

5-Hexylthiophene-fused Porphyrazines: New Soluble Phthalocyanines for Solution-Processed Organic Electronic Devices

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Table of Contents

1. Experimental Section	S2
2. ¹ H NMR Spectrum of 2a	S4
3. UV-vis spectra and Cyclic Voltammetry	S5
4. Single Crystal X-ray structural analysis	S6
5. X-ray Diffraction of thin film	S7
6. OFET devices	S8
7. ¹ H and ¹³ C NMR spectra	S9
8. References	S14

Supporting Information

1. Experimental Section

General. All chemicals and solvents are of reagent grade unless otherwise indicated. CuCN was washed with boiled water for 30 min, then dried at 100 °C *in vacuo*.^{S1} THF was distilled from Na-benzophenone ketyl. Gel permeation chromatography (GPC) was carried out on Japan Analytical Industry (JAI) LC-9204 or LC-918 by using JAI-GEL 1H/2H for **4** or JAI-GEL-3H/4H column assembly for **2a**, respectively. Melting points were uncorrected. Nuclear magnetic resonance (NMR) spectra were obtained in deuterated chloroform at a 400 MHz spectrometer for ¹H with TMS or a residual solvent as internal standard; chemical shifts (δ) are reported in parts per million (ppm). EI-MS spectra were obtained by using an electron impact ionization procedure (70 eV). MALDI-TOF mass spectra were measured by using a dithranol matrix. The molecular ion peaks of the sulfur-containing compounds showed a typical isotopic pattern, and all the mass peaks are reported based on ⁷⁹Br and ³²S.

4-Bromo-2-hexylthiophene^{S2} (**3**): 2-Bromo-5-hexylthiophene (400 mg, 1.62 mmol) was placed in a 50-mL round-bottomed flask under an N₂ atmosphere, and dissolved in THF (20 mL). After cooled at -60 °C, the 0.49 M THF solution of LDA (6.56 mL, 3.24 mmol) was added and stirred at -60 °C for 2 h. The reaction was stopped by addition of MeOH (30 mL), and stirred at -60 °C for 1 h. The solution was gradually warmed up to room temperature. Water was added, and water layer was extracted with hexane (50 mL \times 3). Organic layers were combined, washed with water (100 mL \times 3), and dried over anhydrous MgSO₄. After removal of the drying reagent by filtration, the solution was concentrated under reduced pressure, to give **3** as yellow oil (391 mg, 98%). *R*_f 0.79 (1:1 hexane/CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.00 (d, *J* = 1.6 Hz, 1H), 6.70 (d, *J* = 1.6 Hz, 1H), 2.77 (t, *J* = 7.6 Hz, 2H), 1.65 (m, 2H), 1.34 (m, 6H), 0.88 (t, *J* = 7.2 Hz, 3H); MS (70 eV, EI) *m/z* = 246 (M⁺).

2,3-Dibromo-5-hexylthiophene (**4**): To a 50-mL three-neck flask, **3** (1.0 g, 4.1 mmol) was placed and dissolved in DMF (36 mL). DMF solution (4 mL) of *N*-bromosuccinimide (NBS) (720 mg, 4.1 mmol) was added for 5 min at room temperature. The solution was stirred at room temperature for 12 h. To the solution was added saturated NaHCO₃ aqueous solution (60 mL), and the mixture was stirred at room temperature for 30 min. Aqueous layer was separated, and extracted with hexane (100 mL \times 3). Organic layers were combined, washed with water (100 mL \times 3), and dried over anhydrous MgSO₄. After filtration, the solution was concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography (SiO₂, eluted in 1:1 hexane and CH₂Cl₂), to give **4** as yellow oil (1.23 g, 93%). *R*_f 0.86 (1:1 hexane/CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.04 (t, *J* = 0.8 Hz, 1H), 2.87 (t, *J* = 7.2 Hz, 2H), 1.70 (m, 2H), 1.35 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.5, 28.5, 30.4, 30.9, 31.4, 107.4, 112.7, 126.8, 147.2; MS (70 eV, EI) *m/z* = 324 (M⁺). Obtained product was used to the next reaction without further purification due to difficult separation of a small amount of starting material. Analytical pure sample was obtained by GPC (CHCl₃). Anal. Calcd for C₁₀H₁₄SBr₂: C, 36.83%; H, 4.33%. Found: C, 36.98%; H, 4.26%.

2,3-Dicyano-5-hexylthiophene (**5**): To a 50-mL three-neck flask with a reflux condenser, **4** (300 mg, 0.91 mmol) and CuCN (260 mg, 2.92 mmol) were added and dissolved in *N*-methylpyrrolidone (NMP) (8 mL) under an N₂ atmosphere. The mixture was heated at 210 °C for 6 h. To the solution were added FeCl₃ (1.04 g, 6.44 mmol) and 2 M HCl aqueous solution (20 mL) (Caution!: This operation must conduct in a fume hood because HCN gas generates). The mixture was stirred at 60–70 °C for 30 min. After cooled to room temperature, CH₂Cl₂ (60 mL) was added, and the water layer was extracted with CH₂Cl₂ (60 mL \times 2). Organic layers were combined, washed with 2 M HCl aqueous solution (100 mL \times 2), water (100 mL), saturated NaHCO₃ aqueous solution (100 mL), water (100 mL), brine (150 mL \times 2), and water (100 mL), successively. The solution was dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The crude oil was purified by silica-gel column chromatography (SiO₂, eluted in 1:1 hexane and CH₂Cl₂), to give **5** as pale green oil (133 mg, 66%). *R*_f 0.24 (1:1 hexane/CH₂Cl₂); IR (KBr) 2222 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.04 (t, *J* = 0.8 Hz, 1H), 2.87 (t, *J* = 7.2 Hz, 2H), 1.70 (m, 2H), 1.35 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz,

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CDCl_3) δ 13.9, 22.4, 28.4, 30.1, 31.0, 31.2, 111.1, 112.2, 115.0, 119.1, 126.6, 155.5; MS (70 eV, EI) $m/z = 218$ (M^+); Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{S}$: C, 66.02%; H, 6.46%; N, 12.83%. Found: C, 66.01%; H, 6.66%; N, 12.83%.

