Electronic Supplementary Information for:

Transition metal-catalyzed C-H activation as a route to structurally diverse di(arylthiophenyl)-diketopyrrolopyrroles

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Contents

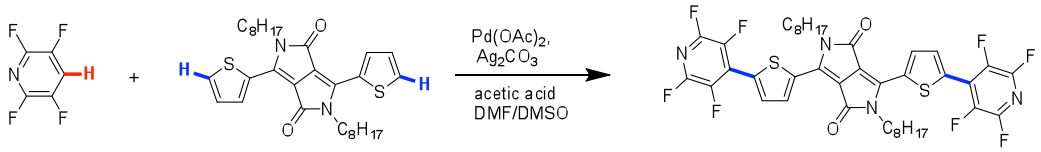
1. Experimental Details

General

Anhydrous DMF, DMSO, DMAc and AcOH were purchased from Aldrich and used as received. $Pd(OAc)_2$ and Ag_2CO_3 were purchased from Strem Chemicals. 2,3,5,6-Tetrafluoropyridine, 2,3,5,6-tetrafluorobenzonitrile and pentafluorobezene were purchased from Acros or Alfa Aesar and used as received. 2,5-Dioctyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**1a**) was synthesized according to a literature procedure[1] from 2,5-dihydro-1,4-dioxo-3,6-dithienylpyrrolo[3,4-*c*]pyrrole, which was prepared by the reaction between 2-thiophene carbonitrile and dimethylsuccinate. Its 2,5-di(2-ethylhexyl) analogue, **1b**, was synthesized in an analogous fashion.

^1H and $^{13}C\{1H\}$ NMR spectra were acquired using a Bruker AMX-400 spectrometer or a Varian Mercury Vx 300, and the signals were referenced to Me_4Si at 0 ppm using either the residual ^1H signal or the ^{13}C signal of the solvent or internal Me_4Si. Most spectra were acquired in $CDCl_3$ in 5 mm NMR tubes, but $^{13}C\{^1H\}$ spectra of the fluoroaryl compounds **2a-c** were acquired in 10 mm NMR tubes using 35 mg of sample in 3 mL 1,1,2,2-CD_2Cl_4. Chromatographic separations were performed using standard flash column chromatography methods using silica gel purchased from Sorbent Technologies (60 Å, 32-63 μm). Electrochemical measurements were carried out under nitrogen in dry deoxygenated 0.1 M tetra-*n*-butylammonium hexafluorophosphate in dichloromethane (ca. 10^{-4} M of analyte) using a conventional three-electrode cell with a glassy carbon working electrode, platinum wire counter electrode, and a Ag wire coated with AgCl as pseudo-reference electrode. Potentials were referenced to ferrocenium/ferrocene using internal ferrocene. Cyclic voltammograms were recorded at a scan rate of 50 $mV.s^{-1}$. UV-vis-NIR spectra were recorded in 1 cm cells using a Varian Cary 5E spectrometer. Fluorescence spectra were acquired using a Horiba FluoroLog-3 spectrometer. Mass spectra were recorded on an Applied Biosystems 4700 Proteomics Analyzer by the Georgia Tech Mass Spectrometry Facility. Elemental analyses were performed by Atlantic Microlabs.

2,5-Dioctyl-3,6-bis(5-(2,3,5,6-tetrafluoropyridin-4-yl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (2a)

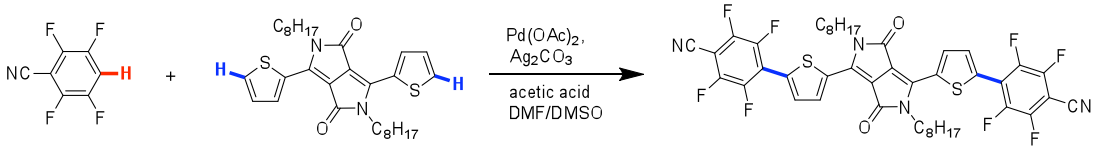


To a septum-capped 500 mL Schlenk flask were added $Pd(OAc)_2$ (22.5 mg, 0.1 mmol), Ag_2CO_3 (1655 mg, 6 mmol), and **1a** (1050 mg, 2 mmol), followed by DMSO (10 mL) and DMF (10 mL),

1. Y. Zou, D. Gendron, R. Badrou-Aïch, A. Najari, Y. Tao, M. Leclerc, *Macromolecules* 2009, **42**, 2891

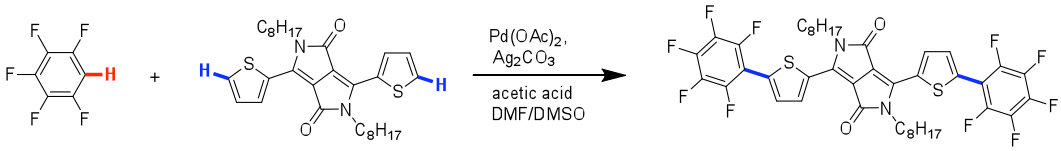
HOAc (240 mg, 4 mmol) and 2,3,5,6-tetrafluoropyridine (1813 mg, 12 mmol) with stirring. The resulting mixture was purged with N_2 for 30 min, screw-capped and heated to 140 °C using an oil bath. After stirring for 8 h, the reaction mixture was cooled to room temperature and diluted with hot $CHCl_3$ (2 L), filtered through Celite® (ca. 50 mL) to remove insoluble inorganic materials, washed with 1 N HCl, brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressue. The residue was purified with silica gel chromatography (500 mL of silica gel, $CHCl_3$ as eluant) to provide **2a** as purple solid (1.3 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, J = 4.4 Hz, 2H), 8.03 (d, J = 4.4 Hz, 2H), 4.13 (t, J = 7.5 Hz, 4H), 1.82-1.72 (m, 4H), 1.48-1.22 (m, 20H), 0.91-0.83 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $C_2D_2Cl_4$) δ 161.14, 144.46 (dt, J_{CF} = 245, 17 Hz), 139.61, 138.92 (dd, J_{CF} = 268, 35 Hz), 135.28, 134.27, 133.50, 131.05, 125.35 (t, J_{CF} = 14 Hz), 110.36, 42.75, 31.78, 30.08, 29.17, 29.16, 26.90, 22.61, 14.03. HRMS (MALDI) *m/z* calcd for $C_{40}H_{39}F_8N_4O_2S_2$ (MH^+), 823.2387; found, 823.2395. Anal. Calc. for $C_{40}H_{38}F_8N_4O_2S_2$: C, 58.38; H, 4.65; N, 6.81. Found: C, 58.35; H, 4.63; N, 6.88.

4,4'-(5,5'-(2,5-Dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-*c*]pyrrole-1,4-diyl)bis(thiophene-5,2-diyl))bis(2,3,5,6-tetrafluorobenzonitrile) (2b)



The same procedure used for **2a** was followed, but using 2,3,5,6-tetrafluorobenzonitrile in place of tetrafluoropyridine, and using 10 mol%, rather than 5 mol%, $Pd(OAc)_2$. Purification by column chromatography with silica gel chromatography provided **2b** as a black solid (45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, J = 4.0 Hz, 2H), 7.93 (d, J = 4.0 Hz, 2H), 4.12 (t, J = 8.0 Hz, 4H), 1.80-1.70 (m, 4H), 1.48-1.22 (m, 20H), 0.88-0.82 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $C_2D_2Cl_4$) δ 161.12, 147.77 (dd, J_{CF} = 262, 17 Hz), 143.68 (dd, J_{CF} = 255, 13 Hz), 139.52, 135.31, 133.96, 133.22, 131.03, 119.51(t, J = 14 Hz), 110.28, 107.26, 92.67 (t, J_{CF} = 17 Hz), 42.74, 31.77, 30.06, 29.18, 29.16, 26.89, 22.60, 14.02. HRMS (MALDI) *m/z* calcd for $C_{44}H_{39}F_8N_4O_2S_2$ (MH^+), 871.2387; found, 871.2359. Anal. Calc. for $C_{44}H_{38}F_8N_4O_2S_2$: C, 60.68; H, 4.40; N, 6.43. Found: C, 60.83; H, 4.42; N, 6.53.

