Supporting Information for:

Charge Transfer in Cross-Conjugated 4,8-Dithienylbenzo[1,2-*b*:4,5-*b*']dithiophene Based Organic Sensitizers

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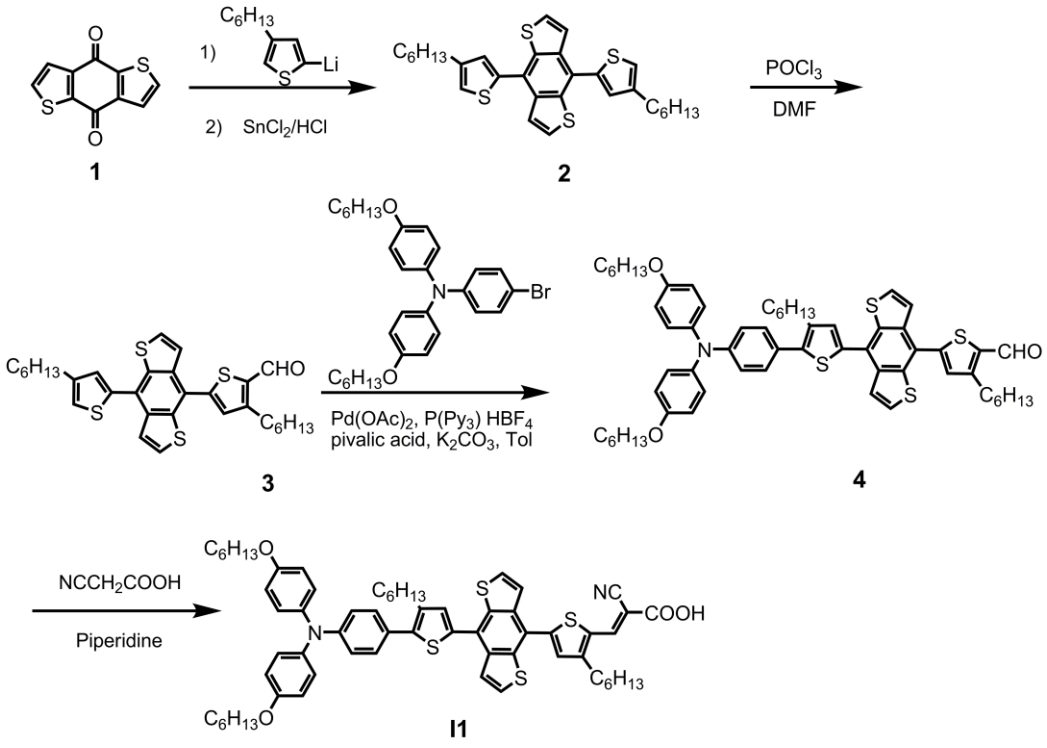
Experimental Section.

Materials and Reagents.

Thiophene, 3-thiophenecarboxylic acid, *N*-bromosuccinimide (NBS) were purchased from J&K Chemical Ltd, China. 4,8-Dehydrobenzo[l,2-*b*:4,5-*b'*]dithiophene-4,8-dione (**1**) was synthesized according to reported method.[1] Organic solvents used in this work were purified using standard process. Other chemicals and reagents were used as received from commercial sources without further purification. Transparent conductive glass (F-doped SnO_2, FTO, 15 Ω, transmittance of 80%, Nippon Sheet Glass Co., Japan) was used as the substrate for the fabrication of TiO_2 thin film electrode.

Synthesis.



Scheme 1. Synthetic route for compound **I1**.

Synthesis of compound 2.

In a 50 mL argon purged flask, *n*-butyllithium (10 mL, 16.0 mmol) was added dropwise to a solution of 3-hexylthiophene (2.68 g, 15.9 mmol) in THF (20 mL) at 0 ^{o}C and then the mixture was stirred for 1 h. Subsequently, 4,8-dehydrobenzo[l,2-*b*:4,5-*b'*]dithiophene-4,8-dione (1.4g, 6.4 mmol) was added into the mixture and then stirred for 1 h at 50 ^{o}C. After cooling the reaction mixture to ambient temperature, a mixture of $SnCl_2$ (12.3 g, 50 mmol) in 10% HCl (24 mL) was added and the mixture was stirred for additional 1.5 h and poured into ice water. Then the mixture was extracted with diethylether twice and the combined organic phases were concentrated to obtain the crude compound **2**. Further purification was carried out by column chromatography on silica gel using petroleum ether as the eluent, which provides pure compound **2** as yellow solid, yield 65% (0.86 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.64 (d, *J* = 5.6 Hz, 2H), 7.46 (d, *J* = 5.6 Hz, 2H), 7.32 (s, 2H), 7.11 (s, 2H), 2.72 (t, *J* = 7.6 Hz, 4H), 1.80 – 1.64 (m, 4H), 1.48 – 1.38 (m, 4H), 1.38 – 1.30 (m, 8H), 0.92 (t, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 143.86, 139.51, 139.25, 136.72, 129.64, 127.84, 124.35, 123.59, 121.18, 31.97, 30.83, 30.72, 29.29, 22.91, 14.39. MS: m/z 522.1545 ($C_{30}H_{34}S_4^+$, calc. 522.1543).

Synthesis of compound 3.

Under argon atmosphere, compound **2** (0.40 g, 0.76 mmol), DMF (0.27 g, 0.76 mmol) and CH_2Cl_2 (20 mL) were placed in a 50 mL three-necked flask. After the mixture was cooled to 0 ^{o}C, 0.07 mL $POCl_3$ (0.90 mmol) was added dropwise, and then

refluxed for 24 h. Cooling to room temperature, the mixture was quenched with 10% NaOAc aqueous solution (30 mL), extracted with dichloromethane (DCM), and then washed with water. After dried over anhydrous sodium sulfate, the crude product was purified by column chromatography on silica gel with hexane/dichloromethane (4/1, v/v) as eluent. Pure compound **3** was obtained as yellow oil, yield 61% (0.26g). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10.14 (s, 1H), 7.65 (d, *J* = 5.6 Hz, 1H), 7.62 (d, *J* = 6.0 Hz, 1H), 7.53 (d, *J* = 5.2 Hz, 1H), 7.48 (d, *J* = 5.6 Hz, 1H), 7.41 (s, 1H), 7.32 (s, 1H), 7.12 (s, 1H), 3.07 (t, *J* = 7.2 Hz, 4H), 2.74 – 2.70 (m, 4H), 1.80 – 1.69 (m, 4H), 1.47 – 1.35 (m, 8H), 0.92 – 0.89 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 182.37, 153.44, 149.00, 143.98, 139.00, 138.00, 136.76, 136.48, 131.79, 129.88, 129.02, 127.78, 125.68, 123.72, 122.92, 122.46, 121.53, 31.95, 31.84, 31.69, 30.80, 30.72, 29.28, 29.25, 28.88, 22.90, 22.84, 14.38, 14.33. MS: m/z 551.1559 ($C_{32}H_{34}OS_4^+$, calc. 551.1526).

Synthesis of compound 4.

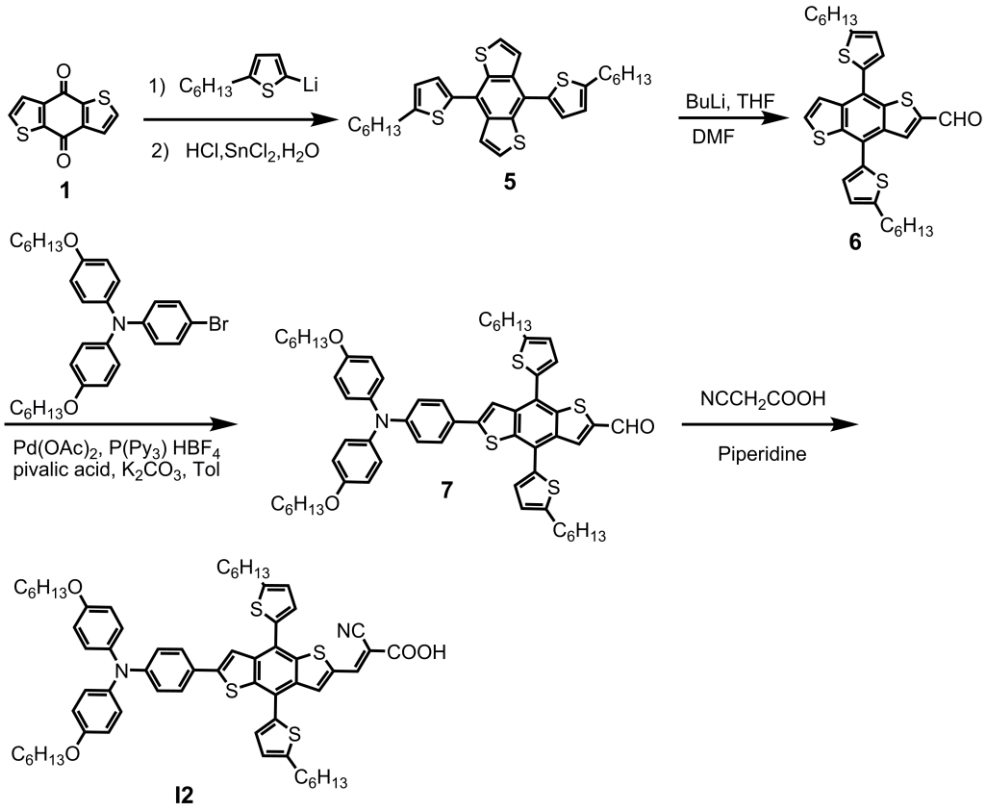
In a Schlenk tube was added K_2CO_3 (2.5 equiv, 0 .74 mmol, 104 mg), $Pd(OAc)_2$ (2 mol%, 0.006 mmol, 1.4 mg), tricyclohexylphosphonium tetrafluoroborate (4 mol%, 0.012 mmol, 4.4 mg), pivalic acid (30 mol%, 0.090 mmol, 9.2 mg) and compound **3** (0.30 mmol, 165 mg). Under argon atmosphere, toluene (1 mL) and 4-bromo-*N*,*N*-bis(4-(hexyloxy)-phenyl)benzeneamine (1.3 equiv, 0.38 mmol, 200 mg) were added. The reaction mixture was then vigorously stirred at 100 ^{o}C for 24 h. After cooling to room temperature, DCM was added. Then the mixture was washed with water and dried over $MgSO_4$. Compound **4** was obtained after purification by

