

Supporting information

Donor–Acceptor Conjugated Polymers Based on thieno[3,2-b]indole (TI) and [2,1,3-b]Benzo-thiadiazole (BT) for High-Performance Polymer Solar Cells

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Supporting Information

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Section 1. General

Materials.

4,4'-Dibromobenzene, 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzo[c][1,2,5]thiadiazole, Pd(PPh₃)₄, and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) were purchased from Energy Chemical, J&K and Suna Tech Inc. Toluene and tetrahydrofuran (THF) were freshly distilled prior to use after processed with Na and benzophenone. Other solvents and reagents were directly used unless mentioned otherwise.

General Measurement and Characterization.

¹H NMR and ¹³C NMR data were measured on a Bruker Ultra Shield Plus AV-400 spectrometer in deuterated chloroform solution at 298 K with tetramethylsilane (TMS, $\delta = 0$ ppm) as the internal standard (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz). Elemental analysis was performed on a Vario EL III Elementar system (Elementar Analyzen-systeme, Hanau, Germany). Elemental analyses are the average of three runs. All samples were measured simultaneously for C, H, N and S. Weight ratio of O was measured individually with IR detection. The elemental fractions of Br were estimated based on the measured values of other elements (C, H, N, S and O). All samples used for EA measurement were purified carefully with silica column chromatography for two or three times. After that, the samples were dissolved in diether (HPLC grade). The sample solution then was filtered through a 0.22 μ m syringe filter to a clean sample vial. After diether was carefully removed under

vacuum, the sample was subjected to EA measurement. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was recorded using a Shimadzu AXIMA-CFR mass spectrometer. Molecular weight and polydispersity of the polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene as standard, *o*-DCB (HPLC grade) as eluent at a flow rate of 1.0 mL/min at 120 °C. Differential scanning calorimetry (DSC) analysis and thermogravimetry analysis (TGA) were performed on a Mettler DSC823e thermal analyzer and a Rigaku TG-DTA 8120 thermal analyzer, respectively, with a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. The absorption spectra were recorded on a Shimadzu UV-3600. In the solid, the polymer films were casted on quartz plates with KW-4A spinner. The electrochemical cyclic voltammetry (CV) was tested in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution with Au disk as working electrode, Pt plate as counter electrode, and Ag/AgNO₃ as reference electrode. The polymer films were coated from chloroform solution (ca. 5 mg/mL). X-Ray diffraction (XRD) investigation on thin films casted from *o*-DCB solutions of polymers was carried out with a Bruker D8 advanced diffractometer equipped with a diffracted-beamed monochromator set for Cu K α ($\lambda=1.5418$ Å) radiation. The data were collected using a Ni-filtered Cu-target tube at room temperature in the 2 θ range from 5° to 45° at an angular rate of 0.2 s/step, with a scan step width of 0.02°. Transmission electron microscopy (TEM) was conducted on a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100 kV. The surface morphology was measured via tapping

mode atomic force microscopy (AFM) (Thermo. Auto Probe C P Res.). The external quantum efficiency (EQE) was performed by a source meter, silicon photodiode and a computer-controlled light source-monochromator-Lock-in system.

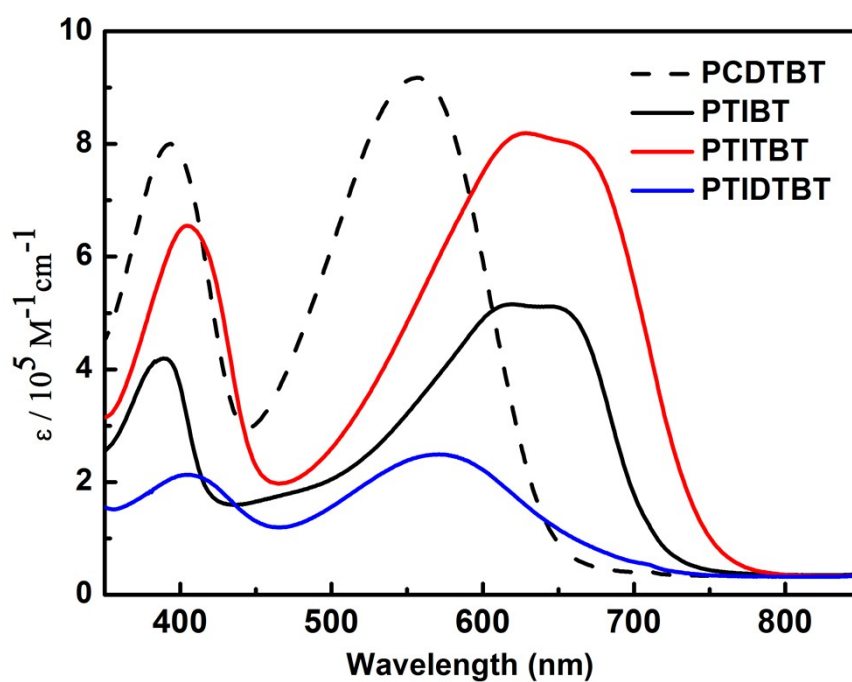


Figure S1. Absorption spectra of PCDTBT, PTIBT, PTITBT, and PTIDTBT in o-DCB with a concentration of 1.0×10^{-6} M.

Section 2. Devices Fabrication and Characterization

BHJ devices.

The BHJ photovoltaic devices were fabricated with the standard configuration as: glass/ITO/PEDOT:PSS/Polymer:PC₇₁BM/Ca/Al. The indium tin oxide (ITO)-coated glass substrates were treated with acetone, following by deionized water, 2-propanol subsequently. The substrates were dried in a laboratory under a nitrogen stream.

The ITO substrate was modified by a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and the thickness of the PEDOT:PSS layer was about 40 nm. *o*-DCB was used in this study as the solvent, the concentration of the polymer:PC₇₁BM blend solution used for spin-coating was 30 mg/mL (polymer/*o*-dichlorobenzene) and filtered through a 0.45 μm poly(tetrafluoroethylene) filter, and spin-casted at 900 for 5 s then 1500 rpm for 30 s onto the PEDOT:PSS layer with a thickness of \sim 110 nm. The as-prepared films were dried under nitrogen atmosphere at room temperature and annealed at 25°C, 80°C, 150°C for 15 min in nitrogen-filled glovebox. Then the devices were completed by evaporating Ca/Al metal electrodes with an area of 0.11 cm² as defined by masks. The current–voltage curves were measured under 100 mW cm⁻² standard AM 1.5G spectrum (Oriel 91160, 300 W).

Hole-Only Devices.

Based on the space-charge-limited currents (SCLC) method, we conducted the hole mobility measurement with the device structure of

ITO/PEDOT:PSS/polymer:PC₇₁BM layer/Al. The SCLC mobility is calculated according to the Mott–Gurney law:

$$J = (9/8)\epsilon_0\epsilon_r\mu_h(V^2/d^3)$$

where J stands for current density, d is the thickness of the active layer, $V (=V_{\text{appl}} - V_{\text{bi}})$ is the internal voltage of the device, V_{appl} is the applied potential and V_{bi} is the built-in voltage, ϵ_0 is permittivity of free space, ϵ_r is the relative permittivity, μ_h is the hole mobility.

Section 3. Devices optimization

Table S1. Device performance of the PSCs based on polymer:PC₇₁BM (1:3, w/w) with different thermal annealing temperature and DIO additive treatment.

Blend	Annealing Temp.(°C)	J _{sc} (mA/cm ²)	Voc (V)	FF (%)	PCE (%)
PTIBT:PC ₇₁ BM	25	5.47	0.66	35.02	1.23
	80	5.58	0.66	35.90	1.31
	150	5.60	0.71	39.70	1.57
	150 ^a	5.86	0.83	33.20	1.61
PTITBT:PC ₇₁ BM	25	14.19	0.66	54.80	5.10
	80	13.63	0.66	56.44	5.11
	150	13.92	0.69	61.80	5.83
	150 ^a	12.72	0.66	56.20	4.73
PTIDTBT:PC ₇₁ BM	25	6.26	0.64	38.33	1.54
	80	7.27	0.60	40.90	1.79
	150	6.29	0.50	37.39	1.17
	80 ^a	3.93	0.63	67.60	1.68

^a: DIO additive.