2,8,14,20-Tetrahexyl-25H,27H-tetrathieno[2,3-b][2'3'-g][2''3''-l][2'''3'''-q]porphyrazine (2a): To a 50 mL round bottomed flask with a reflux condenser, **5** (600 mg, 2.75 mmol) was placed, and dissolved in 1-pentanol (10 mL) under an N_2 atmosphere. After heating at 100 °C, 1-Pentanol solution of 2.6 M lithium pentoxide (10.6 mL, 27.5 mmol) at 80 °C was added. The solution was heated at 130 °C for 11 h. After being cooled at room temperature, acetic acid (50 mL) was added. The solution was stirred at room temperature for 30 min. After removal of solvents under reduced pressure, methanol was added. The precipitates were collected, washed with methanol. Crude product was purified by column chromatography (Al_2O_3 , CH_2Cl_2 as eluant), to give **2a** (145 mg, 24%) as violet powder. Pure sample for elemental analysis was obtained by GPC (CHCl_3) then recrystallization from toluene and ethyl acetate. R_f 0.72 (CH_2Cl_2); Mp. 244–245 °C; IR (KBr) 3291 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.6–7.9 (m, 4H), 3.28 (t, $J = 6.4$ Hz, 8H), 1.68 (m, 32H), 1.03 (t, $J = 6.8$ Hz, 12H), -4.70 (brs, 2H); MS (MALDI-TOF) $m/z = 875.6$ ($\text{M}+\text{H}^+$); Anal. Calcd for $\text{C}_{48}\text{H}_{58}\text{N}_8\text{S}_4$: C, 65.87%; H, 6.68%; N, 12.80%. Found: C, 65.61%; H, 6.62%; N, 12.62%.

Copper complex of 2a (2b): To a 50 mL round bottomed flask with a reflux condenser, **2a** (50 mg, 0.029 mmol) and cupric acetate (60 mg, 0.331 mmol) were placed, and dissolved in 1-pentanol (10 mL). After refluxing for 1 h, the solution was cooled to room temperature. After removal of solvent under reduced pressure, residue was purified by column chromatography (Al_2O_3 , CH_2Cl_2 as eluant), to give **2b** (50 mg, 93%) as green powder. R_f 0.43 (CH_2Cl_2); Mp. >300 °C; MS (MALDI-TOF) $m/z = 936.8$ ($\text{M}+\text{H}^+$); Anal. Calcd for $\text{C}_{48}\text{H}_{56}\text{N}_8\text{S}_4\text{Cu}$: C, 61.54%; H, 6.03%; N, 11.96%. Found: C, 61.84%; H, 6.01%; N, 11.99%.

Supporting Information

2. ^1H NMR Spectrum of **2a**

In the synthesis of **2a**, four possible isomers exist. An NMR spectrum of **2a** measured in CDCl_3 was depicted in Figure S1. One broad peak around -4.7 ppm and four broad peaks around 7.9 ppm were attributed to the protons of N-H in the porphyrazine core and C-H of the thiophene moieties, respectively.

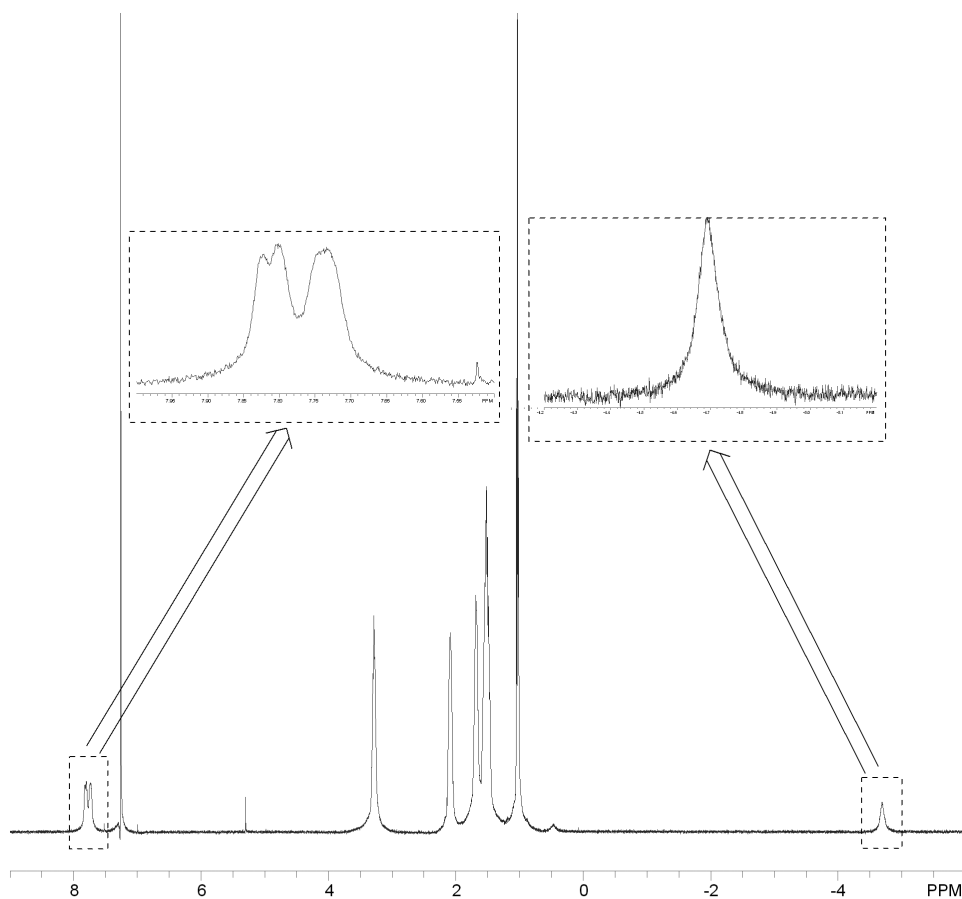


Figure S1. ^1H NMR spectrum of **2a** in CDCl_3 .

