Electronic Supplementary Information

for

Chemodivergent Hydrogenolysis of Eucalyptus Lignin with Ni@ZIF-8 Catalyst

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Contents

1. General Information

Materials: All commercially available compounds were used as received, unless otherwise noted. Methanol and bis(cyclopentadienyl)nickel(II) (98.0%) were purchased from Aladdin. $Zn(NO_3)_2 \cdot 6H_2O$ (99.0%) and 2-methylimididazole (98.0%) were purchased from Energy Chemical. Diethyl ether and dichloromethane were purchased from Beijing Chemical Works. Eucalyptus (*Eucalyptus robusta Smith*, 5 years old) was employed in this paper, which was extracted, crushed and screened into powders in size of 40-60 meshes (0.5 mm-1.0 mm), and dried vacuum at 50 °C for 72 hours before used. Lignin models[1] and polymeric lignin model[2] were synthesized according the literature.

TEM: Transmission electron microscopy (TEM) was carried out by a JEM-2100F FETEM equipped with energy dispersive X-ray spectrometer (EDX) analyses at 100 kV, EDX elemental mapping were operated at 200 kV. Verasa, ULAC-PHI, Inc.) using Al Ka radiation and the C1s peak at 284.8 eV as internal standard.

XRD: The crystallinity index of samples were measured using a Bruker D 8 Advance with a Cu Kα radiation source and theta‑theta diffractometer equipped with a Lynx‑eye position sensitive detector. Samples were scanned from 5° to 60° (2θ) at a speed of 2°/min.

XPS: X-ray photoelectron spectroscopy (XPS) was collected on scanning X-ray microprobe (PHI 5000 Verasa, ULAC-PHI, Inc.) using Al Ka radiation and the C1s peak at 284.8 eV as internal standard.

ICP-AES: The Ni and Zn contents were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP–AES) with a Thermo IRIS Intrepid II XSP emission spectrometer after dissolving the catalyst in a HF solution.

The Brunauer–Emmett–Teller (BET) specific surface areas were measured by using nitrogen adsorption at 77 K on a Beijing Builder Instrument, the sample should be pretreated at 473 K before adsorption.

GPC: GPC analyses were performed on Agilent 1200 instrument equipped with a refraction index detector on a PL-gel 10 μm Mixed-B 7.5 mm ID column, calibrated with polystyrene standards (peaks average molecular weights of 96, 500, 1320, 9,200, 66,000, Ploymer Laboratories Ltd.).

GC and GC-MS：GC and GCMS 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-QP2010SE equipped with a HP-5MS (30 m × 0.25 mm × 0.25 mm) column, respectively. 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.

HPLC: HPLC analysis was conducted on a Shimadzu LC-20A equipped with an aminex HPX-87H column (300 × 7.8 mm) with 9 μm particle size using a differential refractive index detector (RID-20A). The detection temperature was 60 °C, The velocity of the pump was 0.6 mL/min.

NMR: The NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer. Lignin oil and standard samples were dissolved in DMSO-d_6. The central solvent peak at δ_C/δ_H = 39.5/2.49 ppm was used as an internal reference. The standard Bruker implementations of two-dimensional HSQC NMR experiments were used for structural characterization and assignment authentication as reported earlier.

2. Preparation and characterization of Ni@ZIF-8

Preparation of ZIF-8: ZIF-8 was rapidly synthesized at room-temperature according to the literature.[3] Typically, $Zn(NO_3)_2 \cdot 6H_2O$ (3.0 g, 10.1 mmol) was dissolved in 200 mL methanol, then the solution was rapidly poured into a solution of 2-methylimididazole (6.53 g, 79.5 mmol) in 200 mL of methanol under vigorous stirring for 24 h. The mixed solution was gradually emerged turbid and the obtained nanocrystals were separated from the milky dispersion by centrifugation. The synthesized ZIF-8 was washed with deionized water and methanol, soaked in methanol at room-temperature for 48 h, then centrifuged to have the solid and dried at 150 ^{o}C for 8 h under vacuum.

Preparation of Ni@ZIF-8 catalyst: ZIF-8 immobilized Ni using the chemical liquid deposition (CLD) method according to the literature.[4] In a glove-box, a solution of bis(cyclopentadienyl)nickel(II) (0.23 g, 1.2 mmol) in 20 mL anhydrous diethylether was added dropwise to a suspension of ZIF-8 (0.25 g) in 20 mL methanol. After stirring for 24 h, the methanol was removed at room temperature, and the residue was dried at 60 ^{o}C for 24 h under vacuum. The sample was treated in a steam of H_2/N_2 flow (50 mol% H_2) at 300 ^{o}C for 8 h to obtain the black Ni@ZIF-8, which was stored with nitrogen protection.

Characterization of Ni@ZIF-8:

In X-ray photoelectron spectroscopy (XPS) spectra (Figure S1a and b), well-defined peaks with binding energies of 1021.7 and 1046.0 eV are ascribed to the $2p_{3/2}$ and $2p_{1/2}$ of the Zn^{2+} ion in the ZIF-8 framework. The signals for Ni^0, NiO and $Ni(OH)_2$ on the surface are all detected, probably because nickel on the surface can be easily oxidized under air.

Powder X-ray diffraction (XRD) patterns of ZIF-8 and Ni@ZIF-8 display typical characteristic peaks of ZIF-8 at 2θ = 7.4^o, 10.4^o, 12.8^o, 14.8° and 16.5°. Of note, , no visible diffraction of Ni NPs species was detected in the XRD patterns of Ni@ZIF-8, indicating that Ni was controlled in the small size by the framework of ZIF-8 (Figure S1c).

The TEM images show that the Ni atoms in fresh Ni@ZIF-8 were distributed on support as either nanocrystallites with lattice fringe spacing as 0.22 nm or cluster-type (Figure S2a). EDS mapping show the presence of C, N, Zn and Ni elements in Ni@ZIF-8 (Figure S2b).
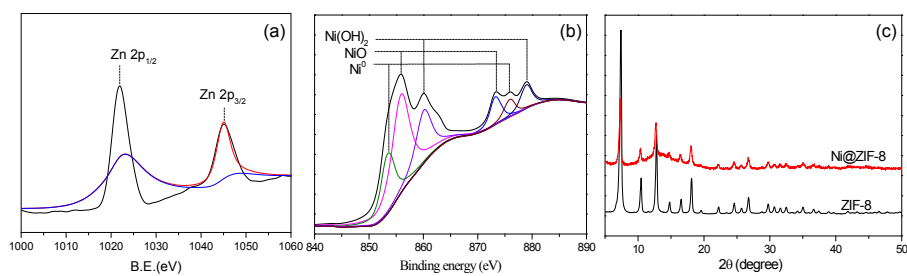
Figure S1. XPS spectra of (a) Zn 2p and (b) Ni 2p. (c) Powder XRD patterns of ZIF-8 and Ni@ZIF-8.
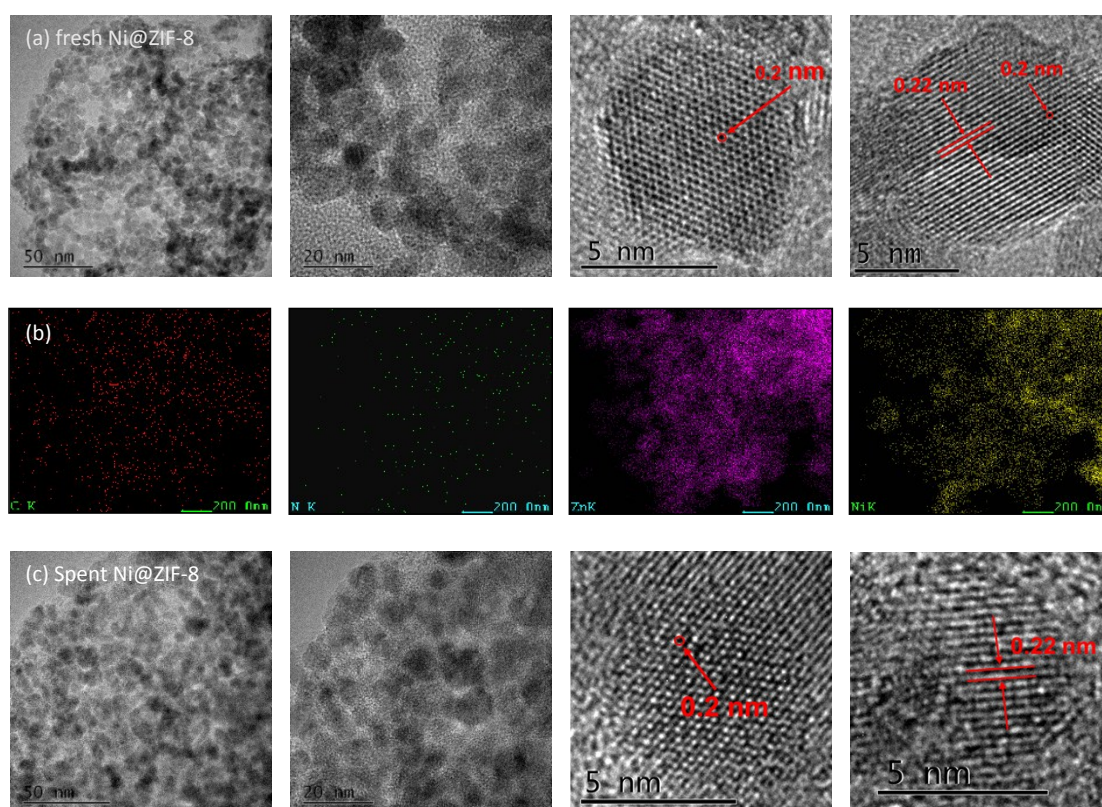

