Monolithic, Hybrid and Particulate Lignin-based Hydrogels for Sustainable CO2 Capture

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Materials

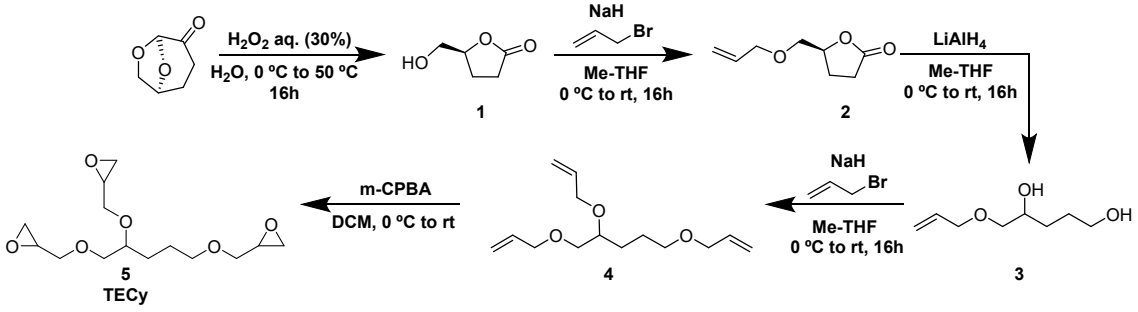
All lignin materials prepared in this work (LNPs, hy-NPs and *c*-hy-LNPs) were prepared from BIOPIVA™ 100 pine Kraft lignin (SKL) (UPM, Finland), previously characterized.[1] The following chemicals were purchased from Merck and used as received: Dihydrolevoglucosenone (Cyrene™), allyl bromide (97%), sodium hydride (NaH, 60% dispersion in mineral oil), lithium aluminum hydride ($LiAlH_4$, 95%) and 3-chloroperbenzoic acid (m-CPBA, ≤ 77%). 2-Methyltetrahydrofuran (2-MeTHF, Merck, 99.5%) was distilled prior to use from CaH_2 and sodium/benzophenone, respectively. Deionized (DI) water and acetone were used throughout the experiments that involve particle formation. Dialysis of particles (LNPs and hy-LNPs) was performed on dialysis tube benzoylated (MWCO 1000) from Merck against deionized water and acetone, respectively. Deuterated chloroform ($CDCl_3$) was purchased from Eurisotop and used as received.

Methods

NMR spectroscopy. ^{1}H, ^{31}P and ^{13}C NMR analyses were performed on a 400 MHz Varian VNMR-S400 NMR instrument at 25°C using deuterated solvents. All chemical shifts are quoted on the δ scale in ppm using the residual solvent as internal standard. **LC/MS** was performed with a Thermo Scientific Vanquish Horizon UHPLC system interfaced with a Thermo scientific Orbitrap ID-X Tribrid Mass Spectrometer. Reaction's products were separated by HILIC chromatography with an ACQUITY UPLC BEH HILIC (2.1 x 150 nm, 1.7 μm) column (Waters). The mobile phase A was 50 mM ammonium acetate in water, and mobile phase B was acetonitrile. Separation was carried out under the following gradient: 0-2 min, isocratic 95% B; 2-6 min decreased to 50% B; 6-7 min, isocratic 50% B; 7-7.2 min, increased to 90% B; 7.2-10.5 min, reequilibration column 95% B. The flow was 0.4 mL min^{-1}. Samples were analyzed in fullScan mode in positive mode. The MS parameters used were scan range, 80-900 *m/z*; spray voltage, 3500 V; sheath gas, 50; auxiliary gas, 10; Ion transfer tube temperature, 300 ºC; vaporizer temperature, 300 ºC; Orbitrap resolution, 120000; RF Lens (%), 60; AGC target, 2^5; maximum injection time, 200 ms. **Transmission electron microscopy (TEM)** microscope operating with an accelerating voltage of 200 kV. Colloidal dispersions of LNPs, hy-LNPs and *c*-hy-LNPs were previously diluted by a factor of 1:40, followed by the deposition and evaporation onto a carbon-coated copper grid. Image J software was

used to process the images. **Scanning electron microscopy (SEM)** images were recorded on a FEI QUANTA 600 FESEM operating at 2−5 kV. Lignin-based hydrogels were fixed into an aluminum plate with carbon tape for the SEM investigation of top surface and cross-sectional surface. **Atomic force microscopy (AFM)** analysis was performed on a MultiMode AFM Nanoscope V (Agilent 5500). The images were obtained in ScanAsyst mode under ambient air conditions with SCANASYST-AIR probes (Bruker). **Dynamic Light Scattering (DLS)** measurements were performed at room temperature on a Zetasizer Nano ZS (Malvern, UK). The zeta potential was determined using a dip cell probe. LNPs, hy-LNPs, *c*-hy-LNPs were diluted by a factor of 30 with deionized water respectively before the analysis. **Thermogravimetric analysis (TGA)** was perfomed using a Mettler Toledo TGA 2 thermobalance. Around 30 mg of CO_2-loaded lignin-based hydrogel was heated up from room temperature to 300 °C at a heating rate of 10 °C min^{-1} under an N_2 atmosphere with a flow rate of 50 cm^3 min^{-1}. A Jasco **FTIR**-680 Plus spectrometer equipped with an attenuated total reflection accessory (ATR) (Golden Gate, Specac Ltd, Teknokroma) was used to record the FTIR spectra of the mixture before and after the curing procedure. Real-time spectra were recorded in the wavenumber range between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 20 scans. **The mechanical properties** of the lignin-based hydrogels were measured using an Instron 5960 universal testing machine (Instron, USA) equipped with a 100 N loaded cell at a strain rate of 1 mm min^{-1}. The mechanical measurements were performed on rectangular shaped hydrogels with dimensions of 0.5 cm × 3 cm using a gauge length of 1 cm. The specimens were conditioned 24 h prior to the measurement and measured at 50% relative humidity (RH) and 25 °C.

Additional experimental section



Scheme 1. Synthetic route towards the preparation of triepoxide derived from the bio-based and green solvent dihydrolevoglucosenone (**TECy**) (**5**).

Synthesis of (*S*)-5-(hydroxymethyl)dihydrofuran-2(3H)-one (1)

In a round-bottom flask, Cyrene™ (30 g, 1 equiv.) was added with 80 mL of deionized water. Once Cyrene™ was dissolved, the reaction flask was placed in an ice-water bath at 0 °C, and H_2O_2 (24 mL, 1 equiv.) was added very slowly. After adding hydrogen peroxide, the ice-water bath was swapped for an oil bath, and a reflux system was connected to the flask. After 1h under stirring at room temperature, the reaction was heated up to 50 °C under stirring overnight. Finally, the solvent was removed under vacuum. Purification of the crude product was carried out trough vacuum distillation (bp = 150 °C at 0.05 mmHg) to afford product **1** as a transparent oil. (96% yield)

^{1}H NMR [$CDCl_3$, TMS, δH (ppm)] (Fig. S1): 4.64 (m, 1H, CH_2-C**H**-O), 3.91 (dd, 1H, OH-C**H**H), 3.66 (dd, 1H, OH-CH**H**), 2.59 (m, 2H, COO-C**H$_2$**-CH_2-CH), 2.32-2.10 (m, 3H, COO-CH_2-C**H$_2$**-CH-CH_2-O**H**).

^{13}C NMR [$CDCl_3$, TMS, δH (ppm)] (Fig. S2): 177.7, 80.8, 64.2, 28.7, 23.2.

Synthesis of (S)-5-((allyloxy)methyl)dihydrofuran-2(3H)-one (2)

In a 100 mL two-neck round bottom flask, NaH (3.6 g, 1.05 equiv.) was rinsed (3 x 10 mL) with anhydrous hexane to remove mineral oil, and after that dispersed in 60 mL of dry 2-MeTHF under inert atmosphere. Then, a solution of **1** (10 g, 1 equiv.) in 20 mL of anhydrous 2-MeTHF was added to the NaH suspension dropwise at 20 °C. The reaction mixture was placed in an ice bath at 0 °C and was left under stirring for 30 min. Then, allyl bromide (8.2 mL, 1.1 equiv.) was added dropwise. After that, the reaction mixture was allowed to reach room temperature and keep under stirring for additional 16 h. Once the reaction is completed, excess of NaH was neutralized by dropwise addition of deionized water at 0 °C. The solvent was removed in vacuum, and then the crude was redissolved in CH_2Cl_2, and rinsed with brine solution (3x 20 mL). The organic layer was dried by the addition of $MgSO_4$, and the solvent was removed in vacuum, to afford **2** as a yellow oil. (75% yield)

^{1}H NMR [$CDCl_3$, TMS, δH (ppm)] (Fig. S3): 5.87 (m, 1H, CH_2=C**H**-CH_2-O), 5.22 (m, 2H, C**H$_2$**=CH-CH_2-O), 4.65 (m, 1H, CH_2-C**H**-O), 4.02 (d, 2H, CH_2=CH-C**H$_2$**-O), 3.66-3.54 (dd, 2H, CH_2=CH-CH_2-O-C**H$_2$**), 2.61 (m, 1H, COO-C**H**H-CH_2-CH), 2.48 (m, 1H, COO-CH**H**-CH_2-CH), 2.29 (m, 1H, COO-CH_2C**H**H-CH), 2.13 (m, 1H, COO-CH_2-CH**H**-CH).