3 UV-vis and Cyclic voltammetry

UV-vis spectra were recorded in toluene solution with a Shimadzu UV-3100 spectrometer. Cyclic voltammetry (CV) measurements were carried out on a potentiostat and a function generator in CH_2Cl_2 containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , 0.1 M) as a supporting electrolyte at a scan rate of 100 mV/s. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. The results of CVs were summarized in Table S1.

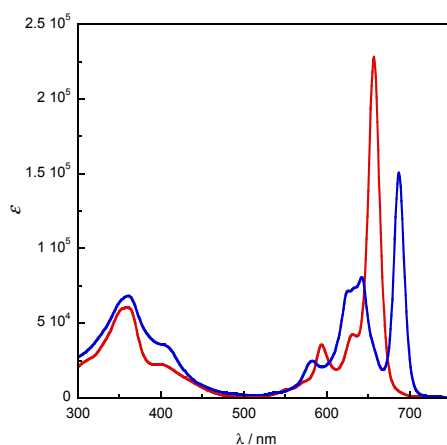


Figure S2. UV-vis spectra of **2a** (blue solid line) and **2b** (red solid line) in toluene.

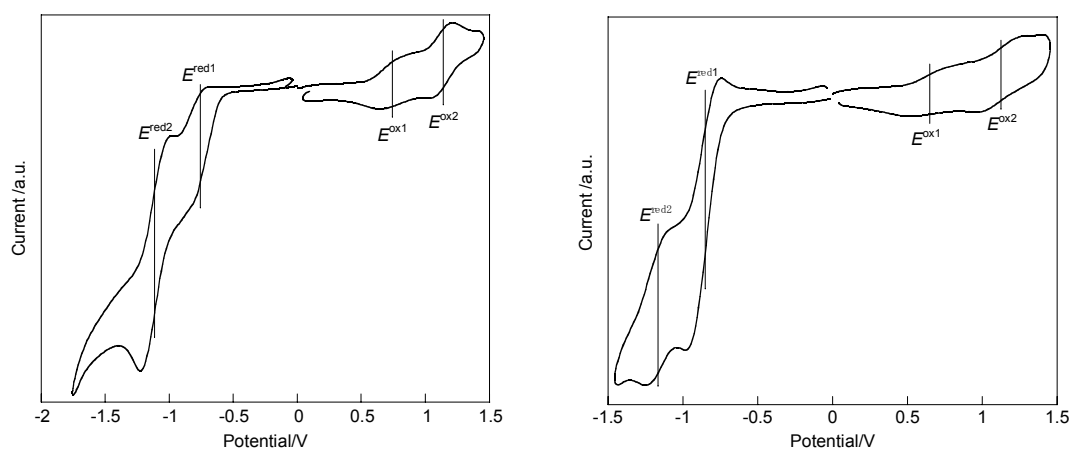


Figure S3. Cyclic voltammograms of **2a** (left) and **2b** (right) in CH_2Cl_2 .

Table S1. Summary of redox potentials of **2a** and **2b**.^a

compound	$E_{1/2}^{\text{red}2}$	$E_{1/2}^{\text{red}1}$	$E_{1/2}^{\text{ox}1}$	$E_{1/2}^{\text{ox}2}$	E_g
2a	-1.14	-0.75	+0.74	+1.12	1.49
2b	-1.19	-0.85	+0.56	+1.10	1.41

^a V vs. Ag/AgCl.

Supporting Information

4. Single crystal X-ray analysis of 2a and 2b

Single crystals suitable for X-ray structural analysis were obtained by recrystallization from toluene and ethyl acetate. The X-ray crystal structural analysis was made on a Rigaku Rapid Imaging Plate (Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$, graphite monochromator, $T = 150 \text{ K}$, $2\theta_{\text{max}} = 55.0^\circ$). The structure was solved by the direct method using SIR92.^{S3} Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in the calculations but not refined. All calculations were performed using the crystallographic software package of TeXsan 1.2^{S4} and SHELXL-97^{S5}. Considering the anisotropic parameters of the sulfur and carbon atoms on the thiophene sites, the extent of disorder was determined to be 0.5. To deal with the disorder, C-S and C-C distances were controlled with DFIX restraints (C-S 1.722, C=C 1.366 (C(α)-C(β)), and C-C 1.412 \AA (C(β)-C(β)). Planarity of the thiophene ring was also constrained. In addition, anisotropic displacement parameters of the disordered atoms were averaged.

Crystal data for **2a**: $\text{C}_{48}\text{H}_{58}\text{N}_8\text{S}_4$, $M = 875.28$, deep violet plate, $0.45 \times 0.45 \times 0.05 \text{ mm}^3$, *monoclinic*, space group $P2_1/c$ (no. 14), $a = 17.173(8)$, $b = 6.043(3)$, $c = 22.63(1) \text{ \AA}$, $\beta = 103.43(2)^\circ$, $V = 2283(6) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 2$, $D_{\text{calc}} = 1.273 \text{ g/cm}^3$, GOF = 0.92, reflections measured 17703, 4960 unique ($R_{\text{int}} = 0.0781$) which were used in all calculations. The final R_1 was 0.091, and the final wR on F_2 was 0.333 (all data). CCDC xxxxx.

