Supporting information

Systematic Diffusion Ordered Spectroscopy for the Selective Determination of Molecular Weight in real Lignins and Fractions arising from Base-Catalyzed Depolymerization Reaction mixtures.

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1. Monomer Groups and retention times

Table S1. Monomer groups and retention times.

Group	Compound	Retention time (min)
Internal Standard	Bromobenzene	8.67
Phenols	Phenol	9.22
Phenols	o-cresol	11.06
Phenols	p-cresol/m-cresol	11.55/11.88
Guaiacols	Guaiacylglycerol-β-guaiacyl ether	12.12
Vanillins	Vanillic acid	12.12
Guaiacols	Guaiacol	12.26
Phenols	2-ethylphenol	13.22
Phenols	3-ethylphenol	14.03
Phenols	4-ethylphenol	14.10
Catechols	Catechol	14.89
Others	3,4-dimethoxyphenol	14.90
Guaicols	4-methylguaiacol	14.95
Guaicols	4-ethylguaiacol	17.18
Catechols	4-methylcatechol	17.33
Syringols	Syringic acid	18.83
Syringols	2,6 dimethoxyphenol (Syringol)	18.88
Guaicols	4-Allylguaiacol, Eugenol	19.12
Phenols	4-hydroxybenzaldehyde	19.25
Guaicols	4-Propylguaiacol	19.33
Catechols	4-ethylcatechol	19.57
Vanillins	Vanillin	20.04
Others	Diphenylether	20.43
Guaicols	Guaiacylketone	22.40
Vanillins	Syringaldehyde	24.50
Vanillins	Acetosyringone	25.60
Syringols	4-methylsyringol	20.82
Vanillins	Acetovanillin	21.79

2. Optimization of the BCD reaction conditions

Table S2. Optimization of the BCD reaction conditions using 0.25 M NaOH (1 % w/v; pH 13.4) and NaOH/ POP_L 25:1. Error is given at 95 % confidence level.

T[a]	t (min)	Soluble fraction (%w)	Monomer (%w yield)	Phenol's (%)	Guaiacol's (%)	Catechol's (%)	Syringol's (%)	Vanillin's (%)
150	60	58	2.2	23	20	0	45	14
	120	63	2.3	27	21	0	40	13
	240	32	3.2	18	18	0	48	15
				22.7 ± 4.0	19.4 ± 1.5	0.0	43.9 ± 3.9	13.8 ± 1.0
175	0	53	1.4	25	16	0	37	21
175	60	61	4.9	24	29	0	39	7
175	120	67	6.8	24	26	0	40	10
175	180	67	8.2	20	29	0	37	9
175	240	39	5.1	27	27	0	37	8
175	300	50	7.1	27	30	0	34	11
				24.5 ± 2.2	26.1 ± 4.2	0.0	37.4 ± 2.0	11.1 ± 4.2
200	0	42	3.1	26	26	0	37	10
200	60	36	6.4	19	36	0	37	8
200	120	40	5.4	22	37	0	34	7
200	180	41	6.6	24	38	0	31	8
200	240	59	9.1	22	36	0	31	11
200	300	61	9.5	23	38	0	29	10
200	360	64	9.7	19	37	0	34	9
200	480	42	6.4	28	44	0	21	7
200	1200	34	5.4	23	48	0	23	6
				22.8 ± 1.9	37.9 ± 3.9	0.0	30.8 ± 3.7	8.5 ± 1.1
200 (PIN_L)	240		4.1	6	81	0	0	3
225	60	67	7.8	22	41	0	31	7
225	60	51	8.2	22	41	1	29	7
225	180	42	6.6	25	45	0	23	7
225	240	54	7.2	20	43	0	27	11
				22.3 ± 2.1	42.2 ± 1.7	0.2 ± 0.4	27.6 ± 3.1	7.8 ± 1.9
250	60	40	6.5	30	48	0	16	6
250	120	48	5.1	27	48	0	18	7
				28.1 ± 2.3	48.4 ± 0.1	0.0	16.8 ± 2.0	6.8 ± 0.5
275	0	51	7.5	19	40	0	31	9
275	60	57	4.9	43	35	8	5	10
275	120	36	2.4	59	26	6	3	6
275	240	58	5.9	65	19	17	0	0
300	0	40	4.4	50	33	6	2	9
300	60	35	3.2	55	18	15	5	6

