Electronic Supplementary Material (ESI) for RSC Advances.

Supplement 1

Figure 1: Lignin content of Solution 1 permeate after XAD-4 resins cycling obtained by UV spectrometry at 280nm

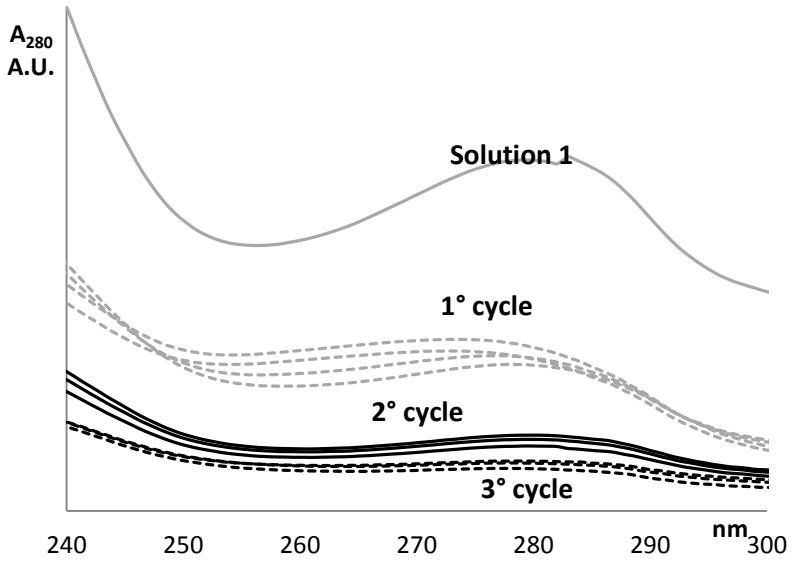
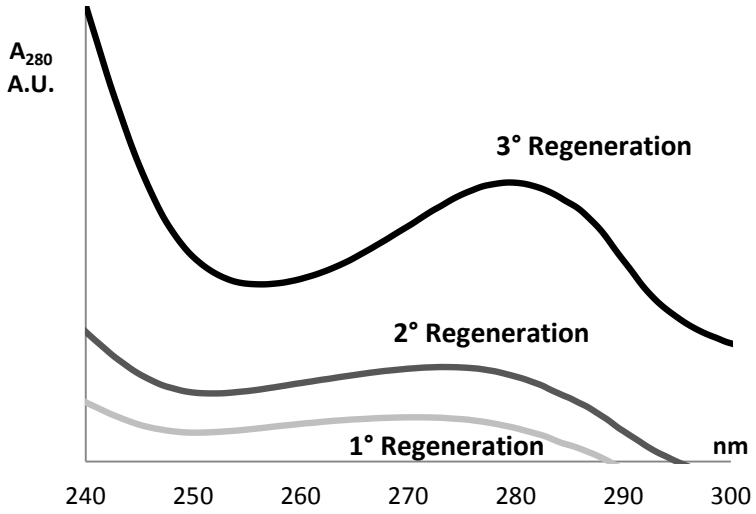


Figure 2: Lignin content of solution 1 retentate (Fraction 2) after XAD-4 resins cycling obtained by UV spectrometry at 280nm



