Supporting Information

Levoglucosenone to 3D-Printed Green Materials: Synthesizing Sustainable and Tunable Monomers for Eco-Friendly Photo-curing

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KEYWORDS Click-chemistry • DLP 3D-printing • Green Chemistry • Levoglucosenone • Photochemistry

Content

Experimental Procedures

Materials

LGO was graciously provided by Circa group. Allyl alcohol was purchased from Acros Organic, diethyl malonate, diethyl adipate and diethyl azelate were purchased from TCI chemicals. Anhydrous magnesium sulfate ($MgSO_4$), triethylamine (Et_3N), hydrogen peroxide (H_2O_2) were purchased from Fisher scientific. Hydrochloric acid, TLC silica gel 60 F_{254} sheets and solvents were purchased from VWR-Avantor Sciences. Novozym435 was purchased from UnivarSolutions, its activity was determined at 9993 $PLU.g^{-1}$. Quantofix peroxid 100 strips were purchased from Macherey-Nagel. Trimethylolpropane tris(3-mercaptopropionate) (TMPMP) was supplied from Sigma Aldrich. Darocure 1173 was purchased from BASF and used as photoinitiator.

Methods for monomers purification and characterization

Flash purifications were performed on a Flash XS, Interchim, equipped with prepacked PF-30SI-HP (30 µm silica gel) columns, Interchim. Mixtures of cyclohexane and ethyl acetate (EtOAc) were used as eluent. TLC plate were eluted in 1:1 cyclohexane:EtOAc eluent.
NMR analyses were recorded on a Bruker Fourier 300. ^1H NMR spectra of samples were recorded at 300 MHz; chemical shifts were reported in parts per million relative to the residual solvent peak (δ = 7.26 for $CDCl_3$). ^{13}C NMR spectra of samples were recorded at 75 MHz, chemical shifts were reported in parts per million relative to the residual solvent peak (δ = 77.16 for $CDCl_3$). $[\alpha]_D$ were recorded on a polarimeter ADP410, Bellingham Stanley. Melting points were measured on a MP50, Mettler Toledo. High-resolution mass spectrometry experiments (HRMS) were performed on a 6545 Q-TOF hybrid quadrupole time-of-flight instrument (Wilmington, DE, USA) equipped with electrospray source ionization, coupled to an Agilent Technologies 1290 UHPLC chromatography system (Santa Clara, CA, USA). The ESI source was operated in the positive and negative ionization mode with following parameters: capillary voltage, 4000 V (positive ionization mode) and 3500 V (negative ionization mode); nozzle voltage, 1000 V (positive ionization mode) and 2000 V (negative ionization mode); gas temperature, 325 °C; gas flow, 11 L/min; nebulizer, 35 psi; fragmentor, 70 V (positive ionization mode) and 120 V (negative ionization mode); sheath gas flow, 12 L/min; sheath gas temperature, 350 °C. Nitrogen N_2 (99.999%) was used as the desolvation gas. The lock mass correction was applied using Agilent reference solution (*m/z* 121.05087 and 922.00979 in positive ionization mode; *m/z* 112.98558 and 1033.98811 in negative ionization mode) for accurate mass measurements. The scan range was *m/z* 100 – 1500 at 2 spectra/sec. All spectra were recorded in continuum mode. Data acquisition was performed using Agilent MassHunter Workstation Data Acquisition B.08.00 software. UHPLC conditions: samples were prepared in MeOH at a concentration of 2 mg/ml and 1 µL was injected. A Zorbax Eclipse plus C18 (1.8 µm, 50 × 2.1 mm; Agilent Technologies, USA) column maintained at 40 °C was used for compounds separation. The elution was performed using 0.4 mL/min mobile phase of 0.1% formic acid with water (A) and 0.1% formic acid with ACN (B) according to the following

gradient (A/B): 95/5 (t = 0 min), 95/5 (t = 1 min), 75/25 (t = 3 min), 50/50 (t = 6 min), 20/80 (t = 8 min), 20/80 (t = 11 min), 0/100 (t = 12 min), 0/100 (t = 15 min), 95/5 (t = 16 min).

Synthesis of HBO-*O*-All

LGO (1 g, 7.9 mmol), allyl alcohol (10 mL, 158 mmol, 20 equiv.) and triethylamine (1.1 mL, 7.9 mmol, 1 equiv.) were stirred at room temperature for 20 h. After concentration of the medium, 1 mL of water was added. At 0 °C, 0.88 mL of hydrogen peroxide 30% solution was added dropwise, then the reaction mixture was allowed to reach room temperature and then was heated at 45 °C for 16 h. Absence of remaining peroxide was tested using quantofix strip and reaction medium was concentrated prior flash purification over silica gel (Table S1). Pure **HBO-*O*-All** was recovered as a pale-yellow oil (777 mg, 63% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (ddt, *J* = 17.3, 10.4, 5.6 Hz, 1H, 7), 5.49 – 4.95 (m, 2H, 8'), 4.51 (q, *J* = 2.9 Hz, 1H, 4), 4.25 (dt, *J* = 7.0, 2.7 Hz, 1H, 3), 4.08 – 3.86 (m, 3H, 5', 6), 3.72 (dd, *J* = 12.5, 3.2 Hz, 1H, 5''), 2.87 (dd, *J* = 18.2, 7.1 Hz, 1H, 2'), 2.54 (dd, *J* = 18.2, 2.9 Hz, 1H, 2'') (Figure S1). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.3 (s, 1), 133.8 (d, 7), 118.0 (t, 8), 85.9 (d, 4), 75.5 (d, 3), 70.4 (t, 6), 62.3 (t, 5), 36.1 (t, 2) (Figure S2). **HRMS** *m/z* calculated $[C_8H_{12}O_4+H]^+$ 173.0808, found 173.0809 **$[\alpha_D]^{23\ °C}$** +16.9 (c. 16.9 g/100 mL AcOEt).

Table S1. T Elution for **HBO-*O*-All** purification

Column volume	%cyclohexane	%ethyl acetate	%methanol
0.0	50	50	0
8.0	20	80	0
10.3	20	80	0
14.0	20	80	0
19.0	0	100	0
23.0	0	100	0
24	0	95	5
26.0	0	95	5

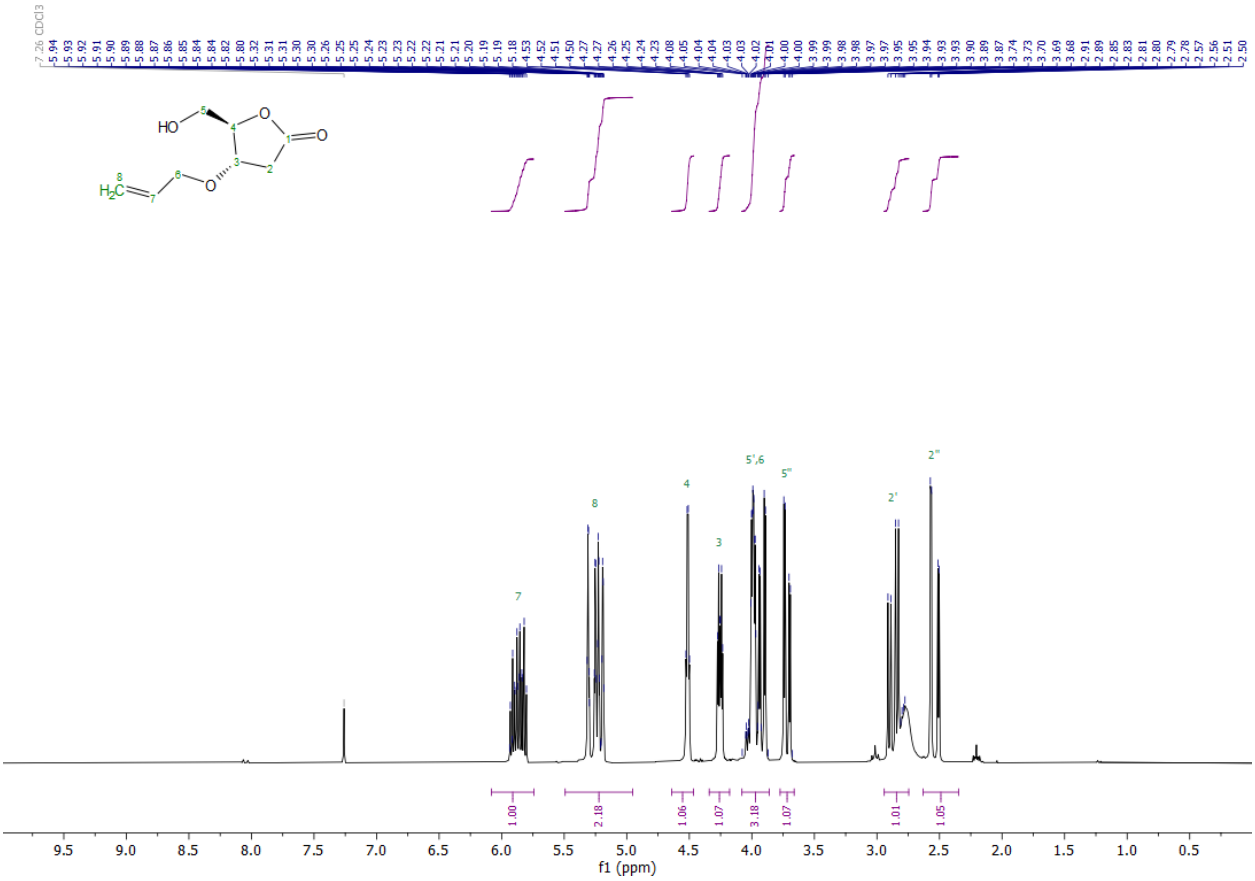

Figure S1. ^{1}H NMR Spectrum of **HBO-*O*-All**

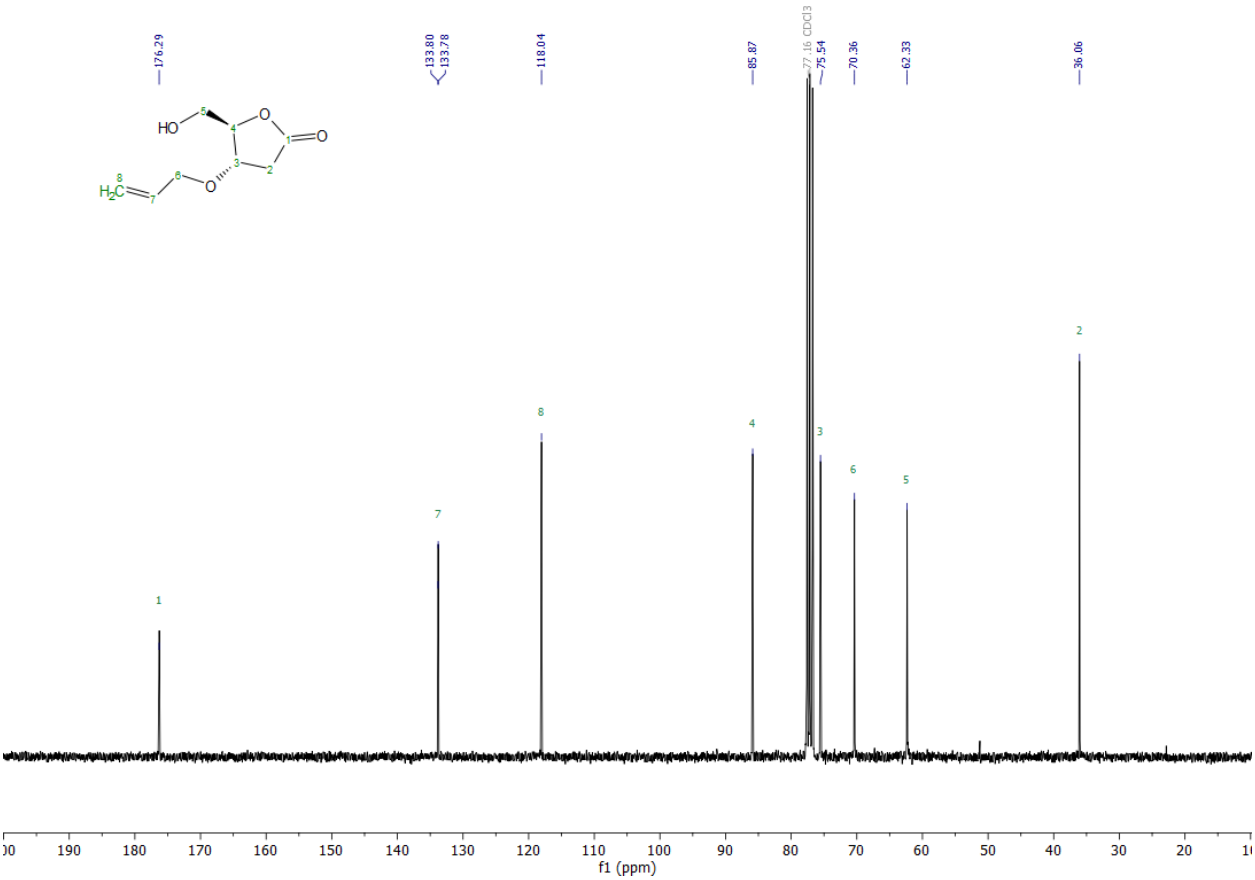

Figure S2. ^{13}C NMR Spectrum of **HBO-*O*-All**

Synthesis of All_N1

Design of experiments

Diethyl malonate (230 µL, 1.5 mmol) and **HBO-*O*-All** (2 to 3 equiv.) were placed in a round bottom flask under reduced pressure (100 mbar) at a set temperature (70, 85 or 100 °C), then Novozym 435 (320 to 960 U.mmol^{-1}) was added and reaction was gently stirred (70 rpm). Aliquots were taken at 1, 2, 3, 5, 7 and 24 h and analyzed by ^{1}H NMR to monitor conversion (ESI, Table S1 and Figure S2). Two additional experiments were conducted at (i) 81.7 °C, 2.7 equiv. of HBO-*O*-All and 144 mg of Nov435, and (ii) 83.1 °C, 2.0 equiv. of HBO-*O*-All and 53 mg of Nov435.

