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A donor-acceptor-acceptor molecule for vacuum-processed organic solar cells with a power conversion efficiency of 6.4%

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Synthetic procedures:

General Methods: All chemicals and reagents were used as received from commercial sources without purification. Solvents for chemical synthesis were purified by distillation. All chemical reactions were carried out under an argon or nitrogen atmosphere. 2-[*N*,*N*-di(*p*-tolyl)amino]thiophene [1] and 5-bromo-2-iodopyrimidine [2] were synthesized according to the published procedures.

Synthesis of [5-(5-bromo-pyrimidin-2-yl)-thiophen-2-yl]-*N*,*N*-di(*p*-tolyl)amine (1). To a stirring solution of 2-[*N*,*N*-di(*p*-tolyl)amino]thiophene (8.31 g, 30 mmol) in anhydrous THF (90 mL) was dropwise added *n*-BuLi (1.6 M, 19.69 mL, 31.5 mmol) at -78 °C under argon atmosphere. The reaction mixture was warmed to -35 °C and stirred for 15 min. $ZnCl_2$ (33 mL of 1 M solution in anhydrous THF, 33 mmol) was then added to the reaction mixture in one portion, after which the reaction mixture was warmed to room temperature and stirred for 30 min. To the above resulting zinc reagent was added 5-bromo-2-iodopyrimidine (8.55 g, 30 mmol), $Pd(PPh_3)_4$ (1.73 g, 1.5 mmol), and anhydrous THF (120 mL). The whole mixture was heated to reflux under argon atmosphere for 2 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with ethyl acetate, the combined extracts were washed with brine, dried over anhydrous magnesium sulfate and filtered. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with CH_2Cl_2/hexane (v/v, 1:2) as eluent to afford **1** as a yellow solid (10.84 g, 83%). M.p. 173-174 °C; IR (KBr) ν 3028, 2916, 1605, 1551, 1374, 1119, 1056, 928 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.55 (s, 2H), 7.71 (d, J = 4.4 Hz, 1H), 7.16-7.10 (m, 8H), 6.43 (d, J = 4.4 Hz, 1H), 2,34 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.5, 158.9, 157.2, 144.4, 134.3, 130.0, 129.8, 128.9, 124.4, 114.7, 114.5, 21.0; HRMS (m/z, FAB^+) Calcd. for $C_{22}H_{18}{}^{79}BrN_3S$ 435.0405, found 435.0411. Calcd. for $C_{22}H_{18}{}^{81}BrN_3S$ 437.0384, found 437.0391.

Synthesis of 2-[5-*N*,*N*-di(*p*-tolyl)aminothiophen-2-yl]-pyrimidine-5-carbaldehyde (2). To a stirring solution of **1** (8.73 g, 20 mmol) in 350 mL anhydrous THF was dropwise added *n*-BuLi (1.6 M, 13.13 mL, 21 mmol) at -100 °C under argon atmosphere. The resulting solution was stirred for 30 min, after which dry ethyl formate (16.15 mL, 200 mmol) was added dropwise over 5 min. After stirring for 30 min, the reaction was quenched with 1.5 M HCl in THF solution (15 mL, 22.5 mmol). The cold bath was removed, and the reaction mixture was stirred for 2 h. The THF was removed by rotary evaporation and the reaction mixture was extracted with

[1] I.-Y. Wu, J. T. Lin, Y.-T. Tao, E. Balasubramaniam, Y. Z. Su and C.-W. Ko, *Chem. Mater.*, 2001, **13**, 2626.
[2] G. Vlád and I. T. Horváth, *J. Org. Chem.*, 2002, **67**, 6550.

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chloroform, the combined extracts were washed with brine, dried over anhydrous magnesium sulfate and filtered. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with CH_2Cl_2 as eluent to afford **2** as an orange solid (3.27 g, 42%). M.p. 176-177 ^oC; IR (KBr) ν 3027, 2918, 2825, 2719, 1694, 1593, 1547, 1209, 1071 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 9.92 (s, 1H), 8.88 (s, 2H), 7.88 (d, J = 4.4 Hz, 1H), 7.20-7.14 (m, 8H), 6.40 (d, J = 4.4 Hz, 1H), 2.36 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.9, 164.1, 162.7, 158.4, 143.7, 135.4, 133.4, 130.2, 127.3, 125.1, 124.1, 113.1, 21.1; HRMS (m/z, FAB^+) Calcd. for $C_{23}H_{19}N_3OS$ 385.1249, found 385.1252.

Synthesis of 2-{[2-(5-*N*,*N*-di(*p*-tolyl)aminothiophen-2-yl)-pyrimidin-5-yl]methylene}malononitrile (DTDCTP). A mixture of **2** (1.54 g, 4.00 mmol), malononitrile (528 mg, 8.00 mmol), and basic aluminum oxide (2.00 g) in dry toluene (60 mL) was stirred and heated at 70 ^oC for 1 h. After the reaction mixture was cooling to room temperature, the basic aluminum oxide residue was removed by filtration and thoroughly washed with toluene. Solvent of the filtrate was removed by rotary evaporation, and the crude product was purified by column chromatography on silica gel with CH_2Cl_2 as eluent to afford **DTDCTP** as a black solid (1.36 g, 78%). M.p. 209 ^oC (DSC); IR (KBr) ν 3024, 2921, 2221, 1587, 1542, 1286, 1107, 1071, 814 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.93 (s, 2H), 7.91 (d, J = 4.4 Hz, 1H), 7.47 (s, 1H), 7.22-7.16 (m, 8H), 6.39 (d, J = 4.4 Hz, 1H), 2.37 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.5, 163.0, 158.2, 152.7, 143.3, 136.1, 135.1, 130.3, 126.6, 125.4, 119.8, 113.7, 112.9, 112.8, 80.1, 21.1; HRMS (m/z, FAB^+) Calcd. for $C_{26}H_{19}N_5S$ 433.1361, found 433.1358.

