Supporting Information

Polycyclic Aromatics with Flanking Thiophenes: Tuning Energy Level and Band Gap of Conjugated Polymers for Bulk Heterojunction Photovoltaics

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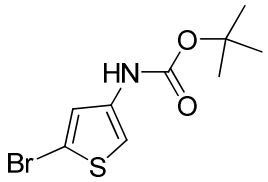
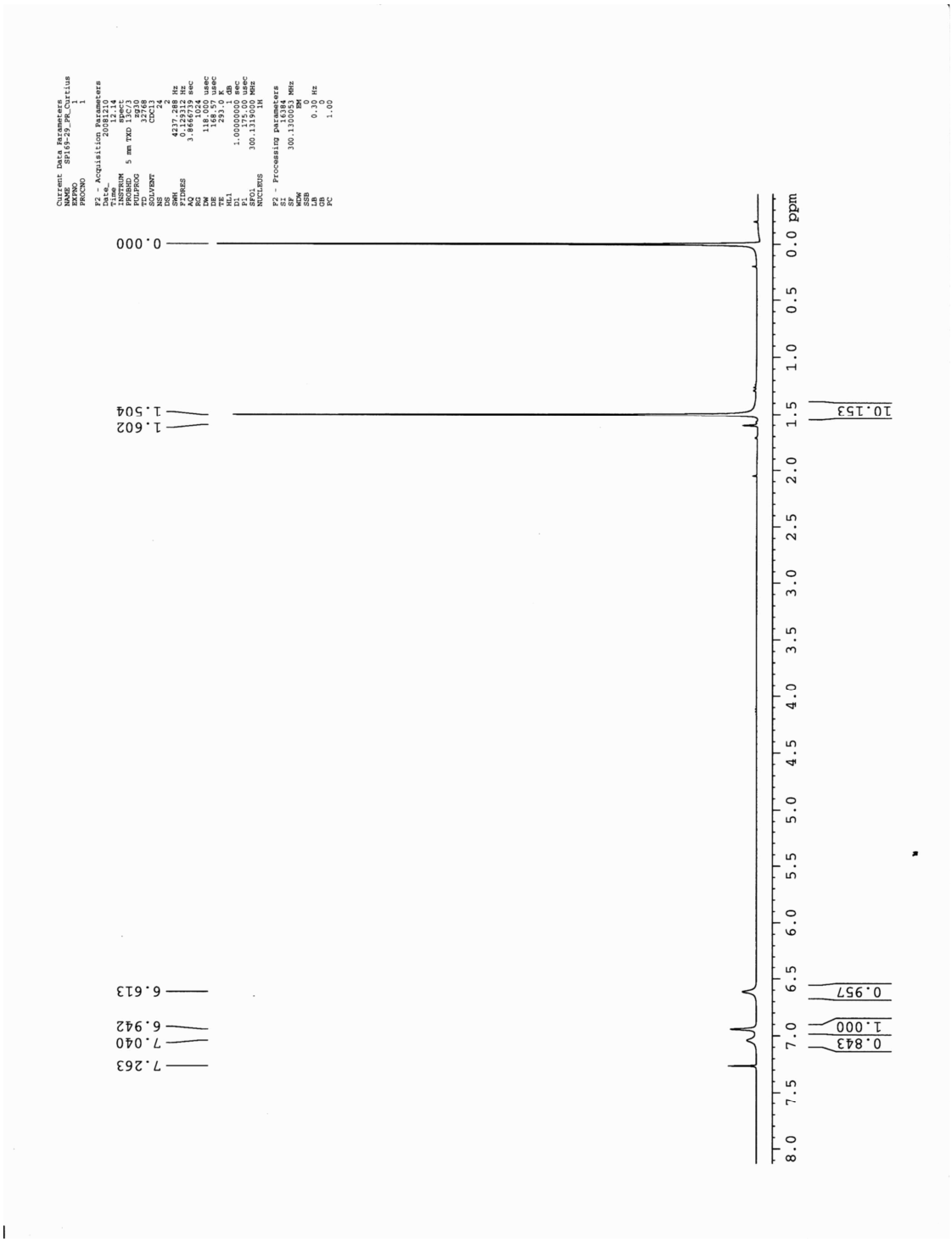
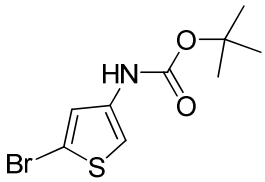
NMR Spectra



