Electronic Supplementary Material (ESI) for Materials Advances.

Supporting information

Optimized charge transport in *N*-substituted isatin-based acceptor-donor-acceptor small molecules by regulating side chain length for solution-processable organic thin-film transistors

Wenyu Cai,[a,c†] Jiyun Lee,[b,†] Yao Zhao,[a] Boseok Kang,[b,*] Guobing Zhang[a,c*]

[a]Special Display and Imaging Technology Innovation Center of Anhui Province, National Engineering Lab of Special Display Technology, Academy of Opto-Electronic Technology, Anhui Province Key Laboratory of Measuring Theory and Precision Instrument, Hefei University of Technology, Hefei 230009, China. Email: gbzhang@hfut.edu.cn

[b]SKKU Advanced Institute of Nanotechnology, Department of Nano Science and Technology, and Department of Nano Engineering, Sungkyunkwan University (SKKU), Suwon 16419, the Republic of Korea. Email: bskang88@skku.edu

[c]School of Chemistry and Chemical Engineering, Key Laboratory of Advance Functional Materials and Devices of Anhui Province

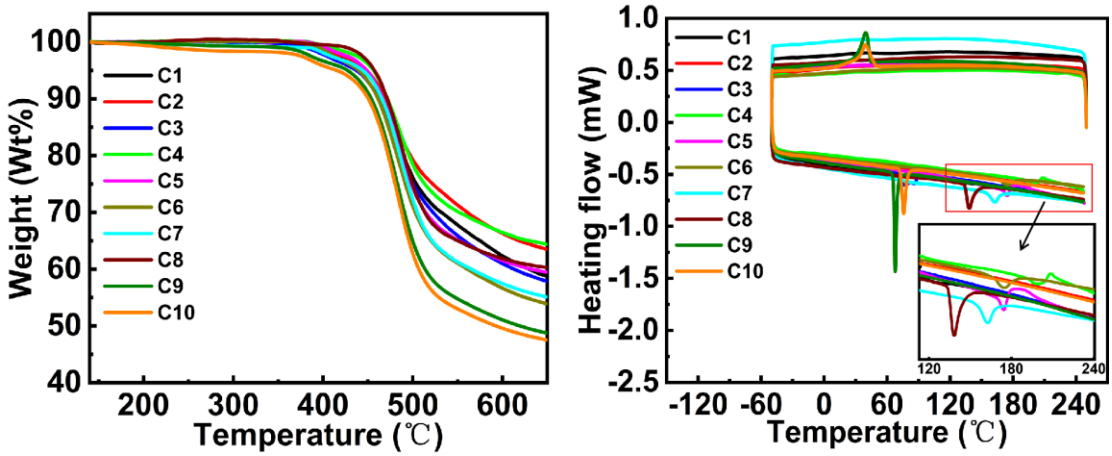


Fig. S1. TG and DSC curves of small molecuels.

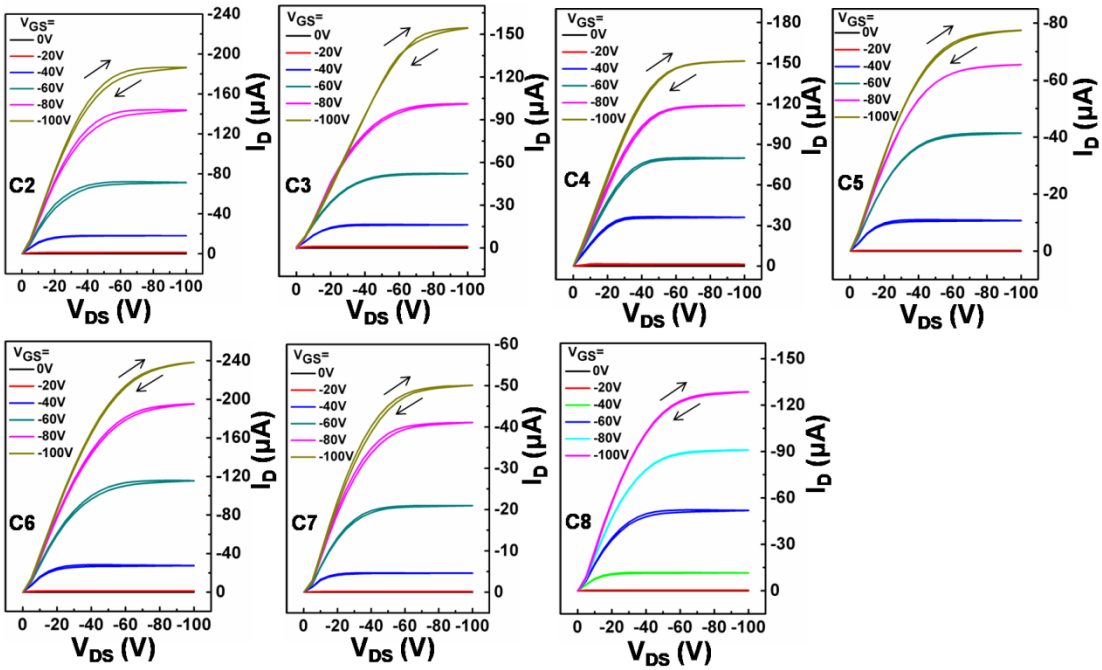


Fig. S2. Typical output curves of small molecule-based devices.

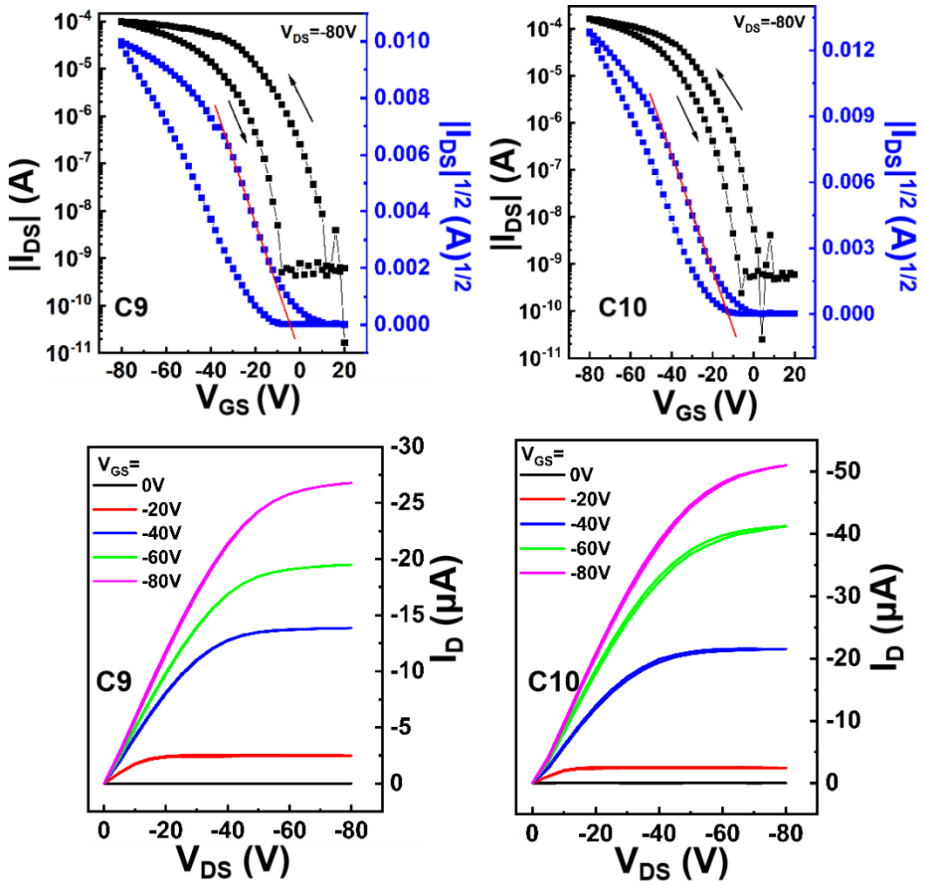


Fig. S3. Transfer and output curves of **C9** and **C10** small molecules.

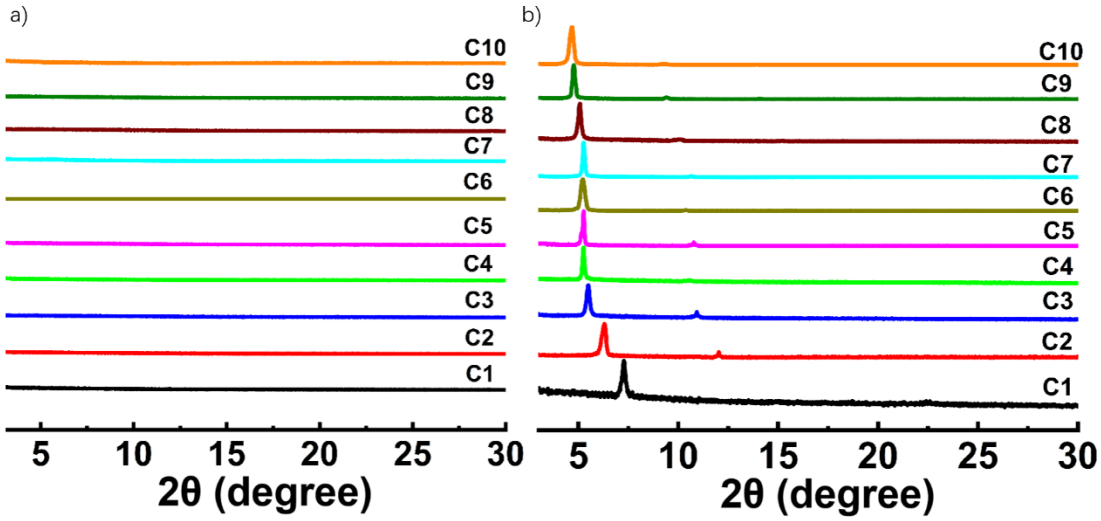


Fig. S4. XRD patterns of small molecule film with and without annealing.

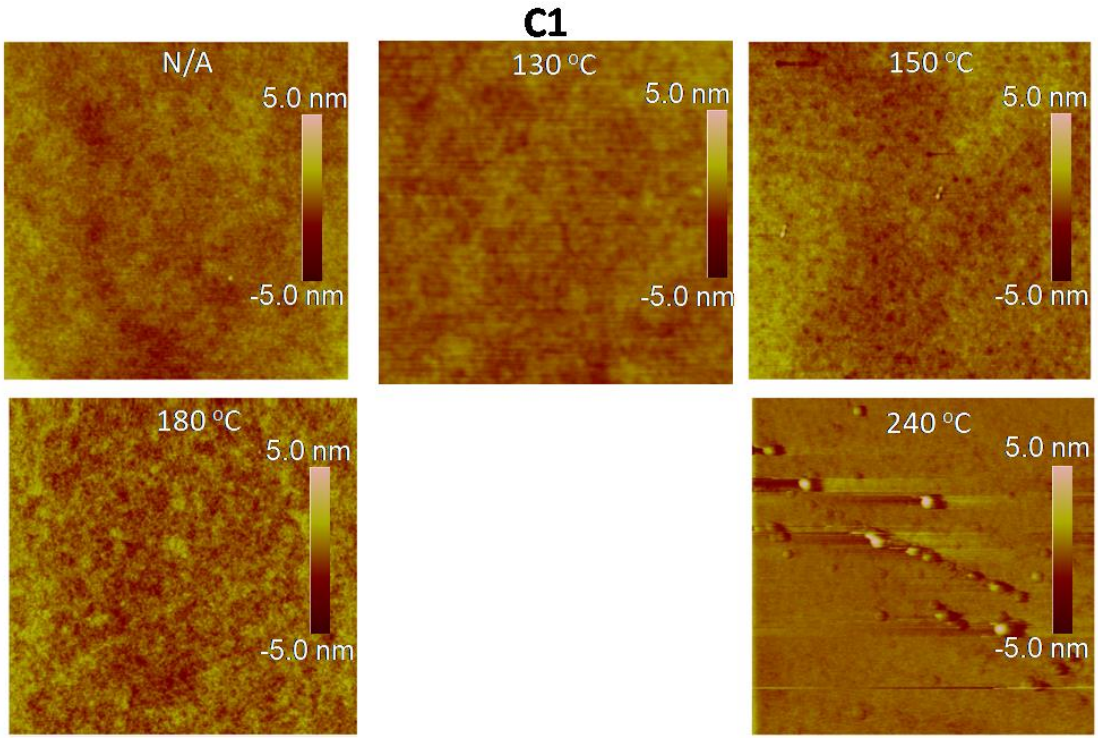


Fig. S5. AFM height images (5×5 μm) of **C1** films spin-coated on OTS-treated SiO_2/Si substrates and annealed at different temperatures.

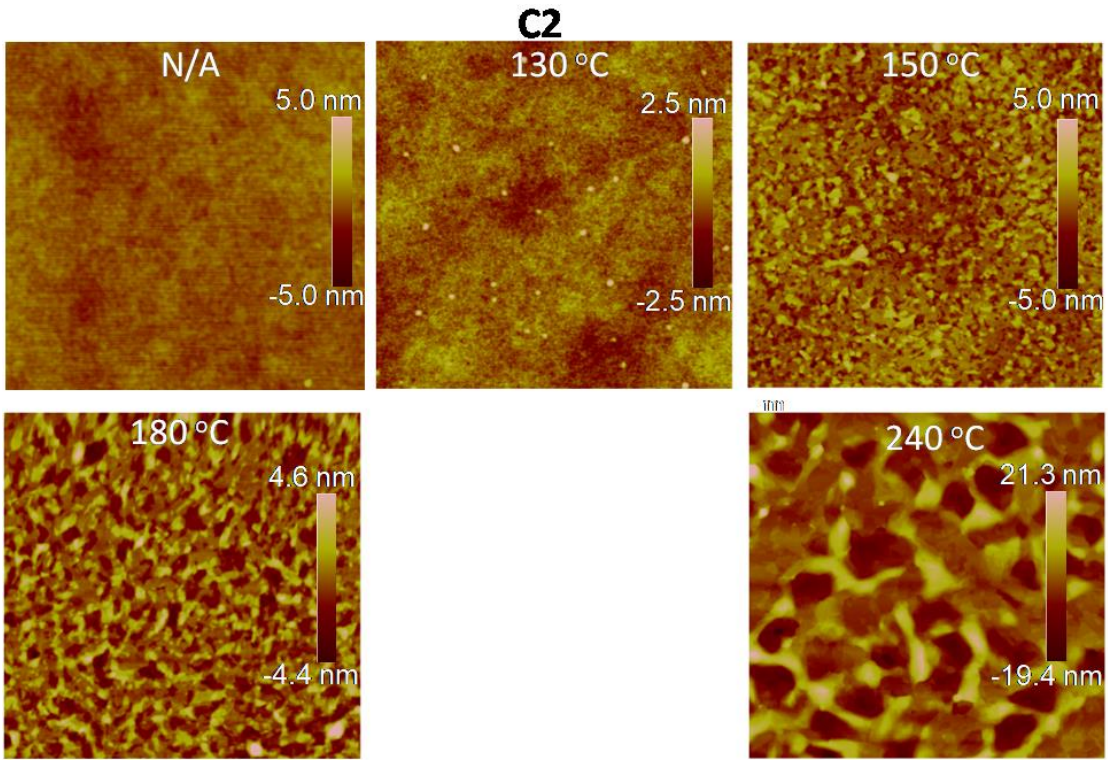


Fig. S6. AFM height images (5×5 μm) of **C2** films spin-coated on OTS-treated SiO_2/Si substrates and annealed at different temperatures.

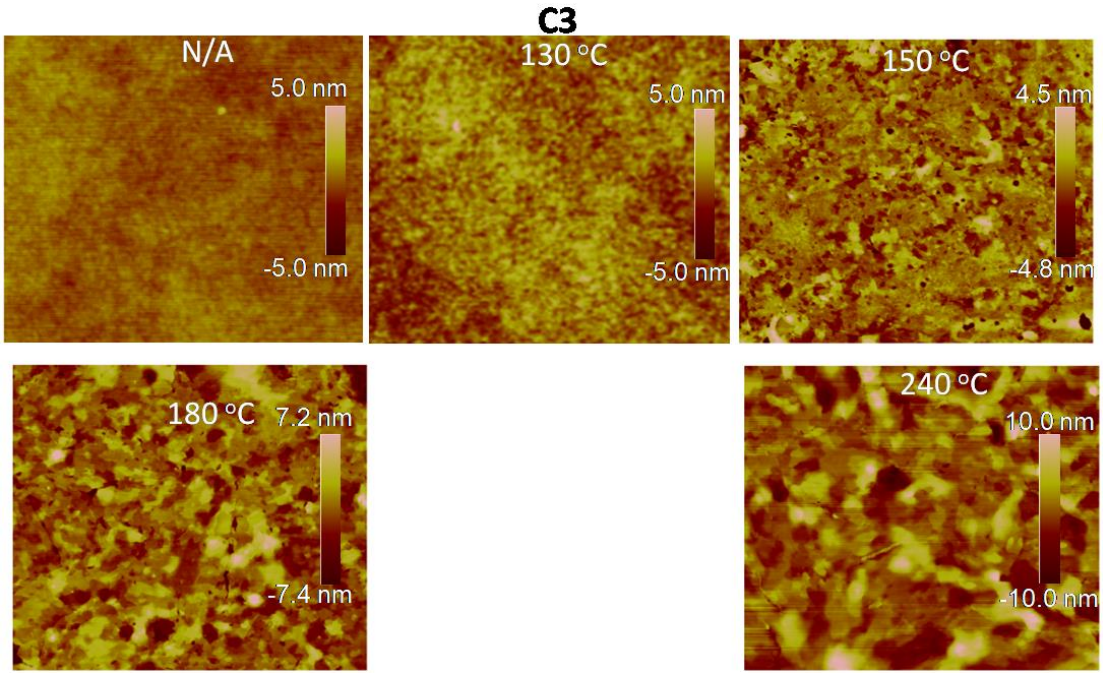


Fig. S7. AFM height images (5×5 μm) of **C3** films spin-coated on OTS-treated SiO_2/Si substrates and annealed at different temperatures.

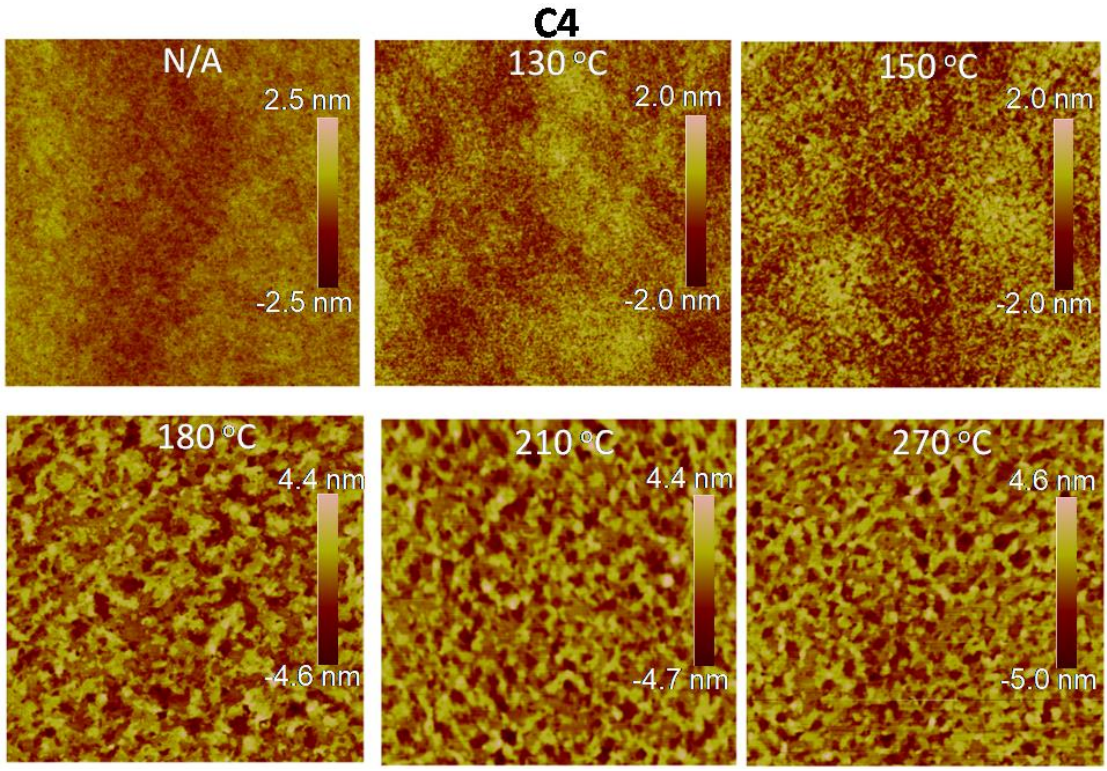


Fig. S8. AFM height images (5×5 μm) of **C4** films spin-coated on OTS-treated SiO_2/Si substrates and annealed at different temperatures.

