

Electronic Supplementary Information (ESI)

Pyrazine-fused isoindigo: a new building block for polymer solar cells with high open circuit voltage

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1. Materials and Characterization

All the starting materials were obtained from HEOWNS and J&K in analytical grade. All chromatographic separations of small molecules were carried out on silica gel (200-300 mesh). All chromatographic separations of polymers were carried out on silica gel (60-80 mesh). Tetrahydrofuran and toluene were dried and distilled by sodium and DMF was dried by calcium hydride and distilled under reduced pressure. Other solvents and chemicals used in this work were analytical grade. BDT2TC8¹ and BTT2TC10² were synthesized according to the relevant literature. The ¹H NMR spectra were measured with Bruker AVANCE 400 spectrometer and ¹³C NMR spectra were measured with Bruker AVANCE 600. The UV-vis absorption spectra of target small molecules and polymers were measured using a T6 UV-vis spectrometer. The average molecular weight and polydispersity index (PDI) of the polymers were determined using Waters 1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. Thermogravimetric analyses (TGA) were carried out on STA PT1600 under flowing N₂ flow at a heating rate of 20 °C min⁻¹ to investigate the thermal stabilities. The thickness of films was measured using a Dektak 6 M surface profilometer. Electrochemical redox potentials were measured by cyclic voltammetry (CV) on a CHI660C electrochemistry station with a three-electrode system. CV was conducted with glassy carbon electrode, which was used as working electrode. The polymer films were coated on the surface of the working electrode and with 0.1 M tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆) (as a supporting electrolyte) in anhydrous acetonitrile solution at a scan rate of 100 mV s⁻¹. A platinum wire was used as a counter electrode and an Ag/AgNO₃ (0.01 M AgNO₃ in acetonitrile) electrode was used as the reference electrode. A ferrocene/ferrocenium couple (FeCp₂⁺/FeCp₂⁰) was used as the internal standard. Potentials were referenced to FeCp₂⁺/FeCp₂⁰, which is -4.80 eV related to vacuum. Highresolution mass spectral data (HRMS) were measured on a Bruker APEX II FT-MS mass spectrometer. Atomic force microscopy (AFM) was performed

using an Agilent 5500 scanning probe microscope on the samples with a silicon tip, in tapping mode.

2. Synthetic Procedures

2,5-Dimethylpyrazine-1,4-dioxide (2)

To a solution of m-CPBA (85% purity, 25.0 g, 101.4 mmol) was added in ethyl acetate (100 mL), 2,5-dimethylpyrazine (7 mL, 64.1 mmol) was added dropwise under the ice water bath and the reaction was stirred at room temperature for 24 hours. The resulting solution was filtered and washed by ethyl acetate (3×100 mL) to get white solid precipitated (7.63 g, 85%). ¹H NMR (400 MHz, D₂O) δ=8.37 (s, 1H), 2.31 (s, 3H). ¹³C NMR (150 MHz, D₂O) δ=146.04, 136.23, 13.86.

2,5-Di(acetoxymethyl)pyrazine (3)

Compound 2 (7.63 g) was added in 80 mL acetic anhydride then reflux for 24 hours. The resulting solution was under reduced pressure to remove the acetic anhydride then get a black residue. The resulting solid was transferred onto a silica gel column and then eluted with a solution of 20% ether acetate in petroleum ether to get a yellow compound, then recrystallized the compound in petroleum ether to get a white crystalline (2.5 g, 20%). ¹H NMR (400 MHz, CDCl₃) δ=8.63 (s, 1H), 5.27 (s, 2H), 2.17 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ=170.42, 150.52, 142.87, 64.51, 20.75.

2,5-Di(hydroxymethyl)pyrazine (4)

Compound 3 (2.5 g, 11 mmol) and CH₃ONa (1.0 g, 18.5 mmol) were added in 80 mL dry methanol under N₂ atmosphere to stir 3 hours at room temperature. The resulting solution was quenched by NH₄Cl (1.5 g) and removed the methanol under reduced pressure. Silica gel column chromatography (10% methanol in chloroform) of the product gave a pale yellow solid (1.25 g, 85%). ¹H NMR (400 MHz, CDCl₃) δ=8.59 (s, 1H), 4.86 (d, J = 4.7 Hz, 2H), 3.07 (s, 1H). ¹³C NMR (150 MHz, CDCl₃) δ=153.37, 141.35, 62.74.

Pyrazine-2,5-dialdehyde (5)

Compound 4 (1.25 g, 8.92 mmol) and activated MnO₂ (6.0 g, 69.00 mmol) was added in dry 1,4-dioxane (40 mL) under reflux for 1 hours and the resulting mixture was filtered and washed by dichloromethane, then concentrate the filtrate under reduced pressure to get the yellow oily matter. The crude product was transferred onto a silica gel column and then eluted with a solution of 50% ether acetate in petroleum ether to get a yellow compound (971 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ=10.26 (s, 1H), 9.33 (s, 1H). ¹³C NMR (150 MHz, CDCl₃) δ=192.48, 149.49, 144.11.

6-bromo-1-octylindoline-2,3-dione (7)

6-bromoisatin (2.6g, 11.5 mmol) and K₂CO₃ (6.9 g 50 mmol) were added in anhydrous DMF (20mL) under N₂ atmosphere to heat to 60°C and n-Octyl bromide (3.5 mL) was added dropwise. Then improve the heating temperature to 80°C for 2 hours. Concentrating the resulting mixture under reduced pressure to get the yellow oily substances and transferred it onto a silica gel column and eluted with a solution of 10% ether acetate in petroleum ether to get a compound 7 (3.9 g, 90%). ¹H NMR (400 MHz, CDCl₃) δ=7.48 (d, *J* = 7.9, 1.2 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.08 (s, 1H), 3.71 (t, *J* = 6.5 Hz, 2H), 1.78–1.12 (m, 12H), 0.90 (d, *J* = 5.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ= 182.31, 157.92, 151.82, 133.48, 126.81, 126.40, 116.23, 113.75, 40.45, 31.69, 29.08, 27.15, 26.80, 22.57, 14.03, 14.00.

6-bromo-1-octylindolin-2-one (8)

To a solution of Zn powder (780 mg) was added in anhydrous THF (15 mL) and TiCl₄ (0.7 mL) was added dropwise under N₂ atmosphere at room temperature. The solution mixture was refluxed for 3 hours then cooled to room temperature. Compound 7 (507 mg, 1.5 mmol) was dissolved in anhydrous THF (5 mL) and added dropwise to the mixture. The solution was quenched by 3.5% HCl (15 mL) after 30 minutes. The mixture solution extracted with DCM (3 × 50 mL) and concentrated the solution under reduced pressure to obtain pale yellow oil. The crude product was purified by a silica gel column and eluted with a solution of 50% ether acetate in petroleum ether to get a compound 8 (413 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ=7.16 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.96 (s, 1H), 3.66 (t, *J* = 7.4 Hz, 2H), 3.46 (s, 2H), 1.72–1.58 (m, 2H), 1.22–1.41 (m, 10H), 0.89 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ =174.57, 146.02, 125.58, 124.74, 123.42, 121.27, 111.62, 40.13, 35.31, 31.73, 29.18, 29.13, 27.29, 26.88, 22.59, 14.05.

BrPzIIG

To a solution of compound 8 (2.94 mmol, 954 mg) and compound 5 (1.47 mmol, 200 mg) was added in absolute ethyl alcohol (20 mL) under N_2 atmosphere and piperidine (0.5 mL) was added dropwise. The reaction mixture was refluxed for 24 hours and filtered. Then recrystallized the crude product by CHCl_3 to get red crystal (825 mg, 75%). ^1H NMR (400 MHz, CDCl_3) δ =9.06 (s, 1H), 8.97 (d, J = 8.3 Hz, 1H), 7.80 (s, 1H), 7.26 (d, J = 9.8 Hz, 1H), 7.02 (s, 1H), 3.79 (t, J = 7.3 Hz, 2H), 1.82–1.63 (m, 2H), 1.49–1.17 (m, 10H), 0.90 (t, J = 6.6 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ =168.36, 148.41, 147.95, 146.00, 131.28, 129.95, 129.48, 125.73, 125.16, 120.29, 111.68, 40.38, 31.77, 29.22, 29.17, 27.45, 26.91, 22.62, 14.08. ESI-HRMS: Calcd. For $\text{C}_{38}\text{H}_{44}\text{Br}_2\text{N}_4\text{O}_2$ $[\text{M}+\text{H}]^+$: 749.1883. Found: 749.1906

BrIIG

The details of synthetic procedure for BrIIG can refer to a manuscript published on *Org. Lett.*³

PzIIG-BDT2TC8

To a solution of BrPzIIG (112 mg, 0.15 mmol) and BDT2TC8 (170 mg, 0.15 mmol) in toluene (6.0 mL) and DMF(0.8 mL) under N_2 atmosphere, tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) (5 mg) and tri(*o*-tolyl)phosphine ($\text{P}(\text{o-Tol})_3$) (10 mg) were added in the solution mixture in the room temperature and improve the temperature to 110 °C for 48 hours. After cooled to room temperature, the solution mixture was poured into methanol (100 mL) and was stirred for 1 h. A dark brown precipitate was collected by filtration. The crude product was purified by a silica gel column (60 to 80 mesh) and eluted with CHCl_3 and concentrate the solution under reduced pressure to get with metallic luster dark brown solid. ^1H NMR (600 MHz, CDCl_3 , δ): 9.0–8.5 (br, 2 H), 8.0–6.5 (br, 12 H), 4.1–3.7 (br, 4 H), 3.4–2.4 (br, 8 H), 2.2–0.7 (br, 90 H). Elemental analysis calculated for $(\text{C}_{88}\text{H}_{118}\text{N}_4\text{O}_2\text{S}_4)_n$: C, 75.92; H, 8.54; N, 4.02. Found: C, 75.43; H, 8.26; N, 3.91.

