Electronic Supplementary Information (ESI)

Structural changes in lignins isolated using an acidic ionic liquid water mixture

Agnieszka Brandt,[a] Long Chen,[b,c] Bart E. van Dongen,[d] Tom Welton[b] and Jason P. Hallett*[,a]

[a]*Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, UK. E-mail: j.hallett@imperial.ac.uk*

[b]*Department of Chemistry, Imperial College London, London, SW7 2AZ, UK.*

[c]*State Key Laboratory of Chemical Engineering, School of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China.*

[d]*School of Earth, Atmospheric, and Environmental Sciences and the Williamson Research Centre for Molecular Environmental Science, University of Manchester, Manchester M13 9PL, UK.*

Table S1: Composition of Miscanthus (determined by NREL protocol xxx)

Glucan	Xylan	Arabinan	Acid-insoluble lignin	Acid-soluble lignin	Ash	Extractives	Mass balance[a]
47.3 ±0.8	20.1±0.	2.2±0.5	22.4±0.1	4.0±0.1	0.6±0.4	2.8±0.1	105.0±2.4

[a] sum of compositional analysis mass fractions prior to normalisation

[HC_4im][HSO_4] synthesis: 1-butylimidazole was mixed with 50 ml water and the mixture cooled to 0°C. Sulfuric acid was added dropwise while stirring. The molar ratio of these two reagents was 1:1. A viscous colourless liquid was obtained.

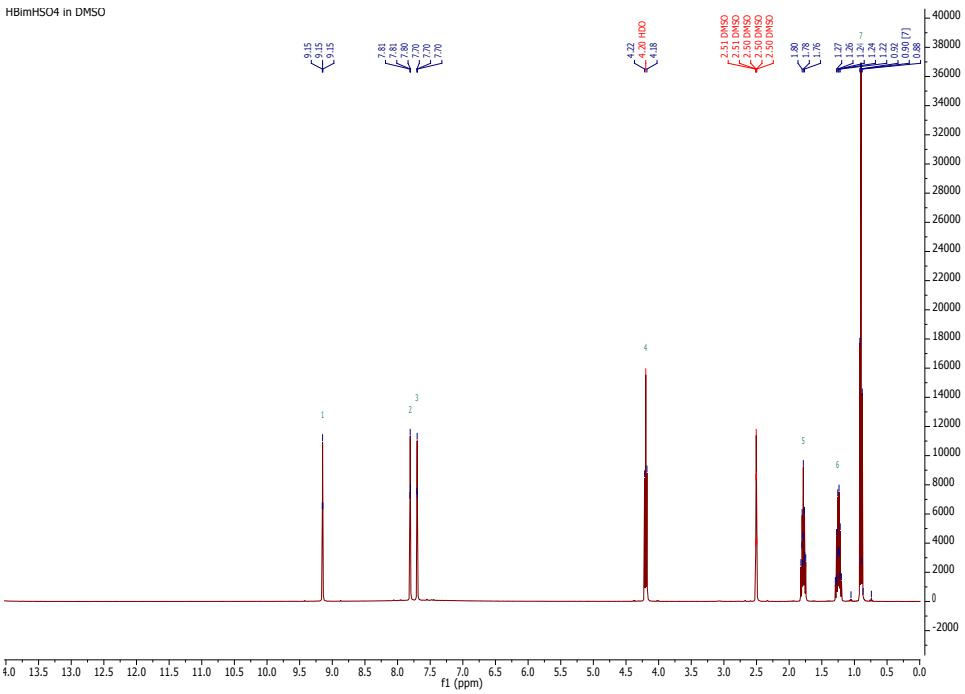

Figure S1. ^{1}H-NMR of [HC_4im[HSO_4]

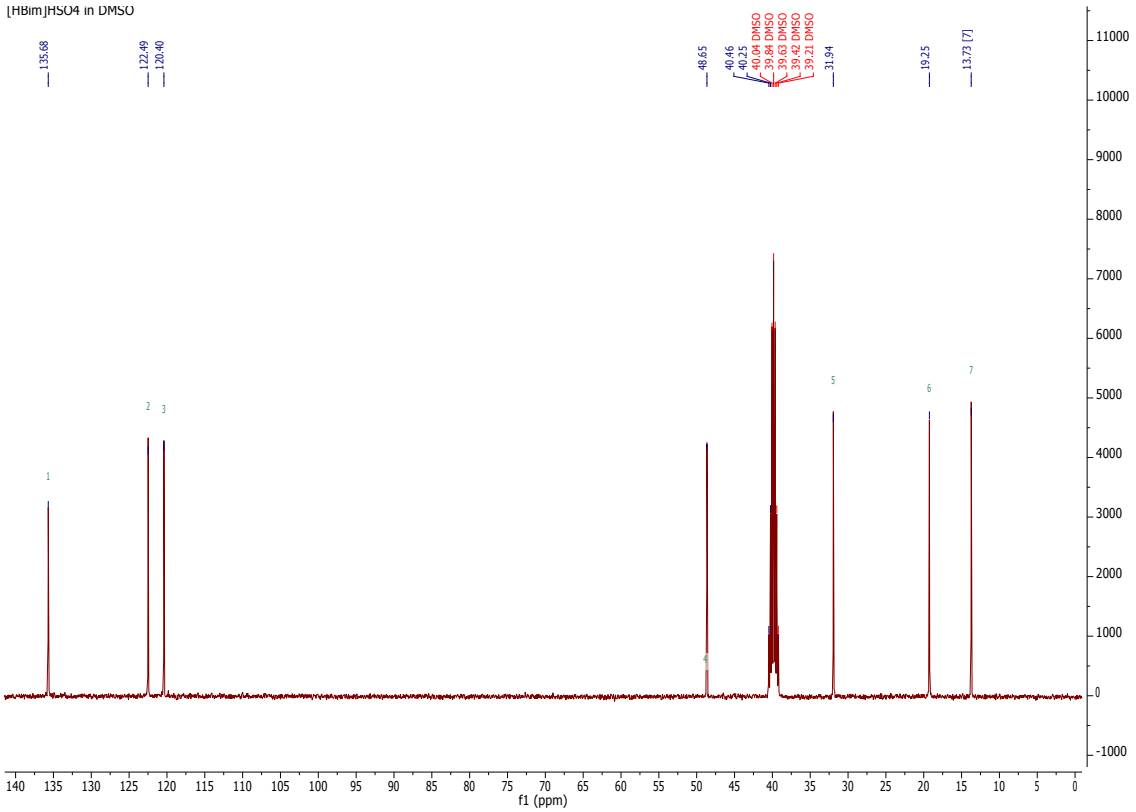

Figure S2. ^{13}C-NMR of [HC_4im[HSO_4]

