Electronic Supplementary Material (ESI) for Polymer Chemistry.

A proof-of-concept study on a fully biobased and degradable polymer network based on vanillin and myrcene

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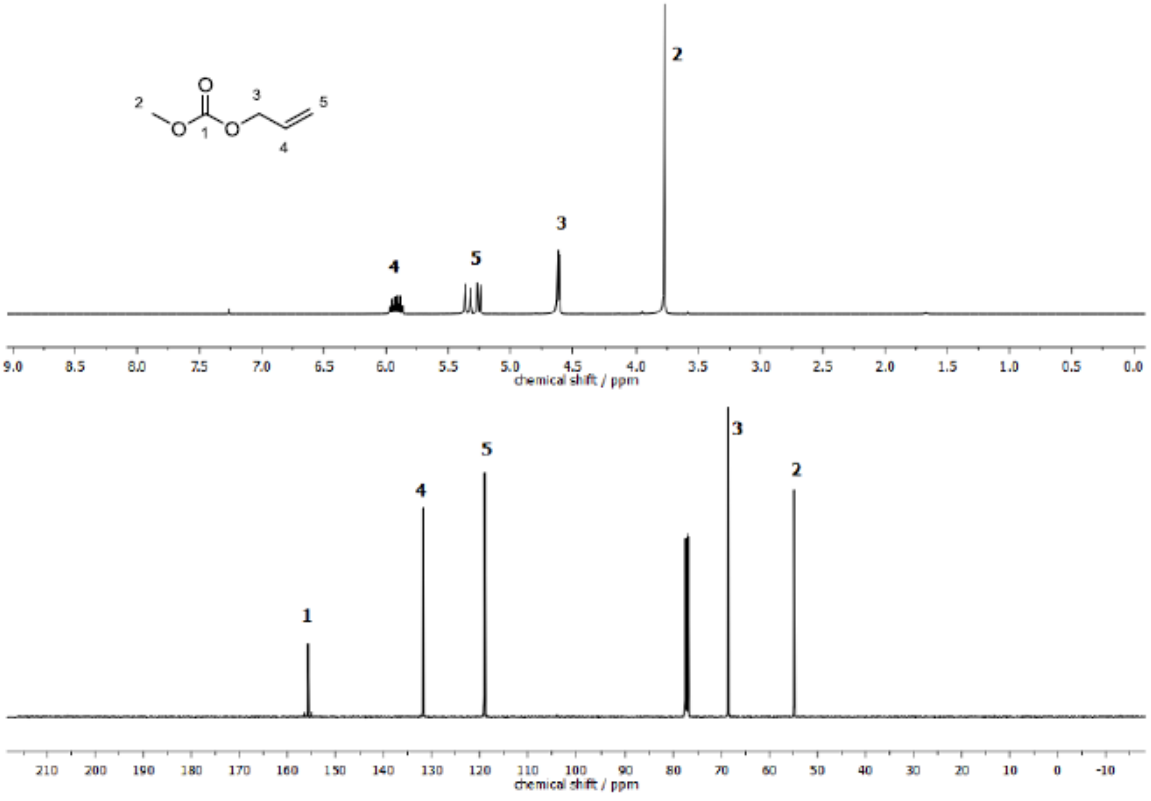


Figure S1. Top: ^{1}H-NMR spectrum of allyl methyl carbonate; bottom: ^{13}C NMR spectrum of allyl methyl carbonate in $CDCl_3$.

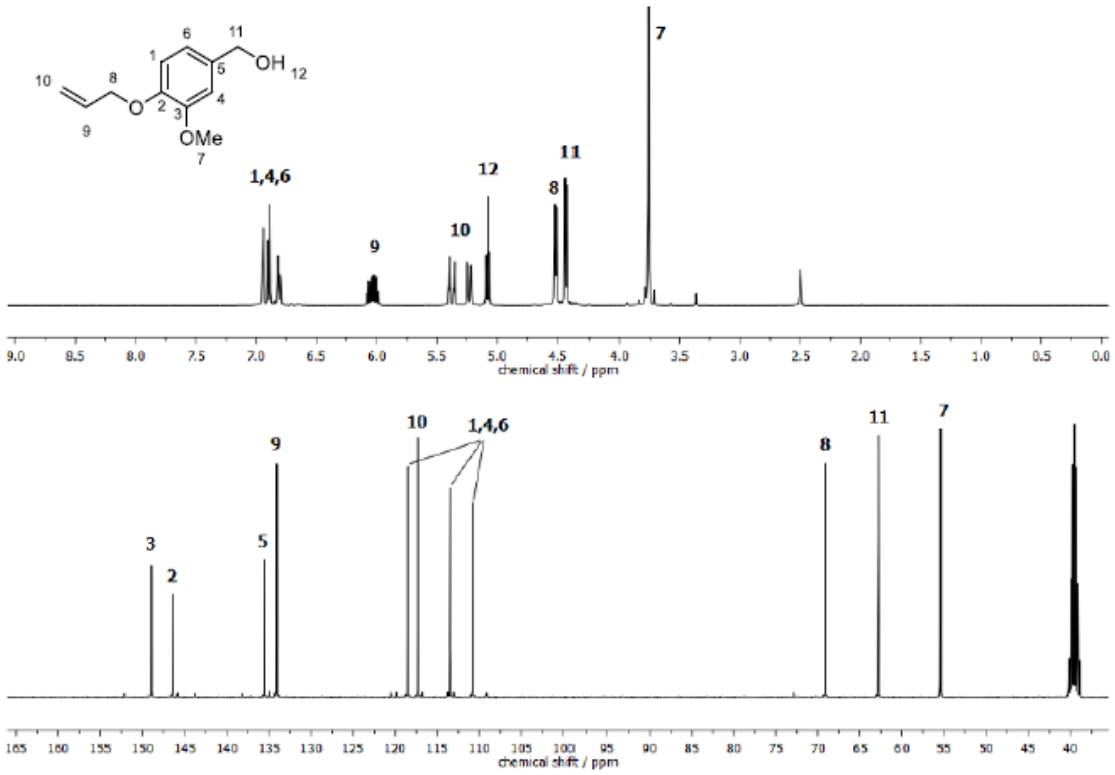


Figure S2. Top: ^{1}H-NMR spectrum of **AVA**; bottom: ^{13}C NMR spectrum of **AVA** in DMSO-d_6.

