ARTICLE

Supplementary information

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A hemicellulose and lignin-first process for corn stover valorization catalyzed by aluminum sulfate in γ-butyrolactone/water co-solvent

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I. The organosolv fractionation of raw biomass

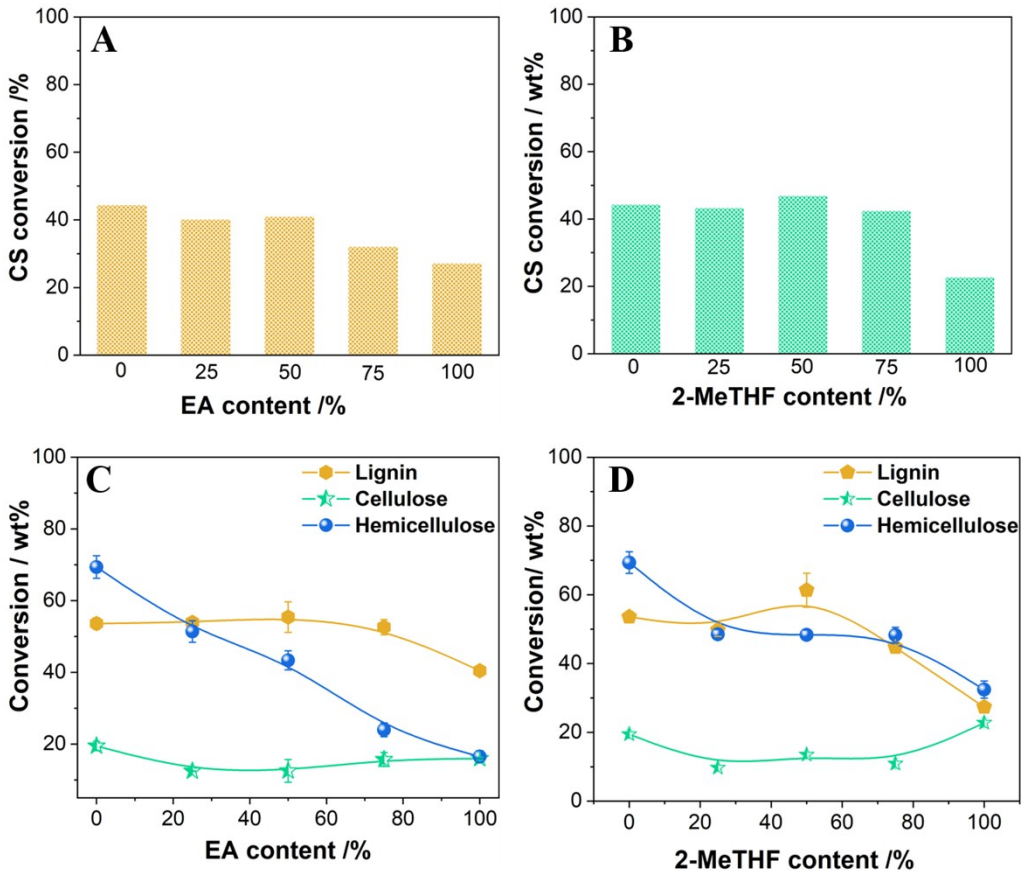


Figure S1 The transformation of corn stover and the three main components in corn stover at 160 °C for 2 h under EA/H_2O and 2-MeTHF/H_2O systems (Reaction condition: 3 g corn stover, 60 mL co-solvent with different organic solvent contents (0, 25, 50, 75 and 100%), 160 °C, 2 h)

