

Supplementary Information

New Dyes for Dye-sensitized Solar Cells Featuring a Carbon-bridged Phenylenevinylene Linker

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Experimental Section

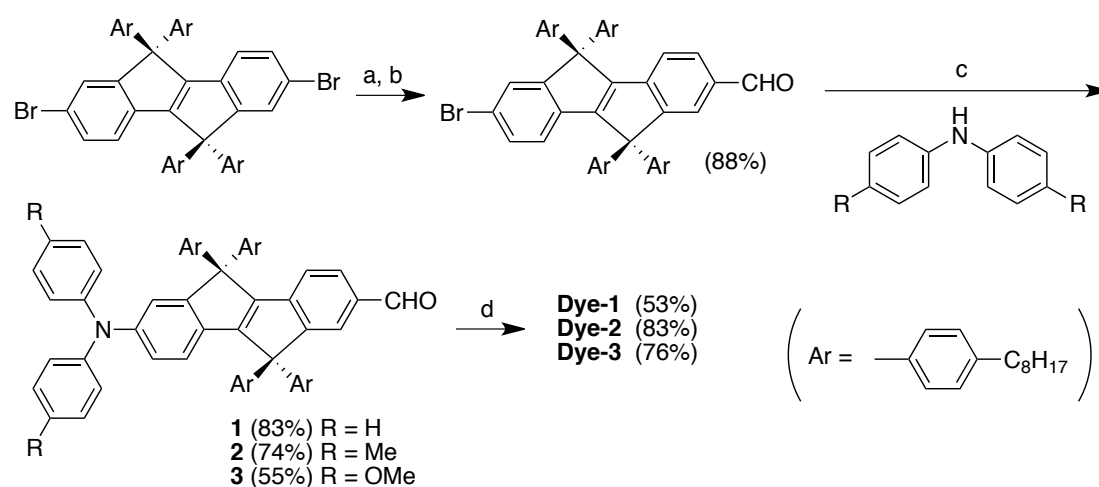
General. All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen or argon. Air- and moisture-sensitive liquids and solutions were transferred via syringe or Teflon cannula. Analytical thin-layer chromatography (TLC) was performed using glass plates precoated with 0.25 mm, 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin-layer chromatography plates were visualized by exposure to ultraviolet light (UV). Organic solutions were concentrated by rotary evaporation at ca. 15 Torr (evacuated with a diaphragm pump). Flash column chromatography was performed as described by Still *et al.*,¹ employing Kanto Silica gel 60 (spherical, neutral, 140–325 mesh).

Materials. Commercial reagents were purchased from Tokyo Kasei Co. and Aldrich Inc., and unless otherwise noted. Butyllithium was purchased from Kanto, passed over a pad of Celite under nitrogen and the concentration was determined by titration with menthol in the presence of 2,2'-bipyridyl. Anhydrous tetrahydrofuran (THF) was purchased from Wako Ltd., and purified by successively passing it over a molecular sieves column, then an alumina column. Lithium (dispersion) was purchased from Wako Co., and was washed with distilled hexane and dried over before use. The water content of the solvent was confirmed with a Karl-Fischer moisture titrator to be less than 20 ppm.

Instruments. Proton nuclear magnetic resonance (¹H NMR) and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded using a JEOL ECA-500 (500 MHz) NMR spectrometer. Chemical data for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the residual protons in the NMR solvent (CDCl₃: δ 7.26). Carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 125 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent (CDCl₃: δ 77.0). The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, br = broad), coupling constant in Hertz

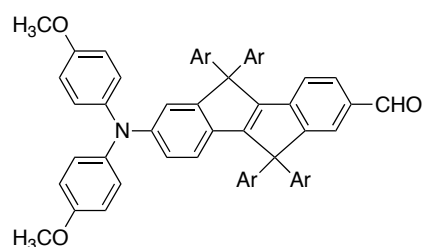
¹ W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2924.

(Hz), and integration. Melting points of solid materials were determined on a Mel-Temp II capillary melting-point apparatus and are uncorrected. Mass spectra were obtained on a JEOL Accu TOF JMS-T100LC. UV-Vis-NIR absorption spectra were recorded on JASCO V-570 spectrophotometer equipped with JASCO Pbs power supply. Fluorescence spectra were recorded on HITACHI F-4500 spectrophotometer. Photoluminescence quantum yields were measured on Hamamatsu Photonics C9920-02 Absolute PL Quantum Yield Measurement System, and absolute quantum yields were determined by using a calibrated integrating sphere system.



Scheme S1. Synthesis of CPV-dyes. (a) *n*-BuLi (1.1 eq), THF, -78 °C, 1 h; (b) DMF (1.1 eq), r. t., 30 min; (c) Diarylamine (2 eq), Pd₂(dba)₃•CHCl₃ (2 mol%), P(*t*-Bu)₃H•BF₄ (16 mol%), *t*-BuONa (2 eq), toluene, 110 °C, overnight; (d) CNCH₂COOH (3 eq), piperidine (3 eq), CH₃CN, 85 °C, overnight.

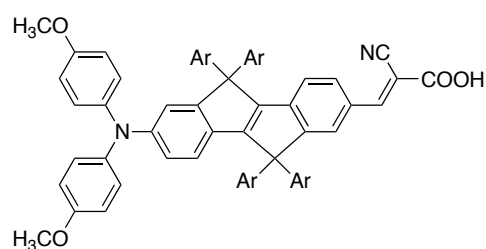
7-[Bis(4-methoxyphenyl)amino]-5,5,10,10-tetrakis(4-octylphenyl)-5,10-dihydroindeno[2,1-*a*]indene-2-carbaldehyde (**3**)



A mixture of compound 7-bromo-5,5,10,10-tetrakis(4-octylphenyl)-5,10-dihydroindeno[2,1-*a*]indene-2-carbaldehyde (0.16 g, 0.150 mmol), Pd₂(dba)₃•CHCl₃ (3 mg, 0.0029 mmol), P(*t*-Bu)₃H•BF₄ (7 mg, 0.024 mmol), di-*p*-anisylamine (69 mg, 0.30 mmol) and NaO*t*-Bu (29 mg, 0.302 mmol) in argon-saturated toluene (6 mL)

was stirred overnight at 110 °C. After cooling to room temperature, the reaction solution was added several drops of saturated ammonium chloride solution. After purification on a silica-gel column (CH₂Cl₂/hexane = 1:6 to 1:1), a yellow compound **3** was obtained from with a yield of 55% (0.101 g). Mp: 92-94 °C; ¹H NMR (500 MHz, THF-*d*₈): δ 0.86-0.88 (m, 12H), 1.28-1.32 (m, 40H), 1.54-1.59 (m, 8H), 2.53-2.56 (m, 8H), 3.71 (s, 6H), 6.51 (d, ³*J* = 8.6 Hz, 1H), 6.74 (d, ³*J* = 8.6 Hz, 4H), 6.92 (d, ³*J* = 9.2 Hz, 4H), 6.99 (d, ³*J* = 8.6 Hz, 1H), 7.02-7.06 (m, 8H), 7.13-7.15 (m, 5H), 7.20-7.23 (m, 5H), 7.59 (d, ³*J* = 7.4 Hz, 1H), 7.86 (s, 1H), 9.80 (s, 1H); ¹³C NMR (125 MHz, THF-*d*₈): δ 14.5, 23.6, 30.26, 30.28, 30.49, 30.52, 30.56, 32.5, 32.6, 32.9, 36.5, 55.6, 63.4, 63.5, 115.5, 118.2, 119.1, 120.8, 122.7, 125.7, 127.5, 129.1, 129.2, 129.3, 130.8, 131.1, 134.8, 140.7, 141.2, 141.5, 142.3, 142.5, 146.0, 149.0, 152.8, 157.3, 158.9, 160.7, 161.3, 191.2; HRMS (APCI+) calcd for C₈₇H₁₀₅NO₃ (M): 1211.8094; found: 1211.8092.

