Supporting Information

Forced Coplanarity of Dithienofluorene-based Non-Fullerene Acceptors to Achieve High-Efficiency Organic Solar Cells

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CONTENT

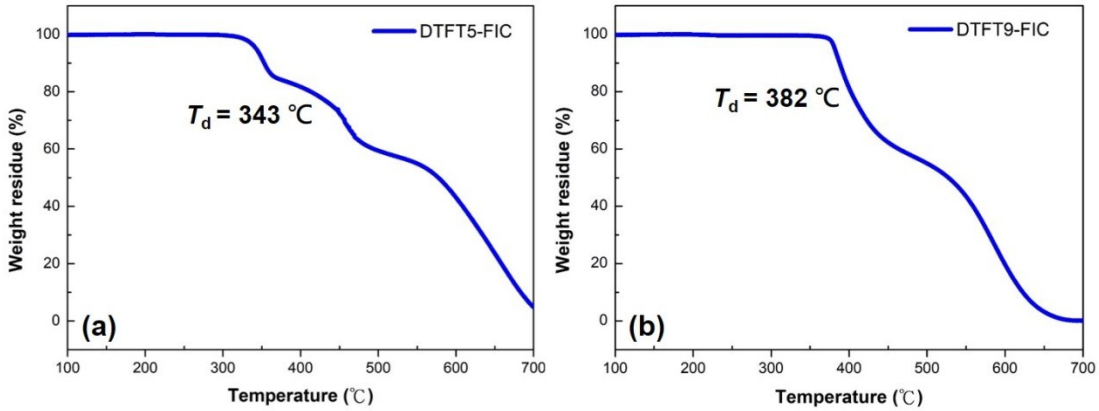


Fig. S1. TGA measurement of a) DTFT5-FIC and b) DTFT9-FIC with a ramping rate of 10 ºC/min.

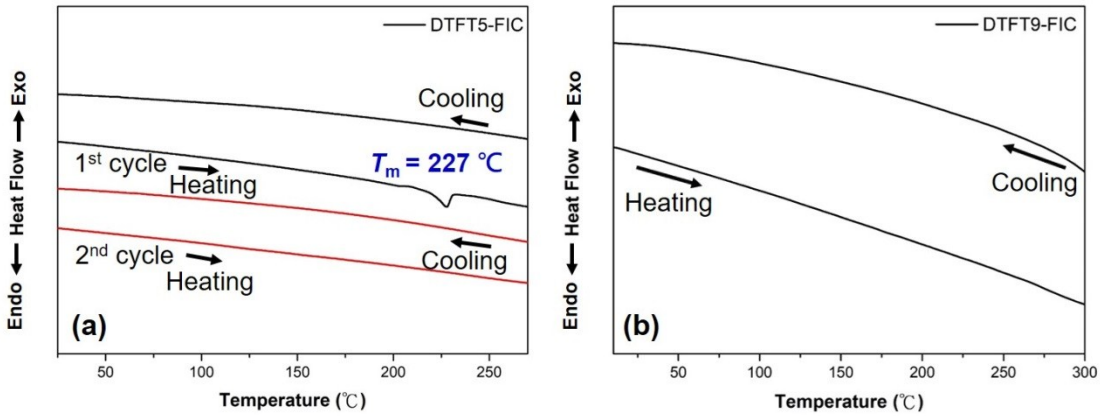


Fig. S2. DSC measurement of a) DTFT5-FIC and b) DTFT9-FIC with a ramping rate of 10 ºC/min.

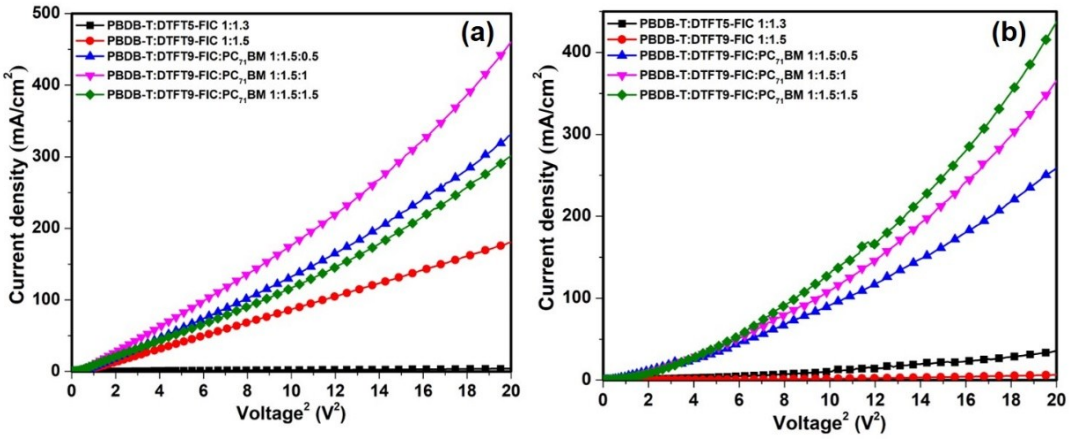


Fig. S3. *J-V* curves of the a) hole-only devices and b) electron-only devices with DTFT5-FIC and DTFT9-FIC contained blend under dark condition.

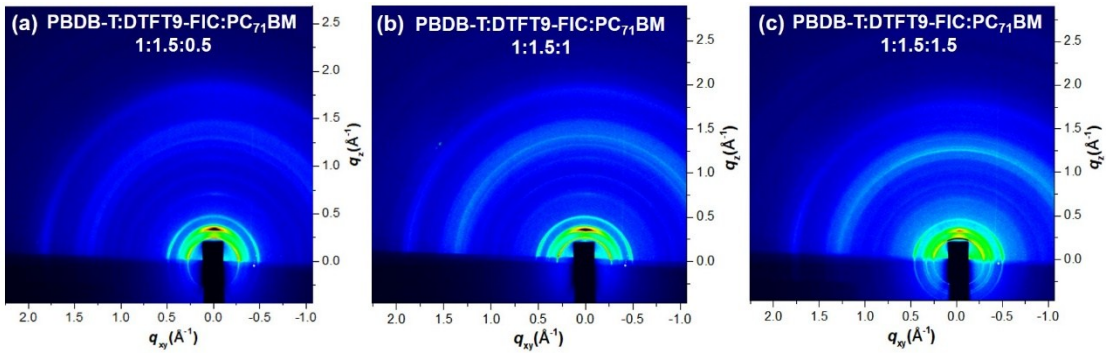


Fig. S4. 2-Dimensional GIWAXS images of the PBDB-T:DTFT9-FIC:$PC_{71}BM$ films with the blending ratio of (a) 1:1.5:0.5 (b) 1:1.5:1, (c) 1:1.5:1.5.

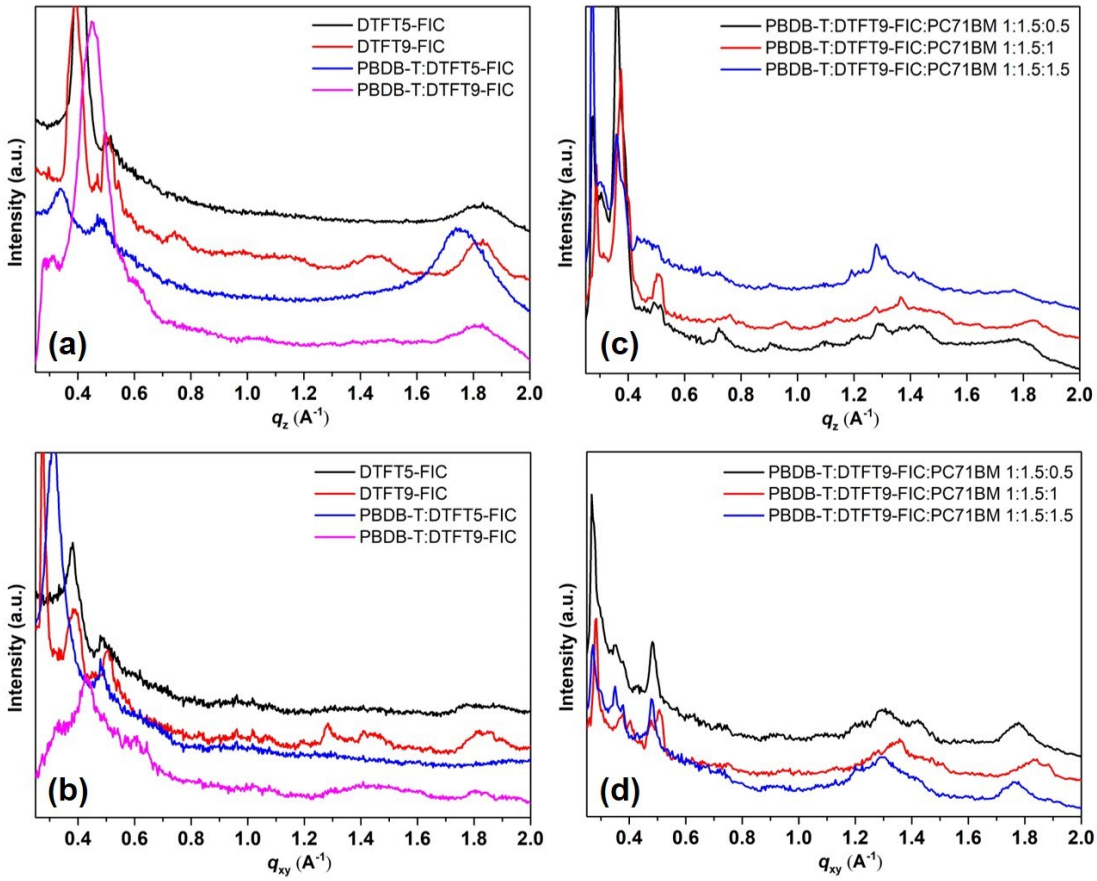


Fig. S5. 1-Dimensional (a) out-of-plane and (b) in-plane GIWAXS patterns of DTFT5-FIC, DTFT9-FIC, PBDB-T:DTFT5-FIC and PBDB-T:DTFT9-FIC film. 1-Dimensional (c) out-of-plane and (d) in-plane GIWAXS patterns of PBDB-T:DTFT9-FIC:$PC_{71}BM$ films.