Supplement 2

Figure 1-4: DSMO+0.5% LiBr SEC chromatograms of LCCs fractions

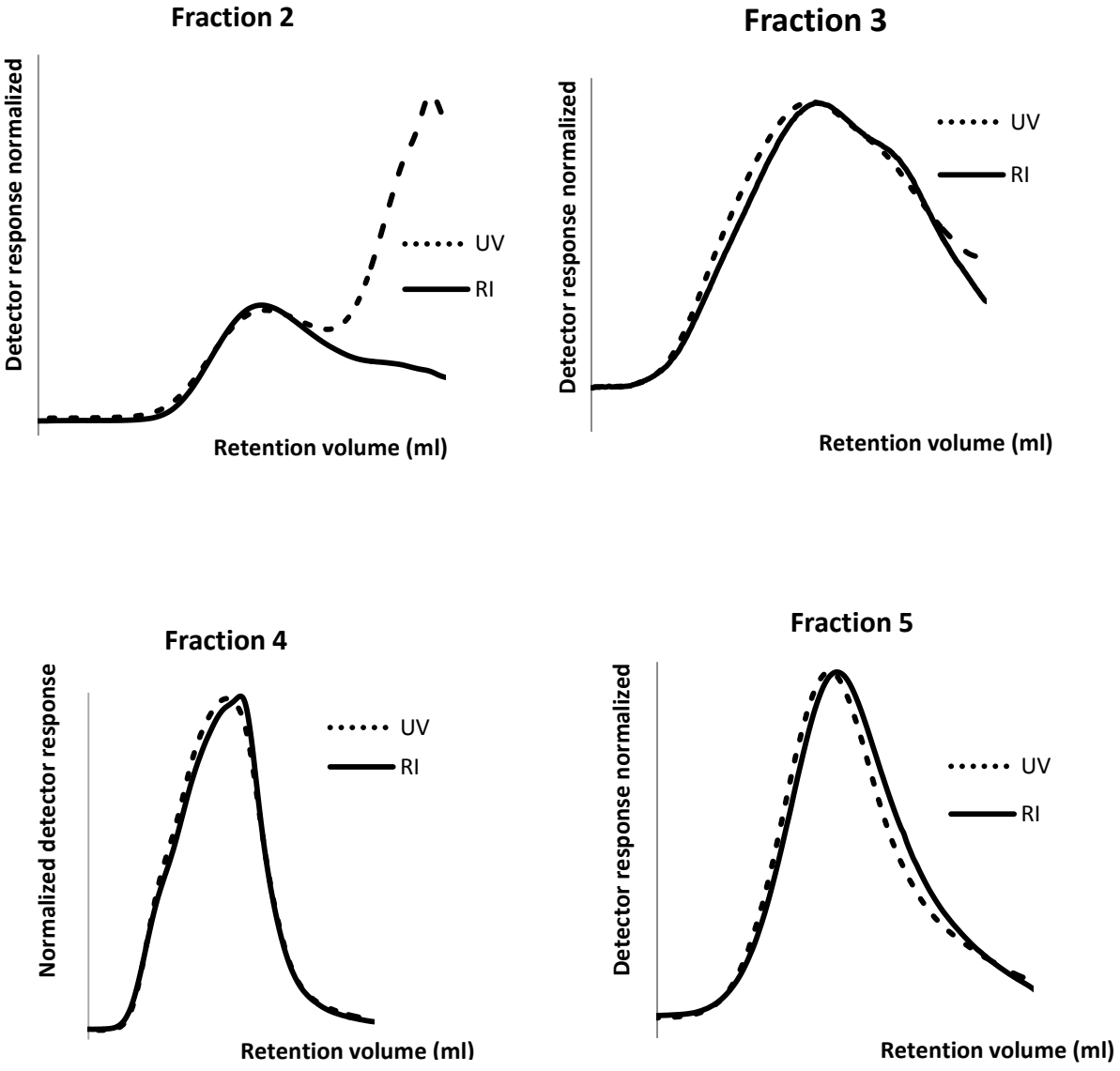
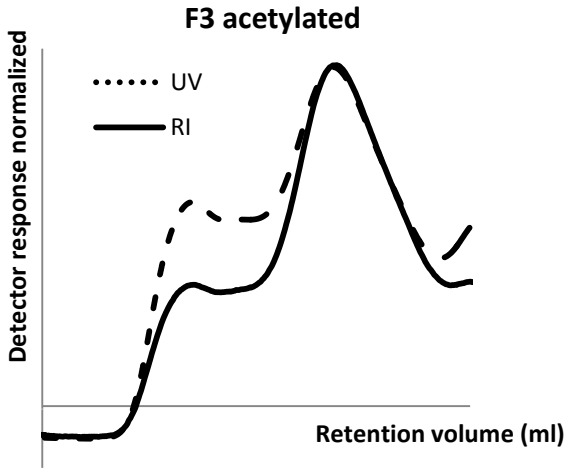


