

Supplementary Information

Solvent-triggered directional lignin valorization towards monomeric acetals or lignin polyols

Xinyue Sun, Junjie Ni, Yuhan Lou, Peng Zhao, Yanyan Yu, Yilin Li, Qi Tang, Haipeng Yu,* Yongzhuang Liu*

Key Laboratory of Bio-based Material Science and Technology (Northeast Forestry University), Ministry of Education, Harbin 150040, PR China

1 Supplementary Methods

1.1 Synthesis of lignin model compounds

1.1.1 Synthesis of M1C1, M2C1 and M3C1:

To synthesize 2-(2-methoxyphenoxy)-1-phenylethaneone (M1C1), α -Bromophenone was used as the raw material. Typically, 30 mmol of α -Bromophenone was dissolved in 100 ml of acetone, next, the solution was slowly added to a mixture of 44.5 mmol of potassium carbonate, 37 mmol of guaiacol, and 100 ml of acetone under continuously stirring. The combined mixture was reflux for 4 hours, with a stirring speed of 300 r/min. Afterwards, the mixture was cooled to room temperature and filtered to obtain an orange liquid. This liquid was concentrated in rotary evaporator until it dried into a solid. The solid was then collected and purified by recrystallization using ethanol. A white or slightly yellow needle-shaped crystals was obtained with a yield of 94.5%, which was identified as M1C1. M2C1 (92.9%) and M3C1 (90.1%) were synthesized following the same procedure, using 4-methoxy- α -Bromophenone and Bromo-3,4-Dimethoxyacetophenone as raw materials, respectively.

1.1.2 Synthesis of 3a, 1a and 2a:

Typically for 3a synthesis, M1C1 was used as raw material. 4.95 mmol of M1C1 was added to a 75 ml ethanol aqueous solution (ethanol concentration of 99.5%) and stirred it at 300 r/min. Subsequently, 5.85 mmol of sodium borohydride was slowly added under continuous stirring at room temperature for 4 hours. The obtained mixture was concentrated using a rotary evaporator and quenched by adding 25 ml of saturated ammonium chloride aqueous solution. The quenched mixture was diluted with water and extracted with ethyl acetate (50mL \times 2). The collected ethyl acetate phase was combined and washed with Brine. Finally, the ethyl acetate phase was dried over anhydrous magnesium sulfate and concentrated to give the final product of 3a (purification by a flash column if necessary). The obtained 3a was white crystals with a yield of 92.3%. 1a (92.1%) and 2a (89.8%) was synthesized following the same procedure.

1.1.3 Synthesis of 4a:

For the synthesis of a more complex lignin model compound, typically 5.05mmol of potassium carbonate and 4.625mmol of M2C1 were added to 50 mL of ethanol aqueous solution (ethanol concentration 99.5%), and the mixture was stirred at room temperature at a speed of 300 r/min. 6.875mmol of formaldehyde aqueous solution (formaldehyde concentration 36% -38%) was slowly added to the mixture and reacted at room temperature. Thin layer chromatography (TLC) was used to monitor the conversion of the raw material. When full conversion of the raw material is observed, 16.5mmol of sodium borohydride was slowly added to the reaction mixture and stirred at room temperature for another 4 hours. Finally, the mixture was cooled to room temperature and concentrated in a rotary evaporator. The concentrated mixture was quenched with 25ml of ammonium chloride saturated aqueous solution and extracted with ethyl acetate (50mL×2), followed by washing with Brine, drying over anhydrous magnesium sulfate. The crude products were purified by chromatography (gradient ethyl acetate in petroleum ether). The purified product 4a was identified by TLC and gave a yield of 64.9%.

1.2 Calculation of monomeric acetal yield from lignin acidolysis

The yield of monomeric acetal from lignin depolymerization was calculated by an external standard method using NMR. Typically, the monomeric products were extracted by DCM and concentrated in vacuum after reaction, 0.5 mmol benzaldehyde was added into the products as external standard. The mixture was further characterized by 2D HSQC NMR. α and β proton of the external standard and monomeric acetals was used for determining the yield of the monomeric acetals (the formula is as follows). The product distribution of syringyl type or guaiacyl type products was calculated according to the S/G ratio (~2).

$$\text{Yield}_{\text{acetals}}\% = \text{SA1} + \text{GA1} + \text{SA2} + \text{GA2}$$

$$\text{SA1} = \frac{\frac{2}{3}M_{S_{A1}} \times n_{ES} \cdot (\text{Integral}A1\beta)}{\text{Integral}ES \times m_L} \times 100\%$$

$$GA1 = \frac{\frac{1}{3}M_{G_A1} \times n_{ES} \cdot (IntegralA1\beta)}{IntegralES \times m_L} \times 100\%$$

$$2 = \frac{\frac{2}{3}M_{S_A2} \times n_{ES} \cdot \left[\frac{1}{2}(IntegralA1\alpha + IntegralA2\alpha) - IntegralA1\beta \right]}{IntegralES \times m_L} \times 100\%$$

$$2 = \frac{\frac{1}{3}M_{G_A2} \times n_{ES} \cdot \left[\frac{1}{2}(IntegralA1\alpha + IntegralA2\alpha) - IntegralA1\beta \right]}{IntegralES \times m_L} \times 100\%$$

IntegralES represents integral of the proton of external standard area; IntegralA1 β represents integral of the proton β of monomeric acetals A1; IntegralA1 α represents integral of the proton α of monomeric acetals A1; IntegralA2 α represents integral of the proton α of monomeric acetals A2; n_{ES} represents the molecular weight of the external standard; M_{S_A1} represents the molar mass of SA1; M_{G_A1} represents the molar mass of GA1; M_{S_A2} represents the molar mass of SA2; M_{G_A2} represents the molar mass of GA2; m_L represents the quality of lignin.

2 Supplementary Figures and Tables

2.1 Lignin model compound

Table S1 Lignin model compound

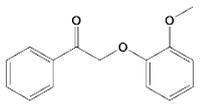
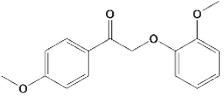
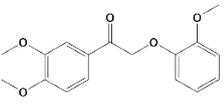
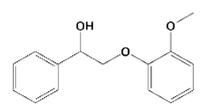
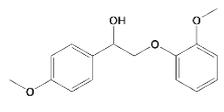
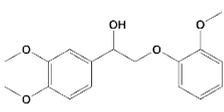
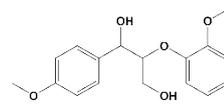
Name	Structure	Digital picture of the products	Yield %
M1C1			94.5
M2C1			92.9
M3C1			90.1
3a			92.3
1a			92.1
2a			89.8
4a			64.9

Table S2 Screen of different organic solvents in biphasic DES for the model compound reactions

Organic phase	Boiling point/°C	Conversion of 1a/%	Selectivity of 1d/%
CPME	106	96.1	60.6
MIBK	116	84.7	64.5
DCM	40	95.5	74.9

Conditions: 100 mg of substrate, 1wt% of catalyst, 100°C, and 1 h. The conversion and selectivity were calculated according to GC results.

