

## Supplementary Information

### Mapping the Transmission Function of Single-Molecule Junctions

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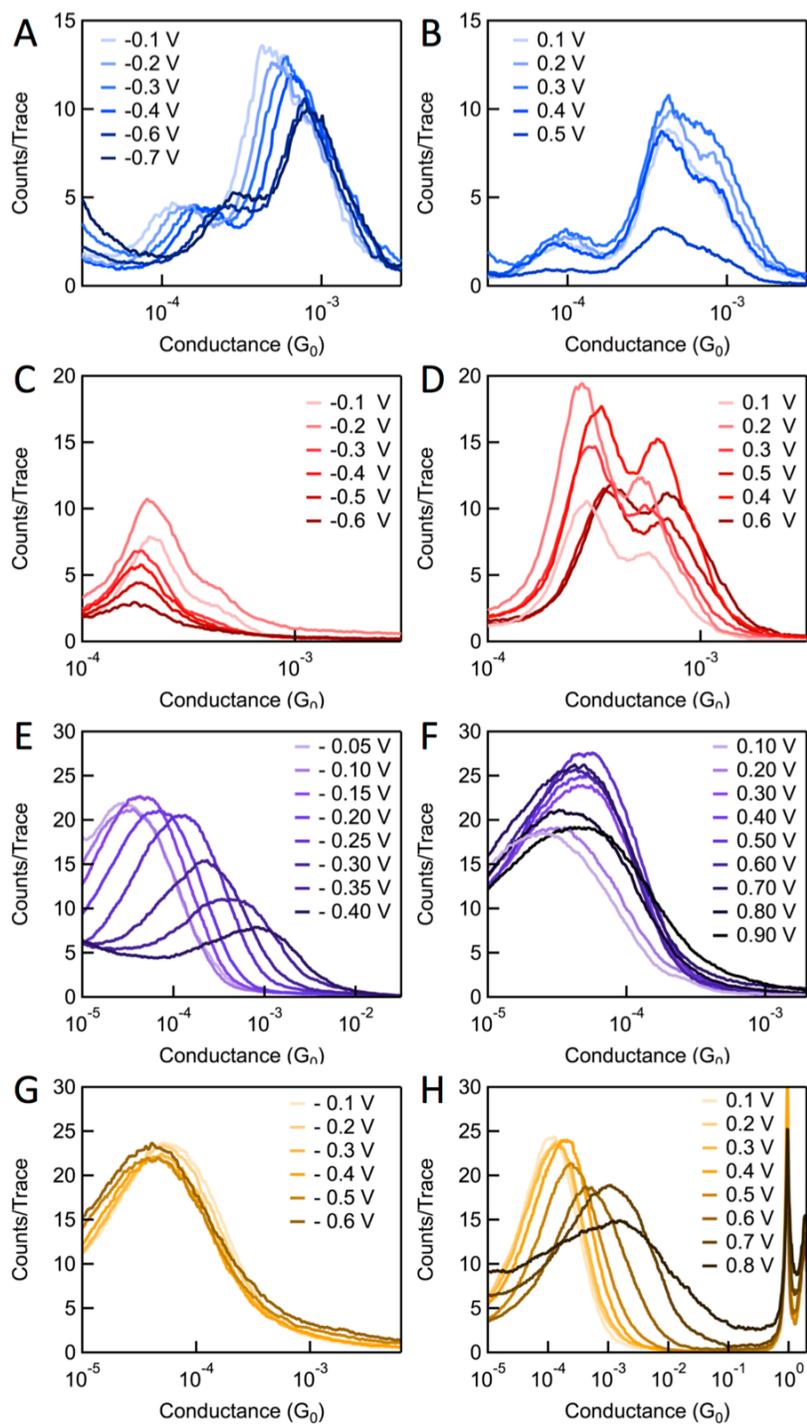
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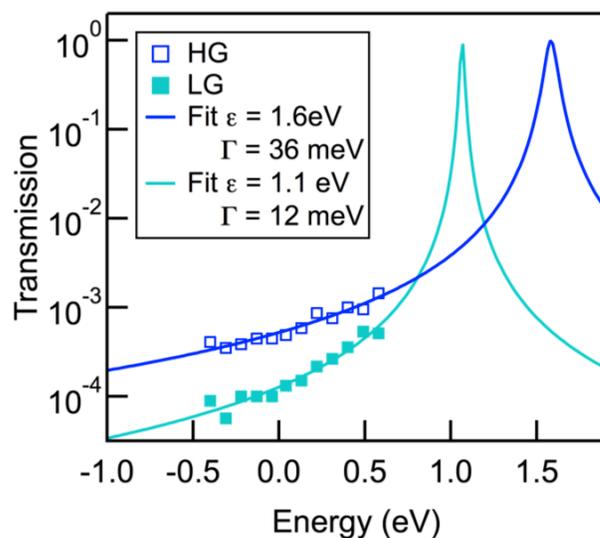
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## 1. Additional Data



*SI Figure S1: Logarithmically binned conductance histograms at all biases studied for: molecule 1 – A and B, molecule – C and D, molecule 3 – E and F, molecule 4 – G and H.*



