

Efficient Nickel-Catalysed Telomerisation on Glycerol Carbonate: A new Linker route for Lignin Functionalisation

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1. Additional study of [Ni] telomerisation on glycerol carbonate

Table SI 1: Additional study of [Ni] telomerisation on glycerol carbonate.

Entry	Ni(COD) ₂ (mol %)	Ligand	THF	Butadiene (eq.)	Time (h)	Base	GC Conversion (%) ^[a]	Yield Hydroalkoxylates (%) ^[a]	Yield Telomeres (%) ^[a]	Ratio GCHA L/B ^[a]	Ratio GCT L/B ^[a]
11	1.5	dppb	0	2	16	-	74	20	54	1/1	3/2
12	1.5	dppe	0	2	16	-	-	0	0	-	-
13	1.5	dppp	0	2	16	-	-	0	0	-	-
14	1.5	PPh ₃	0	2	16	-	-	0	0	-	-
15	1.5	dppf	0	2	16	-	31	29	2	1/1	7/3
1	1.5	dppb	1mL	2	16	-	56	21	35	5/5	6/4
2	1.5	dppb	0.5mL	2	16	-	58	17	41	5/5	6/4
3	1.5	dppb	0.3mL	2	16	-	79	23	56	5/5	6/4
4	1.5	dppb	0	5	1	-	29	26	3	2/8	7/3
5	1.5	dppb	0	5	3	-	88	35	53	4/6	6/4
6	1.5	dppb	0	5	8	-	84	17	67	6/4	6/4
7	1.5	dppb	0	5	16	-	88	18	70	6/4	6/4
8	1.5	dppb	0	5	24	-	76	14	62	5/5	6/4
9	1.5	dppb	0	5	16	KOH	91	34	57	4/6	6/4
10	1.5	dppb	0	5	16	TEA	87	18	69	6/4	6/4

Conditions: 0.4mL glycerol carbonate dried and freeze pump, 0.1eq. of base, degazed THF, Ni(Cod)₂, 1.5eq. diphosphine/Ni or 3eq. of PPh₃/Ni, N₂ atmosphere, 80°C, Schlenk equipped with a Rotaflo stop cock.

a) Conversion and selectivity are determined by gaz chromatography

2. Kinetic of [Ni] telomerisation on glycerol carbonate

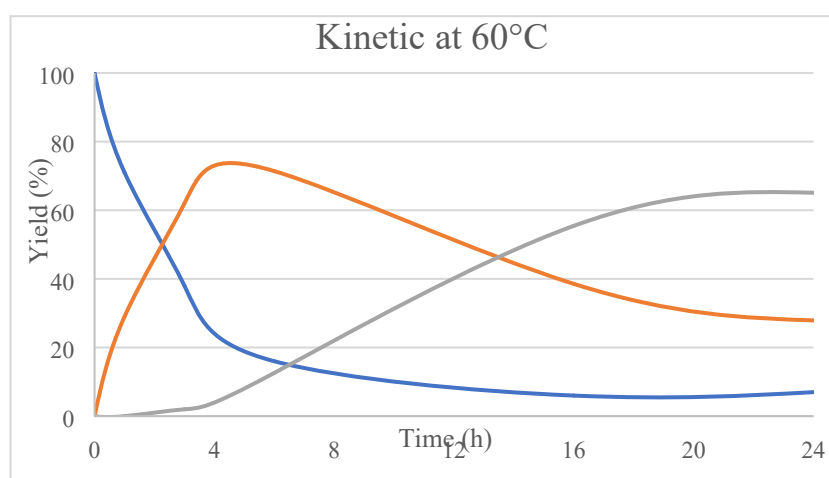


Figure SI 1: Kinetic of telomerisation on glycerol carbonate at 60°C with 1.5 mol% Ni(Cod)₂ and dppb/Ni =1.5 with 2eq. of butadiene. orange: yield in GC-HA ; grey: yield in GC-T ; blue: proportion of unmodified glycerol carbonate.

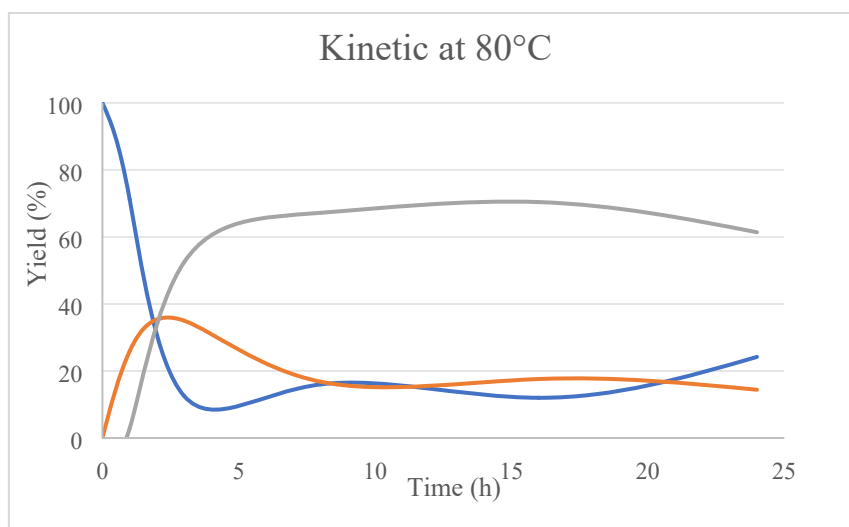
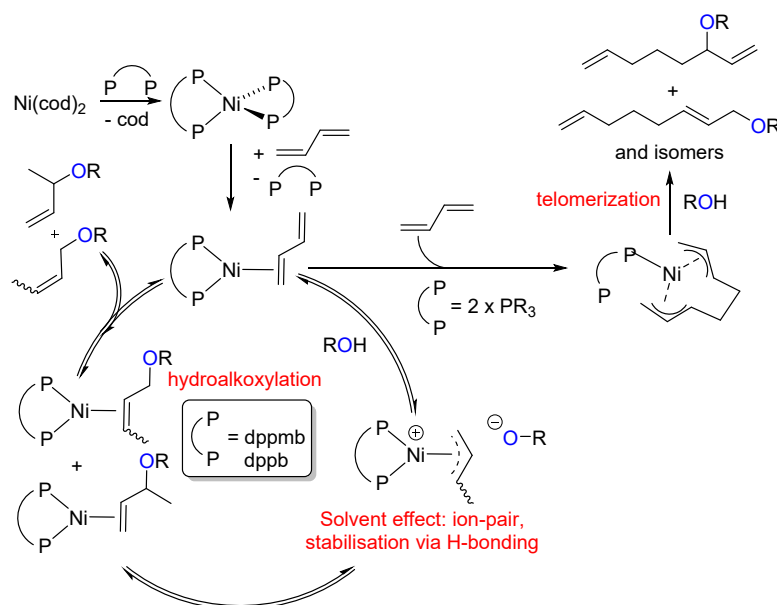


Figure SI 2: Kinetic of telomerisation on glycerol carbonate at 80°C with 1.5 mol% Ni(Cod)₂ and dppb/Ni =1.5 with 5eq. of butadiene. orange: yield in GC-HA ; grey: yield in GC-T ; blue: proportion of unmodified glycerol carbonate.

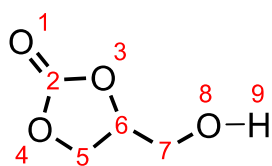
3. Proposed catalytic cycle for the Ni-Catalysed hydroalkoxylation and Telomerisation of Butadiene

We suggested the following catalytic cycle for the nickel-catalyzed hydroalkoxylation reaction in a previous article.¹ Experimental results and DFT calculations showed a reversibility of the process. The use of a diphosphine such as dppb or dppmb reduces the impedes the butadiene oxidative coupling reaction that leads to products of dimerization (right side in the scheme) but doesn't completely suppress it. By using an excess of butadiene and a longer reaction time, the dimerization is likely favored and the product of hydroalkoxylation that is mainly produced at the beginning of the reaction is converted in product of telomerization. The butadiene coupling step is clearly irreversible and the whole process is pushed towards the formation of octadienyl ethers.



¹ *ACS Catal.*, **2017**, *7* (10), 6915–6923 DOI: 10.1021/acscatal.7b00616, "Deciphering the Mechanism of the Nickel-Catalyzed Hydroalkoxylation Reaction: A Combined Experimental and Computational Study" A. Mifleur, D. S. Mérel, A. Mortreux, I. Suisse, F. Capet, X. Trivelli, M. Sauthier, and S. A. Macgregor

4. Glycerol carbonate



¹H NMR (300 MHz, DMSO-*d*₆) δ 5.25 (s, 1H) [9], 4.77 (m, 1H) [6], 4.47 (t, *J* = 8.3 Hz, 1H) [5a], 4.25 (dd, *J* = 8.1, 5.8 Hz, 1H) [5b], 3.69 – 3.56 (dd, 12.6 Hz, 3.3 Hz, 1H) [7a], 3.48 (dd, *J* = 12.6, 3.3 Hz, 1H) [7b].

¹³C NMR (75 MHz, DMSO) δ 155.21 [2], 77.05 [6], 65.90 [5], 60.62 [7].

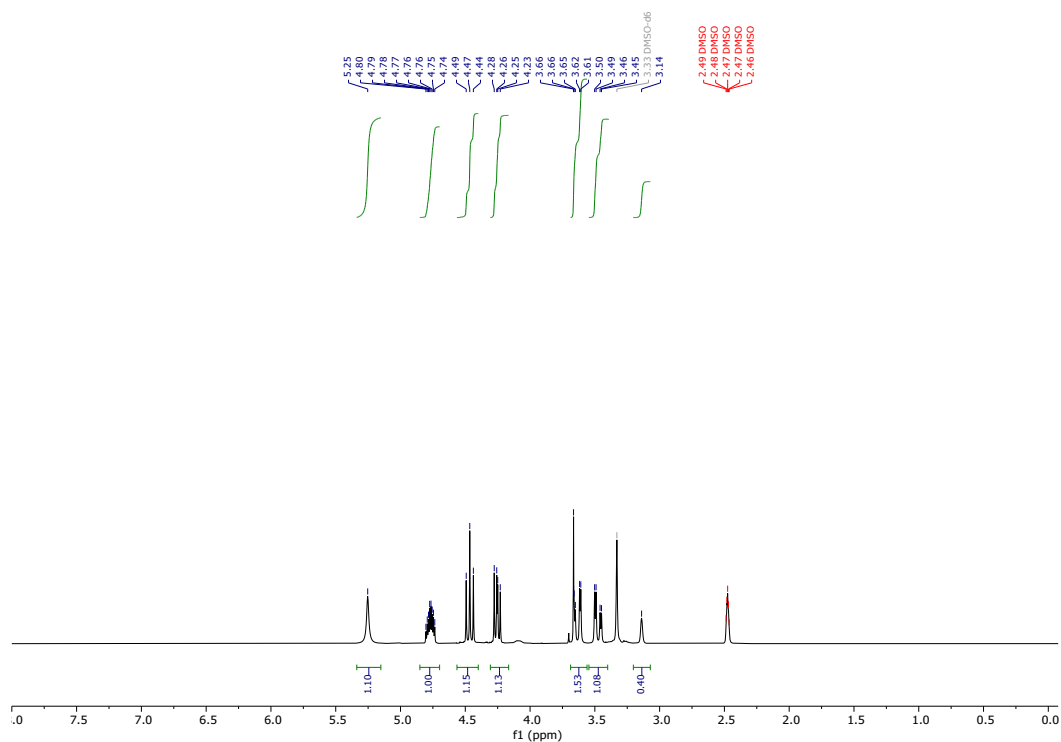


Figure SI 3: ^1H NMR spectra of glycerol carbonate.

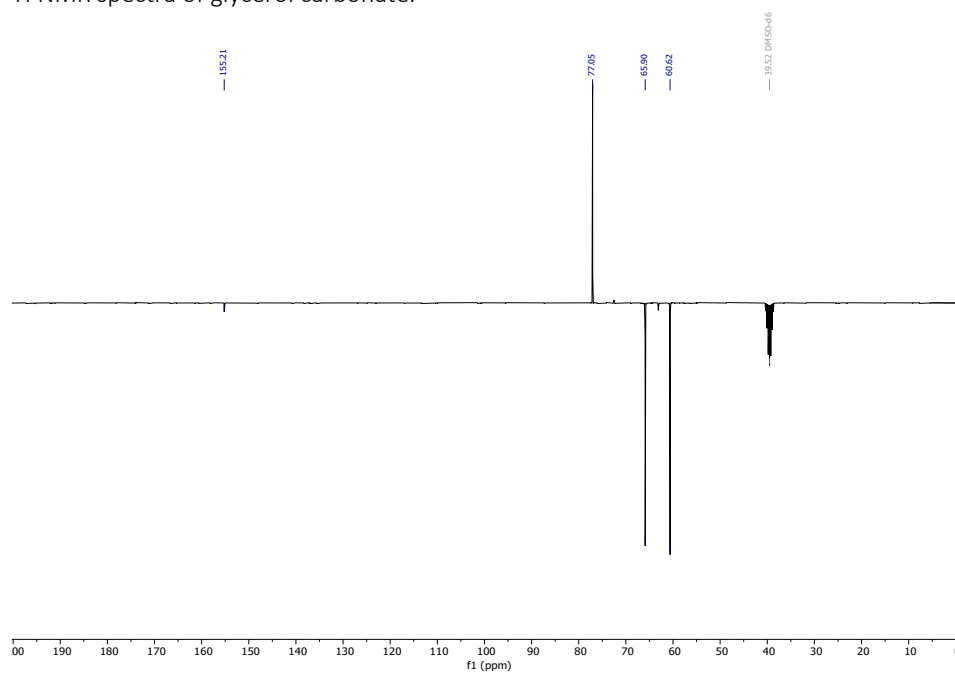
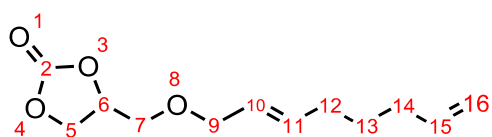


Figure SI 4: ^{13}C NMR spectra of glycerol carbonate

5. Glycerol carbonate telomers (GC-T)

A) Linear telomer GC-T



^1H NMR (300 MHz, Chloroform- d) δ 5.92 – 5.41 (m, 3H) [10-11-15], 5.10 – 4.89 (m, 2H) [16], 4.80 (m, 1H) [6], 4.57

– 4.27 (m, 2H) [5], 4.06 – 3.92 (m, 2H) [9], 3.77 – 3.32 (m, 2H) [7], 2.06 (m, 4H) [12-14], 1.48 (m, 2H) [13]. (2 isomers – Z/E)

¹³C NMR (75 MHz, CDCl₃) δ 155.08 [2], 138.61 [15], 135.69 [11], 125.64 [10], 114.81 [16], 75.17 [6], 72.59 [9], 68.59 [7], 66.52 [5], 33.29 [14], 31.73 [12], 28.29 [13].

