Supplementary Information

Donor-Acceptor Polymers Based on Multi-fused Heptacyclic Structures: Synthesis, Characterization and Photovoltaic Applications

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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. Fourier transform infrared spectroscopy (FTIR) was measured on a Perkin-Elmer One Instrument by preparing KBr Pellets. 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 VE2001GPC, 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 200 °C during 10 min, the samples were cooled down to room temperature. Polymers were dissolved in *o*-dichlorobenzene (ODCB) (10 mg/mL) and $PC_{71}BM$ (purchased from Nano-C) was added (20mg/mL). The solution was then heated at 100 °C during 30 minutes and stirred overnight at room temperature. Prior to deposition, the solution were filtrated (1µm filters) and the substrates transferred in a glove box. The solution of polymer:$PC_{71}BM$ was then spin coated to form the active layer. Different spin coating speed (500 and 1000 rpm) were used in order to tune the thickness. The thickness of **PFDCTBT**:$PC_{71}BM$ layer and **PCDCTBT**:$PC_{71}BM$(1:2, w/w) layer are 70 nm and 90 nm, respectively. 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 cm². 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.

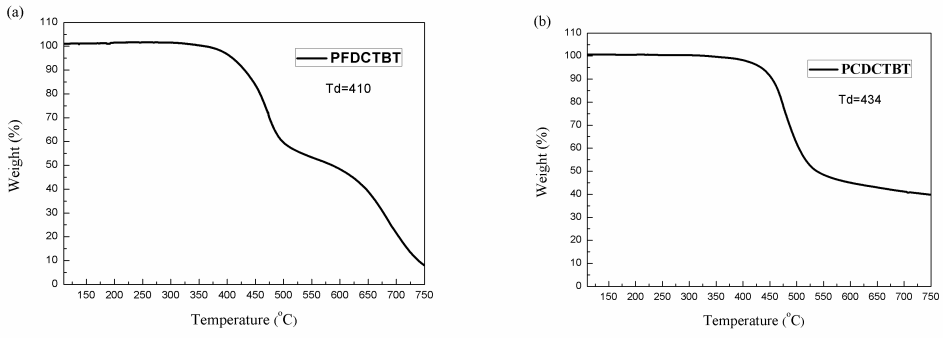


Fig. S1 Thermogravimetric analysis (TGA) of **PFDCTBT** (a) and **PDCDTBT** (b).

DSC Measurements.

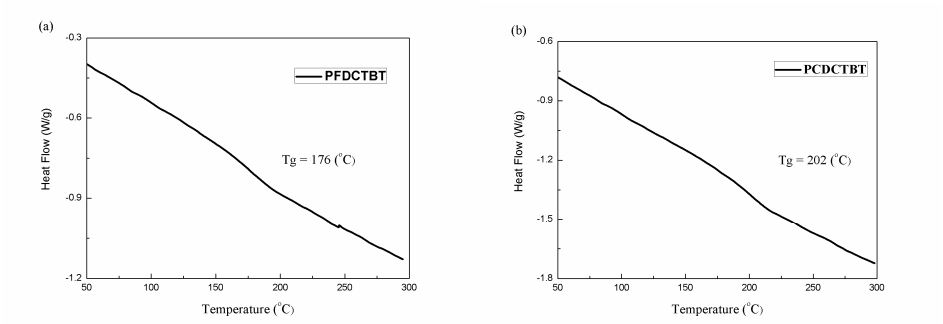


Fig. S2 Differential scanning calorimetry (DSC) of **PFDCTBT** (a) and **PCDCTBT** (b).

Photoluminescence quenching in the film of the PFDCTBT/$PC_{71}BM$ and PCDCTBT/$PC_{71}BM$ (1:2, w/w) blends.

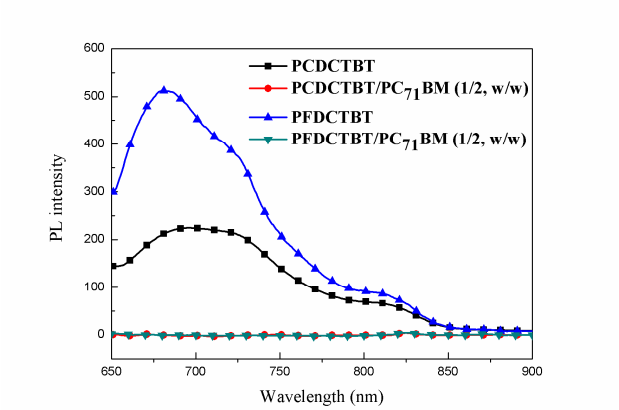


Fig. S3 Emission spectra of **PFDCTBT**, **PDCDTBT, PFDCTBT/$PC_{71}BM$** (1/2, w/w) and **PCDCTBT/$PC_{71}BM$** (1/2, w/w) in the thin film.

Atomic force microscopy images.

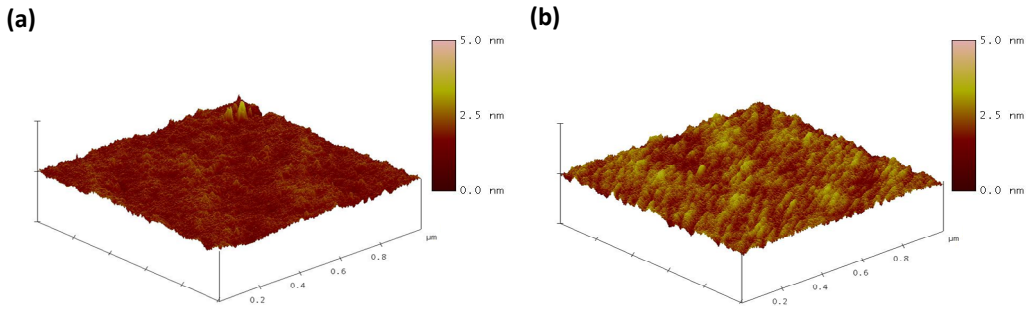


Fig. S4 AFM tapping mode height images of the surface of (a) **PFDCTBT**/$PC_{71}BM$ (1:2, w/w) blend and (b) **PCDCTBT**/$PC_{71}BM$ (1:2, w/w) blend (1.0 □μm × 1.0 μm).

Synthesis of 2,7-Bis(3-ethoxycarbonyl-2-thienyl)-9,9-dioctylfluorene (3a).

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene **1a**[1] (4.6 g, 7.2 mmol), ethyl 2-bromothiophene-3-carboxylate **2**[2] (3.89 g, 16.56 mmol), K_2CO_3 (5.97 g, 43.2 mmol), Aliquant 336 (0.72 g, 1.8 mmol) and $Pd(PPh_3)_4$ (0.83 g, 0.72 mmol) were dissolved in deoxygenated toluene/H_2O (60 mL, 5:1, v/v). The reaction mixture was refluxed at 85℃ for 72 h and then extracted 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 pale yellow sticky product **3a** (4.3g, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz): (t, *J* = 6.7 Hz, 6 H), 1.08-1.19 (m, 30 H), 1.95-2.01 (m, 4 H), 4.19 (q, *J* = 7.2 Hz, 4H), 7.24 (d, *J* = 5.4 Hz, 2 H), 7.46-7.49 (m, 4 H), 7.52 (d, *J* = 5.4 Hz, 2 H), 7.72 (d, *J* = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 14.30, 14.38, 22.81, 24.07, 29.45, 29.49, 30.29, 32.02, 40.24, 55.53, 60.64, 119.53, 124.06, 124.62, 128.65, 129.07, 139.28, 132.64, 141.12, 151.05, 151.53, 163.72; IR (KBr) 3111, 3091, 2954, 2926, 2853, 1722, 1716, 1577, 1528, 1468, 1443, 1379, 1274, 1147, 1085, 1027, 938, 889, 843, 821, 708 cm^{-1}; MS (EI, $C_{43}H_{54}O_4S_2$): Calcd, 699.02; Found, 699.

Synthesis of Compound (5a).

To a solution of compound **3a** (2.1 g, 3.0 mmol) in dry THF (30 mL) was added dropwise 4-(2-ethylhexyloxy)phenyl magnesium bromide **4** which was freshly prepared by reacting 1-(2-ethylhexyloxy)-4-bromobenzene (3.77 g, 13.22 mmol) with magnesium turnings (0.36 g, 14.80 mmol). The reaction mixture was refluxed at 70℃ for 16 h and then quenched with water, followed by extraction with diethyl ether (50 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 deep orange sticky product **5a** (2.8g, 66%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.80 (t, *J* = 6.7 Hz, 6 H), 0.89-1.57 (m, 84 H), 1.69-1.75 (m, 4 H), 2.99 (s, 2 H), 3.84 (d, *J* = 5.4 Hz, 8 H), 6.45 (d, *J* = 5.4 Hz, 2 H), 6.82 (d, *J* = 8.7 Hz, 8 H), 7.03 (s, 2 H), 7.08 (d, *J* = 5.4 Hz, 2 H), 7.16 (d, *J* = 8.7 Hz, 8 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 7.51 (d, *J* = 7.8 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 11.26, 14.24, 22.77, 23.19, 23.85, 24.01, 29.25, 29.37, 29.44, 29.83, 30.08, 30.70, 31.95, 39.52, 39.76, 55.12, 70.59, 80.57, 113.85. 119.88, 122.47, 124.30, 128.93, 129.16, 131.57, 133.70, 139.21, 140.38, 140.56, 144.50, 151.18, 158.63; MS (FAB, $C_{95}H_{130}O_6S_2$): Calcd, 1432.18; Found, 1431.

Synthesis of Compound (6a).

To a solution of compound **5a** (2.5 g, 1.76 mmol) in acetic acid (200 mL) was

added dropwise concentrated H_2SO_4 (3.0 mL). The reaction mixture was refluxed at 85℃for 15 h and then 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, 100/1) to give a deep orange sticky product **6a** (1.27 g, 52%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.79 (t, *J* = 6.6 Hz, 6 H), 0.85-1.48 (m, 80 H), 1.64-1.68 (m, 4 H), 1.96-2.01 (m, 4 H), 3.76 (d, *J* = 5.4 Hz, 8 H), 6.76 (d, *J* = 8.7 Hz, 8 H), 6.97 (d, *J* = 4.8 Hz, 2 H), 7.14 (d, *J* = 8.7 Hz, 8 H), 7.25 (d, *J* = 4.8 Hz, 2H), 7.35 (s, 2 H), 7.47 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 11.25, 14.21, 22.75, 23.17, 23.98, 29.21, 29.38, 29.41, 29.85, 30.25, 30.66, 31.96, 39.56, 40.81, 54.59, 62.03,70.38, 113.87, 114.26, 117.33, 123.15, 127.45, 129.20, 136.22, 137.10, 139.37, 141.31, 151.08, 153.32, 156.61, 158.22; IR (KBr) 3096, 3070, 3035, 2956, 2925, 2870, 2855, 1637, 1608, 1580, 1507, 1464, 1378, 1291, 1246, 1176, 1113, 1034, 868, 822, 719, 658, 615, 522 cm^{-1}; MS (FAB, $C_{95}H_{126}O_4S_2$): Calcd, 1396.14; Found, 1395; elemental analysis (%) Calcd, for $C_{95}H_{126}O_4S_2$: C, 81.73; H, 9.10. Found: C, 81.76; H, 8.89.

Synthesis of Compound (7).

To a solution of **6a** (0.37 g, 0.265 mmol) in chloroform (30 mL) was added *N*-bromosuccimide (0.104 g, 0.583 mmol) in one portion. The reaction was stirred under dark for 12 h at room temperature. The mixture solution was extracted with dichloromethane (50 mL × 3) and water (50 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) to give a black solid **7** (0.367 g, 89%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.79-1.57 (m, 86 H), 1.71-1.76 (m, 4H), 2.03-2.08 (m, 4 H), 3.85 (d, *J* = 5.4 Hz, 8 H), 6.85 (d, *J* = 9.0 Hz, 8 H), 7.04 (s, 2H), 7.19 (d, *J* = 9.0 Hz, 8 H), 7.36 (s, 2 H), 7.53 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 11.24, 14.20, 22.74, 23.16, 23.98, 29.20, 29.36, 29.50, 29.84, 30.18, 30.33, 30.66, 31.57, 31.94, 39.54, 54.66, 62.82, 70.36, 113.54, 113.75, 114.37, 117.32, 126.12, 129.09, 135.95, 136.36, 139.51, 141.54, 151.29, 152.27, 155.41, 158.38; IR (KBr) 3063, 3036, 2957, 2925, 2870, 2855, 1607, 1580, 1507, 1464, 1377, 1291, 1247, 1176, 1113, 1034, 950, 869, 826, 772, 725, 666, 523 cm^{-1}; MS (FAB, $C_{95}H_{124}Br_2O_4S_2$): Calcd, 1553.94; Found, 1553; elemental analysis (%) Calcd, for $C_{95}H_{124}Br_2O_4S_2$: C, 73.43; H, 8.04. Found: C, 73.24; H, 8.01.