column chromatography in 55% yield (163 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10.15 (s, 1H), 7.79 (d, *J* = 5.6 Hz, 1H), 7.64 (d, *J* = 5.6 Hz, 1H), 7.54 (d, *J* = 5.6 Hz, 1H), 7.48 (d, *J* = 5.6 Hz, 1H), 7.42 (s, 1H), 7.38 (s, 1H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.16 – 7.07 (m, 4H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 4H), 3.95 (t, *J* = 6.4 Hz, 4H), 3.07 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 1.85 – 1.73 (m, 8H), 1.46 (dd, *J* = 8.4, 6.1 Hz, 8H), 1.42 – 1.28 (m, 16H), 0.98 – 0.84 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 182.35, 155.91, 153.44, 149.08, 148.53, 140.60, 139.92, 139.16, 139.11, 138.40, 137.97, 136.61, 136.55, 136.36, 131.80, 131.19, 129.98, 129.04, 127.64, 127.15, 125.81, 125.76, 123.95, 122.94, 122.27, 119.88, 115.52, 68.47, 31.98, 31.87, 31.70, 31.31, 29.58, 29.50, 29.27, 29.16, 28.89, 26.03, 22.93, 22.89, 22.86, 14.41, 14.36, 14.33. MS: m/z 993.4315 ($C_{61}H_{71}NO_3S_4^+$, calc. 993.4317).

Synthesis of compound I1.

Under argon atmosphere, a mixture of compound **4** (110 mg, 0.11 mmol) and cyanoacetic acid (20 mg, 0.23 mmol) in acetonitrile (10 mL) was refluxed in the presence of piperidine (0.2 mL) for 8 h. After cooling to room temperature, the mixture was poured into water and extracted with DCM. The combined organic phase was washed with water and brine and dried over anhydrous sodium sulfate. After the removal of the solvent, the residue was purified by flash column chromatography (silica gel, DCM/MeOH = 10/1, v/v). The target product was obtained as red solid with a yield of 88% (104 mg). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 8.24 (s, 1H), 7.87 (dd, *J* = 9.6, 5.6 Hz, 2H), 7.69 (d, *J* = 5.6 Hz, 1H), 7.59 (d, *J* = 5.6 Hz, 1H), 7.53

(s, 1H), 7.45 (s, 1H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 4H), 6.91 (d, *J* = 8.8 Hz, 4H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.93 (t, *J* = 6.4 Hz, 4H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.72 – 1.65 (m, 8H), 1.41 – 1.38 (m, 8H), 1.32 – 1.29 (m, 16H), 0.88 – 0.81 (m, 12H). ^{13}C NMR (100 MHz, THF-d_8, δ ppm):156.09, 152.14, 148.46, 145.65, 145.61, 141.72, 140.57, 139.66, 139.33, 136.85, 136.81, 136.03, 135.96, 135.92, 135.88, 132.08, 131.05, 130.76, 129.74, 126.89, 125.99, 125.93, 123.12, 123.08, 122.29, 119.75, 115.24, 109.71, 67.95, 32.22, 32.00, 31.86, 31.22, 29.88, 29.57, 29.53, 29.23, 29.03, 26.01, 22.85, 22.80, 22.68, 13.95, 13.79, 13.67. MS: *m/z* 1060.4368 ($C_{64}H_{72}N_2O_4S_4^+$, calc. 1060.4375).



Scheme 2. Synthetic route for compound **I2**.

Synthesis of compound 5.

Compound **5** was synthesized similarly as compound **2** and obtained as yellow viscous liquid, yield 58% (0.48g). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.65 (d, *J* = 5.6 Hz, 2H), 7.45 (d, *J* = 5.7 Hz, 2H), 7.29 (d, *J* = 1.6 Hz, 2H), 6.91 (d, *J* = 1.6 Hz 2H), 2.92 (t, *J* = 7.6 Hz, 4H), 1.80 – 1.74 (m, 4H), 1.47 – 1.44 (m, 4H), 1.38 – 1.31 (m, 8H), 0.92 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 147.37, 139.19, 137.19, 136.72, 127.99, 127.67, 124.49, 124.28, 123.66, 31.83, 30.51, 29.94, 29.17, 22.85, 14.36. MS: m/z 522.1544 ($C_{30}H_{34}S_4^+$, calc. 522.1543).

Synthesis of compound 6.

Under argon atmosphere, compound **5** (0.44 g, 0.85 mmol) and THF (30 mL) were placed in a 50 mL three-necked flask. The solution was cooled to -78 °C, then *n*-BuLi (0.60 mL, 1.6 M in hexane，0.96 mmol) was dropwisely added and the solution was stirred for 1 h. Subsequently, anhydrous DMF (0.8 mL, 10.6 mmol) was added and the mixture was stirred overnight at room temperature. Then the mixture was poured into water, extracted with DCM, and dried over anhydrous sodium sulfate. After the removal of the solvent, the target product **6** was purified by column chromatography on silica gel with hexane/dichloromethane (3/1, v/v) as eluent. Yellow solid, yield 71% (0.33 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 10.05 (s, 1H), 8.35 (s, 1H), 7.66 (d, *J* = 5.6 Hz, 1H), 7.57 (d, *J* = 5.6 Hz, 1H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.28 (d, *J* = 3.6 Hz, 1H), 6.95 (d, *J* = 3.6 Hz, 1H), 6.91 (d, *J* = 3.6 Hz, 1H), 2.96 – 2.89 (m, 4H), 1.82 – 1.76 (m, 4H), 1.54 – 1.42 (m, 4H), 1.40 – 1.31 (m, 8H), 0.92 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 184.98, 148.44, 148.03, 143.60, 141.35, 139.76,

139.63, 135.99, 135.48, 134.90, 130.37, 128.64, 128.40, 127.31, 124.87, 124.70, 123.90, 31.84, 31.81, 30.51, 30.49, 29.89, 29.16, 29.14, 22.83, 14.34. MS: m/z 550.1500 ($C_{31}H_{34}OS_4^+$, calc. 550.1492).

Synthesis of compound 7.

Compound **7** was synthesized similarly as compound **4** and obtained as red viscous oil, yield 53% (82 mg). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 10.02 (s, 1H), 8.30 (s, 1H), 7.71 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.30 (d, *J* = 3.6 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 4H), 6.95 (d, *J* = 3.6Hz, 1H), 6.91 (d, *J* = 3.6 Hz, 1H), 6.90 (d, *J* = 6.8 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 4H), 3.94 (t, *J* = 6.4 Hz, 4H), 2.86 – 2.81 (m, 4H), 1.85 – 1.72 (m, 8H), 1.47 – 1.44 (m, 8H), 1.41 – 1.29 (m, 16H), 0.93 – 0.91 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 184.88, 156.14, 149.76, 148.30, 147.83, 142.81, 141.80, 141.19, 140.10, 138.93, 136.25, 136.03, 135.09, 134.98, 128.57, 128.33, 127.51, 127.26, 126.73, 125.24, 124.84, 124.69, 123.75, 119.64, 116.95, 115.53, 68.46, 31.87, 31.84, 30.54, 29.97, 29.95, 29.55, 29.21, 26.02, 22.89, 14.39, 14.33. MS: m/z 993.4318 ($C_{61}H_{71}NO_3S_4^+$, calc. 993.4317).

Synthesis of compound I2.

Compound **I2** was synthesized similarly as compound **I1** and obtained as black solid, yield 90% (80 mg). ^{1}H NMR (400 MHz, THF-d_8, δ ppm): 8.29 (s, 1H), 8.13 (s, 1H), 7.61 (s, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.22 (s, 2H), 6.91 (d, *J* = 8.0 Hz, 4H), 6.85 (s, 2H), 6.72 (d, *J* = 8.0 Hz, 6H), 3.82 (t, *J* = 6.0 Hz, 4H), 2.82 – 2.81 (m, 4H), 1.73 – 1.55 (m, 8H), 1.37 – 1.35 (m, 8H), 1.29 – 1.28 (m, 16H), 0.81 – 0.80 (s, 12H). ^{13}C NMR (100 MHz, THF-d_8, δ ppm): 156.40, 149.84, 147.74, 147.42, 145.62, 145.54,

141.51, 141.07, 140.49, 140.07, 138.60, 137.42, 136.58, 136.30, 136.12, 134.65, 128.77, 128.40, 127.22, 127.09, 125.57, 125.20, 124.79, 124.49, 123.09, 119.41, 116.68, 115.25, 115.09, 67.95, 31.84, 31.81, 26.00, 24.96, 24.76, 24.56, 24.36, 24.16, 22.80, 13.73, 13.67. MS: *m/z* 1060.4371 ($C_{64}H_{72}N_2O_4S_4^+$, calc. 1060.4375).

DSSC Fabrication and Photovoltaic Measurements.