Crystal data for **2b**: $\text{C}_{48}\text{H}_{56}\text{N}_8\text{CuS}_4$, $M = 936.81$, deep violet plate, $0.50 \times 0.30 \times 0.02 \text{ mm}^3$, *monoclinic*, space group $P2_1/c$ (no. 14), $a = 17.007(4)$, $b = 6.058(2)$, $c = 22.801(5) \text{ \AA}$, $\beta = 103.949(5)^\circ$, $V = 2280.0(9) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 2$, $D_{\text{calc}} = 1.364 \text{ g/cm}^3$, GOF = 0.723, reflections measured 21633, 5199 unique ($R_{\text{int}} = 0.124$) which were used in all calculations. The final R_1 was 0.0641, and the final wR on F_2 was 0.2012 (all data). CCDC xxxxx.

5. X-ray diffraction of thin films of **2a** and **2b**

X-ray diffractions of the spin-coated thin films of **2a** and **2b** on bare Si/SiO₂ substrates were obtained with a Rigaku RINT2000 diffractometer with a Cu *K*α source ($\lambda = 1.541 \text{ \AA}$) in air. Their calculated interlayer distances (*d*-spacing) were 16.4 and 15.8 Å, respectively.

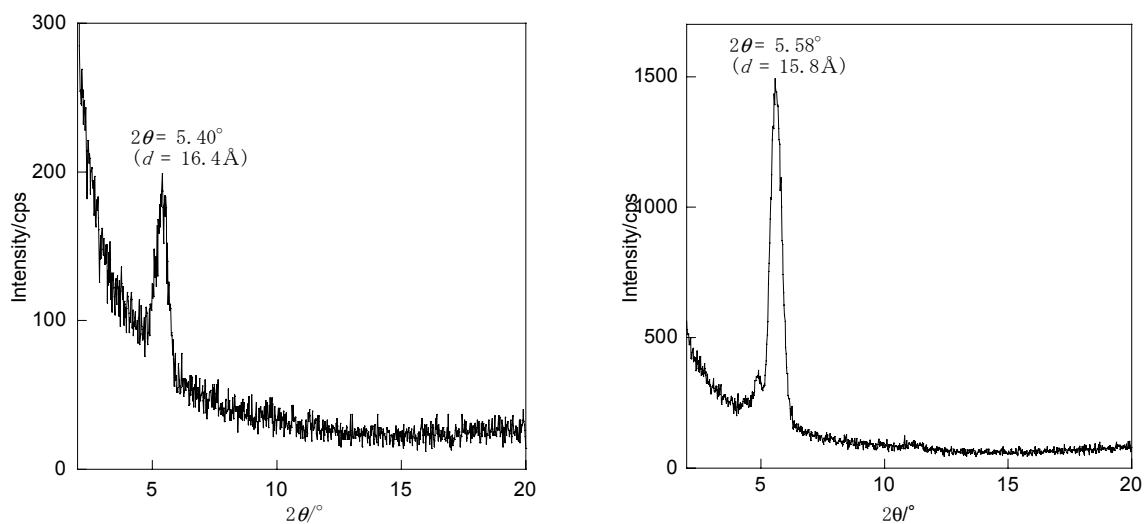


Figure S3. XRDs of the spin-coated thin films of **2a** (left) and **2b** (right).

6. Fabrications and evaluations of OFETs

The Si/SiO₂ substrates were treated in following ways; The SiO₂ surface was modified with an OTS (octyltrichlorosilane) SAM (self-assembled monolayer) by immersing the Si/SiO₂ substrate in 1 mM OTS in toluene at room temperature for 24 h. OFETs were fabricated in a “top-contact” configuration on a heavily doped *n*⁺-Si (100) wafer with 200-nm-thick thermally grown SiO₂ (*C_i* = 17.3 nF cm⁻²). Thin films of **2a** and **2b** were deposited by a spin-coating method using a 0.2 wt % CHCl₃ solution on the Si/SiO₂ substrates. Then the films were annealed under an N₂ atmosphere at 100 °C for 0.5–1 h. On top of the organic thin film, gold films (80 nm) as drain and source electrodes were deposited through a shadow mask. For a typical device, the drain-source channel length (*L*) and width (*W*) are 50 μm and ca. 1.5 mm, respectively. The characteristics of the OFET devices were measured at room temperature in air with a Keithley 6430 subfemtometer and a Keithley 2400 source meter, operated by a LabTracer program and GPIB interface. Field-effect mobility (μ_{FET}) was calculated in the saturation regime ($V_d = -50$ or -60 V) of the I_d using the following equation,

$$I_d = (WC_i/2L) \mu_{\text{FET}} (V_g - V_{\text{th}})^2$$

where *C_i* is the capacitance of the SiO₂ insulator, and V_g and V_{th} are the gate and threshold voltages, respectively. Current on/off ratio ($I_{\text{on}}/I_{\text{off}}$) was determined from the I_d at $V_g = 0$ V (I_{off}) and $V_g = -60$ V (I_{on}).

The output and transfer characteristics of **2a**- and CuPc-based devices fabricated on OTS-modified Si/SiO₂ substrate, where typical p-channel FET characteristics were observed (Figure S4 and S5). The field-effect mobility (μ_{FET}) extracted from the saturation regime is 0.03–0.05 and 0.01–0.02 cm² V⁻¹ s⁻¹ with $I_{\text{on}}/I_{\text{off}}$ of 10⁴–10⁵ and 10⁴, respectively.

