Electronic Supplementary Material (ESI) for Green Chemistry.

# Supporting information

# Transforming technical lignin to structurally defined star-copolymers under ambient conditions

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## Experimental

**Materials.** All the solvents; MeOH, Acetone and Chloroform were used as received. All the reagents ε-caprolactone (CL, 97 %, Sigma Aldrich Sweden), methanesulfonic acid (MSA, 99.5 % Sigma Aldrich Sweden) was used as received. Lignoboost Kraft lignin were kindly provided by Stora Enso.

**Methods.** Nuclear Magnetic Resonance (NMR). $^{1}H$, $^{31}P$, and 2D heteronuclear single quantum coherence (HSQC) results were recorded at room temperature on a Bruker Avance III HD 400 MHz instrument with a BBFO probe equipped with a Z-gradient coil for structural analysis. Data were processed with MestreNova (Mestrelab Research) software using a 90° shifted square sine-bell apodization window; baseline and phase correction were applied in both directions. $^{31}P$ NMR samples were prepared and analyzed according the procedure reported by Argyropolous and others.[1–3]

Gel permeation chromatography (GPC) was performed with a TOSOH EcoSEC HLC-8320GPC system equipped with an EcoSEC RI detector and three PSS PFG 5 µm columns (microguard, 100 Å, and 300 Å). Poly(methyl methacrylate) (PMMA) standards were used for calibration and toluene was used as internal standard.

**Procedures.**

**Fractionation protocol.**

The fractionation procedure was performed in accordance to previous work by Duval and others.[4–6]

**Synthesis of 2-allyloxmethy-2-ethyltrimethylene carbonate (AOMEC)**

The monomer was synthesized via ring-closing depolymerization according to previously reported protocol.[7,8]

**Star-Copolymers based on Lignin, AOMEC and ε-Caprolactone**

All the reactions were performed at ambient temperatures in a 50 ml round bottom flask under magnetic stirring under air if not otherwise stated. In a typical reaction; the freeze-dried methanol fraction derived from the Lignoboost process (1 g) was dissolved in the desired amounts of ε-caprolactone (εCL) (3g, 26 mmol) and 2-allyloxmethy-2-ethyltrimethylene carbonate (AOMEC) (1g, 5 mmol). The reaction flask was shaken for 5 min, and let to equilibrate for 25 min, followed by addition of methanesulfonic acid (0.1 g, 1 mmol). The reaction was left for 18 h at ambient temperature under air. After 18 h a sample was collected and terminated with excess of triethylamine (TEA) to determine the crude conversion. The copolymer was dissolved in $CHCl_3$ and precipitated in MeOH. The total amount of product was 3.8 g, giving the total yield of 76 % The solute was concentrated under air and the molecular weight of both the crude, solute and precipitate was determined by GPC in DMF using PMMA standards.

**Crude polymerization of Star-Copolymers based on Lignin, ε-Caprolactone and AOMEC**

The aforementioned procedure was modified to circumvent the use of; chlorinated solvents, the precipitations step and the use of triethylamine. The polymerization was conducted under the same conditions as before for all the different fractions derived from the Lignoboost process. The terminations was achieved with addition of sodium acetate (0.24 g, 3 mmol) dissolved in 5 ml of MeOH. The mixture was left to evaporate and the star polymer was used crude in the following step.

## Thermally initiated Thiol-Ene crosslinking

The resins where prepared in accordance to earlier work.[9] Typically Trimethylolpropane tris(3-mercaptopropionate) (3MP3 TMP) and a lignin star-copolymer where added to a vial with a 1:1 stoichiometric ratio between thiol and ene functional groups (7,53 mmol/g thiols/$g_{crosslinker}$ & 1 mmol/g enes/$m_{star\ copolymer}$). A few drops of EtOAc and $CHCl_3$ were added to the mixture to ensure dissolution and ease a homogenous mixing of the resin. When the resin had been thoroughly dissolved, a pipette was used to transfer the solution to teflon molds. The solvent was left to evaporate and placed in an oven, heated to 125 °C and left to cure over 22 hours. When the curing had taken place the samples where let to cool down to room temperature before carefully being removed from the mold

