

Electronic Supplementary Material (ESI)

Catalytic oxidative conversion of C/G-type lignin coexisting in Tung nutshell to aromatic aldehydes and acids

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Experimental Section

Lignin Content Analysis

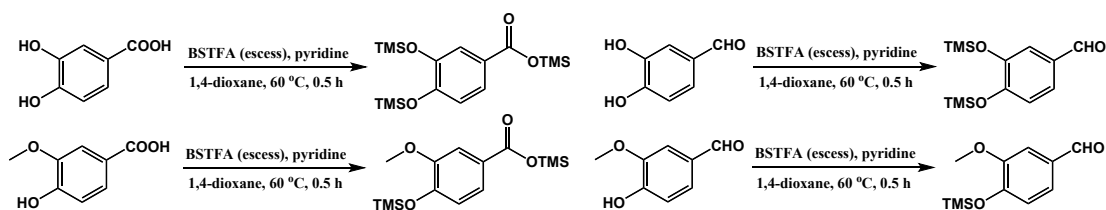
The content of Klason lignin in raw tung nutshell powder was measured by a modified two-stage H₂SO₄ hydrolysis process based on the NREL/TP-510-42618 protocol.^{1, 2} Tung nutshell powder was dried at 105 °C for all night. To remove the fat, waxes, and other residuals, the dried tung nutshell powder (5.00 g) was extracted with the toluene/ethanol co-solvent (2/1, v/v) in a Soxhlet extractor at 105 °C for 12 h. The powder was washed with ethanol and dried at 80 °C for all night to get the extracted tung nutshell (4.14 g). Under an ice-water bath condition, 15 mL of H₂SO₄ (72%, w/w) was added slowly to 1.00 g of the extracted tung nutshell powder. The suspension was stirred in 30 °C water bath for 2 h, and the 72% of H₂SO₄ was then diluted to 4% by adding deionized water (420 mL) for the second hydrolysis. The diluted solution refluxed at 120 °C for 6 h, and the residual was filtered and washed to neutrality by water. Finally, the solid was dried at 105 °C for all night (0.57 g), and the residual weight, denoted as W_h. The lignin content was calculated as follows:

$$\text{Lignin (wt \%)} = \frac{W_h}{W_e} \times 100\%$$

where W_e and W_h are the mass of the extracted tung nutshell powder and the residual solid after H₂SO₄ hydrolysis, respectively. Then Klason lignin content was 57 wt% based on the extracted tung nutshell powder, and 47 wt% based on the raw tung nutshell powder.

Procedure for GC-MS Qualitative Analysis

Qualitative analysis of the Oxidative Depolymerization reaction was performed by Agilent 8890N-5977B GC-MS instrument. The system is equipped with an HP-5 MS capillary column (30.0 mm × 250 μm × 0.25 μm), an Electron Impact (EI) ion source, and Quadrupole Mass Analyzer (QMA). Specific parameters are set as follows: vaporization chamber temperature (280 °C), detector temperature (280 °C), heating procedure: 50 °C (1 min), 200 °C (2 min, heating rate of 10 °C/min) and 250 °C (8 min, heating rate of 10 °C/min). The preparation of silylated samples was as follows (**Scheme S1**): the dried lignin oil (6 mg) was dissolved in 1,4-dioxane (1 mL), then was silylated with the mixture of BSTFA (50 uL) and pyridine (10 uL) at 60 °C for 30 min.^{3, 4} Finally, the silylated reaction solution was filtered with a PTFE filter (0.22 μm) before injection.



Scheme S1. The silylated reaction of protocatechuic acid, protocatechuic aldehyde, vanillic acid, and vanillin before GC-MS analysis.

Procedure for HPLC Quantitative Analysis and Calibration Curve Development

Quantitative analysis on lignin-derived monomers and oligomers was obtained on an Agilent 1260 Infinity II HPLC system equipped with a Supersil ODS2 column (5 μm , 250 mm \times 4.6 mm I. D.) and G7115A Diode Array Detector (UV absorbance at 280 nm) at 35 $^\circ\text{C}$. Solvent A (0.1% of aqueous formic acid) and solvent B (acetonitrile) were used as the mobile phase with a 1.5 mL/min of flow rate. The gradient of solvent B (acetonitrile) is shown in **Table S1**. The 2,6-Dimethoxyphenol was chosen as the internal standard to develop the calibration Curve.

