ELECTRONIC SUPPLEMENTARY INFORMATION FOR

New insights into the structure and composition of technical lignins: a comparative characterisation study

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A. Experimental

Chemicals and materials

Details of chemicals and reagents, used in the three laboratories are described below:

LAB1: ECN

For the organosolv experiments, ethanol 96% v/v was purchased from Merck or Cargill (Alcohol Fortior). An average purity of 94wt% (specified purity of 92.6–95.2wt%) was used in the calculations, H_2SO_4 was purchased from Merck (Emsure 98% for analysis).

For compositional analysis the following chemicals were used: H_2SO_4 from Boom 72% p.a, $BaCO_3$ (Merck, EMSURE® ACS, Reag. Ph. Eur. analytical reagent), and sugar standards: Glucose (Sigma >99.5%), Xylose (Fluka >98%), Mannose, Arabinose, Galactose and Rhamnose (L-rhamnose monohydrate) (all Fluka, HPLC grade, >99%).

For SEC, defined poly(styrene sulphonate) sodium salt standards from Polymer Standards Service (SPS) GmbH (range 1100-32900 g/mol) as well as phenol (GC grade, Sigma-Aldrich ≥99.5%) were used for calibration. 0.5 M NaOH eluent was prepared with anhydrous NaOH pellets (reagent grade, ≥98%, Sigma-Aldrich) and degassed with N_2.

LAB2: WUR

For ^{31}P NMR high grade DMF (anhydrous, 99.8%), pyridine (anhydrous, 99.8%), cyclohexanol (ReagentPlus®, 99%), chromium(III) acetylacetonate (99.99%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphopholane (95%), and $CDCl_3$ (99.8%D, contains 0.03% TMS) were purchased from Sigma-Aldrich.

For alkaline SEC, poly(styrene sulphonate) sodium salt standards were obtained from Polymer Standards Service (SPS) GmbH (range 891 - 258000 g/mol), and phenol (≥99.5%; GC grade) was purchased from Sigma-Aldrich. 50% NaOH solution in water (Emsure® analytical reagent) was obtained from Merck.

For organic SEC, polystyrene standards ranging from 580-3040000 g/mol were obtained from Pressure Chemical Co. and Polymer Laboratories (EasyVials). PMMA standards ranging from 550 - 2140000 g/mol were obtained from Agilent Technologies (EasyVials). The 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) and THF were purchased from Apollo Scientific Limited and Sigma-Aldrich, respectively.

LAB3: UU

Most of the chemicals, reagents and model compounds for [^{1}H;^{13}C]-HSQC identification were purchased from Sigma Aldrich: molecular sieves 3Å (8 to 12 mesh), acetic anhydride (≥99%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%), pyridine (99%), 1-methoxy-4-[2-(4-methoxyphenyl)ethenyl]benzene, 2-furfuraldehyde (99%), 5-hydroxymethylfurfural (99%), chromium(III) acetylacetonate (97%, Acros).

5-methoxymethylfurfural was provided by Avantium (The Netherlands). Deuterated DMSO-d_6 and Chloroform-d_3 were obtained from Buchem. The THF eluent (SEC Method F) was stabilized with 250 ppm of 2,6-di-tert-butyl-4-methyl phenol (BHT) Fischer Scientific and 1% (v/v) of acetic acid.

Lignins

Kraft lignin INDULIN AT (softwood, Meadwestvaco, US) and soda lignin Protobind™ 1000 (mixed wheat straw/ Sarkanda grass, GreenValue S.A., Switzerland) were obtained commercially. Alcell™ organosolv lignin (mixed hardwoods (maple, birch and poplar)) was obtained from Repap Technology, Canada. The three organosolv lignins were extracted from wheat straw (Spain), poplar (supplied by the Kenniscentrum Papier en Karton), and spruce (Denmark) using the acid-catalysed ethanol-based organosolv process developed by the Energy research Centre of the Netherlands (ECN). The wheat straw, poplar wood chips and spruce were dried and cut into < 10 mm, < 4 mm and < 6 mm particles, respectively. The composition of the feedstocks was determined as described previously[1] and is given in Table S1. The organosolv procedure and lignin isolation methods have been reported in detail elsewhere.[1,2] In short, all three feedstocks were pulped at 190 °C for 60 min using H_2SO_4 acidified, 60 wt% aqueous ethanol in a 20 L batch autoclave reactor (Büchi Glas Uster AG, Switzerland). The specific process conditions applied and fractionation results are given in Table S2. According to the biomass source used, the organosolv lignins are labelled OS-W (wheat straw), OS-P (poplar) and OS-S (spruce).

Table S1. Composition of biomass feedstocks used for organosolv process (wt% dry biomass)

Biomass	Extractives		Carbohydrates					Lignin		Ash	Reference
	H_2O	EtOH	Glucan	Xylan	Galactan	Arabinan	Mannan	AIL	ASL		
Wheat straw	11.2	2.0	34.6	21.5	0.5	2.1	0.2	15.1	1.0	8.5	[3]
Poplar	3.8	1.4	48.2	13.7	0.5	<0.2	2.6	20.0	1.9	0.6	NA
Spruce	6.4	0.9	41.6	3.6	1.2	<0.2	10.4	27.3	0.3	0.3	NA

Table S2. Key properties of lignin production

Lignin	Organosolv process conditions			Fractionation results	
	Biomass	L/S (L/kg)[a]	H_2SO_4 (mM)	Pulp yield (% dw)	Lignin yield (%)[b]
OS-W	Wheat straw	11.0	20	47.9	81.8
OS-P	Poplar	6.6	20	44.2	67.2
OS-S	Spruce	5.0	10	51.7	50.7

[a] Liquid-to-solid ratio based on dry weight (dw) biomass feedstock.
[b] Based on lignin content feedstock.

Compositions

The residual carbohydrate content in the lignin samples was analysed following a modified hydrolysis protocol based on TAPPI methods T 222 and 249 (1999),[4] as described previously.[5] First, the material was subjected to hydrolysis in 12 M H_2SO_4 at 30 °C for 1 h and subsequently in 1 M H_2SO_4 at 100 °C for 3 h. The acid-insoluble residue was gravimetrically determined and the ash content herein was quantified after overnight calcination at 550 °C. The acid-insoluble lignin (AIL) content was defined as the amount of ash-free Klason lignin. The hydrolysate was analysed for acid-soluble lignin (ASL) by UV-VIS absorption spectroscopy at 205 nm and the monomeric reducing sugars by High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection (HPAEC-PAD).[6] The ash content of the

lignins samples was determined by calcination at 550 °C in a muffle furnace or by thermogravimetric analysis (TGA).

Elemental analysis

The C, H, N and O elemental composition was measured with an elemental analyser (Carlo Erba Instruments FLASH EA 1112, Wigan, UK). Cl, F and Br were determined using ion chromatography (Dionex IC25, column Dionex AS18) according to NEN-EN-ISO 10304-1 following bomb combustion in a calorimeter (Parr 6300) and subsequent water washing of the combustion residues. The inorganic elemental composition was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Thermo ICAP 6000). The lignins were digested using HNO_3/$HClO_4$/HF before ICP analysis.

FT-IR

Fourier transform infrared spectroscopy measurements were carried out at room temperature on a Bruker Tensor 27 instrument. FTIR data were recorded with a deuterated triglycerine sulphate (DTGS) detector. The samples were recorded using a KBr pellet in transmission mode. The optical resolution of the IR spectra was 4 cm^{-1} and 16 scans were accumulated for each spectrum.

Pyro-GC-MS

Pyrolysis-GC-MS analysis was carried out on an Agilent 7890A 5975C GC/MS equipped with a GERSTEL Thermal Desorption/pyrolysis module and an MPS autosampler. Pyrolysis was performed at 500°C and a polar GC column was used for separation (Phenomenex ZBWAXPlus, 30 m x 0.25 mm x 0.25 µm) using helium as carrier gas. After 5 min at 50 °C, the GC oven temperature was raised to 245 °C with a rate of 10 °C/min. The MS was in electron ionisation (EI) mode, standard electron energy (70 eV) scanning from 29 to 500 amu. Peak deconvolution of the full GC-MS spectrum was performed and the results were verified against the NIST MS library. GC peak identification was performed based on retention times of calibration standards. Finally, the relative occurrence of each identified component was determined based on the peak area of its most prominent mass fragment in the MS spectrum.

NMR

For the ^{31}P-NMR measurements, the lignin samples were analysed in duplicate using the standard phosphitylation procedure.[7,8] A dried solvent mixture composed of pyridine/deuterated chloroform (1.6/1.0 v/v) was protected from moisture with 3 Å molecular sieves. 40 mg of dried lignin was dissolved in the solvent mixture at room temperature overnight under continuous stirring. Stock solutions of the internal standard (cholesterol or cyclohexanol, 19 mg/mL) and relaxation reagent (chromium (III) acetylacetonate, 11.4 mg/mL) were prepared separately using the solvent mixture for dissolution. 200 µl and 50 µL were respectively added to the lignin mixture. Prior analysis, 100 µL of derivatisation reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2- dioxaphospholane) was added and the mixture transferred into a 5-mm-OD NMR tube. ^{31}P NMR spectra were obtained on a Varian 400 MHz NMR spectrometer using a standard phosphorus pulse

programme with a relaxation delay of 10 s and 512 acquired scans. Chemical shifts were referenced from the sharp signal arising from the reaction product between residual water and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane at 132.2 ppm.
The 2D HSQC NMR spectra were acquired on a Bruker Avance II 600 MHz spectrometer equipped with a 5 mm CPTCI ^{1}H-^{13}C/^{15}N/^{2}H cryogenic probe with z-gradients at 25 °C using the Q-CAHSQC pulse program.[9] Matrices of 2048 data points for the ^{1}H-dimension and 128 data points for the ^{13}C-dimension were collected with a relaxation delay of 6 s and spectral widths from 13 to -1 ppm and from 160 to 0 ppm for the ^{1}H and ^{13}C dimensions, respectively. The lignins were dissolved in DMSO-d_6 after overnight stirring (200 mg/750 µL) and chemical shifts were referenced to the solvent signal (2.50/39.5 ppm). The spectra were processed using MestReNova software. Prior to Fourier transformation, FIDs were apodised with a π/2 sine square bell function in both dimensions and zero-filled up to 512 points in the ^{13}C-dimension and 4096 points in the ^{1}H-dimension. A semi-quantitative analysis of the HSQC spectra was performed by integration of correlations peaks in the different regions of the spectra with MestReNova. The relative quantity of side chains involved in the inter-unit and terminal substructures was expressed as a number per 100 aromatic units (S+G).

