

## Supplementary data

**Table S1.** Assignments of carbon chemical shifts ( $\delta$ , ppm) in  $^{13}\text{C}$  NMR spectrum of MWL and formosolv lignin.

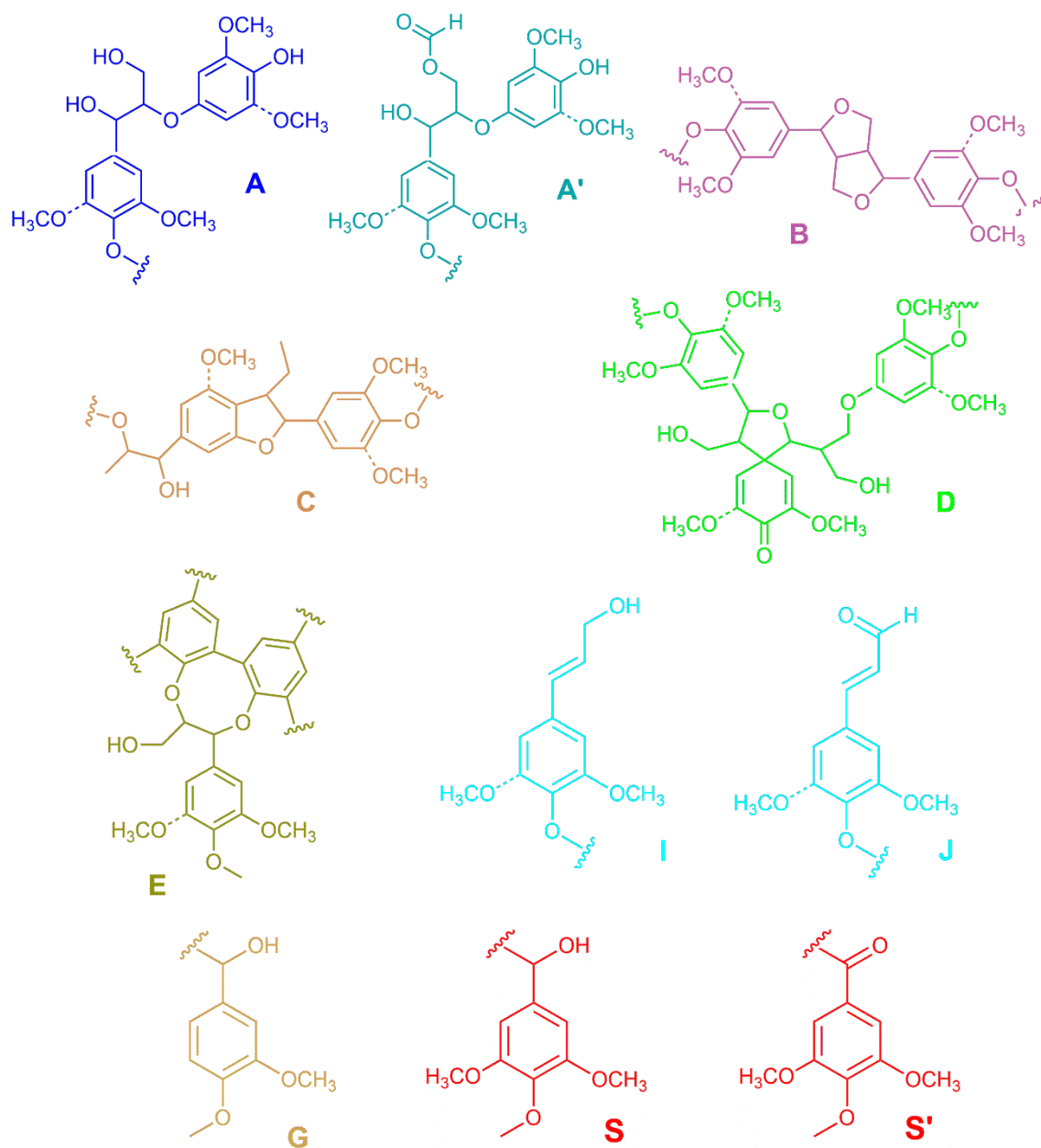
$\delta$ (ppm)	Assignment
<b>Clusters</b>	
161-141	Aromatic C-O
141-124	Aromatic C-C
124-100	Aromatic C-H
169.6	Carbonyl carbon in acetates
162.4, 163.4	Formate groups
158, 161, 167	p-hydroxyphenyl groups
152.2	C <sub>3,5</sub> in etherified S units
149.1	C <sub>3</sub> in etherified G units
138.2	C <sub>4</sub> eth. G + C <sub>3,5</sub> non eth. S + C <sub>4</sub> in S
119.1	Aromatic C <sub>6</sub> of the G structures
114.7	Aromatic C <sub>5</sub> of the G structures
111.1	Aromatic C <sub>2</sub> of the G structures
104.0	C <sub>2,6</sub> in S units
71.9	C <sub><math>\alpha</math></sub> of $\beta$ -O-4'
70-90	C <sub><math>\beta</math></sub> in $\beta$ -O-4', C <sub><math>\alpha</math></sub> in $\beta$ -5' and $\beta$ - $\beta'$
65.6	C in units with oxidized C <sub><math>\alpha</math></sub>
62.9	C in substructures $\beta$ -O-4'
55.9	OCH <sub>3</sub>
29.1	Methylene carbons in $\alpha,\beta$
21.1	CH <sub>3</sub> in acetates
15.3	C <sub>1</sub> -(CH <sub>3</sub> ) of the propyl chain