II. Optimization of reaction conditions for corn stover fractionation

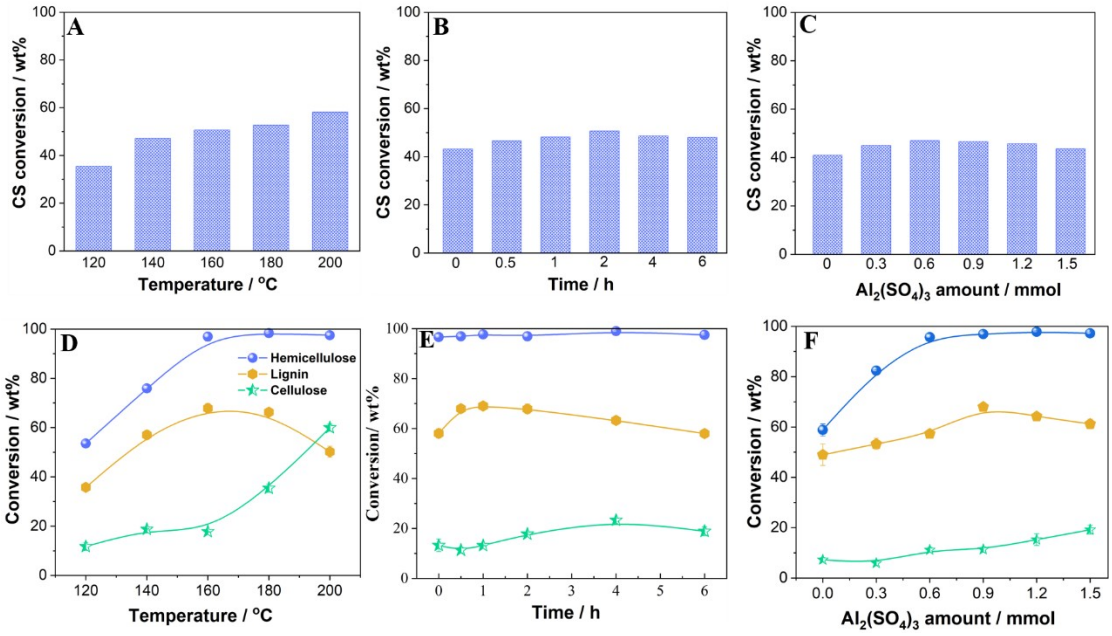


Figure S2 Effects of temperature (A and D), time (B and E) and $Al_2(SO_4)_3$ amounts (C and F) in 25% GBL/H_2O-$Al_2(SO_4)_3$ on the transformation of corn stover and the three main components in corn stover (A and D, 3 g corn stover, 60 mL 25% GBL/H_2O, 0.9 mmol $Al_2(SO_4)_3$, 120-200 °C for 2 h; B and E, 3 g corn stover, 60 mL 25% GBL/H_2O, 0.9 mmol $Al_2(SO_4)_3$, 160 °C for 0-6 h; C and F, 3 g corn stover, 60 mL 25% GBL/H_2O, 160 °C for 0.5 h; 0-1.5 mmol $Al_2(SO_4)_3$)

III. Ion strength of different solutions

Table S1 Ion strength of different solutions without considering salt hydrolysis

Sulfate salt solution	Ion strength (I)/ (mol/kg)[a]	Chloride salt solution	Ion strength (I)/ (mol/kg)[a]
H_2SO_4[b]	0.06	HCl	0.09
$Al_2(SO_4)_3$	0.31	$AlCl_3$	0.25
$Fe_2(SO_4)_3$	0.31	$FeCl_3$	0.25
K_2SO_4	0.19	KCl	0.12
Na_2SO_4	0.19	NaCl	0.12
$CaSO_4$	0.25	$CaCl_2$	0.19

[a] Ion strength of different solutions was calculated using the equation (I=1/2∑b(B)*z(B)^2, b(B) is the molar concentration (mol/kg) of B ion, Z(B) is ion valence of B); [b] Ion strength of H_2SO_4 which considered the secondary ionization is incomplete in Figure S3.

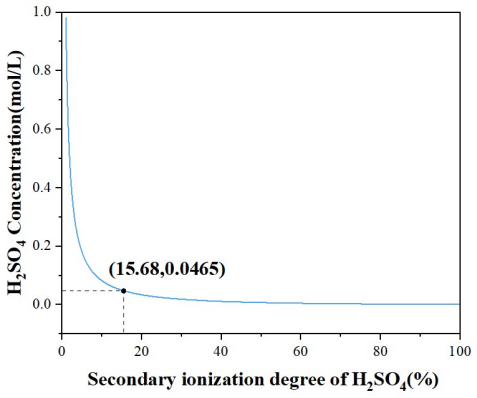


Figure S3 The relationship between H_2SO_4 concentration and its secondary ionization degree

H_2SO_4 is a binary strong acid with a two-stage ionization characteristic. As shown in Figure S3, the first ionization can be complete to produce H^+ and HSO_4^-, while the degree of secondary ionization is related to the concentration of H_2SO_4. The concentration of H_2SO_4 used in this work was 0.0465 mol/L, and the secondary ionization degree was 15.68%, indicating that the secondary ionization was incomplete.

