Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Two-step conversion of Kraft lignin to nylon precursors under mild conditions

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1. Experimental

1.1 Chemicals and materials

Kraft lignin (sulfur content 2.1 wt%), guaiacol, 1,2-dimethoxybenzene, 4-methylguaiacol, 4-propylguaiacol, vanillin, isoeugenol, 4-hydroxy-3-methoxyphenylacetone, phenanthrene, 4-methylbenzyl alcohol, 2-phenoxy-1-phenylethanol (PPE), 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt and 10 wt% Pd loaded carbon were purchased from Sigma-Aldrich. Nickel nitrate hexahydrate, sodium hydroxide, potassium hydroxide, dioxane, dimethyl sulfoxide (DMSO), and acetophenone were obtained from Fisher Scientific. Activated carbon and 2-methoxy-4-vinylphenol were obtained from Alfa-Aesar. Ru (5 wt%) loaded on carbon was purchased from Engelhard. Ruthenium (III) nitrosyl nitrate solution (1.5% Ru) was obtained from Strem Chemicals. Guaiacylglycerol-beta-guaiacyl ether (GGE) was obtained from TCI. Chloroform-d and DMSO-d_6 were purchased from Cambridge Isotope Laboratories. Dihydroconiferyl alcohol was provided from Ark Pharm.

1.2 Synthesis of 1% Ru/Al_2O_3

Ruthenium (III) nitrosyl nitrate solution (1.5 wt% Ru, 0.67 mL, 0.099 mmol Ru) was diluted in 30 mL water. Al_2O_3 (0.99 g, 9.7 mmol) was dispersed in 30 mL water and ultrasonicated for 10 min. Ruthenium (III) nitrosyl nitrate solution was added into Al_2O_3 suspension dropwise with continuous stirring. The mixture was kept at 80 °C with stirring overnight to evaporate the water. The solid was dried in the oven for another 10 h, followed by calcination in air at 350 °C for 2h. Before use, the catalyst was reduced in H_2 at 350 °C for 2h.

1.3 Synthesis of 5% Ni/C

Nickel nitrate hexahydrate (261 mg, 1.4 mmol) was dissolved in 30 mL ethanol. Activated carbon (0.95 g) was dispersed in 30 mL ethanol and ultrasonicated for 10 min. Nickel nitrate solution was added into carbon suspension drop by drop with continuous stirring. The mixture was kept at 65 °C with stirring overnight to evaporate the ethanol. The solid was dried in the oven for another 10 h, followed by calcination in N_2 at 350 °C for 2h. Before use, the catalyst was reduced in H_2 at 350 °C for 2h.

1.4 Depolymerization of lignin

The Kraft lignin was derived from Norway spruce. To remove the water-soluble component, 1 g lignin was dispersed in 200 mL water and stirred at room temperature for 4 h. The mixture was then filtered and dried overnight. The depolymerization reaction was conducted in a 100 mL Parr autoclave reactor. Typically, 100 mg lignin and 25 mL NaOH solution were placed in the reactor. The reactor was sealed and purged 3 times with N_2 to remove air. During the reaction, the reaction mixture was stirred at 200 °C for 8 h. After cooling down to room temperature, the mixture was centrifuged and 3 mL of the supernatant was then extracted with ethyl acetate (3 × 1 mL). The solid was washed using a fritted glass funnel (2.5 μm pores) and recovered for weighting.

For the product analysis, 3 mL of supernatant was extracted with ethyl acetate (3 × 1 mL). The ethyl acetate solution was then tested by GC-MS (Agilent 7890A, 5975C with HP-5MS column) with phenanthrene as the internal standard. The GC column was ramped from 60 °C to 200 °C at a rate of 5 °C min^{-1}, then ramped to 280 °C at a rate of 20 °C min^{-1}, and maintained at 280 °C for another 5 min. The products were determined by comparison to the GC retention times and the MS spectra of reference samples. The *concentrations of products* were calculated based on the calibration curves obtained from at least 6 different concentrations of the standard compounds with phenanthrene as the internal standard (Fig. S1). The *yield of certain monomer* was calculated by the mass of this monomer from GC-MS divided the mass of input lignin (100 mg) times 100 %. The *selectivity of certain monomer* was calculated by the mass of this monomer divided by the mass of the total monomers times 100 %. To recover the lignin after reaction, the solution was neutralized with 1 M HCl to pH 7, and then the precipitated lignin was separated by centrifugation and dried in the oven.

1.5 Reactions of lignin model compounds

The reactions of lignin model compounds followed similar procedures as the lignin depolymerization. The yield of certain product was calculated by the amount (mol) of the product (from GC-MS) divided by the amount (mol) of starting materials times 100 %.

1.6 Conversion of lignin-derived monomers to KA oil

To produce KA oil from lignin-derived monomers, a larger amount of lignin (1.0 g) was used (25 mL 100 mM NaOH) and the depolymerization reaction time was set as 16 h. After the reaction the mixture was centrifuged and the supernatant was then extracted with ethyl acetate (3 × 10 mL) and tested by GC. The solid was transferred to a Büchner funnel (with filter paper of 2.5 μm pores) washed with water and recovered for weighting. The ethyl acetate extract was then removed in a rotary evaporator, the residue was dissolved in water (94 mL) and filtered through a 0.2 μm membrane. The recovered aqueous solution was 94 mL. Then, 25 mL of the above solution and 20 mg Ru/C catalyst was placed in an autoclave reactor (Mettler Toledo EasyMax 102). The reactor was purged 3 times with H_2 and then the H_2 was kept at ambient pressure. The reactor was heated to 150 °C and stirred at 800 rpm for 8 h.

After the reaction, a 3 mL aliquot of the reaction mixture was extracted with ethyl acetate (3 × 1 mL) and analyzed by GC-MS using 4-methylbenzyl alcohol as the internal standard. The GC column temperature was as ramped from 60 to 150 °C at 5 °C min^{-1}, and then ramped to 280 °C at 20 °C min^{-1} holding for 1 min. The conversion of the substrates was calculated from the moles of the products divided by the moles of the substrates times 100 %. The selectivity to certain product was calculated by the moles this product divided by the total amount of all the products times 100 %. Catalyst recyclability tests were carried out for 8 h at 150 °C under 1 bar H_2 using 0.8 mmol commercial guaiacol with a Ru/guaiacol ratio of 1/20 (wt/wt).

