Supporting Information for

Generation of an Elusive Permanent Merocyanine via a Unique Mechanochemical Reaction Pathway

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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. 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 $CHCl_3$ (7.26 ppm), acetone (2.05 ppm), or acetonitrile (1.94 ppm) in deuterated solvent. All ^{13}C NMR spectra were measured in deuterated solvents and are reported in ppm relative to the signals for $^{13}CDCl_3$ (77.16 ppm) or acetone-d_6 (206.26 ppm). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, 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. Reflection measurements were performed on a Cary 5000 UV/Vis/NIR spectrophotometer equipped with an integrating sphere diffuse reflectance accessory (Internal DRA 1800). All reflection measurements were referenced to a LabSphere Spectralon 99% certified reflectance standard. The samples were illuminated through a Spectralon-coated aperture with a diameter of 1 cm, with a beam area of approximately 0.5 cm^2.

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 either a Philips PL-S 9W/01/2P UVB bulb with a narrow emission of 305–315 nm and a peak at 311 nm, or a DR/9W-UVA bulb with peak at 365 nm under ambient conditions unless indicated otherwise. Irradiation with white light was carried out using a 13 W broadband fluorescent lamp (Bayco Model BA-506) filtered through a 425 nm bandpass filter. Irradiation with blue light was applied to PDMS films using a 470 nm LED (ThorLabs M470L3), driver (ledd1B), and collimator (SM1U25-A).

II. Supplementary Figures

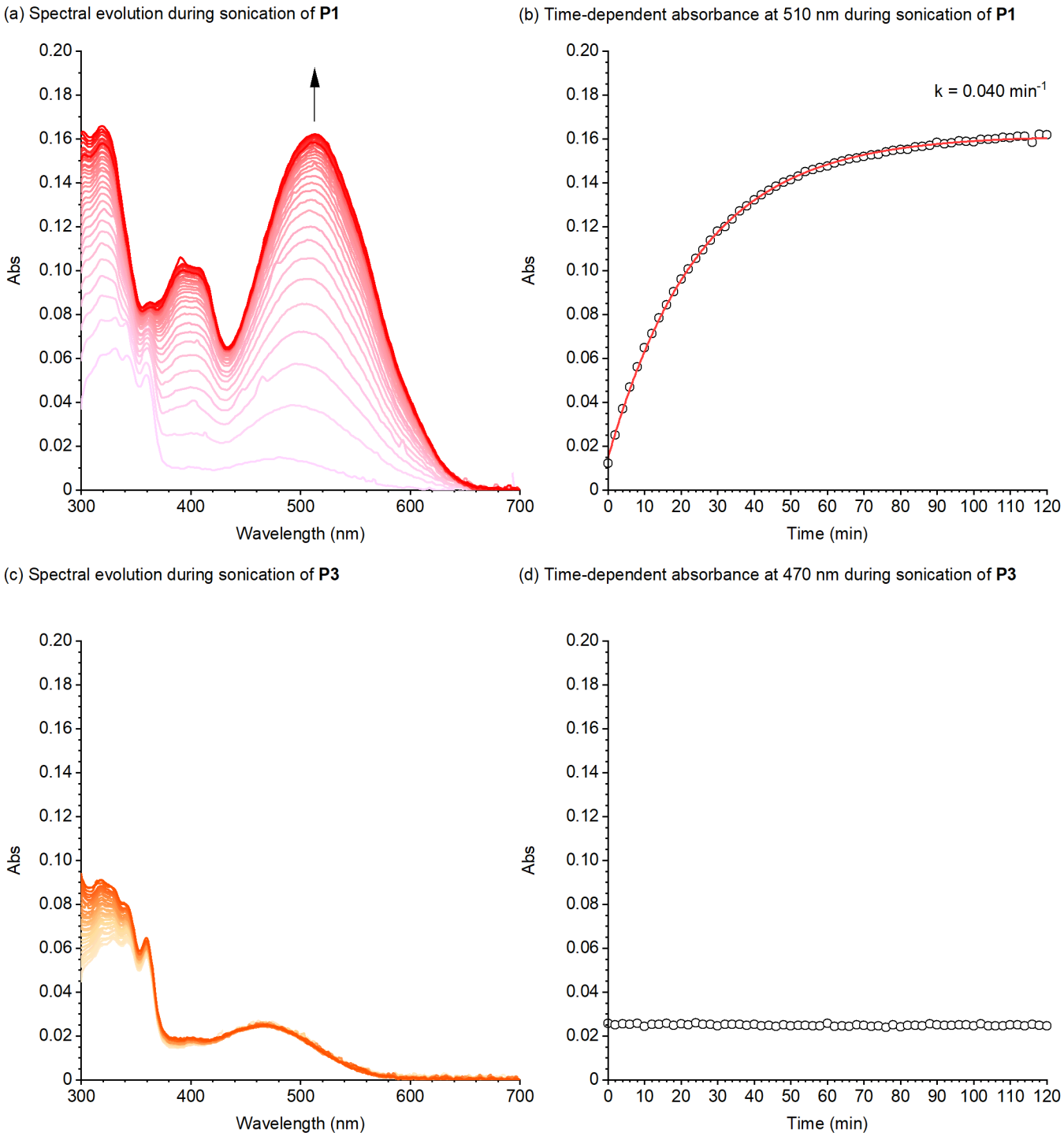


Figure S1. Comparison of sonication experiments performed on solutions (2 mg/mL in THF with 30 mM BHT) of polymer **P1** containing a chain-centered mechanophore and chain-end functional control polymer **P3**. (a) UV-vis spectra acquired at regular intervals during ultrasound-induced mechanical activation of **P1** exhibit an increase in visible absorption with λ_{max} of 510 nm. (b) Fitting time-dependent absorbance at 510 nm to eq S1 yields a rate constant for merocyanine formation of 0.040 min^{-1}. (c,d) No change in visible absorption is observed upon sonication of a solution of chain-end functional control polymer **P3**.

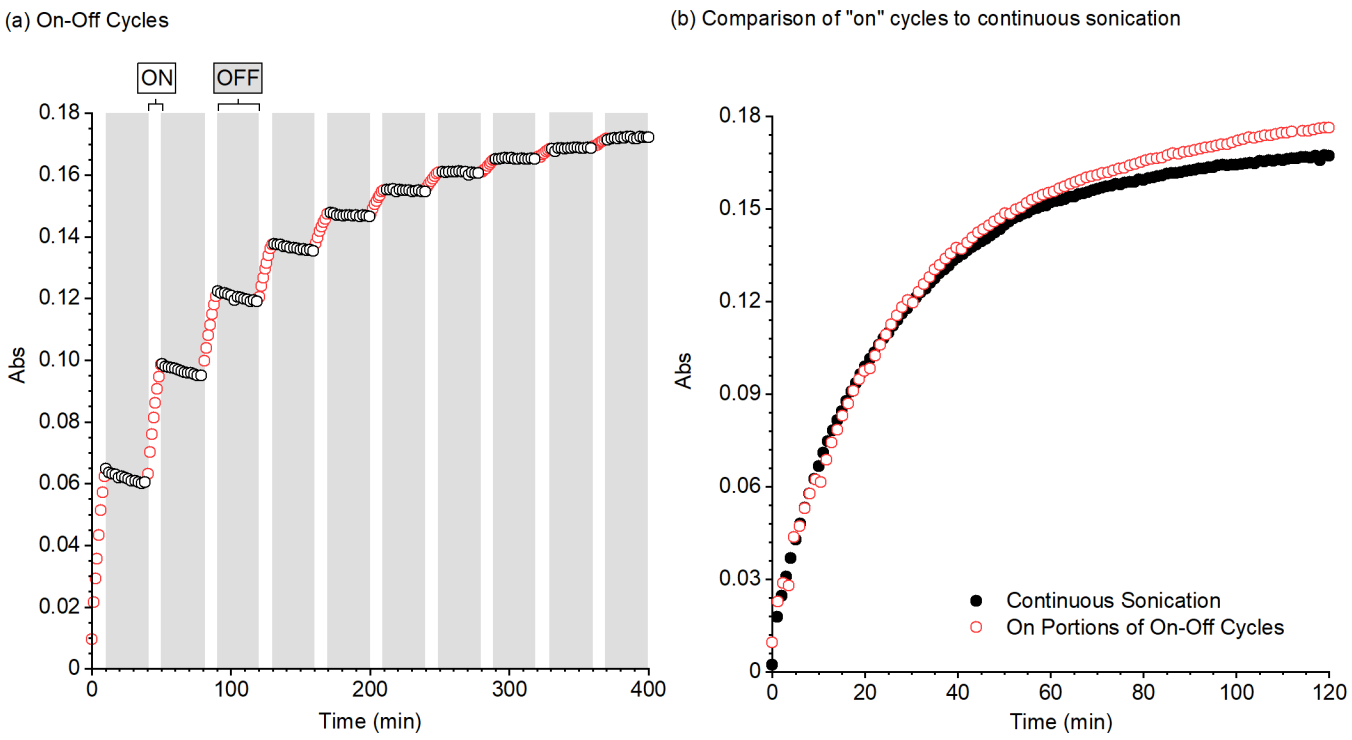


Figure S2. Investigation of the temporal dependence of permanent merocyanine formation. (a) A solution of **P1** (2 mg/mL with 30 mM BHT) was exposed to "on–off" cycles of ultrasonication, alternating between 10 min "on" and 30 min "off". (b) Minimal loss of color is observed during the "off" periods, as demonstrated by comparing only the "on" time from panel a to the mechanochemical activation of **P1** under continuous ultrasonication. Absorbance measured at 510 nm.

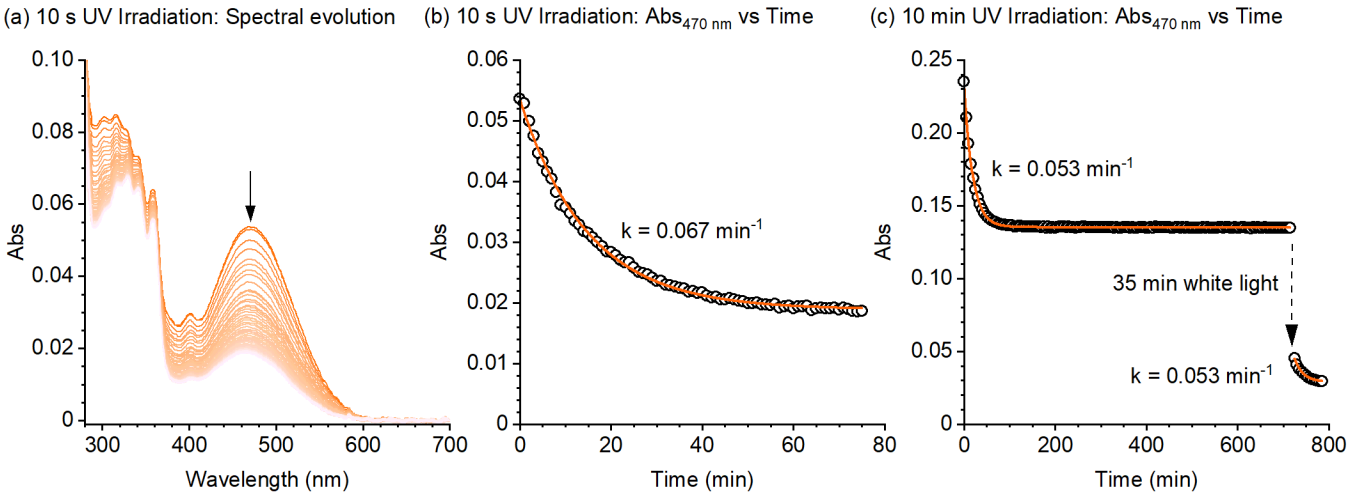


Figure S3. Demonstration of reversion of the photochemically generated merocyanine under ambient conditions or upon irradiation with white light. (a,b) Brief photoactivation of a solution of **P1** with UV light (10 s) produces a merocyanine with λ_{max} of 470 nm that fully reverts after approximately 1 h at room temperature. Fitting the time dependent absorbance at 470 nm to eq S2 yields a reversion rate of 0.067 min^{-1}. (c) Extended irradiation of a solution of **P1** with UV light (10 min) generates a merocyanine with the same λ_{max} of 470 nm, which fades to half the initial absorbance in approximately 1 h, leaving a persistent merocyanine attributed to the exocyclic *trans* isomer. Subsequent irradiation with white light for 35 min leads to additional reversion. Further thermal reversion occurs with the same rate constant observed initially.

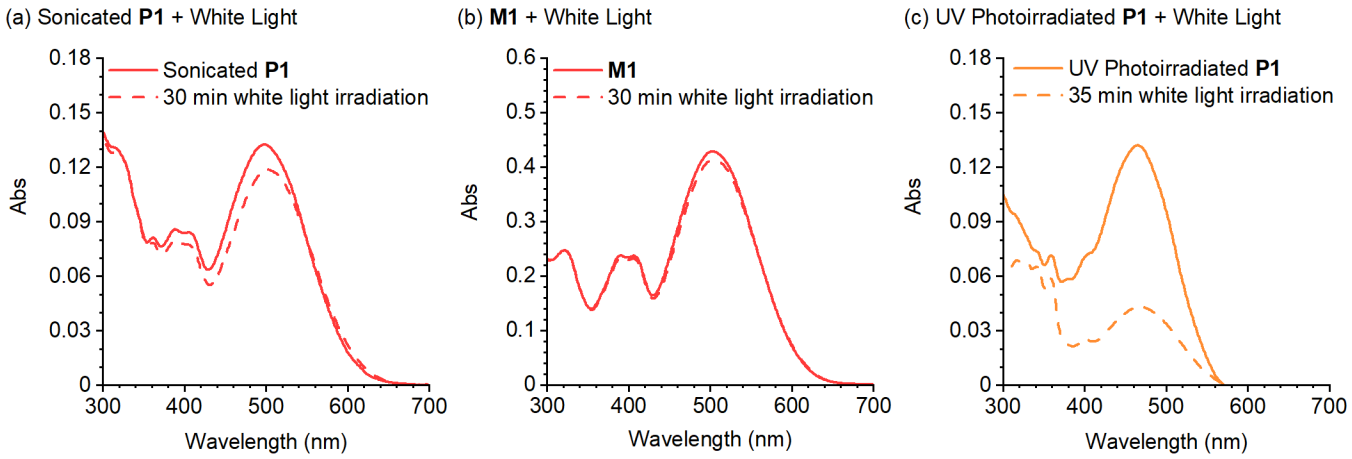


Figure S4. Irradiation of (a) the merocyanine derived from ultrasound-induced mechanochemical activation of **P1** and (b) **M1** with white light for 30 min results in negligible (< 10%) change in visible absorption. (c) Irradiation of the thermally persistent merocyanine generated from photochemical activation of **P1** with white light for 35 min under the same conditions results in 67% attenuation of the visible absorbance at 470 nm (see Figure S3c above).

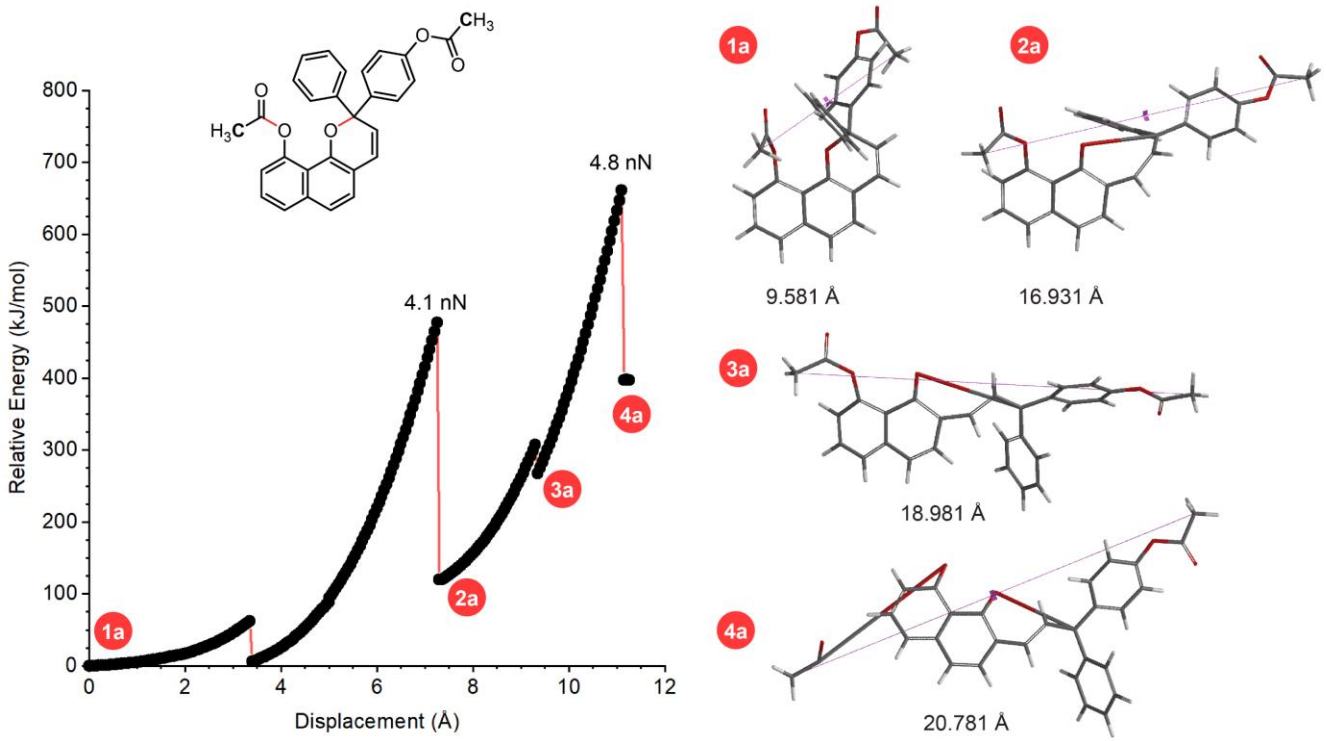


Figure S5. DFT calculations using the constrained geometries simulate external force (CoGEF) method at the B3LYP/6-31G* level of theory for a truncated model reflecting the mechanophore in polymer **P1**. CoGEF calculations predict the ring-opening reaction with an F_{max} value of 4.1 nN followed by further elongation that results in C–O bond scission at a predicted F_{max} value of 4.8 nN. The corresponding computed structures at various points of elongation are shown at right along with the associated constraint distance between the terminal methyl groups.