^{13}C NMR [$CDCl_3$, TMS, δH (ppm)] (Fig. S4): 177.3, 134.2, 117.4, 78.9, 72.5, 71.5, 28.4, 24.1.

Synthesis of 5-(allyloxy)pentane-1,4-diol (3)

In a 250 mL three-neck round bottom flask, under inert atmosphere, $LiAlH_4$ (7.68 g, 2 equiv.) was dispersed with anhydrous 2-MeTHF (160 mL), and a solution of **2** (10 g, 1 equiv.) in 20 mL of 2-MeTHF was added dropwise to the $LiAlH_4$ suspension at 25 °C. The reaction mixture was left under stirring at room temperature overnight. Then, remaining $LiAlH_4$ was neutralized by controlled addition of brine solution at 0 °C. Then the reaction mixture was left to reach room temperature. After that, the reaction mixture was filtrated to remove the white solid precipitated, and the solvent was removed under vacuum. Purification of the crude reaction mixture was performed by flash column chromatography (1:1 Hex/AcOEt) to provide **3** as a transparent oil. (98% yield)

^{1}H NMR [$CDCl_3$, TMS, δH (ppm)] (Fig. S6): 5.87 (m, 1H, CH_2=C**H**-CH_2-O), 5.22 (m, 2H, C**H$_2$**=CH-CH_2-O), 4.65 (m, 1H, CH_2-C**H**-O-), 4.02 (d, 2H, CH_2=CH-C**H$_2$**-O), 3.84 (m, 1H, O-CH_2-C**H**-OH), 3.68 (m, 2H, CH_2-C**H$_2$**-OH), 3.47 (dd, 1H, O-C**H**H-CH-OH), 3.31 (dd, 1H, O-C-H**H**-CH-OH), 2.76 (s, 1H, CH-O-**H**), 2.33 (s, 1H, CH_2-O**H**), 1.72 (q, 2H, C**H$_2$**-CH_2-OH) 1.61 (m, 1H, C**H**H-CH_2-CH_2-OH) 1.50 (m, 1H, CH**H**-CH_2-CH_2-OH).

^{13}C NMR [$CDCl_3$, TMS, δH (ppm)] (Fig. S7): 134.4, 117.4, 74.4, 72.2, 70.3, 62.8, 30.2, 29.1.

Synthesis of 1,2,5-tris(allyloxy)pentane (4)

In a 100 mL two-neck round bottom flask, NaH (2.7 g, 2.1 equiv.) was rinsed (3 x 10 mL) with anhydrous hexane to remove the mineral oil, and then dispersed in anhydrous 2-MeTHF under inert atmosphere. Then, a solution of **3** (5 g, 1 equiv.) in anhydrous 2-MeTHF was added to the NaH suspension dropwise at 20 °C. Then the reaction mixture was placed in an ice bath at 0 °C and was left under stirring for 30 min. After that, allyl bromide (2.2 equiv.) was added dropwise. Subsequently, the reaction was allowed to reach room temperature and stirred for 16 h. Once the reaction is completed, excess of NaH was neutralized by dropwise addition of deionized water at 0 °C. The solvent was removed under vacuum, and the crude was redissolved in CH_2Cl_2, and rinsed with brine solution (3 x 20 mL). The organic layer was dried by the addition of $MgSO_4$, and the

solvent was removed in vacuum. Purification was performed by flash column chromatography (1:1 Hex/AcOEt) to provide **4** as a yellowish oil. (80% yield)

^{1}H NMR [$CDCl_3$, TMS, δH (ppm)] (Fig. S9): 5.86 (m, 3H, CH_2=C**H**-CH_2-O), 5.16 (m, 6H, C**H$_2$**=CH-CH_2-O), 4.13-3.88 (dt, 6H, CH_2=CH-C**H$_2$**-O), 3.51 (m, 1H, O-CH_2-C**H**-O-), 3.44 (m, 4H, CH_2=CH-CH_2-O-C**H$_2$**-CH-O), 1.72 (m, 2H, C**H$_2$**-CH_2-O-) 1.61 (m, 2H, C**H$_2$**-CH_2-CH_2-O-).

^{13}C NMR [$CDCl_3$, TMS, δH (ppm)] (Fig. S10): 135.4, 135.0, 134.8, 116.7, 116.6, 116.4, 77.8, 72.7, 72.2, 71.7, 70.9, 70.3, 28.6, 25.7.

Synthesis of 2,2',2''-((pentane-1,2,5-triyltris(oxy))tris(methylene))tris(oxirane) (TECy) (5)

To a 500 mL round-bottom flask, **4** (3 g, 1 equiv.) was dissolved in 50 mL of DCM. The reaction was placed in an ice bath at 0 °C, and m-CPBA (12.76 g, 4 equiv.) in 130 mL of DCM was added dropwise, and the reaction was let to reach room temperature under stirring until complete consumption of the double bonds was verified mediated ^{1}H NMR. Once the reaction was completed, the crude reaction mixture was rinsed first with a saturated solution of $Na_2S_2O_3$ (3 x 40 mL), and then with brine solution (3 x 40 mL). The organic layer was dried by the addition of $MgSO_4$, and the solvent was removed under vacuum. Purification by flash column chromatography (1:1 Hex/AcOEt) provide **5** as a yellowish oil. (92% yield)

^{1}H NMR [$CDCl_3$, TMS, δH (ppm)] (Fig. S12): 3.90-3.68 (m, 3H, -CH_2-O-C**H$_2$**-CH-CH_2-CH_2-C**H$_2$**-O-), 3.63-3.33 (m, 8H, -C**H$_2$**-O-CH_2-C**H**-CH_2-CH_2-C**H$_2$**-O-), 3.14 (m, 3H, O-CH_2-C**H**-), 2.79 (m, 3H, O-C**H**-H-CH-), 2.60 (m, 3H, O-CH-**H**-CH-), 1.66 (m, 4H, CH-C**H$_2$**-C**H$_2$**-CH_2-O-).

^{13}C NMR [$CDCl_3$, TMS, δH (ppm)] (Fig. S13): 79.1, 79.0, 74.0, 73.9, 72.0, 71.9, 71.4, 71.1, 70.9, 51.1, 50.9, 50.8, 44.5, 44.4, 44.3, 44.1, 28.3, 25.6.

HRMS (LC-Orbitrap-IDX) calculated for $[M+H]^+$ $C_{14}H_{25}O_6^+$ (m/z): 289.1646; found: 289.1643. Calculated for $[M+NH_4]^+$ $C_{14}H_{28}O_6N^+$ (m/z): 306.1911; found: 306.1908. Calculated for $[M+Na]^+$ $C_{14}H_{24}O_6Na^+$ (m/z): 311.1465; found: 311.1461.

Basic stability of *c*-hy-LNPs. *c*-hy-LNPs dispersions (10 mL) were adjusted to pH 13.0 by the addition of 2 mL of NaOH (0.1 M). Samples were incubated under orbital shaking

at 25 °C at different times (e.g. 24 hours, 48 hours and 72 hours). The evolution of particle size and morphology was evaluated by DLS and TEM measurements, respectively.

^{31}P NMR spectroscopy. The content of hydroxyl groups in SKL was determined by ^{31}P NMR spectroscopy. Details of the method used are reported in a standard procedure.[2] Briefly, the dry lignin sample (30 mg) is phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) (0.9 mmol) in the presence of *N*-hydroxy-5-norbornene-2,3-dicarboxylic acid imine (NHND) (0.010 mmol) as an internal standard and chromium(III) acetylacetonate as a relaxation agent. The ^{31}P NMR experiments (256 scans, 10 s relaxation delay) were performed with 90° pulse angle and inverse gated proton decoupling.

