Supporting Information

Synthesis of Ladder-Type π-Conjugated Heteroacenes via Palladium-Catalyzed Double *N*-Arylation and Intramolecular *O*-Arylation

Keiko Kawaguchi, Koji Nakano,* and Kyoko Nozaki*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

e-mail: knakano@chembio.t.u-tokyo.ac.jp, nozaki@chembio.t.u-tokyo.ac.jp

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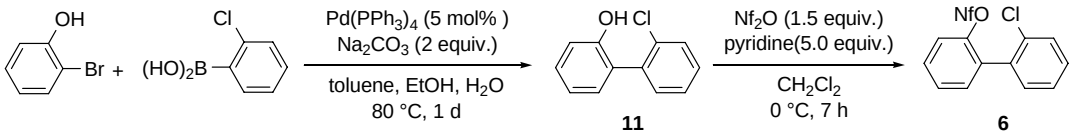
General Methods. All manipulations involving air- and/or moisture-sensitive compounds were carried out in a glove box under argon atmosphere or with the standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11. All the solvents used for reactions were distilled under argon after drying over an appropriate drying reagent or passed through solvent purification columns. Most of reagents were used without further purification unless otherwise specified. Analytical thin-layer chromatography was performed on a glass plates coated with 0.25-mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). For a silica gel column chromatography, Silica gel 60N (spherical neutral, particle size 63-210 μm, Kanto Kagaku Co., Ltd.) was used. NMR spectra were recorded in deuteriochloroform on a 500 MHz spectrometers (^{1}H 500 MHz; ^{13}C 125 MHz). Chemical shifts are reported in ppm relative to the residual protiated solvent peak (7.26 ppm for $CHCl_3$) for ^{1}H and deuteriochloroform (77.16 ppm) or deutrioacetone (206.26 ppm) for ^{13}C. Data are presented in the following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet and/or multiplet resonances, br = broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. Melting points were determined on a melting point apparatus. UV-Vis absorption spectra were recorded on a UV-VIS-NIR scanning spectrophotometer. The recycling preparative GPC was performed with a JAI GEL-1H and -2H columns (chloroform as an eluent). High resolution mass spectra are taken with FAB method. X-ray crystallographic analyses were recorded on a CCD diffractometer.

X-ray Crystallography. A suitable crystal was mounted with mineral oil to the glass fiber and transferred to the goniometer of a diffractmeter with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) to 2θmax = 55°. The structures were solved by direct methods with SIR-97[1] and refined by full-matrix least-squares techniques against $F2$ (SHELXL-97[2]). The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Synthetic Procedures

SCHEME S1.

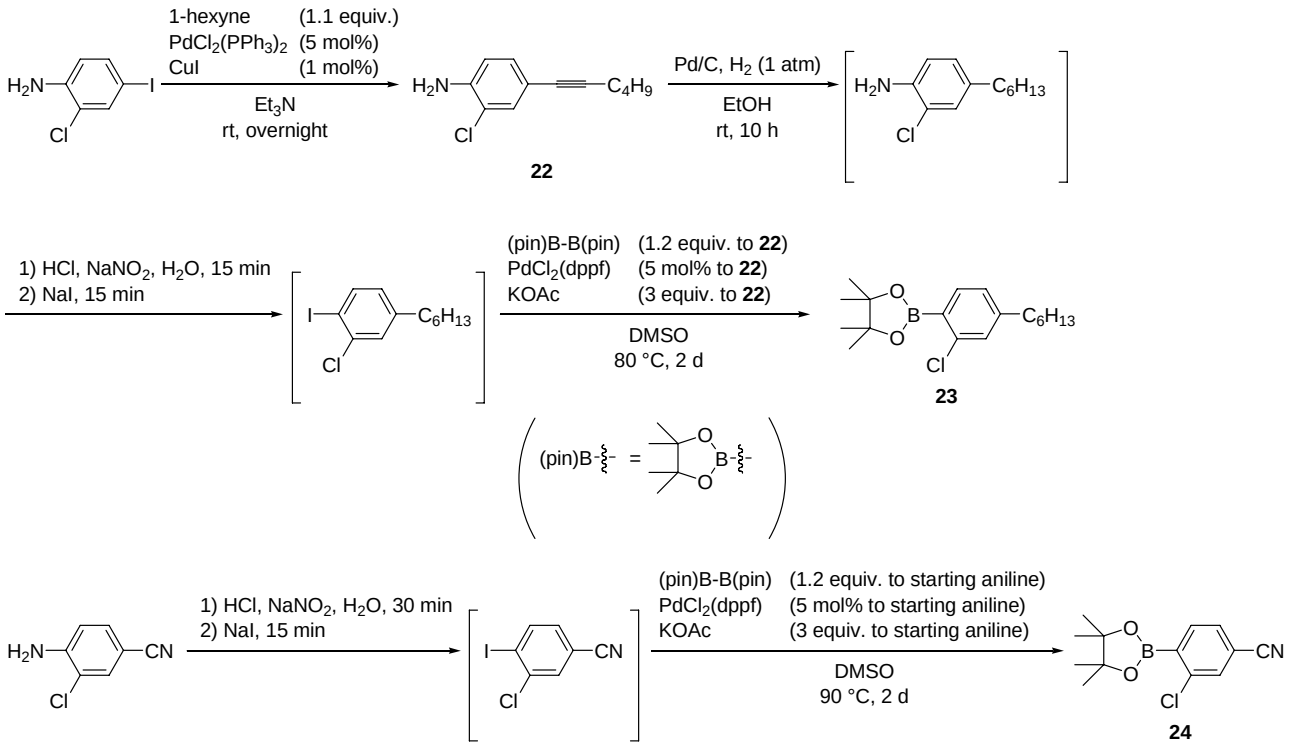


Synthesis of 2'-chlorobiphenyl-2-ol (11). The crude material was obtained by using 2-bromophenol (173 mg, 1.0 mmol), 2-chlorophenylboronic acid (156 mg, 1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.050 mmol), and Na_2CO_3 (212 mg, 2.0 mmol) in toluene (3.0 mL), EtOH (2.0 mL), and H_2O (1.0 mL) (80 °C, 1 d) according to the procedure described for the synthesis of compound **14**. Purification by column chromatography (silica gel; 20% AcOEt in hexane as an eluent, R_f 0.4) provided 179 mg of the title product as a colorless solid (88% yield): mp 145.1−146.4 °C; ^{1}H NMR ($CDCl_3$) δ 7.56−7.52 (m, 1H), 7.38−7.36 (m, 3H), 7.33 (td, J = 7.7, 1.6 Hz, 1H), 7.16 (dd, J = 7.6, 1.6 Hz, 1H), 7.04−7.00 (m, 2H), 4.83 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 152.7, 135.7, 134.2, 132.2, 130.8, 130.2, 129.9, 129.8, 127.4, 126.0, 120.7, 116.0. HRMS-FAB$^+$ (m/z) calcd for $C_{12}H_9ClO$ 204.0342, found 204.0344.

Synthesis of 2'-(1,1,2,2,3,3,4,4,4-nonafluorobutanesulfonyloxy)-2-chlorobiphenyl (6). The crude material was obtained by using **11** (43 mg, 0.21 mmol), triethylamine (0.10 mL, 1.1 mmol), and nonafluorobuthanesulfonic anhydride (0.10 mL, 0.32 mmol) in dichloromethane (2.0 mL) (0 °C, 9 h) according to the procedure described for the synthesis of compound **5**. Purification by column chromatography (silica gel; 14% AcOEt in hexane as an eluent, R_f 0.3) provided 93 mg of the title product

as a colorless solid (91% yield): mp 82.4−83.2 °C; ^{1}H NMR ($CDCl_3$) δ 7.52−7.45 (m, 3H), 7.43−7.40 (m, 2H), 7.39−7.33 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 147.2, 134.6, 133.8, 133.4, 132.5, 132.0, 130.09, 130.07, 129.8, 128.4, 126.8, 121.8, 118.5–109.6 (m, $CF_2CF_2CF_2CF_3$). HRMS-FAB$^+$ (*m*/*z*) calcd for $C_{16}H_8ClF_9O_3S$ 485.9739, found 485.9741.

SCHEME S2.



2-Chloro-4-hexynylaniline (22). A flame-dried 100 mL round-bottom flask containing a magnetic stirring bar was charged with 2-chloro-4-iodoaniline (4.0 g, 15.8 mmol), 1-hexyne (2.0 mL, 17.4 mmol), $PdCl_2(PPh_3)_2$ (554 mg, 0.79 mmol), CuI (31 mg, 0.16 mmol), and triethylamine (30 mL) under argon.

The mixture was stirred at room temperature overnight. The reaction mixture was filtered with a pad of Celite and concentrated. The residue was poured into 5 mL of water, extracted with Et_2O (10 mL × 3). The combined organic layers were washed with 2 *M* aqueous NH_4Cl and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated**.** The crude residue was purified by column chromatography (silica gel; 20% AcOEt in hexane as an eluent, R_f 0.5) to provide 3.1 g of the title product as a colorless oil (96% yield): ^{1}H NMR ($CDCl_3$) δ 7.30 (d, J = 1.9 Hz 1H), 7.10 (dd, J = 8.3, 1.9 Hz, 1H), 6.64 (d, J = 8.3 Hz, 1H), 4.11 (brs, 2H), 2.37 (t, J = 7.1 Hz, 2H), 1.59−1.53 (m, 2H), 1.49−1.42 (m, 2H), 0.94 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 142.6, 132.5, 131.1, 118.7, 115.4, 114.6, 88.9, 79.7, 31.0, 22.1, 19.2, 13.8. HRMS-FAB$^+$ (*m*/*z*) calcd for $C_{12}H_{14}ClN$ 207.0815, found 207.0811.

2-(2-Chloro-4-hexylphenyl)- 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23). A suspension of **22** (340 mg, 6.0 mmol) and palladium (10 wt% on activated carbon; 300 mg) in EtOH (5 mL) was stirred at room temperature under a hydrogen atmosphere (1 atm) for 10 h. The reaction mixture was filtered through a pad of Celite, and then the filtrate was concentrared. After the crude residue was dried under reduced pressure for 1 h, 2-chloro-4-hexylaniline was obtained as colorless oil that was used for next step without further purification.

The crude 2-chloro-4-hexylaniline was dissolved in 3.5 *M* aqueous HCl (8.8 mL) at 0 °C, and then a solution of sodium nitrite (460 mg, 1.1 mmol) in water (5 mL) was added slowly. After the reaction mixture was stirred for 15 min, a solution of sodium iodide (9.9 g, 66.0 mmol) in water (12 mL) was added. The resulting mixture was stirred for further 15 min and extracted with Et_2O (15 mL × 3). The combined

organic layers were washed twice with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. After the residue was dried under reduced pressure for 4 h, 2-chloro-1-iodo-4-hexylbenzene was obtained as a brown oil in almost pure form that was used next step without further purification.

A flame-dried 80 mL Schlenk tube containing a magnetic stirring bar was charged with $PdCl_2$(dppf) (246 mg, 0.14 mmol), KOAc (824 mg, 8.4 mmol), bis(pinacolate)diboron (1.8 g, 7.2 mmol), and the crude 2-chloro-1-iodo-4-hexylbenzene (ca. 2.8 mmol) under argon. After DMSO (15 mL) was added through the septum via syringe, the mixture was degassed by freeze-pump-thaw cycles. The resulting mixture was stirred at 80 ˚C for 2 d under argon. The reaction mixture was cooled to ambient temperature, poured into 5 mL of water, and extracted with Et_2O (30 mL × 3). The organic layers were washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was dried under reduced pressure for 1 h, and used for next step without further purification since **23** was found to decompose under purification conditions [silica gel column chromatography, recycling preparative GPC ($CHCl_3$ as eluent)]. The ^{1}H NMR analysis of the crude residue showed that it contained almost only **23** and bis(pinacolate)diboron (**23**/bis(pinacolate)diboron = 1/0.2). Based on this ratio, the amount of **23** added in the reaction mixture was estimated in the next coupling step. ^{1}H NMR ($CDCl_3$) δ 7.58 (d, J = 7.6 Hz, 1H), 7.14 (s, 1H), 7.01 (d, J = 7.6 Hz, 1H), 2.54 (t, J = 7.6 Hz, 2H), 1.55 (quint, J = 7.3 Hz, 2H), 1.33 (s, 12H), 1.28−1.21 (m, 6H, The signal of methyl groups of bis(pinacolate)diboron overlaps in this range.), 0.87 (t, J = 6.6 Hz, 3H).

2-(2-Chloro-4-cyanophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24). A solution of sodium

nitrite (560 g, 8 mmol) in water (4 mL) was added slowly to a solution of 4-amino-3-chlorobenzonitrile (508 g, 3 mmol) in 5.4 *M* aqueous HCl (3.5 mL) at 0 ˚C with stirring over 30 min. To the resulting mixture was added a solution of sodium iodide (5.5 g, 33 mmol) in water (1.5 mL). The reaction mixture was stirred for further 15 min, and then extracted with $CHCl_3$ (10 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. After the crude residue was dried for 4 h under reduced pressure, 3-chloro-4- iodobenzonitrile was obtained as a white solid in almost pure form that was used for next step without further purification.

A flame-dried 80 mL Schlenk tube containing a magnetic stirring bar was charged with $PdCl_2$(dppf) (114 mg, 0.14 mmol), KOAc (883 mg, 9.0 mmol), bis(pinacolate)diboron (853 mg, 3.4 mmol), and the crude 3-chloro-4- iodobenzonitrile under argon. After DMSO (15 mL) was added through the septum via syringe, the resulting mixture was degassed by freeze-pump-thaw cycles, and stirred at 90 ˚C for 2 day under argon. The reaction mixture was cooled to ambient temperature, poured into 10 mL of water, and extracted with AcOEt (15 mL × 3). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residure was purified by column chromatography (silica gel; 33% AcOEt in hexane as an eluent, R_f 0.4) to provide 696 mg of the title product as a colorless solid (88% yield): mp 137.6−143.2˚C; ^{1}H NMR ($CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 1.4 Hz, 1H), 7.50 (dd, J = 8.0, 1.4 Hz, 1H), 1.36 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 140.3, 137.0, 134.8 (*C*−B), 132.4, 129.2, 117.5, 115.4, 85.0, 24.9. Anal. Calcd for $C_{13}H_{15}BClNO_2$: C, 59.25; H, 5.74; N, 5.32. Found: C, 59.10; H, 5.69; N, 5.29.

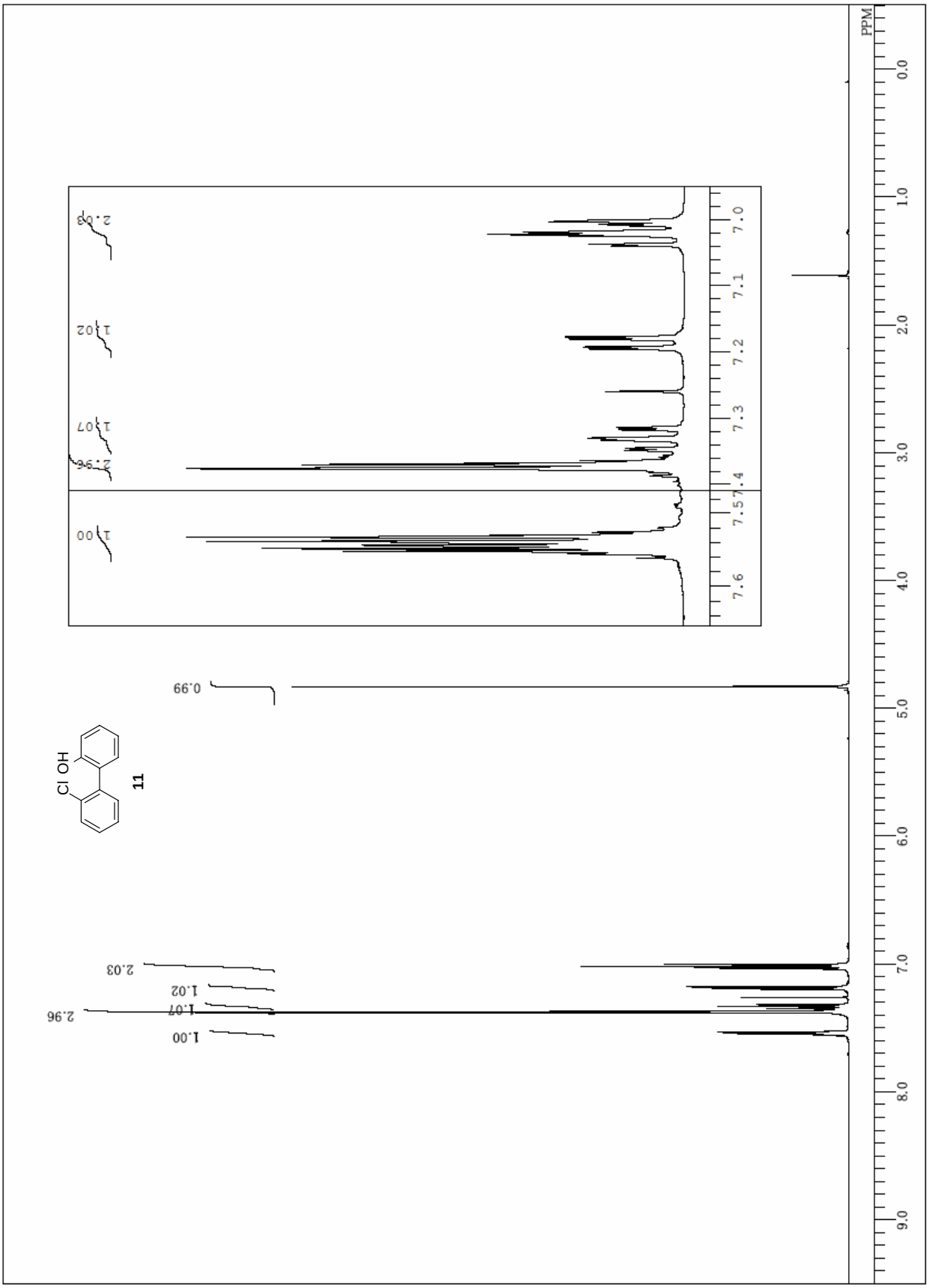


Figure S1. ^{1}H NMR spectrum of **11** ($CDCl_3$, 500 MHz).

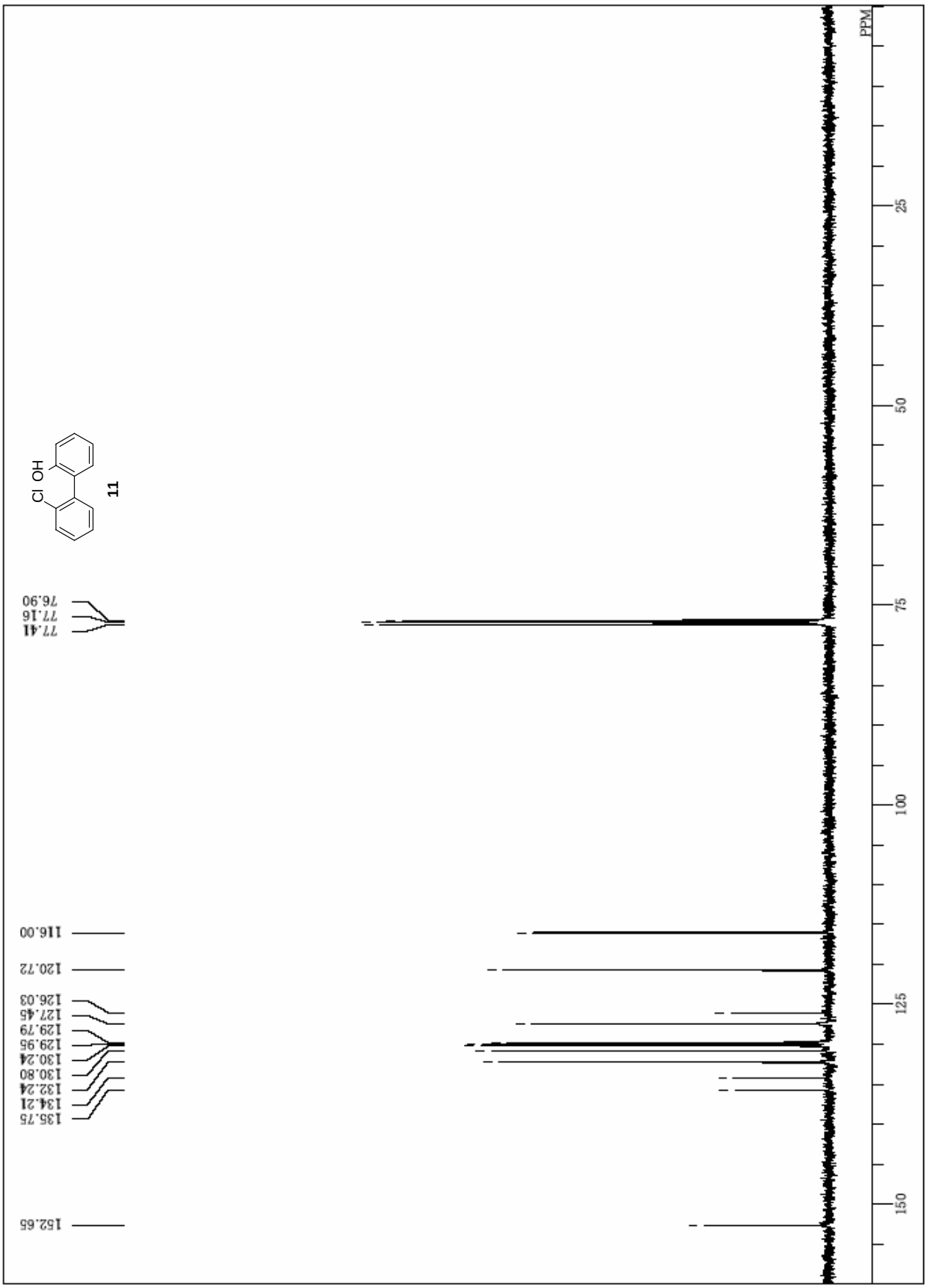


Figure S2. ^{13}C NMR spectrum of **11** ($CDCl_3$, 125 MHz).

