

Supporting information

Enhanced Open Circuit Voltage of Small Molecule Acceptor Containing Angular-Shaped Indacenodithiophene Unit for P3HT-based Organic Solar Cells

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Materials and instruments

All the chemicals were purchased from J&K, Energy Chemical Inc, Sigma–Aldrich and used as received. ^1H NMR and ^{13}C NMR data were taken on a Bruker Ultra Shield Plus AV400 spectrometer in deuterated chloroform (CDCl_3) solution at 298 K with tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard (^1H NMR: 400 MHz, ^{13}C NMR: 100 MHz). Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) with anthracene-1,8,9-triol as matrix was carried out on a Bruker Autoflex III instrument. Thermogravimetry analysis (TGA, Rigaku TG-DTA 8120) measurements were performed on a Rigaku TG-DTA 8120 thermal analyzer at a heating rate of $10^{-1} \text{ }^\circ\text{C min}^{-1}$ under N_2 atmosphere. UV–vis absorption spectrums were collected with a Shimadzu UV–1700 spectrometer. Cyclic voltammograms (CV) experiments of the two small acceptor molecules were executed with a CHI 620C electrochemical analyzer, and a gold disc with a diameter of 2 mm, a Pt wire and an Ag/Ag⁺ electrode were used as the working electrode, counter electrode and reference electrode, respectively. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , 0.1 M) in dry dichloromethane was used as the supporting electrolyte. The surface morphology was obtained via tapping mode atomic force microscopy (AFM) (Veeco Dimension 3100).

BHJ organic solar cells fabrication and characterization

BHJ organic solar cells with a conventional configuration of ITO/PEDOT:PSS/active layer/Ca/Al were fabricated by the following process.

Patterned indium tin oxide (ITO) glass substrates were cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol, and then further treated with Jelight UV-ozone cleaner for 15 min. A thin layer of poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) (~ 30 nm) was formed on ITO substrate by spin coating a PEDOT:PSS aqueous solution and baked for 150 °C for 15 min. After cooling to the room temperature, and the substrates were transferred into glove box. A blend solution of P3HT and the small molecule acceptor in chloroform was spin-coated onto the PEDOT:PSS layer. Finally, a cathode made of Ca and Al layers were then thermally evaporated on the active layer at a pressure of 4.0×10^{-6} mbar via a shadow mask (active area 4 mm²). The current density–voltage characteristics (J–V) of the photovoltaic cells were measured utilizing a Keithley 2400 digital source meter under a simulated AM 1.5G solar irradiation at 100 mW cm². External Quantum Efficiency (EQE) of solar cells were measured using an Oriel Newport system (Model 66902).

Synthesis

Compound (2) In a two-necked RBF (100 mL), Compound 1 (7.60 g, 20 mmol) and 2-thiophenylboric acid (5.60 g, 44 mmol) were dissolved in THF (55 mL), 2M K₂CO₃ solution (25 mL) was added. The mixture was degassed with N₂ flow for 20 min, Pd(PPh₃)₄ (70 mg, 0.60 mmol) was added under N₂ flow. The mixture was stirred at 70 °C under N₂ in dark for 24 h. The mixture was then allowed to cool to room temperature and extracted with CH₂Cl₂ and dried with Na₂SO₄. The

product was purified by silica chromatography with petroleum ether/dichloromethane as the eluent, affording the product as a light yellow solid (5.6 g, 73% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (s, 2H), 7.39 (dd, $J = 4.9, 1.4$ Hz, 2H), 7.09 (dd, $J = 5.2, 3.2$ Hz, 4H), 4.22 (q, $J = 7.1$ Hz, 4H), 1.15 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.71, 140.49, 134.08, 133.45, 131.99, 127.39, 127.06, 126.49, 61.67, 13.79.

1-IDT In a RBF (100 mL), Compound 2 (3.86 g, 10mmol) was dissolved in THF (25 mL). To the solution, p-(octyloxy)phenyl Grignard reagent [obtained by adding a solution of 1-octyl bromide (18.5 g, 65 mmol) in dry THF (20 mL) to a suspension of Mg (1.87 g, 78 mmol) in dry THF (30 mL)] was added dropwisely under N_2 . After the addition finished, The mixture was refluxed overnight at 70 $^\circ\text{C}$. The mixture was poured into ice-water and extracted with ethyl acetate (100 mL). The combined organic fractions were washed with brine, water and dried over Na_2SO_4 . The solvents were removed with reduced vaccum. the crude product was dissolved in acetic acid (125 mL) and then 6 mL of H_2SO_4 was added. The mixture was refluxed for 5 h allowed to cool to room temperature. The combined organic fractions were washed with brine, water and dried over Na_2SO_4 . The solvents were removed with reduced vacuum. The yellow residue was purified by column chromatography over silica gel (petroleum ether as the eluent) to give compound 3 as a yellow solid (3.96 g, 37% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.44 (s, 2H), 7.34 (d, $J = 5.0$ Hz, 2H), 7.18 (d, $J = 8.8$ Hz, 8H), 7.13 (d, $J = 5.0$ Hz, 2H), 6.77 (d, $J = 8.9$ Hz, 8H), 3.90 (t, $J = 6.5$ Hz, 8H), 1.81

– 1.70 (m, 8H), 1.42 – 1.27 (m, 40H), 0.88 (t, J = 6.8 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 158.00, 156.19, 153.76, 141.04, 136.73, 135.02, 128.95, 127.57, 123.04, 117.14, 114.05, 68.00, 61.91, 31.76, 29.37, 29.32, 29.25, 26.09, 22.66, 14.11.

l-IDTSn In a 50 mL Schlenk flask, l-IDT (1.0 g, 1 mmol) was dissolved in THF (20 mL) at -78 °C under N₂ atmosphere, and then 1.6 M n-BuLi (1.3 mL, 2 mmol) was added dropwise. The mixture solution was stirred at -40 °C for 2 h, trimethyltin chloride (1 M, 2.2 mL) was quickly injected into the solution. After stirring at -78 °C for 30 min, the solution was stirred overnight at room temperature, poured into ice-water and extracted with petroleum ether. The organic layer was washed with ammonium chloride solution, water and dried over Na₂SO₄. The crude product l-IDT-Sn as the yellow solid was obtained by rotary evaporation and directly used for the next step without any treatment.

l-IDTBT In a 50 mL Schlenk flask, 7-bromo-benzo[c][1,2,5]thiadiazole-4-carbaldehyde (486 mg, 2 mmol) and l-IDT-Sn (486 mg, 2 mmol) were dissolved in toluene (25 mL) under N₂ atmosphere, the solution was flushed with N₂ for 10 min and then Pd(PPh₃)₄ (35 mg, 0.30 mmol) was added. After flushing with N₂ for 10 min, the reaction solution was heated to 100 °C for 24 h in dark and cooled to the room temperature, and extracted with dichloromethane. The crude product was obtained by rotary evaporation and purified by silica gel column chromatography with petroleum ether/dichloromethane as an eluent, affording the product l-IDT-BT as the red solid with a yield of 56%. ¹H NMR (400 MHz,

