Electronic Supplementary Information (ESI)

Authors: Nicola Giummarella,[a,b] Claudio Gioia[b,c] and Martin Lawoko[a,b]*

A One-Pot Biomimetic Synthesis of Selectively Functionalized Lignins from Monomers: A Green Functionalization Platform

a. Department of Fibre and Polymer Technology, School of Engineering Sciences in Chemistry, Biotechnology and Health, KTH Royal Institute of Technology, Teknikringen 56-58, SE–100 44, Stockholm, Sweden.

b. Wallenberg Wood Science Centre, KTH Royal Institute of Technology, Teknikringen 56-58, SE–100 44, Stockholm, Sweden.

c. Department of Civil, Chemical, Environmental and Materials Engineering , Via Terracini 28, 40131, Universita di Bologna, Italy.

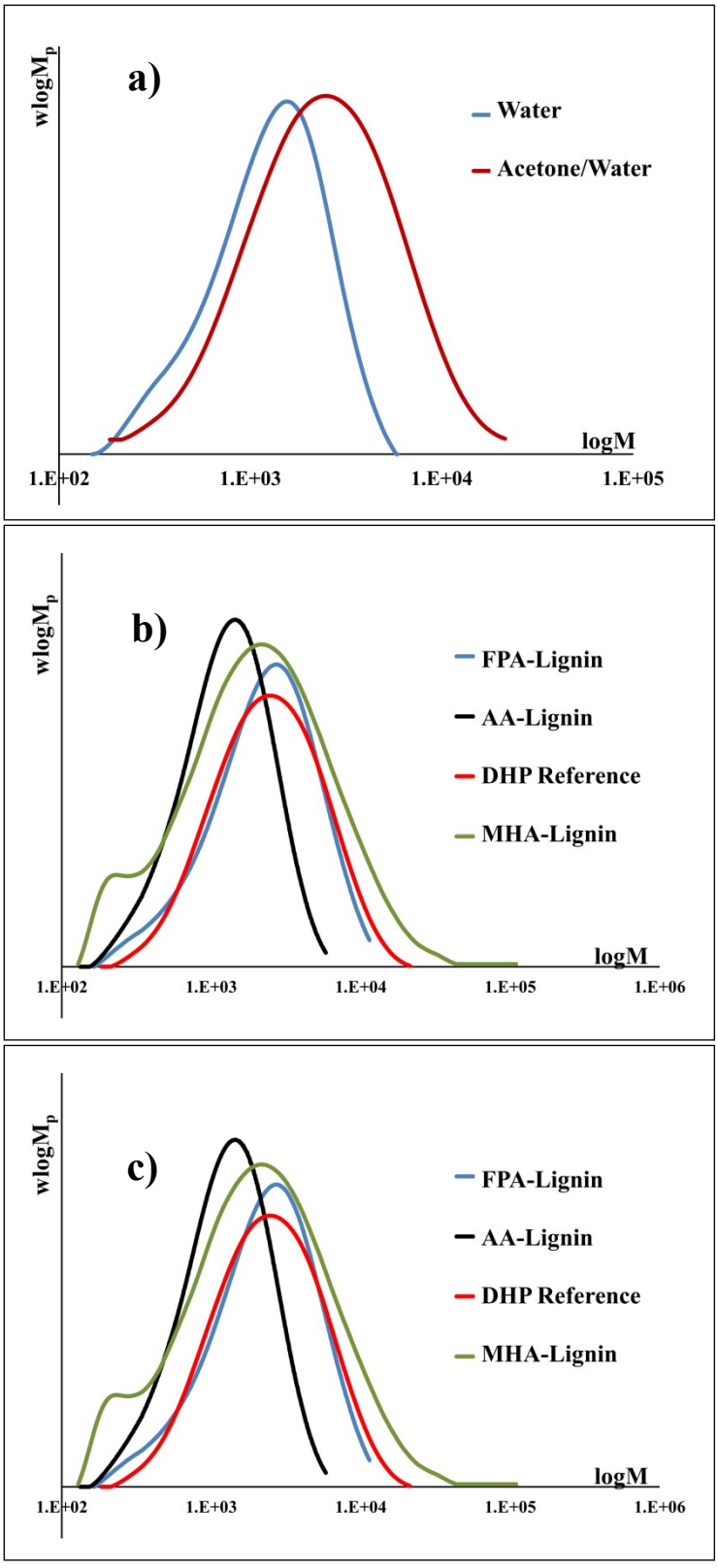
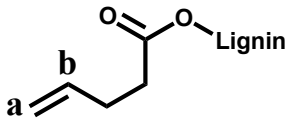


Figure S1: Molecular weights distribution of a) DHPs reference b) functionalized DHP Lignin in water and c) functionalized DHP Lignin in 50% acetone

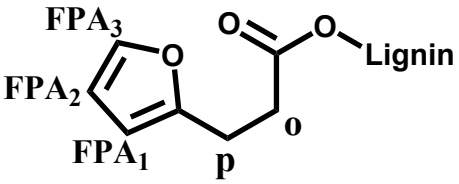
Table S1. Assignment of the main ^{13}C-^{1}H correlation signals of lignin substructures bonds detected in 2D HSQC spectra of DHPs reference and functionalized lignin n DMSO-*d6*.

	δ_C*(ppm)*	δ_H *(ppm)*	Description
1_α	71.4	4.71	C_α/H_α in γ-hydroxylated βO4
$1_{\alpha\ ester}$	74.8	5.92	C_α/H_α in benzyl-ester βO4
1_β	83.5	4.27	C_β/H_β in γ-hydroxylated βO4 in G-units
1_γ	59.4	3.42/3.71	C_γ/H_γ in βO4
2	86.9	5.40	C_α/H_α in Phenylcoumaran
2	53.2	3.42	C_β/H_β in Phenylcoumaran
2	62.8	3.8	C_β/H_β in Phenylcoumaran
3	85.1	4.61	C_α/H_α in resinol structure
3	53.5	3.04	C_β/H_β in resinol structure
3	71.1	3.81/4.15	C_γ/H_γ in resinol structure
4	83.8	4.80	C_α/H_α in Dibenzodioxin
4	85.2	3.91	C_β/H_β in Dibenzodioxin
4	60.4	3.42	C_γ/H_γ in Dibenzodioxin
5	81.2	5.03	C_α/H_α in Spirodienone
5	59.6	2.80	C_β/H_β in Spirodienone
6	129.2	6.46	C_α/H_α in Cinnamyl alcohol
6	128.6	6.23	C_β/H_β in Cinnamyl alcohol
6	61.4	4.06	C_γ/H_γ in Cinnamyl alcohol
-OMe	55.4	3.71	C/H in -OMe in G- units
C_2	110.8	6.93	C_2/H_2 in G-units
C_5	114.9	6.80	C_5/H_5 in G-units
C_6	118.8	6.74	C_6/H_6 in G-units
a*	115.9	4.94	
b*	137.4	5.72	
GE (γ-esters in lignin)*	63.5	4.17-4.27	

*= detected in AA-Lignin, shown in Figure S14

Table S2. Additional assignment of the main ^{13}C-^{1}H correlation signals of FPA-Lignin before and after Dies Alder reaction detected in 2D HSQC spectra in DMSO-*d6*.

