Supporting Information for

Synthesis of Angular-Shaped Naphthodithiophenediimide and its Donor-Acceptor Copolymers as Nonvolatile Polymer Additives for Organic Solar Cells

Chia-Lin Tsai,[a] Tung-Hsien Chan,[a] Han-Cheng Lu,[a] Ching-Li Huang,[a] Kai-En Hung,[a] Yu-Ying Lai*[c] and Yen-Ju Cheng*[ab]

[a]Department of Applied Chemistry, National Yang Ming Chiao Tung University, 1001 University Road, Hsinchu 30010, Taiwan.
[b]Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, 1001 University Road, Hsinchu 30010, Taiwan.
[c]Institute of Polymer Science and Engineering, National Taiwan University, No.1, Sec.4, Roosevelt Road, Taipei 10617, Taiwan.

Corresponding Authors
E-mail: yjcheng@nycu.edu.tw, and yuyinglai@ntu.edu.tw

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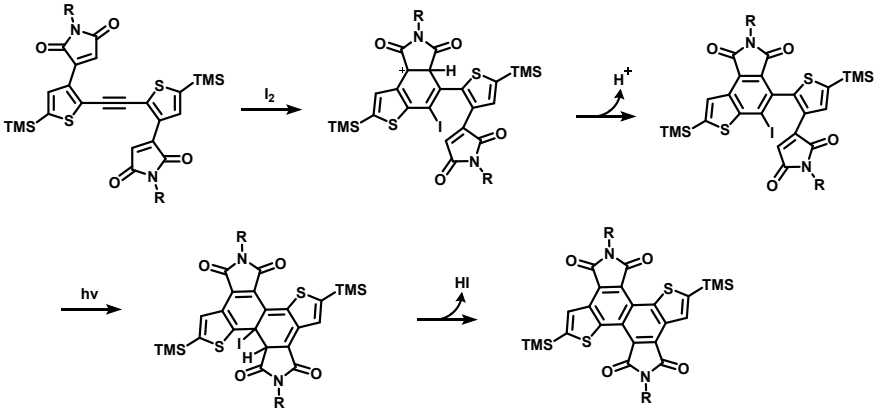
1. General measurement and characterization

Differential scanning calorimetry (DSC) was conducted on a TA Q200 Instrument under nitrogen atmosphere at a heating/cooling rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer Pyris under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. UV-visible spectra were collected by a UV-HITACHI U-4100 UV−vis spectrophotometer. Electrochemical cyclic voltammetry (CV) was conducted on a CH instruments electrochemical analyzer. A carbon glass was used as the working electrode and an Ag/AgCl electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile was the electrolyte. CV curves were calibrated using ferrocene as the standard and the HOMO was set at −4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation HOMO = $-(E_{ox,\ onset} - E_{(ferrocene)onset} + 4.8)$ eV. The LUMO levels were obtained from the equation LUMO = $-(E_{red,\ onset} - E_{(ferrocene)onset} + 4.8)$ eV. 2D-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 10.00120 keV (λ = 1.239851 Å) at a fixed incident angle of 0.08° through a coupled double crystal Si (111)/multilayer (Mo/B4C) monochromator, and the GIWAXS patterns were recorded on a 2D image detector (Pilatus 1MF area detector). ^{1}H and ^{13}C NMR spectra were measured using a Varian 400 MHz instrument spectrometer and obtained in deuterated chloroform ($CDCl_3$) with TMS as the internal reference unless otherwise stated, and chemical shifts (δ) are reported in parts per million.

2. Proposed reaction mechanism for the formation of TMS-aNDTI-C8

Scheme S1 Proposed reaction mechanism for the formation of **TMS-aNDTI-C_8** from compound 7.[1]



3. Molecular weight determination

Determination of molecular-weight data for **PBM** by gel permeation chromatography (GPC) was unsuccessful as a result of its poor solubility in tetrahydrofuran room temperature. Instead, high-temperature GPC with 1,2,4-trichlorobenzene as the eluent at 160 °C was carried out. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) of the polymers were obtained accordingly. The values are summarized in Table S1.

Table S1 Molecular-weight data for **PBM** and **PFBM**.

Polymer	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI (M_w/M_n)
PBM	2,558	3,581	1.4
PFBM	5,622	6,746	1.2

4. Thermal analysis

Thermal properties of polymers were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermal decomposition temperature (T_d) estimated by the 5% weight loss was 240 °C for **PBM** and 243 °C for **PFBM (Fig. S1).**

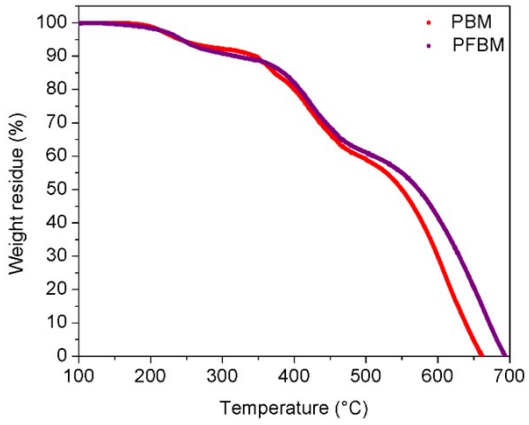


Fig. S1 Thermogravimetric analysis curves of **PBM** and **PFBM** (scan rate: 10 °C min^{-1}).

DSC revealed that no apparent thermal transition within the scanning range of temperature was detected (Fig. S2).

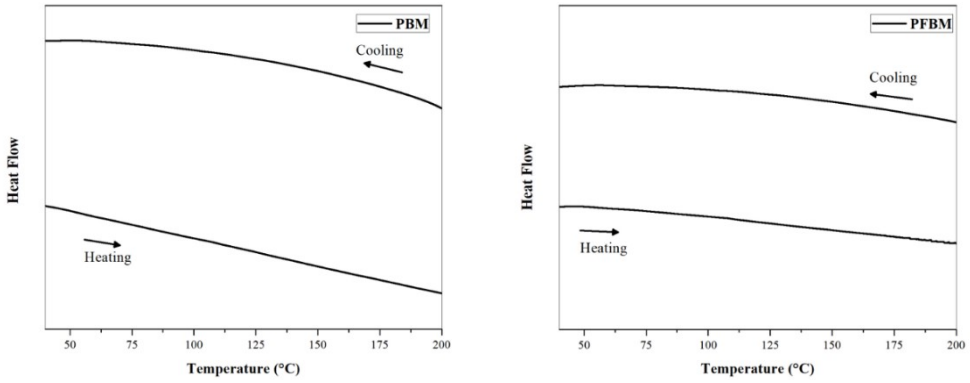


Fig. S2 DSC diagrams of **PBM** and **PFBM** (scan rate: 10 °C min^{-1}).

5. Fabrication and characterization of OFET devices

300 nm thick SiO_2 was deposited on n-doped silicon wafers (C_i = 11 nF cm^{-2}). The substrates were rinsed with sulfuric acid and hydrogen peroxide (30% solution in water) (3 : 1, volume ratio) at room temperature for 1 h, followed by 15 min of sonication in pure water. The substrates were heated on a hot plate in a glovebox at 150 °C to remove water, followed by UV-ozone treatment for 30 min. The SiO_2 wafers were immersed in an *n*-octadecyltrichlorosilane (ODTS) : toluene solution (1 : 100, volume ratio) for 3 h. The surface of the ODTS-treated SiO_2/Si substrates was washed with acetone and heated for 1 h at 100 °C. On the other hand, a 3 mM solution of *N*-(2-Aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS) in trichloroethylene (TCE) was cast onto a UV-ozone cleaned SiO_2/Si wafer to cover the entire surface and was allowed to partially assemble for 10 s. The substrate was then spun at 3000 rpm. Following spin-casting the substrate was put in a closed container with a small vial which containing a few millimeters of ammonium hydroxide solution (28-30% in water) for 20 h at room temperature. The substrates were then rinsed with DI water and sonicated in toluene, acetone, and IPA, respectively. Thin films (40–60 nm in thickness) of the polymers were deposited on SAM-treated SiO_2/Si substrates by spincoating (1000 rpm) their hot $CHCl_3$ solutions (10 mg mL^{-1}). PBM and PFBM were depoisted on the SAM-treated SiO2, AEAPTMS and ODTS, respectively. Thermal annealing was then conducted at 120 °C for 10 min. Gold source and drain electrodes (40 nm in thickness) were deposited by vacuum evaporation on the polymer layer to complete the bottom-gate/top-contact OFET devices as illustrated in Fig. S3. Electrical measurements of all OFET devices were carried out at room temperature in air on a 4156C instrument (Agilent Technologies). The field-effect mobility was calculated at saturation using the equation $I_d = (\mu W C_i/2L)(V_g - V_t)^2$, where I_d is the drain–source current, μ is the field-effect mobility, W is the channel

width (1 mm), L is the channel length (100 μm), C_i is the capacitance per unit area of the gate dielectric layer, V_g is the gate voltage, and V_t is the threshold voltage.

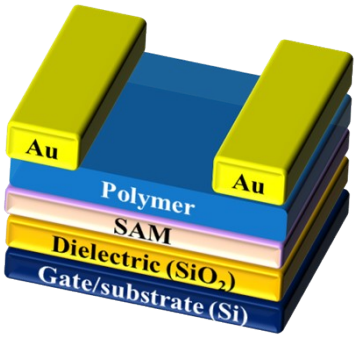


Fig. S3 OFET architecture with the bottom-gate-top-contact (BGTC) configuration.

6. OPV device fabrication

The ZnO precursor was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, Aldrich, 99.9%, 1 g) and ethanolamine ($NH_2CH_2CH_2OH$, Aldrich, 99.5%, 0.28 g) in 2-methoxyethanol ($CH_3OCH_2CH_2OH$, Aldrich, 99.8%, 10 mL) under vigorous stirring for 24 h and spun-cast onto a pre-cleaned ITO substrate, followed by 180 °C baking in the air at relative humidity below 50 % for 20 min. The active layer was deposited by spin-coating a sample solution on the ZnO in the glovebox. The active layer was thermally annealed at 100 °C for 13 min in a glovebox. Then, the devices were covered with shadow masks to define the active area (0.04 mm^2) and were transferred to a thermal evaporator. The electrode consisting of MoO_3 (7 nm) and silver (150 nm) thin layers was thermally evaporated on the active layer sequentially. The solar cells were measured at ca. 25 °C using the Oriel Xenon lamp (450 W) with an AM1.5 filter as the solar simulator. The light intensity was calibrated using a standardized reference silicon solar cell to 100 mW cm^{-2}.

For the active-layer preparation, a PM6:Y6 solution was prepared by dissolving PM6 (solamer, M_n = 39183, PDI = 2.45) and Y6 (solamer) in chloroform at a concentration of 19.8 mg/mL (PM6 and Y6 weight ratio is 1:1.2) with 0.6 vol% 1-chloronaphthalene (CN) and 0.05 wt% **PBM** or **PFBM** polymer additive. Polymer additives are dissolved in chloroform solution with the concentration of 1 mg/mL. 2.0 μL additive polymer solution was introduced into 0.2 mL PM6:Y6 chloroform blending solution, approximately equal to 0.05 wt%. The solution was stirred for 1 h before spin-coating.

7. Energy loss

$E_{g,pv}$ is derived from the intersection of normalized absorption and PL spectra.[2] Subtracting V_{oc} from $E_{g,pv}$ could yield energy loss (E_{loss}).[3] E_{loss} can be further categorized into three contributions, ΔE_1, ΔE_2, and ΔE_3. $V_{oc,SQ}$, the maximum thermodynamic voltage limit based on the Schottky-Queisser limit, SQ)[4,5], is estimated by **Equation (S1)**. $E_{g,pv} - V_{oc,SQ}$ gives ΔE_1, radiative recombination from the absorption above the bandgap. **Equation (S2)** in conjunction with **Equation (S3)** is used to calculate $V_{oc,Rad}$, the radiation voltage limit.[3] $V_{oc,SQ} - V_{oc,Rad}$ gives ΔE_2, radiative recombination from the absorption below the bandgap. $E_{loss} - \Delta E_1 - \Delta E_2$ being equal to $V_{oc,Rad} - V_{oc}$ gives ΔE_3, non-radiation energy loss.[6]

Values for the E_{loss} estimation are summarized in **Table S2**. In the pristine **PM6**:**Y6** device, E_{loss} was 0.588 eV, ΔE_1 was 0.263 eV, ΔE_2 was 0.065 eV, and ΔE_3 was 0.260 eV. In the **PM6**:**Y6**:**PBM** device, ΔE_2 slightly rose from 0.065 eV to 0.069 eV while ΔE_1 and ΔE_3 remained constant. As for the **PM6**:**Y6**:**PFBM** device, ΔE_2 and ΔE_3 slightly dropped to 0.062 eV and 0.259 eV, respectively. ΔE_1 stayed constant. The results confirm that the incorporation of **PBM** and **PFBM** had a marginal influence on the E_{loss}, rationalizing the unaffected V_{oc} values.

Table S2. Values for the E_{loss} estimation for the **PM6**:**Y6**-based BHJ solar devices.

Active layer	V_{oc} (V)	$E_{g,pv}$ (eV)	$V_{oc,SQ}$ (eV)	$V_{oc,Rad}$ (eV)	E_{loss} (eV)	ΔE_1	ΔE_2	ΔE_3
PM6:Y6:PBM	0.83	1.426	1.163	1.094	0.593	0.263	0.069	0.260
PM6:Y6:PFBM	0.83	1.414	1.151	1.093	0.584	0.263	0.062	0.259
PM6:Y6	0.83	1.418	1.155	1.090	0.588	0.263	0.065	0.260

$$V_{OC,SQ} = \frac{k_B T}{q} \ln\left[\frac{J_{SC}}{q\int_{E_g}^{\infty} \varphi_{BB}(E)\mathrm{d}E} + 1\right] \qquad \textbf{Equation (S1)}$$

$$V_{OC,Rad} = \frac{k_B T}{q} \ln\left[\frac{J_{SC}}{\int_{0}^{\infty} \eta_{EQE}(E)\varphi_{BB}(E)\mathrm{d}E} + 1\right] \qquad \textbf{Equation (S2)}$$

$$\varphi_{BB}(E) = \frac{2\pi E^2}{h^3 c^2} \frac{1}{[\exp(E/kT) - 1]} \approx \frac{2\pi E^2}{h^3 c^2} \exp\left(\frac{-E}{kT}\right) \qquad \textbf{Equation (S3)}$$

8. Grazing incidence wide-angle X-ray scattering (GIWAXS)

GIWAXS were implemented at the BL23A SWAXS instrument of Taiwan Light Source (TLS) at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu[7]. A thin film for GIWAXS was spin-coated from a chloroform solution of either sample on a Si wafer (13 × 13 mm^2). With an X-ray beam of 10 keV and incident angles of 0.16°, 0.2°, or 2°, GIWAXS data were collected by using a sample-to-detector (SD) distance of 100, 135.5 or 186 mm. With the sample surface defined as the x-y plane and the incident x-rays in the x-z plane, the scattering vector $q = (q_x, q_y, q_z)$ can expressed as $q_x = 2\pi\lambda^{-1}$ (cos β cos φ – cos α), $q_y = 2\pi\lambda^{-1}$ (cos β sin φ), and $q_z = 2\pi\lambda^{-1}$ (sin α + sin β), with α and β for the incident and exit angles and φ for the scattering angle away from the y-z plane. The in-plane and out-of-plane scattering vector components are respectively defined by q_r and q_z, with $q_r = (q_x^2 + q_y^2)^{1/2}$, as that detailed previously[7]. For GIWAXS, the scattering peak positions were carefully calibrated using the diffraction peaks from Si and LaB6. After converting 2D GIWAXS patterns to those defined with q_r and q_z using the previously stated process,[8, 9] there is a missing wedge of no diffraction information available in the vertical direction of each 2D[10].

As depicted in Fig. S5, both thin films showed the (010) π–π diffraction peaks and the lamella (h00) diffraction peaks in the both in-plane and out-of-plane directions.