HRMS m/z: Calculated for [M+H]⁺ C₁₂H₁₉O₄ 227.1283; Found 227.1297 (Δm = 0.0014m/z)

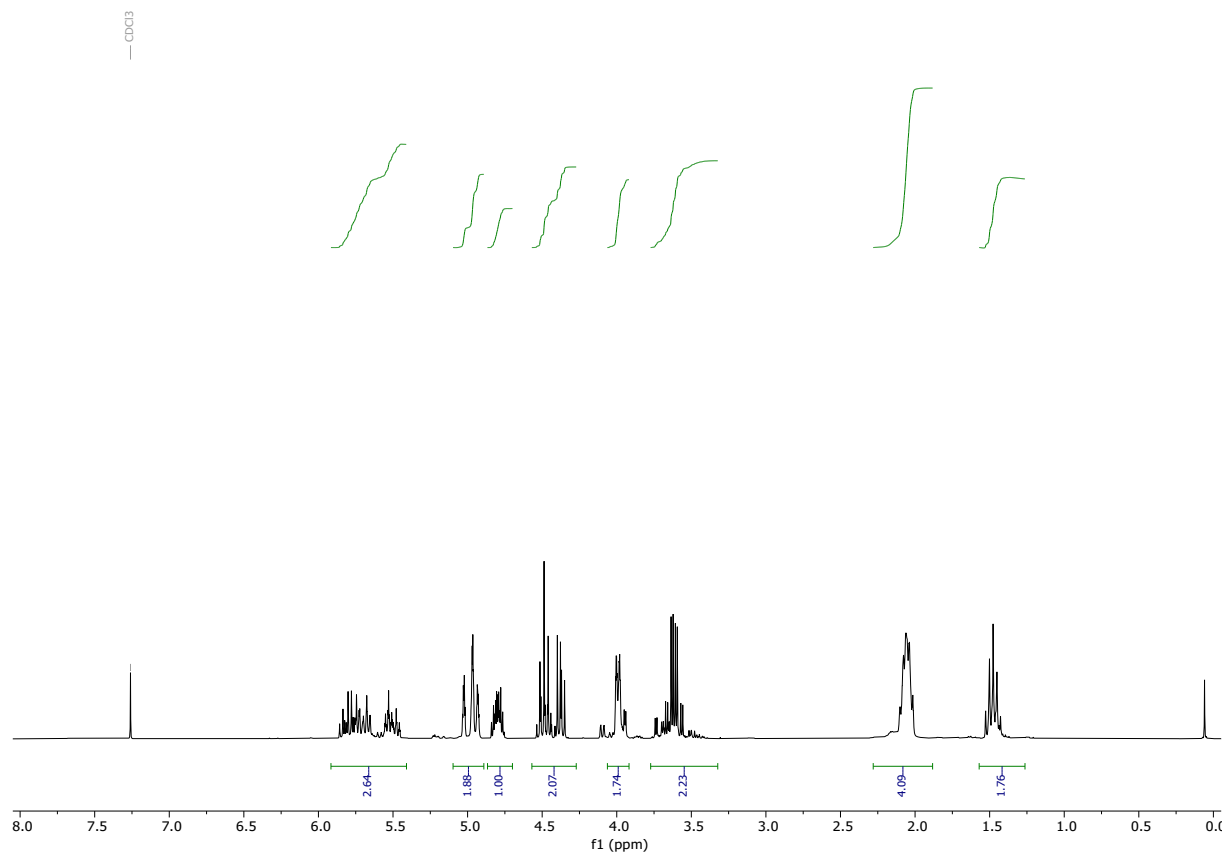


Figure SI 5: ¹H NMR spectra of linear telomer GC-T.

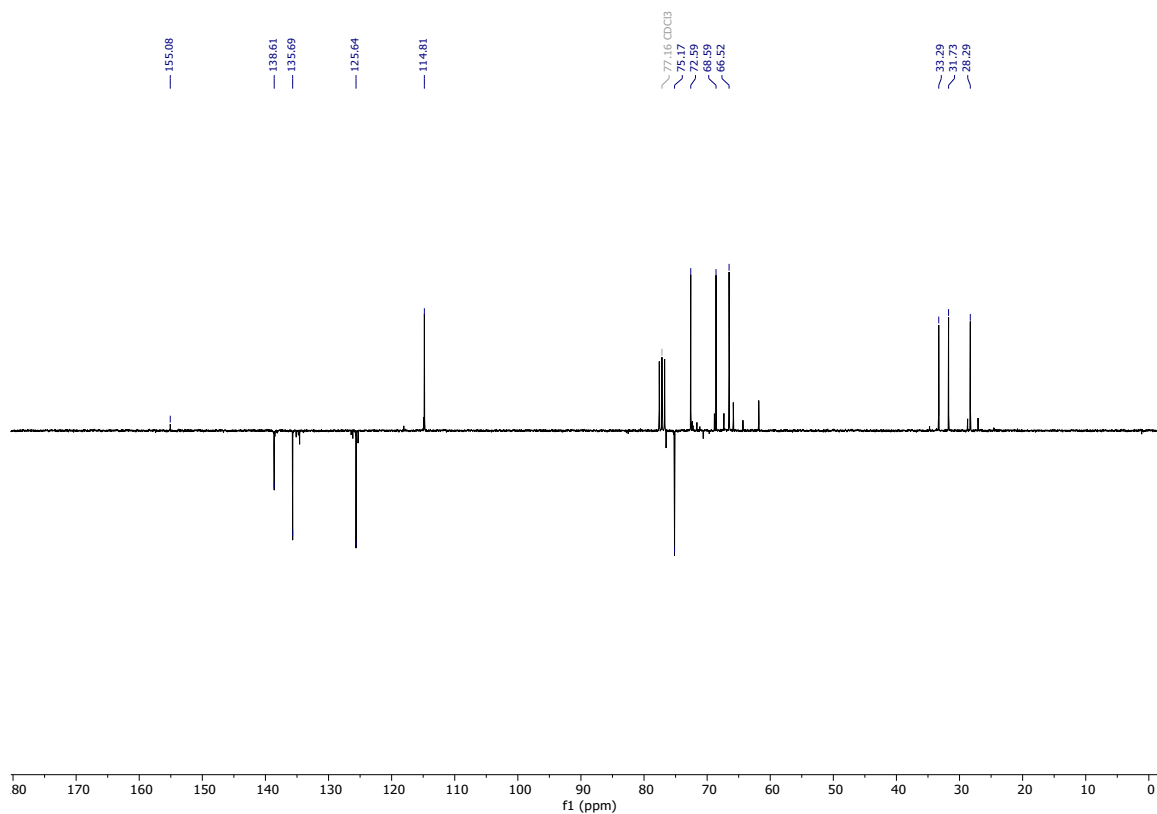
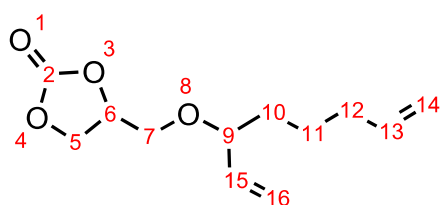


Figure SI 6: ^{13}C NMR spectra of linear telomer GC-T.

B) Branched telomer GC-T



$^1\text{H NMR}$ (300 MHz, Chloroform-*d*) δ 5.88 – 5.54 (m, 2H) [15-13], 5.28 – 5.19 (m, 1H) [16], 5.25 – 5.13 (m, 1H) [16], 5.06 – 4.90 (m, 1H) [14], 4.79 (m, 1H) [6], 4.55 – 4.30 (m, 2H) [5], 3.80 – 3.59 (m, 1H) [9], 3.49 (m, 1H) [7], 2.13 – 1.99 (m, 1H) [10-12], 1.69 – 1.28 (m, 2H) [11]. (stars showing traces of the linear telomer)

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 155.11 [2], 138.66 [15], 138.63 [15], 138.24 [13], 138.12 [13], 118.11 [16], 118.09 [16], 114.88 [14], 114.85 [14], 82.83 [9], 82.54 [9], 75.24 [6], 75.17 [6], 67.42 [7], 67.34 [7], 66.58 [5], 66.49 [5], 34.78 [10], 33.67 [12], 33.65 [12], 24.62 [11], 24.53 [11]. (Two asymmetric centers creating diastereoisomers thus dedoubling of the peaks).

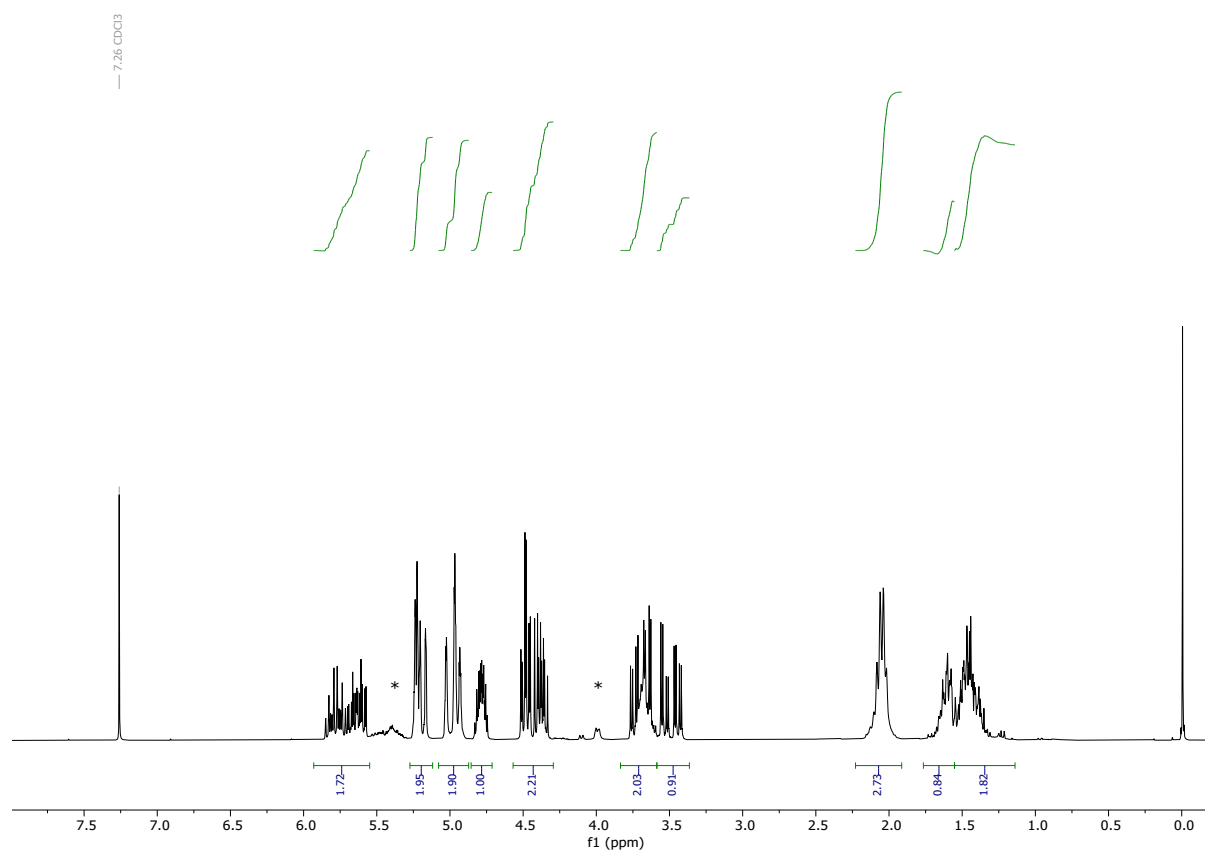


Figure SI 7: ¹H NMR of branched telomer GC-T.

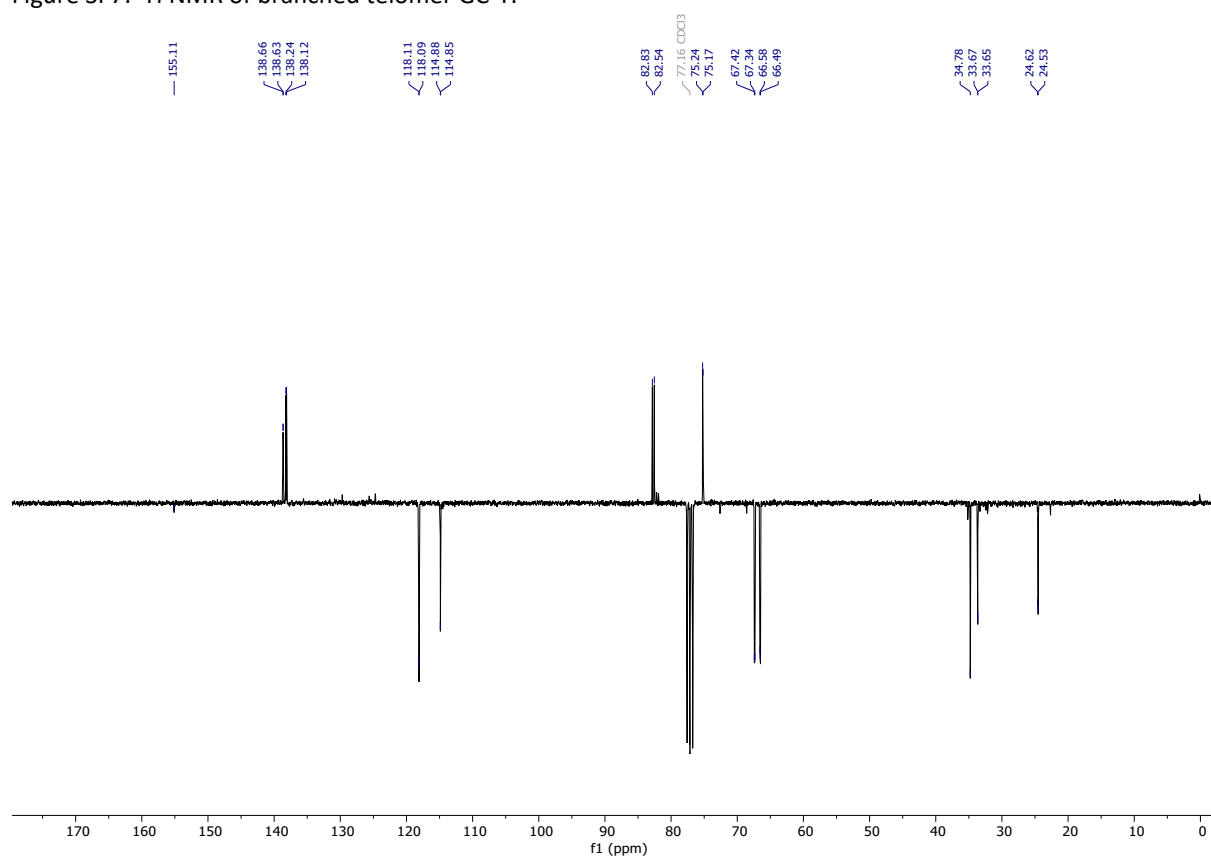
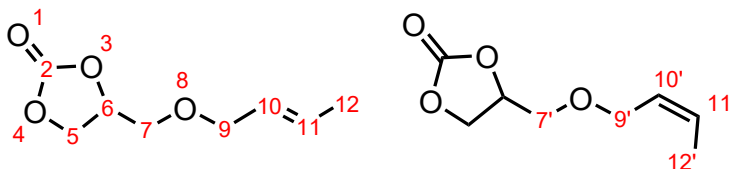


Figure SI 8: ¹³C NMR of branched telomer GC-T.

6. Glycerol carbonate hydroalkoxylate (GC-HA)

A) Linear hydroalkoxylate GC-HA



Linear (2 isomers – Z/E (30/70 ^1H NMR, determined with integration of 4.12 and 3.98 pics)):

^1H NMR (300 MHz, Chloroform-*d*) δ 5.85 – 5.63 (m, 1H) [11-11'], 5.61 – 5.40 (m, 1H) [10-10'], 4.91 – 4.68 (m, 1H) [6], 4.49 (m, 1H) [5a], 4.38 (m, 1H) [5b], 4.12 (d, $J = 6.3$ Hz, 2H, **Z form**) [9'], 3.98 (m, 2H, **E form**) [9], 3.76 – 3.43 (m, 2H) [7-7'], 1.71 (m, 3H, **E form**) [12], 1.66 (m, 3H, **Z form**) [12'].

^{13}C NMR (75 MHz, CDCl_3) δ 155.06 [2], 130.88 (**E form**) [11], 129.27 (**Z form**) [11'], 126.65 (**E form**) [10], 125.83 (**Z form**) [10'], 75.12 [6], 72.57 (**E form**) [9], 68.80 (**Z form**) [7'], 68.60 (**E form**) [7], 67.01 (**Z form**) [7'], 66.53 [5], 17.89 (**E form**) [12], 13.34 (**Z form**) [12'].