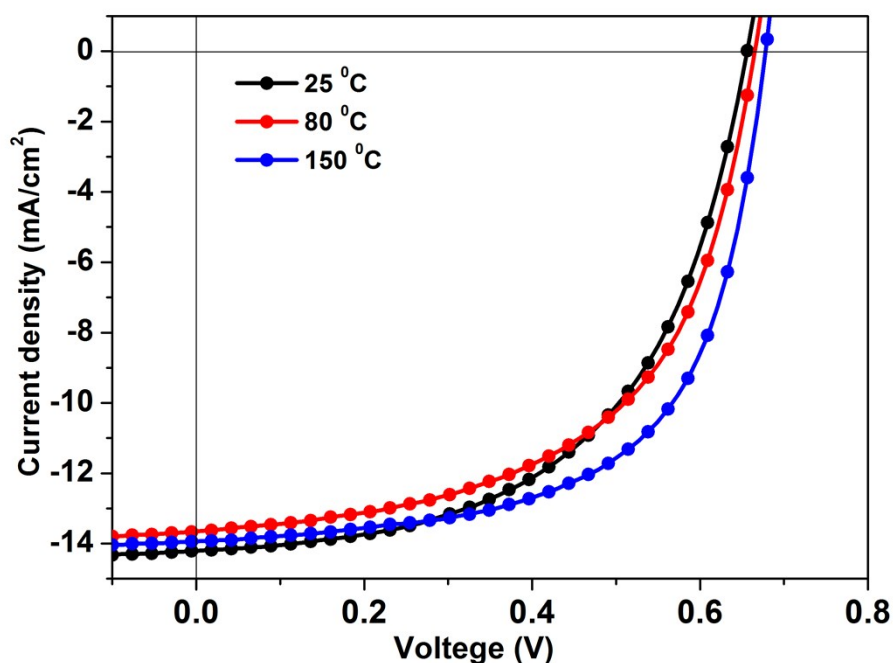


Figure S2. $J-V$ curves of PSCs based on PTITBT:PC₇₁BM (1:3, w/w) with different thermal annealing temperature under simulated AM 1.5 G solar irradiation.

Table S2. Device Performance of the PSCs based on PTITBT:PC₇₁BM (1:3, w/w) with Different Thermal Annealing Temperature and DIO Additive Treatment (for each fabrication condition, 2 typical devices were selected and marked in 1 to 8 accordingly).

Blend	Annealing Temp.(°C)	J _{sc} (mA/cm ²)	Voc (V)	FF (%)	PCE (%)	Device number
PTITBT:PC ₇₁ BM	25	14.40	0.66	53.72	5.08	1
		14.19	0.66	54.80	5.10	2
	80	13.31	0.67	56.86	5.03	3
		13.63	0.66	56.44	5.11	4
	150	13.92	0.69	61.80	5.83	5
		13.76	0.68	60.70	5.71	6
	150 ^a	12.72	0.66	56.18	4.73	7
		12.40	0.66	57.10	4.66	8

a: DIO additive.

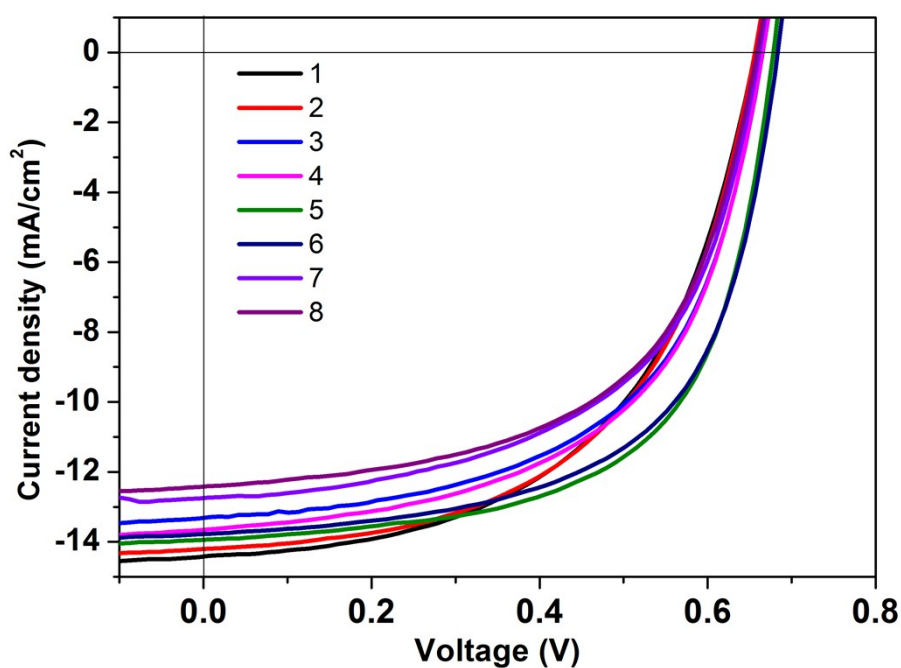


Figure S3. $J-V$ curves of the PSCs based on PTITBT:PC₇₁BM (1:3, w/w) with different thermal annealing temperature and DIO additive treatment under simulated AM 1.5 G solar irradiation (for each fabrication condition, 2 typical devices were selected and marked in 1 to 8 accordingly).

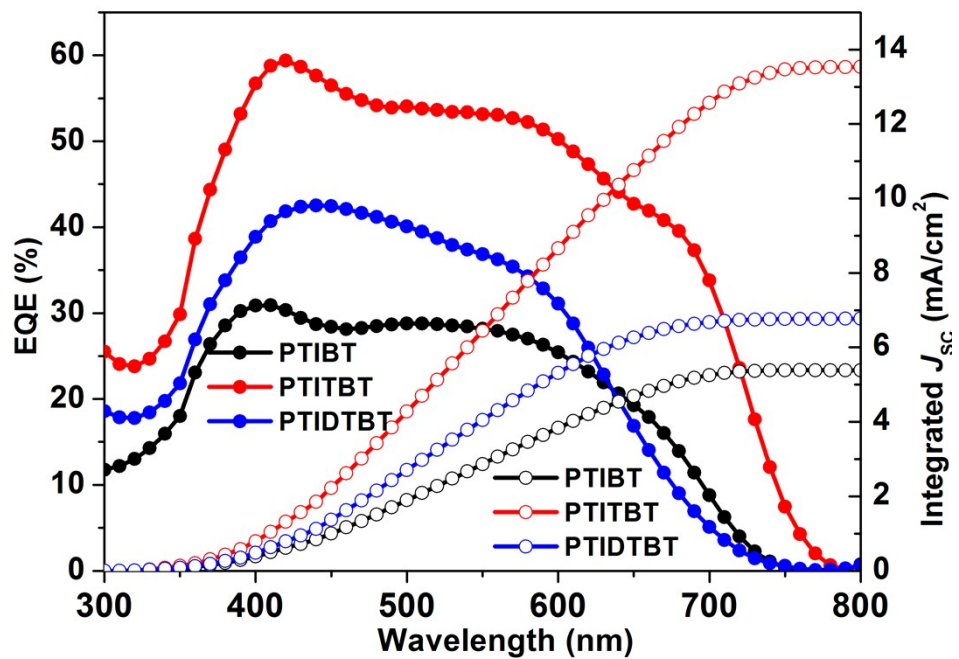


Figure S4. EQE and corresponding integrated J_{sc} curves of PSCs based on polymer:PC₇₁BM (1:3, w/w) with thermal annealing 150 °C under standard solar illumination conditions.

Section 4. SCLC mobility plots

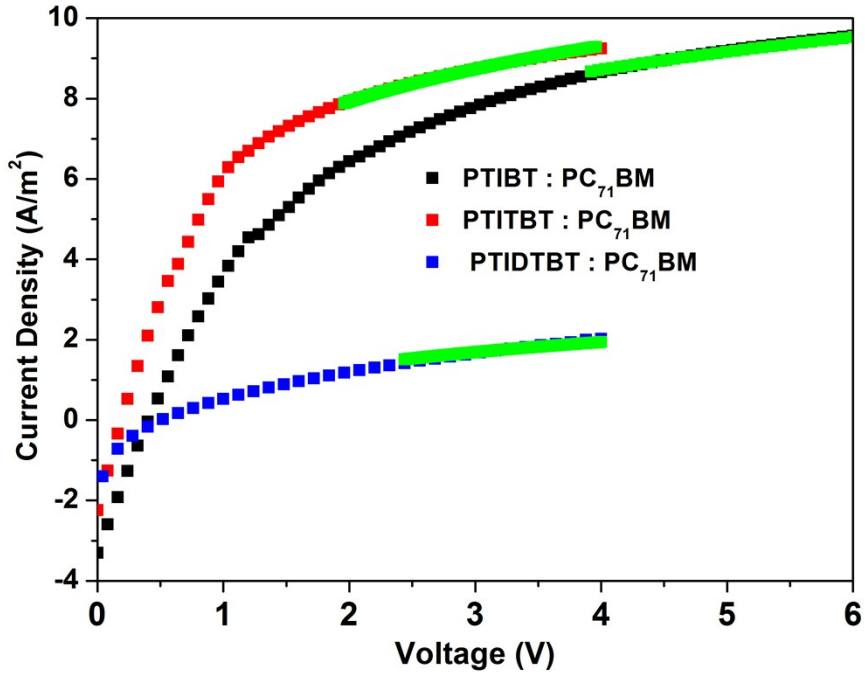


Figure S5. Current density (J)–voltage (V) curves for **PTIBT**, **PTITBT** and **PTIDTBT** based device (the symbols were experimental data for transport of hole and the green lines were fitted according to the space-charge-limited-current model).