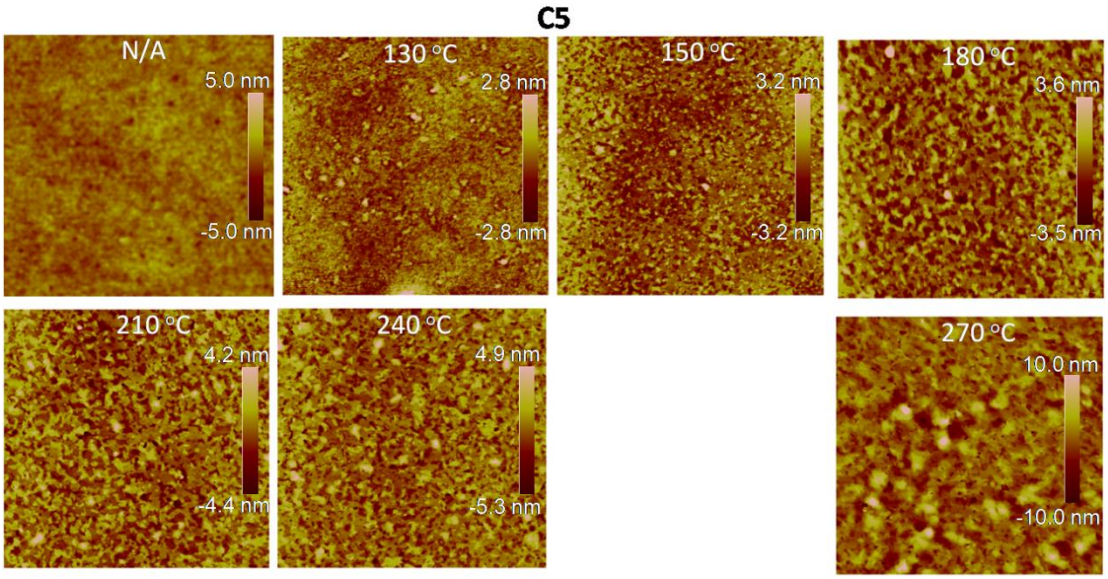


Fig. S9. AFM height images (5 ×5 μm) of **C5** films spin-coated on OTS-treated SiO_2/Si substrates and annealed at different temperatures.

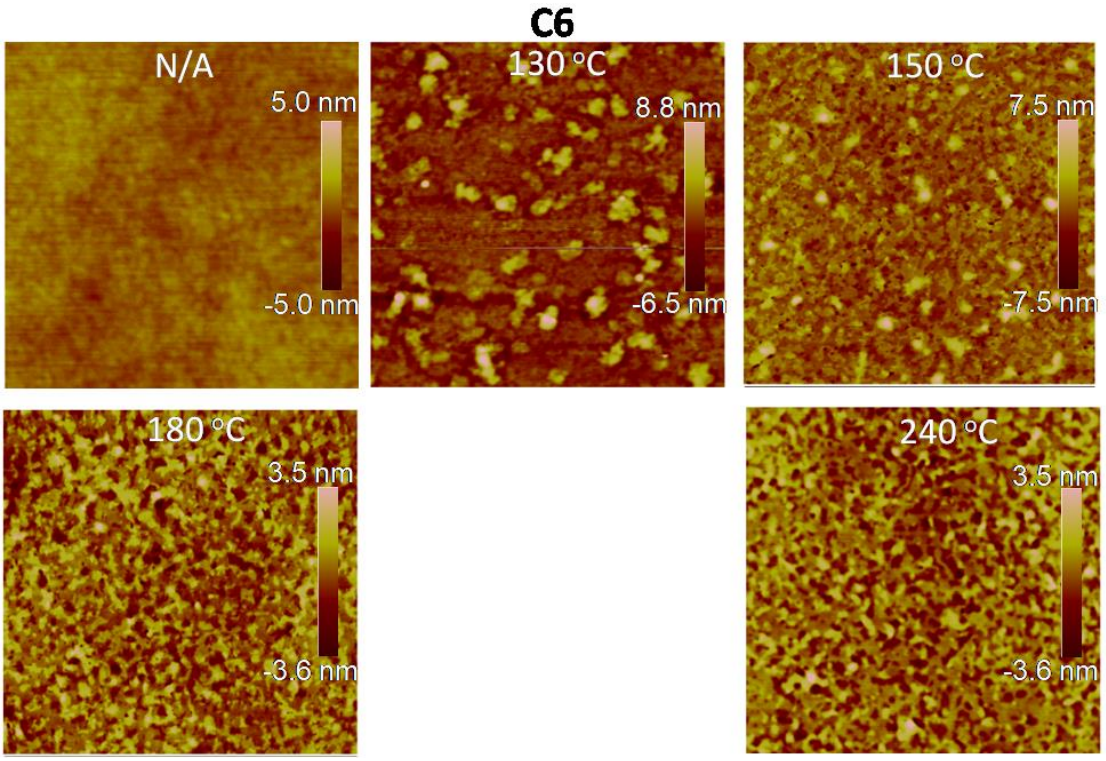


Fig. S10. AFM height images (5 ×5 μm) of **C6** films spin-coated on OTS-treated SiO_2/Si substrates and annealed at different temperatures.

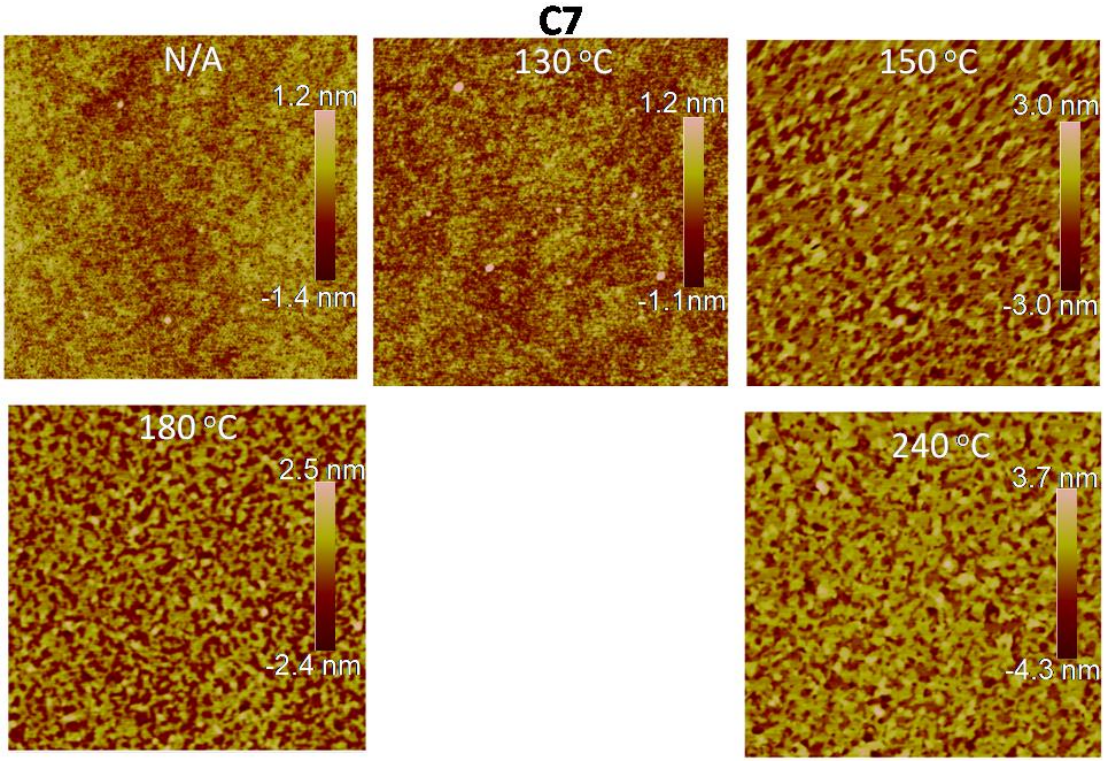


Fig. S11. AFM height images (5 ×5 μm) of **C7** films spin-coated on OTS-treated SiO_2/Si substrates and annealed at different temperatures.

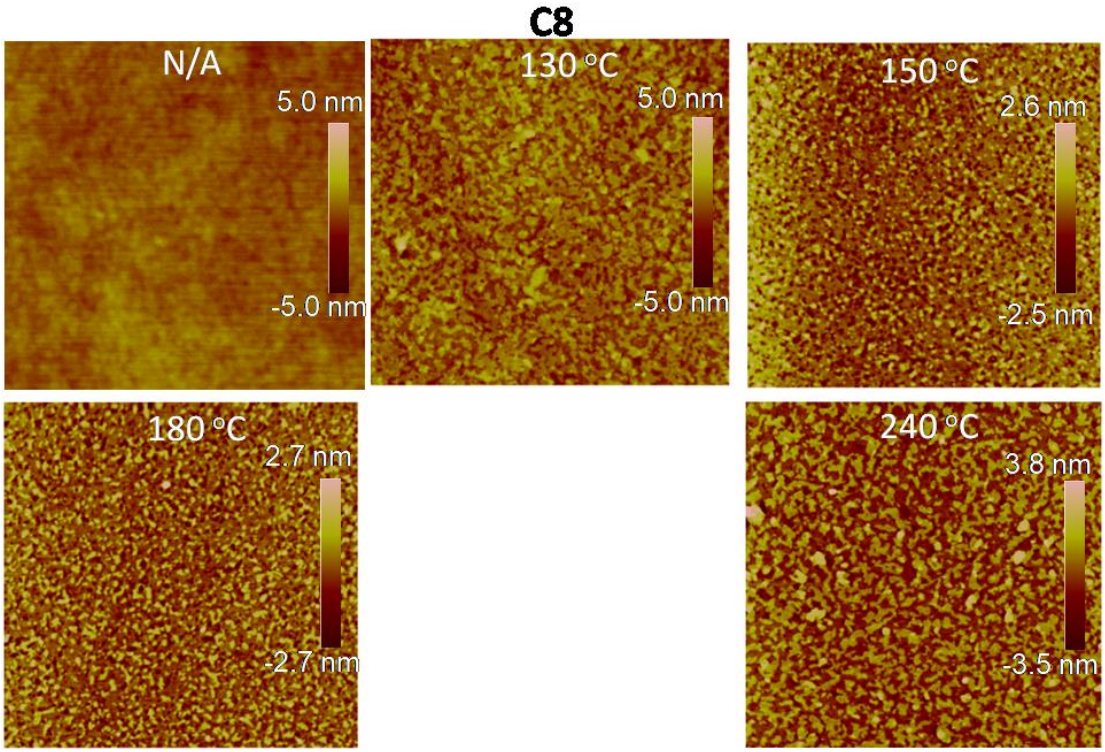


Fig. S12. AFM height images (5 ×5 μm) of **C8** films spin-coated on OTS-treated SiO_2/Si substrates and annealed at different temperatures.

Experimental section

All starting commercially available regents were used as received without further purification. Tetrakis(4-hexylphenyl)-indacenodithieno[3,2-*b*]thiophene-bis-(trimethylstannane) was purchased from Derthon Optoelectronics Materials Science Technology Co. LTD. Other chemicals were obtained from Energy Chemical, J&K Scientific, and Sinopharm Chemical Reagent Co. Ltd., China.

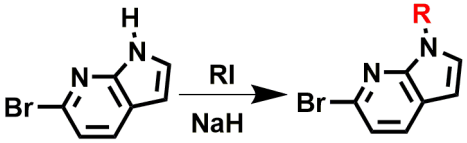
Characterization

Nuclear magnetic resonance (NMR) spectra were obtained by using an Agilent VNMRS600 instrument. Thermogravimetric analysis (TGA) was investigated by using a STA449F5 machine with the ramp rate of 10 ^{o}C/min. UV-vis absorption spectra were obtained using Agilent Cray 5000 model spectrophotometer in chloroform solutions and films spin-coated onto quartz glass. Cyclic voltammetry (CV) characterization was tested using a CHI 660D electrochemical workstation in anhydrous acetonitrile solution (0.1 M tetra-*n*-butylammonium hexafluorophosphate). The platinum (Pt) plate was used as the working electrode, the Pt wire was used as counter electrode. The Ag/Ag^{+} electrode was used as the reference electrode. Grazing-incidence X-ray diffraction (GIXD) experiments were performed using the synchrotron source at the Pohang Accelerator Laboratory (PAL) in Korea. 2D-GIXD patterns were recorded with a 2D CCD detector and X-ray irradiation time was 1 ~ 10 seconds dependent on the saturation level of detector. Diffraction angles were calibrated by a pre-calibrated sucrose (Monoclinic, $P2_1$, a = 10.8631 Å, b = 8.7044 Å, c= 7.7624 Å, β= 102.938^{o}).[S1] Density functional theory (DFT) calculations were performed with the nonlocal hybrid Becke three-parameter Lee-Yang-Parr (B3LYP) function and the 6-31G* basis set after optimizing the geometry of molecules. Atomic force microscopy (AFM) characterization was measured using a SPA300HV instrument.

Fabrication and characterization of OFET device

The field-effect devices were fabricated on a gate of *n*-doped Si (deposited 300 nm SiO_2) with bottom gate/top contact (BG/TC) configuration. The Si substrates were firstly treated with a piranha solution (30 vol% H_2O_2 and 70 vol% H_2SO_4) and then further treated by UV-ozone. The wafer surface continued to be modified with octadecyltrimethoxysilane (OTS) self-assembled monolayers (SAM) which were

referred from the previous literature.[S2] Last, small molecules were dissolved in chloroform solution (5 mg/mL) and the semiconductor films were spin-coated on the OTS-treated Si/SiO_2 substrates at the speed of 4000 rpm. The prepared films were further annealed at the different temperatures (150-270 ^oC) under nitrogen conditions. The gold electrodes were deposited on the semiconductors by thermal evaporation. The OFET devices had a channel length (L) of 130 μm and a channel width (W) of 760 μm. All the devices were measured under ambient conditions via a Keithley 4200 semiconductor analyzer. The field-effect mobility (μ) was calculated using the equation regime: $I_d = (W/2L)Ci\mu(V_g-V_{th})^2$, where I_d is the drain current, L is the channel length, W is the channel width, C_i is the capacitance of the gate dielectric, V_g is the gate-source voltage, and V_{th} is the threshold voltage.



General synthetic procedure for 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine

6-Bromo-7-azaindol was added slowly in the mixture of NaH and dimethylformamide at the 0 ^oC. The reaction was warm to room temperature and stirred for about 20 min. Then RI was added and the mixture was stirred overnight. The reaction was quenched with water and the organic layer was extracted with ethyl acetate. At last, the compound was purified by using flash chromatography on silica gel with petroleum ether.

6-Bromo-1-(2-methyl)-1*H*-pyrrolo[2,3-*b*]pyridine

The used compounds were 6-bromo-7-azaindol (1.5 g, 7.62 mmol), NaH (0.46 g, 11.43 mmol), dimethylformamide (15 mL), and RI (1.4 g, 9.9 mmol). The residue was purified by flash chromatography on silica gel with hexane as eluent to give the titled compound (1.05 g, 65%). ^1H NMR (600 MHz, $CDCl_3$): δ=7.73 (d, 1H), 7.19 (d, 1H), 7.13 (d, 1H), 6.42 (d, 2H), 3.86 (s, 3H).

6-Bromo-1-(2-ethyl)-1*H*-pyrrolo[2,3-*b*]pyridine

The used compounds were 6-bromo-7-azaindol (1.5 g, 7.62 mmol), NaH (0.46 g, 11.43 mmol), dimethylformamide (15 mL), and RI (1.54 g, 9.9 mmol). The residue

was purified by flash chromatography on silica gel with hexane as eluent to give the titled compound (0.96 g, 60%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.72 (d, 1H), 7.18 (t, 1H), 6.43 (d, 1H), 4.31 (q, 2H), 1.35 (t, 3H).

6-Bromo-1-(2-propyl)-1*H*-pyrrolo[2,3-*b*]pyridine

The used compounds were 6-bromo-7-azaindol (1.5 g, 7.62 mmol), NaH (0.46 g, 11.43 mmol), dimethylformamide (15 mL), and RI (1.68 g, 9.9 mmol). The residue was purified by flash chromatography on silica gel with hexane as eluent to give the titled compound (1.08 g, 68%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.72 (d, 1H), 7.18 (t, 1H), 6.43 (d, 1H), 4.23 (t, 2H), 1.88 (m, 2H), 0.93 (t, 3H).

6-Bromo-1-(2-butyl)-1*H*-pyrrolo[2,3-*b*]pyridine

The used compounds were 6-bromo-7-azaindol (1.5 g, 7.62 mmol), NaH (0.46 g, 11.43 mmol), dimethylformamide (15 mL), and RI (1.82 g, 9.9 mmol). The residue was purified by flash chromatography on silica gel with hexane as eluent to give the titled compound (0.93 g, 58%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.72 (d, 1H), 7.18 (d, 1H), 6.43 (d, 1H), 4.26 (t, 2H), 1.83 (m, 2H), 1.33 (m, 2H), 0.94 (t, 3H).

6-Bromo-1-(2-amyl)-1*H*-pyrrolo[2,3-*b*]pyridine

The used compounds were 6-bromo-7-azaindol (1.5 g, 7.62 mmol), NaH (0.46 g, 11.43 mmol), dimethylformamide (15 mL), and RI (1.96 g, 9.9 mmol). The residue was purified by flash chromatography on silica gel with hexane as eluent to give the titled compound (1.13 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.72 (d, 1H), 7.18 (d, 1H), 6.43 (d, 1H), 4.24 (t, 2H), 1.84 (m, 2H), 1.33 (m,2H), 1.29 (t, 2H), 0.88 (t, 3H).

6-Bromo-1-(2-hexyl)-1*H*-pyrrolo[2,3-*b*]pyridine

The used compounds were 6-bromo-7-azaindol (3.0 g, 15.24 mmol), NaH (0.74 g, 18.3 mmol), dimethylformamide (10 mL), and RI (3.6 g, 16.77 mmol). The residue was purified by flash chromatography on silica gel with hexane as eluent to give the titled compound (3.94 g, 92%). ^{1}H NMR (600 MH_z, $CDCl_3$): δ= 7.75 (d, 1H), 7.19 (t, 2H), 6.44 (d, 1H), 4.24 (t, 2H), 1.85 (m, 2H), 1.30 (m, 6H), 0.89 (t, 3H).

6-Bromo-1-(2-heptyl)-1*H*-pyrrolo[2,3-*b*]pyridine

The used compounds were 6-bromo-7-azaindol (1.5 g, 7.62 mmol), NaH (0.46 g, 11.43 mmol), dimethylformamide (15 mL), and RI (2.24 g, 9.9 mmol). The residue

was purified by flash chromatography on silica gel with hexane as eluent to give the titled compound (0.90 g, 57%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.72 (d, 1H), 7.17 (d, 1H), 6.42 (s, 1H), 4.23 (t, 2H), 1.83 (m, 2H), 1.26 (m, 8H), 0.87 (t, 3H).

6-Bromo-1-(2-octyl)-1*H*-pyrrolo[2,3-*b*]pyridine

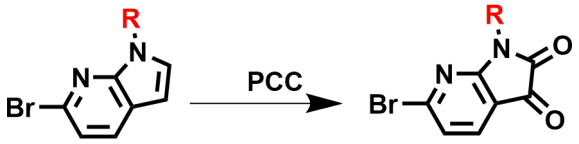
The used compounds were 6-bromo-7-azaindol (1.5 g, 7.62 mmol), NaH (0.46 g, 11.43 mmol), dimethylformamide (15 mL), and RI (2.38 g, 9.9 mmol). The residue was purified by flash chromatography on silica gel with hexane as eluent to give the titled compound (1.05 g, 66%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.71 (d, 1H), 7.17 (d, 1H), 6.41 (s, 1H), 4.23 (t, 2H), 1.83 (m, 2H), 1.26 (m, 10H), 0.87 (t, 3H).

6-Bromo-1-(2-nonyl)-1*H*-pyrrolo[2,3-*b*]pyridine

The used compounds were 6-bromo-7-azaindol (0.75 g, 3.81 mmol), NaH (0.2 g, 4.95 mmol), dimethylformamide (8 mL), and RI (1.26 g, 5.72 mmol). The residue was purified by flash chromatography on silica gel with hexane as eluent to give the titled compound (0.78 g, 63%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72 (d, 1H), 7.17 (d, 2H), 6.42 (s, 1H), 4.23 (t, 2H), 1.83 (m, 2H), 1.28 (m, 12H), 0.87 (t, 3H).

6-Bromo-1-(2-decyl)-1H-pyrrolo[2,3-b]pyridine

The used compounds were 6-bromo-7-azaindol (0.74 g, 3.76mmol), NaH (0.20 g, 4.89 mmol), dimethylformamide (8 mL), and RI (1.25 g, 5.64 mmol). The residue was purified by flash chromatography on silica gel with hexane as eluent to give the titled compound (0.81 g, 64%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.71 (d, 1H), 7.17 (d, 2H), 6.41 (s, 1H), 4.23 (t, 2H), 1.83 (m, 2H), 1.26 (m, 14H), 0.87 (t, 3H).



General synthetic procedure for 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione.

Pyridinium chlorochromate (PCC), 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine, and silica were added in flask with solvent of 1,2-dichloroethane and acetonitrile. The reaction mixture was heated to reflux for 3 h after the addition of $AlCl_3$. After the removal of the organic solvent, the residue was purified by flash chromatography on silica gel to

give the desired monomer.

6-Bromo-1-(2-methyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione

The used compounds were pyridinium chlorochromate (PCC, 3.2 g, 14.91 mmol), 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (1.05 g, 4.97 mmol), silica (3.2 g), $AlCl_3$ (10 mg), 1,2-dichloroethane (15 mL), and acetonitrile (15 mL). The residue was purified by flash chromatography on silica gel with hexane: dichloromethane (2:1) as eluent to give the titled compound (0.57 g, 48%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.63 (d, 1H), 7.27 (d, 1H), 3.35 (t, 3H).

6-Bromo-1-(2-ethyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione

The used compounds were pyridinium chlorochromate (PCC, 2,8 g, 12.78 mmol), 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (0.96 g, 4.26 mmol), silica (2.8 g), $AlCl_3$ (10 mg), 1,2-dichloroethane (15 mL), and acetonitrile (15 mL). The residue was purified by flash chromatography on silica gel with hexane: dichloromethane (3:1) as eluent to give the titled compound (0.50 g, 51%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.63 (d, 1H), 7.27 (d, 1H), 3.8 (t, 2H), 0.92 (t, 3H).