Calculation method for linkage quantification by 2D [^{1}H;^{13}C]-HSQC NMR

Part of the aromatic region is defined as internal standard and the amount of linkages and units are expressed as a number per 100 aromatic units (S+G). As the area of the $S_{2,6}$ correlation peak corresponds to twice the amount of syringyl units (i.e. $S_{2,6}$ peak contains S_2 and S_6 correlations)[10], half of this value was taken. The integral value obtained for $S_{2,6}/2 + G_2$ is then set to 100 Ar.

The amount of linkages and units, expressed as a number per 100 aromatic units (Ar column in Table 3), are determined using the equation:

$$Ar\ X = \frac{\int^{*} X}{100Ar} \times 100 = \frac{\int^{*} X}{\int^{*} S + \int^{*} G} \times 100$$

$\int^{*}$ correspond to the integrals expressed per number of correlations as shown in the following table .

Linkage/unit	Chemical shift of the integrated peak δC/δH (ppm)	The integrals expressed per number of correlations ($\int^{*}$)
β-O-4 (A)	71.9/4.9	$\int_{A\alpha}$
β-5 (B)	87.7/5.5	$\int_{B\alpha}$
β-β (C)	85.5/4.6	$\int_{C\alpha}$
Syringyl (S)	104.2/6.7	$\int_{S2,6}/2$
Guaiacyl (G)	110.2/6.9	$\int_{G2}$
p-hydroxyphenyl (H)	128.2/7.2	$\int_{H2,6}/2$
Tricin (T)	99.5/66.2	$\int_{T6}$
p-benzoate (Pb)	131.6/7.7	$\int_{PB2,6}/2$
p-coumarate (PCA)	130.1/7.5	$\int_{PCA2,6}/2$
Stilbene (St)	126.6/6.9	$\int_{St\alpha,\beta}/2$

In the aliphatic oxygenated region, interunit linkages were estimated from Cα−Hα correlations to avoid possible interference from homonuclear $^{1}H–^{1}H$ couplings as previously described in the literature[11]

Molar mass determination

The molar mass distributions of the lignins as well as acetylated lignins were determined with seven different SEC methods (A-G). A summary of the analytical conditions is given in Table 4. Lignin acetylation, required for methods F-H, was performed using a standard protocol.[12] SEC method A made use of an alkaline eluent. For separation, a column (7.8 mm ID x 300 mm) was packed with 30 µm porous polymer beads (Toyopearl HW-55 F).[5,7] Separation was carried out at 40 °C with a flow rate of 1 mL/min 0.5 M NaOH. Sodium polystyrene sulphonate standards and phenol were used for calibration. Method A' is identical to A, but carried out in a different laboratory. Method B was performed with a PSS MCX column with the same flow and temperature settings as listed for A/A'. The lignins were also analysed by alkaline SEC using a TSKgel GMPWxl column at 30 °C with a 1 mL/min 0.5 M NaOH using sodium polystyrene sulphonate as standards (method C). Method D was performed under the same conditions of method C except now two TSKgel GMPWxl columns were employed. Method E involved the use of 0.7 mL/min of hexafluoroisopropanol (HFIP) + 0.02 M KTFA as eluent at 40 °C, with a PSS PFG column and polymethyl methacrylate (PMMA) as calibration standard. This method was used on both non-acetylated and acetylated lignins. Methods F through H used THF as eluent and were performed on acetylated lignins, only. For Method F, three PL-gel Mixed-E columns were used at 40 °C with a 1 mL/min flow rate of stabilized THF with 250 ppm of 2,5-di-*t*-butylhydroxytoluene and 1 v% of acetic acid using polystyrene standards for calibration and toluene as flow marker. For method G, two GMHhr-M columns were used with same eluent and operated at 40 °C with a 0.5 mL/min flow rate of THF and again using polystyrene as standard. Method H was identical to method G except for the calibration standard used, which, in this case, was PMMA. An ultraviolet spectroscopy detector operated at 280 nm was used for all of the seven SEC methods.

B. Additional results

Table S3. Reproducibility of lignin composition studies based on dry weight

	wt%		Indulin Kraft	Soda P1000	Alcell	OS-W	OS-P	OS-S
Sugars	**Glucan**	LAB1	< 0.1	0.4	0.1	0.2	< 0.1	0.3
		LAB2	0.1	0.6	0.0	0.2	0.2	0.4
		Average	**0.1**	**0.5**	**0.1**	**0.2**	**0.1**	**0.3**
		Std dev		**0.15**	**0.05**	**0.01**		**0.07**
	Xylan	LAB1	0.5	1.4	0.1	0.2	0.2	0.1
		LAB2	0.6	1.6	0.2	0.2	02	0.2
		Average	**0.6**	**1.5**	**0.1**	**0.2**	**0.2**	**0.2**
		Std dev	**0.05**	**0.11**	**0.04**	**0.01**	**0.01**	**0.03**
	Galactan	LAB1	0.5	0.1	< 0.1	< 0.1	< 0.1	< 0.1
		LAB2	0.6	0.2	0.0	0.0	0.0	0.1
		Average	**0.6**	**0.2**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
		Std dev	**0.09**	**0.03**				
	Arabinan	LAB1	0.3	0.3	< 0.1	0.2	< 0.1	< 0.1
		LAB2	0.0	0.1	0.0	0.0	0.0	0.0
		Average	**0.1**	**0.2**	**< 0.1**	**0.1**	**< 0.1**	**< 0.1**
		Std dev	**0.15**	**0.17**		**0.11**		
	Mannan	LAB1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.5
		LAB2	0.1	0.0	0.0	0.0	0.0	0.6
		Average	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**0.6**
		Std dev						**0.13**
	Rhamnan	LAB1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
		LAB2	0.1	0.2	0.0	0.1	0.0	0.0
		Average	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
		Std dev						
Lignin	**Acid Insoluble Lignin**	LAB1	90.3	85.6	93.8	93.8	94.6	95.7
		LAB2	90.3	84.6	94.8	94.4	93.9	95.2
		Average	**90.3**	**85.1**	**94.3**	**94.1**	**94.3**	**95.5**
		Std dev	**0.05**	**0.72**	**0.71**	**0.41**	**0.50**	**0.38**
	Acid Soluble Lignin	LAB1	2.0	5.4	1.9	1.0	1.6	0.9
		LAB2	1.8	5.4	1.9	0.9	1.6	0.7
		Average	**1.9**	**5.4**	**1.9**	**0.9**	**1.6**	**0.8**
		Std dev	**0.17**	**0.03**	**0.01**	**0.13**	**0.06**	**0.08**
Ash			2.6	2.5	< 0.1	<0.1	<0.1	<0.1
Sum		LAB1	96.2	95.8	95.9	95.4	96.4	97.5
		LAB2	96.3	95.1	97.0	95.7	95.9	97.3
		Average	**96.2**	**95.5**	**96.4**	**95.6**	**96.1**	**97.4**
		Std dev	0.07	0.44	0.76	0.24	0.36	0.12

Table S4. Comparison with literature of the composition of the industrial lignins

wt%	Literature reference	Indulin Kraft	Soda P1000	Alcell
Lignin content (ASL+AIL)	This work	92.2	90.5	96.2
	[12]			96.5
	[2]			95.7
	[13]	93.5	90.3	
	[14]		84.2[a]	
Carbohydrates	This work	1.4	2.4	0.2
	[12]			0.3
	[2]			0.1
	[15]		2.6	
	[14]		3.5	
	[16]			0.3
	[17]	2		0.2

[a] only AIL measured

Table S5. Elemental composition of the six lignins

	Element	Indulin Kraft	Soda P1000	Alcell	OS-W	OS-P	OS-S
Elemental composition in wt%, d.b.[a]	C	63	64	67	66	66	68
	H	5.6	5.7	5.9	6.0	5.7	5.8
	N	0.7	0.6	0.2	0.7	0.2	<0.1
	O	27	28	27	28	29	27
Elemental composition from IC in mg/kg, d.b.	Br	*<10*	*<10*	*<10*	*<10*	*<10*	*<10*
	Cl	99	667	12	143	28	19
	F	*<10*	*<10*	*<10*	*<10*	*<10*	*<10*
Elemental from ICP in mg/kg, d.b.	Al	108.8	153.9	1.9	2.8	18.0	2.1
	As	*< 2.2*	*< 2.2*	*< 2.2*	*< 2.2*	*< 2.2*	*< 2.2*
	B	21.2	11.7	3.4	1.3	1.7	< 1.1
	Ba	1.4	2.8	4.2	0.3	0.6	0.2
	Ca	70.3	136.8	338.0	< 26.0	< 26.0	< 26.0
	Cd	*< 0.2*	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
	Co	*< 0.5*	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	Cr	*< 1.4*	1.7	< 1.4	14.7	4.0	< 1.4
	Cu	*< 2.7*	11.0	< 2.7	9.5	47.7	< 2.7
	Fe	52.7	145.2	23.0	147.9	44.1	35.4
	K	1072.0	2142.0	48.0	52.9	21.6	17.1
	Li	*< 0.5*	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	Mg	139.6	68.4	11.4	2.7	7.4	3.9
	Mn	51.3	2.1	13.6	0.3	0.3	3.8
	Mo	*< 1.4*	10.1	< 1.4	3.1	< 1.4	< 1.4
	Na	7161.0	5688.0	< 5.2	< 5.2	< 5.2	< 5.2
	Ni	1.3	3.9	< 0.9	3.4	< 0.9	< 0.9
	P	5.0	28.6	< 4.7	5.3	< 4.7	< 4.7
	S	16752.0	9540.0	162.0	961.4	264.8	164.6
	Sb	*< 5.4*	< 5.4	< 5.4	< 5.4	< 5.4	< 5.4
	Se	*< 2.2*	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2
	Si	196.3	1102.0	< 49.0	< 49.0	54.6	< 49.0
	Sn	*< 1.4*	< 1.4	< 1.4	< 1.4	< 1.4	< 1.4
	Sr	0.4	1.2	0.7	< 0.2	< 0.2	< 0.2
	Ti	1.0	10.6	< 0.5	0.6	0.8	< 0.5
	V	62.2	3.9	< 0.4	< 0.4	< 0.4	< 0.4
	W	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0
	Zn	3.4	6.7	5.2	< 0.8	4.2	< 0.8
Sum (wt%, d.b.)		**99**	**100**	**100**	**101**	**101**	**101**

[a)] d.b.: based on dry weight.

