Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Command-destruct thermosets via photoinduced thiol-catalyzed ß-scission of acyclic benzylidene acetals

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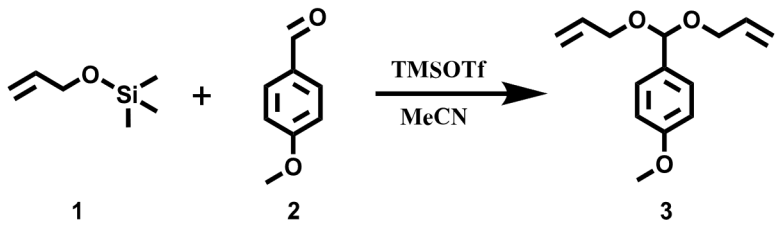
Description of supplementary videos. Supplementary video 1) Time lapse of poly(thioether acetal) networks with excess thiol, stoichiometric thiol/alkene, and excess alkene exposed to UV light. Samples were formulated with 10 mol% photoinitiator. Video playback is 4x real time. Supplementary video 2) Selective photodegradation of poly(thioether acetal) networks using laser irradiation. Networks exhibit complete stability towards 150 mW 633 nm red and 100 mW 532 nm green lasers outside the excitation bands of TPO-L photoinitiator, while undergoing rapid degradation along the path of a 50 mW 405 nm laser at the edge of the excitation region for the TPO-L photoinitiator.

Materials. Allyl alcohol, 4-methoxybenzaldehyde, dry acetonitrile, 2-hydroxy-2-methylpropiophenone (Darocur 1173), hexanes, ethyl acetate, and ether were obtained from Fisher Scientific and used as received. Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) was supplied by Bruno Bock.

Equipment and Instrumentation. Samples in all polymerizations and degradation experiments were irradiated using an Omnicure S-1000B light source using (100W mercury lamp, λ_{max} = 365 nm, 320-500 nm filter) with light guide at a prescribed irradiation intensity calibrated using an International Light Model 1400A calibration radiometer.

FT-IR kinetic data was collected using a Thermo Nicolet 8700 spectrophotometer with a KBr beam splitter and an MCT/A cryogenic detector under an inert nitrogen atmosphere. Data was collected at a resolution of 2 cm^{-1} at 1.37 s intervals. Samples were irradiated at an intensity of 200 mW cm^{-2} with a light guide positioned into the FT-IR environmental chamber. Thiol conversion was monitored using the change in peak area of the S-H stretch at 2550 cm^{-1}, alkene conversion was monitored at 1631 and 3130 cm^{-1}, and ß scission was tracked using the appearance of the benzoate ester peak at 773 cm^{-1} relative to the constant area of the aromatic C-H peak at 1516 cm^{-1}. Free films used for visual observations were subjected to an appreciable degree of heating under the light source and underwent rapid degradation. Therefore, samples for FT-IR kinetics were placed on a heated stage at 60 °C to replicate the bulk process, as the NaCl windows act as a heat sink for thin films.

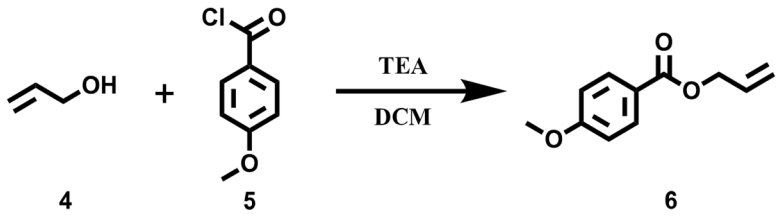
NMR analysis was performed on a Bruker Ascend 600 MHz spectrometer with a sample temperature of 303.1 K. All samples were diluted to 40 mg/mL in $CDCl_3$ or DMSO-D_6 for analysis. All proton experiments were set to a relaxation delay of 5 s and carbon/2D experiments were set to 2 s. All spectra were referenced to solvent shifts in the absence of other internal standards.



1 2 3

Scheme S1. Synthesis of bis-allyl 4-methoxybenzylidene acetal (BAMA, **3**)

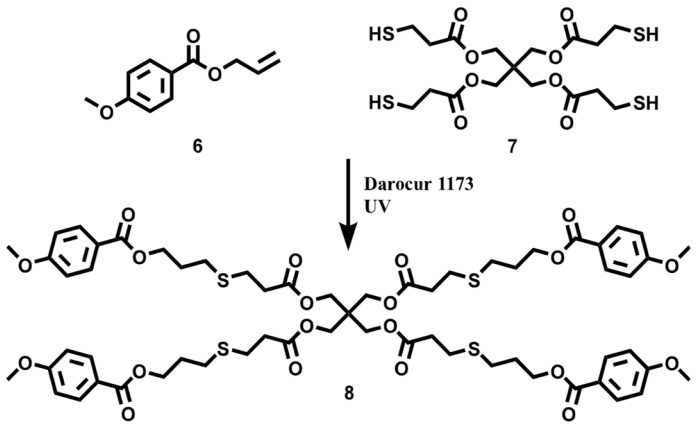
Synthesis of p-methoxybenzylidene bis-allyl acetal (3). p-methoxybenzylidene bis-allyl acetal (BAMA, compound **3**) was synthesized using procedures adapted from literature.[1-3] 200 mL of dry MeCN was added to a flame-dried round bottom flask using a cannula under air-free conditions at 0°C, followed by sequential addition of 20 g p-methoxybenzaldehyde (compound **2**, 146.9 mmol, 1 equiv) and 49.75 g allyloxytrimethylsilane (compound **1**, 382 mmol, 2.6 equiv). The reaction mixture was then sparged with N_2 for 15 minutes. 1.63 g trimethylsilyl triflate catalyst (7.35 mmol, 0.05 equiv, 5 mol% to aldehyde) was added and the reaction was allowed to warm to room temperature and stir overnight. The reaction mixture was quenched by addition of 0.1 equiv triethylamine and equivolumetric amount of 1M sodium bicarbonate under vigorous stirring. Upon addition of bicarb, the crude product formed a pale yellow oil that phase separated to the top of the mixture upon settling. The resultant oil was then diluted in 100 mL ether and washed with 3 x 100 mL portions of 1M bicarb, 2 x 200 mL DI H_2O, and 2 x 200 mL brine. The product was then dried over $MgSO_4$ and concentrated via rotary evaporation. The resultant oil was then purified via column chromatography (5% TEA, 15% EtOAc, 80% hexanes, silica gel support) and concentrated under vacuum to yield 23.41 g (68.1% yeild) of pure acetal **3** as a clear oil. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.35 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.92 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 2H), 5.55 (s, 1H), 5.28 (dq, *J* = 17.2, 1.8 Hz, 2H), 5.14 (dq, *J* = 10.5, 1.6 Hz, 2H), 4.01 (ddt, *J* = 5.2, 3.3, 1.6 Hz, 4H), 3.76 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.20, 134.88, 130.64, 127.64, 116.06, 113.39, 100.21, 65.82, 54.98.



4 5 6

Scheme S2. Synthesis of allyl 4-methoxybenzoate (**6**)

Synthesis of allyl 4-methoxybenzoate (6). 3 g 4-methoxybenzoyl chloride (compound **5**, 17.6 mmol, 1 equiv), 5.1 g allyl alcohol (compound **4**, 87.9 mmol, 5 equiv), and 40 mL dry DCM were added to a flask with magnetic stirring in accordance with literature procedures.[4] 3.56 g triethylamine (35.2 mmol, 2 equiv) was added over the course of 10 mins. The reaction was stirred for 30 mins, quenched with 1M bicarb, and extracted with 2 x 100 mL portions of ether. The combined organic layers were washed with 2 x 100 mL 1M bicarb and 2 x 100 mL brine, dried with $MgSO_4$, and concentrated under rotary evaporation. The resultant compound was purified via flash chromatography (0% → 15% EtOAc in hexanes, silica support) to yield 2.84 g allyl 4-methoxybenzoate (**6**) (14.78 mmol, 83.4%) as a pale yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 9.34 Hz, 2H), 6.92 (d, *J* = 8.89 Hz 2H), 6.04 (ddt, *J* = 17.4, 10.6, 5.6 Hz, 1H), 5.40 (dq, *J* = 17.4, 1.6 Hz, 1H), 5.27 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.80 (dt, *J* = 5.6, 1.5 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.34, 163.76, 132.86, 132.01, 122.98, 118.29, 113.97, 65.60, 55.77.



Scheme S3. Synthesis of tetra tetraallylmethoxybenzoate-PETMP (**8**)

Synthesis of model tetraamethoxybenzoate analog (8). 500 mg pentaerythritol tetrakis(3-mercaptopropionate) (compound **7**, 1.02 mmol, 1 equiv, 4 SH equiv), 1.0 g allyl 4-methoxybenzoate (compound **6**, 5.2 mmol, 5.2 equiv), and 100 mg 2-hydroxy-2-methylpropiophenone (Darocur 1173, 0.61 mmol, 0.6 equiv) were added to a scintillation vial and stirred under UV light for 30 min. The resultant viscous oil was purified via flash chromatography (0% → 20% EtOAc in hexanes, silica support) to yield 1.16 g tetraallylmethoxybenzoate-PETMP (compound **8**, .93 mmol, 91%) as a pale yellow oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.7 Hz, 8H), 6.91 (d, *J* = 8.7 Hz, 8H), 4.36 (t, *J* = 6.2 Hz, 8H), 4.16 (s, 8H), 3.85 (s, 12H), 2.78 (t, *J* = 7.2 Hz, 8H), 2.65 (dt, *J* = 23.0, 7.2 Hz, 16H), 2.03 (p, *J* = 6.4 Hz, 8H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.21, 166.18, 163.39, 131.58, 122.62, 113.64, 63.14, 62.25, 55.43, 34.56, 28.82, 28.79, 26.95.