TiO_2 films (12 μm) composed of a 12 μm nanoparticle (20 nm) layer in direct contact with the FTO substrate was fabricated with a screen printing method and used in this study. The films were sintered at 500 °C for 2 h to achieve good necking of neighboring TiO_2 particles. The sintered films were then treated with 0.05 M $TiCl_4$ aqueous solution at 70 °C for 30 min followed by calcinations at 450 °C for 30 min. When TiO_2 electrodes were cooled down at 120 °C, the electrodes were dipped in dye solutions (0.3 mM in toluene) for 16 h at room temperature. The Pt-coated FTO as a counter electrode and the dye-loaded film were separated by a hot-melt Surlyn film (30 μm) and sealed together by pressing them under heat. The electrolyte was prepared by mixing a redox solution (0.1 M I_2, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazoliumiodide and 0.5 M 4-*tert*-butylpyridine in 3-methoxypropionitrile). The electrolyte was injection into the middle of the counter electrode and film by the two holes on the back of the counter electrode, then sealed with a Surlyn film covered with a thin glass slide under heat.

Characterizations.

UV-vis absorption spectra of dye solutions were recorded with a Shimadzu Model 3100 UV-vis-NIR spectrophotometer in a transmission mode. The PL spectra of the

dye solutions were recorded on a RF-5301PC (Shimadzu) spectrophotometer. Cyclic voltammetry (CV) measurements were performed with an Autolab analyzer using a typical three-electrode electrochemical cell in a solution of tetrabutylammonium hexafluorophosphate (0.1M) in acetonitrile at room temperature under argon. The scan rate was 50 mV/ s. A Pt wire was used as counter electrode, and an Ag/Ag^{+} electrode as reference electrode. The potential of the reference electrode was calibrated by ferrocene, and all potentials mentioned in this work are against normal hydrogen electrode (NHE). The film thickness was measured by a surface profiler (VeecoDektak150, USA). The geometrical and electronic properties of the resulted sensitizers are calculated by density functional methods using the Gaussian 03 program package at the B3LYP/6-31G(d) level. The working performance of the DSSC was tested by recording the current density–voltage (*J*–*V*) curves with a Keithley 2400 source meter (Oriel) under illumination of simulated AM1.5G solar light coming from a solar simulator (Oriel-94043A equipped with a 450 W Xe lamp and an AM1.5G filter). The light intensity was calibrated using a standard Si solar cell (Newport 91150). A black mask with aperture area of 0.2304 cm^2 was used during measurement to avoid stray light.

Figure S1. Calculated frontier molecular orbitals of **I1** and **I2**.

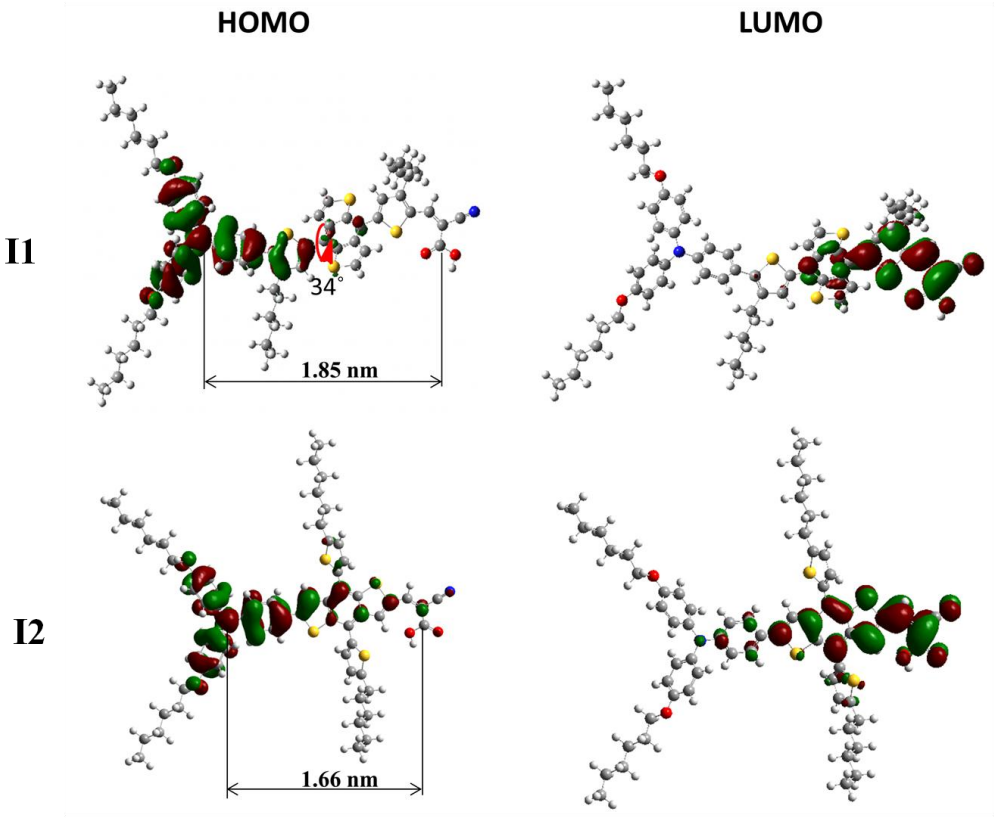


Figure S2. Absorption spectra of **I1** and **I2** on TiO_2 films.

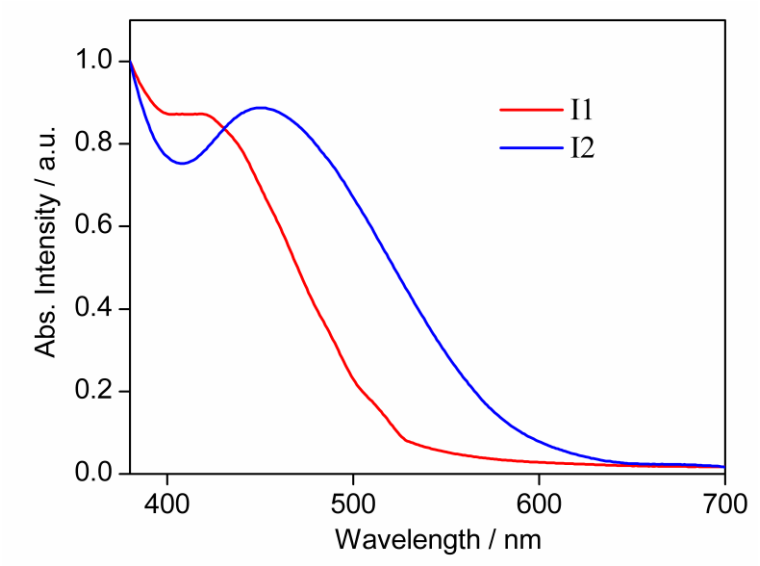


Figure S3. PL spectra of **I1** (a) and **I2** (b) in different solvents.

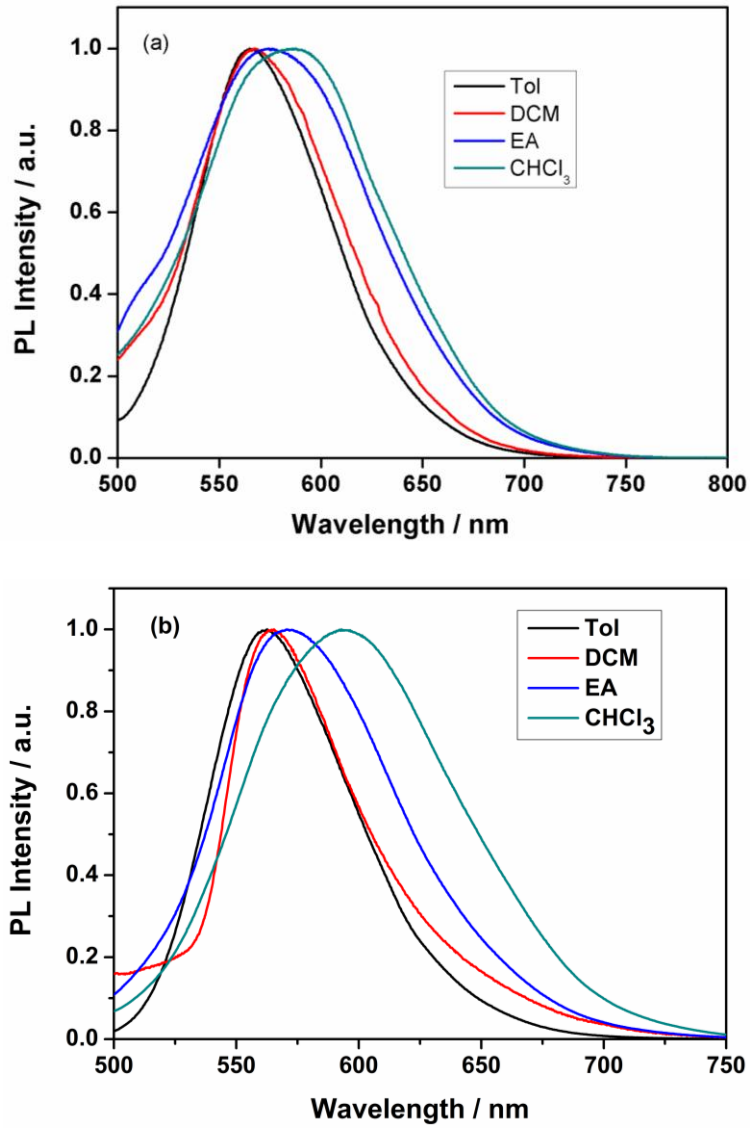


Figure S4. Electron lifetime as a function of charge density at open circuit for the DSSCs based on **I1** and **I2**.