^{1}H NMR

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O
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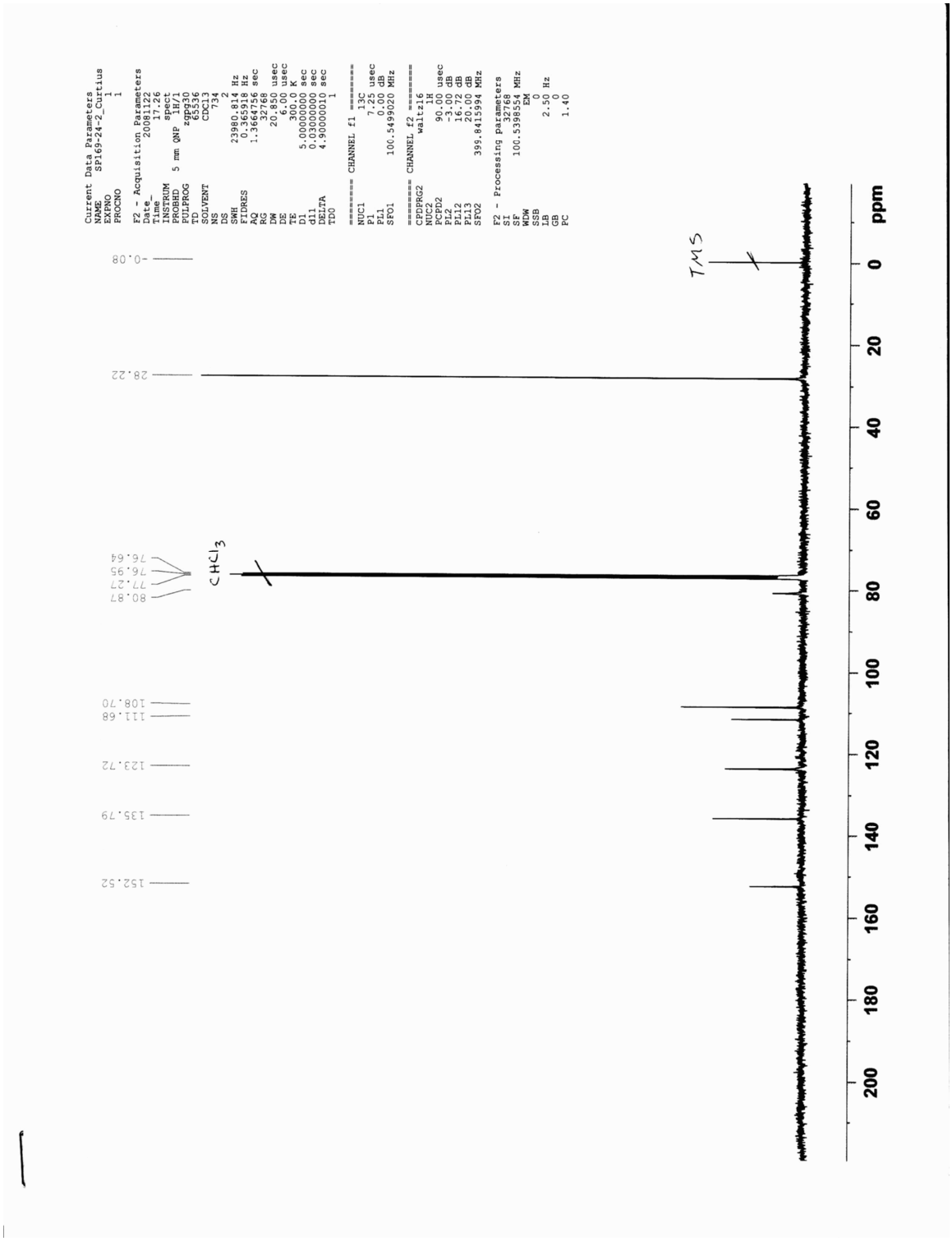
^{13}C NMR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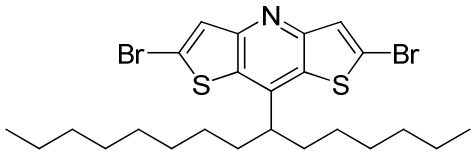
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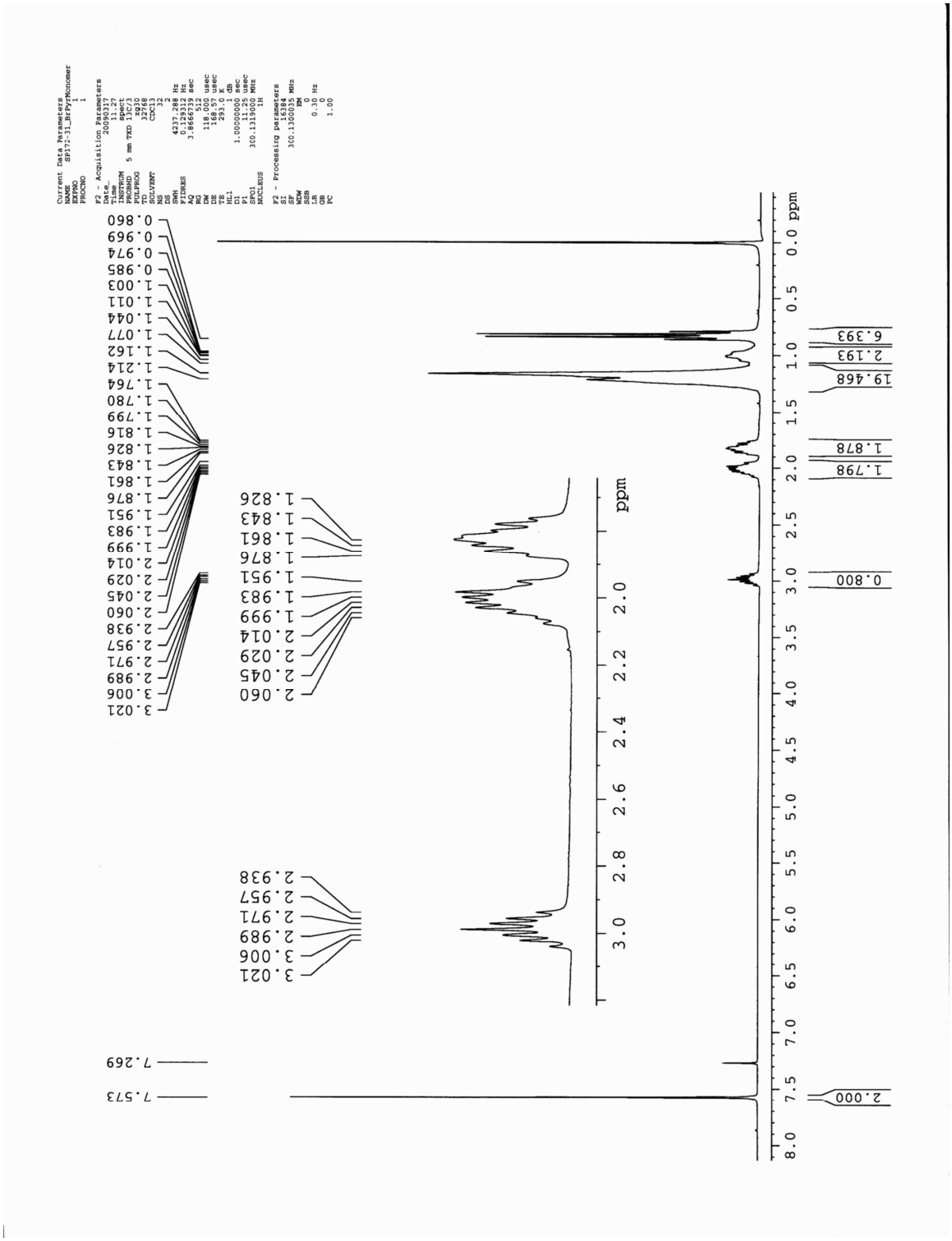
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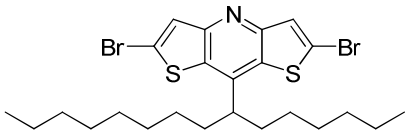
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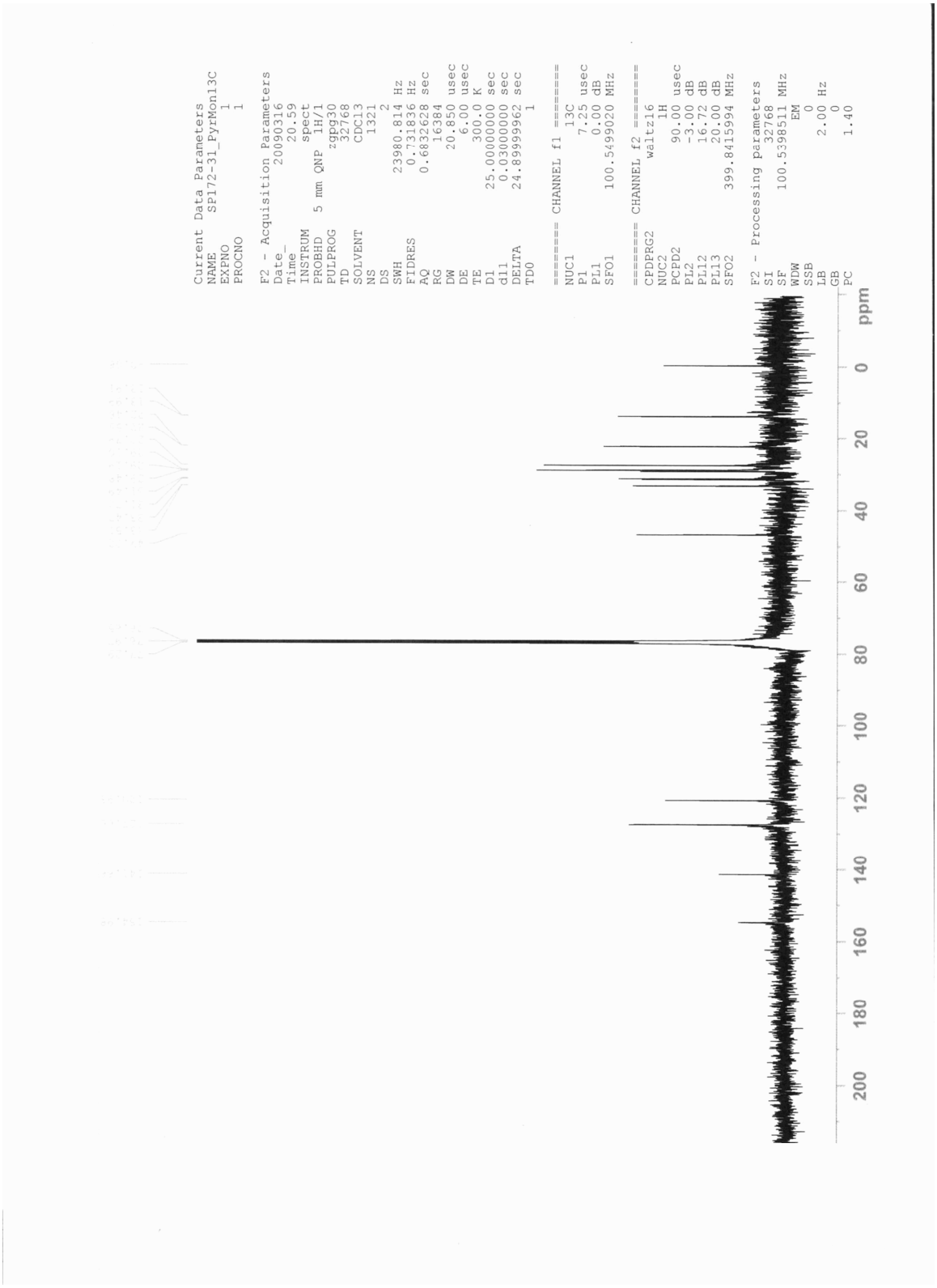
S