External validation of the DoE at optimized conditions

Diethyl malonate (230 µL, 1.5 mmol) and HBO-*O*-All (517 mg, 3 mmol, 2 equiv.) were placed in a round bottom flask under reduced pressure (100 mbar) at desired temperature (82.4 °C), then Novozym 435 (60 mg, 400 U/mmol) was added and the reaction mixture was gently stirred (70 rpm) for 5 h. Productivity and K_{cat} at 5 h were 3.78 and 6.09, respectively, in accordance with predicted values (3.37 +/- 0.5 and 6.45 +/- 0.95, respectively). After 20 h, the reaction mixture was diluted with acetone, enzyme beads were filtered off and filtrate was concentrated. Crude product was recrystallized in ethanol to afford 436 mg (70% yield) of pure **All_N1** as white powder.

mp (°C) 52. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.86 (ddt, $J_{7/8}$ = 17.2, 10.4 Hz, $J_{7/6}$ = 5.6 Hz, 2H, 7), 5.40 – 5.10 (m, 4H, 8), 4.64 (ddd, $J_{4/5b}$ = 4.7 Hz, $J_{4/3\ and\ 4/5a}$ = 3.3 Hz, 2H, 4), 4.37 (dd, $J_{5a/5b}$ = 12.2 Hz, $J_{5a/4}$ = 3.6 Hz, 2H, 5a), 4.28 (dd, $J_{5b/5a}$ = 12.2, $J_{5b/4}$ = 4.7 Hz, 2H, 5b), 4.14 (ddd, $J_{3/2a}$ = 6.8, $J_{3/4\ and\ 3/2b}$ = 3.2 Hz, 2H, 3), 4.00 (ddt, $J_{6/7}$ = 5.8 Hz, $J_{6/8=}$ = 4.4, 1.4 Hz, 4H, 6), 3.45 (s, 2H, b), 2.85 (dd, $J_{2a/2b}$ = 18.2 Hz, $J_{2a/3}$ = 7.1 Hz, 2H, 2a), 2.58 (dd, $J_{2b/2a}$ = 18.2 Hz, $J_{2b/3}$ 3.4 Hz, 2H, 2b) (FigureS3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.4 (s, 1), 165.5 (s, a), 133.6 (d, 7), 118.3 (t, 8), 81.9 (d, 4), 75.3 (d, 3), 70.6 (t, 6), 64.6 (t, 5), 41.1 (t, b), 35.3 (t, 2) (Figure S4). **HRMS** calculated $[C_{19}H_{24}O_{10}+H]^+$ *m/z* 413.1442, found 413.1444. **$[\alpha_D]^{22\ °C}$** + 14.5 (c. 6.02 g/100 mL AcOEt).

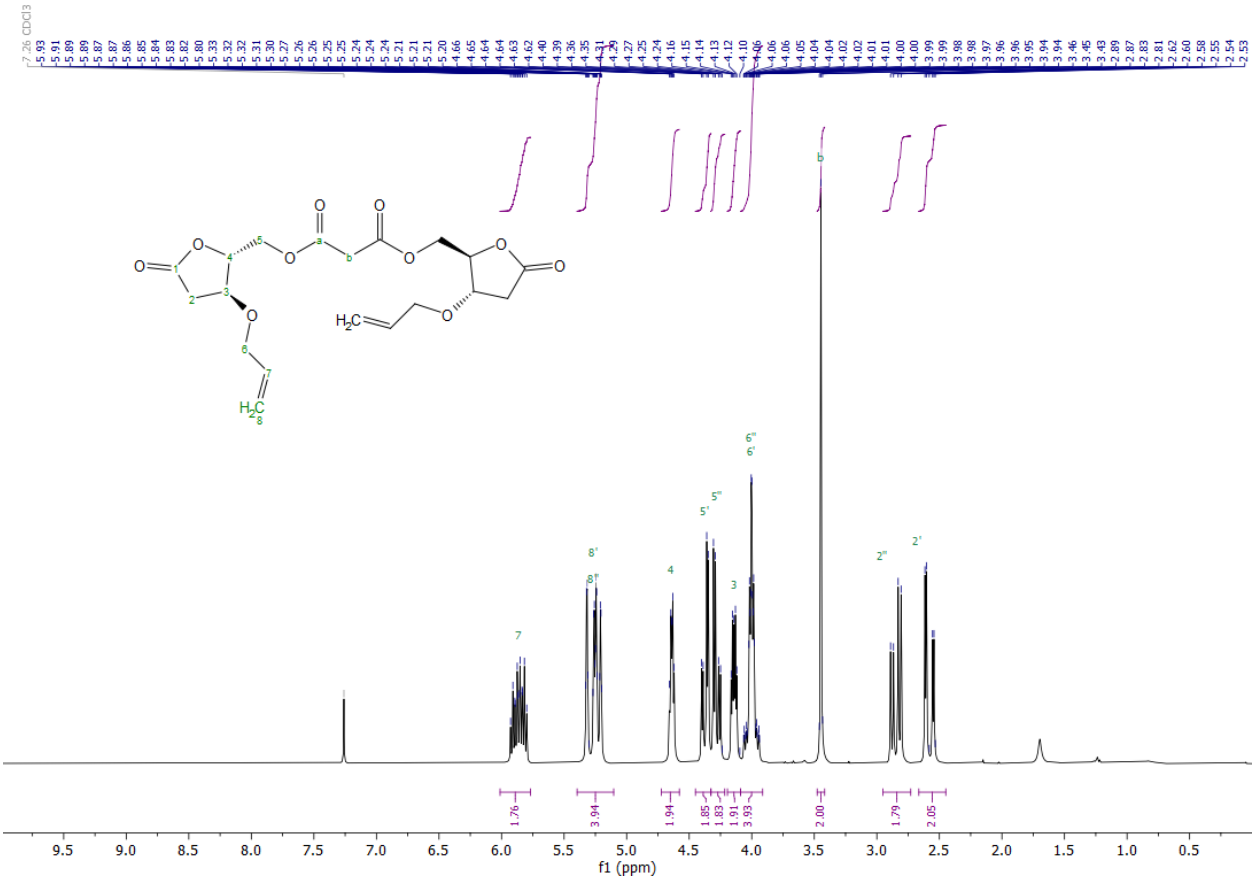

Figure S3. 1H NMR Spectrum of **All_N1**

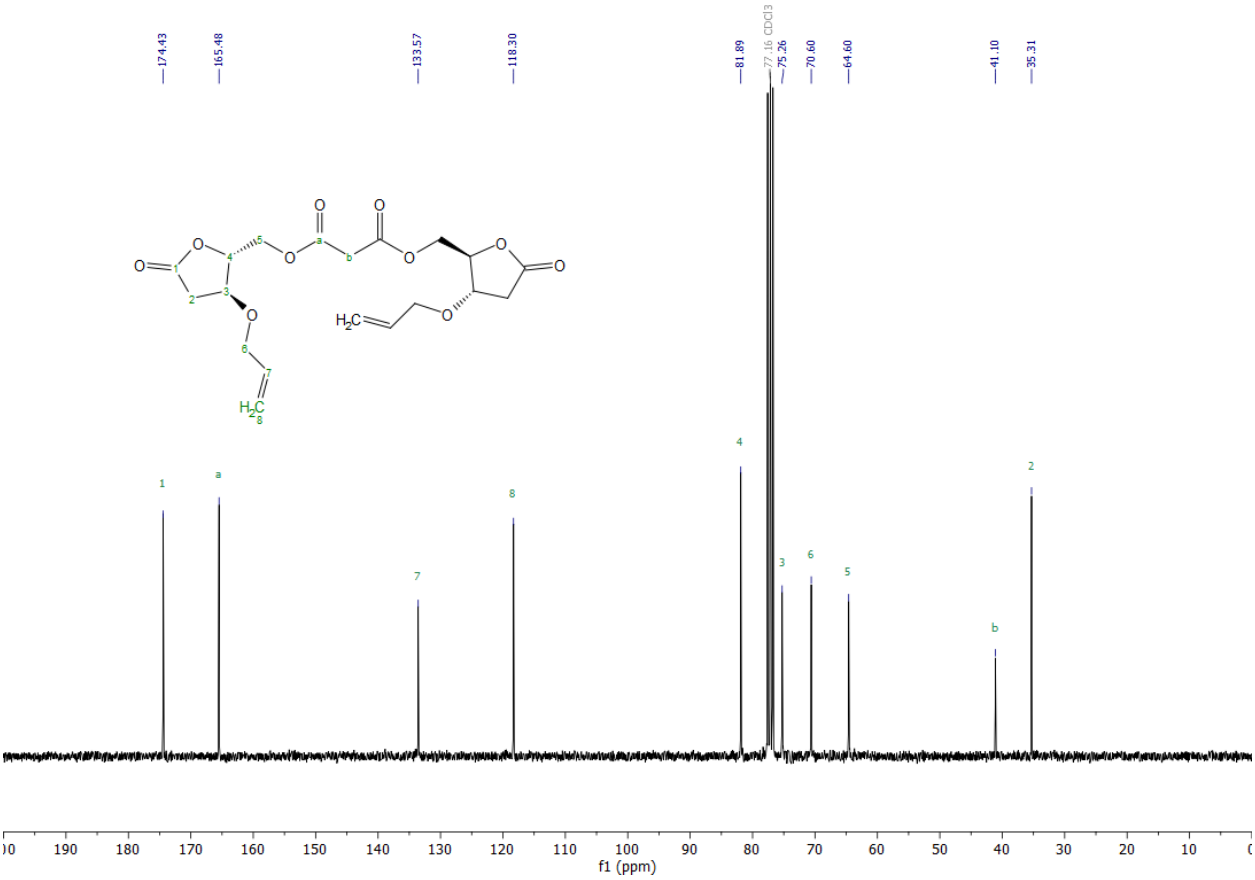

Figure S4. ^{13}C NMR Spectrum of **All_N1**

Synthesis of All_N4

Diethyl adipate (360 µL, 1.8 mmol) and HBO-*O*-All (517 mg, 3 mmol) were placed in a round bottom flask under reduced pressure (100 mbar) at 82.4 °C, then Novozym 435 (60 mg, 333 mg, U/mmol) was added and the reaction mixture was gently stirred (70 rpm) for 20 h. The reaction mixture was then diluted with acetone, enzyme beads were filtered off and filtrate was concentrated. Crude product was purified through flash chromatography (Table S2). In a first fraction, **HBO-*O*-All-Ad** was recovered (132 mg) then 434 mg (64% yield) of pure **All_N4** were recovered in a second fraction.

Table S2. Elution for **All_N4** and **All_N7** purification

Column volume	%cyclohexane	%ethyl acetate
0.0	75	25
3.0	75	25
6.0	70	30
8.9	70	30
11.9	50	50
14.9	30	70
17.0	30	70

HBO-*O*-All-Ad, Colorless oil
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (ddt, *J* = 17.3, 10.4, 5.6 Hz, 1H, 7), 5.36 – 5.19 (m, 2H, 8), 4.69 – 4.60 (m, 1H, 4), 4.34 (dd, *J* = 12.3, 3.6 Hz, 1H, 5'), 4.25 – 4.08 (m, 4H, g, 3, 5''), 4.01 (ddt, *J* = 5.7, 4.2, 1.4 Hz, 2H, 6), 2.82 (dd, *J* = 18.1, 7.0 Hz, 1H, 2'), 2.60 (dd, *J* = 18.1, 3.4 Hz, 1H, 2''), 2.41 – 2.26 (m, 3H, b, e), 1.74-1.60 (m 5H, c, d), 1.25 (t, *J* = 7.2 Hz, 3H, h) (Figure S5). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.5 (s, 1), 173.4 (s, f), 172.8 (s, a), 133.6 (d, 7), 118.4 (t, 8), 82.3 (d, 4), 75.4 (d, 3), 70.6 (t, 6), 63.6 (t, 5), 60.5 (t, g), 35.5 (t, 2), 34.0 (t, b), 33.7 (t, e), 24.4 (t, d), 24.3 (t, c), 14.4 (q, h) (Figure S6). **HRMS** calculated $[C_{16}H_{24}O_7+H]^+$ *m/z* 329.1595, found 329.1594. **$[\alpha_D]^{23\ °C}$** +18.2 (c. 4.5 g/100 mL AcOEt).