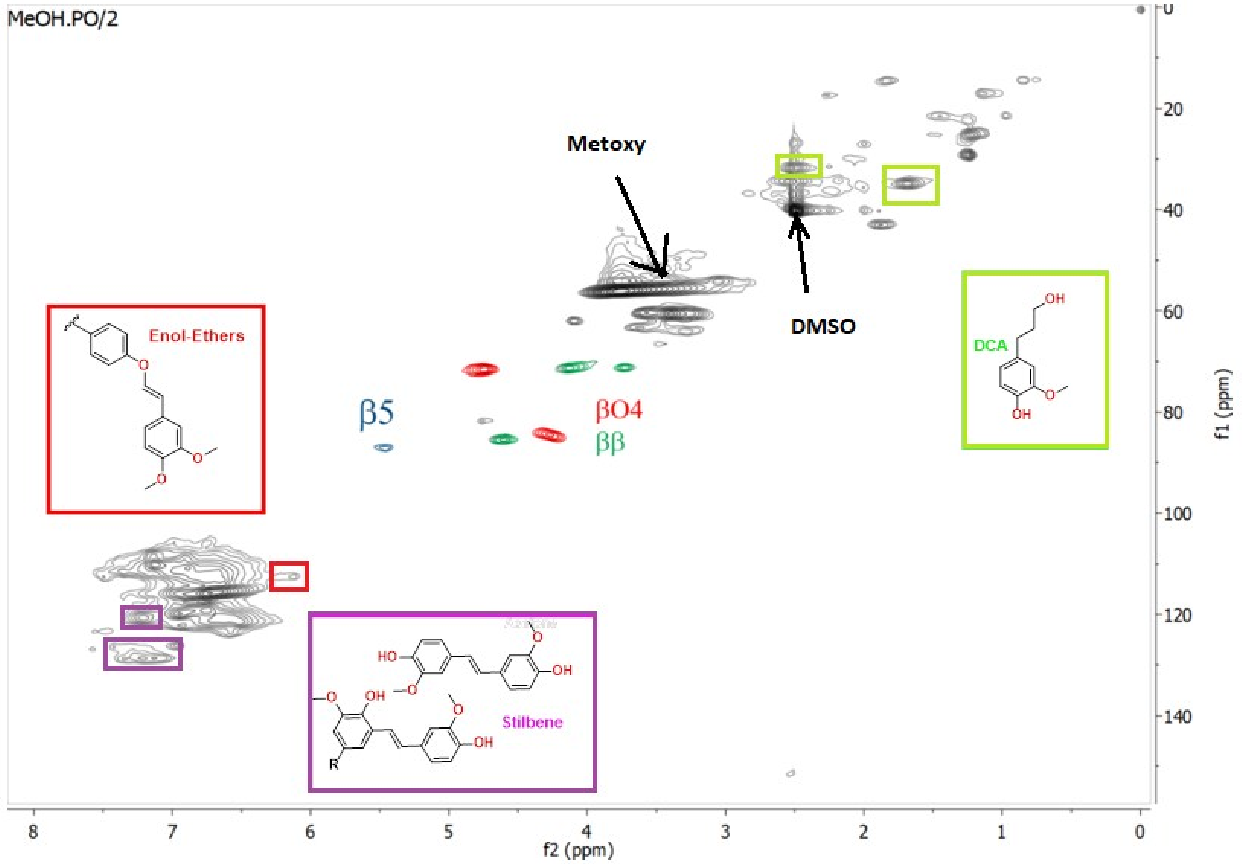


**Figure S1**. Full HSQC NMR spectra in DMSO

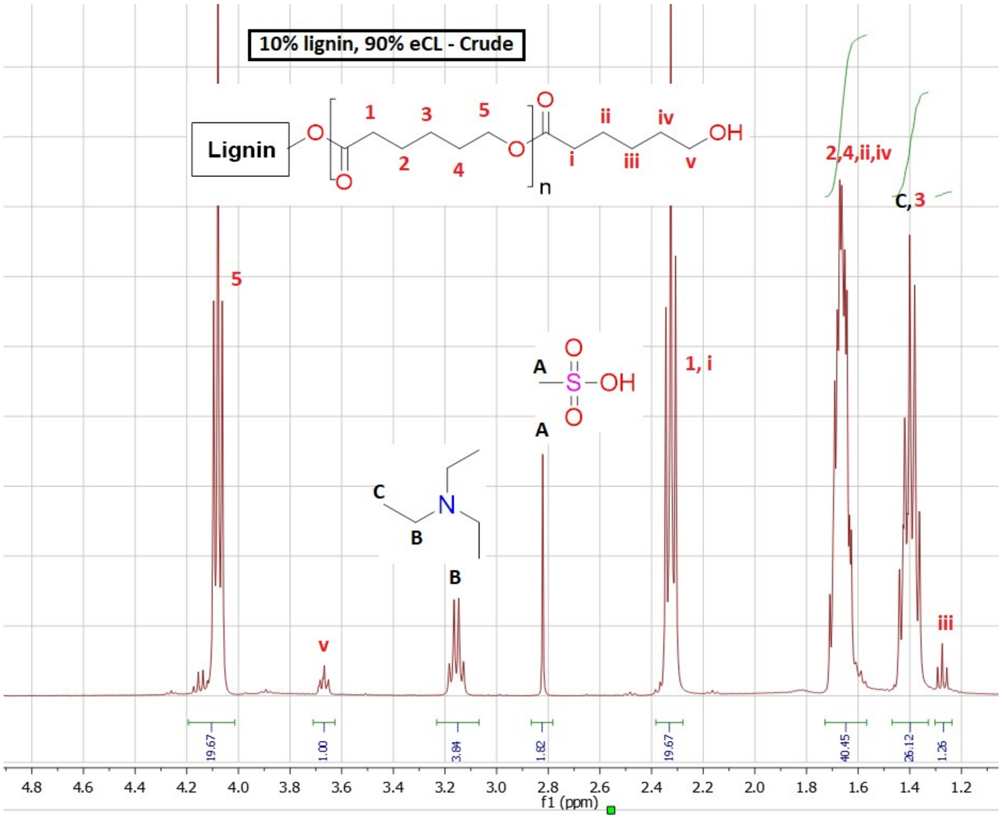


**Figure S2**. Crude $^1$H NMR before precipitation

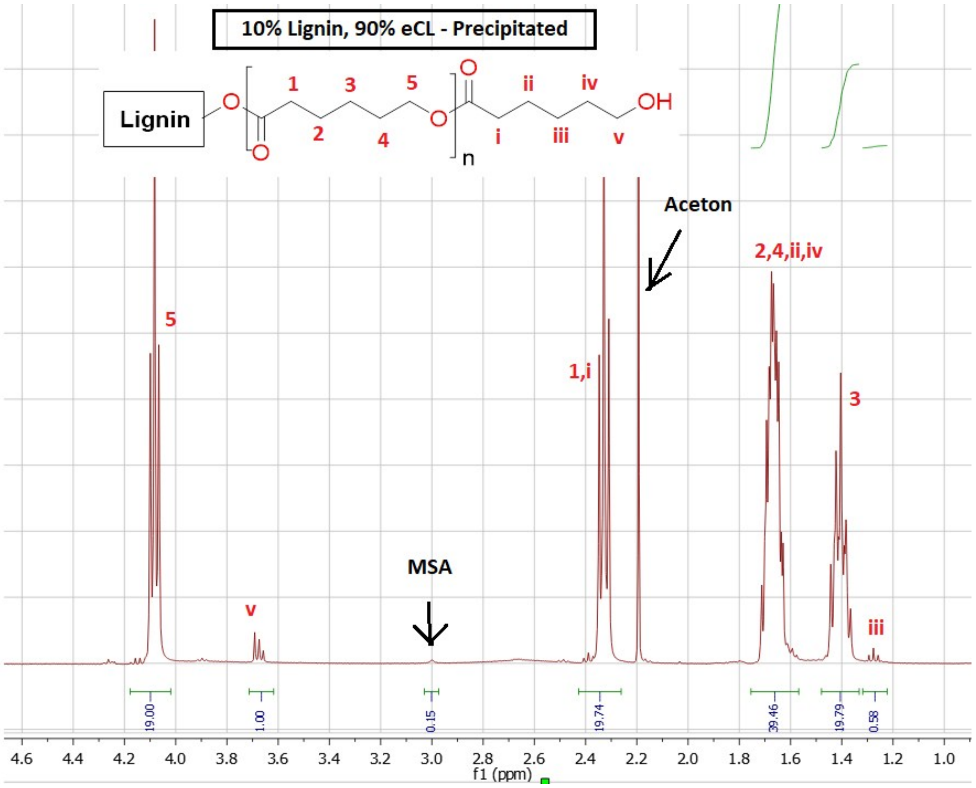


**Figure S3**. $^1$H NMR after precipitation

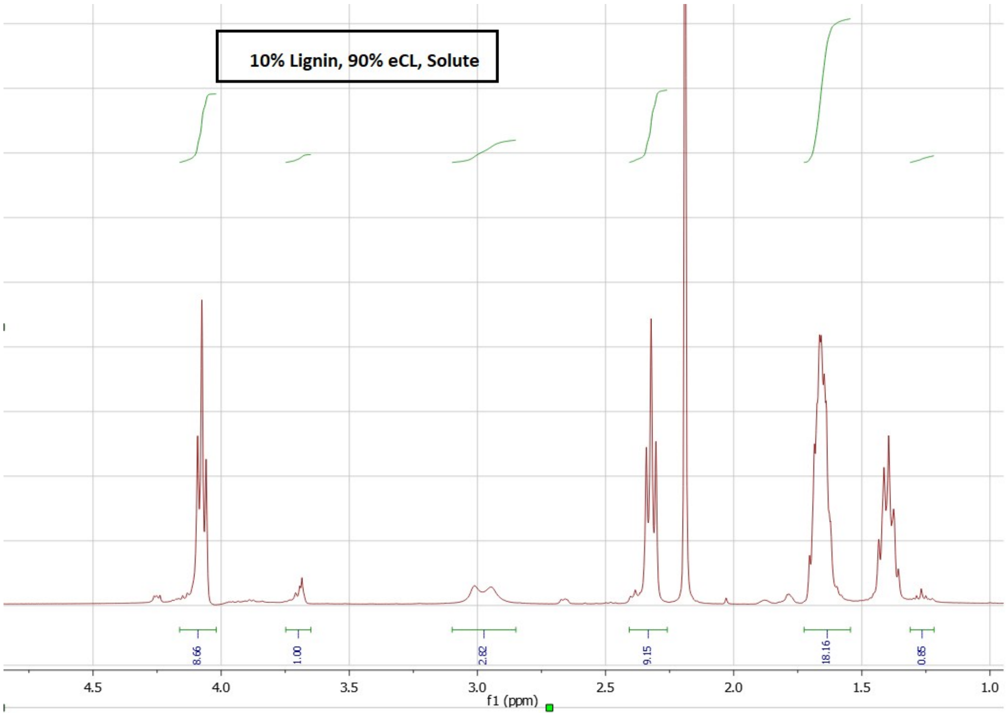


**Figure S4**. $^1$H NMR on the solute

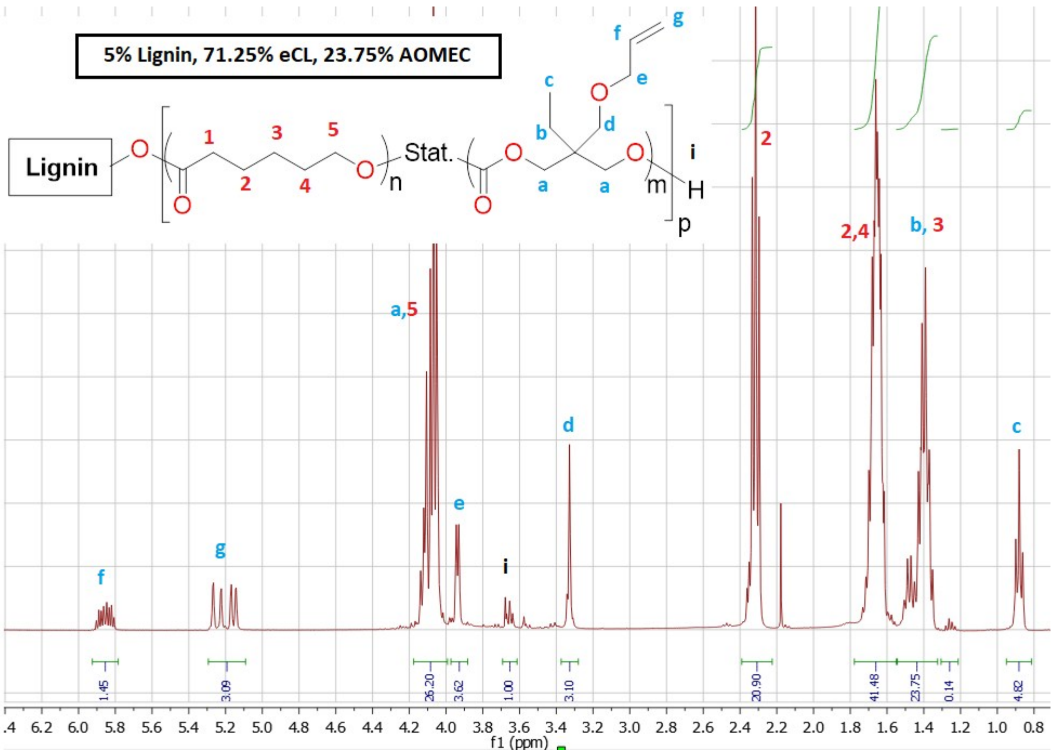


**Figure S5**. $^1$H NMR on the copolymer between AOMEC and εCL and the methanol fraction of ligno-boost

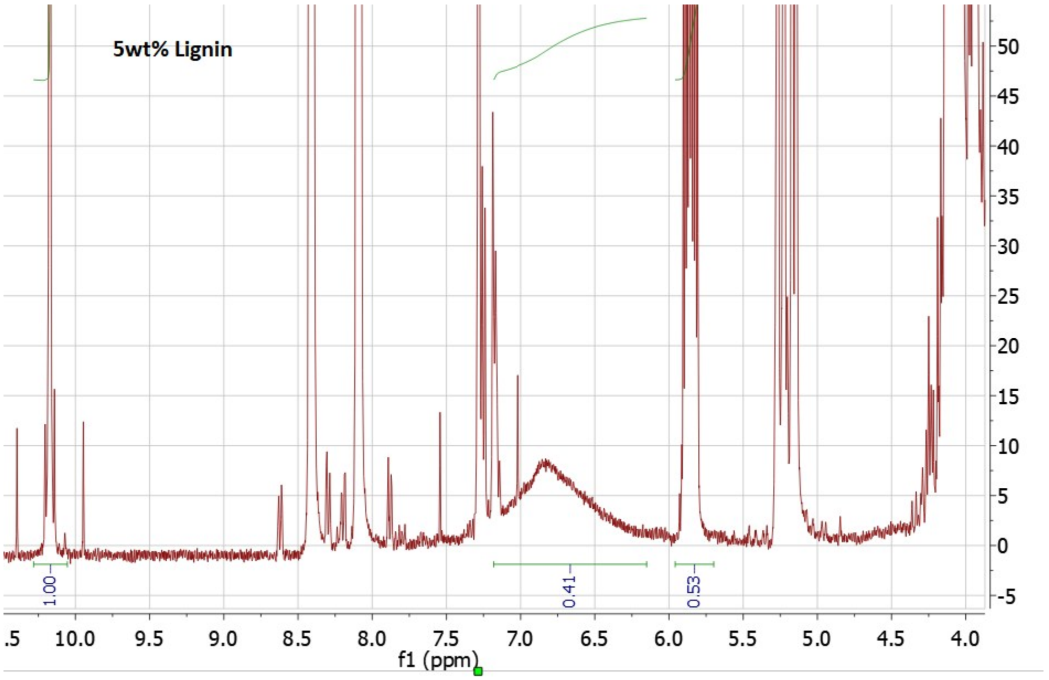