^{13}C NMR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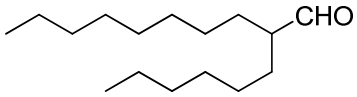
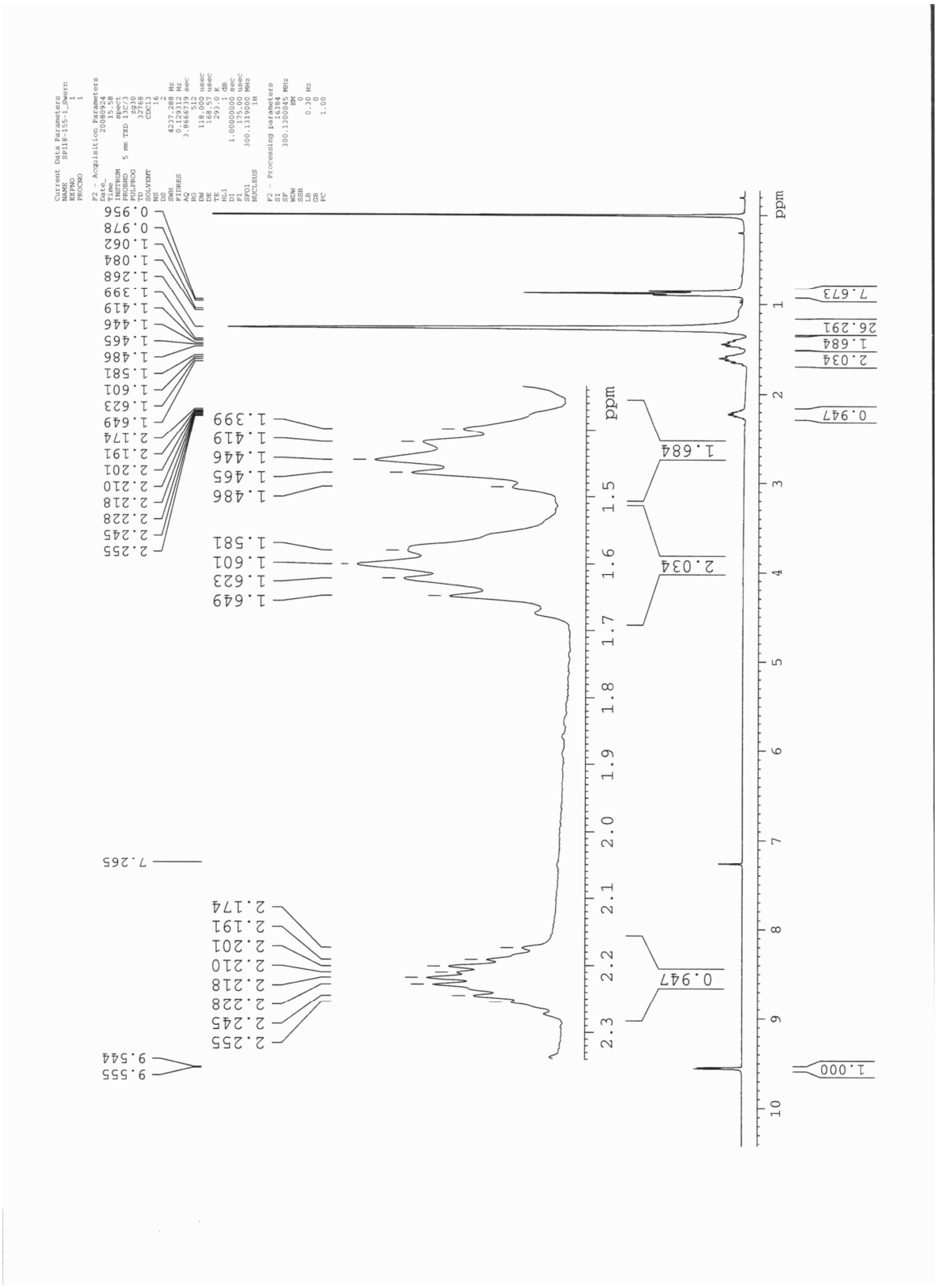

