

Supplementary Information

Synthesis and physical properties of zethrene derivatives bearing donor/acceptor substituents at 7,14-positions

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1. General

^1H and ^{13}C NMR spectra were recorded in CDCl_3 at 30 °C. The chemical shifts were referenced to the residual solvent protons in the ^1H NMR (7.26 ppm) and in the ^{13}C NMR (77.0 ppm). Mass spectral analyses were performed with EI or FAB mode. IR spectra were recorded as a KBr disk. Melting points were measured with a hot-stage apparatus equipped with a thermometer. Column chromatography and TLC were performed with silica gel (70-230 mesh) and pre-coated silica gel plates, respectively. Preparative recycling GPC separation was undertaken using two 600 mm \times 20 mm GPC columns with CHCl_3 as the eluent. All reagents were obtained from commercial suppliers and used as received. Solvents were dried (drying agent in parentheses) and distilled prior to use: Et_3N (KOH), benzene (CaH_2), pyridine (KOH).

UV-vis spectra and fluorescence spectra were measured in spectrograde dichloromethane. Electrochemical measurements were performed in degassed CH_2Cl_2 including $n\text{-Bu}_4\text{NClO}_4$ as supporting electrolyte. Glassy carbon was used as the working electrode. The counter electrode was platinum wire, and reference electrode was Ag/Ag^+ . The potential was corrected against ferrocene (Fc)/ferrocenium (Fc^+) redox couple. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV/s.

A single crystal of **2b** suitable for X-ray diffraction study was subjected to data collection which was conducted with a Rigaku IP detector with graphite monochromated $\text{MoK}\alpha$ radiation. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F_2 by the full-matrix least-squares method using SHELXL-97.¹ Hydrogen atoms were placed at calculated positions and refined "riding" on their corresponding carbon atoms. In the subsequent refinement, the function $\sum w(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \sum (||F_o| - |F_c||) / \sum |F_o|$ and $wR2 = [\sum w (F_o^2 - F_c^2)^2 / \sum (w F_o^2)^2]^{1/2}$.

The DFT calculations were performed with a Gaussian 09 program package.² The geometries of the molecules were optimized by using the B3LYP method with the 6-31G(d) basis set. The nature of the stationary points was assessed by means of vibrational frequency analysis.

2. Synthesis

3,6-Di-*tert*-butyl-1,8-diiodonaphthalene (**6**)

H₂SO₄ (18 M, 4.1 mL) was added to a solution of 1,8-diamino-3,6-di-*tert*-butylnaphthalene (**5**)³ (3.49 g, 12.8 mmol) in EtOH (30 mL) which was cooled to -20 °C. NaNO₂ (2.48 g, 38.7 mmol) dissolved in H₂O (19 mL) was added dropwise at -15 °C to -20 °C followed by the addition of KI (12.8 g, 77.4 mmol) dissolved in H₂O (24 mL). The mixture was kept at -5 °C to 0 °C for 2 h and then heated at 60 °C for 30 min. After cooling to room temperature, the mixture was neutralized with aqueous NaOH solution and extracted with CHCl₃. The organic layer was washed with saturated aqueous Na₂S₂O₃ solution and dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (hexanes) followed by preparative GPC. The crude product was recrystallized from a mixture of hexanes : EtOH = 1 : 1 to afford 1.65 g (26%) of **6** as a yellow solid. mp 108–110 °C; ¹H NMR (400 MHz, CDCl₃, 30 °C) δ 8.38 (d, *J* = 1.6 Hz, 2H), 7.72 (d, *J* = 1.6 Hz, 2H), 1.38 (s, 18H); ¹³C NMR (100 MHz, CDCl₃, 30 °C) δ 149.6, 142.3, 135.3, 128.7, 126.3, 95.7, 34.3, 31.0; IR (KBr) 3064, 2963, 2905, 2867, 1612, 1526, 1479, 1365, 1257, 1165, 964, 879, 627 cm⁻¹; MS (EI) *m/z* 491.9 (M⁺); Anal. Calcd for C₁₈H₂₂I₂: C, 43.93; H, 4.51. Found: C, 44.19; H, 4.59.