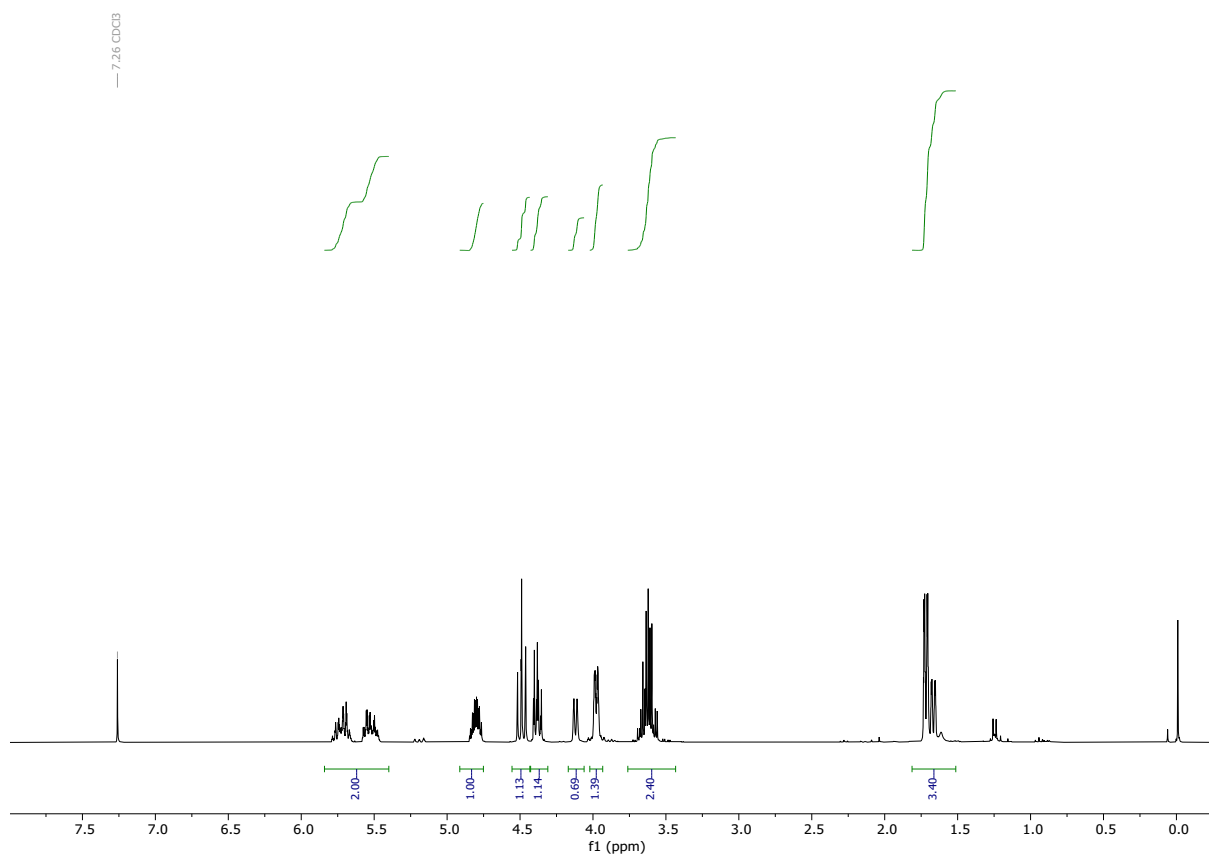


Figure SI 9: ^1H NMR spectra of GC-HA (linear form: mix Z/E) (trace of branched form).

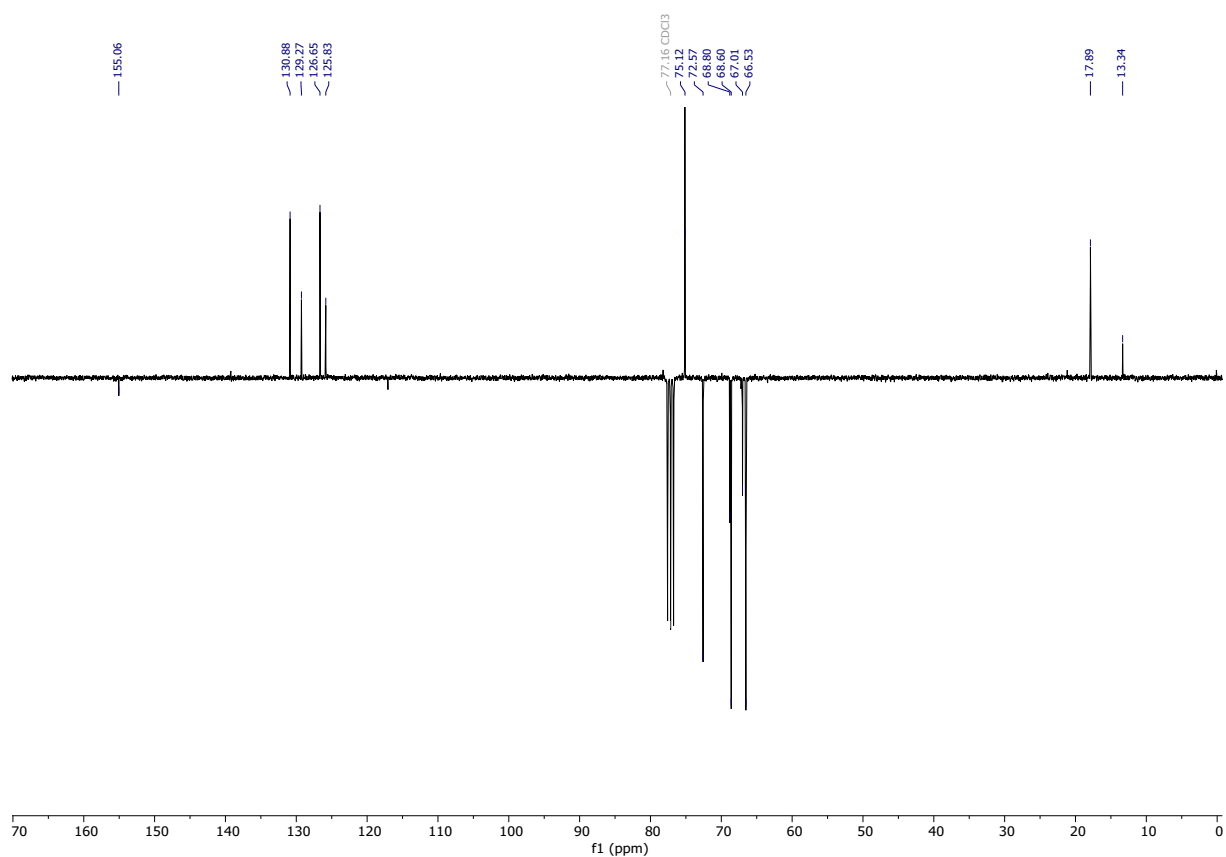
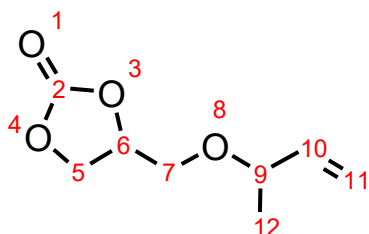


Figure SI 10: ^{13}C NMR spectra of GC-HA (linear form: Z/E mix).

B) Branched hydroalkoxylate GC-HA



^1H NMR (300 MHz, Chloroform-*d*) δ 5.71 (m, 1H) [10], 5.29 – 5.11 (m, 2H) [11], 4.82 (m, 1H) [6], 4.58 – 4.33 (m, 2H) [5], 3.90 (m, 1H) [9], 3.79 – 3.43 (m, 2H) [7], 1.27 (d, $J = 6.4$ Hz, 3H) [12].

^{13}C NMR (75 MHz, CDCl_3) δ 155.16, 139.33 [10], 139.25 [10], 117.07 [11], 78.53 [9], 78.22 [9], 75.22 [6], 67.22 [7], 67.19 [7], 66.59 [5], 66.52 [5], 21.23 [12], 21.17 [12]. (Two asymmetric centers creating diastereoisomers thus dedoubling of the peaks).

HRMS m/z calculated for $[\text{M}+\text{H}]^+$ $\text{C}_8\text{H}_{13}\text{O}_4$ 173.0814 ; Found : 173.0817 ($\Delta m = 0.0003$ m/z).

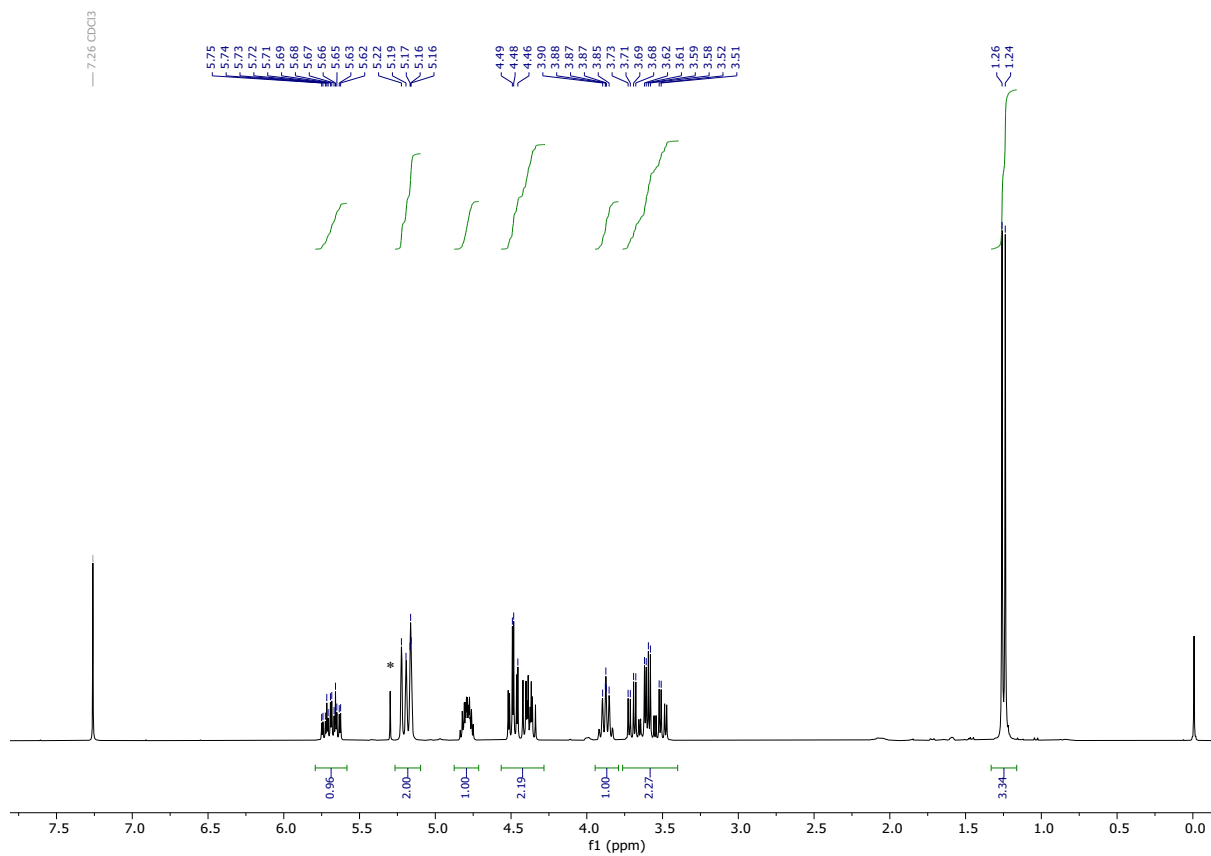


Figure SI 11: ^1H NMR spectra of GC-HA (branched form).

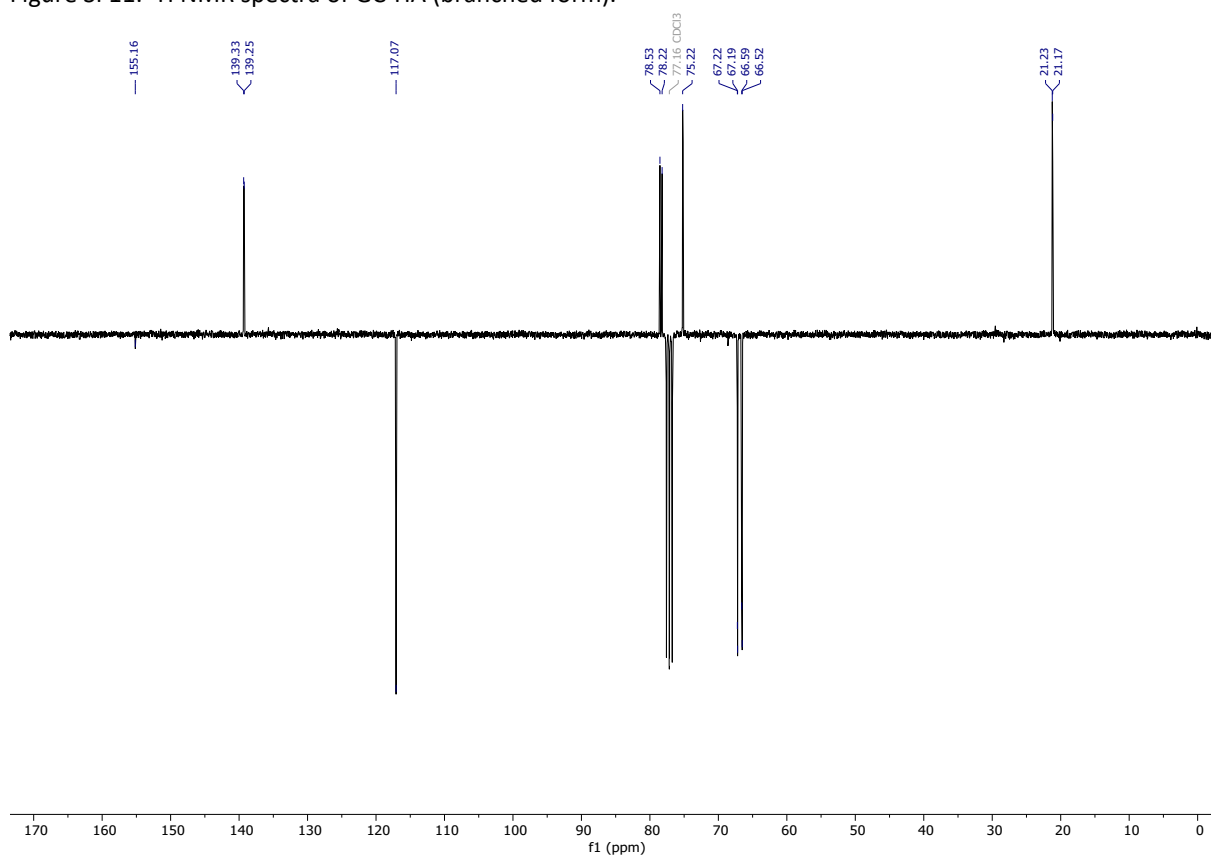


Figure SI 12: ^{13}C NMR spectra of GC-HA (branched form).