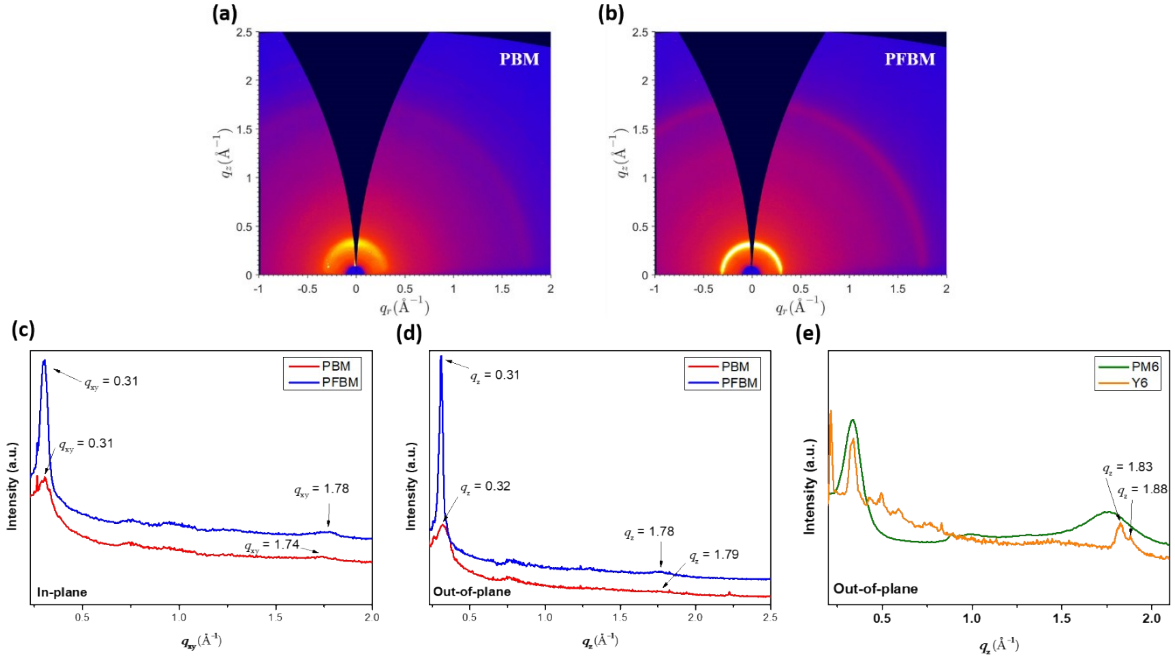
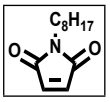
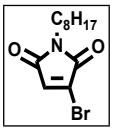


Fig. S4□2-Dimensional GIWAXS images of (a) **PBM** and (b) **PFBM**. 1-Dimensional diffraction patterns of **PBM** and **PFBM** along (c) the in-plane direction (q_{xy}) and (d) the out-of-plane direction (q_z). (e) 1-Dimensional diffraction patterns of **PM6** and **Y6** neat film along the out-of-plane direction (q_z).

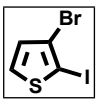
9. Synthesis details



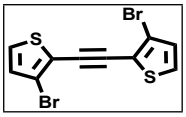
Synthesis of *N*-Octyl maleimide (1a): To a solution of maleic anhydride (3 g, 0.03 mol) and *n*-octyl amine (6 ml, 0.036 mol) in toluene (130ml) was stirred at room temperature for 1 h. To the mixture was added $ZnBr_2$ (6.89 g, 0.03 mol) and a toluene (20 mL) solution of hexamethyldisilazane (8.8 ml, 0.04 mol). The reaction mixture was stirred at 110 °C for 2 h. After being cooled down to room temperature, the reaction mixture was poured into $HCl_{(aq)}$ (0.5 M, 200 mL), and extracted with ethyl acetate (50 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residual oil was purified by column chromatography on silica gel (hexane:ethyl acetate = 1:1) to afford *n*-octyl maleimide as a white crystal. (5.0 g, 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 2H), 3.49 (t, *J* = 8.0 Hz, 2H), 1.65–1.54 (m, 2H), 1.29–1.24 (m, 10H), 0.86 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 129.3, 39.8, 31.7, 29.1, 29.0, 28.4, 26.6, 22.6, 14.0.



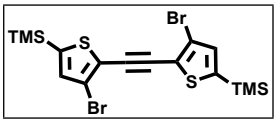
Synthesis of 2-Bromo-*n*-octyl maleimide (2a): To an ether (50 mL) solution of *n*-octyl maleimide (4 g, 0.02 mol) was added bromine (1 mL, 0.02 mol) and the mixture was stirred at room temperature for 1 h. Then triethylamine (2.8 mL, 0.02 mol) was added dropwise under 0 °C. After being stirred at room temperature for 16 h, the reaction mixture was poured into water (50 mL), and extracted with ethyl acetate (25 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was submitted to column chromatography on silica gel (hexane:ethyl acetate = 20:1) to afford 2-bromo-*n*-octyl maleimide as a yellow oil. (4.2 g, 74%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 3.54 (t, *J* = 6.0 Hz, 2H), 1.60–1.56 (m, 2H), 1.28–1.25 (m, 10H), 0.87 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 165.2, 131.7, 131.2, 38.8, 31.7, 29.0, 29.0, 28.4, 26.6, 22.5, 14.0.



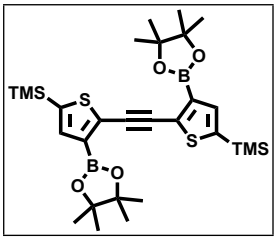
Synthesis of 3-Bromo-2-iodothiophene (3): A solution of 3-bromothiophene (10 g, 0.06 mol), *p*-toluenesulfonic acid (1.05g, 0.006 mol), and *N*-iodosuccinimide (15 g, 0.066 mol) in methanol (60 mL) was stirred at 50 °C for 30 min in the dark. After being cooled down to room temperature, the reaction mixture was poured into saturated $NaOH_{(aq)}$ and extracted with dichloromethane (50 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by vacuum distillation to afford 3-bromo-2-iodothiophene as a pink oil. (13 g, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 5.6 Hz, 1H), 6.90 (d, J = 5.6 Hz, 1H).



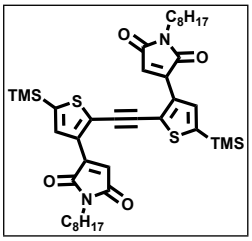
Synthesis of Bis-(3-bromo-2-thienyl)acetylene (4): A mixture of 3-bromo-2-iodothiophene (20 g, 0.069 mol), $PdCl_2(PPh_3)_2$ (2.9 g, 0.004 mol), CuI (1.32 g, 0.007 mol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 60ml, 0.4 mol), trimethylsilylacetylene (5 ml, 0.017 mol), and toluene (200 mL) was stirred at room temperature for 48 h. The mixture was concentrated under reduced pressure and filtrated with celite. Purification by column chromatography gave bis-(3-bromo-2-thienyl)acetylene as a white solid. (5.1 g, 42%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 6.0 Hz, 1H), 7.01 (d, J = 6.0 Hz, 1H).



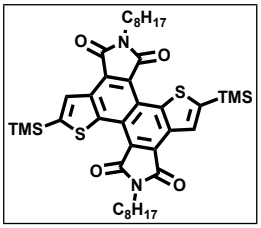
Synthesis of Bis(3-bromo-5-(trimethylsilyl)-2-thienyl)acetylene (5): To a solution of compound **4** (2 g, 0.0057 mol) in anhydrous THF solution (60 mL) was added lithium diisopropylamide (2 M, 11.5 mL) dropwise. The mixture was stirred for 1 h at -78 °C and chlorotrimethylsilane (2.5 ml, 0.0196 mol) was added. After being warmed to room temperature, the reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (50 mL×2). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography using hexane as eluent to afford compound **5** as a yellow solid. (1.9 g, 67%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2H), 0.32 (s, 18H).



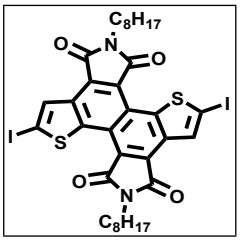
Synthesis of Bis(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)-2-thienyl)acetylene (6): To a solution of compound **5** (1 g, 0.002 mol) in anhydrous THF solution (60 mL) was added *n*-butyllithium solution (2.5 M, 1.8 mL) dropwise for 30 min at -78 °C. Isopropoxyboronic acid pinacol ester (1.24 g, 0.006 mol) was added. After being warmed up to room temperature, the reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (50 mL×2). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was washed with methanol to give compound **6** as a white solid. (0.72 g, 60%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 2H), 1.37 (s, 24H), 0.32 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 139.5, 137.9, 91.1, 83.7, 24.9, -0.1.



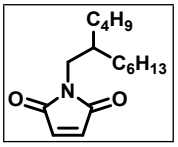
Synthesis of 3,3'-(ethyne-1,2-diylbis(5-(trimethylsilyl)thiophene-2,3-diyl))bis(1-octyl-1*H*-pyrrole-2,5-dione) (7a): A mixture of compound **6** (100 mg, 0.17 mmol), 2-bromo-*N*-octyl maleimide (108 mg, 0.37 mmol), $NaHCO_3$ (43 mg, 0.5 mmol), $Pd(PPh_3)_4$ (20 mg, 0.017 mmol), aliquat 336 (17 mg, 0.04 mmol), toluene (6 mL), and H_2O (3 mL) was degassed and stirred at 90 °C for 2 h. The mixture was poured into brine (50 mL) and extracted with ethyl acetate (50 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was washed with acetone to afford compound **7a** as an orange solid. (35 mg, 27%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.26 (s, 2H), 3.57 (t, J = 8.0 Hz , 4H), 1.63–1.56 (m, 4H), 1.31–1.25 (m, 20H), 0.87 (t, J = 8.0 Hz , 6H), 0.38 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.8, 145.7, 137.6, 134.5, 133.6, 128.8, 124.3, 94.3, 38.2, 31.8, 29.7, 29.1, 28.6, 26.8, 22.6, 14.1, -0.4. HRMS (EI, $M^{+\cdot}$, $C_{40}H_{56}N_2O_4S_2Si_2$): calcd, 748.3220; found, 748.3232.



Synthesis of TMS-aNDTI-C_8: A toluene (10 mL) solution of compound **7a** (50 mg, 0.066 mmol) and iodine (17 mg, 0.066 mmol) was irradiated by a medium-pressure mercury lamp for 16 h. The mixture was poured into saturated $Na_2S_2O_{3(aq)}$ (50 mL) and extracted with toluene (50 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was washed with acetone to furnish **TMS-aNDTI-C_8** as a yellow solid. (20 mg, 40%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 2H), 3.86 (t, *J* = 7.4 Hz, 4H), 1.84–1.78 (m, 4H), 1.29 (m, 20H), 0.87 (t, *J* = 6.6 Hz, 6H), 0.52 (s, 18H). ^{13}C NMR (100 MHz, CDCl3) δ 169.0, 168.1, 150.4, 147.4, 133.8, 128.0, 127.9, 124.4, 122.5, 38.6, 31.8, 29.3, 28.7, 27.0, 22.6, 14.1, 1.02. HRMS (EI, $M^{+\cdot}$, $C_{40}H_{54}N_2O_4S_2Si_2^{+\cdot}$): calcd, 746.3064; found, 746.3055.

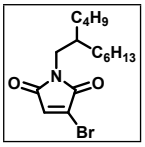


Synthesis of I-aNDTI-C_8: To a solution of **TMS-aNDTI-C_8** (50 mg, 0.067 mmol) in anhydrous dichloromethane (DCM) (5 mL) was added a solution of ICl (22 mg, 0.134 mmol) in anhydrous DCM (1 mL) dropwise at 0 °C. After being warmed up to room temperature for 4 h, the reaction mixture was poured into 5% $Na_2S_2O_{3(aq)}$ (10 mL). The crude product was filtrated and washed with DCM to furnish compound **I-aNDTI-C_8** as a yellow solid. (38 mg, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 2H), 3.85 (t, *J* = 7.4 Hz, 4H), 1.82–1.79 (m, 4H), 1.29 (m, 20H), 0.90-0.88 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 169.8, 168.8, 148.1, 133.4, 132.1, 130.8, 122.1, 119.8, 73.31, 38.6, 31.9, 29.8, 28.6, 27.2, 22.7, 13.9, 0.9.

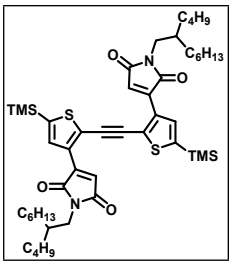


Synthesis of *N*-(2-Butyloctyl) maleimide (1b): To a solution of maleic anhydride (3 g, 0.03 mol) and 2-butyloctyl amine (6.8 g, 0.036mol) in toluene (120ml) was stirred at room temperature for 1 h. To the mixture was added $ZnBr_2$ (6.76 g, 0.03 mol) and a toluene (20 mL) solution of

hexamethyldisilazane (8.5ml, 0.04 mol). The reaction was stirred at 110 °C for 2 h. After being cooled down to room temperature, the reaction mixture was poured into $HCl_{(aq)}$ solution (0.5 M, 200 mL), and extracted with ethyl acetate (50 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the residual oil was purified by column chromatography on silica gel (hexane:ethyl acetate = 1:1) to afford compound **1b** as a white crystal. (5.39 g, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.68 (s, 2H), 3.40 (d, *J* = 7.3 Hz, 2H), 1.76 (d, *J* = 6.0 Hz, 1H), 1.26 (ddd, *J* = 17.1, 12.6, 4.5 Hz, 16H), 0.88 (td, *J* = 6.9, 1.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 133.9, 42.1, 36.9, 31.8, 31.4, 31.0, 29.6, 28.4, 26.2, 23.0, 22.6, 14.1, 14.0.

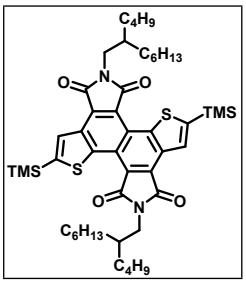


Synthesis of 2-Bromo-*N*-(2-butyloctyl)maleimide (2b): To an ether (50 mL) solution of 2-butyloctyl maleimide (5.39 g, 0.02 mol) was added bromine (1 mL, 0.02 mol) and the mixture was stirred at room temperature for 1 h. Then triethylamine (3.0 mL, 0.02 mol) was added dropwise under 0 °C. After being stirred at room temperature for 16 h, the reaction mixture was poured into water (50 mL), and extracted with ethyl acetate (25 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was submitted to column chromatography on silica gel (hexane:ethyl acetate = 20:1) to afford compound **2b** as a yellow oil. (5.7 g, 81%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 1H), 3.30 (t, *J* = 7.7Hz, 2H), 1.92 – 1.83 (m, 1H), 1.10 (m, 16H), 0.78 – 0.68 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 165.0, 131.5, 130.6, 59.8, 42.4, 36.6, 31.4, 31.0, 30.6, 29.2, 28.0, 25.8, 22.6, 22.3, 13.7.

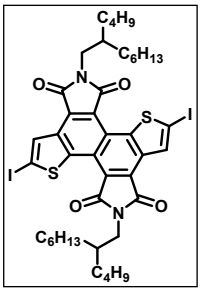


Synthesis of 3,3'-(ethyne-1,2-diylbis(5-(trimethylsilyl)thiophene-2,3-diyl))bis(1-(2-butyloctyl)-1H-pyrrole-2,5-dione) (7b): A mixture of compound **6** (100 mg, 0.17 mmol), compound **2b** (130 mg, 0.037 mmol), $NaHCO_3$ (43 mg, 0.5 mmol), $Pd(PPh_3)_4$ (20 mg, 0.017 mmol), aliquat336 (17 mg, 0.04 mmol), toluene (6 mL), and H_2O (3 mL) was degassed and stirred at 90 °C for 2 h. The mixture was poured into brine (50 mL) and extracted with ethyl acetate (50 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the mixture

was washed with acetone to afford compound **7b** as an orange solid. (32 mg, 22%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.27 (s, 2H), 3.46 (t, *J* = 7.2 Hz , 4H), 1.81 (m, 2H), 1.26 (m, 32H), 0.87 (q, *J* = 6.8 Hz , 12H), 0.38 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 171.1, 145.7, 137.5, 134.5, 133.9, 128.8, 124.2, 94.4, 42.4, 37.0, 31.8, 31.4, 31.1, 29.6, 28.5, 26.2, 23.0, 22.6, 14.1, 14.1, -0.35. HRMS (EI, $M^{+\cdot}$, $C_{40}H_{56}N_2O_4S_2Si_2$): calcd, 748.3220; found, 748.3232.

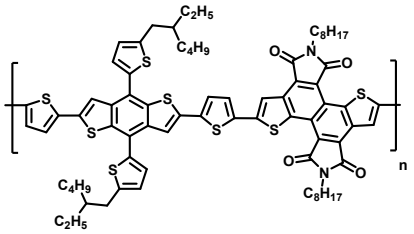


Synthesis of TMS-aNDTI-C_8C_4: A toluene (10 mL) solution of compound **7b** (50 mg, 0.058 mmol) and iodine (15 mg, 0.058 mmol) was irradiated by a medium-pressure mercury lamp for 16 h. The mixture was poured into saturated $Na_2S_2O_{3(aq)}$ (50 mL) and extracted with toluene (50 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the crude product was washed with acetone to furnish **TMS-aNDTI-C_8C_4** as a yellow solid. (16 mg, 32%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 2H), 3.75 (d, *J* = 7.1 Hz, 4H), 2.05 (m, 2H), 1.32(m, 32H), 0.87 (m, 12H), 0.52 (s, 18H). ^{13}C NMR (100 MHz, CDCl3) δ 169.1, 168.2, 150.5, 147.5, 133.9, 128.2, 127.8, 124.2, 122.5, 42.9, 37.1, 31.8, 31.7, 31.5, 31.2, 29.7, 28.5, 26.3, 23.1, 22.7, 14.1, 1.1. HRMS (EI, $M^{+\cdot}$, $C_{40}H_{54}N_2O_4S_2Si_2^{+\cdot}$): calcd, 746.3064; found, 746.3055.