General Measurement and Characterization. ^{1}H and ^{13}C NMR spectra were measured using Varian 400 MHz instrument spectrometer and obtained in deuterated chloroform ($CDCl_3$) with TMS as internal reference unless otherwise stated, and chemical shifts (δ) are reported in parts per million. Absorption spectra were taken on a HP8453 UV-vis spectrophotometer. Differential scanning calorimetery (DSC) was conducted on a TA Q200 Instrument under nitrogen atmosphere at a heating/cooling rate of 10 °C/min. Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer Pyris under nitrogen atmosphere at a heating rate of 10 °C/min. Electrochemical cyclic voltammetry was conducted on a CH instruments electrochemical analyzer. A carbon glass was used as the working electrode and a Ag/AgCl electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile was the electrolyte. CV curves were calibrated using ferrocence as the standard, whose ionization potential is set at -4.8 eV with respect to zero vacuum level. The ionization potential energy levels were obtained from the equation ionization potential = $-(E_{ox}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$ eV. The electron affinity levels were obtained from the equation electron affinity = $-(E_{red}^{onset} - E_{(ferrocene)}^{onset} + 4.8)$ eV. GIWAXS experiments were conducted at National Synchrotron Radiation Research Center (NSRRC) on beamline BL23A in Taiwan. The samples were irradiated with an X-ray

energy of 10.09 keV (λ = 1.23 Å) at a fixed incident angle of 0.08° through a coupled double crystal Si(111)/multilayer (Mo/B4C) monochromator, and the GIXS patterns were recorded on a 2D image detector (Pilatus 1M-F area detector). The thin films for GIXS measurement were prepared under identical conditions used for the OPV devices.

Fabrication and Characterization of OPV Devices. The fabrication of the inverted devices follow the procedures: The ITO-coated glass substrates were cleaned by ultrasonic cleaner in detergent, DI-water, acetone and isopropyl alcohol for 10 min, respectively, and subsequently treated with UV-ozone for 45 min. The ZnO layer was prepared by the ZnO precursor (diethyl Zinc) solution in THF and spin-coated onto the pre-treated ITO-coated glass. The chlorobenzene solution of PBDBD-T:DTFT5-FIC, PBDBD-T:DTFT9-FIC and PBDBD-T:DTFT9-FIC:$PC_{71}BM$ in an different weight ratio with 0.5 vol% DIO as additive were prepared and stired 12 h at 80 °C. Active layers were formed by spin-coating on top of the ZnO/ITO substrate. Moreover, the substrates were thermally annealed at 150 °C for 10 min in the glove box. Finally, the MoO_3 layer (7 nm) and silver anode (150 nm) were deposited by thermal evaporation at a pressure below 10^{-6} torr. The devices without encapsulation were characterized in ambient condition. Current-voltage characteristics were measured by a Keithley 2400 SMU under the irradiation of AM 1.5G San-Yi solar simulator with JIS AAA spectrum.

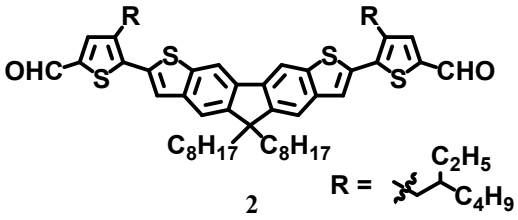
The characteristics of the solar cells were optimized by testing approximately 25 cells. IPCE spectra were measured using a lock-in amplifier with a current preamplifier under short-circuit conditions with illumination by monochromatic light from a 250 W quartz-halogen lamp (Osram) passing through a monochromator (Spectral Products CM110).

Table S1. The optimized condition of the blending solution with PBDBD-T:DTFT5-FIC, PBDBD-T:DTFT9-FIC and PBDBD-T:DTFT9-FIC:$PC_{71}BM$.

Blending system [donor/acceptor]	Blending ratio	Conc.	Solvent	Thermal annealing	Spin rate [rpm]
PBDB-T: DTFT5-FIC	1:1.3	10 mg/ml	CB	120 °C 10 min	3000
PBDB-T: DTFT9-FIC	1:1.3	10 mg/ml	CB	120 °C 10 min	3000
	1:1.5	10 mg/ml	CB	120 °C 10 min	2500
PBDB-T: DTFT9-FIC: $PC_{71}BM$	1:1.5:0.5	10 mg/ml	CB	120 °C 10 min	4000
	1:1.5:1	8.57 mg/ml	CB	150 °C 10 min	3500
	1:1.5:1.5	7.5 mg/ml	CB	150 °C 10 min	3500

Synthetic procedures

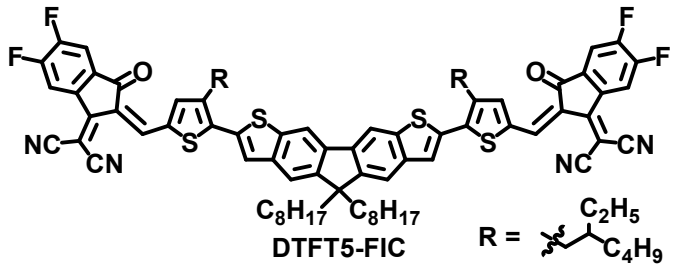
Synthesis of Compound 2.



2

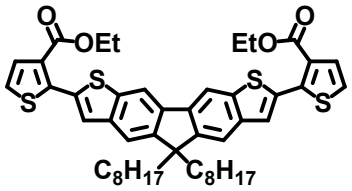
To a degassed toluene (15 mL) solution of compound **1** (950 mg, 1.15 mmol) were added $Pd(PPh_3)_4$ (112 mg, 0.1 mmol), and 5-bromo-4-(2-ethylhexyl)thiophene-2-carbaldehyde (765 mg, 2.52 mmol). The mixture was stirred for 12 h at 110 ℃ and water (15 ml) was then added. The resultant was filtered by celite, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 20/1) to give a yellow solid **2** (800 mg, yield 73.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 2H), 8.17 (s, 2H), 7.74 (s, 2H), 7.61 (s, 2H), 7.54 (s, 2H), 2.87 (d, J = 7.0 Hz, 4H), 2.12 – 2.02 (m, 4H), 1.80 – 1.69 (m, 2H), 1.42 – 1.21 (m, 18H), 1.20 – 0.97 (m, 20H), 0.92 – 0.84 (m, 10H), 0.79 (t, J = 7.1 Hz, 6H), 0.73 – 0.61 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.67, 149.00, 141.76, 141.09, 140.67, 139.80, 139.50, 139.43, 138.90, 134.91, 124.48, 118.00, 113.01, 54.25, 41.63, 40.22, 33.64, 32.53, 31.73, 30.05, 29.70, 29.22, 29.21, 28.71, 25.78, 23.88, 23.03, 22.54, 14.09, 14.02, 10.78; HRMS (FD, $C_{59}H_{78}O_2S_4$): calcd, 946.4879; found, 946.4893.

Synthesis of DTFT5-FIC



2-(5,6-Difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (243 mg, 1.05 mmol) was added into the solution of compound **5** (200 mg, 0.21 mmol) in chloroform (41 mL) with pyridine (1.5 mL). The mixture was deoxygenated with nitrogen for 30 min and then refluxed at 80 ℃ for 3 h. After cooling to room temperature, the reaction was poured into water and the precipitate was filtered off. It was then washed with methanol and hexane. The crude product was purified by column chromatography on silica gel using dichloromethane as the eluent to give a deep blue solid **DTFT5-FIC** (50 mg, yield 17%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 2H), 8.55 (dd, J_1 = 9.0, J_2 = 7.2, 2H), 8.19 (s, 2H), 7.82 – 7.66 (m, 8H), 2.91 (d, J = 6.8 Hz, 4H), 2.15 – 2.05 (m, 4H), 1.83 – 1.75 (m, 2H), 1.45 – 1.24 (m, 18H), 1.21 – 1.05 (m, 20H), 0.94 – 0.86 (m, 10H), 0.79 (t, J = 6.9 Hz, 6H), 0.75 – 0.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.84, 158.25, 153.32, 149.77, 149.39, 149.00, 141.36, 140.49, 139.63, 139.37, 137.65, 134.97, 134.92, 126.82, 125.52, 122.15, 119.40, 118.29, 115.13, 114.91, 114.08, 113.97, 113.23, 112.66, 80.85, 77.32, 77.20, 77.00, 76.68, 70.44, 56.86, 54.29, 51.80, 41.58, 39.93, 37.35, 33.56, 32.54, 31.75, 30.05, 29.25, 28.67, 25.82, 23.97, 23.06, 22.56, 20.27, 14.10, 14.04, 10.76, -0.01; HRMS (FD, $C_{83}H_{82}N_4O_2F_4S_4$): calcd, 1370.5251; found, 1370.5235.

