Supporting Information for

Comparison of the reactivity of isomeric 2*H*- and 3*H*-naphthopyran mechanophores

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I. General Experimental Details

Reagents from commercial sources were used without further purification unless otherwise stated. Methyl acrylate was passed through a short plug of basic alumina to remove inhibitor immediately prior to use. Copper wire was cleaned by rinsing consecutively with 1 M HCl, water, acetone, and dichloromethane immediately prior to use. Dry THF was obtained from a Pure Process Technology solvent purification system. All reactions were performed under a N_2 or argon atmosphere unless specified otherwise. Column chromatography was performed on a Biotage Isolera system using SiliCycle SiliaSep HP flash cartridges.

NMR spectra were recorded using a 400 MHz Bruker Avance III HD with Prodigy Cryoprobe. All ^{1}H NMR spectra are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual dichloromethane (5.32 ppm), acetone (2.05 ppm), or chloroform (7.26 ppm) in deuterated solvent. All ^{13}C NMR spectra were measured in deuterated solvents and are reported in ppm relative to the signals for chloroform (77.16 ppm). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent.

High resolution mass spectra (HRMS) were obtained from a Waters Corp. LCT Premier XE time-of-flight mass spectrometer equipped with an electrospray ionization (ESI) probe, or a JEOL JMS-600H magnetic sector mass spectrometer equipped with a FAB+ probe.

Analytical gel permeation chromatography (GPC) was performed using an Agilent 1260 series pump equipped with two Agilent PLgel MIXED-B columns (7.5 x 300 mm), an Agilent 1200 series diode array detector, a Wyatt 18-angle DAWN HELEOS light scattering detector, and a Optilab rEX differential refractive index detector. The mobile phase was THF at a flow rate of 1 mL/min. Molecular weights and molecular weight distributions were calculated by light scattering using a dn/dc value of 0.062 mL/g (25 °C) for poly(methyl acrylate).

UV-vis absorption spectra were recorded on a Thermo Scientific Evolution 220 spectrometer.

Ultrasound experiments were performed using a Vibra Cell 505 liquid processor equipped with a 0.5-inch diameter solid probe (part #630-0217), sonochemical adapter (part #830-00014), and a Suslick reaction vessel made by the Caltech glass shop (analogous to vessel #830-00014 from Sonics and Materials). Polymer solutions were continuously sampled for UV-vis analysis using a Cole Parmer Masterflex L/S pump system (item #EW-77912-10) composed of an L/S pump head (part #77390-00) and L/S precision variable speed drive (part #07528-20) using 4x6 mm PTFE tubing (part #77390-60) and a quartz flow-through cell (Starna, part #583.4-Q-10/Z8.5), which was connected using M6-threaded PTFE tubing (Starna, part #M6-SET).

Photoirradiation with UV light was performed using a Philips PL-S 9W/01/2P UVB bulb with a narrow emission of 305–315 nm and a peak at 311 nm under ambient conditions unless indicated otherwise. Irradiation with blue light was performed using a 470 nm LED (ThorLabs M470L3), driver (ledd1B), and collimator (SM1U25-A).

II. Supplementary Figures

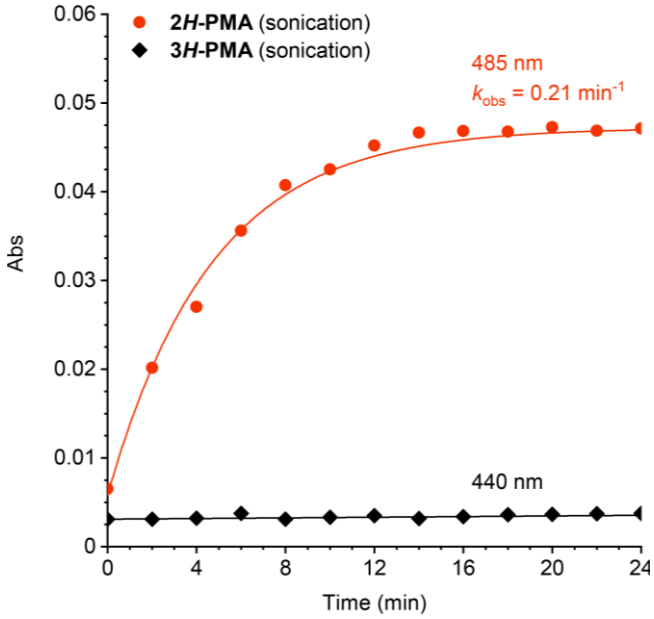


Figure S1. Ultrasound-induced mechanical activation of **2*H*-PMA** and **3*H*-PMA** (2 mg/mL in THF with 30 mM BHT) at 15–20 °C (solution temperature), characterized by synchronous UV-vis absorption spectroscopy monitoring at the λ_{max} of each merocyanine. At this temperature, mechanochemical generation of the merocyanine from **3*H*-PMA** is not observed due to rapid thermal reversion. In contrast, mechanochemical activation of **2*H*-PMA** is observed with rate constant k_{obs} = 0.21 min^{-1} due to the longer lifetime of the merocyanine dye.

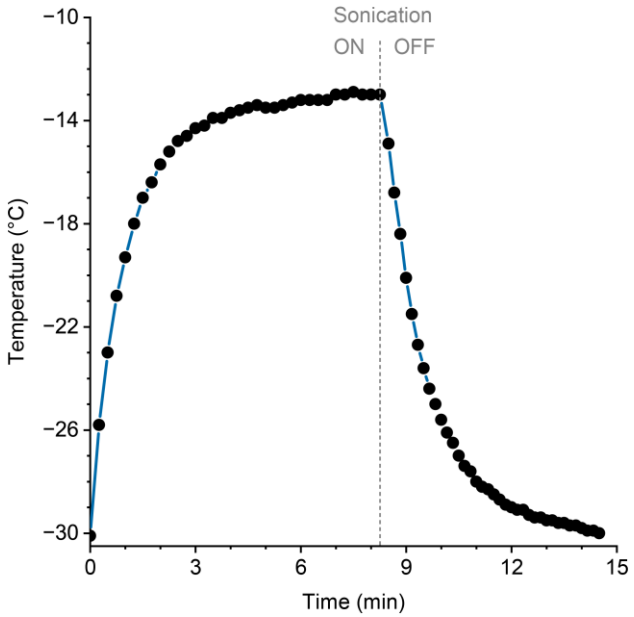


Figure S2. Evolution of solution temperature in the sonication vessel during flow. Application of continuous ultrasound (8.8 ± 0.2 W/cm^2) to the vessel starting at a stable initial temperature of –30 °C results in an increase in temperature that reaches a constant value of –13 °C after approximately 5 min. The effect of this temperature increase is eliminated by initiating sonication prior to the injection of a concentrated polymer sample (see Section VII for details). Upon cessation of ultrasound, the solution temperature returns to approximately –30 °C over a period of approximately 7 min.

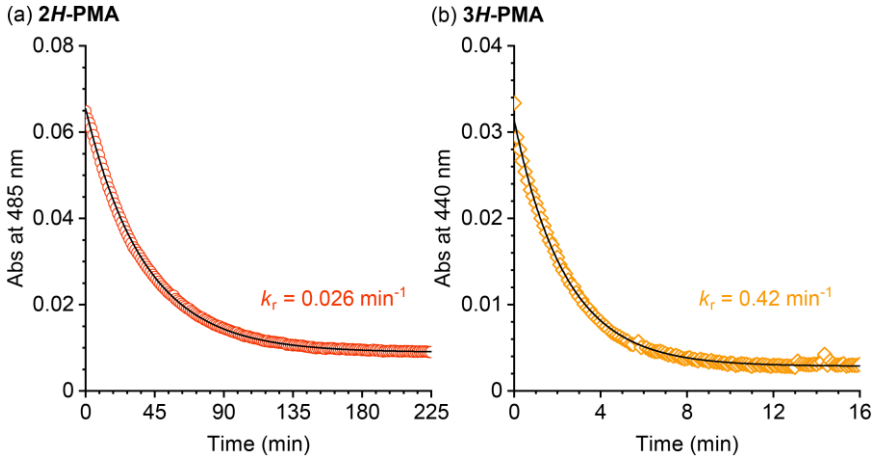
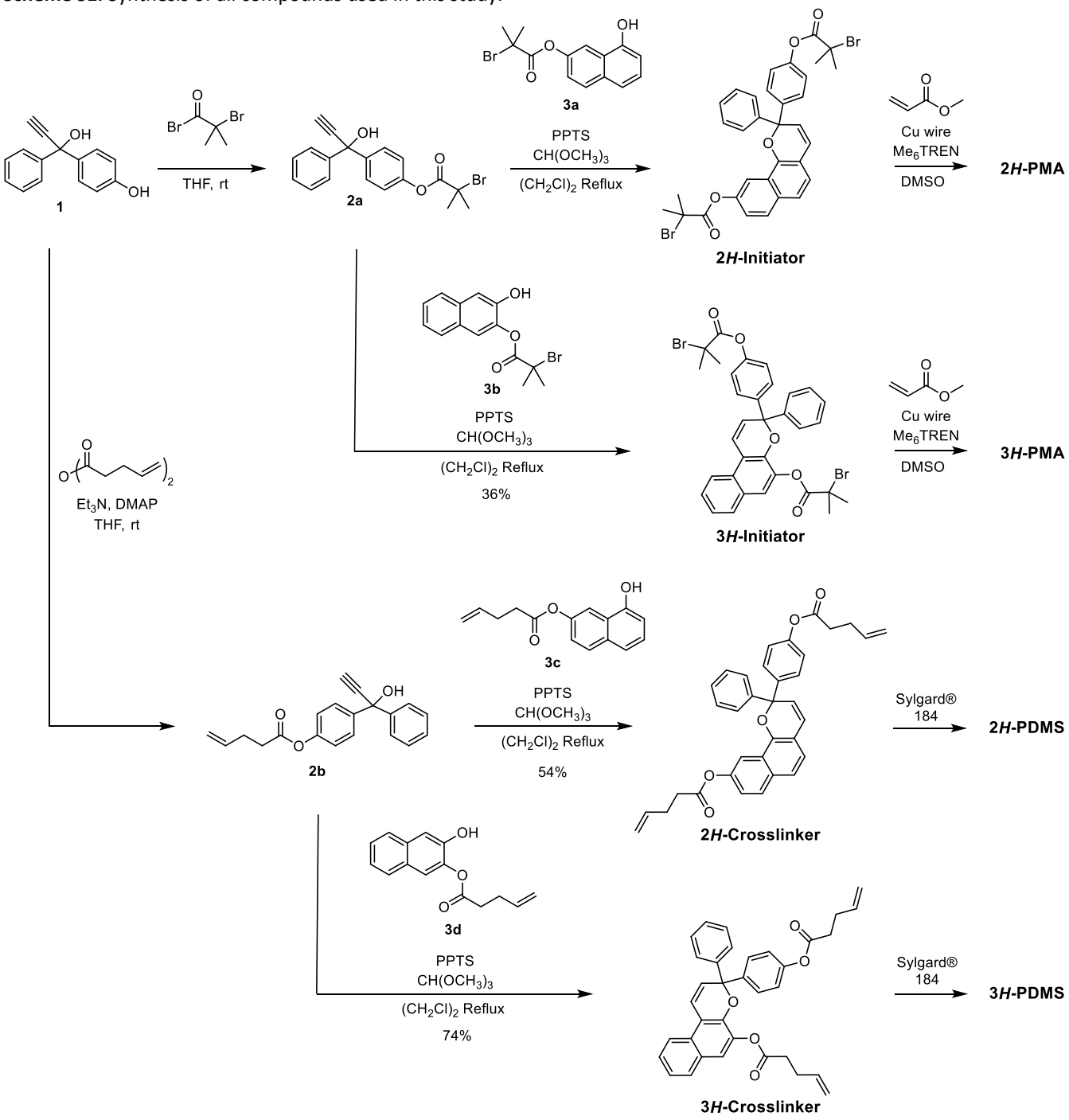


