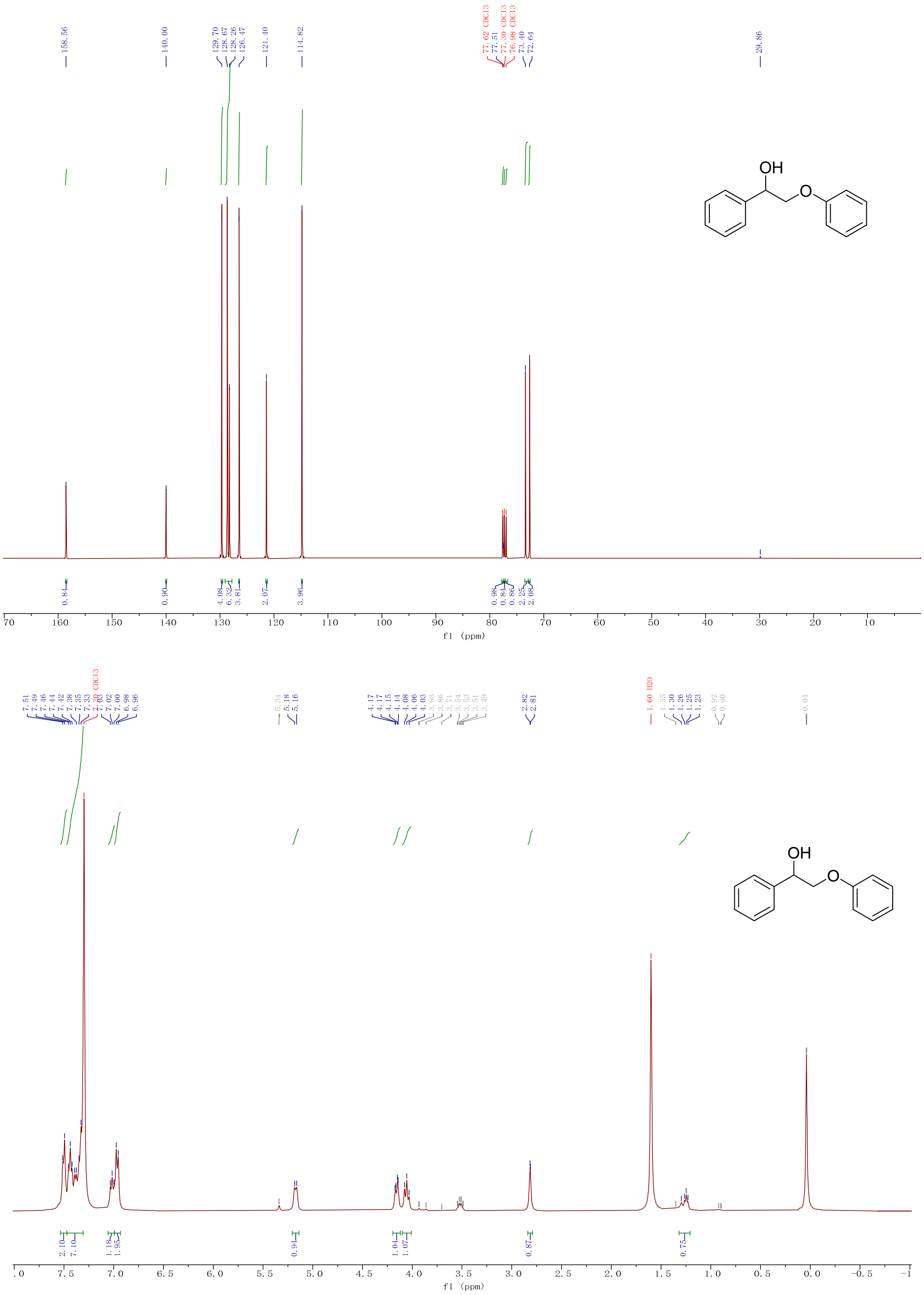
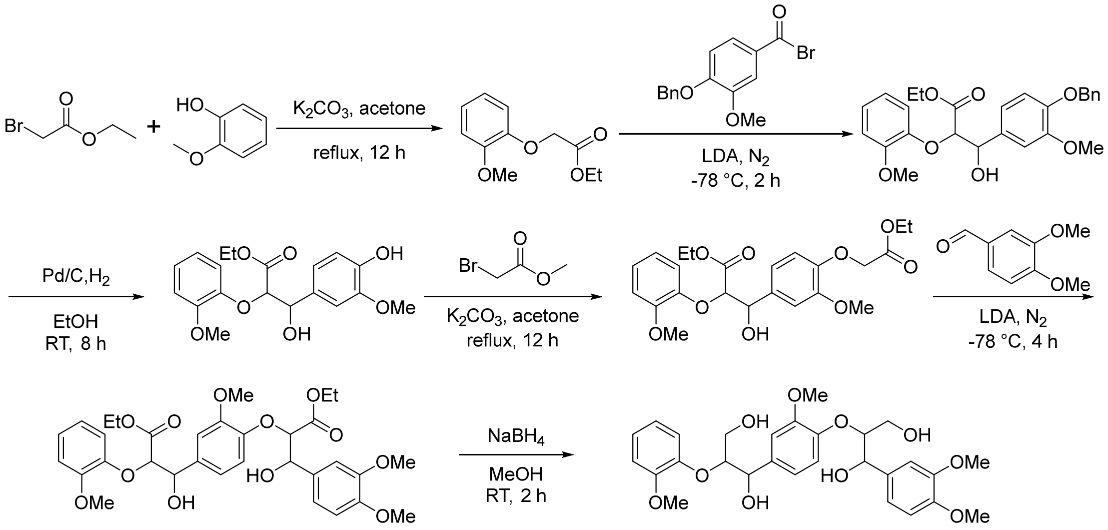


Figure S25. ^{1}H and ^{13}C NMR spectra of lignin model compound **5**.



Scheme S6. Synthesis of trimerical lignin model compounds **6**.[1]

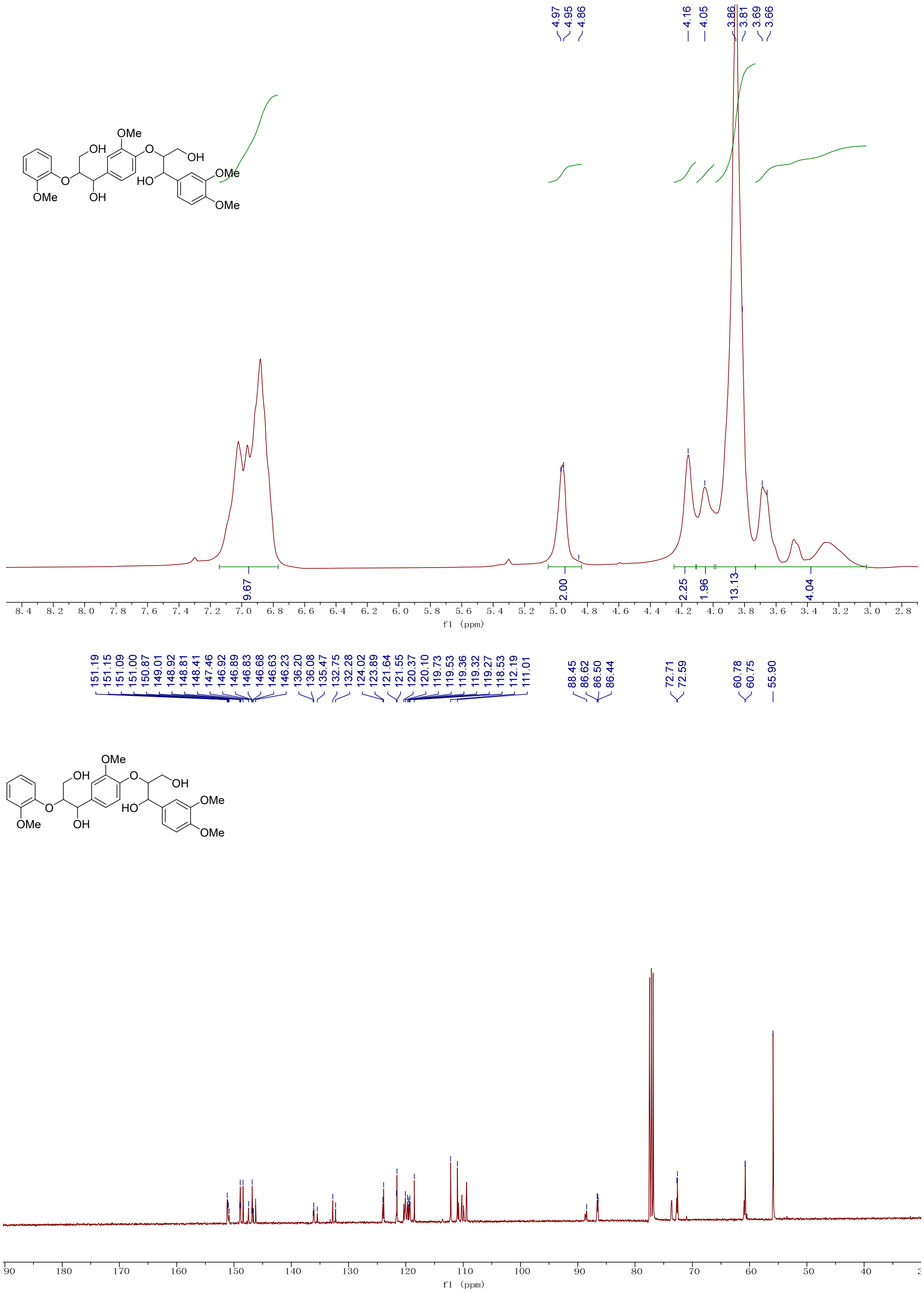


Figure S26. ^{1}H and ^{13}C NMR spectra of trimerical lignin model compound **6**.