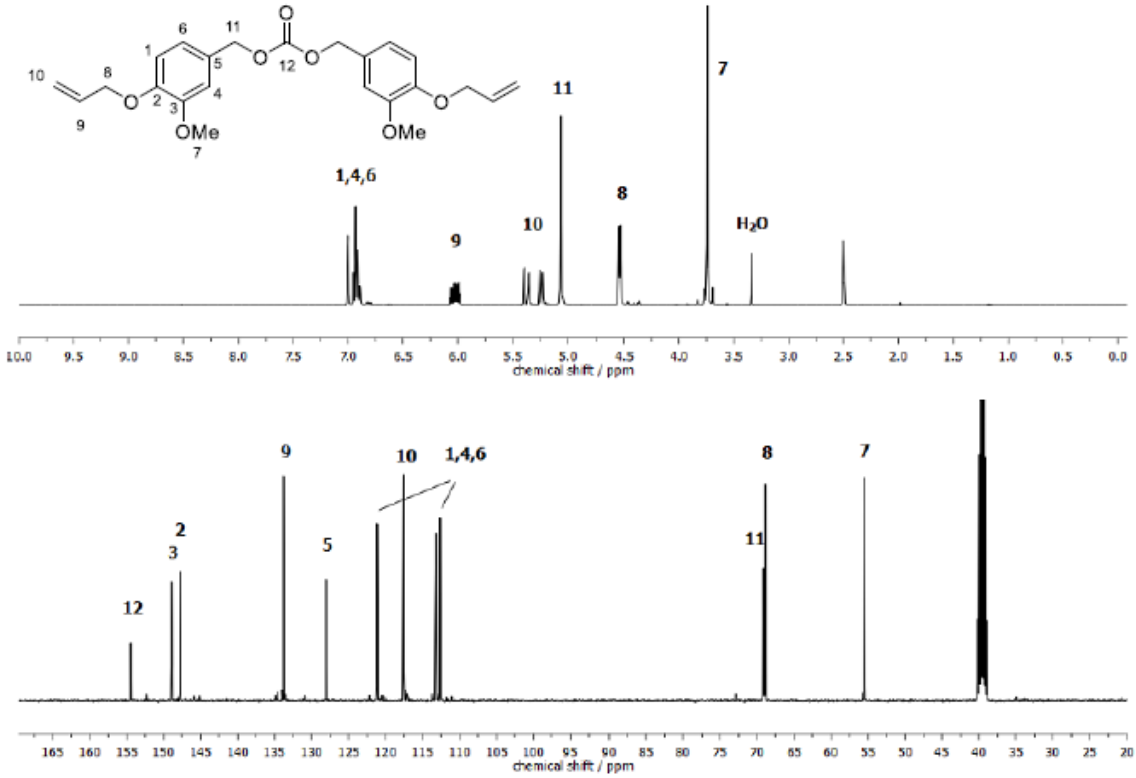


Figure S3. Top: ^{1}H-NMR spectrum of **AVACarb**; bottom: ^{13}C NMR spectrum of **AVACarb** in DMSO-d_6.

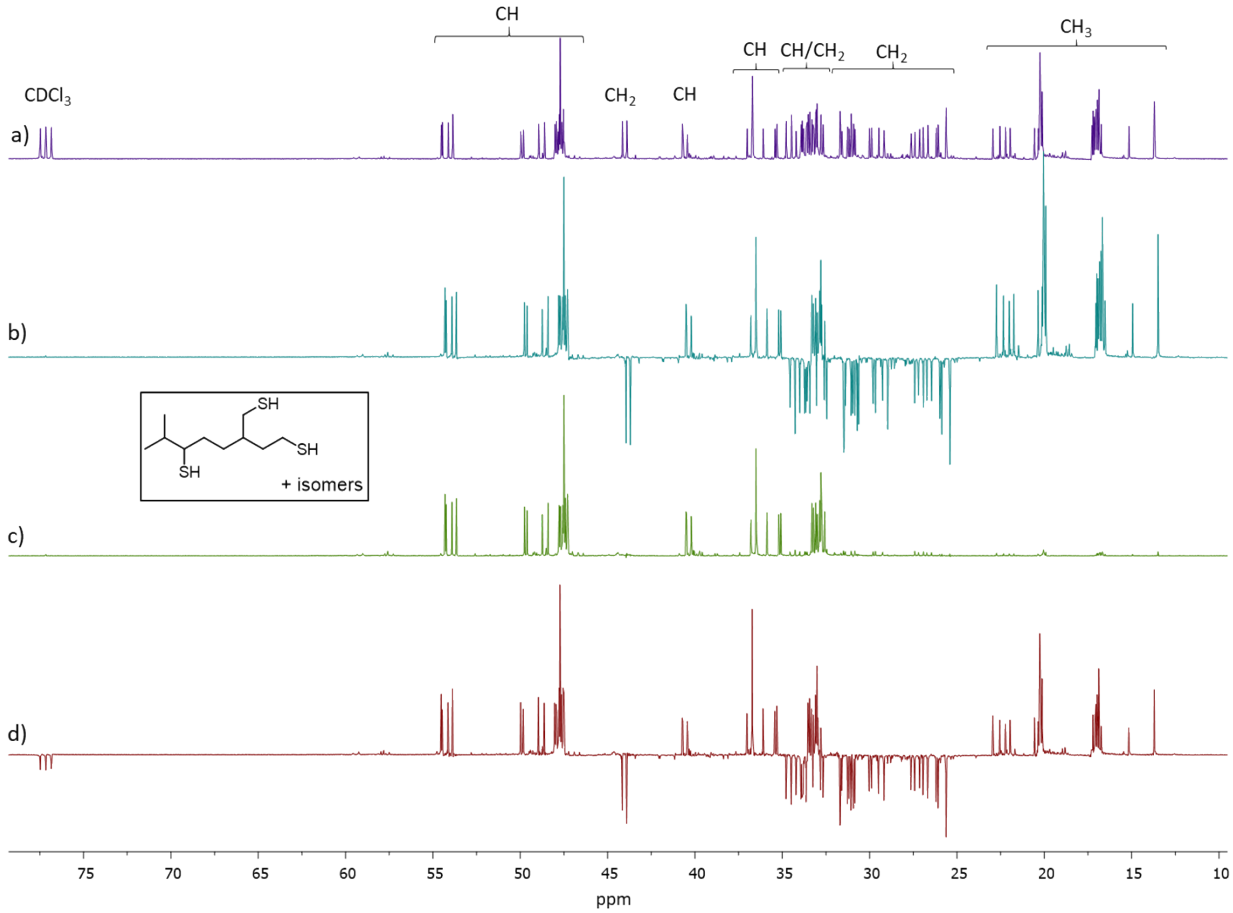


Figure S4. NMR spectra of myrcene trithiol in $CDCl_3$: (a) ^{13}C NMR, (b) Jmod, (c) DEPT 90, (d) DEPT 135