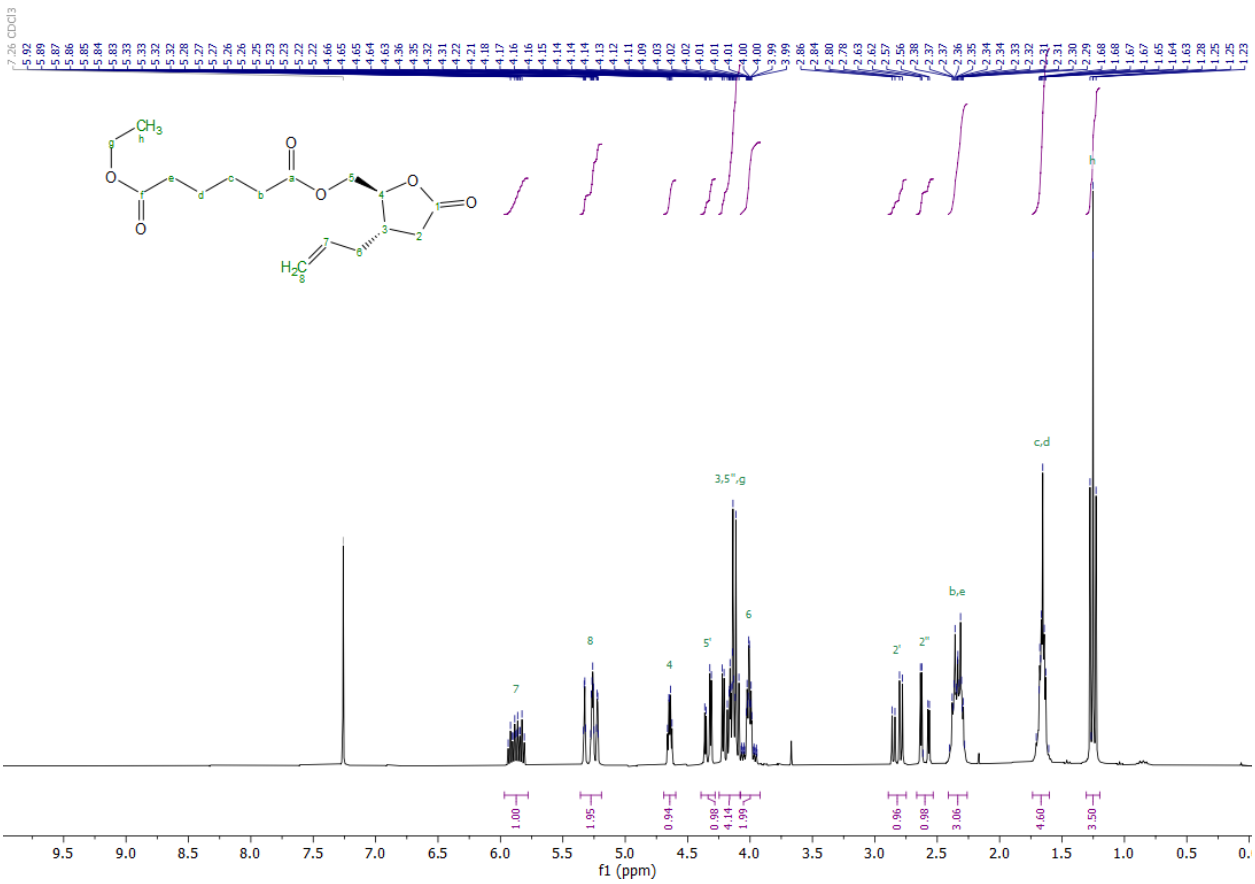

Figure S5. ^{1}H NMR Spectrum of **HBO-*O*-All-Ad**

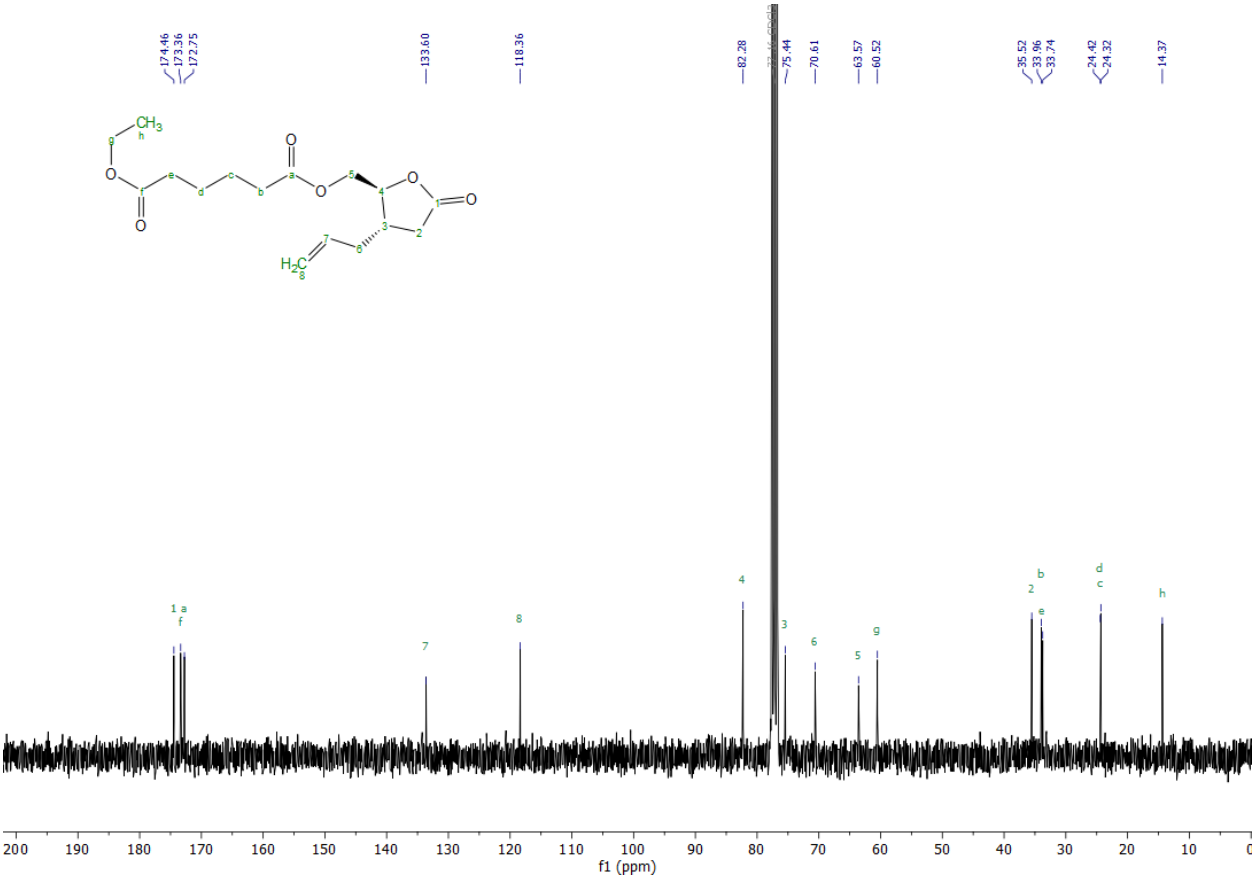

Figure S6. ^{13}C NMR Spectrum of **HBO-*O*-All-Ad**

All_N4, Colorless oil

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (ddt, $J_{7/8}$ = 17.2, 10.3 Hz, $J_{7/6}$ = 5.6 Hz, 2H, 7), 5.40 – 5.16 (m, 4H, 8), 4.64 (ddd, $J_{4/5a,\ 4/5b\ and\ 4/3}$ = 4.3, 3.5, 3.2 Hz, 2H, 4), 4.35 (dd, $J_{5a/5b}$ = 12.3 hz, $J_{5a/4}$ = 3.5 Hz, 2H, 5a), 4.23 – 4.10 (m, 4H, 5b and 3), 4.08 – 3.92 (m, 4H, 6), 2.83 (dd, $J_{2a/2b}$ = 18.1 Hz, , $J_{2a/3}$ = 7.0 Hz, 2H, 2a), 2.60 (dd, $J_{2b/2a}$ = 18.1 Hz, $J_{2b/3}$ = 3.4 Hz, 2H, 2b), 2.42 – 2.29 (m, 4H, b), 1.72 – 1.52 (m, 2H, c) (Figure S7). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.5 (s, 1), 172.6 (s, a), 133.6 (d, 7), 118.3 (t, 8), 82.3 (d, 4), 75.4 (d, 3), 70.6 (t, 6), 63.6 (t, 5), 35.5 (t, 2), 33.6 (t, b), 24.2 (t,c) (Figure S8). **HRMS** calculated $[C_{22}H_{30}O_{10}+H]^+$ *m/z* 455.1912, found 455.1920. **$[\alpha_D]^{22}$** $^{°C}$ +31.2 (c. 12.3 g/100 mL AcOEt).