Figure S2. High-resolution TEM images of (a) fresh Ni@ZIF-8 and (c) spent Ni@ZIF-8; (b) EDS elemental mapping of C, N, Zn and Ni in fresh Ni@ZIF-8.
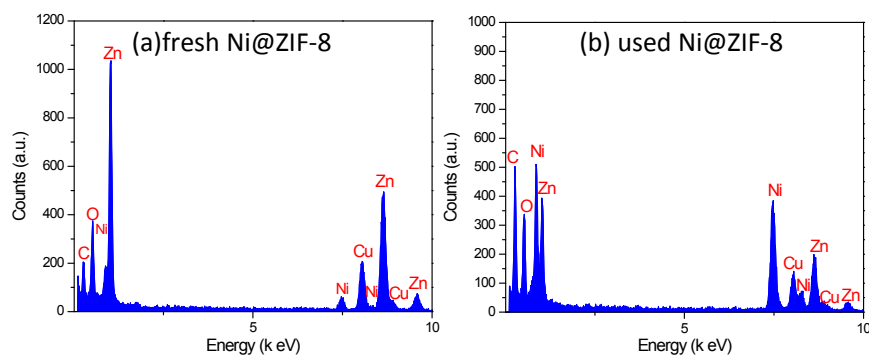

Figure S3. The EDS spectra of (a) fresh Ni@ZIF-8 and (b) used Ni@ZIF-8.

Table S1. ICP-AES analyses for the fresh Ni@ZIF-8 and spent Ni@ZIF-8 catalysts.

sample	Ni content（%）
Fresh Ni@ZIF-8	14
Used Ni@ZIF-8	13.5

By the N_2 adsorption examinations, ZIF-8 shows a specific surface area of 1450 m^2/g and a micropore volume of 0.67 cm^3/g, which are similar to the highest values reported form microscale ZIF-8 (BET surface area: 1630 m^2/g, micropore volume 0.64 cm^3/g). In the case of Ni@ZIF-8, a decreased BET surface area (579 m^2/g) and micropore volume (0.31 cm^3/g) were measured. (Table S2 and Figure S4).

Table S2. N_2 adsorption-desorption of ZIF-8 and Ni@ZIF-8 catalyst.

sample	Specific surface area $(m^2/g)^a$	Pore Volume $(cm^3/g)^b$
ZIF-8	1450	0.67
Ni@ZIF-8	579	0.31

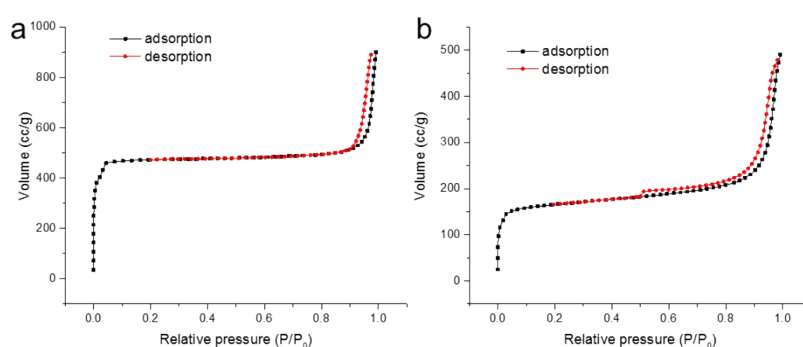[a] BET surface area. [b] BJH desorption cumulative volume of pores.

Figure S4. N_2 adsorption-desorption isotherms of pure ZIF-8 (a) and Ni@ZIF-8 catalyst (b).

3. Ni@ZIF-8-catalysed decomposition of β-O-4 model compounds

General procedure: Lignin model compound **1** (25 mg, 0.08 mmol), Ni@ZIF-8 (5 mg) and MeOH (10 mL) were mixed in a 50 mL stainless steel batch reactor (Parr Instruments Co.), which was then sealed, evacuated and filled with H_2 (3 MPa) at room temperature. After stirring at 260 °C for 8 h, the autoclave was cooled to room temperature and depressurized carefully. Tetradecane (0.005 mmol) solution was added as a standard. The reaction mixture was filtered to remove the MeOH and the filtrate was evaporated to afford an oily product. The oily product was dissolved into CH_2Cl_2 in a 5.0 mL volumetric flask, which was then submitted to GC and GC-MS. The identification and quantification of products were assessed by comparison with authentic samples.
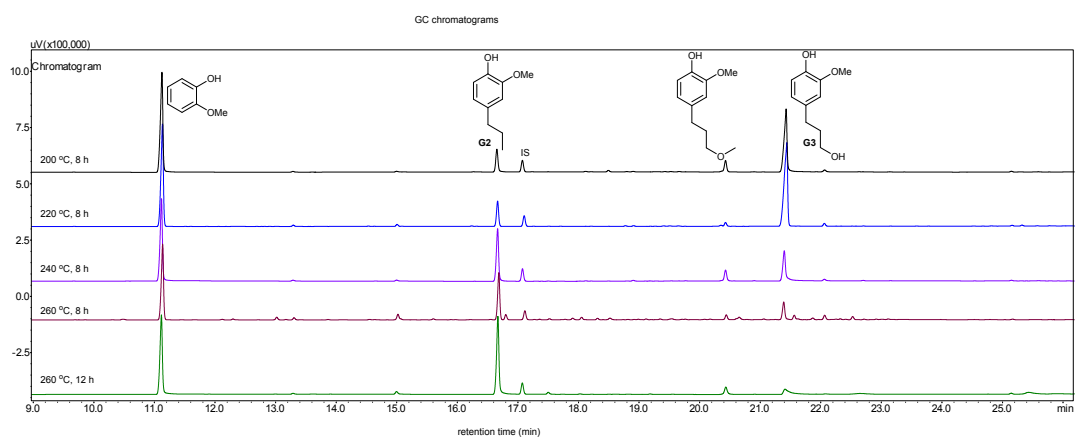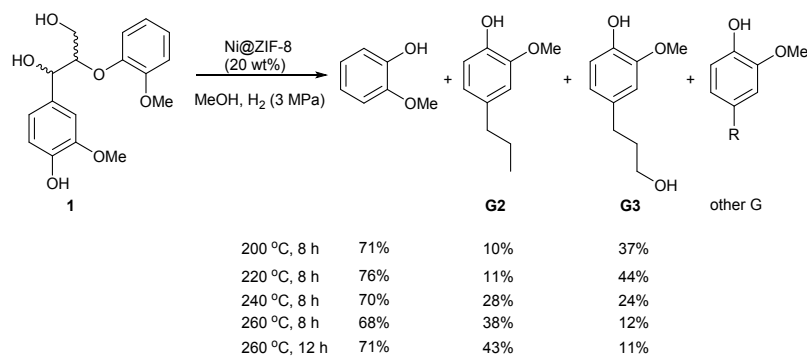

200 °C, 8 h	71%	10%	37%
220 °C, 8 h	76%	11%	44%
240 °C, 8 h	70%	28%	24%
260 °C, 8 h	68%	38%	12%
260 °C, 12 h	71%	43%	11%

