

SUPPLEMENTARY INFORMATION

Tethered PProDOTs: Conformationally Restricted 3,4-Propylenedioxythiophene Based Electroactive Polymers

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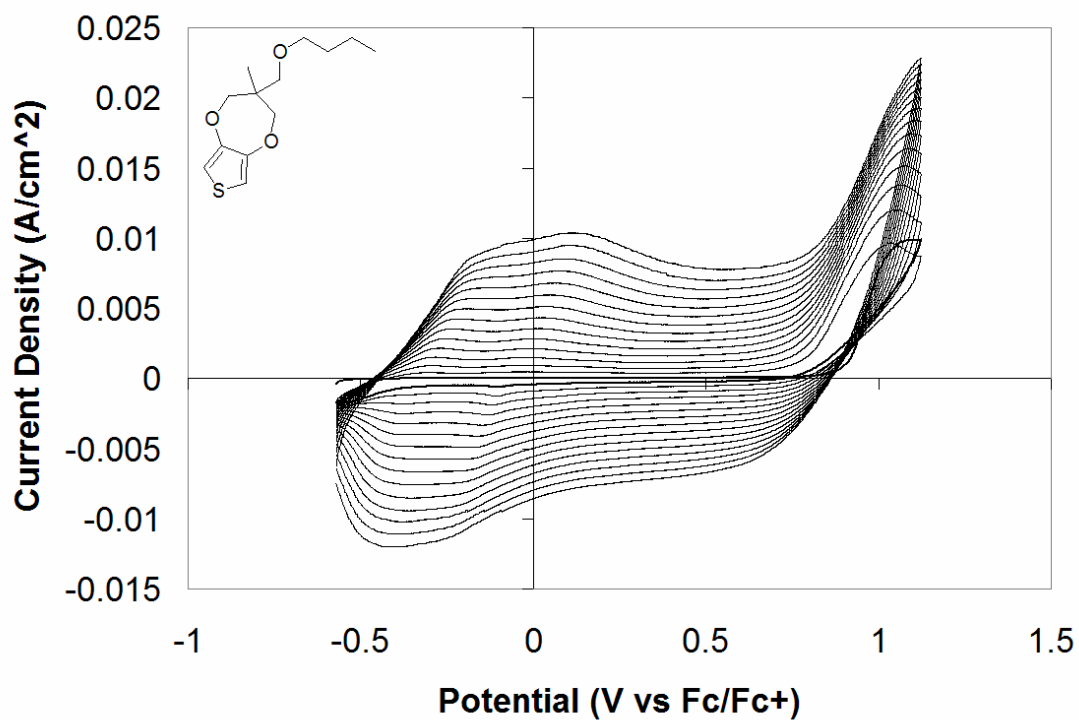


Fig S-1. Electropolymerization of compound 4 in 0.1M TBAP/ACN.

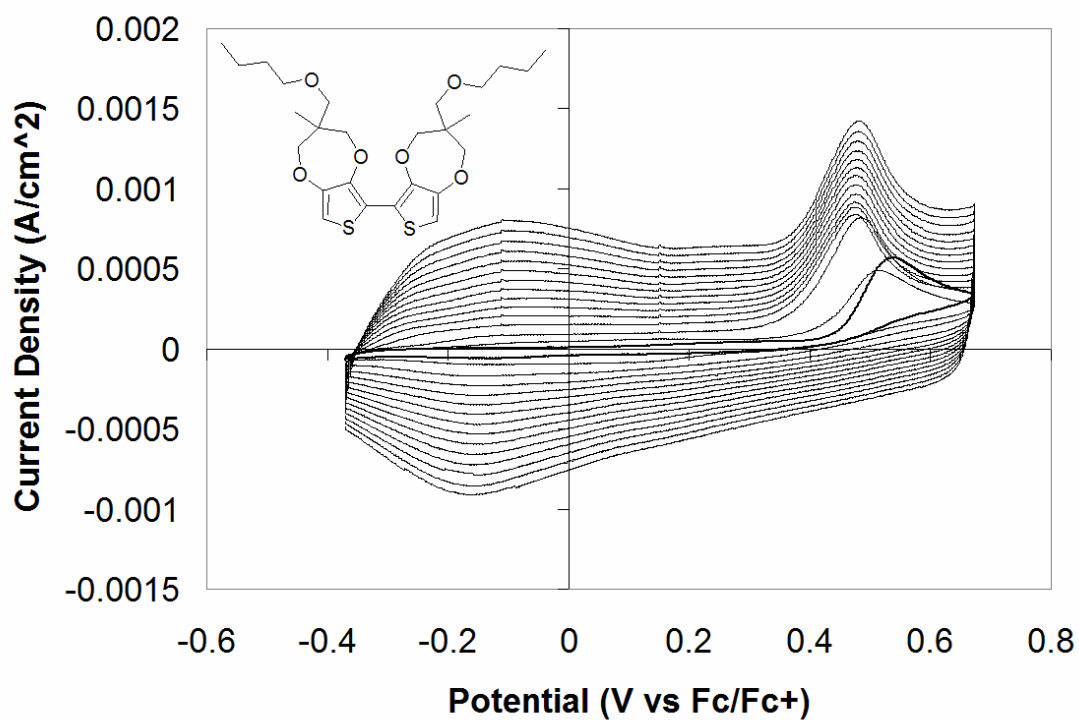


Fig S-2. Electropolymerization of compound 5 in 0.1M TBAP/ACN.