IV. pH values of different salt solutions

Table S2 pH values of different solvent systems before and after reaction

Solvent systems	Initial pH	Final pH
25% GBL/H_2O	5.43	3.70
25% GBL/H_2O-H_2SO_4	1.45	1.63
25% GBL/H_2O-$Al_2(SO_4)_3$	2.97	1.99
25% GBL/H_2O-$Fe_2(SO_4)_3$	2.14	2.97
25% GBL/H_2O-K_2SO_4	5.21	3.72
25% GBL/H_2O-Na_2SO_4	5.06	3.70
25% GBL/H_2O-Ca_2SO_4	4.93	3.60
25% GBL/H_2O-HCl	1.12	1.42
25% GBL/H_2O-$AlCl_3$	2.86	2.28
25% GBL/H_2O-$FeCl_3$	1.84	2.70
25% GBL/H_2O-KCl	4.44	3.61
25% GBL/H_2O-NaCl	4.42	3.52
25% GBL/H_2O-$CaCl_2$	4.91	3.43

Reaction condition: 3 g corn stover, 60 mL 25% GBL/H_2O, sulfate salts with 2.8 mmol SO_4^{2-} or chloride salts with 5.6 mmol Cl^- or mineral acids (2.8 mmol H_2SO_4 and 5.6 mmol HCl), 160 °C for 2 h. pH values were measured after the complete dissolution of metal salts in water at room temperature (initial pH), and after reaction (final pH).

V. Quantum Chemical Calculation

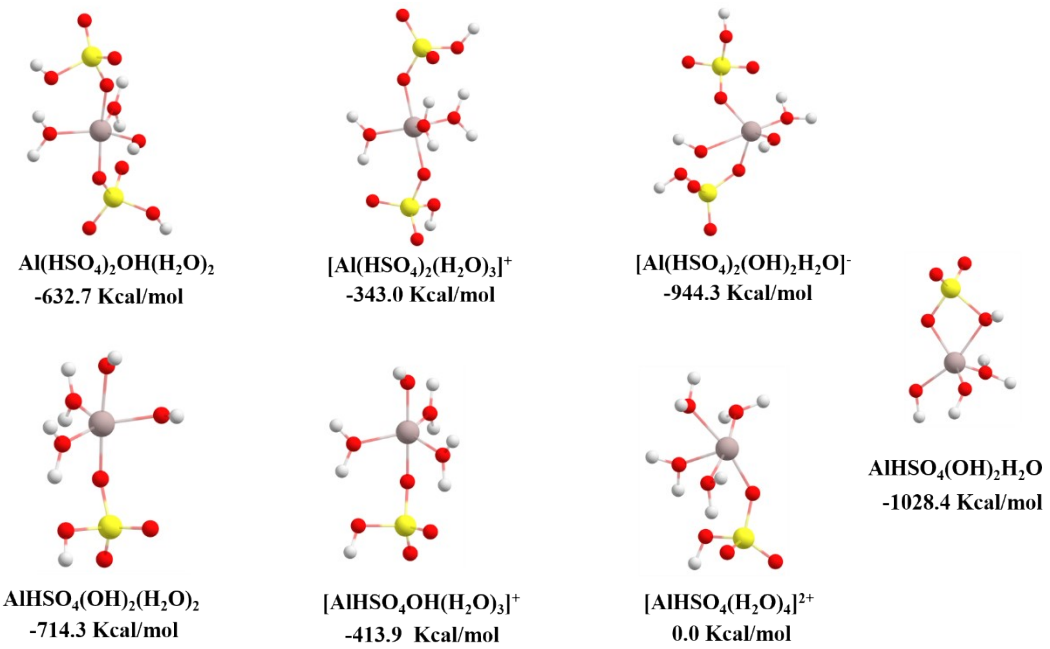


Figure S4 Geometric structures and the relative Gibbs free energy (ΔG, Kcal/mol) of possible $[Al(HSO_4)_p(OH)_m(H_2O)_n]^{3-m-p}$ species

