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Electronic Supplementary Information for

Mechanochemical Activation of an Indole-Fused 2*H*-Benzopyran Generates an Acidochromic Merocyanine Dye Enabling Multicolor Chromomorphic Materials

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I. Materials and Methods

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 soaked in 1 M HCl for 30 min and then rinsed consecutively with water and acetone immediately prior to use. Dry solvents were obtained from a Pure Process Technology solvent purification system. All reactions were performed under a N_2 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 or a 600 MHz Varian spectrometer with 5 mm triple resonance inverse probe. All ^{1}H NMR spectra are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), acetone (2.05 ppm), dichloromethane (5.32 ppm), or dimethyl sulfoxide (2.50 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), acetone (206.26 ppm), dichloromethane (53.84 ppm), or dimethyl sulfoxide (39.52 ppm).

High resolution mass spectra (HRMS) were obtained via direct injection on an Agilent 1260 Infinity II Series HPLC coupled to a 6230 LC/TOF system in electrospray ionization (ESI+) mode.

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). A Thermo Scientific EK45 Immersion Cooler (part #3281452) was used to maintain a constant temperature bath for sonication experiments. 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 white light was carried out using a 13 W broadband fluorescent lamp (Bayco Model BA-506) filtered through a 425 nm bandpass filter.

Compounds **4**, **8**, 2-tetrahydropyranyloxy-1-iodoethane, and *N*-methyl-4-hydroxycarbazole were synthesized following the procedures reported in the literature.[1–3]

II. Supplementary Figures

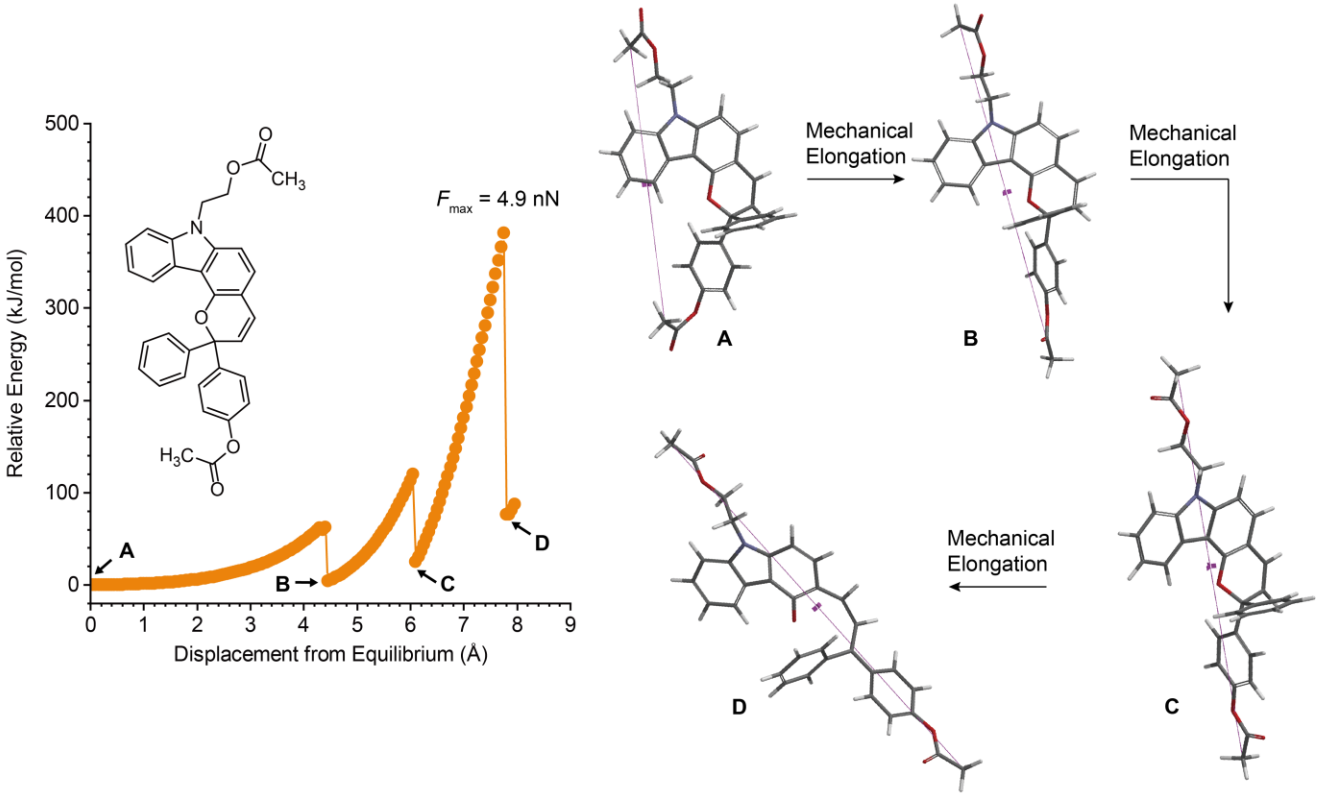


Figure S1. Density functional theory (DFT) calculations using the constrained geometries simulate external force (CoGEF) method performed on an indole-fused benzopyran models predict a ring-opening reaction upon mechanical elongation. The structures at various points in the CoGEF profile are shown at right, corresponding to the positions labeled A–D. Calculations were performed at the B3LYP/6-31G* level of theory. The carbon atoms of the terminal methyl groups were used to define the distance constraint. The features at ~4.4 and ~6.0 Å displacement associated with the formation of structures B and C, respectively, correspond to minor conformational changes.

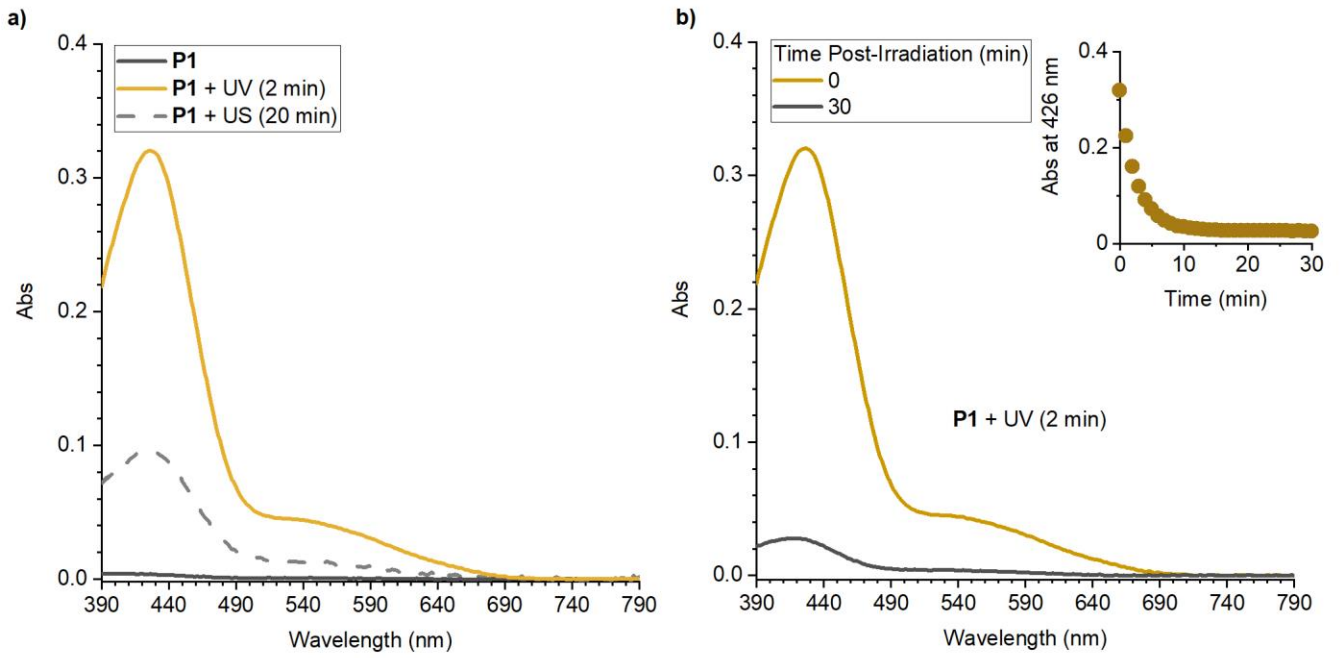


Figure S2. (a) UV-vis absorption spectra of **P1** (2 mg/mL in CH_3CN with 30 mM BHT) before and after photoirradiation with 311 nm UV light at room temperature for 2 min, compared to after continuous ultrasonication at −15 °C for 20 min. (b) Upon cessation of photoirradiation (20 °C), **MC** reverts to the ring-closed benzopyran rapidly in the dark. Inset shows the fading profile of **MC** monitored at 426 nm upon cessation of photoirradiation.

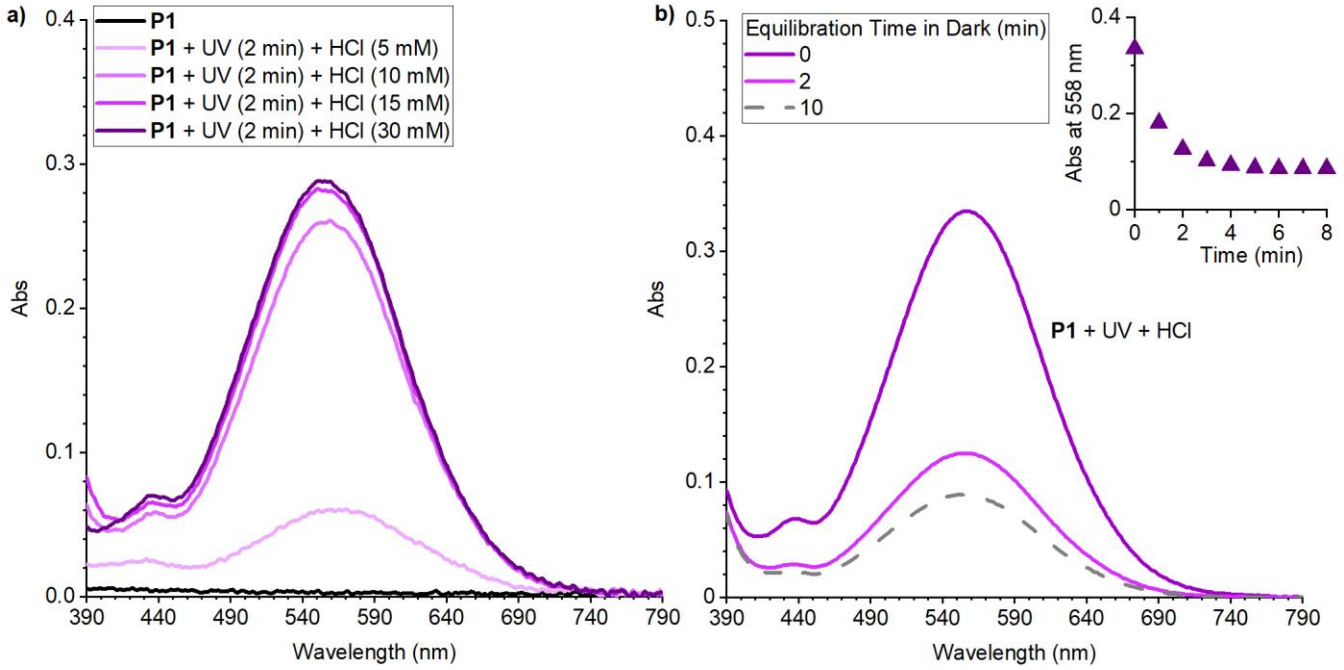


Figure S3. (a) UV-vis absorption spectra of **P1** (2 mg/mL in CH_3CN with 30 mM BHT) before and after photoirradiation with 311 nm UV light for 2 min and subsequent treatment with hydrochloric acid to produce a solution with the indicated concentration, resulting in a new absorption peak at 558 nm. (b) UV-Vis absorption behavior of **P1** following photoirradiation with 311 nm UV light for 2 min and subsequent treatment with HCL (15 mM) during subsequent equilibration in the dark (20 °C). Attenuation of the visible absorption peak at 558 nm is observed without added base, suggesting an acid-mediated decomposition pathway.