Figure 5: DSMO+0.5%LiBr SEC chromatograms of fractions 3 acetylated



Supplement 3

	Retention time	*M+*	*Fragments*						*Inter-units bond*
Monomers	5.14	194(10)	152(90)	137(100)					βO4
	5.52	208(10)	166(80)	151(100)					
	5.86	208(20)	166(80)	137(85)					
	6.76	206(10)	164(100)	149(35)					
	7.4	222(5)	180(30)	151(100)					
	9.51	266(10)	224(75)	164(100)	149(35)	137(65)			
Dimers	15.4	372(0.1)	330(20)	288(100)	259(40)				β1
	16.65	414(0.1)	372(25)	330(100)	315(30)	273(25)	150(18)	137(20)	55
	17.1	400(0.1)	358(20)	316(100)	287(20)	255(10)	241(8)		55
	17.43	414(0.1)	372(30)	330(100)	315(30)	301(10)	287(5)	259(10)	55
	17.64	414(0.1)	372(10)	330(100)	301(30)	269(10)	179(10)	150(55)	55
	18.24	414(0.1)	372(40)	330(100)	301(50)	269(10)	254(8)	227(5)	55
	18.62	358(1)	316(40)	274(50)	137(100)				β1
	19.52	386(1)	344(40)	302(60)	165(40)	137(100)			β5
	19.89	400(0.1)	358(50)	316(80)	179(50)	137(100)			β5
	20.18	414(0.1)	372(30)	330(10)	193(100)	137(20)			β5
	20.92	400(1)	358(60)	316(90)	179(60)	137(100)			β5
	21.51	356(20)	314(100)	285(15)					4O5

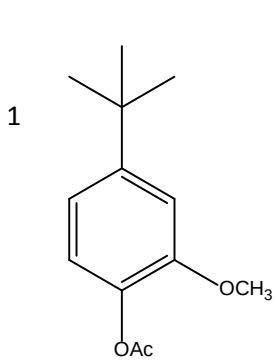
Table 1 Selected monomers and dimers fragments of fraction 5 GC MS spectra degraded by thioacidolysis and Raney-nickel desulphuration.

The mass (m_x) of uncondensed βO4 linkages have been calculated according to:

$$\frac{A_{IS}}{m_{IS}} = \frac{A_x}{m_x} R_f$$

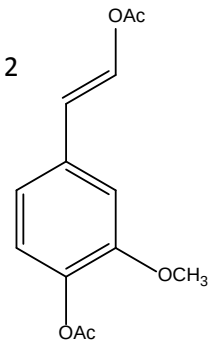
Where A_{is} and m_{is} are the GC MS area and mass of internal standard respectively, R_f is the response factor and A_x is the area of the peaks belonging to a specific interunit linkage.

Figure 1: Response factor and structures of model compounds used for quantitative characterization of βO4(1 and 2) and dimers (3)



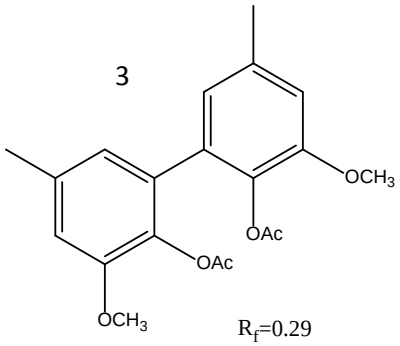
$R_{f=}1.24$

4-(*tert*-butyl)-2-methoxyphenyl acetate



R_f=0.32

2-methoxy-4-(3-oxopropyl)phenyl acetate



R_f=0.29

3,3'-dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diyl diacetate

To obtain the value in percentage,

$$\%_x = (^{m_x}/_{m_s}) x100$$

Where m_s it the mass of the lignin sample injected.

The percentage of βO4 accounts for only non-condensed etherified units in lignin and takes into consideration as thioacidolysis´ yield 76% whereas the percentages of the other most common interunit linkages, namely β1, 55, 4O5, β5 and have been calculated using R_f=0.29 which has been obtained from 55 dimer model compound (Structure 3 in Figure 1)

Supplement 4

Figure 1: HSQC 2D-NMR of acetylated phenyl mannopyranoside and model compounds.