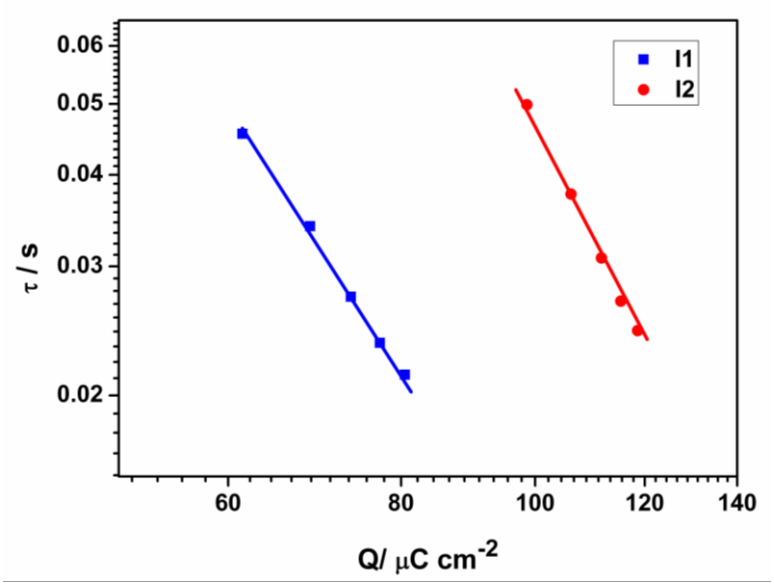


Figure S5. ^{1}H NMR spectrum of compound **2**.

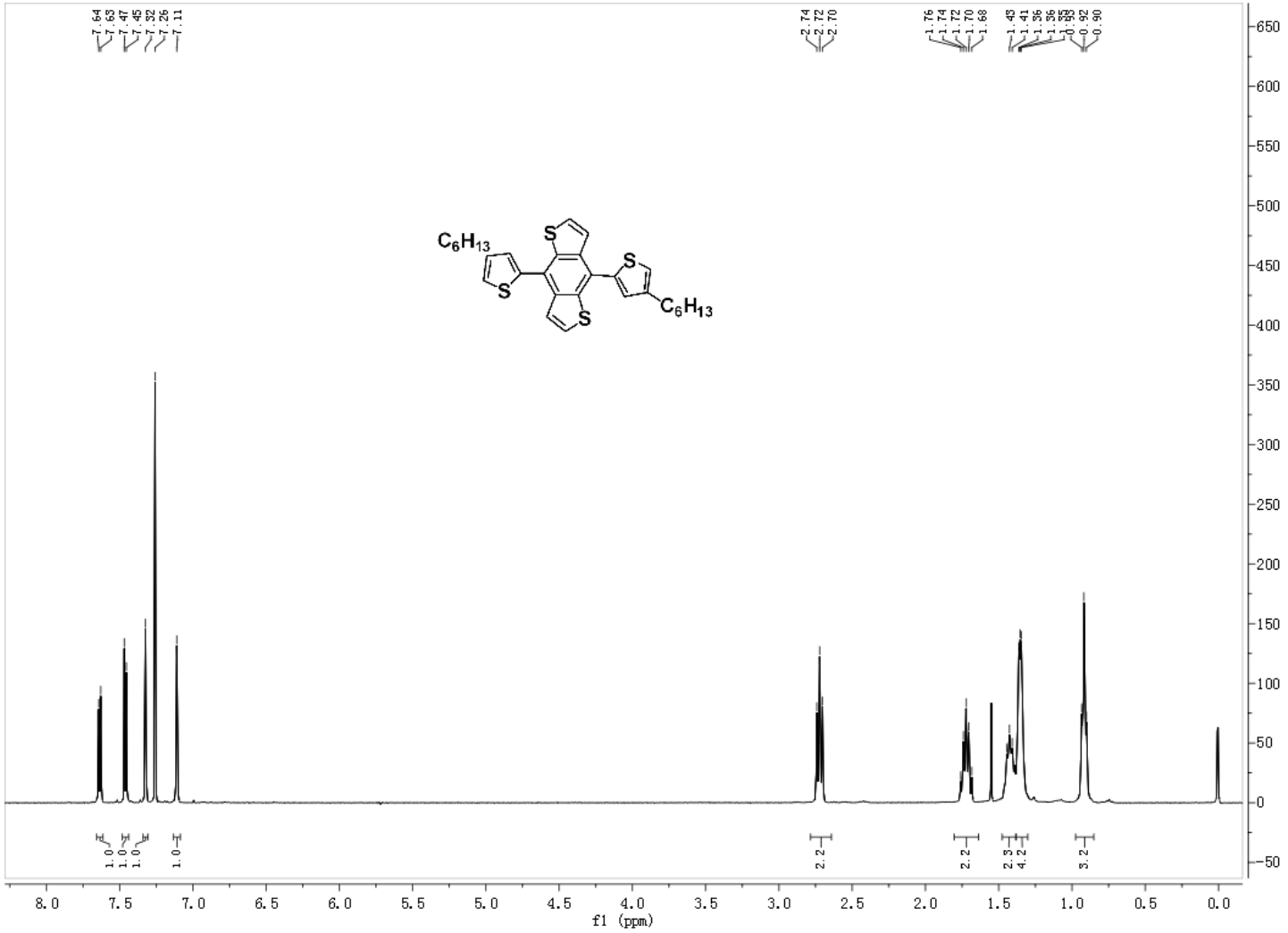


Figure S6. ^{1}H NMR spectrum of compound **3**.

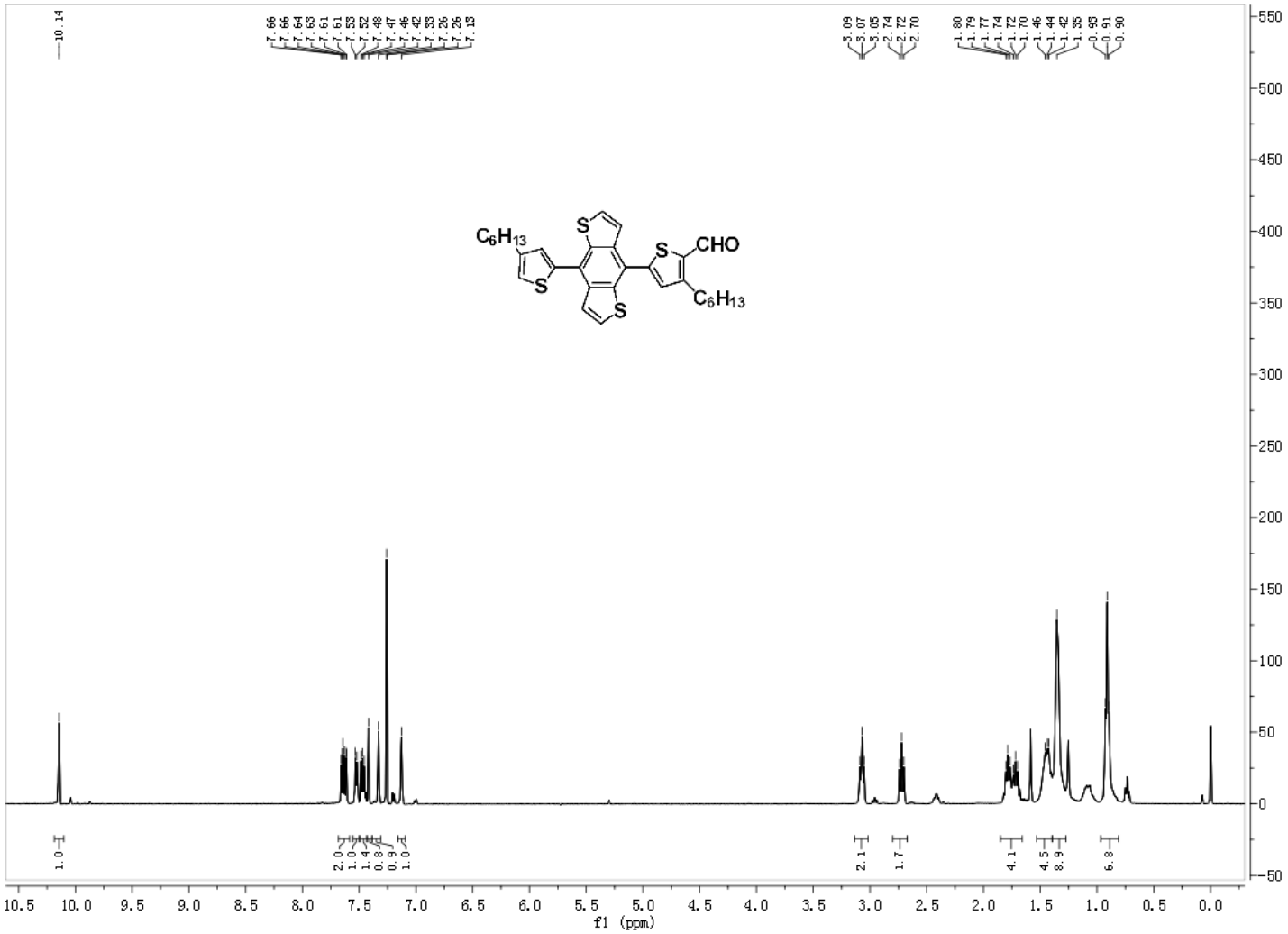


Figure S7. ^{1}H NMR spectrum of compound **4**.