Table S1. HPLC gradient profile for lignin monomer quantitation

Retention time (min)	Percentage of B mobile phase (%)
0	10
20	17
30	40
35	90
37	90
39	10
41	10

The standard solutions of the four different lignin-derived monomers (protocatechuic acid, protocatechuic aldehyde, vanillic acid, and vanillin) were obtained by the following steps: a certain amount of the four monomers and 15 mg of 2,6-dimethoxyphenol internal standard were transferred to a 25 mL of volumetric flask to obtain the standard solutions (denoted as A, acetonitrile as solvent). And the B~F standard solutions were prepared using the same method only changing the amount of the four monomers. Controlling the concentrations gradient were 0.008, 0.04, 0.16, 0.32, 0.48, and 1.2 mg/mL for the A~F standard solutions, respectively. It should be noted that the yield of the furfural by-product was calculated by the single-point method. The mass ratio of monomers to tung nutshell (mg/g) was calculated as the quantitative yield of products:

$$\text{monomer Yield (mg/g)} = \frac{\text{mass of detected monomers}}{\text{total mass of initial tung nutshell powder}}$$

Table S2. The retention time for each product by the HPLC analysis.

Compound	Retention Time (min)
Protocatechuic acid	5.07
Protocatechuic aldehyde	7.76
Vanillic acid	10.29
Vanillin	15.47
Furfural	6.34

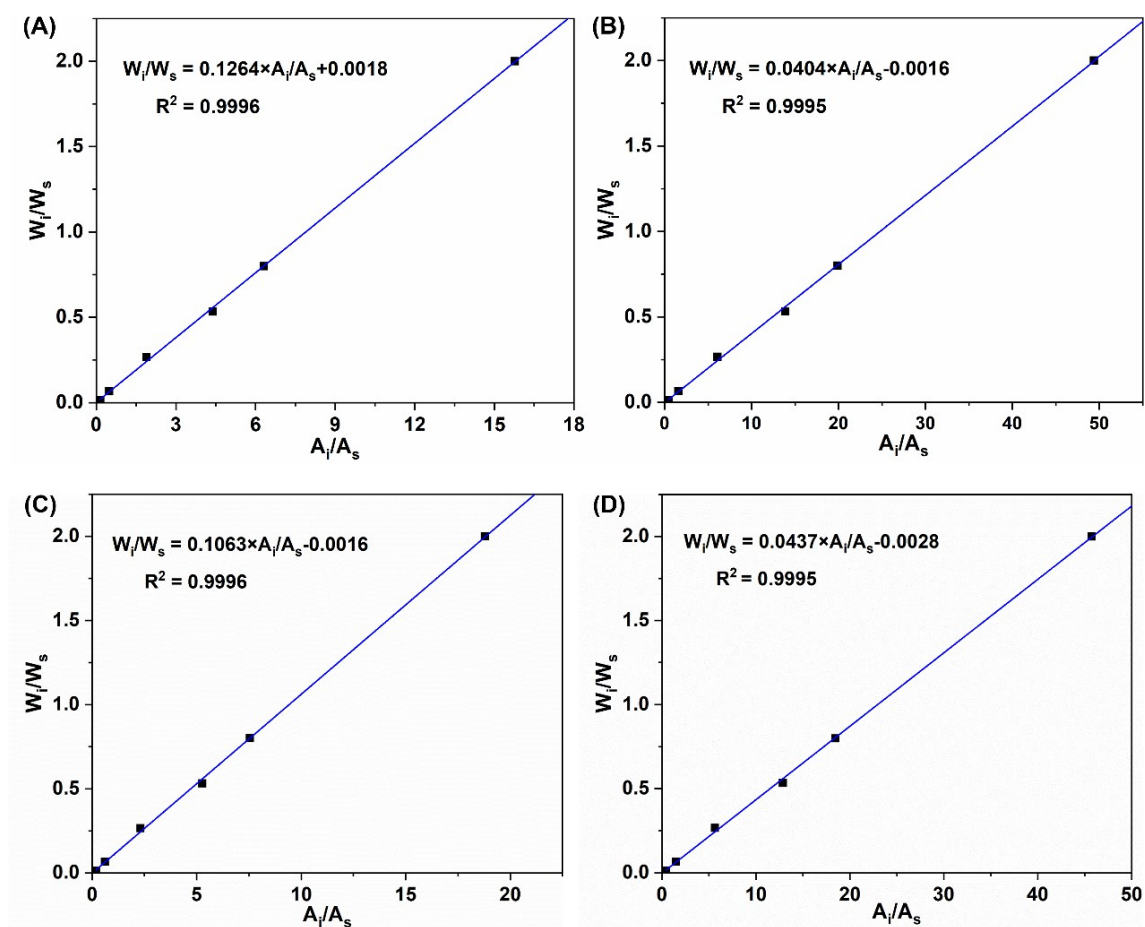


Figure S1. Internal standard curve of (A) protocatechuic acid; (B) protocatechuic aldehyde, (C) vanillic acid, and (D) vanillin

Procedure for Gel Permeation Chromatography Analysis

The Gel Permeation Chromatography (GPC) analysis was carried out on a Waters e2695 system equipped with a PL-gel 10 μm Mixed-B 7.5 mm I. D. column and UV detector (254 nm) at 50 °C, using THF ($1 \text{ mL} \cdot \text{min}^{-1}$) as eluent.^{5, 6} Before the injection, the dried lignin oils were solubilized in THF to prepare the 4 mg/ml of samples. Weight-average (M_w) was determined based on a calibration curve of polystyrene standards (370-42400 g/mol) and toluene (92 g/mol).