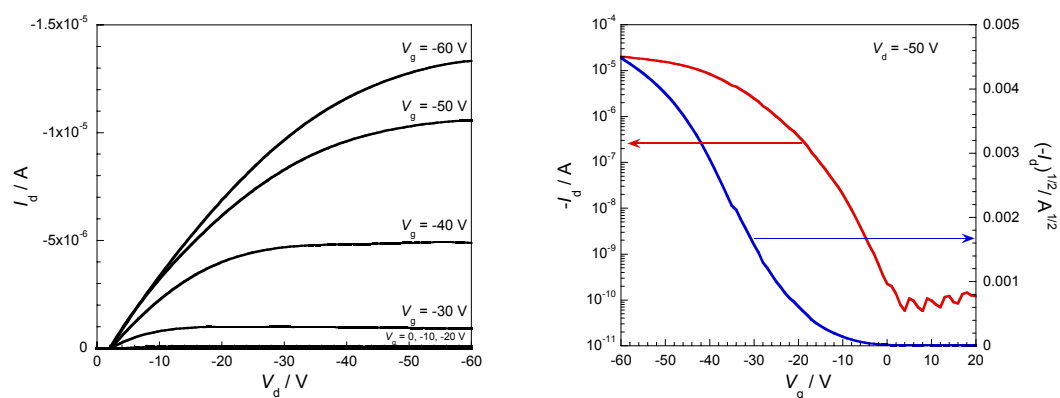


Figure S4. FET characteristics solution processed **2a**-based OFET.

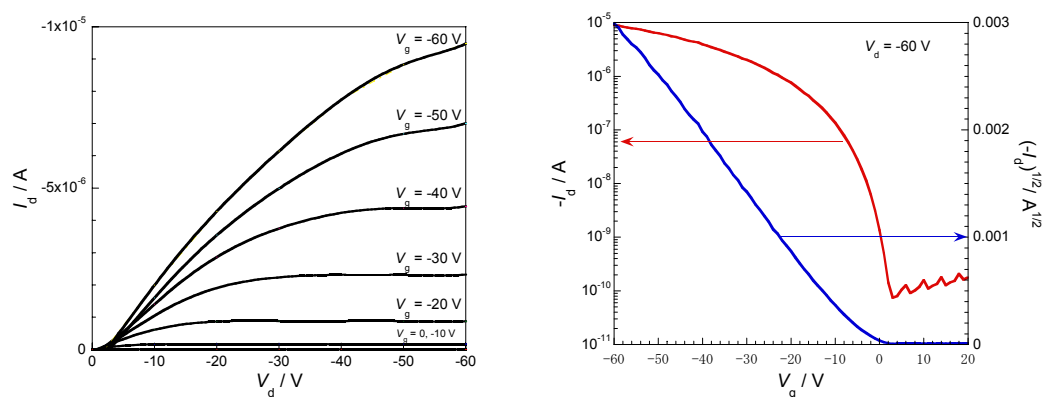


Figure S5. FET characteristics solution processed CuPc-based OFET.

Thin film of CuPc (4 Å/sec) was deposited by vapor deposition on the Si/SiO₂ substrates at 100 °C.

7. ^1H and ^{13}C NMR spectra

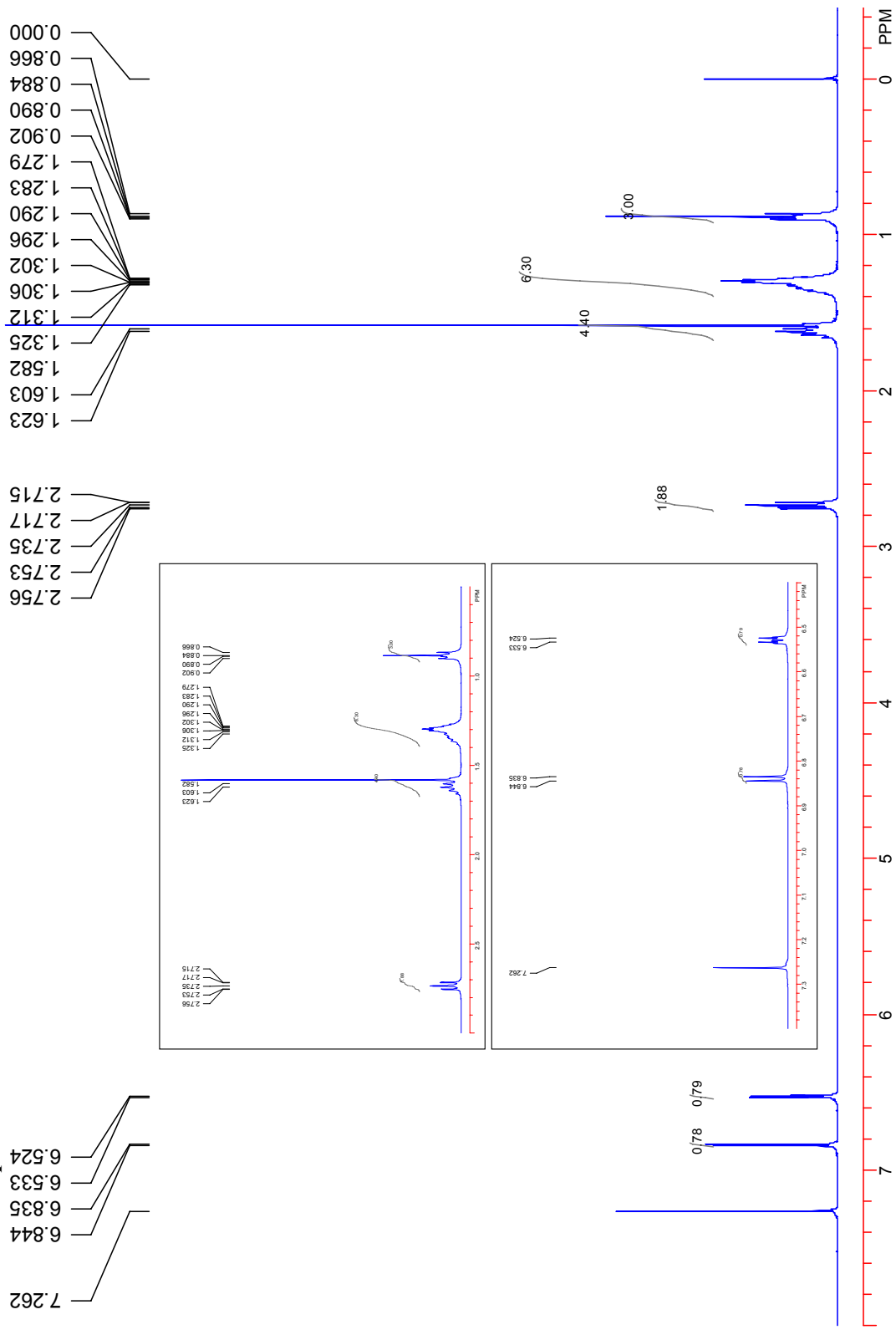


Figure S6. ^1H NMR of **3** in CDCl_3 .