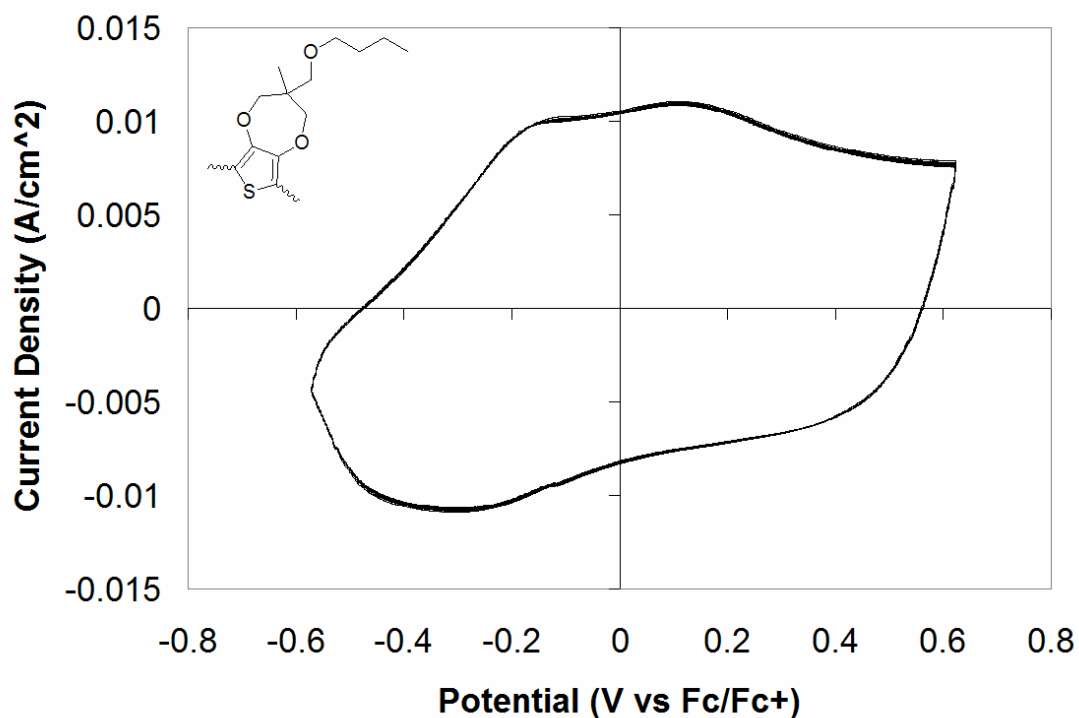


Fig S-3. Repeated scan CV of Poly4 in 0.1M TBAP/ACN.

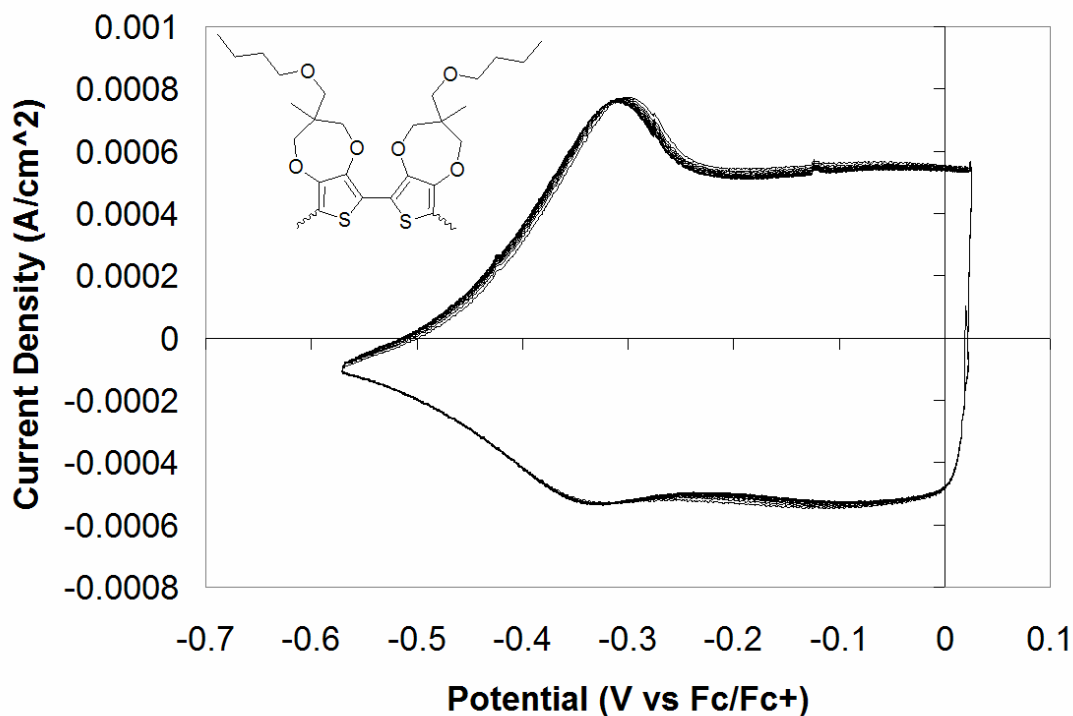


Fig S-4. Repeated scan CV of Poly5 in 0.1M TBAP/ACN.

Compound	¹ H NMR Shift #1	¹ H NMR Shift #2	Shift 1:Shift 2 Integral Ratio
3c	6.51	6.49	0.85
3d	6.49	6.48	0.85
3e	6.500	6.498	1.00

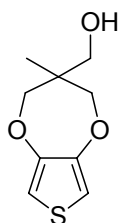
Table S-1. Competitive ¹H NMR data for the macrocyclic derivatives

Experimental Section

Materials. All reagents were obtained either from Aldrich or Fisher Scientific. All electrochemical solvents were distilled prior to use except for propylene carbonate, which was used as is. ITO-coated glass slides (7 x 50 x 0.6 mm, 20 Ω/□) were obtained from Delta Technologies and were cleaned *via* ultrasound in acetone.

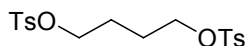
Instrumentation. NMR spectra were measured on a Gemini-300 FT-NMR, a VXR 300 FT-NMR, or a Mercury-300 FT-NMR. High resolution mass spectrometry was performed on a Finnigan MAT 95Q Hybrid Sector or a Bruker APEX II FTICR. UV-vis-NIR spectra were recorded on a Varian Cary 5E UV-vis-NIR spectrophotometer. Elemental analysis was performed at Robertson Microlit, Madison NJ. TGA data was

measured with a Perkin-Elmer TGA 7 thermogravimetric analyzer. Electrochemistry was performed on a Princeton Applied Research model 273A potentiostat/galvanostat. Electrochemical measurements were performed in a three-electrode cell configured with a Pt button (0.02 cm²) working electrode, a Pt flag counter electrode, and a Ag/Ag⁺ (10 mM in TBAP/ACN) reference electrode, which was calibrated to the ferrocene/ferricinium redox couple. Electrochemistry on ITO/glass electrodes was performed in a three-electrode cell with ITO/glass as the working electrode, a Pt wire counter electrode, and a silver wire pseudoreference electrode. Contact to the ITO slides was made using conductive Cu tape (1131) purchased from 3M. Digital photographs were taken with a Canon PowerShot A75 digital camera by front illumination with a halogen lamp onto a white background. Colorimetry was measured using a Minolta CS-100 chroma meter, during which samples were placed into an in-house fabricated dark box and illuminated from behind with a D50 (5000K) light source.