CDCl₃) δ 10.69 (s, 2H), 8.22 – 8.19 (m, 4H), 7.99 (d, J = 7.6 Hz, 2H), 7.55 (s, 4H), 7.27 (s, 2H), 7.25 (d, J = 2.1 Hz, 4H), 6.84 (d, J = 8.9 Hz, 8H), 3.91 (t, J = 6.5 Hz, 8H), 1.78 – 1.71 (m, 8H), 1.44 – 1.25 (m, 40H), 0.88 – 0.84 (t, J = 7.0 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 188.46, 158.30, 157.91, 154.70, 153.82, 152.13, 146.03, 141.55, 135.91, 135.68, 133.64, 132.77, 129.04, 125.78, 125.12, 123.06, 118.09, 114.43, 68.00, 62.48, 31.81, 29.35, 29.29, 29.23, 26.08, 22.65, 14.10.

l-IDTBTRh In a 50 mL Schlenk flask, IDT-BT (422 mg, 0.3 mmol) and 3-ethylrhodanine (113 mg, 0.7 mmol) were dissolved in dry CHCl₃ (20 mL) under N₂ atmosphere, two drops of piperidine were added. The mixture solution was stirred for 24 h at the room temperature and extracted with dichloromethane. The organic layer was dried over Na₂SO₄ and concentrated on a rotary evaporator to give the crude product. Further purification was carried out by silica gel column chromatography with petroleum ether/dichloromethane as an eluent to obtain the target compound l-IDTBTRh. (422 mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ 8.49 (s, 2H), 8.17 (s, 2H), 7.94 (d, J = 7.8 Hz, 2H), 7.68 (d, J = 7.9 Hz, 2H), 7.53 (s, 2H), 7.27 (s, 4H), 7.25 (s, 4H), 6.84 (d, J = 8.9 Hz, 8H), 4.26 – 4.21 (dd, J = 12.2, 9.0 Hz, 4H), 3.93 (t, J = 6.5 Hz, 8H), 1.78 – 1.72 (m, 8H), 1.44 – 1.25(m, 40H), 0.88 – 0.84 (m, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 192.91, 167.50, 158.28, 157.90, 154.63, 154.45, 151.59, 145.17, 141.92, 136.04, 135.67, 131.15, 130.01, 129.07, 127.04, 125.01, 124.77, 124.57, 124.04, 117.98, 114.42, 68.00,

62.47, 39.92, 31.82, 29.36, 29.30, 29.24, 26.09, 22.66, 14.11, 12.33. MALDI-TOF-MS (m/z) 1692.03 for [M]⁺.

Compound 3, a-IDT, a-IDTSn, a-IDTBT and a-IDTBTRh: According to the similar procedure of compound 3, a-IDT, a-IDTSn, a-IDTBT and a-IDTBTRh were synthesized, respectively.

Compound 3 ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 2H), 7.36 (dd, J = 4.9, 3.0 Hz, 2H), 7.31 (dd, J = 2.9, 1.3 Hz, 2H), 7.13 (dd, J = 4.9, 1.3 Hz, 2H), 4.19 (q, J = 7.1 Hz, 4H), 1.13 (t, J = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 167.98, 140.18, 135.47, 133.59, 131.51, 128.41, 125.32, 122.87, 61.40, 13.83.

a-IDT ¹H NMR (400 MHz, CDCl₃) δ 7.39 (s, 2H), 7.24 (d, J = 4.8 Hz, 2H), 7.15 (d, J = 8.8 Hz, 8H), 6.97 (d, J = 4.9 Hz, 2H), 6.76 (d, J = 8.8 Hz, 8H), 3.90 (t, J = 6.5 Hz, 8H), 1.81 – 1.68 (m, 8H), 1.48 – 1.23 (m, 40H), 0.88 (t, J = 6.8 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 157.98, 156.18, 153.76, 141.03, 136.72, 135.00, 128.89, 127.47, 122.92, 117.10, 114.23, 67.97, 61.73, 31.81, 29.35, 29.30, 29.23, 26.07, 22.65, 14.09.

a-IDTBT ¹H NMR (400 MHz, CDCl₃) δ 10.71 (s, 2H), 8.48 (s, 1H), 8.21 (d, J = 7.6 Hz, 2H), 7.96 (d, J = 7.5 Hz, 2H), 7.63 (s, 2H), 7.28 (s, 8H), 6.84 (d, J = 8.9 Hz, 8H), 3.93 (t, J = 6.5 Hz, 8H), 1.78 – 1.71 (m, 8H), 1.44 – 1.25 (m, 40H), 0.88 – 0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 188.49, 159.28, 158.35, 154.06, 153.80, 152.15, 145.87, 143.36, 136.56, 135.03, 133.56, 132.68, 129.08, 125.43, 123.46, 121.80, 118.30, 114.46, 68.01, 63.71, 31.82, 29.36, 29.29, 29.24, 26.08, 22.66, 14.11.

a-IDTBTRh ^1H NMR (400 MHz, CDCl_3) δ 8.49 (s, 2H), 8.39 (s, 2H), 7.90 (d, $J = 7.7$ Hz, 2H), 7.66 (m, 4H), 7.28 (s, 6H), 6.83 (d, $J = 9.0$ Hz, 10H), 4.26 – 4.21 (dd, $J = 7.0$ Hz, 4H), 3.90 (t, $J = 6.4$ Hz, 8H), 1.77 – 1.71 (m, 8H), 1.42 – 1.25 (m, 40H), 0.88 – 0.84 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 192.92, 167.46, 158.49, 158.31, 154.41, 154.10, 151.62, 145.74, 143.66, 136.65, 135.05, 131.06, 129.91, 129.06, 126.98, 124.96, 124.86, 124.44, 120.76, 118.28, 114.42, 67.99, 63.68, 39.93, 31.83, 29.37, 29.29, 29.26, 26.08, 22.67, 14.13, 12.33. MALDI-TOF-MS (m/z) 1692.04 for $[\text{M}]^+$.

TGA plots

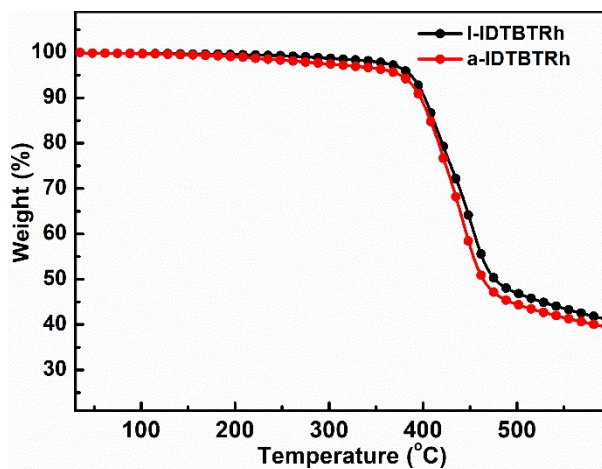


Figure S1. TGA plots of l-IDTBTRh and a-IDTBTRh at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere.