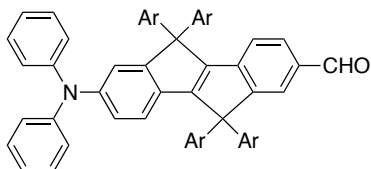
3-{7-[Bis(4-methoxyphenyl)amino]-5,5,10,10-tetrakis(4-octylphenyl)-5,10-dihydroindeno[2,1-*a*]inden-2-yl}-2-cyanoacrylic acid (Dye-3)



A mixture of compound **3** (90 mg, 0.074 mmol), cyanoacetic acid (19 mg, 0.223 mmol) and piperidine (22 μL, 0.222 mmol) in degassed and anhydrous acetonitrile (30 mL) was stirred overnight at 85 °C in the presence of molecular sieve (4 Å). After evaporation of the solvent, the residue was purified on a silica-gel column (CH₂Cl₂/MeOH = 100:0 to 100:10) to give a black compound **Dye-3** with a yield of 76% (72 mg). Mp: 90-92 °C; ¹H NMR (500 MHz, THF-*d*₈): δ 0.85-0.87 (m, 12H), 1.28 (brs, 40H), 1.56-1.59 (m, 8H), 2.52-2.56 (m, 8H), 3.71 (s, 6H), 6.52 (d, ³*J* = 9.4 Hz, 1H), 6.74 (d, ³*J* = 8.6 Hz, 4H), 6.92 (d, ³*J* = 8.6 Hz, 4H), 6.98-7.03 (m, 9H), 7.13-7.16 (m, 5H), 7.20-7.22 (m, 5H), 7.90 (s, 1H), 8.07 (s, 1H), 8.11 (s, 1H); ¹³C NMR (125 MHz, THF-*d*₈): δ 14.5, 23.6, 30.27, 30.29, 30.49, 30.52, 30.6, 30.7, 32.5, 32.6, 32.9, 36.5, 55.6, 63.4, 63.6, 115.4, 118.2, 119.2, 121.1, 122.7, 127.5, 129.1,

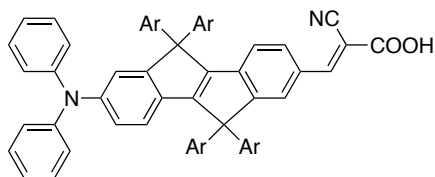
129.2, 129.3, 131.2, 140.7, 141.2, 141.5, 142.2, 142.3, 149.0, 153.1, 157.3, 158.9, 160.7; HRMS (APCI+) calcd for C₉₀H₁₀₆N₂O₄ (M): 1278.8152; found: 1278.8154.

7-(Diphenylamino)-5,5,10,10-tetrakis(4-octylphenyl)-5,10-dihydroindeno[2,1-*a*]indene-2-carbaldehyde (1)



Yellow oily solid (83%). ¹H NMR (500 MHz, THF-*d*₈): δ 0.85-0.89 (m, 12H), 1.27-1.32 (m, 40H), 1.57-1.59 (m, 8H), 2.52-2.56 (m, 8H), 6.68 (d, ³*J* = 8.0 Hz, 1H), 6.93-6.96 (m, 2H), 6.98 (d, ³*J* = 8.6 Hz, 4H), 7.03 (d, ³*J* = 8.0 Hz, 4H), 7.06 (d, ³*J* = 8.0 Hz, 4H), 7.09 (d, ³*J* = 8.6 Hz, 1H), 7.13-7.16 (m, 8H), 7.22 (d, ³*J* = 7.4 Hz, 4H), 7.26 (d, ³*J* = 8.0 Hz, 1H), 7.28 (s, 1H), 7.61 (d, ³*J* = 8.0 Hz, 1H), 7.88 (s, 1H), 9.82 (s, 1H); ¹³C NMR (125 MHz, THF-*d*₈): δ 14.5, 23.6, 30.25, 30.28, 30.49, 30.51, 30.53, 30.55, 32.49, 32.55, 32.9, 36.47, 32.50, 63.5, 63.6, 121.2, 122.3, 122.9, 124.0, 125.5, 125.8, 129.15, 129.20, 129.26, 130.0, 130.8, 133.1, 135.1, 140.6, 140.9, 142.4, 142.5, 145.7, 147.9, 148.5, 154.0, 159.1, 160.8, 160.9, 191.3; TOF MS (APCI+): 1151.7 [M]⁺; Anal. Calcd for C₈₅H₁₀₁NO: C, 88.57; H, 8.83; N, 1.22; Found: C, 88.21; H, 9.11; N, 1.08.

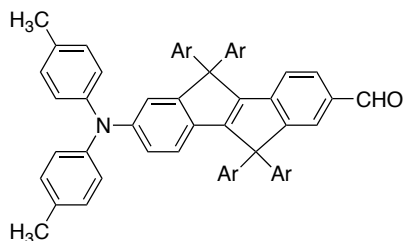
2-Cyano-3-{7-(diphenylamino)-5,5,10,10-tetrakis(4-octylphenyl)-5,10-dihydroindeno[2,1-*a*]inden-2-yl}acrylic acid (Dye-1)



Dark-red solid (53%). Mp: 98-100 °C; ¹H NMR (500 MHz, THF-*d*₈): δ 0.85-0.87 (m, 12H), 1.27-1.32 (m, 40H), 1.56-1.58 (m, 8H), 2.52 (overlapped with water signal, 8H), 6.68 (d, ³*J* = 8.0 Hz, ⁴*J* = 1.7 Hz, 1H), 6.93-7.03 (m, 14H), 7.08 (d, ³*J* = 8.0 Hz, 1H), 7.14-7.16 (m, 8H), 7.21-7.22 (m, 1H), 7.28 (d, ⁴*J* = 1.7 Hz, 1H), 7.89 (s, 1H), 8.08 (s, 1H), 8.12 (s, 1H); ¹³C NMR (125 MHz, THF-*d*₈): δ 14.5, 23.6, 30.27, 30.30, 30.50, 30.53, 30.55, 30.57, 32.4, 32.5, 32.9, 36.5, 63.4, 63.7, 121.2, 121.4, 122.3, 122.8, 123.9, 125.4, 129.16, 129.20, 129.24, 129.3, 130.0, 131.1, 133.3, 140.7,

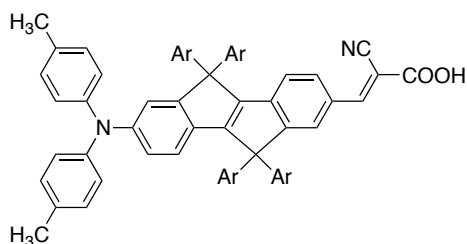
141.0, 142.33, 142.37, 147.7, 148.5, 154.3, 159.0, 160.7; HRMS (APCI+) calcd for $C_{88}H_{102}N_2O_2$ (M): 1218.7941; found: 1218.7939.