FPA-Lignin		
	δ_C*(ppm)*	δ_H *(ppm)*
FPA_1	105.7	5.99
FPA_2	110.7	6.32
FPA_3	141.5	7.47
o	32.5	2.56
p	23.9	2.78
Diels Alder product		
d_1	135.5	6.35
e_1	135.2	6.42
a_1	79.8	4.99
b_1	51.3	2.94
c_1	49.6	2.74
d_2	137.8	6.30
e_2	137.4	6.45
a_2	78.0	5.12
b_2	49.3	3.55
c_2	50.5	3.15
M_α	135.8	6.74



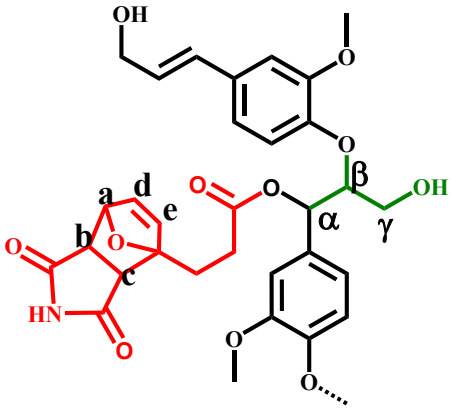
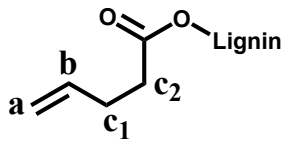
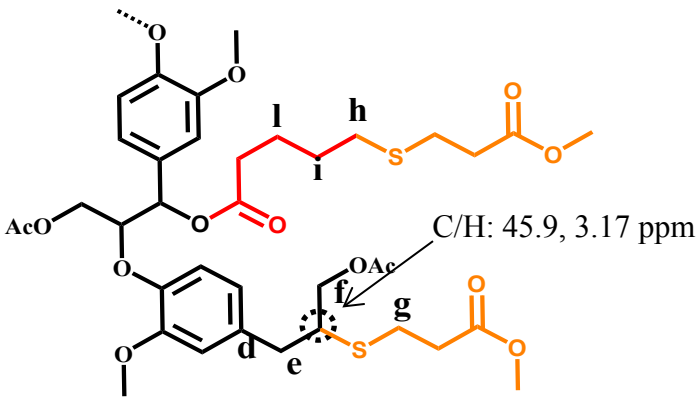


Table S3: : Assignment of main ^{13}C-^{1}H correlation signals in Acetone-*d6* of lignin substructures detected in 2D HSQC spectra of acetylated AA-Lignin before and after thiolene reaction.

	δ_C*(ppm)*	δ_H *(ppm)*	Description
$1_{\alpha\ ester}$	74.3	6.05	C_α/H_α in benzyl-ester βO4
1_β	79.7	4.84	C_β/H_β in γ-hydroxylated βO4 in G-units
1_γ	63.1	4.03,4.48	C_γ/H_γ in βO4
2	87.7	5.56	C_α/H_α in Phenylcoumaran
2	50.3	3.77	C_β/H_β in Phenylcoumaran
2	65.1	4.36	C_γ/H_γ in Phenylcoumaran
3	85.4	4.71	C_α/H_α in resinol structure
3	54.4	3.10	C_β/H_β in resinol structure
3	71.6	3.86/4.24	C_γ/H_γ in resinol structure
4	84.5	4.92	C_α/H_α in Dibenzodioxin
4	82.6	4.29	C_β/H_β in Dibenzodioxin
4	62.6	4.23	C_γ/H_γ in Dibenzodioxin
6_α	133.6	6.63	C_α/H_α in Cinnamyl alcohol
6_β	121.9	6.26	C_β/H_β in Cinnamyl alcohol
6	64.6	4.67	C_γ/H_γ in Cinnamyl alcohol
-OMe	55.51	3.83	C/H in -OMe in G- units
C_2	111.0	7.06	C_2/H_2 in G-units
C_5	119.6	6.96	C_5/H_5 in G-units
C_6	122.42	7.01	C_6/H_6 in G-units
a	114.9	4.93	
b	136.9	5.80	
c_1	28.6	2.31	
c_2	33.2	2.45	
After thiolene reaction			
e	38.1	2.75/2.89	
f	65.8	4.05/4.12	
g	26.2	2.75	
h	31.1	2.47	
i	28.7	1.53	
l	23.8	1.62	

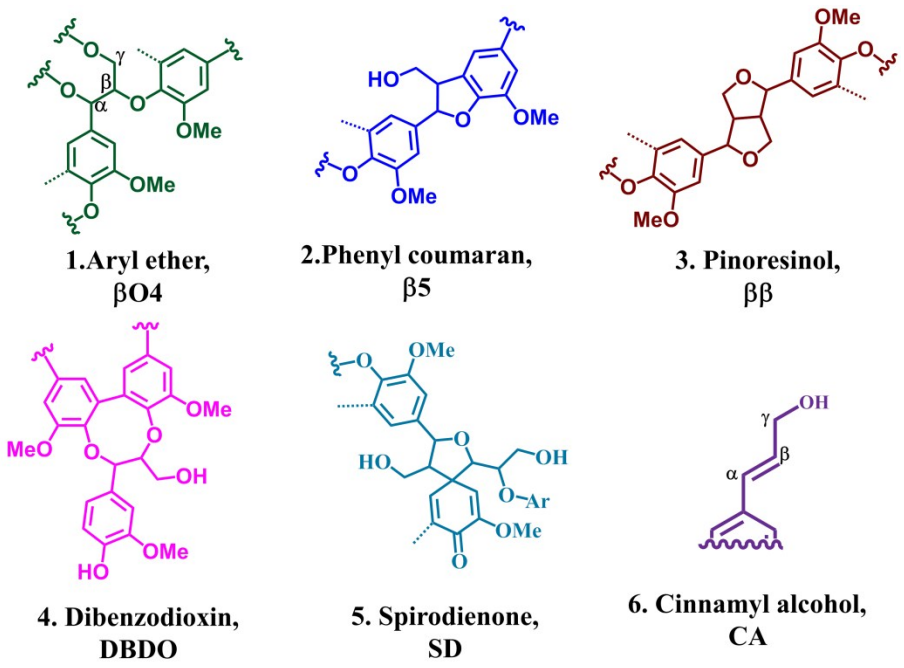


Figure S2: Structures of lignin inter-monolignol linkages and end group detected in NMR studies