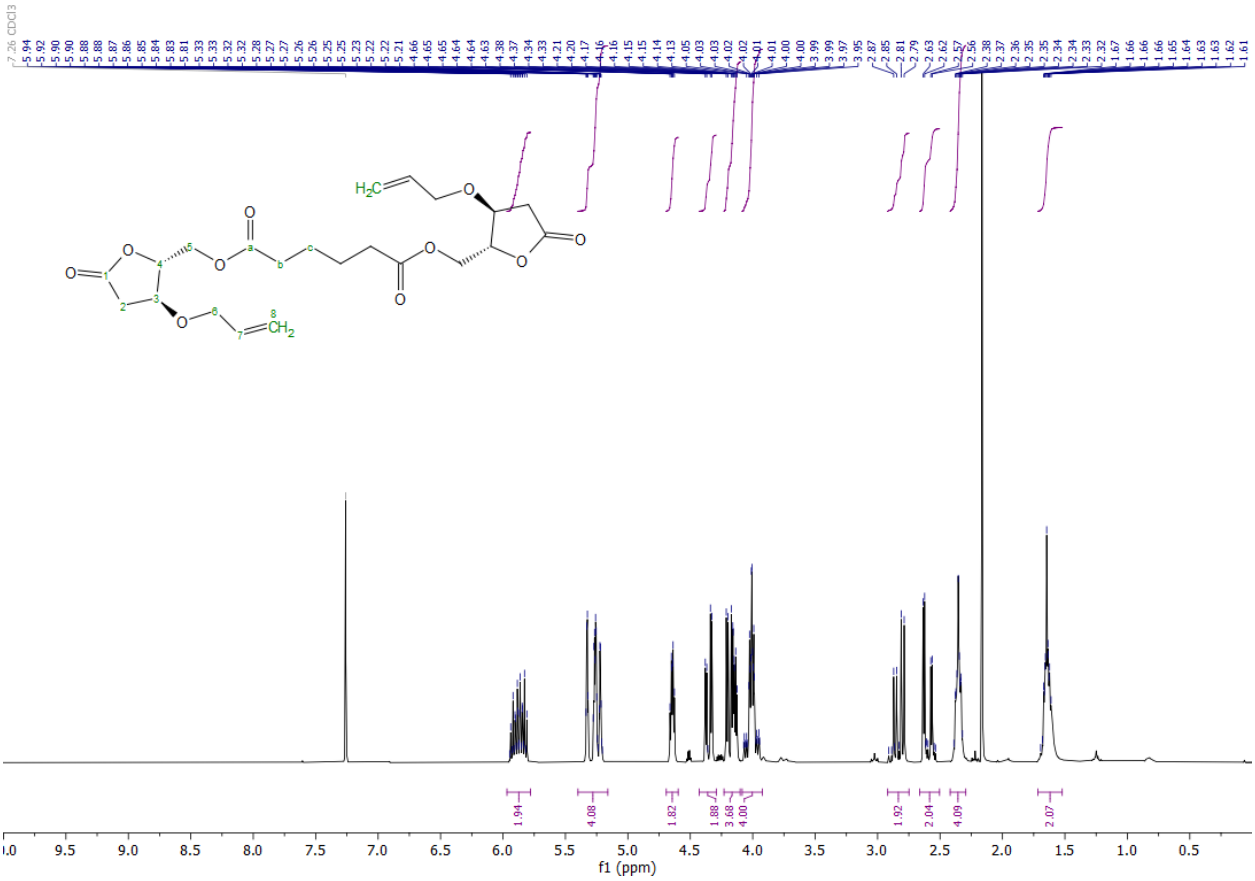

Figure S7. 1H NMR Spectrum of **All_N4**

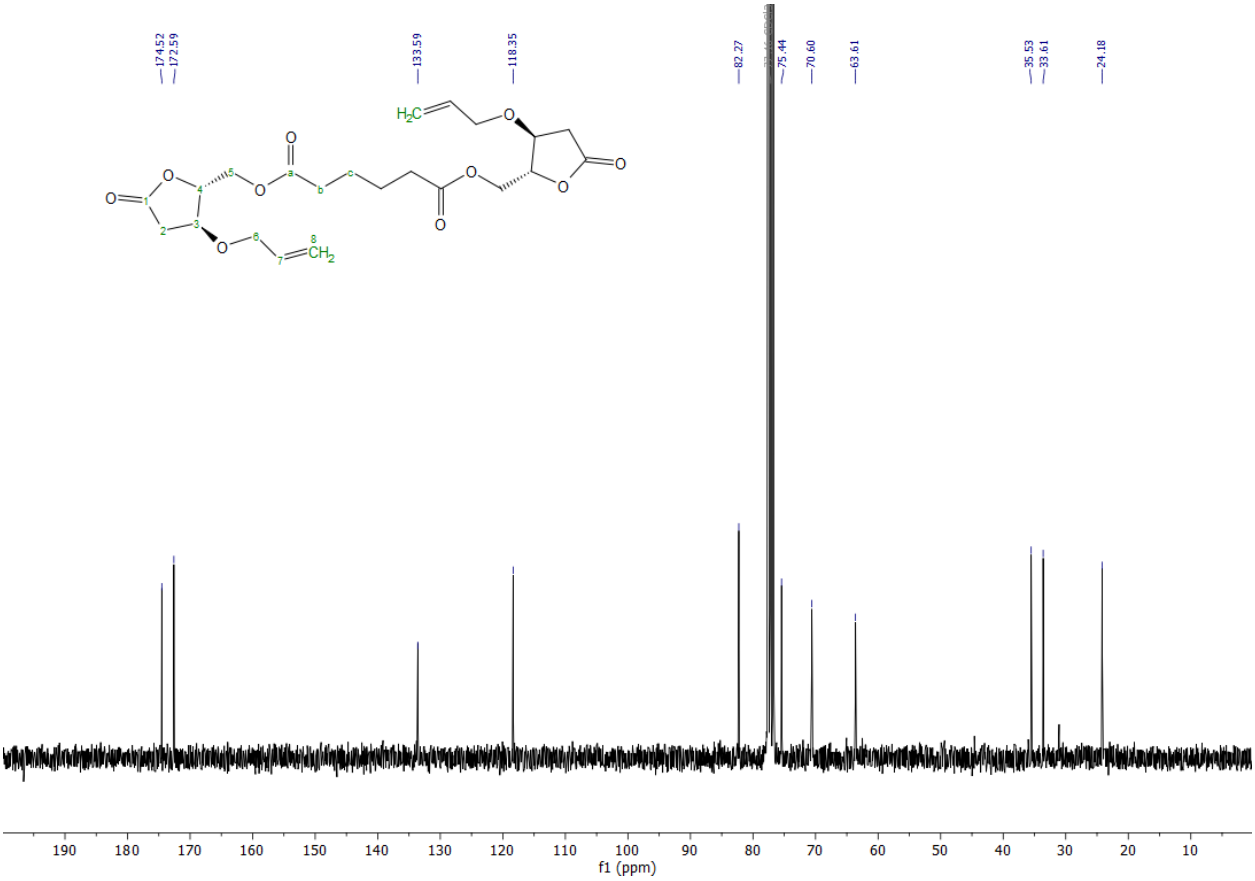

Figure S8. ^{13}C NMR Spectrum of **All_N4**

Synthesis of All_N7

Diethyl azelate 90% (419 µL, 1.5 mmol) and HBO-*O*-All (517 mg, 3 mmol) were placed in a round bottom flask under reduced pressure (100 mbar) at 82.4 °C, then Novozym 435 (60 mg, 400 U/mmol) was added and the reaction mixture was gently stirred (70 rpm) for 20 h. The reaction mixture was then diluted with acetone, enzyme beads were filtered off and filtrate was concentrated. Crude product was purified through flash chromatography (Table S2). In a first fraction, **HBO-*O*-All-Az** was recovered (136 mg) then 523 mg (70% yield) of pure **All_N7** were recovered in a second fraction.

HBO-*O*-All-Az, colorless oil
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (ddt, *J* = 17.3, 10.4, 5.6 Hz, 1H, 7), 5.40 – 5.17 (m, 2H, 8'), 4.65 (q, *J* = 3.5 Hz, 1H, 4), 4.33 (dd, *J* = 12.3, 3.6 Hz, 1H, 5'), 4.23 – 4.07 (m, 4H, j, 3, 5''), 4.01 (ddt, *J* = 5.6, 4.1, 1.4 Hz, 2H, 6), 2.82 (dd, *J* = 18.1, 7.0 Hz, 1H, 2'), 2.60 (dd, *J* = 18.1, 3.3 Hz, 1H, 2''), 2.30 (dt, *J* = 11.9, 7.5 Hz, 4H, b, h), 1.66 – 1.56 (m, 4H, c, g), 1.32 (d, *J* = 4.5 Hz, 6H, d, e, f), 1.25 (t, *J* = 7.1 Hz, 3H, k) (Figure S9). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.5 (s, 1), 173.9 (s, i), 173.2 (s, a), 133.6 (d, 7), 118.3 (t, 8), 82.3 (d, 4), 75.5 (d, 3), 70.6 (t, 6), 63.5 (t, 5), 60.3 (t, j), 35.5 (t, 2), 34.4 (t, h), 34.1 (t, b), 29.0 (t, d, e, f), 25.0 (t, g), 24.8 (t, c), 14.4 (q, k) (Figure S10). **HRMS** calculated $[C_{19}H_{30}O_7+H]^+$ *m/z* 371.2065, found 371.2065. **$[\alpha_D]^{22\ °C}$** +12.8 (c. 10.4 g/100 mL AcOEt).