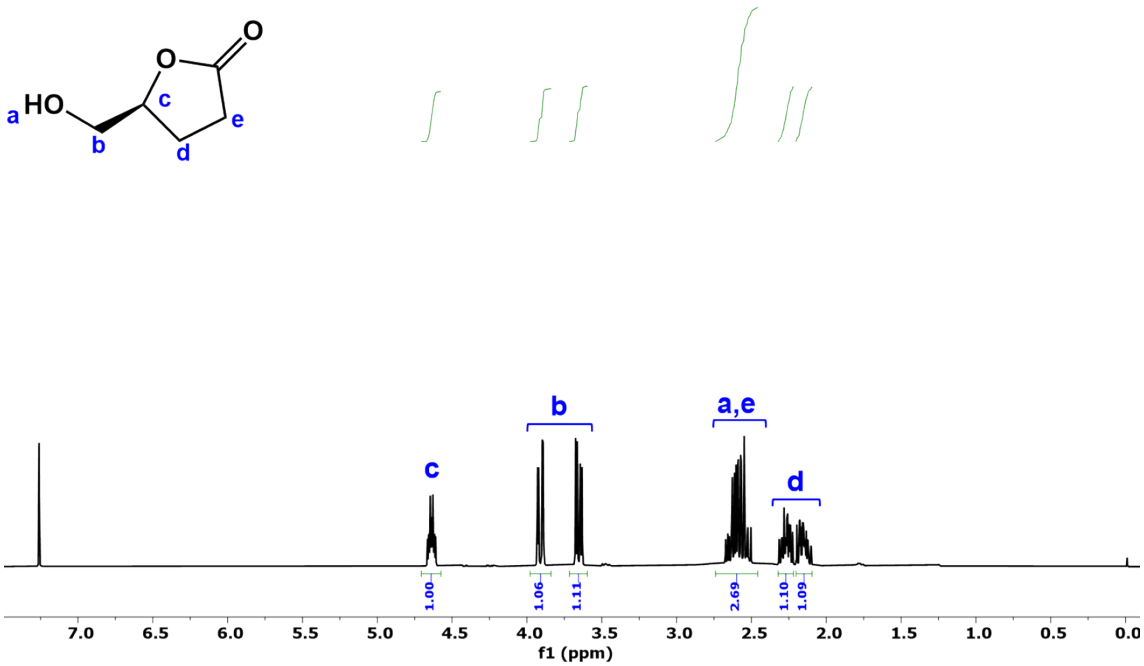


Figure S1. ^{1}H NMR spectrum of **1** (δ (ppm), $CDCl_3$)

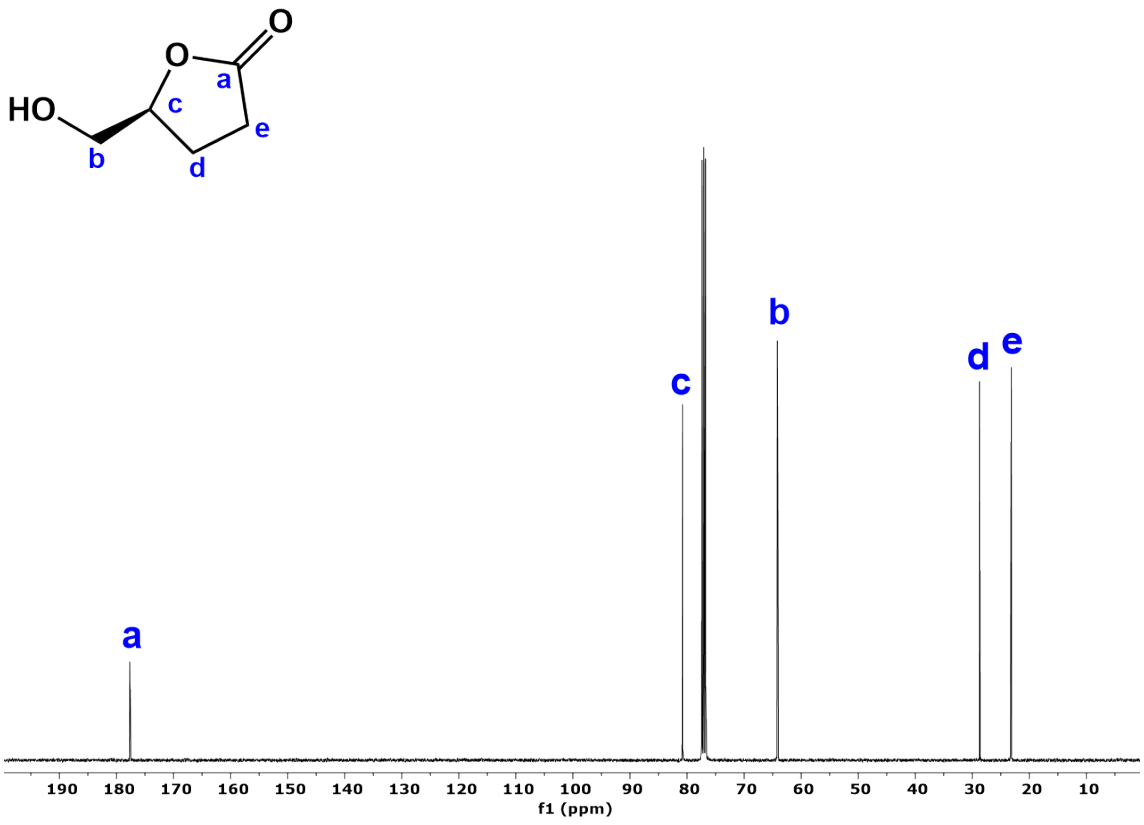


Figure S2. ^{13}C NMR spectrum of **1** (δ (ppm), $CDCl_3$)

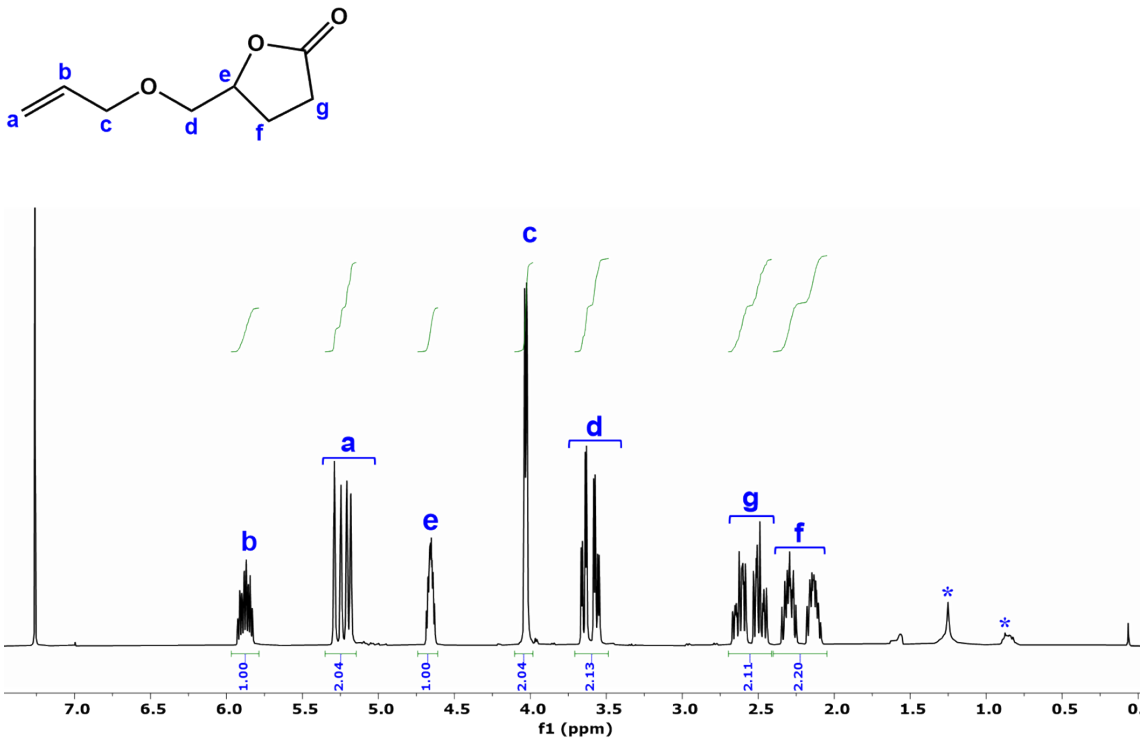


Figure S3. ^{1}H NMR spectrum of **2** (δ (ppm), $CDCl_3$). Marked signals (*) correspond to mineral oil.

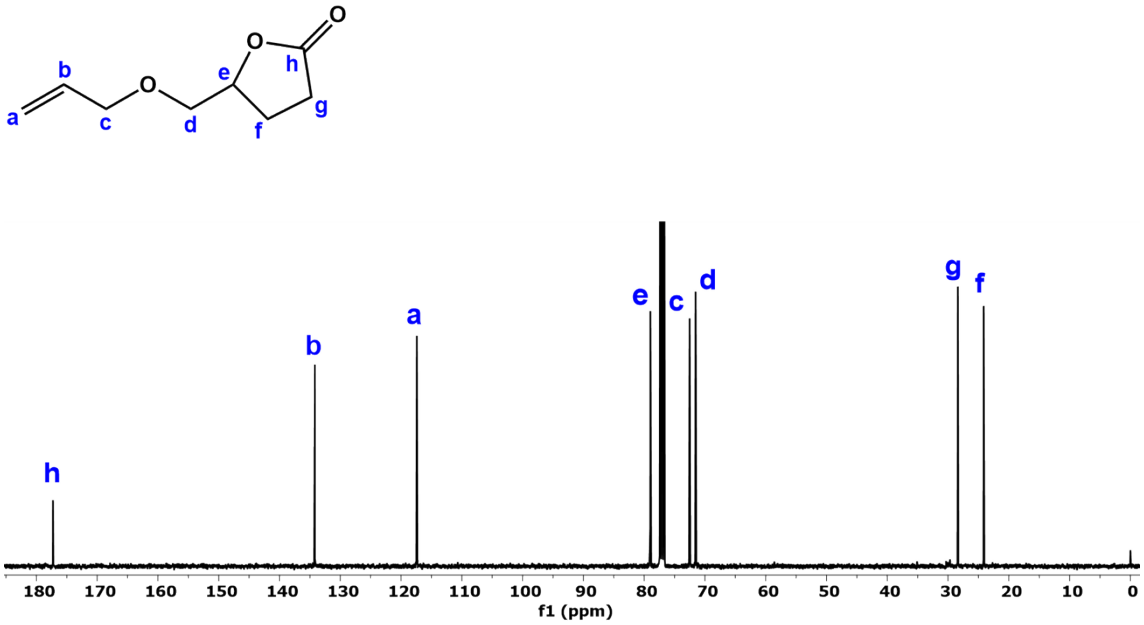


Figure S4. ^{13}C NMR spectrum of **2** (δ (ppm), $CDCl_3$)