PzIIG-BTT2TC10

To a solution of BrPzIIG (112 mg, 0.15 mmol) and BTT2TC10 (203 mg, 0.15 mmol) in toluene (6.0 mL) and DMF (0.8 mL) under N₂ atmosphere, tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) (5 mg) and tri(*o*-tolyl)phosphine (P(*o*-Tol)₃) (10 mg) were added in the solution mixture in the room temperature and improve the temperature to 110 °C for 48 hours. After cooled to room temperature, the solution mixture was poured into methanol (100 mL) and was stirred for 1 h. A dark brown precipitate was collected by filtration. The crude product was purified by a silica gel column (60 to 80 mesh) and eluted with CHCl₃ and concentrate the solution under reduced pressure to get with metallic luster dark brown solid. ¹H NMR (600 MHz, CDCl₃, δ): 8.8–8.4 (br, 2 H), 7.8–6.4 (br, 12 H), 4.3–3.9 (br, 4 H), 3.3–2.4 (br, 8 H), 2.1–0.7 (br, 106 H). Elemental analysis calculated for (C₁₀₀H₁₃₄N₄O₂S₆)_n: C, 74.30; H, 8.36; N, 3.47. Found: C, 73.86; H, 8.07; N, 3.28.

3. Polymer Solar Cells Device Fabrication

The structure of the solar cell device was Glass / ITO / PFN / Active Layer / MoO₃ / Ag. The conductive polymer, PFN, was spin-coated onto ITO-coated glass substrates. The polymers and PCBM were blended at different ratio as the active layer to spin-coated from CB solution (without DIO additive and with DIO additive) onto the PFN layer. The spin-coating process was finished in a glove box. MoO₃ (10 nm) was deposited via a mask in vacuum onto the active layer and Ag (100 nm) were deposited onto the MoO₃ layer as the top electrodes. The accurate area of every device is 10 mm². The thickness of the PzIIG-BDT2TC8 based active layer and PzIIG-BTT2TC10 based active layer are controlled in the range of 60-70 nm and 50-60 nm, respectively. PCE was calculated from J-V characteristics recorded by a Keithley 2400 source meter under illumination of an AM1.5G solar simulator with an intensity of 100 mW cm⁻² (Model SS-50A, Photo Emission Tech., Inc.). The light intensity was determined by a standard silicon photodiode. IPCE were calculated from the photocurrents at short-circuit conditions. The currents were measured by a Keithley 485 picoammeter under illumination of monochromatic light (MS257) through the ITO side of the devices.

4. Additional Data

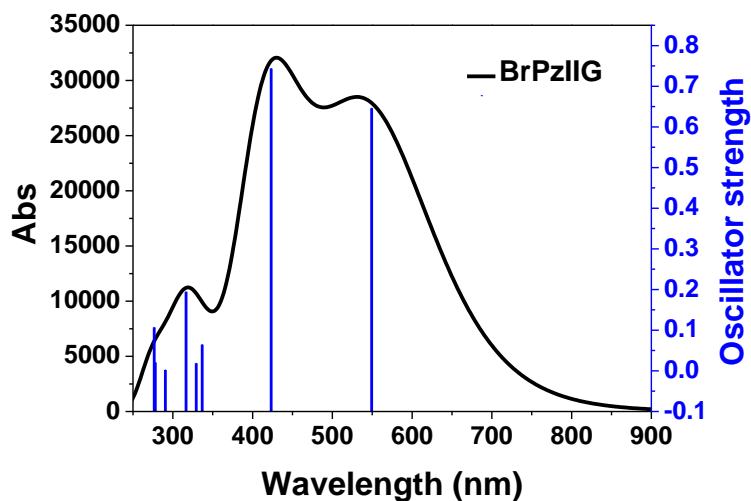


Fig. S1 Simulated absorption spectrum of BrPzIIG by TD-DFT calculations at the B3LYP/6-311G (d, p) level.

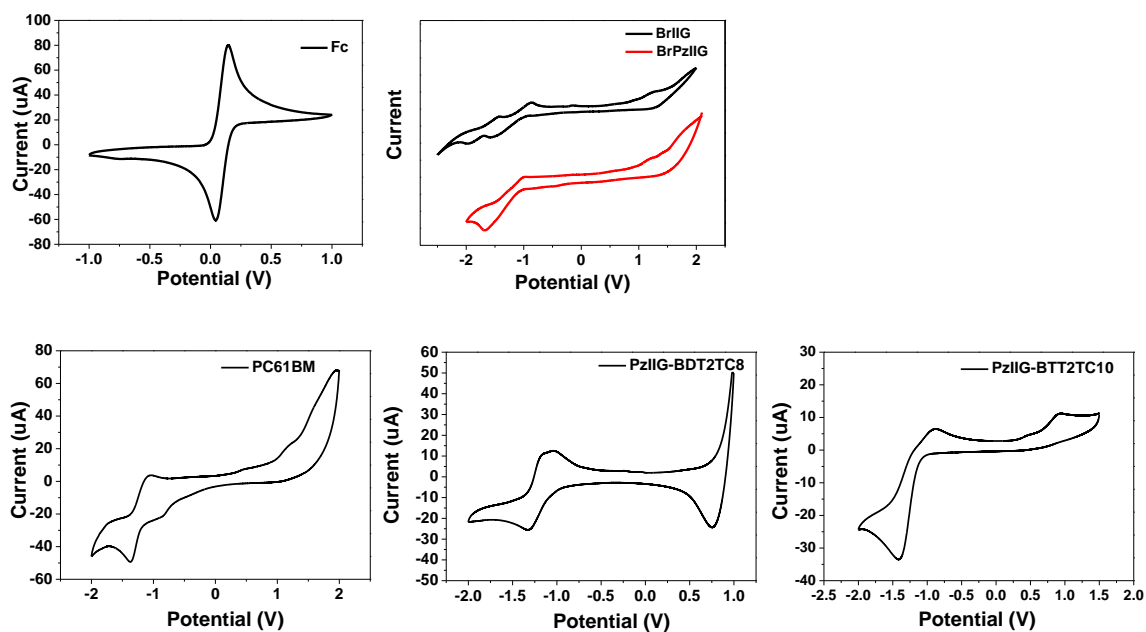


Fig. S2. Cyclic voltammograms of BrPzIIG and BrIIG in solutions and thin film cyclic voltammograms of PzIIG-BDT2TC8 and PzIIG-BTT2TC10 on a glassy carbon electrode in 0.1 mol / L Bu_4NPF_6 acetonitrile solution.

BrIIG

$$\text{HOMO} = -[E_{\text{onset}}^{\text{ox}} - E_{1/2\text{ferrocene}} + 4.80] = -(1.07 - 0.10 + 4.80) \text{ eV} = -5.77 \text{ eV}$$

$$\text{LUMO} = -[E_{\text{onset}}^{\text{red}} - E_{1/2\text{ferrocene}} + 4.80] = -(-1.04 - 0.10 + 4.80) \text{ eV} = -3.66 \text{ eV}$$

$$\text{Gap} = 2.11 \text{ eV}$$

BrPzIIG

$$\text{HOMO} = -[E_{\text{onset}}^{\text{ox}} - E_{1/2\text{ferrocene}} + 4.80] = -(0.99 - 0.10 + 4.80) \text{ eV} = -5.69 \text{ eV}$$

$$\text{LUMO} = -[E_{\text{onset}}^{\text{red}} - E_{1/2\text{ferrocene}} + 4.80] = -(-1.02 - 0.10 + 4.80) \text{ eV} = -3.68 \text{ eV}$$

$$\text{Gap} = 2.01 \text{ eV}$$

PzIIG-BDT2TC8

$$\text{HOMO} = -[E_{\text{onset}}^{\text{ox}} - E_{1/2\text{ferrocene}} + 4.80] = -(0.78 - 0.10 + 4.80) \text{ eV} = -5.48 \text{ eV}$$

$$\text{LUMO} = -[E_{\text{onset}}^{\text{red}} - E_{1/2\text{ferrocene}} + 4.80] = -(-1.06 - 0.10 + 4.80) \text{ eV} = -3.64 \text{ eV}$$

