

Fully bio-based Cellulose nanofiber/epoxy composites with both sustainable production and selective matrix deconstruction towards infinite fiber recycling systems

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Supplementary Information

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1. General information

^1H NMR spectra were recorded with a Bruker 400 (400 MHz) spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm, δ) and are referenced to a deuterated solvent as an internal standard. ^{13}C NMR spectra were recorded with a Bruker 400 (100 MHz) spectrometer as solutions.

FT-IR spectra were recorded using Spectrum 100 Fourier transform infrared (FT-IR) spectrometer (PerkinElmer, USA) equipped with a Golden Gate diamond ATR (Gaseby Specac Ltd, UK).

The SEM images were obtained using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800, Japan). All samples were Pt/Pd sputtered under vacuum (Cressington R208, UK).

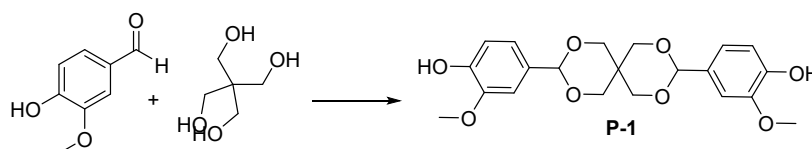
Energy dispersive X-ray spectroscopy (EDS) mapping was performed at an acceleration voltage of 5 kV using FE-SEM equipped with an X-Max 80mm² silicon drift detector (Oxford Instruments, UK).

Dynamic mechanical thermal analysis (DMTA) was carried out using a DMA Q800 (TA Instruments, USA). Specimens of 20 × 5.0 × 0.5 mm³ were subjected to a strain of 0.05% of the sample length with a frequency of 1 Hz in tensile mode with a heating rate of 3.0 °C min⁻¹.

Thermal transitions were studied using Mettler Toledo DSC1 equipped with a sample robot. Measurements were performed with a heating/cooling rate of 10 °C min⁻¹ in a nitrogen atmosphere (flow rate, 50 mL min⁻¹).

Unless otherwise stated, all chemicals were purchased from Sigma Aldrich.

2.1 Preparation of 4,4'-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2-methoxyphenol) (P-1)

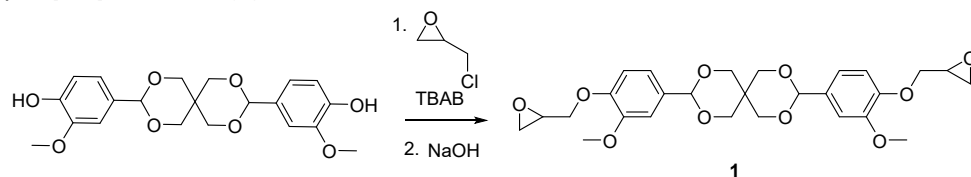


Vanillin (5g, 33 mmol), bio-based pentaerythritol (*Perstrop*) (2.46 g, 18 mmol), catalyst: p-TSA·H₂O (150mg, 0.79 mmol, 4.8 mol%), or Amberlyst15 (dry, hydrogen form; 350 mg), an additive (if used): triethylorthoformate (4.9 g, 33 mmol) and γ -valerolactone (GVL; 30 mL) were placed in a round bottom flask, equipped with a stir bar. When the reaction was performed under reduced pressure, the flask was sealed with a septum and connected to a vacuum pump (2-5 mbar). The reaction was performed at room temperature overnight. In a case of Amberlyst15, upon the completion of the reaction, the catalyst was separated from the reaction mixture via filtration followed by washing with water. A solution of Na₂CO₃ (9g in 250 mL of water) was added to the reaction mixture and the reaction mixture was left in a fridge for several hours. The product precipitated from the solution as a white solid. The product was collected from the solution via filtration followed by an extensive washing with water. The product was dried under reduced pressure overnight. ^1H and ^{13}C NMR spectra match those previously reported. ^[1]

Table S1. Synthesis of 4,4'-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2-methoxyphenol)

Entry	Catalyst	Additive	Pressure, mbar	Yield of P-1, %
1	p-TSA·H ₂ O	none	2-5	69
2	p-TSA·H ₂ O	HC(OMe) ₃	1013	65
3	Amberlyst15	none	2-5	70

2.2 Preparation of 3,9-bis(3-methoxy-4-(oxiran-2-ylmethoxy)phenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (**1**)

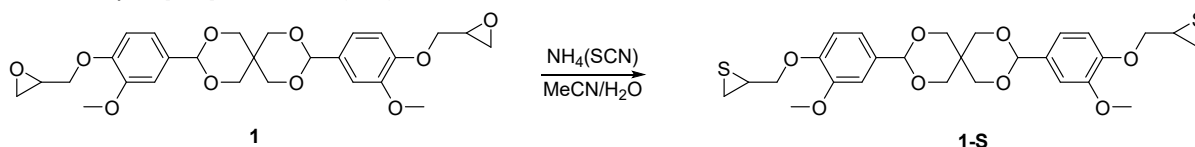


Compound **1** was prepared following a previously published procedure. ^[1]

P-1 (5 g, 12.3 mmol), epichlorohydrin (30 mL), and tetrabutylammonium bromide (0.47g, 1.5 mol%) were added into a round bottom flask equipped with a stir bar and a reflux condenser, the mixture was reacted at 80 °C for 3 hours. After being cooled to 5 °C, 5 g of 40 wt% aqueous sodium hydroxide solution (0.05 mol of NaOH) was added dropwise into the flask. The reaction mixture left to react at room temperature for 4 hours. The product precipitated as a white solid, the mixture was filtered and washed with ethanol and water. **P-2** was obtained in 80% yield after drying under reduced pressure for 2 hours.

¹H and ¹³C NMR spectra match those previously reported. ^[1]

2.3 preparation of 3,9-bis(3-methoxy-4-(thiiran-2-ylmethoxy)phenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (**1-S**)



1-S was prepared according to modified literature procedure.^[2] **1** (1g, 1.9 mmol) was dissolved in MeCN, NH₄SCN (0.3g, 4 mmol) was dissolved in H₂O. The solution of NH₄SCN was added to the solution of **1** in MeCN, the reaction mixture was stirred overnight. MeCN was removed by rotary evaporator. The product was extracted with DCM.

3. Preparation thermosets

3.1. Preparation of thermosets for DSC analysis

A certain amount of compound **1** (c.a. 100 mg) and a corresponding hardener (succinic anhydride, succinic acid or citric acid) were placed in an open vial and placed in an oven preheated to a certain temperature (170 °C or 200 °C). The polymerization was performed in melt for 1.5 hours.

Table S2. Curing of **1** with different hardeners

Entry	Hardener	1 /hardener, mol/mol	Water, wt% ^a	Gel content ^b , %
1	Succinic anhydride	1/2	-	98
2	Succinic acid	1/2	157	89
3	Succinic acid	1/2	350	90
3	Citric acid	3/4	320	97

^aWt% of total mass of **1** and a hardener. ^b Cured thermoset was placed in a vial containing chloroform. The vial was sealed and kept at 80 C for 16 h. The dried solid residue was washed with chloroform and dried to give gel content of a thermoset.

3.1. Preparation of a thermoset for DMTA analysis

Films for DMTA analysis were prepared as follows. **1** and succinic anhydride (molar ratio 1/2) were dissolved in a minimal amount of DMF. A solution was transferred to a Teflon mold with pipette. The mold was placed in an oven. The reaction was performed at 170 °C, for 1.5 hours.

Table S3. Storage modulus of a neat epoxy thermoset (succinic anhydride as a hardener) and CNF-epoxy composites

Composite	Preparation method	Storage modulus, 30° C, GPa	Storage modulus, 120 ° C, GPa	Storage modulus, 180 ° C, GPa
MeCN_ succinic anhydride (33wt% CNF)	Solvent exchange	4.5±0.6	2.64±0.05	0.86
H ₂ O_Succinic acid (42 wt% CNF)	Water-based	6.5±1.4	3.5±0.9	2.1±0.8
H ₂ O_Citric acid (40 wt% CNF)	Water-based	7.6±0.7	6.8±0.9	4.9±0.5
Neat epoxy	Melt	1.15±0.3	0.0014±0.0005	0.00077±0.00005

4. Preparation of Holo-CNF

Holo-CNF was prepared according to the previously published procedure.^[3] Briefly, holocellulose fibers were obtained using a mild peracetic acid (PAA) delignification on *Picea abies* spruce. Spruce pieces were treated with PAA (4 wt % in water, pH 4.8 before reaction) for 45 min at 85 °C. Four rounds of PAA treatments were performed. The final fibers were washed with 0.01 M NaOH and then extensively with deionized water to remove residual chemicals. Then they were subjected to mechanical defibrillation using a kitchen blender (3 hp, 30 000 rpm, Vitamix Vita-Prep 3, USA) for 15 min.

5. Preparation of Holo-CNF wet cake

Holo-CNF films were prepared via a vacuum filtration of a diluted CNF suspension. 250 mg (dry basis) of CNF was diluted with 600 mL of DI water. The suspension was mixed using an ULTRA-TURRAX mixer (IKA T25, Germany) at 12,000 rpm for 45 s, and then subjected to vacuum filtration. The obtained CNF wet cake contained c.a. 80-85 wt% of water.

6. Preparation of Holo-CNF wet cake containing spirodiepoxide **1**

250 mg (dry basis) of CNF and 250 mg of **1** were diluted with 600 mL of DI water. The obtained suspension was mixed using an ULTRA-TURRAX mixer (IKA T25, Germany) at 12,000 rpm for 45 s, and then subjected to vacuum filtration.