Synthesis of polymer thermosets. Polymer discs were prepared by combining pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) and MA in varying stoichiometries based on functionality. Samples were prepared in 1.1:1, 1:1, and 1:1.1 thiol:ene stoichiometry with addition of 10 mol% 2-hydroxy-2-methylpropiophenone (Darocur 1173) as a photoinitiator. These resin stocks were then vortex mixed for one minute and centrifuged to remove air bubbles. 200 µL aliquots of resin were placed between glass slides using 500 µm PTFE spacers. The resins were cured at an intensity of 200 mW cm^{-2} for 3s per side.

Photodegradation and analysis of the degradation products. 1 g PETMP (compound **7**, 2.05 mmol, 1.1 SH equiv), 872 mg BAMA (compound **3**, 3.7 mmol, 1.0 alkene equiv), and 122 mg Darocur 1173 (0.74 mmol, 10 mol% wrt alkene) were added to a vial and vortex mixed for 1 min. 200 µL aliquots of resin were placed between glass slides using 500 µm PTFE spacers and cured at an intensity of 200 mW cm^{-2} for 3s per side to form polymer network **9**. The resultant discs were irradiated at 400 mW cm^{-2} to induce photodegradation. The liquid degradation products were collected as drops from the polymer disc. The viscous liquid degradation products from multiple discs were combined and purified via flash chromatography (hexanes → EtOAc, silica support) to remove residual photoinitiator, initiator fragments, and partially degraded oligomeric species to yield the simplest and most abundant photodegradation product. The samples collected for analysis eluted from 60-70% EtOAc. The resultant bis-propyl, bis-propyloxy(4-methoxybenzoyl)-PETMP (**10**) was dried under vacuum at 75°C overnight and analyzed via NMR spectroscopy. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.9 Hz, 4H), 6.91 (d, *J* = 8.9 Hz, 4H), 4.37 (t, *J* = 6.3 Hz, 4H), 4.16 (d, *J* = 1.5 Hz, 8H), 3.85 (s, 6H), 2.76 (dt, *J* = 26.6, 7.2 Hz, 8H), 2.69 – 2.58 (m, 12H), 2.51 – 2.46 (t, J = 7.84, 4H), 2.03 (p, *J* = 6.5 Hz, 4H), 1.59 (h, *J* = 7.3 Hz, 4H), 0.97 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.46, 166.30, 163.51, 131.71, 122.75, 113.76, 63.27, 62.42, 62.35, 55.55, 42.22, 34.82, 34.69, 34.33, 28.95, 28.92, 27.07, 26.97, 22.97, 13.55.

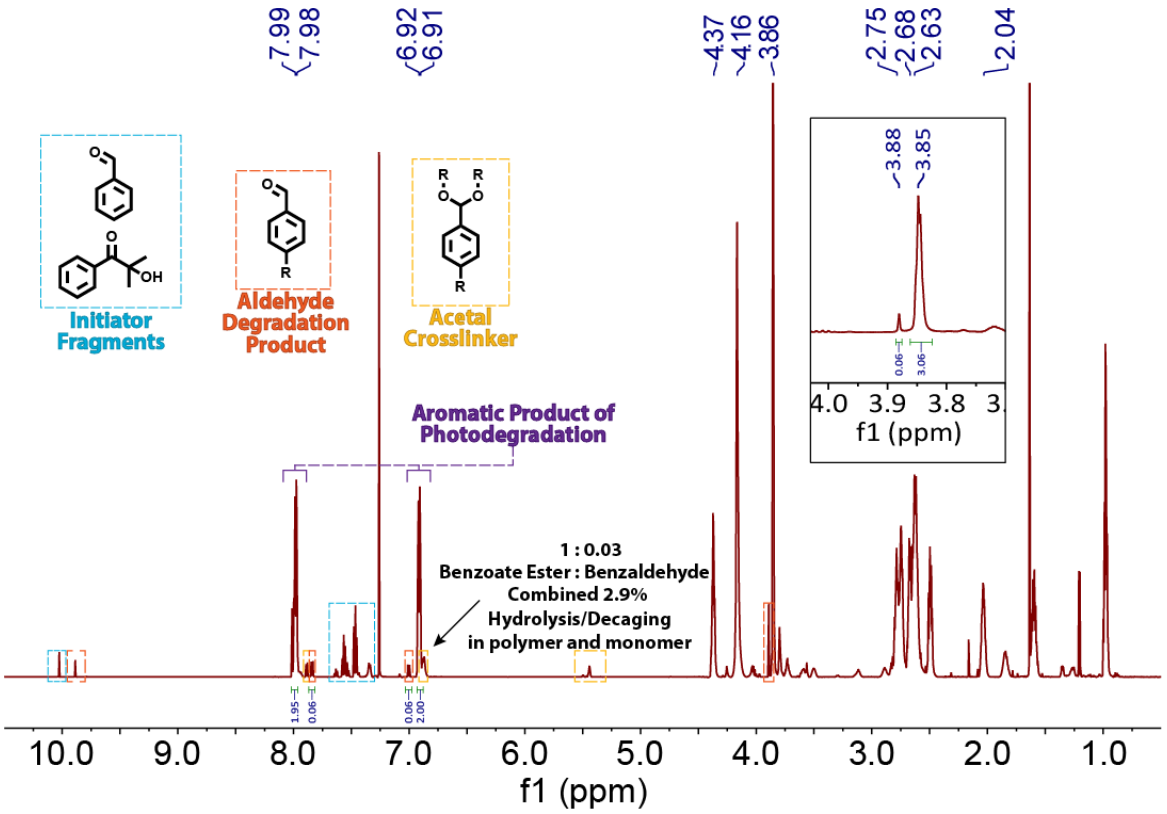


Fig. S1. NMR of crude photodegradation products to show lack of competing hydrolysis/decaging reactions. The areas integrated represent only 4-methoxybenzoate ester and 4-methoxybenzaldehyde aromatic and methoxy shifts. Complete assignments and integrations listed in NMR data section.

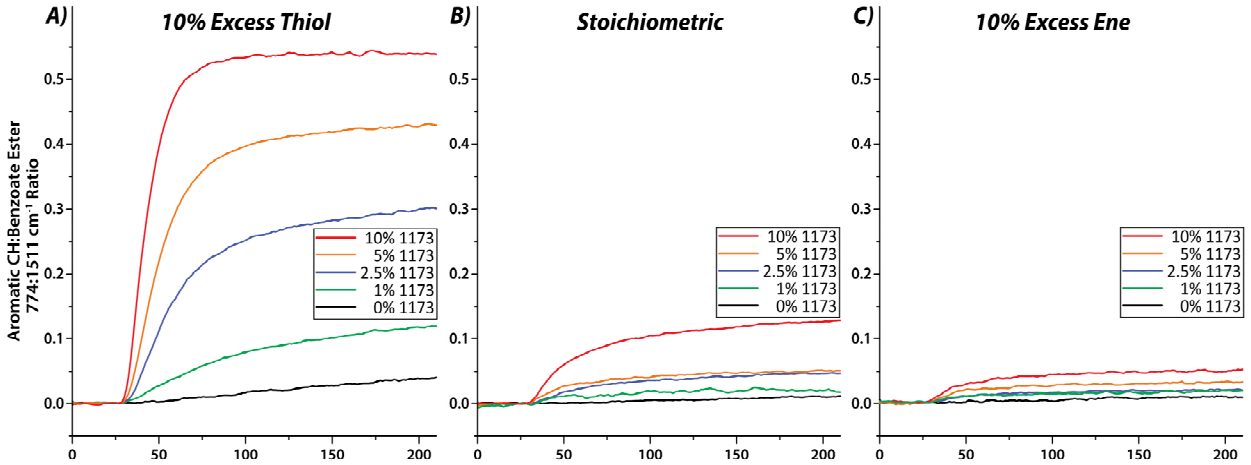


Fig. S2. Initiator concentration dependence of BAMA:PETMP network degradation at 200 mW cm^{-2} irradiation.