7. Characterization of the native lignins

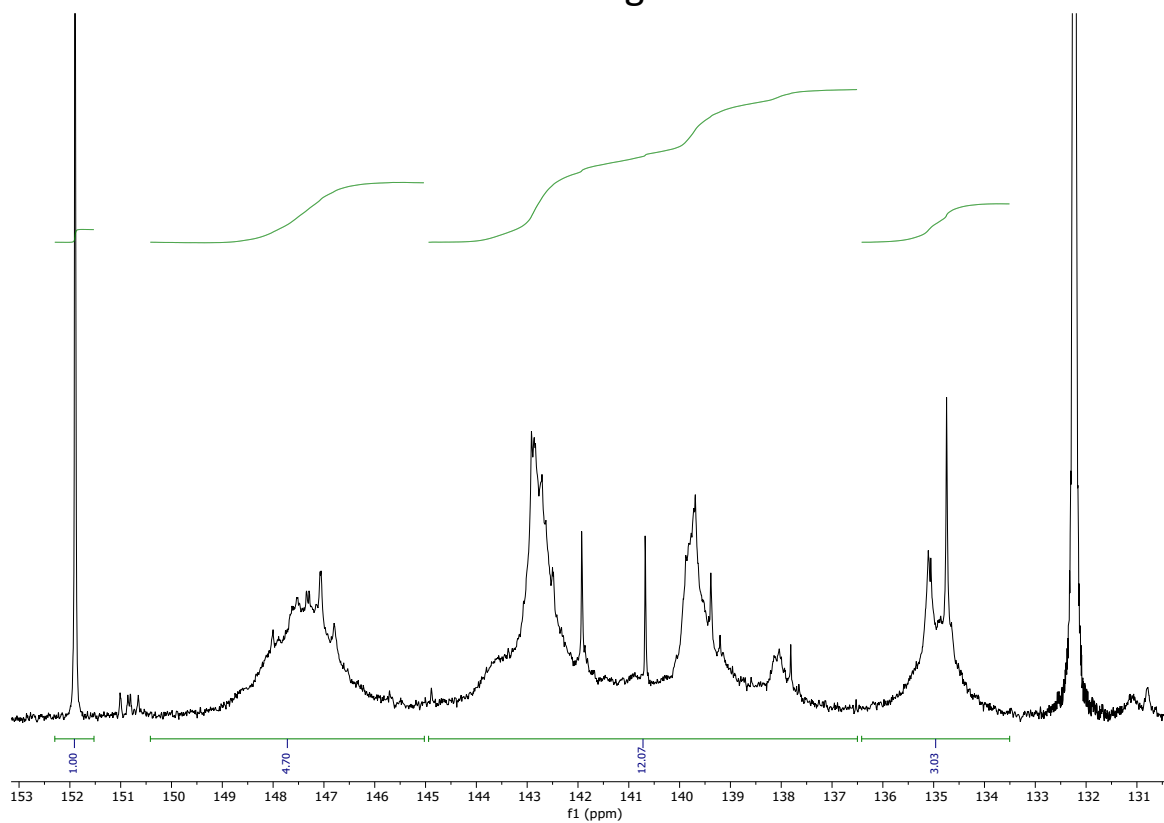


Figure SI 13: ^{31}P NMR spectra of soda lignin

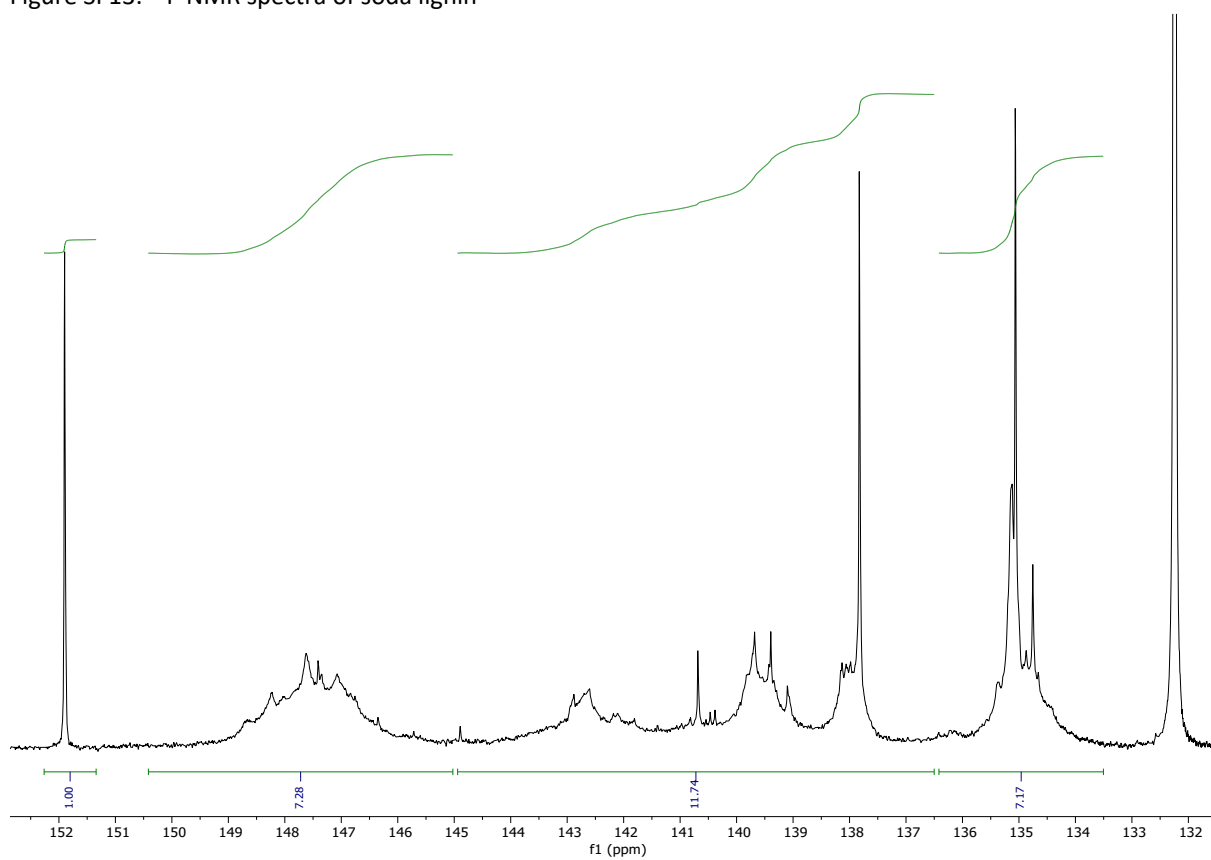


Figure SI 14: ^{31}P NMR of organosolv lignin.

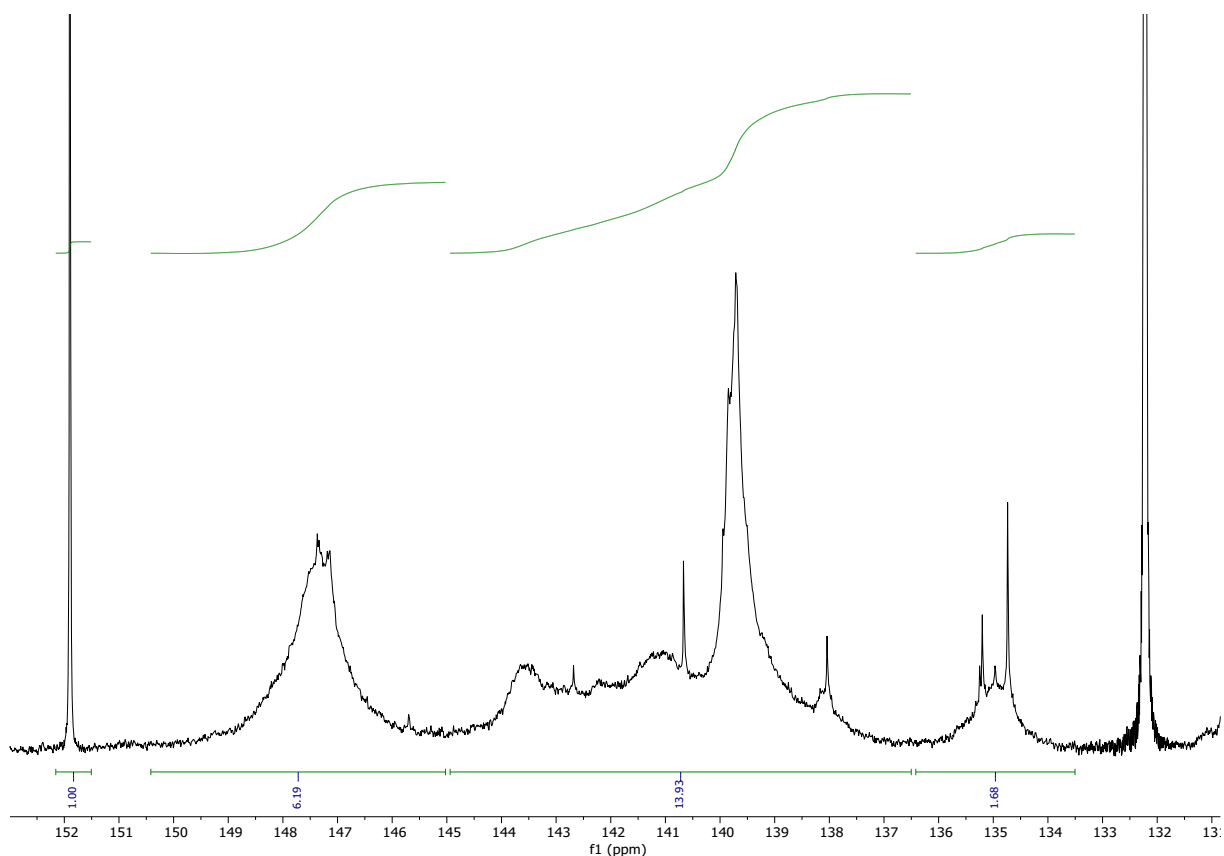


Figure SI 15: ^{31}P NMR of kraft lignin.

Table SI 2: ^{31}P analysis of lignins - titration of hydroxyl groups

Lignin	Aliphatic OH mmol/g [ini-OH _{Al}]	Phenolic OH mmol/g [ini-OH _{Ph}]	Total OH mmol/g [ini-OH _{Tot}]	Carboxylic Acid mmol/g [ini-COOH]	Total reactive groups [React-Groups]
Kraft	1.9	4.2	6.1	0.5	6.6
Organosolv	2.4	3.1	5.5	1.5	7.0
Soda	1.5	3.9	5.4	1	6.4

8. Methods for calculating degrees of substitution, lignin masses and estimation of transcarbonation

The calculations are based on the assumption that for each hydroxyl group functionalized via a cyclic carbonate, a new hydroxyl group is generated. A second assumption is that transcarbonation occurs in a statistically balanced manner between aliphatic OH from lignin and Grafted aliphatic OH. Thus the data needed to calculate the degrees of substitution are obtained from the ^{31}P NMR of modified lignins. Two peaks are shown corresponding to the unmodified aliphatic hydroxyl groups, and the newly grafted aliphatic *hydroxyl* groups on the lignin. These can be seen in figure SI 16 below. As the two peaks are relatively close, a deconvolution of the signals was performed to gain more accuracy.

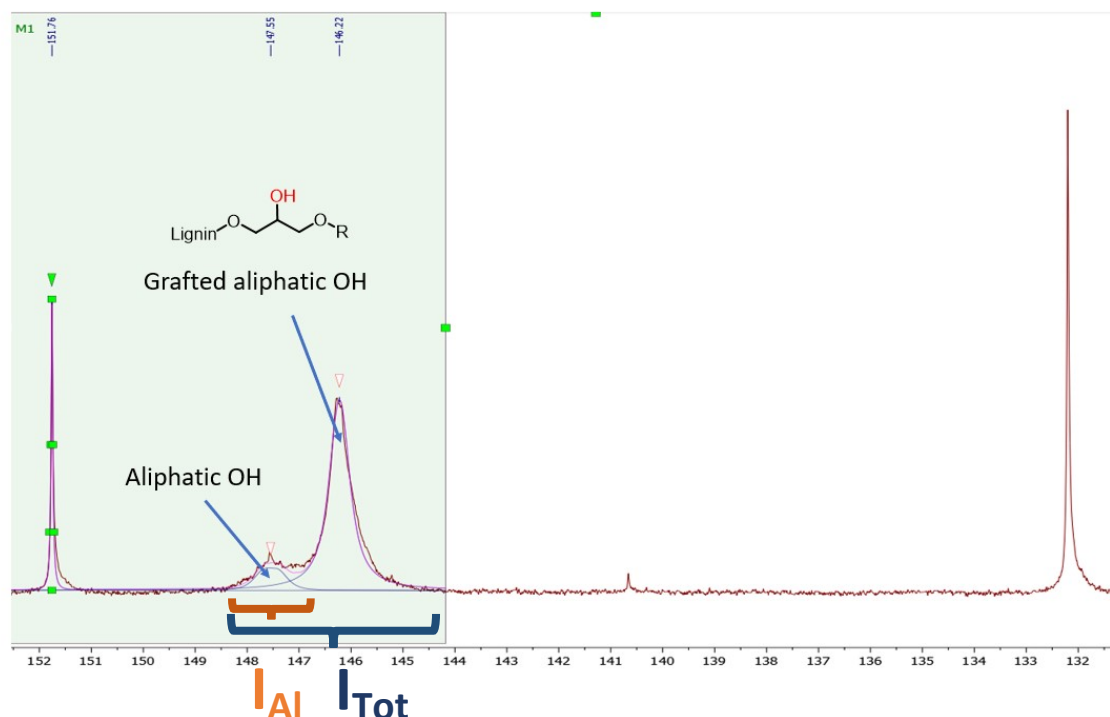


Figure SI 16 : Line fitting of the aliphatic OH peak of modified lignin.

As phenols and carboxylic acids are shown to be fully substituted on the ^{31}P NMR. The calculation of the degree of substitution of aliphatic alcohols and total alcohols can be calculated as follows:

$$\text{Substitution Degree OH aliphatics} = \left(1 - \frac{I_{Al} \times [\text{Reactive groups}]}{I_{Tot} \times [\text{ini-OH}_{Al}]}\right) * 100$$

$$\text{Substitution Degree OH Total} = \left(1 - \frac{I_{Al} \times [\text{Reactive groups}]}{I_{Tot} \times [\text{ini-OH}_{Tot}]}\right) * 100$$

I_{Al} = ^{31}P NMR integration of unmodified aliphatic hydroxyl groups as shown in Figure SI16 relative to the internal standard

I_{Tot} = ^{31}P NMR integration of total grafted aliphatic hydroxyl groups as shown in Figure SI16 relative to the internal standard

[Reactive groups] = Total concentration of reactive groups subject to opening of cyclic carbonates initially present in technical lignins (OH tot + COOH) as shown in table SI2

[ini-OH_{Al}] = Concentration of aliphatic hydroxyl groups initially present in technical lignins (OH tot + COOH) as shown in table SI2

[ini-OH_{Tot}] = Concentration of total hydroxyl groups initially present in technical lignins (OH tot + COOH) as shown in table SI2

Thus, with all substitution degrees, the addition in mass per gram of lignin related to chain grafting can be determined as follow. And so on to the % weight of lignin in the final product.

Added Weight

$$= ([SD-OH_{ph}] \times [ini-OH_{ph}] \times M_a) + ([SD-OH_{Al}] \times [ini-OH_{Al}] \times M_b) + ([SD-COOH] \times [ini-COOH] \times M_a)$$

[SD-OH_x] = Substitution degree of corresponding reactive group (x)

[ini-OH_x] = amount of corresponding reactive group (x) initially present in technical lignins as shown in table SI2

Ma = Molar mass of the ether-grafted chain (depends on GCT or GC-HA)

Mb = Molar mass of the carbonate grafted chain (depends on GCT or GC-HA)

The cross-linking bonds associated with transcarbonation do not generate hydroxyl groups when converting an aliphatic alcohol. To estimate the rate of transcarbonation, one should therefore compare the number of hydroxyl groups effectively obtained, compared to the hydroxyl groups expected in ³¹P NMR.

Estimated Carbonate Transesterification [% OH]

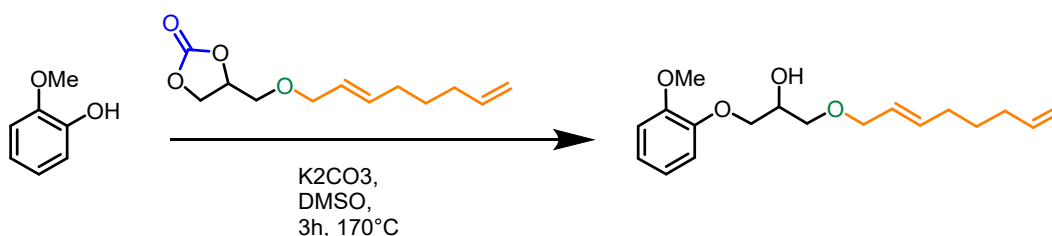
$$= \left(1 - \frac{ITot \times \frac{n_{EI}}{m_{sample}}}{\% Lignin Weight \times [Reactive groups]} \right) * 100$$

n_{EI} = Number of moles of internal standard in ³¹P NMR tube

m_{sample} = mass of modified lignin added to the ³¹P NMR tube

9. Model molecules

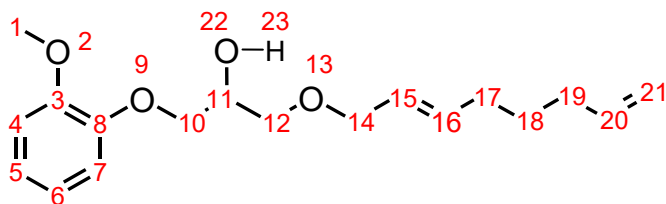
A) GCT grafted on guaiacol



Scheme SI 1: Synthesis of model molecule with GCT.