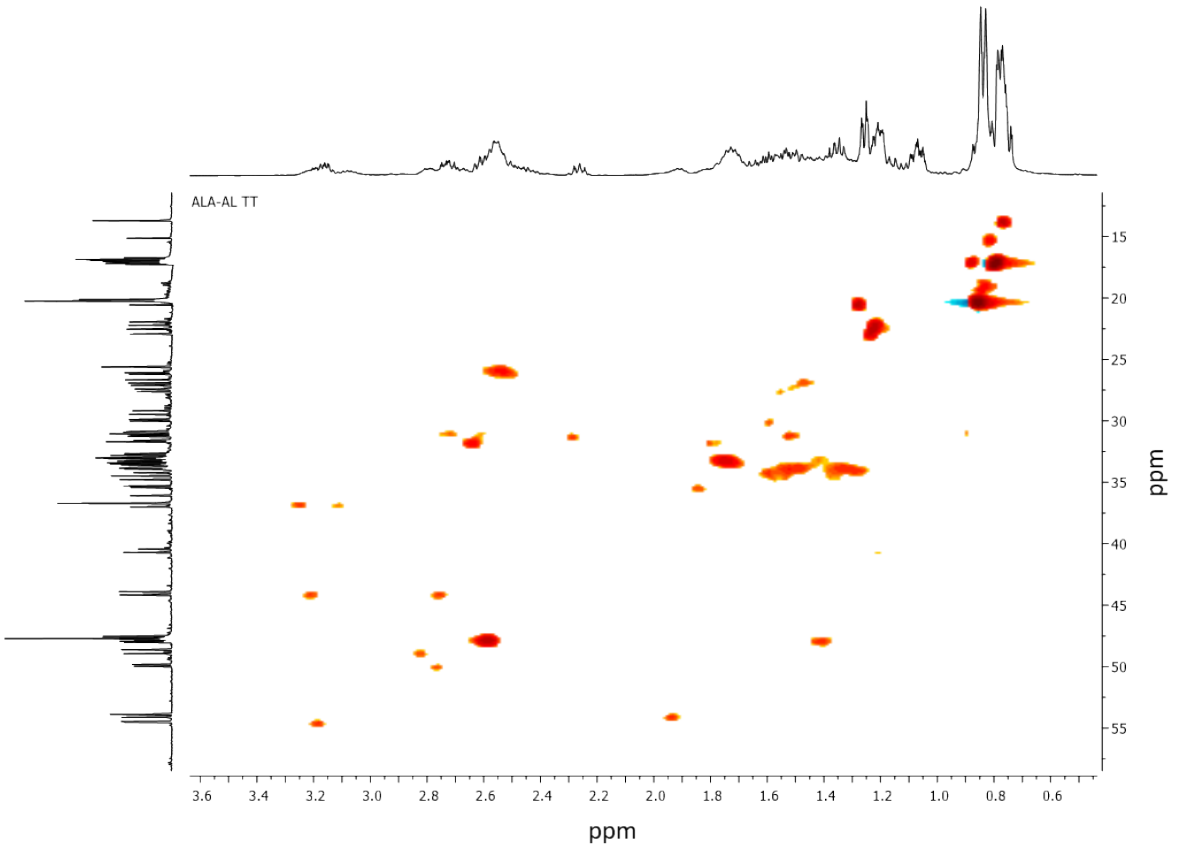
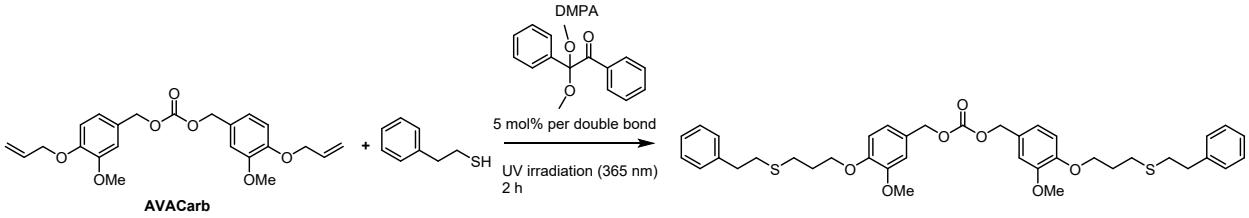


Figure S5. HSQC analysis of myrcene trithiol in $CDCl_3$

Synthesis of the model thiol-ene adduct



Scheme S1. Synthesis of a model thiol-ene adduct from **AVACarb**

In a reactor vessel, **AVACarb** (10 mg, 0.024 mmol) was mixed with 2-phenylethanethiol (6.5 µL, 0.048 mmol) in a double bond:thiol ratio of 1:1. Then, DMPA (5 mol% per double bond) was added. To ensure homogeneity, degassed chloroform (0.1 mL) was added into the reactor vessel. The resulting solution was placed into the UV oven under UV irradiation (365 nm, 50% power) for 2 hours.