3,6-Di-*tert*-butyl-1,8-bis[(trimethylsilyl)ethynyl]naphthalene (**7**)

A mixture of **6** (501 mg, 1.02 mmol), (trimethylsilyl)acetylene (580 μL, 4.1 mmol), Pd(PPh₃)₂Cl₂ (220 mg, 0.31 mmol) and CuI (69 mg, 0.36 mmol) in Et₃N was heated at 100 °C under an argon atmosphere for 1 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (hexanes : AcOEt = 100 : 1) to afford 329 mg (75%) of **7** as a colorless solid. mp 165–166 °C; ¹H NMR (400 MHz, CDCl₃, 30 °C) δ 7.79 (d, *J* = 2.0 Hz, 2H), 7.67 (d, *J* = 2.0 Hz, 2H), 1.39 (s, 18H), 0.31 (s, 18H); ¹³C NMR (100 MHz, CDCl₃, 30 °C) δ 147.8, 134.9, 134.0, 127.0, 125.3, 119.8, 106.0, 101.5, 34.5, 31.1, 0.4; IR (KBr) 3058, 2966, 2906, 2872, 2141, 1609, 1375, 1247, 889, 856 cm⁻¹; HRMS (EI) *m/z* Calcd for C₂₈H₄₀Si₂ [M⁺] 432.2669, Found: 432.2655.

Tetra-*tert*-butyl-1,6-dinaphthotetradehydro[10]annulene (**3b**)

An aqueous solution of NaOH (4.0 M, 270 μL, 1.1 μmol) was added to a solution of **6** (150 mg, 305 μmol), **7** (120 mg, 277 μmol), Pd(PPh₃)₄ (112 mg, 97.1 μmol), CuI (26 mg, 140 μmol) and DBU (0.29 mL, 1.94 mmol) in benzene (16 mL) and pyridine (4 mL), which had been degassed by bubbling argon for 20 min. After the mixture was stirred under an argon atmosphere at room temperature for 16 h, the solvents were removed under reduced pressure. The residue was

subjected to silica-gel column chromatography (hexanes : $\text{CHCl}_3 = 20 : 1$). The solid product was washed with hexanes to give 37.5 mg (26%) of **3b** as a yellow solid. mp 153 °C dec.; ^1H NMR (400 MHz, CDCl_3 , 30 °C) δ 7.76 (d, $J = 2.0$ Hz, 4H), 7.71 (d, $J = 2.0$ Hz, 4H), 1.44 (s, 36H); ^{13}C NMR (100 MHz, CDCl_3 , 30 °C) δ 148.2, 134.5, 129.6, 128.3, 125.2, 120.6, 95.4, 34.7, 31.1; IR (KBr) 3057, 2962, 2868, 1608, 1595, 1362, 885, 786, 644 cm^{-1} ; HRMS (EI) m/z Calcd for $\text{C}_{40}\text{H}_{44} [\text{M}^+]$ 524.3423, Found: 524.3443.

2,5,9,12-Tetra-tert-butyl-7,14-diiodozethrene (4b)