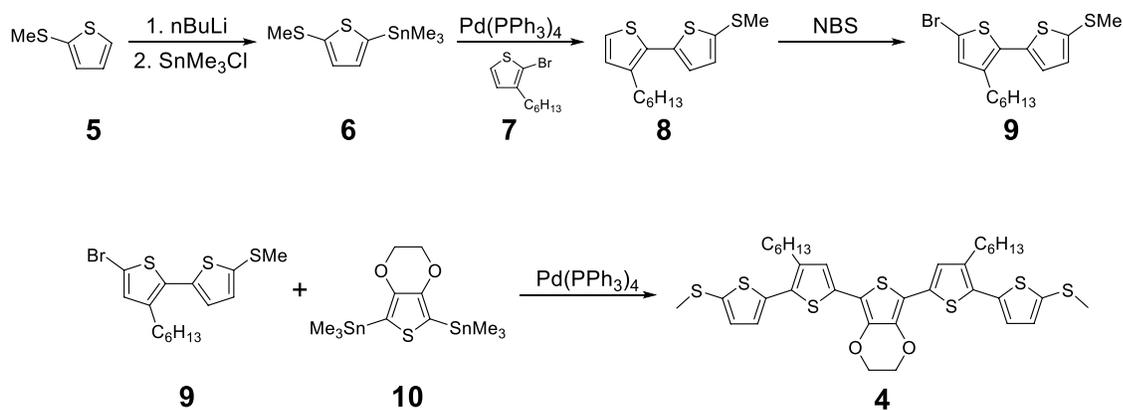
*SI Figure S2: Lorentzian fit to transmission data for Molecule 1:*

## 2. General Experimental Details

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR were recorded on either a Bruker Avance III 400 (400MHz) or Avance III 500 (500MHz) spectrometer, in chloroform solution (residual solvent peak at  $\delta = 7.26\text{ppm}$ ) unless stated otherwise. Mass spectra were obtained at the Columbia University mass spectrometry facility using a XEVO G2-XS Waters<sup>®</sup> equipped with a QTOF detector with multiple inlet and ionization capabilities including electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and atmospheric solids analysis probe (ASAP). The base peaks were usually obtained as  $[\text{M}]^+$  or  $[\text{M}+\text{H}]^+$  ions.

## 3. Synthetic Details

4,4'-bipyridine (molecule **1**), 4,4''-*p*-diaminoterphenyl (molecule **2**), 2-(methylthio)thiophene (**5**) and 2-bromo-3-hexylthiophene (**7**) were purchased from Sigma and used without further purification, as was 3,4-ethylenedioxythiophene which was converted to compound **10** by a previously reported method.<sup>1</sup> The synthesis of molecule **3** has been reported elsewhere.<sup>2</sup> Scheme 1 shows the synthetic route to molecule **4**. All palladium coupling and lithiation reactions were done in oven-dried glassware using dry solvents from a solvent still.



