

Towards Environmentally Friendly Processing in Molecular Semiconductors

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Materials and Methods

General Details: Preparations were carried out on a bench top or under an atmosphere of dry, O₂-free N₂ employing both Schlenk line techniques and a Vacuum Atmospheres inert atmosphere glove box. Toluene was dried over sodium/benzophenone, distilled under vacuum, and stored over molecular sieves (4 Å). Chloroform was dried over calcium hydride, distilled under vacuum, and stored over molecular sieves (4 Å). Anhydrous Chlorobenzene and Ethyl Acetate were purchased from Sigma Aldrich, degassed and stored over Molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Company and dried at 140 °C under vacuum for 24 hours prior to use. Deuterated solvents were (CD₂Cl₂, CDCl₃) purchased from Cambridge Isotopes Laboratory and used as received. All reactants and reagents are commercially available and used as received, unless otherwise noted.

Materials: Compound 4H-cyclopenta[2,1-b:3,4-b']dithiophene was purchased from AstarPharma and used without further purification. 4,7-dibromopyridal[2,1,3]thiadiazole was purchased from 1-Material and used without further purification. 2-furylmethanol, 2-thiophenemethanol, 1-bromo-2-methoxyethane, 2-(tributylstannyl)thiophene and 2-(tributylstannyl)furan were purchased from Sigma Aldrich and used as received. 5-hexyl-2,2'-bifuran was synthesized according to previous reports.^[1] Compounds 1, 16 and 17 (Scheme S2) were prepared according previous reports.^[2]

NMR: ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance-500 MHz spectrometer at 25°C unless otherwise noted. ¹H and ¹³C NMR spectra are referenced to SiMe₄ using the residual solvent peak impurity of the given solvent. Chemical shifts are reported in ppm and coupling constants in Hz as absolute values.

UV-vis: UV-visible spectroscopy were recored using either a Beckman Coulter DU 800 series or Perkin Elmer Lambda 750 spectrophotometer at room temperature unless otherwise noted. All solution UV-vis experiments were run in CHCl₃. Films were prepared by spin-coating CHCl₃ solutions onto quartz substrates. Films were annealed directly on a hot plate for 2 minutes.

Mass Spectrometry: Full scan, low resolution FD and high resolution ESI mass spectrometry was carried out at the Department of Chemsitry spectrometry facility, University of California, Santa Barbara.

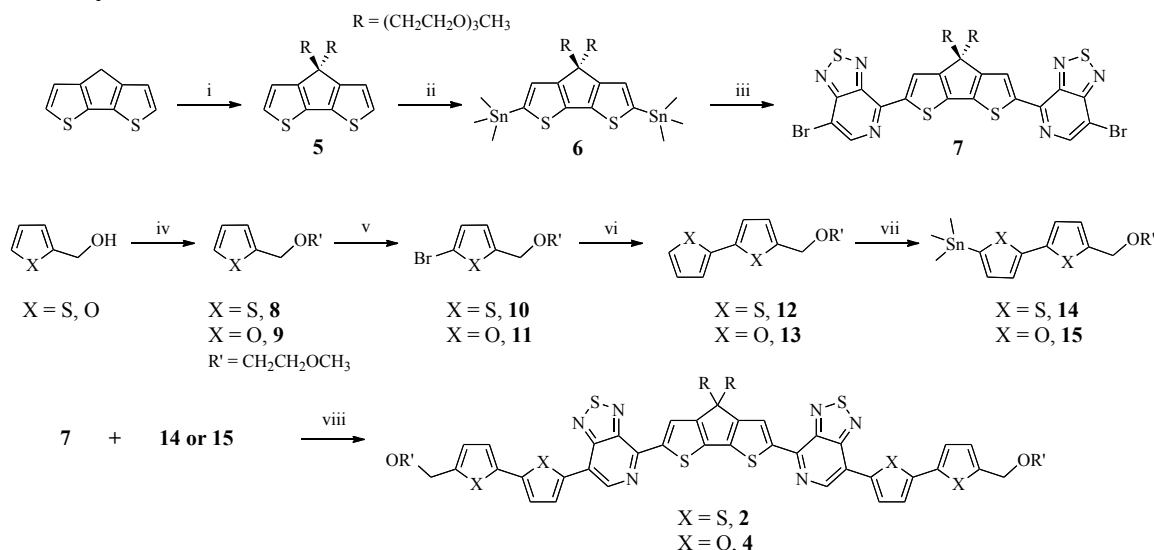
Profilometry: The active layer thicknesses were determined using an Ambios XP-100 Stylus profilometer.

Solubility Measurements: The solubility of each compound in chlorobenzene and ethyl acetate was determined as follows: A saturated solution of each compound was stirred for 48 hours at room temperature then allowed to stand still for 12 hours. The slurry was then filtered through a 1 µm PTFE filter. The filtrate is assumed to be a saturated solution. A 50 µL aliquot was then diluted with chlorobenzene or ethyl acetate. The UV-vis absorption spectrum was acquired and the concentration determined using a standard calibration curve. The calibration curve was prepared by measuring the absorbance of 5 solutions of a given compound in chlorobenzene or

ethyl acetate with known concentrations and plotting λ_{\max} vs. concentration. In each case a linear relationship was observed.

Thin Film Transistor Device Fabrication: Field-effect transistors were fabricated in a bottom-gate, top-contact configuration with highly doped n-type silicon wafers as the gate electrode and 200 nm of hexamethyldisilazane (HMDS) passivated SiO₂ as the gate dielectric. Silicon wafers were cleaned by sequential sonication and rinsing with 70:30 H₂SO₄:H₂O solution, acetone, and isopropyl alcohol. HMDS passivation was applied by spin coating at 3000 rpm for 60 seconds, followed by drying at 150 °C for 1 hour. Compound **4** was dissolved in dry, degassed ethyl acetate at concentration of 5 mg/mL. The ethyl acetate was boiled off and the molecule was redissolved in dry, degassed ethyl acetate. This procedure was repeated three times before using the resulting 5 mg/mL solution, which was spun cast directly at a rate of 2000 rpm. Thermally evaporated Au electrodes were used as the source and drain, with a channel width of either 1, 2 or 3 mm and a channel length of 40 μ m. Output and transfer characteristics of the device were measured in vacuum (10^{-8} torr).

General Synthesis:

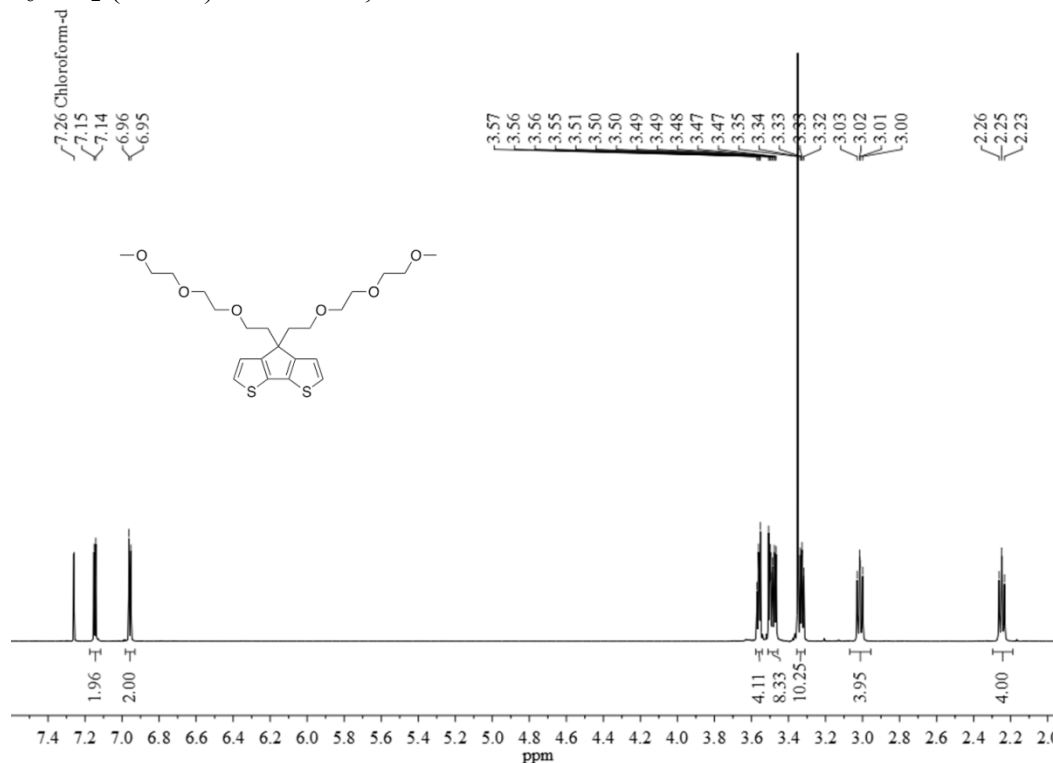


Scheme S1. Synthetic entry to Compounds **2** and **4**. (i) 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane, KOH, NaI (cat), DMSO, r.t. (ii) n-BuLi, (CH₃)₃SnCl, THF, -78 °C. (iii) 4,7-dibromopyridal[2,1,3]thiadiazole, cat. Pd(PPh₃)₄, Toluene, Microwave Heating 160 °C. (iv) KH, 1-bromo-2-methoxyethane, THF, 0 °C → r.t. (v) NBS, DMF, 0 °C → r.t. (vi) 2-(Tributylstannyl)thiophene or 2-(Tributylstannyl)furan, cat. Pd(PPh₃)₄, Toluene, 90 °C, 2d. (vii) n-BuLi, (CH₃)₃SnCl, THF, -78 °C. (viii) cat. Pd(PPh₃)₄, Toluene, 90 °C, 2d.