Synthesis of Compound (M1).

To a solution of **7** (0.367 g, 0.236 mmol) in dry THF (20 mL) was added a 1.7 M solution of *t*-BuLi in hexane (0.83 mL, 1.4 mmol) dropwise at -78 ^{o}C. After stirring at -78 ^{o}C for 30 min, 1.0 M solution of chlorotrimethylstannane in THF (1.9 mL, 1.9

mmol) was introduced by syringe to the solution. The mixture solution was warmed up to room temperature and stirred for 12 h. The mixture solution was quenched with water and extracted with diethyl ether (50 mL × 3) and water (50 mL). After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/Et3N, v/v, 50/1) to give a deep orange sticky product **M1** (0.394 g, 97%). ^{1}H NMR ($CDCl_3$,300 MHz): 0.35 (s, 18 H), 0.66-1.48 (m, 86 H), 1.64-1.68 (m, 4 H), 1.94-2.02 (m, 4 H), 3.76 (d, *J* = 5.7 Hz, 8 H), 6.76 (d, *J* = 9.0 Hz, 8 H), 6.99 (s, 2 H), 7.14 (d, *J* = 9.0 Hz, 8 H), 7.33 (s, 2 H), 7.43 (s, 2 H); IR (KBr) 3038, 3005, 2956, 2924, 2854, 1660, 1629, 1596, 1507, 1465, 1349, 1292, 1247, 1177, 1084, 1032, 1014, 870, 822, 690, 664, 551 cm^{-1} MS (FAB, $C_{101}H_{142}O_4S_2Sn_2$): Calcd, 1721.76; Found, 1721.

N-Heptadecanyl-2,7-bis(3-ethoxycarbonyl-2-thienyl)-9H-carbazole(3b).

2,7-Bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolan-2′-yl)-N-9″-heptadecanylcarbazole **1b**[3] (2.43 g, 3.7 mmol), ethyl 2-bromothiophene-3-carboxylate **2** (2.0 g, 8.51 mmol), K_2CO_3 (3.06 g, 22.2 mmol), Aliquant 336 (0.37 g, 0.93 mmol) and $Pd(PPh_3)_4$ (0.43 g, 0.37 mmol) were dissolved in deoxygenated toluene/H_2O (36 mL, 5:1, v/v). The reaction mixture was refluxed at 85℃ for 72 h and then extracted 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, 40/1) to give a colorless sticky product **3b** (2.05g, 79%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.80 (t, *J* = 6.6 Hz, 6 H), 1.14-1.33 (m, 30 H), 1.89- 1.96 (m, 2 H), 2.24-2.30 (m, 2 H), 4.18 (q, *J* = 6.6 Hz, 4 H), 4.51-4.58 (m, 1 H), 7.26 (d, *J* = 5.4 Hz, 2 H), 7.37 (br, 2 H), 7.55 (d, *J* = 5.4 Hz, 3 H), 7.75 (br, 1 H), 8.09 (br, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 14.18, 22.71, 27.04, 29.33, 29.46, 29.55, 29.83, 31.88, 33.87, 56.82, 69.56, 110.47, 113.27, 119.69, 119.96, 121.11, 122.41, 124.04, 128.31, 128.50, 130.14, 130.48, 131.16, 138.81, 142.18, 152.15, 163.69 (Multiplecarbon peaks result from phenomenon of atropisomerism [3]);□IR (KBr) 3110, 3091, 2953, 2926, 2854, 1715, 1625, 1600, 1563, 1523, 1456, 1445, 1434, 1400, 1380, 1369, 1332, 1269, 1228, 1145, 1085, 1028, 1000, 941, 909, 842, 805, 788, 709, 652, 566, 516 cm^{-1}; MS (FAB, $C_{43}H_{55}NO_4S_2$): Calcd, 714.03; Found, 714.

Synthesis of Compound (5b).

To a solution of compound **3b** (2.05 g, 2.87 mmol) in dry THF (30 mL) was added dropwise 4-(2-ethylhexyloxy)phenyl magnesium bromide **4** which was freshly prepared by reacting 1-(2-ethylhexyloxy)-4-bromobenzene (3.70 g, 13 mmol) with magnesium turnings (0.35 g, 14.3 mmol). The reaction mixture was refluxed at 70℃

for 16 h and then quenched with water followed by extraction with diethyl ether (50 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 colorless sticky product **5b** (1.9 g, 46%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.70-1.52 (m, 86 H), 1.69-1.75 (m, 8 H), 3.30 (d, *J* = 7.2 Hz, 2 H), 3.82 (d, *J* = 5.7 Hz, 8 H), 6.44 (d, *J* = 5.1 Hz, 2 H), 6.79-6.83 (m, 8 H), 7.11-7.19 (m, 13 H), 7.37 (br, 1 H), 7.91 (t, *J* = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 11.26, 11.28, 14.21, 14.24, 21.32, 22.76, 22.82, 23.21, 24.00, 26.66, 29.25, 29.42, 29.54, 29.58, 29.83, 30.32, 30.45, 30.68, 31.02, 31.56, 31.64, 31.94, 32.06, 33.55, 34.35, 35.00, 39.54, 56.36, 70.61, 80.62, 80.82, 82.16, 110.17, 112.63, 113.77, 120.51, 120.71, 121.06, 121.35, 121.79, 122.68, 123.19, 124.12, 124.59, 125.65, 128.37, 129.09, 129.22, 131.76, 132.02, 132.30, 135.88, 138.89, 139.69, 140.59, 140.79, 142.29, 143.52, 144.11, 158.64 (Multiple carbon peaks result from phenomenon of atropisomerism[3]);□IR (KBr) 3317(br), 3066, 3039, 2957, 2926, 2856, 1660, 1606, 1581, 1508, 1460, 1379, 1330. 1297, 1246, 1173, 1034, 971, 831, 809, 777, 724, 666 cm^{-1}; MS (FAB, $C_{95}H_{131}NO_6S_2$): Calcd, 1447.19; Found, 1447.

Synthesis of Compound (6b).

Compound **5b** (1.9 g, 1.31 mmol) was dissolved in acetic acid (400 mL). The reaction mixture was refluxed at 85℃ for 2 h and then 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/ethyl acetat, v/v, 50/1) to give a deep orange sticky product **6b** (1.8g, 97%). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.76-0.90 (m, 18 H), 1.15-1.68 (m, 72 H), 1.93-2.00 (m, 2 H), 2.28-2.32 (m, 2 H), 3.76 (d, *J* = 5.7 Hz, 8 H), 4.55-4.58 (m, 1 H), 6.75 (d, *J* = 8.7 Hz, 8 H), 6.99 (d, *J* = 5.1 Hz, 2 H), 7.18 (d, *J* = 8.7 Hz, 8 H), 7.27 (d, *J* = 5.1 Hz, 2 H), 7.37 (br, 1 H), 7.51 (br, 1 H), 7.81 (d, *J* = 10.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 11.33, 14.30, 22.81, 22.93, 23.26, 24.06, 27.21, 29.29, 29.42, 29.56, 29.72, 29.93, 30.74, 31.98, 32.16, 34.00, 39.62, 57.01, 61.64, 70.44, 99.76, 102.38, 114.30, 117.38, 122.58, 123.36, 127.50, 129.20, 134.73, 137.86, 142.37, 145.59, 156.90, 158.25 (Multiple carbon peaks result from phenomenon of atropisomerism[3]);□IR (KBr) 3096, 3071, 3034, 2956, 2924, 2870, 2854, 1671, 1626, 1606, 1580, 1507, 1457, 1378, 1336, 1291, 1246, 1175, 1112, 1083, 1033, 1015, 1004, 971, 869, 821, 806, 712, 656, 540, 524 cm^{-1}; MS (FAB, $C_{95}H_{127}NO_4S_2$): Calcd, 1411.16; Found, 1411; elemental analysis (%) Calcd, for

$C_{95}H_{127}NO_4S_2$: C, 80.86; H, 9.07; N, 0.99. Found: C, 80.95; H, 9.40; N, 1.16.

Synthesis of Compound (M2).

To a solution of **6b** (0.8 g, 0.57 mmol) in dry THF (20 mL) was added a 1.7 M solution of *t*-BuLi in hexane (4.0 mL, 6.8 mmol) dropwise at -78 ^{o}C. After stirring at -78 ^{o}C for 30 min, 1.0 M solution of chlorotrimethylstannane in THF (8.0 mL, 8.0 mmol) was introduced by syringe to the solution. The mixture solution was warmed up to room temperature and stirred for 12 h. The mixture solution was quenched with water and extracted with diethyl ether (50 mL × 3) and water (50 mL). After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/Et3N, v/v, 50/1) to give a deep orange sticky product **M2** (0.9 g, 92%). ^{1}H NMR ($CDCl_3$,300 MHz): 0.37 (s, 18 H), 0.77-1.46 (m, 86 H), 1.62-1.68 (m, 4 H), 1.94 (br, 2 H), 2.30 (br, 2 H), 3.76 (d, J = 5.7 Hz, 8 H), 4.55 (br, 1 H), 6.75 (d, J = 8.7 Hz, 8 H), 7.02 (s, 2 H), 7.19 (d, J = 8.7 Hz, 8 H), 7.35 (br, 1 H), 7.50 (br, 1 H), 7.77 (d, J = 10.8 Hz, 2 H); IR (KBr) 3062, 3036, 2957, 2925, 2854, 1655, 1628, 1606, 1581, 1507, 1465, 1378, 1341, 1291, 1245, 1176, 1113, 1033, 1014, 916, 873, 825, 770, 719, 661, 600, 531, 513 cm^{-1}; MS (FAB, $C_{101}H_{143}NO_4S_2Sn_2$): calcd, 1736.77; found, 1736.

Synthesis of PFDCTBT.

To a solution of dry and deoxygenated toluene (15 mL) was introduced **M1** (0.5063 g, 0.294 mmol), 4,7-dibromo-2,1,3-benzothiadiazole **8** (86.4 mg, 0.294 mmol), and $Pd(PPh_3)_4$ (16.2 mg, 0.014 mmol). The reaction mixture was refluxed at 120℃ for 72 h. The solution was dropwise added into methanol. The precipitate was collected by filtration and washed by Soxhlet extraction with methanol/acetone (1/1, v/v) sequentially for three days. The product was re-dissolved in THF. 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 out. The purified polymer was collected by filtration and dried under vacuum for 1 day to give dark violet solid (230 mg, yield 51%, M_n = 8.6 kDa, PDI = 1.89). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.77-1.48 (m, 86 H), 1.64-1.66 (m, 4 H), 2.03- 2.17 (m, 4 H), 3.78 (br, 8 H), 6.75-6.82 (m, 8 H), 7.13-7.16 (m, 2 H), 7.19-7.23 (m, 8 H), 7.45-7.51 (m, 2 H), 7.84 (br, 2 H), 8.02 (br, 2 H).