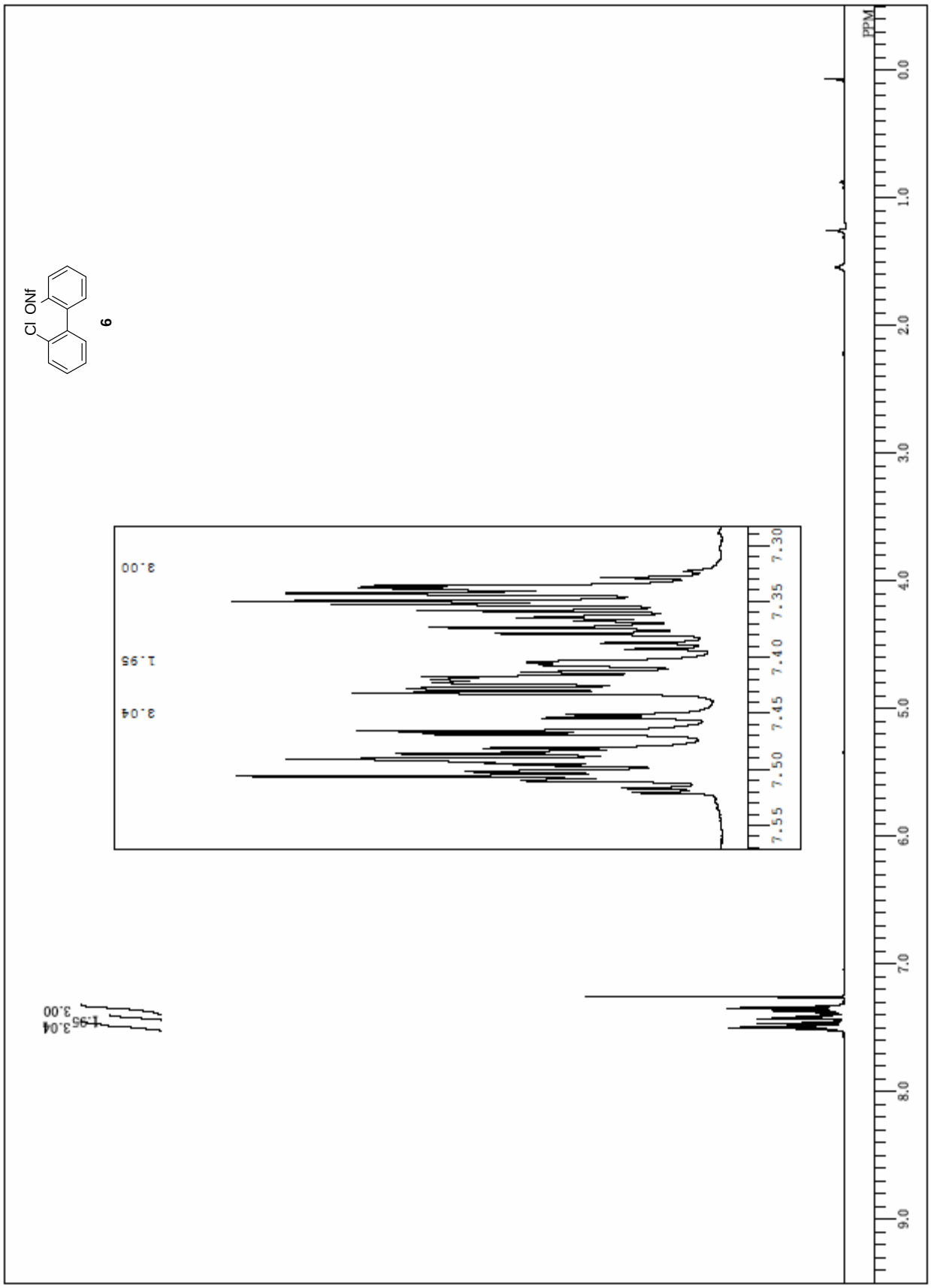


Figure S3. ^{1}H NMR spectrum of **6** ($CDCl_3$, 500 MHz).

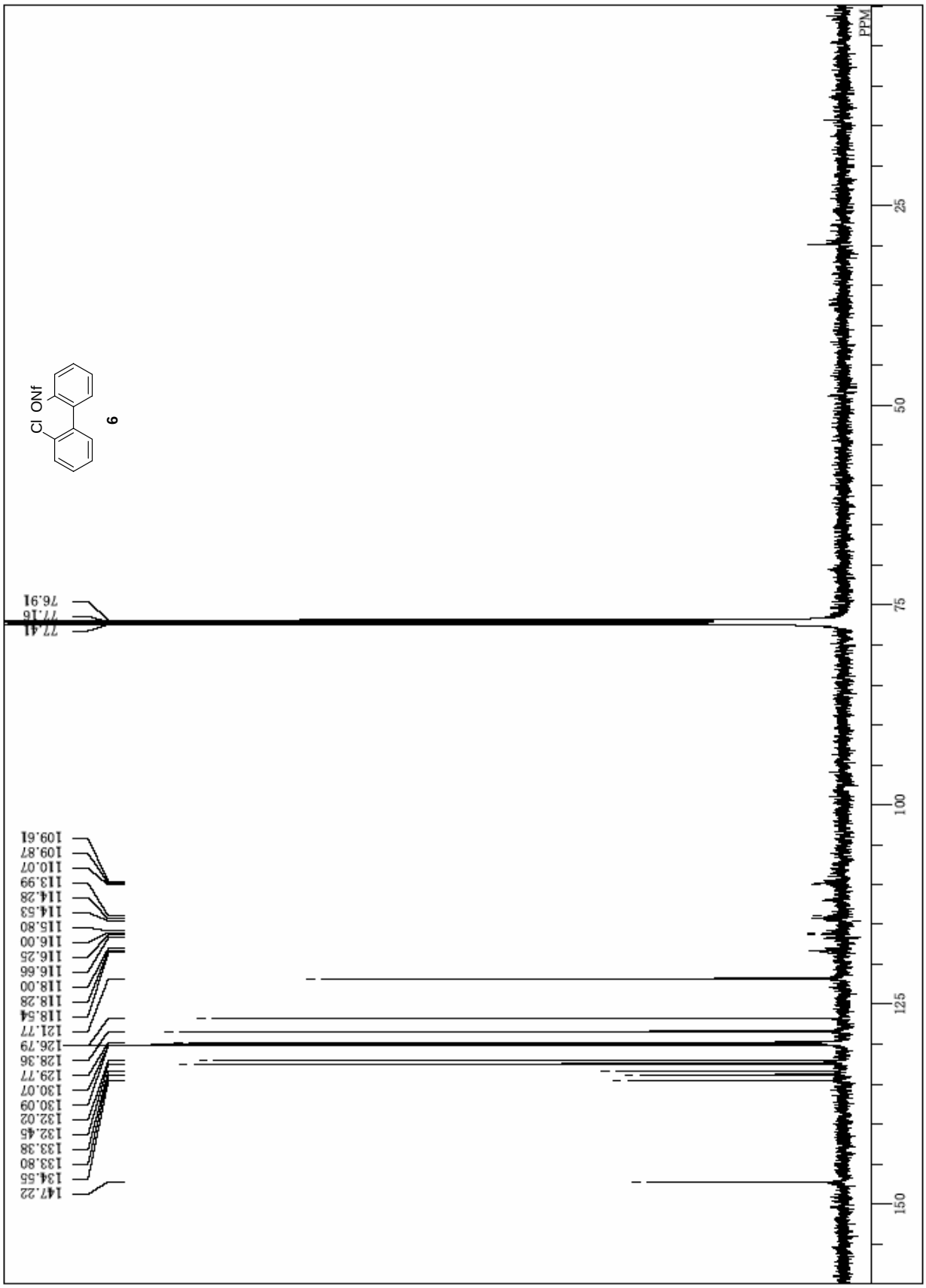


Figure S4. ^{13}C NMR spectrum of **6** ($CDCl_3$, 125 MHz).

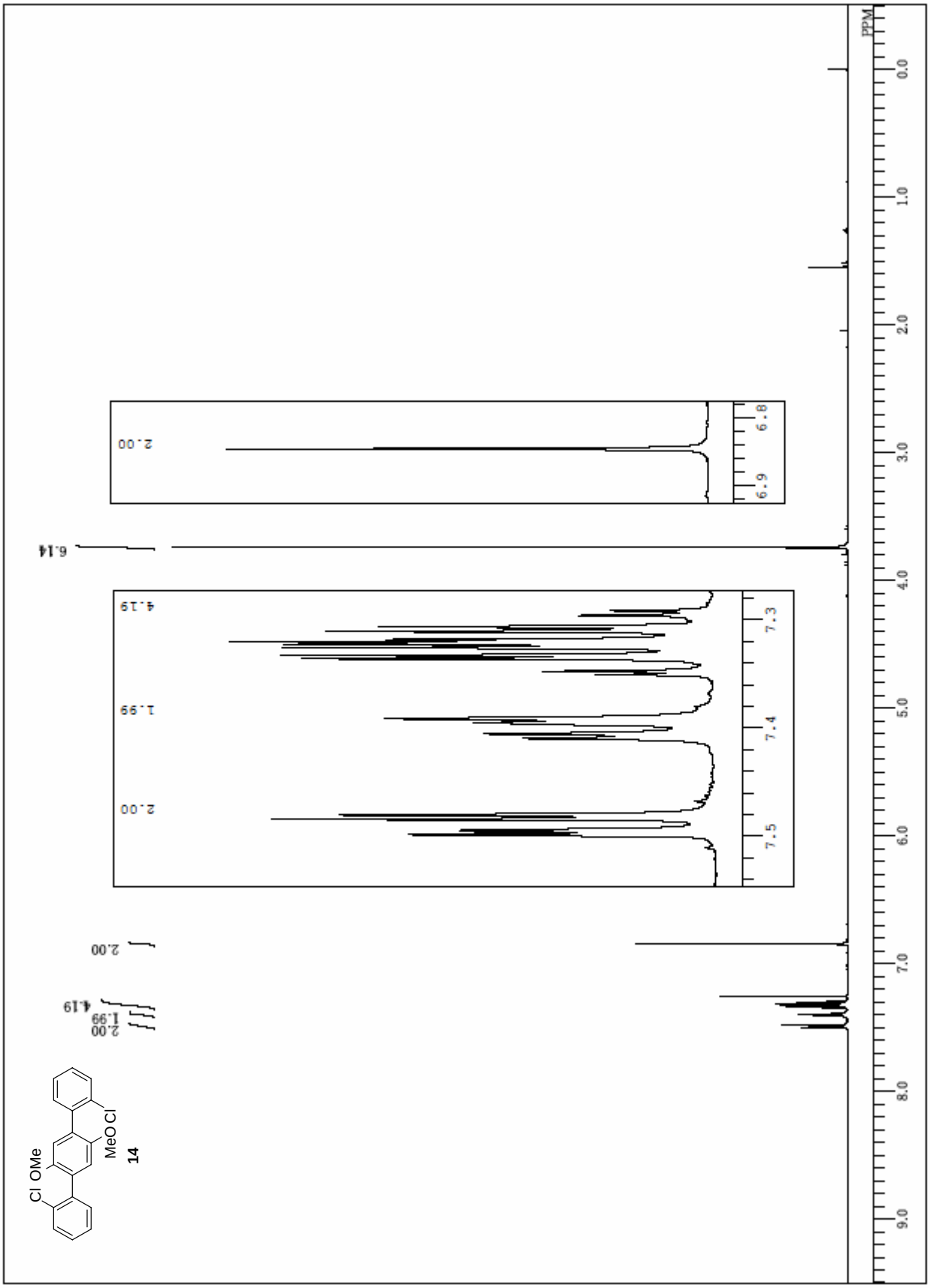


Figure S5. ^{1}H NMR spectrum of **14** ($CDCl_3$, 500 MHz).

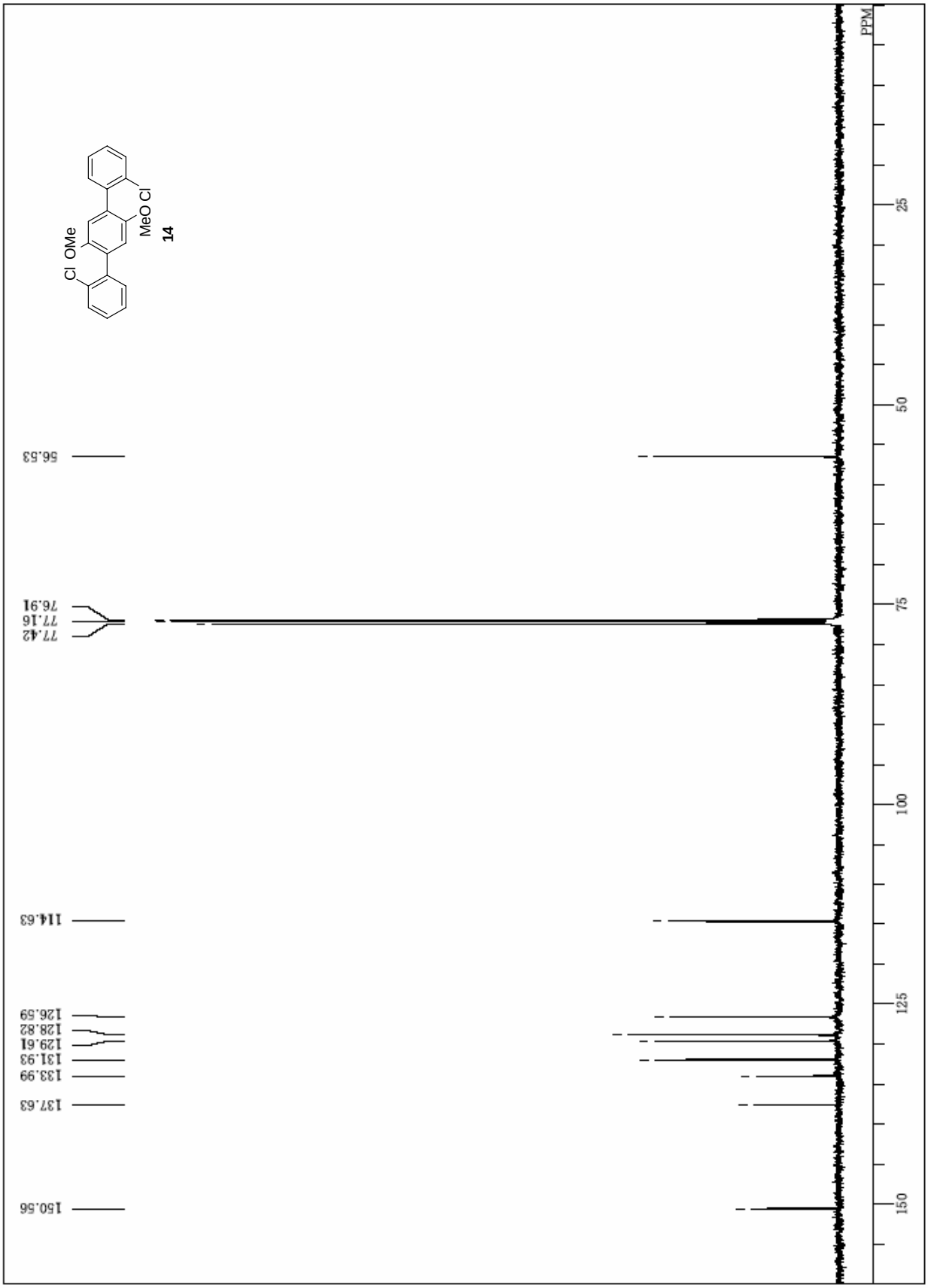


Figure S6. ^{13}C NMR spectrum of **14** ($CDCl_3$, 125 MHz).

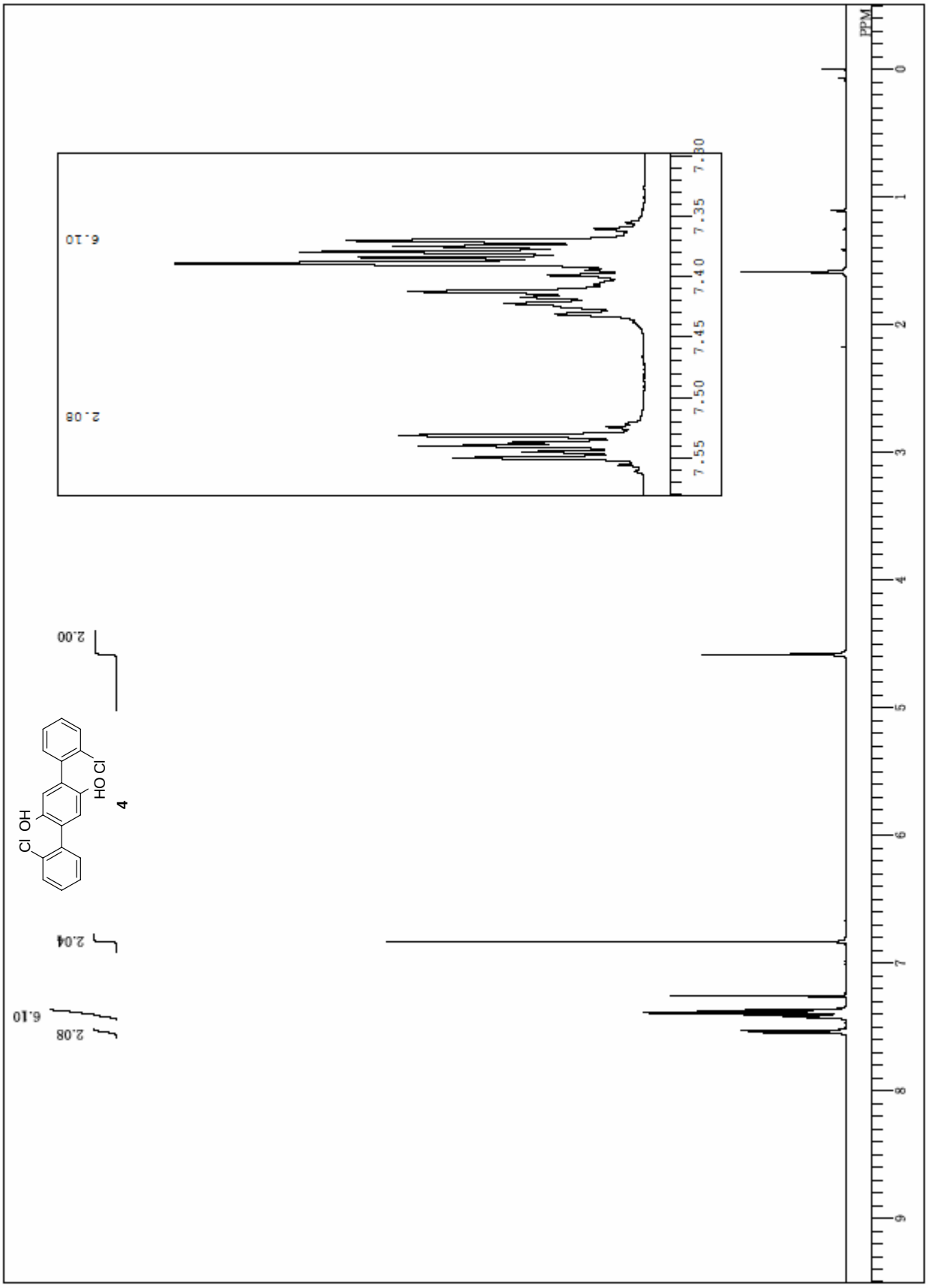


Figure S7. ^{1}H NMR spectrum of **4** ($CDCl_3$, 500 MHz).

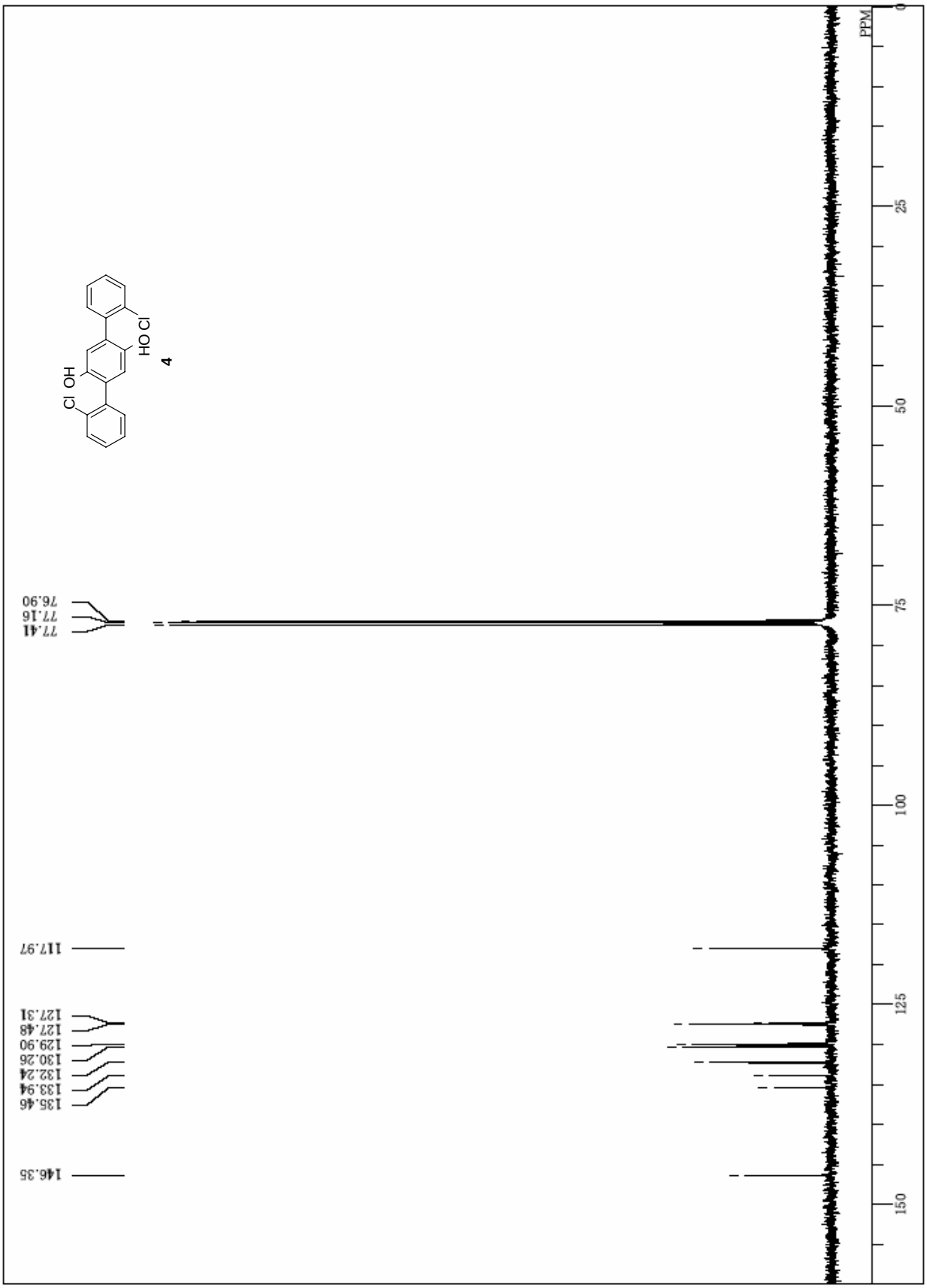


Figure S8. ^{13}C NMR spectrum of **4** ($CDCl_3$, 125 MHz).

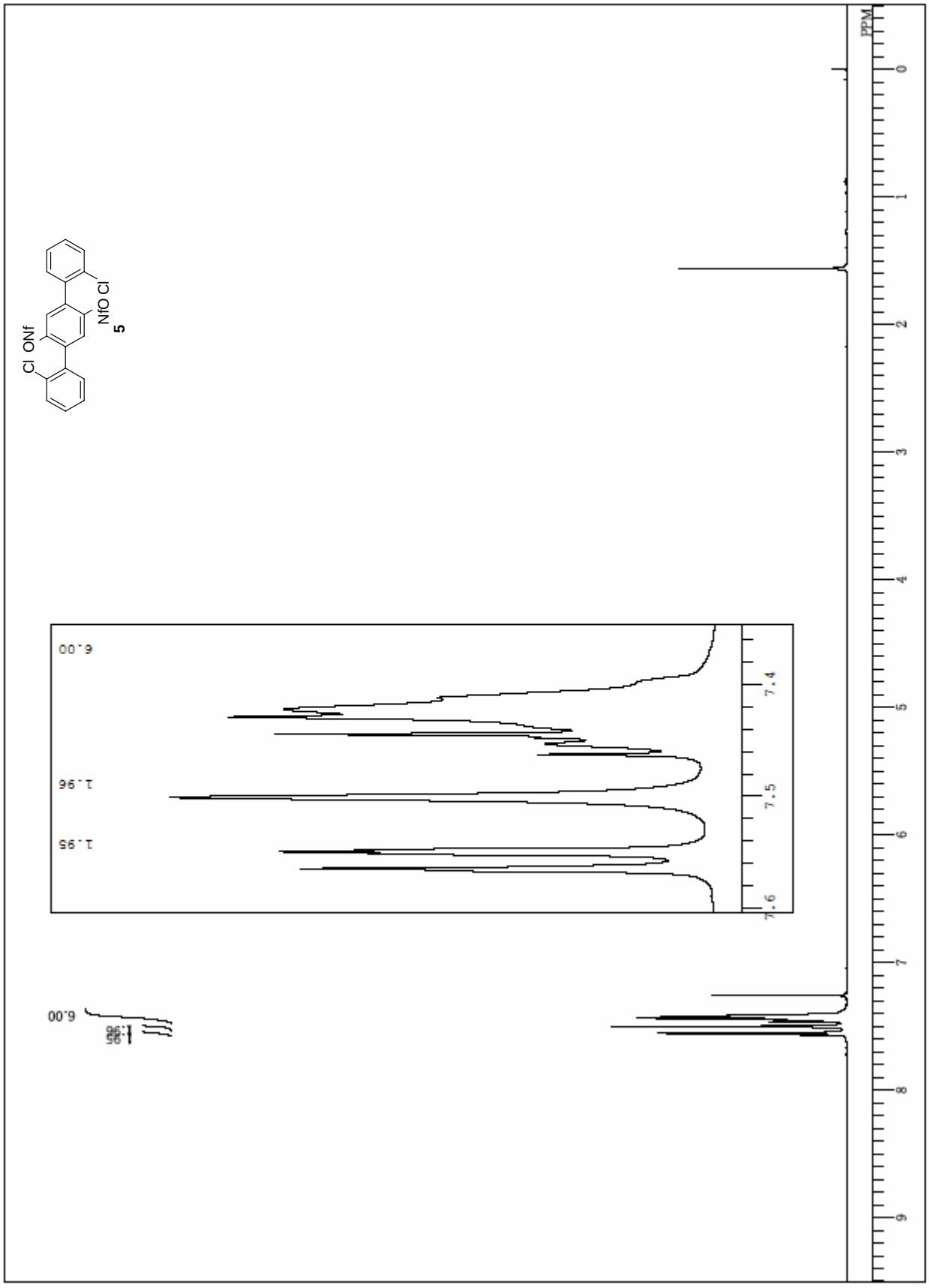


Figure S9. ^{1}H NMR spectrum of **5** ($CDCl_3$, 500 MHz).

