Electronic Supplementary Information for

Disassembling Catechyl and Guaiacyl/Syringyl Lignins Coexisted in Euphorbiaceae Seed Coats

Shihao Su, Shuizhong Wang, Guoyong Song*

[a]Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083, P. R. China.
Email: songg@bjfu.edu.cn

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1. Materials

The seeds of Jatropha (*Jatropha carcas L.*), Candlenut (*Aleurites moluccana (L.) Willd*) and Tung (*Vernicia fordii (Hemsl.) Airy Shaw*) grow up in Yunnan Province, China. Castor (*Ricinus communis L.*) seeds were obtained from Shandong Province, China. Pd/C (Pd content: 5 wt %) was purchased from Energy Chemical. Dioxane, methanol, ethanol and n-butyl alcohol were purchased from Sinopharm. Cellulase and xylanase are purchased from Shandong Longcote Enzyme Preparation Co., Ltd. All commercially available chemical reagents were used without further purification.

The seeds were washed with deionized water to remove dust and were then dried. After cracked with hammers or pliers, the coats can be readily peeled from kernel. The dried seed coats were ground into powder (20-60 mesh), which were then extracted with ethanol/toluene (1:2, *v*/*v*) to remove some waxes and then dried under vacuum before use.

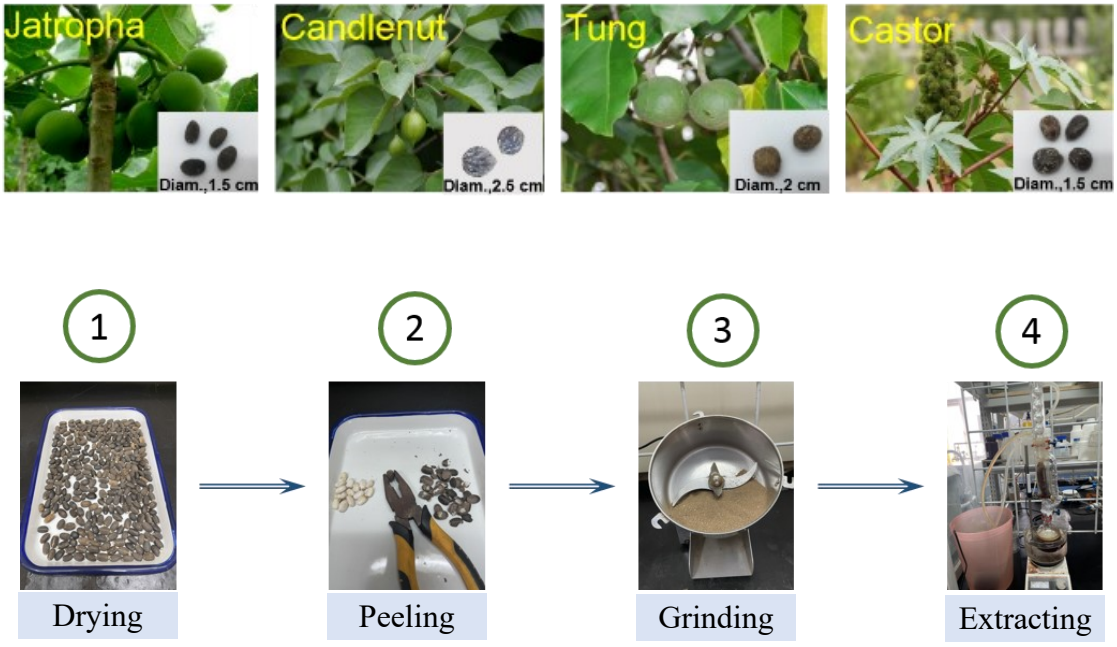


Figure S1. The pre-treatment of Euphorbiaceae plant seeds.

2. The preparation of C-lignin samples

Klason lignin (KL): Klason lignin was prepared according to NREL/TP-510-42618 protocol.[40, 41] The power of Jatropha seed coats (20~60 mesh, 2 g) was treated with 12 M sulfuric acid (20 mL) at 30 ºC for 1 h, to which deionized water (560 mL) was added. After further heating at 120 ºC for 1 h, the mixture was filtered through a filter crucible (filter diameter 4-7 um). The solid phase was obtained as Klason lignin (900 mg).