$$\text{Gap} = 1.84 \text{ eV}$$

PzIIG-BTT2TC10

$$\text{HOMO} = -[E_{\text{onset}}^{\text{ox}} - E_{1/2\text{ferrocene}} + 4.80] = -(0.70 - 0.10 + 4.80) \text{ eV} = -5.40 \text{ eV}$$

$$\text{LUMO} = -[E_{\text{onset}}^{\text{red}} - E_{1/2\text{ferrocene}} + 4.80] = -(-1.12 - 0.10 + 4.80) \text{ eV} = -3.58 \text{ eV}$$

$$\text{Gap} = 1.82 \text{ eV}$$

PC₆₁BM

$$\text{HOMO} = -[E_{\text{onset}}^{\text{ox}} - E_{1/2\text{ferrocene}} + 4.80] = -(1.32 - 0.10 + 4.80) \text{ eV} = -6.02 \text{ eV}$$

$$\text{LUMO} = -[E_{\text{onset}}^{\text{red}} - E_{1/2\text{ferrocene}} + 4.80] = -(-0.69 - 0.10 + 4.80) \text{ eV} = -4.01 \text{ eV}$$

$$\text{Gap} = 2.01 \text{ eV}$$

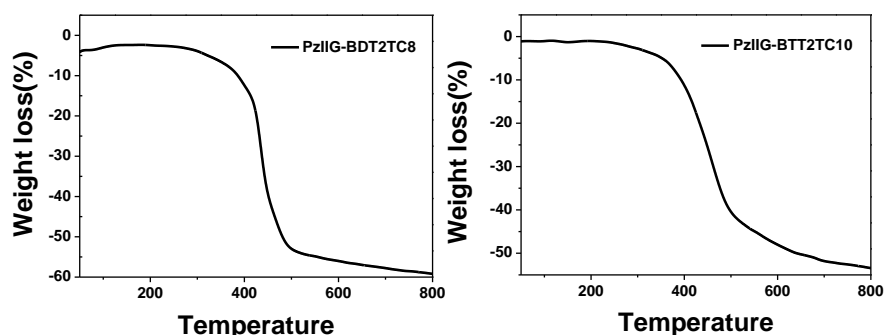
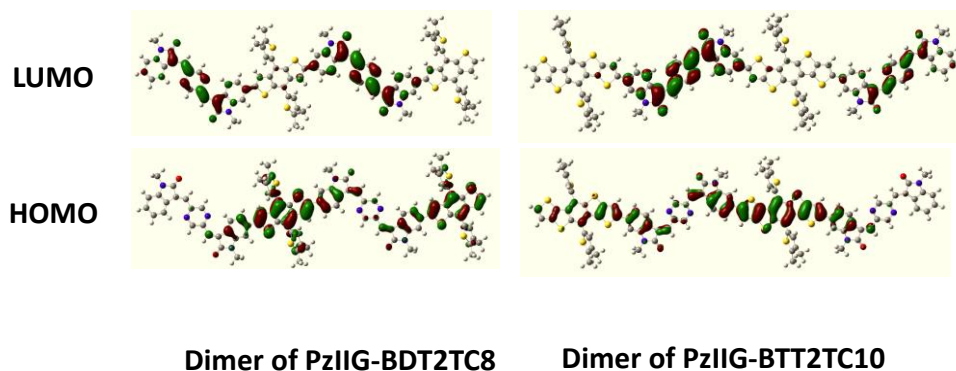


Fig. S3 TGA plot of PzIIG-BDT2TC8 and PzIIG-BTT2TC10 collected under N₂ at a heating rate of 20 °C / min.



Dimer of PzIIG-BDT2TC8 HOMO= -5.06 eV LUMO= -3.06 eV

Dimer of PzIIG-BTT2TC10 HOMO= -5.06 eV LUMO= -3.06 eV

Fig. S4. HOMO and LUMO energy levels of dimers of PzIIG-BDT2T and PzIIG-BTT2T based on DFT calculations at the B3LYP/6-31G (d) level.

Hole mobility measurement

The device structure for the space charge limited current (SCLC) studies is ITO / PEDOT:PSS / active layer / MoO₃ (10 nm) / Ag (100 nm).⁴ The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation: $J = (9/8) \epsilon_0 \epsilon_r \mu ((V^2) / (d^3))$, where J is the current, μ is the zero-field mobility, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{app}), $V = V_{app} - V_{bi} - V_s$. The hole mobility can be calculated from the slope of the $J^{1/2}$ -V curves. The effective area was 10 mm². The film thickness of PzIIG-BDT2TC8 and PzIIG-BTT2TC10 are 62 nm and 57 nm, respectively.

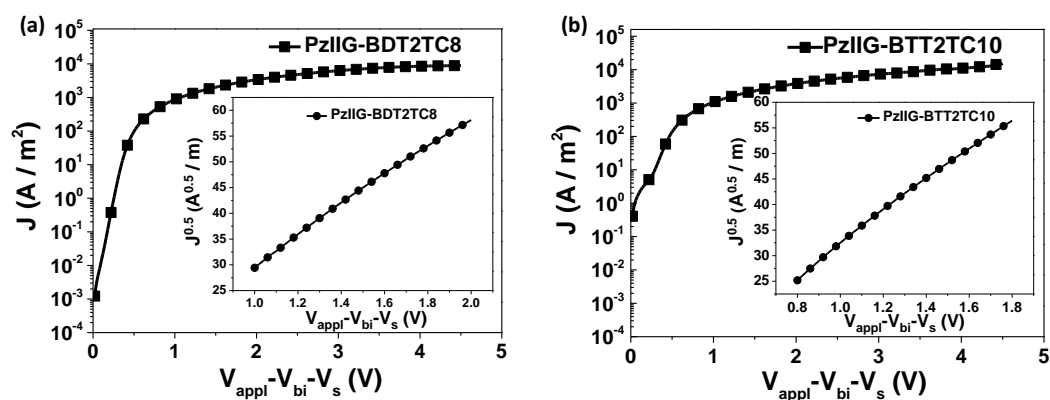


Fig. S5 J-V characteristics of the SCLC measurement of PzIIG-BDT2TC8 and PzIIG-BTT2TC10.