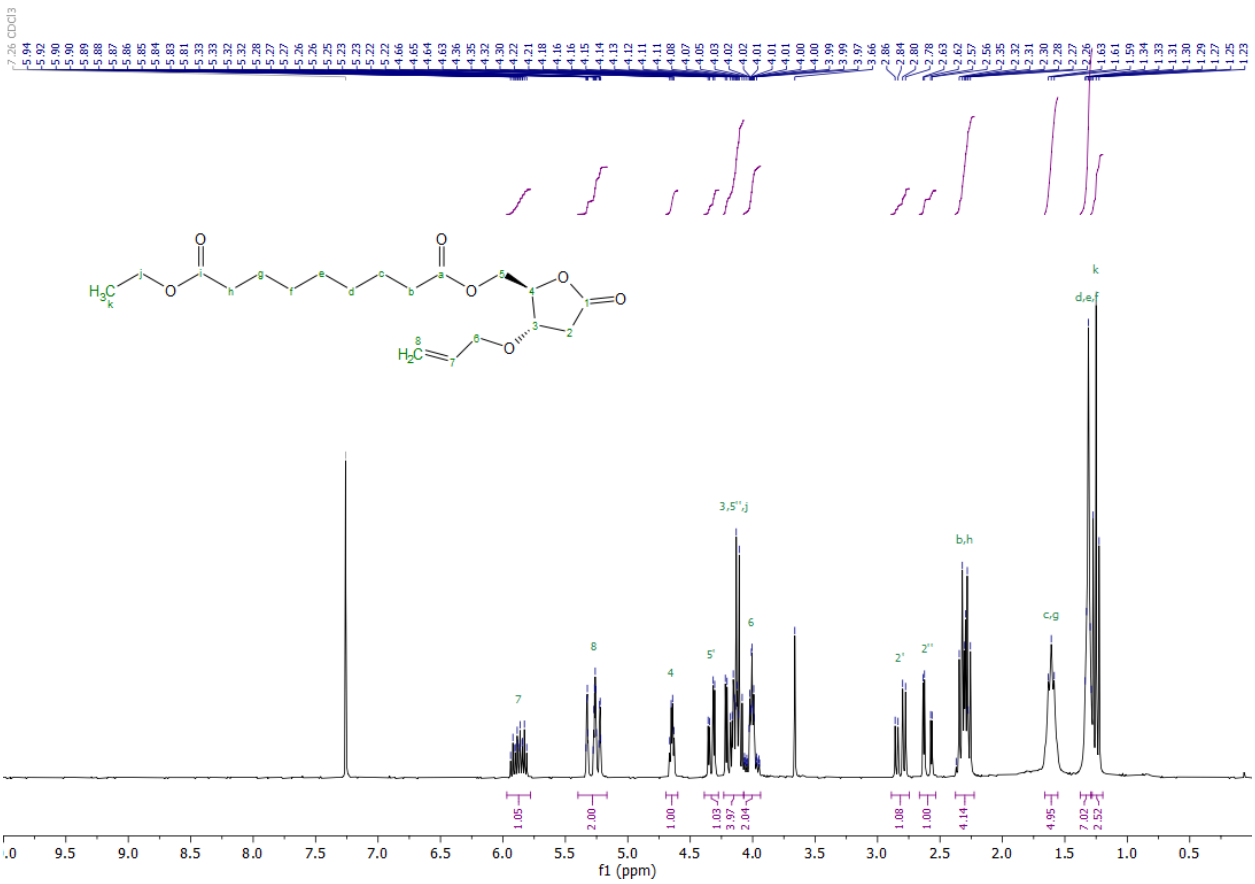

Figure S9. ^{1}H NMR Spectrum of **HBO-*O*-All-Az**

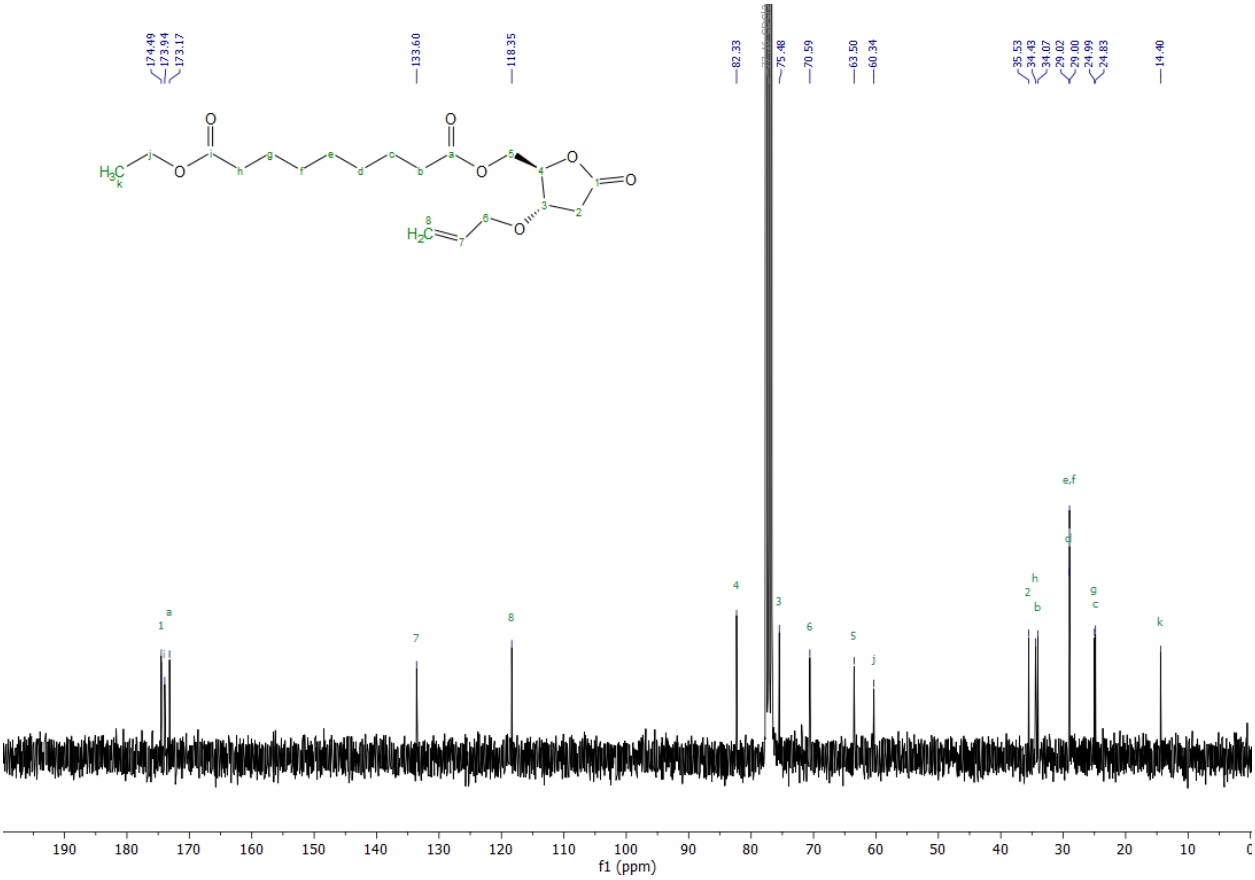

Figure S10. ^{13}C NMR Spectrum of **HBO-*O*-All-Az**

All_N7, White solid

mp (°C) 33.5. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.86 (ddt, $J_{7/8}$ = 17.3, 10.4 Hz, $J_{7/6}$ = 5.6 Hz, 2H, 7), 5.35 – 5.17 (m, 4H, 8), 4.64 (ddd, $J_{4/5a,\ 4/5b\ and\ 4/3}$ = 4.0, 3.5 2.8 Hz, 2H, 4), 4.33 (dd, $J_{5a/5b}$ = 12.3 Hz, $J_{5a/4}$ = 3.5 Hz, 2H, 5a), 4.22 – 4.08 (m, 4H, 5b, 3), 4.07 – 3.92 (m, 4H, 6), 2.81 (dd, $J_{2a/2b}$ = 18.1 Hz, $J_{2a/3}$ = 7.0 Hz, 2H, 2a), 2.59 (dd, $J_{2b/2a}$ = 18.1 Hz, $J_{2b/3}$ = 3.3 Hz, 2H, 2b), 2.31 (t, $J_{b/c}$ = 7.5 Hz, 4H, b), 1.69 – 1.47 (m, 4H, c), 1.36-1.24 (m, 6H, d, e) (Figure S11). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.5 (s, 1), 173.1 (s, a), 133.6 (d, 7), 118.3 (t, 8), 82.3 (d, 4), 75.5, 75.4 (d, 3), 70.5 (t, 6), 63.5 (t, 5), 35.5, 35.4 (t, 2), 34.0 (t, b), 28.9 (t, d and e), 24.7 (t, c) (Figure S12). **HRMS** calculated $[C_{25}H_{36}O_{10}+H]^+$ *m/z* 497.2381, found 497.2385. **$[\alpha_D]^{23\ °C}$** +30.7 (c. 5.64 g/100mL AcOEt).

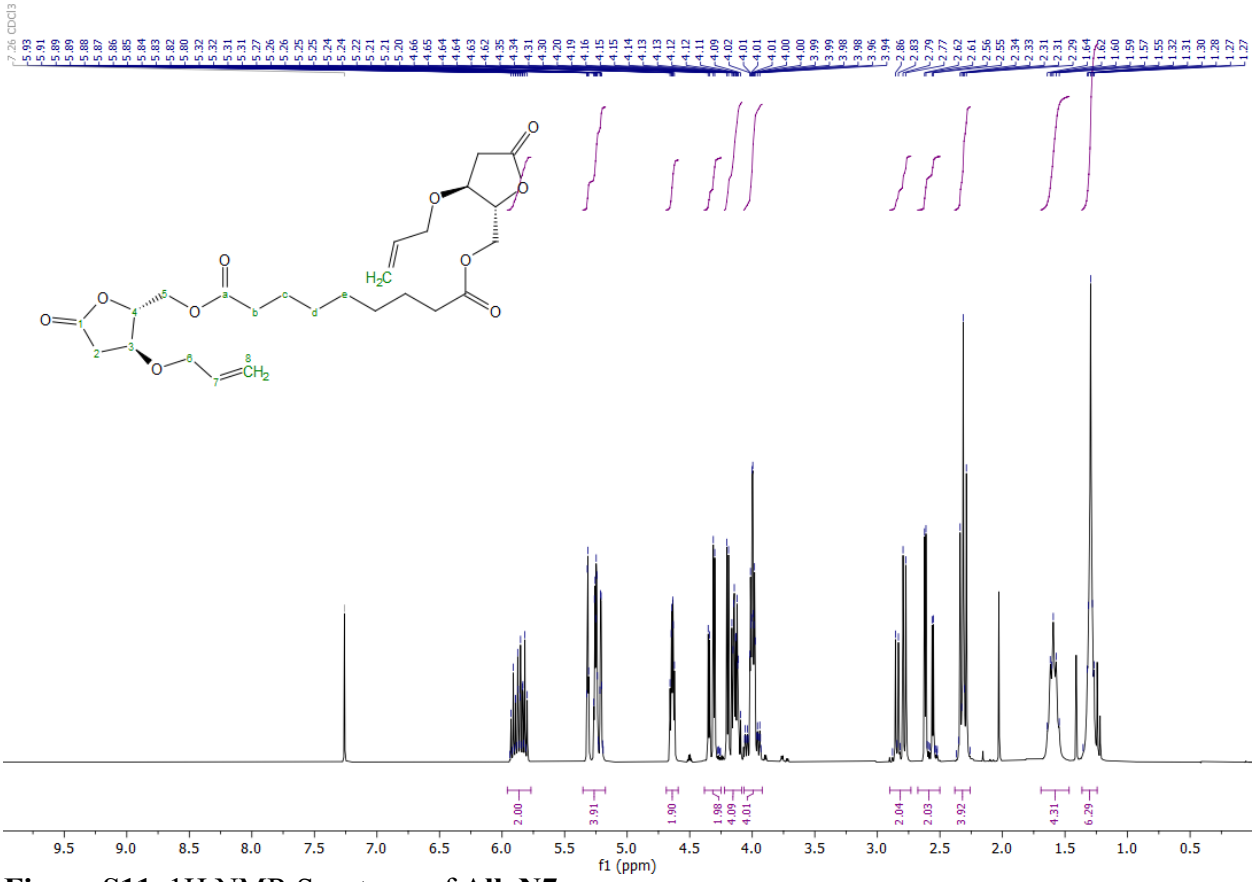

Figure S11. 1H NMR Spectrum of **All_N7**

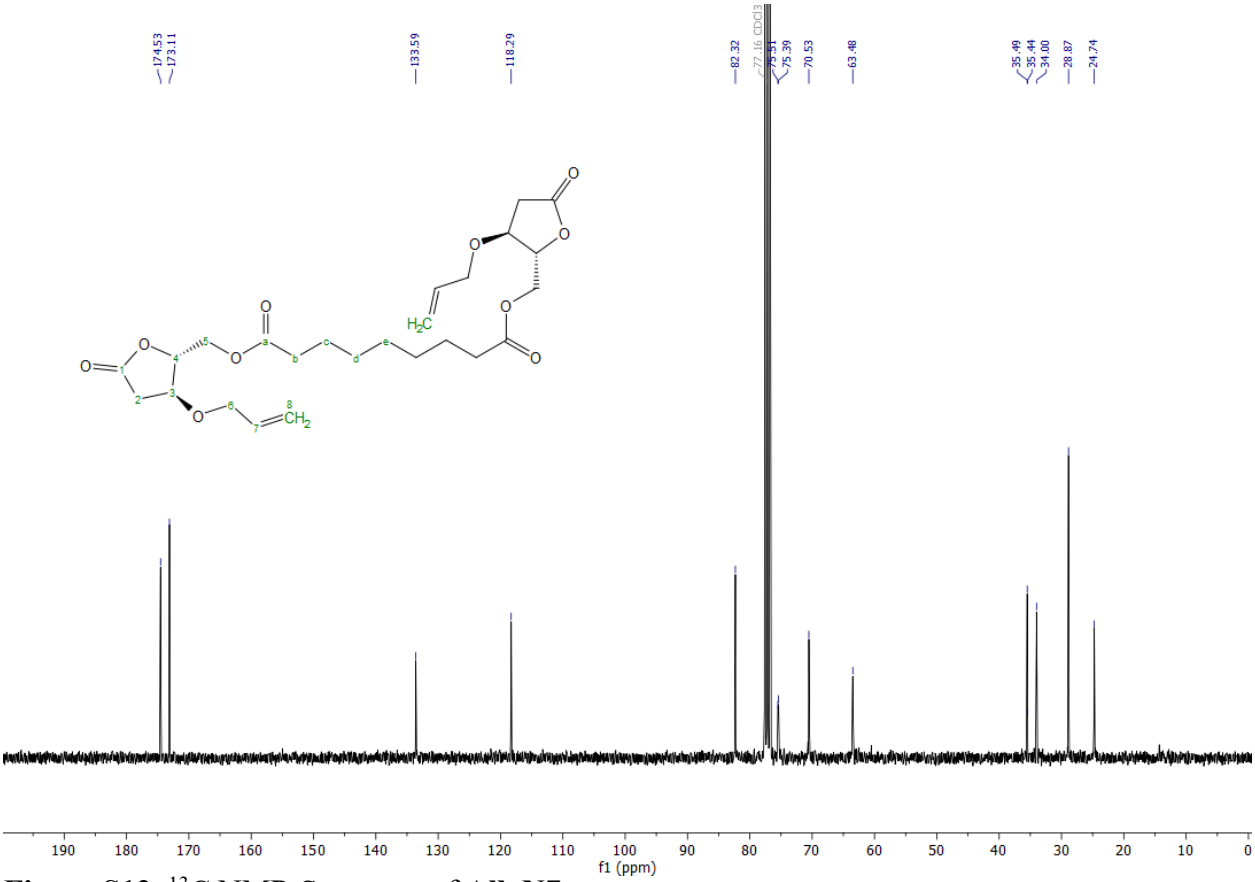

Figure S12. ^{13}C NMR Spectrum of **All_N7**

Formulation and Photocuring

The three synthetized allyl ether were tested for thiol-ene photocuring process, so a commercial thiol (TMPMP) was used in the formulations. The ratio between ene and thiol was kept at 1:1 molar ratio and 3 wt% of photoinitiator, Darocure 1173, was added to the mixture of monomers. All the data are collected in Table 1. The formulations containing **ALL_N1** and **ALL_N7** were heated to allow the melting of the ene monomers in order to mixing properly. Then all the formulations were kept in an ultrasound bath for 5 minutes in order to disperse uniformly all components. Successively, the formulations were cured in silicon mold to create the samples for DMTA, DSC, TGA and tensile analysis. A Flood DMAX UV lamp was used as a UV-source. The light intensity was set around 100 mW/cm^2 and the irradiation time was one minute. The emission spectrum of the UV lamp was from 275 to 500 nm with a maximum located to 365 nm. The left-over formulations were kept in brown vials to avoid the light contact and used for successive curing and sample preparation.

Table S3. Schematic report of the amount of monomers and PI used for the formulation tested.

FORMULATION	ENE MONOMER		THIOL MONOMER		MOLAR RATIO THIOL-ENE	PI 3 wt%
	/	[g]	/	[g]		[g]
All_N1_TMPMP	All_N1	1.000	TMPMP	0.643	1:1	0.051
All_N4_TMPMP	All_N4	1.000	TMPMP	0.585	1:1	0.049
All_N7_TMPMP	All_N7	1.000	TMPMP	0.535	1:1	0.047

Real-time Fourier transform IR (real-time FTIR)

The photo-curing process was followed in real-time by means of a Nicolet iS 50 Spectrometer. A SiC wafer was used as substrates for the transmission analysis. The liquid formulations were coated on the substrate with film-bar guaranteeing a thickness of 12 μm. A Hamamatsu LIGHTINGCURE LC8 was employed as UV-source and the UV-light was directed on the sample by an optic fiber. The lamp intensity was set to 5% corresponding about 4 mW/cm^2. The spectra were collected with a spectral resolution of 4 cm^{-1}. All the data were handled by Onmic software developed by Thermo Fisher Scientific. The conversion curves were collected by monitoring the disappearance of the thiol peaks at 2570 cm^{-1} and the carbon-carbon double bond at 1640 cm^{-1}. The peak at 1730 cm^{-1} was taken as reference. It was assumed to be unaffected by UV-irradiation since it belonged to the C=O bending of the ester that was not involved into the curing reaction. Equation 1 was used to calculate the conversion for the exposure time.

$$Conversion\ (\%) = \frac{\left(\frac{A_{fun}}{A_{ref}}\right)_{t=0} - \left(\frac{A_{fun}}{A_{ref}}\right)_{t}}{\left(\frac{A_{fun}}{A_{ref}}\right)_{t=0}} \times 100 \qquad \text{(Eq. 1)}$$

where A_{fun} is the area of the functional group under investigation (*e.g.*, area of the thiol at 2570 cm^{-1}) while A_{ref} is the area of the peak at 1730 cm^{-1}. The area was normalized to give the conversion and then an average of three measure was taken.

