Electronic supplementary information:

Thermal and nonlinear optical studies of newly synthesized EDOT based bent-core and hockey-stick like liquid crystals

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1. General methods

All the chemicals and reagents were AR-grade quality and procured from Sigma-Aldrich. The solvents employed in the reactions were dried and distilled using standard protocols prior to use. The progress, completion of the reactions and purity of all the compounds were primarily determined by thin layered chromatography (TLC, make – Merck). The crude compounds were purified by column chromatography using silica gel mesh powder of mesh size 100–200 were used as a stationary phase. The molecular structure and purity of all compounds were established with the aid of data access from spectroscopic and elemental analysis methods. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using Shimadzu – 8400 in Nujol liquid paraffin; only major peaks were reported in cm^{-1} (wave number). Nuclear magnetic resonance spectroscopy ^{1}H NMR were recorded on Bruker machine at 500 MHz and ^{13}C NMR at 125 MHz using deuterated chloroform ($CDCl_3$) as a solvent and chemical shifts are given in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard ($CDCl_3$: ^{1}H NMR: δ = 7.23 ppm; ^{13}C NMR = 77.0 ppm). The patterns (splitting or multiplicity) of the ^{1}H NMR signals are represented as s = singlet, d = doublet, t = triplet, m = multiplet and coupling constants (J) are mentioned in Hz. Elemental analysis was carried out using Elementar Vario MICRO Select instrument. The microscopic textures were recorded on sample placed between ordinary glass slides using Olympus BX51 polarising optical microscope attached with a digital camera (Olympus, Tokyo, Japan) in conjunction with Mettler FP82HT hot stage controlled by Mettler FP90 central processor. The phase transition temperature and associated enthalpy values for all the liquid crystalline compounds using 2–4 mg of samples were determined by METTLER TOLEDO DSC 3 STAR^{e} system with PC system operating on STAR^{e} software. Prior to the use, the instrument was calibrated using pure indium and zinc. DSC traces were recorded at scan rate of 10 ºC min^{-1} under continuous flow of nitrogen gas. X-ray diffraction studies were performed on powder samples in Lindemann capillaries with Cu *K*α (λ = 1.54060 Å) radiation using DY 1042-Empyrean (PANalytical) X-ray diffractometer comprising a programmable divergence slit and PIXcel 3D detector. Thermal stability of mesogens were obtained by using TGA 4000 thermogravimetric analysis (TGA) instrument.

2. DFT calculations

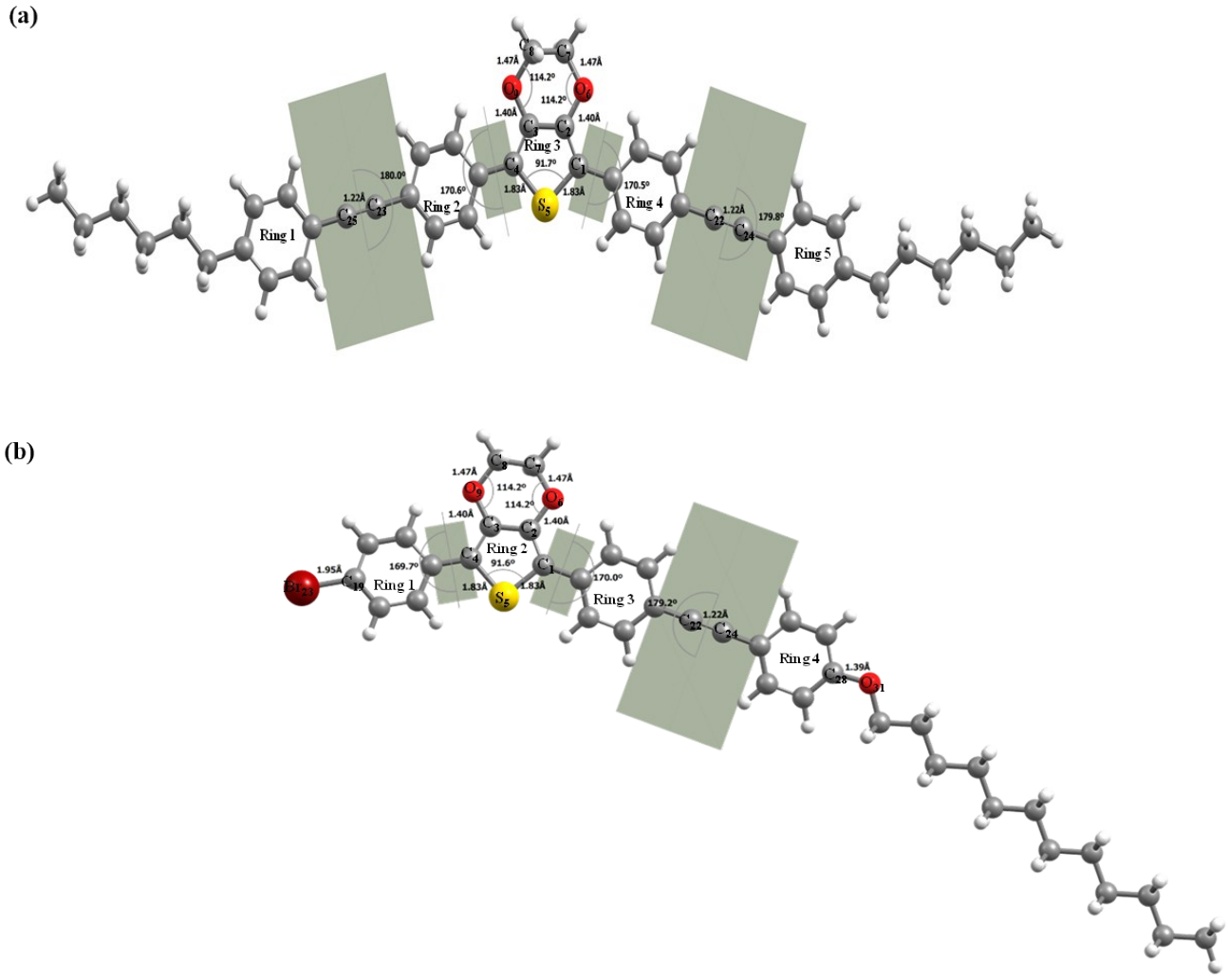


Fig. S1. DFT optimized molecular structures: (a) bent-core mesogen 9b and (b) hockey-stick like mesogen 10d.

3. NLO experimental set up

The open aperture Z-scan technique was used to characterize the nonlinear optical transmission of all the novel mesogenic compounds 9a–9b and 10a–10e at the wavelength of 532 nm, using 5 ns laser pulses obtained from a frequency doubled Nd:YAG laser (Minilite I, Continuum). The laser output was spatially filtered to obtain a nearly perfect Gaussian beam profile.