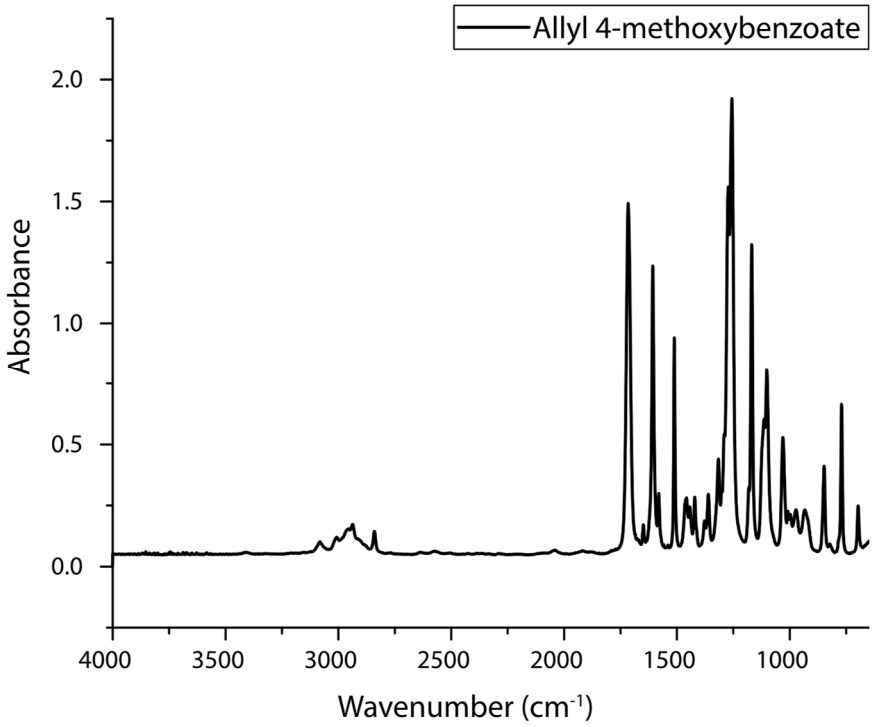


Figure S3. FT-IR Spectra of compound **6**

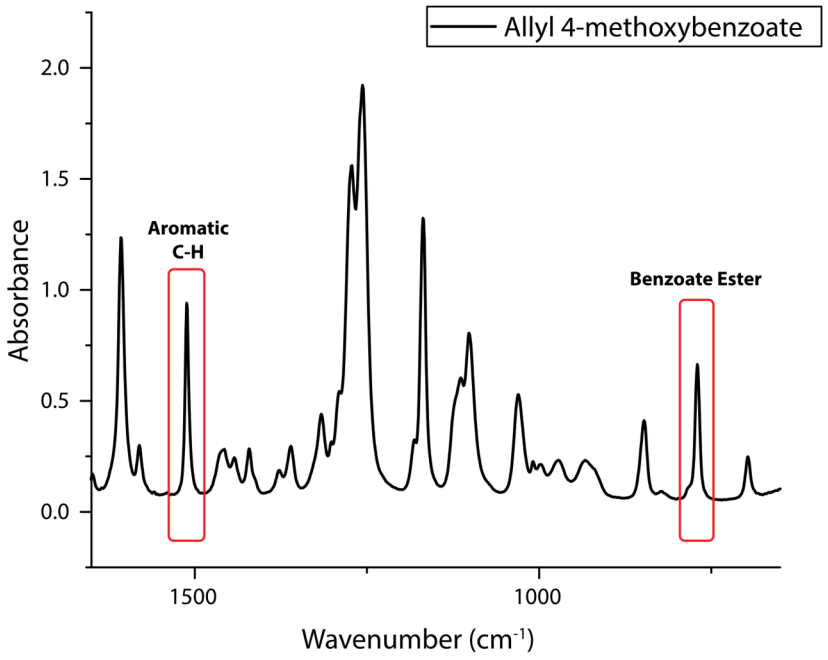


Fig. S4. FT-IR of allyl-methoxybenzoate control compound **6**. Benzoate ester peak at 774 cm^{-1} corresponds to the same peak observed in the degradation process. The ratio of the highlighted benzoate ester peak to the highlight aromatic peak is used to quantify acetal ß-scission to form benzoate esters.

FTIR Kinetic Analysis

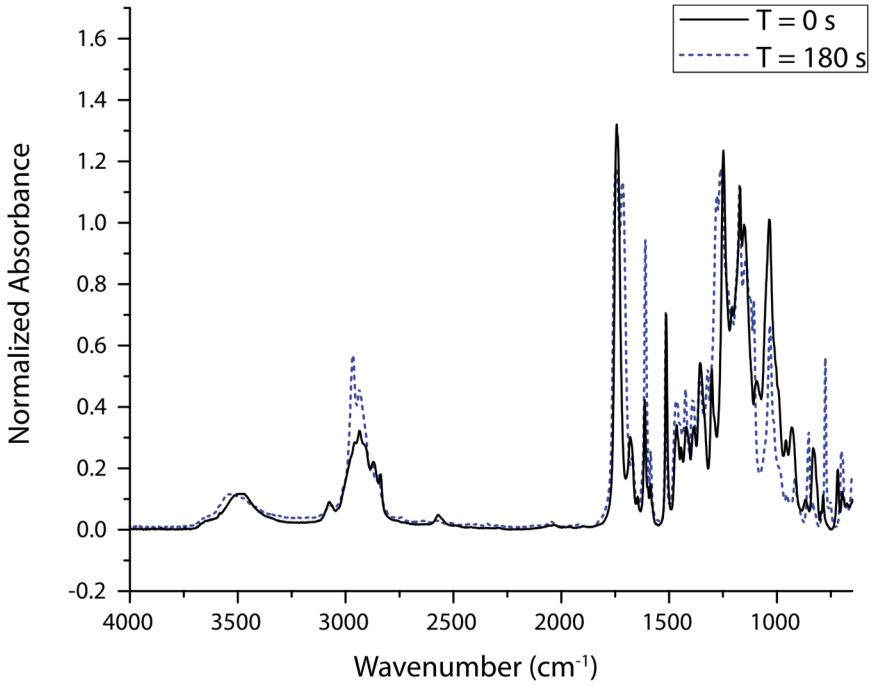


Fig. S5. PETMP-acetal resin prior to irradiation (solid black) and after 180 s irradiation at 200 mW cm^{-2} (dashed blue).

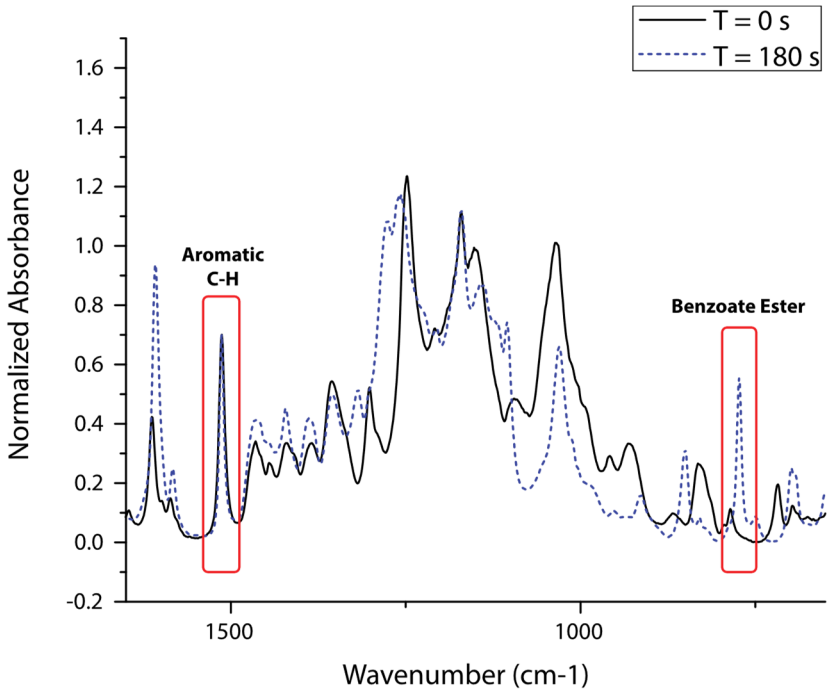


Fig. S6. Spectra of PETMP-acetal resin prior to irradiation (solid black) and after 180 s irradiation at 200 mW cm^{-2} (dashed blue) cropped to the region of interest. As in figure S.2, the highlighted regions indicate the peaks tracked to obtain kinetic information.