Guaiacol (0.5g, 4mmol, 1eq.), telomer glycerol carbonate (5.43g, 24mmol, 6eq.), K₂CO₃ (55.5mg, 0.4mmol, 0.1eq.) were added in a Schlenck equipped with a Rotaflo stop cock and then placed under

inert atmosphere. DMSO dried and degazed (2.7mL, 9eq.) was then added. The reaction mixture was heated at 170°C during 3h. The yield was determined by gaz chromatography (47%). Linear isomer of telomer glycerol carbonate was chosen for being easier to separate on flash silica column chromatography (80-20 petroleum ether-ethyl acetate) with 33% of isolated yield.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.06 – 6.76 (m, 4H) [3-4-5-6-7-8], 5.91 – 5.39 (m, 3H) [15-16-20], 5.10 – 4.88 (m, 2H) [21], 4.30 – 3.93 (m, 5H) [10-11-14], 3.85 (s, 3H) [1], 3.69 – 3.40 (m, 2H) [12], 2.93 (s, 1H) [23], 2.16 – 1.94 (m, 4H) [17-19], 1.48 (m, 2H) [18].

¹³C NMR (75 MHz, CDCl₃) δ 150.05 [3], 148.30 [8], 138.73 [20], 134.89 [16], 126.37 [15], 122.24 [5], 121.11 [6], 115.37 [7], 114.77 [21], 112.07 [4], 72.33 [14], 71.63 [10], 70.72 [12], 69.18 [11], 55.97 [1], 33.35 [19], 31.80 [17], 28.35 [18].

HRMS m/z calculated for [M+H]⁺ C₁₈H₂₇O₄ 307.1909 ; Found : 307.1886 (Δ m = 0.0023 m/z).

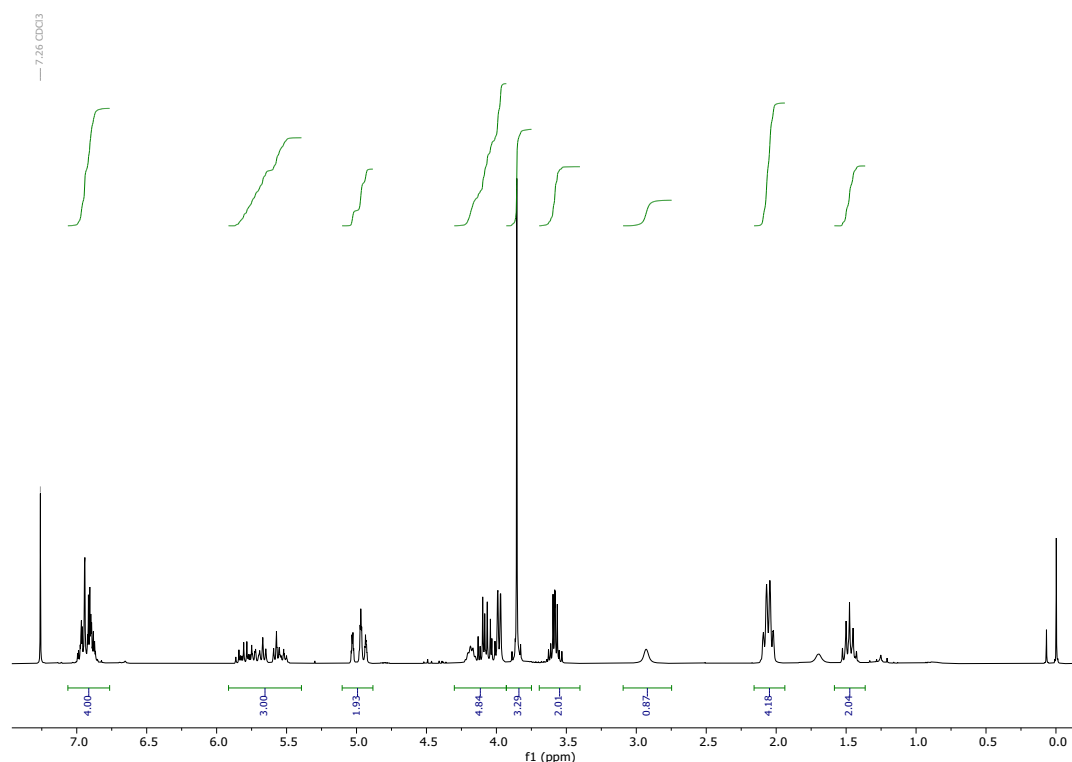


Figure SI 17: ¹H NMR spectra of modified guaiacol by opening GC-T.

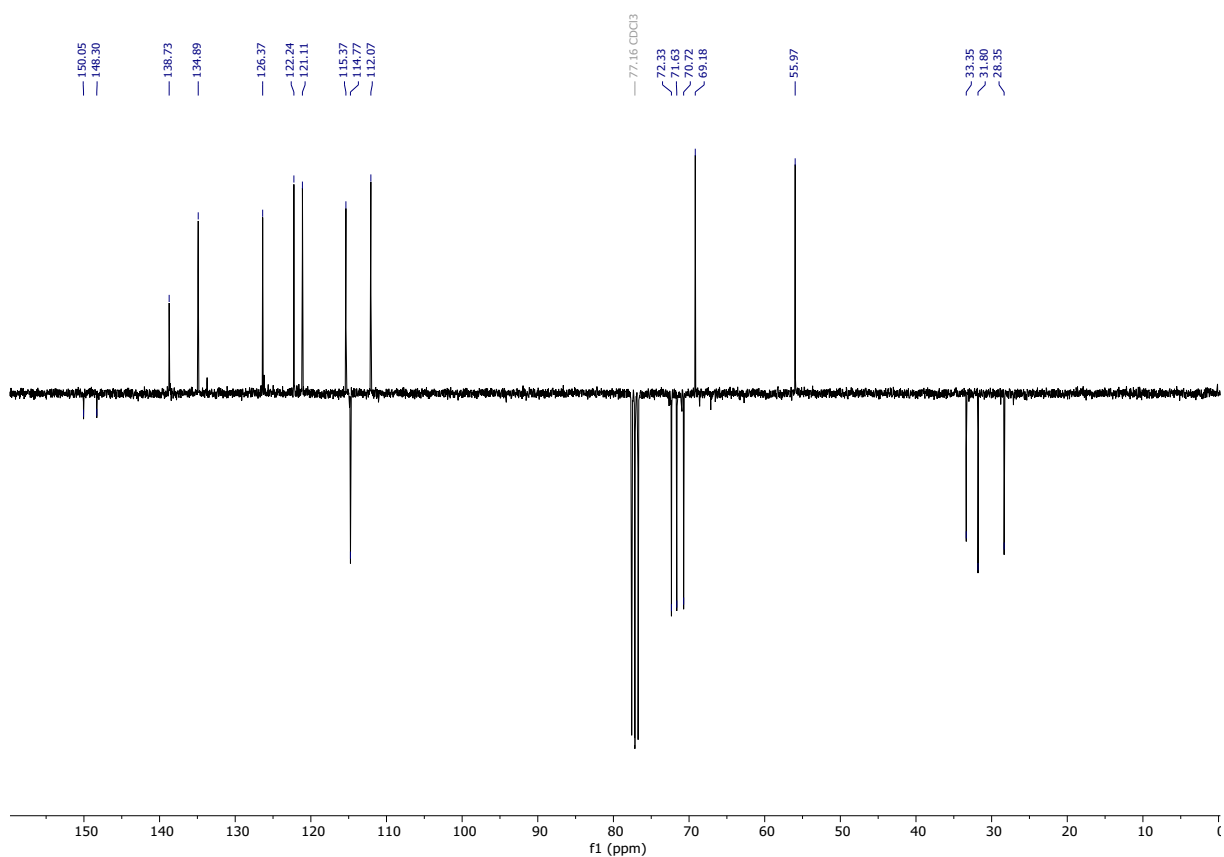
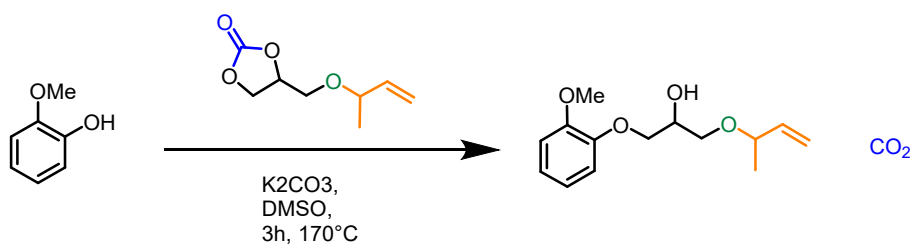


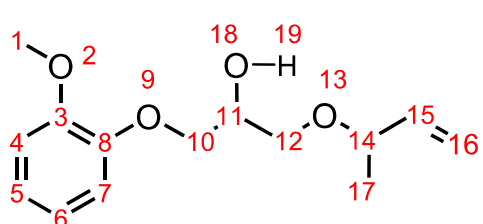
Figure SI 18: ^{13}C NMR spectra of modified guaiacol by opening GC-T.

B) GC-HA grafted on guaiacol



Scheme SI 2: Synthesis of model molecule with GC-HA.

Guaiacol (0.5g, 4mmol, 1eq.), hydroalkoxylate glycerol carbonate branched (4.1g, 24mmol, 6eq.), K_2CO_3 (55.5mg, 0.4mmol, 0.1eq.) were gathered in a Schlenk equipped with a Rotaflo stop cock and then placed under inert atmosphere. DMSO dried and degazed (2.7mL, 9eq.) was then added. The reaction mixture was put at 170°C during 3h. The yield was determined by gaz chromatography (47%). Branched isomer of hydroalkoxylate glycerol carbonate was chosen for being easier to separate on flash silica column chromatography (80-20 petroleum ether-ethyl acetate) with 48% of isolated yield.



^1H NMR (300 MHz, Chloroform- d) δ 7.06 – 6.87 (m, 4H) [3-4-5-6-7-8], 5.75 (m, 1H) [15], 5.32 – 5.08 (m, 2H) [16], 4.28 – 3.99 (m, 3H) [14-10], 3.88 (m, 4H) [1-11], 3.75 – 3.42 (m, 2H) [12], 2.99 – 2.82 (m, 1H) [19], 1.28 (d, J = 6.4 Hz, 3H) [17].

^{13}C NMR (75 MHz, CDCl_3) δ 150.09 [3], 148.37 [8], 140.06 [15], 122.21 [6], 121.11 [5], 116.29 [16], 115.39 [4], 112.12 [7], 77.83 [14], 71.65 [10], 69.26 [12], 69.08 [11], 55.99 [1], 21.29 [17].

HRMS m/z calculated for $[\text{M}+\text{H}]^+$ $\text{C}_{14}\text{H}_{21}\text{O}_4$ 253.1440 ; Found : 253.1426 ($\Delta m = 0.0014$ m/z).

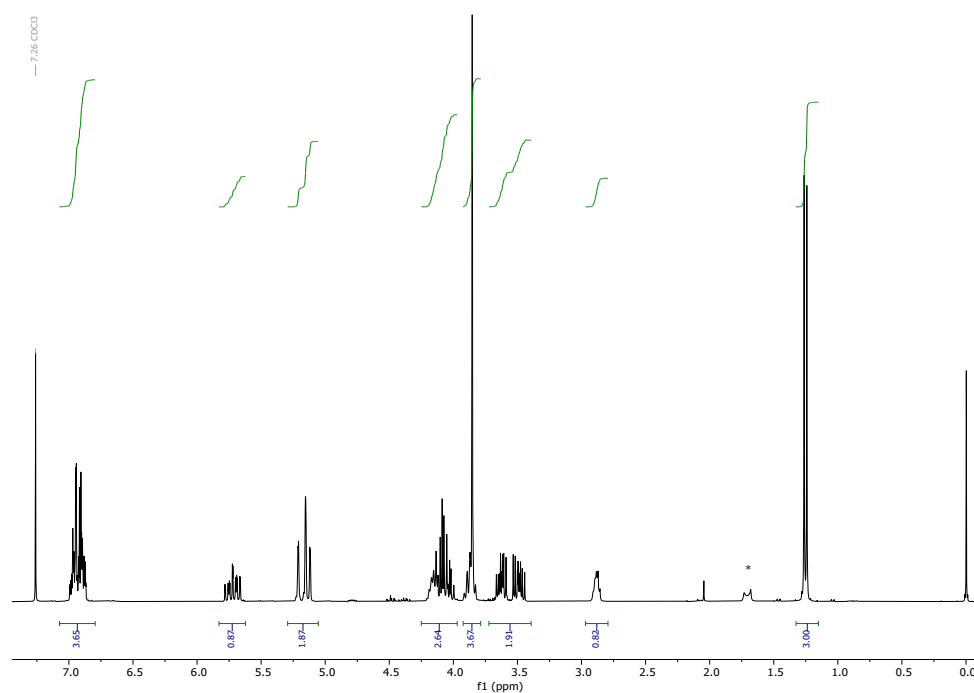


Figure SI 19: ^1H NMR spectra of modified guaiacol by opening of GC-HA.

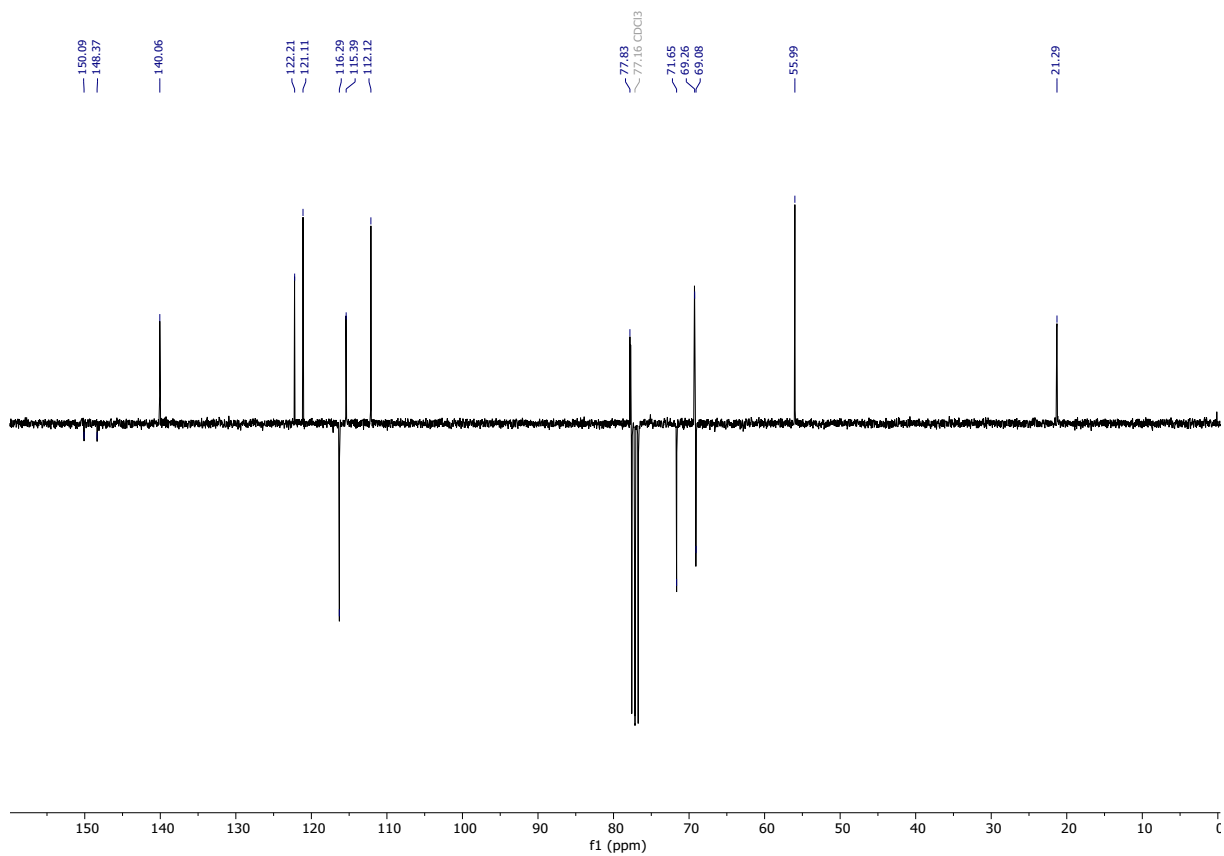


Figure SI 20: ^{13}C spectra of modified guaiacol obtained by opening of GC-HA.