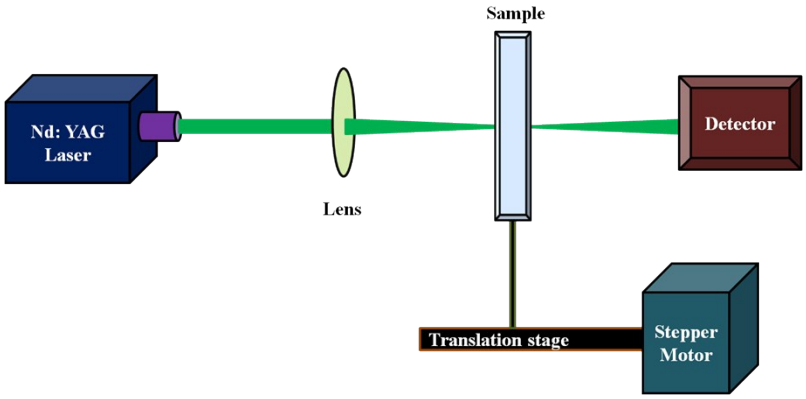
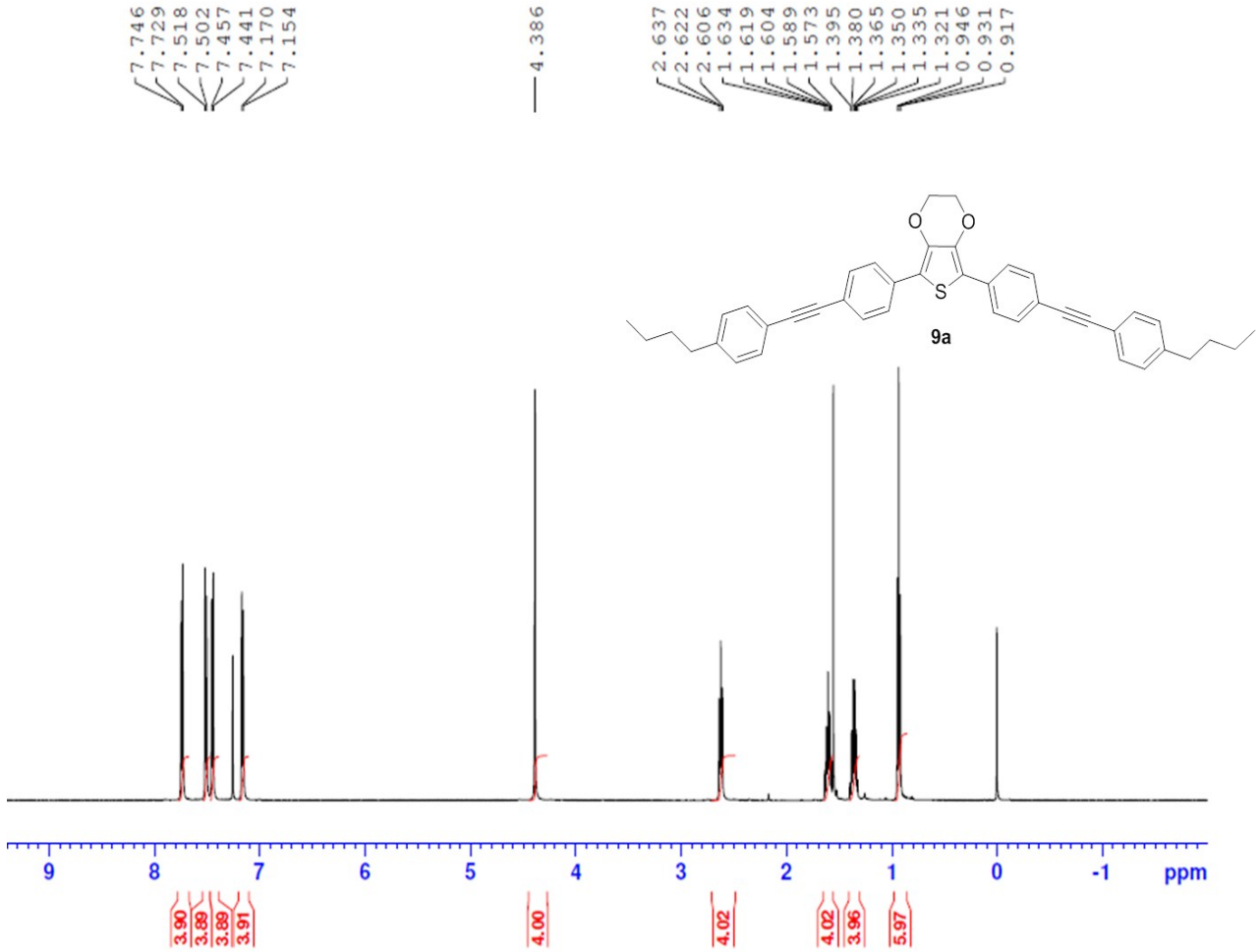


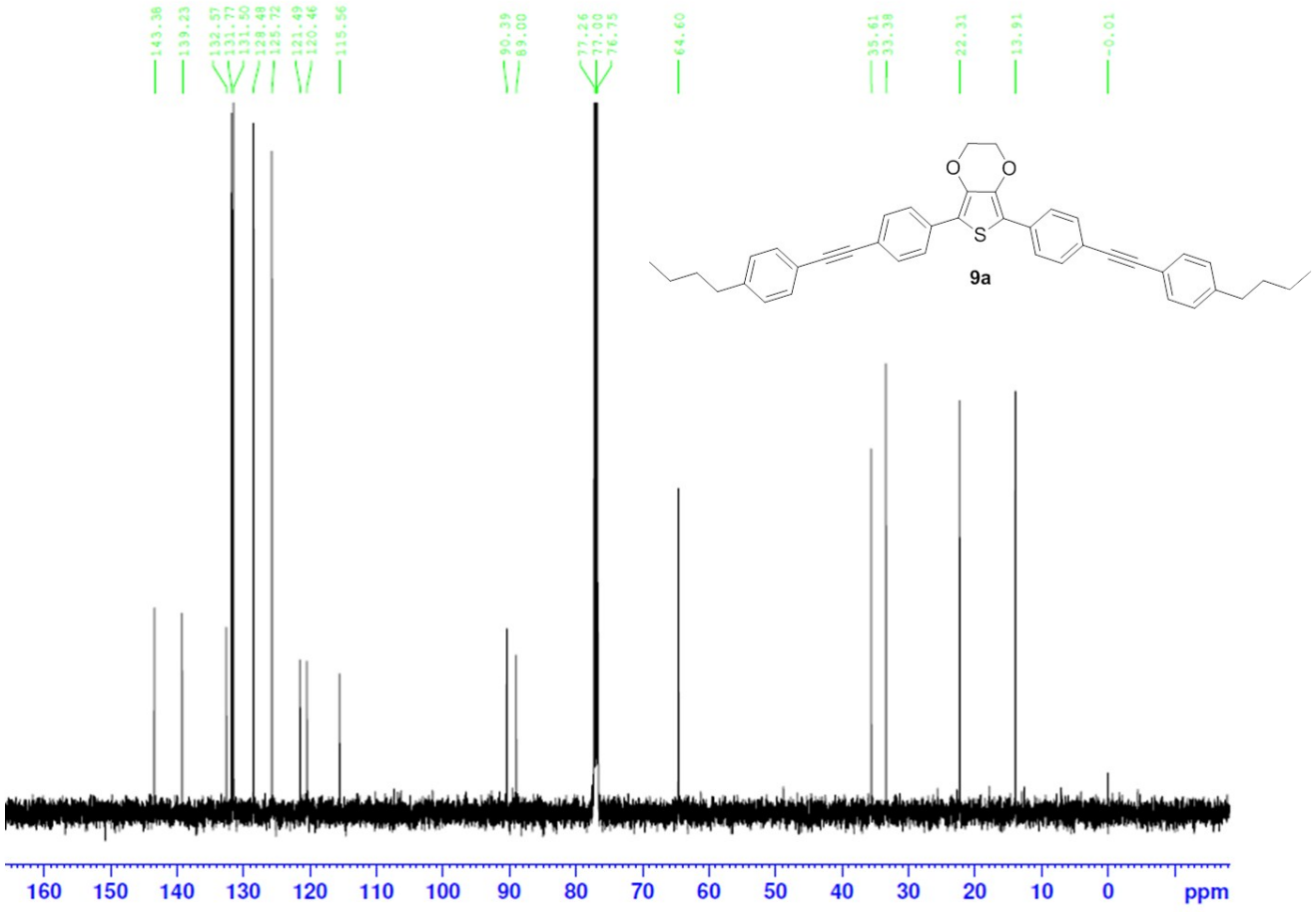
Fig. S2 Schematic illustration of the open aperture Z-scan setup used for nonlinear transmission measurements.