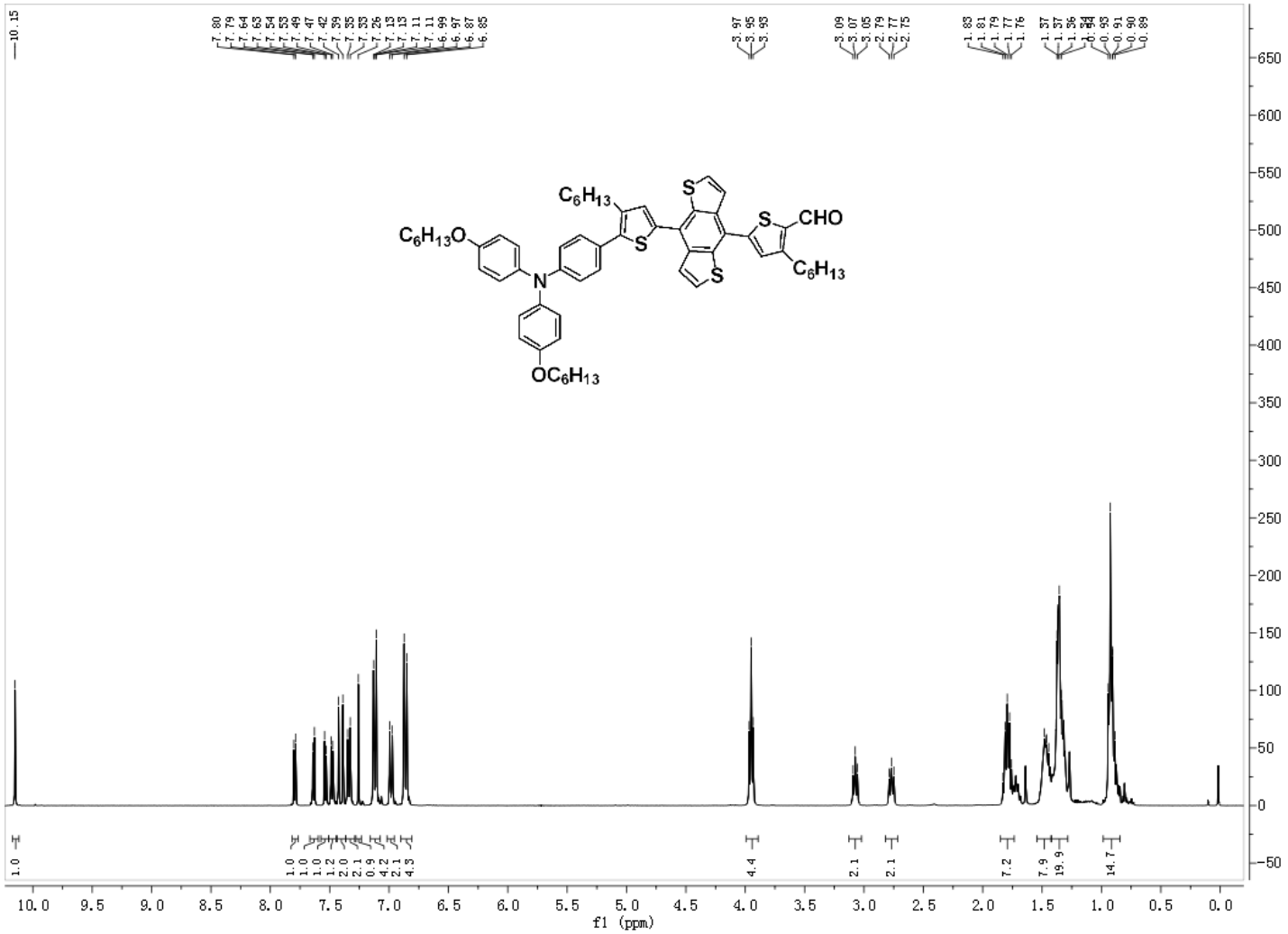


Figure S8. ^{1}H NMR spectrum of compound **I1**.

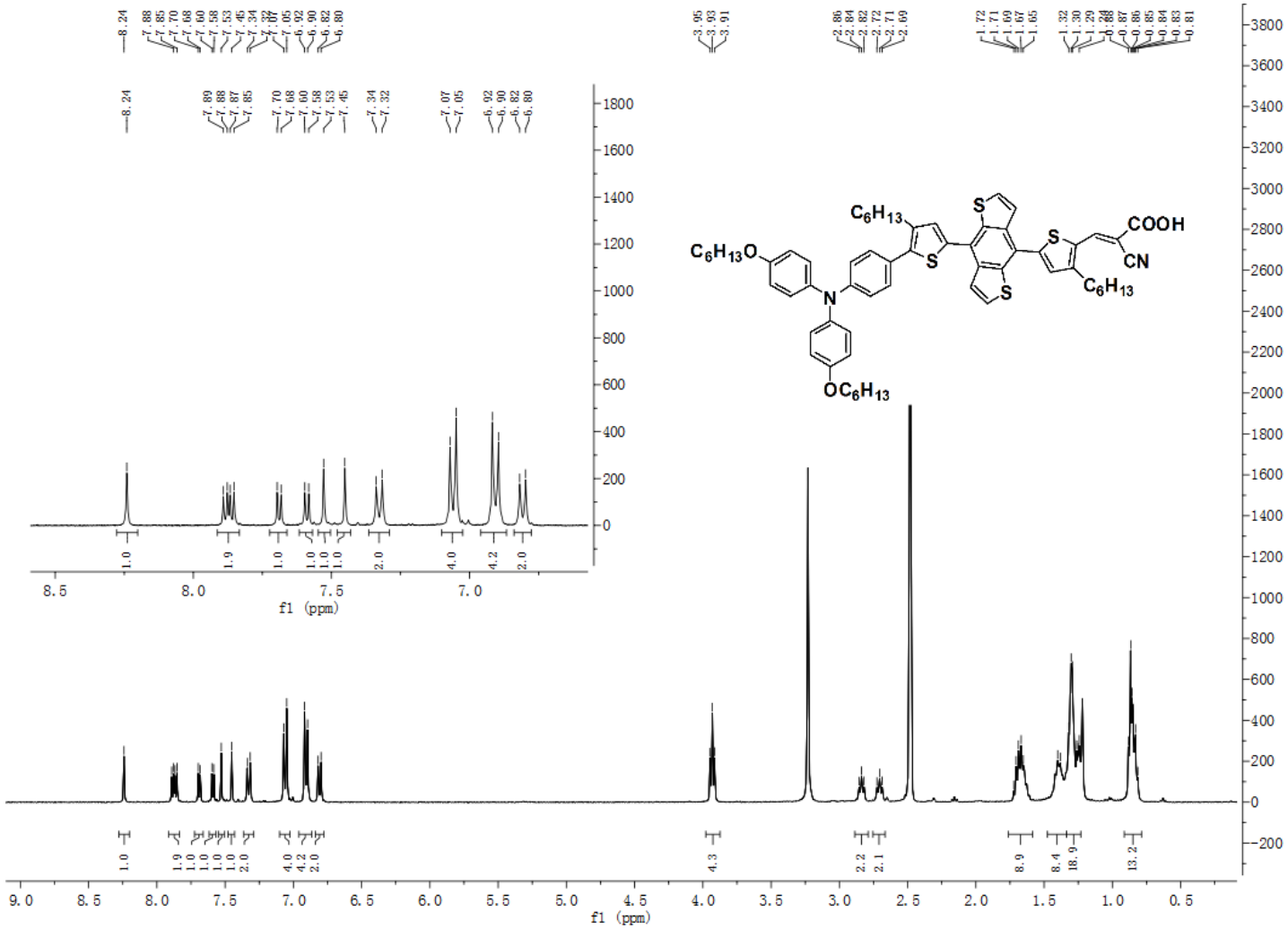


Figure S9. ^{13}C NMR spectrum of compound **I1**.