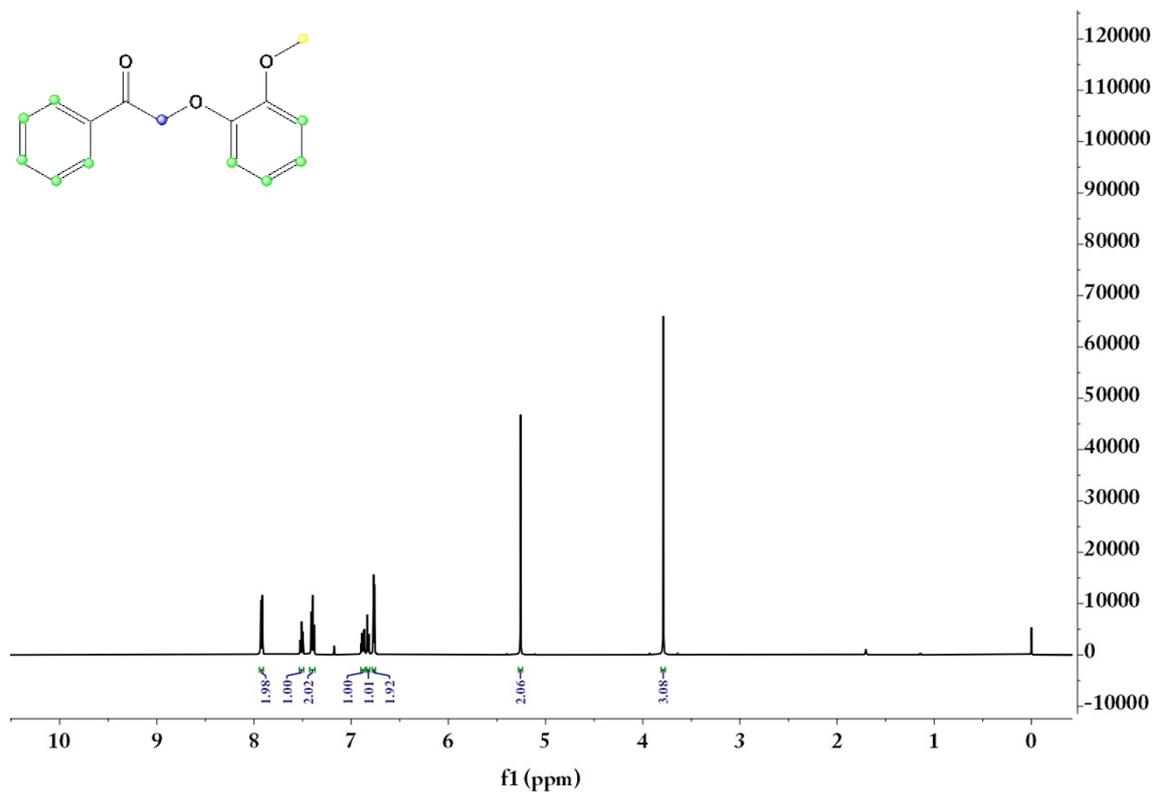


Fig.S1 ¹H NMR (CDCl₃) spectrum of M1C1

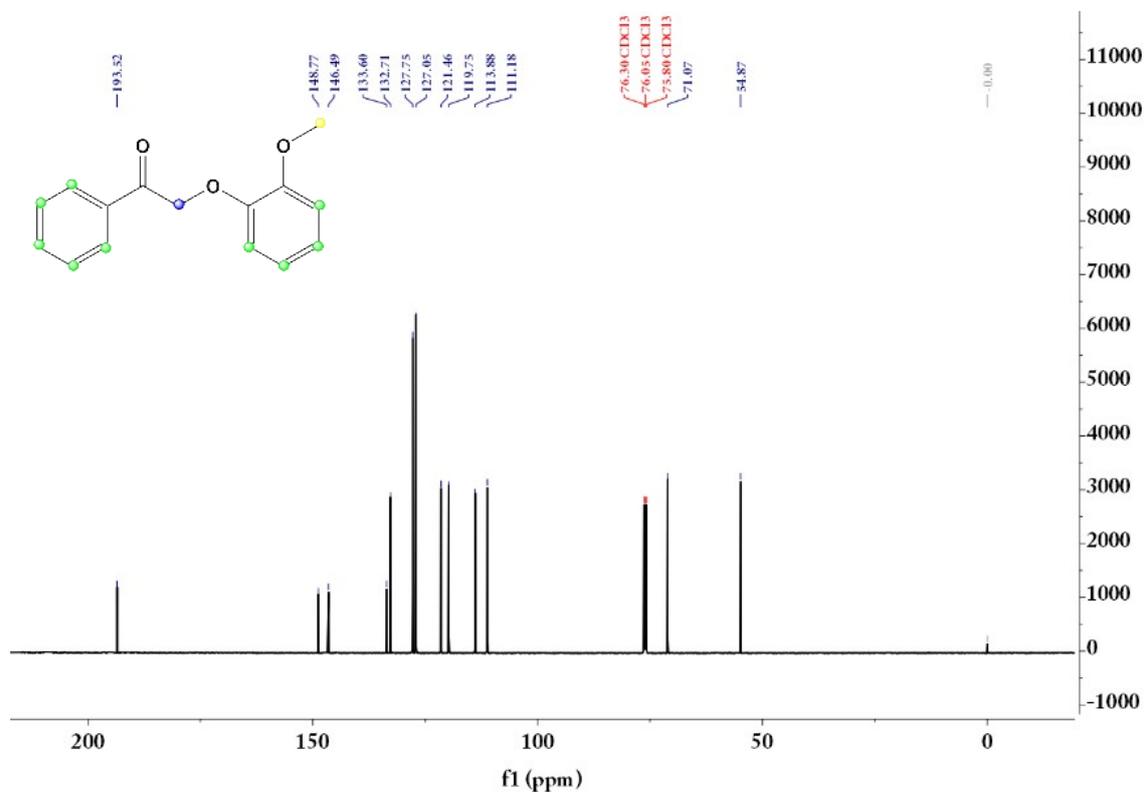


Fig.S2 ¹³C NMR (CDCl₃) spectrum of M1C1

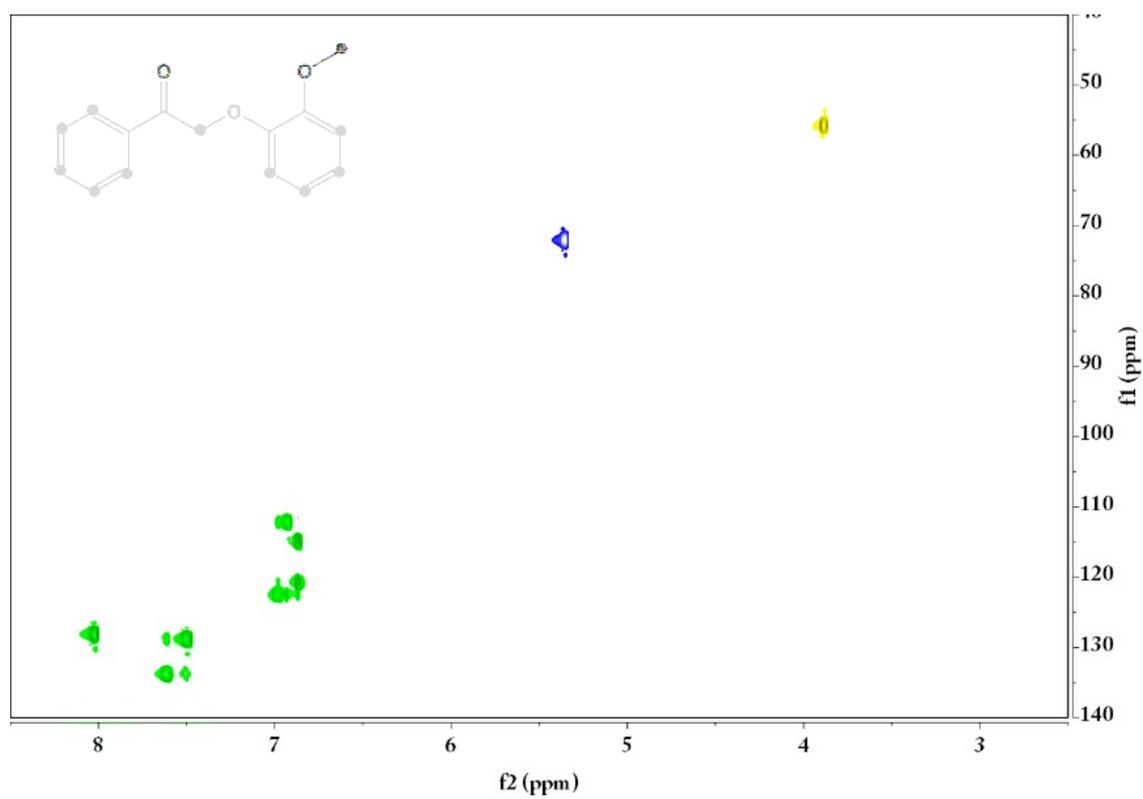


Fig.S3 2D HSQC NMR spectra of MIC1

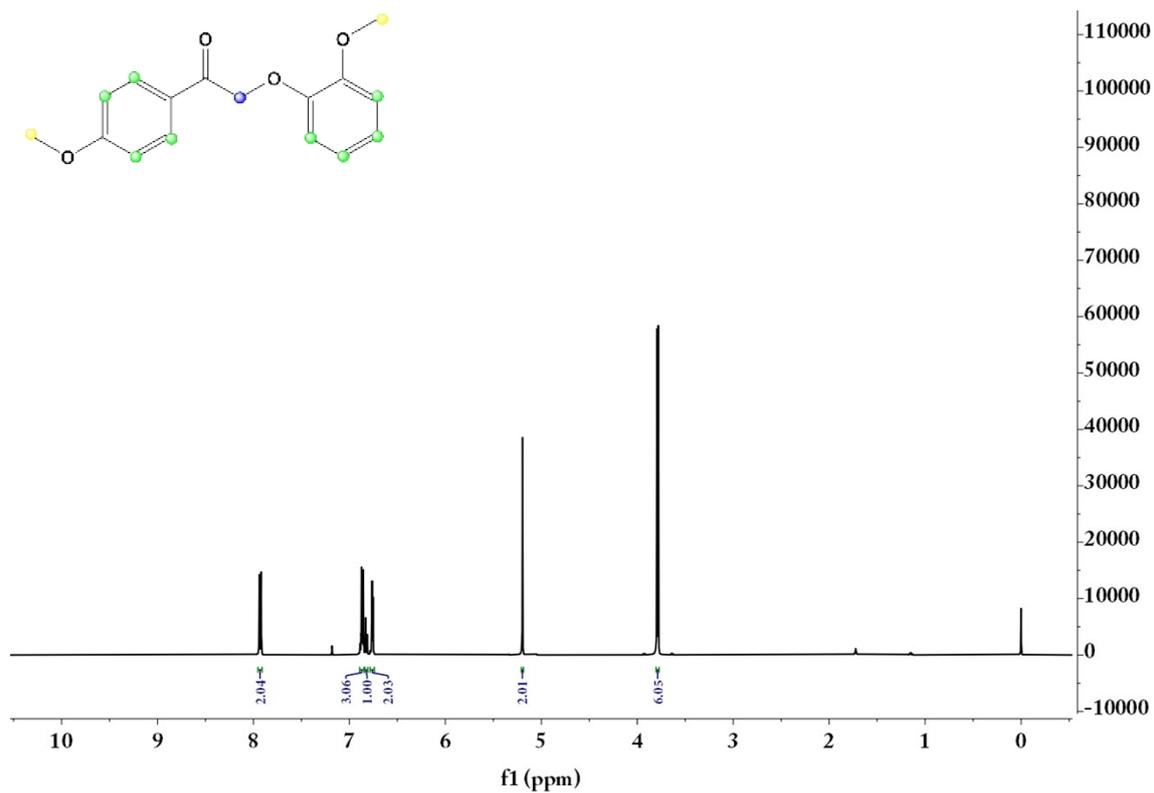


Fig.S4 ¹H NMR (CDCl₃) spectrum of M2C1

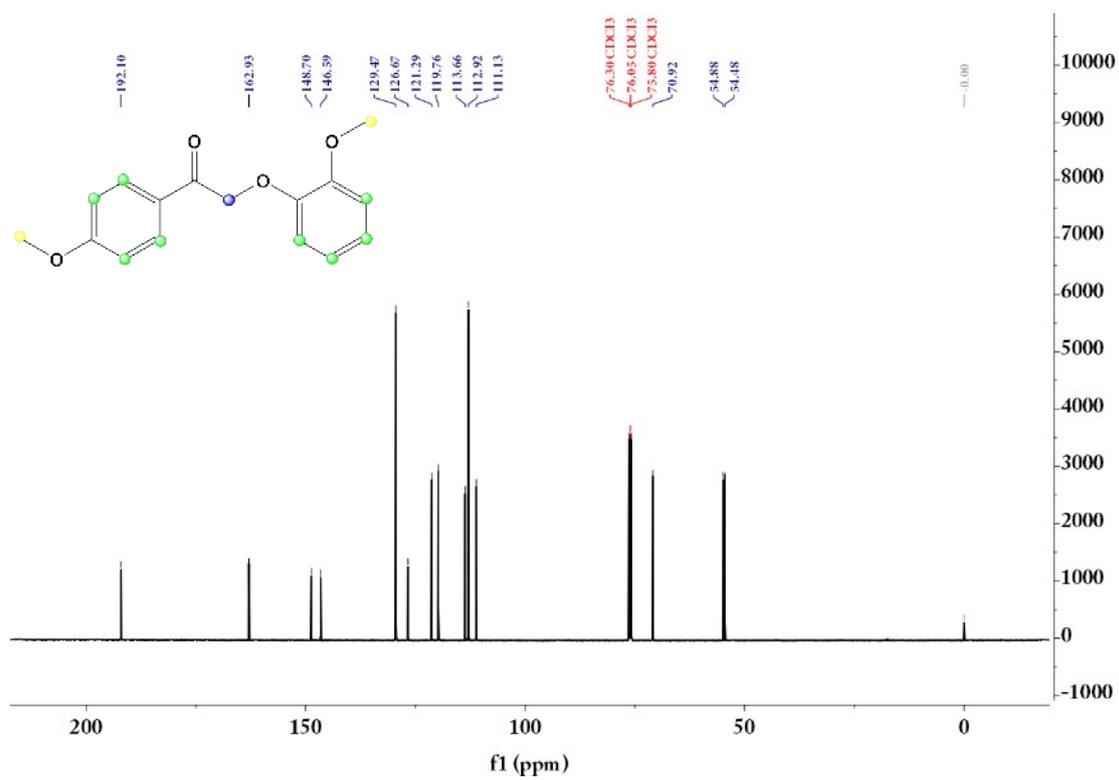


Fig.S5 ¹³C NMR (CDCl₃) spectrum of M2C1

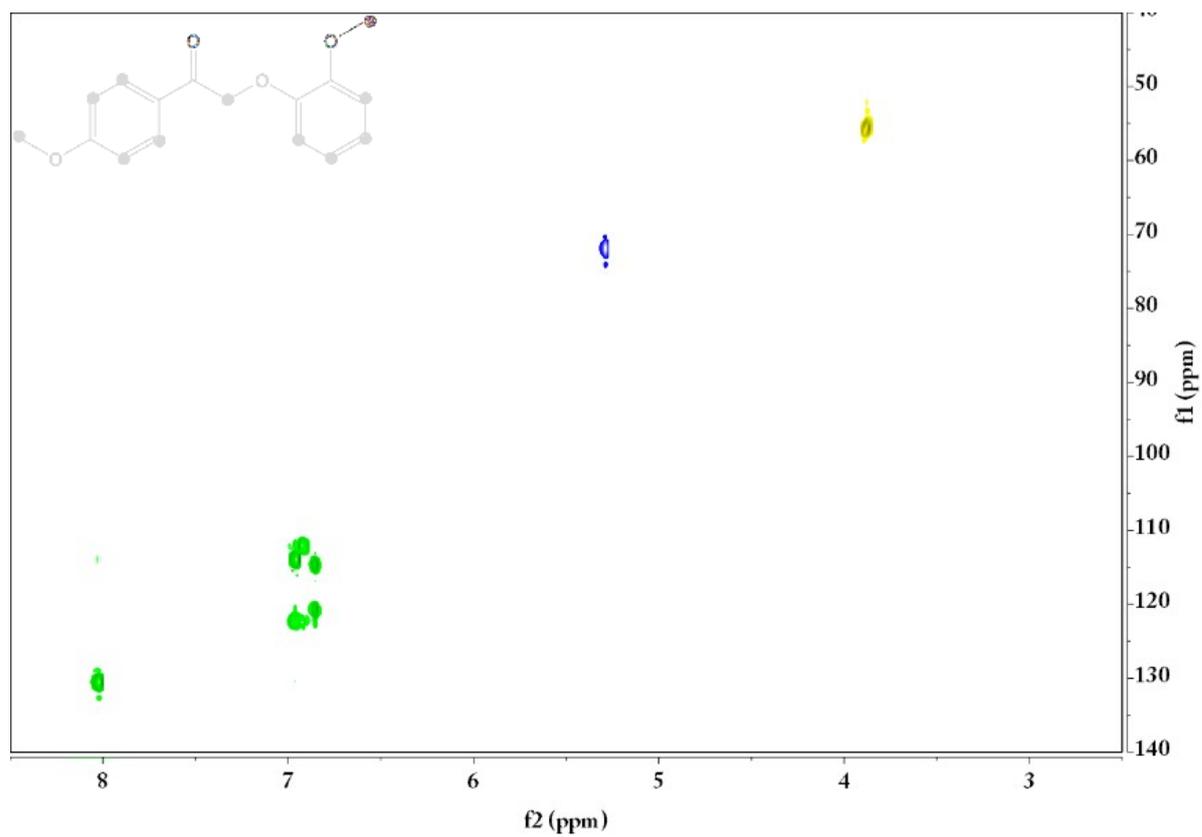
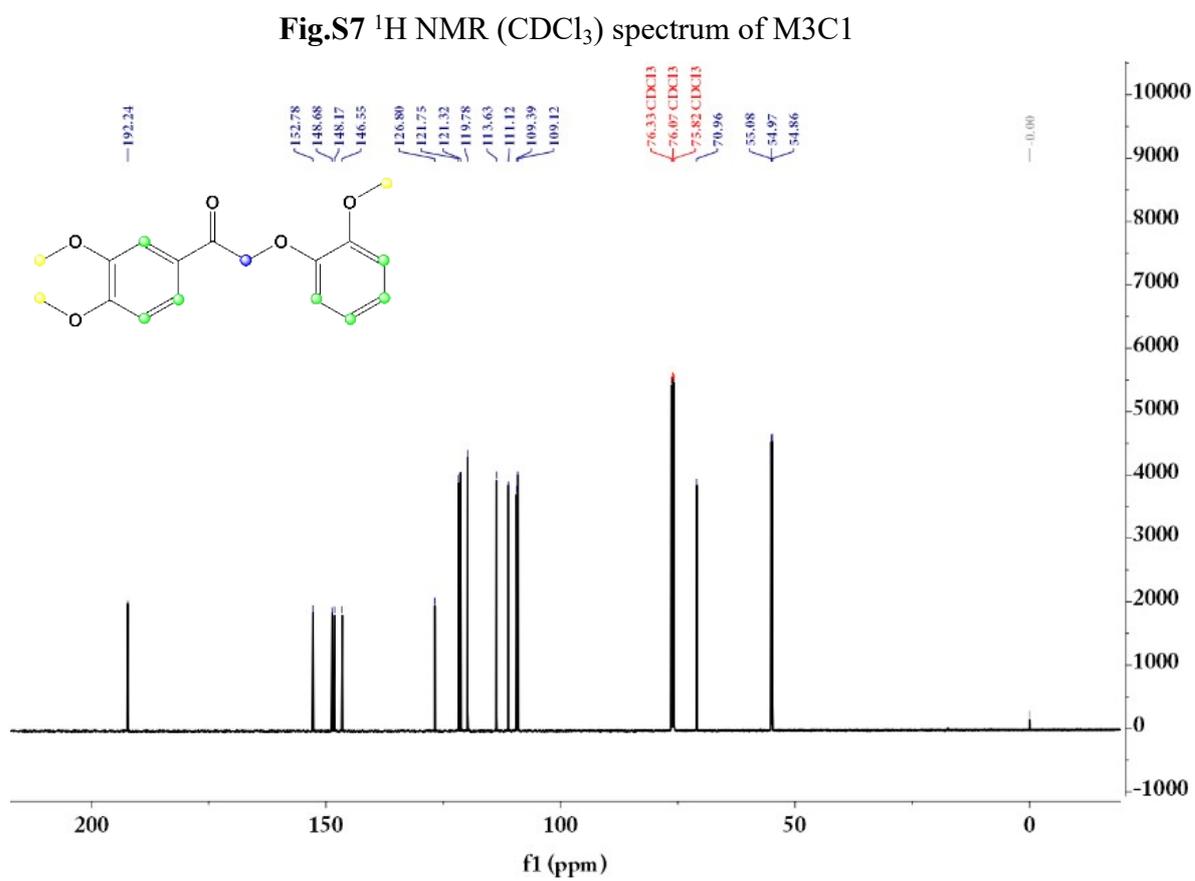
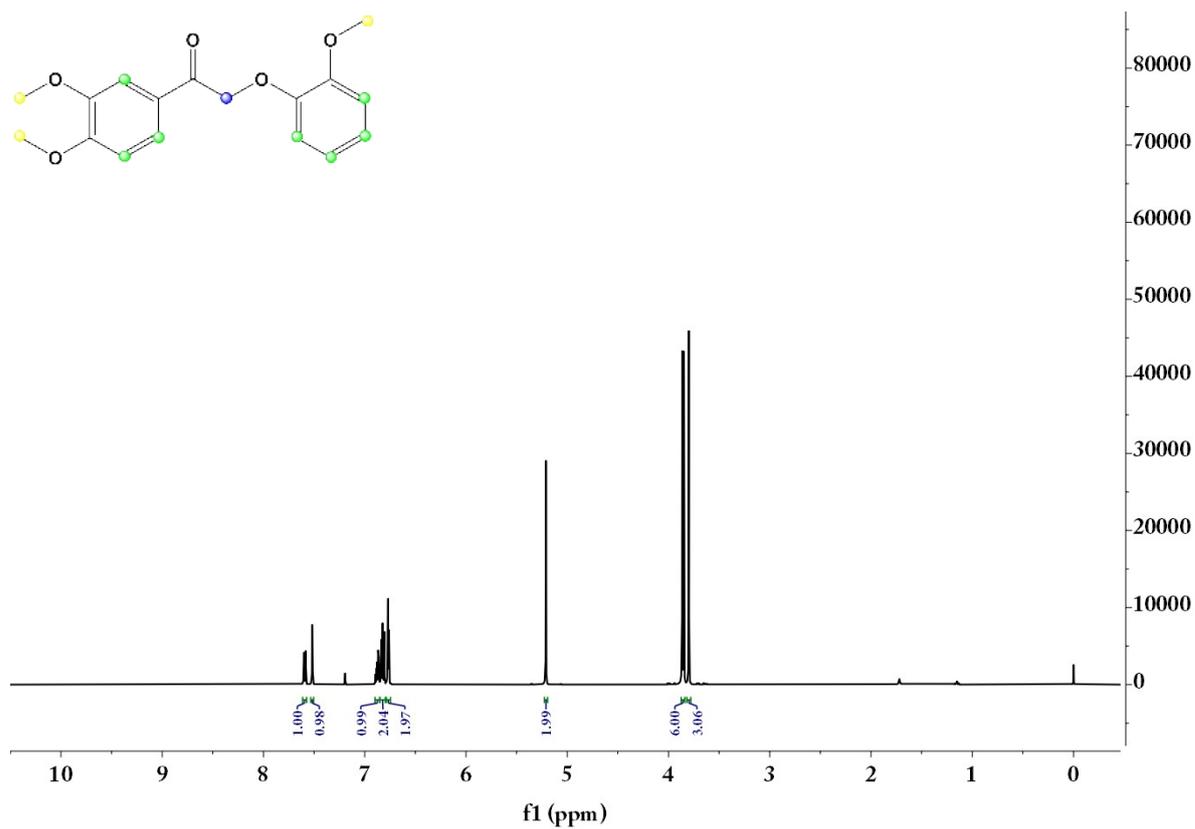