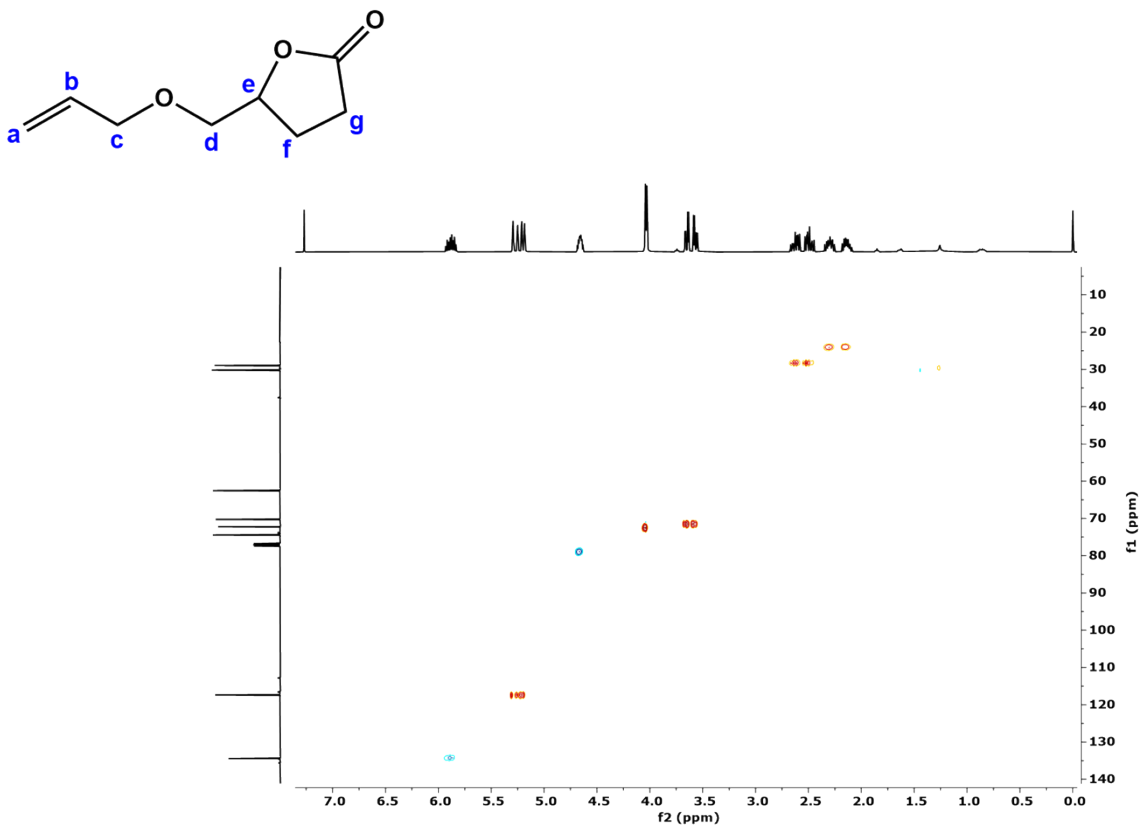


Figure S5. 2D ^{1}H-^{13}C HSQC NMR spectrum of **2** (δ (ppm), $CDCl_3$)

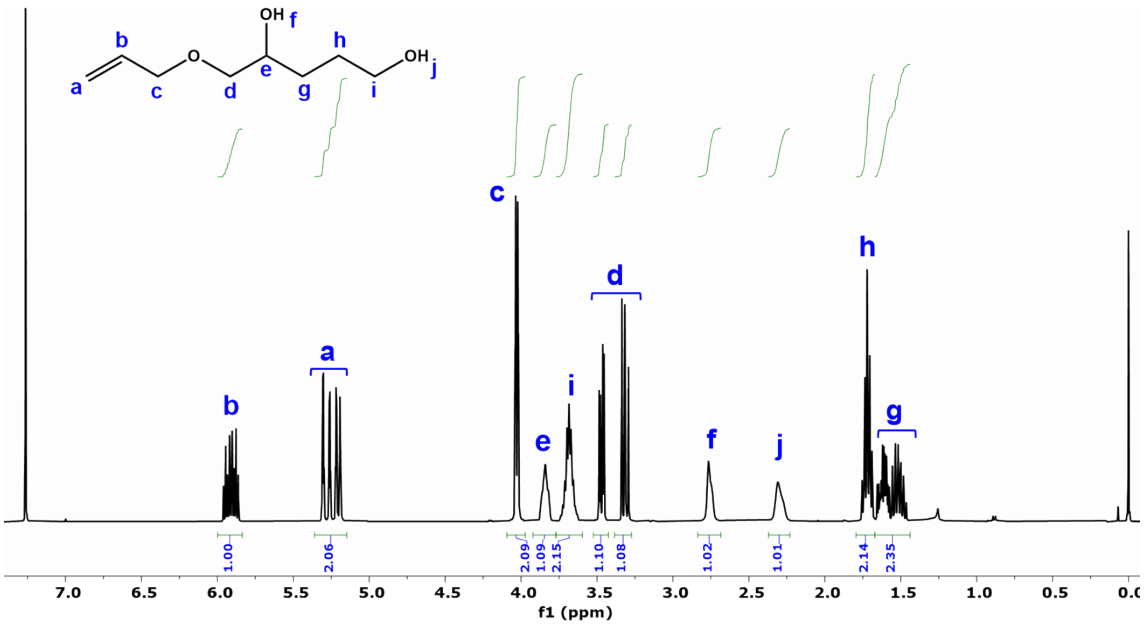


Figure S6. ^{1}H NMR spectrum of **3** (δ (ppm), $CDCl_3$)

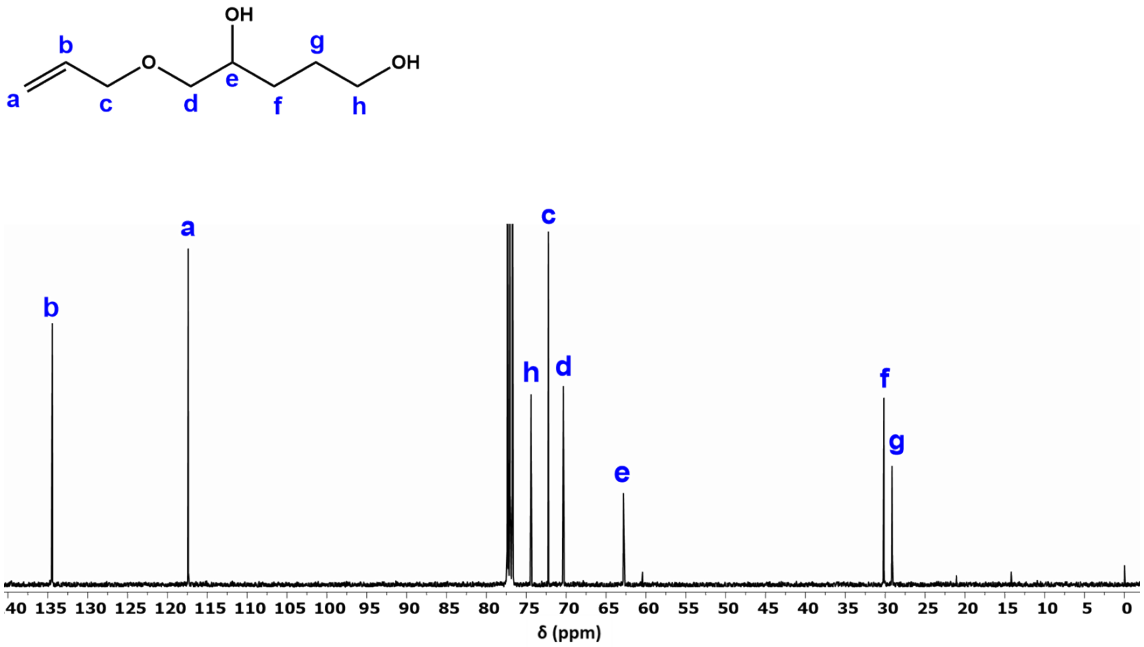


Figure S7. ^{13}C NMR spectrum of **3** (δ (ppm), $CDCl_3$)