Enzyme lignin (EL): The ball-milled Jatropha seed coats (300 mesh, 10 g) was treated with cellulase (200000 μ/g, 750 mg) and xylanase (290000 μ/g, 750 mg) in a citrate buffer (200 mL, pH = 4.8) at 50 °C for 48 h. After enzymatic hydrolysis, the solid residue was collected by centrifugation, which was treated with cellulase and xylanase again. The insoluble solid was collected, washed with deionized water, and freeze-drying to afford **EL** (7.8 g).

Enzymatic mild acidolysis lignin (EMAL): The suspension of enzyme lignin (5 g) in an acidic dioxane/H_2O mixture (85:15 *v*/*v*, 500 mL, [HCl] = 4 mM) was refluxed under nitrogen for 4 h. After filtration, the soluble fraction was neutralized with $NaHCO_3$, followed by evaporation to afford a thick solution. Upon the treatment of HCl aqueous solution (pH = 2.0), a precipitate was formed, which was allowed to equilibrate at 4 °C overnight. The **EMAL** sample was collected by centrifugation, washing with HCl aqueous solution (pH = 2.0), and freeze-drying (515 mg).

Cellulolytic enzyme lignin (CEL): The suspension of enzyme lignin (5 g) in dioxane/H_2O (96:4 *v*/*v*, 500 mL) was refluxed under nitrogen for 24 h. After filtration, the soluble fraction was concentrated and acidized to pH = 2.0 (adjusted by HCl aqueous solution). Collecting the resulted precipitate, and followed freeze-drying afforded **CEL** (400 mg).

Alkali lignin (AL): The ball-milled Jatropha seed coats (300 mesh, 5 g), NaOH (0.8 g), anthraquinone (0.025 g) and water (30 mL) was placed into reactor and heated at 160 ºC for 2 h. The black liquid was collected by filtration and adjusted the acidity of solution (pH = 2) to generate a precipitate, which was allowed to equilibrate at 4 ºC overnight. The **AL** was obtained by centrifugation, washing with HCl aqueous solution (pH = 2.0), and freeze-drying (850 mg).

Milled wood lignin (MWL): The suspension of ball-milled Jatropha seed coats (300 mesh, 10 g) in dioxane/water (96:4, *v*/*v*, 100 mL) was stirred under N_2 at room temperature for 48 h. The soluble fraction was collected by filtration and

the solid residue was treated with dioxane/water again. The combined soluble fraction was concentrated and acidified to pH = 2.0 with 6 M HCl solution. The formed precipitate was collected by centrifugation and freeze-drying to give **MWL** (950 mg).

Ethanol organosolv lignin (EOL): The Jatropha seed coats (20~60 mesh, 10 g) was treated with EtOH/H_2O (65/35, *v*/*v*, 100 mL) in the presence of H_2SO_4 (12 mM) at 170 °C for 1 h. The soluble fraction was obtained by filtration and concentrated to afford a thick solution, which was acidified to pH = 2.0 with 6 M HCl solution. The formed precipitate was collected by centrifugation and freeze-drying to give **EOL** (700 mg).

Butanol organosolv lignin (BL): BL (1.05 g) was prepared by following the analogous procedure of **EOL** by using ^{n}BuOH instead of EtOH starting from Jatropha seed coats (20~60 mesh, 10 g).

Dioxane lignin (DL): Concentrated HCl (150 μL) was added to the suspension of seed coats (20~60 mesh, 10 g) in dioxane (100 mL), where [HCl] was estimated as 18 mmol L^{-1}. The mixture was heated at 85 °C under N_2 for 3 h, and solid residue was removed by centrifugation. The supernatant liquid was concentrated through evaporation to afford a thick solution, which was acidified to pH = 2.0 with 6 M HCl solution. The formed precipitate was collected by centrifugation and freeze-drying to give **DL** (1 g).