Photo dynamic scanning calorimetry (photo-DSC) and Dynamic scanning calorimetry (DSC)

Photo-DSC was used to monitoring the photo-curing process. A Mettler TOLEDO DSC-1 equipped with Gas Controller GC100 was used to perform the analysis. The DSC was further equipped with a mercury lamp, Hamamatsu LIGHTINGCURE LC8, with an optic fiber to direct irradiate the samples. The emission of UV-light was centered at 365 nm and the light intensity was set at 5%. About 5-10 mg of photocurable formulation was placed in an open aluminum pan (40 mL), whereas an empty pan was used as reference. The tests were done at different temperature (25 °C, 50 °C and 80 °C) and in controlled atmosphere (N_2 flow of 40 mL/min). An initial time of two minutes was used to stabilize the sample. The samples were

irradiated two times for 5 min in order to proper evaluate the UV-curing. The second run was done to confirm the complete curing and create the base line. The second curve was subtracted from the first to obtain the curve related to the curing only. The integration of the final thermogram gave the evolution of the heat of polymerization.
The thermal properties of cured sample were analyzed by DSC. A Mettler TOLEDO DSC-1 equipped with Gas Controller GC100 was employed to carry the tests. Samples of about 5-10 mg were sealed in 40 μL aluminum pans and analyzed by DSC. The data were analyzed with Mettler Toledo STARe software V9.2. The following method was used to analyze the different thermoset. The starting temperature was set at room temperature; the first heating goes from 25 to 100 °C in order to eliminate the thermal history of the polymers; after that the chamber was again cooled until – 40 °C was reached and finally was a second heating from – 40 °C to 250 °C applied. After each dynamic steps, isothermal steps of 5 min were done to stabilize the chamber and the sample. The heating and the cooling rates were set at 10 °C/min and the analysis was performed in a controlled atmosphere with a N_2 flow rate of 40 mL/min. All the data were analyzed with Mettler Toledo STARe software V9.2.

Photo-rheology and Viscosity

The curing process was studied by means of photo-rheology with an Anton Paar MC 302 rheometer (Physica MCR 302, Graz, Styria). The rheometer was set with a plate-plate geometry; the outside diameter of the upper metal disk was 25 mm and a quartz disk was used as bottom support in order to guarantee the irradiation of the sample. The distance between the plate was set as 200 μm. which correspond about 150 μL of the formulation between the plates. A Hamamatsu LIGHTINGCURE LC8 was used as UV-source and the light was directed on the sample by means of an optic fiber. The light intensity provided on the surface of the sample was 5% of the intensity of the lamp that correspond to 4 mW/cm^2. The lamp was turned on after 60 second of stabilization and the measurements were performed in oscillatory condition at frequency of 1 Hz, with strain 1%. The tests were done in isothermal condition at 25 °C, 50 °C and 80 °C. The thermal stability was test after 2000 seconds by starting the irradiation.
The Anton Paar MC 302 rheometer (Physica MCR 302, Graz, Styria) was also used for viscosity measurements. The geometry was set as plate-plate with both metal-based disk. Two different temperatures were tested, 25 and 80 °C. The distance between the plate was 200 mm. The viscosity was measured by applying an increase shear stress from 0.01 to 1000 1/s.

Gel content

The gel content percentage (% gel) was evaluated on UV-cured samples. About 500 mg samples were tested, the curing was done using silicon mold as describe in the previous paragraph. The determination of gel content was done by evaluating the weight loss after 24 h extraction with chloroform at room temperature. The samples after the immersion were allowed to dry for 24 h in air and a final stage at 50 °C for 2 hours was done to completely remove trace of solvent. % gel was calculated according to Equation 2.

$$\% \, gel = \frac{W_1}{W_0} * 100 \qquad \text{(Eq. 2)}$$

where W_1 is the weight of the dry film after the treatment with chloroform and W_0 is the weight of the dry sample before the treatment.

Dynamic mechanical thermal analysis (DMTA)

The dynamic-mechanical analysis of the photocured thermosets was carried out with a Triton Technology instrument. The heating rate was 3°C/min and the initial temperature of – 40°C was achieved by cooling down the test chamber with liquid nitrogen. The instrument applied uniaxial tensile stress at frequency of 1 Hz. The measurement was done to detect the T_g as maximum of *Tan δ* curve and to monitor the trend of the storage modulus; the tests were stopped after the rubbery plateau. The samples were UV-cured in a silicon mold with average dimension of 0.2 x 3.5 x 12 mm. Equation 3 is derived from the statistical theory of rubber elasticity and gives an estimation of the density of cross-links.

$$\nu_c = \frac{E'}{3RT} \qquad \text{(Eq. 3)}$$

where ν_c is the number of crosslinks per volume of the crosslinked network, *E*' is the storage modulus in the rubbery plateau (T_g + 50 °C), *R* is the gas constant and *T* is the temperature expressed in Kelvin.

Tensile test

The mechanical properties of the thermoset were investigated by tensile test. The stress-strain curve was registered using a tensile instrument (MTS QTestTM/10 Elite, MTS System Corporation) combined with a measurement software (TestWorks® 4, MTS System Corporation). A 1 KN load cell was used, and the traverse speed of the machine was set as 5 mm/min. The Young's modulus (E) was evaluated as the tangent of the curve up to the linear region (around 20% of total elongation). The result was the average value of 5 measurement.

Contact angle

In order to evaluate surface properties, contact angle test was measured against water. The formulations were UV-cured with a thickness of 500 µm. The contact angle test was performed on the free surface. The instrument used was a Drop Shape Analyzer, DSA100, Krüss. Five measurements were taken to have an average value.

Thermogravimetric analysis (TGA)

The thermal stability of the UV-cured coatings was studied by TGA analysis by means of a Mettler Toledo TGA1. About 10-15 mg of sample were placed in alumina crucibles and heated from 25 °C to 700 °C with a heating ramp of 10 K/min. Inert atmosphere was guarantee by flow of Ar at 40 mL/min. The analysis was done evaluating different features: T_5, temperature at which the sample lost 5 wt %; T_{peak}, temperature at peak of degradation, evaluated as peak of the first derivative and final char residue, analyzed as wt%.

Chemical degradation

The UV-cured samples (50-75 mg) were immersed into an alkaline solution of NaOH 2 M (2 mL) and gently stirred on a thermoregulate mixer at 25 °C, 120 rpm. The samples were recovered from the solution, washed with deionized water, dried and weight. A weight loss evaluation was done considering the initial weight of the samples, triplicate measures of each time were performed. The Equation 4 was used for the evaluation.

$$\text{Not degraded sample (\%)} = \frac{W_1}{W_0} * 100 \quad \text{(Eq. 4)}$$

where W_1 is the weight of the dry film after the treatment in NaOH and W_0 is the weight of the dry sample before the treatment.

3D Printing

The 3D-printing DLP process was performed with an Asiga (Alexandria, Australia) MAX X UV 27 DLP printer operating a 385 nm LED light source. CAD models were designed and exported to .stl files to be uploaded into the proprietary printer software Asiga Composer. Light intensity was set to 40 mW/cm^2 and the layer thickness was 50 nm. The printing parameters were set according to the best result achieved. After the printing process, samples were immersed in an isopropanol and left for 15 minutes in an ultrasound bath to remove the unpolymerized formulations present on the surface. Subsequently, samples were subjected to UV-postcuring performed in a RobotFactory (Mirano, Italy) UV chamber equipped with a medium-pressure mercury lamp for 1 min.

3D Scanning

The printed object was scanned with a 3Shape (Copenhagen, Denmark) E3 scanner to verify the precision and accuracy of the print. The sample was coated with magnesium stearate in order to limit the reflection of light on the transparent structure, and then positioned on a platform by means of a sticky paste to ensure the correct acquisition of images. The resulting scanned image was then compared to the original CAD model by means of CA Analyzer software (3Shape, Copenhagen, Denmark) to generate the deviation analysis and map.

Results and Discussion

Synthesis of monomers

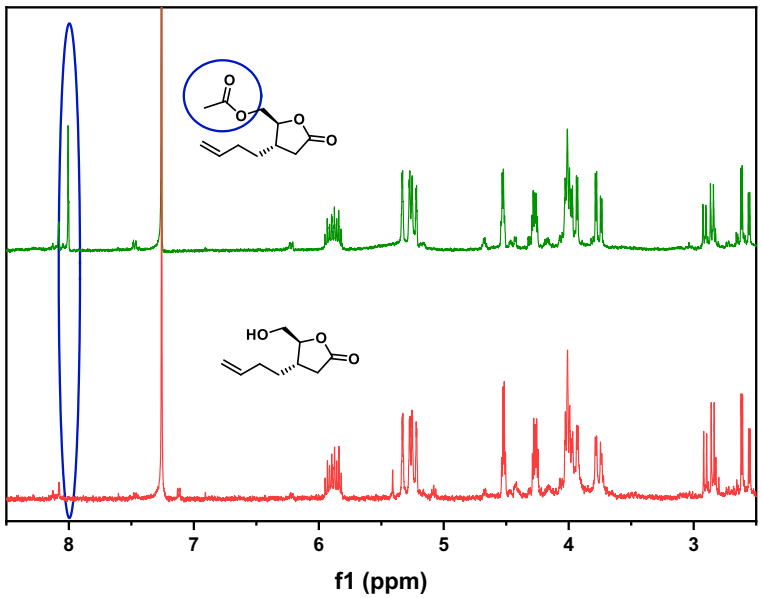

Figure S13. ^{1}H-NMR spectra of crude mixture after Baeyer-Villiger oxidation with (red) or without (green) addition of water.

Table S4. Matrix of the DoE and results at 5 h of reaction

Exp Name	Run Order	Temp. (°C)	CAL-B ($U.mmol^{-1}$)	M_{th} Cal-B (mg)	Weight (mg)	HBO-O-Allyl (equiv.)	m_{th} HBO-O-Allyl	Weight (mg)	Diethyl malonate	HBO-O-All-M	All_N1	Productivity ($mmol.min^{-1}$)	PseudoKcat
N1	7	70	320	48	48	2.5	646	646	6.9%	43.7 %	49.4 %	2.471	51.49
N2	14	100	320	48	48	2.5	646	647	0.0%	92.8 %	7.2%	0.361	7.52
N3	1	70	960	144	141	2.5	646	646	0.0%	23.6 %	76.4 %	3.822	27.11
N4	13	100	960	144	145	2.5	646	647	0.0%	32.0 %	68.0 %	3.398	23.44
N5	15	70	640	96	96	2	517	516	2.9%	32.3 %	64.8 %	3.240	33.75
N6	11	100	640	96	96	2	517	516	0.0%	33.5 %	66.5 %	3.327	34.66
N7	3	70	640	96	98	3	775	776	0.0%	33.7 %	66.3 %	3.313	33.81
N8	5	100	640	96	97	3	775	776	0.0%	89.5 %	10.5 %	0.524	5.40
N9	4	85	320	48	48	2	517	520	0.0%	22.5 %	77.5 %	3.875	80.74
N10	8	85	960	144	144	2	517	517	1.4%	21.0 %	77.6 %	3.880	26.94
N11	2	85	320	48	47	3	775	779	9.8%	64.5 %	25.7 %	1.286	27.37
N12	12	85	960	144	145	3	775	776	0.0%	17.9 %	82.1 %	4.106	28.32
N13	9	85	640	96	98	2.5	646	646	1.7%	24.1 %	74.2 %	3.712	37.88
N14	6	85	640	96	96	2.5	646	646	0.0%	12.1 %	87.9 %	4.396	45.80
N15	10	85	640	96	97	2.5	646	645	0.0%	21.0 %	79.0 %	3.950	40.72
N16	16	81.7	960	144	144	2.67	690	690	0.0%	20.4 %	79.6 %	3.978	27.63
N17	17	83.1	352	53	53	2	517	517	3.6%	32.6 %	63.8 %	3.778	60.94
Predicted	18	82.4	400	60	#	2	517	#	#	#	#	3.037<3.715<4.393	55.00<64.47<73.94
Validation	19	82.4	400	60	62	2	517	517	0.0%	24.4 %	75.6 %	3.778	6.09E-02

