Electronic Supplementary Information for

A Modular Approach to Mechanically Gated Photoswitching with Color-Tunable Molecular Force Probes

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I. General Experimental Details

Reagents from commercial sources were used without further purification unless otherwise stated. Methyl acrylate was passed through a short plug of basic alumina to remove inhibitor immediately prior to use. Copper wire was cleaned prior to use by soaking in 1 M HCl for 15 min, and then rinsed thoroughly with deionized water and dried. Dry solvents were obtained from a Pure Process Technology solvent purification system. All reactions were performed under a N_2 or Ar atmosphere unless specified otherwise. Column chromatography was performed manually using Silicycle SiliaFlash F60 silica gel or on a Biotage Isolera system using SiliCycle SiliaSep HP flash cartridges or Buchi FlashPure C18 30 µm spherical reverse phase cartridges.

NMR spectra were recorded using a 400 MHz Bruker Avance III HD with Prodigy Cryoprobe, a 400 MHz Bruker Avance Neo, a 500 MHz Varian Inova, or a 300 MHz Varian spectrometer. 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), or methanol (3.31 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 (29.84 or 206.26 ppm), or methanol (49.00 ppm). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad, app = apparent.

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

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 an 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 inside a sound abating enclosure 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). UV irradiation 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.

Crosslinked polymer samples with a thickness of approximately 1 mm were cut with a 2 mm hammer-driven hole punch. Compression experiments were performed using a hydraulic press under a force of 10 tons. Photographs were captured using a Google Pixel 5 and corrected for exposure in Adobe Photoshop.

II. Supplementary Figures and Tables

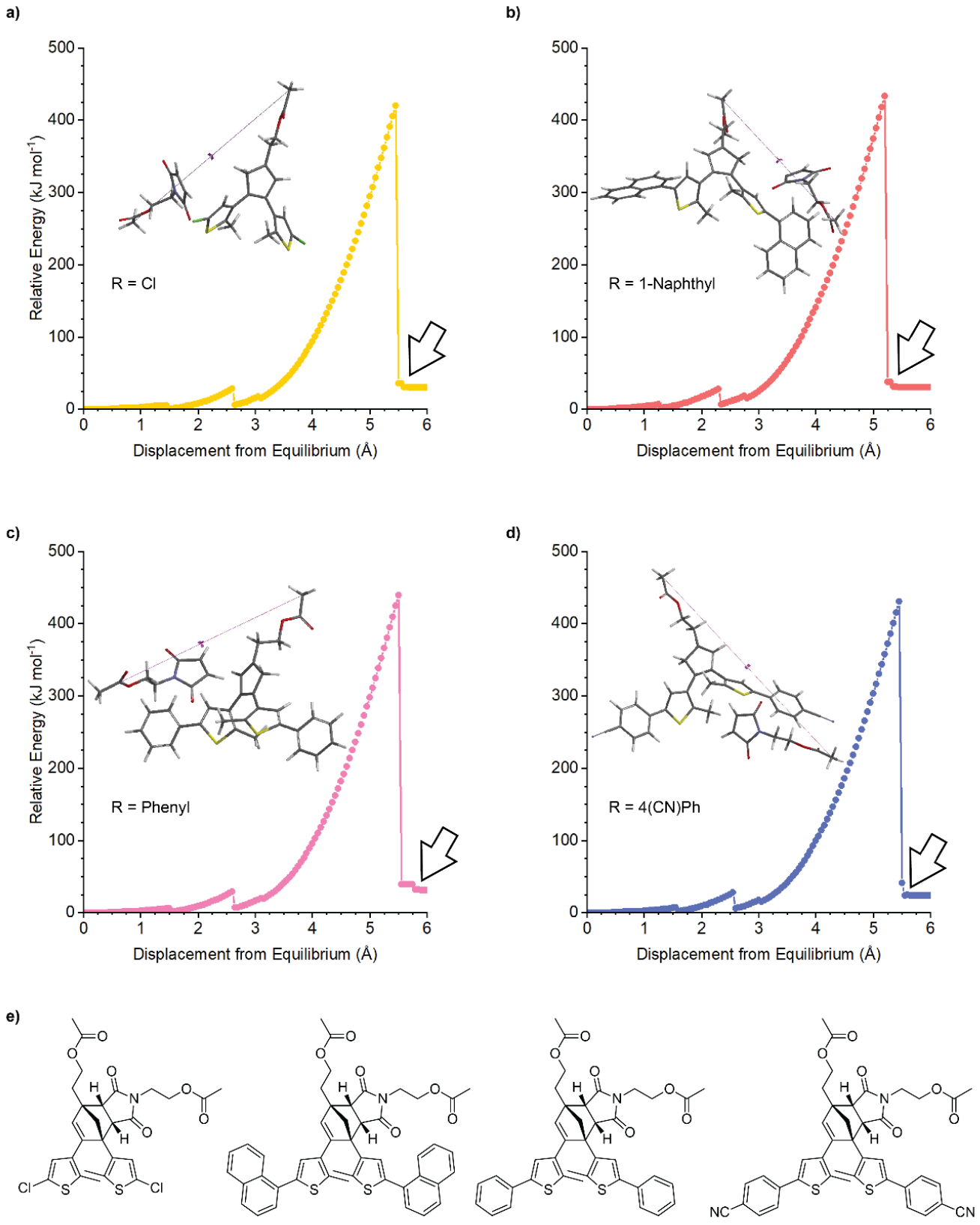


Figure S1. DFT calculations using the constrained geometries simulate external force (CoGEF) method at the B3LYP/6-31G* level of theory for a) chloro-substituted, b) naphthyl-substituted, c) phenyl-substituted, and d) 4-cyanophenyl-substituted cyclopentadiene–maleimide mechanophores. The computed structures of products following the mechanochemical reaction are shown, which correspond to the position on the CoGEF profile indicated by an arrow. e) Structures of truncated models used for CoGEF calculations. The reaction is predicted to occur with a maximum force (F_{max}) of 4.9 nN for all four compounds.

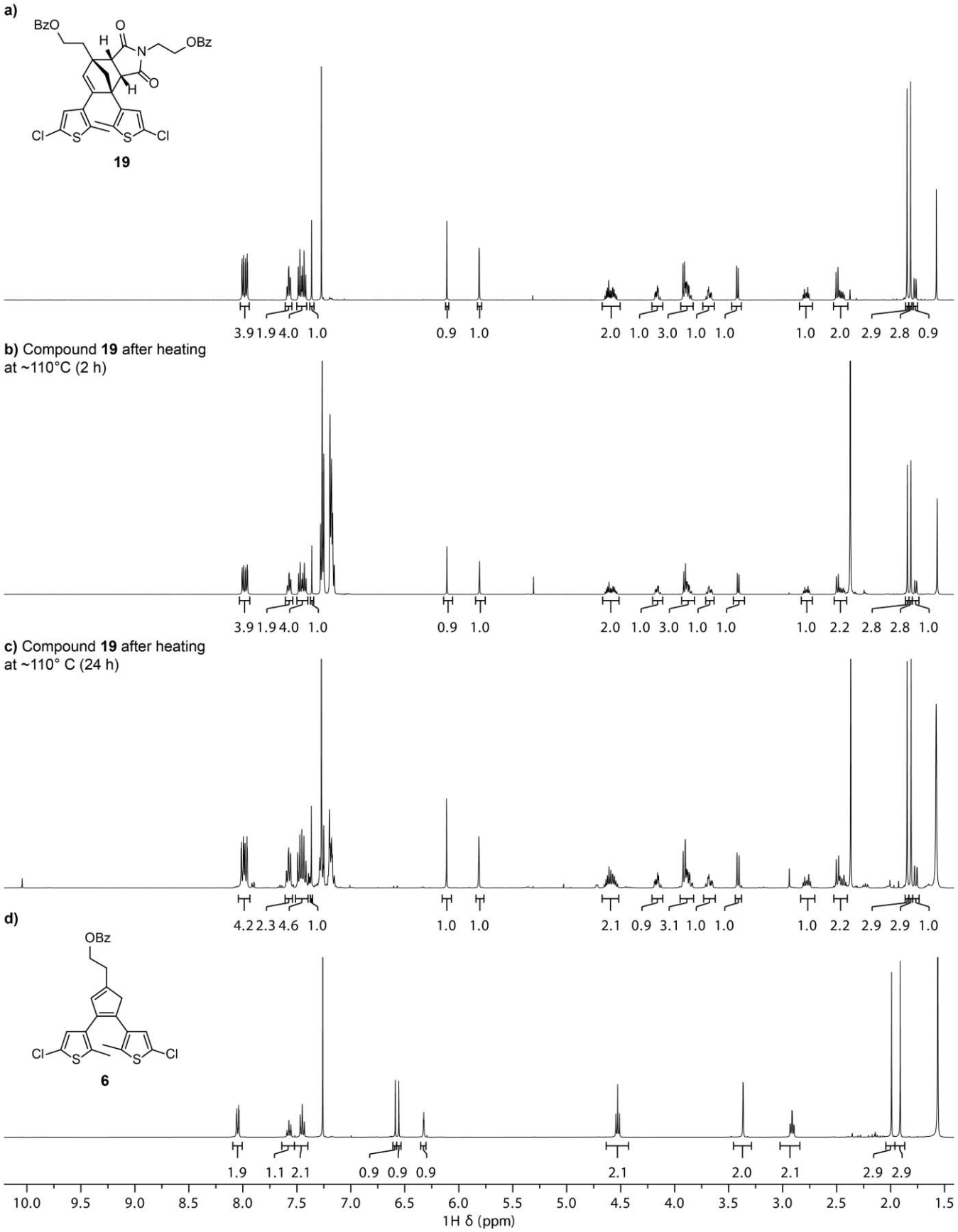


Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of cyclopentadiene–maleimide Diels–Alder adduct **19** a) before, and after heating in refluxing toluene for b) 2 h and c) 24 h, demonstrating the thermal stability of the adduct. d) The ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of cyclopentadiene **6** is included for reference.

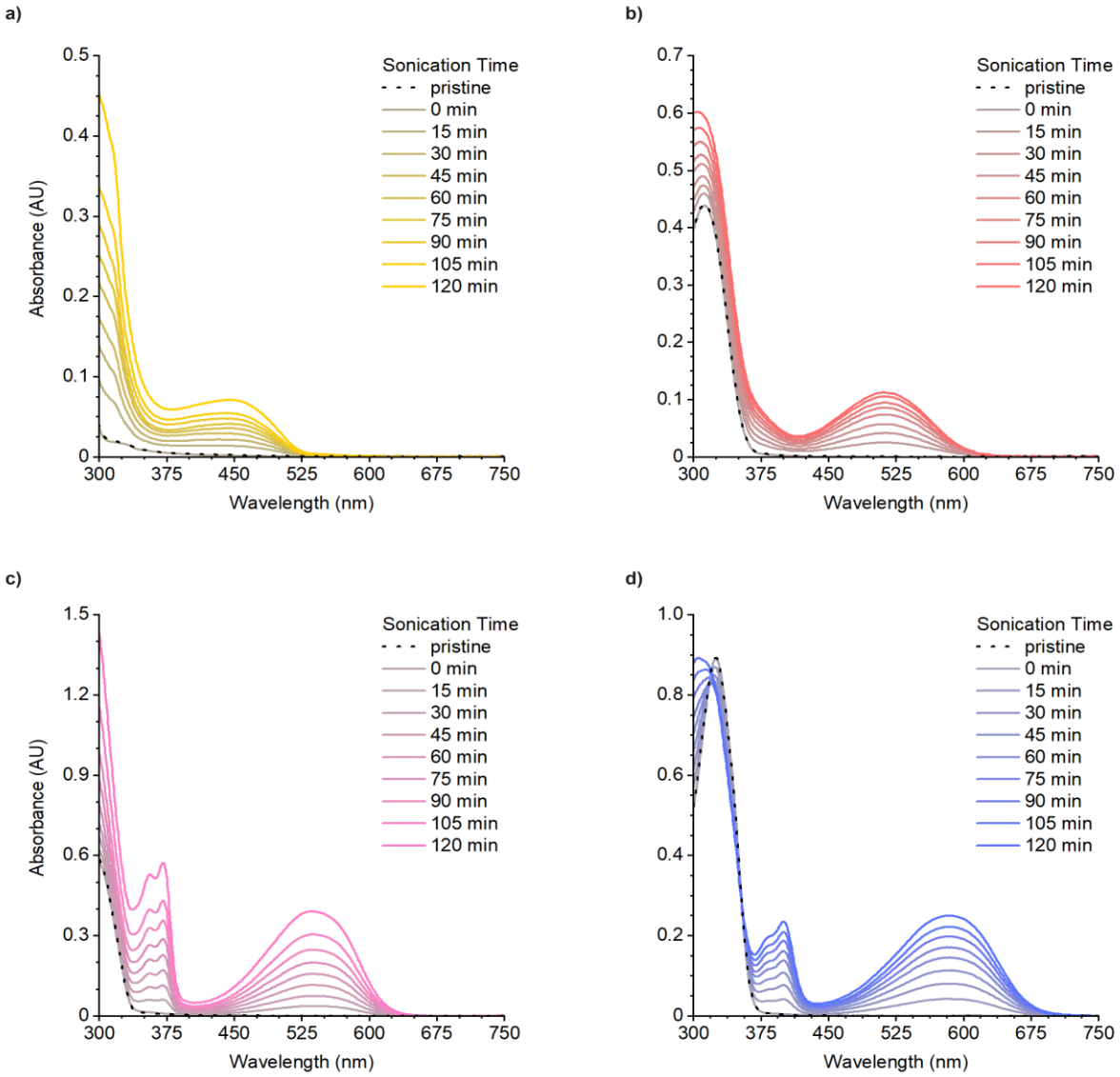


Figure S3. UV-vis absorption spectra of a) **10a**, b) **10b**, c) **10c**, and d) **10d** (2 mg/mL in THF) as a function of ultrasonication time and after irradiation with UV light. Spectra of pristine polymers were acquired before UV irradiation or ultrasonication. All other spectra were acquired after the indicated duration of ultrasonication, and after irradiation with a 311 nm UV lamp for 60 s. The increasing absorbance in the visible region of the spectra is indicative of progressively greater mechanophore conversion with increasing sonication time, resulting in increasing concentration of the diarylethene photoswitches.

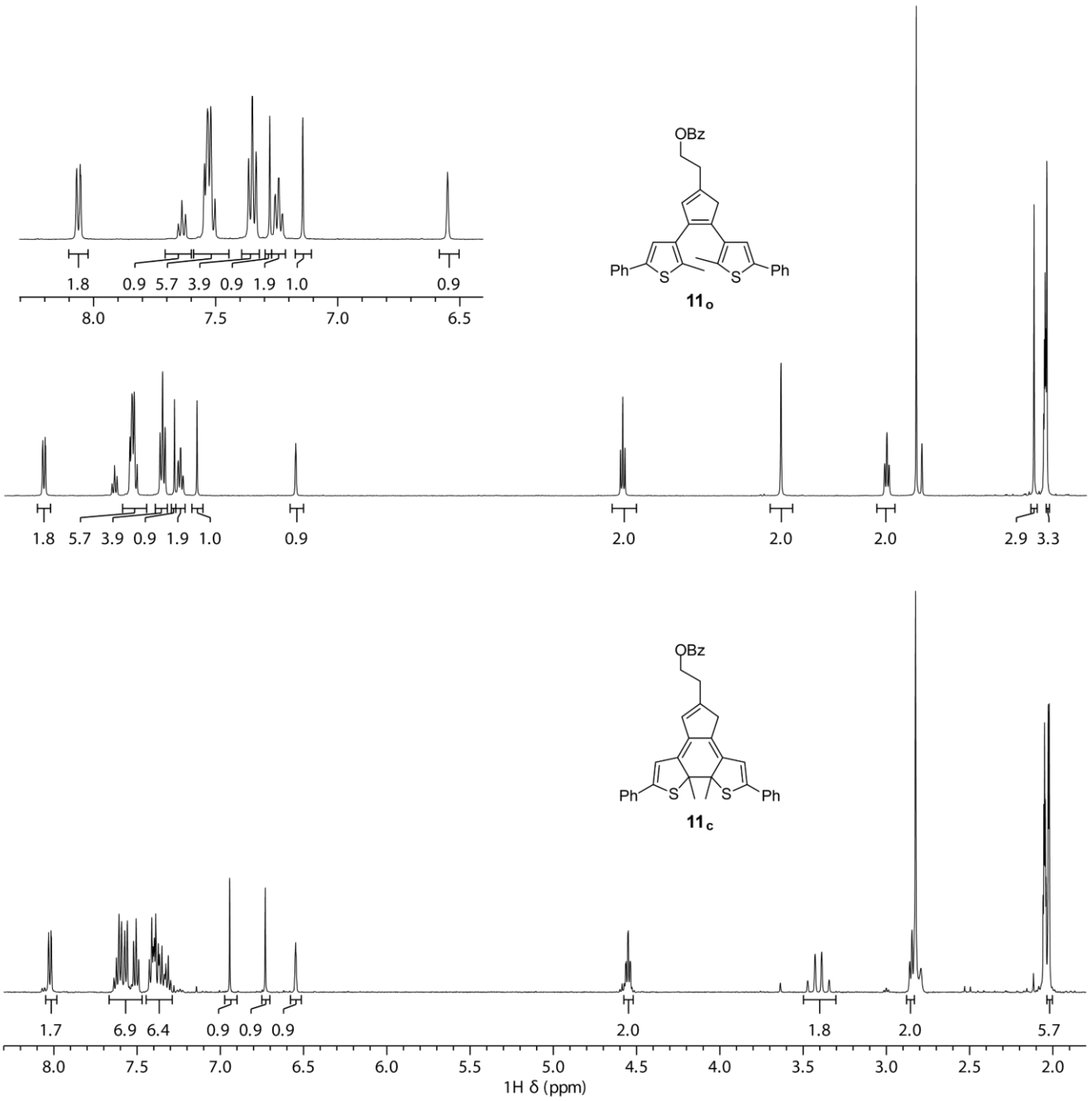


Figure S4. ^{1}H NMR spectra (500 MHz, acetone-d_6) of **11_o** (*top*) and the same sample after irradiation with 311 nm light for 60 min (*bottom*) displaying nearly complete conversion to **11_c** (**11_c**:**11_o** = 18:1).

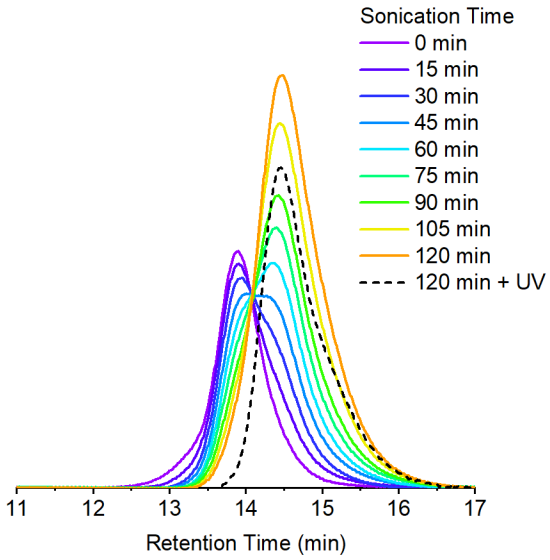


Figure S5. GPC traces (RI response) of aliquots of **10c** collected over the course of ultrasound-induced mechanical activation demonstrating features characteristic of mid-chain scission. A GPC measurement monitored using a UV-vis detector (491–581 nm) performed on the sample after 120 min of ultrasonication and UV irradiation (λ = 311 nm, 60 s) reveals a peak with a retention time corresponding to that of the polymer fragments, indicating the formation of a polymer-bound photoswitch upon polymer chain scission.

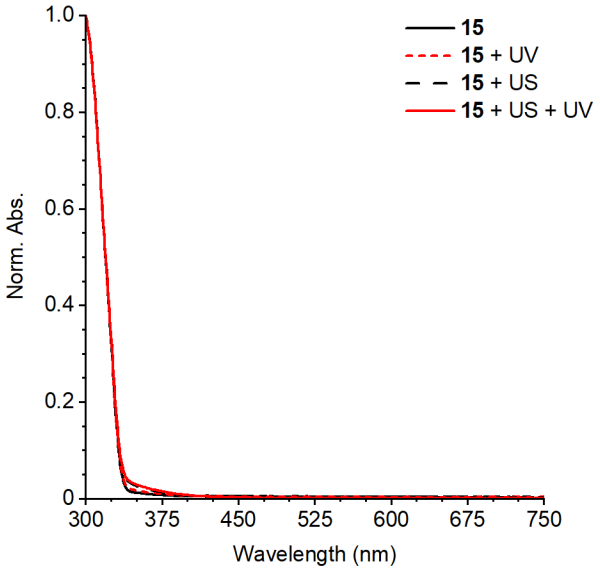


Figure S6. UV-vis absorption spectra of chain-end functional control polymer **15** (2 mg/mL in THF) before and after being subjected to combinations of ultrasonication (120 min) and UV photoirradiation (λ = 311 nm, 60 s). Negligible changes in the absorption spectra are observed supporting that the activation of polymers **10a**–**d** is mechanochemical in nature.

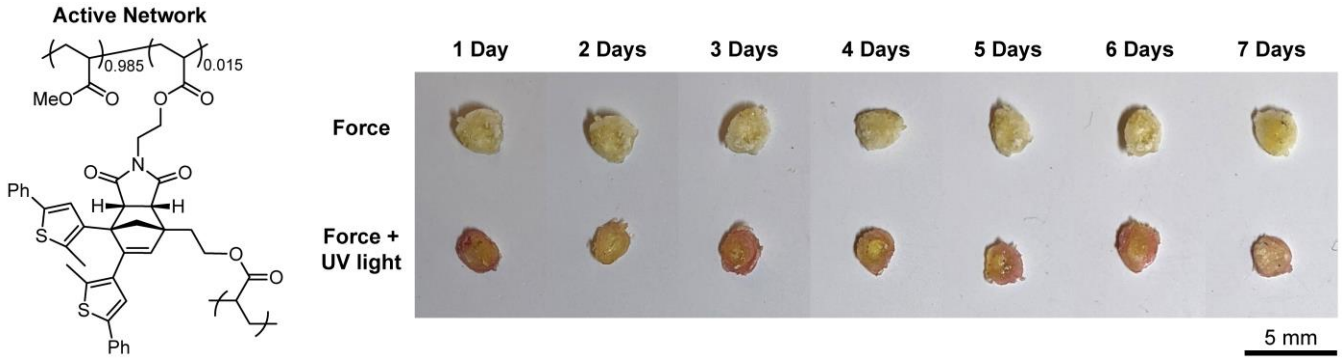


Figure S7. Structure of the active PMA network containing 1.5 mol% of a mechanophore crosslinker and photographs of samples of the polymer network after being subjected to combinations of compressive force and UV irradiation. Each sample was subjected to uniaxial compression (10 tons, 5 min) on the same day and subsequently stored in the dark at room temperature under air. The photochromic behavior of the samples was then analyzed on successive days following the initial compression experiment. *Top row:* a polymer sample subjected to compressive force that was not irradiated with UV light, as a reference. *Bottom row:* polymer samples irradiated with UV light (311 nm, 5 min) on the indicated day after the initial compression. The photochromic behavior of the mechanically activated material is evident for one week, demonstrating the persistence of the mechanically gated photoswitching response.