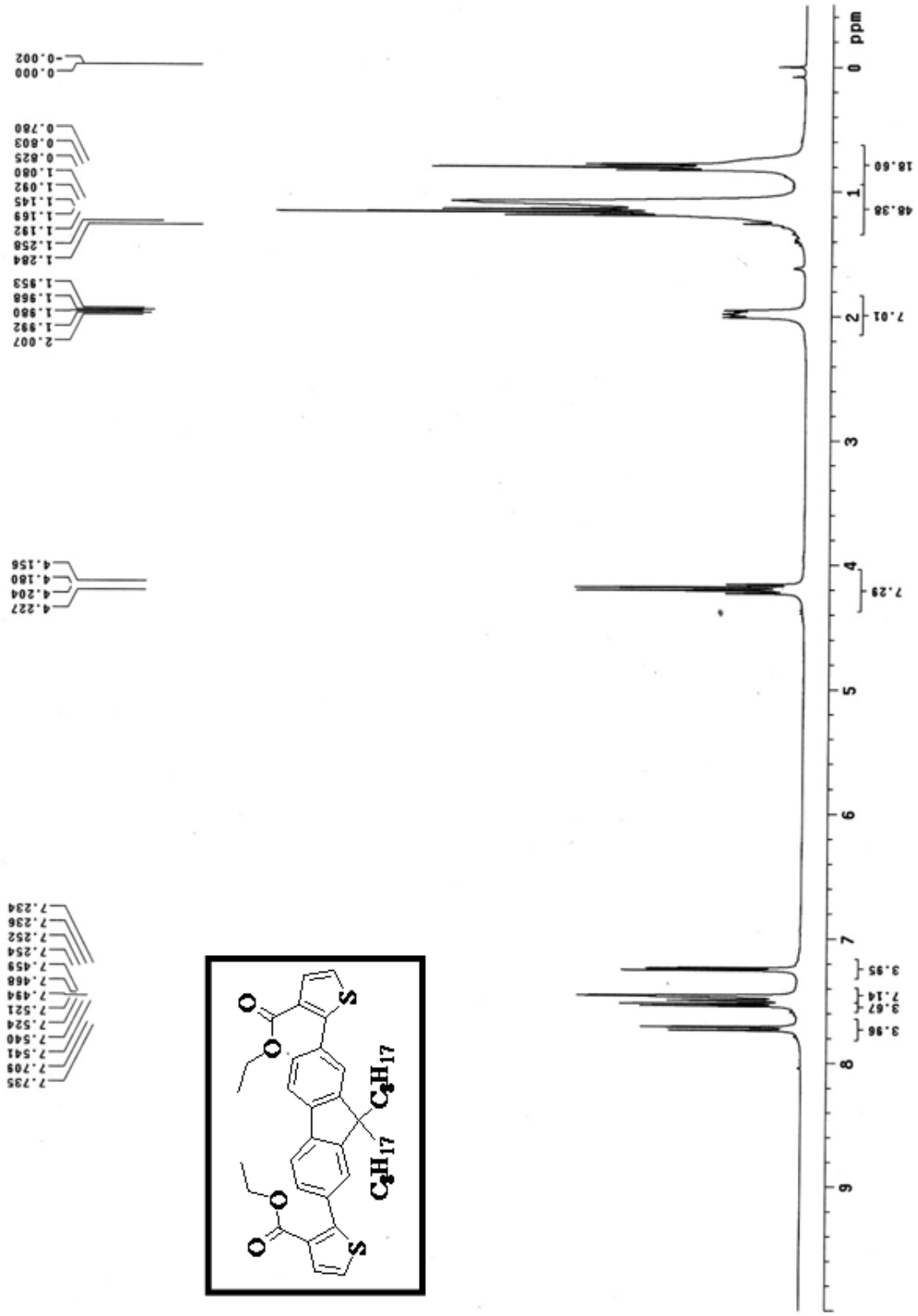
Synthesis of PCDCTBT.

To a solution of in dry deoxygenated toluene (15 mL) was introduced **M2** (0.570 g, 0.328 mmol), 4,7-dibromo-2,1,3-benzothiadiazole **8** (96.4 mg, 0.328 mmol), and $Pd(PPh_3)_4$ (18.9 mg, 0.0164 mmol). The reaction mixture was refluxed at 120℃ for

72 h. The solution was dropwise added into methanol. The precipitate was collected by filtration and washed by Soxhlet extraction with methanol/acetone (1/1, v/v) sequentially for three days. The product was dissolved in THF. 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 out. The purified polymer was collected by filtration and dried under vacuum for 1 day to give a dark violet solid (220 mg, yield 43%, M_n = 8.2 kDa, PDI = 1.59). ^{1}H NMR ($CDCl_3$, 300 MHz): 0.79-1.48 (m, 86 H), 1.64-1.66 (m, 4 H), 2.01 (br, 2 H), 2.33 (br, 2 H), 3.77 (br, 8 H), 4.60 (br, 1 H), 6.74-6.81 (m, 8 H), 6.90-7.01 (m, 2 H), 7.17-7.30 (m, 8 H), 7.47 (br, 1 H), 7.60 (br, 1 H), 7.86 (br, 2 H), 8.00 (br, 2 H).