Section 5. NMR spectra

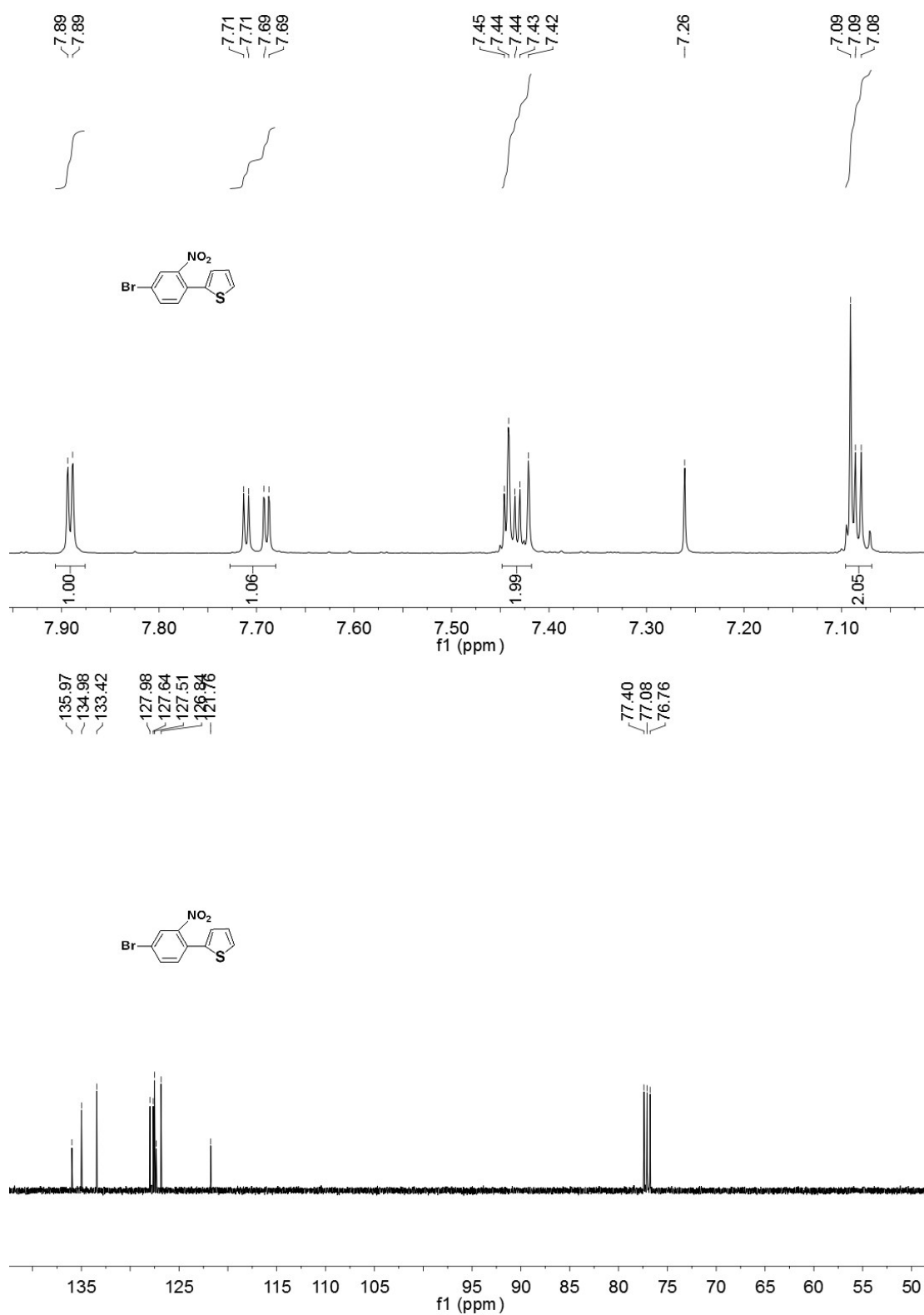


Figure S6. ¹H and ¹³C NMR spectra of **2** in CDCl₃.

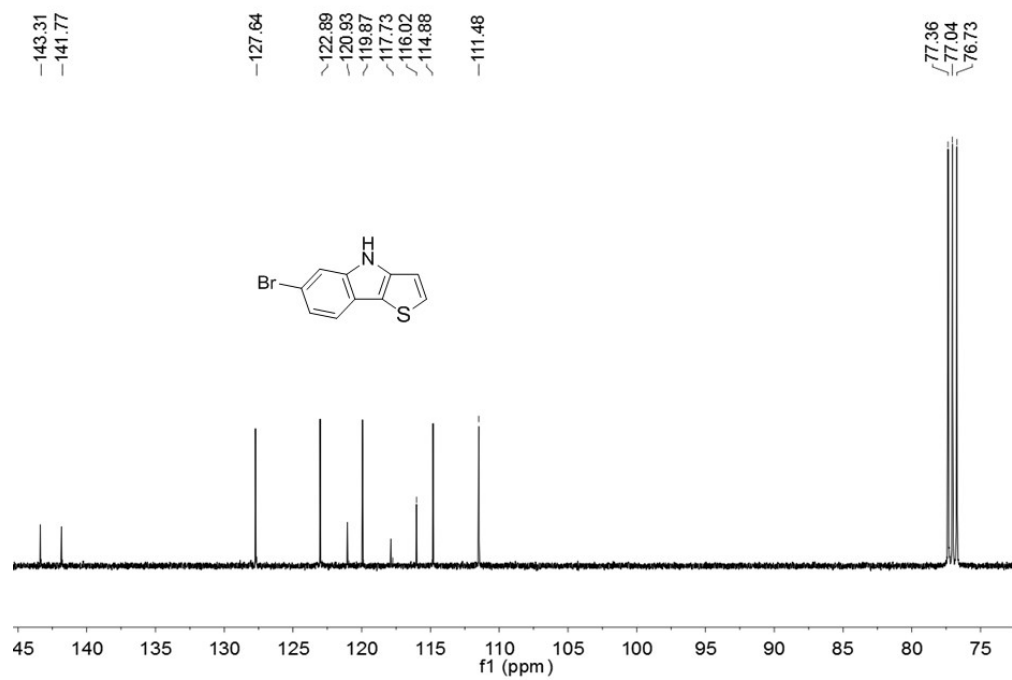
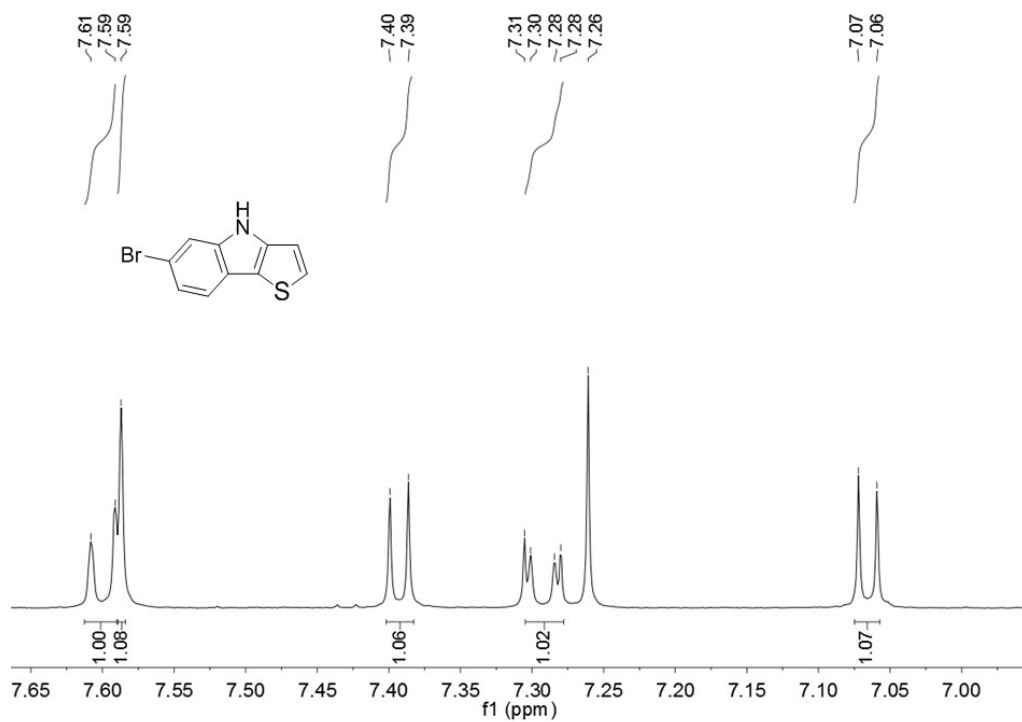


Figure S7. ^1H and ^{13}C NMR spectra of **3** in CDCl_3 .