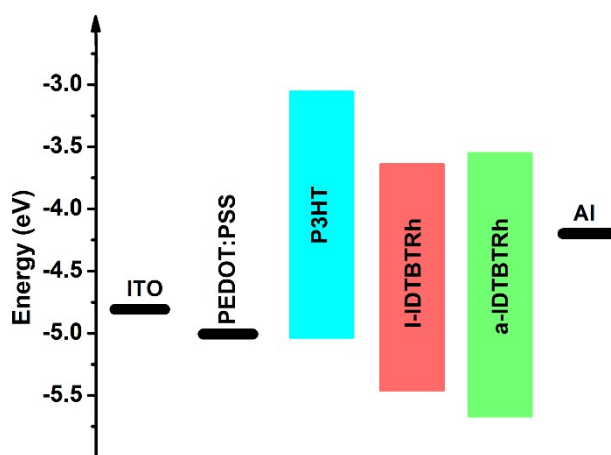


Figure S2. Energy level diagram of the device with a conventional non-fullerene sequential layer of ITO/PEDOT:PSS/P3HT:small molecule acceptors/Ca/Al.

Devices optimization

Table S1. Device performance of the organic solar cells based on P3HT:I-IDTBTRh (w/w, 1:0.8) and P3HT:a-IDTBTRh (w/w, 0.8:1) under the thermal annealing at 100 °C for 10 min.

Blend	Solvent	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
P3HT:I-IDTBTRh	CF	8.04	0.85	59.0	4.03
	CB	9.42	0.82	51.0	3.94
	<i>o</i> -DCB	5.62	0.84	68.0	3.21
P3HT:a-IDTBTRh	CF	5.11	0.91	45.0	2.09
	CB	3.52	0.90	42.0	1.33
	<i>o</i> -DCB	3.50	0.82	53.0	1.52

Table S2. Device performance of the PSCs based on P3HT:acceptors with different D/A ratio (from 0.5:1 to 1:0.5) under the thermal annealing at 100 °C for 10 min.

Blend	D/A (w/w)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
P3HT:I-IDTBTRh	0.5:1	7.03	0.81	49.0	2.79
	0.6:1	9.21	0.83	61.0	4.66
	0.8:1	8.37	0.83	60.0	4.17
	1:1	9.10	0.83	60.0	4.53
	1:0.8	9.45	0.84	63.0	5.00
	1:0.6	8.91	0.85	65.0	4.92
	1:0.5	8.85	0.84	55.0	4.09
P3HT:a-IDTBTRh	0.5:1	5.26	0.91	47.0	2.25
	0.6:1	5.13	0.91	45.0	2.10
	0.8:1	5.43	0.91	48.0	2.37

1:1	4.70	0.92	40.0	1.73
1:0.8	4.89	0.91	40.0	1.78

Table S3. Device performance of the organic solar cells based on P3HT:l-IDTBTRh (w/w, 1:0.8) and P3HT:a-IDTBTRh (w/w, 0.8:1) with different thermal annealing temperature (from 110 to 150 °C).

Blend	Annealing Temp.(°C)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
P3HT:l-IDTBTRh	110	8.55	0.84	68.0	4.88
	120	7.98	0.85	69.0	4.68
	130	8.44	0.85	69.0	4.95
	140	8.81	0.86	71.0	5.38
	150	8.37	0.86	71.0	5.11
P3HT:a-IDTBTRh	110	5.23	0.91	49.0	2.33
	120	5.00	0.92	55.0	2.53
	130	4.61	0.91	51.0	2.14
	140	5.15	0.92	53.0	2.51
	150	4.89	0.92	56.0	2.52

Table S4. Device performance of the organic solar cells based on P3HT:l-IDTBTRh (w/w, 1:0.8) and P3HT:a-IDTBTRh (w/w, 0.8:1) with different solvent additives.

Blend	additive	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
P3HT:l-IDTBTRh	none	8.81	0.86	71.0	5.38
	1%DIO	7.81	0.84	66.0	4.33
	1%CN	8.56	0.85	70.0	5.09
	1%DPE	8.00	0.83	64.0	4.25
P3HT:a-IDTBTRh	none	5.00	0.92	55.0	2.53
	1%DIO	5.12	0.91	58.0	2.70
	1%CN	4.65	0.92	55.0	2.35
	1%DPE	4.65	0.91	52.0	2.20