A solution of **3b** (43.5 mg, 82.9 μmol) and iodine (88.4 mg, 348 μmol) in CHCl_3 was stirred at room temperature under an argon atmosphere for 6 h. During the reaction, the mixture was protected from room light by covering the flask with an aluminum foil. The mixture was diluted with CHCl_3 and washed with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution. The aqueous layer was extracted with CHCl_3 twice. The combined organic layer was dried over MgSO_4 and the solvent was removed under reduced pressure. Silica-gel column chromatography (hexanes) gave 77.0 mg (68%) of **4b** as a red solid. mp 209–210 °C; ^1H NMR (400 MHz, CDCl_3 , 30 °C) δ 8.52 (d, $J = 1.2$ Hz, 2H), 8.20 (d, $J = 1.2$ Hz, 2H), 7.81 (d, $J = 1.2$ Hz, 2H), 7.71 (d, $J = 1.2$ Hz, 2H), 1.49 (s, 18H), 1.48 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3 , 30 °C) δ 149.6, 147.9, 141.4, 132.7, 132.6, 132.2, 131.7, 128.8, 125.3, 124.0, 123.9, 99.9, 35.1, 31.3, 31.2; IR (KBr) 3057, 2960, 2904, 2867, 1476, 1362, 1245, 1211, 948, 891, 877, 648 cm^{-1} ; MS (FAB) m/z 778.1 (M^+); Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{I}_2$: C, 61.71, H, 5.70, Found: C, 61.60; H, 5.81.

7,14-Dibromo-2,5,9,12-tetra-tert-butylzethrene (4c)

A 40 mL solution of IBr in CHCl_3 (11 mM, 40 mL, 440 μmol) was added to **3b** (95.5 mg, 182 μmol) under argon and the mixture was stirred at room temperature for 4 h. After the mixture was diluted by CHCl_3 , it was washed with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ solution. The aqueous layer was extracted with CHCl_3 twice. The combined organic layer was dried over MgSO_4 and the solvent was removed under reduced pressure. The residue was subjected to silica-gel column chromatography (hexanes) to give 74.5 mg (60%) of **4c** as a red solid. mp 158–160 °C; ^1H NMR (400 MHz, CDCl_3 , 30 °C) δ 8.63 (d, $J = 1.6$ Hz, 2H), 8.23 (d, $J = 1.6$ Hz, 2H), 7.79 (d, $J = 1.6$ Hz, 2H), 7.72 (d, $J = 1.6$ Hz, 2H), 1.48 (s, 18H), 1.47 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3 , 30 °C) δ 149.2, 148.2, 135.3, 132.6, 130.9, 129.5, 128.8, 125.3, 125.2, 124.2, 123.7, 119.8, 35.1, 35.0, 31.3, 31.1; IR (KBr) 2961, 2905, 2869, 1463, 1363, 953, 880, 650, 417 cm^{-1} ; HRMS (EI) m/z Calcd for $\text{C}_{40}\text{H}_{44}\text{Br}_2 [\text{M}^+]$ 684.1794, Found: 684.1796.

2,5,9,12-Tetra-tert-butyl-7,14-bis(phenylethynyl)zethrene (2a)

To a solution of **4b** (15.4 mg, 19.7 μmol), $\text{Pd}(\text{PPh}_3)_4$ (9.5 mg, 8.2 μmol) and CuI (2.7 mg, 14.2

μmol) in degassed Et₃N (6 mL) was added phenylacetylene (30 μL, 28mg, 260 μmol) under an argon atmosphere. After stirring at room temperature for 6 h, the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (hexanes : CHCl₃ = 10 : 1) to afford 12.6 mg (89%) of **2a** as a purple solid. mp 249–250 °C; ¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.09 (d, *J* = 1.6 Hz, 2H), 8.35 (d, *J* = 1.6 Hz, 2H), 7.81 (d, *J* = 1.6 Hz, 2H), 7.71 (d, *J* = 1.6 Hz, 2H), 7.59–7.57 (m, 4H), 7.37–7.35 (m, 6H), 1.50 (s, 18H), 1.39 (s, 18H); ¹³C NMR (100 MHz, CDCl₃, 30 °C) δ 149.2, 148.9, 137.9, 132.9, 131.8, 131.6, 130.0, 128.4, 128.1, 126.1, 124.8, 124.6, 123.7, 123.5, 123.0, 115.9, 93.9, 90.4, 35.02, 35.00, 31.5, 31.4; IR (KBr) 3053, 2961, 2905, 2868, 2179, 1594, 1479, 1464, 1362, 1246, 1212, 883, 754 cm⁻¹; HRMS (FAB) *m/z* Calcd for C₅₆H₅₄ [M⁺]: 726.4226, Found: 726.4216.