8. Hydrogenolysis of lignin model compounds

In a typical reaction, β-*O*-4' model compounds (12.5 mg), Pd-Zn@NC (6.5 mg) and MeOH (10 mL) were mixed into a 50 mL stainless steel batch reactor (Parr Instruments Co.), which was then flushed with N_2 for three times and pressurized with desired amount of H_2 at room temperature. The reaction was carried out at different temperatures for a certain time with a magnetic stirring at 800 rpm. After completion, the autoclave was cooled and depressurized carefully. Then the reaction mixture was filtered, and the insoluble fraction was washed with dichloromethane (DCM). Subsequently, the solution fraction was extracted with DCM and the resulting lignin oily product was obtained after removing all volatiles under a vacuum condition. An external standard (1,3,5-trimethoxybenzene) was added to the lignin oil solution in DCM, which was subjected to GC and GC-MS for analysis. The identification and quantification of lignin monomers in the oily product were assessed by comparison. The identification and quantification of lignin monomers in the oily product were assessed by comparison with authentic samples acquired from commercial purchase or independent synthesis as described previously.[1]

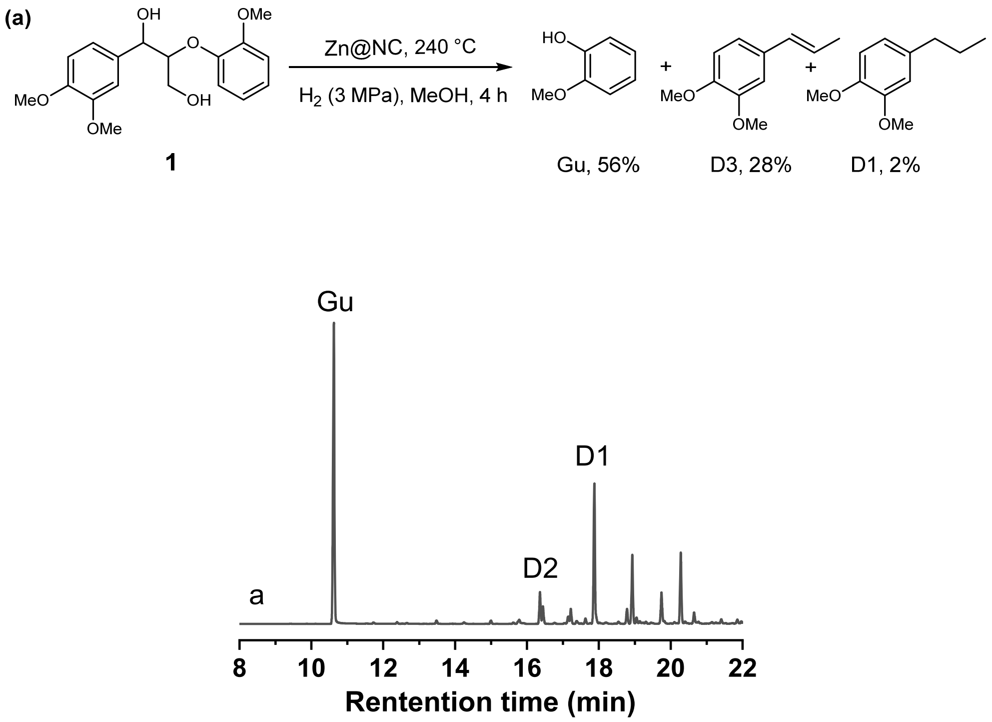


Figure S27. Zn@NC-catalyzed hydrogenolysis of lignin model compound **1**.

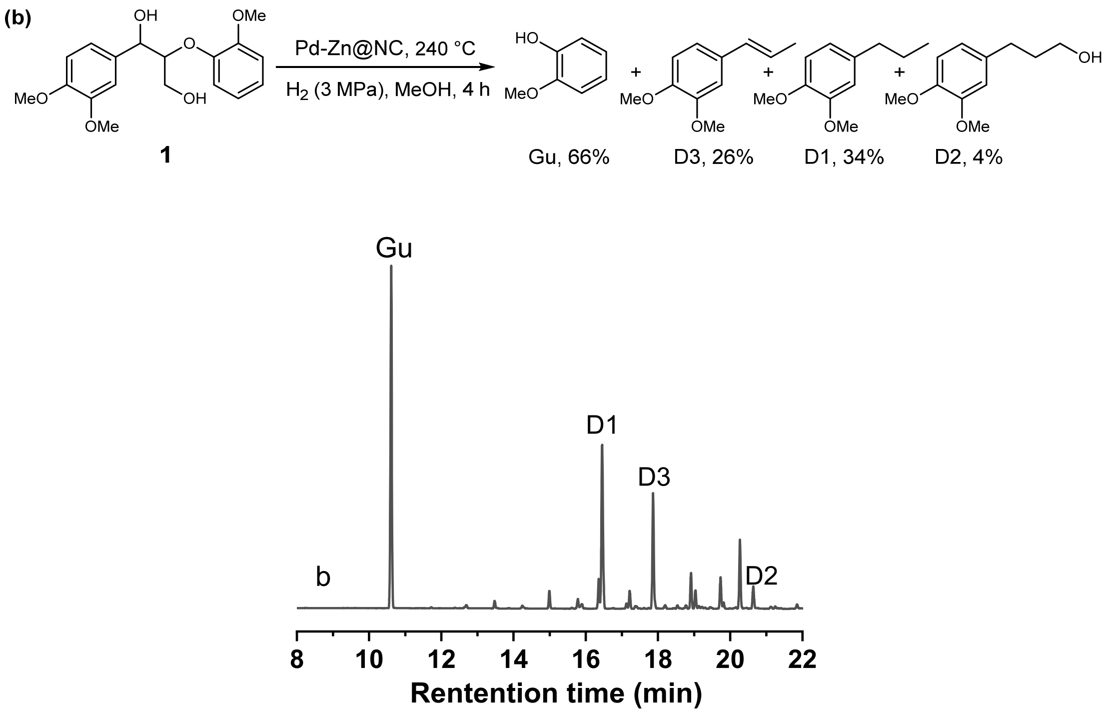


Figure S28. Pd-Zn@NC-catalyzed hydrogenolysis of lignin model compound **1**.

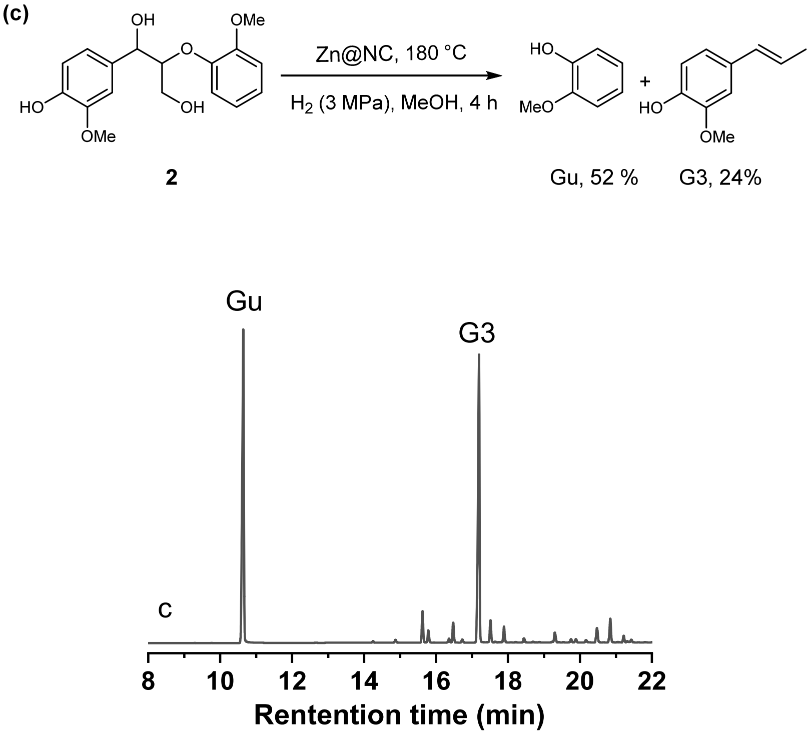


Figure S29. Zn@NC-catalyzed hydrogenolysis of lignin model compound **2**.

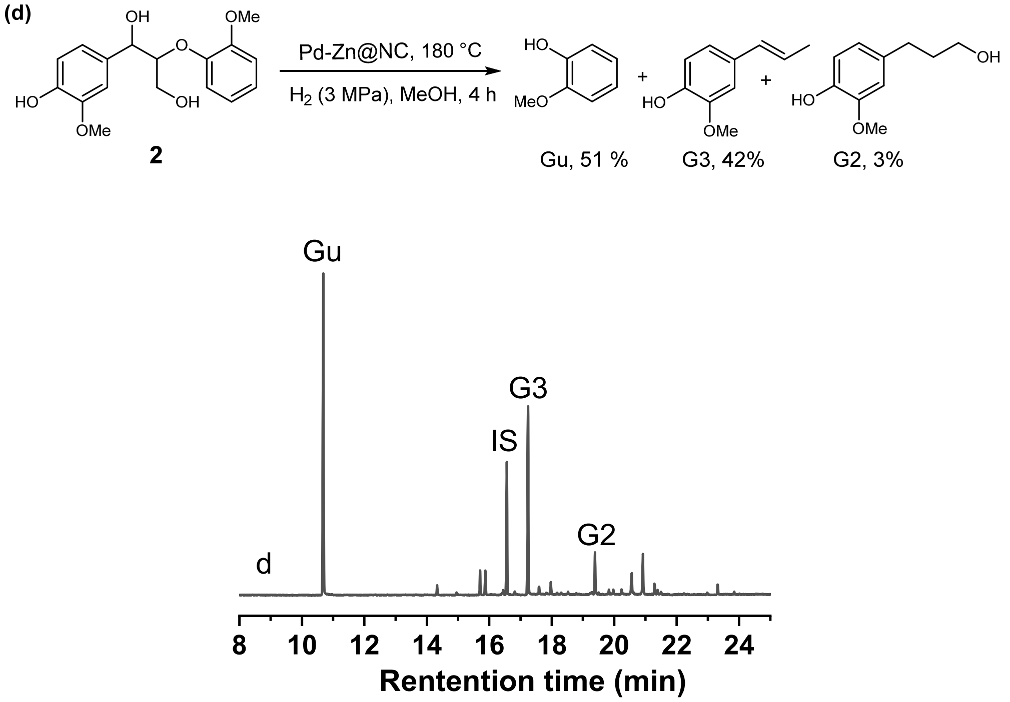


Figure S30. Pd-Zn@NC-catalyzed hydrogenolysis of lignin model compound **2**.