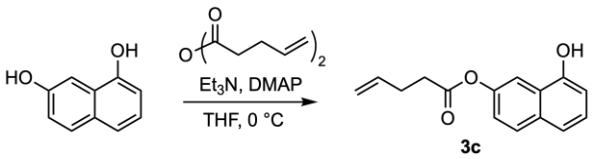
Figure S3. Merocyanine reversion at –13 °C in THF after photochemical activation with UV light (311 nm, 2 min) monitored at λ_{max}. (a) The merocyanine derived from **2*H*-PMA** reverts with a rate constant k_r = 0.026 min^{-1} and corresponding half-life of $t_{1/2}$ = 27 min, while (b) the merocyanine derived from **3*H*-PMA** reverts with a rate constant k_r = 0.42 min^{-1} and corresponding half-life of $t_{1/2}$ = 1.7 min.

III. Synthetic Details

Scheme S1. Synthesis of all compounds used in this study.



Compounds **1**,[1] **2a**,[2] **2b**,[2] **3a**,[2] **3b**,[3] and **2*H*-Initiator**[2] were prepared according to previously reported procedures.



3c

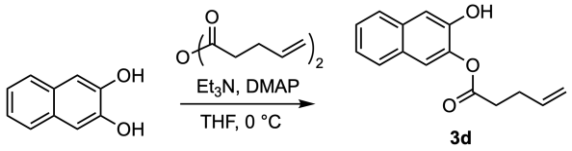
8-hydroxynaphthalen-2-yl pent-4-enoate (3c). To a flame-dried 2-neck 250 mL RBF equipped with a stir bar was added 1,7-dihydroxynaphthalene (2.00 g, 12.5 mmol) and catalytic N,N-dimethylaminopyridine (15.3 mg, 0.125 mmol). The flask was evacuated and backfilled with N_2 three times. Anhydrous THF (50 mL) and triethylamine (2.1 mL, 15.0 mmol) were added sequentially via syringe under N_2. The solution was cooled to 0 °C in ice. Pentenoic anhydride (2.30 mL, 12.5 mmol) was added dropwise via syringe over 10 min at 0 °C. After stirring for 20 h, the reaction was diluted with 100 mL EtOAc, washed with saturated aqueous NH_4Cl (100 mL), saturated aqueous $NaHCO_3$ (100 mL), and brine (100 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by column chromatography on silica gel (0–50% EtOAc/hexanes). A second chromatographic separation on silica gel (0–35% EtOAc/hexanes with 1% triethylamine) provided the title compound as a brown oil (508 mg, 17%).

TLC (25% EtOAc/hexanes): R_f = 0.36

^{1}H NMR (400 MHz, Acetone-d_6) δ: 9.15 (s, 1H), 7.90 (d, *J* = 2.5 Hz, 1H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.30 (app dd, *J* = 8.2, 7.5 Hz, 1H), 7.25 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.95 (dd, *J* = 7.5, 1.0 Hz, 1H), 5.97 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.17 (app dq, *J* = 17.2, 1.7 Hz, 1H), 5.06 (ddt, *J* = 10.3, 1.9, 1.3 Hz, 1H), 2.75 td, *J* = 7.3, 0.5 Hz, 2H), 2.55 – 2.47 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 172.7, 151.5, 147.8, 136.4, 132.9, 129.3, 125.8, 124.9, 121.5, 120.2, 116.2, 113.4, 109.2, 33.9, 29.0.

HRMS (FAB, *m/z*): calcd for $[C_{15}H_{14}O_3]^+$ $(M)^+$, 242.0943; found, 242.0949.



3d

3-hydroxynaphthalen-2-yl pent-4-enoate (3d). To a flame-dried 2-neck 250 mL RBF equipped with a stir bar was added 2,3-dihydroxynaphthalene (721 mg, 4.82 mmol) and catalytic N,N-dimethylaminopyridine (58.9 mg, 0.482 mmol). The flask was evacuated and backfilled with N_2 three times. Anhydrous THF (40 mL) and triethylamine (0.86 mL, 6.2 mmol) were added sequentially via syringe under N_2. The solution was cooled to 0 °C in an ice bath. Pentenoic anhydride (1.0 mL, 5.5 mmol) was added dropwise via syringe over 10 min at 0 °C. After stirring for 16 h, the reaction was diluted with EtOAc (100 mL) and washed sequentially with saturated aqueous NH_4Cl (100 mL), saturated aqueous $NaHCO_3$ (100 mL), and brine (100 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by column chromatography on silica gel (5–40% EtOAc/hexanes) to provide the title compound as a white solid (892 mg, 76%).

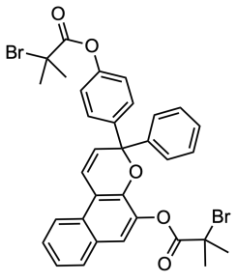
TLC (25% EtOAc/hexanes): R_f = 0.36

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.65 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.58 (d, *J* = 0.6 Hz, 1H), 7.40 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.34 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.30 (s, 1H), 5.97 (ddt, *J* = 17.2, 10.2, 6.4 Hz, 1H), 5.49 (s, 1H), 5.21 (app dq, *J* = 17.2, 1.6 Hz, 1H), 5.15 (app dq, *J* = 10.2, 1.3 Hz, 1H), 2.80 (t, *J* = 7.3, 0.6 Hz, 2H), 2.63 – 2.53 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 171.7, 146.2, 139.3, 136.6, 132.6, 128.6, 127.5, 126.4, 126.3, 124.4, 120.1, 116.4, 112.3, 33.7, 29.0.

HRMS (FAB, *m/z*): calcd for $[C_{15}H_{15}O_3]^+$ $(M+H)^+$, 243.1021; found, 243.1036.

General Procedure A for the Synthesis of Naphthopyrans. Naphthopyrans were synthesized following the procedure by Zhao and Carreira.[4] To a flame-dried 2-neck round bottom flask equipped with a stir bar and reflux condenser was added the appropriate propargyl alcohol, naphthol, and a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS). The flask was evacuated and backfilled with N_2 three times followed by the sequential addition of 1,2-dichloroethane and trimethyl orthoformate via syringe. The reaction was heated to reflux and stirred for the indicated amount of time. Upon completion, the reaction was cooled to room temperature, concentrated with celite, and purified by column chromatography on silica gel.



3*H*-Initiator

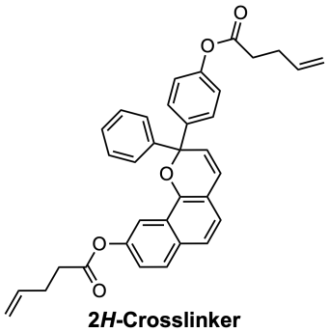
4-(5-((2-bromo-2-methylpropanoyl)oxy)-3-phenyl-3H-benzo[f]chromen-3-yl)phenyl 2-bromo-2-methylpropanoate (3*H*-Initiator). The title compound was prepared using General Procedure A with compound **3b** (311 mg, 1.01 mmol), compound **2a** (442 mg, 1.18 mmol) added as a solution in 1,2-dichloroethane, PPTS (35.5 mg, 0.141 mmol), trimethyl orthoformate (0.33 mL, 3.0 mmol), and 1,2-dichloroethane (10 mL). After reacting for 18 h, purification by column chromatography on silica gel (0–35% EtOAc/hexanes) followed by a second chromatographic separation on silica gel (5–15% EtOAc/hexanes) produced the title compound as a pale, peach-colored foamy solid (243 mg, 36%).