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Absorption spectra of DTDCTP

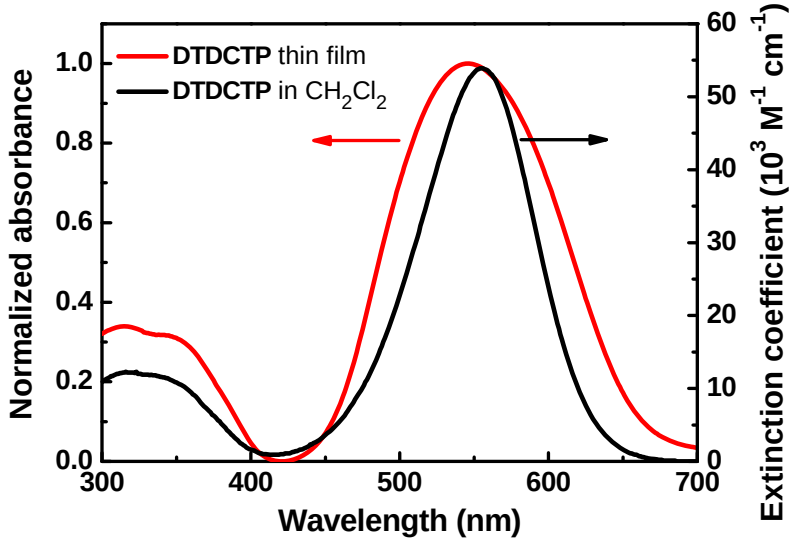

Fig. S1 Absorption spectra of **DTDCTP** in CH_2Cl_2 and a vacuum-deposited thin film.

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Crystal data for DTDCTP

Crystal structure determinations:

Crystallographic data were collected at 295(2) K on a Oxford Gemini A CCD diffractometer using graphite-monochromatized Cu-Kα radiation (λ = 1.54178 Å). Cell parameters were retrieved and refined using CrysAlis Pro software on all observed reflections. Data reduction was performed with the CrysAlis Pro software. The structures were solved and refined with SHELXL programs.[3] The hydrogen atoms were included in calculated positions and refined using a riding mode.

Table S1 Crystal Data for **DTDCTP**

	DTDCTP
Empirical formula	$C_{60}H_{50}N_2OS$
Formula weight	847.08
Crystal dimensions/mm^3	0.20 × 0.15 × 0.10
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	7.9834 (3)
b/Å	10.1056 (4)
c/Å	14.4674 (5)
α (°)	80.452 (3)
β (°)	79.680 (3)
γ (°)	80.471 (3)
Cell volume/Å^3	1121.24 (7)
Z	2
Density (calc)/g cm^{-3}	2.509
F (000)	896
Temperature/K	295(2)
Wavelength/Å	1.54178
No. of reflns collected	12110
No. of indep reflns (R_{int})	4084 (0.0364)
R(*F*), *wR2* [I > 2σ(I)]	0.0486, 0.1398
R(*F*), wR_2 (all data)	0.0609, 0.1544

[3] Sheldrick, G. M. SHELXL-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.

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Device fabrication and measurement

Organic compounds including synthesized **DTDCTP**, and purchased fullerenes C_{60} or C_{70} and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were subject to purification at least once by temperature-gradient sublimation before use in this study. The organic and metal oxide thin films and metal electrodes were deposited on indium tin oxide (ITO) coated glass substrates in a high vacuum chamber with base pressure ~ $1x10^{-6}$ Torr. The sheet resistance of ITO is ~ 15Ω/sq. The deposition was performed at a rate of 2-3 Å with the substrate held at room temperature. Thicknesses were monitored using a crystal oscillator during deposition and were verified later with spectroscopic ellipsometry. The active areas of the cells were carefully measured (intersect area between the Ag cathode and ITO anode) device-by-device by using calibrated optical microscope and had an average size of 5 mm^2. Devices were encapsulated by using a UV-cured sealant (*Everwide Chemical Co., Epowide EX*) and a cover glass under the dry nitrogen atmosphere after fabrication and were measured in air. Current density-voltage characteristics were measured with a SourceMeter *Keithley* 2636A under illumination of AM1.5G solar light from a xenon lamp solar simulator (*Abet Technologies*). The incident light intensity was calibrated as 100mW/cm^2. Taking the spectral mismatch between the solar simulator used in this work and the AM 1.5G reference spectrum (IEC 60904) as well as mismatch of photoresponse spectral coverage of the reference cell (KG5 filtered Si diode) and the **DTDCTP** cell into account, the mismatch factor M is calculated to be 0.994.[4] The devices were all measured without a mask (the J_{SC} values of cells measured with and without a mask had been examined and the differences were always less than 2%). The external quantum efficiency spectra were taken by illuminating chopped monochromatic light with a continuous-wave bias white light (from halogen lamp) on the solar cells. The photocurrent signals were extracted with lock-in technique using a current preamplifier (*Stanford Research System*) followed by a lock-in amplifier (*AMETEK*). The EQE measurement is fully computer-controlled and the intensity of monochromatic light is carefully calibrated with optical power meter (*Ophir Optronics*). Organic films for photoelectron spectroscopy and ellipsometry measurements were prepared by vacuum-deposition on fused silica substrates. The HOMO values of thin films were acquired with a photoelectron spectrometer (*Riken Keiki Co. Ltd.*). Ellipsometry measurements were carried out with *J. A. Woollam Inc. V-VASE* variable-angle spectroscopic ellipsometer. Simulation program is coded with *Matlab* software (*The MathWorks, Inc.*) and performed with dual-core *Intel*-CPU personal computer. AFM images were taken with

[4] V. Shrotriya, G. Li, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Adv. Mater.*, 2006, **16**, 2016.