1.7 Analysis of Lignin by solution NMR

The ^{1}H NMR, ^{13}C NMR, HSQC, and DOSY analyses were performed in a Bruker Avance III Spectrometer (600 MHz). For raw Kraft lignin, 200 mg sample was dissolved in 1 mL DMSO-d_6 with the addition of 10 mg 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt as the internal reference. To precipitate the lignin sample after the reaction, 1 M HCl was added to the solution until pH 7. The solid was then filtered, dried, and dissolved in 1 mL DMSO-d_6 with the addition of 10 mg 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt as the internal reference. For ^{1}H NMR, the number of scans (NS) was 16 and the recording time was 80 s. For ^{13}C NMR, the NS was 4096 and the recording time was 4.5 h. For HSQC NMR, the NS was 32 and the recording time was 5 h. For DOSY NMR, the NS was 64 and the recording time was 6.4 h.

1.8 Quadrupole time of flight mass spectrometry (Q-TOF MS)

The measurements were carried out in an Agilent Accurate-Mass Q-TOF 6540 MS/MS with positive electrospray ionization (ESI) method. For each run, 1 μL sample was injected. The m/z range from 100 to 3000 Da was recorded.

1.9 Solid-state NMR

All solid-state NMR spectra were acquired using a Bruker Avance III, 400 MHz MAS-DNP system, equipped with a 264 GHz gyrotron and a 3.2-mm low temperature MAS probe operating at 105 K. Lignin samples were impregnated with 15 mM solutions of the AMUPol biradical (Cortecnet) in water, tightly packed into 3.2-mm sapphire rotors, sealed with Teflon inserts, pre-spun on the bench at room temperature and then spun at low temperature in the NMR probe at 10 kHz. The 'on/off' DNP enhancements for the raw lignin and the extracted residue were around 5 and 10, respectively. The CPMAS spectra were acquired using a 2.5 μs ^{1}H excitation pulse and a 2 ms CP contact time. To maximize the sensitivity, the recycle delays were set to $1.3T_1$, as determined using a saturation recovery experiment, which corresponded to 1.55 s for the raw lignin and 1.69 s for the extracted residue. 128 scans were accumulated for both samples. The refocused INADEQUATE spectra were acquired using 32 t_1 increments of 33.3 μs with 2048 scans per increment; the double-quantum excitation/refocusing times of 3 ms were used with the magnitude of ^{13}C radiofrequency field set at 78 kHz.

2. Supplementary Figures

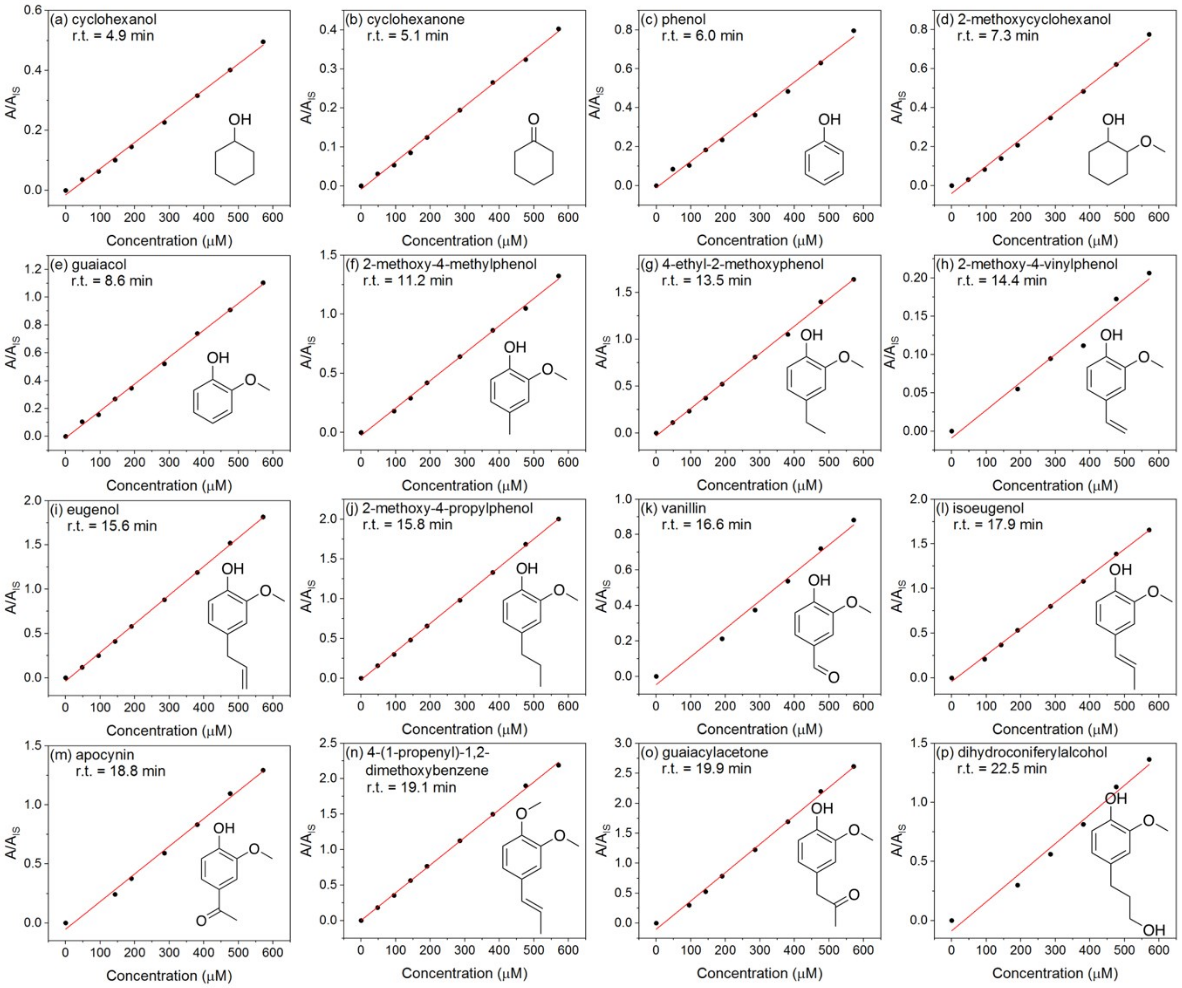

Fig. S1 Calibration curves of gas chromatogram with standard compounds (A: GC peak area of the calibrated compound, A_{IS}: GC peak area of the internal standard).