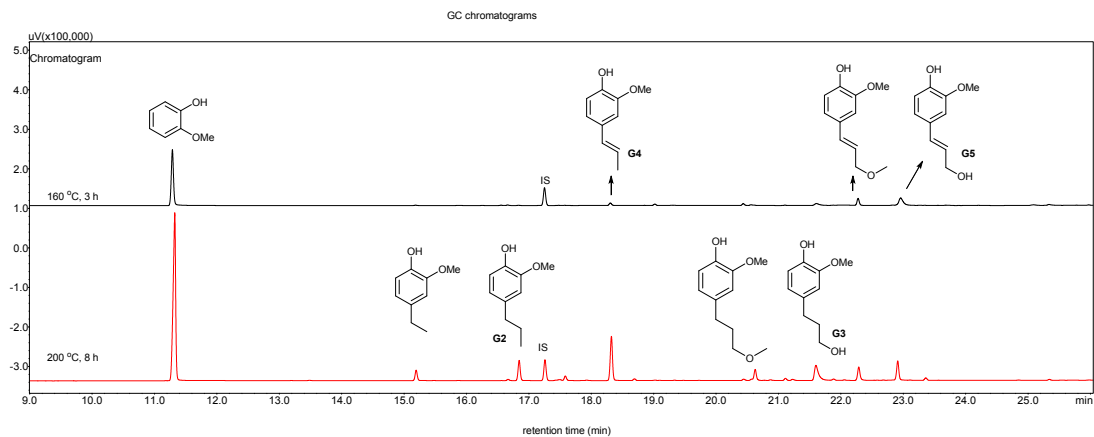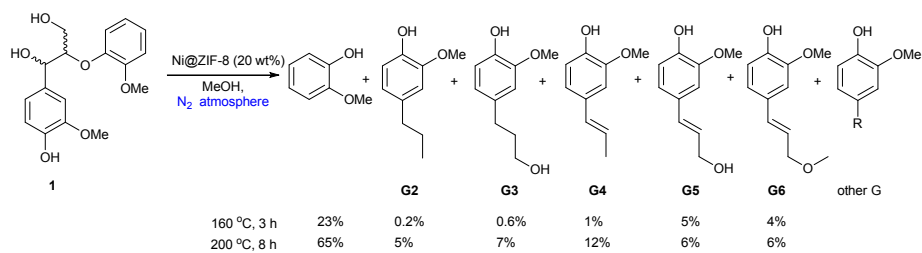**Figure S5**. Ni@ZIF-8-catalyzed decomposition of β-O-4 model compound **1** under H_2

Figure S6. Ni@ZIF-8-catalyzed decomposition of β-O-4 model compound **1** under N$_2$
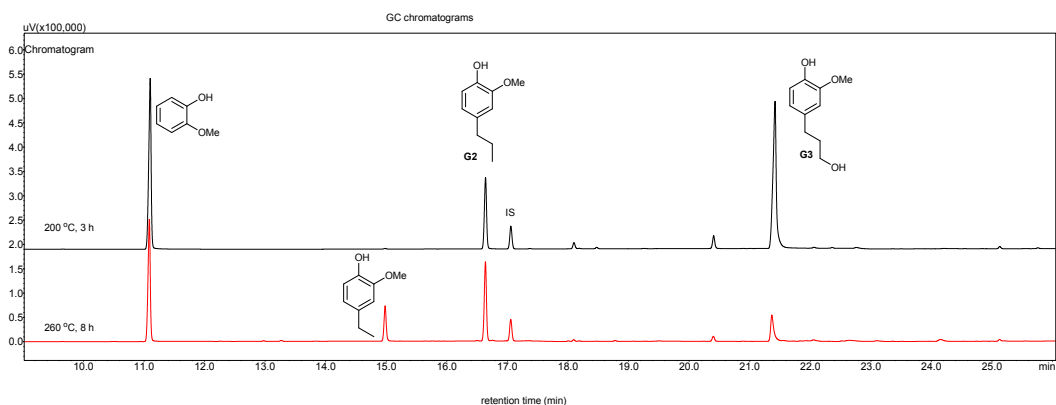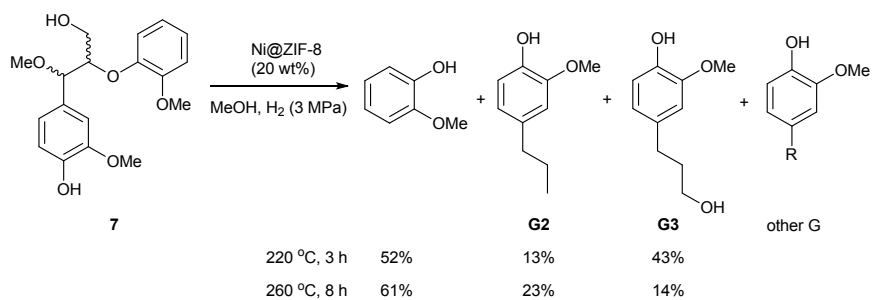

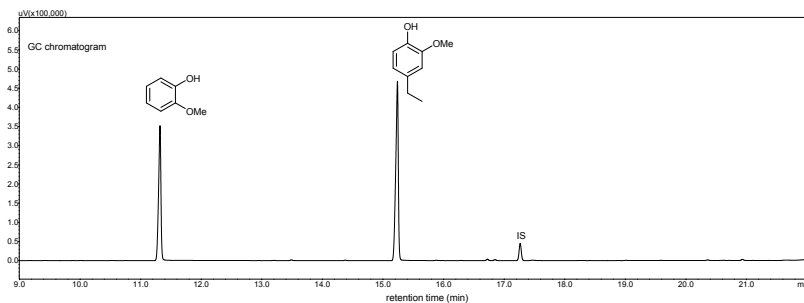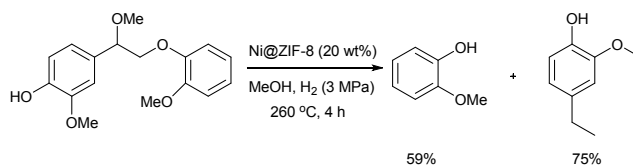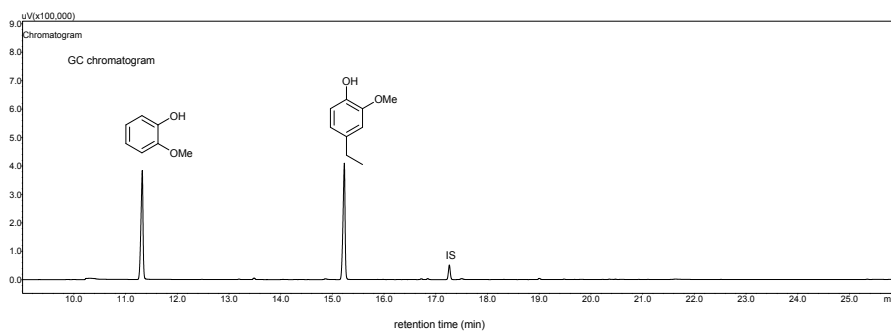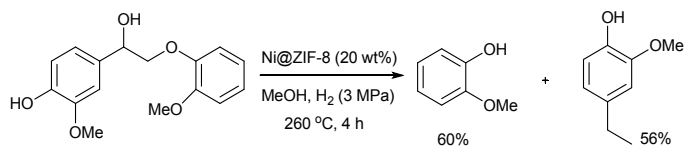**Figure S7**. Ni@ZIF-8-catalyzed decomposition of β-O-4 model compound **7**
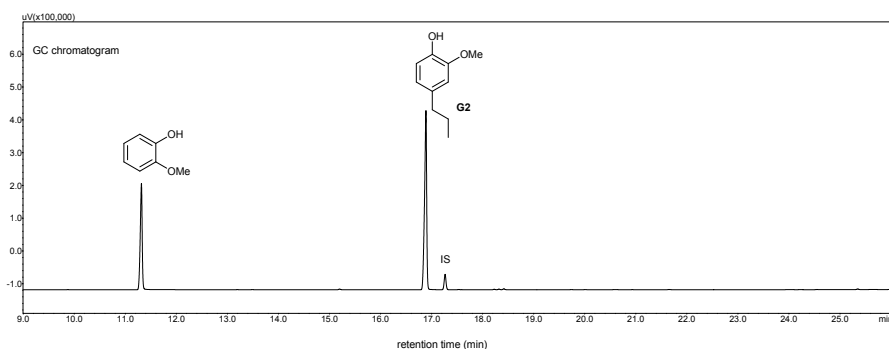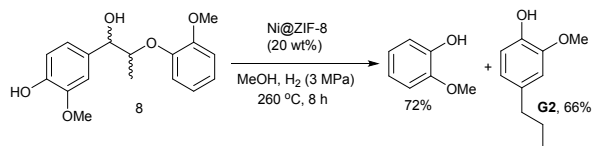
Figure S8. Decomposition of model compounds with Ni@ZIF-8 catalyst