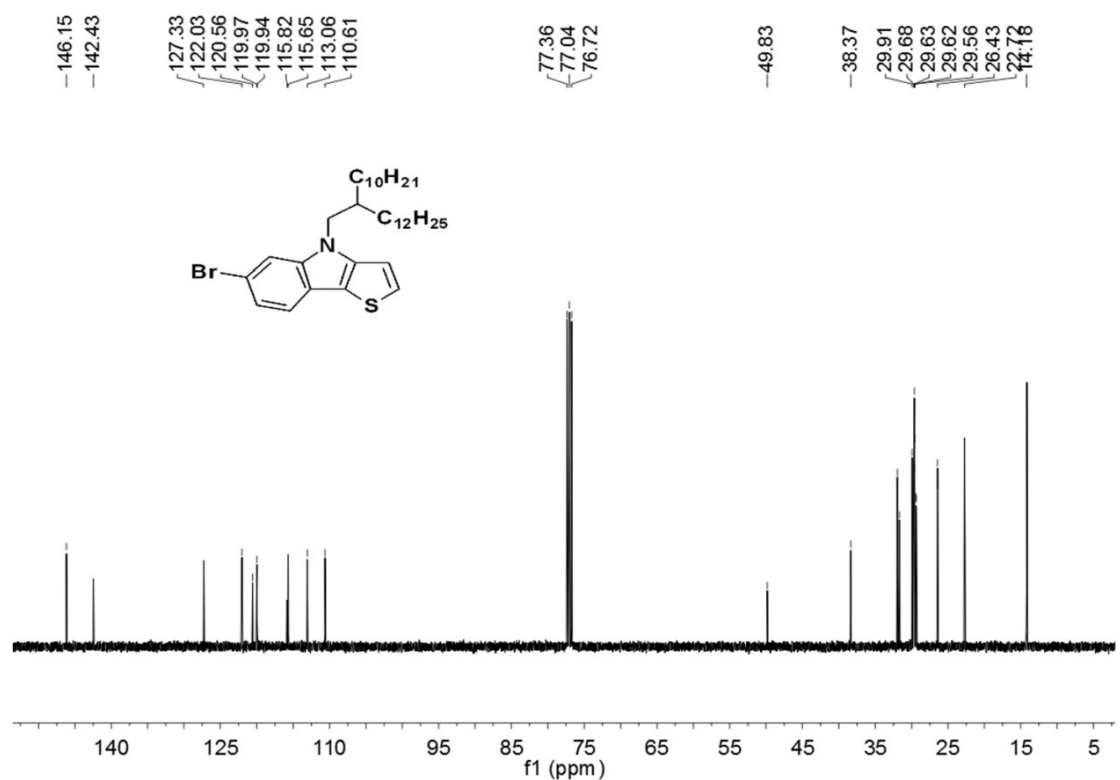
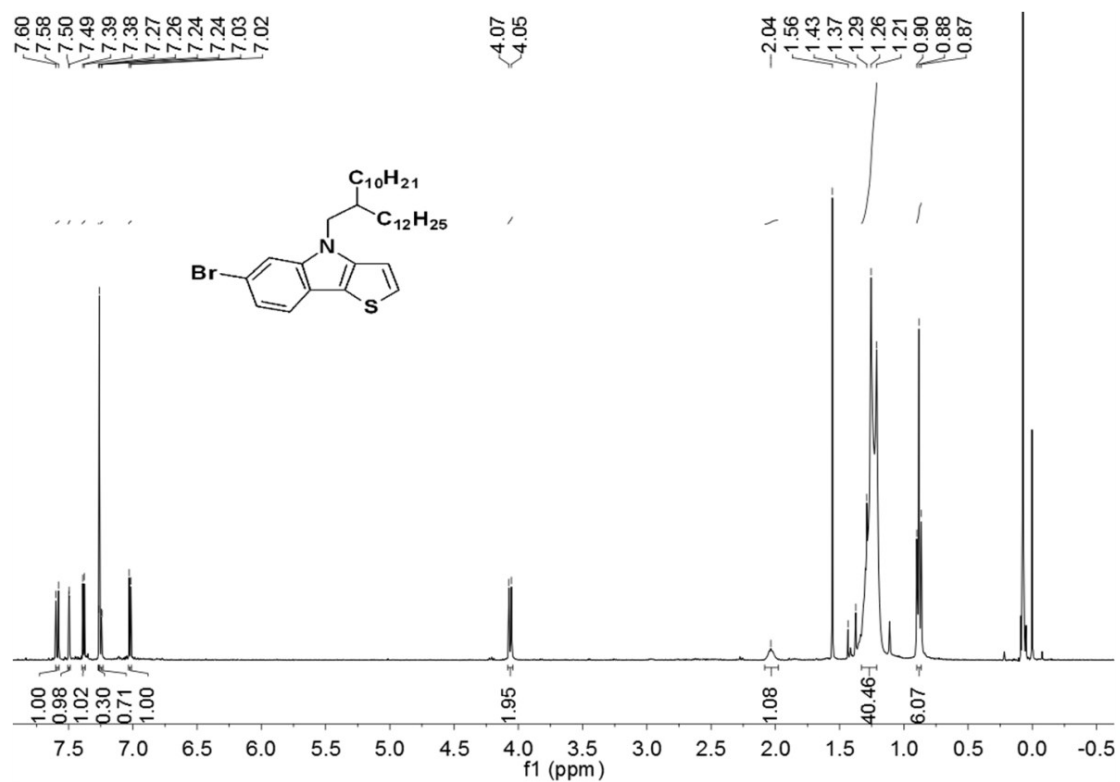


Figure S8. ¹H and ¹³C NMR spectra of **4** in CDCl₃.

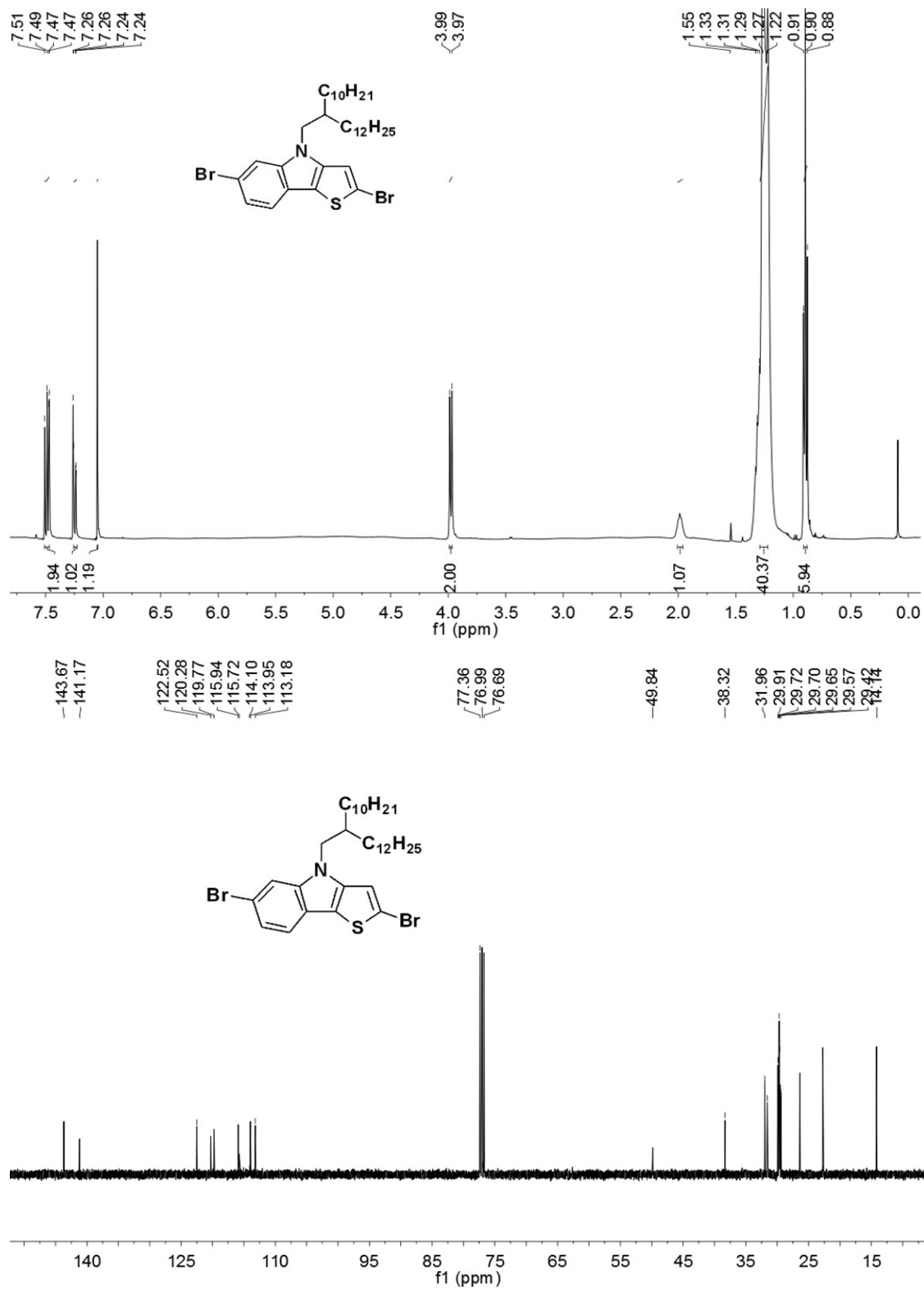


Figure S9. ¹H and ¹³C NMR spectra **M1** in CDCl₃.