6-Bromo-1-(2-propyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione

The used compounds were pyridinium chlorochromate (PCC, 2.9 g, 13.56 mmol), 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (1.08 g, 4.52 mmol), silica (2.9 g), $AlCl_3$ (10 mg), 1,2-dichloroethane (15 mL) and acetonitrile (15 mL). The residue was purified by flash chromatography on silica gel with hexane: dichloromethane (3:1) as eluent to give the titled compound (0.57 g, 48%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.64 (d, 1H), 7.28 (d, 1H), 3.85 (t, 2H)，1.42 (m, 2H), 0.92 (t, 3H).

6-Bromo-1-(2-butyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione

The used compounds were pyridinium chlorochromate (PCC, 2.4 g, 11.0 mmol), 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (0.93 g, 3.67 mmol), silica (2.4 g), $AlCl_3$ (10 mg), 1,2-dichloroethane (15 mL) and acetonitrile (15 mL). The residue was purified by flash chromatography on silica gel with hexane: dichloromethane (3:1) as eluent to give the titled compound (0.56 g, 49%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.64 (d, 1H), 7.28 (d, 1H), 3.85 (t, 2H)，1.77-1.72 (m, 2H), 1.42-1.36 (m, 2H), 0.98 (t, 3H).

6-Bromo-1-(2-amyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione

The used compounds were pyridinium chlorochromate (PCC, 2.74 g, 12.69 mmol), 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (1.13 g, 4.23 mmol), silica (2.74 g), $AlCl_3$ (10 mg), 1,2-dichloroethane (15 mL) and acetonitrile (15 mL). The residue was purified by flash chromatography on silica gel with hexane: dichloromethane (5:1) as eluent to give the titled compound (0.53 g, 42%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.64 (d, 1H), 7.28 (d, 1H), 3.85 (t, 2H)，1.77-1.72 (m, 2H), 1.42-1.29 (m, 4H), 0.92 (t, 3H).

6-Bromo-1-(2-hexyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione

The used compounds were pyridinium chlorochromate (PCC, 9.0 g, 41.6 mmol), 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (3.9 g, 13.9 mmol), silica (2.9 g), $AlCl_3$ (10 mg), 1,2-dichloroethane (25 mL) and acetonitrile (25 mL). The residue was purified by flash chromatography on silica gel with hexane: ether (1:5) as eluent to give the titled compound (2.1 g, 49%). ^{1}H NMR (600 MH_z, $CDCl_3$): δ= 7.63 (d, 1H), 7.27 (d, 1H), 3.82 (t, 2H), 1.75 (m, 2H), 1.35 (m, 6H), 0.89 (t, 3H).

6-Bromo-1-(2-heptyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione

The used compounds were Pyridinium chlorochromate (PCC, 2.0 g, 9.2 mmol), 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (0.9 g, 3.1 mmol), silica (2.0 g), $AlCl_3$ (10 mg), 1,2-dichloroethane (15 mL) and acetonitrile (15 mL). The residue was purified by flash chromatography on silica gel with hexane: dichloromethane (5:1) as eluent to give the titled compound (0.41 g, 42%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.64 (d, 1H), 7.28 (d, 1H), 3.84 (t, 2H)，1.77-1.72 (m, 2H), 1.40-1.27 (m, 8H), 0.89 (t, 3H).

6-Bromo-1-(2-octyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione

The used compounds were Pyridinium chlorochromate (PCC, 2.2 g, 10.2 mmol), 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (1.05 g, 3.4 mmol), silica (2.2 g), $AlCl_3$ (10 mg), 1,2-dichloroethane (15 mL) and acetonitrile (15 mL). The residue was purified by flash chromatography on silica gel with hexane: dichloromethane (5:1) as eluent to give the titled compound (0.49 g, 43%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.64 (d, 1H), 7.28 (d, 1H), 3.84 (t, 2H)，1.77~1.72 (m, 2H), 1.38~1.27 (m, 10H), 0.89 (t, 3H).

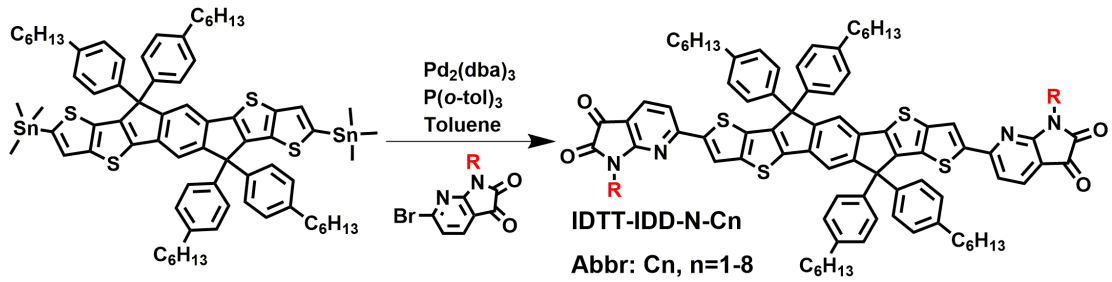
6-Bromo-1-(2-nonyl)-1H-pyrrolo[2,3-b]pyridine-2,3-dione

The used compounds were Pyridinium chlorochromate (PCC, 1.56 g, 7.24 mmol), 6-bromo-1H-pyrrolo[2,3-b]pyridine (0.78 g, 2.41 mmol), silica (2.2 g), $AlCl_3$ (3mg),

1,2-dichloroethane (15 mL) and acetonitrile (15 mL). The residue was purified by flash chromatography on silica gel with hexane: dichloromethane (3:1) as eluent to give the titled compound (0.50 g, 58%). ^{1}H NMR (600 MHz, $CDCl_3$):δ= 7.64 (d, 1H), 7.28 (d, 1H), 3.84 (t, 2H)，1.77~1.72 (m, 2H), 1.38~1.27 (m, 12H), 0.89 (t, 3H).

6-Bromo-1-(2-decyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione

The used compounds were Pyridinium chlorochromate (PCC, 1.55 g, 7.2 mmol), 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (0.81 g, 2.4 mmol), silica (2.2 g), $AlCl_3$ (3 mg), 1,2-dichloroethane (15 mL) and acetonitrile (15 mL). The residue was purified by flash chromatography on silica gel with hexane: dichloromethane (3:1) as eluent to give the titled compound (0.51 g,56%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 7.64 (d, 1H), 7.28 (d, 1H), 3.84 (t, 2H)，1.77~1.72 (m, 2H), 1.38~1.27 (m, 14H), 0.89 (t, 3H).



General synthetic procedure for small molecules (C1-C8)

Distannylated monomer (0.16 mmol), and 6-bromo-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione (0.37 mmol) were added to the Schlenk tube with toluene (8 mL). The mixture was purged with nitrogen flow for about 40 min. Tri(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$, 4.4 mg), tri-*o*-tolylphosphine (P(*o*-tolyl)$_3$, 6 mg) was added quickly and the mixture was heated to 105 ^{o}C for 18 h. After being cooled to room temperature, the mixture was poured into 100 mL H_2O and extracted with dichloromethane for three times. After removing the solvent, the residue was purified by silica gel column chromatography using a mixture of petroleum ether/diethyl ether/dichloromethane (5:1:1) to give the small molecule.

IDTT-IDD-N-C1 (C1): The used compounds were 6-bromo-1-(2-methyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione (0.042 g, 0.17 mmol), distannylated monomer (0.1 g, 0.074 mmol), $Pd_2(dba)_3$ (4.4 mg), P(*o*-tolyl)$_3$ (6 mg),

and toluene (10 mL). The residue was purified by flash chromatography on silica gel with hexane: ethyl acetate: dichloromethane (10:1:1) as eluent to give the titled compound (80 mg, 80%). ^{1}HNMR (600 MHZ, $CDCl_3$): δ= 8.03 (s, 2H), 7.75 (d, 2H), 7.58 (s, 2H), 7.30 (d, 2H), 7.22 (d, 8H), 7.13 (d, 8H), 3.96 (t, 4H), 2.59 (t, 8H), 1.59 (m, 6H), 1.26-1.40 (m, 26 H), 0.86 (t, 18H).

^{13}C NMR (150 MHz, $CDCl_3$): δ= 13C NMR (150 MHz, CDCl3): δ=180.09, 164.28, 159.62, 158.38, 154.25, 147.20, 146.75, 144.02, 143.13, 142.16, 139.50,138.19, 136.25, 133.07, 128.65, 127.93, 121.85, 117.54, 113.48, 109.60, 63.06, 35.58, 31.68, 31.27, 29.15, 25.18, 22.57, 14.04.

Elemental analysis: calcd for $C_{84}H_{82}N_4O_4S_4$: C, 75.30, H, 6.17, N, 4.18. Found: C, 75.48, H, 6.15, N, 4.04.

IDTT-IDD-N-C2 (C2): The used compounds were 6-bromo-1-(2-ethyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione (0.044 g, 0.17 mmol), distannylated monomer (0.1 g, 0.074 mmol), $Pd_2(dba)_3$ (4.4 mg), P(*o*-tolyl)$_3$ (6 mg), and toluene (10 mL). The residue was purified by flash chromatography on silica gel with hexane: ethyl acetate: dichloromethane (10:1:1) as eluent to give the titled compound (70 mg, 70%).

^{1}H NMR (600 MHz, $CDCl_3$): δ= 8.03 (s, 2H), 7.75 (d, 2H), 7.58 (s, 2H), 7.30 (d, 2H), 7.22 (d, 8H), 7.13 (d, 8H), 3.96 (t, 4H), 2.59 (t, 8H), 1.59 (m, 6H), 1.26-1.40 (m, 26 H), 0.86 (t, 18H).

^{13}C NMR (150 MHz, $CDCl_3$): δ= 180.46, 164.44, 159.42, 158.32, 154.29, 147.12, 146.77, 144.23, 143.18, 142.21, 139.62, 138.22, 136.36, 133.15, 128.65, 127.95, 121.81, 117.63, 113.27, 109.47, 63.08, 39.22, 35.62, 31.70, 31.30, 31.28, 29.72, 29.18, 27.44, 26.48, 22.60, 22.49, 14.09, 14.03.

Elemental analysis: calcd for $C_{86}H_{86}N_4O_4S_4$: C, 75.51, H, 6.34, N, 4.10. Found: C, 75.77, H, 6.554, N, 4.16.

IDTT-IDD-N-C3 (C3): The used compounds were 6-bromo-1-(2-propyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione (0.046 g, 0.17 mmol), distannylated monomer (0.1 g, 0.074 mmol), $Pd_2(dba)_3$ (4.4 mg), P(*o*-tolyl)$_3$ (6 mg), and toluene (10

mL). The residue was purified by flash chromatography on silica gel with hexane: ethyl acetate: dichloromethane (10:1:1) as eluent to give the titled compound (73 mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$): δ= 8.04 (s, 2H), 7.77 (d, 2H), 7.58 (s, 2H), 7.32 (d, 2H), 7.22 (d, 8H), 7.13 (d, 8H), 3.88 (t, 4H), 2.59 (t, 8H), 1.85 (m, 4H), 1.59 (m, 6H), 1.26-1.33 (m, 26 H), 1.03 (t, 6H),0.86 (t, 18H).

^{13}C NMR (150 MHz, $CDCl_3$): δ= 180.44, 164.45, 159.49, 158.34, 154.30, 147.12, 146.77, 144.14, 143.18, 142.21, 139.62, 138.17, 138.36, 133.19, 128.66, 127.96, 121.91, 117.62, 113.35, 109.45, 63.08, 40.82, 35.61, 31.70, 31.28, 29.72, 29.16, 22.59, 21.05, 14.09, 11.52.

Elemental analysis: calcd for $C_{88}H_{90}N_4O_4S_4$: C, 75.72, H, 6.50, N, 4.01. Found: C, 76.00, H, 6.78, N, 4.11.

IDTT-IDD-N-C4 (C4): The used compounds were 6-bromo-1-(2-butyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione (0.049 g, 0.17 mmol), distannylated monomer (0.1 g, 0.074 mmol), $Pd_2(dba)_3$ (4.4 mg), P(*o*-tolyl)$_3$ (6 mg), and toluene (10 mL). The residue was purified by flash chromatography on silica gel with hexane: ethyl acetate: dichloromethane (10:1:1) as eluent to give the titled compound (70 mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$): δ= 8.01 (s, 2H), 7.76 (d, 2H), 7.56 (s, 2H), 7.32 (d, 2H), 7.22 (d, 8H), 7.13 (d, 8H), 3.88 (t, 4H), 2.59 (t, 8H), 1.85 (m, 4H), 1.59 (m, 6H), 1.26-1.44 (m, 30 H), 1.03 (t, 6H),0.86 (t, 12H).

^{13}C NMR (150 MHz, $CDCl_3$): δ= 180.43, 164.44, 159.42, 158.31, 154. 31, 147.10, 146.78, 144.27, 143.18, 142.20, 139.62, 138.24, 136.38, 133.15, 128.65, 127.95, 121.77, 117.62, 113.24, 109.46, 63.07, 38.89, 35.60, 31.69, 31.27, 29.66, 29.15, 22.58, 20.09, 14.08, 13.73.

Elemental analysis: calcd for $C_{90}H_{94}N_4O_4S_4$: C, 75.91, H, 6.65, N, 3.93. Found: C, 75.82, H, 6.69, N, 4.12.

IDTT-IDD-N-C5 (C5): The used compounds were 6-bromo-1-(2-amyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione (0.049 g, 0.17 mmol), distannylated monomer (0.1 g, 0.074 mmol), $Pd_2(dba)_3$ (4.4 mg), P(*o*-tolyl)$_3$ (6 mg), and toluene (10

mL). The residue was purified by flash chromatography on silica gel with hexane: ethyl acetate: dichloromethane (10:1:1) as eluent to give the titled compound (65 mg, 65%).

^{1}H NMR (600 MHz, $CDCl_3$): δ= 8.01 (s, 2H), 7.76 (d, 2H), 7.56 (s, 2H), 7.32 (d, 2H), 7.22 (d, 8H), 7.13 (d, 8H), 3.88 (t, 4H), 2.59 (t, 8H), 1.85 (m, 4H), 1.59 (m, 6H), 1.26-1.42 (m, 34 H), 0.86 (m, 18H).

^{13}C NMR (150 MHz, $CDCl_3$): δ= 180.44, 164.44, 159.41, 158.32, 154.30, 147.10, 146.79, 144.29, 143.17, 142.20, 139.62, 138.26, 136.37, 133.14, 128.64, 127.95, 121.73, 117.62, 113.22, 109.46, 63.07, 39.17, 35.61, 31.70, 31.29, 29.17, 28.96, 27.18, 22.59, 22.21, 14.08, 14.00.

Elemental analysis: calcd for $C_{92}H_{98}N_4O_4S_4$: C, 76.10, H, 6.80, N, 3.86. Found: C, 76.03, H, 6.83, N, 3.56.

IDTT-IDD-N-C6 (C6): The used compounds were 6-bromo-1-(2-hexyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione (0.12 g, 0.37 mmol), distannylated monomer (0.22 g, 0.16 mmol), $Pd_2(dba)_3$ (4.4 mg), P(*o*-tolyl)$_3$ (6 mg), and toluene (8 mL). The residue was purified by flash chromatography on silica gel with hexane: ether: dichloromethane (5:1:1) as eluent to give the titled compound (120 mg, 50%).

^{1}H NMR (600 MH_z, $CDCl_3$): δ= 8.04 (s, 2H), 7.78 (d, 2H), 7.60 (s, 2H), 7.32 (d, 2H), 7.22 (d, 8H), 7.14 (d, 8H), 3.91 (t, 4H), 2.60 (t, 8H), 1.82 (m, 4H), 1.61 (m, 6H), 1.25-1.45 (m, 38 H), 0.88 (t, 18H).

^{13}C NMR (150 MHz, CDCl3): δ= 183.05, 167.08, 162.05, 160.95, 156.94, 149.76, 149.43, 146.87, 145.81, 144.85, 142.25, 140.85, 139.00, 135.78, 131.30, 130.60, 124.45, 120.24, 115.90, 112.12, 65.73, 41.87, 38.25, 34.34, 33.92, 31.81, 30.08, 29.11, 25.22, 25.12, 16.71, 16.65, 2.65.

Elemental analysis: calcd for $C_{94}H_{102}N_4O_4S_4$: C, 76.28, H, 6.95, N, 3.79. Found: C, 76.35, H, 6.82, N, 3.93.

IDTT-IDD-N-C7 (C7): The used compounds were 6-bromo-1-(2-heptyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione (0.055 g, 0.17 mmol), distannylated monomer (0.1 g, 0.074 mmol), $Pd_2(dba)_3$ (4.4 mg), P(*o*-tolyl)$_3$ (6 mg), and toluene (10 mL). The residue was purified by flash chromatography on silica gel with hexane:

ethyl acetate: dichloromethane (10:1:1) as eluent to give the titled compound (68 mg, 68%).

^{1}H NMR (600 MHz, CDCl3): δ= 8.01 (s, 2H), 7.74 (d, 2H), 7.56 (s, 2H), 7.28 (d, 2H), 7.20 (d, 8H), 7.11 (d, 8H), 3.87 (t, 4H), 2.55 (t, 8H), 1.77 (m, 4H), 1.56 (m, 6H), 1.23-1.44 (m, 42 H), 0.84 (m, 18H).

^{13}C NMR (150 MHz, $CDCl_3$): δ= 180.46, 164.43, 159.42, 158.33, 154.29, 147.12, 146.77, 144.19, 143.17,142.20, 139.62, 138.19, 136.35, 133.15, 128.65, 127.95, 121.86, 117.62, 113.30, 109.48, 63.08, 39.24, 35.62, 31.70, 31.29, 29.72, 29.18, 28.82, 27.52, 26.81, 22.59, 14.11, 14.08.

Elemental analysis: calcd for $C_{96}H_{106}N_4O_4S_4$: C, 76.45, H, 7.08, N, 3.71. Found: C, 76.32, H, 7.05, N, 3.63.

IDTT-IDD-N-C8 (C8): The used compounds were 6-bromo-1-(2-octyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione (0.058 g, 0.17 mmol), distannylated monomer (0.1 g, 0.074 mmol), $Pd_2(dba)_3$ (4.4 mg), P(*o*-tolyl)$_3$ (6 mg), and toluene (10 mL). The residue was purified by flash chromatography on silica gel with hexane: ethyl acetate: dichloromethane (10:1:1) as eluent to give the titled compound (79 mg, 79%). ^{1}H NMR (600 MHz, $CDCl_3$): δ= 8.01 (s, 2H), 7.77 (d, 2H), 7.56 (s, 2H), 7.32 (d, 2H), 7.22 (d, 8H), 7.13 (d, 8H), 3.86 (t, 4H), 2.59 (t, 8H), 1.85 (m, 4H), 1.59 (m, 6H), 1.23-1.44 (m, 46 H), 0.86 (m, 18H).

^{13}C NMR (150 MHz, $CDCl_3$): δ= 180.45, 164.41, 159.36, 158.22, 154.22, 147.12, 146.73, 144.15, 143.12, 142.18, 139.52, 138.08, 136.29, 133.15, 128.59, 127.92, 121.85, 117.59, 113.32, 109.33, 63.04, 39.23, 35.59, 31.75, 31.68, 31.28, 29.17, 29.16, 29.13, 27.52, 26.68, 22.64, 22.57, 14.08, 14.06.

Elemental analysis: calcd for $C_{98}H_{110}N_4O_4S_4$: C, 76.62, H, 7.22, N, 3.65. Found: C, 76.51, H, 7.35, N, 3.54.

IDTT-IDD-N-C9 (C9): The used compounds were 6-bromo-1-(2-nonyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione (0.069 g, 0.20 mmol), distannylated monomer (0.1105 g, 0.082 mmol), $Pd_2(dba)_3$ (4.3 mg), P(*o*-tolyl)$_3$ (5 mg), and toluene (10 mL). The residue was purified by flash chromatography on silica gel with hexane: ethyl acetate: dichloromethane (10:1:1) as eluent to give the titled compound (90 mg,

89%).

^{1}H NMR (600 MHz, $CDCl_3$): δ= 8.01 (s, 2H), 7.77 (d, 2H), 7.56 (s, 2H), 7.32 (d, 2H), 7.22 (d, 8H), 7.13 (d, 8H), 3.86 (t, 4H), 2.59 (t, 8H), 1.85 (m, 4H), 1.59 (m, 7H), 1.23-1.44 (m, 49 H), 0.86 (m, 18H).

^{13}C NMR (150 MHz, $CDCl_3$): δ= 180.45, 164.40, 159.41, 158.30, 154.26, 147.09, 146.73, 144.15, 143.15, 142.18, 139.60, 138.14, 136.34, 133.15, 128.63, 127.92, 121.85, 117.60, 113.29, 109.45, 63.05, 39.24, 35.60, 31.86, 31.68, 31.28, 29.49, 29.22, 29.16, 27.54, 26.87, 22.64, 22.57, 14.11, 14.07.

IDTT-IDD-N-C10 (C10): The used compounds were 6-bromo-1-(2-decyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione (0.067 g, 0.18 mmol), distannylated monomer (0.1018 g, 0.076 mmol), $Pd_2(dba)_3$ (4.4 mg), P(*o*-tolyl)$_3$ (5.3 mg), and toluene (10 mL). The residue was purified by flash chromatography on silica gel with hexane: ethyl acetate: dichloromethane (10:1:1) as eluent to give the titled compound (91 mg, 90%).

^{1}H NMR (600 MHz, $CDCl_3$): δ= 8.01 (s, 2H), 7.77 (d, 2H), 7.56 (s, 2H), 7.32 (d, 2H), 7.22 (d, 8H), 7.13 (d, 8H), 3.86 (t, 4H), 2.59 (t, 8H), 1.85 (m, 4H), 1.59 (m, 8H), 1.23-1.44 (m, 50 H), 0.86 (m, 18H).