**Scheme 1.** Synthesis of molecule **4**.

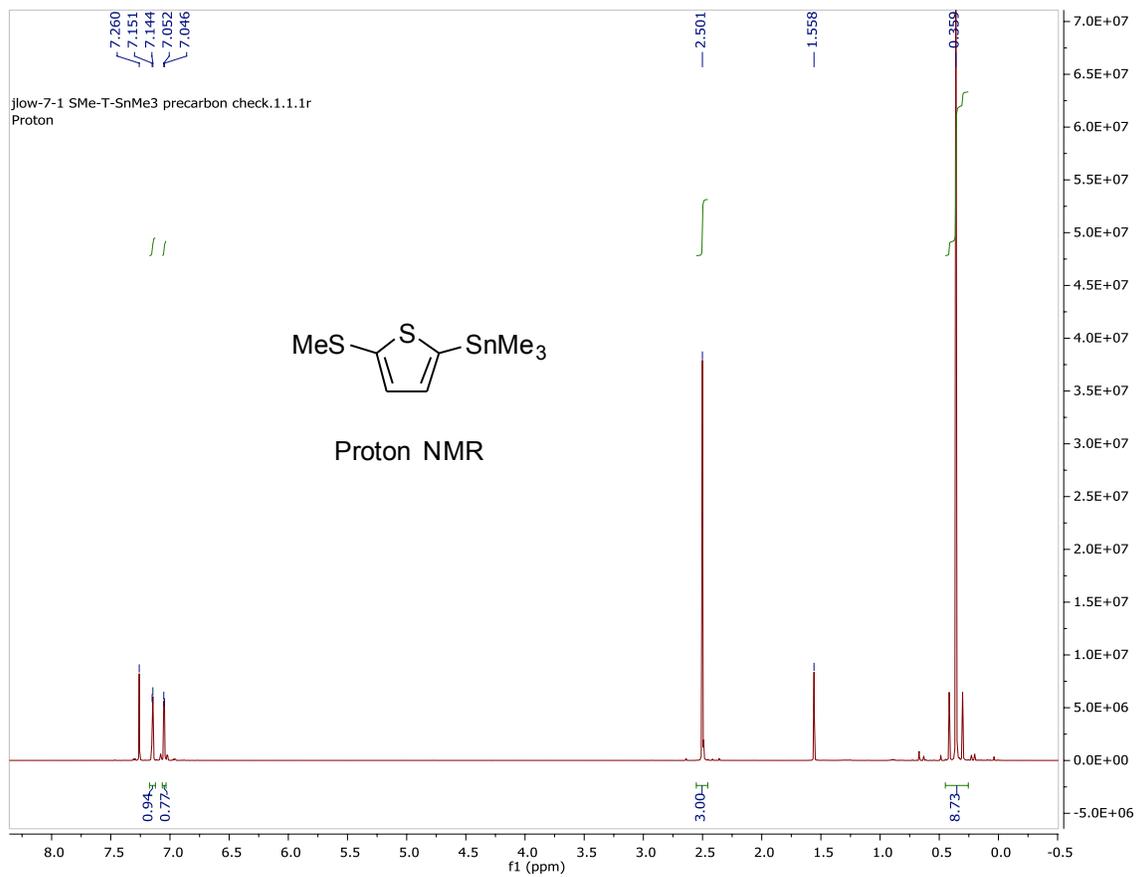
*2-methylthio-5-trimethylstannylthiophene*, (**6**). 2-(methylthio)thiophene (**5**) (8.14g, 62.5mmol, 1eq) was placed in a schlenk flask which was evacuated and refilled with nitrogen. Dry THF (30mL) was added and the solution was cooled to  $-78^{\circ}\text{C}$ . n-Butyl lithium (2.5M in hexanes, 26.3mL, 65.7mmol, 1.05eq) was added dropwise and the solution was stirred for 1h at  $-78^{\circ}\text{C}$ , then half an hour at  $0^{\circ}\text{C}$ . The solution was cooled again to  $-78^{\circ}\text{C}$  and trimethyltin chloride (13.1g, 65.7mmol, 1.05eq) was added in one portion and the reaction was allowed to warm to room temperature overnight. 5mL of water was then added to quench the reaction and the volatile solvents were removed. The residue was dissolved in DCM, washed with water and dried over  $\text{MgSO}_4$ . The solvent was removed and the product was obtained as a dark brown oil (17.8g, 97%). The crude product was used without further purification.  $^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ ),  $\delta$  7.15 (d,  $J = 3.2$  Hz, 1H), 7.05 (d,  $J = 3.2$  Hz, 1H), 2.50 (s, 3H) 0.36 (s, 9H).  $^{13}\text{C-NMR}$  (500MHz,  $\text{CDCl}_3$ )  $\delta$  142.37, 141.18, 135.49, 131.37, 22.00, -8.22. HRMS (ASAP+) Calculated for  $\text{C}_8\text{H}_{14}\text{S}_2\text{Sn}$ : 293.9559; Observed: 293.9557.