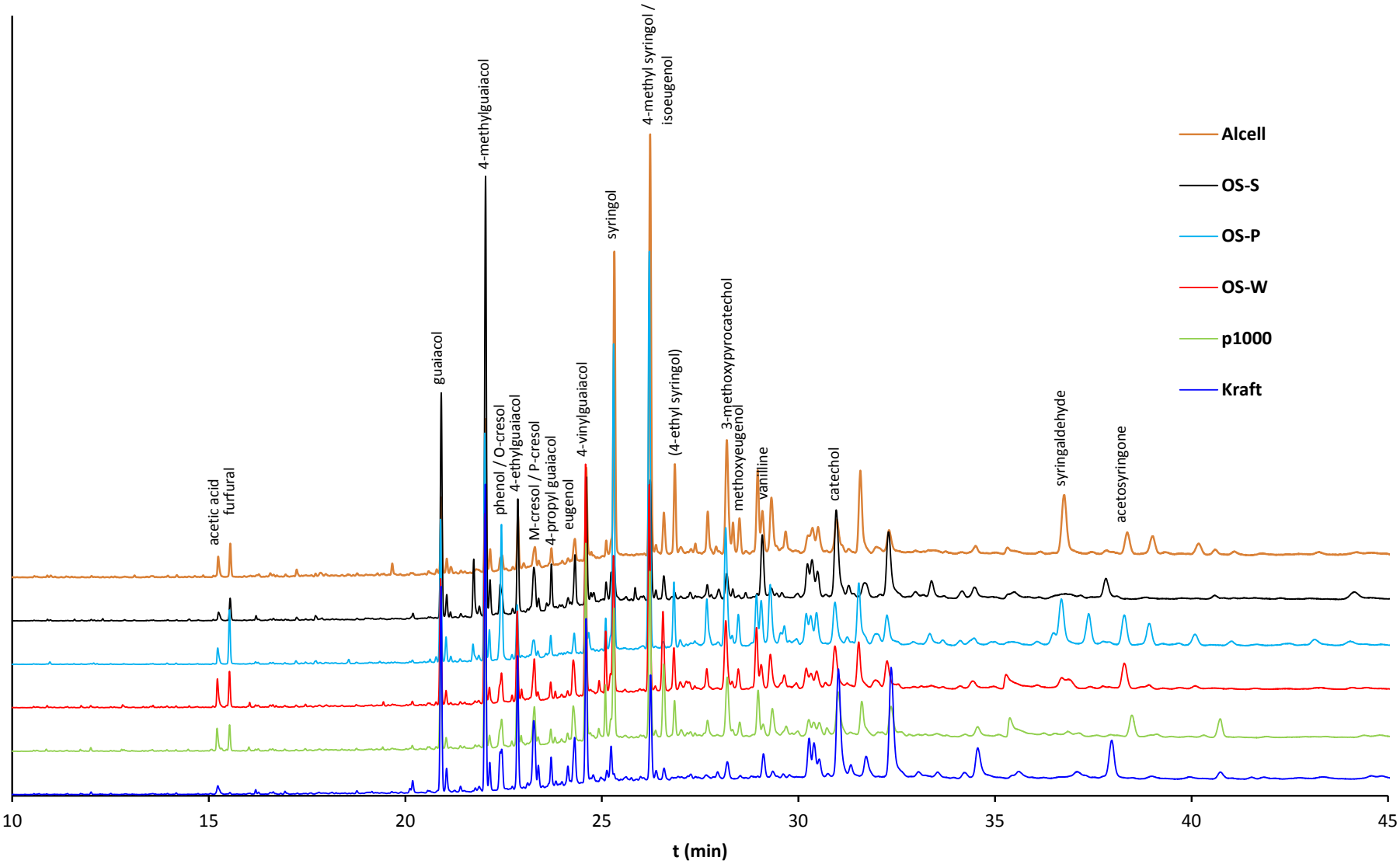


Fig. S1 Pyrograms with components as identified by NIST library and confirmed by retention time of standards.

Table S6. Relative distribution of Pyro-GC-MS products

Component			Retention time (min)	Indulin	P1000	Alcell	OS-W	OS-P	OS-S
Non-aromatics (% of total Py-GC-MS products identified based on MS spectrum)									
Fatty acids[a]	Saturated	tetradecanoic , ethyl ester	23.0	-	*0.4*[b]	-	*0.4*	-	-
		hexadecanoic , ethyl ester	25.1	-	*2.0*	*0.5*	*2.2*	*0.9*	*0.6*
		n-hexadecanoic	35.4	-	*0.3*	-	-	-	-
		heptadecanoic , ethyl ester	25.8	-	-	-	-	-	*0.4*
		octadecanoic , ethyl ester	27.4	-	-	*0.3*	-	-	-
	Unsaturated	linoleic acid , ethyl ester	28.3	-	-	*0.4*	-	-	-
		9,12-octadecadienoic , ethyl ester	28.3	-	-	*0.4*	-	-	-
Other	Alcohols	methanol	4.7	*1.2*	*1.3*	*1.5*	*1.3*	*2.0*	*1.0*
		ethanol	5.4	-	*3.8*	*1.4*	*4.4*	*4.7*	*3.4*
	Carbohydrate-derived	acetic acid	15.2	0.5	1.3	1.1	1.5	0.8	0.5
		furfural	15.5	-	1.7	2.0	2.3	2.9	1.6
Aromatics (% of total aromatic Py-GC-MS products identified based on MS spectrum)									
G-type[c]	Guaiacol	2-methoxyphenol	20.9	12.1	7.5	4.3	8	7.1	14.4
	4-methyl guaiacol	2-methoxy-4-methylphenol	22.0	15.3	9.2	7.7	10.6	10.4	20.6
	4-ethyl guaiacol	2-methoxy-4-ethylphenol	22.9	10.4	7.2	4.0	7.6	3.7	9.6
	4-propyl guaiacol	2-methoxy-4-propylphenol	23.7	3.0	1.8	1.7	1.9	1.7	4.8
	Eugenol	2-methoxy-4-(2-propenyl)phenol	24.3	1.6	0.9	0.7	0.9	0.6	2.1

	p-vinyl guaiacol	2-methoxy-4-vinylphenol	24.6	9.3	13.2	5.1	14.1	3.4	7.7
	Isoeugenol[d]	2-methoxy-4-(1-propenyl)-phenol	26.2	6.1	3.9	3.1	7.8	2.1	5.1
	3-methoxy catechol	3-methoxy-1,2-benzenediol	28.1	-	2.5	4.8	2.7	4.3	-
	Vanillin	4-hydroxy-3-methoxybenzaldehyde	29.0	1.1	0.6	1.9	1.2	1.7	3.4
S-type	Syringol	2,6-dimethoxyphenol	25.3	-	8.8	16.4	8.4	14.6	(2.2)[g]
	4-methyl syringol[e]	4-methyl 2,6-dimethoxyphenol	26.2	-	8.0	18.5	9.1	16.9	-
	4-ethyl syringol[f]	4-ethyl 2,6-dimethoxyphenol	26.8	-	*(2.9)*	*(5.7)*	-	*(3.7)*	-
	Methoxy eugenol	4-(2-propenyl)-syringol	28.5	-	0.7	1.4	0.9	1.0	-
	Syringaldehyde	4-hydroxy-3,5-dimethoxybenzaldehyde	36.7	-	-	1.8	0.3	1.2	-
	Acetosyringone	1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone	38.3	-	0.9	0.7	0.9	0.9	-
P-type	Phenol		22.4	3.3	2.8	1.1	2.7	10.2	1.7
	O-cresol	2-methylphenol	22.4	1.8	0.9	0.6	0.8	0.8	1.6
	P-cresol	4-methylphenol	23.3	3.5	2.5	0.9	2.4	1.2	2.1
	M-cresol	3-methylphenol	23.3	1.2	0.5	0.4	0.5	0.3	0.8
C-type	Catechol	1,2-benzenediol	31.0	6.5	3.0	2.3	-	2.4	5.7

a) For all fatty acids, except n-hexadecanoic acid, the ethyl ester derivative was identified.

b) Components identified by comparison of their MS spectrum with the NIST library without verification of the retention time with a calibration standard are given in italics.

c) Aromatic components classified according to Wang et al.[18] Only aromatic components shown which were confirmed using a calibration standard. Aromatics shown represent 75 (Indulin) - 88% (OS-P) of total aromatics identified based on MS spectrum.

d) Most probably trans-isoeugenol. In addition, a minor peak at 25.2 min was found in all samples except Indulin lignin, which possibly represents cis-isoeugenol (<1.5% of total aromatics). See also Wang et al. [18]

e) Component identified by retention time and MS spectrum of standard.

f) Component neither available in NIST library nor as calibration standard. Identification made by comparison of MS spectra with 4-methyl syringol and elution order, but should be treated with caution.

g) Component has been identified based on MS spectrum with a low probability of ~80% and is therefore given between brackets.