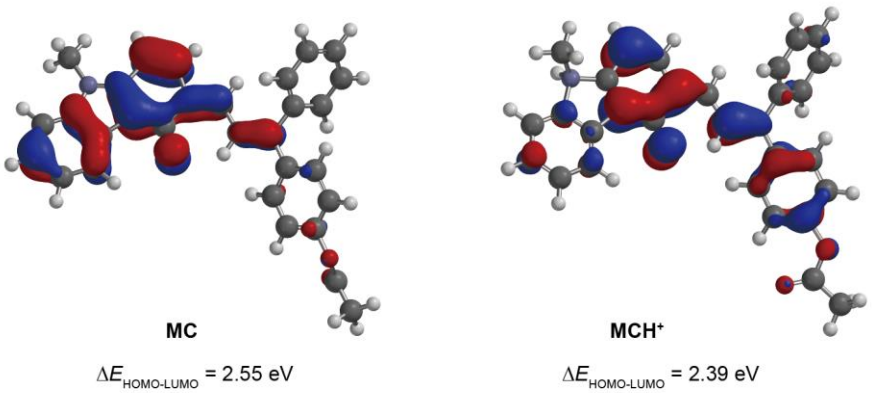


Figure S4. HOMO diagrams for **MC** and **MCH**$^+$. Protonation of **MC** results in a smaller HOMO-LUMO energy gap and greater electron delocalization, consistent with the bathochromically shifted absorption peak observed experimentally. Geometries are optimized at the B3LYP/6-31G* level of theory using Spartan.

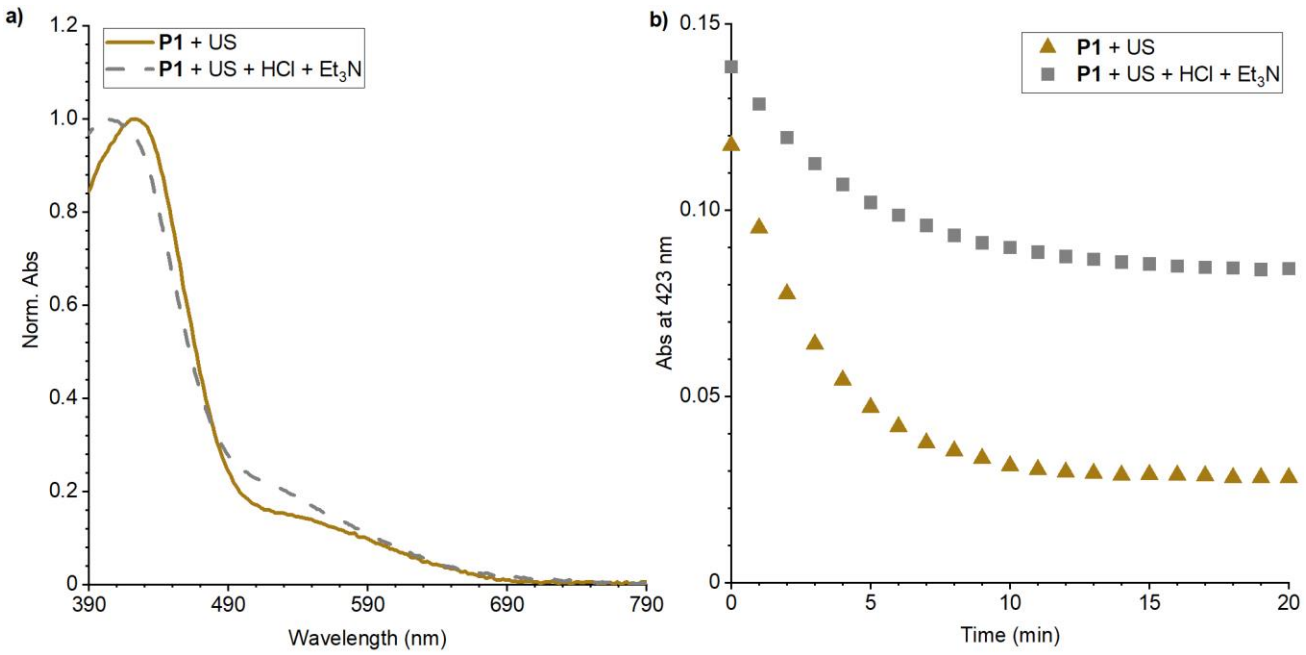


Figure S5. (a) UV-vis absorption spectra of a sonicated solution of **P1** in CH_3CN (2 mg/mL with 30 mM BHT, continuous ultrasonication at −15 °C for 20 min) before and after treatment with HCl (15 mM) and Et_3N (30 mM). (b) Fading profiles of mechanically generated **MC** and regenerated **MC** by treating **MCH**$^+$ with Et_3N (30 mM) as described in Figure 2. Changes in absorbance are monitored at 423 nm at room temperature in the dark.

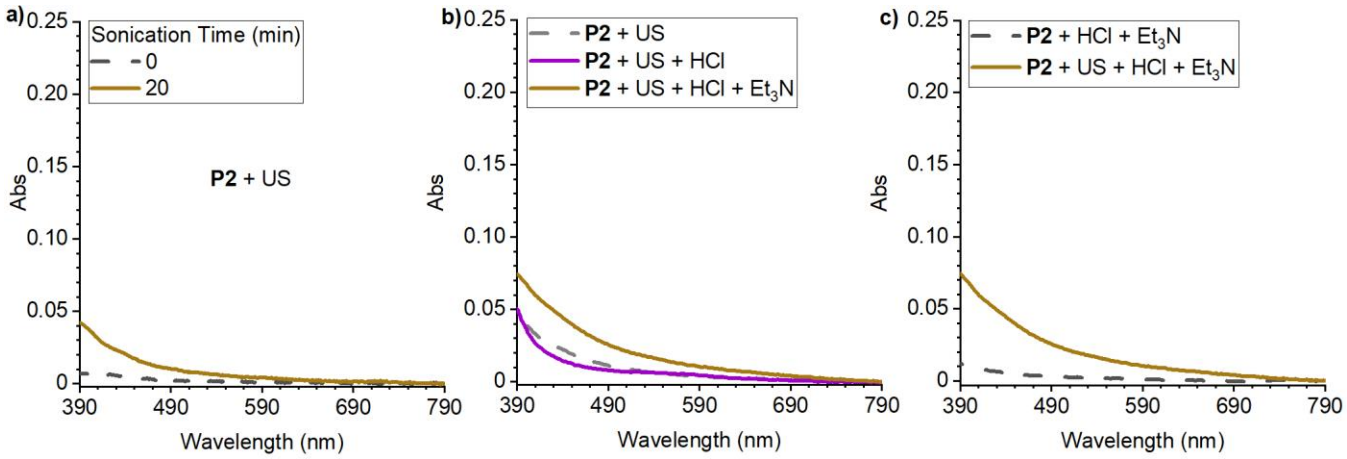


Figure S6. (a) UV-vis absorption spectra of chain-end control polymer **P2** in CH_3CN (2 mg/mL with 30 mM BHT) before and after continuous ultrasonication at −15 °C for 20 min. (b) UV-vis absorption spectra of sonicated **P2** in CH_3CN (2 mg/mL with 30 mM BHT) before and after successive treatment with HCl (15 mM) and Et_3N (30 mM), indicating that the acidochromic behavior originates exclusively from the mechanically activated benzopyran. (c) UV-vis absorption spectra obtained after treating a similar solution of **P2** with HCl (15 mM) and Et_3N (30 mM) successively, with and without first being subjected to ultrasonication.

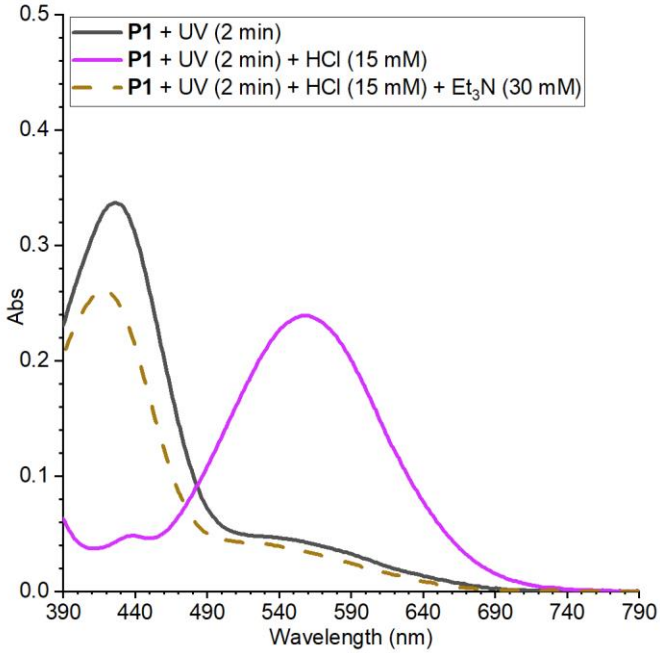
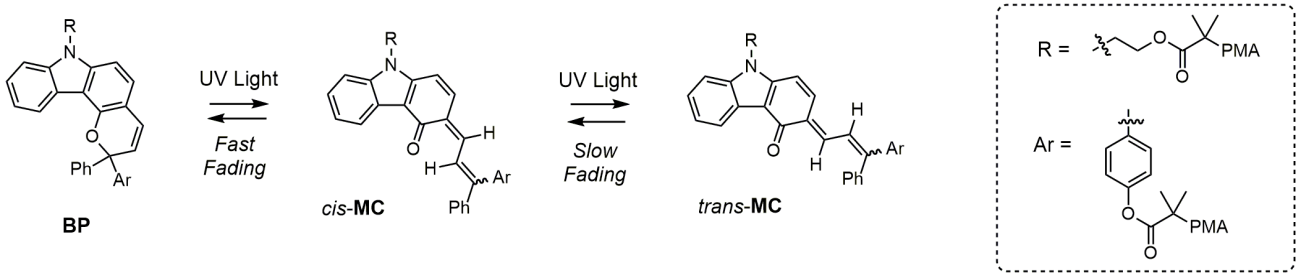


Figure S7. UV-vis absorption spectra of **P1** (2 mg/mL in CH_3CN with 30 mM BHT) after irradiation with 311 nm UV light for 2 min and successive treatment with HCl (15 mM) and triethylamine (30 mM). The absorption peak of the regenerated **MC** upon treatment with triethylamine is hypsochromically shifted by 8 nm compared to the photogenerated **MC**, similar to results from sonication experiments.