Decomposition of deuterated β-O-4 mimic with Ni@ZIF-8
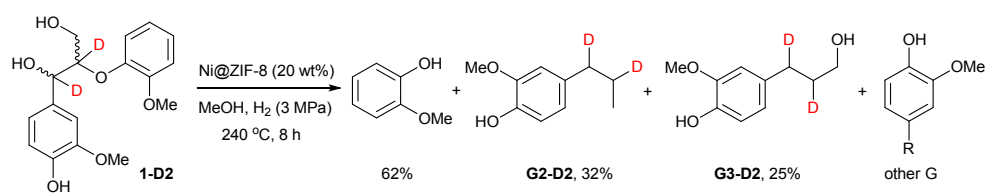
Ni@ZIF-8-catalyzed hydrogenolysis of **1-D2** reaction was performed at 240 °C for 8 h. After reaction, the oily product was initially analyzed by GC and GC-MS, which indicated that both **G2** and **G3** were generated in 32% and 23% yields, respectively. The molecular weights of **G2-D2** and **G3-D2** in oily product were determined as 168.1 and 184.1 g mol^{-1}, respectively, being consistent with the authentic samples. Through silica gel column chromatography (PE/EtOAc), pure **G3-D2** was isolated in 21% yield. ^{1}H NMR spectrum analysis confirmed that the α- and β-D still remained in **G3-D2**.
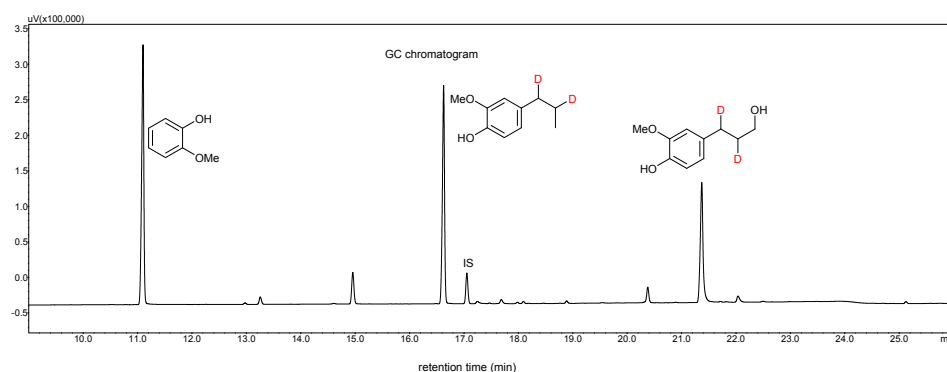
Figure S9. Gas chromatogram of the monomers from decomposition of deuterated β-O-4 mimic
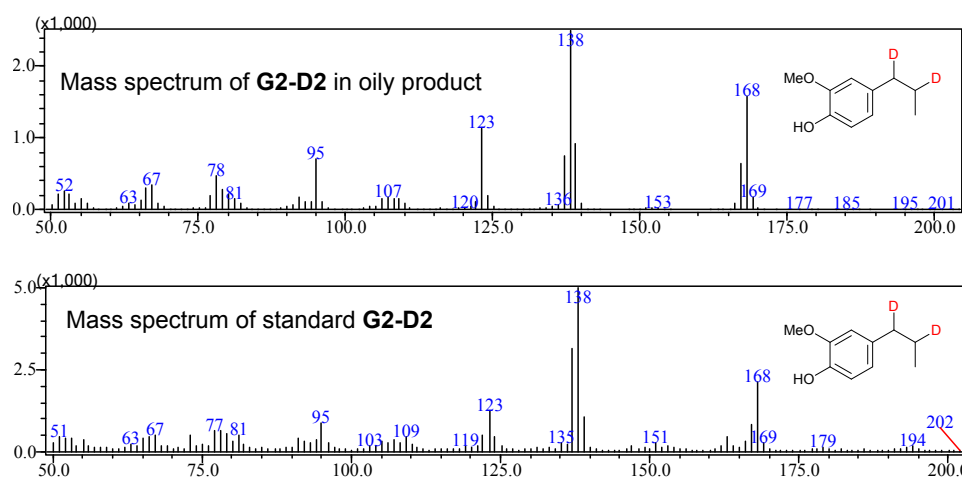
Figure S10. Mass spectra of **G2-D2** in oily product and standard sample