NMR Spectra of Compounds

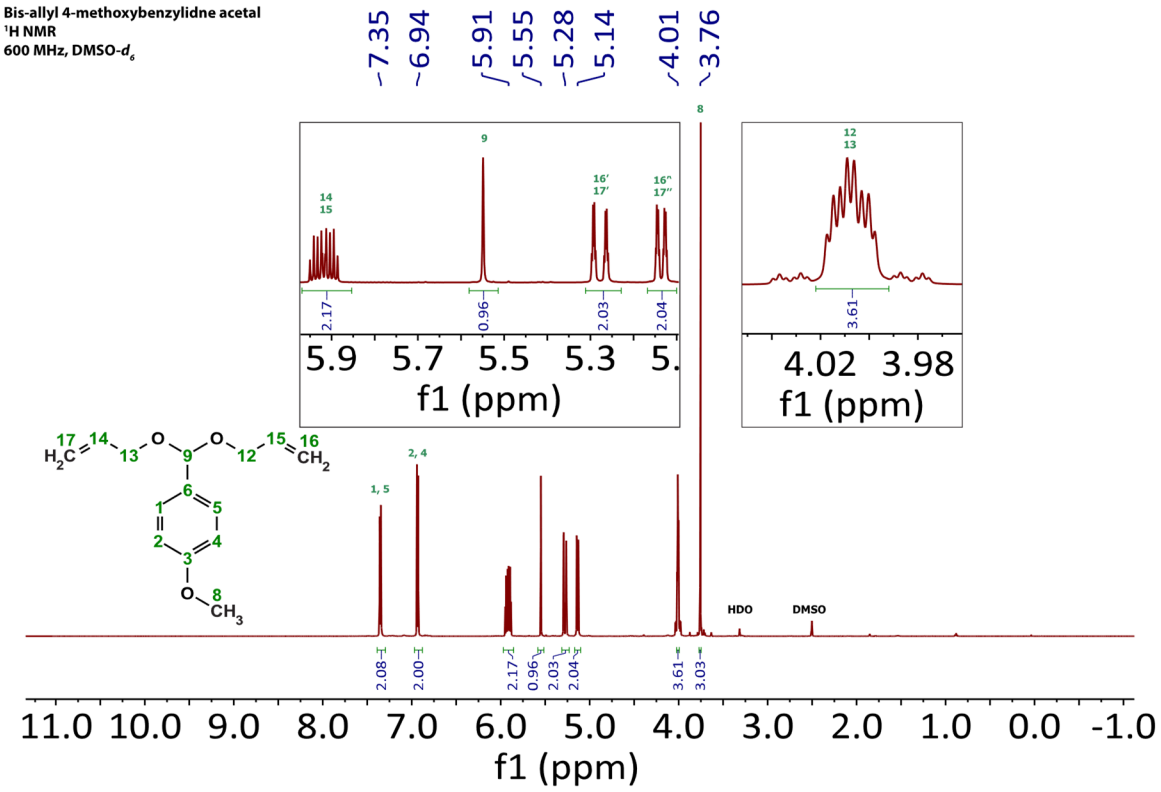


Figure S.7: ^{1}H NMR Spectrum of BAMA (**3**)

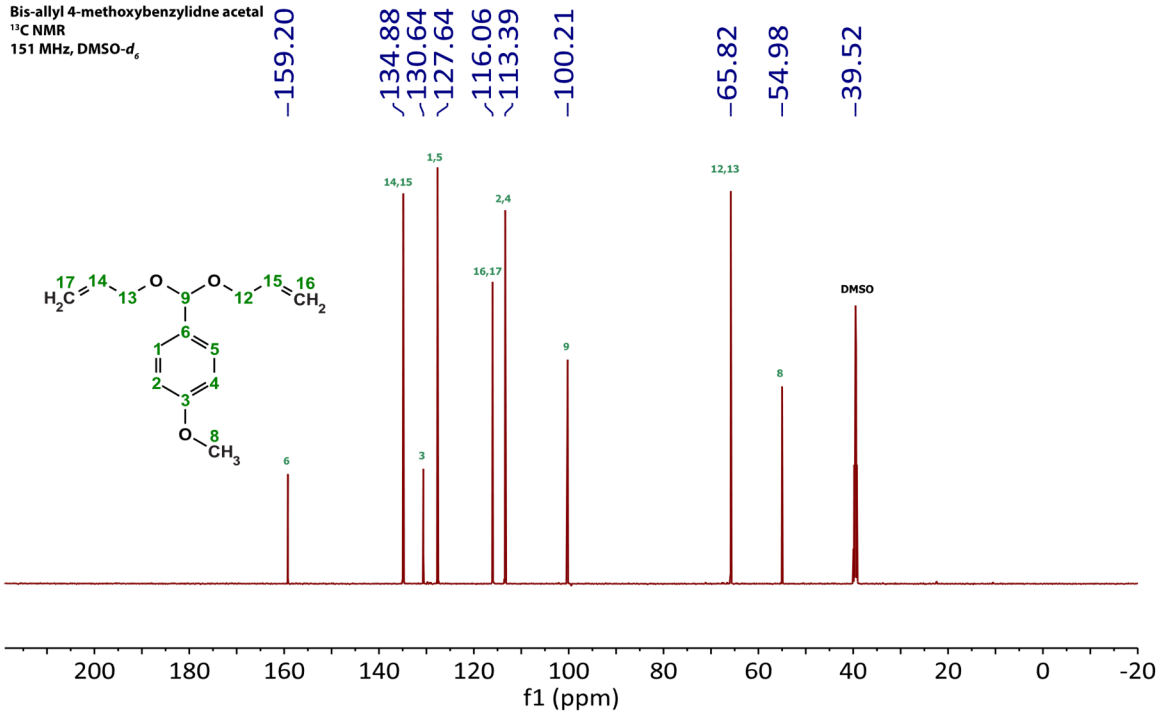


Fig. S8. ^{13}C NMR Spectrum of BAMA (**3**)

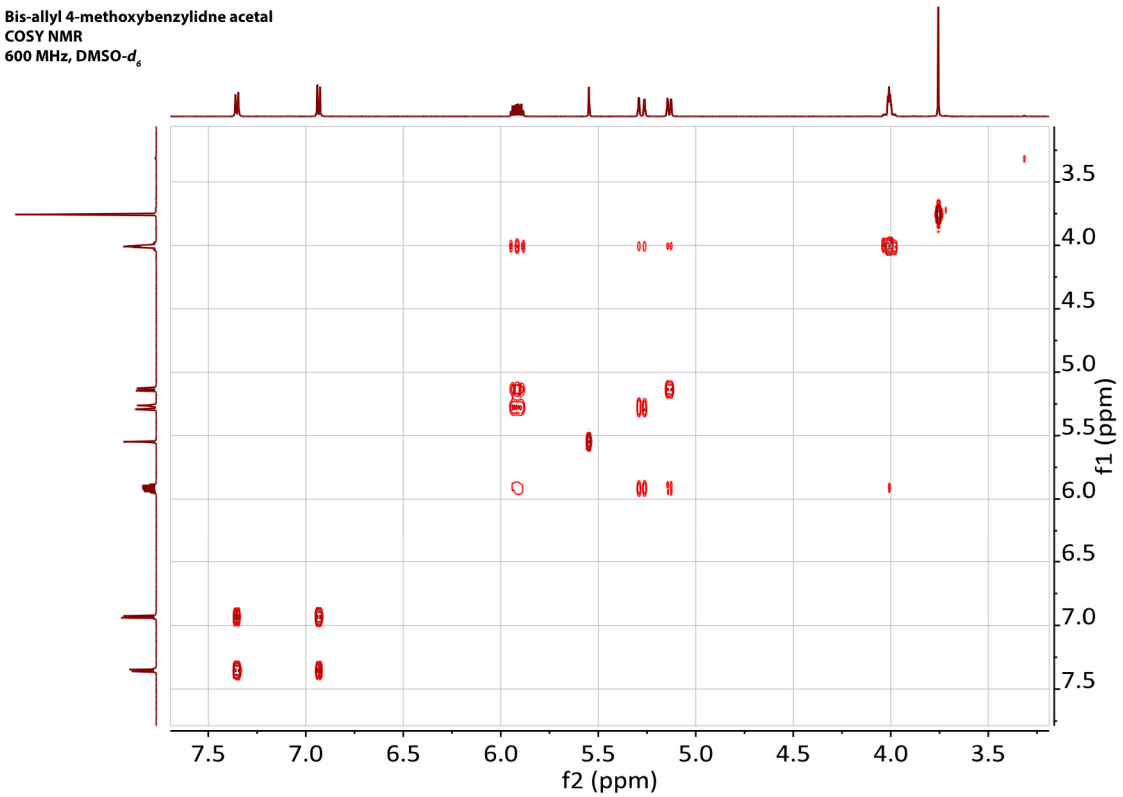


Fig. S9. COSY NMR Spectrum of BAMA (**3**)

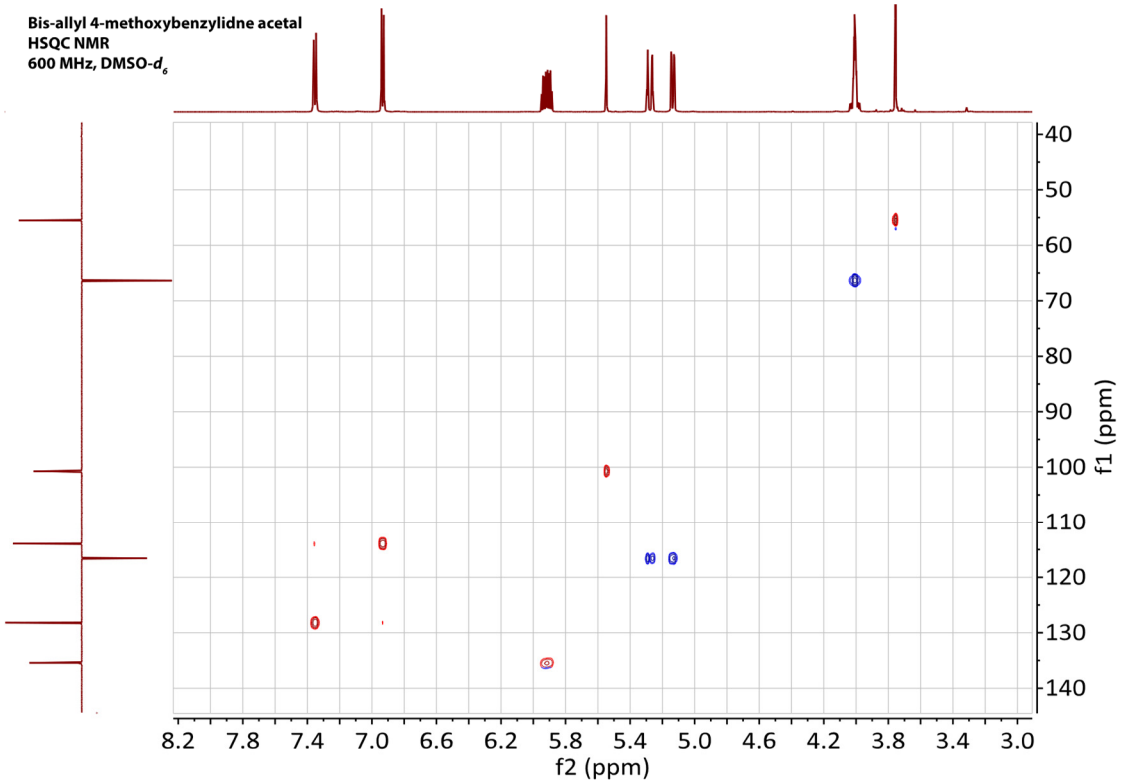


Fig. S10. HSQC NMR Spectrum of BAMA (**3**)