NMR Spectrum

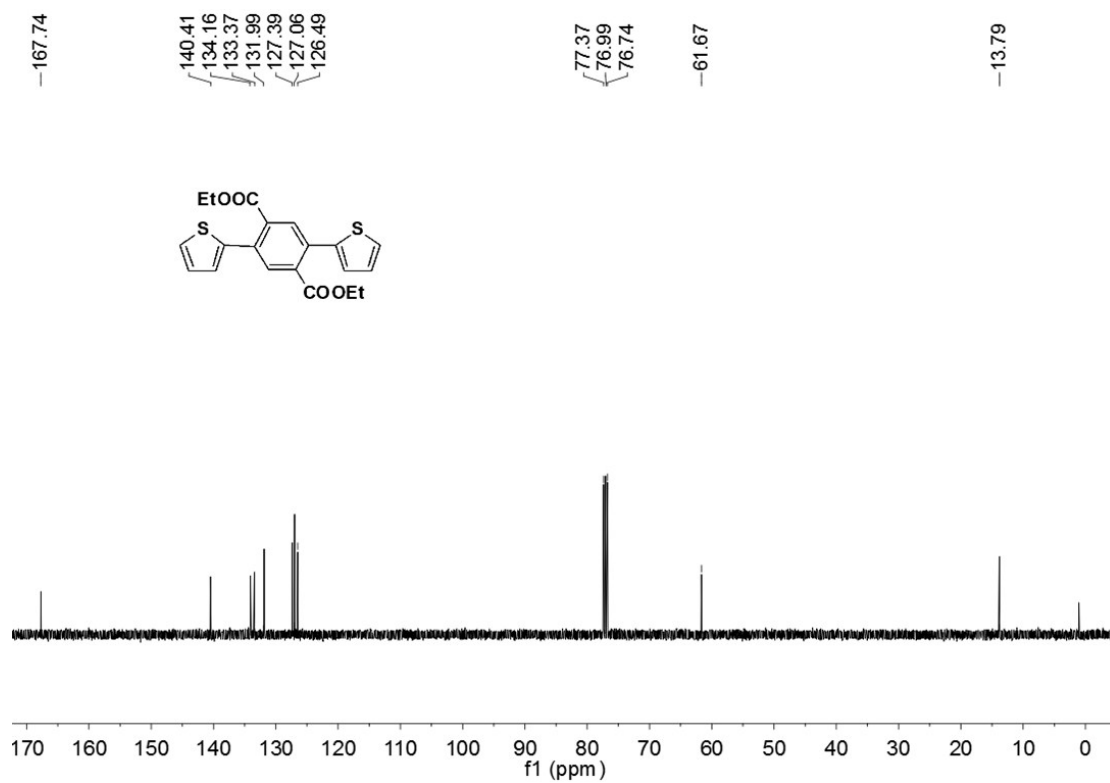
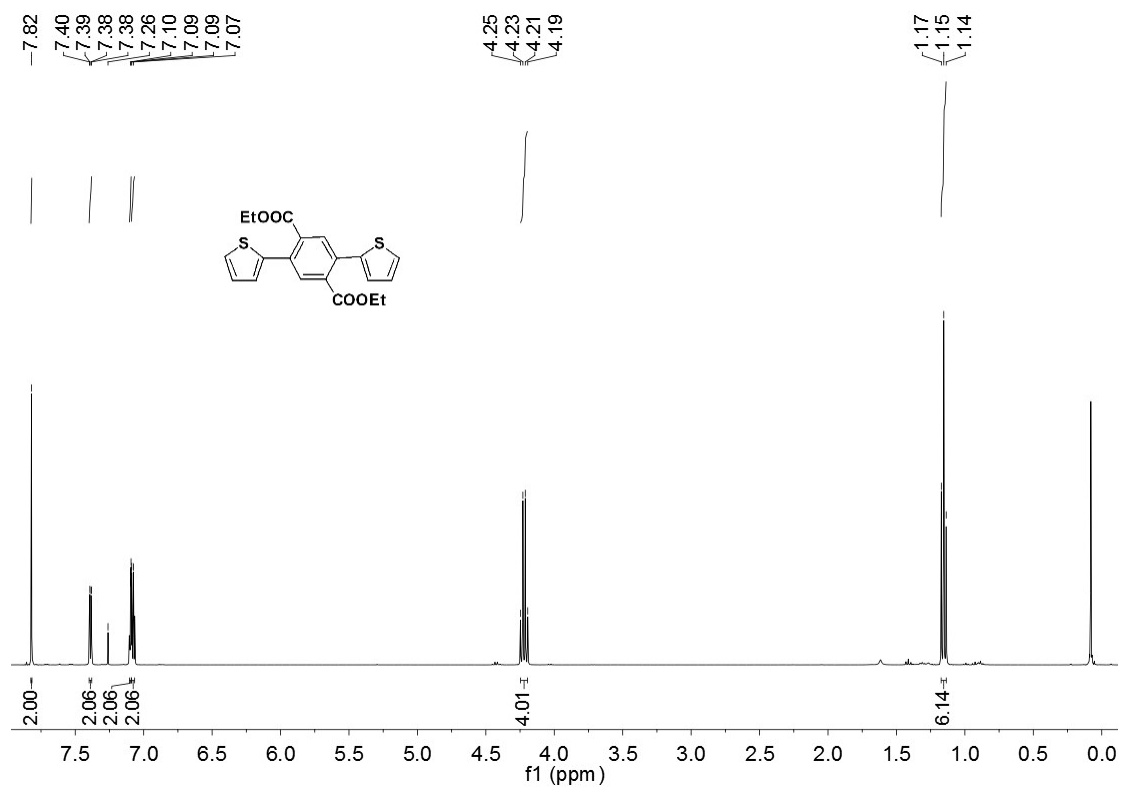


Figure S3. ¹H and ¹³C NMR spectra of compound **2** in CDCl₃.

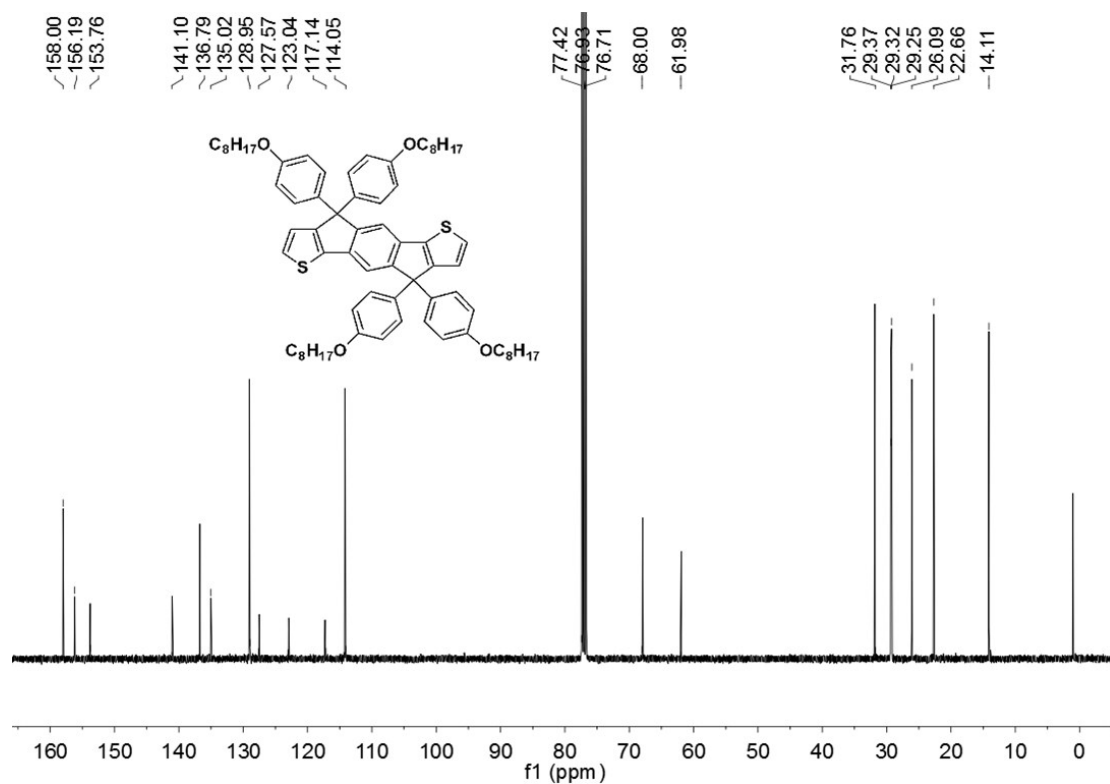
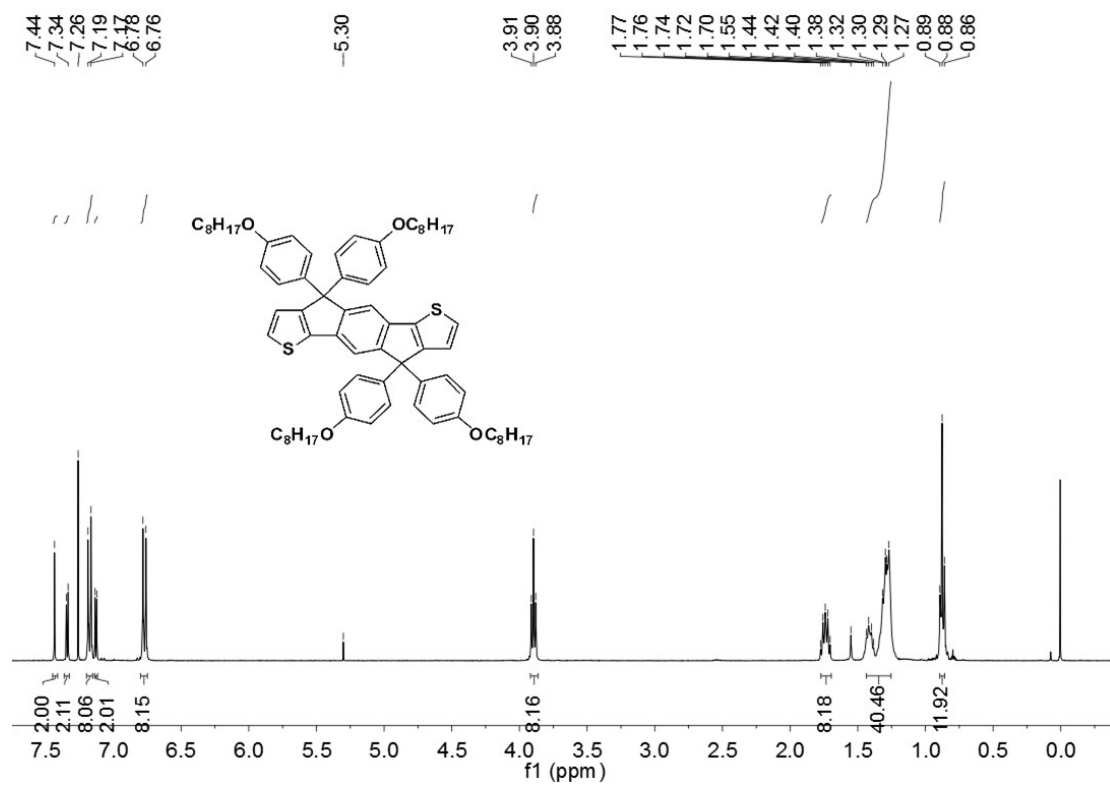