References

1. Q. Hou, Q. Zhou, Y. Zhang, W. Yang, R. Yang and Y. Cao, *Macromolecules*, 2004, **37**, 6299.
2. M. Pomerantz, A. S. Amarasekara and H. V. R. Dias, *J. Org. Chem*., 2002, **67***,* 6931.
3. N. Blouim, A. Michaud and M. Leclerc, *Adv. Mater*., 2007, **19**, 2295.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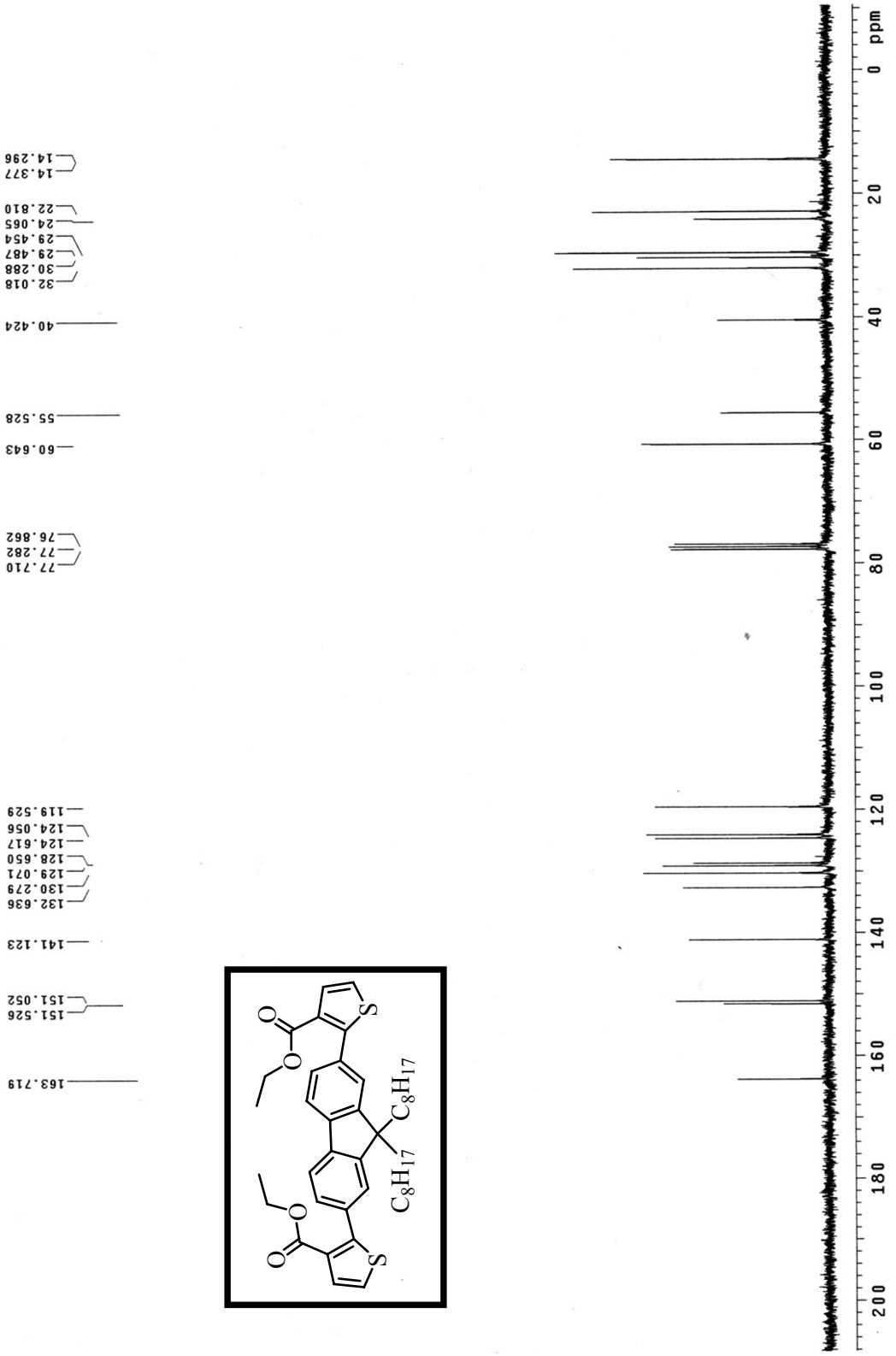
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O