^{13}C NMR (150 MHz, $CDCl_3$): δ= 180.44, 164.40, 159.40, 158.30, 154.26, 147.09, 146.74, 144.15, 143.15, 142.17, 139.59, 138.14, 136.34, 133.14, 128.62, 127.92, 121.85, 117.59, 113.28, 109.46, 63.05, 39.23, 35.59, 31.87, 31.68, 31.27, 29.54, 29.33, 29.20, 29.16, 27.54, 26.87, 22.67, 22.57, 14.11, 14.06.

NMR

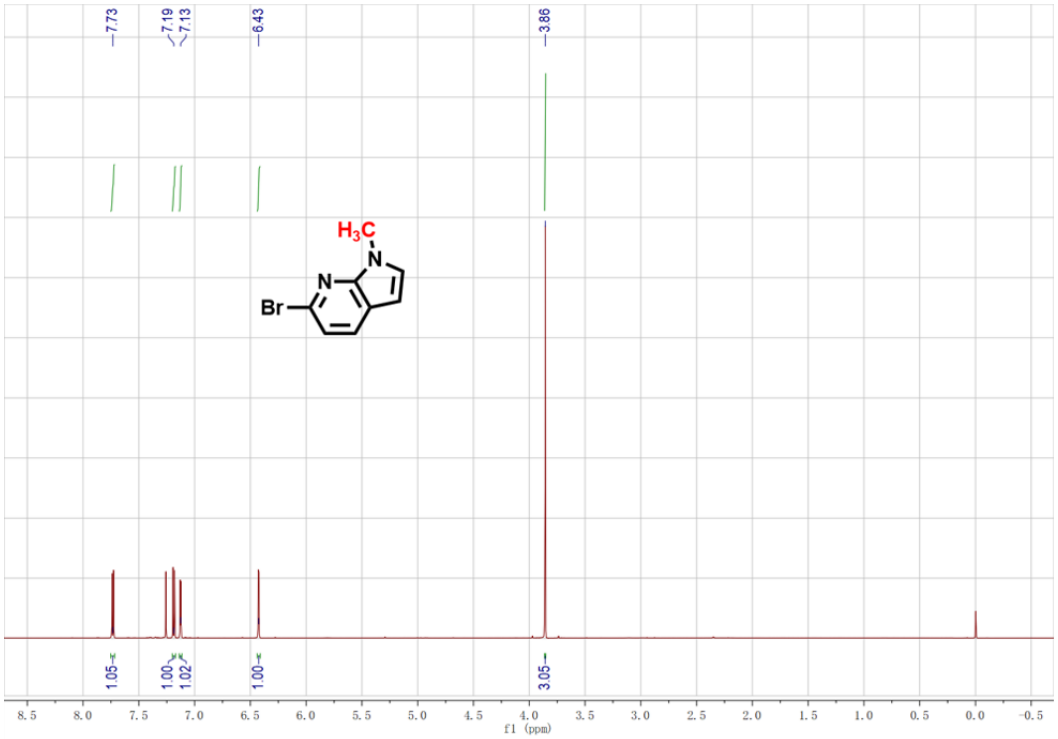


Fig. S13. ^{1}H spectrum of 6-bromo-1-(2-methyl)-1*H*-pyrrolo[2,3-*b*]pyridine in $CDCl_3$.

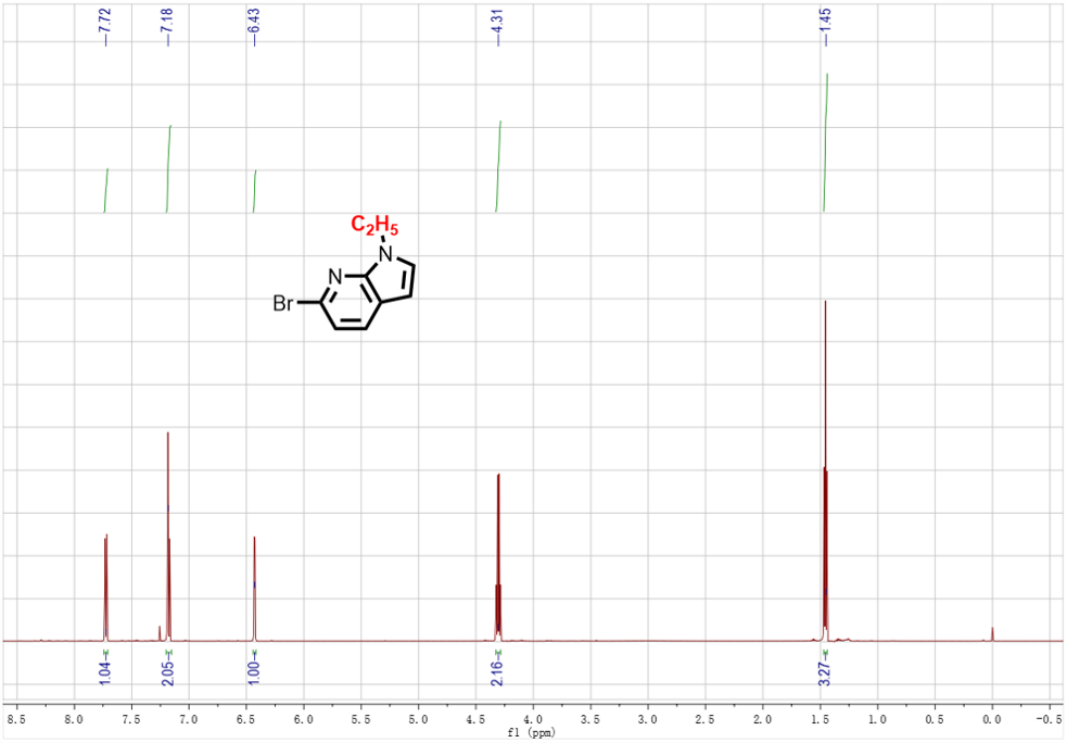


Fig. S14. ^{1}H spectrum of 6-bromo-1-(2-ethyl)-1*H*-pyrrolo[2,3-*b*]pyridine in $CDCl_3$.

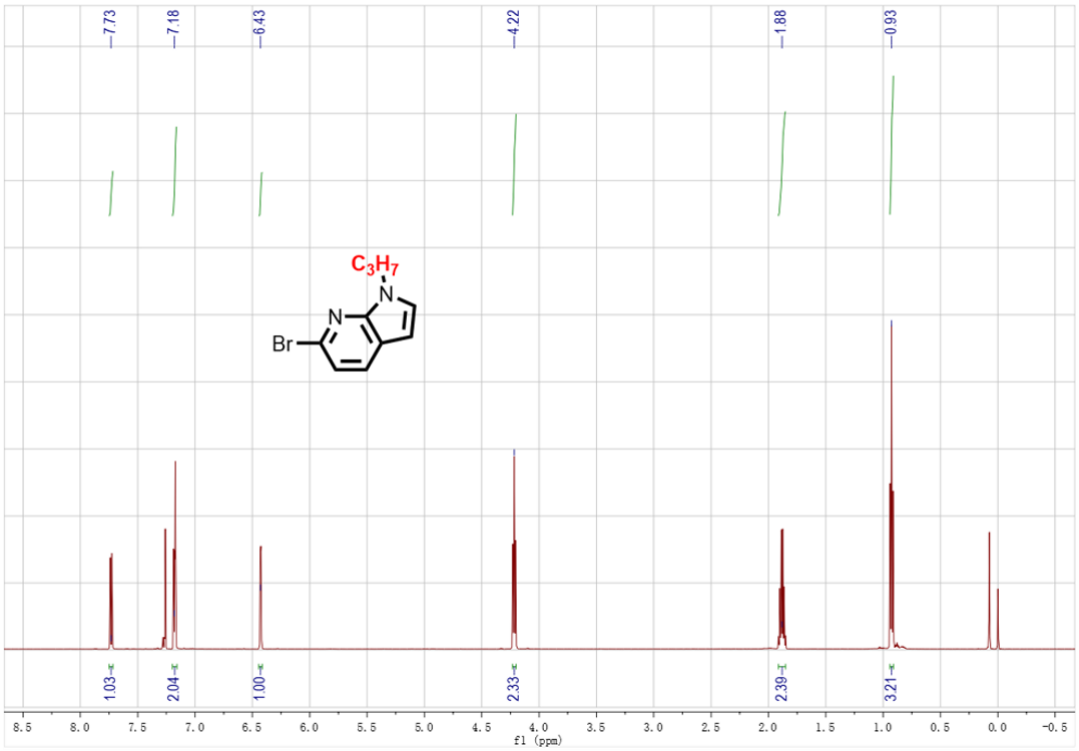


Fig. S15. ^{1}H spectrum of 6-bromo-1-(2- propyl)-1*H*-pyrrolo[2,3-*b*]pyridine in $CDCl_3$.

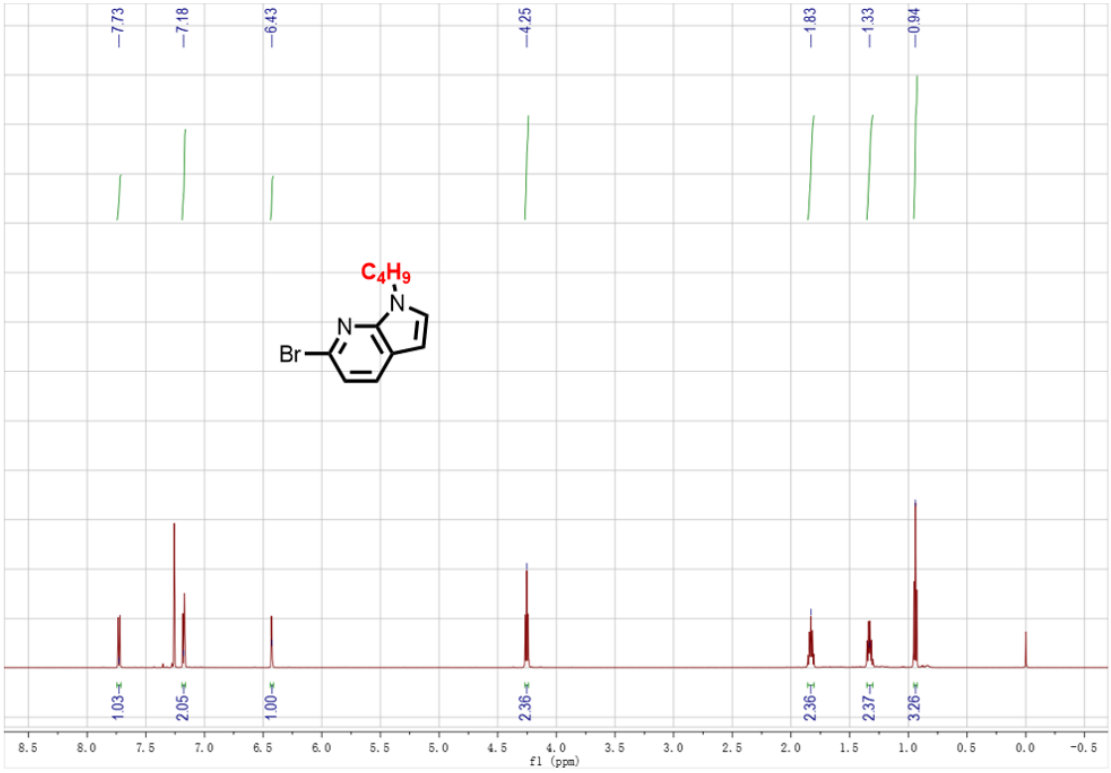


Fig. S16. ^{1}H spectrum of 6-bromo-1-(2-butyl)-1*H*-pyrrolo[2,3-*b*]pyridine in $CDCl_3$.

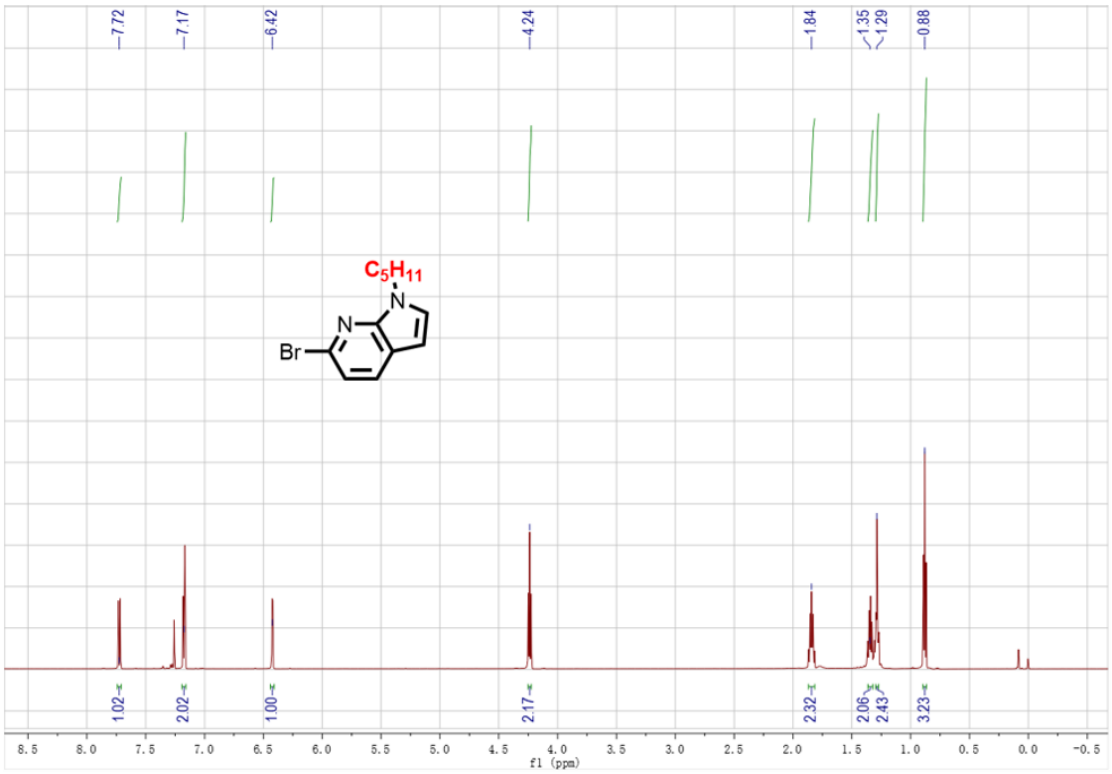


Fig. S17. ^{1}H spectrum of 6-bromo-1-(2-amyl)-1*H*-pyrrolo[2,3-*b*]pyridine in $CDCl_3$.

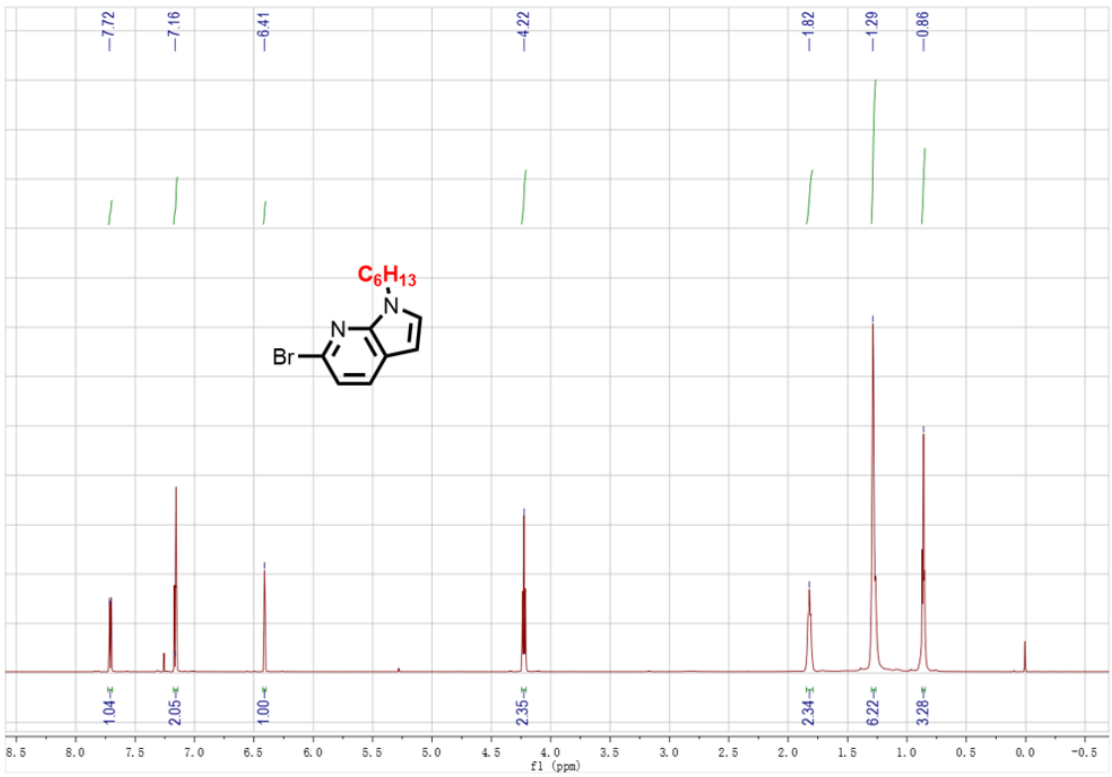


Fig. S18. ^{1}H spectrum of 6-bromo-1-(2-hexyl)-1*H*-pyrrolo[2,3-*b*]pyridine in $CDCl_3$.

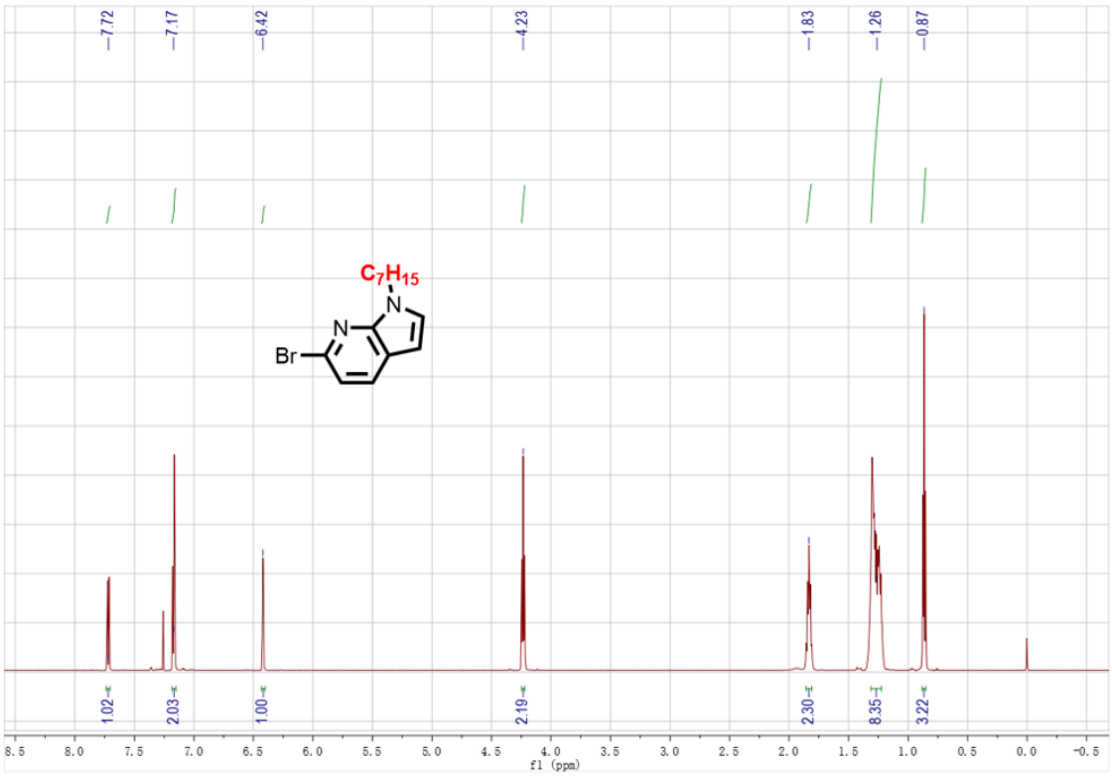


Fig. S19. ^{1}H spectrum of 6-bromo-1-(2-heptyl)-1*H*-pyrrolo[2,3-*b*]pyridine in $CDCl_3$.

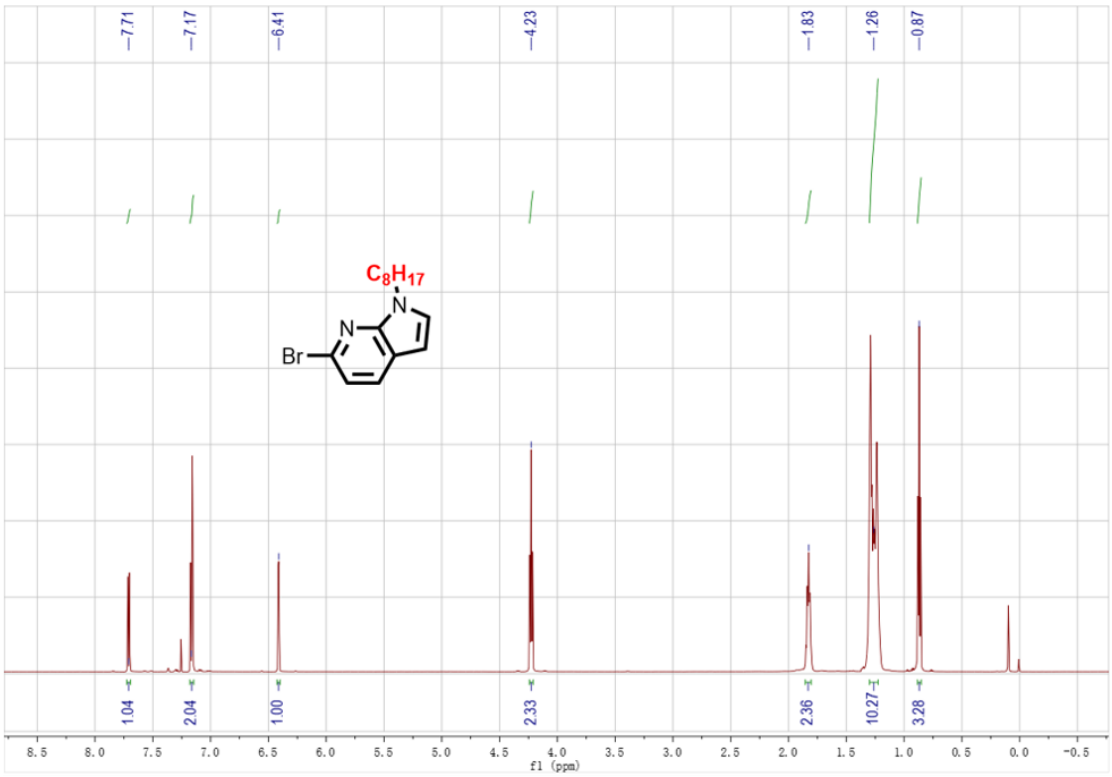


Fig. S20. ^{1}H spectrum of 6-bromo-1-(2- octyl)-1*H*-pyrrolo[2,3-*b*]pyridine in $CDCl_3$.