Table S7. Reproducibility of the quantification of ^{31}P NMR measurements[a]

mmol function /g lignin		**Aliphatic OH**	**5-substitued OH**	**Guaiacyl OH**	***p* Hydroxy OH**	**COOH**	**Free COOH /Tricin**
Indulin Kraft	LAB3	1.79	1.31	1.30	0.16	0.33	0.05
	LAB2	2.36	1.67	2.02	0.28	0.48	0.02
	Avg	**2.07**	**1.49**	**1.66**	**0.22**	**0.40**	**0.04**
	Std Dev	**0.40**	**0.25**	**0.51**	**0.08**	**0.11**	**0.02**
Soda P1000	LAB3	1.26	1.73	0.73	0.40	0.80	0.14
	LAB2	1.35	1.95	0.91	0.54	0.98	0.00
	Avg	**1.31**	**1.84**	**0.82**	**0.47**	**0.89**	**0.07**
	Std Dev	**0.06**	**0.16**	**0.12**	**0.10**	**0.12**	**0.10**
Alcell	LAB3	1.04	1.68	0.58	0.11	0.22	0.00
	LAB2	1.20	2.26	0.78	0.20	0.36	0.00
	Avg	**1.12**	**1.97**	**0.68**	**0.16**	**0.29**	**0.00**
	Std Dev	**0.11**	**0.41**	**0.15**	**0.06**	**0.10**	**0.00**
OS-W	LAB3	1.27	1.24	0.92	0.38	0.21	0.20
	LAB2	1.34	1.33	1.08	0.50	0.29	0.24
	Avg	**1.31**	**1.28**	**1.00**	**0.44**	**0.25**	**0.22**
	Std Dev	**0.05**	**0.06**	**0.11**	**0.08**	**0.06**	**0.03**
OS-P	LAB3	0.80	1.83	0.58	0.18	0.07	0.00
	LAB2	1.06	2.41	0.89	0.33	0.14	0.04
	Avg	**0.93**	**2.12**	**0.73**	**0.25**	**0.11**	**0.02**
	Std Dev	**0.18**	**0.41**	**0.22**	**0.11**	**0.05**	**0.03**
OS--S	LAB3	1.43	1.21	1.44	0.08	0.06	0.00
	LAB2	1.71	1.14	1.87	0.17	0.13	0.06
	Avg	**1.57**	**1.18**	**1.65**	**0.12**	**0.10**	**0.03**
	Std Dev	**0.19**	**0.05**	**0.30**	**0.06**	**0.05**	**0.04**

[a]Internal standard: LAB3 cholesterol, LAB2 cyclohexanol

Table S8. Comparison of quantified ^{31}P NMR measurement on the industrial lignins with literature

mmol function/g lignin	Literature reference	Indulin Kraft	Soda P1000	Alcell
Aliphatic OH	This work[a]	1.79	1.26	1.04
	This work[b]	2.36	1.35	1.20
	[19]	2.35	1.76	1.08
	[5]			1.46
	[20]		1.60	
	[21]			1.28
	[17]	2.34		1.10
5-substitued OH	This work[a]	1.31	1.73	1.68
	This work[b]	1.67	1.95	2.26
	[19]	1.36	1.37	1.81
	[5]			2.19
	[20]		1.10	
	[21]			1.69
	[17]	1.91		2.81
Guaiacyl OH	This work[a]	1.30	0.73	0.58
	This work[b]	2.02	0.91	0.78
	[19]	1.88	0.76	0.70
	[5]			0.82
	[20]		0.80	
	[21]			0.64
	[17]	1.96		0.80
***p* Hydroxy OH**	This work[a]	0.16	0.40	0.11
	This work[b]	0.28	0.54	0.20
	[19]	0.22	0.50	0.20
	[5]			0.23
	[20]		0.40	
	[21]			0.11
	[17]	0.26		0.13
COOH	This work[a]	0.33	0.80	0.22
	This work[b]	0.48	0.98	0.36
	[19]	0.49	1.11	0.30
	[5]			0.35
	[20]		0.90	
	[21]			0.26
	[17]	0.39		0.23

Analysis conditions: all studies presented in this table used 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane as phosphitylating agent and different internal standards listed below

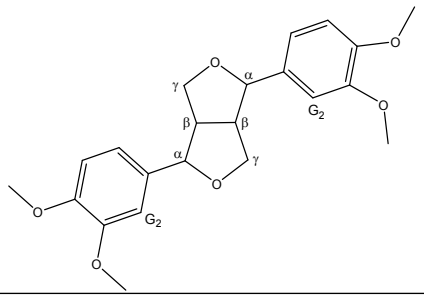
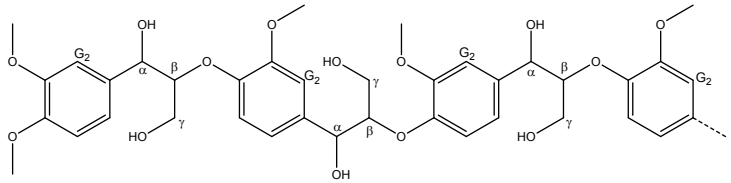
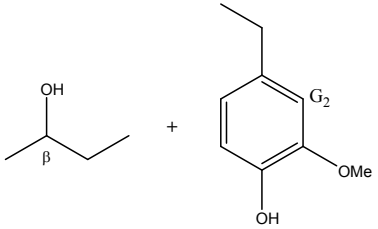
[a]: cholesterol

[b]: cyclohexanol

[5,19,20]: cyclohexanol

[17,21]: cholesterol

Table S9. Results from quantification of model compounds by [^{1}H;^{13}C]-HSQC NMR

		α	β	γ	G2	G5	G6	Nb linkage per 100 Ar exp	Nb linkage per 100 Ar th
β-β 	Processing 1[a]	1	**0.84**	**2**	**1.05**	**0.78**	**0.88**	**95.2**	**100**
	Processing 2[a]	1	**0.76**	**1.89**	**1**	**0.73**	**0.80**	**100**	**100**
	Average							**97.6**	
	Std dev							**2.38**	
β-O-4 polymer 	Processing 1[a]	**1**	**0.92**	**1.41**	**1**	**0.79**	**0.88**	**100**	**100**
	Processing 2[a]	**1**	**0.92**	**1.38**	**0.99**	**0.83**	**0.89**	**101**	**100**
	Average							**100.5**	
	Std dev							**0.51**	
Mixture[b] 	Processing 1[a]		**3.02**		**1**			**300**	**330**
	Processing 2[a]		**2.8**		**1.01**			**280**	**330**
	Average							**290**	
	Error							**12%**	

[a] The raw data were processed twice: the same zero filling and apodisation methods were applied. However, the phase correction and integration of peaks were adjusted and measured manually.

[b] The mixture was prepared with 1 Eq of 4-ethyl guaiacol (0.06 mmol) and 3.3 Eq of 2-butanol (0.20 mmol).

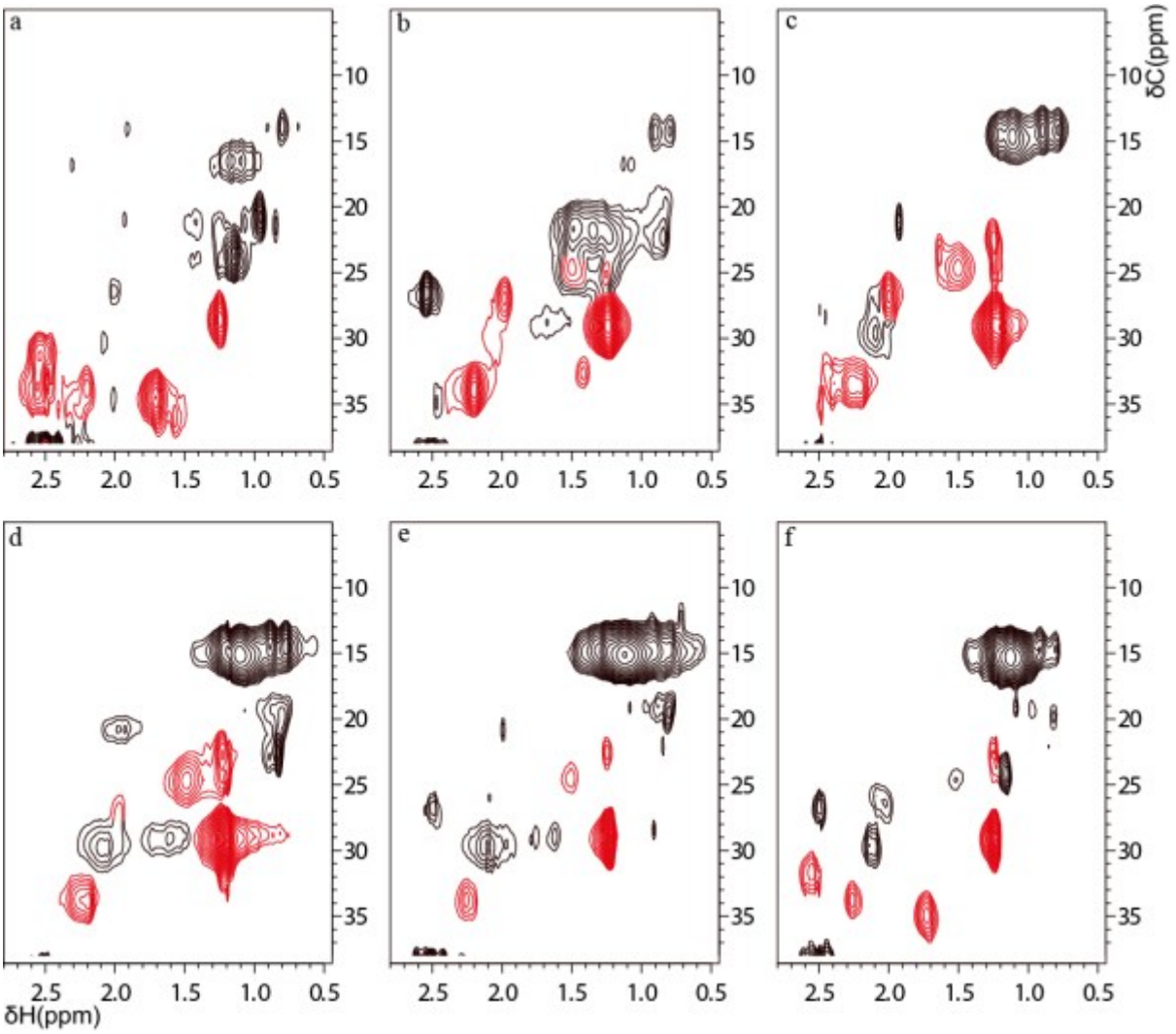


Fig. S2 Aliphatic chain regions of the 2D [^{1}H;^{13}C]-HSQC NMR spectra of lignins. CH_2 signals are colored in red; (a) Indulin Kraft, (b) soda P1000, (c) Alcell, (d) OS-W, (e) OS-P, (f) OS-S.