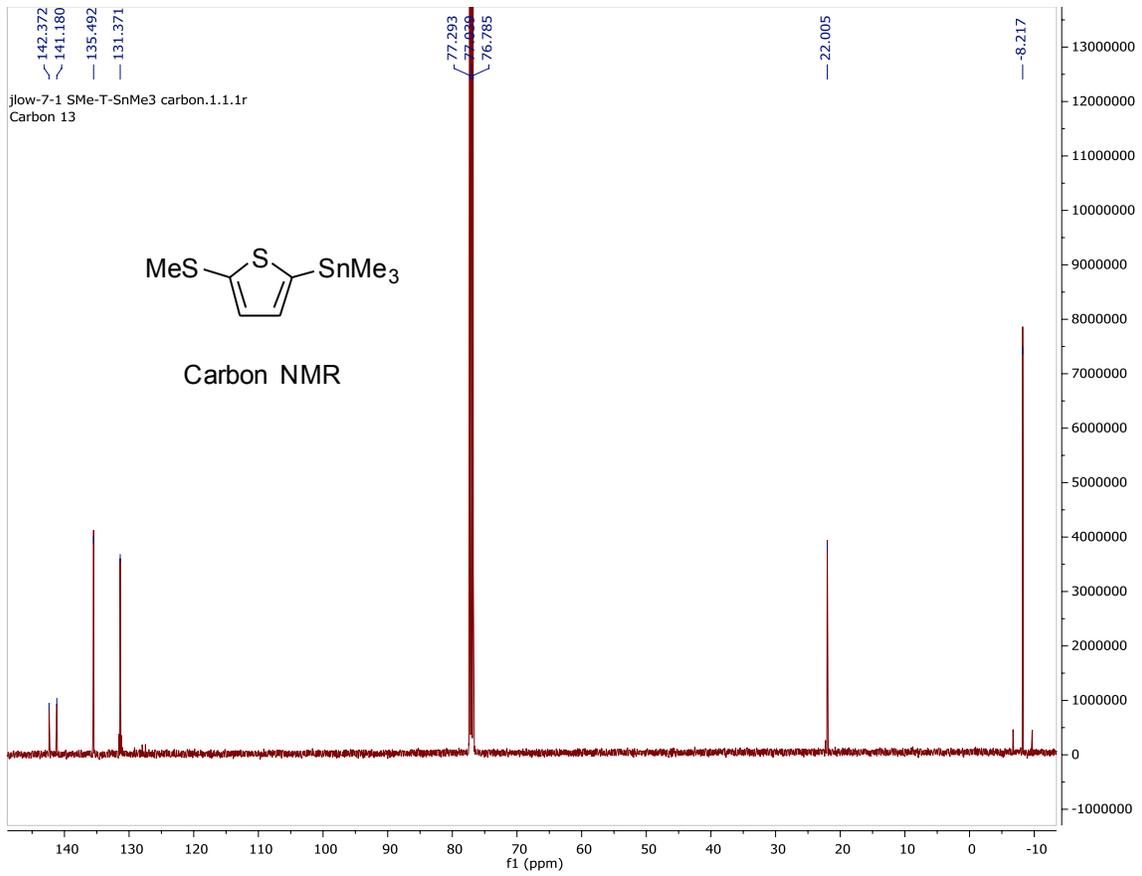
*3-hexyl-5'-(methylthio)-2,2'-bithiophene*, (**8**). Compound **6** (1.19g, 4.05mmol, 1eq), compound **7** (1.00g, 4.05mmol, 1eq) and  $\text{Pd}(\text{PPh}_3)_4$  (233mg, 5% eq) were placed in a sealed reaction vial which was evacuated and refilled with nitrogen. Dry toluene (15mL) was added and the reaction was stirred at  $110^{\circ}\text{C}$  for 24h. The solvent was removed and the residue was dissolved in DCM, washed with water and dried over  $\text{MgSO}_4$ . After removal of solvent, the crude product was purified by column chromatography (silica gel, hexanes as eluent). The product was isolated as a yellow oil (0.970g, 81%).  $^1\text{H-NMR}$  (400MHz,  $\text{CDCl}_3$ ),  $\delta$  7.16 (d,  $J = 5.2$  Hz, 1H), 7.02 (d,  $J = 3.7$  Hz, 1H), 6.94 (d,  $J = 3.7$  Hz, 1H), 6.92 (d,  $J = 5.2$  Hz, 1H), 2.73 (t,  $J = 7.6$  Hz, 2H), 2.52 (s, 3H), 1.62 (m, 2H), 1.40 – 1.26 (m, 6H), 0.88 (t, 3H).  $^{13}\text{C-NMR}$  (500MHz,  $\text{CDCl}_3$ )  $\delta$  139.84, 138.65, 136.81, 131.44, 130.28, 130.00, 126.05, 123.89, 31.68, 30.71, 29.22, 29.19, 22.64, 22.21, 14.13. HRMS (ASAP+) Calculated for  $\text{C}_{15}\text{H}_{21}\text{S}_3$ : 297.0805; Observed: 297.0808.