Procedure for 2D HSQC NMR Analysis

The 2D Heteronuclear Single Quantum Coherence Nuclear Magnetic Resonance (2D HSQC NMR) spectra were performed on a Bruker DRX-600 NMR spectrometer using the standard Bruker pulse sequence hsqcetgpsi.2. 40 mg of dried lignin oil dissolved in 0.5 mL of DMSO- d_6 to prepare the test samples. The parameters were set according to our previously reported method.⁷ The spectral width of 10.3 and 165 ppm (receiver gain: 208) was acquired in the f2 (^1H) and f1 (^{13}C) dimensions, respectively. Acquisition time (130 ms), relaxation delay time (1.5 s), 24 scan times (24), and 1024 data points (1024) were set for recording. The spectra were processed by MestReNova software using a squared cosine bell in both f1 and f2 dimensions. The peak of DMSO- d_6 ($\delta_{\text{C}}/\delta_{\text{H}}=39.52/2.49$ ppm) was used as the signal correction.

Supplementary Experimental Results

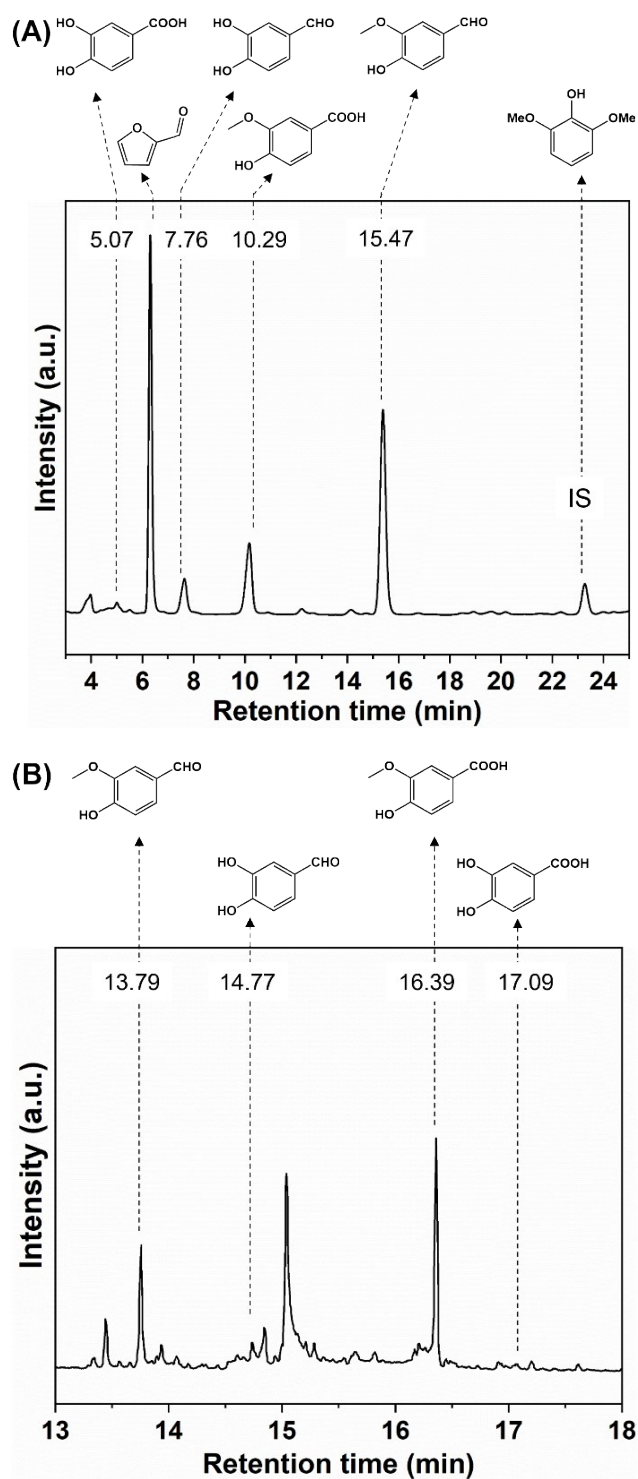


Figure S2. Oxidative depolymerization of tung nutshell lignin analyzed by (A) HPLC, (B) GC-MS. Reaction conditions: tung nutshell (0.2 g), CuCl_2 (21.4 mg, 10.7 wt%), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (20 mL, 8/2, v/v), air (2 MPa), 190 °C, 0.5 h.