**Figure S6**. $^1$H NMR for determination of the lignin content in the copolymer

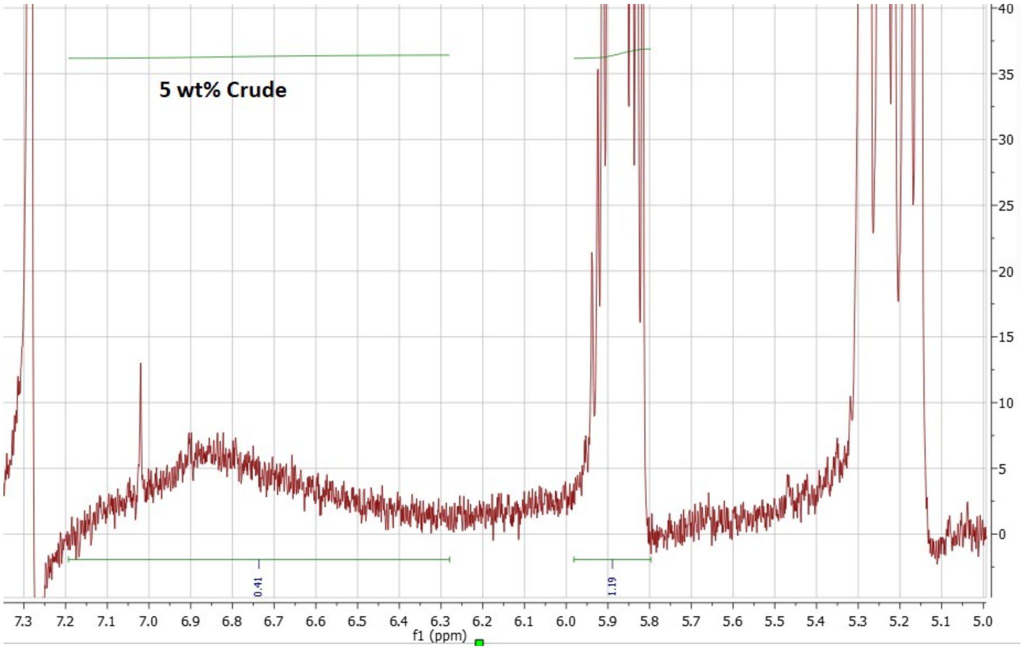


**Figure S7**. $^1$H NMR for determination of the lignin content in the copolymer¨

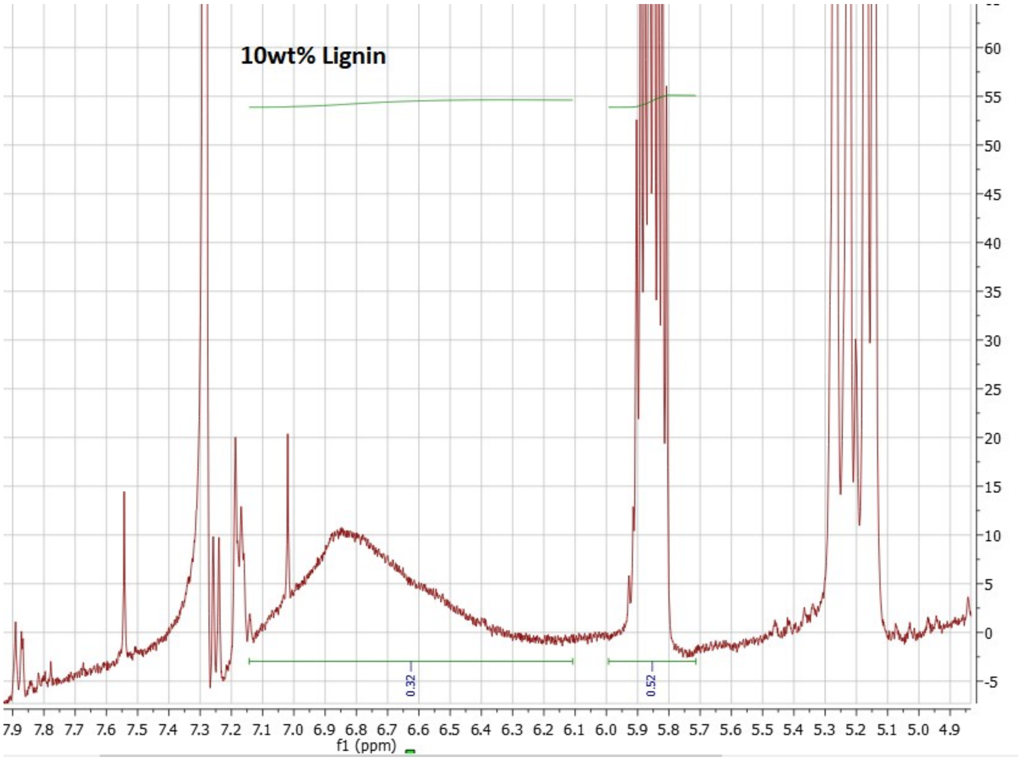


**Figure S8**. $^1$H NMR for determination of the lignin content in the copolymer

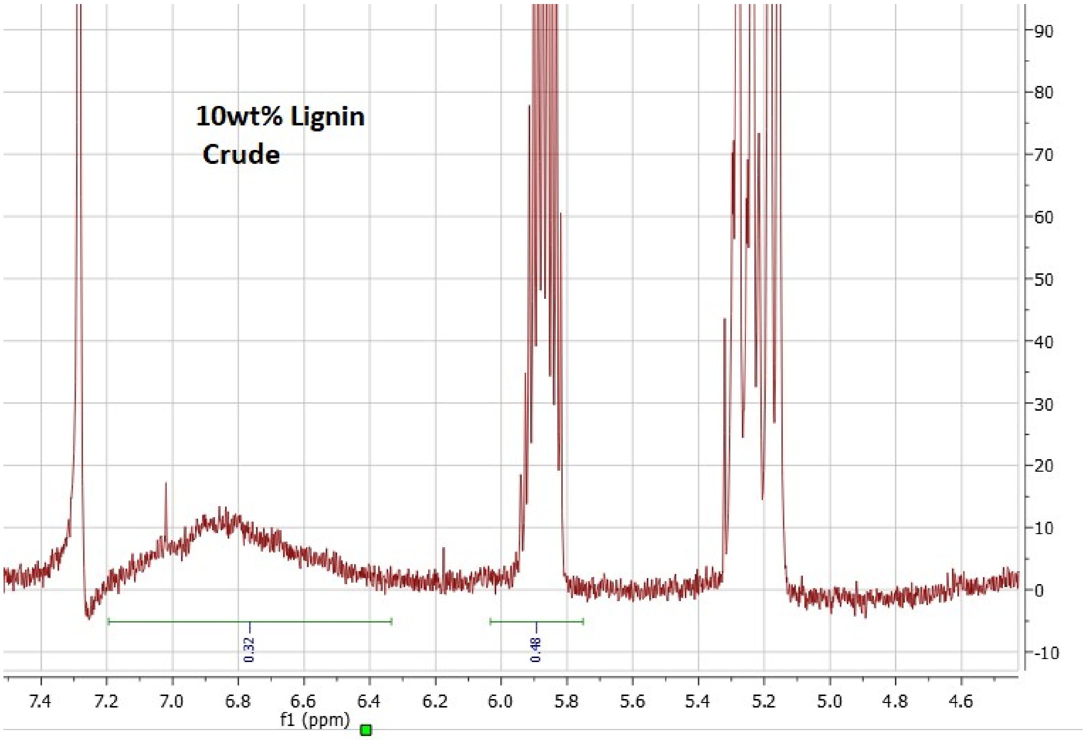


**Figure S9**. $^1$H NMR for determination of the lignin content in the copolymer

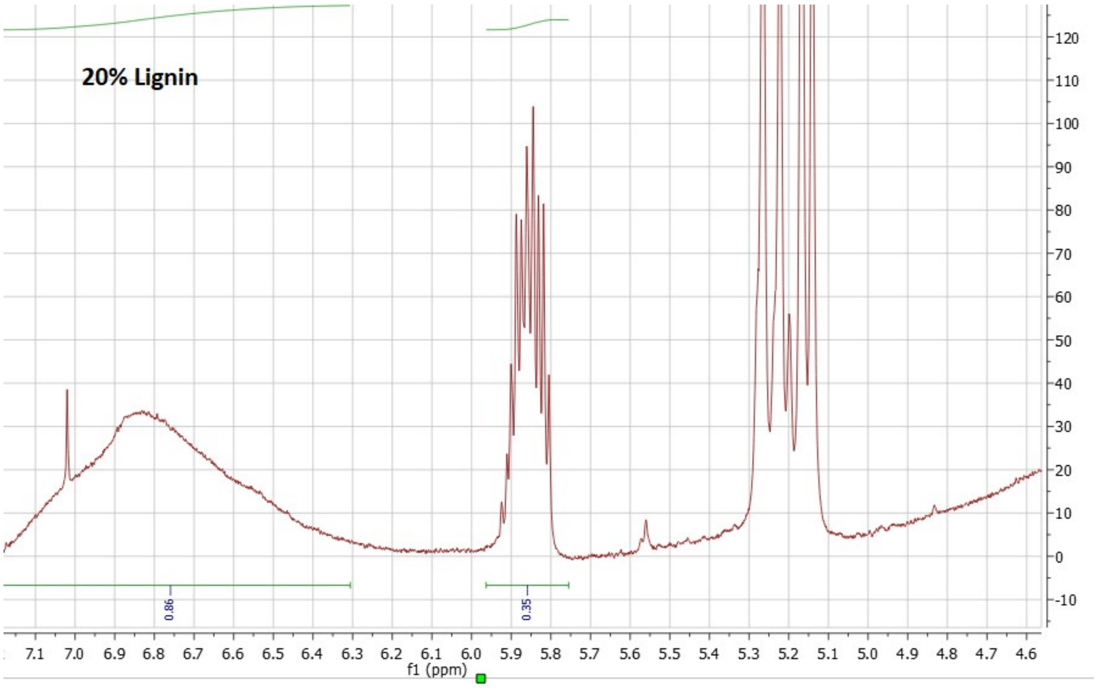