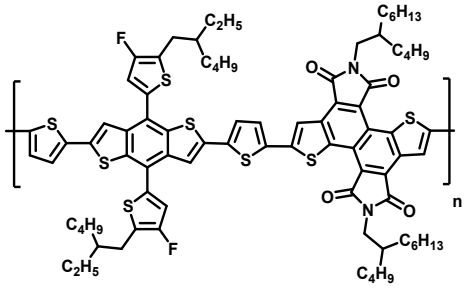


Synthesis of I-aNDTI-C_8C_4: To a solution of **TMS-aNDTI-C_8C_4** (50 mg, 0.058 mmol) in anhydrous dichloromethane (DCM) (5 mL) was added a solution of ICl (25 mg, 0.145 mmol) in anhydrous DCM (1 mL) dropwise at 0 °C. After being warmed up to room temperature for 4 h, the reaction mixture was poured into 5% $Na_2S_2O_{3(aq)}$ (10 mL). The crude product was filtrated and washed with DCM to furnish **I-aNDTI-C_8C_4** as a yellow solid. (40 g, 71%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 2H), 3.73 (d, *J* = 7.1 Hz, 4H), 1.98 (m, 2H), 1.31 (m, 32H), 0.86 (m, 12H). ^{13}C NMR (100 MHz, CDCl3) δ 169.0,

168.2, 148.2, 133.7, 132.3, 131.1, 122.5, 120.3, 73.8, 42.9, 37.1, 31.8, 31.7, 31.5, 31.2, 29.7, 28.5, 26.3, 23.1, 22.7, 14.1.



Synthesis of PBM: To a 20 mL seal tube were introduced **I-aNDTI-C_8** (80 mg, 0.09356 mmol), **BDT-T-Sn** (100 mg, 0.09356 mmol), P(*o*-tolyl)$_3$ (2.62 mg, 0.0086 mmol), $Pd_2(dba)_3$ (1.97 mg, 0.0021 mmol) and dry chlorobenzene (3.2 ml). The mixture was degassed by bubbling nitrogen for 10 min at room temperature and stirred at 145 °C under nitrogen for 72 hr. The reaction mixture was added into methanol dropwise. The precipitate was collected by filtration and washed by Soxhlet extraction with acetone, hexane, THF, and chlorobenzene sequentially for three days. After filtration and removal of the solvent, the polymer was re-dissolved in chlorobenzene again and added into methanol to re-precipitate out. The purified polymer was collected by filtration and dried under vacuum for 1 day to give a dark red solid of **PBM**. (32 mg, M_n = 2558, M_w = 3581, PDI = 1.40). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.14–0.38 (br, 8H), 0.99–1.03 (br, 24H), 1.44–1.86 (br, 84H), 2.89–2.98 (br, 4H), 3.83 (br, 2H), 6.80–7.12 (br, 12H).



Synthesis of PFBM: To a 20 mL seal tube were introduced **I-aNDTI-C_8C_4** (87.5 mg, 0.09051 mmol), **FBDT-T-Sn** (100 mg, 0.09051 mmol), P(*o*-tolyl)$_3$ (2.53 mg, 0.0083 mmol), $Pd_2(dba)_3$ (1.9 mg, 0.0021 mmol) and dry chlorobenzene (3.2 ml). The mixture was degassed by bubbling nitrogen for 10 min at room temperature and stirred at 145 °C under nitrogen for 72 hr. The solution was added into methanol dropwise. The precipitate was collected by filtration and washed by Soxhlet extraction with acetone, hexane, THF, and chlorobenzene sequentially for three days. After filtration and removal of the solvent, the polymer was re-dissolved in chlorobenzene again and added into methanol to re-precipitate out. The purified polymer was collected by filtration and dried under vacuum for 1 day to give a dark red solid of **PFBM**. (35 mg, M_n = 5622, M_w = 6746, PDI = 1.20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07–

0.08 (br, 58H), 0.86–1.06 (br, 59H), 1.25–1.85 (br, 99H), 2.00–2.22 (br, 4H), 2.83–2.87 (br, 8H), 3.75–3.82 (br, 4H), 5.32（1H), 6.80–7.12 (br, 10H), 7.46–7.64 (br, 3H).