TLC (25% EtOAc/hexanes): R_f = 0.55

^{1}H NMR (400 MHz, CD_2Cl_2) δ: 8.00 (d, *J* = 8.5, Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.45 (m, 6H), 7.43 – 7.36 (m, 2H), 7.33 (m, 2H), 7.31 – 7.23 (m, 1H), 7.13 – 7.05 (m, 2H), 6.32 (d, *J* = 10.0 Hz, 1H), 2.11 (s, 6H), 2.03 (s, 6H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ: 170.2, 170.0, 150.2, 144.1, 142.9, 142.4, 139.2, 128.8, 128.38, 128.36, 128.30, 128.22, 128.20, 127.9, 127.0, 126.7, 124.7, 121.5, 120.74, 120.72, 119.8, 116.0, 83.0, 55.4, 54.9, 31.3, 30.7.

HRMS (FAB, *m/z*): calcd for $[C_{33}H_{28}Br_2O_5]^+$ $(M)^+$, 662.0304; found, 662.0290



2*H*-Crosslinker

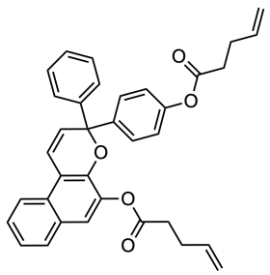
4-(9-(pent-4-enoyloxy)-2-phenyl-2H-benzo[h]chromen-2-yl)phenyl pent-4-enoate (2*H*-Crosslinker). The title compound was prepared using General Procedure A with **3c** (145 mg, 0.598 mmol), **2b** (220 mg, 0.718 mmol) added as a solution in 1,2-dichloroethane, PPTS (18 mg, 0.072 mmol), trimethyl orthoformate (0.15 mL, 1.4 mmol), and 1,2-dichloroethane (6 mL). After reacting for 4 h, purification by column chromatography on silica gel (0–15% EtOAc/hexanes with 1% triethylamine) followed by a second chromatographic separation on silica gel (10–80% dichloromethane/hexanes) provided the title compound as a red oil (171 mg, 54%).

TLC (25% EtOAc/hexanes): R_f = 0.53

^{1}H NMR (400 MHz, Acetone-d_6) δ: 8.05 (d, *J* = 2.3 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.61 – 7.54 (m, 4H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.32 – 7.23 (m, 3H), 7.14 – 7.07 (m, 2H), 6.90 (d, *J* = 9.7 Hz, 1H), 6.46 (d, *J* = 9.7 Hz, 1H), 5.93 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 2H), 5.14 (m, 2H), 5.03 (m, 2H), 2.76 (td, *J* = 7.4, 0.5 Hz, 2H), 2.65 (td, J = 7.3, 0.6 Hz, 2H), 2.54 – 2.47 (m, 2H), 2.46 – 2.39 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ: 171.8, 171.6, 150.1, 148.6, 147.5, 144.8, 142.6, 136.5, 136.4, 132.8, 129.3, 128.34, 128.27, 127.8, 127.7, 127.0, 125.1, 124.5, 123.9, 121.9, 121.3, 120.6, 116.1, 116.0, 113.0, 83.2, 33.8, 33.7, 29.0, 28.98.

HRMS (FAB, *m/z*): calcd for $[C_{35}H_{30}O_5]^+$ $(M)^+$, 530.2093; found, 530.2078



3*H*-Crosslinker

4-(5-(pent-4-enoyloxy)-3-phenyl-3H-benzo[f]chromen-3-yl)phenyl pent-4-enoate (3*H*-Crosslinker). The title compound was prepared using General Procedure A with **3d** (300 mg, 1.24 mmol), **2b** (455 mg, 1.49 mmol) added as a solution in 1,2-dichloroethane, PPTS (37.3 mg, 0.149 mmol), trimethyl orthoformate (0.31 mL, 2.8 mmol), and 1,2-dichloroethane (12 mL). After reacting for 4 h, purification by column chromatography on silica gel (0–15% EtOAc/hexanes with 1% triethylamine) followed by a second chromatographic separation on silica gel (0–10% Et_2O/CH_2Cl_2:hexanes (1:1)) produced the title compound as an orange oil (484 mg, 74%).

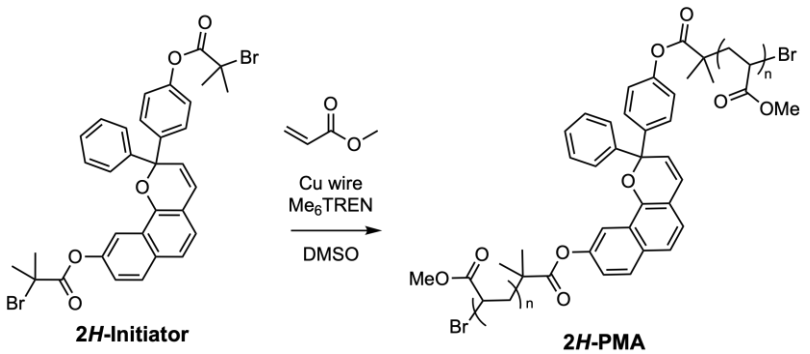
TLC (25% EtOAc/hexanes): R_f = 0.55

^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.98 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.43 (m, 6H), 7.42 – 7.31 (m, 4H), 7.31 – 7.24 (m, 1H), 7.08 – 7.00 (m, 2H), 6.32 (d, *J* = 9.9 Hz, 1H), 6.00 – 5.83 (m, 2H), 5.13 (m, 2H), 5.03 (m, 2H), 2.82 – 2.75 (m, 2H), 2.64 (td, *J* = 7.4, 0.8 Hz, 2H), 2.58 – 2.50 (m, 2H), 2.50 – 2.43 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 171.5, 171.2, 150.1, 144.2, 143.1, 142.1, 139.4, 136.5, 136.4, 128.8, 128.28, 128.26, 128.24, 128.21, 128.1, 127.8, 127.0, 126.5, 124.5, 121.5, 121.3, 121.0, 119.6, 116.1, 116.0, 115.8, 83.0, 33.7, 33.5, 29.1, 29.0.

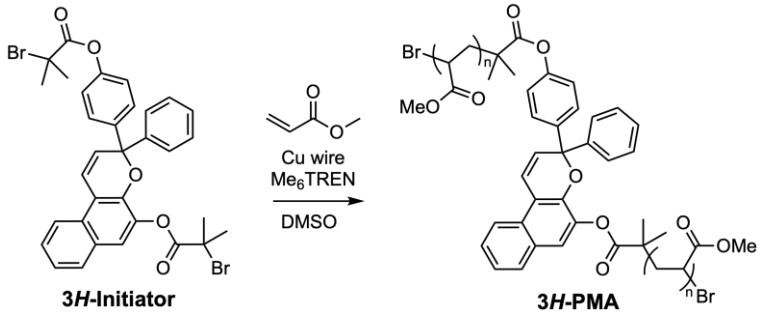
HRMS (FAB, *m/z*): calcd for $[C_{35}H_{30}O_5]^+$ $(M)^+$, 530.2093; found, 530.2084

General Procedure B for the Synthesis of Poly(Methyl Acrylate) (PMA) Polymers Incorporating a Chain-Centered Naphthopyran. Polymers were synthesized by controlled radical polymerization following the procedure by Nguyen *et al*.[5] A flame-dried Schlenk flask was charged with freshly cut 20 G copper wire (2 cm), initiator, DMSO, and methyl acrylate. The flask was sealed and the solution was degassed via three freeze-pump-thaw cycles, then backfilled with nitrogen and warmed to room temperature. Me_6TREN was added via microsyringe and the reaction was stirred at room temperature for the indicated amount of time. Upon completion of the polymerization, the flask was opened to atmosphere and diluted with a minimal amount of CH_2Cl_2. The polymer was precipitated 3x into methanol cooled with dry ice and then dried under vacuum.



2*H*-Initiator **2*H*-PMA**

Polymer **2*H*-PMA.** Synthesized using General Procedure B with initiator **2*H*-Initiator** (8.3 mg, 0.012 mmol), methyl acrylate (3.4 mL, 37 mmol), DMSO (3.4 mL), and Me_6TREN (17 µL, 0.063 mmol). Polymerization for 2.5 h provided the title polymer as a tacky pale peach-colored solid (1.4 g, 43%). M_n = 155 kg/mol, $Đ$ = 1.07.



3*H*-Initiator **3*H*-PMA**

Polymer **3*H*-PMA.** Synthesized using General Procedure B with initiator **3*H*-Initiator** (10.0 mg, 0.015 mmol), methyl acrylate (4.9 mL, 54 mmol), DMSO (4.9 mL), and Me_6TREN (20 µL, 0.075 mmol). Polymerization for 3 h provided the title polymer as a tacky colorless solid (1.6 g, 34%). M_n = 149 kg/mol, $Đ$ = 1.07.