VI. The yield of small molecular products mainly from hemicellulose

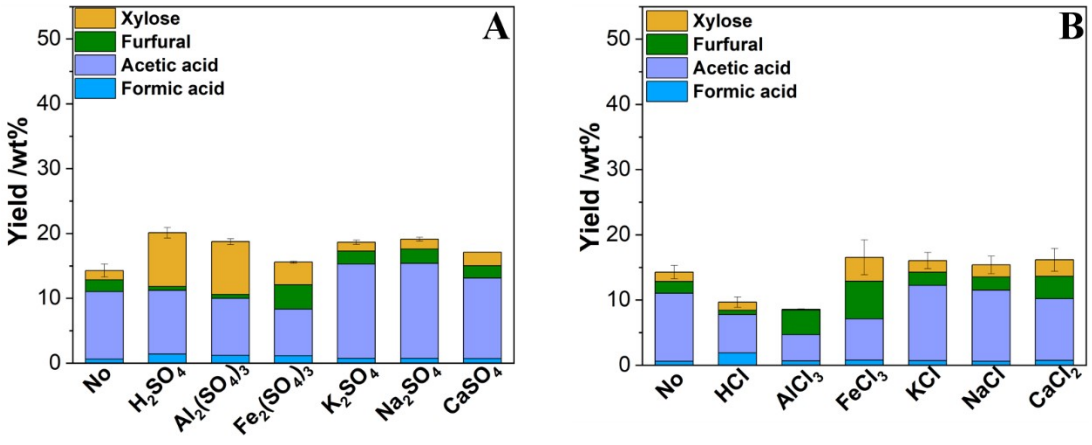


Figure S5 Effects of sulfate salts, chloride salts and mineral acids (H_2SO_4 and HCl) in 25% GBL/H_2O co-solvent on the yield of small molecular products mainly from hemicellulose in corn stover at 160 °C for 2 h (Reaction condition: 3 g corn stover, 60 mL 25% GBL/H_2O, 160 °C for 2 h, sulfate salts with 2.8 mmol SO_4^{2-} or chloride salts with 5.6 mmol Cl^- or mineral acids (2.8 mmol H_2SO_4 and 5.6 mmol HCl), the yield of small molecular products was based on the weight of corn stover)

VII. GC-FID analysis of monophenol yield from lignin

Table S3 The yield of monophenols obtained from different systems

Products	Yield/% (based on the weight of lignin)						
	H_2O[a]	25GBL[a]	50GBL[a]	75GBL[a]	100 GBL[a]	$Al_2(SO_4)_3$-2h[b]	$Al_2(SO_4)_3$-0.5h[c]
Phenol	0.000	0.026	0.058	0.103	0.172	0.075	0.045
O-cresol	0.051	1.375	11.969	5.251	1.009	0.029	0.000
2,3-dihydrobenzofuran	0.000	0.020	0.000	0.000	0.000	0.068	0.304
P-cresol	0.003	0.000	0.000	0.000	0.033	0.047	0.039
Guaiacol	0.000	0.117	0.274	0.392	0.963	0.046	0.042
4-ethylphenol	0.000	0.010	0.000	0.039	0.047	0.011	0.361
4-methyl guaiacol	0.000	0.038	0.046	0.050	0.217	0.049	0.269
4-vinylphenol	0.455	1.127	2.388	1.461	1.915	1.684	3.287
4-propyl phenol	0.007	0.009	0.133	0.160	0.351	0.385	1.770
4-ethyl guaiacol	0.000	0.028	0.079	0.000	0.083	0.187	0.418
4-vinyl guaiacol	0.574	1.184	1.994	0.884	0.690	2.055	4.317
Syringol	0.000	0.035	0.000	0.043	0.127	0.032	0.022
Eugenol	0.001	0.021	0.069	0.000	0.000	0.095	0.062
3-(4-Hydroxy-3-methoxyphenyl)-1-propanol	0.001	0.000	0.066	0.000	0.000	0.040	0.049
Syringaldehyde	0.014	0.000	0.000	0.000	0.000	0.135	0.187
4-(3-Hydroxypropyl)-2,6-dimethoxyphenol	0.010	0.000	0.000	0.000	0.000	0.000	0.033
Total yield	1.115	3.989	17.077	8.384	5.607	4.937	11.204