**Figure S10**. $^1$H NMR for determination of the lignin content in the copolymer

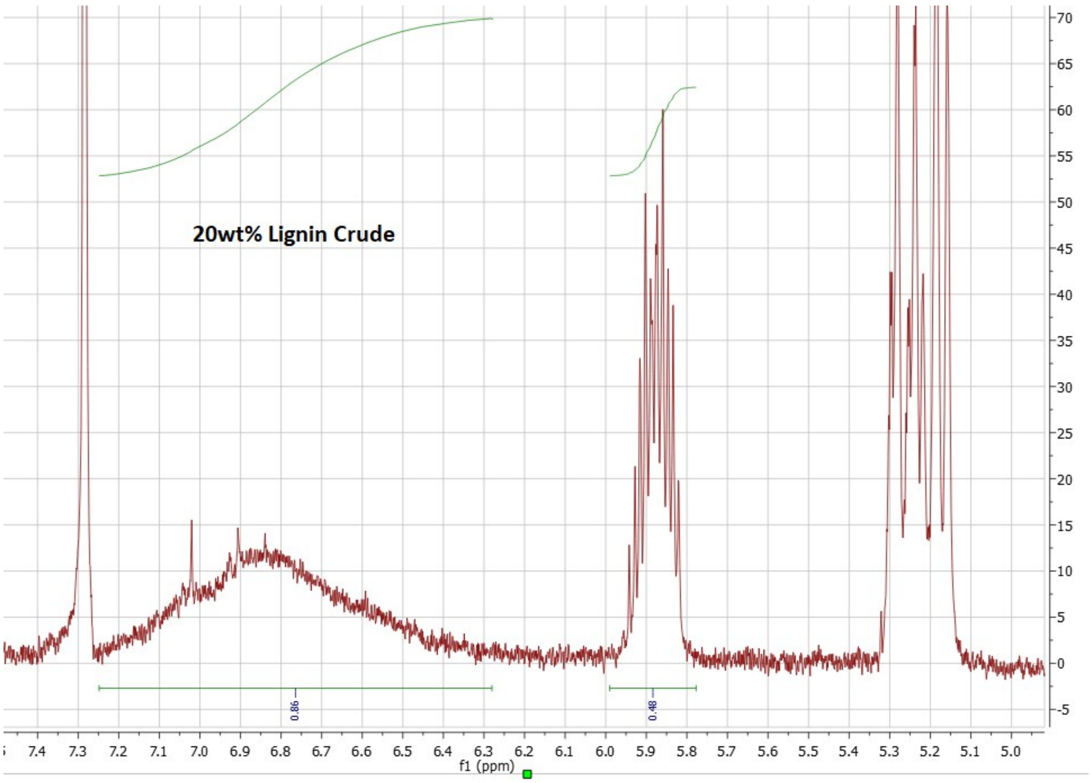


**Figure S11**. $^1$H NMR for determination of the lignin content in the copolymer

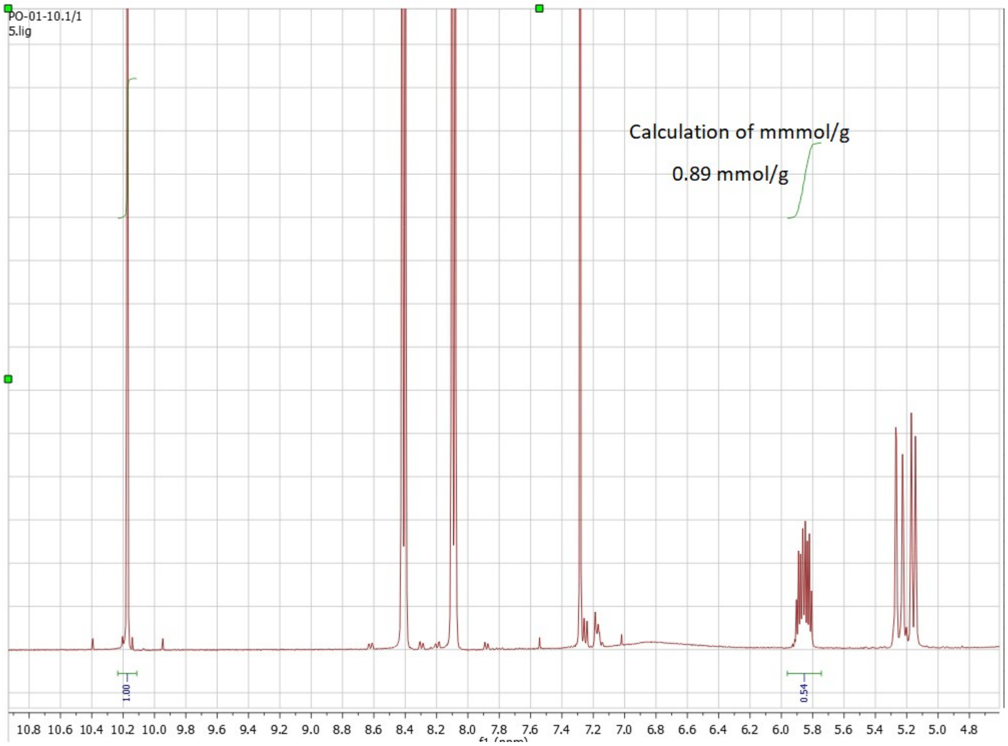


**Figure S12**. $^1$H NMR for determination of the allyl content in the copolymer with -Nitrobenzaldehyde as internal standard

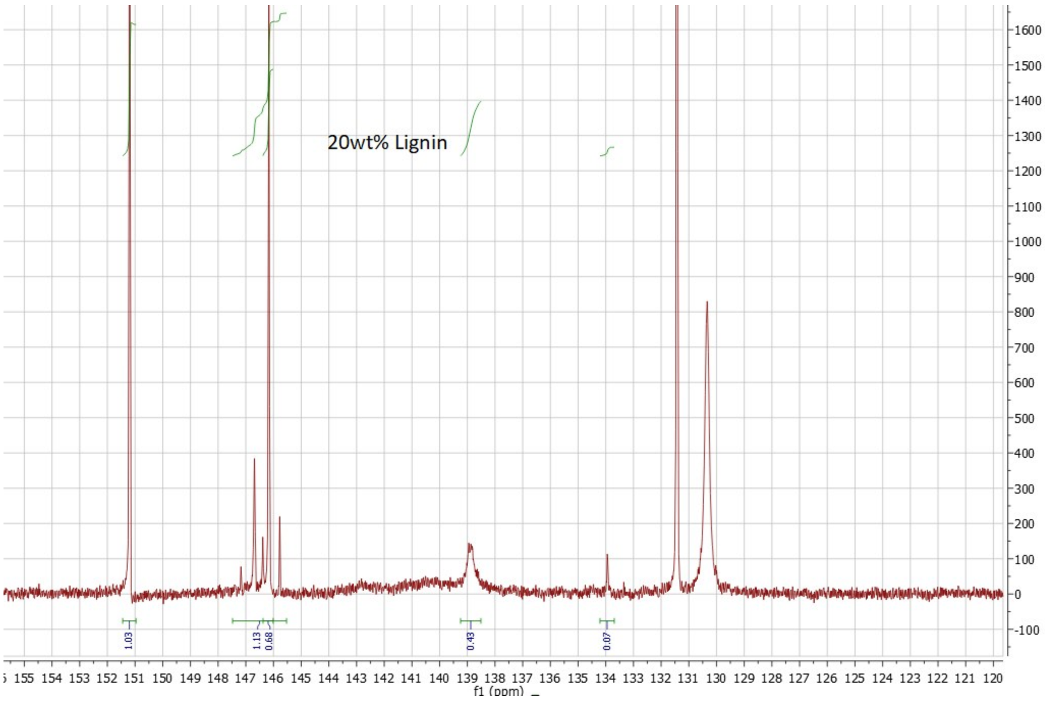


**Figure S13**. $^1$H NMR for determination of the allyl content in the copolymer with -Nitrobenzaldehyde as internal standard