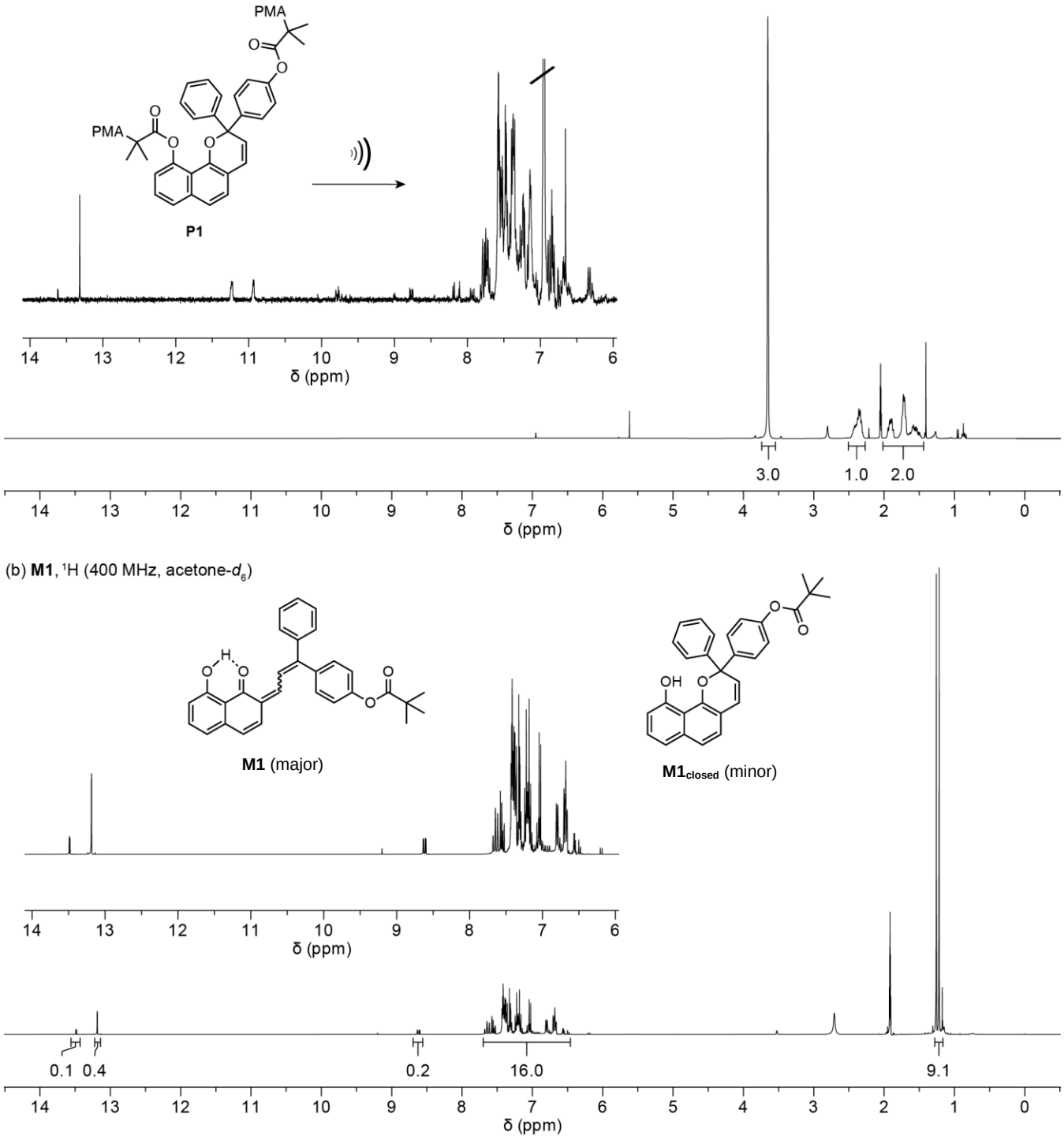


Figure S6. ^{1}H NMR spectra of (a) **P1** after ultrasonication (125 min), and (b) **M1**. Polymer **P1** was precipitated into hexanes and dried under vacuum prior to analysis. In the spectrum for **P1**, the peak at 6.95 ppm is residual BHT and peaks at 10.94 and 11.23 ppm are attributed to peroxide impurities resulting from the decomposition of THF. The small singlet at 9.34 ppm in the spectrum of **M1** is attributed to the significantly more shielded hydroxyl proton of the minor ring-closed naphthopyran (**M1$_{closed}$**).

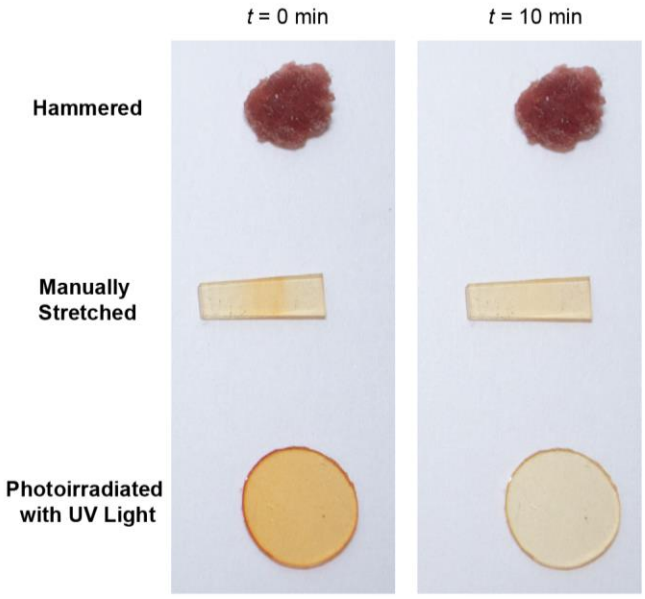


Figure S7. Photographs of **PDMS$_{active}$** films containing a mechanophore crosslinker after being subjected to repeated hammering, manual tension, and UV irradiation (365 nm) immediately after activation and then 10 min later. Manual stretching and UV light generate a transient yellow-orange color that quickly fades. In contrast, mechanical activation using a hammer generates a distinct red coloration that does not fade.

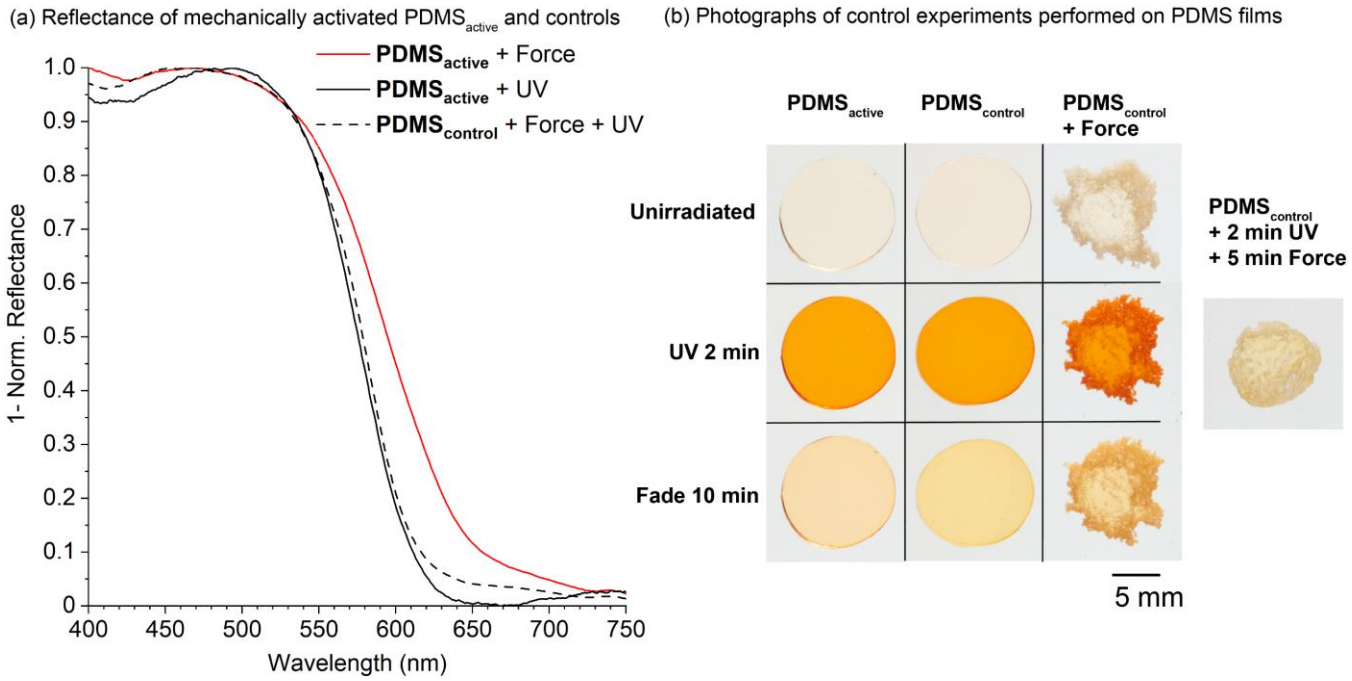
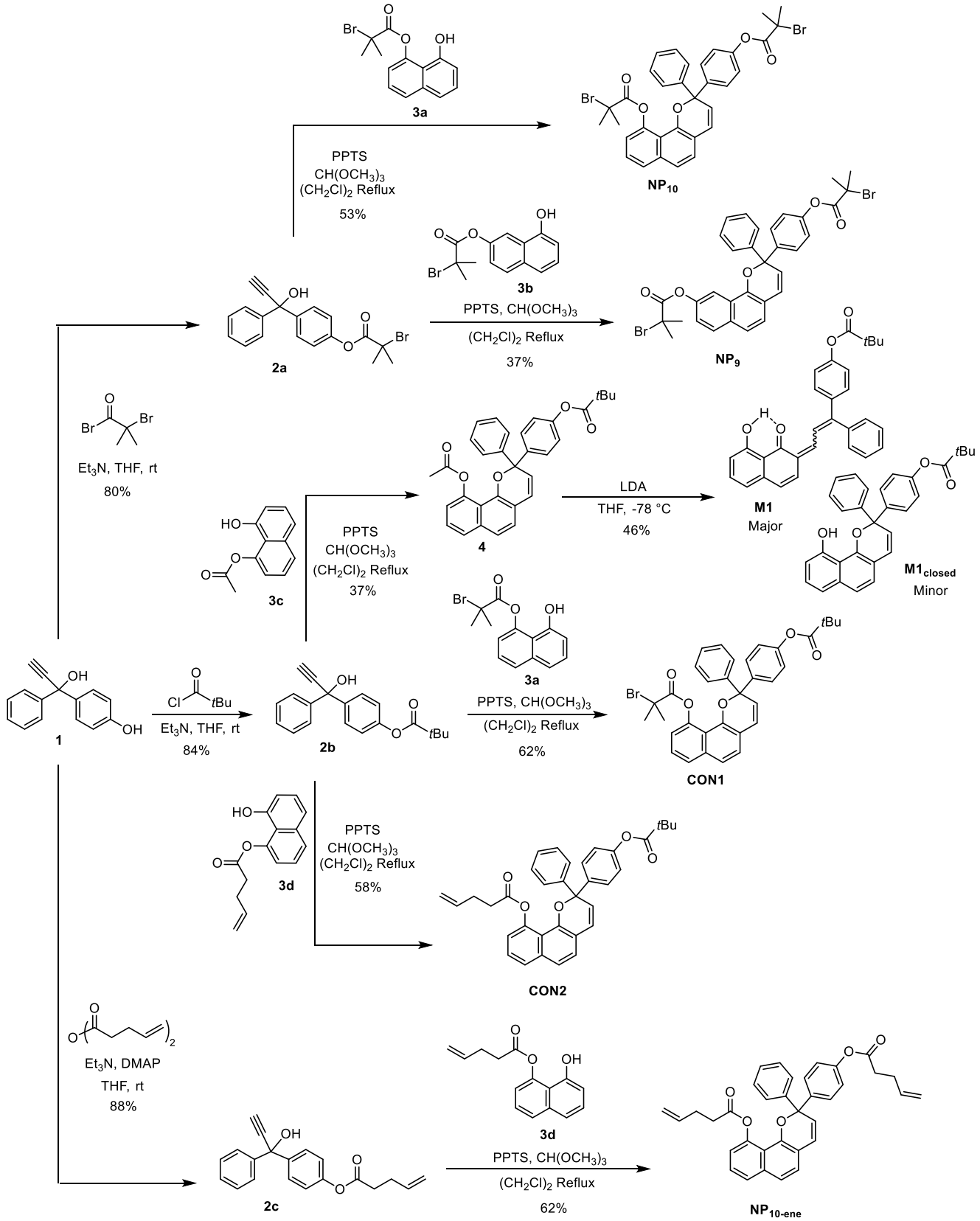
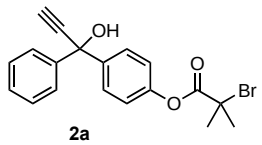


Figure S8. (a) Reflectance measurements and (b) photographs of a mechanophore-crosslinked active PDMS material (**PDMS$_{active}$**) and a control PDMS network incorporating a mono-functional naphthopyran moiety (**PDMS$_{control}$**) after being subjected to combinations of mechanical force by repeated hammering and UV light (365 nm). The control material exhibits similar reflection after being subjected to mechanical force and UV light as **PDMS$_{active}$** after UV irradiation, in contrast to the bathochromically shifted reflection observed for **PDMS$_{active}$** following mechanical activation. The control film turns yellow-orange under UV light and the color quickly fades in all cases. Fading is accelerated in the photoactivated control film after being hammered for 5 min.

III. Synthetic Details

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





2a

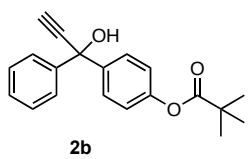
4-(1-hydroxy-1-phenylprop-2-yn-1-yl)phenyl 2-bromo-2-methylpropanoate (2a). To a flame-dried 2-neck 50 mL RBF equipped with a stir bar was added **1** (773 mg, 3.45 mmol). The flask was evacuated and backfilled with N_2 three times. Anhydrous THF (20 mL) and then triethylamine (0.65 mL, 4.7 mmol) were added via syringe under N_2. α-bromoisobutyryl bromide (0.42 mL, 3.4 mmol) was added dropwise via syringe over 10 min under N_2 at room temperature. After stirring for 19 h, the reaction was diluted with EtOAc (100 mL), washed with DI water (100 mL), saturated aqueous $NaHCO_3$ (100 mL), and brine (50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude yellow oil was purified by column chromatography on silica gel (5–30% EtOAc/hexanes) to yield the product as a pale yellow oil that solidified upon trituration with hexanes (1.01 g, 78%).

TLC (25% EtOAc/hexanes): R_f = 0.57

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 – 7.57 (m, 4H), 7.38 – 7.26 (m, 3H), 7.13 – 7.07 (m, 2H), 2.89 (s, 1H), 2.86 (s, 1H), 2.06 (s, 6H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 170.3, 150.4, 144.2, 142.5, 128.5, 128.2, 127.5, 126.1, 120.9, 86.2, 76.0, 74.0, 55.4, 30.7.

HRMS (FAB, *m/z*): calcd for $[C_{19}H_{17}BrO_3]^+$ $(M)^+$, 372.0361; found, 372.0372.



2b

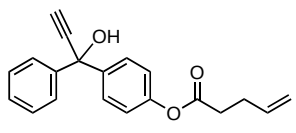
4-(1-hydroxy-1-phenylprop-2-yn-1-yl)phenyl pivalate (2b). To a flame-dried 2-neck 100 mL RBF equipped with a stir bar was added **1** (922 mg, 4.11 mmol). The flask was evacuated and backfilled with N_2 three times. Anhydrous THF (30 mL) and subsequently triethylamine (0.80 mL, 5.7 mmol) was added via syringe under N_2. Pivaloyl chloride (0.58 mL, 4.7 mmol) was added dropwise via syringe over 10 min at room temperature. After stirring for 20 h, the reaction was diluted with 100 mL EtOAc, washed with 10% aqueous NH_4Cl (100 mL), saturated aqueous $NaHCO_3$ (100 mL) and brine (50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to a yellow oil. The crude material purified by column chromatography on silica gel (10–30% EtOAc/hexanes) to yield the product as a pale yellow solid (1.06 g, 83%).

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

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 – 7.57 (m, 4H), 7.37 – 7.27 (m, 3H), 7.05 – 7.00 (m, 2H), 2.88 (s, 1H), 2.86 (s, 1H), 1.35 (s, 9H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ: 177.1, 150.8, 144.3, 141.8, 128.5, 128.1, 127.3, 126.1, 121.4, 86.3, 75.8, 74.1, 39.2, 27.2.

HRMS (FAB, *m/z*): calcd for $[C_{20}H_{20}O_3]^+$ $(M)^+$, 309.1491; found, 309.1471.



2c

4-(1-hydroxy-1-phenylprop-2-yn-1-yl)phenyl pent-4-enoate (2c). To a flame-dried 2-neck 50 mL RBF equipped with a stir bar was added **1** (307 mg, 1.37 mmol) and catalytic N,N-dimethylaminopyridine (10 mg, 0.08 mmol). The flask was evacuated and

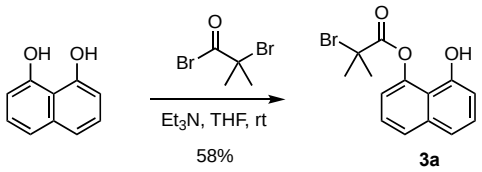
backfilled with N_2 three times. Anhydrous THF (20 mL) and subsequently triethylamine (0.23 mL, 1.6 mmol) was added via syringe under N_2. Pentenoic anhydride (0.28 mL, 1.5 mmol) was added dropwise via syringe over 10 min room temperature. After stirring for 22 h, the reaction was diluted with 100 mL EtOAc, washed with DI water (50 mL), saturated aqueous $NaHCO_3$ (50 mL) and brine (30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude material purified by column chromatography on silica gel (0–30% EtOAc/hexanes) to yield the product as a pale yellow oil (371 mg, 88%).

TLC (25% EtOAc/hexanes): R_f = 0.51

^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.69 – 7.62 (m, 4H), 7.37 – 7.30 (m, 2H), 7.28 – 7.22 (m, 1H), 7.10 – 7.05 (m, 2H), 5.92 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.77 (s, 1H), 5.13 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.03 (dq, *J* = 10.2, 1.4 Hz, 1H), 3.38 (d, *J* = 0.6 Hz, 1H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.50 – 2.39 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ: 171.8, 151.1, 146.7, 144.4, 137.7, 128.9, 128.2, 127.9, 126.7, 122.1, 116.0, 87.8, 76.5, 74.0, 34.0.

HRMS (FAB, *m/z*): calcd for $[C_{20}H_{19}O_3]^+$ $(M+H)^+$, 307.1334; found, 307.1327.



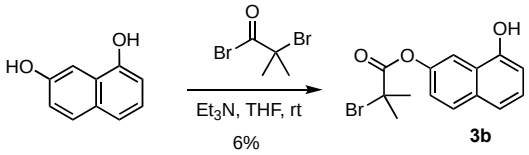
8-hydroxynaphthalen-1-yl 2-bromo-2-methylpropanoate (3a). To a flame-dried 2-neck 100 mL RBF equipped with a stir bar was added 1,8-dihydroxynaphthalene (2.31 g, 14.4 mmol). The flask was evacuated and backfilled with N_2 three times. Anhydrous THF (40 mL) and then triethylamine (2.60 mL, 18.6 mmol) were added via syringe under N_2, followed by the dropwise addition of α-bromoisobutyryl bromide (2.00 mL, 16.3 mmol) via syringe over 10 min at room temperature. After stirring for 19 h, the reaction was diluted with 100 mL EtOAc, washed with aqueous 10% NH_4Cl (2 x 100 mL), saturated aqueous $NaHCO_3$ (100 mL), and brine (50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude material was dissolved in hot toluene (50 mL) and recrystallized in the dark to yield the product as grey crystals (2.57 g, 58%).

TLC (25% EtOAc/hexanes): R_f = 0.49

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.32 (dd, *J* = 8.3, 7.6 Hz, 1H), 7.17 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.06 (s, 1H), 6.85 (dd, *J* = 7.6, 1.1 Hz, 1H), 2.43 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 169.8, 151.6, 146.3, 137.0, 127.3, 127.0, 125.5, 120.6, 117.8, 117.0, 111.8, 55.5, 31.0.

HRMS (ESI, *m/z*): calcd for $[C_{14}H_{13}BrO_3]^+$ $(M+H)^+$, 309.0126; found, 309.0151.



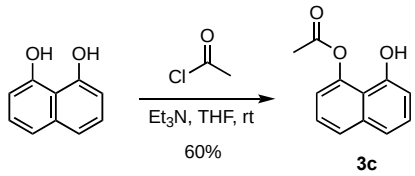
8-hydroxynaphthalen-2-yl 2-bromo-2-methylpropanoate (3b). To a flame-dried 2-neck 100 mL RBF equipped with a stir bar was added 1,7-dihydroxynaphthalene (2.99 g, 18.7 mmol). The flask was evacuated and backfilled with N_2 three times. Anhydrous THF (60 mL) and subsequently triethylamine (3.40 mL, 24.4 mmol) was added via syringe under N_2. α-bromoisobutyryl bromide (2.25 mL, 18.5 mmol) was added dropwise via syringe over 10 min under N_2 at room temperature. After stirring for 17 h, the reaction was diluted with 150 mL EtOAc, washed with DI water (100 mL, aqueous layer turns pink), saturated aqueous $NaHCO_3$ (100 mL), and brine (50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated onto celite. The material was partially purified by column chromatography on silica gel (10–100% EtOAc/hexanes), then product-containing fractions were loaded onto a plug of basic alumina and washed with 25% EtOAc/hex to remove diester side product, and lastly the product and its constitutional isomer were eluted with 5% MeOH/CH_2Cl_2. A second silica column was run (10–50% EtOAc/hexanes with 1% triethylamine) and then a third (25–100% 10–50% EtOAc/hexanes with 1% triethylamine) to finally yield the pure product as a grey solid (341 mg, 6%).