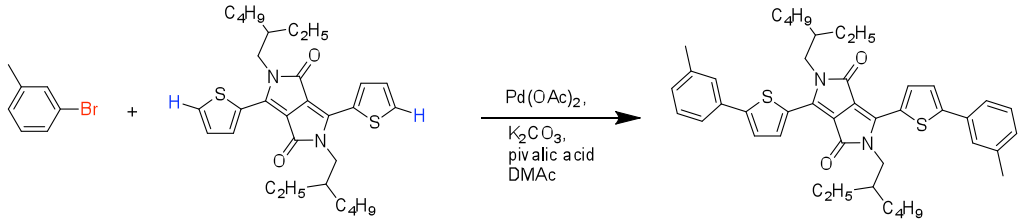
2,5-Dioctyl-3,6-bis(5-(perfluorophenyl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (2c)



The same procedure used for **2a** was followed, but using pentafluorobenzene in place of tetrafluoropyridine. Purification by column chromatography with silica gel chromatography

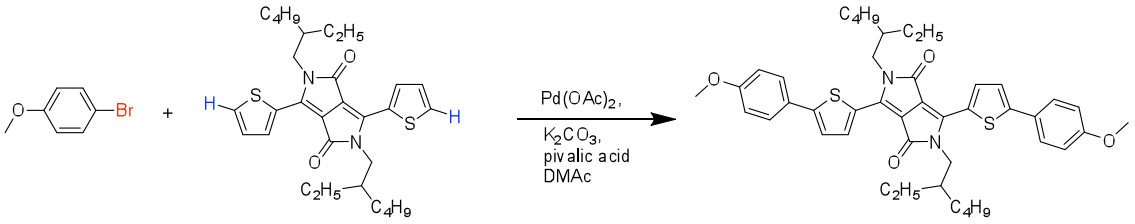
provided **2c** as purple solid (23%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (d, J = 4.2 Hz, 2H), 7.71 (d, J = 4.2 Hz, 2H), 4.10 (t, J = 7.8 Hz, 4H), 1.82-1.70 (m, 4H), 1.48-1.22 (m, 20H), 0.88-0.82 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $C_2D_2Cl_4$) δ 160.97, 142.87-142.78 (m), 139.45-139.13 (m), 136.98-136.85 (m), 134.83, 131.78, 131.33, 131.16-131.06 (m), 109.15, 108.95-108.91 (m), 42.36, 31.50, 30.58, 29.77, 28.90, 26.62, 22.33, 13.74 (one aromatic ^{13}C resonance not observed, presumably due to overlap). HRMS (MALDI) *m/z* calcd for $C_{42}H_{39}F_{10}N_2O_2S_2$ (MH^+), 857.2293; found, 857.2301. Anal. Calc. for $C_{42}H_{38}F_{10}N_2O_2S_2$: C, 58.87; H, 4.47; N, 3.27. Found: C, 58.52; H, 4.23; N, 3.26.

2,5-Bis(2-ethylhexyl)-3,6-bis(5-(*m*-tolyl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (3a)



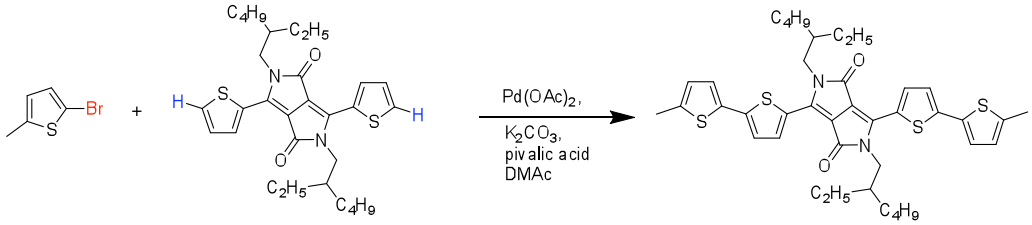
2,5-Bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**1b**, 1 mmol, 524 mg), K_2CO_3 (4.5 equiv, 4.5 mmol, 622 mg), $Pd(OAc)_2$ (10 mol %, 0.1 mmol, 22 mg), and pivalic acid (1 eq., 1 mmol, 102 mg) were weighed to air and placed in a round-bottomed Schlenk flask equipped with a magnetic stir bar. The flask was purged with argon for 30 min, and dimethyl acetamide (DMAc) (20 mL), 3-bromotoluene (3 mmol, 364 mg) were then added. The reaction mixture was vigorously stirred at 100 °C for 3 h, then cooled to room temperature, diluted with hot $CHCl_3$ (300 mL), filtered through Celite® (1 cm) to remove inorganic solids, washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified using column chromatography (300 ml of silica gel, 50% hexane in $CHCl_3$ as eluant) to provide **3a** as black solid (600 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 4.0 Hz, 2H), 7.51-7.47 (m, 4H), 7.45 (d, J = 4.0 Hz, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 4.14-4.02 (m, 4H), 2.42 (s, 6H), 2.00-1.92 (m, 2H), 1.45-1.25 (m, 16H), 0.92-0.82 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.78, 149.91, 139.91, 138.92, 136.75, 133.12, 129.66, 129.06, 128.71, 126.81, 124.40, 123.33, 108.15, 45.98, 39.26, 30.41, 28.63, 23.70, 23.14, 21.45, 14.10, 10.59. HRMS (MALDI) *m/z* calcd for $C_{44}H_{52}N_2O_2S_2$ (M^+), 704.3470; found, 704.3529. Anal. Calc. for $C_{44}H_{52}N_2O_2S_2$: C, 74.96; H, 7.43; N, 3.97. Found: C, 75.14; H, 7.48; N, 3.82.

2,5-Bis(2-ethylhexyl)-3,6-bis(5-(4-methoxyphenyl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (3b)



The same procedure used for **3a** was followed, but using 4-bromoanisole in place of 3-bromotoluene. Purification by column chromatography with silica gel chromatography provides **3b** as dark solid (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, J = 4.4 Hz, 2H), 7.64 (d, J = 8.8 Hz, 4H), 7.38 (d, J = 4.0 Hz, 2H), 6.98 (d, J = 8.8 Hz, 4H), 4.16-4.06 (m, 4H), 3.89 (s, 6H), 2.02-1.92 (m, 2H), 1.45-1.25 (m, 16H), 0.92-0.85 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.79, 160.27, 149.76, 139.77, 136.90, 127.93, 127.52, 126.05, 123.46, 114.60, 107.92, 55.45, 45.97, 39.23, 30.37, 28.58, 23.70, 23.13, 14.10, 10.61. HRMS (MALDI) *m/z* calcd for $C_{44}H_{52}N_2O_4S_2$ (M^+), 736.3368; found, 736.3362. Anal. Calc. for $C_{44}H_{52}N_2O_4S_2$: C, 71.70; H, 7.11; N, 3.80. Found: C, 71.85; H, 7.14; N, 3.75.