Fig.S6 2D HSQC NMR (CDCl_3) spectra of M2C1



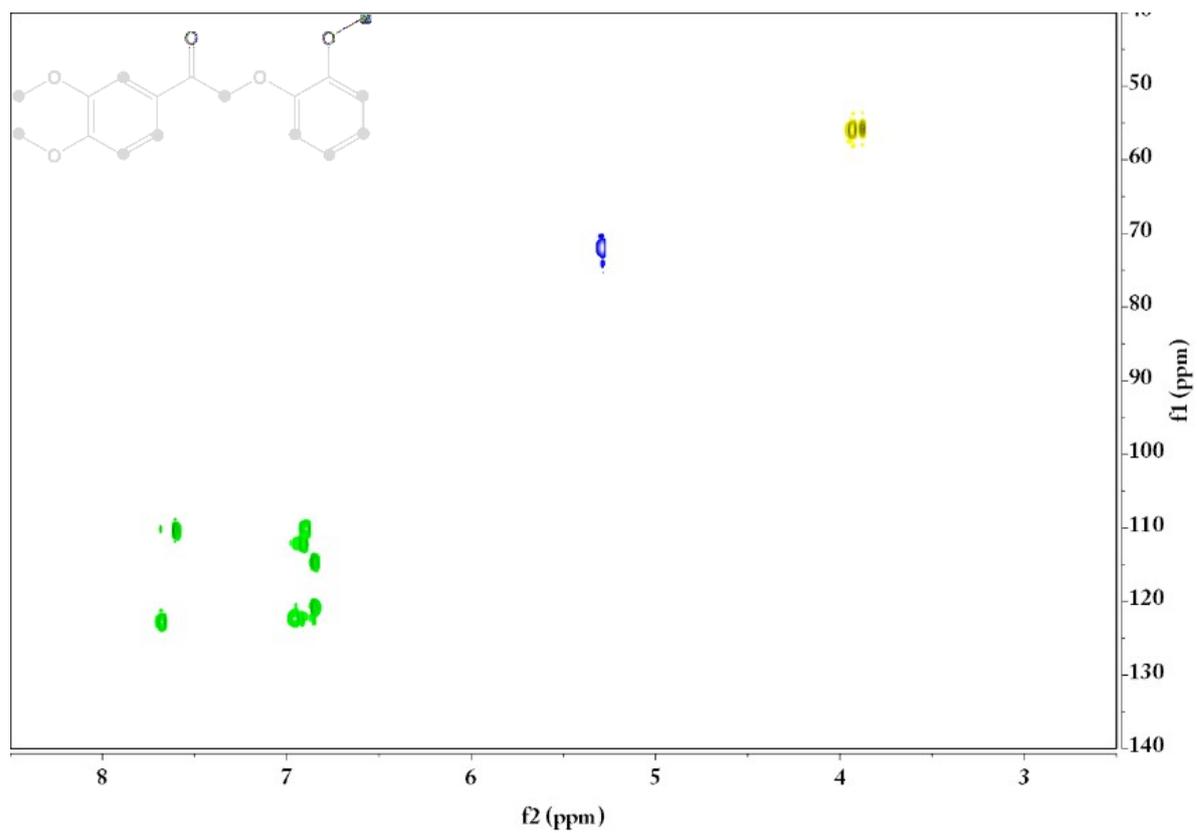


Fig.S9 2D HSQC NMR (CDCl₃) spectra of M3C1

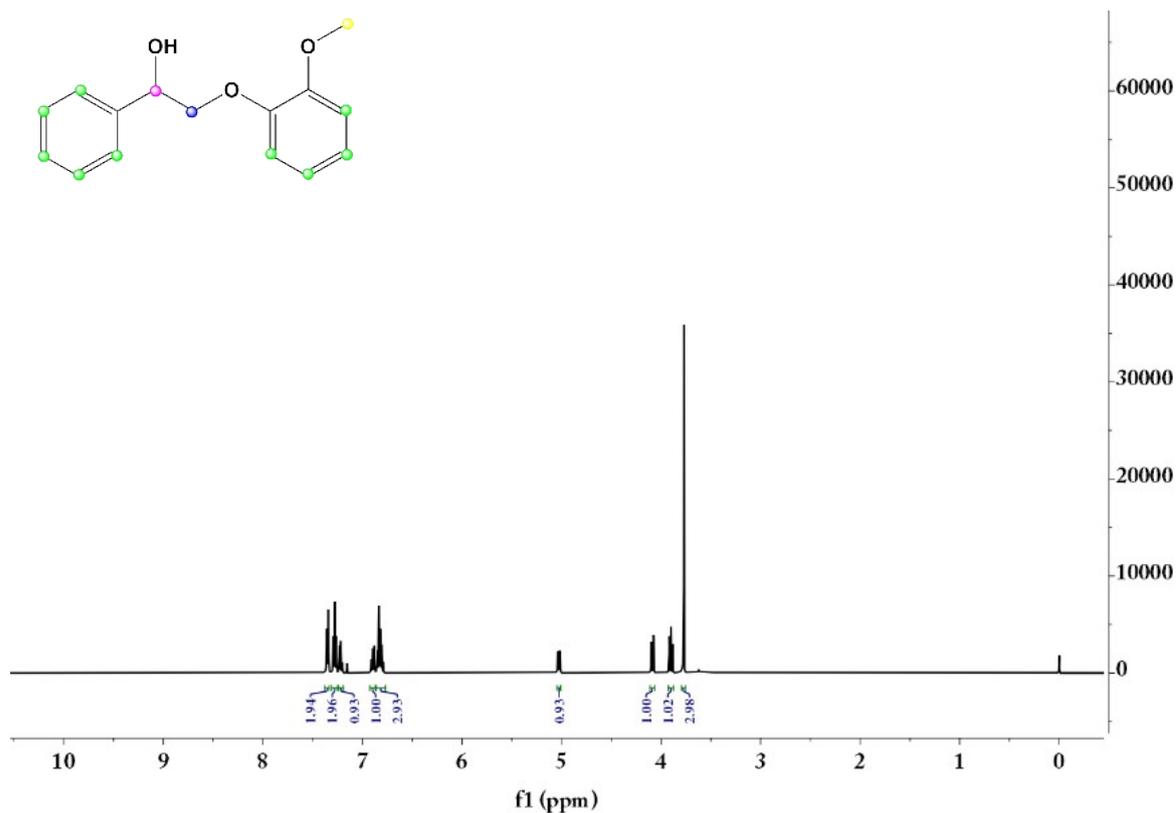


Fig.S10 ^1H NMR (CDCl_3) spectrum of 3a

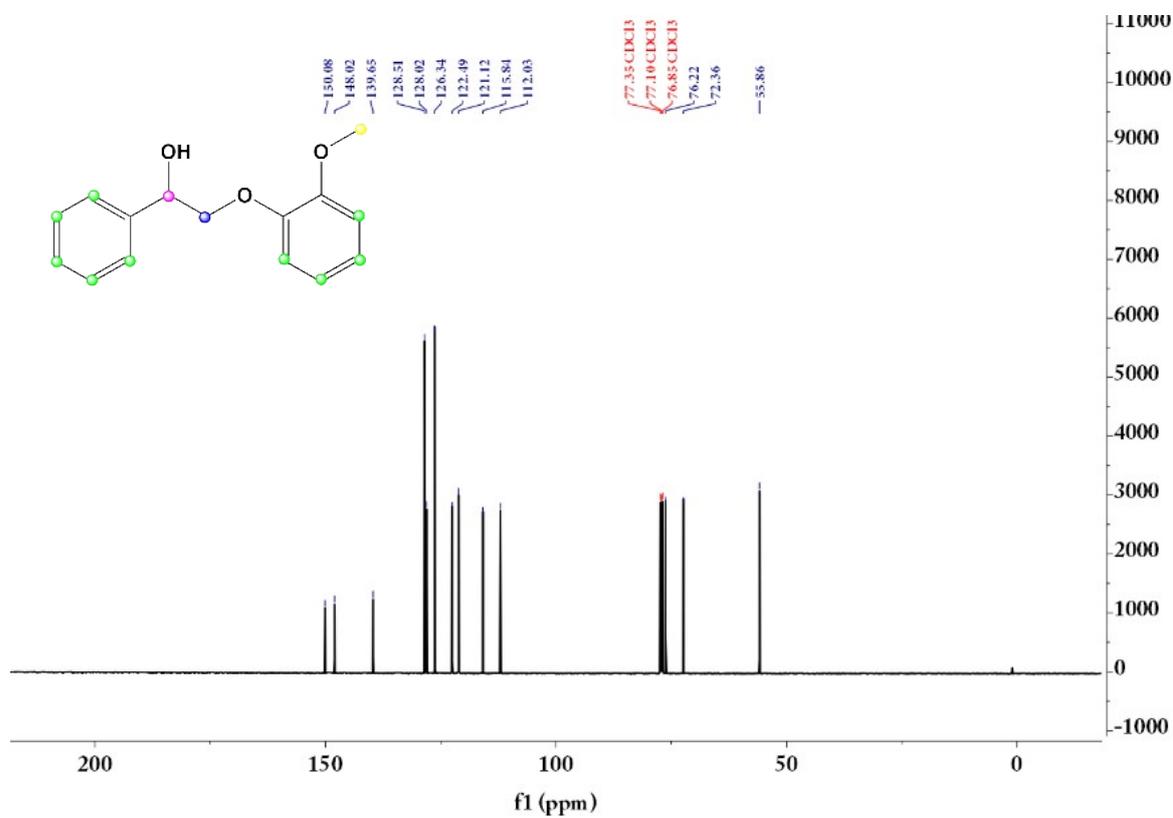


Fig.S11 ^{13}C NMR (CDCl_3) spectrum of 3a

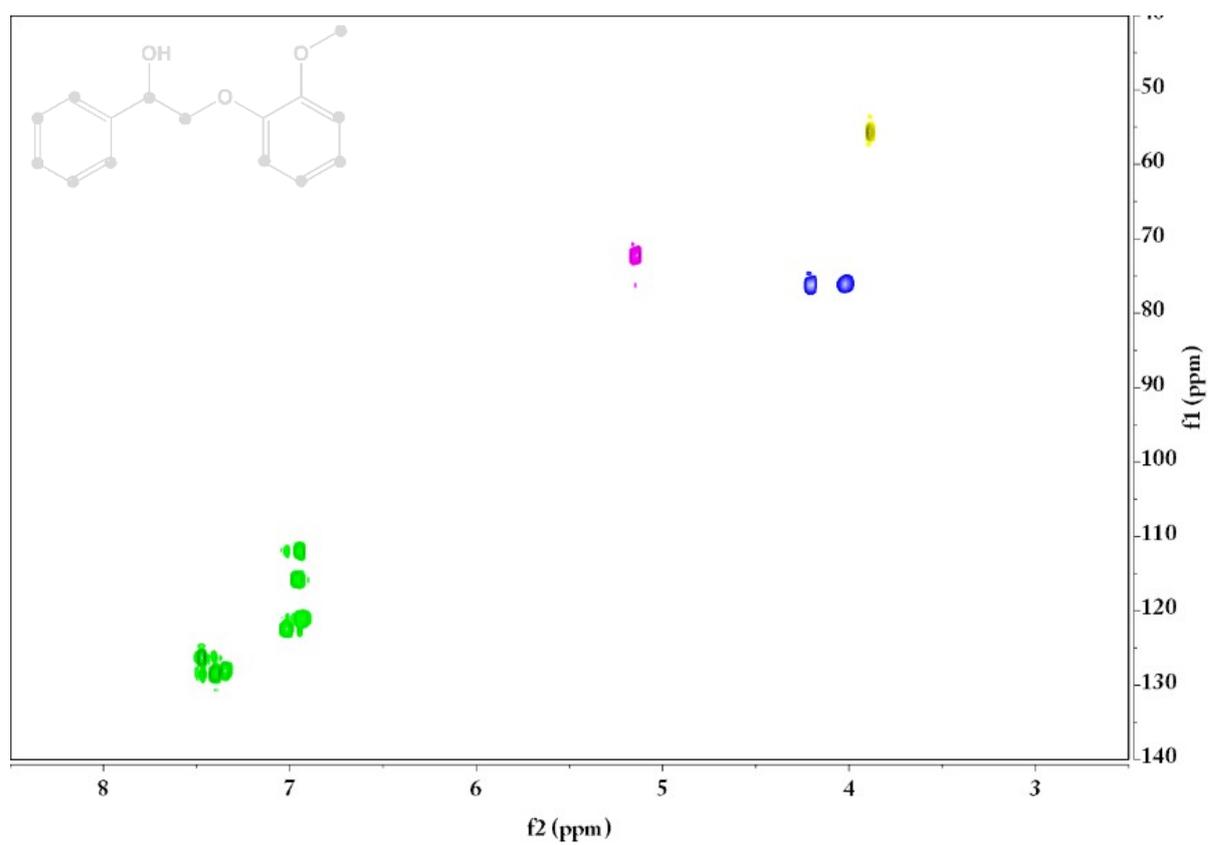


Fig.S12 2D HSQC NMR (CDCl_3) spectra of 3a

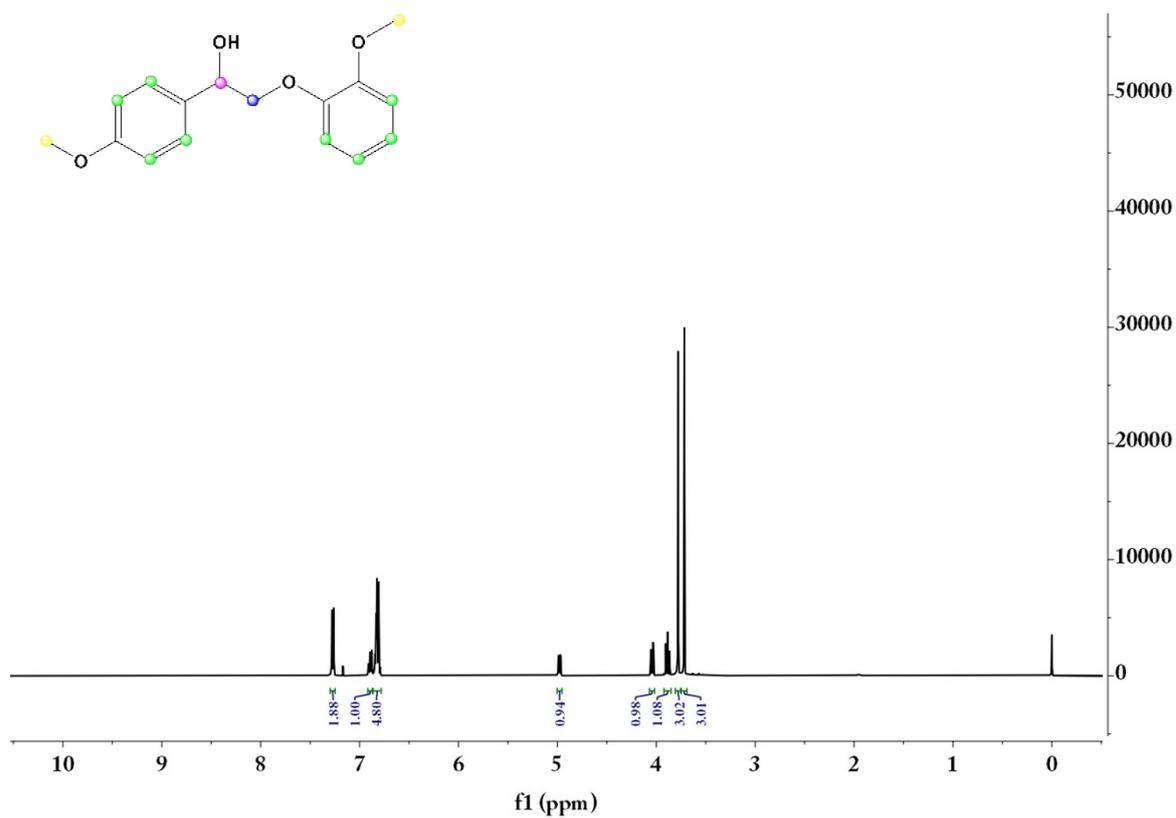


Fig.S13 ¹H NMR (CDCl₃) spectrum of 1a

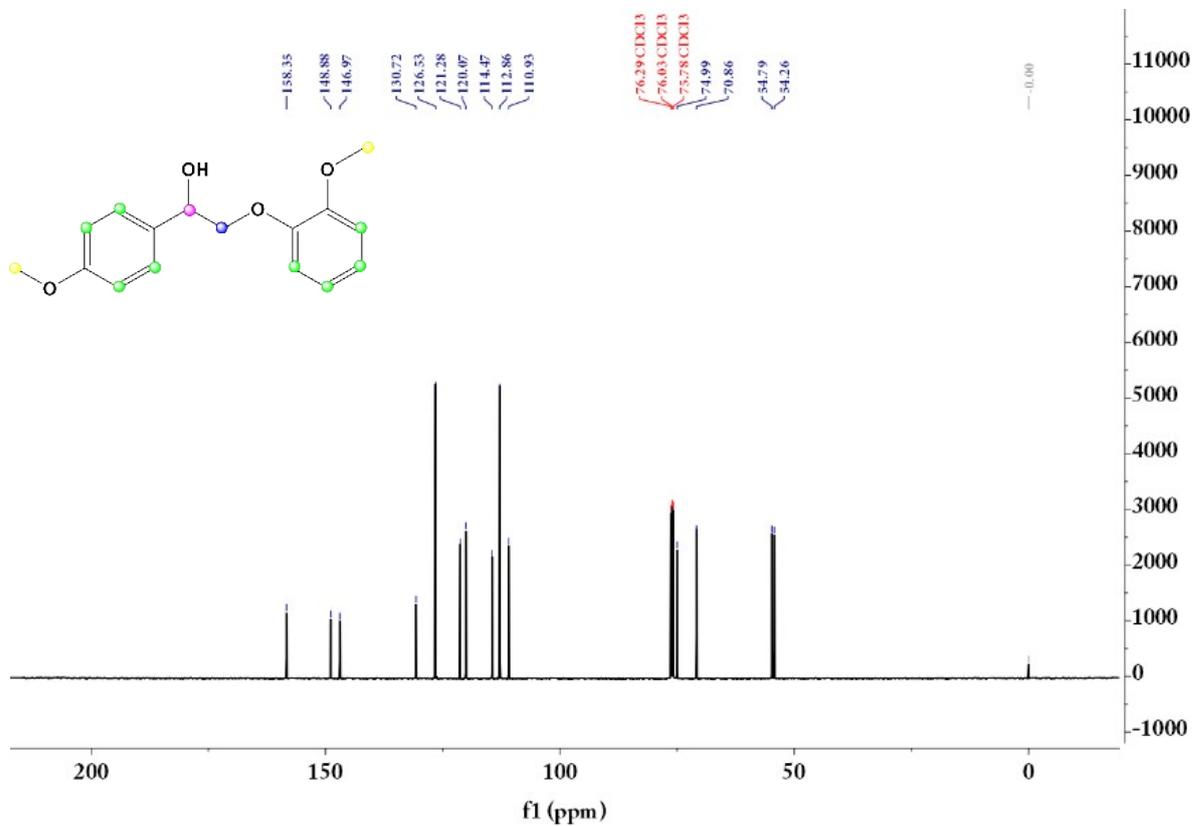