7-(Di-*p*-tolylamino)-5,5,10,10-tetrakis(4-octylphenyl)-5,10-dihydroindeno[2,1-*a*]indene-2-carbaldehyde (2)



Yellow oily solid (74%). 1H NMR (500 MHz, THF- d_8): δ 0.84-0.87 (m, 12H), 1.25-1.29 (m, 40H), 1.55-1.57 (m, 8H), 2.23 (m, 6H), 2.48-2.54 (m, 8H), 6.58 (dd, $^3J = 8.0$ Hz, $^4J = 2.2$ Hz, 1H), 6.84 (d, $^3J = 8.6$ Hz, 4H), 6.95 (d, $^3J = 8.6$ Hz, 4H), 7.00-7.14 (m, 9H), 7.13 (d, $^3J = 8.6$ Hz, 4H), 7.19 (d, $^3J = 8.6$ Hz, 4H), 7.21-7.23 (m, 2H), 7.58 (d, $^3J = 8.0$ Hz, 1H), 7.86 (s, 1H), 9.79 (s, 1H); ^{13}C NMR (125 MHz, THF- d_8): δ 14.4, 20.9, 23.6, 30.2, 30.44, 30.48, 32.4, 32.5, 32.9, 36.4, 63.4, 63.5, 120.0, 121.0, 121.1, 122.8, 125.6, 129.07, 129.18, 129.23, 130.5, 130.7, 132.2, 133.5, 134.9, 140.6, 141.0, 142.3, 142.4, 145.8, 146.0, 148.2, 153.4, 158.9, 160.6, 161.1, 191.2; TOF MS (APCI+): 1179.4 [M] $^+$; Anal. Calcd for $C_{87}H_{105}NO$: C, 88.50; H, 8.96; N, 1.19; Found: C, 88.32; H, 9.14; N, 1.16.

2-Cyano-3-{7-(di-*p*-tolylamino)-5,5,10,10-tetrakis(4-octylphenyl)-5,10-dihydroindeno[2,1-*a*]inden-2-yl}acrylic acid (Dye-2)



Dark-red solid (83%). Mp: 106-108 °C; 1H NMR (500 MHz, THF- d_8): δ 0.84-0.86 (m, 12H), 1.18-1.38 (m, 40H), 1.50-1.62 (m, 8H), 2.23 (s, 6H), 2.52 (overlapped with water signal, 8H), 6.58 (d, $^3J = 8.0$ Hz, 1H), 6.85 (d, $^3J = 8.6$ Hz, 4H), 6.95 (d, $^3J = 8.6$ Hz, 4H), 7.00-7.02 (m, 9H), 7.13 (d, $^3J = 8.0$ Hz, 4H), 7.18-7.23 (m, 6H), 7.85 (brs, 1H), 8.04 (s, 1H), 8.08 (s, 1H); ^{13}C NMR (125 MHz, THF- d_8): δ 13.5, 20.0, 22.6, 29.29, 29.31, 29.52, 29.55, 29.57, 29.60, 29.7, 31.5, 31.6, 31.9, 35.5, 62.4, 62.7, 119.1,

120.21, 120.25, 121.8, 124.7, 127.2, 128.16, 128.24, 128.35, 129.3, 129.6, 130.1, 131.4, 132.5, 139.8, 140.1, 141.3, 141.4, 145.1, 147.2, 152.8, 158.0, 159.6; HRMS (APCI+) calcd for $C_{90}H_{106}N_2O_2$ (M): 1246.8254; found: 1246.8237.

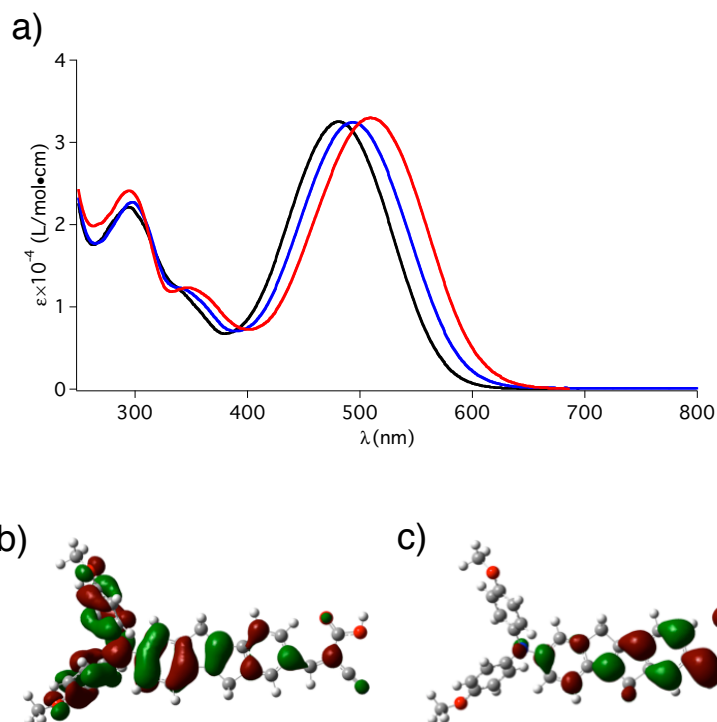


Figure S1. (a) UV-Vis absorption spectra of **Dye-1** (black), **Dye-2** (blue), **Dye-3** (red) in dichloromethane. (b) Spatial distribution of HOMO coefficient of **Dye-3** at B3LYP/6-31G** level. (c) LUMO coefficient.

Solar cell fabrication and characterization.

The TiO_2 photoanodes were prepared by screen printing onto fluorine-doped tin oxide (FTO, Solar 4 mm thickness, 10 ohms per sq, Nippon Sheet Glass) conducting glass. A total film thickness of $10 + 5 \mu m$ was used. The transparent layer consists of the particles of ~ 20 nm diameter anatase particles that gave a mesoporous layer. To render high PCE, a $\sim 5\text{-}\mu m$ scattering layer (400 nm diameter, Catalysts & Chemicals Ind. Co. Ltd. (CCIC), HPW-400) was deposited on the transparent layer. The TiO_2 electrodes were immersed into a 0.1-mM dye solutions 1:4 mixture of tetrahydrofuran and ethanol, and kept for 5 h at room temperature. The electrolyte consists of 1M 1,3-dimethylimidazolium iodide, 0.05 M iodine, 0.05 M LiI, 0.05M GuNCS and 0.5 M 4-tert-butylpyridine in 15/85 (v/v) mixture of valeronitrile and acetonitrile. The dye-adsorbed TiO_2 electrode and thermally platinized counter

electrode on FTO (TEC 15 ohms per sq, Pilkington) were assembled into a sealed sandwich type cell with a gap of a hot-melt ionomer film, Surlyn (25 μm , Du-Pont). A self-adhesive, anti-reflecting, ultraviolet cutoff film ($\lambda < 380 \text{ nm}$, ARKTOP, ASAHI Glass) was attached to the top of active area to decrease light reflection loss. For photovoltaic measurements of the DSSCs, the irradiation source was a 450 W xenon light source (Osram XBO 450) with a filter (Schott 113), whose power was regulated to the AM 1.5G solar standard by using a reference Si photodiode equipped with a colour-matched filter (KG-3, Schott) to reduce the mismatch in the region of 350–750 nm between the simulated light and AM 1.5G to less than 4%. The measurement-settling time between applying a voltage and measuring a current for the J – V characterization of DSSCs was fixed to 80 ms. The incident photon to collected electron conversion efficiency (IPCE) measurement was plotted as function of wavelength by using the light from a 300-W xenon lamp (ILC Technology), which was focused through a Gemini-180 double monochromator (Jobin Yvon) onto the photovoltaic cell under test. A computer-controlled monochromator was incremented through the spectral range (300–900 nm) to generate a photocurrent action spectrum with a sampling interval of 10 nm and a current sampling time of 4 s. To reduce scattered light from the edge of the glass electrodes of the dyed TiO_2 layer, a light-shading mask was used on the DSSCs, so the active area of DSCs was fixed to 0.16 cm^2 .

