Supplementary Information

Diindenothieno[3,2-*b*]thiophene Arene for Efficient Organic Photovoltaics with an Extra High Open-Circuit Voltage of 1.14 eV

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General Measurement and Characterization. All chemicals are purchased from Aldrich or Acros and used as received unless otherwise specified. ^{1}H and ^{13}C NMR spectra were measured using a Varian 300 MHz instrument spectrometer. Differential scanning calorimeter (DSC) was measured on a TA Q200 Instrument and thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Pyris under nitrogen atmosphere at a heating rate of 10 °C/min. Absorption spectra were collected on a HP8453 UV-vis spectrophotometer. The molecular weight of polymers were measured by the GPC method on a Viscotek VE2001 GPC, and polystyrene was used as the standard (THF as the eluent). The electrochemical cyclic voltammetry (CV) was conducted on a Autolab ADC 164. A Carbon glass coated with a thin polymer film was used as the working electrode and standard calomel electrode as the reference electrode, while 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in acetonitrile was the electrolyte. CV curves were calibrated using ferrocence as the standard, whose oxidation potential is 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 of polymer were obtained from the equation LUMO = $-(E_{red}{}^{onset} - E_{(ferrocene)}{}^{onset} + 4.8)$ eV. Surface topography was investigated using Veeco Nanoscope 3100 AFM and standard tips (type Tap 300; L, 135 m; FREQ, 300 MHz; k, 40 N/m).

Device Fabrication.

First, ITO/Glass substrates were ultrasonically cleaned sequentially in detergent, water, acetone and *iso*-propanol (IPA). Then, the substrates were covered by a 30 nm thick layer of PEDOT:PSS (Clevios P provided by Stark) by spin coating . After annealing in air at 150 °C during 30 min, the samples were cooled down to room temperature. **PDITTBT** was dissolved in *o*-dichlorobenzene (ODCB) (6 mg/mL) and

$PC_{71}BM$ (purchased from Nano-C) was added to reach the desired ratio. **PDITTDTBT** was dissolved in *o*-dichlorobenzene (ODCB) (6 mg/mL) and $PC_{71}BM$ or DMPCBA was added to reach the desired ratio. The solution was then heated at 100 °C and stirred overnight . Prior to deposition, the solution were filtrated (0.45 μm filters) and the substrates transferred in a glove box. The solution of polymer:$PC_{71}BM$ or DMPCBA was then spin coated to form the active layer. Different spin coating speed were used in order to tune the thickness. After drying, the samples were annealed during 10 min. The detailed processing parameters (spin coating speed; annealing temperature/time) are shown as follows: **PDITTBT**/$PC_{71}BM$ (1200 rpm; 120 ℃/10 min), **PDITTDTBT**/$PC_{71}BM$ (1400 rpm; 130 □/10 min) and **PDITTDTBT**/DMPCBA (1000 rpm; 130 ℃/10 min). The cathode made of calcium (35 nm thick) and Aluminum (100 nm thick) was sequentially evaporated through a shadow mask under high vacuum ($< 10^{-6}$ Torr). Each sample consists of 4 independent pixels defined by an active area of 0.04 cm^2. Finally, the devices were encapsulated and *I-V* curves were measured in air. In order to investigate the hole mobilities of the different polymer films, unipolar devices have been prepared following the same procedure except that the Ca/Al cathode is replaced by evaporated gold (40 nm). The hole mobilities were calculated according to space charge limited current theory (SCLC). The J-V curves were fitted according to the following equation:

$$J = \frac{9}{8}\varepsilon\mu\frac{V^2}{L^3}$$

Where ε is the dielectric permittivity of the polymer, μ is the hole mobility and L is the film thickness (distance between the two electrodes)

TGA measurements.

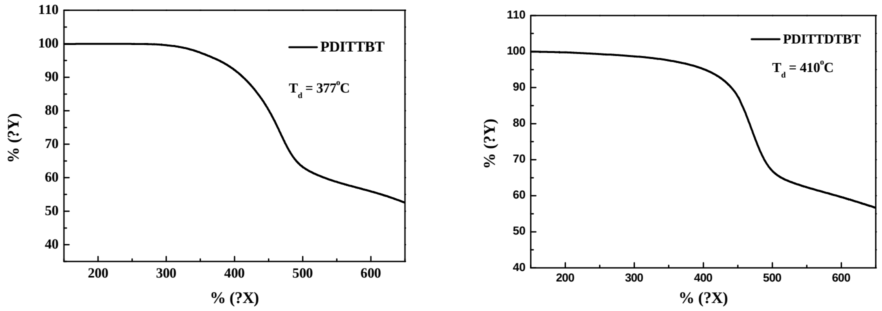


Fig. S1 Thermogravimetric analysis (TGA) of **PDITTBT** (left) and **PDITTDTBT** (right).

DSC Measurements.

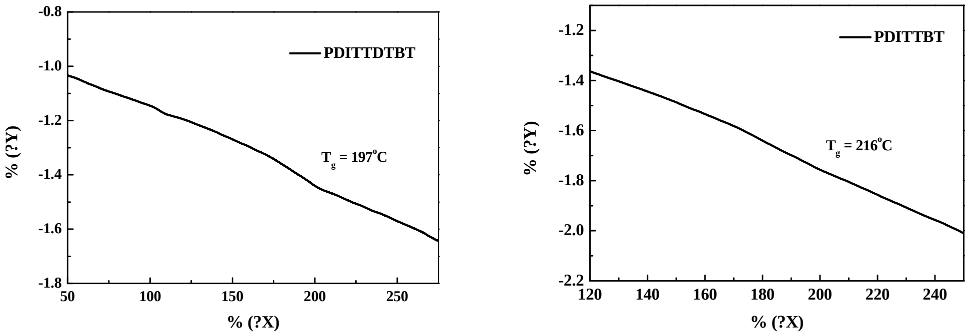


Fig. S2 Differential scanning calorimetry (DSC) of **PDITTBT** and **PDITTDTBT**.

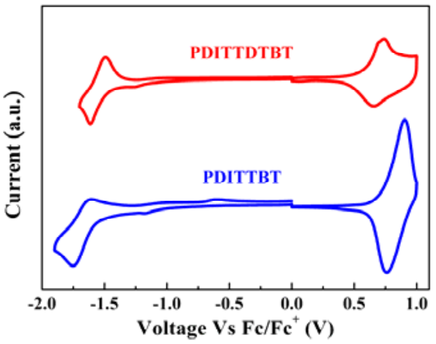


Fig. S3 Cyclic voltammograms of **PDITTBT** and **PDITTDTBT** in the thin film at a scan rate of 80 mV s^{-1}.

Atomic force microscopy images.