2,5-Bis(2-ethylhexyl)-3,6-bis(5-(perfluorophenyl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3c)



The same procedure used for **3a** was followed, using 2-bromo-5-methylthiophene in place of 3-bromotoluene. Purification by column chromatography with silica gel chromatography provided **3c** as dark solid (39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, J = 4.4 Hz, 2H), 7.22 (d, J = 4.0 Hz, 2H), 7.12 (d, J = 4.4 Hz, 2H), 6.73 (dd, J = ca. 4, <1 Hz, 2H), 4.10-4.00 (m, 4H), 2.52 (d, J < 1 Hz, 6H), 1.94-1.88 (m, 2H), 1.38-1.22 (m, 16H), 0.90-0.85 (m, 12H). The ^{1}H NMR spectrum is very similar to that reported for the same compound in CD_2Cl_2 in ref. 2. HRMS (MALDI) *m/z* calcd for $C_{40}H_{48}N_2O_2S_4$ (M^+), 716.2599; found, 716.2590.

2. H. Bürckstümmer, A. Weissenstein, D. Bialas and F. Würthner, *J. Org. Chem.*, 2011, **76**, 2426

2. Emission Spectra

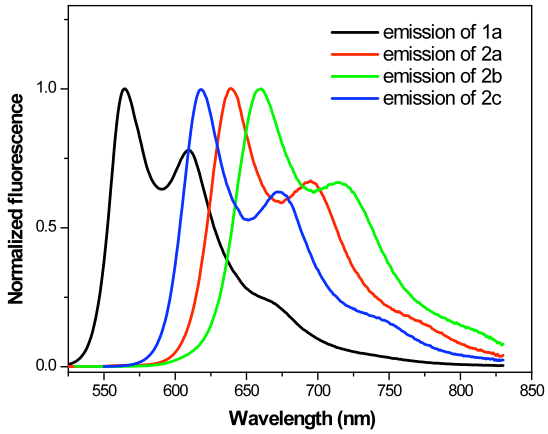


Fig. S1. Normalized emission spectra of compounds **1a** and **2a-c** in $CHCl_3$ (λ_{ex} = 500 nm).

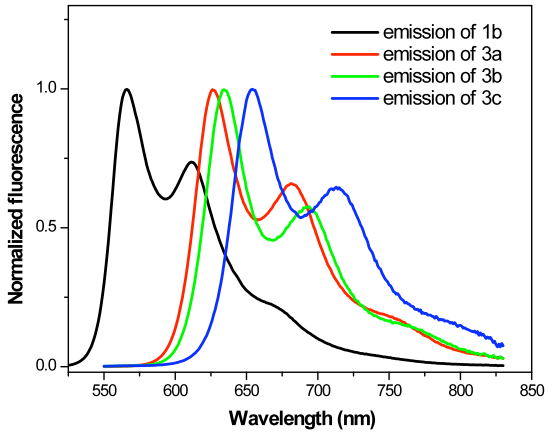


Fig. S2. Normalized emission spectra of compounds **1b** and **3a-c** in $CHCl_3$ (λ_{ex} = 500 nm).