10. NMR spectra

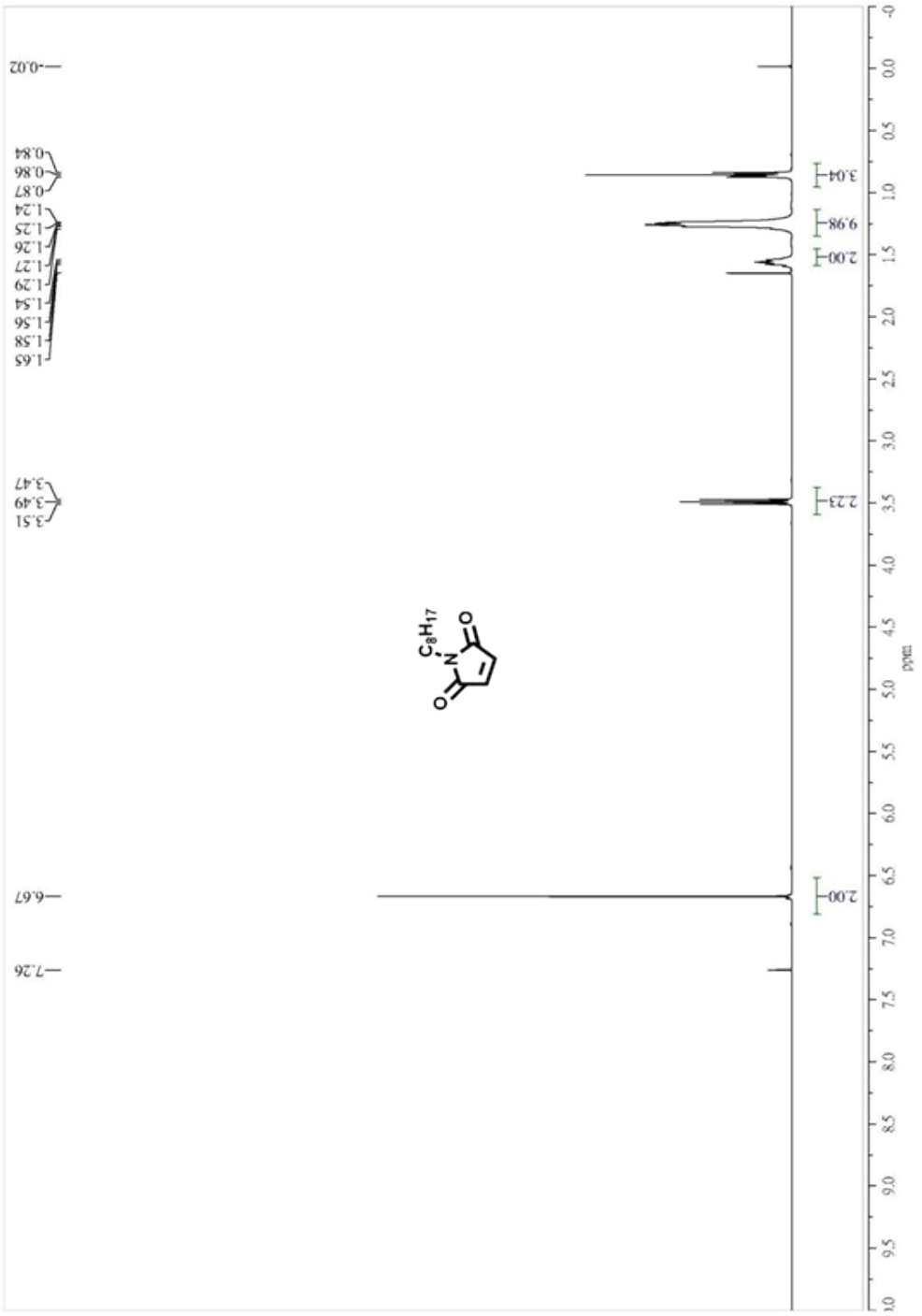


Fig. S5 Compound **1a** ^{1}H NMR spectrum

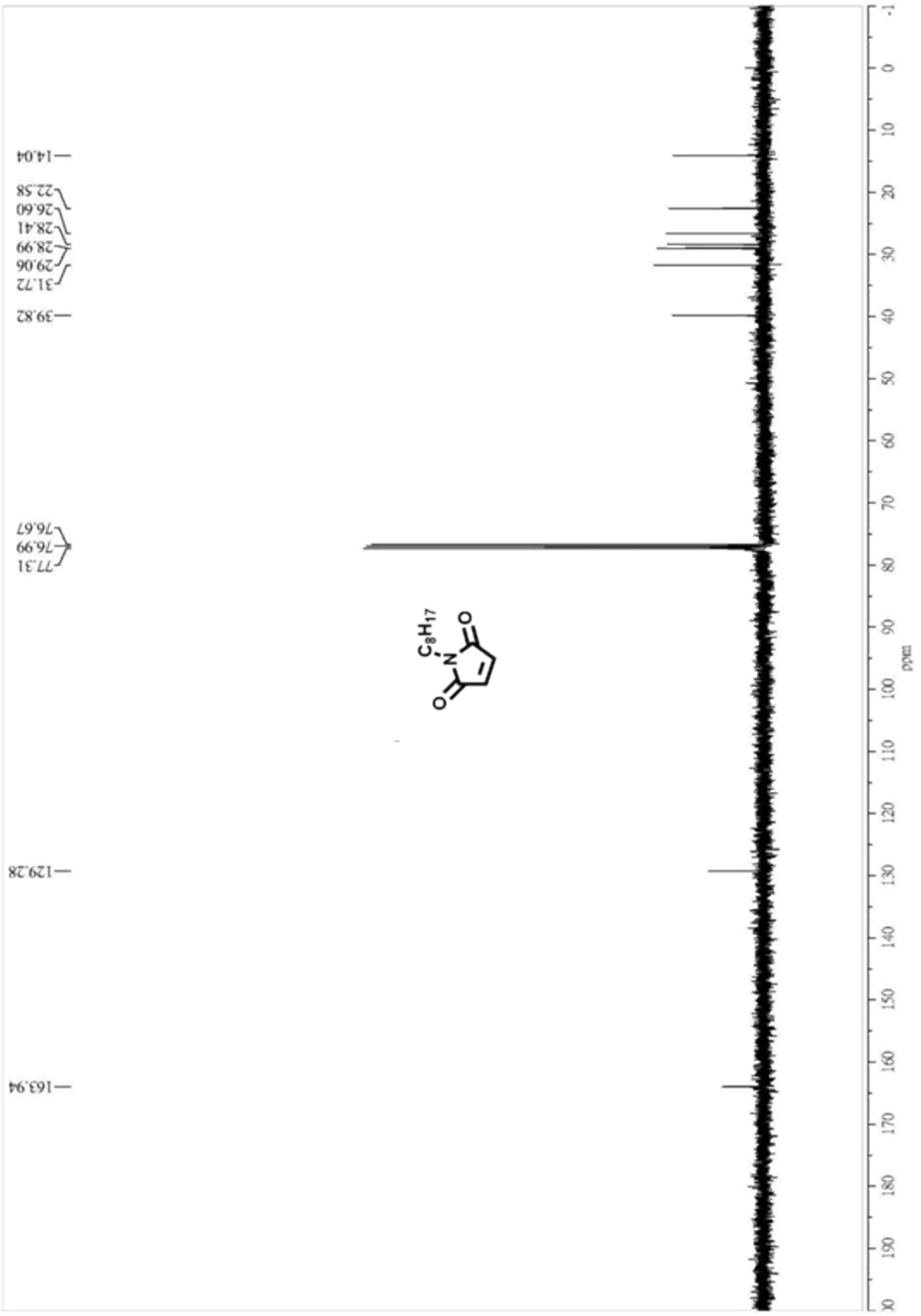


Fig. S6 Compound **1a** ^{13}C NMR spectrum

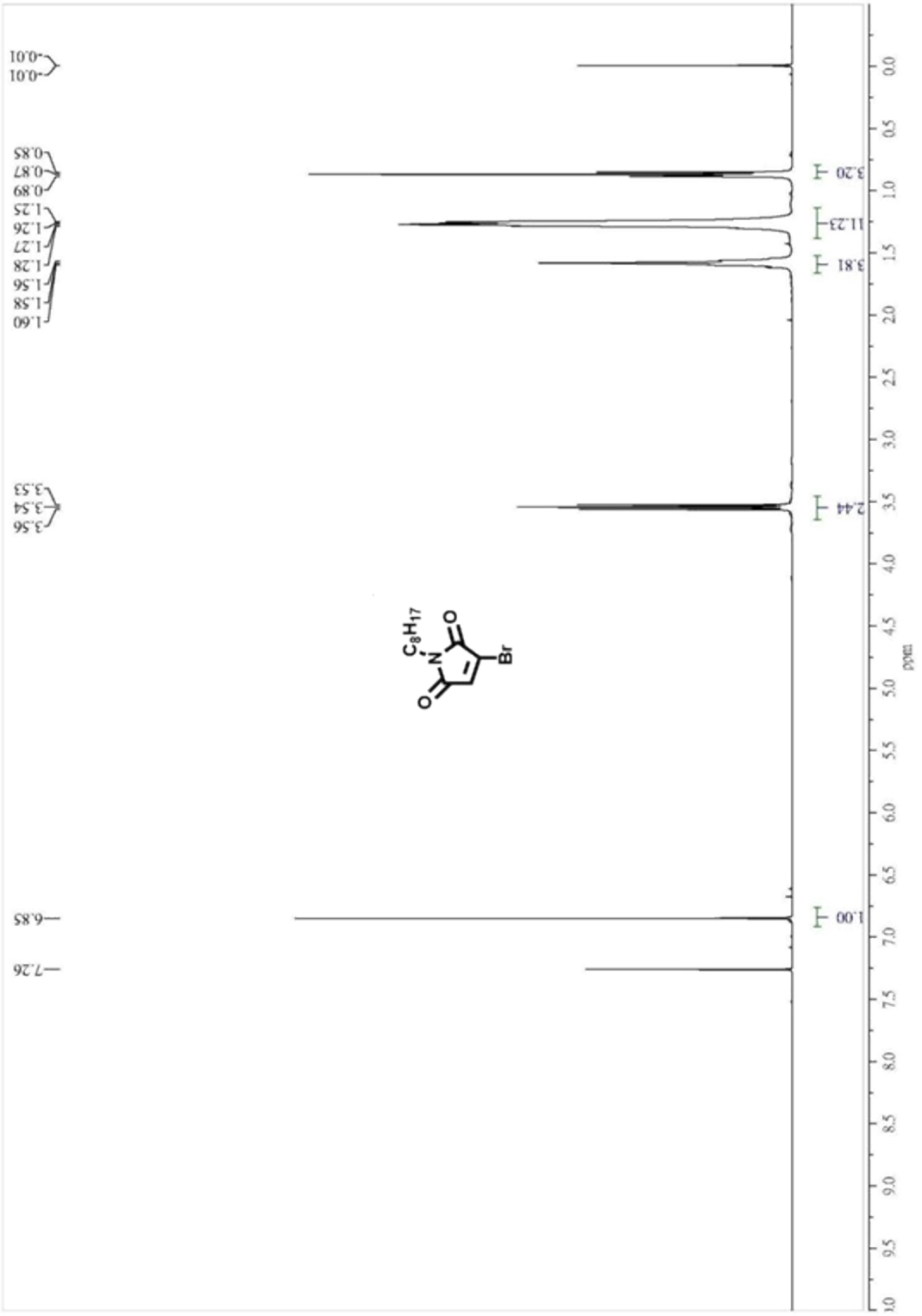


Fig. S7 Compound **2a** ^{1}H NMR spectrum

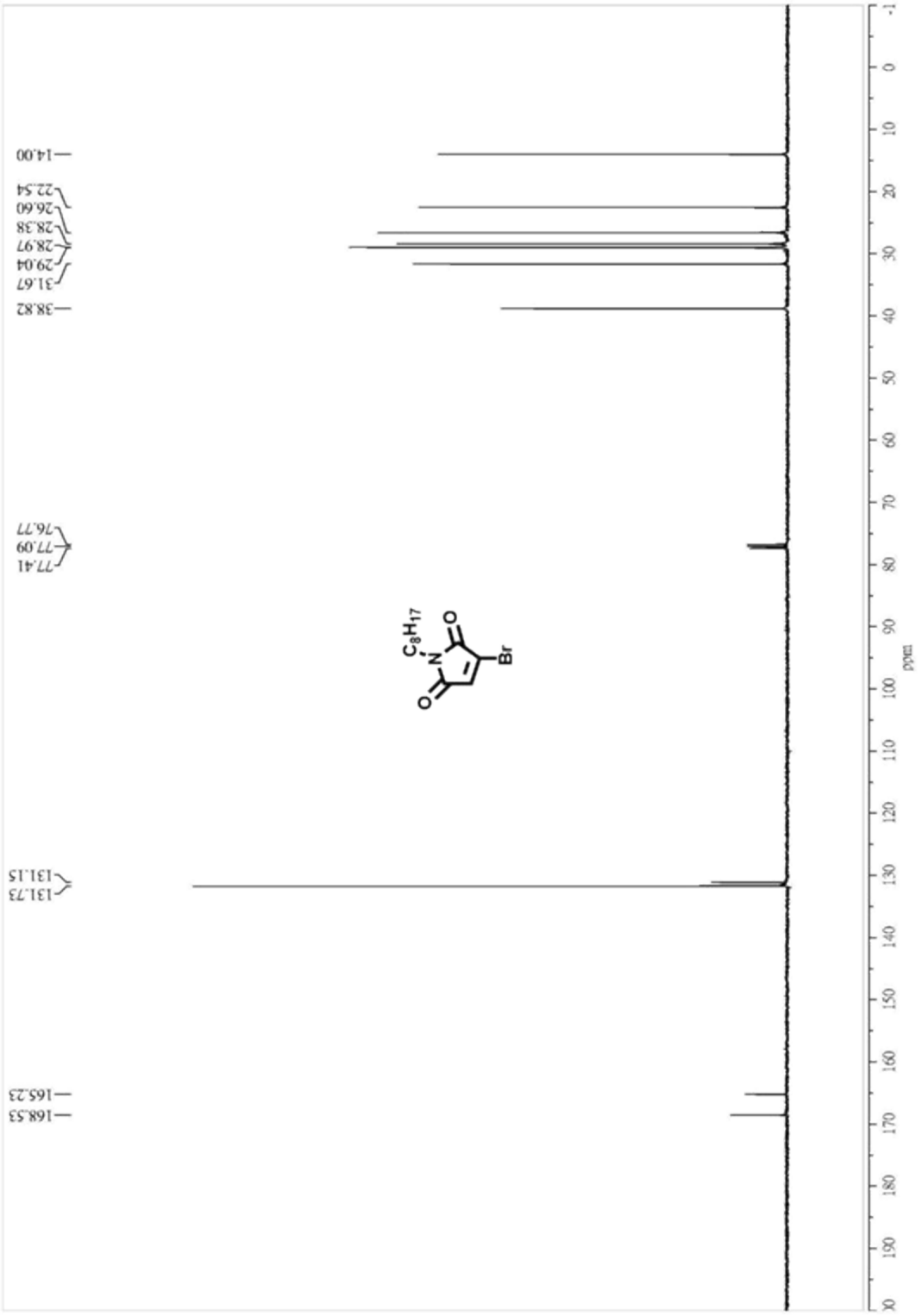


Fig. S8 Compound **2a** ^{13}C NMR spectrum

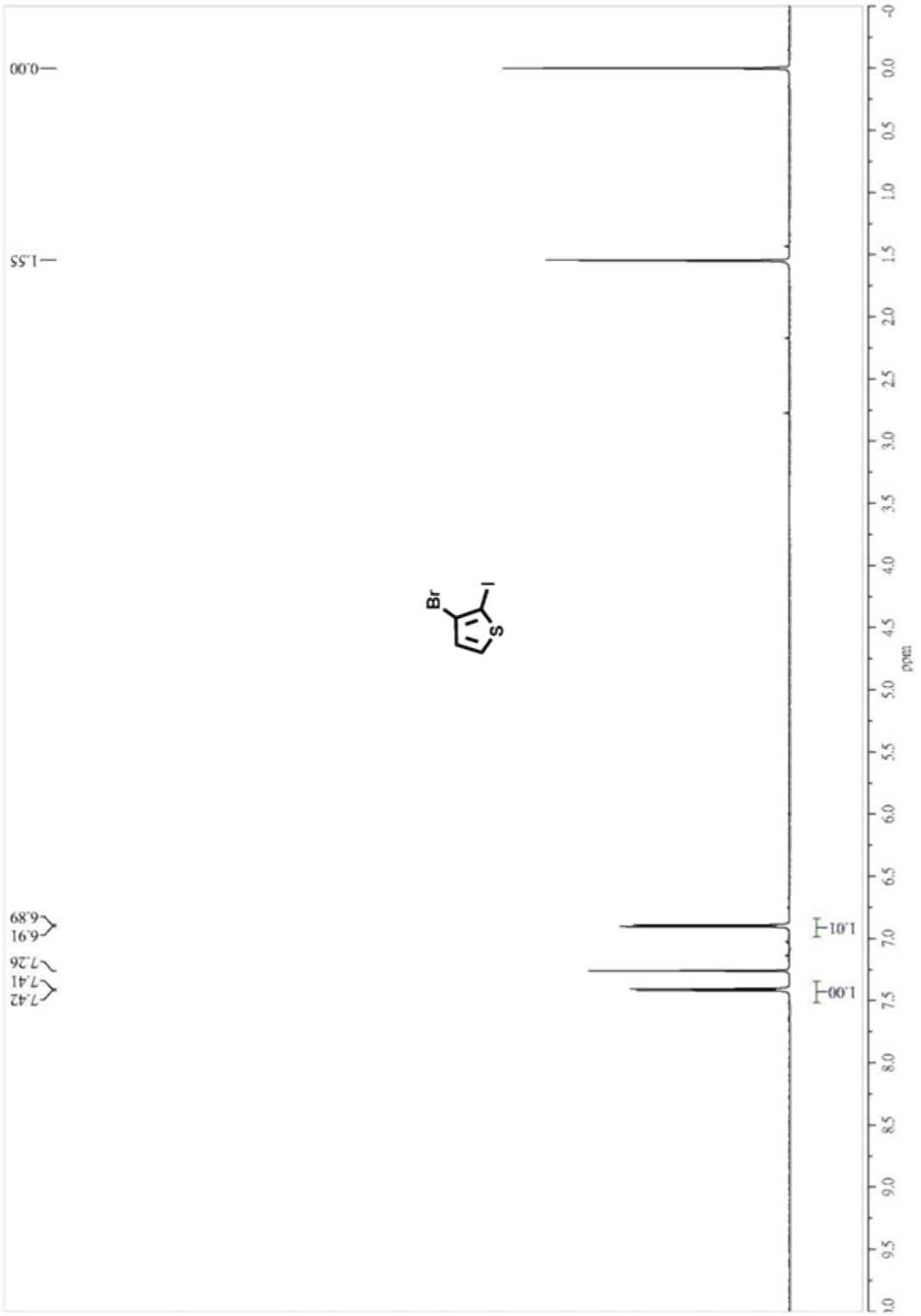


Fig. S9 Compound **3** ^{1}H NMR spectrum

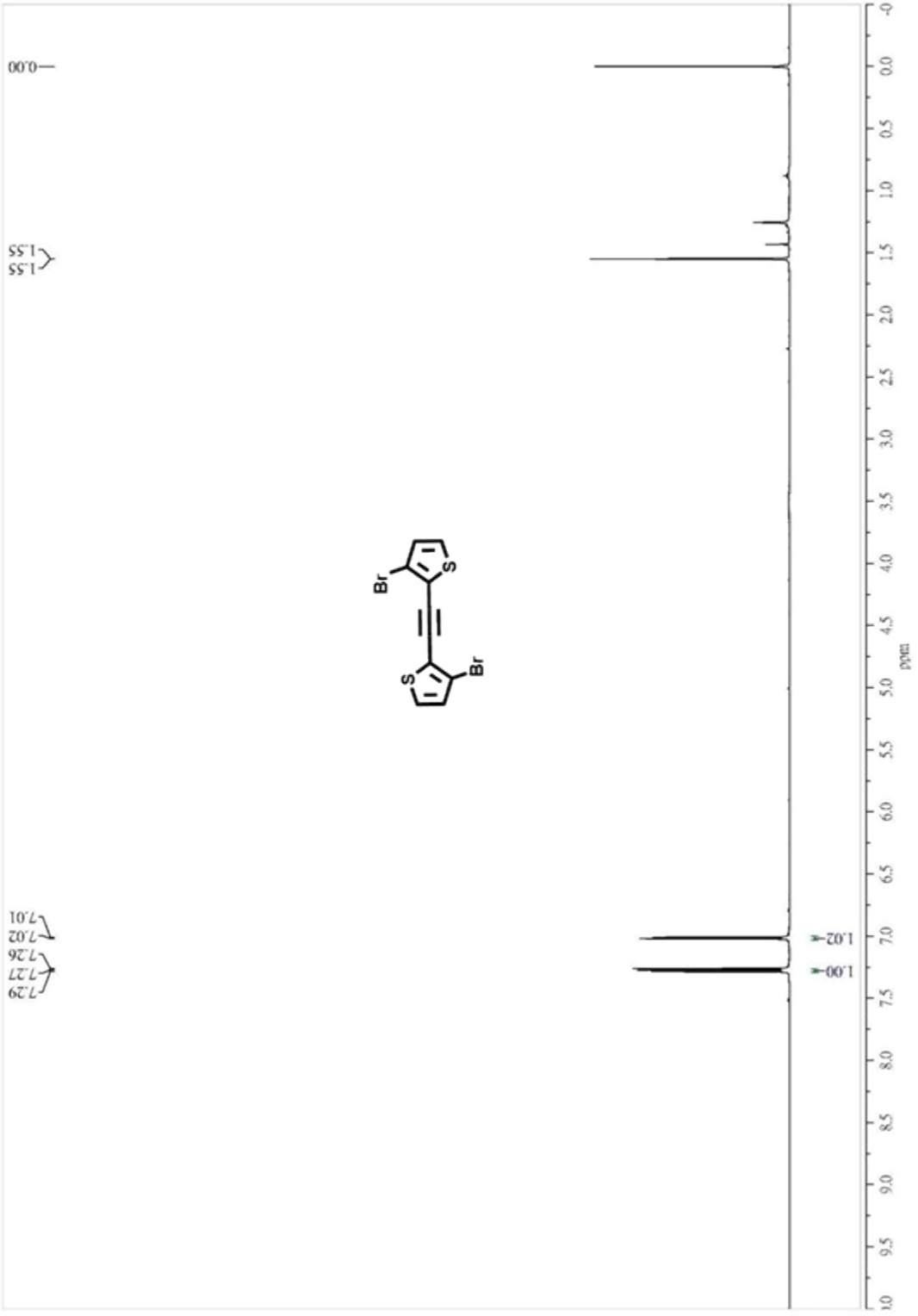