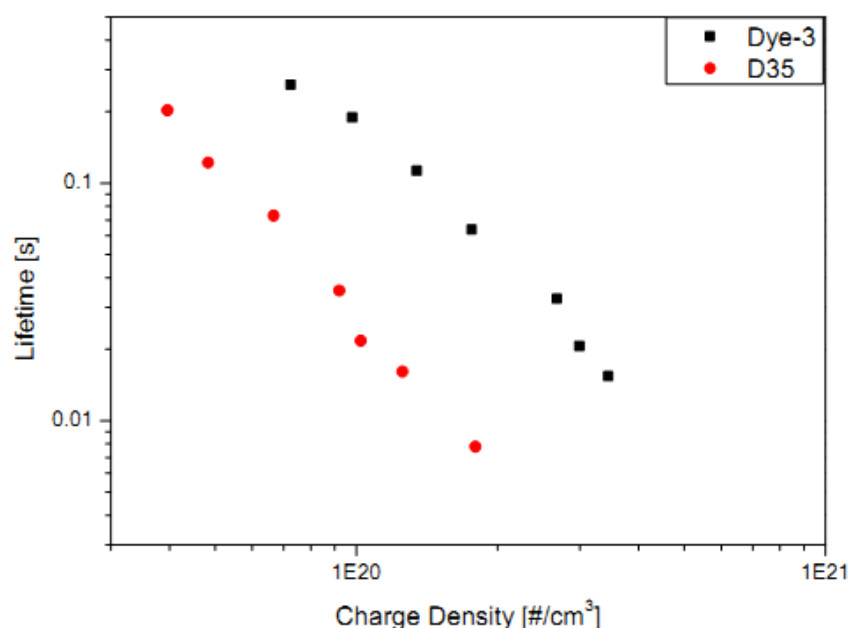


Figure 2. Electron lifetimes of **Dye-3** and **D35** sensitized solar cells as function of the charge density.

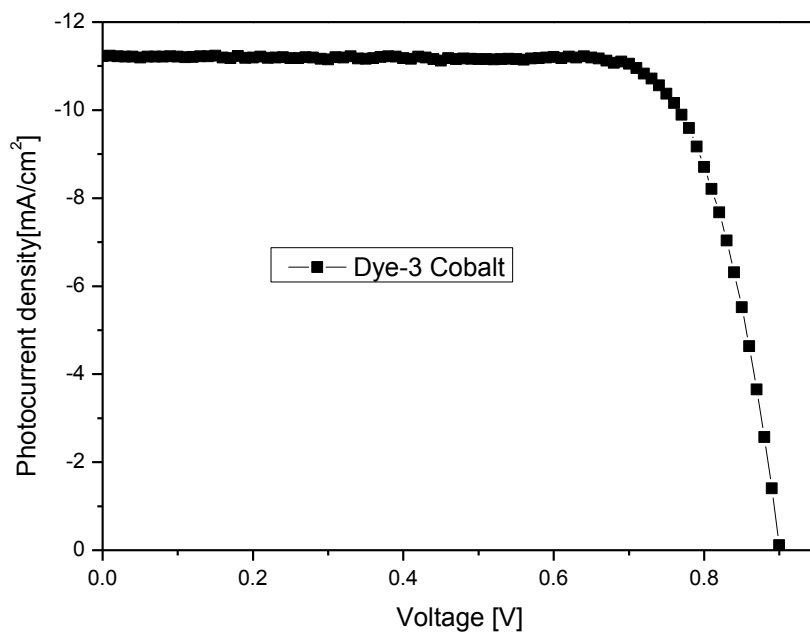


Figure S3. Photocurrent voltage curve obtained for **Dye-3** using Co(II/III)(bipy)₃ based redox electrolyte. The TiO₂ photoanodes used for the cobalt based cells has a total film thickness of ~ 9 μm, consisting of 5 μm transparent layer and 4 μm scattering layer to render higher power conversion efficiency. The electrolyte consists of 0.25 M Co(bpy)₃(TFSI)₂, 0.055 M Co(bpy)₃(TFSI)₃, 0.1 M LiTFSI, and 0.5 M 4-tert-butylpyridine in acetonitrile. The following photovoltaic performance parameter are derived from the *J-V* curve: J_{SC} 11.23 mA/cm², V_{OC} 0.9 V, ff 0.772 and PCE 7.54 %.