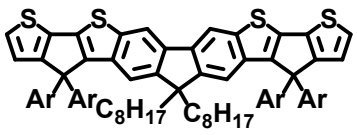
Synthesis of Compound 3.



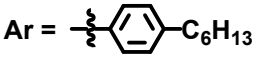
3

To a degassed toluene (5 mL) solution of compound **1** (800 mg, 0.97 mmol) were added $Pd(PPh_3)_4$ (112 mg, 0.1 mmol), PPh_3 (51 mg, 0.19 mmol), and ethyl 2-bromothiophene-3-carboxylate (568 mg, 2.42 mmol). The mixture was stirred for 12 h at 110 ℃ and water (10 mL) was then added. The resultant was filtered by celite, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane as the eluent to give a yellow oil **3** (487 mg, yield 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 2H), 7.81 (s, 2H), 7.75 (s, 2H), 7.58 (d, J = 5.4 Hz, 2H), 7.31 (d, J = 5.4 Hz, 2H), 4.38 (q, J = 6.8 Hz, 4H), 2,12 – 2.04 (m, 4H), 1.37 (t, J = 6.4 Hz, 6H), 1.24 – 1.01 (m, 20H), 0.83 (t, J = 6.5 Hz, 6H), 0.61 – 0.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.88, 8.17, 7.74, 7.61, 7.54, 7.26, 2.88, 2.86, 2.09, 2.08, 2.07, 2.06, 2.05, 1.76, 1.74, 1.73, 1.71, 1.42, 1.40, 1.38, 1.37, 1.35, 1.34, 1.33, 1.32, 1.31, 1.29, 1.28, 1.26, 1.20, 1.18, 1.16, 1.15, 1.09, 1.08, 1.07, 1.06, 1.04, 0.92, 0.90, 0.88, 0.87, 0.85, 0.84, 0.81, 0.79, 0.77, 0.68, 0.08, 0.00; HRMS (FD, $C_{47}H_{54}O_4S_4$): calcd, 810.2899; found, 810.2873.

Synthesis of Compound 4.

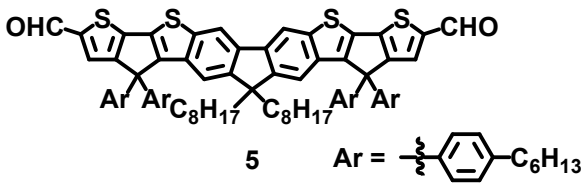


4



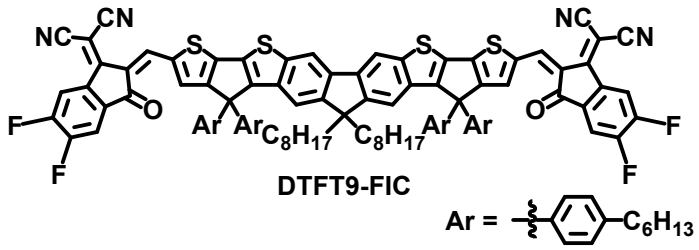
A Grignard reagent was prepared by the following procedure. To a suspension of magnesium turnings (90 mg, 3.7 mmol) and 3-4 drops of 1,2-dibromoethane in dry THF (3 mL) was slowly added 1-bromo-4-hexylbenzene (893 mg, 3.7 mmol) dropwise, and the mixture was stirred for 1 h. To a solution of compound **3** (300 mg, 0.37 mmol) in dry THF (15 mL) under nitrogen was added 4-hexylbenzene 1-magnesium bromide (1.2 mL, 1.48 mmol) dropwise at room temperature. The resulting mixture was refluxed at 80 ℃ for 16 h. The reaction solution was extracted with diethyl ether (50 mL × 3) and ammonium chloride solution (150 mL), dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was used for next reaction without purification. To a solution of the product (500 mg, 0.37 mmol) of previous step in octane (38 mL) was added acetic acid (3.8 mL) and sulfuric acid (0.38 mL, 7.08 mmol) slowly. The resulting solution was stirred for 4 h at 65 ℃. After removal of the octane under reduced pressure, the residue was extracted by sodium carbonate solution (50 mL × 3) and diethyl ether (50 mL × 2). The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 100/1) to give an orange solid **4** (250 mg, yield 50 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 2H), 7.37 (s, 2H), 7.26 (d, J = 4.8 Hz, 2H), 7.17 (d, J = 8.0 Hz, 8H), 7.13 (d, J = 4.8 Hz, 2H), 7.02 (d, J = 7.9 Hz, 8H), 2.51 (t, J = 8.0 Hz, 8H), 1.76 – 1.71 (m, 4H), 1.53 (d, J = 7.9 Hz, 8H), 1.29 – 1.08 (m, 36H), 0.97 – 0.81 (m, 26H), 0.59 – 0.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.75, 150.34, 148.67, 142.53, 141.54, 139.53, 137.09, 136.87, 136.78, 133.92, 128.19, 128.15, 126.48, 123.02, 116.05, 114.31, 77.32, 77.00, 76.68, 62.39, 53.70, 41.01, 35.58, 31.87, 31.69, 31.36, 30.34, 29.61, 29.39, 29.21, 24.01, 22.71, 22.60, 14.06; HRMS (FD, $C_{91}H_{110}S_4$): calcd, 1330.7485; found, 1330.7459.

Synthesis of Compound 5.



$POCl_3$ (144 mg, 2.5 mmol) was added dropwise to a solution of anhydrous DMF (3.52 mL) and stirred for 30 min at 0 ℃ Compound **5** (600 mg, 0.45 mmol) dissolved in 1,2-dichloroethene (40 mL) was added slowly and the mixture was stirred for 12 h at room temperature. The mixture was poured into a S-5 saturated aqueous solution of CH_3COOK and stirred for another 30 min. Then it was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, v/v, 10/1) to give an orange solid **6** (360 mg, yield 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (s, 2H), 8.17 (s, 2H), 7.74 (s, 2H), 7.41 (s, 2H), 7.17 (d, J = 8.0 Hz, 8H), 7.05 (d, J = 7.9 Hz, 8H), 2.52 (t, J = 8.0 Hz, 8H), 1.77 – 1.69 (m, 4H), 1.57 - 1.49 (m, 8H), 1.34 – 1.06 (m, 36H), 0.99 – 0.78 (m, 26H), 0.55 – 0.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.88, 8.17, 7.74, 7.61, 7.54, 7.26, 2.88, 2.86, 2.09, 2.08, 2.07, 2.06, 2.05, 1.76, 1.74, 1.73, 1.71, 1.42, 1.40, 1.38, 1.37, 1.35, 1.34, 1.33, 1.32, 1.31, 1.29, 1.28, 1.26, 1.20, 1.18, 1.16, 1.15, 1.09, 1.08, 1.07, 1.06, 1.04, 0.92, 0.90, 0.88, 0.87, 0.85, 0.84, 0.81, 0.79, 0.77, 0.68, 0.08, 0.00; HRMS (FD, $C_{93}H_{110}O_2S_4$): calcd, 1386.7383; found, 1386.7391.

Synthesis of DTFT9-FIC



2-(5,6-Difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (105 mg, 0.46 mmol) was added to the solution of compound **5** (118 mg, 0.085 mmol) in chloroform with pyridine (0.6 mL). The mixture was deoxygenated with nitrogen for 30 min and then refluxed at 80 ℃ for 18 h. After cooling to room temperature, the reaction was poured into water and the precipitate was filtered off. It was then washed with methanol and hexane. The crude product was purified by column chromatography on silica gel using DCM as the eluent to give a dark blue solid **DTFT9-FIC** (32 mg, yield 21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 2H), 8.52 (dd, J_1 = 9.8 Hz, J_2 = 6.0 Hz, 2H), 8.16 (s, 2H), 7.75 (s, 2H), 7.66 (dd, J_1 = 7.6 Hz, J_2 = 3.8 Hz, 2H), 7.45 (s, 2H), 7.17 (d, J = 8.2 Hz, 8H), 7.07 (d, J = 8.2 Hz, 8H), 2.53 (t, J = 7.6 Hz, 8H), 1.77 – 1.71 (m, 4H), 1.51 (s, 8H), 1.36 – 1.04 (m, 36H), 1.02 – 0.78 (m, 26H), 0.50 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.92, 162.09, 157.96, 157.81, 152.95, 149.64, 146.02, 142.59, 139.87, 139.00, 138.19, 137.55, 136.97, 133.51, 128.64, 128.13, 119.95, 117.81, 115.19, 114.36, 112.66, 68.47, 62.63, 53.92, 40.94, 35.58, 31.82, 31.66, 31.35, 30.22, 29.51, 29.43, 29.14, 24.22, 22.68, 22.57, 14.04; HRMS (FD, $C_{117}H_{114}N_4O_2F_4S_4$): calcd, 1810.7753; found, 1810.7802.