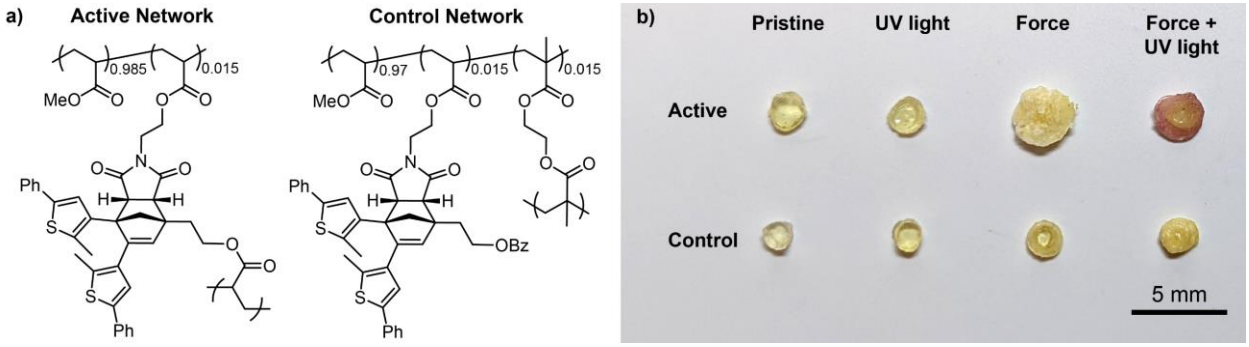
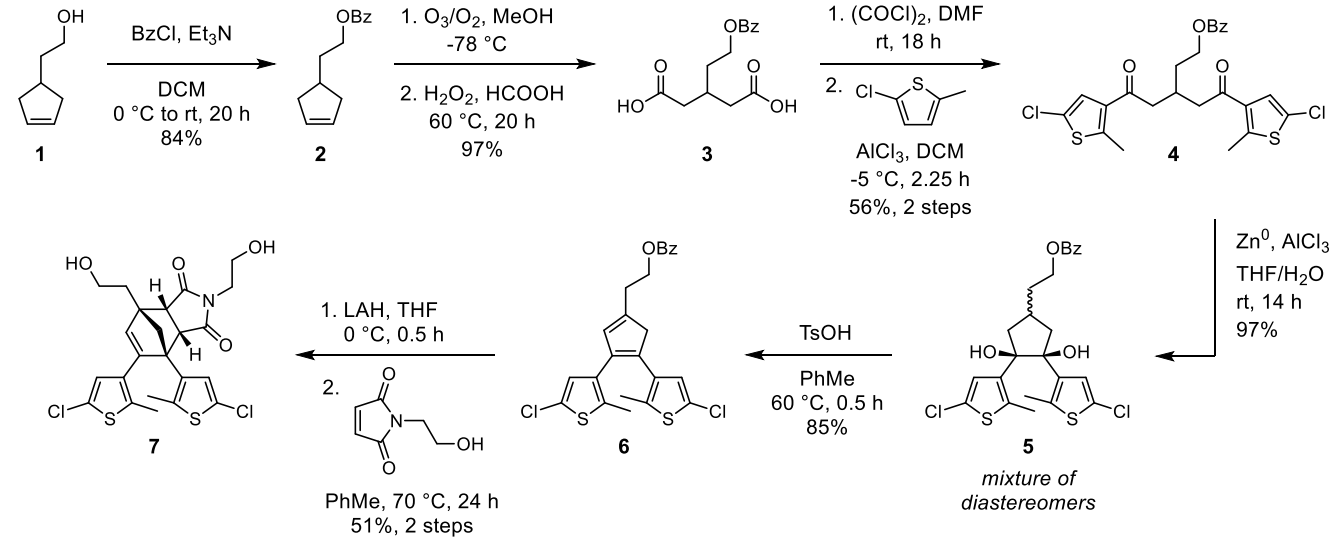
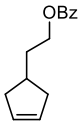


Figure S8. a) Structures of the active and control PMA networks containing 1.5 mol% of a mechanophore crosslinker and pendant group, respectively. The control network was crosslinked with 1.5 mol% of a mechanochemically inactive ethylene glycol dimethacrylate crosslinker. b) Photographs of the active and control PMA networks before and after being subjected to combinations of mechanical force and UV light irradiation. From left to right: pristine samples, after irradiation with 311 nm light (5 min), after uniaxial compression (10 tons for 5 min), and samples after uniaxial compression (10 tons for 5 min) and subsequent irradiation with 311 nm light (5 min). Color is only produced in the active network following the sequence of compression followed by UV irradiation, indicating that the DAE photoswitch is successfully revealed under mechanical force. The control samples display no change in color in response to any stimuli, indicating that force must be transferred across the cyclopentadiene–maleimide junction to activate the mechanophore. Greater deformation is observed for the active network compared to the control network, suggesting that the mechanochemical sensitivity of the mechanophore crosslinker influences macroscopic fracture behavior.

III. Synthetic Details

Scheme S1. Synthesis of Mechanophore Diol **7**





2

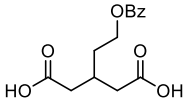
2-(cyclopent-3-en-1-yl)ethyl benzoate (2). A flame-dried round bottom flask equipped with a stir bar was charged with 2-(cyclopent-3-en-1-yl)ethan-1-ol **1**[1] (8.13 g, 72.5 mmol), triethylamine (50.0 mL, 359 mmol), and dry DCM (200 mL). The solution was cooled to 0 °C in an ice/water bath and benzoyl chloride (25.0 mL, 215 mmol) was added slowly with stirring. Immediately after the addition was complete, the reaction was removed from the ice bath and warmed to room temperature over 20 h. The organic layer was washed with saturated $NaHCO_3$ (3 x 100 mL) and once with brine (100 mL). The organics were dried with Na_2SO_4, filtered, and concentrated under vacuum. The crude mixture was purified by silica gel chromatography (0–15% EtOAc/hexanes) to provide the title compound as colorless oil (13.2 g, 84%).

TLC (10% EtOAc/hexanes): R_f = 0.45

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.20 – 7.90 (m, 2H), 7.61 – 7.52 (m, 1H), 7.49 – 7.39 (m, 2H), 5.69 (s, 2H), 4.36 (t, *J* = 6.7 Hz, 2H), 2.72 – 2.49 (m, 2H), 2.49 – 2.37 (m, 1H), 2.16 – 2.01 (m, 2H), 1.89 (q, *J* = 6.9 Hz, 2H) ppm.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 166.9, 133.0, 130.6, 130.0, 129.7, 128.5, 64.4, 39.0, 35.3, 34.8 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{14}H_{17}O_2]^+$ $(M+H)^+$ 217.1223, found 217.1227.



3

3-(2-(benzoyloxy)ethyl)pentanedioic acid (3). A round bottom flask equipped with a stir bar was charged with **2** (1.62 g, 7.49 mmol) and methanol (50 mL). The solution was cooled to −78 °C in a dry ice/acetone bath and a

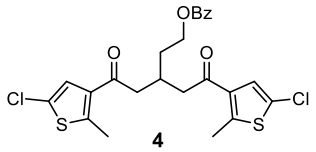
stream of O_2/O_3 was bubbled through the solution until it became blue. To remove excess ozone, O_2 was bubbled through the solution until the blue color disappeared. After warming to room temperature, the solution was diluted with formic acid (50 mL) and concentrated partially under vacuum to remove methanol. This process was repeated 2×, after which the residue was dissolved in formic acid (50 mL) in a round bottom flask equipped with a reflux condenser. Hydrogen peroxide (35 wt% in water, 6.50 mL, 75.6 mmol) was added and the reaction, which was then heated to 60 °C. After 20 h the solution tested negative for peroxides and was cooled to room temperature. The products were extracted into EtOAc (5 x 50 mL), and the combined organics were washed once with brine (50 mL), dried with Na_2SO_4, filtered, and concentrated to provide the title compound as a white solid (2.04 g, 97%).

TLC (5 % MeOH/DCM): R_f = 0.13

^{1}H NMR (400 MHz, CD_3OD) δ: 8.10 – 7.97 (m, 2H), 7.64 – 7.54 (m, 1H), 7.47 (ddt, *J* = 8.0, 6.7, 1.2 Hz, 2H), 4.40 (t, *J* = 6.4 Hz, 2H), 2.65 – 2.39 (m, 5H), 1.90 (app q, *J* = 6.4 Hz, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_3OD) δ: 176.1, 168.0, 134.2, 131.5, 130.6, 129.5, 63.9, 39.2, 33.7, 30.6 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{14}H_{17}O_6]^+$ $(M+H)^+$ 281.1020, found 281.1049.



4

5-(5-chloro-2-methylthiophen-3-yl)-3-(2-(5-chloro-2-methylthiophen-3-yl)-2-oxoethyl)-5-oxopentyl benzoate (4). A flame-dried round bottom flask equipped with a magnetic stir bar was charged with **3** (1.72 g, 6.14 mmol). The atmosphere was evacuated and refilled with N_2 3×. Dry DCM (100 mL) was added, followed by dry DMF (10 drops, cat.). Oxalyl chloride (5.30 mL, 61.8 mmol) was added slowly, after which the reaction stirred at room temperature. After 15 h, it was concentrated under vacuum and re-dissolved in a minimal amount of dry DCM. The catalyst was removed by syringe filtration, after which the products were concentrated under vacuum to provide the crude material as a brown oil that was used in the next step without further purification.

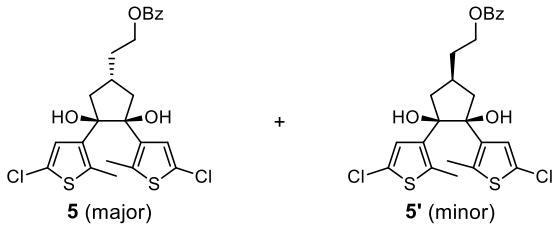
A flame-dried round bottom flask equipped with a magnetic stir bar was charged with $AlCl_3$ (1.88 g, 14.1 mmol). The atmosphere was evacuated and refilled with N_2 3×. Anhydrous DCM (110 mL) was added and the flask was cooled to -5 °C in an ice/brine bath. The acyl chloride was added as a solution in DCM (10 mL), followed by 2-chloro-5-methylthiophene[2] (1.30 mL, 11.86 mmol). The reaction stirred at -5 °C for 2.25 h, after which it was quenched with deionized water (50 mL). The aqueous layer was washed with DCM (3 x 30 mL), and the combined organics were washed with brine (30 mL), dried with Na_2SO_4, and filtered. The products were separated by silica gel chromatography (0–20% EtOAc/hexanes), yielding the title compound as a light yellow oil (1.53 g, 56% over 2 steps).

TLC (10% EtOAc/hexanes): R_f = 0.70

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 – 7.88 (m, 2H), 7.54 (ddt, *J* = 8.8, 7.0, 1.3 Hz, 1H), 7.40 (ddt, *J* = 7.8, 6.6, 1.1 Hz, 2H), 7.19 (s, 2H), 4.39 (t, *J* = 6.3 Hz, 2H), 3.11 – 2.77 (m, 5H), 2.63 (s, 5H), 1.95 (app q, *J* = 6.2 Hz, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 194.4, 166.6, 148.3, 135.0, 133.1, 130.2, 129.6, 128.5, 126.9, 125.5, 63.0, 45.7, 32.9, 28.2, 16.2 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{24}H_{23}Cl_2O_4S_2]^+$ $(M+H)^+$ 509.0410, found 509.0414.



5 (major) **5'** (minor)

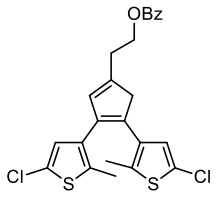
2-((1r,3R,4S)-3,4-bis(5-chloro-2-methylthiophen-3-yl)-3,4-dihydroxycyclopentyl)ethyl benzoate (5 and diastereomer 5'). An oven-dried round bottom flask was charged with Zn^0 powder (4.85 g, 74.2 mmol) in the glovebox. The flask was sealed and removed from the box. $AlCl_3$ (6.11 g, 45.8 mmol) was added to the flask and the atmosphere was evacuated and refilled with N_2 3×. The flask was placed in a room temperature water bath and H_2O (50 mL) was added slowly, followed by **4** in a solution of dry THF (50 mL). The reaction was allowed to stir at room temperature for 14 h, after which the solids were removed by filtration through celite. The celite was flushed with EtOAc (200 mL) and the organics were washed with $NaHCO_3$ (3 x 100 mL) and once with brine (100 mL). The organics were dried with Na_2SO_4, filtered, and concentrated to provide the title compounds as a white solid (4.72 g, 97%). The product was retrieved as a mixture of diastereomers that were not separated before the next step.

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

^{1}H NMR (400 MHz, $CDCl_3$, major diastereomer): 8.05 – 7.98 (m, 2H), 7.59 – 7.53 (m, 1H), 7.46 – 7.39 (m, 2H), 6.38 (s, 2H), 4.34 (t, 2H, *J* = 6.6 Hz), 3.51 (s, 2H, -OH), 2.75 (app quint, 1H, *J* = 8.1 Hz), 2.29 – 2.05 (m, 10 H), 2.03 – 1.94 (m, 2H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, major diastereomer) δ: 166.9, 137.3, 136.2, 133.2, 130.1, 129.7, 128.5, 127.5, 123.5, 86.5, 64.3, 46.4, 34.0, 31.7, 15.0 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{24}H_{24}Cl_2O_4S_2]^{+\cdot}$ $(M)^{+\cdot}$ 510.0493, found 510.0506.



6

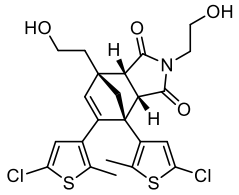
2-(3,4-bis(5-chloro-2-methylthiophen-3-yl)cyclopenta-1,3-dien-1-yl)ethyl benzoate (6). A round bottom flask equipped with a magnetic stir bar was charged with **5** (588 mg, 1.15 mmol). Dry toluene (40 mL) was added and the solution was heated to 60 °C. p-Toluenesulfonic acid monohydrate (40.0 mg, 0.210 mmol) was added in one portion and the reaction stirred for 30 min open to the atmosphere. The reaction was then cooled to room temperature and washed with saturated $NaHCO_3$ (3 x 15 mL) and brine (15 mL). The organics were dried with Na_2SO_4, filtered, and concentrated. The products were purified by silica gel chromatography (0–10% EtOAc/hexanes), yielding the title compound as an orange solid (464 mg, 85%).

TLC (25% EtOAc/hexanes): R_f = 0.78

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 – 7.98 (m, 2H), 7.65 – 7.51 (ddt, *J* = 7.9, 6.9, 1.3 Hz 1H), 7.45 (m, 2H), 6.60 (s, 1H), 6.57 (s, 1H), 6.33 (app quint, *J* = 1.3 Hz, 1H), 4.53 (t, *J* = 6.7 Hz, 2H), 3.37 (d, *J* = 1.1 Hz, 2H), 2.91 (td, *J* = 6.7, 1.4 Hz, 2H), 1.99 (s, 3H), 1.91 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ: 166.6, 143.9, 136.8, 135.0, 134.1, 133.9, 133.7, 133.1, 133.0, 131.9, 130.3, 129.7, 128.5, 127.4, 127.1, 125.6, 125.4, 64.3, 47.8, 30.2, 14.4, 14.2 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{24}H_{20}Cl_2O_2S_2]^{+\cdot}$ $(M)^{+\cdot}$ 474.0282, found 474.0301.



7

(3aS,4S,7S,7aR)-4,5-bis(5-chloro-2-methylthiophen-3-yl)-2,7-bis(2-hydroxyethyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione (7). A flame-dried round bottom flask was charged with LAH (19.9 mg, 0.524 mmol) and the atmosphere was evacuated and backfilled with N_2 3×. THF (2 mL) was added and the mixture was cooled to 0 °C. A solution of **6** (251 mg, 0.528 mmol) in THF (1 mL) was added slowly, after which the reaction was allowed to stir at 0 °C for 30 min. It was quenched with saturated NH_4Cl (3 mL) and the products were extracted into Et_2O (3 x 5 mL). During each extraction, the combined organic and aqueous layers were sonicated for approximately 30 s in a bath sonicator in order to liberate the reduced product from Al salt aggregates. The combined organics were washed with brine (5 mL), dried with Na_2SO_4, and filtered. The products were purified by silica gel chromatography (0–50% EtOAc/hexanes), yielding 2-(3,4-bis(5-chloro-2-methylthiophen-3-yl)cyclopenta-1,3-dien-1-yl)ethan-1-ol as a light yellow oil contaminated with a roughly equimolar amount of benzyl alcohol. It was used directly in the next step without further purification to avoid decomposition.

A flame-dried round bottom flask was charged with *N*-(2-hydroxyethyl)maleimide[3] (748 mg, 5.30 mmol) and the atmosphere was evacuated and refilled with N_2 3×. 2-(3,4-bis(5-chloro-2-methylthiophen-3-yl)cyclopenta-1,3-dien-1-yl)ethan-1-ol was added as a solution in dry toluene (5.0 mL) and the reaction was stirred at 70 °C for 24 h. The reaction was cooled to room temperature and concentrated. The crude mixture was separated by reverse phase chromatography on a C18 column (45–60% MeCN/H_2O) to provide the title compound as a white solid (148 mg, 51% over 2 steps). Alternatively, silica gel chromatography (0–10% MeOH/DCM) followed by recrystallization from toluene also afforded the pure *endo* product.

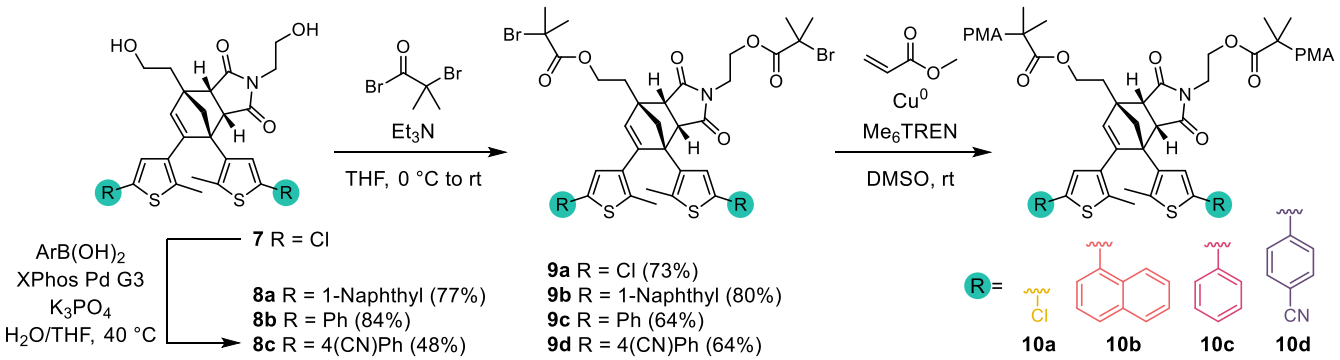
TLC (5% MeOH/DCM): R_f = 0.43

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 7.47 (s, 1H), 6.20 (s, 1H), 6.13 (s, 1H), 4.15 (d, *J* = 7.7 Hz), 3.86 (td, *J* = 6.5, 0.9 Hz), 3.83 – 3.79 (m, 1H, -OH), 3.60 (t, 1H, J = 6.0 Hz, -OH), 3.54 (d, *J* = 7.7 Hz), 3.41 – 3.29 (m, 2H), 3.25 – 3.14 (m, 2H), 2.58 (d, *J* = 9.0 Hz), 2.47 – 2.35 (m, 4H), 2.17 (dt, *J* = 14.3, 6.5 Hz), 2.01 (s, 3H), 1.88 (dd, *J* = 9.0, 1.1 Hz) ppm.

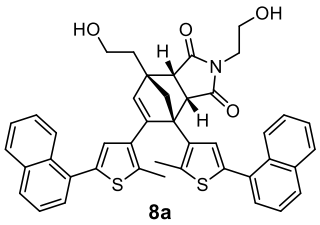
$^{13}C\{^{1}H\}$ NMR (101 MHz, $(CD_3)_2CO$) δ: 177.9, 177.6, 143.6, 136.2, 136.1, 135.9, 135.8, 132.4, 130.4, 127.7, 124.0, 123.4, 62.1, 61.8, 60.0, 58.9, 56.1, 52.0, 51.3, 41.1, 35.5, 15.1, 14.4 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{23}H_{24}Cl_2NO_4S_2]^{+}$ $(M+H)^{+}$ 512.0519, found 512.0524.

Scheme S2. Differentiation of **7** and Synthesis of Mechanophore-Centered PMA Polymers



General Procedure A for Suzuki–Miyaura Cross-Coupling of Thienyl Chlorides with Aryl Boronic Acids. A round bottom flask was charged with the appropriate thienyl chloride (1.0 equiv), XPhos Pd G3 (0.1 equiv), K_3PO_4 (6 equiv), and the appropriate aryl boronic acid (4 equiv). The atmosphere was evacuated and refilled with N_2 3×. Degassed water was added, followed by dry THF, and the reaction was stirred at the indicated temperature for the indicated amount of time. Upon completion, the reaction was cooled to room temperature (if applicable) and diluted with EtOAc (10 mL). The organics were washed with 1 M NaOH (3 x 5 mL), then the combined aqueous layer was extracted once with EtOAc (5 mL). The organic layers were combined and washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure.



8a

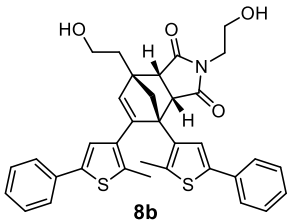
(3aS,4S,7S,7aR)-2,7-bis(2-hydroxyethyl)-4,5-bis(2-methyl-5-(naphthalen-1-yl)thiophen-3-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione (8a). Synthesized according to general procedure A with **7** (100 mg, 0.195 mmol), XPhos Pd G3 (16.5 mg, 0.0195 mmol), K_3PO_4 (250 mg, 1.18 mmol), and 1-naphthaleneboronic acid (134 mg, 0.779 mmol). It was purified by silica gel chromatography (0–10% MeOH/DCM) to yield the title compound as a light brown solid (105 mg, 77%).

TLC (5% MeOH/DCM): R_f = 0.37

^{1}H NMR (400 MHz, CD_3OD) δ: 8.10 (m, 1H), 7.89 – 7.78 (m, 3H), 7.73 (m, 2H), 7.69 (s, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.28 (m, 3H), 7.17 – 7.08 (m, 2H), 6.95 (ddd, 1H, *J* = 8.3, 6.8, 1.3 Hz), 6.80 (s, 1H), 6.17 (s, 1H), 4.19 (d, 1H, *J* = 7.7 Hz), 3.93 (td, 2H, *J* = 6.7, 1.1 Hz), 3.47 (d, 1H, *J* = 7.7 Hz), 3.43 – 3.37 (m, 2H), 3.24 (t, 2H, *J* = 6.6 Hz), 2.66 (d, 1H, *J* = 8.9 Hz), 2.61 (s, 3H), 2.50 (dt, 1H, *J* = 13.8, 6.7 Hz), 2.30 – 2.15 (m, 4H), 1.90 (dd, 1H, *J* = 8.9, 1.0 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, CD_3OD) δ: 179.1, 178.9, 145.9, 138.0, 137.9, 137.4, 137.1, 136.9, 135.4, 135.3, 135.0, 133.7, 133.6, 133.4, 132.64, 132.62, 132.0, 129.8, 129.13, 129.10, 129.06, 129.0, 128.7, 128.6, 127.9, 127.3, 127.0, 126.8, 126.7, 126.6, 126.12, 126.06, 63.0, 62.6, 60.6, 59.4, 56.3, 52.9, 51.7, 41.1, 35.9, 15.4, 14.6 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{43}H_{38}NO_4S_2]^+$ $(M+H)^+$ 696.2237, found 696.2250.



8b

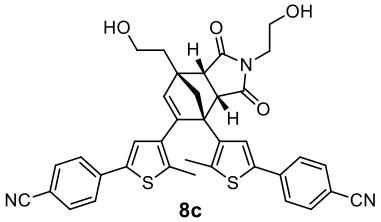
(3aS,4S,7S,7aR)-2,7-bis(2-hydroxyethyl)-4,5-bis(2-methyl-5-phenylthiophen-3-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione (8b). Synthesized according to general procedure A with **7** (200 mg, 0.390 mmol), XPhos Pd G3 (33 mg, 0.039 mmol), K_3PO_4 (495 mg, 2.33 mmol), and phenylboronic acid (190 mg, 1.56 mmol). It was purified by silica gel chromatography (0–10% MeOH/DCM) to yield the title compound as a light brown solid (195 mg, 84%).