Compound **G3-D2.** **¹H NMR** (400 MHz, CDCl₃): δ 6.82 (d, J = 8 Hz, 1H), 6.70 – 6.68 (m, 2H), 5.56 (s, 1H, ArO$\underline{H}$), 3.87 (s, 3H), 3.67 (d, J = 6.4 Hz, 2H, γ-C$\underline{H}_2$), 2.62 – 2.61 (m, 1H, α-C$\underline{H}$D), 1.87 – 1.83 (m, 1H, β-C$\underline{H}$D). MS (EI) found for $C_{10}H_{12}D_2O_3$: 184.1.
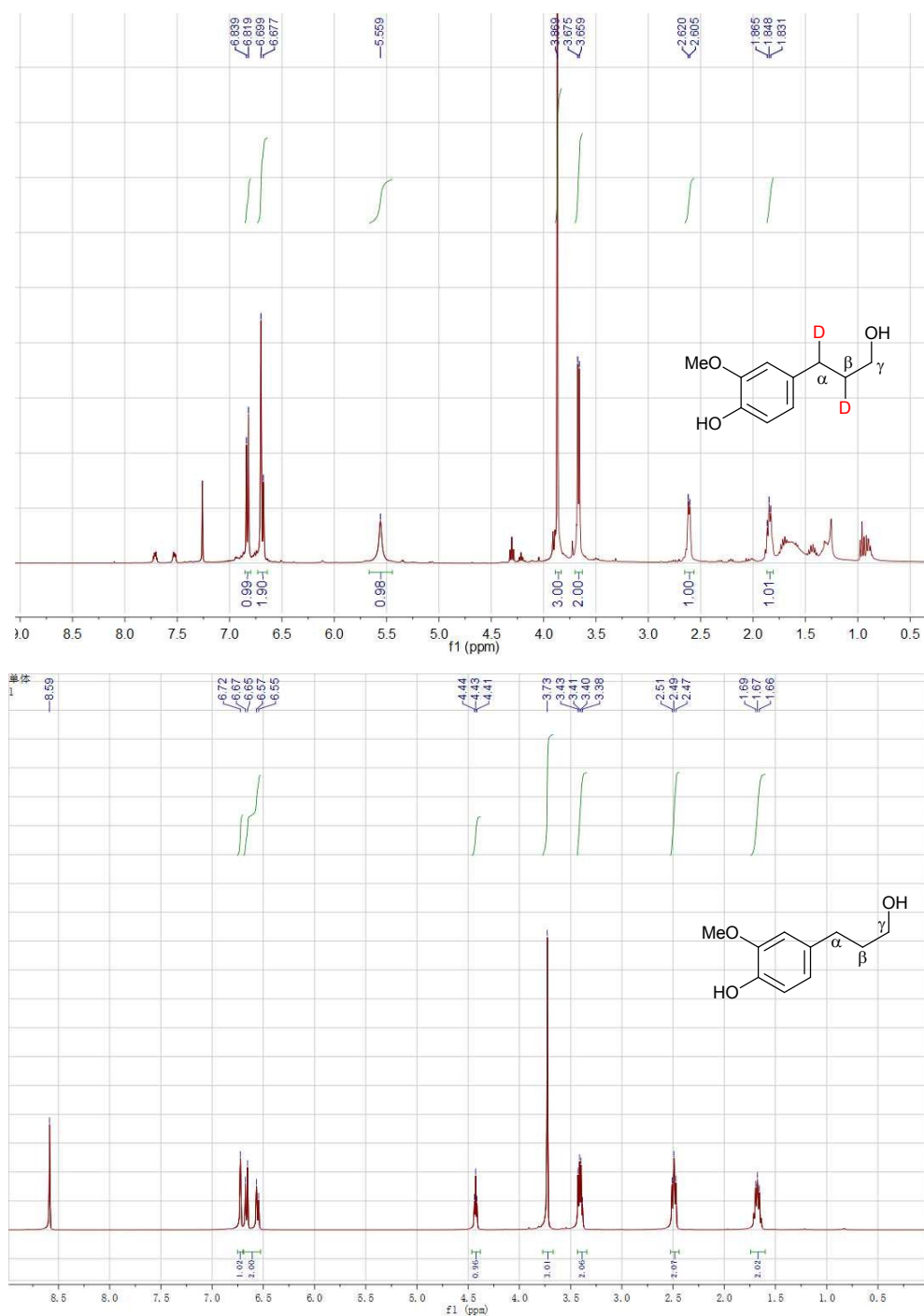
Figure S11. ¹H NMR spectra of **G3-D2** and **G3**
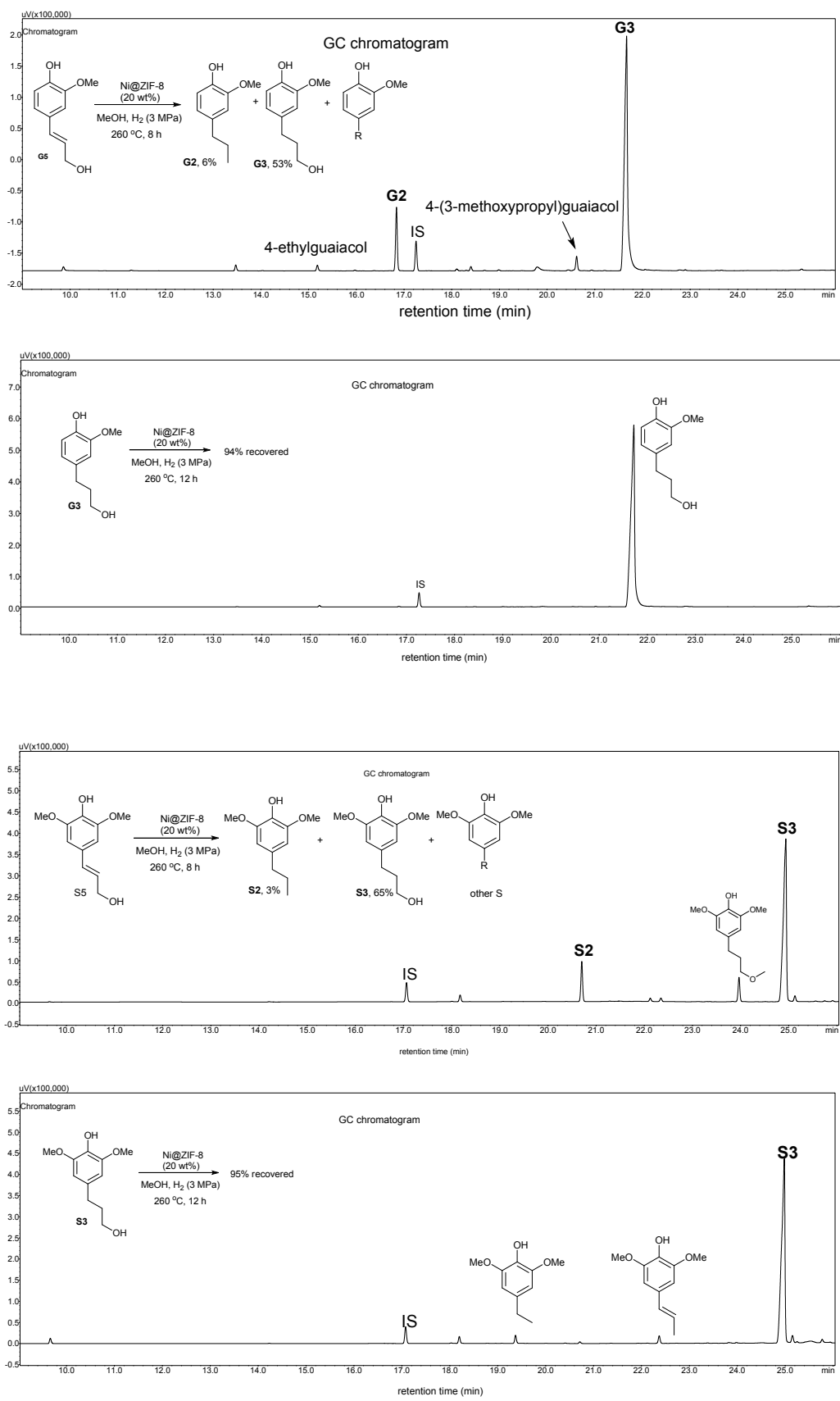
Figure S12. The reactivity of monomeric phenols over Ni@ZIF-8

4. Catalytic hydrogenolysis of synthetic lignin polymer

General procedure: Synthetic lignin polymer (25 mg), Ni@ZIF-8 (5 mg), MeOH (10 mL) were mixed in 50 mL stainless steel batch reactor (Parr Instruments Co.), which was sealed, evacuated and filled with H_2 (3 MPa) at room temperature. After heated, the reaction mixture was cooled to room temperature. The reaction mixture was filtered and evaporated to obtain an oily product, which was then dissolved in CH_2Cl_2 and analyzed by GC and GC-MS.
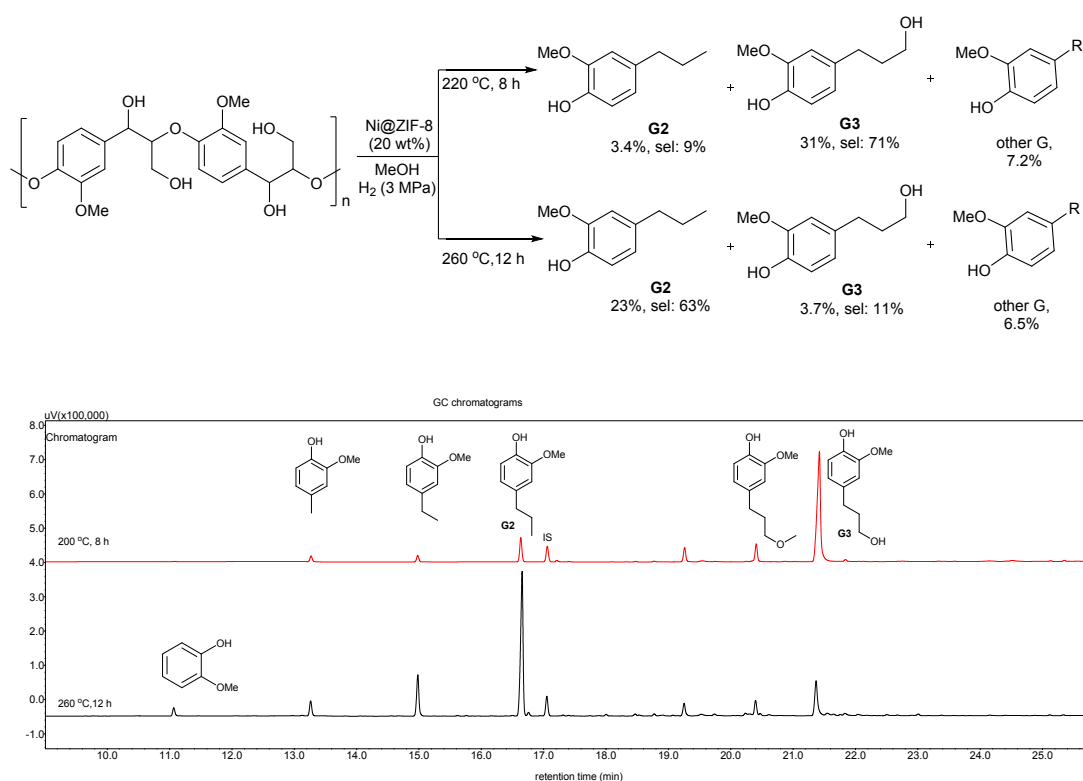
Figure S13. Gas chromatogram of the monomers from hydrogenolysis of synthetic lignin polymer.

5. Chemical composition of eucalyptus sawdust

General procedure: Firstly, the Eucalyptus sawdust (particles size: 0.5 mm-1.0 mm) was extracted with toluene/ethanol (2:1, v/v) in a Soxhlet instrument for 12 h, and then dried at 50 °C under vacuum for 8 h. The chemical composition was determined followed by National Renewable Energy laboratory's (NREL) standard analytical procedure. The Eucalyptus sawdust (300 mg) was milled and hydrolyzed at room temperature with 72 wt% sulfuric acid solution (3.0 mL) for 1 h. Deionized water (84.0 mL) was then added to dilute sulfuric acid (*ca.* 3%). This mixture was heated at 120 °C for 1 h in the autoclave. After cooling, the mixture was filtered through a mixed cellulose ester (MCE) membrane filter (0.2 μm). The amount of acid insoluble lignin (AIL, Klason lignin) was determined by measurement the weight of residue after drying. The concentration of acid soluble lignin (ASL) was determined by UV spectra by measuring the absorbance of the soluble fraction at 205 nm. The determination of monomeric sugars in the aqueous soluble fraction performed on HPAEC system (Dionex ICS 3000, USA) equipped with a Carbopac TM PA-20 column (3 mm × 150 mm, Dionex, Sunnyvale, USA) and an amperometric detector, by comparison with authentic samples. These samples were conducted in triplicate.