CHO

^{1}H NMR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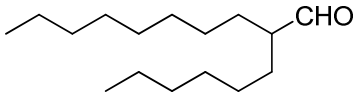
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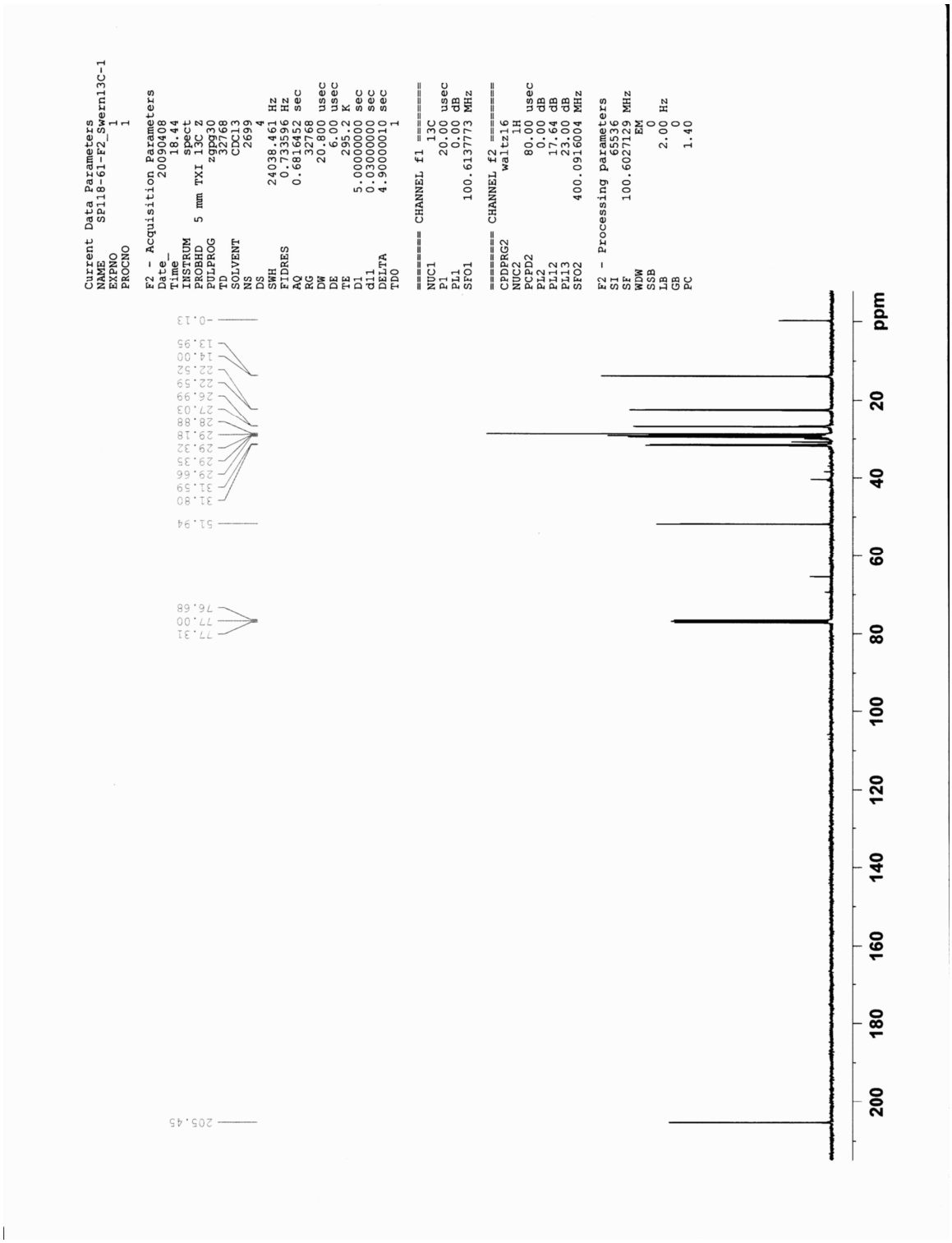
^{13}C NMR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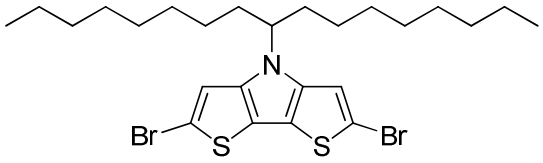
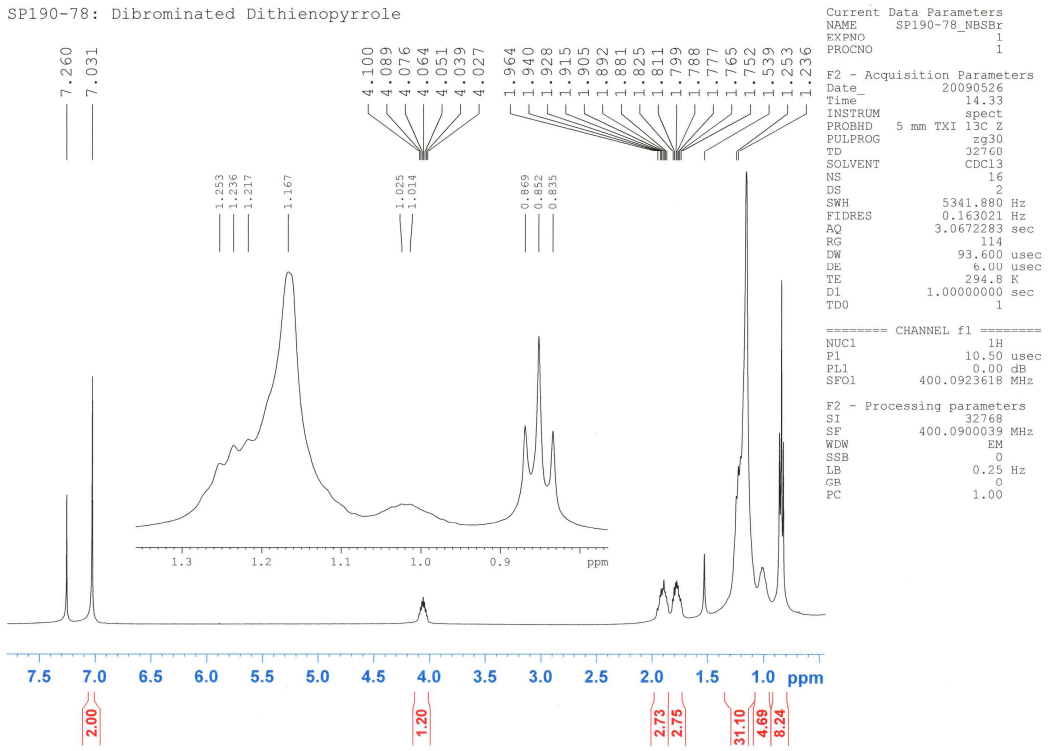
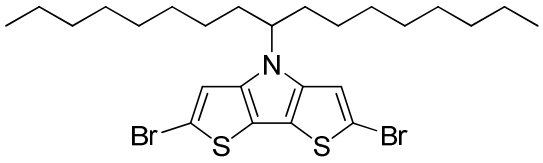