Supporting Information

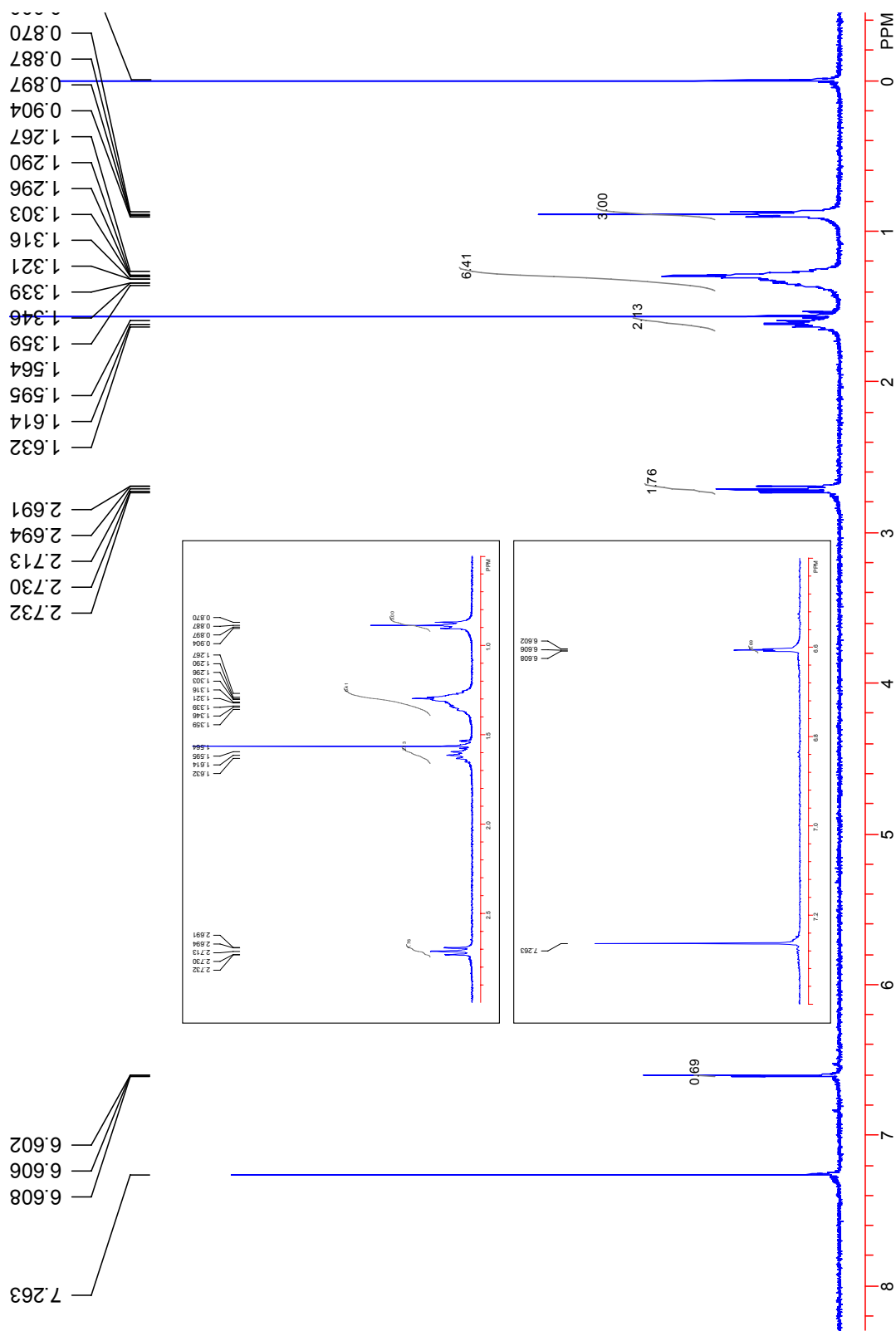
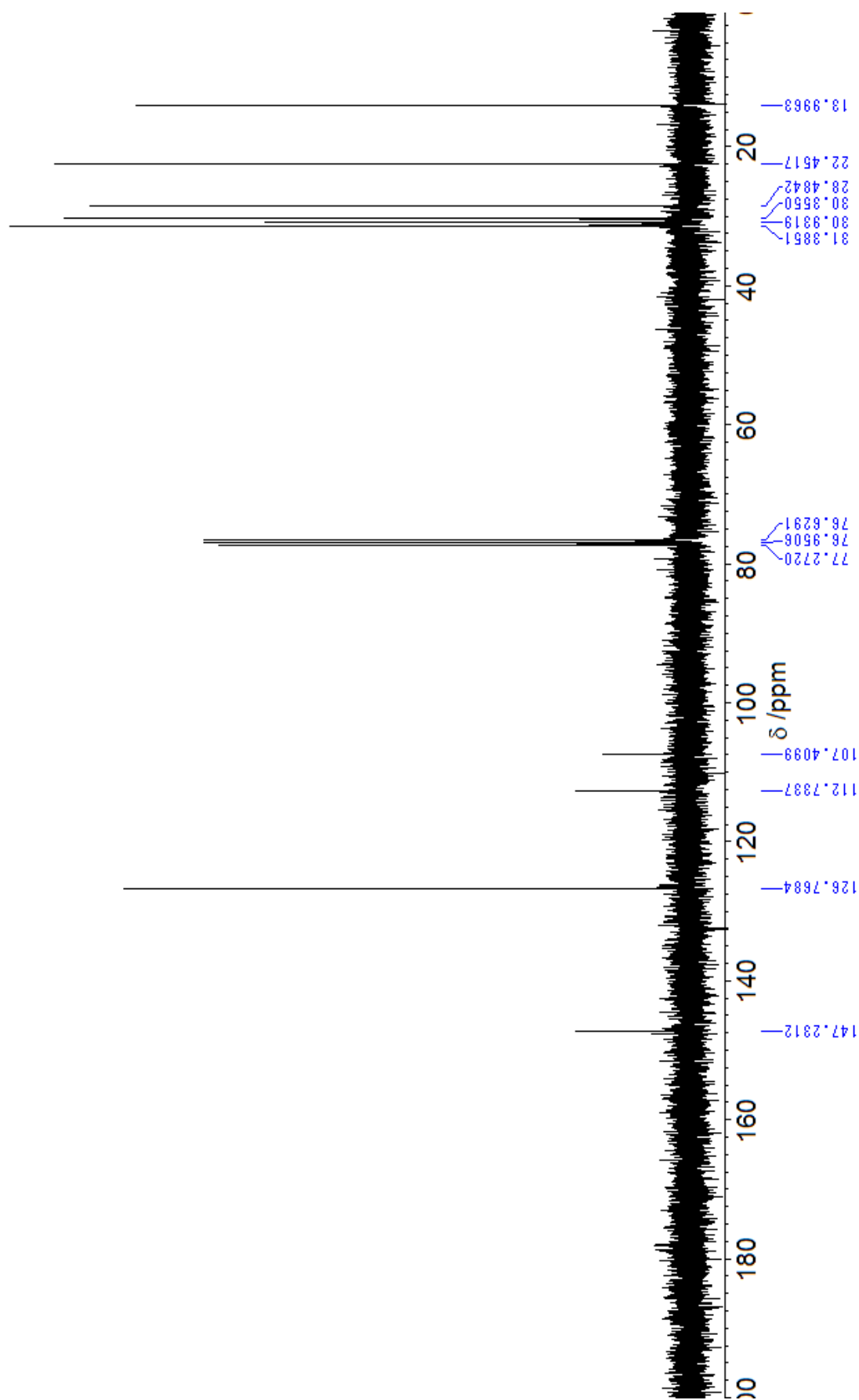