[a] GBL/H_2O co-solvent with different contents of GBL

[b] 25%GBL/H_2O with 0.9 mmol $Al_2(SO_4)_3$ at 160 °C for 2 h

[c] 25%GBL/H_2O with 0.9 mmol $Al_2(SO_4)_3$ at 160 °C for 0.5 h

VIII. GC-FID spectra

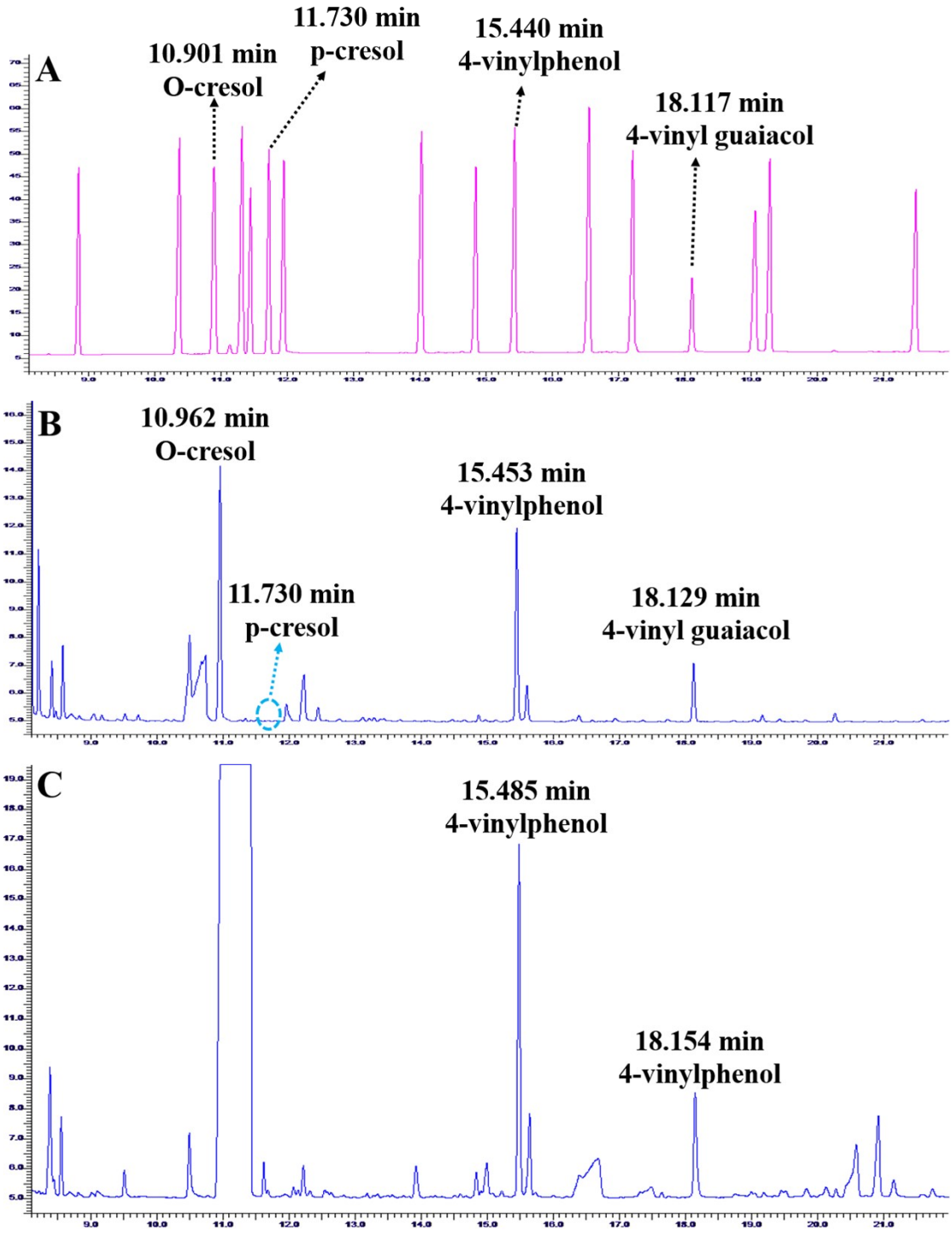


Figure S6 GC-FID spectra of monophenol mixture standards (A), liquid fraction obtained from 25% GBL/H_2O (B) and 25% GBL/H_2O-$Al_2(SO_4)_3$ (C) system