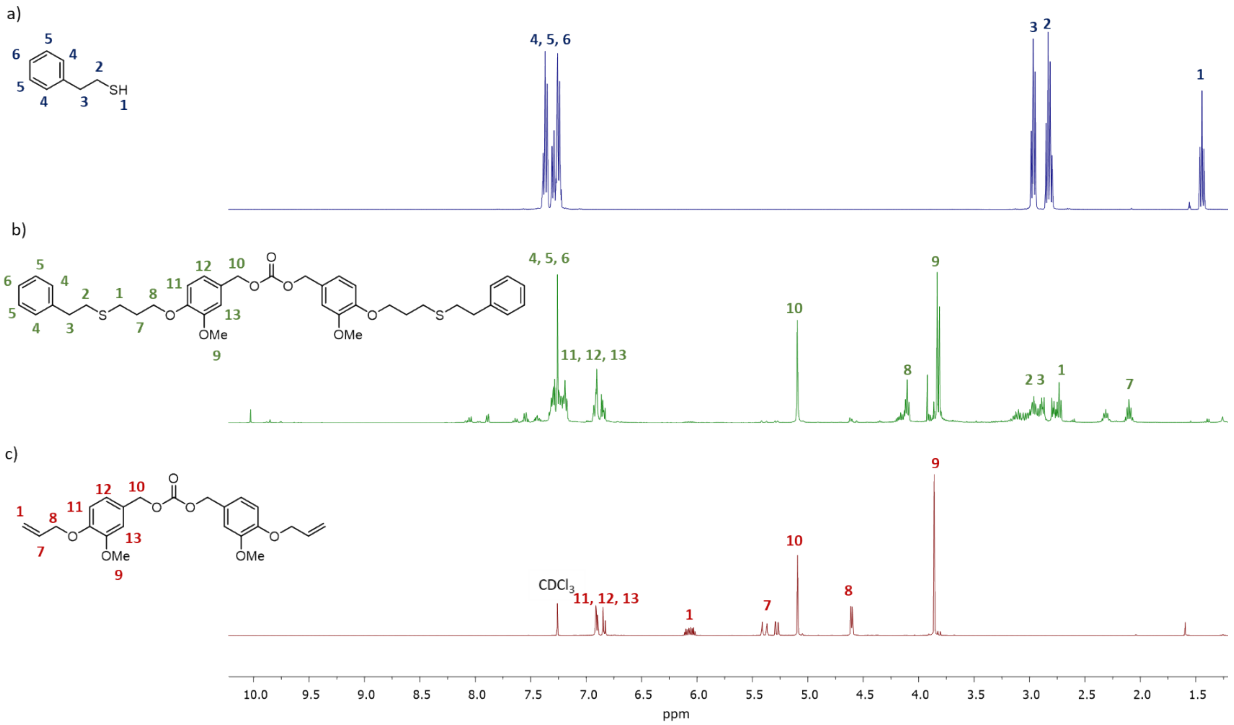


Figure S6. ^{1}H NMR spectra of 2-phenylethanethiol (a), the crude reaction mixture after synthesis of the model thiol-ene adduct (b) and **AVACarb** (c).

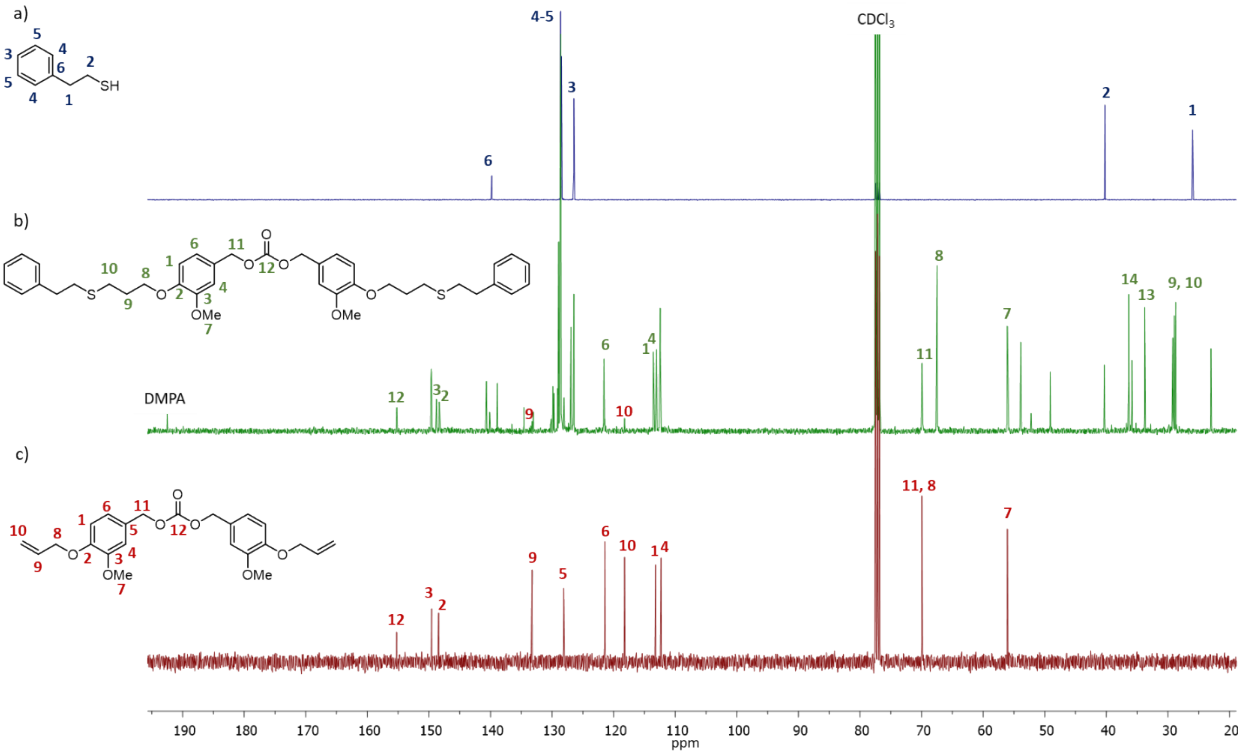


Figure S7. ^{13}C NMR spectra of 2-phenylethanethiol (a), the crude reaction mixture after synthesis of the model thiol-ene adduct (b) and **AVACarb** (c).