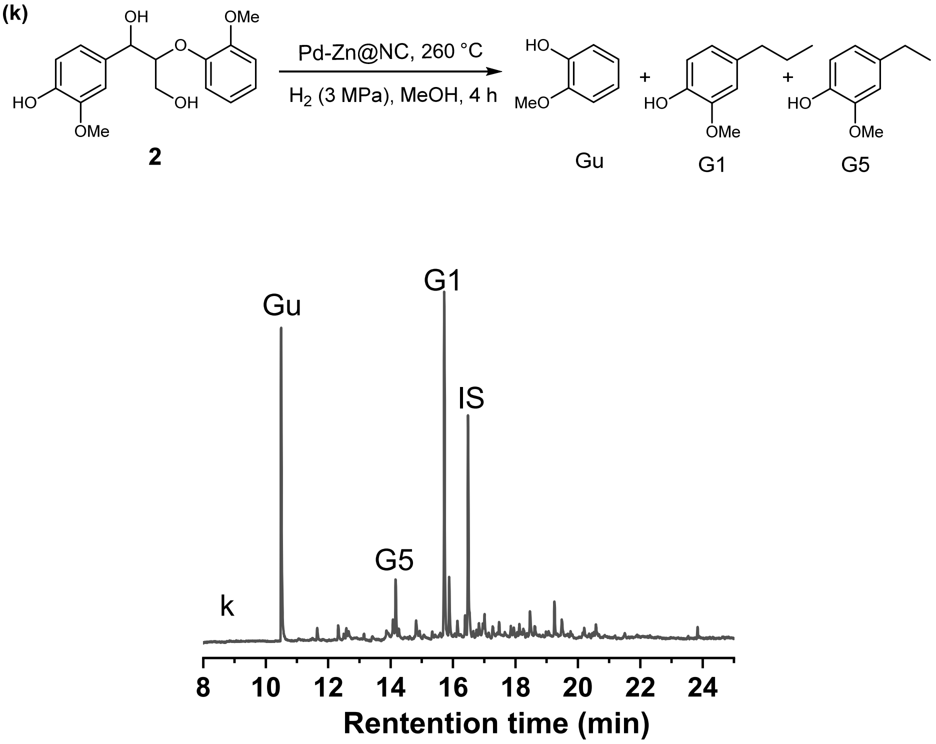


Figure S31. Pd-Zn@NC-catalyzed hydrogenolysis of lignin model compound **2**.

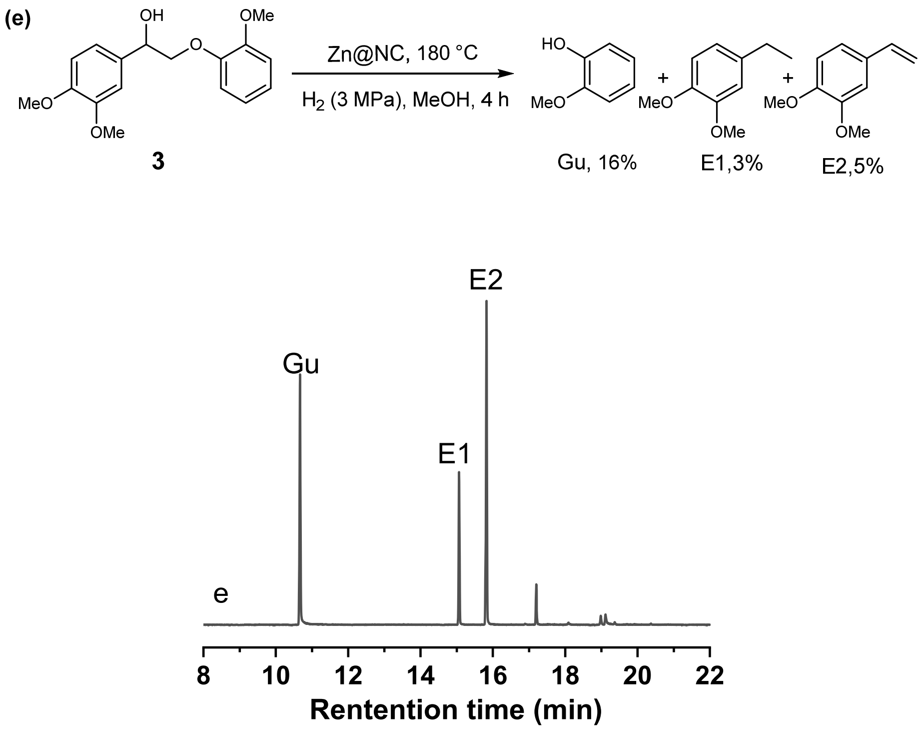


Figure S32. Zn@NC-catalyzed hydrogenolysis of lignin model compound **3**.

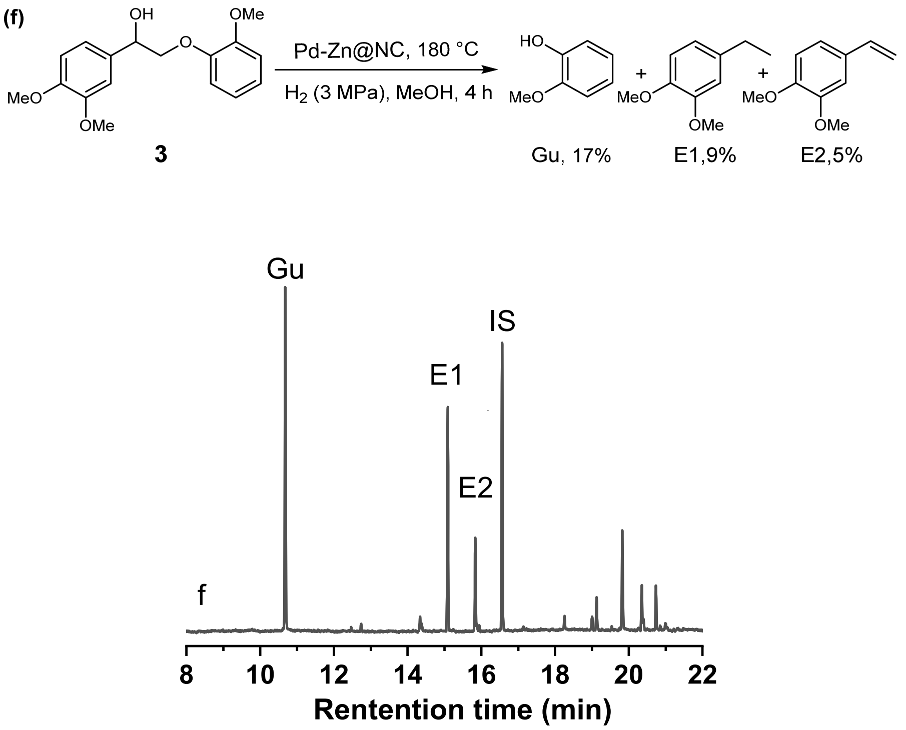


Figure S33. Pd-Zn@NC-catalyzed hydrogenolysis of lignin model compound **3**.

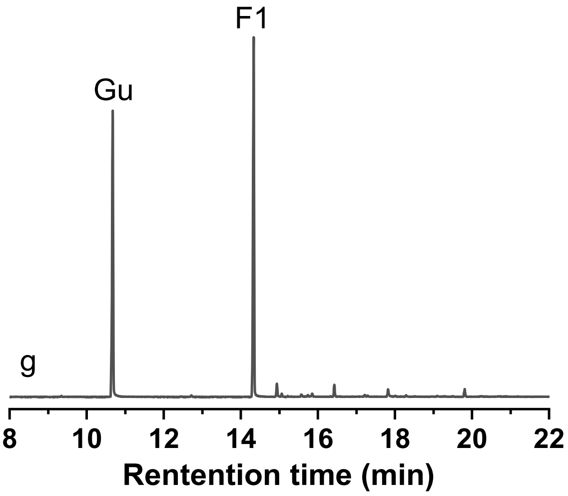


Figure S34. Zn@NC-catalyzed hydrogenolysis of lignin model compound **4**.

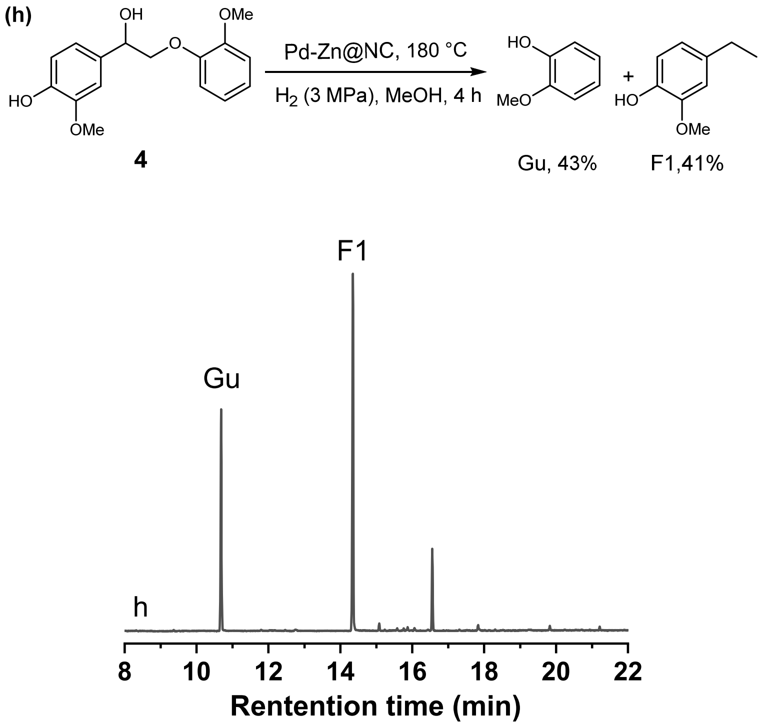


Figure S35. Pd-Zn@NC-catalyzed hydrogenolysis of lignin model compound **4**.