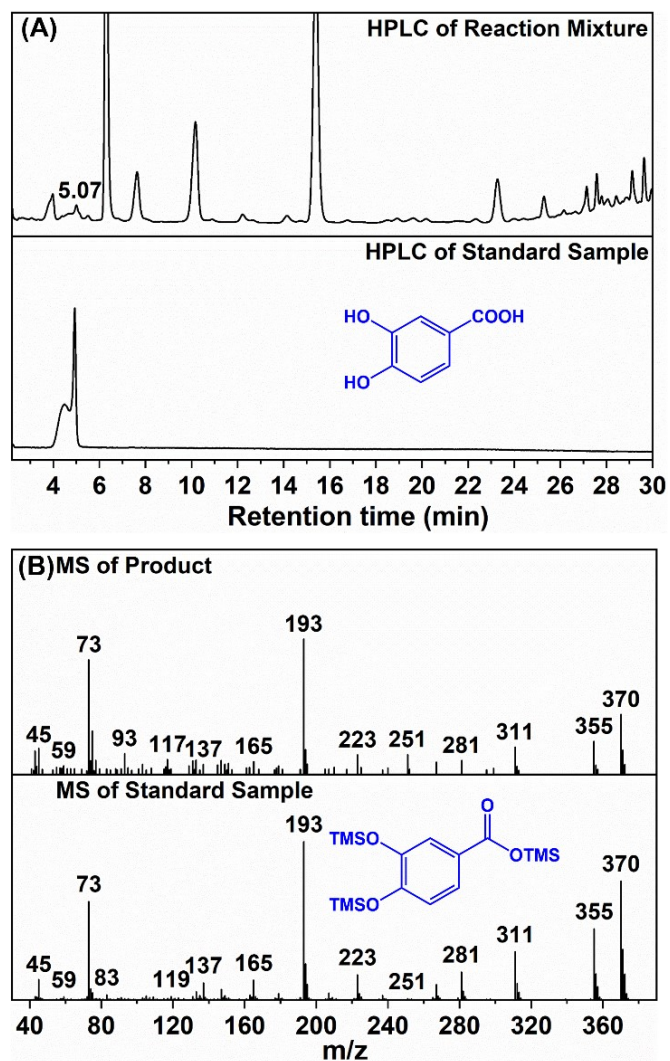


Figure S3. Oxidative depolymerization of tung nutshell lignin and the protocatechuic acid standard sample analyzed by (A) HPLC, (B) MS. Reaction conditions: tung nutshell (0.2 g), CuCl_2 (21.4 mg, 10.7 wt%), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (20 mL, 8/2, v/v), air (2 MPa), 190 °C, 0.5 h.

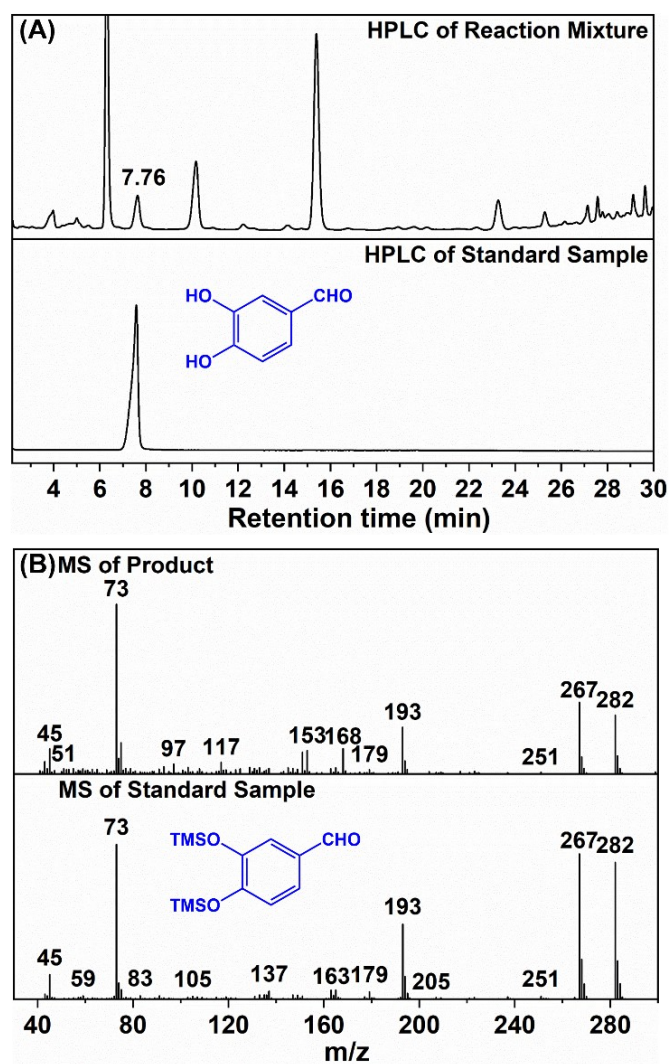


Figure S4. Oxidative depolymerization of tung nutshell lignin and protocatechuic aldehyde standard sample analyzed by (A) HPLC, (B) MS. Reaction conditions: tung nutshell (0.2 g), CuCl_2 (21.4 mg, 10.7 wt%), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (20 mL, 8/2, v/v), air (2 MPa), 190 °C, 0.5 h.