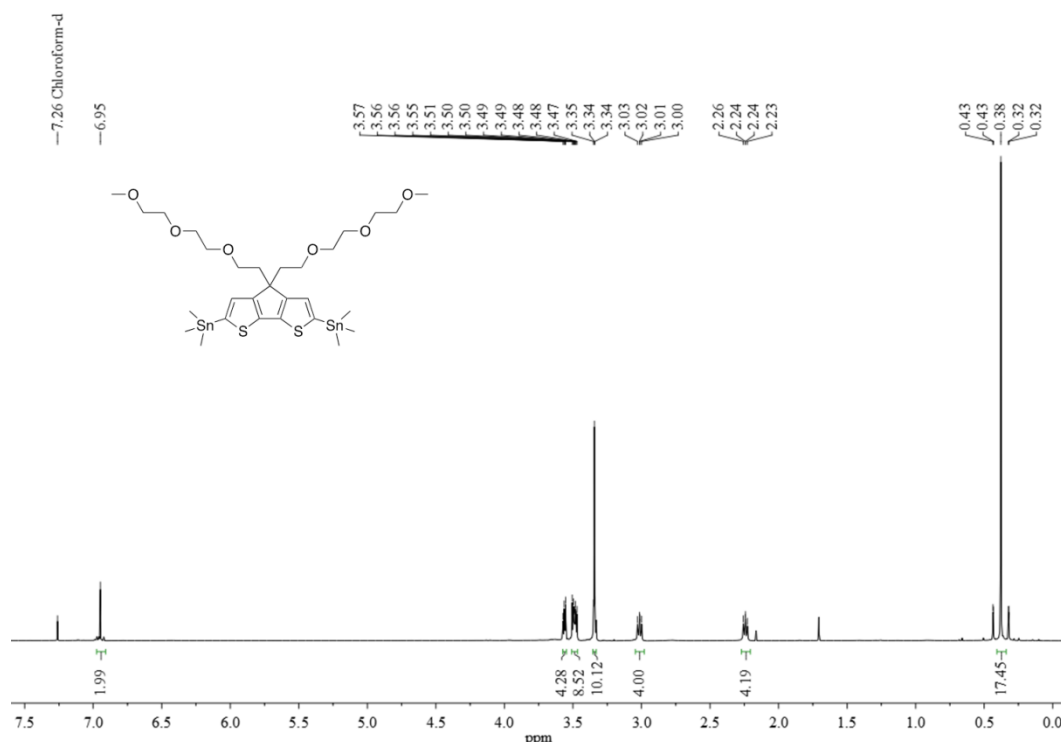
Detailed Procedures:

Synthesis of **4,4-Di[2-[2-(2-methoxyethoxy)ethoxy]ethyl]4H-cyclopenta[2,1-b:3,4-b']dithiophene (5)**: 4H-cyclopenta[2,1-b:3,4-b']dithiophene (.500 g. 2.80 mmol) was dissolved

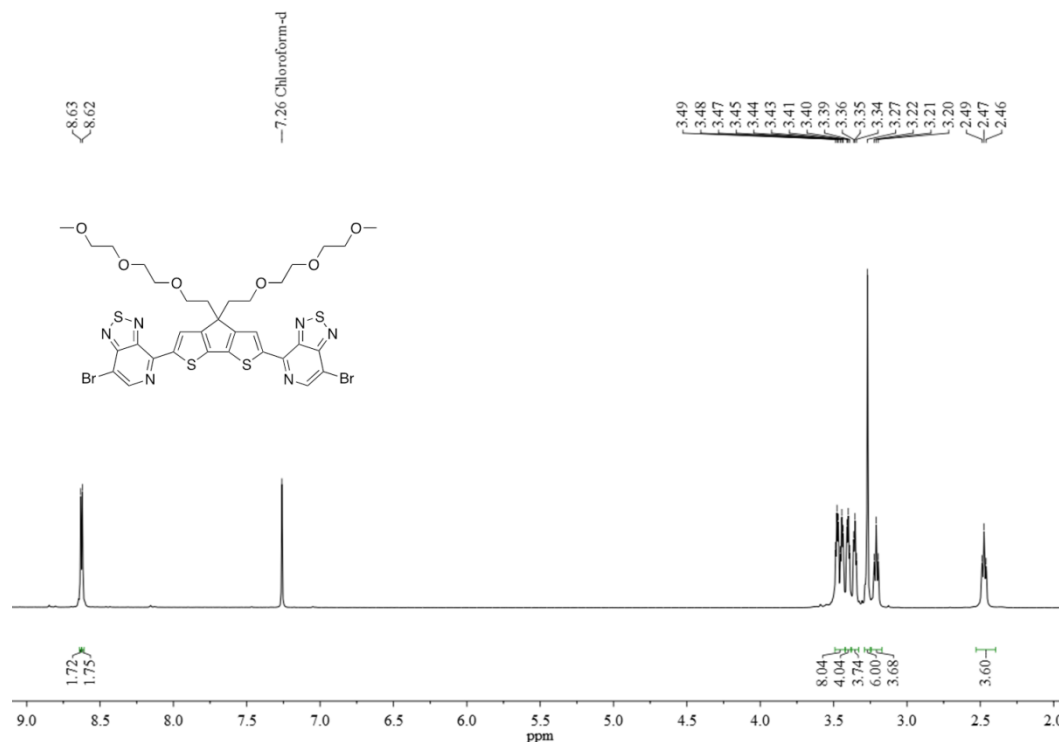
in DMSO and Argon was bubbled through the solution for 10 minutes before adding KOH (.629 g, 11.2 mmol), NaI (.02 g) and 1-bromo-2-(2-(2-methoxyethoxy)ethoxy)ethane (1.40 g, 6.17 mmol). The solution was stirred under argon overnight. Water was added and the mixture was extracted with diethyl ether. The combined organics were washed with brine, dried over MgSO₄ and filtered. The resulting oil was purified using silica gel column chromatography (diethyl ether/acetone) to yield 1.07 g (81%) of a slightly yellow oil. ¹H NMR (500 MHz, CDCl₃) δ = 7.15 (d, 2H), 6.96 (d, 2H), 3.62 – 3.52 (m, 4H), 3.52 – 3.46 (m, 8H), 3.36 – 3.30 (m, 10H), 3.01 (t, 4H), 2.25 (t, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 156.51, 136.55, 125.00, 121.73, 77.16, 71.92, 70.56, 70.48, 70.09, 67.64, 59.02, 49.24, 37.55. HRMS (ESI) *m/z*, calcd for C₂₃H₃₄O₆NaS₂ (M+Na)⁺: 493.1695; found: 493.1685.