Veeco Nanoscope 3100 atomic force microscope. The film preparation conditions for the AFM measurements were kept the same as device fabrication for accurate comparison. The electron and hole mobilities of the **DTDCTP**:C_{70} mixed layer were carried out with the space-charge-limited-current (SCLC) method. Devices for mobility measurements were deposited on patterned ITO glass which was treated by UV ozone after cleaning, the hole mobility device was configured as: ITO/MoO_3 (1 nm)/**DTDCTP**:C_{70} (100 nm)/MoO_3 (10 nm)/Al (100 nm), the electron mobility device was configured as: ITO/Mg (5nm)/**DTDCTP**:C_{70} (100 nm)/Ca (5 nm)/Al (100 nm), current density-voltage characteristics were also measured with a SourceMeter *Keithley* 2636A.

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Device characteristics of DTDCTP:C_{60} PMHJ solar cells with different thicknesses of DTDCTP:C_{60} and DTDCTP layers

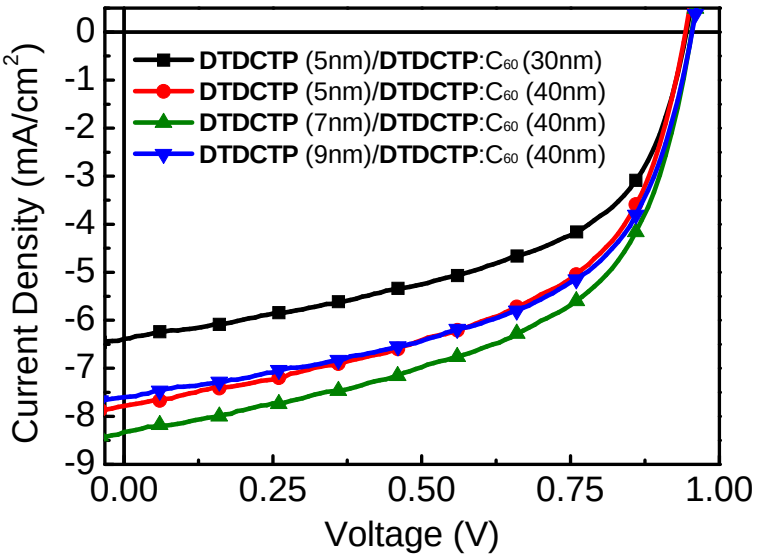

Fig. S2 J-V characteristics of **DTDCTP**:C_{60} PMHJ solar cells. The device structures are: ITO/MoO_3 (20 nm)/**DTDCTP** (5, 7, 9 nm)/**DTDCTP**:C_{60} (1:1, 30, 40 nm)/C_{60} (20 nm)/BCP (10 nm)/Ag (150 nm).

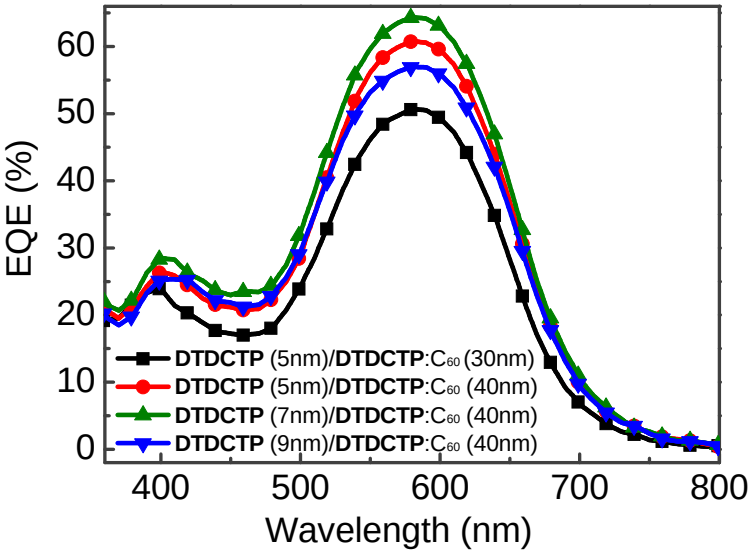

Fig. S3 External quantum efficiency spectra of **DTDCTP**:C_{60} PMHJ solar cells.

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Table S2: Performance Parameters of DTDCTP:C_{60} Devices

Device	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η_{PCE} (%)
DTDCTP (5nm)/**DTDCTP**:C_{60} (30 nm)	0.94	6.4	0.53	3.1
DTDCTP (5nm)/**DTDCTP**:C_{60} (40 nm)	0.94	7.7	0.53	3.9
DTDCTP (7nm)/**DTDCTP**:C_{60} (40 nm)	0.95	8.3	0.54	4.3
DTDCTP (9nm)/**DTDCTP**:C_{60} (40 nm)	0.95	7.6	0.54	3.9

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Device characteristics of DTDCTP:C_{70} PMHJ solar cells with different thicknesses of the C_{70} layer

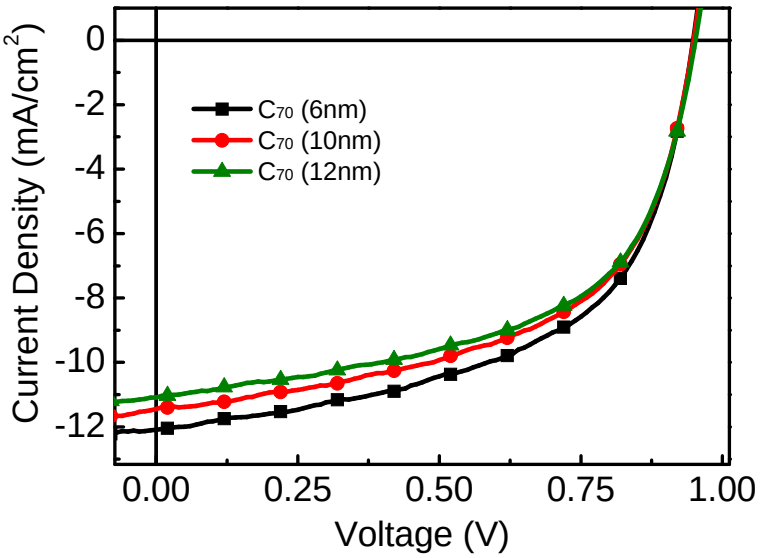

Fig. S4 J-V characteristics of **DTDCTP**:C_{70} PMHJ solar cells. The device structures are: ITO/MoO_3 (20 nm)/**DTDCTP** (7 nm)/**DTDCTP**:C_{70} (1:1, 40 nm)/C_{70} (6, 10, 12 nm)/BCP (10 nm)/Ag (150 nm).