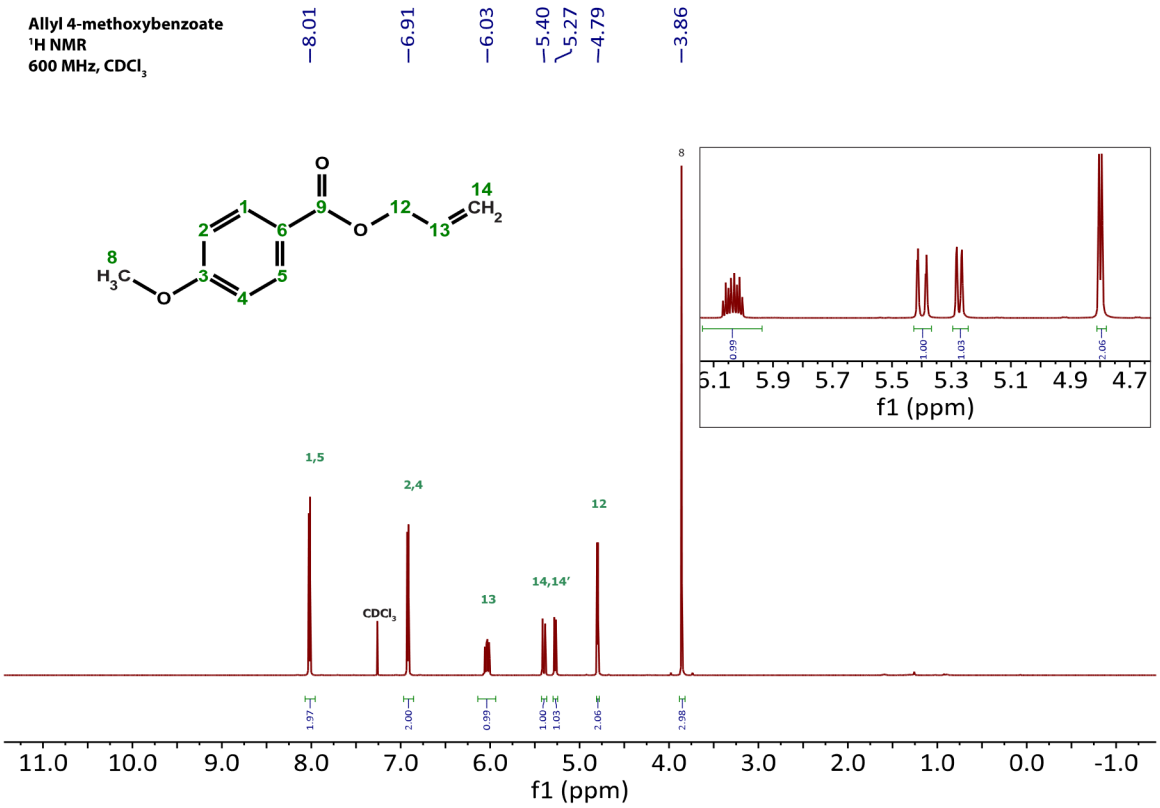


Fig. S11. ^{1}H NMR Spectrum of **6**

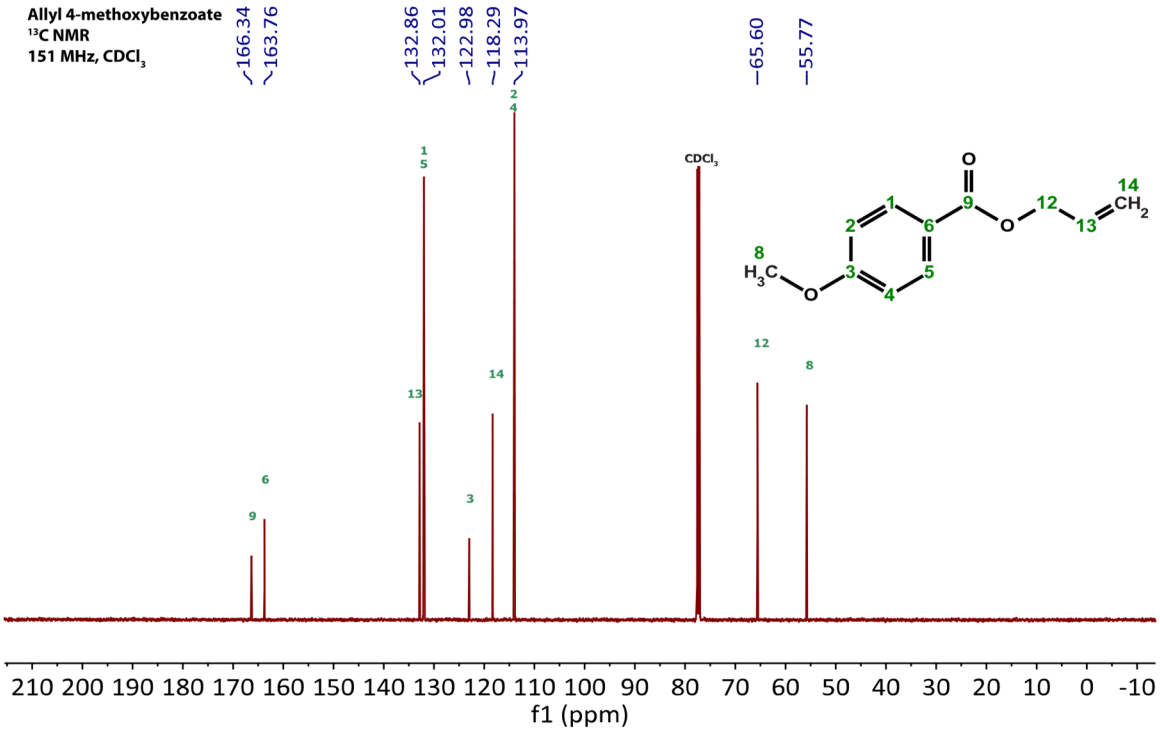


Fig. S12. ^{13}C NMR Spectrum of **6**

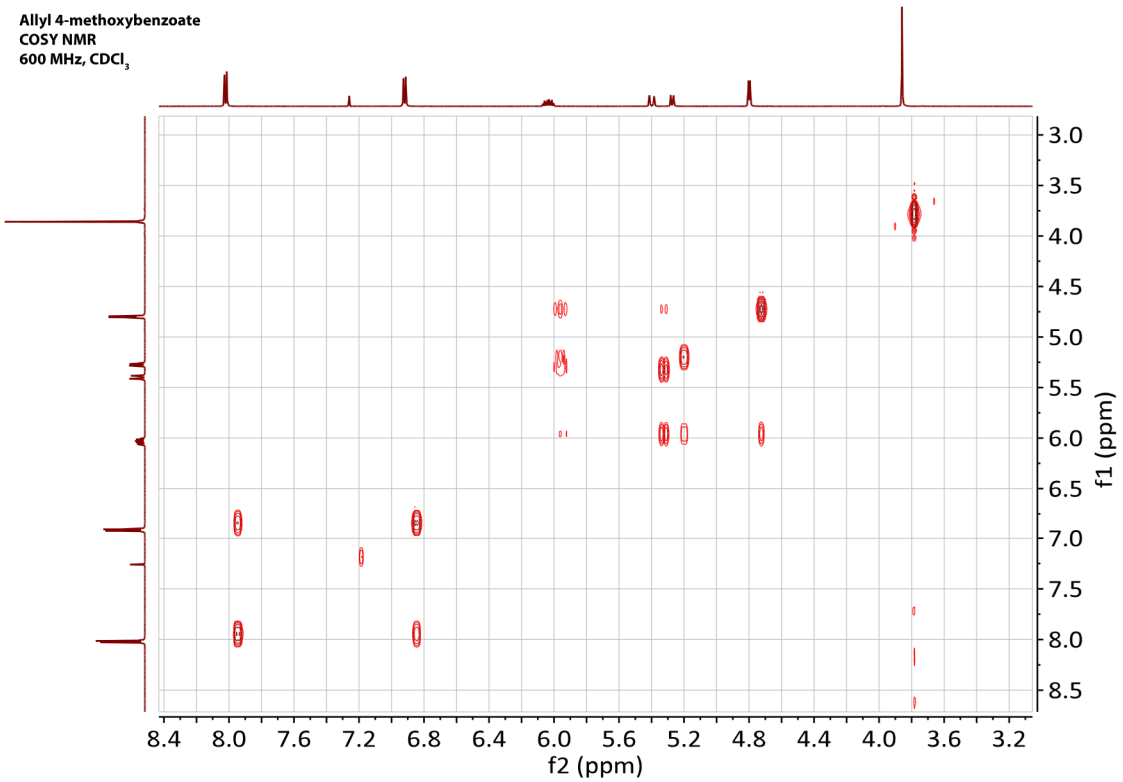


Fig. S13. COSY NMR Spectrum of **6**

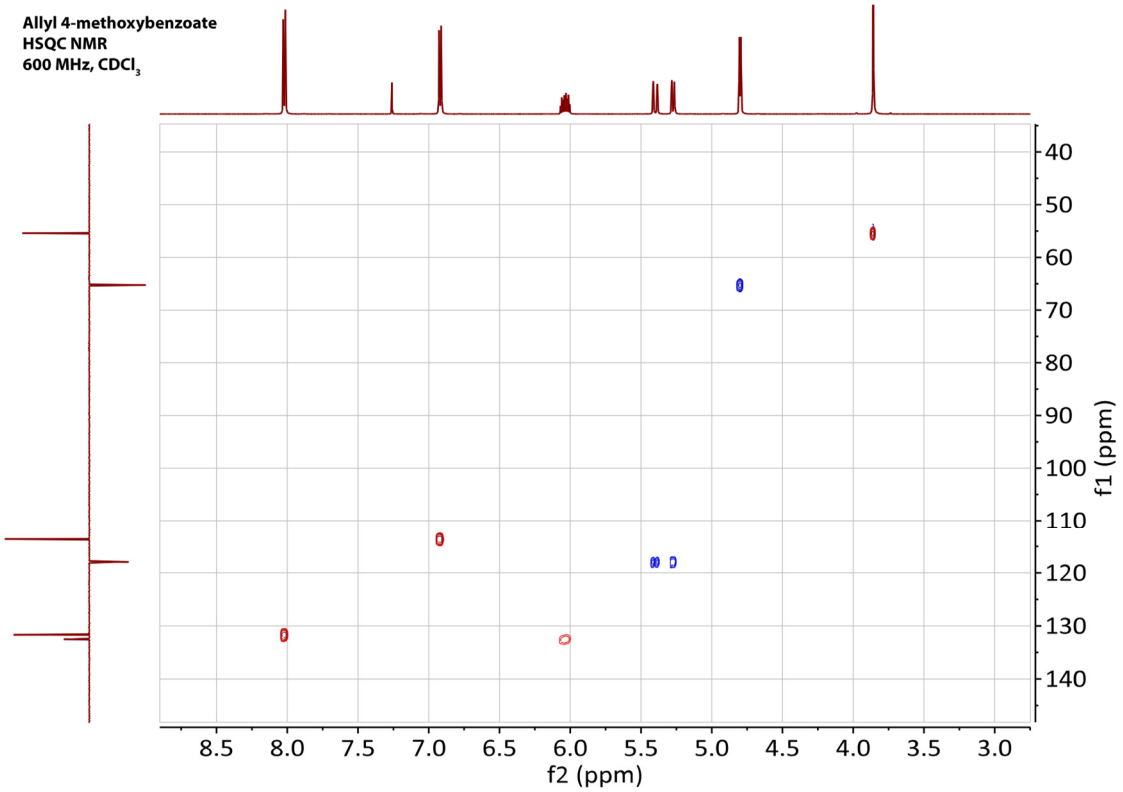


Fig. S14. HSQC NMR Spectrum of **6**

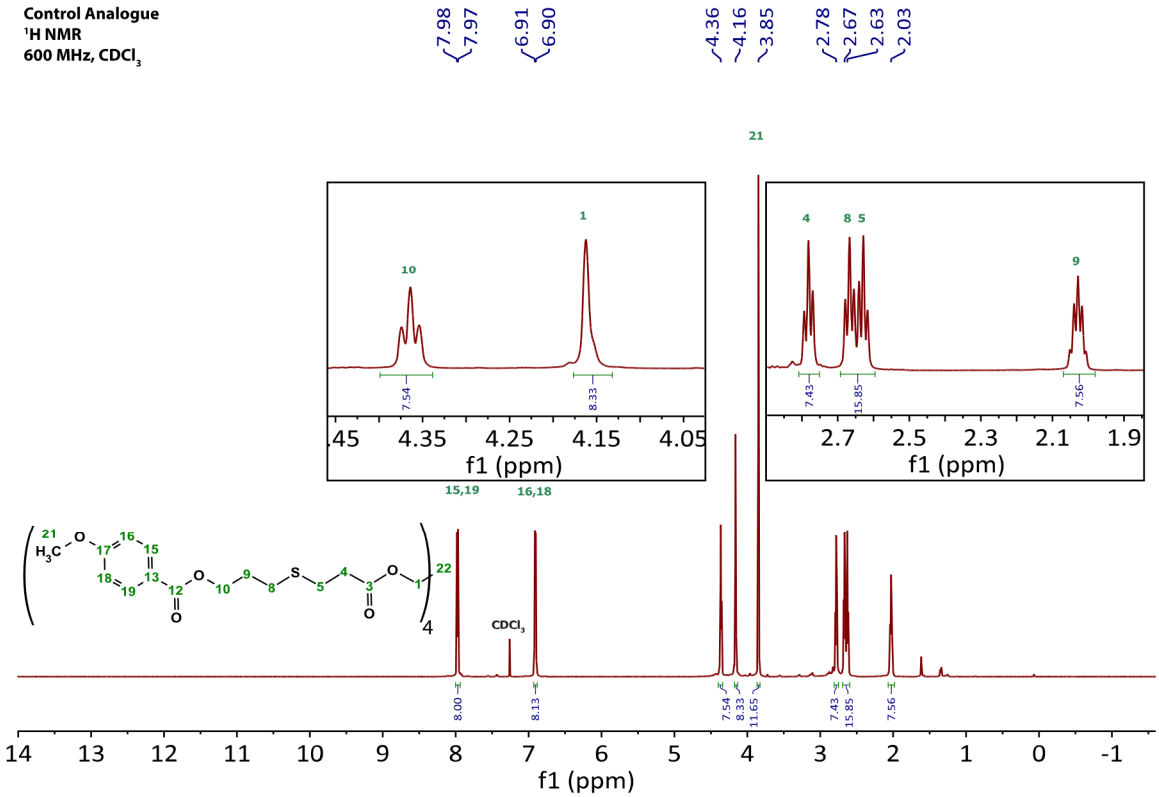


Fig. S15. ^{1}H NMR Spectrum of **8**

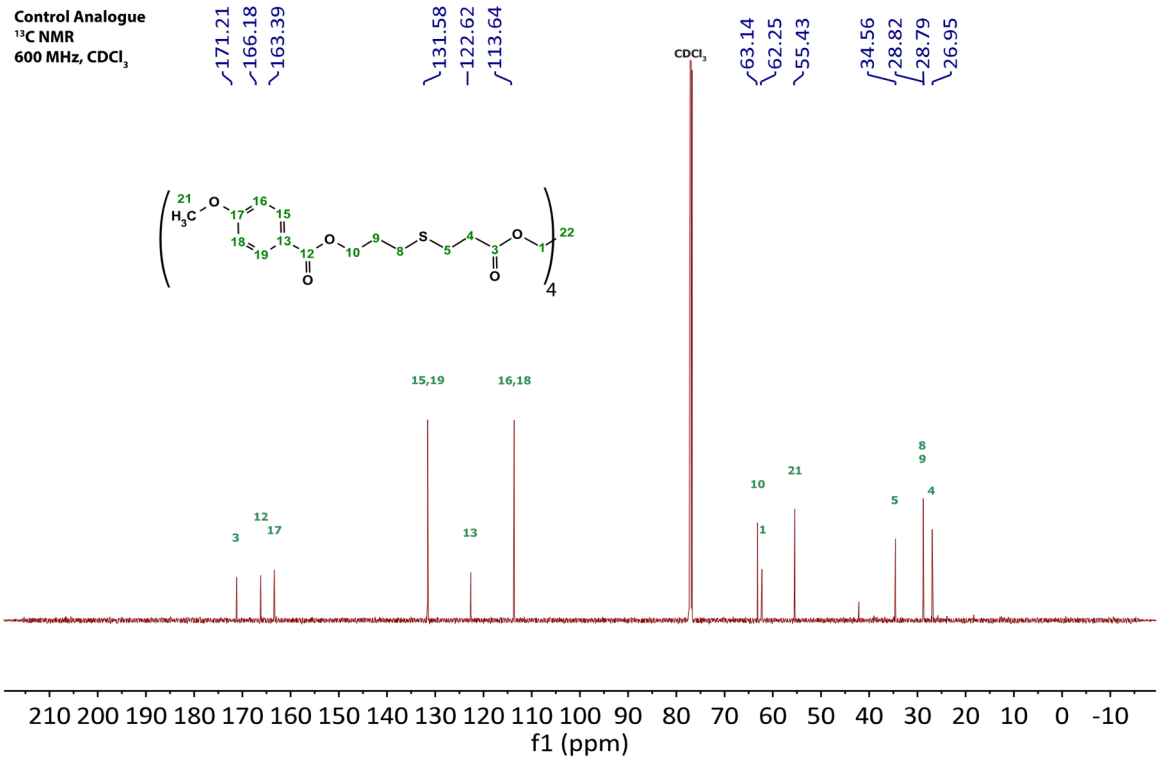


Fig. S16. ^{13}C NMR Spectrum of **8**