**Table S2.** Assignments of  $^{13}\text{C}$ - $^1\text{H}$  correlation signals in the HSQC NMR spectrum of the obtained lignin fractions.

Labels	$\delta_{\text{C}}/\delta_{\text{H}}$ (ppm)	Assignment
C	53.9/3.5	C -H in phenylcoumaran substructures (C)
B	54.3/3.1	C -H in resinol substructures (B)
-OCH <sub>3</sub>	56.1/3.2-56.2/3.7	C-H in methoxyls
E	56.0/3.41	C -H in $\beta$ -1' substructures (E)
A	60.2/3.7-60.4/3.2	C -H in substructures (A)
D	60.4/2.7	C -H in spirodienone substructures (D)
I	62.1/4.1	C -H in cinnamyl (sinapyl/coniferyl) alcohol end-groups (I)

B	71.6/3.8-71.7/4.2	C -H in resinol substructures (B)
A (G)	71.8/4.7	C -H in $\beta$ -O-4' linked to a G unit (A)
A (S)	72.5/4.9	C -H in $\beta$ -O-4' linked to a S unit (A)
D	81.8/5.04	C -H in spirodienone substructures (D)
E	83.4/4.8	C -H in dibenzodioxin substructures (E)
B	85.5/4.7	C -H in resinol substructures (B)
A (G)	86.5/4.1	C -H in $\beta$ -O-4' linked to a G unit (A)
A (S)	84.4/4.3	C -H in $\beta$ -O-4' linked to a S unit (A)
E	86.6/3.8	C -H in dibenzodioxin substructures (E)
C	87.5/5.5	C -H in phenylcoumaran substructures (C)
S <sub>2,6</sub>	104.4/6.7	C <sub>2,6</sub> -H <sub>2,6</sub> in etherified syringyl units (S)
J <sub>2,6-5</sub>	106.7/7.0	Cinnamyl aldehyde end-groups in S-units (J)
S' <sub>2,6</sub>	107.1/7.3-107.0/7.2	C <sub>2,6</sub> -H <sub>2,6</sub> in syringyl units with $\alpha$ oxidization (S')
G <sub>2</sub>	111.6/7.0	C <sub>2</sub> -H <sub>2</sub> in guaiacyl units (G)
G <sub>5</sub>	115.5/6.7-115.8/6.9	C <sub>5</sub> -H <sub>5</sub> in guaiacyl units (G)
G <sub>6</sub>	119.7/6.8	C <sub>6</sub> -H <sub>5</sub> in guaiacyl units (G)
J	126.7/6.8	C -H in cinnamyl (sinapyl/coniferyl) aldehyde end-groups (J)
I	128.9/6.2	C -H in cinnamyl (sinapyl/coniferyl) alcohol end-groups (I)
H <sub>2,6</sub>	128.9/7.2	<i>p</i> -hydroxyphenyl units (H)
I	129.2/6.5	C -H in cinnamyl (sinapyl/coniferyl) alcohol end-groups (I)
F	162.0/8.2	Formates (F)

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**Figure S1.** Main substructures identified in MWL and PFL of Paulownia. **(A)** Arylglycerol -aryl ethers; **(A')** -OH acylated arylglycerol -aryl ethers; **(B)** resinols; **(C)** phenylcoumarans; **(D)** spirodienones; **(E)** dibenzodioxocins; **(I)** cinnamyl alcohol end-groups; **(J)** cinnamaldehyde end-groups; **(G)** guaiacyl units; **(S)** syringyl units; **(S')**, oxidized syringyl units bearing a carbonyl group at C .