Fig. S14 ¹³C NMR (CDCl₃) spectrum of 1a

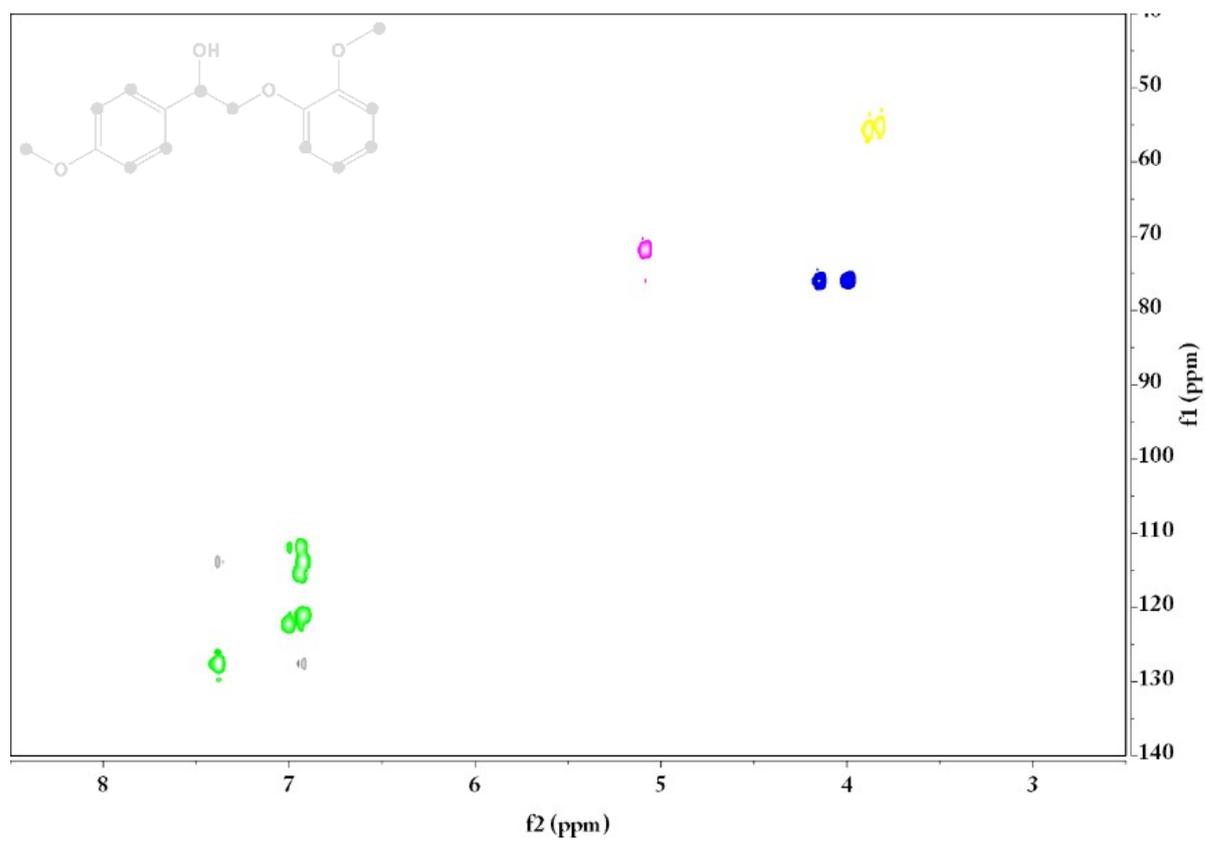


Fig.S15 2D HSQC NMR (CDCl_3) spectra of 1a

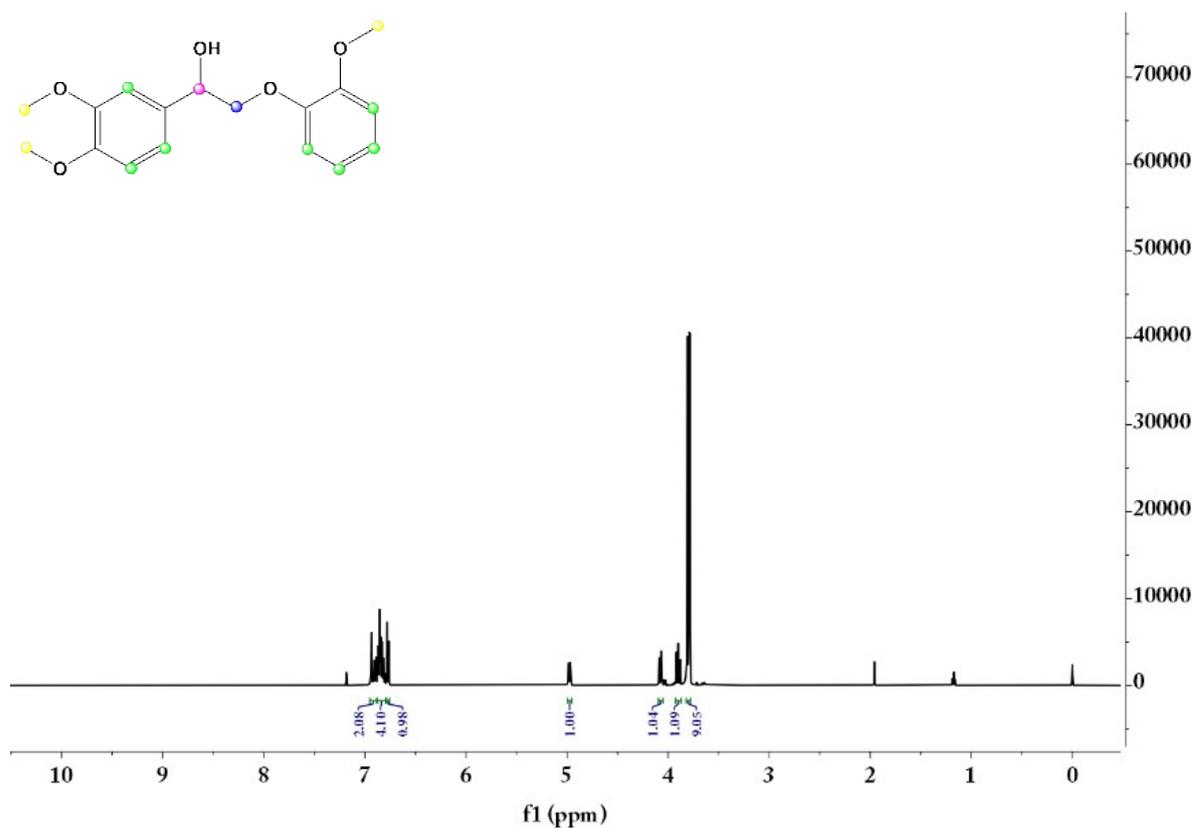


Fig.S16 ^1H NMR (CDCl_3) spectrum of 2a

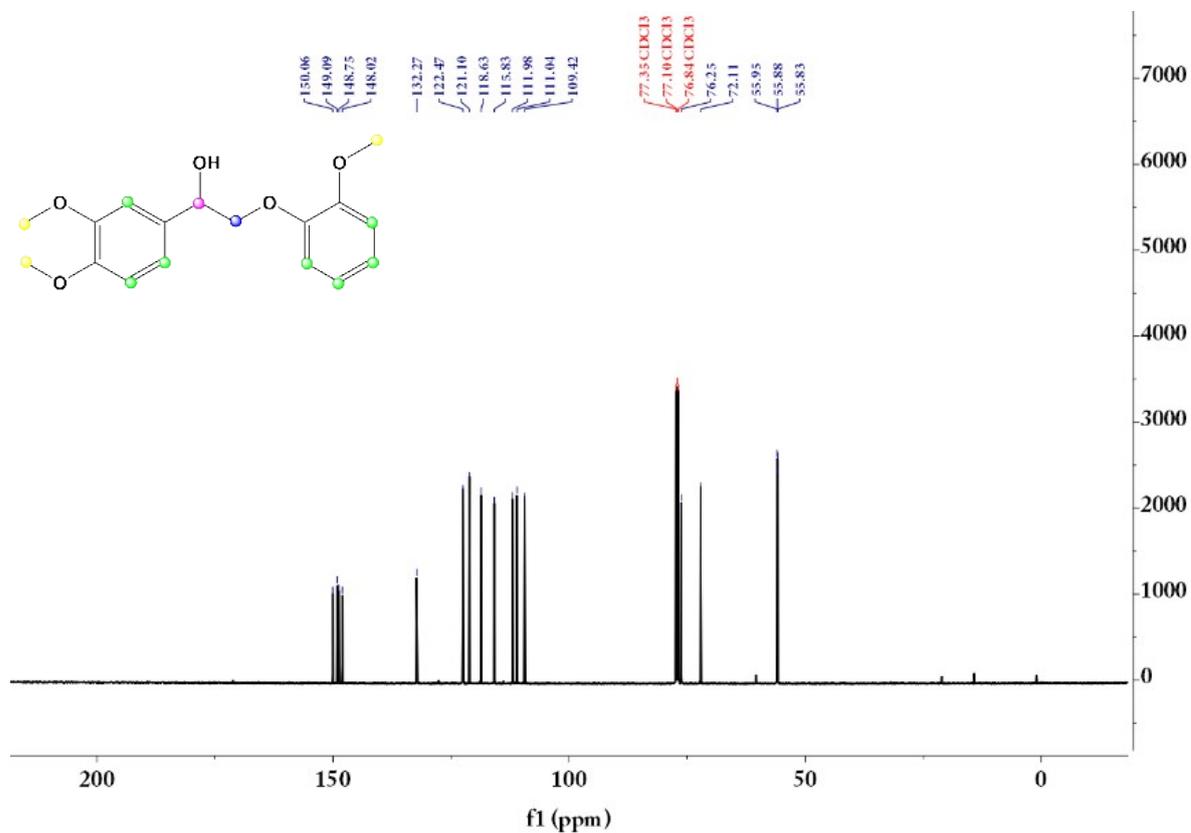


Fig.S17 ^{13}C NMR (CDCl_3) spectrum of 2a

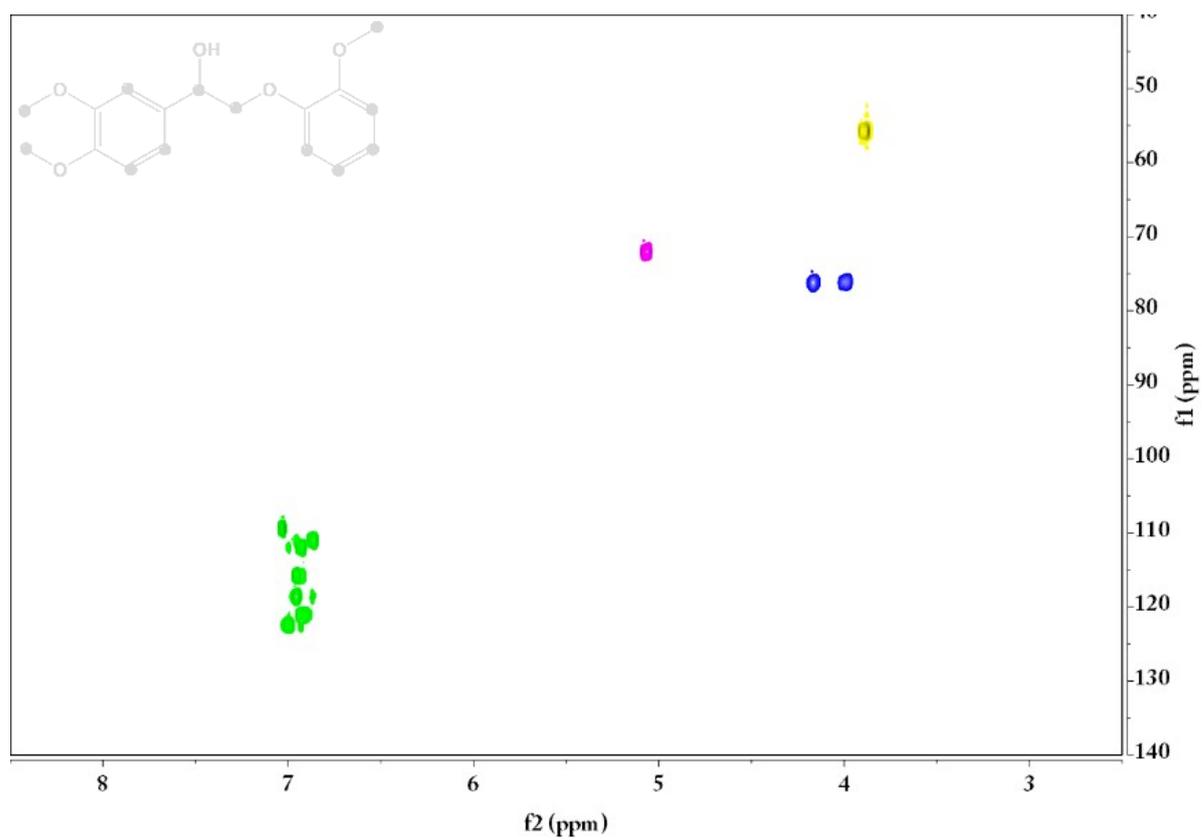


Fig.S18 2D HSQC NMR (CDCl_3) spectra of 2a

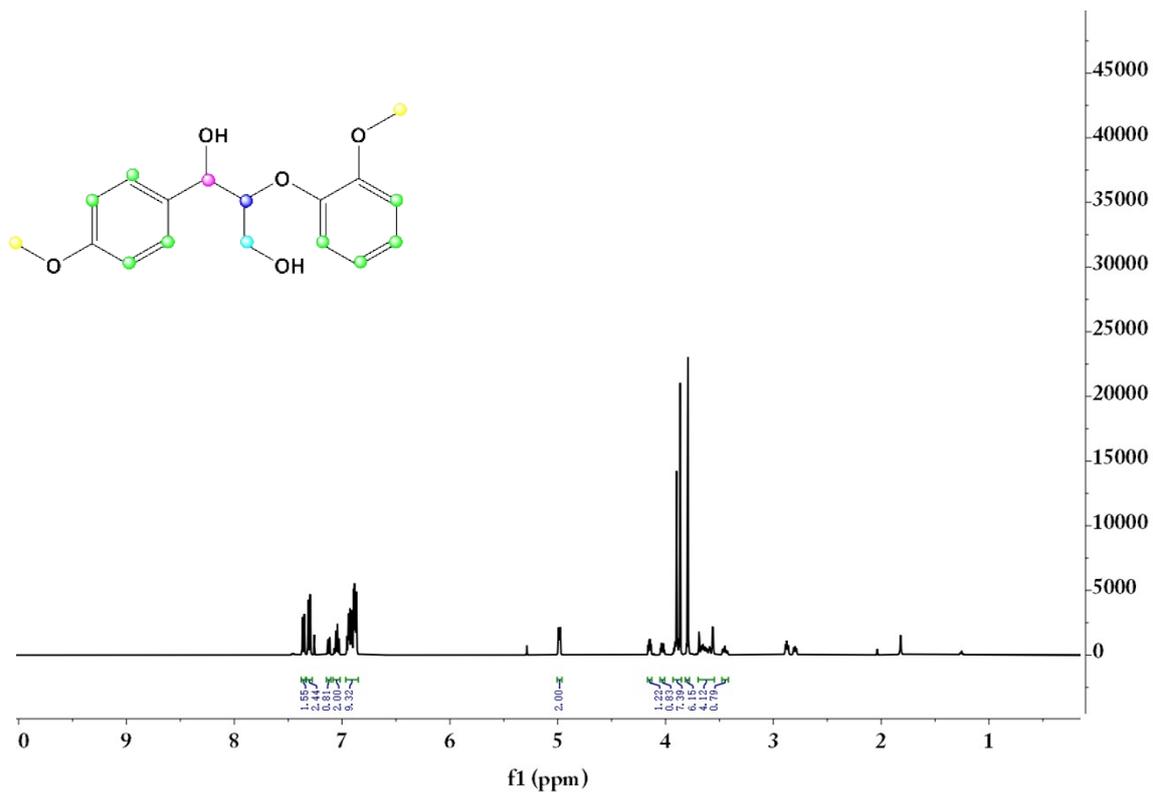


Fig.S19 ¹H NMR spectrum of lignin model compound 4a

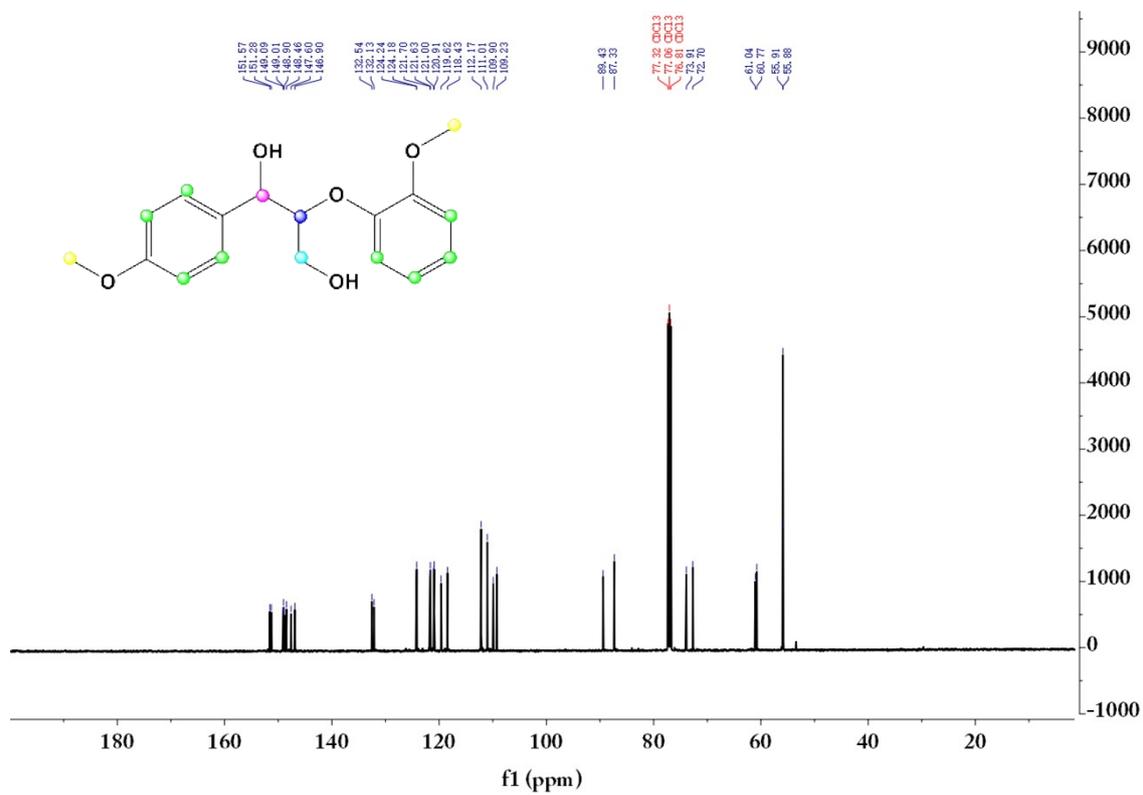