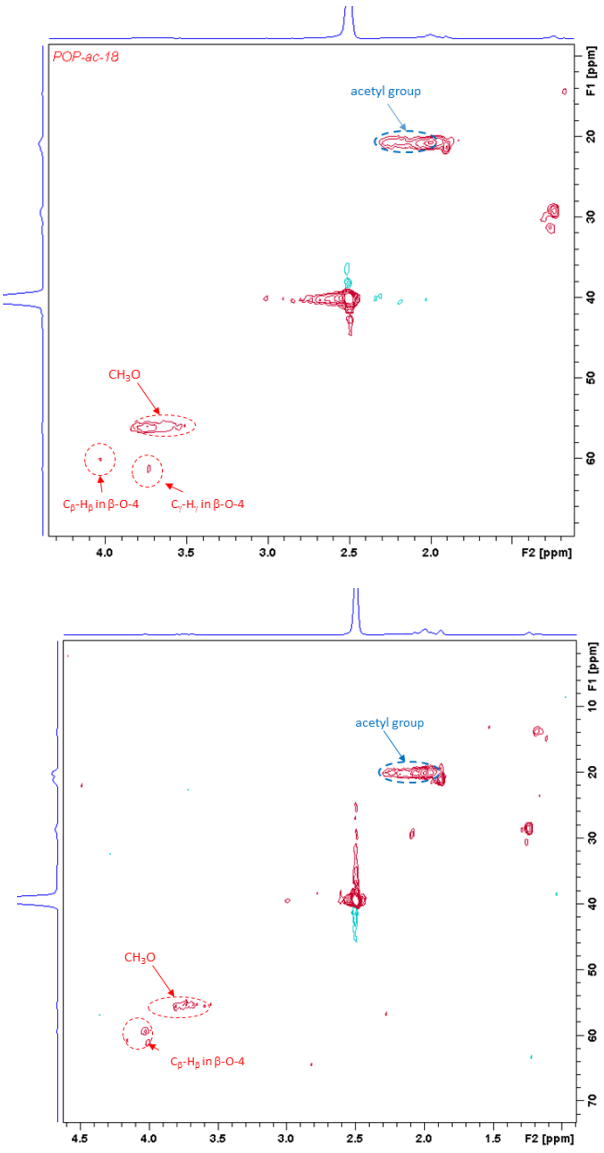
300	120	44	3.4	66	18	12	3	0
300	240	46	2.5	71	14	14	0	0

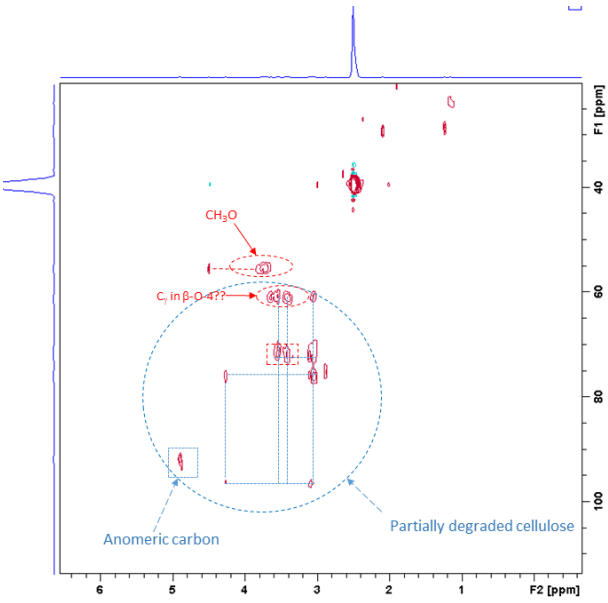
.

S accounts for syringyl groups; G account for guaiacyl groups; P accounts for phenyl units