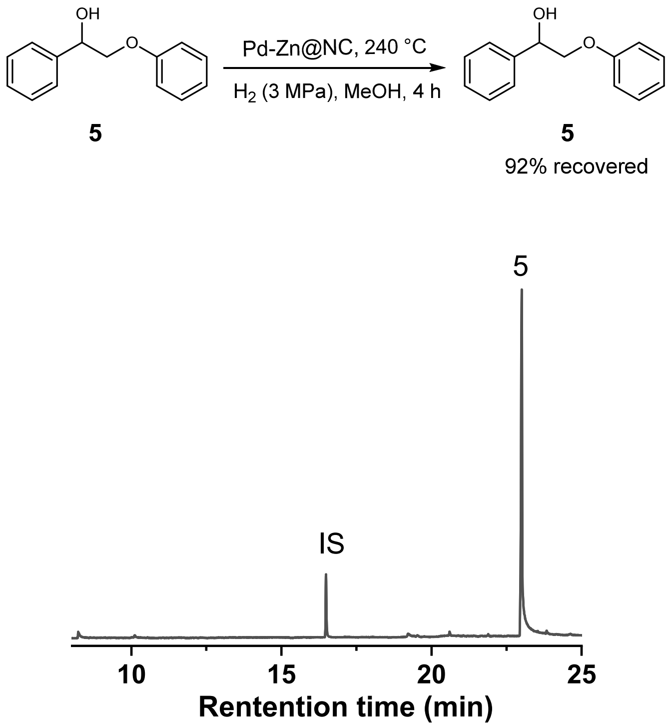


Figure S36. Pd-Zn@NC-catalyzed hydrogenolysis of lignin model compound **5**.

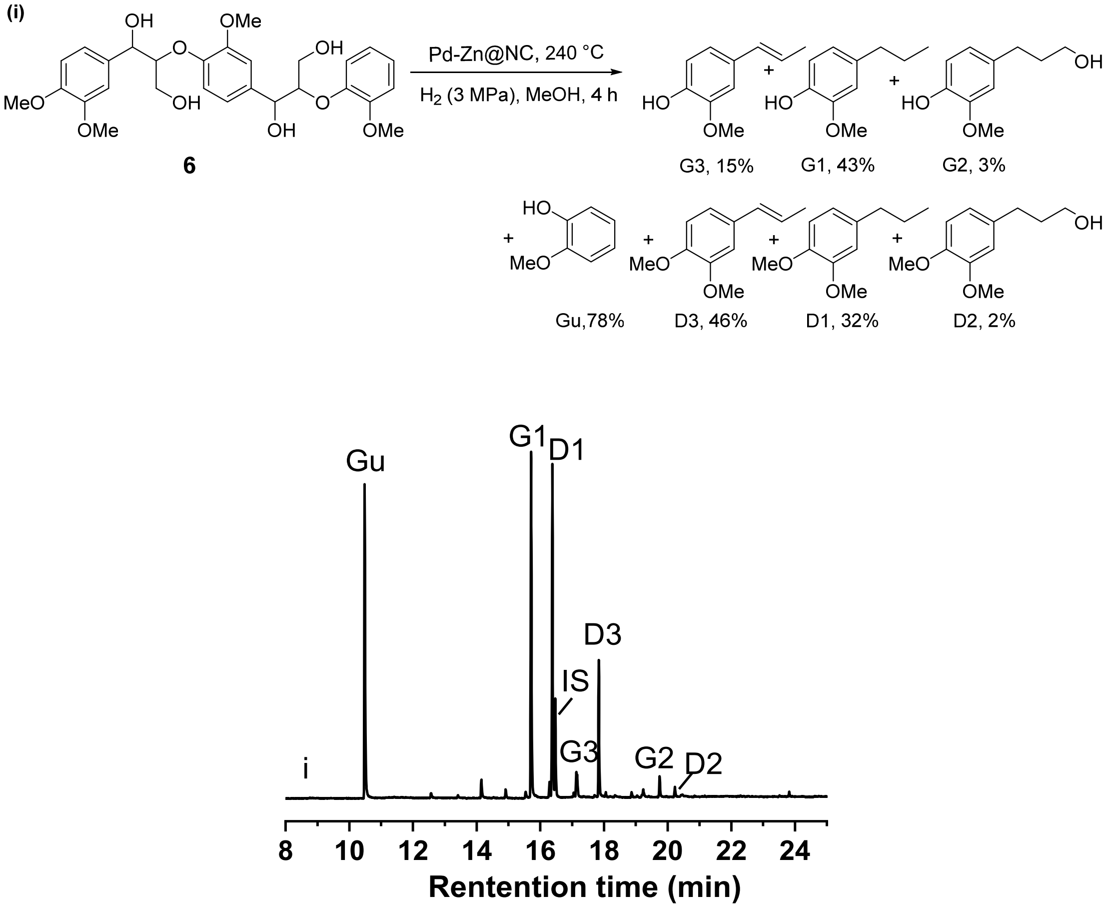


Figure S37. Pd-Zn@NC-catalyzed hydrogenolysis of lignin model compound **6**.

9. Hydrogenolysis of softwoods and hardwoods over Zn@NC and Pd-Zn@NC catalysts

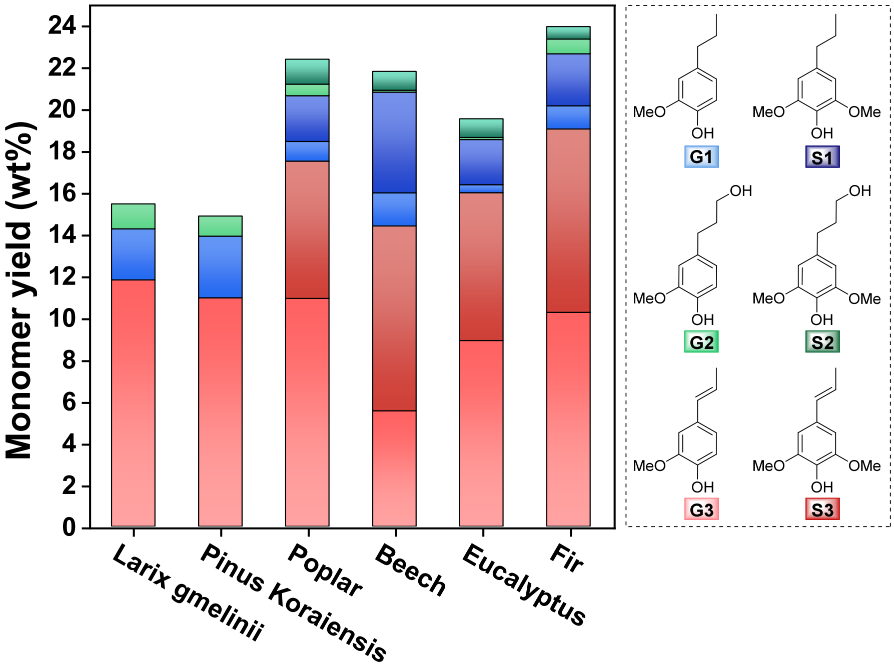
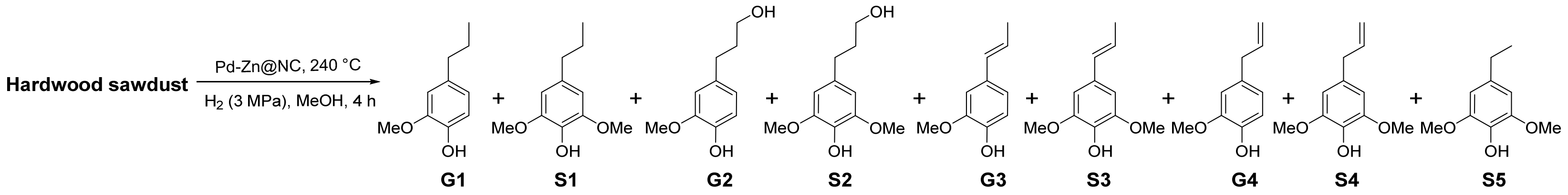


Figure S38. Pd-Zn@NC-catalyzed hydrogenolysis of lignocellulose. Reaction conditions: sawdust (50 mg), Pd-Zn@NC (6.5 mg), MeOH (10 mL), H_2 (3 MPa), 240 °C, 4 h.

Table S12 Hydrogenolysis of different hardwood sawdusts for 4 h.[a]



Entry	Sawdust	Phenolic monomers yield (wt%)								Selectivity (%)[b]
		G1	G2	G3	S1	S2	S3	others	Total monomers	
1	Beech	1.6	0.1	5.5	4.8	0.9	8.9	3.1	24.9	58
2	Poplar	0.9	0.6	10.9	2.2	1.2	6.6	2.5	24.9	70
3	Fir	1.1	0.7	10.3	2.5	0.6	8.8	2.4	26.4	72
4	Eucalyptus	0.4	0.1	8.9	2.2	0.9	7.1	2.6	22.2	72
5	Birch	2.4	0.2	5.2	7.5	1.8	5.3	3.9	26.4	40

[a] Reaction conditions: Hardwood sawdust (50 mg), Pd-Zn@NC (6.5 mg), MeOH (10 mL), H_2 (3 MPa), 240 °C, 4 h.

[b] Contribution of G/S3 to total yield in phenolic monomer products.

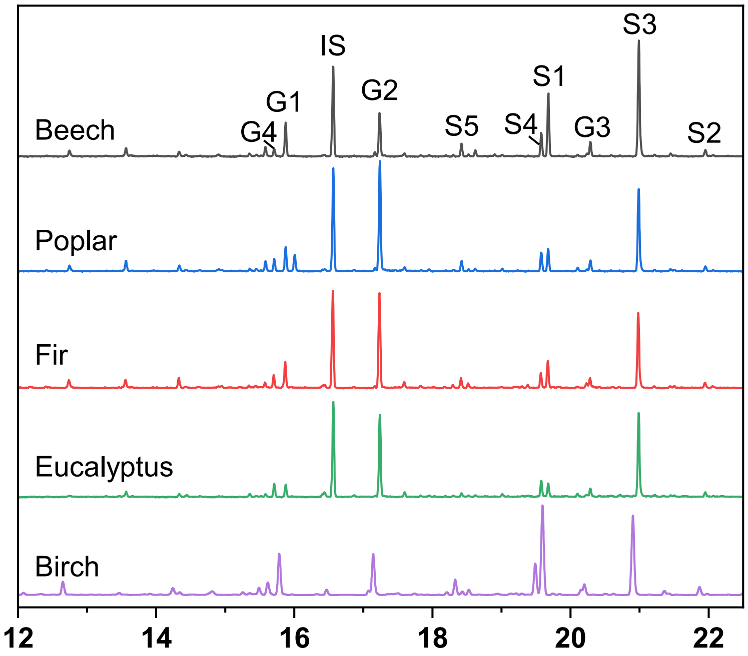


Figure S39. GC chromatogram of the monomers obtained from hydrogenolysis of different hardwood sawdusts.