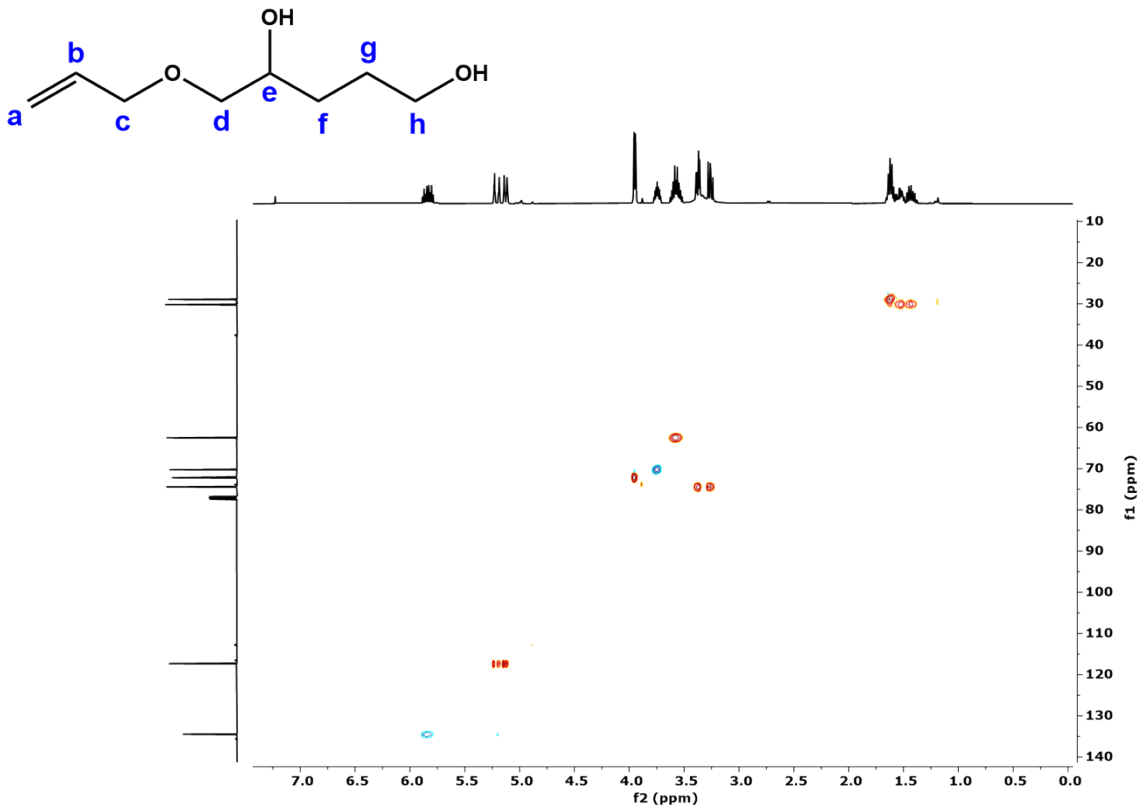


Figure S8. 2D ^{1}H-^{13}C HSQC NMR spectrum of **3** (δ (ppm), $CDCl_3$)

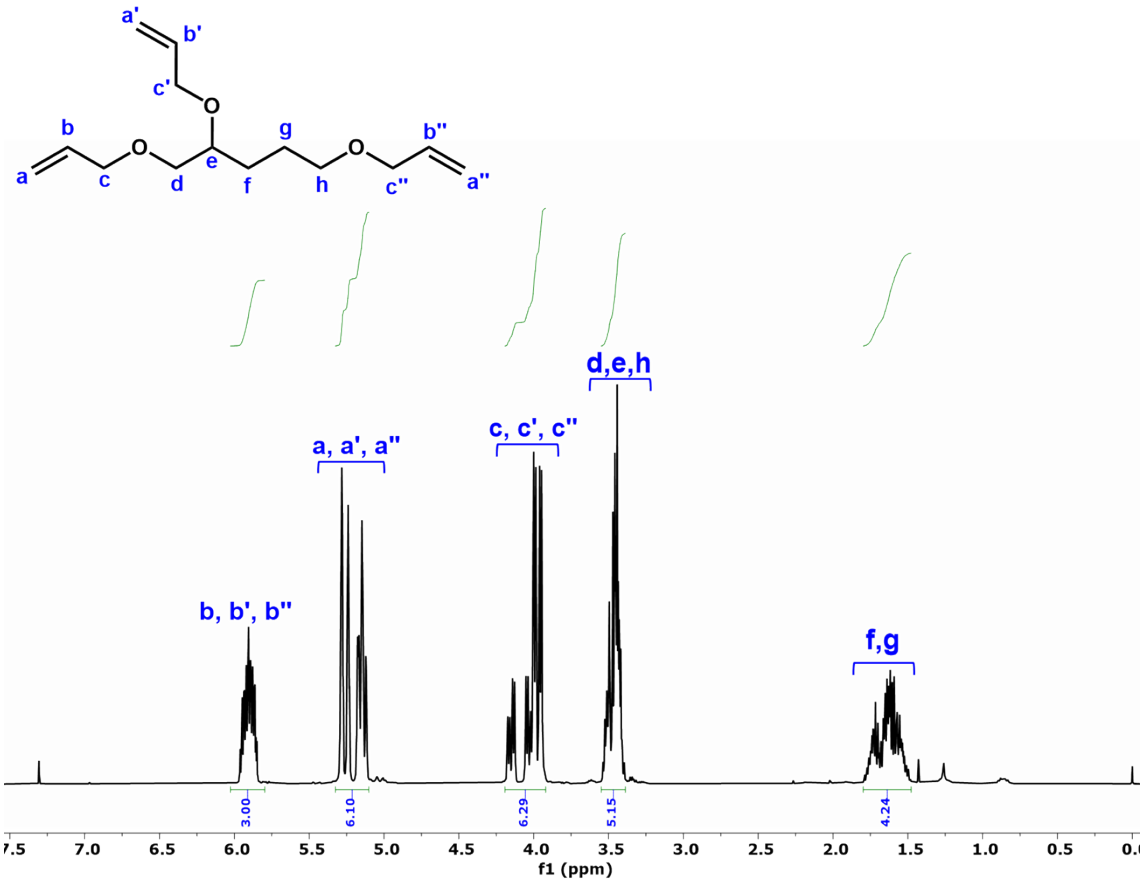


Figure S9. ^{1}H NMR spectrum of **4** (δ (ppm), $CDCl_3$)

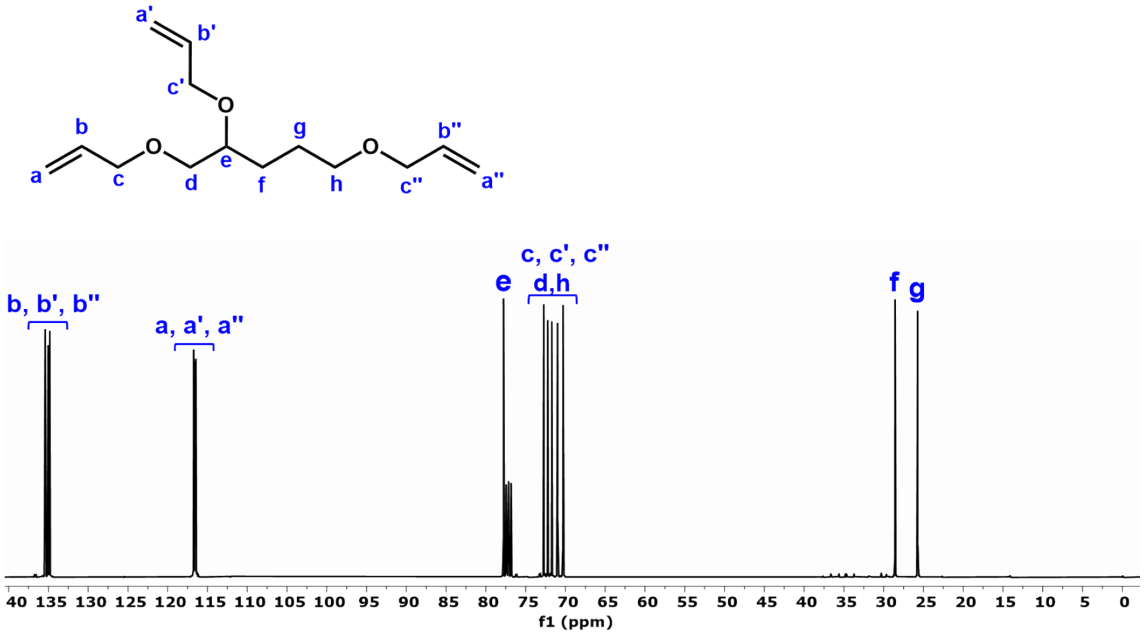


Figure S10. ^{13}C NMR spectrum of **4** (δ (ppm), $CDCl_3$)