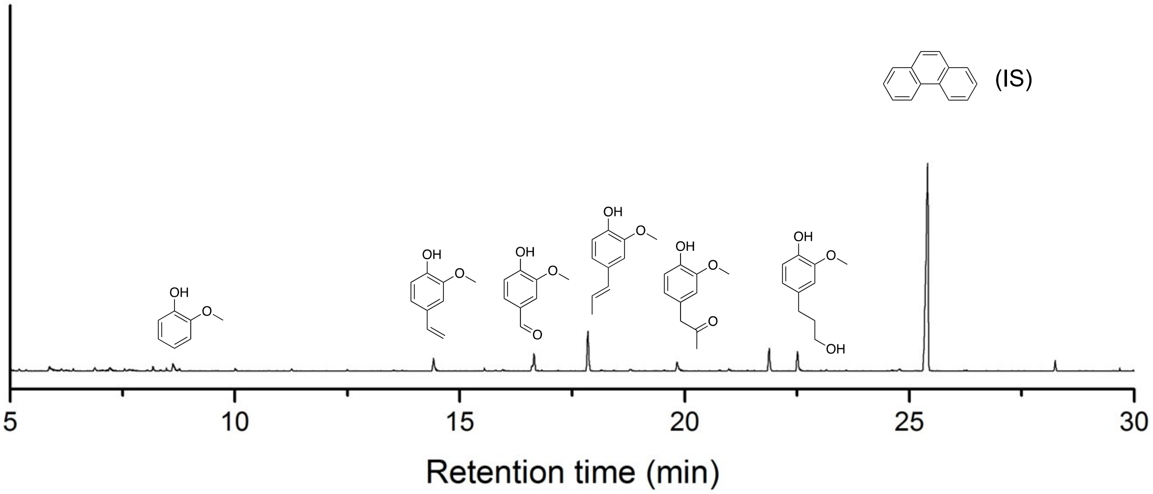

Fig. S2 Gas chromatogram of the reaction of Kraft lignin in methanol. Reaction conditions: 100 mg Kraft lignin, 25 mL methanol, 200 °C, 1 bar N_2, 8h.

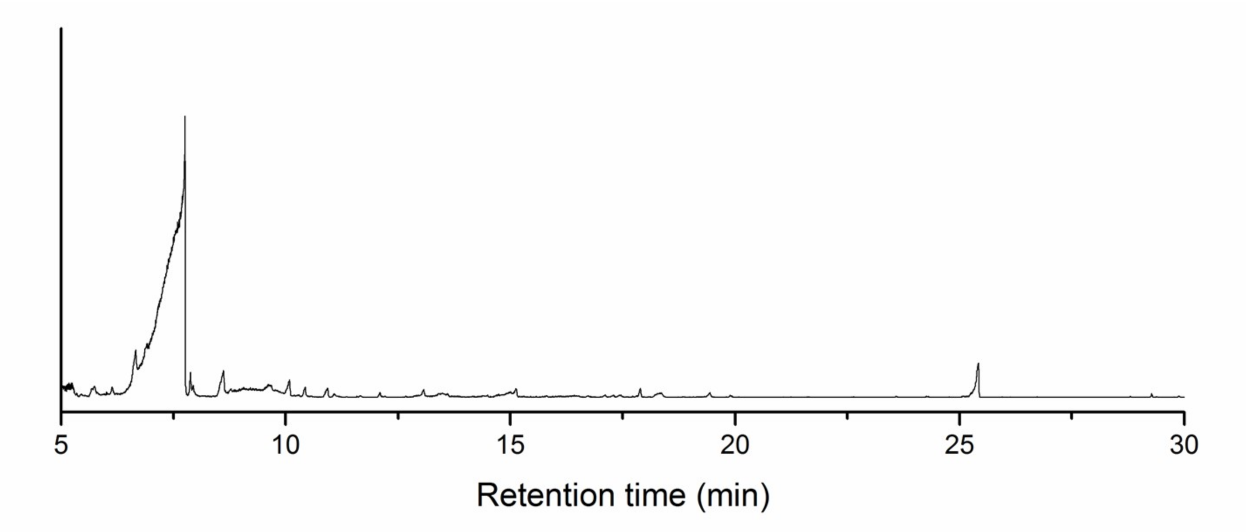

Fig. S3 Gas chromatogram of reaction of Kraft lignin in dioxane. Reaction conditions: 100 mg Kraft lignin, 25 mL dioxane, 200 °C, 1 bar N_2, 8h. The large peak at 7.5 min came from the solvent.

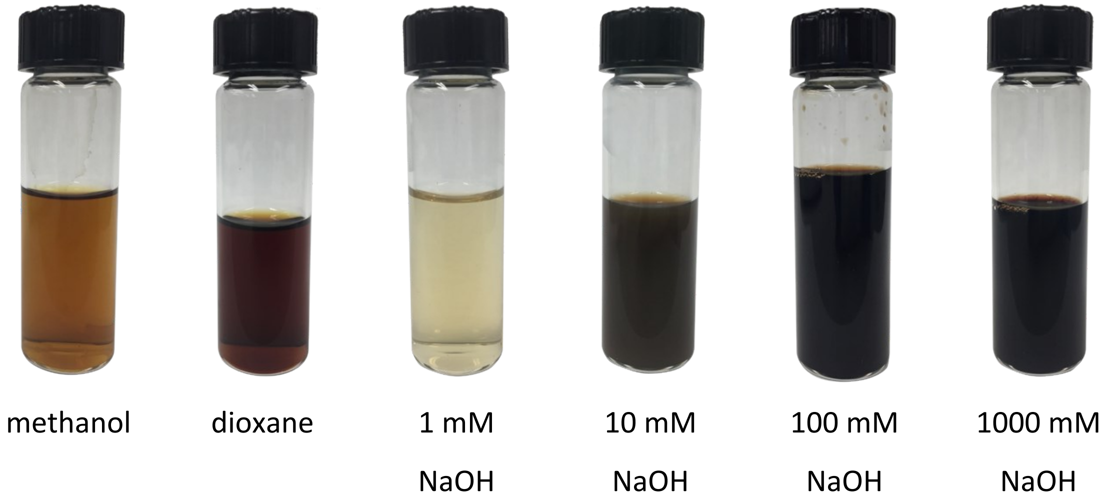

Fig. S4 Supernatants obtained after filtration from the reaction of lignin in different solvents. Reaction conditions: 100 mg Kraft lignin, 25 mL solvent/solution, 1 bar N_2, 200 °C, 8h. The color of the solution is indicative of the amount of lignin dissolved in liquid. The amounts of solid residue are given in **Table S1**.