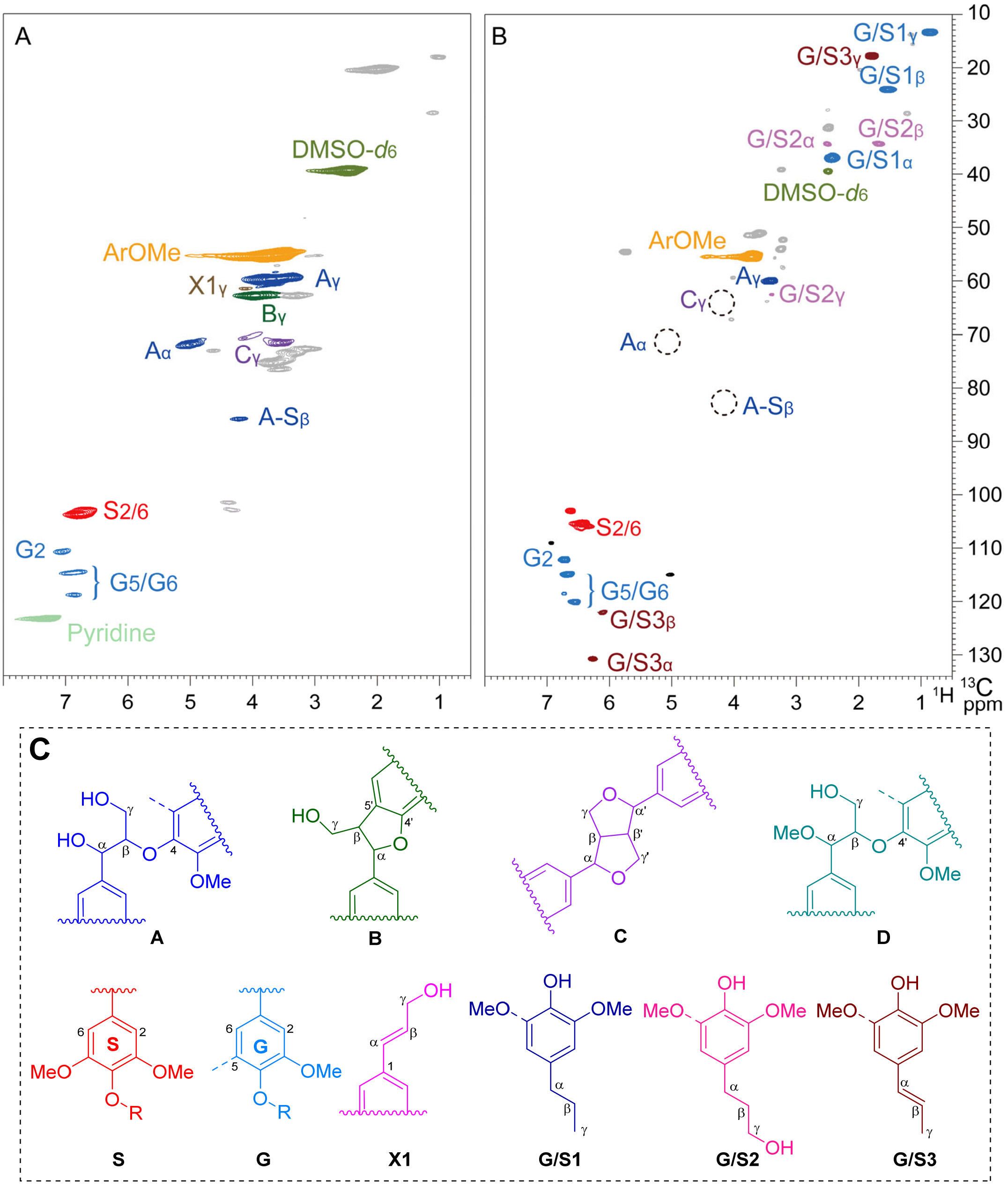


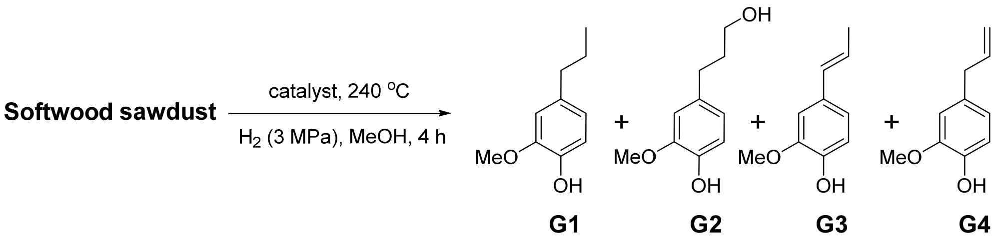
Figure S40. Characterization of Eucalyptus lignin and oily products.

(A) 2D HSQC NMR spectrum of double enzymatic hydrolysis lignins (DEL) isolated from Eucalyptus (dissolved in DMSO-*d*6).

(B) 2D HSQC NMR spectrum of oily product from Pd-Zn@CN-catalyzed reaction (dissolved in DMSO-*d*6).

(C) Main structures presented in the 2D HSQC NMR spectra: (**A**) β-*O*-4′ alkyl-aryl ether, (**B**) β-5′ phenylcoumaran, (**C**) β-β′ resinol, (**D**) α-OH with methylated β-*O*-4′ alkyl-aryl ether, (**G**) guaiacyl units, (**X1**) cinnamyl alcohol end-groups, (**G/S1**) dihydroeugenol/syringylpropane, (**G/S2**) dihydroconiferyl alcohol/sinapyl alcohol, and (**G/S3**) isoeugenol/sinapine.

Table S13 Hydrogenolysis of different softwood sawdust.[a]



Entry	Sawdust	Catalyst	Phenolic monomers yield (wt%)					Selectivity (%)[b]
			G1	G2	G3	Others	Total monomers	
1	*Pinus yunnanensis*	Zn@NC	0.6	ND[c]	11.7	1.6	13.9	84
2	*Pinus yunnanensis*	Pd-Zn@NC	4.1	0.6	11.7	1.6	18.1	65
3	*Larix gmelinii*	Pd-Zn@NC	11.8	2.5	1.2	1.6	17.1	7
4	*Pinus Koraiensis*	Pd-Zn@NC	11.0	3.0	1.0	1.1	16.0	6

[a] Reaction conditions: Softwood sawdust (50 mg), catalyst (6.5 mg), MeOH (10 mL), H_2 (3 MPa), 240 °C, 4 h.

[b] Contribution of G/S3 to total yield in phenolic monomer products.

[c] ND, not detectable.

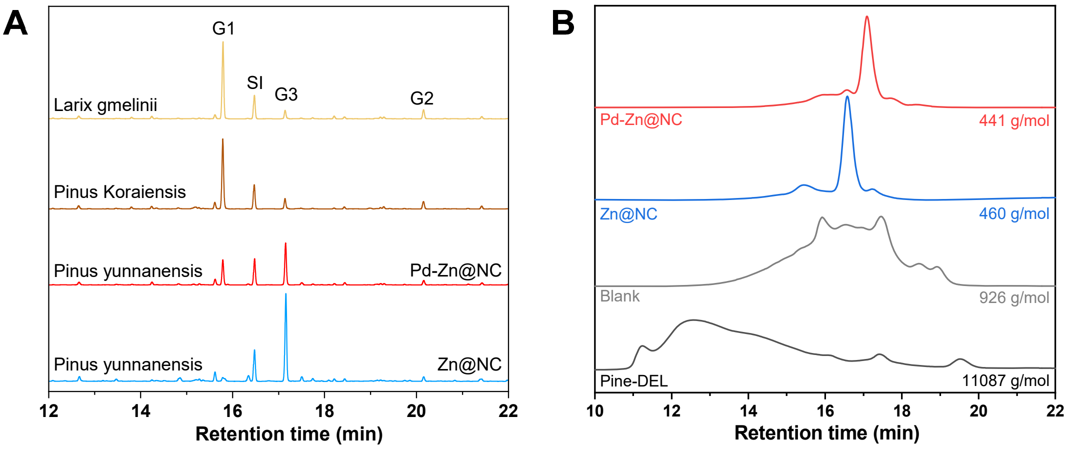
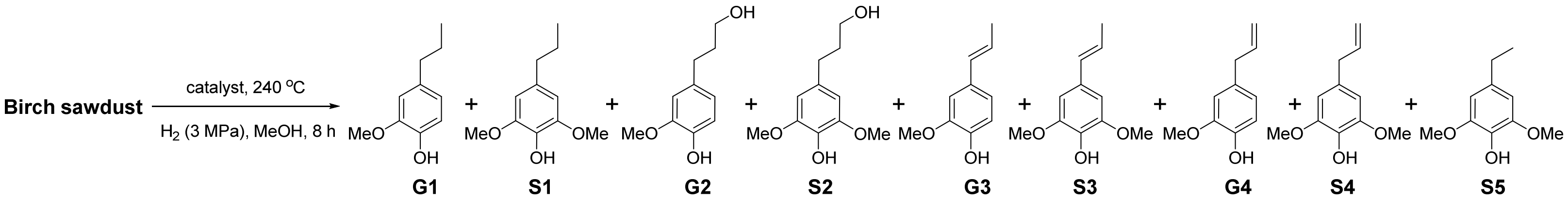


Figure S41. (A) GC chromatogram of the monomers obtained from hydrogenolysis of different softwood sawdusts. (B) Molecular weight distribution of Pine lignin and oily products obtained from hydrogenolysis of *Pinus yunnanensis* sawdust via GPC analysis

Table S14 Hydrogenolysis of Birch for 8 h.[a]



Entry	Sawdust	Catalyst	Phenolic monomers yield (wt%)								Selectivity (%)[b]
			G1	G2	G3	S1	S2	S3	others	Total monomers	
1	Birch	Zn@NC	0.3	0.2	4.5	3.9	ND	7.5	1.0	17.2	70
2	Birch	Pd-Zn@NC	5.2	1.1	4.9	15.5	4.5	5.5	1.9	38.6	27

[a] Reaction conditions: Birch sawdust (50 mg), catalyst (6.5 mg), MeOH (10 mL), H_2 (3 MPa), 240 °C, 8 h.