IV. Characterization of Linear PMA Polymers

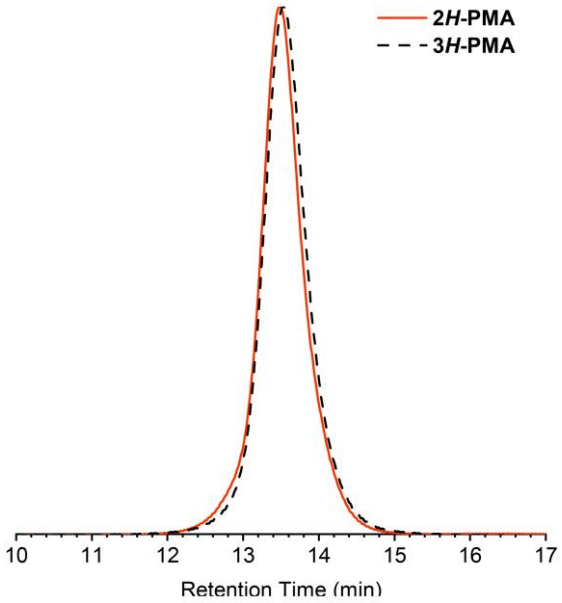


Figure S4. GPC traces (refractive index response) normalized to peak height for **2*H*-PMA** and **3*H*-PMA**.

V. Preparation of PDMS Materials

PDMS materials incorporating naphthopyran (~1.5 wt%) were prepared following previously reported procedures using the two-part Sylgard® 184 elastomer kit (Dow Corning).[1,6] PDMS films approximately 0.5 mm thick were cut into 3 x 15 mm strips for testing.

General Procedure C for the Preparation of PDMS Materials. The naphthopyran crosslinker was dissolved in a minimal amount of xylene in a 20 mL scintillation vial. Sylgard® 184 prepolymer base was added and the contents were thoroughly mixed in a vortex mixer with intermittent gentle heating to form a homogeneous dispersion. Sylgard® 184 curing agent was added and the contents were mixed thoroughly using a vortex mixer. The mixture was pipetted onto a clean 5 cm x 5 cm delrin plate, which was placed inside a vacuum chamber and evacuated under high vacuum (~30 mTorr) for 4 h. The delrin plate was then transferred to an oven and cured at 80 °C overnight. After curing, the plate was removed from the oven and the PDMS film was peeled off and cut into strips.

2*H*-PDMS was synthesized using General Procedure C with **2*H*-Crosslinker** (30.7 mg, 0.058 mmol), xylenes (0.2 mL), Sylgard® 184 prepolymer base (1.956 g), and Sylgard® 184 curing agent (0.195 g). After curing, the films were irradiated with blue light (470 nm) for 30 min to reduce initial coloration.

3*H*-PDMS was synthesized using General Procedure C with **3*H*-Crosslinker** (31.4 mg, 0.059 mmol), xylenes (0.2 mL), Sylgard® 184 prepolymer base (1.975 g), and Sylgard® 184 curing agent (0.197 g).

VI. DFT Calculations (CoGEF)

CoGEF calculations were performed using Spartan ’18 Parallel Suite according to previously reported methods.[7,8] Ground state energies were calculated using DFT at the B3LYP/6-31G* level of theory. Truncated models of each mechanophore with terminal acetoxy groups were used in the calculations. For each structure, the equilibrium conformations of the unconstrained molecule were initially calculated using molecular mechanics (MMFF) followed by optimization of the equilibrium geometries using DFT (B3LYP/6-31G*). Starting from the equilibrium geometry of the unconstrained molecules (energy = 0 kJ/mol), the distance between the terminal methyl groups of the truncated structures was increased in increments of 0.05 Å and the energy was minimized at each step. The maximum force associated with the mechanochemical reaction was calculated from the slope of the curve immediately prior to bond cleavage using the final two contiguous data points.

VII. Details for Photoirradiation and Sonication Experiments

In order to continuously monitor reaction progress by UV-vis absorption spectroscopy, a previously described experimental setup[3,9] was assembled using a peristaltic pump to transport solution from the reaction vessel through a quartz flow cell in a UV-vis spectrometer and return the solution to the reaction vessel. The flow rate through the system was maintained at 8 mL/min, corresponding to a setting of 50 RPM on the peristaltic pump at the selected occlusion. The UV-vis spectrometer was programmed to acquire either full spectra or absorbance at predefined wavelengths at regular time intervals. Absorbance measurements at wavelengths of 440, 485, and 700 nm were acquired every 10 s during continuous photoirradiation or sonication of polymer solutions. The absorbance values measured at 700 nm were subtracted from the absorbance values monitored at 440 or 485 nm at each time point to account for drift during the experiments.

General Procedure for Sonication Experiments. A sonication vessel was placed onto the sonication probe and allowed to cool under a stream of N_2. The vessel was charged with THF, which contained 30 mM BHT (19.0 mL) to avoid decomposition side reactions resulting from free radicals generated during sonication.[10] An additional 6.2 mL of stabilized THF was pumped into the dead space of the circulatory setup. Teflon inlet and outlet tubes were inserted into the solution in the sonication vessel through punctured septa, and the pump was engaged to start the flow of solution through the system. The sonication vessel was submerged in either an ethanol bath maintained at −45 ± 2 °C with an immersion chiller or an ice bath maintained at 0 ± 2 °C, and the solution was sparged with N_2 for 30 min. The system was then maintained under an inert atmosphere for the duration of the experiment. Continuous sonication at 20 kHz (8.8 ± 0.2 W/cm^2) was initiated and run for approximately 5 min to allow the temperature inside the reaction vessel to equilibrate to –13 °C (ethanol bath) or 15–20 °C (ice bath), as measured by a thermocouple inserted into the solution (Digi-Sense EW-91428-02 thermometer with Digi-Sense probe EW-08466-83). Separately, a concentrated solution of polymer (1.0 mL, 52.4 mg/mL in stabilized THF) was sparged with N_2 for 30 min. This solution was then injected into the sonication vessel to provide a total system volume of 26.2 mL (2.0 mg/mL of polymer) and reaction progress was monitored by UV-vis absorption spectroscopy. Sonication intensity was calibrated via the literature method.[11] The entire system was kept in the dark for the duration of the experiment. Complete experimental data for the ultrasound-induced

mechanochemical generation and reversion of merocyanine dyes derived from **2*H*-PMA** and **3*H*-PMA** are provided in Figures S5 and S6 below.

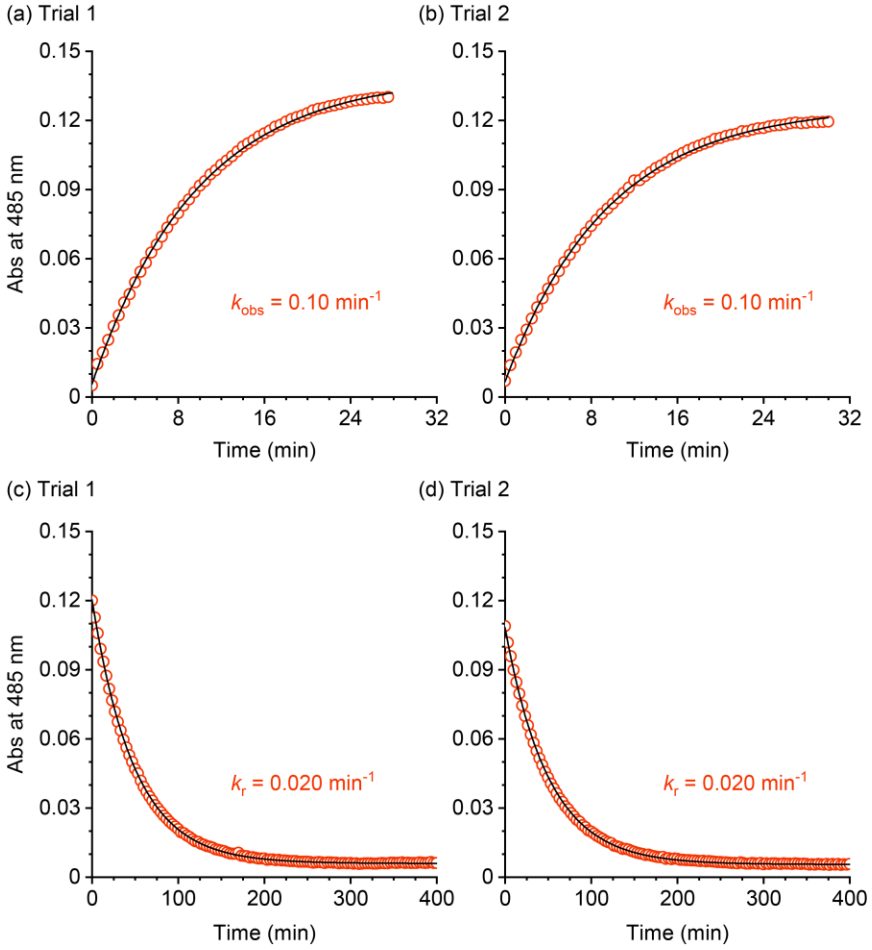


Figure S5. Ultrasound-induced mechanical activation of **2*H*-PMA** (2 mg/mL in THF with 30 mM BHT) at –13 °C and subsequent thermal reversion at approximately –30 °C, monitored at λ_{max} = 485 nm. (a,b) The forward reaction occurs with an observed rate constant of k_{obs} = 0.10 min^{-1} averaged over two replicate experiments. (c,d) Thermal reversion of the merocyanine at –30 °C measured from the same polymer solutions after cessation of ultrasound occurs with an average rate constant of k_r = 0.020 min^{-1} corresponding to a half-life of $t_{1/2}$ = 35 min. Note that the temperature of the polymer solution quickly equilibrates to approximately –30 °C when the ultrasound is turned off (see Figure S2).

