Electronic Supporting Information (ESI)

Expanding the Thiol–X Toolbox: Photoinitiation and Materials Application of the Acid-Catalyzed Thiol–ene (ACT) Reaction

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1. Materials and Instrumentation

All reagents, unless otherwise stated, were purchased from Millipore Sigma. Vinyl pyrrolidinone (VPy) and Vinylacetamide (MeVAc) were purchased from Combi-Blocks. Ethyl mercaptopropionate (EMP) and methane sulfonic acid (MSA) was purchased from TCI America. Deuterated dichloromethane (DCM) was purchased from Oakwood Chemicals and deuterated dimethylsulfoxide (DMSO) was purchased from Fisher Scientific. Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) was donated from Thiochem. Solution phase kinetics performed on an AVIII 400 MHz Nuclear Magnetic Resonance Spectrometer (NMR; Bruker). All thermoset formulations were mixed using a DAC 150.1 FVZ-K speedmixer (Flacktek). A UV-Omnicure 200 lamp (Excelitas) equipped with an external 365, 405, or 470 nm wavelength interference filters was used to initiate the photopolymerizations. Intensities were determined using a NIST traceable radiometer and photometer (International Light). Polymerizations of crosslinked materials were conducted in a Nicolet iS50 Fourier Transform Infrared Spectrometer (FTIR; ThermoFisher Scientific). Thermomechanical analysis consisting of frequency sweep-temperature ramps on the polymer networks were performed using a Q800 Dynamic Mechanical Analyzer (DMA; TA Instruments).

2. Experimental Procedures

2.1. Varying Thiol and Vinyl Concentrations for Kinetic Modeling

Varying thiol (benzyl mercaptan; BM) concentration with respect to constant vinyl (VPy) concentration: To a vial was added DCM (calculated to make total final volume 600 µL), BM (0.05, 0.1, 0.2, 0.4, and 0.8 mmol), VPy (0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and tetramethylurea (TMU; 3 mol% to total vinyl functional groups). Upon transfer to an NMR tube, the initial NMR spectra was recorded as t = 0. To the NMR tube, MSA (1.5 mol% to vinyl functional groups) was added and the NMR spectra was recorded every 30 seconds for 10 min. The product peak (δ = 5.63) was integrated in relation to the internal standard, mesitylene (δ = 6.86). Initial rates were determined by taking the slope of linear region of the reaction (within the first 1 to 2 min).

Varying vinyl (VPy) concentration with respect to constant thiol (BM) concentration: To a vial was added DCM (calculated to make total final volume 600 µL), BM (0.2 mmol), VPy (0.05, 0.1, 0.2, 0.4, and 0.8 mmol), mesitylene (0.2 mmol, 1 eq), and TMU (3 mol% to total thiol functional groups). Upon transfer to an NMR tube, the initial NMR spectra was recorded as t = 0. To the NMR tube, MSA (1.5 mol% to thiol functional groups) was added and the NMR spectra was recorded every 30 seconds for 10 min). The product peak (δ = 5.63) was integrated in relation to the internal standard, mesitylene (δ = 6.86). Initial rates were determined by taking the slope of linear region of the conversion versus time data.

Varying methane sulfonic acid (MSA) catalyst concentration with respect to constant thiol (BM) and vinyl (VPy) concentration: To a vial was added DCM (calculated to make total final volume 600 µL), BM (0.2 mmol), VPy (0.2 mmol), mesitylene (0.2 mmol, 1 eq), and TMU (3 mol% to total thiol functional groups). Upon transfer to an NMR tube, the initial NMR spectra was recorded as t = 0. To the NMR tube, MSA (0.75, 1.5, 3, 6, and 12 mol% to thiol functional groups) was added and the NMR spectra was recorded every 30 seconds for 10 min). The product peak (δ = 5.63) was integrated in relation to the internal standard,

mesitylene (δ = 6.86). Initial rates were determined by taking the slope of linear region of the conversion versus time data.

The kinetic data obtained was fit using OriginPro® graphing and data analysis software (OriginLab Corp.) (see **Figure S1** and **Figure S2**).

2.2. Testing Thiol Substrates

To a vial was added DCM (calculated to make total final volume 600 µL), thiol (0.2 mmol), VPy (0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (3 mol% to total thiol functional groups). The solutions were transferred to an NMR tube where an initial NMR spectra was recorded as t = 0. To the NMR tube, MSA (1.5 mol% to thiol functional groups) was added and the NMR spectra was recorded every 30 s for 10 min.

2.3. Testing Vinyl Substrates

To a vial was added DCM (calculated to make total final volume 600 µL), EMP (0.2 mmol), vinyl (0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (3 mol% to total thiol functional groups). The solutions were transferred to an NMR tube where they were measured to get the initial time point (t = 0). MSA (1.5 mol% to vinyl functional groups) was added and the reaction was monitored with time points at every 30 s for 10 min.

2.4. One Pot Sequential Thiol-X Initiations

To a single NMR tube was added deuterated DMSO (calculated to make total final volume 600 µL), EMP (0.6 mmol, 3 eq), DMA (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), and tert-butyl N-allylcarbamate (tBAC; 0.2 mmol, 1 eq). The initial time point was measured by NMR prior to the addition of any of catalyst. To initiate the thiol-Michael reaction, dimethylphenylphosphine (DMPP; 2.5 mol% to total acrylamide functional groups) was added to the NMR tube and allowed to mix for 16 h. Once complete, the ACT reaction was initiated with the addition MSA (5 mol%) and mixed for 16 h. Finally, Irgacure-819 (I-819; 5 mol%), a visible light photoinitiator, was added to the NMR tube in order to initiate the thiol-ene reaction. The NMR tube was subjected to 405 nm light at an intensity of 20 mW/cm^2 for 30 min. Completion of the individual reactions were verified by NMR prior to initiating the subsequent reaction.

2.5. Photoinitiation of ACT Reaction using Photochromic Acid

To a vial was added DCM (calculated to bring final volume to 600 µL), BzM or EMP (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), TMU (3 mol%), and mesitylene (0.2 mmol, 1 eq). The samples were split into two equal portions in which both received the corresponding photochromic photoacid (SP1, SP2, or SP3) (1.5 mol%). Then the samples were transferred to NMR tubes, and each sample was measured via NMR (t = 0 min). Then one sample was left in the dark for 30 min and the other was subjected to 470 nm irradiation (20 mW/cm^2, 30 min). The NMR spectra were recorded for the sample that was left in the dark for 30 min and for the other sample that was irradiated for 30 min.

2.6. UV-Vis of SP3

To a 20 mL vial was added the synthesized photochromic photoacid, SP3 (5.27 mg, 0.01 mmol), followed by 20 mL of DMSO to make a solution of 0.5 mM SP3 in DMSO. The solution was well mixed and from this solution was taken 1 mL which was further diluted in 9 mL of DMSO to make a 0.05 mM solution of SP3 in DMSO. The sample was then placed in a cuvette and measured to get the dark absorbance spectrum.

Next, the sample was irradiated from the top down in 3s intervals using 470 nm light (20 mW/cm^2). After each irradiation, the sample measured by UV-Vis.

3. ACT Reaction using Various Vinyl and Thiol substrates

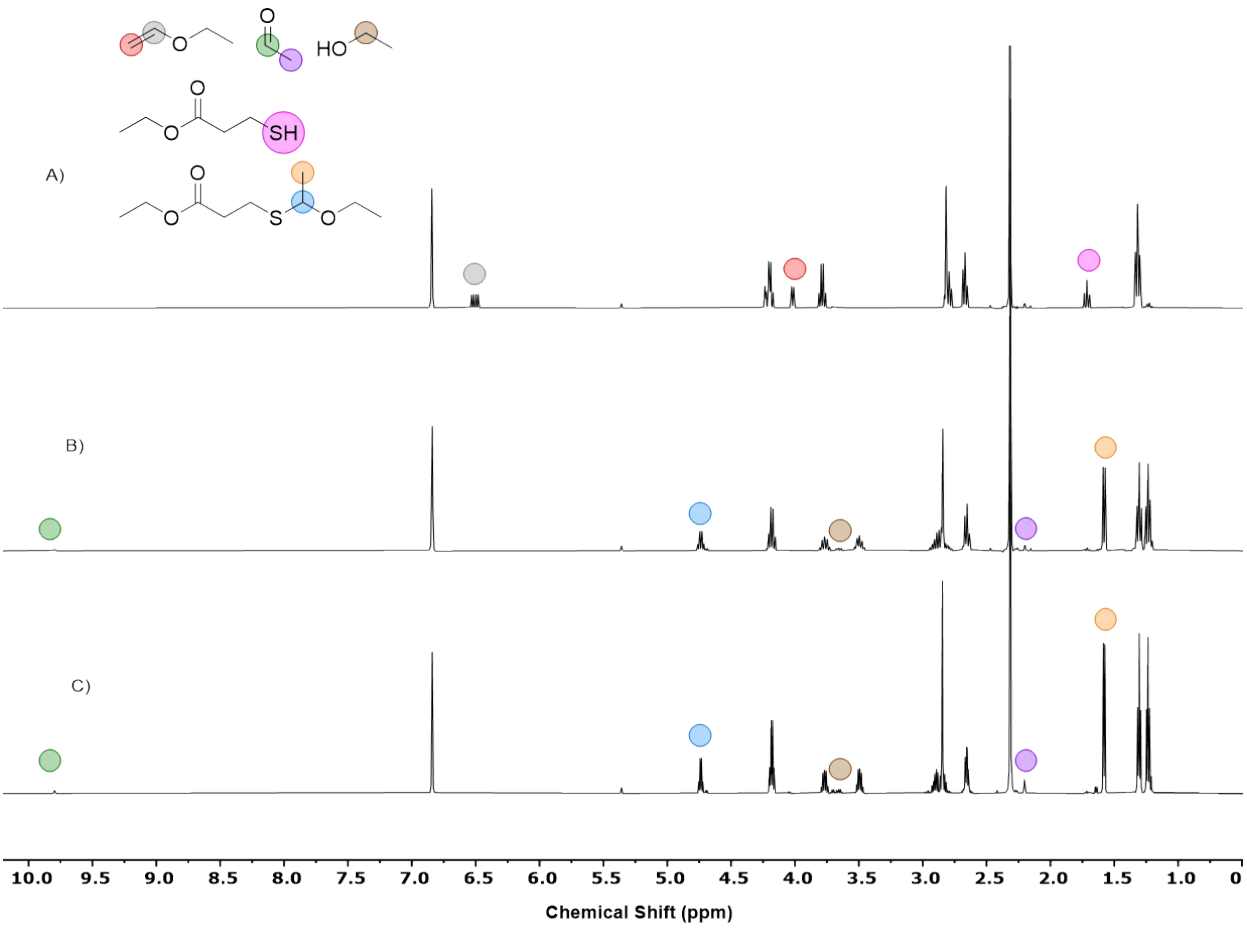


Figure S1. A) Reaction with EMP (0.2 mmol, 1 eq), ethyl vinyl ether (EVE; 0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (15 mol%) prior to adding the acid catalyst at t = 0 min. B) Post addition of MSA (1.5 mol%) at t = 10 min (94% conversion based on tertiary carbon product proton, blue circle). C) Reaction time at 16 h (96% conversion based on tertiary carbon product proton, blue circle).

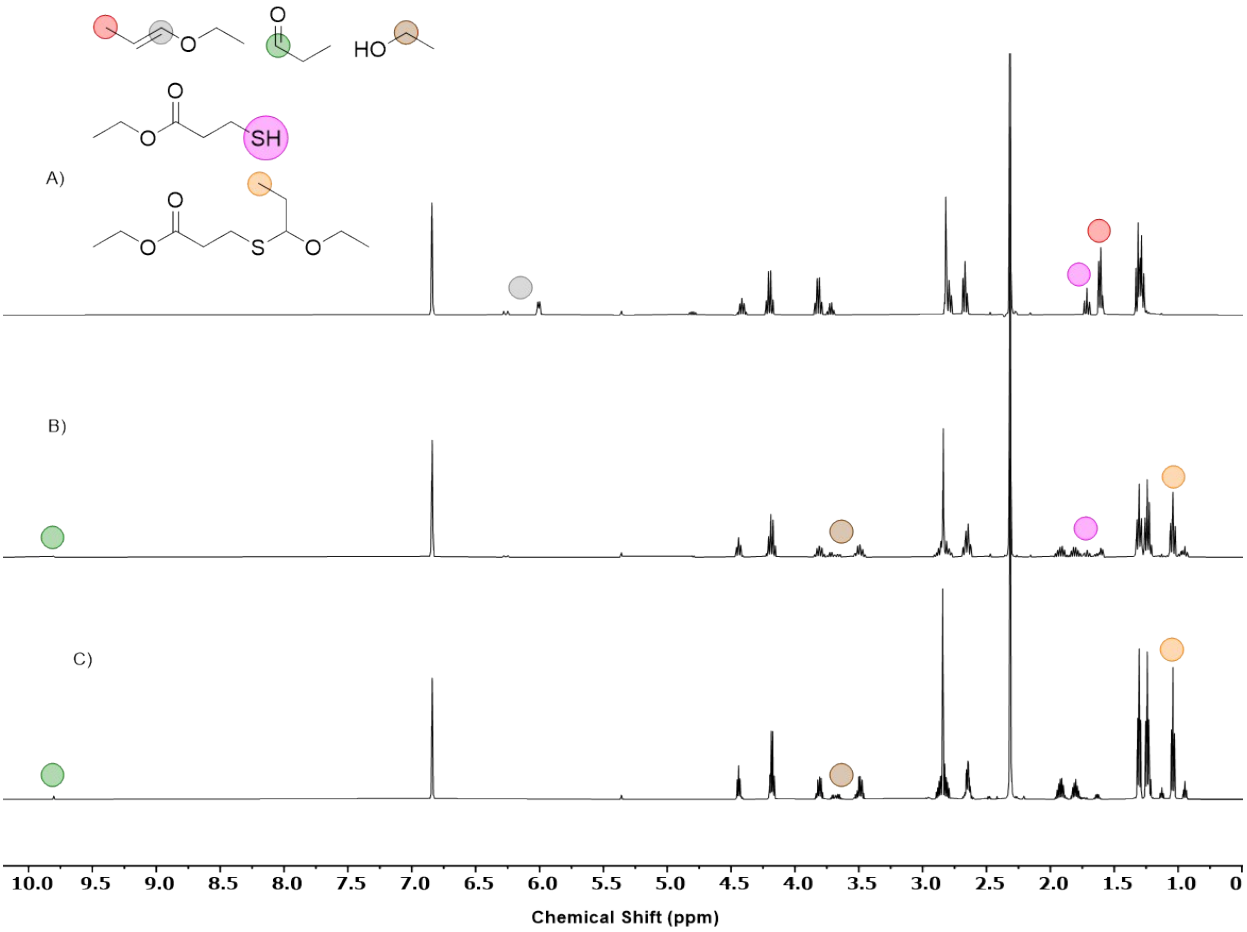


Figure S2. A) Reaction with EMP (0.2 mmol, 1 eq), 1-ethyoxypropene (PVE; 0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (15 mol%) prior to adding the acid catalyst at t = 0 min. B) Post addition of MSA (1.5 mol%) at t = 10 min (70% conversion based on thiol proton, pink circle). C) Reaction time at 16 h (88% conversion based on thiol proton, pink circle).

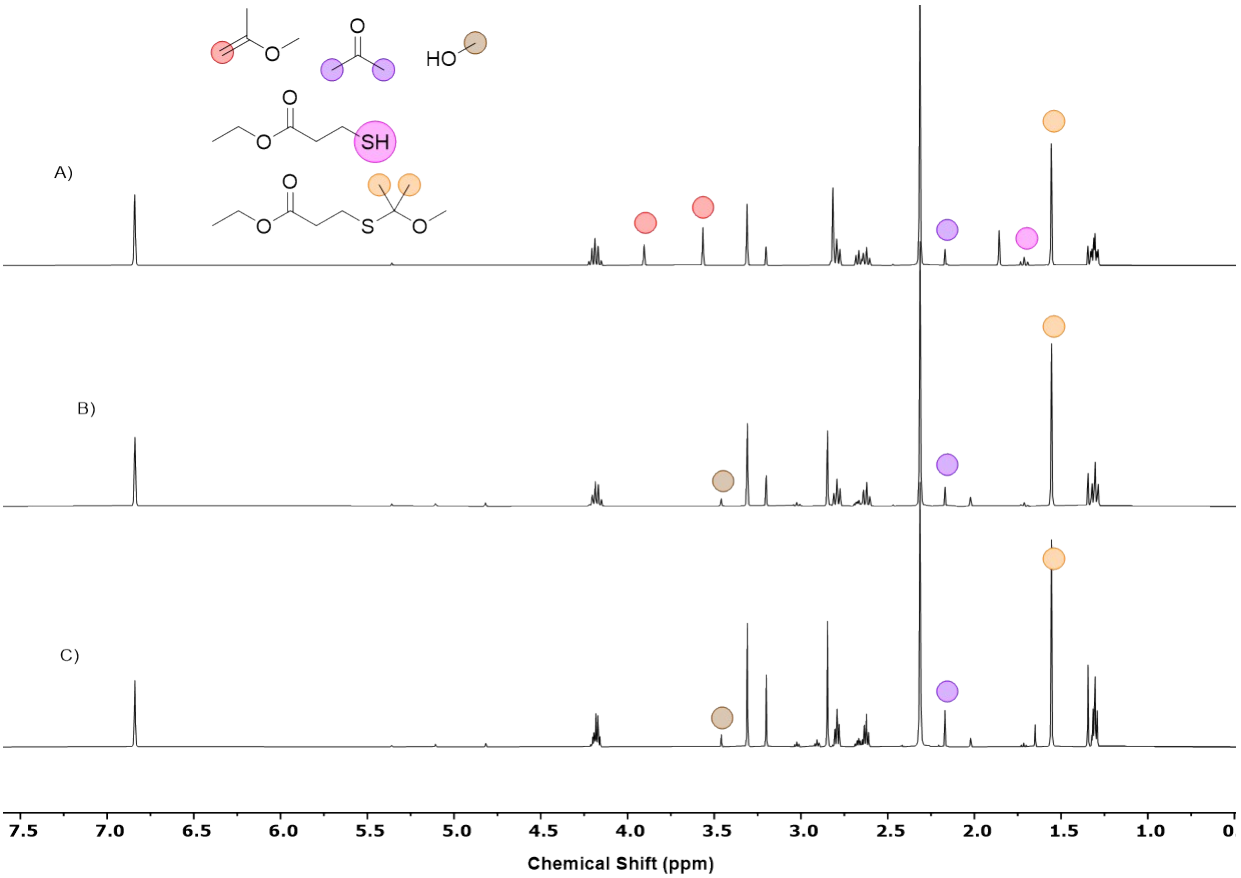


Figure S3. A) Reaction with EMP (0.2 mmol, 1 eq), 2-methoxypropene (iPVE; 0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (15 mol%) prior to adding the acid catalyst at t = 0 min (53% conversion based on thiol proton, pink circle). B) Post addition of MSA (1.5 mol%) at t = 10 min (81% conversion based on thiol proton, pink circle). C) Reaction time at 16 h (84% conversion based on thiol proton, pink circle). The high conversion prior to the addition of the acid catalyst is likely a result of the minor acidity associated with the commercially available thiol (as noted in the manuscript).