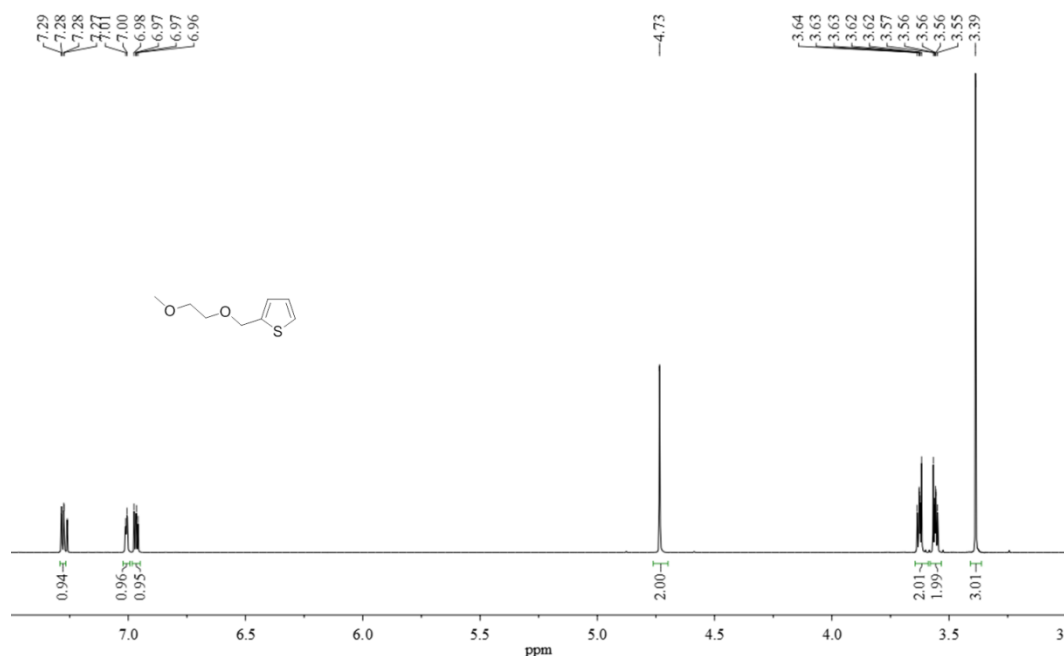
Synthesis of **4,4-Di[2-[2-(2-methoxyethoxy)ethoxy]ethyl]-2,6-bis(trimethylstannyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (6)**: Compound **5** (.500 g, 1.06 mmol) was dissolved in dry, degassed THF and cooled to -78 °C. n-Butyllithium (1.46 mL, 1.6 M) was then added and the solution was stirred at -78 °C for 90 minutes before injecting trimethyltin chloride (.529 g, 2.66 mmol). The reaction was stirred overnight, quenched with water and extracted with diethyl ether. The combined organics were washed with water, dried over MgSO₄ and filtered. The resulting light brown oil was used without further purification. Recovered yield: .78 g (92%). ¹H NMR (CDCl₃): δ 6.95 (s, 2H), 3.56 (m, 4H), 3.52 – 3.47 (m, 8H), 3.34 (s, 10H), 3.01 (t, 4H), 2.24 (t, 4H), 0.38 (s, 18H). ¹³C NMR (126 MHz, CDCl₃) δ 158.43, 142.41, 137.88, 129.17, 71.90, 70.60, 70.49, 70.05, 67.76, 59.01, 48.02, 37.79, -8.03.



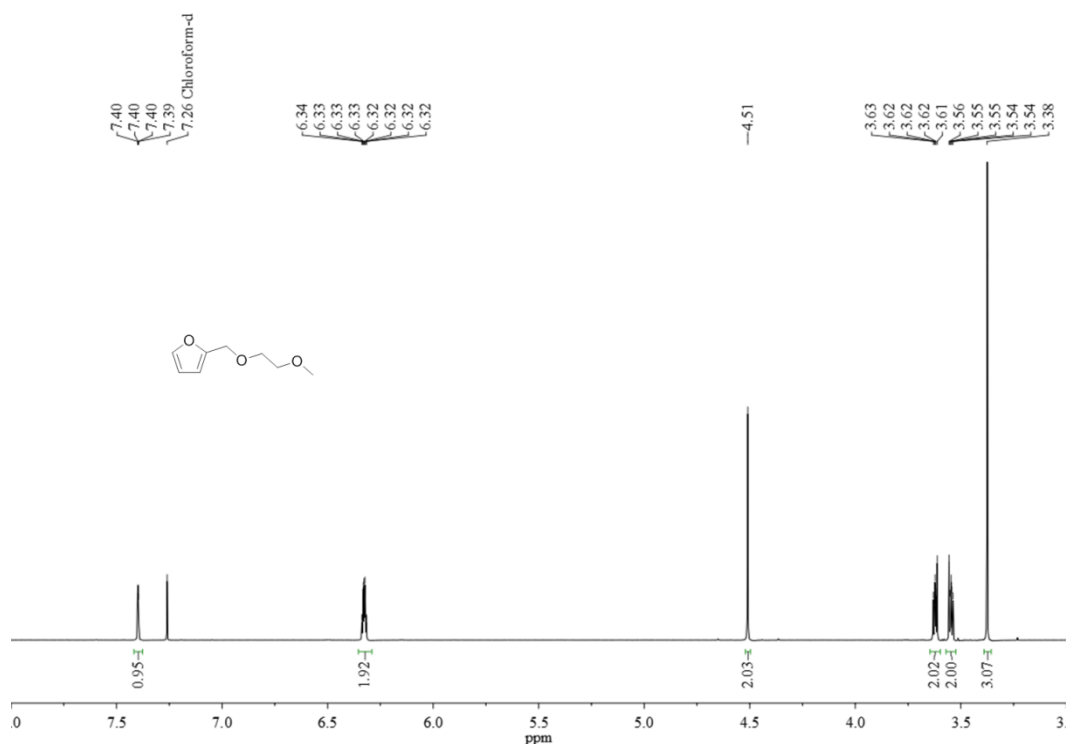
Synthesis of **4,4'-(4,4-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(7-bromo-[1,2,5]thiadiazolo[3,4-c]pyridine) (7)**: In a N₂ filled glove box a 20 mL microwave tube was charged with 4,7-dibromopyridal[2,1,3]thiadiazole (1.04 g, 3.53 mmol), Compound **6** (1.13 g, 1.42 mmol), Pd(PPh₃)₄, toluene (15 mL), and sealed with a Teflon® cap. Using a Biotage microwave reactor with stirring (900 rpm), the reaction mixture was heated to 80 °C for 5 minutes, 120 °C for 5 minutes, and 160 °C for 60 minutes. Upon cooling, the purple residue was passed through a short silica/K₂CO₃ (9:1) plug eluting with CHCl₃ (1% Et₃N) (~500 mL). All volatiles were removed *in vacuo* to give the crude product as a dark sticky solid. The material was then purified by flash chromatography using a diethyl ether/CHCl₃ (3% Et₃N) gradient. The collected solid was then slurried in hexanes, filtered and further purified by soxhlet extraction with hexanes. After drying under vacuum, 0.82 g (64%) of a dark solid was collected. **¹H NMR (500 MHz, CDCl₃)** δ 8.63 (s, 2H), 8.62 (s, 2H), 3.48 (t, *J* = 4.7 Hz, 4H), 3.44 (t, *J* = 4.9 Hz, 4H), 3.40 (t, *J* = 4.7 Hz, 4H), 3.35 (t, *J* = 4.9 Hz, 4H), 3.27 (s, 6H), 3.21 (t, *J* = 7.1 Hz, 4H), 2.47 (t, *J* = 7.2 Hz, 4H). **¹³C NMR (126 MHz, CDCl₃)** δ 160.57, 156.53, 147.89, 147.62, 146.10, 143.97, 142.75, 127.27, 107.87, 77.16, 71.97, 70.65, 70.59, 70.37, 67.75, 59.09, 50.79, 37.76. **LRMS (FD)** *m/z* = 898.