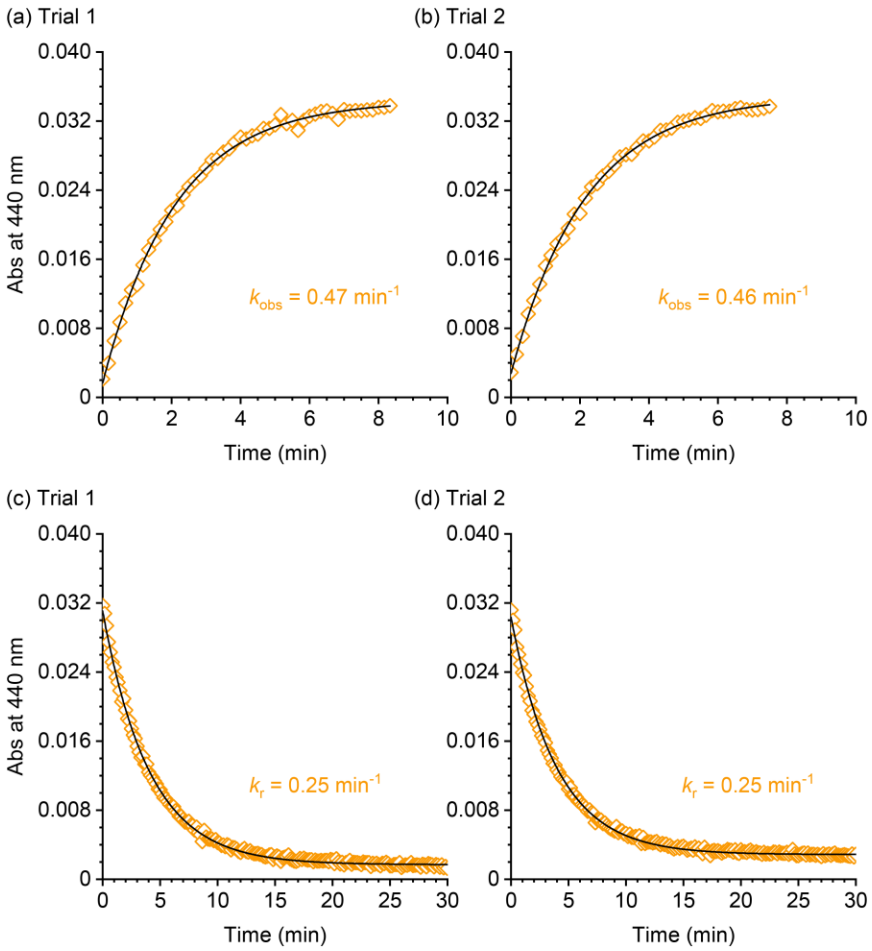


Figure S6. Ultrasound-induced mechanical activation of **3*H*-PMA** (2 mg/mL in THF with 30 mM BHT) at –13°C and subsequent thermal reversion at approximately –30 °C, monitored at λ_{max} = 440 nm. (a,b) The forward reaction occurs with an observed rate constant of k_{obs} = 0.47 min^{-1} averaged over two replicate experiments. (c,d) Thermal reversion of the merocyanine at –30 °C measured from the same polymer solutions after cessation of ultrasound occurs with an average rate constant of k_r = 0.25 min^{-1} corresponding to a half-life of $t_{1/2}$ = 2.8 min. Note that the temperature of the polymer solution quickly equilibrates to approximately –30 °C when the ultrasound is turned off (see Figure S2).

General Procedure for Photoirradiation Experiments. Absorption spectra of photochemically generated merocyanines were measured at room temperature (~20 °C) by exposing a solution of the polymer (2.0 mg/mL in THF) in a two-sided quartz cuvette to a UV light source (λ = 311 nm) positioned ~2 inches away for 60 s. The cuvette was immediately placed into the spectrometer and the absorption spectrum was collected. To monitor thermal reversion of photochemically generated merocyanines at –13 °C, an identical procedure as the one used for sonication experiments was employed with continuous flow and synchronous UV-vis measurements, except a 20% ethanol/ethylene glycol dry ice bath maintained at −30 ± 2 °C was used to cool the reaction vessel containing the polymer solution. The temperature of the solution inside the reaction vessel equilibrated to –13 °C as measured by a thermocouple inserted into the solution (Digi-Sense EW-91428-02 thermometer with Digi-Sense probe EW-08466-83). The solution was exposed to a UV light source (λ = 311 nm) positioned ~3.5 inches away for 2 min, and then the thermal reversion of the photochemically generated merocyanine was monitored by UV-vis absorption

spectroscopy. The entire system was kept under an inert atmosphere in the dark for the duration of the experiment.

VIII. Kinetic Analysis

Determination of reaction kinetics from UV-vis spectroscopy. The kinetics of the ring-opening reaction under sonication, or thermal ring-closure after sonication or UV irradiation, was evaluated by fitting time-dependent absorbance traces monitored at λ_{max} to expressions of first-order kinetics using OriginPro 2020. Data corresponding to product formation is fit to eq S1:

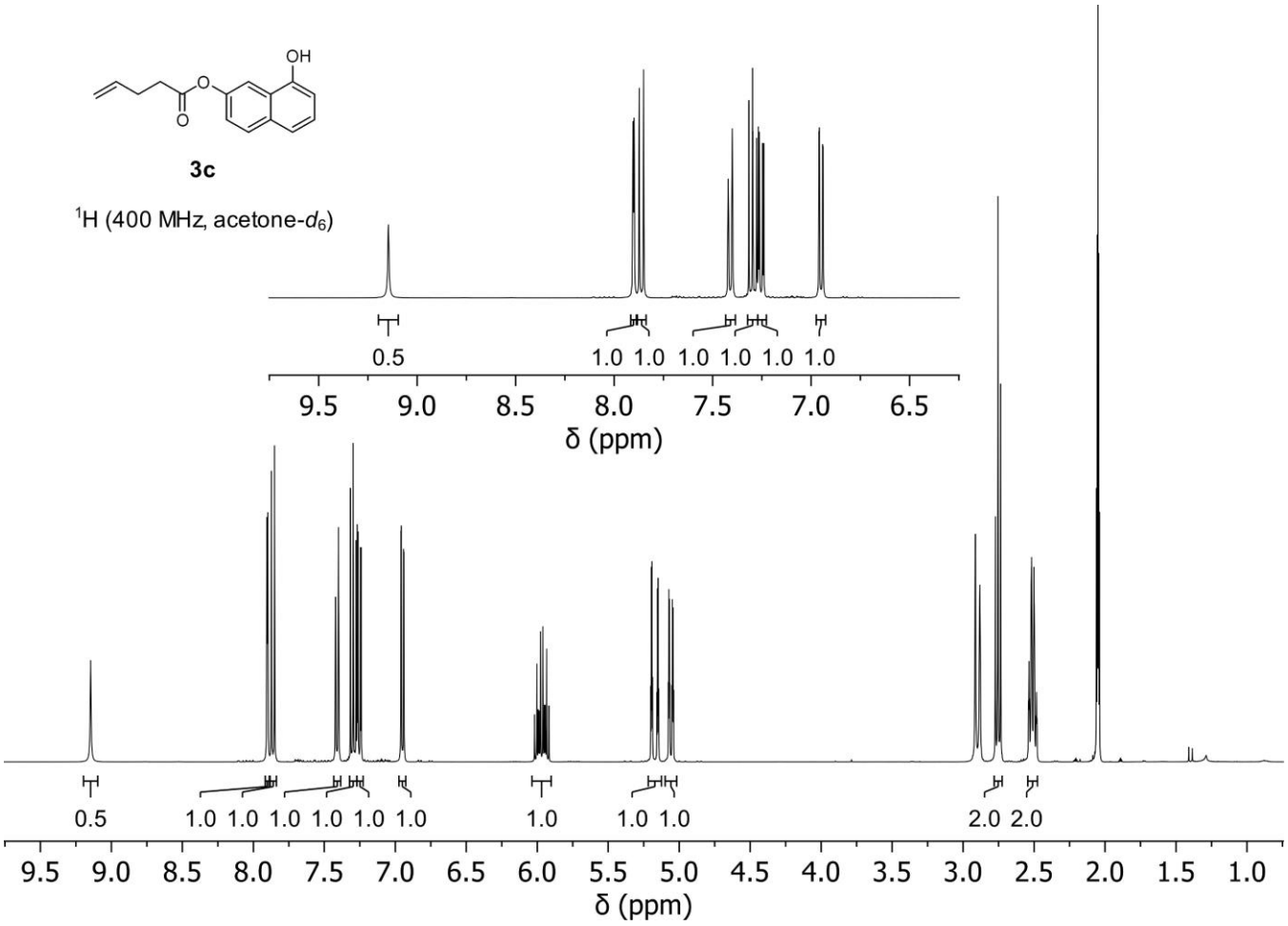
$$A(t) = A\left(1 - e^{-kt}\right) + c \tag{S1}$$