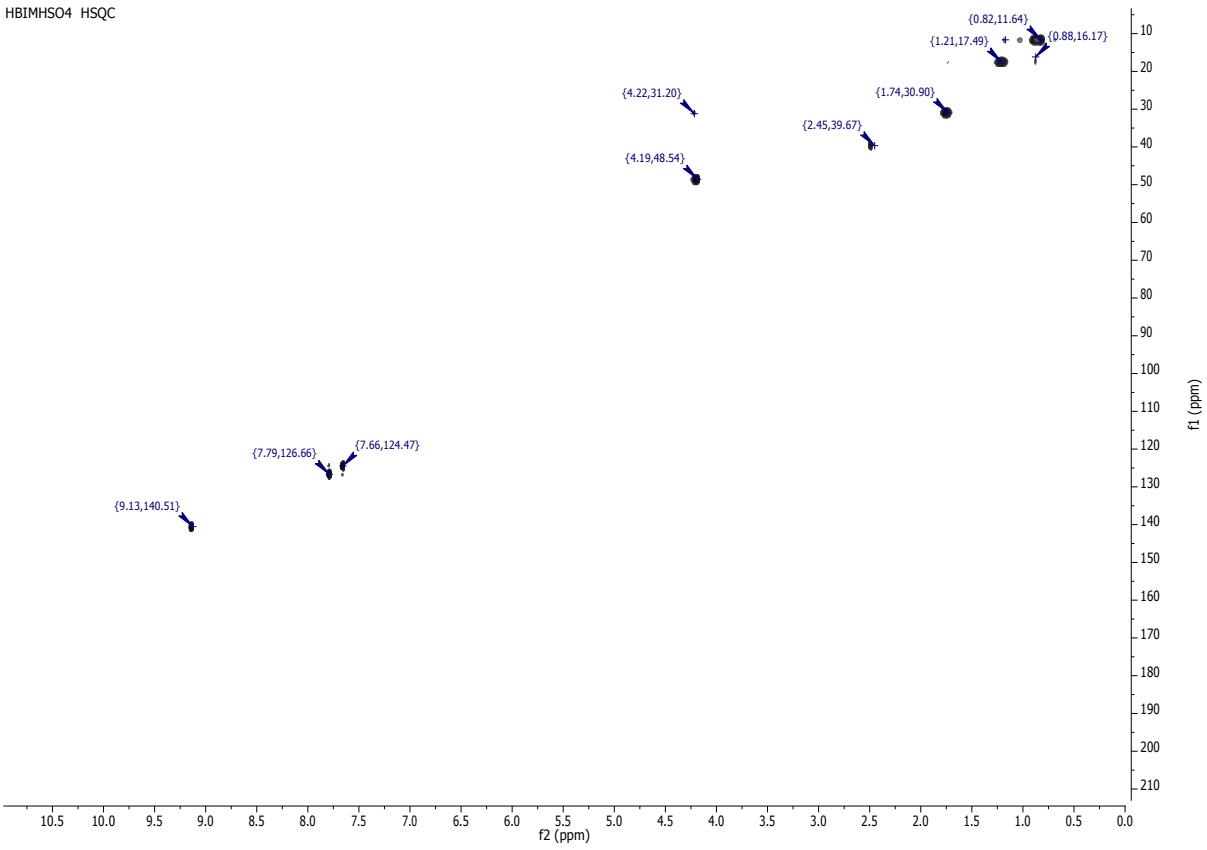

Figure S3. HSQC NMR of [HC_4im[HSO_4]