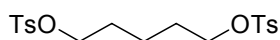


(3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methanol (1). To a 500-mL RB flask outfitted with a magnetic stir bar, condenser, and an argon atmosphere was added 3,4-dimethoxythiophene (2.00 g, 13.9 mmol), 1,1,1-Tris(hydroxymethyl)ethane (2.50 g, 20.8 mmol), *p*-toluenesulfonic acid hydrate (0.26 g, 1.39 mmol), and toluene (200 mL). The reaction was heated to 100 °C for 12 hours and the pale green solution was cooled to room temperature, washed twice with deionized water, and concentrated *via* rotary evaporation. The crude mixture was purified *via* silica gel flash chromatography (1:1 = Hexanes: Et₂O) to yield 2.47 g (89 %) of a white solid. TLC *R_f* = 0.22 (Silica, 1:1 = Hexanes:Et₂O); mp 61.8 – 62.1 °C; ¹H NMR (300 MHz, CDCl₃): δ 6.48 (s, 2H), 3.91 (dd, 4H, *J* = 115 Hz, *J* = 13.7 Hz), 3.75 (s, 2H), 1.68 (t, 1H, *J* = 6.3 Hz), 0.95 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 157.6, 105.9, 76.7, 66.0, 44.0, 17.2; HRMS (EI): Calcd for C₉H₁₂O₃S ([M]⁺), 200.0507, found *m/z*, 200.0514; Anal. Calcd for C₉H₁₂O₃S: C, 53.98; H, 6.04 %, found: C, 54.07; H, 6.13 %.

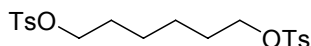
Alkylene Ditosylates (2a-h) General Procedure. To a 500-mL RB flask outfitted with a magnetic stir bar, addition funnel, and argon atmosphere was added α,ω-alkylenediol (96.0 mmol) and pyridine (20 – 100 mL). The flask was cooled to ~0 °C in an ice bath. A mixture of *p*-toluenesulfonyl chloride (202 mmol) and pyridine (55 mL) was added to the addition funnel and its contents were added drop-wise over a period of 30 minutes. The reaction was stirred at 0 °C for two hours, where it became a solid white mass. The mixture was poured into water (400 mL) under vigorous stirring and the resulting white precipitate was vacuum filtered and recrystallized in hot methanol to yield the final product.



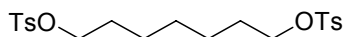
1,3-Bis(*p*-toluenesulfonyloxy)butane (2a). Yield, 74% of flaky white crystals. mp 58.1 – 59.2 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.76 (d, 4H, J = 9.3 Hz), 7.35 (d, 4H, J = 9.3 Hz), 3.99 (t, 4H, J = 4.0 Hz), 2.45 (s, 6H), 1.70 (p, 4H, J = 4.0 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 145.2, 133.1, 130.1, 128.1, 69.6, 25.3, 21.9; HRMS (ESI-FTICR-MS): Calcd for C₁₈H₂₃O₆S₂ ([M + H]⁺), 399.0931, found *m/z*, 399.0933; Anal. Calcd for C₁₈H₂₂O₆S₂: C, 54.25; H, 5.56 %, found: C, 54.26; H, 5.57 %.



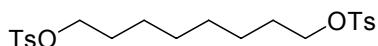
1,5-Bis(*p*-toluenesulfonyloxy)pentane (2b). Yield, 76% of shiny white, flaky crystals. mp = 72.7 – 73.0 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.77 (dd, 2H, J = 7.3 Hz, J = 2.0 Hz), 7.35 (dd, 2H, J = 7.3 Hz, J = 2.0 Hz), 3.97 (t, 4H, J = 7.0 Hz), 2.46 (s, 6H), 1.61 (p, 4H, J = 7.6 Hz), 1.40 – 1.32 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 145.1, 133.2, 130.1, 128.1, 70.2, 28.4, 21.9, 21.7; HRMS Calcd. for C₁₉H₂₄O₆S₂: 412.1014, Found: 412.1006; Elemental anal. calcd. for C₁₉H₂₄O₆S₂: C, 55.32; H, 5.86; found: C, 55.38; H, 5.75.



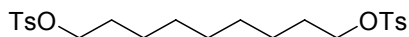
1,6-Bis(*p*-toluenesulfonyloxy)hexane (2c). Yield, 82% of a white solid. mp 72.0 – 75.3 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.77 (d, 4H, J = 9.3 Hz), 7.34 (d, 4H, J = 9.3 Hz), 3.97 (t, 4H, J = 7.3 Hz), 2.17 (s, 6H), 1.58 (p, 4H, J = 7.3 Hz), 1.26 (p, 4H, J = 7.3 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 145.0, 133.2, 130.1, 128.1, 70.5, 28.8, 25.0, 21.9; HRMS (ESI-FTICR-MS): Calcd for C₂₀H₂₆NaO₆S₂ ([M + Na]⁺), 449.1063, found *m/z*, 449.1067; Anal. Calcd for C₂₀H₂₆O₆S₂: C, 56.32; H, 6.14 %, found: C, 56.69; H, 6.42 %.



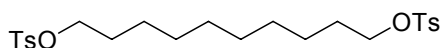
1,7-Bis(*p*-toluenesulfonyloxy)heptane (2d). Yield, 91% of a white solid. mp 74.2 – 74.7 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.77 (d, 4H, J = 9.3 Hz), 7.34 (d, 4H, J = 9.3 Hz), 3.98 (t, 4H, J = 7.3 Hz), 2.16 (s, 6H), 1.58 (p, 4H, J = 7.3 Hz), 1.32 – 1.10 (m, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 145.0, 133.2, 130.0, 128.1, 70.7, 28.8, 28.4, 25.3, 21.8; HRMS (ESI-FTICR-MS): Calcd for C₂₁H₂₈NaO₆S₂ ([M + Na]⁺), 463.1220, found *m/z*, 463.1220; Anal. Calcd for C₂₁H₂₈O₆S₂: C, 57.25; H, 6.41 %, found: C, 57.43; H, 6.54 %.



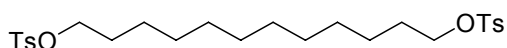
1,8-Bis(*p*-toluenesulfonyloxy)octane (2e). Yield, 91% of a white solid. mp 76.3 – 77.4 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.78 (d, 4H, J = 9.3 Hz), 7.34 (d, 4H, J = 9.3 Hz), 4.00 (t, 4H, J = 7.0 Hz), 2.45 (s, 6H), 1.61 (p, 4H, J = 7.0 Hz), 1.31 – 1.15 (m, 8H); ¹³C NMR (75 MHz, CDCl₃): δ 144.9, 133.4, 130.0, 128.1, 70.8, 29.0, 28.9, 25.4, 21.9; HRMS (ESI-FTICR-MS): Calcd for C₂₂H₃₀NaO₆S₂ ([M+Na]⁺), 477.1376, found *m/z*, 477.1371; Anal. Calcd for C₂₂H₃₀O₆S₂: C, 58.12; H, 6.65 %, found: C, 58.13; H, 6.72 %.