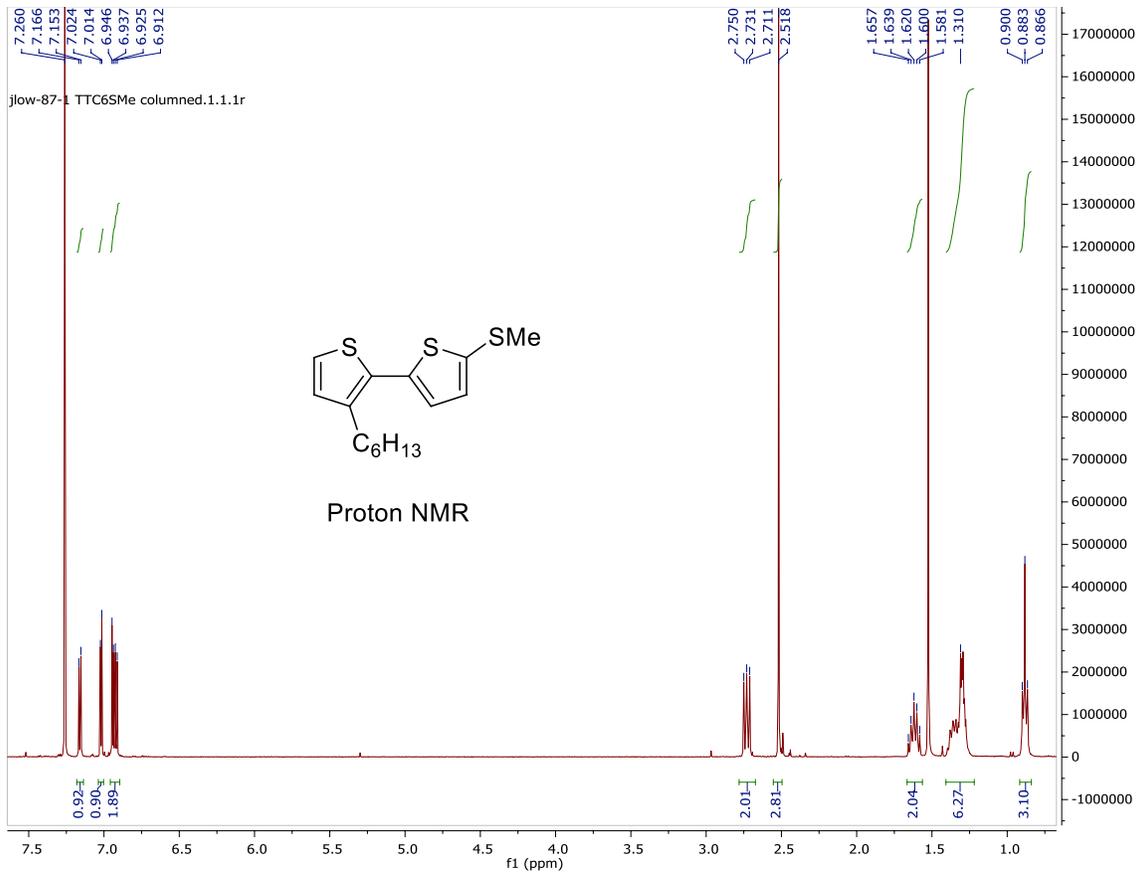
*5-bromo-3-hexyl-5'-(methylthio)-2,2'-bithiophene*, (**9**). Compound **8** (536mg, 1.81mmol, 1eq) was dissolved in a mixture of chloroform (10mL) and acetic acid (10mL), then protected from light. *N*-bromosuccinimide (338mg, 1.89mmol, 1.05eq) was added in one portion and the reaction was stirred for 1h at room temperature. Water was then added to quench the reaction. The mixture was extracted thrice with chloroform. The organic layer was washed with sodium bicarbonate and water, then dried over MgSO<sub>4</sub>. After removal of solvent, the crude product was purified by column chromatography (silica gel, hexanes as eluent). The product was isolated as a yellow oil (537mg, 79%). <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>), δ 7.00 (d, *J* = 3.7 Hz, 1H), 6.89 (d, *J* = 3.7 Hz, 1H), 6.88 (s, 1H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.52 (s, 3H), 1.58 (p, *J* = 7.4 Hz, 2H), 1.40 – 1.26 (m, 6H), 0.88 (m, 3H). <sup>13</sup>C-NMR (500MHz, CDCl<sub>3</sub>) δ 140.45, 137.67, 137.04, 132.60, 131.73, 131.21, 126.49, 110.62, 31.62, 30.56, 29.12, 29.09, 22.60, 22.06, 14.11. HRMS (ESI+) Calculated for C<sub>15</sub>H<sub>19</sub>S<sub>3</sub>Br: 373.9832; Observed: 373.9832.