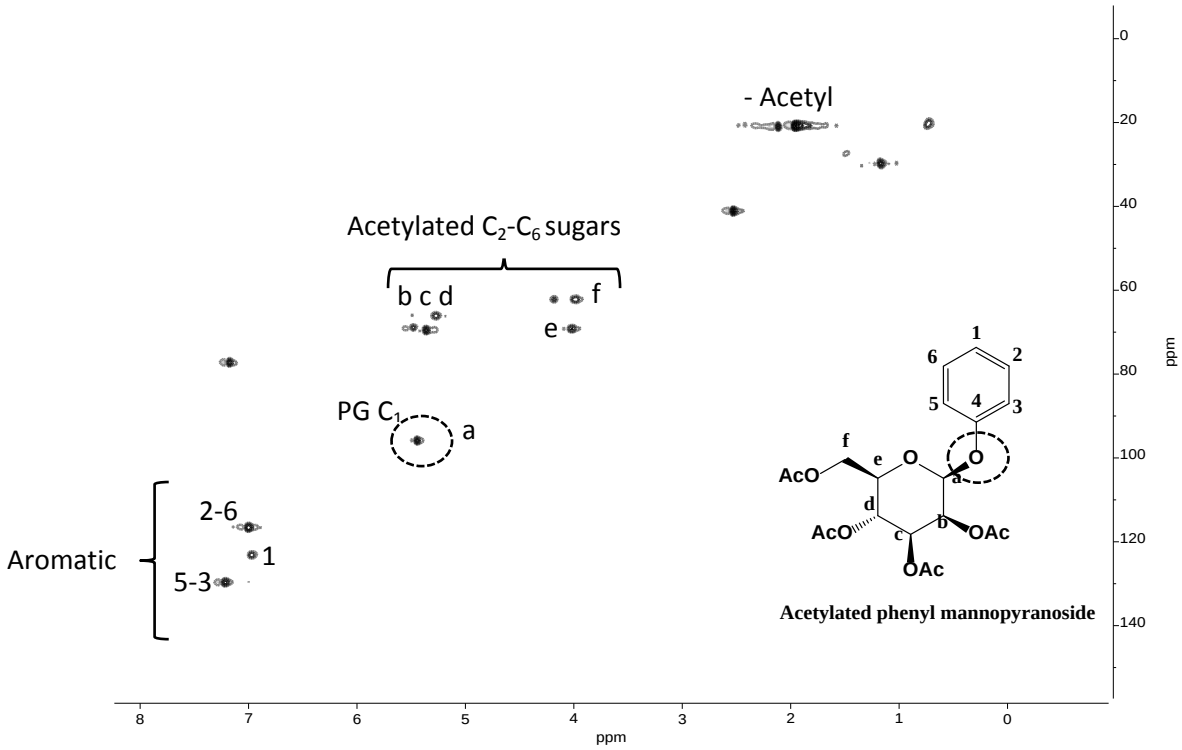
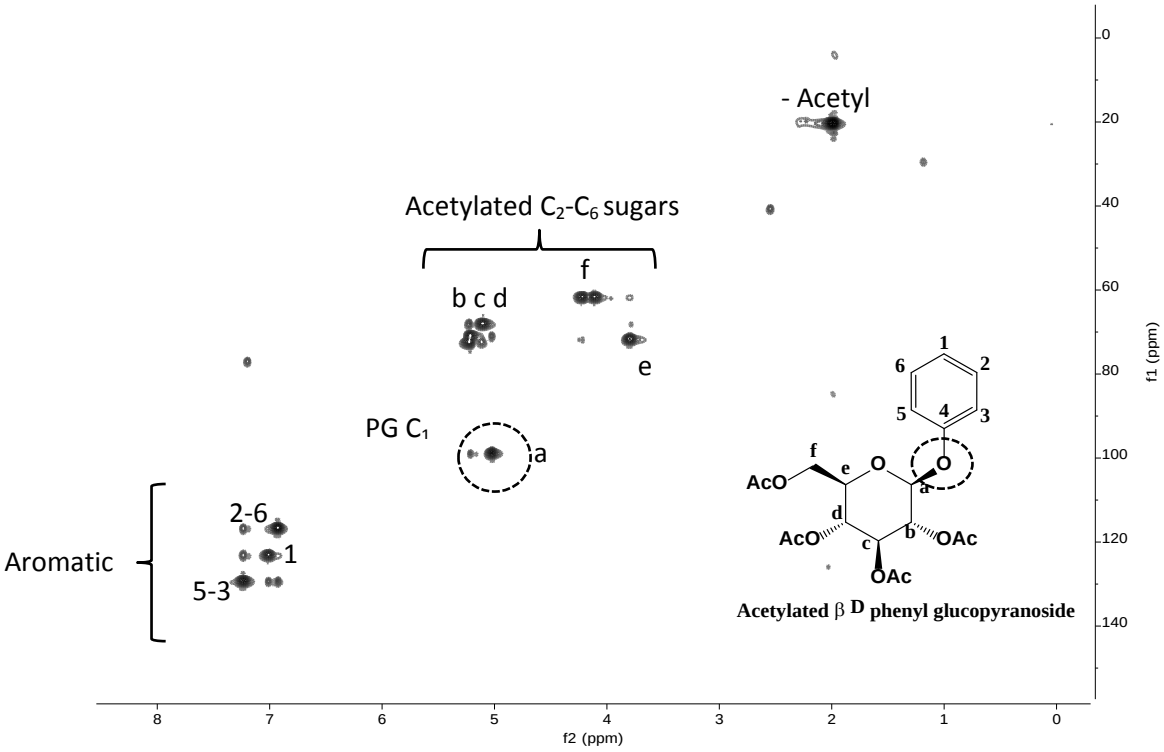