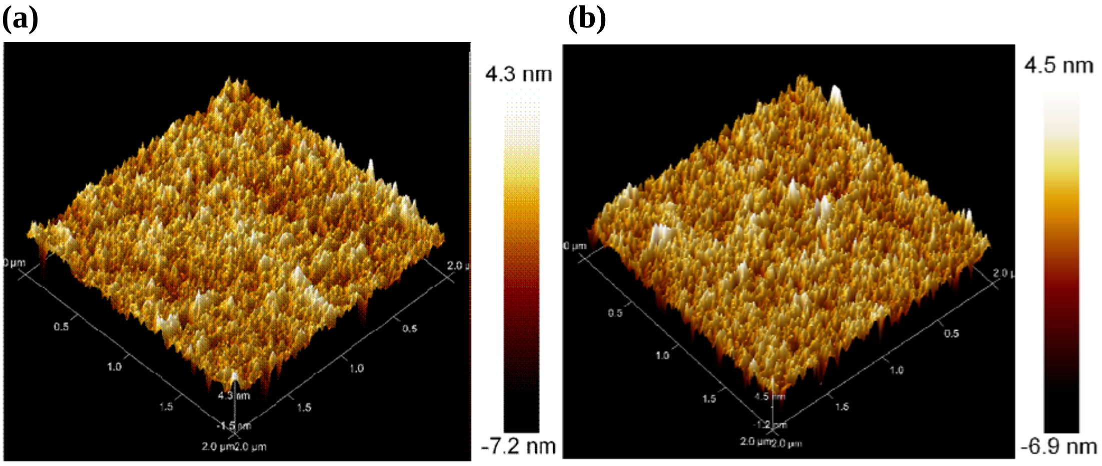


Fig. S4 AFM tapping mode height images of the surface of (a) **PDITTDTBT**/PC$_{71}$BM (1:4, w/w) blend and (b) **PDITTDTBT**/DMPCBA (1:3.5, w/w) blend (2.0 µm × 2.0 µm).

Table S1 Photovoltaic performances of the devices.

Copolymers	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
PDIDTDTBT	0.7	5.3	44	1.65
PDITTBT	0.88	7.46	41.4	2.7
PDITTDTBT	0.92	10.71	58.4	5.8
PDITTDTBT[a]	1.14	8.97	35.5	3.6

[a] The device incorporates **DMPCBA** as the acceptor.

Synthesis of Compound 3. Compound **1**[1] (2.00 g, 4.3 mmol), compound **2** (2.4 g, 10.3 mmol), and $Pd(PPh_3)_4$ (0.25 g, 0.2 mmol) were dissolved in deoxygenated toluene (43 mL). The reaction mixture was refluxed at 130 °C for 16 h. After cooling down to rt, the mixture was extracted with dichloromethane (100 mL × 3) and water (100 mL). The collected 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, 20/1) to give a golden solid product **3** (1.65g, 88%). ^{1}H NMR ($CDCl_3$, 300 MHz): 1.14 (t, J = 7.2 Hz, 6 H), 4.23 (q, J = 7.1 Hz, 4 H), 7.20 (s, 2 H), 7.40-7.50 (m, 2 H), 7.50-7.60 (m, 4 H) 7.76 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz):□13.85, 61.28, 118.59, 128.06, 129.50, 130.95, 131.21, 132.17, 134.06, 139.37, 143.26, 168.56.

Synthesis of Compound 5. To a solution of compound **3** (4.00 g, 9.16 mmol) in dry THF (100 mL) was added dropwise compound **4** which was freshly prepared by reacting 1-(octyloxy)-4-bromobenzene (26.10 g, 91.51 mmol) with magnesium turnings (2.23 g, 91.73 mmol). The reaction mixture was refluxed at 70 °C for 16 h and then quenched with water, followed by extraction with diethyl ether (100 mL × 3) and water (100 mL). The collected 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, 30/1) to give a light yellow sticky product **5** (7.5g, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.88 (t, J = 6.5 Hz, 12 H), 1.20-1.50 (m, 40 H), 1.78 (m, 8 H), 3.42 (s, 2 H), 3.95 (t, *J* = 6.5 Hz, 8 H), 6.26 (s, 2 H), 6.81 (d, *J* = 9.0 Hz, 8 H), 7.05 (d, *J* = 9.0 Hz, 8 H), 7.19-7.35 (m, 8 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 14.08, 22.65, 26.08, 29.24, 29.32, 29.40, 31.81, 68.02, 82.82, 113.71, 120.06, 126.80, 127.67, 129.18, 130.35, 133.06, 134.20, 139.14, 139.91, 144.08, 147.16, 158.30.

Synthesis of Compound DITT. To a solution of compound **5** (3.00 g, 2.56 mmol) in acetic acid (72 mL) was added one drop concentrated H_2SO_4. The reaction mixture was refluxed at 85 °C for 4 h. After cooling down to rt, the mixture was extracted with ethyl acetate (100 mL × 4) and water (500 mL). The collected 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/diethyl ether, v/v, 80/1) to give a deep orange sticky product **DITT** (2.16 g, 74%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.87 (t, *J* = 6.6 Hz, 12 H), 1.20-1.55 (m, 40 H), 3.88 (t, *J* = 6.5 Hz, 8 H), 6.78 (d, *J* = 8.9 Hz, 8 H), 7.16 (d, *J* = 8.9 Hz, 8 H), 7.20-7.30 (m, 4 H), 7.35 (d, *J* = 7.8 Hz, 2 H), 7.38 (d, *J* = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 14.32, 22.87, 26.28, 29.45, 29.51, 29.57, 32.02, 62.67, 68.10, 98.82, 114.44, 119.15, 125.95, 127.71, 129.41, 135.29, 136.18, 137.93, 142.62, 147.36, 153.75, 158.41.

Synthesis of Compound Br-DITT. To a solution of **DITT** (0.50 g, 0.44 mmol) and iron(III) chloride (9.3 mg) in chloroform (15.4 mL) was added bromine (0.14 g, 0.89 mmol) dropwise at rt. The resulting solution was stirred for 12 h at rt and then was quenched by saturated sodium thiosulfate solution (20 mL). The mixture solution was extracted with chloroform (50 mL × 3) and water (20 mL). 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/diethyl ether, v/v, 80/1) to give a pale-yellow solid **Br-DITT** (0.55 g, 97%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.87 (t, *J* = 6.3 Hz, 12 H), 1.20-1.50 (m, 40 H), 1.74 (m, 8 H), 3.89 (t, *J* = 6.5

Hz, 8 H), 6.80 (d, *J* = 9.0 Hz, 8 H), 7.12 (d, *J* = 9.0 Hz, 8 H), 7.20 (d, *J* = 8.1 Hz, 2 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 7.48 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 14.08, 22.63, 26.04, 29.20, 29.24, 29.32, 31.78, 62.61, 67.89, 114.38, 119.45, 120.09, 129.06, 130.66, 134.10, 136.16, 136.57, 141.60, 147.37, 155.51, 158.39.

Synthesis of Compound B-DITT. To a solution of **Br-DITT** (1.00 g, 0.77 mmol) in dry THF (26.5 mL) was added a 2.5M solution of *n*-BuLi (1.0 mL in hexane, 2.44 mmol) dropwise at −78 °C. The resulting mixture was stirred for 1 h at −78 °C. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.58 g, 3.12 mmol) was added to the mixture solution dropwise. The mixture was allowed to warm up to rt and then stirred for 16 h. Water (150 mL) was added to the reaction which was then extracted with ethyl acetate (300 mL × 3). The combined organic layer ws 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, 40/1) and then recrystallized from hexane to give a pale-yellow solid **B-DITT** (0.57 g, 53%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.86 (t, *J* = 5.9 Hz, 12 H), 1.20-1.1.40 (m, 40 H), 1.72 (m, 64 H), 3.88 (t, *J* = 6.5 Hz, 8 H), 6.77 (d, *J* = 8.6 Hz, 8 H), 7.16 (d, *J* = 8.6 Hz, 8 H), 7.34 (d, *J* = 7.5 Hz, 2 H), 7.73 (d, *J* = 7.5 Hz, 2 H), 7.78 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 14.09, 22.63, 24.88, 26.03, 29.20, 29.25, 29.32, 31.78, 62.35, 67.80, 83.64, 114.14, 118.30, 129.29, 131.41, 134.60, 134.82, 136.48, 140.50, 142.66, 148.28, 152.73, 157.79, 158.08.