O
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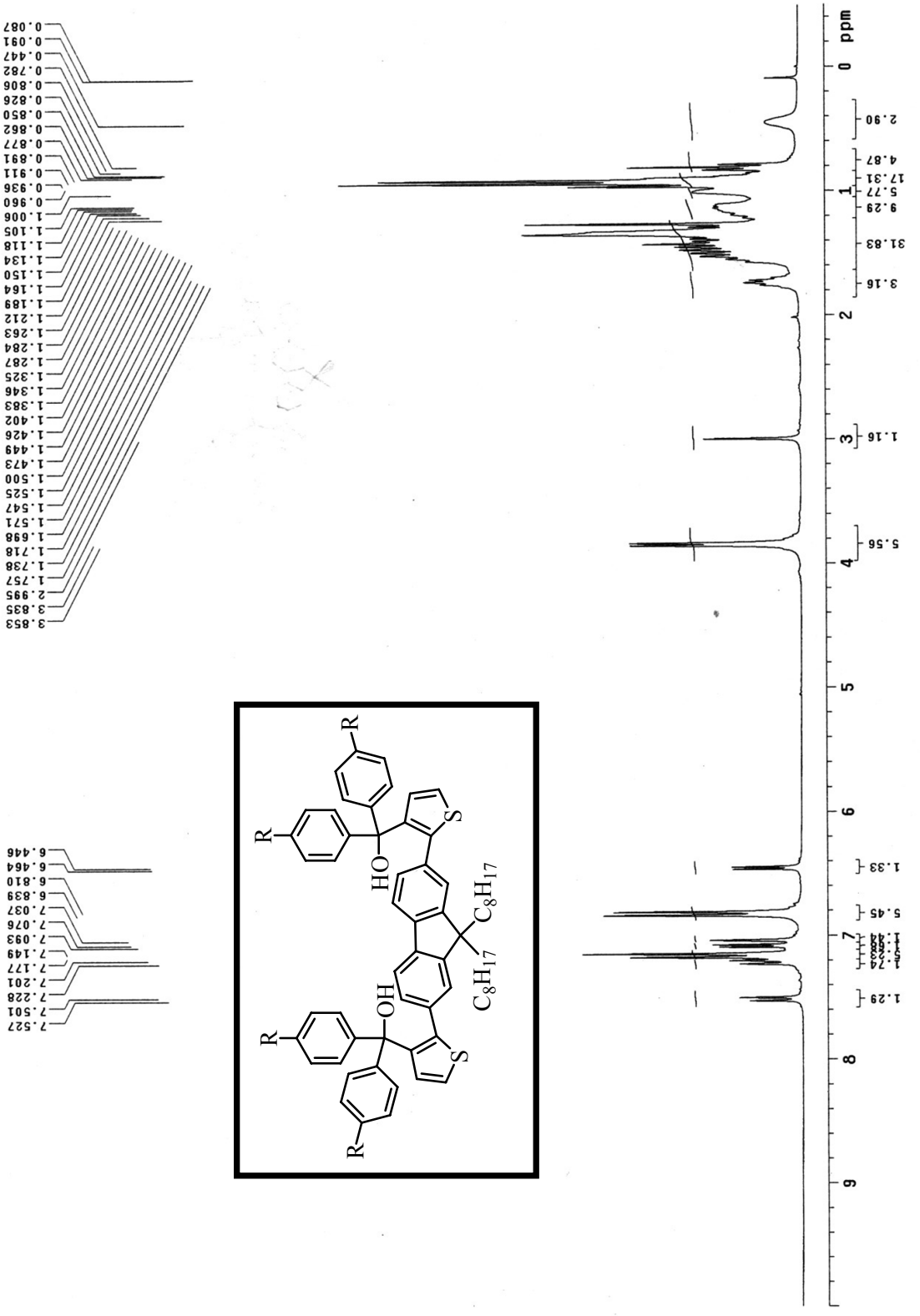
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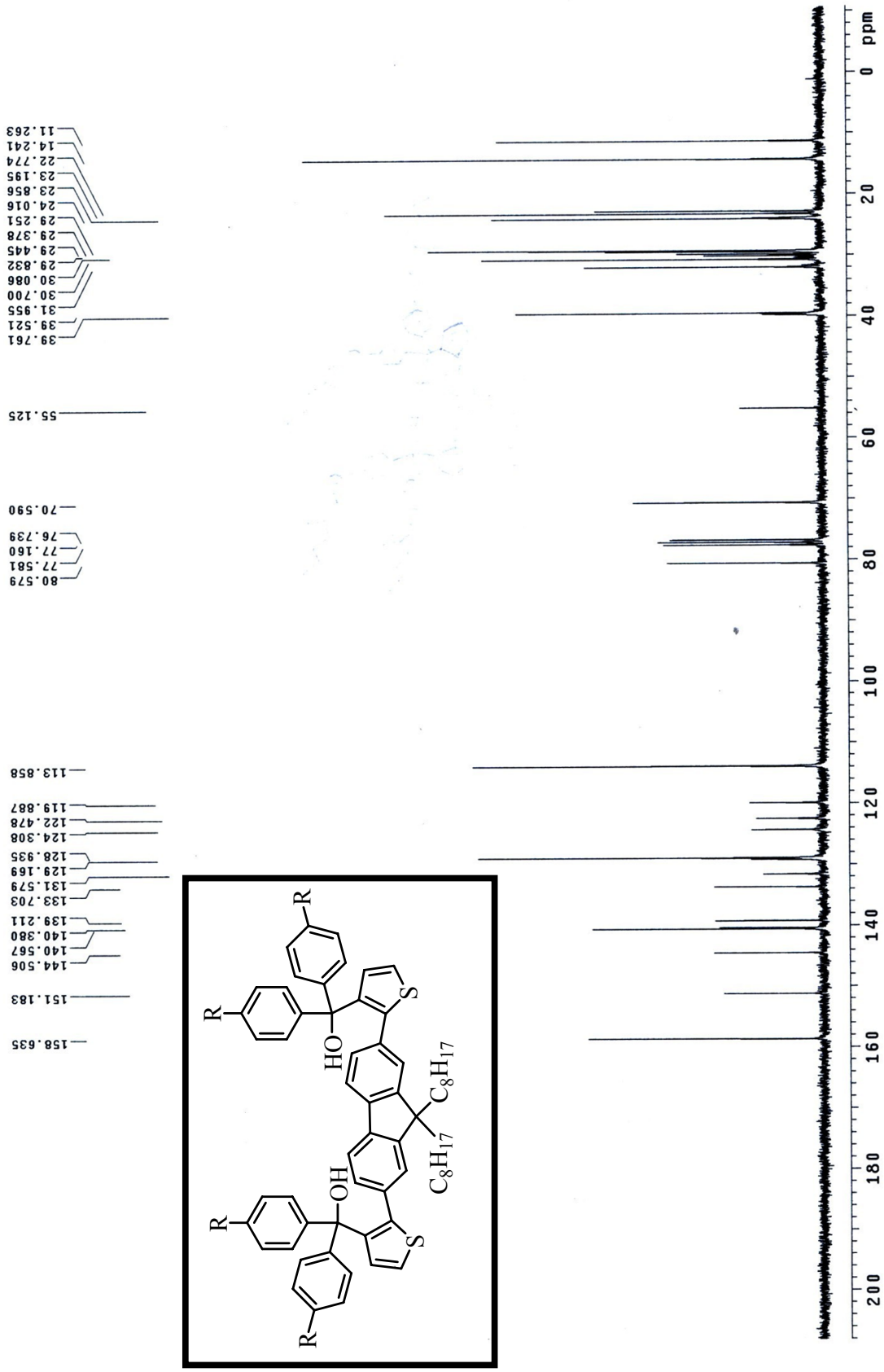
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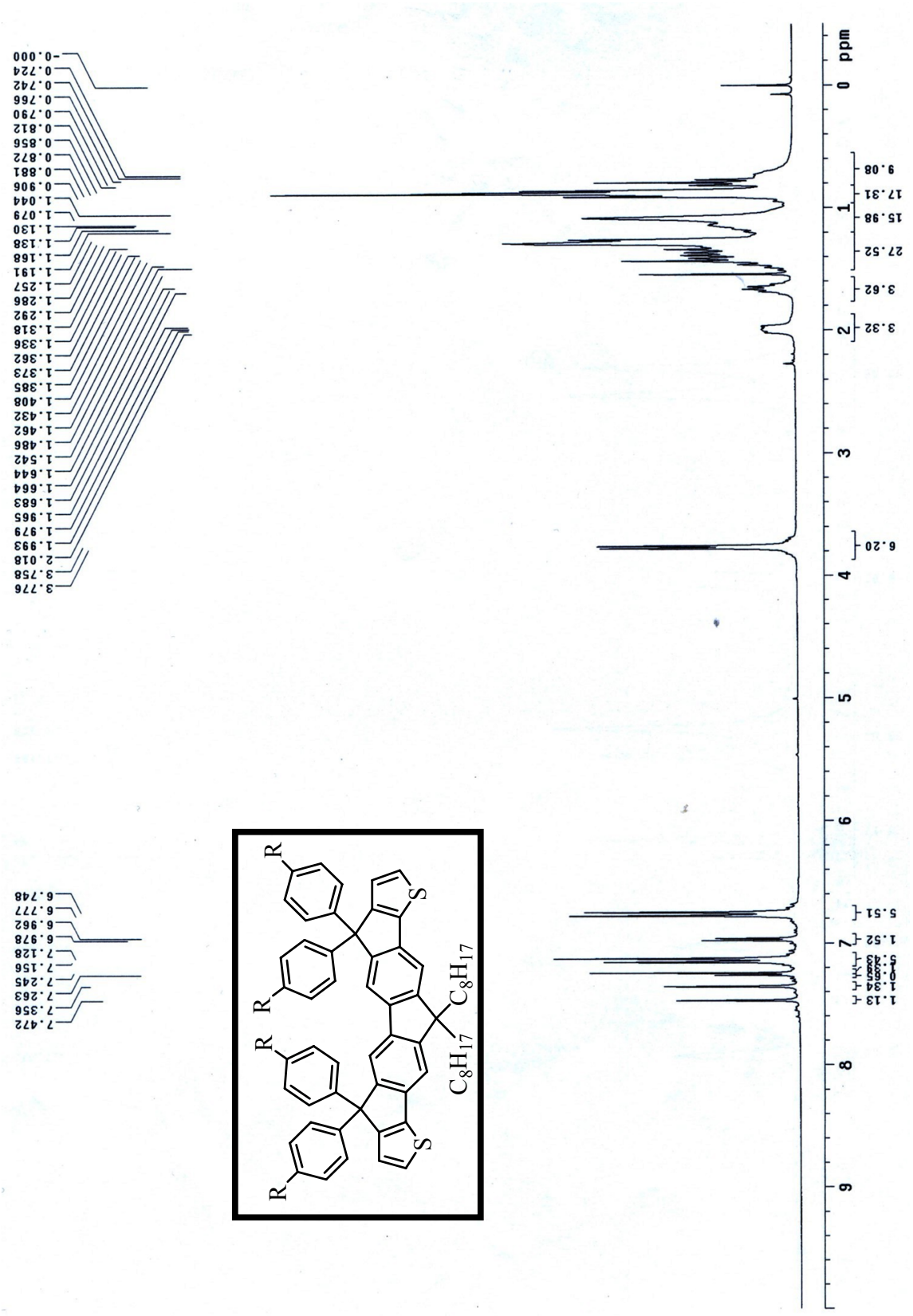
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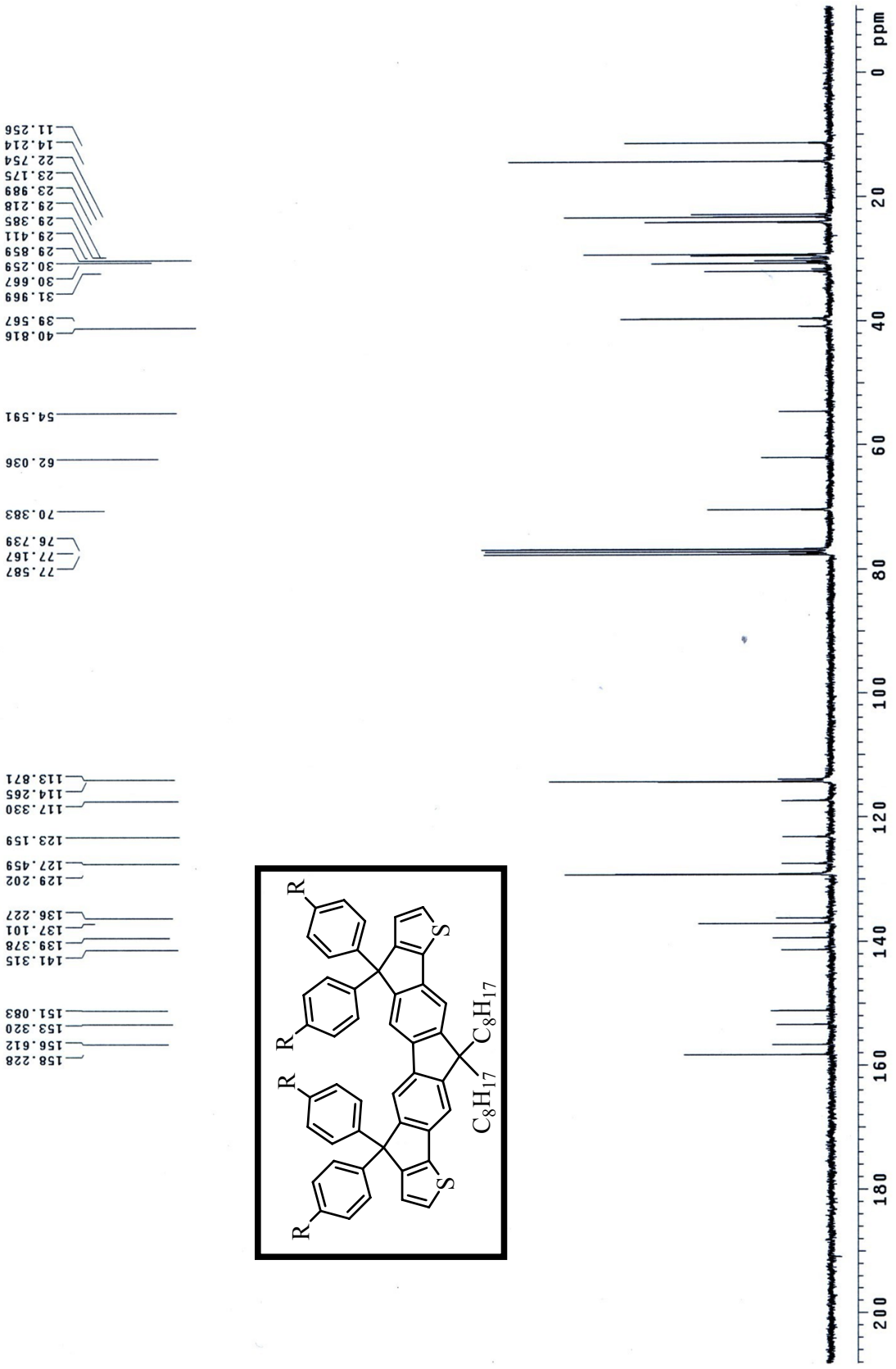