Amount of **1** in the wet cakes was assessed by ^1H NMR with an internal standard via soaking a piece of wet cake in d_6 -DMSO.

7. Preparation of CNF-epoxy composites in water system

CNF-epoxy composites with citric and succinic acids as hardeners were prepared as follows. CNF wet cake, containing spirodiepoxide **1**, was immersed into a water solution of succinic acid (5 wt%) or citric acid (5.4 wt%) and left overnight. The concentration of the corresponding acid was chosen based on an assumption that wet cake containing spirodiepoxide **1** uptakes c.a. 80wt% of the solution. The ratio between **1** and a corresponding acid was assessed by ^1H NMR via soaking a piece of wet cake in d_6 -DMSO. The molar ratio between epoxy groups of **1** and carboxyl groups of succinic acid was found to be 1/2.34 ($2 \times 4.68/4 = 2.34$) (Figure S1). The molar ratio between epoxy groups of **1** and carboxyl groups of citric acid was found to be 1/3.3 ($3 \times 2.21/2 = 3.3$) (Figure S2). Assuming that each carboxyl group is consumed either via primary reaction with an epoxide (epoxide opening, Figure S3a) or via a secondary reaction (condensation with hydroxyl group released upon an opening of an epoxide, Figure S3b) a ratio between epoxy and carboxyl groups should be 1/2. In case of citric acid one carboxyl group is sterically hindered, which makes it less reactive thus an excess of carboxyl group is desirable.

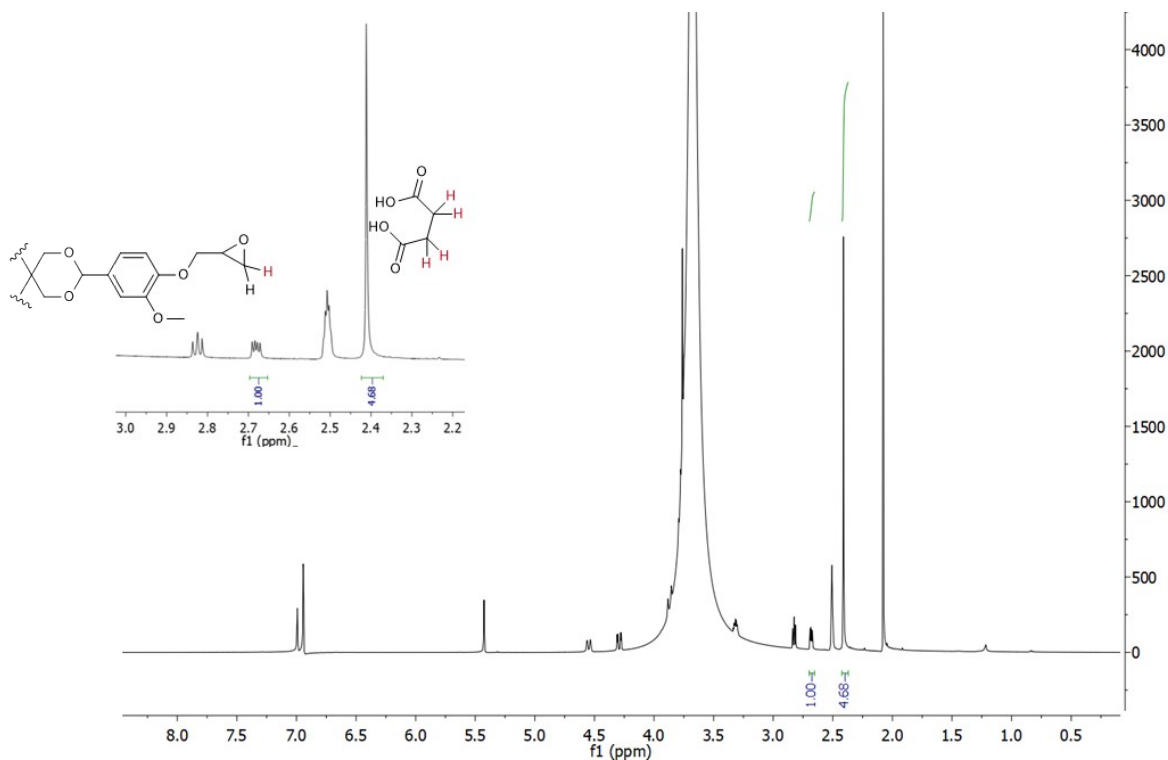


Figure S1. Ratio between spirodiepoxide **1** and succinic acid.

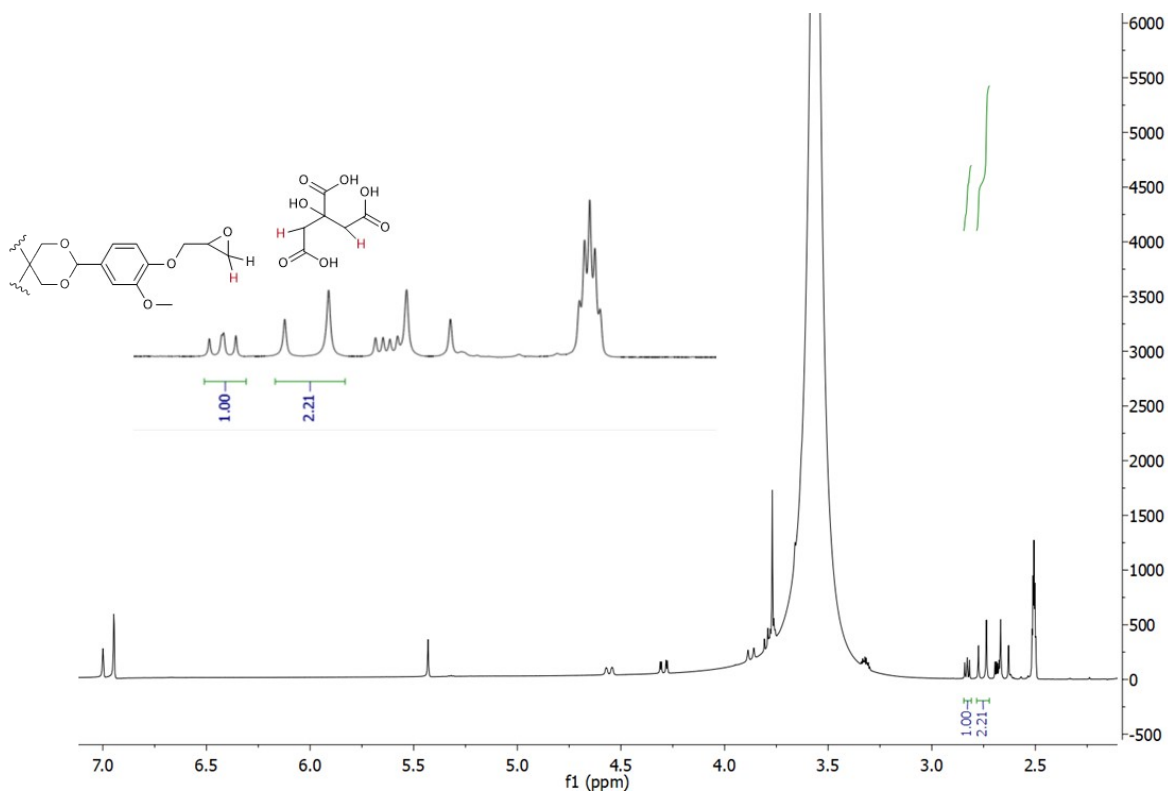


Figure S2. Ratio between spirodiepoxide **1** and citric acid.

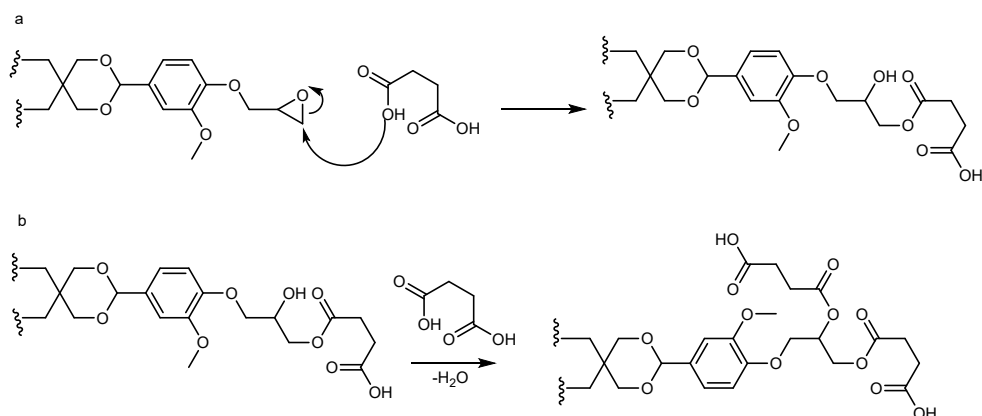


Figure S3. a. Primary reaction of carboxylic acids with epoxides (ring opening). b. secondary reactions of carboxylic acids with hydroxyl groups.

The impregnated CNF-epoxy wet cake was placed between two Teflon-coated metal plates (prior the reaction metal plates were kept at room temperature) and placed in a preheated to 170 °C oven. The curing was carried out at 170 °C for 1.5 hours followed 30 mins at 200 °C. The curing resulted in yellowish light-brownish films.