4. Characterization: ^{1}H and ^{13} NMR spectroscopy

Supplementary information Fig. S3 ^{1}H NMR



Supplementary information Fig. S3 ^{13}C NMR



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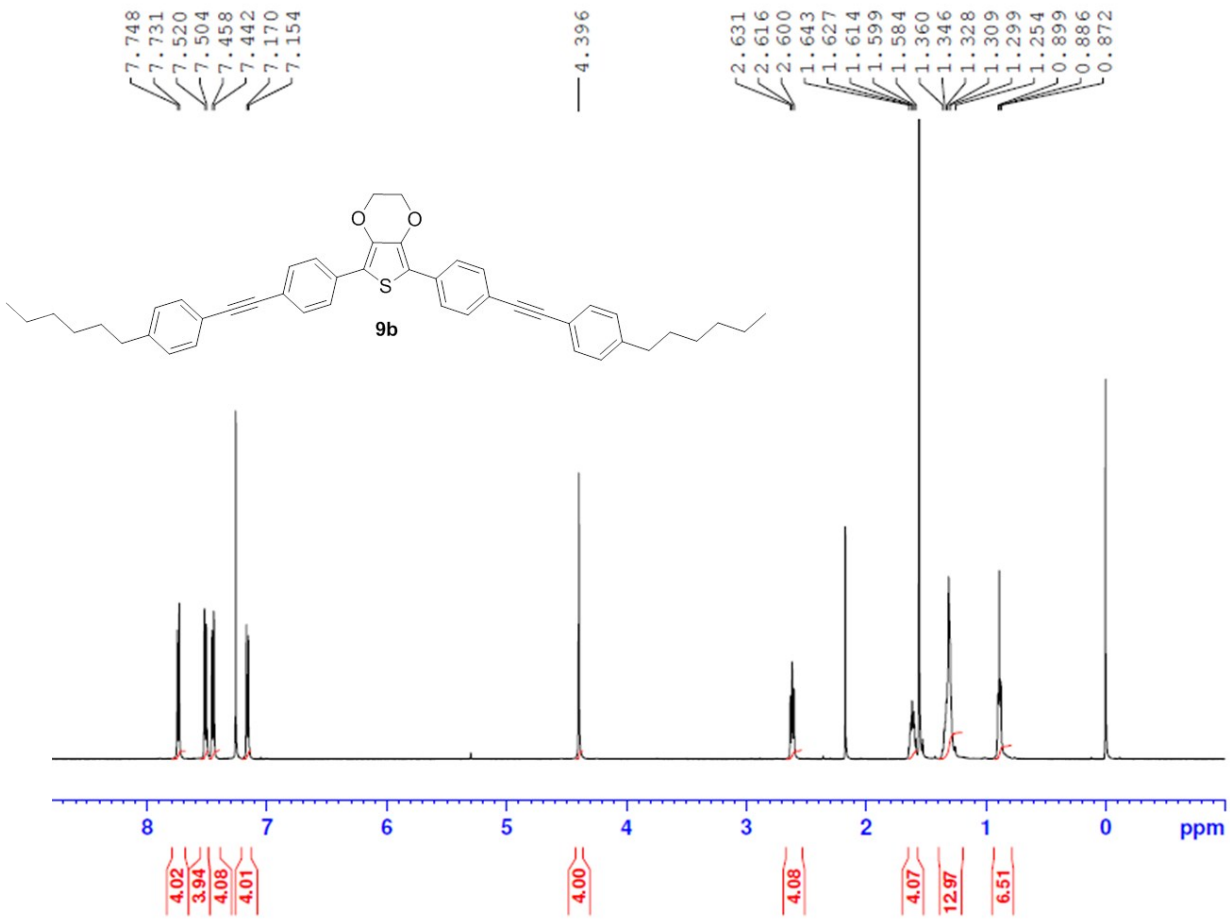