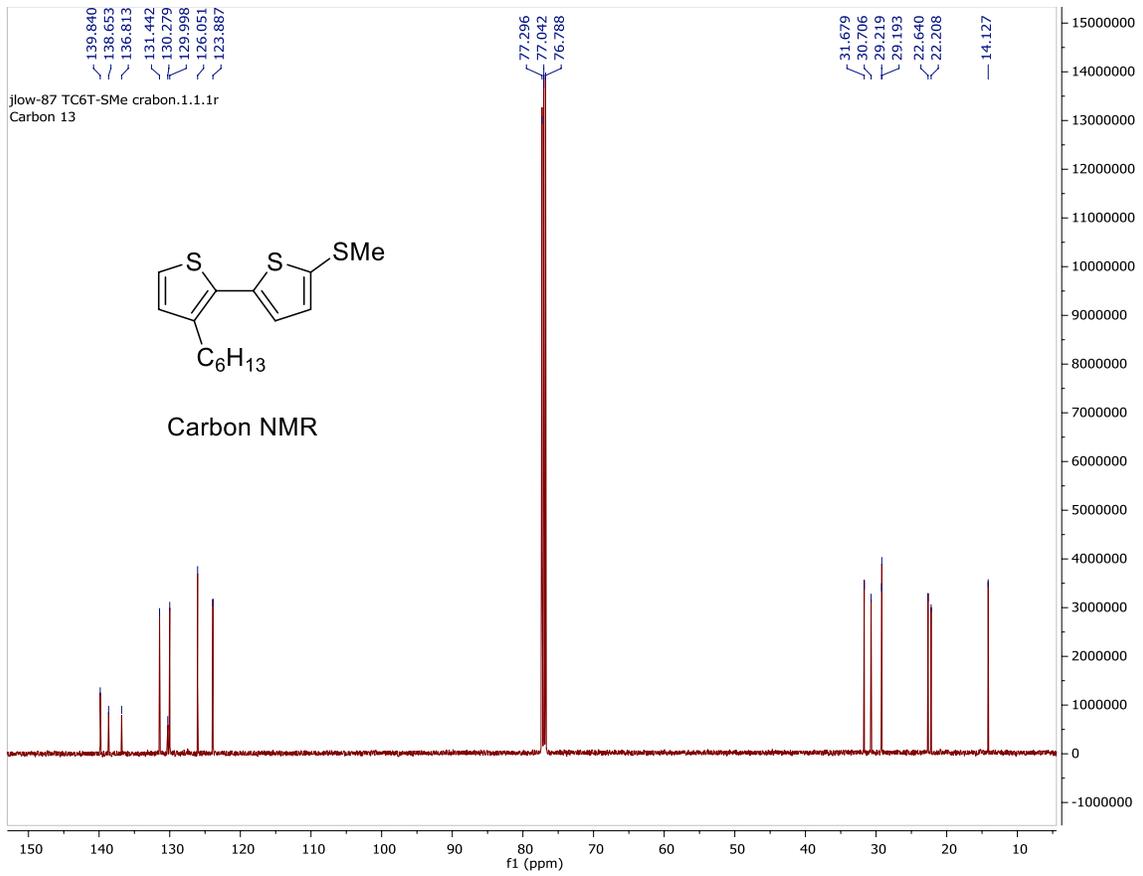
Molecule **4**. Compound **9** (245mg, 0.653mmol, 2.1eq), compound **10** (145mg, 0.311mmol, 1eq) and Pd(PPh<sub>3</sub>)<sub>4</sub> (17mg, 5% eq) were placed in a sealed reaction vial which was evacuated and refilled with nitrogen. Dry chlorobenzene (5mL) was added and the reaction was stirred at 120°C for 24h. The solvent was removed and the residue was dissolved in DCM, washed with water and dried over MgSO<sub>4</sub>. After removal of solvent, the crude product was purified by column chromatography (silica gel, 20% DCM in hexanes as eluent). The product was then recrystallized from acetonitrile (with a small amount of DCM) to yield an orange crystalline solid (83mg, 37%). <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>, 320K), δ 7.04 (s, 2H), 7.02 (d, *J* = 3.7 Hz, 2H), 6.96 (d, *J* = 3.7 Hz, 2H), 4.39 (s, 4H), 2.73 (t, *J* = 6.2 Hz, 4H), 2.52 (s, 6H), 1.66 (m, 4H), 1.43 – 1.29 (m, 12H), 0.90 (t, 6H). <sup>13</sup>C-NMR (500MHz, CDCl<sub>3</sub>) δ 139.92, 138.59, 137.77, 136.66, 132.34, 131.48, 129.08, 125.78, 125.58, 109.54, 65.01, 31.67, 30.51, 29.37, 29.24, 22.63, 22.19, 14.11. HRMS (ASAP+) Calculated for C<sub>36</sub>H<sub>43</sub>O<sub>2</sub>S<sub>7</sub>: 731.1308; Observed: 731.1304. Note: The <sup>1</sup>H-NMR spectrum at 300K in chloroform showed broad, unresolved peaks in the aromatic region. These became sharp when the sample was heated to 320K. <sup>13</sup>C-NMR was performed at room temperature.