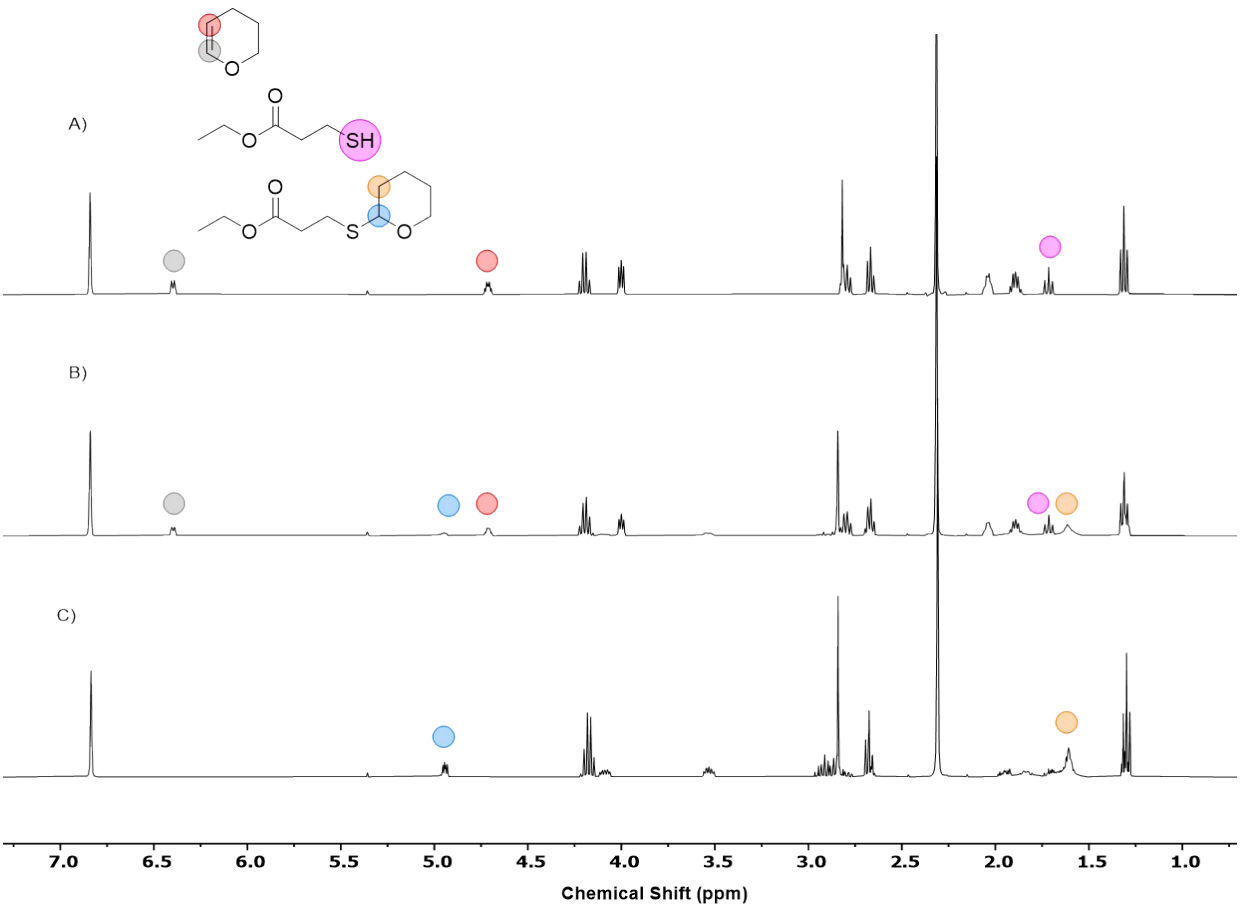


Figure S4. A) Reaction with EMP (0.2 mmol, 1 eq), Dihydropyran (DHP; 0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (15 mol%) prior to adding the acid catalyst at t = 0 min. B) Post addition of MSA (1.5 mol%) at t = 10 min (28% conversion based on tertiary carbon product proton, blue circle). C) Reaction time at 16 h (97% conversion based on tertiary carbon product proton, blue circle).

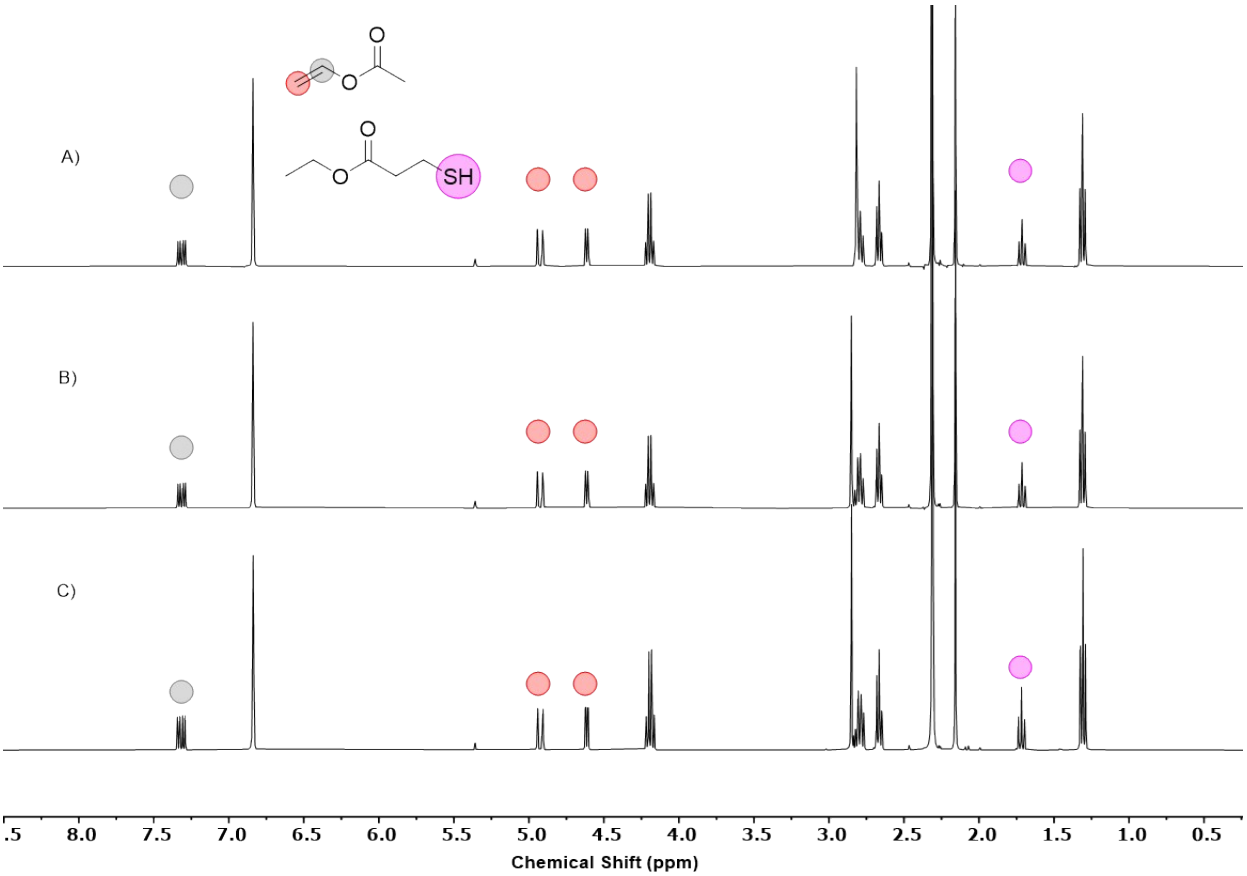


Figure S5. A) Reaction with EMP (0.2 mmol, 1 eq), vinyl acetate (Vest; 0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (15 mol%) prior to adding the acid catalyst at t = 0 min. B) Post addition of MSA (1.5 mol%) at t = 10 min (0% conversion). C) Reaction time at 16 h (< 1% conversion, minor product formation).

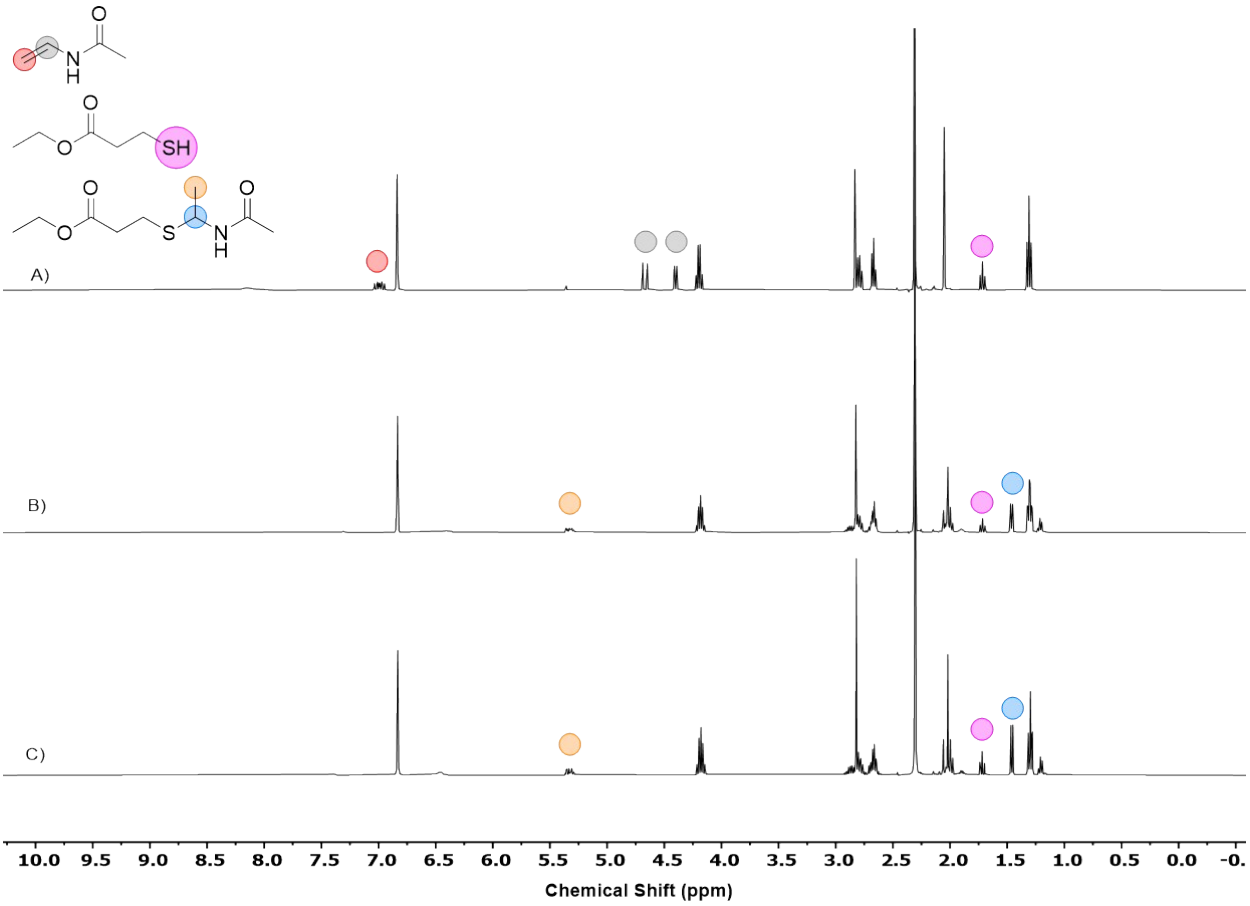


Figure S6. A) Reaction with EMP (0.2 mmol, 1 eq), Vinyl acetamide (HVAc; 0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (15 mol%) prior to adding the acid catalyst at t = 0 min. B) Post addition of MSA (1.5 mol%) at t = 10 min (44% conversion based on thiol proton, pink circle). C) Reaction time at 16 h (48% conversion based on thiol proton, pink circle). The triplet associated with the methyl group of the acetamide at δ = 2.01 ppm suggests significant homopolymerization takes place with the HVAc substrate resulting in lower conversion to the desired product, as noted in the manuscript.

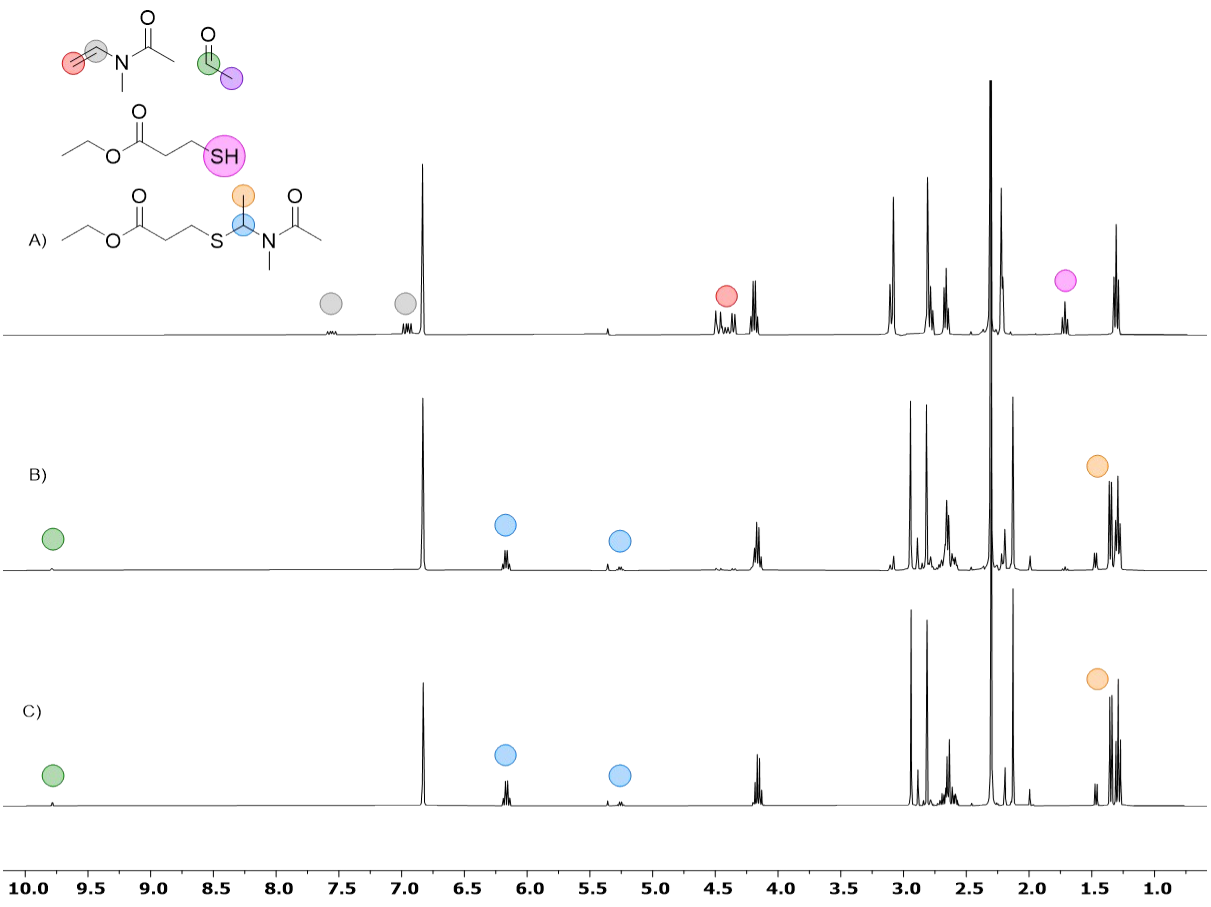


Figure S7. A) Reaction with EMP (0.2 mmol, 1 eq), MeVAc (0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (15 mol%) prior to adding the acid catalyst at t = 0 min. B) Post addition of MSA (1.5 mol%) at t = 10 min (88% conversion based on tertiary carbon product proton, blue circle). C) Reaction time at 16 h (94% conversion based on tertiary carbon product proton, blue circle).

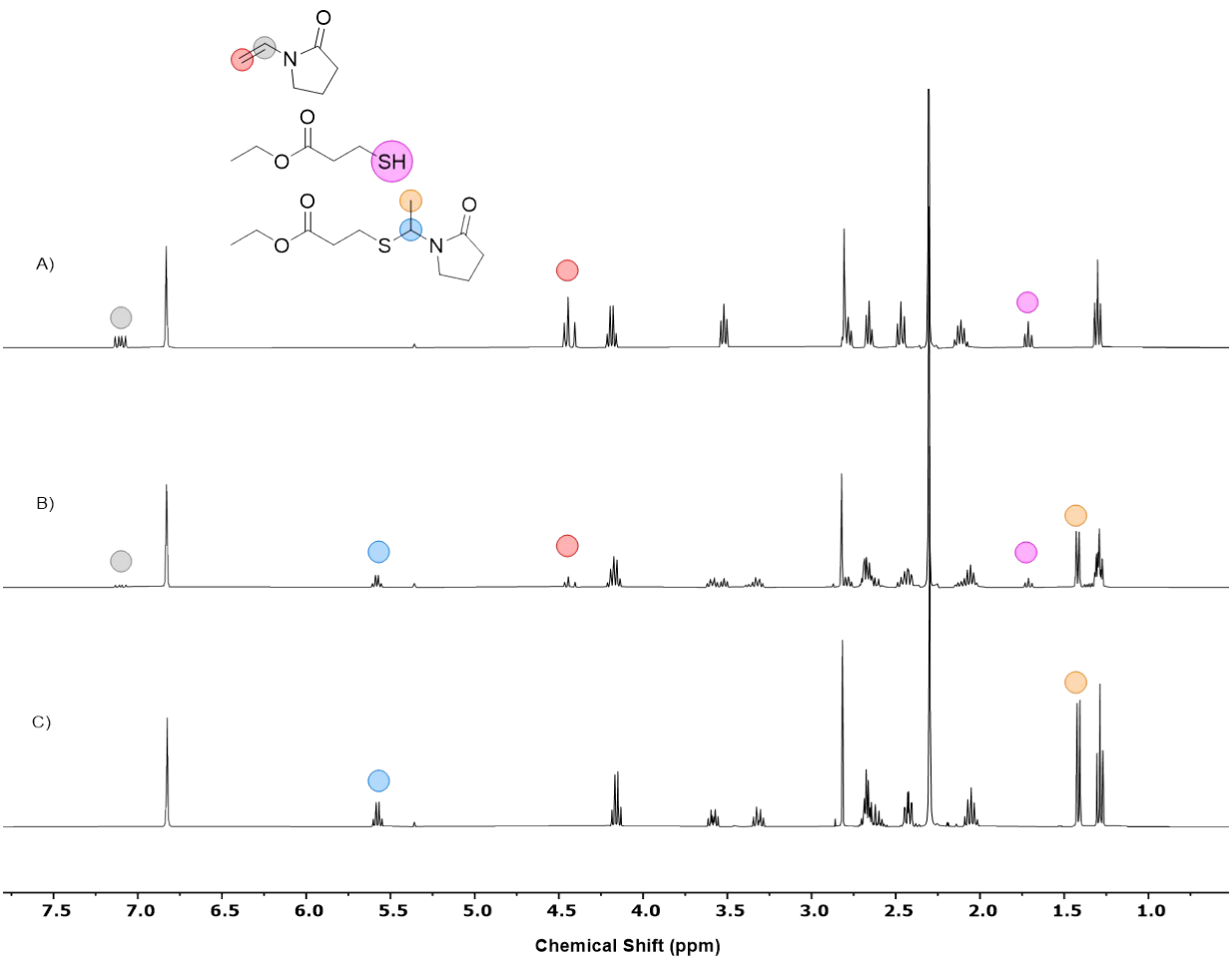


Figure S8. A) Reaction with EMP (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (15 mol%) prior to adding the acid catalyst at t = 0 min. B) Post addition of MSA (1.5 mol%) at t = 10 min (72% conversion based on tertiary carbon product proton, blue circle). C) Reaction time at 16 h (quantitative conversion based on tertiary carbon product proton, blue circle).