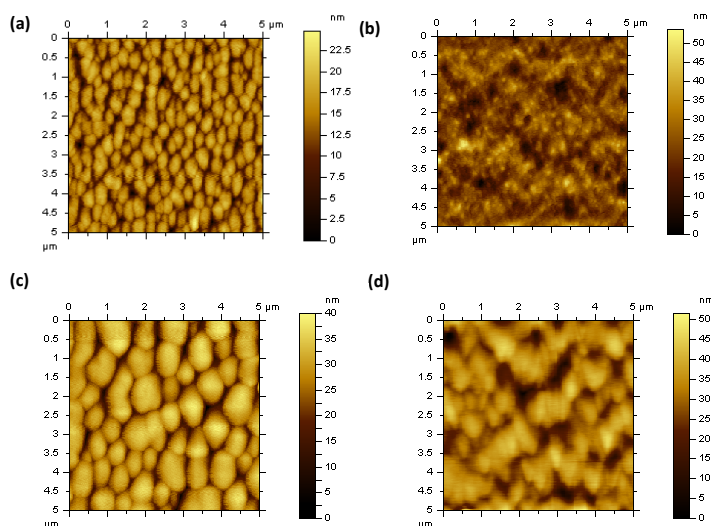
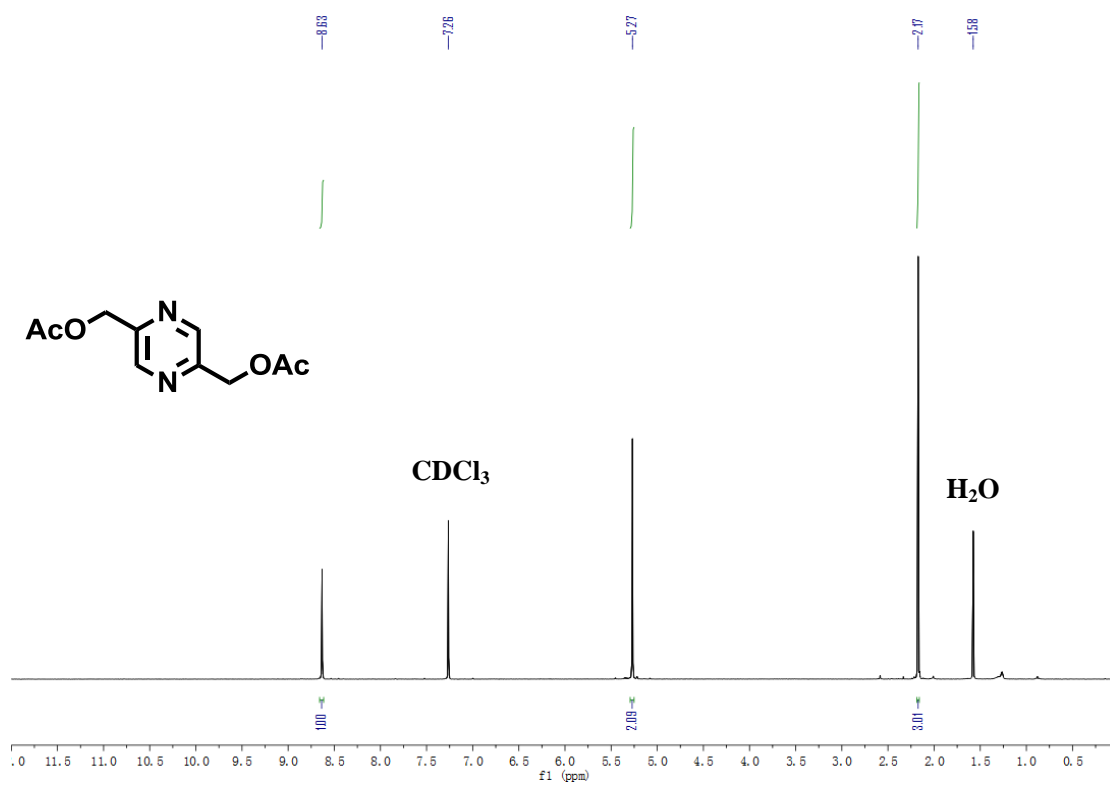
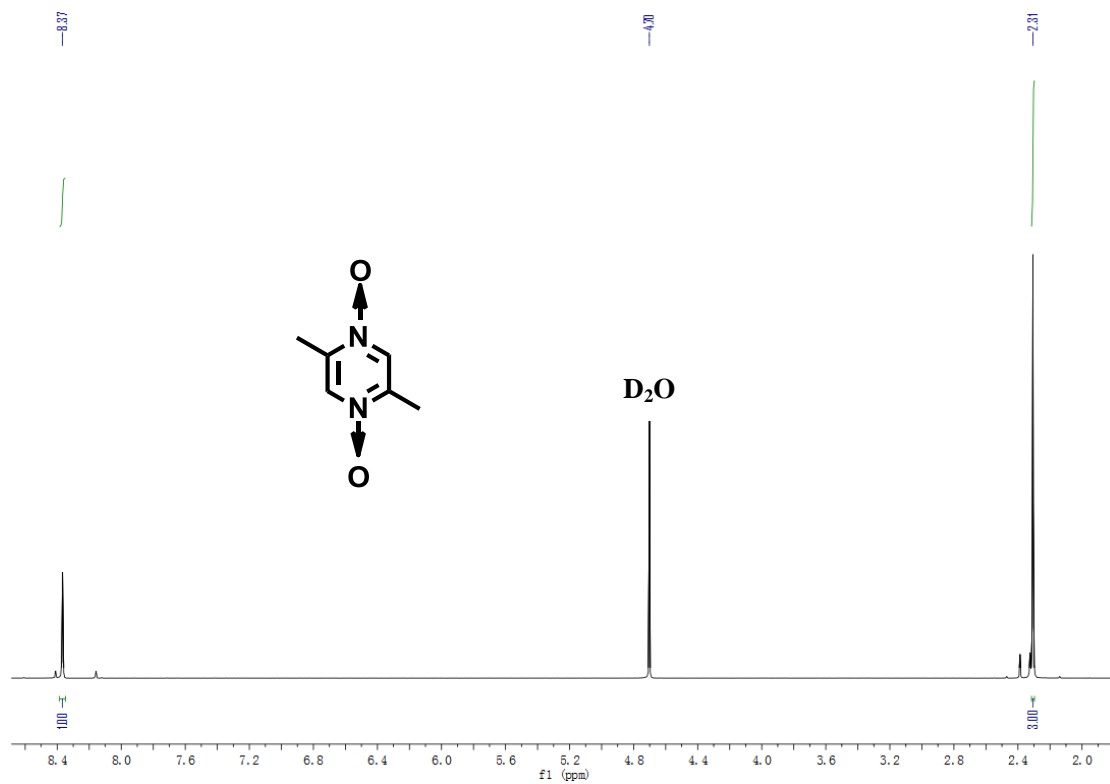
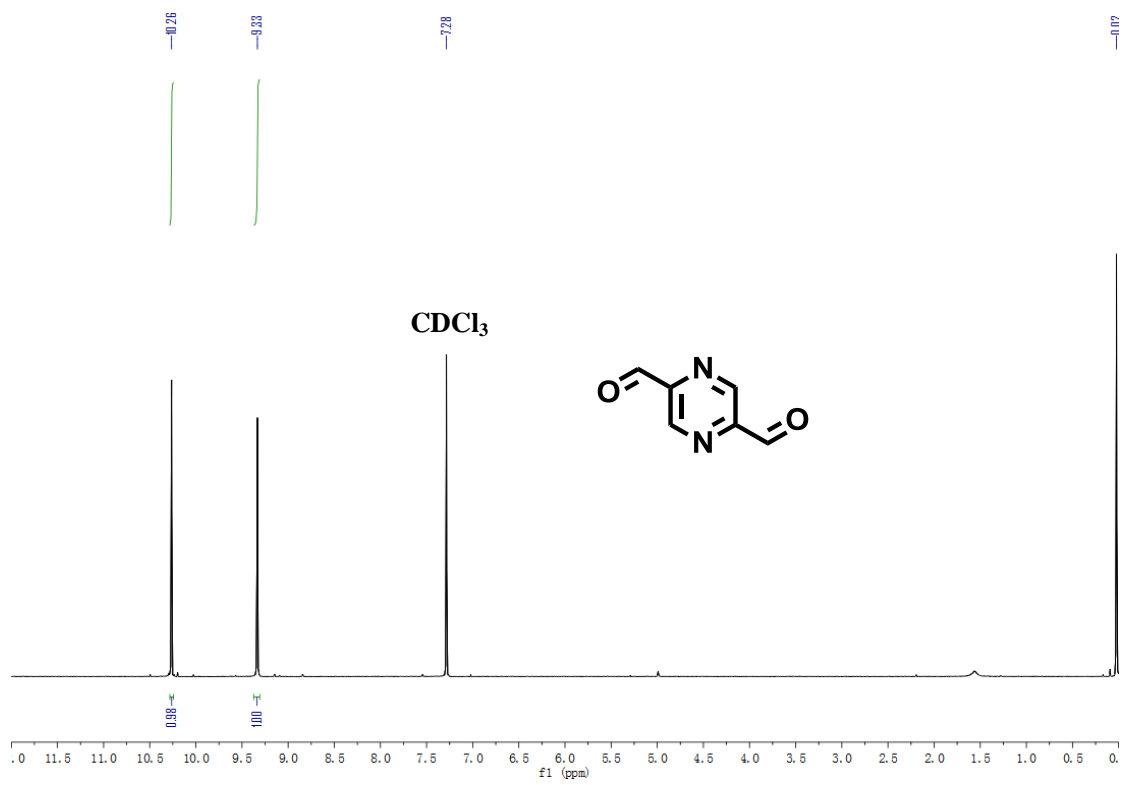