3. Characterizations

HSQC NMR analysis

2D HSQC NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer by using lignin samples (50 mg) dissolved in DMSO-d_6 (0.5 mL). The central solvent peak at δ_C/δ_H 39.5/2.49 ppm was used as an internal reference. HSQC cross-peaks assigned by comparison with C-lignin dimer and previous literatures' reports.[1-3] A semi-quantitative analysis of the HSQC cross-peak intensities were performed in the side-chain region, and volume integration of peaks of benzodioxane (I_α), resinol (II_α) and cinnamyl alcohol end-unit (IV, IV_α) gave the corresponding ratios.

Quantitative ^{13}C NMR analysis

Quantitative ^{13}C NMR spectra were acquired on a Bruker Avance 600 MHz spectrometer under decoupled mode with a relaxation time as 10 second. The sample was prepared as followed: an isolated C-lignin sample (100 mg), 1,3,5-trioxane (internal standard) and $Cr(acac)_3$ (relaxation reagent, 2 mg) were dissolved in DMSO-d_6 (0.5 mL).

GPC analysis

Lignin sample (10 mg) was treated with a 1:1 mixture of acetic anhydride/pyridine (1.0 mL) at room temperature under N_2 for 72 h. After removing the volatiles under vacuum, the acetylated lignin was dissolved in THF (*ca*. 2 mg mL^{-1}) and filtered through a PTFE filter (0.45 μm). The average molecular weight was determined on Shimadzu LC-20AD 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^{-1}). The average molecular weight was calibrated with polystyrene standards.

Thioacidolysis analysis

Thioacidolysis analysis was performed according to previous reports.[1, 4-6] In brief, 30 mg samples (seed coats or isolated lignin samples) were treated with BF_3-etherate (0.2 M, 5 mL) in a dioxane/ethanethiol (8.75:1, *v*/*v*) at 100 °C for 4 h. The reaction mixture was extracted by dichloromethane. After the removal of all volatiles of the organic phase under vacuum, the resulted residue was

dissolved in anhydrous THF, which was treated with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) at 65 °C for 1 h under N_2 before GC-MS analysis. The ratios of C/(G+S) were calculated based on the integrations of doublets in the GC-MS profile corresponding to α,β,γ-trithioethylpropyl-substituted catechol, guaiacol and syringol. All the analyses were repeated at least twice.