TLC (25% EtOAc/hexanes): R_f = 0.45

^{1}H NMR (400 MHz, Acetone-d_6) δ: 9.20 (br s, 1H), 7.99 (d, *J* = 2.5 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.31 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.99 (dd, *J* = 7.5, 1.0 Hz, 1H), 2.13 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ: 170.9, 153.7, 148.8, 133.9, 130.0, 127.2, 125.9, 121.7, 119.8, 113.8, 109.6, 57.2, 30.8.

HRMS (FAB, *m/z*): calcd for $[C_{14}H_{13}BrO_3]^+$ $(M)^+$, 308.0048; found, 308.0076.



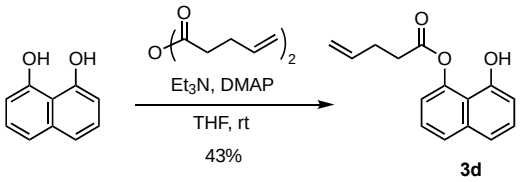
8-hydroxynaphthalen-1-yl acetate (3c). To a flame-dried 2-neck 50 mL RBF equipped with a stir bar was added 1,8-dihydroxynaphthalene (1.01 g, 6.30 mmol). The flask was evacuated and backfilled with N_2 three times. Anhydrous THF (20 mL) and subsequently triethylamine (1.10 mL, 7.89 mmol) was added via syringe under N_2. Acetyl chloride (0.50 mL, 7.0 mmol) was added dropwise via syringe over 10 min at room temperature. After stirring for 3.5 h, the reaction was diluted with 100 mL EtOAc, washed with DI water (50 mL), 10% aqueous NH_4Cl (50 mL), and brine (50 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude material was recrystallized from toluene in the dark to yield the product as beige crystals (0.76 g, 60%).

TLC (25% EtOAc/hexanes): R_f = 0.26

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.32 (dd, *J* = 8.3, 7.6 Hz, 1H), 7.17 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.06 (s, 1H), 6.85 (dd, *J* = 7.6, 1.1 Hz, 1H), 2.43 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ: 168.8, 151.8, 146.0, 137.0, 127.2, 126.6, 125.6, 120.6, 118.6, 117.1, 111.5, 21.6.

HRMS (FAB, *m/z*): calcd for $[C_{12}H_{10}O_3]^+$ $(M)^+$, 202.0630; found, 202.0638.



3d

8-hydroxynaphthalen-1-yl pent-4-enoate (3d). To a flame-dried 2-neck 50 mL RBF equipped with a stir bar was added 1,8-dihydroxynaphthalene (687 mg, 4.29 mmol) and catalytic N,N-dimethylaminopyridine (5.5 mg, 0.045 mmol). The flask was evacuated and backfilled with N_2 three times. Anhydrous THF (15 mL) and subsequently triethylamine (0.72 mL, 5.2 mmol) was added via syringe under N_2. Pentenoic anhydride (0.89 mL, 4.7 mmol) was added dropwise via syringe over 10 min room temperature. After stirring for 15 h, the reaction was diluted with 100 mL EtOAc, washed with DI water (50 mL), saturated aqueous $NaHCO_3$ (50 mL) and brine (30 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude material purified by column chromatography on silica gel (5–30% EtOAc/hexanes) and subsequently recrystallized from toluene to yield the product as colorless crystals (444 mg, 43%).

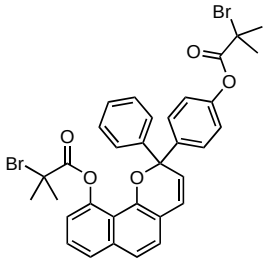
TLC (25% EtOAc/hexanes): R_f = 0.56

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.33 (app t, *J* = 7.9 Hz, 1H), 7.16 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.11 (d, *J* = 2.1 Hz, 1H), 6.86 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.93 (ddt, *J* = 16.9, 10.1, 6.4 Hz, 1H), 5.19 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.12 (dq, *J* = 10.2, 1.4 Hz, 1H), 2.87 – 2.77 (m, 2H), 2.63 – 2.53 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ: 170.7, 151.9, 146.0, 137.0, 136.1, 127.2, 126.6, 125.6, 120.5, 118.6, 117.0, 116.5, 111.5, 34.1, 28.7.

HRMS (FAB, *m/z*): calcd for $[C_{15}H_{14}O_3]^+$ $(M)^+$, 242.0943; found, 242.0930.

General Procedure A for Naphthopyran Synthesis. Naphthopyrans were synthesized following the procedure by Zhao and Carreira.[1] 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.



NP_{10}

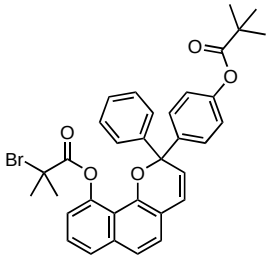
4-(10-((2-bromo-2-methylpropanoyl)oxy)-2-phenyl-2H-benzo[h]chromen-2-yl)phenyl 2-bromo-2-methylpropanoate (NP_{10}). The title compound was prepared using General Procedure A with **3a** (283 mg, 0.915 mmol), **2a** (475 mg, 1.27 mmol) added as a solution in 1,2-dichloroethane, PPTS (22 mg, 0.088 mmol), trimethyl orthoformate (0.30 mL, 2.7 mmol), and 1,2-dichloroethane (10 mL) for 7 h. Purification by column chromatography on silica gel (5–40% EtOAc/hexanes) yielded the title compound as a pink foamy solid (322 mg, 53%).

TLC (25% EtOAc/hexanes): R_f = 0.57 (Merocyanine R_f = 0.50)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.46 – 7.35 (m, 4H), 7.35 – 7.27 (m, 3H), 7.17 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.66 (d, *J* = 9.6 Hz, 1H), 6.11 (d, *J* = 9.6 Hz, 1H), 2.04 (s, 6H), 1.55 (s, 3H), 1.54 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.7, 170.2, 150.4, 147.4, 147.0, 144.4, 142.2, 137.1, 129.1, 128.6, 128.3, 128.2, 127.8, 127.2, 126.1, 125.6, 124.0, 121.6, 120.8, 119.5, 118.8, 117.5, 83.6, 57.1, 55.4, 30.7, 29.7, 29.6.

HRMS (ESI, *m/z*): calcd for $[C_{33}H_{29}Br_2O_5]^+$ $(M+H)^+$, 663.0382; found, 663.0399.



CON1

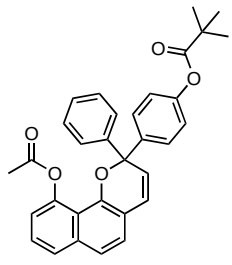
4-(10-((2-bromo-2-methylpropanoyl)oxy)-2-phenyl-2H-benzo[h]chromen-2-yl)phenyl pivalate (CON1). The title compound was prepared using General Procedure A with **3a** (181 mg, 0.585 mmol), **2b** (204 mg, 0.662 mmol), PPTS (8.0 mg, 0.032 mmol), trimethyl orthoformate (0.20 mL, 1.8 mmol), and 1,2-dichloroethane (9 mL) for 17 h. Purification by column chromatography on silica gel (10–60% CH_2Cl_2/hexanes) yielded the title compound as a pink foamy solid (219 mg, 62%).

TLC (25% EtOAc/hexanes): R_f = 0.66 (Merocyanine form R_f = 0.60)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.47 – 7.35 (m, 4H), 7.35 – 7.27 (m, 3H), 7.18 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 7.04 – 6.98 (m, 2H), 6.65 (d, *J* = 9.6 Hz, 1H), 6.11 (d, *J* = 9.6 Hz, 1H), 1.56 (s, 3H), 1.54 (s, 3H), 1.34 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 177.1, 170.7, 150.8, 147.4, 147.0, 144.5, 141.6, 137.1, 128.9, 128.7, 128.2, 128.1, 127.9, 127.2, 126.0, 125.5, 123.8, 121.6, 121.2, 119.5, 118.8, 117.5, 83.6, 57.1, 39.2, 29.7, 29.6, 27.2.

HRMS (ESI, *m/z*): calcd for $[C_{34}H_{32}BrO_5]^+$ $(M+H)^+$, 599.1433; found, 599.1441.



4

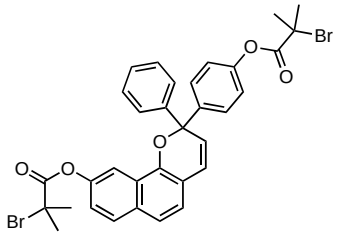
4-(10-acetoxy-2-phenyl-2H-benzo[h]chromen-2-yl)phenyl pivalate (4). The title compound was prepared using General Procedure A with **3c** (519 mg, 2.57 mmol), **2b** (905 mg, 2.93 mmol), PPTS (32.7 mg, 0.130 mmol), trimethyl orthoformate (0.70 mL, 6.4 mmol), and 1,2-dichloroethane (20 mL) for 19 h. The crude reaction mixture was filtered over basic alumina, eluted with EtOAc, and purification by column chromatography on silica gel (0–25% EtOAc/hexanes) yielded the title compound as pink foamy solid (466 mg, 37%).

TLC (25% EtOAc/hexanes): R_f = 0.47

^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.69 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.59 – 7.52 (m, 4H), 7.47 – 7.30 (m, 5H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.14 – 7.08 (m, 3H), 6.83 (d, *J* = 9.7 Hz, 1H), 6.34 (d, *J* = 9.7 Hz, 1H), 1.68 (s, 3H), 1.32 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ: 177.2, 170.4, 152.0, 148.1, 147.7, 145.5, 142.9, 138.0, 129.7, 129.4, 129.0, 128.9, 128.4, 127.3, 127.1, 126.3, 124.7, 122.24, 122.22, 121.1, 120.2, 118.3, 84.5, 39.7, 27.4, 20.8.

HRMS (ESI, *m/z*): calcd for $[C_{32}H_{29}O_5]^+$ $(M+H)^+$, 493.2015; found, 493.2005.



NP$_9$

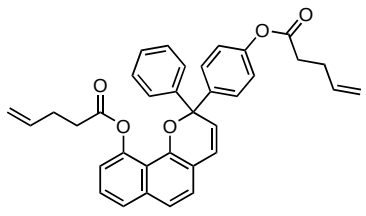
4-(9-((2-bromo-2-methylpropanoyl)oxy)-2-phenyl-2H-benzo[h]chromen-2-yl)phenyl 2-bromo-2-methylpropanoate (NP$_9$). The title compound was prepared using General Procedure A with **3b** (308 mg, 0.997 mmol), **2a** (436 mg, 1.17 mmol), which was added as a solid, PPTS (34.5 mg, 0.137 mmol), trimethyl orthoformate (0.33 mL, 3.0 mmol), and 1,2-dichloroethane (10 mL) for 18 h. Purification by column chromatography on silica gel (5–40% EtOAc/hexanes) yielded the title compound as a pink foamy solid (246 mg, 37%).

TLC (25% EtOAc/hexanes): R_f = 0.57 (Merocyanine R_f = 0.50)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, *J* = 2.5 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.57 – 7.46 (m, 4H), 7.39 – 7.27 (m, 4H), 7.23 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.14 – 7.08 (m, 2H), 6.75 (d, *J* = 9.8 Hz, 1H), 6.17 (d, *J* = 9.7 Hz, 1H), 2.13 (s, 6H), 2.04 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 170.5, 170.3, 150.2, 148.7, 147.5, 144.7, 142.8, 132.9, 129.5, 128.5, 128.4, 127.9, 127.8, 127.1, 125.0, 124.7, 123.9, 121.0, 120.8, 120.7, 116.2, 112.7, 83.3, 55.7, 55.4, 30.9, 30.7.

HRMS (ESI, *m/z*): calcd for $[C_{33}H_{29}Br_2O_5]^+$ $(M+H)^+$, 663.0382; found, 663.0390.



NP$_{10\text{-ene}}$

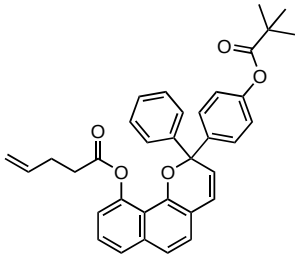
4-(10-(pent-4-enoyloxy)-2-phenyl-2H-benzo[h]chromen-2-yl)phenyl pent-4-enoate (NP$_{10\text{-ene}}$). The title compound was prepared using General Procedure A with **3d** (102 mg, 0.420 mmol), **2c** (148 mg, 0.483 mmol) added as a solution in 1,2-dichloroethane, PPTS (9.4 mg, 0.037 mmol), trimethyl orthoformate (0.14 mL, 1.3 mmol), and 1,2-dichloroethane (6 mL) for 2 h. Purification by column chromatography on silica gel (0–10% EtOAc with 1% triethylamine/hexanes) yielded the title compound as a dark orange-red oil (138 mg, 62%).

TLC (25% EtOAc/hexanes): R_f = 0.57 (Merocyanine R_f = 0.50)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.56 – 7.45 (m, 4H), 7.40 – 7.27 (m, 5H), 7.12 (d, *J* = 8.3 Hz, 1H), 7.08 – 6.98 (m, 3H), 6.66 (d, *J* = 9.7 Hz, 1H), 6.12 (d, *J* = 9.6 Hz, 1H), 5.89 (ddt, *J* = 16.8, 10.2, 6.4 Hz, 1H), 5.70 – 5.57 (m, 1H), 5.13 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.07 (dq, *J* = 10.3, 1.4 Hz, 1H), 4.99 – 4.95 (m, 1H), 4.93 (dt, *J* = 2.6, 1.7 Hz, 1H), 2.65 (td, *J* = 7.3, 0.8 Hz, 2H), 2.49 (tdd, *J* = 7.6, 6.0, 1.1 Hz, 2H), 2.20 – 2.06 (m, 2H), 2.06 – 1.94 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ: 172.6, 171.6, 150.4, 147.5, 146.6, 144.6, 142.1, 137.3, 136.9, 136.5, 129.0, 128.3, 128.2, 128.0, 127.8, 126.8, 126.1, 125.6, 124.1, 121.5, 121.3, 1220.2, 119.3, 117.3, 116.2, 115.5, 83.7, 33.8, 33.1, 29.1, 28.6.

HRMS (FAB, *m/z*): calcd for $[C_{35}H_{30}O_5]^+$ $(M)^+$, 530.2093; found, 530.2094.



CON2

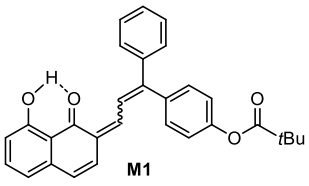
2-phenyl-2-(4-(pivaloyloxy)phenyl)-2H-benzo[h]chromen-10-yl pent-4-enoate (CON2). The title compound was prepared using General Procedure A with **3d** (180 mg, 0.743 mmol), **2b** (309 mg, 1.00 mmol) added as a solid, PPTS (9.6 mg, 0.038 mmol), trimethyl orthoformate (0.25 mL, 2.3 mmol), and 1,2-dichloroethane (6 mL) for 2 h. Purification by column chromatography on silica gel (0–10% EtOAc with 1% triethylamine/hexanes) yielded the title compound as a pink foamy solid (229 mg, 58%).

TLC (25% EtOAc/hexanes): R_f = 0.66

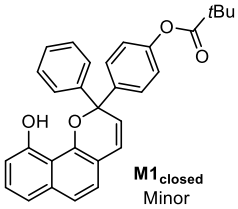
^{1}H NMR (400 MHz, Acetone-d_6) δ: 7.73 – 7.66 (m, 1H), 7.59 – 7.51 (m, 5H), 7.48 – 7.30 (m, 6H), 7.26 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.15 – 7.07 (m, 3H), 6.83 (dd, *J* = 9.7, 1.1 Hz, 1H), 6.34 (dd, *J* = 9.7, 1.0 Hz, 1H), 5.75 – 5.60 (m, 1H), 5.01 – 4.88 (m, 2H), 2.17 – 2.07 (m, 4H), 1.32 (d, *J* = 0.7 Hz, 9H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, Acetone-d_6) δ: 177.1, 172.5, 152.0, 148.2, 147.7, 145.5, 142.8, 138.0, 137.9, 129.7, 129.6, 129.1, 129.0, 128.5, 127.4, 127.1, 126.4, 124.7, 122.30, 122.27, 121.2, 120.3, 118.4, 115.7, 84.6, 39.7, 33.7, 29.3, 27.4.

HRMS (FAB, *m/z*): calcd for $[C_{35}H_{33}O_5]^+$ $(M+H)^+$, 533.2328; found, 533.2345.



M1
Major



M1$_{closed}$
Minor

4-(3-(8-hydroxy-1-oxonaphthalen-2(1H)-ylidene)-1-phenylprop-1-en-1-yl)phenyl pivalate (M1). Lithium diisopropylamine was freshly prepared in a flame-dried 25 mL round bottom flask. Anhydrous THF (7 mL) and diisopropylamine (0.50 mL, 3.5 mmol) were added via syringe under N_2. The flask was cooled to –78 °C and n-butyllithium (2.5 M in hexanes, 1.4 mL, 3.5 mmol) was added via syringe under N_2. The reaction was stirred for 2 h. To a separate flame dried 100 mL 2-neck round bottom flask equipped with a stir bar was added **4** (210 mg, 0.426 mmol) and the vessel was evacuated and backfilled with N_2 three times. Anhydrous THF (10 mL) was added via syringe under N_2, the solution was cooled to –78 °C, and LDA solution (1.0 mL, 0.39 mmol) was added dropwise via syringe, upon which the coral pink solution immediately turned yellow. After 2 h, the reaction was removed from the cooling bath and immediately diluted with EtOAc (100 mL) and 10% aqueous NH_4Cl solution (120 mL). Upon dilution, the organic layer initially becomes deep indigo in color, but the organic layer becomes a deep burgundy red color upon washing with aqueous acid. The organic layer was washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated. Purification by column chromatography on silica gel (0–25% EtOAc/hexanes) yielded the product as a red foamy solid (80.3 mg, 46%). The product is a mixture of merocyanine stereoisomers that readily interconvert and contains ~10% ring-closed

naphthopyran as a minor product based on integrations of the hydroxyl resonances in the ^{1}H NMR spectrum measured in acetonitrile-d_3.

TLC (25% EtOAc/hexanes): R_f = 0.66, 0.58 (stereoisomers)

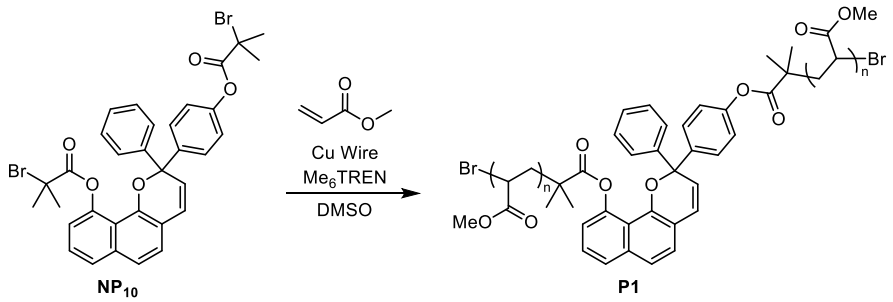
^{1}H NMR (400 MHz, acetone-d_6) δ: 13.63 (s, 0.04H, -O*H*), 13.61 (s, 0.04H, -O*H*), 13.322 (s, 0.2H, -O*H*), 13.319 (s, 0.2H, -O*H*), 9.34 (s, 0.01H, -O*H*, **M1$_{closed}$**), 8.76 (d, *J* = 12.2 Hz, 0.09H), 8.75 (d, *J* = 12.3 Hz, 0.09H), 7.85 – 6.59 (m, 16H), 6.33 (d, *J* = 9.9 Hz, 0.03H, **M1$_{closed}$**) 1.40 – 1.30 (m, 9H).