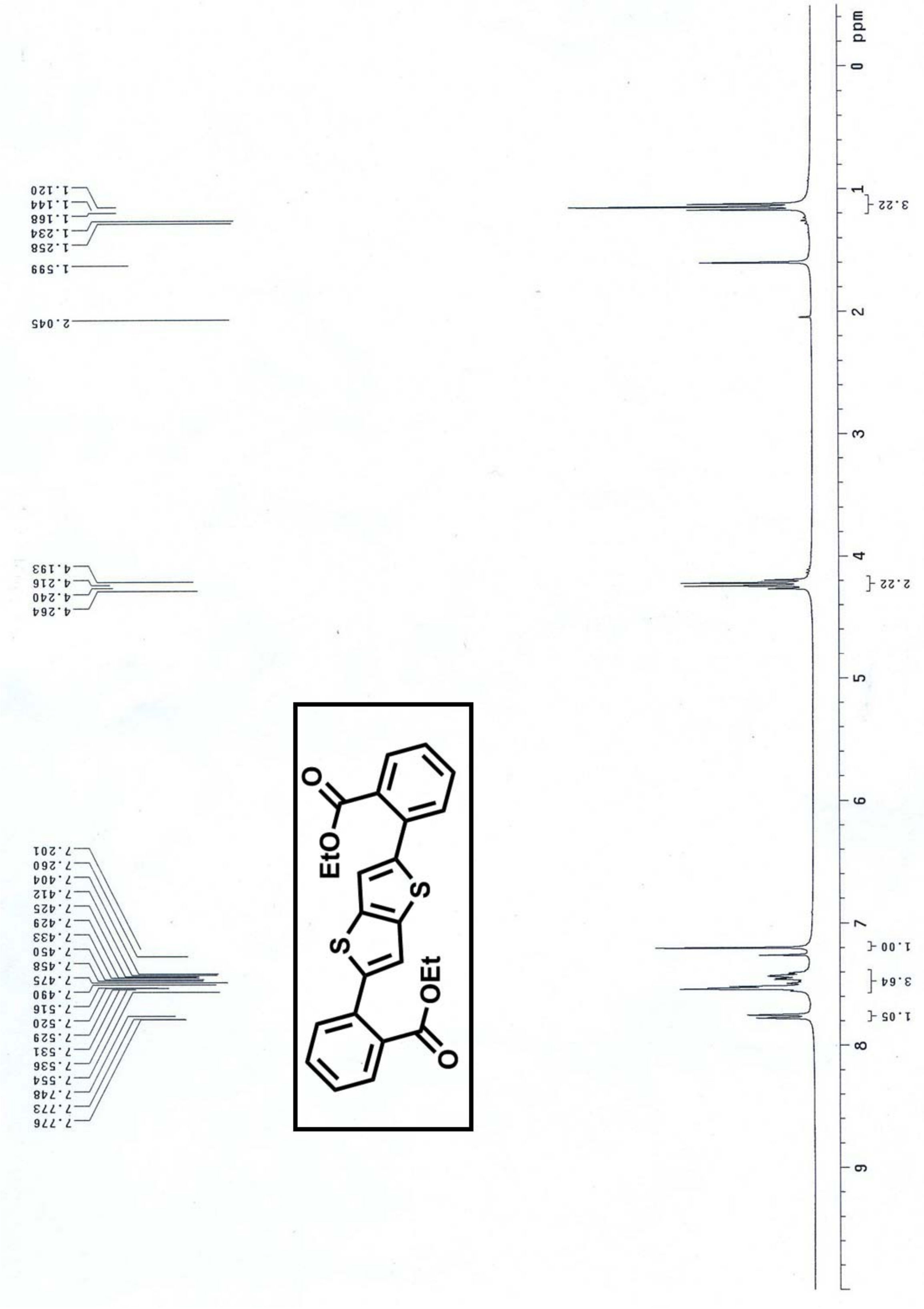
Synthesis of PDITTBT. To a 25 mL round bottom flask was introduced **B-DITT** (216.8 mg, 0.16 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (46 mg, 0.16 mmol), $Pd(PPh_3)_4$ (3.6 mg, 0.0031 mmol), K_2CO_3 (163.3 mg, 1.18 mmol), Aliquat 336 (27 mg, 0.07 mmol), degassed toluene (5 mL), and degassed H_2O (1 mL). The mixture was heated to 90 °C under argon for 72 h. The mixture was added into methanol dropwise. The precipitate was collected by filtration and washed by Soxhlet extraction with acetone, hexane and THF sequentially for three days. The Pd-thiol gel (Silicycle Inc.) was added to above THF solution to remove the residual Pd catalyst. After filtration and removal of the solvent, the polymer was re-dissolved in THF again and added into methanol to re-precipitate. The purified polymer was collected by filtration and dried under vacuum for 1 day to give a red solid (103 mg, 52%, M_n = 19.0 kDa, PDI = 1.76). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.75-0.90 (m, 12 H), 1.00-1.50 (m, 40 H), 1.65-1.80 (m, 8 H), 3.80-4.00 (m, 8 H), 6.70-6.90 (m, 8 H), 7.15-7.40 (m, 8 H), 7.40-7.55 (m, 2 H), 7.60-7.80 (m, 2 H), 7.90-8.10 (m, 4 H).