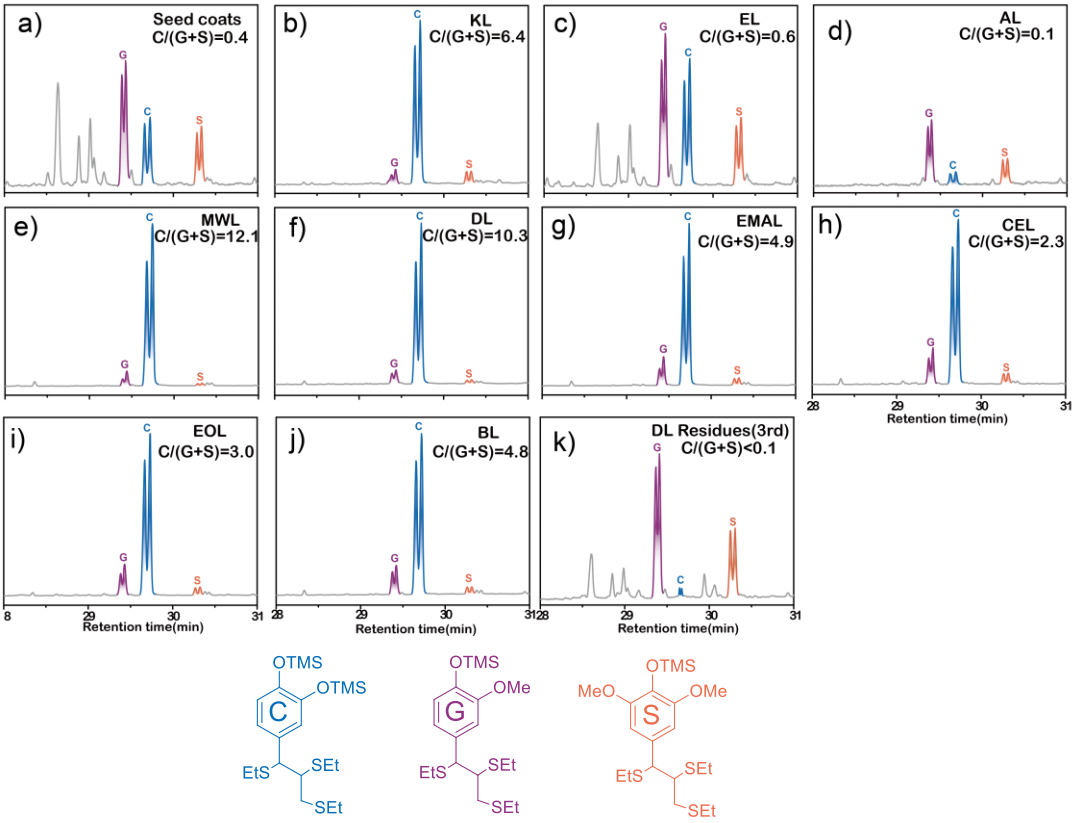


Figure S2. GC chromatograms of thioacidolysis products from Jatropha seed coats (a) **seed coats sawdust**, (b) **KL**, (c) **EL**, (d) **AL**, (e) **MWL**, (f) **DL**, (g) **EMAL**, (h) **CEL**, (i) **EOL**, (j) **BL** and (k) **DL solid residue** after three-time dioxane (36 mM HCl) extraction.

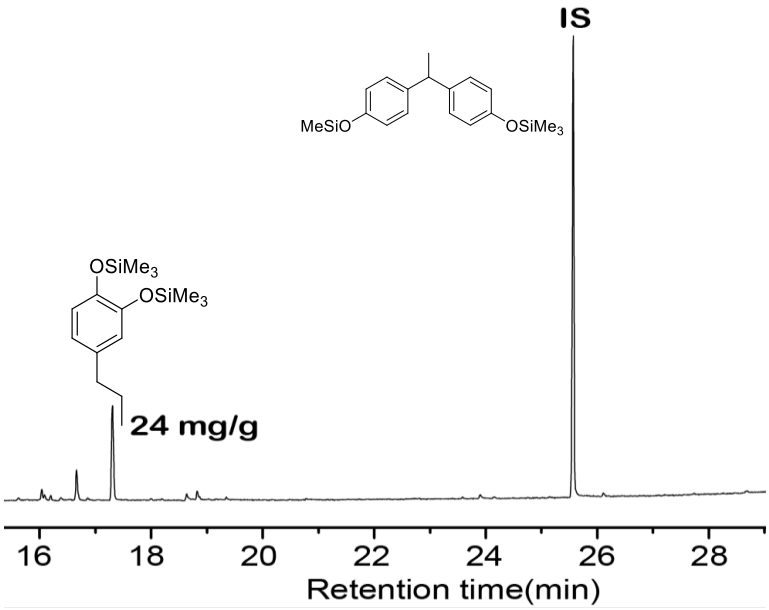


Figure S3. GC spectrum of monomeric products from thioacidolysis and subsequent desulfurization over Raney nickel.