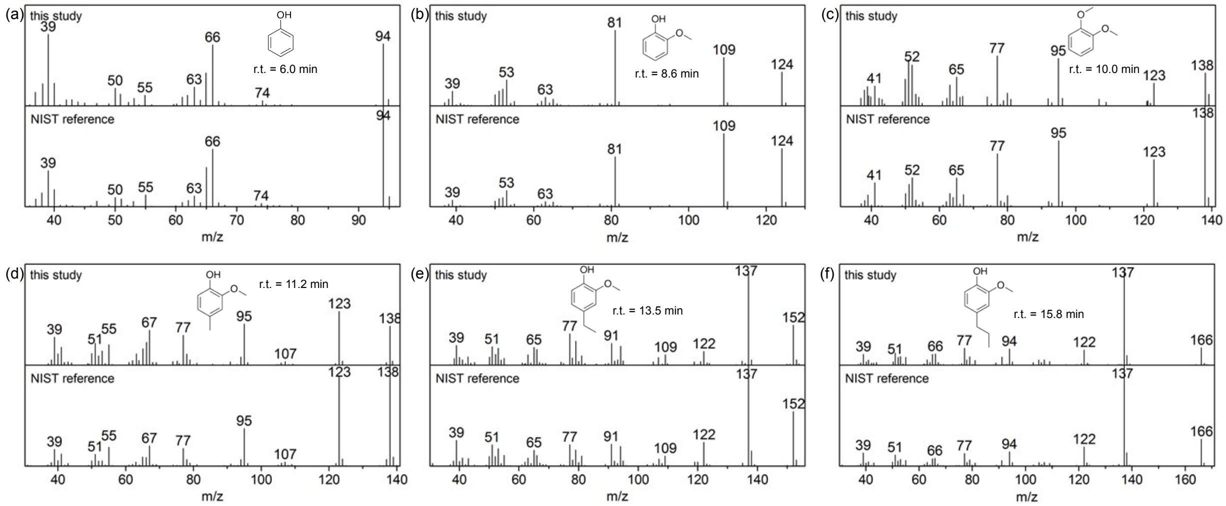

Fig. S5 Comparison of the mass spectra of compounds identified from this study and NIST database references. (a) phenol, (b) guaiacol, (c) 1,2-dimethoxybenzene, (d) 4-methylguaiacol, (e) 4-ethylguaiacol, and (f) 4-propylguaiacol.

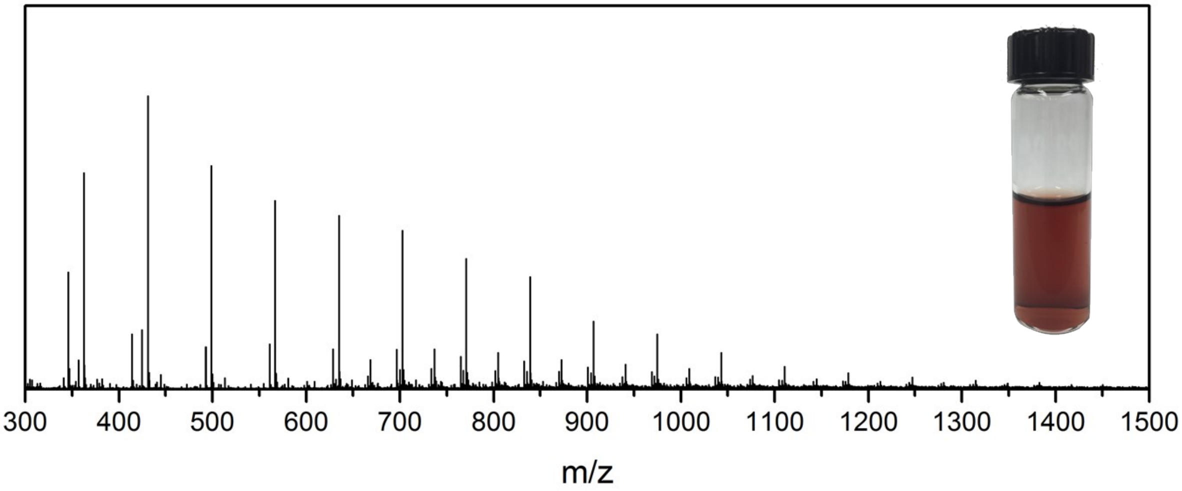

Fig. S6 Mass spectrum of solution after guaiacol reaction in 1000 mM NaOH. Reaction conditions: guaiacol 2 mM, 200 °C, 1 bar N_2, 8h.

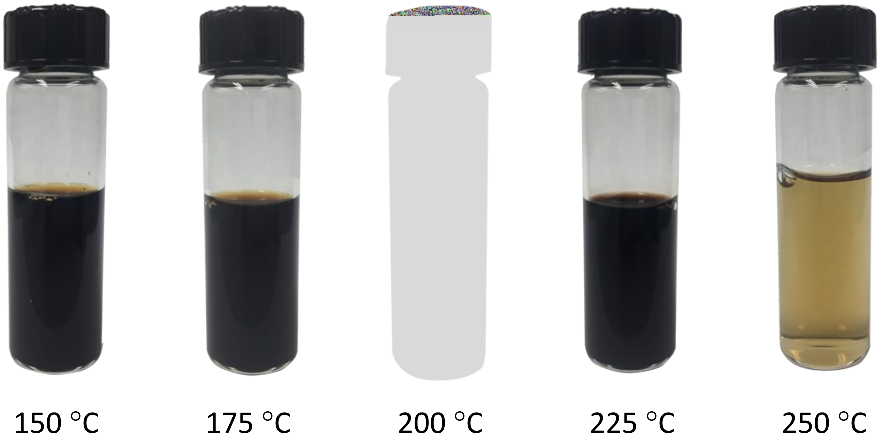

Fig. S7 Supernatants obtained after filtration from the reaction of lignin at different temperatures. Reaction conditions: 100 mg Kraft lignin, 25 mL 100 mM NaOH solution, 1 bar N_2, 8h. The amounts of solid residue are given in **Table S1**.