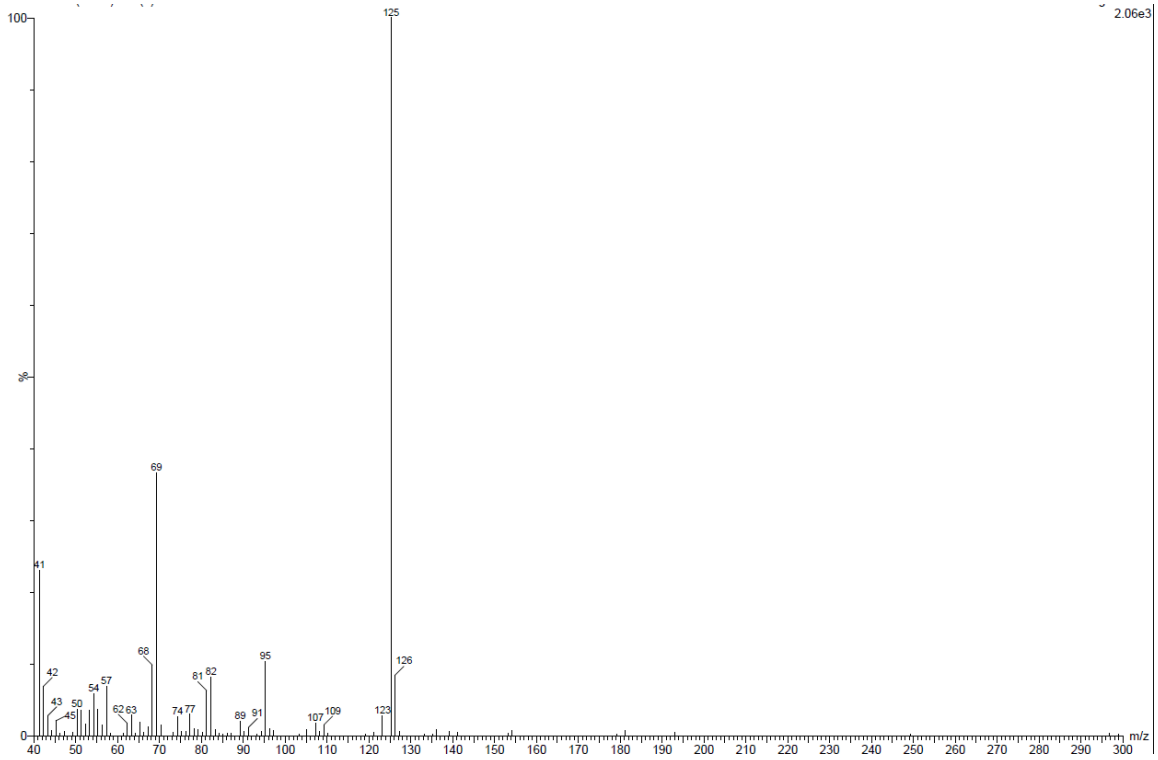

Figure S4. Mass spectrum (positive) of $[HC_4im][HSO_4]$

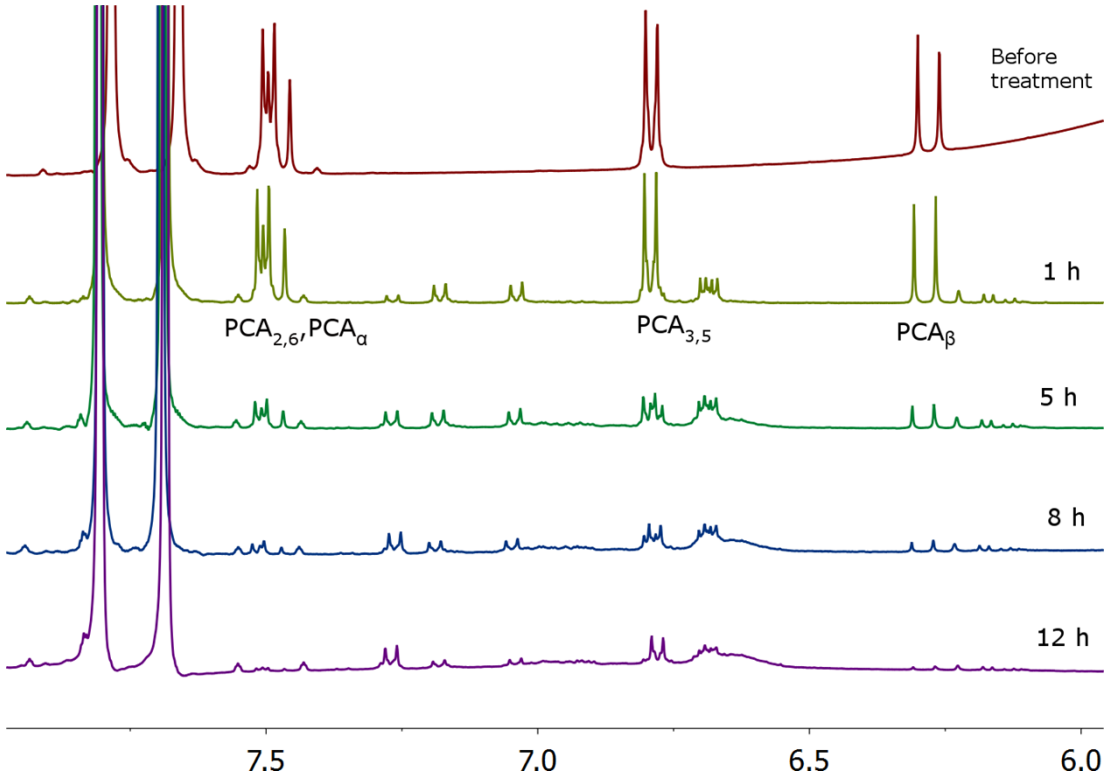

Figure S5. Stack of ^{1}H-NMR spectra recorded during incubation of p-coumaric acid (PCA) in a $[HC_4im][HSO_4]$water mixture at 120°C. The spectra represent the Ionosolv solution, not the precipitate.

Table S2. Assignment of the most important ^{13}C-^{1}H cross-signals in the HSQC NMR spectra

Label	δ_C /δ_H (ppm)	Assignment
C_β	53.5/3.46	C_β - H_β in phenylcoumaran substructures (C)
B_β	53.0/3.05	C_β - H_β in β–β (resinol) substructures (B)
C_γ	53.1/3.45	C_γ - H_γ in phenylcoumaran substructures
Methoxyl	55.6/3.73	C - H in methoxyl (-OCH_3) groups
A_γ and X_γ	59.5/3.40-3.72	C_γ- H_γ in β–*O*–4 substructures (A), primary hydroxyl groups in condensed lignin
Ara_5	64.2/4.32 and 64.4/4.12	C_5-H_5 of arabinofuranose
H_γ	66.9/4.15	C_γ - H_γ in Hibbert's ketone
B_γ	71.0/4.18 and 71.0/3.80	C_γ - H_γ in β–β (resinol) substructures (B)
A_α	71.7/4.86	C_α - H_α in β–*O*–4 substructures (A)
$Ara_{2,3,4}$	74.1-83.7/4.0-3.6	C_2 - H_2 , C_3-H_3 and C_4-H_4 of arabinofuranose
B_α	84.8/4.63	C_α - H_α in β – β (resinol) substructures (B)
A_β	86.7/4.17	C_β - H_β in β–*O*–4 substructures linked to S-type units (A)
C_α	86.9/5.45	C_α - H_α in phenyl coumaran substructures (C)
A_β(S/G-G)	83.5/4.28	C_β - H_β in β–*O*–4 substructures linked to a G unit (A)
A_β(S/G-S)	85.8/4.11	C_β - H_β in β–*O*–4 substructures linked to a S unit (A)
$S_{2,6}$	103.5/6.69	C_2-H_2 and C_6–H_6 in syringyl units (S)
G_2	110.5/6.99	C_2 - H_2 in guaiacyl units (G)
PCA_β and FA_β	113.5/6.27	C_2 - H_2 in ferulate (FA)
G_5	114.9/6.71 and 116.7/6.94	C_5 - H_5 in guaiacyl units (G)
G_6	118.5/6.76	C_6 - H_6 in guaiacyl units (G)
$H_{2,6}$	127.1/7.17	C_2 - H_2 and C_6 - H_6 *p*-hydroxyphenyl units (H)
$PCA_{2,6}$	130.0/7.46	C_2 - H_2 and C_6 - H_6 in *p*-coumarate (PCA)

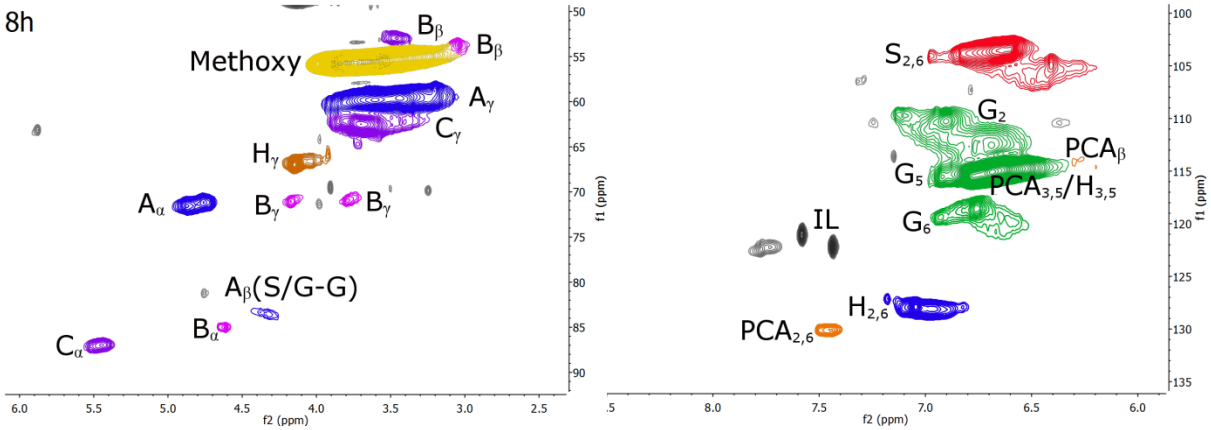

Figure S6. Assigned side chain (left) and aromatic (right) -regions of the HSQC NMR for 8 h Ionosolv lignin