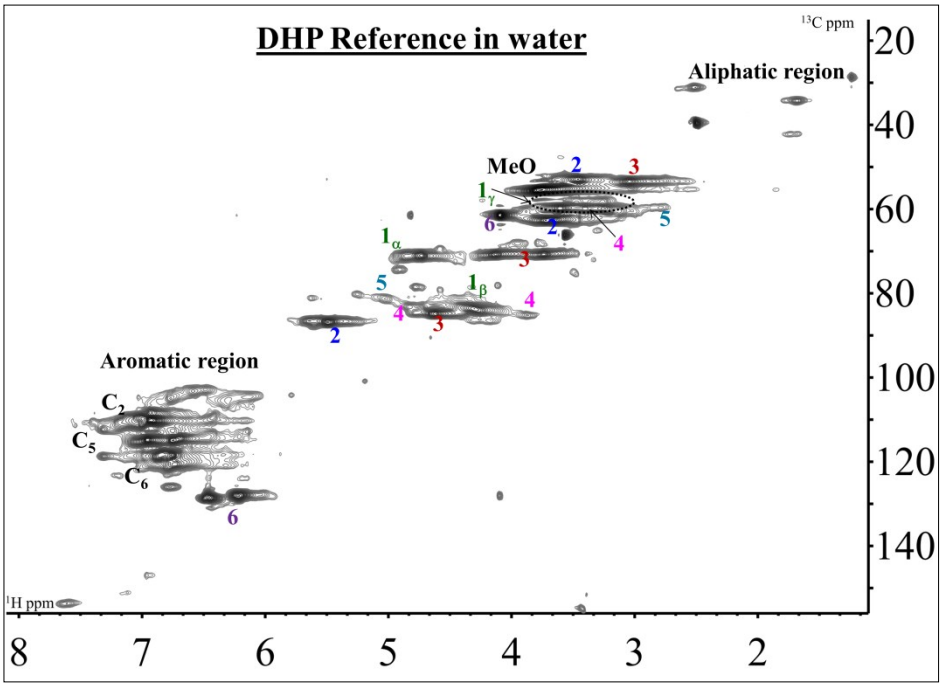


Figure S3: HSQC spectrum in DMSO-*d6* of DHP reference polymerized in water. MeO= Methoxy group