10. ^1H NMR of modified lignins

A) Lignins modified by GC-T

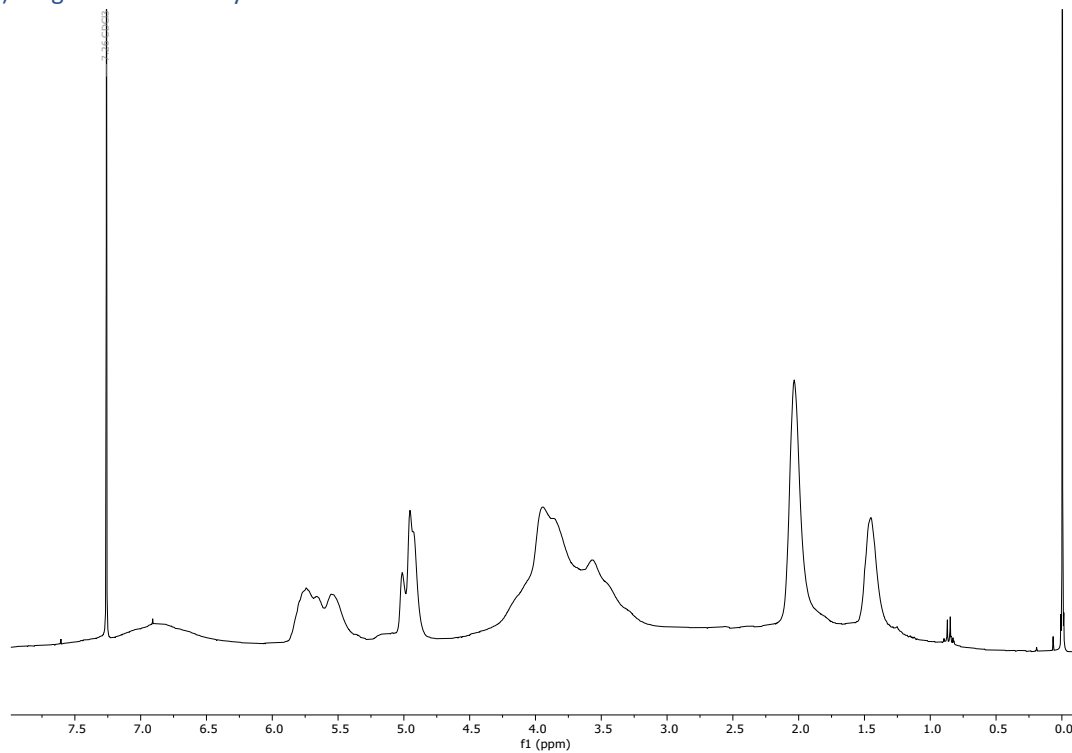


Figure SI 21: ^1H kraft lignin modified by GC-T.

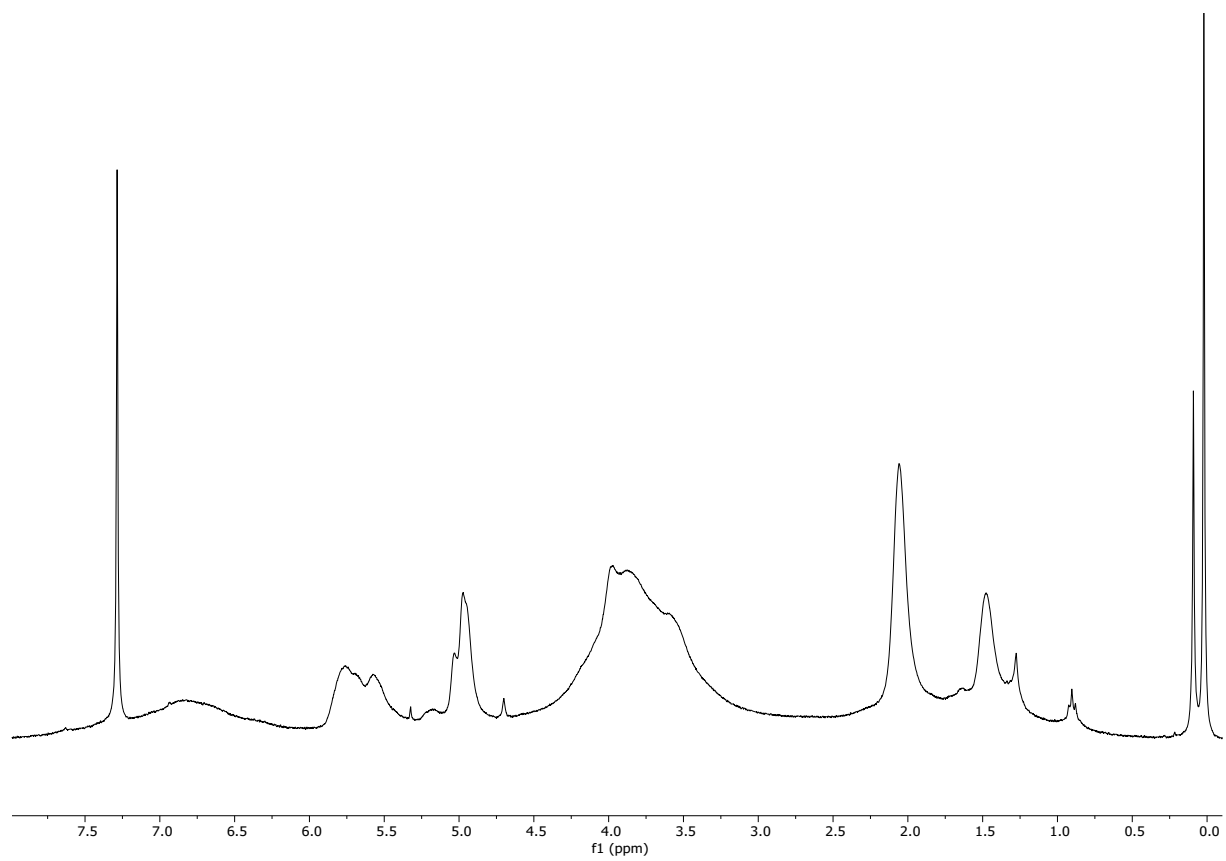


Figure SI 22: ¹H Organosolv lignin modified by GC-T.

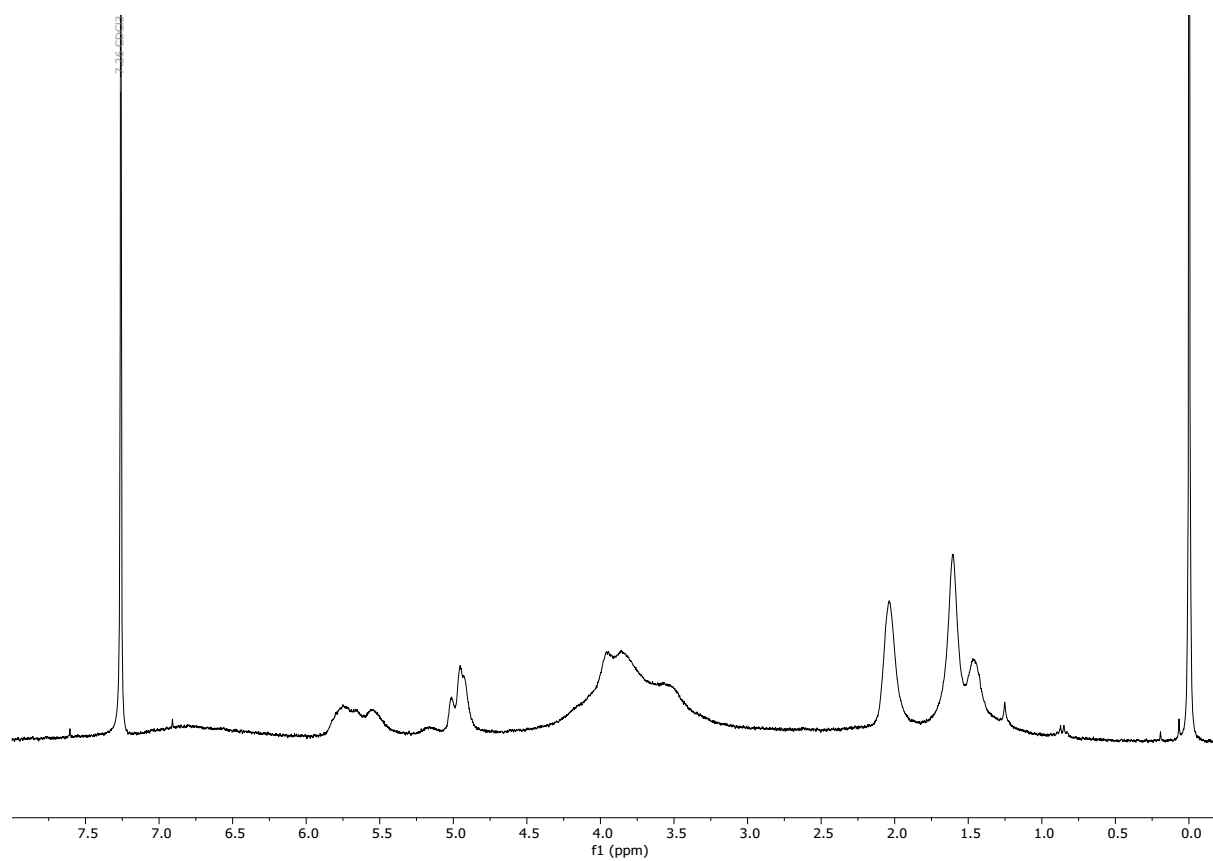


Figure SI 23: ¹H Soda lignin modified by GC-T.

B) Lignins modified by GC-HA

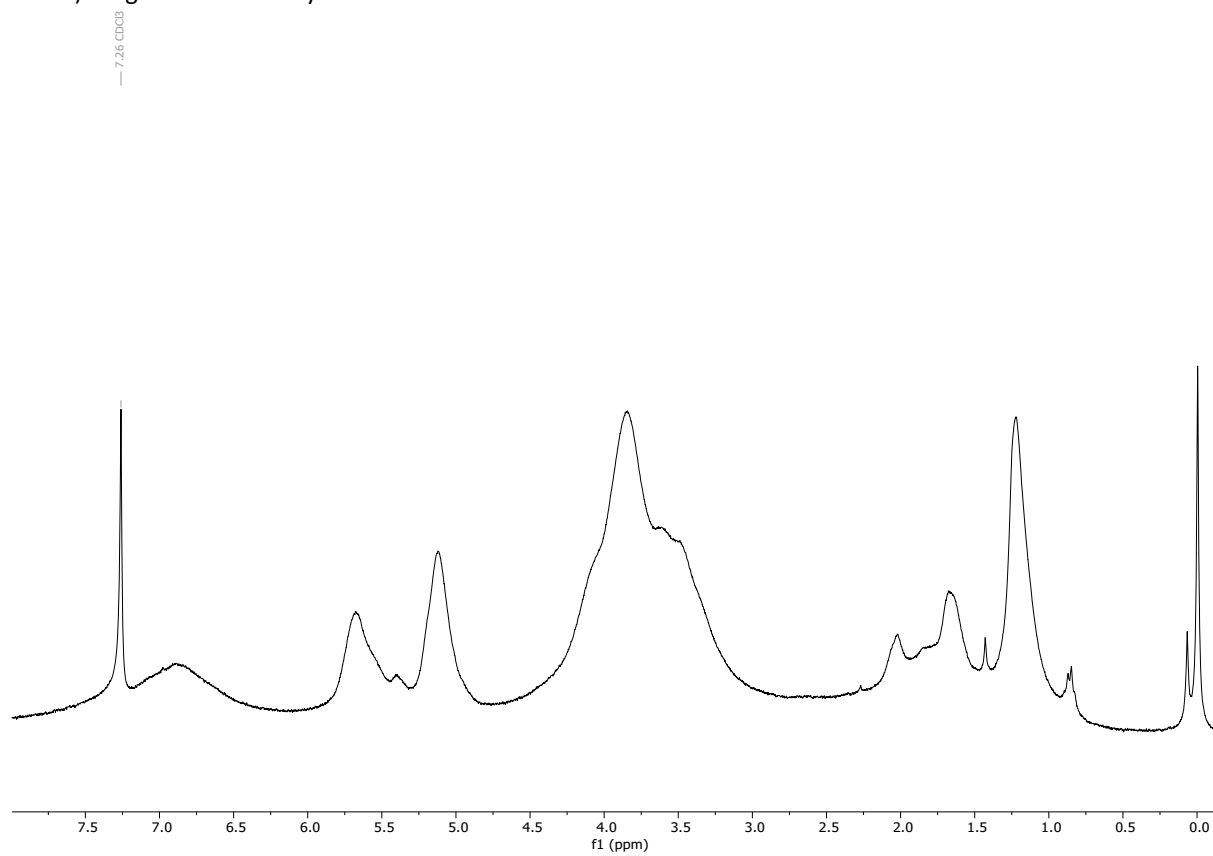


Figure SI 24: ¹H kraft lignin modified by GC-HA.

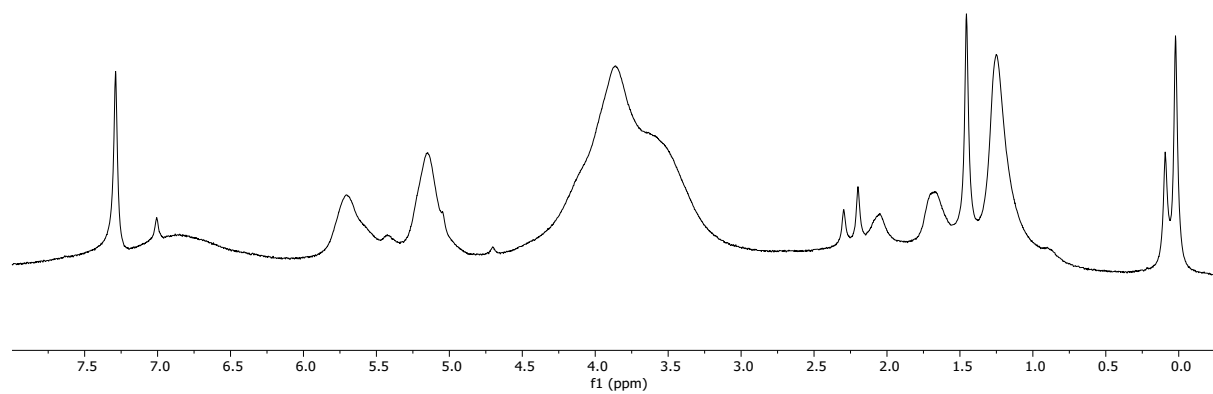


Figure SI 25: ^1H Organosolv lignin modified by GC-HA.