1,9-Bis(*p*-toluenesulfonyloxy)nonane (2f). Yield, 88% of a white solid. mp 76.8 – 77.4 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.77 (d, 4H, J = 9.3 Hz), 7.34 (d, 4H, J = 9.3 Hz), 3.99 (t, 4H, J = 7.3 Hz), 2.16 (s, 6H), 1.61 (p, 4H, J = 7.3 Hz), 1.32 – 1.13 (m, 10H); ¹³C NMR (75 MHz, CDCl₃): δ 144.9, 133.3, 130.0, 128.1, 70.8, 29.3, 28.9, 25.4, 21.8; HRMS (ESI-FTICR-MS): Calcd for C₂₃H₃₂NaO₆S₂ ([M]⁺), 491.1533, found *m/z*, 491.1507; Anal. Calcd for C₂₃H₃₂O₆S₂: C, 58.95; H, 6.88 %, found: C, 59.28; H, 7.24 %.

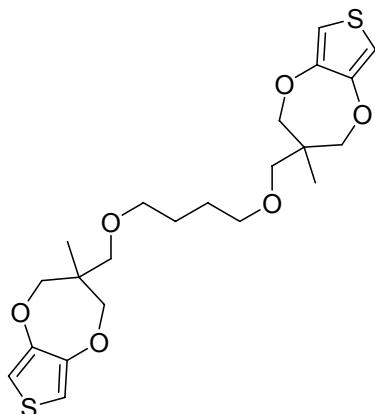


1,10-Bis(*p*-toluenesulfonyloxy)decane (2g). Yield 85% of a white powder. mp = 103.2 – 103.7 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.79 (dd, 2H, J = 7.7 Hz, J = 1.7 Hz), 7.34 (d, 2H, J = 7.3 Hz), 4.01 (t, 4H, J = 7.3 Hz), 2.45 (s, 6H), 1.62 (p, 4H, J = 7.3 Hz), 1.35 – 1.17 (m, 12H); ¹³C NMR (75 MHz, CDCl₃): δ 147.5, 144.9, 130.0, 128.1, 70.9, 29.4, 29.1, 29.0, 25.5, 21.9; HRMS Calcd. for C₂₄H₃₄O₆S₂: 482.1797, Found: 482.1795; Elemental anal. calcd. for C₂₄H₃₄O₆S₂: C, 59.72; H, 7.10; found: C, 59.81; H, 7.39.

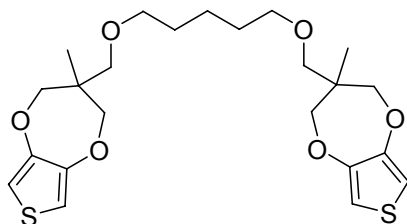


1,12-Bis(*p*-toluenesulfonyloxy)dodecane (2h). Yield, 89% of a white solid. mp 71.2 – 72.2 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.79 (d, 4H, J = 9.7 Hz), 7.34 (d, 4H, J = 9.7 Hz), 4.02 (t, 4H, J = 7.0 Hz), 2.45 (s, 6H), 1.63 (p, 4H, J = 7.0 Hz), 1.35 – 1.17 (m, 16H); ¹³C NMR (75 MHz, CDCl₃): δ 144.8, 133.5, 130.0, 128.1, 70.9, 29.61, 29.55, 29.1, 29.0, 25.5, 21.9; HRMS (ESI-FTICR-MS): Calcd for C₂₆H₃₈NaO₆S₂ ([M+Na]⁺), 533.2002, found *m/z*, 533.2020; Anal. Calcd for C₂₆H₃₈O₆S₂: C, 61.15; H, 7.50 %, found: C, 61.14; H, 7.68 %.

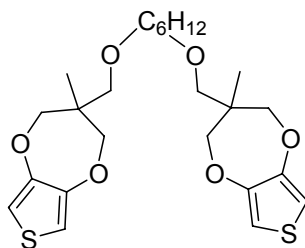
Tethered ProDOTs (3a-h) General Procedure. To a 100-mL RB flask outfitted with a magnetic stir bar and an argon atmosphere was added compound **1** (2.70 g, 13.5 mmol) and anhydrous DMF (50 mL). The reaction was chilled to 0 °C and sodium hydride (60% suspension in mineral oil, 1.35 g, 33.7 mmol) was added. The reaction was stirred for 1 hour, where evolution of hydrogen appeared to be finished. To the reaction, α,ω-alkylene ditosylate (compounds **2a-h**) (6.74 mmol) was added and the reaction was stirred for 10 hours while carefully maintaining a ~0 °C temperature. Twice during the 10 hour time period, a 0.25 g aliquot of sodium hydride suspension was added to the reaction. When finished, the reaction was poured into DI water (250 mL) and the resulting cloudy suspension was extracted with 3x 100 mL of Et₂O. The organic layers were combined and washed with water, brine, dried over anhydrous sodium sulfate, and concentrated under vacuum. The crude mixture was purified *via* flash chromatography on silica gel.



1,4-bis((3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methoxy)butane (3a). The crude mixture was purified *via* silica gel flash chromatography (4:1 = Hexanes: Et₂O) to yield 1.35 g (59%) of a clear oil. TLC R_f = 0.33 (Silica Gel, 4:1 = Hexanes: Et₂O); mp 75.2 – 76.8 °C; ¹H NMR (300 MHz, CDCl₃): δ 6.47 (s, 4H), 3.84 (dd, 8H, J = 101 Hz, J = 13 Hz), 3.49 (t, 4H, J = 5.2 Hz), 3.45 (s, 4H), 1.62 (p, 4H, J = 5.2 Hz), 0.97 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 150.1, 105.8, 77.0, 73.5, 71.7, 43.6, 26.5, 17.7; HRMS (EI): Calcd for C₂₂H₃₀O₆S₂ ([M]⁺), 454.1484, found *m/z*, 454.1489; Anal. Calcd for C₂₂H₃₀O₆S₂: C, 58.12; H, 6.65 %, found: C, 58.37; H, 6.83 %.