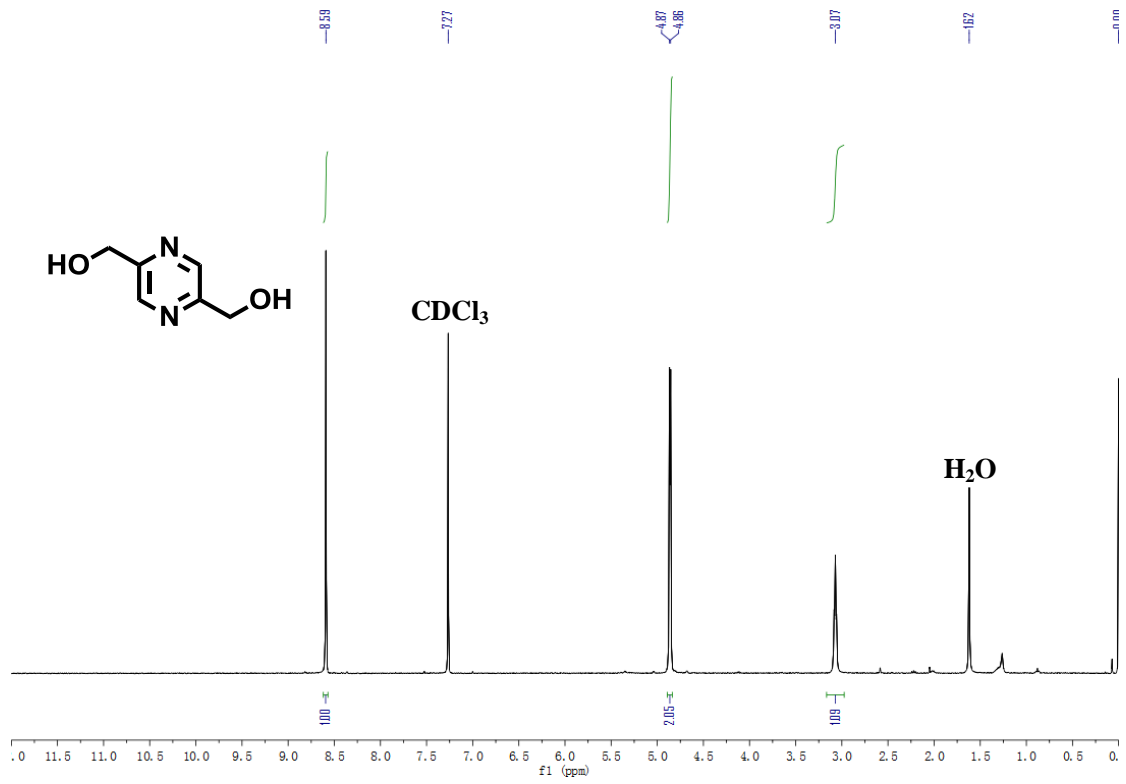
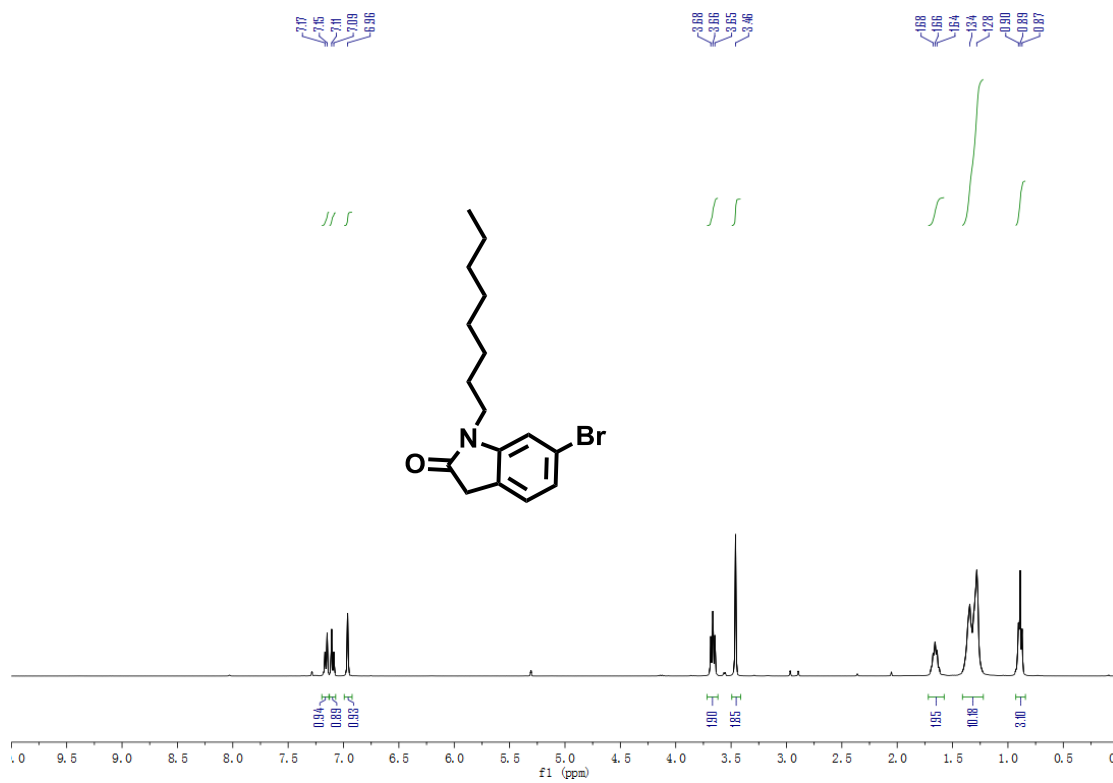
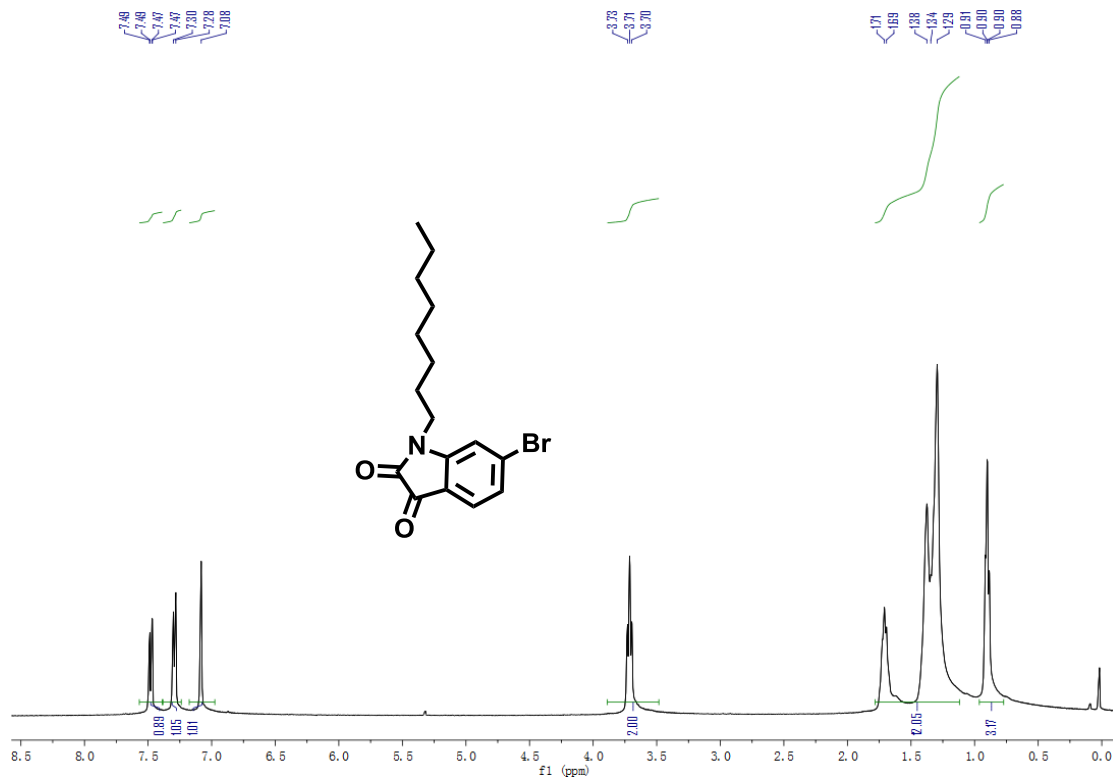