Figure S4. ¹H and ¹³C NMR spectra of monomer **1-IDT** in CDCl₃.

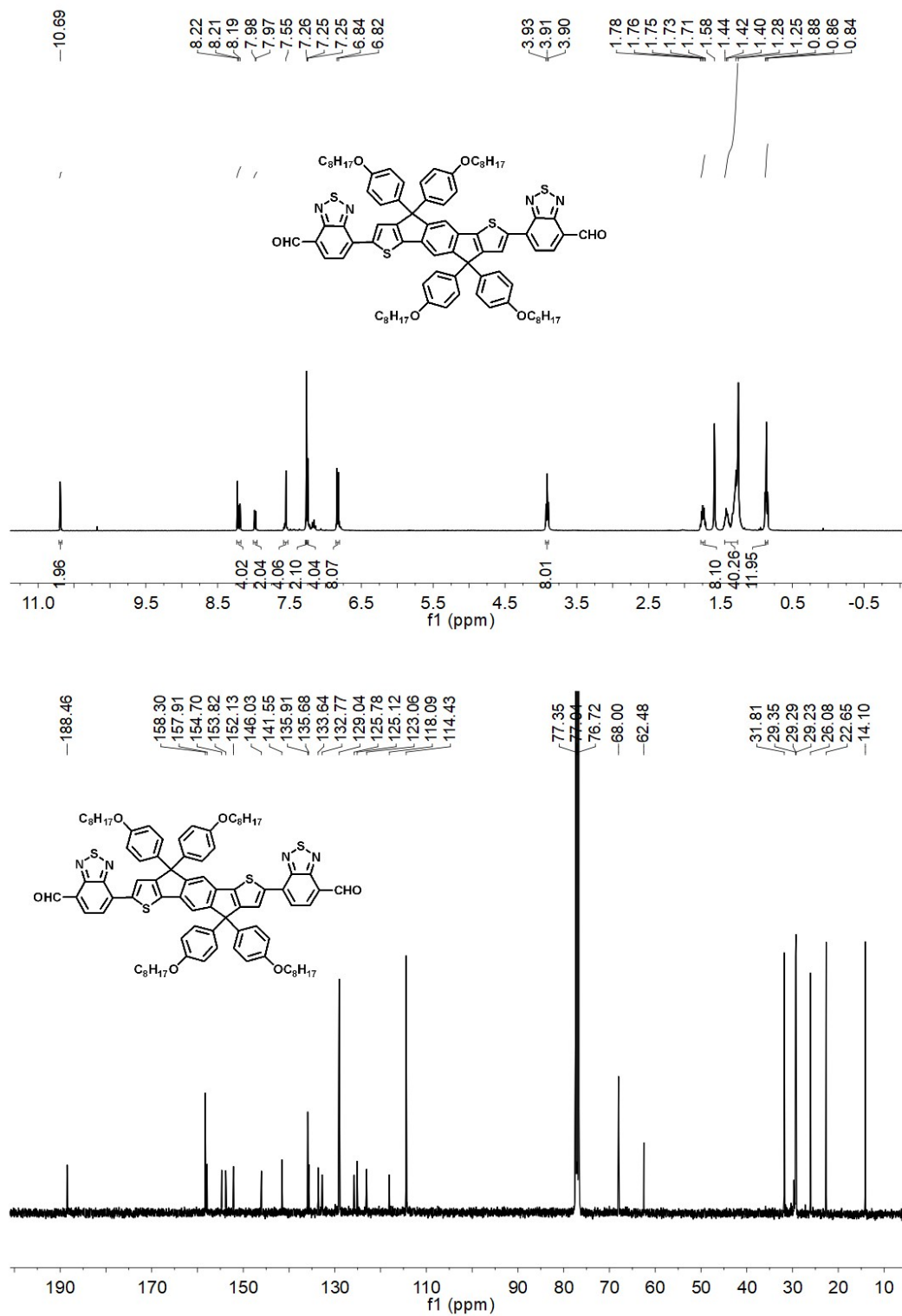


Figure S5. ¹H and ¹³C NMR spectra of compound I-IDTBT in CDCl₃.