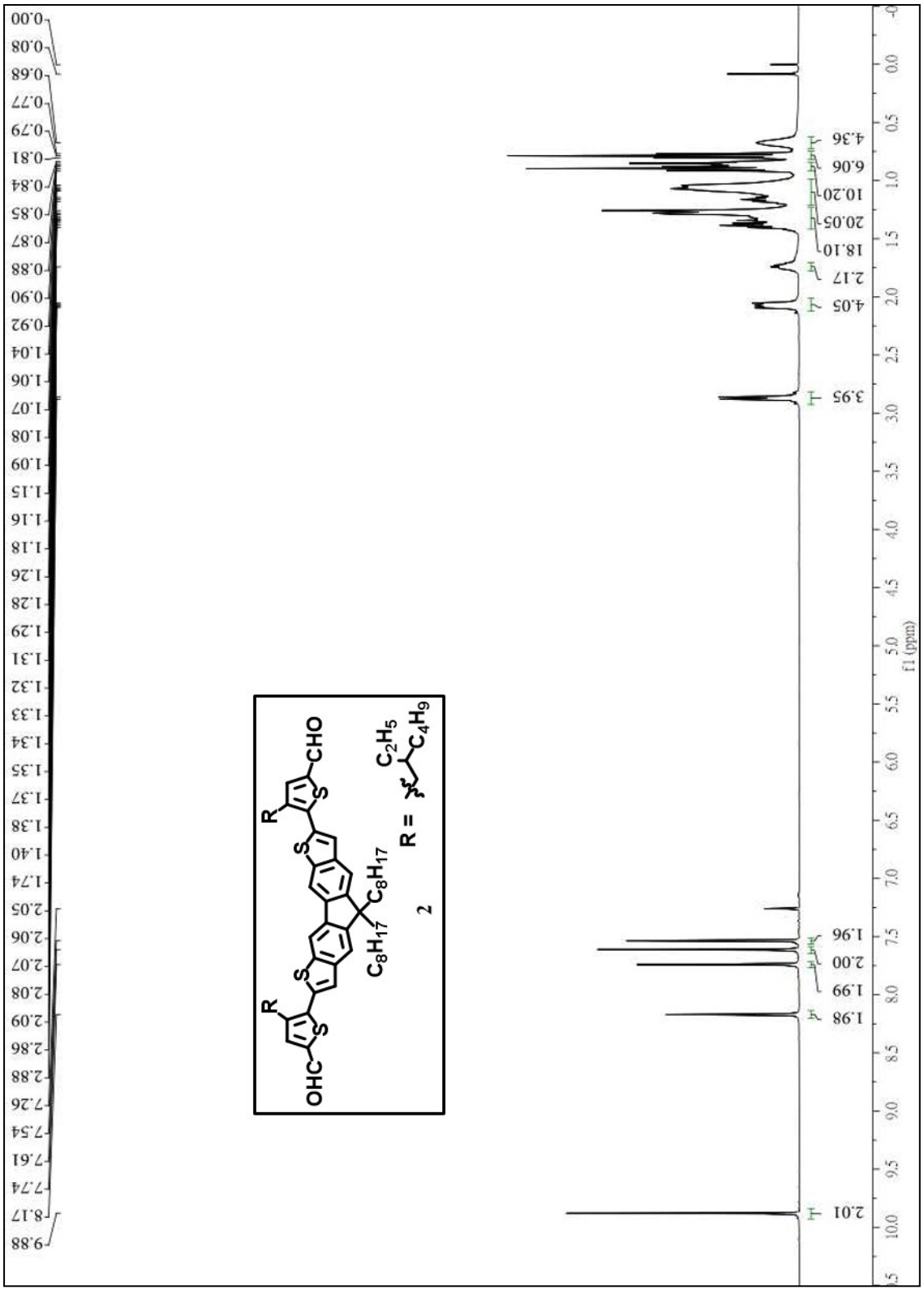


Fig. S4. ^{1}H NMR spectrum of compound **2.**

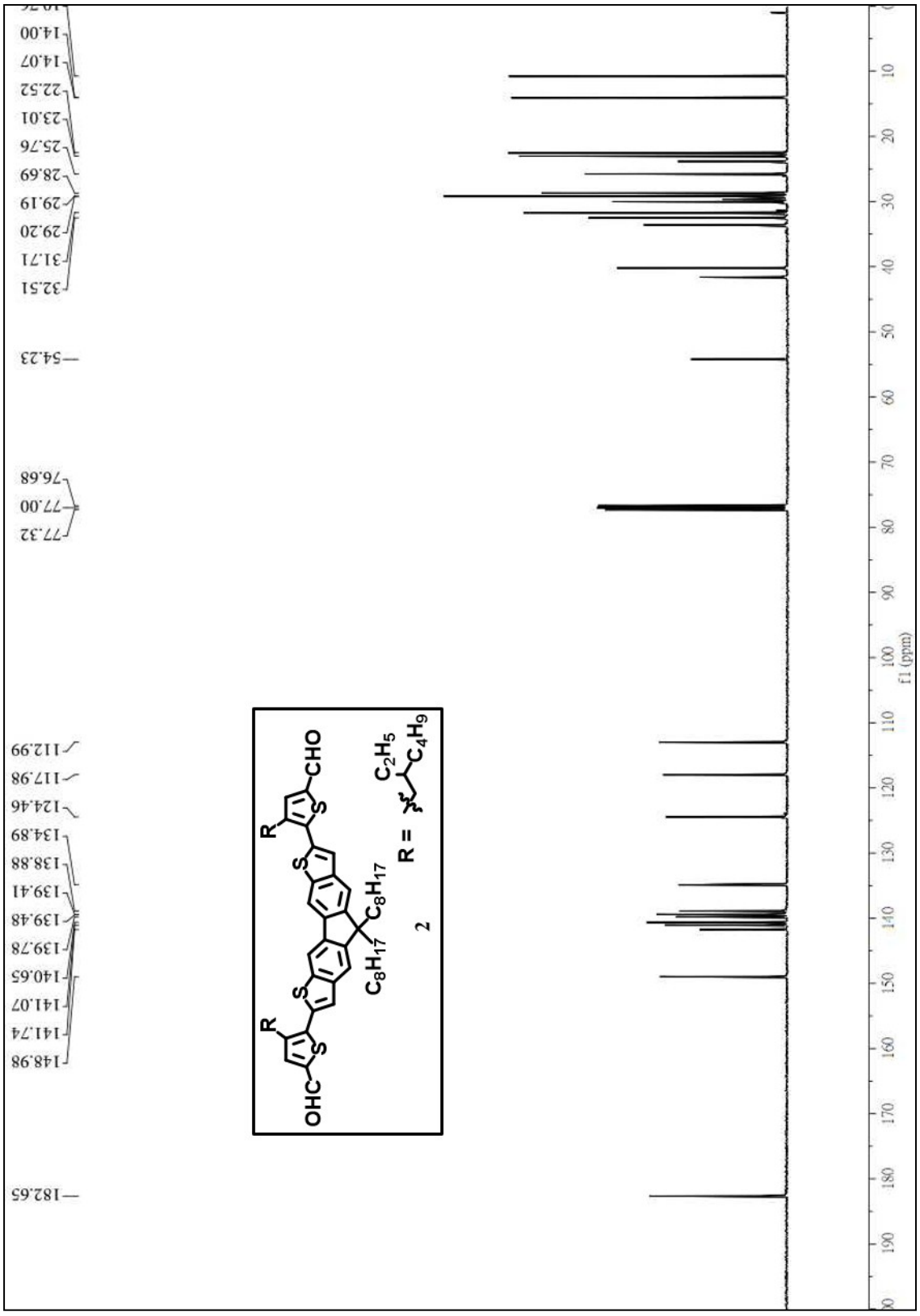


Fig. S5. ^{13}C NMR spectrum of compound **2.**

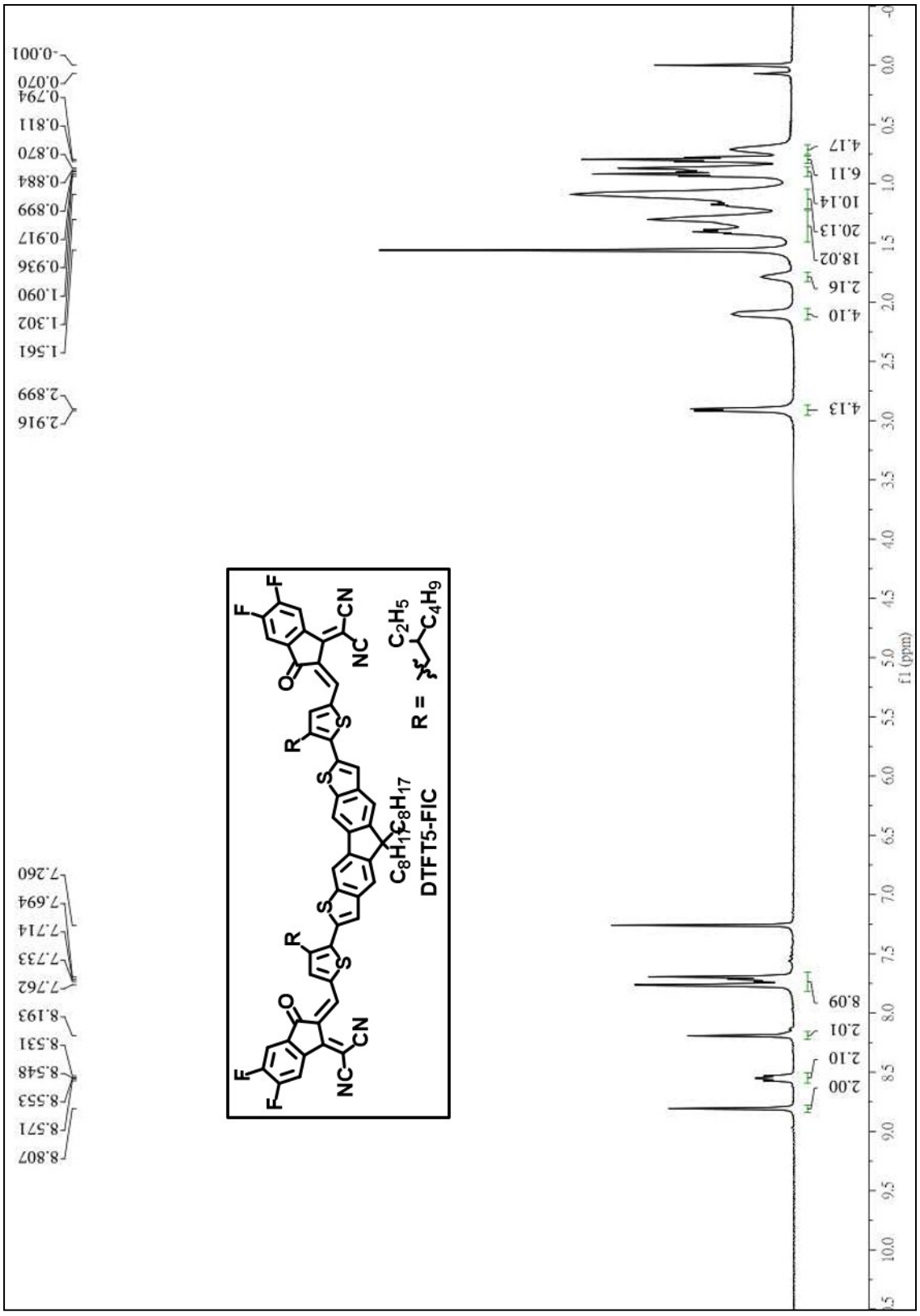