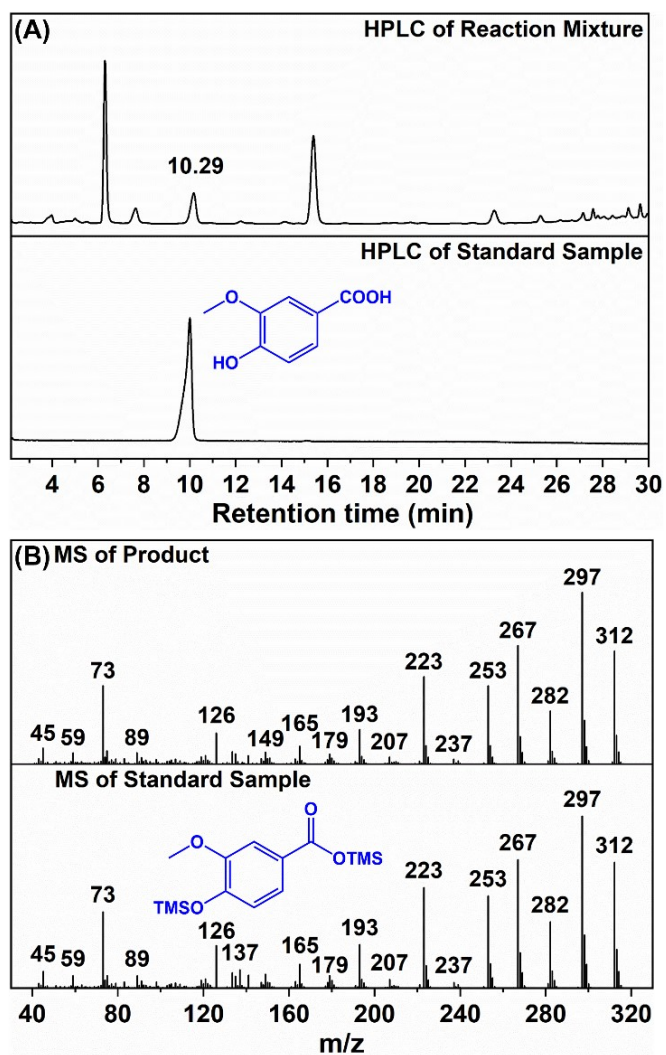


Figure S5. Oxidative depolymerization of tung nutshell lignin and the vanillic acid standard sample analyzed by (A) HPLC, (B) MS. Reaction conditions: tung nutshell (0.2 g), CuCl_2 (21.4 mg, 10.7 wt%), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (20 mL, 8/2, v/v), air (2 MPa), 190 °C, 0.5 h.

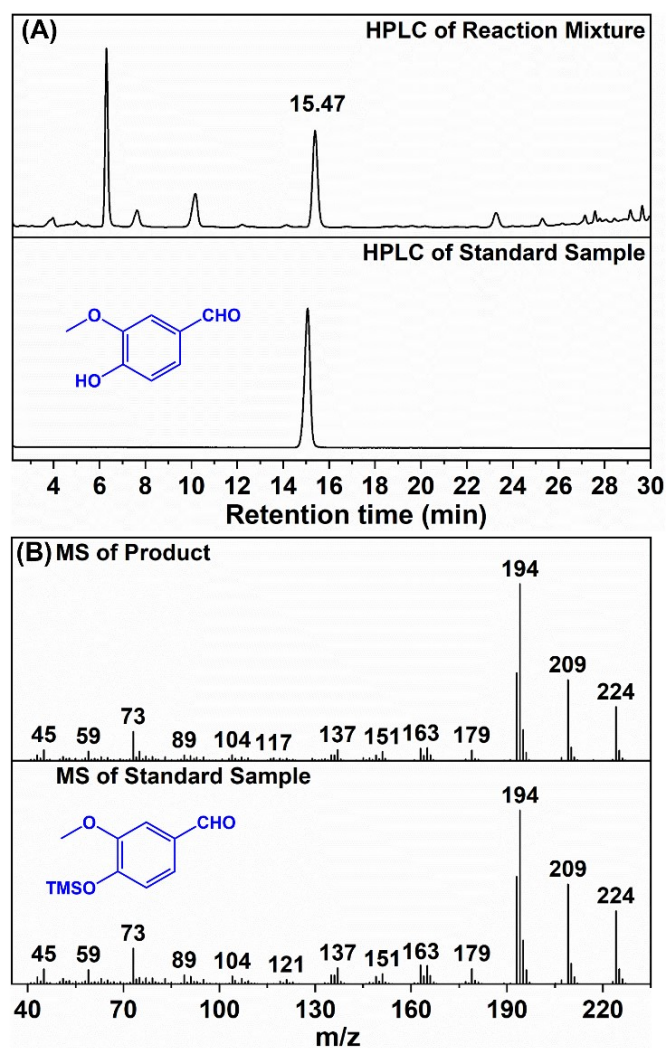


Figure S6. Oxidative depolymerization of tung nutshell lignin and the vanillin standard sample analyzed by (A) HPLC, (B) MS. Reaction conditions: tung nutshell (0.2 g), CuCl_2 (21.4 mg, 10.7 wt%), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (20 mL, 8/2, v/v), air (2 MPa), 190 °C, 0.5 h.