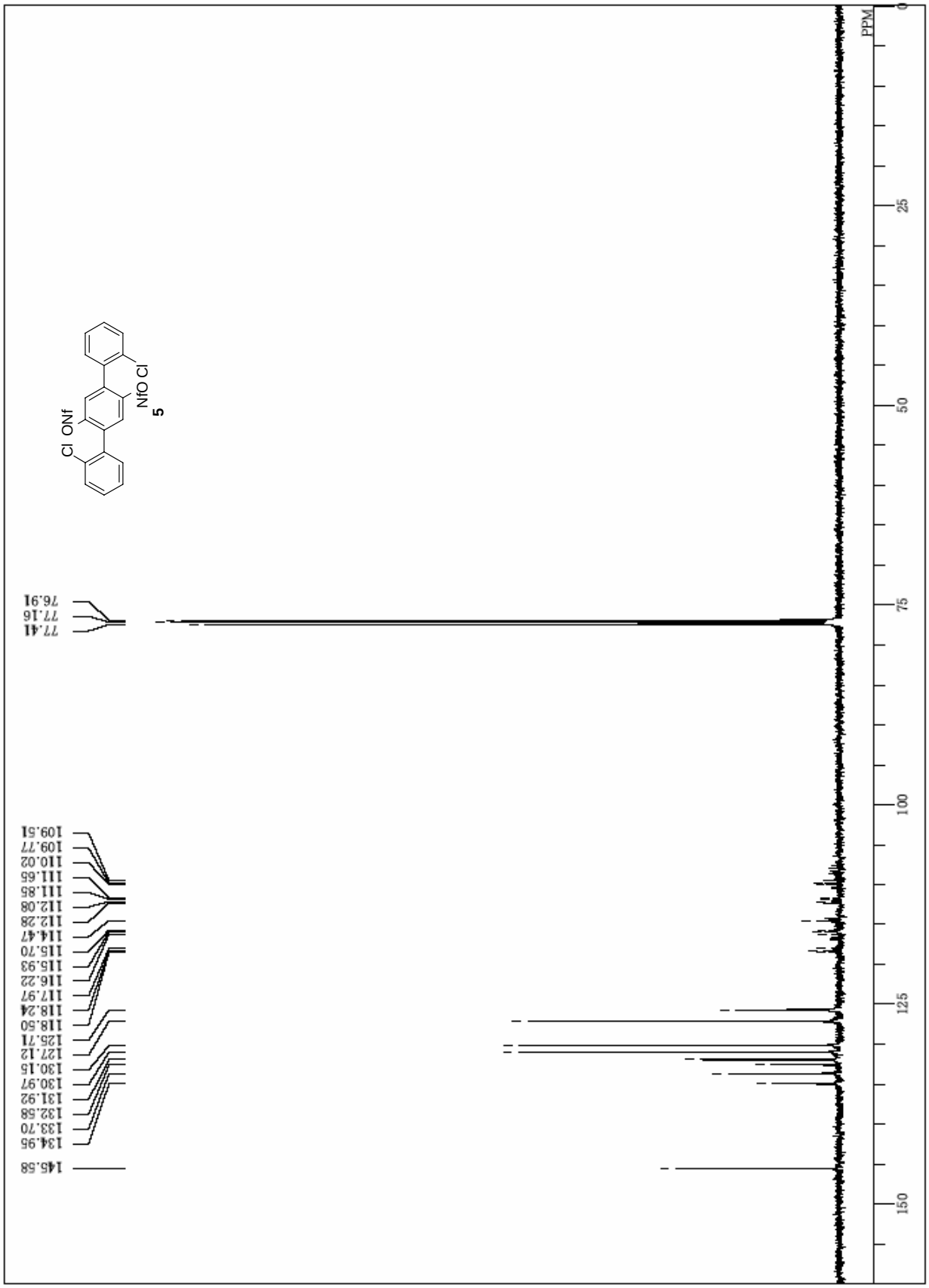


Figure S10. ^{13}C NMR spectrum of **5** ($CDCl_3$, 125 MHz).

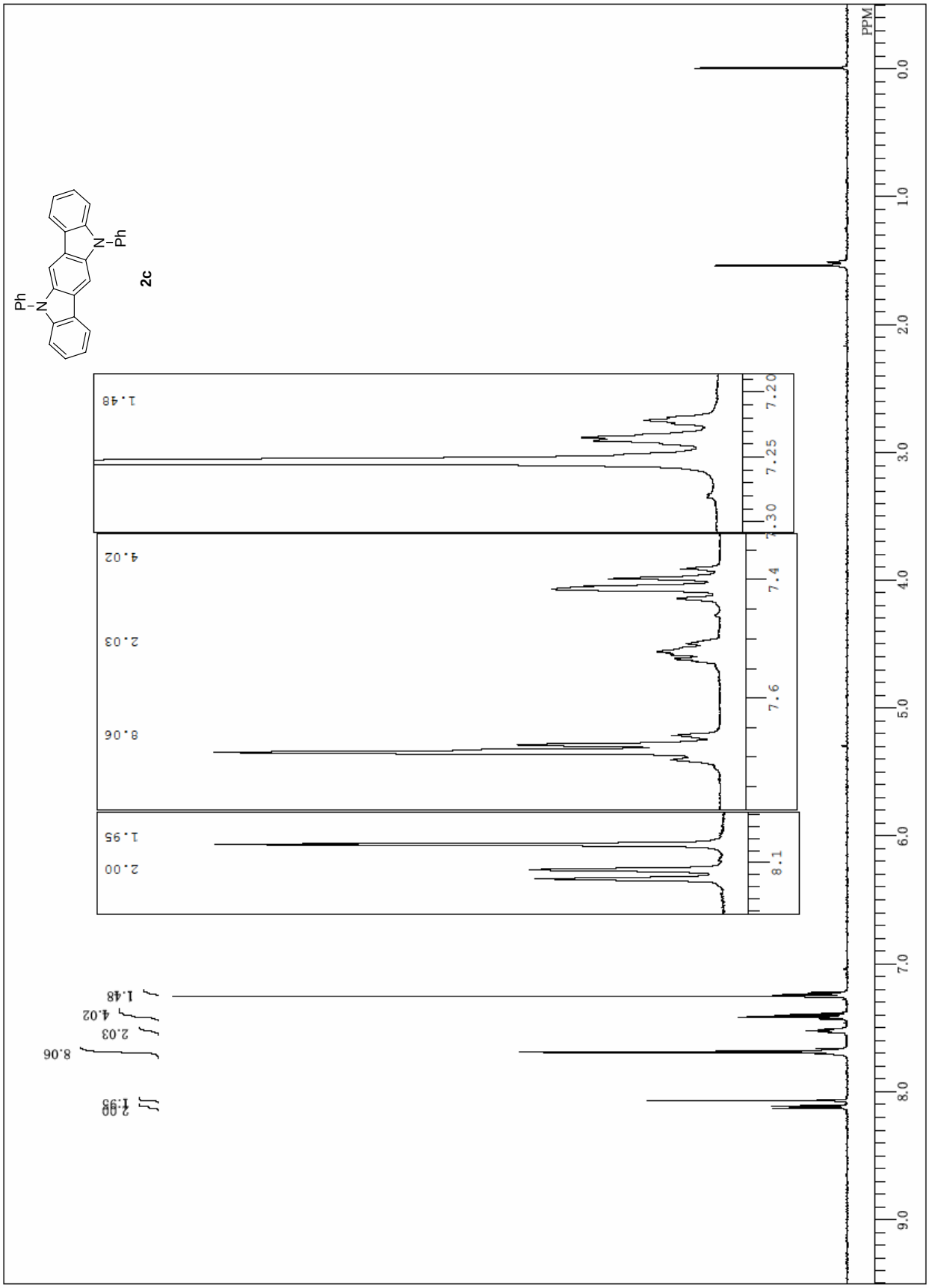


Figure S11. ^{1}H NMR spectrum of **2c** ($CDCl_3$, 500 MHz).

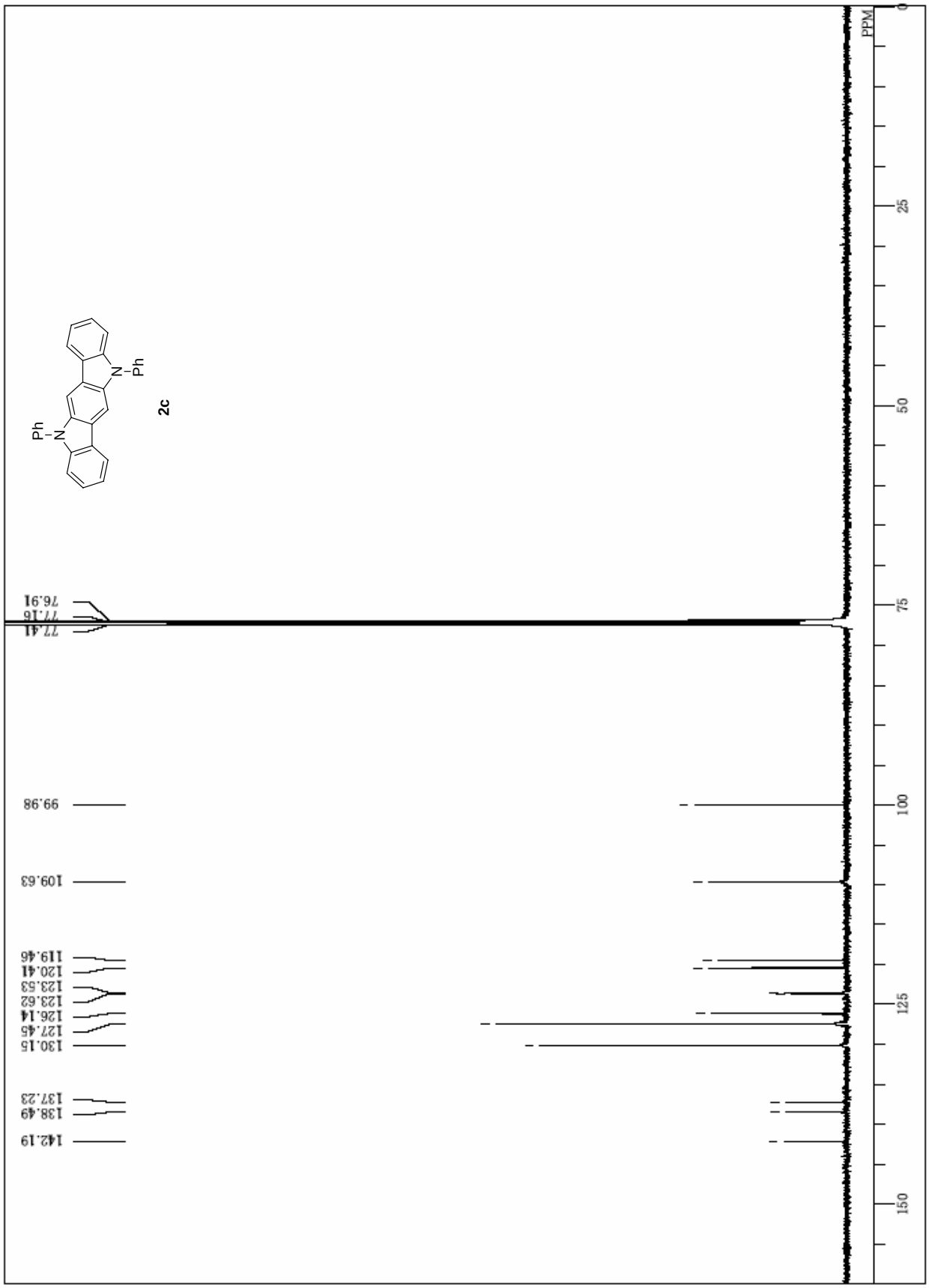


Figure S12. ^{13}C NMR spectrum of **2c** ($CDCl_3$, 125 MHz).

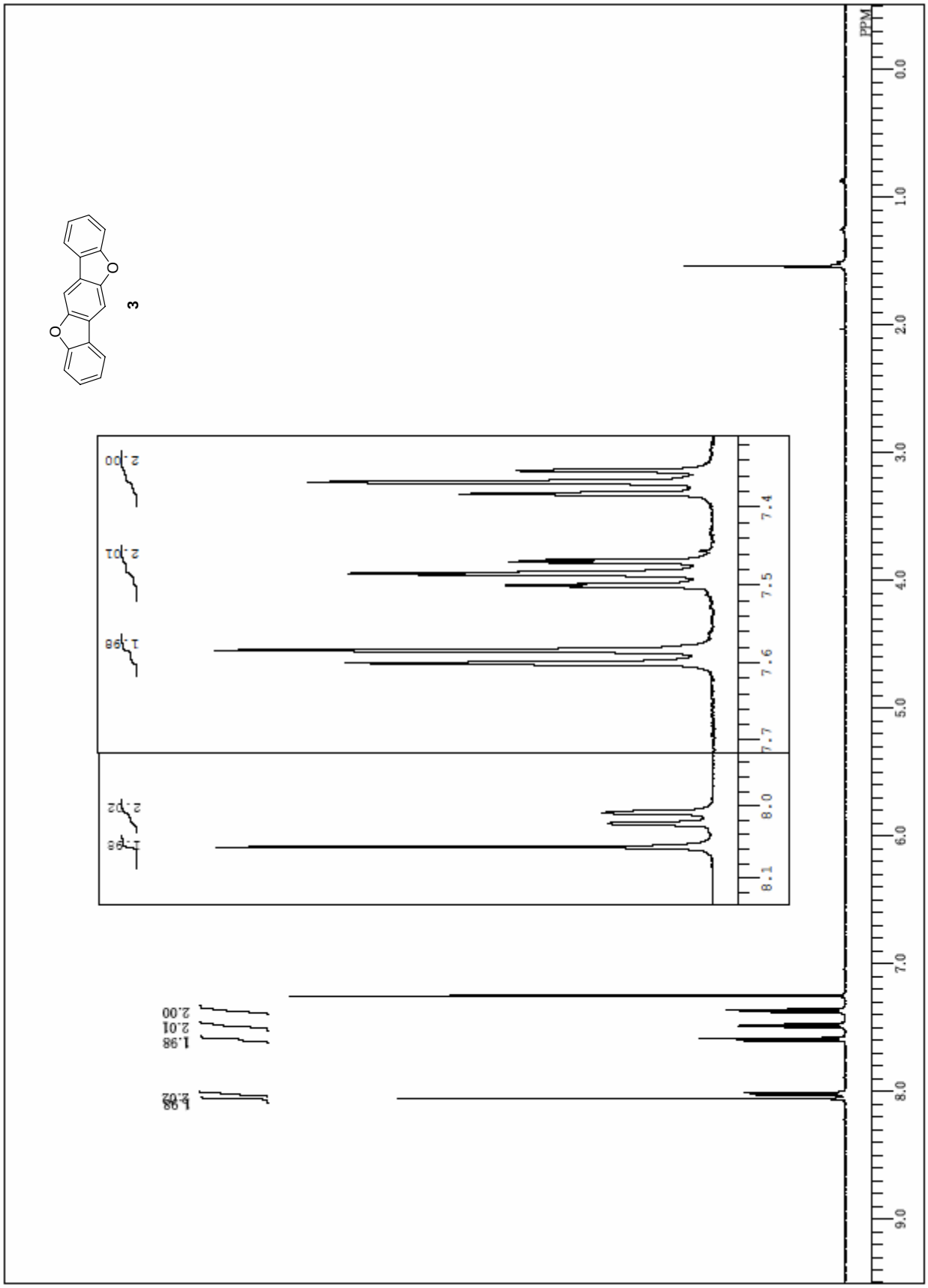


Figure S13. ^{1}H NMR spectrum of **3** ($CDCl_3$, 500 MHz).

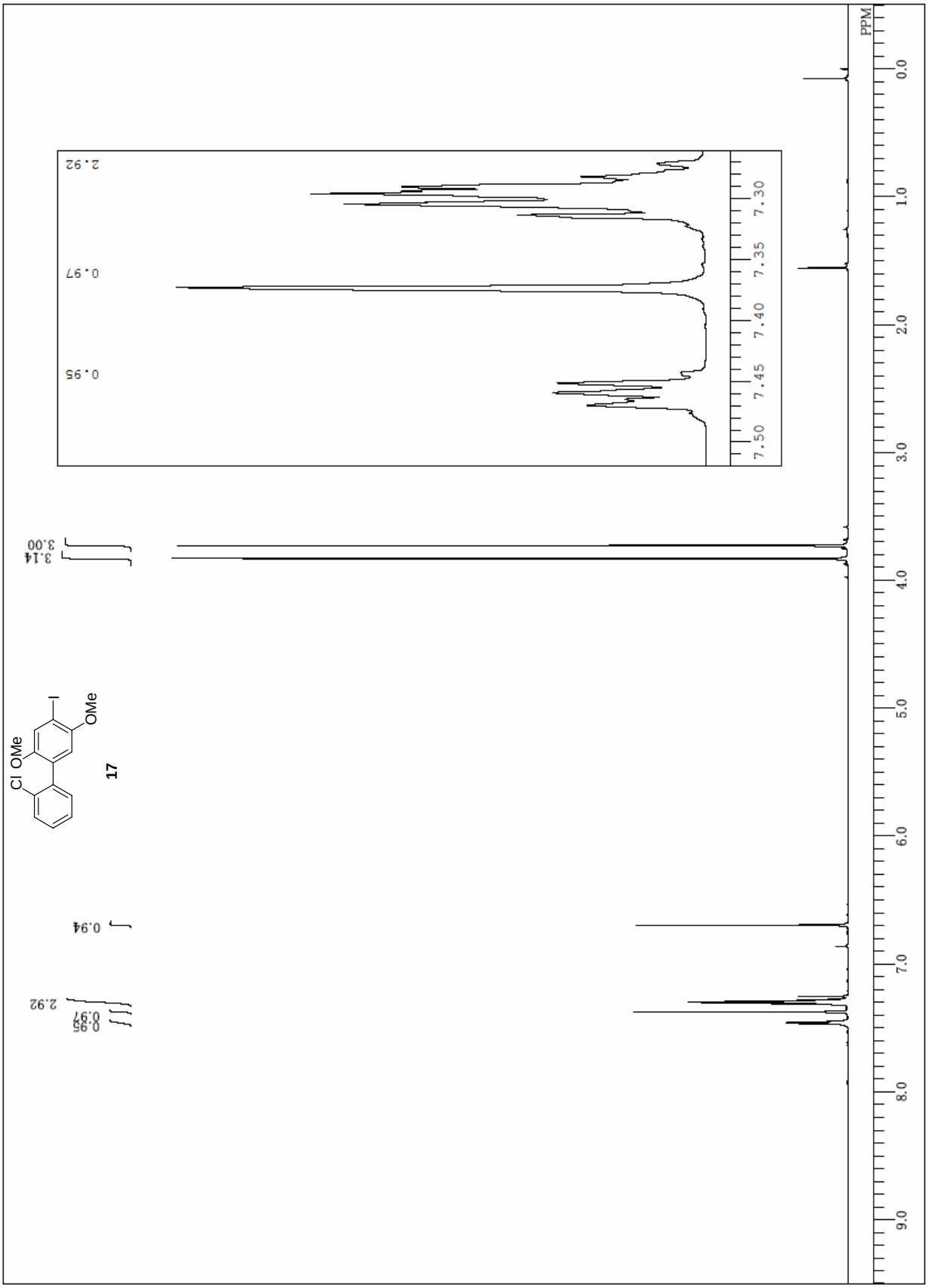


Figure S14. ^{1}H NMR spectrum of **17** ($CDCl_3$, 500 MHz).

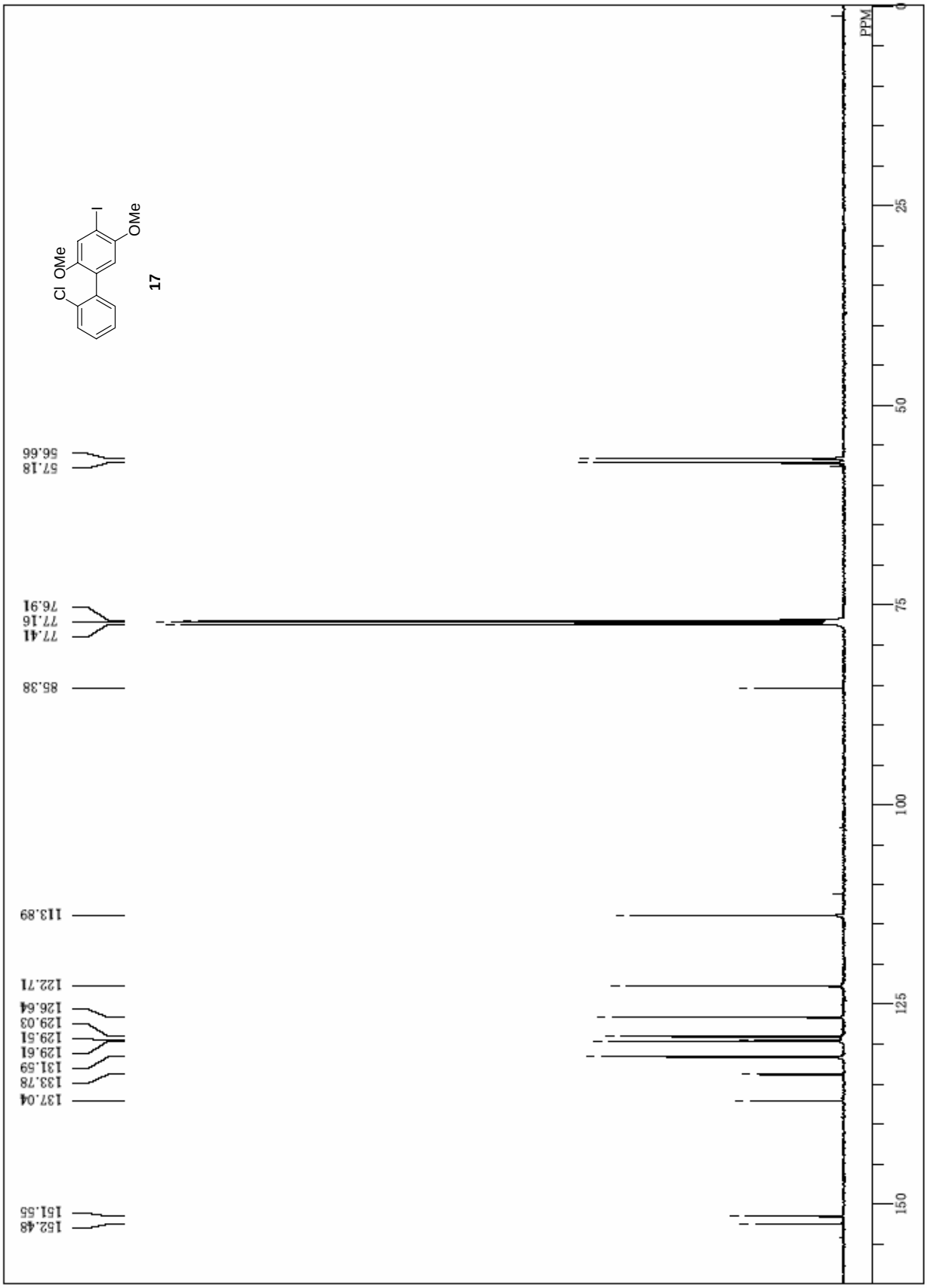


Figure S15. ^{13}C NMR spectrum of **17** ($CDCl_3$, 125 MHz).