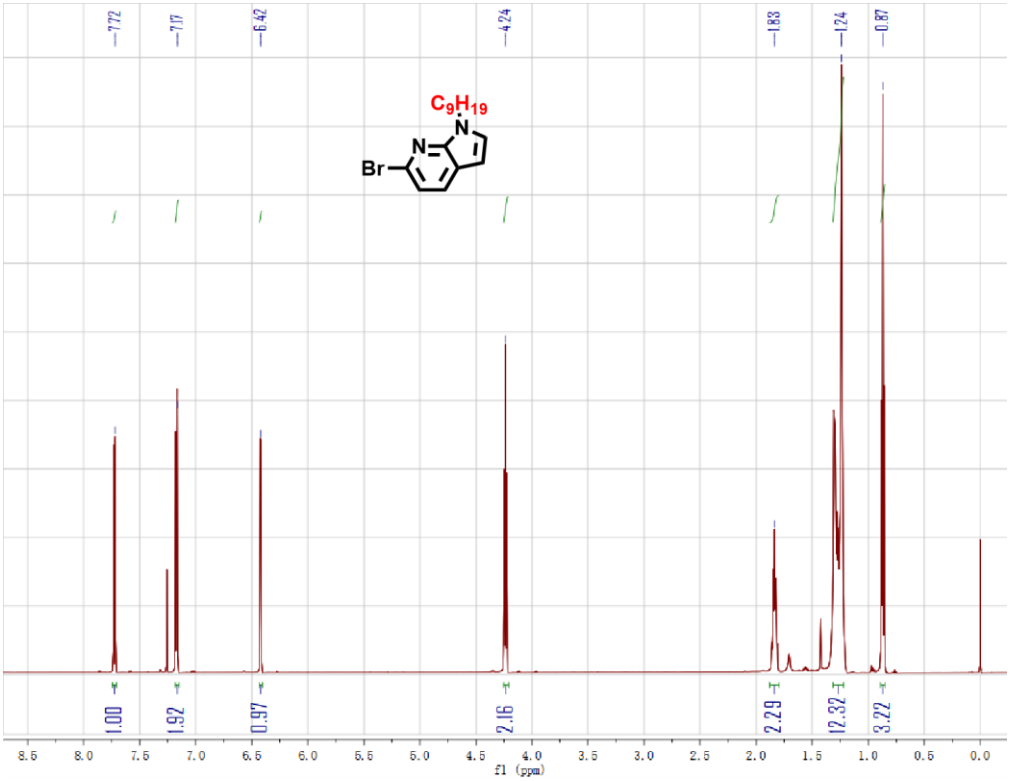


Fig. S21. ^{1}H spectrum of 6-bromo-1-(2-nonyl)-1*H*-pyrrolo[2,3-*b*]pyridine in $CDCl_3$.

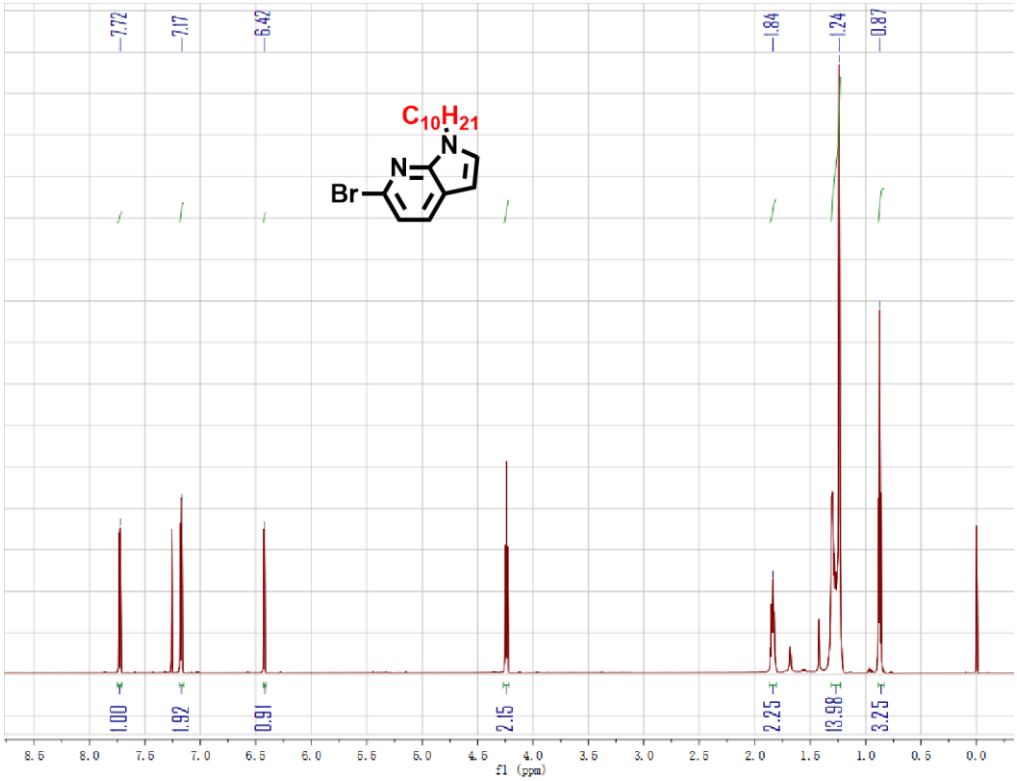


Fig. S22. ^{1}H spectrum of 6-bromo-1-(2-decyl)-1*H*-pyrrolo[2,3-*b*]pyridine in $CDCl_3$.

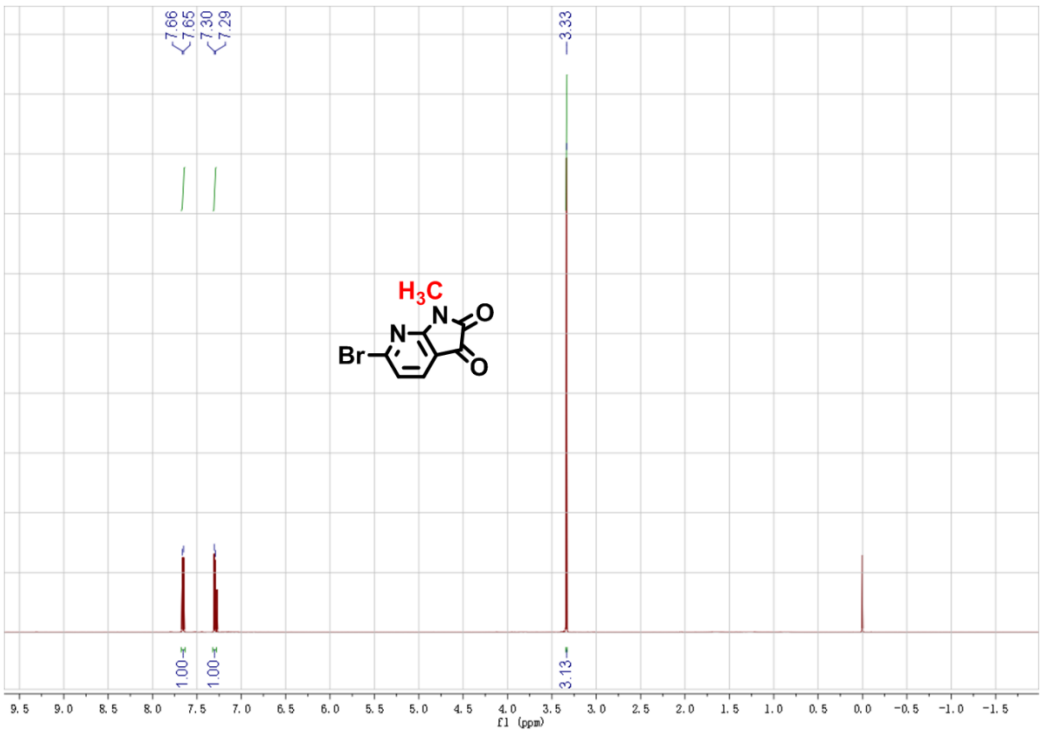


Fig. S23. ^{1}H spectrum of 6-bromo-1-(2-methyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione in $CDCl_3$.

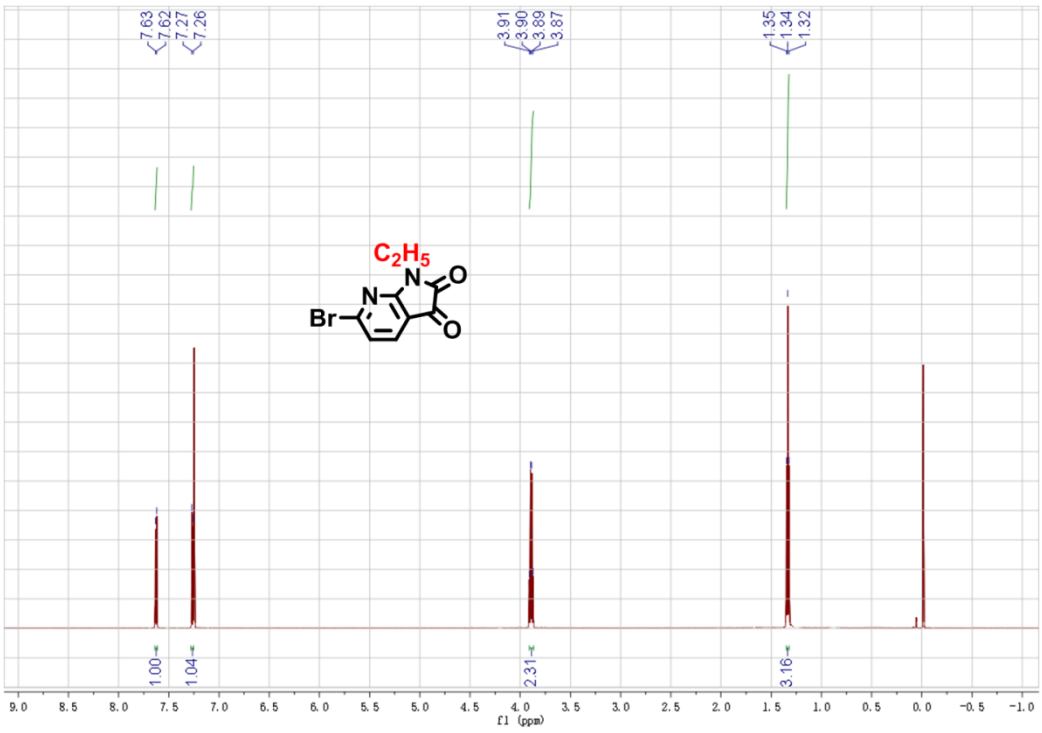


Fig. S24. ^{1}H spectrum of 6-bromo-1-(2-ethyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione in $CDCl_3$.

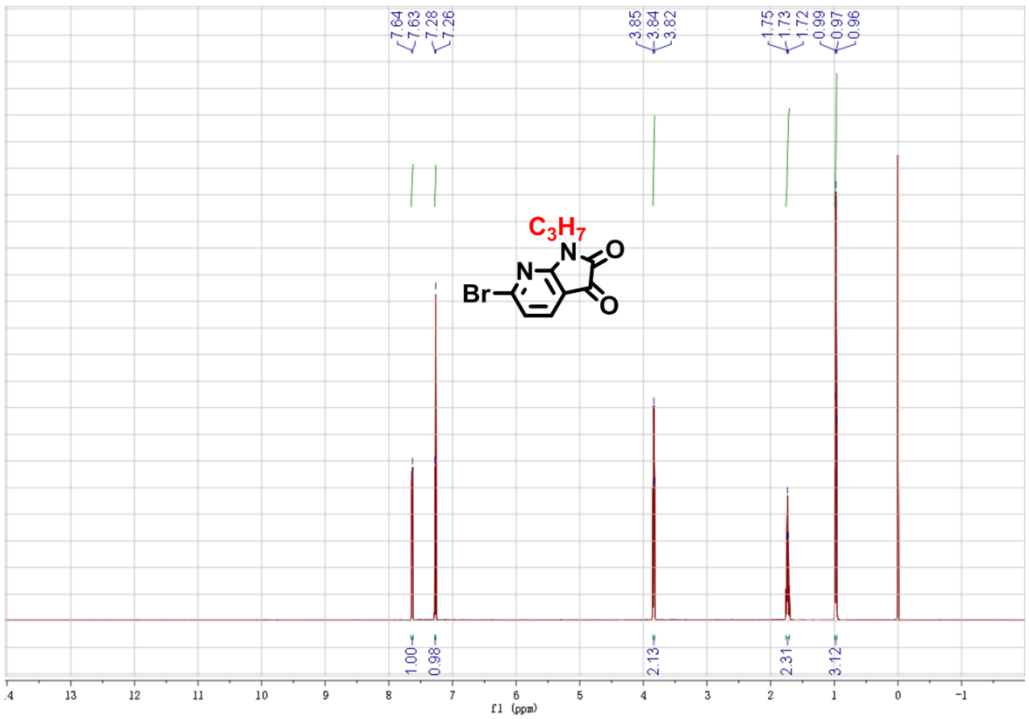


Fig. S25. ^{1}H spectrum of 6-bromo-1-(2-propyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione in $CDCl_3$.

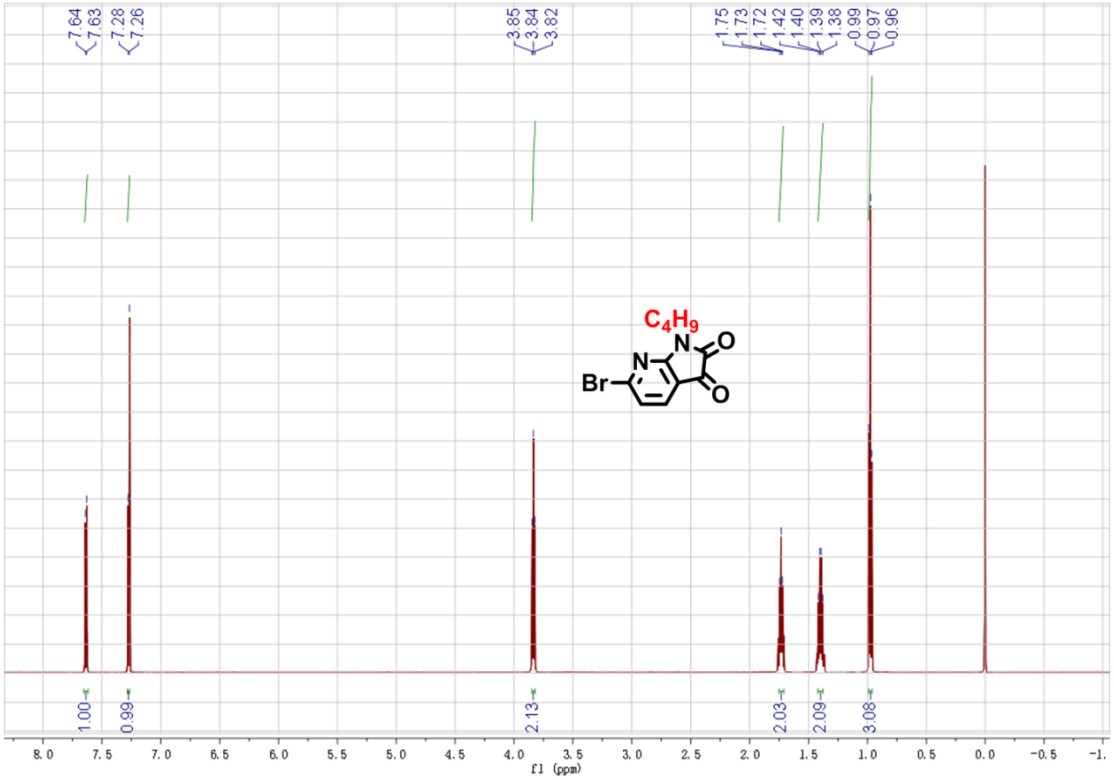


Fig. S26. ^{1}H spectrum of 6-bromo-1-(2-butyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione in $CDCl_3$.

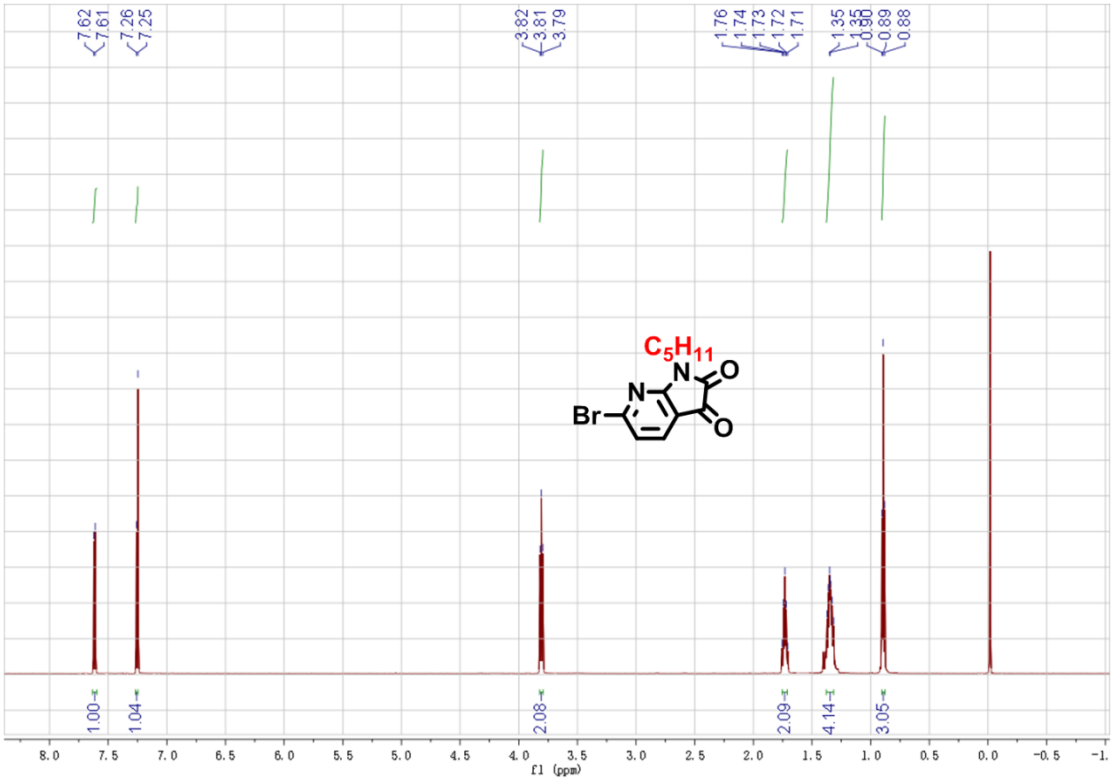


Fig. S27. ^{1}H spectrum of 6-bromo-1-(2-amyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione in $CDCl_3$.

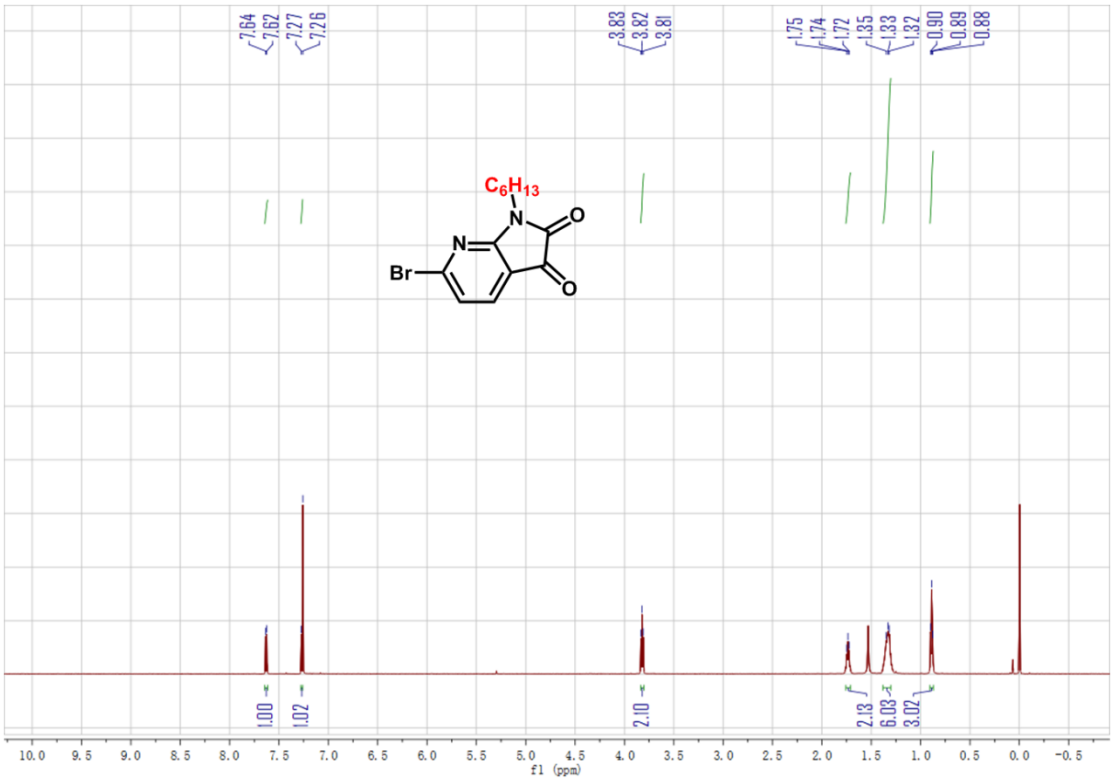


Fig. S28. ^{1}H spectrum of 6-bromo-1-(2-hexyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione in $CDCl_3$.