2,5,9,12-Tetra-*tert*-butyl-7,14-bis[[4-(*N,N*-dimethylamino)phenyl]ethynyl]zethrene (2b)

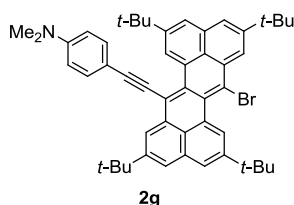
A solution of **4b** (43.7 mg, 56.1 μmol), [4-(*N,N*-dimethylamino)phenyl]acetylene⁴ (97.8 mg, 673 μmol), Pd(PPh₃)₄ (20.7 mg, 17.9 μmol) and CuI (6.7 mg, 35.1 μmol) in degassed Et₃N (6 mL) was stirred under an argon atmosphere at room temperature for 6 h. The solvent was removed under reduced pressure and the product was purified by silica-gel column chromatography (hexanes : CHCl₃ = 1 : 1). The crude product was subjected to preparative GPC separation for further purification to afford 32.6 mg (71%) of **2b** as a blue solid. mp 195–196 °C; ¹H NMR (400 MHz, CDCl₃, 30 °C) δ 9.17 (d, *J* = 1.6 Hz, 2H), 8.37 (d, *J* = 1.6 Hz, 2H), 7.78 (d, *J* = 1.6 Hz, 2H), 7.67 (d, *J* = 1.6 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 4H), 6.69 (d, *J* = 8.8 Hz, 4H), 3.02 (s, 12H), 1.50 (s, 18H), 1.43 (s, 18H); ¹³C NMR (100 MHz, CDCl₃, 30 °C) δ 150.0, 149.0, 148.7, 136.7, 133.1, 132.9, 132.0, 130.4, 125.8, 125.0, 123.9, 123.0, 122.8, 116.3, 111.9, 110.8, 95.5, 88.5, 40.2, 35.04, 34.99, 31.6, 31.5; IR (KBr) 3093, 3043, 2959, 2901, 2865, 2804, 2160, 1604, 1529, 1479, 1443, 1358, 1189, 1164, 883, 814 cm⁻¹; HRMS (FAB) *m/z* Calcd for C₆₀H₆₄N₂ [M⁺]: 812.5070, Found: 812.5097.

2,5,9,12-Tetra-*tert*-butyl-7,14-bis[(dinitrophenyl)ethynyl]zethrene (2c)

A solution of **4b** (40.3 mg, 51.7 μmol), (4-nitrophenyl)acetylene⁵ (39.4mg, 268 μmol), Pd(PPh₃)₄ (11.9 mg, 10.3 μmol) and CuI (3.2 mg, 17 μmol) in Et₃N (13 mL) was stirred under an argon atmosphere at a room temperature for 2.5 h. After the solvent was removed under reduced pressure, the residue was subjected to silica-gel column chromatography (hexanes : CHCl₃ = 1 : 1) to afford 27.1 mg (64%) of **2c** as a blue solid. mp 255 °C dec.; ¹H NMR (400 MHz, CDCl₃, 30 °C) δ 8.95 (d, *J* = 1.6 Hz, 2H), 8.28 (d, *J* = 1.6 Hz, 2H), 8.26 (d, *J* = 9.2 Hz, 4H), 7.88 (d, *J* = 1.6 Hz, 2H), 7.78 (d, *J* = 1.6 Hz, 2H), 7.69 (d, *J* = 9.2 Hz, 4H), 1.51 (s, 18H), 1.39 (s, 18H); ¹³C NMR (100 MHz, CDCl₃, 30 °C) δ 149.5, 149.2, 146.9, 139.2, 133.0, 132.3, 131.1, 130.4, 129.6, 126.5, 125.4, 124.6, 124.2, 123.8, 123.2, 115.3, 96.1, 91.6, 35.08, 35.05,

31.5, 31.4; IR (KBr) 2961, 2907, 2865, 2172, 1591, 1519, 1477, 1362, 1339, 1105, 883, 852, 748 cm^{-1} ; HRMS (EI) m/z Calcd for $\text{C}_{36}\text{H}_{52}\text{O}_4\text{N}_2$ [M^+]: 816.3927, Found: 816.3908.