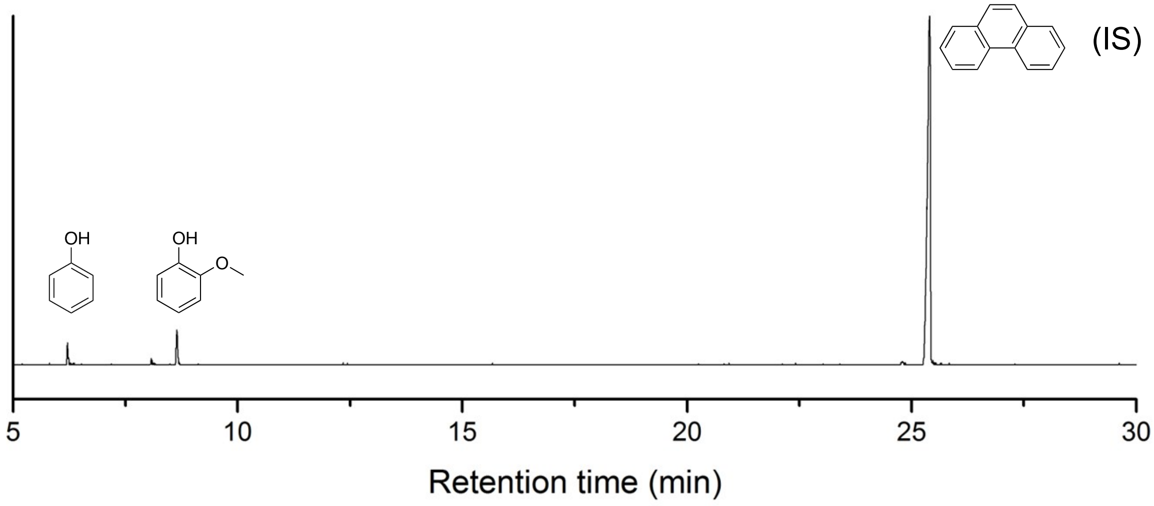

Fig. S8 Gas chromatogram of the reaction of guaiacol in dilute alkali solution at 250 °C. Reaction conditions: 0.2 mmol guaiacol, 25 mL 100 mM NaOH solution, 1 bar N_2, 8h.

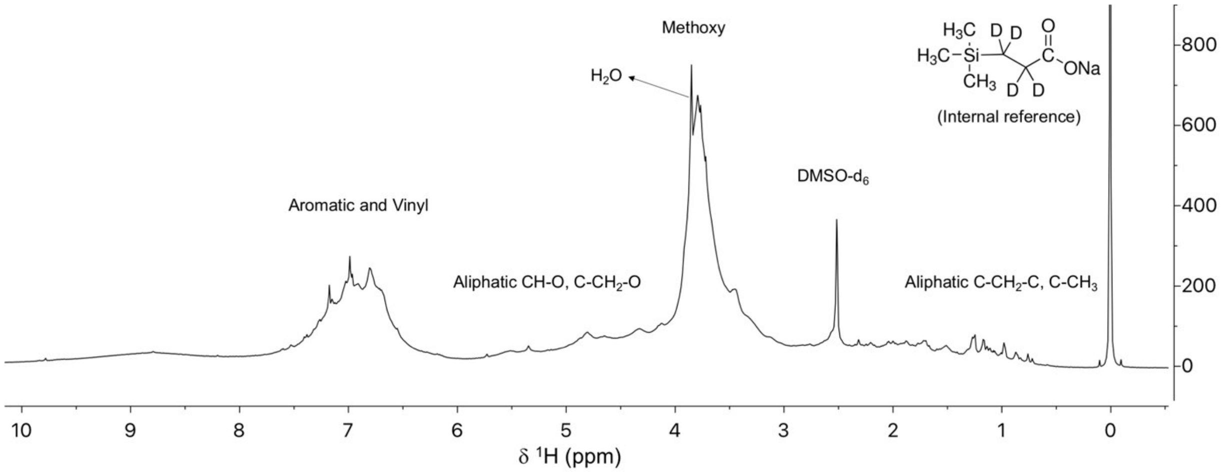

Fig. S9 ^{1}H NMR spectrum of Kraft lignin dissolved in DMSO-*d*$_6$. 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt was added as the internal reference.

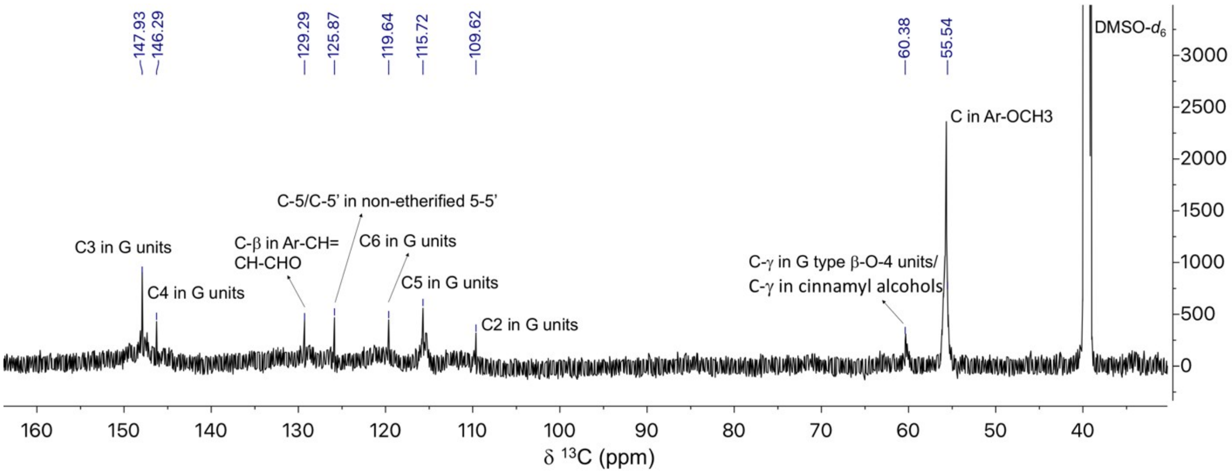

Fig. S10 ^{13}C NMR spectrum of Kraft lignin dissolved in DMSO-d_6.