Figure 2: HSQC 2D-NMR of acetylated phenyl β D glucopyranoside model compounds.



Supplement 5

	Signal	δ_C	δ_H	Description
Lignin singnals in DMSO-d_6	1_α	71.5	4.79	C_α-H_α in βO4
	1_β	84.4	4.29	C_β-H_β in βO4
	2_α	87.5	5.47	C_α-H_α in β5
	2_γ	62.1	3.82	C_γ-H_γ in β5
	3_α	83.8	4.80	C_α-H_α in DBO
	3_β	85.8	3.92	C_β-H_β in DBO
	3_γ	60.4	3.42	C_γ-H_γ in DBO
	4_β	54.0	3.05	C_β-H_β in ββ
	4_γ	71.5	4.16	C_γ-H_γ in ββ
	4_γ	71	3.78	C_γ-H_γ in ββ
	5_α	82	5.05	C_α-H_α in SD
	5_β	59.9	2.80	C_β-H_β in SD
	6_α	129/129.3	6.28/6.47	C_α-H_α in Coniferyl Alchool
	6_γ	62.0	4.10	C_γ-H_γ in Coniferyl Alchool
	7_β	126.6	6.79	C_β-H_β in Coniferyl Aldehyde
	8_{C6}	122.1	7.65	α–C=O
	9	56.1	3.76	Methoxy

Table 1: Assignment of main ^{13}C-^{1}H 2D HSQC correlation signals from lignin compounds of original samples.

	Signal	δ_C	δ_H	Description
Acetylated Lignin signals in $CDCl_3$	1_α	74.2	6.02	C_α-H_α in βO4
	1_β	80.1	4.62	C_β-H_β in βO4
	2_α	88.2	5.56	C_α-H_α in β5
	2_β	50.4	3.86	C_γ-H_γ in β5
	3_β	82.1	4.21	C_β-H_β in DBO
	4_β	54.4	3.12	C_β-H_β in $\beta\beta$
	5_α	81.5	5.11	C_α-H_α in SD
	5_β	60	3.39	C_β-H_β in SD
	9	56.1	3.80	Methoxy

Table 2: Assignment of main ^{13}C-^{1}H 2D HSQC correlation signals from lignin compounds acetylated samples.

	Signal	δ_C	δ_H	Description
LCCs signals in DMSO-d_6	PG	99-104	4.8-5.3	Phenyl Glycoside
	$BE_1(\alpha)$	80.1-81.2	4.21-4.68	Benzyl ether to C6/C5
	$BE_2(\alpha)$	81.7	5.04	Benzyl ether to C2/C3 in α
	γ-ester	62.7	4.31	γ-ester