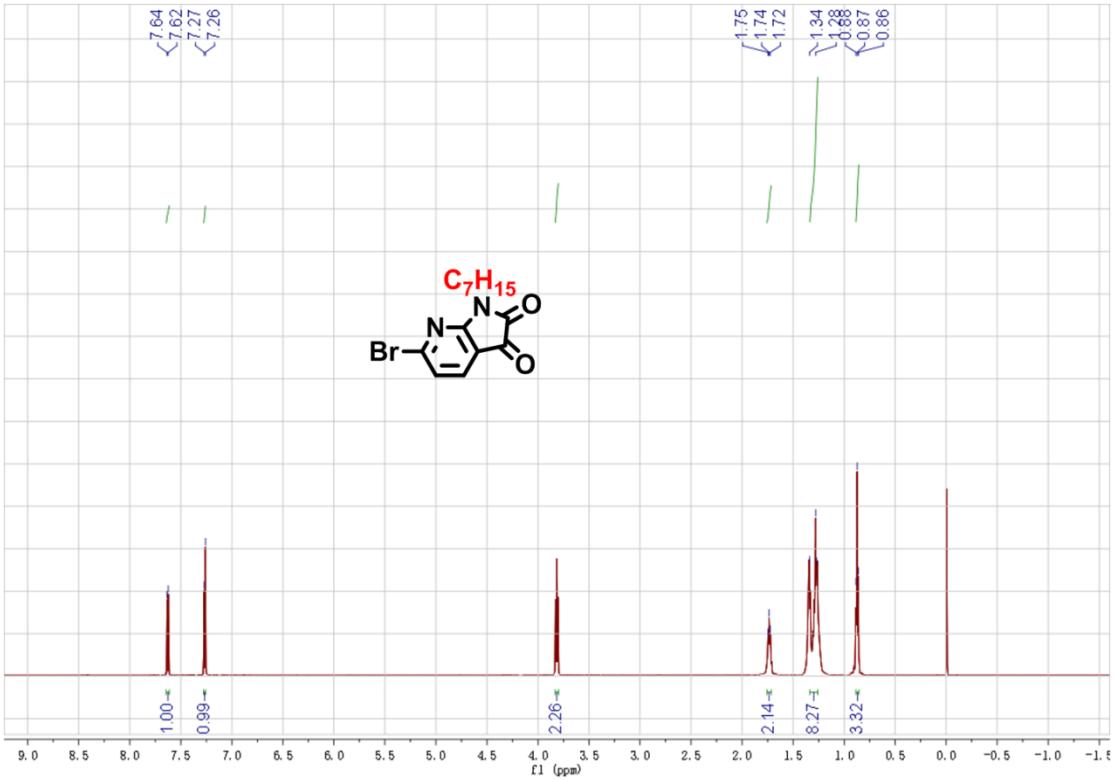


Fig. S29. ^{1}H spectrum of 6-bromo-1-(2-heptyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione in $CDCl_3$.

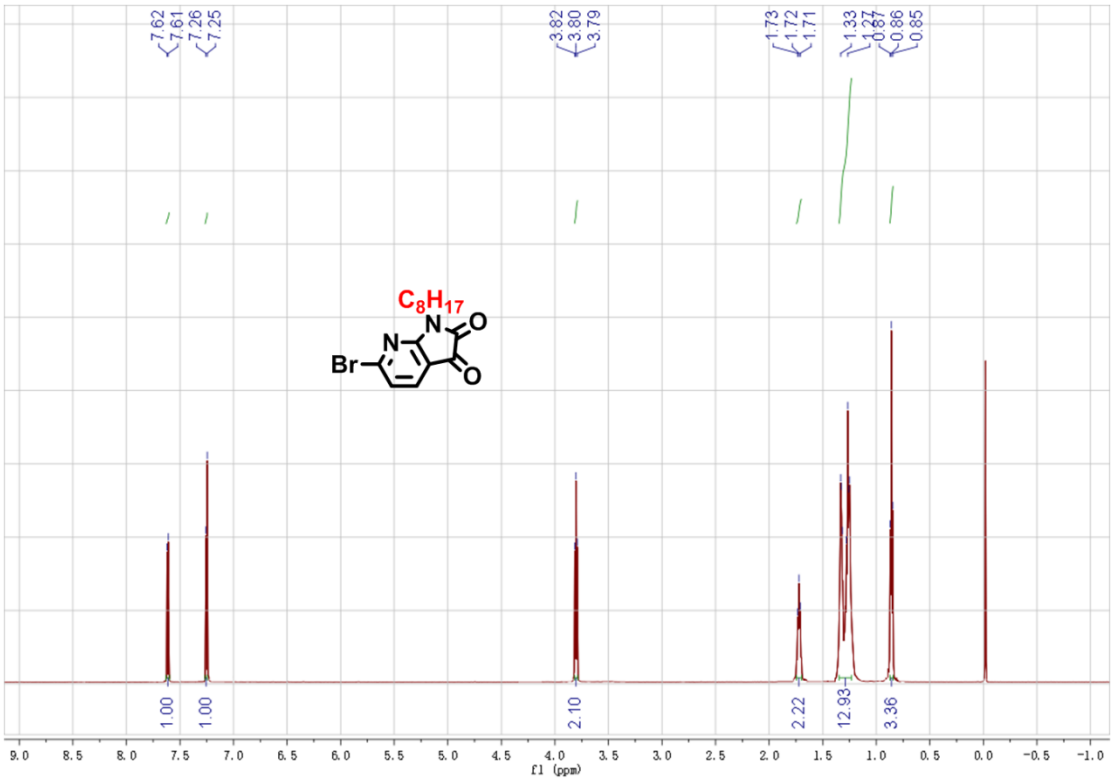


Fig. S30. ^{1}H spectrum of 6-bromo-1-(2-octyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione in $CDCl_3$.

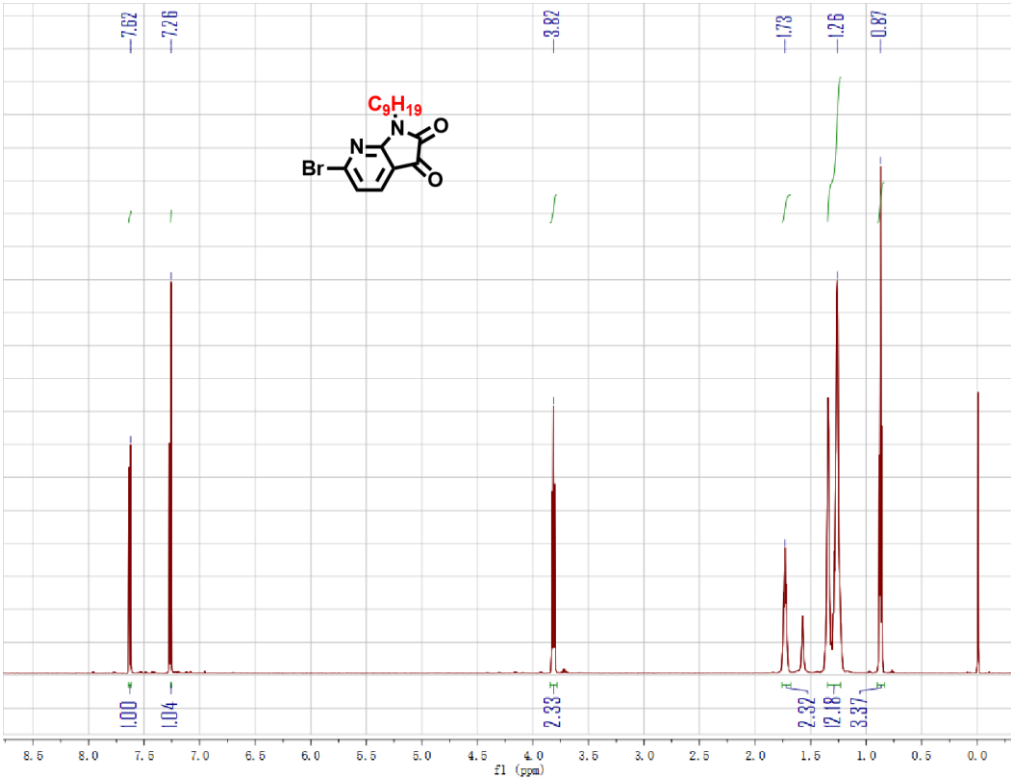


Fig. S31. ^{1}H spectrum of 6-bromo-1-(2-nonyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione in $CDCl_3$.

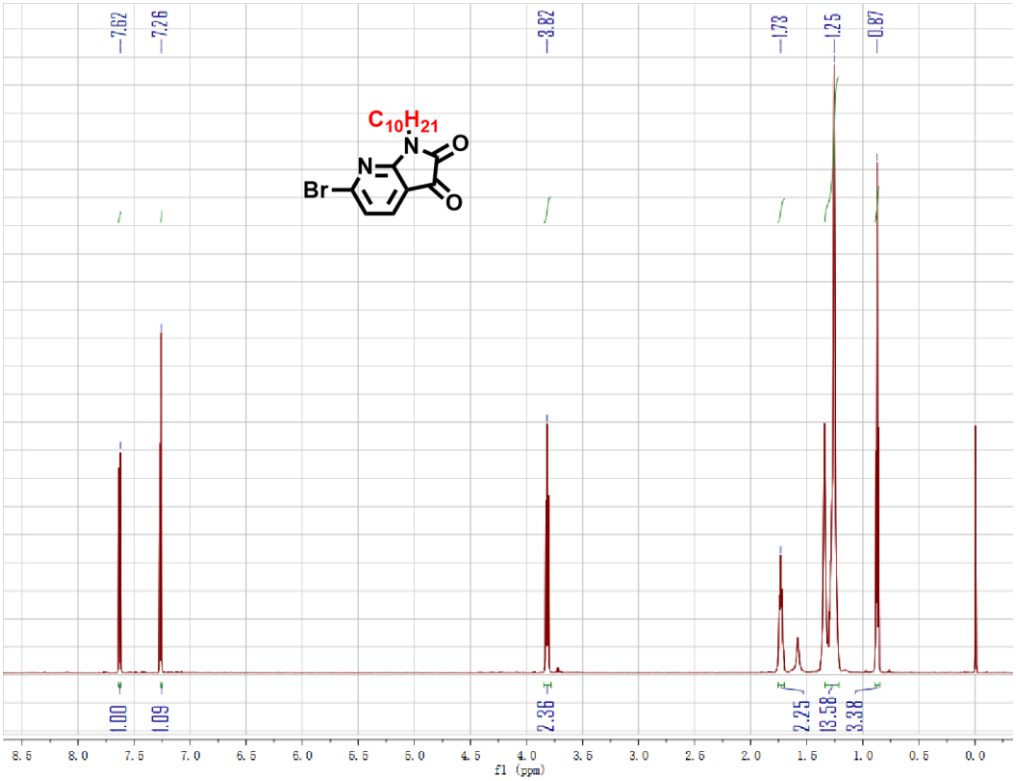


Fig. S32. ^{1}H spectrum of 6-bromo-1-(2-decyl)-1*H*-pyrrolo[2,3-*b*]pyridine-2,3-dione in $CDCl_3$.

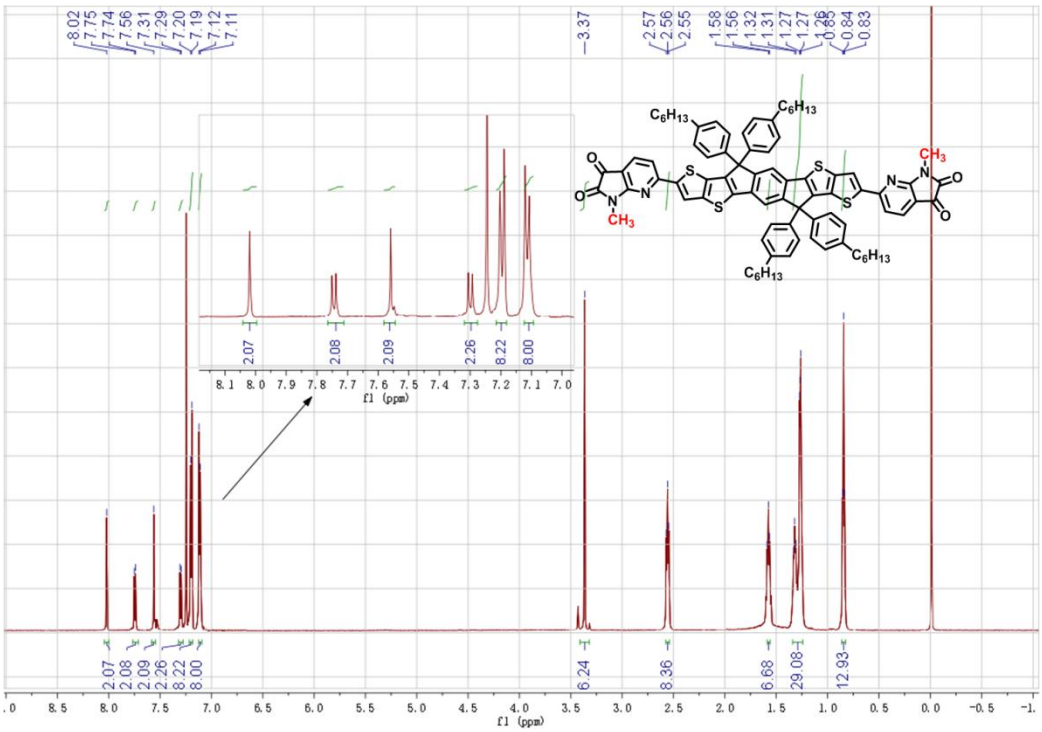


Fig. S33. ^{1}H spectrum of **C1** in $CDCl_3$.

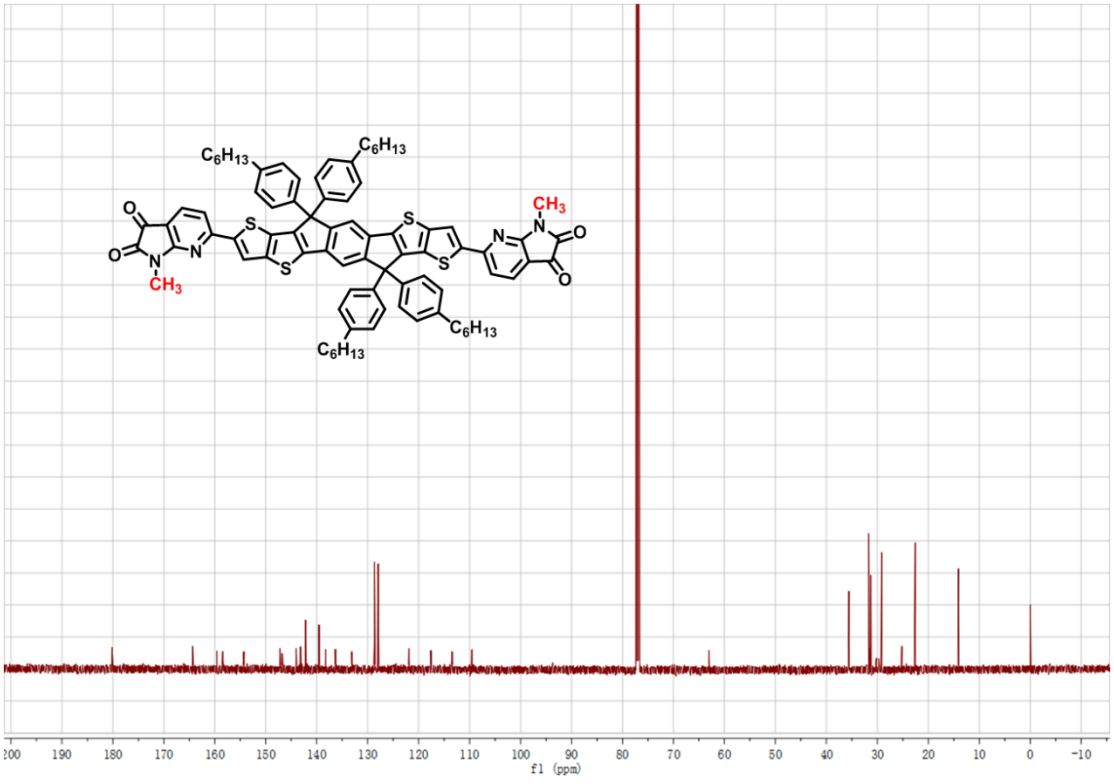


Fig. S34. ^{13}C spectrum of **C1** in $CDCl_3$.

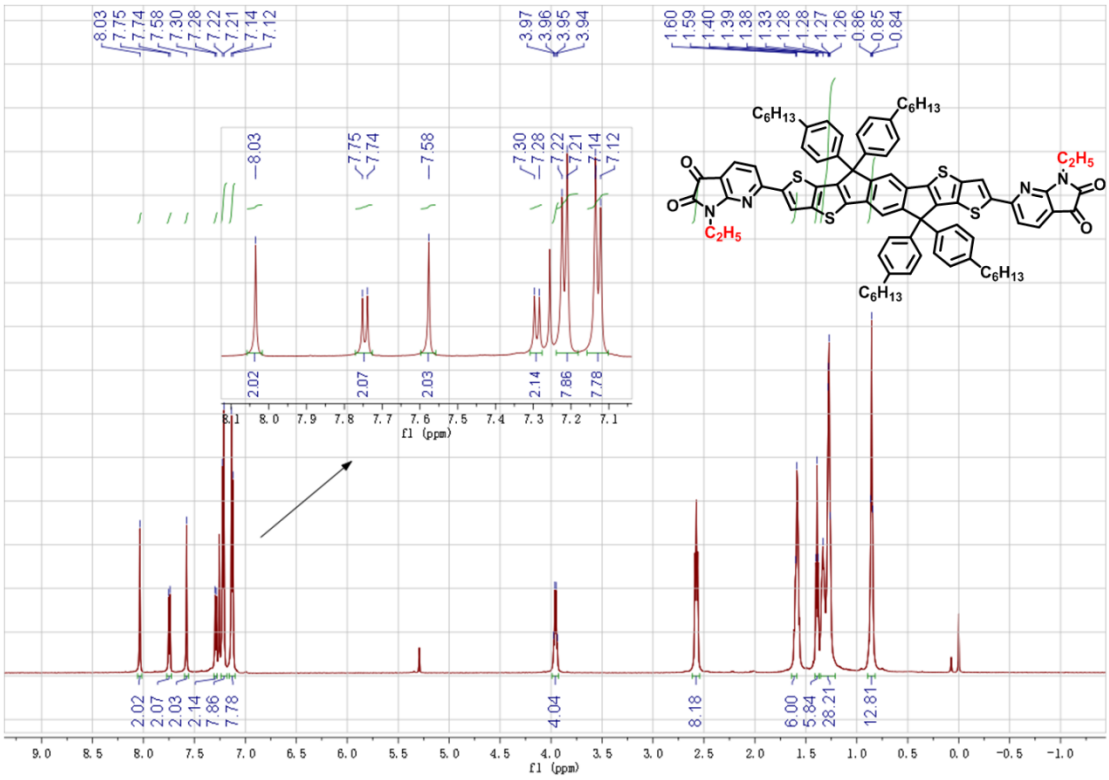


Fig. S35. ^{1}H spectrum of **C2** in $CDCl_3$.

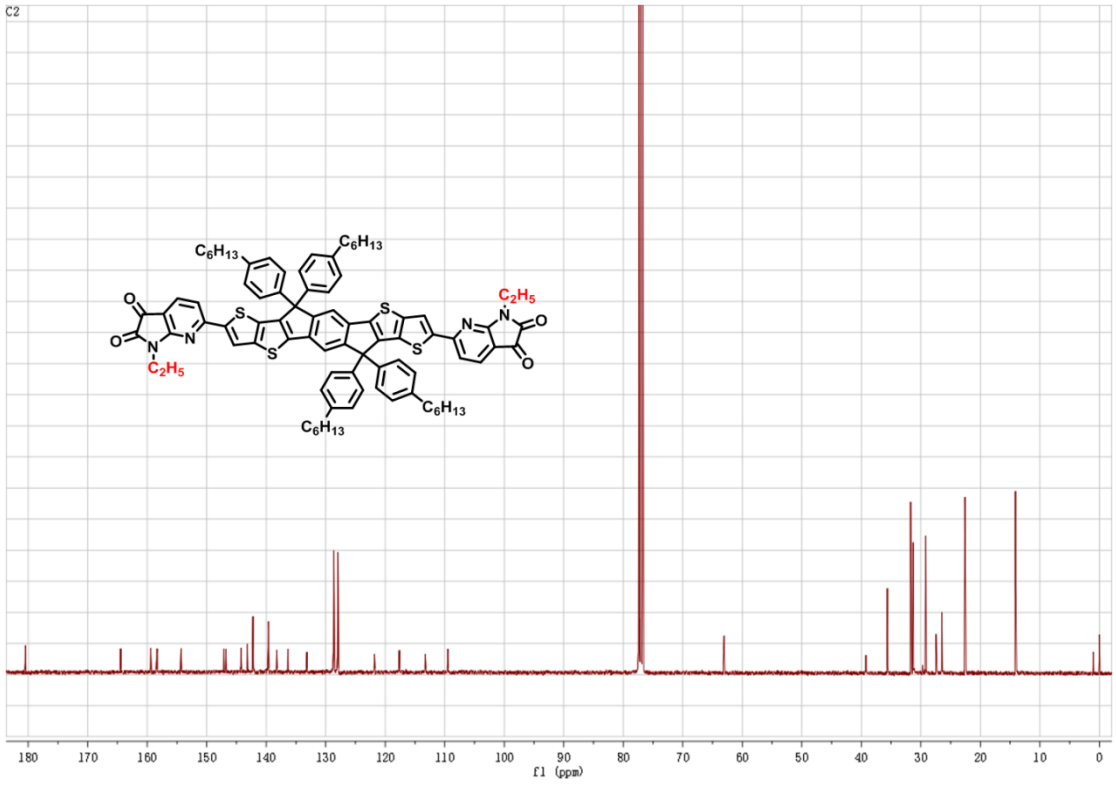


Fig. S36. ^{13}C spectrum of **C2** in $CDCl_3$.