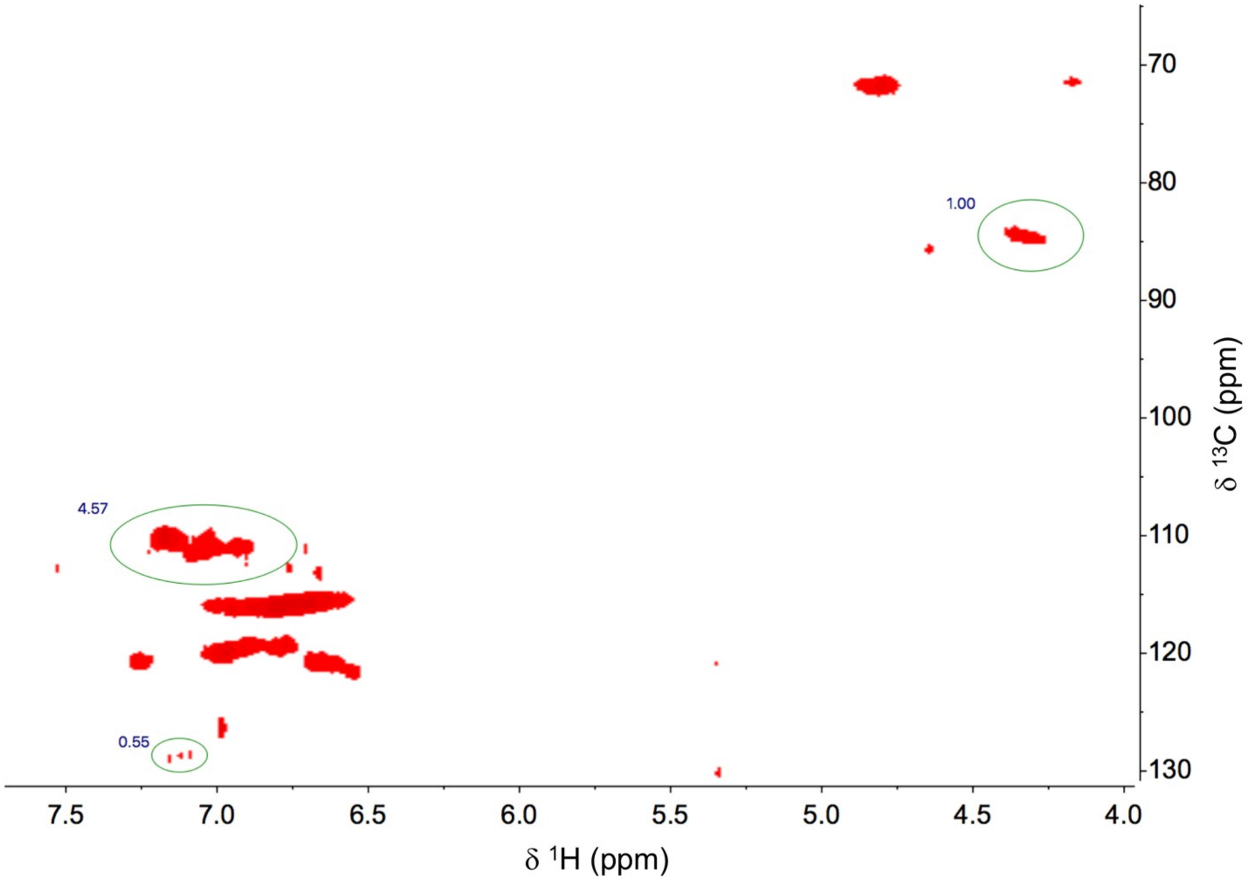

Fig. S11 HSQC (in DMSO-d6) of lignin before the reaction. The amount of β-O-4 units per 100 C9 units = 100 × 1/[4.57 + (0.55/2) = 20.6.[1]