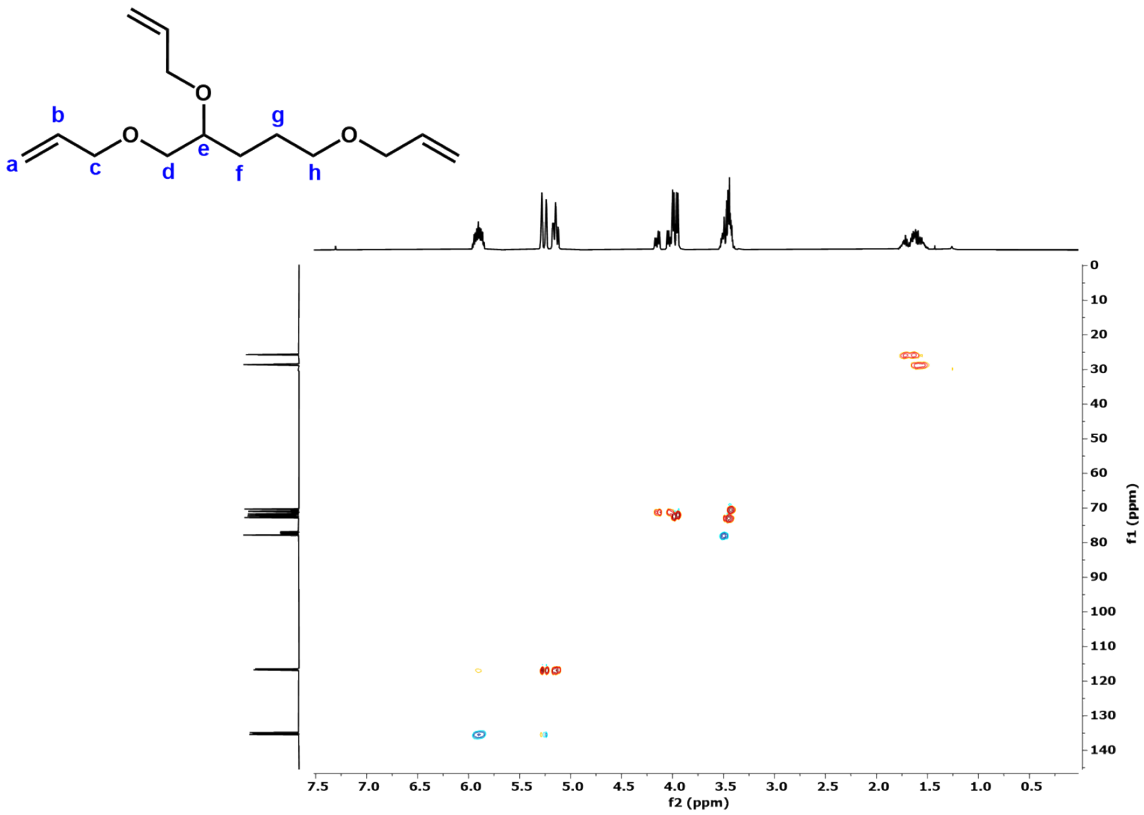


Figure S11. 2D ^{1}H-^{13}C NMR spectrum of **4** (δ (ppm), $CDCl_3$)

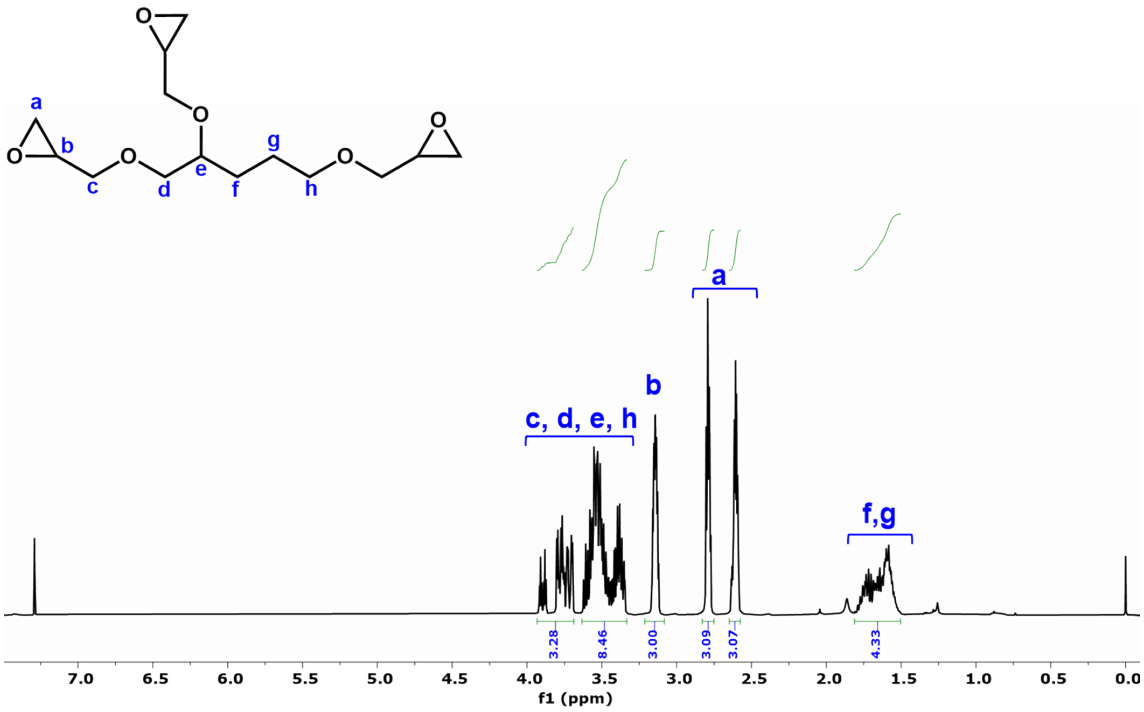


Figure S12. ^{1}H NMR spectrum of **5** (δ (ppm), $CDCl_3$)

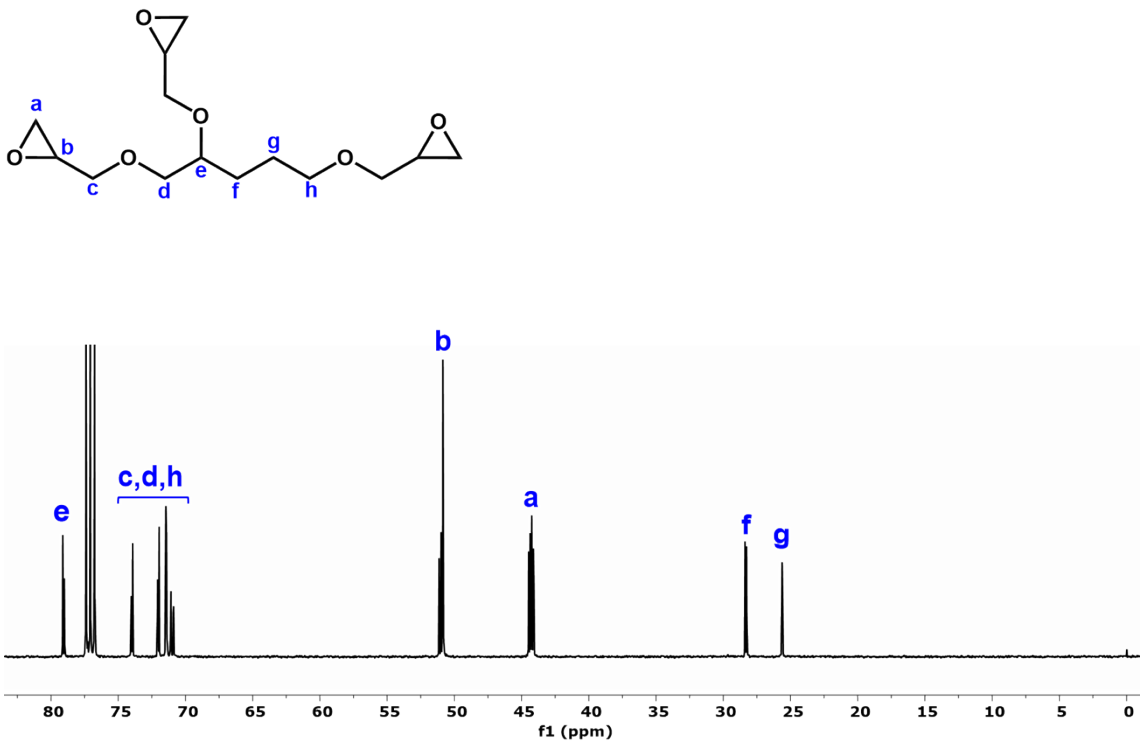


Figure S13. ^{13}C NMR spectrum of **5** (δ (ppm), $CDCl_3$)