Table S10. ^{13}C and ^{1}H assignments of the lignin signals in 2D [^{1}H;^{13}C] HSQC spectra[a]

label	δC/δH (ppm)	Assignment
Bβ	53.1/3.4	Cβ−Hβ in phenylcoumaran substructures (B)
Cβ	53.5/3.1	Cβ−Hβ in β−β′ resinol substructures (C)
−OCH3	55.6/3.73	C−H in methoxyls
Aγ	59.4/3.4 and 3.7	Cγ−Hγ in γ− hydroxylated β-O- 4′ substructures (A)
Iγ	61/4.1	Cγ−Hγ in cinnamyl alcohol end-groups (I)
Bγ	63.4/3.6	Cγ−Hγ in phenylcoumaran substructures (B)
Hkγ	67.5/4.2	Cγ−Hγ in Hibbert ketone structures[b]
Cγ	71.2/4.2	Cγ−Hγ in β−β′ resinol substructures (C)[b]
Aα	71.9/4.9	Cα−Hα in β-O-4′ substructures (A)
X2	73/3.1	C2−H2 in xylan substructures (X)
X3	74/3.3	C3−H3 in xylan substructures (X)
X4	75.7/3.5	C4−H4 in xylan substructures (X)
Aβ	80.4/4.5, 84.4/4.4 and 85.6/4.2	Cβ−Hβ in β-O-4′ substructures (A)
Aoxβ	83/5.2	Cβ−Hβ in α-oxidized β-O-4′ substructures (Aox)
Cα	85.5/4.6	Cα−Hα in β−β′ resinol substructures (C)
Bα	87.7/5.5	Cα−Hα in phenylcoumaran substructures (B)
T8	94.4/6.6	C8−H8 in tricin units (T)
T6	99.5/66.2	C6−H6 in tricin units (T)
T2,6	104.5/7.4	C2−H2 and C6-H6 in tricin units (T)
S2,6	104.2/6.7	C2−H2 and C6−H6 in syringyl units (S)
T3	107/7.2	C3−H3 in tricin units (T)
S′2,6	107.4/7.4	C2−H2 and C6−H6 in syringyl units with α oxidization(S′)
G2	110.2/6.9	C2−H2 in guaiacyl units (G)
Fa2	111.5/7.3	C2−H2 in ferulate (Fa)
G5/G6	115/6.7 and 119.7/6.8	C5−H5 and C6−H6 in guaiacyl units (G)
Fa6	123.1/7.1	C6−H6 in ferulate (Fa)
HMF	123.6/7.5	C3− H3 in 5-O-substituted furfurals -like units
Stα, β	126.6/6.9	Cα−Hα and Cβ−Hβ in stilbene structures (St)
H2,6	128.2/7.2	C2,6−H2,6 in *p*-hydroxyphenyl units (H)
Iα	130.6/6.3	Cα−Hα in cinnamyl alcohol end-groups (I)
Pca2,6	130.1/7.5	C2−H2 and C6−H6 in *p*-coumarate (Pca)
Pb2,6	131.6/7.7	C2−H2 and C6−H6 in p-benzoate (Pb)
HMF	179/9.6	Cα−Hα in 5-O-substituted furfurals -like units

[a] Signals were assigned by comparison with the literature.

[b] The second peak corresponding to Cγ−Hγ in β−β′ resinol substructures and the peak Cα−Hα in Hibbert's ketone structures were not observed due to overlap in the T1 dimension with the negative methoxy signal.

Table S11. Results and reproducibility of quantification of lignin linkages and units by [^{1}H;^{13}C] HSQC NMR

	Sample	Processing	β-O-4[a]	β-5[a]	β-β[a]	Stilbene[a]	Pca[a]	Pb[a]	Tricin[a]	S (%)[b]	G (%)[b]	H (%)[b]	S/G ratio	H/G ratio
Indulin Kraft	I	1	4.3	0.5	0.7	2.0	0.0	0.0	0.0	0	97	3	0.0	0.0
		2	5.8	0.5	1.0	2.3	0.0	0.0	0.0	0	97	3	0.0	0.0
	II	1	6.9	0.1	0.9	2.8	0.0	0.0	0.0	0	96	4	0.0	0.0
		2	7.3	0.1	1.4	2.1	0.0	0.0	0.0	0	97	3	0.0	0.0
	Average		**6.1**	**0.3**	**1.0**	**2.3**	**0.0**	**0.0**	**0.0**	**0.0**	**96.8**	**3.3**	**0.0**	**0.0**
	Standard deviation		**1.2**	**0.2**	**0.2**	**0.3**	**0.0**	**0.0**	**0.0**	**0.0**	**0.4**	**0.4**	**0.0**	**0.0**
Soda P1000	I	1	3.4	0.0	0.7	0.0	3.5	0.0	0.0	49	40	11	1.2	0.3
		2	3.5	0.0	0.8	0.0	3.3	0.0	0.0	51	37	12	1.4	0.3
	II	1	3.8	0.0	0.7	0.0	2.7	0.0	0.0	50	39	11	1.3	0.3
		2	2.9	0.0	0.5	0.0	3.2	0.0	0.0	48	42	10	1.2	0.2
	Average		**3.4**	**0.0**	**0.7**	**0.0**	**3.2**	**0.0**	**0.0**	**49.5**	**39.5**	**11.0**	**1.3**	**0.3**
	Standard deviation		**0.3**	**0.0**	**0.1**	**0.0**	**0.3**	**0.0**	**0.0**	**1.1**	**1.8**	**0.7**	**0.1**	**0.0**
Alcell	I	1	4.0	0.8	2.0	0.6	0.0	0.0	0.0	59	41	0	1.4	0.0
		2	4.8	0.3	2.3	0.3	0.0	0.0	0.0	61	39	0	1.6	0.0
	II	1	6.5	1.0	3.6	0.4	0.0	0.0	0.0	67	33	0	2.1	0.0
		2	6.1	1.1	3.3	0.2	0.0	0.0	0.0	64	36	0	1.8	0.0
	Average		**5.3**	**0.8**	**2.8**	**0.4**	**0.0**	**0.0**	**0.0**	**62.8**	**37.2**	**0.0**	**1.7**	**0.0**
	Standard deviation		**1.0**	**0.3**	**0.7**	**0.2**	**0.0**	**0.0**	**0.0**	**3.2**	**3.2**	**0.0**	**0.2**	**0.0**
OS-W	I	1	3.1	3.0	0.0	0.3	1.6	0.0	2.4	37	60	3	0.6	0.0
		2	4.0	4.3	0.2	0.7	2.2	0.0	2.7	38	59	4	0.6	0.1
	II	1	4.9	5.1	0.0	0.5	2.5	0.0	4.1	40	57	3	0.7	0.1
		2	5.8	5.8	0.0	0.3	2.3	0.0	4.1	40	57	3	0.7	0.1
	III	1	3.8	4.4	0.0	0.3	2.3	0.0	3.5	40	58	3	0.7	0.0
		2	4.0	4.5	0.1	0.3	2.5	0.0	3.9	37	60	3	0.6	0.0
	Average		**4.3**	**4.5**	**0.1**	**0.4**	**2.2**	**0.0**	**3.5**	**38.7**	**58.5**	**3.2**	**0.7**	**0.1**
	Standard deviation		**0.8**	**0.8**	**0.1**	**0.1**	**0.3**	**0.0**	**0.6**	**1.3**	**1.2**	**0.3**	**0.0**	**0.0**
OS-P	I	1	0.2	2.4	1.1	0.1	0.0	8.7	0.0	47	53	0	0.9	0.0
		2	0.0	1.0	1.1	0.0	0.0	10.5	0.0	53	47	0	1.1	0.0
	II	1	0.0	1.9	1.2	0.1	0.0	9.0	0.0	57	43	0	1.3	0.0
		2	0.0	1.8	1.1	0.0	0.0	9.6	0.0	56	44	0	1.3	0.0
	Average		**0.1**	**1.8**	**1.1**	**0.0**	**0.0**	**9.4**	**0.0**	**53.3**	**46.7**	**0.0**	**1.2**	**0.0**
	Standard deviation		**0.1**	**0.5**	**0.0**	**0.0**	**0.0**	**0.7**	**0.0**	**3.9**	**3.9**	**0.0**	**0.2**	**0.0**
OS-S	I	1	0.0	2.3	0.1	0.7	0.0	0.0	0.0	0	100	0	0.0	0.0
		2	0.0	3.0	0.3	1.0	0.0	0.0	0.0	0	100	0	0.0	0.0
	II	1	0.0	3.6	0.2	0.6	0.0	0.0	0.0	0	100	0	0.0	0.0
		2	0.0	4.4	0.2	0.8	0.0	0.0	0.0	0	100	0	0.0	0.0
	Average		**0.0**	**3.3**	**0.2**	**0.7**	**0.0**	**0.0**	**0.0**	**0.0**	**100.0**	**0.0**	**0.0**	**0.0**
	Standard deviation		**0.0**	**0.8**	**0.1**	**0.2**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**

[a]Expressed as a number per 100 aromatic units (S+G) [b]Molar percentage (S+G+H=100)

Table S12. Interunit linkages of various lignins reported in literature, measured by [^{1}H;^{13}C] HSQC NMR and expressed per 100 Ar units

Literature reference	Lignin *biomass origin*	β-O-4	β-β	β-5
This work	Indulin Kraft	6.1	1.0	0.3
	Soda P1000	3.4	0.7	0
	Alcell	5.3	2.8	0.8
	OS-W	4.3	0.1	4.5
	OS-P	0.1	1.1	1.8
	OS-S	0	0.2	3.5
[22]	Soda P1000	6	1.4	0.5
[23]	Indulin Kraft	7	4	4
	Alcell	8	3	3
[24]	EMAL *wheat straw*	66	5	10
	Steam explosion *wheat straw*	51	3	16
[25]	MWL *wheat straw*	29.8	5.4	1.3
	CEL *wheat straw*	36.5	5.7	0.9
[15]	Soda *wheat straw*	3.7	1.9	0.4
	AFEX *wheat straw*	37.1	4.3	3.4
	Organosolv *poplar*	12.1	5.0	4.4
	Ammonia *poplar*	44.9	2.3	9.0
[26]	Hydrotropic *birch*	15.0	3.2	3.3
	Modified hydrotropic *birch*	11.8	3.0	3.2
[27]	MWL *Oliver*	50.8	14.1	2.7
	Hydrothermally treated MWL *Oliver*	31.5	11.1	4.7
	Organosolv *Oliver*	Tr	3.2	Tr
	Hydrothermally treated Organosolv *Oliver*	Tr	2.7	Tr
[28]	MWL *bamboo*	41.4	5.6	3.6
	Alkaline *bamboo*	46.2	6.4	2.5
	Dissolved *bamboo*	35.2	6.9	3.2