For characterizing the rate of thermal ring-closure, the time-dependent absorbance signal is fit to eq S2:

$$A(t) = A\left(e^{-kt}\right) + c \tag{S2}$$

X. References

1. Robb, M. J., Kim, T. A., Halmes, A. J., White, S. R., Sottos, N. R., Moore, J. S. *J. Am. Chem. Soc.*, 2016, **138**, 12328–12331.
2. McFadden, M. E., Robb, M. J. *J. Am. Chem. Soc.*, 2021, **143**, 7925–7929.
3. McFadden, M. E., Robb, M. J. *J. Am. Chem. Soc.*, 2019, **141**, 11388–11392.
4. Zhao, W., Carreira, E. M. *Org. Lett.*, 2003, **5**, 4153–4154.
5. Nguyen, N. H., Rosen, B. M., Lligadas, G., Percec, V. *Macromolecules*, 2009, **42**, 2379–2386.
6. Gossweiler, G. R., Hewage, G. B., Soriano, G., Wang, Q., Welshofer, G. W., Zhao, X., Craig, S. L. *ACS Macro Lett.*, 2014, **3**, 216–219.
7. Beyer, M. K. *J. Chem. Phys.*, 2000, **112**, 7307–7312.
8. Klein, I. M., Husic, C. C., Kovács, D. P., Choquette, N. J., Robb, M. J. *J. Am. Chem. Soc.*, 2020, **142**, 16364–16381.
9. May, P. A., Munaretto, N. F., Hamoy, M. B., Robb, M. J., Moore, J. S. *ACS Macro Lett.*, 2016, **5**, 177–180.
10. Yang, J., Horst, M., Werby, S. H., Cegelski, L., Burns, N. Z., Xia, Y. *J. Am. Chem. Soc.*, 2020, **142**, 14619–14626.
11. Berkowski, K. L., Potisek, S. L., Hickenboth, C. R., Moore, J. S. *Macromolecules*, 2005, **38**, 8975–8978.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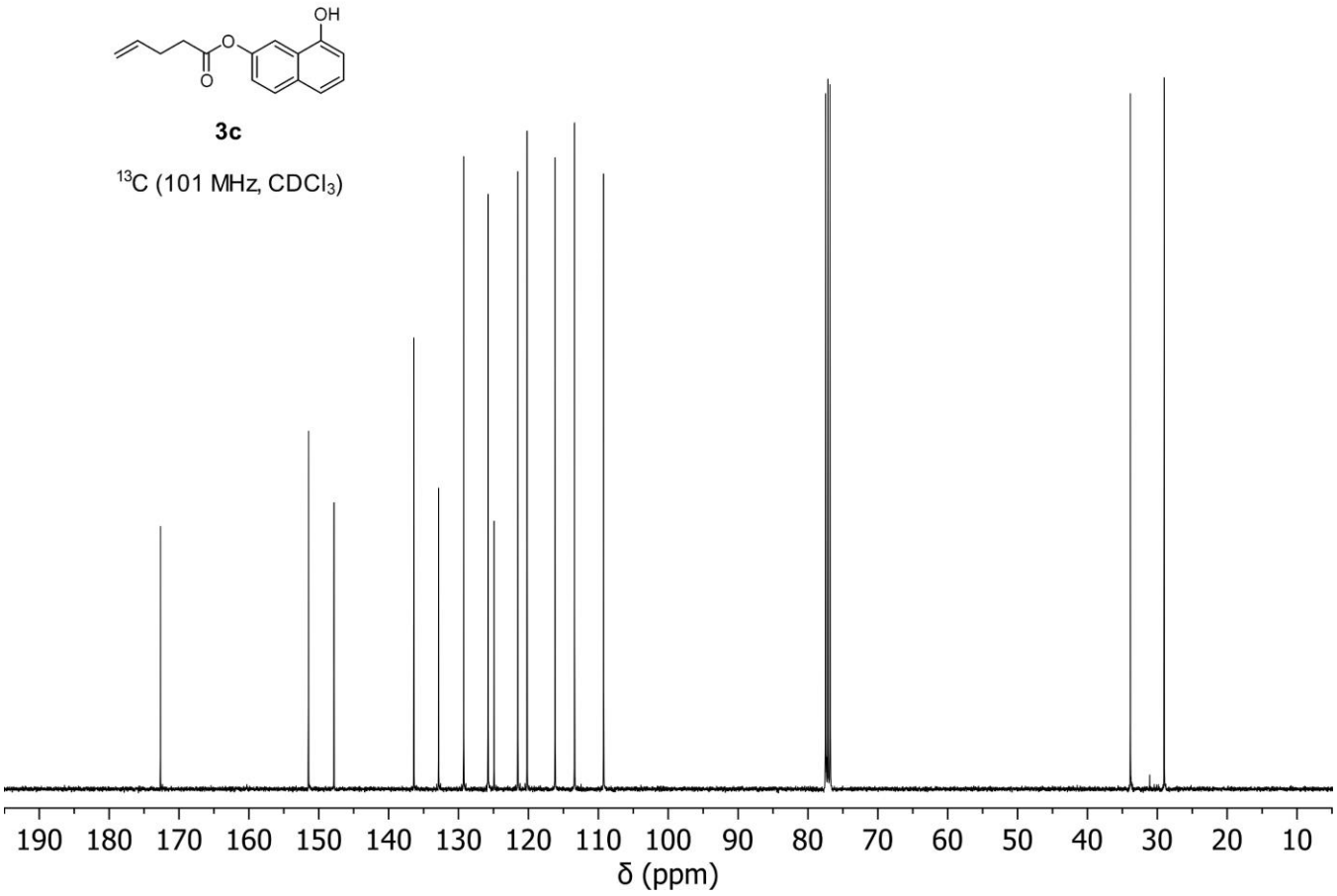
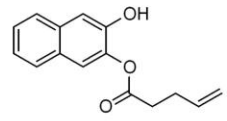
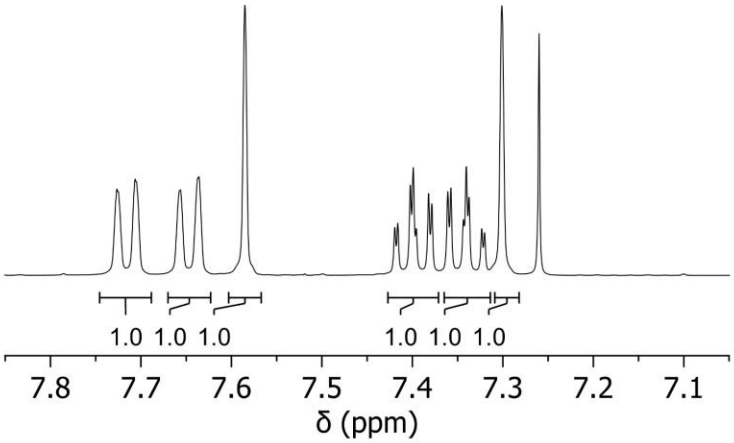
O
O
3c
^{1}H (400 MHz, acetone-d_6)
0.5
1.0 1.0 1.0 1.0 1.0 1.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5
δ (ppm)
0.5
1.0 1.0 1.0 1.0 1.0 1.0
1.0
1.0 1.0
2.0 2.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
δ (ppm)

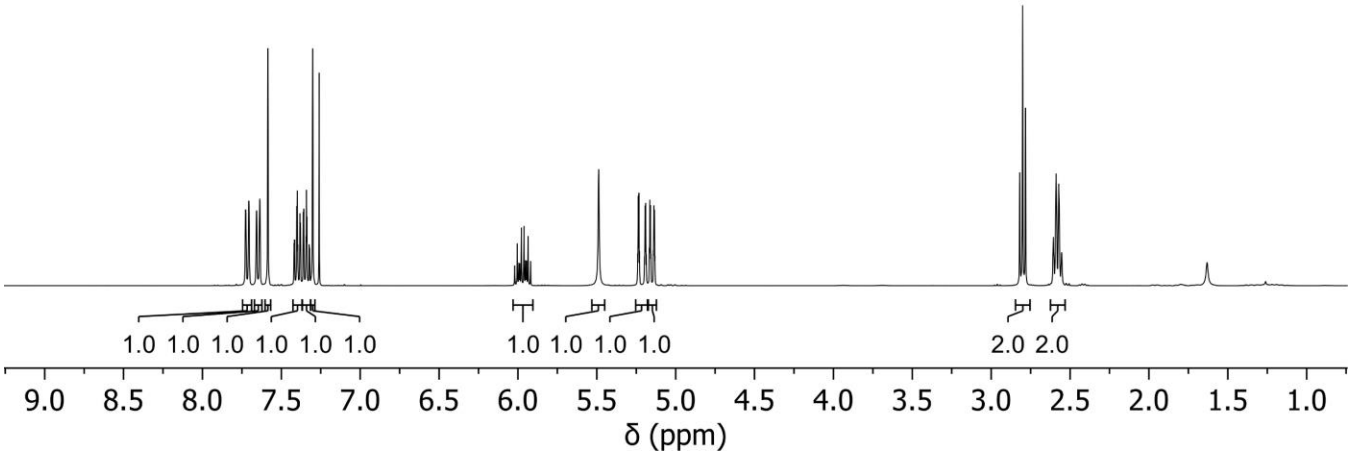

OH
O
O
3c
^{13}C (101 MHz, $CDCl_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ (ppm)

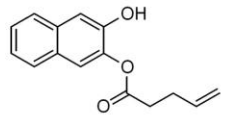


3d

^{1}H (400 MHz, $CDCl_3$)