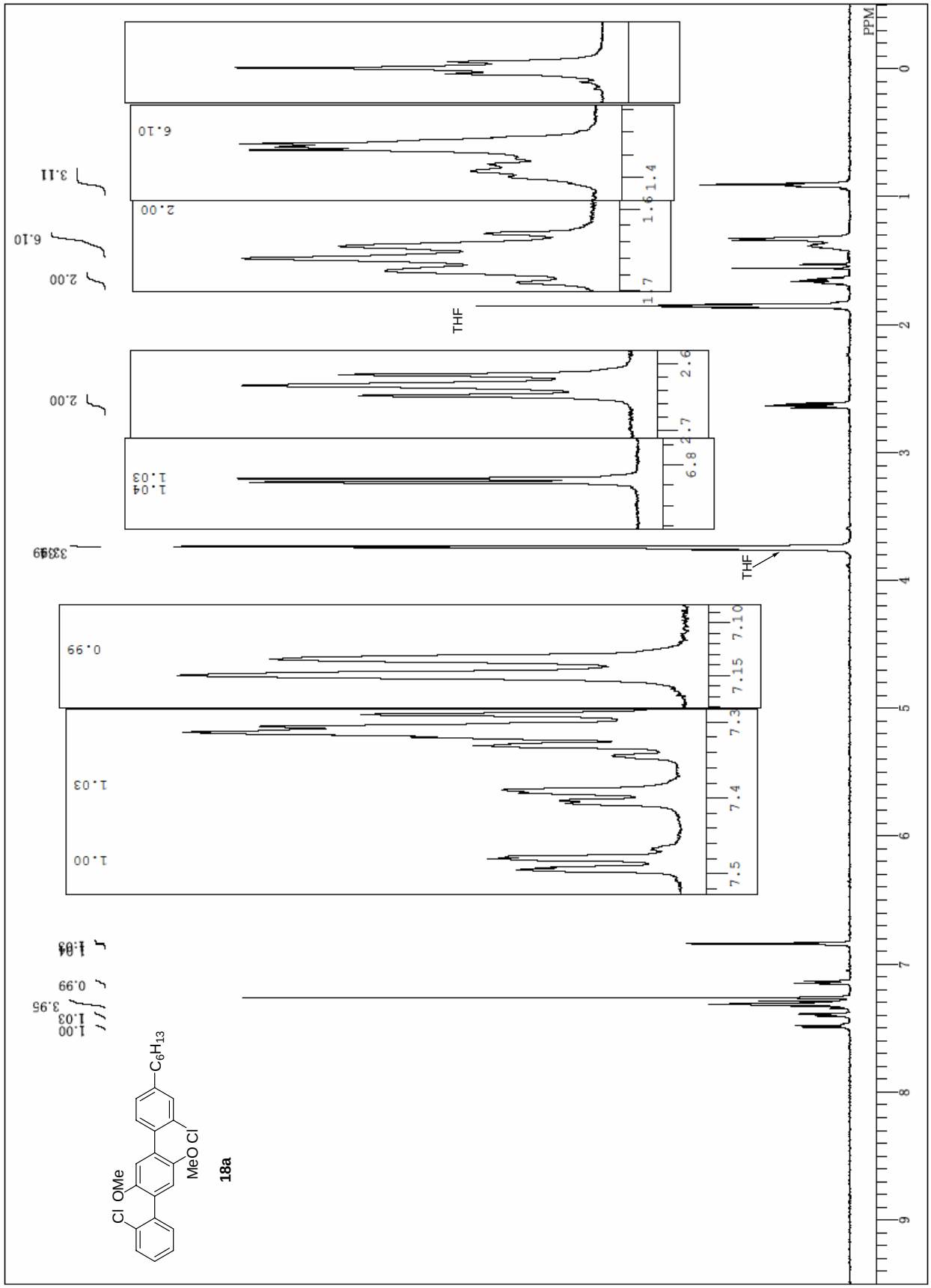


Figure S16. ^{1}H NMR spectrum of **18a** ($CDCl_3$, 500 MHz).

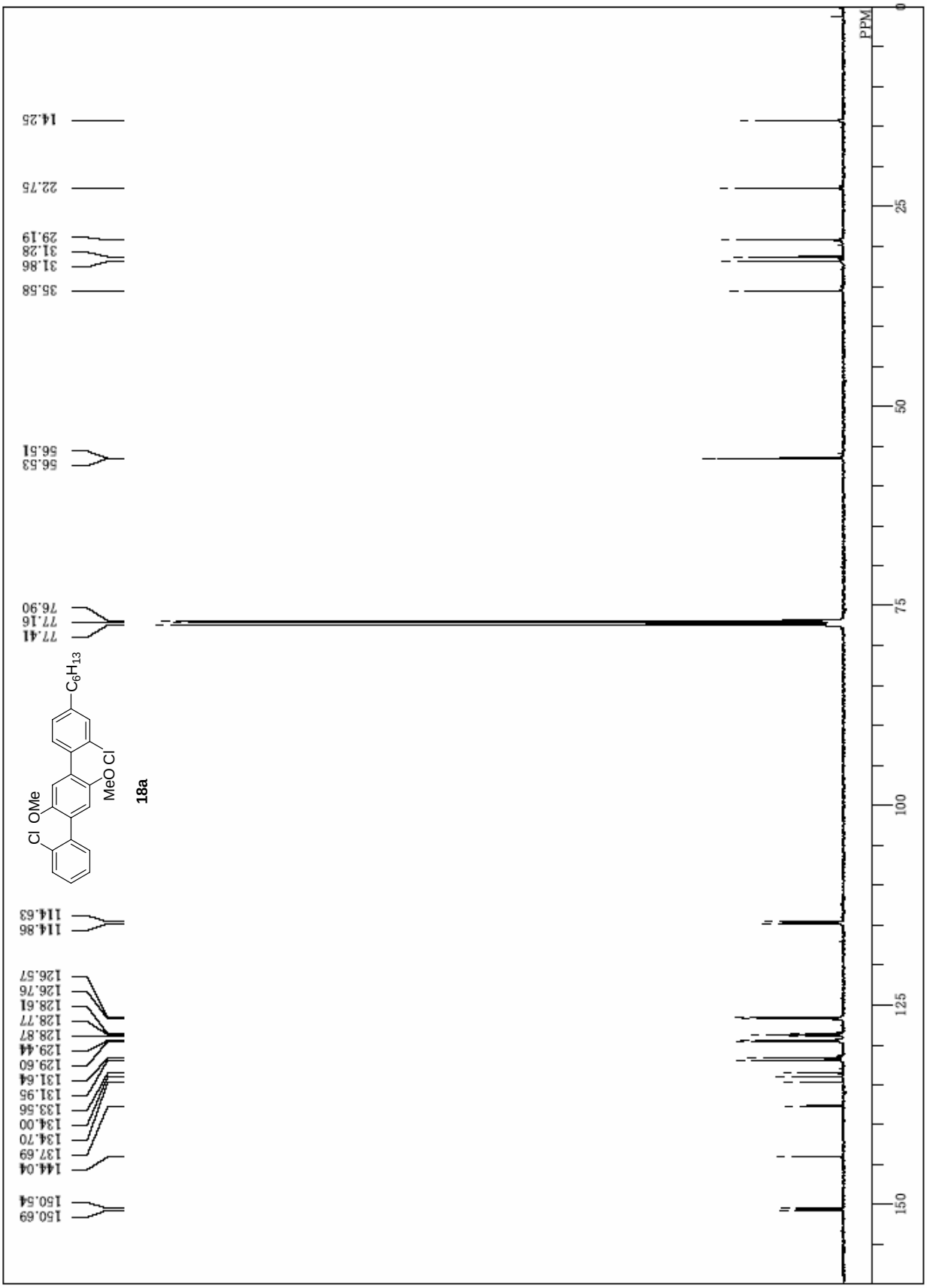


Figure S17. ^{13}C NMR spectrum of **18a** ($CDCl_3$, 125 MHz).

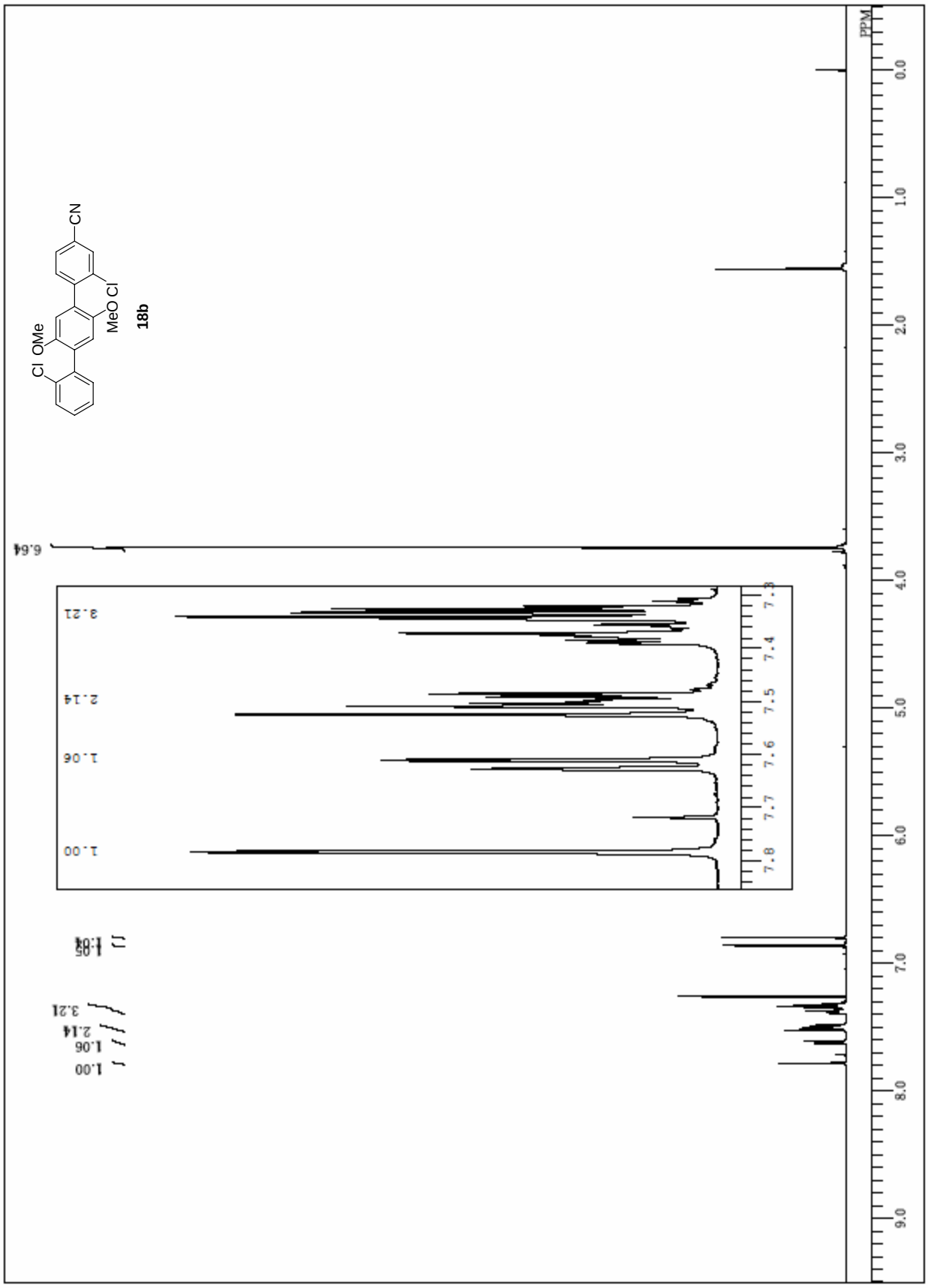


Figure S18. ^{1}H NMR spectrum of **18b** ($CDCl_3$, 500 MHz).

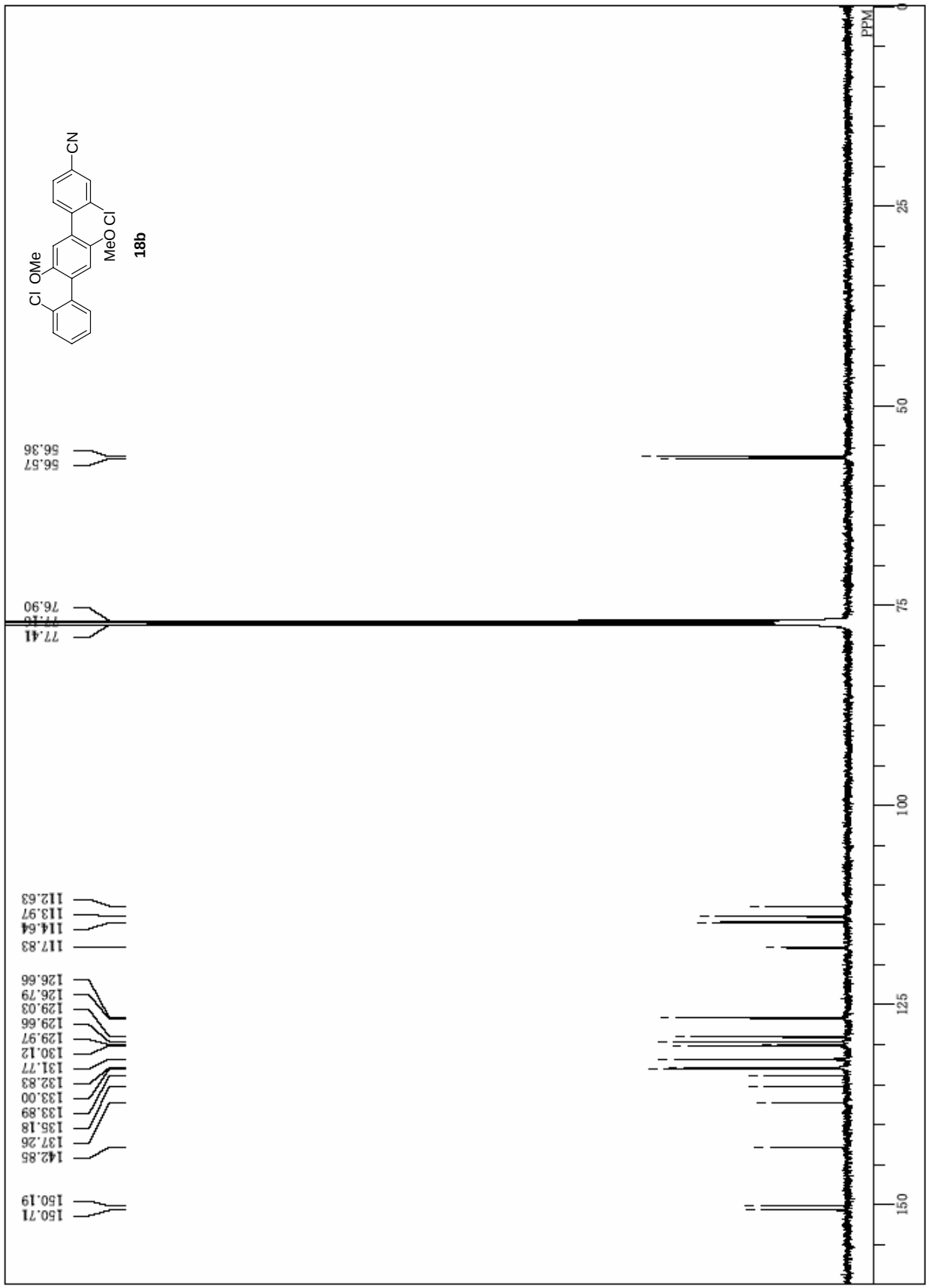


Figure S19. ^{13}C NMR spectrum of **18b** ($CDCl_3$, 125 MHz).

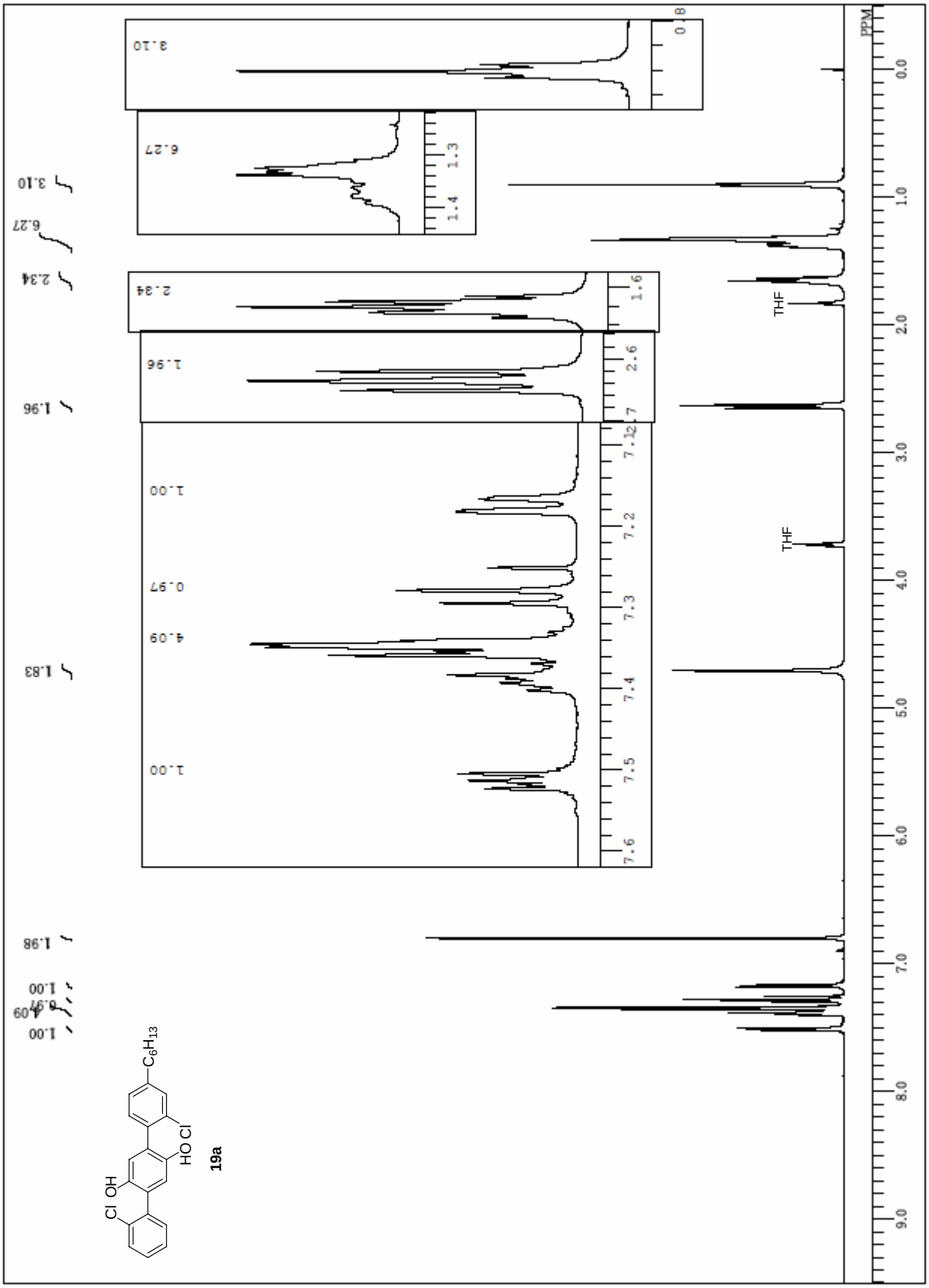


Figure S20. ^{1}H NMR spectrum of **19a** ($CDCl_3$, 500 MHz).

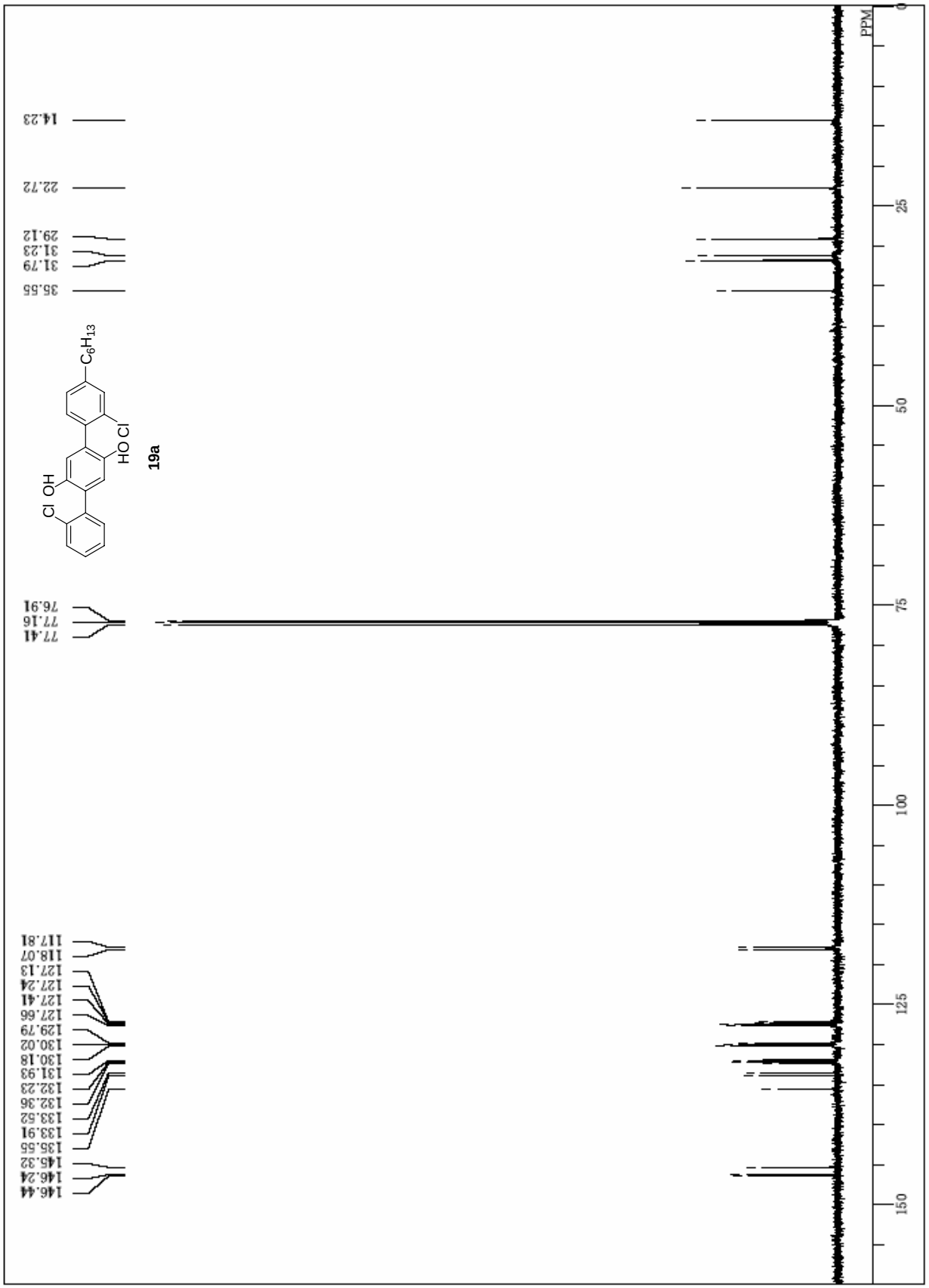


Figure S21. ^{13}C NMR spectrum of **19a** ($CDCl_3$, 125 MHz).