Fig. S10 Compound **4** ^{1}H NMR spectrum

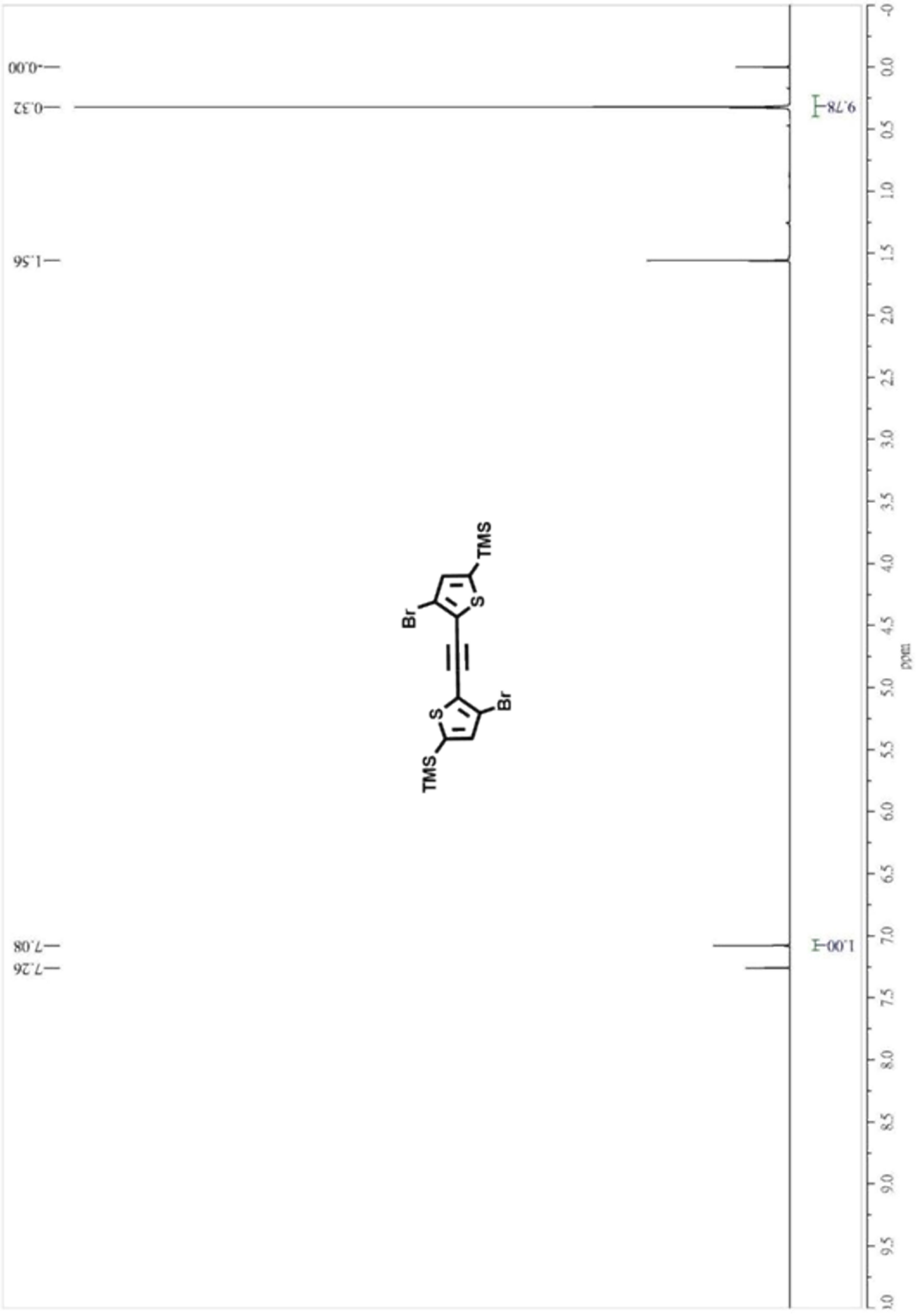


Fig. S11 Compound **5** ^{1}H NMR spectrum

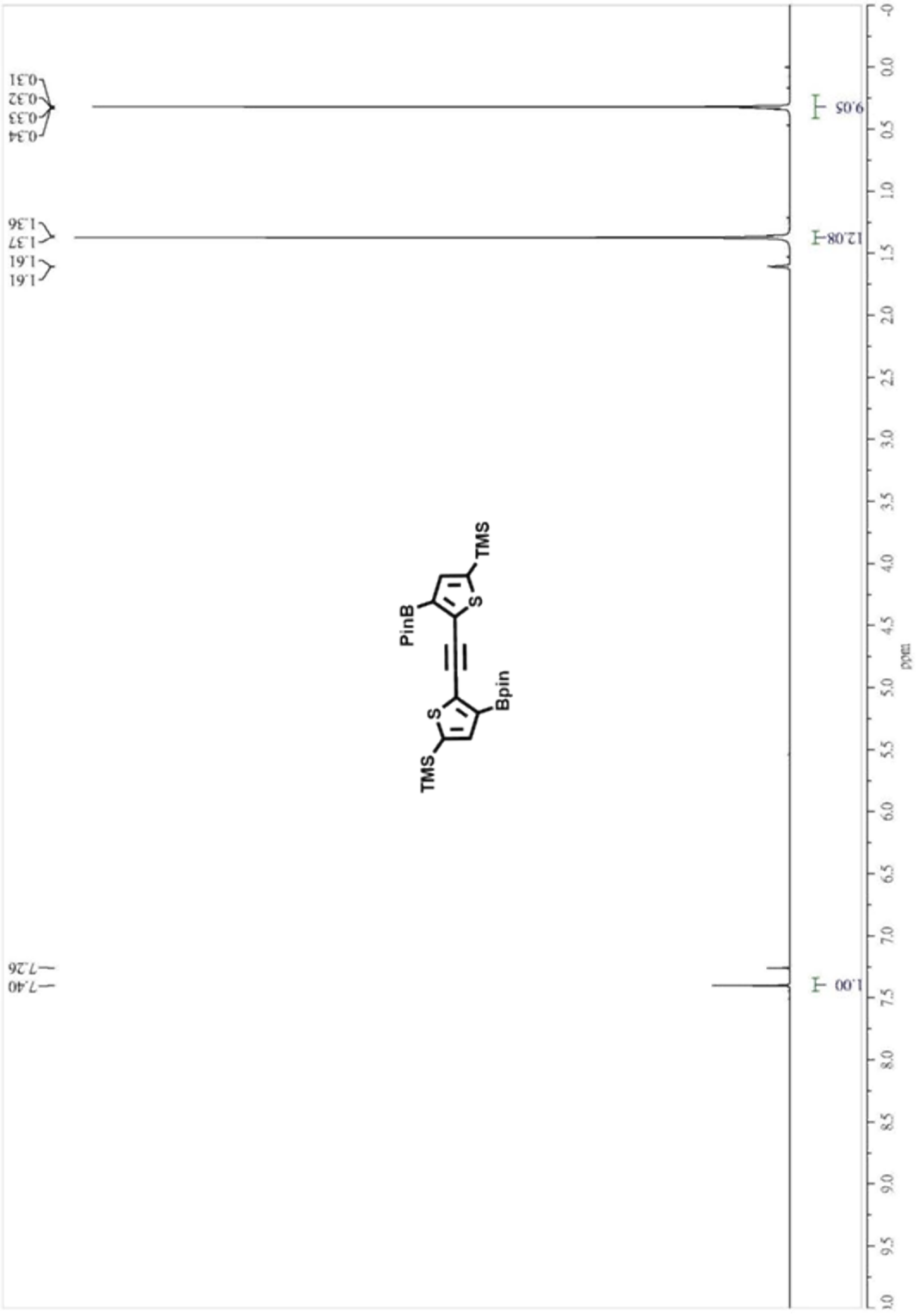


Fig. S12 Compound **6** ^{1}H NMR spectrum

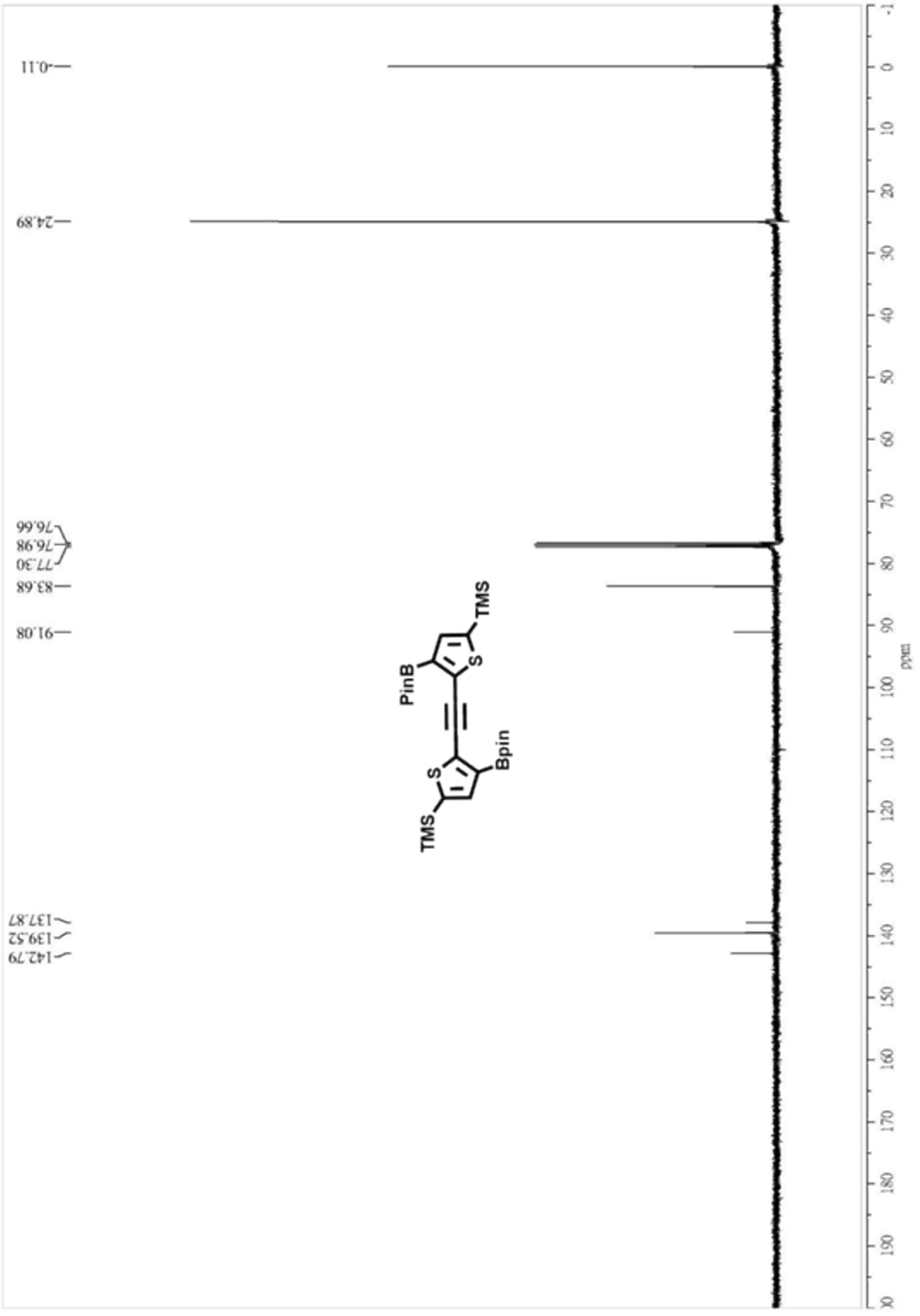


Fig. S13 Compound **6** ^{13}C NMR spectrum

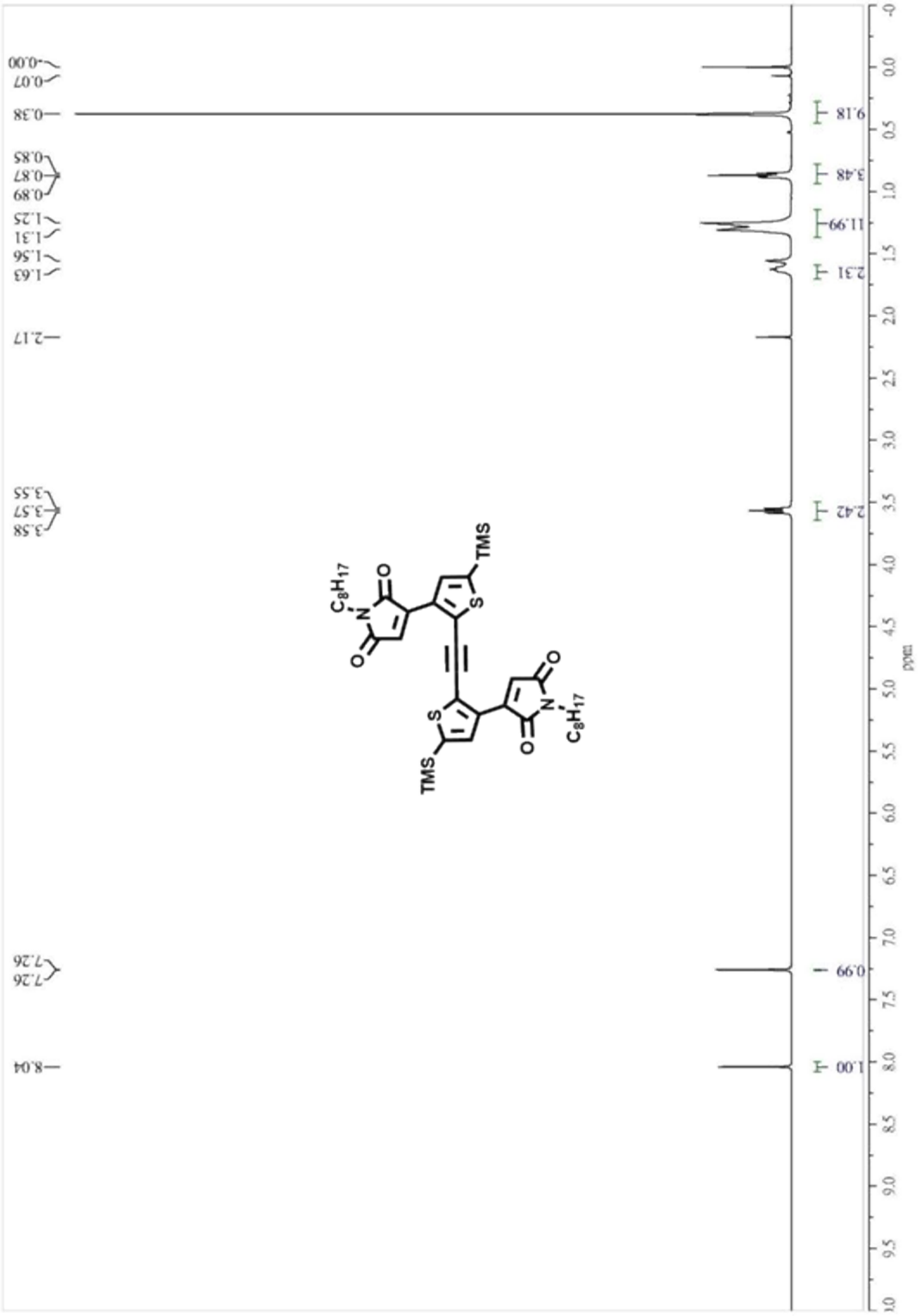


Fig. S14 Compound **7a** ^{1}H NMR spectrum

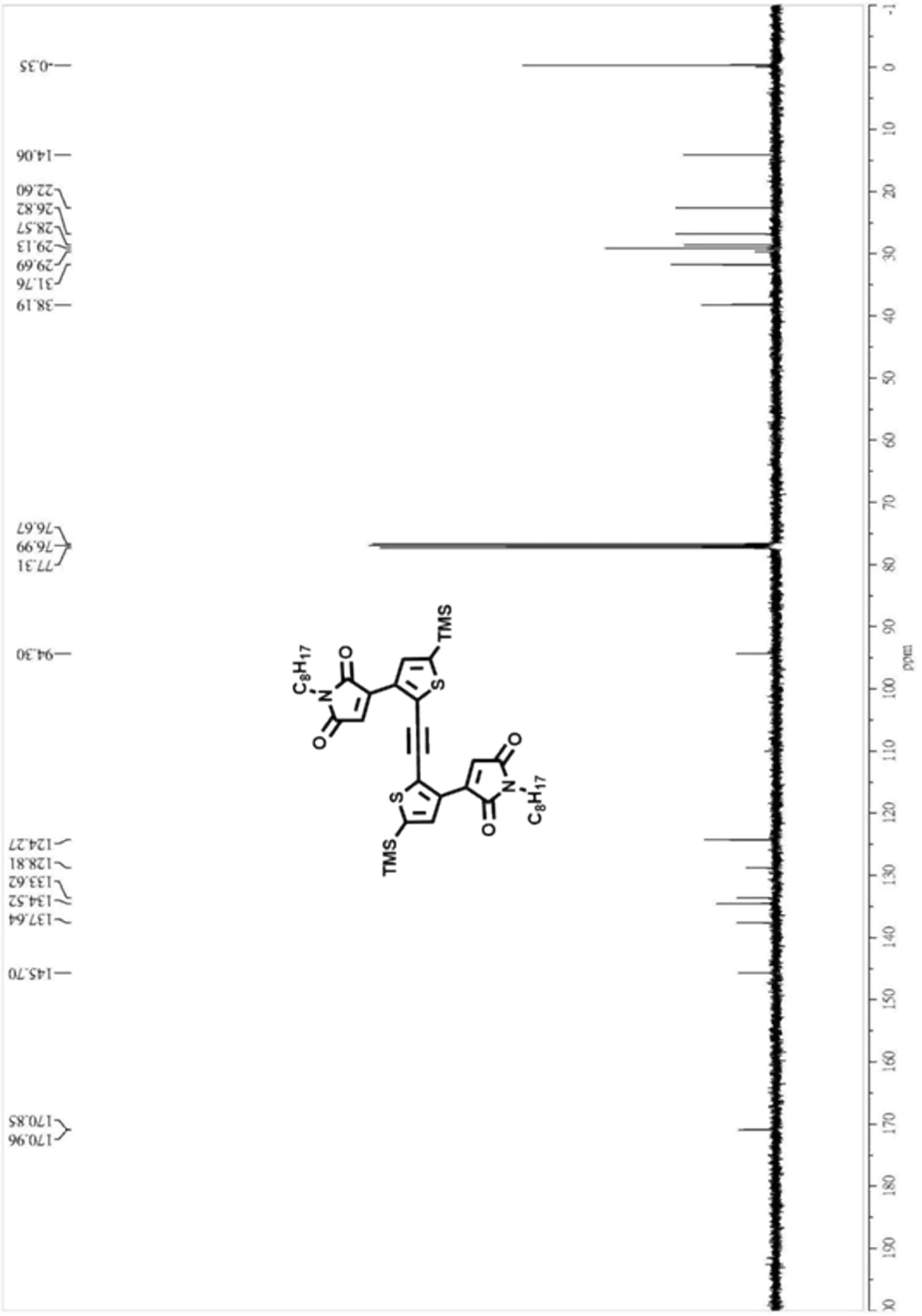