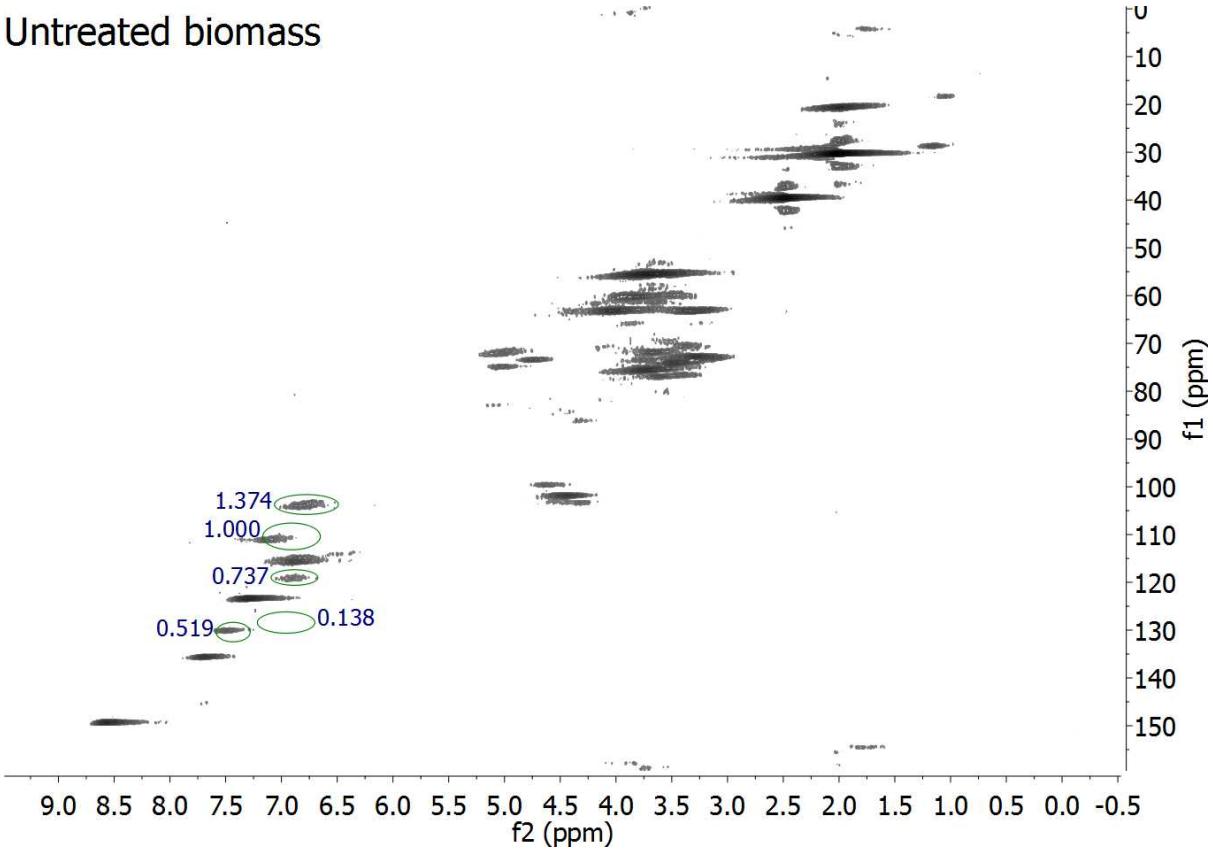

Figure S7. HSQC NMR of native *Miscanthus giganteus*

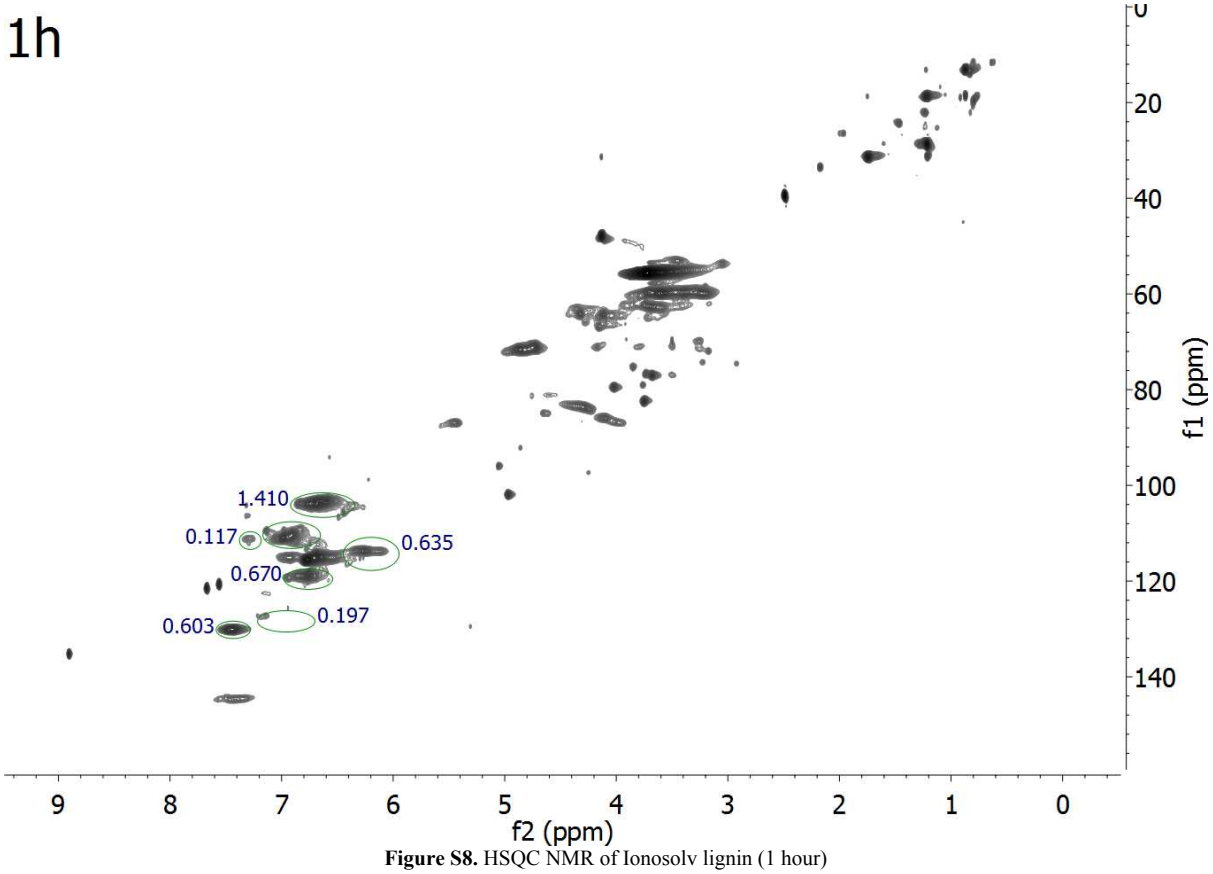

Figure S8. HSQC NMR of Ionosolv lignin (1 hour)