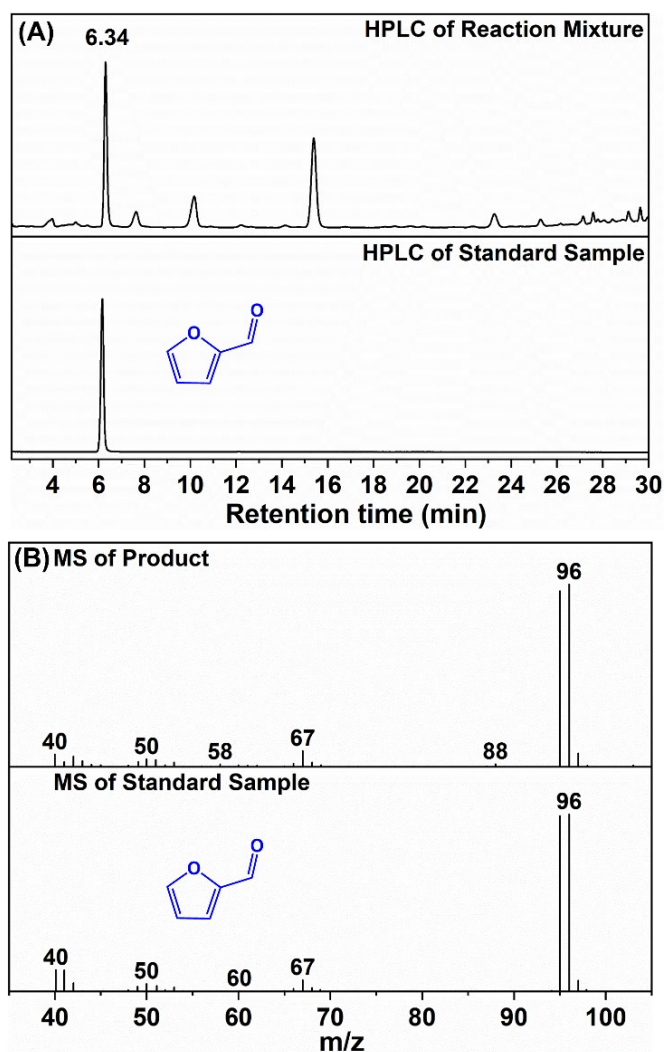


Figure S7. Oxidative depolymerization of tung nutshell lignin and furfural standard sample analyzed by (A) HPLC, (B) MS. Reaction conditions: tung nutshell (0.2 g), CuCl_2 (21.4 mg, 10.7 wt%), $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (20 mL, 8/2, v/v), air (2 MPa), 190 °C, 0.5 h. Note: for the MS result, the furfural product was detected when the reaction was conducted at the 1,4-dioxane solvent for 4 h due to a higher yield.

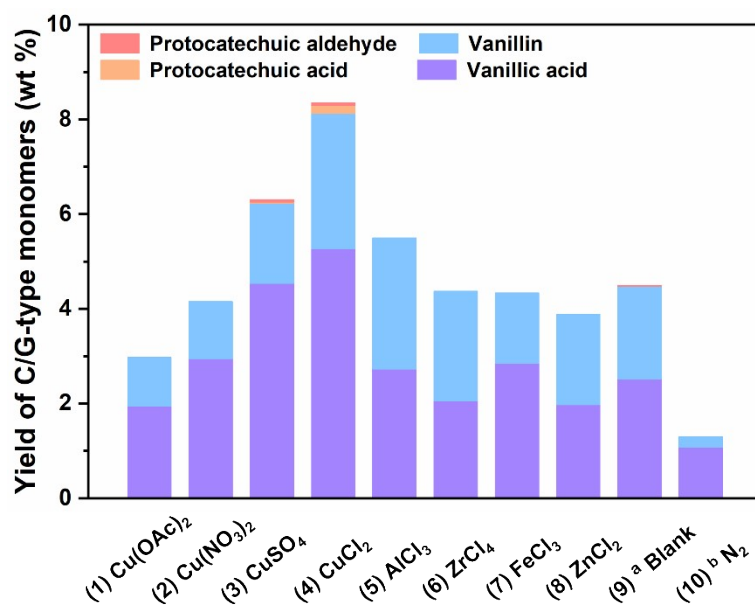


Figure S8. Yields of lignin-derived monomers from Tung nutshell oxidation depolymerization catalyzed by different transition-metal-based salts. Reaction conditions: Tung nutshell (0.2 g), Transition-metal based salts (0.1253 mmol), CH₃CN (20 mL), Air (2 MPa), 190 °C, 4 h. ^a Entry 9: no catalyst; ^b Entry 10: CuCl₂ catalyst under N₂ atmosphere; Keep the same molar metal as 0.1253 mmol for Entry 1-8. Note: For comparison with Figure 1 in the manuscripts, the yields were based on the content of Klason lignin in raw Tung nutshell powder (47 wt %).