NMR Charts

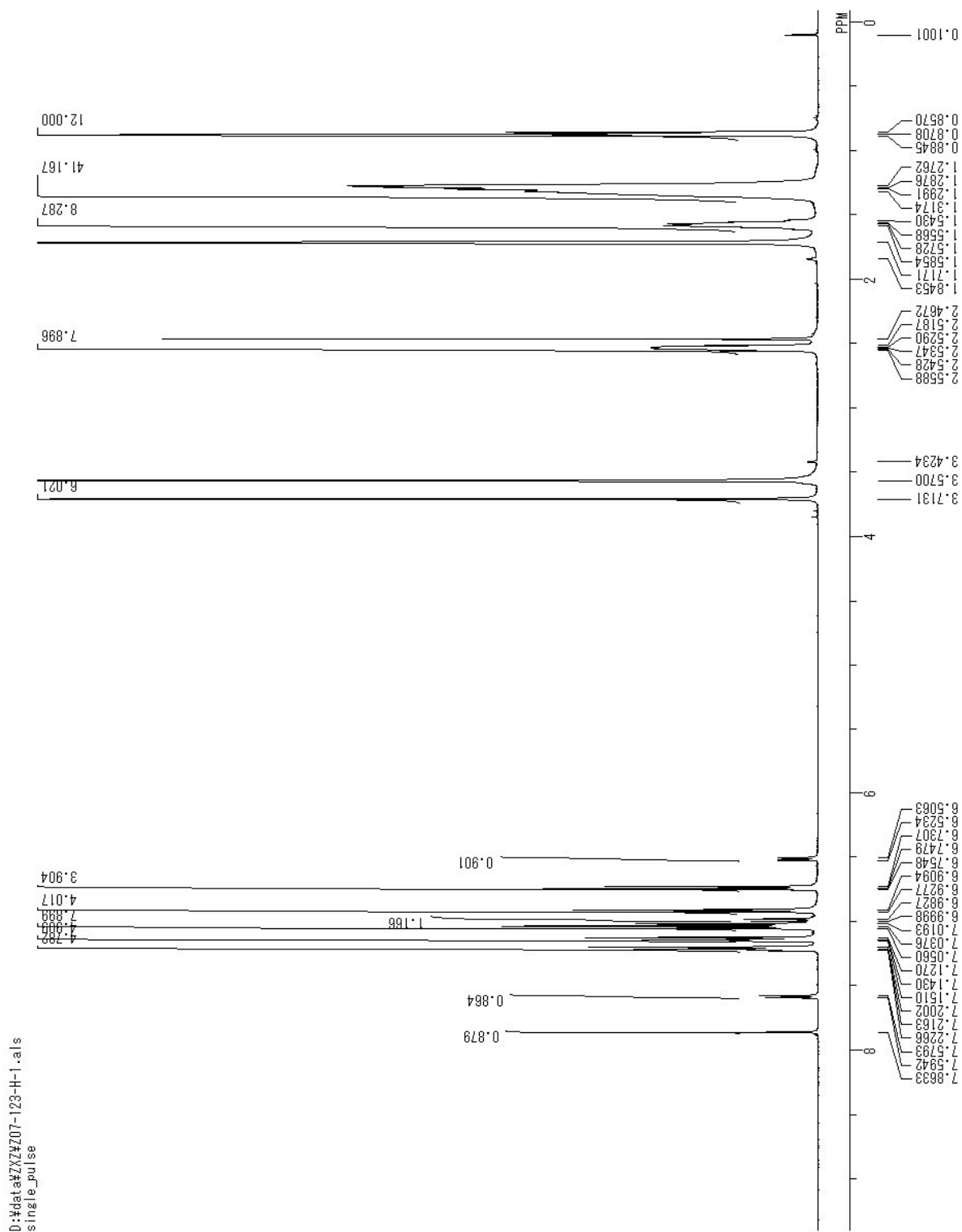


Figure S4. ^1H NMR ($\text{THF-}d_8$) spectrum of compound **3**.

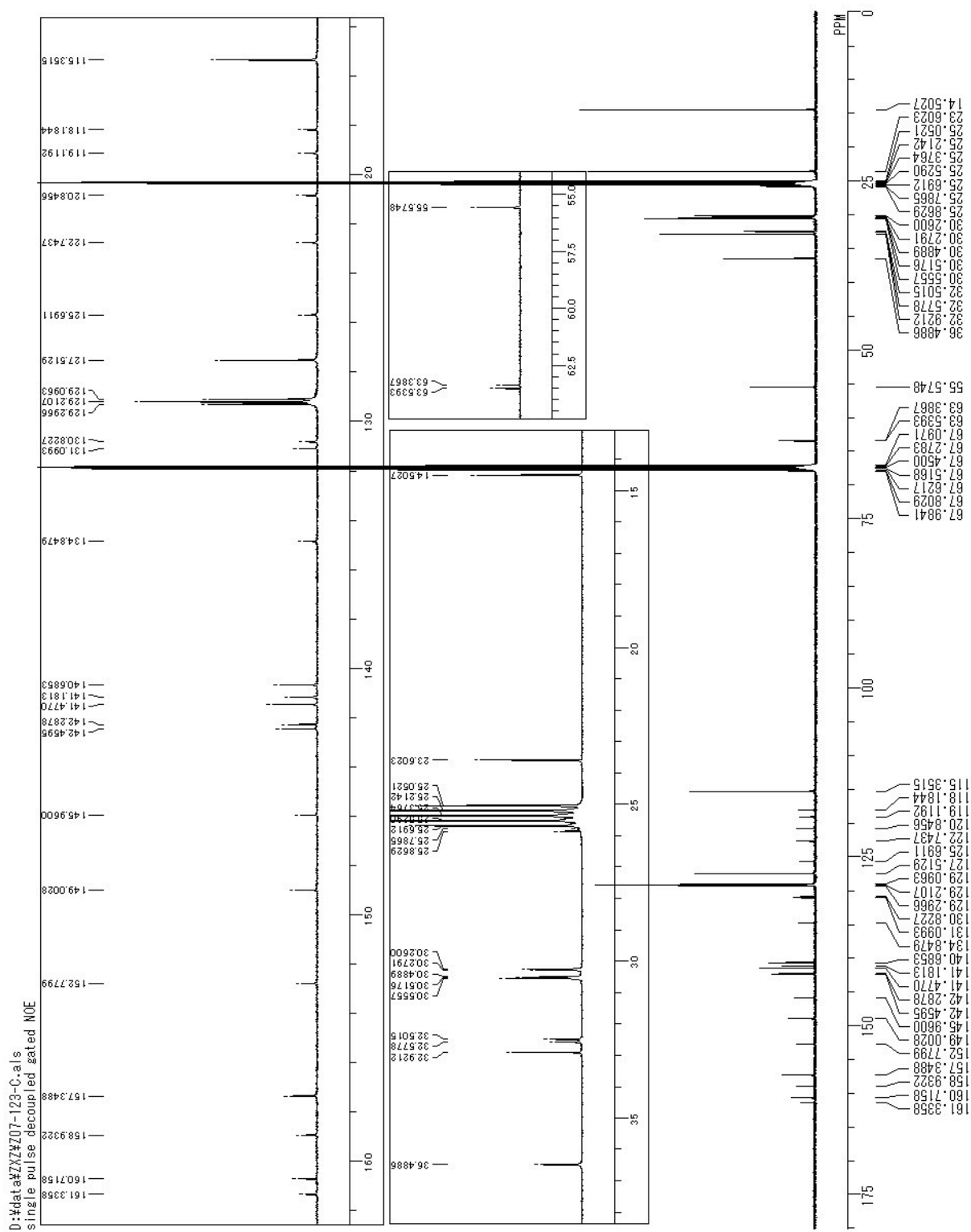


Figure S5. ^{13}C NMR ($\text{THF-}d_8$) spectrum of compound **3**.