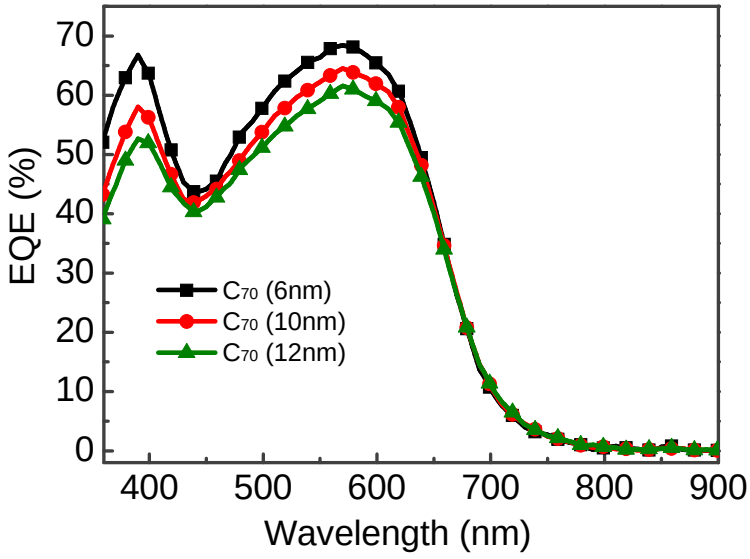

Fig. S5 External quantum efficiency spectra of **DTDCTP**:C_{70} PMHJ solar cells.

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Table S3: Performance Parameters of DTDCTP:C_{70} Devices

Device	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η_{PCE} (%)
C_{70} (6 nm)	0.95	12.1	0.56	6.4
C_{70} (10 nm)	0.95	11.4	0.56	6.1
C_{70} (12 nm)	0.95	11.1	0.57	6.0

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Electron and hole mobilities for the DTDCTP:C_{70} mixed layer

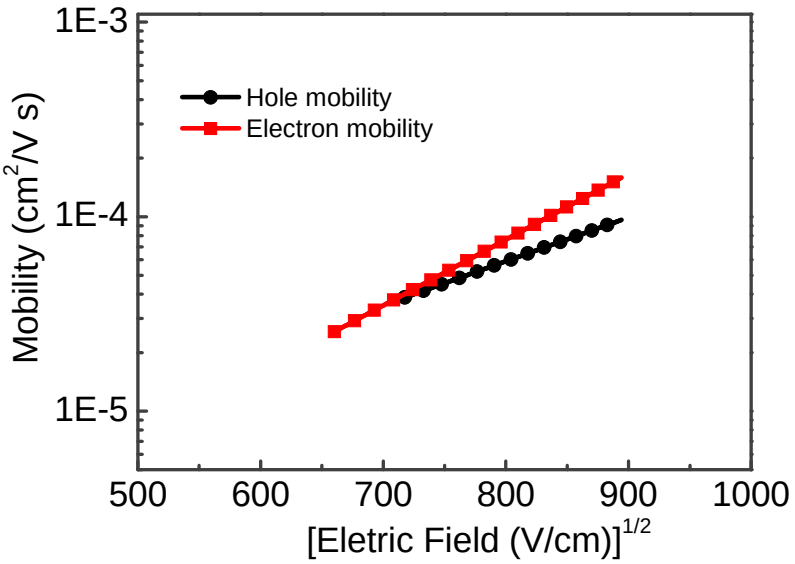

Fig. S6 Electron and hole mobilities for the **DTDCTP**:C_{70} mixed layer.

Table S4: Performance Parameters of DTDCTP:C_{70} Mobility Devices

Device	**Zero field mobility(cm^2/V s)**	**β ($cm^{0.5}V^{-0.5}$)**
Hole	9.20631E-7	5.843E-3
Electron	1.49738E-7	8.753E-3

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The total absorption, IQE, and EQE spectra of the DTDCTP:C_{70} device

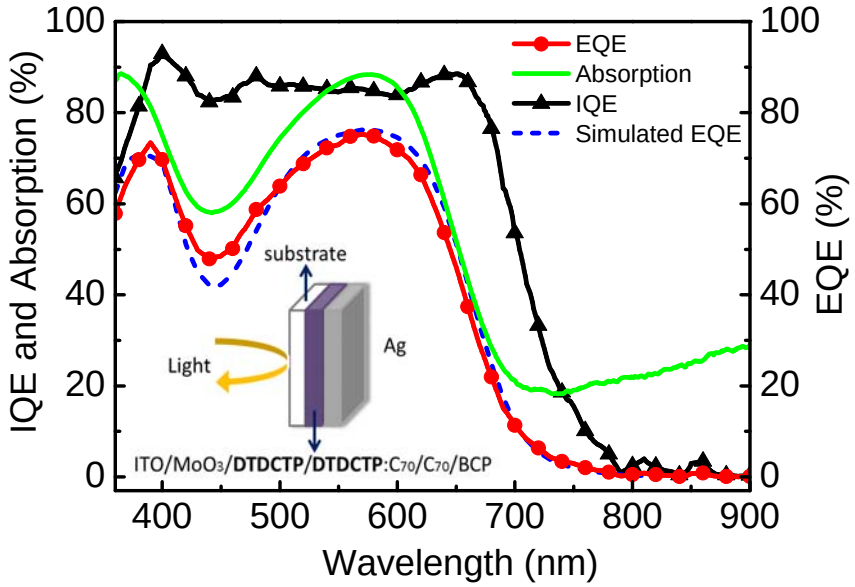

Fig. S7 IQE, EQE and total absorption spectra of the **DTDCTP**:C_{70} device. The dash line shows the simulated EQE spectrum with the assumption that 95% of excitons generated in the mixed layer are successfully collected at the electrodes. Inset: Illustration of the total absorption measurement in a normal-incident reflection geometry with the complete device.