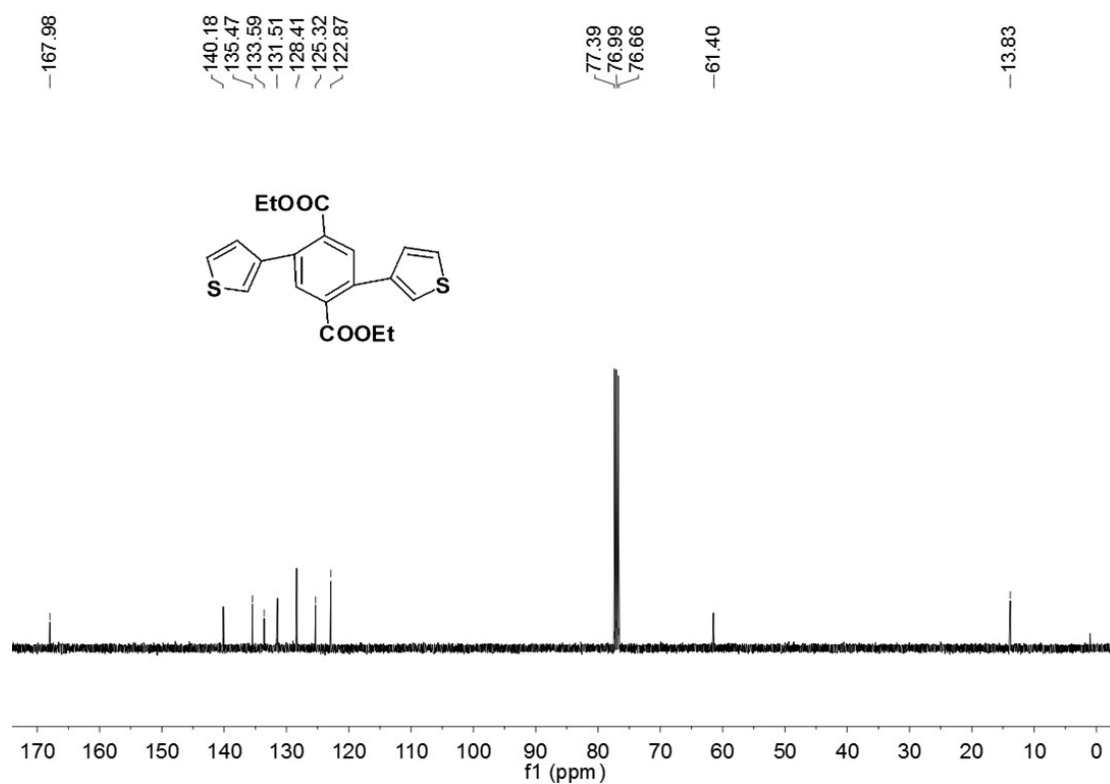
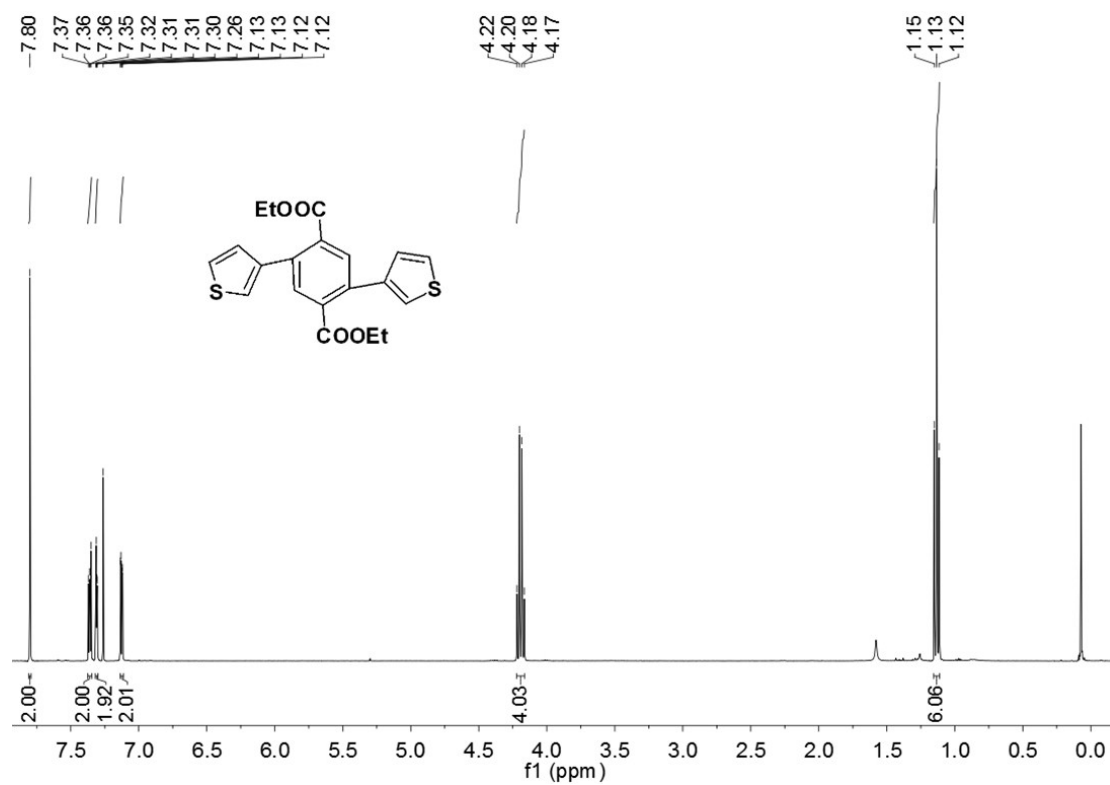


Figure S7. ¹H and ¹³C NMR spectra of compound **3** in CDCl₃.