TLC (5% MeOH/DCM): R_f = 0.39

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ: 8.07 (s, 1H), 7.68 – 7.64 (m, 2H), 7.44 (t, 2H, *J* = 7.8 Hz), 7.31 (td, 1H, *J* = 7.3, 1.2 Hz), 7.22 (dd, 2H, *J* = 8.0, 1.6 Hz), 7.17 – 7.08 (m, 3H), 6.72 (s, 1H), 6.16 (s, 1H), 4.31 (d, 1H, *J* = 7.7 Hz), 3.92 (ddd, 2H, *J* = 10.4, 7.6, 5.0 Hz), 3.81 (t, 1H, *J* = 5.2 Hz, -OH), 3.58 (d, 1H, *J* = 7.6 Hz), 3.51 (t, 1H, *J* = 6.0 Hz, -OH), 3.34 (dd, 2H, *J* = 7.1, 5.9 Hz), 3.18 (qd, 2H, *J* = 6.7, 2.1 Hz), 2.67 (d, 1H, *J* = 8.9 Hz), 2.53 (s, 3H), 2.46 (dt, 1H, *J* = 13.5, 6.5 Hz), 2.23 (dt, 1H, *J* = 14.4, 6.5 Hz), 2.09 (s, 3H), 1.94 (dd, 1H, *J* = 9.0, 1.0 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2CO$) δ: 178.0, 177.8, 144.6, 139.4, 138.0, 137.8, 136.8, 136.6, 135.6, 135.4, 134.7, 133.5, 129.9, 129.6, 128.2, 128.0, 127.7, 126.2, 125.8, 125.7, 62.4, 61.7, 60.2, 59.0, 56.1, 52.2, 51.5, 41.1, 35.8, 15.5, 14.7 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{35}H_{34}NO_4S_2]^+$ $(M+H)^+$ 596.1924, found 596.1931.



8c

4,4'-(((3aS,4S,7S,7aR)-2,7-bis(2-hydroxyethyl)-1,3-dioxo-1,2,3,3a,7,7a-hexahydro-4H-4,7-methanoisoindole-4,5-diyl)bis(5-methylthiophene-4,2-diyl))dibenzonitrile (8c). Synthesized according to general procedure A with **7** (100 mg, 0.195 mmol), XPhos Pd G3 (16.2 mg, 0.0191 mmol), K_3PO_4 (246 mg, 1.16 mmol), and 4-(cyanophenyl)boronic acid (115 mg, 0.783 mmol). It was purified by silica gel chromatography (0–10% MeOH/DCM) to yield the title compound as a white solid (60 mg, 48%).

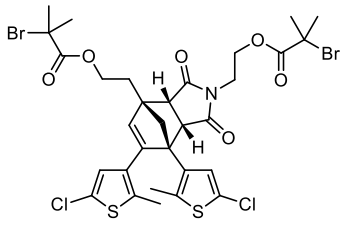
TLC (5% MeOH/DCM): R_f = 0.37

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 8.27 (s, 1H), 7.85 (s, 4H), 7.56 (d, 2H, *J* = 8.2 Hz), 7.35 (d, 2H, *J* = 8.2 Hz), 6.82 (s, 1H), 6.22 (s, 1H), 4.38 (d, 1H, *J* = 7.7 Hz), 3.94 – 3.87 (m, 2H), 3.83 (t, 1H, *J* = 5.1 Hz, -OH), 3.61 (d, 1H, *J* = 7.7 Hz), 3.54 (t, 1H, *J* = 6.0 Hz, -OH), 3.35 (t, 2H, *J* = 6.6 Hz), 3.18 (app q, 2H, *J* = 6.8 Hz), 2.69 (d, 1H, *J* = 9.0 Hz), 2.57 (s, 3H), 2.47 (dt, 1H, *J* = 13.6, 6.7 Hz), 2.23 (dt, 1H, *J* = 13.6, 6.4 Hz), 2,13 (s, 3H), 1.97 (d, 1H, *J* = 9.0 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2CO$) δ: 178.2, 177.7, 144.0, 139.7, 139.6, 139.52, 139.50, 138.5, 137.3, 136.0, 135.7, 134.1, 133.9, 133.6, 130.4, 127.6, 126.5, 126.0, 119.4, 119.2, 111.1, 110.8, 62.3, 61.6, 60.2, 60.0, 59.0, 58.9, 56.3, 52.1, 51.5, 41.1, 35.7, 15.5, 14.8 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{37}H_{31}N_3O_4S_2]^+$ $(M+H)^+$ 646.1829, found 646.1846.

General Procedure B for the Synthesis of Polymerization Initiators and Crosslinkers by Esterification. A flame-dried round bottom flask was charged with the appropriate diol (1.0 equiv) and the atmosphere was evacuated and refilled 3× with N_2. Dry THF (1.5 mL) was added and the solution was cooled to 0 °C in an ice/water bath. Triethylamine (7.0 equiv) was added, followed by either α-bromoisobutyryl bromide or acryloyl chloride (5.0 equiv). Immediately after the addition, the reaction was removed from the bath to warm to room temperature and stirred for the indicated amount of time. The reaction mixture was then diluted with EtOAc (5 mL) and the solution was washed with saturated $NaHCO_3$ (3 x 5 mL) and then brine (5 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure.



9a

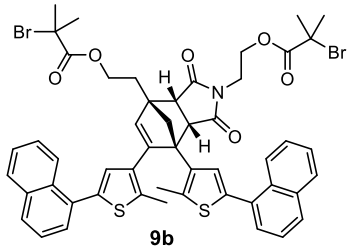
((3aR,4S,7S,7aS)-6,7-bis(5-chloro-2-methylthiophen-3-yl)-1,3-dioxo-3,3a,7,7a-tetrahydro-1H-4,7-methanoisoindole-2,4-diyl)bis(ethane-2,1-diyl) bis(2-bromo-2-methylpropanoate) (9a). Synthesized according to general procedure B with **7** (80 mg, 0.16 mmol), triethylamine (150 µL, 1.08 mmol), and α-bromoisobutyryl bromide (100 µL, 0.811 mmol). It stirred for 17 h before being worked up and purified by silica gel chromatography (0–50% EtOAc/hexanes) and the title compound was retrieved as a light yellow solid (92 mg, 73%).

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

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.33 (s, 1H), 6.13 (s, 1H), 5.98 (s, 1H), 4.51 – 4.36 (m, 2H), 4.16 (dt, 1H, *J* = 11.5, 5.0 Hz), 3.96 – 3.85 (m, 2H), 3.60 (t, 2H, *J* = 5.4 Hz), 3.39 (d, 1H, *J* = 7.8 Hz), 2.59 (dt, 1H, *J* = 15.0, 5.6 Hz), 2.51 (d, *J* = 9.1 Hz), 2.44 – 2.35 (m, 4H), 1.96 – 1.91 (m, 9H), 1.91 (s, 3H), 1.89 (s, 3H), 1.80 (dd, 1H, *J* = 9.1, 1.1 Hz) ppm.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 176.1, 176.0, 171.7, 171.4, 144.9, 135.2, 134.9, 133.6, 132.7, 130.4, 128.7, 126.3, 125.0, 124.6, 63.8, 62.6, 61.9, 61.5, 55.8, 55.7, 54.9, 51.3, 50.7, 37.4, 30.88, 30.87, 30.85, 30.8, 30.6, 15.4, 14.4 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{31}H_{34}Br_2Cl_2NO_6S_2]^+$ $(M+H)^+$ 809.9546, found 809.9565.



9b

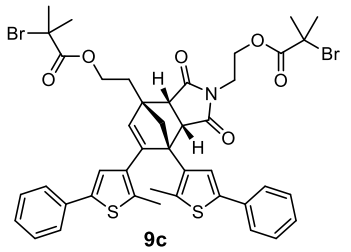
((3aR,4S,7S,7aS)-6,7-bis(2-methyl-5-(naphthalen-1-yl)thiophen-3-yl)-1,3-dioxo-3,3a,7,7a-tetrahydro-1H-4,7-methanoisoindole-2,4-diyl)bis(ethane-2,1-diyl) bis(2-bromo-2-methylpropanoate) (9b). Synthesized according to general procedure B with **8a** (80 mg, 0.12 mmol), triethylamine (112 µL, 0.804 mmol), and α-bromoisobutyryl bromide (71 µL, 0.57 mmol). Stirred for 15 h before being worked up and purified by silica gel chromatography (10–40% EtOAc/hexanes) and the title compound was retrieved as a light yellow solid (91 mg, 80%).

TLC (25% EtOAc/hexanes): R_f = 0.38

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 8.21 (d, 1H, *J* = 8.6 Hz), 7.99 – 7.93 (m, 1H), 7.92 – 7.85 (m, 2H), 7.85 – 7.77 (m, 2H), 7.73 (s, 1H), 7.50 – 7.33 (m, 5H), 7.27 (tt, 2H, *J* = 6.8, 5.1 Hz), 7.12 (ddd, 1H, *J* = 8.3, 6.8, 1.3 Hz), 6.86 (s, 1H), 6.33 (s, 1H), 4.63 – 4.51 (m, 2H), 4.38 (d, 1H, *J* = 7.8 Hz), 4.07 (dt, 1H, *J* = 11.5, 5.0 Hz), 3.86 (ddd, 1H, *J* = 11.7, 7.5, 5.0 Hz), 3.68 – 3.53 (m, 3H), 2.79 (d, 1H, *J* = 8.8 Hz), 2.73 – 2.64 (m, 4H), 2.46 (ddd, 1H, *J* = 14.1, 7.8, 6.3 Hz), 2.35 (s, 2H), 2.11 (d, 1H, *J* = 8.7 Hz), 1.97 (s, 6H), 1.89 – 1.85 (m, 6H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $(CD_3)_2CO$) δ: 177.9, 177.1, 171.9, 171.6, 146.2, 137.7, 137.1, 137.0, 136.7, 136.5, 135.0, 134.9, 134.2, 133.22, 133.19, 133.1, 132.3, 132.12, 132.09, 129.3, 129.1, 129.02, 128.97, 128.9, 128.5, 128.4, 127.7, 127.3, 126.8, 126.7, 126.5, 126.3, 126.11, 126.06, 64.7, 63.3, 62.8, 62.6, 57.4, 57.1, 55.8, 52.5, 51.3, 37.6, 31.5, 31.04, 31.03, 30.99, 15.5, 14.7 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{51}H_{48}Br_2NO_6S_2]^+$ $(M+H)^+$ 992.1285, found 922.1307.



9c

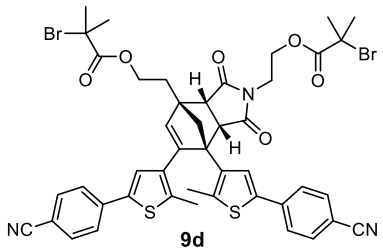
((3aR,4S,7S,7aS)-6,7-bis(2-methyl-5-phenylthiophen-3-yl)-1,3-dioxo-3,3a,7,7a-tetrahydro-1H-4,7-methanoisoindole-2,4-diyl)bis(ethane-2,1-diyl) bis(2-bromo-2-methylpropanoate) (9c). Synthesized according to general procedure B with **8b** (50 mg, 0.084 mmol), triethylamine (82 µL, 0.59 mmol), and α-bromoisobutyryl bromide (52 µL, 0.42 mmol). It stirred for 15 h before being worked up and purified by silica gel chromatography (0–35% EtOAc/hexanes) and the title compound was retrieved as a light yellow solid (48 mg, 64%).

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

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92 (s, 1H), 7.66 – 7.61 (m, 2H), 7.41 (t, 2H, *J* = 7.6 Hz), 7.30 (t, 1H, *J* = 7.4 Hz), 7.22 – 7.17 (m, 2H), 7.15 – 7.06 (m, 2H), 6.59 (s, 1H), 6.05 (s, 1H), 4.57 – 4.41 (m, 2H), 4.17 – 4.08 (m, 2H), 3.87 (ddd, 1H, *J* = 11.4 Hz, 6.7 Hz, 4.5 Hz), 3.66 – 3.53 (m, 2H), 3.45 (d, 1H, *J* = 7.8 Hz), 2.71 – 2.61 (m, 2H), 2.51 (s, 3H), 2.45 (ddd, 1H, J = 14.4, 8.1, 6.0 Hz), 2.06 (s, 3H), 1.96 (s, 6H), 1.93 – 1.87 (m, 7H) ppm.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 176.4, 176.3, 171.8, 171.5, 145.7, 139.7, 138.3, 136.6, 136.5, 135.5, 134.7, 134.3, 131.6, 131.4, 129.0, 128.8, 127.3, 126.9, 126.7, 125.9, 125.4, 124.2, 63.9, 62.7, 62.0, 61.4, 55.9, 55.7, 55.1, 51.6, 51.0, 37.3, 30.92, 30.91, 30.86, 30.85, 30.8, 15.8, 14.7 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{43}H_{44}Br_2NO_6S_2]^+$ $(M+H)^+$ 892.0972, found 892.0981.



9d

((3aR,4S,7S,7aS)-6,7-bis(5-(4-cyanophenyl)-2-methylthiophen-3-yl)-1,3-dioxo-3,3a,7,7a-tetrahydro-1H-4,7-methanoisoindole-2,4-diyl)bis(ethane-2,1-diyl) bis(2-bromo-2-methylpropanoate) (9d). Synthesized according to general procedure B with **8c** (40 mg, 0.062 mmol), triethylamine (60 µL, 0.430 mmol), and α-bromoisobutyryl bromide (38 µL, 0.31 mmol). It stirred for 15 h before it was worked up and purified by silica gel chromatography (30–70% EtOAc/hexanes) and the title compound was retrieved as a light yellow solid (37 mg, 64%).

TLC (25% EtOAc/hexanes): R_f = 0.13

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (s, 1H), 7.69 (s, 4H), 7.39 (d, 2H, *J* = 8.5 Hz), 7.25 – 7.21 (m, 2H), 6.65 (s, 1H), 6.10 (s, 1H), 4.56 – 4.41 (m, 2H), 4.18 – 4.09 (m, 2H), 3.87 (ddd, 1H, *J* = 11.4, 6.8, 4.4 Hz), 3.67 – 3.53 (m, 2H), 3.49 (d, 1H, *J* = 7.8 Hz), 2.71 – 2.61 (m, 2H), 2.53 (s, 3H), 2.47 (ddd, 1H, *J* = 13.9, 8.0, 5.6 Hz), 2.08 (s, 3H), 1.95 (s, 6H), 1.93 – 1.86 (m, 7H) ppm.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 176.6, 176.0, 171.7, 171.5, 144.9, 139.2, 139.1, 138.6, 138.5, 137.3, 136.3, 136.2, 133.0, 132.7, 132.6, 132.1, 128.5, 126.0, 125.7, 125.4, 118.9, 110.6, 110.1, 63.8, 62.5, 61.8, 61.5, 55.83, 55.78 55.2, 51.4, 51.0, 37.4, 30.92, 30.90, 30.86, 30.8, 30.7, 15.9, 14.9 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{45}H_{42}Br_2N_3O_6S_2]^+$ $(M+H)^+$ 942.0877, found 942.0883.

General Procedure C for the Synthesis of Poly(Methyl Acrylate) (PMA) Polymers Incorporating a Cyclopentadiene–Maleimide Mechanophore. Polymers were synthesized by controlled radical polymerization following the procedure by Nguyen *et al*.[4] 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 N_2 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. Following completion of the polymerization, the flask was opened to atmosphere and diluted with a minimal amount of DCM. The polymer was precipitated 3× into methanol cooled with dry ice and then dried under vacuum to afford the polymer.

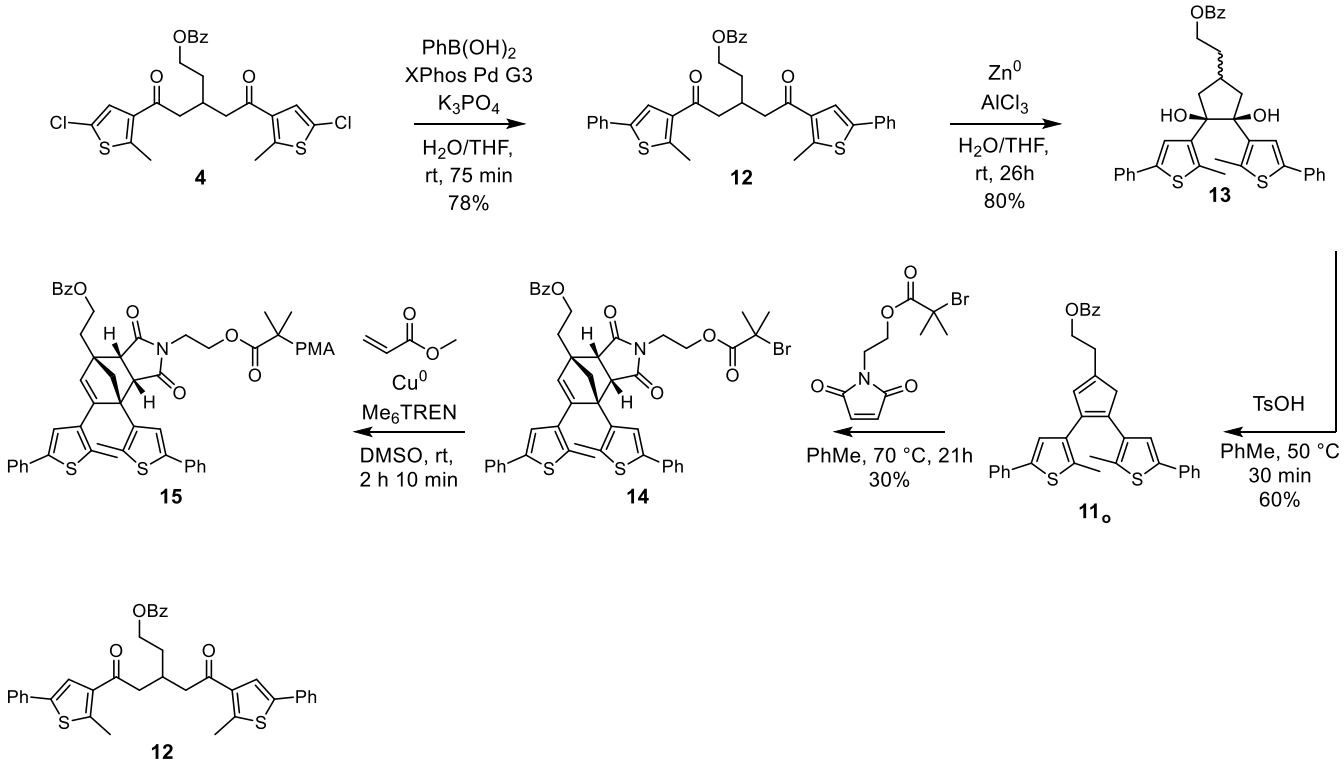
Polymer 10a. Synthesized using general procedure C with **9a** (10.0 mg, 0.0123 mmol), methyl acrylate (1.56 mL, 17.2 mmol), DMSO (1.56 mL), and Me_6TREN (13.0 µL, 0.0486 mmol). Polymerization for 55 min provided the title polymer as a tacky white solid (837 mg, 56%). M_n = 111 kg/mol; $Đ$ = 1.05.

Polymer 10b. Synthesized using general procedure C with **9b** (6.7 mg, 0.0067 mmol), methyl acrylate (850 µL, 9.38 mmol), DMSO (850 µL), and Me_6TREN (6.2 µL, 0.023 mmol). Polymerization for 35 min provided the title polymer as a tacky white solid (427 mg, 52%). M_n = 112 kg/mol; $Đ$ = 1.07.

Polymer 10c. Synthesized using general procedure C with **9c** (10.0 mg, 0.0112 mmol), methyl acrylate (1.42 mL, 15.7 mmol), DMSO (1.42 mL), and Me_6TREN (12.0 µL, 0.0449 mmol). Polymerization for 55 min provided the title polymer as a tacky white solid (639 mg, 47%). M_n = 105 kg/mol; $Đ$ = 1.06.

Polymer 10d. Synthesized using general procedure C with **9d** (10.2 mg, 0.0108 mmol), methyl acrylate (1.37 mL, 15.1 mmol), DMSO (1.37 mL), and Me_6TREN (9.9 µL, 0.037 mmol). Polymerization for 35 min provided the title polymer as a tacky white solid (663 mg, 51%). M_n = 96 kg/mol; $Đ$ = 1.06.

Scheme S3. Synthesis of Chain-End Functional Control PMA Polymer **15**



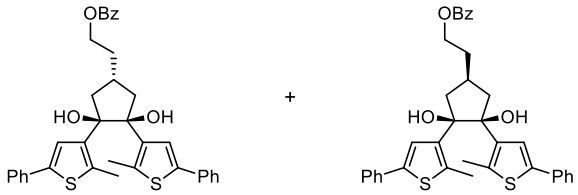
5-(2-methyl-5-phenylthiophen-3-yl)-3-(2-(2-methyl-5-phenylthiophen-3-yl)-2-oxoethyl)-5-oxopentyl benzoate (12). Synthesized according to general procedure A using **4** (1.00 g, 1.69 mmol), XPhos Pd G3 (166 mg, 0.196 mmol), K_3PO_4 (2.49 g, 11.7 mmol), and phenylboronic acid (957 mg, 7.85 mmol) in H_2O (12.0 mL) and THF (6.0 mL) at room temperature for 75 min. Purified by silica gel chromatography (0–25% EtOAc/hexanes) and the title compound was retrieved as a brown solid (909 mg, 78%).

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

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.95 (dd, 2H, *J* = 8.3, 1.3 Hz), 7.65 (s, 2H), 7.53 (dd, 4H, *J* = 8.2, 1.3 Hz), 7.47 (ddt, 1H, *J* = 8.7, 7.4, 1.3 Hz), 7.36 (t, 4H, *J* = 7.7 Hz), 7.34 – 7.27 (m, 4H), 4.45 (t, 2H, *J* = 6.3 Hz), 3.20 – 3.10 (m, 3H), 2.75 (s, 6H), 2.04 (app q, 2H, *J* = 6.1 Hz) ppm.

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 195.6, 166.7, 149.2, 139.8, 136.5, 133.6, 133.0, 130.2, 129.6, 129.1, 128.5, 127.9, 125.8, 123.9, 63.1, 46.0, 32.9, 28.6, 16.5 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{36}H_{32}O_4S_2]^{+\cdot}$ $(M)^{+\cdot}$ 593.1815, found 593.1829.



13 (major) **13'** (minor)

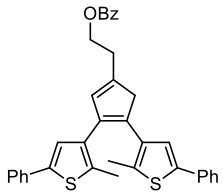
2-(3,4-dihydroxy-3,4-bis(2-methyl-5-phenylthiophen-3-yl)cyclopentyl)ethyl benzoate (13 and diastereomer 13'). An oven-dried round bottom flask was charged with Zn^0 powder (134 mg, 2.05 mmol) in the glovebox. The flask was sealed and removed from the box. $AlCl_3$ (244 mg, 1.83 mmol) was added to the flask and the atmosphere was evacuated and refilled with N_2 3×. The flask was placed in a room temperature water bath and H_2O (2.0 mL) was added slowly, followed by **12** (114 mg, 0.192 mmol) in a solution of dry THF (2.0 mL). The reaction was allowed to stir at room temperature for 26 h, after which the solids were removed by filtration through celite. The celite was flushed with EtOAc (15 mL) and the organics were washed with $NaHCO_3$ (3 x 5 mL) and once with brine (5 mL). The organics were dried with Na_2SO_4, filtered, and concentrated. The products were separated by silica gel chromatography (0–50% EtOAc/hexanes), yielding the title compounds as white solid (91 mg, 80%). The product was isolated as a mixture of diastereomers which were not separated before the next step.