3. HSQC-NMR spectra and SEC chromatograms

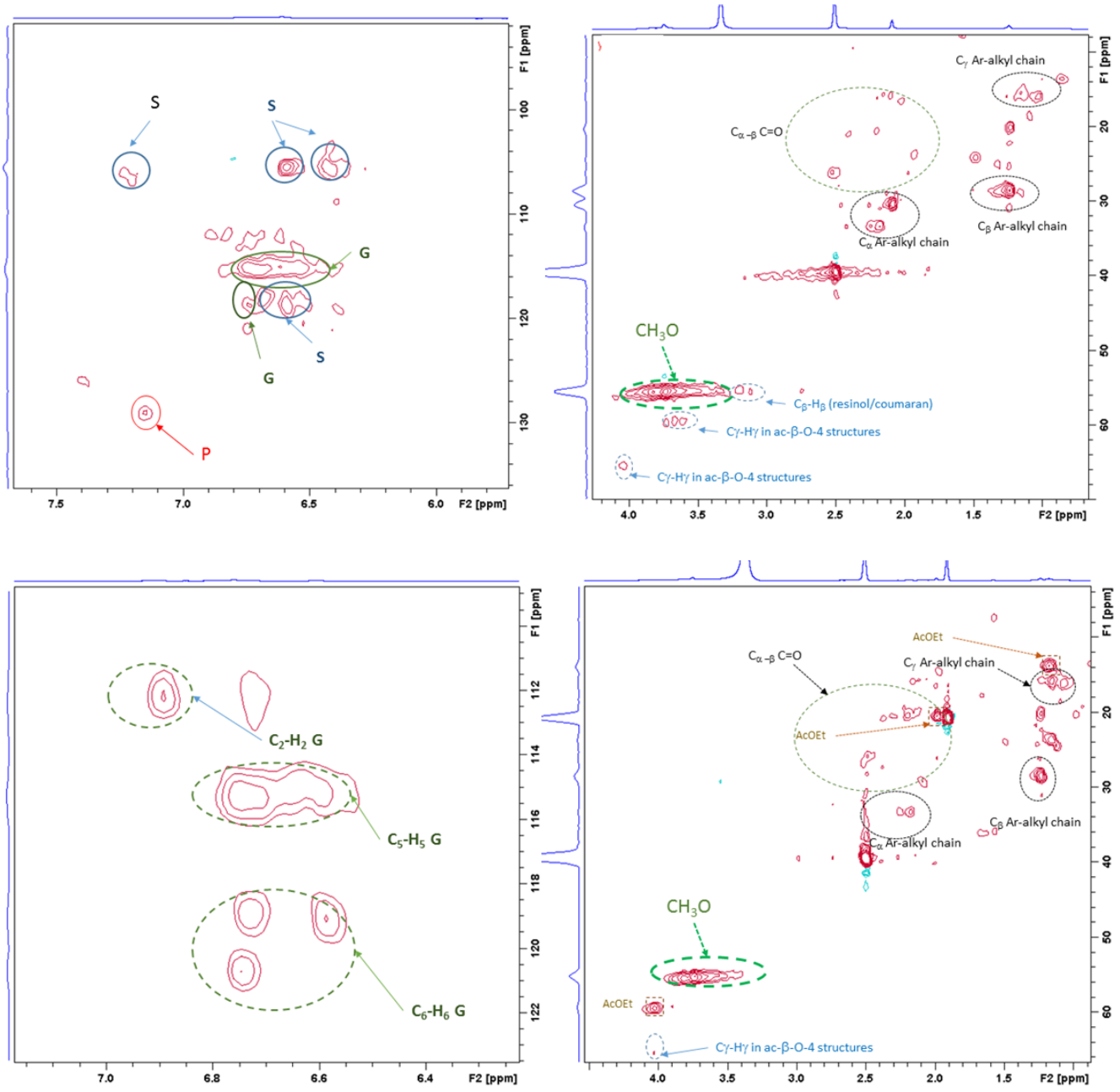
Figure S1. HSQC spectra for acetylated POP_L (top), acetylated PIN_L (middle) and HSQC-TOCSY for PIN_L




CH3O
Cγ in β-O-4??
Anomeric carbon
Partially degraded cellulose
F1 [ppm]
F2 [ppm]
40
60
80
100
6
5
4
3
2
1

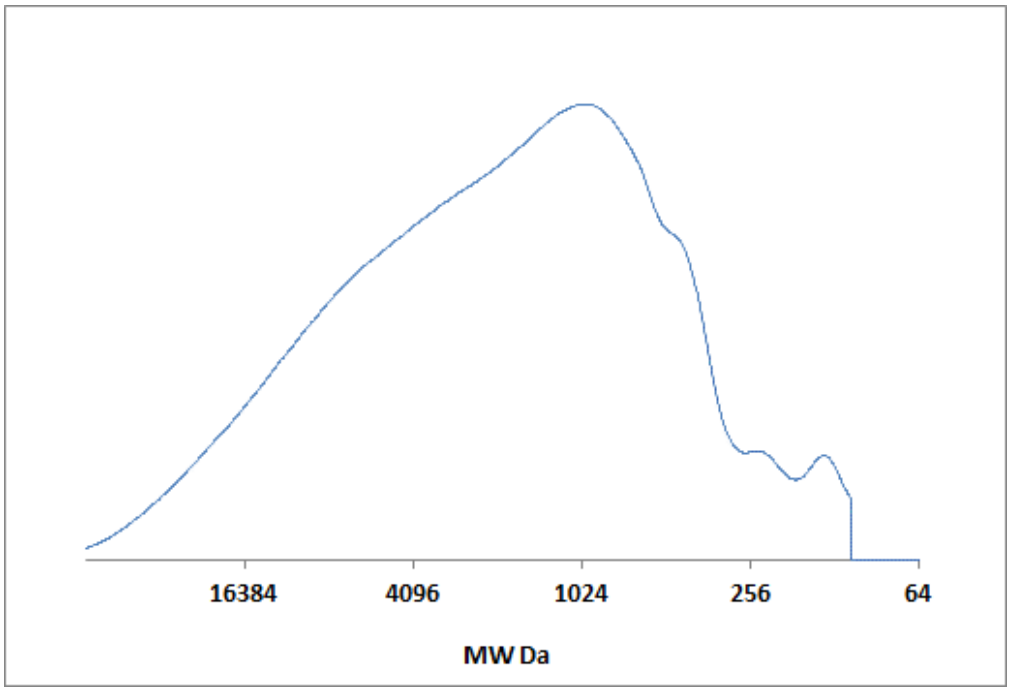
3. HSQC-NMR spectra and SEC chromatograms