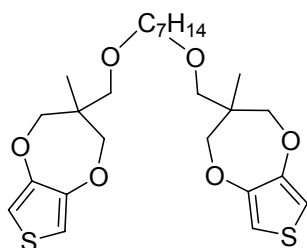


1,5-bis((3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methoxy)pentane (3b). The crude mixture was purified *via* silica gel flash chromatography (4:1 = Hexanes: Et₂O) to yield 1.61 g (71%) of a clear oil. TLC R_f = 0.55 (Silica, 4:1 = Hexanes: Et₂O); ¹H NMR (300 MHz, CDCl₃): δ 6.47 (s, 4H), 3.86 (dd, 8H, J = 99.0 Hz, J = 13.0 Hz), 3.45 (s, 4H), 3.43 (t, 4H, J = 7.0 Hz), 1.61 (p, 4H, J = 7.3 Hz), 1.36 – 1.46 (m, 2H), 0.98 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 150.1, 105.7, 77.1, 73.5, 71.9, 43.6, 29.6, 23.0, 17.7; HRMS (EI): Calcd for C₂₃H₃₂O₆S₂ ([M]⁺), 468.1640, found *m/z*, 468.1612; Anal. Calcd for C₂₃H₃₂O₆S₂: C, 58.95; H, 6.88 %, found: C, 59.14; H, 7.14 %.



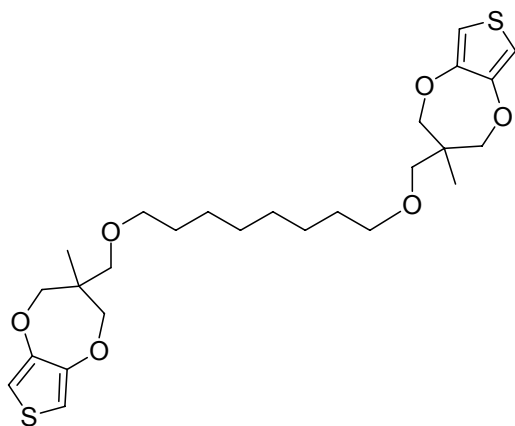
1,6-bis((3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methoxy)hexane

(3c). The crude mixture was purified *via* silica gel flash chromatography (17:3 = Hexanes: Et₂O) to yield 2.84 g (87%) of a clear oil. TLC R_f = 0.47 (Silica Gel, 4:1 = Hexanes: Et₂O); ¹H NMR (300 MHz, CDCl₃): δ 6.47 (s, 4H), 3.86 (dd, 8H, J = 100 Hz, 13.7 Hz), 3.44 (s, 4H), 3.42 (t, 4H, J = 7.3 Hz), 1.56 (p, 4H, J = 7.3 Hz), 1.38 – 1.24 (m, 4H), 0.98 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 150.1, 105.8, 77.1, 73.5, 71.9, 43.6, 29.7, 26.2, 12.7; HRMS (ESI-FTICR-MS): Calcd for C₂₄H₃₄NaO₆S₂ ([M + Na]⁺), 505.1689, found m/z , 505.1681; Anal. Calcd for C₂₄H₃₄O₆S₂: C, 59.72; H, 7.10 %, found: C, 60.23; H, 7.40 %.



1,7-bis((3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methoxy)heptane

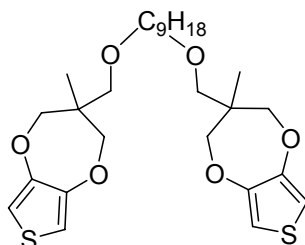
(3d). The crude mixture was purified *via* silica gel flash chromatography (17:3 = Hexanes: Et₂O) to yield 2.85 g (85%) of a clear oil. TLC R_f = 0.52 (Silica Gel, 4:1 = Hexanes: Et₂O); ¹H NMR (300 MHz, CDCl₃): δ 6.47 (s, 4H), 3.86 (dd, 8H, J = 99 Hz, J = 13.3 Hz), 3.44 (s, 4H), 3.42 (t, 4H, J = 7.3 Hz), 1.55 (p, 4H, J = 7.3 Hz), 1.37 – 1.24 (m, 6H), 0.98 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 150.1, 105.7, 77.1, 73.5, 72.0, 43.6, 29.7, 29.5, 26.3, 17.7; HRMS (ESI-FTICR-MS): Calcd for C₂₅H₃₆NaO₆S₂ ([M + Na]⁺), 519.1846, found m/z , 519.1860; Anal. Calcd for C₂₅H₃₆O₆S₂: C, 60.45; H, 7.31 %, found: C, 60.65; H, 7.56 %.



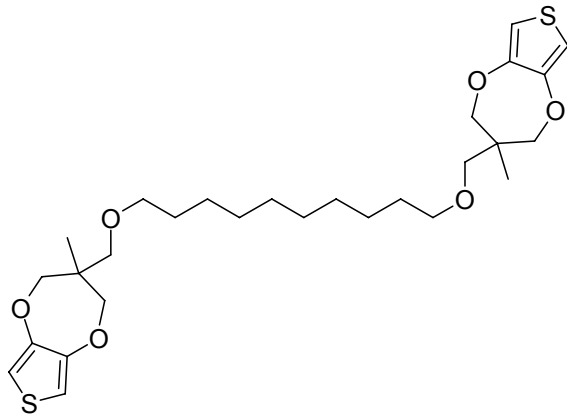
1,8-bis((3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methoxy)octane

(3e). The crude mixture was purified *via* silica gel flash chromatography (9:1 = Hexanes: Et₂O) to yield 3.34 g (90%) of a clear oil. TLC R_f = 0.47 (Silica Gel, 4:1 = Hexanes: Et₂O); ¹H NMR (300 MHz, CDCl₃): δ 6.47 (s, 4H), 4.01 (d, 4H, J = 13 Hz), 3.71 (d, 4H, J = 13 Hz), 3.44 (s, 4H), 3.42 (t, 4H, J = 7.3 Hz), 1.55 (p, 4H, J = 7.3 Hz), 1.36 – 1.28 (m,

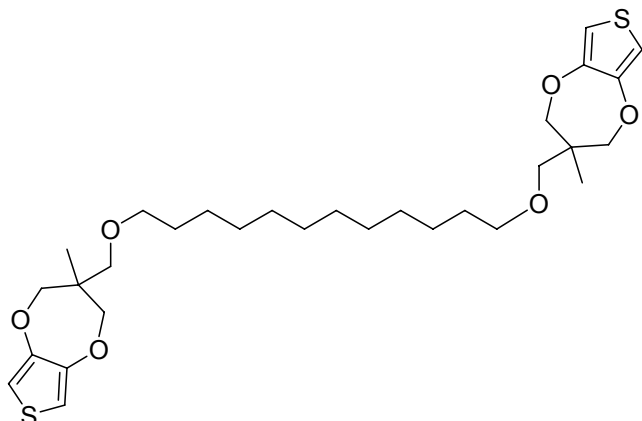
8H), 0.98 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 150.1, 105.7, 77.0, 73.5, 72.0, 43.6, 29.7, 29.6, 26.3, 17.7; HRMS (ESI-FTICR-MS): Calcd for $\text{C}_{26}\text{H}_{38}\text{NaO}_6\text{S}_2$ ($[\text{M}+\text{Na}]^+$), 533.2002, found m/z , 533.1998; Anal. Calcd for $\text{C}_{26}\text{H}_{38}\text{O}_6\text{S}_2$: C, 61.15; H, 7.50 %, found: C, 61.59; H, 7.92 %.