TLC (25% EtOAc/hexanes): R_f = 0.48

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 8.07 – 8.04 (m, 2H), 7.64 – 7.59 (m, 1H), 7.52 – 7.46 (m, 2H), 7.36 –7.41 (m, 4H), 7.30 – 7.24 (m, 4H), 7.23 – 7.17 (m, 2H), 7.02 (s, 2H), 4.86 (s, 2H), 4.47 (t, 2H, *J* = 6.5 Hz), 2.93 (app quint, 1H, *J* = 8.6 Hz), 2.53 – 2.44 (m, 2H), 2.43 – 2.35 (m, 8H), 2.18 (app q, 2H, *J* = 6.9 Hz) ppm.

^{13}C{^{1}H} (101 MHz, $(CD_3)_2CO$) δ: 166.8, 141.2, 137.7, 137.4, 135.5, 133.9, 131.5, 130.2, 129.6, 129.4, 127.7, 126.5, 126.0, 87.1, 65.1, 47.6, 34.7, 32.8, 15.6 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{36}H_{34}O_4S_2]^{+\cdot}$ $(M)^{+\cdot}$ 594.1899, found 594.1904.



11_o

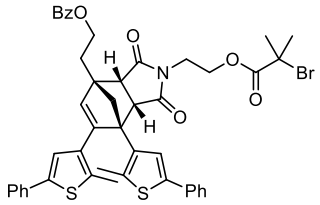
2-(3,4-bis(2-methyl-5-phenylthiophen-3-yl)cyclopenta-1,3-dien-1-yl)ethyl benzoate (11_o). A round bottom flask equipped with a magnetic stir bar was charged with **13** (150 mg, 0.252 mmol). Dry toluene (7.5 mL) was added and the solution was heated to 50 °C. p-Toluenesulfonic acid monohydrate (9.5 mg, 0.050 mmol) was added in one portion and the reaction stirred for 30 min open to the atmosphere. The reaction was then cooled to room temperature and washed with saturated $NaHCO_3$ (3 x 5 mL) and brine (5 mL). The organics were dried with Na_2SO_4, filtered, and concentrated. The products were purified by C18 reverse phase chromatography (80–100% MeCN/H_2O), yielding the title compound as a purple solid (84 mg, 60%).

TLC (25% EtOAc/hexanes): R_f = 0.73

^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ: 8.06 (m, 2H), 7.63 (m, 1H), 7.57 – 7.49 (m, 6H), 7.35 (t, 4H, *J* = 7.6 Hz), 7.28 (s, 1H), 7.24 (td, 2H, *J* = 7.3, 1.4 Hz), 7.14 (s, 1H), 6.56 (s, 1H), 4.59 (t, 2H, *J* = 6.6 Hz), 3.64 (d, 2H, *J* = 1.2 Hz), 3.00 (td, 2H, *J* = 6.7, 1.3 Hz), 2.12 (s, 3H), 2.04 (s, 3H) ppm.

$^{13}C\{^{1}H\}$ NMR (126 MHz, $(CD_3)_2CO$) δ: 166.7, 145.0, 140.7, 140.3, 137.9, 137.1, 136.9, 136.6, 135.5, 135.3, 135.2, 134.4, 133.9, 132.8, 131.4, 130.2, 129.8, 129.4, 128.1, 128.0, 126.0, 125.88, 125.86, 125.4, 64.9, 48.3, 30.8, 14.7, 14.4 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{36}H_{30}O_2S_2]^{+\cdot}$ $(M)^{+\cdot}$ 558.1687, found 558.1694.



14

2-((3aR,4S,7S,7aS)-2-(2-((2-bromo-2-methylpropanoyl)oxy)ethyl)-6,7-bis(2-methyl-5-phenylthiophen-3-yl)-1,3-dioxo-1,2,3,3a,7,7a-hexahydro-4H-4,7-methanoisoindol-4-yl)ethyl benzoate (14). A flame-dried round bottom flask was charged with 2-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl 2-bromo-2-methylpropanoate[5] (121 mg, 0.417 mmol) and the atmosphere was evacuated and refilled with N_2 3×. A solution of **11_o** (121 mg, 0.217 mmol) in dry toluene (3.0 mL) was added and the reaction was stirred at 70 °C for 21 h. The reaction was cooled to room temperature and concentrated. The products were separated by C18 reverse phase chromatography (80–100% MeCN/H_2O). The resulting light brown solid was recrystallized from acetone, yielding the title compound as a white solid (55 mg, 30%).

TLC (25% EtOAc/hexanes): R_f = 0.32

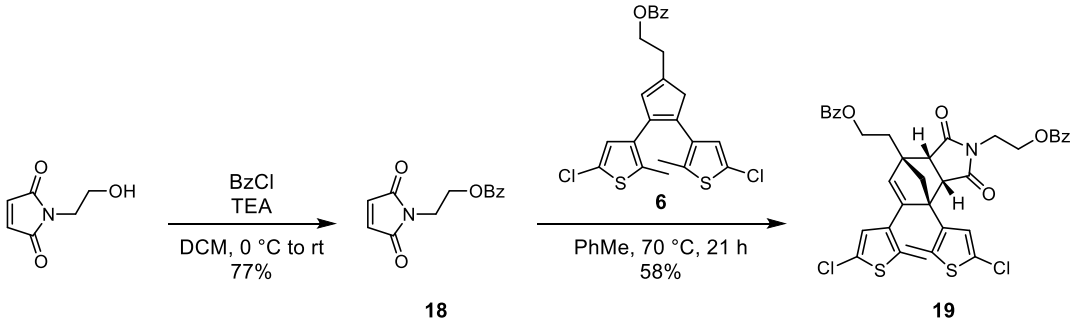
^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.08 – 8.03 (m, 2H), 7.91 (s, 1H), 7.66 – 7.61 (m, 2H), 7.58 (dt, 1H, *J* = 7.3, 1.3 Hz), 7.45 (t, 2H, *J* = 7.8 Hz), 7.41 (t, 2H, *J* = 7.7 Hz), 7.32 – 7.28 (m, 1H), 7.19 (dd, 2H, *J* = 7.9, 1.7 Hz), 7.14 – 7.06 (m, 3H), 6.59 (s, 1H), 6.09 (s, 1H), 4.72 – 4.61 (m, 2H), 4.18 – 4.09 (m, 2H), 3.85 (ddd, 1H, *J* = 11.4, 6.7, 4.5 Hz), 3.66 – 3.54 (m, 2H), 3.44 (d, 1H, *J* = 7.8 Hz), 2.82 (dt, 1H, *J* = 14.9, 5.9 Hz), 2.68 (d, 1H, *J* = 9.0 Hz), 2.49 (dt, 1H, *J* = 15.0, 6.6 Hz), 2.41 (s, 3H), 1.98 (s, 3H), 1.91 (s, 3H), 1.90 – 1.85 (m, 4H) ppm.

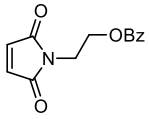
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ: 176.4, 176.3, 171.5, 166.7, 145.5, 139.7, 138.3, 136.6, 136.5, 135.6, 134.7, 134.4, 133.3, 131.64, 131.58, 130.2, 129.7, 129.0, 128.8, 128.7, 127.3, 126.9, 126.7, 125.9, 125.4, 124.2, 62.8, 62.7, 62.0, 61.2, 55.9, 55.3, 51.9, 50.9, 37.4, 31.2, 30.9, 15.6, 14.6 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{46}H_{32}BrNO_6S_2]^{+}$ $(M+H)^{+}$ 848.1710, found 848.1728.

Synthesis of Chain-End Functional Control Polymer 15. Synthesized using general procedure C with **14** (10.0 mg, 0.0118 mmol), methyl acrylate (1.50 mL, 16.6 mmol), DMSO (1.50 mL), and Me_6TREN (6.3 µL, 0.024 mmol). Polymerization for 130 min provided the title polymer as a tacky white solid (689 mg, 48%). M_n = 96 kg/mol; $Đ$ = 1.04.

Scheme S4. Synthesis of Diester Cyclopentadiene–Maleimide Diels–Alder Adduct **19**





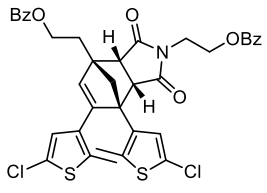
2-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)ethyl benzoate (18). A flame-dried round bottom flask equipped with an addition funnel was charged with *N*-(2-hydroxyethyl)maleimide (996 mg, 7.06 mmol). DCM (24 mL) and triethylamine (5.00 mL, 35.9 mmol) were added and the solution was cooled to 0 °C in an ice bath. A solution of benzoyl chloride (1.65 mL, 14.2 mmol) in DCM (24 mL) was added dropwise via addition funnel. Immediately following the addition, the reaction was removed from the ice bath and allowed to warm to room temperature. After stirring for 18 h, the organic layer was washed with saturated $NaHCO_3$ (3 x 30 mL) and brine (30 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated under vacuum. The crude mixture was purified by silica gel chromatography (0–25% EtOAc/hexanes) to provide the title compound as a light yellow solid (1.33 g, 77%).

TLC (25% EtOAc/hexanes): R_f = 0.41

^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.02–7.94 (m, 2H), 7.59–7.51 (m, 1H), 7.47–7.39 (m, 2H), 6.73 (s, 2H), 4.48–4.41 (m, 2H), 3.99–3.92 (m, 2H) ppm.

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 170.5, 166.5, 134.4, 133.3, 129.8, 129.7, 128.6, 62.3, 37.0 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{13}H_{12}NO_4]^+$ $(M+H)^+$ 246.0761, found 246.0761



((3aR,4S,7S,7aS)-6,7-bis(5-chloro-2-methylthiophen-3-yl)-1,3-dioxo-3,3a,7,7a-tetrahydro-1H-4,7-methanoisoindole-2,4-diyl)bis(ethane-2,1-diyl) dibenzoate (19). A flame-dried round bottom flask was charged with **18** (59 mg, 0.241 mmol) and then sealed and evacuated and refilled with N_2 3×. A solution of **6** (101 mg, 0.212 mmol) in toluene (2.0 mL) was added and the reaction was heated to 70 °C for 21 h. After cooling to room temperature, the reaction was filtered and the collected solids were washed with toluene to yield the title compound as a white solid. A second crop was isolated from the filtrate and recrystallized from toluene to provide additional product as a white solid (88 mg combined, 58%).

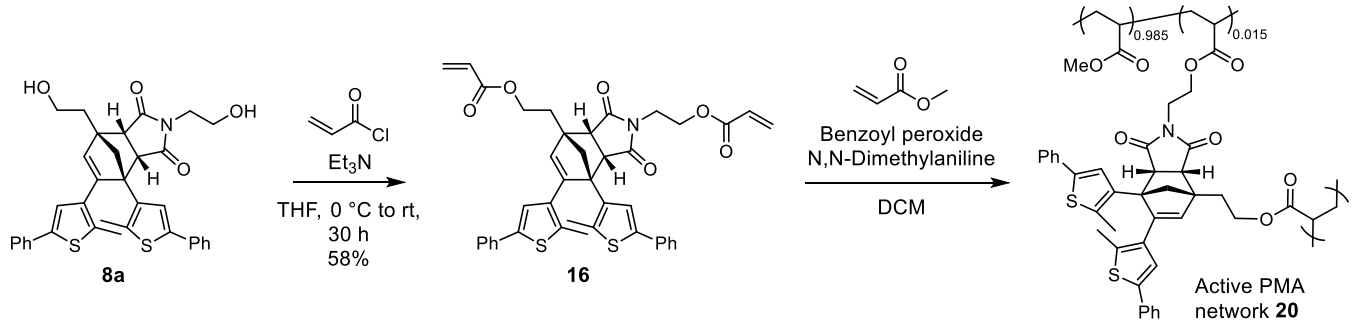
TLC (25% EtOAc/hexanes): R_f = 0.16

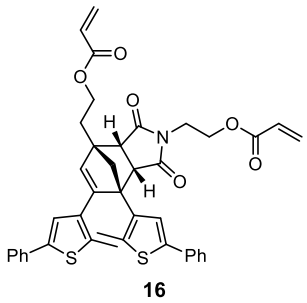
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (ddd, 4H, *J* = 16.4, 8.4, 1.4 Hz), 7.59–7.53 (m, 2H), 7.49–7.39 (m, 4H), 7.35 (s, 1H), 6.10 (s, 1H), 5.80 (s, 1H), 4.66–4.50 (m, 2H), 4.19–4.11 (m, 1H), 3.94–3.81 (m, 3H), 3.72–3.63 (m, 1H), 3.41 (d, 1H, *J* = 7.8 Hz), 2.82–2.73 (dt, 1H, *J* = 14.9, 6.0 Hz), 2.52–2.40 (m, 2H), 1.84 (s, 3H), 1.80 (s, 1H), 1.76 (dd, 1H, *J* = 9.0, 1.1 Hz) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 176.3, 176.1, 166.5, 165.6, 144.3, 135.1, 134.8, 133.6, 133.3, 133.0, 130.2, 130.0, 129.8, 129.62, 129.58, 128.58, 128.55, 125.8, 124.9, 124.8, 62.4, 61.9, 61.6, 61.5, 55.0, 51.7, 50.3, 37.4, 31.1, 14.4, 14.2 ppm.

HRMS (FAB, *m/z*): calcd for $[C_{37}H_{31}Cl_2NO_6S_2]^{+\cdot}$ (M)$^{+\cdot}$ 719.0970, found 719.0991.

Scheme S5. Synthesis of Mechanophore-Crosslinked Active PMA Network **20**




16

((3aR,4S,7S,7aS)-6,7-bis(2-methyl-5-phenylthiophen-3-yl)-1,3-dioxo-3,3a,7,7a-tetrahydro-1H-4,7-methanoisoindole-2,4-diyl)bis(ethane-2,1-diyl) diacrylate (16). Synthesized using general procedure B with **9c** (100 mg, 0.168 mmol), acryloyl chloride (68 µL, 0.84 mmol) and triethylamine (160 µL, 1.15 mmol) in dry THF (2.0 mL). The reaction stirred for 30 h before it was worked up and purified by silica gel chromatography (0–50% EtOAc/hexanes) to yield the title compound as a white solid (69 mg, 58%).

TLC (25% EtOAc/hexanes): R_f = 0.16

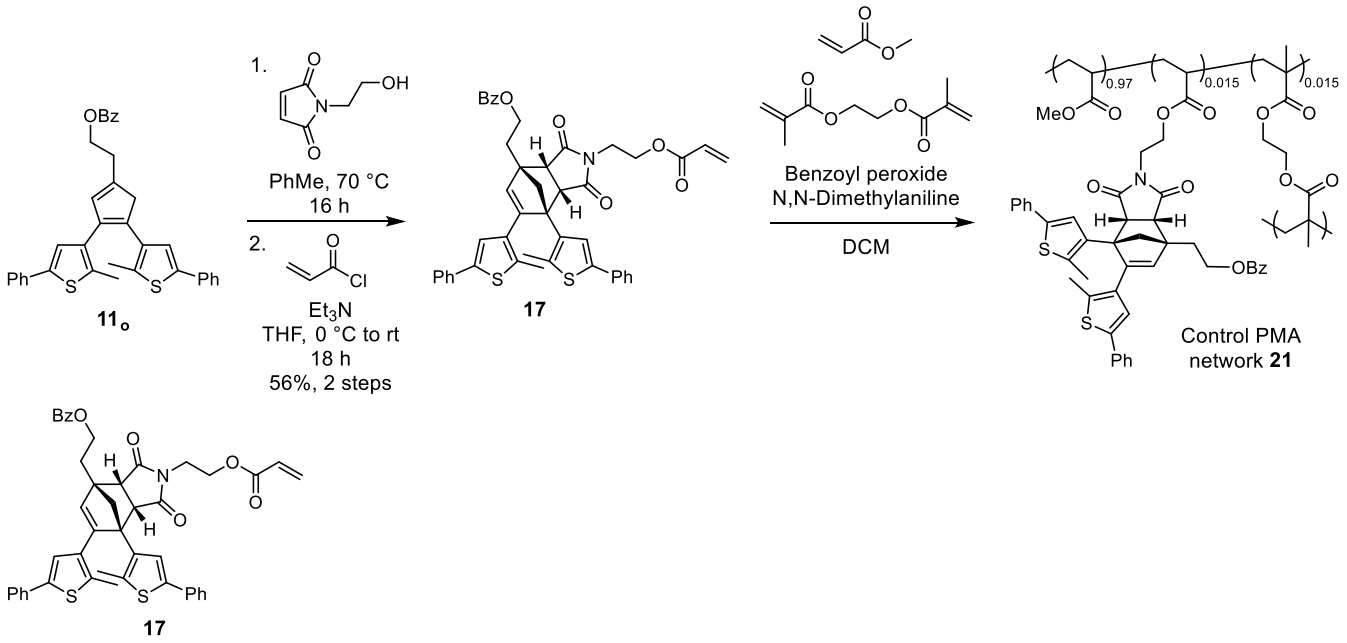
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92 (s, 1H), 7.64 (dd, 2H, *J* = 8.1, 1.2 Hz), 7.41 (t, 2H, *J* = 7.7 Hz), 7.30 (t, 1H, *J* = 7.3 Hz), 7.20 (dd, 2H, *J* = 7.6, 1.9 Hz), 7.15 – 7.06 (m, 3H), 6.59 (s, 1H), 6.44 (dd, 1H, *J* = 17.3, 1.4 Hz), 6.31 (dd, 1H, *J* = 17.2, 1.5 Hz), 6.14 (dd, 1H, *J* = 17.3, 10.4 Hz), 5.97 (s, 1H), 5.93 – 5.84 (m, 2H), 5.74 (dd, 1H, *J* = 10.4, 1.5 Hz), 4.50 (t, 2H, *J* = 6.4 Hz), 4.12 (d, 1H, *J* = 7.8 Hz), 4.05 – 3.97 (m, 1H), 3.82 – 3.74 (m, 1H), 3.66 – 3.56 (m, 2H), 3.40 (d, 1H, *J* = 7.8 Hz), 2.71 (dt, 1H, *J* = 14.8, 6.3 Hz), 2.59 (d, 1H, *J* = 9.0 Hz), 2.44 (s, 3H), 2.40 (dt, 1H, *J* = 15.1, 6.7 Hz), 2.02 (s, 3H), 1.83 (d, 1H, *J* = 9.0 Hz) ppm.

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ: 176.5, 176.4, 166.2, 165.6, 145.4, 139.7, 138.4, 136.41, 136.38, 135.6, 134.7, 134.4, 131.7, 131.5, 131.31, 131.28, 129.0, 128.8, 128.4, 128.0, 127.3, 126.9, 126.6, 125.9, 125.4, 124.2, 62.2, 62.0, 61.3, 61.1, 55.1, 51.6, 50.8, 37.5, 31.0, 15.6, 14.6 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{42}H_{40}BrNO_6S_2Na]^+$ $(M+Na)^+$ 726.1954, found 726.1954.

Synthesis of Active PMA network 20. Bis-acrylate functionalized mechanophore crosslinker **16** (50 mg, 0.071 mmol, 1.5 mol%) and benzoyl peroxide (3.9 mg, 0.016 mmol) were combined in a scintillation vial with a stir bar. The atmosphere was purged with N_2 for 10 min, after which methyl acrylate (420 µL, 4.63 mmol) was added and the mixture was stirred until homogeneous. N,N-dimethylaniline (4.0 µL, 0.032 mmol) was added via microsyringe and the solution was stirred again for 3 minutes, after which the vial was cooled to 8 °C for 22 h. The material was subsequently dried under vacuum for 2 days to yield a clear, slightly yellow polymer.

Scheme S6. Synthesis of Control PMA Network **21**



2-((3aR,4S,7S,7aS)-2-(2-(acryloyloxy)ethyl)-6,7-bis(2-methyl-5-phenylthiophen-3-yl)-1,3-dioxo-1,2,3,3a,7,7a-hexahydro-4H-4,7-methanoisoindol-4-yl)ethyl benzoate (17). A flame-dried round bottom flask was charged with *N*-(2-hydroxyethyl)maleimide (53 mg, 0.38 mmol) and the atmosphere was evacuated and refilled with N_2 3×. A solution of $\mathbf{11_o}$ (93 mg, 0.166 mmol) in dry toluene (3.0 mL)was added and the reaction was stirred at 70 °C for 16 h. The reaction was then cooled to room temperature and concentrated in vacuo. Then, the crude mixture was dissolved in dry THF (3.0 mL) and esterified according to general procedure B with acryloyl chloride (45 µL, 0.56 mmol) and triethylamine (130 µL, 0.933 mmol). It stirred for 18 h before being worked up and purified by silica gel chromatography (0–50% EtOAc/hexanes) to yield a light brown solid. It was recrystallized from acetone to yield the title compound as colorless crystals (73 mg, 56% over 2 steps).

TLC (50% EtOAc/hexanes): R_f = 0.48

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09 – 9.03 (m, 2H), 7.92 (s, 1H), 7.66 – 7.61 (m, 2H), 7.60 – 7.55 (m, 1H), 7.45 (t, 2H, *J* = 7.7 Hz), 7.41 (t, 2H, *J* = 7.7 Hz), 7.33 – 7.27 (m, 1H), 7.21 – 7.16 (m, 2H), 7.22 – 7.06 (m, 3H), 6.58 (s, 1H), 6.30 (dd, 1H, *J* = 17.3, 1.5 Hz), 6.01 (s, 1H), 5.88 (dd, 1H, *J* = 17.3, 10.4 Hz), 5.72 (dd, 1H, *J* = 10.5, 1.4 Hz), 4.72 – 4.62 (m, 2H), 4.12 (d, 1H, *J* = 7.8 Hz), 4.05 – 3.98 (m, 1H), 3.78 (ddd, 1H, *J* = 11.4, 6.5, 4.8 Hz), 3.67 – 3.56 (m, 2H), 3.44

(d, 1H, *J* = 7.7 Hz), 2.82 (dt, 1H, *J* = 14.8, 6.0 Hz), 2.67 (d, 1H, *J* = 9.0 Hz), 2.50 (dt, 1H, *J* = 14.3 Hz, 6.6 Hz), 2.38 (s, 3H), 1.97 (s, 3H), 1.88 (d, 1H, *J* = 9.0 Hz) ppm.

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ: 176.5, 176.4, 166.7, 165.6, 145.5, 139.7, 138.3, 136.48, 136.47, 135.6, 134.7, 134.4, 133.3, 131.7, 131.4, 131.3, 130.2, 129.7, 129.0, 128.8, 128.7, 128.0, 127.3, 126.9, 126.7, 126.0, 125.4, 124.2, 62.7, 62.1, 61.3, 61.2, 55.2, 51.8, 50.8, 37.6, 31.2, 15.6, 14.6 ppm.

HRMS (ESI, *m/z*): calcd for $[C_{45}H_{40}NO_6S_2]^+$ $(M+H)^+$ 754.2292, found 754.2296.

Synthesis of Control PMA network 21. A scintillation vial was charged with benzoyl peroxide (2.3 mg, 0.0095 mmol) and the atmosphere was purged with N_2 for 10 min. Ethylene glycol dimethacrylate (11.8 µL, 0.063 mmol, 1.5 mol %) and methyl acrylate (380 mL, 4.19 mmol) were added, followed by **17** (47 mg, 0.062 mmol, 1.5 mol %) as a solution in dry DCM (300 µL). The mixture was stirred until homogeneous, then N,N-dimethylaniline (1.6 µL, 0.013 mmol) was added and the solution was stirred for 3 min. The vial was kept at 8 °C for 23 h, after which the material was dried under vacuum for 4 days to yield a clear, light brown polymer.