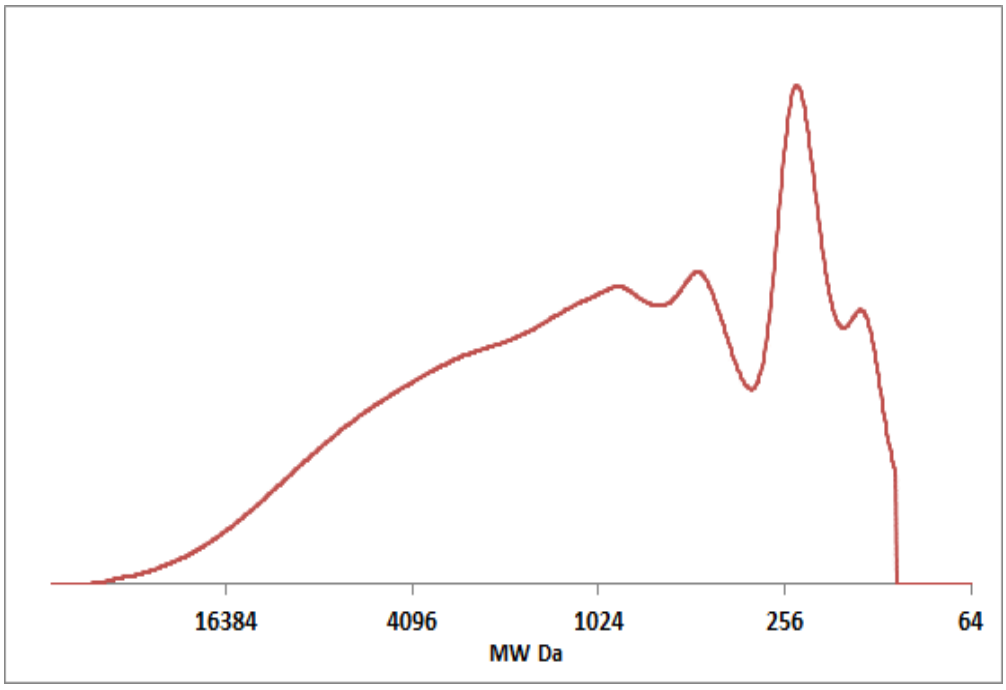
Figure S2. HSQC for sample **1** (top) and sample **6** (bottom)



3. HSQC-NMR spectra and SEC chromatograms

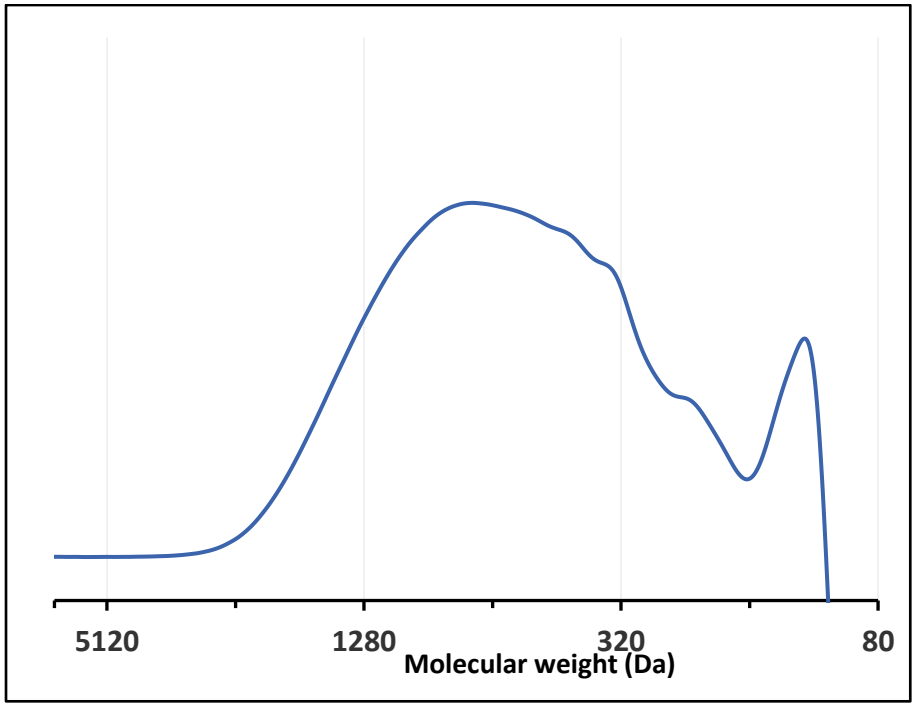
Figure S3. top) SEC for POP_L; bottom) SEC for PIN_L