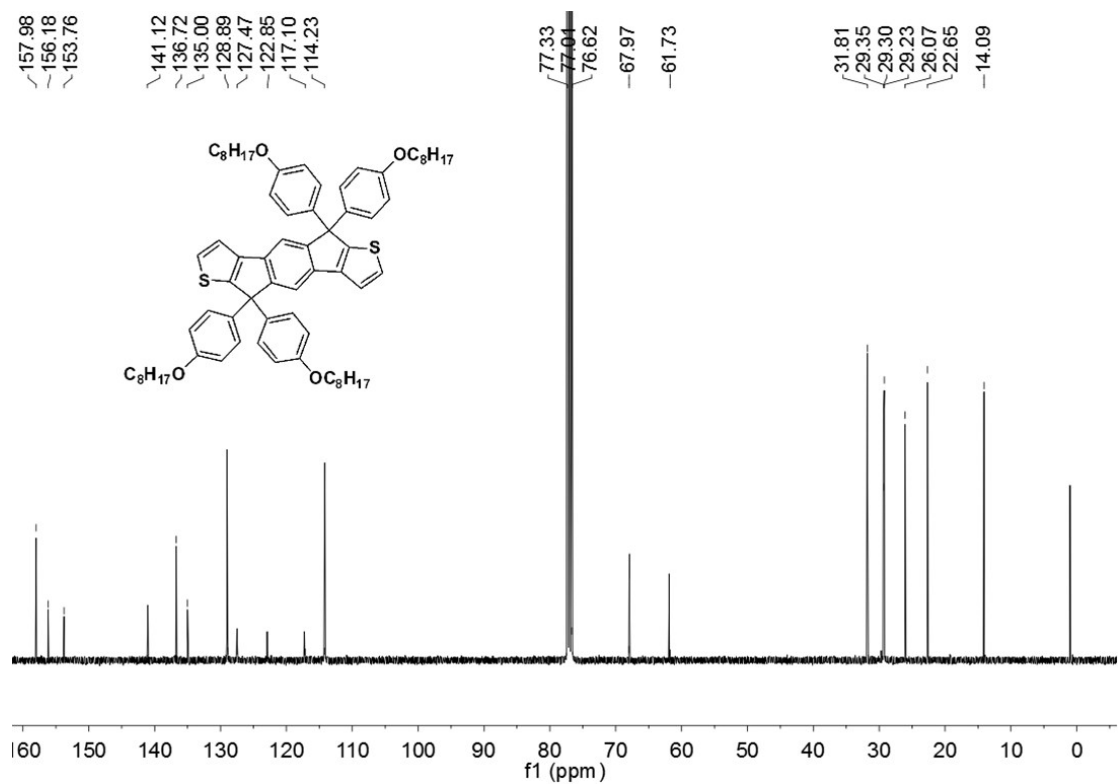
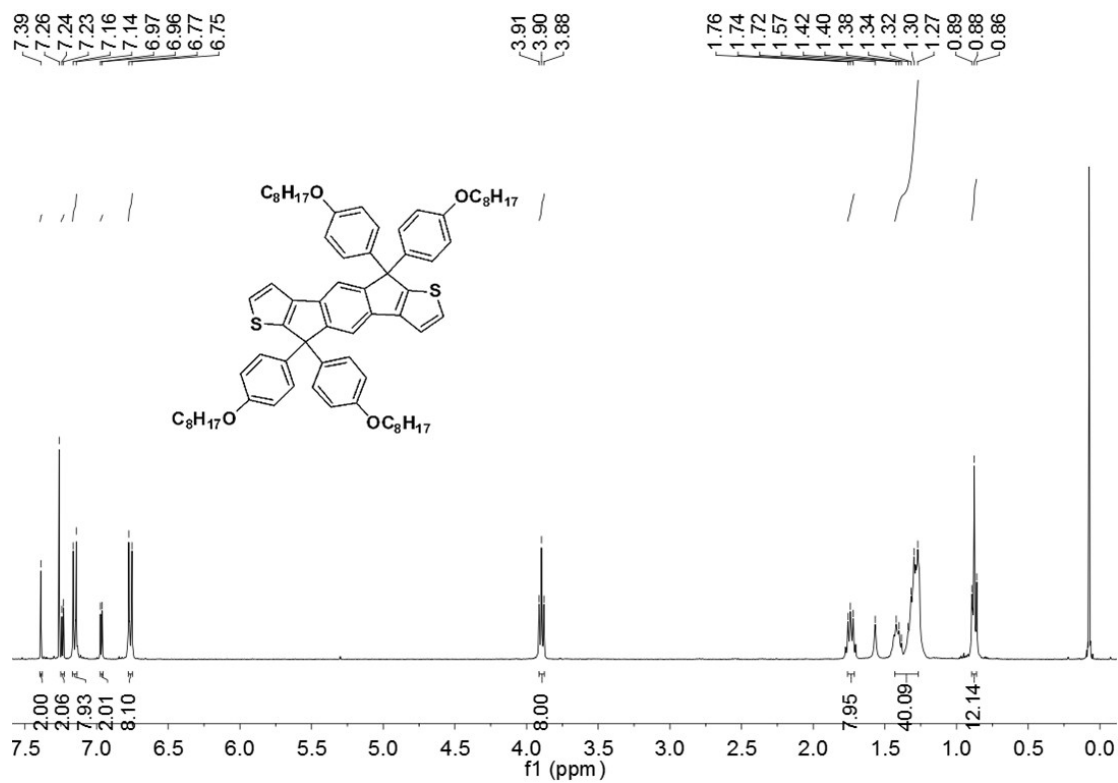


Figure S8. ¹H and ¹³C NMR spectra of monomer a-IDT in CDCl₃.

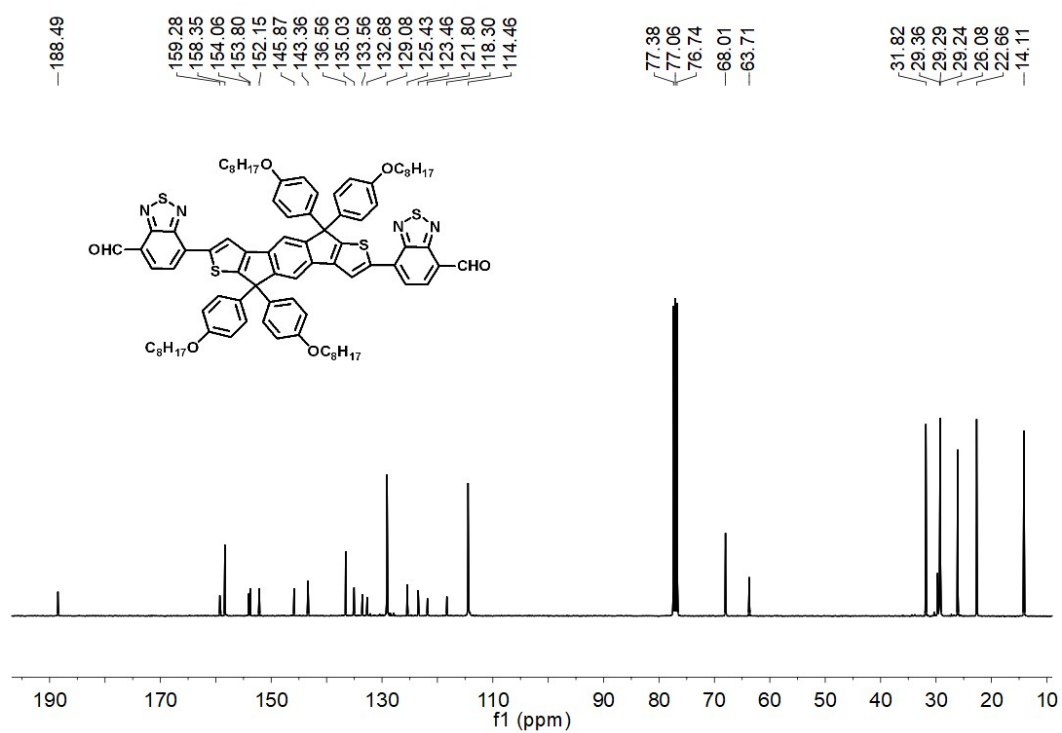
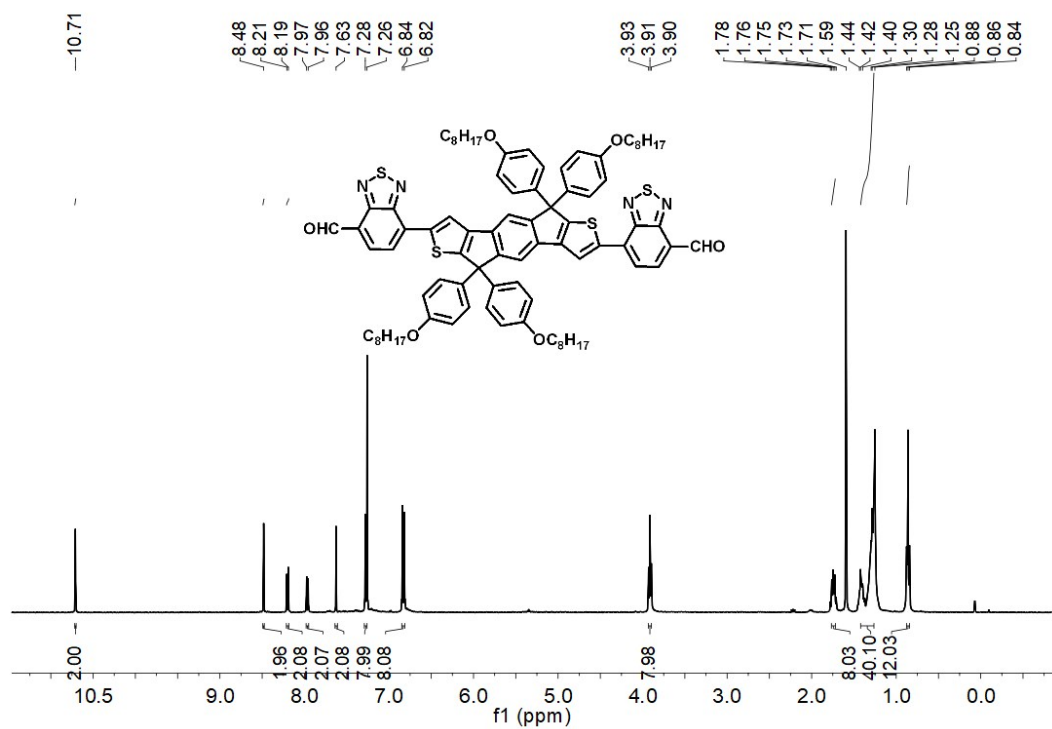