IV. GPC Chromatograms of All Polymers

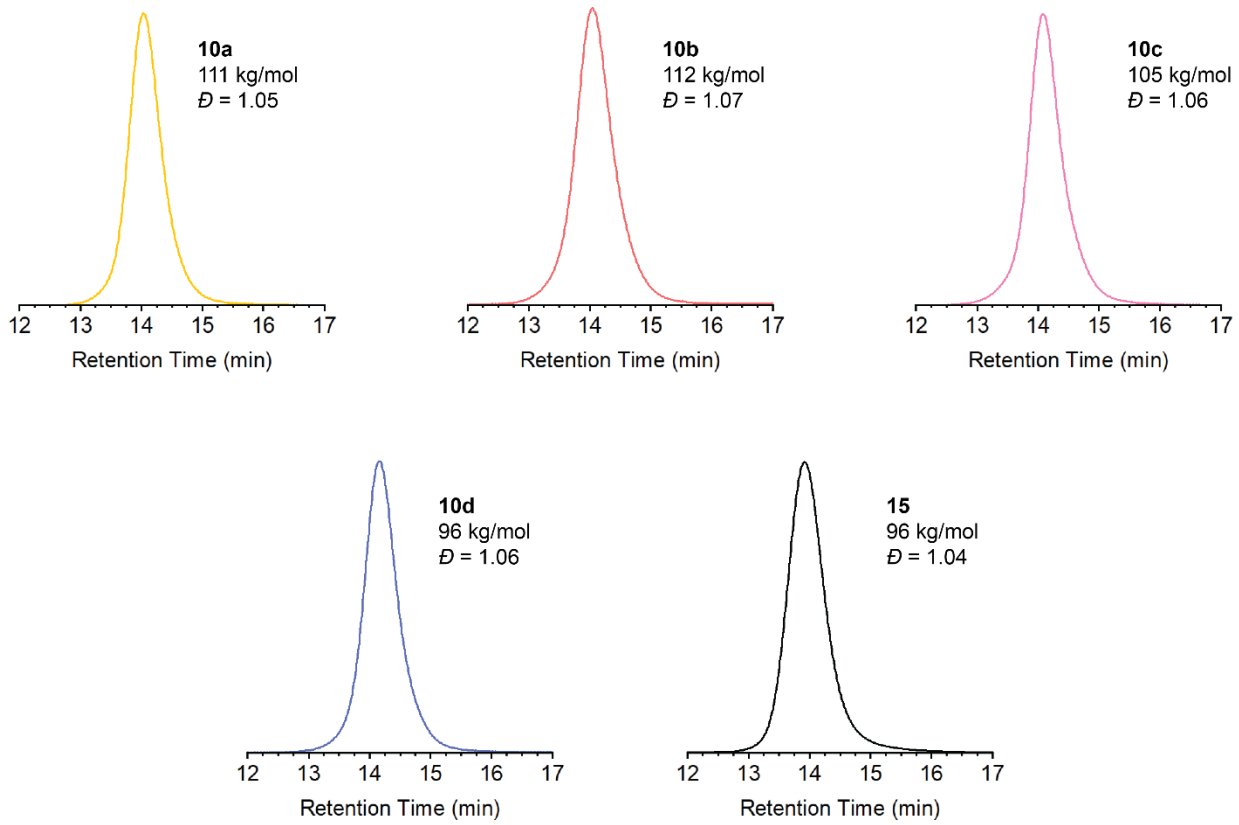


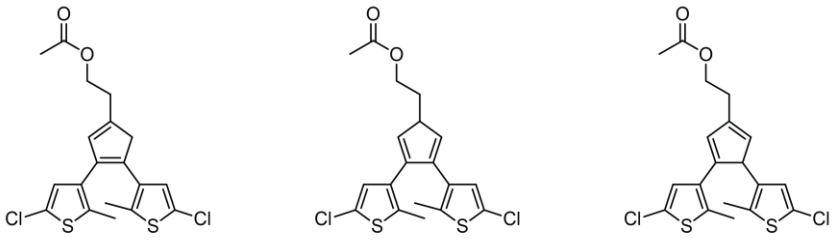
Figure S9. GPC traces (refractive index response), M_n, and dispersity (*Đ*) for functional polymers **10a**–**d** and chain-end functional control polymer **15**.

V. DFT Calculations

CoGEF calculations were performed using Spartan '18 Parallel Suite according to previously reported methods.[6,7] Ground state energies were calculated using DFT at the B3LYP/6-31G* level of theory. For each model, an initial equilibrium conformer calculation was performed using Molecular Mechanics (MMFF), followed by an unconstrained equilibrium geometry calculation. 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. Calculations were run until a chemical transformation was predicted to occur, as evidenced by the rupture and reorganization of one or more covalent bonds. The maximum force associated with the mechanochemical reaction was calculated from the slope of the curve immediately prior to the predicted chemical reaction. For all four truncated structures, a formal retro-[4+2] cycloaddition reaction was predicted with a maximum force of 4.9 nN.

Energy calculations were performed on three possible cyclopentadiene tautomers shown in Scheme S7 using Spartan '18 Parallel Suite. Simplified structures with benzoate esters replaced by acetate esters were investigated to establish the relative energies of each tautomer. Equilibrium geometries and the corresponding Gibbs free energy for each tautomer were calculated at the M06-2X/6-31G* level of theory.

Scheme S7. Structures of Cyclopentadiene Tautomers and Calculated Relative ΔG Values



VI. Details for Sonication/Photoirradiation Experiments

An oven-dried sonication vessel was fitted with a Teflon screw cap sealed with an O-ring and was allowed to cool under a stream of dry Ar. The probe tip was situated 1 cm above the bottom of the sonication vessel. The vessel was charged with a solution of the polymer in dry THF (2.0 mg/mL, 20.0–25.0 mL) and immersed in an ice/water bath. The solution was sparged continuously with Ar beginning 15 min prior to sonication and for the duration of the sonication experiment. Pulsed ultrasound (1 s on/2 s off, 25% amplitude, 20 kHz, 11.6 W/cm^2) was then applied to the system. At 15 minute intervals of sonication time, aliquots were removed from the sonication vessel and analyzed by UV-vis absorption spectroscopy. The solution in the cuvette was then irradiated with 311 nm UV light for 60 s and the sample was reanalyzed by UV-vis spectroscopy. Ultrasonication intensity was calibrated using the method described by Berkowski *et al*.[8]

VII. Photographs of Solutions of Polymers 10a and 10b (2 mg/mL).

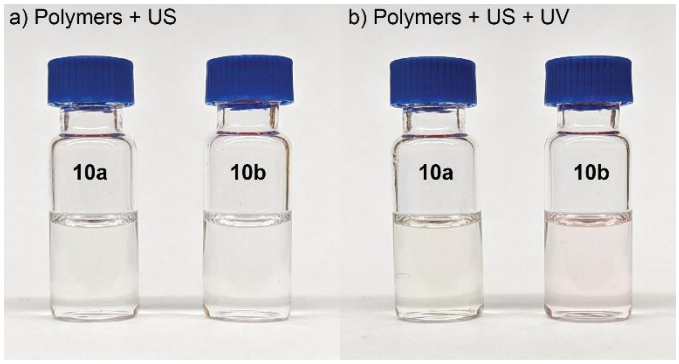


Figure S10. (a) Photographs of solutions of polymers **10a** and **10b** at their original concentrations (2 mg/mL in THF) after being subjected to ultrasonication (120 min), and (b) the same solutions after irradiation with UV light (311 nm, 120 s).

VIII. References

(1) Wilt, J. W.; Massie, S. N.; Dabek, R. B. Reaction of 2-(.DELTA.3-cyclopentenyl)ethyl bromide with tri-n-butyltin hydride. Cyclization to norbornane. *J. Org. Chem.* **1970**, *35*, 2803–2806.

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(3) Heo, Y.; Sodano, H. A. Self-Healing Polyurethanes with Shape Recovery. *Adv. Funct. Mater.* **2014**, *24*, 5261–5268.

(4) Nguyen, N. H.; Rosen, B. M.; Lligadas, G.; Percec, V. Surface-Dependent Kinetics of Cu(0)-Wire-Catalyzed Single-Electron Transfer Living Radical Polymerization of Methyl Acrylate in DMSO at 25 °C. *Macromolecules* **2009**, *42*, 2379–2386.

(5) Stevenson, R.; De Bo, G. Controlling Reactivity by Geometry in Retro-Diels–Alder Reactions under Tension. *J. Am. Chem. Soc.* **2017**, *139*, 16768–16771.

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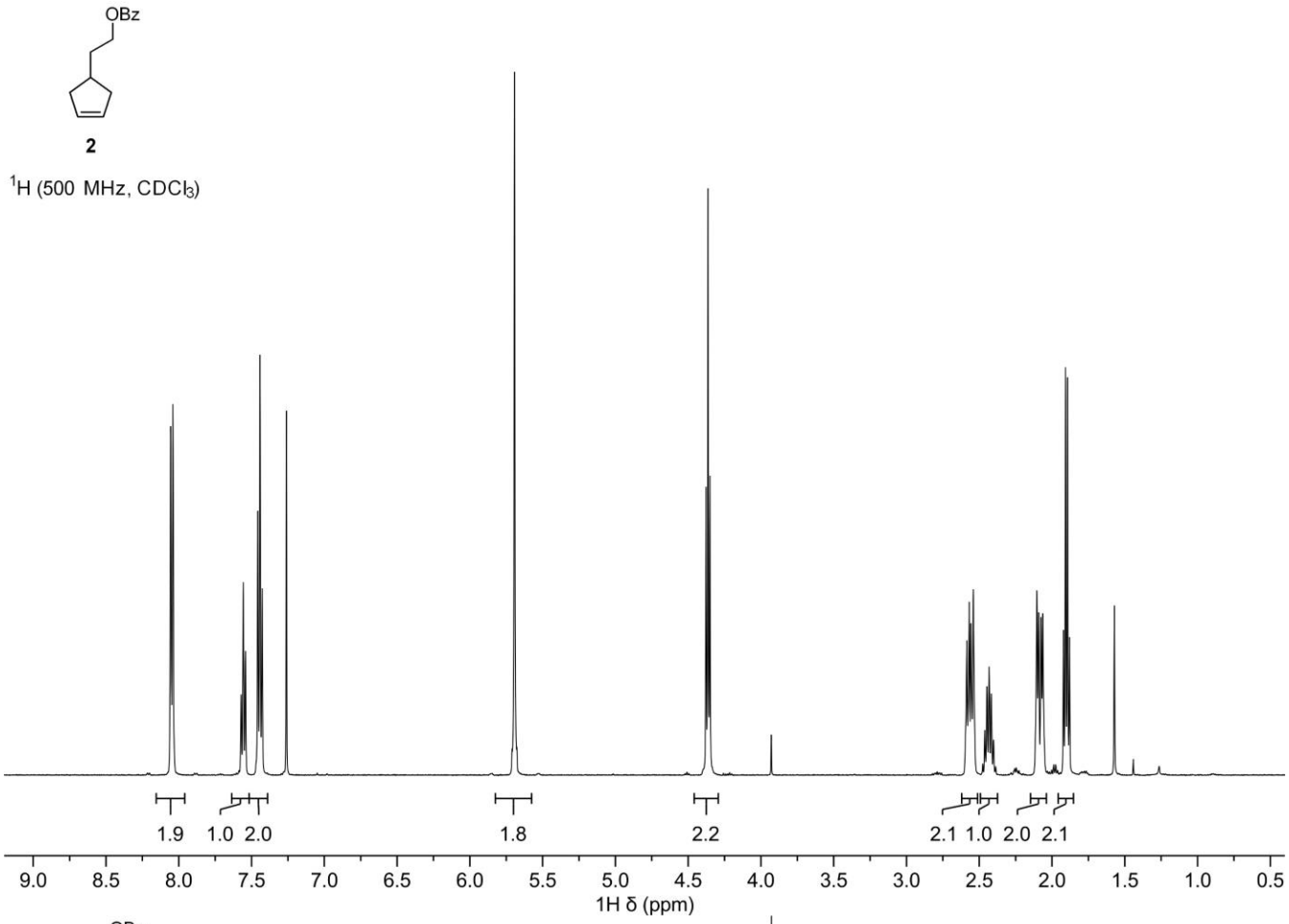
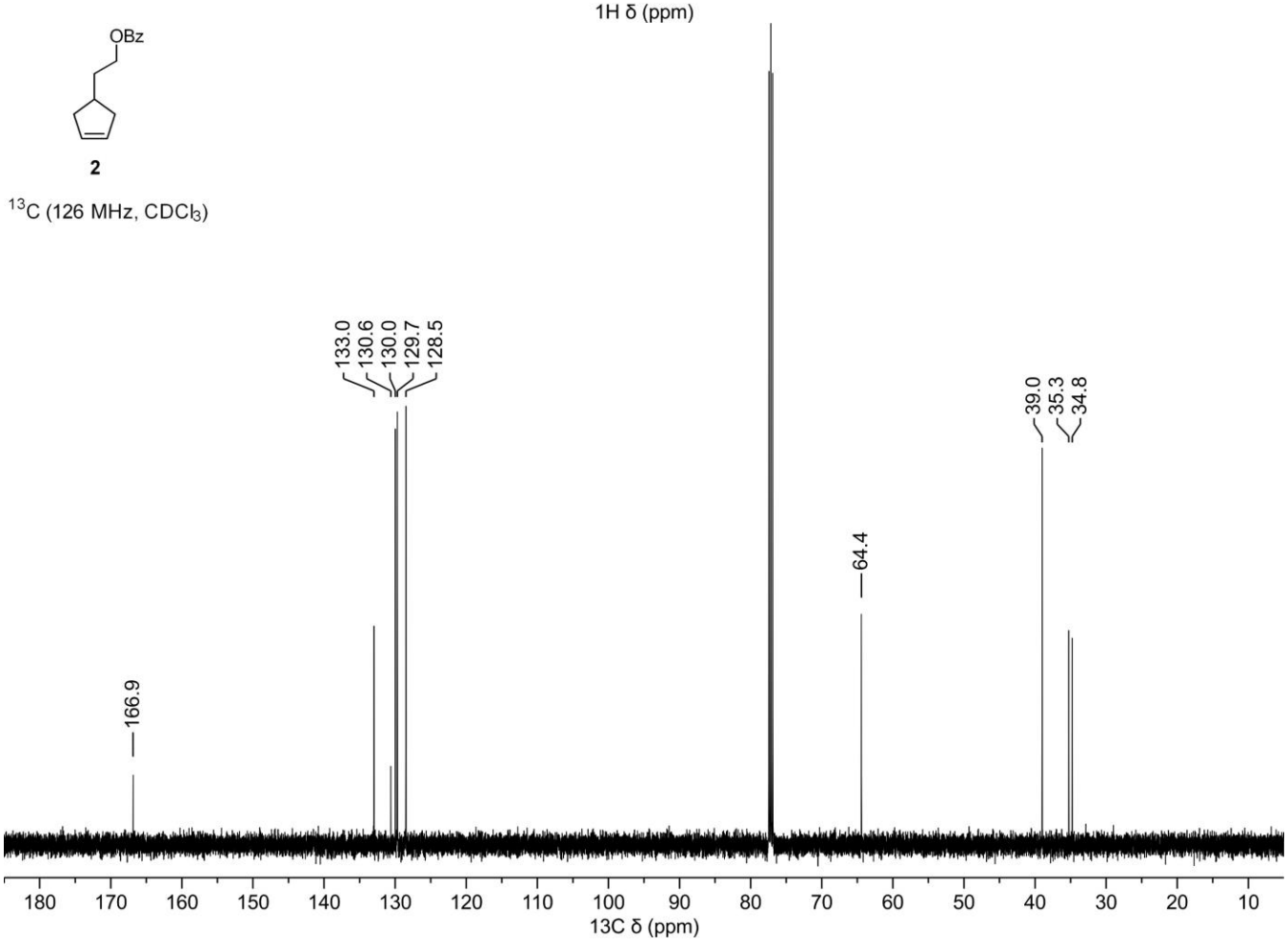
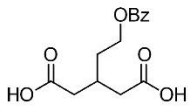
(8) Berkowski, K. L.; Potisek, S. L.; Hickenboth, C. R.; Moore, J. S. Ultrasound-Induced Site-Specific Cleavage of Azo-Functionalized Poly(ethylene glycol). *Macromolecules* **2005**, *38*, 8975–8978.

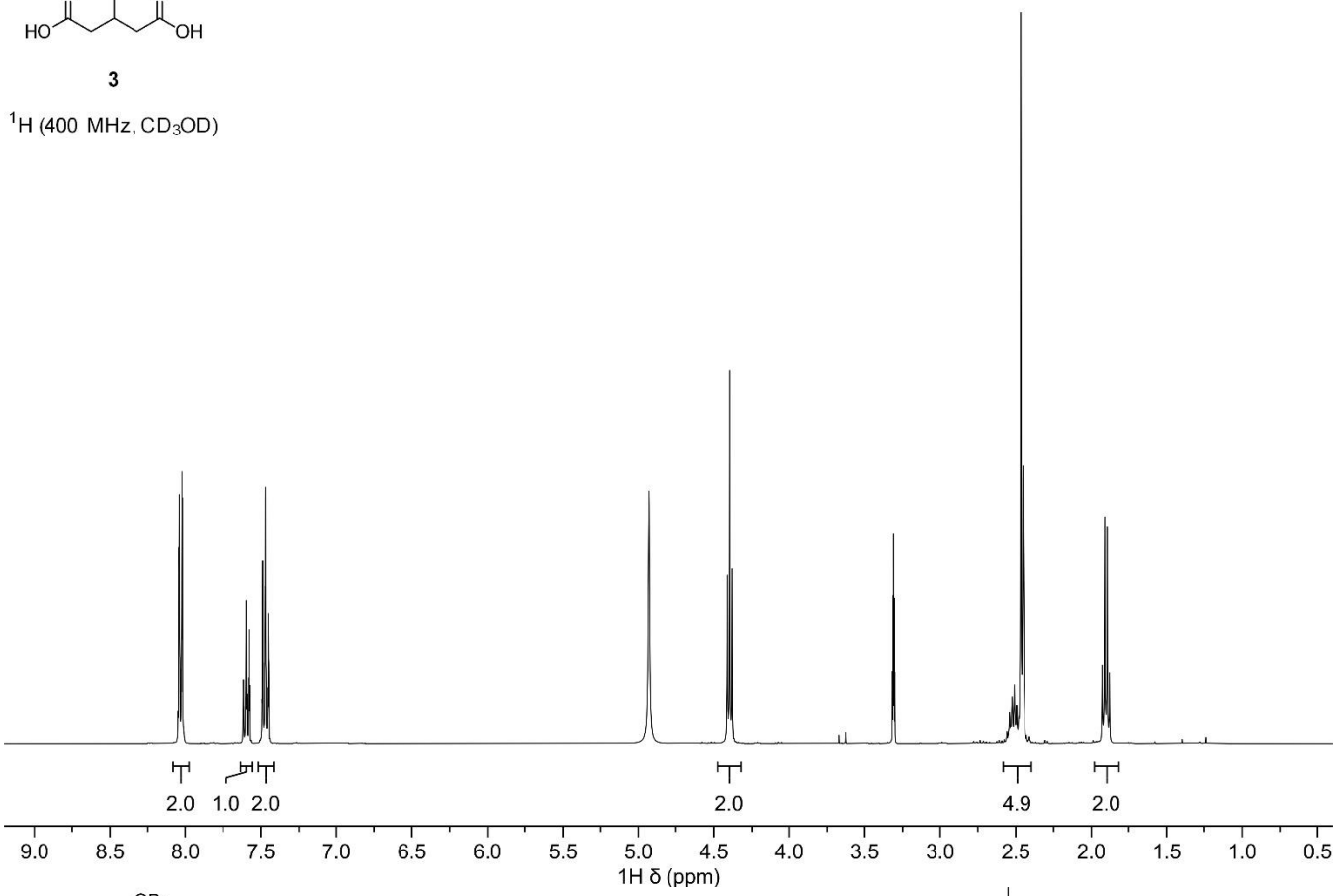

OBz
2
1H (500 MHz, CDCl3)
1.9
1.0
2.0
1.8
2.2
2.1
1.0
2.0
2.1
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
1H δ (ppm)

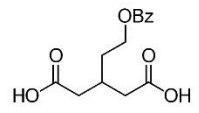

OBz
2
13C (126 MHz, CDCl3)
166.9
133.0
130.6
130.0
129.7
128.5
64.4
39.0
35.3
34.8
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
13C δ (ppm)



3

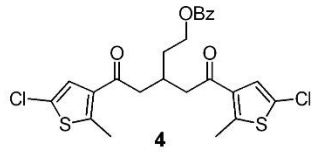
^{1}H (400 MHz, CD_3OD)





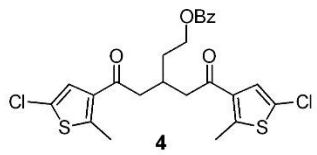
3

^{13}C (101 MHz, CD_3OD)