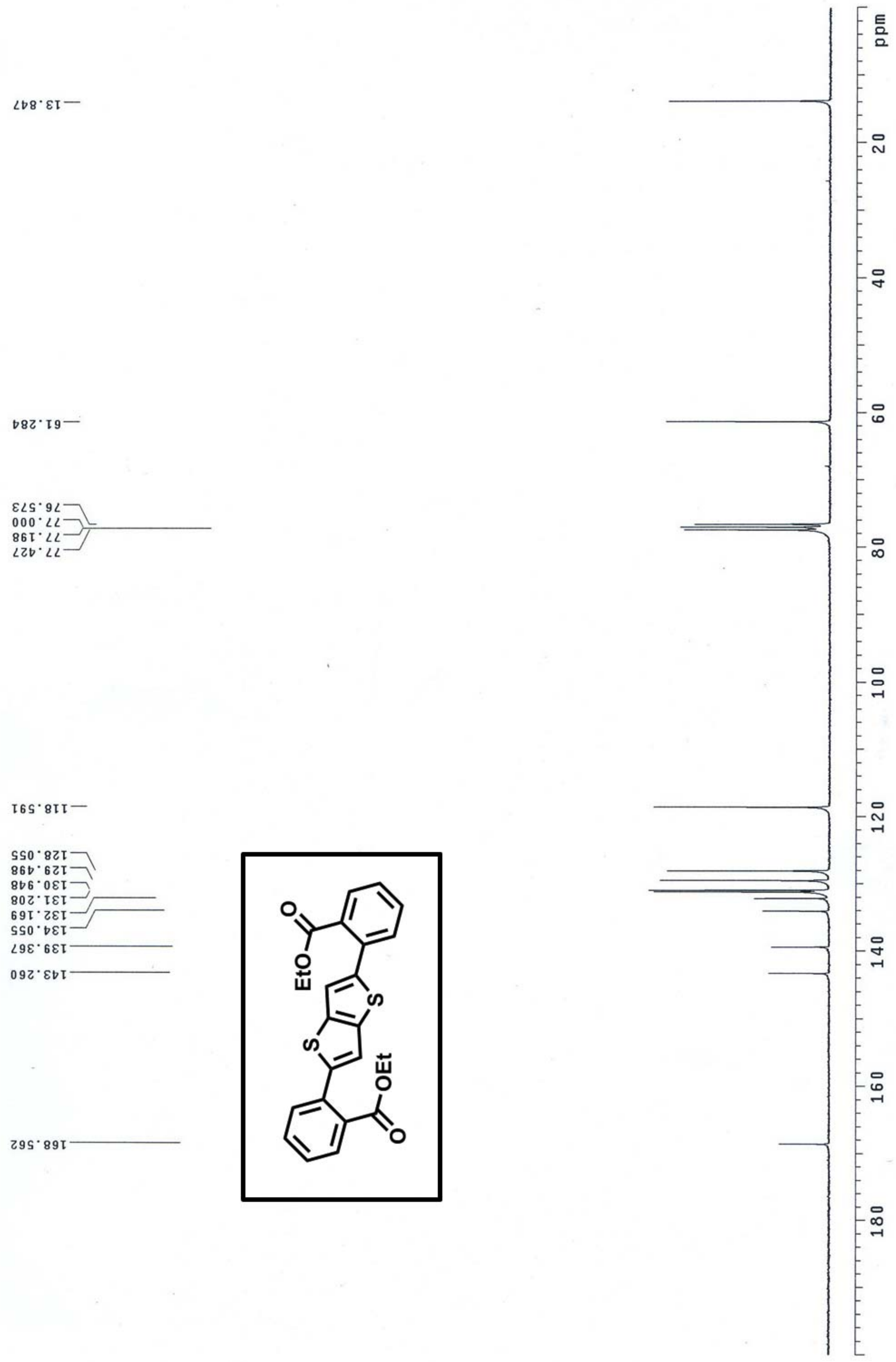
Synthesis of PDITTDTBT. To a 25 mL round bottom flask was introduced **B-DITT** (216.8 mg, 0.16 mmol), 4,7-bis(5-bromothiophene-2-yl)2,1,3-benzothiadiazole (71.5 mg, 0.16 mmol), $Pd(PPh_3)_4$ (3.6 mg, 0.0031 mmol), K_2CO_3 (163.3 mg, 1.18 mmol), Aliquat 336 (27 mg, 0.07 mmol), degassed toluene (5 mL), and degassed H_2O (1 mL). The mixture was heated to 90 °C under argon gas for 72 h. The solution was added into methanol dropwise. The precipitate was collected by filtration and washed by Soxhlet extraction with acetone, hexane and THF sequentially for three days. The Pd-thiol gel (Silicycle Inc.) was added to above THF solution to remove the residual Pd catalyst. After filtration and removal of the solvent, the polymer was re-dissolved in THF again and added into methanol to re-precipitate. The purified polymer was collected by filtration and dried under vacuum for 1 day to give a dark red solid (130 mg, 58%, M_n = 8.1 kDa, PDI = 2.1). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.75-0.90 (m, 12 H), 1.05-1.45 (m, 40 H), 1.70-1.80 (m, 8 H), 3.80-4.00 (m, 8 H), 6.75-6.90 (m, 8 H), 7.10-7.25 (m, 8 H), 7.35-7.45 (m, 4 H), 7.60-7.75 (m, 4 H), 7.80-7.90 (m, 2 H), 8.05-8.15 (m, 2 H).

References

1. M. Sato, A. Asami, G. Maruyama, M. Kosuge, J. Nakayama, S. Kumakura, T.

Fujihara and K. Unoura, *J. Organomet. Chem.*, 2002, **654**, 56.