Fig.S20 ¹³C NMR spectrum of lignin model compound 4a

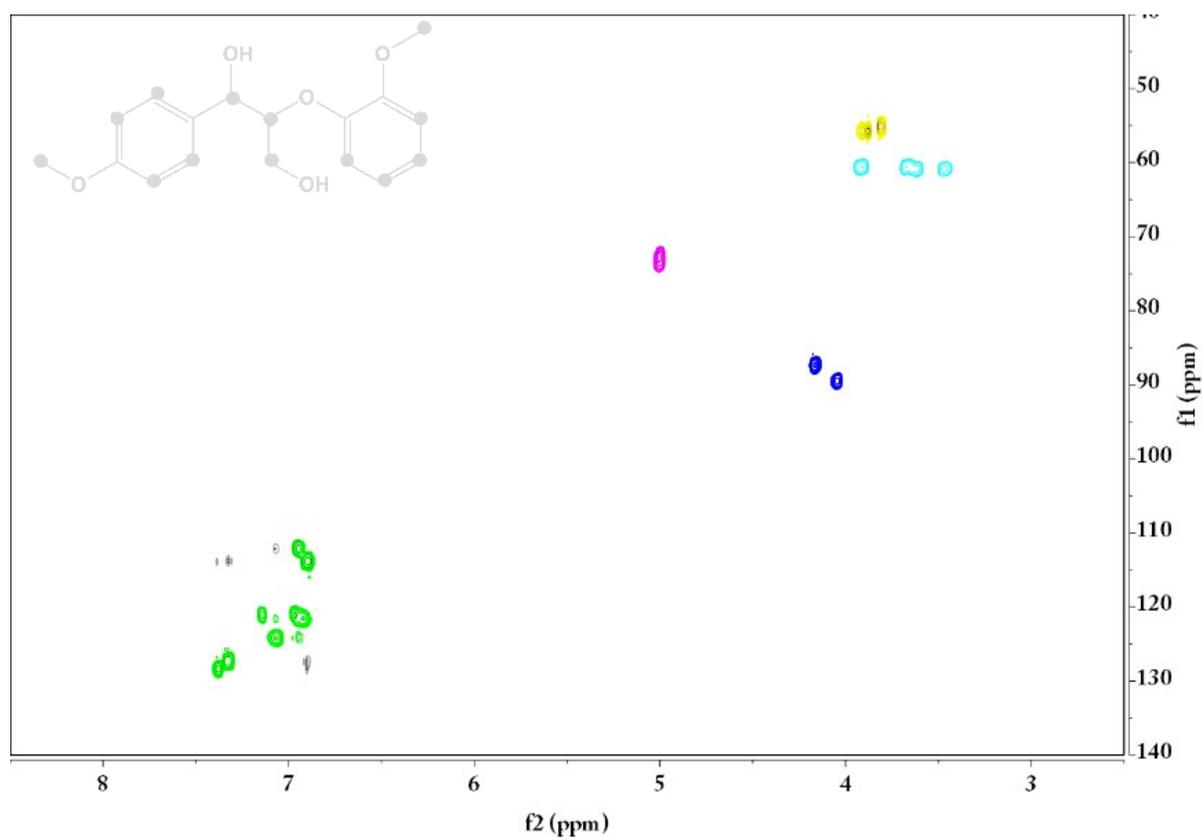


Fig.S21 2D-HSQC NMR spectra of lignin model compound 4a

2.2 Depolymerization of lignin model compound in acidified DES

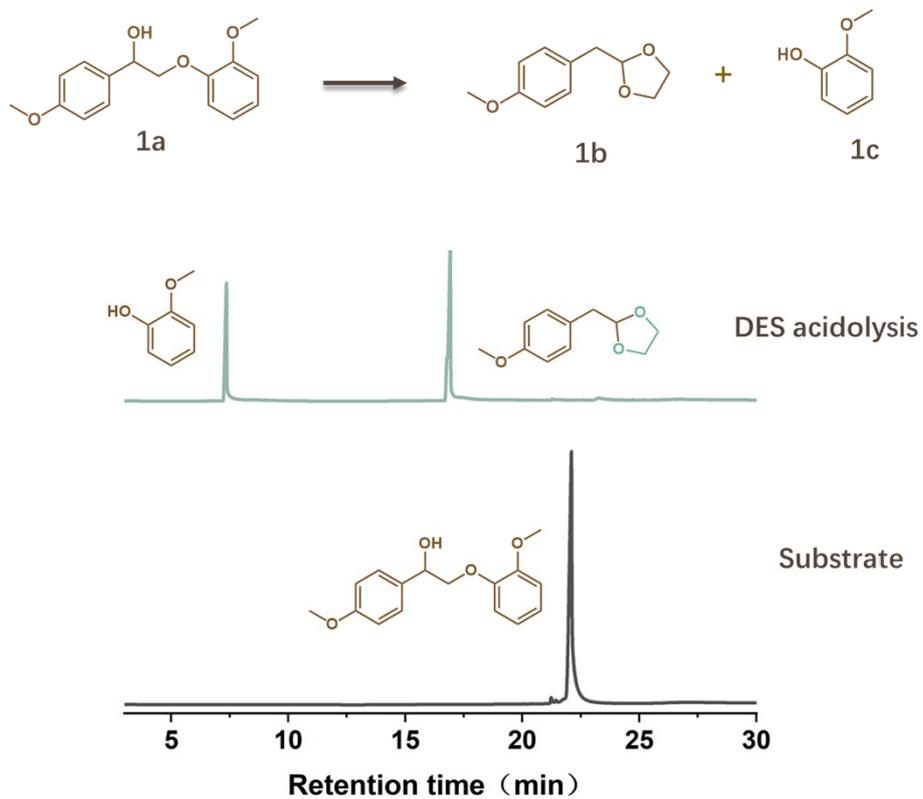


Fig.S22 GC spectra of lignin model compound 1a conversion at DES (AlCl_3 acidified ChCl/EG) acidolysis conditions.

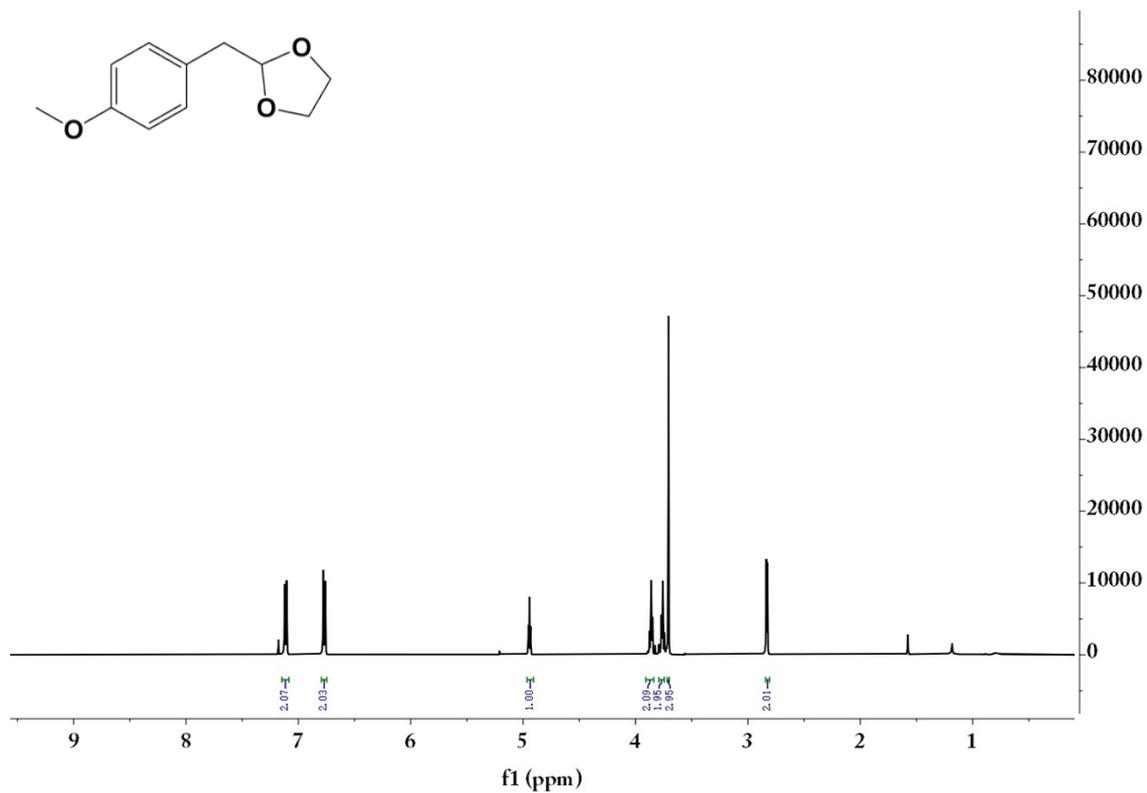


Fig.S23 ¹H NMR spectrum of 1b (1a acetal)

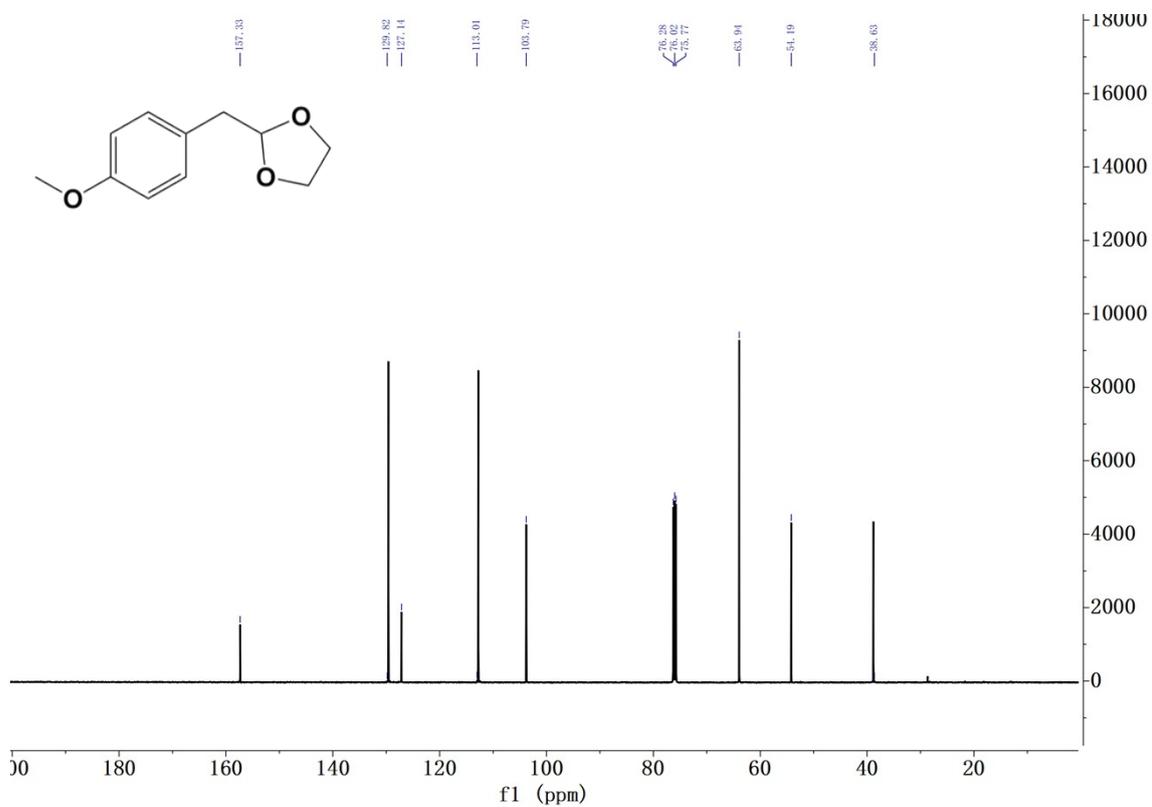


Fig.S24 ¹³C NMR spectrum of 1b (1a acetal)