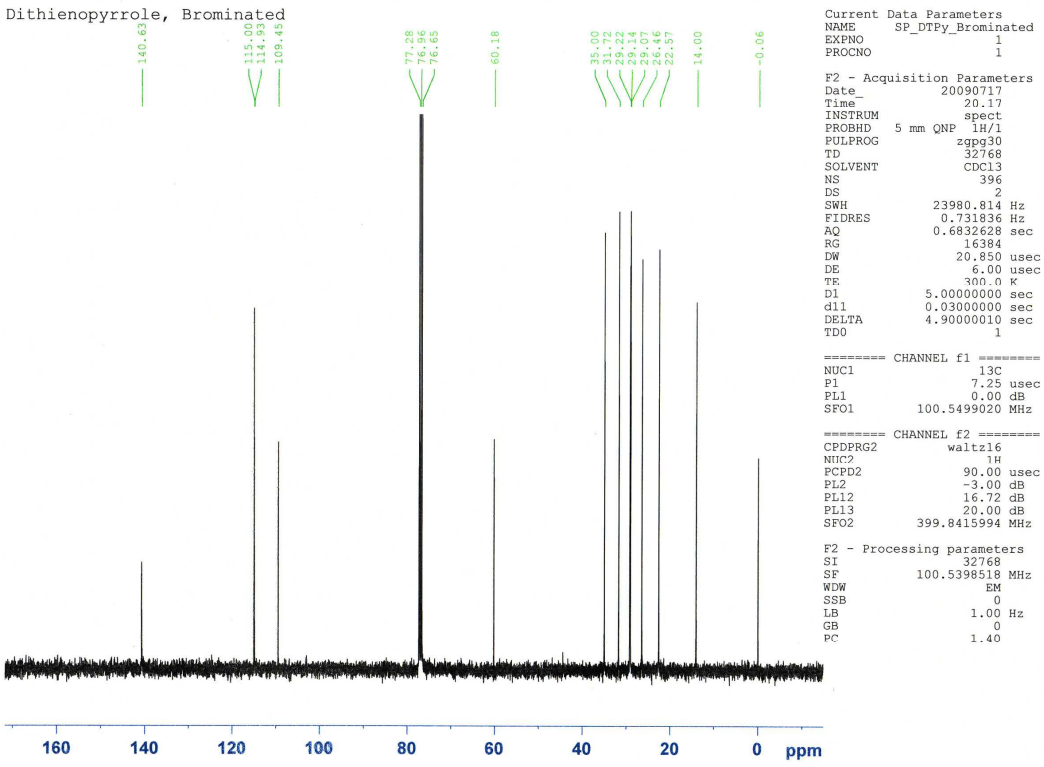
^{1}H NMR



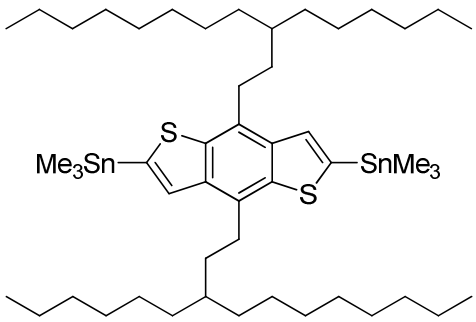
^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.03 (s, 2H), 4.06 (m, 1H), 1.92 (m, 2H), 1.79 (m, 2H), 1.17 (m, 24H), 0.85 (t, J = 6.8 Hz, 6H).



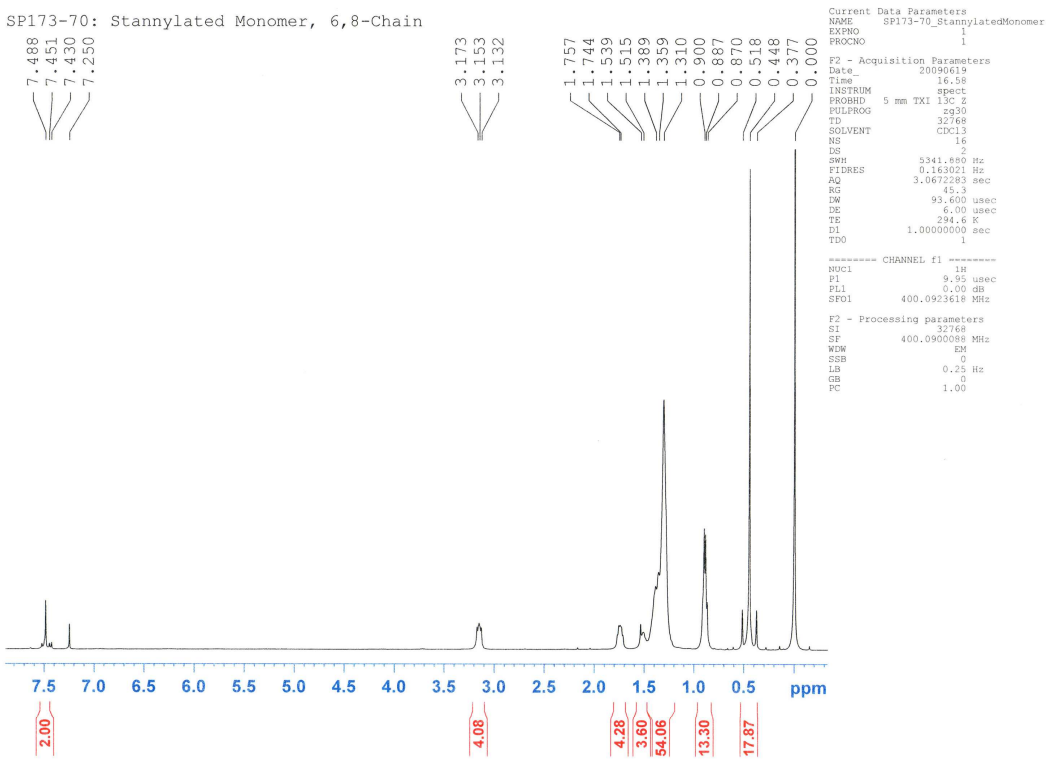
^{13}C NMR



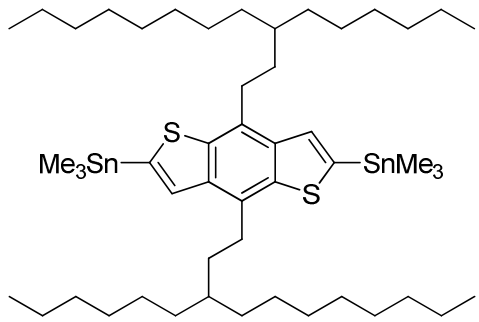
^{13}C NMR ($CDCl_3$, 100 MHz, δ): 140.63, 115.00, 114.93, 109.45, 60.18, 35.00, 31.72, 29.22, 29.14, 29.07, 26.46, 22.57, 14.00.