3. Cyclic Voltammograms

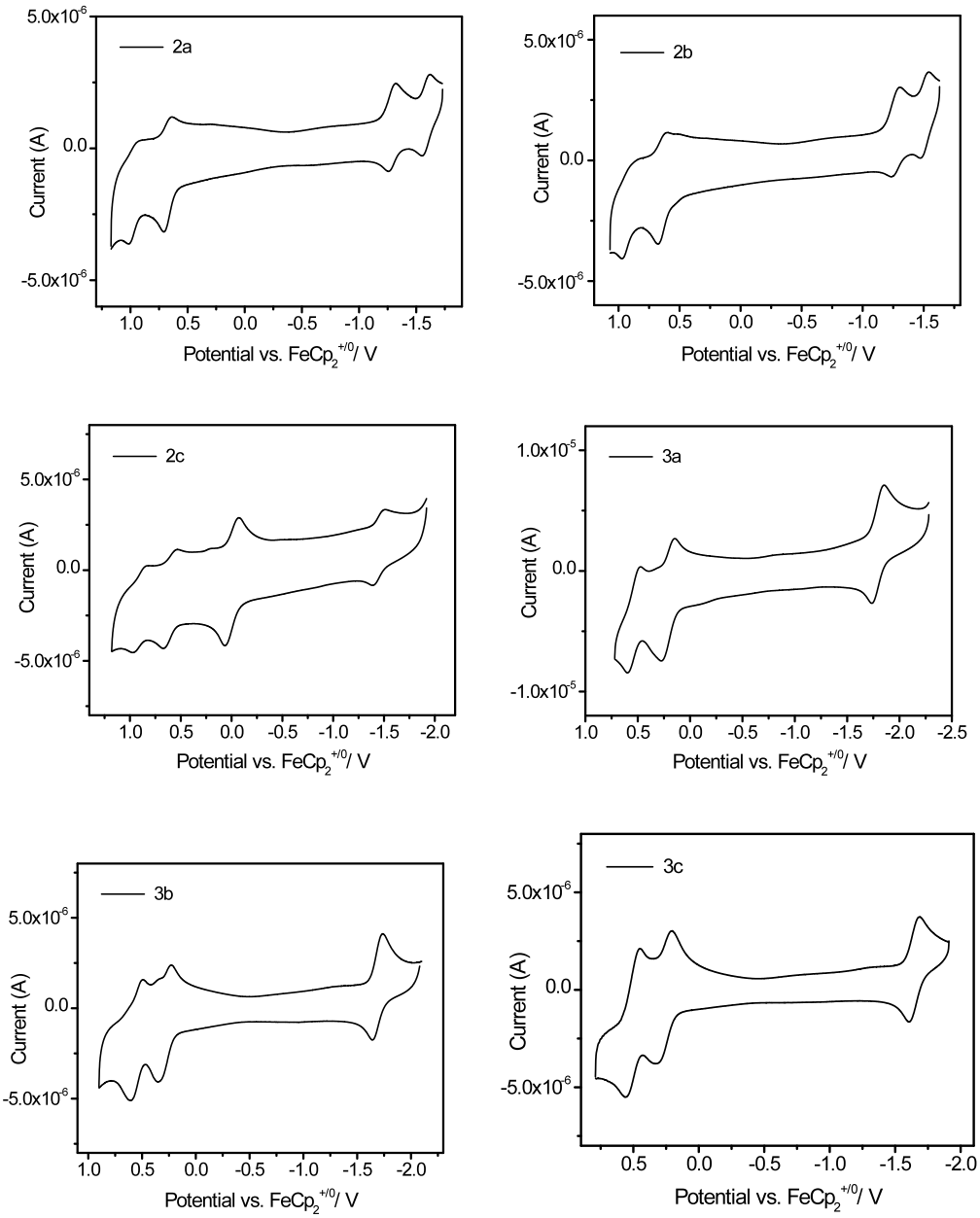
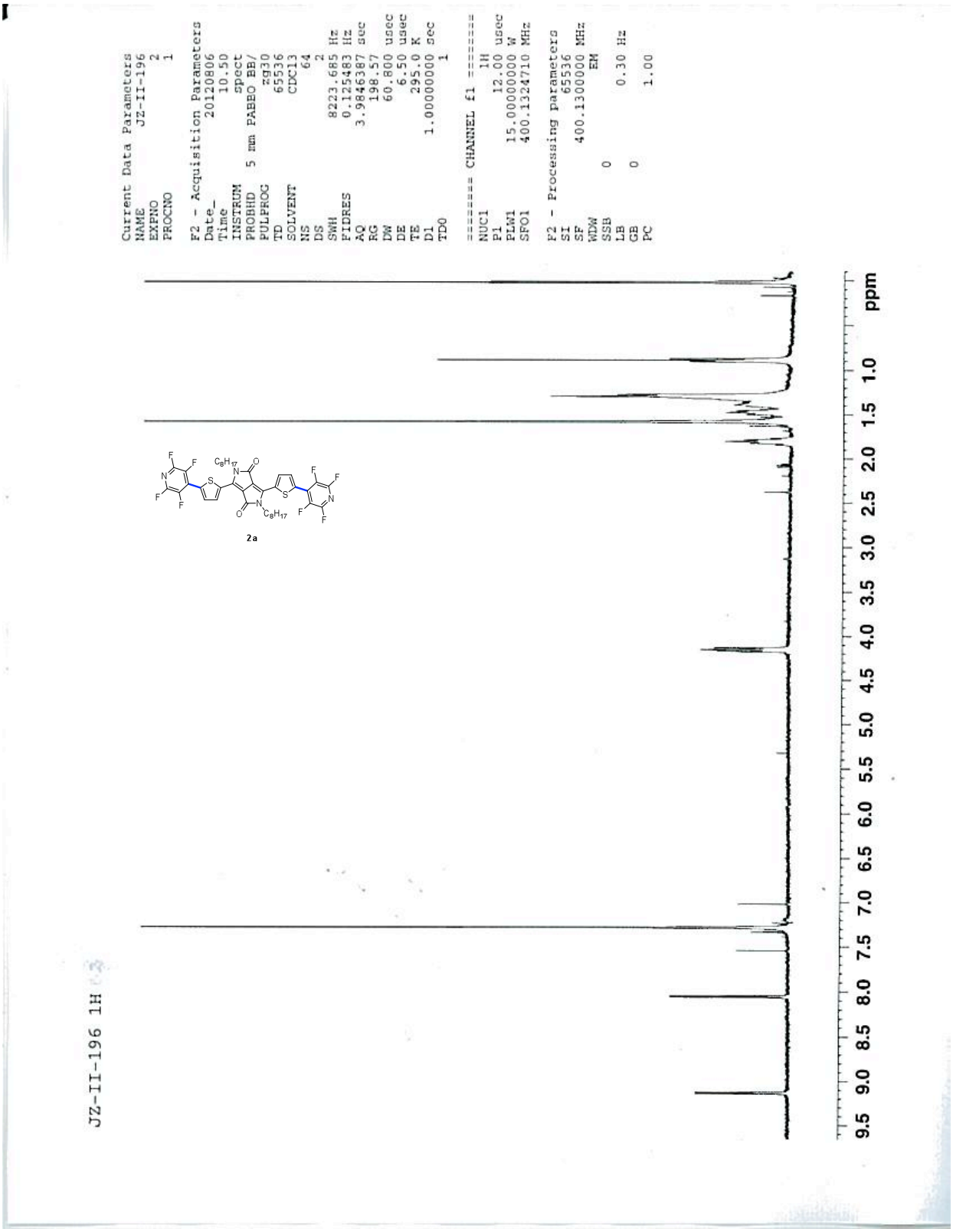
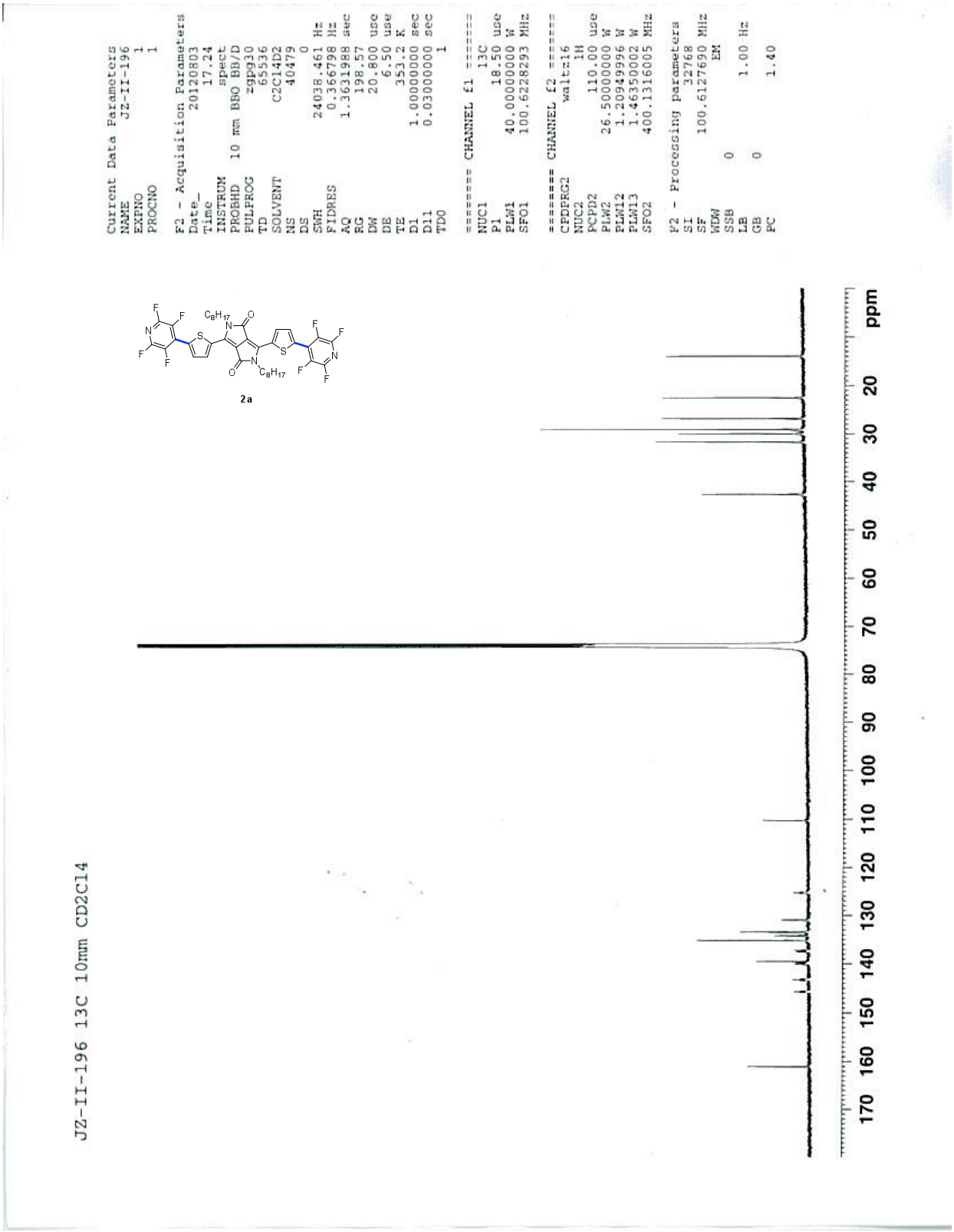


Fig. S3. Cyclic voltammograms of **2a-c** and **3a-b** in CH_2Cl_2 / 0.1 M $^nBu_4NPF_6$.[3]