8. Preparation of CNF-epoxy composites via solvent exchange method

CNF-epoxy composites with succinic anhydride as a hardener were prepared as follows. CNF wet cake was immersed in organic solvent (MeCN) in order to exchange water to MeCN. The solvent was changed 3 times (approximately every 3 hours). Then the solvent exchanged CNF wet cake was immersed into a solution of spirodiepoxide **1** and succinic anhydride (25 wt% of **1**, 10 wt% of succinic anhydride in MeCN) at 70 °C. The CNF wet cake was left in the solution of monomers overnight. Then the impregnated CNF-epoxy wet cake was placed between two Teflon-coated metal plates (prior the

reaction metal plates were kept at room temperature) and placed in a preheated to 170 °C oven. The curing was carried out at 170 °C for 1.5 hours followed 30 mins at 200 °C. The curing resulted in brownish films.

9. Disintegration of CNF-epoxy composites and recovery of CNF film

CNF-epoxy composites with succinic anhydride as a hardener were disintegrated as follows. The film of the composite material was placed in a 0.5M HCl solution (acetone/water, 1:1, v/v) and the reaction vessel was sealed. The reaction was carried out at 80 °C overnight. The CNF film was then removed from the solution and washed with water. The preparation of the “2nd generation” CNF-epoxy composites was performed following a general procedure (see Section 8), using the recovered CNF film. In order to demonstrate the possibility of a reshaping, after the impregnation a piece of CNF film was cut and rolled to form a tube. The shape was fixed using a clamp.

The solution containing depolymerized fragments of the thermoset was kept at 90 °C for additional 12 hours. Upon the completion of the reaction, the reaction mixture was neutralized with NaOH. Acetone was removed from the reaction mixture under reduced pressure, using rotary evaporator. The water phase was then extracted with EtOAc 3 times. The solvent was removed from the combined organic fractions using rotary evaporator. For the quantification, an aliquot of the reaction mixture was then dissolved in DMSO-d₆, containing 4-nitrobenzaldehyde as an internal standard. ¹H NMR and ¹³C of the crude product in CDCl₃ is shown in Figure S4 and S5 respectively.

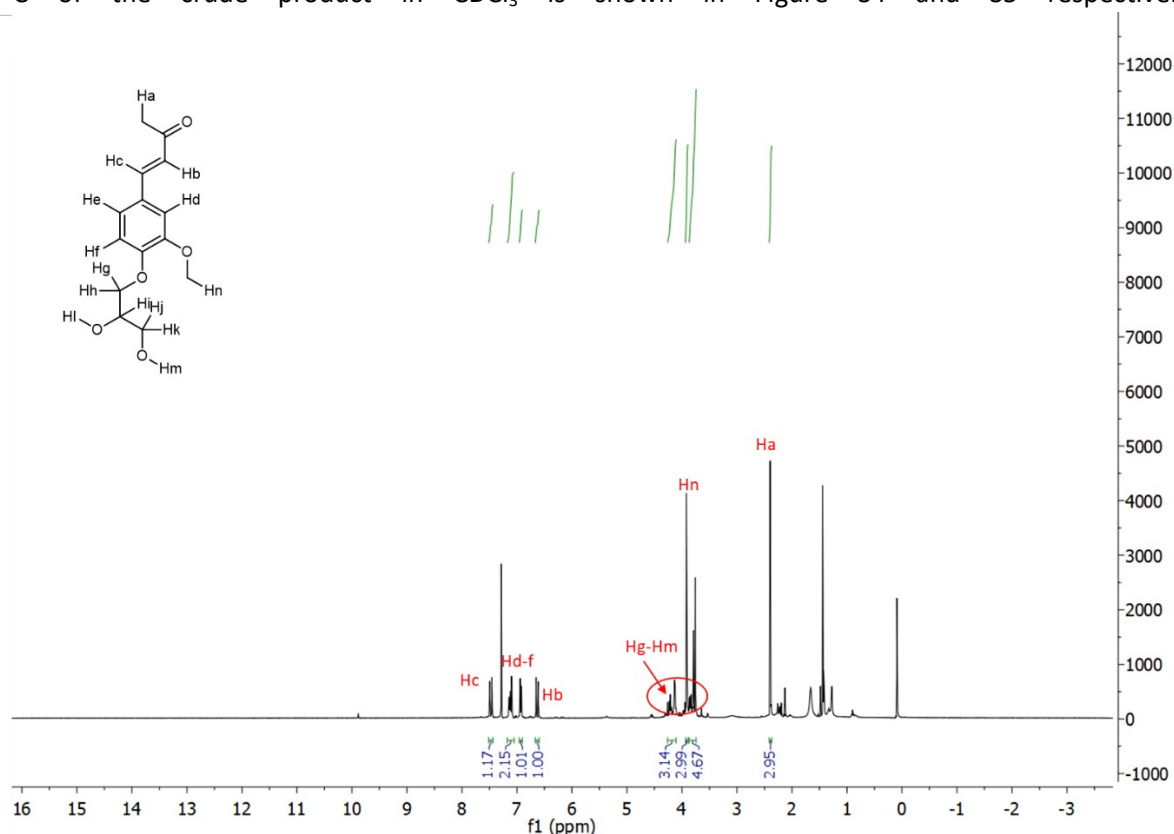


Figure S4. Crude ¹H NMR of an organic phase of the depolymerized epoxy thermoset.

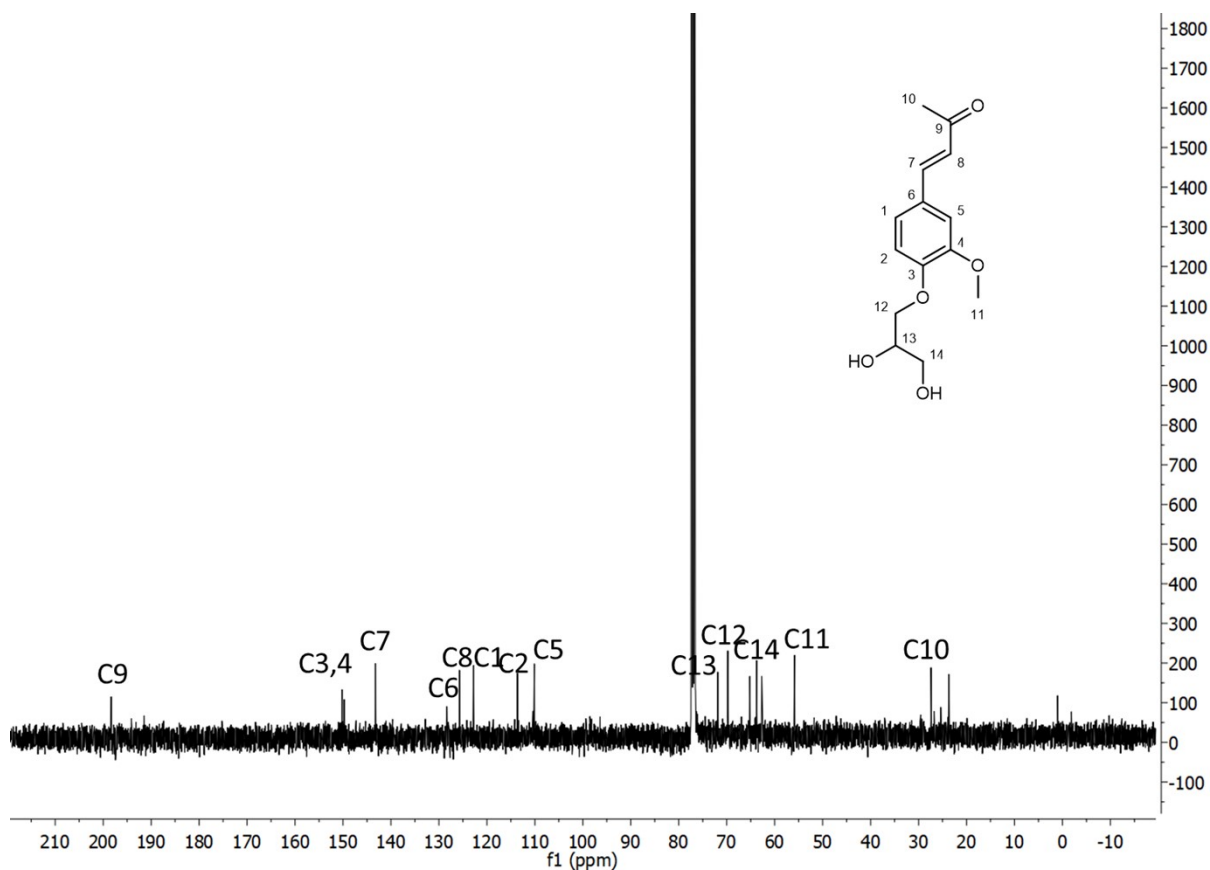


Figure S5. Crude ^{13}C NMR of an organic phase of the depolymerized epoxy thermoset.

Analysis of NMR spectra revealed that product **2** is a main product formed upon the depolymerization of the thermoset. A condensation of vaniline-derived monomer with acetone was evidenced by the presence of distinct signal of protons of methyl group (Ha), together with signals of double bond (Hb and Hc) in addition to a peak of carbonyl group in ^{13}C NMR (C9). An absence of other signals in aromatic region evidenced that product **2** is the only aromatic product formed via the depolymerization of the thermoset. Additional signals can be observed in aliphatic and ether bonds region, which can probably be attributed to byproducts derived from homocoupling of acetone.

Water fraction was evaporated and an aliquot of a solid residue was re-dissolved in D_2O with p-TSA (para-toluenesulfonic acid) as an internal standard for a quantification of succinic acid and pentaerythritol (Figure S6-7).