[b] Contribution of G/S3 to total yield in phenolic monomer products.

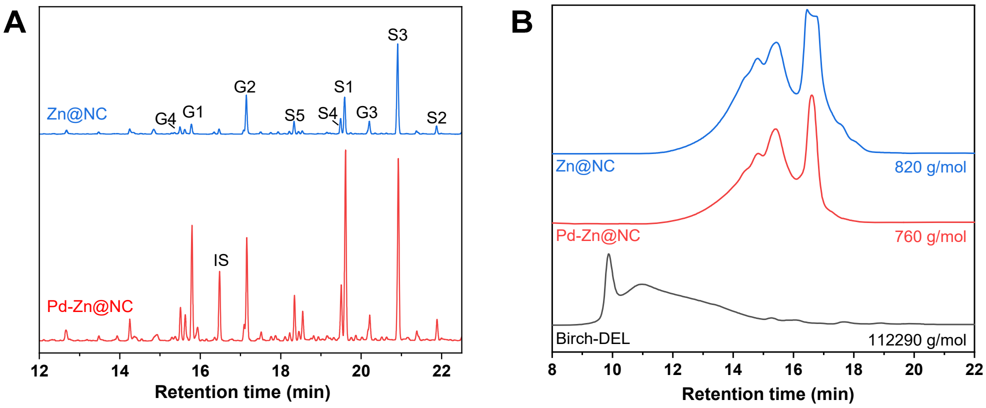
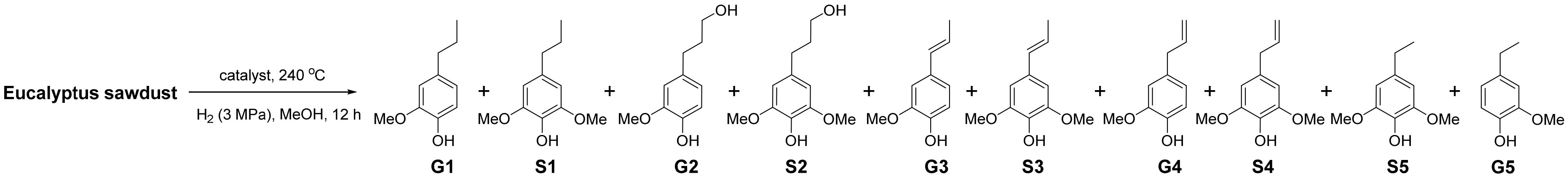


Figure S42. (A) GC chromatogram of the monomers obtained from hydrogenolysis of Birch sawdust. (B) Molecular weight distribution of Birch lignin and oily products obtained from hydrogenolysis of Birch sawdust via GPC analysis.

Table S15 Hydrogenolysis of Eucalyptus sawdust for 12 h.[a]



Entry	Sawdust	Catalyst	Phenolic monomers yield (wt%)								Selectivity (%)[b]
			G1	G2	G3	S1	S2	S3	others	Total monomers	
1	Eucalyptus	Zn@NC	3.6	0.0	3.0	11.2	0.0	4.8	2.1	24.8	31
2	Eucalyptus	Pd-Zn@NC	11.7	1.0	0.0	31.1	2.1	0.0	3.7	49.6	0
3	Eucalyptus	Pd/C	2.4	8.1	0	3.6	12.2	0	16.5	42.8	0

[a] Reaction conditions: Eucalyptus sawdust (50 mg), catalyst (6.5 mg), MeOH (10 mL), H_2 (3 MPa), 240 °C, 12 h.

[b] Contribution of G/S3 to total yield in phenolic monomer products.

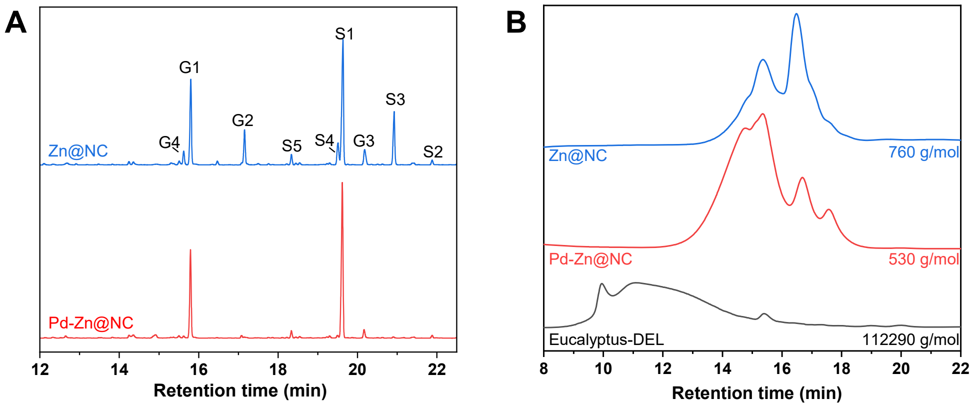


Figure S43. (A) GC chromatogram of the monomers obtained from hydrogenolysis of Eucalyptus sawdust. (B) Molecular weight distribution of Eucalyptus lignin and oily products obtained from hydrogenolysis of Eucalyptus sawdust via GPC analysis.

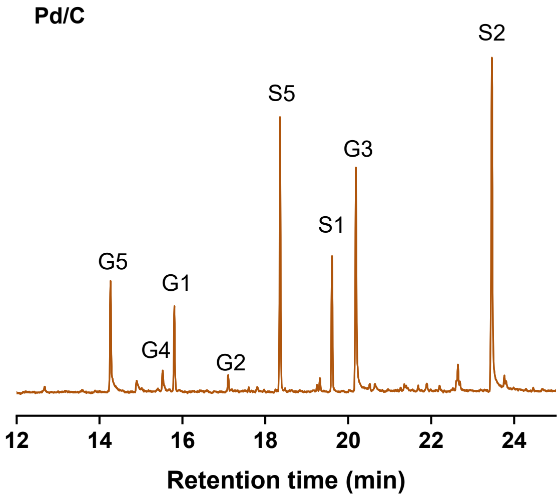


Figure S44. Pd/C-catalyzed hydrogenolysis of Eucalyptus sawdust.

10. Identification and quantitation of phenolic monomers

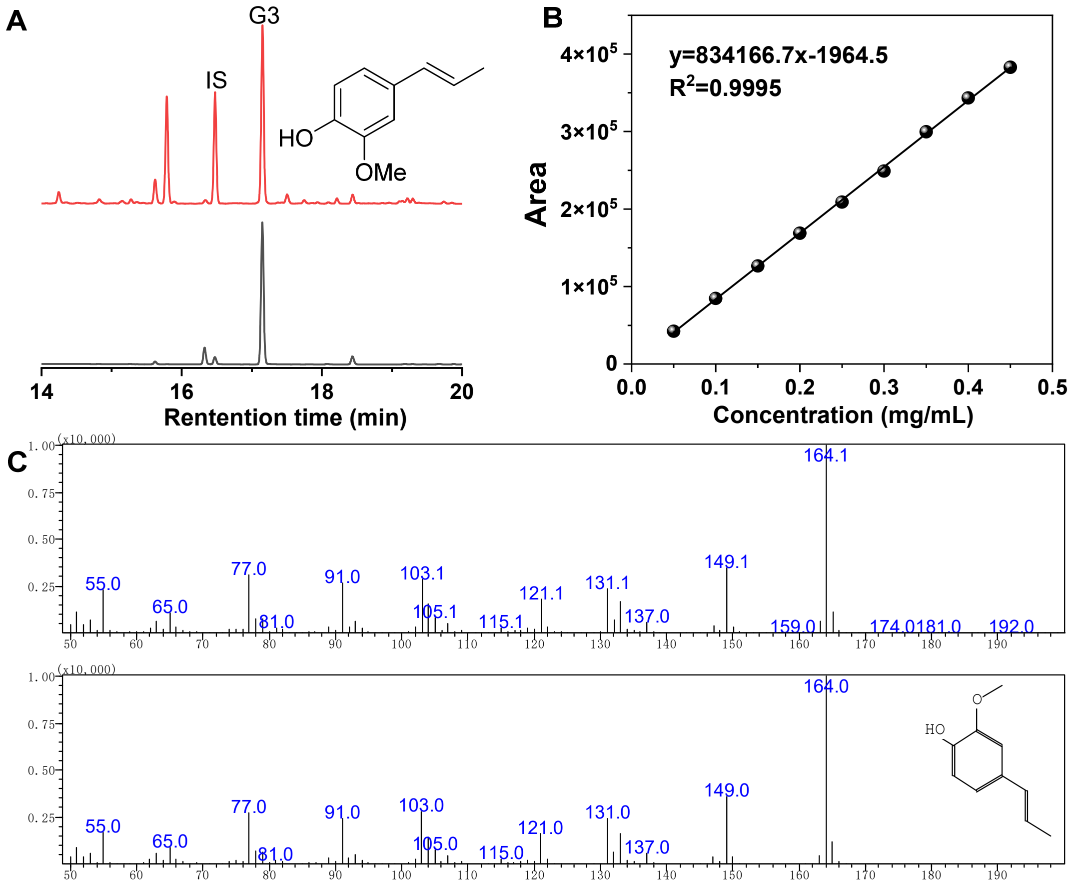


Figure S45. CAS: 97-54-1, isoeugenol (**G3**) was prepared following previously reported procedure.[7] (A) GC spectra of product derived from lignin depolymerization and standard sample **G3**. (B) Standard curve line of **G3**. (**C**) Mass spectra of standard sample **G3**.