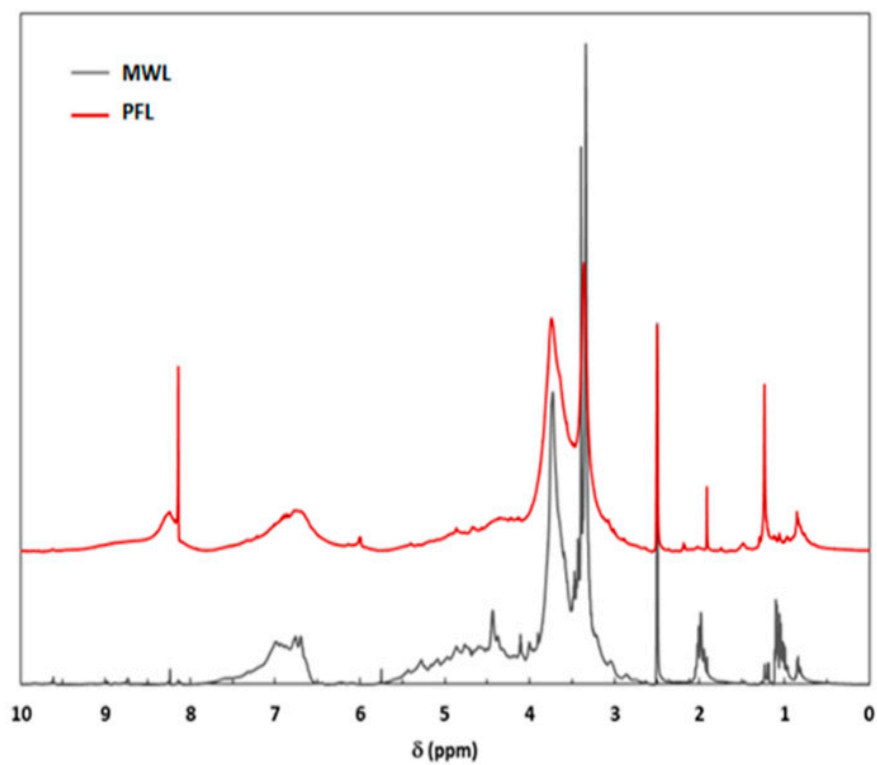


Figure S2. <sup>1</sup>H NMR spectra of MWL and formosolv Paulownia lignin.

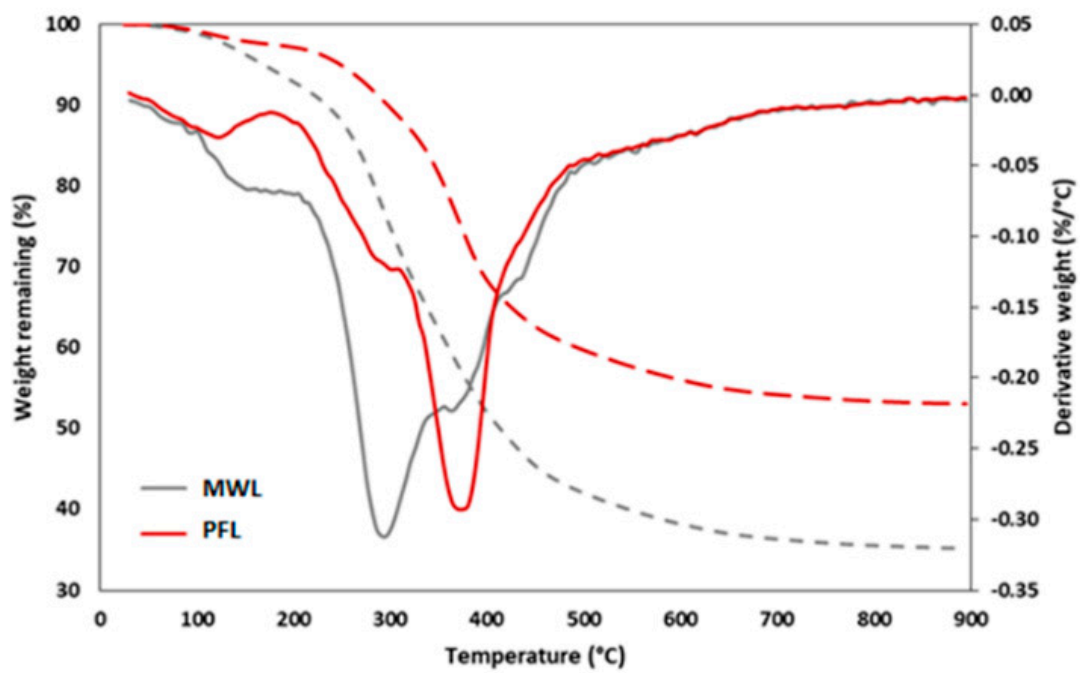


Figure S3. TGA (dashed) and DTG (bold) curves of MWL and PFL.