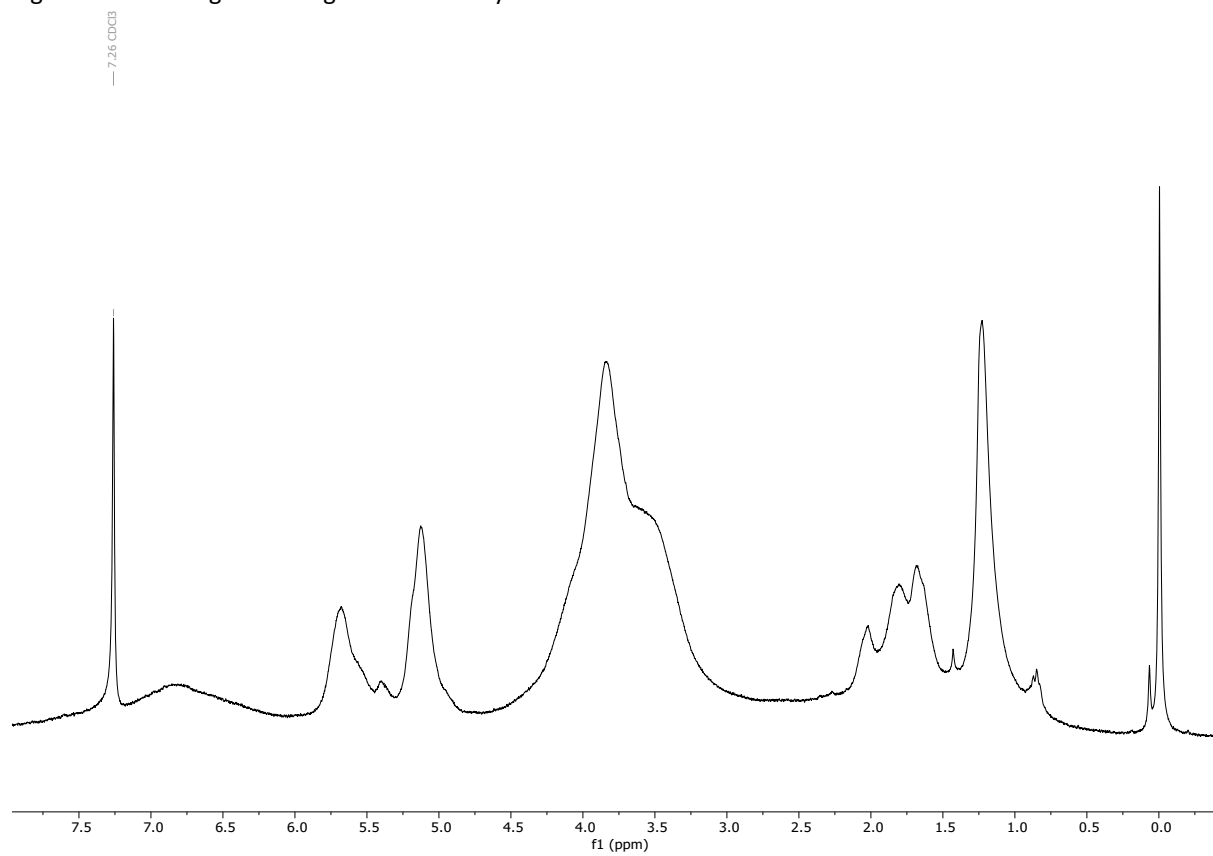


Figure SI 26: ^1H Soda lignin modified by GC-HA.

C) Lignins modified by mix GC-T/GC-HA

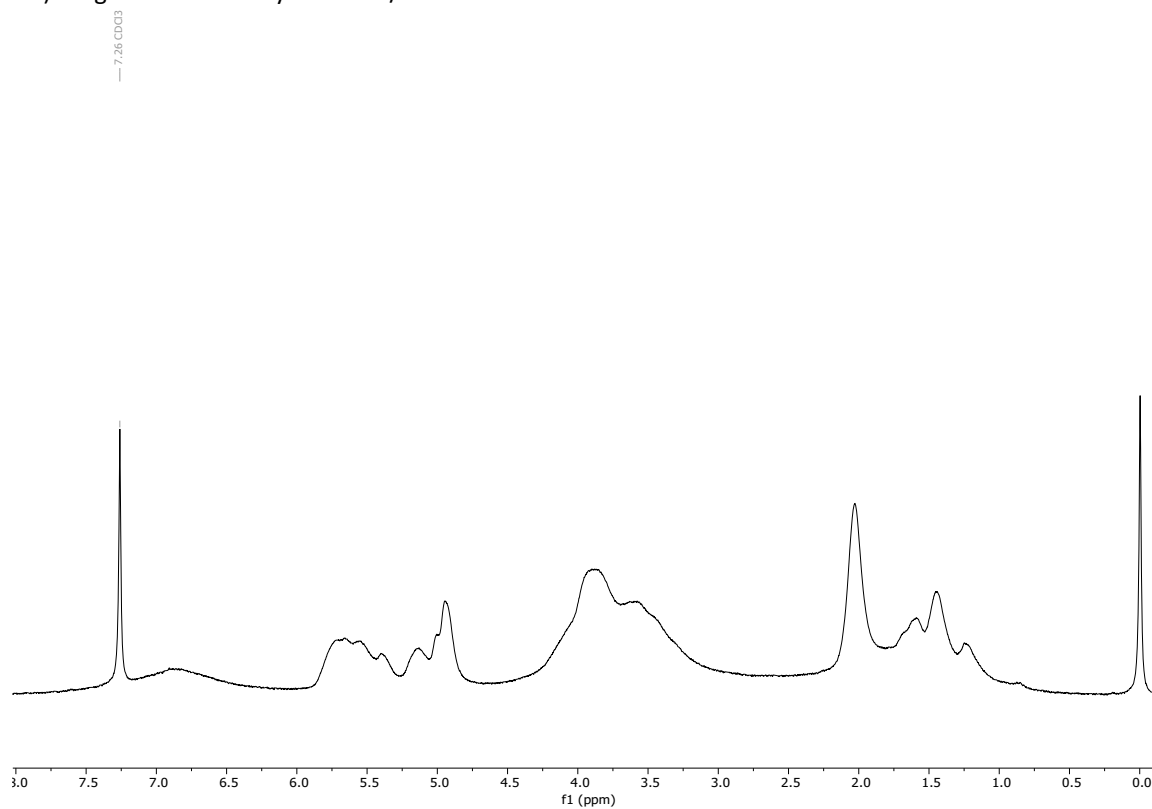


Figure SI 27: ¹H kraft lignin modified by mix GC-T/GC-HA.

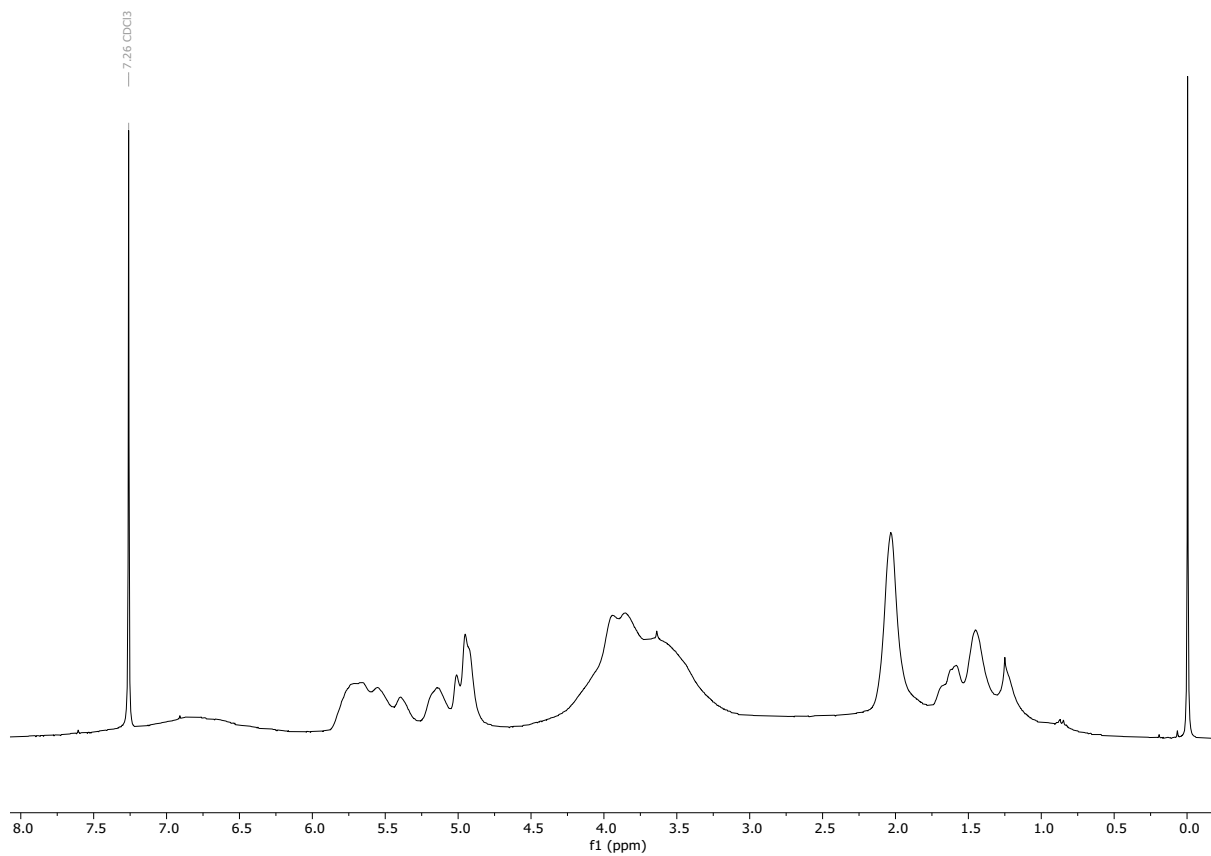


Figure SI 28: ¹H Organosolv lignin modified by mix GC-T/GC-HA.

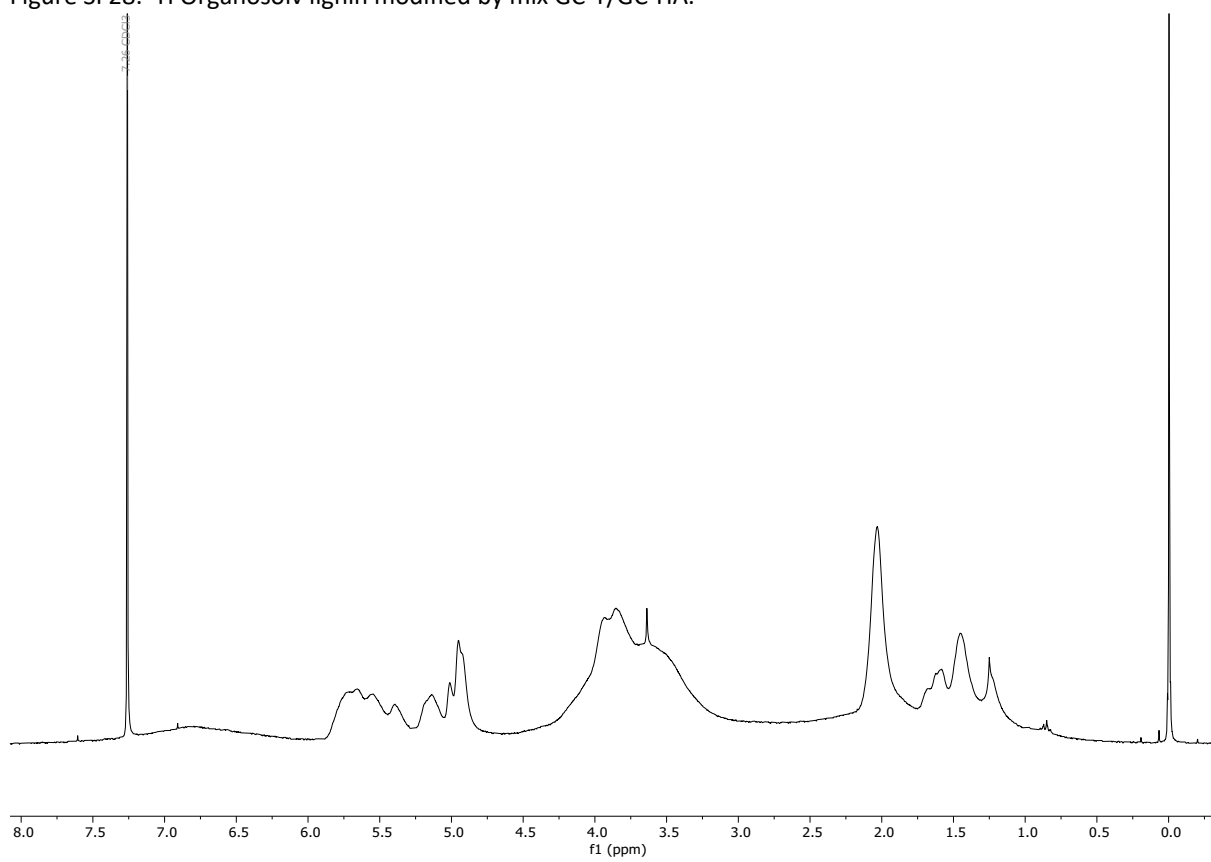


Figure SI 29: ¹H Soda lignin modified by mix GC-T/GC-HA.

11. GPC analysis of modified and unmodified lignin

Table SI 3: GPC analysis of unmodified and modified lignin.

Entry	Modification	Lignin type	Mn (g/mol)	Mw (g/mol)	D
1	Native	Kraft	857,7	1521	1,77
2	Native	Soda	740,9	1288	1,74
3	Native	Organosolv	835,9	1182	1,41
4	GC-T	Kraft	6700	56000	8.4
5	GC-T	Soda	4729	13460	2,85
6	GC-T	Organosolv	4460	16420	3,68
7	GC-HA	Kraft	5298	27080	5,11
8	GC-HA	Soda	3885	11830	3,05
9	GC-HA	Organosolv	4172	21730	5,21
10	Mix	Kraft	6544	33330	5,09
11	Mix	Soda	5351	36190	6,76
12	Mix	Organosolv	5300	20000	3.8

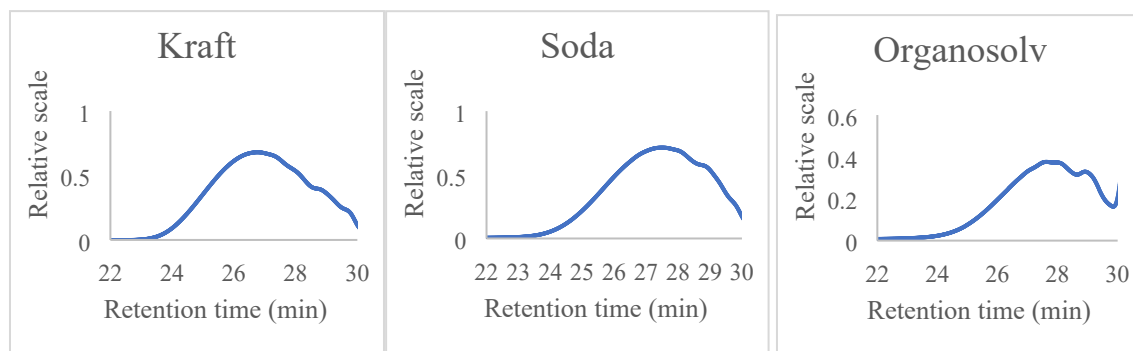


Figure SI 30: GPC analysis of Kraft, Soda and Organosolv lignin.

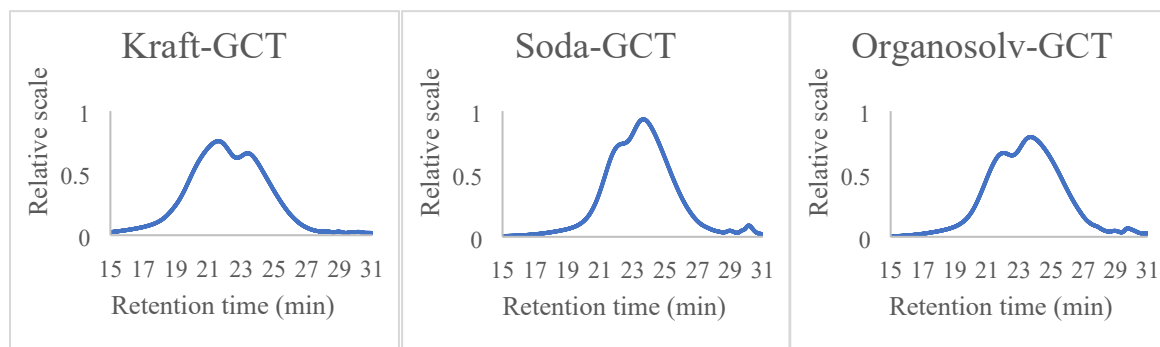


Figure SI 31: GPC analysis of Kraft, Soda and Organosolv modified by GC-T.

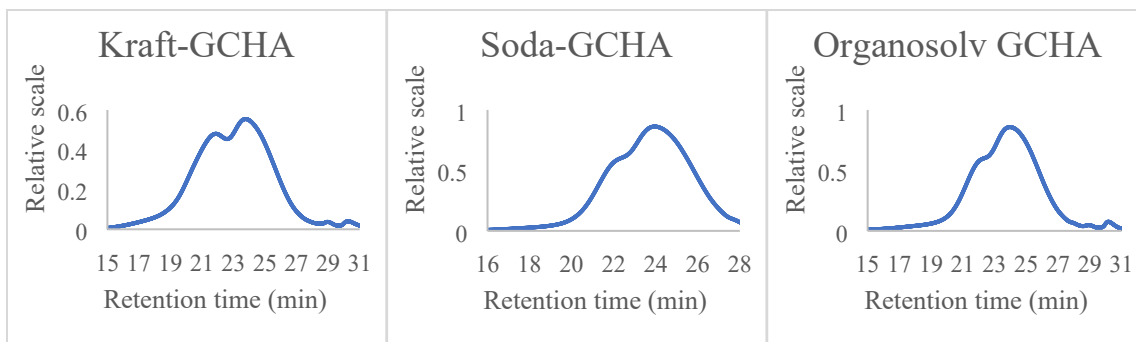


Figure SI 32: GCP analysis of Kraft, Soda and Organosolv modified by GC-HA.