Table S3. The composition of Eucalyptus sawdust[a]

Entry	Substrate	AIL[b] (wt %)	ASL[c] (wt %)	Cellulose (wt %)	Hemicellulose (wt %)	Extraction (wt %)
1	Eucalyptus	23.8	3.2	41.6	16.9	3.2

[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.

6. The reductive catalytic fractionation of eucalyptus sawdust

General procedure: In a typical catalytic lignin hydrogenolysis on Eucalyptus sawdust experiment, extracted eucalyptus sawdust (size 0.5-1.0 mm, 500 mg), Ni@ZIF-8 (50 mg) and MeOH (10 mL) were mixed into a 100 mL stainless steel batch reactor (Parr Instruments Co.). The reactor was sealed, flushed with N_2 about three times and pressurized with 3 MPa H_2 at room temperature. The mixture was stirred at 400 rpm and heated at desired temperature. After reaction, the reactor was cooled to room temperature and depressurized. The reaction mixture was filtered through a nylon 66 membrane filter (0.2μm), thus forming soluble (lignin oil) and insoluble fractions (carbohydrate pulp and catalyst).

Lignin products analysis

Degree of delignification

For the soluble fraction, the methanol was removed under vacuum to give crude "lignin oil", which was weighted to determine the degree of delignification (based on Klason lignin weight).

Monomers analysis

To analyze the lignin monomers after hydrogenolysis, the lignin oil and a standard (tetradcane) was solubilized in dichloromethane in a 10 mL volumetric flask. A aliquot (10 μL) was then analyzed on a GC (Shimadzu GC2010 series, equipped with a HP-5 column and a flame ionization detector (FID)) and GC-MS (Shimadzu GC2010 series equipped with a HP-5 MS column and a Mass Spectroscopy detector), respectively. The following operating conditions were used: injection temperature of 553 K, column heating program: 323 K (3 min), 10 K/min to 553 K, detection temperature of 563 K (for FID). The quantification of lignin monomers in the oil products were assessed by comparison with authentic samples acquired from commercial purchase or independent synthesis.

Gel permeation chromatography (GPC) analysis

GPC analyses of lignin oil (THF solution, *ca*. 2 mg/mL) were performed on Agilent 1260 equipped with a PL-gel 10 μm Mixed-B 7.5 mm I.D. column (mixed) and UV detection detector (254 nm) at 50 °C, using THF as the solvent (1 mL/min), which were calibrated with polystyrene standards (peaks average molecular weights of 180, 550, 870, 1320, Polymer Laboratories Ltd.).

Table S4. Depolymerization of eucalyptus sawdust under different catalysts[a]

Entry	catalyst	total monomers	guaiacyl monomers				syringyl monomers					Delignification[b] (wt %)
			G2	G3			S2	S3				
1	**No**	4.4	ND	ND	0.4	0.2	ND	ND	0.5	1.7	0.3	47%
2	**ZIF-8**	12.9	ND	ND	ND	0.8	0.4	ND	3.7	4.6	2.8	70%

[a] Reaction conditions: eucalyptus sawdust (500 mg), MeOH (10 mL), 220 °C, 4 h, H_2 (3 MPa) catalyst (50 mg).

[b] Based on the weight of dichloromethane extracted fraction (Klason lignin).

Table S5. RCF of eucalyptus sawdust under different solvents[a]

Entry	Solvent	phenolic monomers yield (wt%)							Selectivity (mol %)		S/G	Delignification (wt %)
		G2	S2	G3	S3	other G	other S	total monomers	2	3		
1	**MeOH**	1.2	2.6	9.7	24.2	0.8	3.9	42.0	10	80	2.2	86
2	**EtOH**	0.9	3.1	9.3	18.2	0.3	0.4	32.7	13	82	1.8	80
3	***i*PrOH**	0.4	1.4	8.3	18.8	1.0	0.5	30.4	6	88	1.8	78

[a] Reaction conditions: eucalyptus sawdust (500 mg), catalyst (50 mg), H_2 (3 MPa), 220 °C, 12 h , solvent (10 mL).
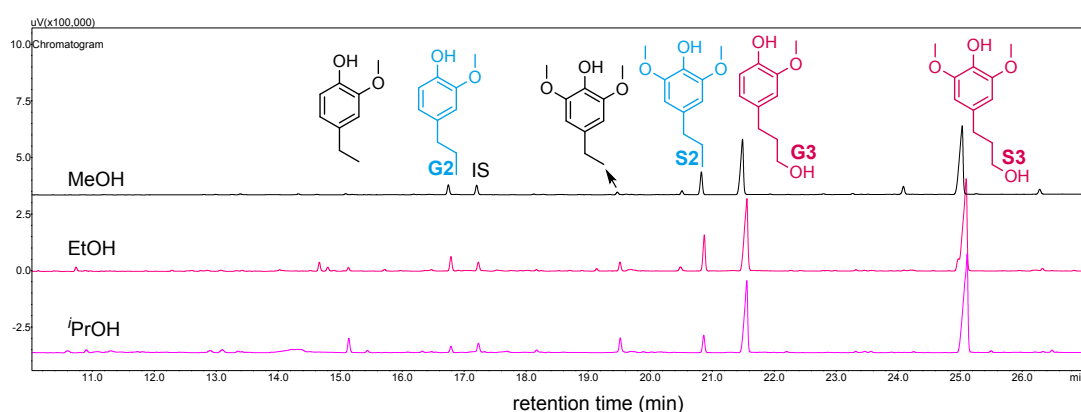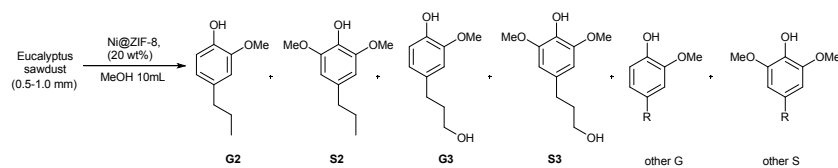

Figure S14. Gas chromatogram of the monomers from RCF of eucalyptus sawdust under different solvents

Table S6. RCF of eucalyptus sawdust under various conditions [a]

Entry	Recation conditions		Phenolic monomers yield (wt %)						Selectivity (mol %)		S/G	Delignification[b] (wt%)
			G2	S2	G3	S3	others	total monomers	2	3		
1		1 atm N₂	1.3	1.6	2.0	1.8	11.3	20.8	24	23	1.9	46
2	220°C	1 MPa H₂	2.2	2.1	5.2	2.5	10.8	24.0	42	23	2.0	50
3	4h	3 MPa H₂	2.3	5.1	4.9	10	9.8	32.1	26	47	2.2	66
4		4 MPa H₂	2.3	5.3	5.0	11	9.7	33.3	24	50	2.2	70
5		160°C, 4 h	ND	2.3	ND	3.2	1.0	6.6	84	0	1.5	15
6		190°C, 4 h	0.3	4.1	0.4	7.0	2.1	13.8	86	5	1.9	28
7	3 MPa H₂	240°C, 4 h	3.1	3.6	7.1	6.2	8.2	28.2	41	35	2.5	83
8		260°C, 8 h	6.8	3.2	16.4	6.3	11.5	44.3	55	20	2.1	92
9		260°C, 12 h	6.4	2.3	15.0	3.2	9.4	36.3	64	15	1.8	95

[a] Reaction conditions: eucalyptus sawdust (500 mg), Ni@ZIF-8 (50 mg), MeOH (10 mL).