3. The sample of **2c** also contains internal ferrocene.

4. NMR Spectra of New Compounds

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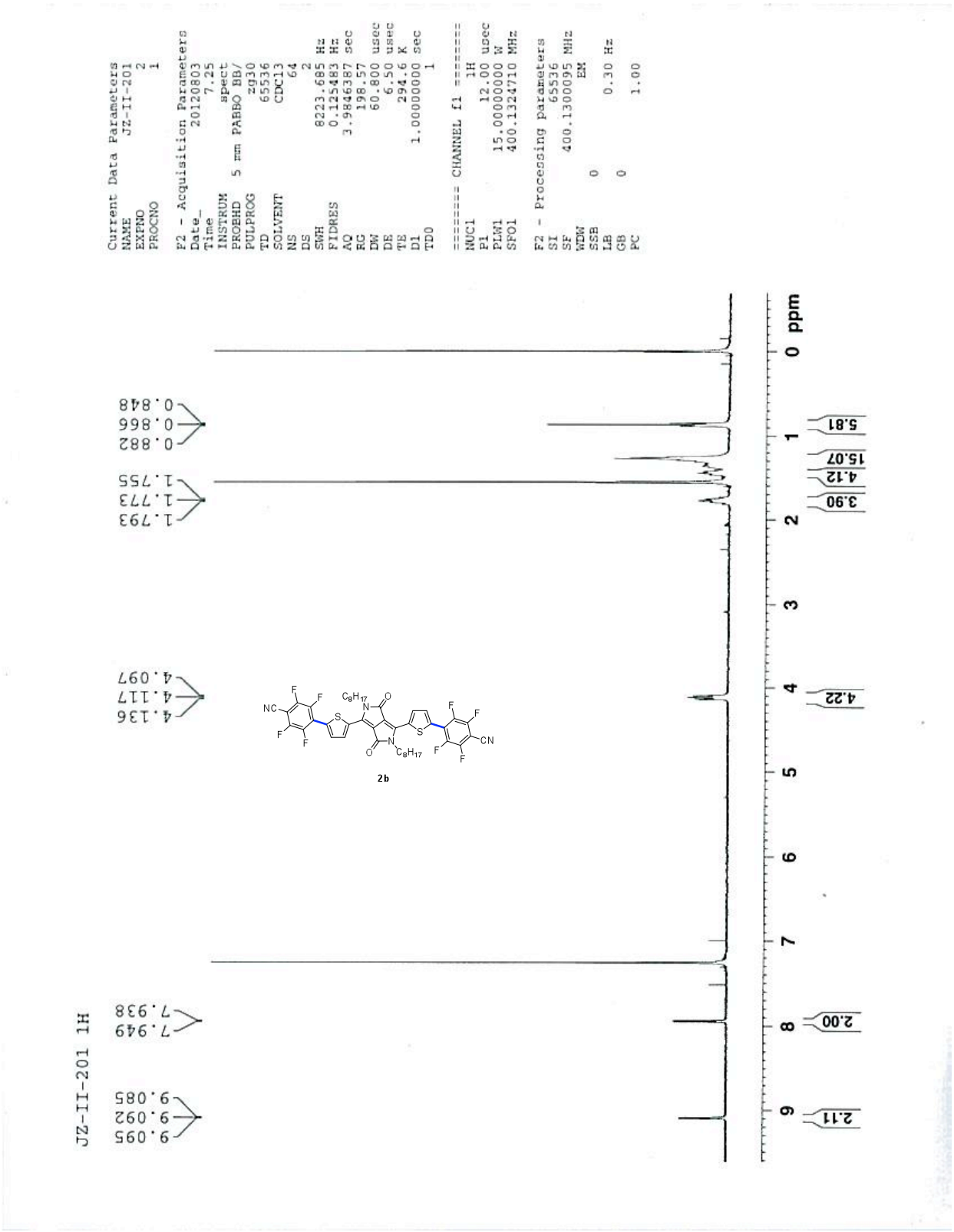