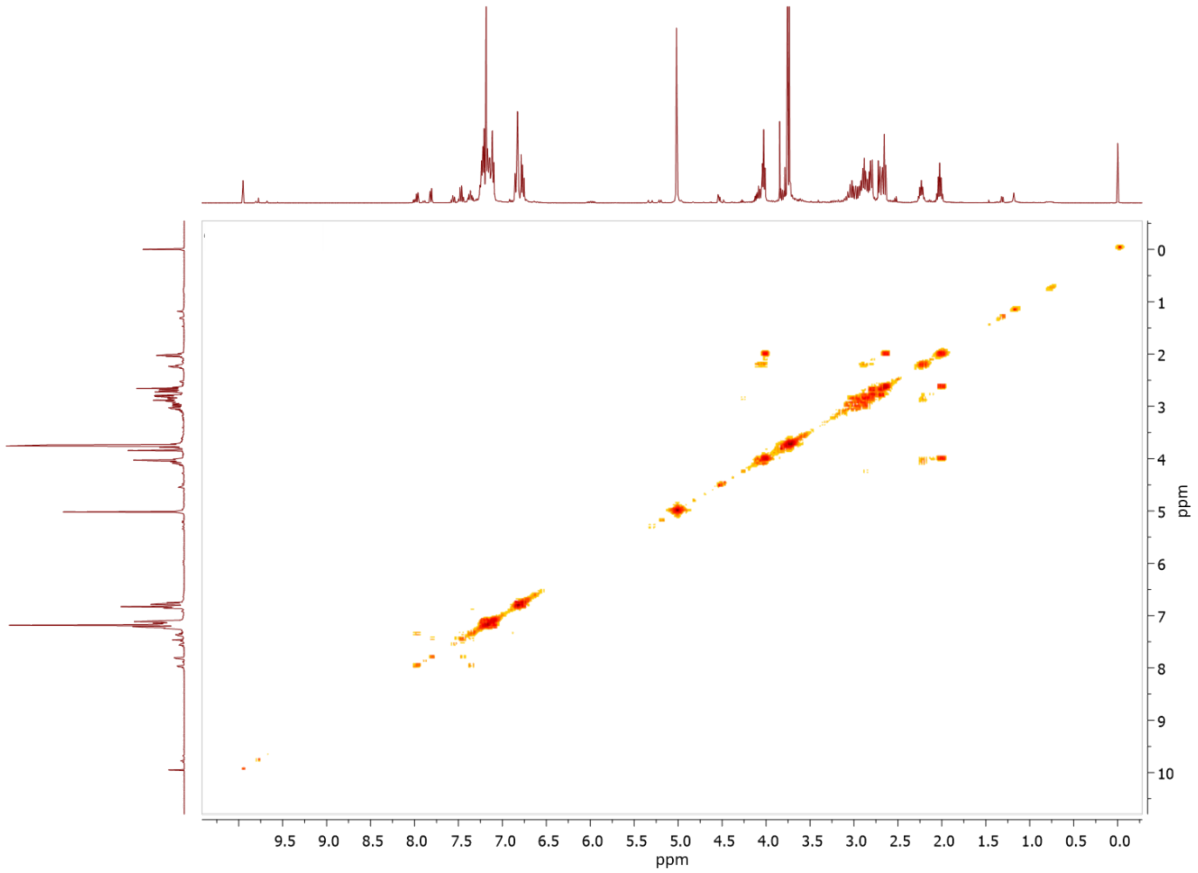


Figure S8. COSY analysis the crude reaction mixture after synthesis of the model thiol-ene adduct in $CDCl_3$.

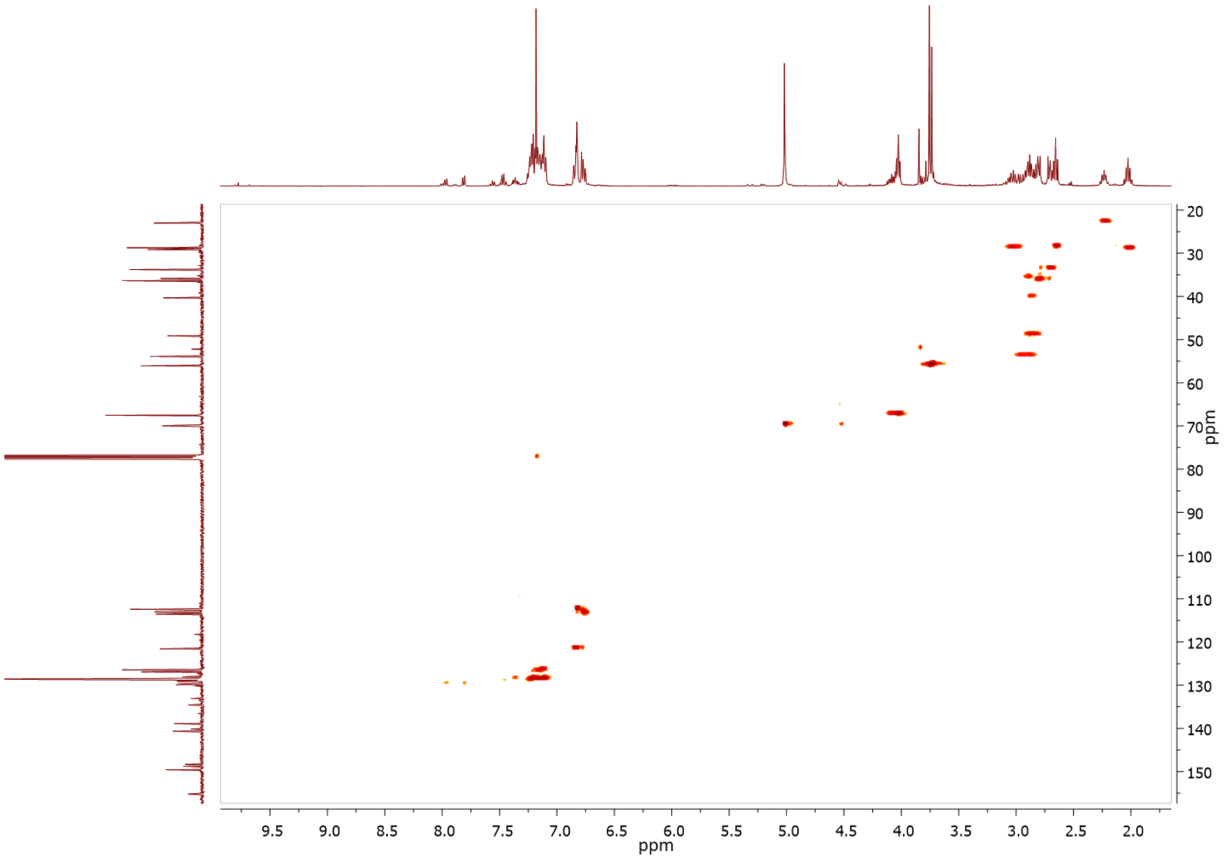


Figure S9. HSQC analysis the crude reaction mixture after synthesis of the model thiol-ene adduct in $CDCl_3$.

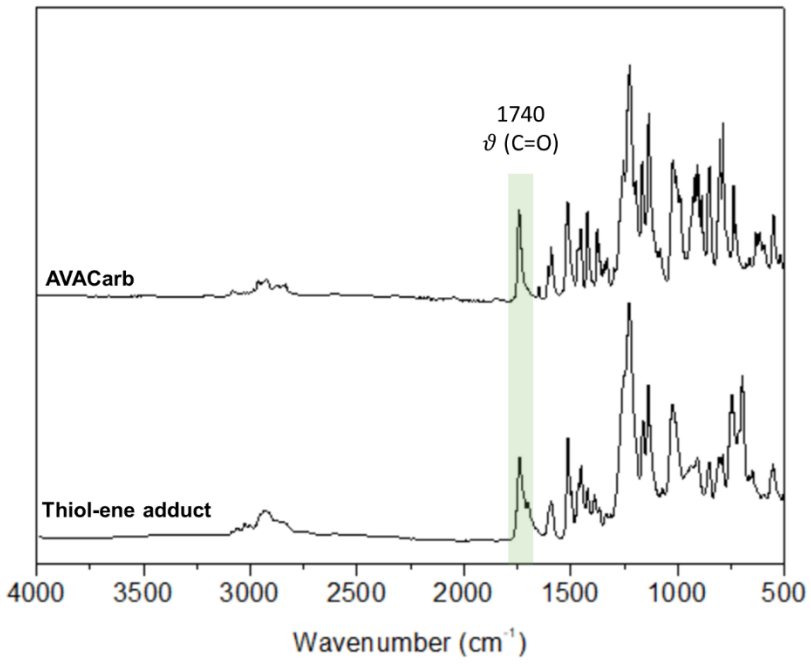


Figure S10. FTIR spectra of AVACarb (top) and the crude reaction mixture after synthesis of the model thiol-ene adduct.