Fig. S6 AFM images ($5 \times 5 \mu\text{m}^2$) of the active layers from PzIIG-BDT2TC8 : PC₇₁BM (1 : 2) blends processed from (a) CB, (b) 3% (wt.) of DIO in CB; AFM images ($5 \times 5 \mu\text{m}^2$) of the active layers from PzIIG-BTT2TC10 : PC₇₁BM (1 : 2) blends processed from (c) CB, (d) 3% (wt.) of DIO in CB.

Fig. S7 ^1H NMR spectra of the target molecules.







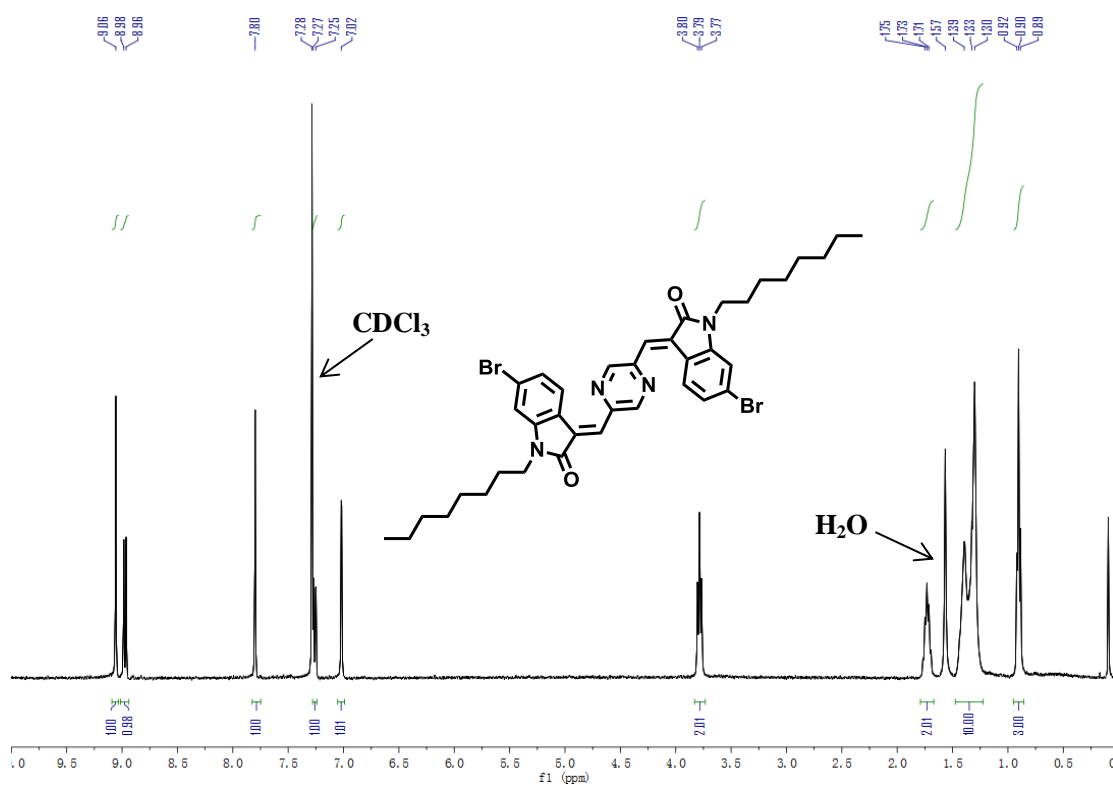
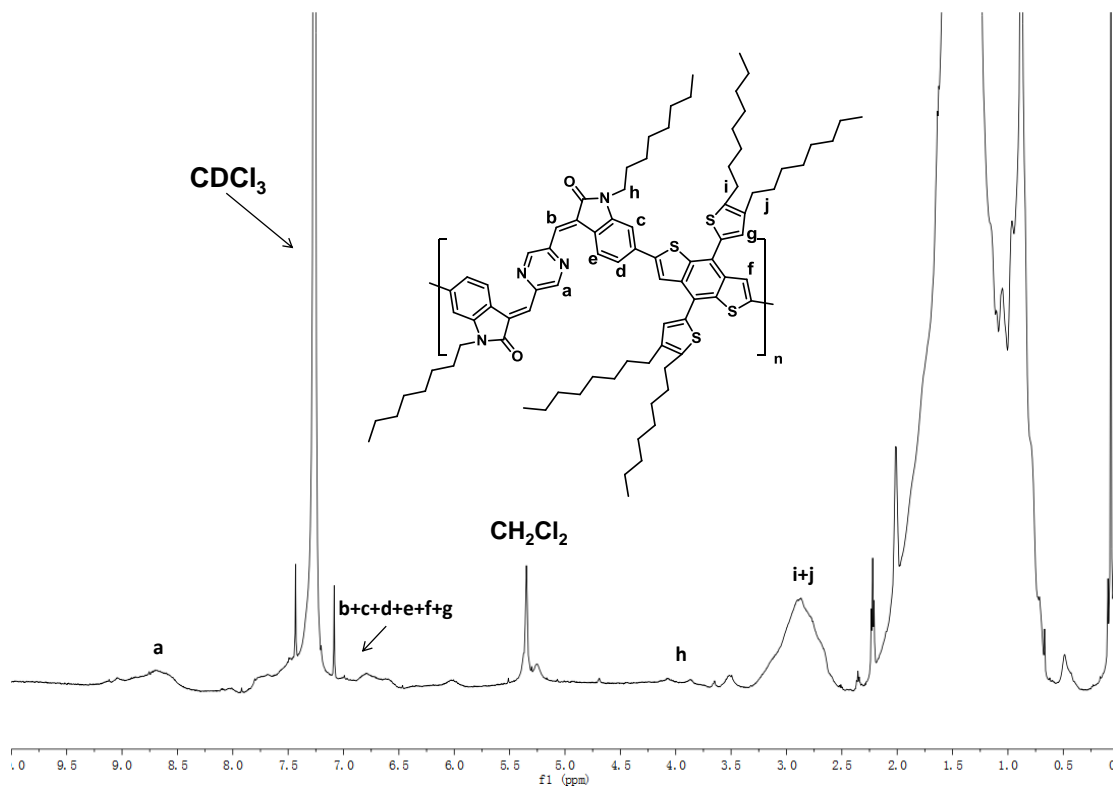


Fig. S8 ¹H NMR spectra of PzIIG-BDT2TC8 and PzIIG-BTT2TC10.