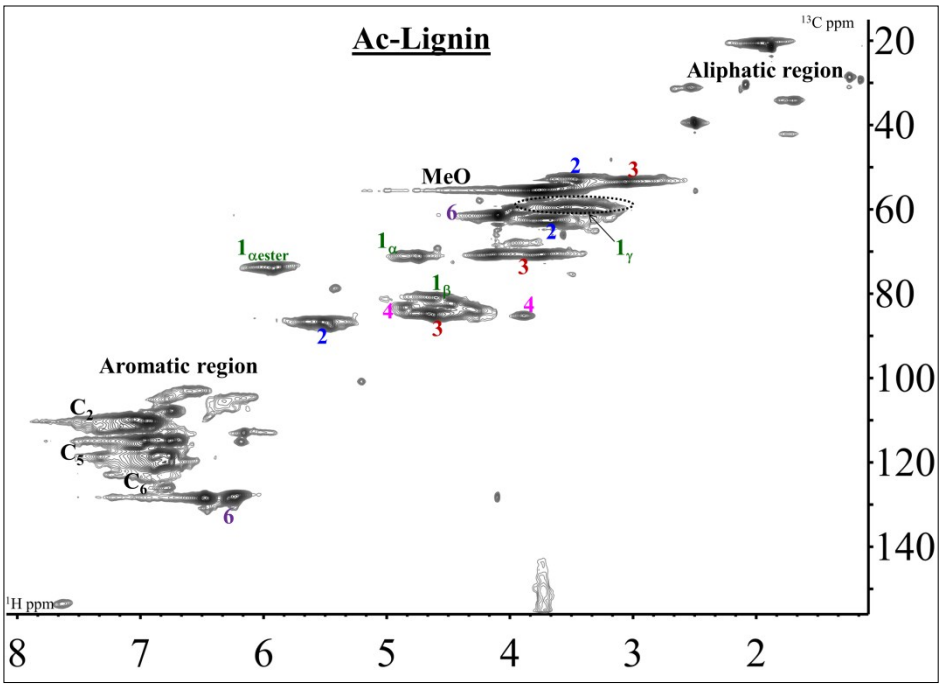


Figure S4: HSQC spectrum in DMSO-*d6* of Ac-Lignin polymerized in water

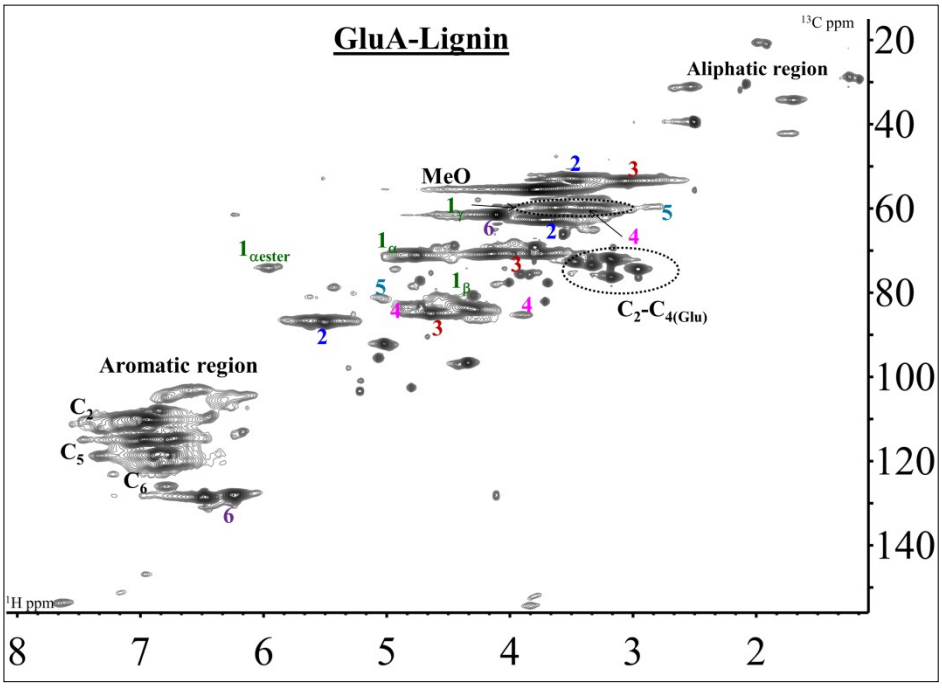


Figure S5: HSQC spectrum in DMSO-*d6* of GluA-Lignin polymerized in water

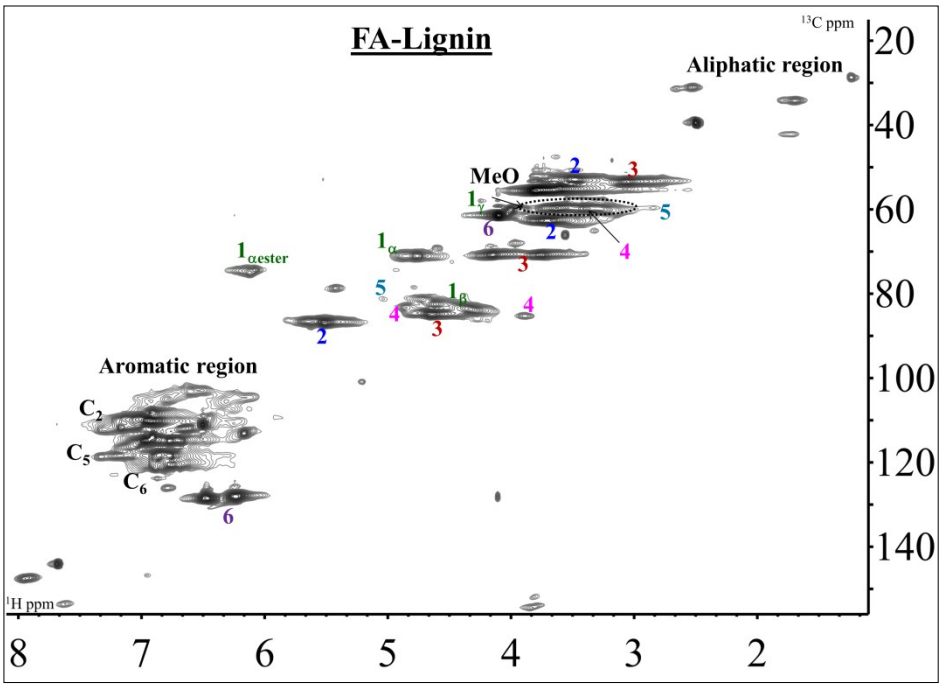


Figure S6: HSQC spectrum in DMSO-*d6* of FA-Lignin polymerized in water

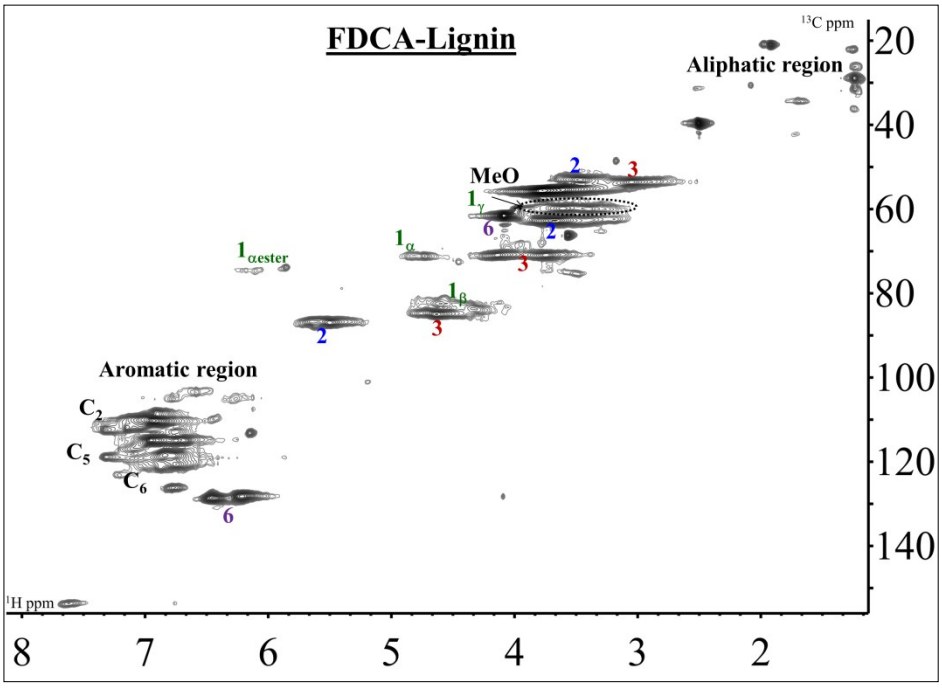


Figure S7: HSQC spectrum in DMSO-*d6* of FDCA-Lignin polymerized in water

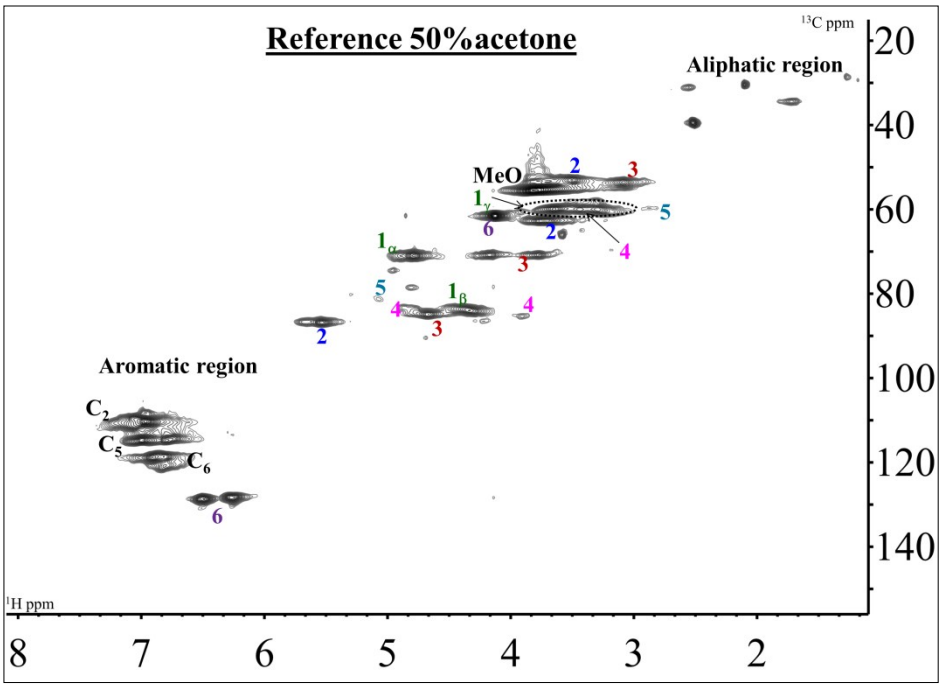


Figure S8: HSQC spectrum in DMSO-*d6* of DHP reference polymerized in 50% acetone