Fig. S15 Compound **7a** ^{13}C NMR spectrum

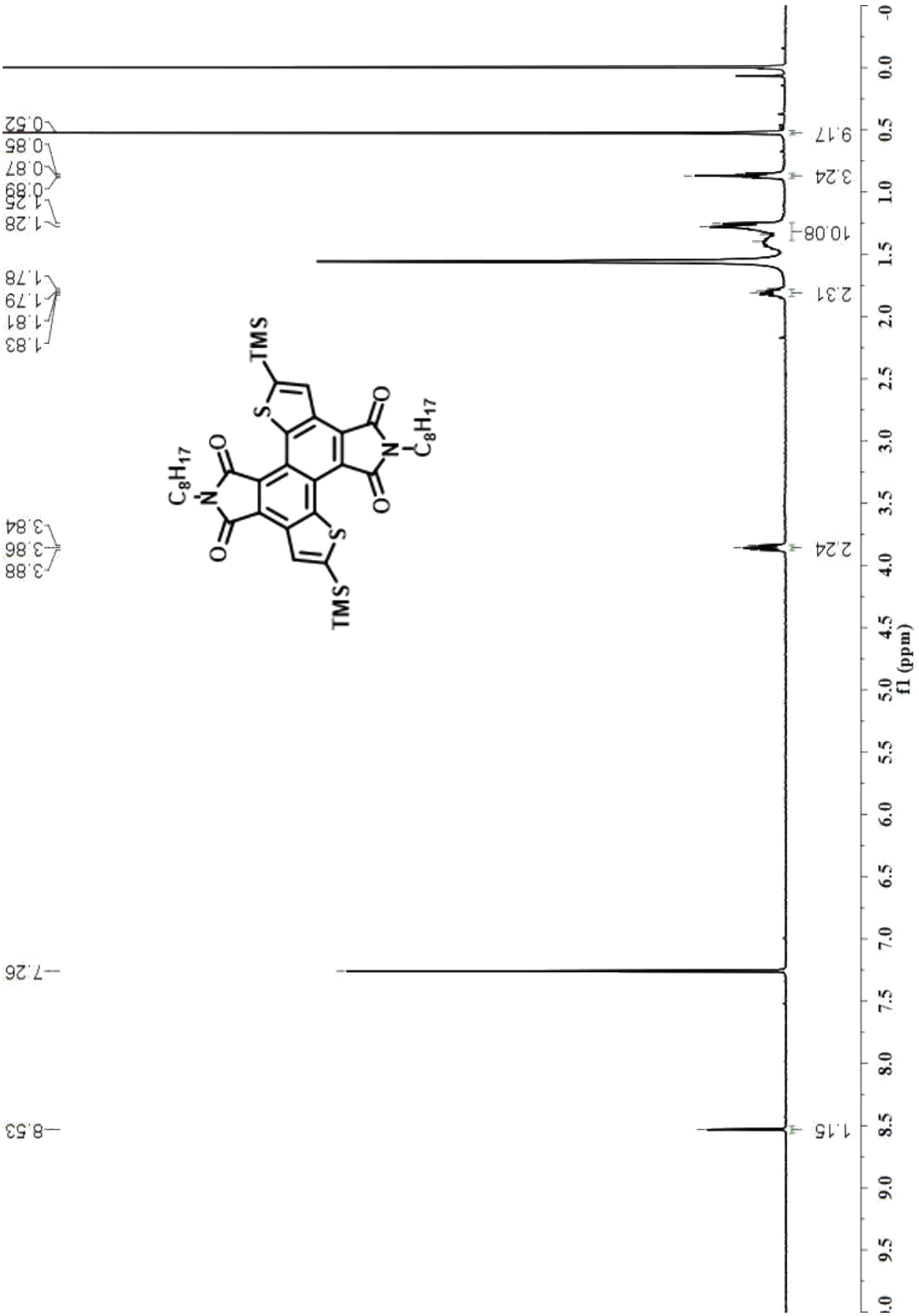


Fig. S16 **TMS-aNDTI-C_8** ^{1}H NMR spectrum

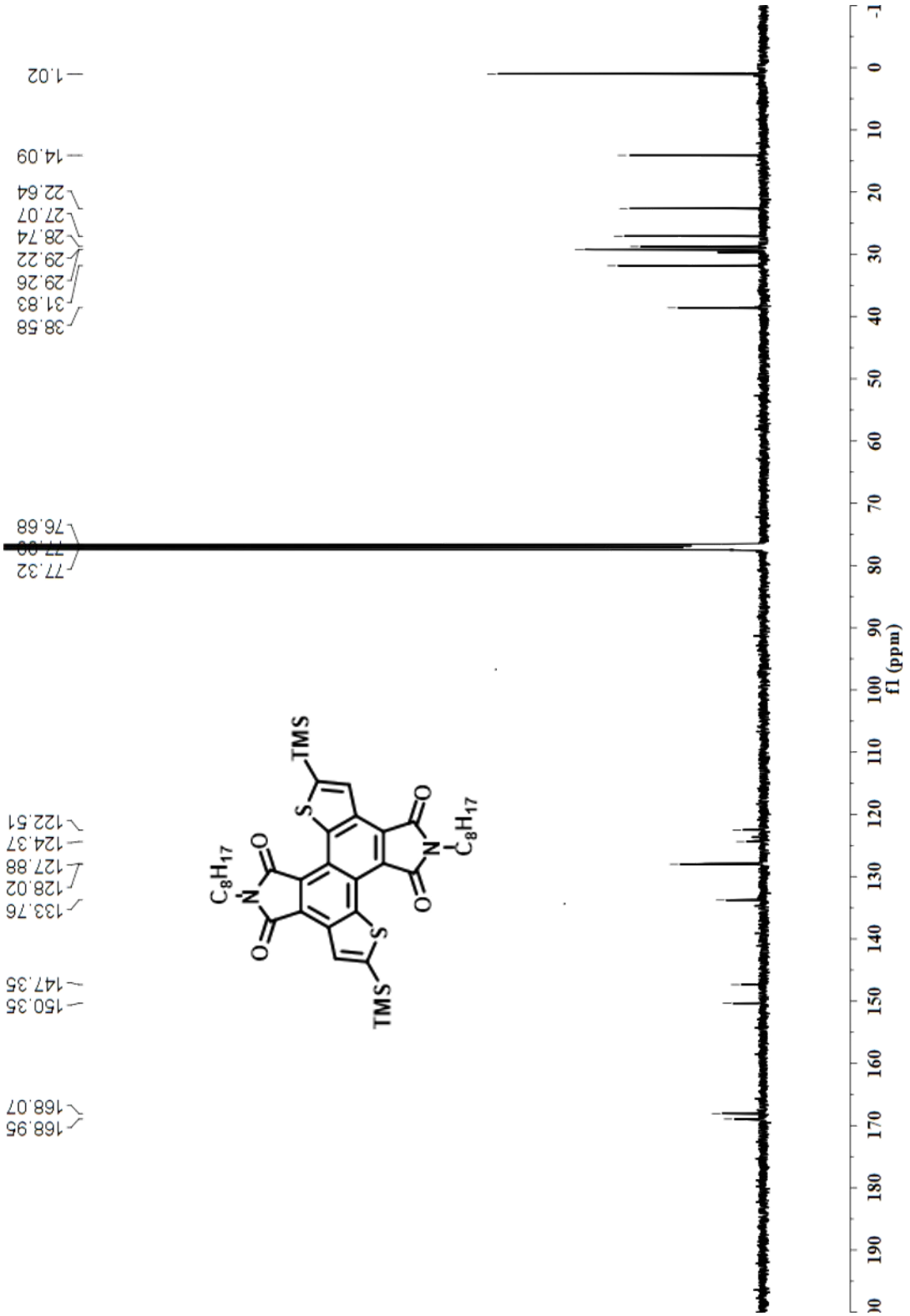


Fig. S17 **TMS-aNDTI-C_8** ^{13}C NMR spectrum

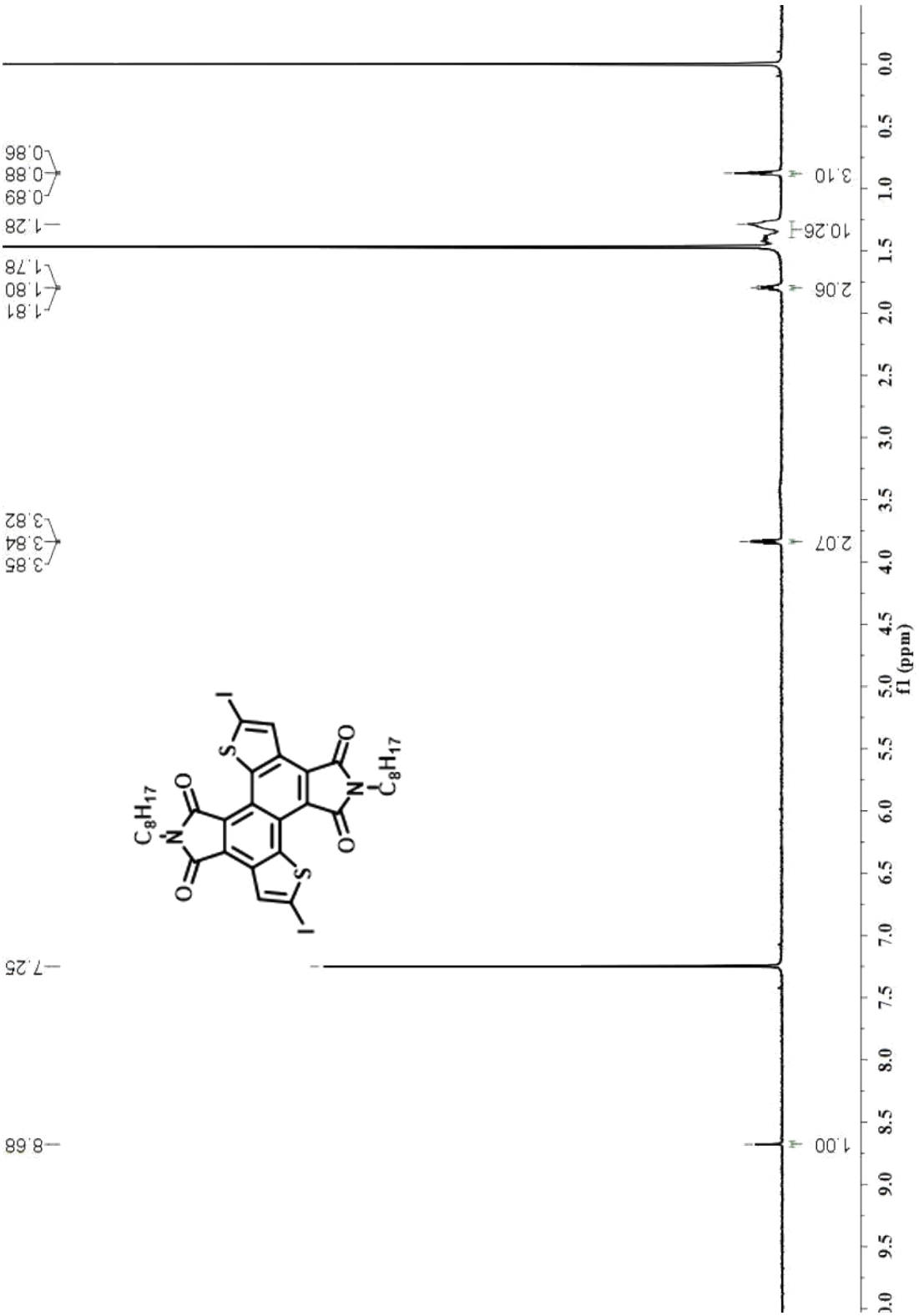


Fig. S18 **I-aNDTI-C_8** ^{1}H NMR spectrum

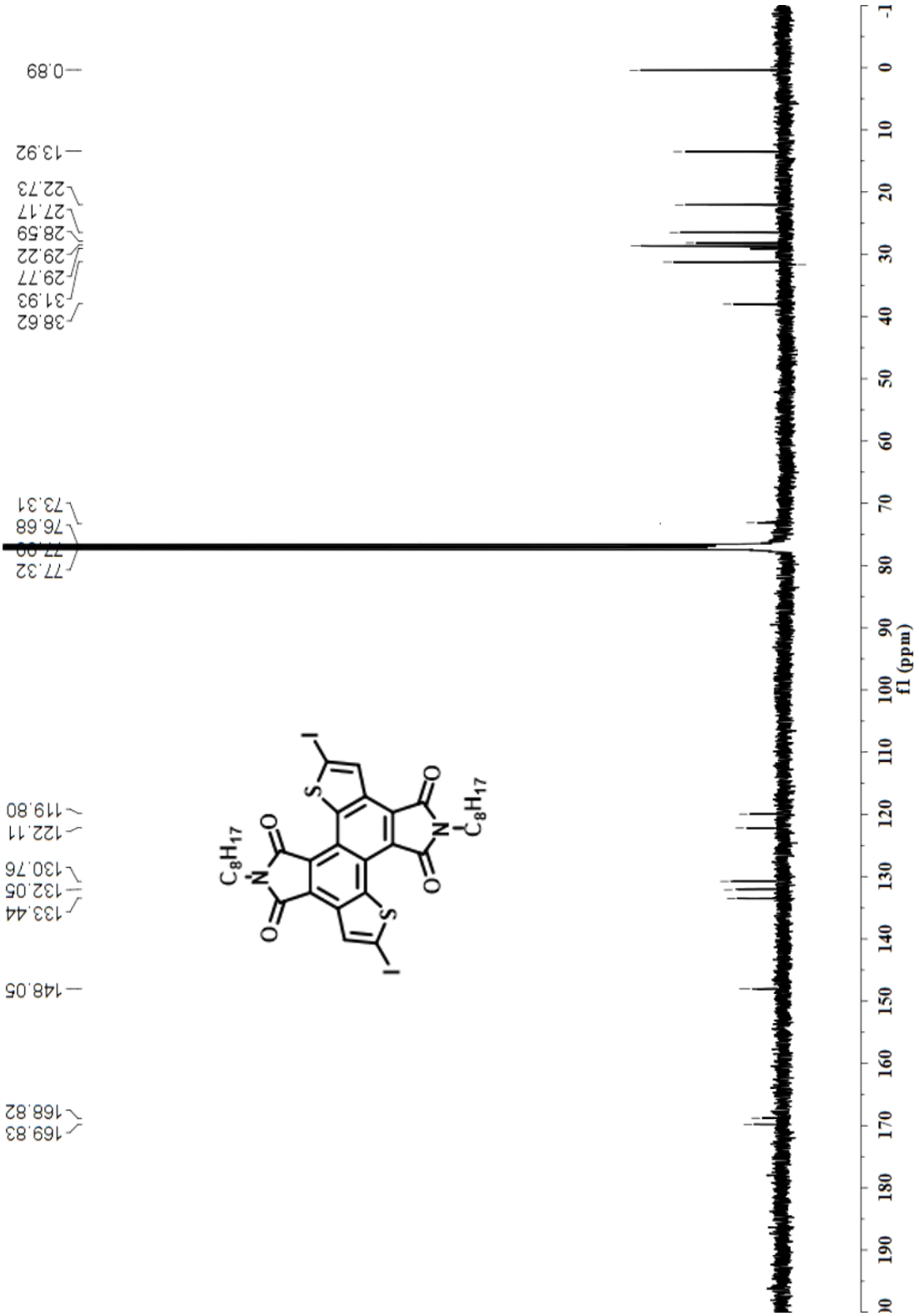


Fig. S19 **I-aNDTI-C_8** ^{13}C NMR spectrum

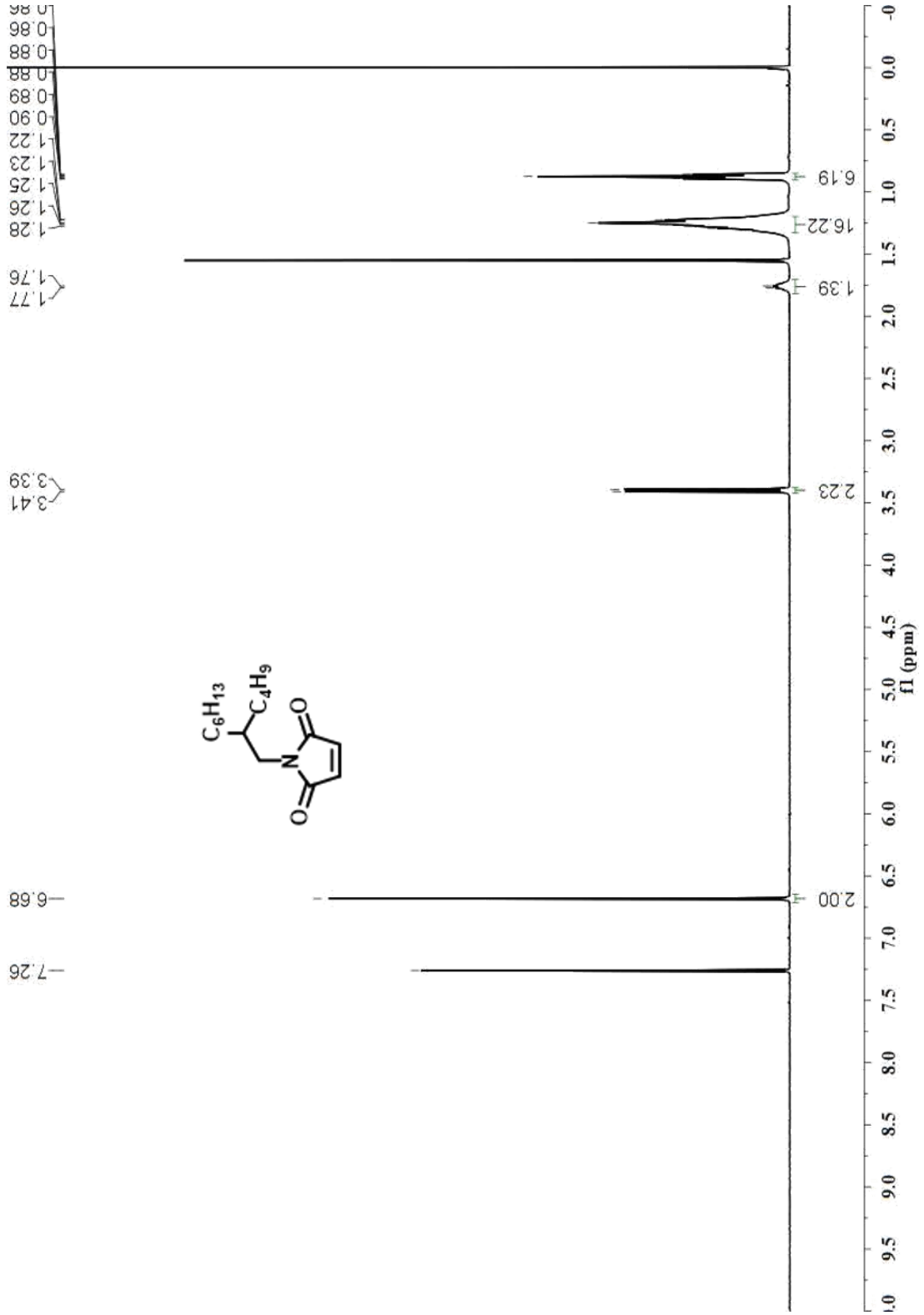


Fig. S20 Compound **1b** ^{1}H NMR spectrum