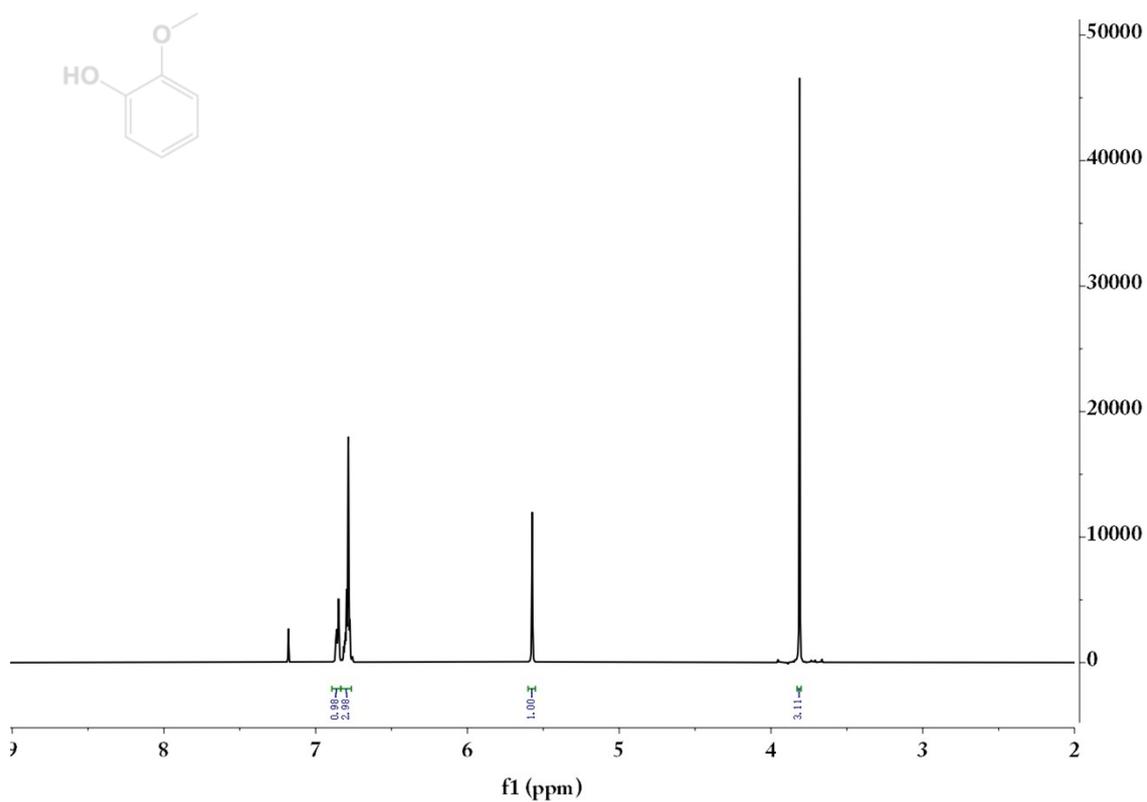


Fig.S25 ^1H NMR spectrum of 1c (1a guaiacol)

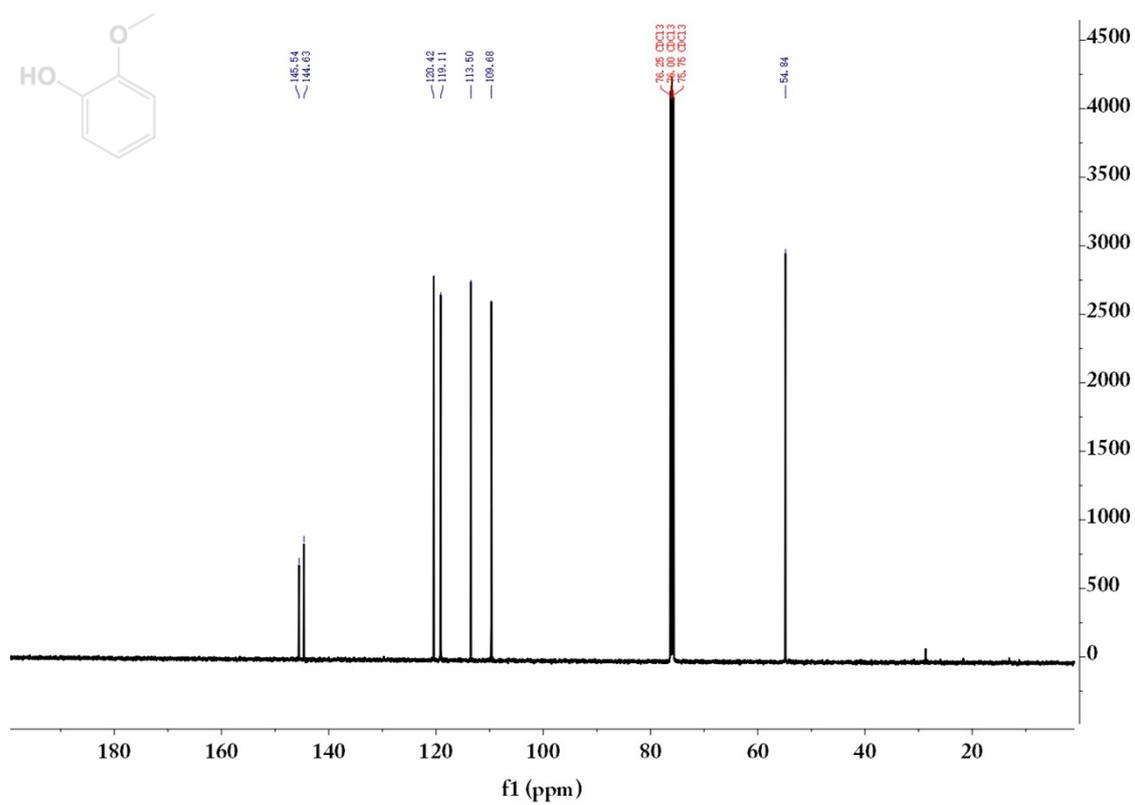


Fig.S26 ^{13}C NMR spectrum of 1c (1a guaiacol)

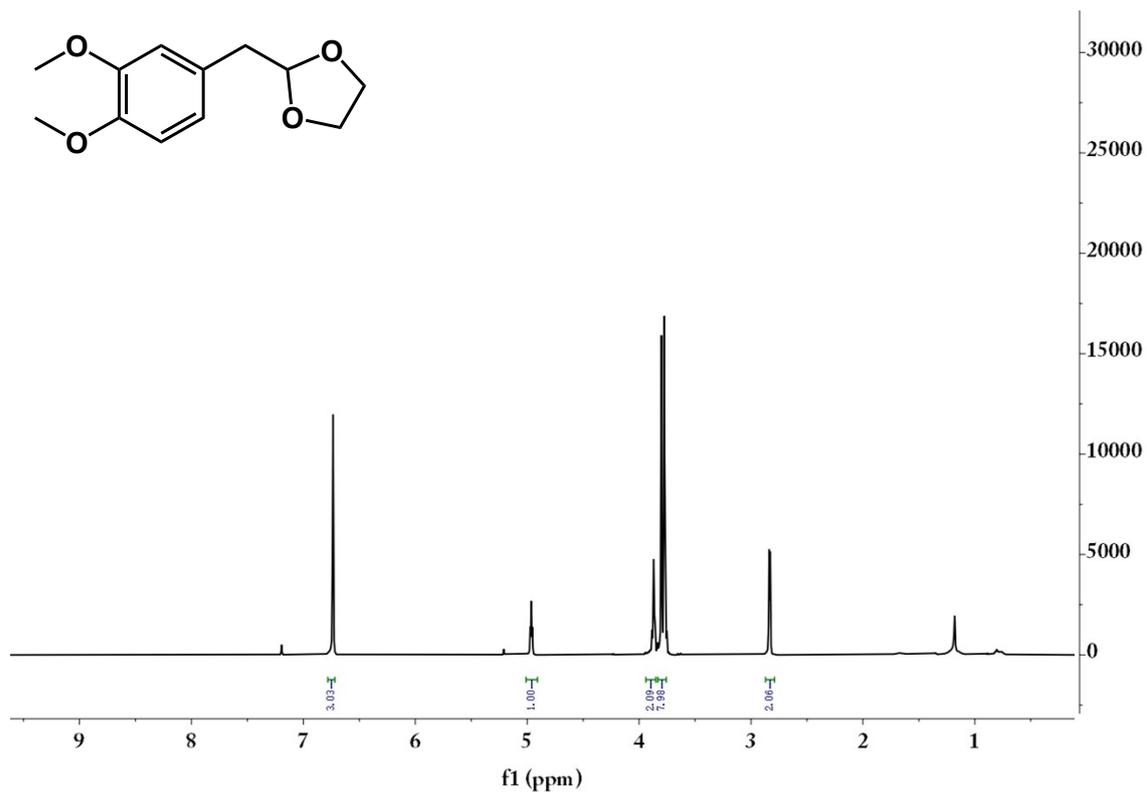


Fig.S27 ¹H NMR spectrum of 1b (2a acetal)

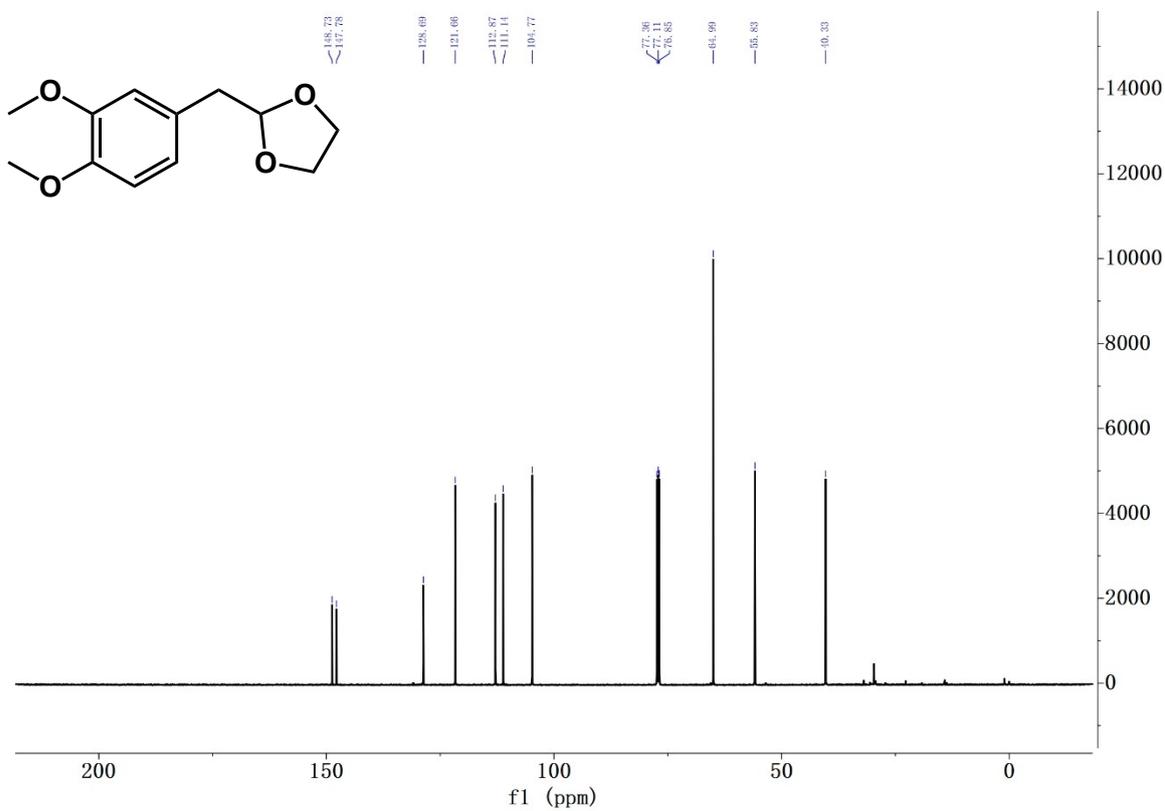


Fig.S28 ¹³C NMR spectrum of 2b (2a acetal)

2.2 Reaction of lignin model compound in biphasic DES

2.2.1 1a reaction

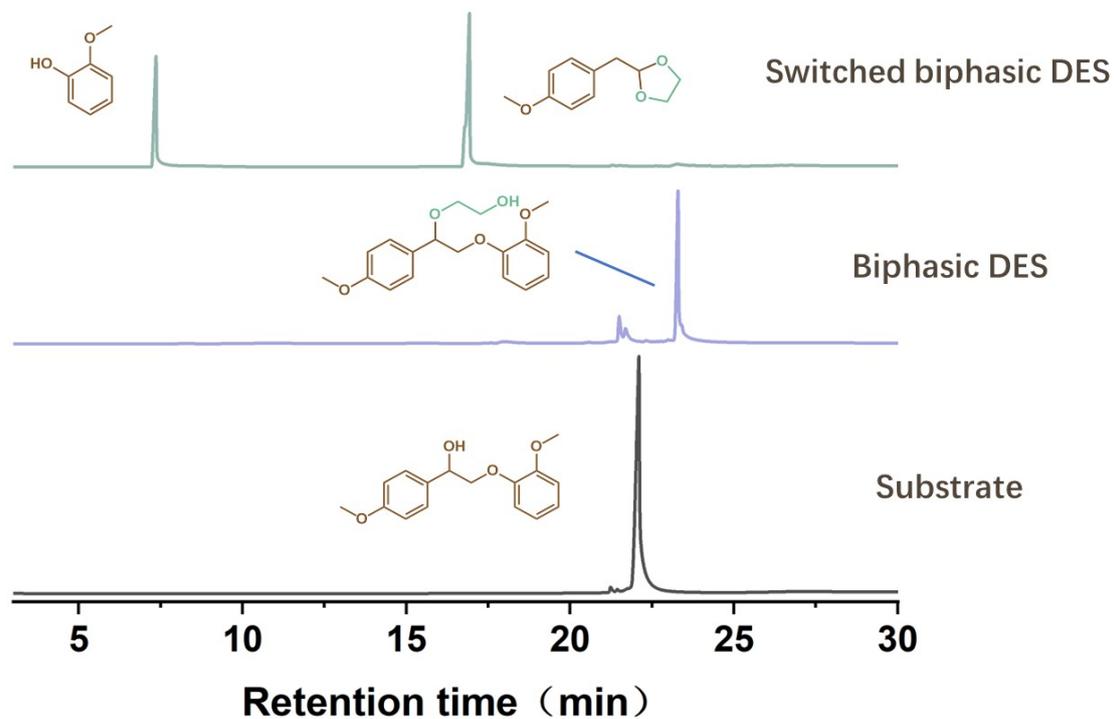
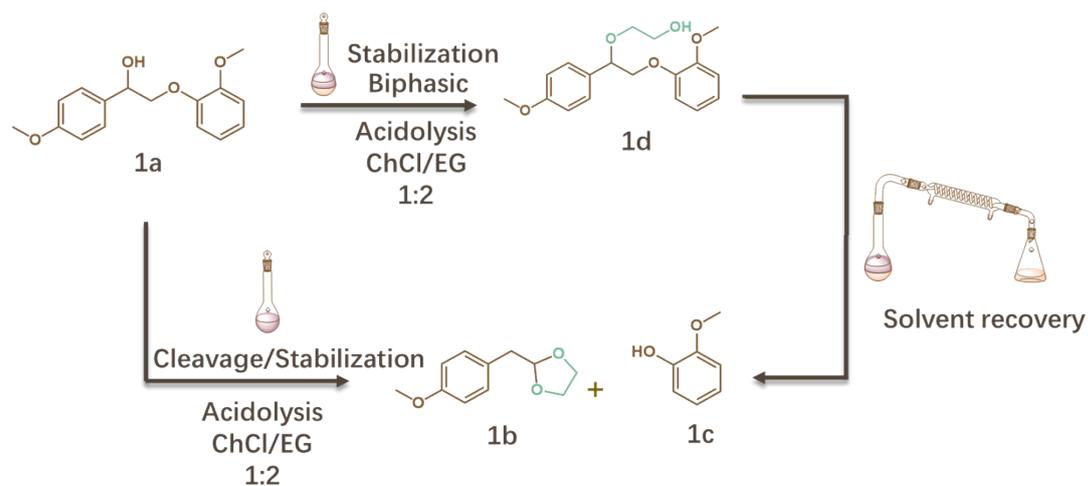