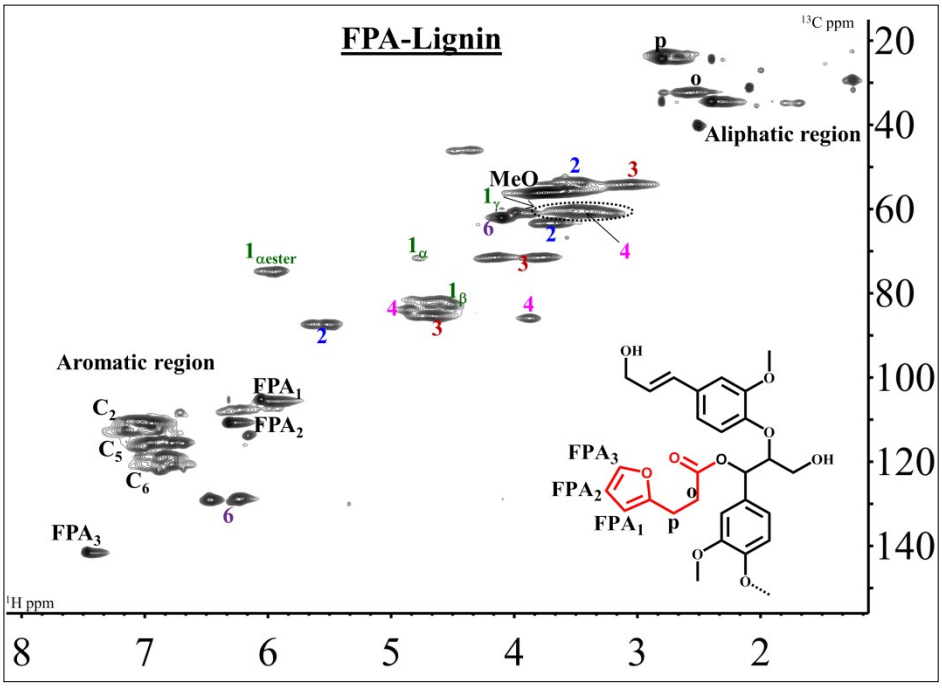


Figure S9: HSQC spectrum in DMSO-*d6* of FPA-Lignin polymerized in 50% acetone

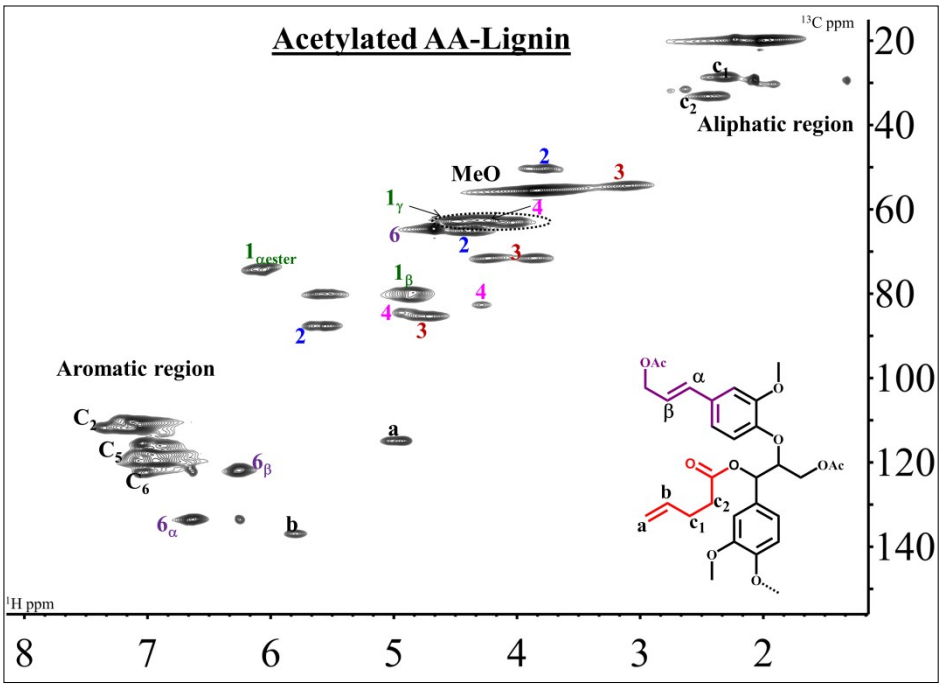


Figure S10: HSQC spectrum in Acetone-*d6* of acetylated AA-Lignin polymerized in 50% acetone