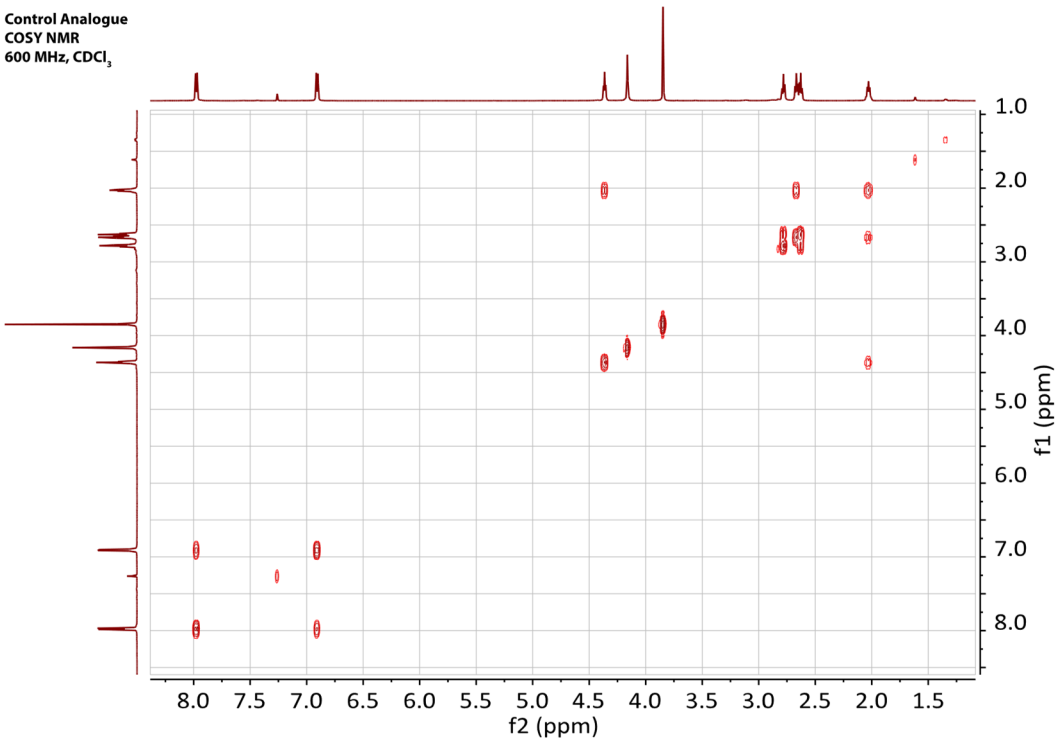


Fig. S17. COSY NMR Spectrum of **8**

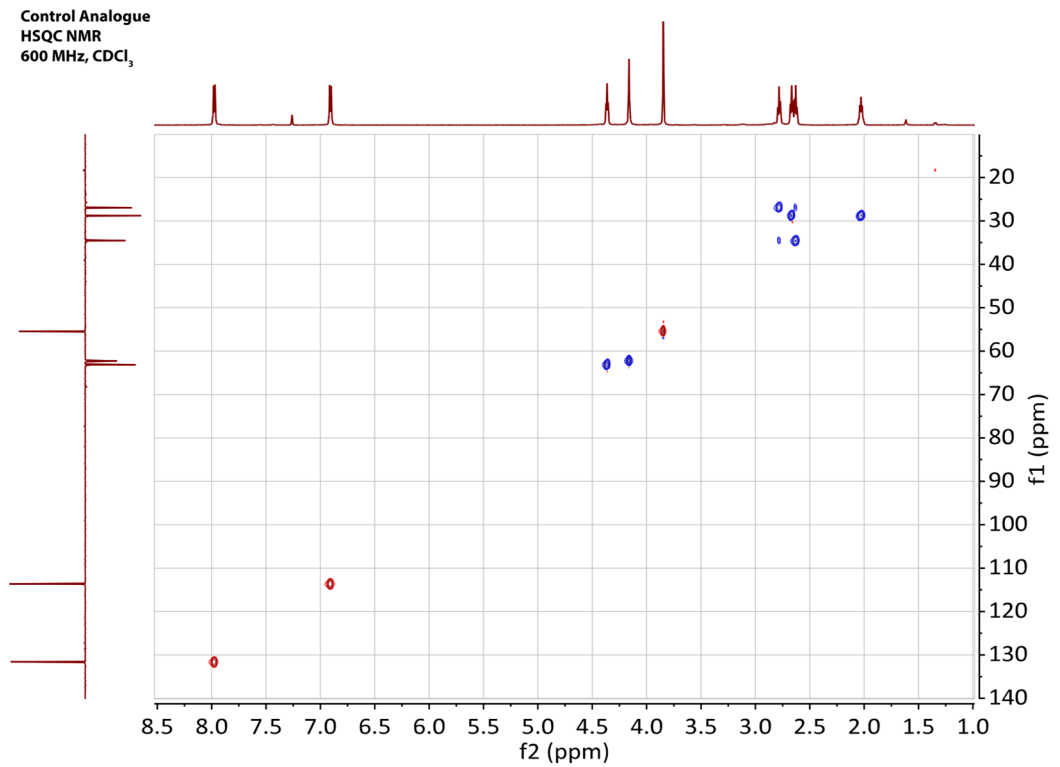


Fig. S18. HSQC NMR Spectrum of **8**

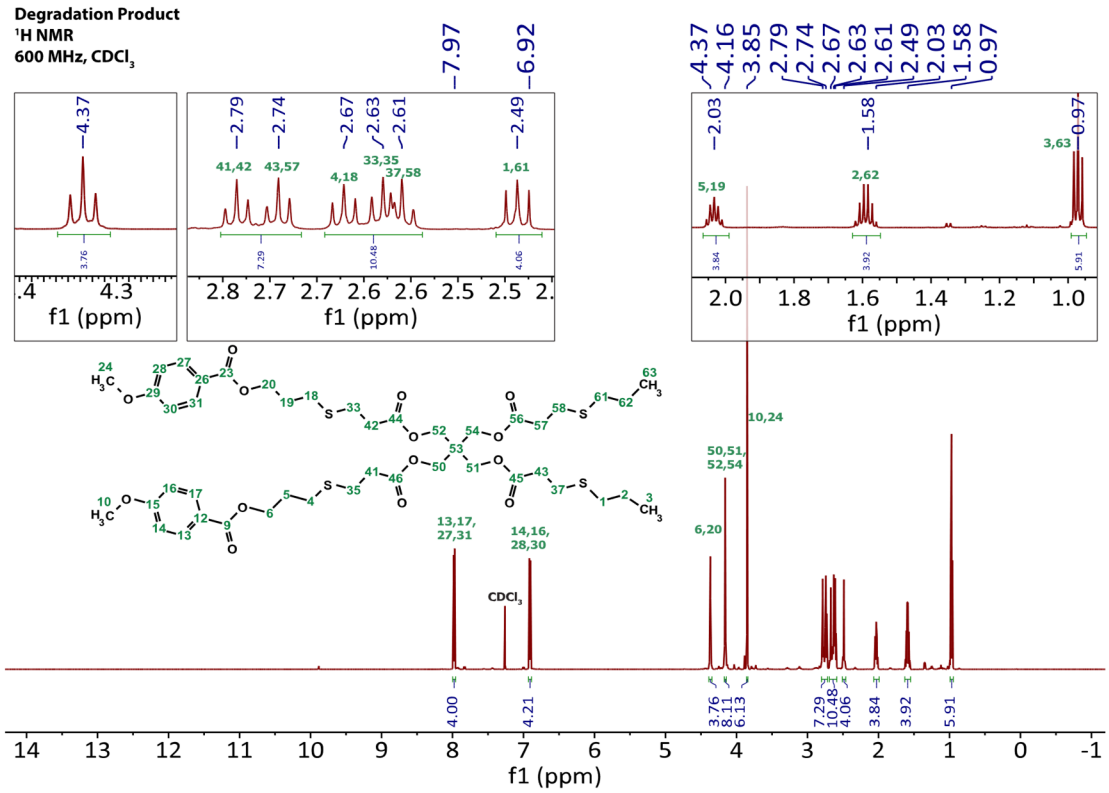


Fig. S19. ^{1}H NMR Spectrum of **10**

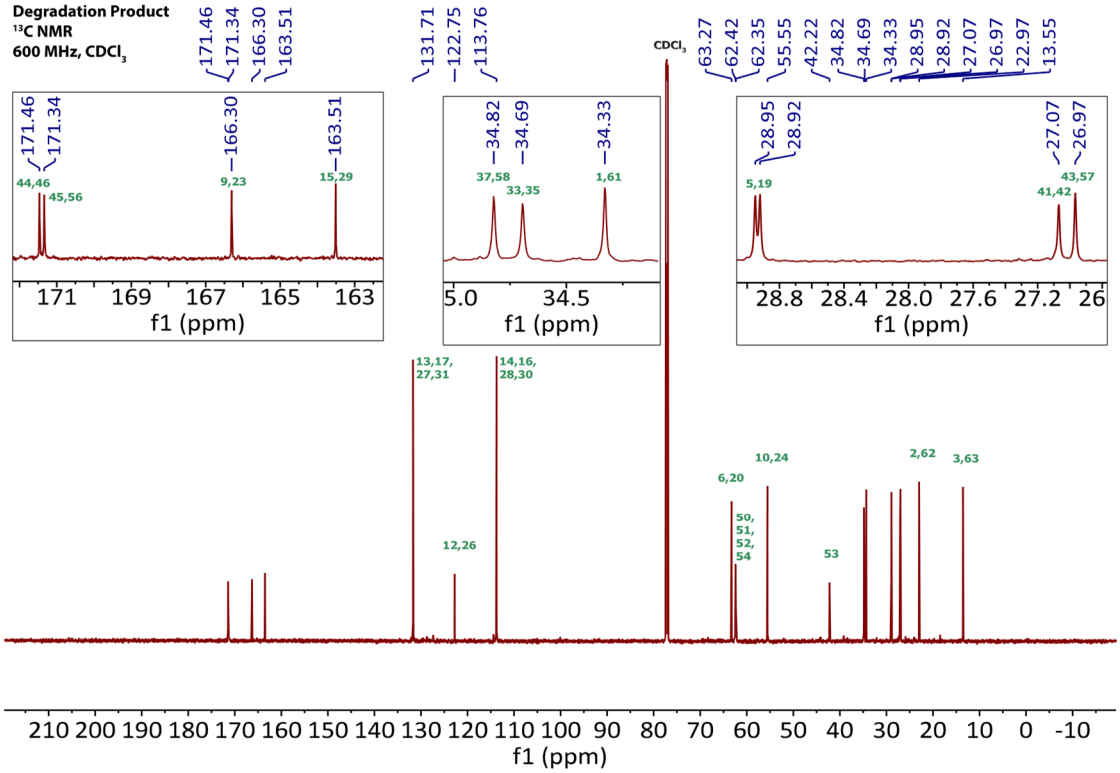


Fig. S20. ^{13}C NMR Spectrum of **10**

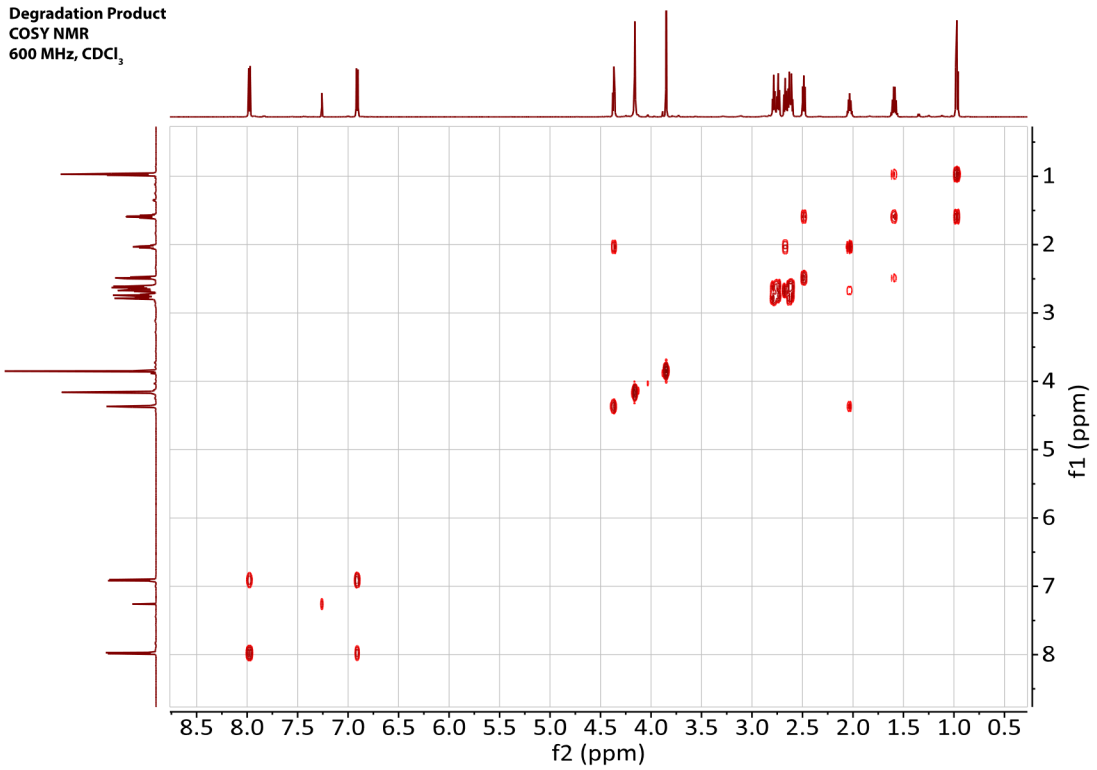


Fig. S21. COSY NMR Spectrum of **10**

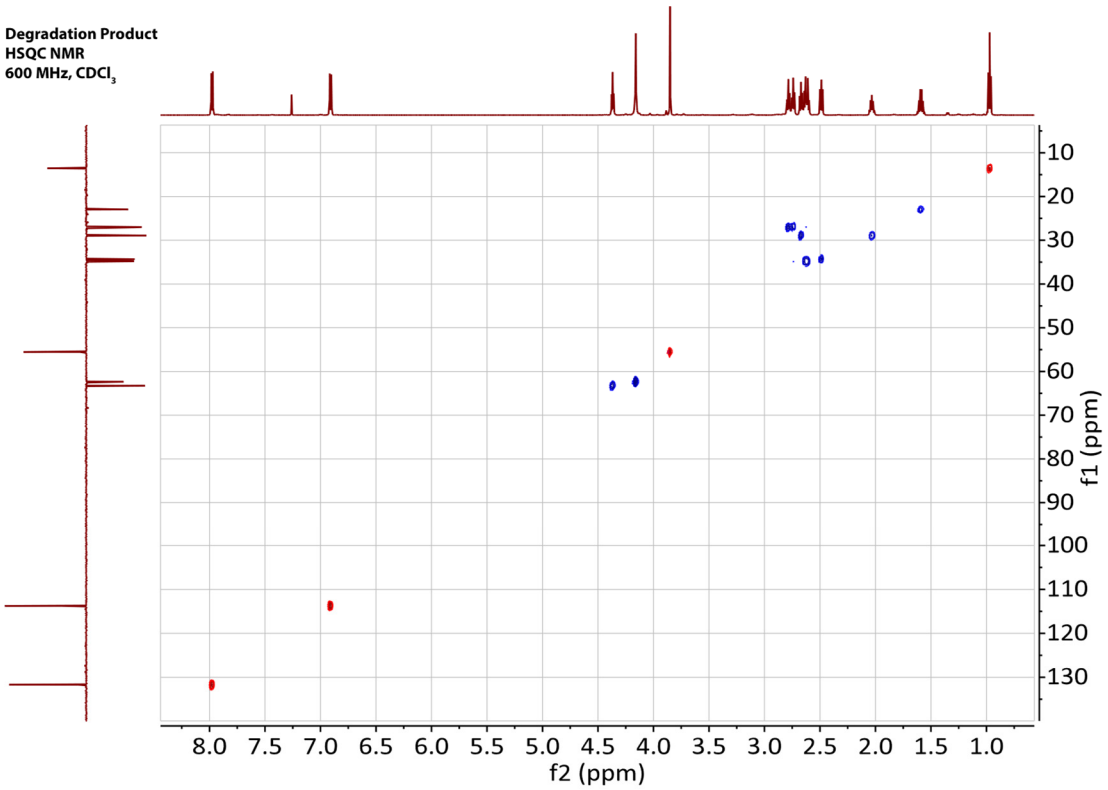


Fig. S22. HSQC NMR Spectrum of **10**