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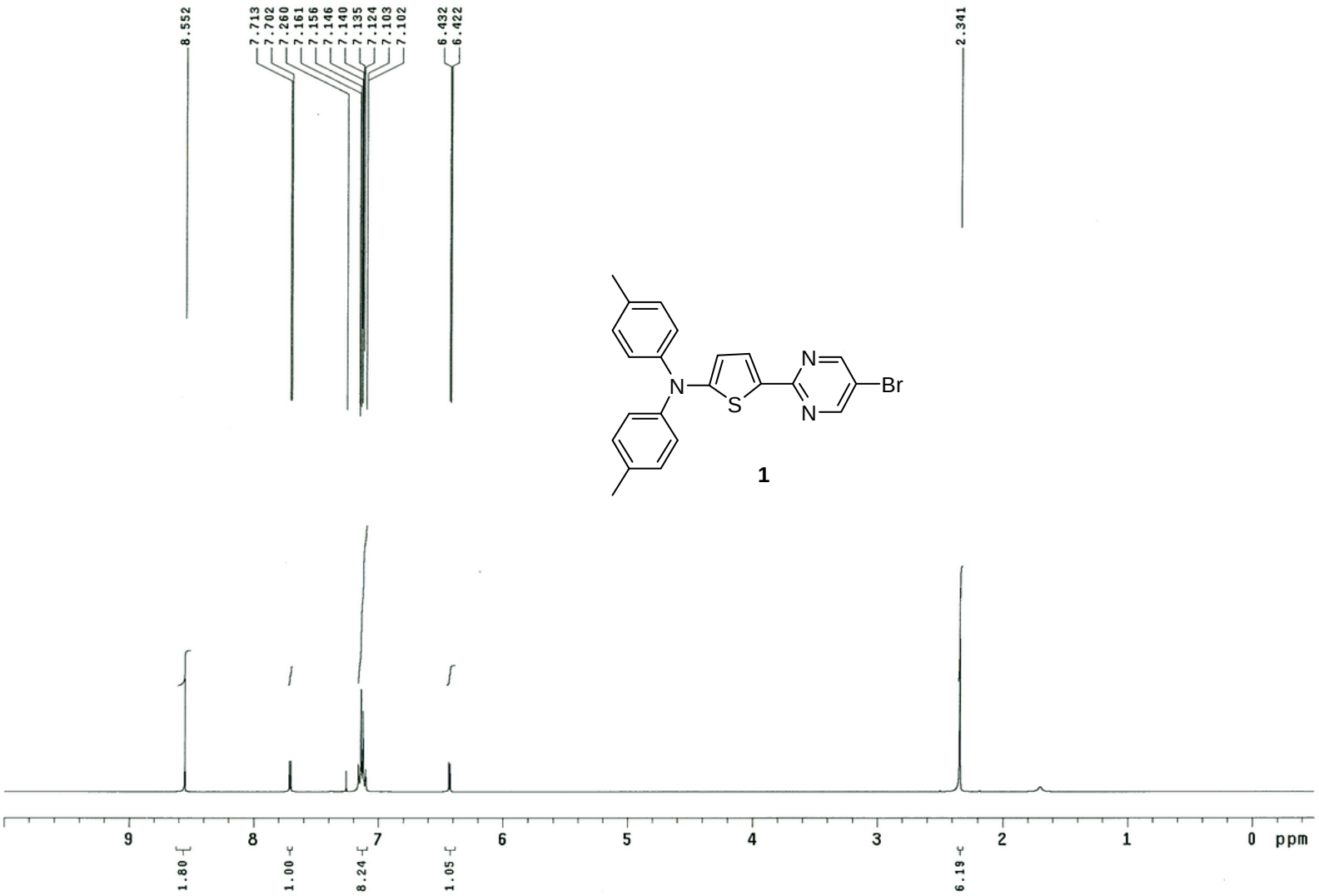