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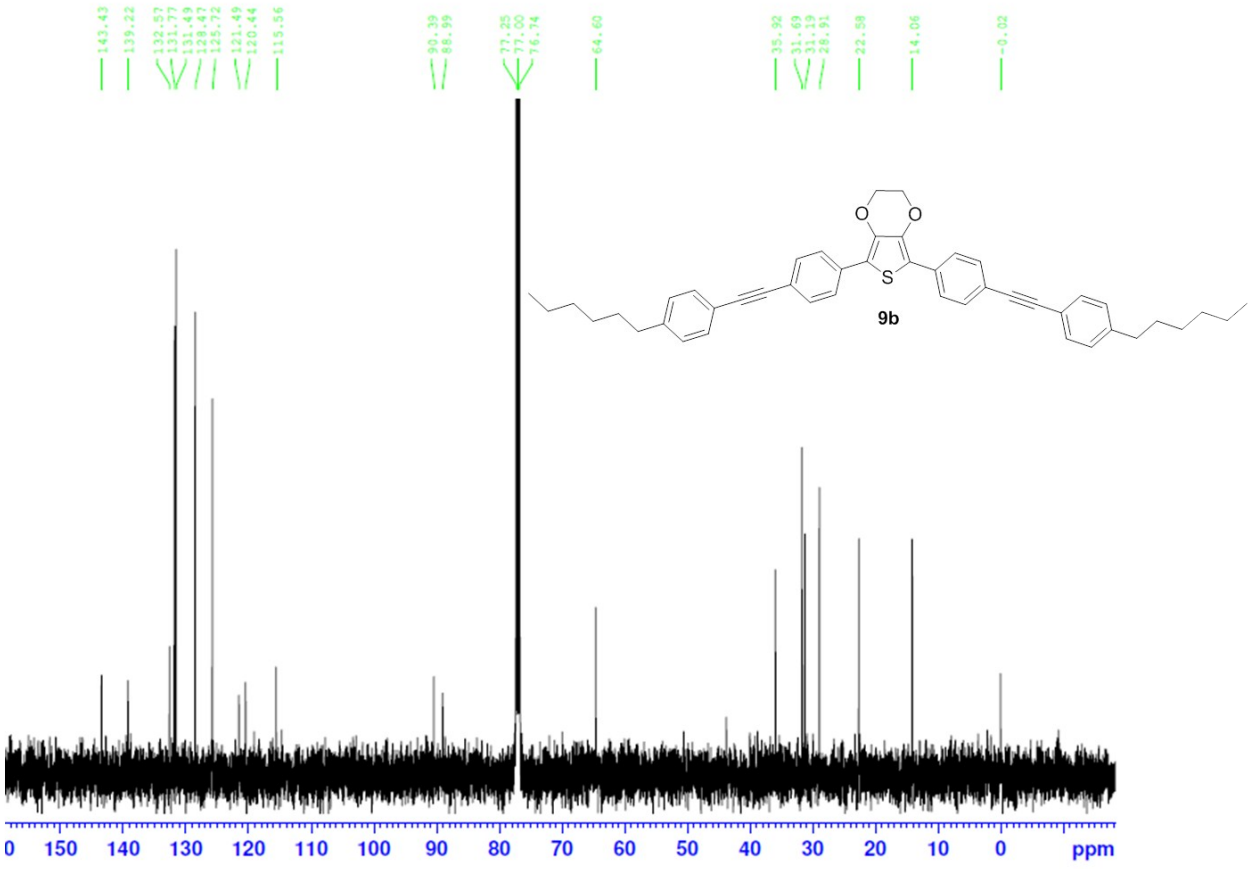

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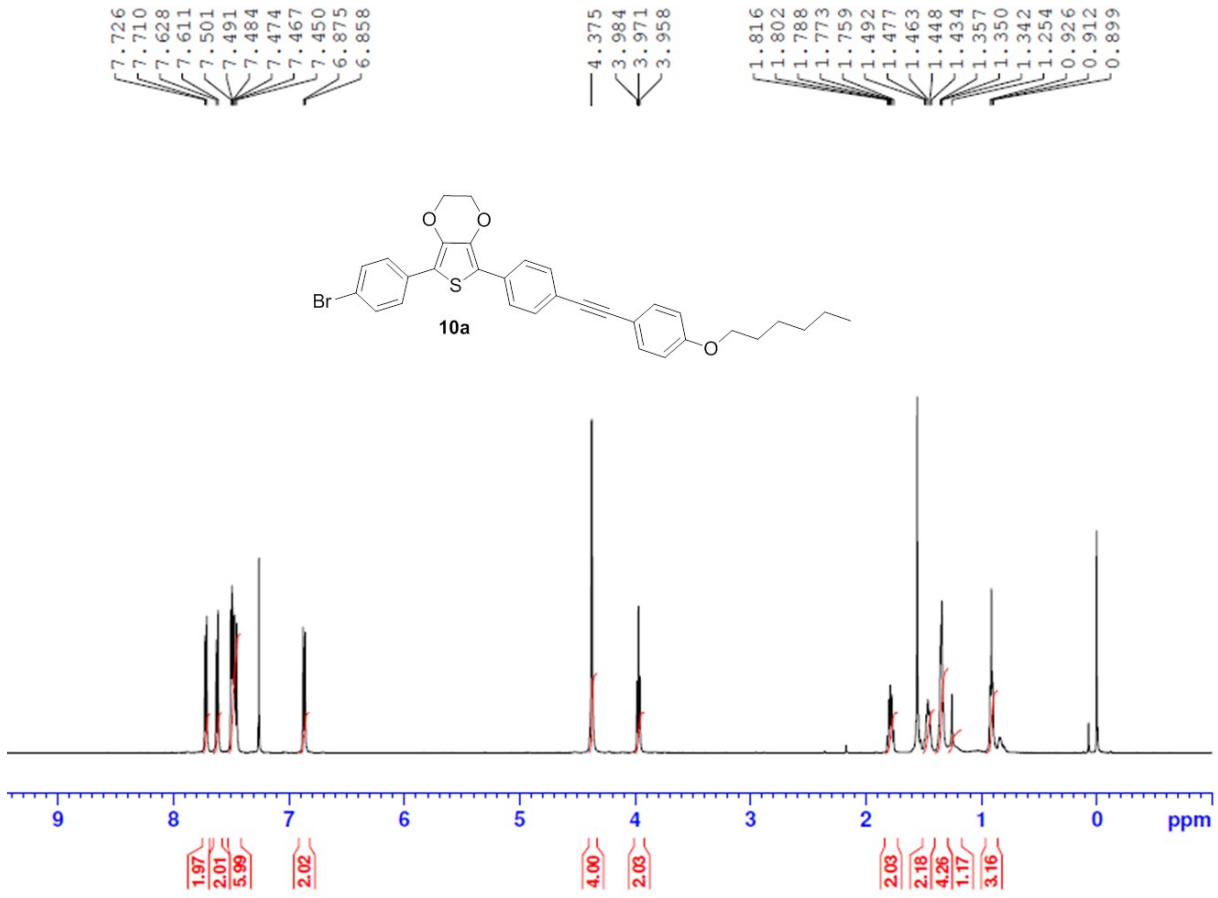