Method: LC-ESI/MS analysis

LC-ESI/MS analysis were performed on a Linear Ion Trap mass spectrometer (LTQ, Thermo Fisher Scientific) linked to Vanquish liquid chromatography system (Thermo Fisher Scientific) consisted of pump VF-P20-A, a UV-VIS detector (VF-V40-4 set at 280 nm), a column oven (VH-C10-A) and an autosampler (VF-A10-A). Identification was based on full-scan MS covering m/z 150–2000 and in MSn mode. Raw data were analysed by Xcalibur software (Thermo Fisher Scientific). HPLC-MSn analysis was performed in positive electrospray ionisation (ESI) mode with a LC column Nucleodur 100-C5 C18 ec (250 X 4 mm, 5□m) from Macherey-Nagel maintained at 25◦C. The mobile phase consisted of acetonitrile with a flow rate of 0,7mL/min. The sample was dissolved in a mixture CHCL3/ACN (1/10, v/v). Injection volume was 10 □L. Electrospray source parameters were as follows: heater temperature 45°C, capillary voltage +49 V, tube lens voltage +120V, capillary temperature 275◦C, sheath and auxiliary gas flow (N2) 50 and 10, sweep gas 0, spray voltage 5 kV.

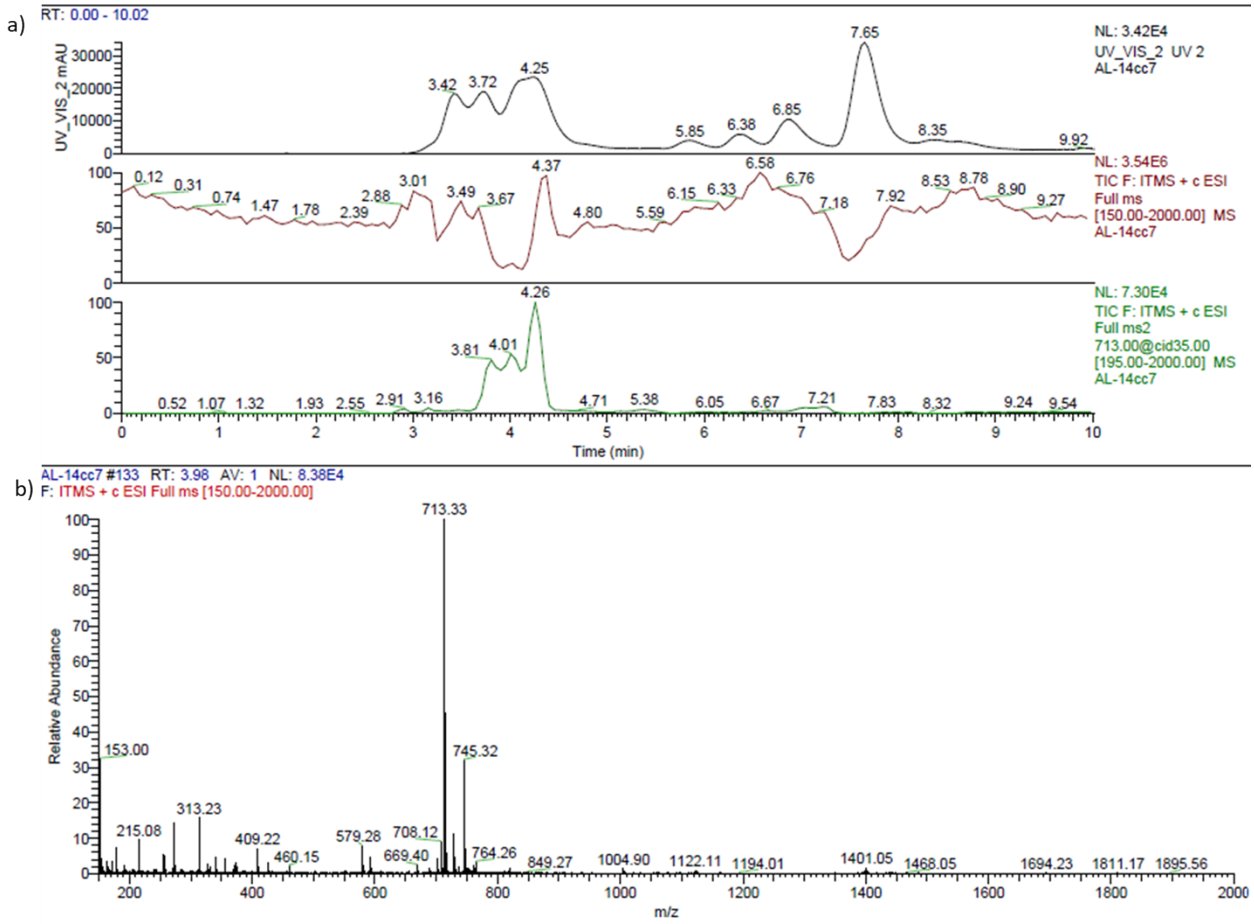


Figure S11. LC chromatogram of the crude reaction mixture after synthesis of the model thiol-ene adduct (a), ESI-MS spectrum of the peak at around 4 min of retention time revealing the mass of the expected product $[M+Na]^+$.

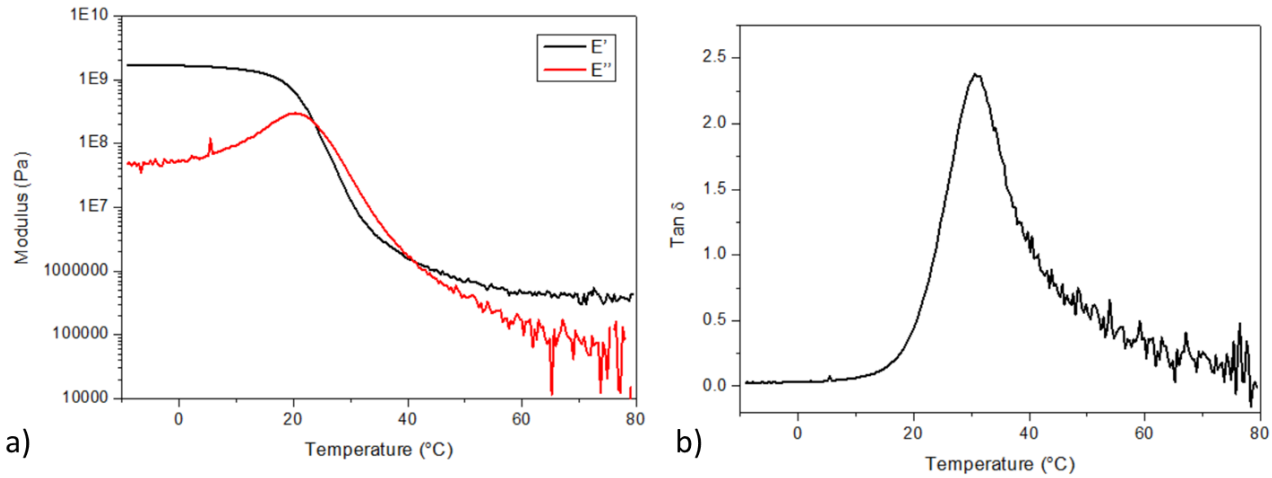


Figure S12. DMA analysis of the polymer network: evolution of the storage and loss moduli with the temperature (a) and tan δ (b).