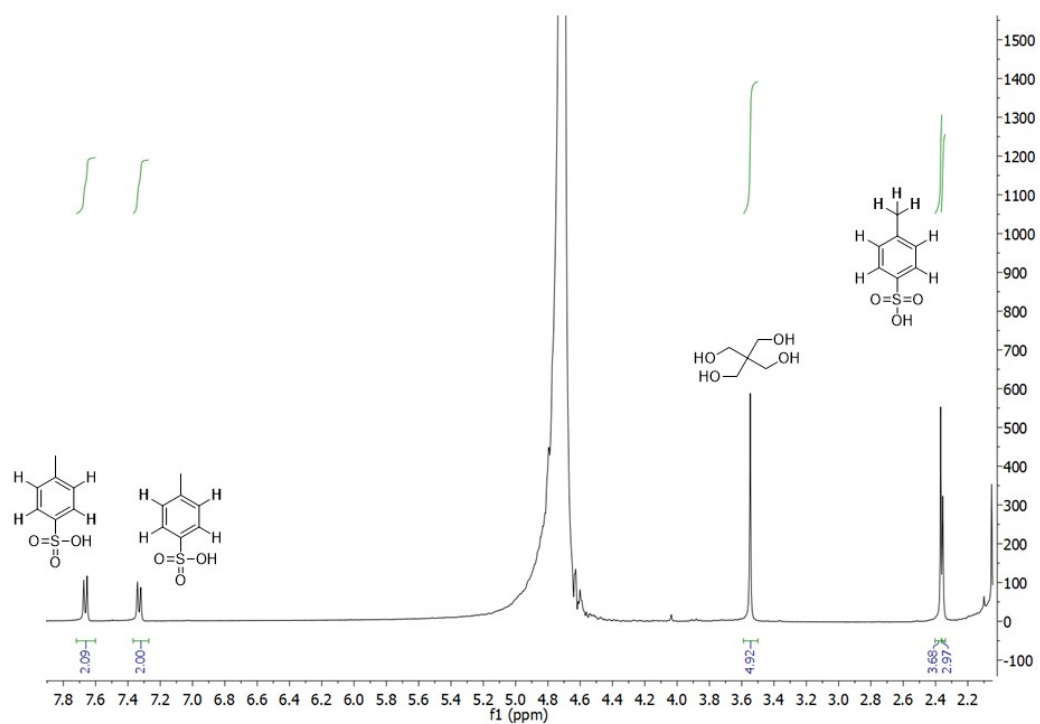


Figure S6. Crude ^1H NMR of water phase of the depolymerized epoxy thermoset (2-8 ppm).

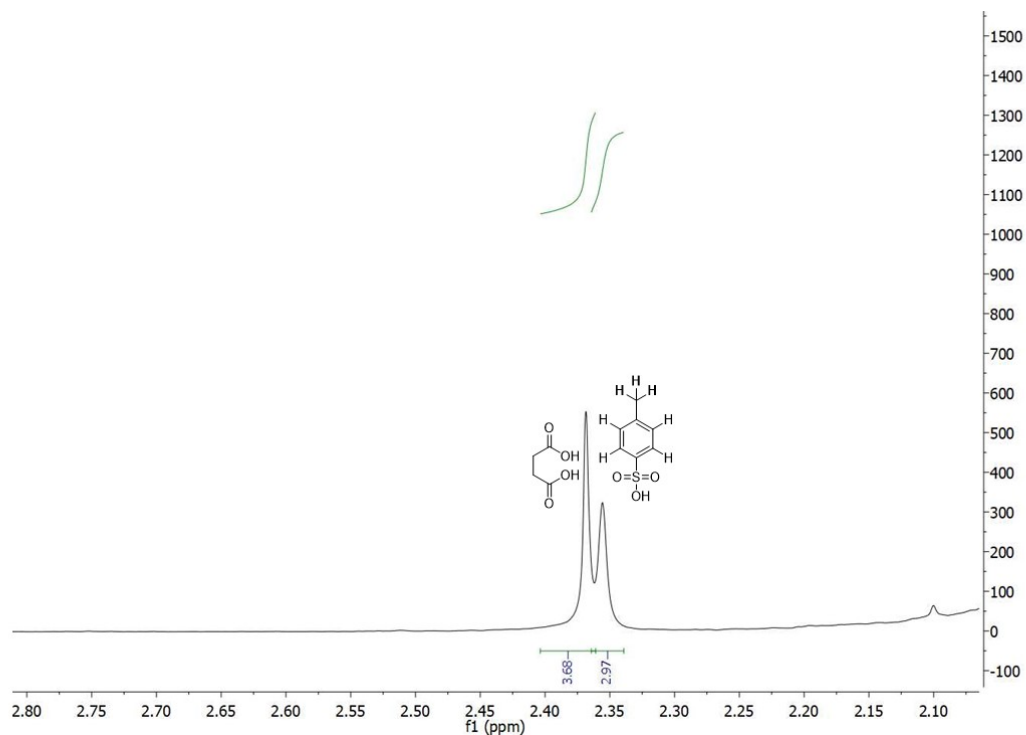
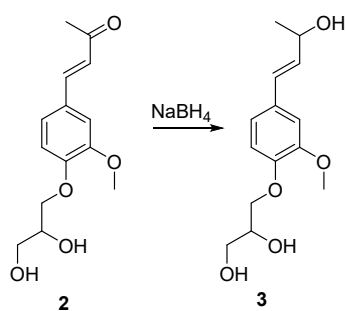


Figure S7. Crude ^1H NMR of water phase of the depolymerized epoxy thermoset (2-3 ppm).

10. Reactions of crude product 2.

10.1 Reduction of 2 with NaBH_4 to product 3



Crude product **2** (30 mg) was dissolved in MeOH (4 mL), then NaBH₄ (10 mg) was added to the reaction mixture in one portion. The reaction mixture was stirred at room temperature for 4 hours. The reaction mixture was quenched with NH₄Cl (saturated solution). MeOH was removed from the reaction mixture using rotary evaporator. Product **3** was extracted with dichloromethane.

Crude ¹H NMR and ¹³C NMR spectra of the crude reaction mixture are presented in Figures S8-9 respectively.

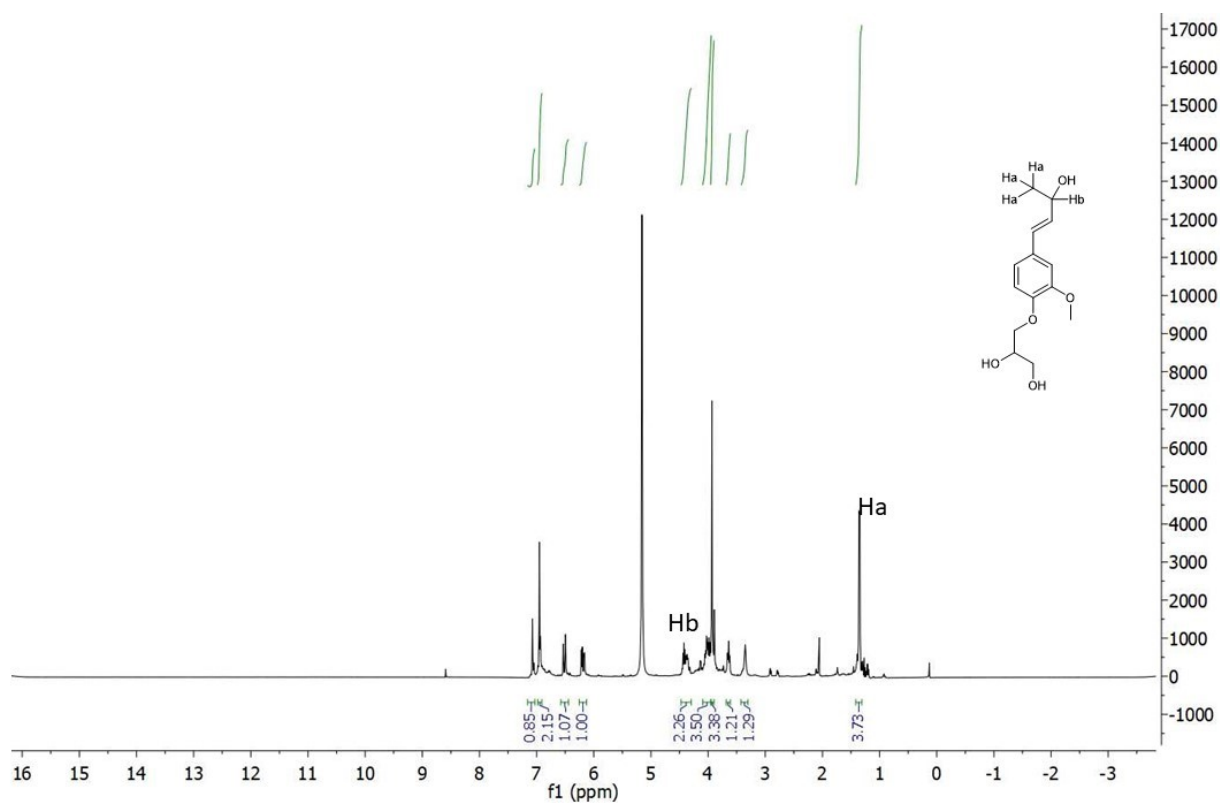


Figure S8. Crude ¹H NMR of product **3**.