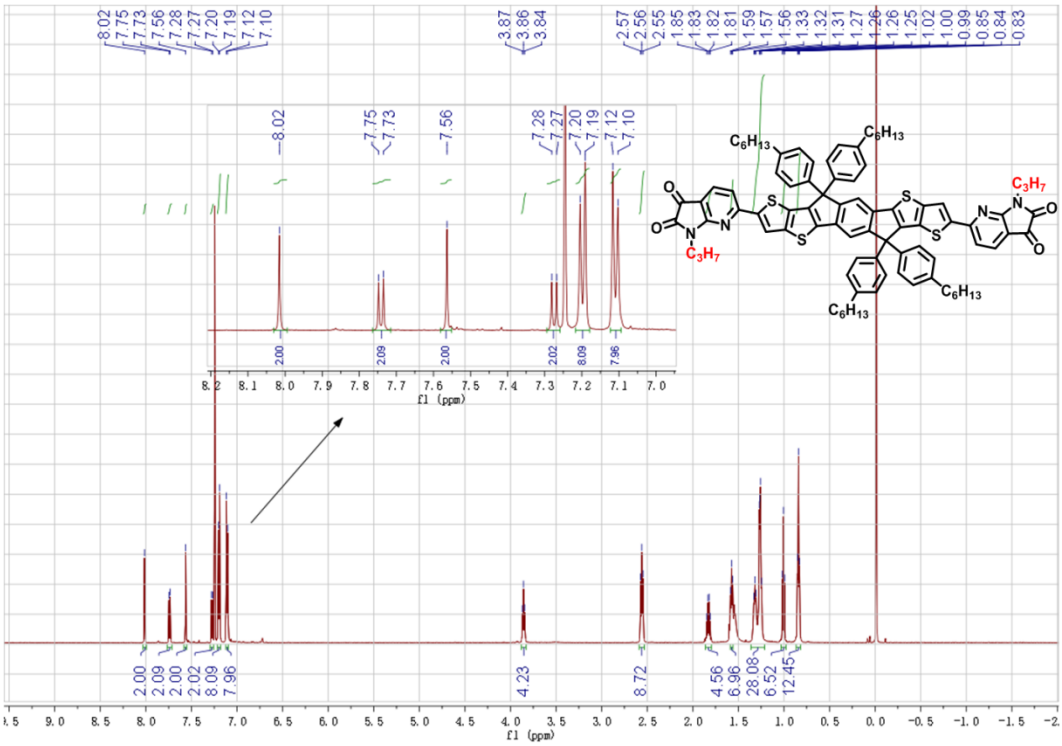


Fig. S37. ^{1}H spectrum of **C3** in $CDCl_3$.

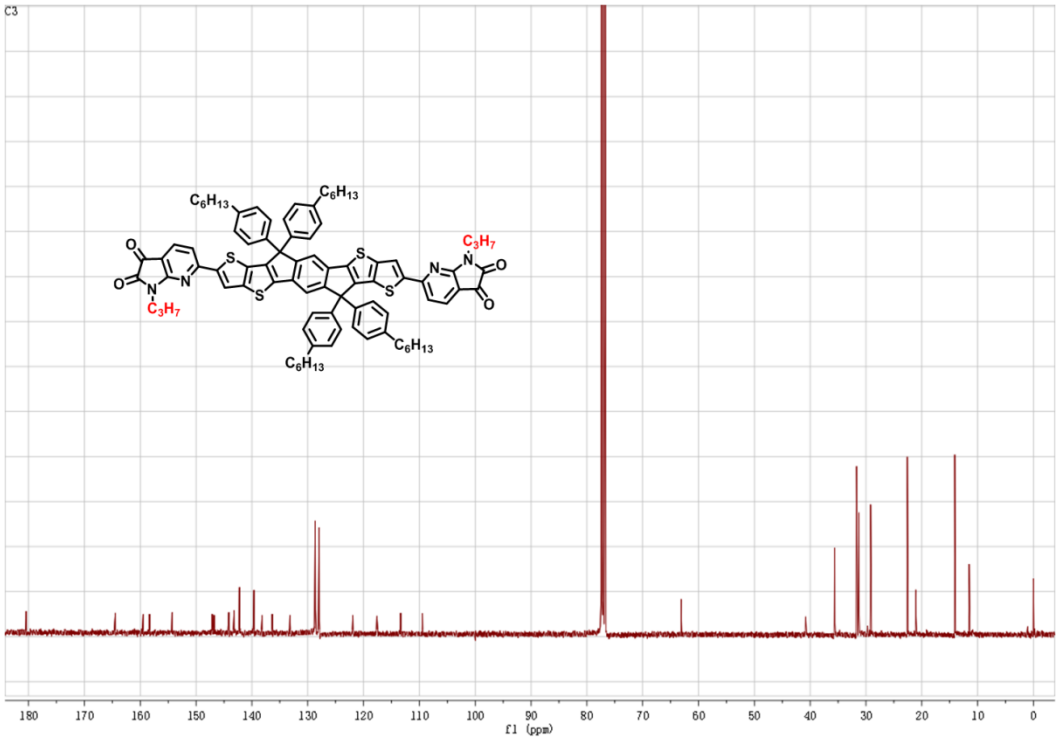


Fig. S38. ^{13}C spectrum of **C3** in $CDCl_3$.

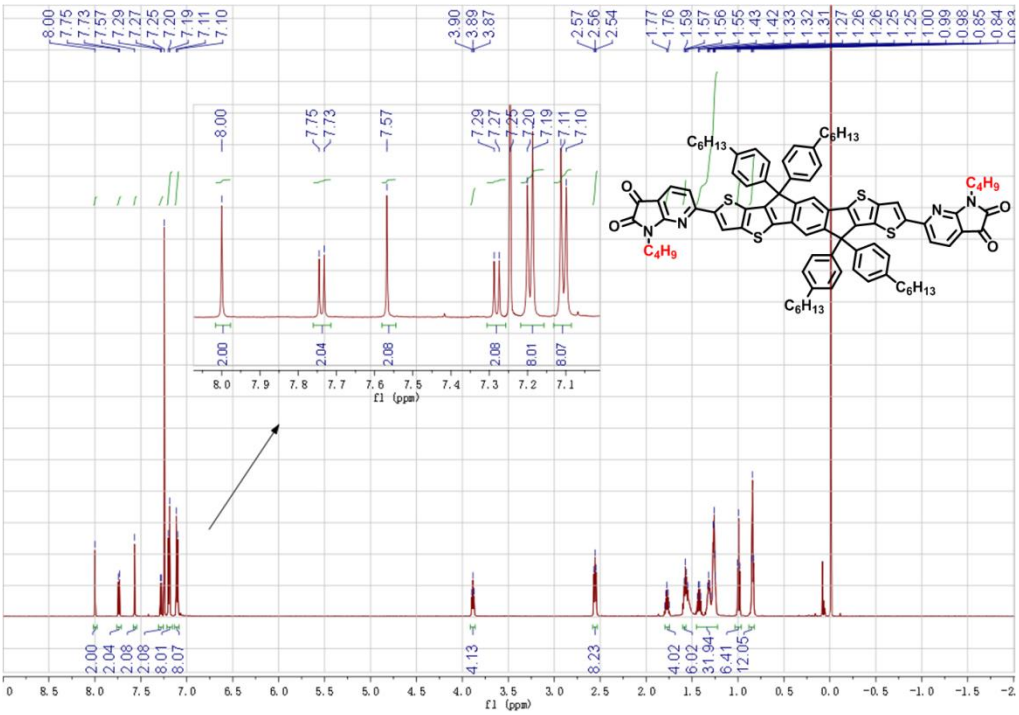


Fig. S39. ^{1}H spectrum of **C4** in $CDCl_3$.

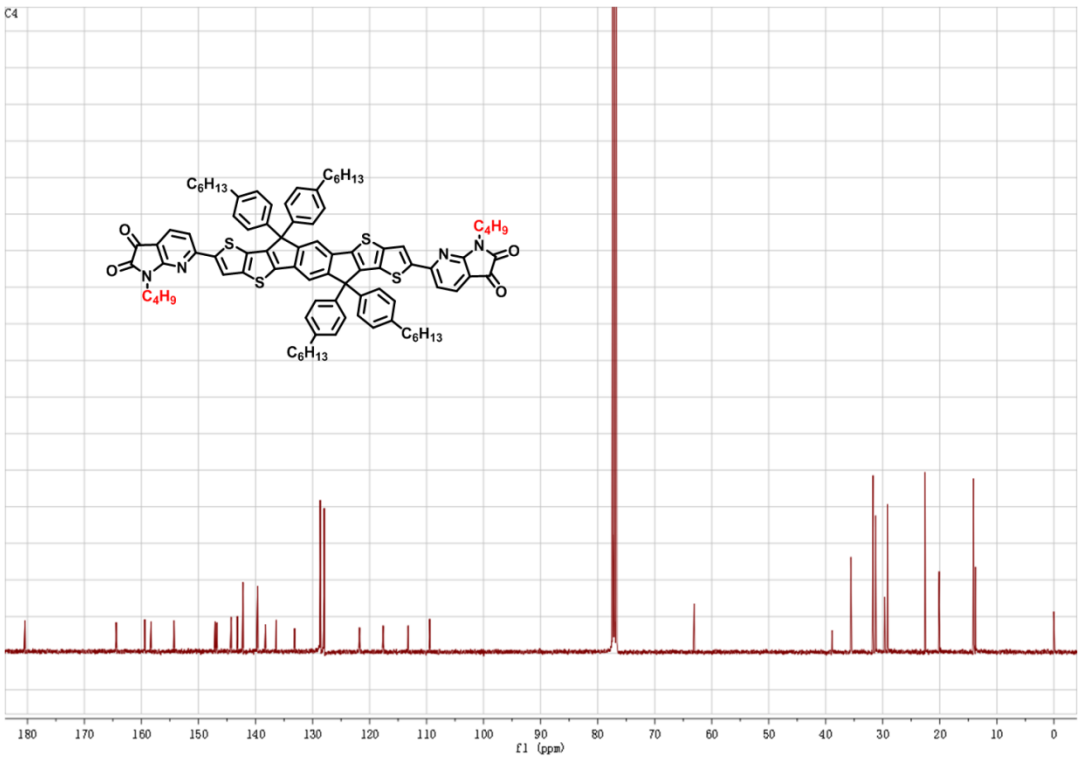


Fig. S40. ^{13}C spectrum of **C4** in $CDCl_3$.

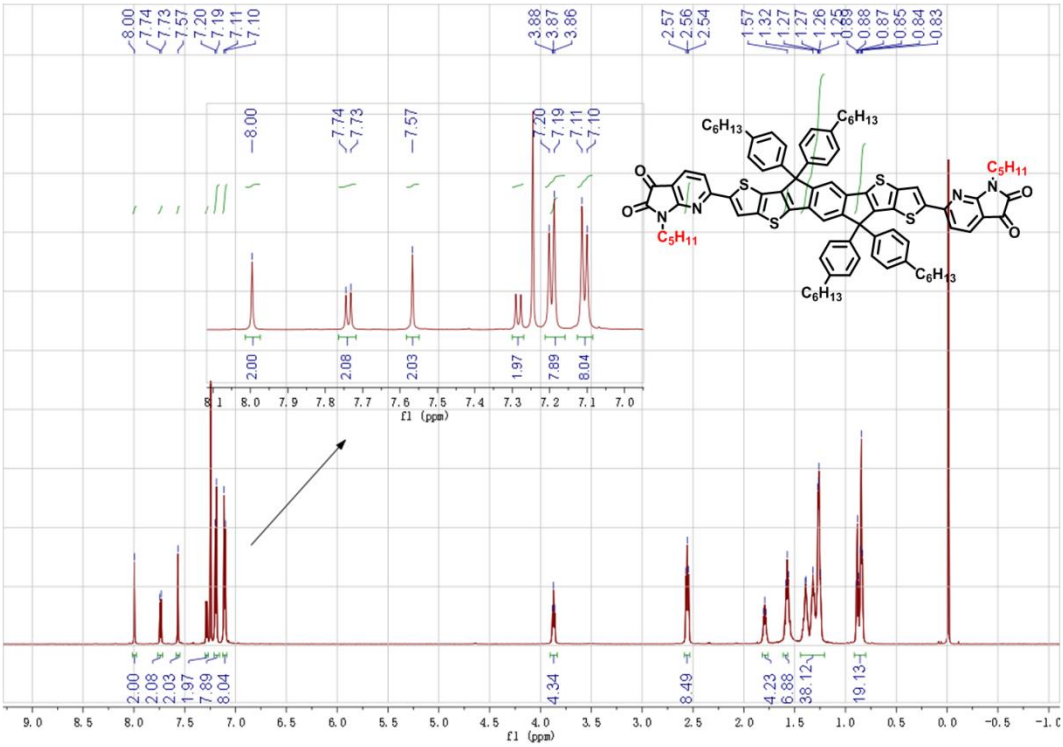


Fig. S41. ^{1}H spectrum of **C5** in $CDCl_3$.

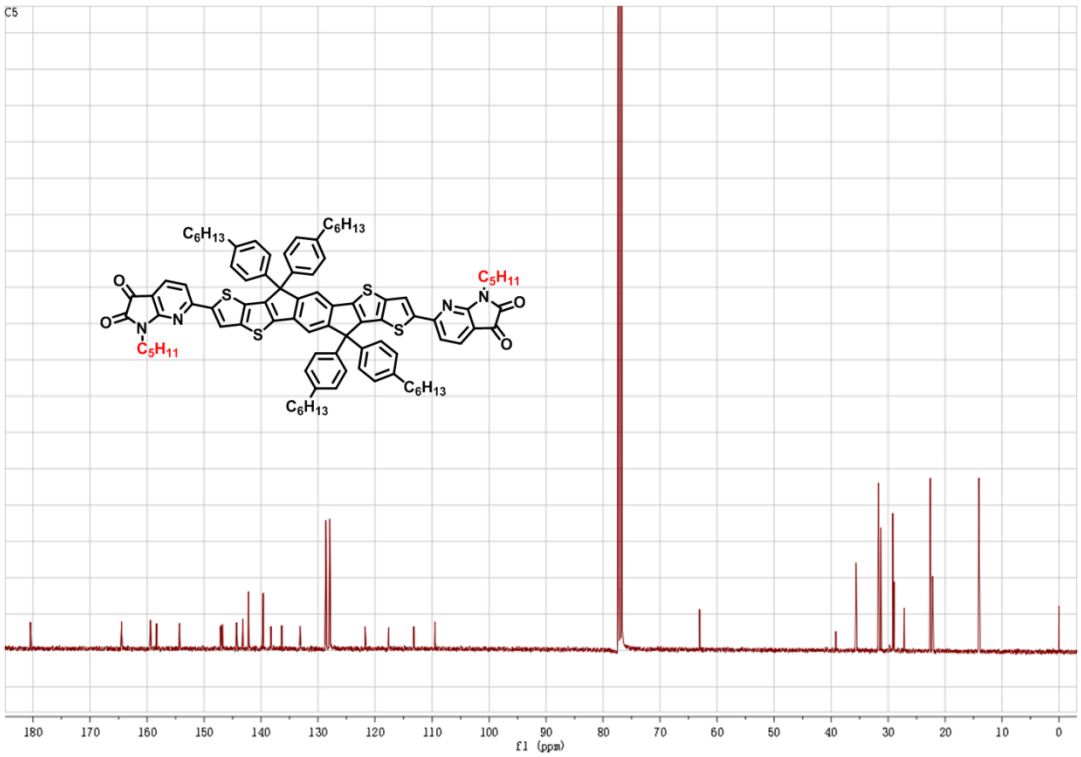


Fig. S42. ^{13}C spectrum of **C5** in $CDCl_3$.

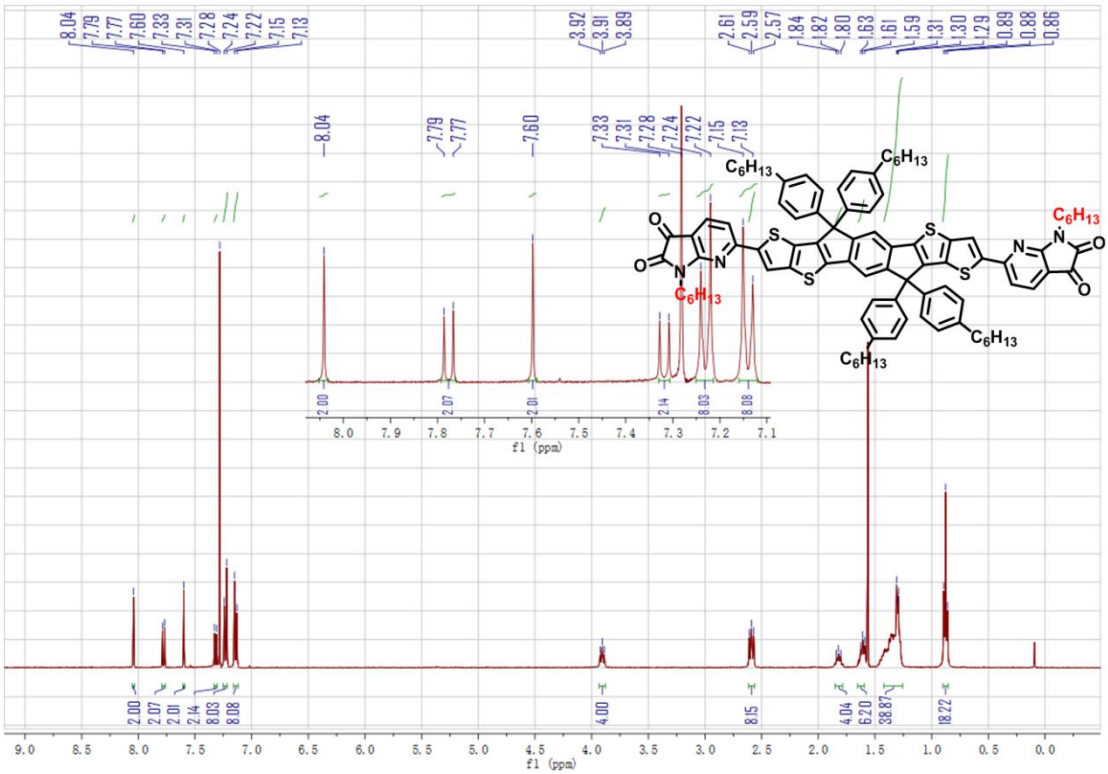


Fig. S43. ^{1}H spectrum of **C6** in $CDCl_3$.

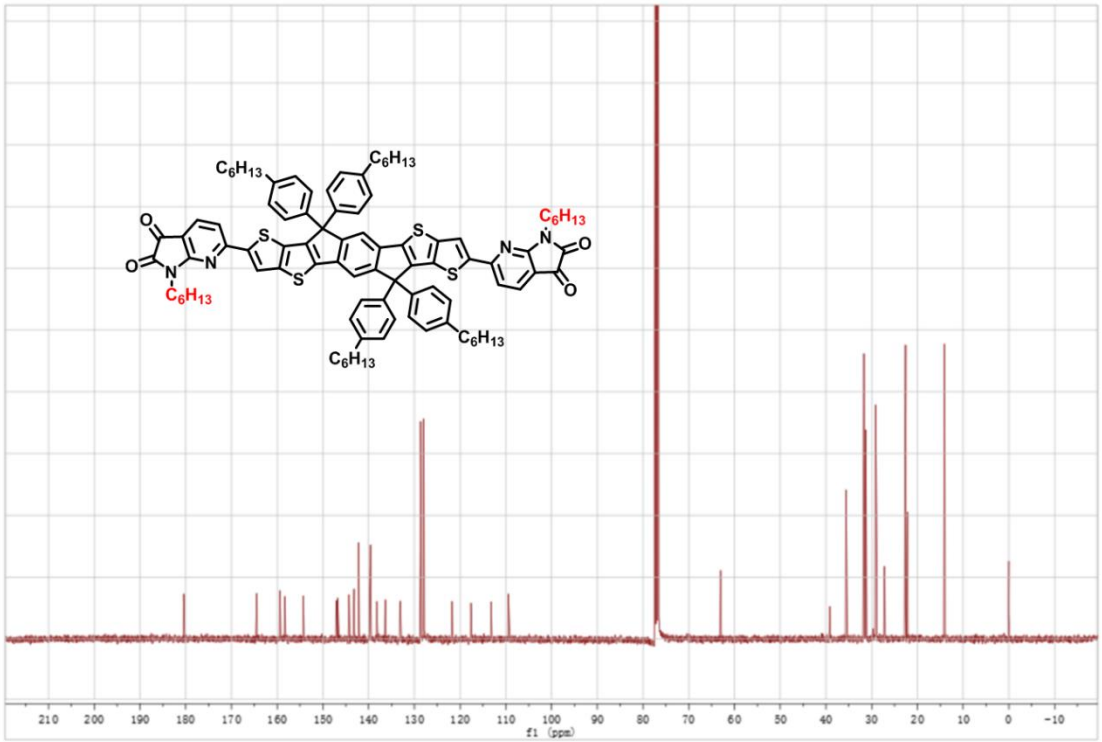


Fig. S44. ^{13}C spectrum of **C6** in $CDCl_3$.