Scheme S1. Photochemical ring-opening reaction and alkene isomerization reaction to generate *cis*- and *trans*-merocyanine products.



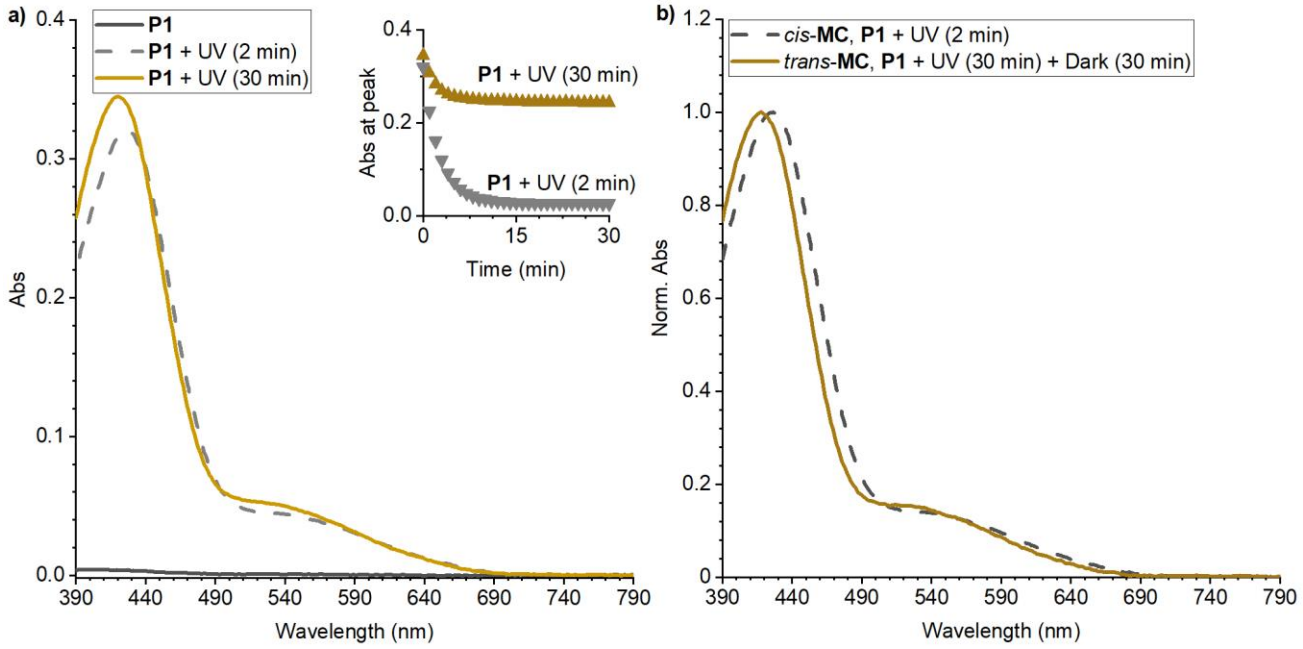


Figure S8. (a) UV-vis absorption spectra of **P1** (2 mg/mL in CH_3CN with 30 mM BHT) before and after photoirradiation with 311 nm UV light (2 min or 30 min) to generate a mixture of *cis*- and *trans*-**MC**. Extended photoirradiation favors the formation of *trans*-**MC**. The inset shows comparison of fading profiles monitored at λ_{max}. The more thermally persistent species is attributed to *trans*-**MC**. (b) Normalized spectra of *cis*- and *trans*-**MC** generated upon photoirradiation of **P1** with 311 nm UV light. The absorption peak of **MC** with *trans* exocyclic alkene geometry is hypsochromically shifted to 418 nm.

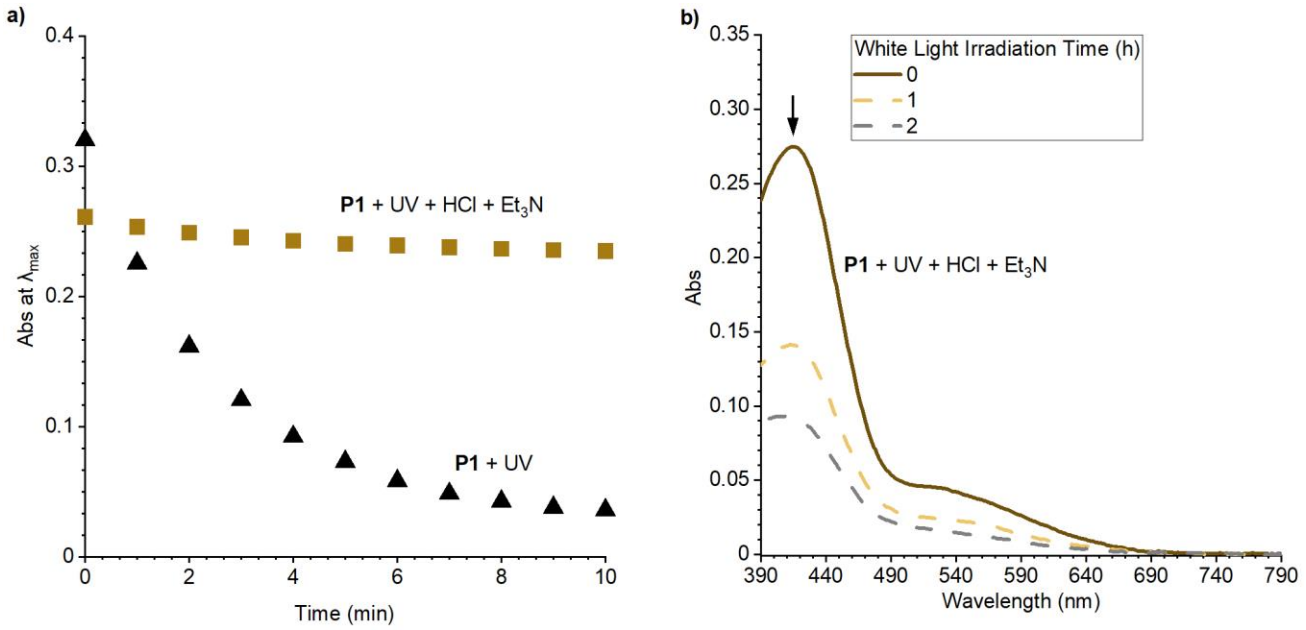


Figure S9. (a) Fading profiles of photogenerated **MC** (311 nm, 2 min) before and after treatment with HCl (15 mM) and Et_3N (30 mM) as illustrated in Figure S6. Changes in absorbance are monitored at λ_{max} at room temperature in the dark. (b) Photoirradiation of the solution of **P1** previously subjected to UV light/HCl/Et_3N using white light for the indicated time results in attenuation of the visible absorbance at 418 nm.

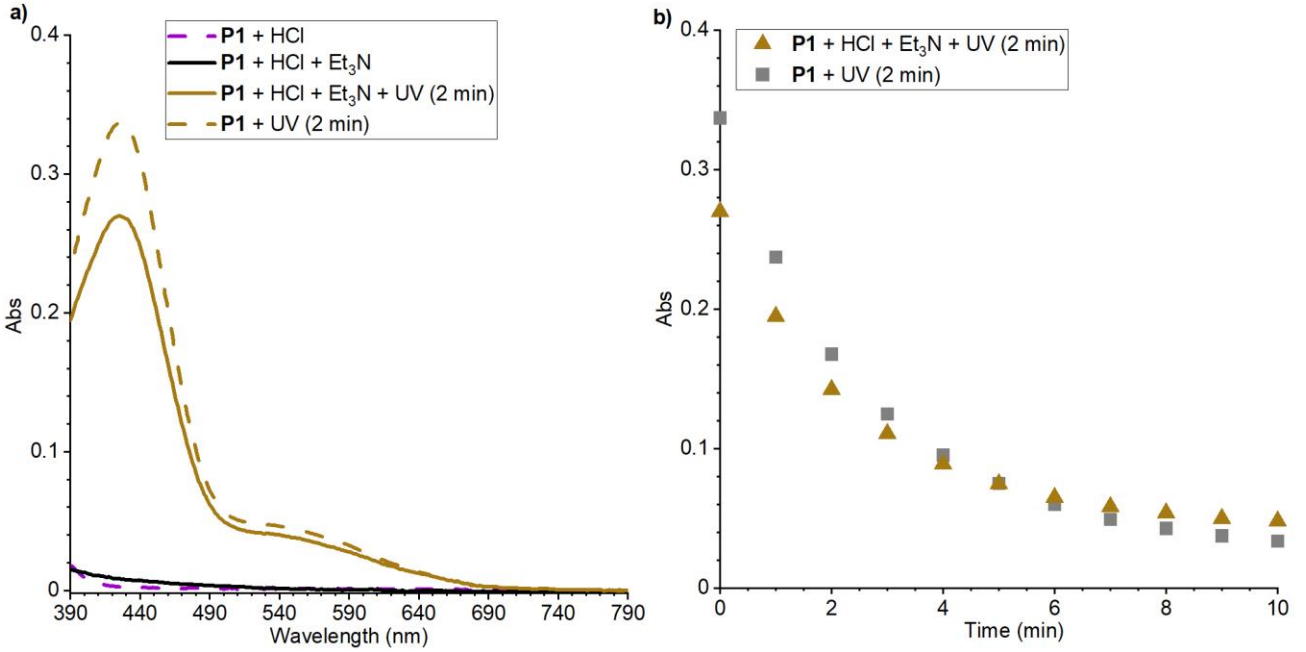
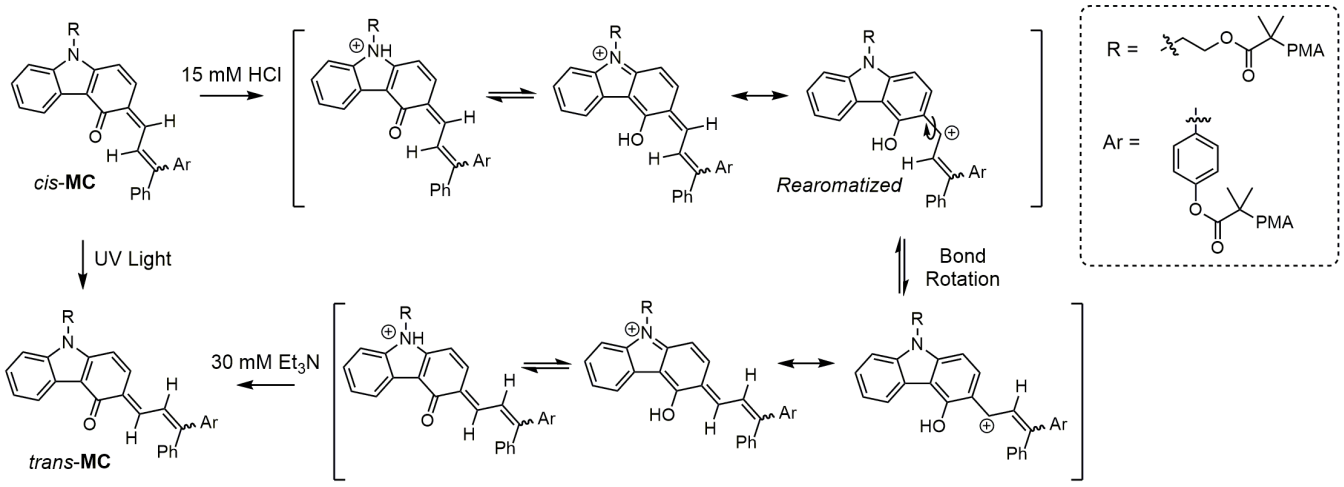