EMAL: enzymatic mild acidolysis lignin
MWL: milled wood lignin
CEL: cellulolytic enzyme lignin
AFEX: ammonia fiber expansion

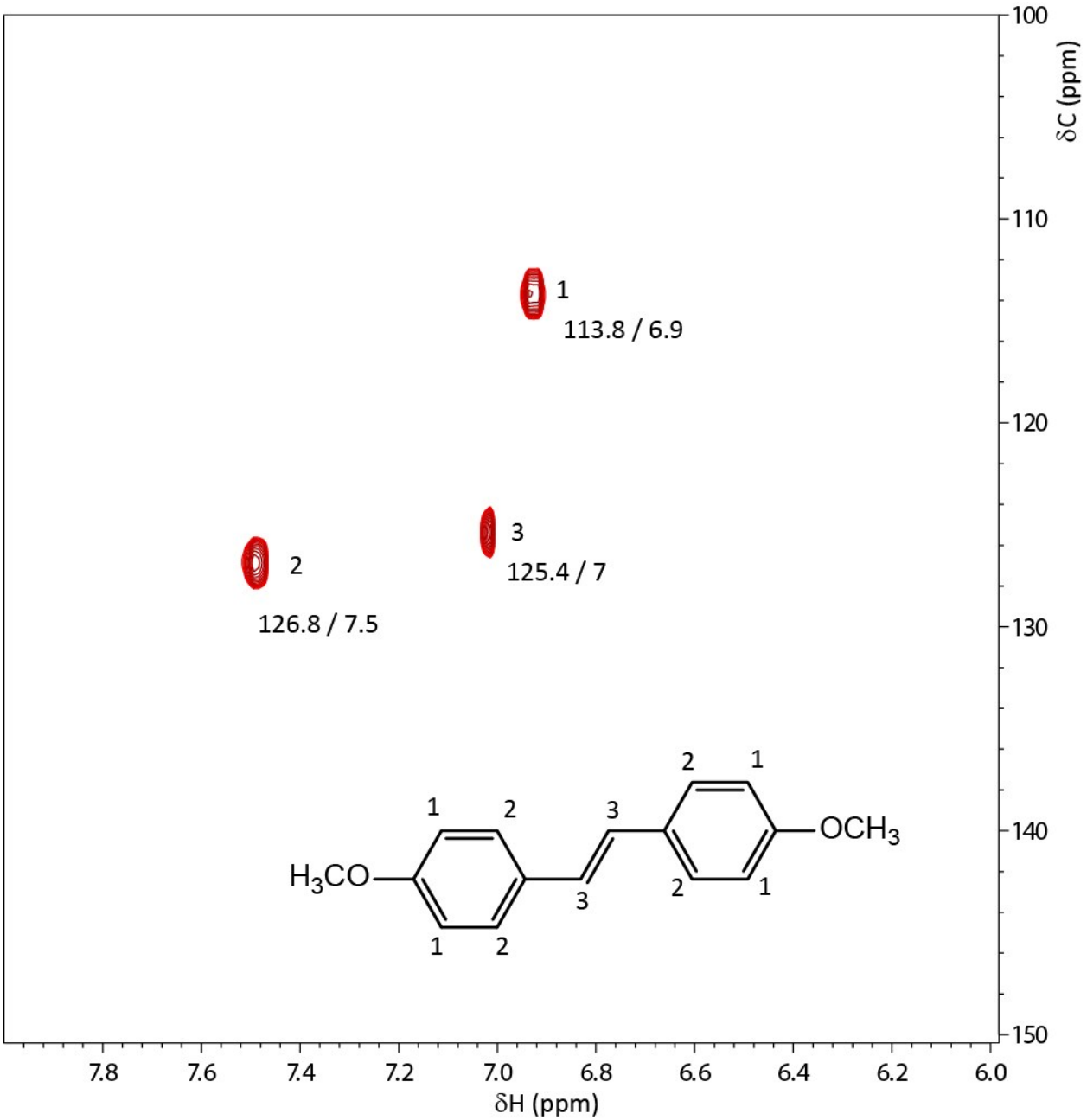


Fig. S3 2D [^{1}H;^{13}C]-HSQC NMR spectrum of 1-methoxy-4-[2-(4-methoxyphenyl)ethenyl]benzene (stilbene unit) recorded at 318.5 K. The stilbene compound was not soluble at room temperature.

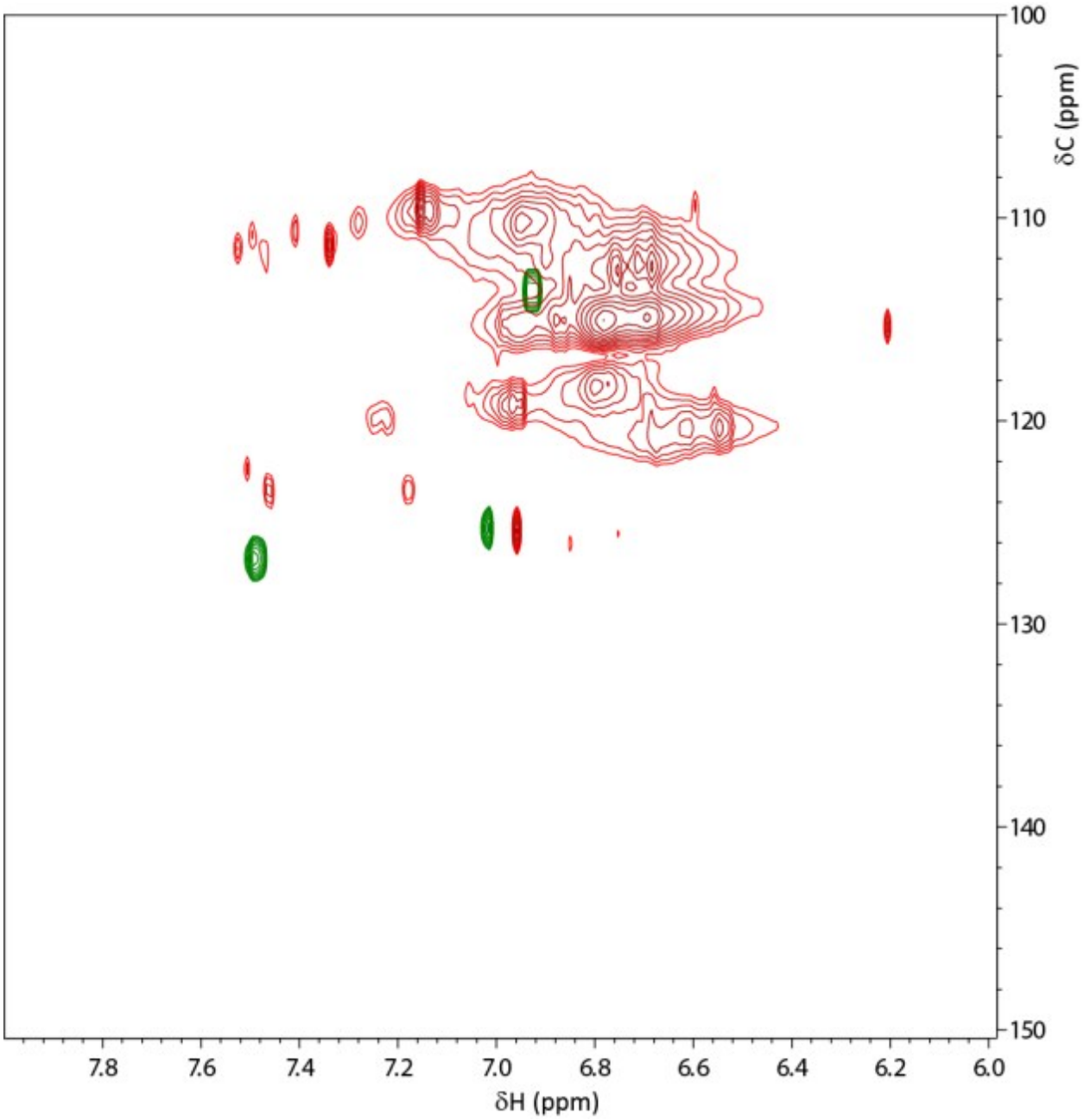


Fig. S4 2D [^{1}H;^{13}C]-HSQC NMR spectra of 1-methoxy-4-[2-(4-methoxyphenyl)ethenyl]benzene (stilbene unit, green) and OS-S (red)recorded at 318.5 K.