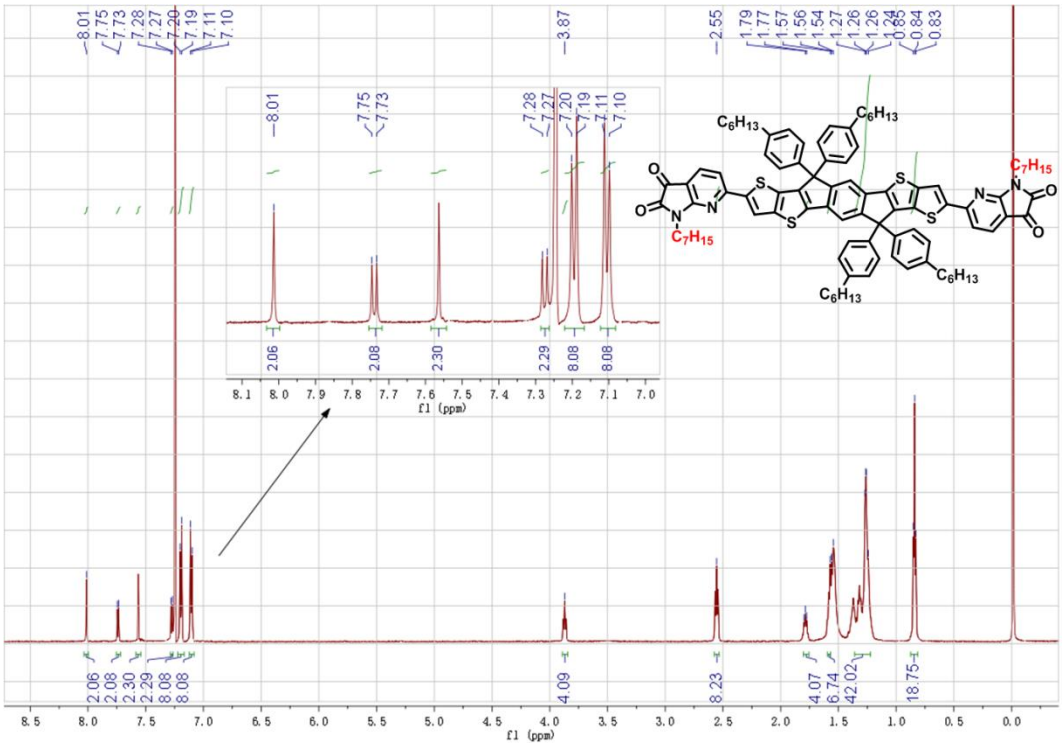


Fig. S45. ^{1}H spectrum of **C7** in $CDCl_3$.

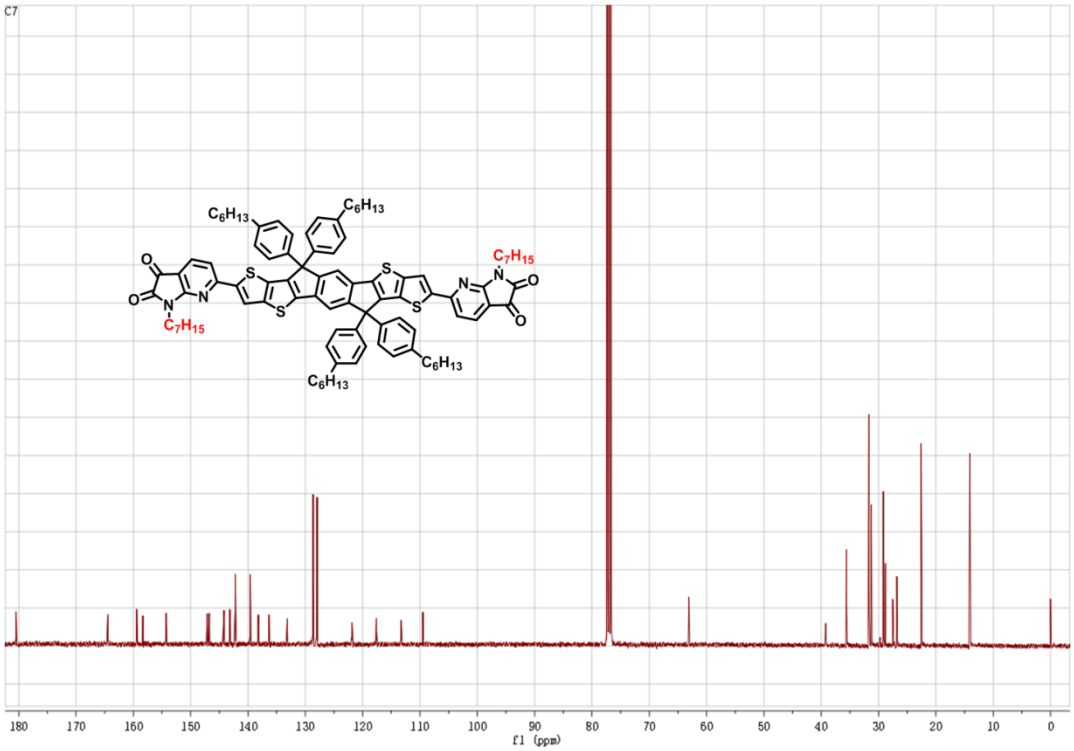


Fig. S46. ^{13}C spectrum of **C7** in $CDCl_3$.

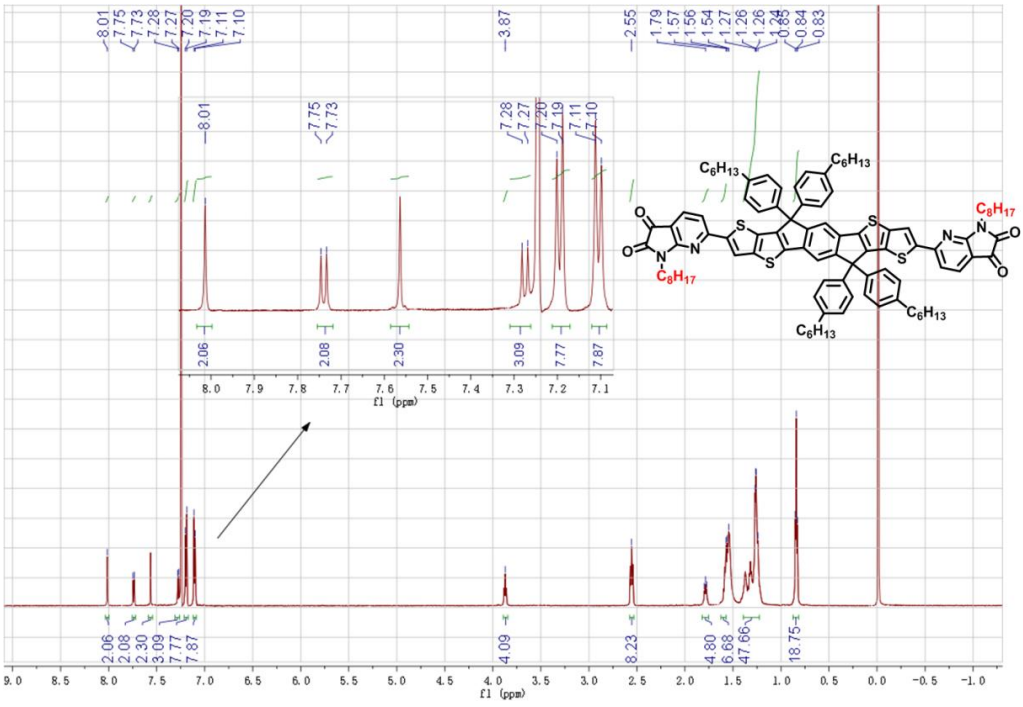


Fig. S47. ^{1}H spectrum of **C8** in $CDCl_3$.

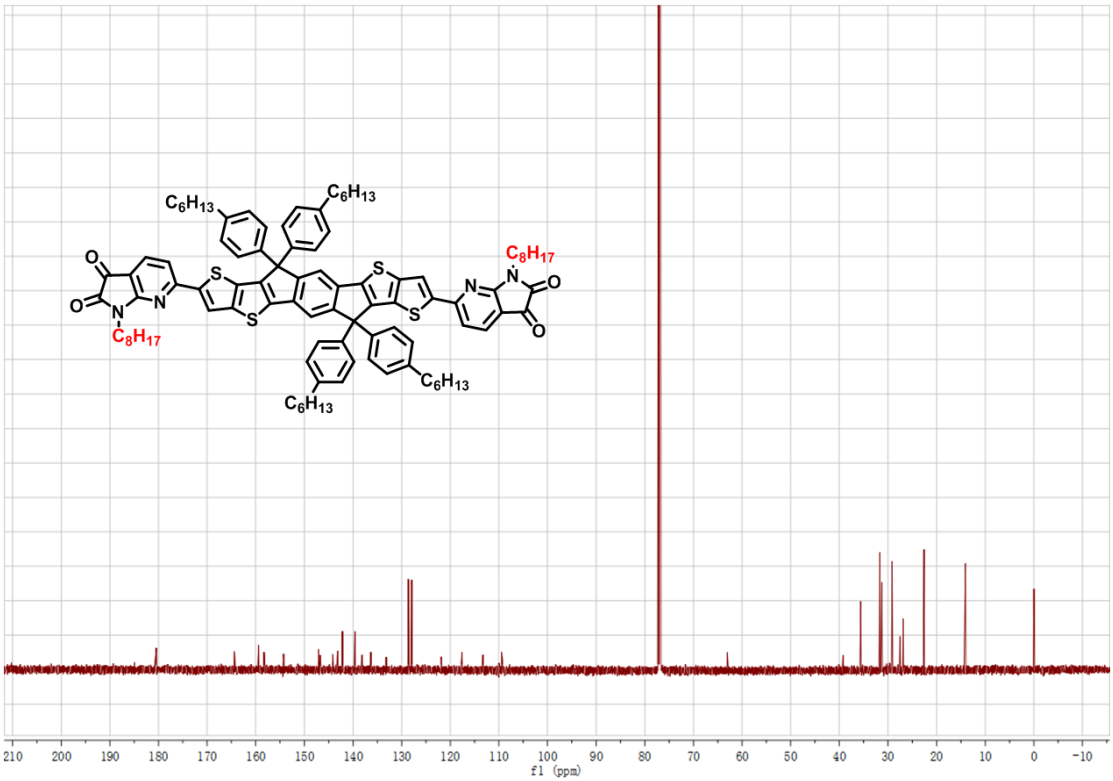


Fig. S48. ^{13}C spectrum of **C8** in $CDCl_3$.

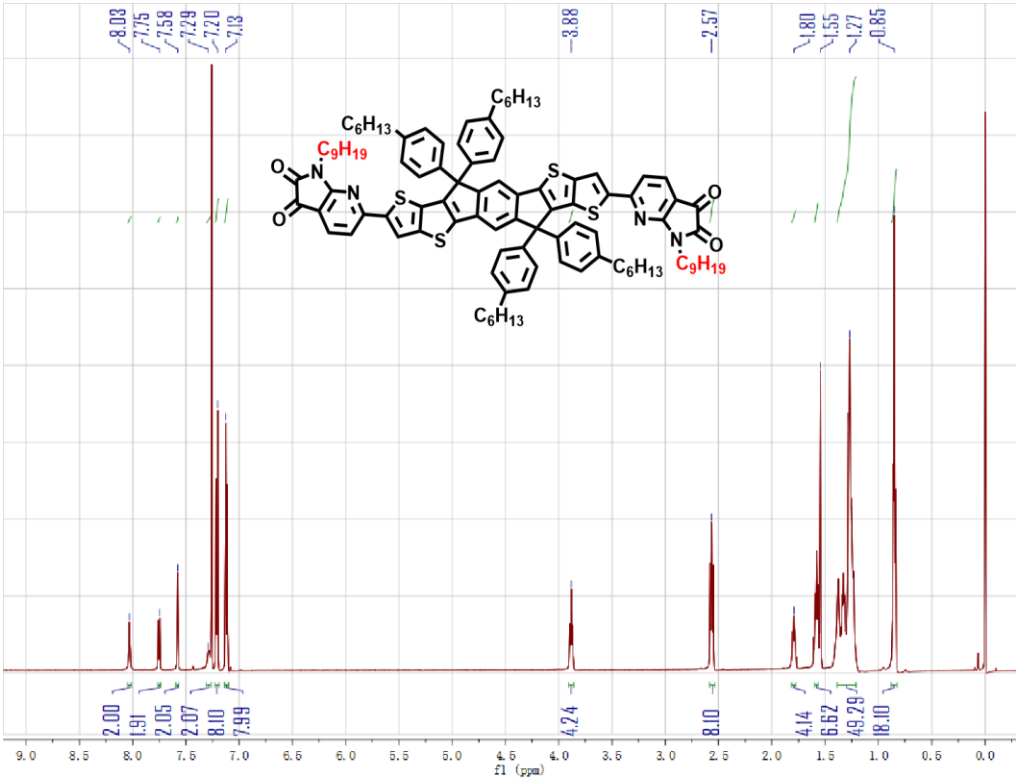


Fig. S49. ^{1}H spectrum of **C9** in $CDCl_3$.

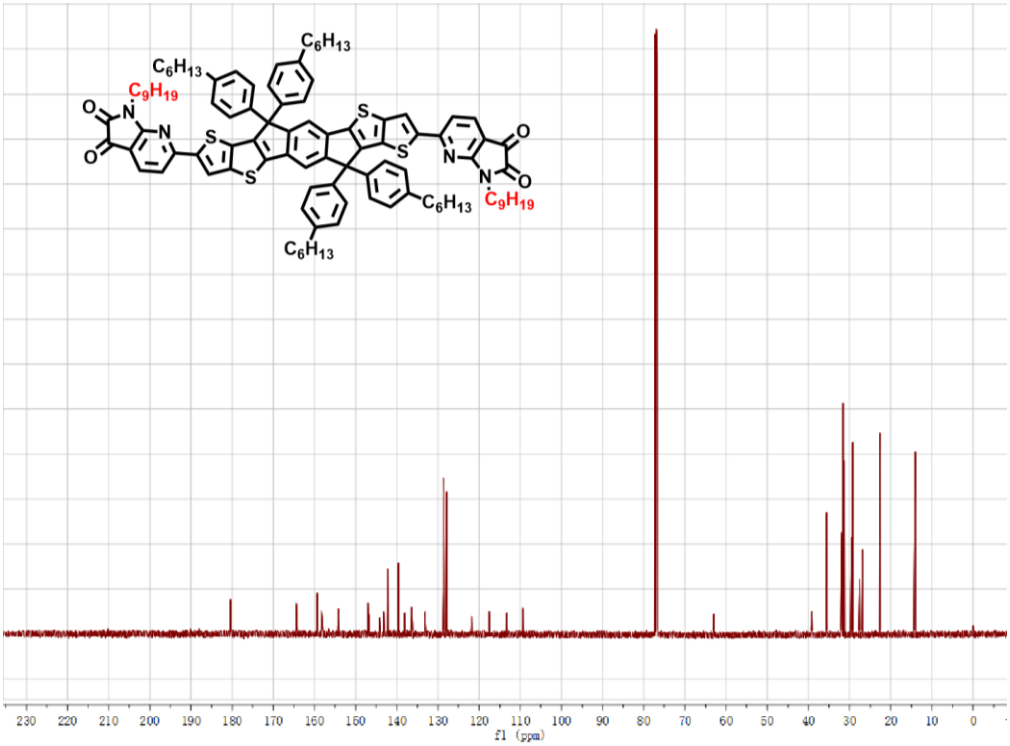


Fig. S50. ^{13}C spectrum of **C9** in $CDCl_3$.

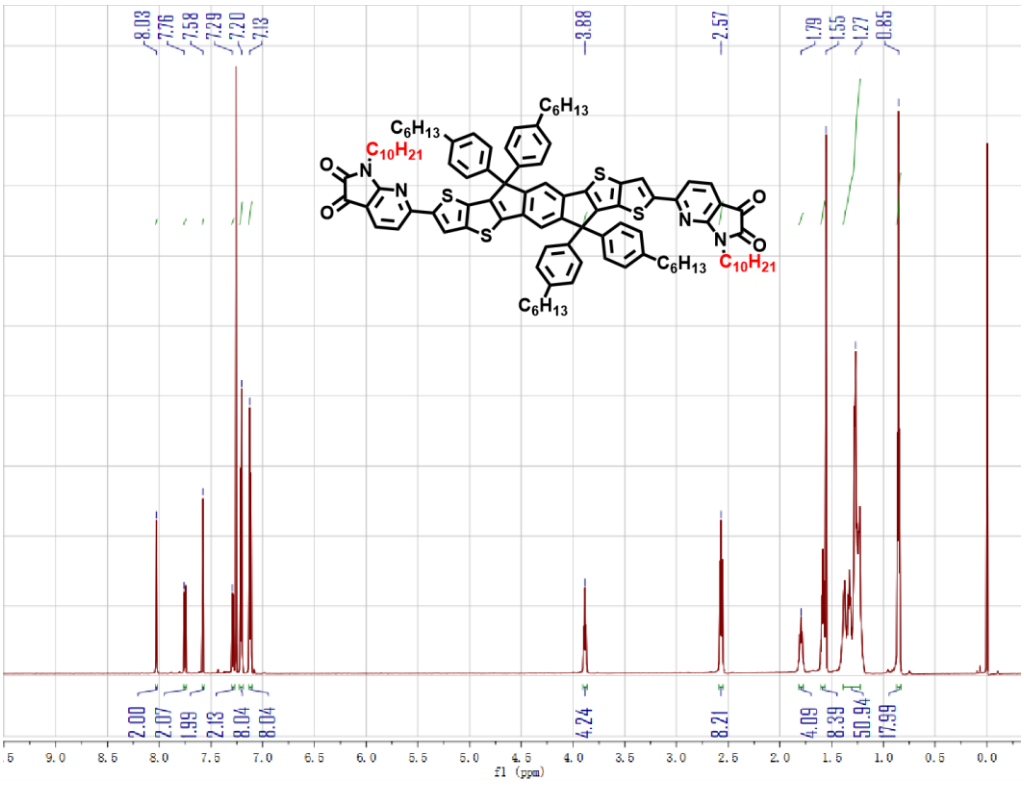


Fig. S51. ^{1}H spectrum of **C10** in $CDCl_3$.

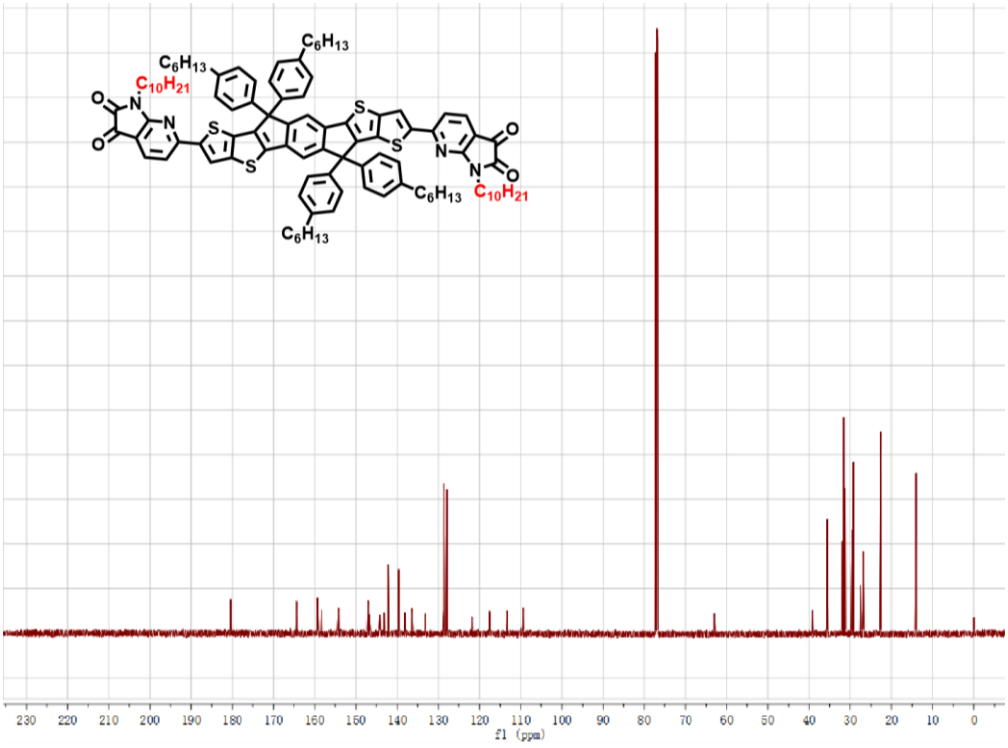


Fig. S52. ^{13}C spectrum of **C10** in $CDCl_3$.

[S1] R. C. Hynes and Y. Le Page, *J. Appl. Cryst.***1991**, *24*, 352.

[S2] Y. Ito, A. A. Virkar, S. Mannsfeld, J. H. Oh, M. Toney, J. Locklin, Z. Bao, *J. Am. Chem. Soc.* **2009**, 131, 9396.