^{1}H NMR (400 MHz, acetonitrile-d_3) δ: 13.60 (s, 0.2H, -O*H*), 13.58 (s, 0.2H, -O*H*), 13.24 (s, 0.5H, -O*H*), 9.25 (s, 0.1H, -O*H,* **M1$_{closed}$**), 8.67 (d, *J* = 12.1 Hz, 0.2H), 8.64 (d, *J* = 12.2 Hz, 0.2H), 7.69 – 6.55 (m, 16H), 6.25 (d, *J* = 9.8 Hz, 0.1H, **M1$_{closed}$**), 1.38 – 1.30 (m, 9H).

^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ: 189.30, 189.26, 176.13, 176.12, 164.5, 164.2, 163.8, 157.5, 155.82, 155.78, 155.7, 152.7, 152.6, 152.0, 146.8, 141.4, 141.2, 140.1, 140.0, 139.83, 139.79, 138.82, 138.80, 138.78, 138.6, 138.4, 136.70, 136.67, 136.65, 136.62, 135.8, 132.4, 132.1, 132.0, 131.3, 131.0, 130.93, 130.88, 130.84, 130.82, 130.80, 130.0, 129.9, 129.8, 129.6, 129.2, 128.9, 128.8, 128.7, 128.63, 128.57, 128.5, 128.4, 128.2, 126.8, 126.5, 126.2, 125.1, 125.0, 124.8, 124.12, 124.07 123.6, 123.54, 123.51, 122.5, 122.3, 122.1, 121.91, 121.86, 121.84, 121.79, 121.7, 119.20, 119.17, 119.13, 119.10, 118.5, 116.34, 116.30, 116.24, 116.20, 116.0, 115.9, 115.4, 38.83, 38.80, 26.5, 26.42, 26.38.

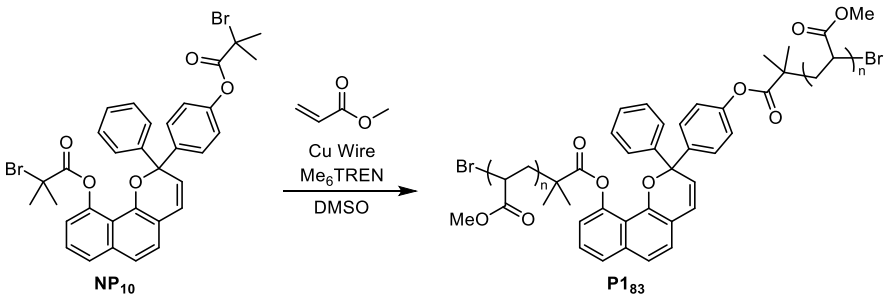
HRMS (ESI, *m/z*): calcd for $[C_{30}H_{27}O_4]^+$ $(M+H)^+$, 451.1909; found, 451.1921

General Procedure B for the Synthesis of Poly(Methyl Acrylate) (PMA) Polymers Incorporating a 2*H*-Naphthopyran. Polymers were synthesized by controlled radical polymerization following the procedure by Nguyen *et al*.[2] 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 to afford the polymer.

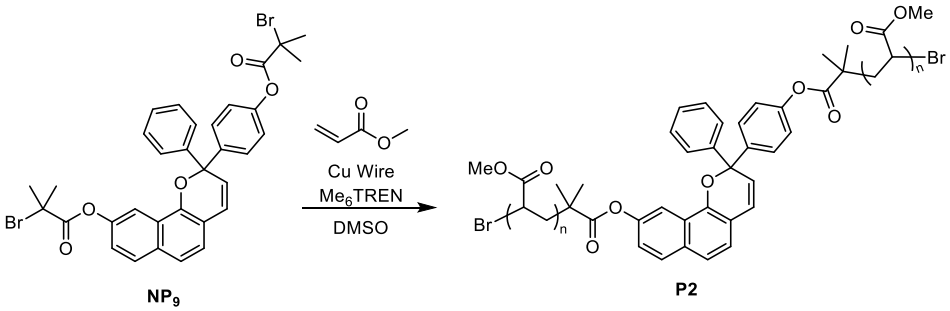


NP$_{10}$ **P1**

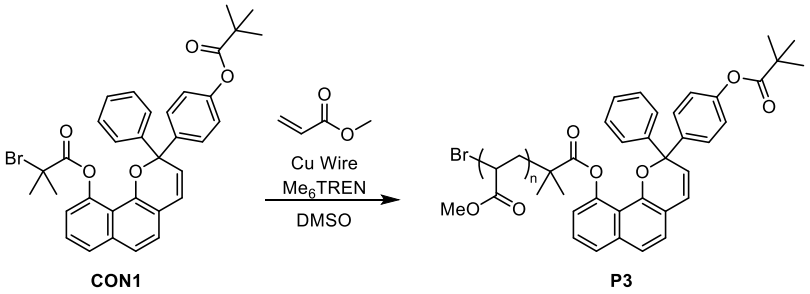
Polymer **P1.** Synthesized using General Procedure B with initiator **NP$_{10}$** (14.0 mg, 0.021 mmol), methyl acrylate (6.8 mL, 76 mmol), DMSO (6.8 mL), and Me_6TREN (28 μL, 0.10 mmol). Polymerization for 5 h provided the title polymer as a tacky orange solid (1.6 g, 25%). M_n = 178 kg/mol, $Đ$ = 1.13.



Polymer **P1$_{83}$.** Synthesized using General Procedure B with initiator **NP$_{10}$** (16.7 mg, 0.0251 mmol), methyl acrylate (2.6 mL, 29 mmol), DMSO (2.6 mL), and Me_6TREN (34 µL, 0.13 mmol). Polymerization for 2.5 h provided the title polymer as a tacky orange solid (440 mg, 25%). M_n = 83.1 kg/mol, $Đ$ = 1.15.



Polymer **P2.** Synthesized using General Procedure B with initiator **NP$_9$** (13.9 mg, 0.0209 mmol), methyl acrylate (6.7 mL, 74 mmol), DMSO (6.7 mL), and Me_6TREN (30 µL, 0.11 mmol). Polymerization for 4.5 h provided the title polymer as a tacky orange solid (2.5 g, 39%). M_n = 174 kg/mol, $Đ$ = 1.06.



Polymer **P3.** Synthesized using General Procedure B with initiator **CON1** (9.1 mg, 0.015 mmol), methyl acrylate (5.3 mL, 59 mmol), DMSO (5.3 mL), and Me_6TREN (20 µL, 0.075 mmol). Polymerization for 3 h provided the title polymer as a tacky orange solid (1.2 g, 24%). M_n = 183 kg/mol, $Đ$ = 1.07.

IV. Characterization of Linear PMA Polymers.

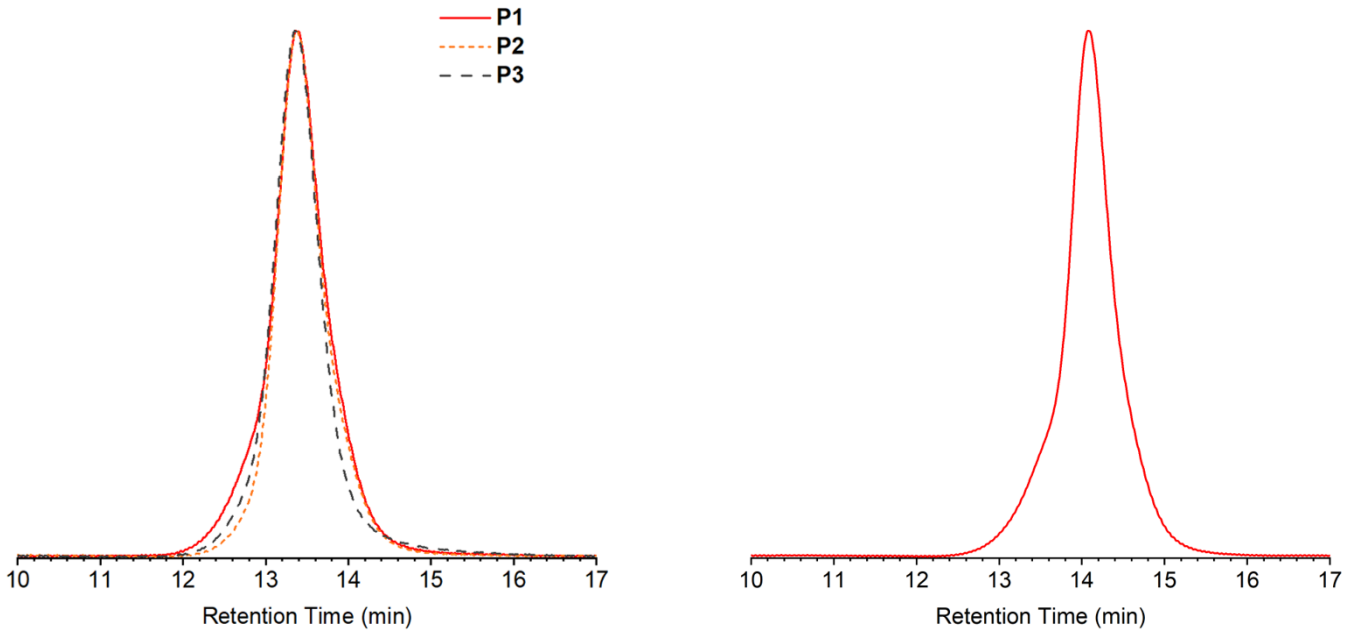


Figure S9. GPC traces (refractive index response) normalized to peak height for **P1**, **P2**, and **P3** (left), and **P1$_{83}$** (right).

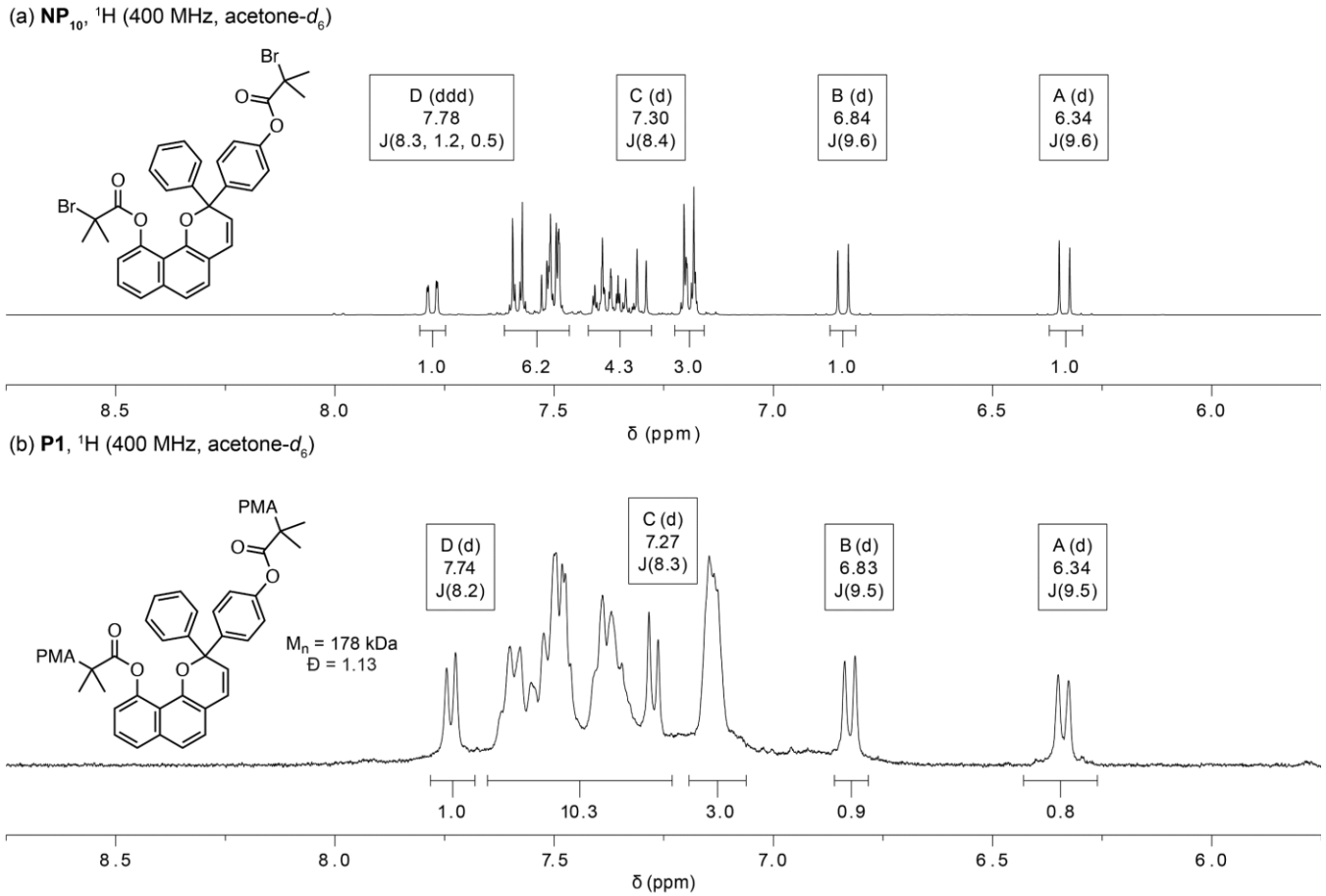


Figure S10. Partial ^{1}H NMR spectra of (a) small molecule initiator **NP$_{10}$**, and (b) polymer **P1** demonstrating successful incorporation of the initiator into the polymer chain.

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).[3,4] PDMS films approximately 0.5 mm thick were cut into 8 mm diameter disks using a hole punch unless otherwise specified.

General Procedure for Preparation of PDMS Materials. A representative procedure is provided for the preparation of **PDMS$_{active}$** incorporiating naphthopyran crosslinker **NP$_{10\text{-}ene}$**. Naphthopyran crosslinker **NP10-ene** (30.4 mg) was dissolved in xylene (0.3 mL) in a 20 mL scintillation vial. Sylgard® 184 prepolymer base (1.93 g) was added and the contents were thoroughly mixed in a vortex mixer with intermittent gentle heating to form a homogeneous, orange dispersion. Sylgard® 184 curing agent (0.193 g) 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 3 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 either cut into strips with a razor blade or cut into uniform 8 mm circles using a hole punch. A similar procedure was followed for preparation of **PDMS$_{control}$** using **CON2**. A sample of PDMS without any additional naphthopyran was also prepared similarly as a blank. PDMS samples containing naphthopyran were irradiated with blue light (470 nm) for 30 min to reduce initial coloration.

VI. DFT Calculations (CoGEF)

CoGEF calculations were performed using Spartan ’18 Parallel Suite according to previously reported methods.[5,6] Ground state energies were calculated using DFT at the B3LYP/6-31G* level of theory. For each mechanophore, the equilibrium conformations of the unconstrained molecule was 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. CoGEF results are shown in Figure S5 for a truncated model reflecting the mechanophore in **P1**, while the results for a truncated model reflecting the mechanophore in **P2** with attachment at the 9-position of the naphthopyran are illustrated below in Figure S11. In contrast to the C–O bond scission reaction predicted for the naphthopyran in **P1**, the naphthopyran in **P2** is predicted to undergo cleavage of the terminal C–C bond upon full extension.

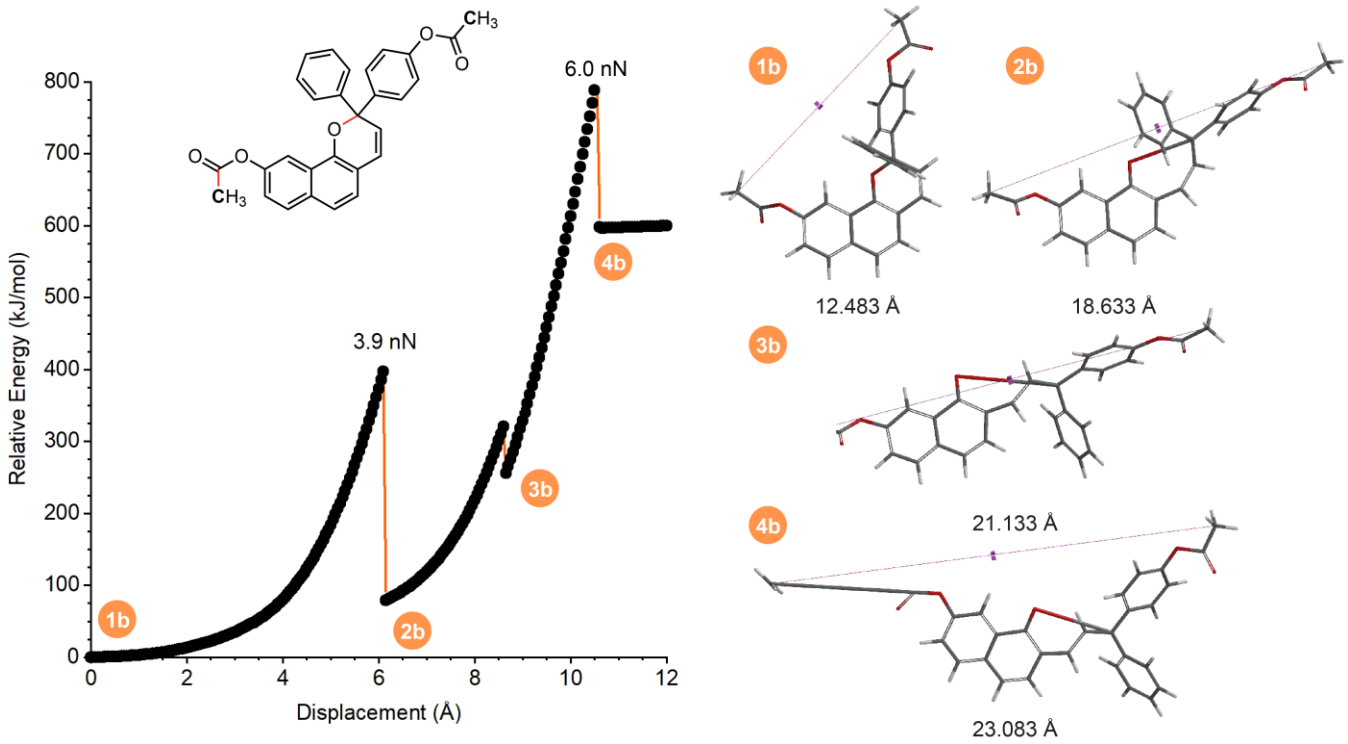


Figure S11. DFT calculations using the constrained geometries simulate external force (CoGEF) method at the B3LYP/6-31G* level of theory for a truncated model reflecting the mechanophore in polymer **P2**. CoGEF calculations predict the ring-opening reaction with an F_{max} value of 3.9 nN followed by further elongation that results in C–C bond scission at a predicted F_{max} value of 6.0 nN. The corresponding computed structures at various points of elongation are shown at right along with the associated constraint distance between the terminal methyl groups.

VII. Details for Photoirradiation and Sonication Experiments

In order to continuously monitor reaction progress by UV-vis absorption spectroscopy, a previously reported experimental setup[7,8] 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 470, 485, 510 nm, 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 470, 485, or 510 nm at each time point to account for drift during the experiments. The two traces in Figure 1b are normalized to their respective maximum absorbance values.

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.[9] 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 an ice bath and the solution was sparged with N_2 for 30 min. The system was then maintained under an inert atmosphere for the duration of

sonication. Continuous sonication at 20 kHz (8.77 ± 0.19 W/cm^2) was initiated and run for approximately 5 min to allow the temperature inside the reaction vessel to equilibrate to 15–20 °C, 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.[10] The entire system was kept in the dark for the duration of the experiment.

General Procedure for Photoirradiation Experiments. To monitor thermal reversion of the photochemically generated merocyanine, a two-sided quartz cuvette was charged with a solution of the polymer in THF (2.0 mg/mL, 1.0 mL, with 1 mM BHT) and then exposed to a UV light source (λ = 311 nm) positioned 2 in away for either 10 s or 10 min (see Figure S3). The cuvette was immediately placed into the spectrometer and absorption was monitored over time. To monitor the photochemical ring-opening reaction, a four-sided quartz cuvette was fitted with a septum with holes for inlet and outlet tubes. The cuvette was charged with a solution of the polymer in THF (2.0 mg/mL, 3.0 mL, with 1 mM BHT). An additional 6.2 mL of polymer solution was pumped into the dead space of the circulatory setup. Teflon inlet and outlet tubes were inserted into the solution in the cuvette through the septum and the pump was engaged to start the flow of solution through the system. Photoirradiation experiments were performed at room temperature (19–22 °C). The cuvette was then exposed to a UV light source (λ = 311 nm) positioned 2 in away. The total volume of the apparatus was 9.2 mL, with 3.0 mL contained in the cuvette. At any given time, only 3.0 mL of solution (out of the total 9.2 mL) was inside of the cuvette and exposed to UV irradiation. The entire system was protected from outside light for the duration of the experiment.