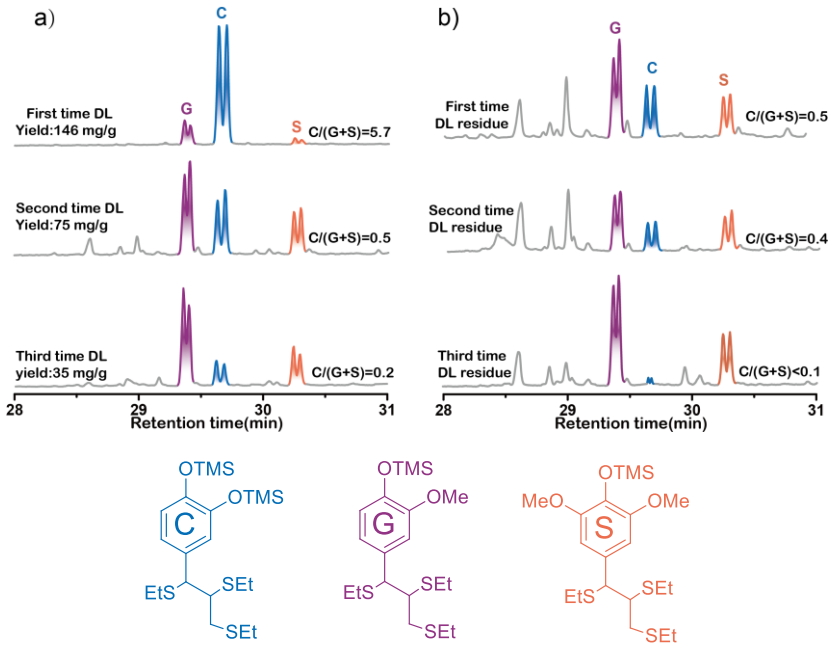


Figure S4. (a) The yield of lignin and thioacidolysis analysis of sequent extracted lignin samples. (b) Thioacidolysis analysis of solid residue after extraction. Reaction condition: Jatropha seed coats (1.0 g), 1,4-dioxane (20 mL), 85 °C, HCl (36 mM), N_2, 3 h.

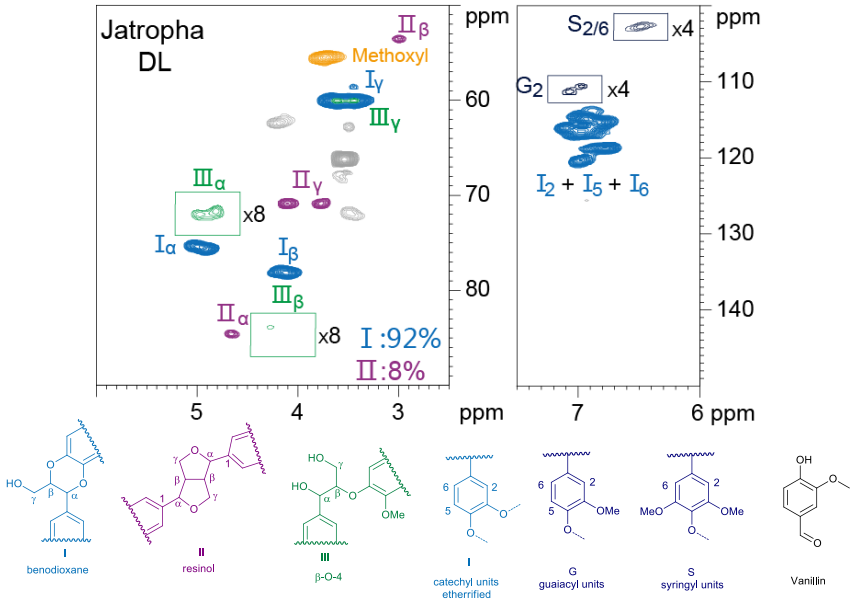


Figure S5. Expanded aliphatic side-chain and aromatic regions regions of 2D NMR spectra of **DL** isolated from Jatropha seed coats, box with x4 or x8 indicates regions that were scaled fourfold or eightfold.

Table S1. NMR data for the signal assignments in jatropha lignin samples and lignin oily products in DMSO-d_6.