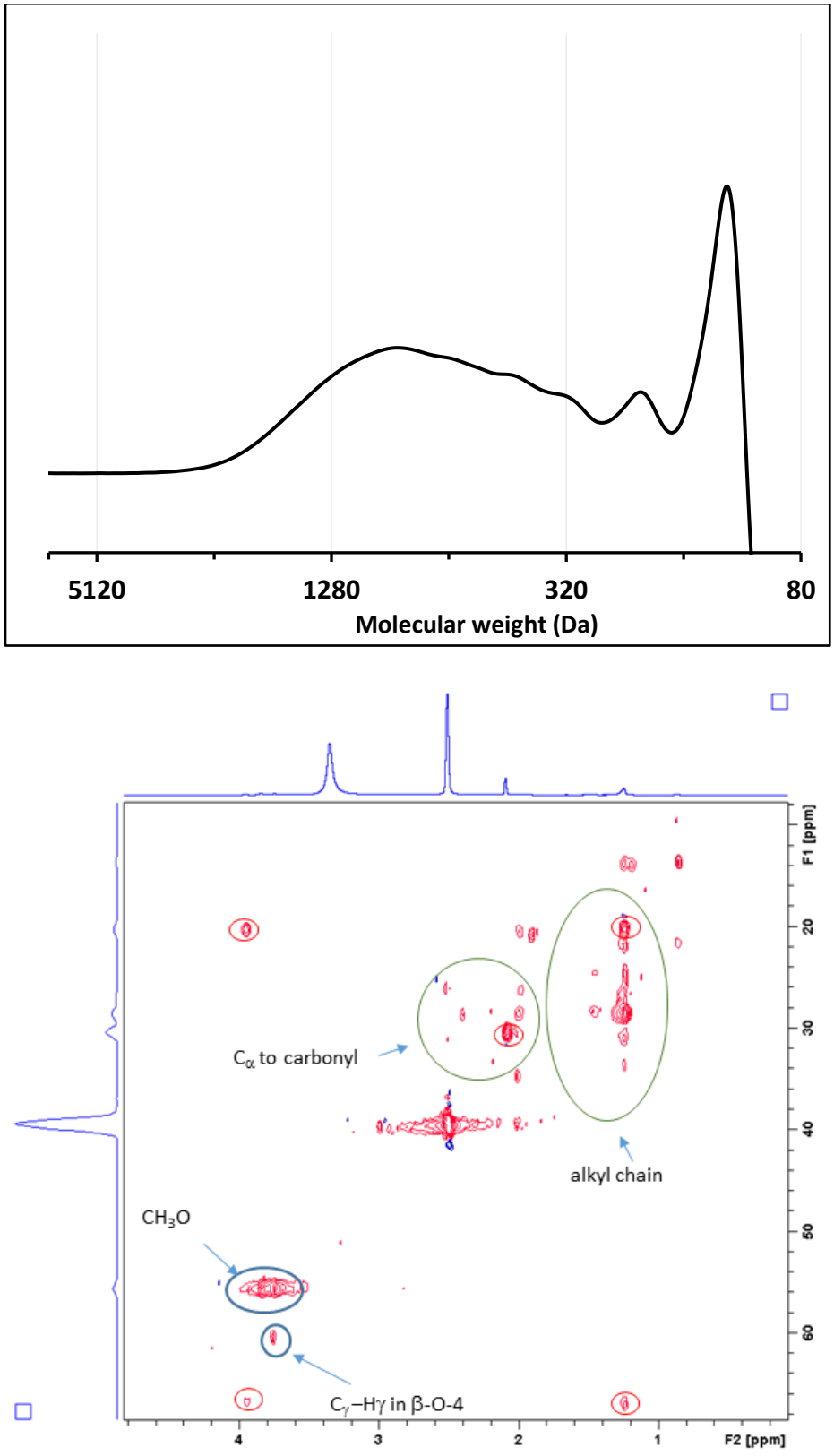
3. HSQC-NMR spectra and SEC chromatograms

Figure S4. SEC for BCD of PIN_L at 200 ºC for 240 min, sample 6.