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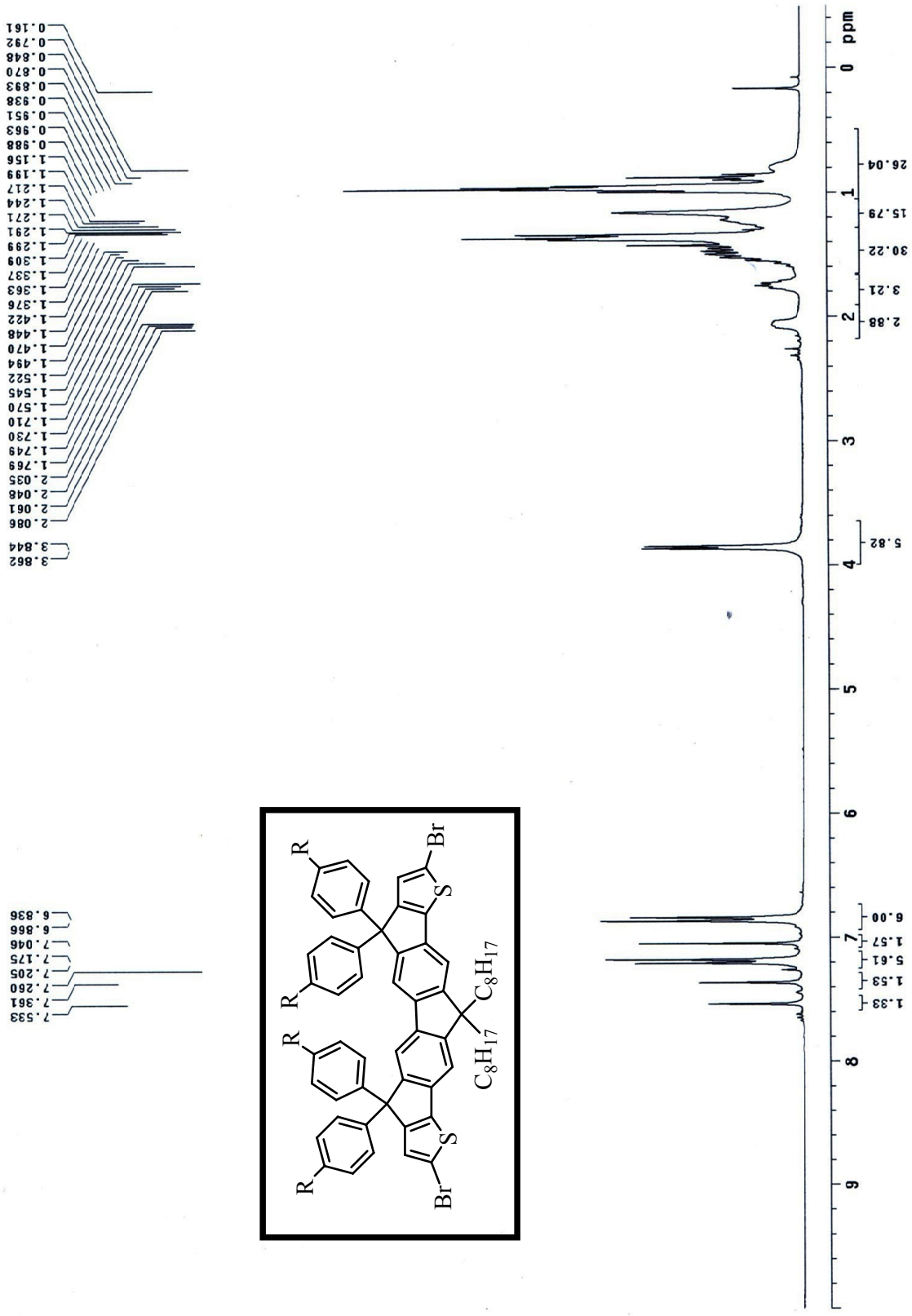
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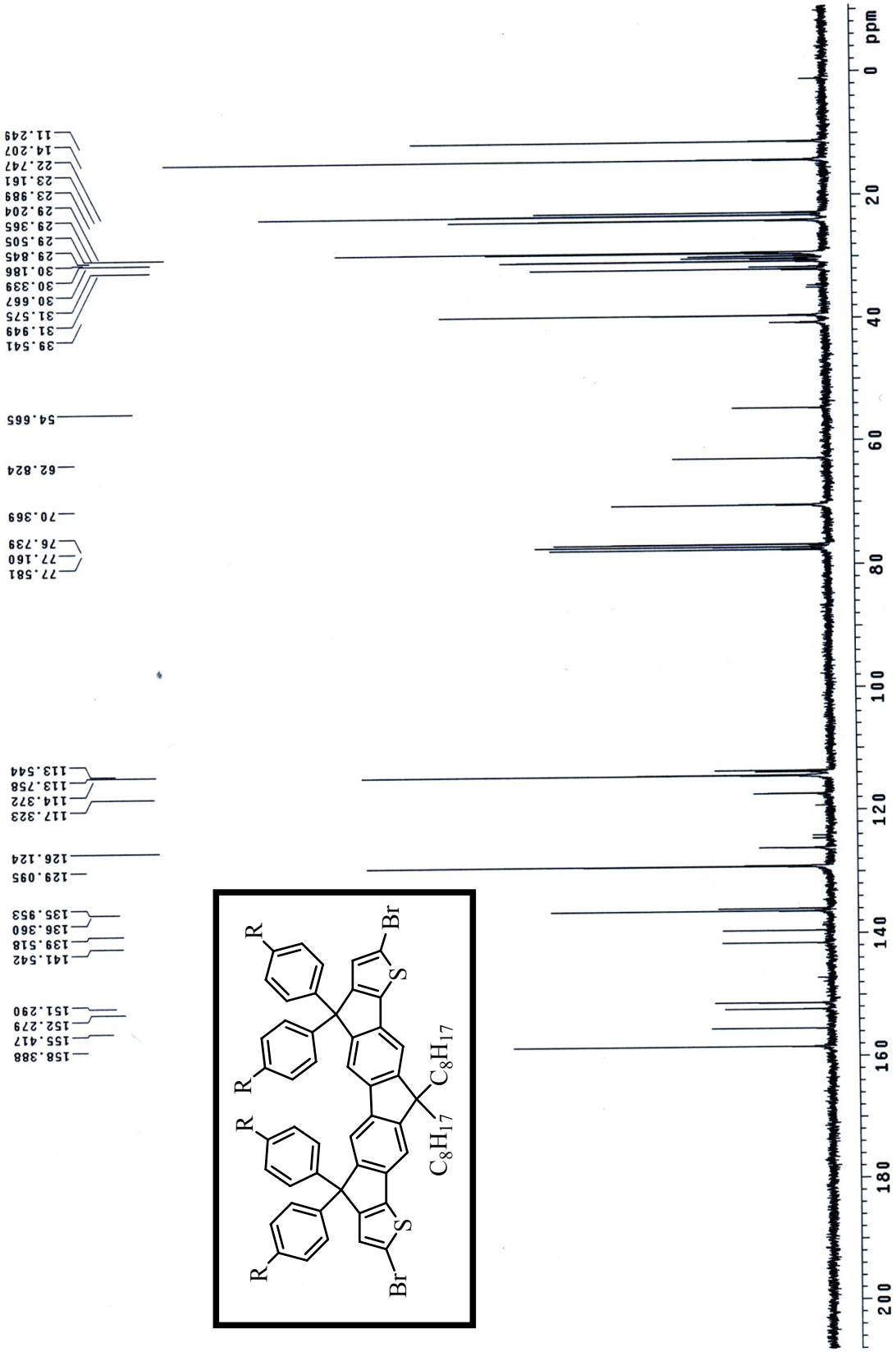
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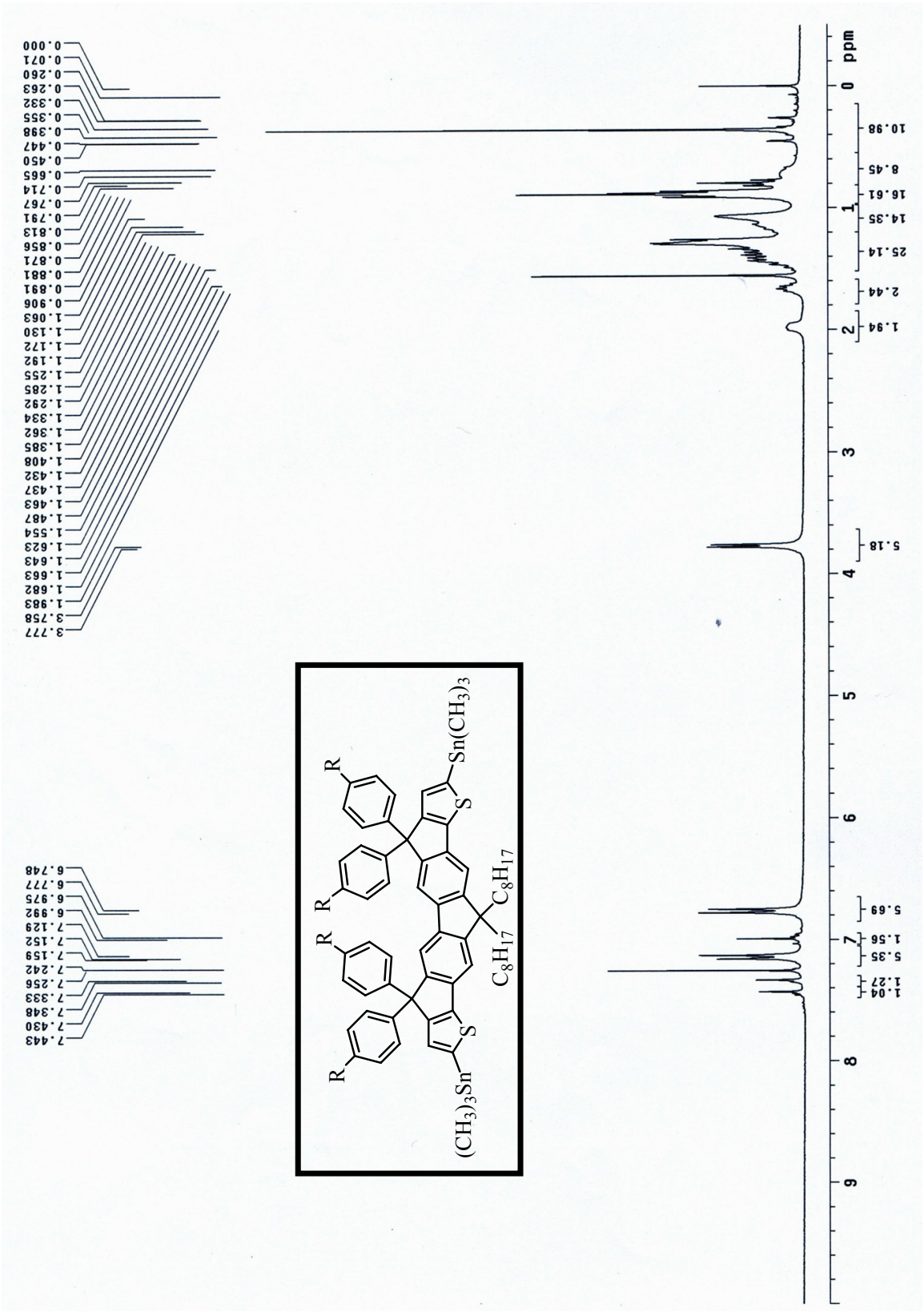
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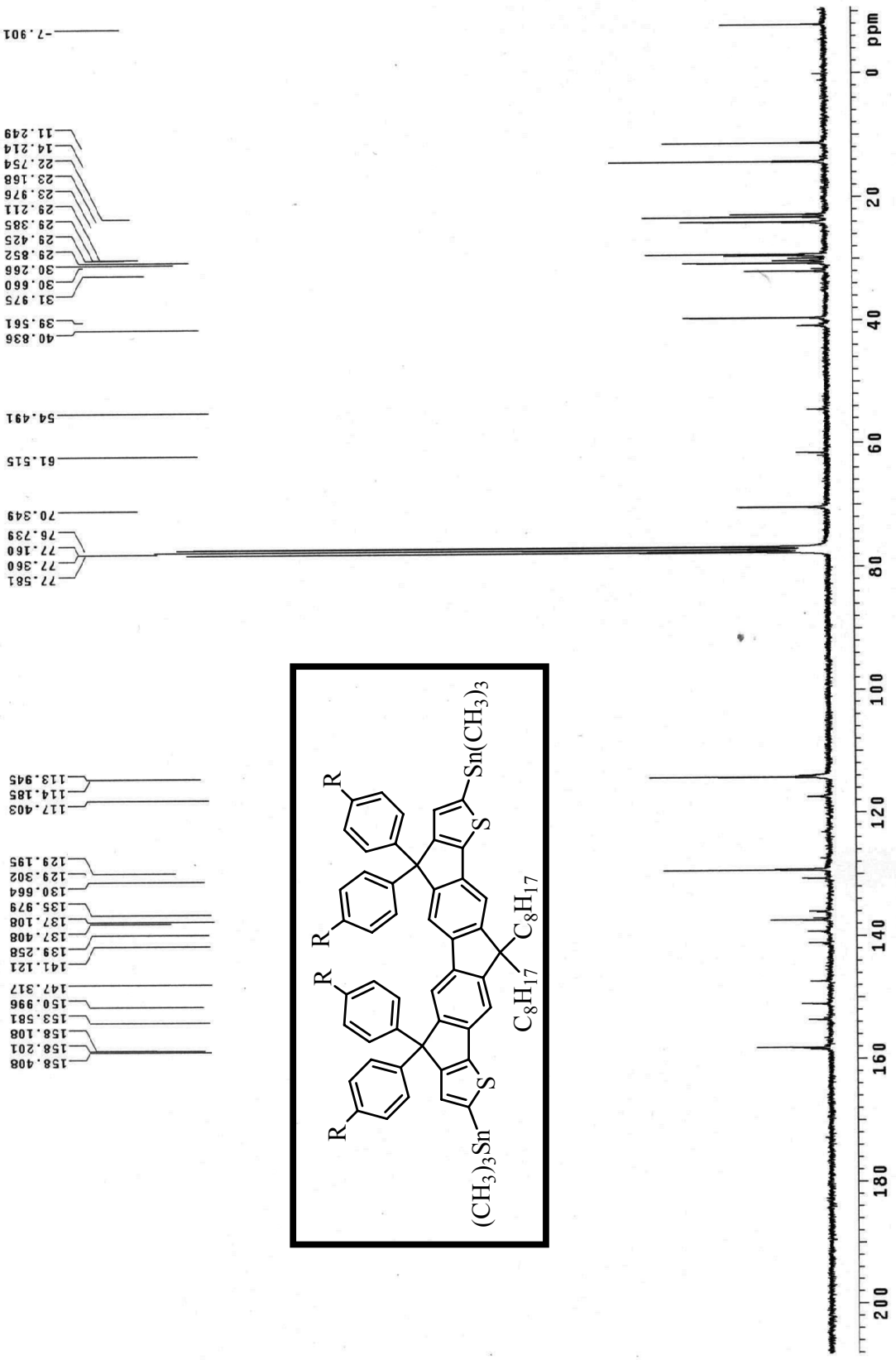
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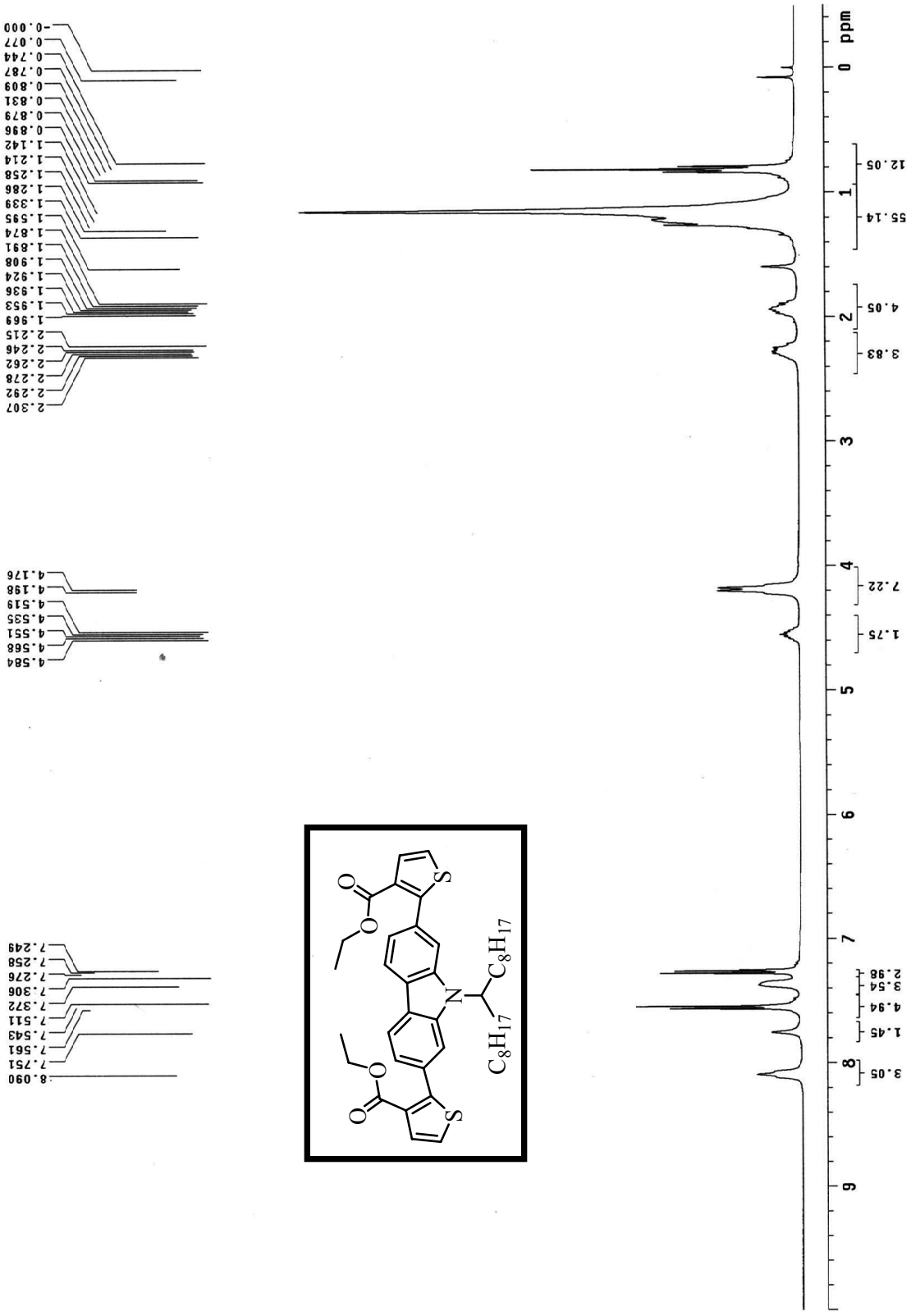