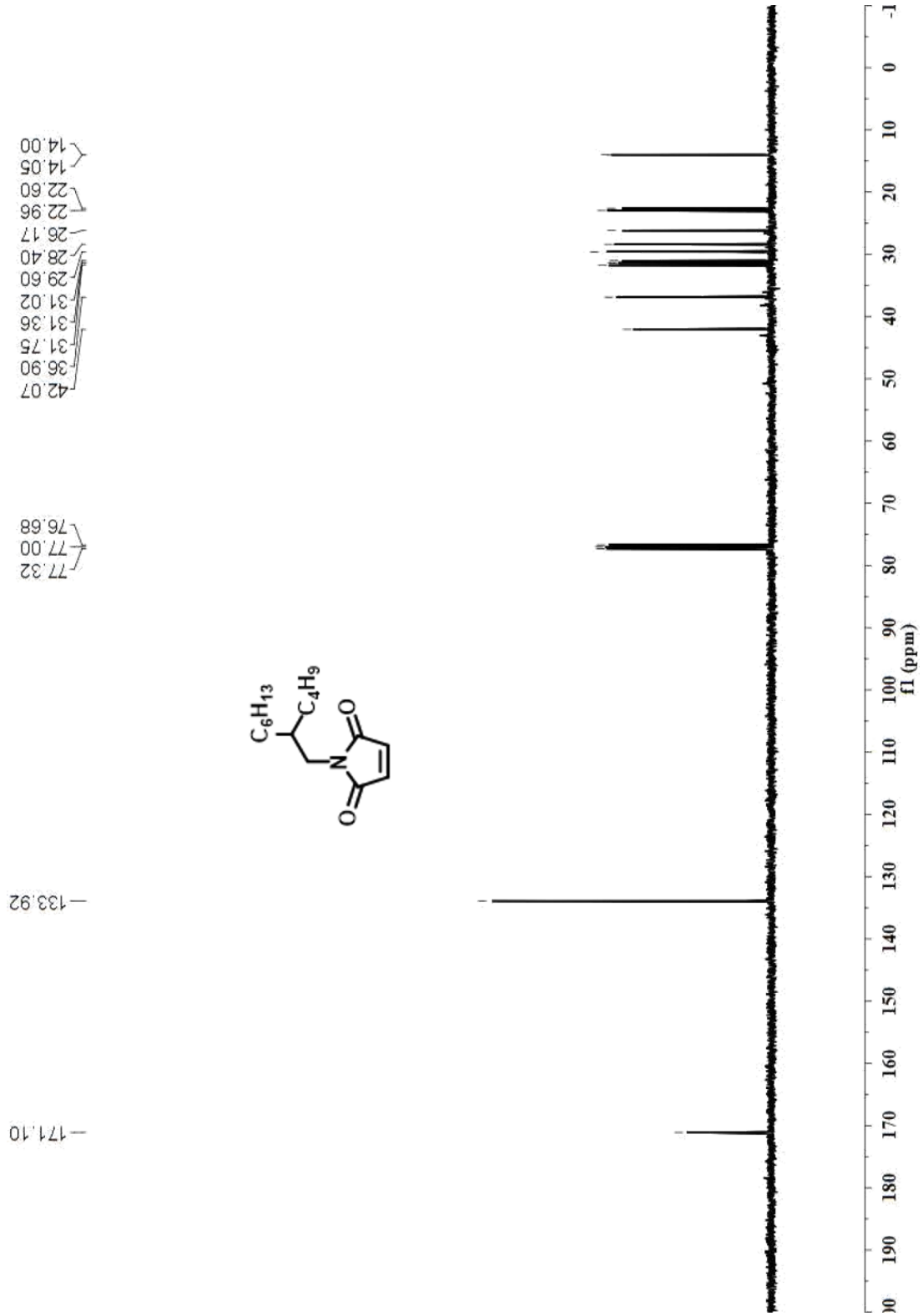


Fig. S21 Compound **1b** ^{13}C NMR spectrum

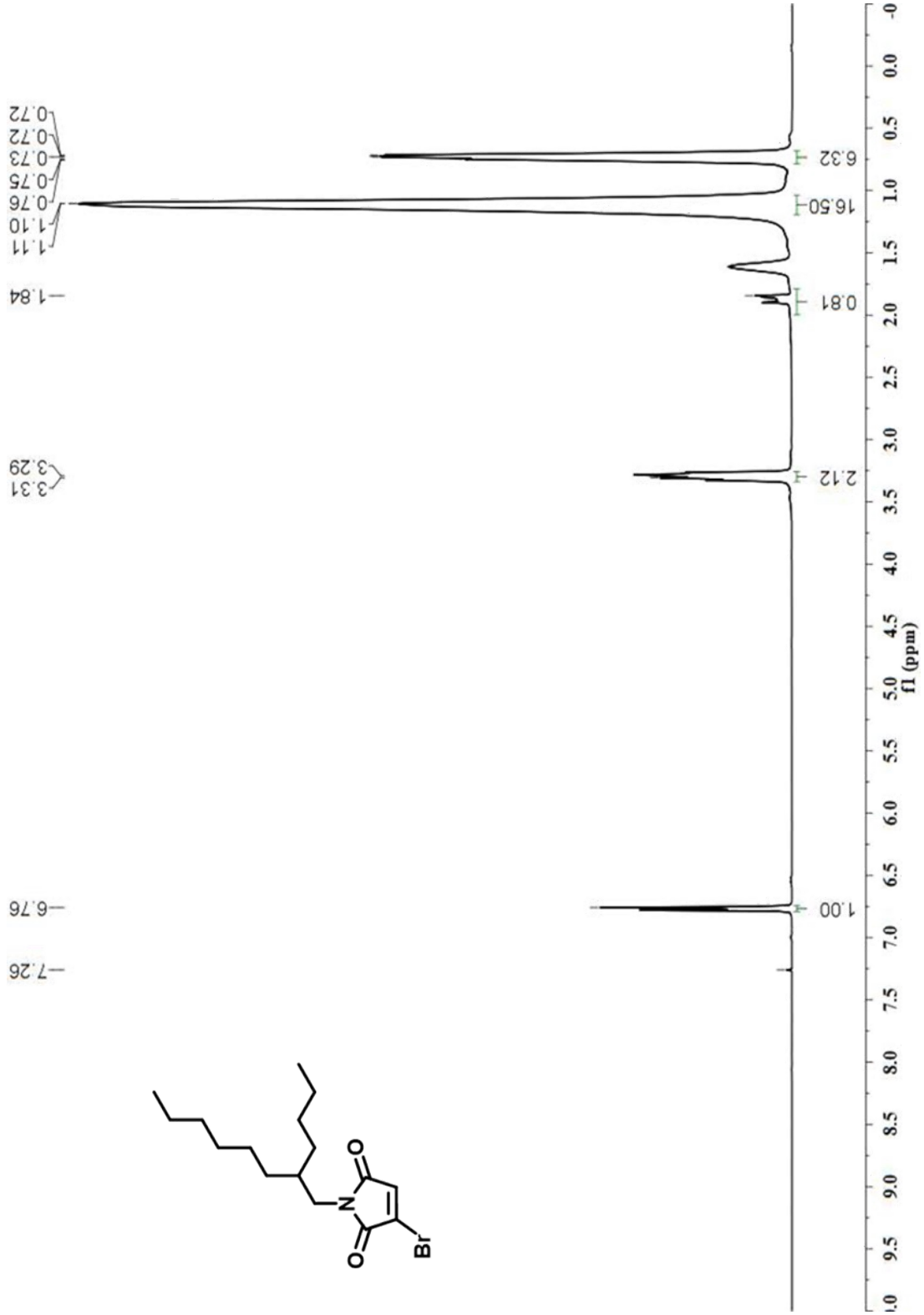


Fig. S22 Compound **2b** ^{1}H NMR spectrum

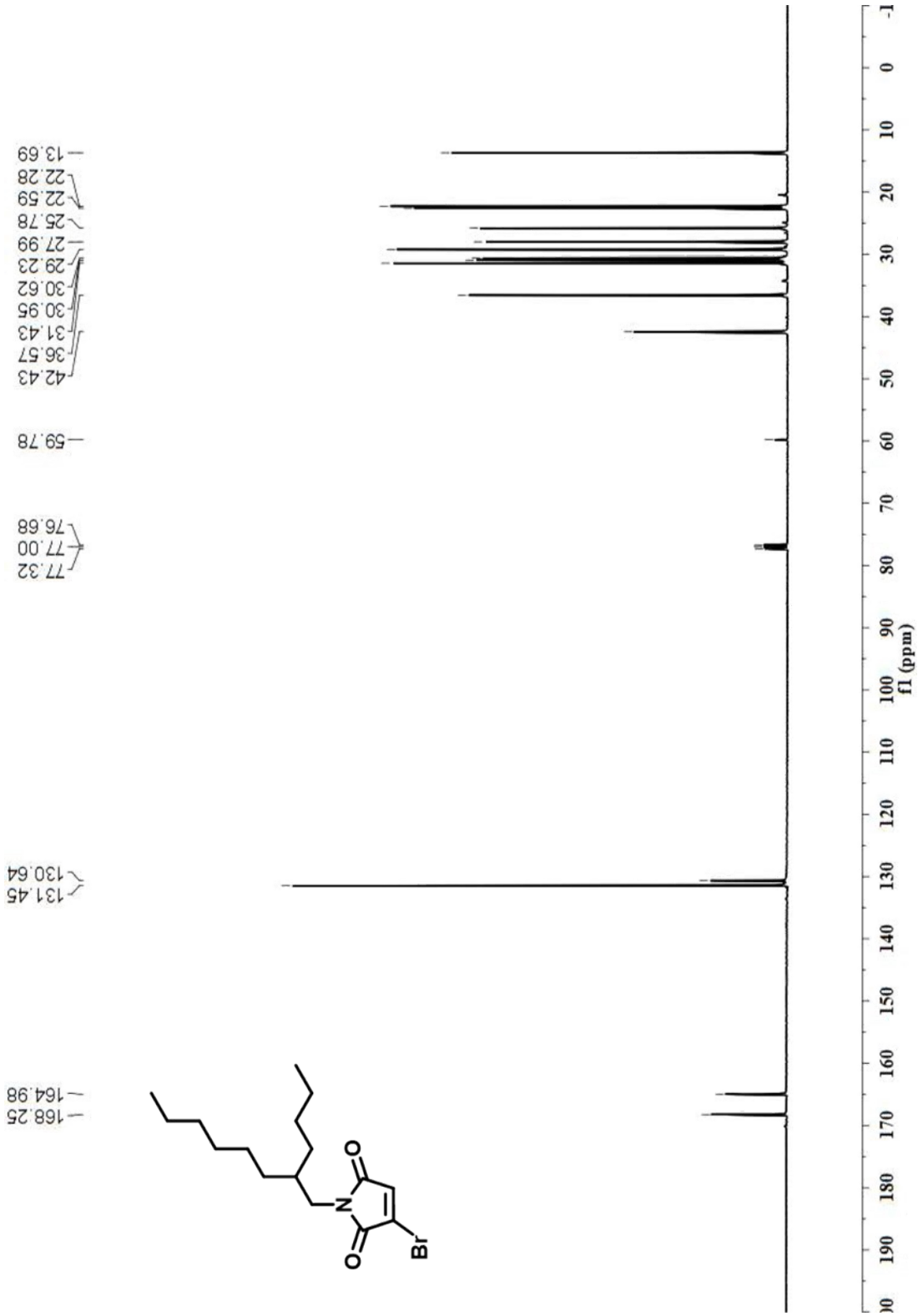


Fig. S23 Compound **2b** ^{13}C NMR spectrum

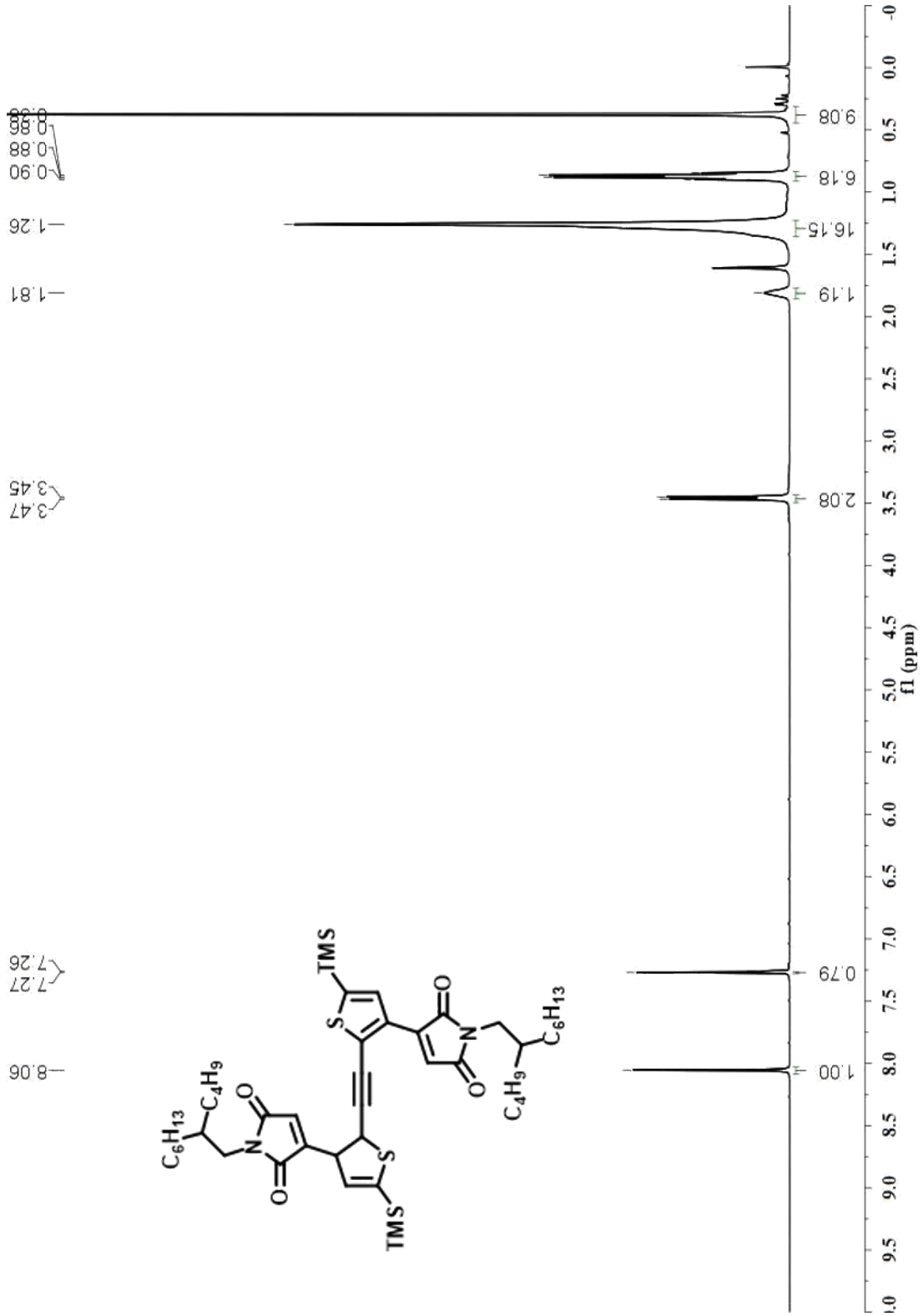


Fig. S24 Compound **7b** ^{1}H NMR spectrum

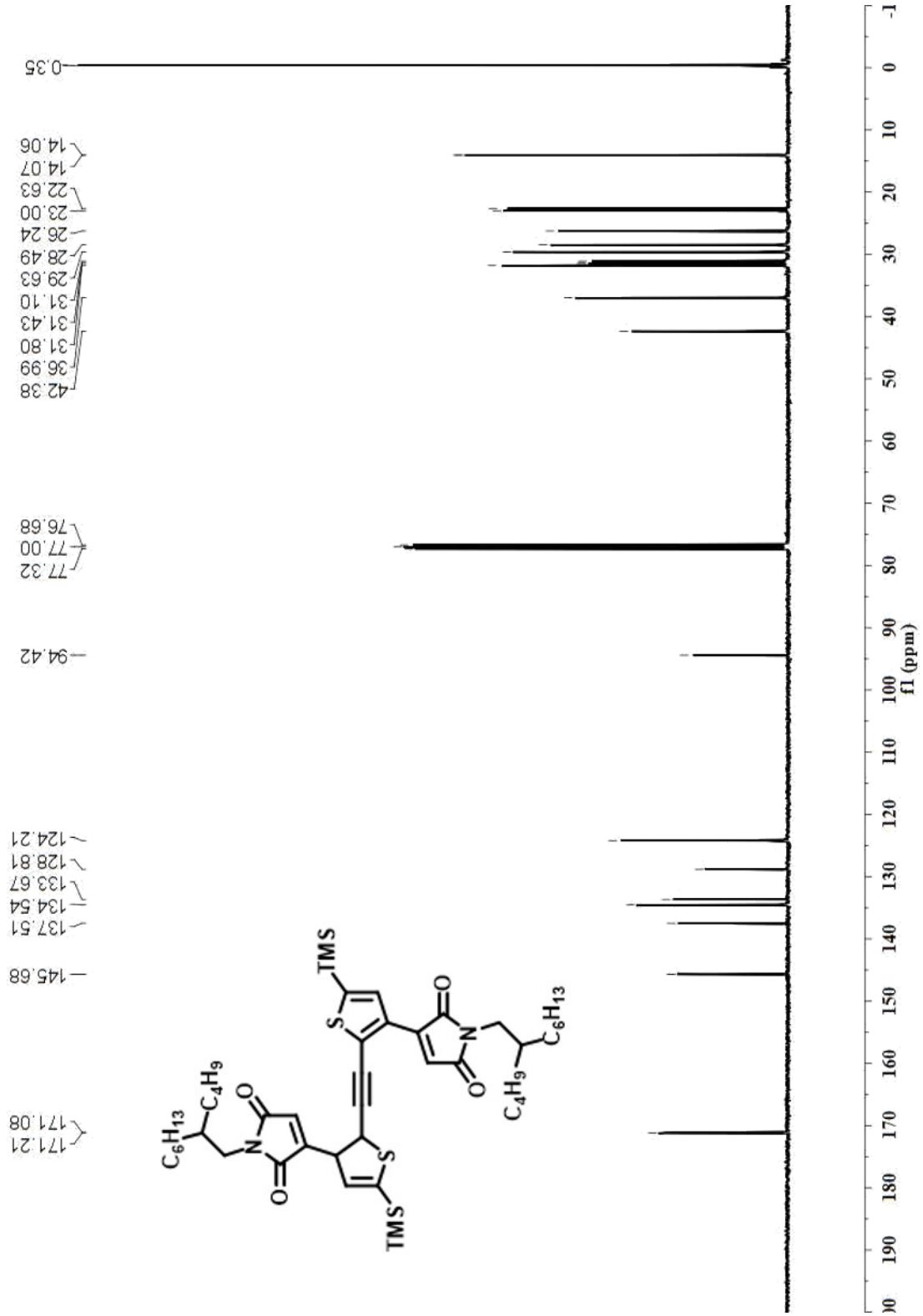


Fig. S25 Compound **7b** ^{13}C NMR spectrum

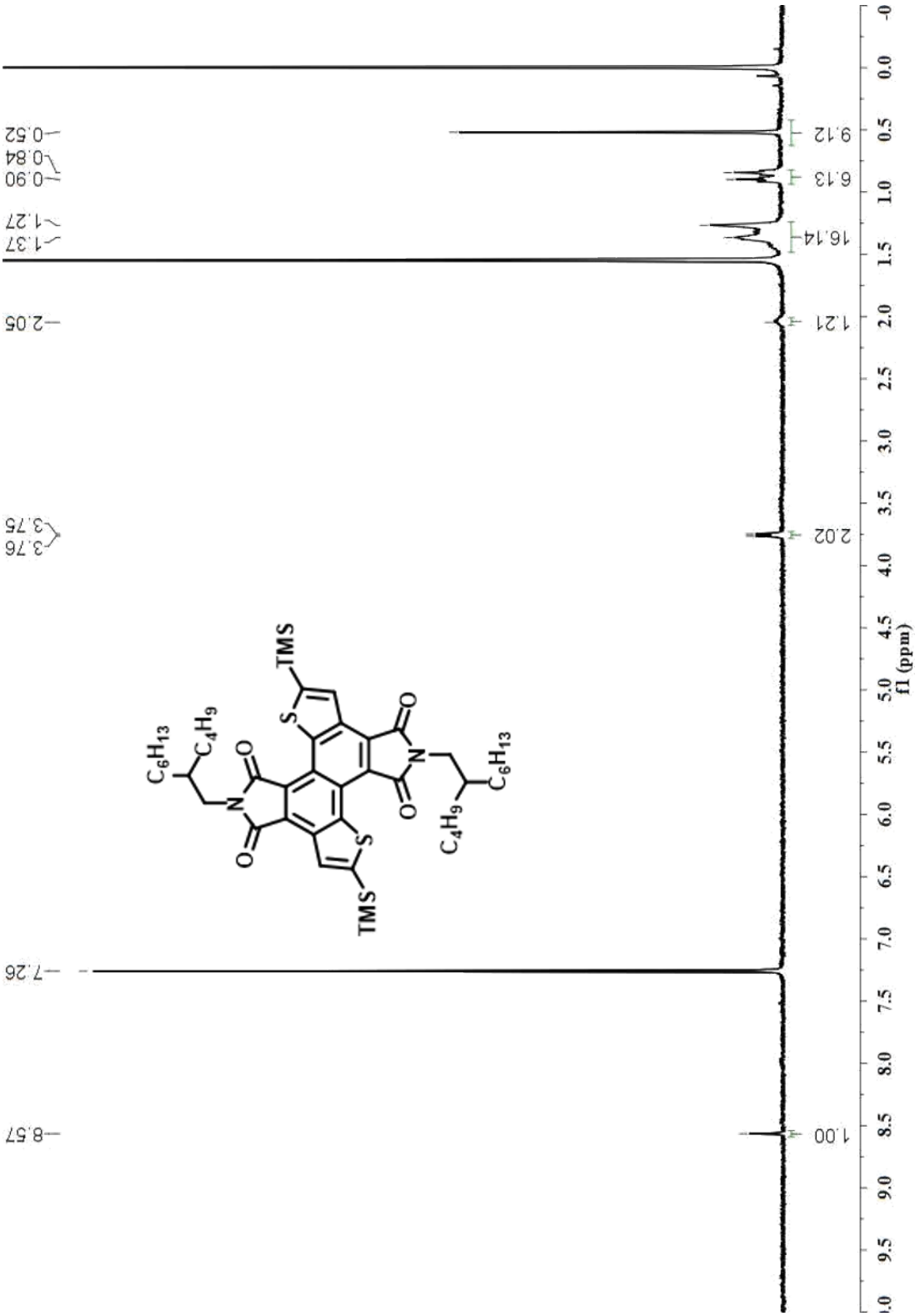