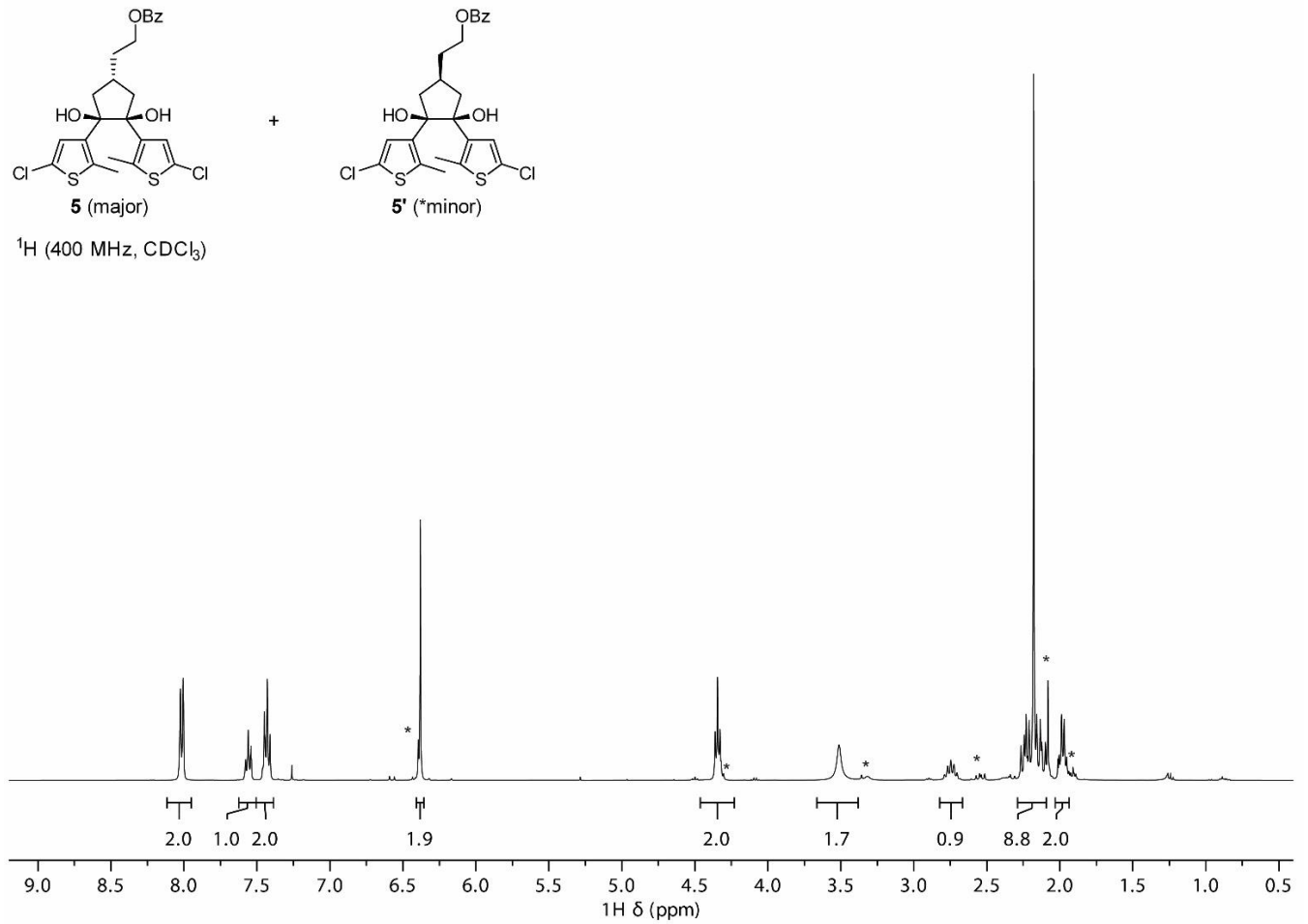
4

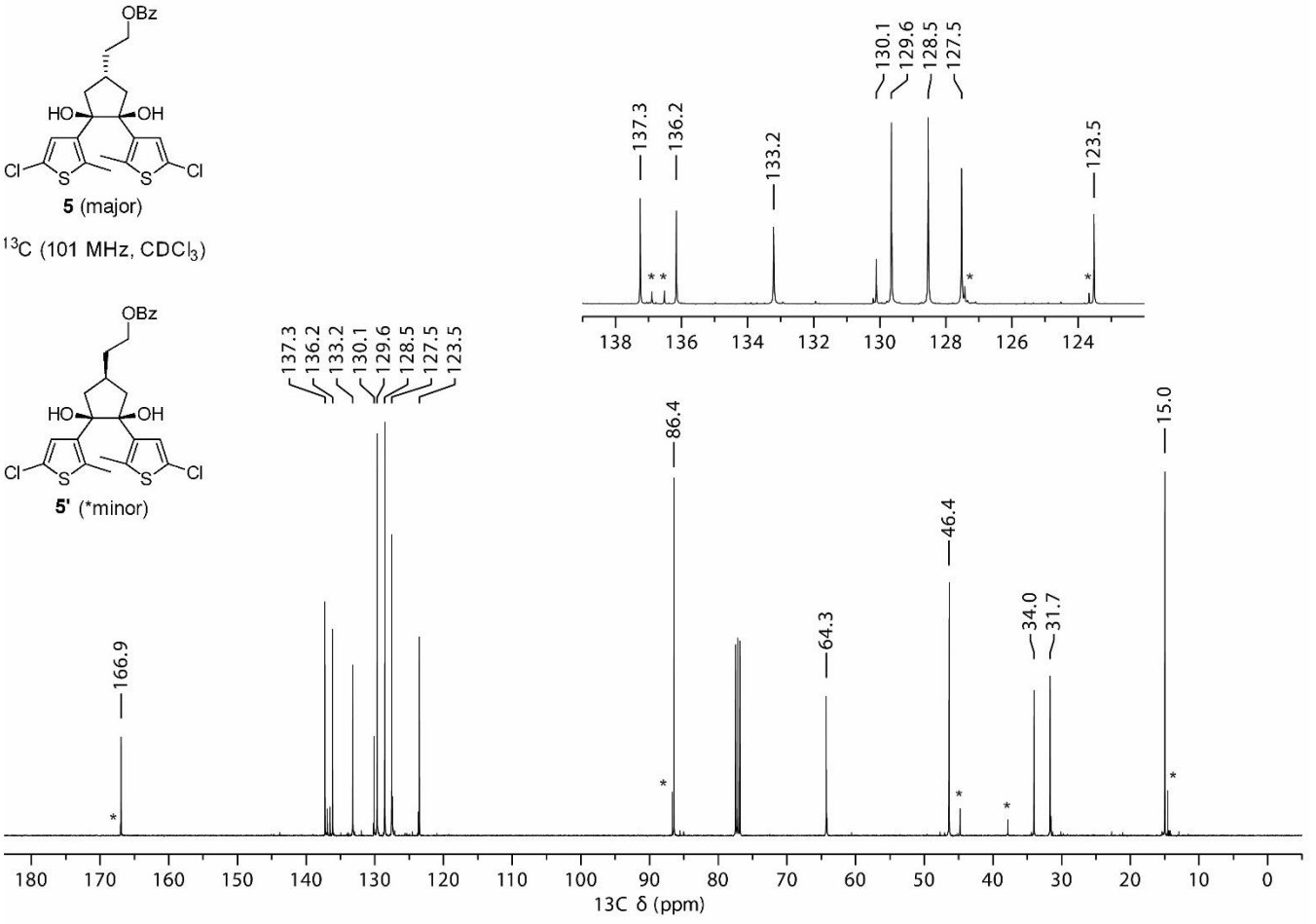
^{1}H (400 MHz, $CDCl_3$)

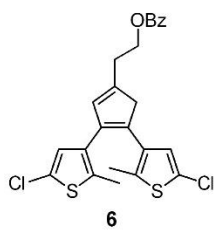


4

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

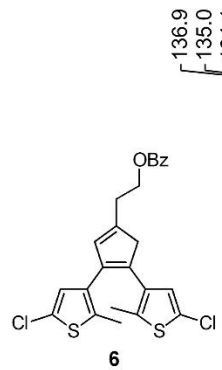

OBz
HO
OH
Cl
S
Cl
+
5 (major)
5' (*minor)
1H (400 MHz, CDCl3)
2.0 1.0 2.0 1.9 2.0 1.7 0.9 8.8 2.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
1H δ (ppm)


OBz
HO
OH
Cl
S
Cl
5 (major)
13C (101 MHz, CDCl3)
137.3
136.2
133.2
130.1
129.6
128.5
127.5
123.5
138 136 134 132 130 128 126 124
5' (*minor)
166.9
86.4
64.3
46.4
34.0
31.7
15.0
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C δ (ppm)



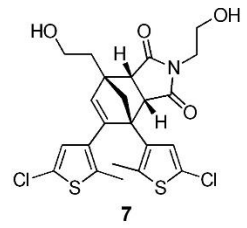
6

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



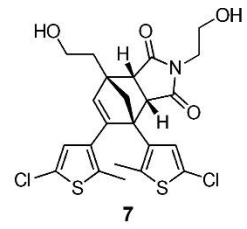
6

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



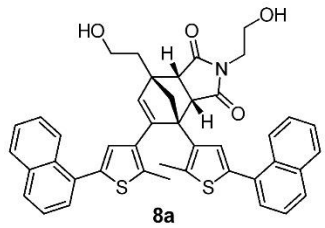
7

^{1}H (500 MHz, $(CD_3)_2CO$)



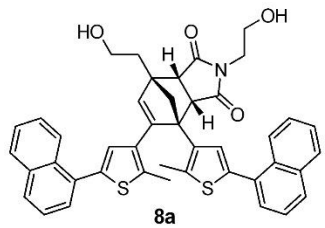
7

^{13}C (101 MHz, $(CD_3)_2CO$)



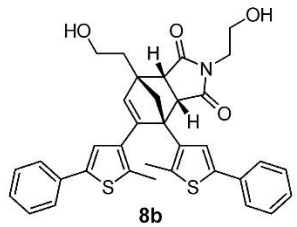
8a

^{1}H (400 MHz, CD_3OD)



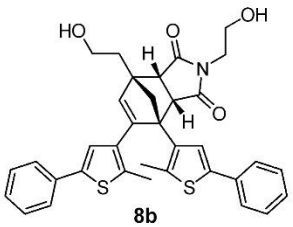
8a

^{13}C (101 MHz, CD_3OD)



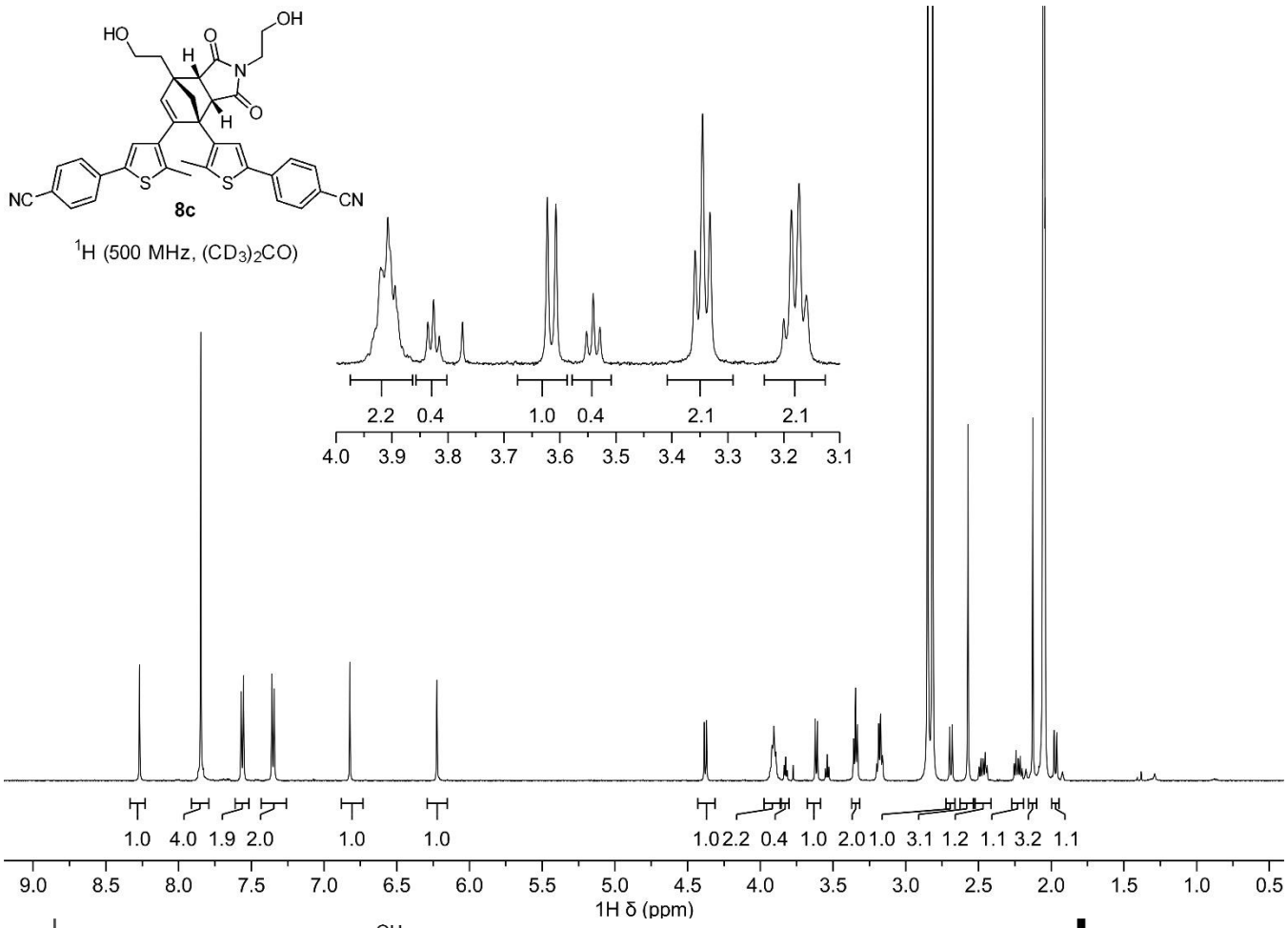
8b

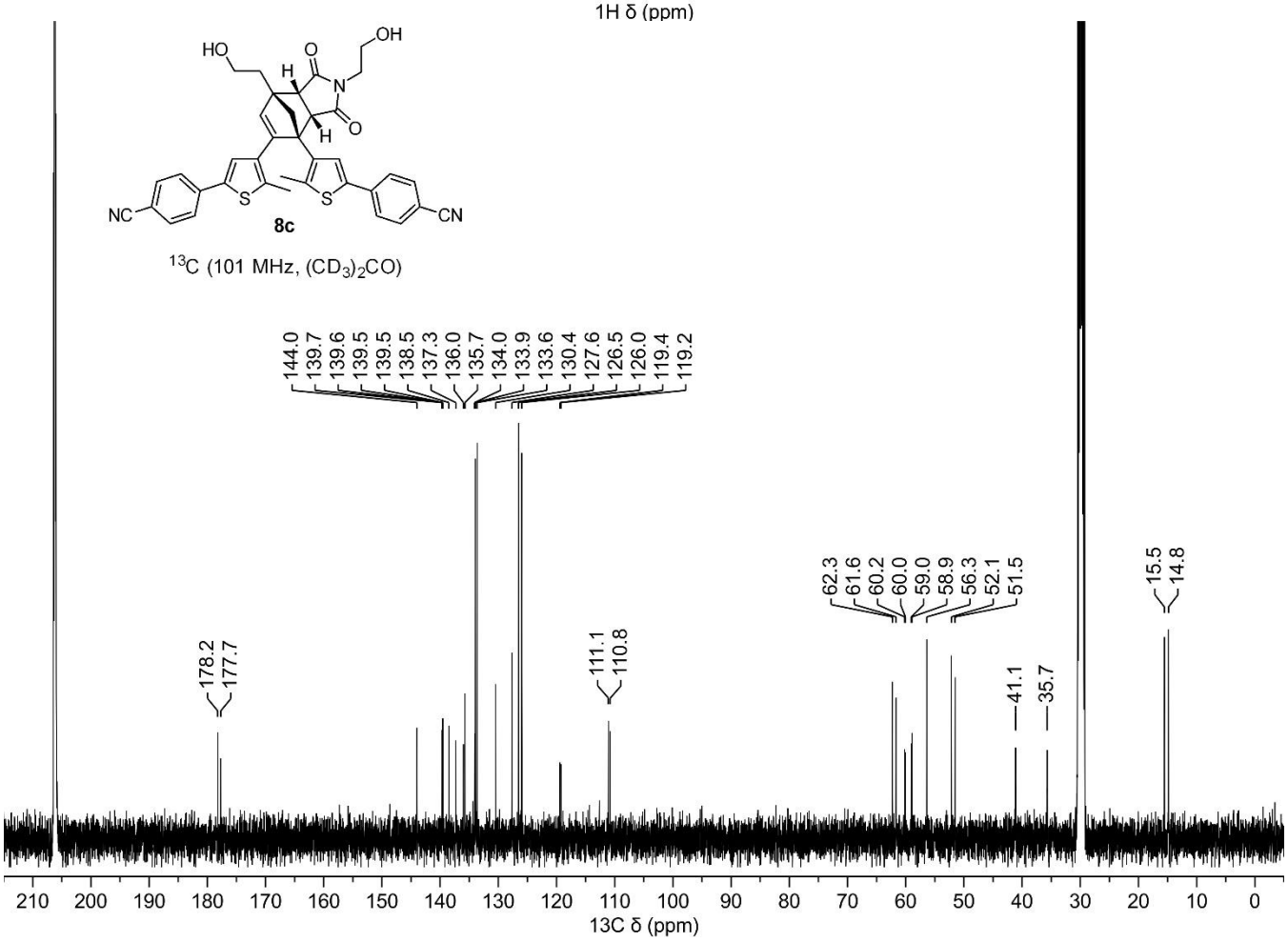
^{1}H (400 MHz, $(CD_3)_2CO$)

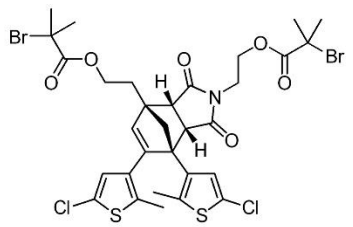


8b

^{13}C (101 MHz, $(CD_3)_2CO$)

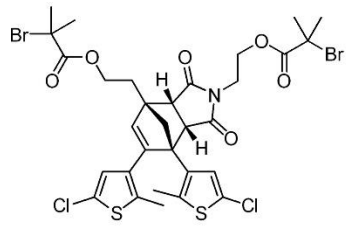

HO
OH
O
N
H
O
H
NC
S
S
CN
8c
^{1}H (500 MHz, $(CD_3)_2CO$)
2.2 0.4 1.0 0.4 2.1 2.1
4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1
1.0 4.0 1.9 2.0 1.0 1.0 1.0 2.2 0.4 1.0 2.0 1.0 3.1 1.2 1.1 3.2 1.1
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
1H δ (ppm)


HO
OH
O
N
H
O
H
NC
S
S
CN
8c
^{13}C (101 MHz, $(CD_3)_2CO$)
144.0
139.7
139.6
139.5
139.5
138.5
137.3
136.0
135.7
134.0
133.9
133.6
130.4
127.6
126.5
126.0
119.4
119.2
178.2
177.7
111.1
110.8
62.3
61.6
60.2
60.0
59.0
58.9
56.3
52.1
51.5
41.1
35.7
15.5
14.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C δ (ppm)



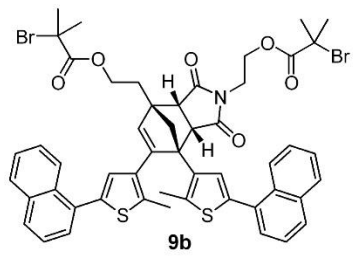
9a

^{1}H (500 MHz, $CDCl_3$)



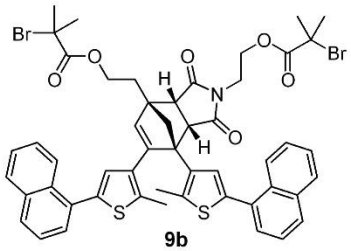
9a

^{13}C (126 MHz, $CDCl_3$)



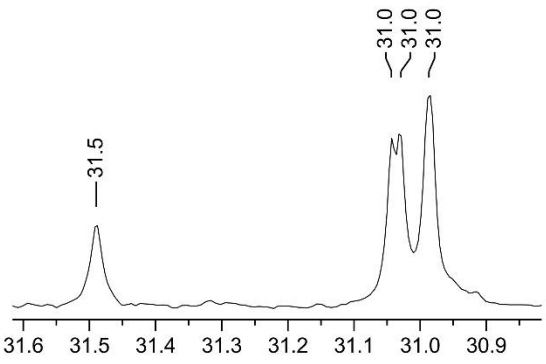
9b

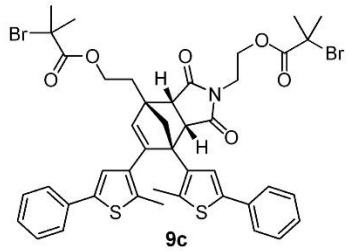
^{1}H (500 MHz, $(CD_3)_2CO$)



9b

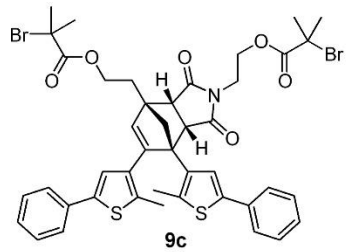
^{1}H (101 MHz, $(CD_3)_2CO$)





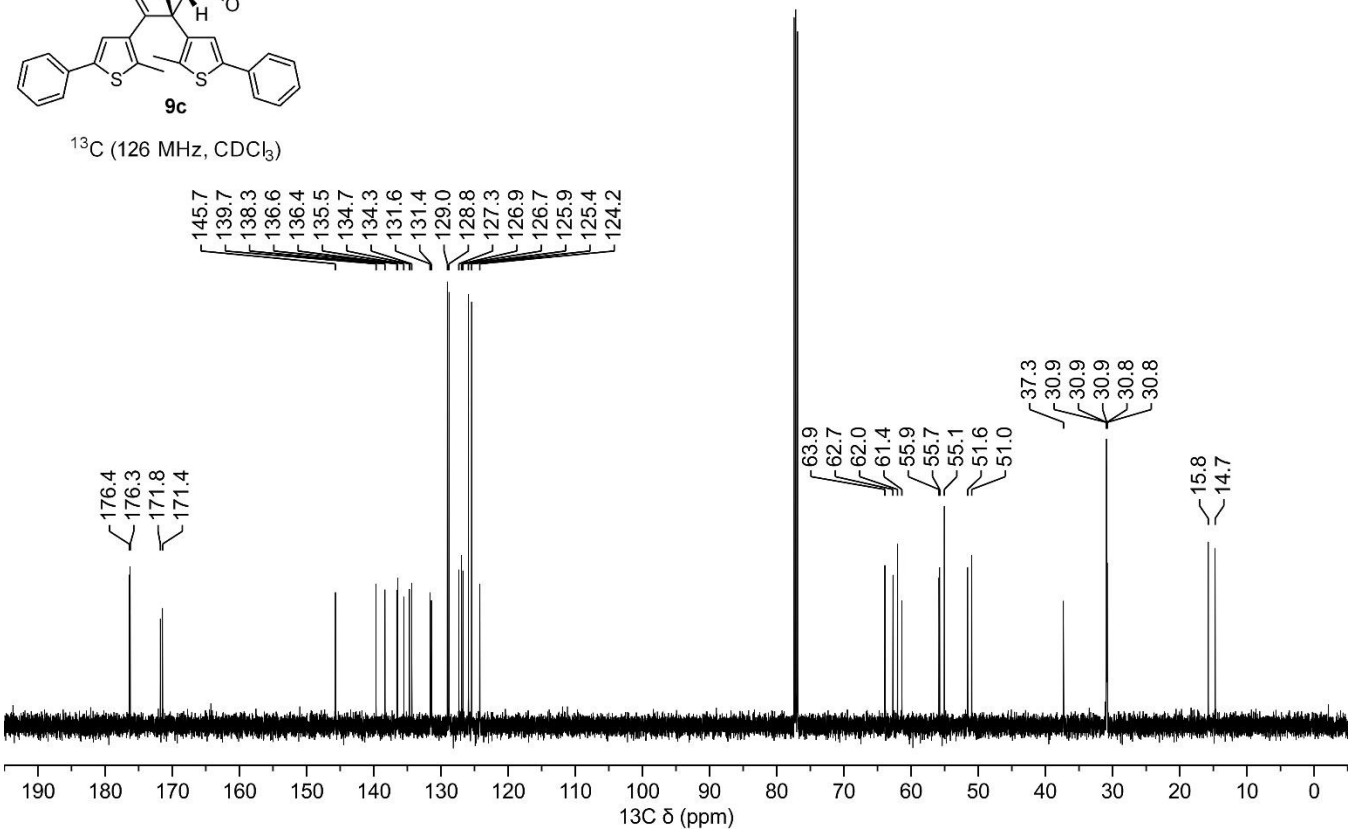
9c

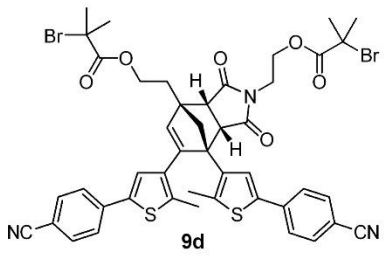
^{1}H (500 MHz, $CDCl_3$)