Lable	δ_C/δ_H (ppm)	Assignment
I_α	75.4/4.83	C_α-H_α in benzodioxane substructures (I)
I_β	77.9/4.06	C_β-H_β in benzodioxane substructures (I)
I_γ	59.9/3.34-3.55	C_γ-H_γ in benzodioxane substructures (I)
II_α	84.5/4.62	C_α-H_α in β-β resinol substructures (II)
II_β	53.4/3.04	C_β-H_β in β-β resinol substructures (II)
II_γ	70.7/3.74-4.09	C_γ-H_γ in β-β resinol substructures (II)
III_α	71.6/4.85	C_α-H_α in β-O-4 substructures (III)
III_β	86.6/4.09	C_β-H_β in β-O-4 substructures (III)
III_γ	59.5/3.1-3.79	C_γ-H_γ in β-O-4 substructures (III)
IV_α	127.9/6.42	C_α-H_α in cinnamyl alcohol end-units (IV)
IV_β	128.7/6.20	C_β-H_β in cinnamyl alcohol end-units (IV)
IV_γ	61.4/4.10	C_γ-H_γ in cinnamyl alcohol end-units (IV)
G_2	110.7/6.92	C_2-H_2 in guaiacyl units (G)
G_5	114.5/6.68	C_5-H_5 in guaiacyl units (G)
G_6	119.0/6.77	C_6-H_6 in guaiacyl units (G)
I_2,I_5,I_6	115.8/6.77, 116.5/6.95, 118.6/6.70, 120.4/6.95	C_2-H_2, C_5-H_5, C_6-H_6, in catechol units (I)

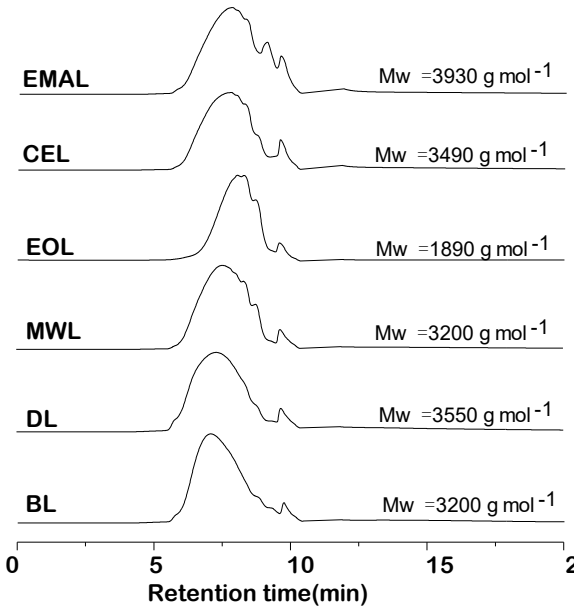


Figure S6. Molecular weight distribution of lignin samples isolated from jatropha seed coats.

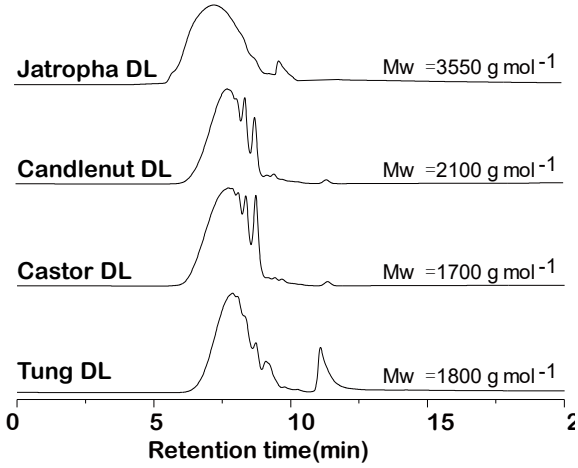
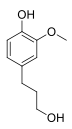
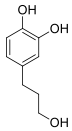
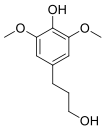


Figure S7. Molecular weight distribution of lignin samples isolated from different seed coats.

4. Catalytic hydrogenolysis

In a typical reaction, C-lignin sample (50 mg), Pd/C (10 mg) and methanol (10 mL) were charged in a 50 mL Parr autoclave with a magnetic stirring. The reactor was purged with nitrogen, and then was pressured to H_2 (3 MPa) at room temperature. After reaction was carried at 230 ºC for 4 h, the autoclave was cooled with water and depressurized carefully. The soluble fraction was obtained by filtration and evaporated under vacuum. The residue was dissolved in anhydrous THF (5 mL) containing an external standard (tetradecane), which was then treated with BSTFA at 65 °C for 1 h under N_2. The resulted mixture was analyzed on GC-MS (Shimadzu QP2010SE equipped with an HP-5 MS column) and GC (Shimadu 2010 equipped with an HP-5 column). Catechol monomers were identified and quantified by comparison with authentic samples from independent synthesis.[7]

Table S2. Pd/C catalyzed depolymerizaion of various samples.