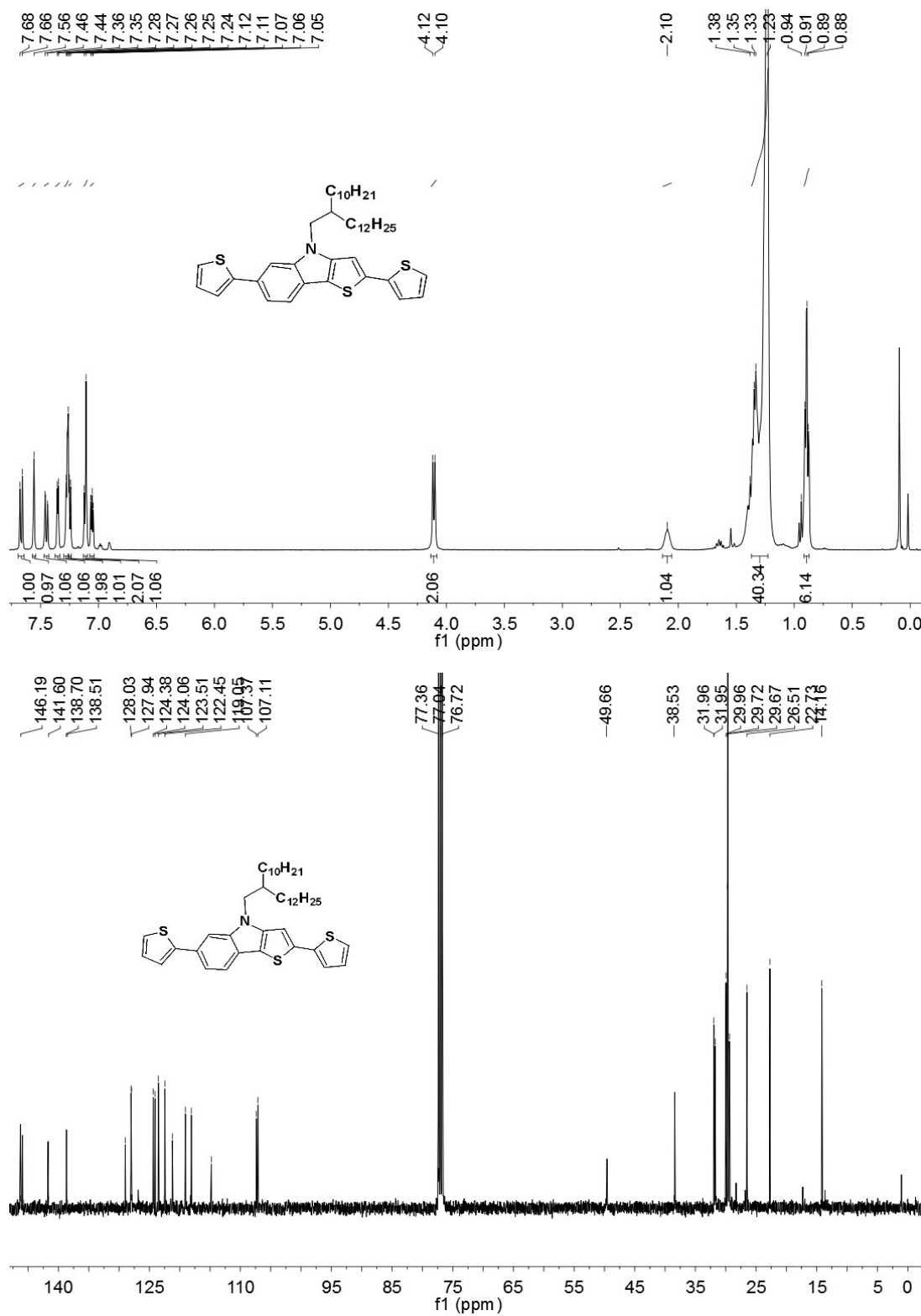


Figure S10. ¹H and ¹³C NMR spectra of **5** in CDCl₃.

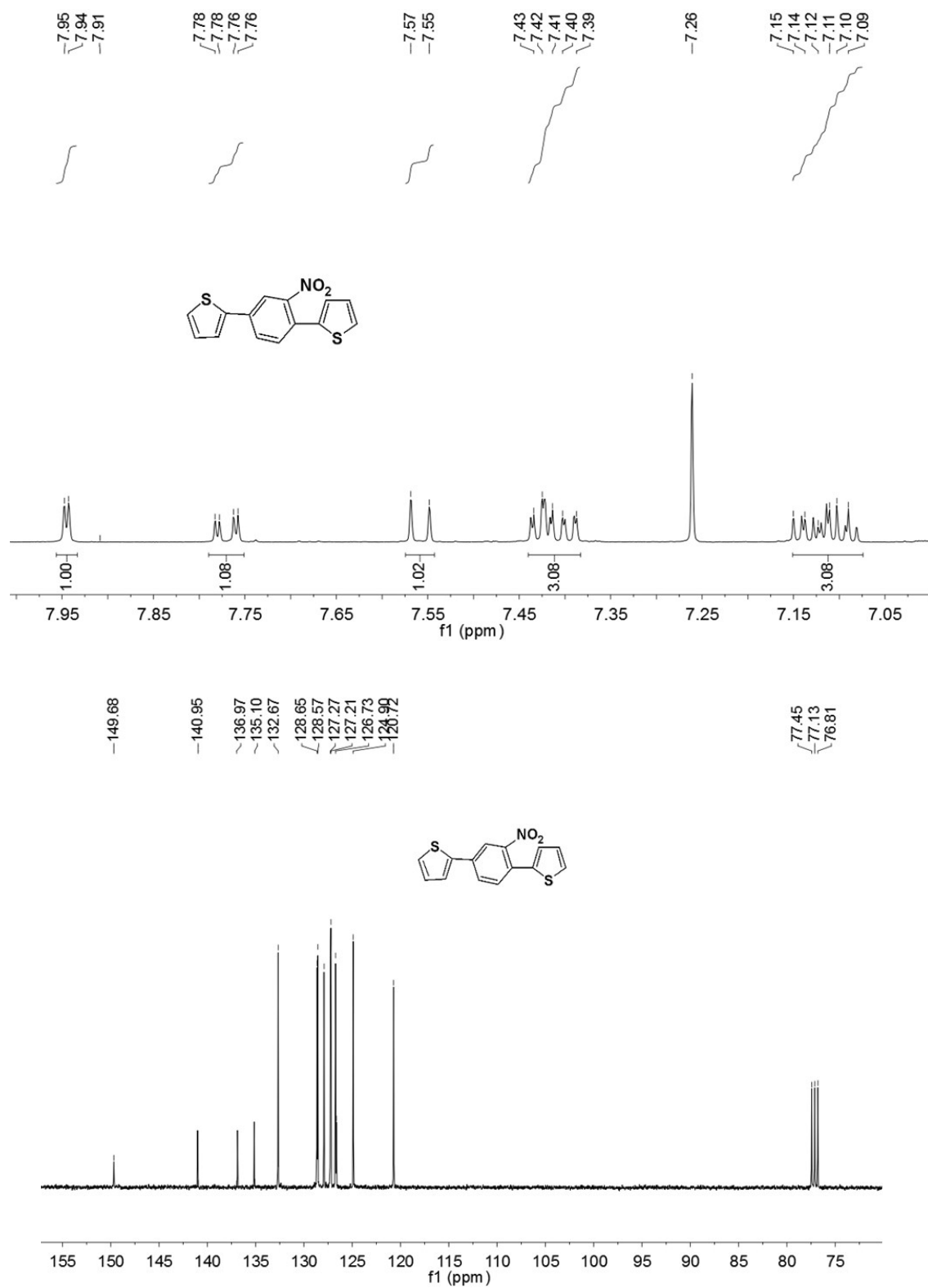


Figure S11. ¹H and ¹³C NMR spectra of **6** in CDCl₃.