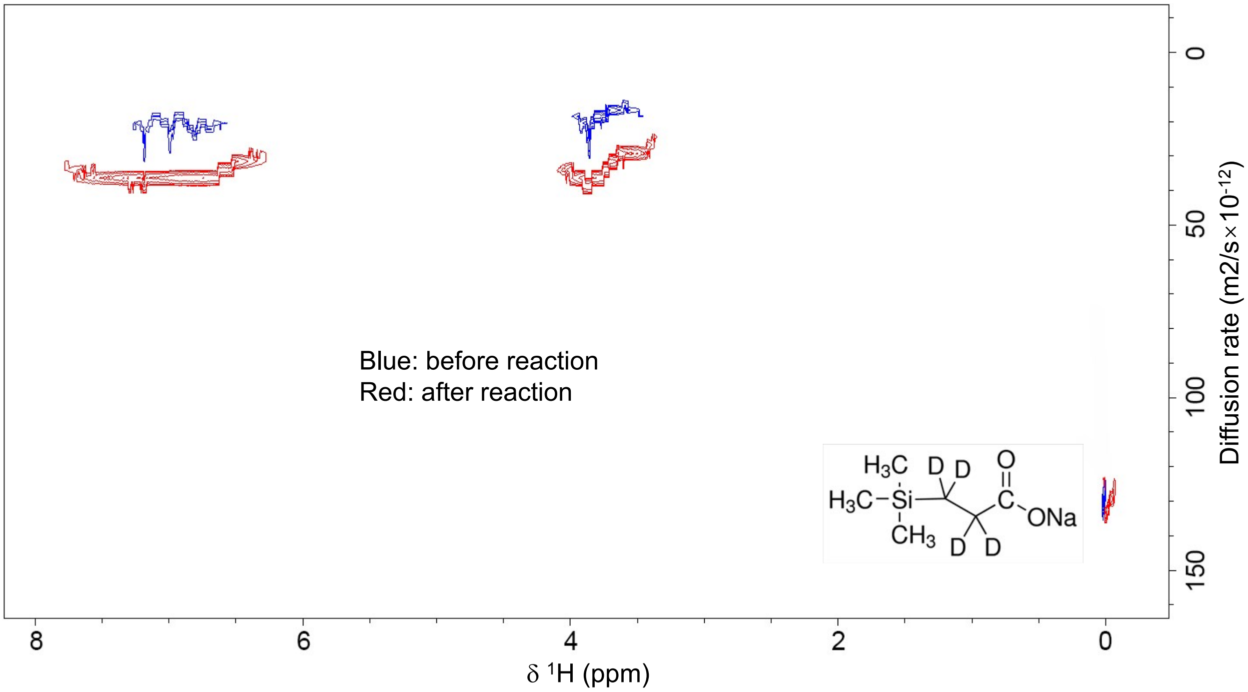

Fig. S12 DOSY NMR of lignin before and after reaction in NaOH (1 g Kraft lignin, 25 mL 100 mM NaOH, 200 °C, 1 bar N_2, 16 h).

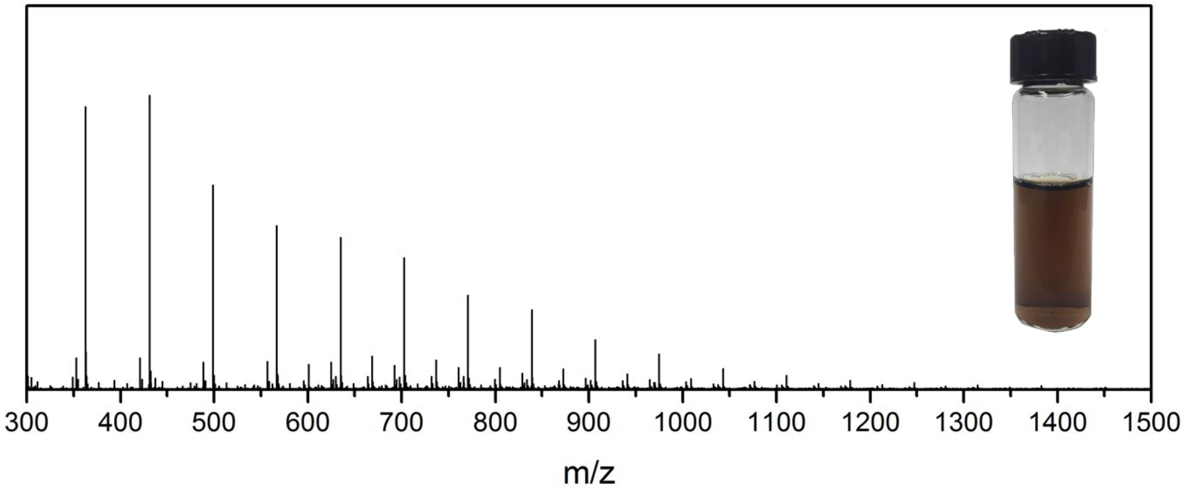

Fig. S13 Mass spectrum of the solution after acetophenone reaction in 100 mM NaOH. Reaction conditions: acetophenone 2 mM, 200 °C, 1 bar N_2, 4h.

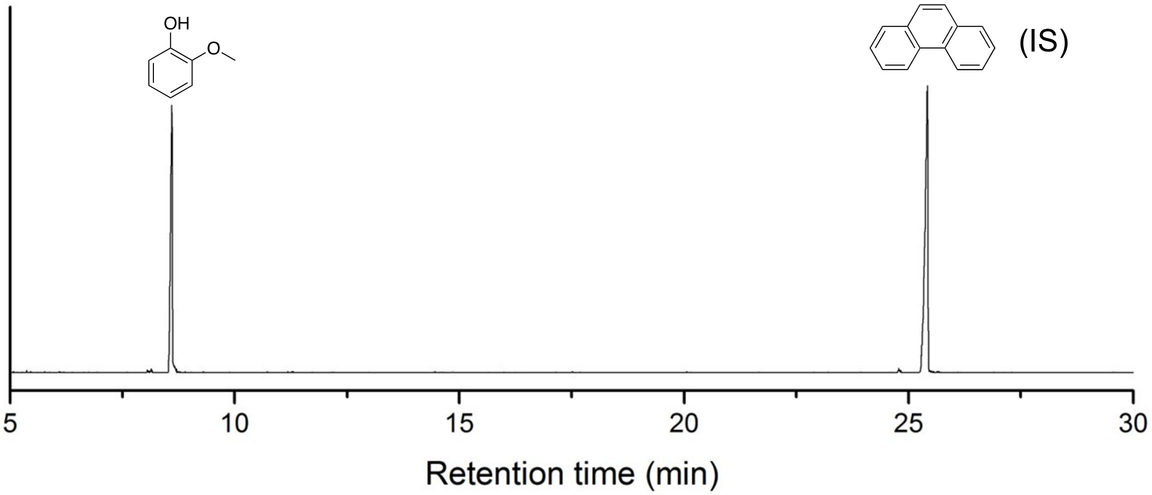

Fig. S14 Gas chromatogram of the reaction of guaiacylglycerol-beta-guaiacyl ether (GGE) in alkaline solution. Reaction conditions: 0.05 mmol GGE, 25 mL 100 mM NaOH solution, 200 °C, 1 bar N_2, 8h.

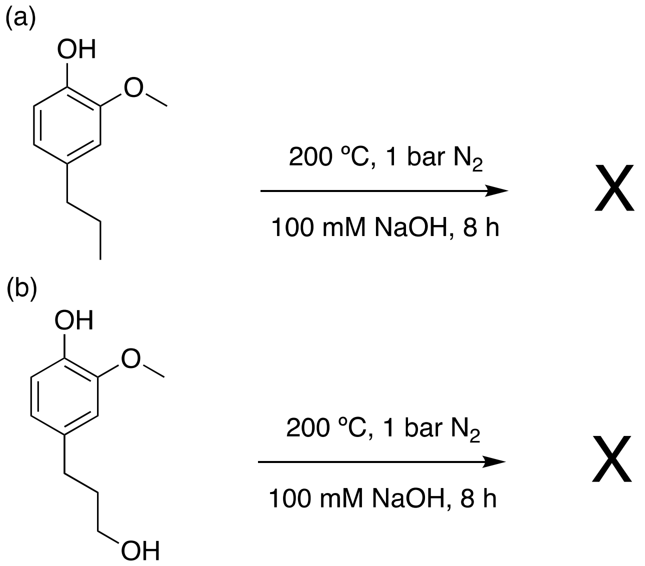

Fig. S15 No conversion was observed for the treatment of propylguaiacol or dihydroconiferyl alcohol in NaOH solution.