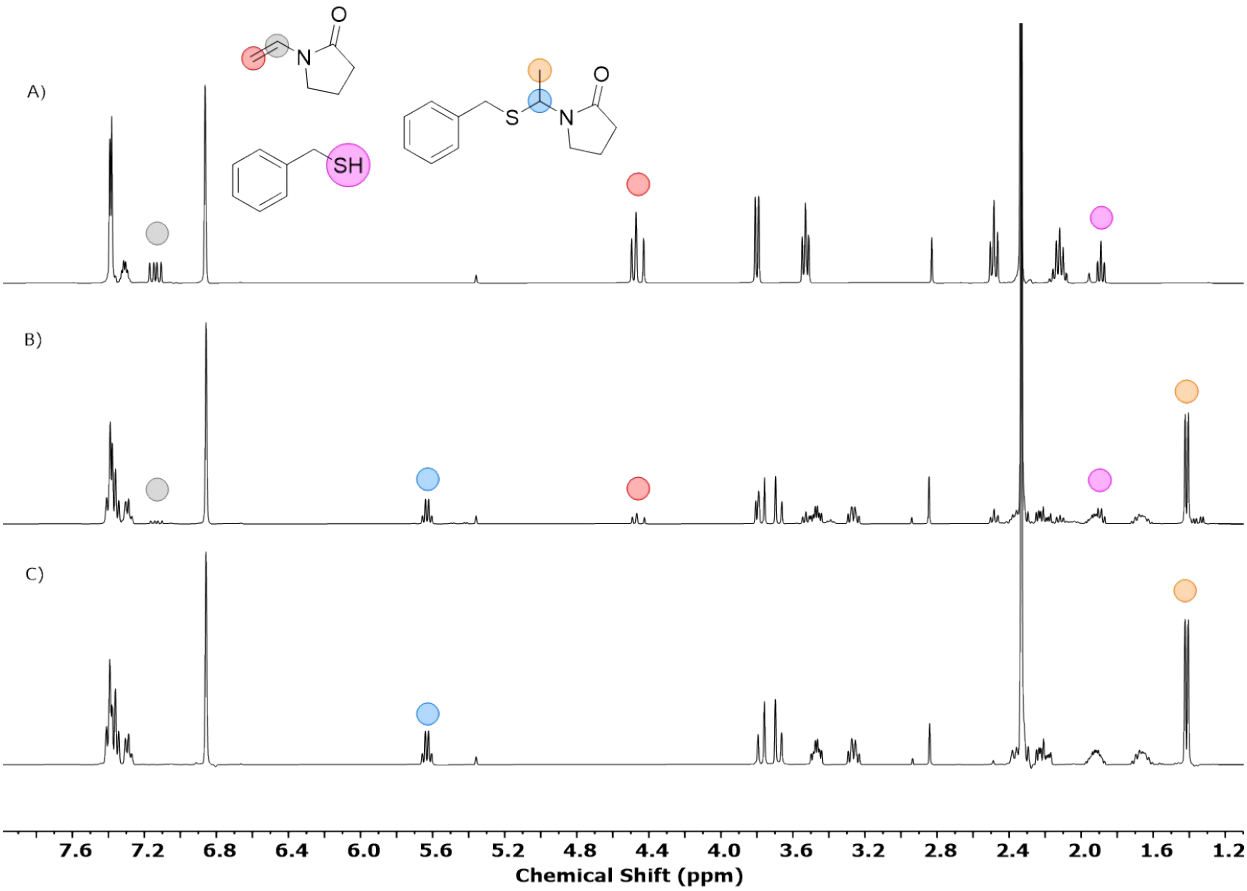


Figure S9. A) Reaction with BzM (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (3 mol%) prior to adding the acid catalyst at t = 0 min. B) Post addition of MSA (1.5 mol%) at t = 10 min (80% conversion based on tertiary carbon product proton, blue circle). C) Reaction time at 16 h (quantitative conversion based on tertiary carbon product proton, blue circle).

4. Kinetic Modeling of ACT Reaction

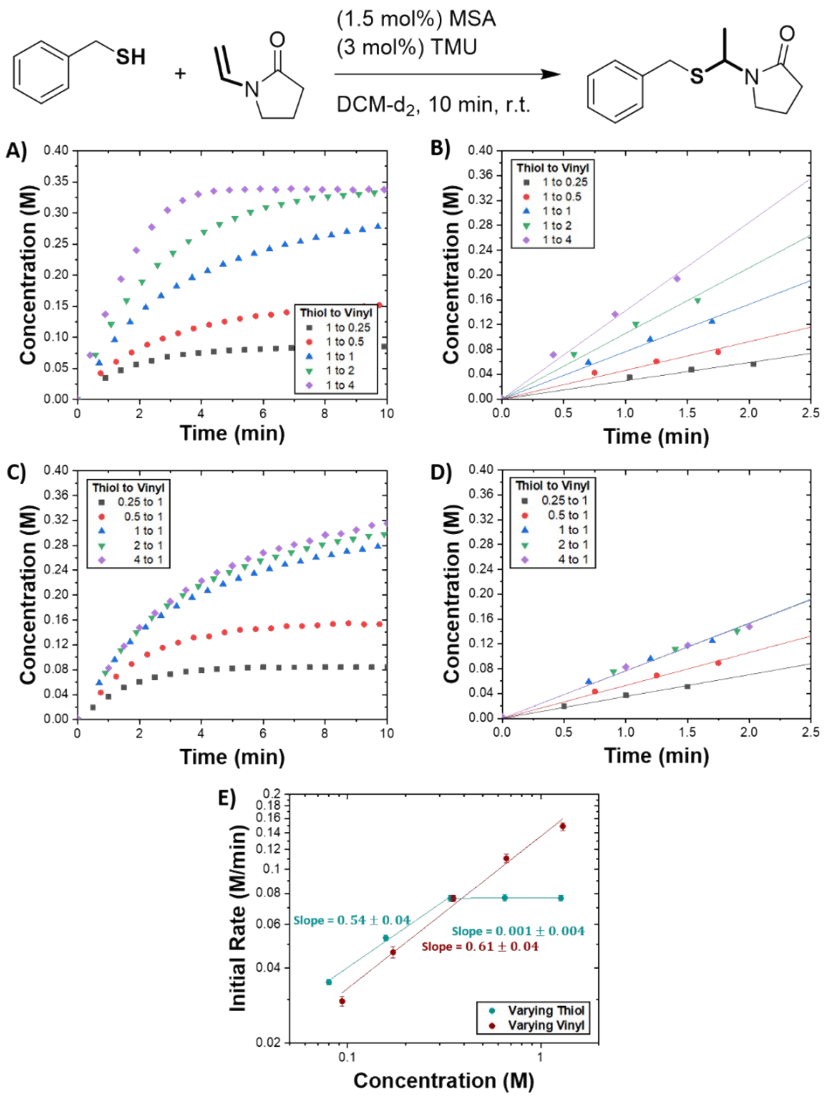


Figure S10. A) Reactions were run with BM (0.2 mmol, 1 eq), VPy (0.05, 0.1, 0.2, 0.4, and 0.8 mmol), TMU (3 mol%), MSA (1.5 mol%), and DCM (calculated to achieve a final volume of 600 µL) with mesitylene (0.2 mmol, 1 eq) as an internal standard. B) Initial rates were determined by taking the slope of the first four time points of the reaction. C) Reactions were run with BM (0.05, 0.1, 0.2, 0.4, and 0.8 mmol), VPy (0.2 mmol, 1 eq), TMU (3 mol%), MSA (1.5 mol%), and DCM (calculated to achieve a final volume of 600 µL) with mesitylene (0.2 mmol, 1 eq) as an internal standard. D) Initial rates were determined by taking the slope of the first four time points of the reaction. E) Compilation of initial rates with respect to concentration of the vinyl and thiol functional groups. Increasing vinyl concentration with respect to constant thiol concentration resulted in an increase in the initial rate that followed a linear relationship with a slope of 0.61 ± 0.04. When the thiol concentration was the limiting reagent, an increase in the initial rate was observed with a slope of 0.54 ± 0.04; however, the initial rates plateaued to near zero order kinetics, with a slope of 0.001 ± 0.004, upon switching the thiol from the limiting to the excess reagent. These findings are consistent with typical vinyl hydrolysis kinetics, which are dependent on both vinyl and acid catalyst concentrations.[1,2] In vinyl hydrolysis, the rate determining step is the vinyl protonation followed by rapid decomposition of the vinyl group into acetaldehyde and alcohol in the presence of water. In conjunction with the findings that demonstrate that water influences the reaction rate and can result in changes in the initial rate of thiol consumption at low concentrations (shown below in **Figure S15** and **Figure S16**), a proposed mechanism was constructed and is shown below in Figure S3. Errors reported are of the error in the initial rate slopes determined from (B) and (D).

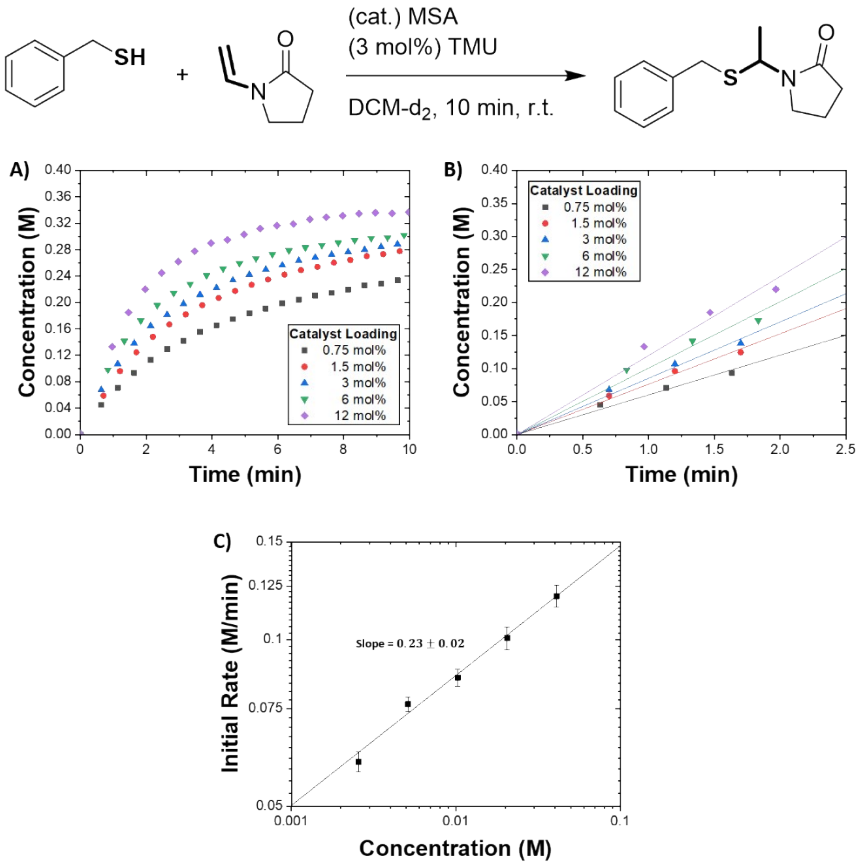


Figure S11. A) Reactions were run with BM (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), TMU (3 mol%), MSA (0.75, 1.5, 3, 6, and 12 mol%), and DCM (calculated to achieve a final volume of 600 µL) with mesitylene (0.2 mmol, 1 eq) as an internal standard. B) Initial rates were determined by taking the slope of the first four time points. C) Initial rate was plotted against concentration to determine the order for the catalyst, **resulting in a linear relationship with a slope of 0.23 ± 0.02 and suggesting a dependence on catalyst concentration.** The error reported is of the initial rate slopes.

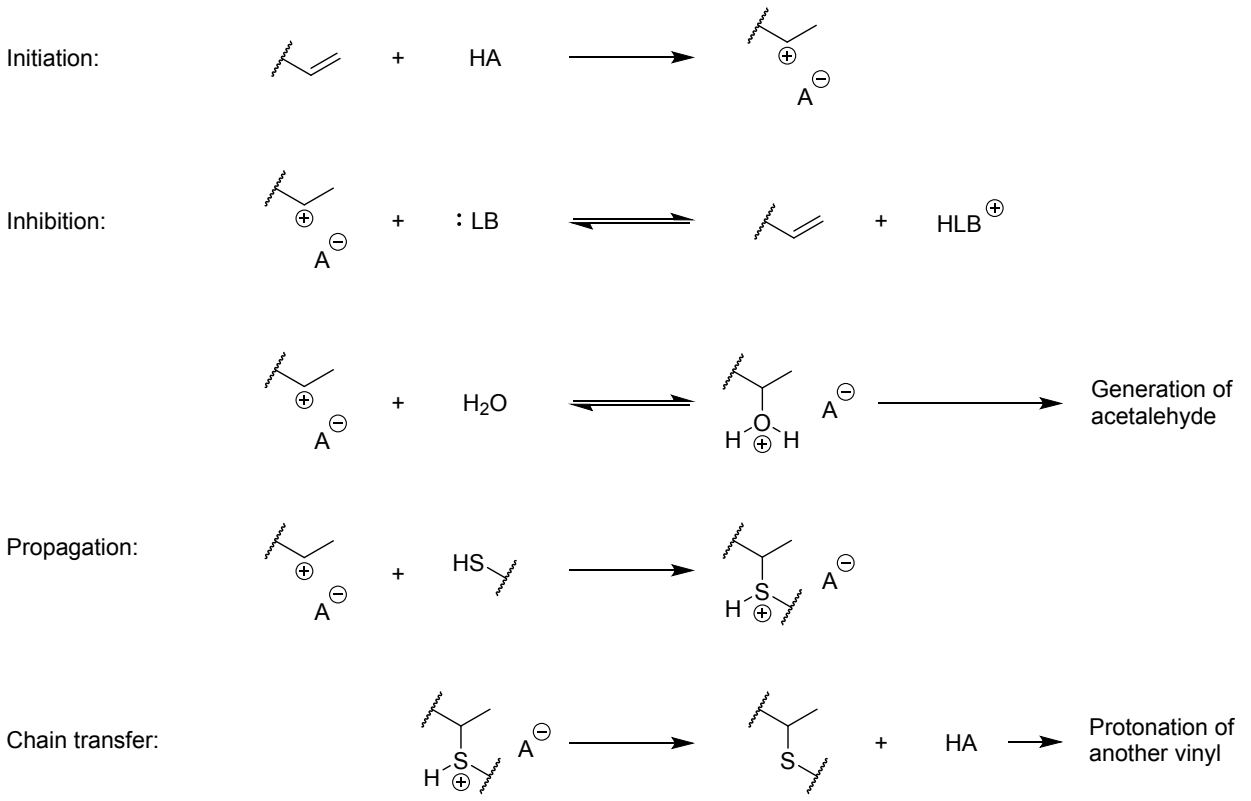


Figure S12. Proposed elementary reaction steps for the ACT reaction in solution. After initiation by protonation of the vinyl group, a carbenium ion forms. The carbenium ion can then undergo quenching by water, deactivation via a Lewis base (LB), or propagation via electrophilic addition of the thiol to the carbenium center. After propagation, the protonated sulfonium intermediate dissociates into the acetal product and free acid, which can undergo another protonation reaction with vinyl.

5. Intermediate Formation During ACT Conjugation and Water Effects

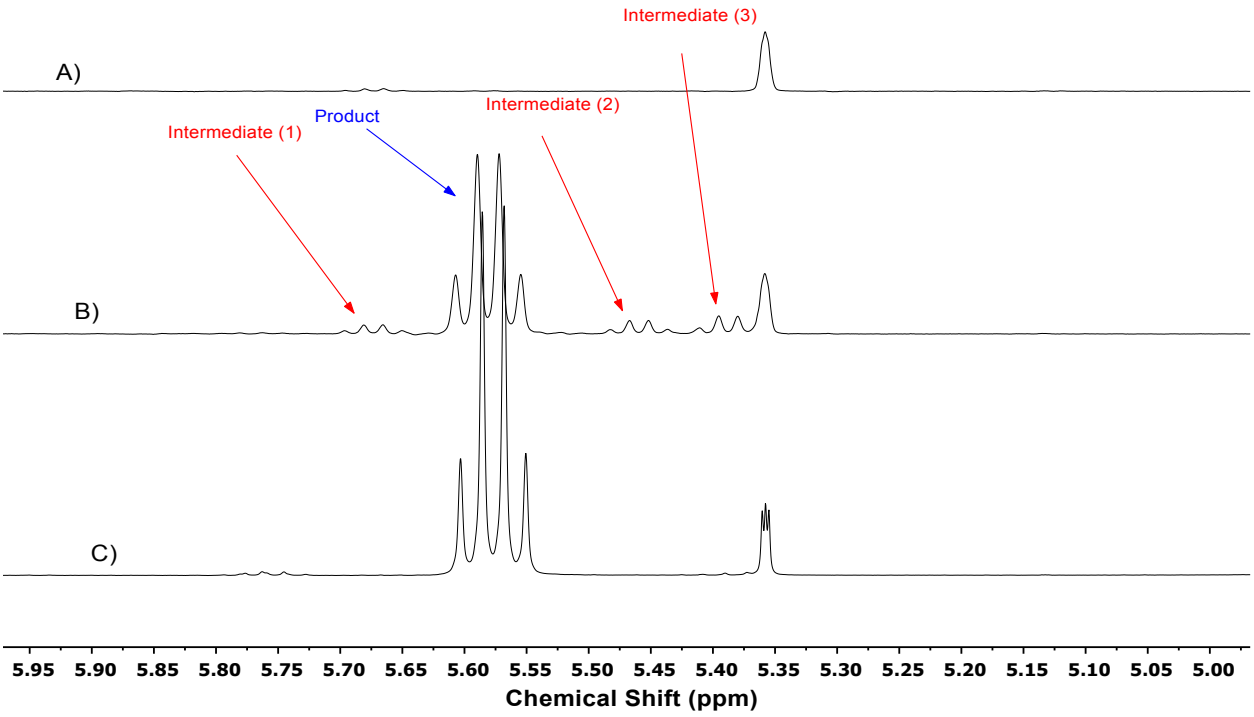


Figure S13. A) Reaction with EMP (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), mesitylene (1 eq), and TMU (15 mol%) in DCM prior to adding the acid catalyst at t = 0 min. B) Post addition of MSA (1.5 mol%) at t = 10 min. C) Reaction time at 16 h where the reaction had completed and near quantitative conversions were achieved. The intermediate peaks 1 is speculated to be water addition to the protonated vinyl, while intermediates 2 and 3 are the protonated vinyl and sulfonium ion prior to dissociation, respectively.