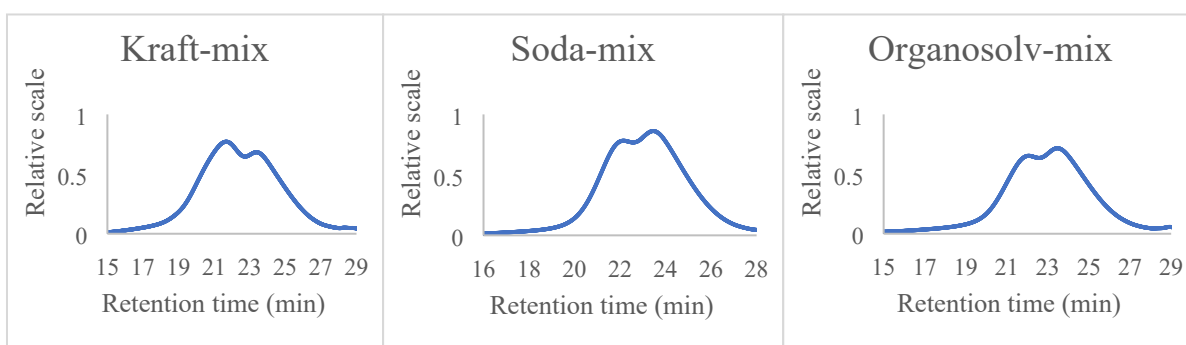


Figure SI 33: GCP analysis of Kraft, Soda and Organosolv-mix.

12. ^{13}C and 2D NMR of native and modified lignin

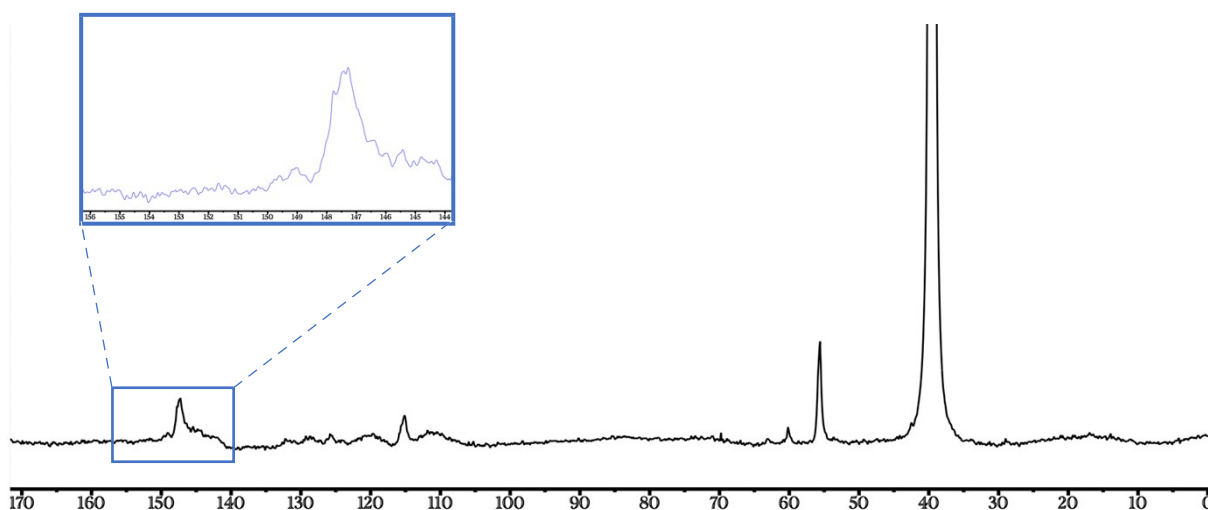


Figure SI 34: ^{13}C NMR spectrum of Kraft lignin in DMSO-d_6 .

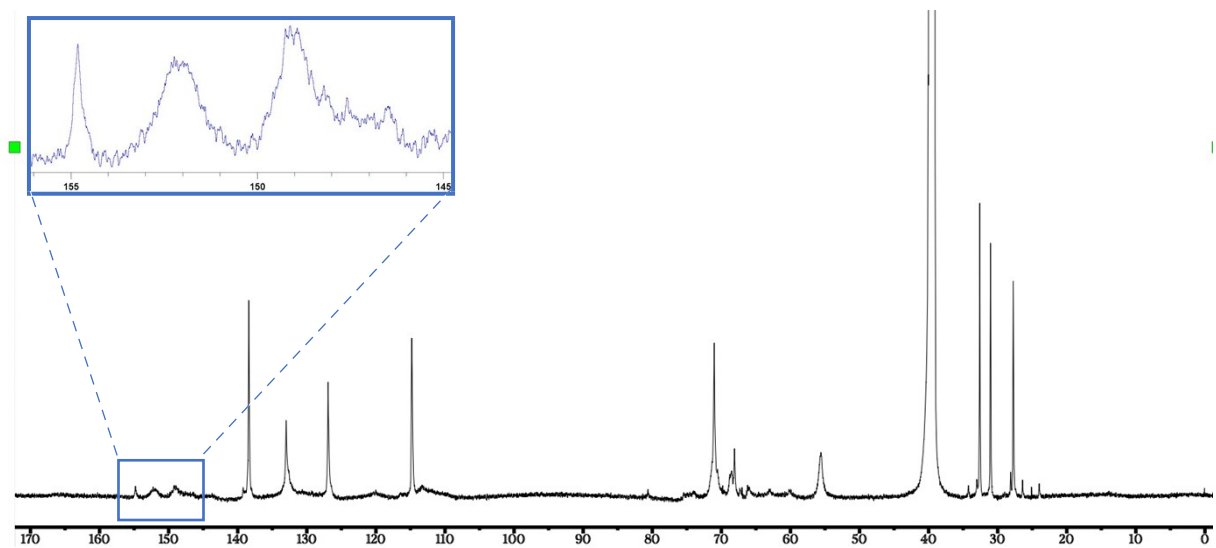


Figure SI 35: ^{13}C NMR of modified Kraft GC-T lignin in DMSO-d_6 .

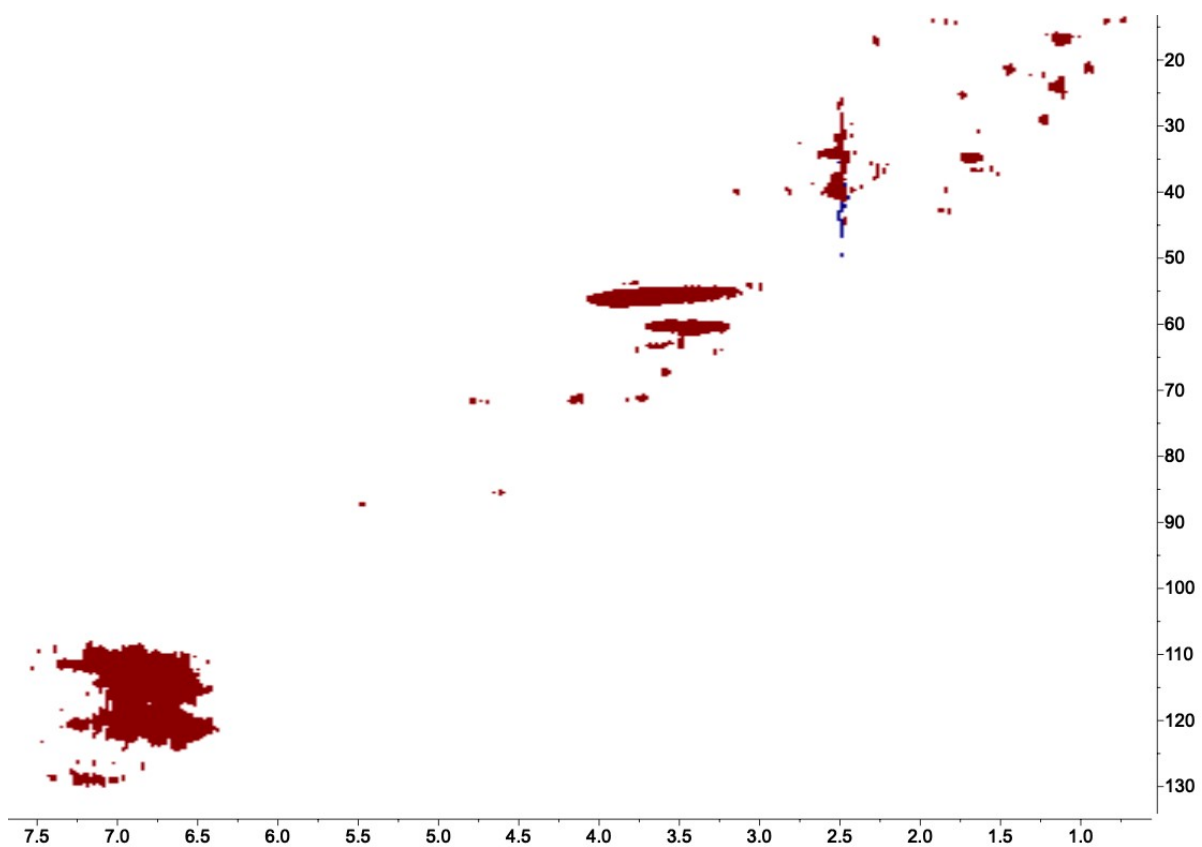


Figure SI 36: 2D HSQC NMR spectrum of technical Kraft lignin in DMSO-d_6 .

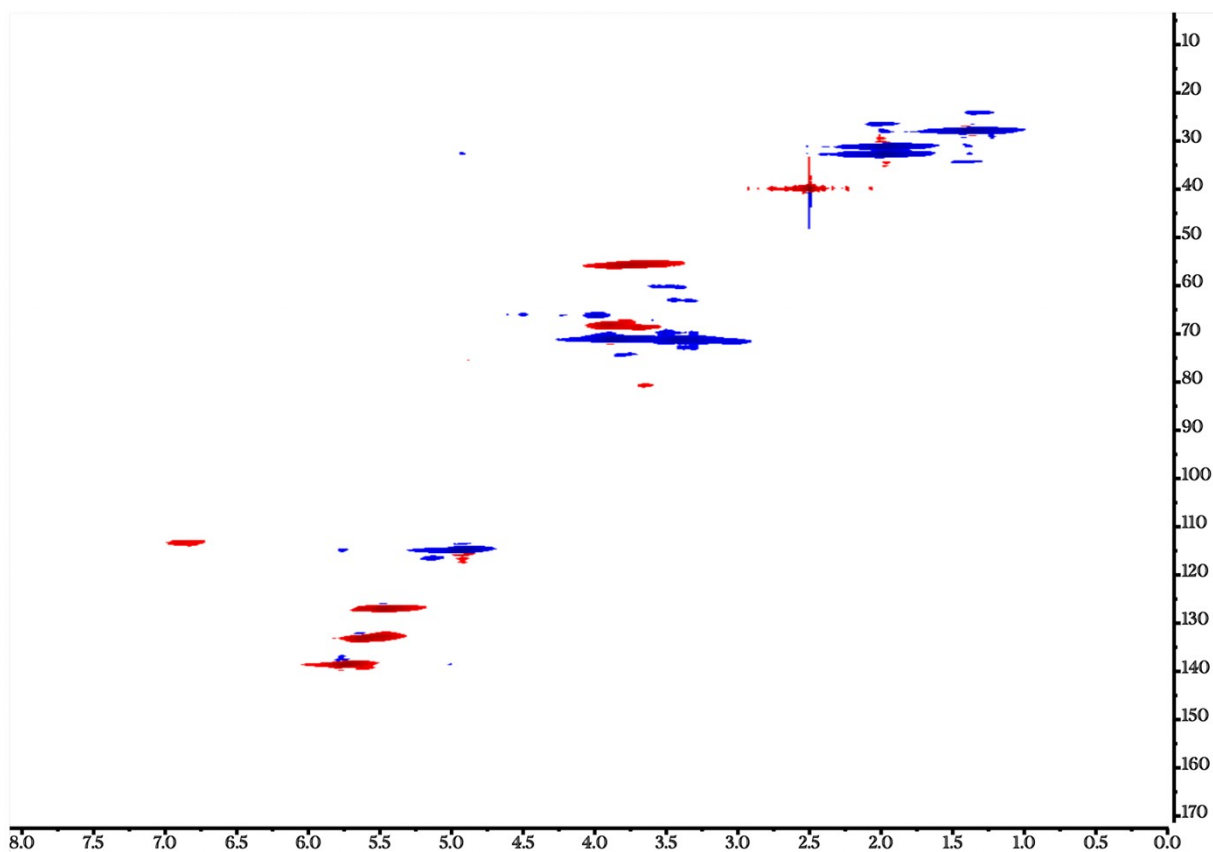


Figure SI 37: 2D HSQC-DEPT NMR spectrum of modified Kraft GC-T lignin in DMSO-d₆.

13. DSC curve of modified and unmodified lignin

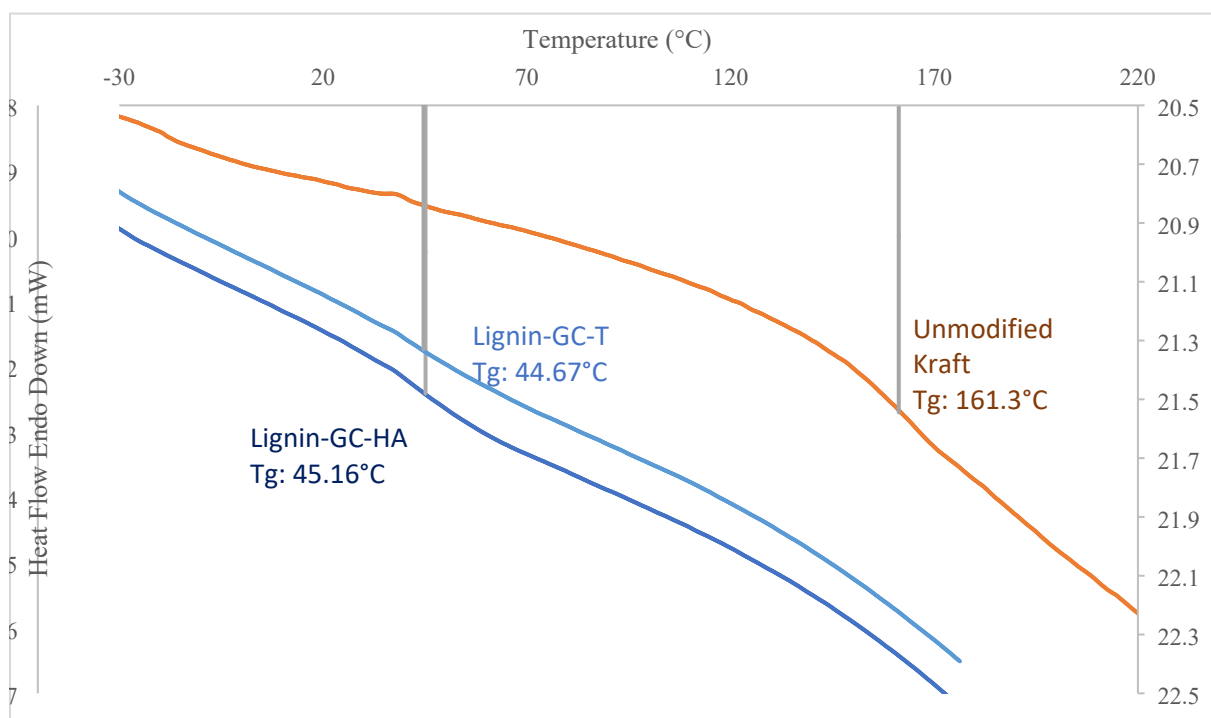


Figure SI 38: DSC curve of modified and unmodified lignin.