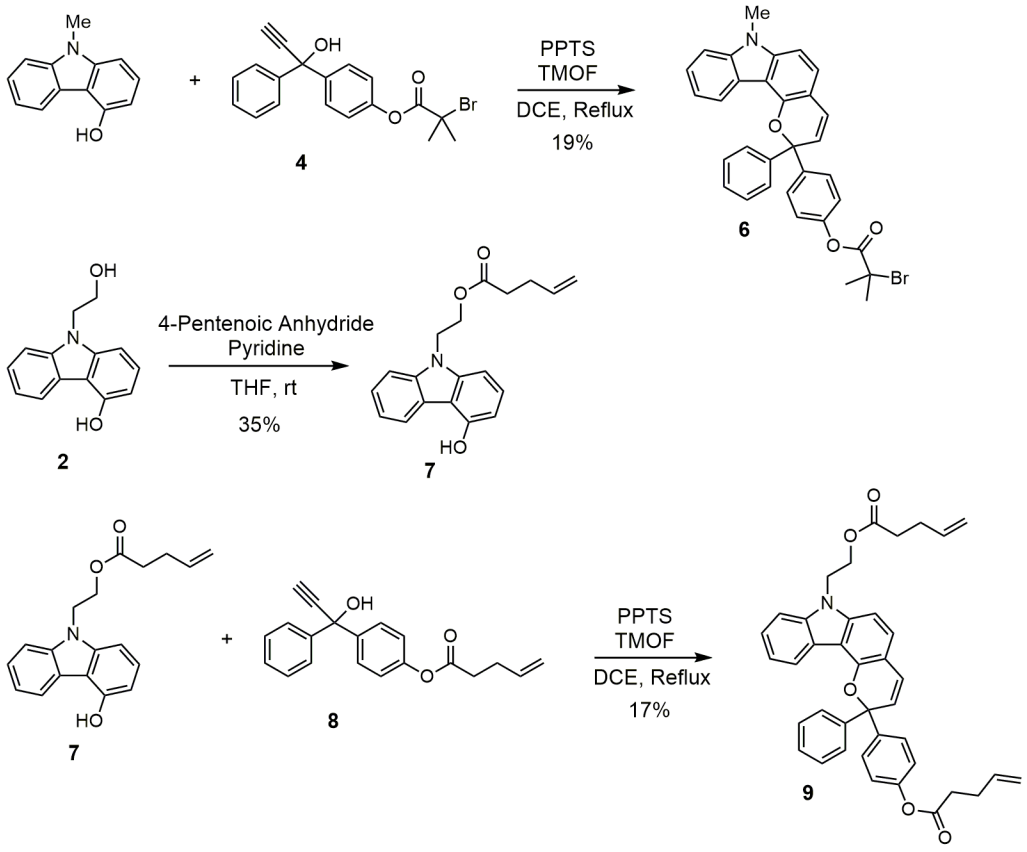
Figure S10. Control experiments illustrating that treatment of **P1** in CH_3CN (2 mg/mL with 30 mM BHT) with hydrochloric acid (15 mM) followed by triethylamine (30 mM) generates minimal changes in visible absorption. Photoirradiation (311 nm, 2 min) of this same solution produces a merocyanine product with similar absorption and reversion properties as that produced without prior acid-base treatment.

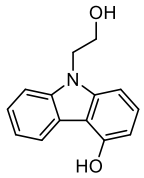
Scheme S2. Proposed mechanism of acid-mediated alkene isomerization.



III. Synthetic Details

Scheme S3. Synthesis of compounds used in the study not included in Scheme 2.





2

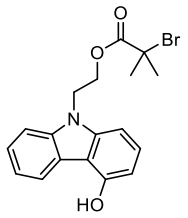
9-(2-hydroxyethyl)-9H-carbazol-4-ol (2). A flame-dried round-bottom flask equipped with a stir bar was charged with **1** (570 mg, 3.11 mmol). The flask was evacuated and backfilled with N_2 three times. Dry THF (10 mL) was added via syringe, followed by the addition of dry DMF (0.30 mL, 3.9 mmol) under N_2. The flask was subsequently cooled in an ice bath, a suspension of NaH (300 mg, 12.5 mmol) in 5 mL dry THF was added slowly via syringe, and the mixture was warmed to room temperature. After stirring for 10 min, 2-tetrahydropyranyloxy-1-iodoethane[2] (790 mg, 3.10 mmol) dissolved separately in 5 mL dry THF was added via syringe to the mixture. After the complete addition, the mixture was heated to reflux overnight. Upon completion, the flask was removed from heat and the reaction was subsequently cooled in an ice bath, quenched with H_2O, and diluted with ethyl acetate. HCl (1 M) was added until the pH of the aqueous phase was < 5, and the aqueous phase was extracted with ethyl acetate three times. The organic layers were combined, washed with H_2O three times, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Next, the crude mixture and pyridinium *p*-toluenesulfonate (100 mg, 0.398 mmol) were added to a round-bottom flask and the flask was evacuated and backfilled with N_2 three times. MeOH (10 mL) was added via syringe and the mixture was heated to reflux. After 12 h, the flask was cooled to room temperature and concentrated under reduced pressure. The crude mixture was then purified by column chromatography on silica gel (0–30% ethyl acetate/hexanes) to produce the title compound as a light brown solid (192 mg, 27%).

TLC (40% EtOAc/hexanes): R_f = 0.47

^{1}H NMR (400 MHz, acetone-d_6) δ: 9.03 (s, 1H), 8.35 – 8.23 (m, 1H), 7.60 – 7.49 (m, 1H), 7.38 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.24 (dd, *J* = 8.0 Hz, 1H), 7.17 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.07 (dd, *J* = 8.2, 0.7 Hz, 1H), 6.67 (dd, *J* = 7.8, 0.7 Hz, 1H), 4.46 (t, *J* = 5.8 Hz, 2H), 4.09 – 4.02 (m, 1H), 4.01 – 3.93 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, acetone-d_6) δ: 154.4, 143.6, 141.0, 127.1, 125.1, 123.4, 123.2, 119.4, 112.0, 109.4, 105.2, 101.6, 61.0, 46.4.

HRMS (ESI, *m/z*): calcd for $[C_{14}H_{14}NO_2]^+$ $(M+H)^+$, 228.1019; found, 228.1027.



3

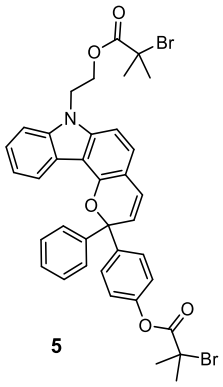
2-(4-hydroxy-9H-carbazol-9-yl)ethyl 2-bromo-2-methylpropanoate (3). A oven-dried vial equipped with a stir bar was charged with **2** (45 mg, 0.20 mmol) and the vial was evacuated and backfilled with N_2 three times. Dry THF (2 mL) was added via syringe, followed by the addition of pyridine (25 uL, 0.31 mmol) under N_2. The flask was subsequently cooled in an ice bath, α-bromoisobutyryl bromide (29 µL, 0.23 mmol) was added via syringe, and the mixture was warmed to room temperature. After stirring for 72 h, the solid precipitate was filtered off and discarded. The filtrate was diluted with ethyl acetate and washed with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (0–15% EtOAc/hexanes) to afford title compound as a pale yellow solid (45 mg, 60%).

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

^{1}H NMR (400 MHz, CD_2Cl_2) δ: 8.32 – 8.23 (m, 1H), 7.52 – 7.44 (m, 2H), 7.36 – 7.21 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 4.65 – 4.59 (m, 2H), 4.58 – 4.53 (m, 2H), 1.70 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ: 172.0, 152.5, 142.8, 140.2, 126.9, 125.4, 123.1, 122.5, 119.9, 111.5, 108.8, 105.6, 102.0, 64.1, 56.1, 42.0, 30.7.

HRMS (ESI, *m/z*): calcd for $[C_{18}H_{19}BrNO_3]^+$ $(M+H)^+$, 376.0543; found, 376.0647.



5

4-(7-(2-((2-bromo-2-methylpropanoyl)oxy)ethyl)-2-phenyl-2,7-dihydropyrano[3,2-c]carbazol-2-yl)phenyl 2-bromo-2-methylpropanoate (5). A flame-dried round-bottom flask equipped with a stir bar was charged with **3** (70 mg, 0.19 mmol), **4**[1] (83 mg, 0.22 mmol), and pyridinium *p*-toluenesulfonate (6 mg, 0.02 mmol). The flask was evacuated and backfilled with N_2 three times. Dichloroethane (10 mL) was added via syringe, followed by the

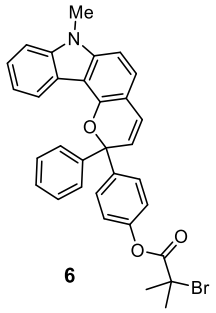
addition of trimethyl orthoformate (0.15 mL, 1.1 mmol) under N_2. After stirring at reflux for 1.5 h, the flask was removed from heat and the crude mixture was concentrated under reduced pressure, and purified by column chromatography on silica gel (0–15% ethyl acetate/hexanes) followed by a reverse-phase chromatographic separation on a C18 column (60–95% acetonitrile/H_2O) to produce the title compound as a yellow solid (23 mg, 27%).

TLC (15% EtOAc/hexanes): R_f = 0.46

^{1}H NMR (400 MHz, CD_2Cl_2) δ: 8.46 – 8.40 (m, 1H), 7.67 – 7.57 (m, 4H), 7.50 – 7.44 (m, 2H), 7.38 – 7.31 (m, 2H), 7.30 – 7.23 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.11 – 7.04 (m, 2H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 9.8 Hz, 1H), 6.14 (d, *J* = 9.7 Hz, 1H), 4.60 – 4.55 (m, 2H), 4.55 – 4.49 (m, 2H), 2.02 (s, 6H), 1.66 (d, *J* = 2.2 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ: 171.8, 170.3, 150.0, 148.8, 145.3, 143.5, 142.5, 140.3, 128.4, 127.6, 127.0, 125.5, 124.9, 124.6, 124.5, 123.3, 122.3, 120.8, 120.2, 112.6, 111.8, 108.5, 101.6, 83.1, 63.6, 55.6, 55.5, 41.5, 30.7, 30.6.

HRMS (ESI, *m/z*): calcd for $[C_{37}H_{34}Br_2NO_5]^+$ $(M+H)^+$, 730.0798; found, 730.0801.