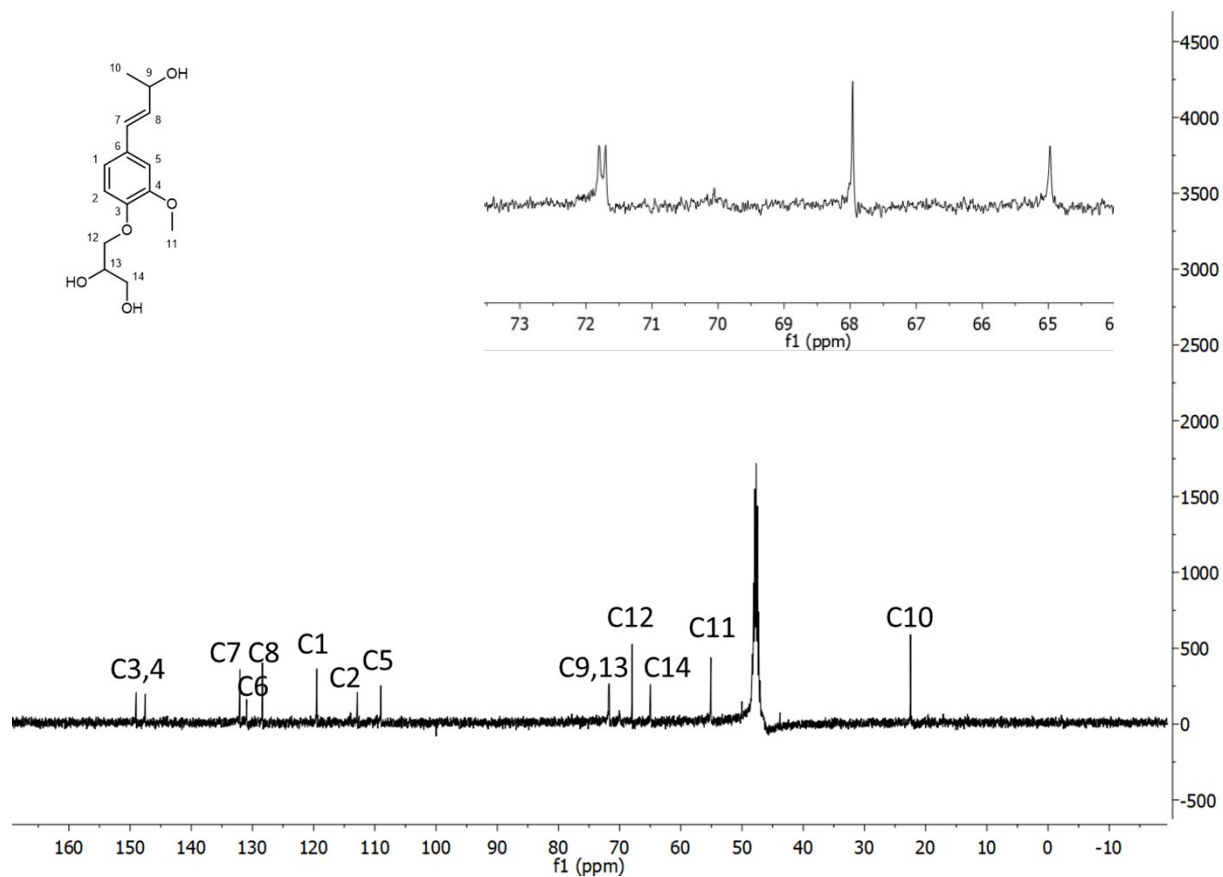
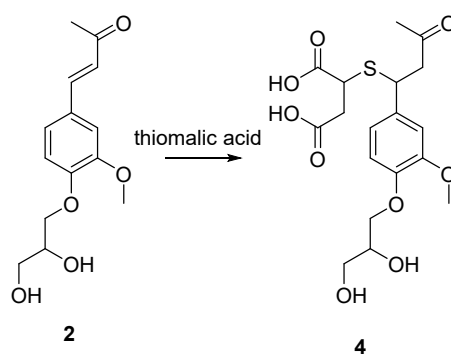


Figure S9. Crude ¹³C NMR of product **3**.

Reduction of the keto group in **2** was apparent by the high shift of the protons of methyl group (Ha) and an appearance of a new signal (Hb).

10.2 Reaction of **2** with thiomalic acid



The reaction was performed following a modified literature procedure.^[4] Compound **2** (30 mg) was suspended in water (2 mL), thiomalic acid (40 mg) was added to the reaction mixture and the vial was sealed. The reaction was performed for 12 hours at 100 °C. The crude ¹H and ¹³C NMR spectra presented in Figures S10-11. The crude reaction mixture contained unreacted thiomalic acid and two diastereoisomers of product **4**.

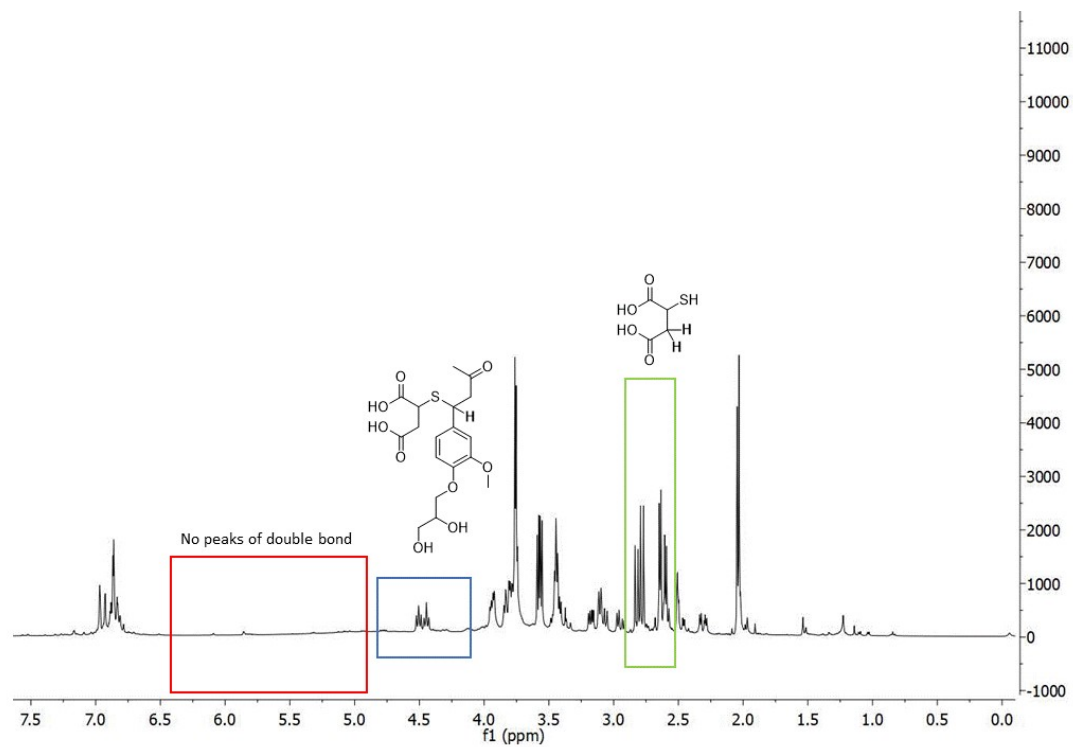


Figure S10. Crude ^1H NMR of product **4**.

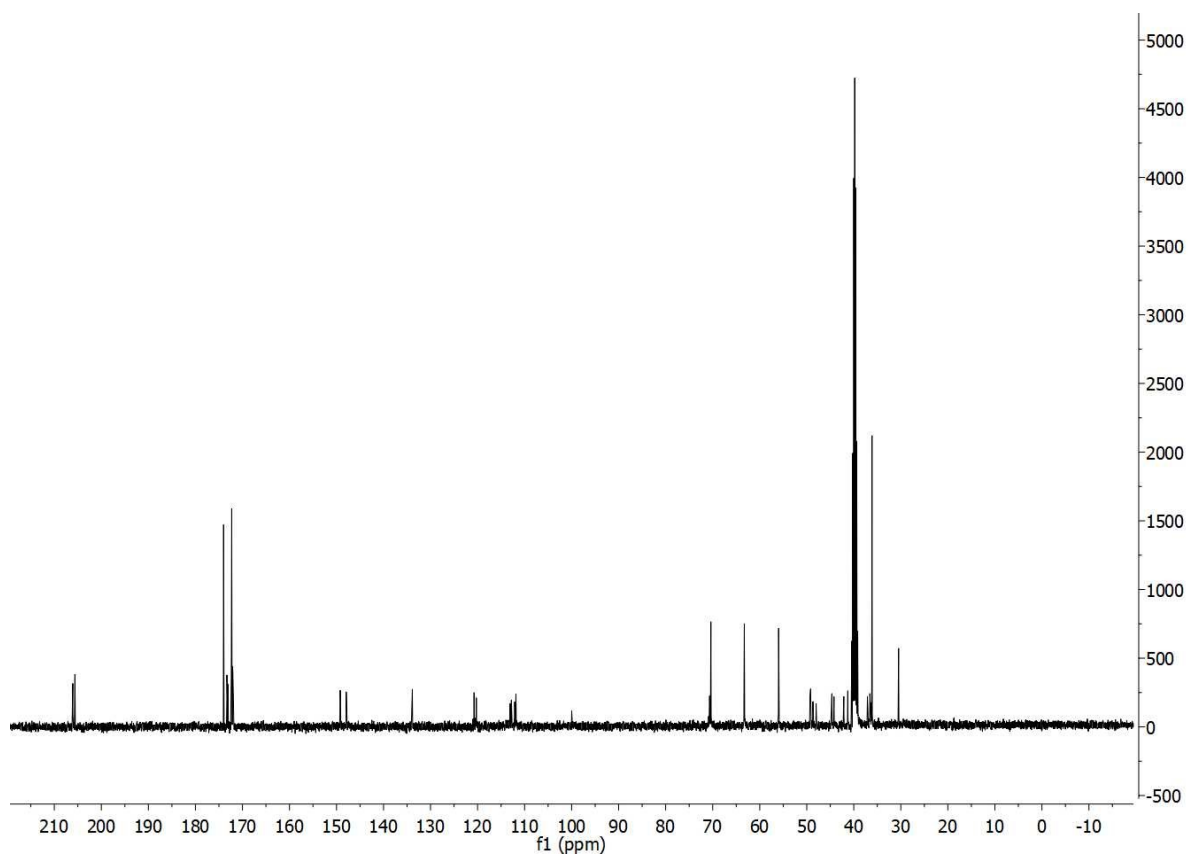


Figure S11. Crude ^{13}C NMR of product **4**.