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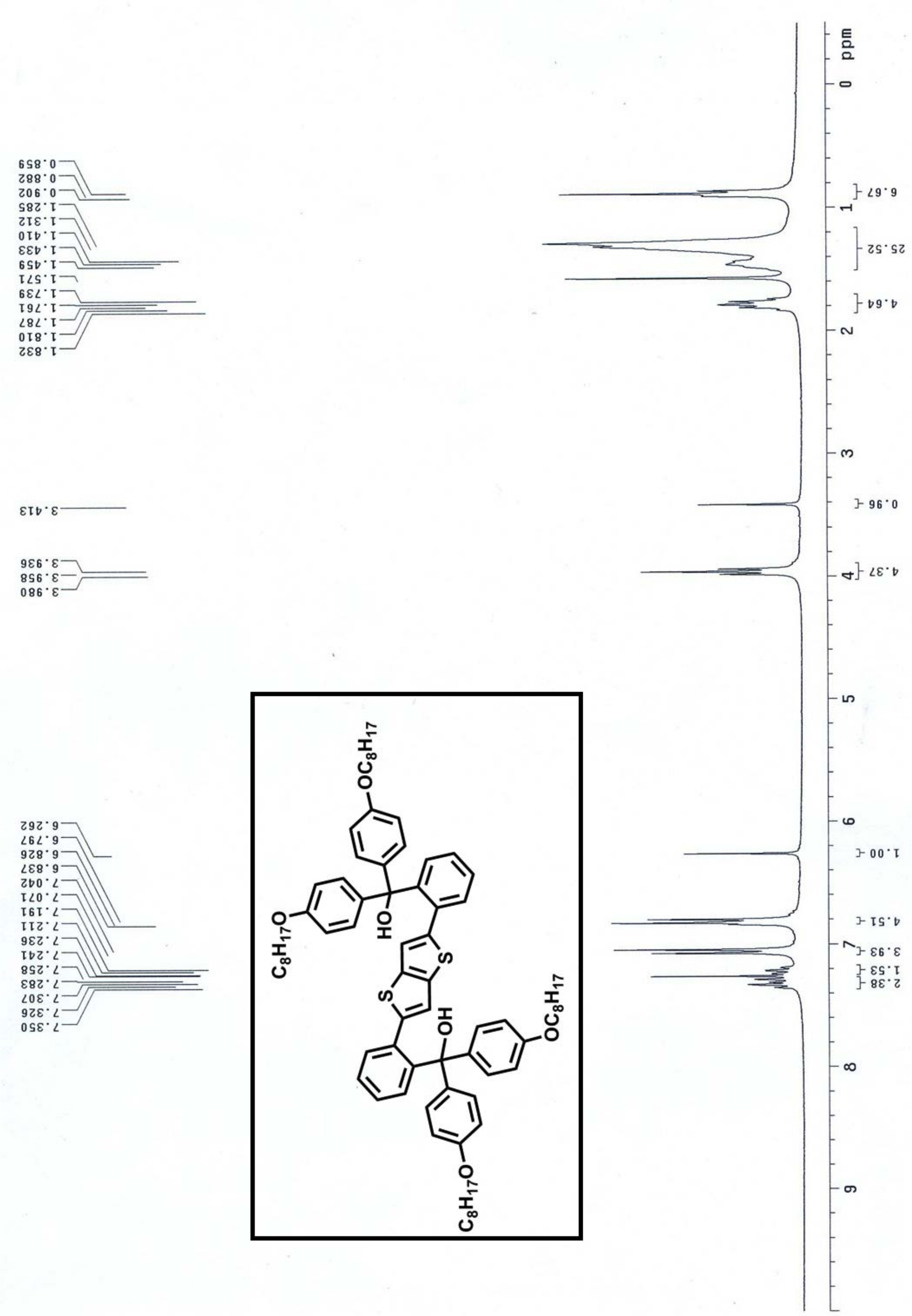
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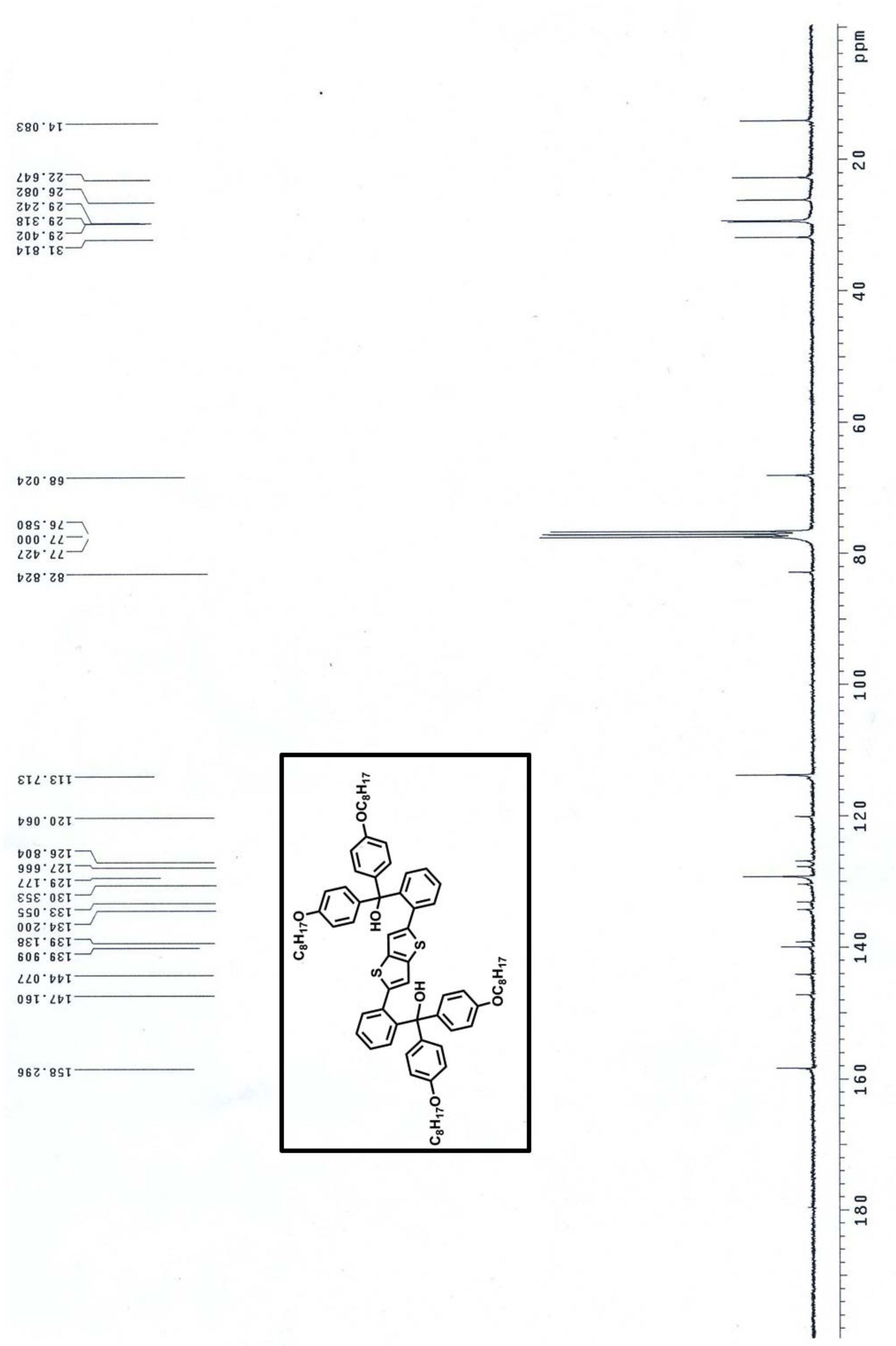
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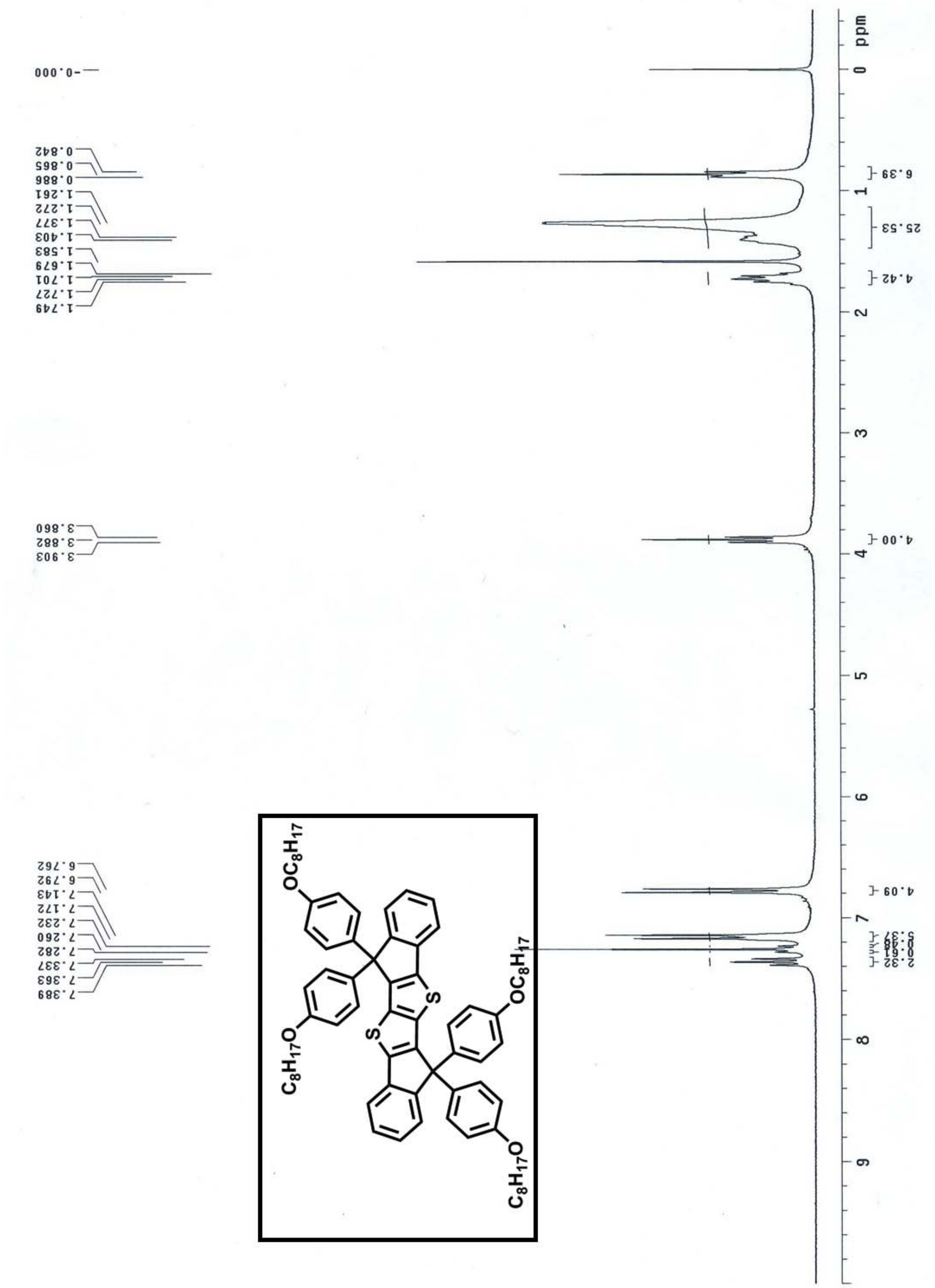
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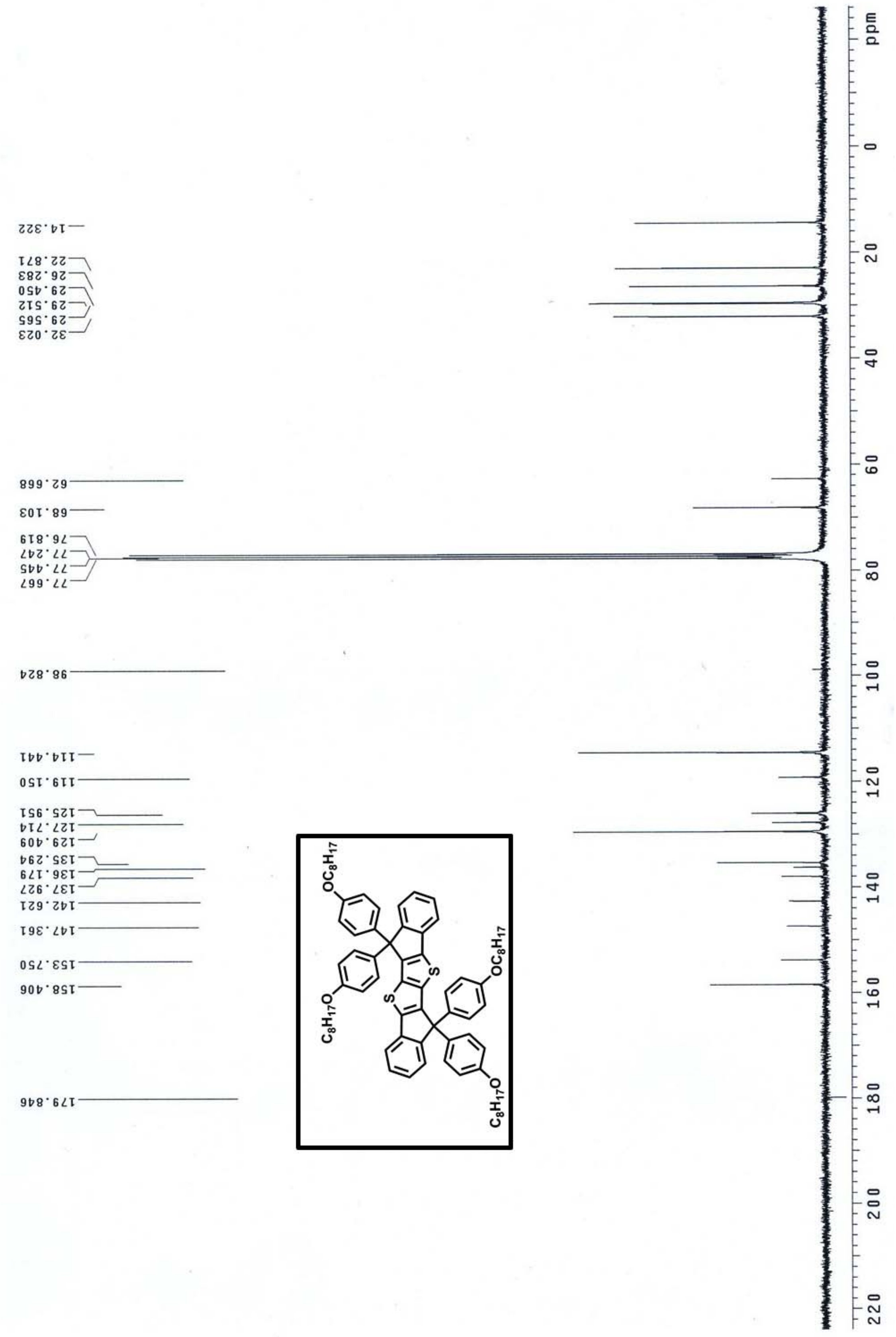