7-Bromo-2,5,9,12-tetra-*tert*-butyl-14-[[4-(*N,N*-dimethylamino)phenyl]ethynyl]zethrene (2g)



To a mixture of **4c** (101 mg, 148 μmol), $\text{Pd}(\text{PPh}_3)_4$ (51.2 mg, 44.4 μmol) and CuI (9.9 mg, 52 μmol) was added a solution of [4-(*N,N*-dimethylamino)phenyl]acetylene (3.4 mM, 103 μmol) in degassed Et_3N (30 mL) under an argon atmosphere. After stirring at room temperature for 2 h, the solvent was removed under reduced pressure. The residue was subjected to silica-gel column chromatography (hexanes : CHCl_3 = 1 : 1) to afford 27.7 mg of a reddish solid product containing **2g**. This product was subjected to next Sonogashira coupling without further purification. 25.2 mg (21%) of **2b** was also obtained and 35.4 mg (35 %) of the starting material **4c** was recovered.

2,5,9,12-Tetra-*tert*-butyl-7-[[4-(*N,N*-dimethylamino)phenyl]ethynyl]-14-[(nitrophenyl)ethynyl]zethrene (2d)

To a mixture of **2g** (45.0 mg, 60.1 μmol), $\text{Pd}(\text{PPh}_3)_4$ (24.1 mg, 21.0 μmol) and CuI (4.6 mg, 24 μmol) was added a solution of (4-nitrophenyl)acetylene (6.84 mM, 171 μmol) in degassed Et_3N (25 mL) under an argon atmosphere. After stirring at room temperature for 2.5 h, the solvent was removed under reduced pressure. The residue was subjected to silica-gel column chromatography (hexanes : CHCl_3 = 1 : 1) followed by preparative GPC to afford 39.0 mg (80%) of **2e** as a dark blue solid. mp 138–140 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3 , 30 $^\circ\text{C}$) δ 9.19 (s, 1H), 8.93 (d, J = 1.6 Hz, 1H), 8.45 (d, J = 1.2 Hz, 1H), 8.24 (d, J = 8.8 Hz, 2H), 8.20 (s, 1H), 7.85 (d, J = 1.2 Hz, 1H), 7.80 (s, 1H), 7.74 (s, 1H), 7.71 (s, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 3.03 (s, 6H), 1.52 (s, 9H), 1.50 (s, 9H), 1.44 (s, 9H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3 , 30 $^\circ\text{C}$) δ 150.1, 149.4, 149.1, 149.0, 148.7, 146.7, 139.9, 136.1, 133.2, 133.1, 132.8, 132.2, 131.7, 131.4, 130.8, 130.2, 129.9, 126.3, 125.9, 125.2, 124.9, 124.7, 124.3, 123.9, 123.8, 123.6, 123.5, 122.1, 117.4, 114.2, 111.9, 110.3, 97.1, 96.4, 91.1, 88.1, 40.2, 35.09, 35.07, 35.02, 34.97, 31.52, 31.47, 31.44, 31.42; IR (KBr) 2961, 2362, 2168, 1606, 1591, 1520, 1338, 883, 853, 815 cm^{-1} ; HRMS (EI) m/z Calcd for $\text{C}_{58}\text{H}_{58}\text{N}_2\text{O}_2$ [M^+] 814.4498, Found: 814.4528.