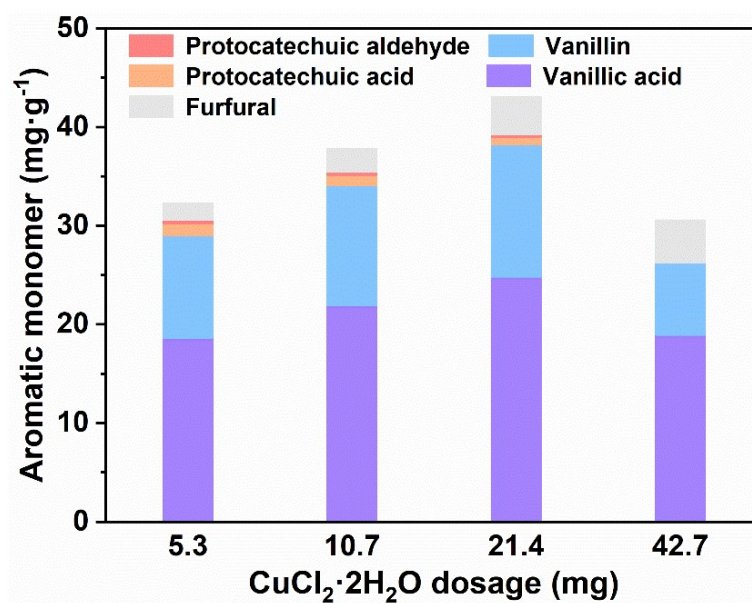
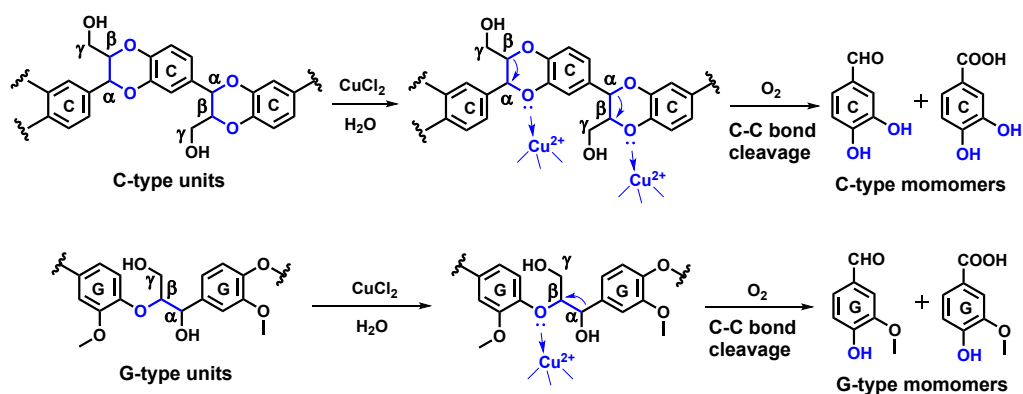


Figure S9. Yields of aromatic monomers from tung nutshell oxidation depolymerization catalyzed by various amounts of CuCl_2 catalyst. Reaction conditions: 0.2 g of tung nutshell, 20 mL of CH_3CN , 2 MPa of air, 190 °C, 4 h. Note: 5.3 mg, 10.7 mg, 21.4 mg and 42.7 mg of CuCl_2 catalyst were corresponding to 0.0311 mmol, 0.0628 mmol, 0.1255 mmol, and 0.2504 mmol, respectively.

Table S3. The summary of state-of-the-art results of C-lignin valorization and this work.