Fig. S6. ^{1}H NMR spectrum of **DTFT5-FIC.**

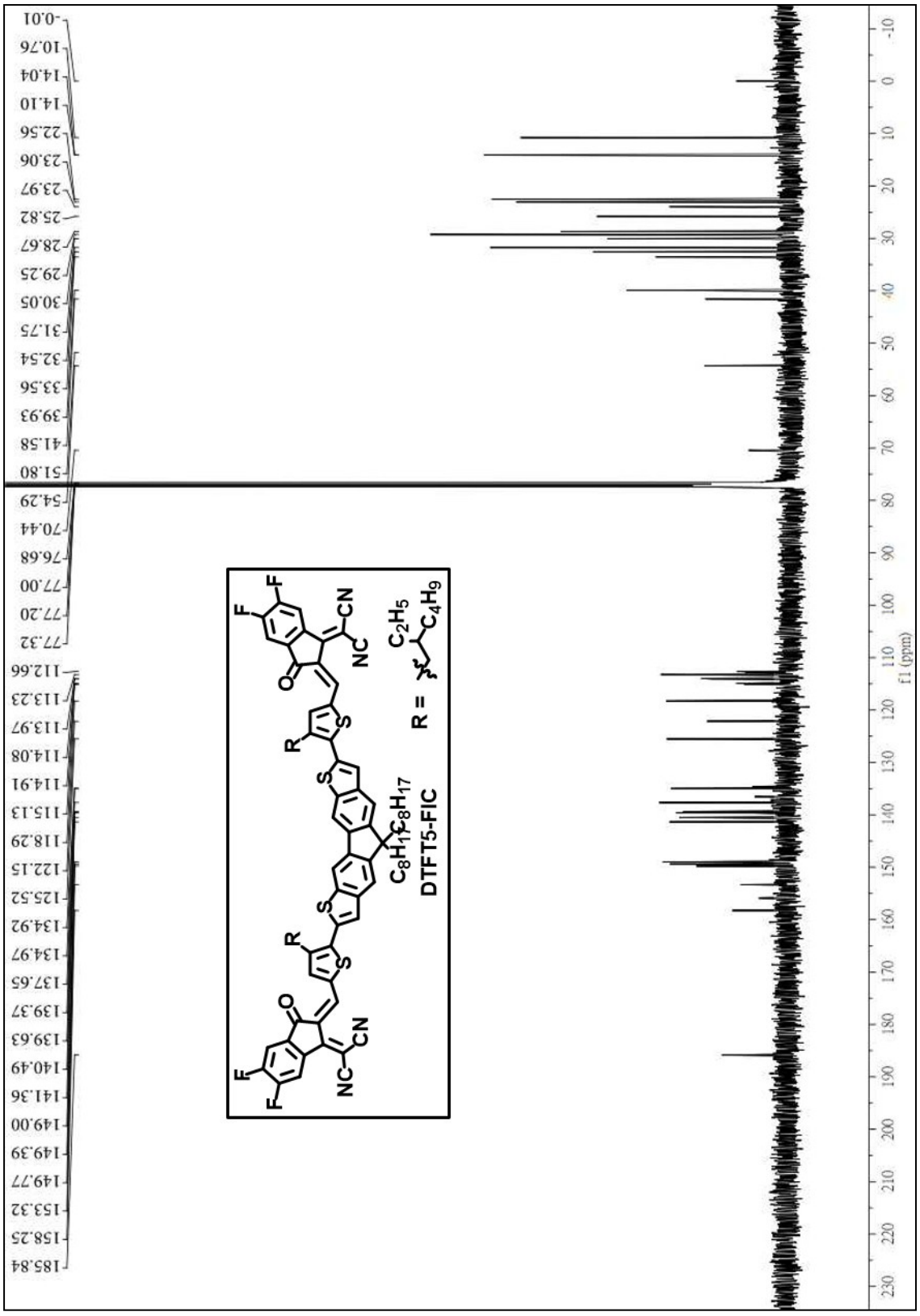


Fig. S7. ^{13}C NMR spectrum of **DTFT5-FIC.**

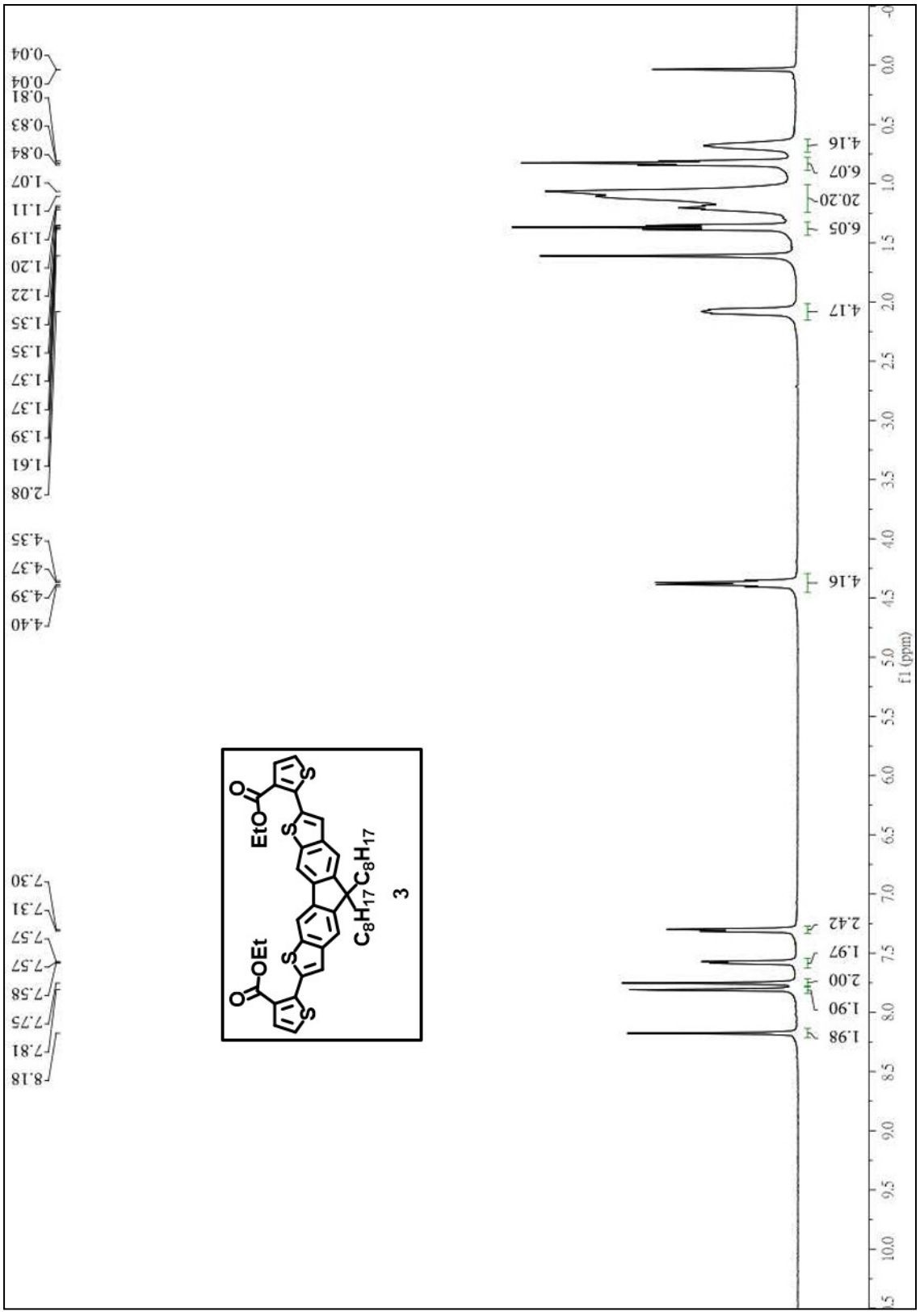


Fig. S8. ^{1}H NMR spectrum of compound **3.**