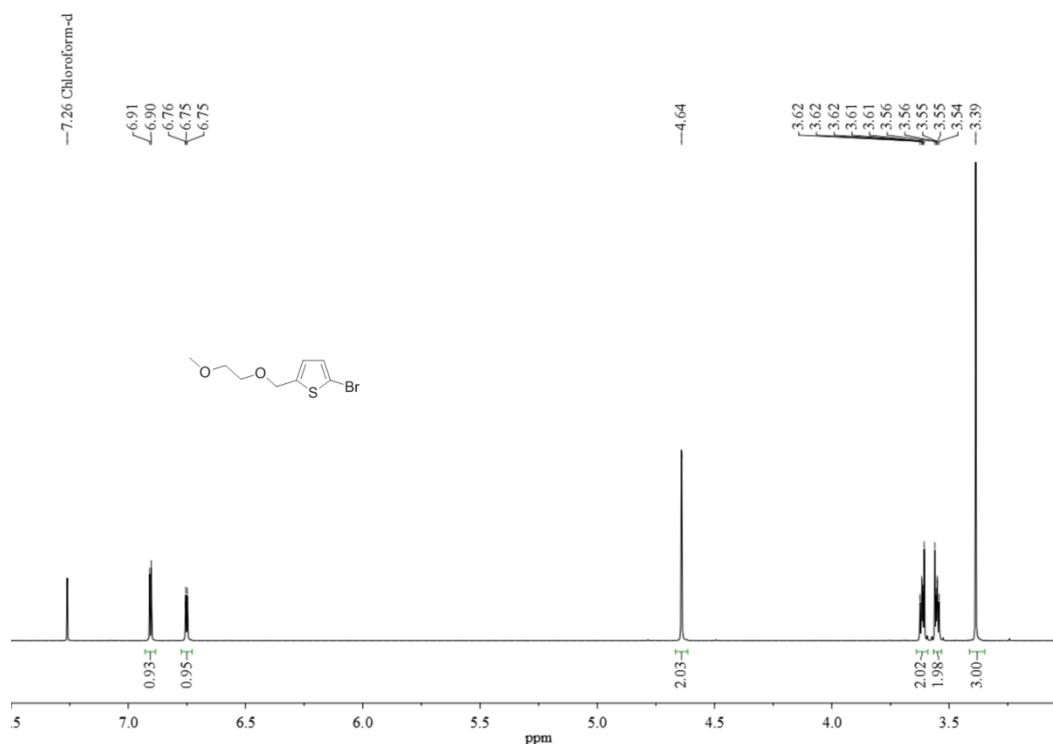
Synthesis of 2-((2-methoxyethoxy)methyl)thiophene (8): In a N₂ filled glove box a round bottom flask was charged with NaH (.420 g) and THF and cooled using an ice bath. A solution of thiophene-2-methanol (2.0 g, 17.5 mmol) in dry, degassed THF was added via cannula and the mixture was stirred for 30 minutes. To this a THF solution of 2-bromoethyl methyl ether (2.38 g, 17.3 mmol) was added via cannula and allowed to stir at room temperature overnight. The reaction was quenched with water and extracted with diethyl ether. Combined organics were washed with brine. The material was then purified by flash chromatography (hexanes/diethyl ether gradient) to obtain 1.75 g (58%) of a colorless liquid. ¹H NMR (500 MHz, Chloroform-d) δ 7.28 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.01 (dd, *J* = 3.3, 1.0 Hz, 1H), 6.97 (dd, *J* = 5.0, 3.4 Hz, 1H), 4.73 (s, 2H), 3.66 – 3.59 (m, 2H), 3.58 – 3.53 (m, 2H), 3.39 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 141.05, 126.75, 126.73, 125.98, 77.16, 72.07, 69.03, 67.82, 59.19.



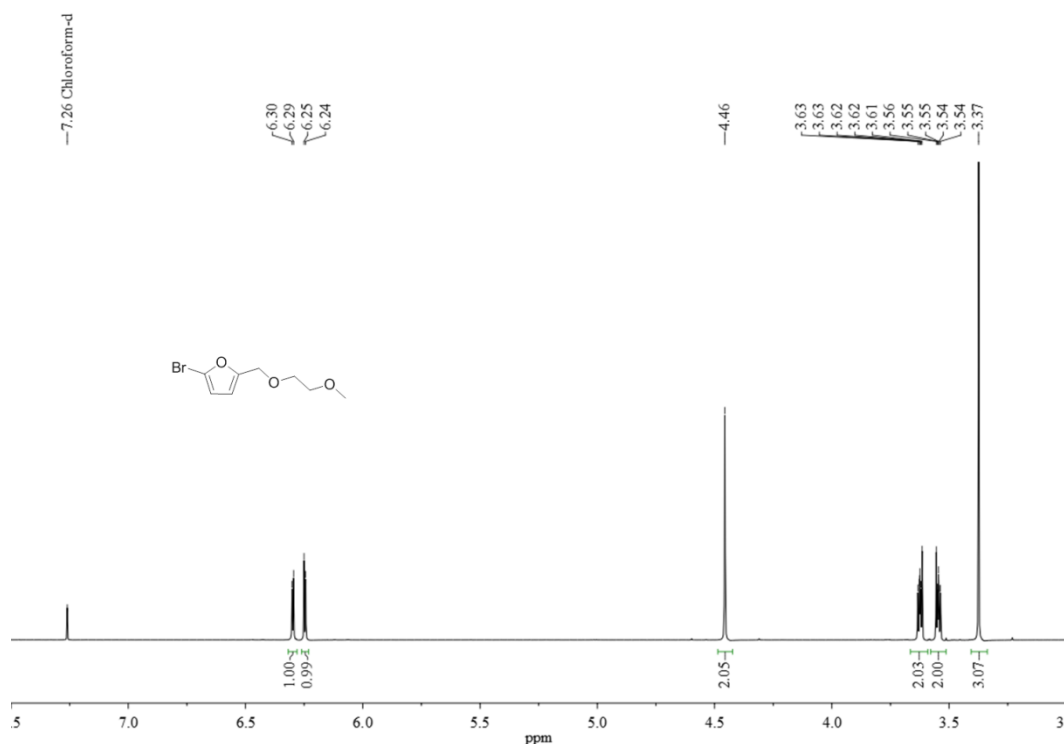
Synthesis of 2-((2-methoxyethoxy)methyl)furan (9): In a N₂ filled glove box a round bottom flask was charged with NaH (1.223 g, 0.051 mol) and THF and cooled using an ice bath. A solution of furfuryl alcohol (5.0 g, 0.051 mol) in dry, degassed THF was added via cannula and the mixture was stirred for 30 minutes. To this a THF solution of 2-bromoethyl methyl ether (7.08 g, 0.051 mol) was added via cannula and allowed to stir at room temperature overnight. The reaction was quenched with water and extracted with diethyl ether. Combined organics were washed with brine. The material was then purified by flash chromatography (hexanes/diethyl ether gradient) to obtain 3.16 g (40%) of a colorless liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.40 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.34 – 6.31 (m, 2H), 4.51 (s, 2H), 3.65 – 3.60 (m, 2H), 3.57 – 3.53 (m, 2H), 3.38 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 151.87, 142.89, 110.37, 109.52, 77.16, 72.01, 69.29, 65.24, 59.18. LRMS (FI): *m/z* = 156.08.



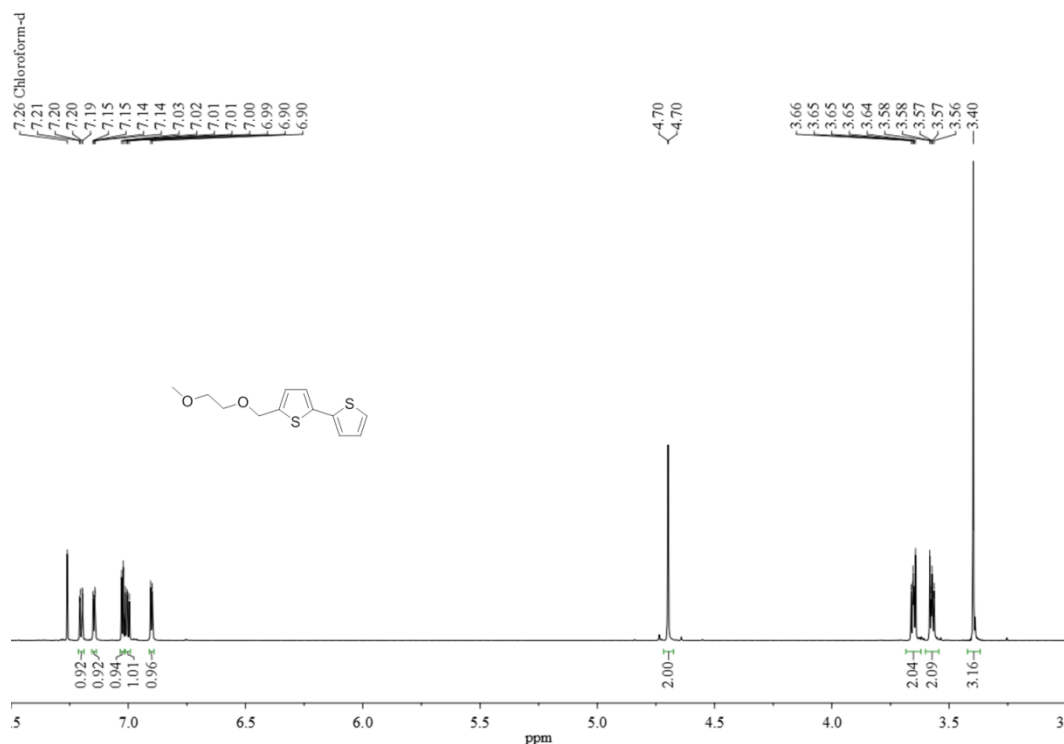
Synthesis of 2-bromo-5-((2-methoxyethoxy)methyl)thiophene (10): Compound **8** (.70 g, 4.06 mmol) was dissolved in dry, degassed DMF and cooled with an ice water bath in the dark. NBS (.796 g, 4.47 mmol) was added, the mixture was allowed to warm to room temperature and stirred for 2 hours. Water was added and the compound was extracted with diethyl ether. Combined organics were washed with brine. The material was then purified by flash chromatography (hexanes/diethyl ether gradient) to obtain .765 g (75%) of a colorless liquid. ¹H NMR (500 MHz, CDCl₃) δ 6.90 (d, *J* = 3.6 Hz, 1H), 6.75 (d, *J* = 3.6 Hz, 1H), 4.64 (d, *J* = 0.8 Hz, 2H), 3.64 – 3.59 (m, 2H), 3.57 – 3.50 (m, 2H), 3.39 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 142.99, 129.53, 126.92, 112.63, 77.16, 72.05, 69.17, 67.98, 59.25. HRMS (EI): *m/z*, calcd for C₈H₁₁O₂SBr (M)⁺: 249.9663; found: 249.9668.