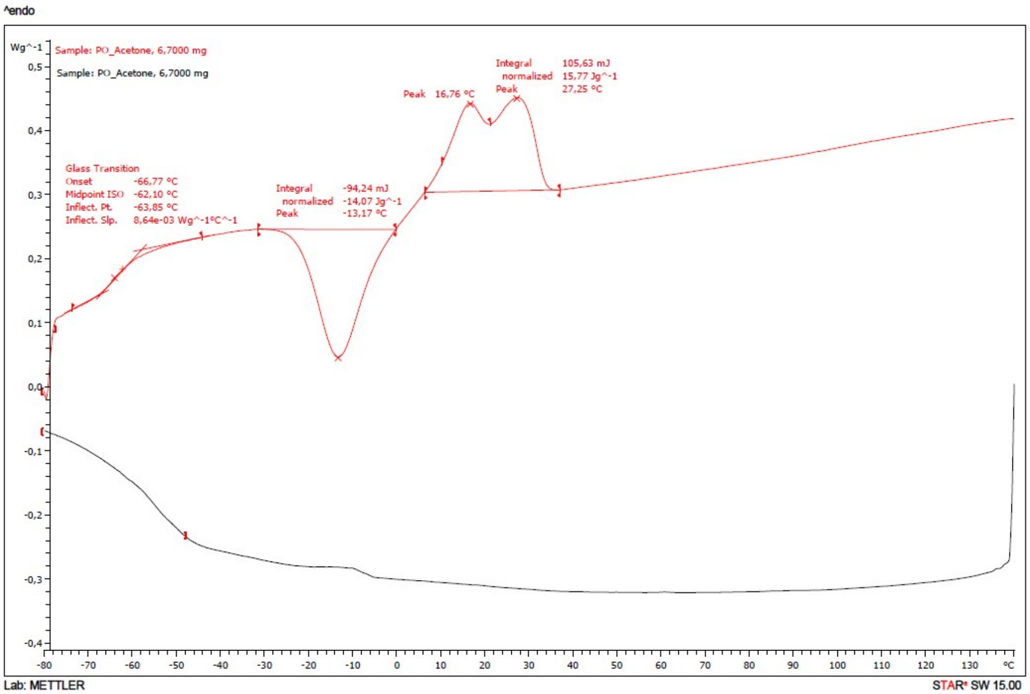


**Figure S14**. DSC curves of the copolymer based on the acetone fraction

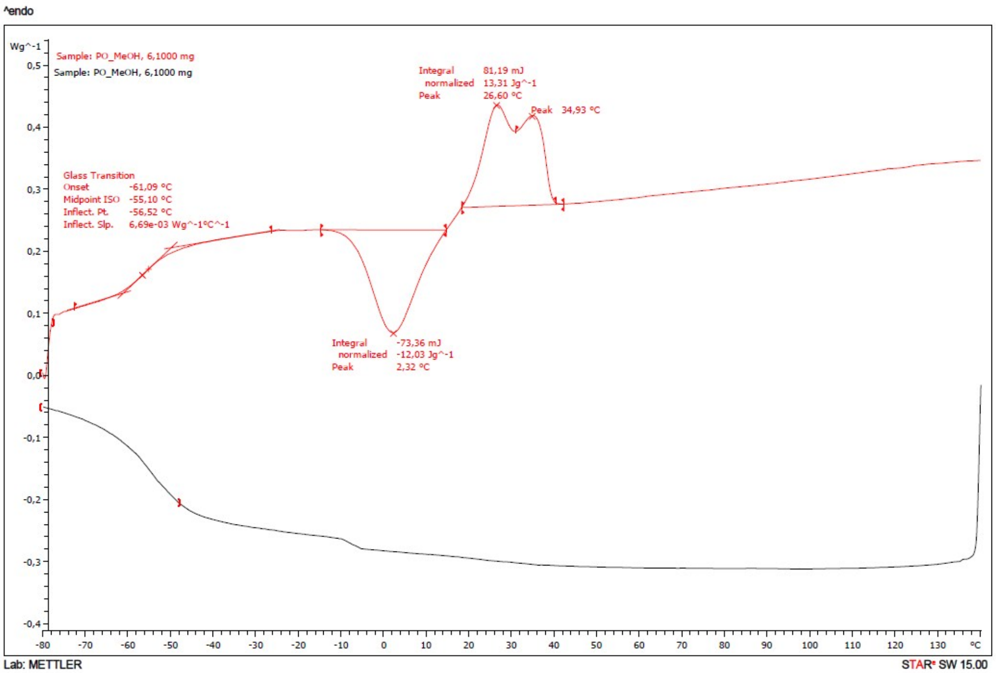


**Figure S15**. DSC curves of the copolymer based on the methanol fraction

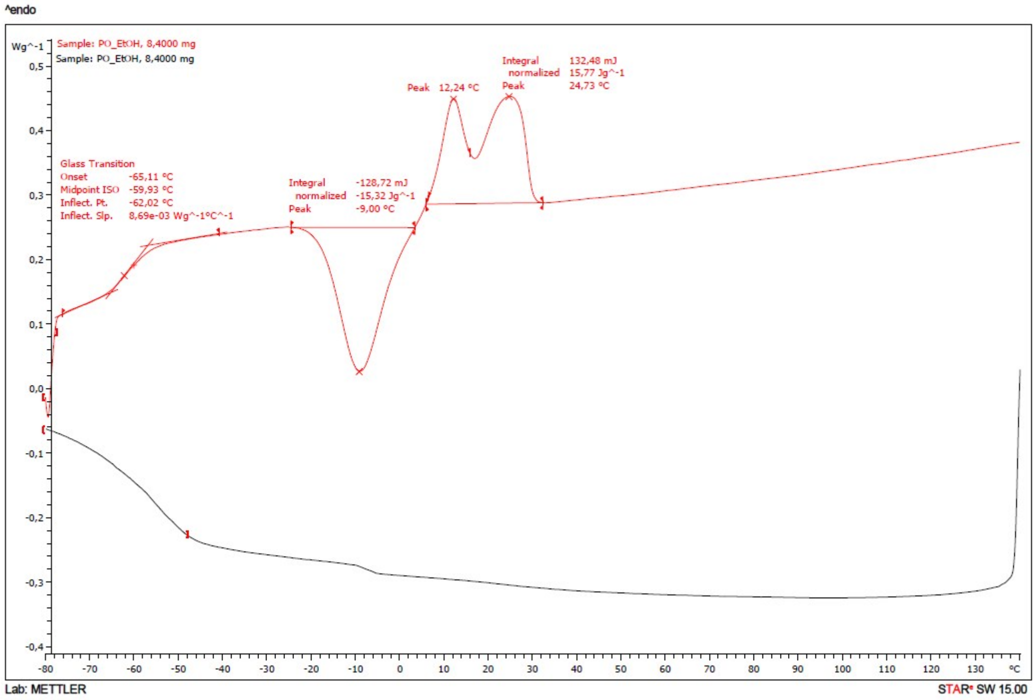


**Figure S16**. DSC curves of the copolymer based on the ethanol fraction

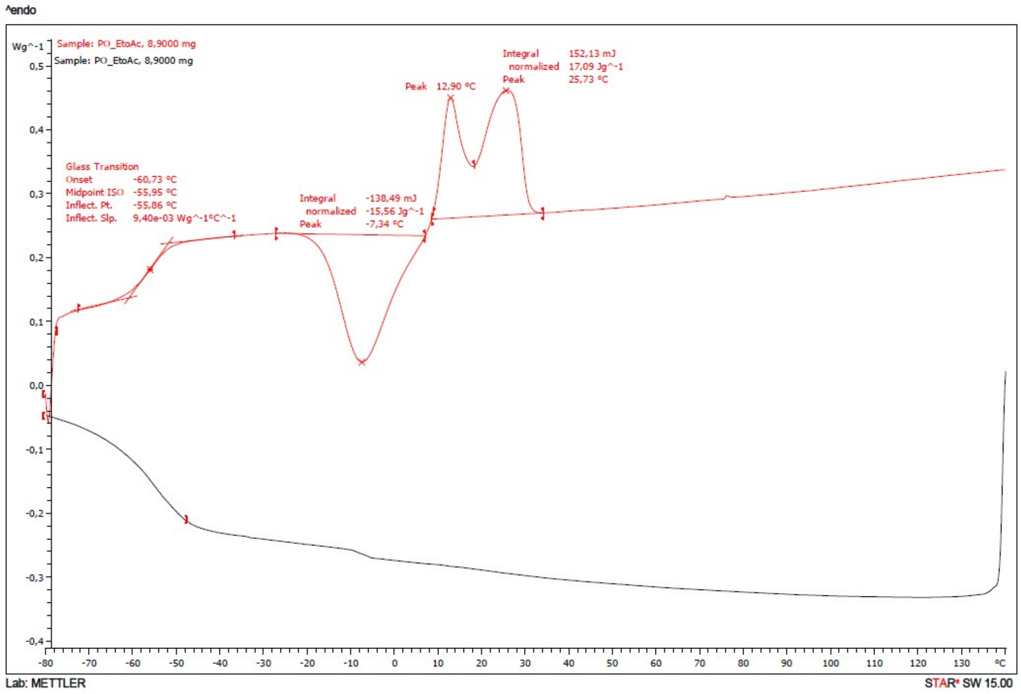
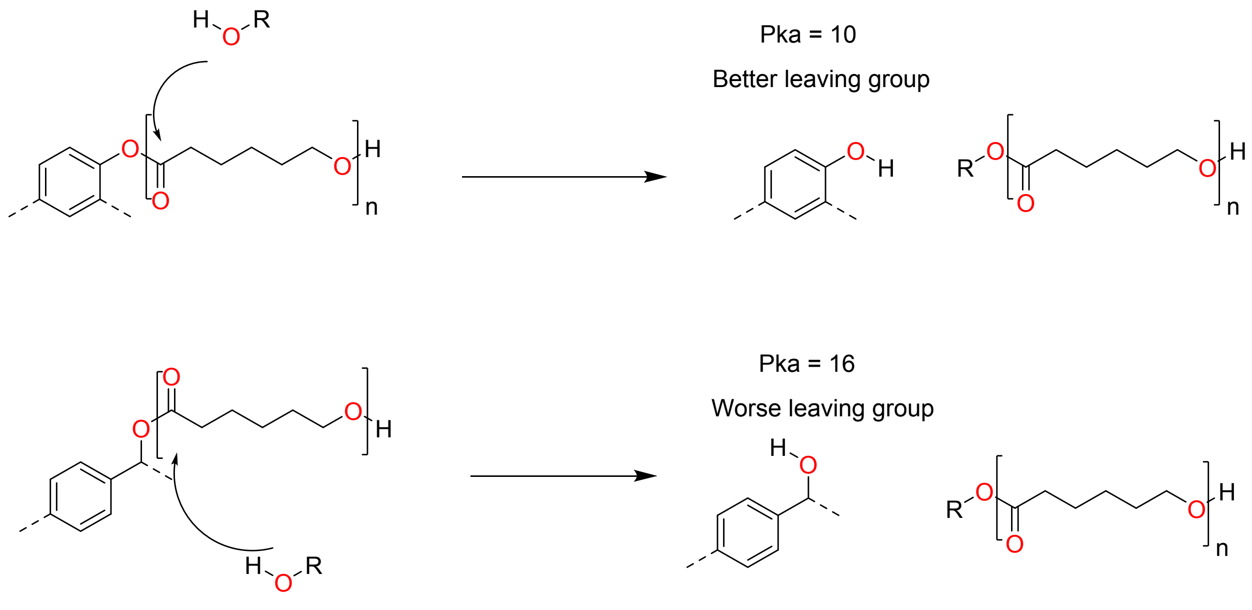


**Figure S17**. DSC curves of the copolymer based on the ethyl acetate fraction