Fig. S26 **TMS-aNDTI-C_8C_4** ^{1}H NMR spectrum

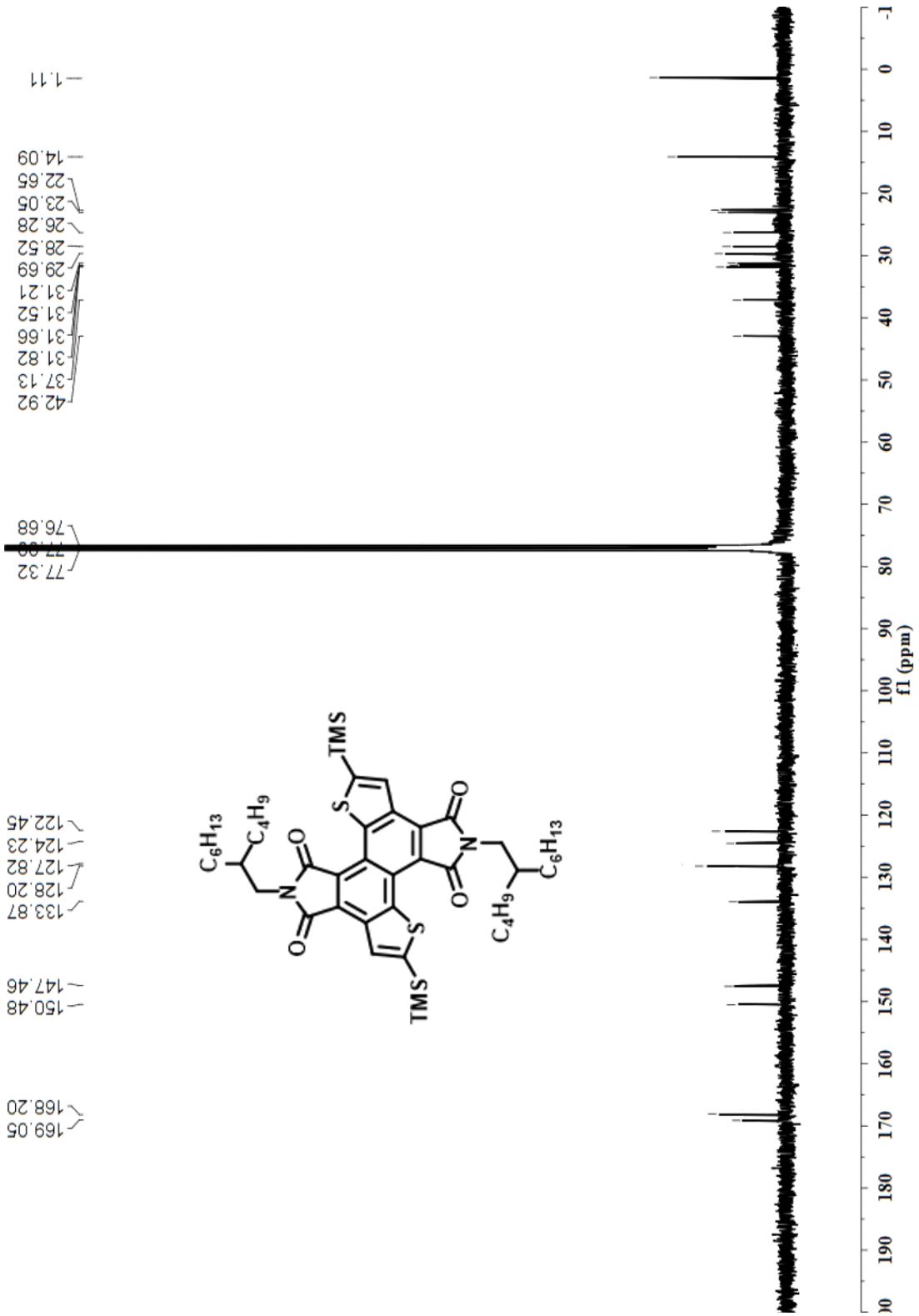


Fig. S27 **TMS-aNDTI-C_8C_4** ^{13}C NMR spectrum

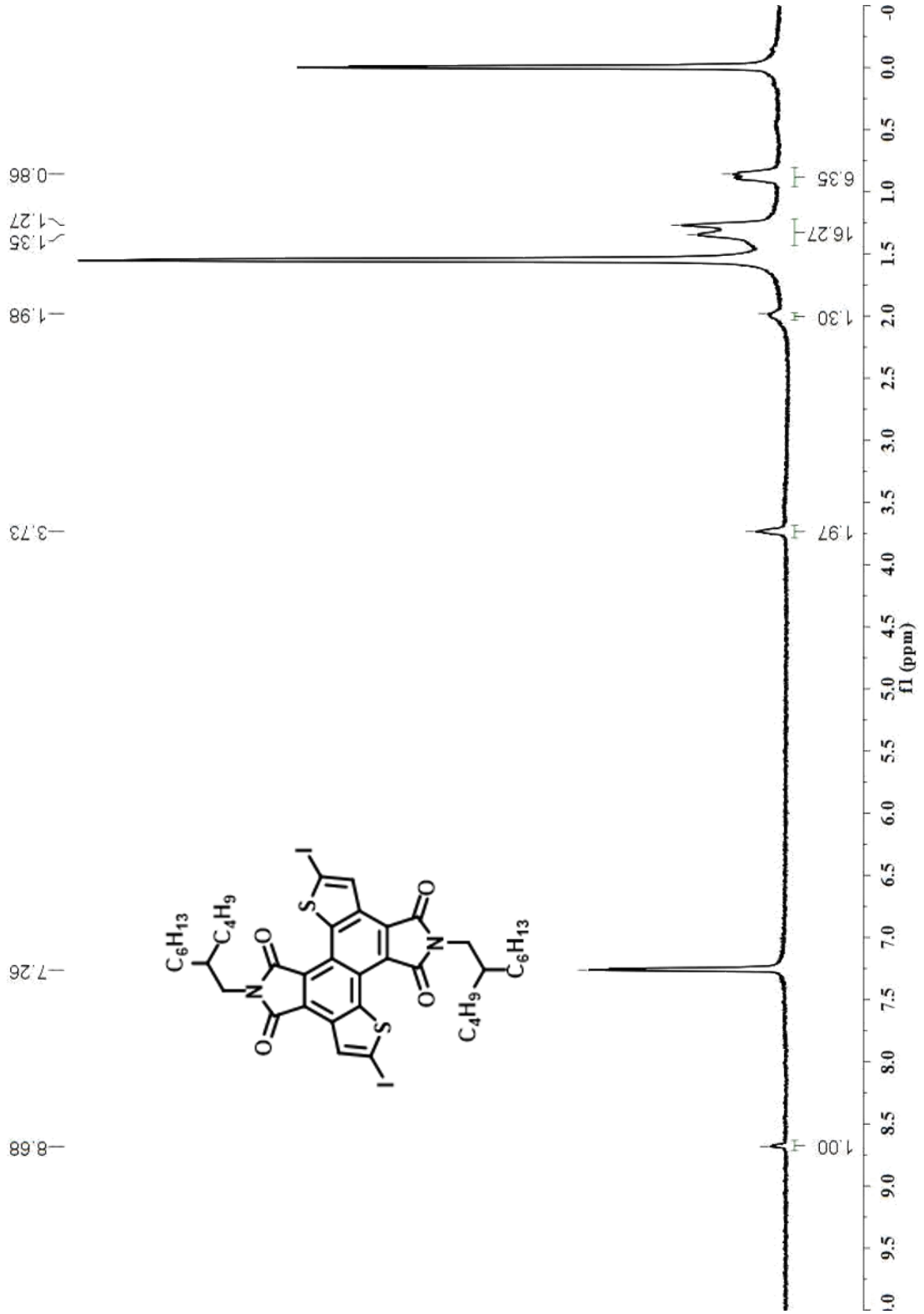


Fig. S28 **I-aNDTI-C_8C_4** ^{1}H NMR spectrum

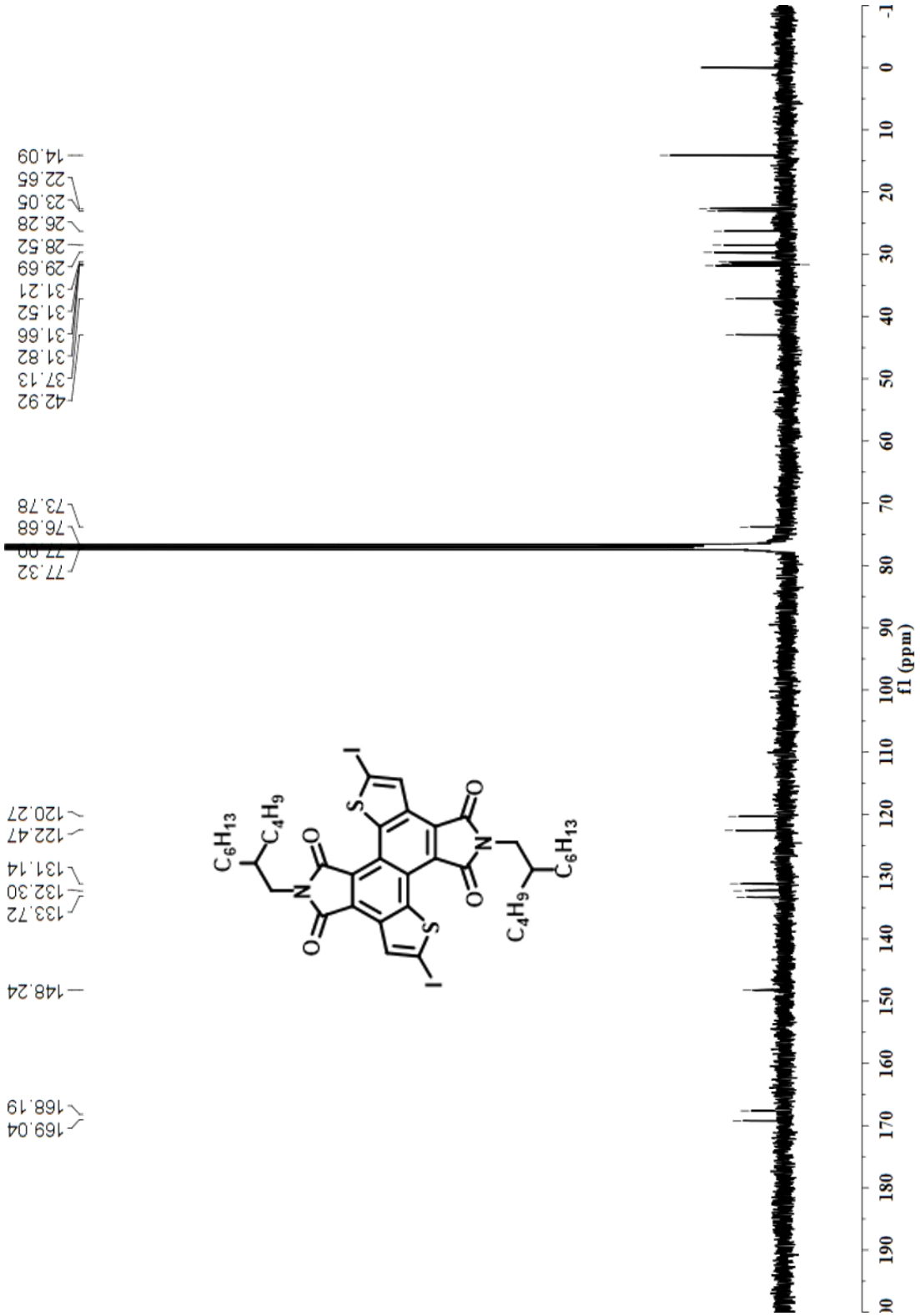


Fig. S29 **I-aNDTI-C_8C_4** ^{13}C NMR spectrum

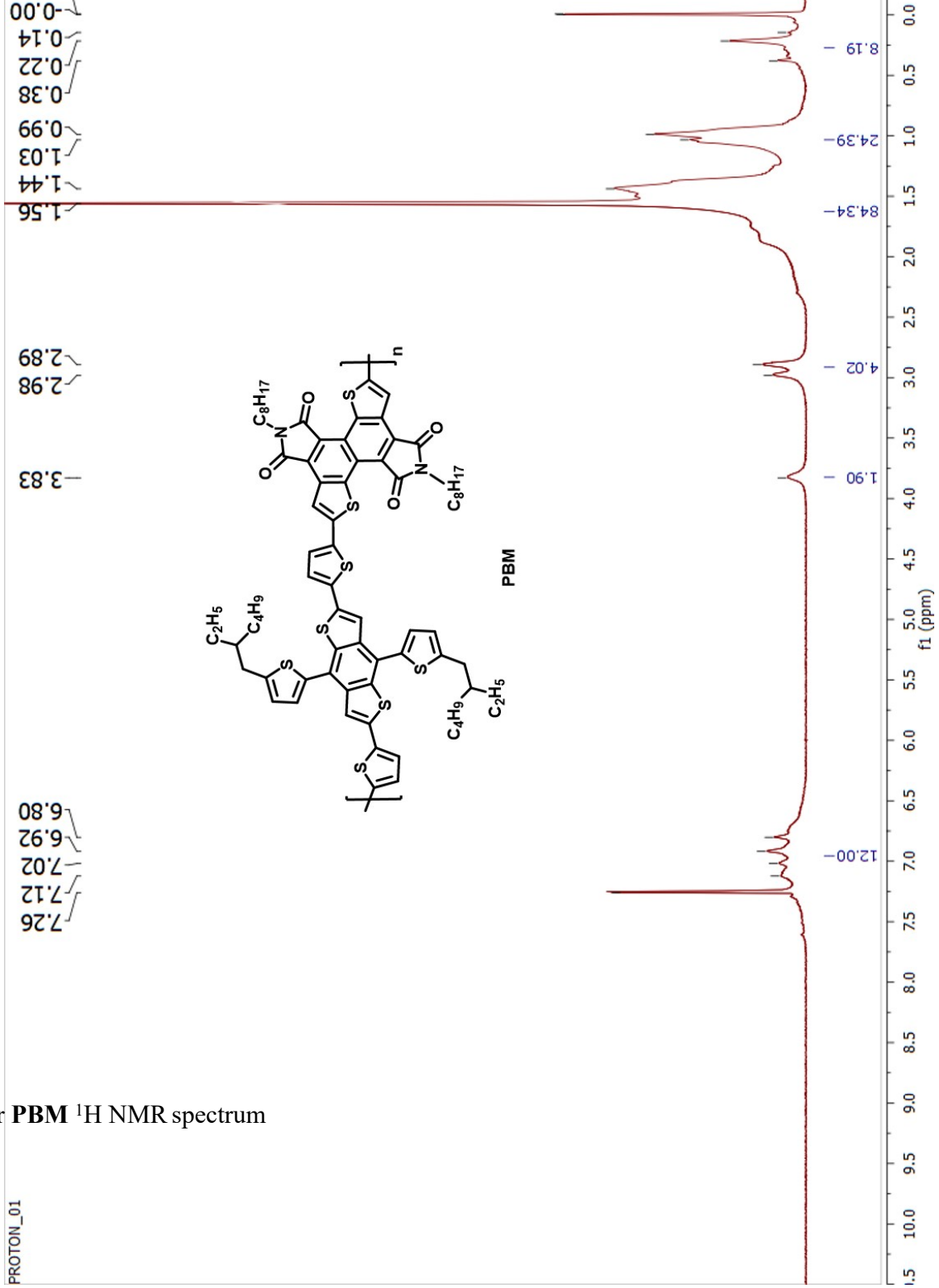


Fig. S30 Polymer **PBM** ^{1}H NMR spectrum

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