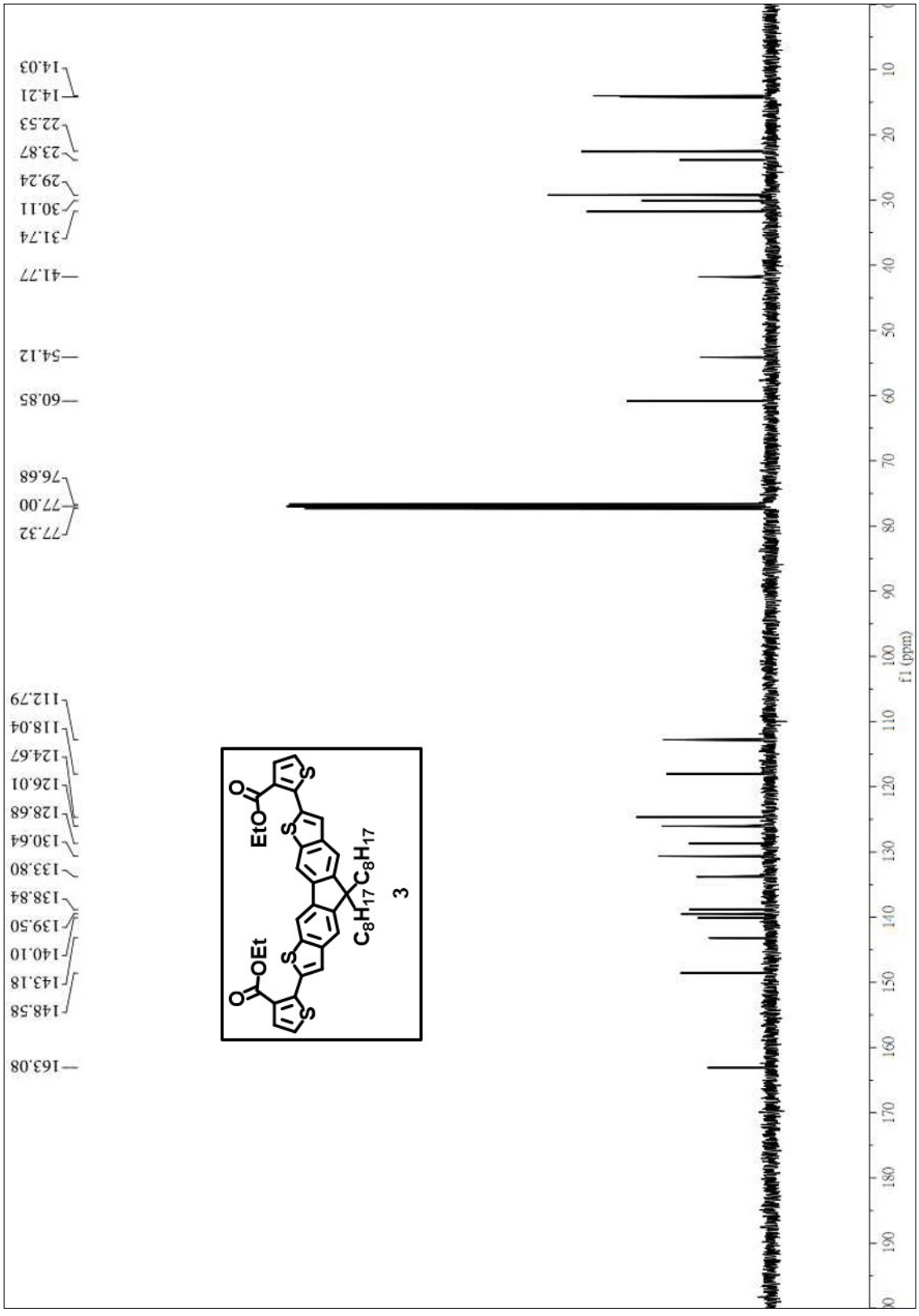


Fig. S9. ^{13}C NMR spectrum of compound **3.**

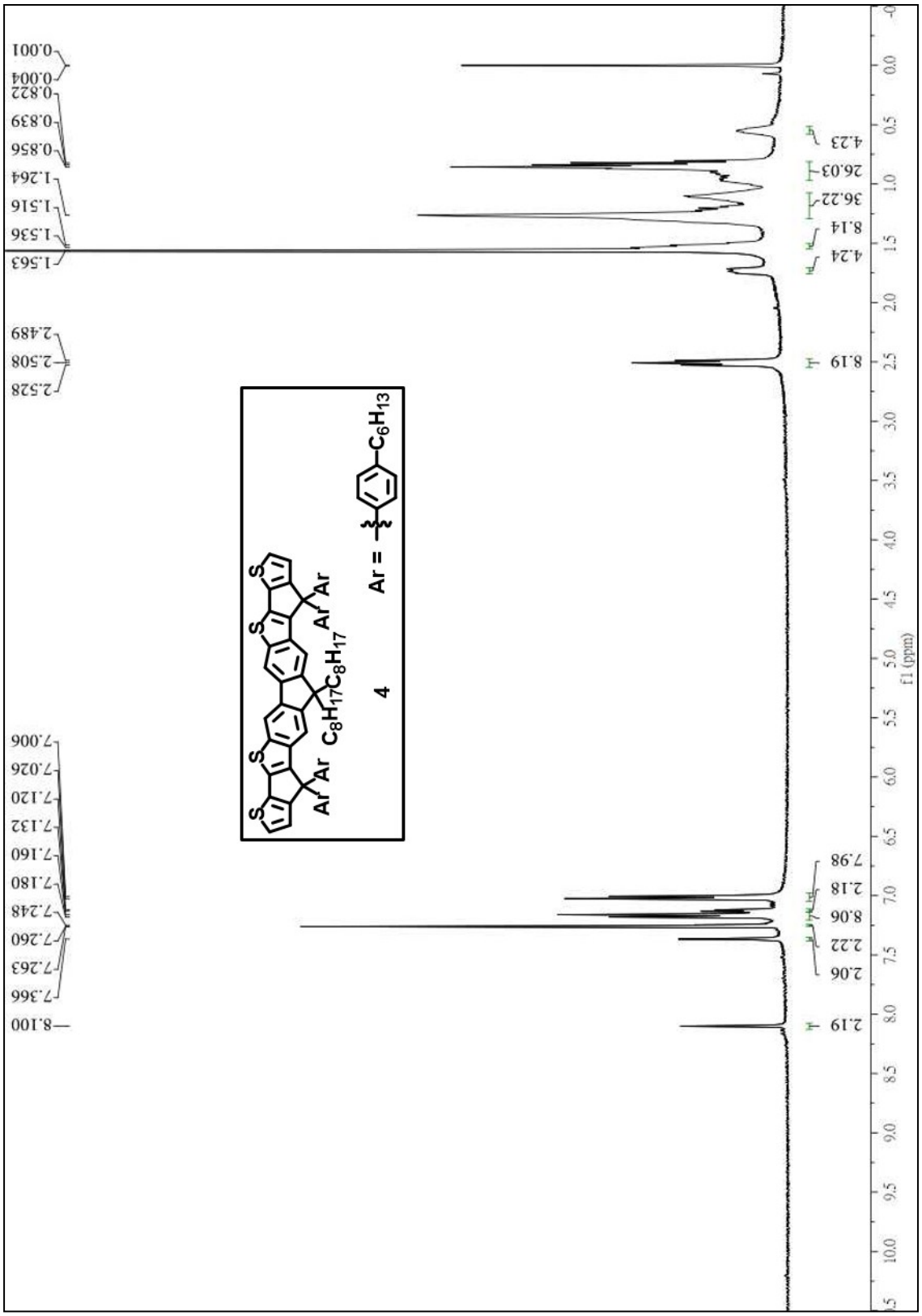


Fig. S10. ^{1}H NMR spectrum of compound **4.**