Fig.S29 GC spectra of two conversion paths for lignin model compound 1a

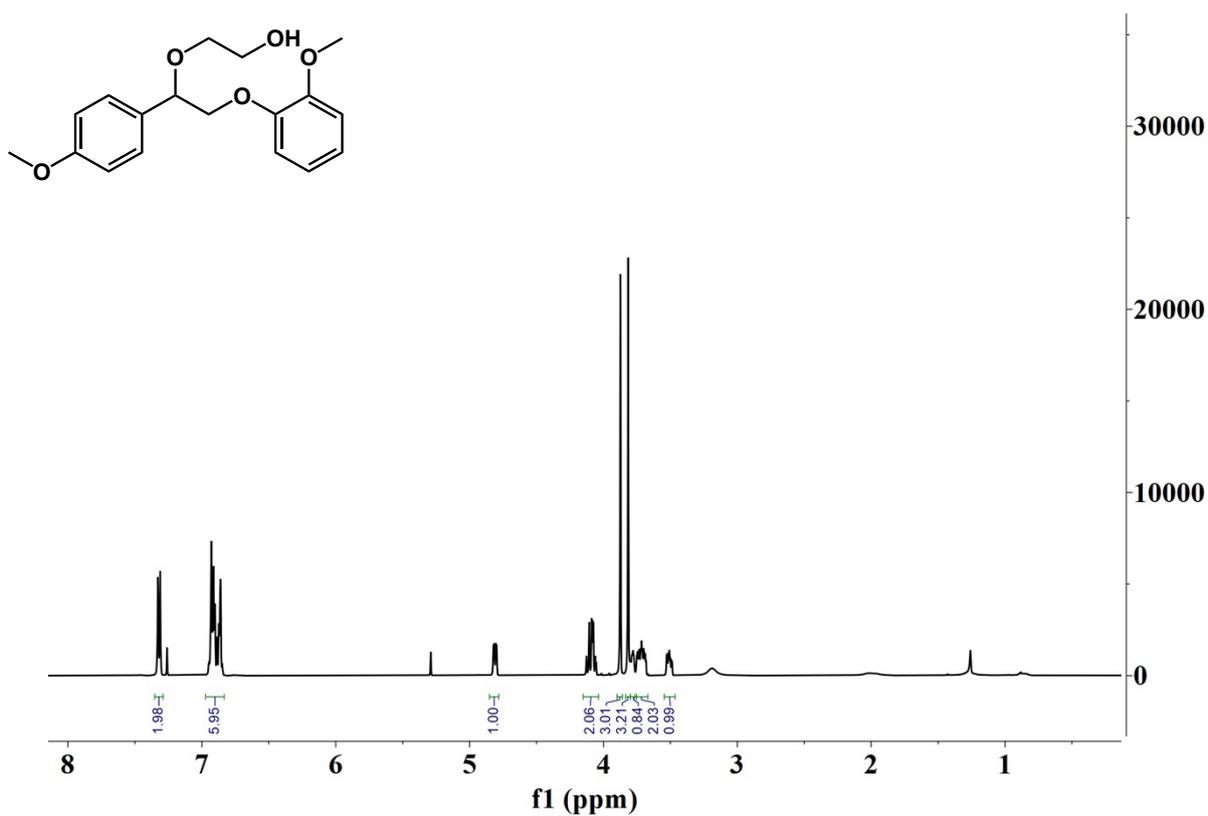


Fig.S30 ¹H NMR spectrum of 1d (1a biphasic reaction product)

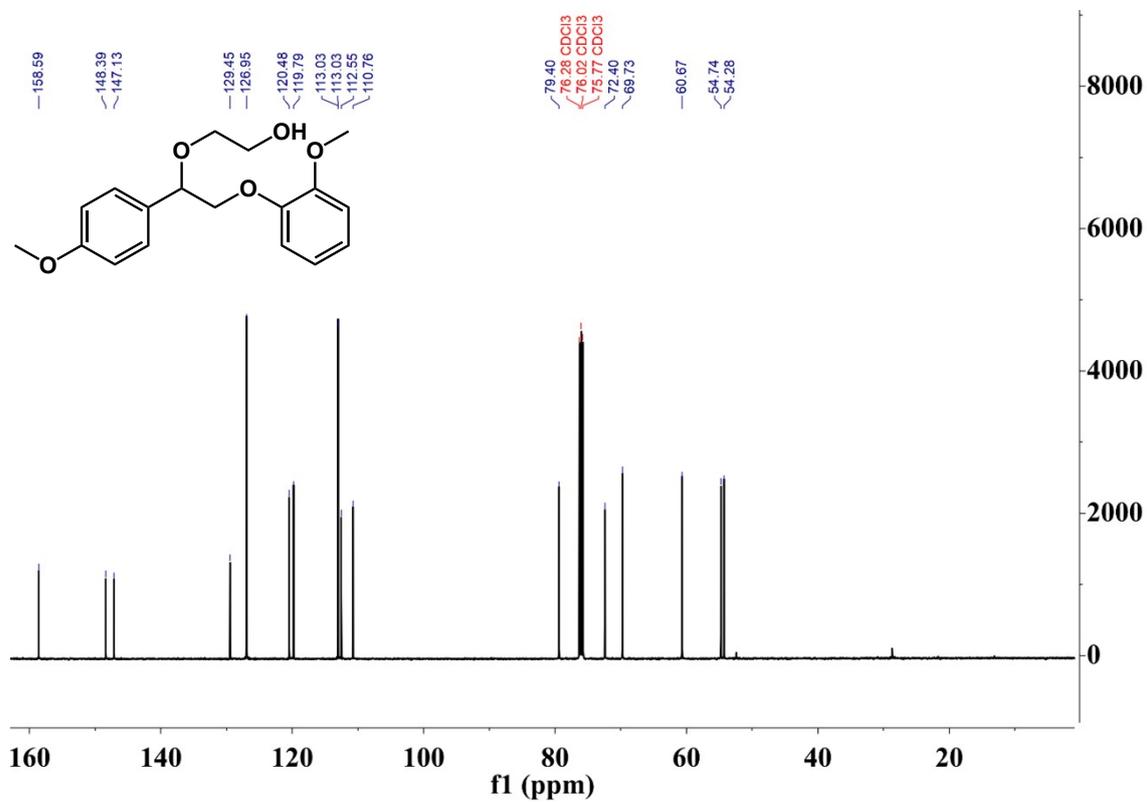


Fig.S31 ¹³C NMR spectrum of 1d (1a biphasic reaction product)

2.2.2 2a reaction

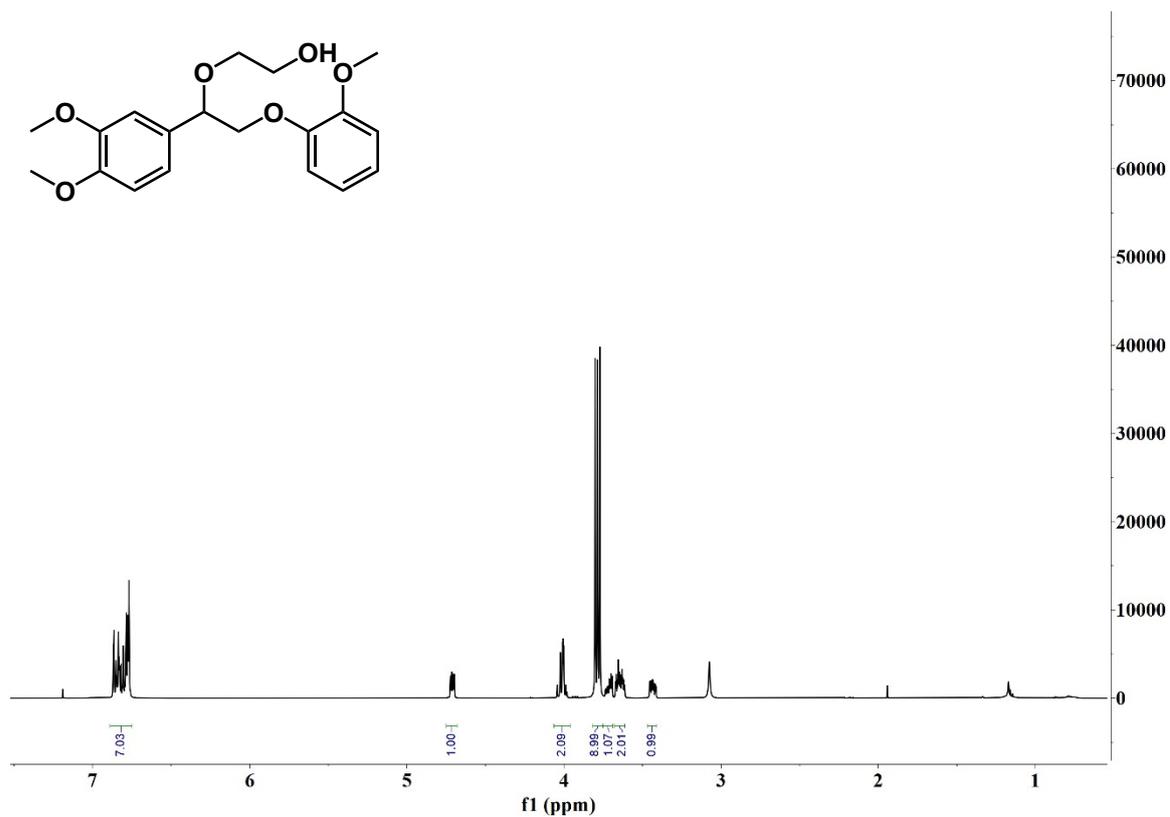


Fig.S32 ¹H NMR spectrum of 2d (2a biphasic reaction product)

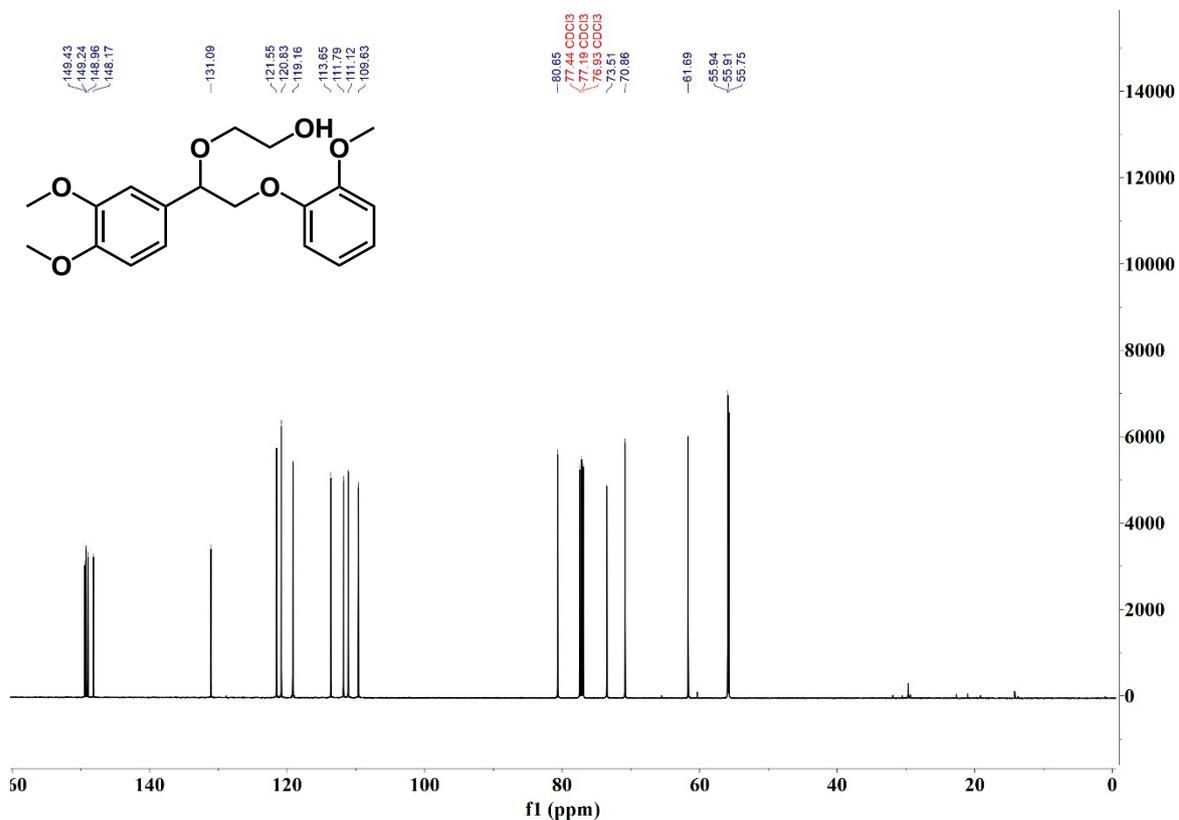


Fig.S33 ¹³C NMR spectrum of 2d (2a biphasic reaction product)

2.2.3 4a reaction

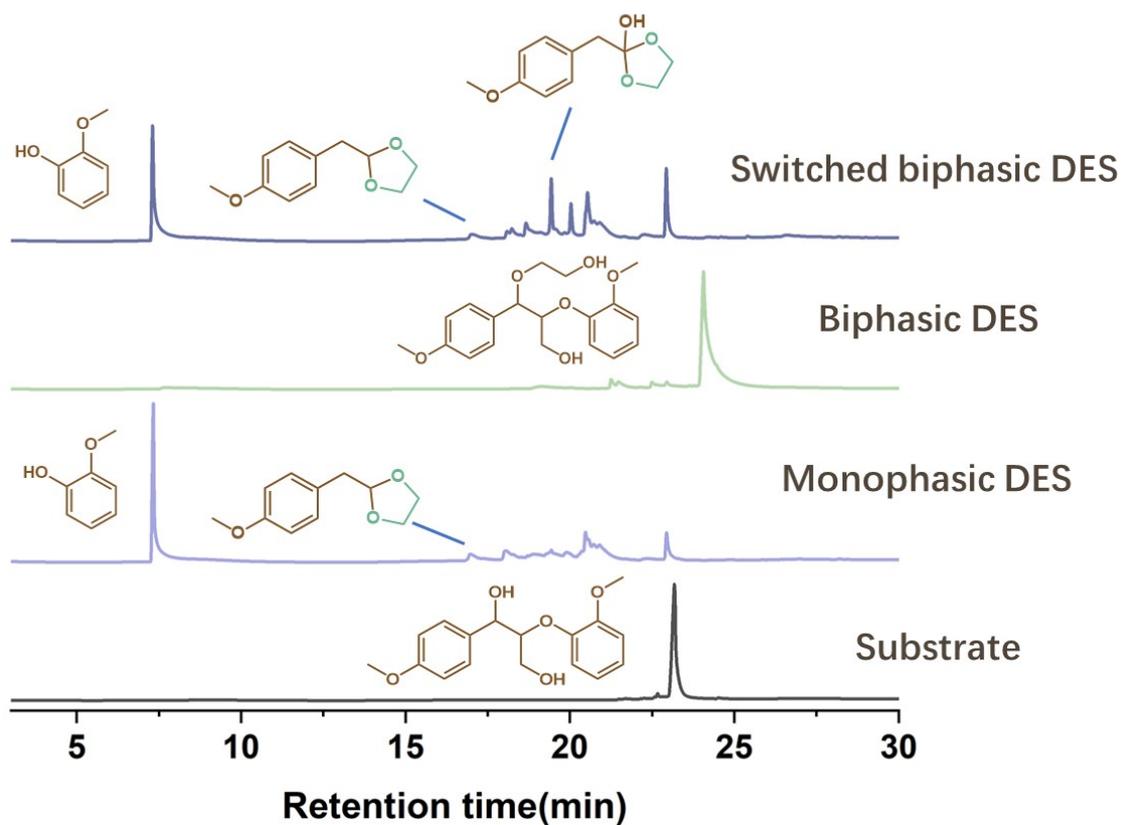


Fig.S34 GC spectra of two conversion paths for lignin model compound 4a

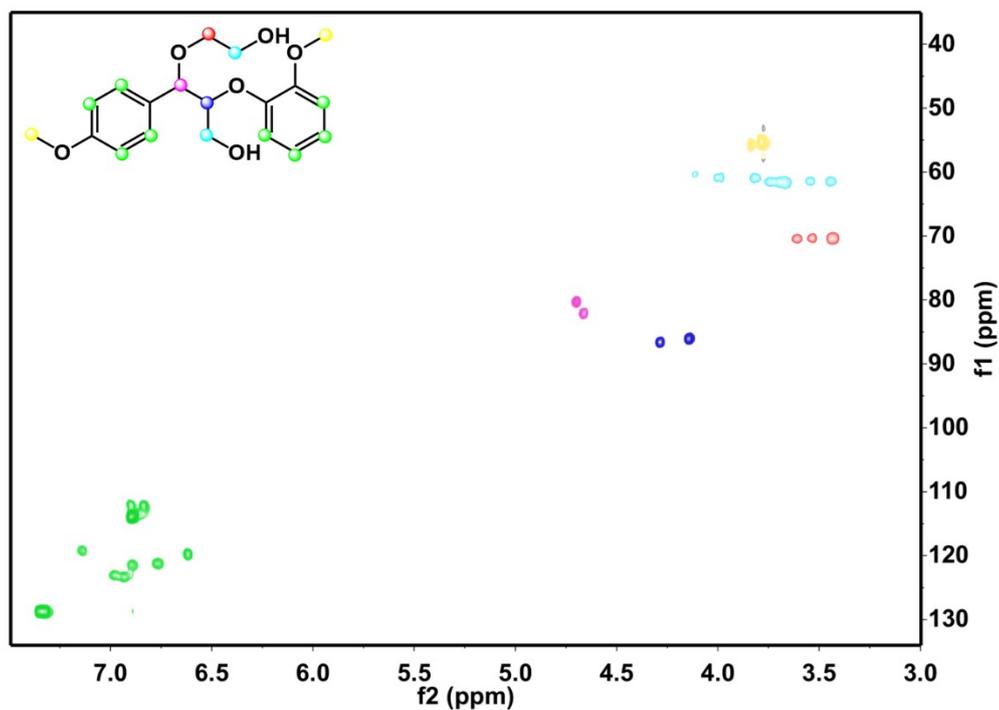


Fig.S35 HSQC NMR spectrum of 2d (4a biphasic reaction product)