VIII. Description of Control Experiments

Sonication of lower molecular weight polymer $\mathbf{P1_{83}}$. To explore whether a persistent colored species is still generated at lower forces than those experienced by **P1** (M_n = 178 kDa, $Đ$ = 1.13), a lower molecular weight PMA polymer with the same chain-centered mechanophore was synthesized (**$\mathbf{P1_{83}}$**, M_n = 83.1 kDa, $Đ$ = 1.15). **$\mathbf{P1_{83}}$** was subjected to ultrasound-induced mechanical force for 2 h under identical conditions as those used for **P1**, and then the solution was monitored for 5 h after cessation of ultrasound. As shown below in Figure S12, minimal reversion is observed after sonication was stopped as evidenced by the nearly constant absorbance monitored at 470 and 510 nm. These results indicate that at lower forces transduced by shorter polymer chains,[11] generation of the permanent merocyanine species is still nearly exclusively observed. Note that only partial conversion is achieved after sonication for 2 h due to the slower reaction kinetics compared to that of **P1**.

Sonication of chain-end functional control polymer P3. To confirm that the ring-opening and ester C(O)–O cleavage reactions observed for **P1** containing a chain-centered 2*H*-naphthopyran mechanophore were due to mechanical force, a chain-end functional control polymer (**P3**) was synthesized and exposed to ultrasound-induced mechanical force under identical conditions. As shown in Figure S1, no changes in absorption were detected during sonication of chain-end functional control polymer **P3**, supporting that the ring-opening reaction is mechanically mediated.[12] In order to rule out that the ester C(O)–O cleavage is a thermally or otherwise non-mechanically mediated process, a second control experiment was devised. Chain-end functional control polymer

P3 was first irradiated with UV light (311 nm, 5 min) as a 52.4 mg/mL solution, and subsequently injected into the sonication vessel and subjected to continuous ultrasonication as described above. As shown below in Figure S13, the photochemically generated merocyanine steadily reverts during sonication as evidenced by the attenuation of visible absorption. In addition, a shift in λ_{max} is not observed, indicating that the C(O)–O ester bond is not cleaved.

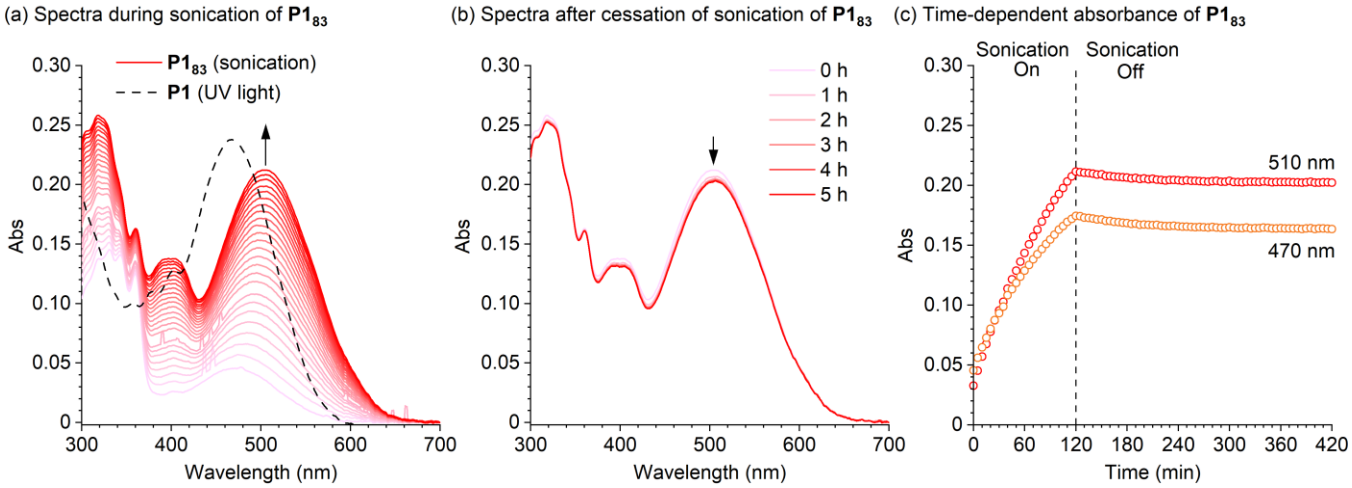


Figure S12. Characterization of ultrasound-induced mechanical activation and subsequent thermal reversion for a lower molecular weight polymer (**P1$_{83}$**) with a chain-centered 2H-NP mechanophore analogous to **P1**. (a) UV-vis absorption spectra acquired at regular intervals during ultrasound-induced mechanical activation of **P1$_{83}$** (pink and red solid traces) exhibit an increase in visible absorption that is significantly bathochromically shifted compared to the photochemical merocyanine product. Note that only partial conversion is achieved after sonication for 2 h. The absorption spectrum of **P1** after irradiation with UV light (311 nm, 10 min) is included for comparison with a λ_{max} of 470 nm (black dashed trace). (b,c) Spectra and time-dependent absorbance at 470 and 510 nm acquired over a period of 5 h after cessation of ultrasound illustrating minimal thermal reversion.

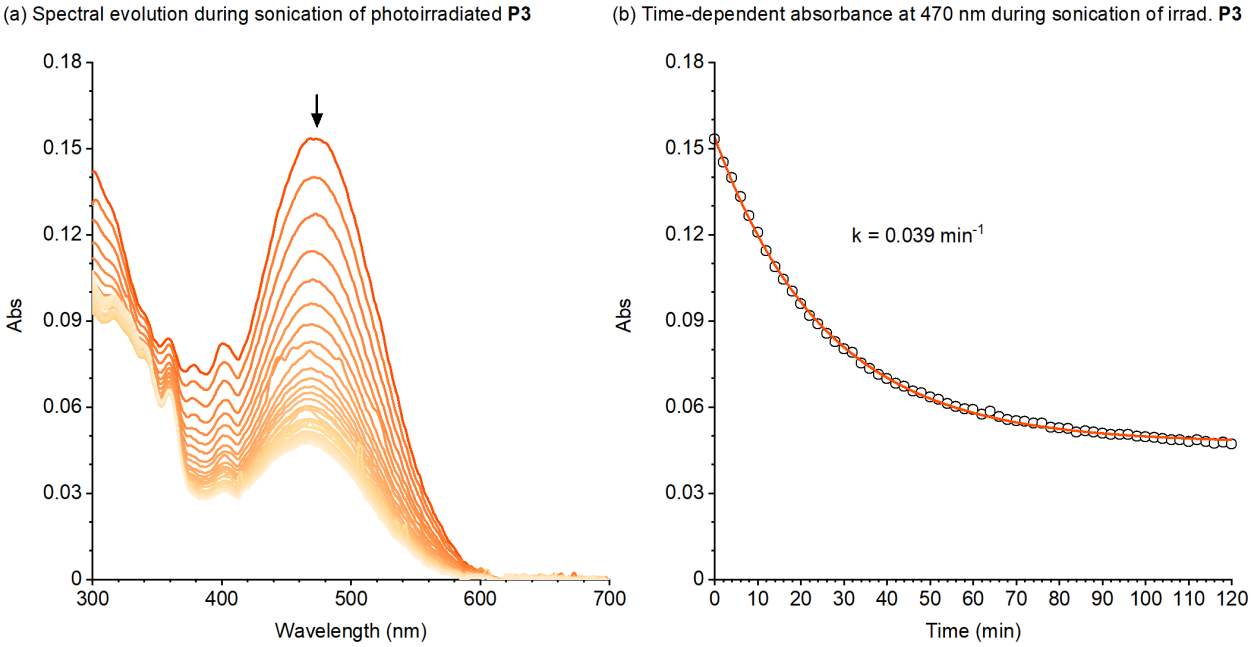


Figure S13. Sonication of chain-end control polymer **P3** after initial photochemical activation with UV light does not result in a permanent merocyanine. A solution of **P3** was irradiated with UV light (311 nm, 5 min) and subsequently subjected to ultrasound. In addition, no bathochromic shift in λ_{max} is observed, which would occur upon ester C(O)–O bond cleavage.

IX. Kinetic Analysis

Determination of reaction kinetics from UV-vis spectroscopy. The kinetics of mechanochemical product formation, or thermal ring-closure after UV irradiation, was evaluated by fitting time-dependent absorbance traces at λ_{max} to first-order exponential decay using OriginPro 2020. For tracking mechanochemical product formation, the data is fit to eq S1:

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

For tracking thermal ring-closure (UV-vis) or ultrasound-induced mechanical chain scission (GPC-RI), the time-dependent signal is fit to eq S2:

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

Determination of polymer chain scission kinetics from GPC measurements. To determine relative rates of polymer chain scission, sonication experiments were performed on **P1** and **P2**, during which aliquots (1 mL) were taken at regular time intervals for GPC analysis. Aliquots were removed from the sonication reactions via a N_2-flushed syringe during continuous sonication as described in section VI, filtered through a 0.45 µm PTFE syringe filter, and submitted for GPC analysis. GPC traces for the ultrasound-induced chain scission of **P1** and **P2** are shown in Figure S14 . GPC traces were normalized by area and the rate of chain scission was determined by plotting the attenuation of the RI response at the retention time (t_R) corresponding to the initial polymer peak as a function of sonication time. The time dependent GPC-RI response is fit to eq S2 to determine the rate of chain scission.[13]

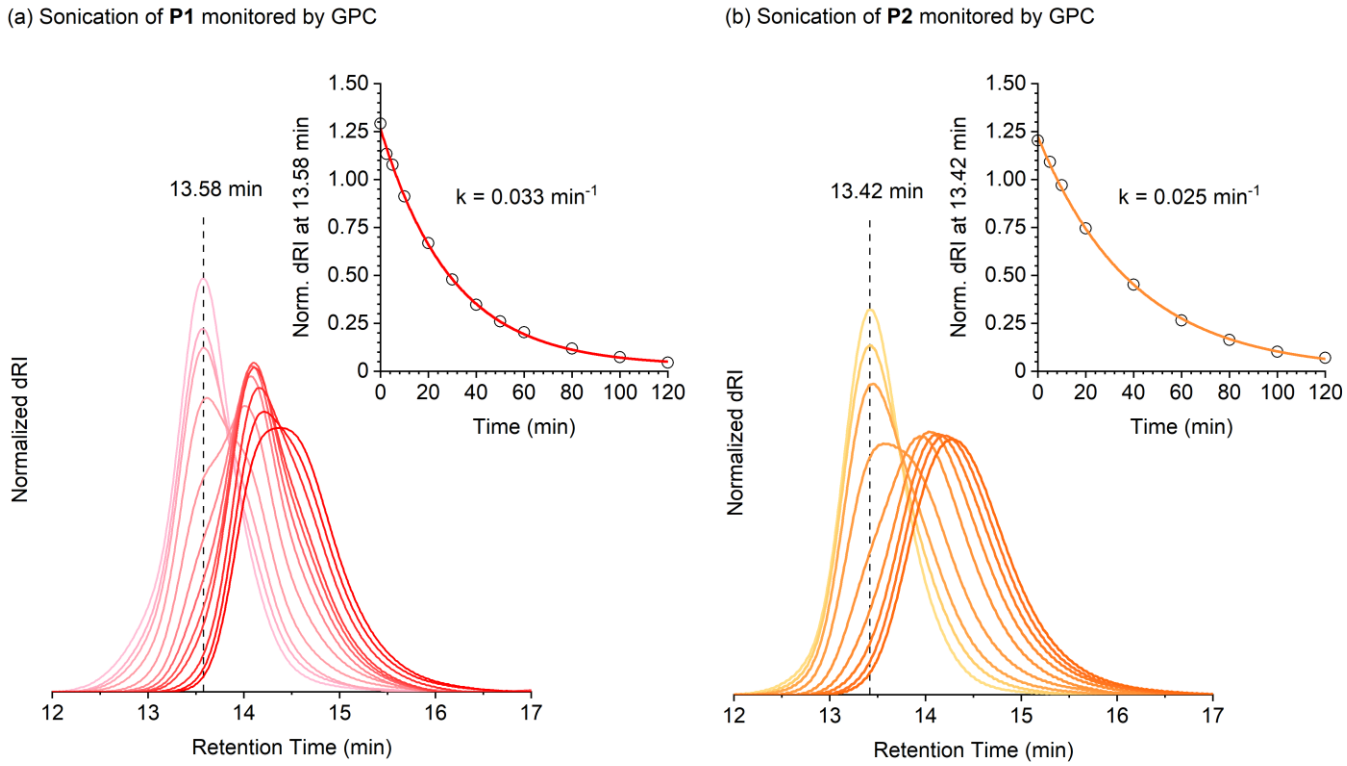


Figure S14. Ultrasound-induced mechanical chain cleavage of **P1** and **P2** monitored by GPC. (a) The rate of chain scission for **P1** determined from time-dependent attenuation of the RI signal at t_R = 13.58 min was found to be 0.033 min^{-1}. (b) The rate of chain scission for **P2** was found to be 0.025 min^{-1} by monitoring the RI signal at t_R = 13.42 min.

X. Characterization of Activation and Fading in PDMS Materials

PDMS films were activated mechanically either manually in tension or by repeated strikes with a hammer with the film placed between sheets of weigh paper on a hard flat surface, or photochemically by irradiation with UV light (λ_{max} = 365 nm). Films were placed between two vertical glass slides and photographed against a white background. Digital images were acquired in RAW mode with a Nikon D3200 DSLR camera. Images were cropped and standardized to a white balance temperature of 5300 and tint of +34 and an exposure of +1.50 in Adobe Photoshop using the Adobe Color profile. Reflectance measurements were performed to spectroscopically characterize the color of the PDMS materials. Spectra were acquired using an integrating sphere accessory to account for variation in surface roughness and scattering. Samples were loaded against a black sample holder. Reflectance spectra were normalized by defining the maximum and minimum value between 450 and 800 nm as 1 and 0, respectively (see Figure S15). In order to make a clear comparison to solution-phase absorption data, reflectance data are plotted in Figure 4 as the inverse, i.e., "1 − norm. reflectance".

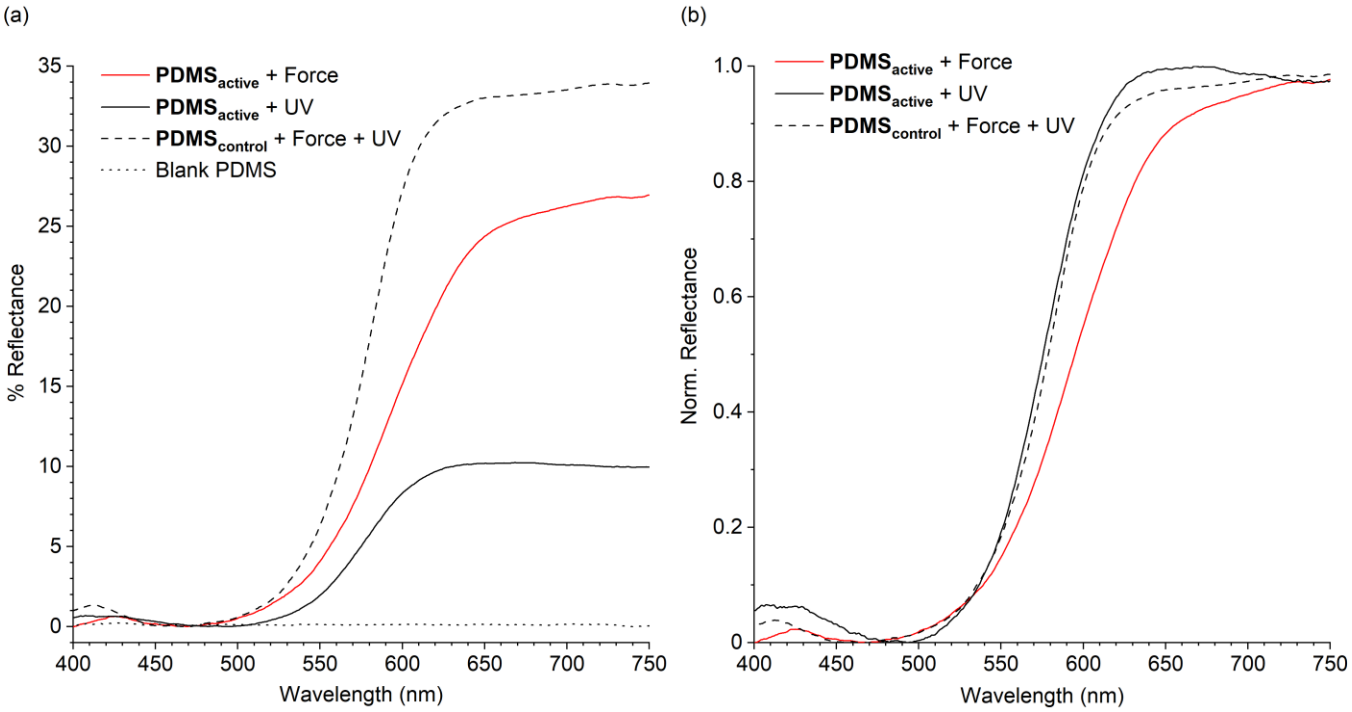


Figure S15. (a) UV-vis reflectance spectra acquired using an integrating sphere for samples of **PDMS$_{active}$** and **PDMS$_{control}$** after being subjected to combinations of mechanical force by repeated hammering and/or irradiation with UV light (365 nm). These are the same spectra depicted in Figure S8. The reflectance spectrum of a blank PDMS sample that does not contain naphthopyran is also shown. (b) The reflectance spectra shown in panel (a) after normalization to define the maximum value between 450–800 nm as 1.