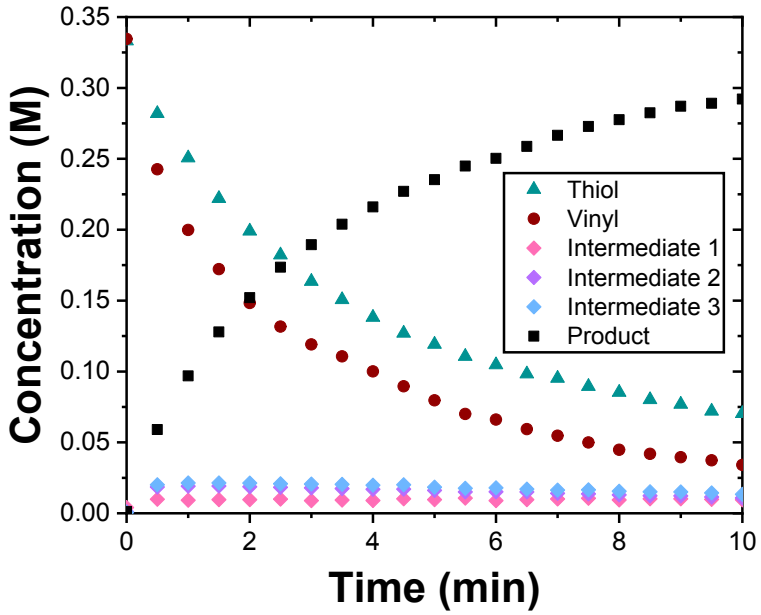


Figure S14. Reaction with EMP (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (15 mol%) initiated with MSA (1.5 mol%). Reaction was performed in deuterated DCM (calculated to achieve final volume of 600 µL). During the reaction, the thiol (green triangles) and vinyl (maroon circles) do not convert at the same rate resulting in an offset. This is indicative of intermediate formation after vinyl protonation. The reaction showed no thiol or vinyl remaining after 16 h demonstrating a final 1:1 stoichiometric reaction in producing the final product (black squares). The intermediates (pink, purple, and blue diamonds) show a rapid initial formation and then remain at a fairly constant concentration for the remainder of the reaction.

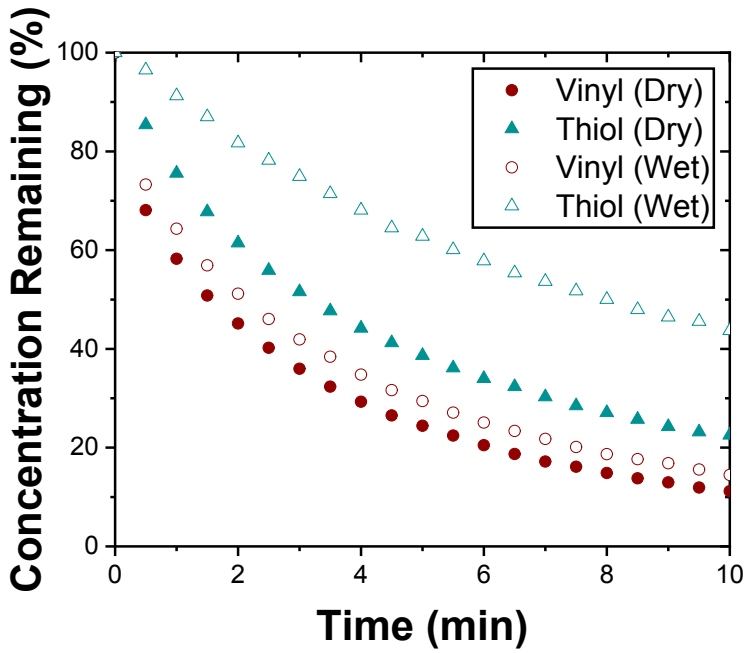


Figure S15. Reaction with EMP (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (15 mol%) initiated with MSA (1.5 mol%). Reaction was performed in either dry or wet deuterated DCM (calculated to achieve final volume of 600 µL). Dry deuterated DCM was used as received, while wet DCM was shaken with water and then separated via extraction funnel and used directly in the reaction. The presence of water results in a larger offset between vinyl and thiol conversion indicating the active role water plays in inhibiting the reaction kinetics.

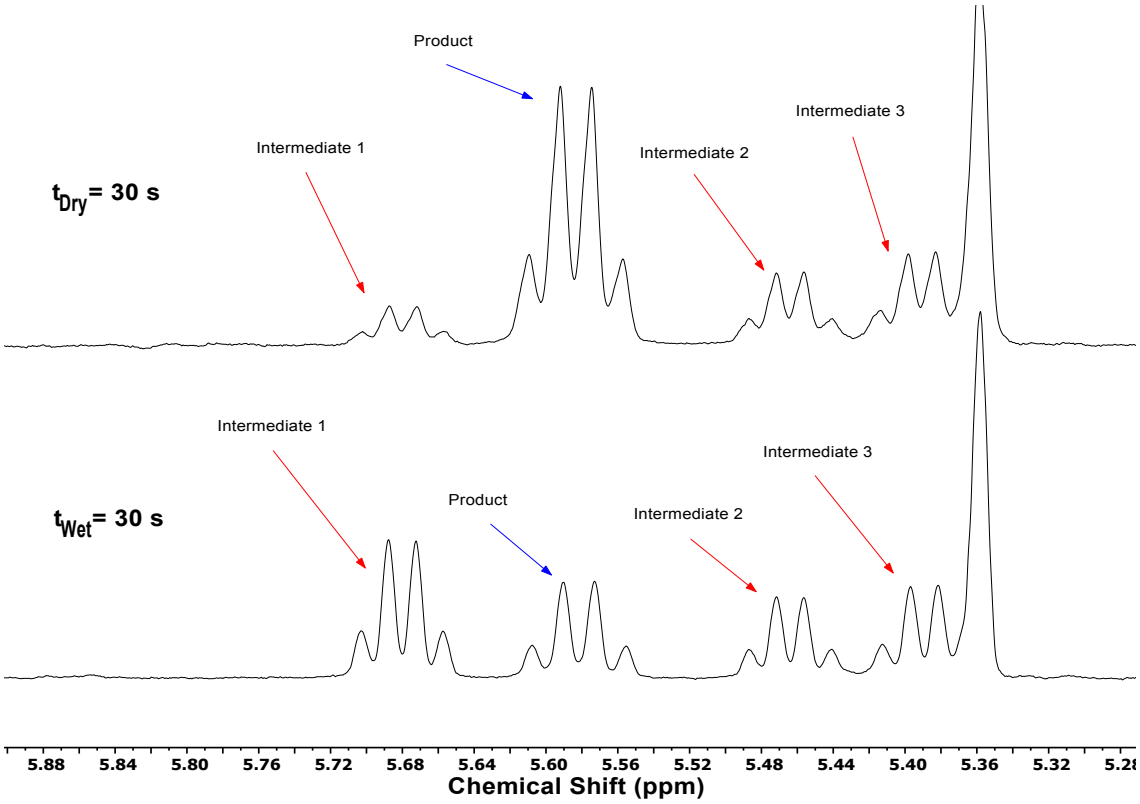


Figure S16. Reaction with EMP (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (15 mol%) initiated with MSA (1.5 mol%). Reaction was performed in either dry or wet deuterated DCM (calculated to achieve final volume of 600 µL). Dry deuterated DCM was used as received, while wet DCM was shaken with water and then separated via extraction funnel and used directly in the reaction. The presence of water results in a larger intermediate 1 peak at t = 30 s suggesting water addition to the carbenium ion. As this is a reversible process, complete disappearance of all three intermediate peaks were observed over 16 h and the reaction proceeded to quantitative conversions.

6. Lewis base and Solvent Effects

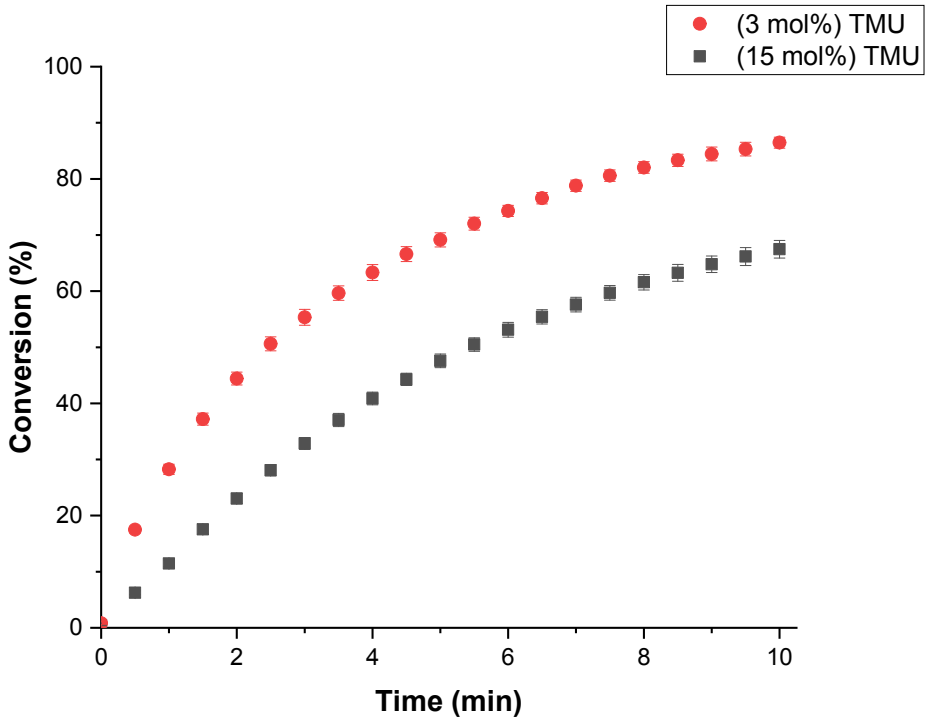


Figure S17. Product formation kinetics comparing the reaction between EMP (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (3 mol% or 15 mol%) catalyzed by MSA (1.5 mol%) in DCM (600 µL). Inhibition of the kinetics occur with increasing Lewis base amount driving vinyl equilibrium into the deactivated state.

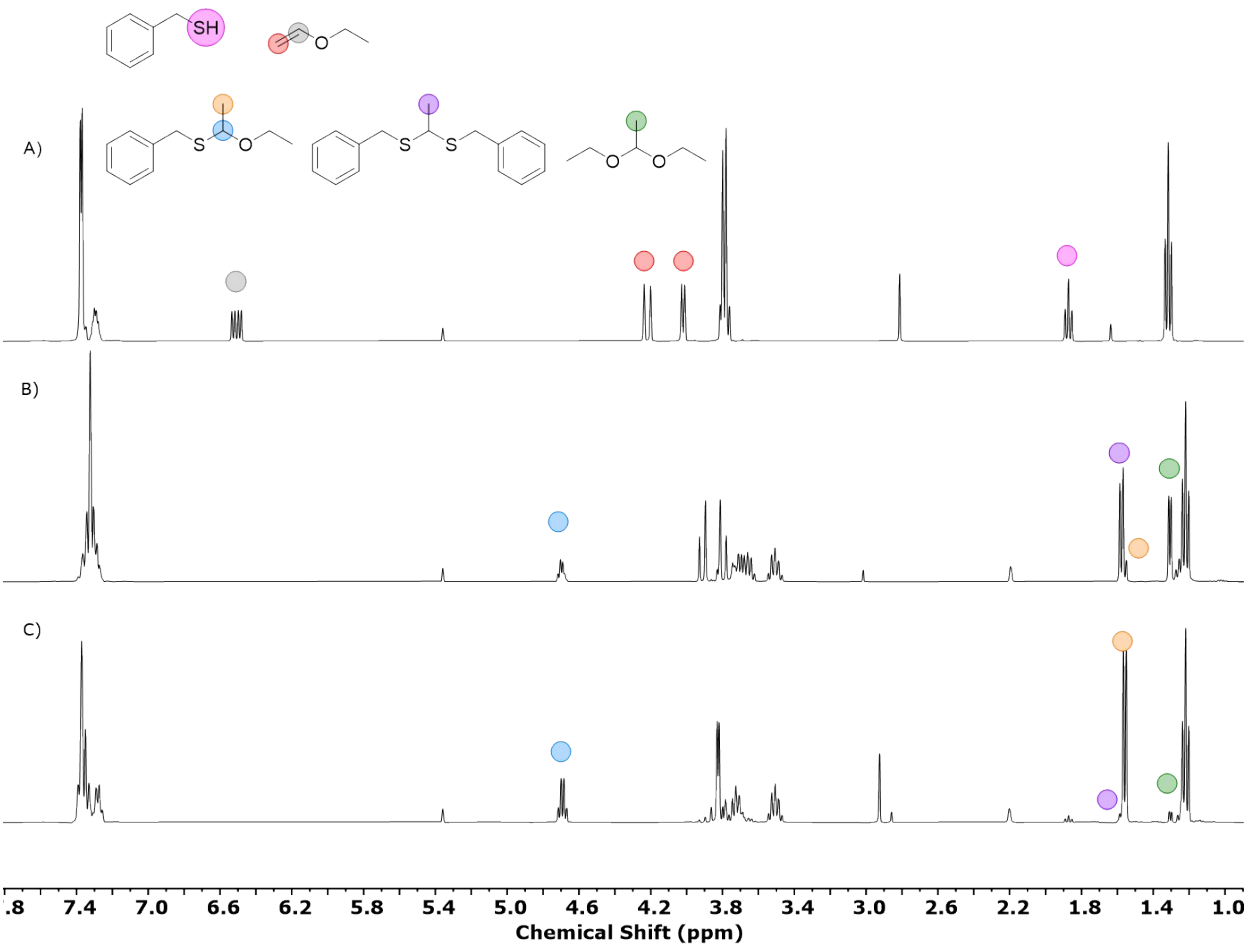


Figure S18. A) BzM (0.2 mmol), EVE (0.2 mmol), TMU (3 mol%) in DCM (600 µL) prior to adding an acid catalyst (t = 0 min). B) At t = 30 min post addition of MSA (1.5 mol%) with no TMU. Degradation of the desired product results in the formation of both O,O- (42% conversion) and S,S-acetal (47% conversion) side products along with minor amounts of the desired S,O-acetal product (11% conversion). Once the vinyl degrades, both an alcohol and acetaldehyde are generated, which can undergo a reaction with either the alcohol or thiol groups to form an acetal with any available nucleophile. It has been shown thiols can displace O or N groups on acetals in the presence of dilute acid to form dithioacetals.[3] C) At t = 30 min post addition of MSA (1.5 mol%) with the larger TMU (3 mol%). The dithioacetal formation is hindered because TMU acts as a weak base preventing acidic hydrolysis of the formed acetal bond. The resulting reaction result in minor formation of the undesired O,O- (< 5% conversion) and S,S-acetals (< 5% conversion), while the major product is the desired S,O-acetal (87% conversion).

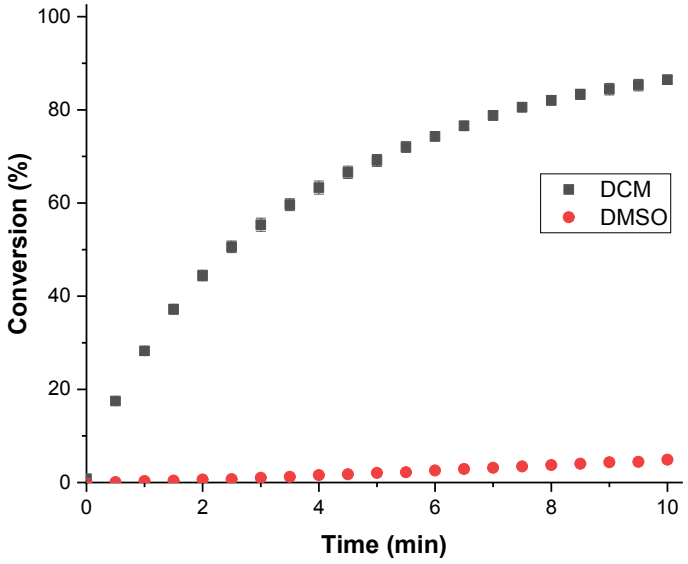


Figure S19. Kinetic comparison of the reaction between EMP (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), mesitylene (0.2 mmol, 1 eq), and TMU (3 mol% or 15 mol%) catalyzed by MSA (1.5 mol%) in DCM (600 µL) and DMSO (600 µL). As shown with increasing TMU, inhibition of the kinetics occurs with increasing Lewis base amount driving vinyl equilibrium into the deactivated state. In the extreme case where the Lewis base is the solvent, a small induction period is observed, followed by a slow rate of conversion. However, in the case of VPy, the reaction still proceeds to quantitative conversions after 16 h.

7. Solution-Phase Photoinitiation of the ACT Reaction

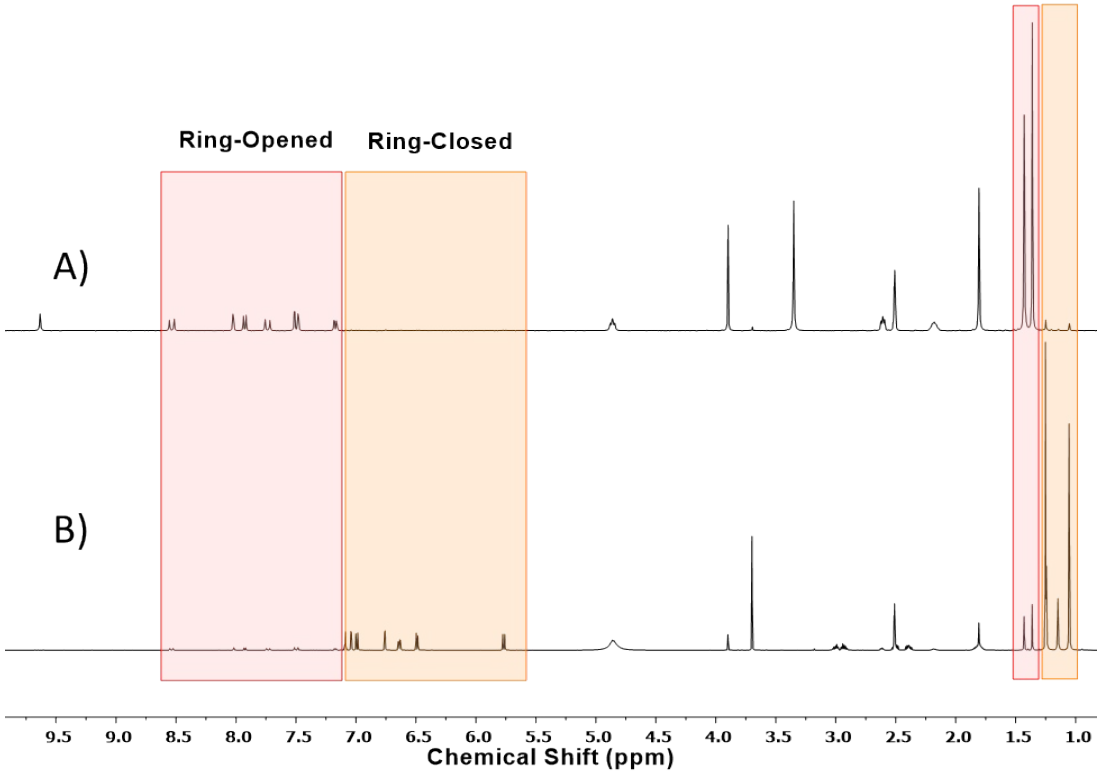


Figure S20. NMR spectrum of synthesized photochromic photoacid, SP3, with corresponding ring-opened (pink) and ring-closed (orange) chemical shifts labeled A) before and B) after irradiation with 20 mW/cm^2 470 nm of light for 30 min.