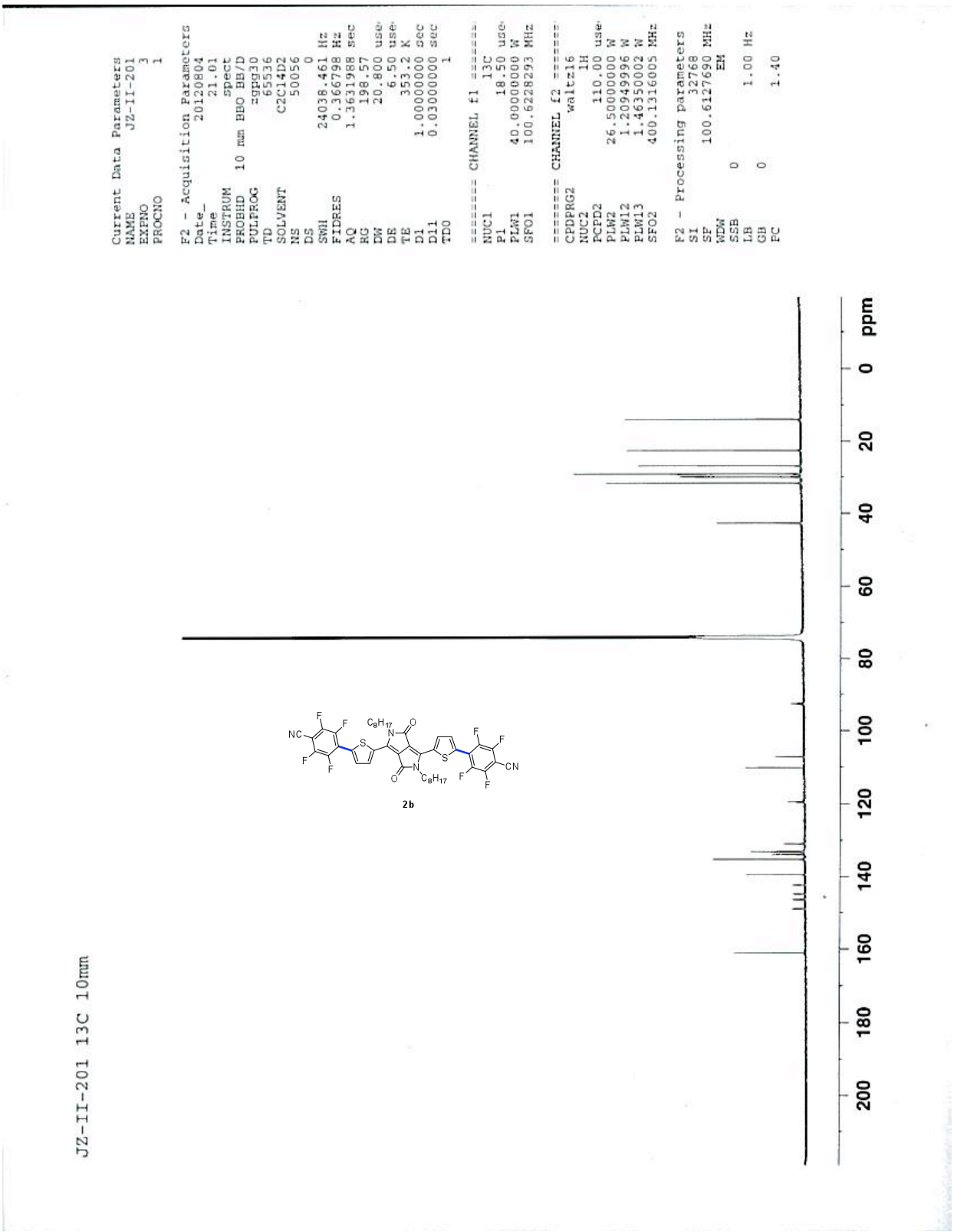

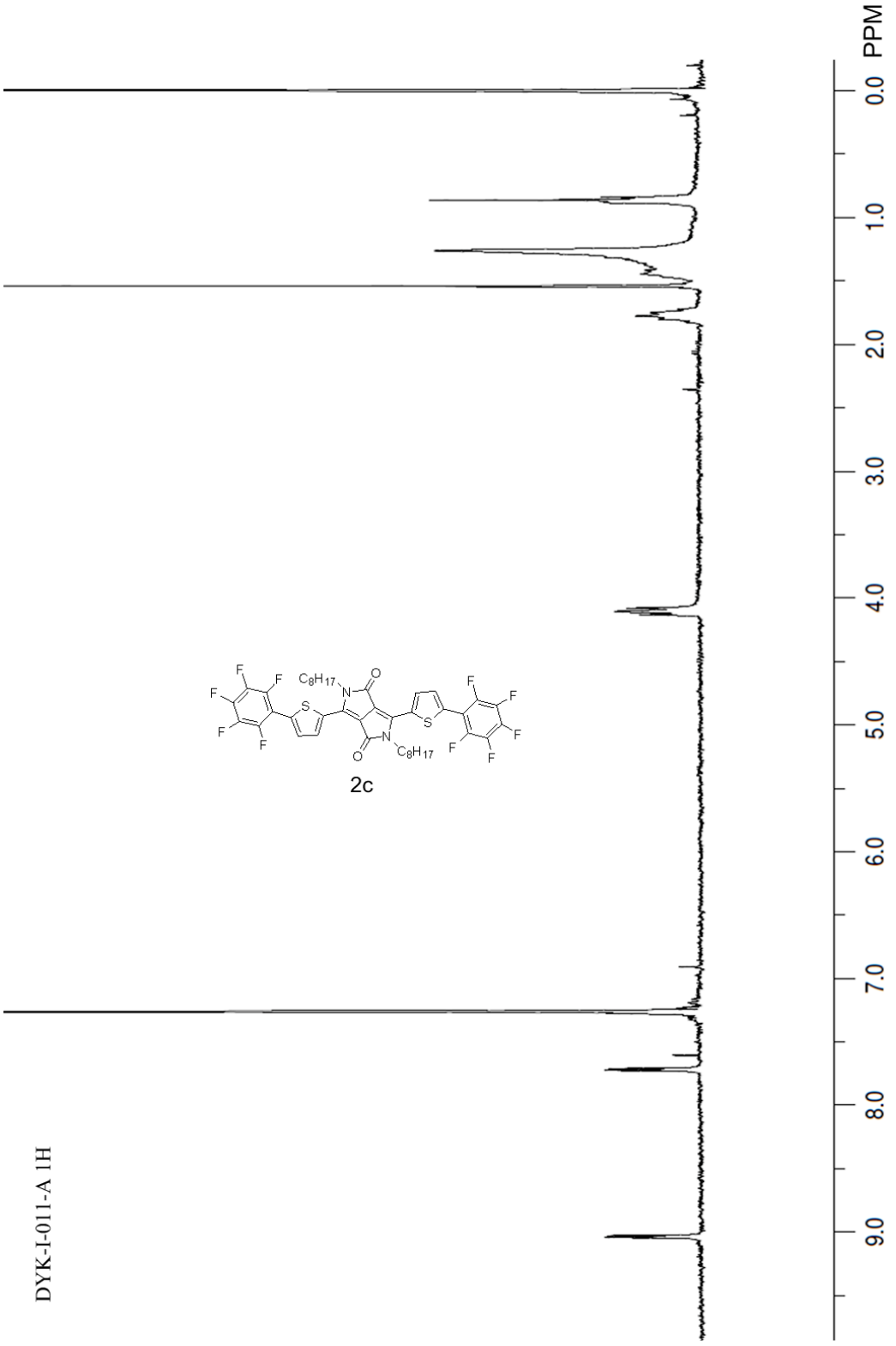

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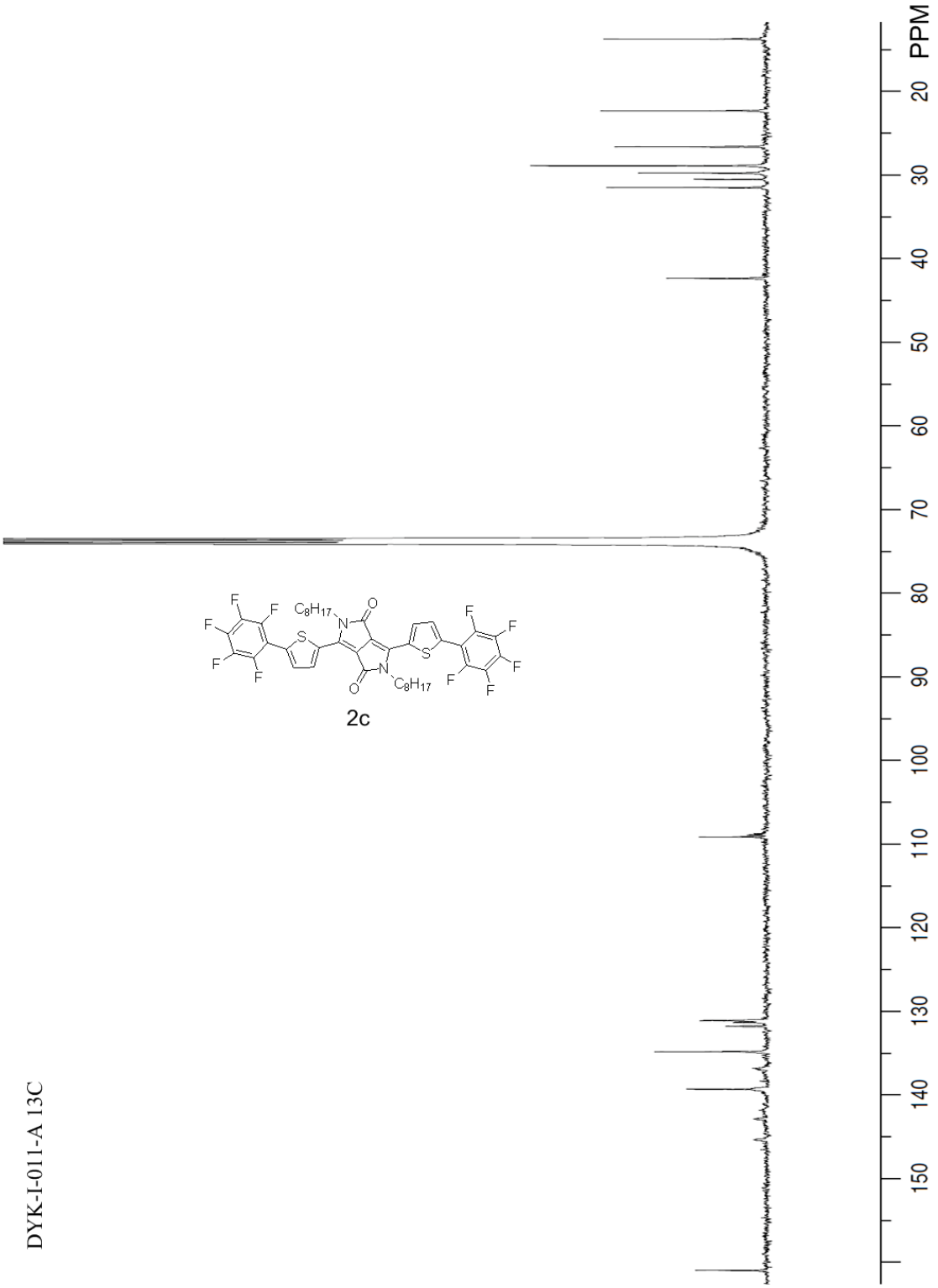