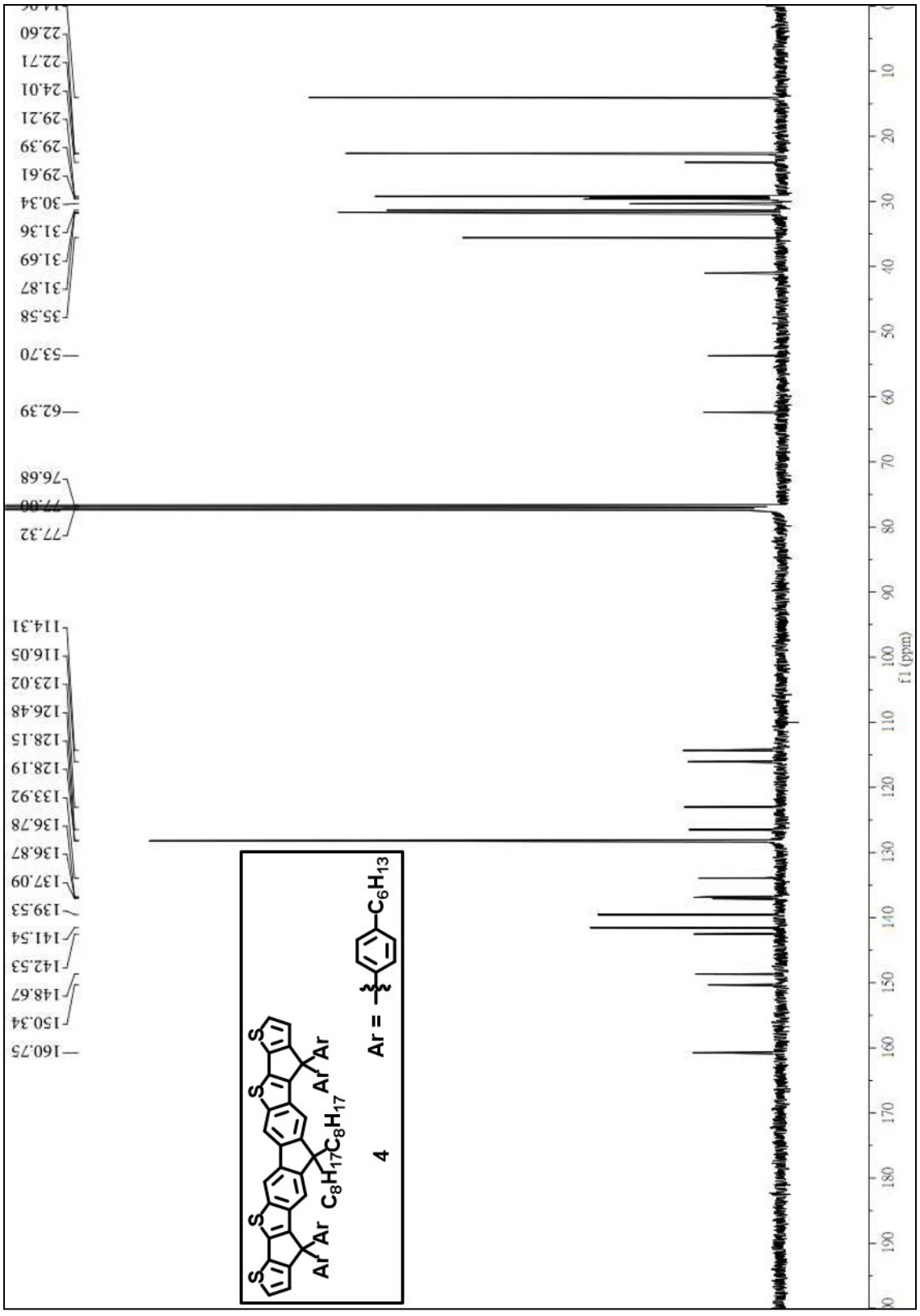


Fig. S11. ^{13}C NMR spectrum of compound **4.**

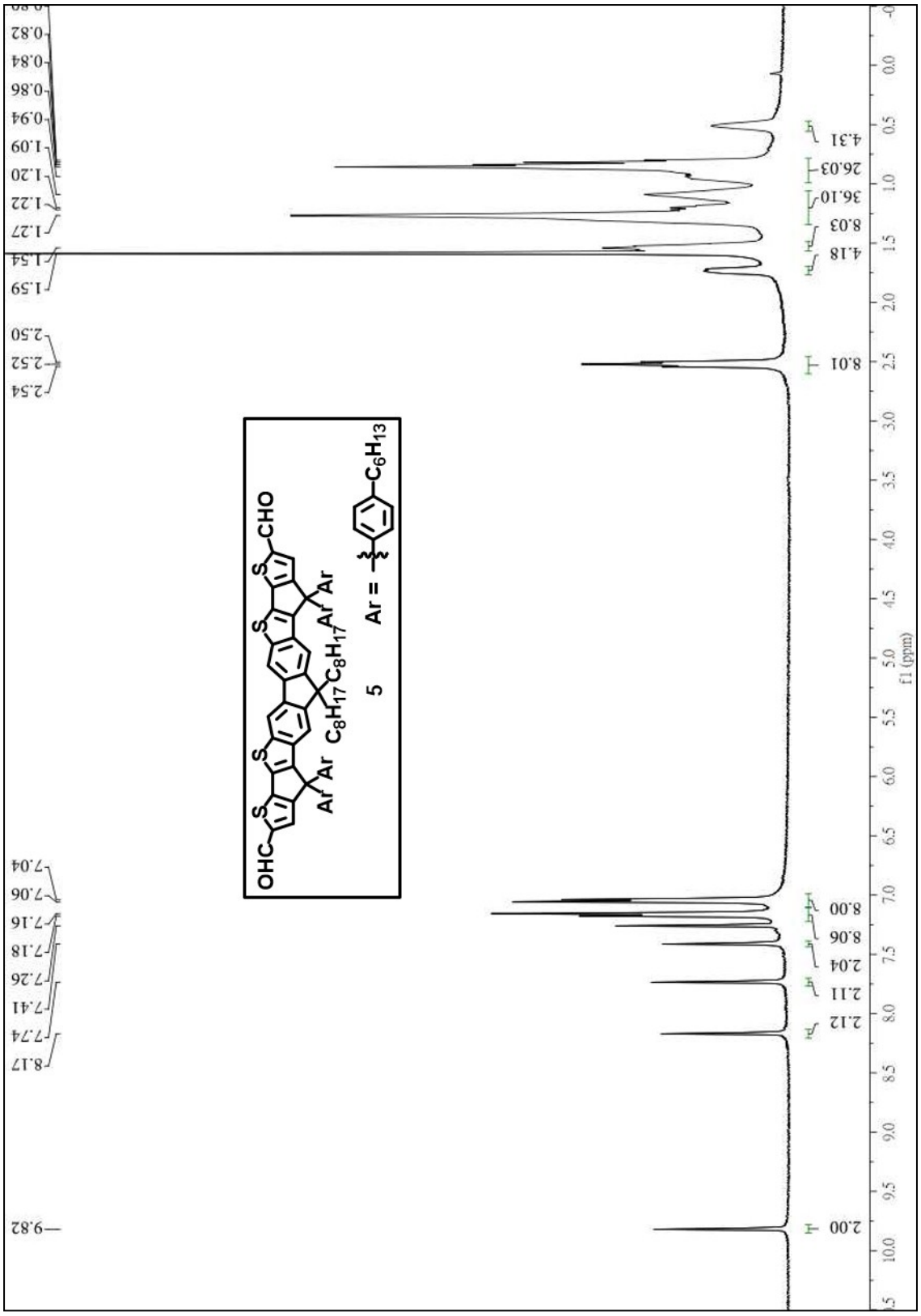


Fig. S12. ^{1}H NMR spectrum of compound **5.**

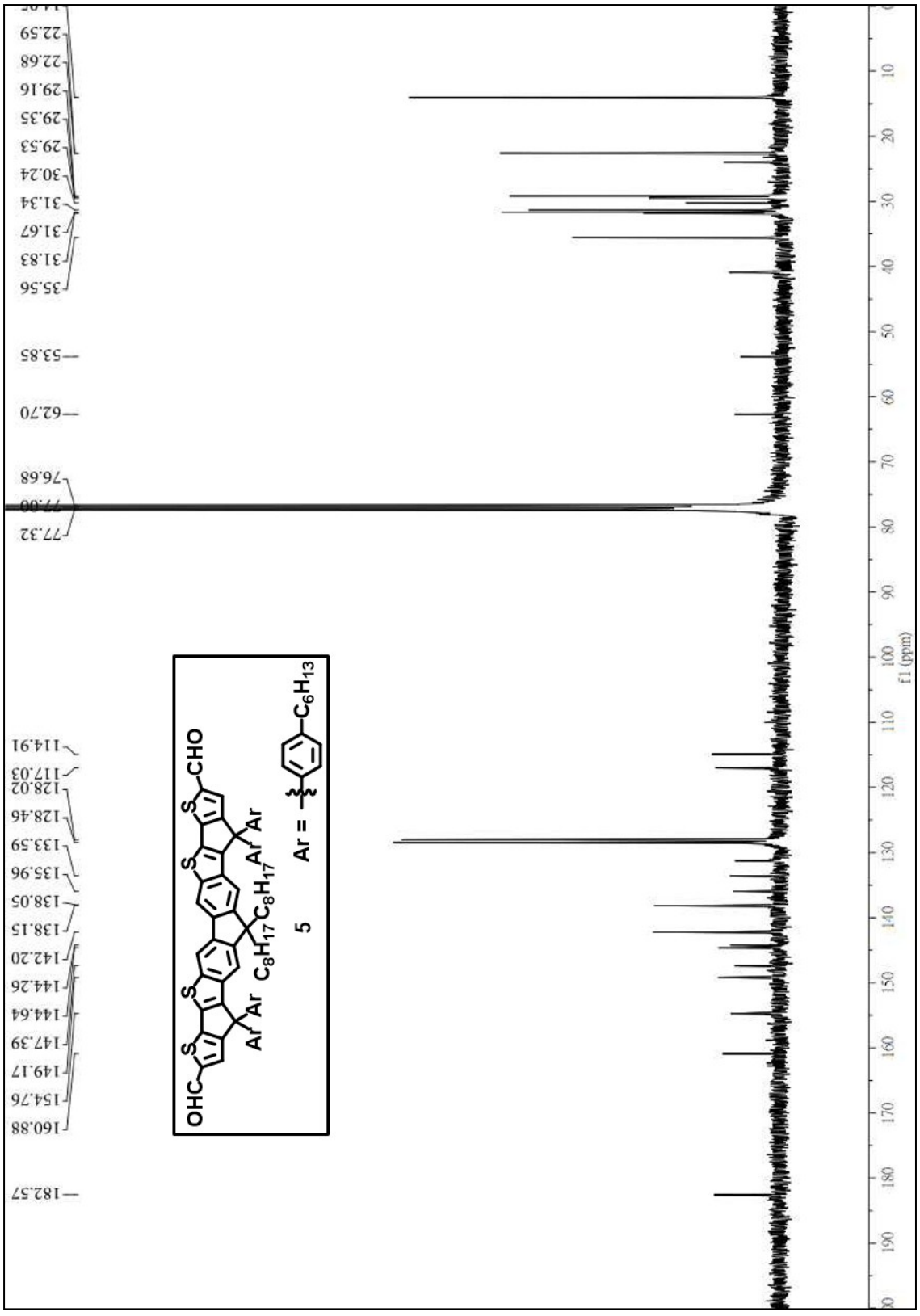