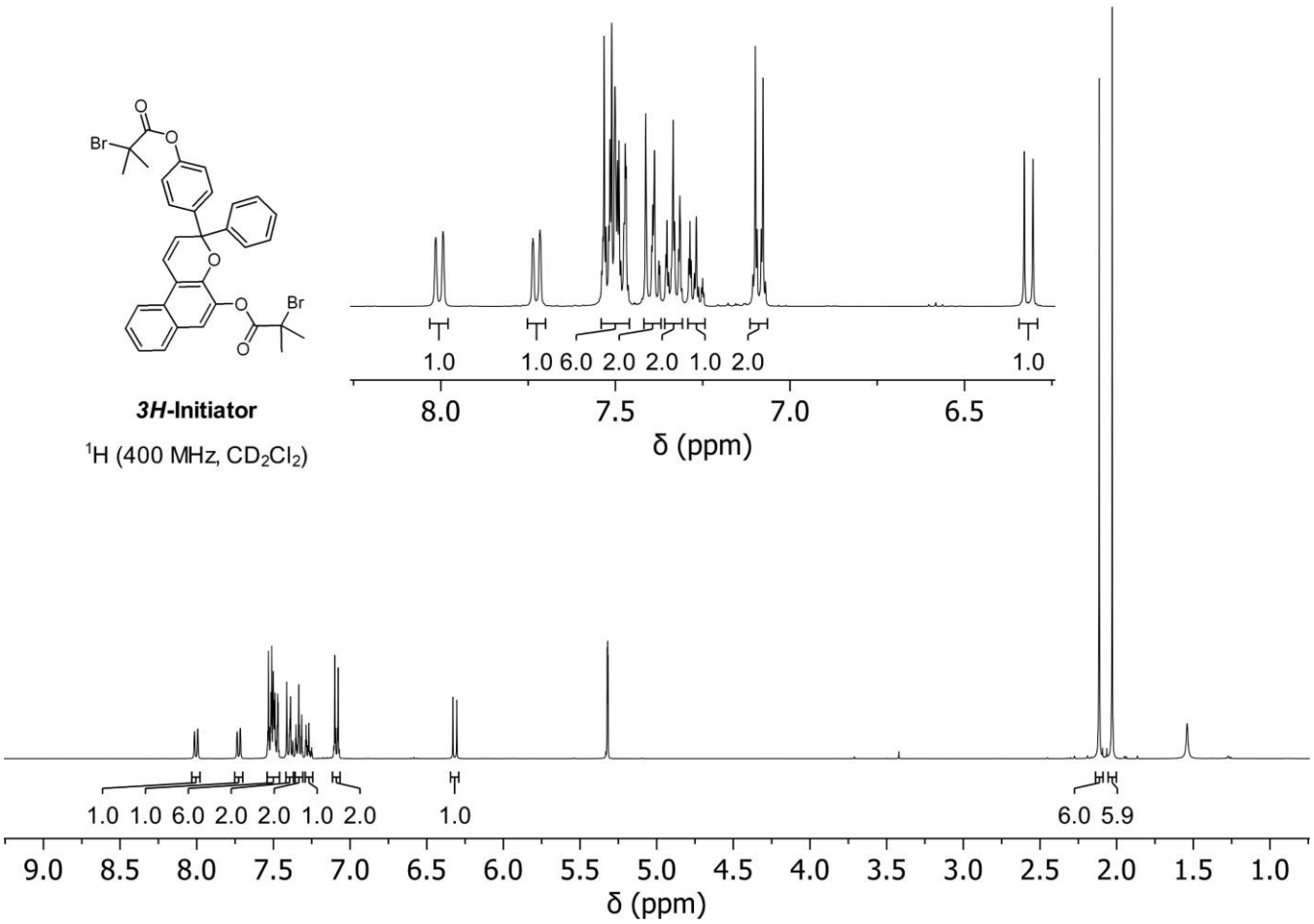






3d

^{13}C (101 MHz, $CDCl_3$)



***3H*-Initiator**

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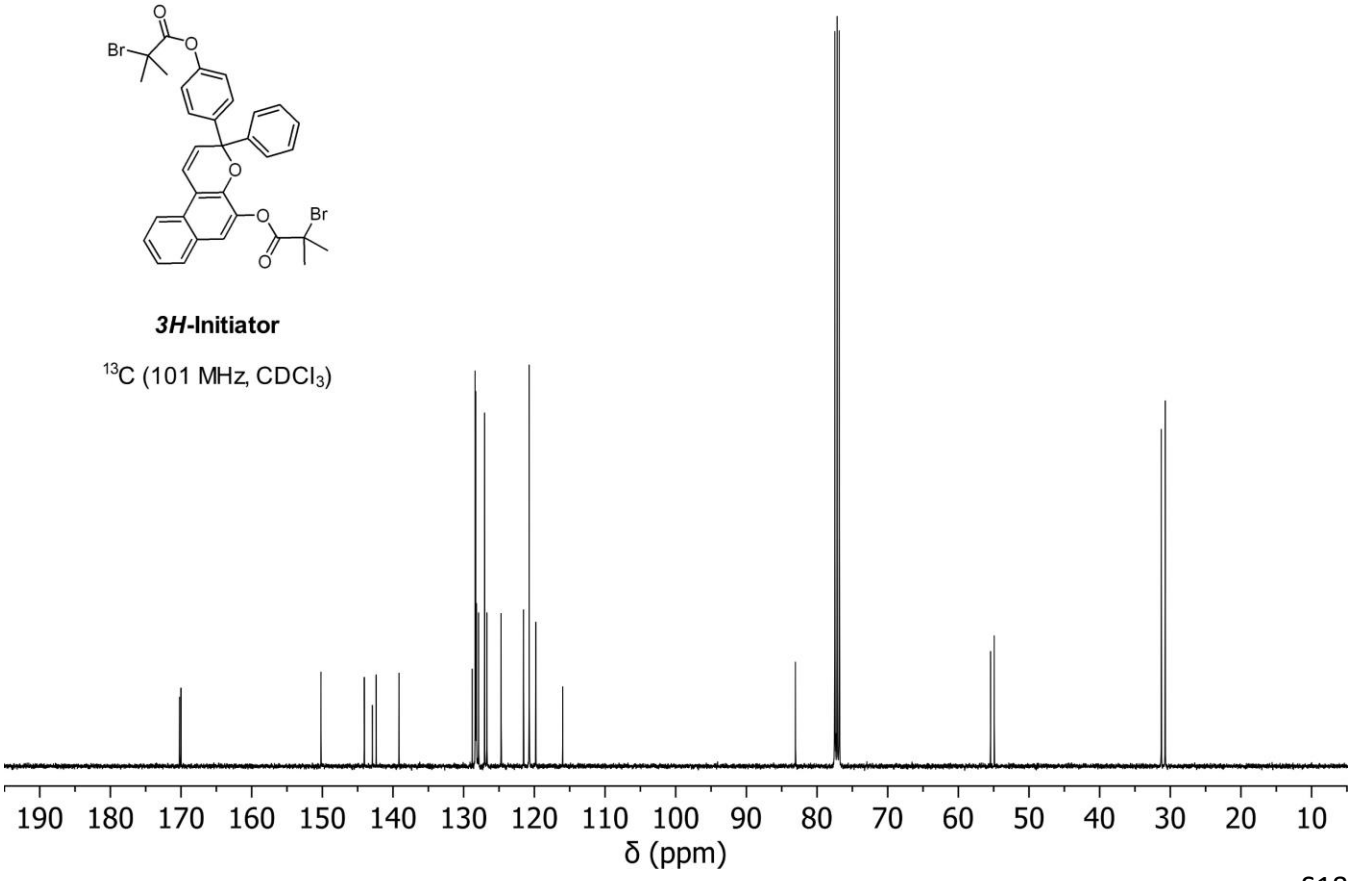
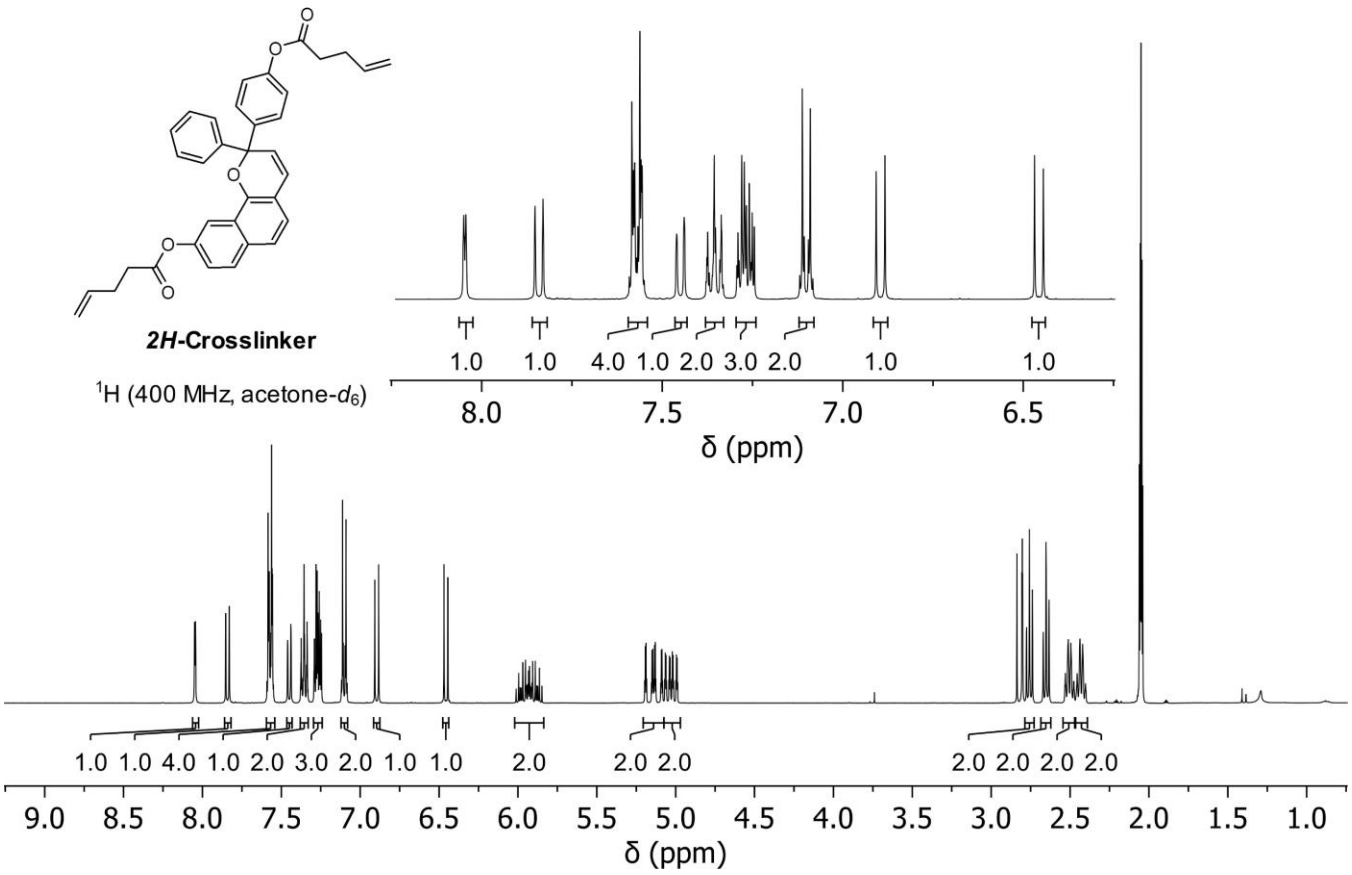