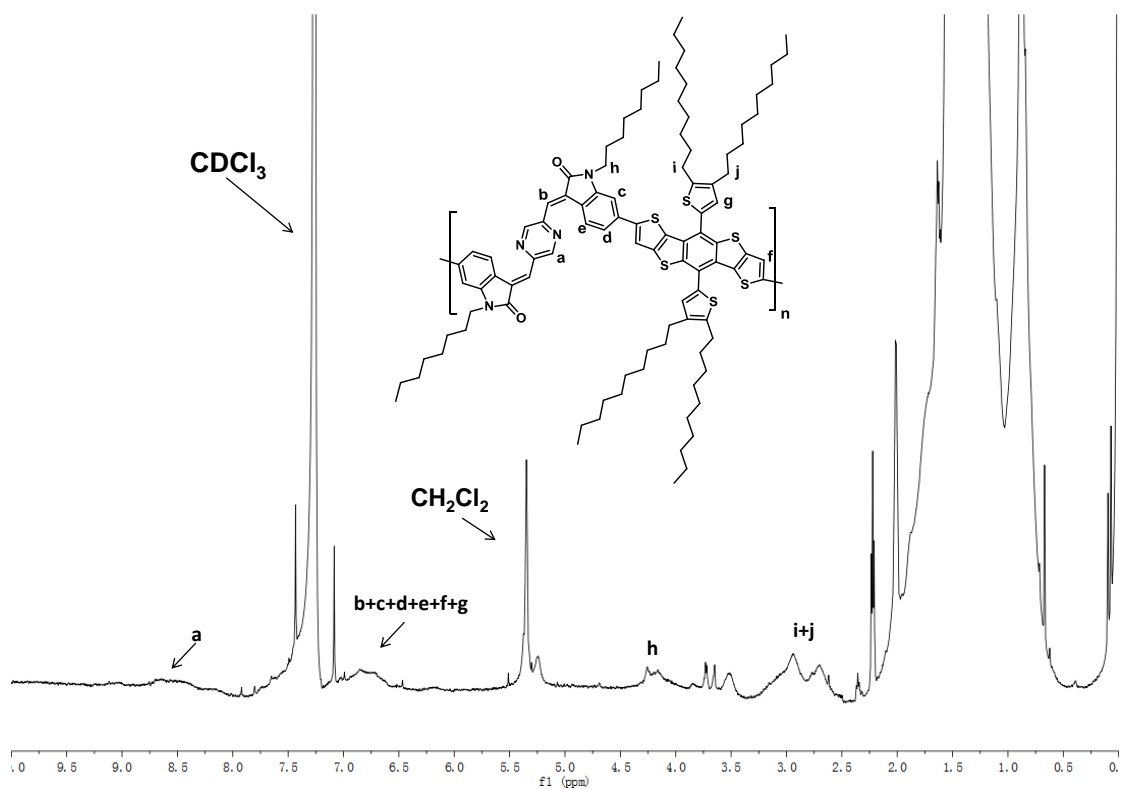
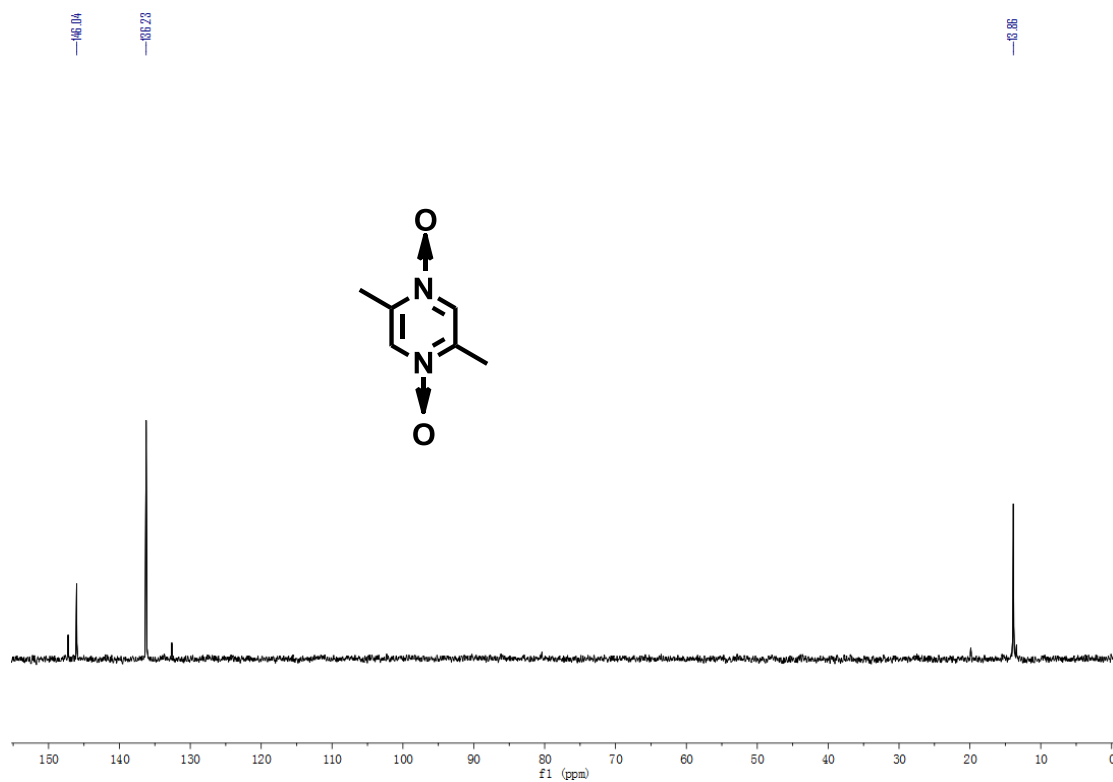
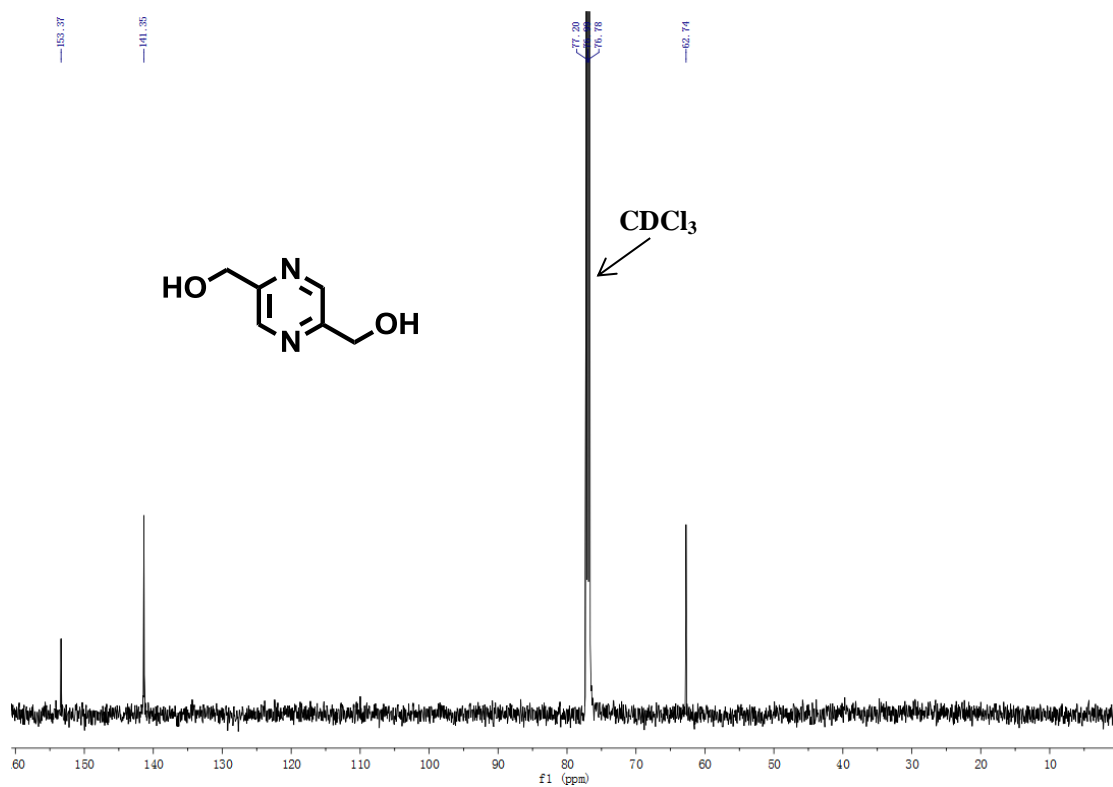
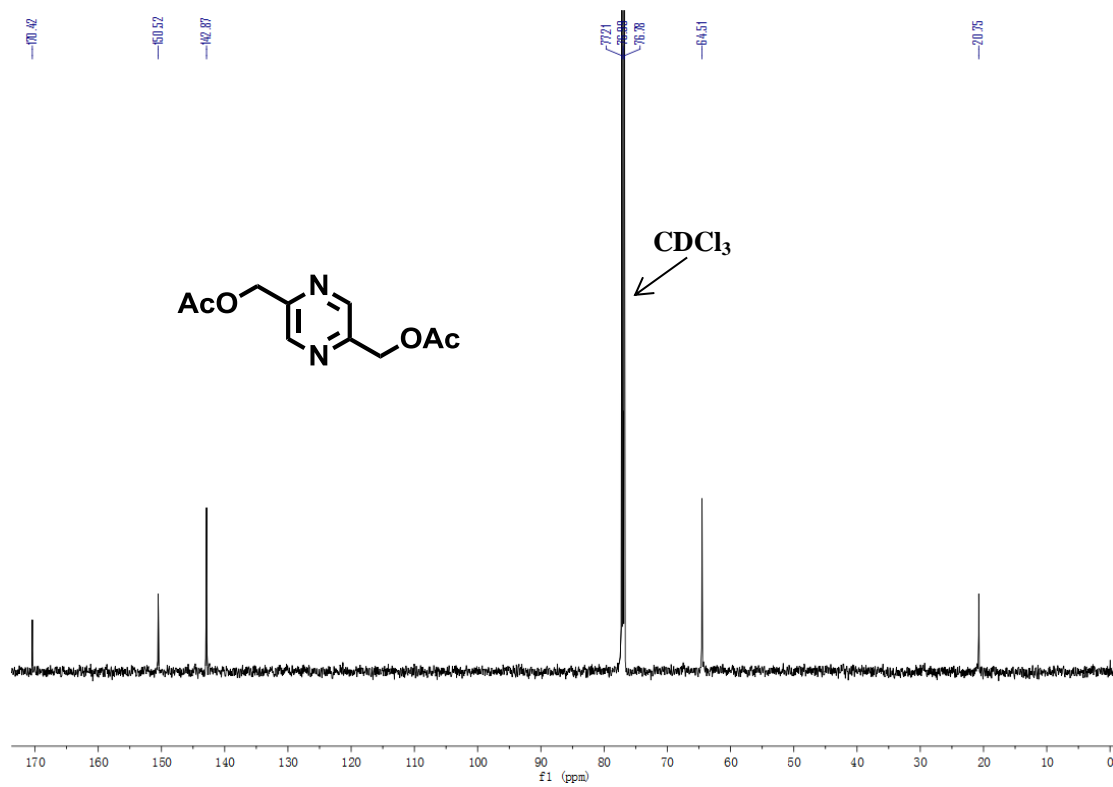
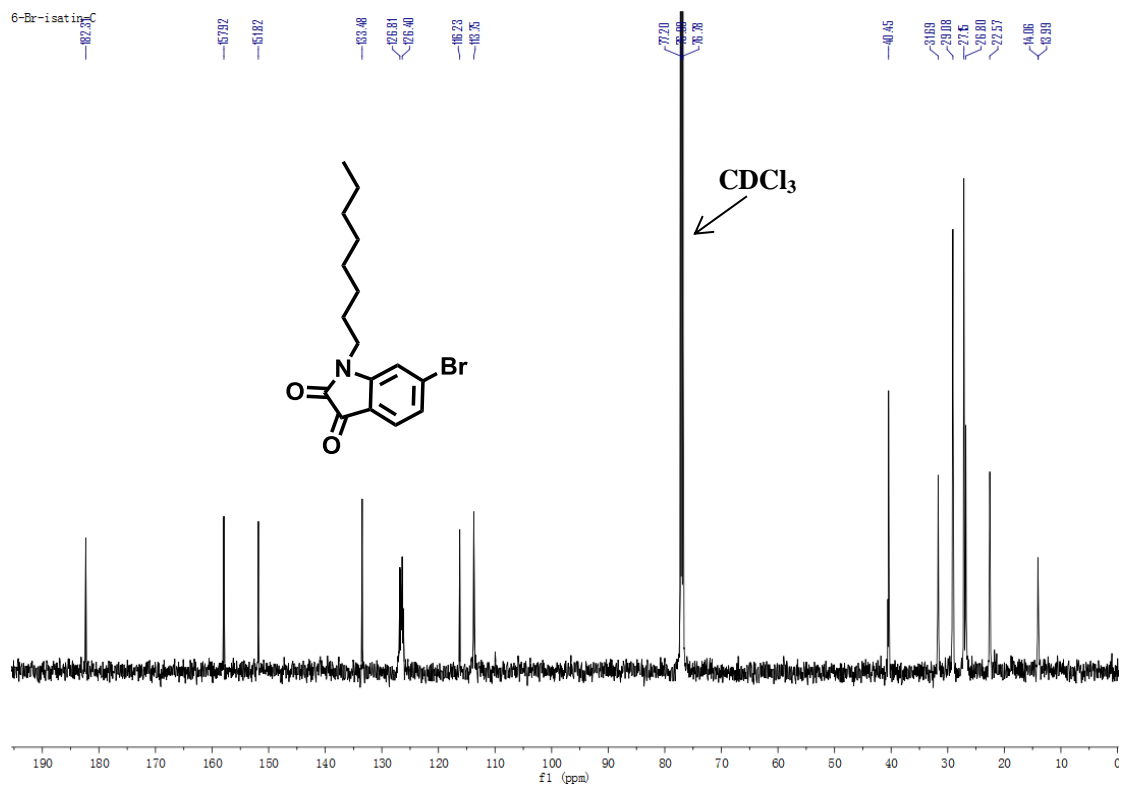