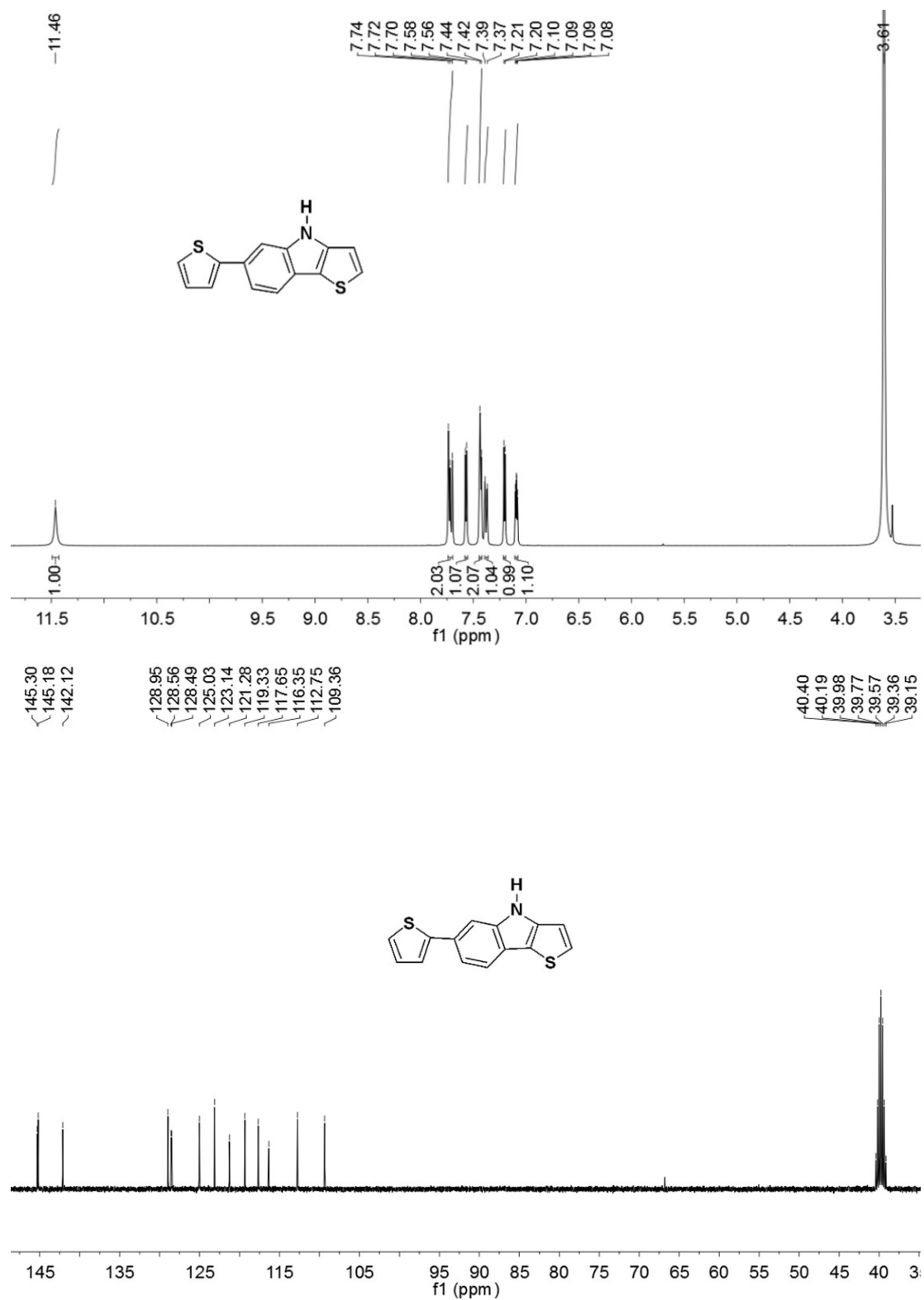


Figure S12. ¹H and ¹³C NMR spectra of 7 in DMSO-d₆.

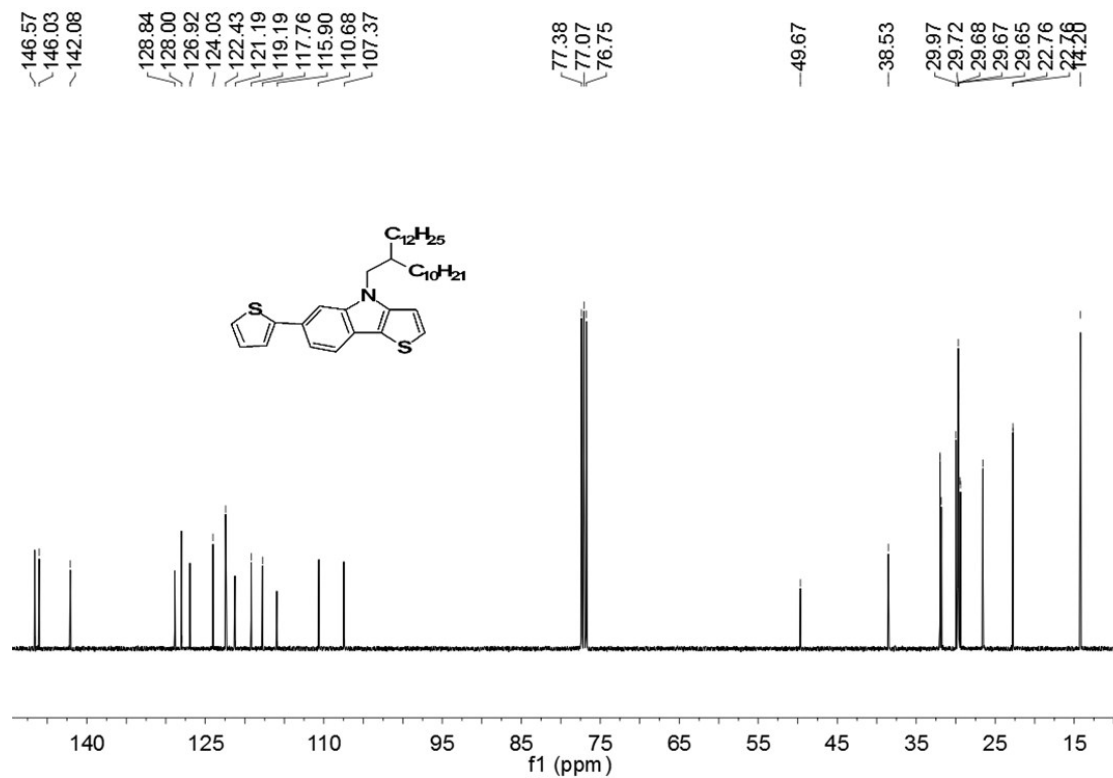
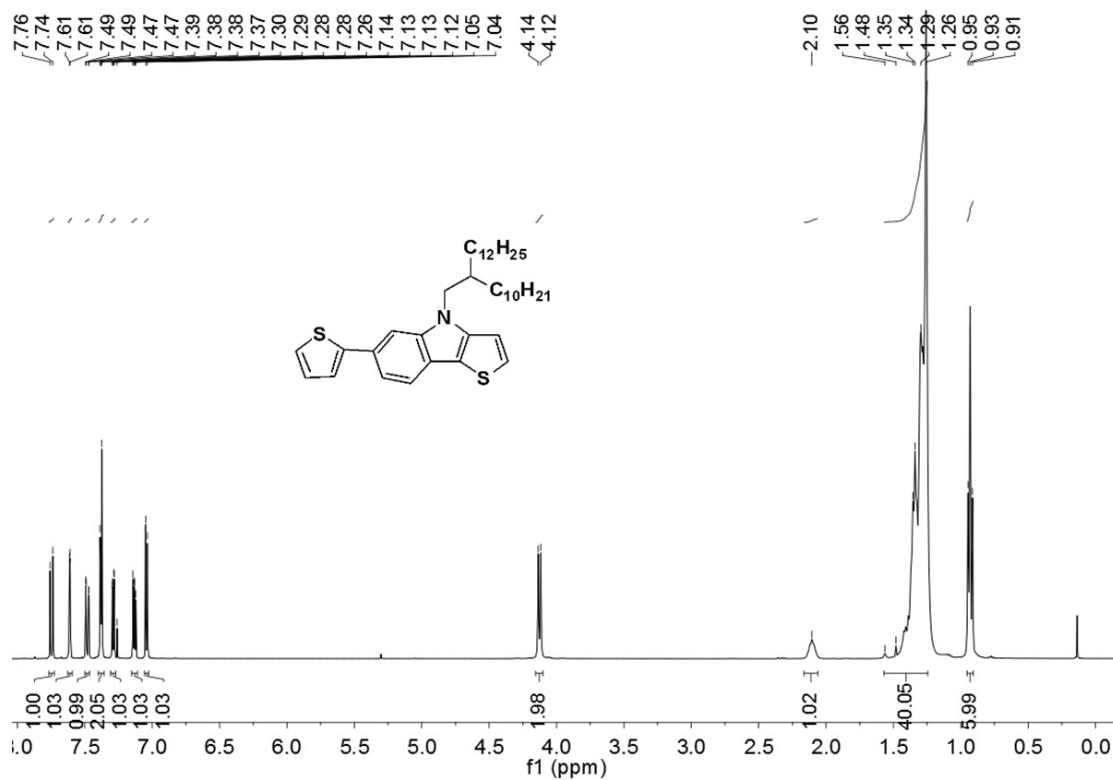


Figure S13. ¹H and ¹³C NMR spectra of **8** in CDCl₃.