XI. References

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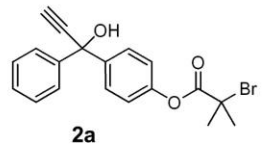
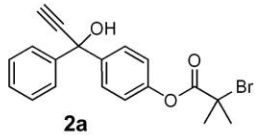


2a

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



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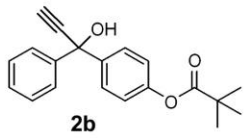

2b

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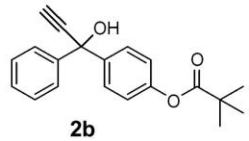

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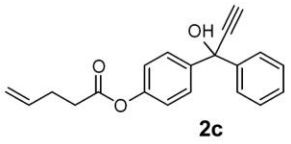

2c

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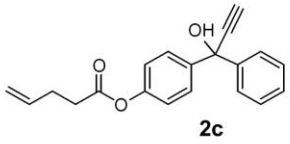

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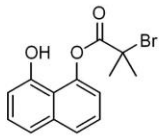

3a

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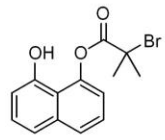
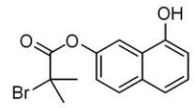


3a

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



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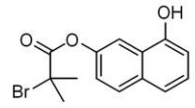
^{1}H (400 MHz, acetone-d_6)



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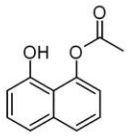

3c

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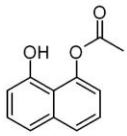

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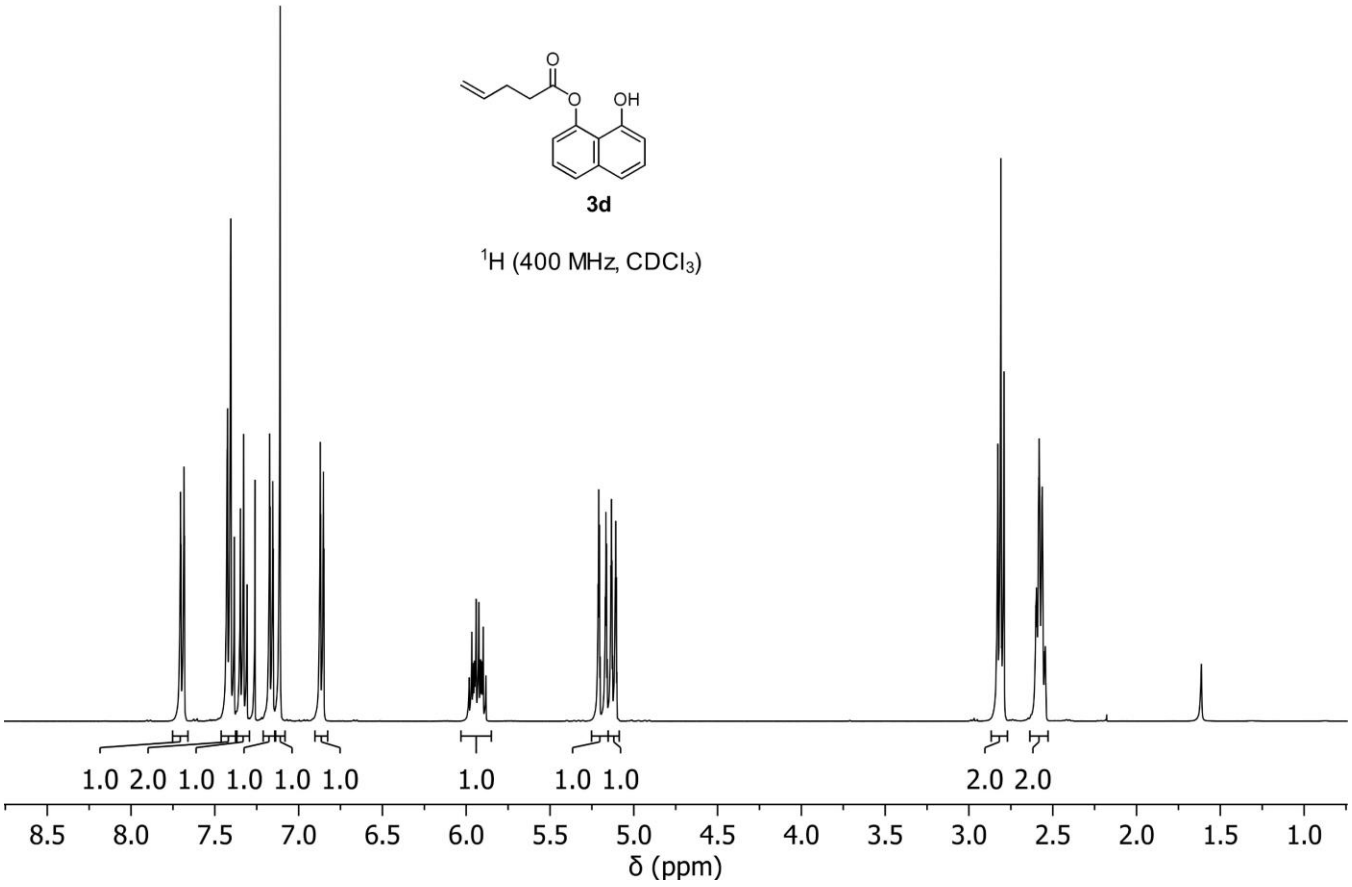
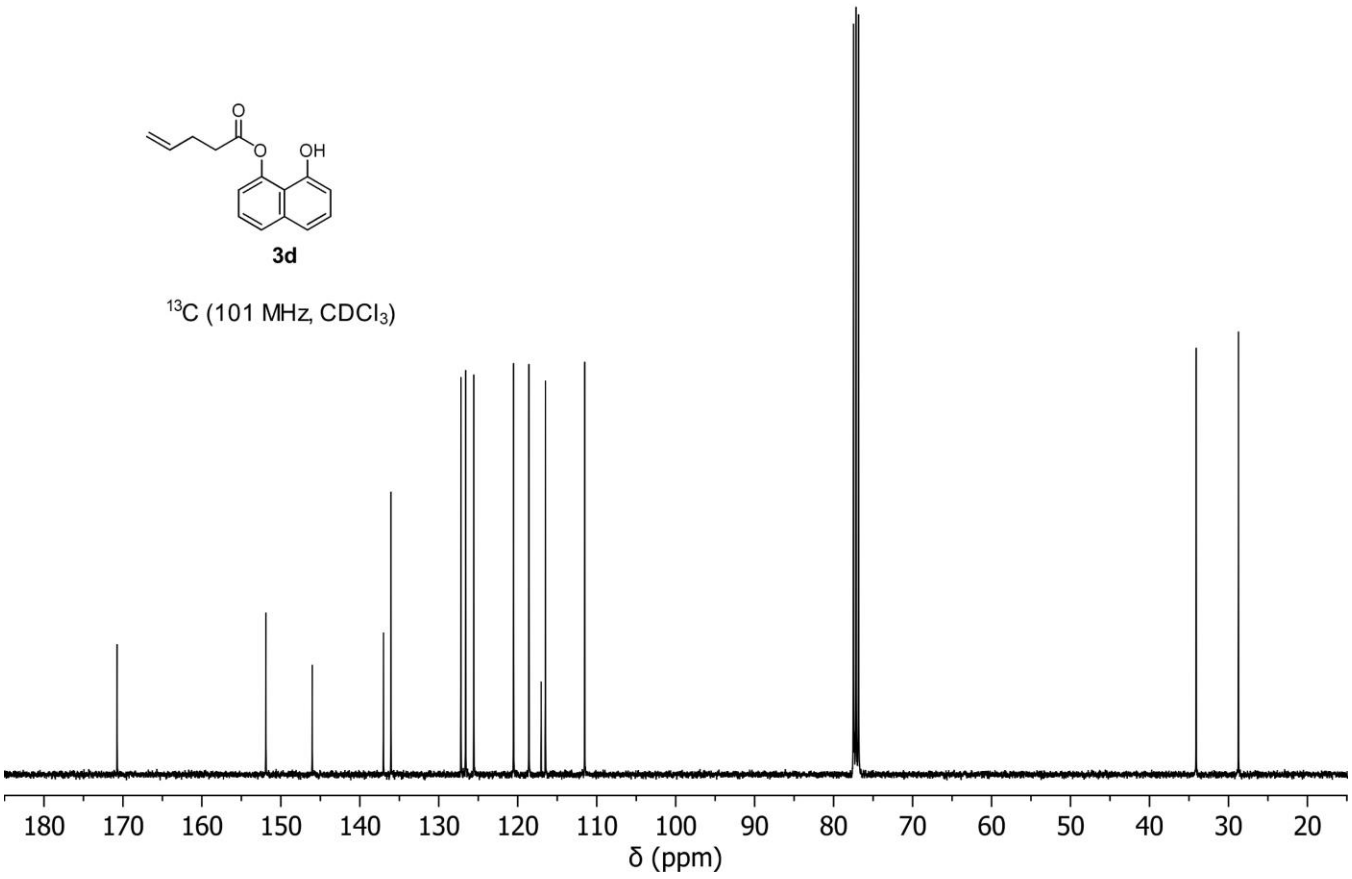
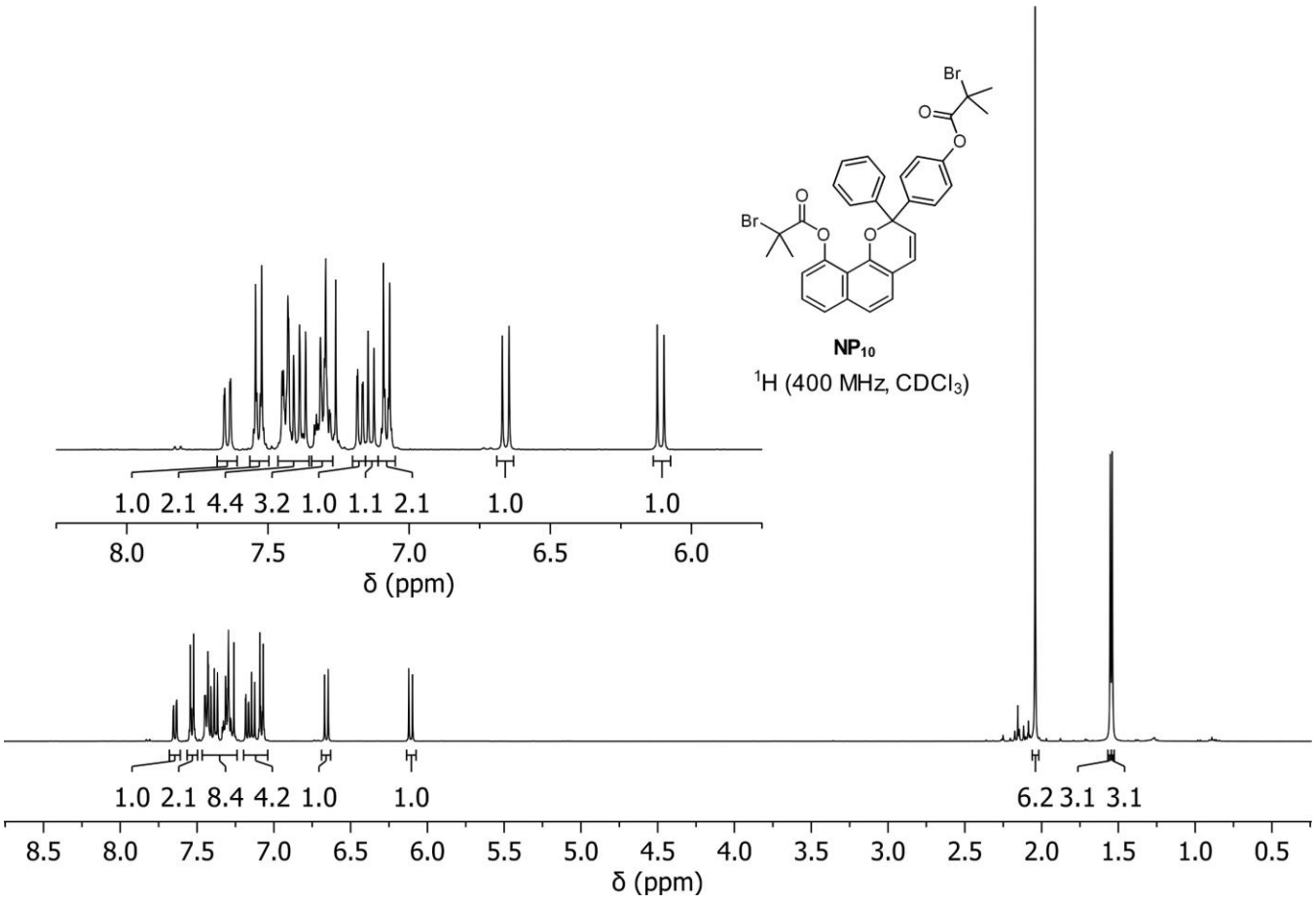
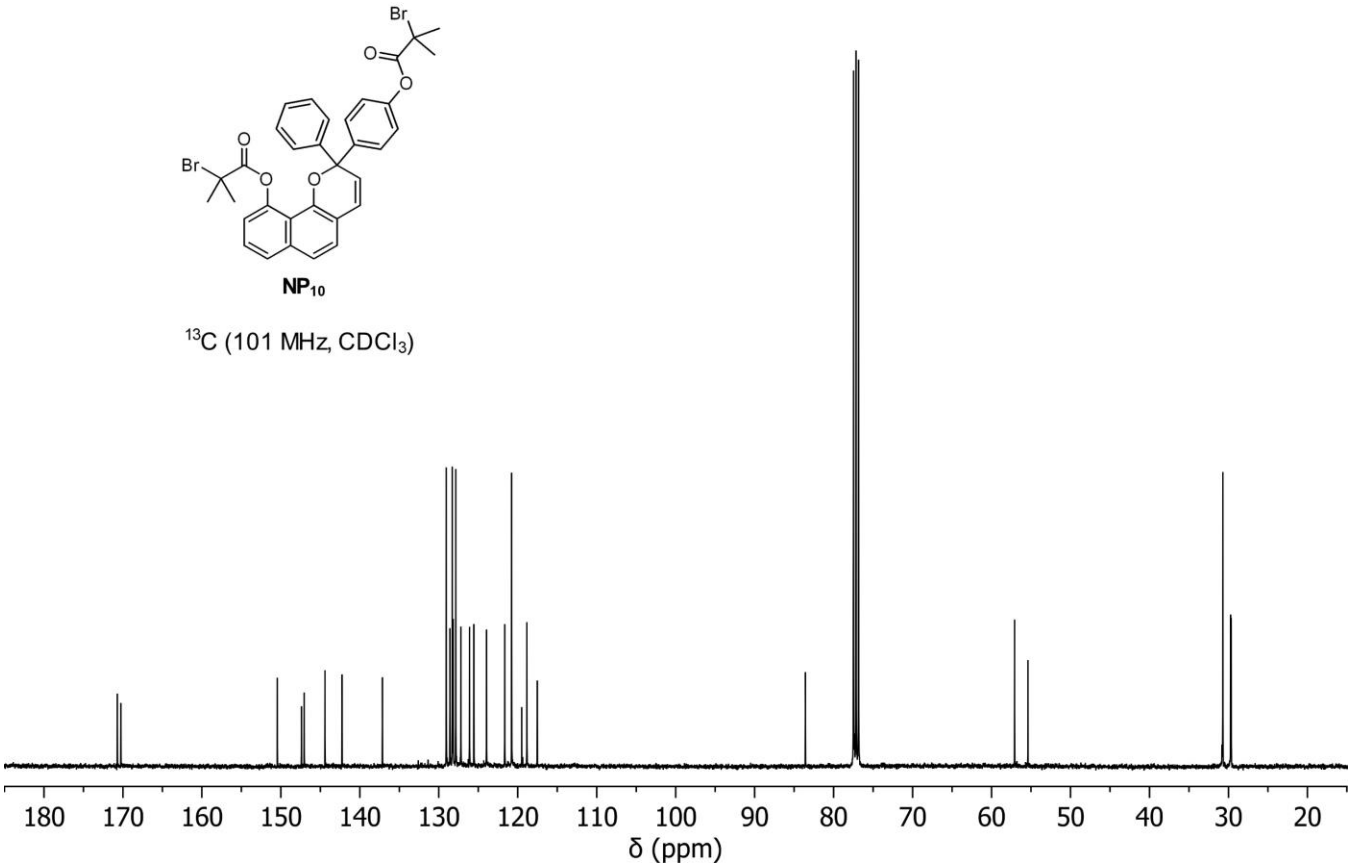
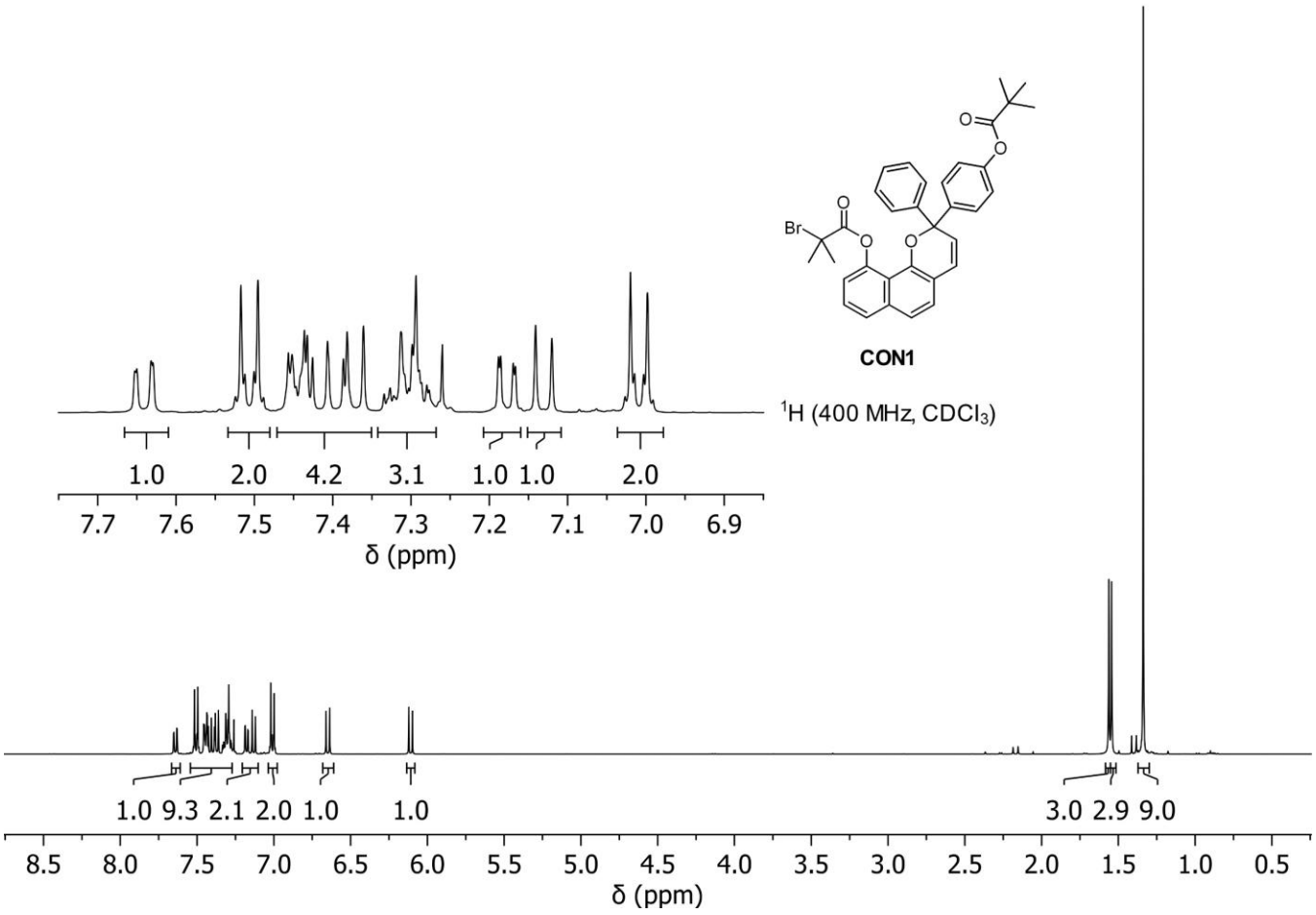

3d
^{1}H (400 MHz, $CDCl_3$)
1.0 2.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0 2.0 2.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
δ (ppm)


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


Br
O
O
Br
O
O
O
NP10
1H (400 MHz, CDCl3)
1.0 2.1 4.4 3.2 1.0 1.1 2.1 1.0 1.0
8.0 7.5 7.0 6.5 6.0
δ (ppm)
1.0 2.1 8.4 4.2 1.0 1.0
6.2 3.1 3.1
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 0.5
δ (ppm)


Br
O
O
Br
O
O
NP10
13C (101 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
δ (ppm)