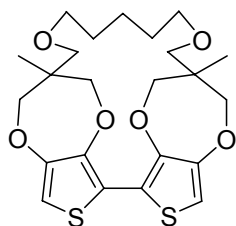
1,9-bis((3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methoxy)nonane (3f). The crude mixture was purified *via* silica gel flash chromatography (17:3 = Hexanes: Et_2O) to yield 2.72 g (79%) of a clear oil. TLC R_f = 0.56 (Silica Gel, 4:1 = Hexanes: Et_2O); ^1H NMR (300 MHz, CDCl_3): δ 6.47 (s, 4H), 3.86 (dd, 8H, $J = 99$ Hz, $J = 13$ Hz), 3.44 (s, 4H), 3.42 (t, 4H, $J = 7.3$ Hz), 1.55 (p, 4H, $J = 7.3$ Hz), 1.36 – 1.24 (m, 10H), 0.98 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 150.1, 105.7, 77.1, 73.5, 72.0, 43.6, 29.8, 29.6, 26.3, 17.7; HRMS (ESI-FTICR-MS): Calcd for $\text{C}_{27}\text{H}_{40}\text{NaO}_6\text{S}_2$ ($[\text{M}]^+$), 547.2159, found m/z , 547.2168; Anal. Calcd for $\text{C}_{27}\text{H}_{40}\text{O}_6\text{S}_2$: C, 61.80; H, 7.68 %, found: C, 62.14; H, 7.95 %.



1,10-bis((3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methoxy)decane (3g). The crude mixture was purified *via* silica gel flash chromatography (4:1 = Hexanes: Et_2O) to yield 2.63 g (61%) of a clear oil. TLC R_f = 0.62 (Silica, 3:1 = Hexanes: Et_2O); ^1H NMR (300 MHz, CDCl_3): δ 6.47 (s, 4H), 3.86 (dd, 8H, $J = 98.0$ Hz, $J = 13.0$ Hz), 3.44 (s, 4H), 3.42 (t, 4H, $J = 7.3$ Hz), 1.55 (p, 4H, $J = 7.3$ Hz), 1.28 (br, 12H), 0.98 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 150.1, 105.7, 77.1, 73.5, 72.1, 43.6, 29.8, 29.7, 26.3, 17.7; HRMS (EI): Calcd for $\text{C}_{28}\text{H}_{42}\text{O}_6\text{S}_2$ ($[\text{M}]^+$), 538.2423, found m/z , 538.2417; Anal. Calcd for $\text{C}_{28}\text{H}_{42}\text{O}_6\text{S}_2$: C, 62.42; H, 7.86 %, found: C, 62.82; H, 8.30 %.

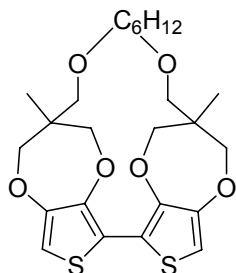


1,12-bis((3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-3-yl)methoxy)dodecane (3h). The crude mixture was purified *via* silica gel flash chromatography (9:1 = Hexanes: Et₂O) to yield 3.30 g (80%) of a clear oil. TLC R_f = 0.51 (Silica Gel, 4:1 = Hexanes: Et₂O); ¹H NMR (300 MHz, CDCl₃): δ 6.47 (s, 4H), 4.01 (d, 4H, J = 13 Hz), 3.72 (d, 4H, J = 13 Hz), 3.44 (s, 4H), 3.42 (t, 4H, J = 7.0 Hz), 1.55 (p, 4H, J = 7.0 Hz), 1.37 – 1.24 (m, 16 H), 0.99 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 150.1, 105.7, 77.1, 73.5, 72.1, 43.6, 29.81, 29.76, 29.68, 26.3, 17.7; HRMS (ESI-FTICR-MS): Calcd for C₃₀H₄₆NaO₆S₂ ([M + Na]⁺), 589.2628, found m/z , 589.2604; Anal. Calcd for C₃₀H₄₆O₆S₂: C, 63.57; H, 8.18 %, found: C, 64.23; H, 8.64 %.

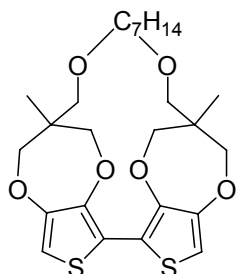


C5 Macrocycle (4b). All glassware was flame-dried prior to use. To a 100-mL round bottom flask equipped with a magnetic stir bar, septum, and an argon atmosphere was added compound **3b** (0.48 g, 1.02 mmol), and anhydrous THF (50 mL). The reaction was chilled in a CO₂/acetone bath, and a solution of *n*-Butyllithium (2.5M in hexanes, 1.02 mL) was added drop-wise *via* syringe. The reaction was stirred for 30 minutes and then warmed to room temperature, during which a white precipitate was seen to form and the solution became yellow. The solution was transferred to a pressure equalizing addition funnel, and its contents were added very slowly (over a period of 30 minutes) to a refluxing mixture of iron (III) acetylacetonate (0.90 g, 2.55 mmol). The reaction was stirred for 30 minutes, cooled to room temperature, concentrated *in vacuo*, and purified *via* gravity column chromatography on silica gel (2:1 = Petroleum Ether: Et₂O) to yield 72 mg (15%) of a white solid. For x-ray analysis, the solid was recrystallized from CDCl₃ *via* petroleum ether vapor diffusion. TLC R_f = 0.60 (Silica, 2:1 = Petroleum Ether: Ether); mp 128.5 – 129.0 °C; ¹H NMR (300 MHz, CDCl₃): δ 6.47 (s, 2H), 4.14 (dd, J = 160 Hz, J = 13 Hz), 3.89 (dd, J = 54 Hz, J = 13 Hz), 3.52 – 3.37 (m, 4H), 3.36 (dd, 4H, J = 111 Hz, J = 10 Hz), 1.52 (m, 4H), 1.26 (m, 2H), 1.11 (s, 6H); ¹³C NMR (75

MHz, CDCl₃): δ 150.6, 146.2, 114.6, 104.7, 77.6, 77.1, 74.2, 71.9, 44.1, 29.8, 25.0, 18.2;
HRMS (EI): Calcd for C₂₃H₃₀O₆S₂ ([M]⁺), 466.1484, found *m/z*, 466.1496.