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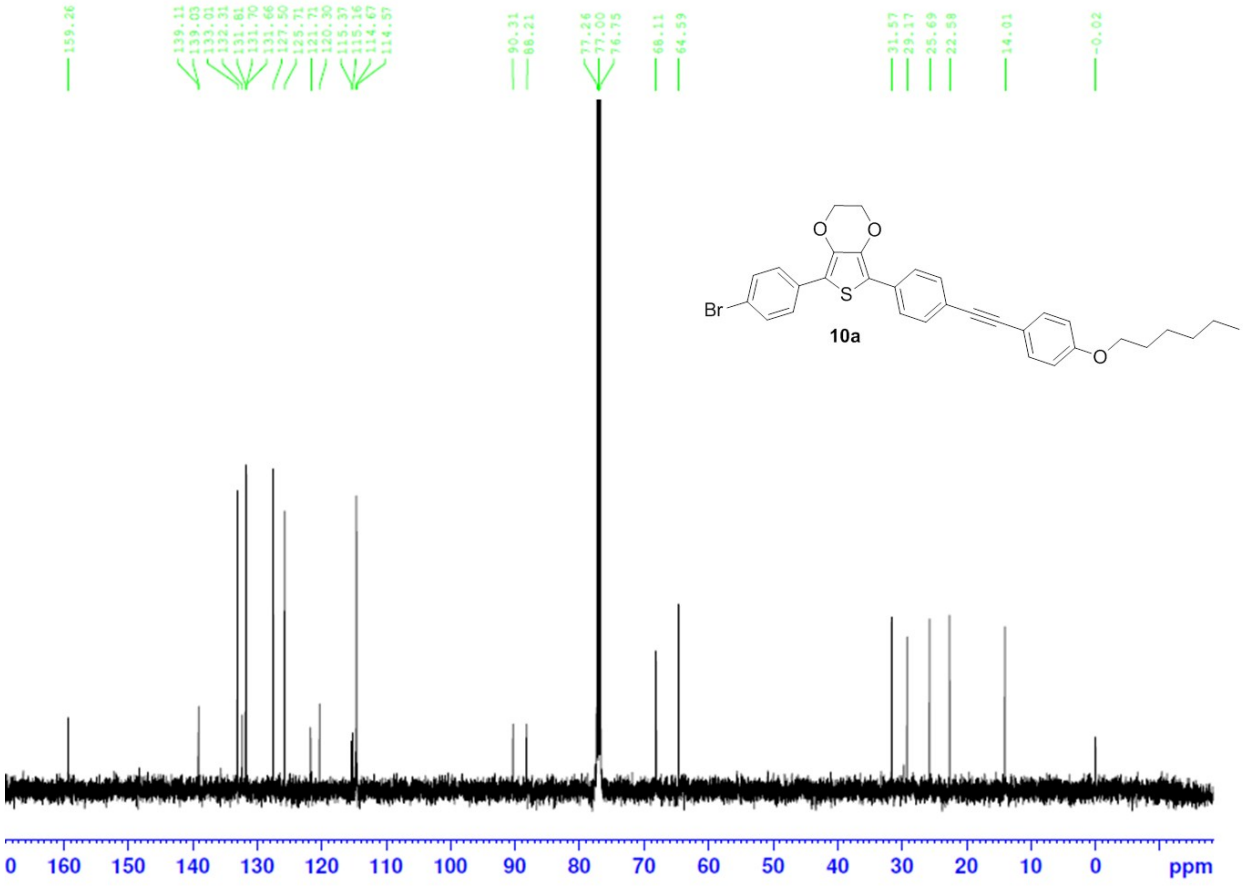

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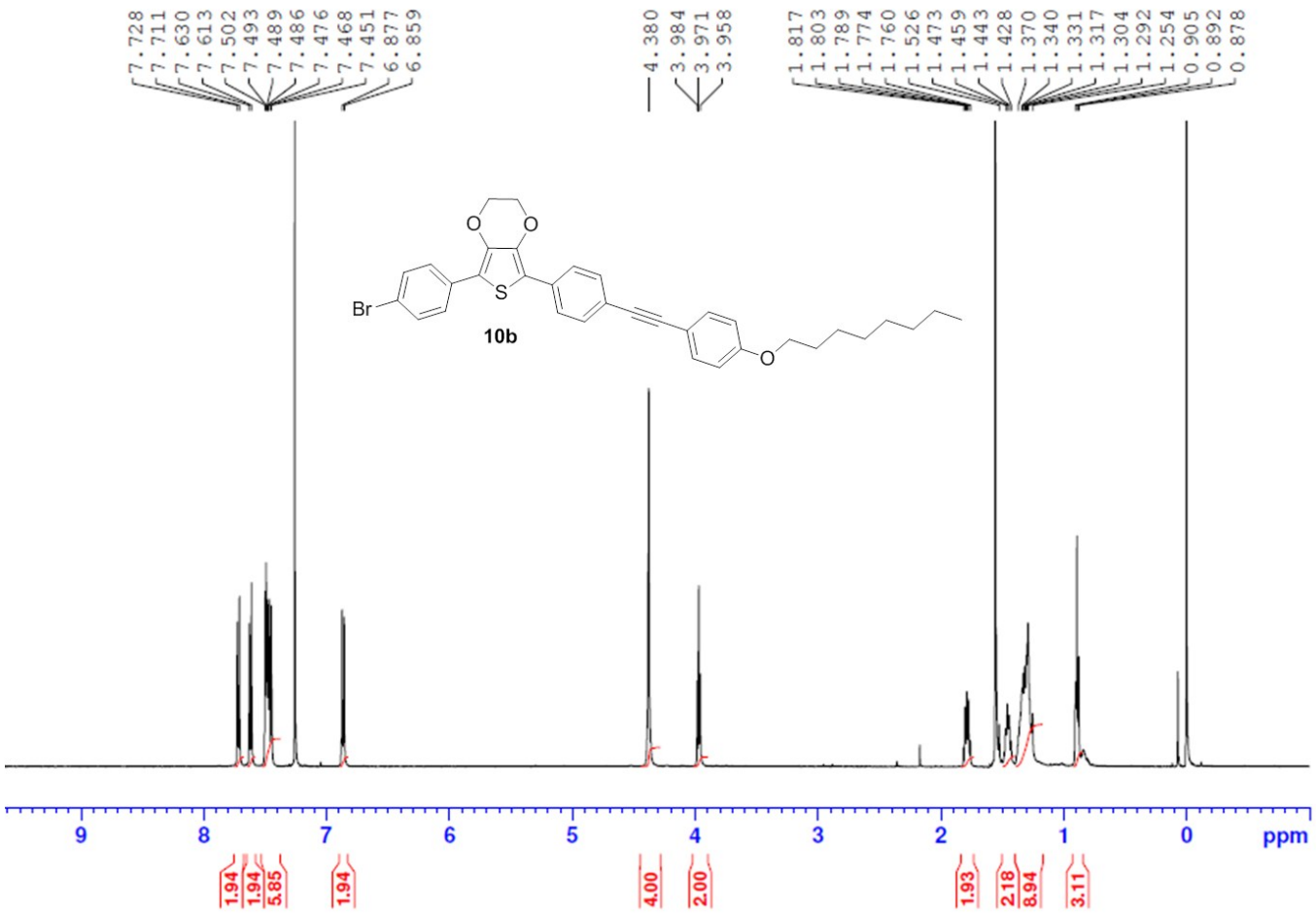