6

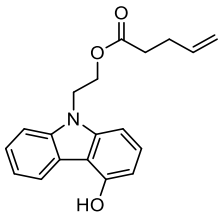
4-(7-methyl-2-phenyl-2,7-dihydropyrano[3,2-c]carbazol-2-yl)phenyl 2-bromo-2-methylpropanoate (6). A flame-dried round-bottom flask equipped with a stir bar was charged with *N*-methyl-4-hydroxycarbazole[3] (30 mg, 0.15 mmol), **4** (60 mg, 0.17 mmol), and pyridinium *p*-toluenesulfonate (14 mg, 0.056 mmol). The flask was evacuated and backfilled with N_2 for three times. Dichloroethane (5 mL) was added via syringe, followed by the addition of trimethyl orthoformate (0.20 mL, 1.9 mmol) under N_2. After stirring at reflux for 1 h, the flask was removed from heat and the crude mixture was concentrated under reduced pressure, and purified by column chromatography on silica gel (0–15% ethyl acetate/hexanes) followed by a reverse-phase chromatographic separation on a C18 column (60–95% acetonitrile/H_2O) to produce the title compound as a yellow solid (16 mg, 19%).

TLC (15% EtOAc/hexanes): R_f = 0.57

^{1}H NMR (400 MHz, CD_2Cl_2) δ: 8.46 – 8.38 (m, 1H), 7.69 – 7.57 (m, 4H), 7.51 – 7.43 (m, 1H), 7.41 – 7.38 (m, 1H), 7.37 – 7.31 (m, 2H), 7.29 – 7.22 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.11 – 7.05 (m, 2H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 9.8 Hz, 1H), 6.14 (d, *J* = 9.7 Hz, 1H), 3.79 (s, 3H), 2.02 (s, 6H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ: 170.6, 150.4, 148.7, 145.6, 144.0, 143.5, 141.4, 128.7, 128.5, 127.9, 127.1, 125.6, 125.1, 125.0, 124.7, 123.2, 122.0, 121.1, 119.9, 112.6, 111.6, 108.7, 102.0, 83.2, 56.1, 30.8, 29.6.

HRMS (ESI, *m/z*): calcd for $[C_{32}H_{27}BrNO_3]^+$ $(M+H)^+$, 552.1169; found, 552.1205.



7

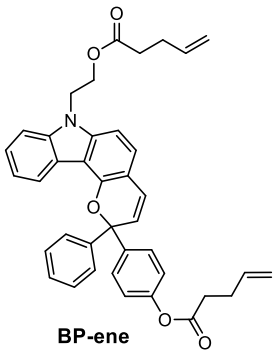
2-(4-hydroxy-9H-carbazol-9-yl)ethyl pent-4-enoate (7). A oven-dried vial equipped with a stir bar was charged with **2** (94 mg, 0.41 mmol) and the vial was evacuated and backfilled with N_2 three times. Dry THF (2 mL) was added via syringe, followed by the addition of pyridine (35 uL, 0.44 mmol) under N_2. The flask was subsequently cooled in an ice bath, 4-pentenoic anhydride (75 µL, 0.41 mmol) was added via syringe and the mixture was warmed to room temperature. After stirring for 72 h, the filtrate was diluted with ethyl acetate and washed with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (0–20% EtOAc/hexanes) to afford title compound as a pale yellow solid (45 mg, 35%).

TLC (15% EtOAc/hexanes): R_f = 0.48

^{1}H NMR (400 MHz, acetone-d_6) δ: 9.11 (s, 1H), 8.40 – 8.23 (m, 1H), 7.61 – 7.51 (m, 1H), 7.45 – 7.36 (m, 1H), 7.29 – 7.23 (m, 1H), 7.22 – 7.16 (m, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 5.68 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 1H), 4.97 – 4.80 (m, 2H), 4.65 (t, *J* = 5.5 Hz, 2H), 4.49 (t, *J* = 5.5 Hz, 2H), 2.25 – 2.18 (m, 2H), 2.17 – 2.11 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) δ: 173.1, 152.5, 142.8, 140.3, 137.1, 126.9, 125.4, 123.1, 122.4, 119.8, 115.5, 111.5, 108.7, 105.4, 101.9, 62.4, 42.4, 33.6, 28.9.

HRMS (ESI, *m/z*): calcd for $[C_{19}H_{20}NO_3]^+$ $(M+H)^+$, 310.1438; found, 310.1475.



BP-ene

4-(7-(2-(pent-4-enoyloxy)ethyl)-2-phenyl-2,7-dihydropyrano[3,2-c]carbazol-2-yl)phenyl pent-4-enoate (BP-ene). A flame-dried round-bottom flask equipped with a stir bar was charged with **7** (49 mg, 0.16 mmol), **8**[1] (58 mg, 0.19 mmol), and pyridinium *p*-toluenesulfonate (5 mg, 0.02 mmol). The flask was evacuated and backfilled with N_2 three times. Dichloroethane (10 mL) was added via syringe, followed by the addition of trimethyl orthoformate (0.10 mL, 0.95 mmol) under N_2. After stirring at reflux for 2 h, the flask was removed from heat and the crude mixture was concentrated under reduced pressure, and purified by column chromatography on silica gel (0–25% ethyl acetate/hexanes) followed by a reverse-phase chromatographic separation on a C18 column (60–95% acetonitrile/H_2O) to produce the title compound as a yellow waxy solid (16 mg, 17%).

TLC (25% EtOAc/hexanes): R_f = 0.33

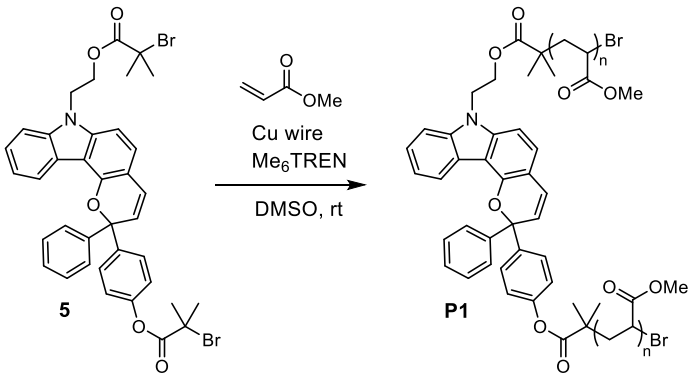
^{1}H NMR (400 MHz, acetone-d_6) δ: 8.52 – 8.41 (m, 1H), 7.70 – 7.64 (m, 4H), 7.61 – 7.57 (m, 1H), 7.51 – 7.43 (m, 1H), 7.38 – 7.32 (m, 2H), 7.30 – 7.23 (m, 2H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.14 – 7.06 (m, 3H), 6.88 (d, *J* = 9.8 Hz, 1H), 6.28 (d, *J* = 9.8 Hz, 1H), 5.89 (ddt, *J* = 16.8, 10.3, 6.5 Hz, 1H), 5.66 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 1H), 5.15 – 5.06 (m, 1H), 5.03 – 4.96 (m, 1H), 4.92 – 4.79 (m, 2H), 4.63 (t, *J* = 5.4 Hz, 2H), 4.48 (t, *J* = 5.4 Hz, 2H), 2.64 (t, *J* = 7.3 Hz, 2H), 2.46 – 2.38 (m, 2H), 2.24 – 2.19 (m, 2H), 2.16 – 2.10 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ: 173.0, 171.6, 150.0, 148.8, 145.4, 143.2, 142.6, 140.4, 136.5, 136.4, 128.3, 128.2, 127.6, 127.0, 125.4, 124.9, 124.5, 124.3, 123.3, 122.3, 121.3, 120.0, 116.1, 115.7, 112.4, 111.7, 108.3, 101.4, 83.2, 62.1, 41.9, 33.7, 33.4, 29.0, 28.7.

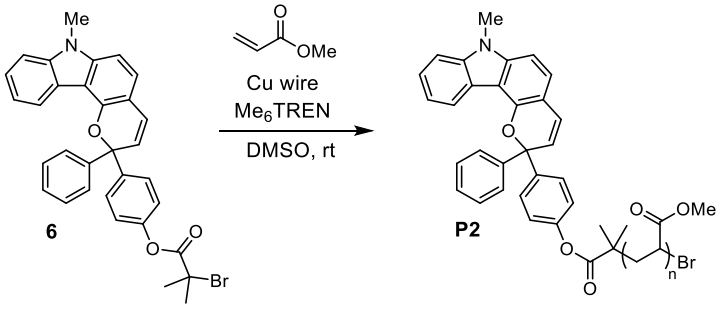
HRMS (ESI, *m/z*): calcd for $[C_{39}H_{36}NO_5]^+$ $(M+H)^+$, 598.2588; found, 598.2677.

General Procedure for the Synthesis of Poly(Methyl Acrylate) (PMA) Polymers Incorporating a Benzopyran Unit. Polymers were synthesized by controlled radical polymerization following the procedure by Nguyen *et al*.[4] A flame-dried Schlenk flask equipped with a stir bar 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 DCM. The polymer was precipitated 3x into methanol cooled with dry ice and then dried under vacuum. The GPC traces for each polymer are shown below in Figure S11.



P1. Synthesized according to the general procedure using bis-initiator **5** (9.0 mg, 0.012 mmol), Me_6TREN (13 µL, 0.048 mmol), DMSO (3.50 mL), and methyl acrylate (3.50 mL, 37.0 mmol). Polymerization for 4 h afforded the title polymer as a tacky white solid (1.25 g, 37%). M_n = 149 kg/mol, $Đ$ = 1.25.



P2. Synthesized according to the general procedure using mono-functional initiator **6** (2.5 mg, 0.0045 mmol), Me_6TREN (5.0 µL, 0.018 mmol), DMSO (1.50 mL), and methyl acrylate (1.50 mL, 13.6 mmol). Polymerization for 110 min afforded the title polymer as a tacky pale yellow solid (380 mg, 27%). M_n = 191 kg/mol, $Đ$ = 1.29.

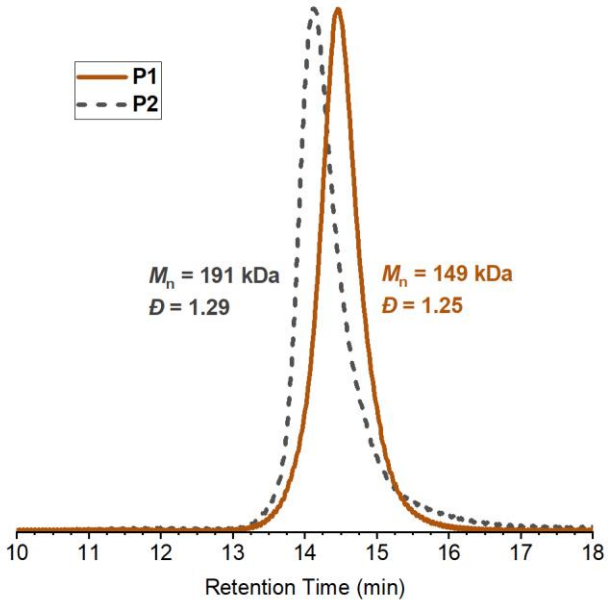


Figure S11. GPC traces (RI response) normalized to peak height for **P1** and **P2**.