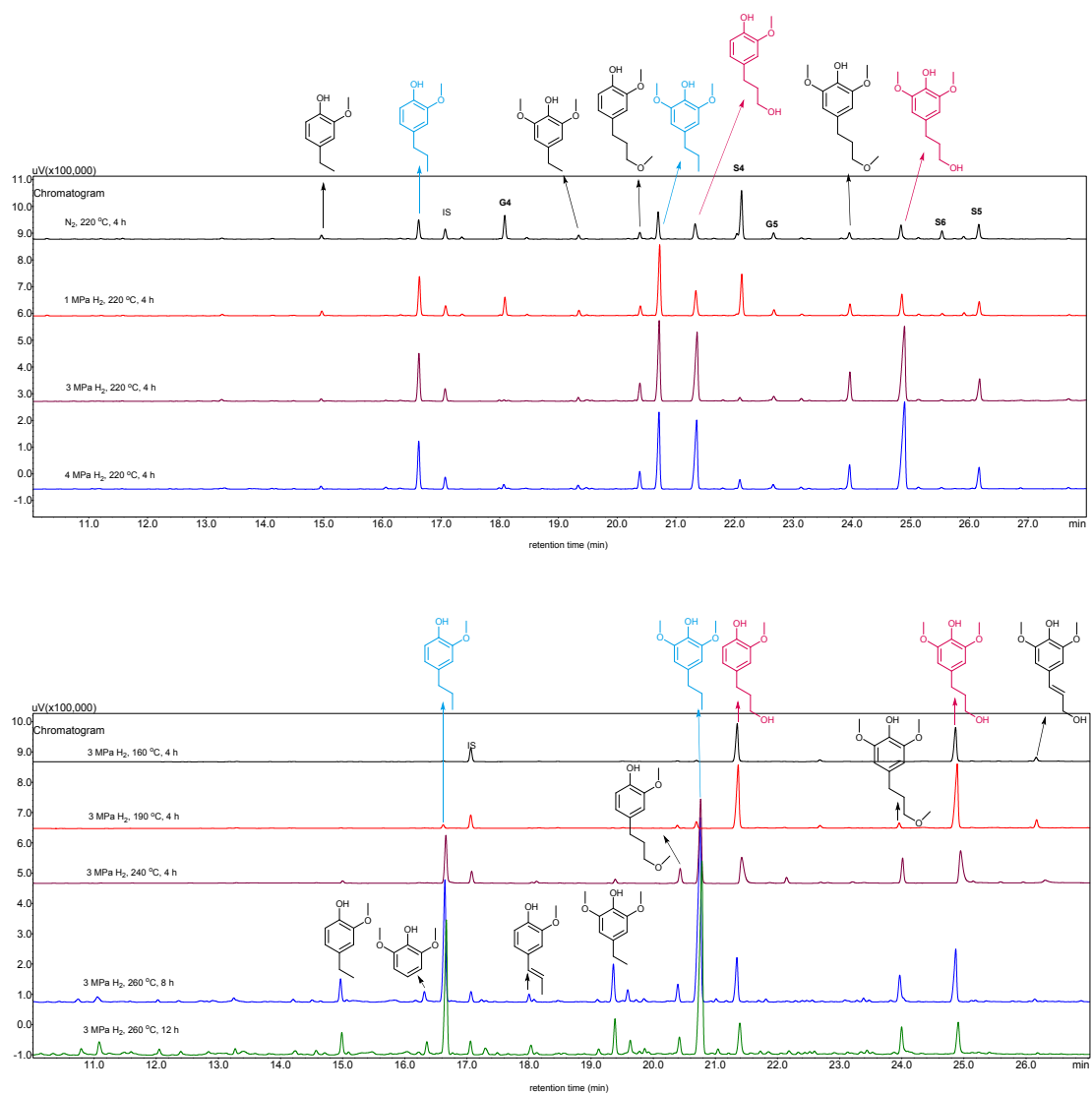[b] Based on the weight of dichloromethane extracted fraction (Klason lignin).

Figure S15. Gas chromatogram of the monomers from RCF of eucalyptus sawdust under various conditions

Table S7. Time profile of RCF of eucalyptus sawdust with Ni@ZIF-8 at 220ºC [a]

Entry	Time (h)	phenolic monomers yield (wt %)					Selectivity (mol %)		S/G	Delignification[b] (wt %)	M_w (g/mol)
		G2	**S2**	**G3**	**S3**	total monomers	**2**	**3**			
1	1	1.0	1.4	2.4	3.2	14.0	20	39	1.4	53	1024
2	2	2.3	4.5	2.8	4.5	18.9	38	37	1.7	46	1071
3	3	2.9	7.1	4.7	9.5	28.3	39	49	2.1	54	1010
4	4	2.3	4.9	5.1	10.0	32.1	25	46	1.8	66	1070
5	5	1.7	3.8	5.7	11.7	32.4	38	37	1.7	74	1071
6	6	1.4	3.4	7.0	14.2	33.4	16	63	1.9	70	1214
7	7	1.4	3.4	6.8	14.7	35.0	16	61	1.9	70	1056
8	8	1.5	3.6	7.0	14.8	35.3	16	61	1.9	87	918
9	10	1.5	3.8	8.8	20.1	41.5	14	68	2.2	74	1042
10	12	1.2	2.6	9.7	24.2	42.0	10	80	2.2	86	925

continued

Entry	Time (h)	phenolic monomers yield (wt %)									
		Other G					Other S				
1	1	ND	ND	0.7	0.8	0.7	ND	1.2	1.2	0.5	1.6
2	2	ND	ND	0.7	0.8	0.7	ND	1.2	1.2	0.5	1.6
3	3	ND	0.2	ND	0.3	ND	0.2	ND	2.8	ND	ND
4	4	ND	0.3	ND	1.8	0.6	ND	0.2	3.6	ND	3.0
5	5	ND	0.3	ND	2.2	1.4	0.2	ND	3.9	ND	2.2
6	6	ND	0.3	ND	1.3	0.5	0.2	ND	2.6	ND	2.4
7	7	ND	0.3	ND	5.2	0.9	0.2	ND	3.7	ND	2.0
8	8	0.2	0.6	ND	1.8	ND	0.3	ND	3.8	ND	1.8
9	10	ND	ND	ND	1.5	ND	0.3	ND	3.3	ND	2.4
10	12	ND	ND	ND	0.8	ND	0.3	ND	2.0	ND	1.6

[a] Reaction conditions: eucalyptus sawdust (500 mg), Ni@ZIF-8 (50 mg), MeOH (10 mL), H_2 (3 MPa), 220 ºC.

[b] Based on the weight of dichloromethane extracted fraction (Klason lignin).

Observation of the possible intermediates

In model reaction and RCF of eucalyptus sawdust, a single peak (retention time: 29.04 min) corresponding to mass of 318 g/mol was found in the gas chromatogram. It may be ascribed to **α-OMe-8**.
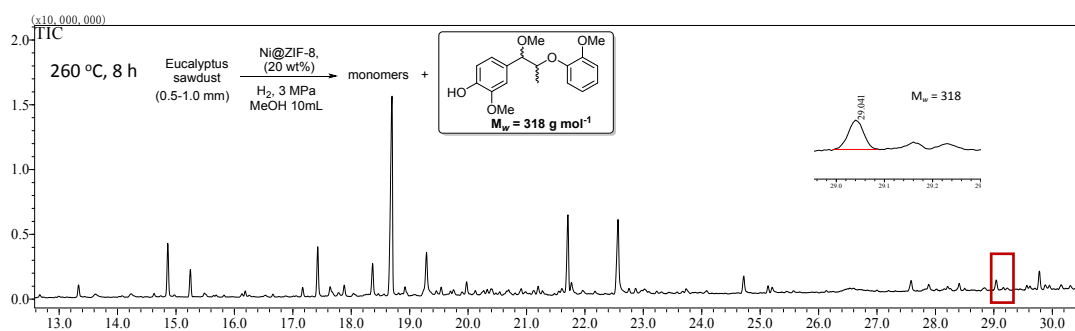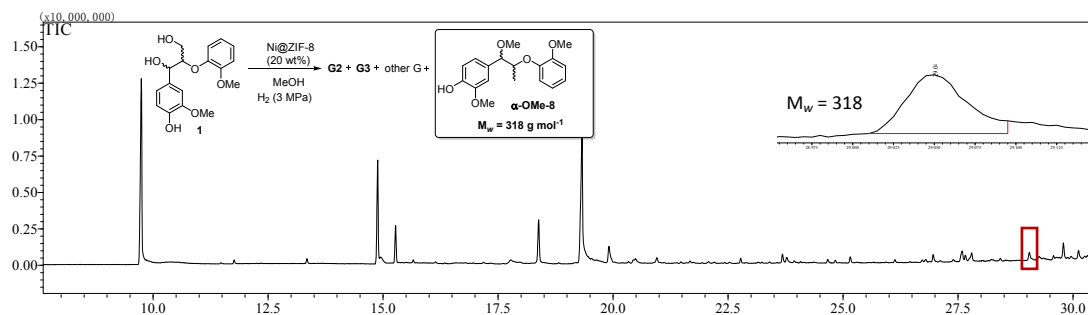

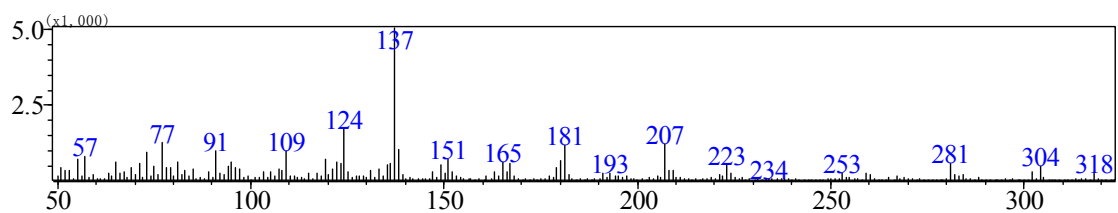**Figure S16.** The observation of **α-OMe-8 in** gas chromatograms.