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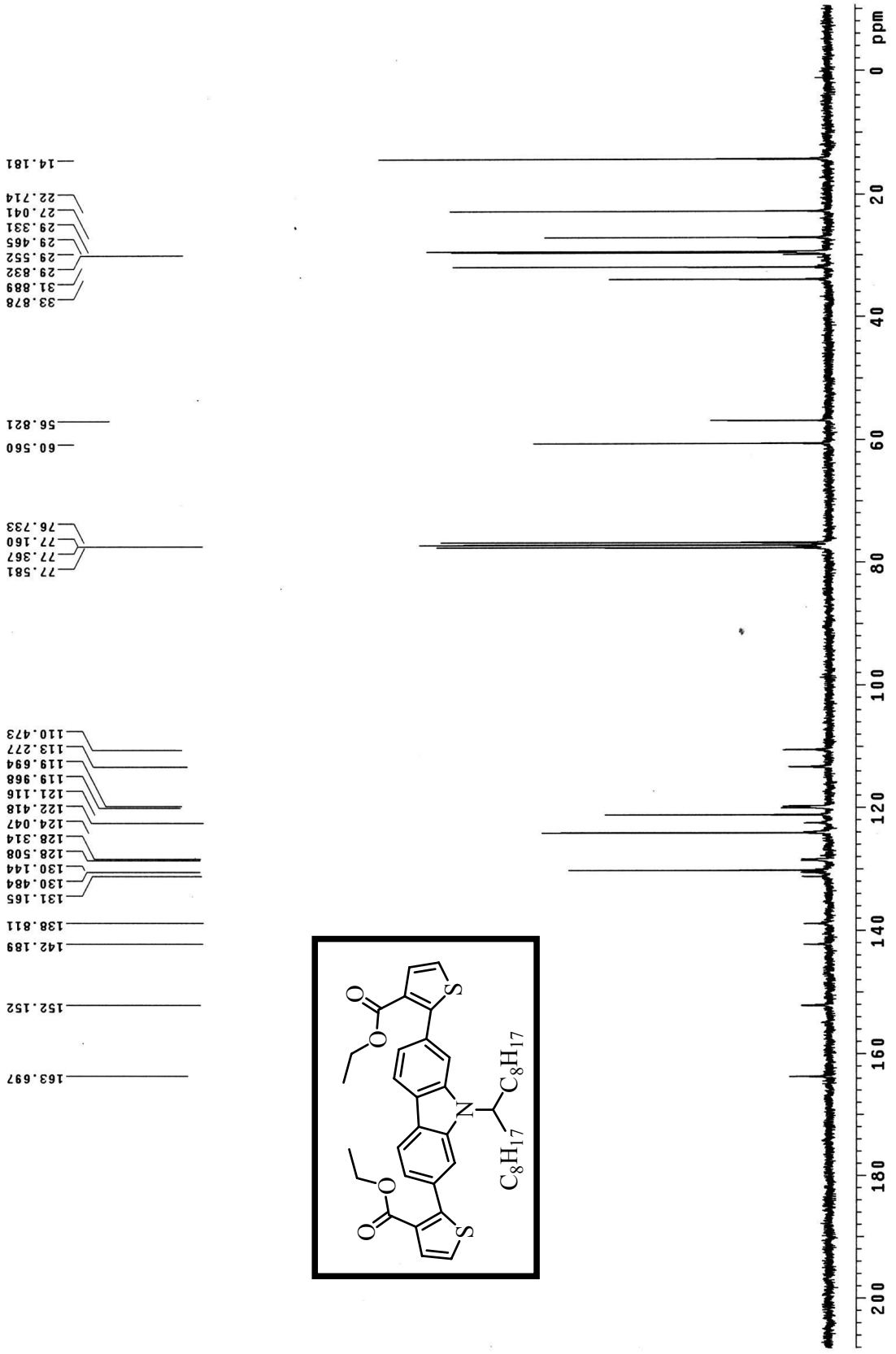
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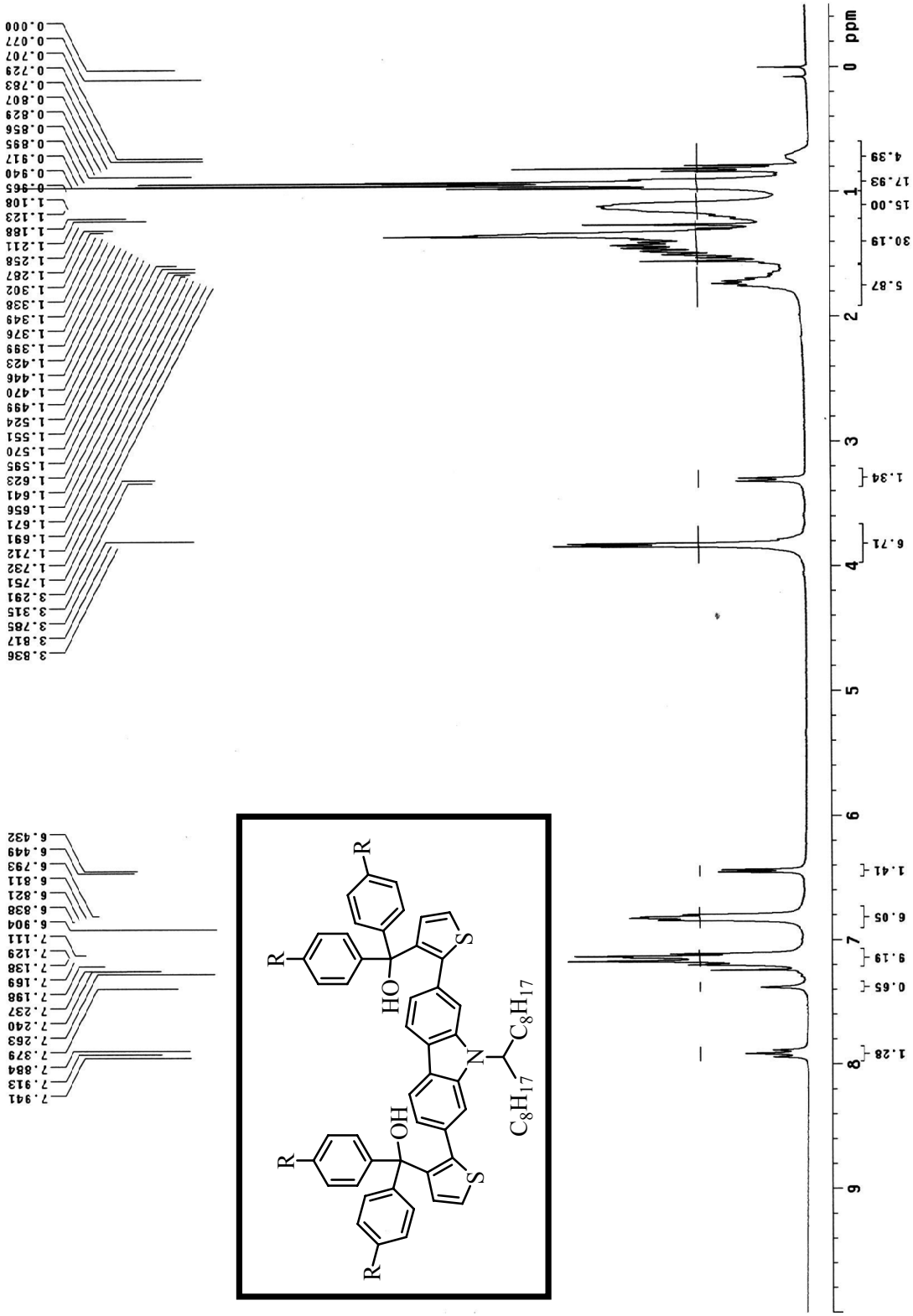
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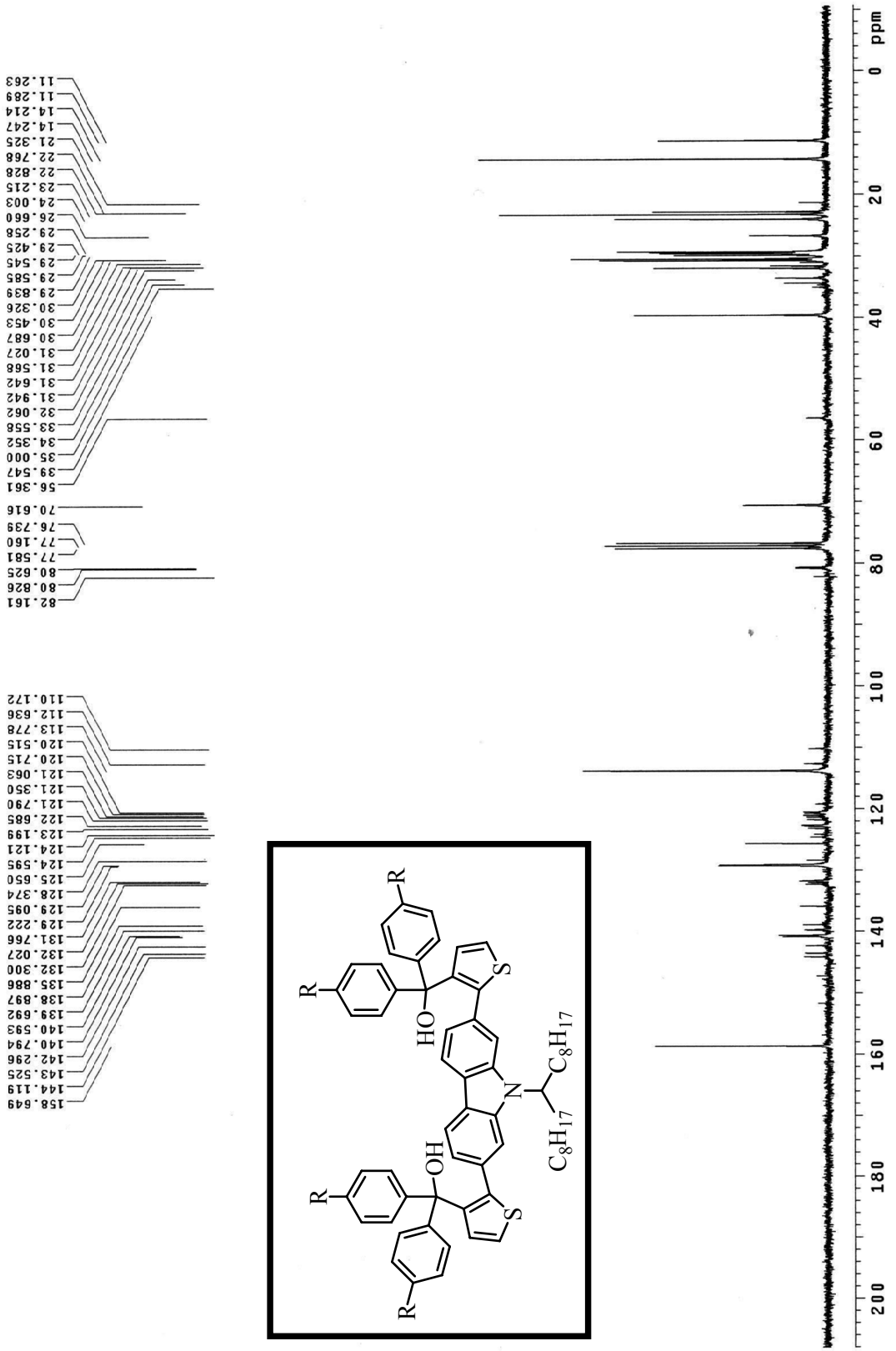
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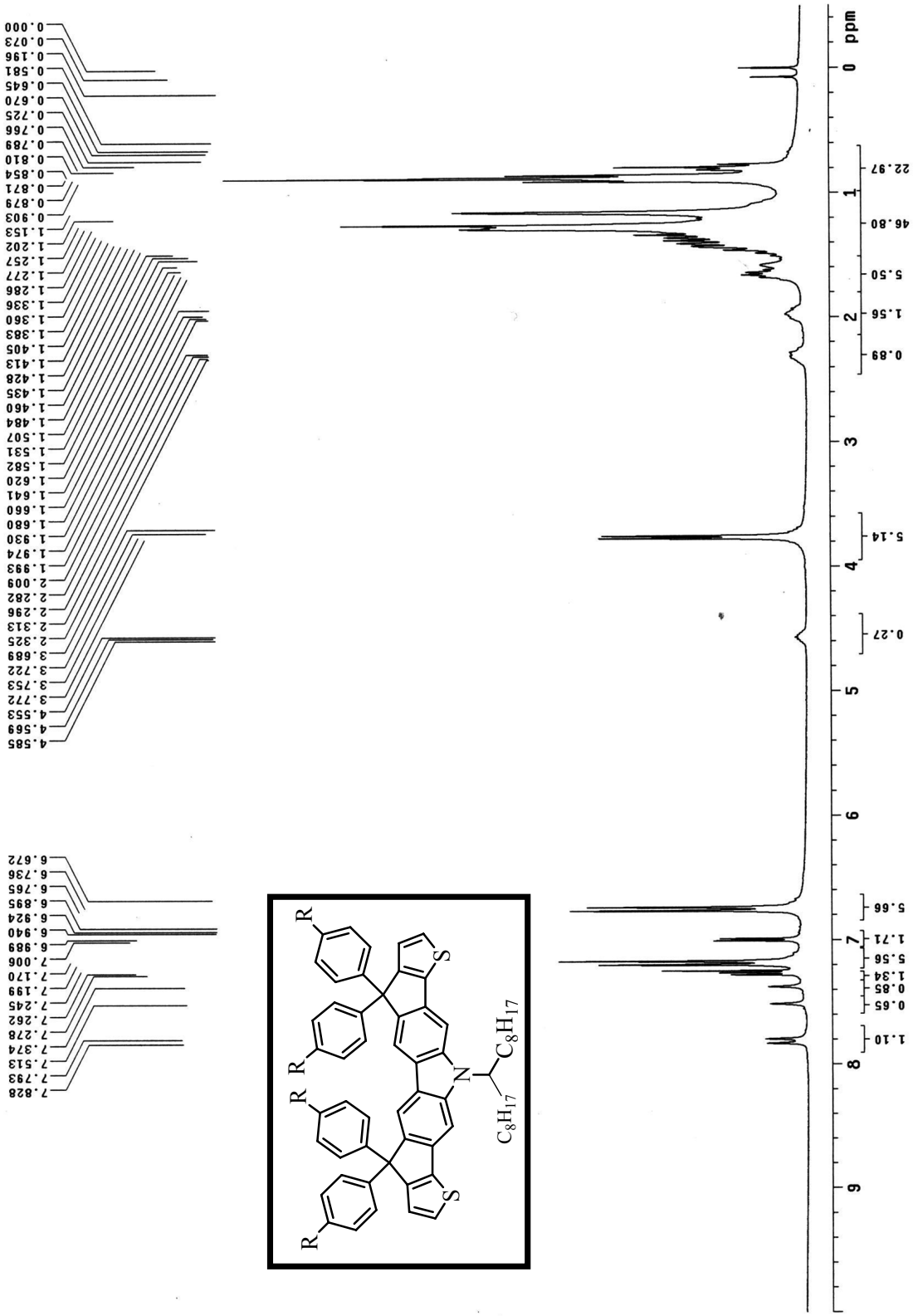