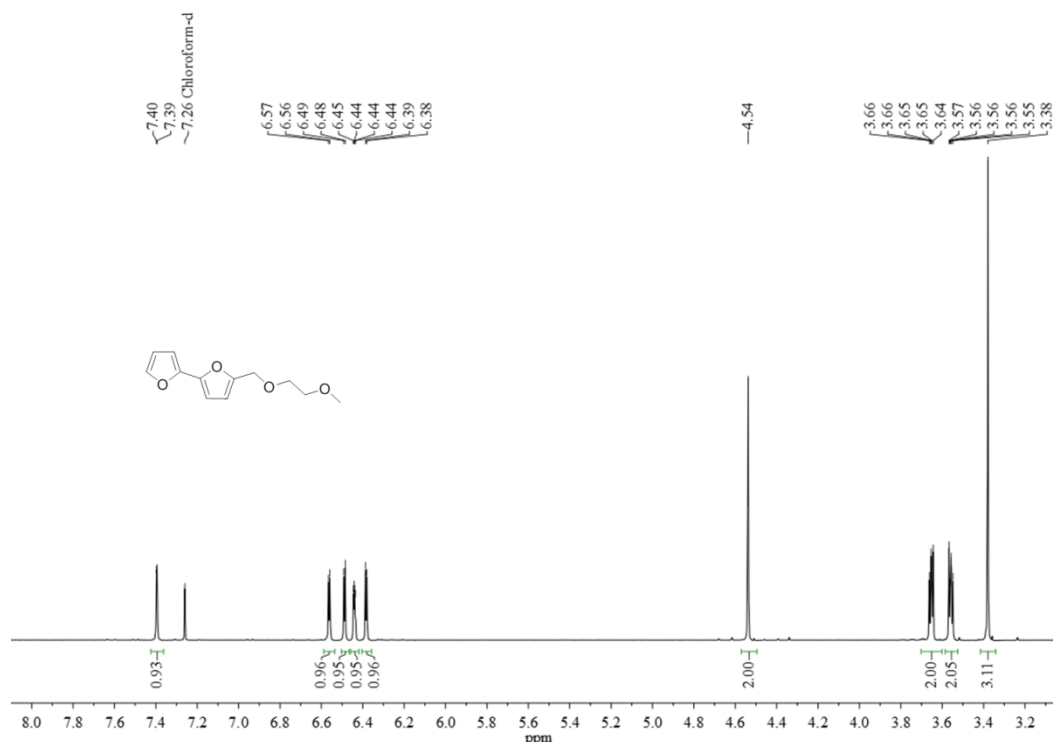
Synthesis of 2-bromo-5-((2-methoxyethoxy)methyl)furan (11): Compound **9** (1.69 g, 11 mmol) was dissolved in dry, degassed DMF and cooled with an ice water bath in the dark. NBS (2.118 g, 12 mmol) was added, the mixture was allowed to warm to room temperature and stirred for 2 hours. Water was added and the compound was extracted with diethyl ether. Combined organics were washed with brine. The material was then purified by flash chromatography (hexanes/diethyl ether gradient) to obtain 1.344 g (53%) of a colorless liquid. ¹H NMR (500 MHz, CDCl₃) δ 6.30 (d, *J* = 3.2 Hz, 1H), 6.25 (d, *J* = 3.4 Hz, 1H), 4.46 (s, 2H), 3.65 – 3.59 (m, 2H), 3.58 – 3.52 (m, 2H), 3.37 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.98, 122.18, 112.24, 112.10, 71.96, 69.44, 65.07, 59.19. HRMS (ESI): *m/z* calcd for C₈H₁₁O₃NaBr (M+Na)⁺: 256.9789; found: 256.979.



Synthesis of 5-((2-methoxyethoxy)methyl)-2,2'-bithiophene (12): In a N₂ filled glove box a 20 mL microwave tube was charged with Compound **10** (.764 g, 3.05 mmol), 2-(tributylstannyl)thiophene (1.14 g, 3.05 mmol), cat. Pd(PPh₃)₄, toluene (5 mL), and sealed with a Teflon® cap. Using a Biotage microwave reactor with stirring (900 rpm), the reaction mixture was heated to 80 °C for 5 minutes, 120 °C for 5 minutes, and 150 °C for 60 minutes. Upon cooling, the residue was passed through a short silica/K₂CO₃ (9:1) plug eluting with CHCl₃. All volatiles were removed *in vacuo* to give the crude product, which was then purified by flash chromatography using a hexanes/diethyl ether gradient. After drying under vacuum, 0.45 g (58%) of a colorless liquid was collected. **¹H NMR** (500 MHz, CDCl₃) δ 7.20 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.15 (dd, *J* = 3.5, 1.1 Hz, 1H), 7.02 (d, *J* = 3.7 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.90 (d, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 0.7 Hz, 2H), 3.71 – 3.61 (m, 2H), 3.61 – 3.52 (m, 2H), 3.40 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 140.07, 137.92, 137.44, 127.77, 127.26, 124.39, 123.69, 123.20, 71.95, 68.96, 67.84, 59.09. **HRMS (ESI):** calcd for C₁₂H₁₄O₂NaS₂ (M+Na)⁺: 277.0333; found: 277.0324.