9c

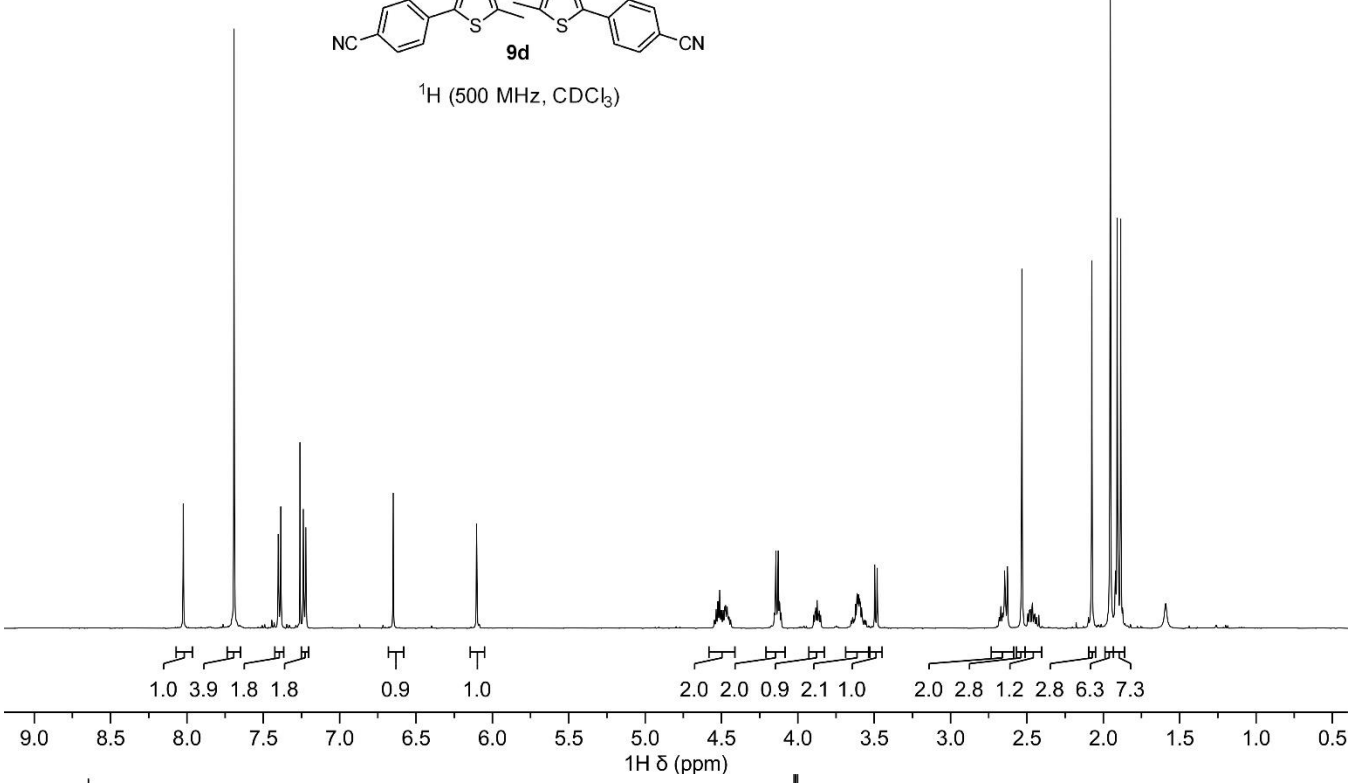
^{13}C (126 MHz, $CDCl_3$)

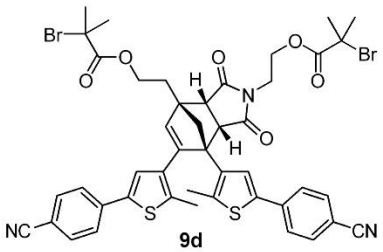




9d

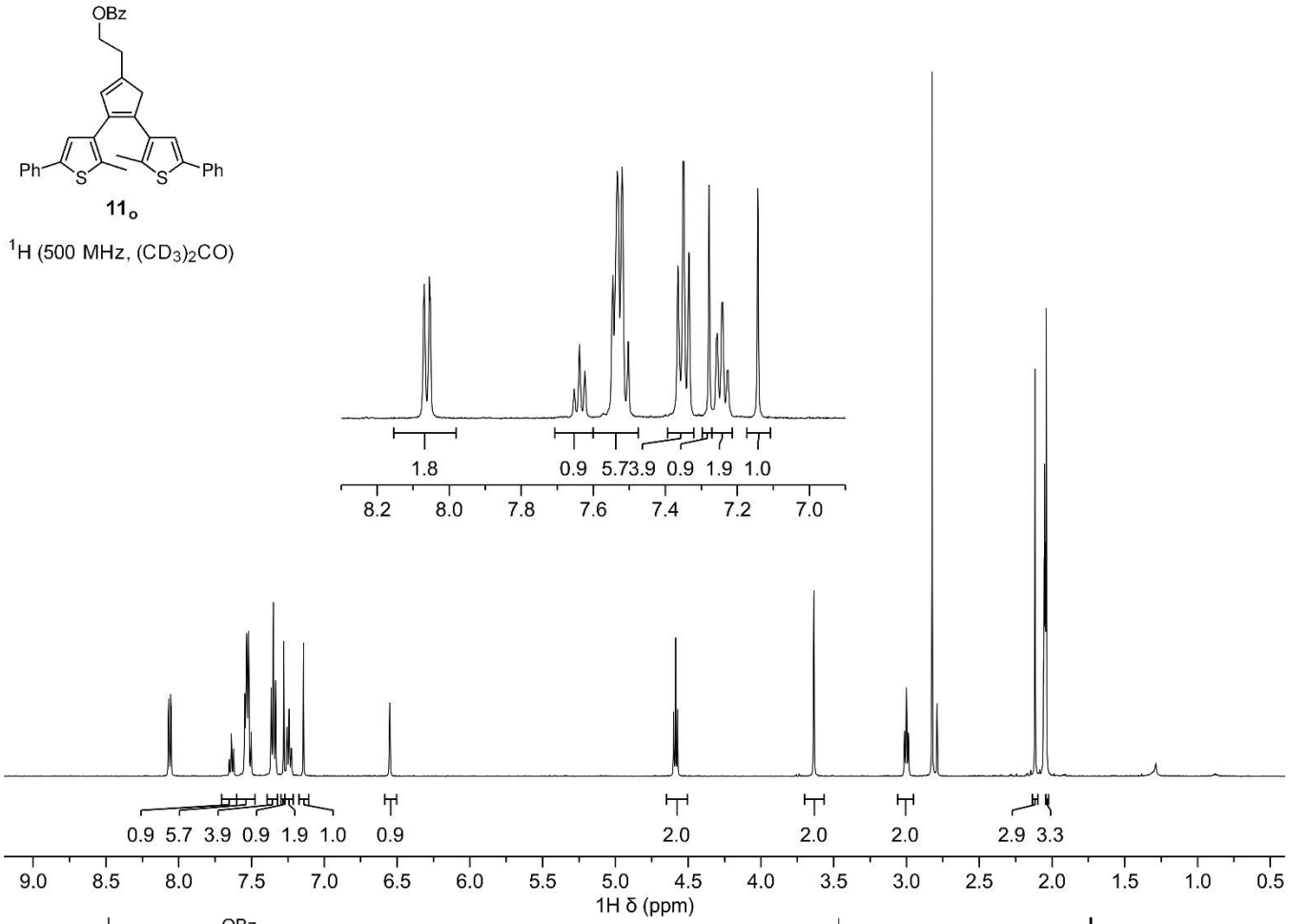
^{1}H (500 MHz, $CDCl_3$)

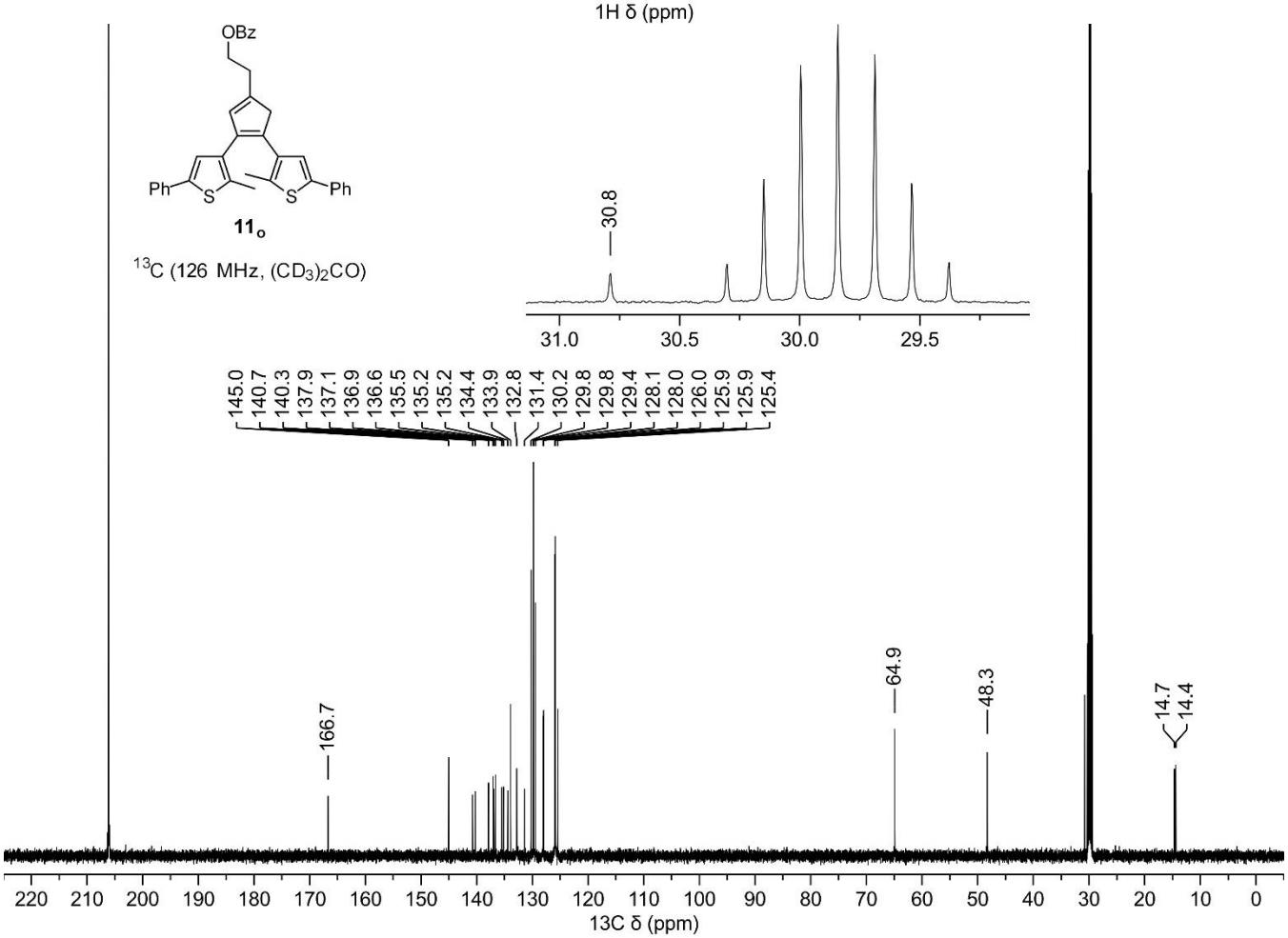


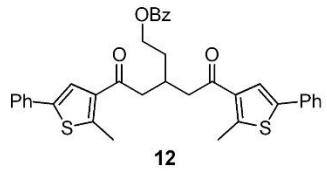


9d

^{13}C (126 MHz, $CDCl_3$)

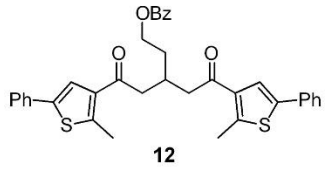

OBz
Ph
S
S
Ph
11o
1H (500 MHz, (CD3)2CO)
1.8
0.9 5.7 3.9 0.9 1.9 1.0
8.2 8.0 7.8 7.6 7.4 7.2 7.0
0.9 5.7 3.9 0.9 1.9 1.0 0.9 2.0 2.0 2.0 2.9 3.3
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
1H δ (ppm)


OBz
Ph
S
S
Ph
11o
13C (126 MHz, (CD3)2CO)
30.8
31.0 30.5 30.0 29.5
145.0 140.7 140.3 137.9 137.1 136.9 136.6 135.5 135.2 135.2 134.4 133.9 132.8 131.4 130.2 129.8 129.8 129.4 128.1 128.0 126.0 125.9 125.9 125.4
166.7
64.9
48.3
14.7
14.4
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C δ (ppm)



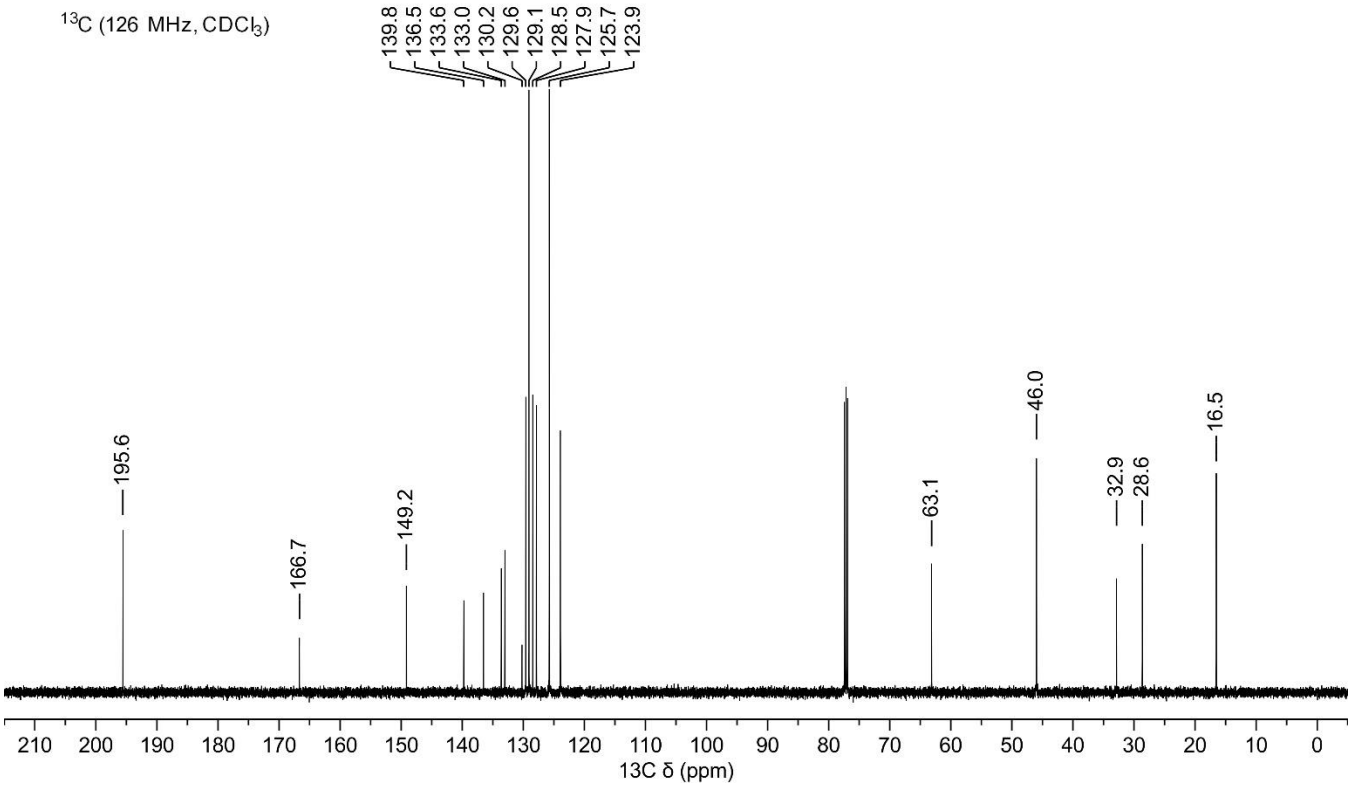
12

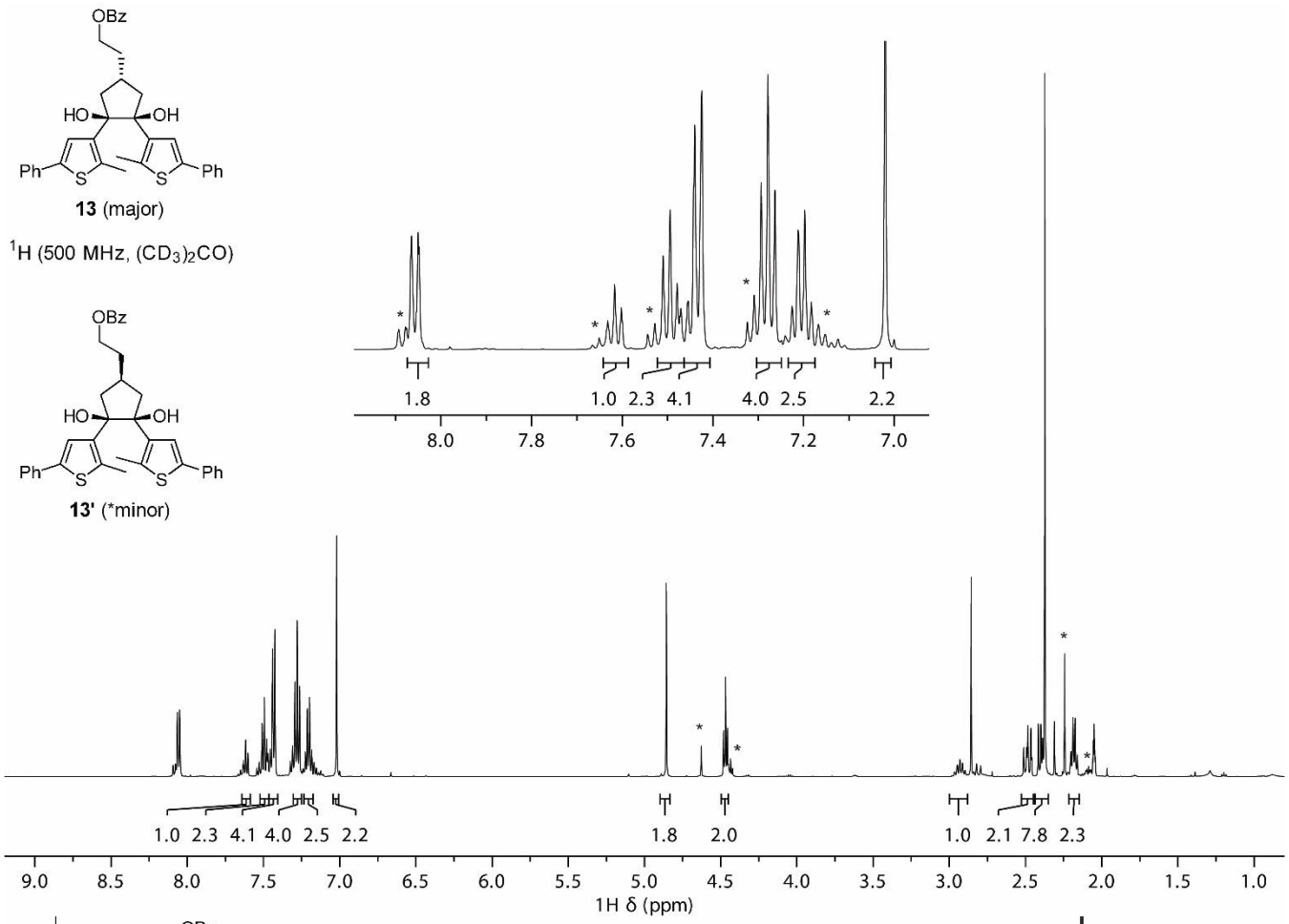
^{1}H (500 MHz, $CDCl_3$)

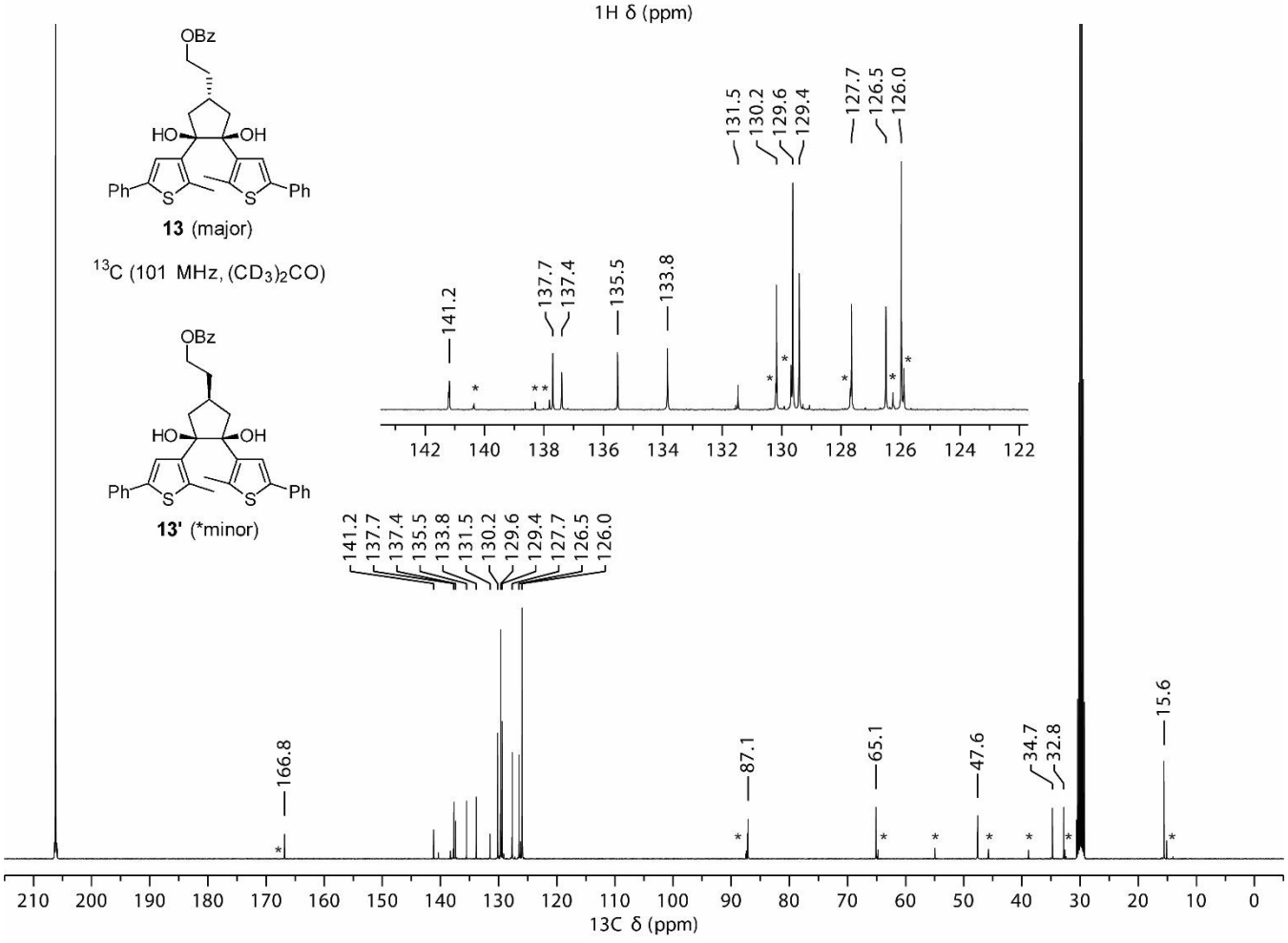


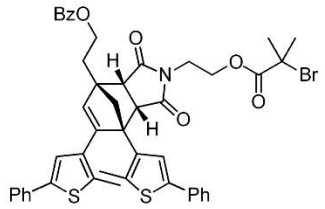
12

^{13}C (126 MHz, $CDCl_3$)