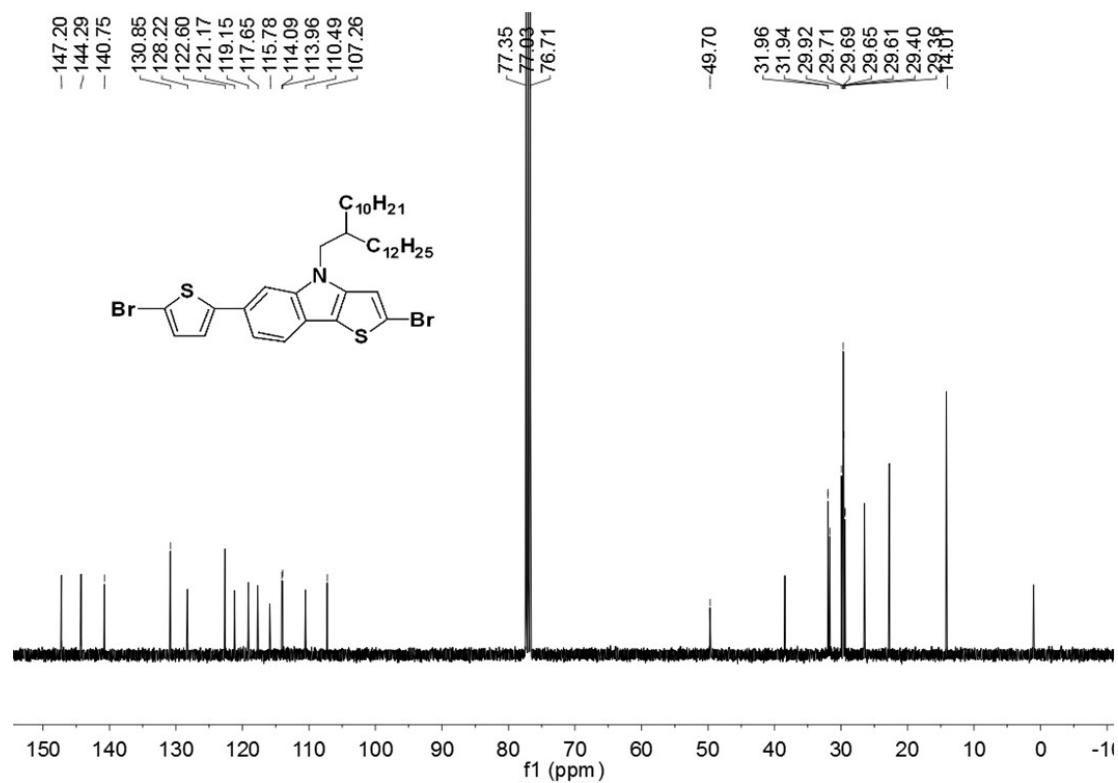
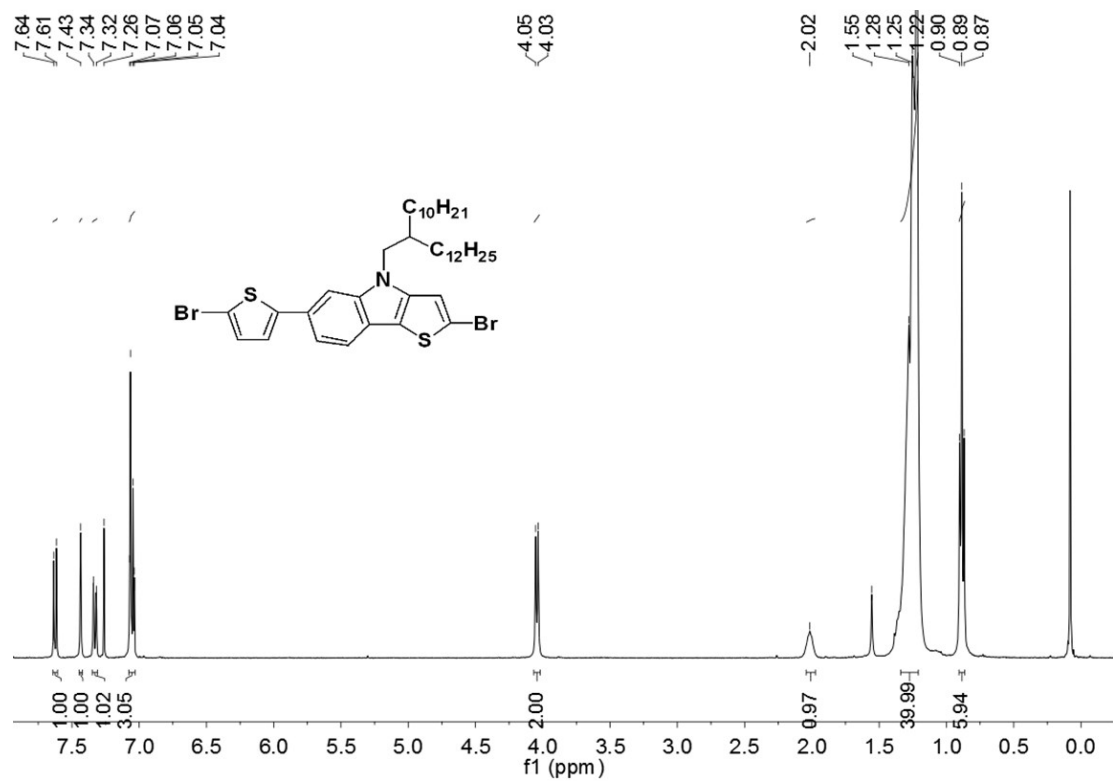


Figure S14. ¹H and ¹³C NMR spectra of M2 in CDCl₃.

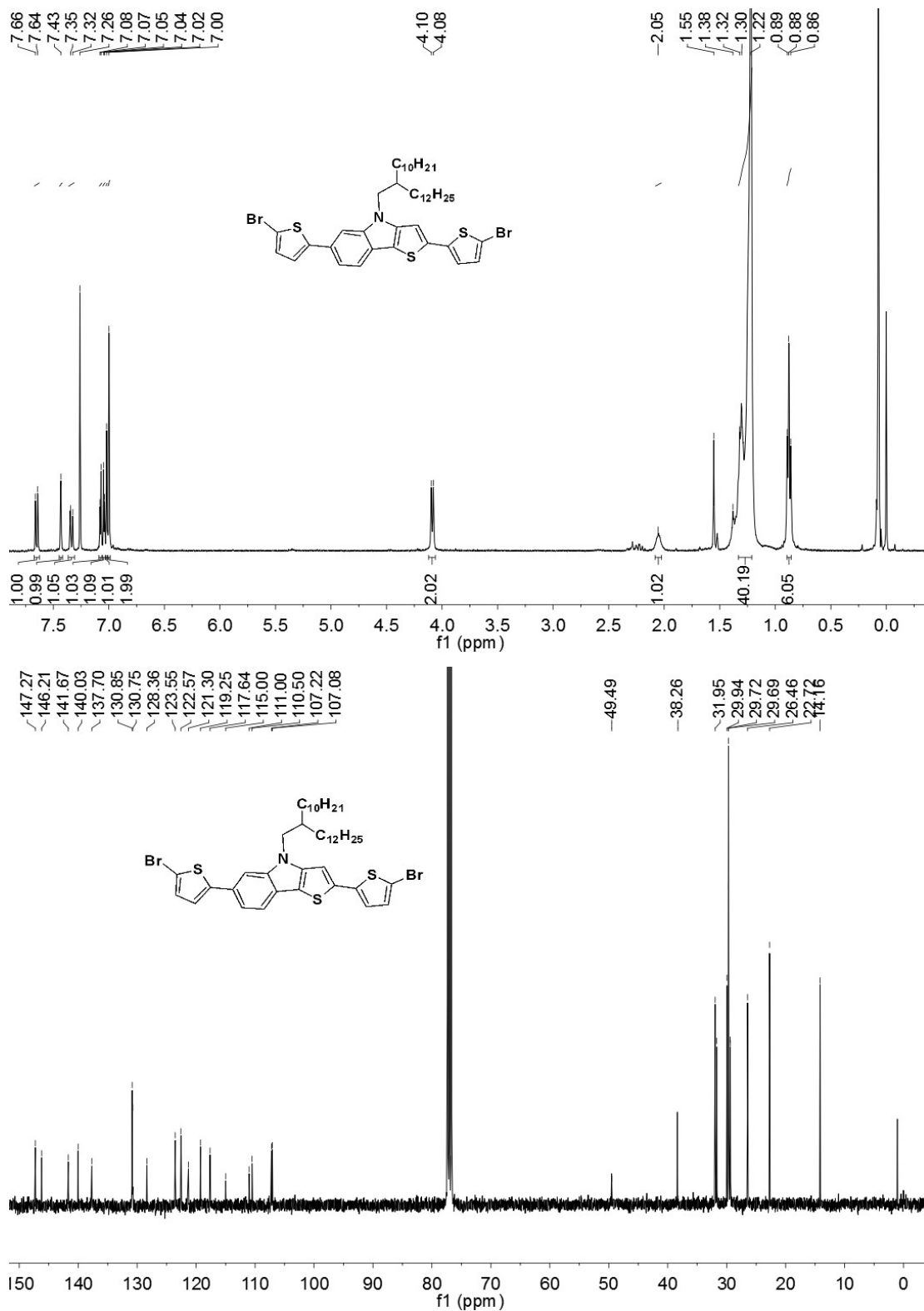


Figure S15. ¹H and ¹³C NMR spectra of **M3** in CDCl₃.