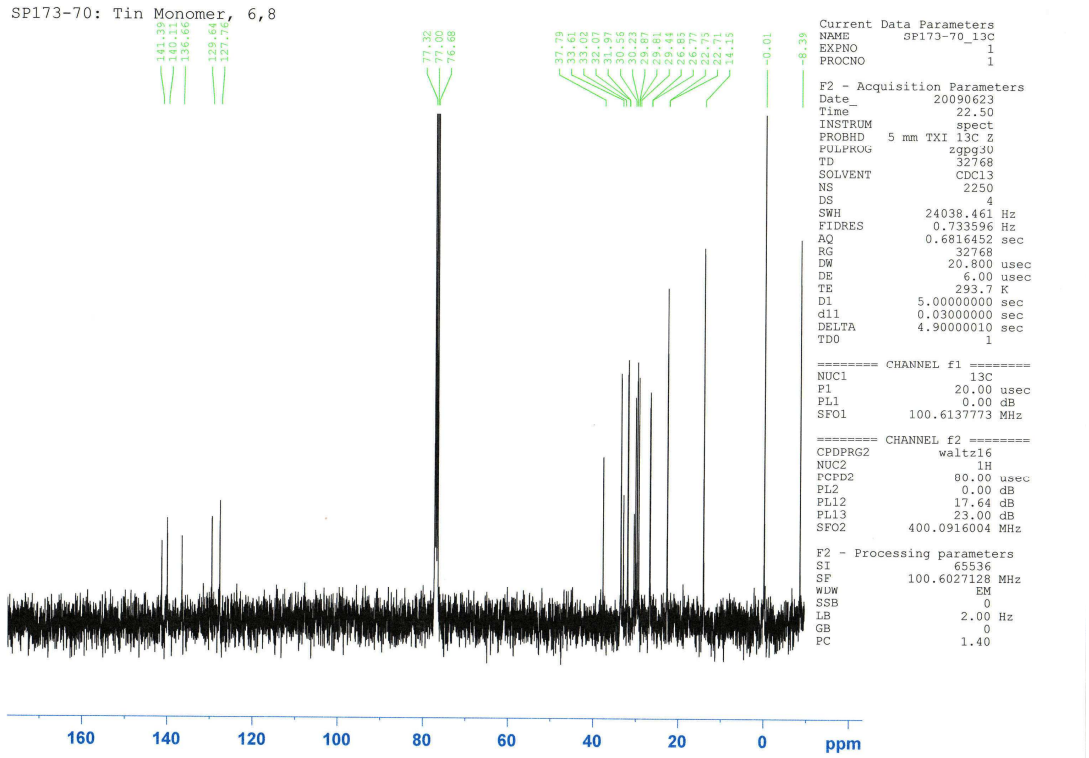
^{1}H NMR



^{1}H NMR ($CDCl_3$, 400 MHz, δ): 7.45 (s, $J_{Sn\text{-}H}$ = 14.8 Hz, 2H), 3.15 (t, J = 8.4 Hz, 4H), 1.74 (m, 4H), 1.31 (m, 50H), 0.89 (m, 12H), 0.45 (s, $J_{Sn\text{-}H}$ = 28.4 Hz, 18H).



^{13}C NMR



^{13}C NMR ($CDCl_3$, 100 MHz, δ): 141.39, 140.11, 136.66, 129.64, 127.76, 37.79, 33.61, 33.02, 32.07, 31.97, 30.56, 30.23, 29.87, 29.81, 29.44, 26.85, 26.77, 22.75, 22.71, 14.15, -8.39.

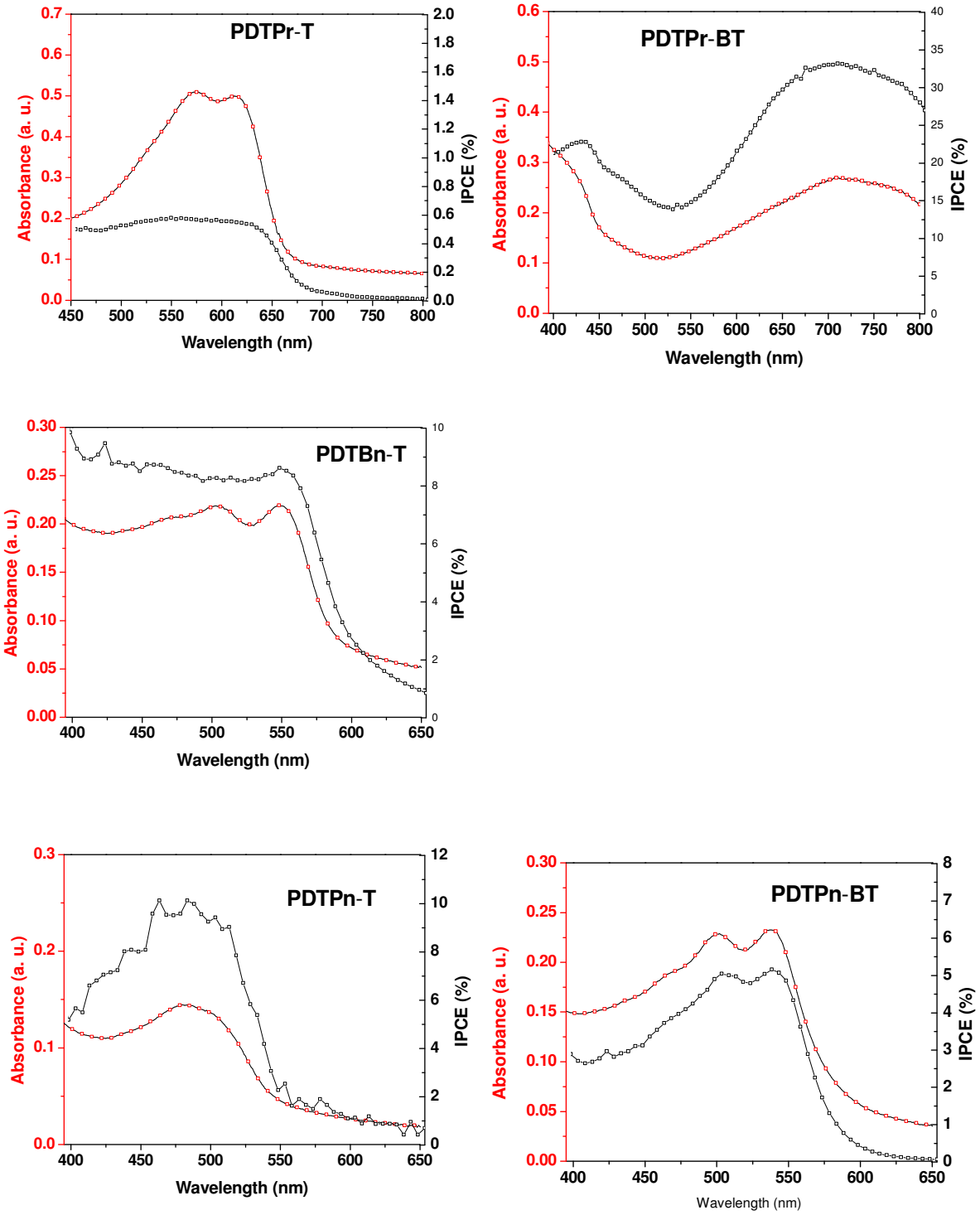


Figure S1. IPCE spectrum of BHJ photovoltaic device of ITO/PEDOT:PSS (45nm)/polymer:PCBM/Ca (30nm)/Al (100nm) and the optical absorptions for the corresponding film of the blend.