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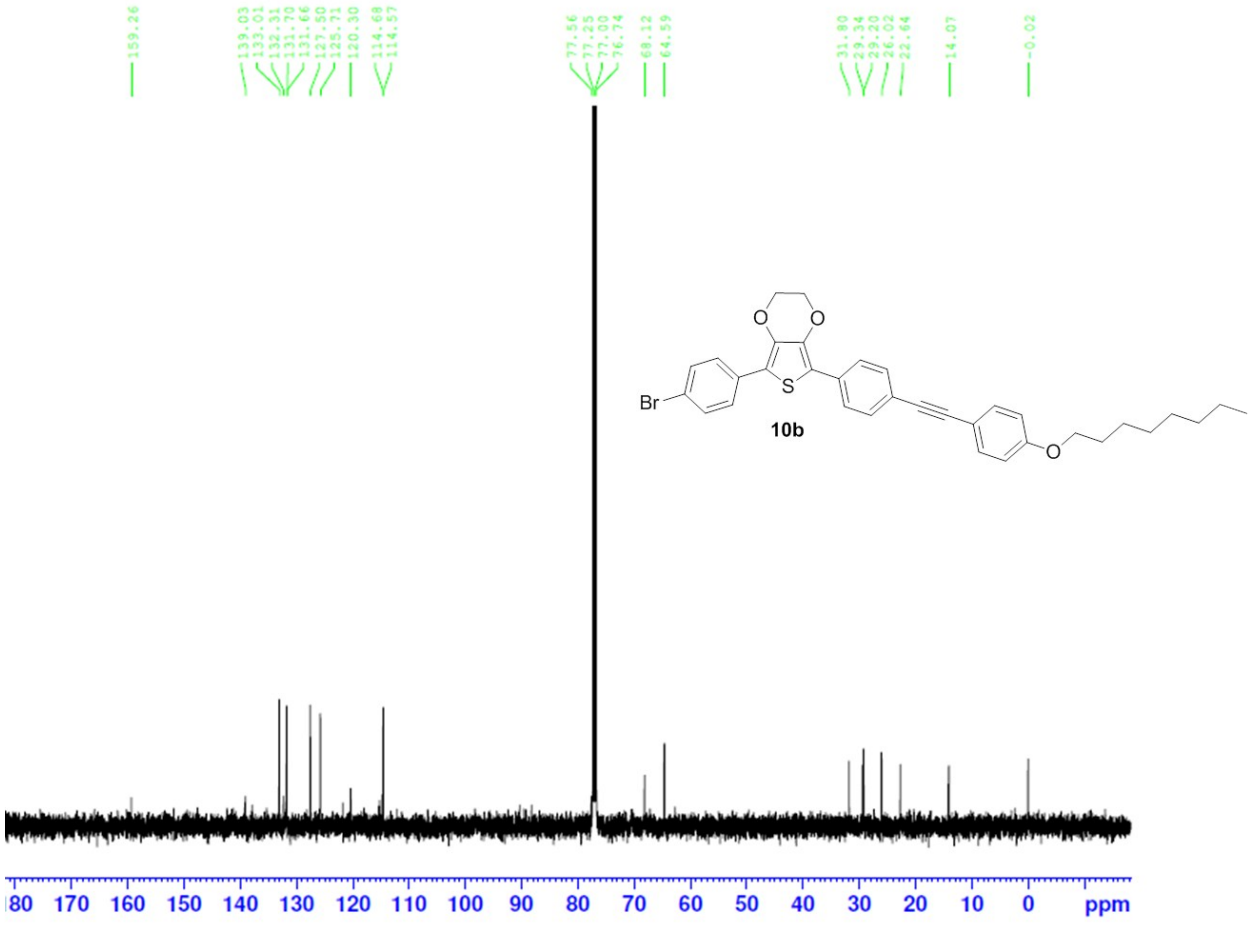

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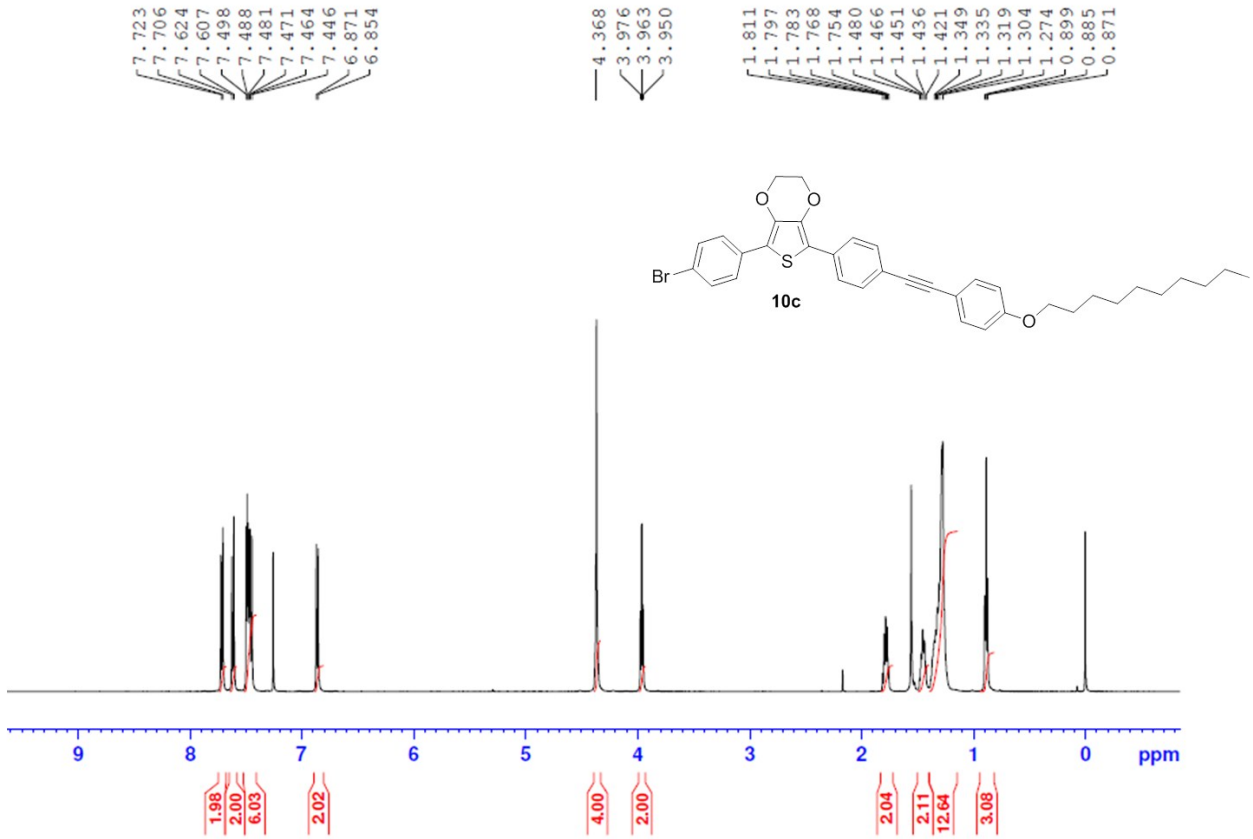