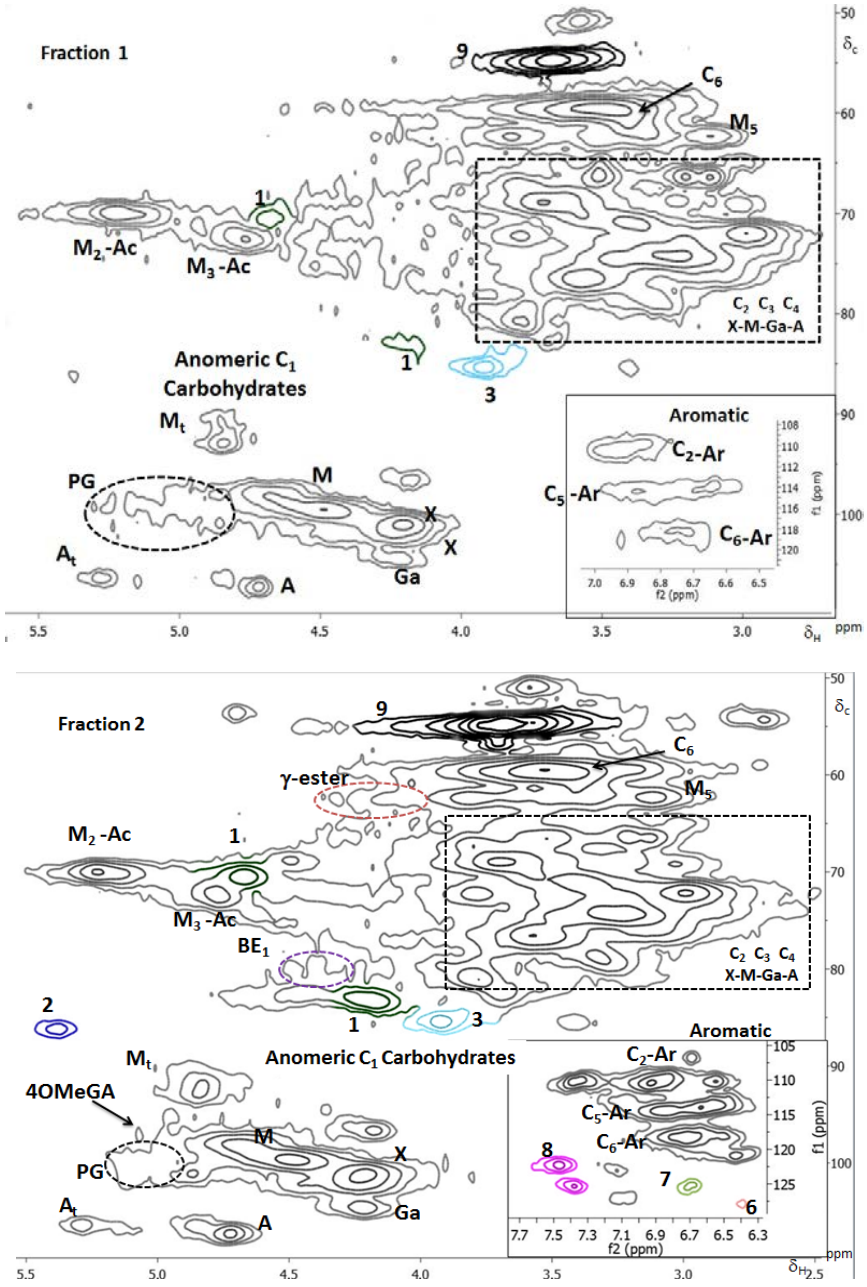
Table 3: Assignment of main ^{13}C-^{1}H 2D HSQC correlation signals from lignin carbohydrate signals of original samples.

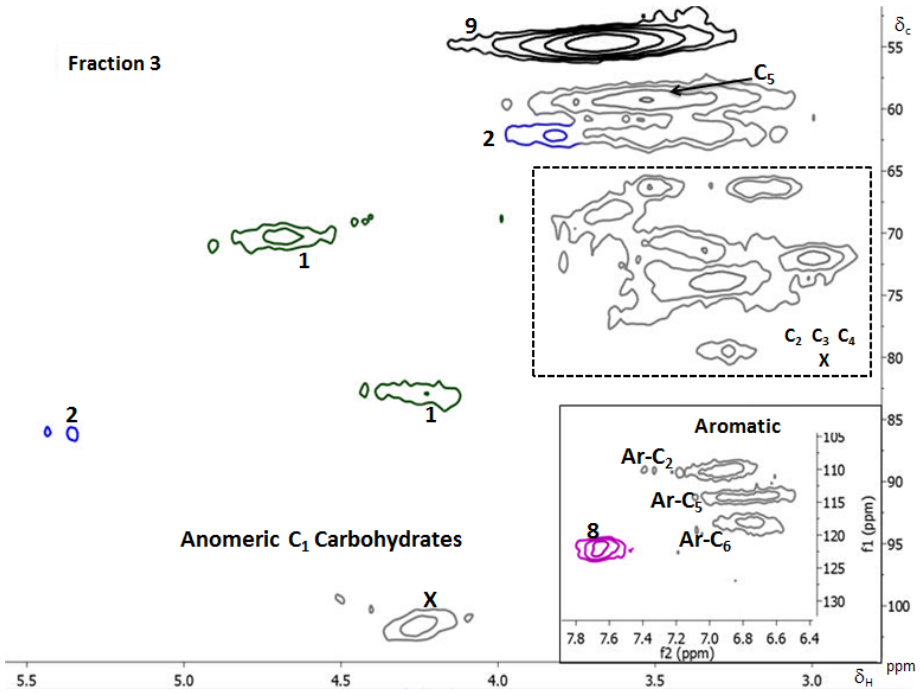
	Signal	δ_C	δ_H	Description
Acetylated LCCs signals in in $CDCl_3$	PG(M)	99.1	5.41	Phenyl Glycoside to mannose
	PG(Glu)	100.5	5.16	Phenyl Glycoside to glucose
	$BE_1(\alpha)$	83.9	4.75	Benzyl ether to C6/C5
	BE_1(C6)	62.3	3.29	Benzyl ether to C6/C5
	$BE_2(\alpha)$	81.5	4.91-5.16	Benzyl ether to C2/C3 in α
	BE_2(C2-C3)	78.5	3.63	Benzyl ether to C2/C3 in xylan