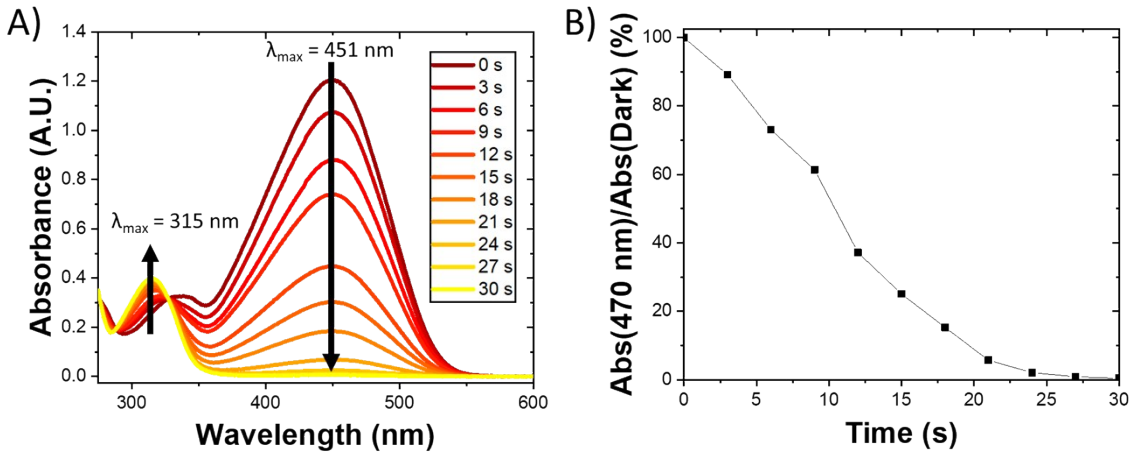


Figure S21. A solution of SP3 (50 µM in DMSO) was irradiated with light (5 mW/cm², 3 s) and measured at each time interval. A) UV-Vis shows the disappearance of the 451 nm peak associated with the ring-opened form of SP3. The increase at 315 nm corresponds to the ring-closed form of SP3. B) Kinetics following the disappearance of the 451 nm peak.

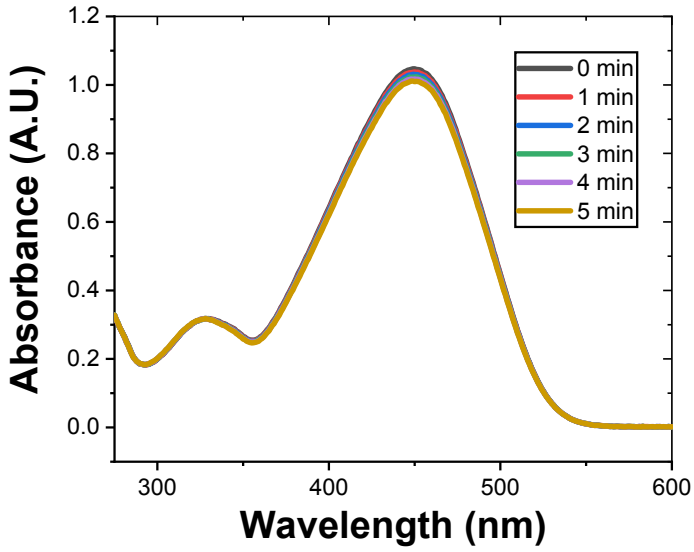


Figure S22. A solution of SP3 (50 µM in DMSO) in the dark measured via UV-Vis every minute for 5 min, showing no change in the spectrum in the absence of light.

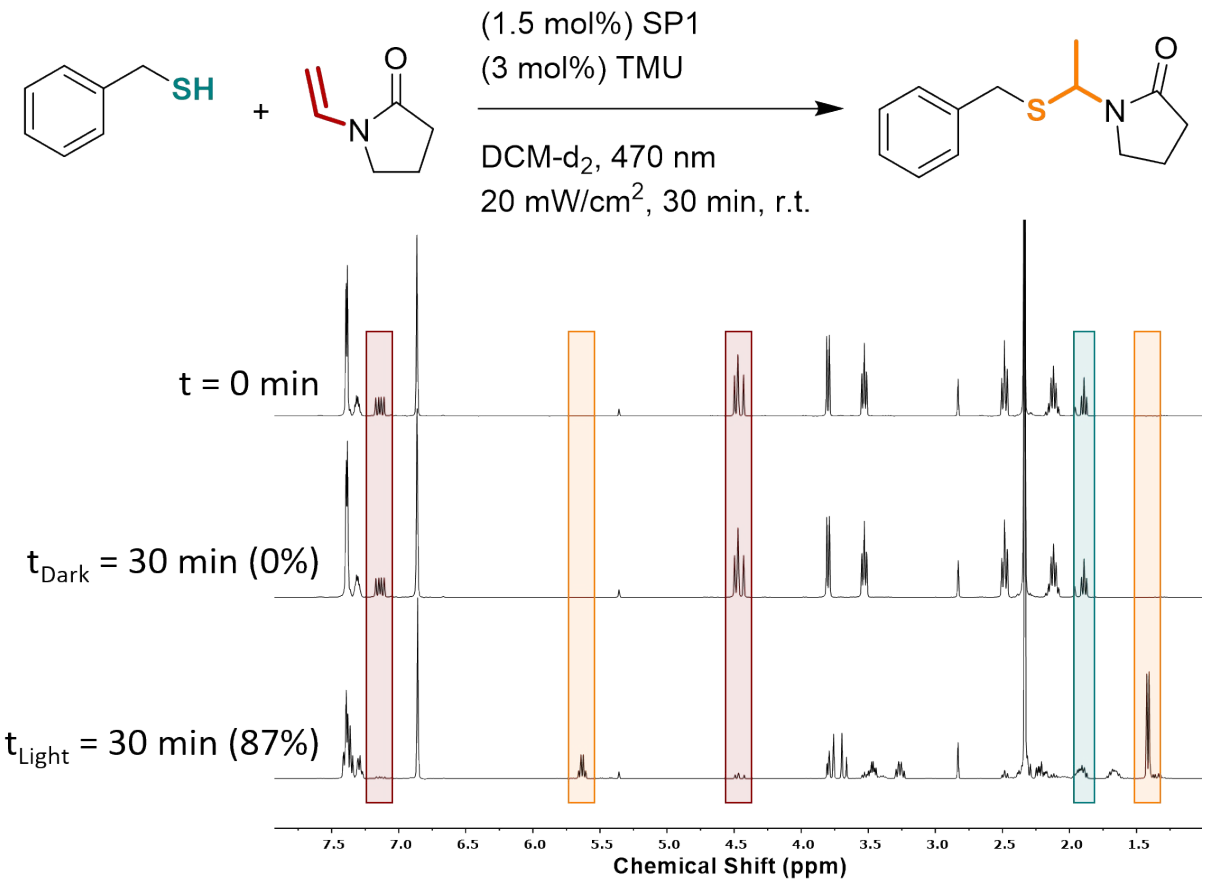


Figure S23. Photoactivation of the ACT reaction using a synthesized photochromic photoacid (SP1) inspired by spiropyran.[4] A sample of BzM (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), TMU (3 mol%), and mesitylene (0.2 mmol, 1 eq) were dissolved in DCM (600 µL). The sample was split into two equal portions in which both received SP1 (1.5 mol%). One sample was left in the dark for 30 min and the other was subjected to 470 nm irradiation (20 mW/cm^2, 30 min). At t = 0, the sample was prior to being split into two separate samples, t_{dark} = 30 min is the sample that was left in the dark with the SP1, and t_{Light} = 30 min was the sample irradiated with light. As can be seen by the maroon boxes, the vinyl peaks only disappear upon irradiation with 470 nm light. Additionally, the product peaks (orange) only appear in the presence of light.

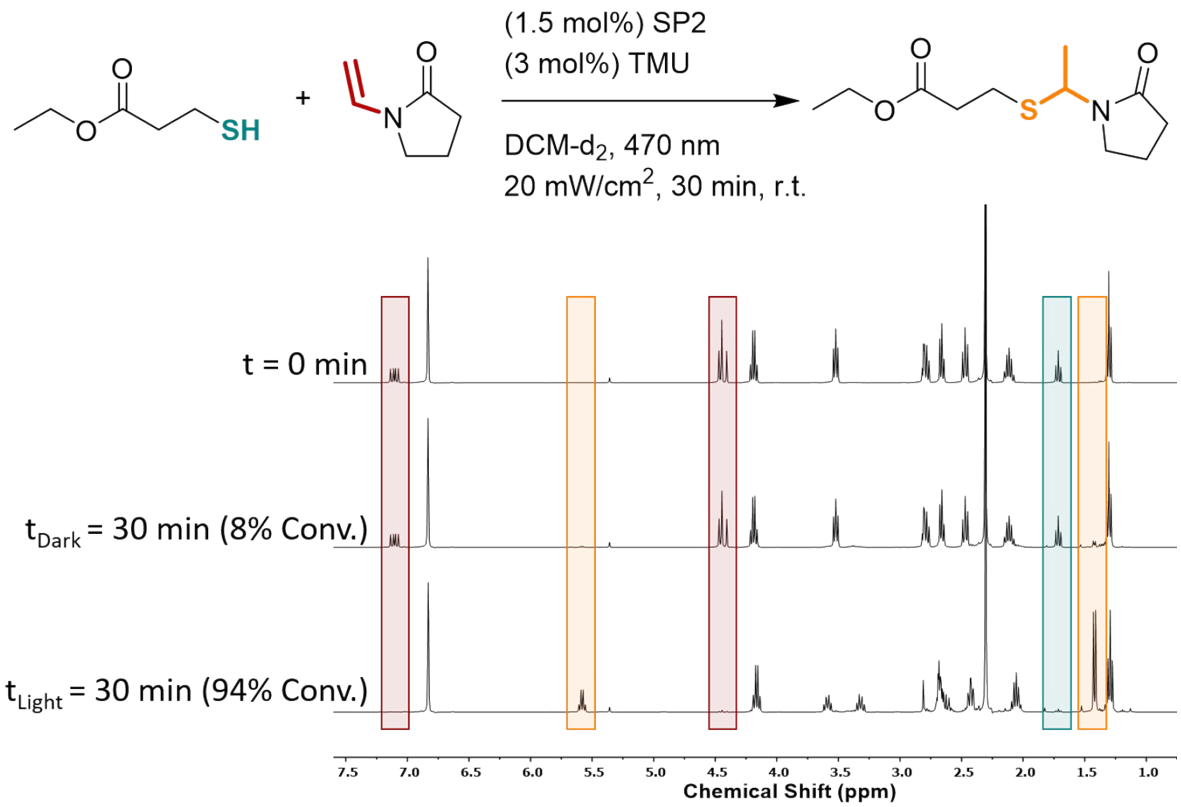


Figure S24. Photoactivation of the ACT reaction using a photochromic photoacid (SP2) developed from Zayas et al.[5] A sample of EMP (0.2 mmol, 1 eq), VPy (0.2 mmol, 1 eq), TMU (3 mol%), and mesitylene (0.2 mmol, 1 eq) were dissolved in DCM (600 µL). The sample was split into two equal portions in which both received SP2 (1.5 mol%). One sample was left in the dark for 30 min and the other was subjected to 470 nm irradiation (20 mW/cm^2, 30 min). At t = 0 is the sample prior to being split into two separate portions, t_{dark} = 30 min is the sample that was left in the dark with the SP2, and t_{Light} = 30 min was the sample irradiated with light. As can be seen by the maroon boxes, the vinyl peaks disappear upon irradiation with 470 nm light, while some of the vinyl (8%) converts in the dark indicating dark acidity.

8. Crosslinked Polymer Network Synthesis

8.1. ACT formulation

The photochromic photoacid (SP3) was dissolved into PETMP at (0.54 wt.% of PETMP) with the use of minimal DCM. Upon vortexing and dissolution of SP3, the mixture was concentrated to remove the DCM. The SP3-PETMP mixture and 1,4 cyclohexane dimethanol divinyl ether (CDDE) were combined at a 1:1 (thiol:vinyl) stoichiometric ratio resulting in a final 0.27 wt% of SP3. The sample was then speed mixed at 2500 RPM for two minutes. Finally, the resin was deposited between two glass slides separated by plastic shims (0.25 mm thickness). The average film dimensions were 0.25 mm by 4 mm by 25 mm (thickness x width x length).

8.2. Thiol-ene (TE) Formulation

PETMP and CDDE were combined at a 1:1 (thiol:vinyl) stoichiometric ratio. Irgacure 651 (I-651) was added at a 0.2 wt.% resin loading. The sample was then speed mixed at 2500 RPM for two minutes. Finally, the resin was deposited between two glass slides separated by plastic shims (0.25 mm thickness). The average film dimensions were 0.25 mm by 4 mm by 25 mm (thickness x width x length).

8.3. Photopolymerization and In-situ FTIR

The ACT photopolymerizations were conducted at 470 nm with an intensity of 20 mW/cm^2. The thiol-ene polymerizations were conducted at 365 nm with an intensity of 15 mW/cm^2. The thiol-Michael polymerization was conducted in the dark. The polymerization was monitored by tracking the FTIR absorbance of thiol (2620-2530 cm^{-1}) and vinyl ether (6205-6175 cm^{-1}).

8.4. Polymer Network Characterization

The thickness and width of the films were measured using a digital caliper. Dynamic mechanical analysis (DMA) was performed over a temperature range of -50°C to 100°C and temperature ramp of 3°C/min. The frequency and strain were kept at 1 Hz and 0.1% where the specimen exhibited linear properties.

9. Polymer Network Formation Kinetics

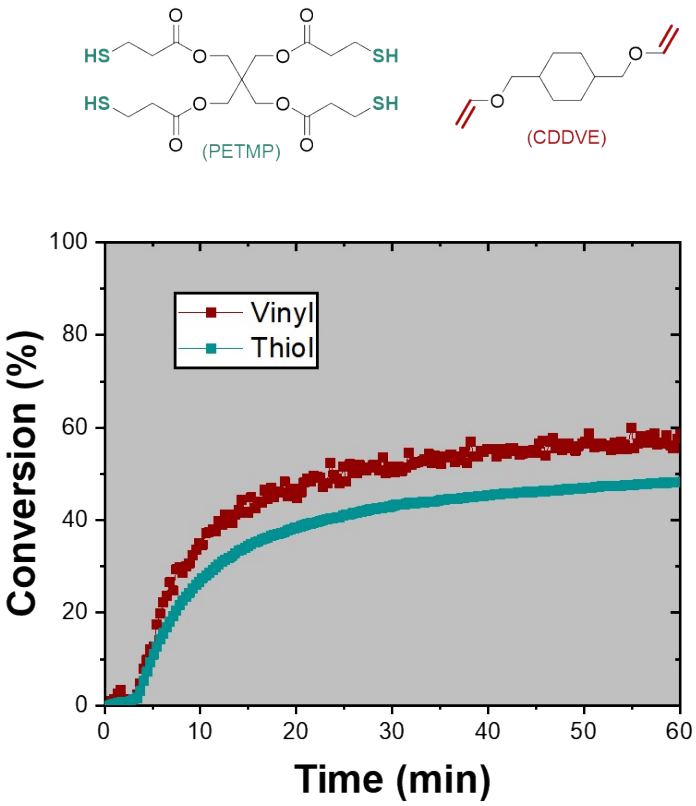


Figure S25. Conversion versus time of an ACT thermoset polymerized in the dark and in the absence of the photochromic photoacid, SP3. The formulation of the film is a 1 to 1 stoichiometric ratio of thiol to vinyl using monomers PETMP and CDDE.

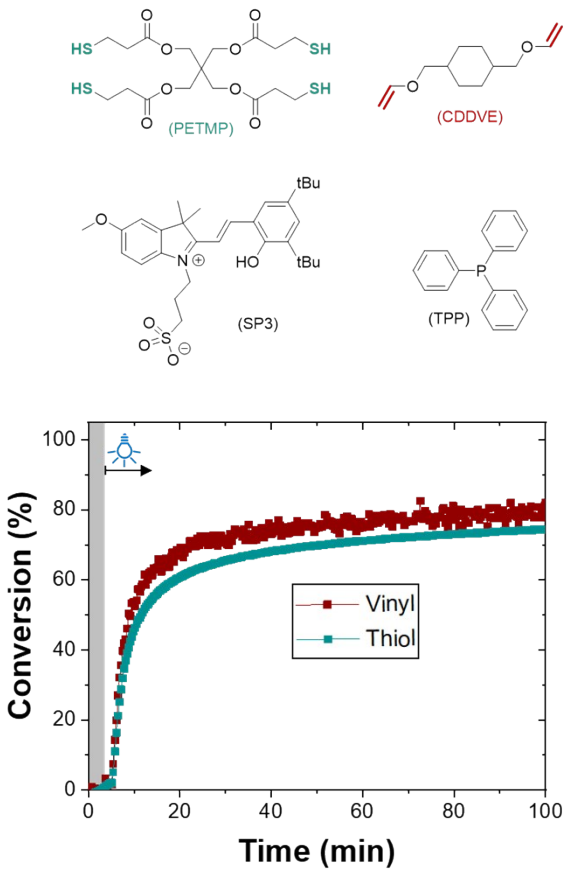


Figure S26. The ACT reaction shows lower final conversions when both SP3 and TPP are present in the resin. The ACT formulation was made using a 1 to 1 thiol to vinyl stoichiometric ratio of monomers PETMP and CDDVE with both SP3 (0.27 wt%) and TPP (2 wt%) present. The resin was initiated after 2 min in the dark with 470 nm light at 20 mW/cm^2. The ACT reaction shows a plateauing conversion for the thiol around 70% that slowly increases over longer periods of time. Additionally, the TPP reduces the overall dark acidity of the resin and improves temporal control over the initiation.