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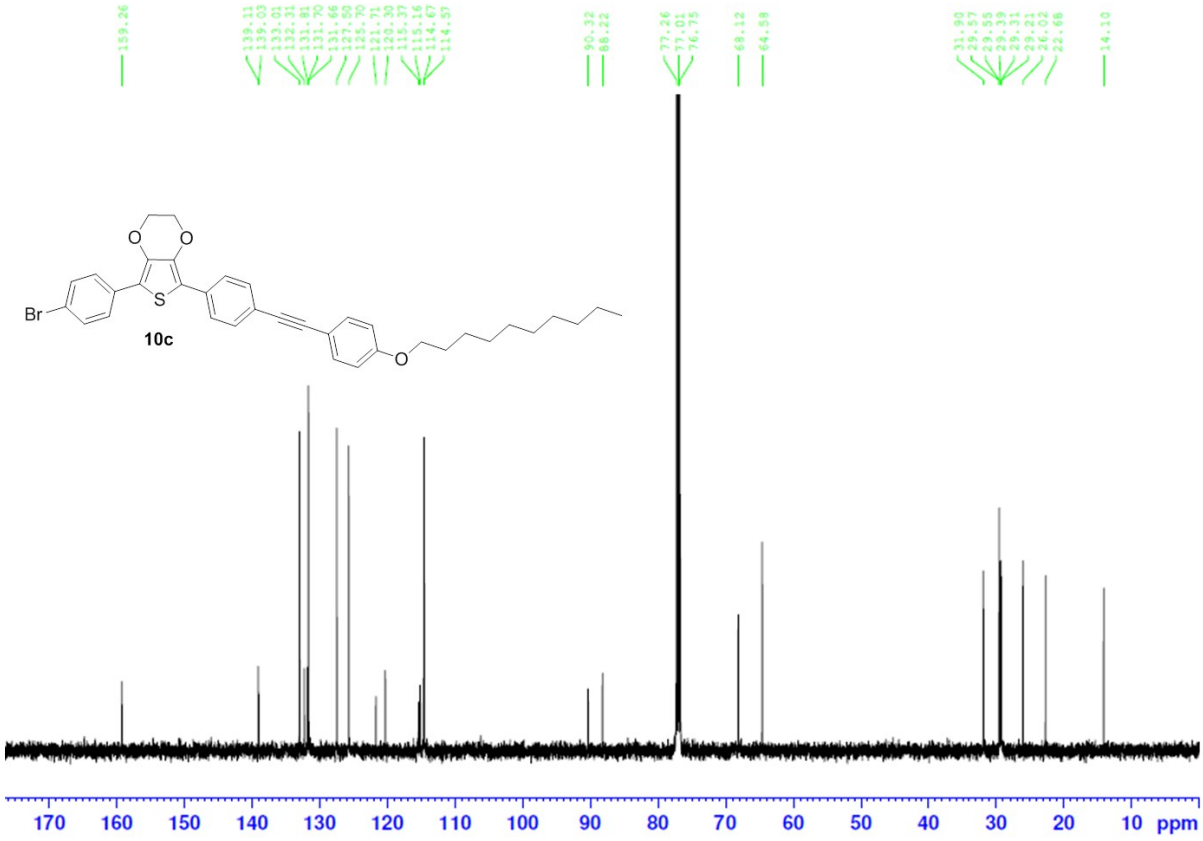

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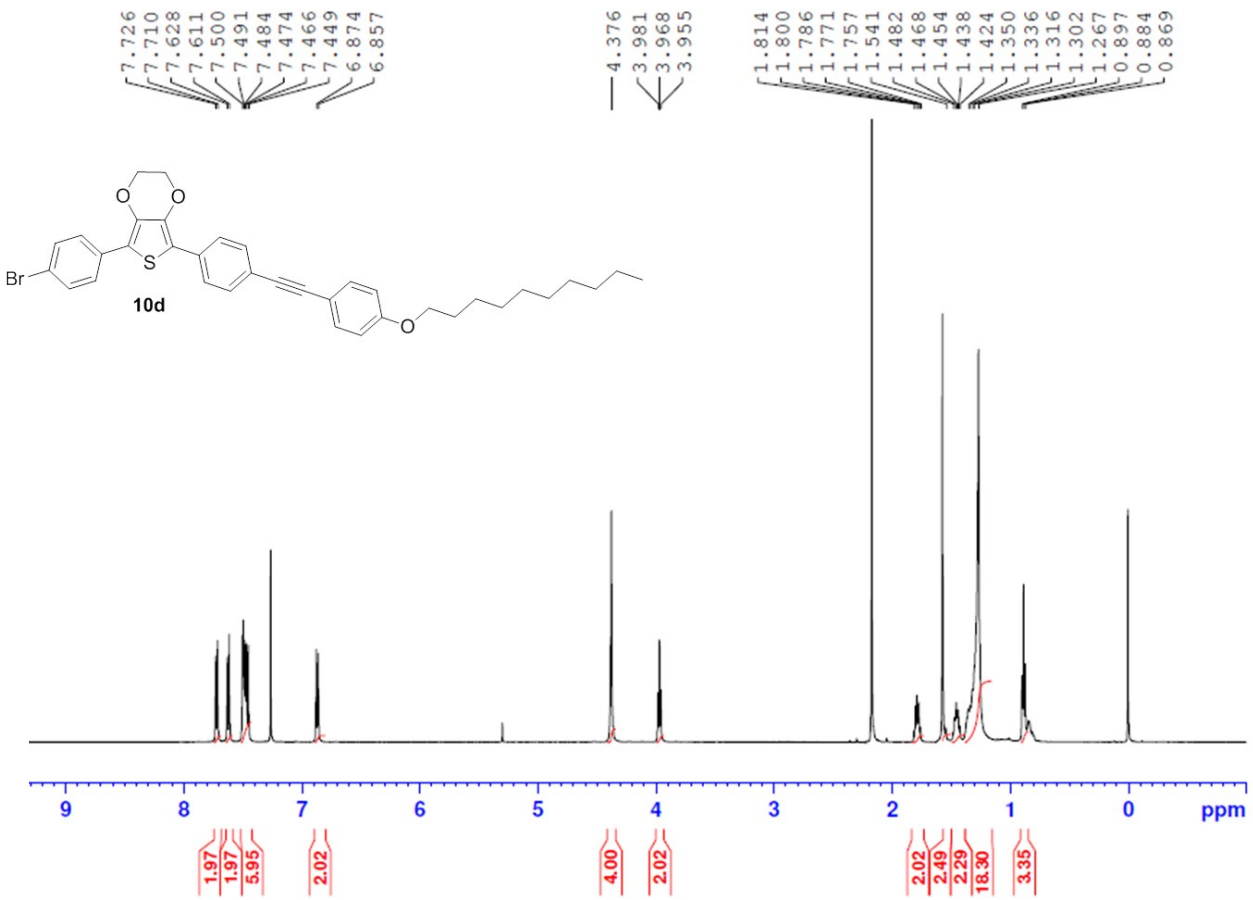