IV. PDMS Materials

PDMS materials incorporating 2*H*-benzopyran (~1.3 wt%) were prepared following previously reported procedures using the two-part Sylgard® 184 elastomer kit (Dow Corning).[5,6] PDMS sheets approximately 0.5 mm thick were cut into 1 cm x 1 cm samples for testing.

General Procedure for Preparation of PDMS Materials. Benzopyran crosslinker **BP-ene** (10 mg) was dissolved in xylenes (0.1 mL) in a 20 mL scintillation vial. Sylgard® 184 prepolymer base (752 mg) was added and the mixture was thoroughly mixed in a vortex mixer to form a homogenous, pale brown opaque dispersion. Sylgard® 184 curing agent (78 mg) was added and the contents were mixed vigorously using a vortex mixer for 10 min. The mixture was then pipetted onto a 2.5 cm x 2.5 cm Delrin plate which was placed inside a vacuum chamber and evacuated under high vacuum (< 50 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 cut into 1 cm x 1 cm samples with a razor blade.

Details of the Patterning Procedure Applied to PDMS Films. The stamp used in the patterning experiments to apply localized compression was 3D printed from poly(lactic acid) with embossed features in the shape of a wavy pattern,[7] as illustrated in Figure 3 in the main text. The stamp was manually compressed into a 1 cm^2 film under a weight of ~75 kg to achieve mechanochemical activation without causing irreversible deformation or tearing of the PDMS. After compression, the films were immersed in a solution of hydrochloric acid (15 mM in DCM) for 20 s and subsequently dried with paper towel. All steps were conducted under ambient light and atmosphere. The hydrochloric acid solution was prepared by adding a 4 M HCl solution in dioxane to DCM to afford the indicated concentration.

V. DFT Calculations (CoGEF)

CoGEF calculations were performed using Spartan '20 Parallel Suite according to previously reported methods.[8,9] 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. 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 carbon atoms in 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.

VI. Details for Photoirradiation and Sonication Experiments

General Procedure for Sonication Experiments. A sonication vessel was placed onto the sonication probe and charged with a 2 mg/mL solution of polymer in CH_3CN containing 30 mM BHT (20.0 mL), which was added to minimize decomposition side reactions resulting from free radicals generated during sonication.[10,11] The sonication vessel was submerged in a −45 °C bath and degassed by sparging with N_2 for 30 min. The inert gas line was then removed into the headspace of the reaction vessel and the system was maintained under an inert atmosphere throughout the sonication experiment. Continuous sonication was then initiated (20 kHz, 20% amplitude, 8.4 ± 0.4 W/cm^2). The temperature inside the reaction vessel equilibrated to −15 °C, as measured by a thermocouple inserted into the solution (Digi-Sense EW-91428-02 thermometer with Digi-Sense probe EW-08466-83). The entire system was kept in the dark for the duration of the experiment. Aliquots (0.4 mL) were removed at 0, 1, 5, 10, 15, 20 min. The aliquots were added directly into the quartz cuvette inside of the UV-vis spectrometer and the collection of absorption spectra was immediately initiated. After the intended amount of time, sonication was stopped. A quartz cuvette charged with freshly sonicated solution (1 mL) was immediately treated with hydrochloric acid (4 N in dioxane) via microsyringe to provide a concentration of 15 mM HCl. If applicable, triethylamine (Et_3N) was added immediately to the cuvette with the freshly acidified solution via microsyringe to provide a concentration of 30 mM Et_3N. UV-vis absorption spectra were acquired immediately after the treatment with acid or base. Sonication intensity was calibrated according to the literature method.[12]

General Procedure for Photoirradiation Experiments. Photoirradiation experiments were performed in a quartz cuvette at room temperature in batch. A quartz cuvette was charged with a solution of polymer (2 mg/mL in CH_3CN containing 30 mM BHT, 1 mL total volume). The quartz cuvette was then exposed to a UV light source (λ = 311 nm) positioned ~2 in away. After the intended amount of time, photoirradiation was stopped and a UV-vis absorption spectrum was immediately recorded. Hydrochloric acid solution was prepared by adding 4 M HCl in dioxane into CH_3CN to make an HCl stock solution (1 M in CH_3CN) and the HCl stock solution was added to the quartz cuvette containing the freshly irradiated solution via microsyringe to provide an indicated concentration of HCl. If applicable, triethylamine (Et_3N) was added immediately to the cuvette containing the freshly acidified solution via microsyringe to provide a concentration of 30 mM Et_3N. UV-vis absorption spectra were acquired immediately after the treatment with acid or base.

VII. References

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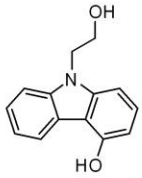
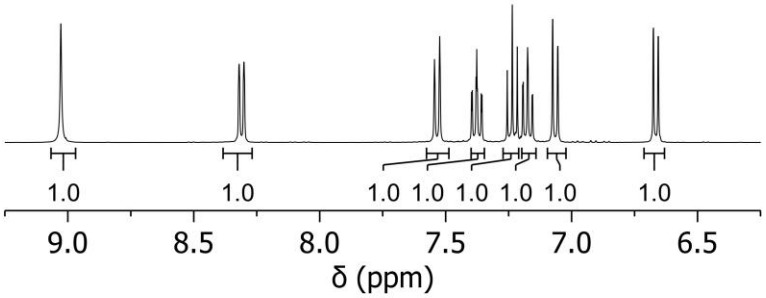
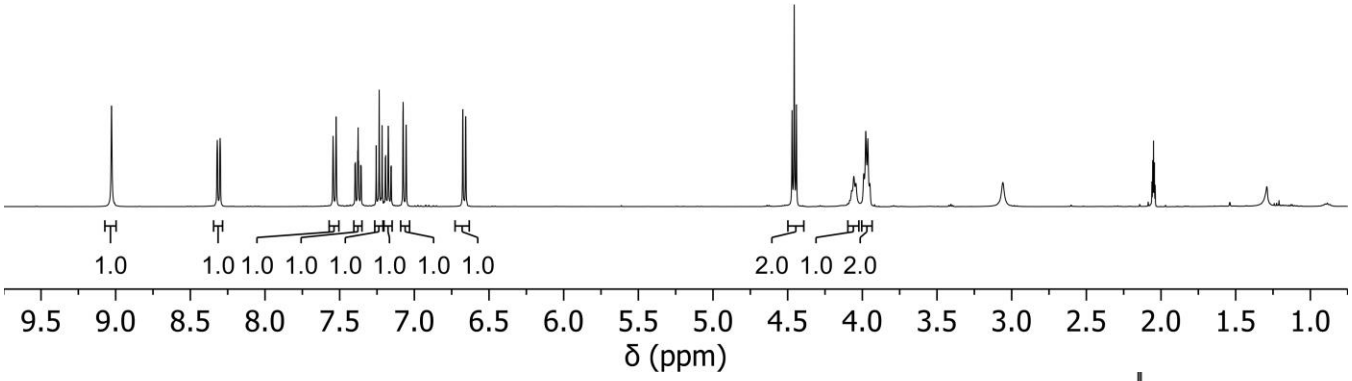
VIII. ^{1}H and ^{13}C NMR Spectra