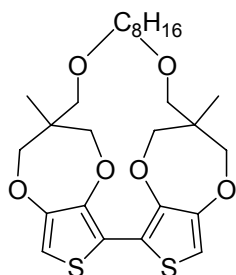


C6 Macrocycle (4c). All glassware was carefully dried before use. Flask *A*: to a 500-mL RB flask containing a stir bar and an argon atmosphere and outfitted with a pressure equalizing addition funnel was added Fe(acac)₃ (2.19 g, 6.21 mmol) and anhydrous THF (275 mL). The mixture was heated to 60 °C. Flask *B*: to a 125-mL 2-neck RB flask containing a stir bar and an argon atmosphere and outfitted with a septum was added compound **3c** (0.75 g, 1.55 mmol) and anhydrous THF (125 mL). The mixture was chilled in an acetone/CO₂ bath and *n*-butyllithium in hexanes (2.5 M, 2.07 mL) was added drop wise *via* syringe. The reaction was stirred for 30 minutes and warmed to room temperature. To the resulting white suspension was added anhydrous HMPA (0.93 g, 5.18 mmol). The contents of Flask *B* were cannulated into the addition funnel of Flask *A* and its contents were added drop-wise very slowly to the mixture in Flask *A*. After addition, the reaction was stirred for another 30 minutes and then cooled to room temperature. After filtering through a bed of Celite™ (THF as the eluent), the solution was concentrated *in vacuo* and purified *via* flash chromatography on silica gel (4:1 = Hexanes:Et₂O) to yield 0.27 g (36%) of a white solid. 2% *de*. TLC *R_f* = 0.35 (Silica Gel, 4:1 = Hexanes:Et₂O); ¹H NMR (300 MHz, CDCl₃): δ 6.51 (s, 1.7H), 6.49 (s, 2.0H), 4.30 (d, 2.0H, *J* = 13 Hz), 4.15 (d, 1.7H, *J* = 13 Hz), 3.98 (d, 2.0 H, *J* = 14 Hz), 3.92 – 3.74 (m, 9.8H), 3.57 (d, 2.0H, *J* = 10Hz), 3.52 (d, 1.7H, *J* = 10 Hz) 3.45 – 3.42 (m, 8H), 3.19 (d, 2H, *J* = 10 Hz), 1.64 – 1.39 (m, 10.8H), 1.09 (s, 5.2H), 1.08 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 150.9, 150.5, 147.2, 146.4, 130.0, 128.1, 105.4, 105.2, 78.2, 78.1, 74.14, 74.09, 71.8, 71.6, 70.0, 43.9, 43.8, 30.4, 29.7, 29.6, 28.2, 27.7, 26.7, 17.8, 17.5; HRMS (CI): Calcd for C₂₄H₃₂O₆S₂ ([M]⁺), 480.1640, found *m/z*, 480.1642.



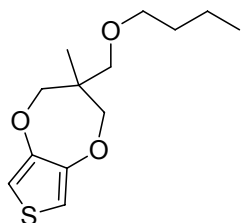
C7 Macrocycle (4d). All glassware was carefully dried before use. Flask *A*: to a 500-mL RB flask containing a stir bar and an argon atmosphere and outfitted with a pressure

equalizing addition funnel was added $\text{Fe}(\text{acac})_3$ (2.13 g, 6.03 mmol) and anhydrous THF (275 mL). The mixture was heated to 60°C . Flask *B*: to a 125-mL 2-neck RB flask containing a stir bar and an argon atmosphere and outfitted with a septum was added compound **3d** (1.00 g, 2.01 mmol) and anhydrous THF (125 mL). The mixture was chilled in an acetone/ CO_2 bath and *n*-butyllithium in hexanes (2.5 M, 2.01 mL) was added drop wise *via* syringe. The reaction was stirred for 30 minutes and warmed to room temperature. To the resulting white suspension was added anhydrous HMPA (1.81 g, 10.1 mmol). The contents of Flask *B* were canulated into the addition funnel of Flask *A* and its contents were added drop-wise very slowly to the mixture in Flask *A*. After addition, the reaction was stirred for another 30 minutes and then cooled to room temperature. After filtering through a bed of Celite™ (THF as the eluent), the solution was concentrated *in vacuo* and purified *via* flash chromatography on silica gel (4:1 = Hexanes: Et_2O) to yield 0.19 g (19%) of a white solid. 3% *d.e.* TLC R_f = 0.25 (Silica Gel, 4:1 = Hexanes: Et_2O); ^1H NMR (300 MHz, CDCl_3): δ 6.49 (s, 1.7H), 6.48 (s, 2.0H), 4.27 (d, 2.0H, J = 13 Hz), 4.15 (d, 1.7H, J = 13 Hz), 3.98 – 3.67 (m, 14.1H), 3.53 – 3.36 (m, 10H), 3.26 – 3.17 (m, 4H) 1.60 – 1.28 (m, 13.2H), 1.09 (s, 5.2H), 1.08 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 150.7, 150.2, 147.2, 146.3, 115.0, 113.8, 105.2, 105.0, 78.0, 77.4, 77.2, 74.6, 74.0, 71.3, 71.1, 44.0, 43.9, 29.2, 29.0, 28.3, 28.0, 26.1, 25.9, 17.8, 17.7; HRMS (CI): Calcd for $\text{C}_{25}\text{H}_{34}\text{O}_6\text{S}_2$ ($[\text{M}]^+$), 494.1797, found m/z , 494.1813.

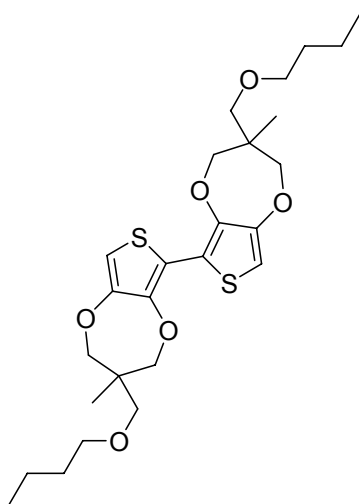


C8 Macrocycle (4e). All glassware was carefully dried before use. Flask *A*: to a 500-mL RB flask containing a stir bar and an argon atmosphere and outfitted with a pressure equalizing addition funnel was added $\text{Fe}(\text{acac})_3$ (5.19 g, 14.7 mmol) and anhydrous THF (275 mL). The mixture was heated to 60°C . Flask *B*: to a 125-mL 2-neck RB flask containing a stir bar and an argon atmosphere and outfitted with a septum was added compound **3e** (2.50 g, 4.90 mmol) and anhydrous THF (125 mL). The mixture was chilled in an acetone/ CO_2 bath and *n*-butyllithium in hexanes (1.28 M, 9.57 mL) was added drop wise *via* syringe. The reaction was stirred for 30 minutes and warmed to room temperature. To the resulting white suspension was added anhydrous HMPA (2.63 g, 14.7 mmol). The contents of Flask *B* were canulated into the addition funnel of Flask *A* and its contents were added drop-wise very slowly to the mixture in Flask *A*. After addition, the reaction was stirred for another 30 minutes and then cooled to room temperature. After filtering through a bed of Celite™ (THF as the eluent), the solution was concentrated *in vacuo* and purified *via* flash chromatography on silica gel (4:1 = Hexanes: Et_2O) to yield 0.19 g (8%) of a white solid. ^1H NMR (300 MHz, CDCl_3): δ 6.50 (s, 2H), 6.498 (s, 2H), 4.29 (d, 2H, J = 13 Hz), 4.16 (d, 2H, J = 13 Hz), 4.00 – 3.69 (m,