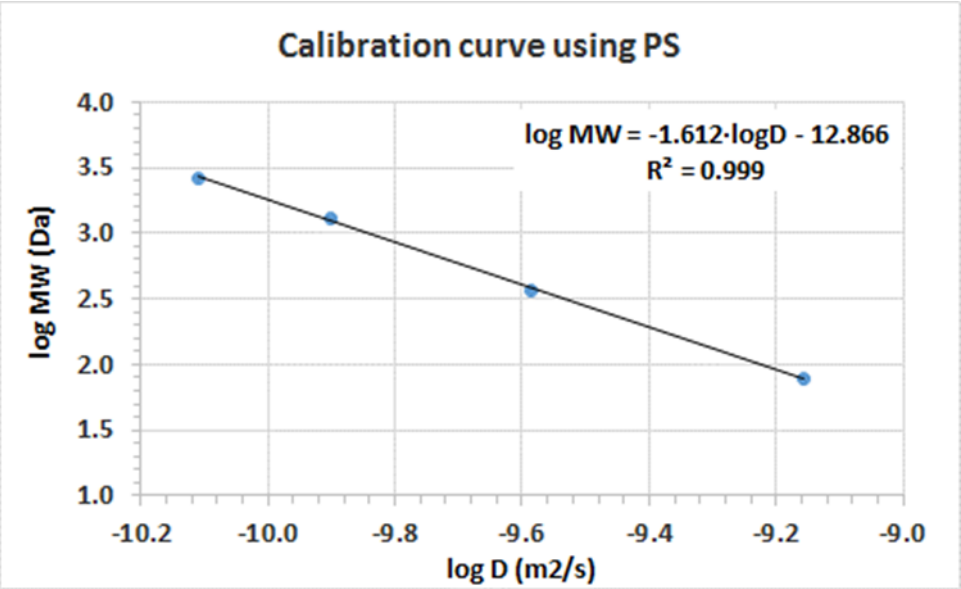
3. HSQC-NMR spectra and SEC chromatograms

Figure S5. Normalized SEC (top) and HSQC-TOCSY(bottom) for BCD of POP_L at 200 ºC for 30 min under microwave irradiation., sample **5**



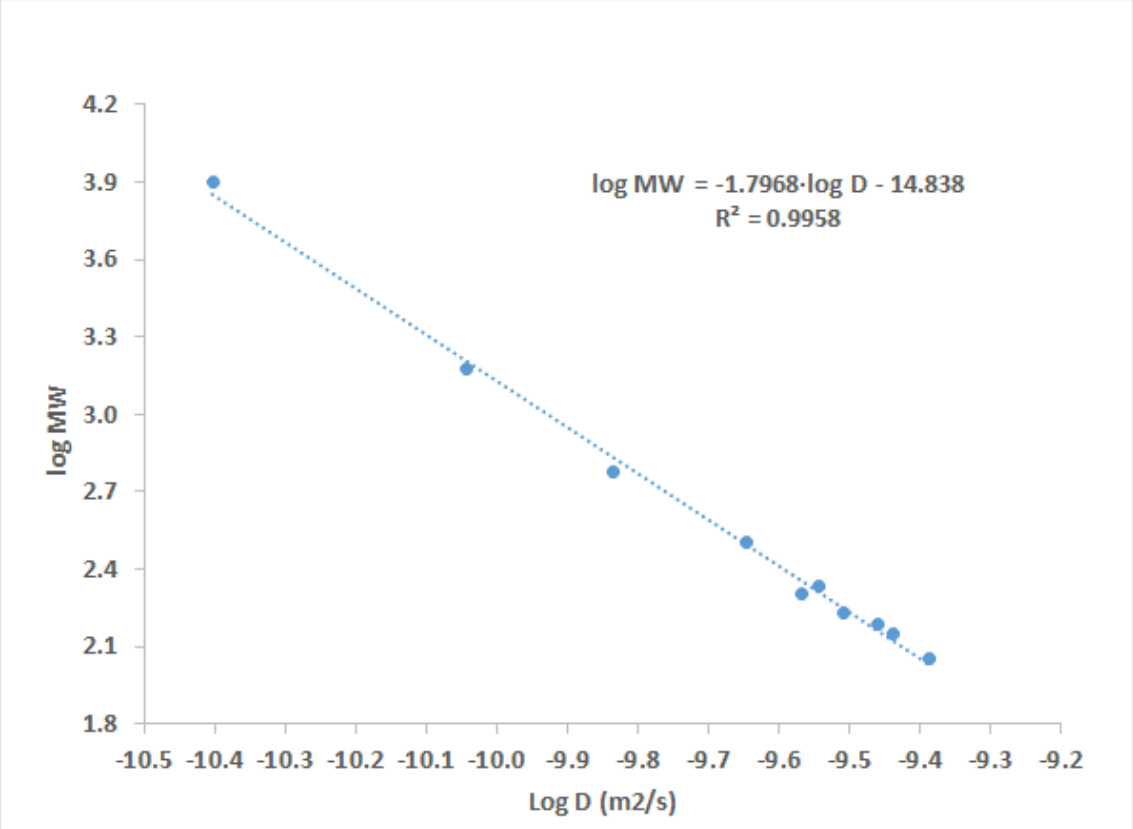
4. Calibration curve of logMW and logD using DOSY for PS