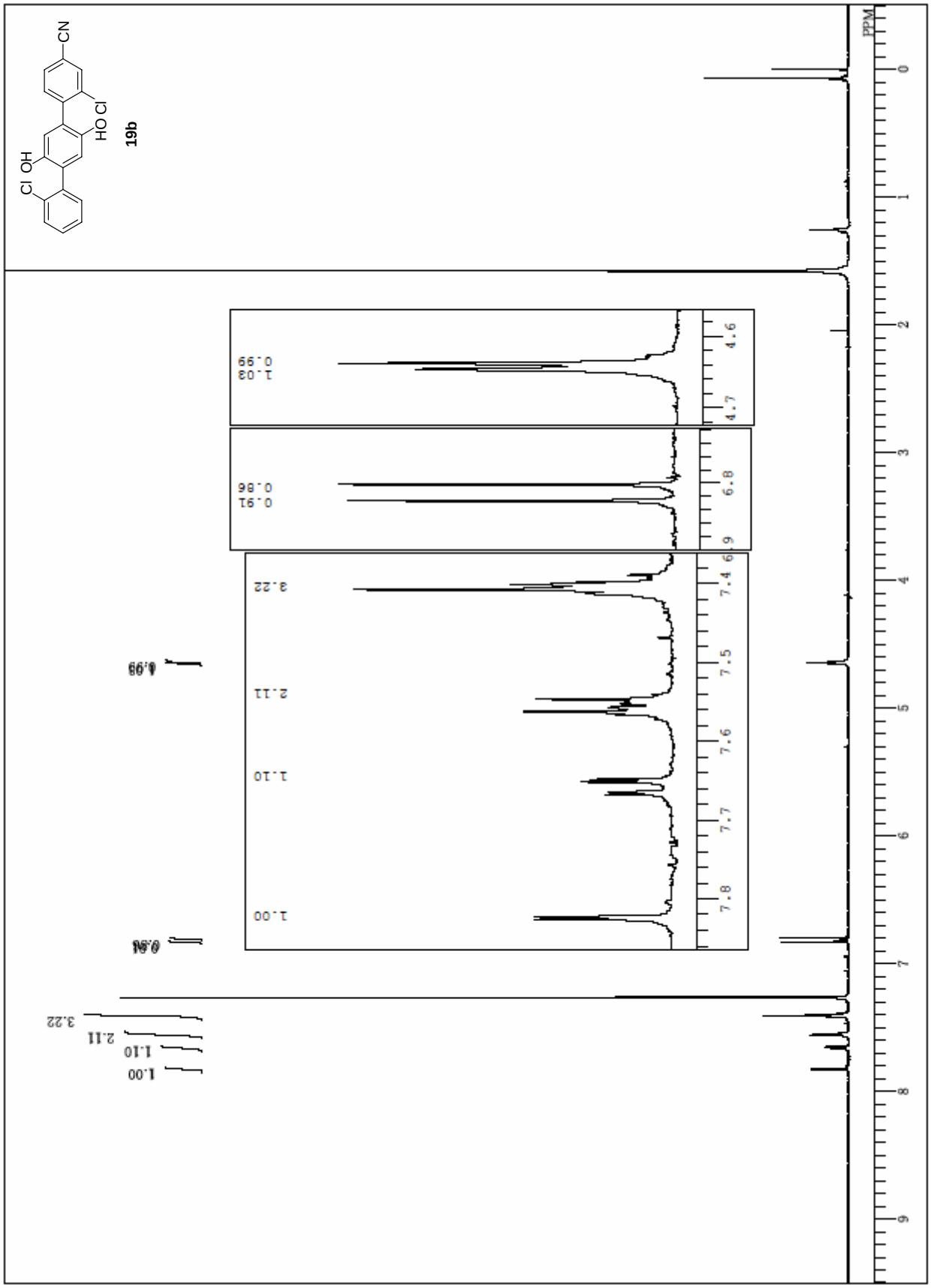


Figure S22. ^{1}H NMR spectrum of **19b** ($CDCl_3$, 500 MHz).

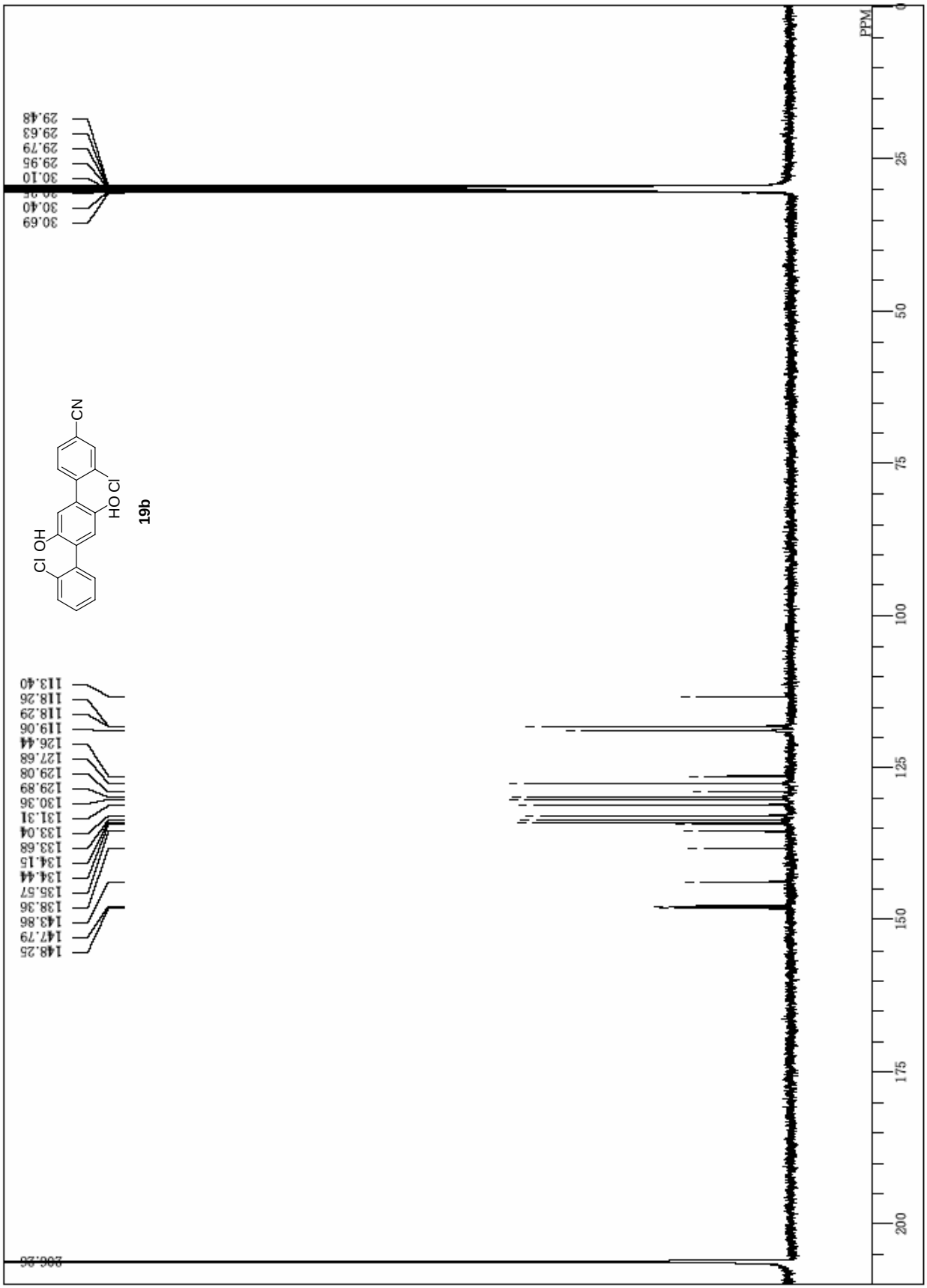


Figure S23. ^{13}C NMR spectrum of **19b** (acetone-d^6, 125 MHz).

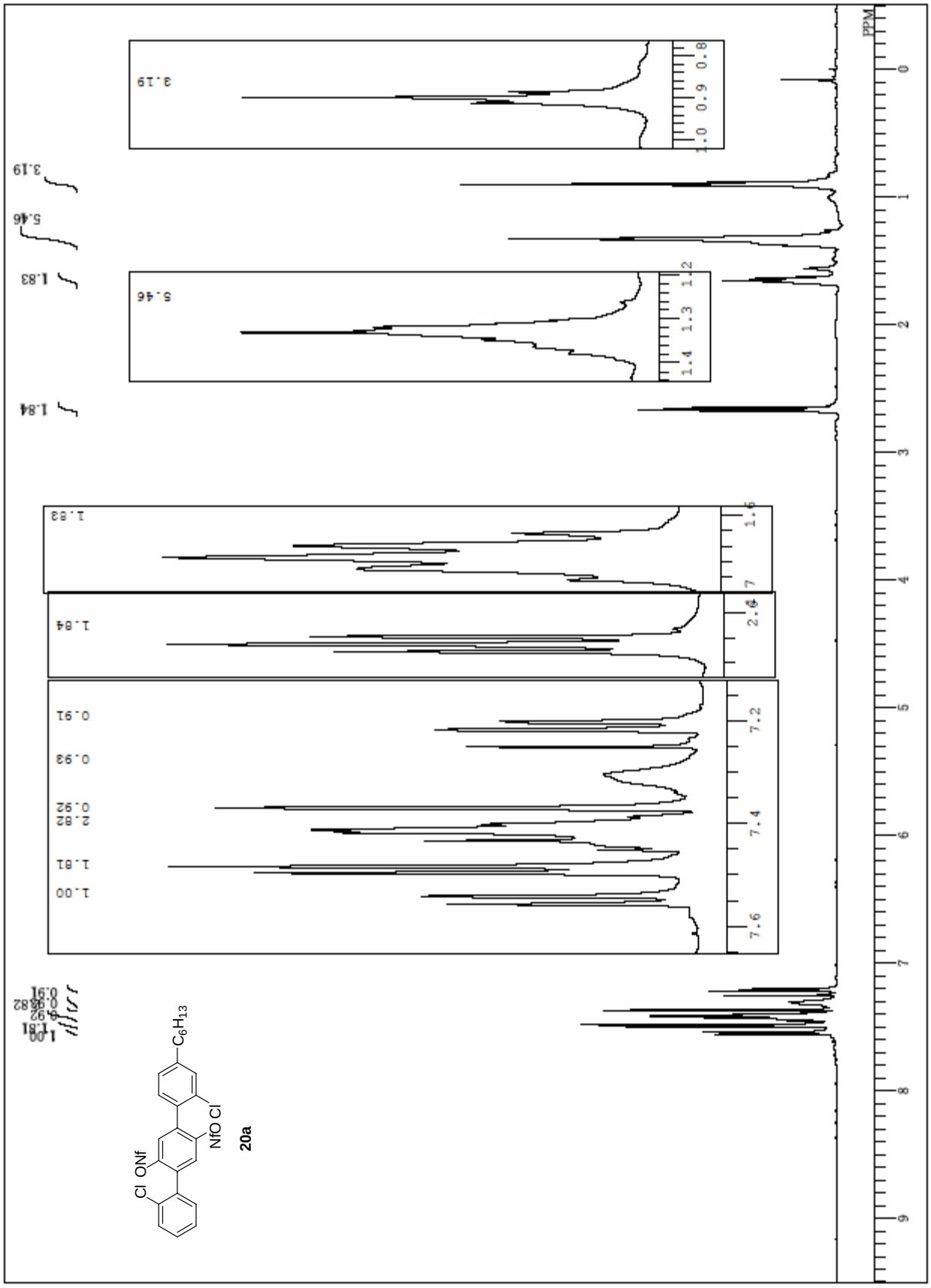


Figure S24. ^{1}H NMR spectrum of **20a** ($CDCl_3$, 500 MHz).

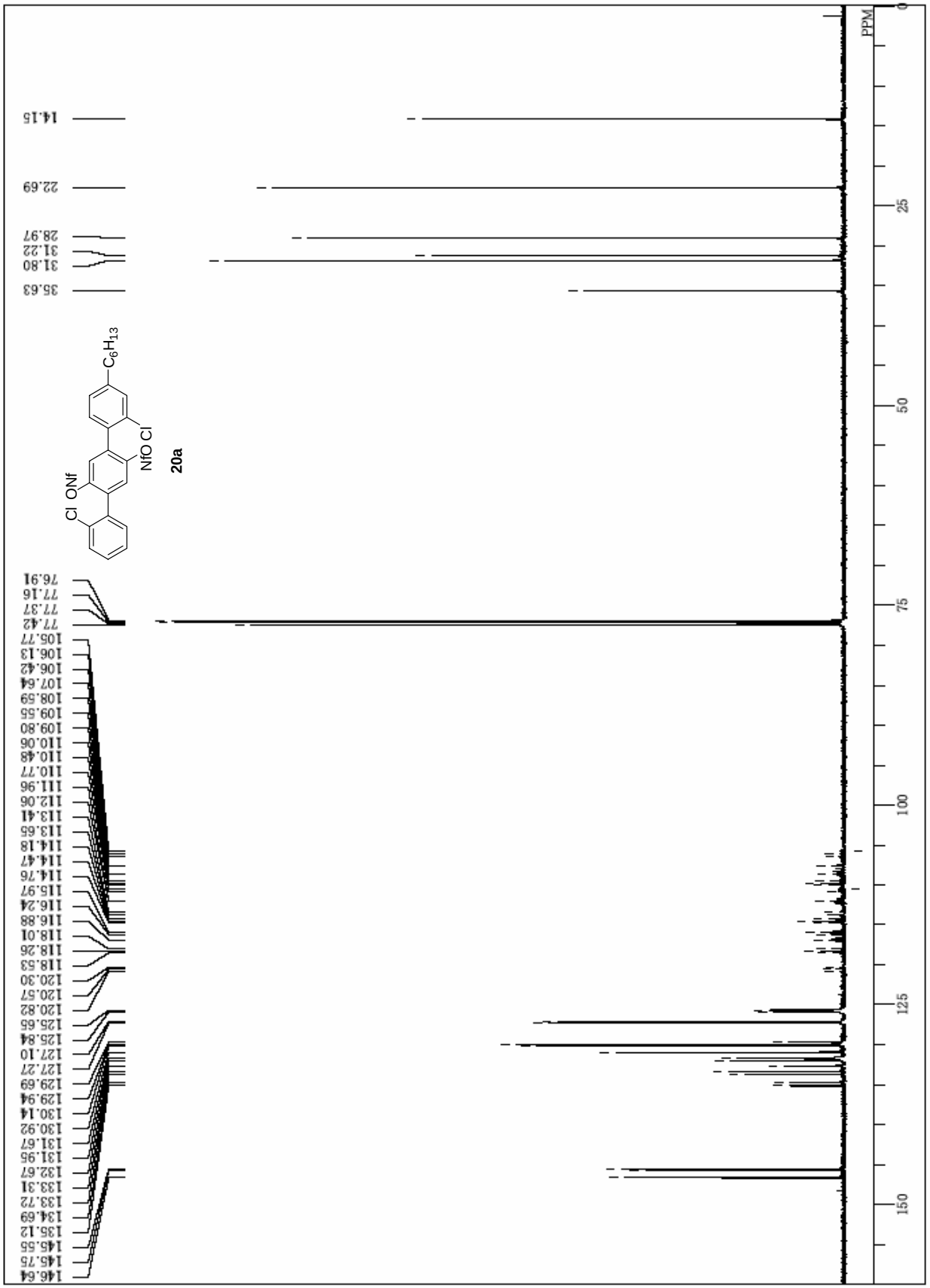


Figure S25. ^{13}C NMR spectrum of **20a** ($CDCl_3$, 125 MHz).

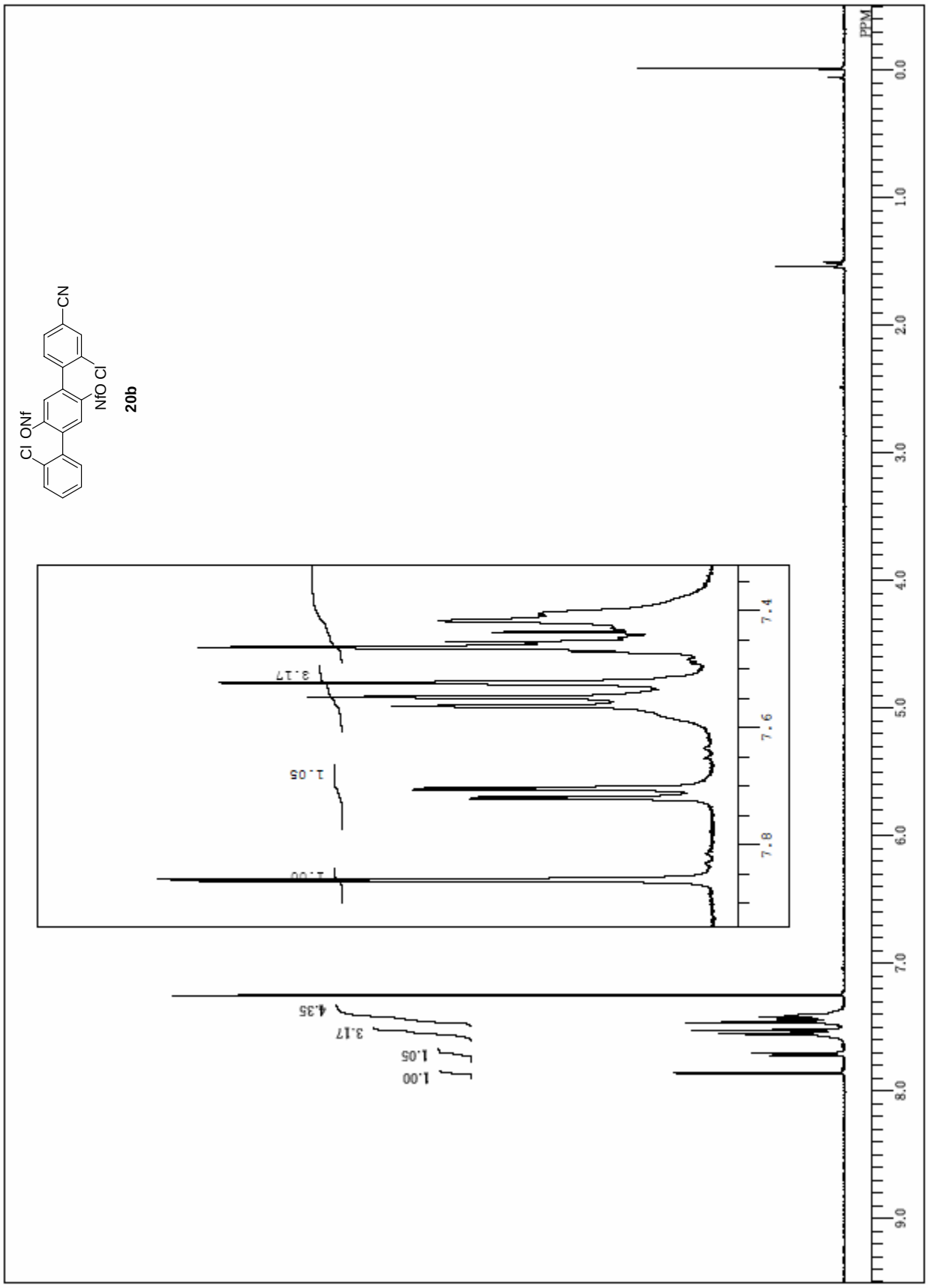


Figure S26. ^{1}H NMR spectrum of **20b** ($CDCl_3$, 500 MHz).

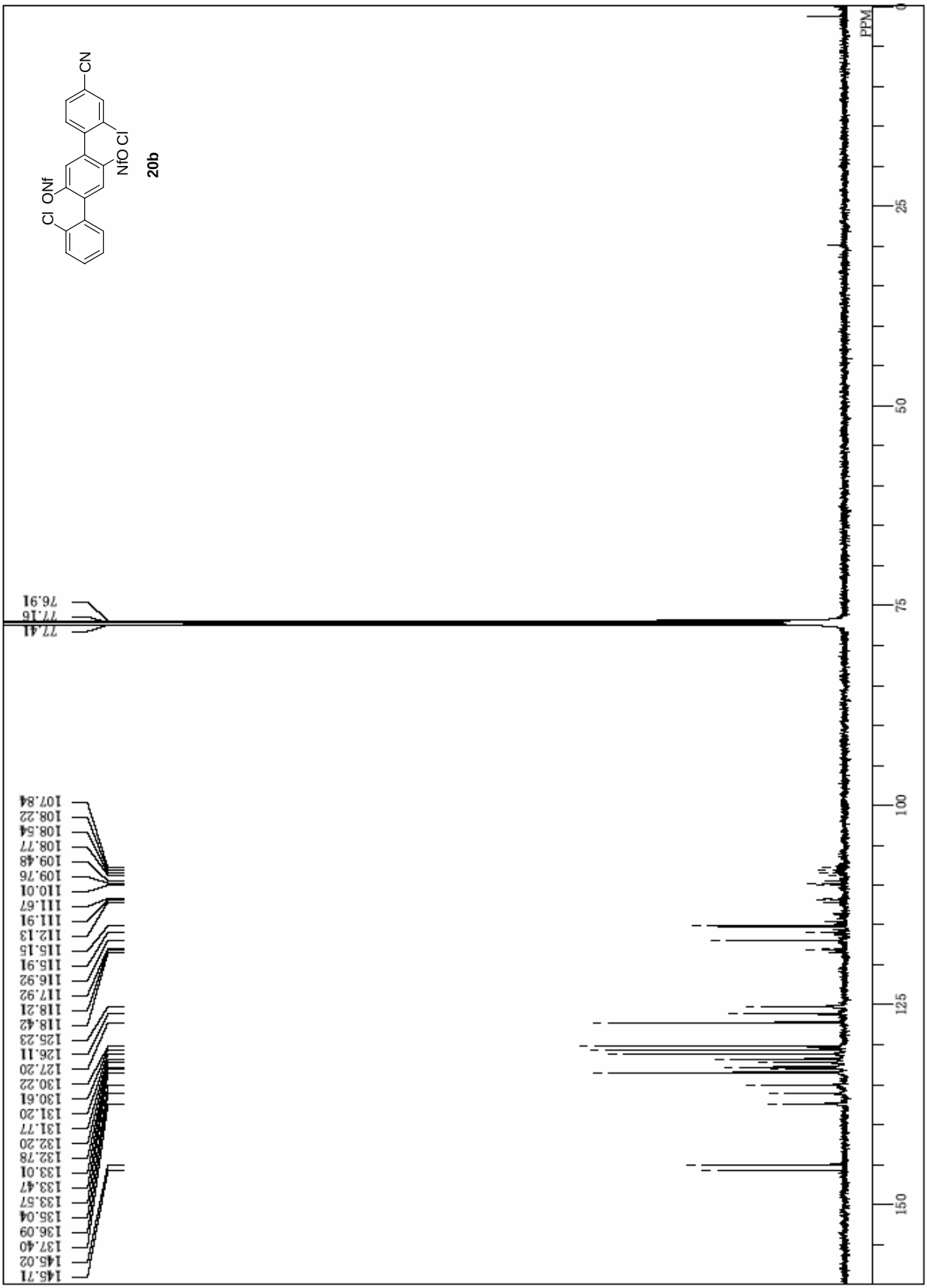


Figure S27. ^{13}C NMR spectrum of **20b** ($CDCl_3$, 125 MHz).