**Scheme S1** Mechanistic explanation to the presence of aryl-OH



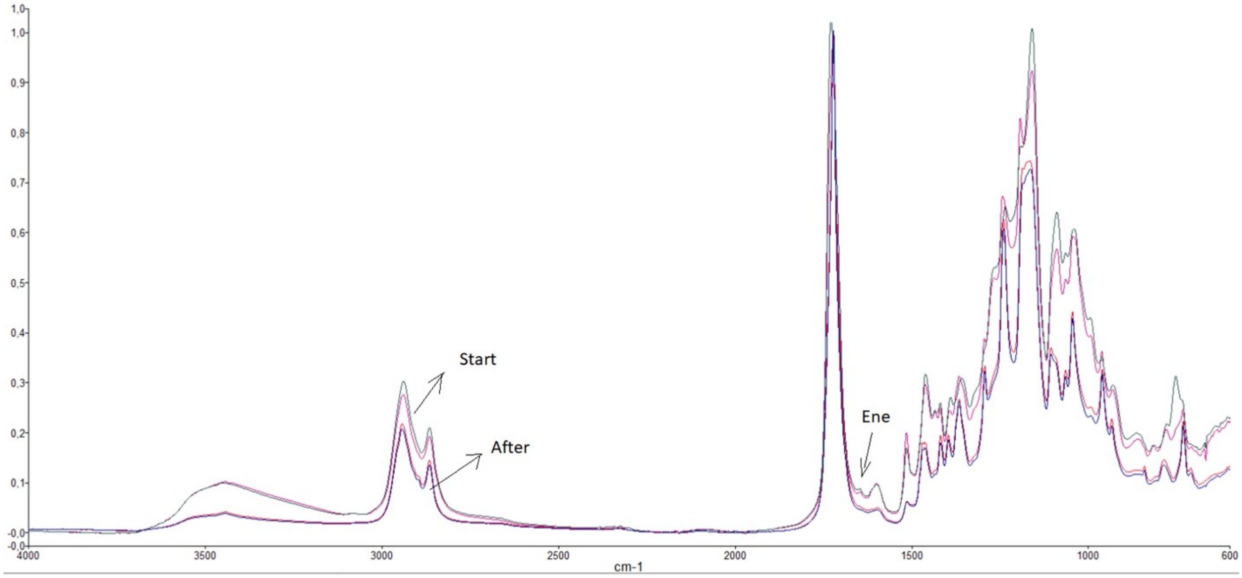


**Figure S18**. FTIR before and after curing

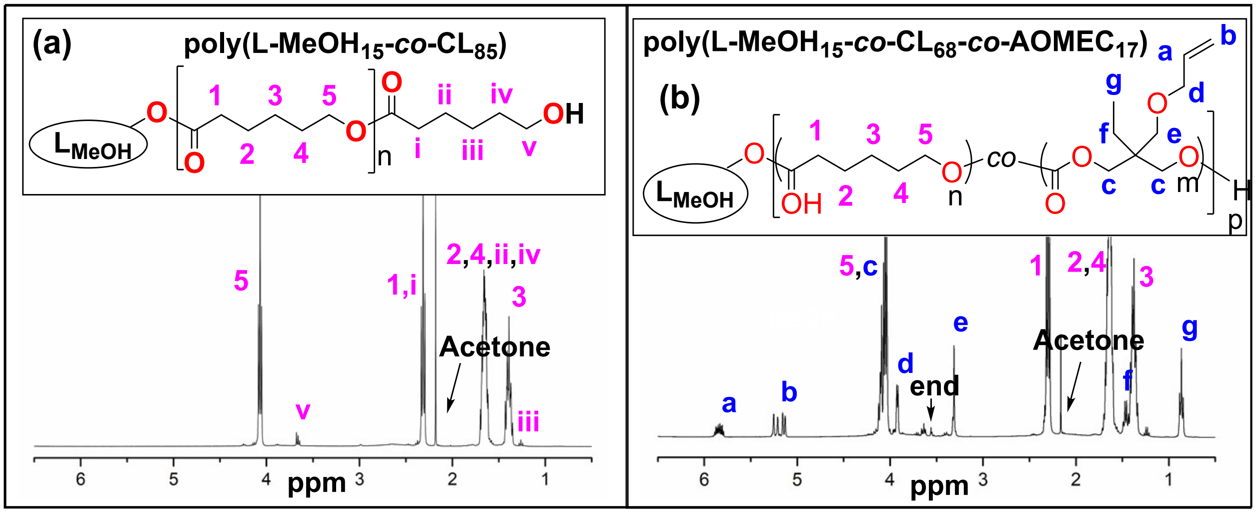


**Fig.2.** $^1$H NMR on the precipitated Lignin starcopolymers in $CDCl_3$, **(a)** 15 wt% lignin MeOH fraction with 85 wt% εCL as determined from $^1$H NMR**, (b)** 15 wt% lignin MeOH fraction with 68 wt% εCL and 17 wt% AOMEC as determined from $^1$H NMR. Both polymerization was perfromed at r.t. for 18 h with 2 wt% MSA.