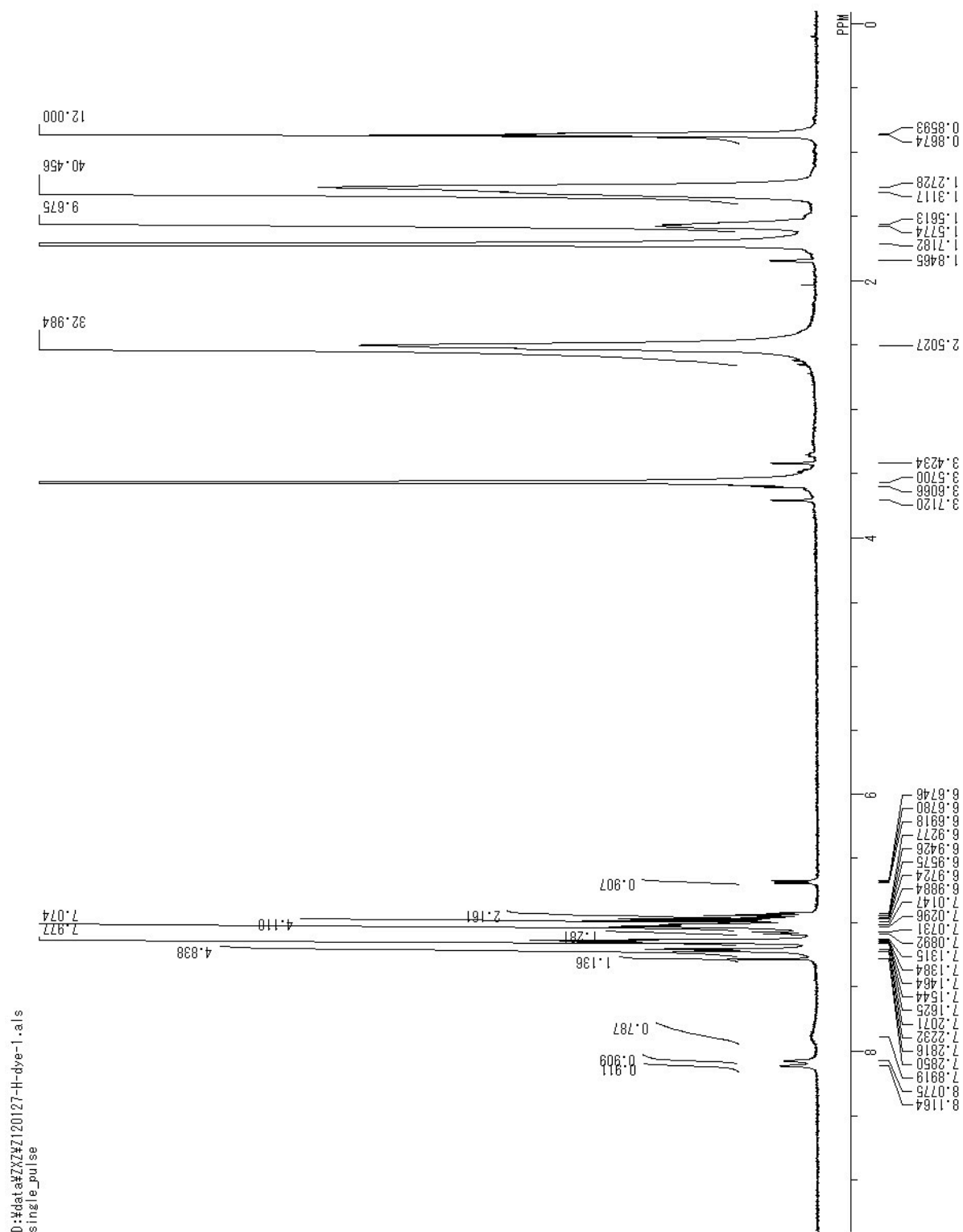


Figure S6. ^1H NMR ($\text{THF-}d_8$) spectrum of compound **Dye-1**.

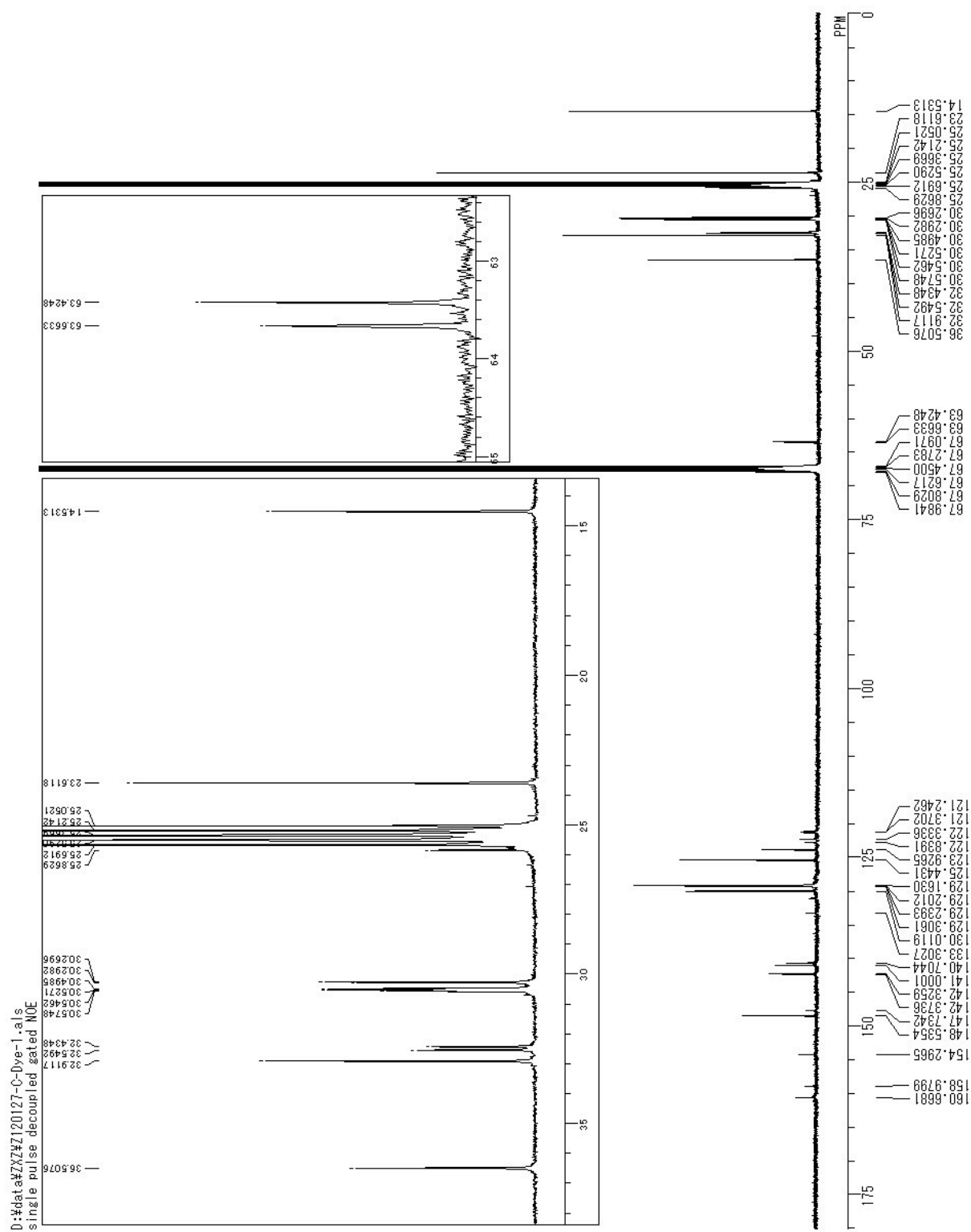


Figure S7. ^{13}C NMR ($\text{THF-}d_8$) spectrum of compound **Dye-1**.