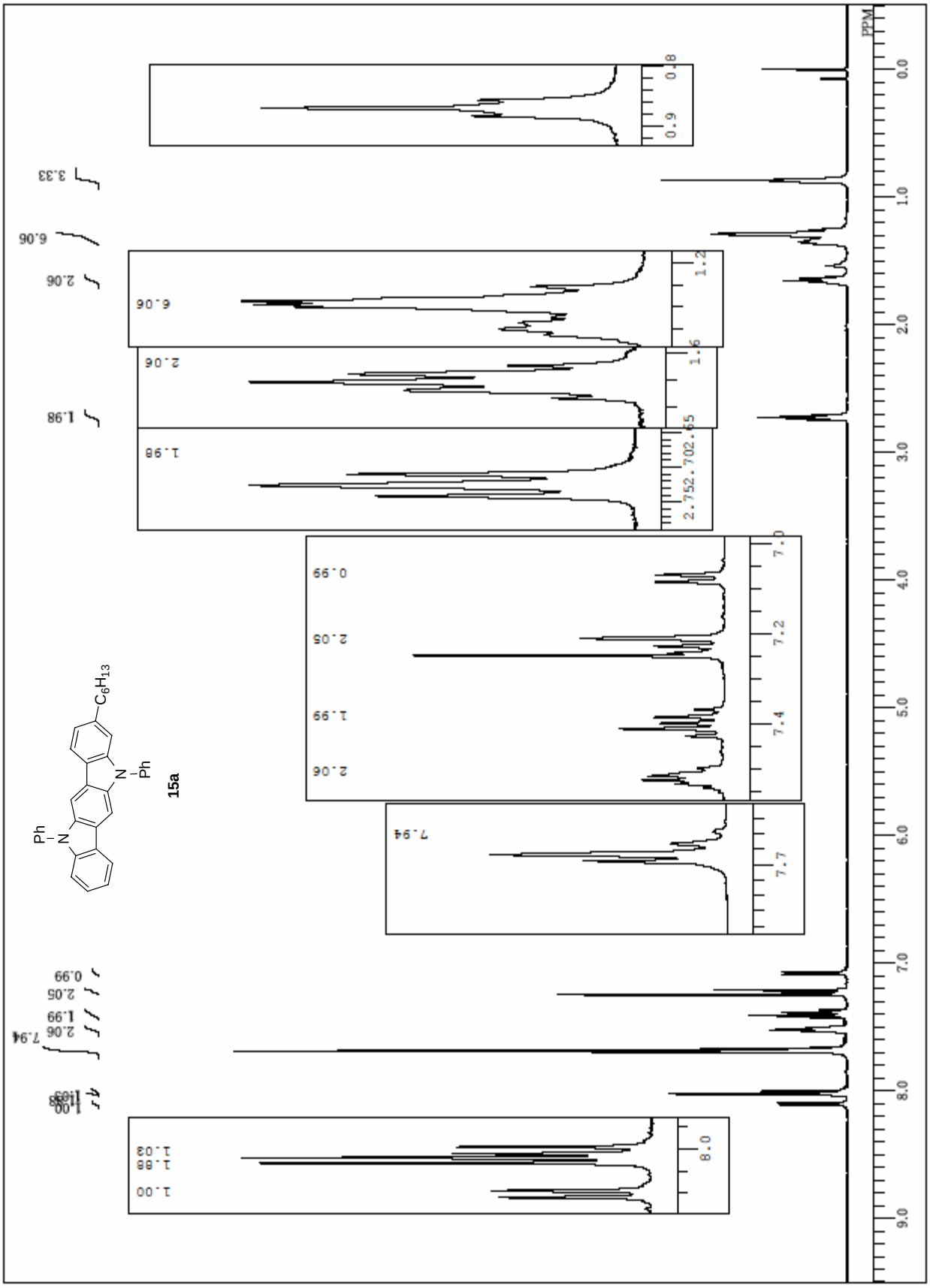


Figure S28. ^{1}H NMR spectrum of **15a** ($CDCl_3$, 500 MHz).

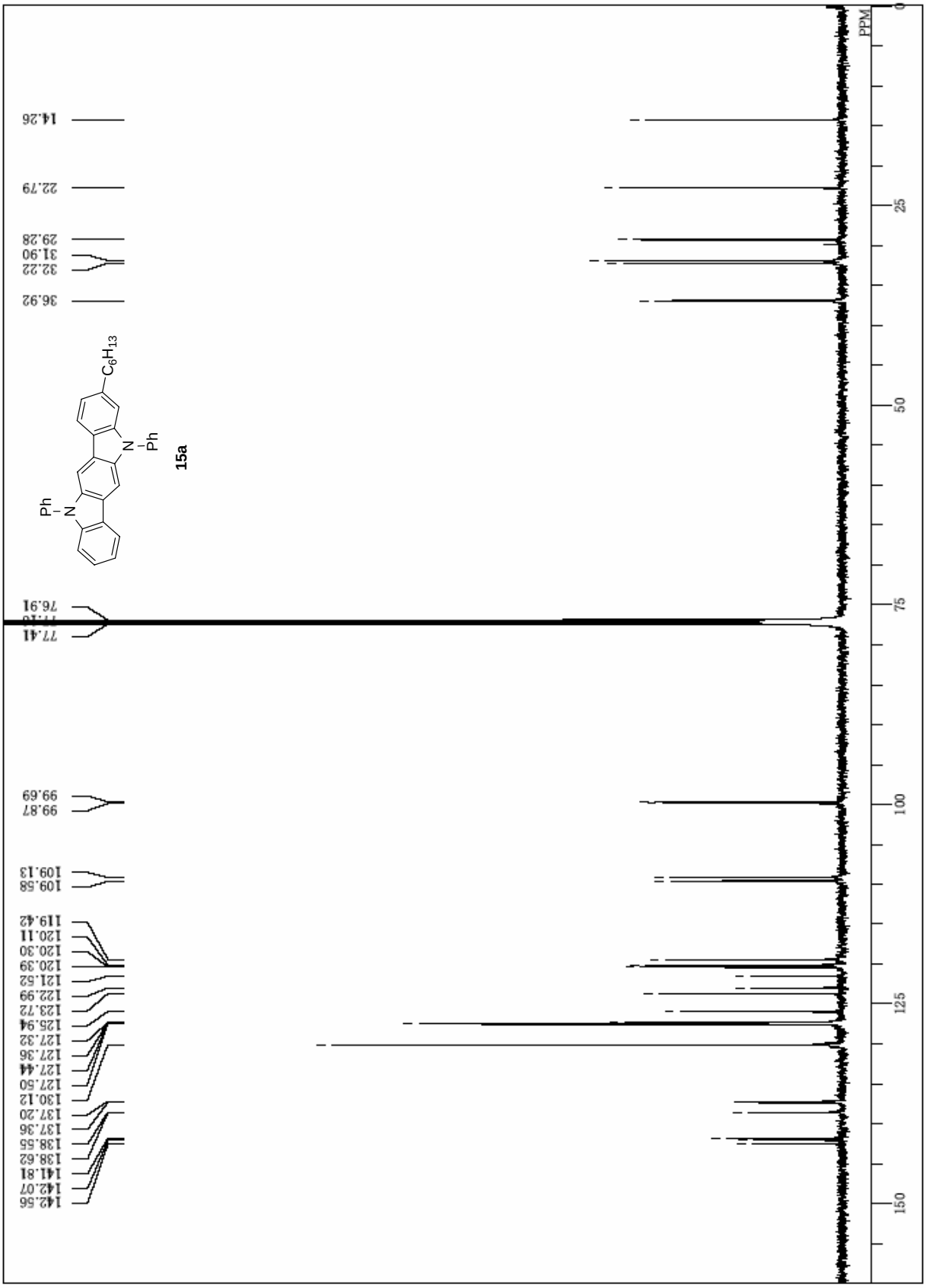


Figure S29. ^{13}C NMR spectrum of **15a** ($CDCl_3$, 125 MHz).

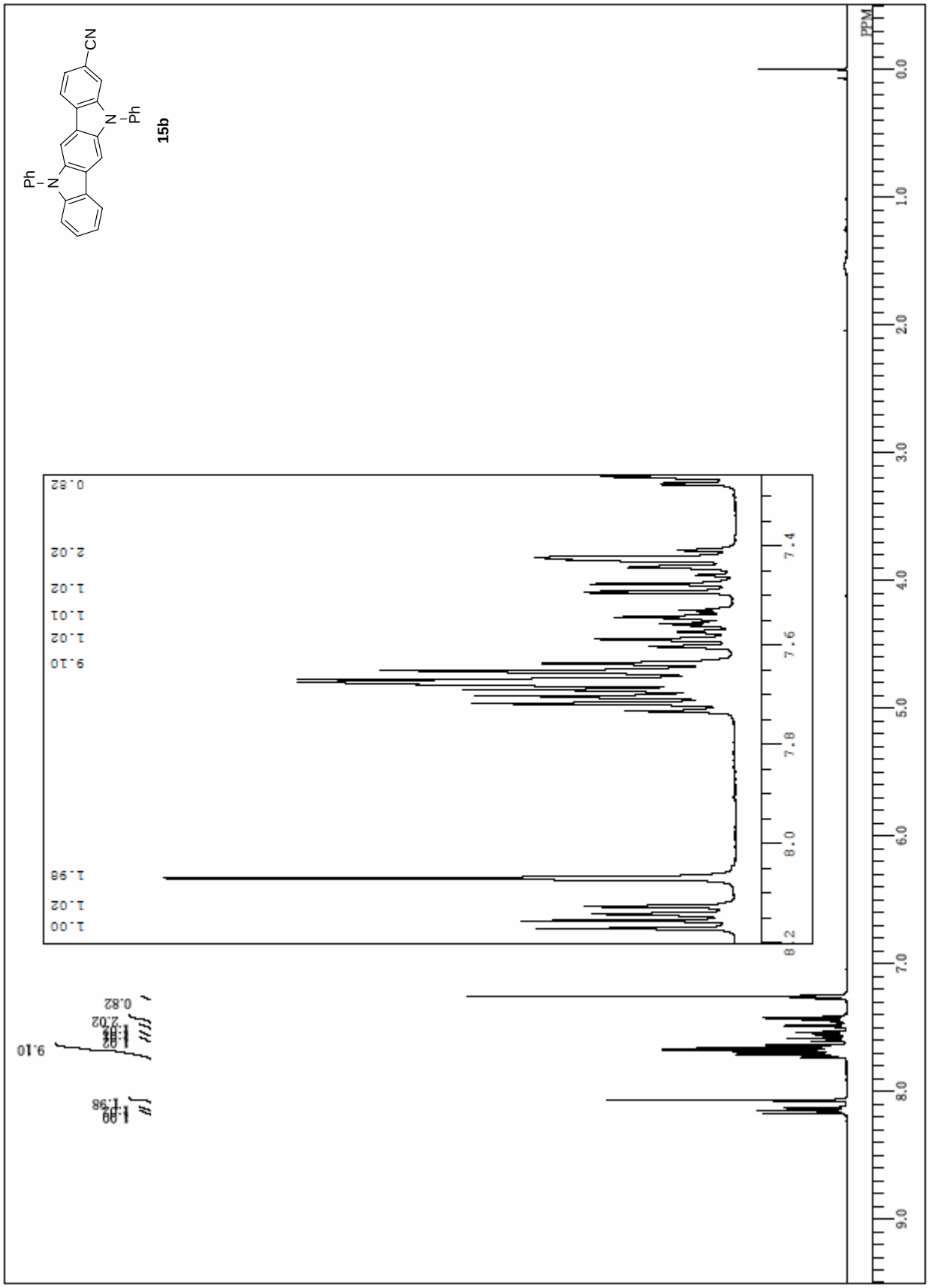


Figure S30. ^{1}H NMR spectrum of **15b** ($CDCl_3$, 500 MHz).

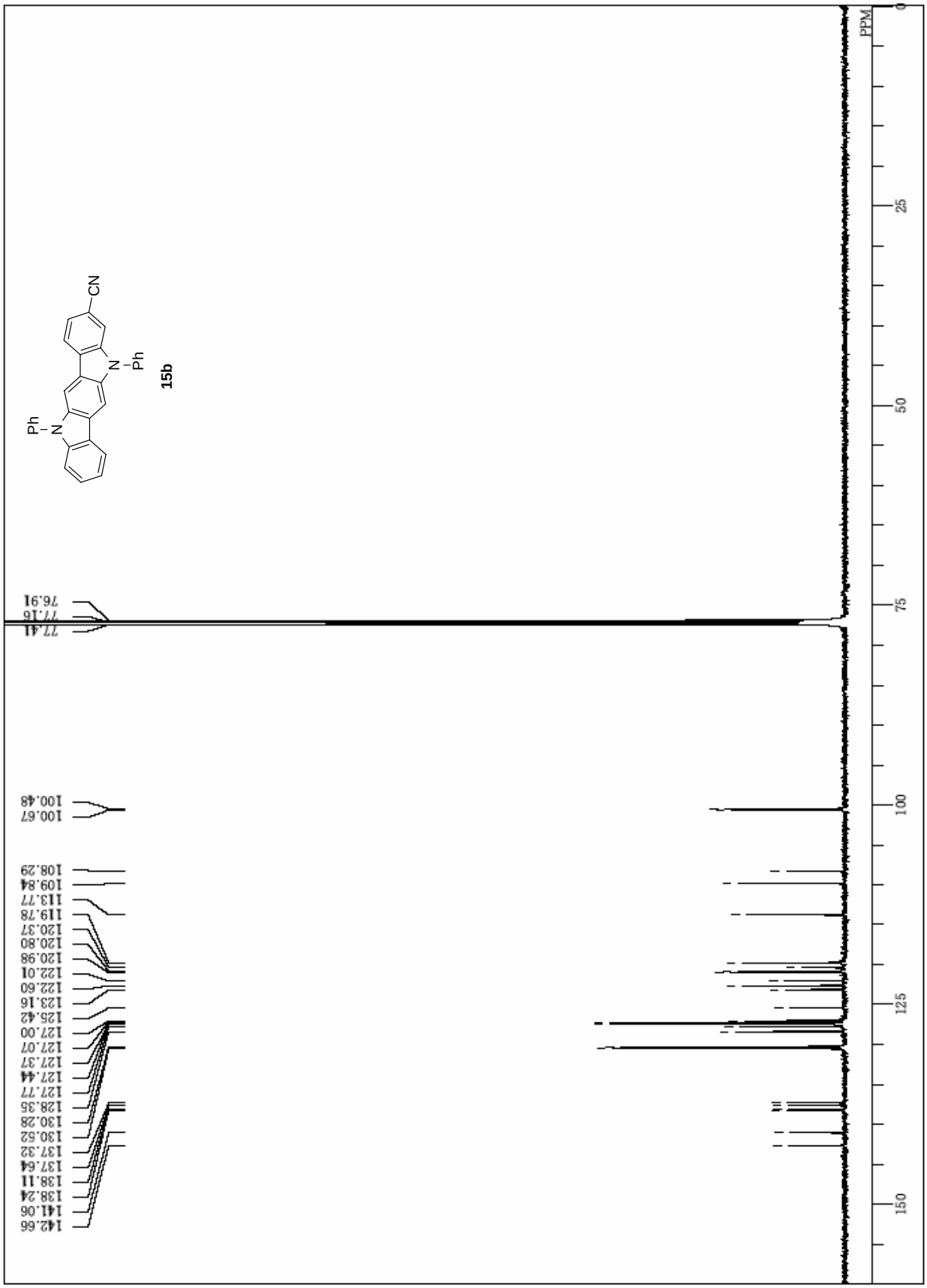


Figure S31. ^{13}C NMR spectrum of **15b** ($CDCl_3$, 125 MHz).

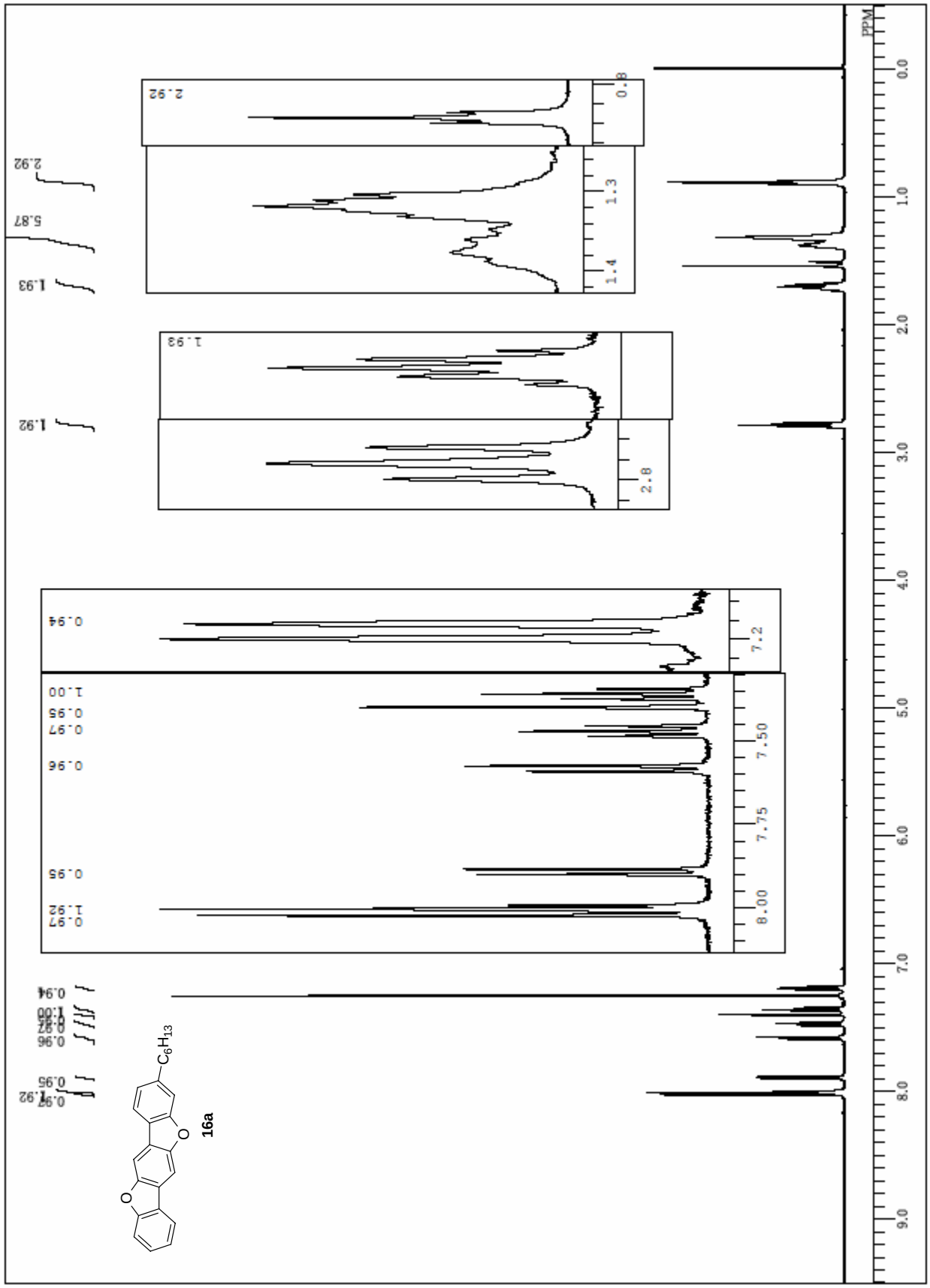


Figure S32. ^{1}H NMR spectrum of **16a** ($CDCl_3$, 500 MHz).

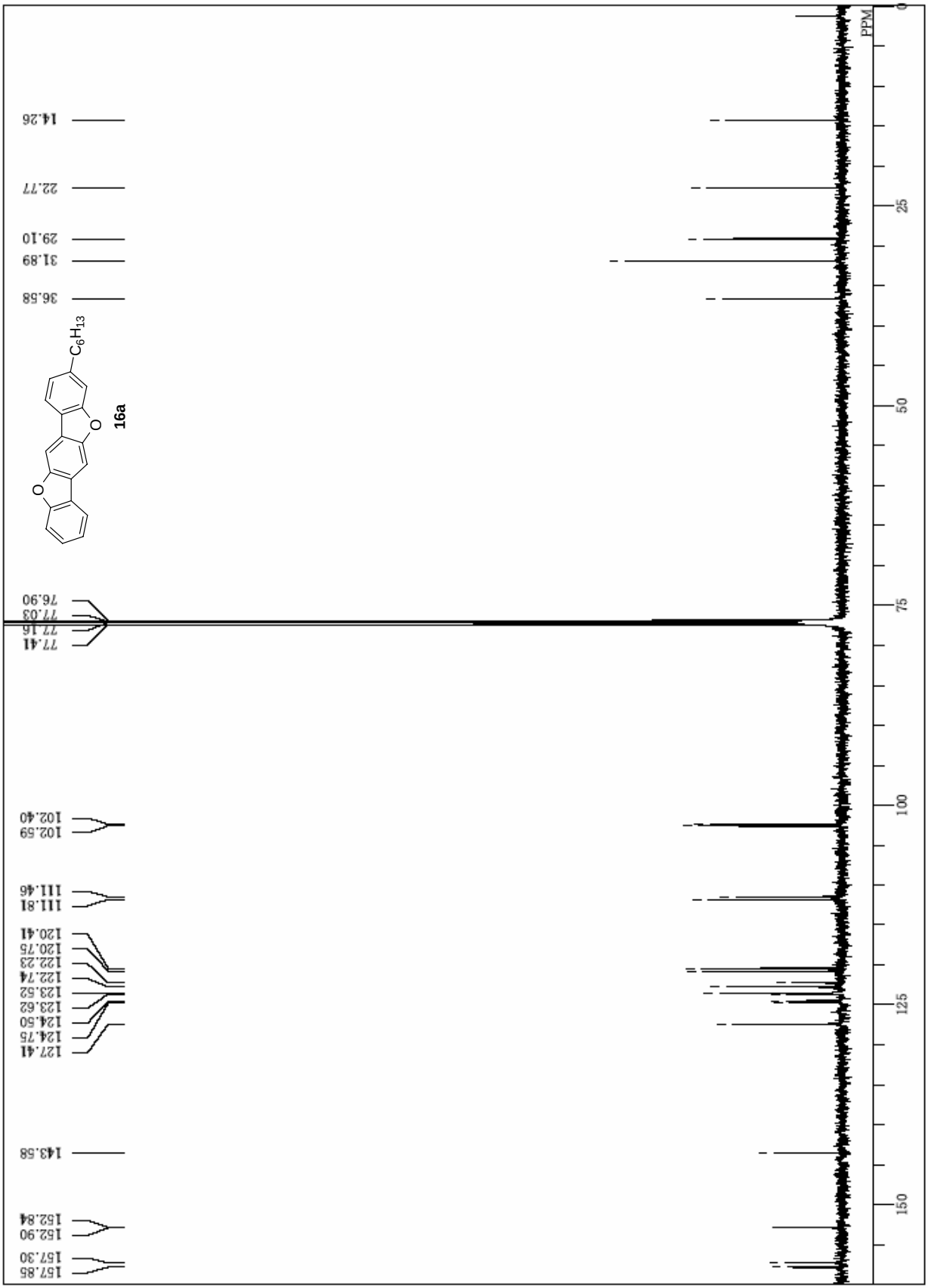


Figure S33. ^{13}C NMR spectrum of **16a** ($CDCl_3$, 125 MHz).