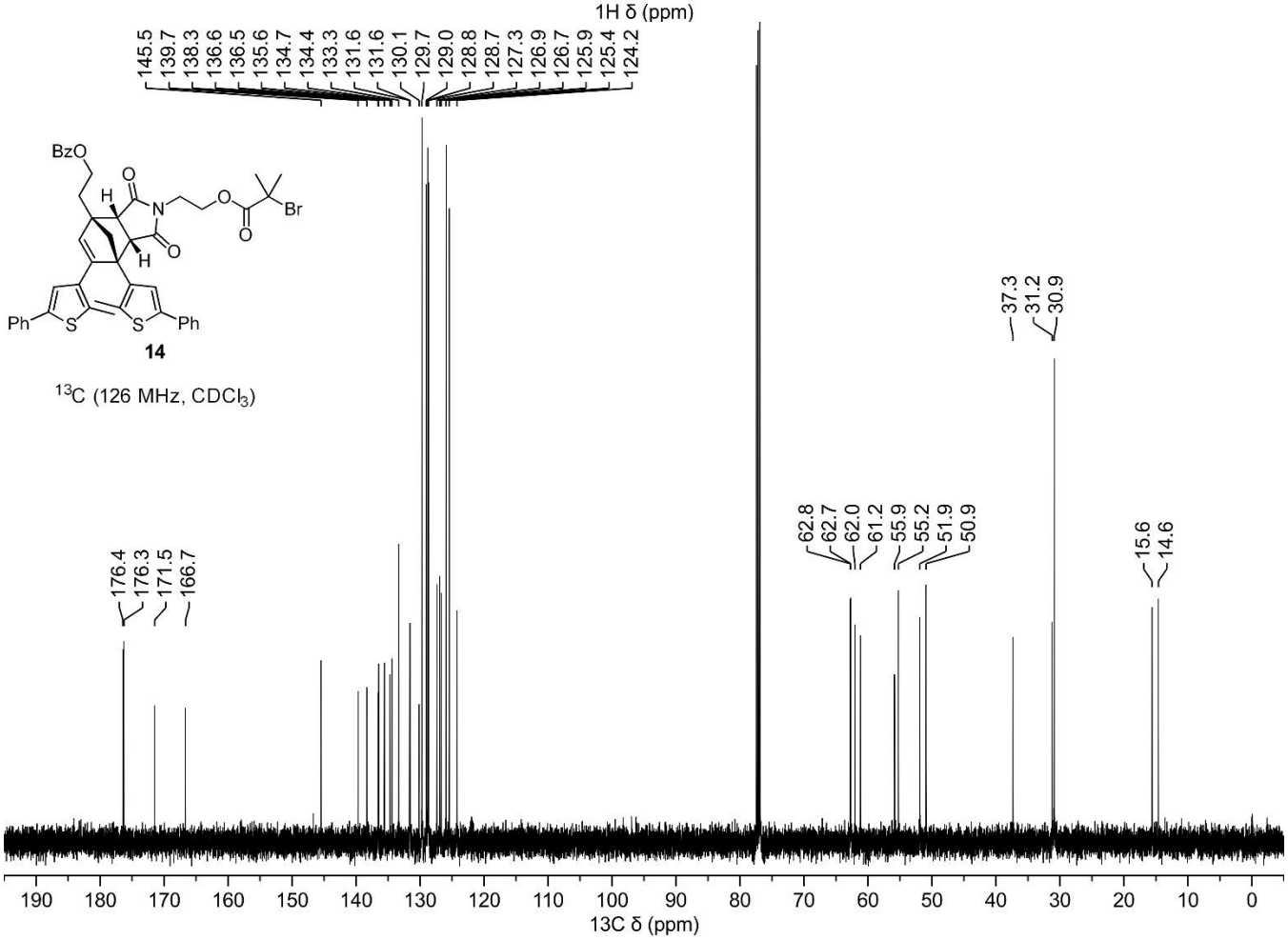

OBz
HO
OH
Ph
S
S
Ph
13 (major)
1H (500 MHz, (CD3)2CO)
13' (*minor)
1.8
1.0 2.3 4.1
4.0 2.5
2.2
8.0 7.8 7.6 7.4 7.2 7.0
1.0 2.3 4.1 4.0 2.5 2.2
1.8 2.0
1.0 2.1 7.8 2.3
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
1H δ (ppm)


OBz
HO
OH
Ph
S
S
Ph
13 (major)
13C (101 MHz, (CD3)2CO)
13' (*minor)
141.2
137.7
137.4
135.5
133.8
131.5
130.2
129.6
129.4
127.7
126.5
126.0
142 140 138 136 134 132 130 128 126 124 122
166.8
87.1
65.1
47.6
34.7
32.8
15.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
13C δ (ppm)



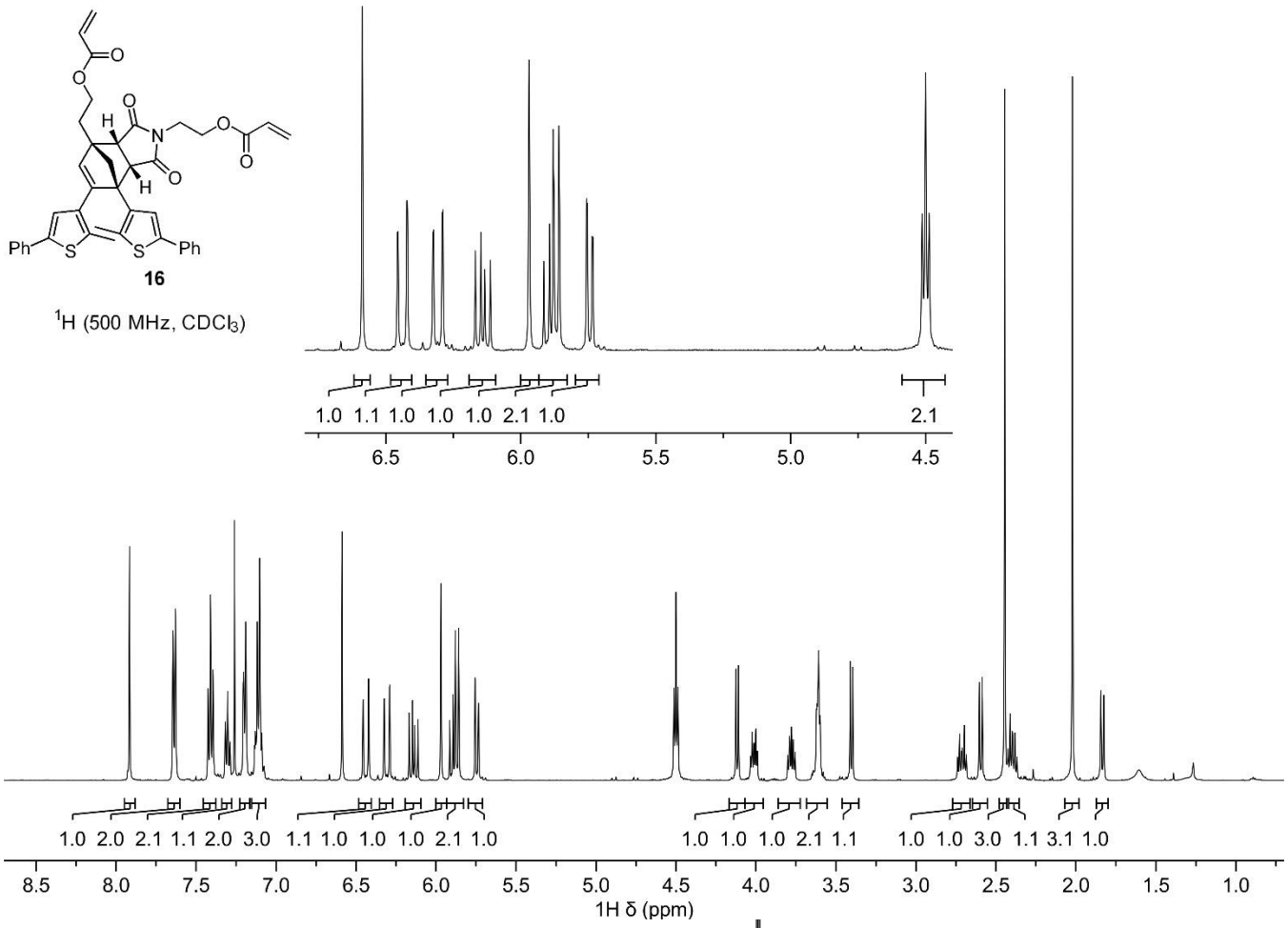
14

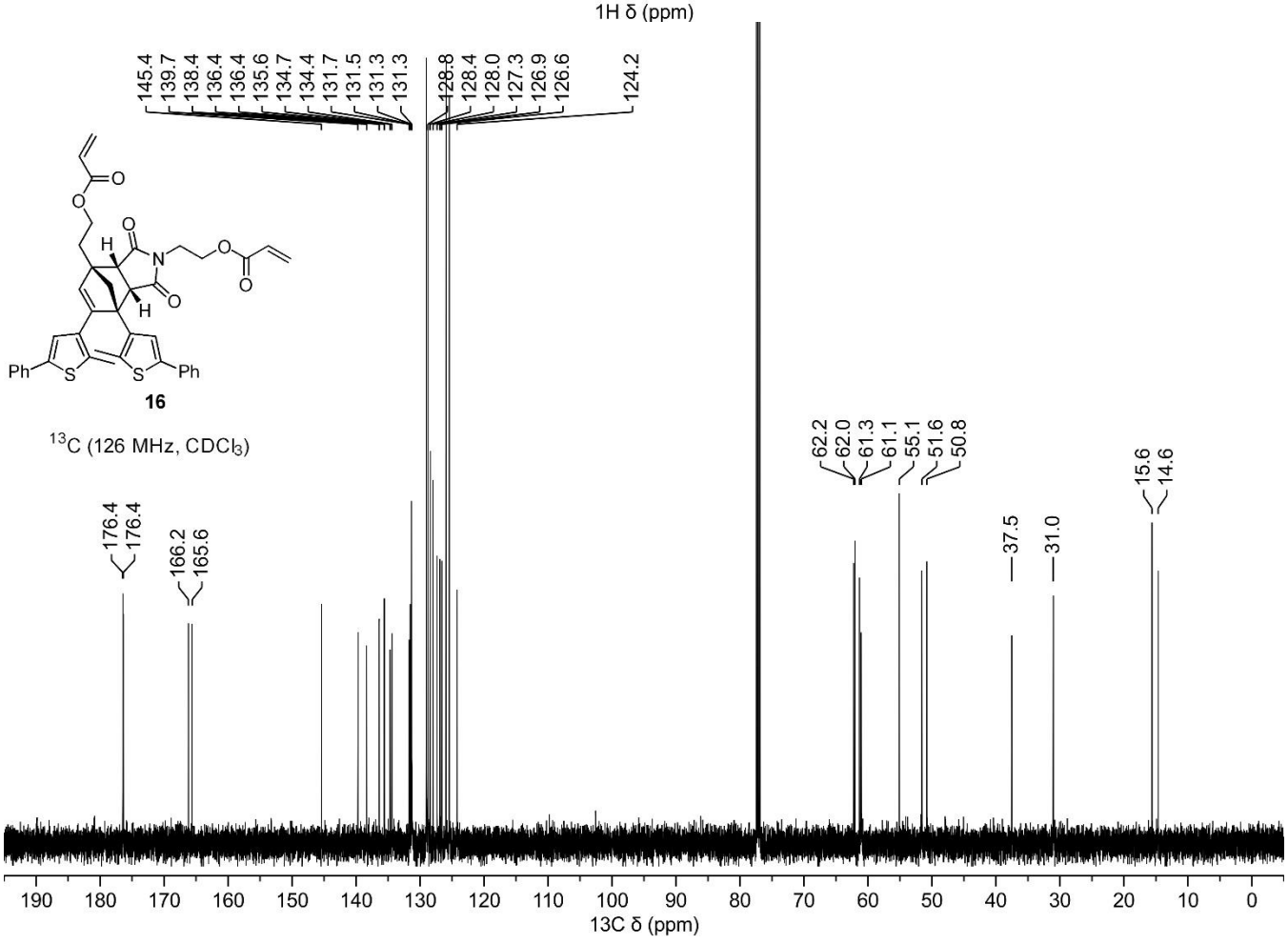
^{1}H (500 MHz, $CDCl_3$)

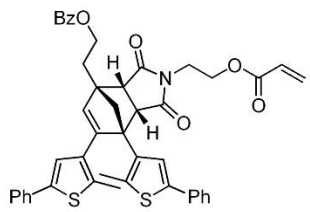


14

^{13}C (126 MHz, $CDCl_3$)

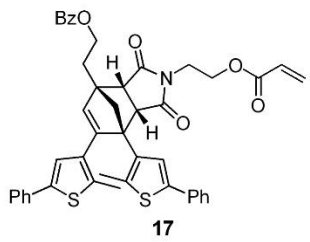

16
1H (500 MHz, CDCl3)
1.0 1.1 1.0 1.0 1.0 2.1 1.0
2.1
1.0 2.0 2.1 1.1 2.0 3.0 1.1 1.0 1.0 1.0 2.1 1.0
1.0 1.0 1.0 2.1 1.1
1.0 1.0 3.0 1.1 3.1 1.0
1H δ (ppm)


145.4
139.7
138.4
136.4
136.4
135.6
134.7
134.4
131.7
131.5
131.3
131.3
128.8
128.4
128.0
127.3
126.9
126.6
124.2
16
13C (126 MHz, CDCl3)
176.4
176.4
166.2
165.6
62.2
62.0
61.3
61.1
55.1
51.6
50.8
37.5
31.0
15.6
14.6
13C δ (ppm)



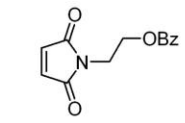
17

^{1}H (500 MHz, $CDCl_3$)



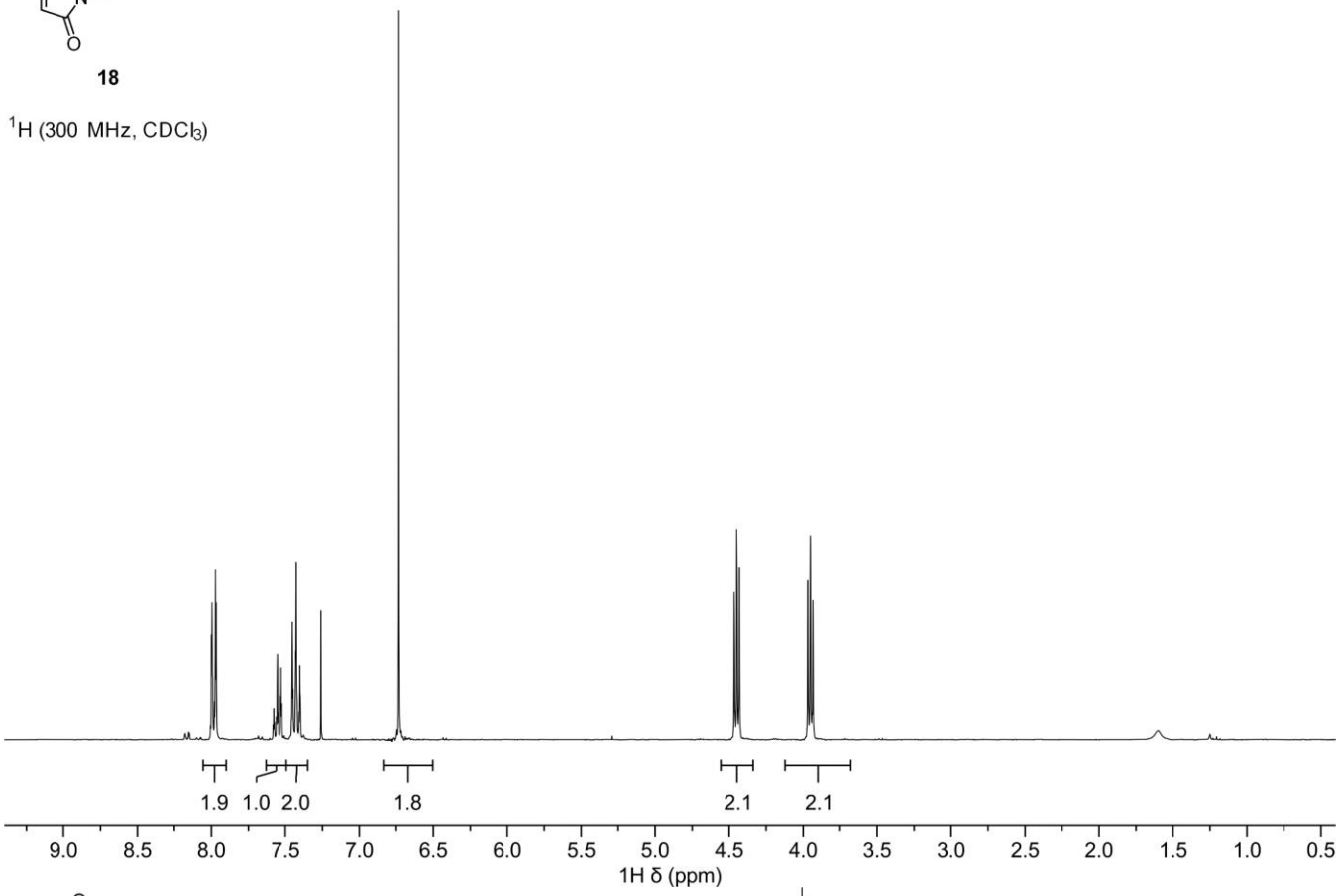
17

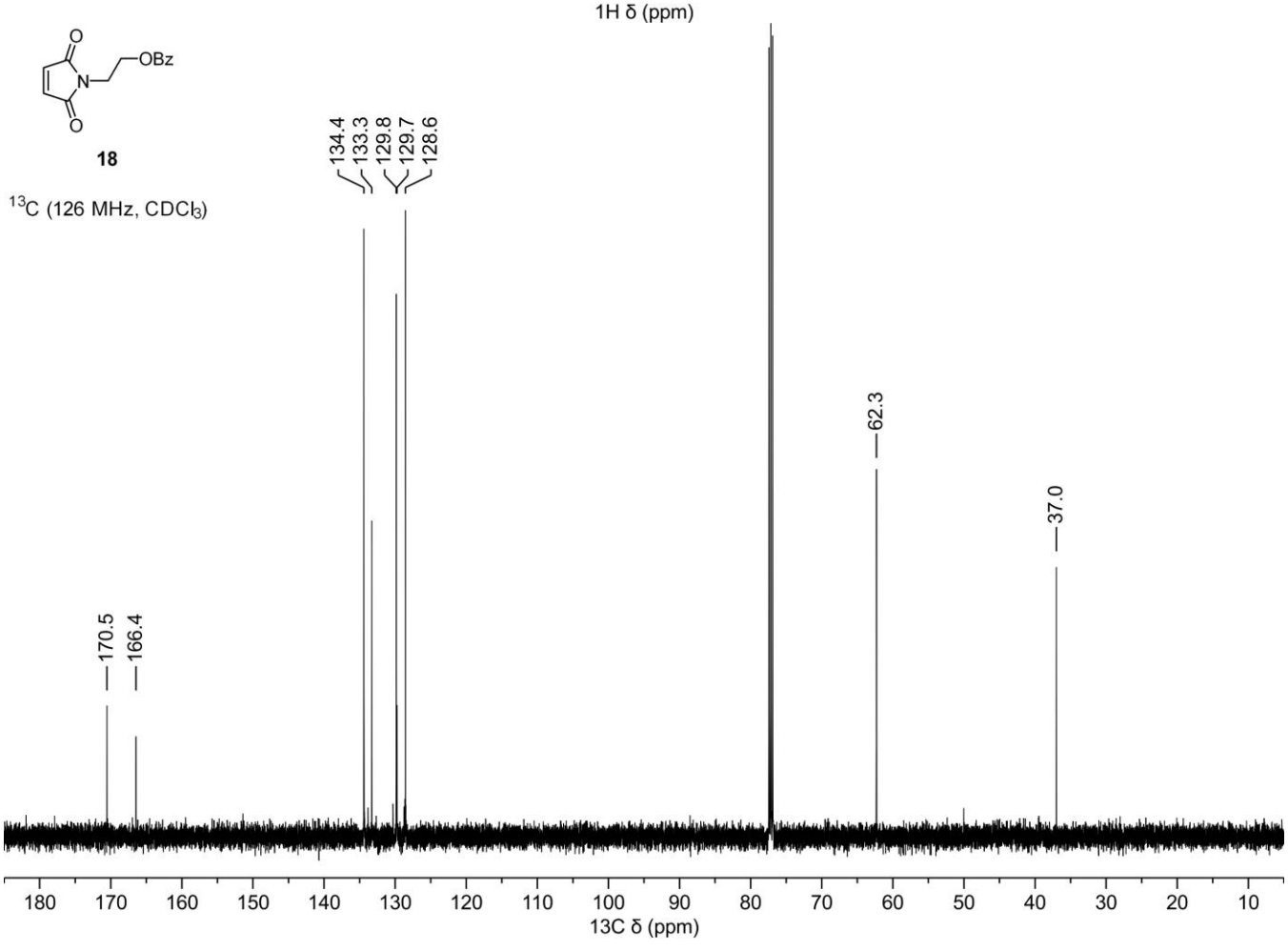
^{13}C (126 MHz, $CDCl_3$)



18

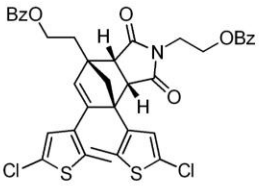
^{1}H (300 MHz, $CDCl_3$)





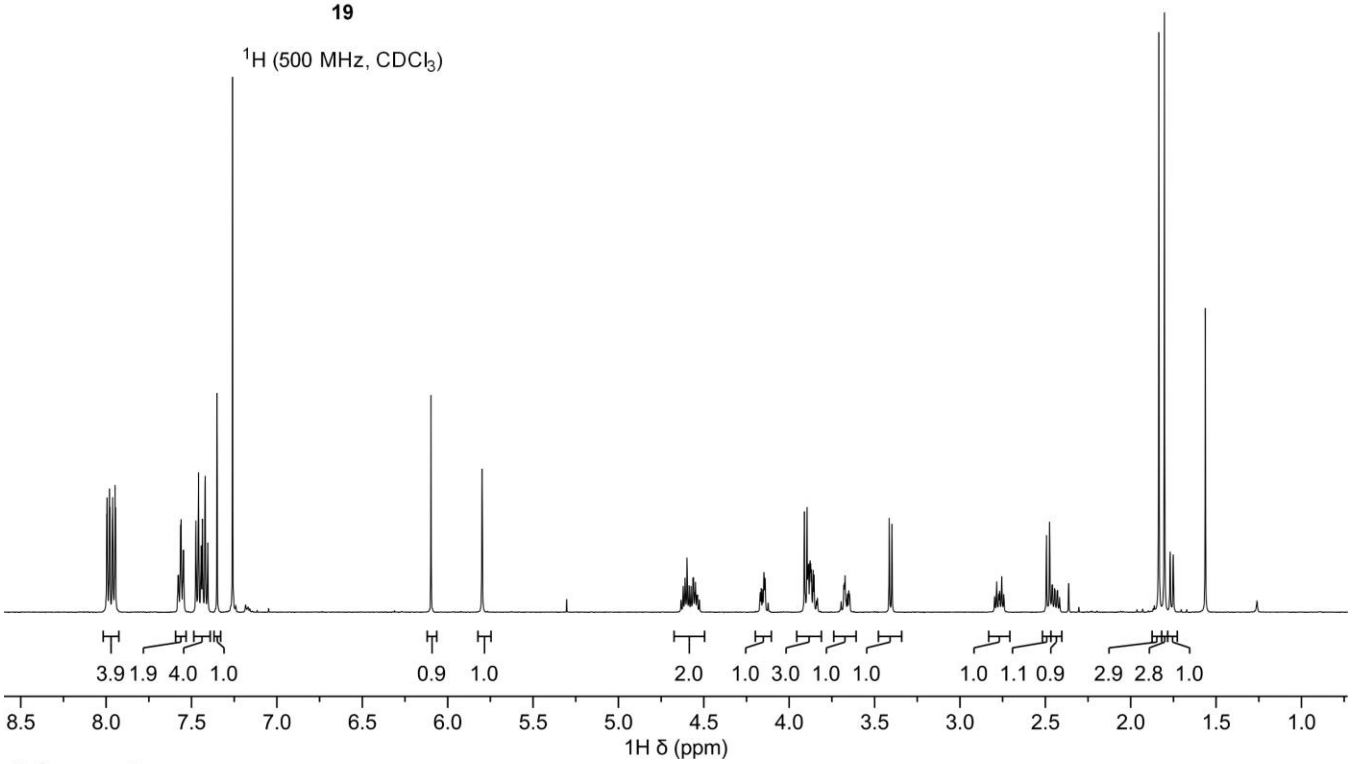
18

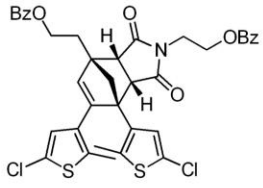
^{13}C (126 MHz, $CDCl_3$)



19

^{1}H (500 MHz, $CDCl_3$)





19

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