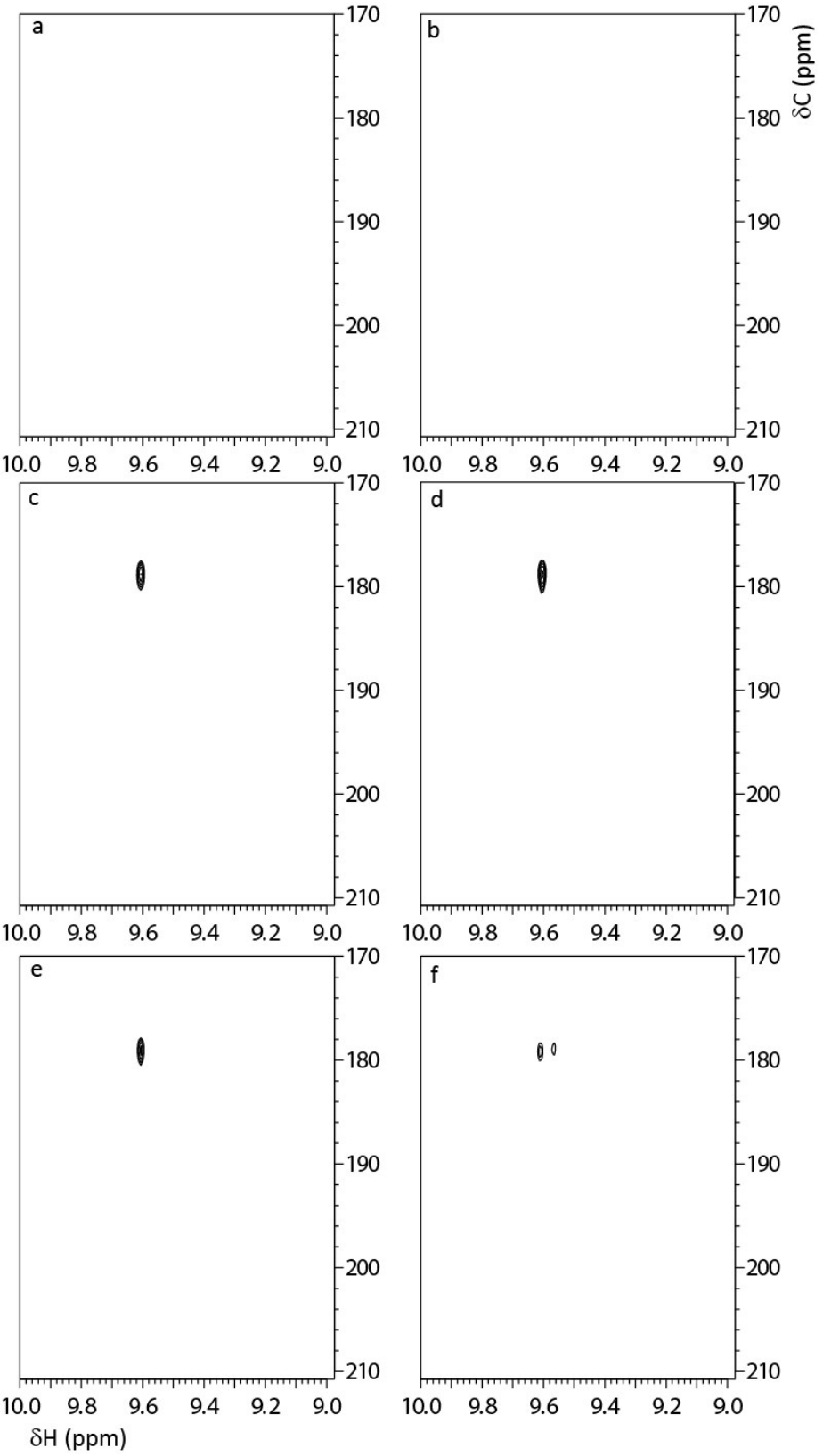


Fig. S5 Aldehyde region in the 2D [^{1}H;^{13}C]-HSQC NMR spectra of lignins. (a) Indulin Kraft, (b) soda P1000 (c) Alcell, (d) OS-W, (e) OS-P, (f) OS-S.

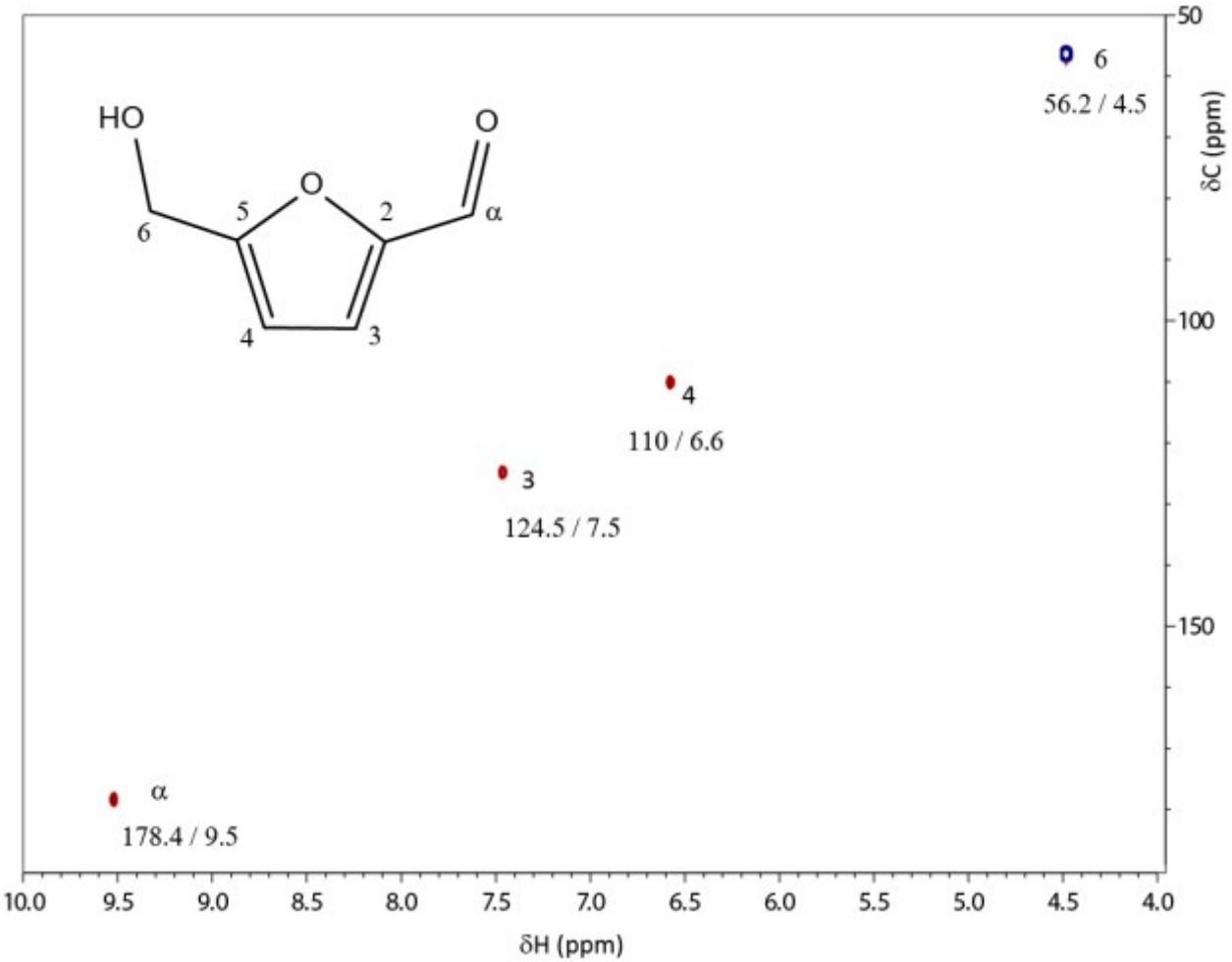


Fig. S6 2D [^{1}H;^{13}C] HSQC NMR spectrum of 5-hydroxymethylfurfural.

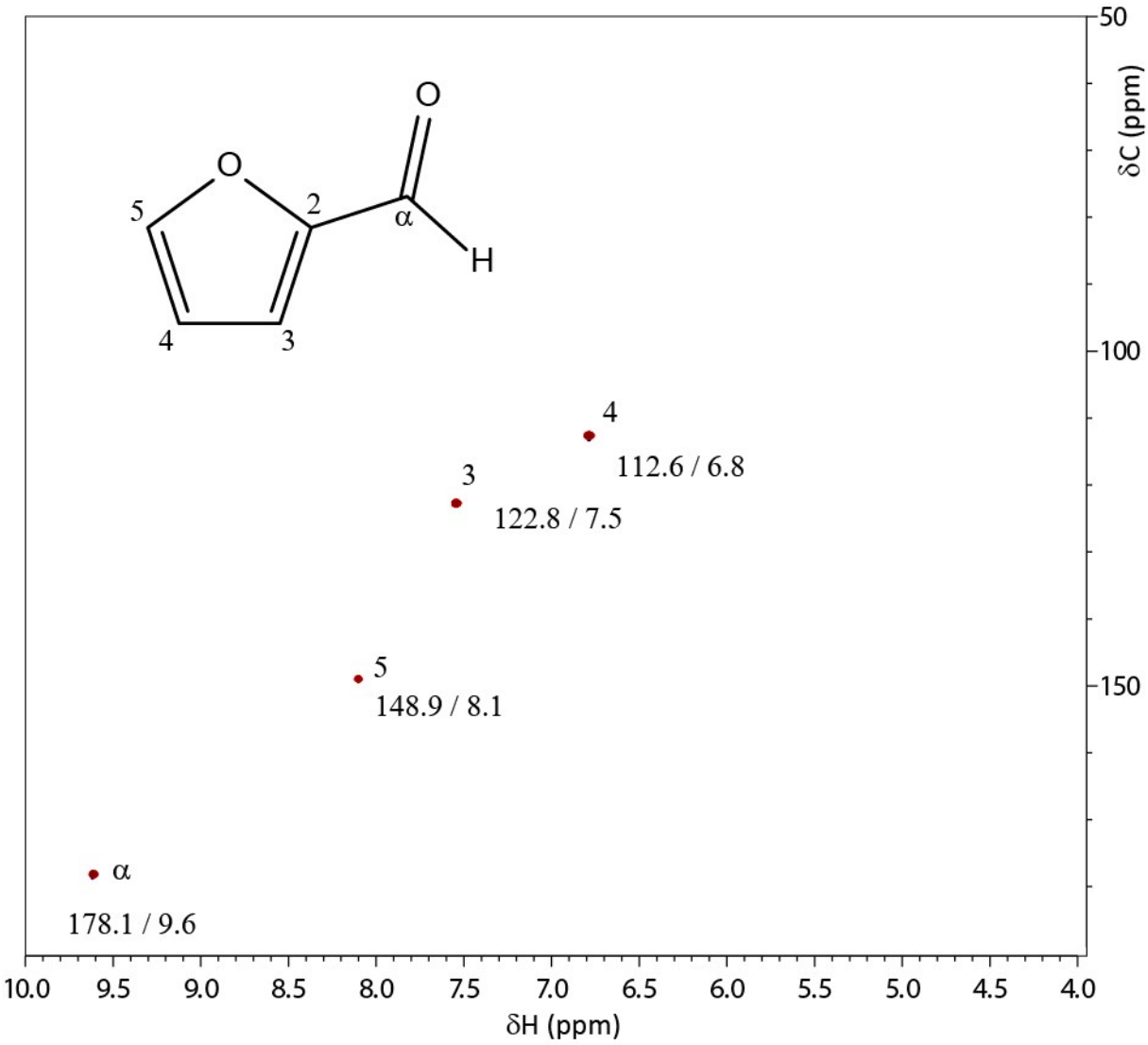


Fig. S7 2D [^{1}H;^{13}C] HSQC NMR spectrum of furfuraldehyde.