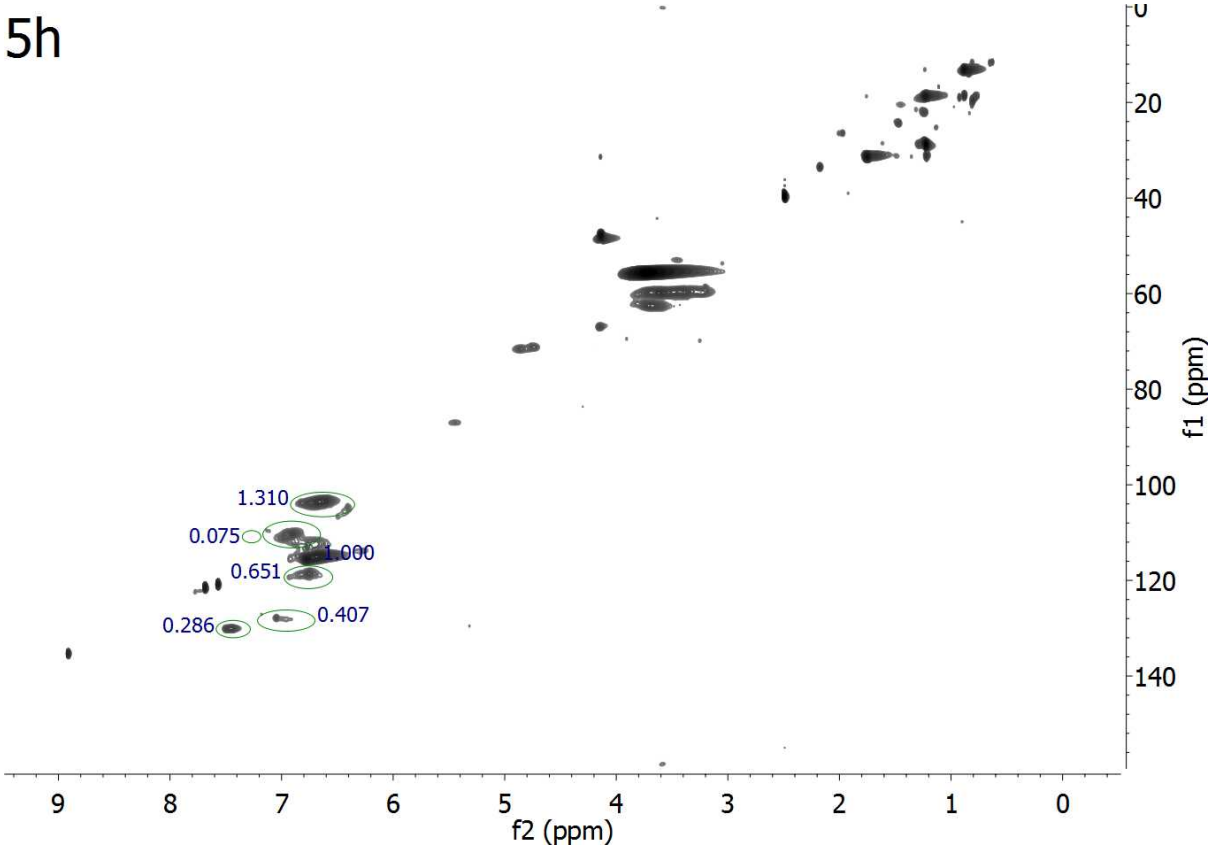

Figure S9. HSQC NMR of Ionosolv lignin (5 hours)

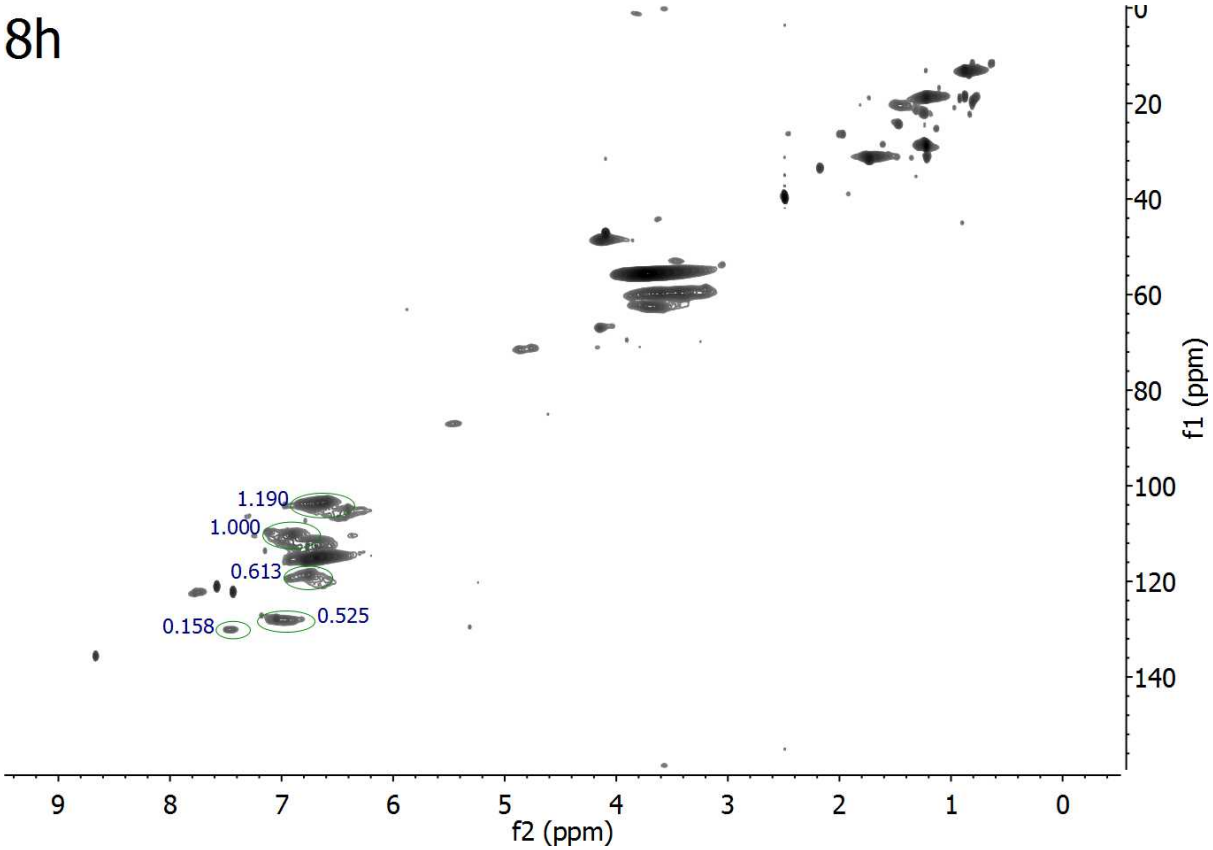

Figure S10. HSQC NMR of Ionosolv lignin (8 hours)

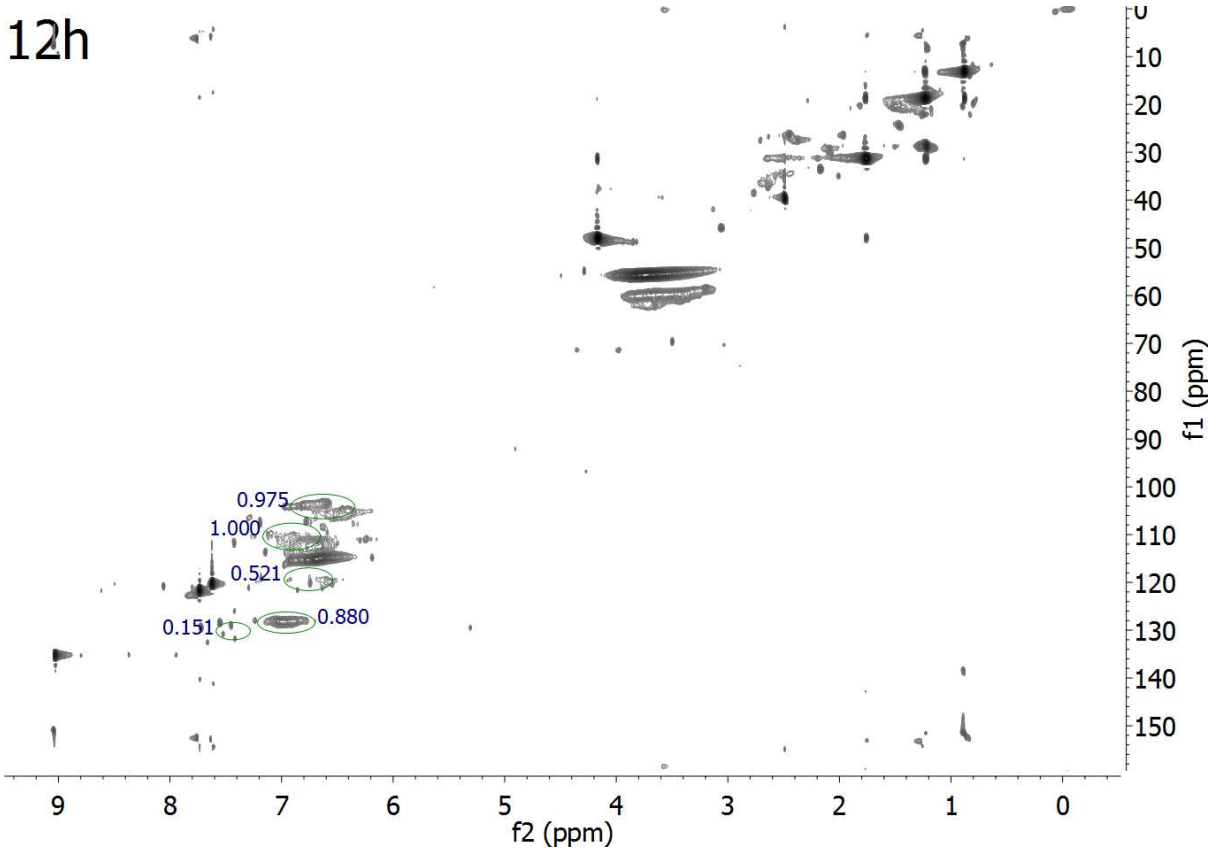

Figure S11. HSQC NMR of Ionosolv lignin (12 hours)