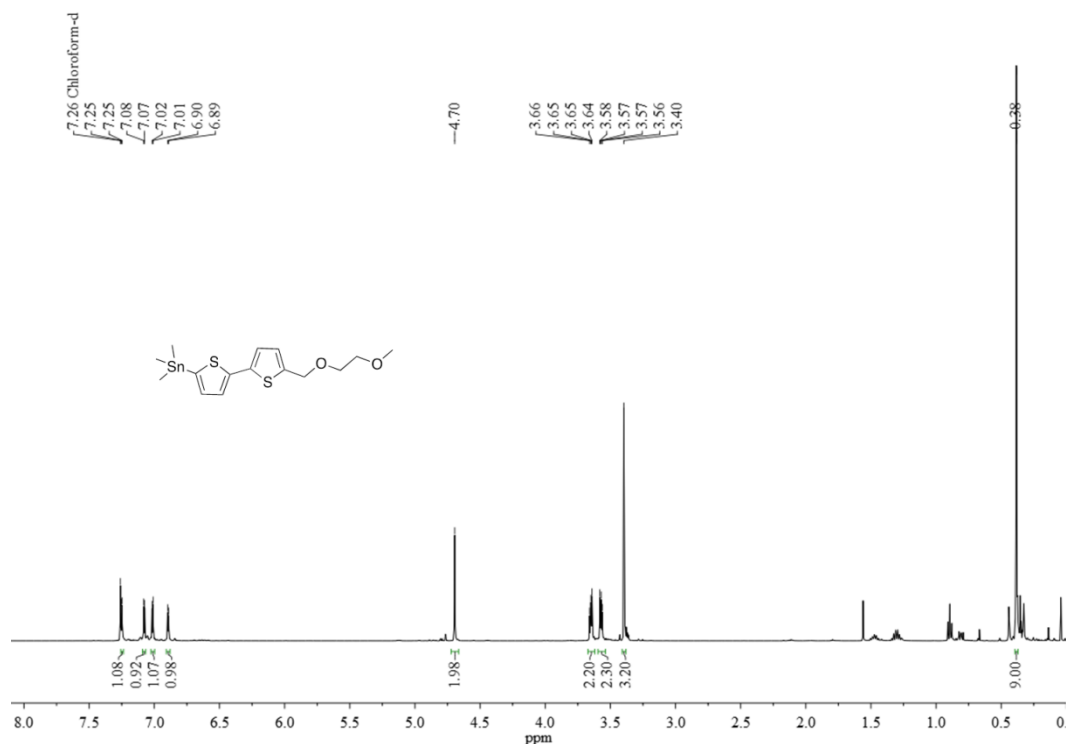


Synthesis of 5-((2-methoxyethoxy)methyl)-2,2'-bifuran (13): In a N₂ filled glove box a 20 mL microwave tube was charged with Compound **11** (2.73 g, 11.6 mmol), 2-(tributylstannyl)furan (4.97 g, 13.9 mmol), cat. Pd(PPh₃)₄, toluene (10 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 85 °C for 48 hr. Upon cooling, the residue was passed through a short silica/K₂CO₃ (9:1) plug eluting with CHCl₃. All volatiles were removed *in vacuo* to give the crude product, which was then purified by flash chromatography using a hexanes/diethyl ether gradient. After drying under vacuum, 1.7 g (66%) of a colorless liquid was collected. **¹H NMR** (500 MHz, CDCl₃) δ 7.40 (d, *J* = 1.6 Hz, 1H), 6.56 (d, *J* = 3.4 Hz, 1H), 6.49 (d, *J* = 3.4 Hz, 1H), 6.44 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.38 (d, *J* = 3.3 Hz, 1H), 4.54 (s, 2H), 3.70 – 3.62 (m, 2H), 3.60 – 3.51 (m, 2H), 3.38 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 151.18, 146.89, 146.59, 141.94, 111.48, 111.40, 105.85, 105.50, 72.00, 69.29, 65.24, 59.18. **HRMS (EI):** *m/z* calcd for C₁₂H₁₄O₄ (M)⁺: 222.0892; found: 222.0906.



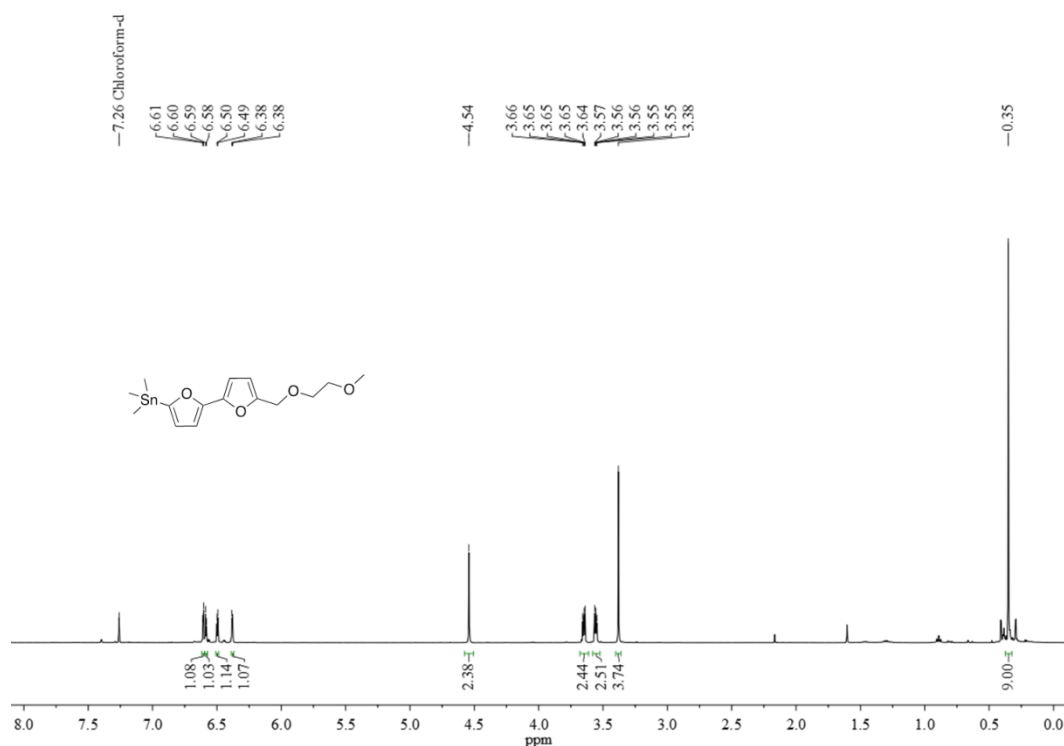
Synthesis of (5'-((2-methoxyethoxy)methyl)-[2,2'-bithiophen]-5-yl)trimethylstannane (14):

Compound **12** (.45 g, 1.77 mmol) was dissolved in dry, degassed THF and cooled to -78 °C. n-Butyllithium (1.6 mL, 1.6 M) was then added and the solution was stirred at -78 °C for 30 minutes, allowed to warm to room temperature and stirred for 60 minutes, and finally cooled back to -78 °C for 30 minutes before injecting trimethyltin chloride (.705 g, 3.53 mmol). The reaction was stirred overnight, quenched with water and extracted with diethyl ether. The combined organics were washed with water, dried over MgSO₄ and filtered. The resulting light brown oil was used without further purification. Recovered yield: .68 g (92%). ¹H NMR (CDCl₃): δ 7.28 (d, *J* = 3.3 Hz, 1H), 7.10 (d, *J* = 3.3 Hz, 1H), 7.04 (d, *J* = 3.6 Hz, 1H), 6.92 (d, *J* = 3.6 Hz, 1H), 4.72 (s, 2H), 3.70 – 3.64 (m, 2H), 3.62 – 3.57 (m, 2H), 3.42 (s, 3H), 0.41 (s, 9H). ¹³C{¹H} NMR (CDCl₃): δ 143.05, 139.87, 138.21, 137.62, 135.97, 127.45, 125.08, 123.14, 77.16, 72.09, 69.05, 68.00, 59.22, -8.08.

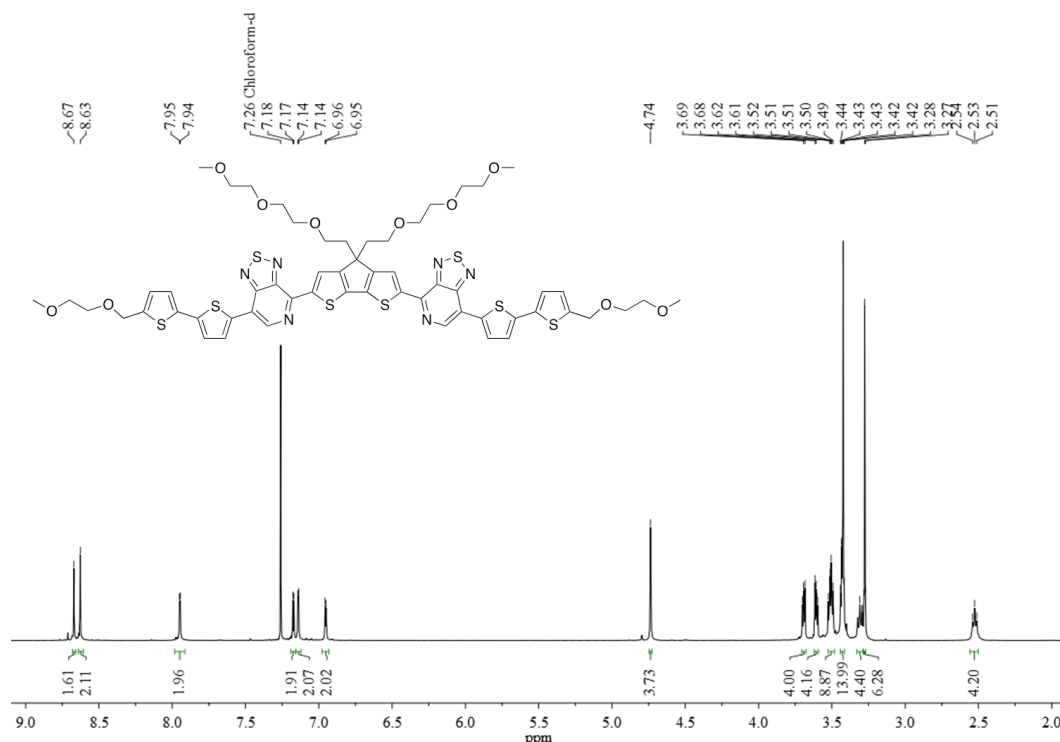


Synthesis of (5'-((2-methoxyethoxy)methyl)-[2,2'-bifuran]-5-yl)trimethylstannane (15):