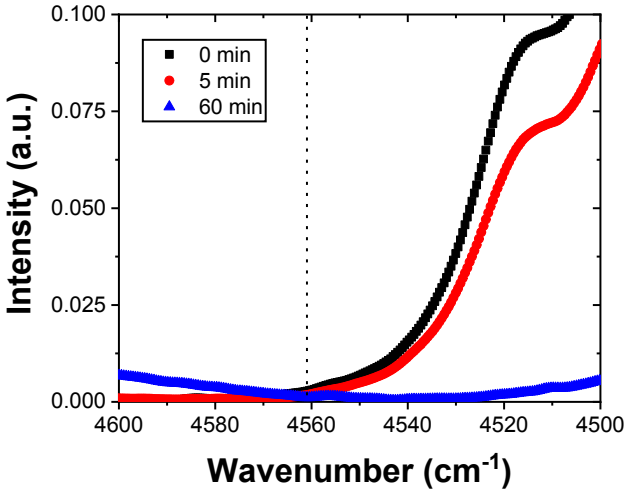
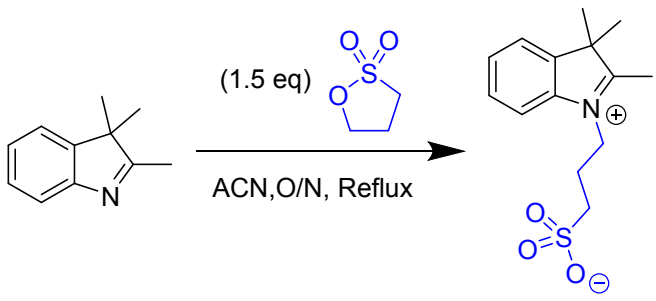


Figure S27. FTIR spectrum showing no change in the 4561 cm^{-1} peak (dashed line) and thus negligible acetaldehyde formation. This result suggests that the offset between the thiol and vinyl conversions likely owe to minor homopolymerization.

10. Photochromic Photoacid Synthesis



1

Reaction conditions were adapted from work previously reported by Li and coworkers.[6] To an oven dried, N_2 purged 50 mL round bottom flask was added 2,3,3-trimethyl-3*H*-Indole (2 g, 12.58 mmol, 1 eq) followed by 10 mL of anhydrous ACN. Propane sulfone (2.32 g, 18.86 mmol, 1.5 eq) was added to the mixture and the solution was heated to reflux and left to react in the dark overnight. The following day, the purple precipitate was filtered and first washed with a minimal amount of ACN and then washed with excess acetone. The solid was collected and dried under high vac to produce compound **1** as a purple solid (3.47 g, 98%). The NMR was in good agreement with previously reported synthesis.

^{1}H NMR (600 MHz, DMSO) δ 8.06 (dd, *J* = 7.0, 1.8 Hz, 1H), 7.89 – 7.78 (m, 1H), 7.71 – 7.54 (m, 2H), 4.70 – 4.64 (m, 2H), 2.84 (s, 3H), 2.63 (t, *J* = 6.5 Hz, 2H), 2.17 (dtd, *J* = 14.5, 7.6, 3.6 Hz, 2H), and 1.54 (s, 6H) ppm.

^{13}C NMR (151 MHz, DMSO) δ 196.16, 141.58, 140.85, 128.97, 128.59, 123.06, 115.11, 53.77, 47.02, 46.25, 23.42, 21.70, and 13.44 ppm.

$[M + H]^+$ Calculated for $C_{14}H_{19}NO_3S$: 282.37; Found: 282.45

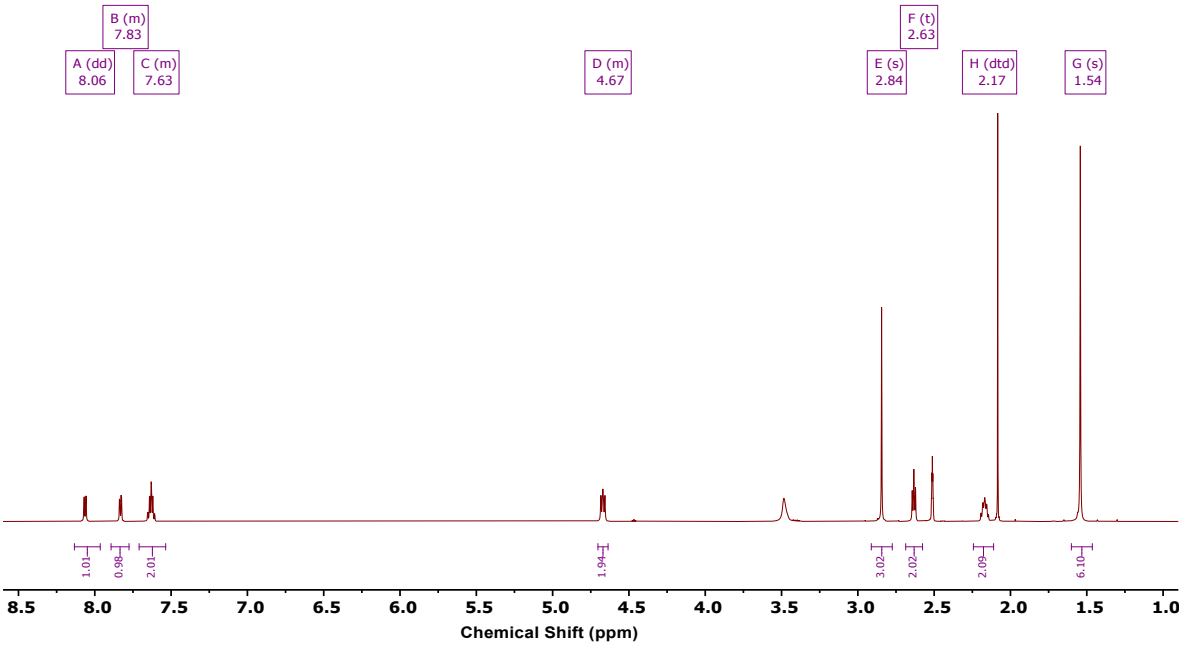


Figure S28. ^{1}H NMR of compound **1** (600 MHz, DMSO).

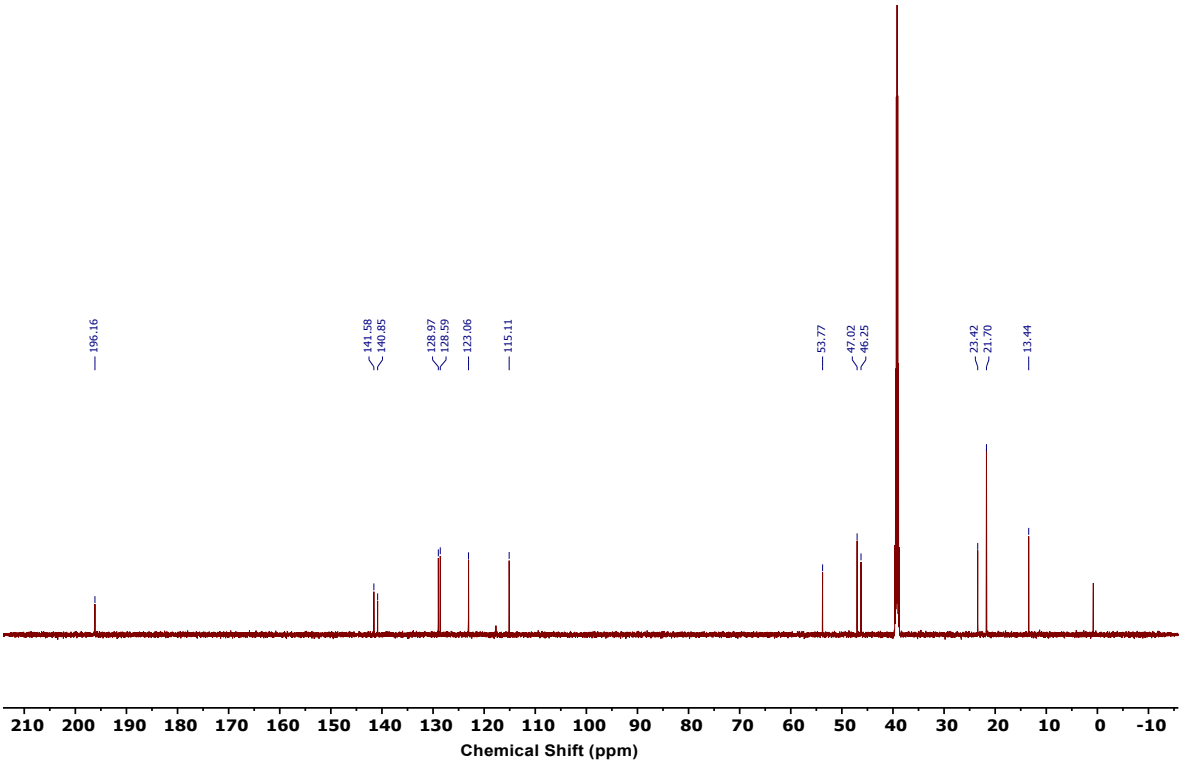
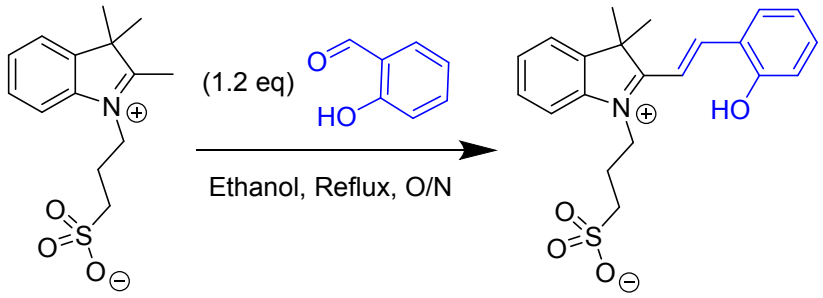


Figure S29. ^{13}C NMR of compound **1** (151 MHz, DMSO).



1 **2 (SP1)**

Reaction conditions were adapted from work previously reported by Shi and coworkers.[4] To a N_2 purged 100 mL round bottom flask was added compound **1** (3.47 g, 12.35, 1 eq) followed by ethanol (15 mL). 2-hydroxybenzyaldehyde (1.58 mL, 14.80 mmol, 1.2 eq) was added dropwise to the reaction and the solution was heated at reflux overnight. The following day, the orange precipitate was filtered and washed with ethanol followed by diethyl ether. The solid was collected and dried via high vac to produce compound **2** (SP1, 3.25 g, 68%) as an orange solid. The NMR was in good agreement with previously reported synthesis.

^{1}H NMR (600 MHz, DMSO) δ 11.04 (s, 1H), 8.61 (d, *J* = 16.4 Hz, 1H), 8.29 (dd, *J* = 8.0, 1.7 Hz, 1H), 8.08 – 7.98 (m, 1H), 7.93 – 7.83 (m, 2H), 7.68 – 7.56 (m, 2H), 7.49 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H), 7.11 – 6.90 (m, 2H), 4.82 (t, *J* = 8.0 Hz, 2H), 2.66 (t, *J* = 6.4 Hz, 2H), 2.26 – 2.11 (m, 2H), and 1.78 (s, 6H) ppm.

^{13}C NMR (151 MHz, DMSO) δ 182.22, 159.48, 149.15, 143.95, 141.40, 136.21, 130.24, 129.59, 123.44, 121.81, 120.53, 117.08, 115.55, 111.93, 52.38, 47.80, 46.01, 26.91, and 25.07 ppm.

$[M + H]^+$ Calculated for $C_{21}H_{23}NO_4S$: 386.48; Found: 386.29

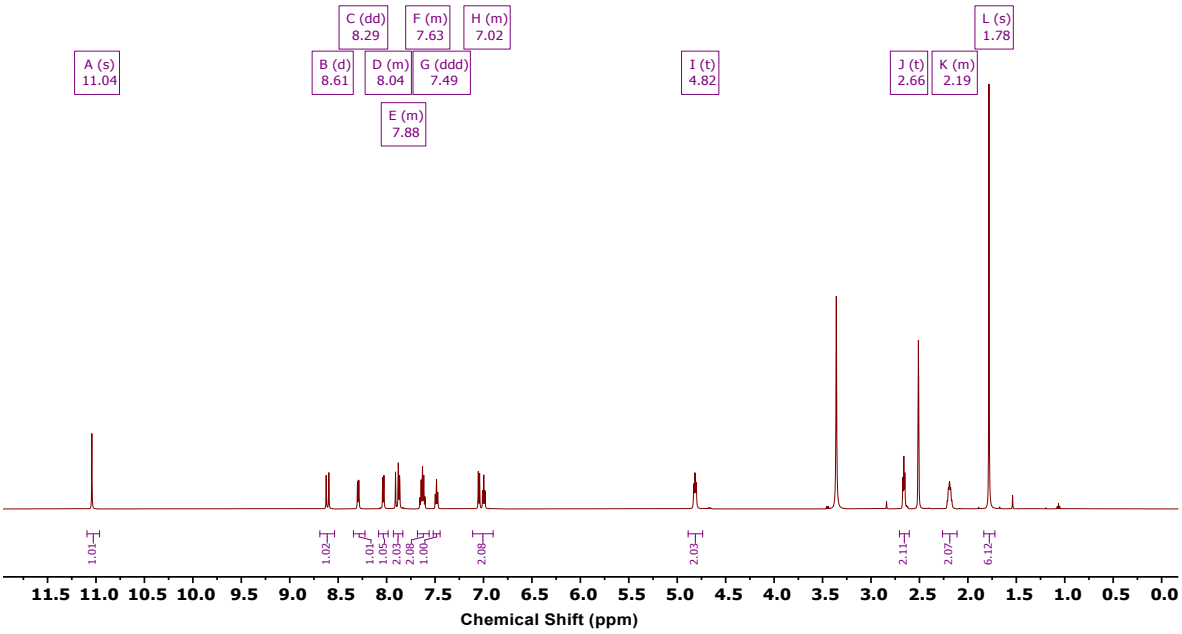


Figure S30. ^{1}H NMR of compound **2** (SP1, 600 MHz, DMSO).

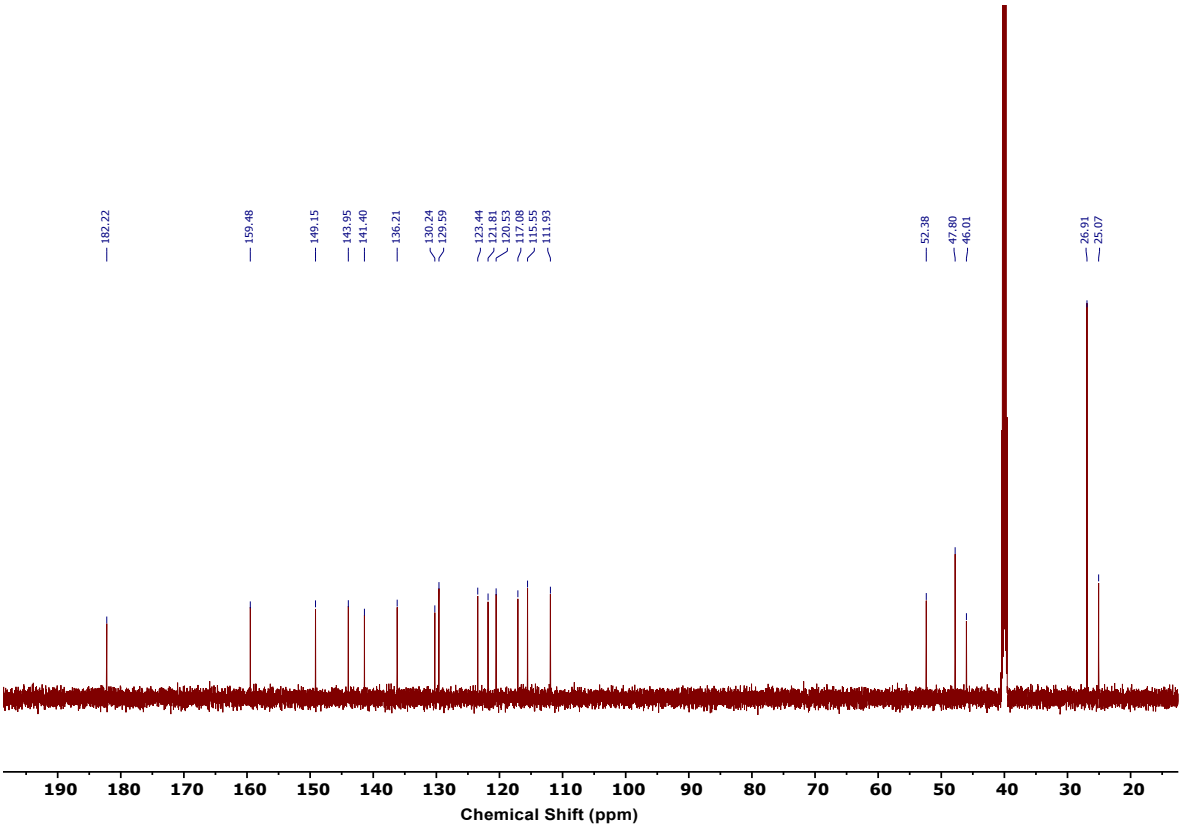
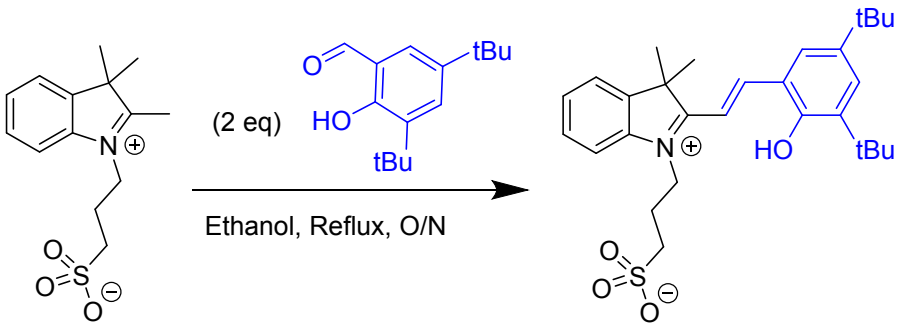


Figure S31. ^{13}C NMR of compound **2** (SP1, 151 MHz, DMSO).



1 **3 (SP2)**

Reaction conditions were adapted from work previously reported by Read de Alaniz and coworkers.[5] To a N_2 purged 100 mL round bottom flask was added compound **1** (2.66 g, 9.45 mmol, 1 eq) followed by ethanol (25 mL). 3,5-di-tert-butyl-2-hydroxybenzaldehyde (4.86 g, 20.79 mmol, 2 eq) was added to the reaction and the solution was heated at reflux overnight. The following day, the solution was cooled in a freezer for 2 h and the orange precipitate was filtered and washed with cold ethanol followed by diethyl ether. The solid was collected, dried via high vac, and dried a second time in an oven set to 130 °C to produce compound **3** (SP2, 2.35 g, 50%) as an orange solid. NMR was in good agreement with previously reported synthesis.

^{1}H NMR (600 MHz, CD_3OH) δ 8.82 (d, *J* = 16.1 Hz, 1H), 8.03 (d, *J* = 2.4 Hz, 1H), 7.99 – 7.88 (m, 1H), 7.88 – 7.72 (m, 2H), 7.72 – 7.56 (m, 3H), 4.99 – 4.89 (m, 2H), 3.11 – 2.88 (m, 2H), 2.54 – 2.32 (m, 2H), 1.90 (s, 6H), and 1.46 (d, *J* = 39.8 Hz, 18H) ppm.

^{13}C NMR (151 MHz, CD_3OH) δ 182.81, 155.31, 152.07, 144.65, 143.59, 140.77, 140.42, 130.93, 129.24, 129.21, 125.48, 122.83, 122.59, 114.56, 110.75, 52.43, 45.07, 34.78, 34.35, 30.50, 28.95, 25.74, and 24.00 ppm.