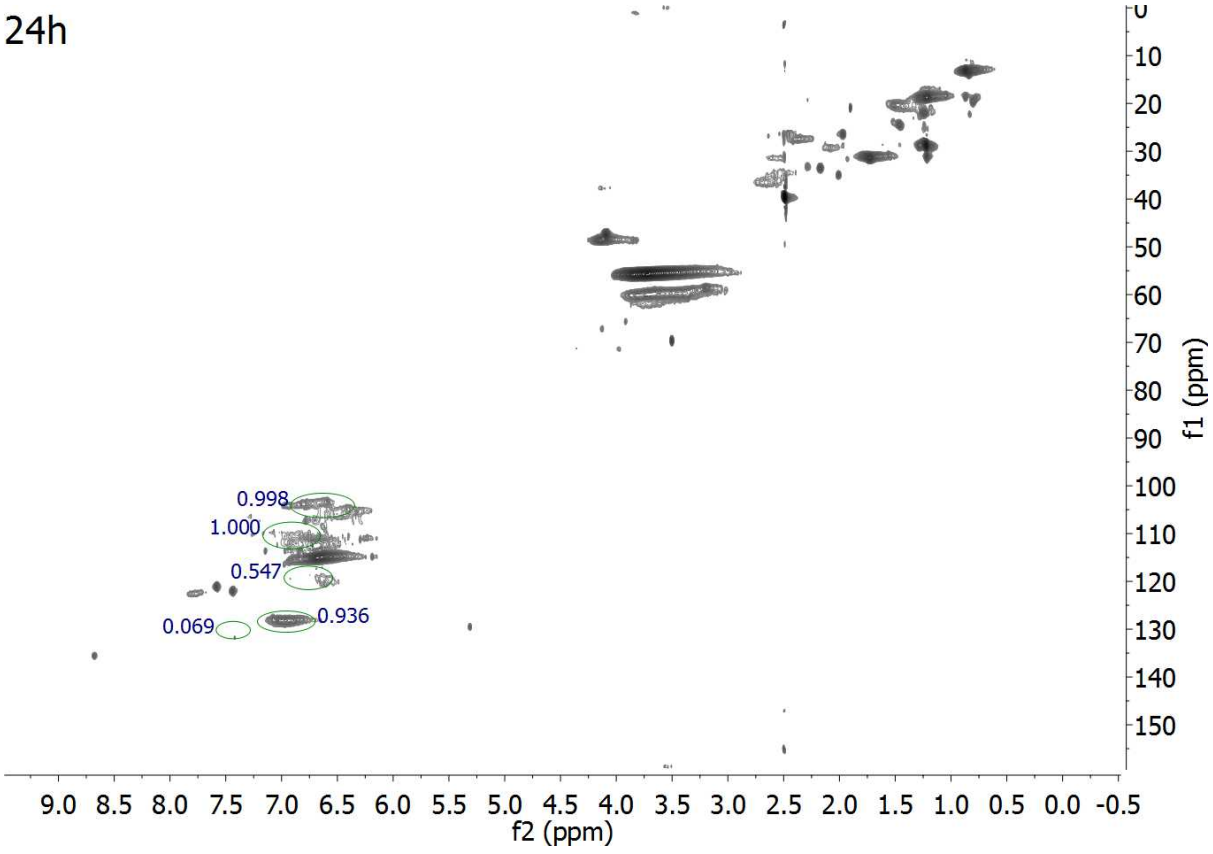

Figure S12. HSQC NMR of Ionosolv lignin (24 hours)

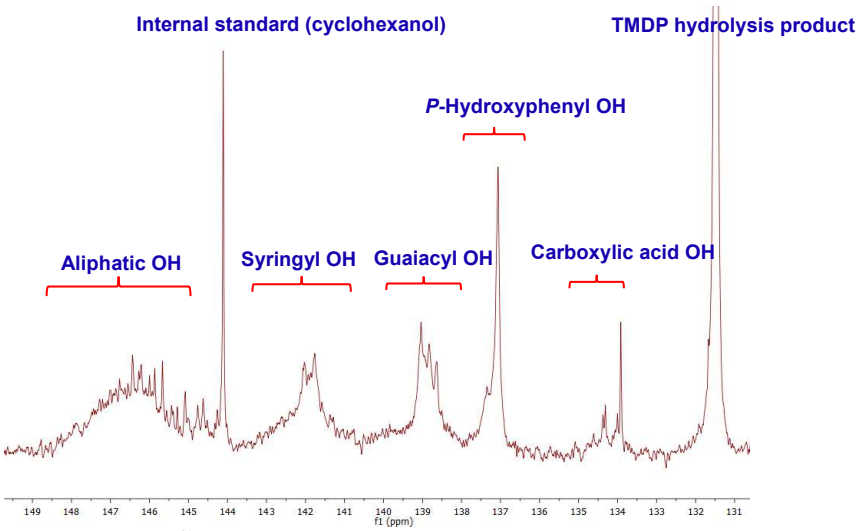

Figure S13.[31]P-NMR of recovered cellulose after 1 hour of Ionosolv pretreatment