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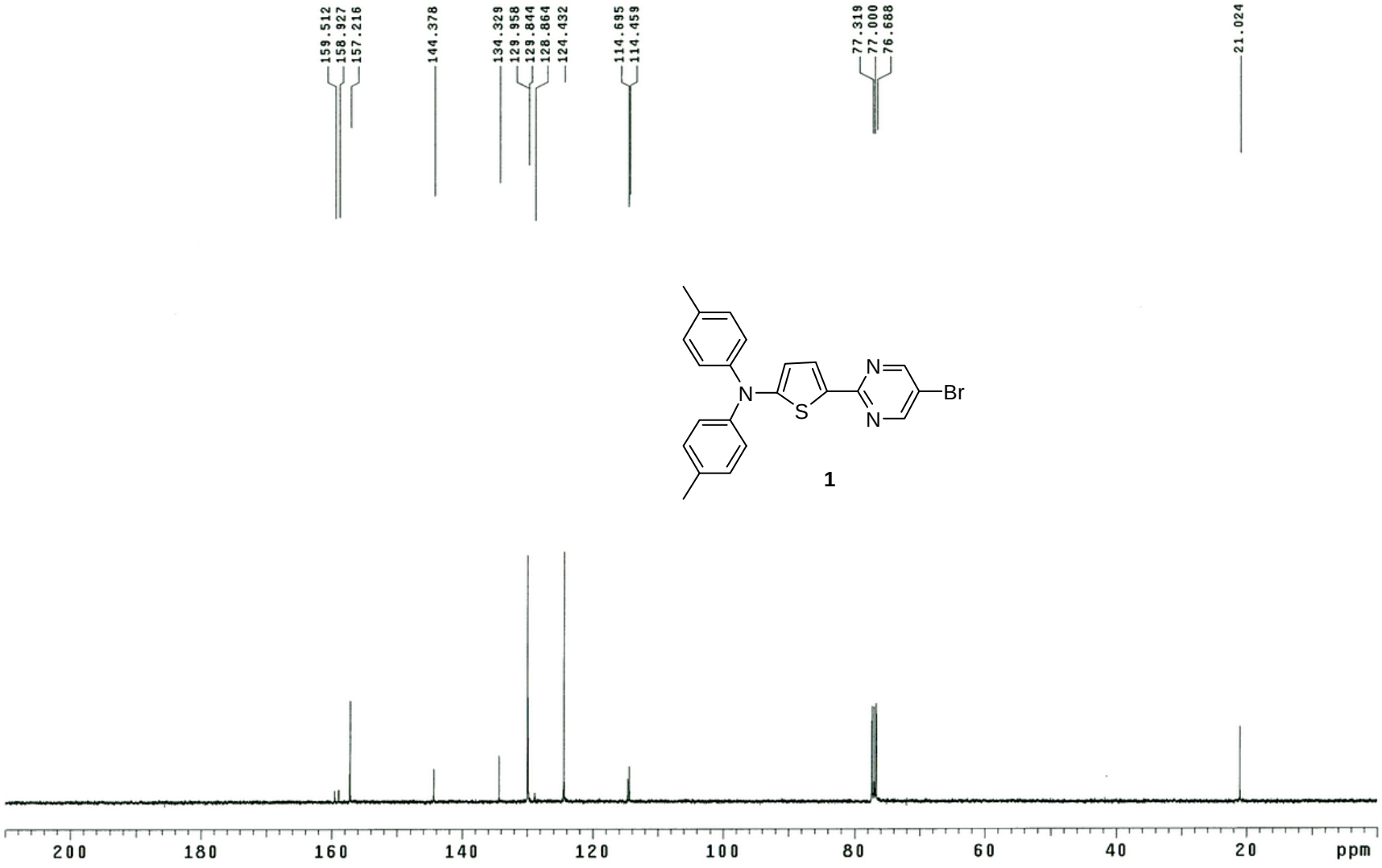

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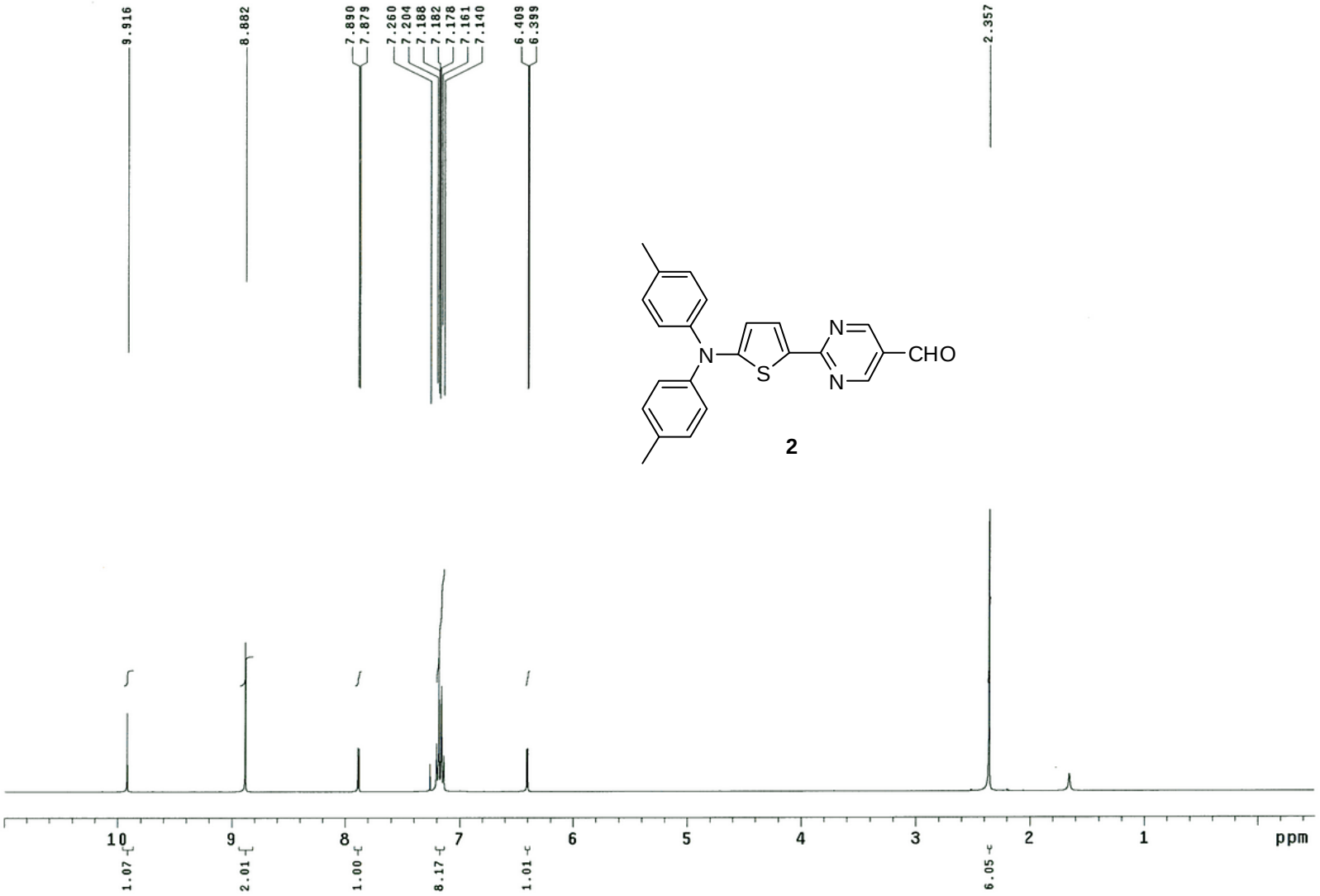