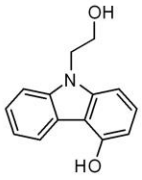


2

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

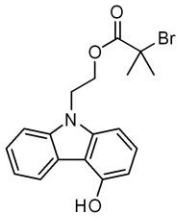






2

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



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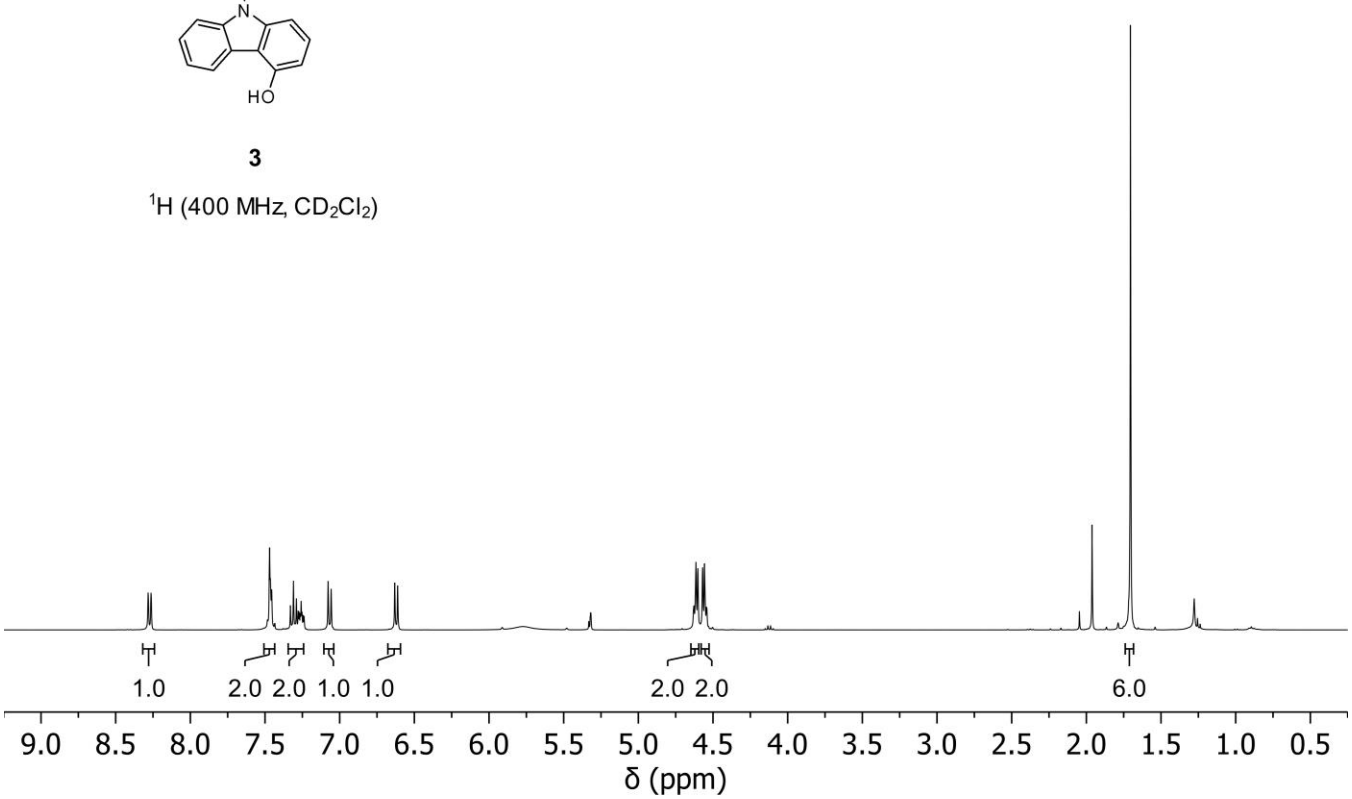
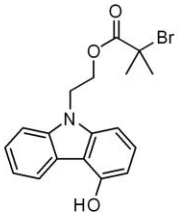
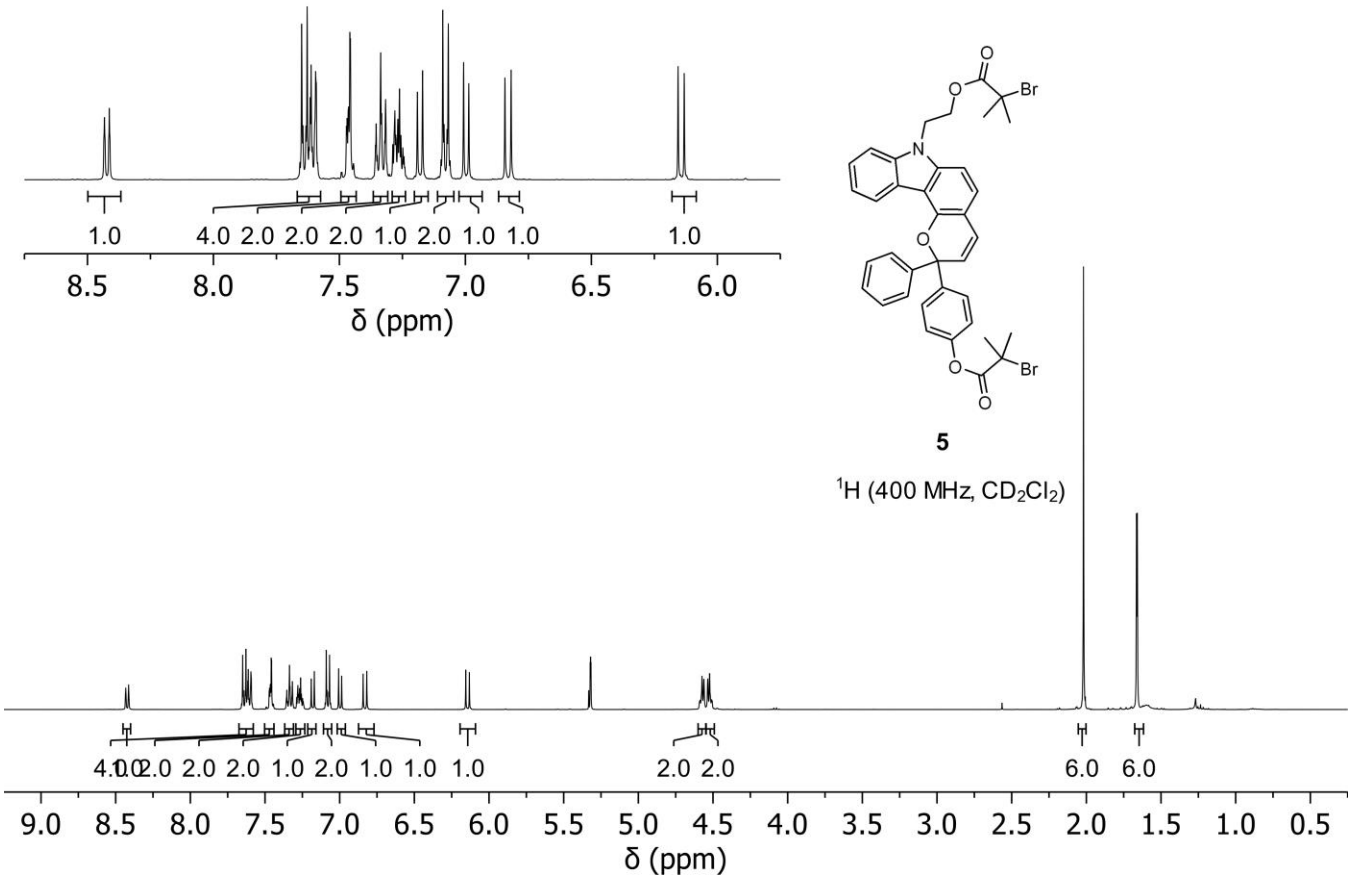




3

^{13}C (101 MHz, CD_2Cl_2)


1.0
4.0 2.0 2.0 2.0 1.0 2.0 1.0 1.0
1.0
8.5
8.0
7.5
7.0
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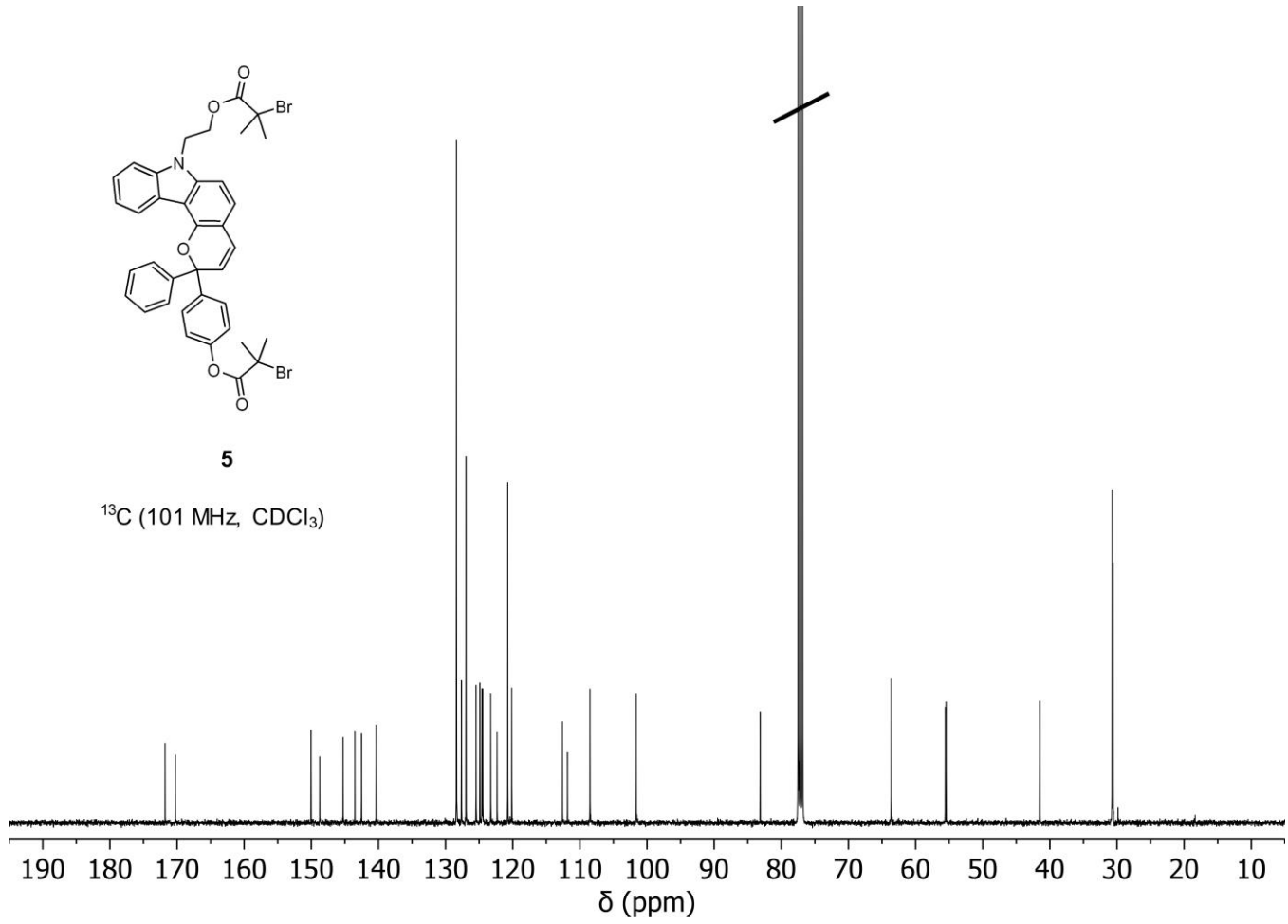
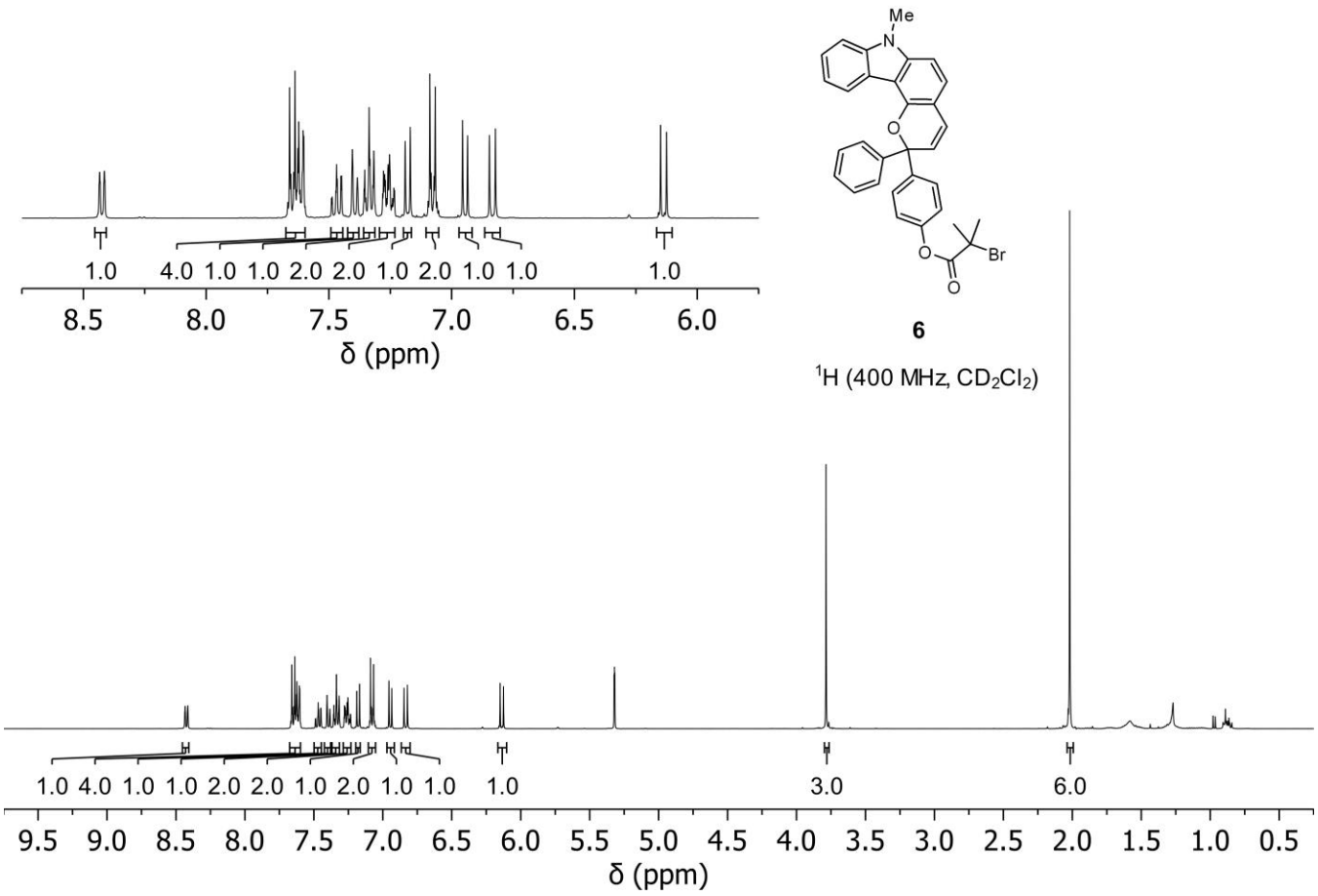
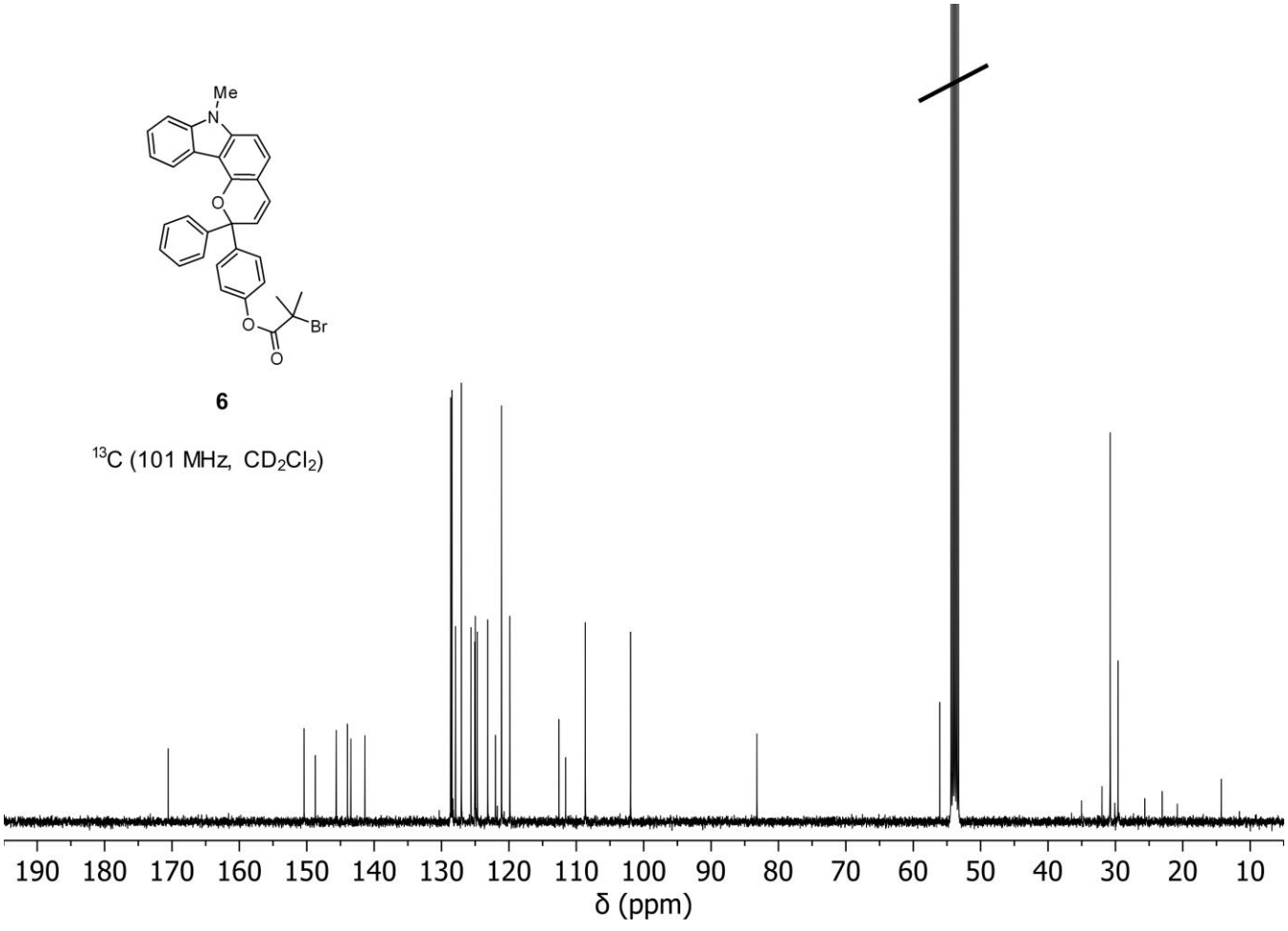
6.0
δ (ppm)
Br
O
N
O
O
Br
O
5
^{1}H (400 MHz, CD_2Cl_2)
4.00 2.0 2.0 2.0 1.0 2.0 1.0 1.0 1.0
2.0 2.0
6.0 6.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
δ (ppm)