Entry	Sample	Monomer yield (mg/g)			C/(G+S) monomers molar ratio
					
1	**Sawdust**	0.6	1.9	0.4	2.1
2	**EL**	1.9	3.2	0.6	1.4
3	**DL Residue**	5.2	0.6	1.3	0.1
4	**DL**	0.8	35.6	0.4	31.2
5	**BL**	1.2	32.1	0.6	20.3
6	**EOL**	1.3	30.2	0.7	19.6

Reaction conditions: lignin sample or sawdust (50 mg), Pd/C (10 mg), MeOH (10 mL), H_2 (3 MPa), 230 ºC, 4 h.

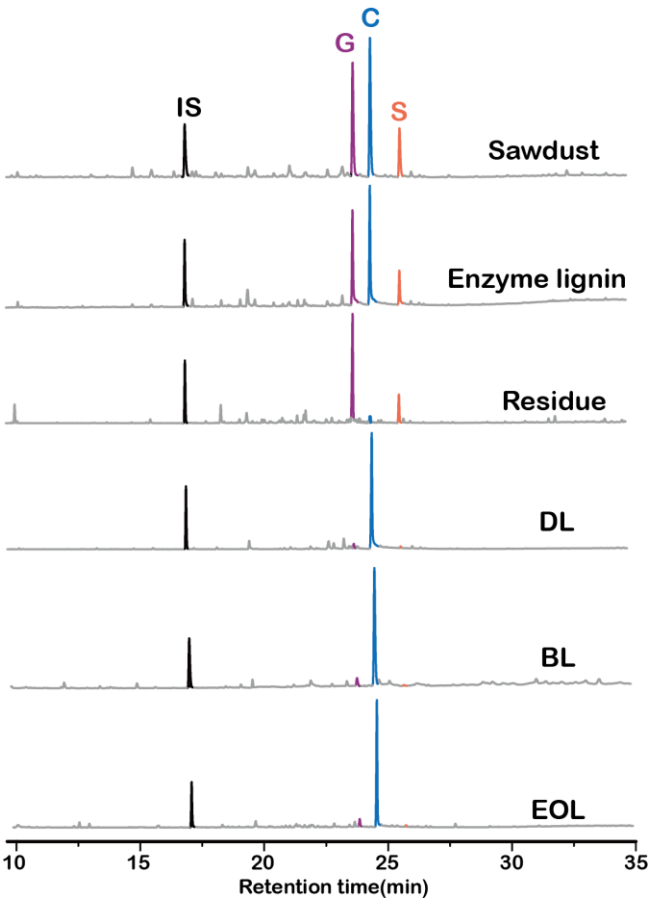
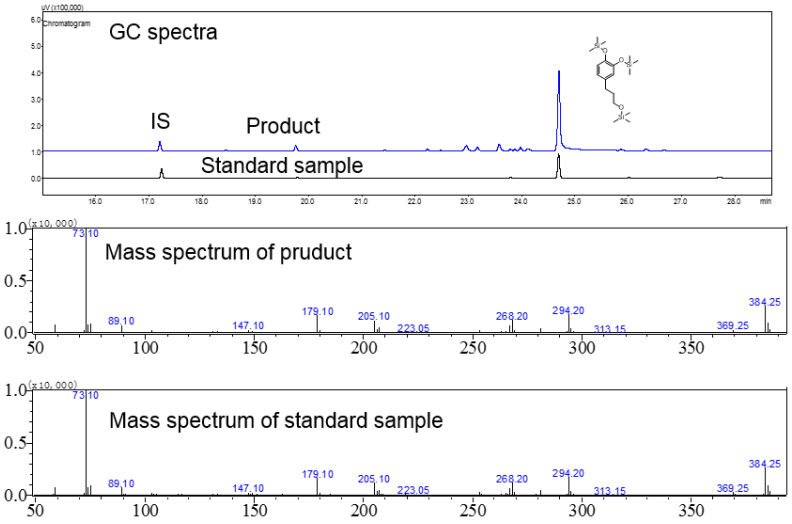


Figure S8. Gas chromatograms of monomers from Pd/C-catalysed hydrogenolysis of various lignin samples.