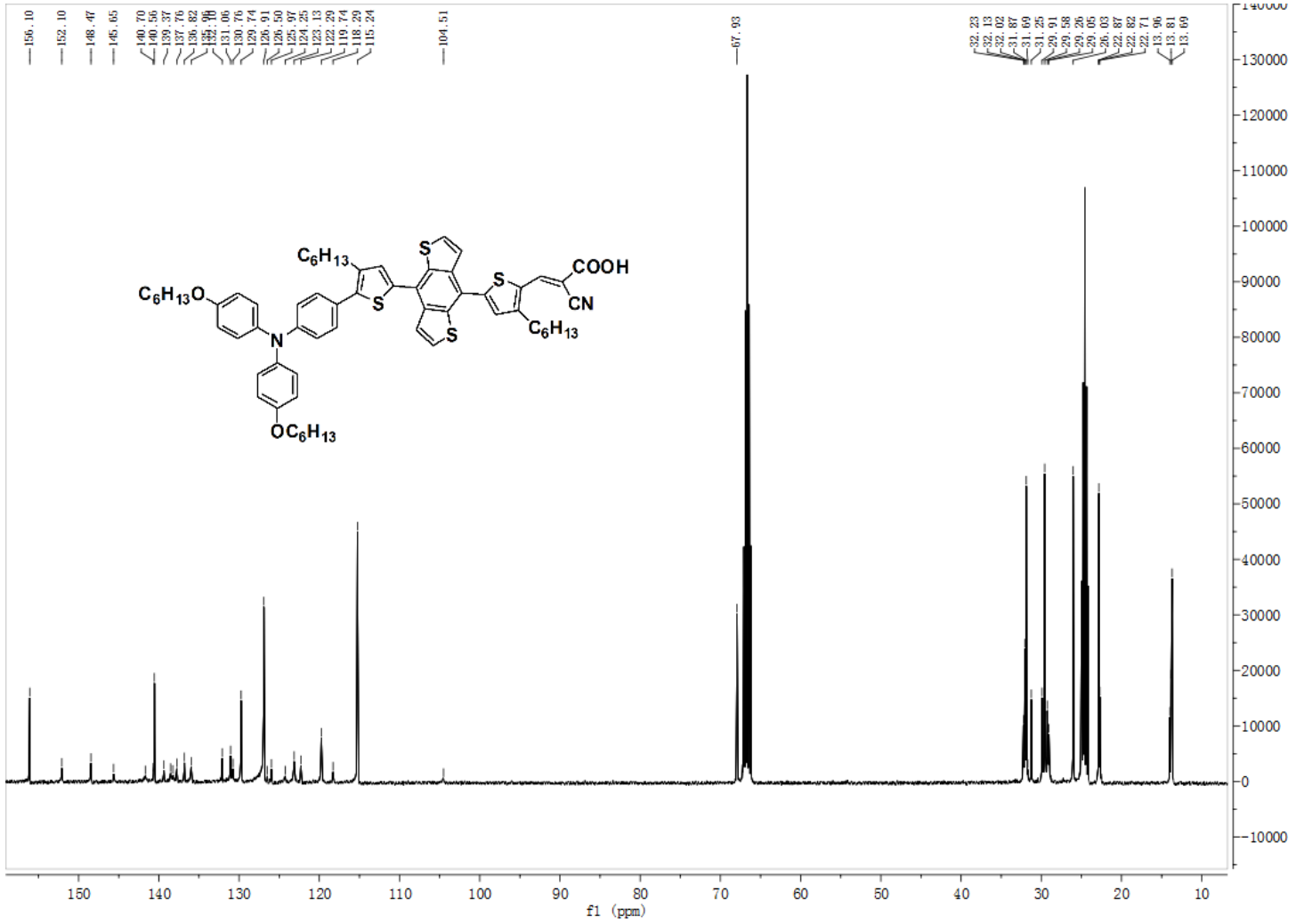


Figure S10. MS spectrum of compound **I1**.

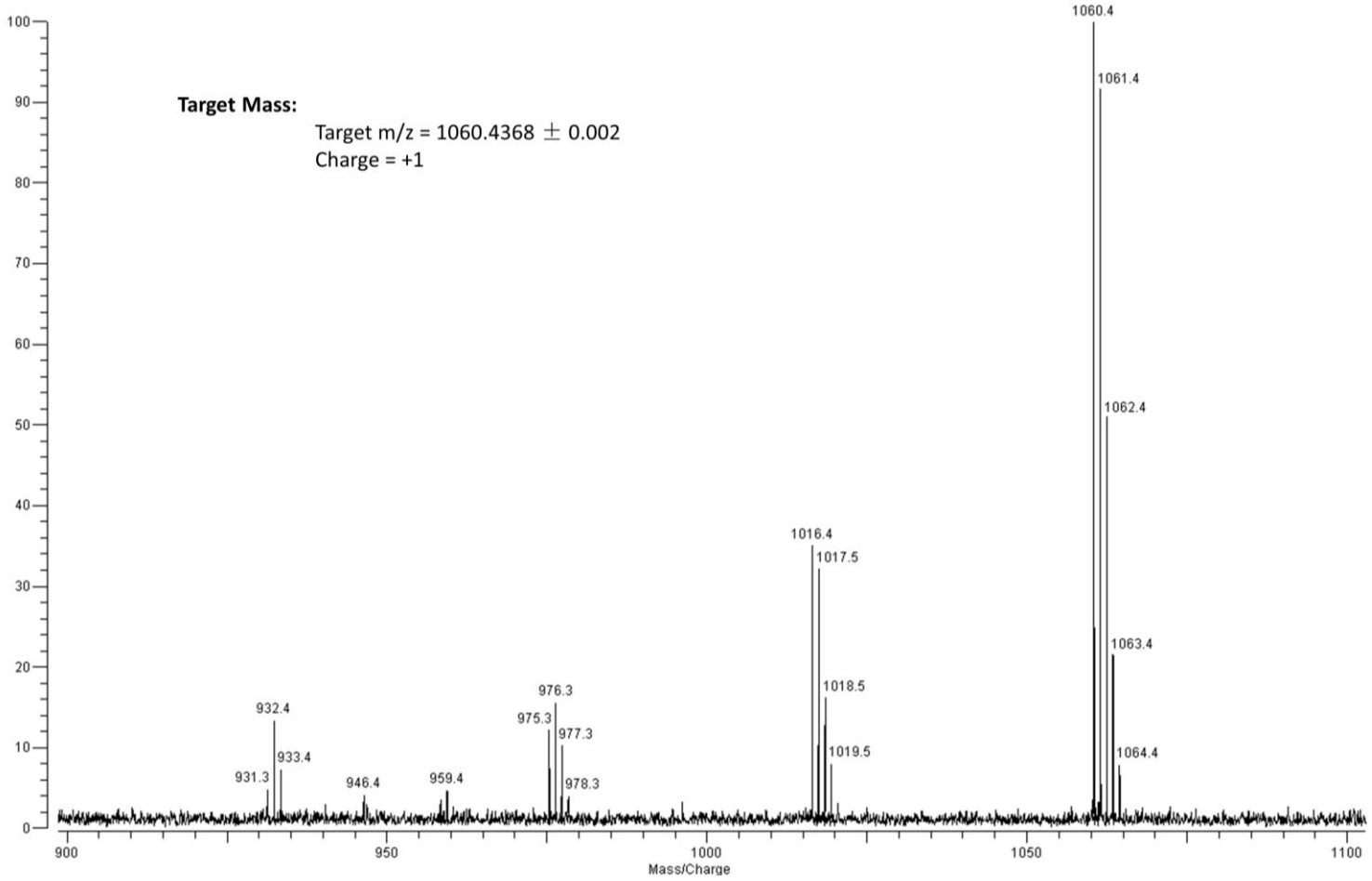


Figure S11. ^{1}H NMR spectrum of compound **5**.

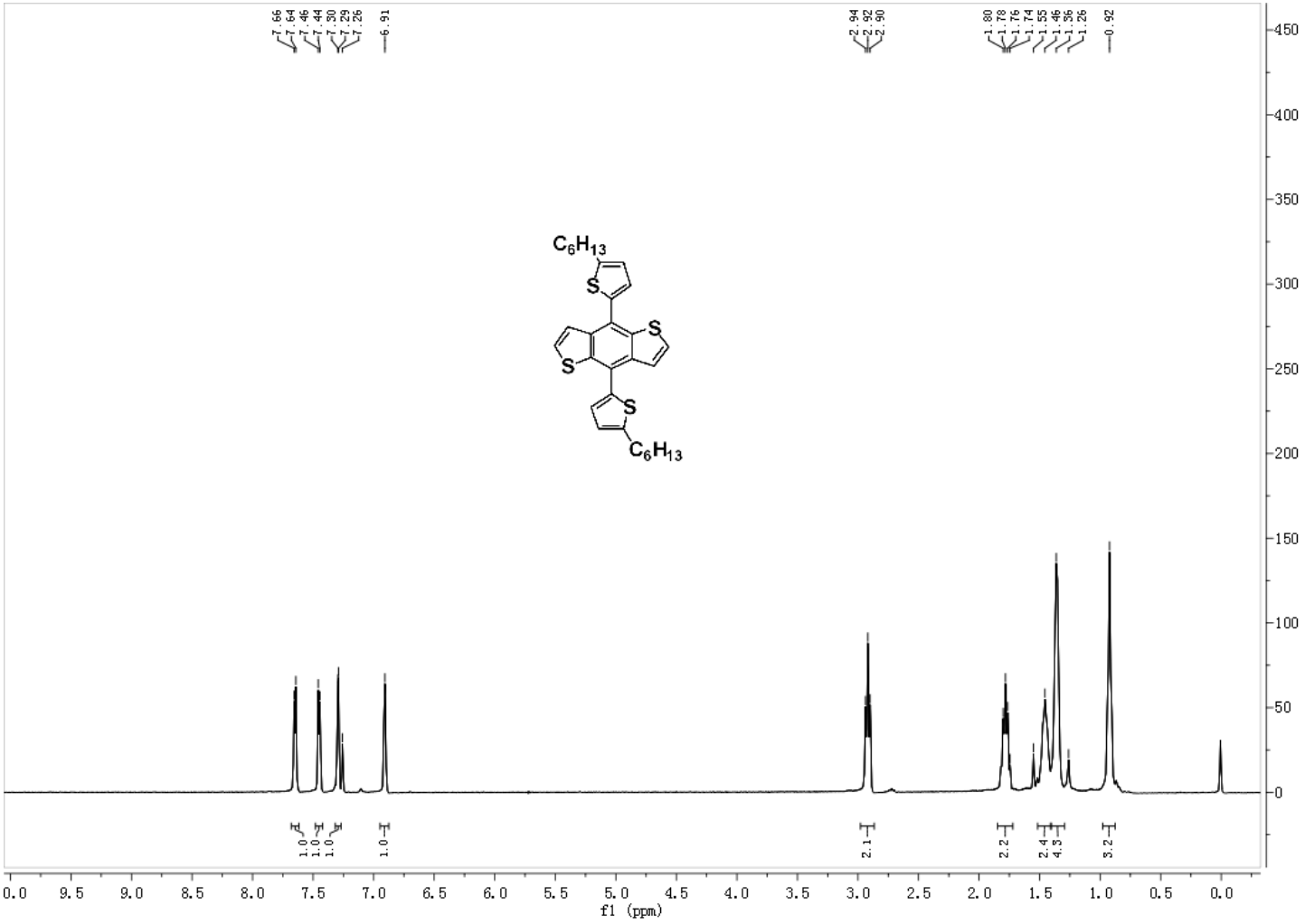


Figure S12. ^{1}H NMR spectrum of compound **6**.