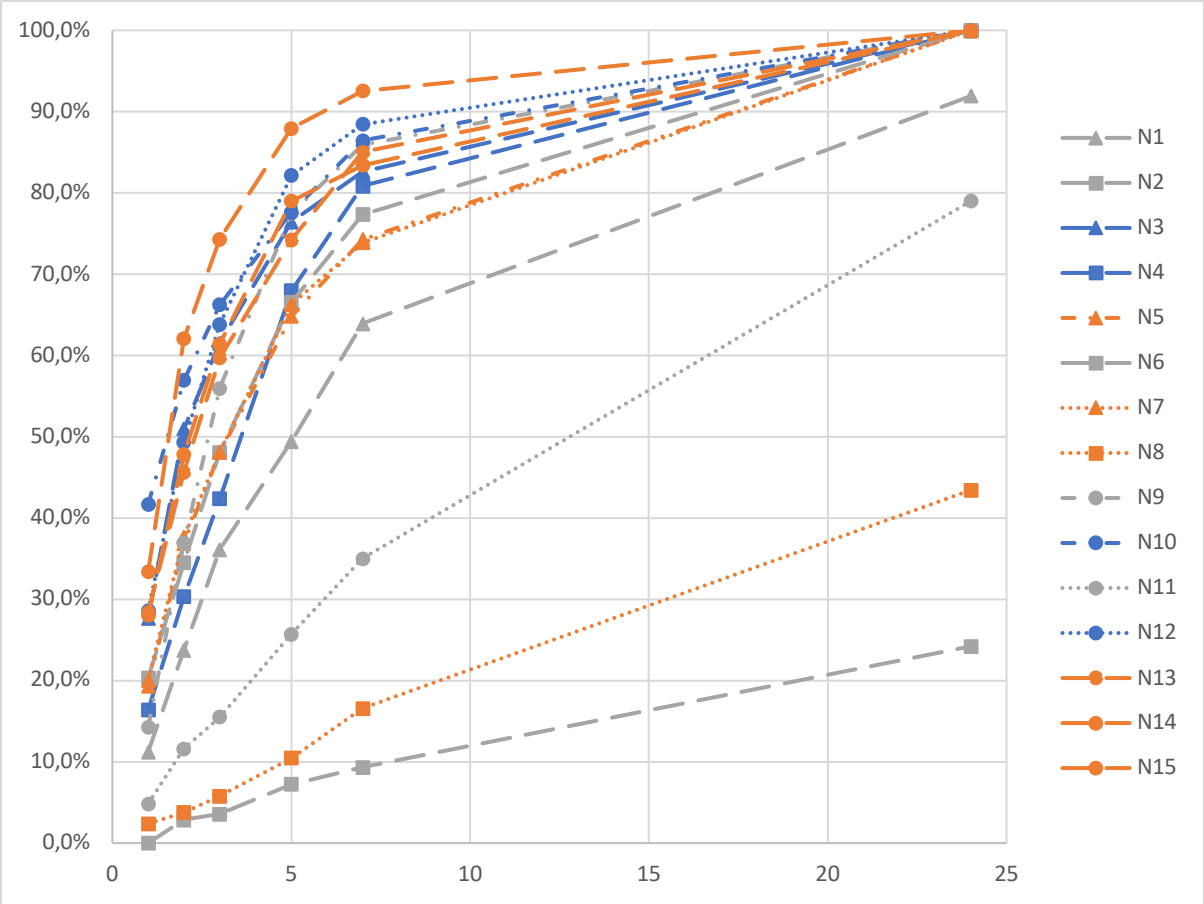

Figure S14. Amount of All_N1 in function of time determined by NMR. Grey (320 PLU.mmol^{-1}), Orange (640 PLU.mmol^{-1}) and Blue (960 PLU.mmol^{-1}). Square (100 °C), Circle (85 °C), triangle (70 °C). Dotted (3 equiv), long dash (2.5 equiv) and dotted-dash (2 equiv).

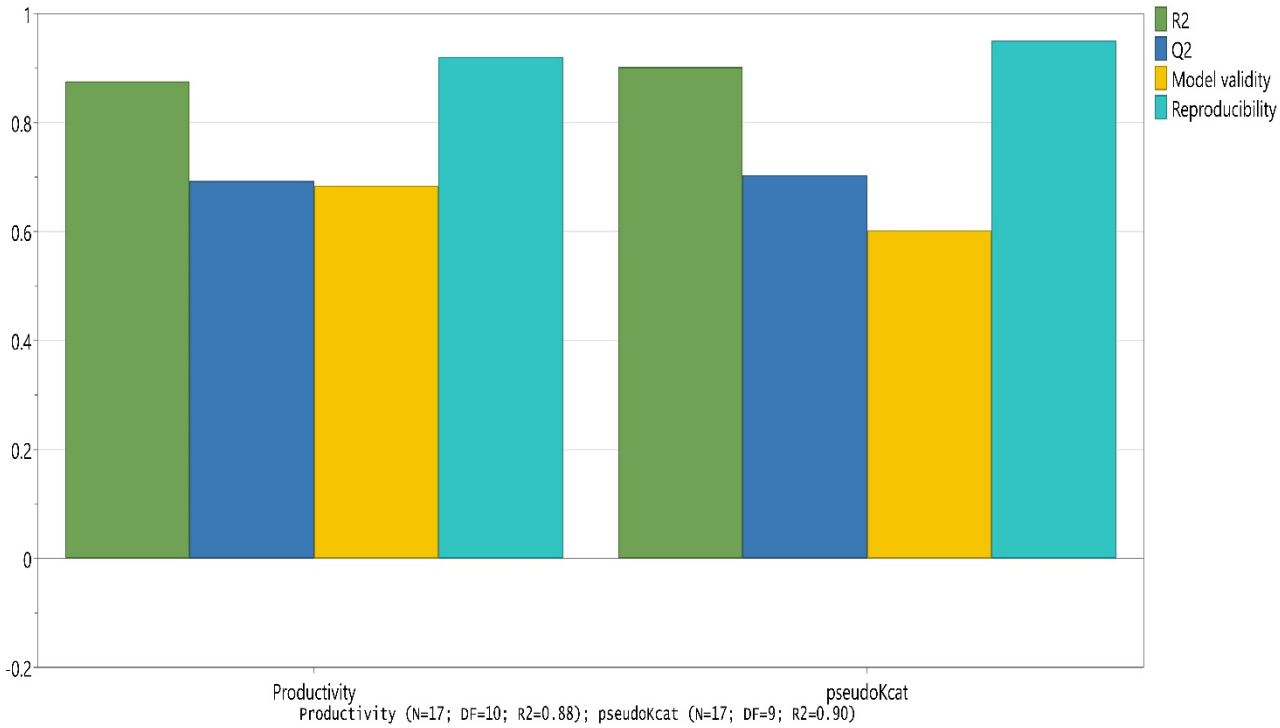

Figure S15. Summary plot for productivity and pseudoKcat.

Table S5. Ratio of the NMR integral between the signal at 4.52 ppm corresponding to H4 of **HBO-O-All** or the signal at 1.25 ppm corresponding to CH3 moiety of **HBO-O-All-Ad** or **HBO-O-All-Az** and allyl peak at 5.88 ppm normalized at 1.

Ratio peaks	*5 h*			*20 h*		
	n = 1	n = 4	n = 7	n = 1	n = 4	n = 7
4.52/5.88	0.35	0.59	0.28	0.32	0.37	0.09
1.25/5.88	0.34	1.97	1.34	0	1.27	0.84

UV-Curing

Figure S16 shows the spectra collected at different time intervals for the formulation containing **All_N7_TMPMP**. The disappearance of the S-H and C=C was visible after few second of irradiation confirming the fast-curing reaction.

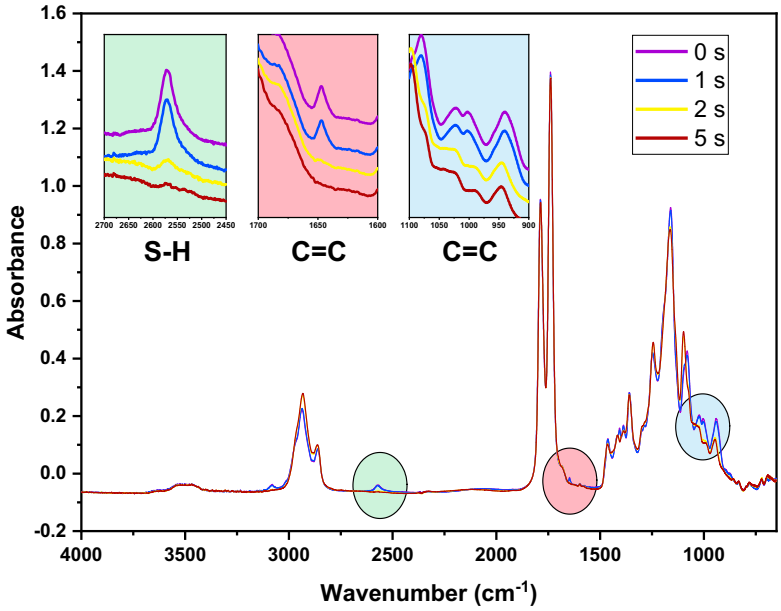

Figure S16. FTIR spectra detected for the thiol-ene formulation containing **All_N7** recorded at different irradiation time. The inserts highlight the thiol peak at 2570 cm^{-1} (green box), carbon double bond peak at 1640 cm^{-1} (red box) and the other region characteristic of C=C around 1025 cm^{-1} (blue box).

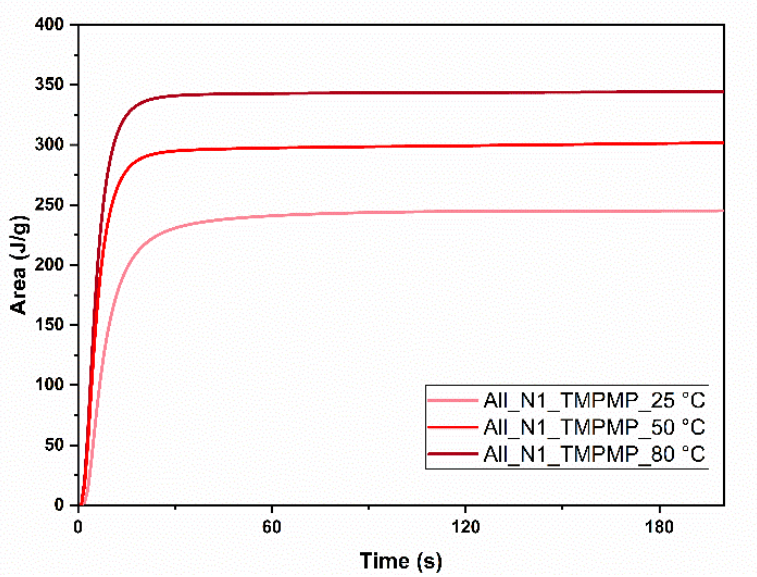

Figure S17. Integral derived from the exothermic peak representing the heat release for the photopolymerization.

Table S6. Results obtained from DSC analysis. Temperature of analysis, height of the peak (h_{peak}), Time at peak (t_{peak}), time to 95% of heat evolution ($t_{95\%DSC}$), total heat flow (ΔH), double bond conversion (DC_{DCS}) evaluated as ratio between heat flow at the set temperature and heat flow for theoretical total conversion (ΔH_{max}).

FORMULATION	**Temperature**	**h_{peak}**	**t_{peak}**	**ΔH**	**DC_{DCS} ($\Delta H/\Delta H_{max.}$)**
	[°C]	[W/g]	[W/g]	[J/g]	[%]
All_N1_TMPMP	25	26 ± 2	5.0 ± 1.0	245 ± 26	71
	50	38 ± 3	4.0 ± 0.5	301 ± 11	88
	80	51 ± 8	3.5 ± 1.0	344 ± 18	≈ 100
All_N4_TMPMP	25	59 ± 5	4.0 ± 1.0	380 ± 8	≈ 100
	50	46 ± 4	4.0 ± 1.0	338 ± 13	89
	80	50 ± 10	3.5 ± 0.5	308 ± 13	81
All_N7_TMPMP	25	61 ± 6	3.5 ± 0.5	368 ± 12	≈ 100
	50	34 ± 5	4.5 ± 1.0	320 ± 10	87
	80	45 ± 8	4.0 ± 1.0	299 ± 22	81

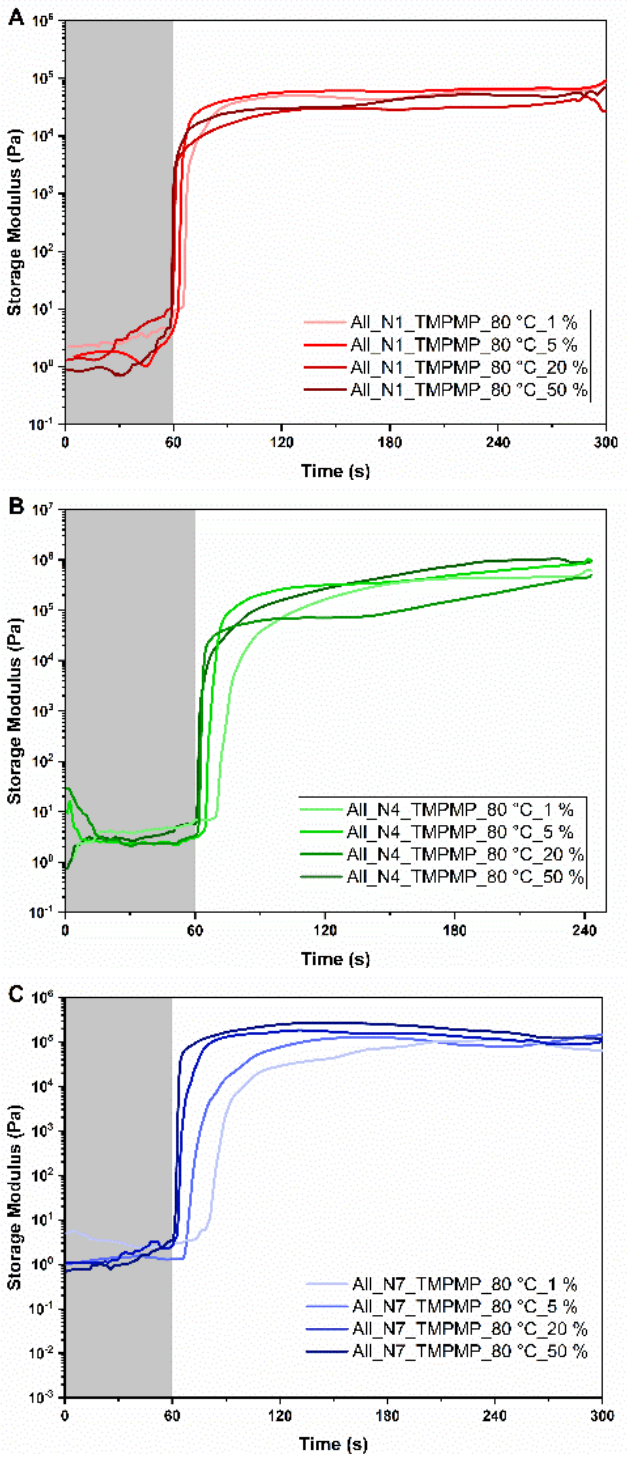

Figure S18. Photorheological curves for **All_N1_TMPMP** (A), **All_N4_TMPMP** (B) and **All_N7_TMPMP** (C) obtained at different light intensity, from 100% to 1% of percentage of lamp emission at 80 °C.