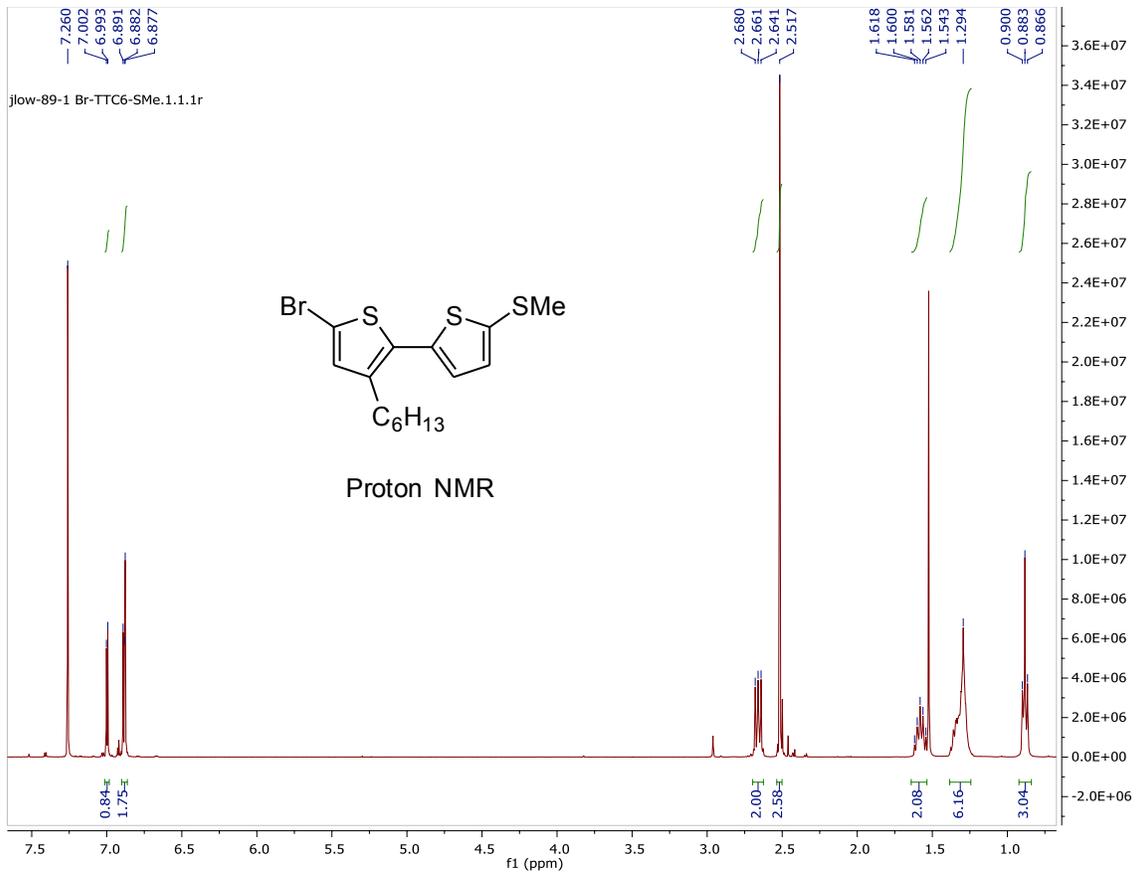
## 4. NMR Spectra

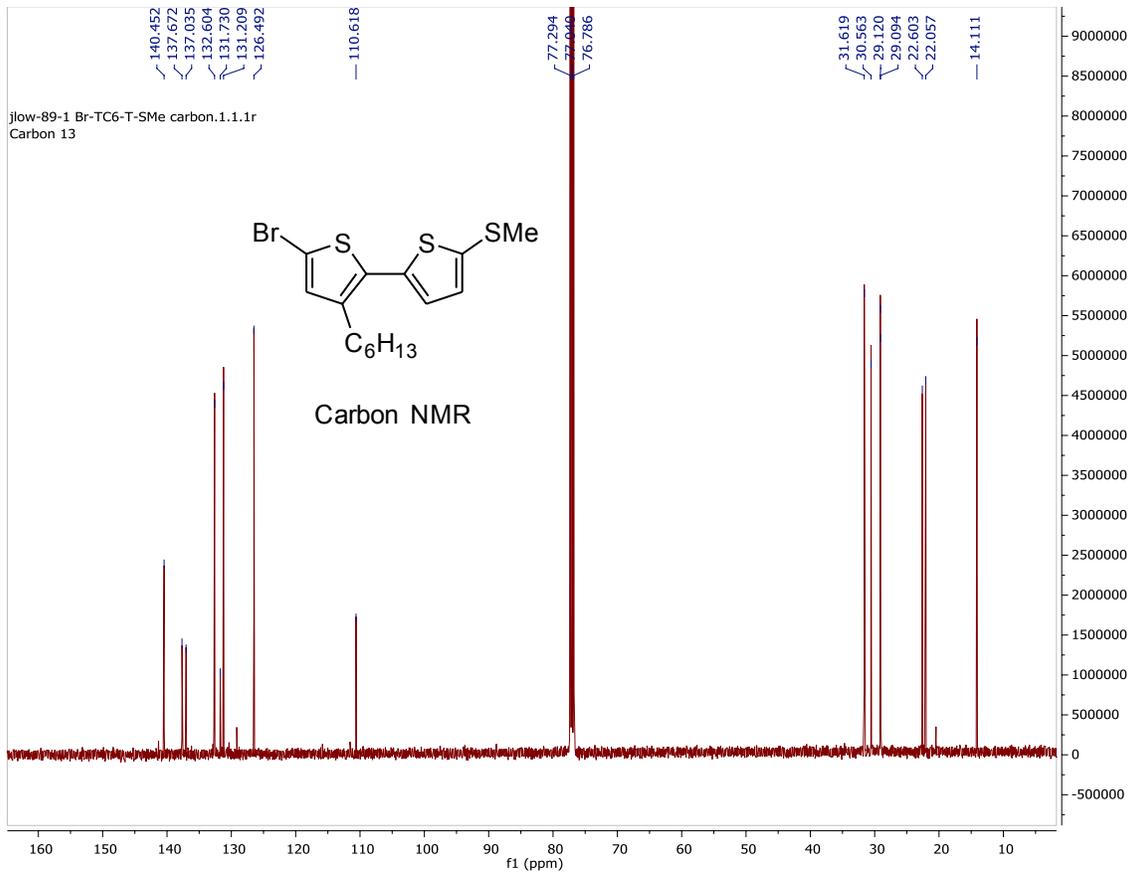


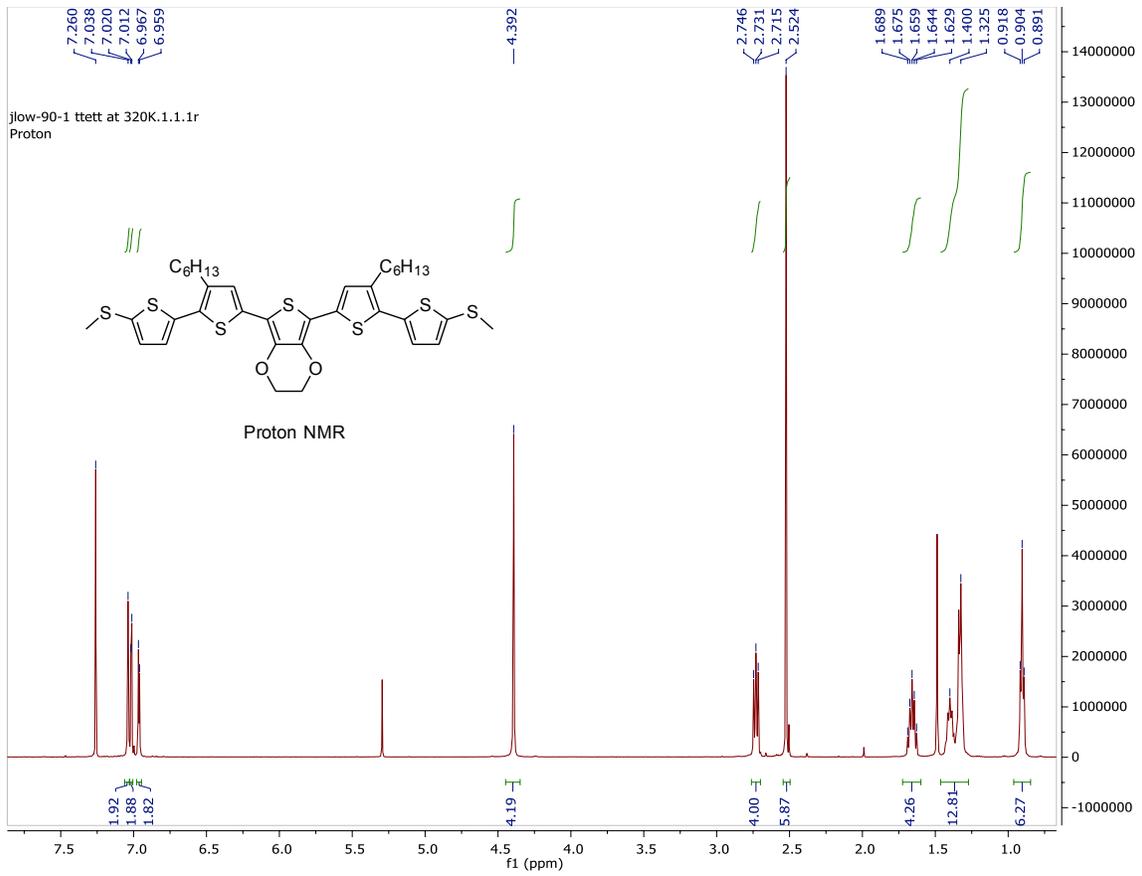


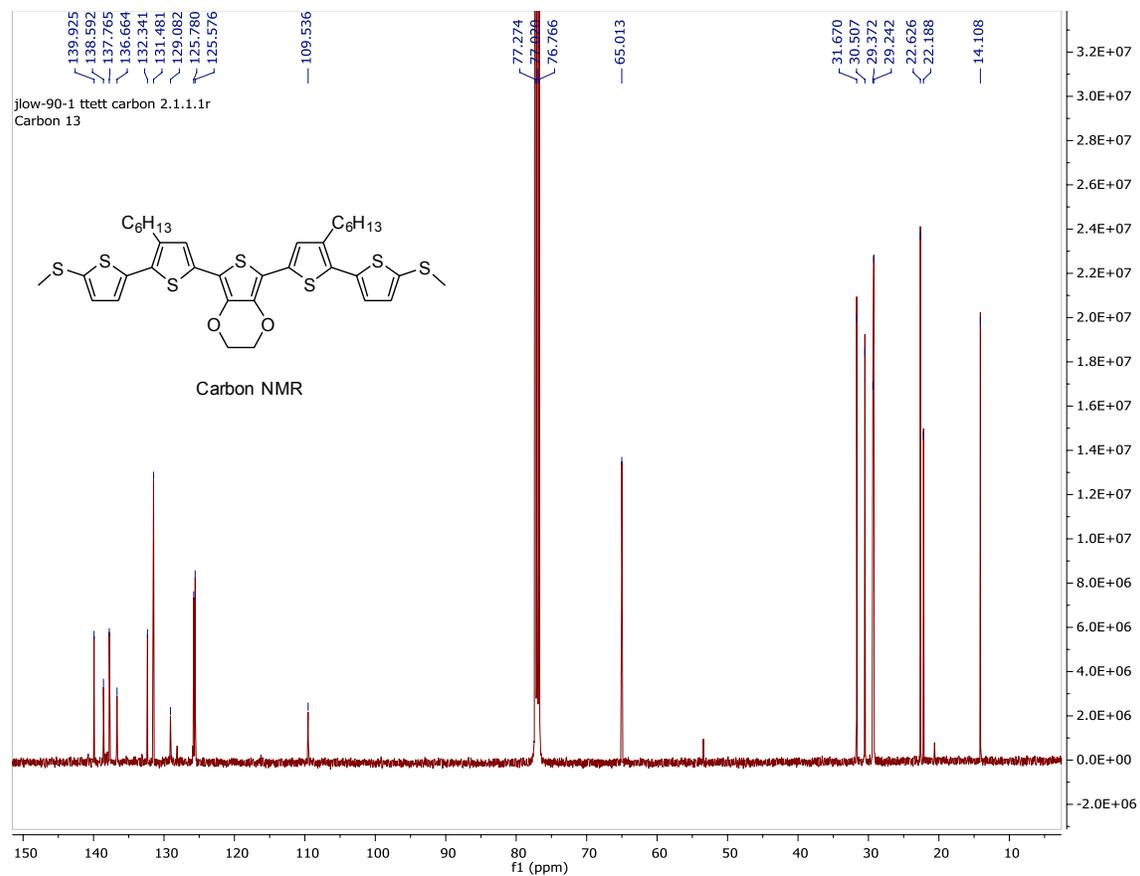












## 5. References

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- (2) Dell, E. J.; Capozzi, B.; Xia, J.; Venkataraman, L.; Campos, L. M. *Nat. Chem.* **2015**, *7*, 209.