Compound	MW (Da)	log MW	log D ($m^2 \cdot s^{-1}$)
DMSO	78	1.892	-9.155
PS 370	370	2.568	-9.586
PS 1300	1300	3.114	-9.900
PS 2600	2600	3.415	-10.109



5. Calibration curve of log MW and log D using DOSY for PEG and monomeric phenols, VG and PE.

	MW (Da)	LogD (m_2/s)	log MW real	Predicted MW	MW error	MW % error
Guaiacol+H_2O	142	-9.440	2.153	133.4	-8.7	-6.1
Vanillin+H_2O	170	-9.509	2.231	177.9	7.7	4.5
Phenol+H_2O	112	-9.386	2.050	106.9	-5.2	-4.6
Syringol	154	-9.460	2.188	145.2	-8.9	-5.8
VG	320	-9.647	2.506	314.9	-5.5	-1.7
PE	214	-9.543	2.331	204.7	-9.6	-4.5
PEG200	200	-9.569	2.301	228.0	28.0	14.0
PEG600	600	-9.836	2.778	688.2	88.2	14.7
PEG1500	1500	-10.044	3.176	1627.5	127.5	8.5
PEG8000	8000	-10.403	3.903	7188.5	-811.5	-10.1



Multiple Linear Regression lunes, 18 de noviembre de 2019 16:21:21

Data source: Data 1 in Lignina2_calibracionDOSY_refDMSO.JNB

Log MW_5 = -14,837 - (1,797 $LogD_{dmso}$)

N = 10 Missing Observations = 1

R = 0,998 Rsqr = 0,996 Adj Rsqr = 0,995

Standard Error of Estimate = 0,040

	Coefficient	Std. Error	t	P	VIF
Constant	-14,837	0,401	-36,960	<0,001	
$LogD_{dmso}$	-1,797	0,0414	-43,363	<0,001	1,000

Analysis of Variance:

	DF	SS	MS	F	P
Regression	1	3,013	3,013	1880,343	<0,001
Residual	8	0,0128	0,00160		
Total	9	3,025	0,336		