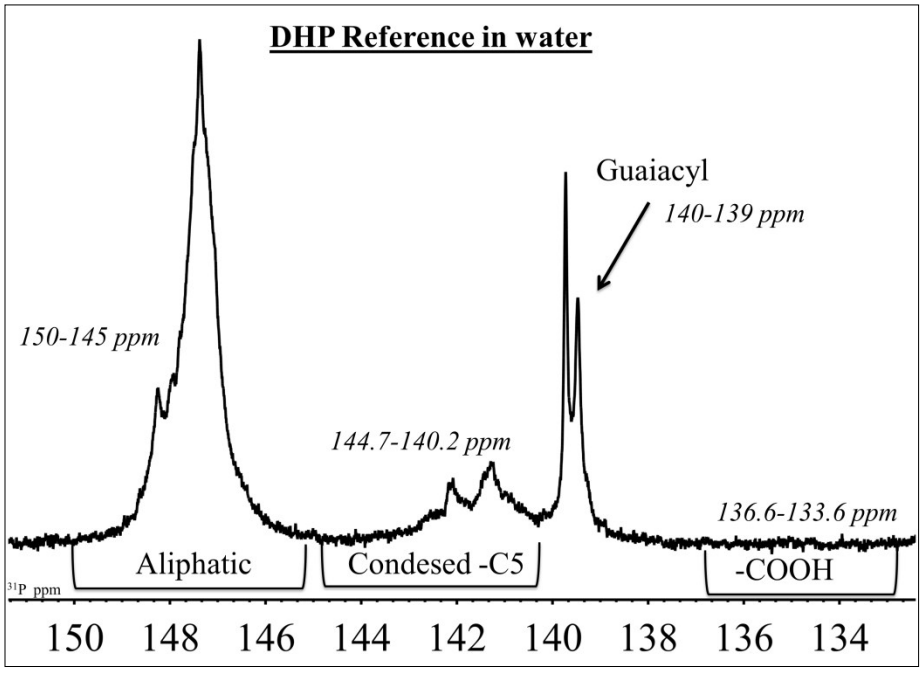


Figure S11: ^{31}P NMR of reference DHP polymerized in water

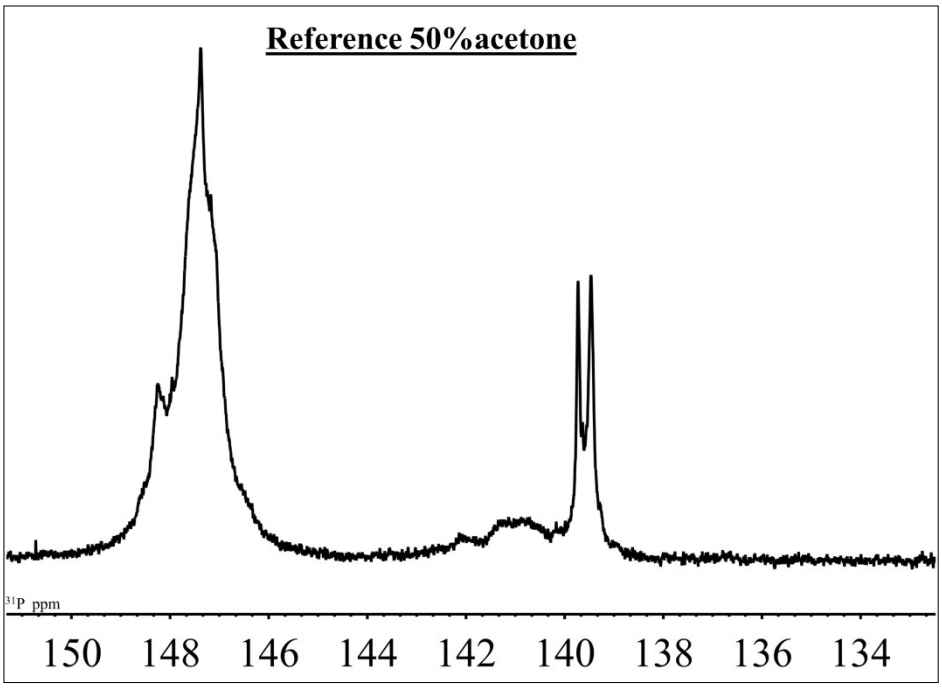


Figure S12: ^{31}P NMR of reference DHP polymerized in 50% acetone

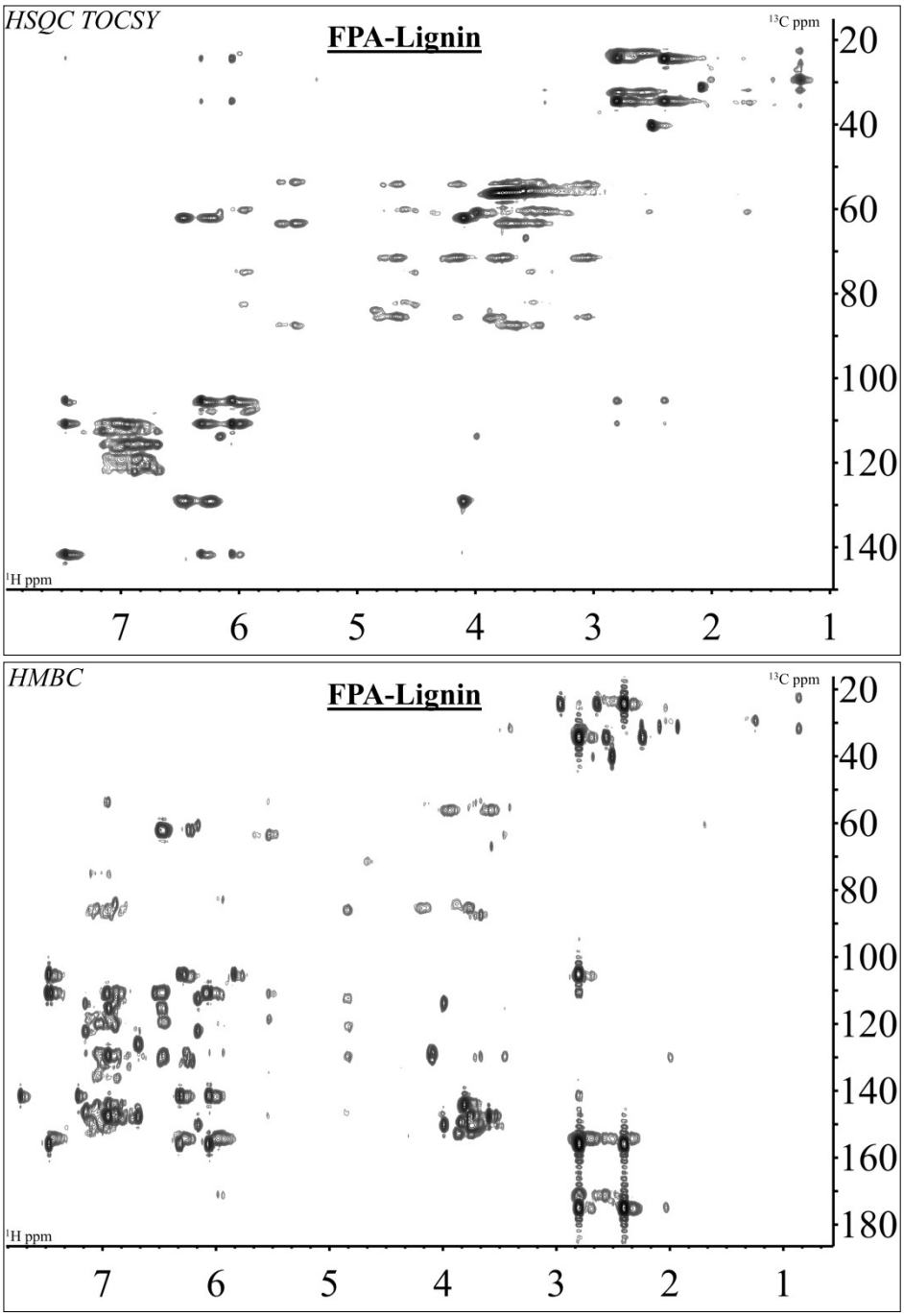


Figure S13: HSQC TOCSY and HMBC spectra in DMSO-*d6* of FPA-Lignin

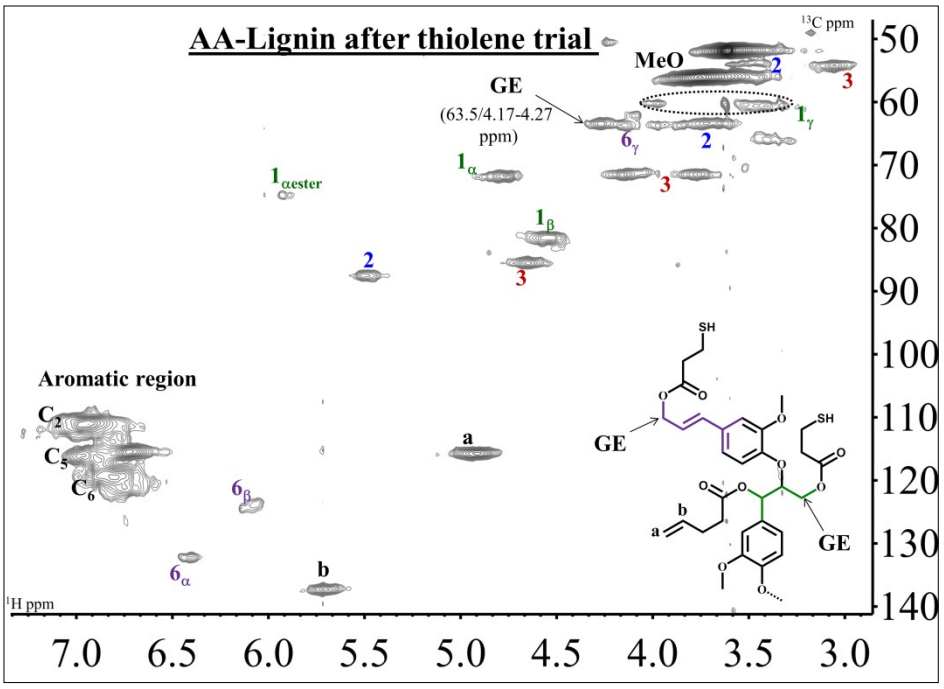


Figure S14: HSQC spectrum in DMSO-*d6* of AA-Lignin after thiolene trial. GE peak shows Cγ acylations (Assignments of characteristic peaks are listed in Table S1).