Figure S9. 1H and ^{13}C NMR spectra of compound **a-IDTBT** in CDCl₃.

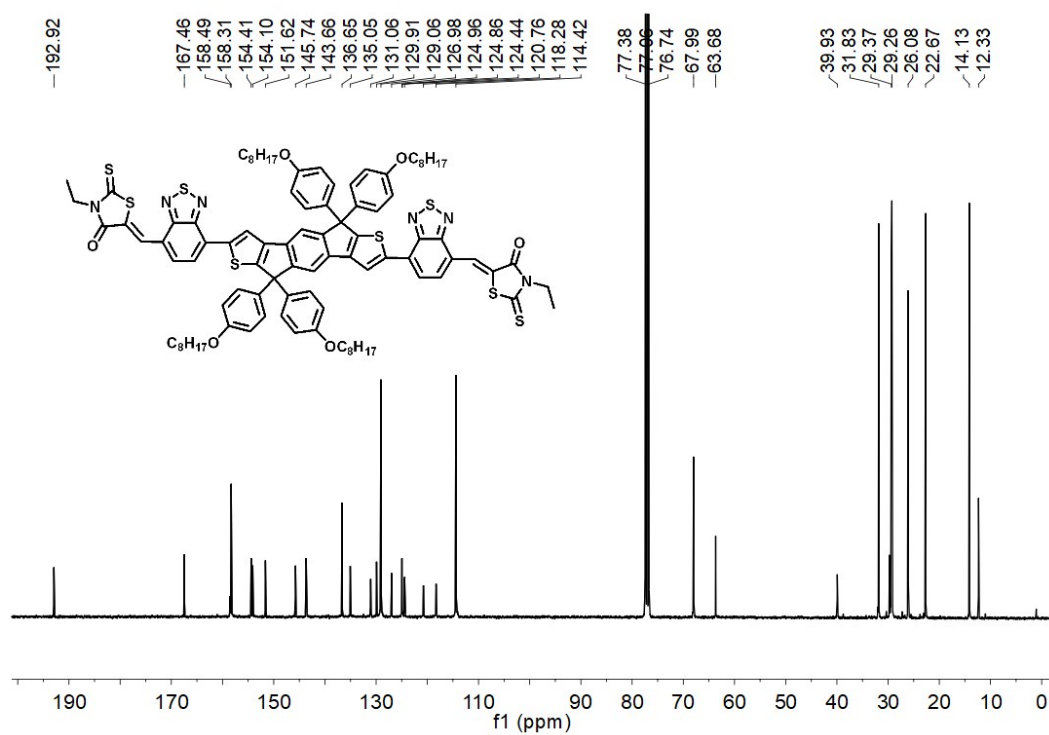
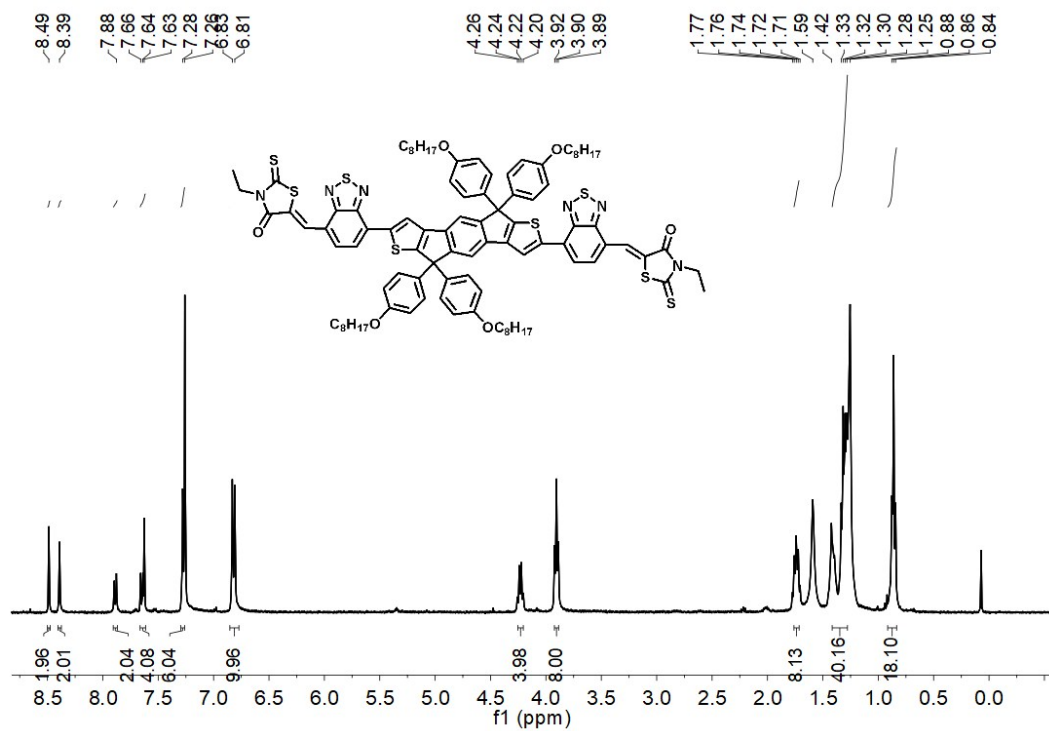


Figure S10. ¹H and ¹³C NMR spectra of target compound a-IDTBTRh in CDCl₃.