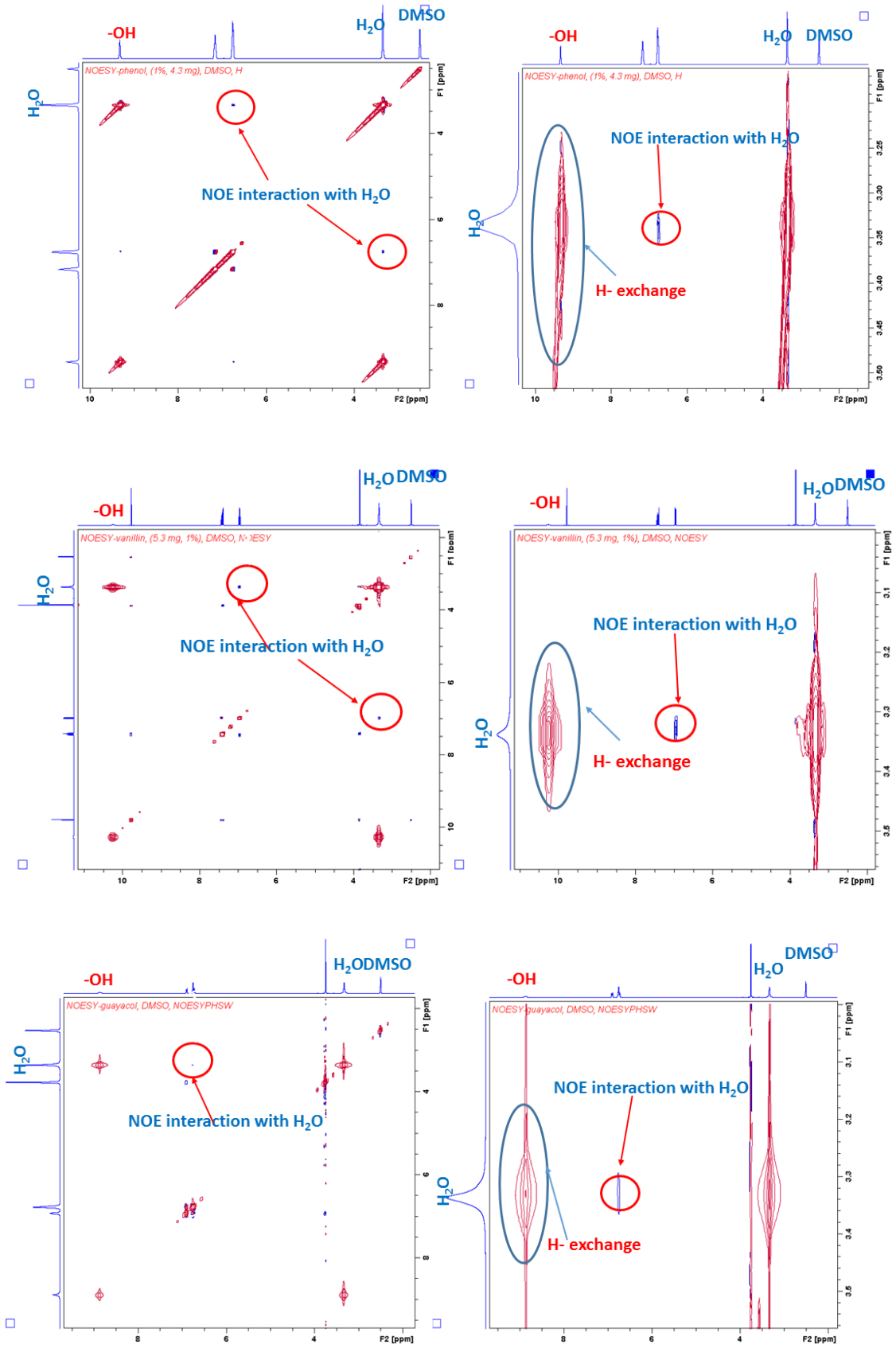
The dependent variable Col 7 can be predicted from a linear combination of the independent variables:

	P
$LogD_{dmso}$	<0,001

All independent variables appear to contribute to predicting $LogD_{dmso}$ ($P < 0.05$).
Normality Test (Shapiro-Wilk) Passed (P = 0,189)
Constant Variance Test (Spearman Rank Correlation): Passed (P = 0,199)
Power of performed test with alpha = 0,050: 1,000

6. NOESY spectra for phenol (top) vanillin (middle) and guaiacol (bottom)

Figure S6. NOESY spectra for phenol (top) vanillin (middle) and guaiacol (bottom).



7. Integration regions used in the determination of averaged diffusion coefficients

$$ln\left(\frac{I}{I_0}\right) = -\gamma^2\delta^2{G_z}^2 D\left[\Delta + \left(\frac{4\delta}{3} + 3\tau/2\right)\right]$$

I_0: intensity at very low gradient value

I: intensity at a given gradient value

γ: gyromagnetic ratio

δ: length of the bipolar gradient pulse

Gz: gradient strength

Δ: time between pulses (d20)

τ: gradient ringdown delay

Table S3. Integration regions used in the determination of averaged diffusion coefficients. R^2 correspond to the correlation between experimental and calculated values for I.

	Aromatic		Aliphatic 1		Aliphatic 2	
Sample	Chemical shift (ppm)	R^2	Chemical shift (ppm)	R^2	Chemical shift (ppm)	R^2
POP_L	7.474 - 6.357	0.510	3.946 - 3.609	0.796	2.384 - 1.104	0.990
1	7.690 - 6.842	0.997	2.435 - 2.017	0.997	1.617 - 0.946	0.998
2	7.649 - 6.249	0.999	2.426 - 1.951	0.984	1.873 - 0.831	0.996
3	7.730 - 6.155	0.998	2.402 - 1.958	0.994		nm
4	7.663 - 6.33	1.000	2.453 - 1.951	0.995	1.851 - 0.726	0.999
5	nm	nm	3.178 - 2.720	0.999	2.384 - 0.593	0.997
PIN_L	8.134 - 6.424	0.991	4.714 - 3.730	0.990	2.249 - 0.647	0.987
6	7.717 - 6.31	0.999	2.411 - 1.966	0.997	1.832 - 0.74	0.999

8. ^{31}P NMR spectra for derivatized samples

Figure S7. ^{31}P spectra for derivatized samples 3 (top), 2 (middle),and 5 (bottom)