CON1
^{1}H (400 MHz, CDCl$_3$)
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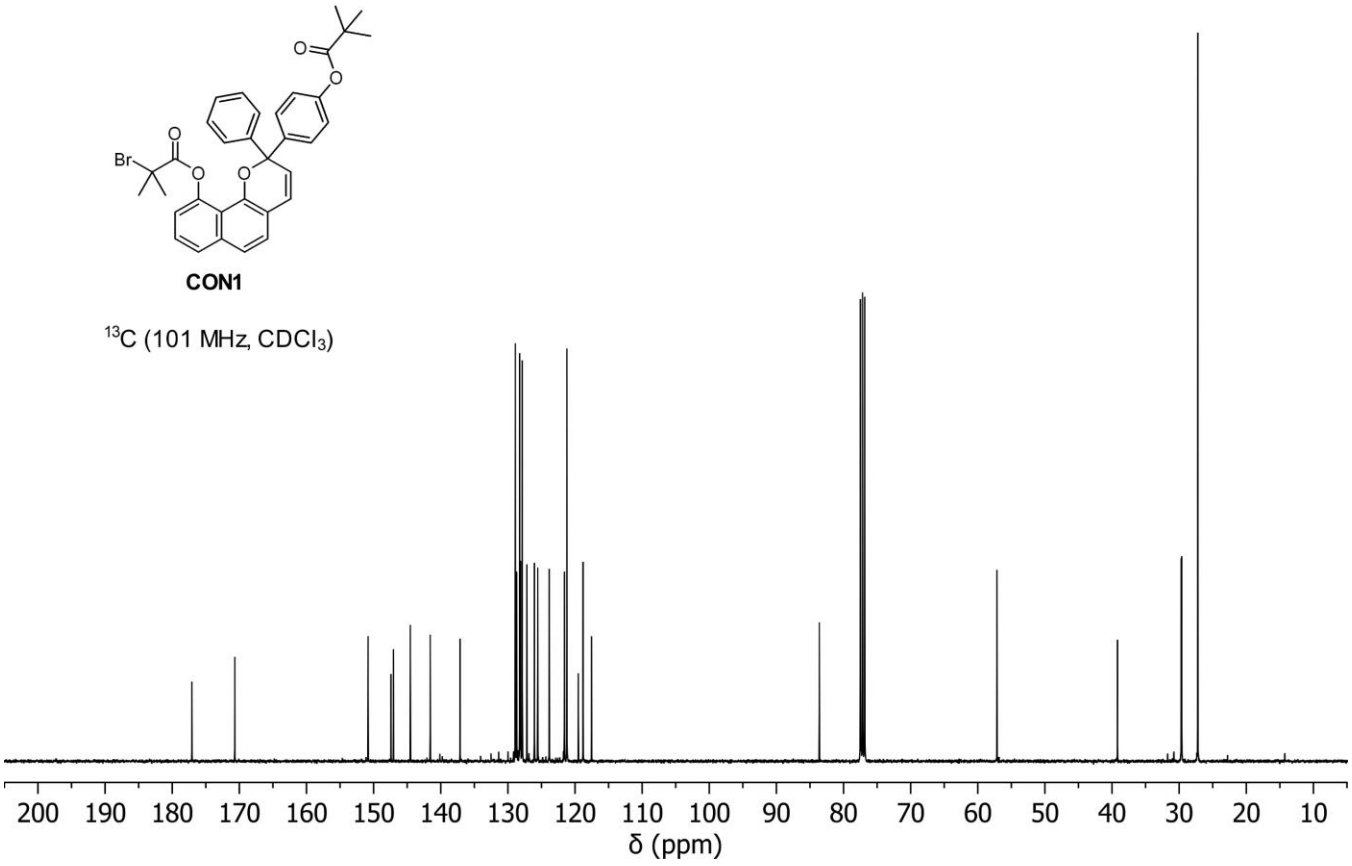
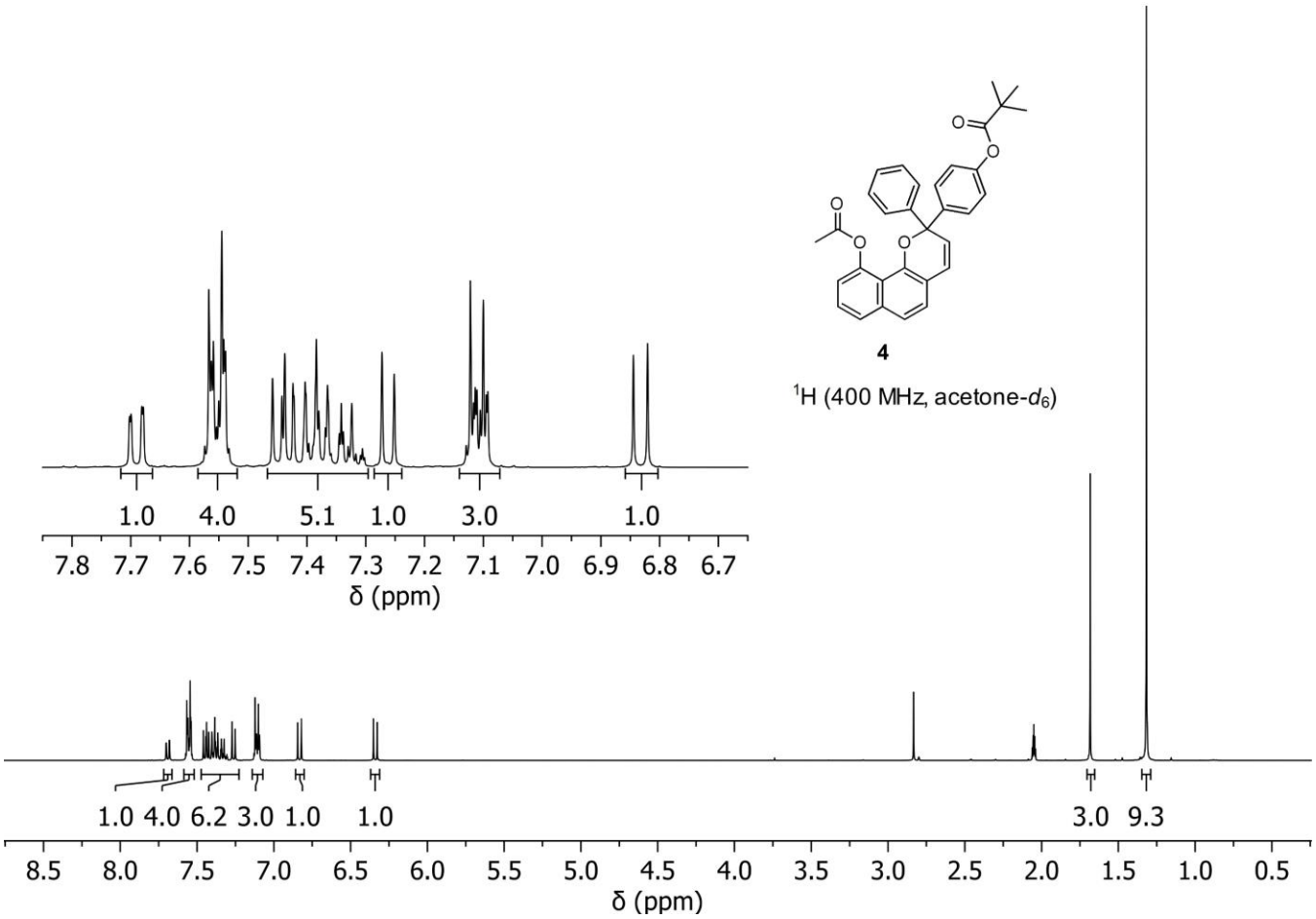
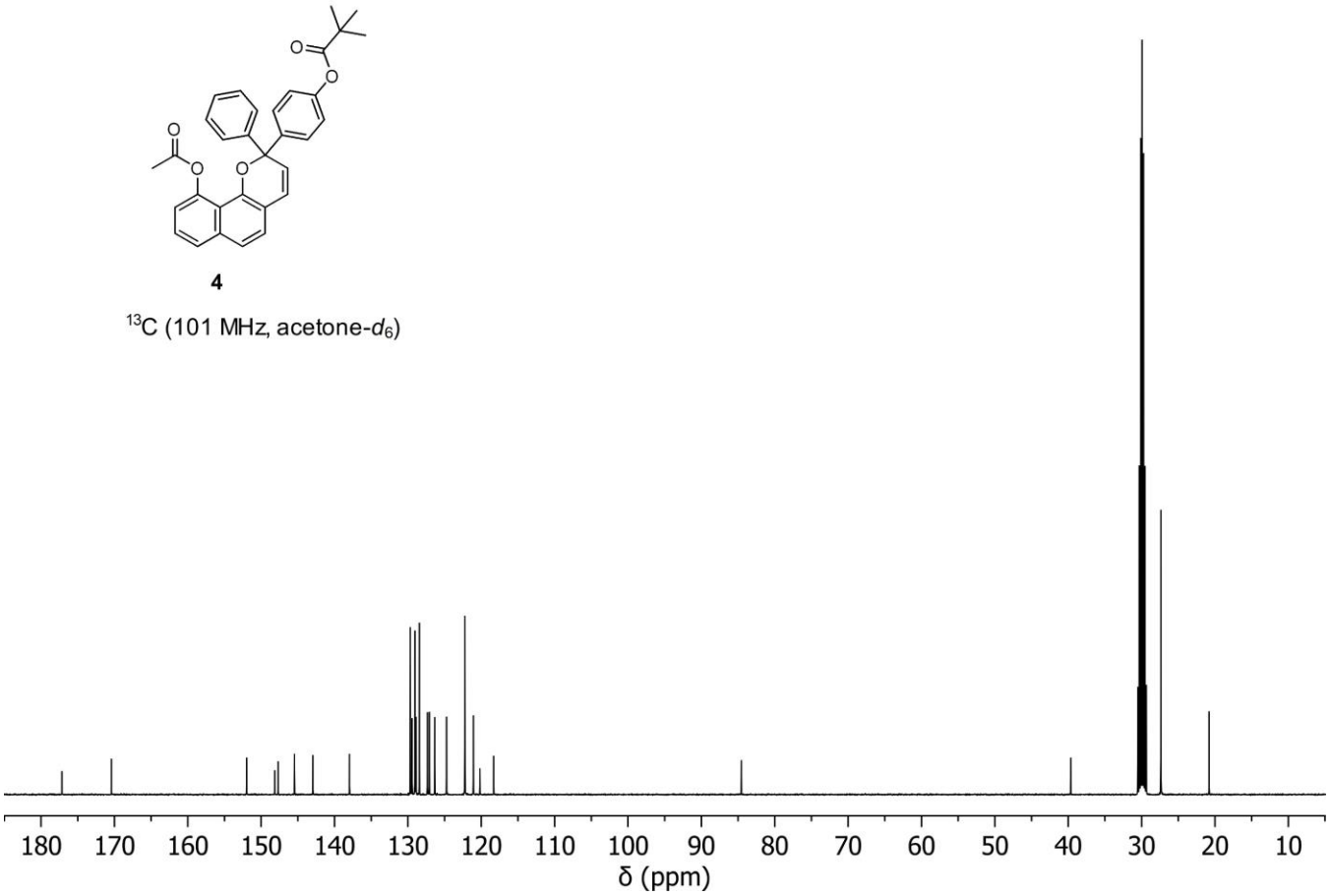
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
δ (ppm)
1.0 9.3 2.1 2.0 1.0 1.0
3.0 2.9 9.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
δ (ppm)


CON1
^{13}C (101 MHz, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ (ppm)



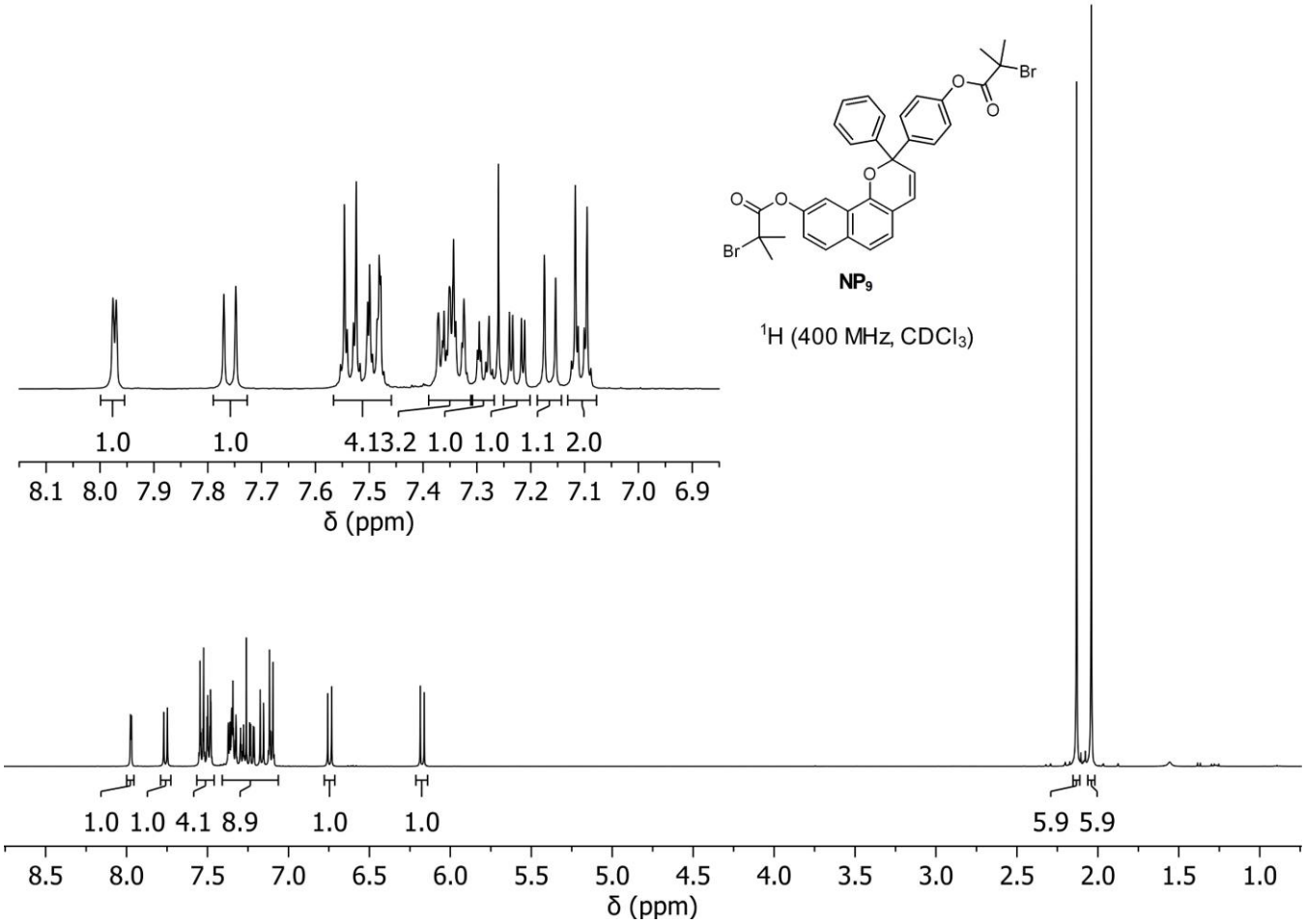
4

^{1}H (400 MHz, acetone-d_6)



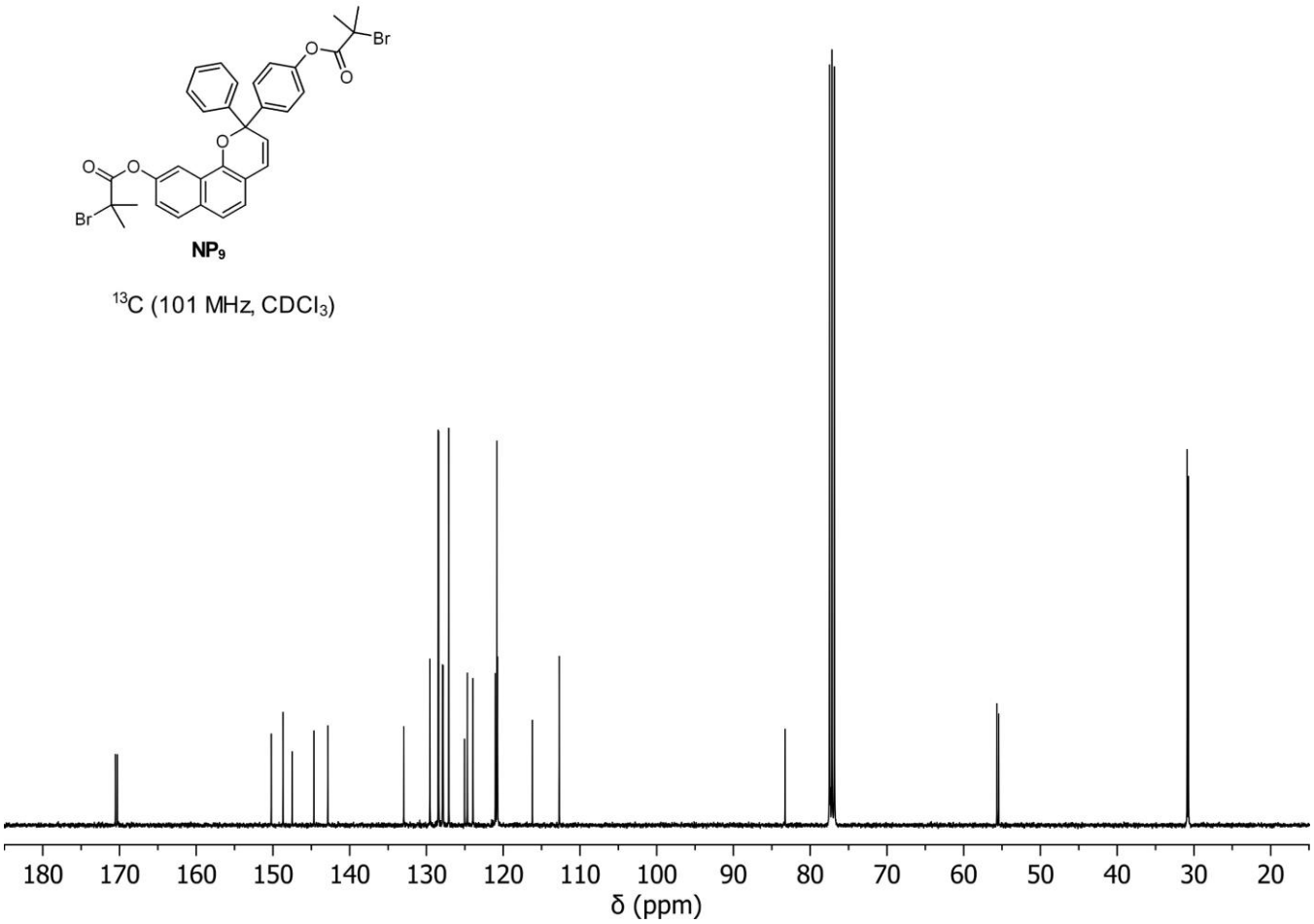
4

^{13}C (101 MHz, acetone-d_6)



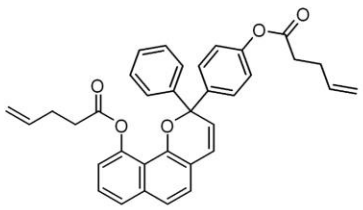
NP$_9$

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



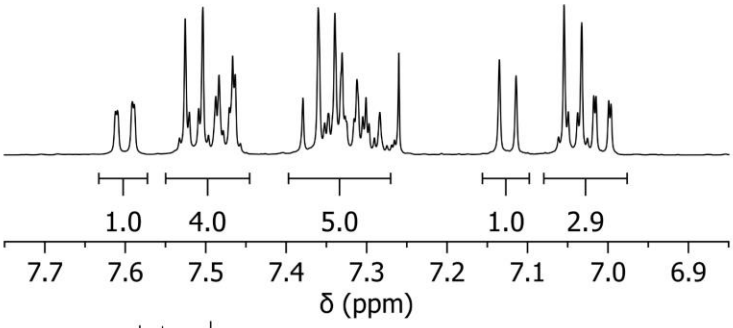
NP$_9$

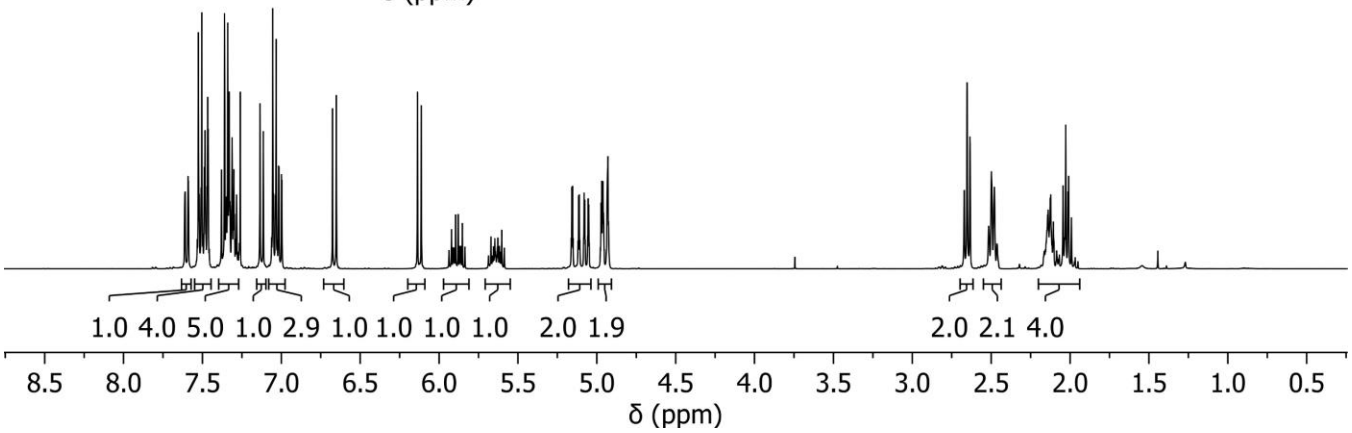
^{13}C (101 MHz, $CDCl_3$)