2.3 Lignin reaction

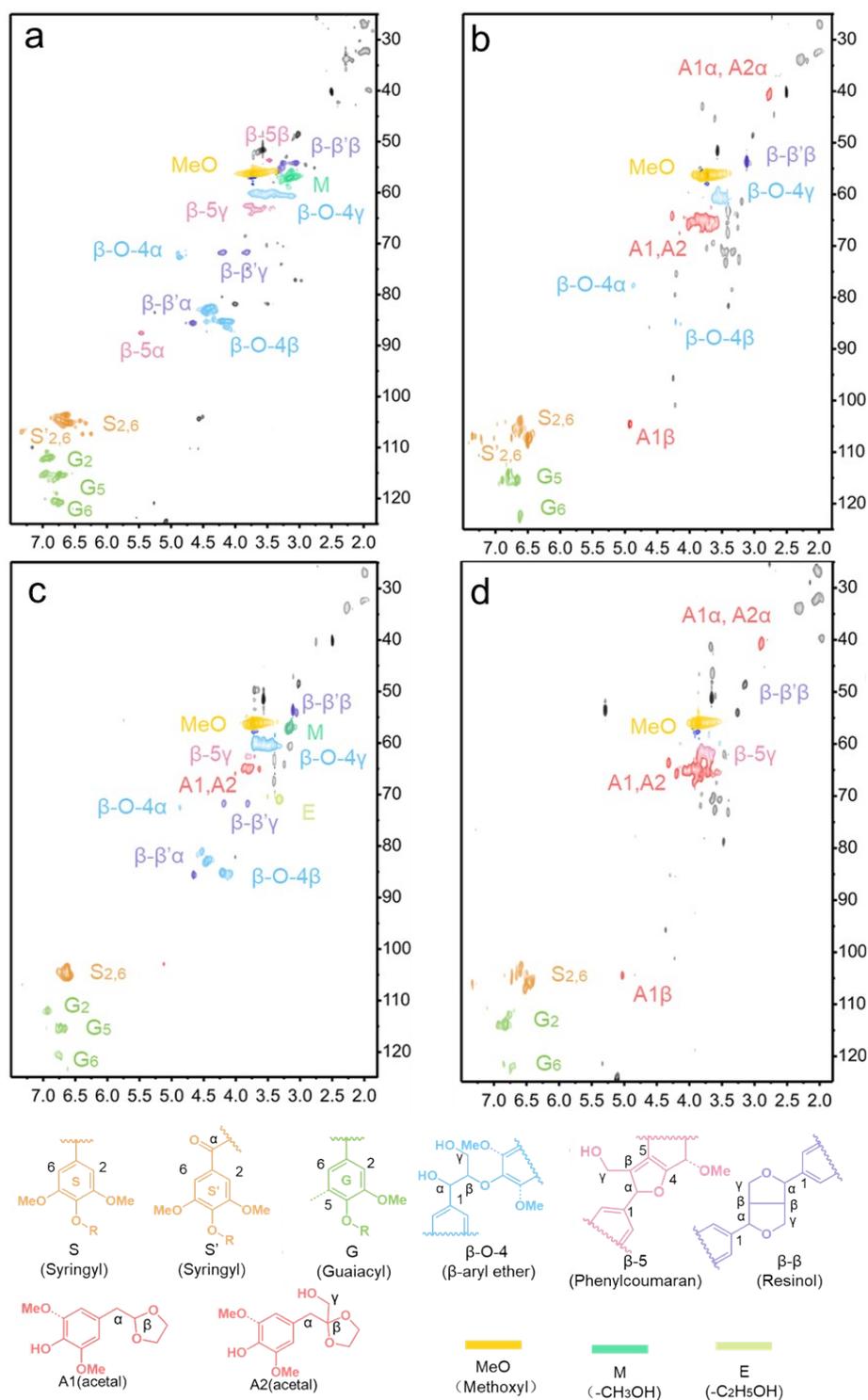


Fig.S36 2D-HSQC NMR spectra of lignin (a) Preparation of lignin from wood powder treated with methanol (b) Reaction results of lignin under DES acidolysis conditions (c) Reaction results of lignin in DES and DCM biphasic solvents (d) Lignin undergoes biphasic reaction followed by switched monophasic DES reaction.

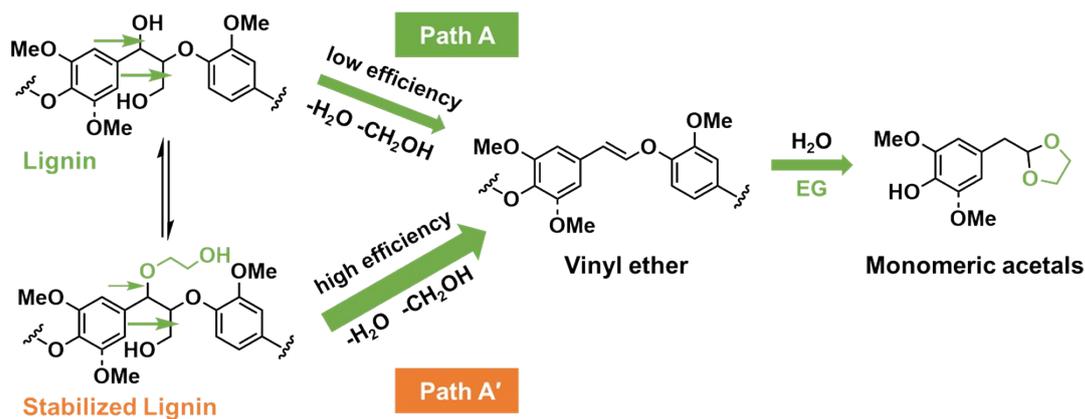


Fig. S37 Proposed reaction pathways of lignin from Path A and Path A'

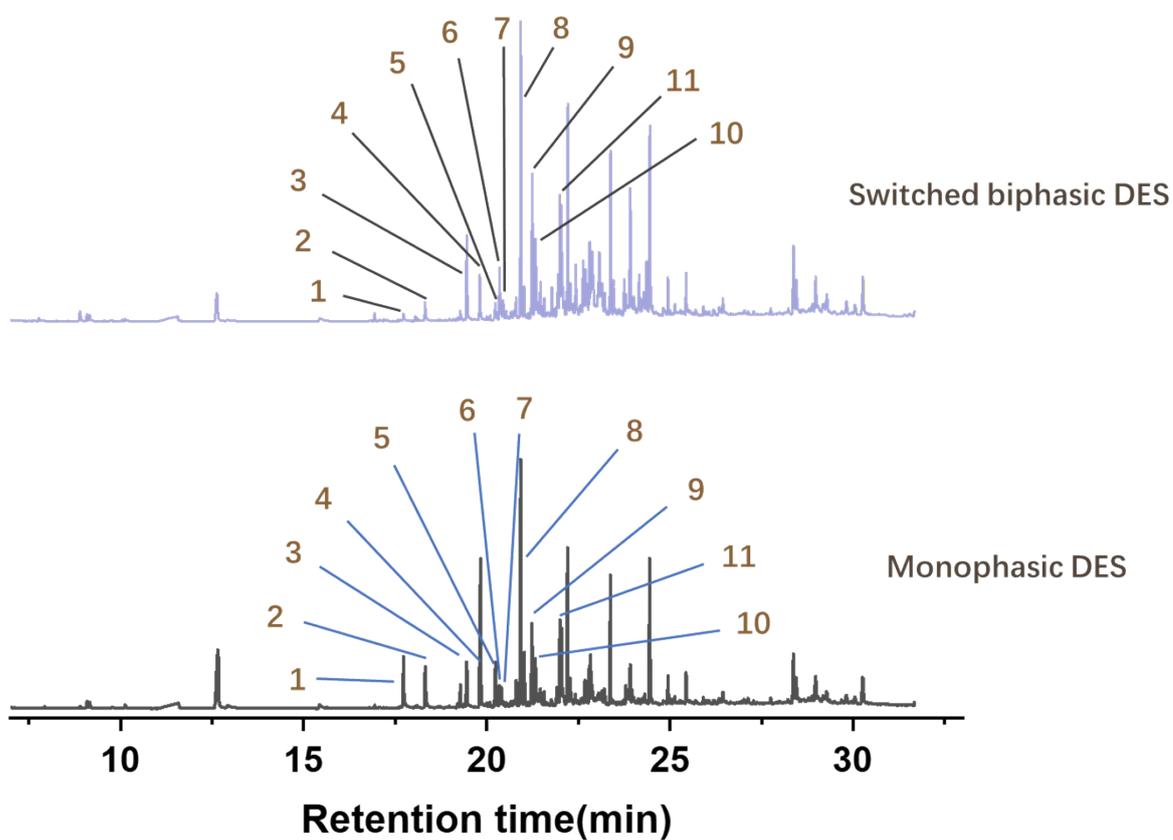


Fig.S38 GC-MS of lignin reaction products under Switched biphasic DES and monophasic DES acidolysis conditions respectively

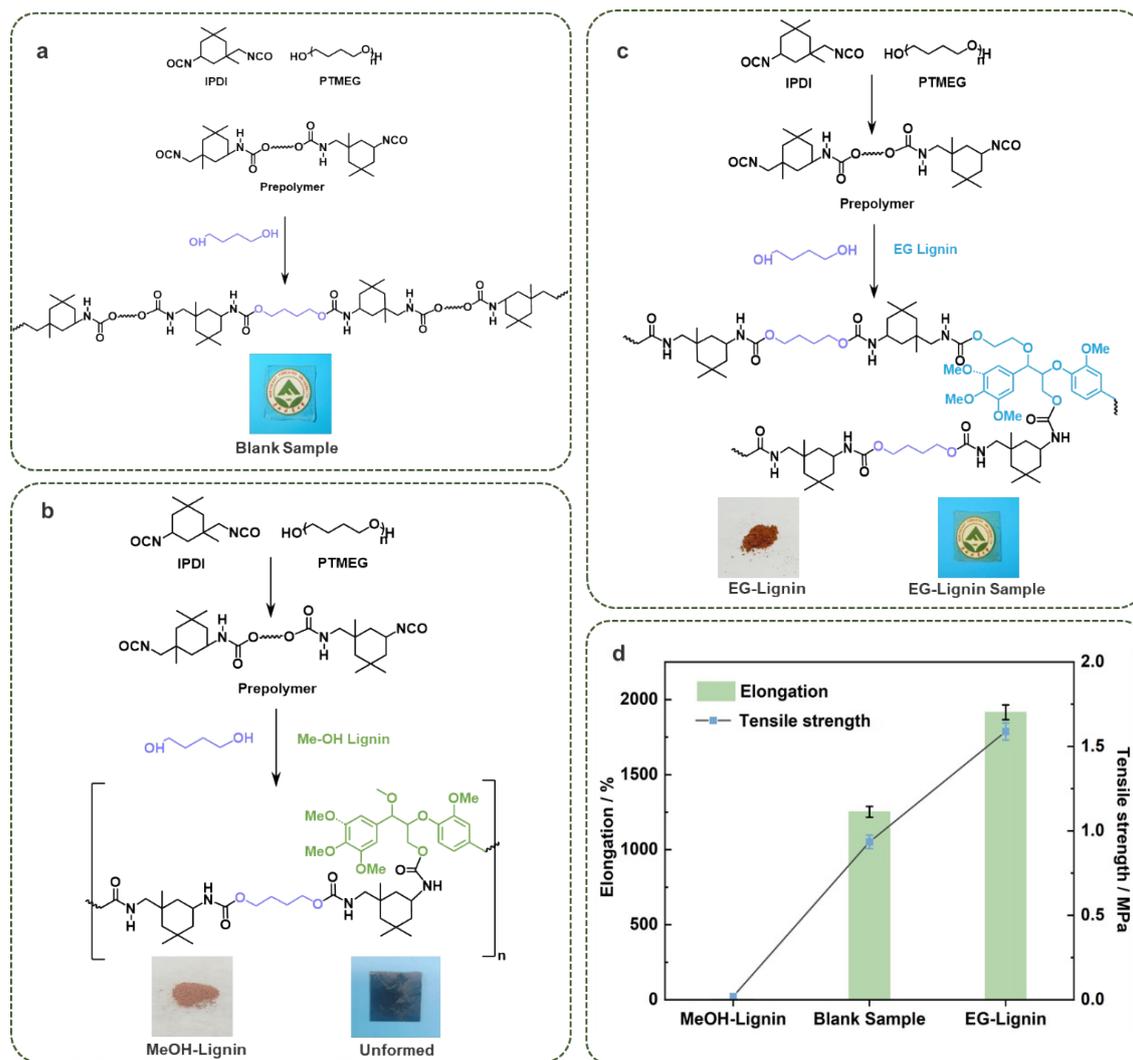
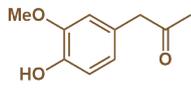
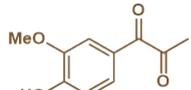
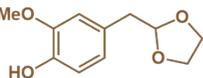
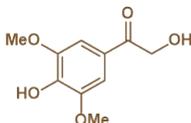
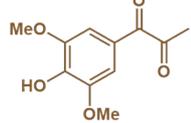
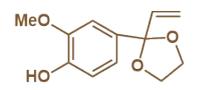
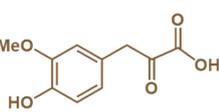
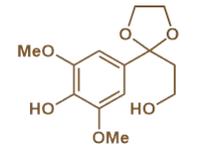
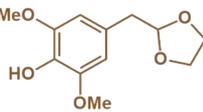
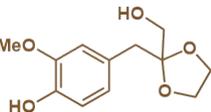
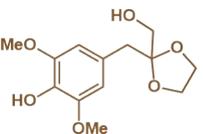


Fig. S39 Synthesis procedure of PU samples (a) Blank sample, (b) The sample with 10wt% methanosolv lignin (MeOH-lignin) incorporation, (c) the sample with 10wt% lignin polyols (EG-lignin) incorporation, and (d) mechanical performance of the prepared samples.

Table S3 Overview of GC-MS signals, identification, and designation obtained from the depolymerization using DES acidolysis and biphasic DES acidolysis conditions

Entry	Ret. ^a (min)	Ret. ^b (min)	Found mass (m/z)	Identification	Type of units
1	17.727	17.723	180		G
2	18.318	18.314	194		G
3	19.446	19.454	210		G
4	19.829	19.805	210		S
5	20.237	20.232	224		S
6	20.342	20.347	224		G
7	20.526	20.526	210		G
8	20.921	20.925	270		S
9	21.230	21.243	240		S
10	21.459	21.467	240		G
11	21.915	21.923	270		S

(a)DES acidolysis. (b) Biphasic reaction followed by switched monophasic DES reaction.