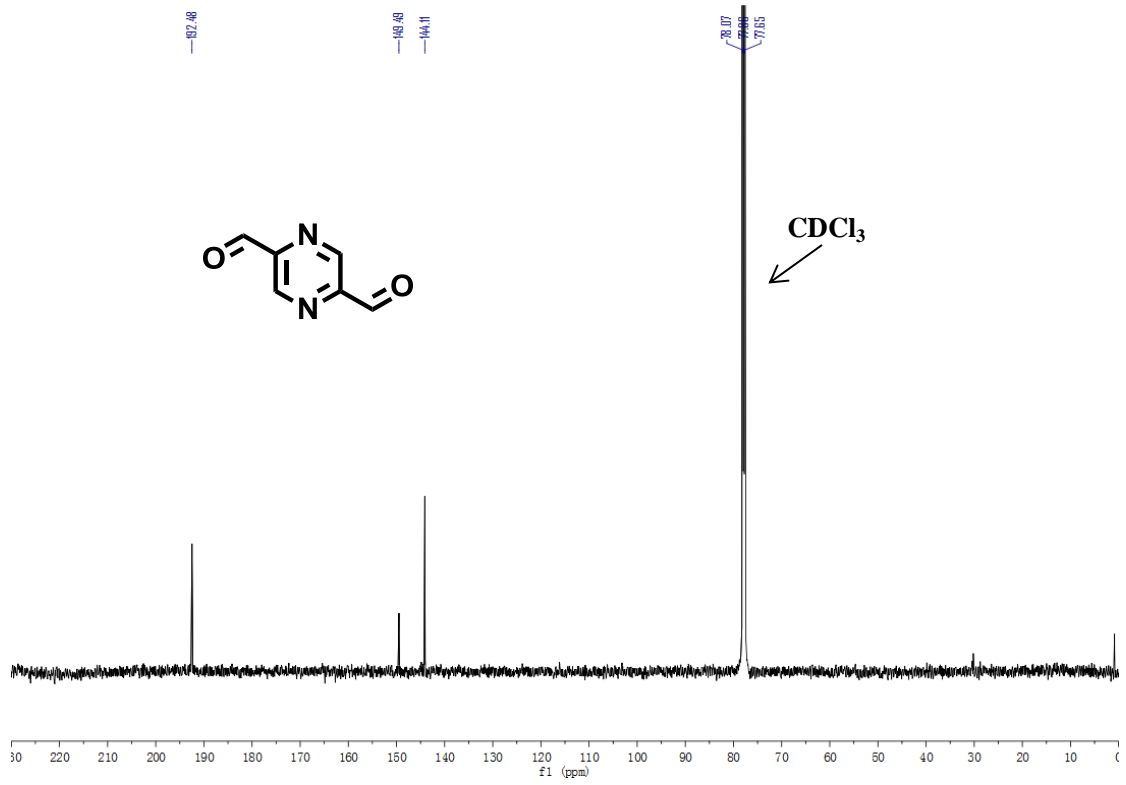
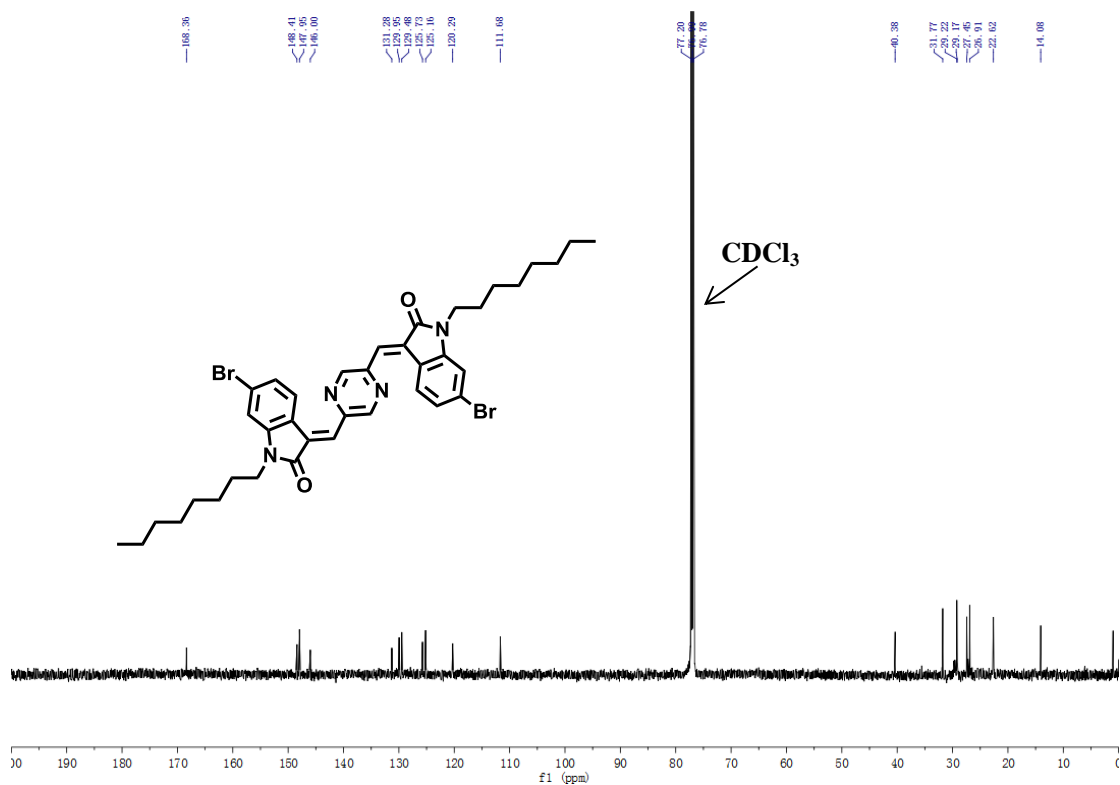
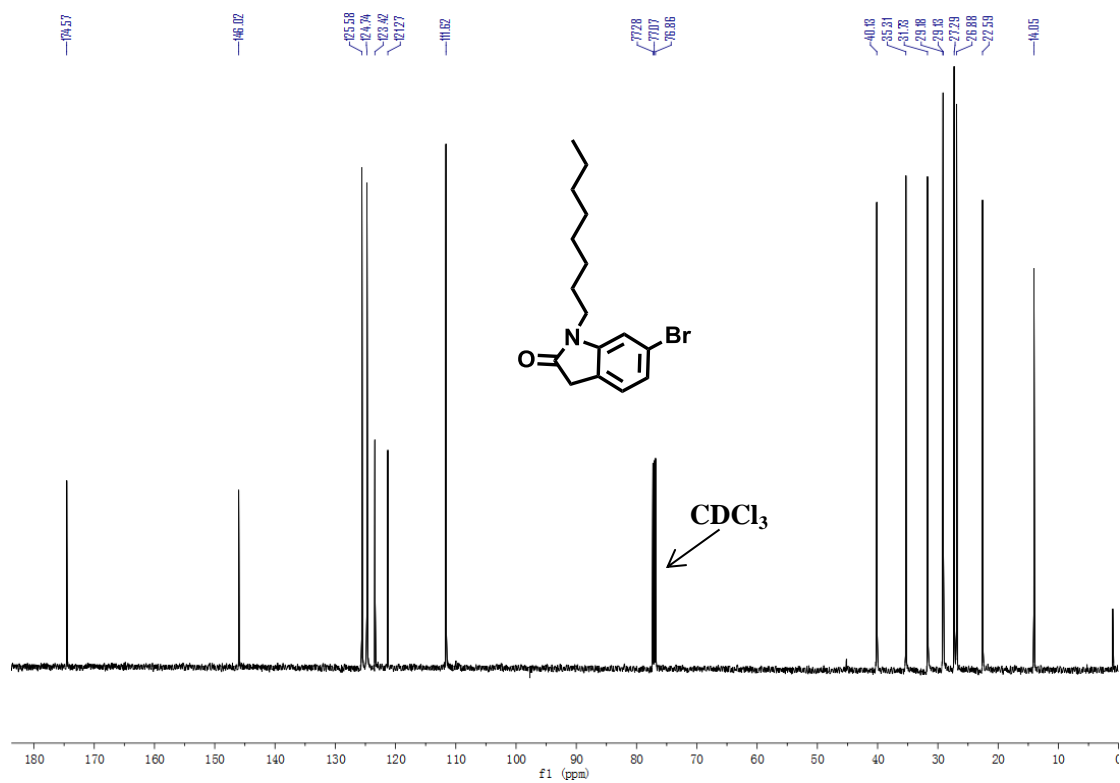


Fig. S9 ^{13}C NMR Spectra of the target molecules.









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