IX. 2D HSQC NMR analysis

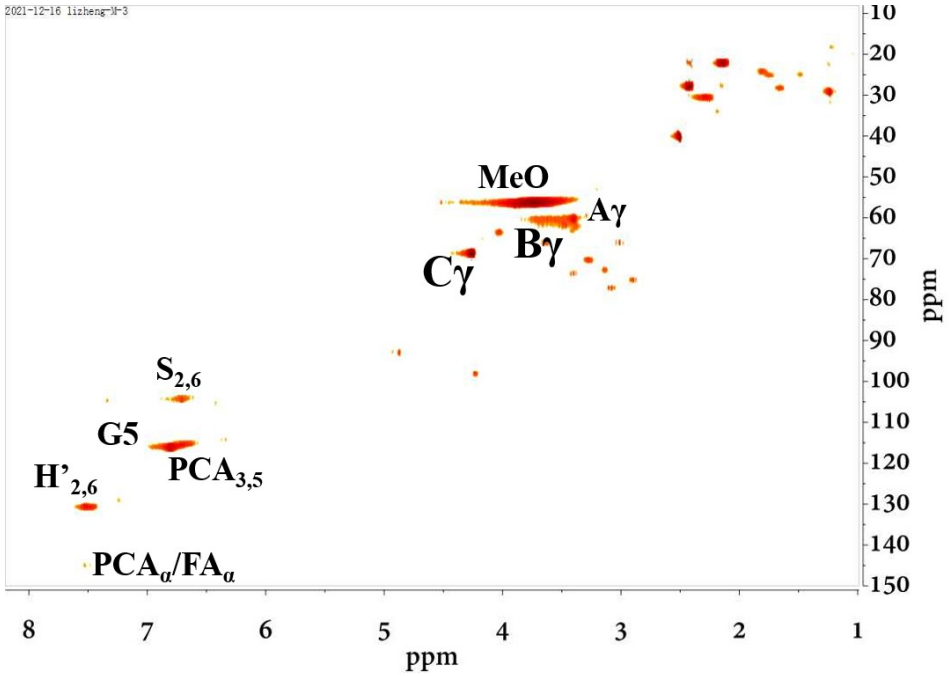


Figure S7 2D HSQC NMR results of liquid fraction obtained from 25% GBL/H_2O-$Al_2(SO_4)_3$ system at 160 °C for 0.5 h

Table S4 Assignment of main lignin ^{13}C-^{1}H correlation signals in 2D HSQC NMR spectra [1-2]

Lables	δ_C/ δ_H	Assignment
A_γ	59.8/3.61	C_γ-H_γ in β-O-4' structure(A)
A'_γ	63.0/4.36	C_γ–H_γ in γ-acylated β–O–4 (A')
B_γ	62.2/3.76	C_γ-H_γ in phenylcoumaran (B)
C_γ	71.2/3.82-4.18	C_γ–H_γ in β-β' resinol (C)
$H'_{2,6}$	130.8/7.56	$C_{2,6}$-$H_{2,6}$ in oxidized(C=O) p-hydroxyphenyl units(H')
$H_{2,6}$	128.2/7.19	$C_{2,6}$-$H_{2,6}$ in p-hydroxyphenyl units(H)
G_5	115.3/6.80	C_5-H_5 in guaiacyl units(G)
MeO	56.0/3.71	C-H in methoxyls
$PCA_{3,5}$	115.5/6.77	C_3-H_3 and C_5-H_5 in p-coumarate structure (PCA)
PCA_α/FA_α	144.4/7.51	C_α-H_α in p-coumarate structure (PCA) and ferulate (FA)
$S_{2,6}$	104.4/6.72	$C_{2,6}$-$H_{2,6}$ in syringyl units(S)