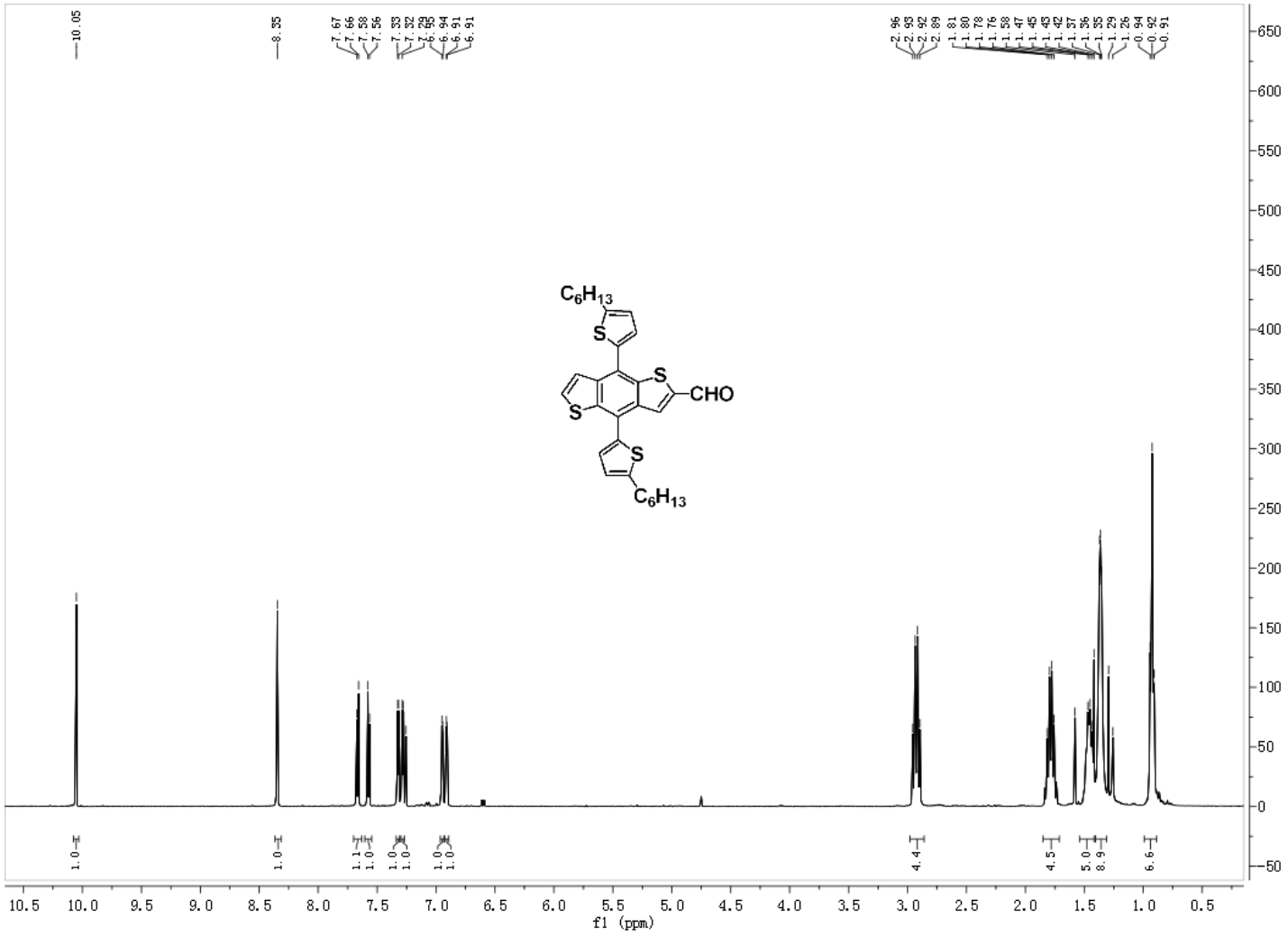


Figure S13. ^{1}H NMR spectrum of compound **7**.

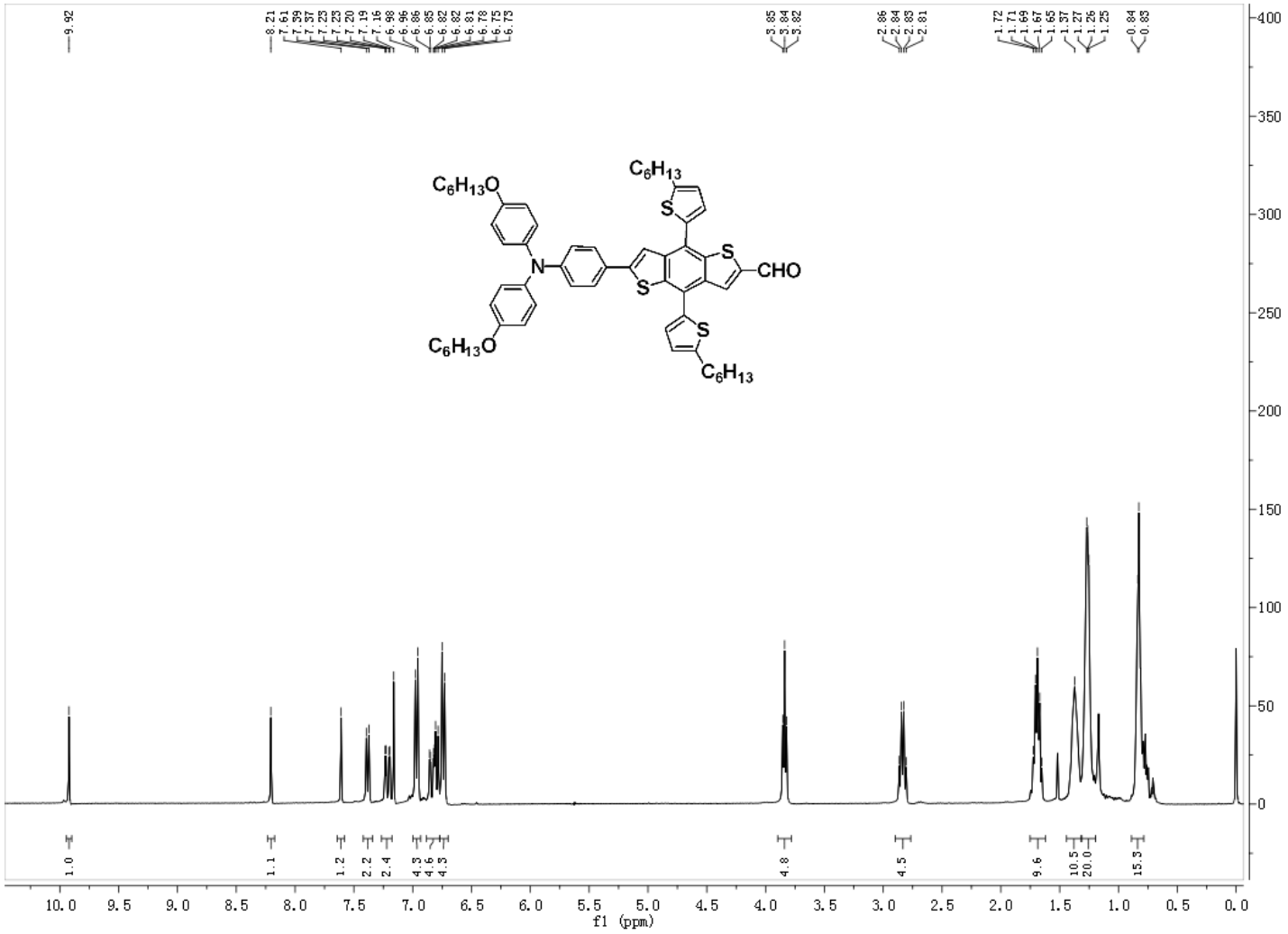


Figure S14. ^{1}H NMR spectrum of compound **I2**.