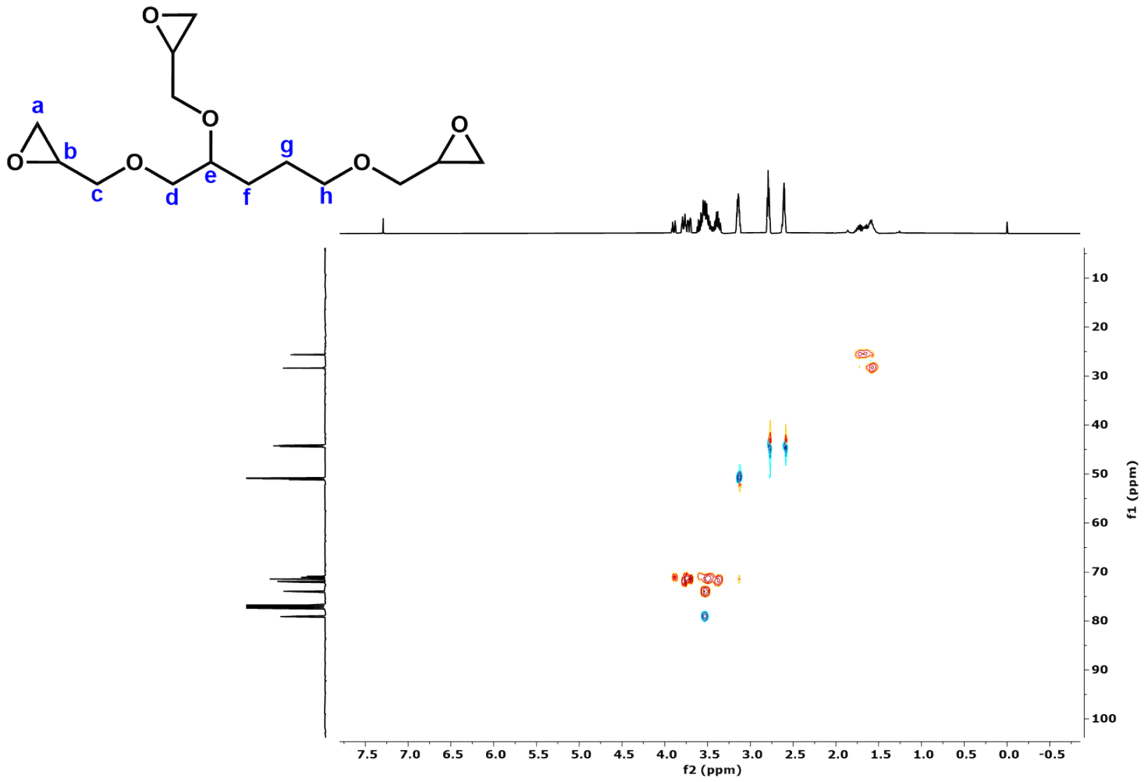
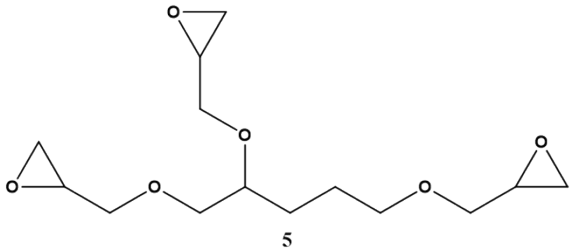


Figure S14. 2D ^{1}H-^{13}C HSQC NMR spectrum of **5** (δ (ppm), $CDCl_3$)



5

Chemical Formula: $C_{14}H_{24}O_6$
Exact Mass: 288,16

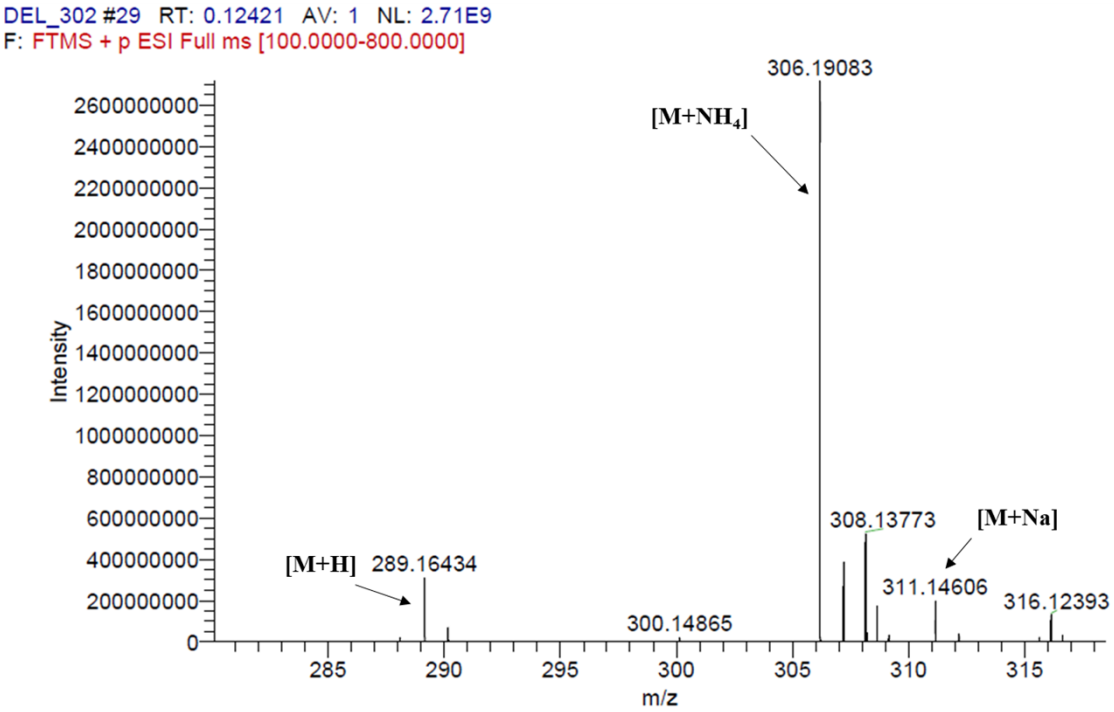


Figure S15. MS spectra of **5**.

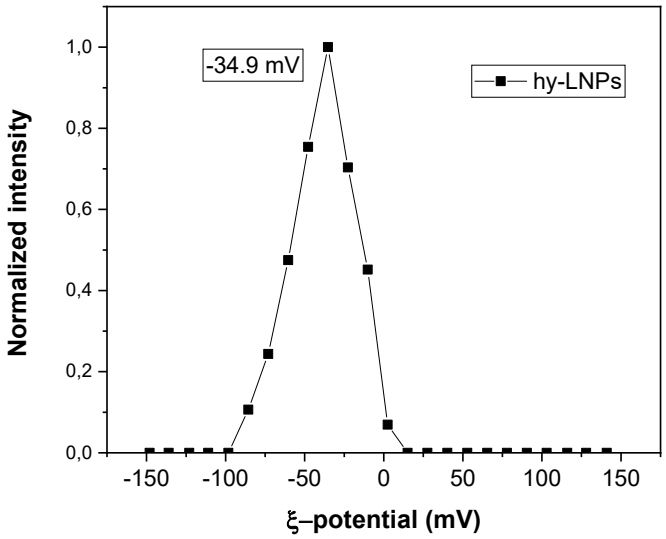


Figure S16. ζ-potential distributions of hy-LNPs employed in this work.

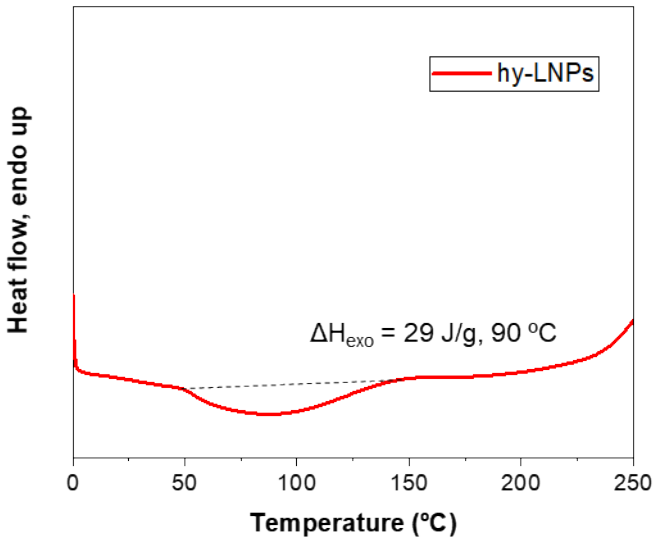


Figure S17. DSC thermogram corresponding to the dynamic curing at 10 °C min^{-1} of freeze-dried hy-LNPs.

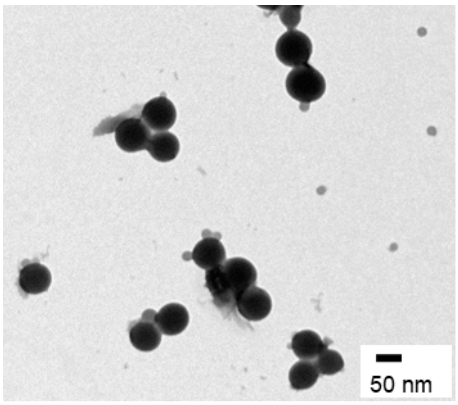


Figure S18. Transmission electron microscopy (TEM) images of *c*-hy-LNPs

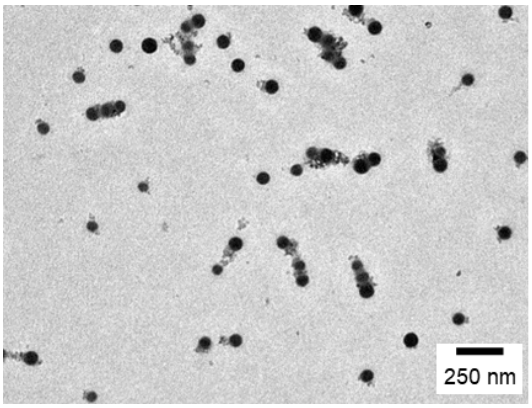


Figure S19. Transmission electron microscopy (TEM) images of *c*-hy-LNPs after being exposed to basic conditions (pH = 13) for 24 hours.