$[M + H]^+$ Calculated for $C_{29}H_{39}NO_4S$: 498.69; Found: 498.67

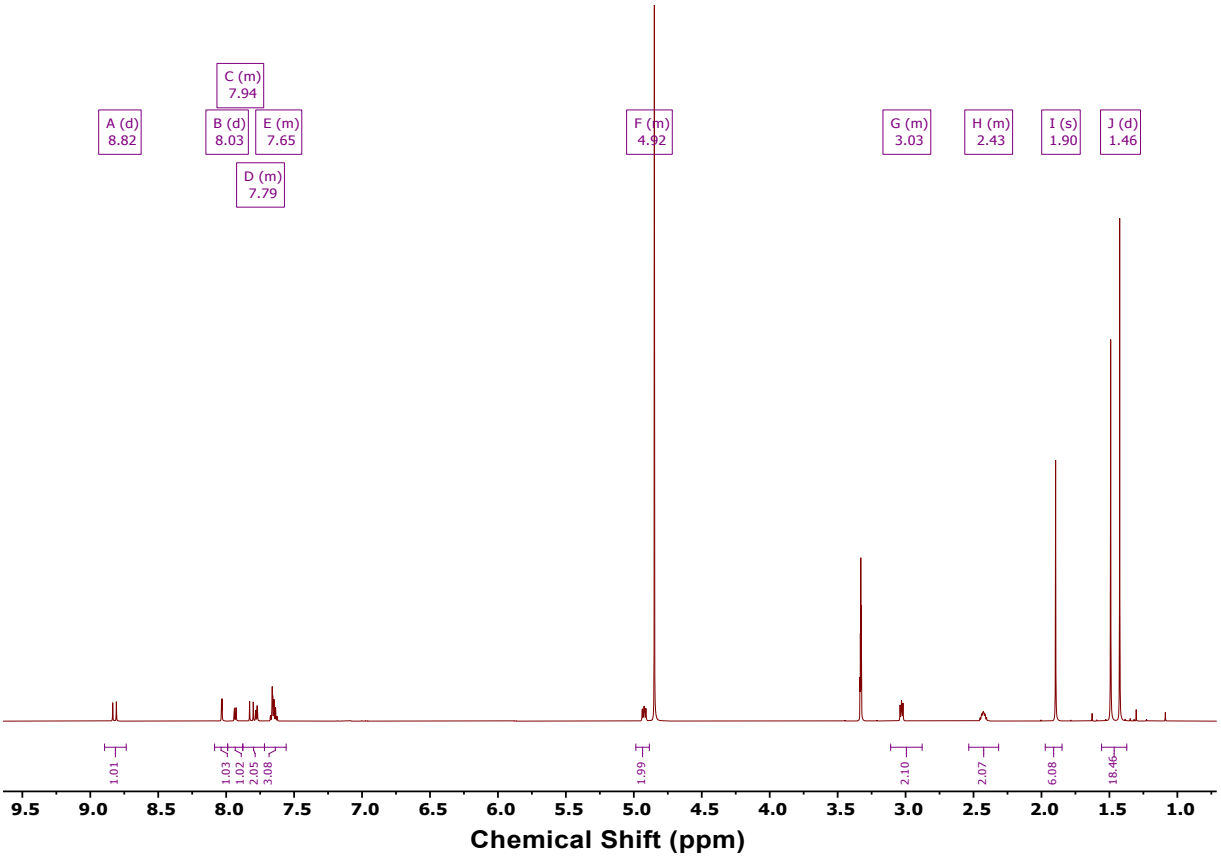


Figure S32. ^{1}H NMR of compound **3** (SP2, 600 MHz, CD_3OH).

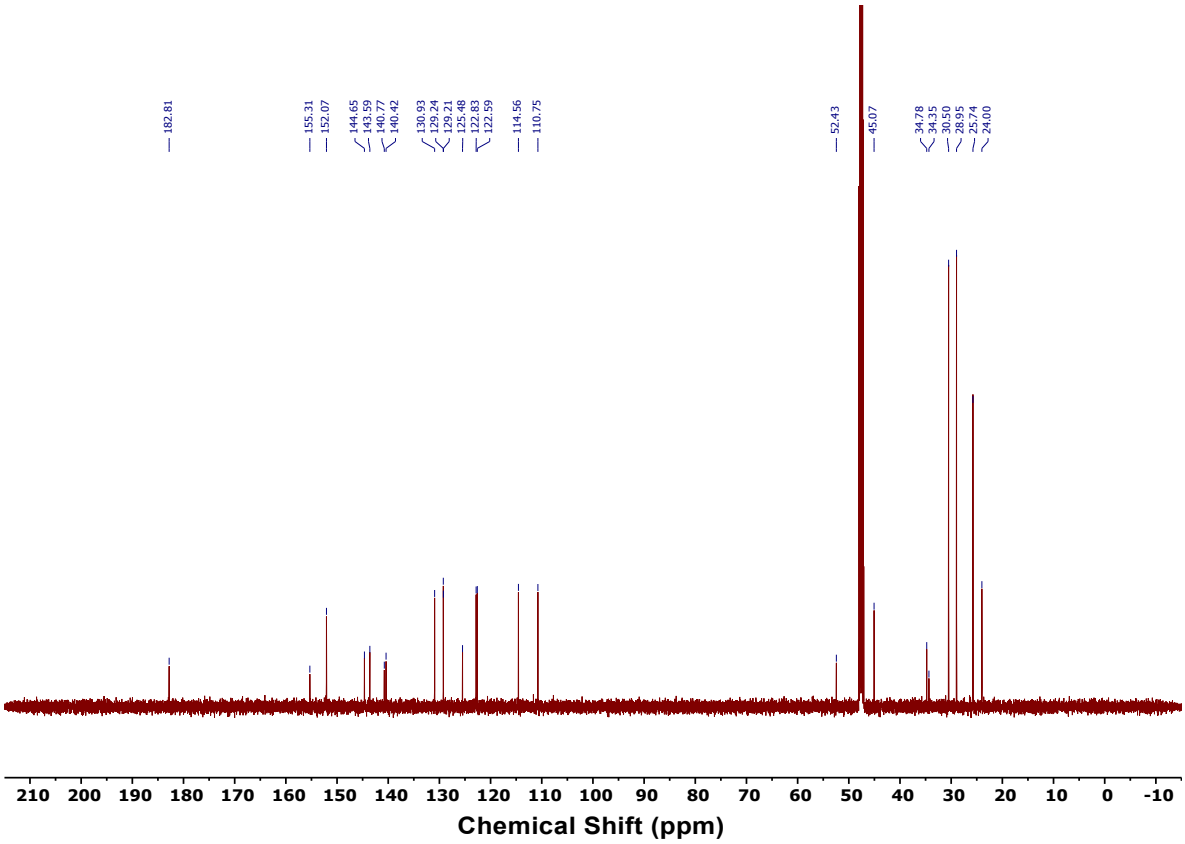


Figure S33. ^{13}C NMR of compound **3** (SP2, 151 MHz, CD_3OH).

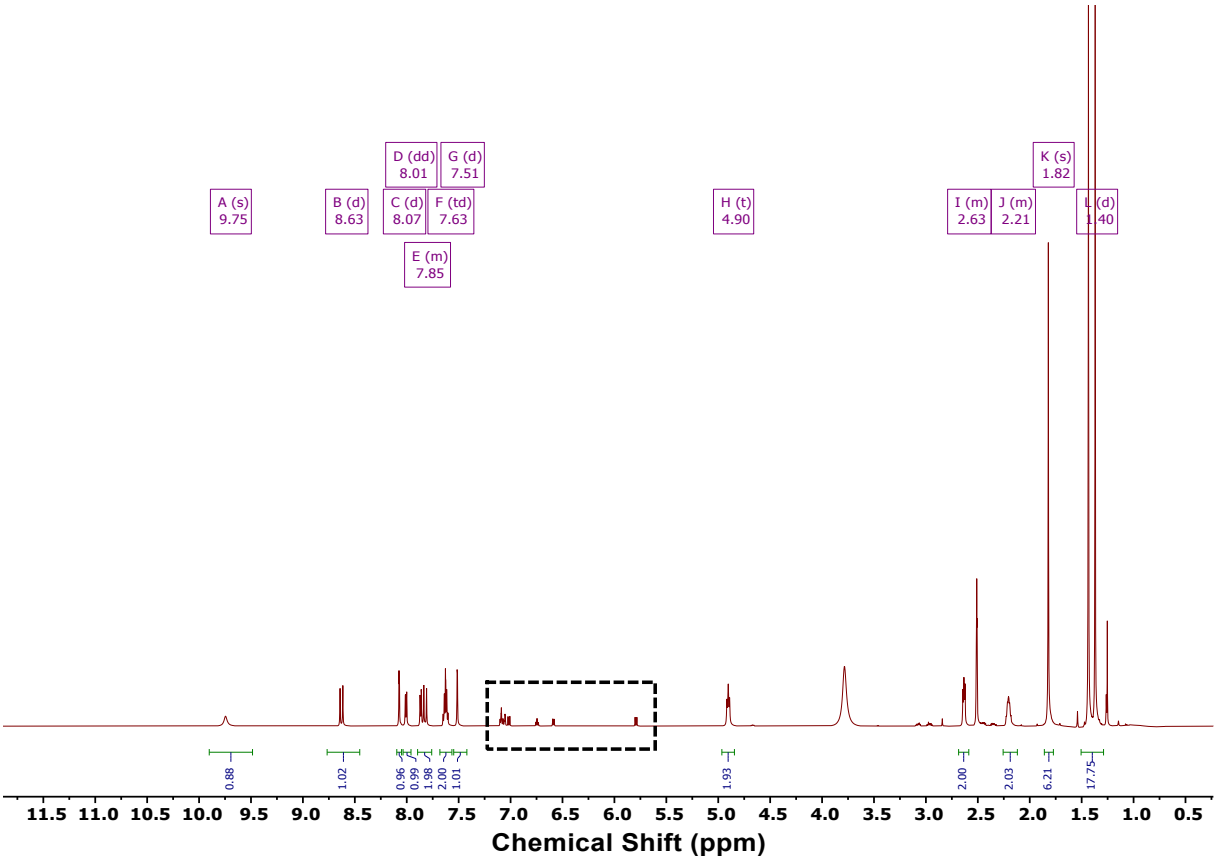
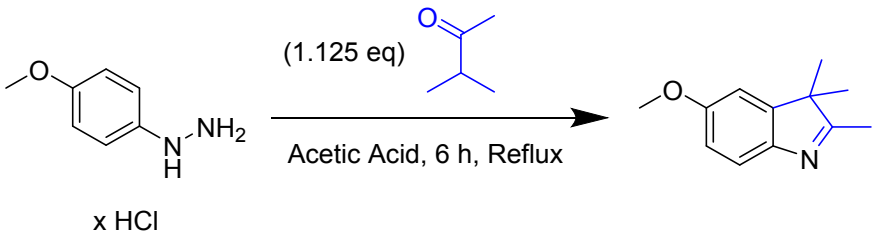


Figure S34. ^{1}H NMR of compound **3** (SP2, 600 MHz, DMSO) in DMSO highlighting (black dashed square) the ring closed isomerized photoacid in the dark. The presence of the ring closed structure is associated with dark acidity.



4

Reaction conditions were adapted from work previously reported by Read de Alaniz and coworkers.[7] To a N_2 purged 100 mL round bottom flask was added 4-methoxyphenylhydrazine hydrochloride (6.96 g, 40 mmol, 1 eq) followed by acetic acid (25 mL). Next, methyl isopropyl ketone (4.82 mL, 45 mmol, 1.125 eq) was added and the reaction was refluxed for 6 h. Upon completion of the reaction, as determined by TLC, the solution was cooled to room temperature and transferred to an extraction vessel. The solution was quenched with 1M NaOH (200 mL) and the aqueous layer was washed with EtOAc (3x, 100 mL). The organic phases were combined and washed with 1M NaOH (3x, 100 mL) and sat. NaCl (100 mL). The organic phase was collected, dried over Na_2SO_4, filtered, and concentrated to produce compound **4** as a red oil (6.2 g, 82%).

^{1}H NMR (400 MHz, DMSO) δ 7.32 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 6.81 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.76 (s, 3H), 2.16 (s, 3H), 1.22 (s, 6H).

^{13}C NMR (101 MHz, DMSO) δ 185.61, 157.86, 147.98, 147.63, 119.93, 112.61, 108.61, 55.86, 53.76, 23.10, and 15.32 ppm.

$[M + H]^+$ Calculated for $C_{12}H_{15}NO$: 190.26; Found: 190.25

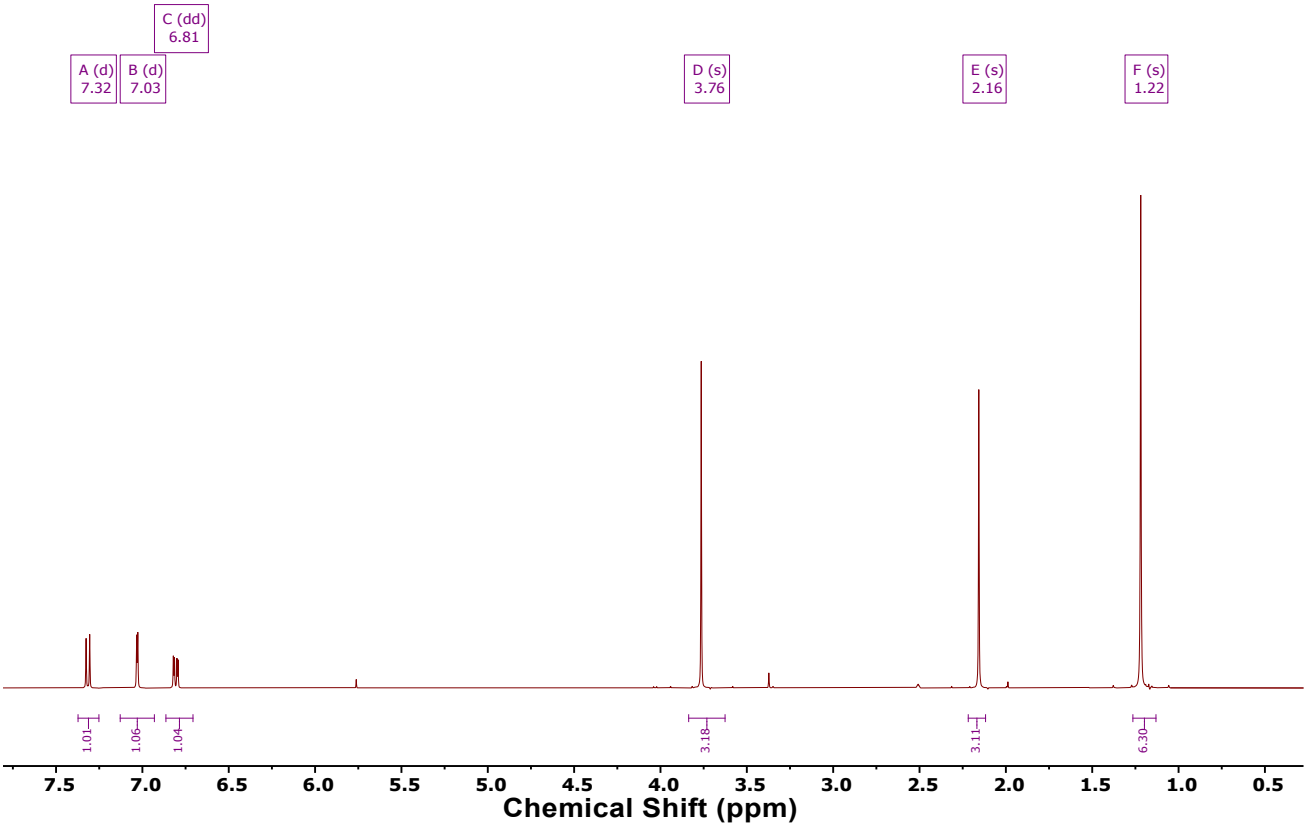


Figure S35. ^{1}H NMR of compound **4** (400 MHz, DMSO).

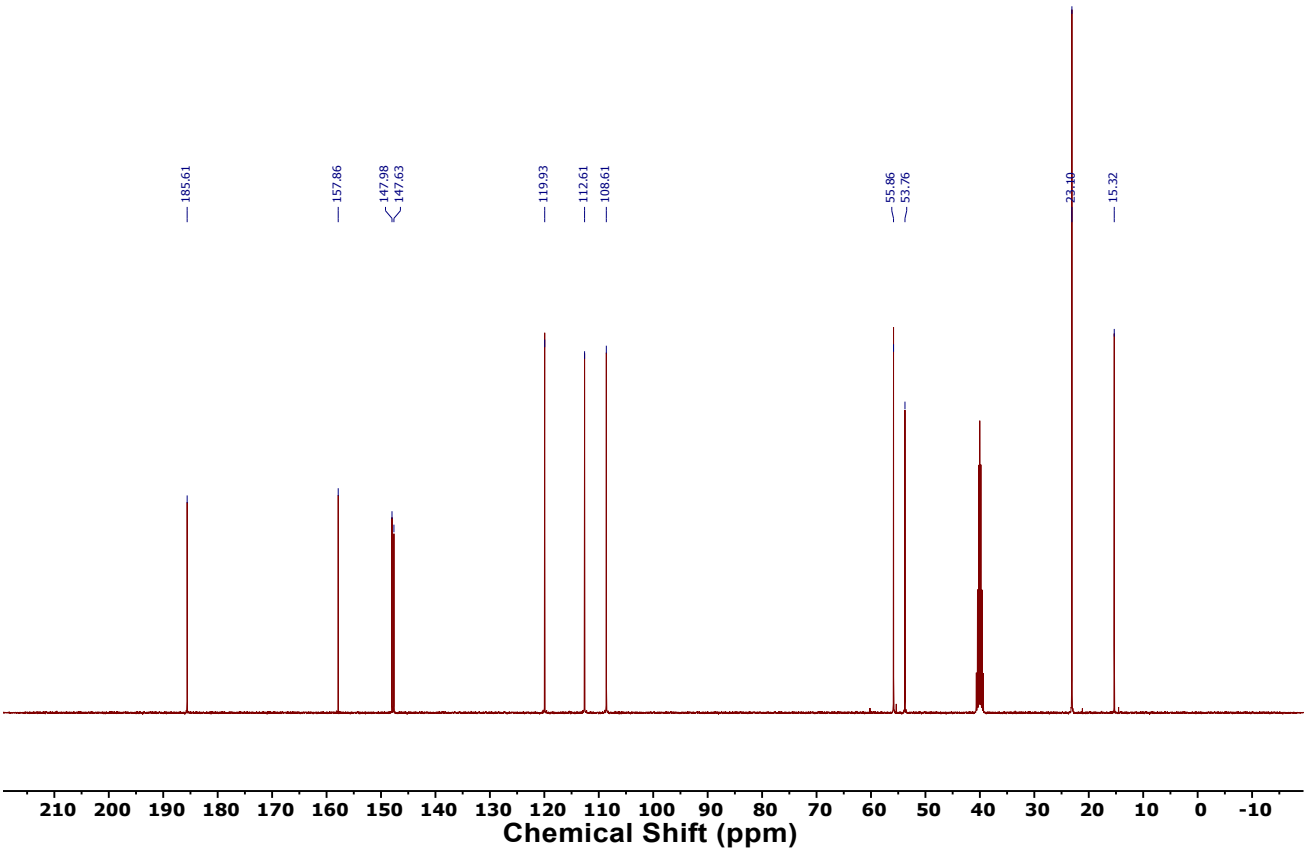
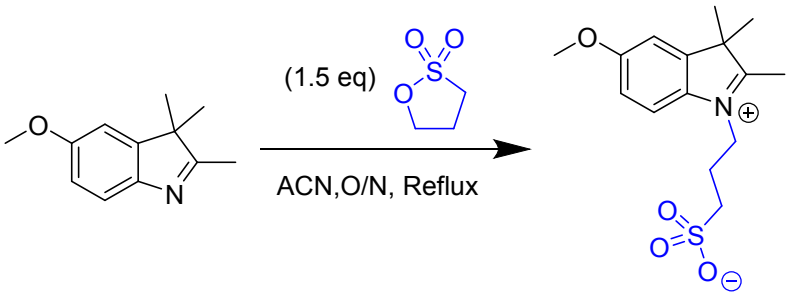


Figure S36. ^{13}C NMR of compound **4** (101 MHz, DMSO).