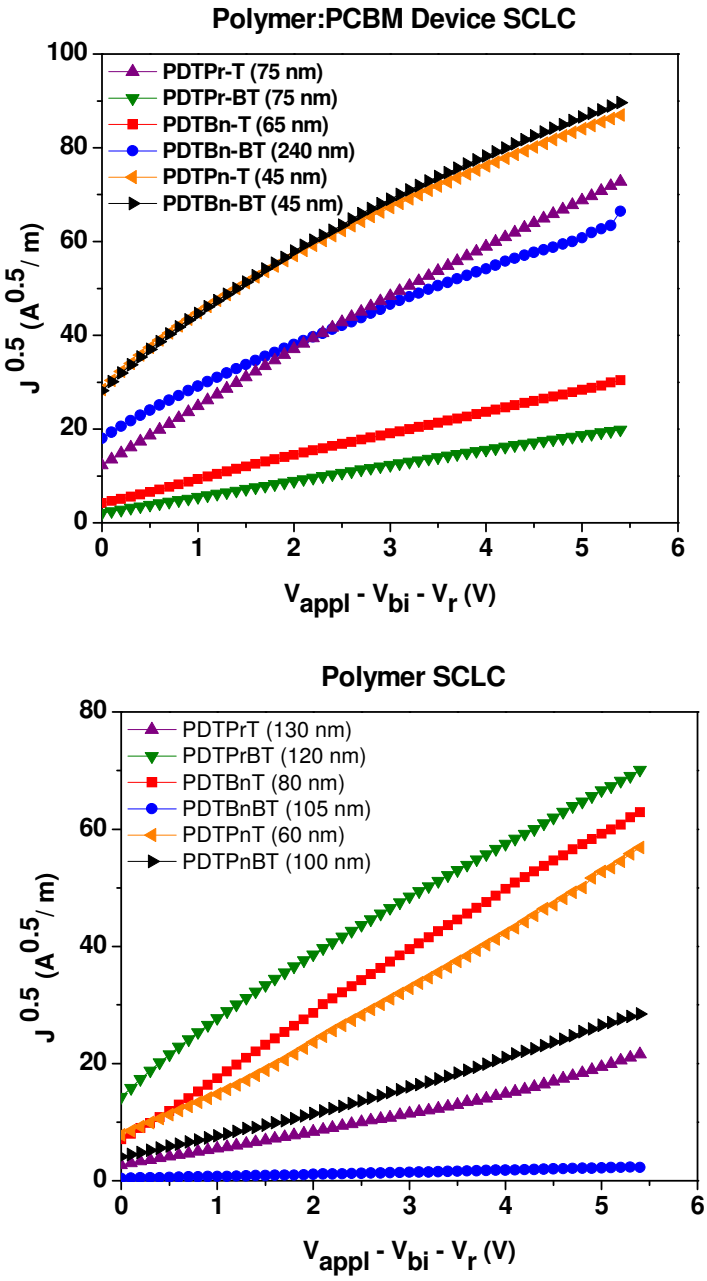


Figure S2. *Top:* $J^{0.5}$ vs V plots for the polymer films at room temperature from a hole-only BHJ device of ITO/PEDOT:PSS (45nm)/polymer:PCBM/Pd (40nm). *Bottom:* $J^{0.5}$ vs V plots for the polymer films at room temperature from a polymer-only device of ITO/PEDOT:PSS (45nm)/polymer /Al (100nm). In both Figures, the thickness of the films is indicated, and the solid lines are fits to the data points using $J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{L^3}$.

Additional characterization data provided below for **PDTBn-T**.

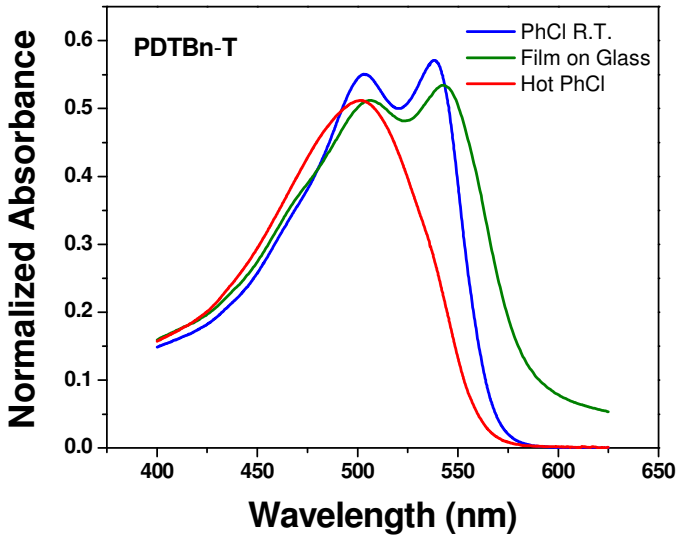


Figure S3. UV-Vis spectra of **PDTBn-T** in boiling chlorobenzene solution, the same solution at room temperature, and from a spun cast film on glass. The bathochromic shift from hot solvent to room temperature solvent and from cold solvent to solid film is typical for planar conjugated polymers. The second red shifted absorption peak is attributed to extension of the conjugation over two dimensions, and aggregation of the polymer backbones.

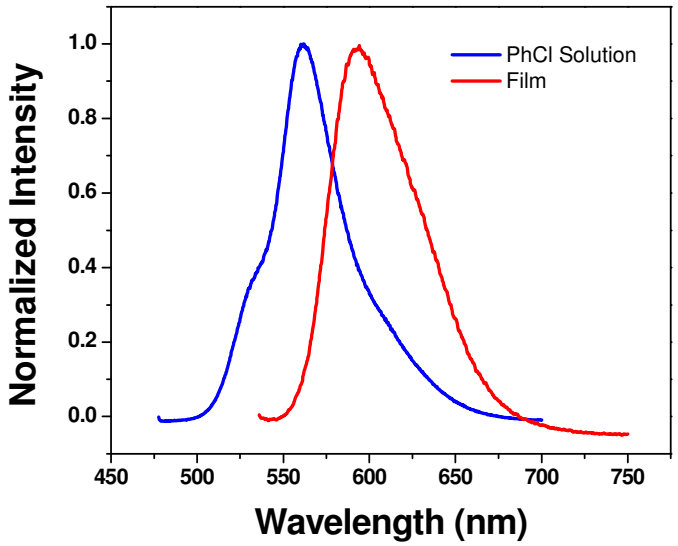


Figure S4. Fluorescence spectra for **PDTBn-T**. The solution spectra was excited at 475 nm, the film spectra was excited at 525 nm. The resulting red shift in the solid film is typical for conjugated polymers, due to increased inter-chain interaction.