1. Amato, D. V.; Amato, D. N.; Blancett, L. T.; Mavrodi, O. V.; Martin, W. B.; Swilley, S. N.; Sandoz, M. J.; Shearer, G.; Mavrodi, D. V.; Patton, D. L., A bio-based pro-antimicrobial polymer network via degradable acetal linkages. *Acta Biomaterialia* **2018,** *67*, 196-205.
2. Tsunoda, T.; Suzuki, M.; Noyori, R., A facile procedure for acetalization under aprotic conditions. *Tetrahedron Letters* **1980,** *21* (14), 1357-1358.
3. Amato, D. N.; Amato, D. V.; Mavrodi, O. V.; Martin, W. B.; Swilley, S. N.; Parsons, K. H.; Mavrodi, D. V.; Patton, D. L., Pro-Antimicrobial Networks via Degradable Acetals (PANDAs) Using Thiol–Ene Photopolymerization. *ACS Macro Letters* **2017,** *6* (2), 171-175.
4. Yue, Q.; Yang, T.; Yang, Y.; Zhang, C.; Zhang, Q.; Li, D., Divergent Reactivity of (Diacyloxyiodo)arenes under Palladium Catalysis: Controlled Allylic C−H Acyloxylation and Vinylic Arylation. *Asian Journal of Organic Chemistry* **2017,** *6* (7), 936-942.