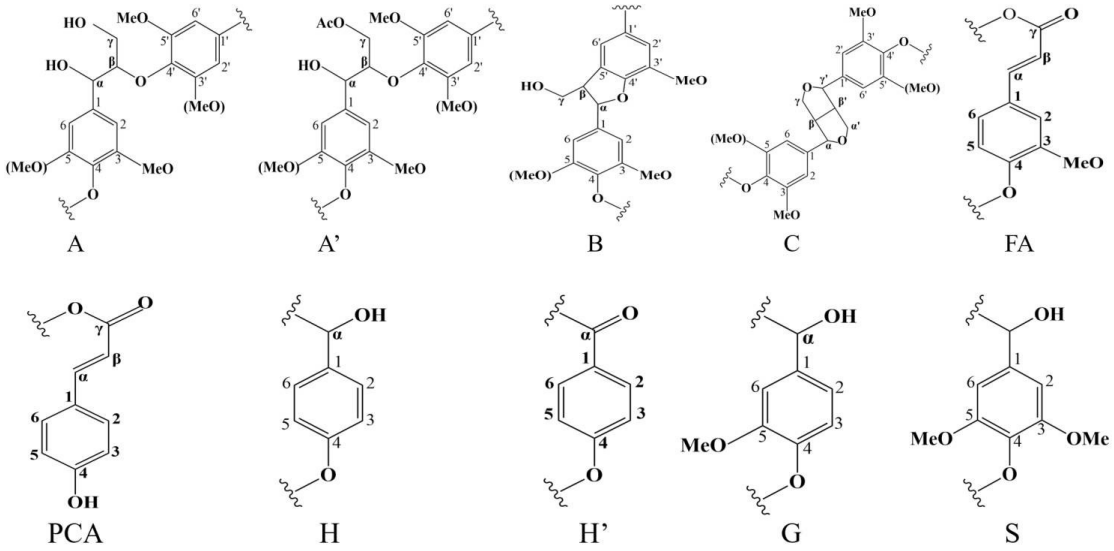


Figure S8 Main structures present in 2D HSQC NMR spectra assignment of Table S4

X. ESI-MS results

The lignin-derived oligomers according to the molecular weights described in Figure 4 (C-F) were listed below:

m/z(166.09)=m(148.05)+NH_4^+

m/z(182.06)=m(164.05)+NH_4^+

m/z(217.11)=m(194.06)+Na^+

m/z(261.13)=m(260.10)+H^+

m/z(283.16)=m(260.10)+Na^+

m/z(309.18)=m(290.12)+H_2O+H^+

m/z(325.15)=m(302.08)+Na^+

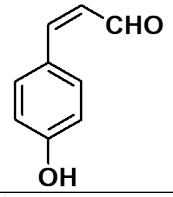
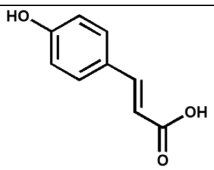
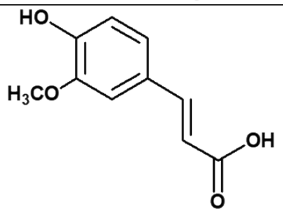
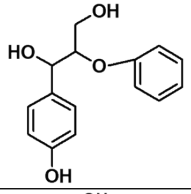
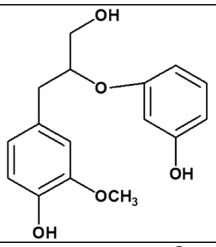
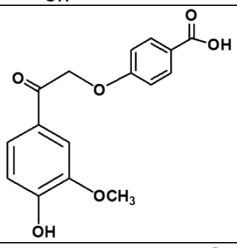
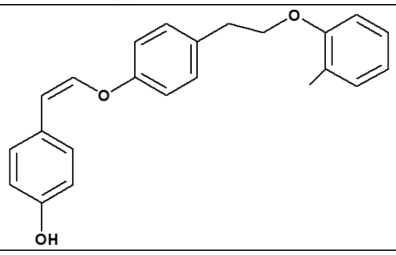
m/z(347.16)=m(346.16)+ H^+

m/z(365.16)=m(346.16)+H_2O+H^+

m/z(437.13)=m(3xylose-2H_2O)+Na^+=m(414.14) +Na^+

m/z(453.10)=m(3xylose-2H_2O)+K^+= m(414.14)+K^+

Table S5 Possible chemical structures of lignin-derived oligomers

Entry	Molecular weight	Molecular formula	Chemical structure
1	148.0524	$C_9H_8O_2$	
2	164.0473	$C_9H_8O_3$	
3	194.0579	$C_{10}H_{10}O_4$	
4	260.1049	$C_{15}H_{16}O_4$	
5	290.1154	$C_{16}H_{18}O_5$	
6	302.0790	$C_{16}H_{14}O_6$	
7	346.1569	$C_{23}H_{22}O_3$	

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