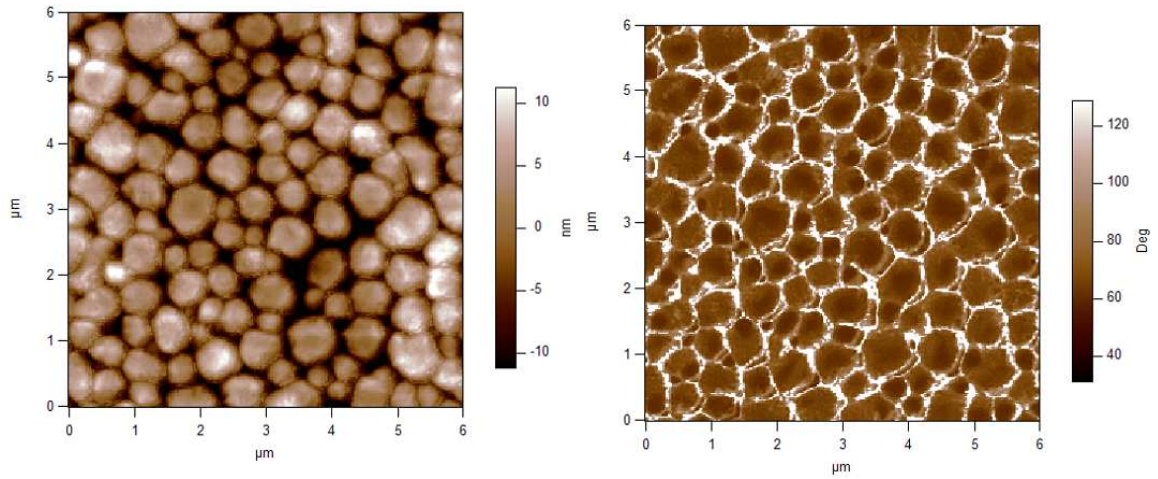


Figure S5. Atomic Force Microscope (AFM) images of **PDTBn-T**:PCBM film in a 1:2 ratio blend. Observed large scale phase segregation is not optimal for bulk heterojunction performance (left: height image; right: phase image).

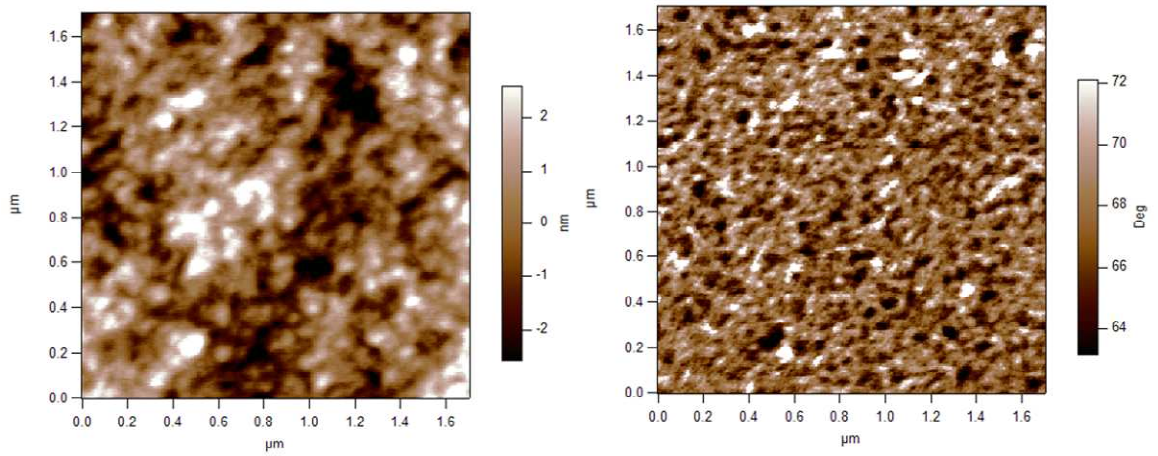


Figure S6. AFM images of pure **PDTBn-T** film spun cast from chlorobenzene (left: height image; right: phase image).

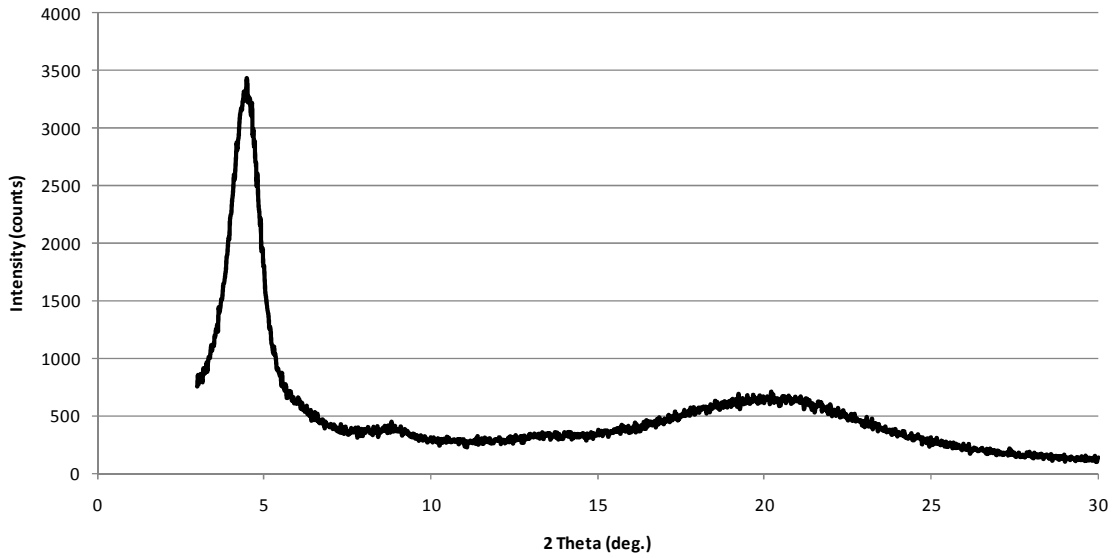


Figure S7. Powder X-Ray Diffraction of pure **PDTBn-T**. $2\theta \approx 4.55°$ corresponds to an inter-chain spacing of 19.4 Å or 1.94 nm (100 direction); $2\theta \approx 19.45°$ corresponds to an face to face stacking distance of 4.55 Å or 0.46 nm (010 direction).