The absence of signals corresponding to double in **2** and an appearance of characteristic signals of protons adjacent to sulfur at ~ 4.5 ppm evidence the formation of product **3**.

11. FT-IR measurements

Spirodiepoxy **1**, CNF films (including the recovered film) and CNF-epoxy composites were analyzed by FT-IR. Comparison of the spectra is presented in Figure S12.

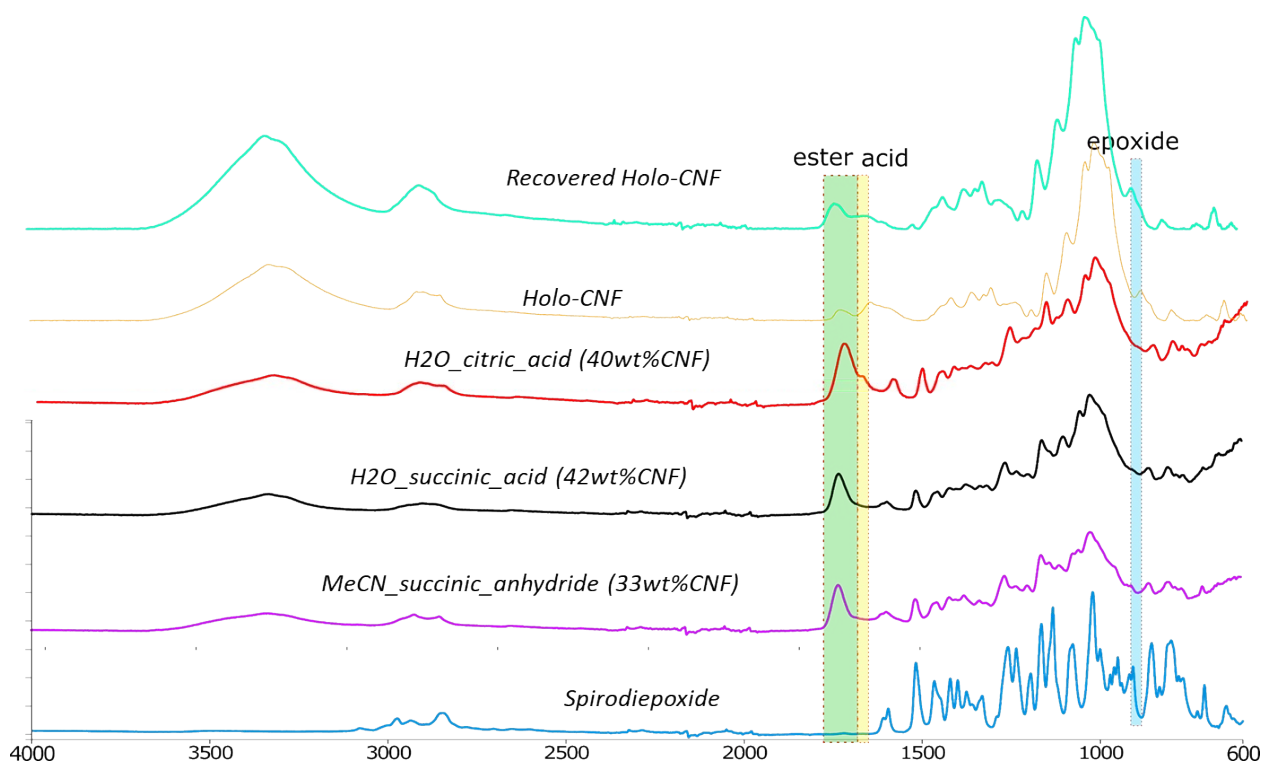


Figure S12. FT-IR spectra of CNF films, CNF-epoxy composites and spirodiepoxy **1**.

12. Schematic representation of covalent interactions between CNF and epoxy thermostets

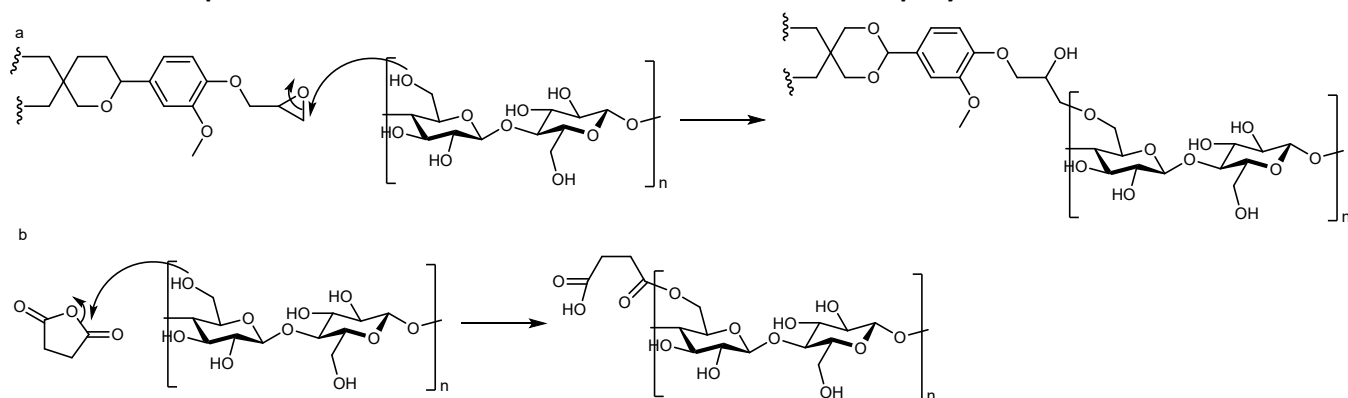


Figure S13. Schematic representation of possible covalent interactions between Diepoxy **1** and CNF (a) and succinic anhydride and CNF (b).