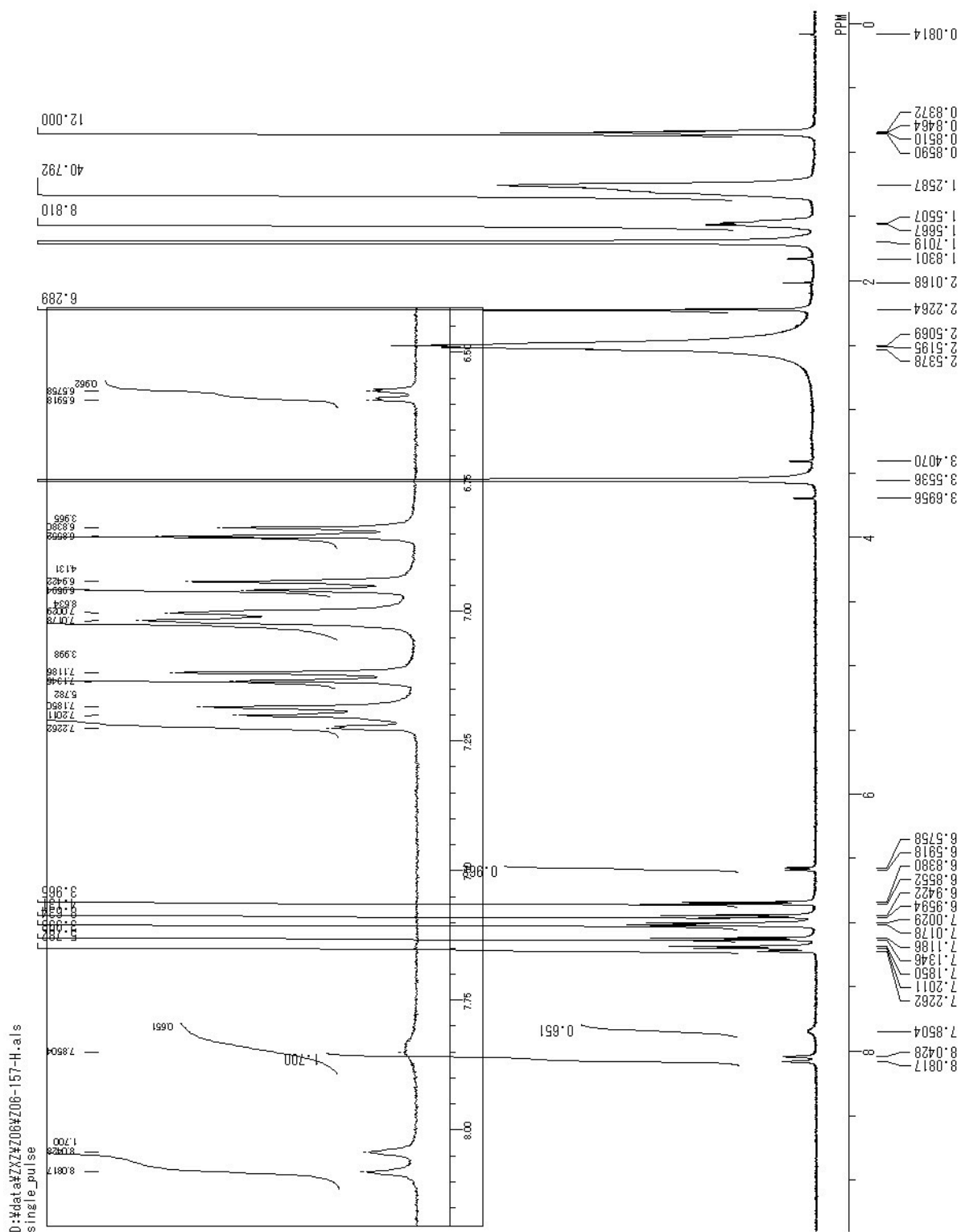


Figure S8. ^1H NMR ($\text{THF-}d_8$) spectrum of compound Dye-2.

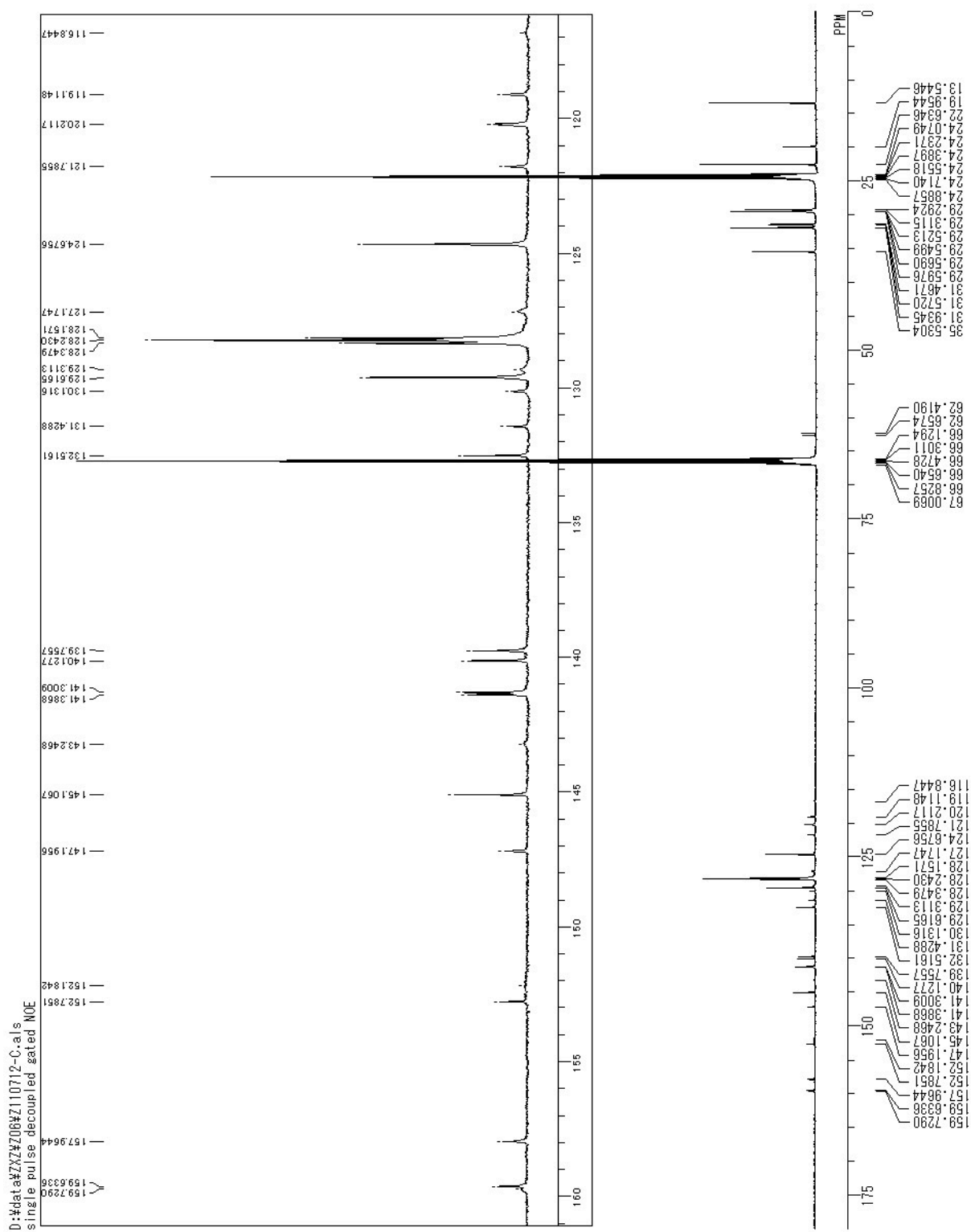


Figure S9. ^{13}C NMR ($\text{THF-}d_8$) spectrum of compound **Dye-2**.