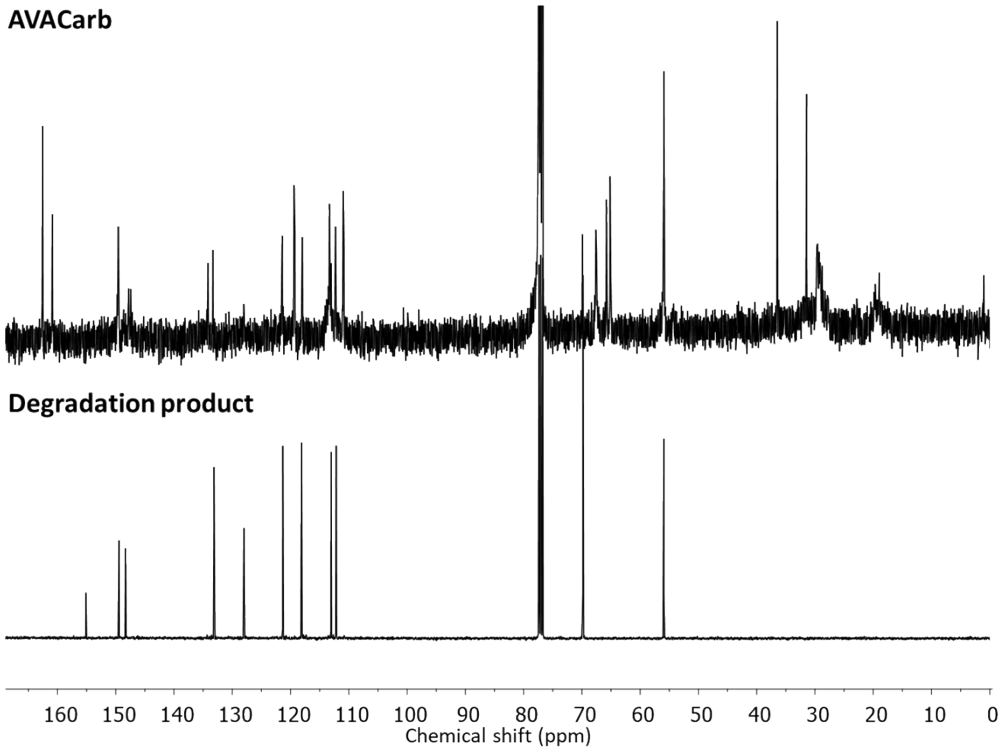


Figure S13. ^{13}C NMR spectra of AVACarb (top) and polymer network degradation product (bottom) in $CDCl_3$.

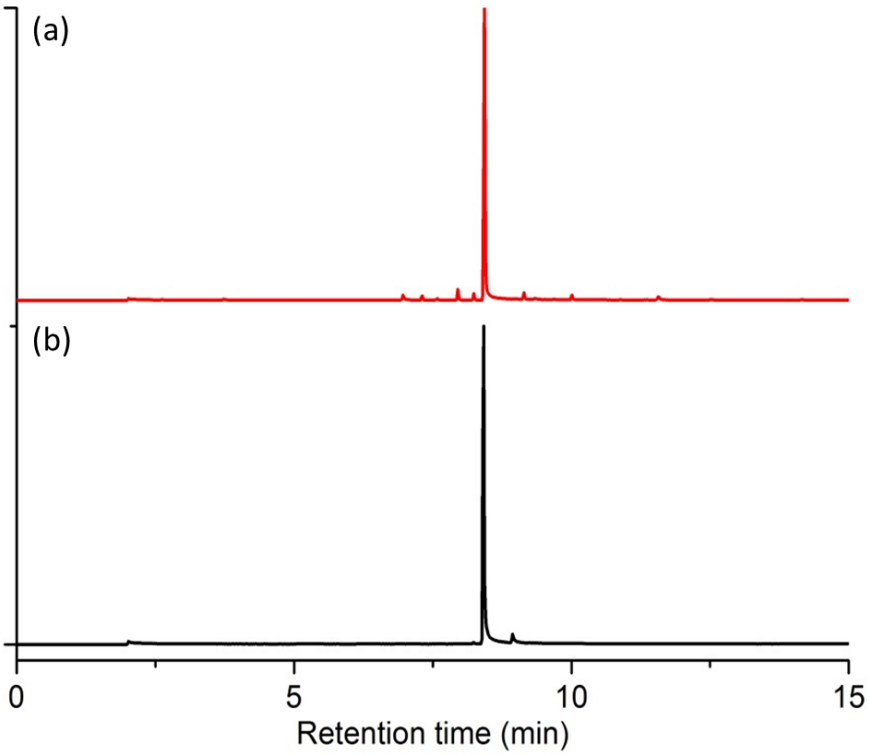


Figure S14. GC-MS chromatogram of (a) allylated vanillyl alcohol (**AVA**) and (b) degradation product of **AVACarb**.

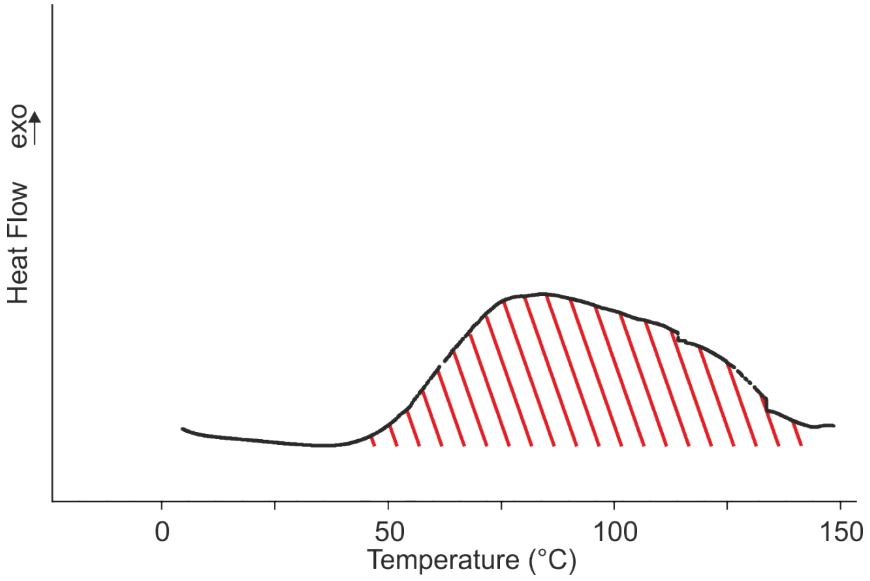


Figure S15. DSC thermogram of the repolymerization of the polyols in the presence of HMDI and catalyst showing the exotherm of the repolymerization into polyurethane (1st heating).