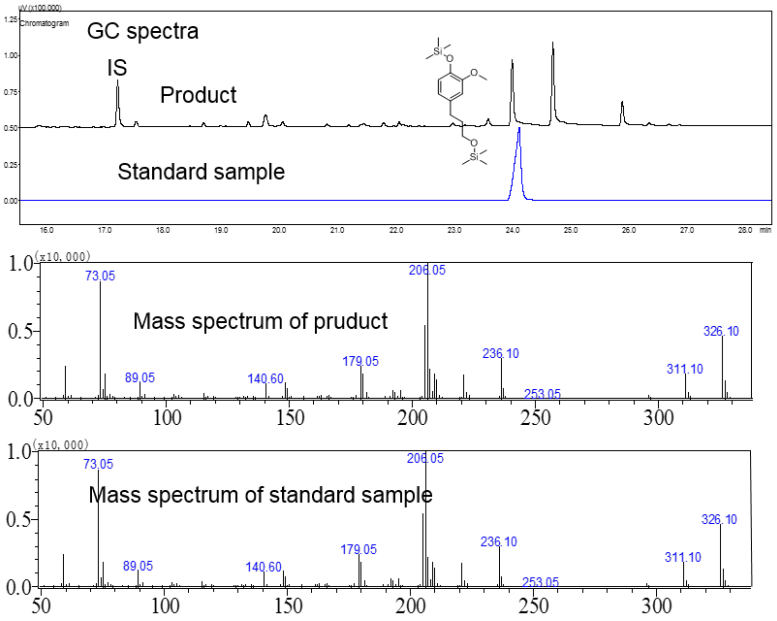
5. Authentic samples

All authentic monomers were synthesized independently and characterized by NMR spectra.

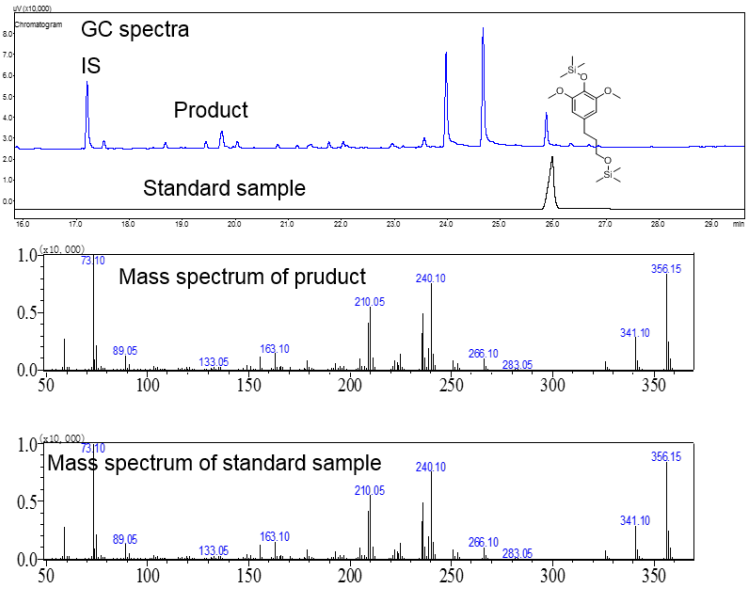
4-(3-hydroxypropyl)-benzene-1,2-diol



4-(3-hydroxypropyl)-2-methoxyphenol



4-(3-hydroxypropyl)-2,6-dimethoxyphenol



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