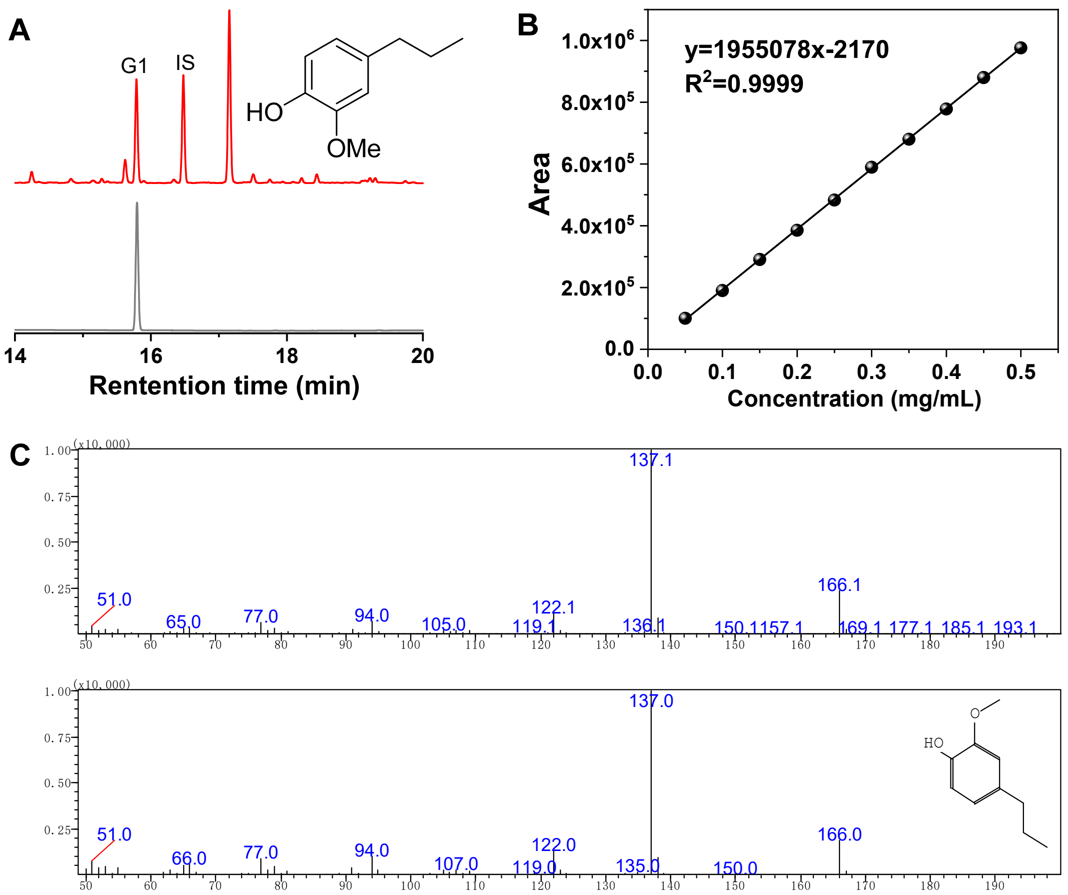


Figure S46. CAS: 2785-87-7, 2-methoxy-4-propylphenol (**G1**) was commercially available. (A) GC spectra of product derived from lignin depolymerization and standard sample **G1**. (B) Standard curve line of **G1**. (**C**) Mass spectra of standard sample **G1**.

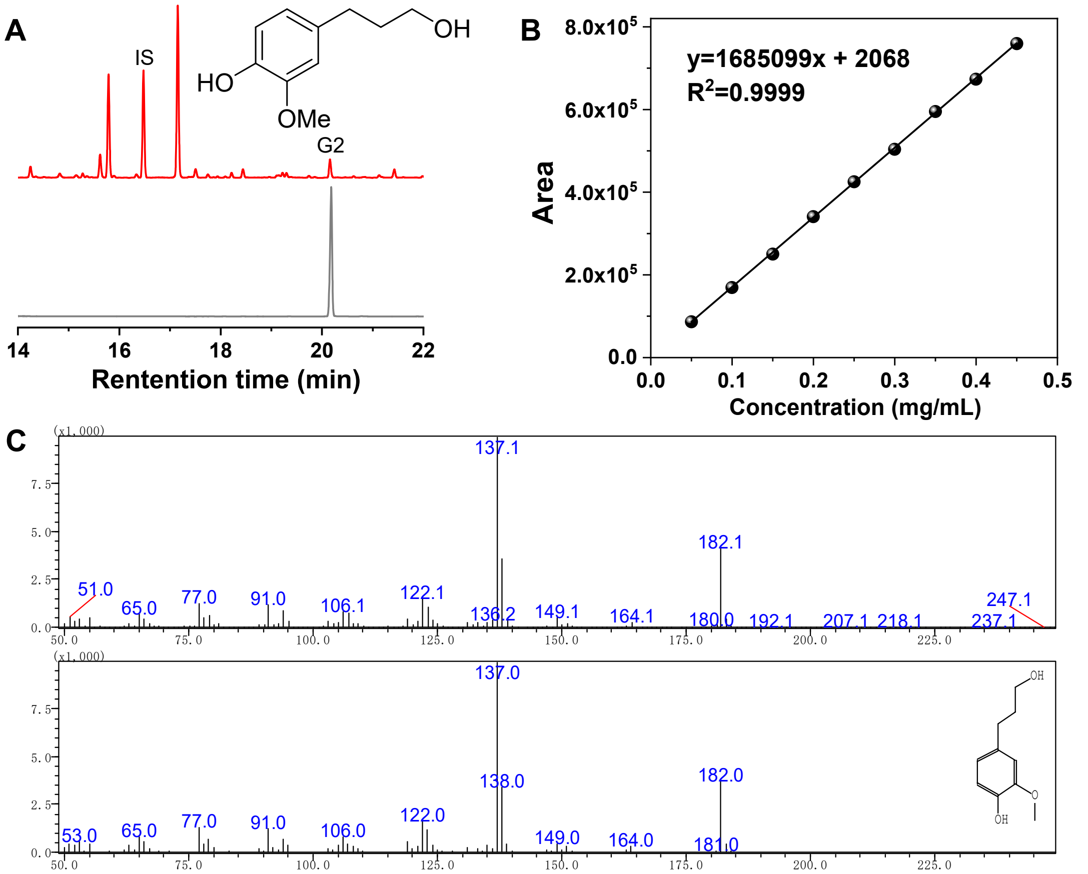


Figure S47. CAS: 2305-13-7, 4-hydroxy-3-methoxybenzenepropanol (dihydroconiferyl alcohol, **G2**) was prepared following previously reported procedures.[7] (A) GC spectra of product derived from lignin depolymerization and standard sample **G2**. (B) Standard curve line of **G2**. (**C**) Mass spectra of standard sample **G2**.

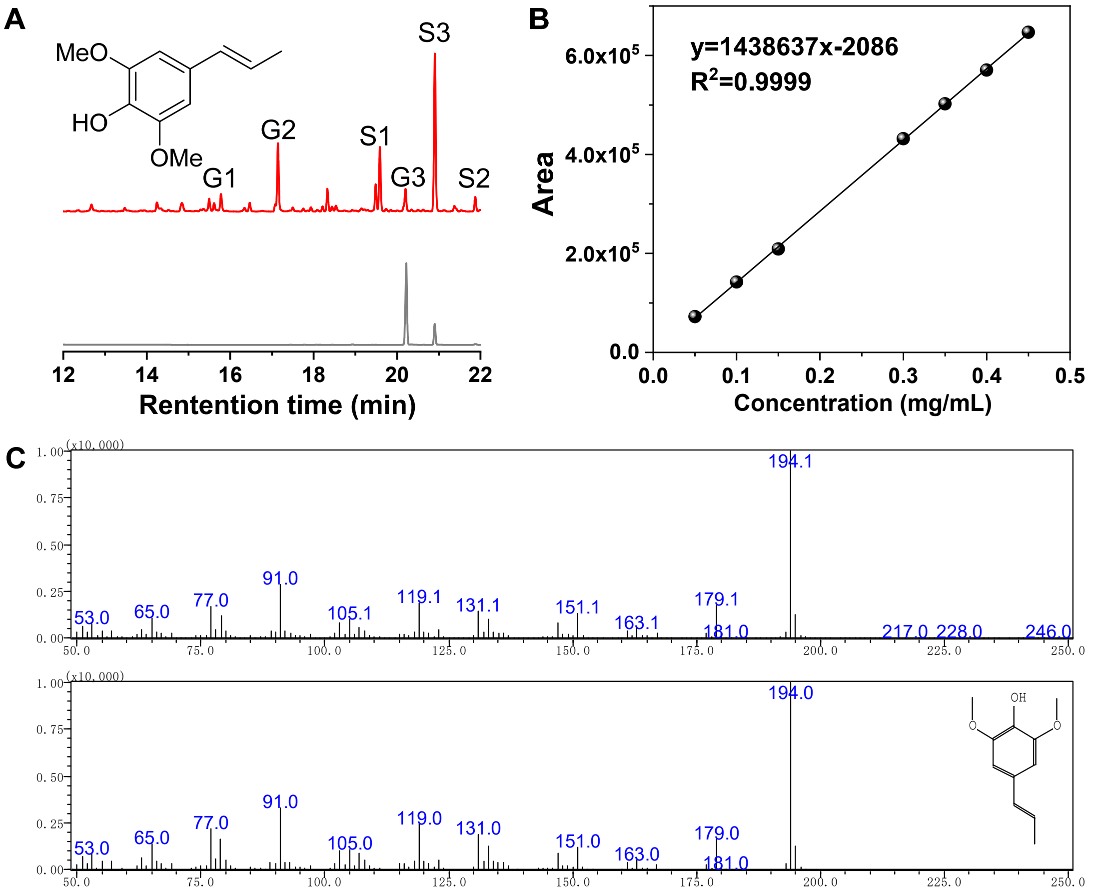


Figure S48. CAS: 6635-22-9, 4-propenyl-2,6-dimethoxyphenol (sinapine, **S3**) was prepare following previously reported procedures.[8,9] (A) GC spectra of product derived from lignin depolymerization and standard sample **S3**. (B) Standard curve line of **S3**. (**C**) Mass spectra of standard sample **S3**.