Entry	Feedstock	Process	Catalyst	Conditions	Product (Yield)	Reference
1	vanilla seeds	<i>Catalytic Hydrogenolysis</i>	Ni/C	H ₂ , CH ₃ OH, 250 °C, 3 h	Propylcatechol (6 %)	4
2	Vanilla seeds	<i>Catalytic Hydrogenolysis</i>	Pd/C	H ₂ , CH ₃ OH, 200 °C, 4 h	Propanolcatechol (79 %)	8
3	castor seeds	<i>Catalytic Hydrogenolysis</i>	Pd/C	H ₂ , CH ₃ OH, 200 °C, 4 h	Propanolcatechol (81 %)	9
4	Jatropha seeds	<i>Catalytic Hydrogenolysis</i>	Pd/C	H ₂ , CH ₃ OH, 230 °C, 4 h	Propanolcatechol (71 %)	10
5	castor seeds	<i>Catalytic Hydrogenolysis</i>	Pd/C	H ₂ , DES, 180 °C, 12 h	Propylcatechol (50.1 mg/g)	11
6	castor seeds	<i>Catalytic Hydrogenolysis</i>	Ru/ZnO/C	H ₂ , CH ₃ OH, 200 °C, 4 h	Propenylcatechol (51 %)	6
7	castor seeds	<i>Hydrogenolysis-Functionalization</i>	Ru/ZnO/C	Methylation-Oxidation-Cyclization	Annuloline natural products (81 %)	12
8	Chinese tallow seeds	<i>Hydrogenolysis-Isocyanation</i>	Pd/C	H ₂ , CH ₃ OH, 220 °C, 4 h	Propanolcatechol (129 mg/g)	13
9	Catechol monomer	<i>Hydrogenation-Amination-Coupling-</i>	Pd/C	H ₂ , ammonia water, 220 °C, 1 h	Phenazine (81 %)	14
10	Catechol monomer	<i>Oxidative cleavage</i>	(NH ₄) ₂ Fe(SO ₄) ₂	HCOOH, H ₂ O ₂ , 20 °C, 4 h	muconic acid (84 %)	15
11	Vanilla seeds	<i>Electrospinning</i>	/	/	carbon fiber	16
12	Tung seeds	<i>Catalytic Oxidation</i>	CuCl ₂	Air, CH ₃ CN/H ₂ O, 190 °C, 4 h	C/G-type aldehydes/acids (60.8 mg/g)	<i>This Work</i>



Scheme S2. Possible process about CuCl_2 catalytic conversion of C/G-lignin to the protocatechuic aldehyde, protocatechuic acid, vanillin, and vanillic acid.

Note: The role of CuCl_2 catalyst was cautiously discussed here. On the one hand, Metal chlorides as Lewis acid catalysts can be used to depolymerize lignin. The Lewis acid sites was conducive to reduce the dissociation energy of β -O-4 linkage, and thus promoting on the cleavage of ether bonds.¹⁷⁻²⁰ On the other hand, it was reported that Cu-based catalysts have potential in the oxidative conversion of lignin,²¹⁻²⁴ and exhibited good activity in the C-C bond oxidative cleavage, where the C_β -H bond activation probably was the rate-determining step.^{25, 26} In this work, we believed the Cu^{2+} Lewis acid sites were probably exposed by hydrolysis at the $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ co-solvent.^{27, 28} Then, the Cu^{2+} could interact with the O atom of the lignin units and furtherly weaken the C-C bond, which would contribute to cleavage of the C or G linkages and final formation of the protocatechuic aldehyde, protocatechuic acid, vanillin, and vanillic acid.

Table S4. 2D HSQC NMR for the signal assignments in tung nutshell lignin samples.^{9, 10, 29, 30}

Feature regions	δ_C/δ_H Signal (ppm)	Characteristic Groups
Alkyl linkage structure on the side chain of aromatics ($\delta_C/\delta_H = 50-100/2.5-6.0$ ppm)	56.37/3.74	Ar-OCH ₃ group
	72.35/4.89	C _{α} -H _{α} of β -O-4 linkage (A)
	84.25/4.31, 86.66/4.13	C _{β} -H _{β} of β -O-4 linkage (A)
	60.22/3.71	C _{γ} -H _{γ} of β -O-4 linkage (A)
	87.66/5.42	C _{α} -H _{α} of β -5 linkage (B)
	53.74/3.46	C _{β} -H _{β} of β -5 linkage (B)
	63.35/3.71	C _{γ} -H _{γ} of β -5 linkage (B)
	85.69/4.65	C _{α} -H _{α} of β - β linkage (E)
	54.11/3.07	C _{β} -H _{β} of β - β linkage (E)
	71.75/3.82, 71.75/4.18	C _{γ} -H _{γ} of β - β linkage (E)
	75.67/5.24	C _{α} -H _{α} of <i>cis</i> -benzodioxane (Dc)
	77.76/4.40	C _{β} -H _{β} of <i>cis</i> -benzodioxane (Dc)
	60.64/3.38	C _{γ} -H _{γ} of <i>cis</i> -benzodioxane (Dc)
	76.21/4.86	C _{α} -H _{α} of <i>trans</i> -benzodioxane
78.76/4.09	C _{β} -H _{β} of <i>trans</i> -benzodioxane	
65.30/3.44	C _{γ} -H _{γ} of <i>trans</i> -benzodioxane	
Characteristics of aromatics structure ($\delta_C/\delta_H = 100-135/6.0-8.0$ ppm)	110.99/6.92	C ₂ -H ₂ of G unit
	115.21/6.76	C ₅ -H ₅ of G unit
	119.48/6.59	C ₆ -H ₆ of G unit
	117.33/6.97	C ₂ -H ₂ , C ₅ -H ₅ , or C ₆ -H ₆ of C unit
	116.02/6.77	
120.79/6.95		

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