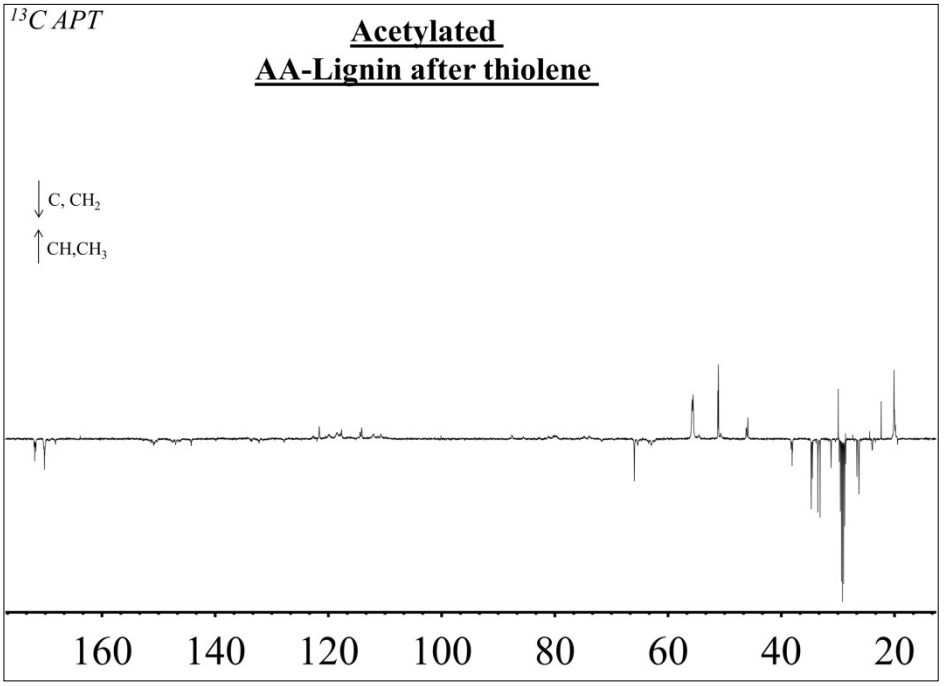


Figure S15: ^{13}C Attached proton test in Acetone-*d6* of acetylated AA-Lignin after thiolene chemistry

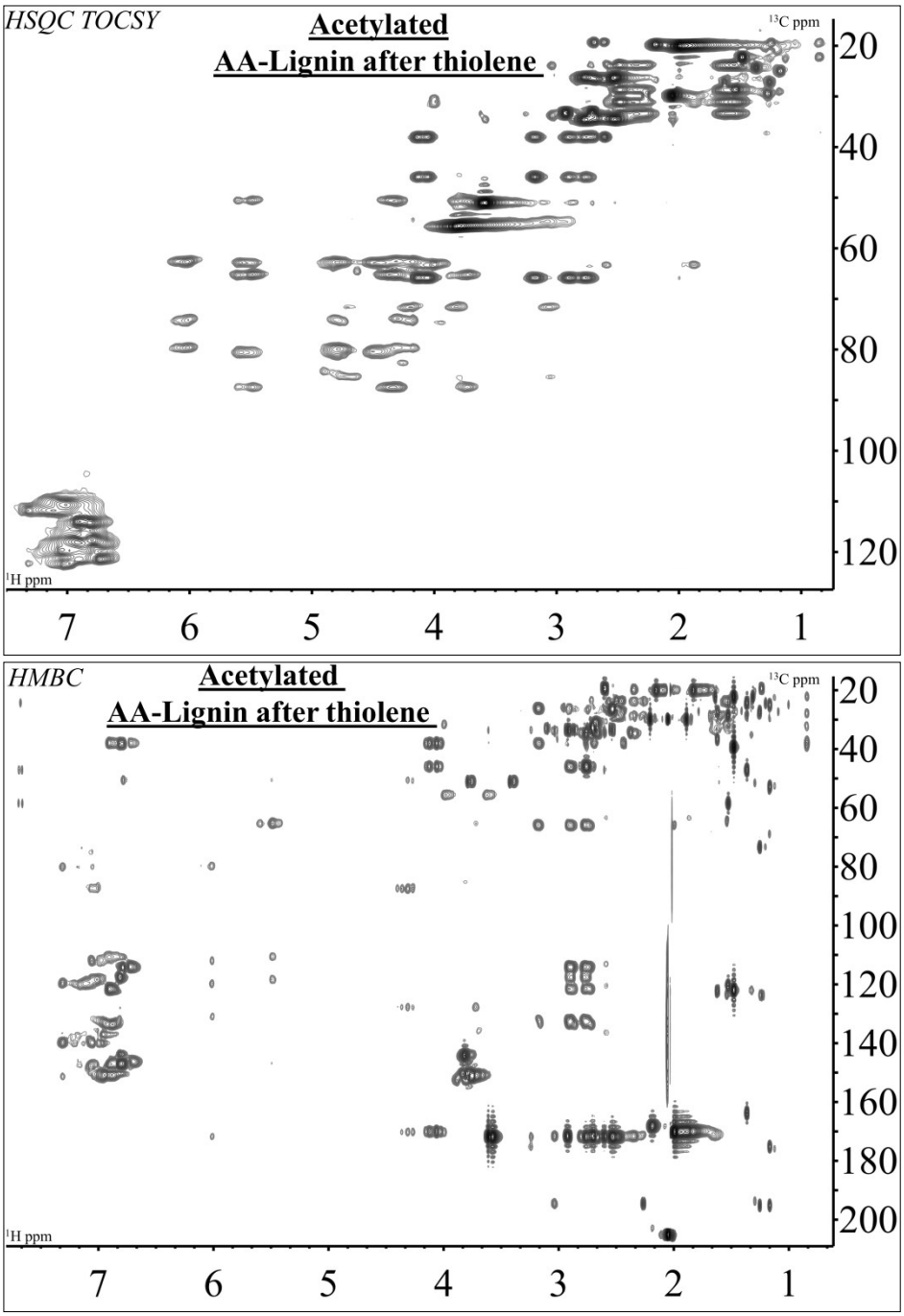


Figure S16: HSQC TOCSY and HMBC spectra in Acetone-*d6* of acetylated AA-Lignin after thiolene chemistry