Fig. S13. ^{13}C NMR spectrum of compound **5.**

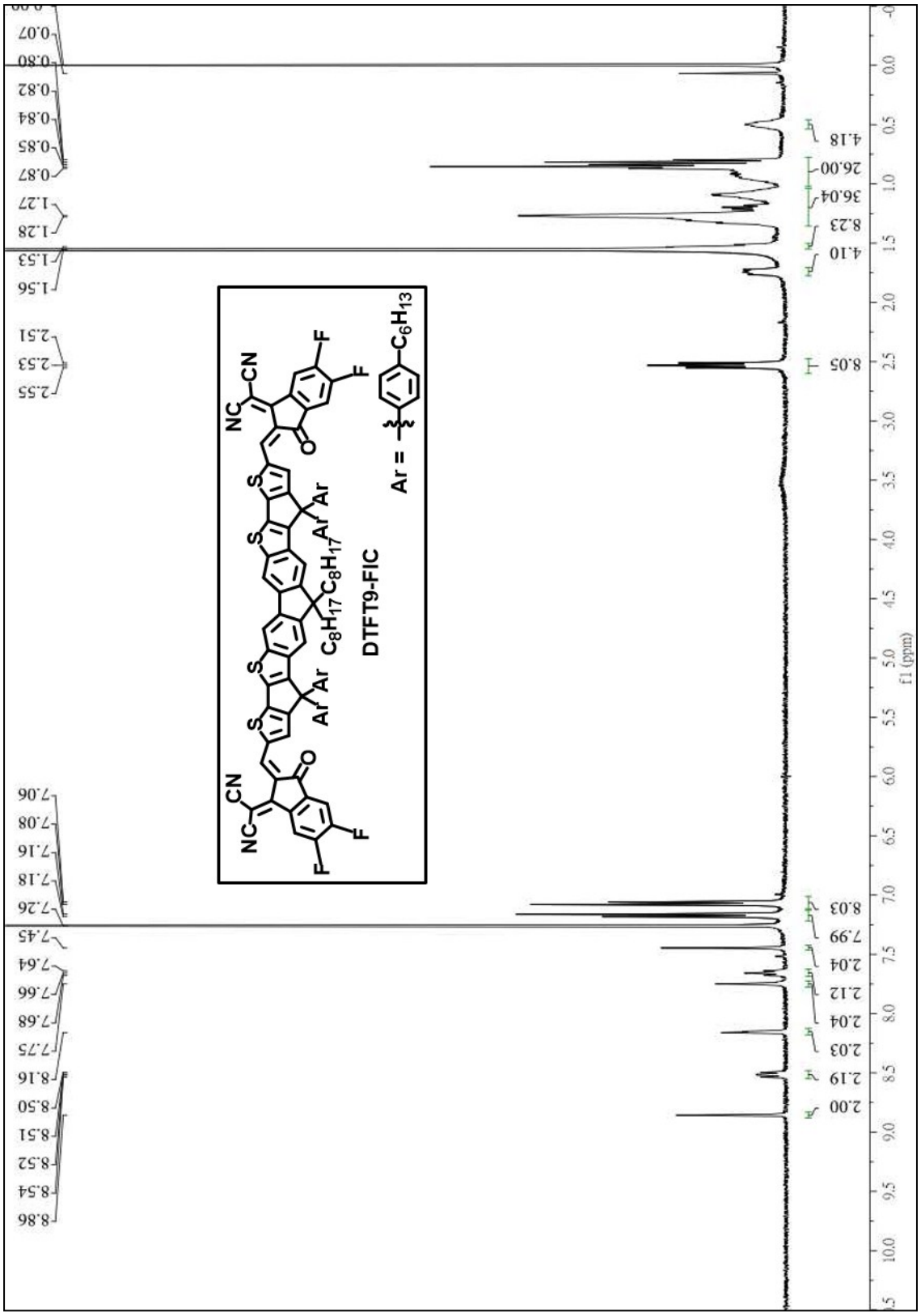


Fig. S14 ^{1}H NMR spectrum of **DTFT9-FIC.**

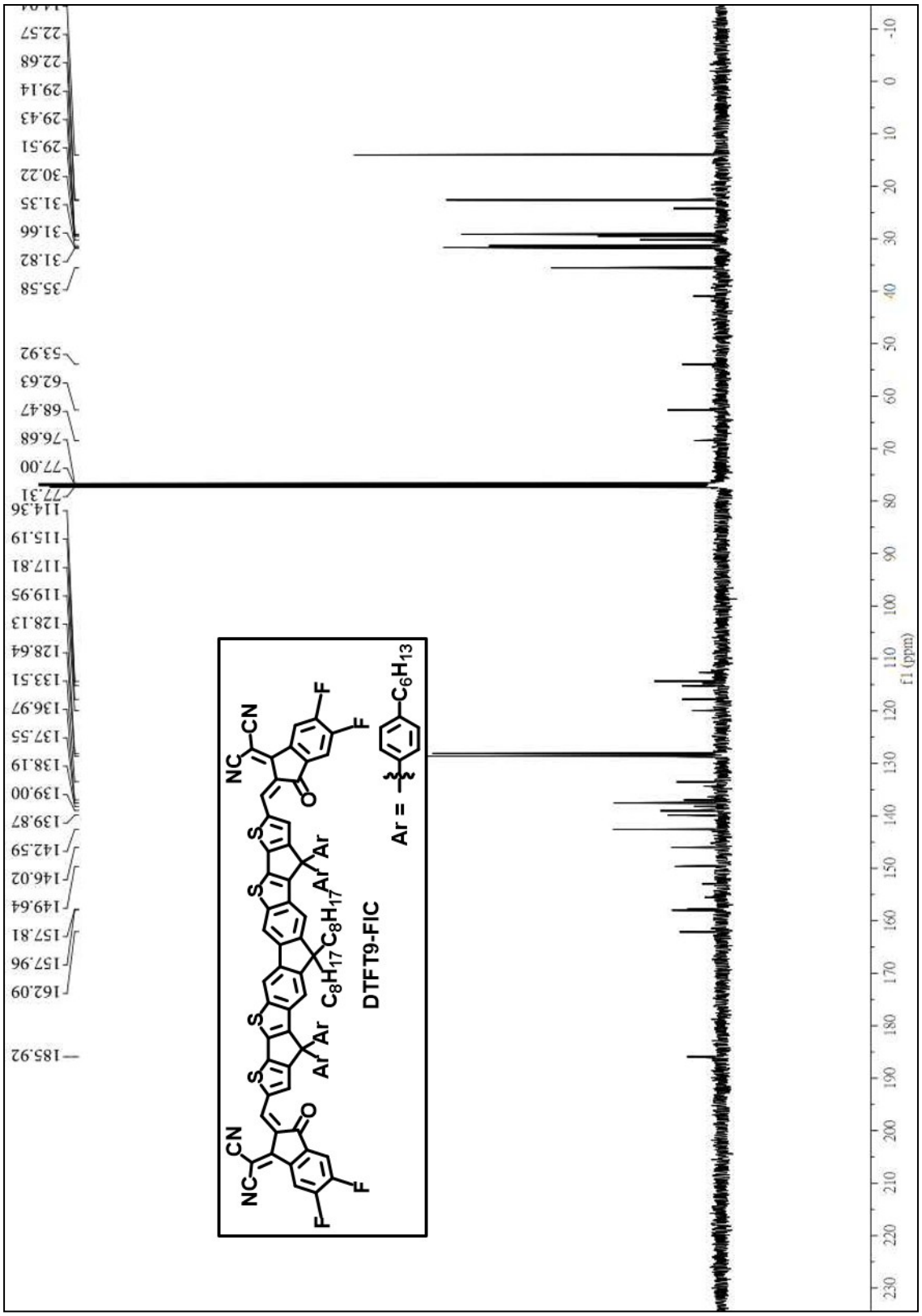


Fig. S15. ^{13}C NMR spectrum of **DTFT9-FIC.**