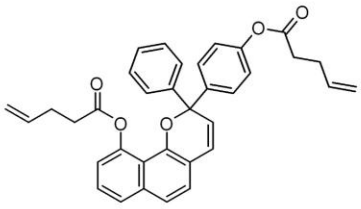


NP$_{10\text{-ene}}$

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

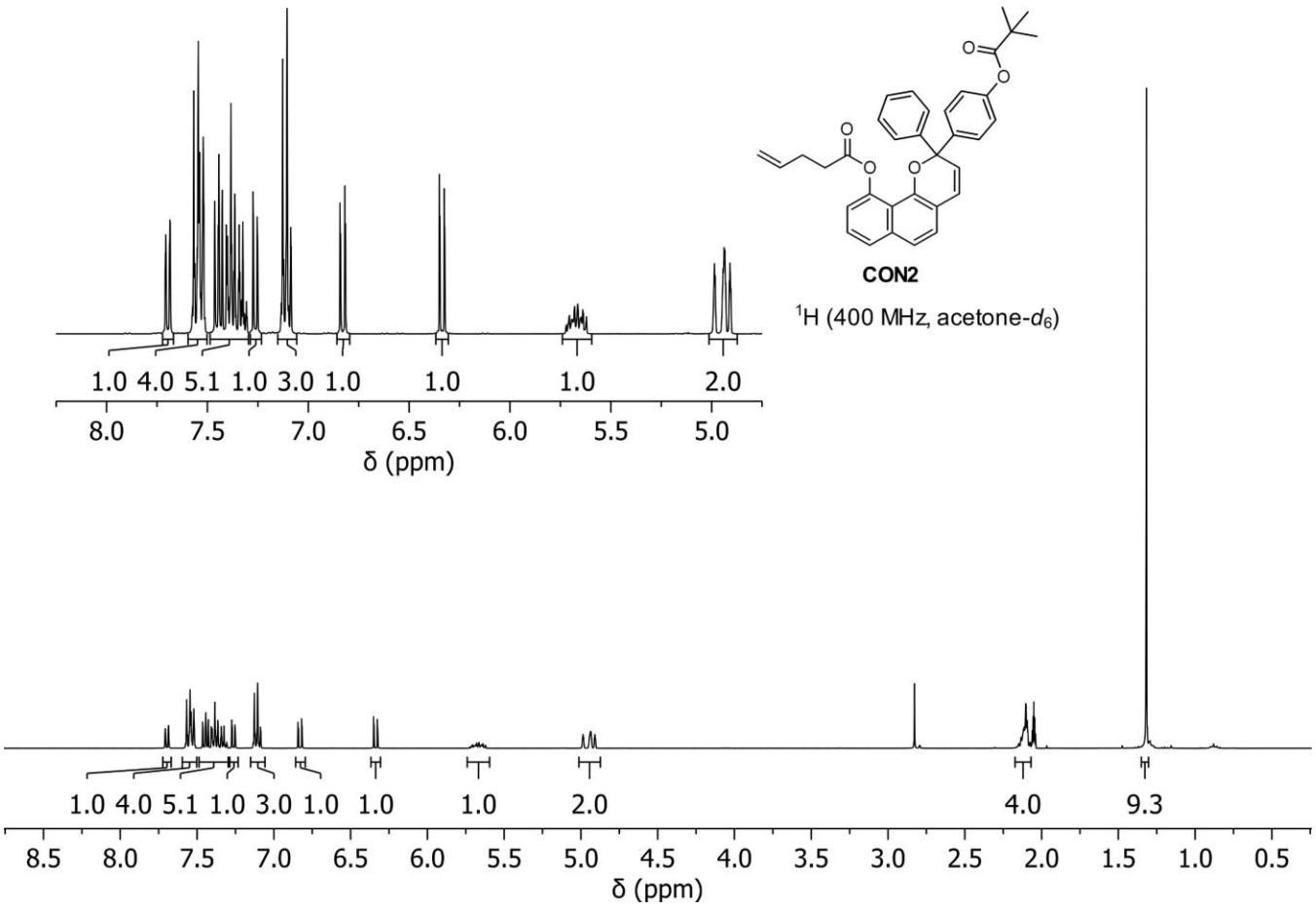






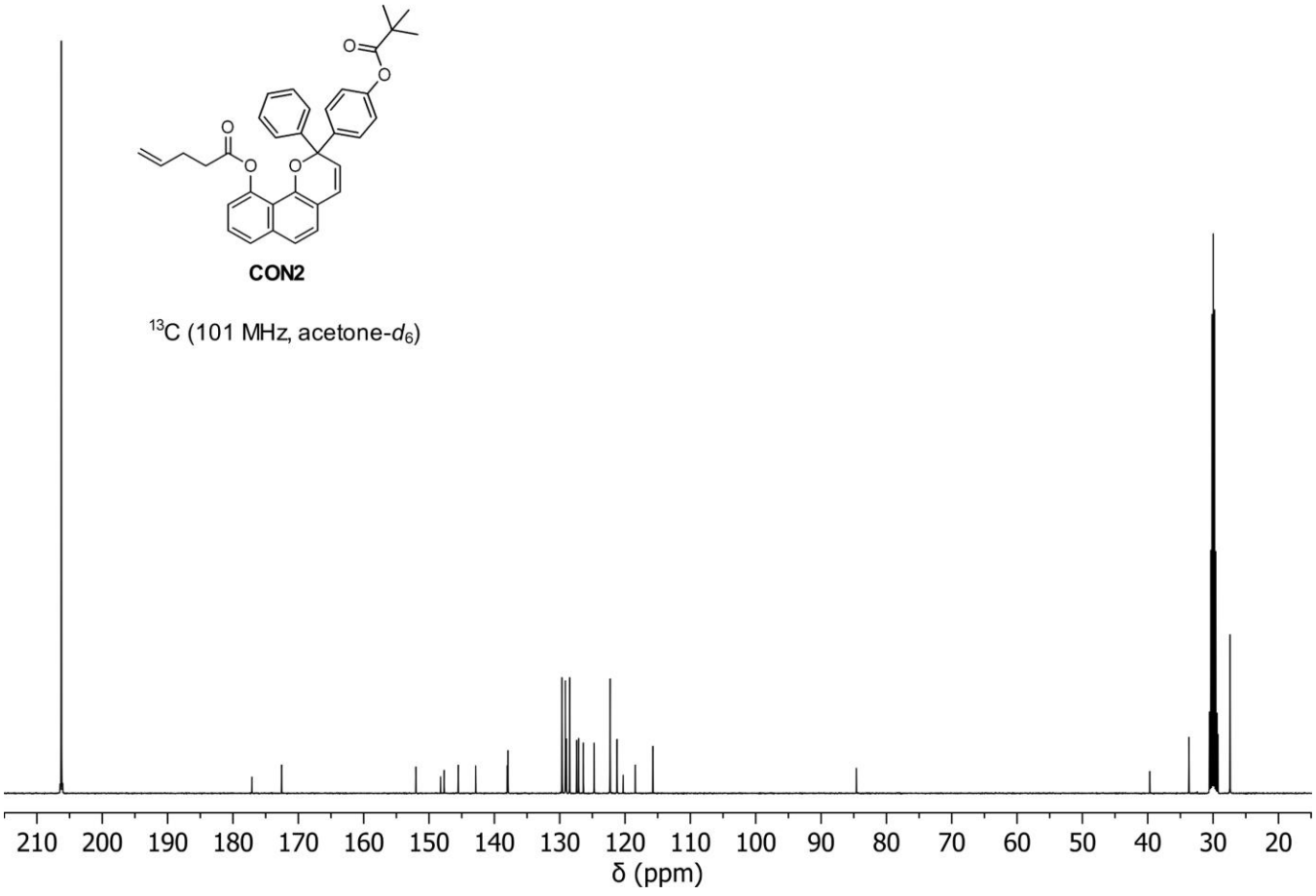
NP$_{10\text{-ene}}$

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



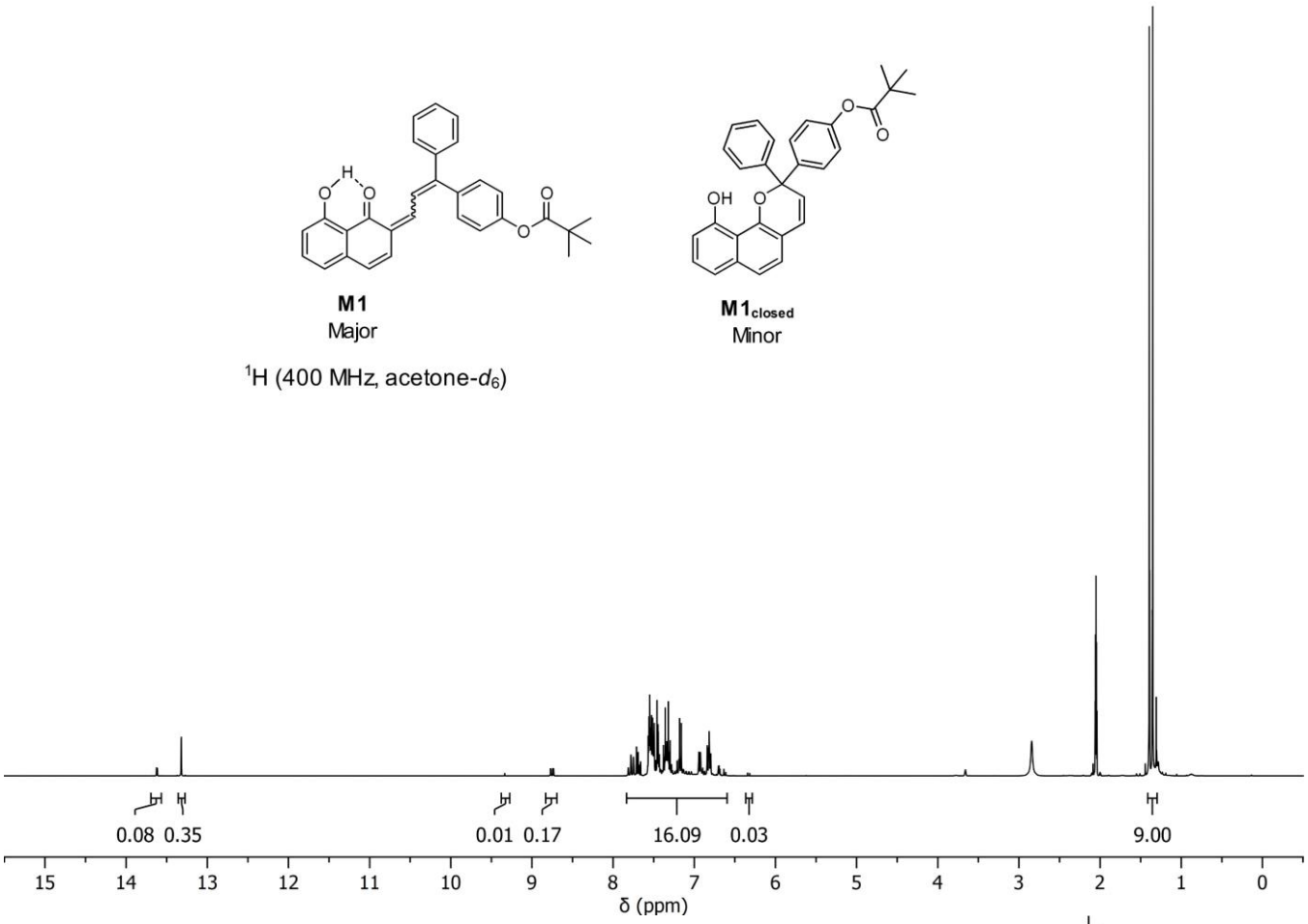
CON2

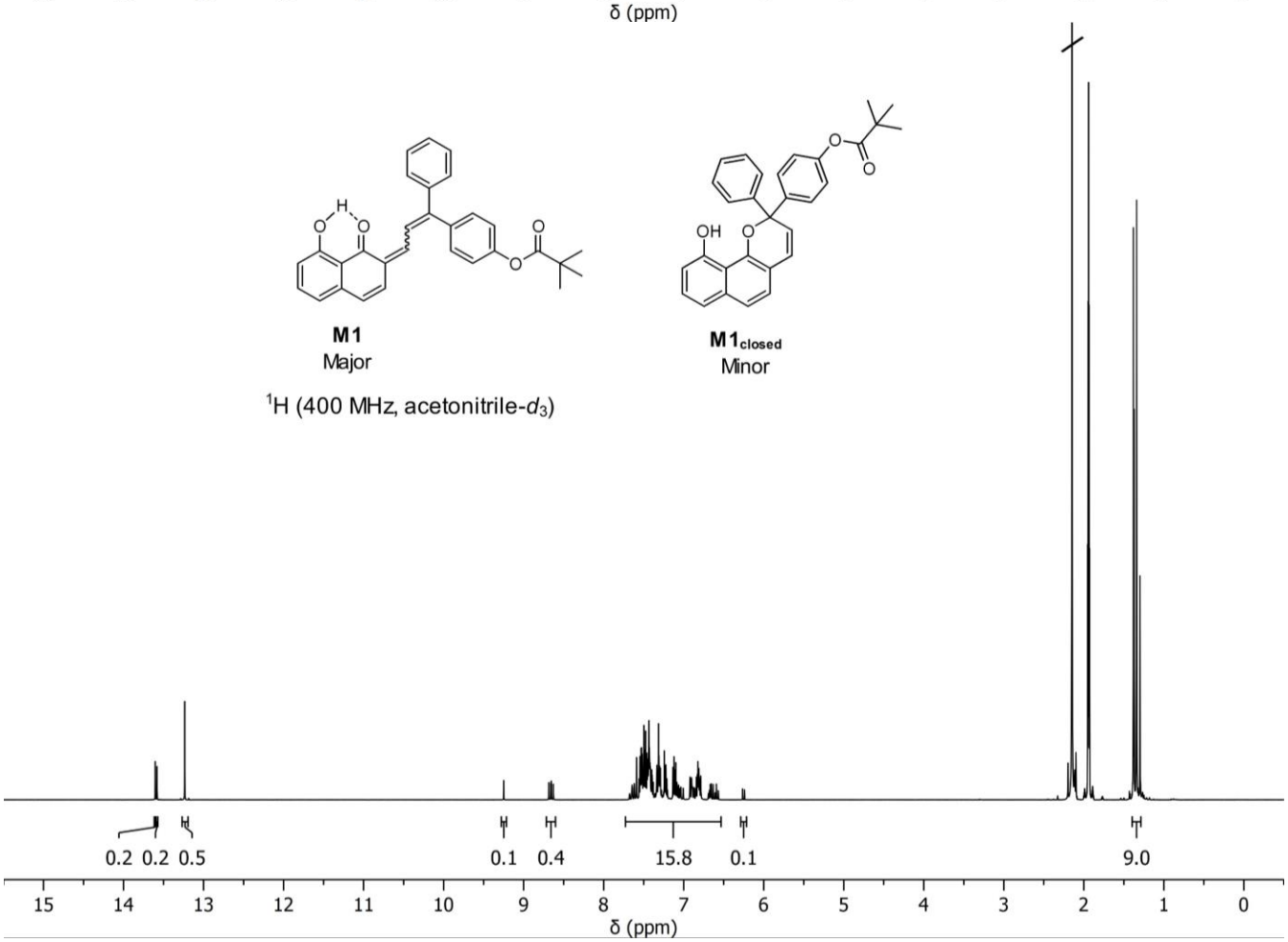
^{1}H (400 MHz, acetone-d_6)

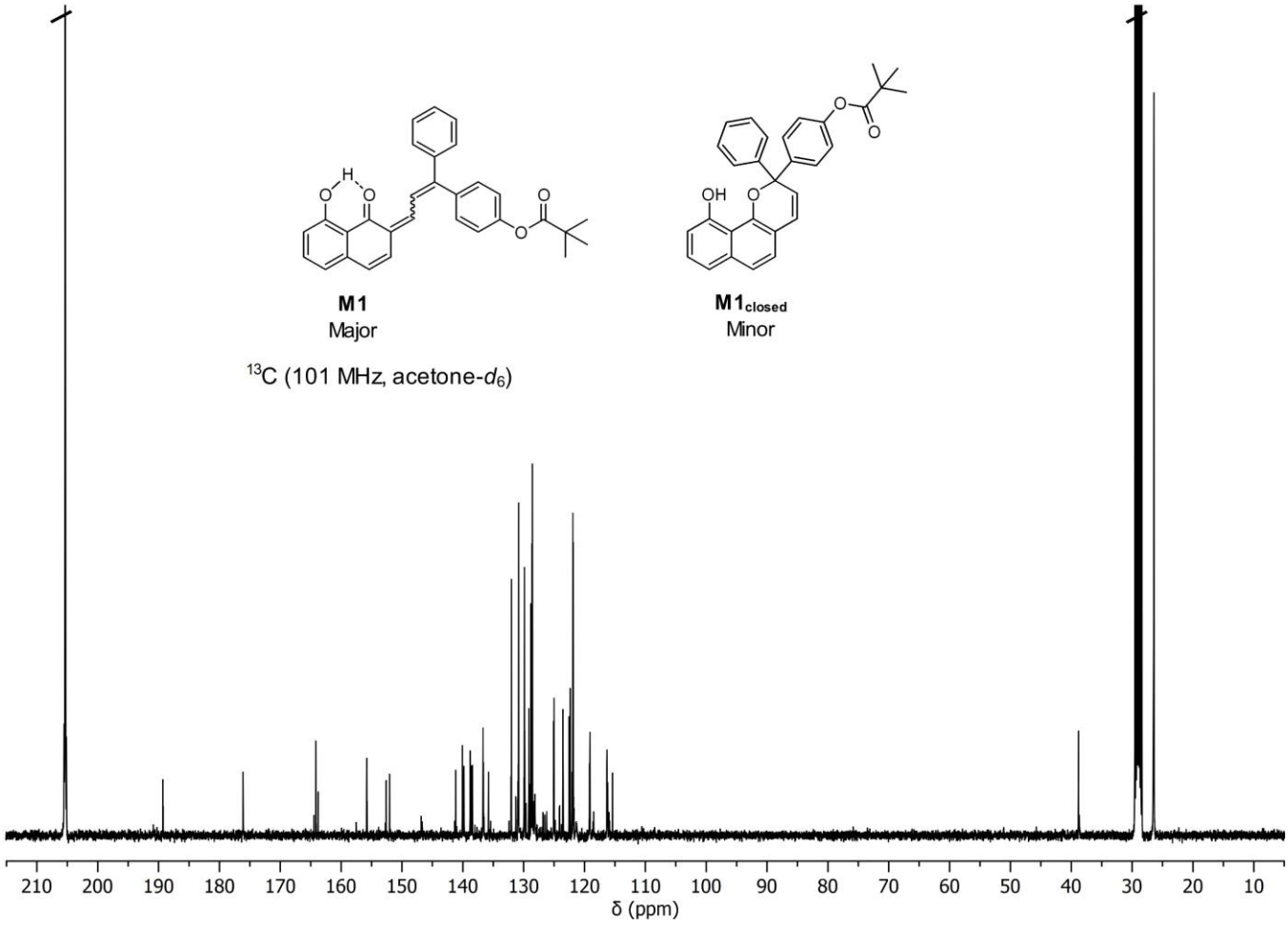


CON2

^{13}C (101 MHz, acetone-d_6)


M1
Major
M1closed
Minor
1H (400 MHz, acetone-d6)
0.08 0.35
0.01 0.17
16.09
0.03
9.00
δ (ppm)


M1
Major
M1closed
Minor
1H (400 MHz, acetonitrile-d3)
0.2 0.2 0.5
0.1 0.4
15.8
0.1
9.0
δ (ppm)


M1
Major
M1closed
Minor
13C (101 MHz, acetone-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ (ppm)