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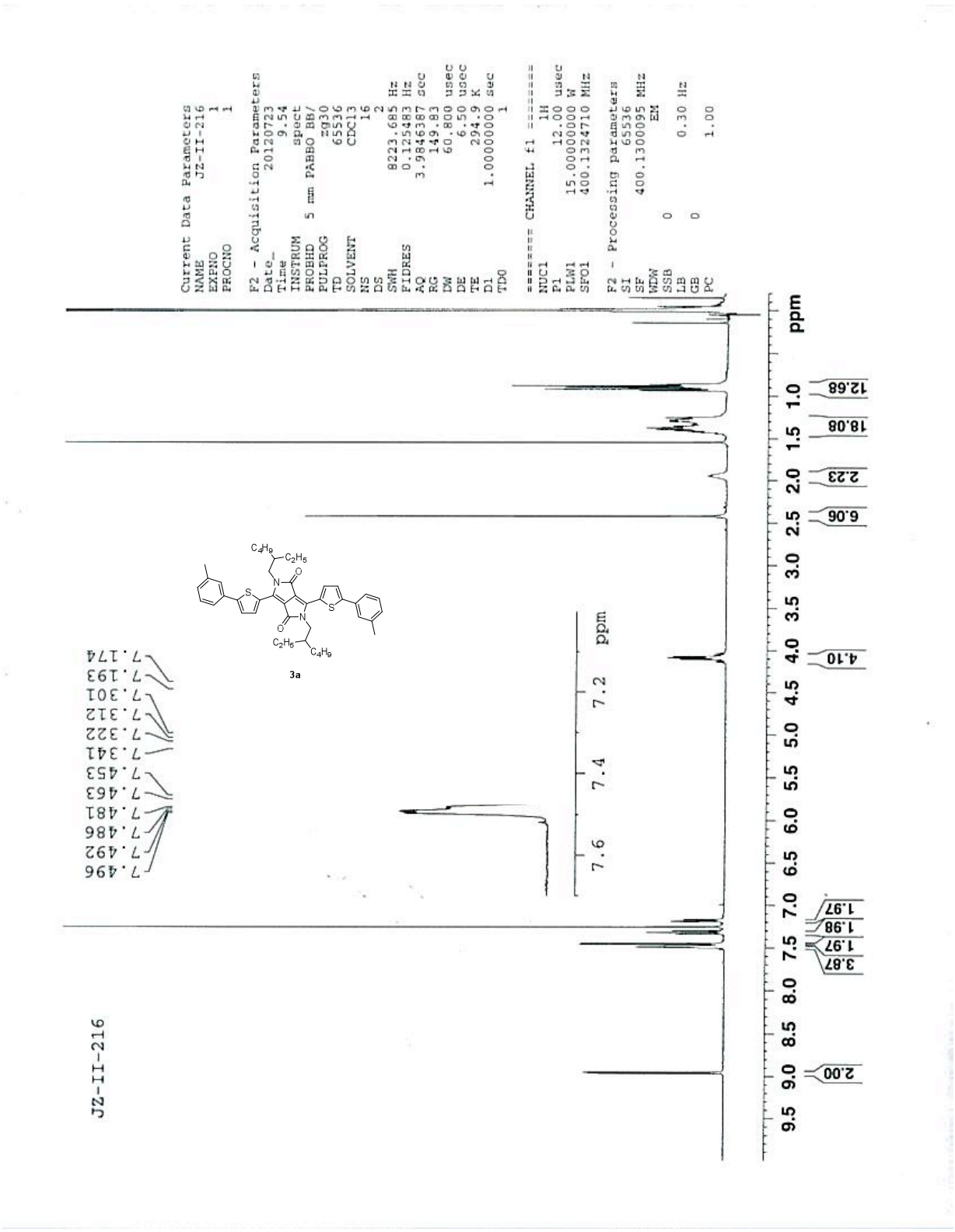
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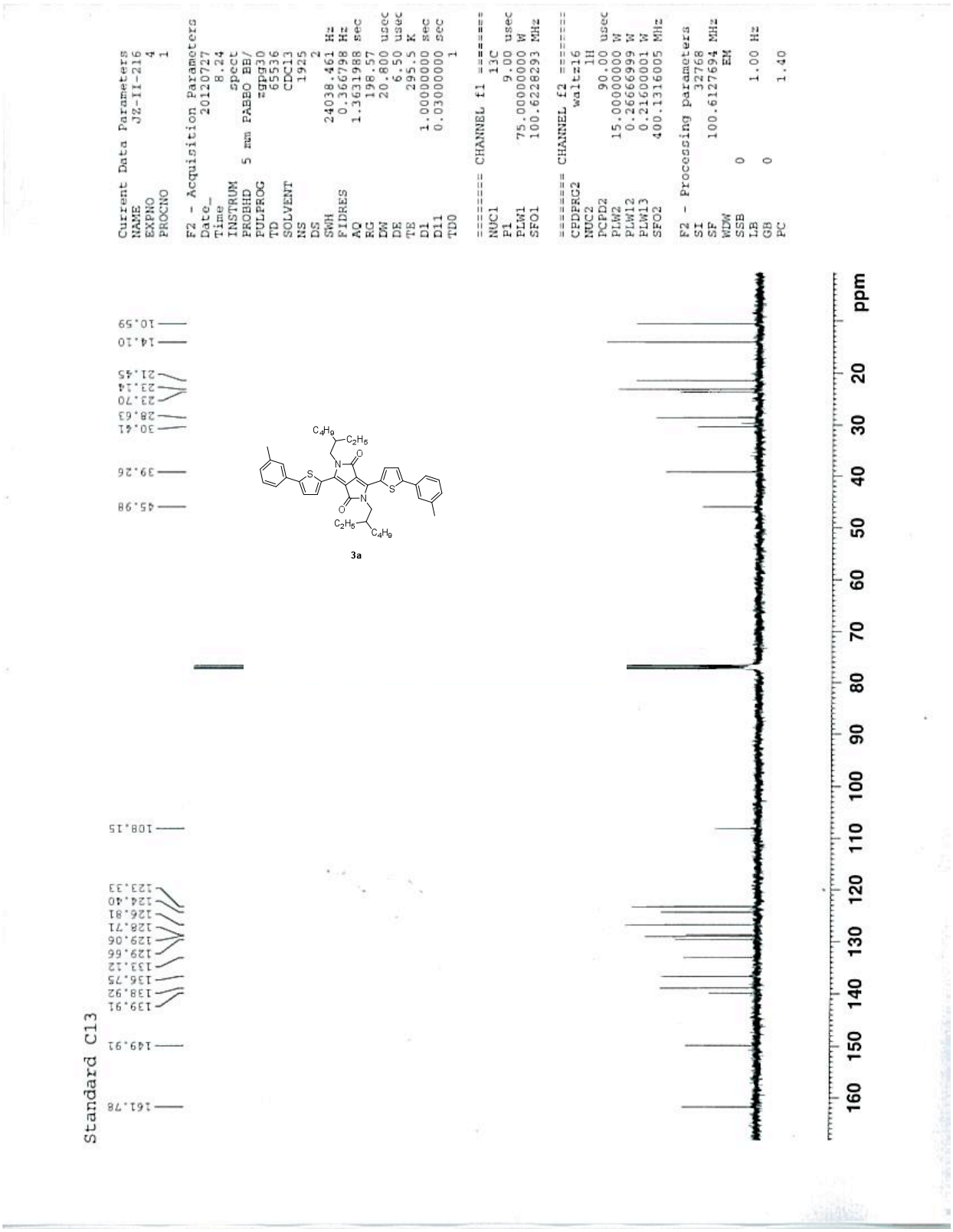