***3H*-Initiator**

^{13}C (101 MHz, $CDCl_3$)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1H (400 MHz, acetone-d6)
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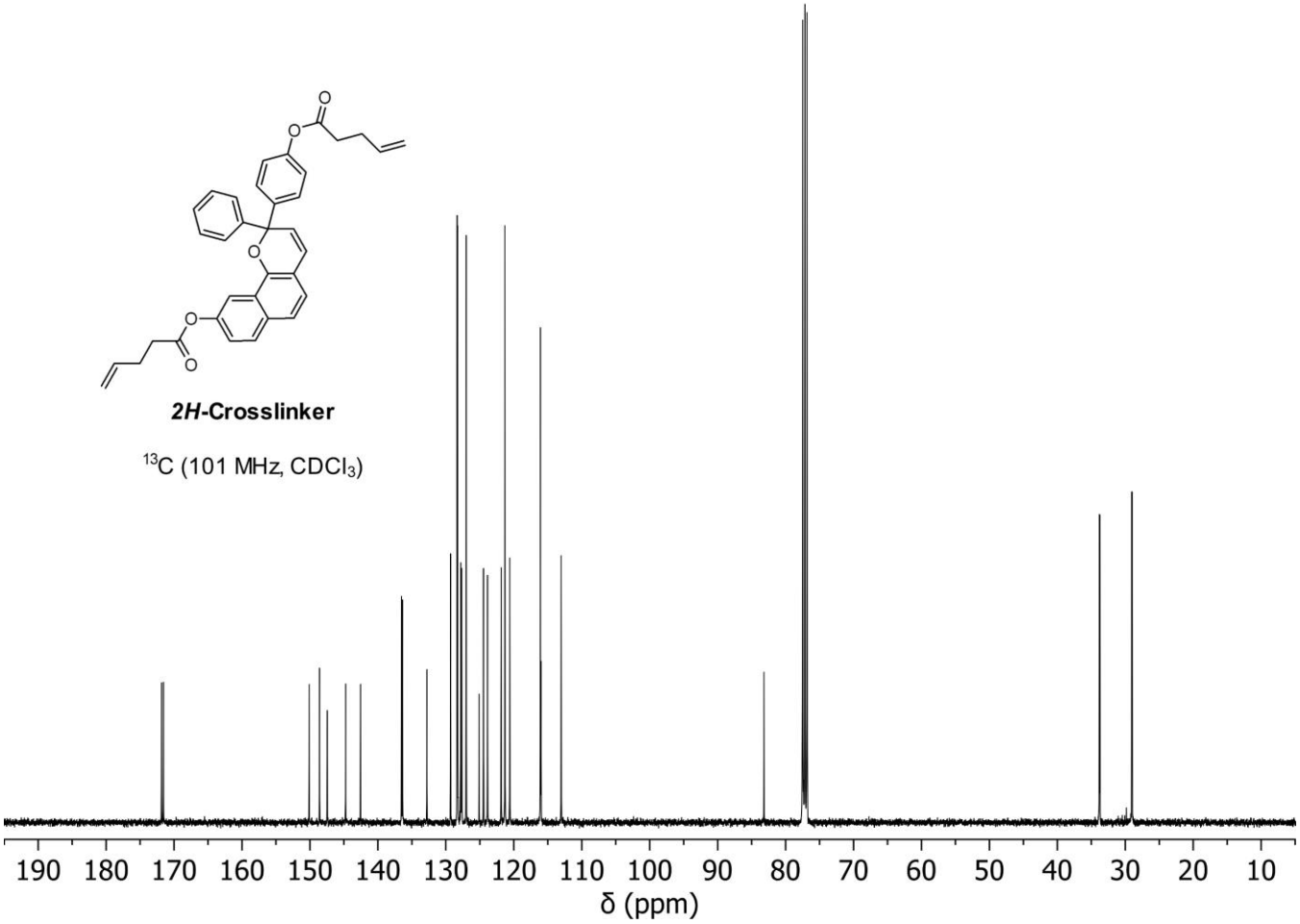
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
δ (ppm)
1.0 1.0 4.0 1.0 2.0 3.0 2.0 1.0 1.0
8.0 7.5 7.0 6.5
δ (ppm)


2H-Crosslinker
13C (101 MHz, CDCl3)
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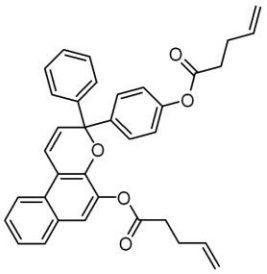
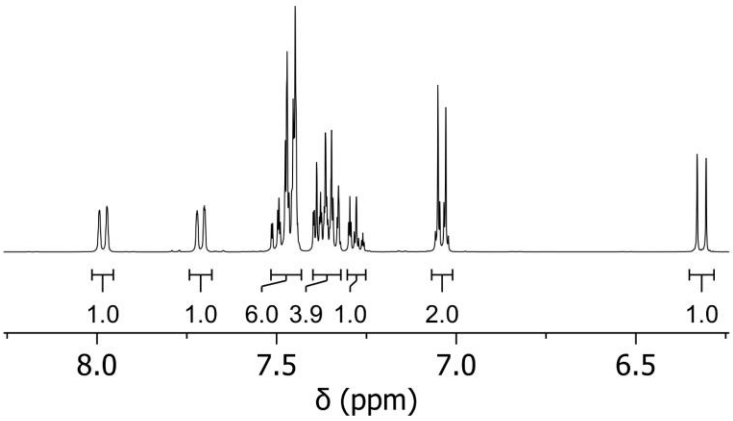
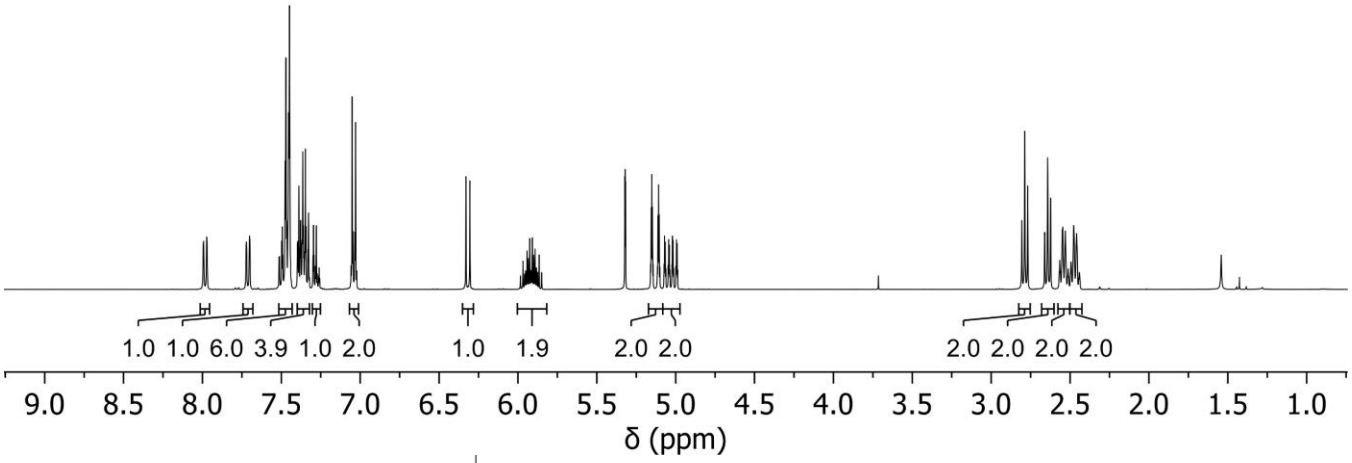
δ (ppm)

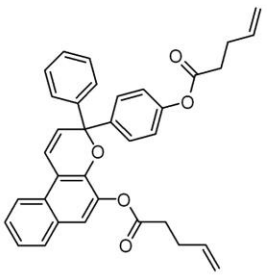


***3H*-Crosslinker**

^{1}H (400 MHz, CD_2Cl_2)







***3H*-Crosslinker**

^{13}C (101 MHz, $CDCl_3$)