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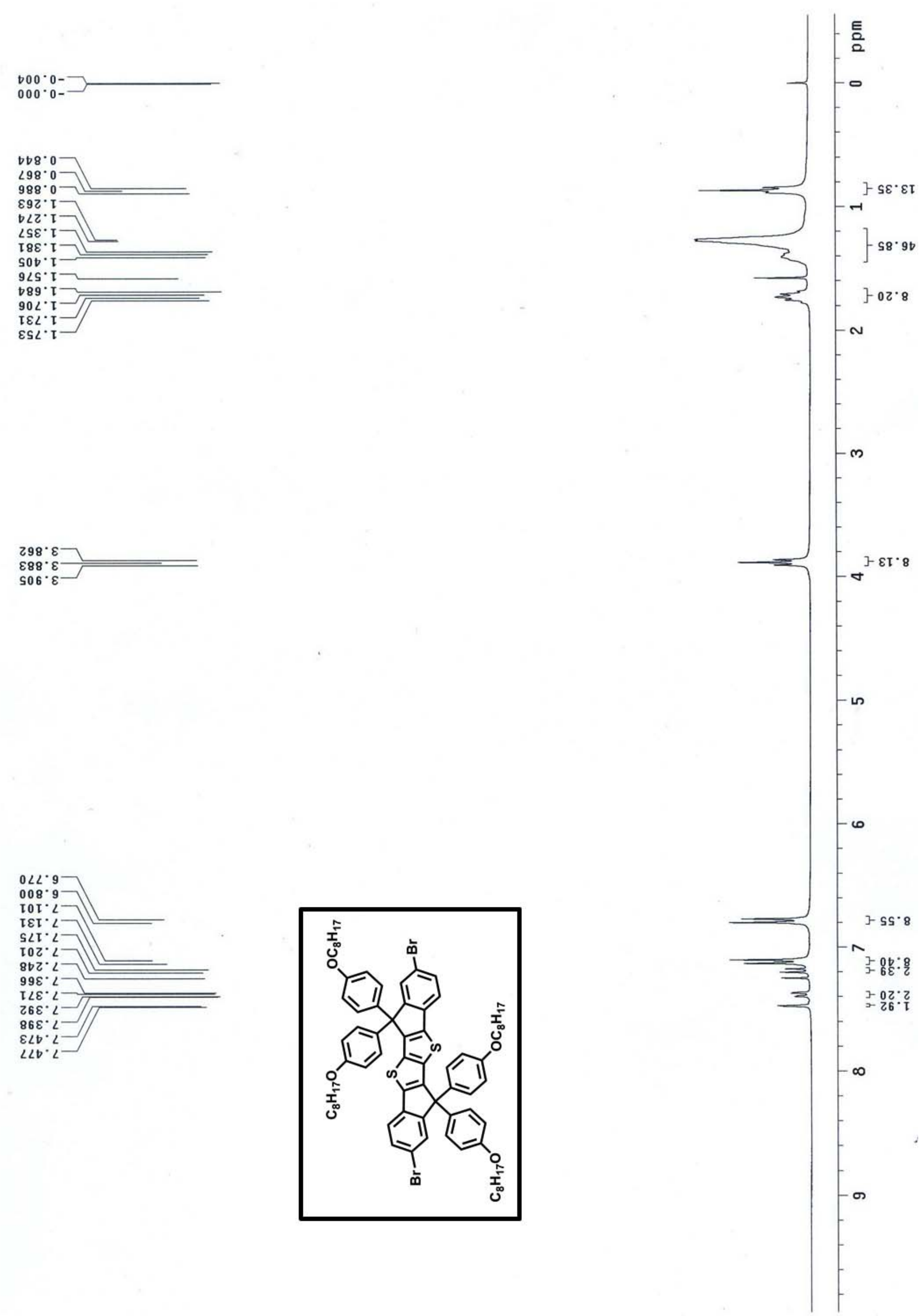
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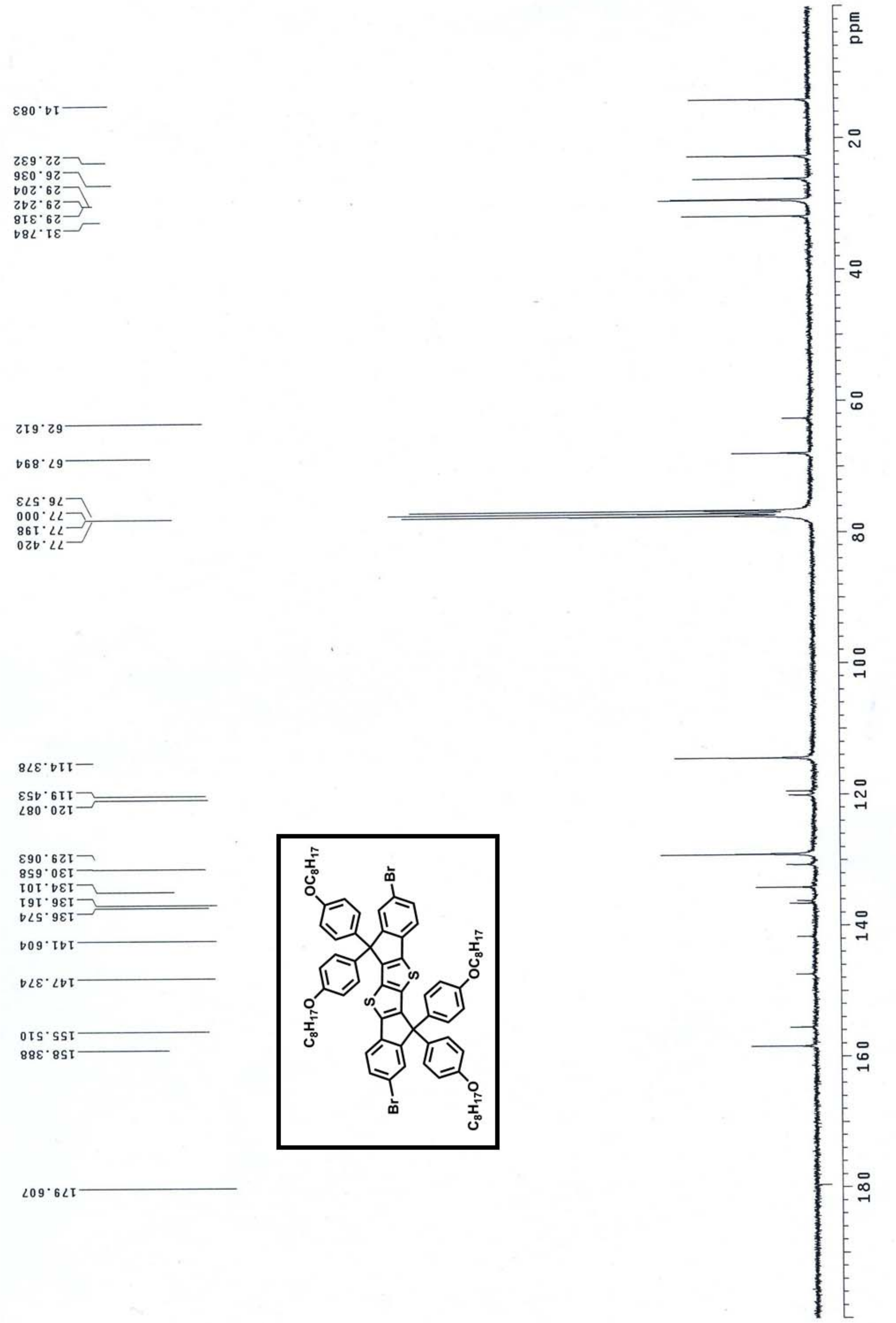
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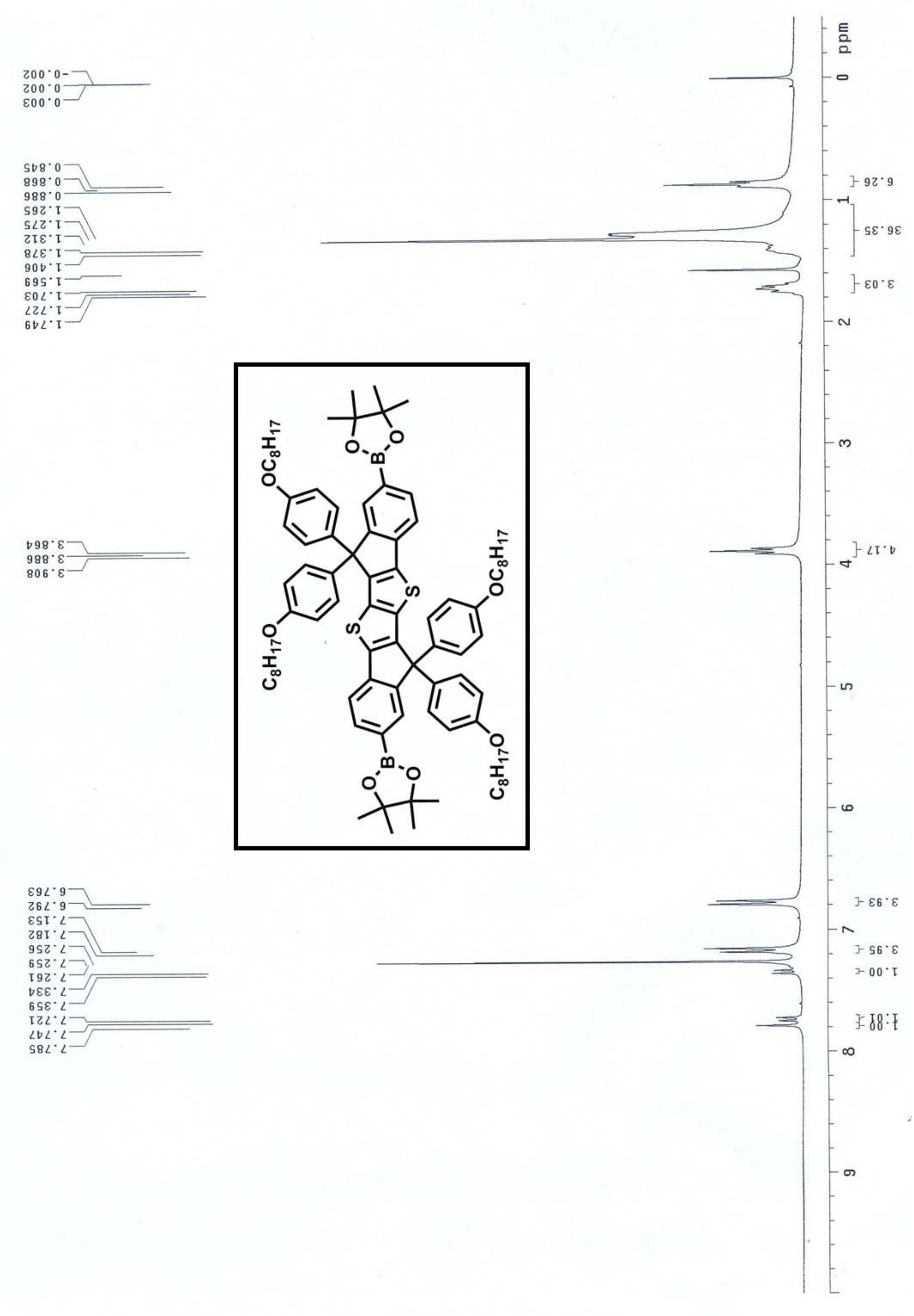