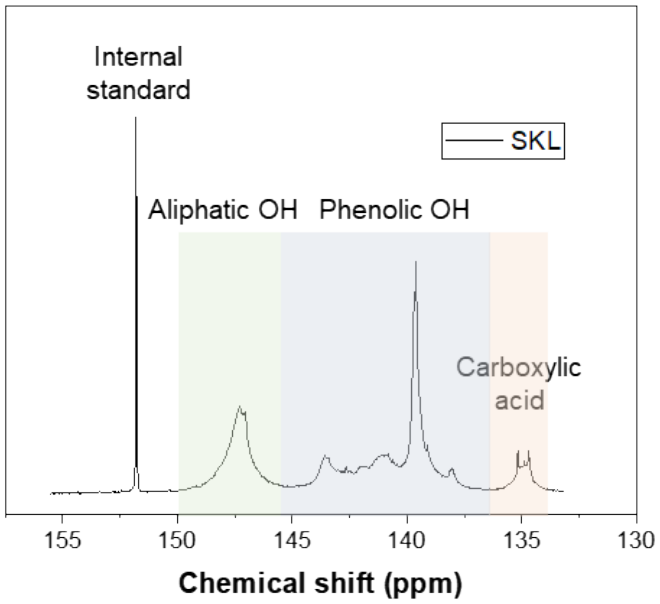


Figure S20. Quantitative ^{31}P NMR spectra of SKL employed in this work.

Table S1. Concentration of Aliphatic and Phenolic OH of SKL according to quantitative ^{31}P NMR.

Sample	Aliphatic OH	Phenolic OH	Carboxylic acid	Total OH
SKL	1.88	4.04	0.28	6.21

[a] Unit mmol/g.

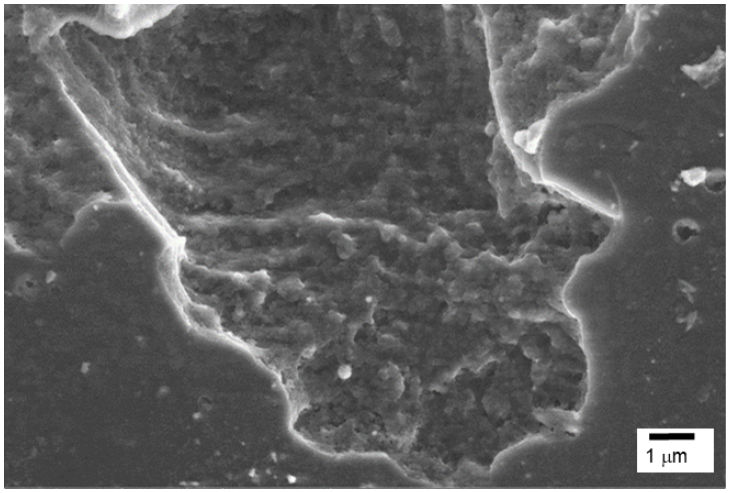


Figure S21. Scanning electron microscopy (SEM) micrograph of cross-sectional surface of *c*-hy-LNPs@gel.

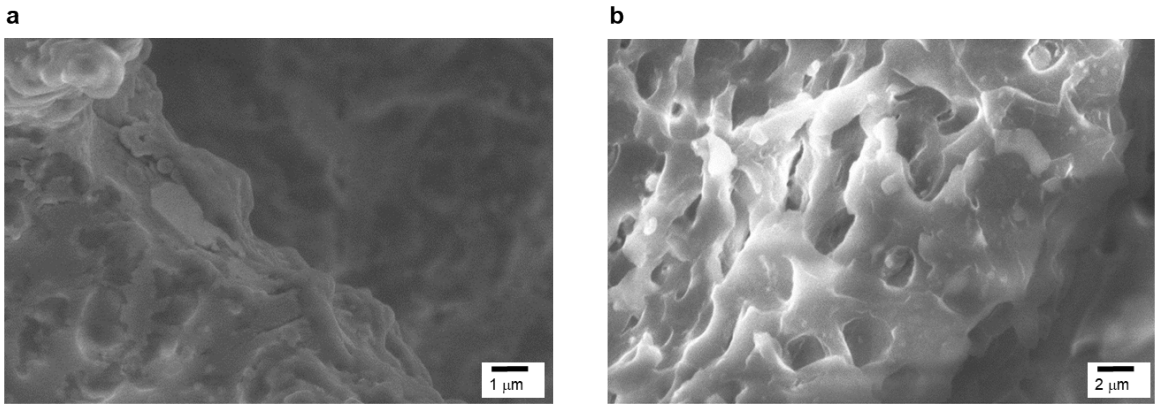


Figure S22. Scanning electron microscopy (SEM) micrographs of top surface of (a) hybrid@gel and (b) SKL@gel.

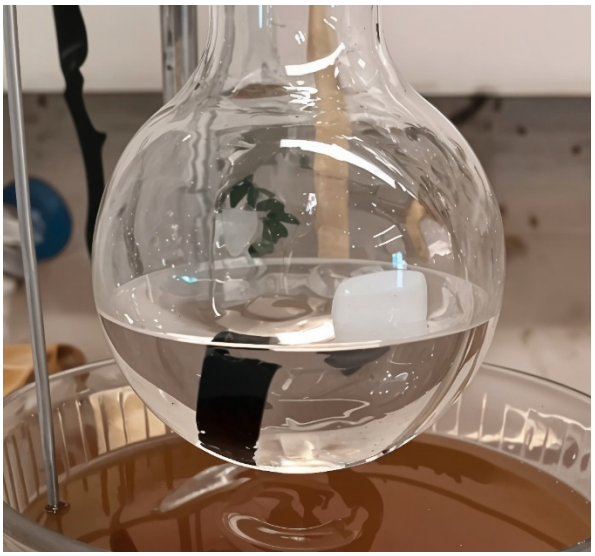


Figure S23. Extraction of particulate lignin-based hydrogel with tetrahydrofuran at 70 °C after 48 hours. The clear solution confirms the absence of LNP leaching, and, along with the gel content calculation (>98%), indicates the complete integration of LNPs within the hydrogel matrix.

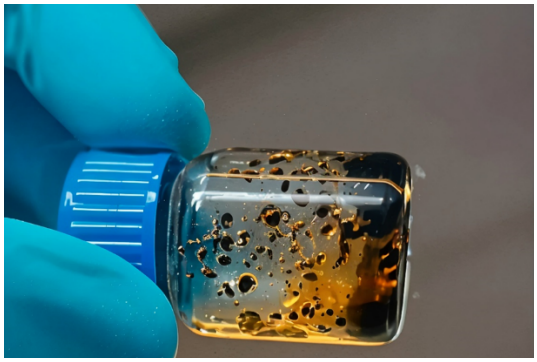


Figure S24. Digital image of particulate lignin-based AIHs after a 2-hour hydration process with a DEA-aqueous solution using 7.5 wt% hydrogel based on the liquid amine solution. Small portions of liquid solution can be observed, attributed to the squeezing of the amine solution from the hydrogel due to an inappropriate balance between the hydrogel and the liquid amine solution.

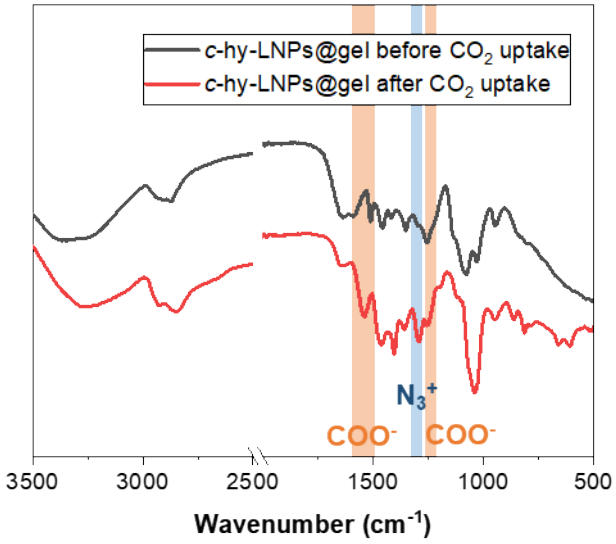


Figure S25. FTIR spectra of lignin-based AIHs (*c*-hy-LNPs@gel) after (red plot) and before (black plot) the absorption of CO_2.

[1] A. Moreno, J. Delgado-Lijarcio, J. C. Ronda, V. Cádiz, M. Galià and M. H. Sipponen, *Small*, **2023**, *19*, 2205672.

[2] X. Meng, C. Crestini, H. Ben, N. Hao, Y. Pu, A. J. Ragauskas and D. S. Argyropoulos, *Nat. Protoc.* **2019**, *14*, 2627-2647.