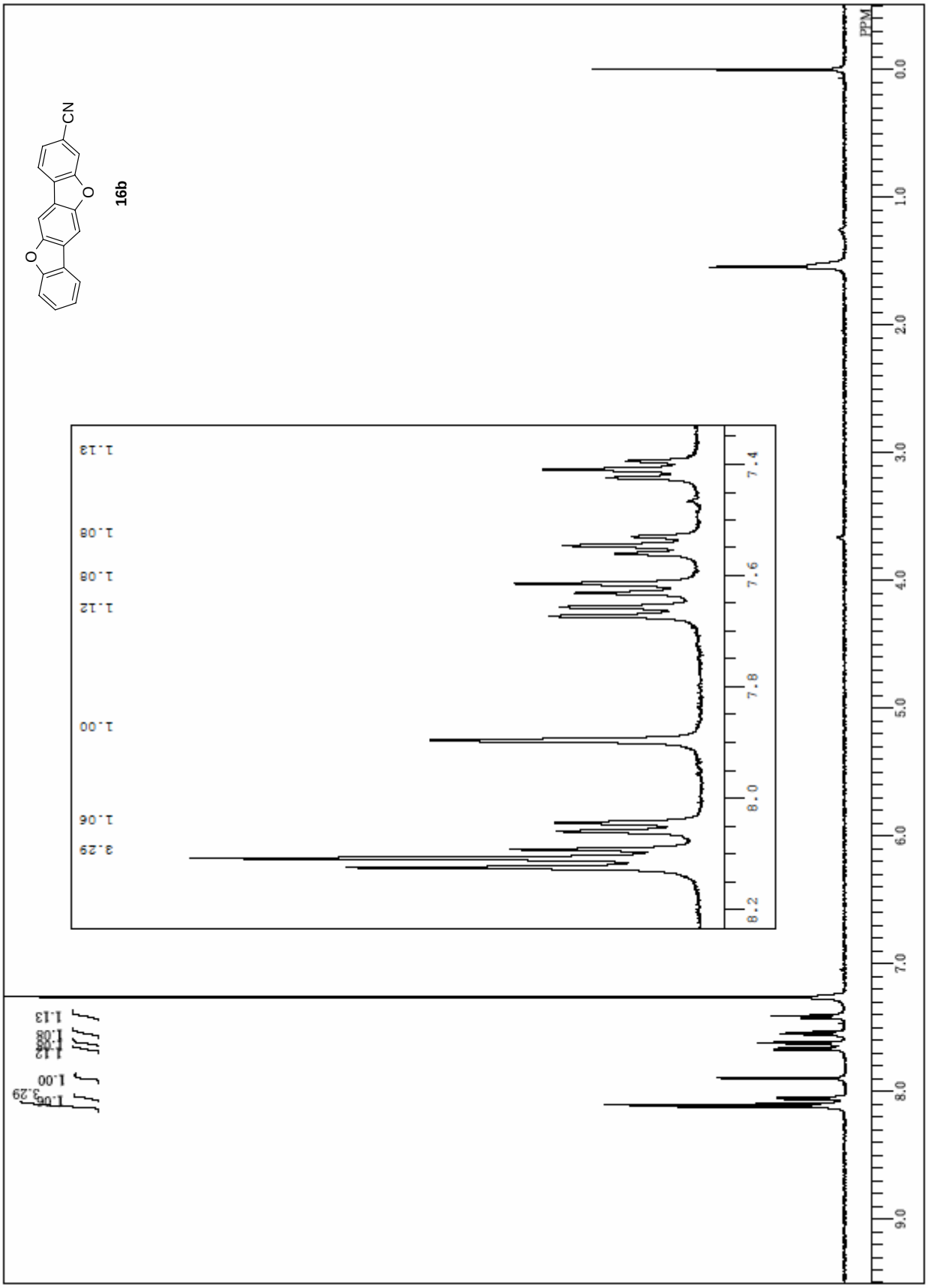


Figure S34. ^{1}H NMR spectrum of **16b** ($CDCl_3$, 500 MHz).

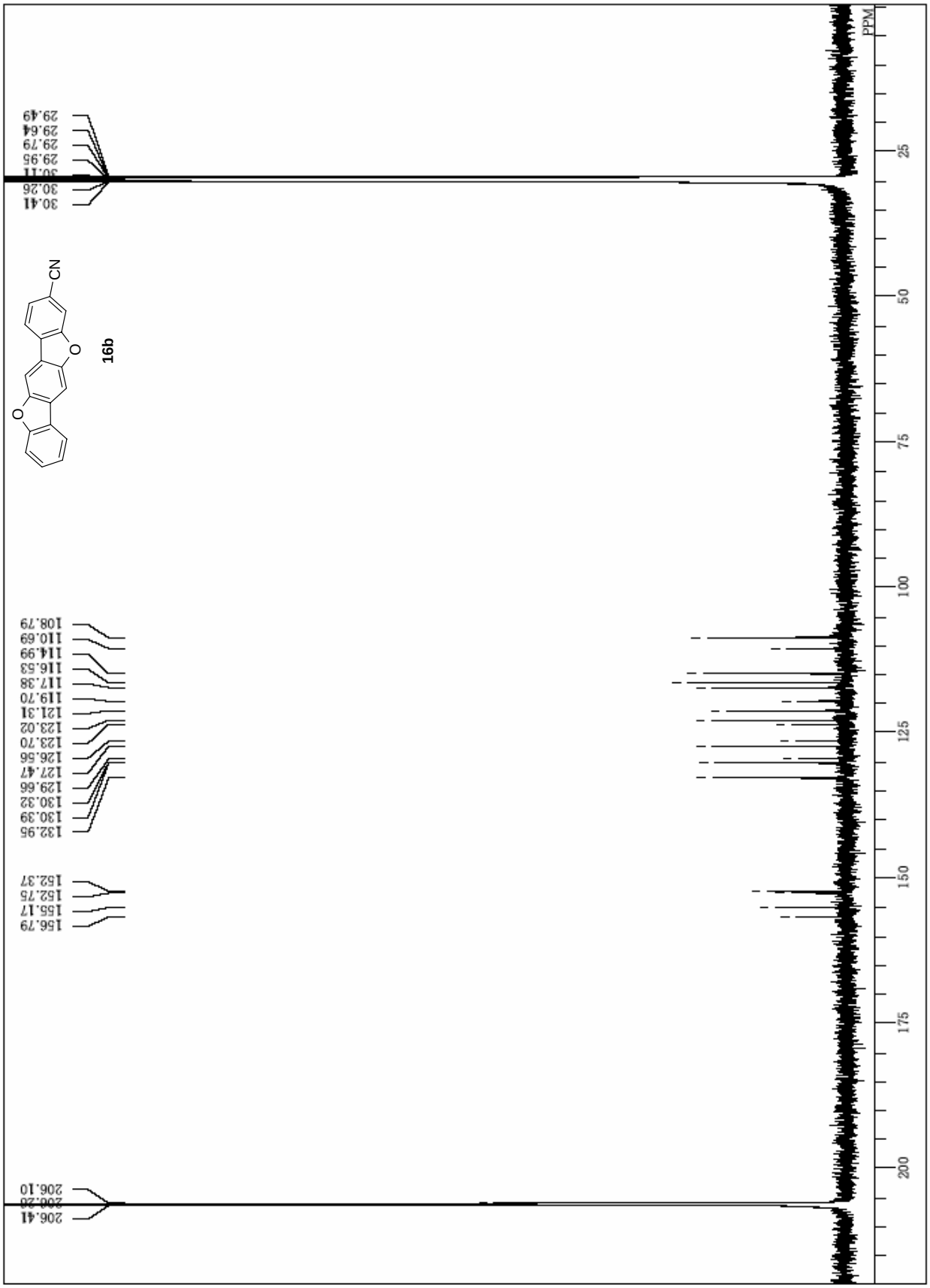


Figure S35. ^{13}C NMR spectrum of **16b** (acetone-d^6, 125 MHz).

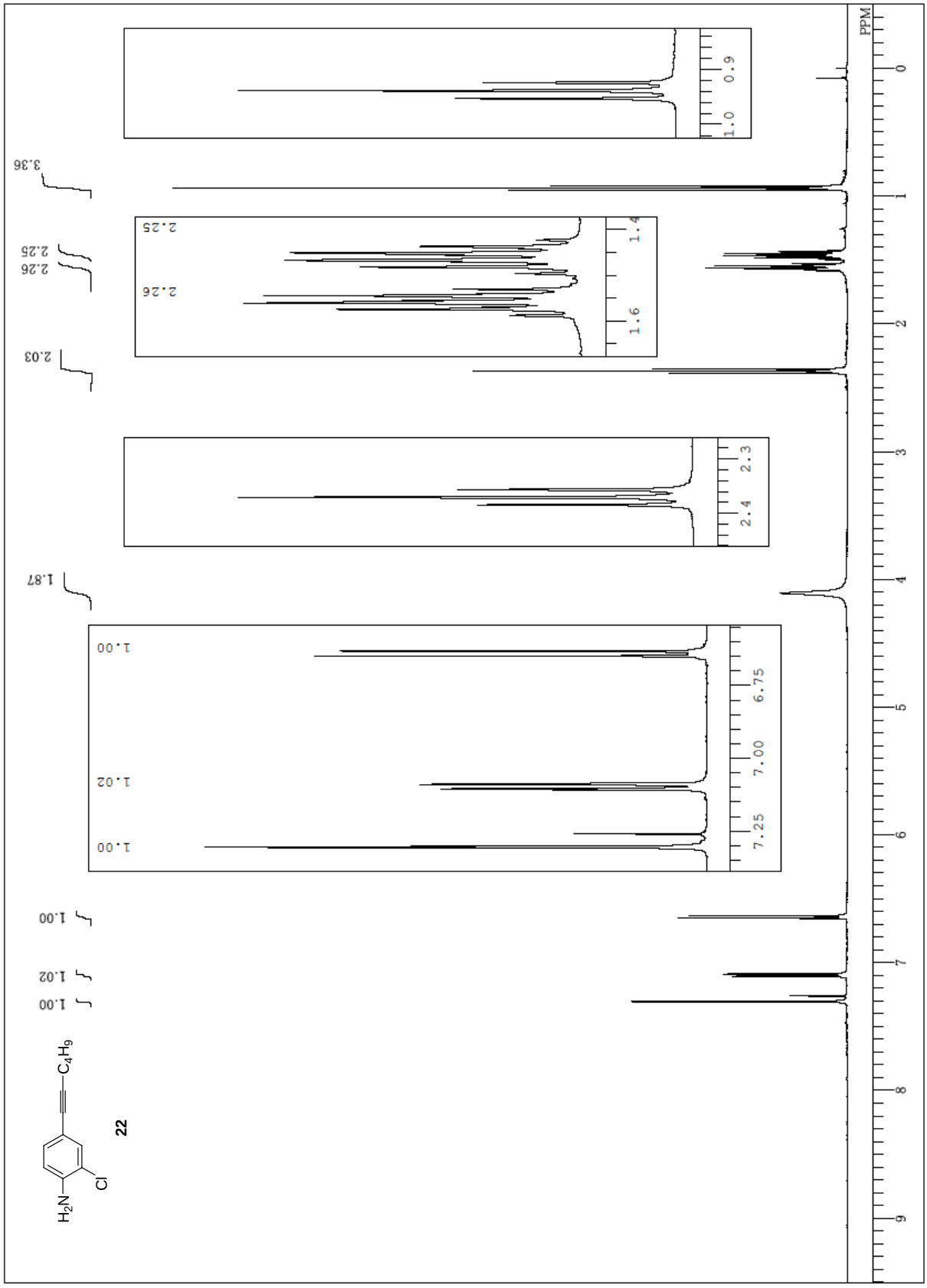


Figure S36. ^{1}H NMR spectrum of **22** ($CDCl_3$, 500 MHz).

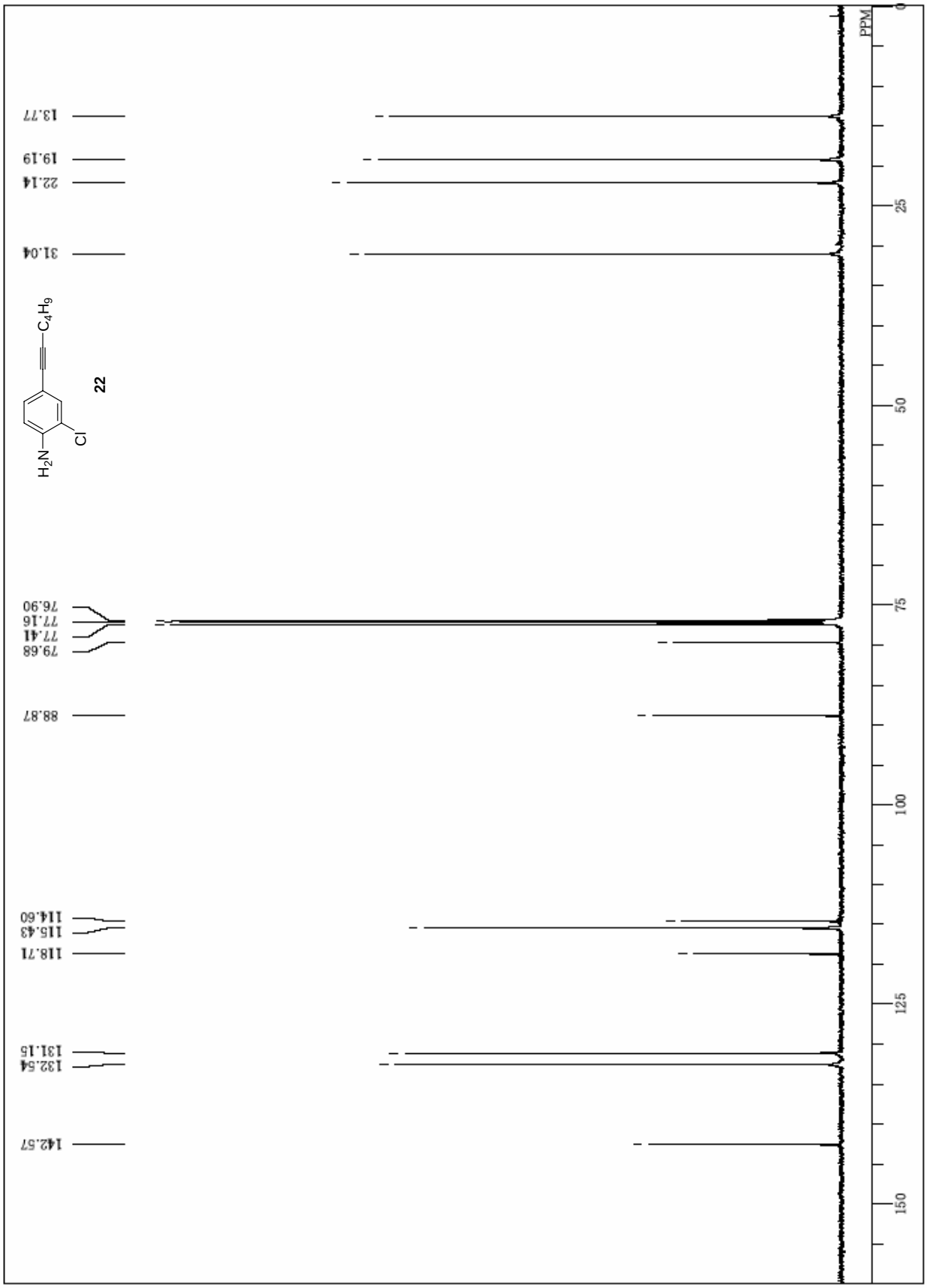


Figure S37. ^{13}C NMR spectrum of **22** ($CDCl_3$, 125 MHz).

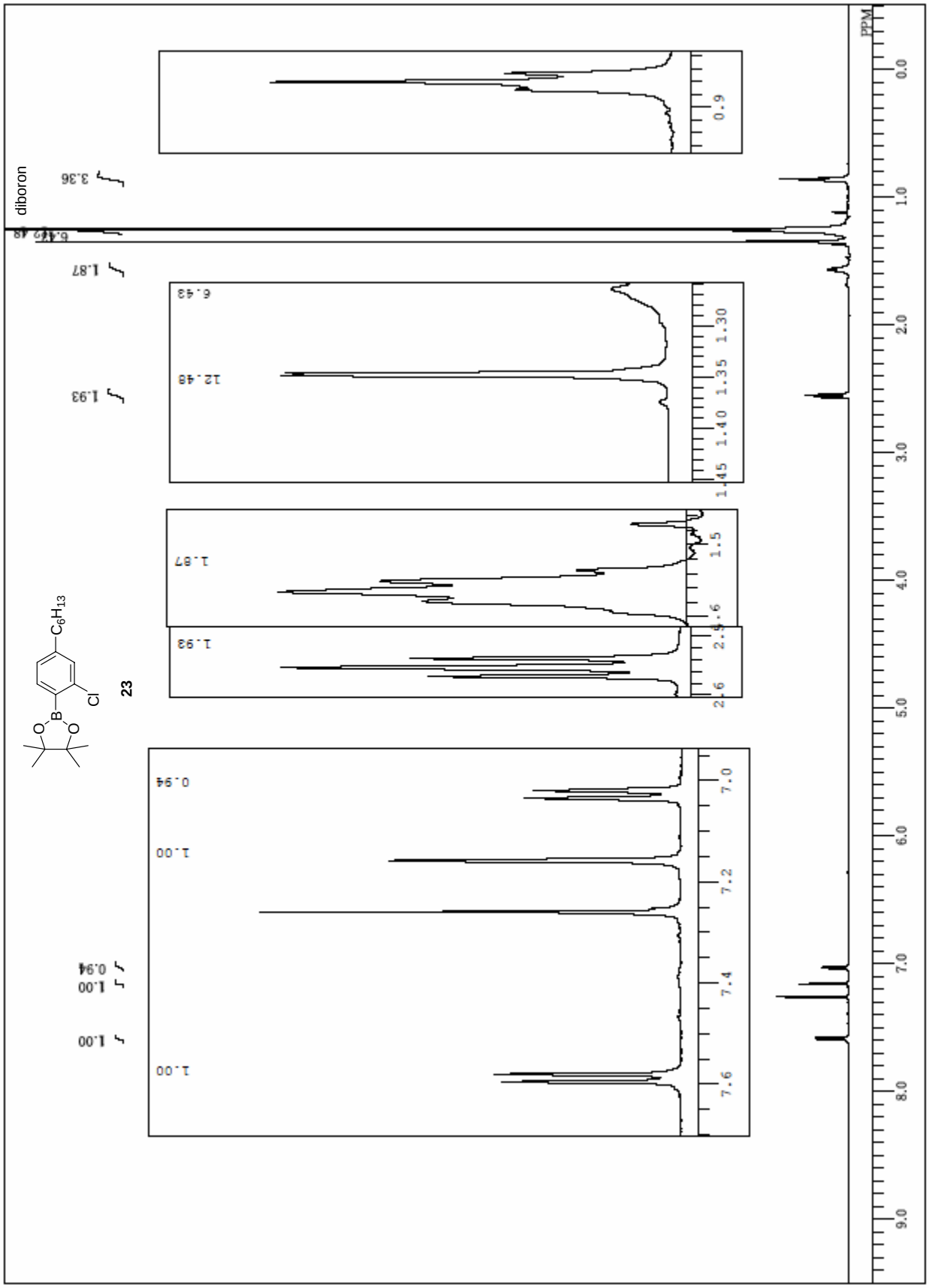


Figure S38. ^{1}H NMR spectrum of **23** ($CDCl_3$, 500 MHz).

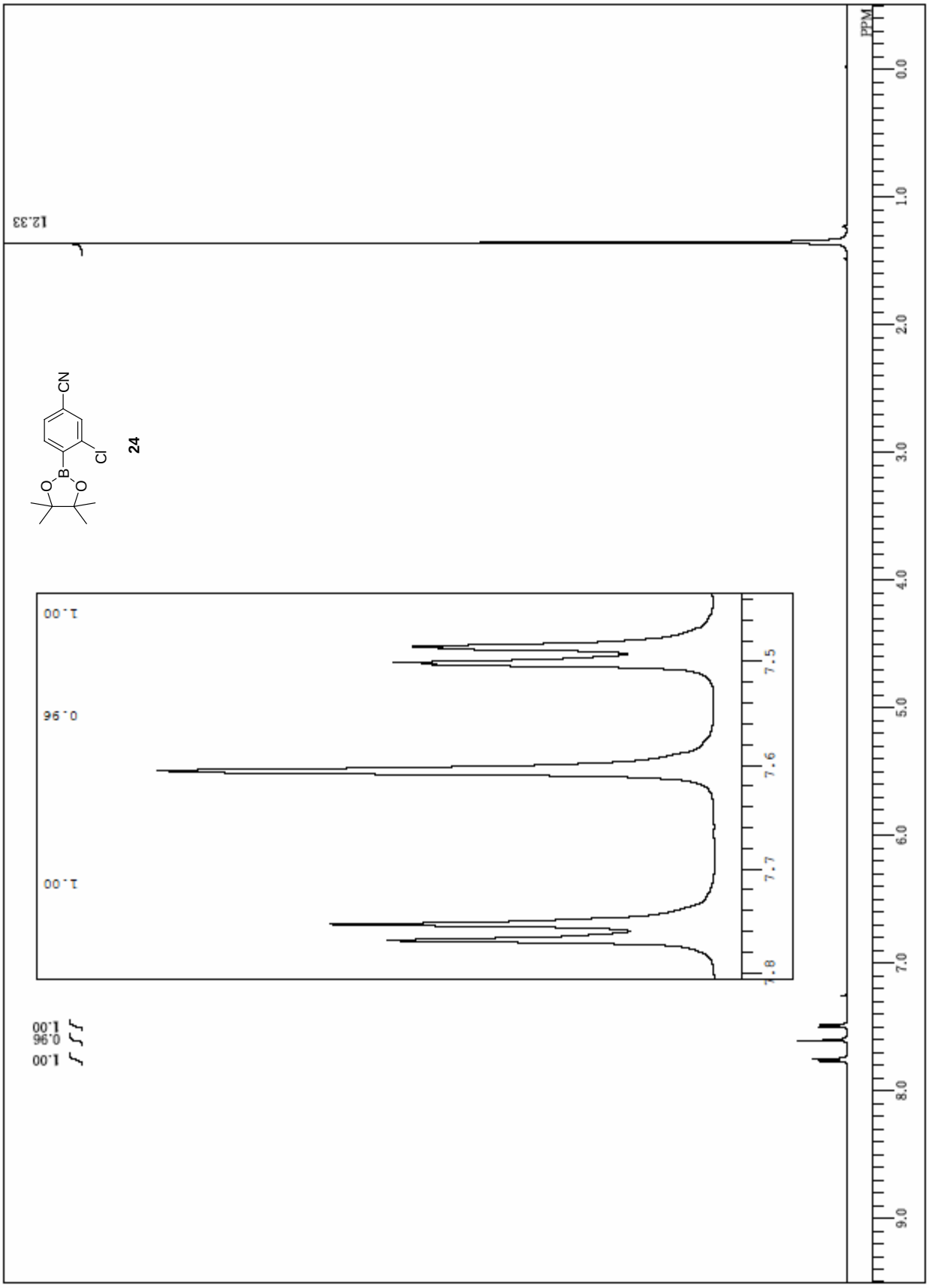


Figure S39. ^{1}H NMR spectrum of **24** ($CDCl_3$, 500 MHz).