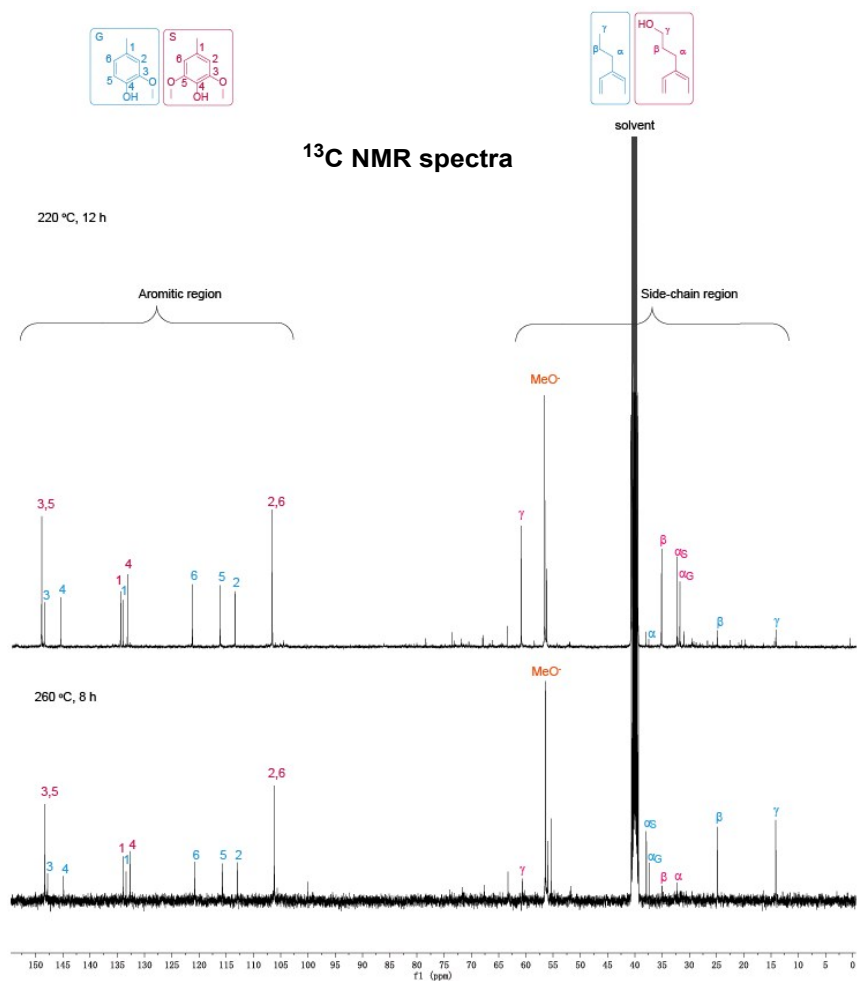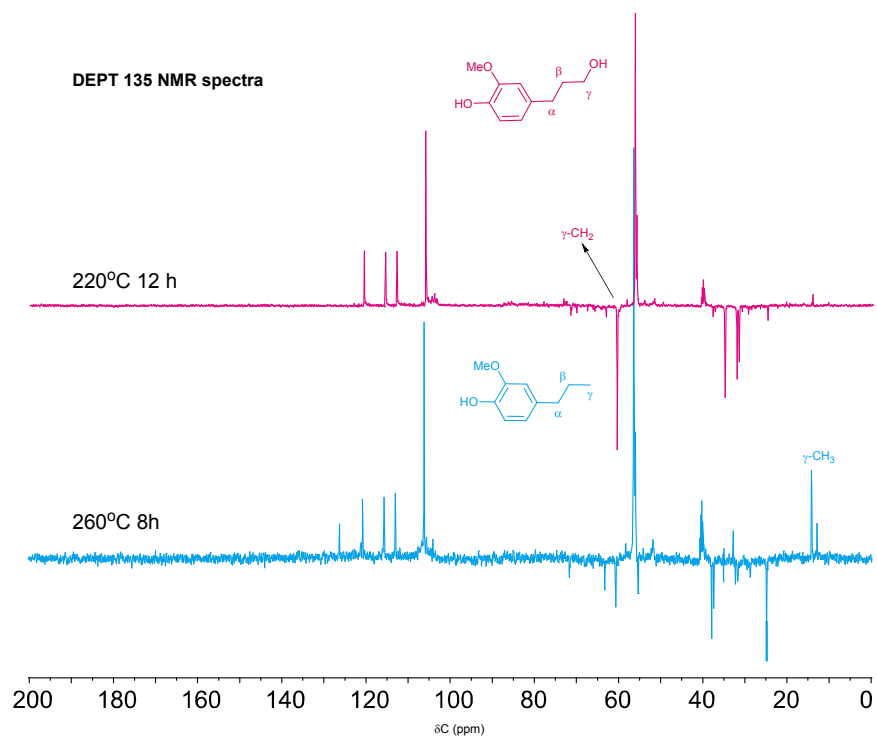**Figure S17.** Mass spectrum of **α-OMe-8.**

Figure S18. DEPT 135 NMR spectra (upper) and ^{13}C NMR spectra (down) of lignin oils.

Table S8. The recycling ability of Ni@ZIF-8

| Entry | run | phenolic monomers yield (wt%) | | | | | | | Selectivity (mol %) | | S/G | Delignification (wt%) |
		G2	S2	G3	S3	other G	other S	total monomers	2	3		
1[a,b]	1	4.6	13.9	2.1	8.7	4.3	6.0	39.7	50	26	2.2	95
2[c]	2	4.9	14.7	2.6	3.9	3.0	5.9	35.1	57	17	2.0	92
3[c]	3	2.8	8.1	4.6	5.9	2.3	6.2	29.8	38	33	1.8	90

[a] Reaction conditions: eucalyptus sawdust (3 g), Ni@ZIF-8 (0.3 g), MeOH (60 mL), H_2 (3 MPa), 260 °C, 8 h; [b] fresh Ni@ZIF-8 was used; [c] spent Ni@ZIF-8 was used.

Table S9. The sugar retention of the two optimized conditions for Ni@ZIF-8 catalysed Eucalyptus sawdust[a]

| Entry | Temp. (°C) | Time (h) | Sugar retention[b] (wt%) | | |
			C5	C6	total
1	220	12	78	90	87
2	260	8	67	90	84

[a] Reaction conditions: eucalyptus sawdust (500 mg), Ni@ZIF-8 (50 mg), MeOH (10 mL), H_2 (3 MPa).

[b] Based on the amount of C5, C6 in the sugar fractions of eucalyptus sawdust.

7. References

1. a) S. Kawai, K. Okita, Sugishita K, Sugishita, A. Tanaka and H. Ohash, *J. Wood Sci.*, 1999, **45**, 440-443; b) S. K. Badamali, R. Luque, J. H. Clark and S. W. Breeden, *Catal. Commun.*, 2011, **12(11)**, 993-995.

2. a) T. Kishimoto, Y. Uraki and M. Ubukata, *Org. Biomol. Chem.*, 2006, **4(7)**, 1343-1347; b) B. Biannic, J. J. Bozell. *Org. Lett.*, 2013, **15(11)**, 2730-2733.

3. J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mater.*, 2009, **21**, 1410-1412

4. P. -Z. Li, K. Aranishi and Q. Xu, *Chem. Commun.*, 2012, **48**, 3173-3175