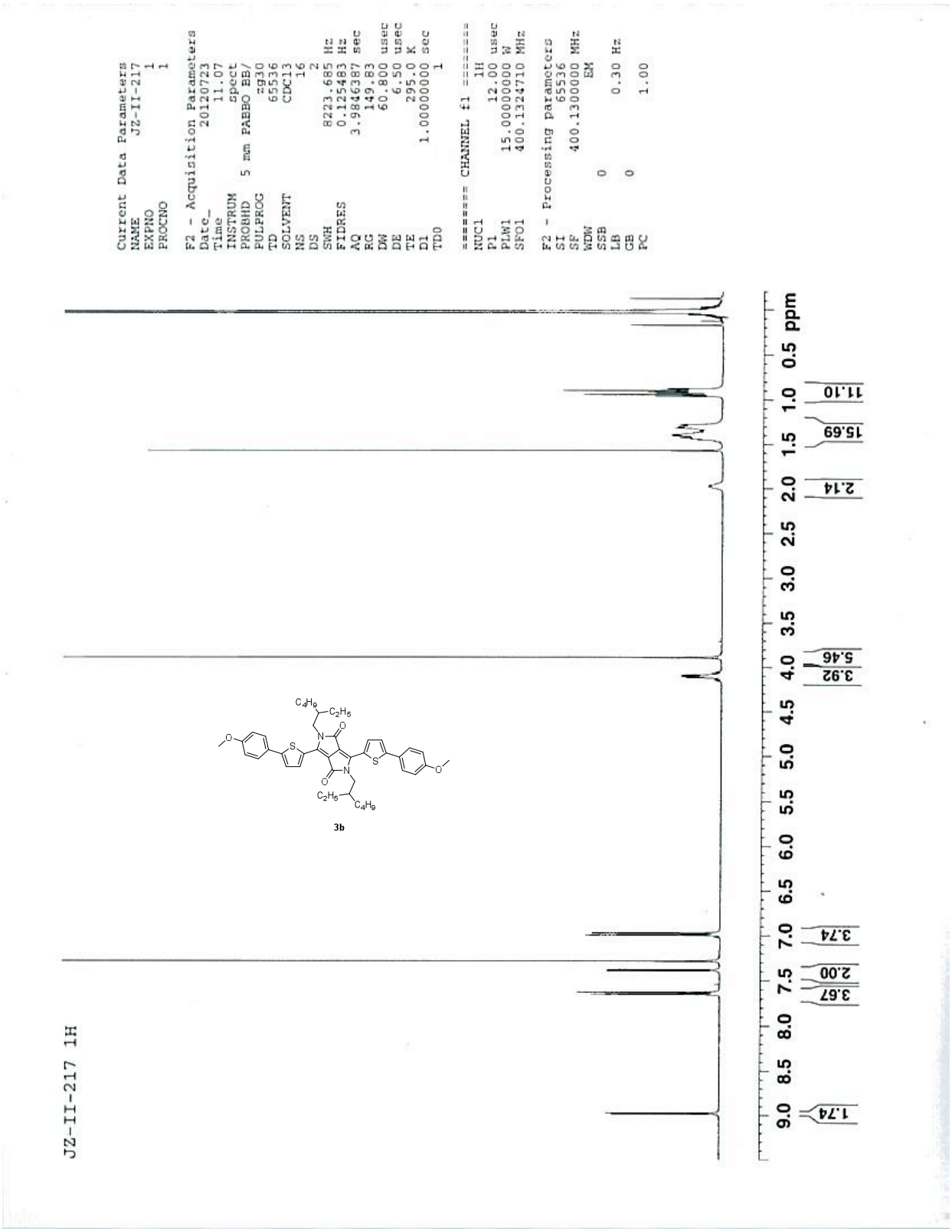
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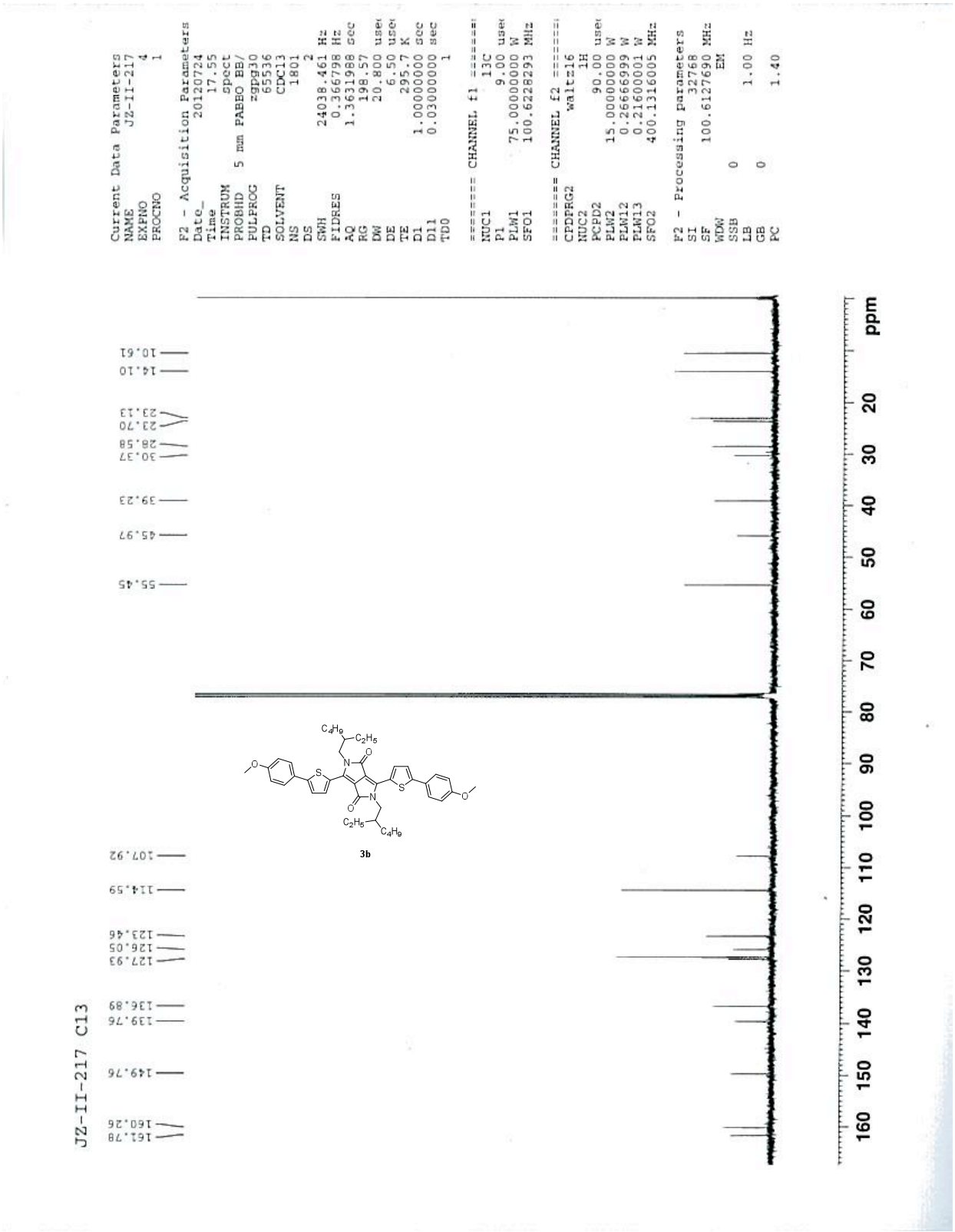
3b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INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1801
DS 2
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 198.57
DW 20.800 use
DE 6.50 use
TE 295.7 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 use
PLW1 75.00000000 W
SFO1 100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 use
PLW2 15.00000000 W
PLW12 0.26666999 W
PLW13 0.21600001 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
JZ-II-217 C13
10.61
14.10
23.13
23.70
28.58
30.37
39.23
45.97
55.45
107.92
114.59
123.46
126.05
127.93
136.89
139.76
149.76
160.26
161.78
3b
ppm