**Figure S19**. $^1$H NMR of the precipitated copolymers on lignin.

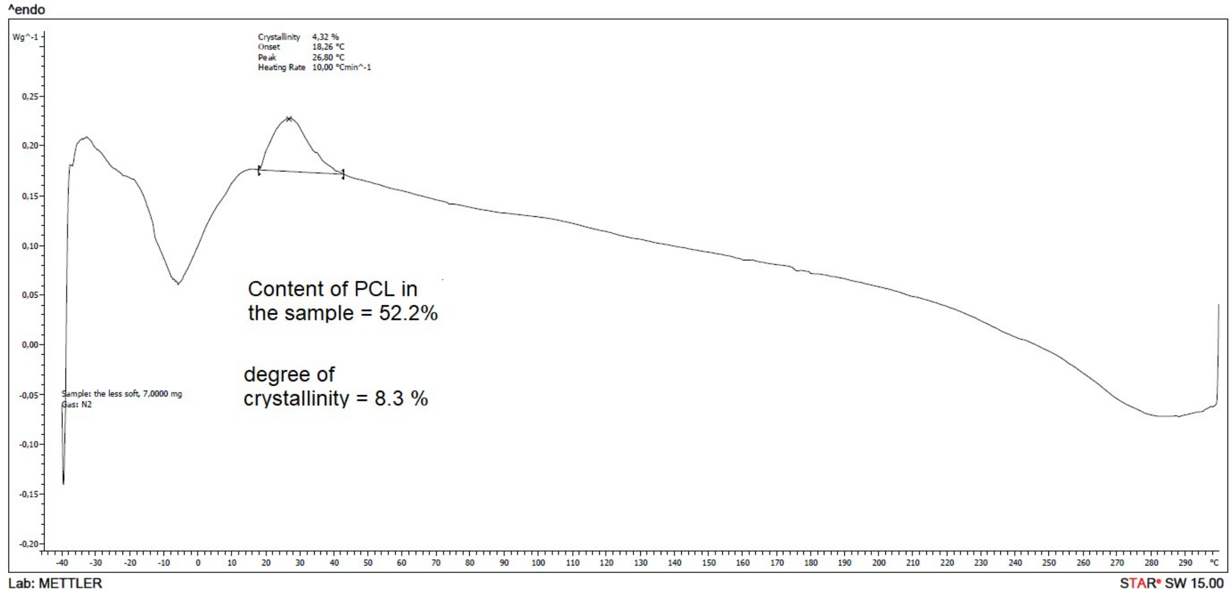


**Figure S20**. DSC curves of the cross-linked copolymer based on the ethanol fraction

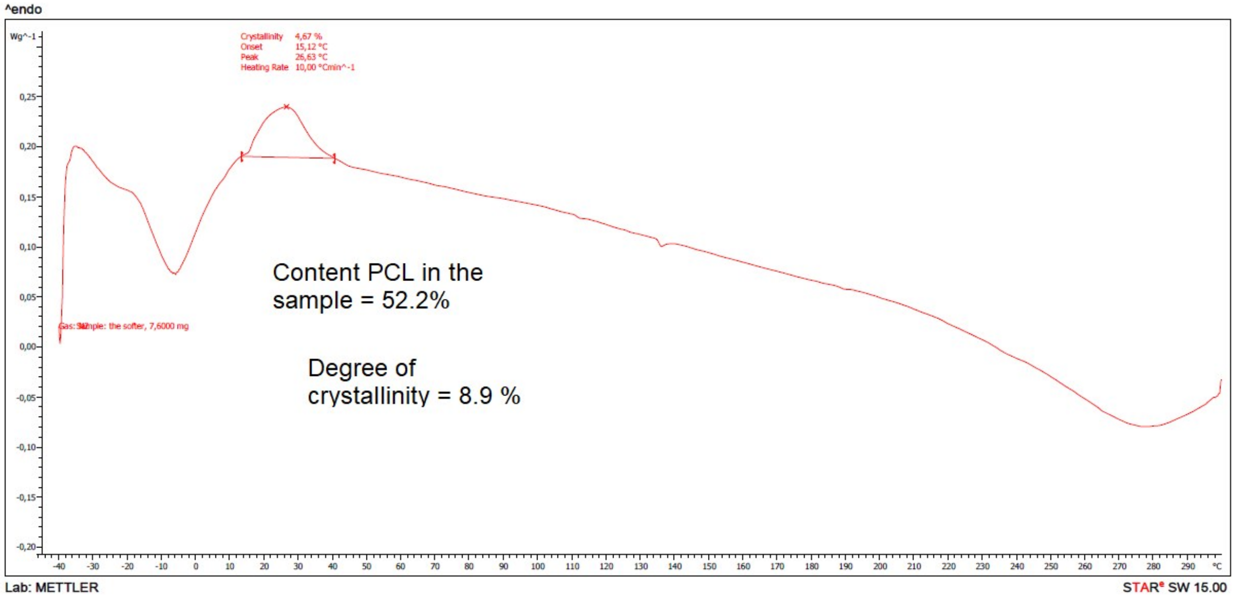
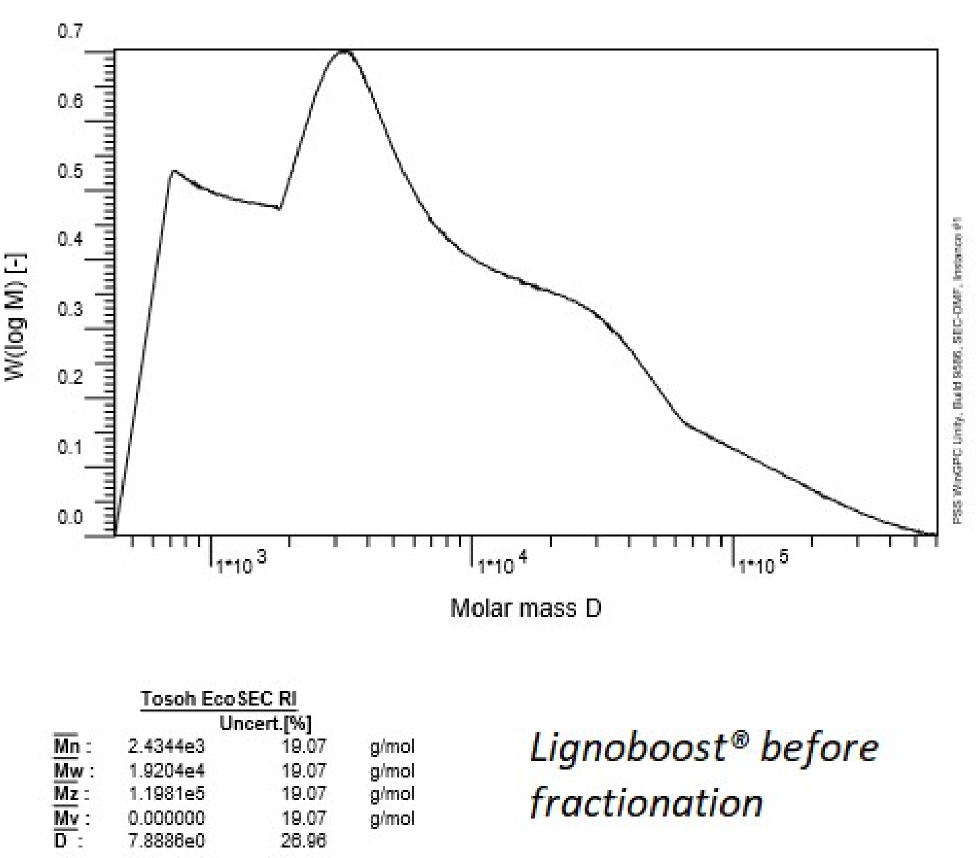


**Figure S21**. DSC curves of the cross-linked copolymer based on the ethyl acetate fraction



| | Tosoh EcoSEC RI | Uncert.[%] | |
|---|---|---|---|
| $\overline{Mn}$ : | 2.4344e3 | 19.07 | g/mol |
| $\overline{Mw}$ : | 1.9204e4 | 19.07 | g/mol |
| $\overline{Mz}$ : | 1.1981e5 | 19.07 | g/mol |
| $\overline{Mv}$ : | 0.000000 | 19.07 | g/mol |
| D : | 7.8886e0 | 26.96 | |