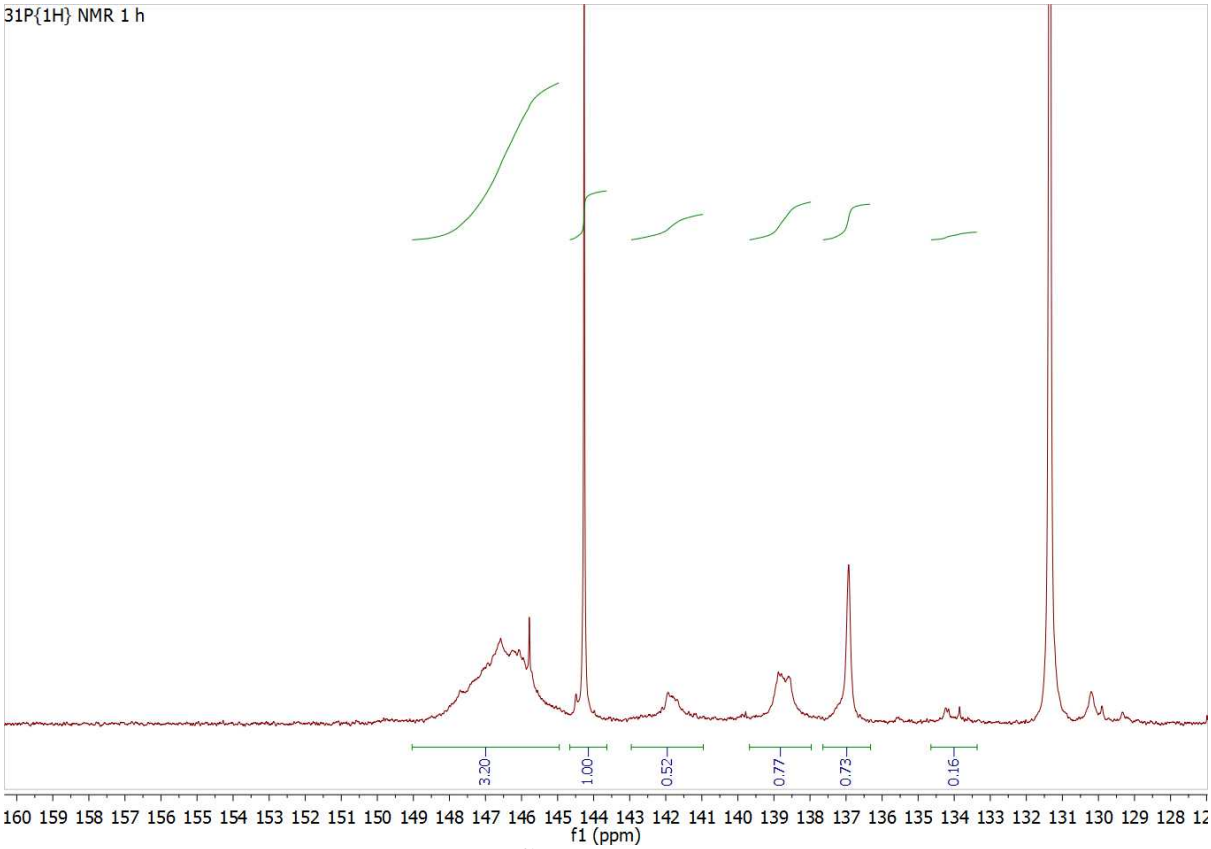

Figure S14.[31]P-NMR of 1 h Ionosolv lignin

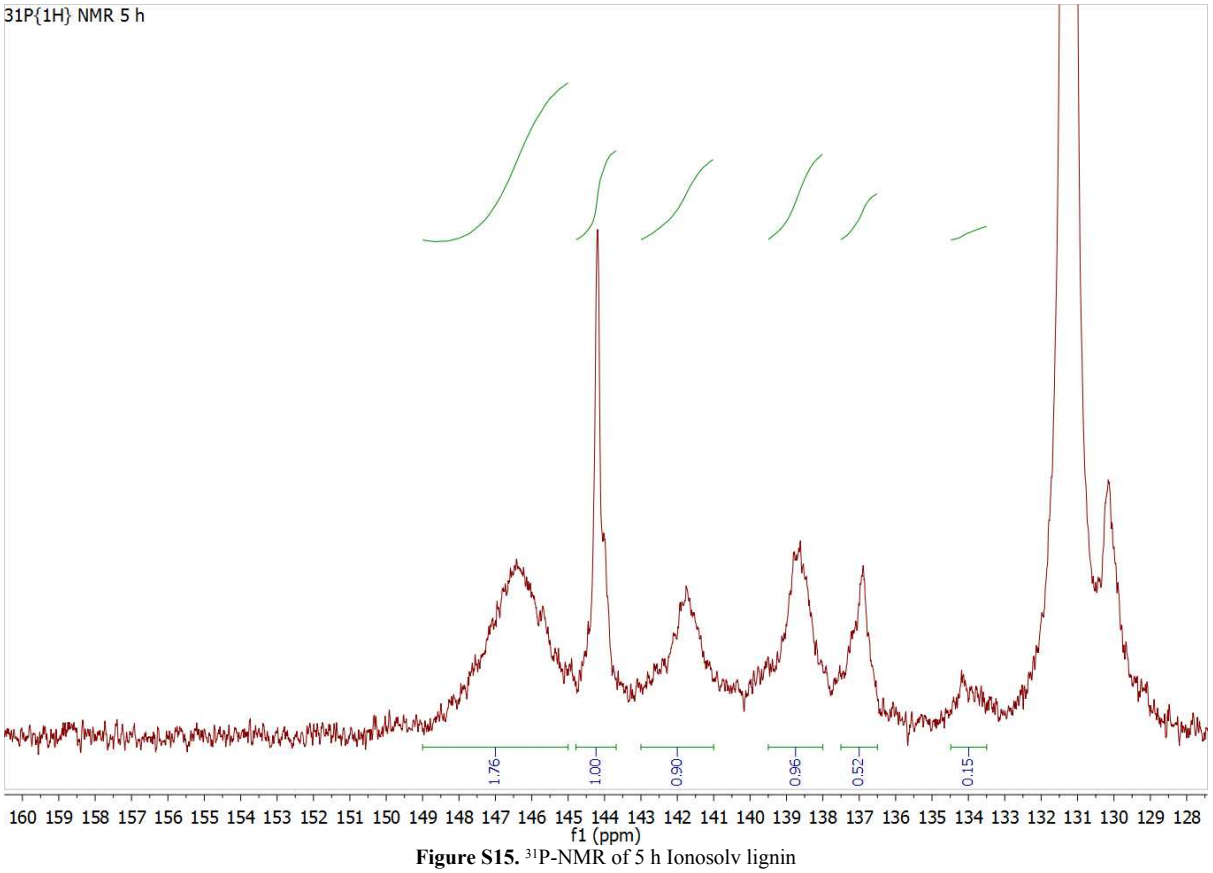

Figure S15. ^{31}P-NMR of 5 h Ionosolv lignin

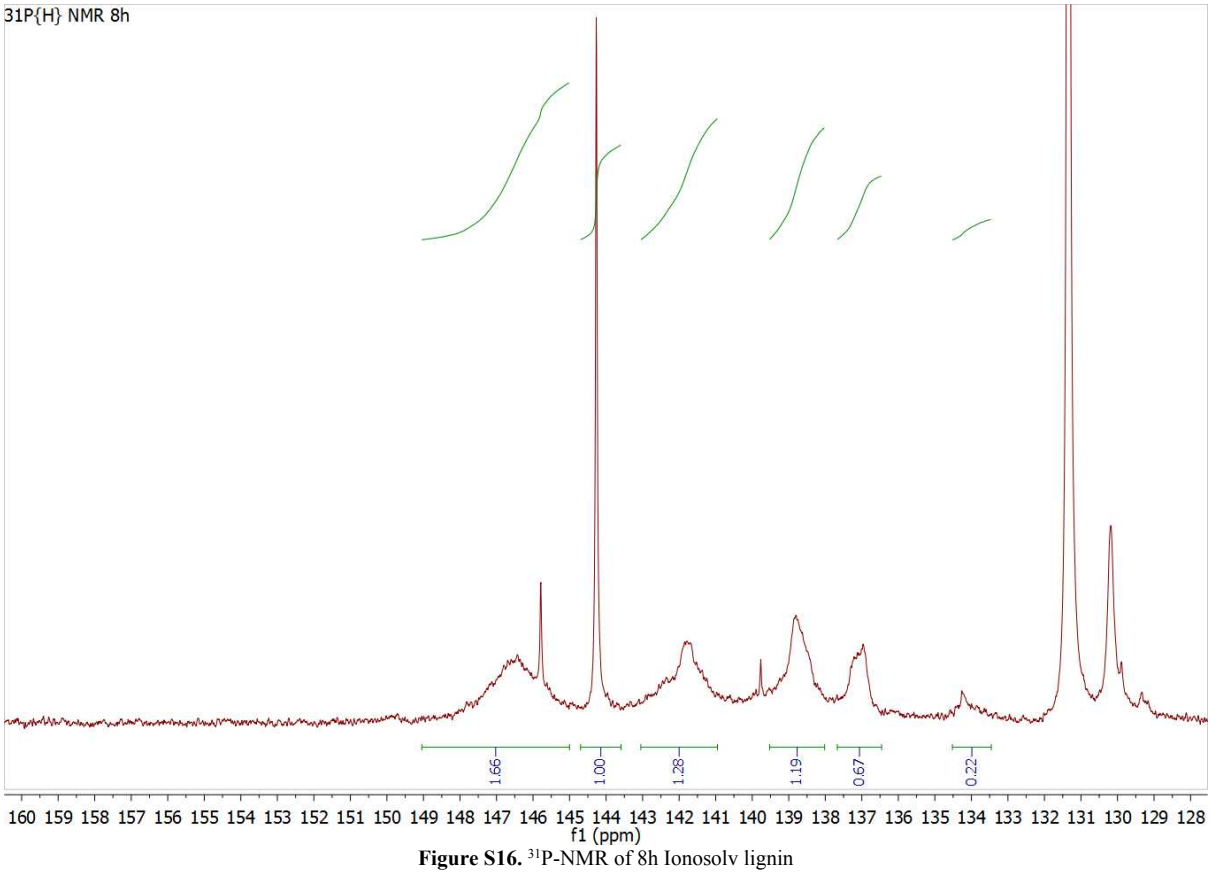

Figure S16. ^{31}P-NMR of 8h Ionosolv lignin

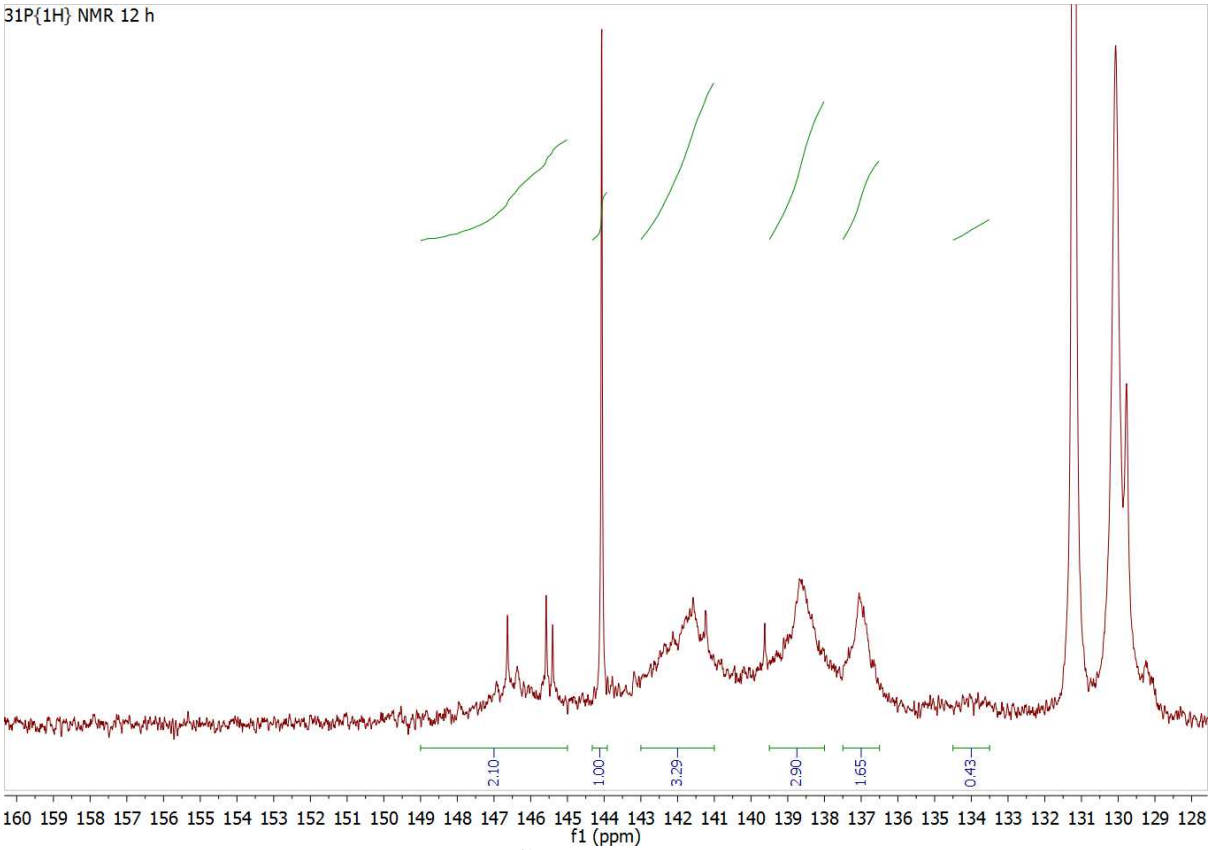

Figure S17. ^{31}P-NMR of 12 h Ionosolv lignin

Table S3. Determination of the concentration of the hydroxyl groups in lignin by ^{31}P-NMR analysis

Hydroxyl group	NMR shift	1 hour (mmol/g)	5 hours (mmol/g)	8 hours (mmol/g)	12 hours (mmol/g)	Tendency
Aliphatic	149-145	2.792	1.582	1.361	1.509	Decrease, slight increase
Syringyl	143-141	0.454	0.733	1.047	2.365	Increase
Guaiacyl	139.5-138	0.672	0.759	0.969	2.085	Increase
p-Hydroxyphenyl	137.5-136.5	0.637	0.410	0.611	1.187	Slight decrease, increase