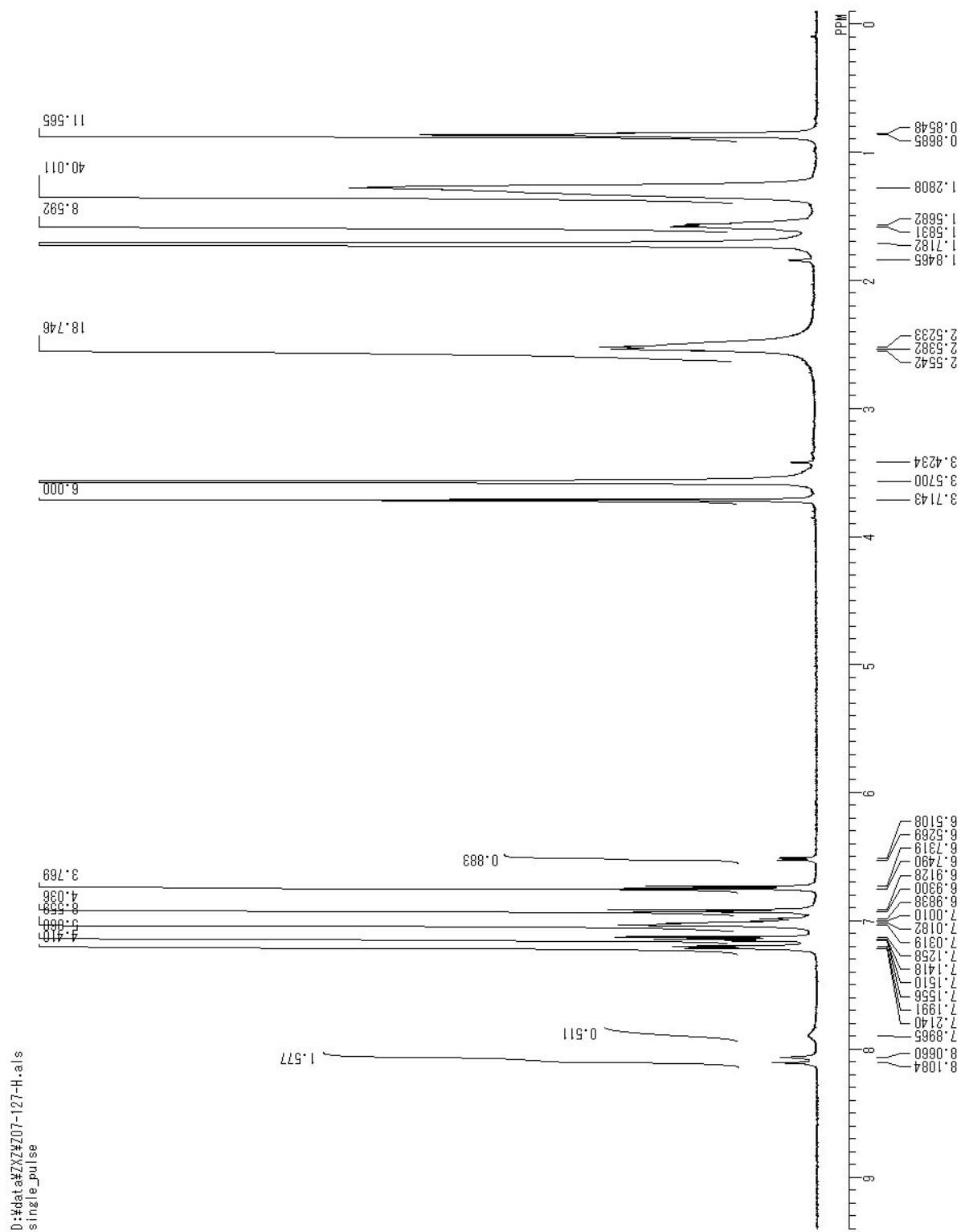


Figure S10. ^1H NMR ($\text{THF-}d_8$) spectra of compound **Dye-3**.

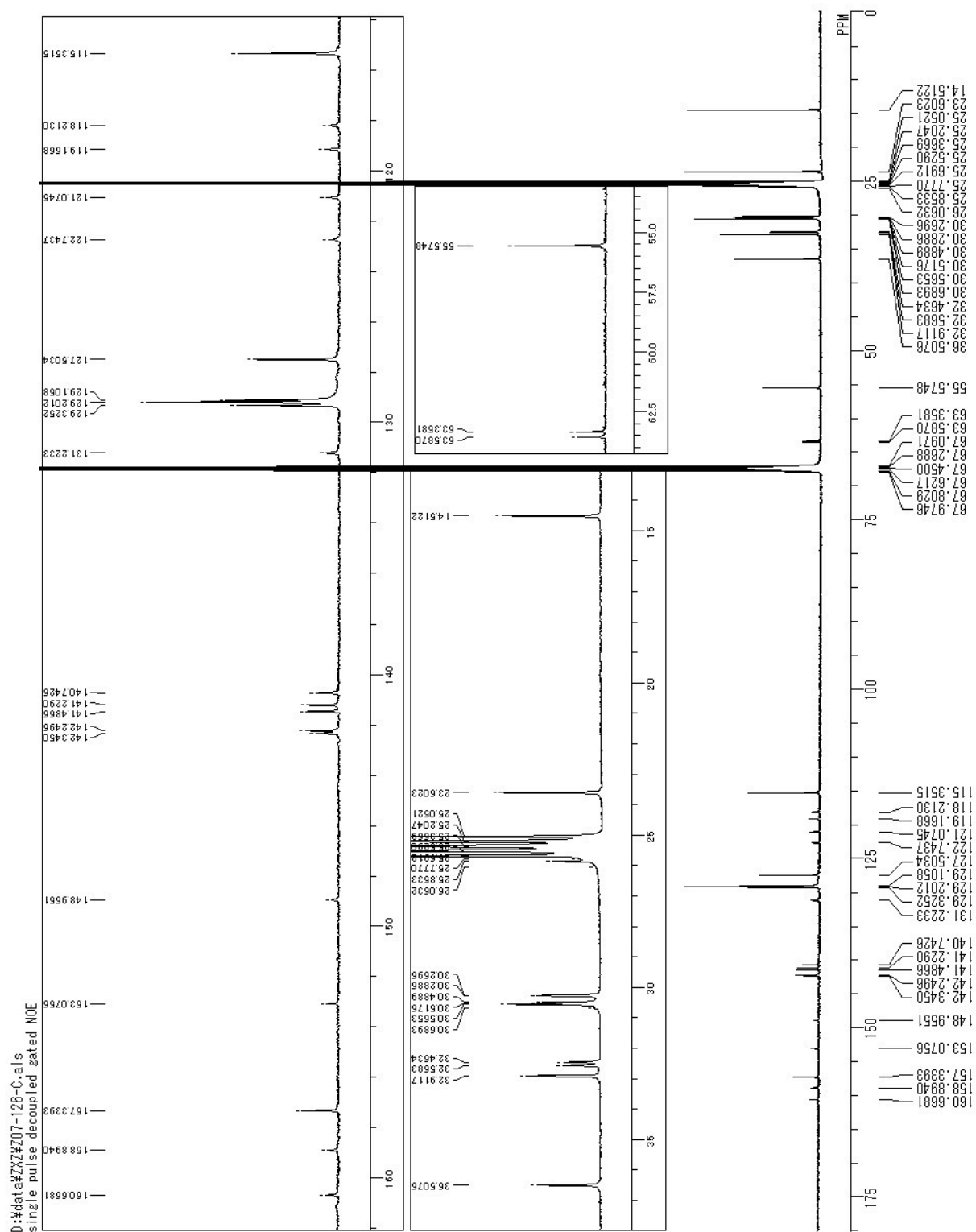


Figure S11. ^{13}C NMR ($\text{THF-}d_8$) spectrum of compound **Dye-3**.