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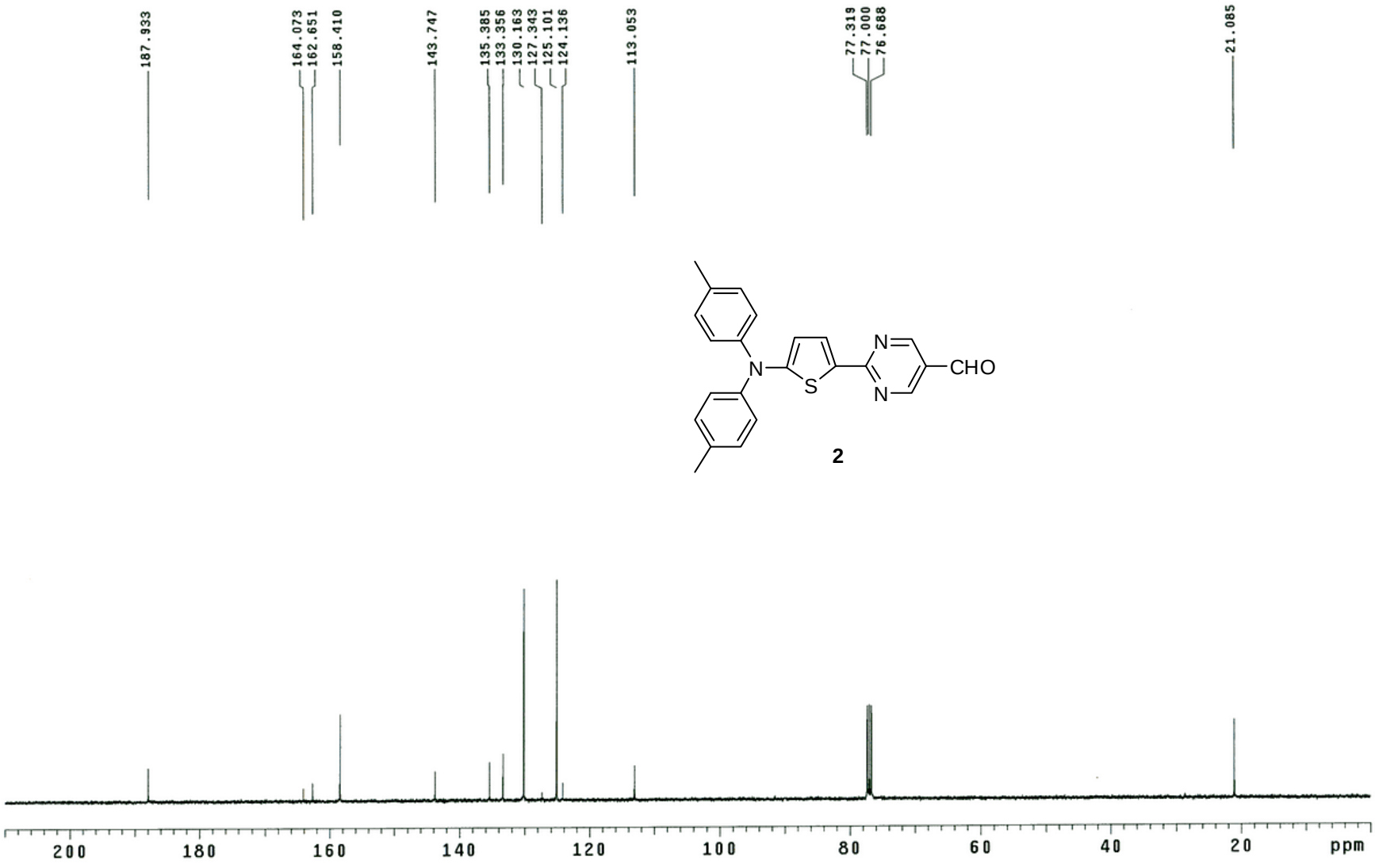