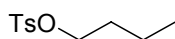
14H), 3.53 – 3.33 (m, 11H), 3.25 – 3.18 (m, 4H), 1.58 – 1.24 (m, 24H), 1.12 (s, 6H), 1.03 (s, 6H); HRMS (CI): Calcd for C₂₅H₃₄O₆S₂ ([M]⁺), 508.1953, found *m/z*, 508.1954.



3-Butoxymethyl-3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (5). Into a 50-mL RB flask outfitted with an argon atmosphere, and containing a stir bar, was added compound **1** (1.00 g, 5.00 mmol) and *N,N*-Dimethylformamide (25 mL). While solution stirred, NaH (60% suspension in mineral oil, 0.40 g, 10.00 mmol) was slowly added. After 20 minutes of stirring, the flask was chilled in an ice bath, and butyl 4-methylbenzenesulfonate (1.37 g, 6.00 mmol) was added. After 1 hour of stirring, NaH suspension (0.25 g, 6.25 mmol) was added, and 2 hours later an additional portion of NaH suspension (0.40 g, 10.00 mmol) was added to the flask. After 30 minutes, an additional portion of butyl 4-methylbenzenesulfonate was added to the flask (0.13 g, 0.60 mmol). The reaction stirred for 30 more minutes, and afterwards was quenched with water (100 mL), extracted 3 times with Et₂O, washed once with water, and washed once with brine. Product was purified *via* flash chromatography on silica gel (9:1 = Hexanes: Et₂O) to yield 0.82 g (63%) of colorless oil TLC *R_f* = 0.49 (silica gel, 9:1 = Hexanes: Et₂O); ¹H NMR (300 MHz, CDCl₃): δ 6.47 (s, 2H), 3.86 (dd, 4H, *J* = 99 Hz, *J* = 13 Hz), 3.45 (s, 2H), 3.43 (t, 2H, *J* = 7.3 Hz), 1.54 (p, 2H, *J* = 7.6 Hz), 1.36 (m, 2H, *J* = 7.6 Hz), 0.99 (s, 3H), 0.92 (t, 3H, *J* = 8.0 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 150.1, 105.7, 77.1, 73.5, 71.7, 43.6, 31.9, 19.6, 17.7, 14.1; HRMS (EI): Calcd for C₁₃H₂₀O₃S ([M]⁺), 256.1133, found *m/z*, 256.1125; Anal. Calcd for C₁₃H₂₀O₃S: C, 60.91; H, 7.86 %, found: C, 60.93; H, 8.10 %.



3-(butoxymethyl)-6-(3-(butoxymethyl)-3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepin-6-yl)-3-methyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine (6). Into a flame-dried 3 neck 100 mL flask outfitted with an argon atmosphere, and equipped with a stir bar, condenser, and 2 stoppers, was added compound **5** (0.328 g, 1.28 mmol) and freshly distilled THF (50 mL). While stirring, the flask was chilled to -78 °C and n-butyllithium (0.66 mL, 1.54 mmol) was added. After 1 hour of stirring, the flask was warmed to room temperature and iron (III) acetylacetonate (0.59 g, 1.66 mmol) was added to the solution. The flask stirred at reflux for 3 hours and was afterwards warmed to room temperature. The product was purified *via* flash chromatography on silica gel (16:1 = Hexanes: Et₂O) to yield 0.051 g (15 %) of an off-white solid. TLC R_f = 0.16 (silica gel, 16:1 = Hexanes: Et₂O); ¹H NMR (300 MHz, CDCl₃): δ 6.40 (s, 2H), 3.95 (dd, 4H, J = 105.7 Hz, J = 13.3 Hz), 3.87 (dd, 4H, J = 106.7 Hz, J = 13 Hz), 3.53-3.42 (m, 8H), 1.55 (p, 4H, J = 7.6 Hz), 1.37 (m, 4H, J = 9 Hz), 1.01 (s, 6H), 0.92 (t, 6H, J = 8.3 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 149.5, 145.1, 115.6, 103.3, 77.0, 76.8, 73.3, 71.5, 43.5, 31.6, 19.3, 17.3, 13.9; HRMS (EI): Calcd for C₂₆H₃₈O₆S₂ ([M]⁺), 510.2110, found *m/z*, 510.2109.



Butyl 4-Methylbenzenesulfonate. Into a 100-mL RB flask outfitted with an argon atmosphere, and containing a stir bar was added 1-butanol (5.00 g, 67 mmol) and pyridine (100 mL). The flask was chilled in an ice bath, and after 5 minutes of stirring, p-Toluenesulfonyl chloride (19.30 g, 101 mmol) was added. The solution was stirred for 2 hours and was then poured into a flask of ice cold 3 M HCl (500 mL). After 10 minutes of vigorous stirring, a thick white precipitate formed. The supernatant liquid was decanted off and the solid melted at room temperature. Product was purified *via* flash chromatography on silica gel (6:1 = Hexanes: Et₂O) to yield 9.52 g (62%) of a colorless oil. TLC R_f = .2 (silica gel, 6:1 = Hexanes: Et₂O); ¹H NMR (300 MHz, CDCl₃): δ 7.77 (d, 2H, J = 9.3 Hz), 7.34 (d, 2H, J = 9.3 Hz), 4.02 (t, 2H, J = 7.0 Hz), 2.44 (s, 3H), 1.62 (p, 2H, J = 7.3 Hz), 1.33 (m, 2H, J = 8.0 Hz), 0.85 (t, 3H, J = 8.3 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 144.8, 133.4, 130.0, 128.0, 70.6, 31.0, 21.8, 18.8, 13.5; HRMS (ESI-FTICR-MS): Calcd for C₁₁H₁₆NaO₃S ([M + Na]⁺), 251.0712, found *m/z*, 251.0705; Anal. Calcd for C₁₁H₁₆O₃S: C, 57.87; H, 7.06 %, found: C, 57.60; H, 7.37 %.