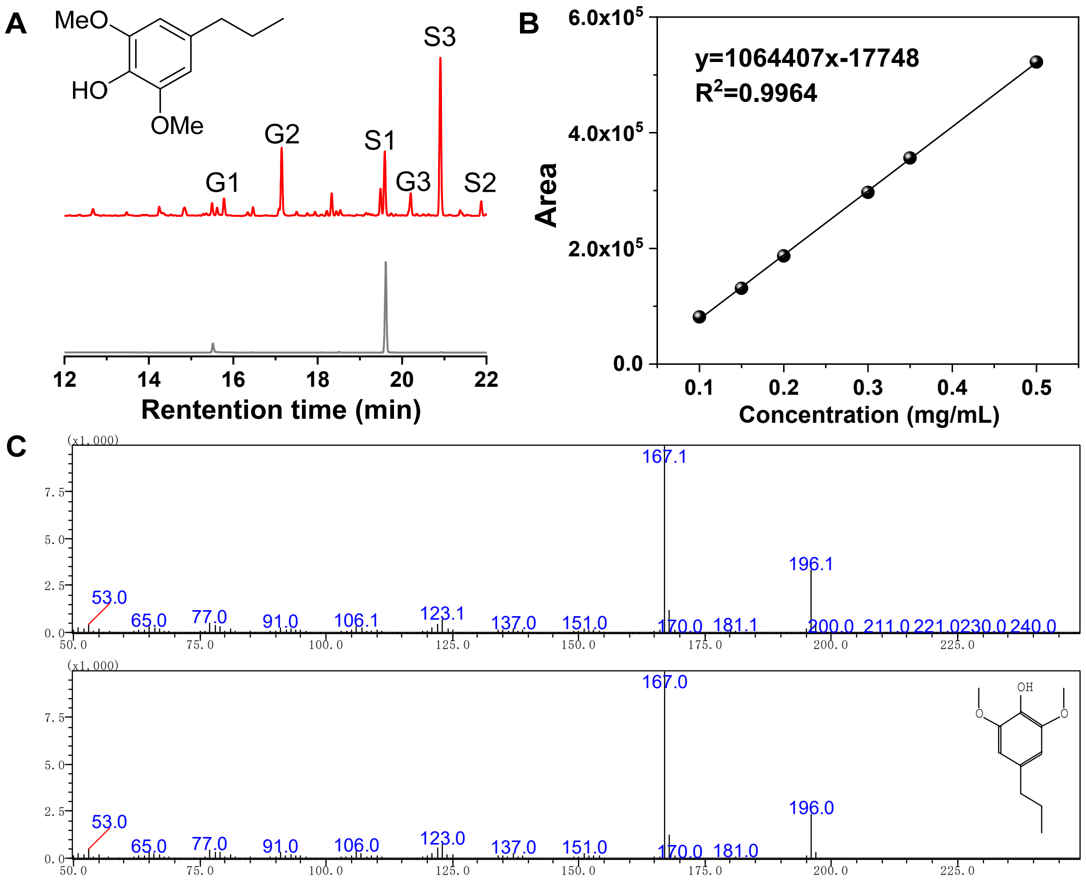


Figure S49. CAS: 6766-82-1, 2,6-dimethoxy-4-propylphenol (**S1**) was prepared following previously reported procedures.[8] (A) GC spectra of product derived from lignin depolymerization and standard sample **S1**. (B) Standard curve line of **S1**. (C) Mass spectra of standard sample **S1**.

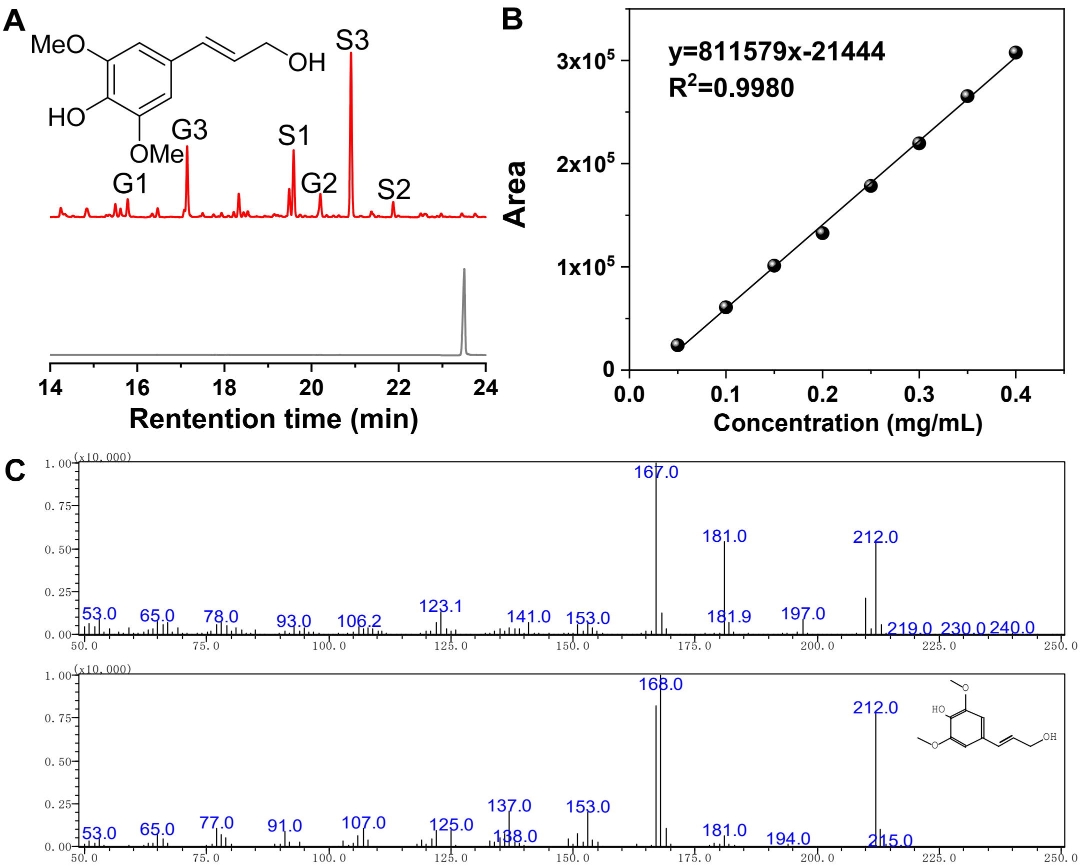


Figure S50. CAS:20736-25-8, 4-(3-hydroxypropyl)-2,6-dimethoxyphenol (sinapyl alcohol, **S2**) was prepared following previously reported procedure.[10] (A) GC spectra of product derived from lignin depolymerization and standard sample **S2**. (B) Standard curve line of **S2**. (**C**) Mass spectra of standard sample **S2**.

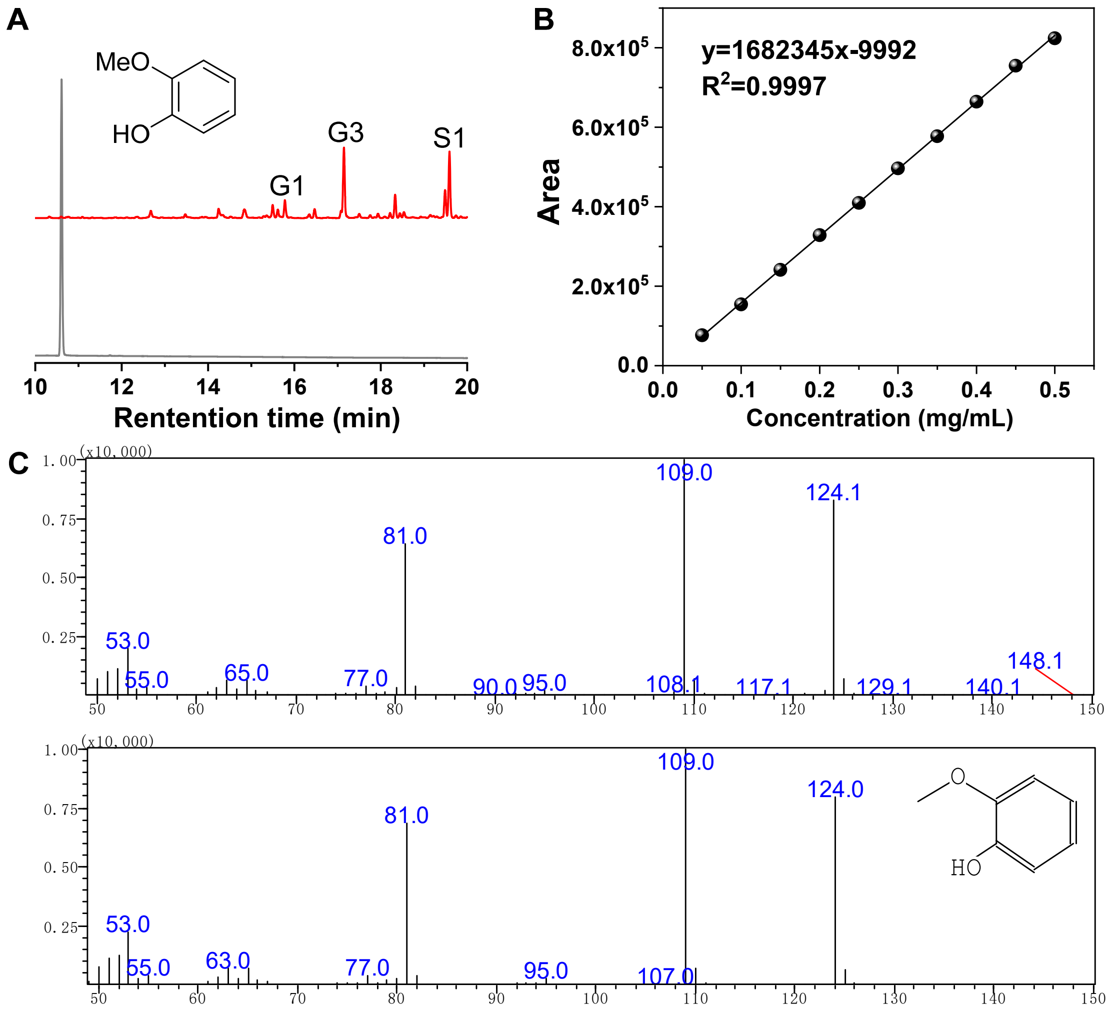


Figure S51. CAS: 90-05-1, 2-methoxyphenol (**Gu**) was commercially available. (A) GC spectra of product derived from lignin depolymerization and standard sample **Gu**. (B) Standard curve line of **Gu**. (**C**) Mass spectra of standard sample **Gu**.

11. Supplementary references

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