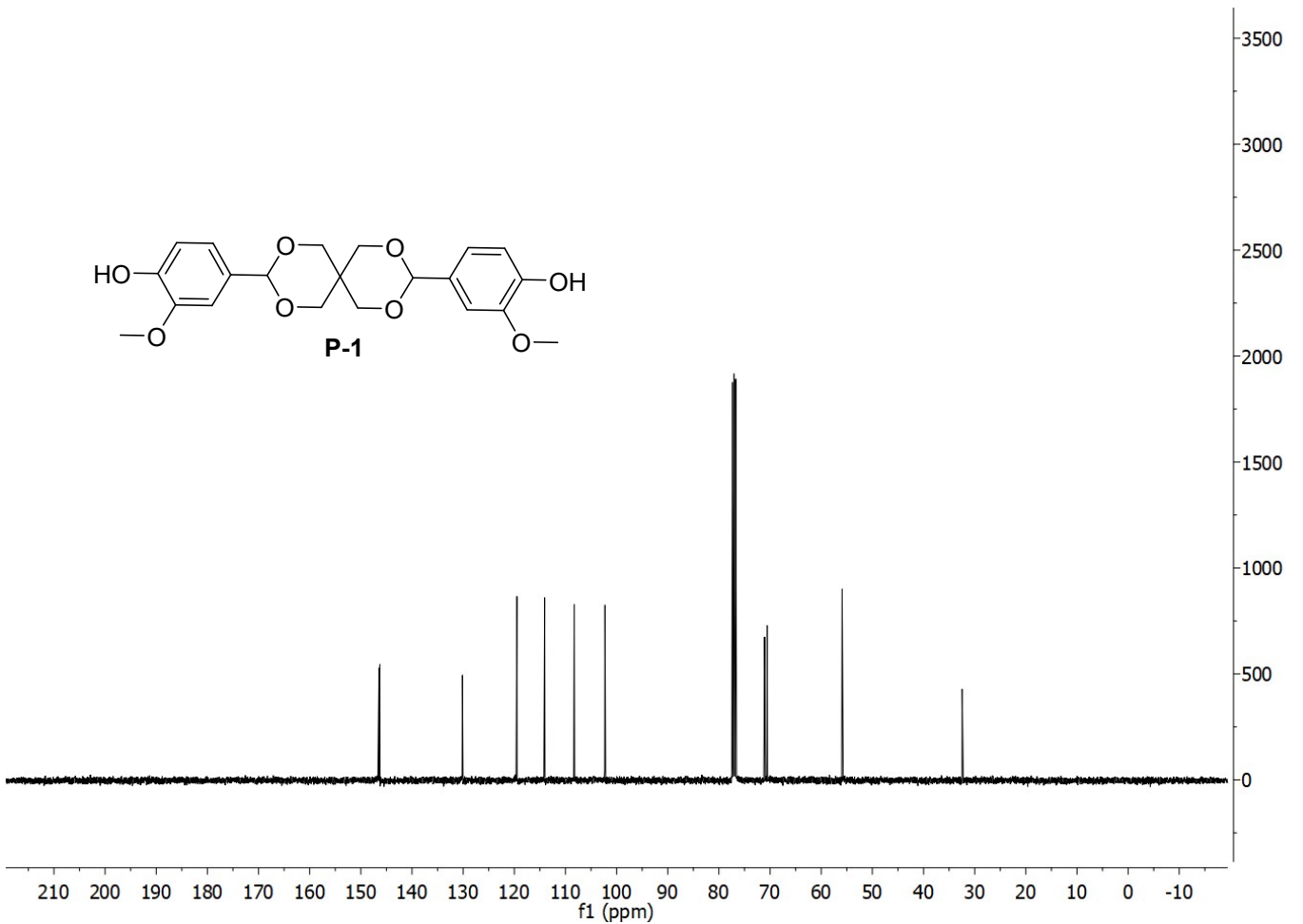
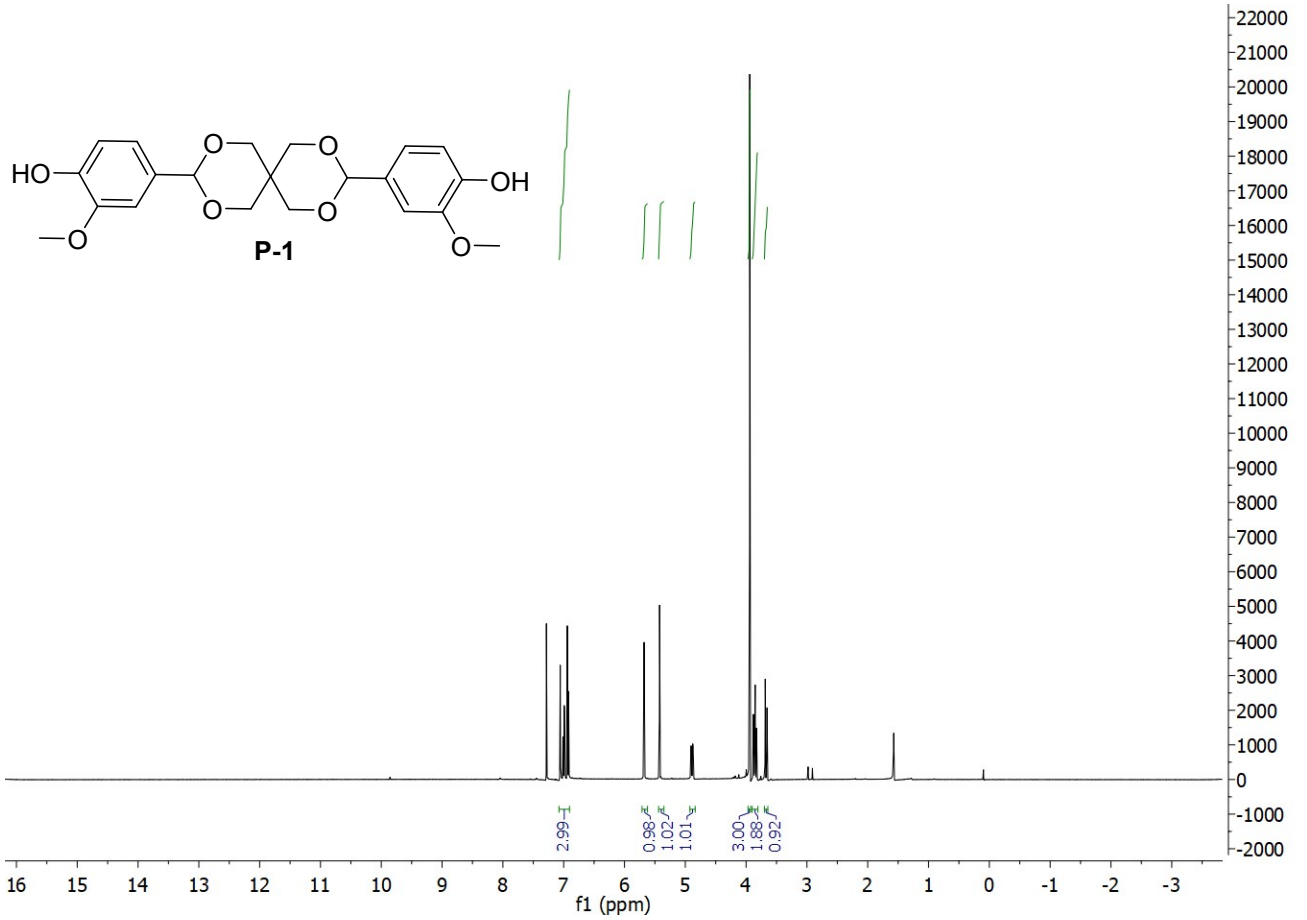
13. Tensile testing

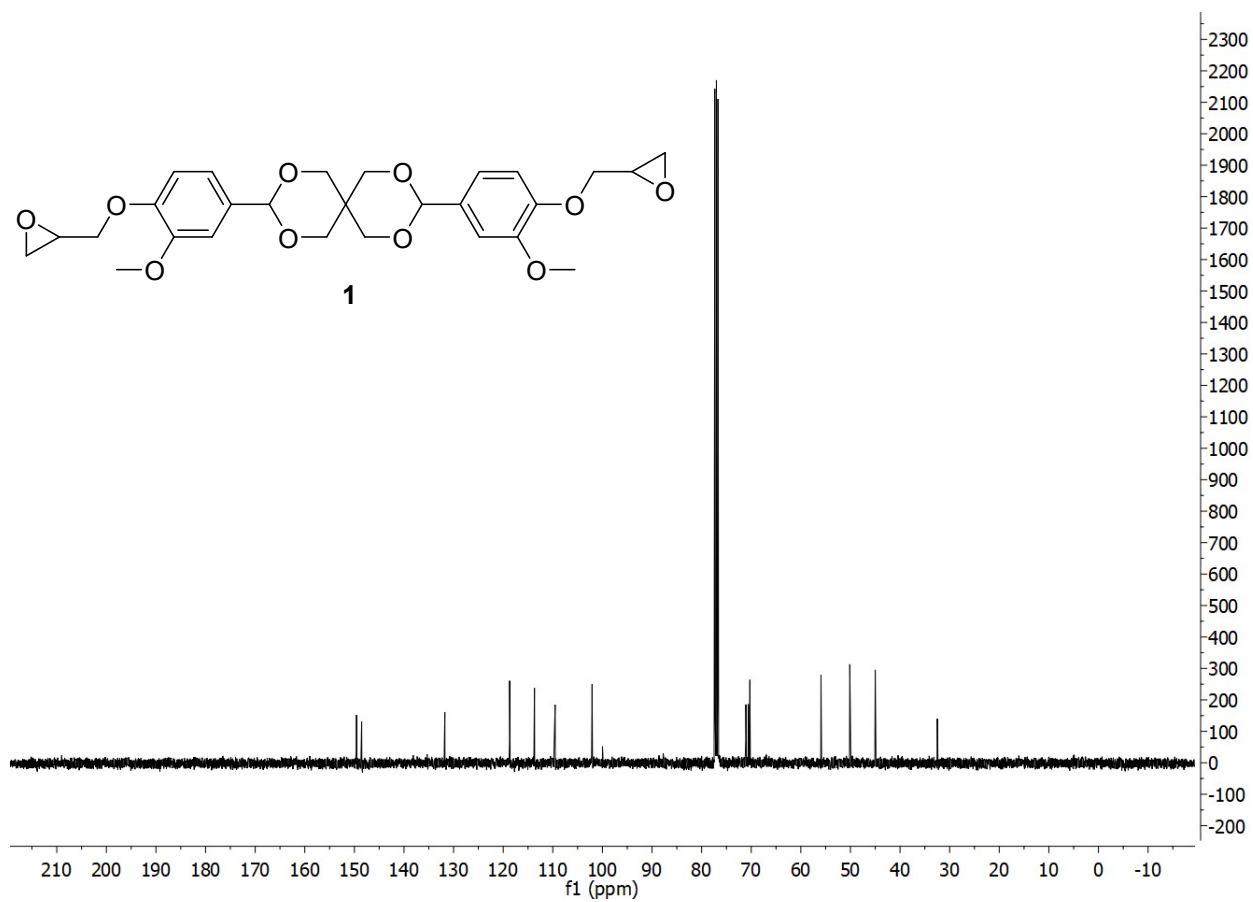
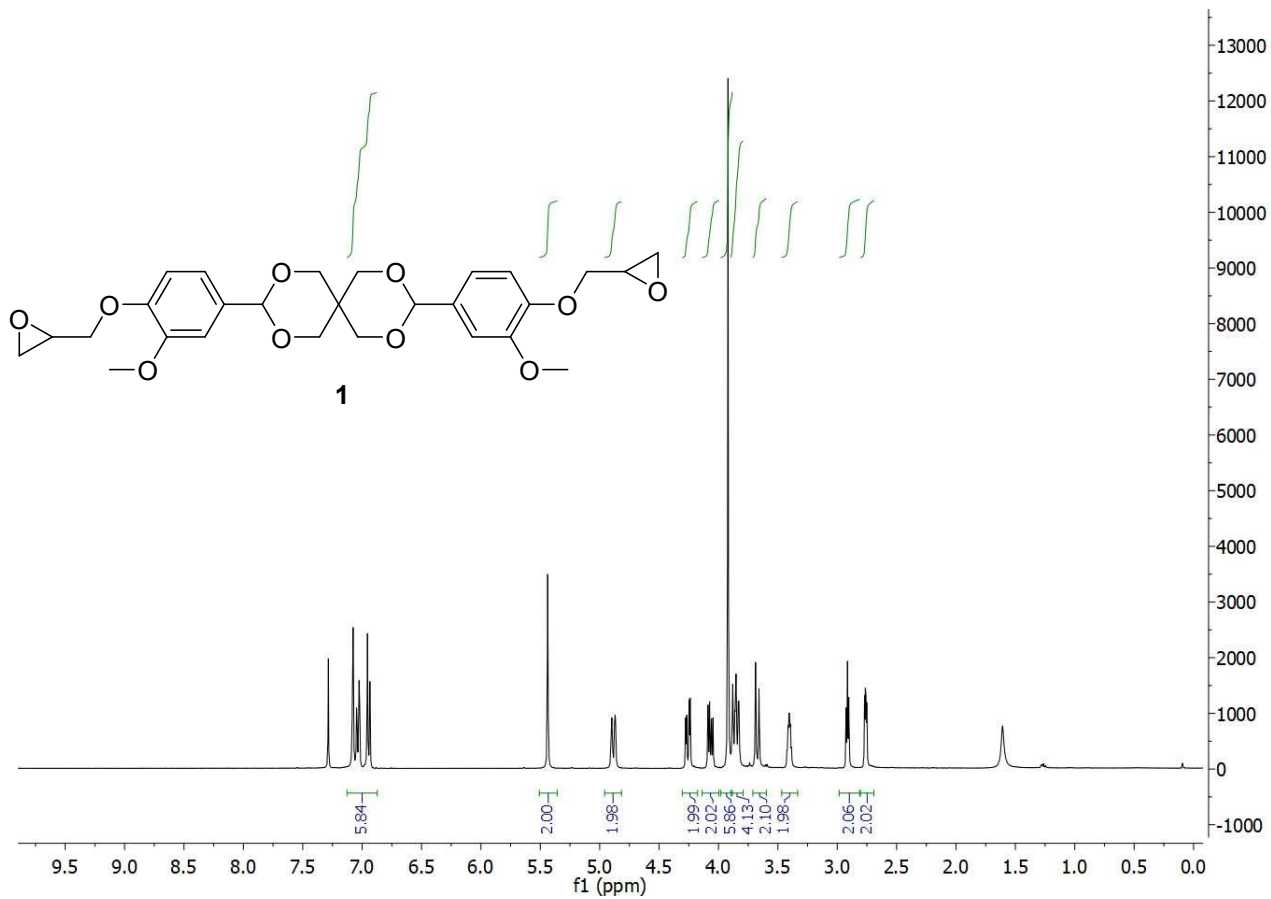
The tensile properties of the samples were determined using a universal testing machine (Instron 5944, USA) equipped with a 2 kN load cell and a video extensometer. Five samples (2.5 mm × 0.5 cm) were preconditioned for 48 h at 50% RH before measurement. The tests were carried out at a temperature of 22 °C and 50% RH, with a 10% min⁻¹ strain rate and.