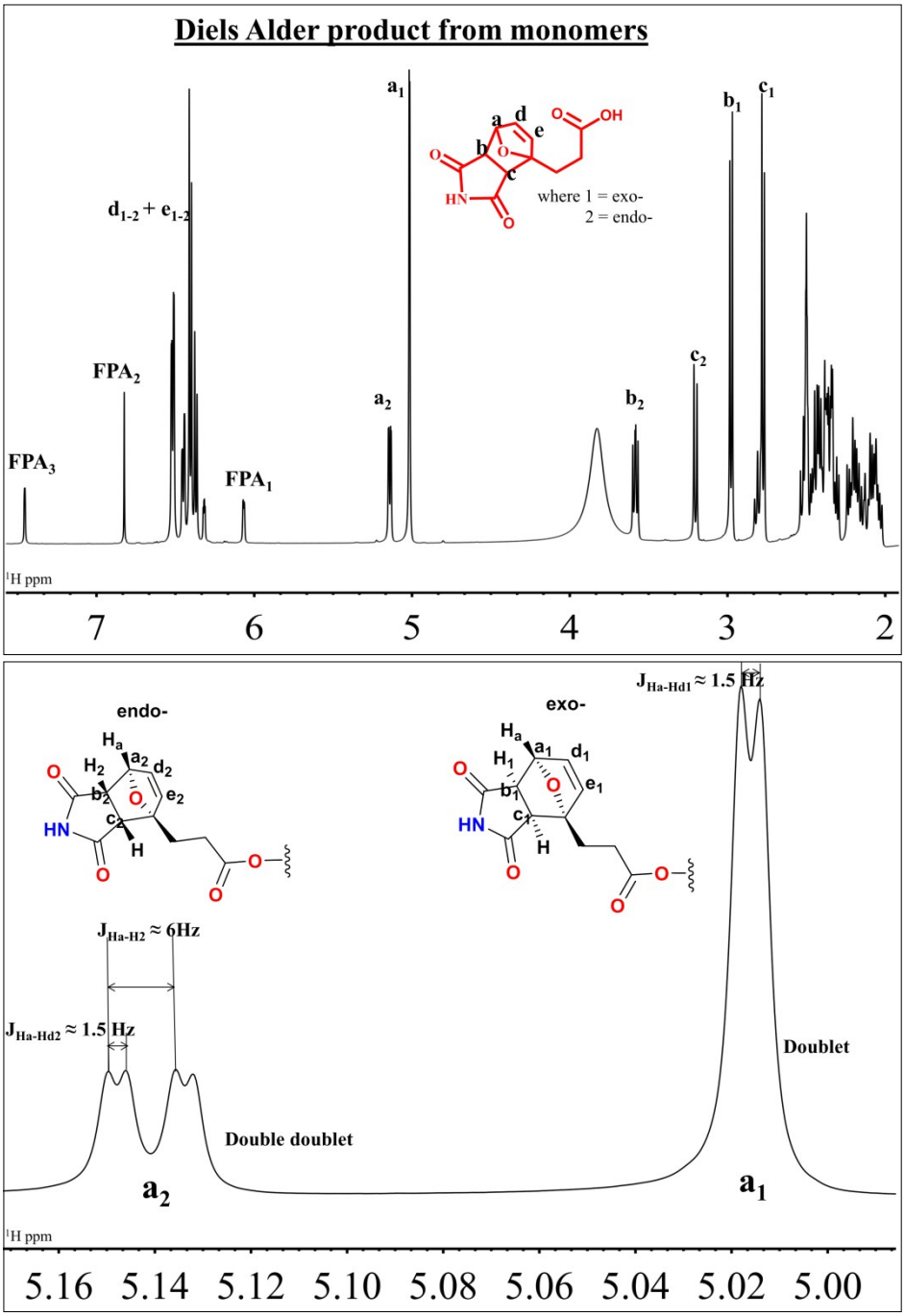


Figure S17: ^{1}H spectrum and its expansion utilized for analysis and assignment of Diels Alder product obtained with M and FPA monomers

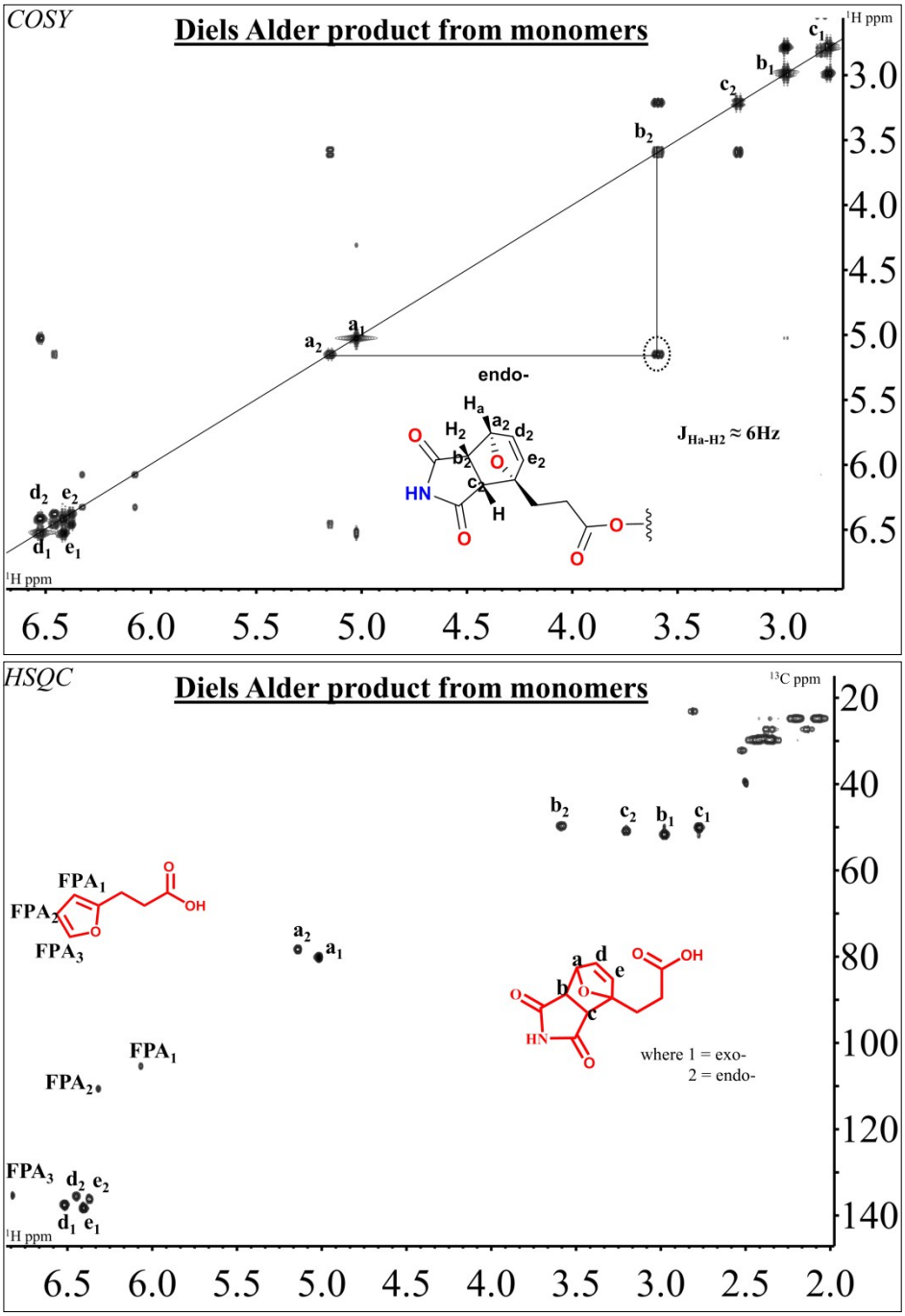


Figure S18: COSY-90 and HSQC spectra in DMSO-*d6* of Diels Alder product obtained with M and FPA monomers