*Lignoboost® before fractionation*

**Figure S22**. SEC trace for the initial *Lignoboost®*

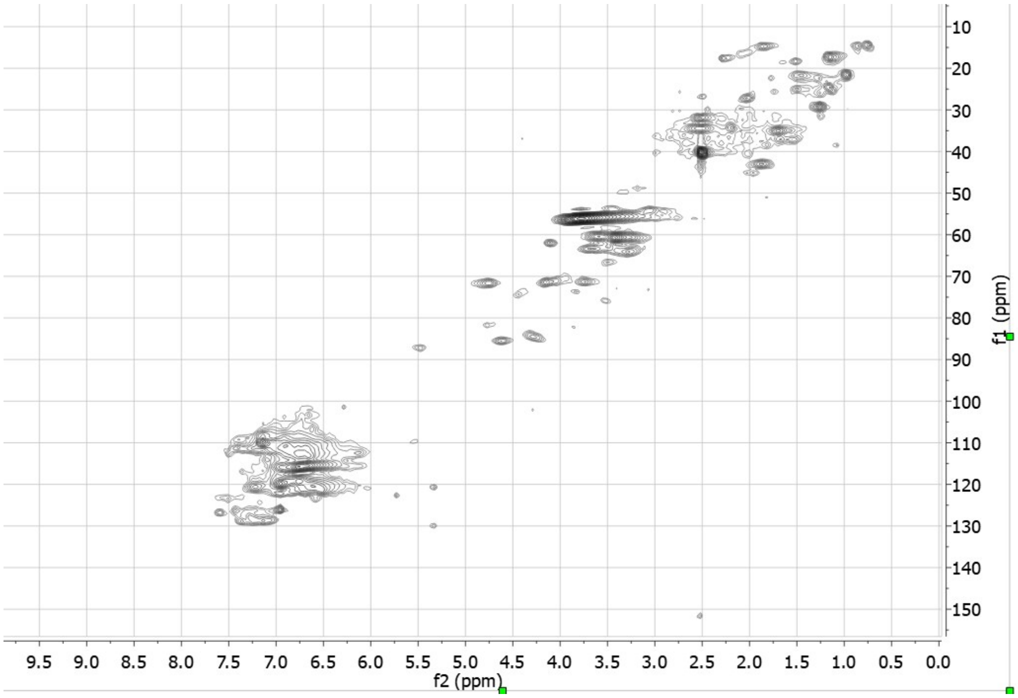


**Figure S23**. HSQC on the initial *Lignoboost®*

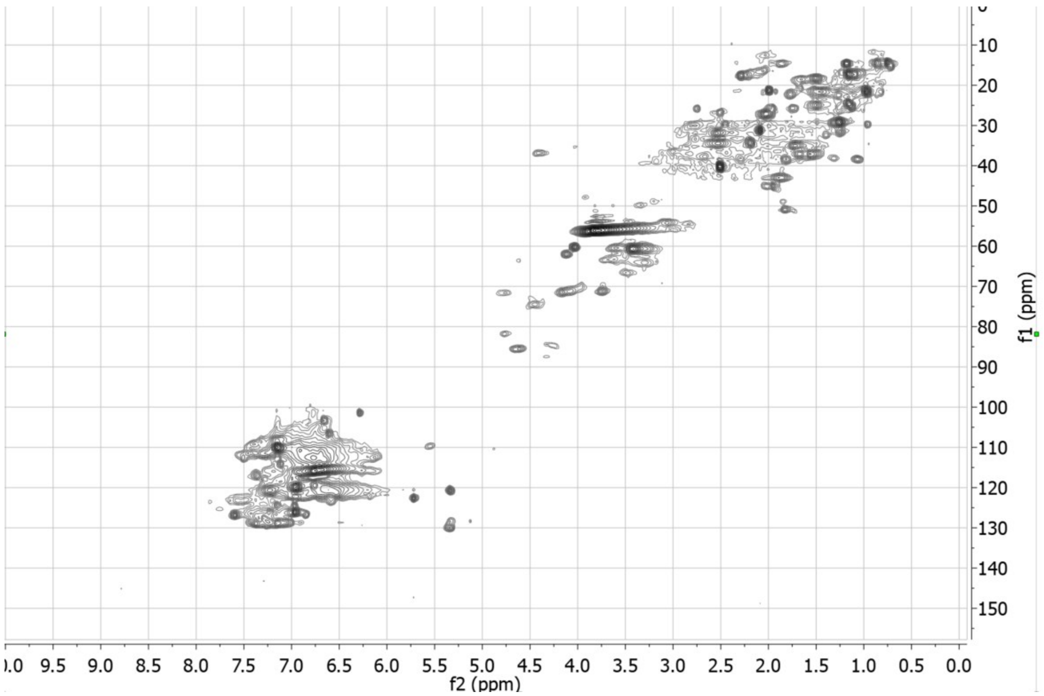


**Figure S24**. HSQC on the EtOAc fraction

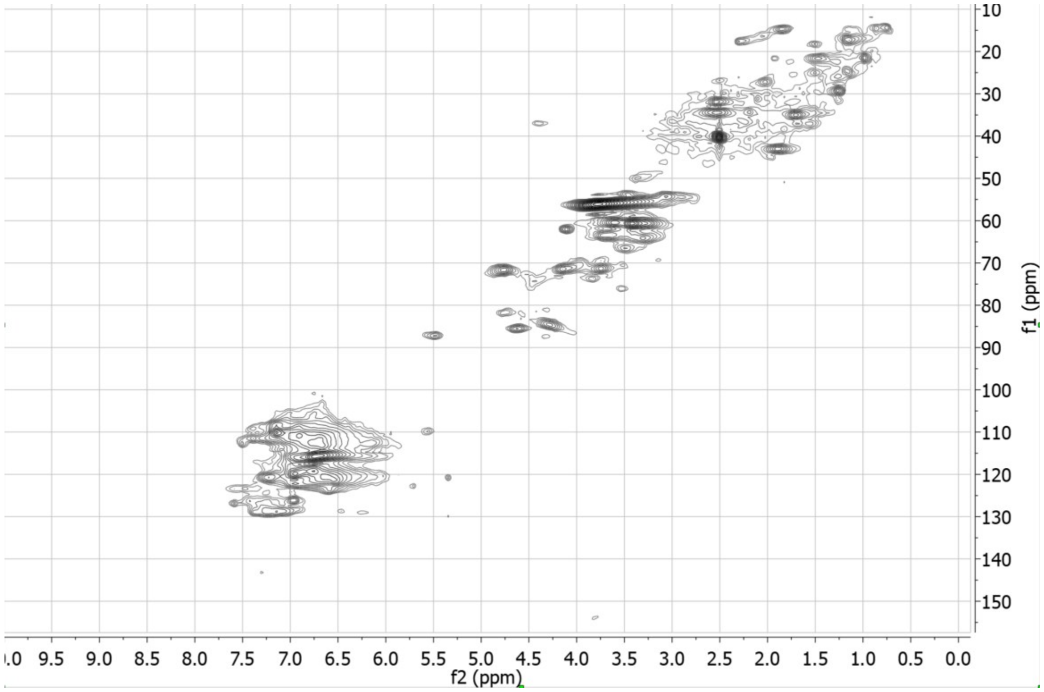


**Figure S25**. HSQC on the EtOH fraction

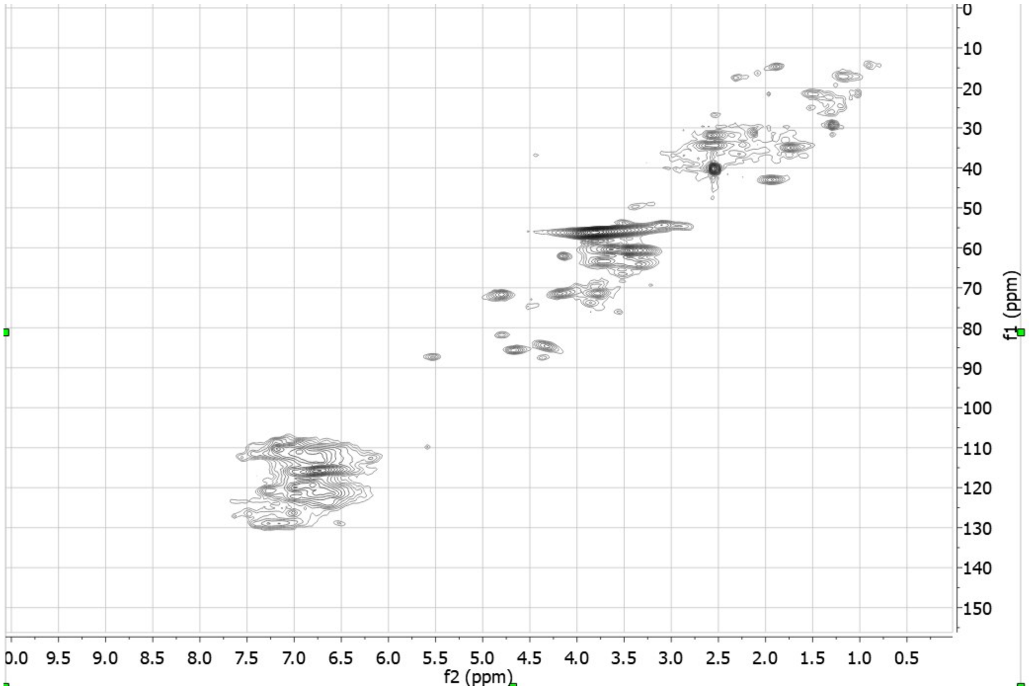


**Figure S26**. HSQC on the MeOH fraction

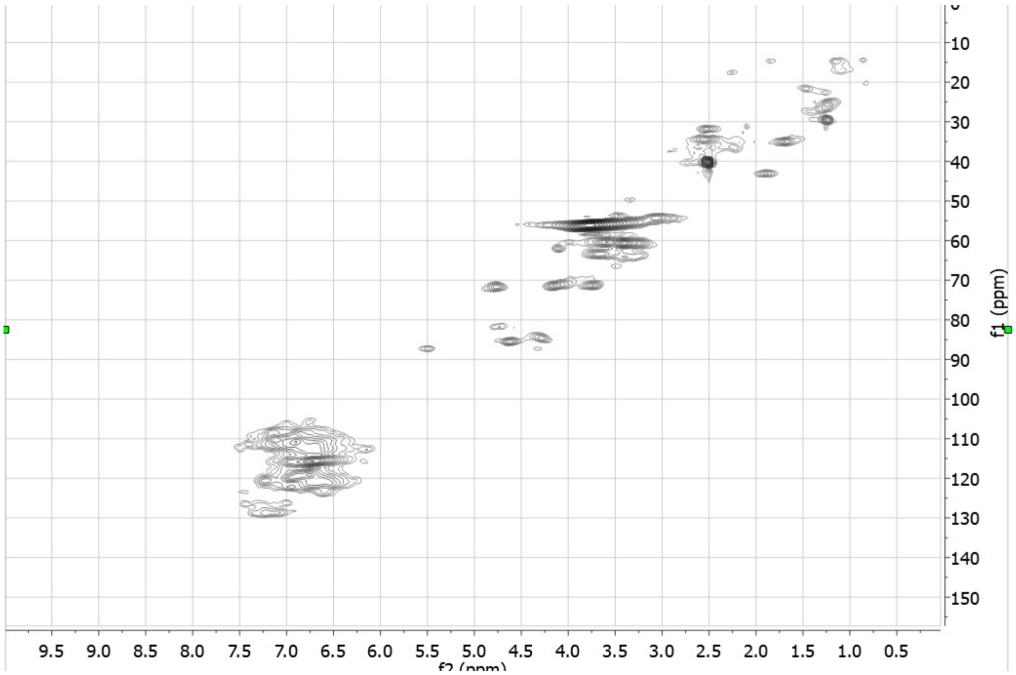


**Figure S27**. HSQC on the Acetone fraction

# References

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