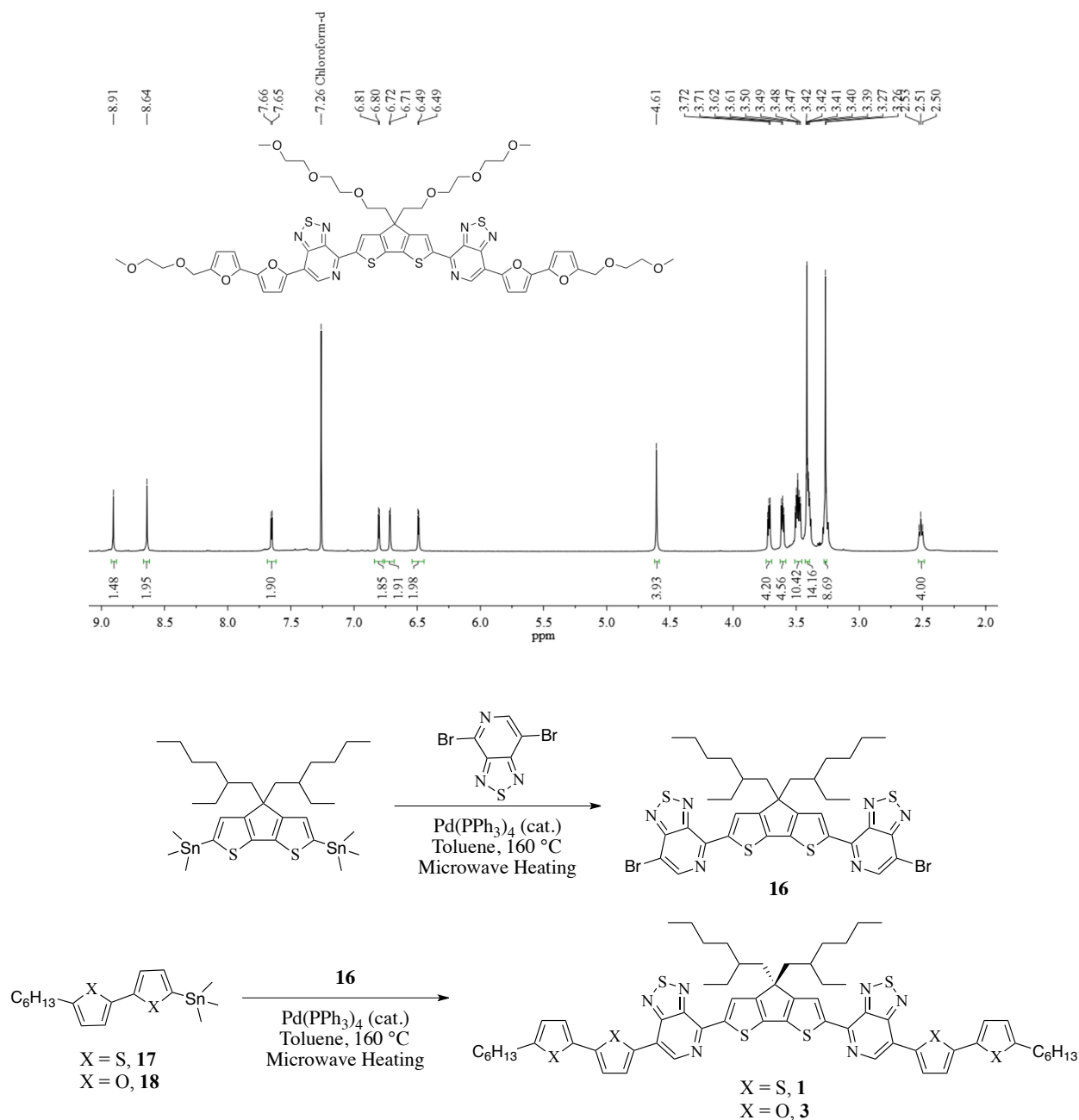
Compound **13** (1.6 g, 7.23 mmol) was dissolved in dry, degassed THF and cooled to -78 °C. *n*-Butyllithium (6.77 mL, 1.6 M) was then added and the solution was stirred at -78 °C for 30 minutes, allowed to warm to room temperature and stirred for 60 minutes, and finally cooled back to -78 °C for 30 minutes before injecting trimethyltin chloride (2.88 g, 14.45 mmol). The reaction was stirred overnight, quenched with water and extracted with diethyl ether. The combined organics were washed with water, dried over MgSO₄ and filtered. The resulting light brown/red oil was used without further purification. Recovered yield: 2.54 g (91%). ¹H NMR (CDCl₃) δ 6.61 (d, *J* = 3.2 Hz, 1H), 6.59 (d, *J* = 3.2 Hz, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 6.38 (d, *J* = 3.3 Hz, 1H), 4.54 (s, 2H), 3.67 – 3.63 (m, 2H), 3.58 – 3.53 (m, 2H), 3.38 (s, 3H), 0.35 (s, 9H). ¹³C{¹H} NMR (CDCl₃): δ 161.00, 150.91, 147.52, 141.94, 122.67, 111.42, 105.69, 105.61, 77.16, 72.01, 69.19, 65.29, 59.18, -8.91.



Synthesis of **4,4'-(4,4-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(7-(5'-((2-methoxyethoxy)methyl)-[2,2'-bithiophen]-5-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine) (2)**: In a N₂ filled glove box a 5 mL microwave tube was charged with compound **7** (.150 g, .167 mmol), compound **14** (.143 g, .342 mmol), cat. Pd(PPh₃)₄, toluene (3 mL), and sealed with a Teflon® cap. Using a Biotage microwave reactor with stirring (900 rpm), the reaction mixture was heated to 80 °C for 5 minutes, 120 °C for 5 minutes, and 150 °C for 60 minutes. Upon cooling, the residue was passed through a short silica/K₂CO₃ (9:1) plug eluting with CHCl₃ (3% NEt₃). All volatiles were removed *in vacuo* to give the crude product, which was then purified by flash chromatography using a hexanes/CHCl₃ (3% NEt₃) gradient. After drying under vacuum, 0.09 g (43%) of a dark solid was collected. ¹H NMR (500 MHz, CDCl₃) δ 8.67 (s, 2H), 8.63 (s, 2H), 7.95 (d, 2H), 7.17 (d, 2H), 7.14 (d, 2H), 6.95 (d, 2H), 4.74 (s, 4H), 3.71 – 3.68 (m, 4H), 3.62 – 3.59 (m, 4H), 3.53 – 3.49 (m, 8H), 3.43 (m, 14H), 3.30 (t, 4H), 3.28 (s, 6H), 2.53 (t, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 160.48, 154.74, 147.96, 146.12, 144.90, 142.47, 141.04, 140.68, 139.13, 137.64, 135.67, 128.54, 127.58, 126.36, 124.66, 123.91, 119.75, 77.16, 72.13, 72.00, 70.70, 70.62, 70.41, 69.26, 68.03, 67.94, 59.28, 59.11, 50.65, 37.72. LRMS (FD): *m/z*: 1244.