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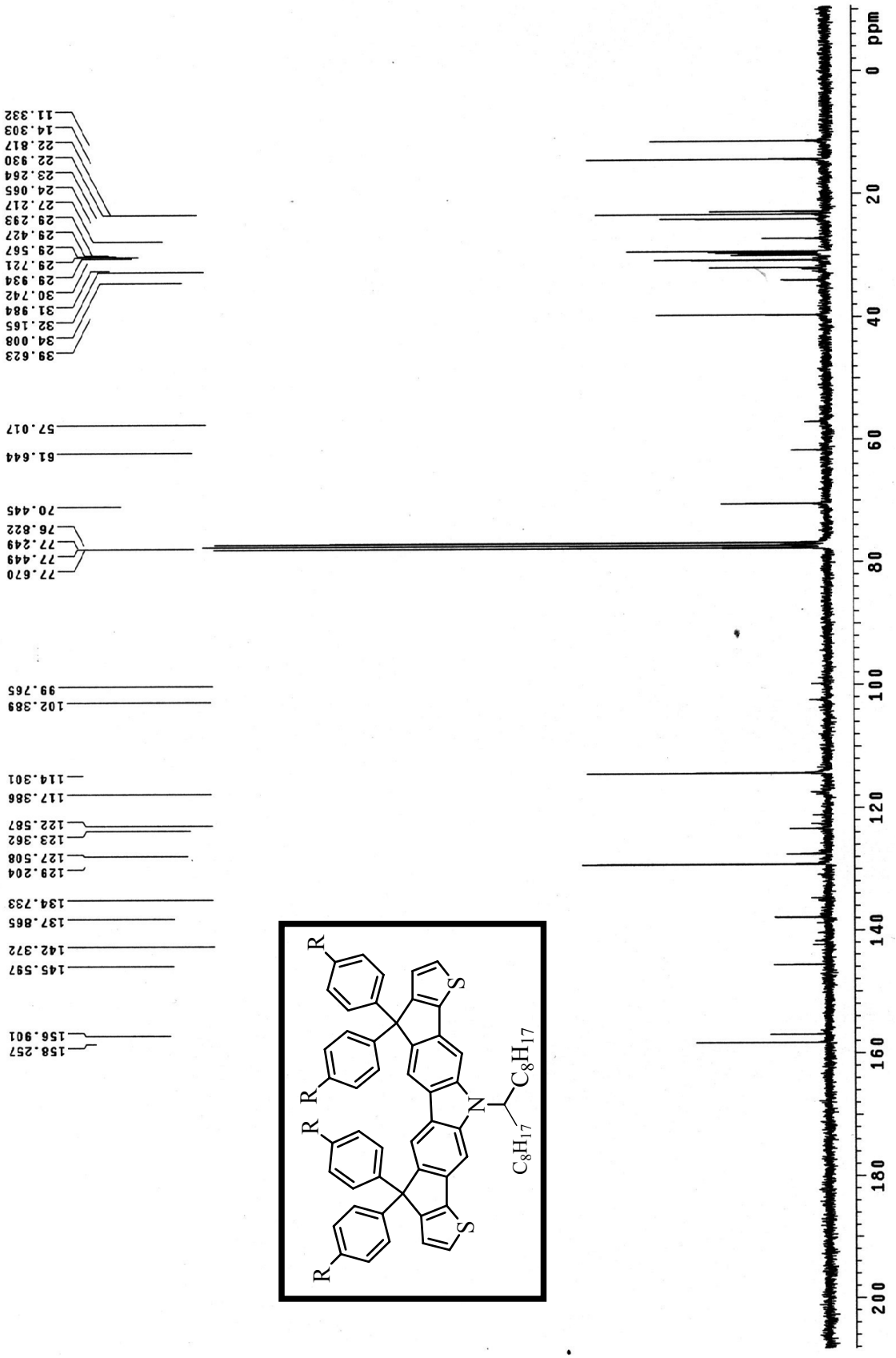
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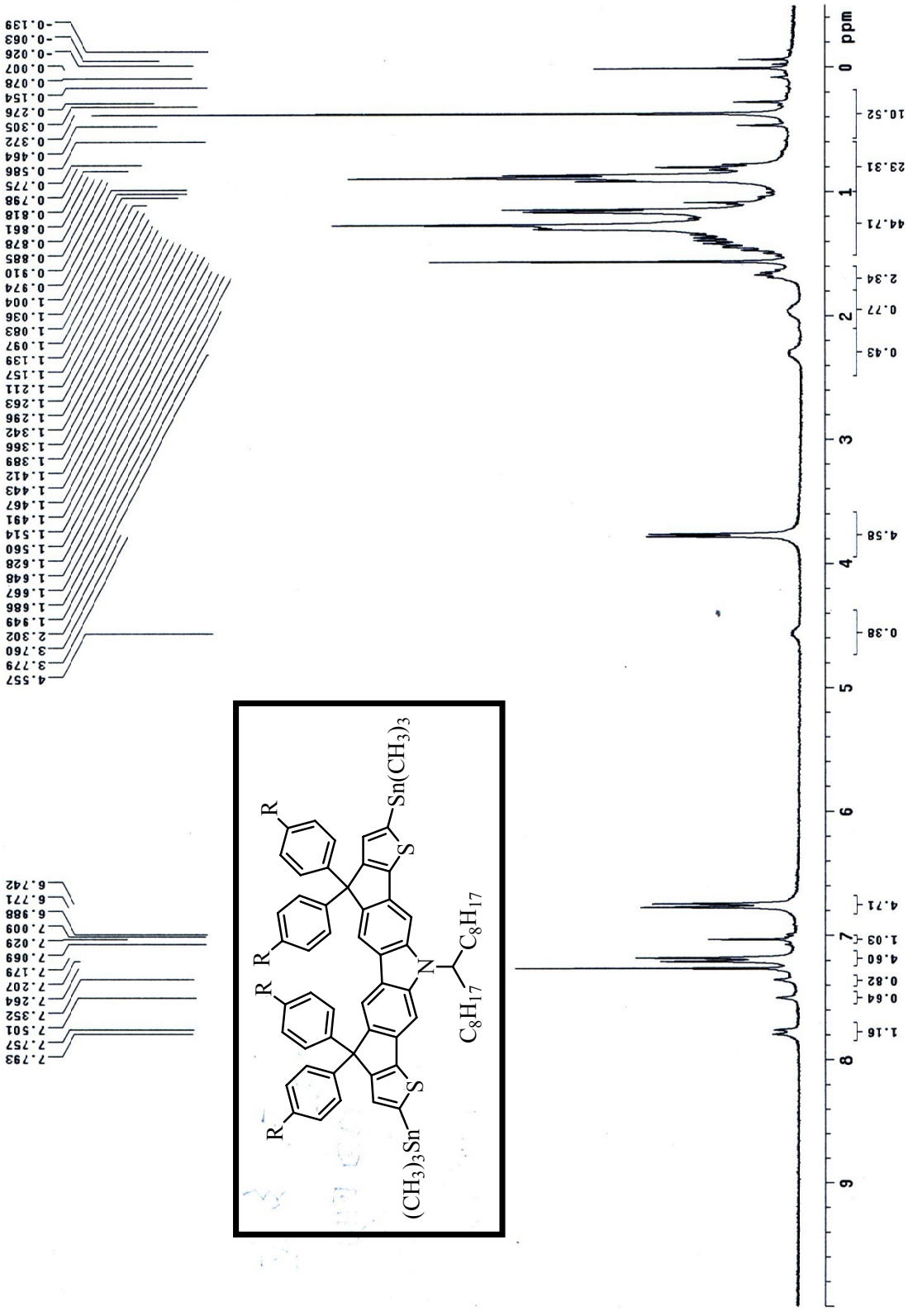
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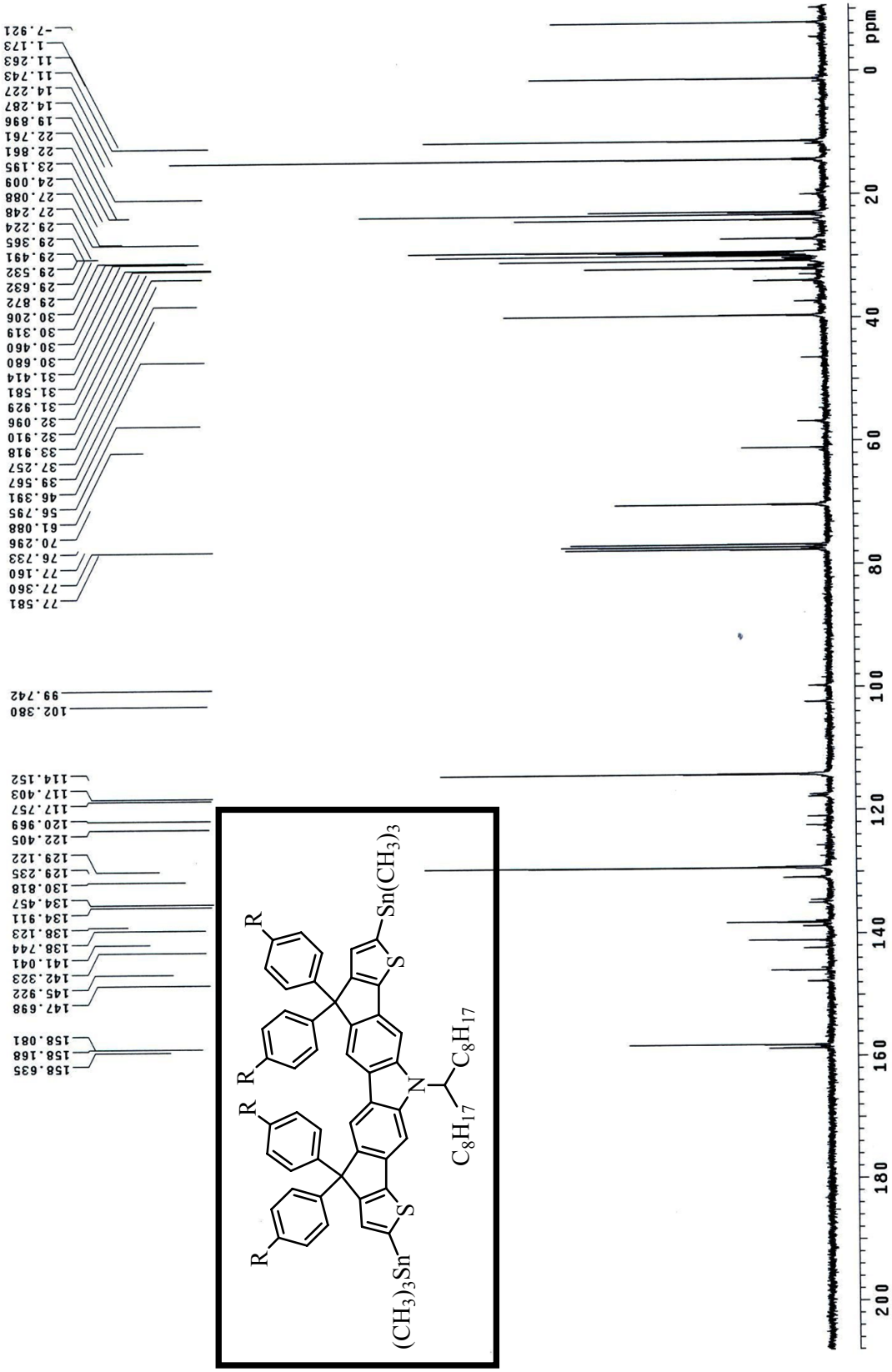
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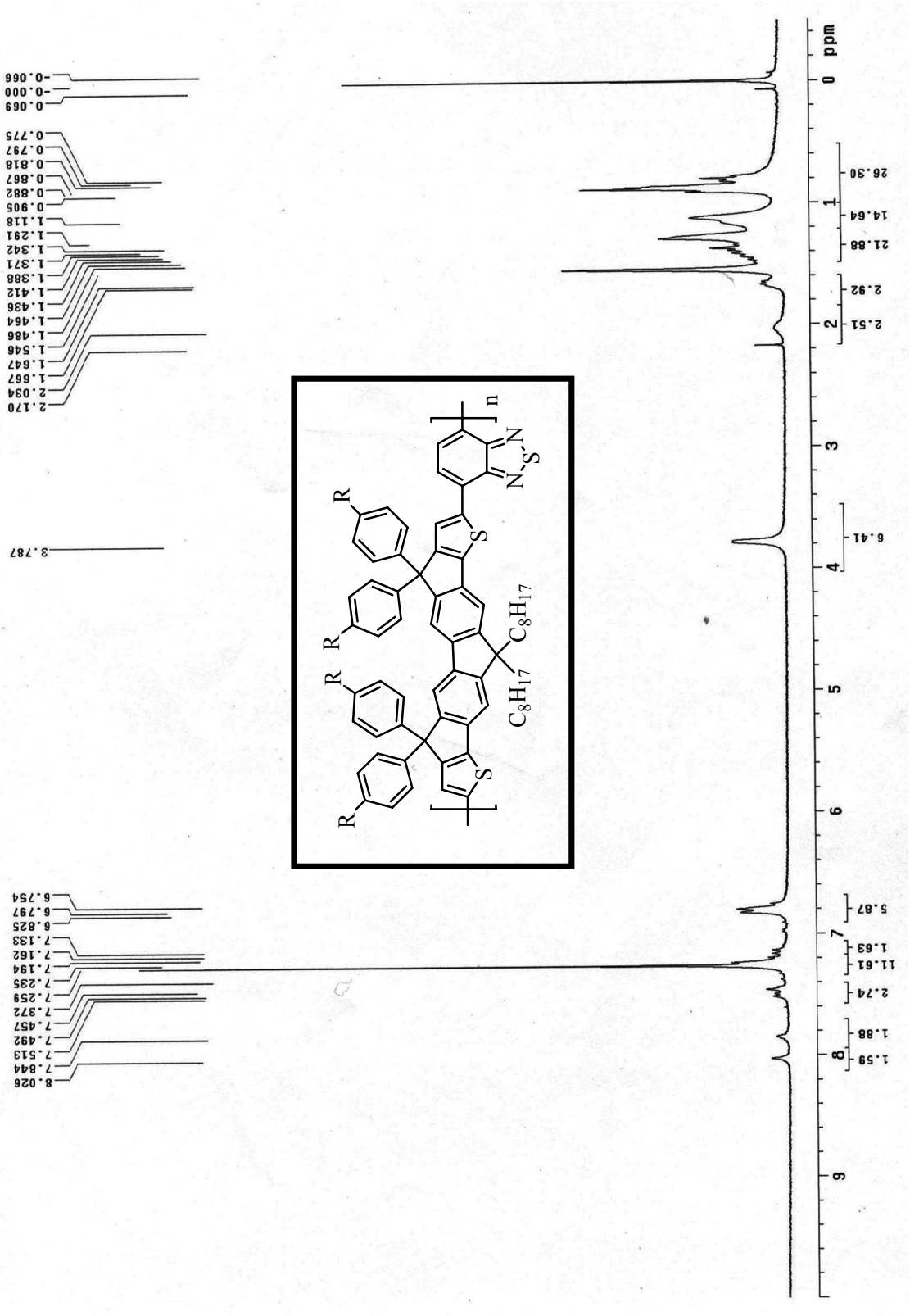
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