Figure S7. ¹H NMR of 4 in CDCl₃.

**Figure S8.** ^{13}C NMR of 4 in CDCl_3 .

Supporting Information

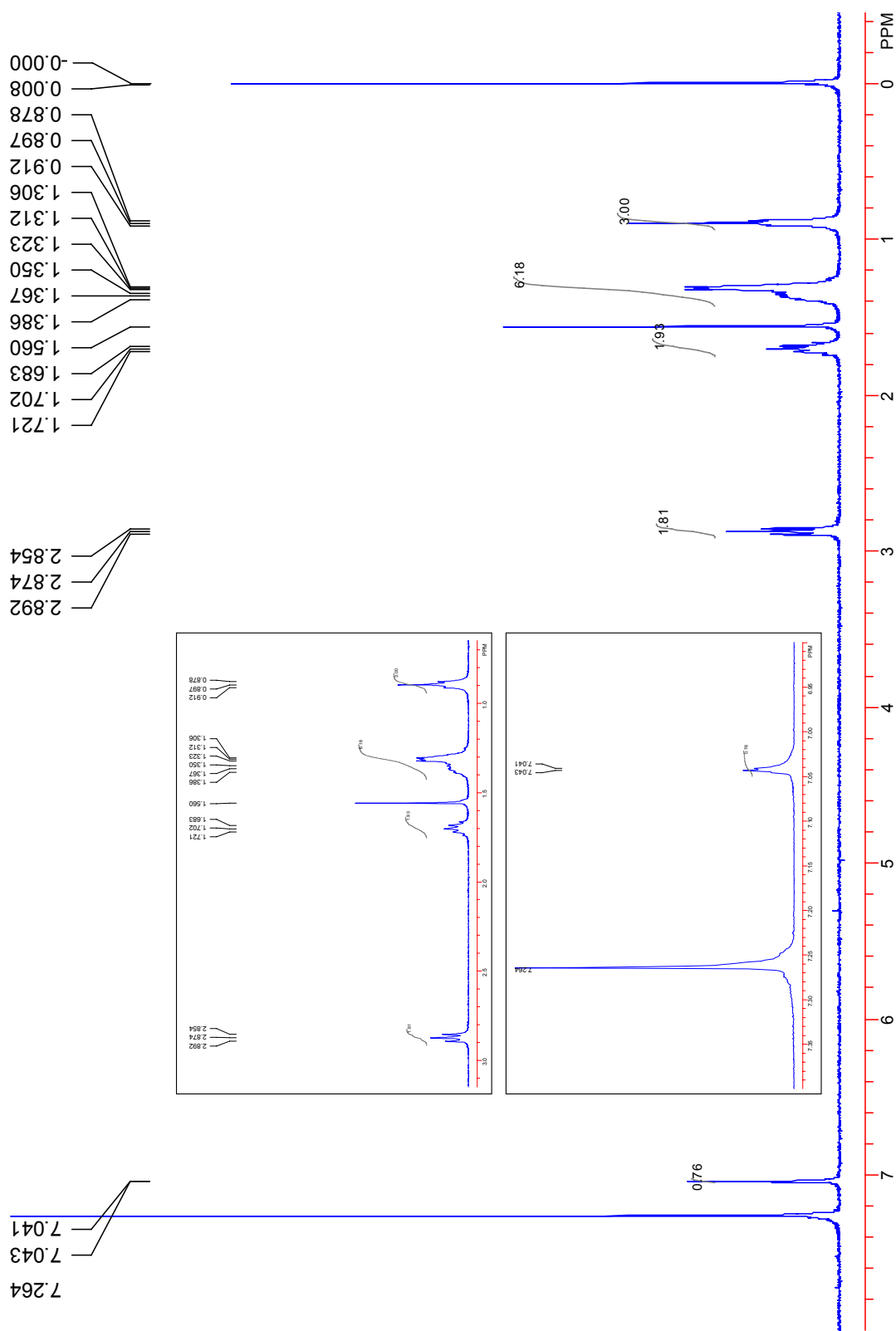
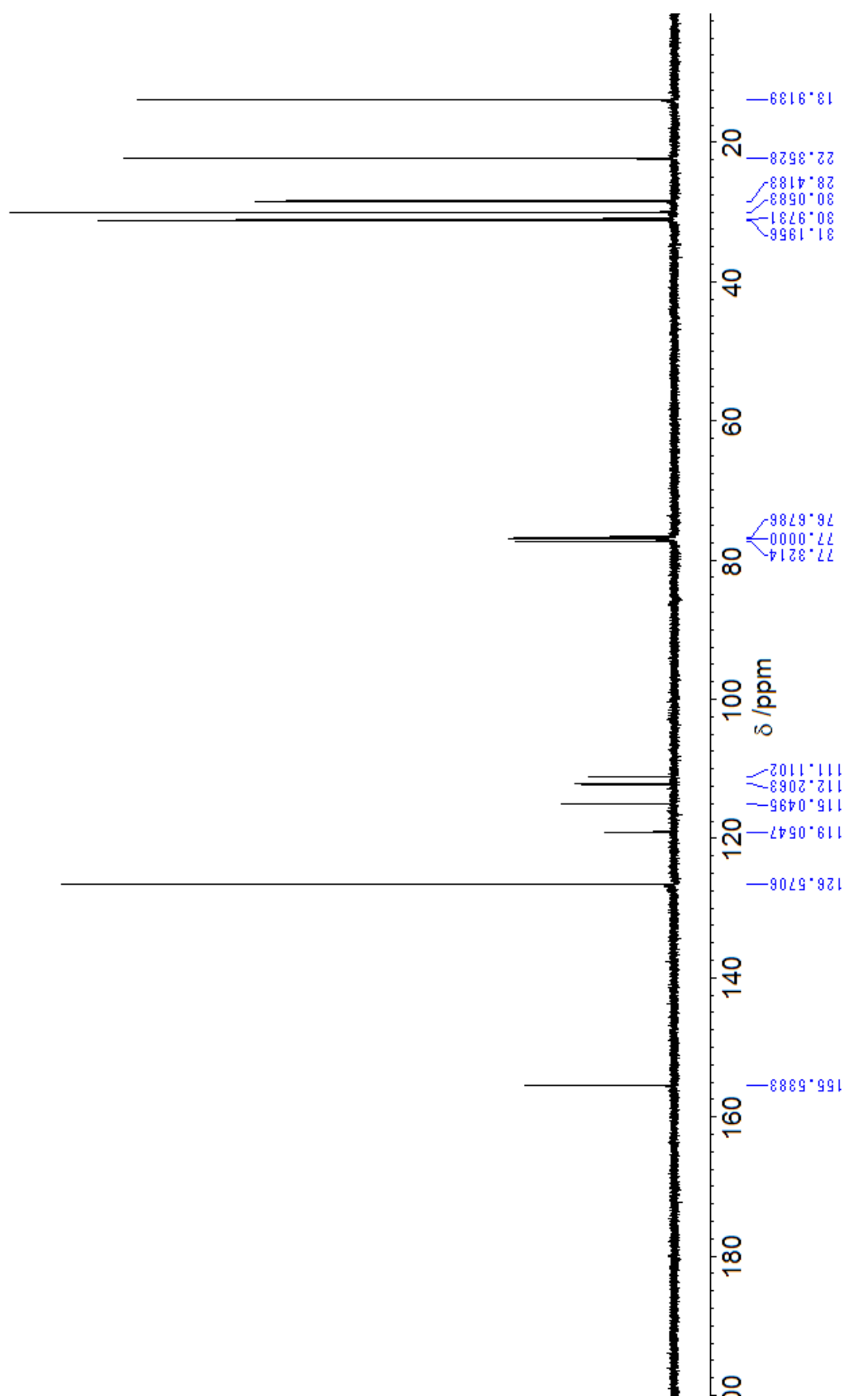


Figure S9. ^1H NMR of **5** in CDCl_3 .

Figure S10. ^{13}C NMR of **5** in CDCl_3 .

Supporting Information

8. References

- S1. *Purification of Laboratory Chemicals*, 5th ed. W. L. F. Armarego and C. L. L. Chai, Eds., Elsevier, New York, 2003, pp 416.
- S2. J. L. Brusso, O. D. Hirst, A. Dadvand, S. Ganesan, F. Cicoira, C. M. Robertson, R. T. Oakley, F. Rosei and D. F. Perepichka, *Chem. Mater.*, 2008, **20**, 2484.
- S3. SIR-92: A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Cryst.*, 1994, **27**, 435.
- S4. teXsan: Single Crystal Structure Analysis Software, Version 1.2; Molecular Structure Corporation and Rigaku Corporation, 2000.
- S5. SHELXL-97: G. M. Sheldrick, Program for the Refinement of Crystal Structures. University of Goettingen, Germany, 1997.