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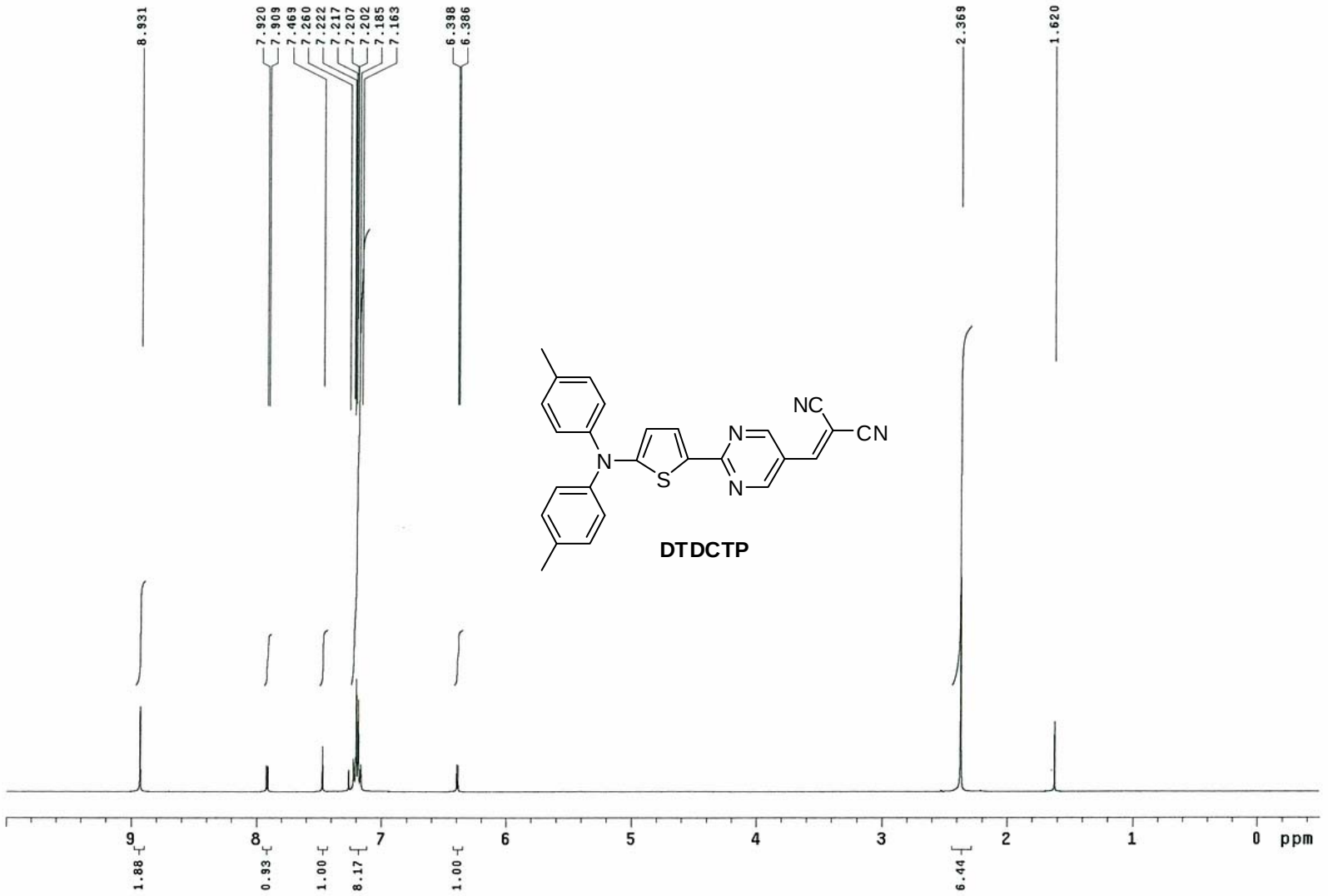
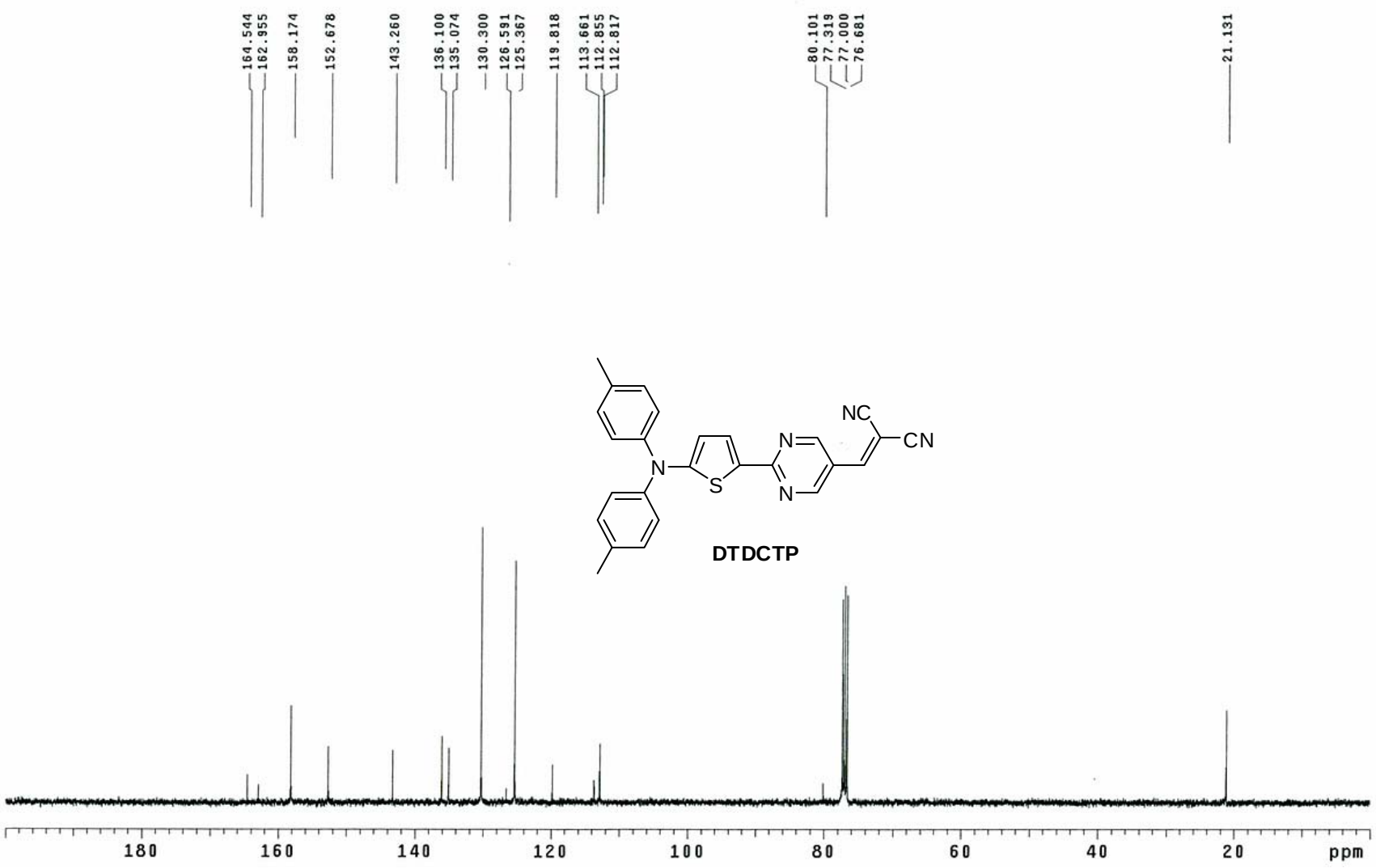
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