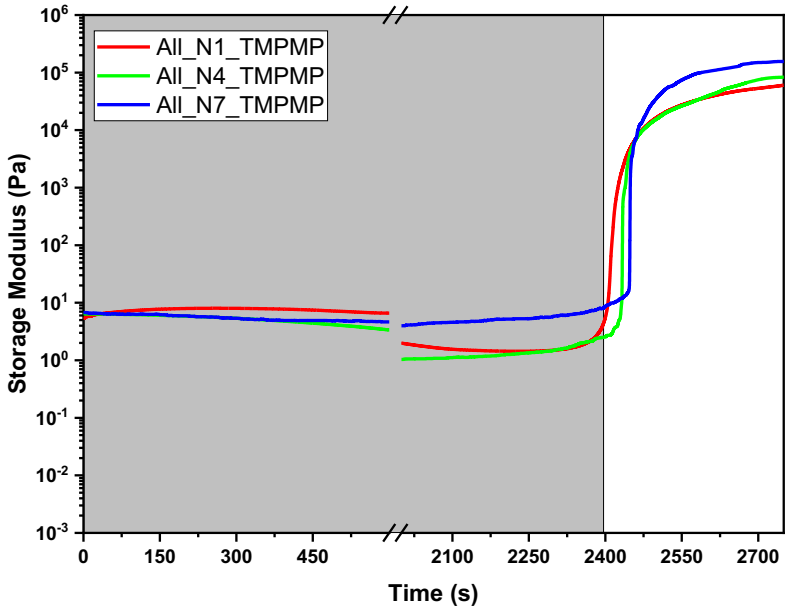

Figure S19. Photorheology of the three thiol-ene photocurable formulations kept at 80 °C for 40 minutes before irradiations

Thermo-mechanical and surface properties characterization of UV-cured network

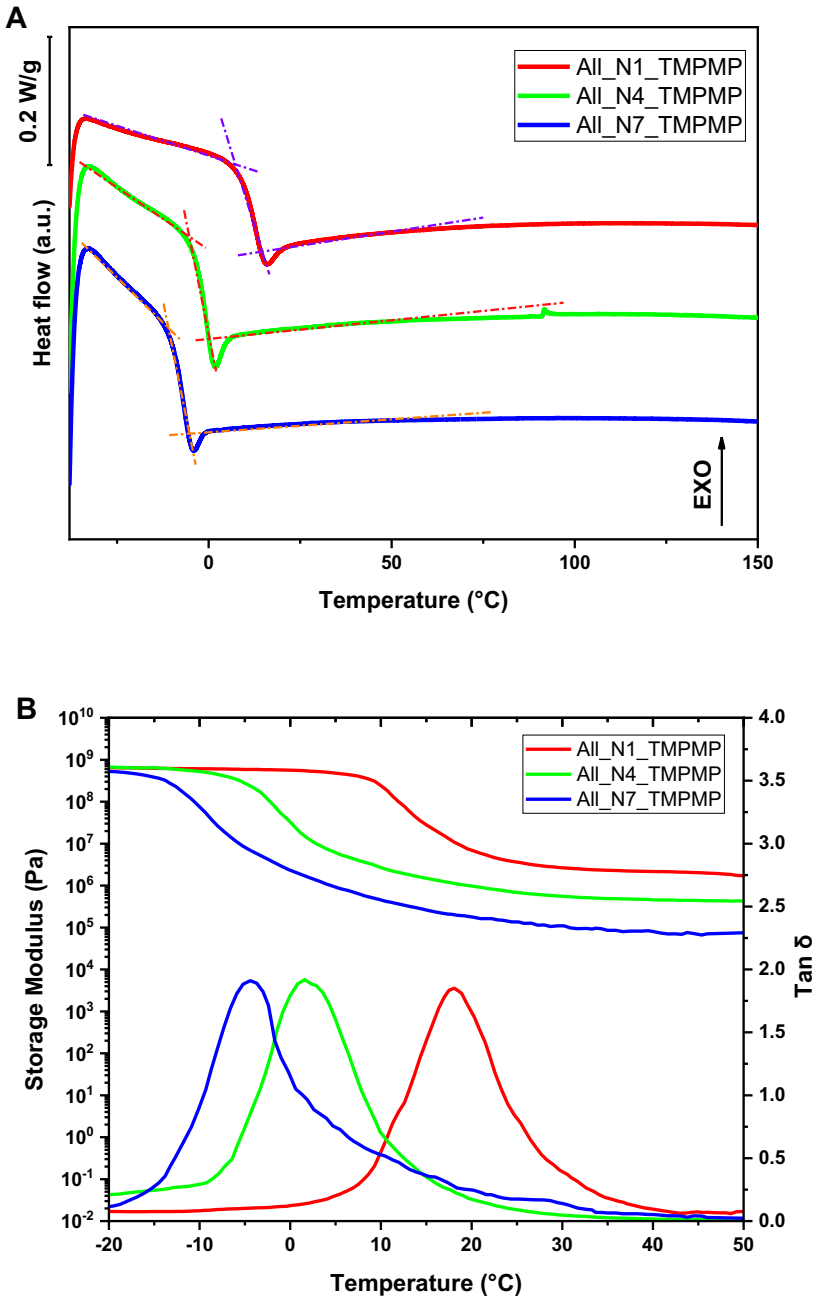

Figure S20. (A) thermogram of the three different UV-cured thiol-ene formulations; red line for the formulation containing **All_N1**, green line for the formulation **All_N4_TMPMP** and blue line for the formulation containing **All_N7**. The detection of the T_g is shown with dash-dot line for each thermoset. (B) DMTA result for the UV-cured thiol-ene networks; red line for formulation **All_N1_TMPMP**, green line for the formulation containing **All_N4** and blue line for the formulation containing **All_N7**. Storage modulus and Tan δ development as a function of the temperature are reported.

Table S7. Tensile test outcomes obtained for the three thermosets. Young's modulus (E), strength at break (σ), elongation at break (ε).

FORMULATION	E	σ	ε
	[MPa]	[MPa]	[%]
All_N1_TMPMP	4.2 ± 0.7	3.1 ± 0.5	100 ± 12
All_N4_TMPMP	3.5 ± 0.2	1.7 ± 0.3	62 ± 10
All_N7_TMPMP	3.2 ± 0.3	1.2 ± 0.3	46 ± 10

Thermal and chemical degradation

Table S8. Results derived from TGA, T_5 (temperature at 5% weight loss), T_{peak} (temperature at derivative peak), *Char* (percentage of residual weight at 700 °C).

FORMULATION	T_5	T_{peak}	Char
	[°C]	[°C]	[%]
All_N1_TMPMP	308	352	2.3
All_N4_TMPMP	301	346	2.2
All_N7_TMPMP	298	335	2.3

3D-printing

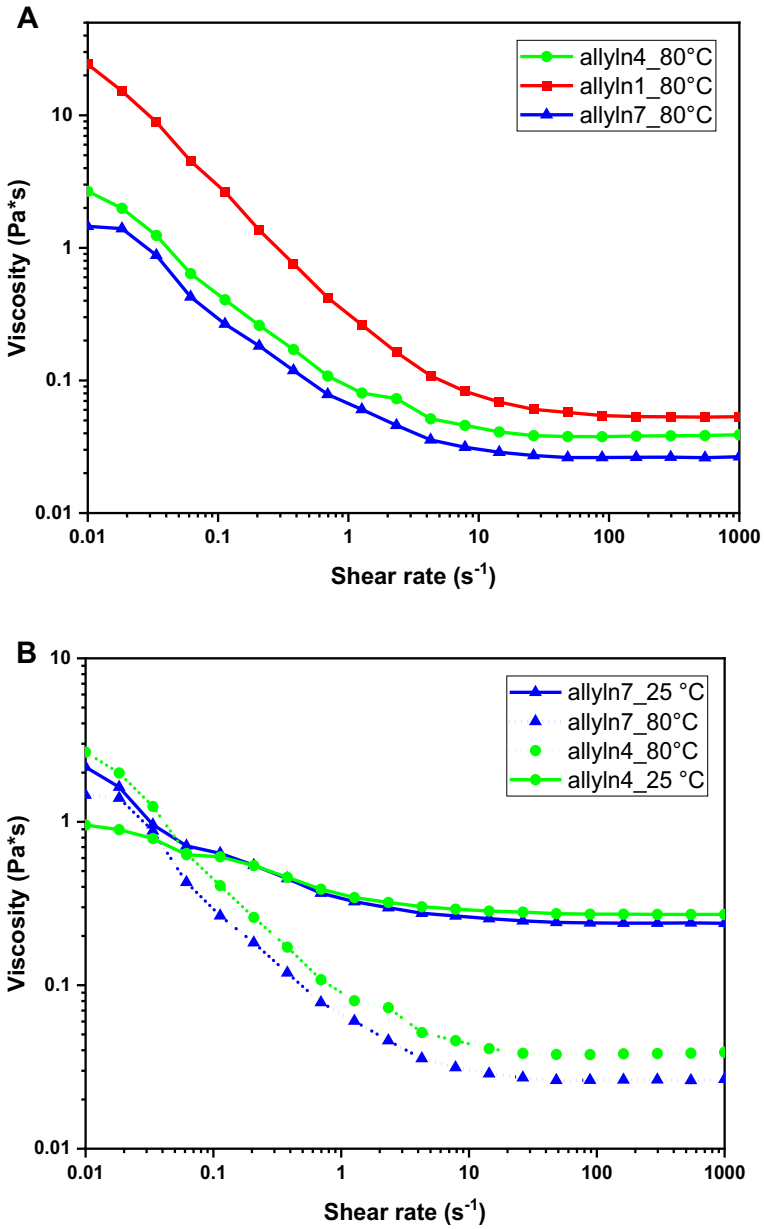

Figure S21. (A) Viscosity for the three resins at 80 °C. (B) Viscosity for **All_N4** and **All_N7** at 25 °C.

Figure S22. Honeycomb structure made by **All_N4.**

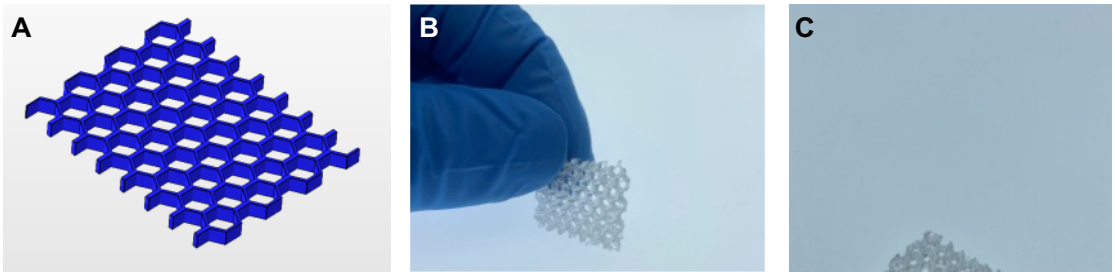

Figure S23. 3D-printed grid formed by hexagonal hole by **All_N7**.