Br
O
N
O
O
Br
O
5
^{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)



6

^{1}H (400 MHz, CD_2Cl_2)



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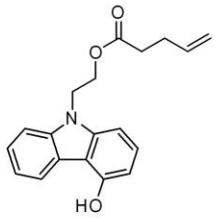
^{13}C (101 MHz, CD_2Cl_2)



7

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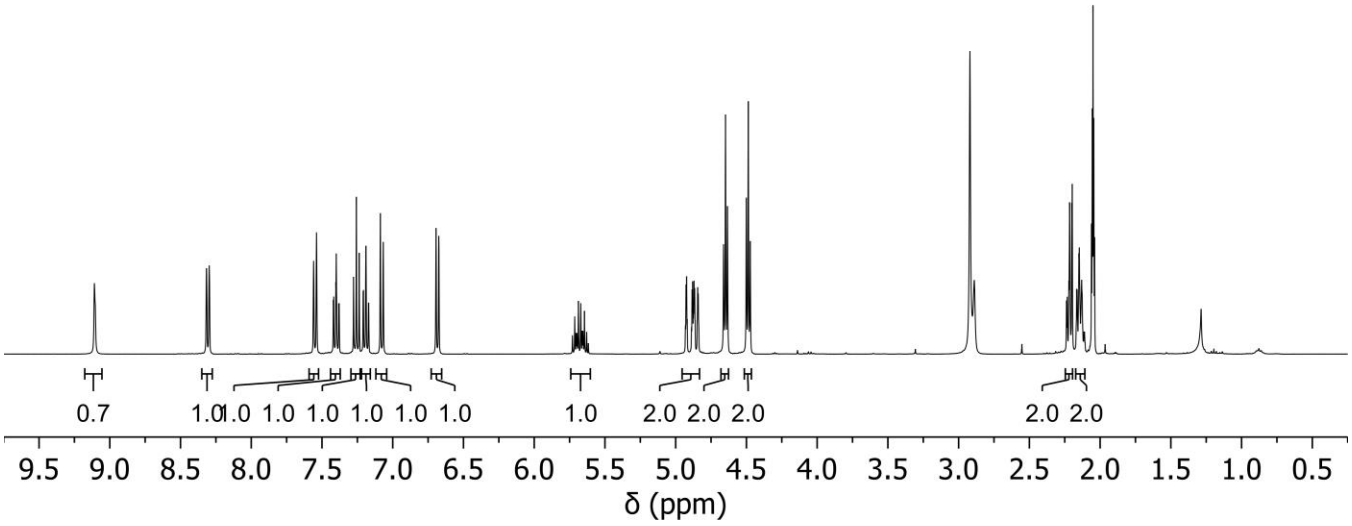

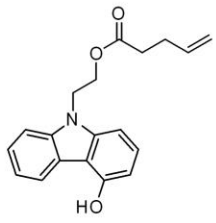

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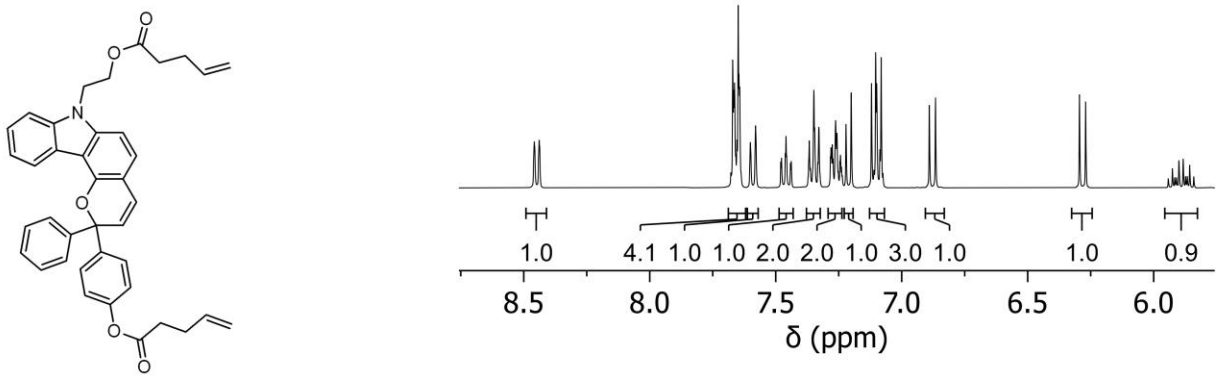
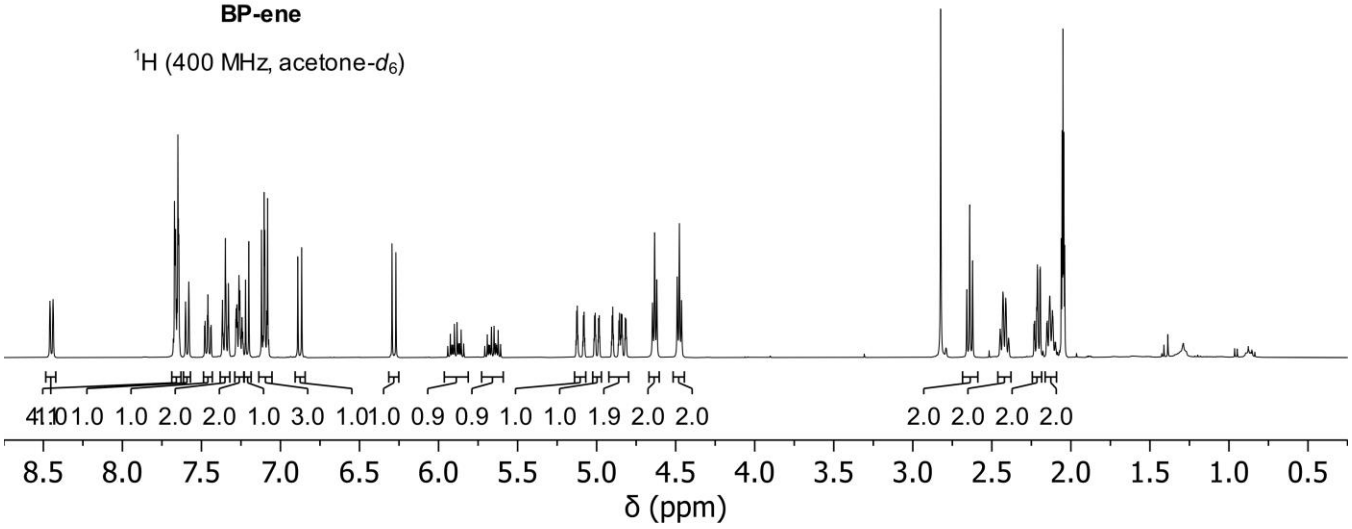


BP-ene

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



BP-ene

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