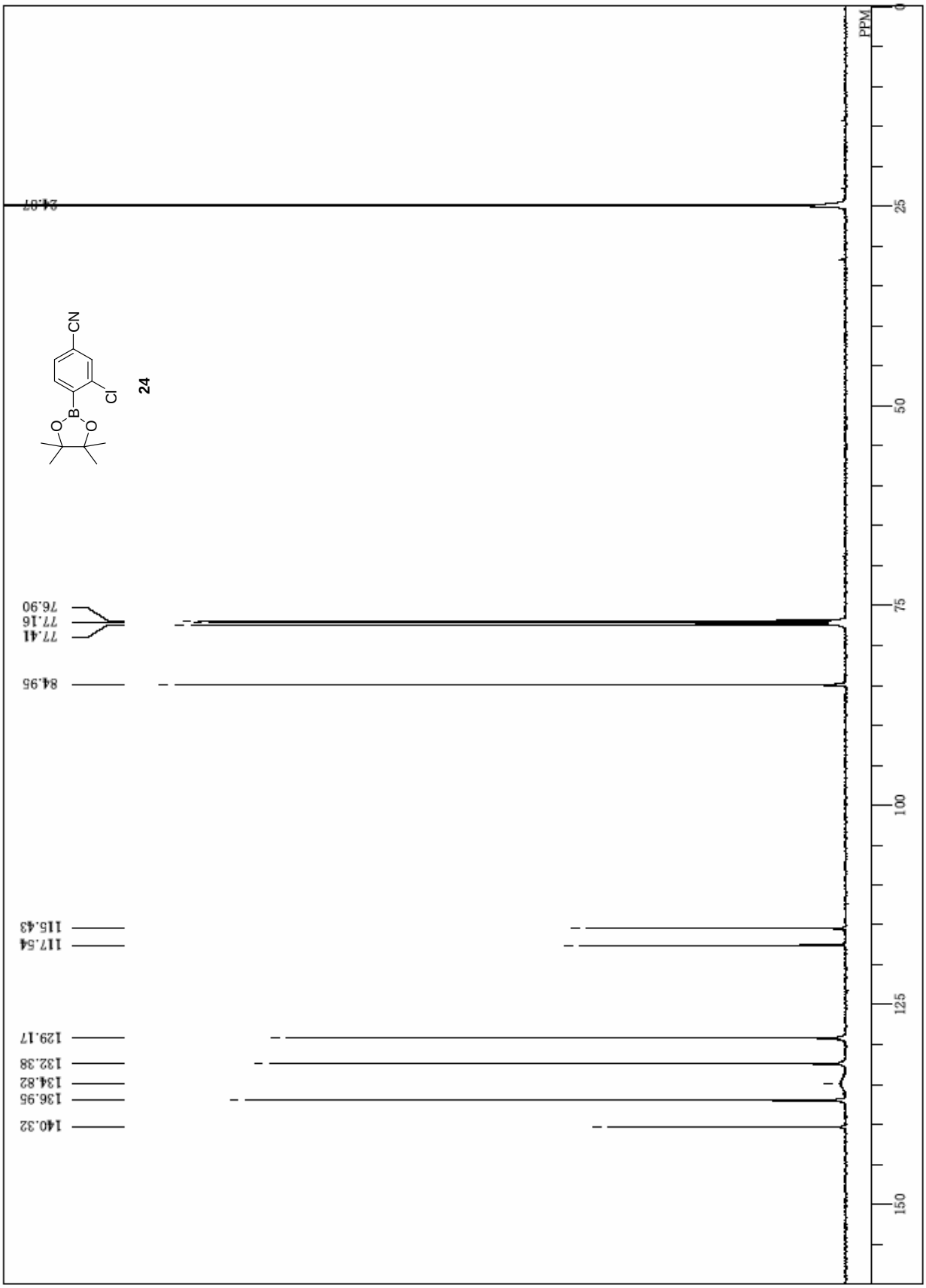


Figure S40. ^{13}C NMR spectrum of **24** ($CDCl_3$, 125 MHz).

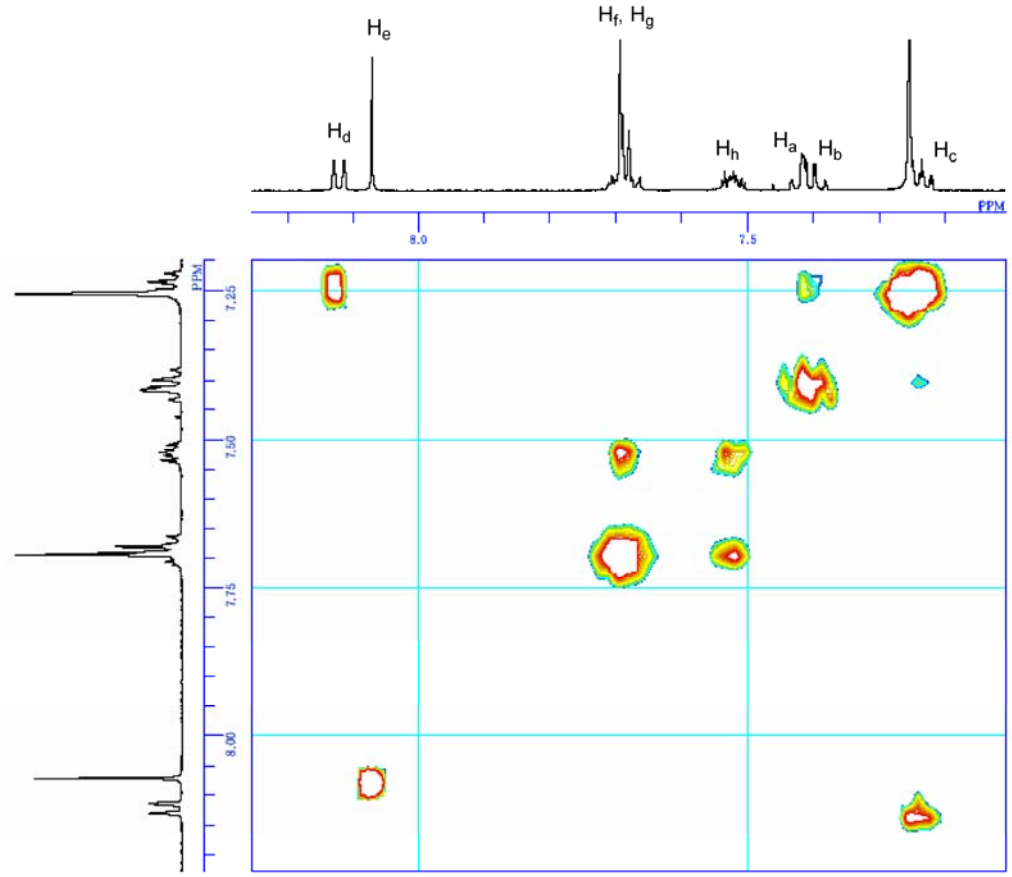


Figure S41. $^{1}H–^{1}H$ COSY spectrum of **2c** ($CDCl_3$).

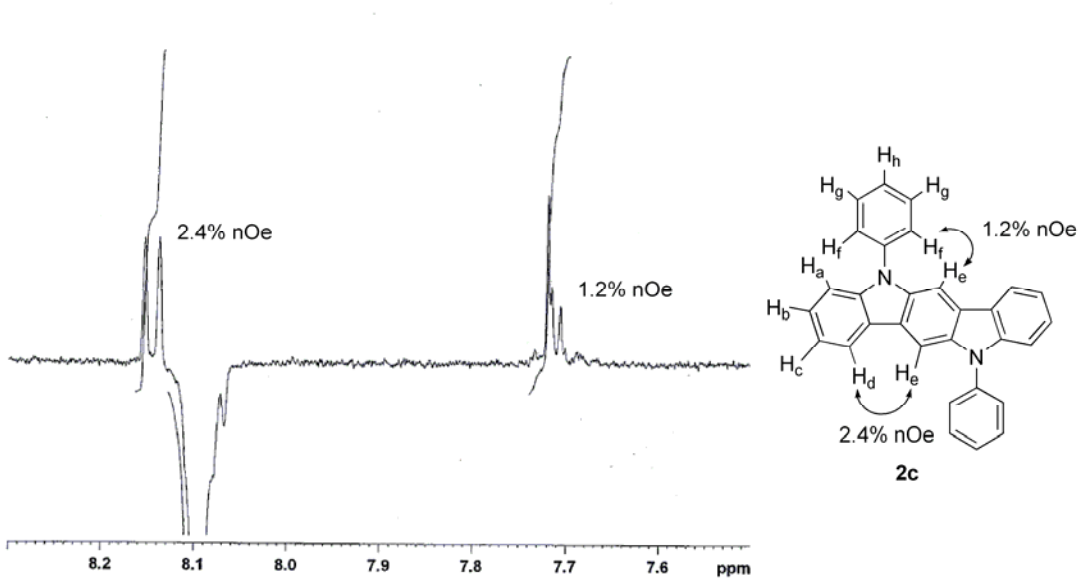


Figure S42. nOe spectrum of **2c** ($CDCl_3$).

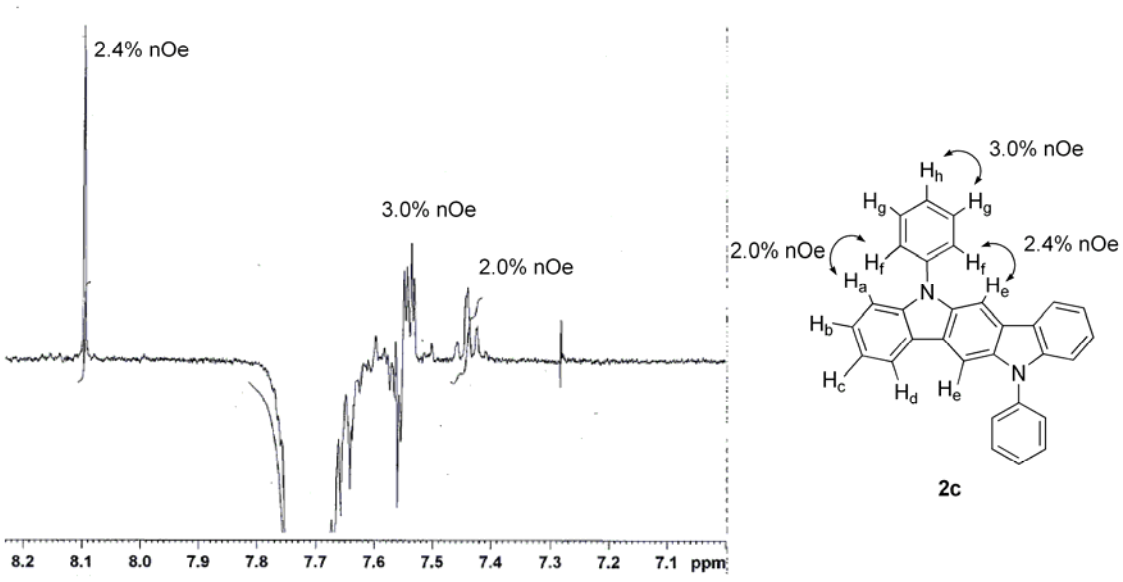


Figure S43. nOe spectrum of **2c** ($CDCl_3$).

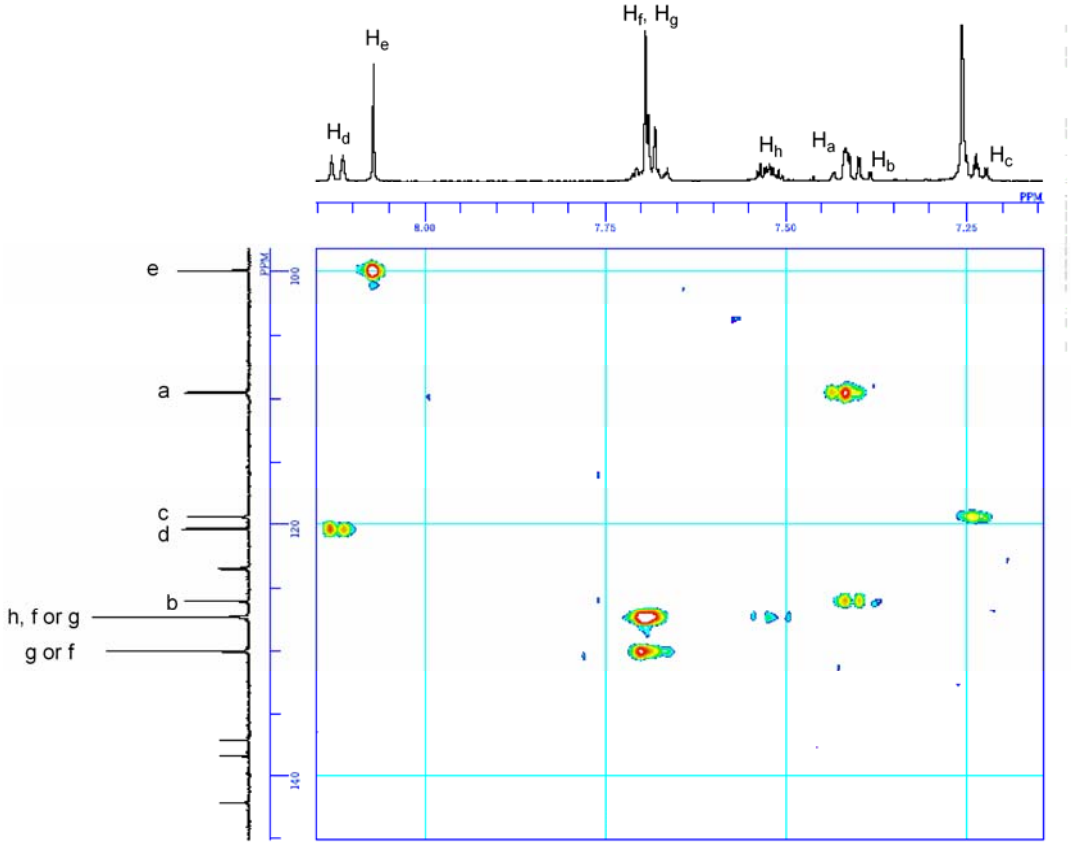


Figure S44. HMQC spectrum of **2c** ($CDCl_3$).

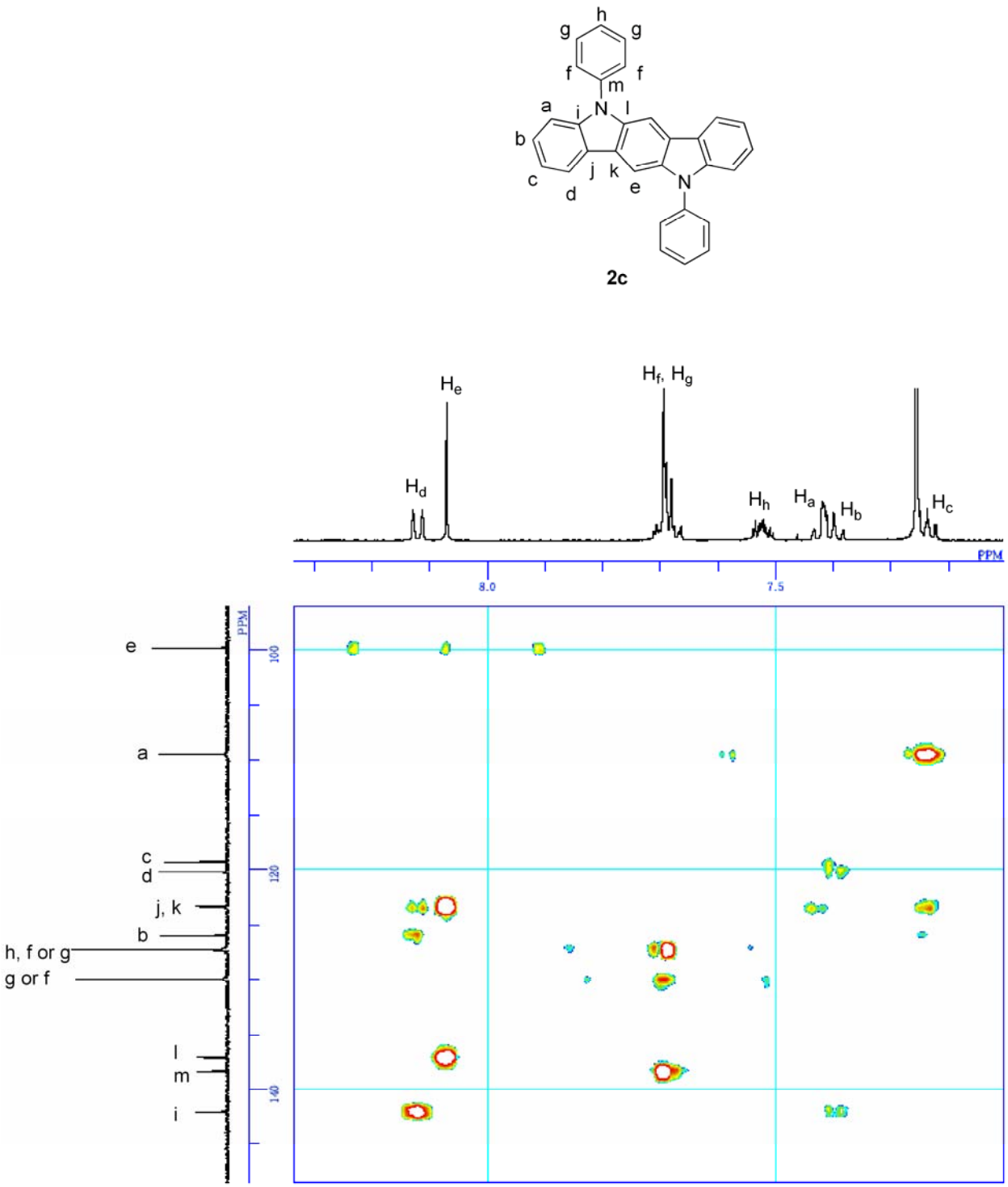


Figure S45. HMBC spectrum of **2c** ($CDCl_3$).

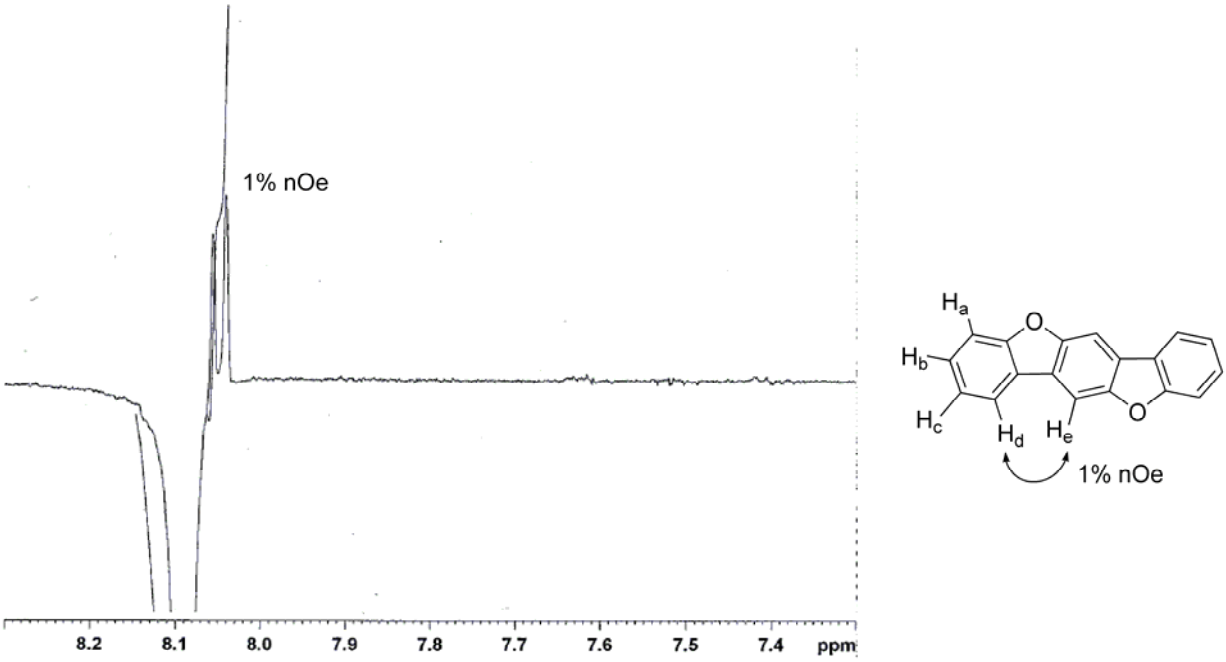


Figure S46. nOe spectrum of **3** ($CDCl_3$).

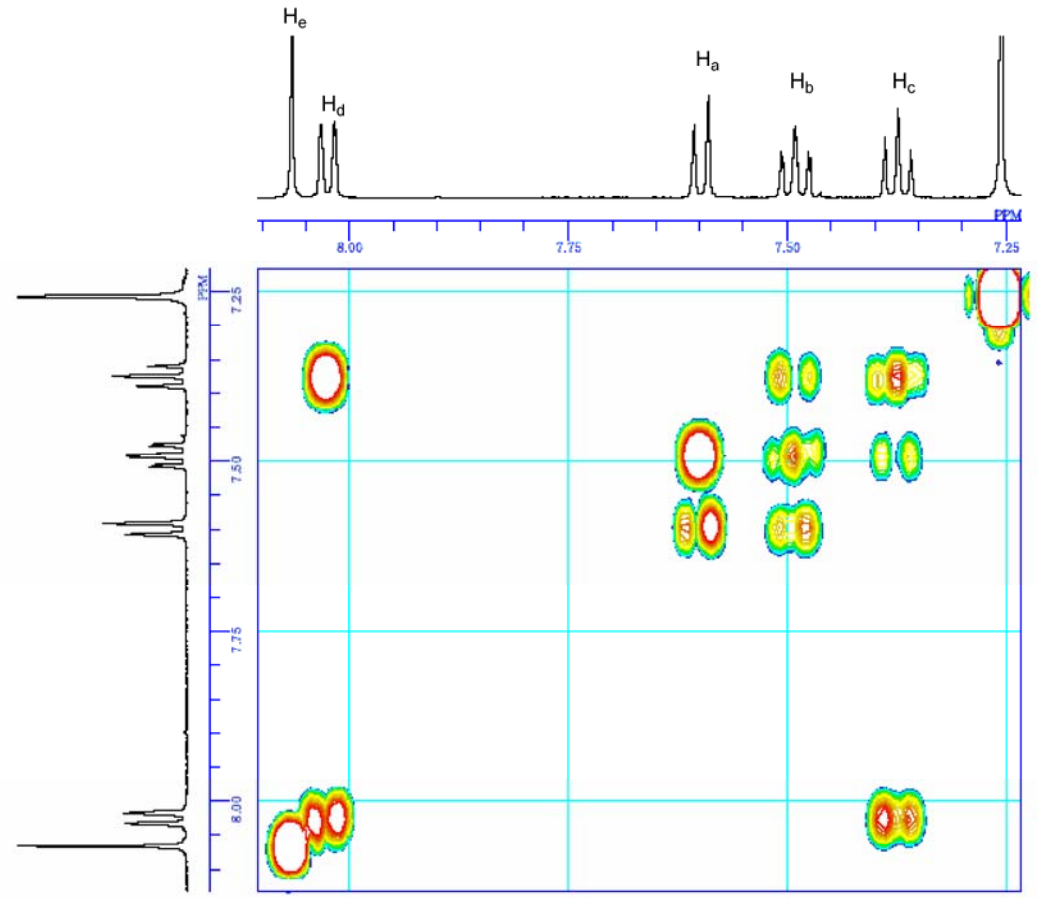


Figure S47. $^1H–^1H$ COSY spectrum of **3** ($CDCl_3$).

References

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