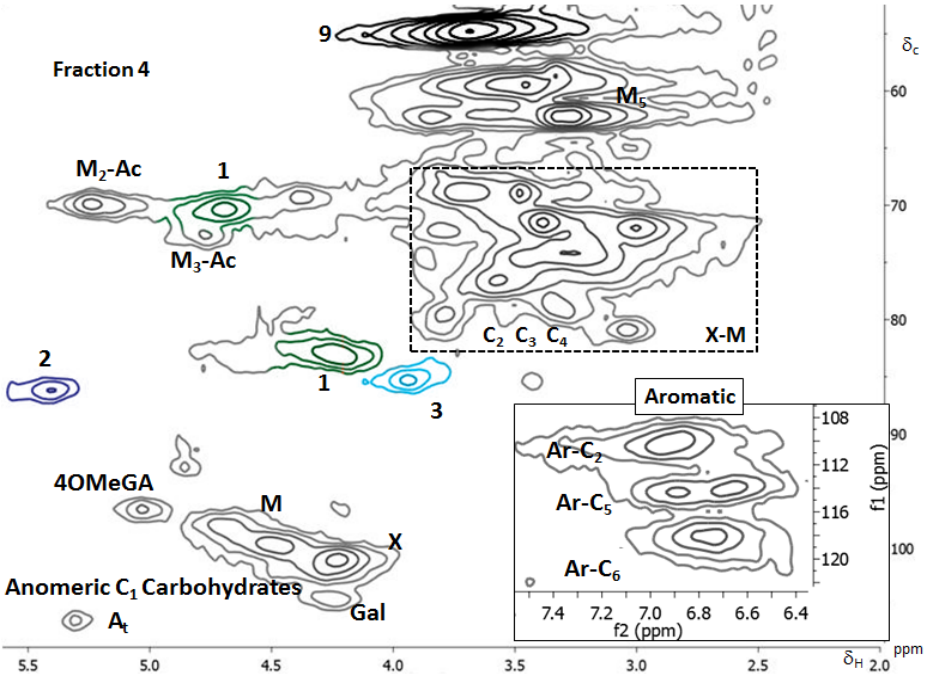
Table 4: Assignment of main ^{13}C-^{1}H 2D HSQC correlation signals from lignin carbohydrate signals of acetylated samples.

Supplement 6

Figure 1-4: 2D HSQC of Fraction 1-4 respectively in in d6-DMSO. In the figure M=Mannose, X=Xylan, Ga=Galactose, A=Arabinose, Gl=Glucose, Ar-C=Carbon in the aromatic, Ac=Acetylated, 4OMeGA=4OMethyl glucuronic acid, GU= Galacturonic acid. The subscript t stands for the carbohydrate terminal reducing end whereas the number in subscript indicates the carbon number either in the aromatic and sugar ring. In the right bottom corner it has been expanded and reported the aromatic region in the δ_H/δ_C area.




Fraction 3
9
C5
2
1
1
2
C2 C3 C4
X
Aromatic
Ar-C2
Ar-C5
Ar-C6
8
Anomeric C1 Carbohydrates
X
f1 (ppm)
f2 (ppm)
δc
δH
ppm


Fraction 4
9
M5
M2-Ac
1
M3-Ac
C2 C3 C4
X-M
2
1
3
Aromatic
Ar-C2
Ar-C5
Ar-C6
4OMeGA
M
X
Anomeric C1 Carbohydrates
At
Gal
f1 (ppm)
f2 (ppm)
δc
δH
ppm