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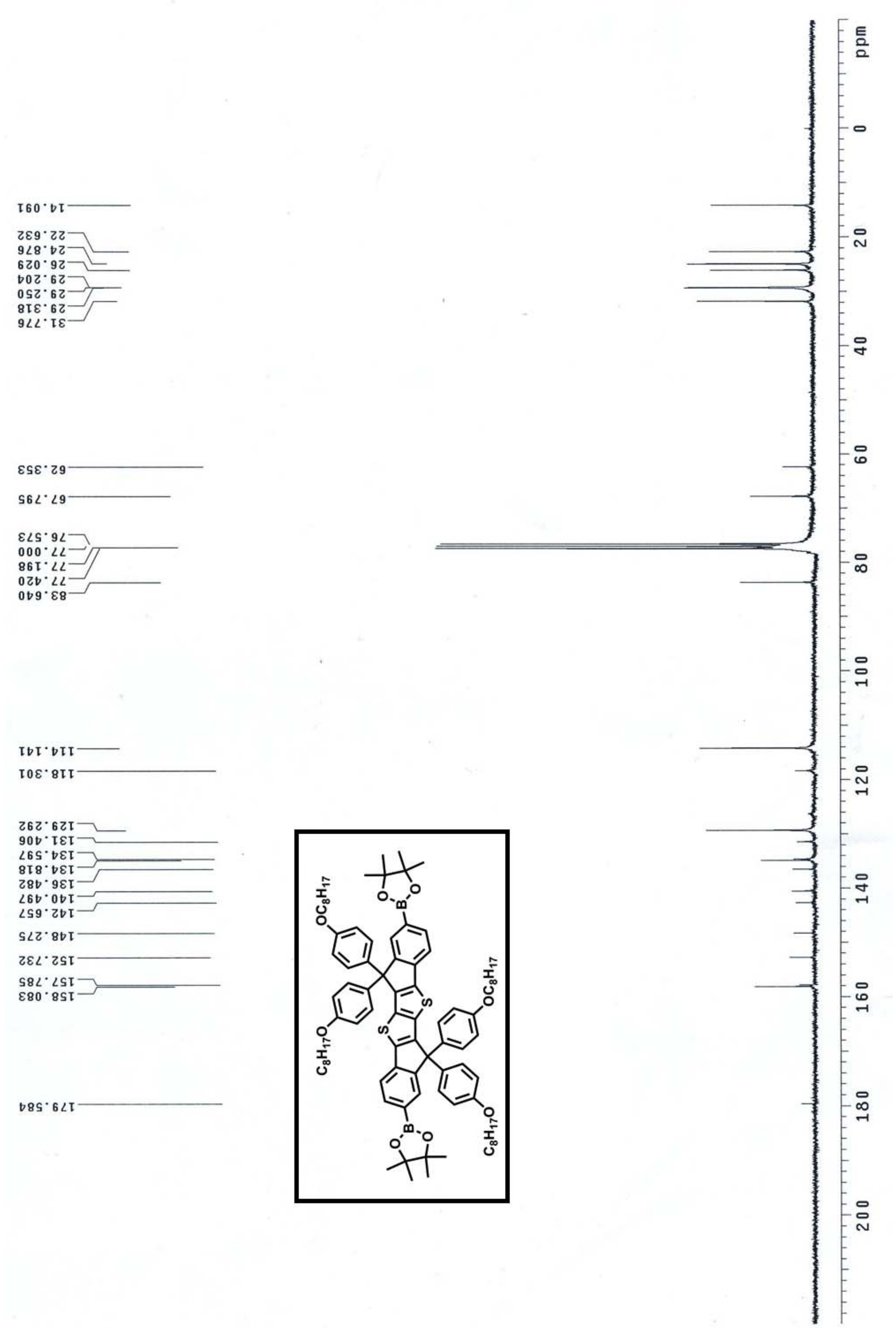
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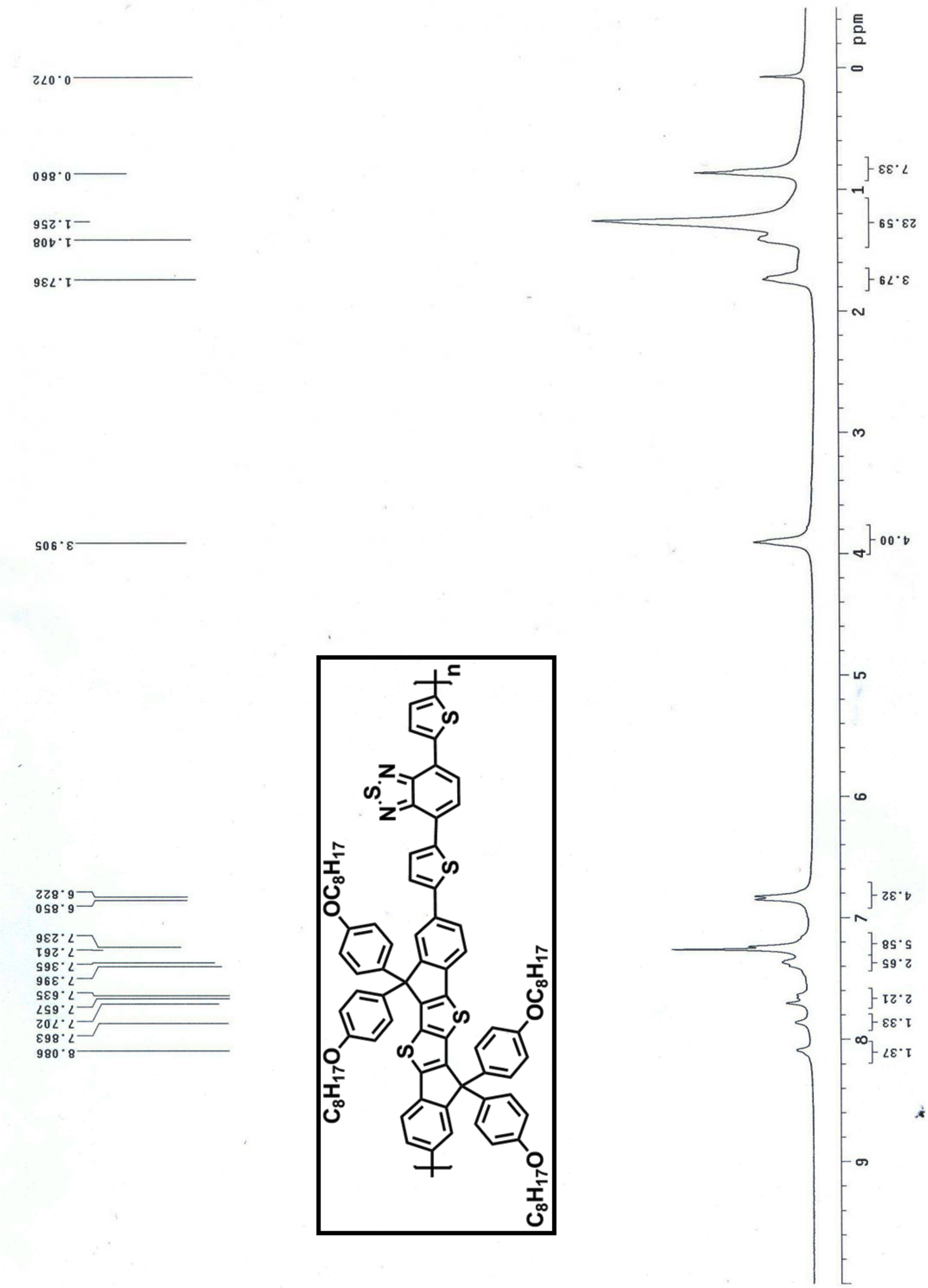
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7.396
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7.657
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7.863
8.086
7.33
23.59
3.79
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4.32
5.58
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2.21
1.33
1.37
ppm
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9
OC_8H_{17}
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OC_8H_{17}
$C_8H_{17}O$
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