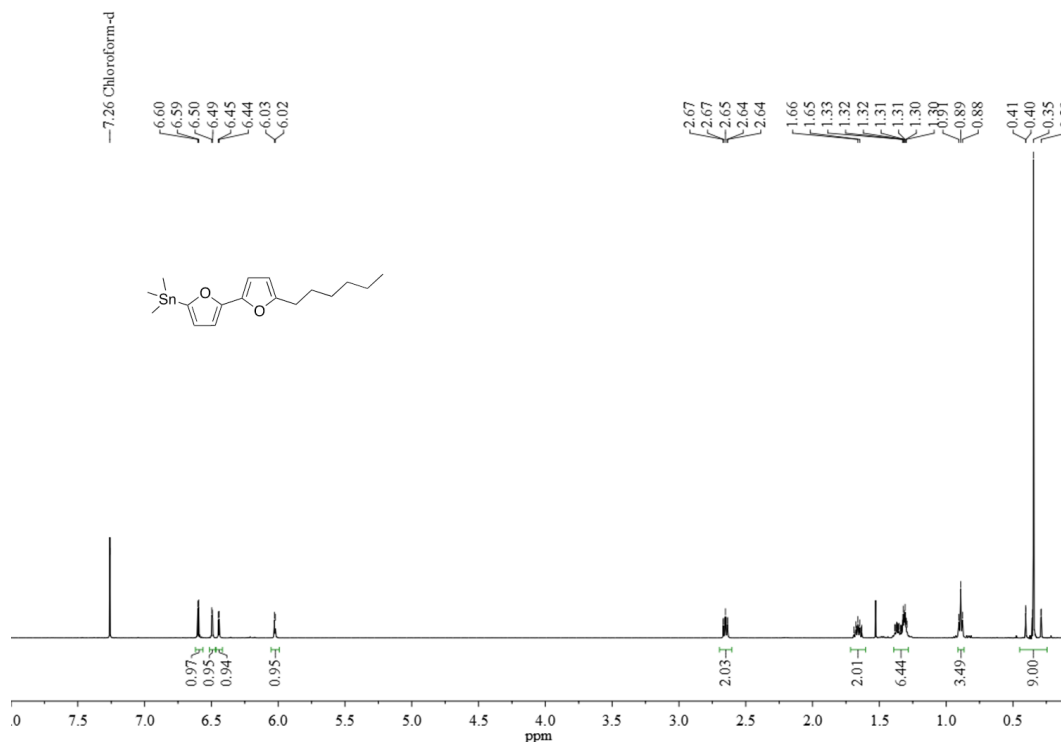
Synthesis of 4,4'-(4,4-bis(2-(2-methoxyethoxy)ethoxy)ethyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diylbis(7-(5'-((2-methoxyethoxy)methyl)-[2,2'-bifuran]-5-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine) (4): In a N₂ filled glove box a 5 mL microwave tube was charged with compound **7** (.100 g, .11 mmol), compound **15** (.094 g, .24 mmol), cat. Pd(PPh₃)₄, toluene (3 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 85 °C for 48 hr. Upon cooling, the residue was passed through a short silica/K₂CO₃ (9:1) plug eluting with CHCl₃ (3% NEt₃). All volatiles were removed *in vacuo* to give the crude product, which was then purified by flash chromatography using a hexanes/CHCl₃ (3% NEt₃) gradient. After drying under vacuum, 0.075 g (58%) of a dark solid was collected. ^1H NMR (500 MHz, CDCl₃) δ 8.91 (s, 2H), 8.64 (s, 2H), 7.65 (d, J = 3.6 Hz, 2H), 6.80 (d, J = 3.5 Hz, 2H), 6.72 (d, J = 3.2 Hz, 2H), 6.49 (d, J = 3.3 Hz, 2H), 4.61 (s, 4H), 3.76 – 3.68 (m, 4H), 3.63 – 3.58 (m, 4H), 3.51 – 3.46 (m, 10H), 3.43 – 3.39 (m, 14H), 3.28 – 3.26 (m, 8H), 2.51 (t, J = 7.2 Hz, 4H). ^{13}C NMR (126 MHz, CDCl₃) δ 160.38, 153.61, 152.08, 147.99, 147.89, 146.98, 146.46, 146.00, 145.04, 142.43, 139.20, 126.34, 115.71, 115.14, 111.79, 108.55, 107.27, 77.16, 72.06, 71.98, 70.68, 70.60, 70.40, 69.48, 67.85, 65.33, 59.09, 37.86. LRMS (FD): m/z : 1180.



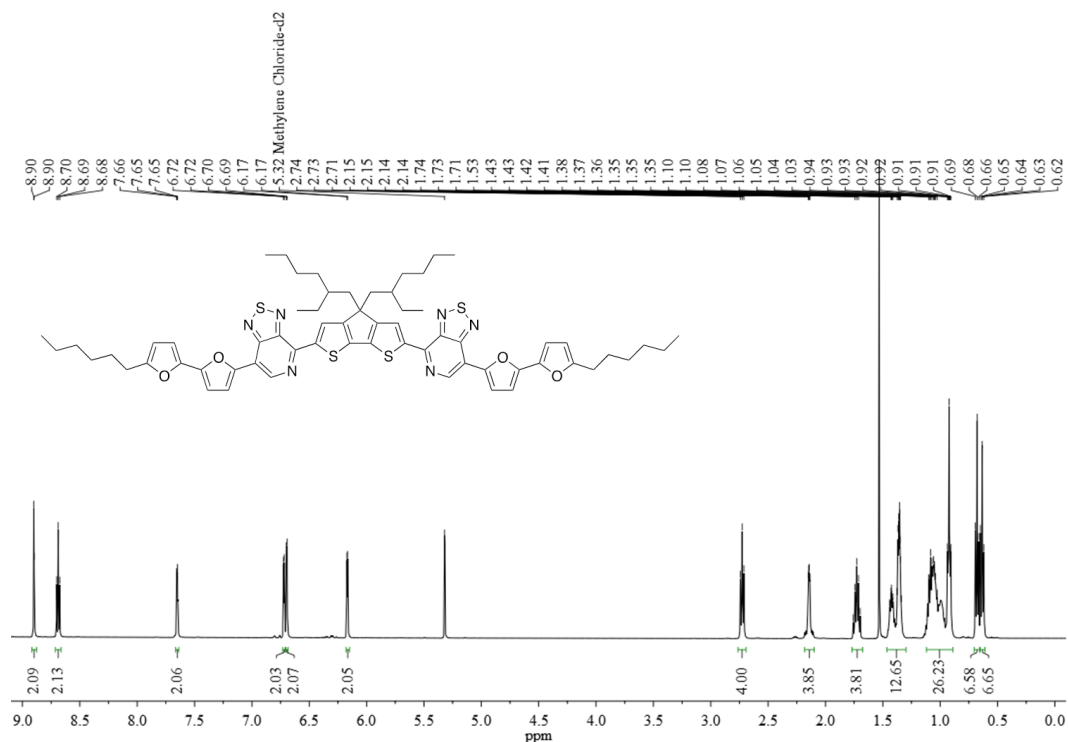
Scheme S2. Synthetic entry to Compounds **1** and **3**. Compounds **1**, **16** and **17** were prepared according to reference 2.

Synthesis of (5'-hexyl-[2,2'-bifuran]-5-yl)trimethylstannane (18**):** 5-hexyl-2,2'-bifuran (.39 g, 1.78 mmol) was dissolved in dry, degassed THF and cooled to -78 °C. n-Butyllithium (1.45 mL, 1.6 M) was then added and the solution was stirred at -78 °C for 30 minutes, allowed to warm to room temperature and stirred for 60 minutes, and finally cooled back to -78 °C for 30 minutes before injecting trimethyltin chloride (.57 g, 2.86 mmol). The reaction was stirred overnight, quenched with water and extracted with diethyl ether. The combined organics were washed with water, dried over MgSO₄ and filtered. The resulting light yellow liquid used without further purification. Recovered yield: .625 g (92%). ¹H NMR (500 MHz, CDCl₃) δ 6.60 (d, 1H), 6.49

(d, 1H), 6.44 (d, 1H), 6.03 (d, 1H), 2.69 – 2.58 (m, 2H), 1.66 (p, 2H), 1.39 – 1.28 (m, 6H), 0.91 – 0.87 (m, 3H), 0.35 (s, 9H).



Synthesis of **4,4'-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(7-(5'-hexyl-[2,2'-bifuran]-5-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine) (3)**: In a N₂ filled glove box a 20 mL microwave tube was charged with compound **16** (.268 g, .323 mmol), compound **18** (.258 g, .677 mmol), cat. Pd(PPh₃)₄, toluene (10 mL), and sealed with a Teflon® cap. Using a Biotage microwave reactor with stirring (900 rpm), the reaction mixture was heated to 80 °C for 5 minutes, 120 °C for 5 minutes, and 150 °C for 60 minutes. Upon cooling, the residue was passed through a short silica/K₂CO₃ (9:1) plug eluting with CHCl₃ (3% NEt₃). All volatiles were removed *in vacuo* to give the crude product, which was then purified by flash chromatography using a hexanes/CHCl₃ (3% NEt₃) gradient. After drying under vacuum, .202 g (57%) of a dark solid was collected. **¹H NMR** (500 MHz, CD₂Cl₂) δ 8.90 (s, 2H), 8.69 (t, 2H), 7.70 – 7.58 (m, 2H), 6.72 (d, 2H), 6.70 (d, 2H), 6.17 (d, 2H), 2.73 (t, 4H), 2.14 (m, 4H), 1.73 (p, 4H), 1.50 – 1.29 (m, 12H), 1.21 – 0.85 (m, 24H), 0.68 (t, 6H), 0.63 (t, 6H). **¹³C NMR** (126 MHz, CD₂Cl₂) δ 162.31, 158.11, 154.07, 148.59, 148.02, 147.93, 146.57, 144.96, 144.90, 143.22, 139.39, 127.60, 116.08, 115.35, 107.97, 107.60, 54.99, 54.43, 54.22, 54.00, 54.00, 53.79, 53.77, 53.57, 43.65, 36.11, 34.90, 32.17, 29.47, 29.16, 28.71, 28.61, 28.23, 23.42, 23.19, 14.43, 14.38, 11.14. **LRMS (FD)**: *m/z*: 1104.



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- [2] G. C. Welch, R. C. Bakus, S. J. Teat, G. C. Bazan, *Journal of the American Chemical Society* **2013**, 135, 2298-2305.