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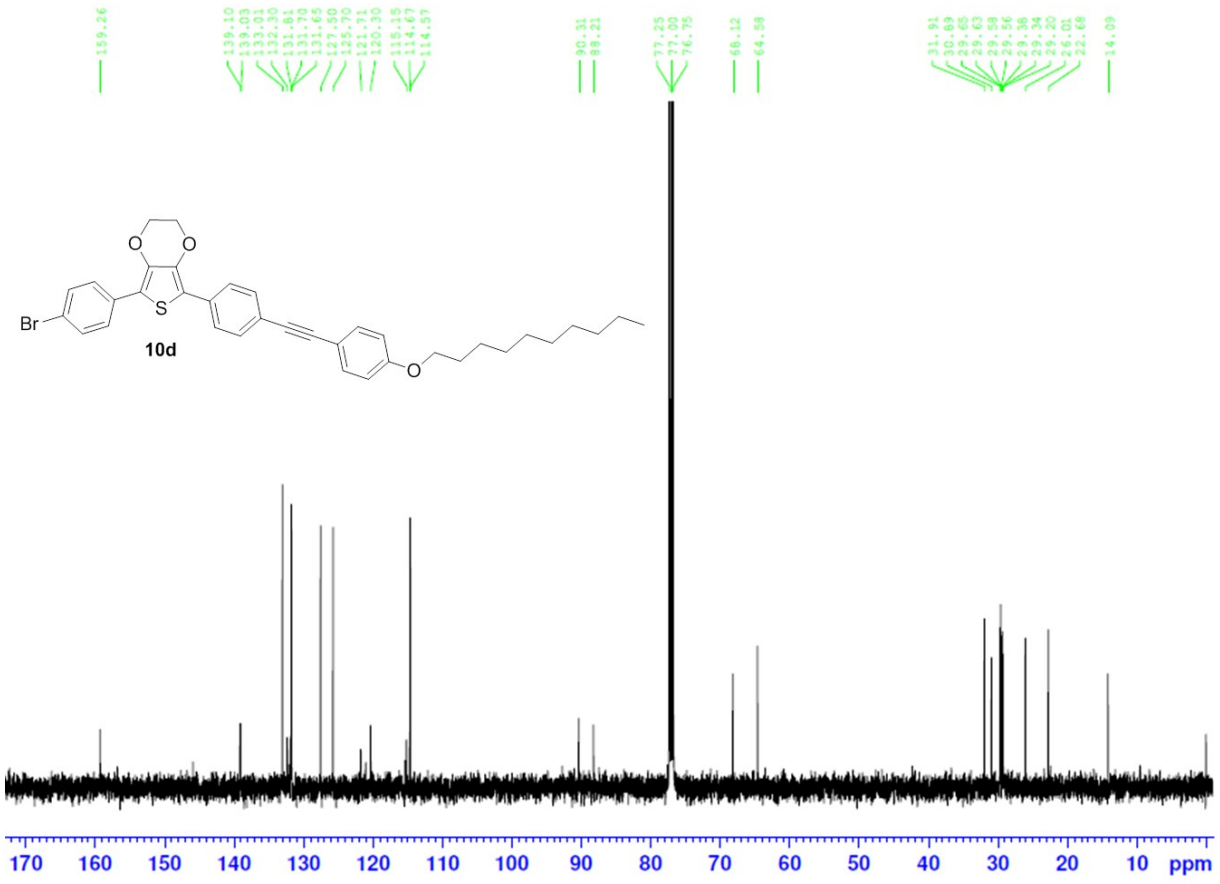

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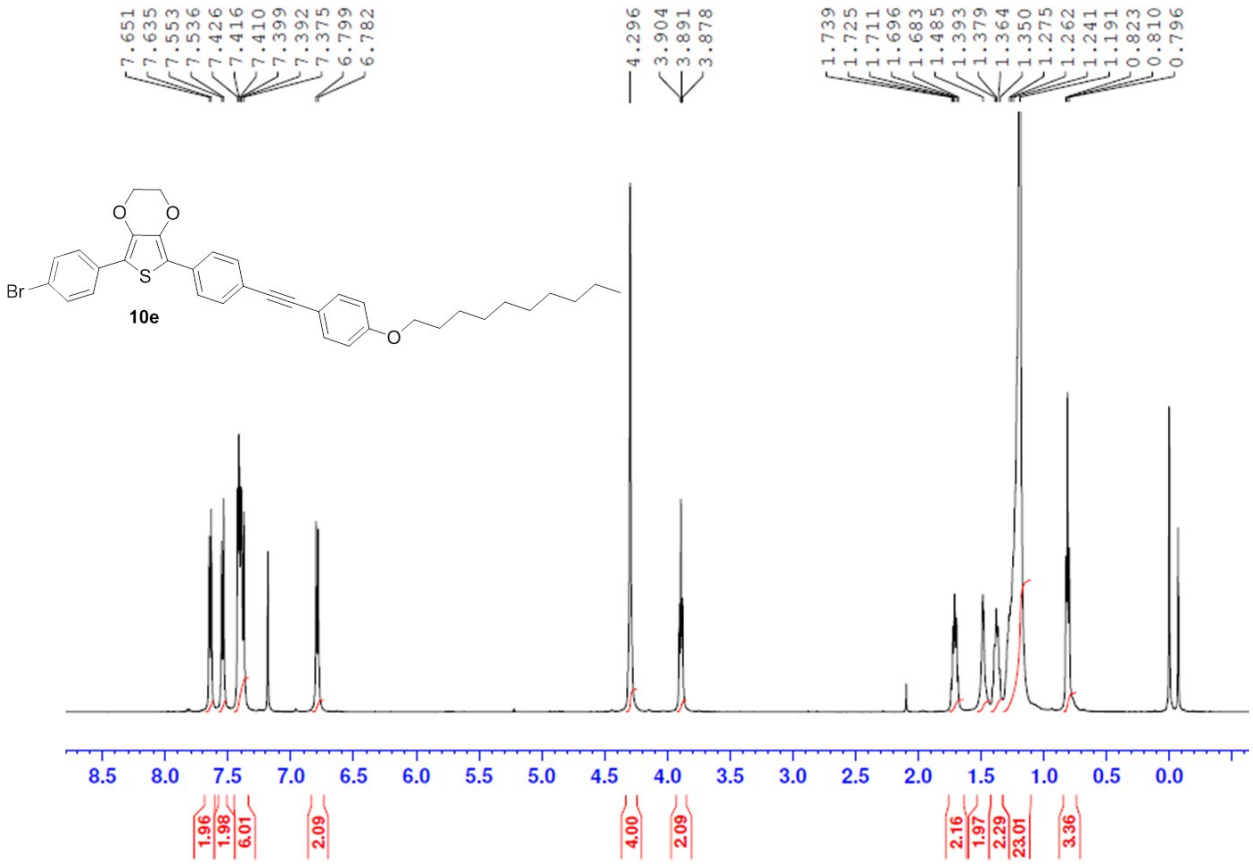

Supplementary Information Fig. S9 ^{1}H NMR