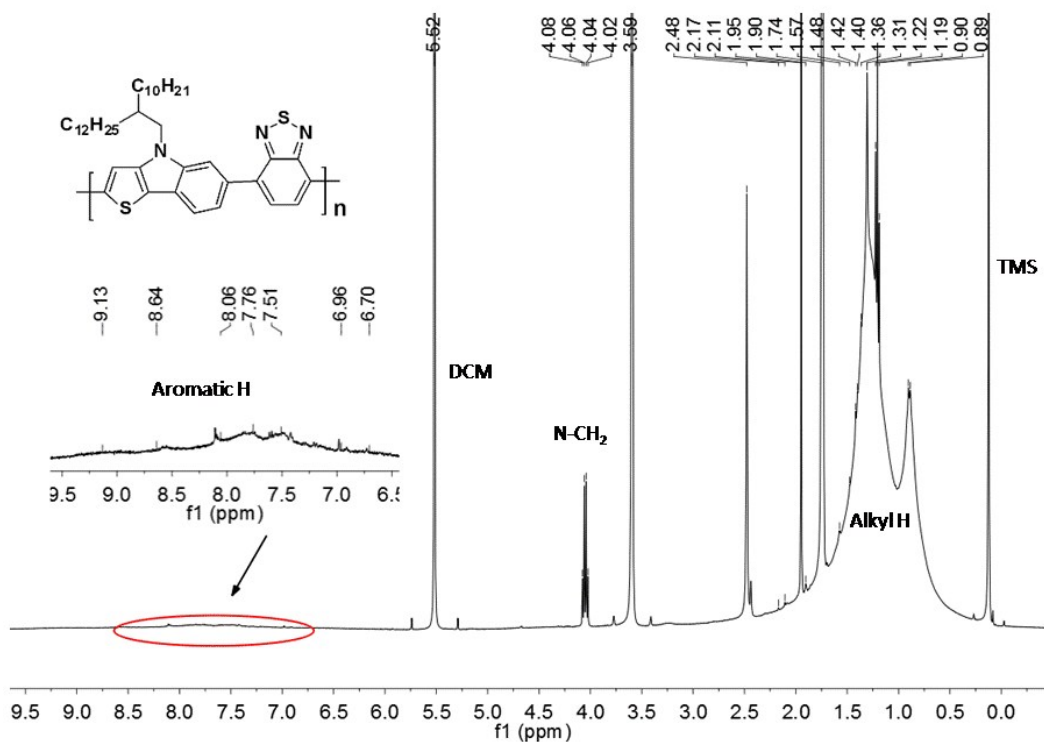


Figure S16. ¹H NMR spectrum of the copolymer PTIBT in THF-d₈

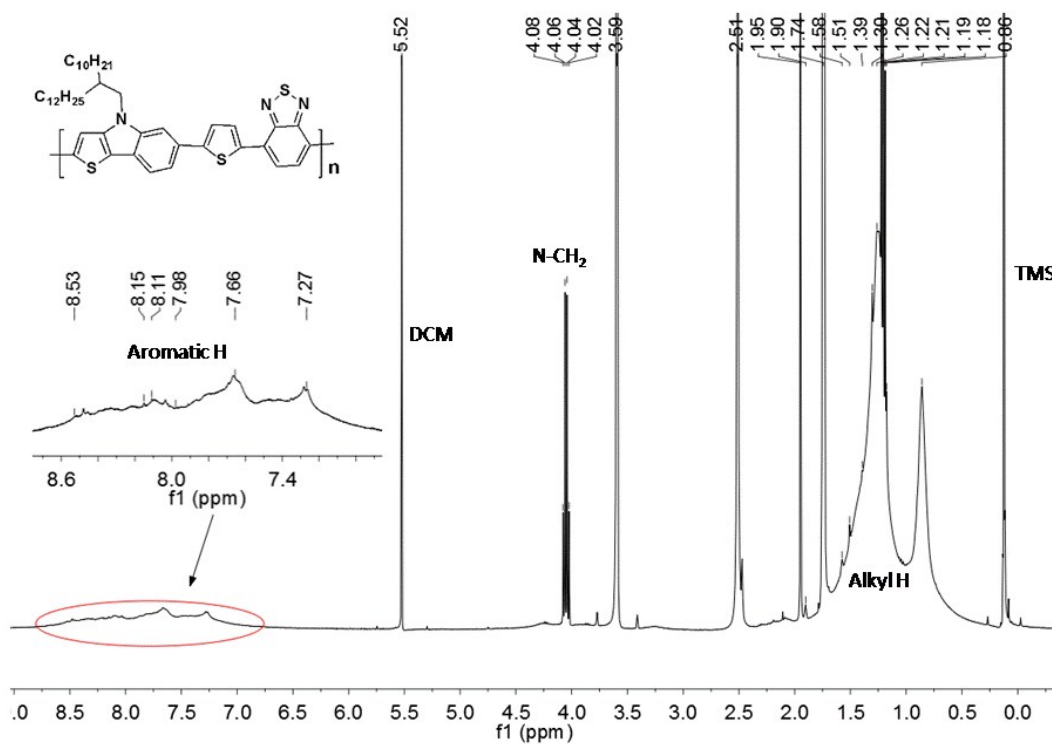


Figure S17. ¹H NMR spectrum of the copolymer PTITBT in THF-d₈

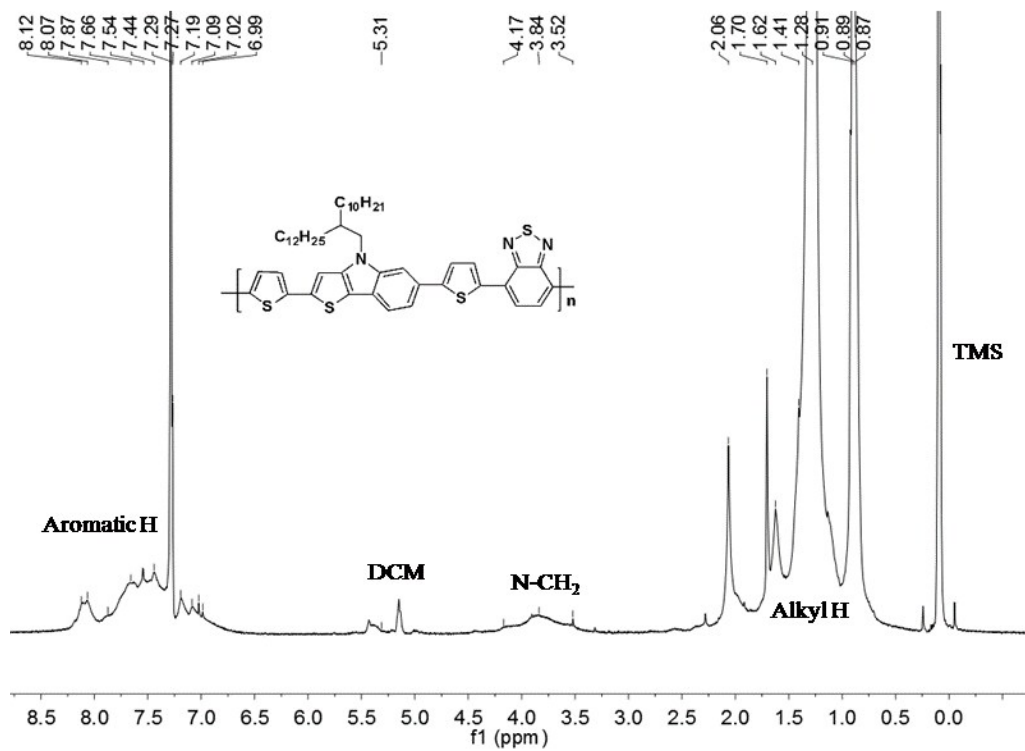


Figure S18. ^1H NMR spectrum of PTIDTBT in CDCl_3 .