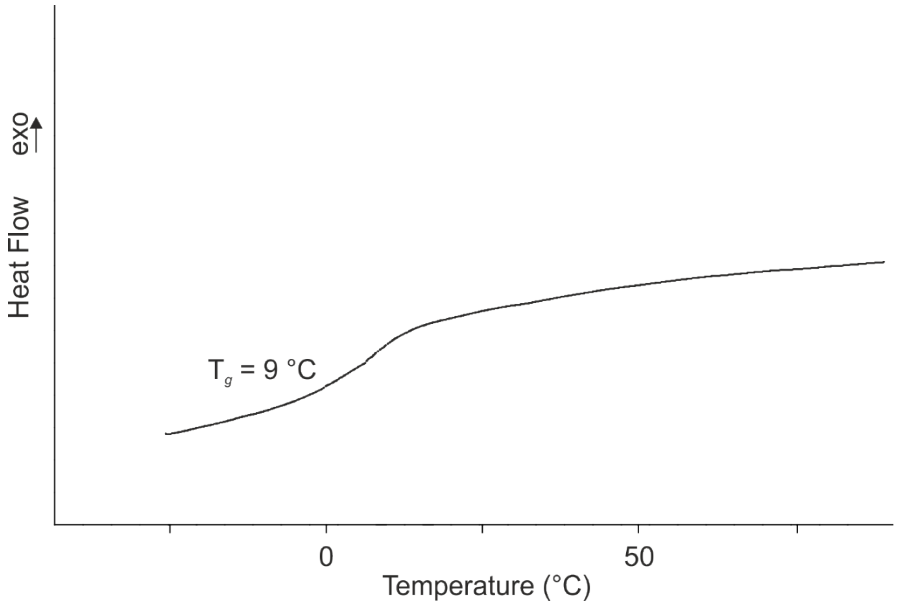


Figure S16. DSC thermogram of the repolymerization of the polyols in the presence of HMDI showing the glass transition (9 °C) of the resulting polyurethane (1st cooling).

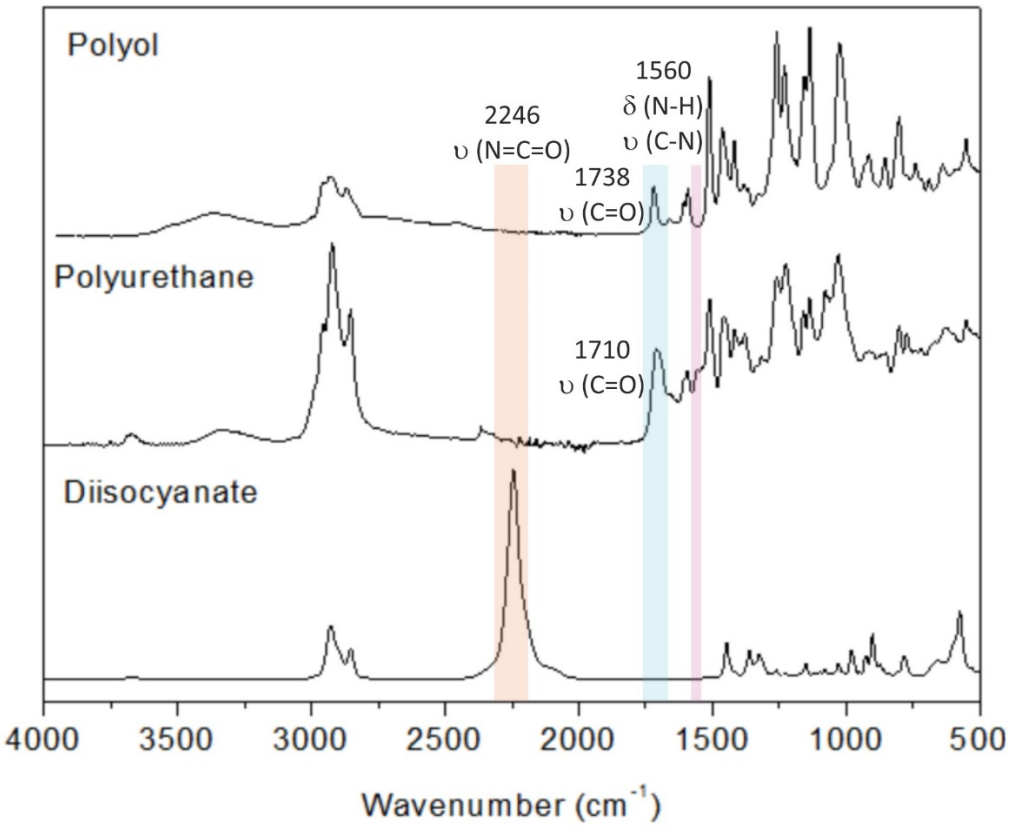
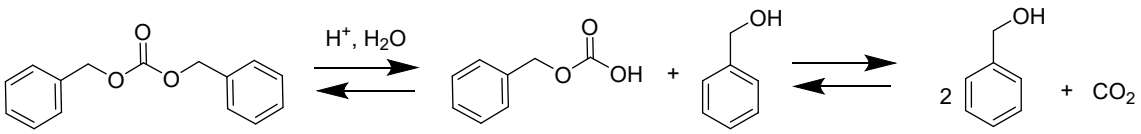


Figure S17. FTIR spectra of polyols (top), HMDI (bottom) and the resulting polyurethane (middle).



Scheme S2. Formation of carbonic acid benzylester from dibenzyl carbonate under acidic conditions.[1, 2]

Table S1. Examples of biobased commercially available polyols including OH content[3]

Biobased molecule	OH content (mg KOH/g)	Application	Producer	Product name
Rapeseed oil	56-120	Flexible PU	Stahl	Recal Bio
Castor oil	102 -168	Flexible PU	Eagle CHemicals	T series
Soybean oil	70-110	Flexible PU	Cargill	BiOH
Soybean oil	145 - 460	All	BASF	Sorvemol
Rapeseed oil	360-410	Rigid PU	Polylab	Biopolyol

References

1. C. M. Comisar, S. E. Hunter, A. Walton and P. E. Savage, *Industrial & Engineering Chemistry Research*, 2008, **47**, 577-584.
2. J. Østergaard and C. Larsen, *Molecules*, 2007, **12**, 2396-2412.
3. H. Sardon, D. Mecerreyes, A. Basterretxea, L. Avérous and C. Jehanno, *ACS Sustainable Chemistry & Engineering*, 2021, **9**, 10664-10677.