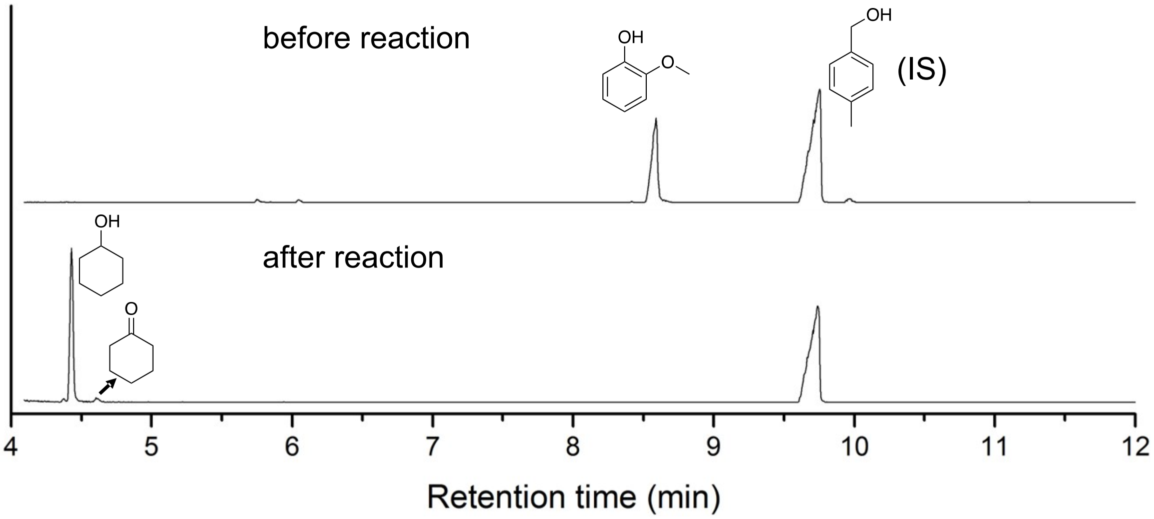

Fig. S16 Gas chromatogram of the reaction of lignin-derived guaiacol to KA oil with 5% Ru/C catalyst. Reaction conditions: 1 bar H_2, 150 °C, 8h in water.

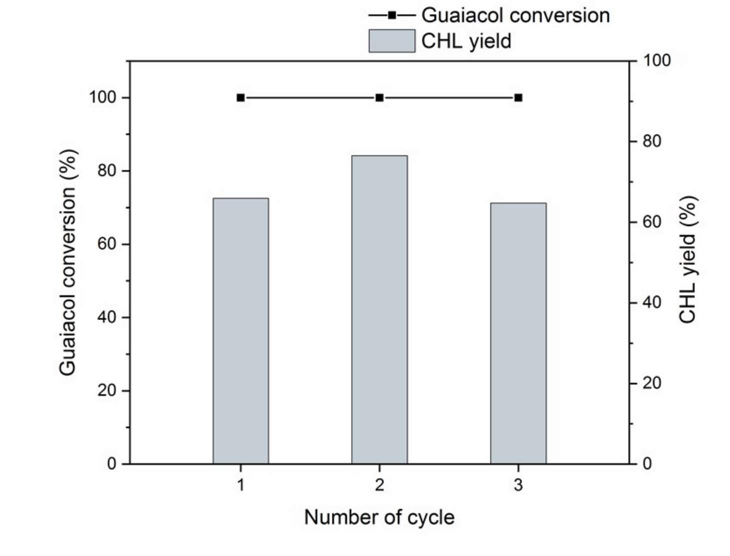

Fig. S17 Stability test of 5% Ru/C catalyst for guaiacol reaction in 3 cycles. Reaction conditions: Ru/guaiacol = 1/20 (wt/wt), 1 bar H_2, 150 °C, 8 h.

3. Supplementary Tables

Table S1. Residue after filtration of lignin reaction. [a]

entry	solvent	temperature (°C)	residue after filtration (%)[b]
1	methanol	200	66.9
2	dioxane	200	17.0
3	1 mM NaOH	200	45.2
4	10 mM NaOH	200	7.8
5	100 mM NaOH	200	4.3
6	1000 mM NaOH	200	2.9
7	100 mM KOH	200	1.9
8	100 mM NaOH	150	3.3
9	100 mM NaOH	175	3.6
10	100 mM NaOH	225	5.4
11	100 mM NaOH	250	69.3
12	100 mM NaOH[c]	200	4.8

[a] Reaction conditions: 100 mg lignin, 25 mL solvent/solution, 1 bar N_2, 8 h; [b] Pore size 2.5 μm; [c] reaction in 1 bar air.

Table S2. Assignment of peaks of ^{13}C NMR of Kraft lignin.[2–4]

chemical shift (ppm)	assignment	chemical shift (ppm)	assignment
147.93	C-3 in G units	115.72	C5 in G units
146.29	C-4 in G units	109.62	C2 in G units
129.29	C-β in Ar-CH=CH-CHO	60.38	C-γ in G type β-O-4 units/C-γ in cinnamyl alcohols
125.87	C-5/C-5’ in non-etherified 5-5’	55.54	C in Ar-OCH_3
119.64	C-6 in G units		

Table S3. Chemical shifts of the aromatic ring carbons and their arrangement determined from DNP-enhanced ^{13}C refocused INADEQUATE.

Site[a]	Kraft lignin	Post-treatment Kraft lignin
C1	130	135
C2	120	120
C3	145	145
C4	145	145
C5	120	120
C6	120	125

[a]The carbon sites are ordered such that C1 is bound to C6 and C2; C2 is bound to C1 and C3 and so forth.

References

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