4 **5**

Reaction conditions were adapted from work previously reported by Li and coworkers.[6] To an oven dried, N_2 purged 50 mL round bottom flask was added compound **4** (3 g, 15.7 mmol, 1 eq) followed by anhydrous ACN (15 mL). Propane sultone (2.89 g, 23.7 mmol, 1.5 eq) was added to the mixture and the solution was heated to reflux and left to react in the dark overnight. The following day, the light purple precipitate was filtered and washed with a minimal amount of ACN and excess acetone. The solid was collected and dried under high vac to produce compound **5** as a grey/purple solid (4.6 g, 94%).

^{1}H NMR (600 MHz, DMSO) δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 2.5 Hz, 1H), 7.15 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.71 – 4.50 (m, 2H), 3.87 (s, 3H), 2.79 (s, 3H), 2.62 (t, *J* = 6.6 Hz, 2H), 2.15 (ddt, *J* = 8.5, 6.5, 3.7 Hz, 2H), 2.09 (s, 2H), and 1.52 (s, 6H) ppm.

^{13}C NMR (151 MHz, DMSO) δ 193.54, 160.55, 143.99, 134.35, 116.41, 114.29, 109.34, 56.04, 53.90, 47.33, 46.55, 23.84, 22.10, 13.50, 1.11.

$[M + H]^+$ Calculated for $C_{15}H_{21}NO_4S$: 312.40; Found: 312.45

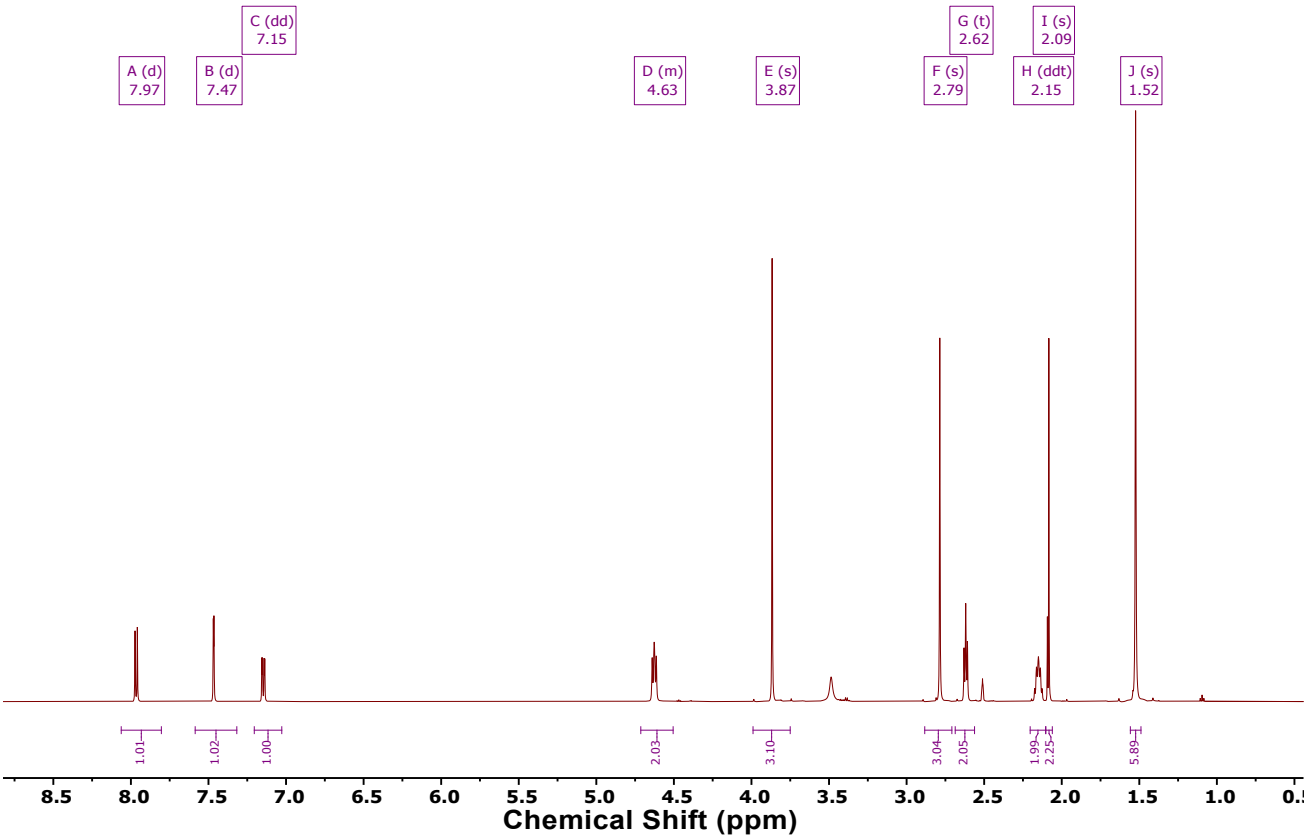


Figure S37. ^{1}H NMR of compound **5** (600 MHz, DMSO).

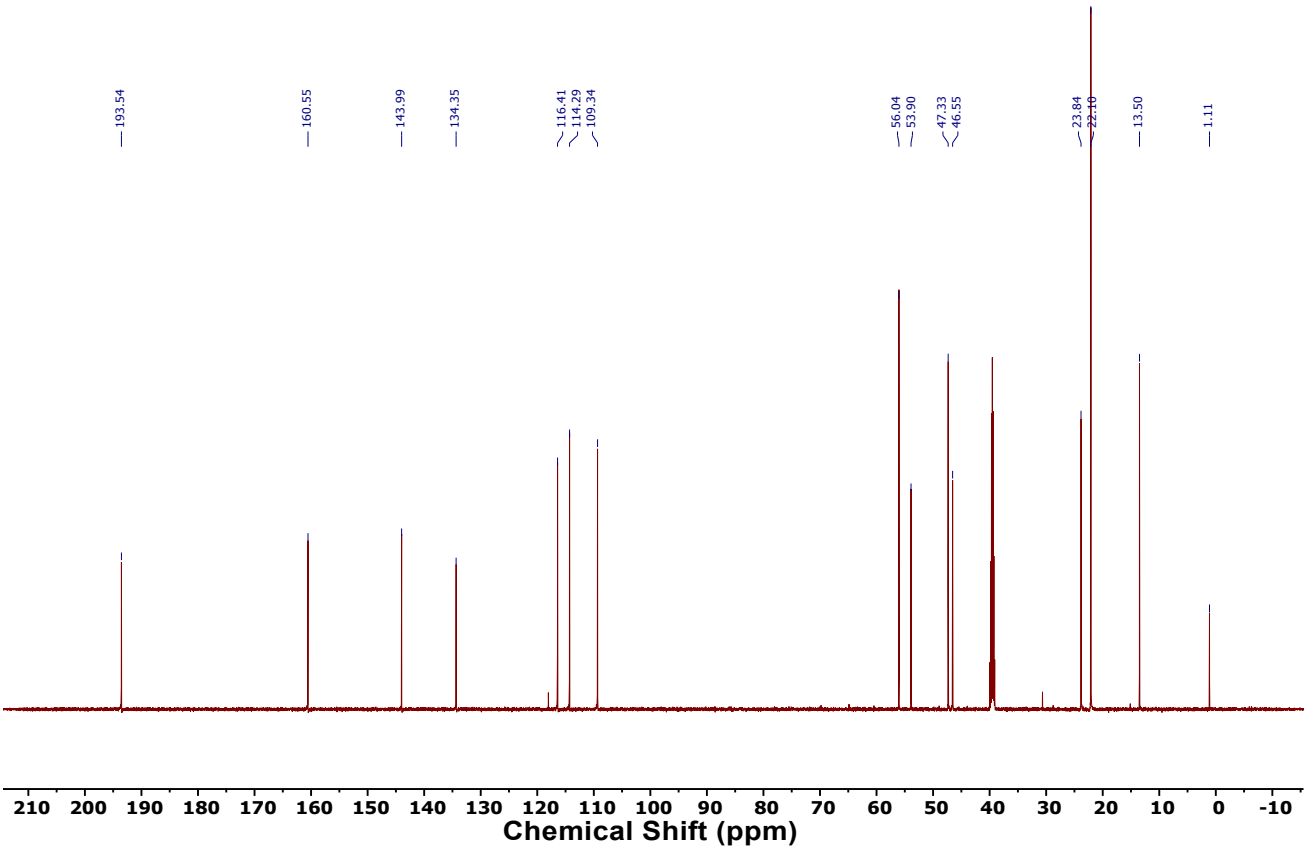
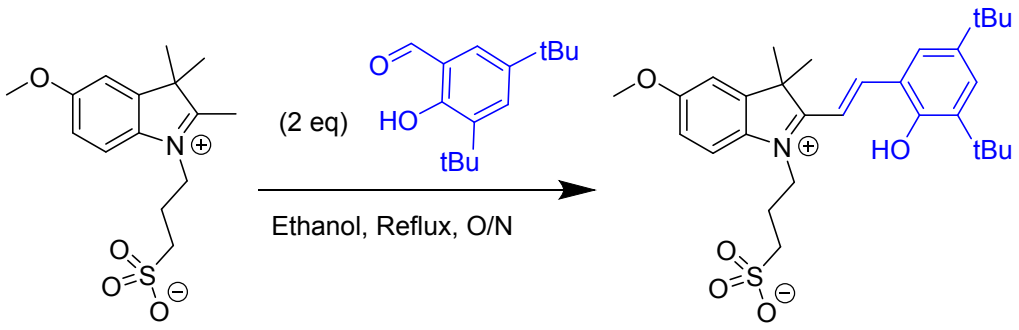


Figure S38. ^{13}C NMR of compound **5** (101 MHz, DMSO).



5 **6 (SP3)**

Reaction conditions were adapted from work previously reported by Read de Alaniz and coworkers.[5] To a N_2 purged 100 mL round bottom flask was added compound **5** (3.5 g, 11.2 mmol, 1 eq) followed by ethanol (25 mL). 3,5-di-tert-butyl-2-hydroxybenzaldehyde (5.79 g, 24.7 mmol, 2 eq) was added to the reaction and the solution was heated at reflux overnight. The following day, the solution was cooled in a freezer for 2 h and the orange precipitate was filtered and washed with cold ethanol followed by diethyl ether. The solid was collected, dried via high vac to produce compound **6** (SP3, 1.52 g, 25%) as a yellow solid.

^{1}H NMR (400 MHz, DMSO) δ 9.63 (s, 1H), 8.53 (d, *J* = 16.1 Hz, 1H), 8.02 (d, *J* = 2.3 Hz, 1H), 7.93 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 16.1 Hz, 1H), 7.50 (dd, *J* = 12.4, 2.4 Hz, 2H), 7.17 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.86 (t, *J* = 7.7 Hz, 2H), 3.90 (s, 3H), 2.61 (t, *J* = 6.3 Hz, 2H), 2.18 (s, 2H), 1.81 (s, 6H), 1.43 (s, 9H), and 1.36 (s, 9H) ppm.

^{13}C NMR (151 MHz, DMSO) δ 180.24, 161.19, 155.14, 148.88, 146.46, 143.88, 140.10, 134.51, 129.72, 125.48, 123.26, 116.68, 115.33, 112.15, 109.19, 56.61, 52.54, 47.55, 45.92, 35.39, 34.96, 31.85, 31.82, 30.24, 30.05, 26.61, and 25.31 ppm.

$[M + H]^+$ Calculated for $C_{30}H_{41}NO_5S$: 528.72; Found: 528.79

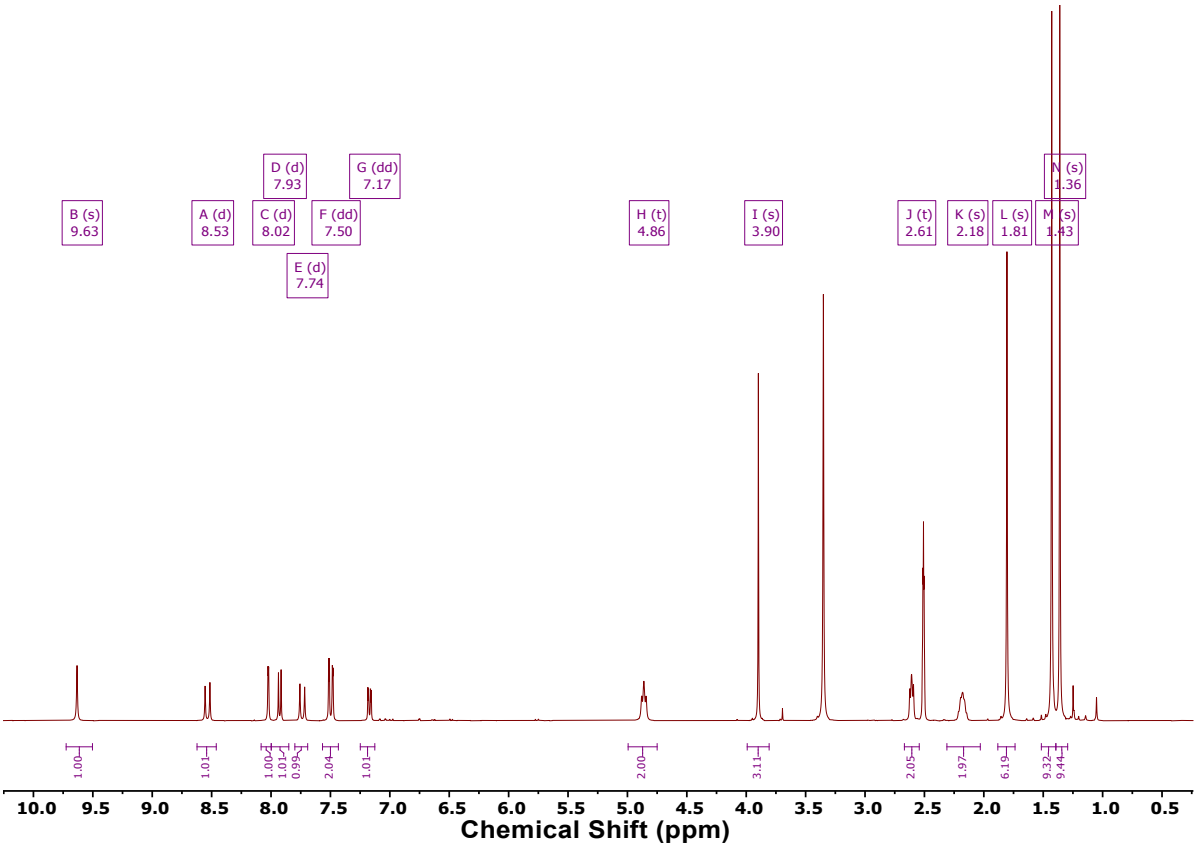


Figure S39. ^{1}H NMR of compound **6** (SP3, 400 MHz, DMSO). Note the lack of ring-closed form present as compared to SP2 in DMSO highlighting the lower dark acidity and higher stability SP3's ring-opened form.

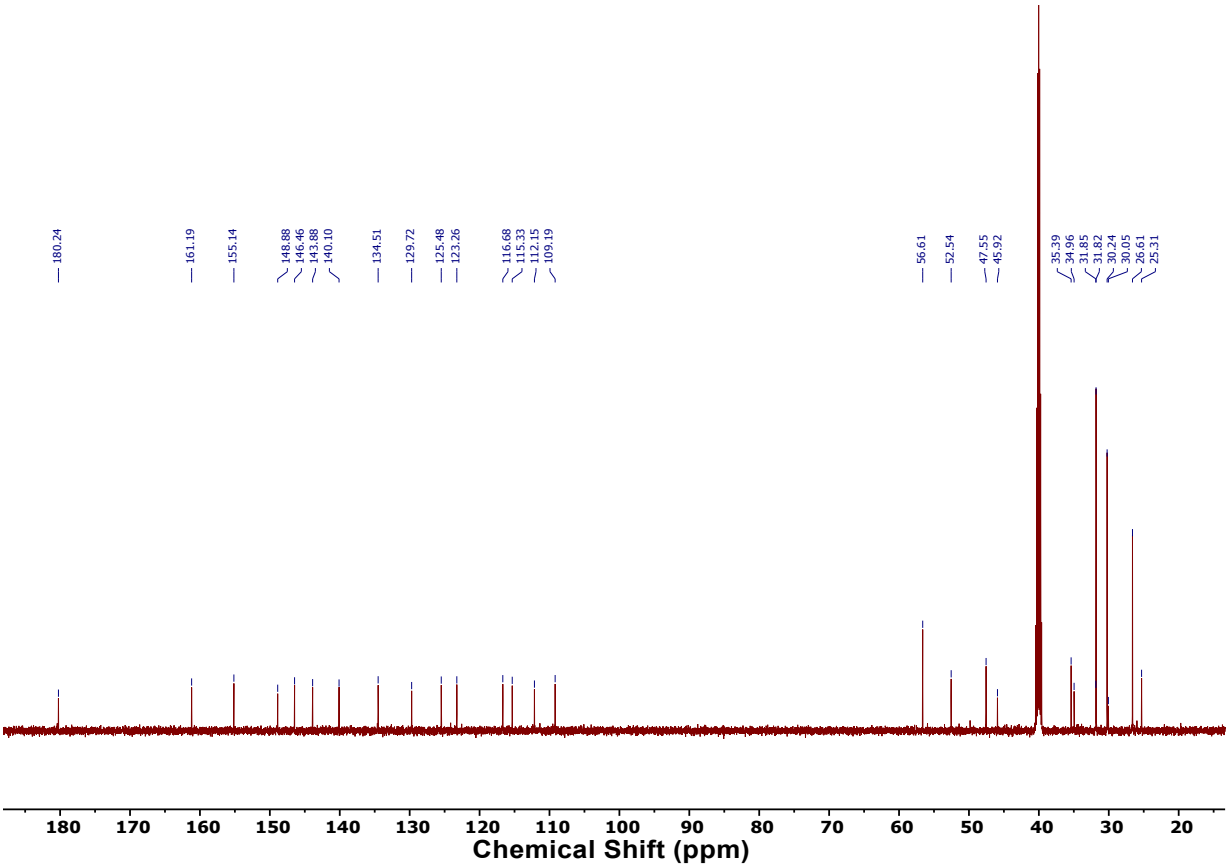


Figure S40. ^{13}C NMR of compound **6** (SP3, 101 MHz, DMSO).

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