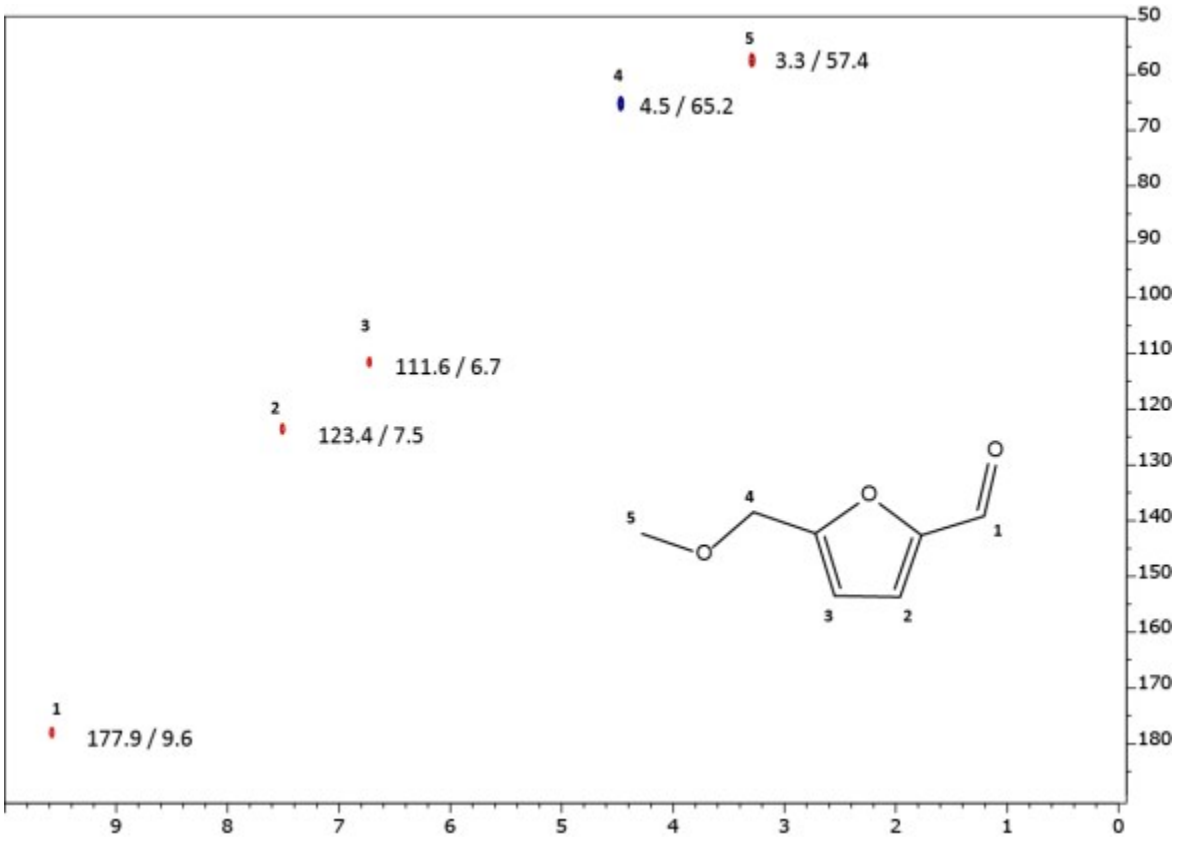


Fig. S8 2D [^{1}H;^{13}C] HSQC NMR spectrum of 5-(methoxymethyl)furfural.

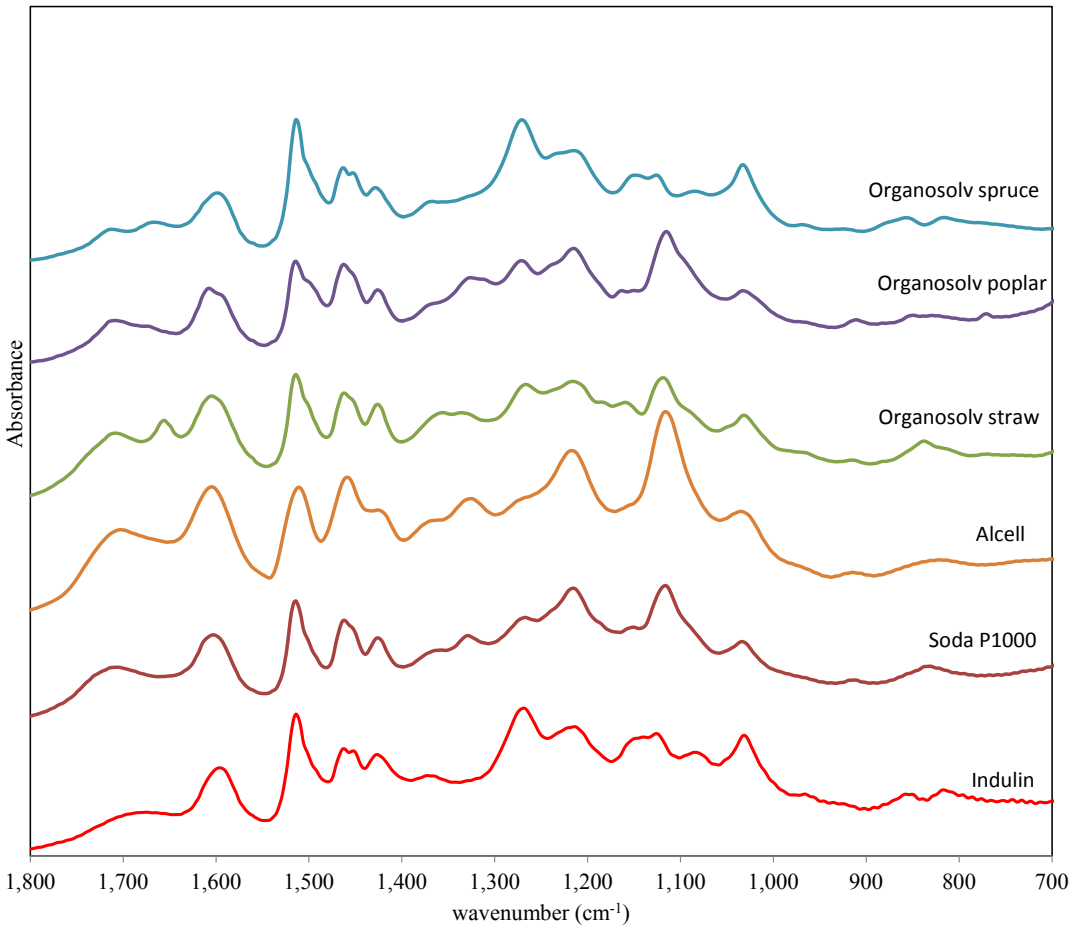


Fig. S9. FT-IR spectra of the six lignins studied (KBr pellets).

Table S13. Analytical details of the SEC methods (identical to Table 4 in the main text, reproduced for convenience)

Method	Solvent	Column	Column Mw specifications (g/mol)	Standard[b]	Acetylated lignin
A	0.5M NaOH	home-packed	1000-700000	SPS	No
A'[a]	0.5M NaOH	home-packed	1000-700000	SPS	No
B	0.5M NaOH	PSS MCX	100-35000	SPS	No
C	0.5M NaOH	TSKgel GMPWxl	500-8000000	SPS	No
D	0.5M NaOH	2 x TSKgel GMPWxl	500-8000000	SPS	No
E/E'	*HFIP*	PSS PFG	100-1000000	PMMA	No / yes
F	THF	3 x PL-gel Mixed-E	up to 25000	PS	Yes
G	THF	2 x GMHhr-M	100-3000000	PS	Yes
H	THF	2 x GMHhr-M	100-3000000	PMMA	Yes

[a] method A' is identical to method A, but was run at a different laboratory
[b] SPS: sodium polystyrene sulphonate; PMMA: poly(methyl methacrylate); PS: sodium polystyrene

Table S14. Molar masses (Mw, Mn) expressed in g/mol and polydispersity (PD) of lignins measured with different SEC methods (A-E). See Table S13 for method denomination.

	Method A			Method A'			Method B			Method C			Method D			Method E		
	Mw	Mn	PD	Mw	Mn	PD	Mw	Mn	PD	Mw	Mn	PD	Mw	Mn	PD	Mw	Mn	PD
Indulin Kraft	5930	700	8.4	4250	1560	2.7	3310	1350	2.5	5290	440	11.9	4290	530	8.1	6010	1090	5.6
Soda P1000	3880	700	5.5	3140	1350	2.3	2410	1160	2.1	4110	550	7.5	3270	620	5.2	4540	990	4.5
Alcell	3160	610	5.1	3570	1390	2.6	2910	1150	2.5	3200	500	5.8	2580	600	4.3	2840	950	3.0
OS-W	2700	530	5.1	2290	1160	2.0	1720	1040	1.7	2500	400	6.2	1960	450	4.4	3350	870	3.9
OS-P	2560	570	4.5	2200	1080	2.0	1700	960	1.8	2630	530	5.0	2180	570	3.8	2640	830	3.1
OS-S	2830	500	5.6	2520	1250	2.0	2120	1160	1.8	2530	360	7.1	2030	420	4.9	5550	910	5.6

Table S15. Molar masses (Mw, Mn) expressed in g/mol and polydispersity (PD) of acetylated lignins measured with different SEC methods (E-H). See Table S13 for method denomination.

	Method F			Method G			Method H			Method E'		
	Mw	Mn	PD	Mw	Mn	PD	Mw	Mn	PD	Mw	Mn	PD
Indulin Kraft	4480	1100	4.1	1450	320	4.5	2270	560	4.1	11300	1440	7.8
Soda P1000	3260	940	3.5	730	220	3.5	1180	400	3.0	6030	1140	5.3
Alcell	3550	1060	3.3	2460	640	3.8	3570	860	4.2	6700	1510	4.5
OS-W	1810	890	2.0	590	230	2.6	960	400	2.4	2940	990	3.0
OS-P	1970	950	2.1	690	310	2.2	1140	540	2.1	3040	1060	2.9
OSS	2130	970	2.2	970	380	2.6	1570	650	2.4	3280	1070	3.1

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