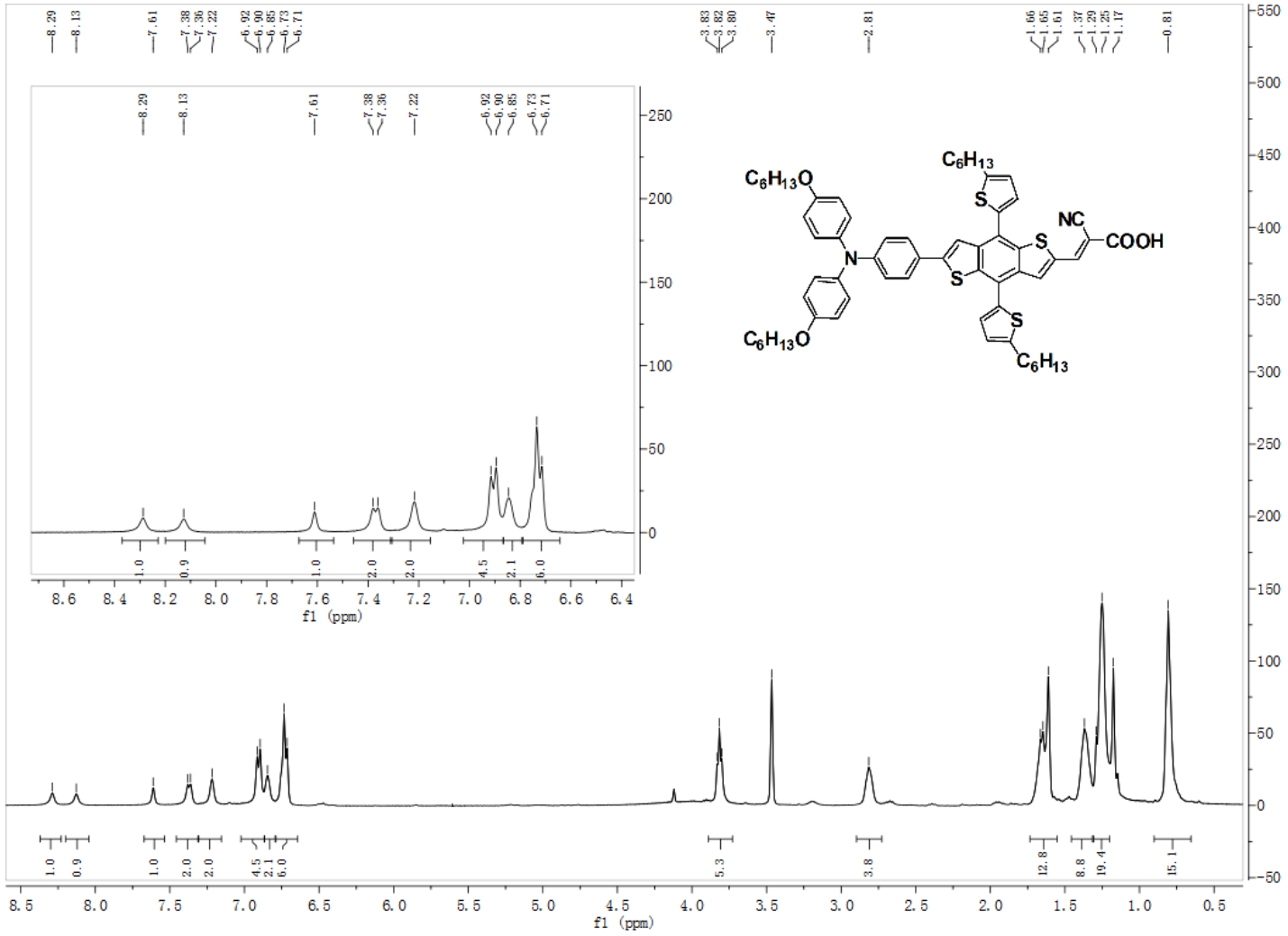


Figure S15. ^{13}C NMR spectrum of compound **I2**.

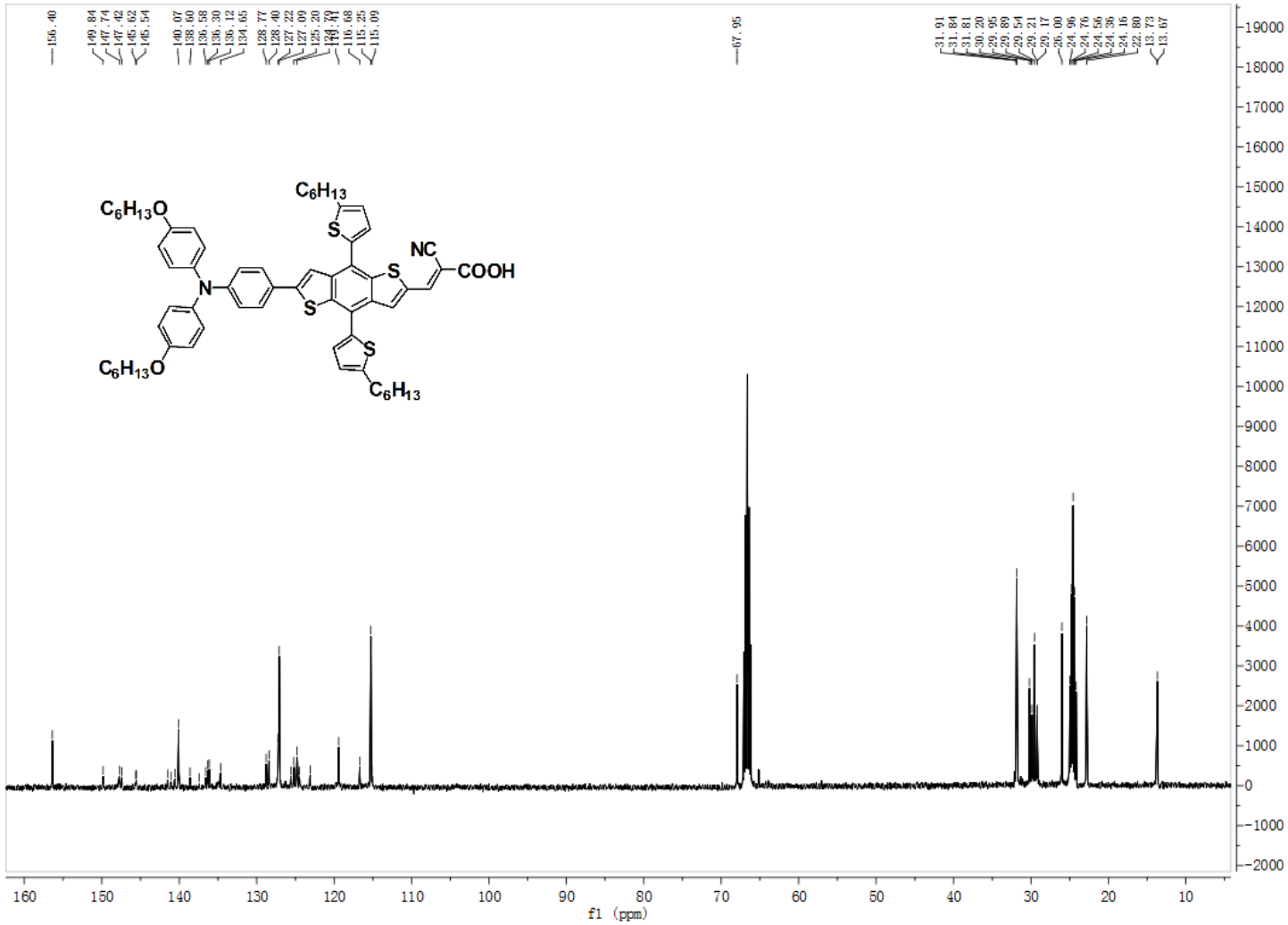
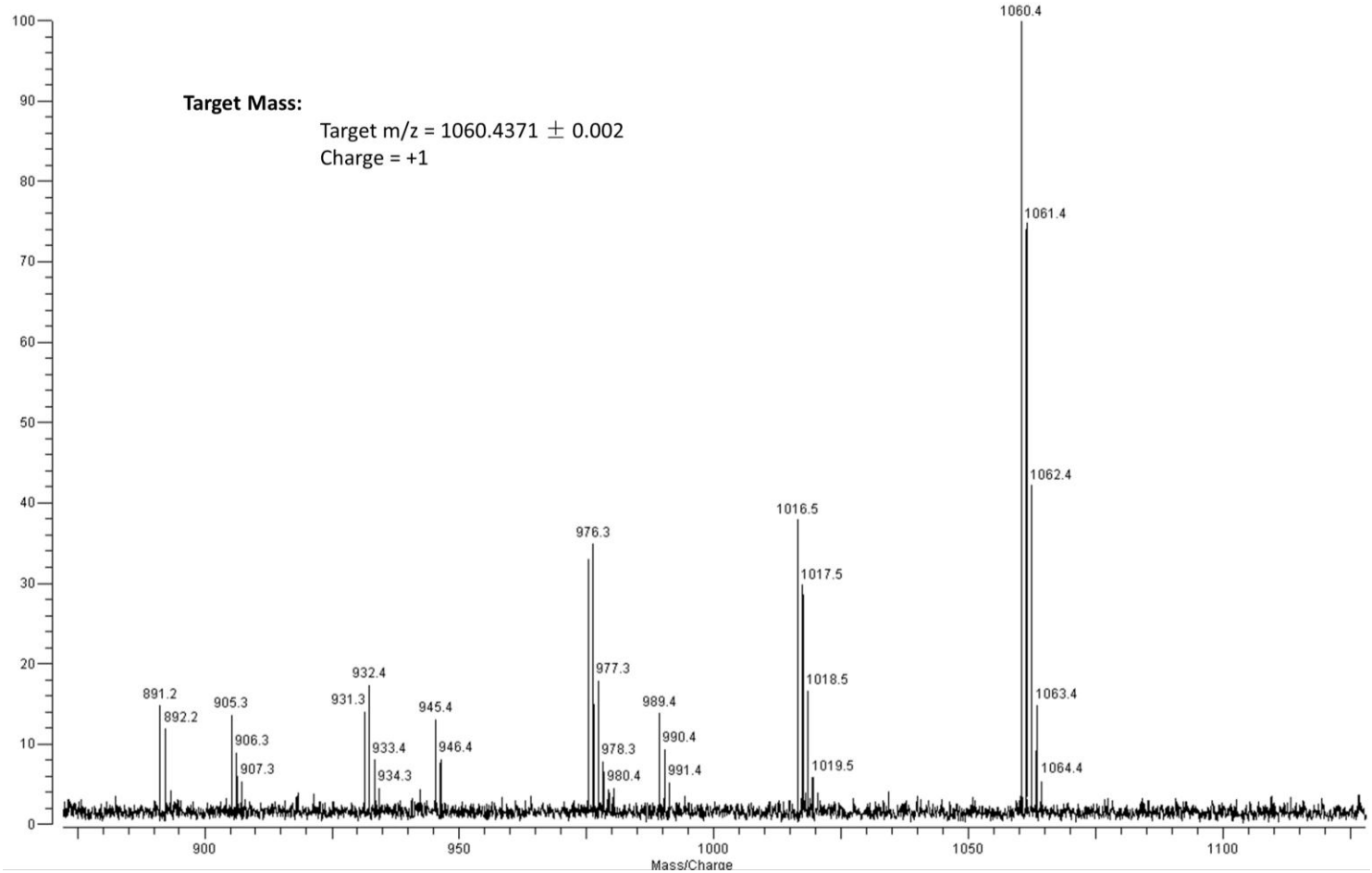


Figure S16. MS spectrum of compound **I2**.



References:

[1] J. Hou, M. H. Park, S. Zhang, Y. Yao, L. Chen, J. Li, and Y. Yang, *Macromolecules*., 2008, **41**, 6012.