Carboxylic	134.5-133.5	0.140	0.113	0.175	0.305	Slight increase

Table S4: Elemental analysis raw data

	C (%)	H (%)	N (%)	S (%)
1 h 1	59.86	5.40	0.71	1.03
1 h 2	59.84	5.56	0.71	0.96
5 h 1	61.38	5.48	1.17	1.38
5 h 2	61.58	5.66	1.13	1.24
8 h 1	62.54	5.48	1.03	1.14
8 h 2	62.59	5.47	0.96	1.09
12 h 1	58.62	5.35	3.32	3.57
12 h 2	58.31	5.29	3.38	3.88

Table S5: IL content, cation/anion ratio and C and H contributions of IL to elemental analysis (wt%)

	Cation content (%)	Anion content (%)	Sum IL (%)	Cation/anion ratio	H contribution from cation (%)	C contribution from cation (%)
1 h	3.17	3.02	6.19	0.82	0.31	2.15
5 h	5.13	3.97	9.10	1.00	0.50	3.48
8 h	4.44	3.38	7.82	1.02	0.43	3.01
12 h	14.96	11.29	26.25	1.03	1.46	10.12

Table S6: corrected values for elemental composition of lignin

	C (%)	H (%)
1h	61.51	5.51
5h	63.81	5.58
8h	64.61	5.47
12 h	65.54	5.24