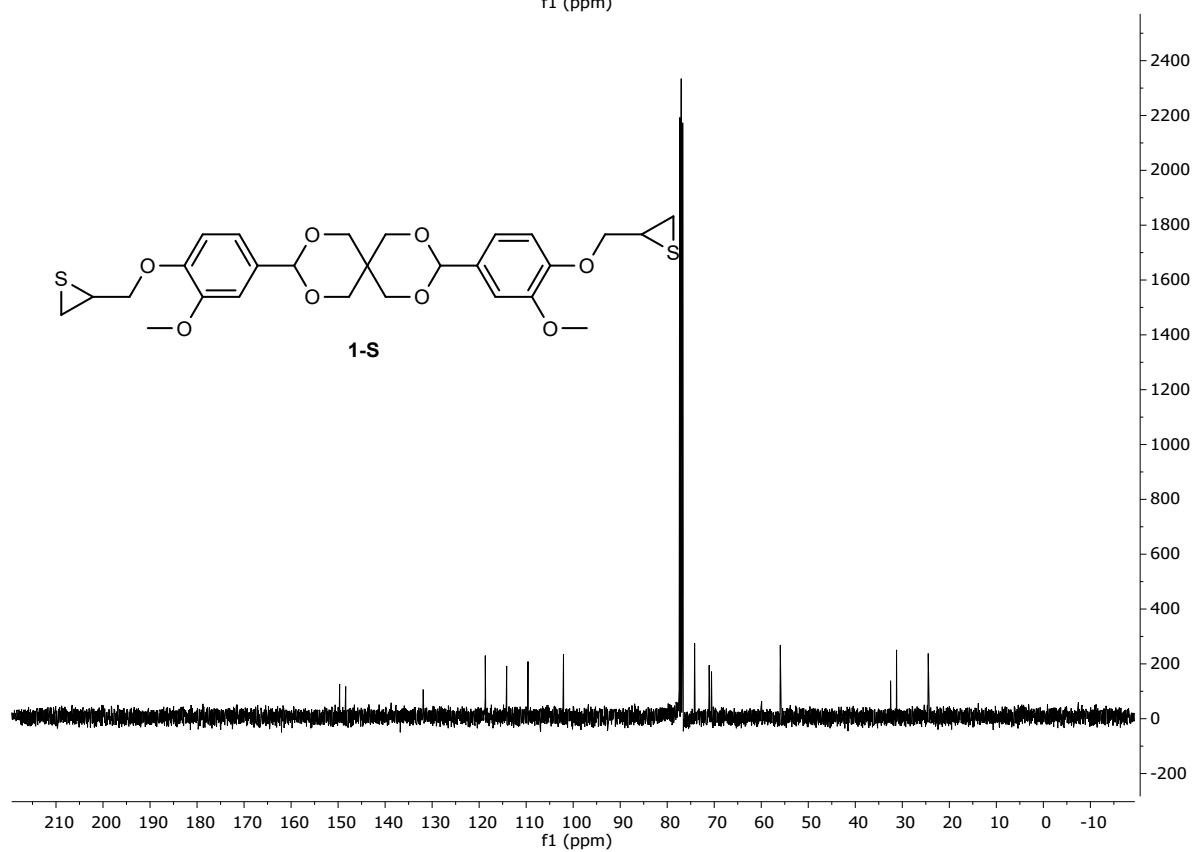
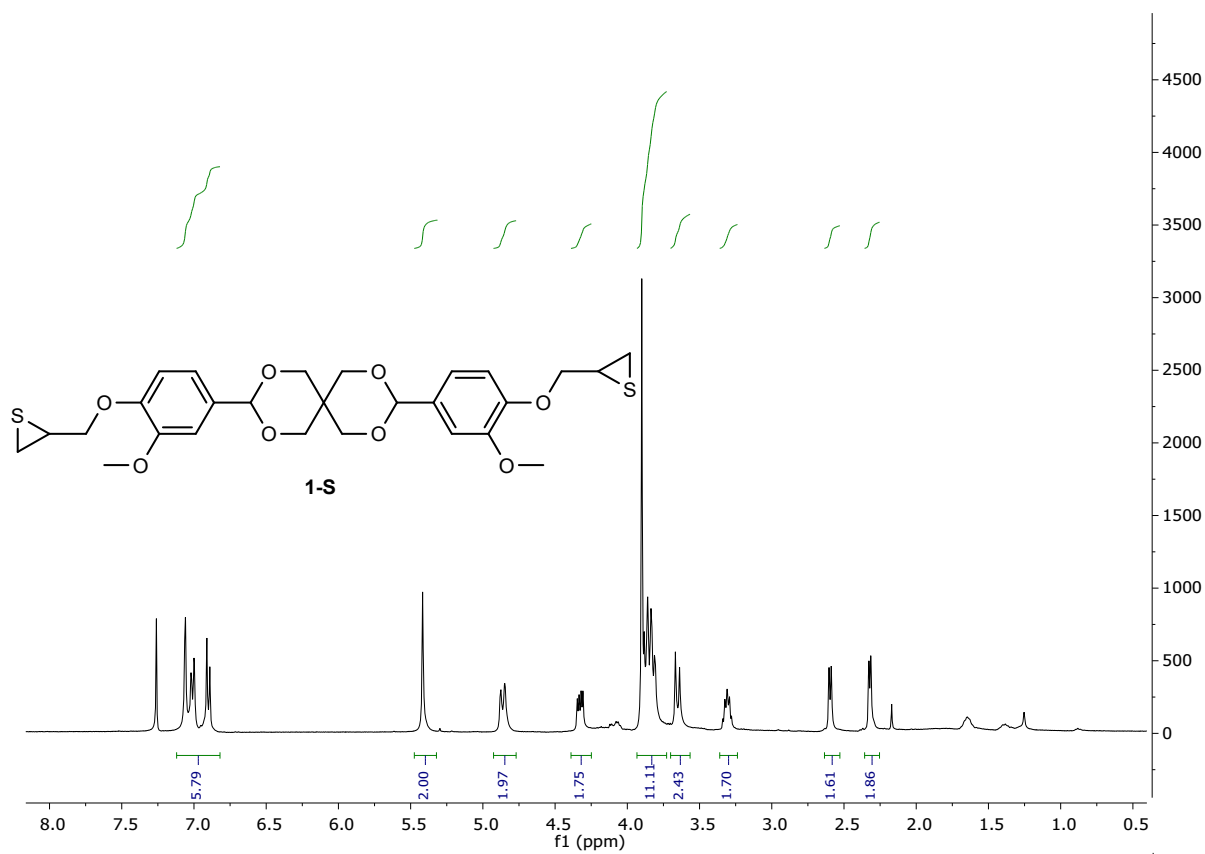
Table S4. Tensile properties of composites

Entry	Sample	Tensile strength, MPa	Young modulus, GPa
1	MeCN_succinic_anhydride	127 ±14	4±0.4
2	2 nd generation MeCN_succinic_anhydride	105±10	3±0.2

Appendix







References

- [1] S. Ma, J. Wei, Z. Jia, T. Yu, W. Yuan, Q. Li, S. Wang, S. You, R. Liu, J. Zhu, *Journal of Materials Chemistry A* **2019**, *7*, 1233-1243.

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