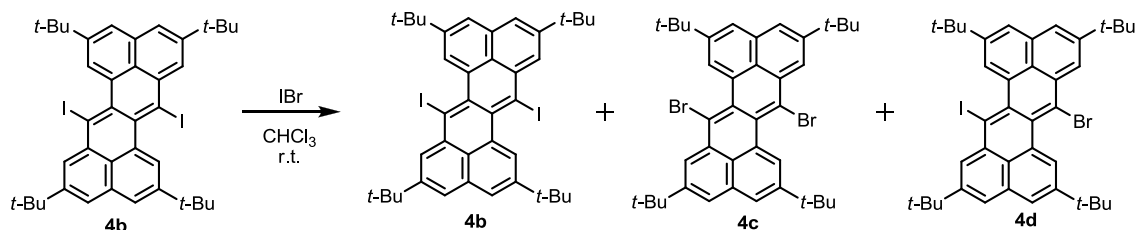
2,5,9,12-Tetra-*tert*-butyl-7,14-bis[(trimethylsilyl)ethynyl]zethrene (2e)

To a solution of **4b** (20.5 mg, 26.3 μmol), $\text{Pd}(\text{PPh}_3)_4$ (7.6 mg, 6.6 μmol) and CuI (1.5 mg, 7.9 μmol) in degassed Et_3N (15 mL) was added (trimethylsilyl)acetylene (69 μL , 48 mg, 260 μmol) under an argon atmosphere. After stirring at 60 $^\circ\text{C}$ for 6 h, the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography (hexanes) to afford 9.8 mg (52%) of **2e** as a purple solid. mp 189 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3 , 30 $^\circ\text{C}$) δ 9.05 (s, 2H), 8.23 (s, 2H), 7.79 (s, 2H), 7.67 (s, 2H), 1.49 (s, 18H), 1.48 (s, 18H), 0.33 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3 , 30 $^\circ\text{C}$) δ 149.0, 148.6, 138.0, 132.7, 131.6, 129.6, 126.6, 124.6, 124.5, 123.42, 123.35, 115.9, 105.8, 100.1, 35.3, 35.0, 31.6, 31.3, 0.5; IR (KBr) 2958, 2902, 2864, 2360, 2121, 1477, 1363, 1249, 842, 758, 647 cm^{-1} ; HRMS (EI) m/z Calcd for $\text{C}_{50}\text{H}_{62}\text{Si}_2$ [M^+] 718.4390, Found: 718.4420.

2,5,9,12-Tetra-tert-butyl-7,14-bis[(tri-iso-propylsilyl)ethynyl]zethrene (2f)

To a solution of **4b** (20.1 mg, 25.7 μmol), $\text{Pd}(\text{PPh}_3)_4$ (7.4 mg, 6.4 μmol) and CuI (1.5 mg, 7.7 μmol) in degassed Et_3N (15 mL) was added (tri-iso-propylsilyl)acetylene (120 μL , 260 μmol) under an argon atmosphere. After stirring at 70 $^\circ\text{C}$ for 8 h, the solvent was removed under reduced pressure. The product was purified by silica-gel column chromatography (hexanes) to afford 9.1 mg (40%) of **2f** as a purple solid. mp 190 $^\circ\text{C}$ dec.; ^1H NMR (400 MHz, CDCl_3 , 30 $^\circ\text{C}$) δ 8.84 (s, 2H), 8.24 (s, 2H), 7.79 (s, 2H), 7.66 (s, 2H), 1.47 (s, 18H), 1.44 (s, 18H), 1.24-1.12 (m, 42H); ^{13}C NMR (100 MHz, CDCl_3 , 30 $^\circ\text{C}$) δ 149.1, 148.7, 139.1, 132.7, 132.0, 129.7, 126.6, 125.1, 124.7, 123.5, 123.2, 115.4, 107.3, 94.3, 35.1, 35.0, 31.6, 31.3, 19.0, 11.9; IR (KBr) 2960, 2865, 2114, 1464, 1363, 1245, 990, 883, 737, 646 cm^{-1} ; HRMS (FAB) m/z Calcd for $\text{C}_{62}\text{H}_{86}\text{Si}_2$ [M^+] 886.6268, Found: 886.6276.

3. Reaction of diiodozethrene **4b** with IBr



Respective amount of IBr (Table below) in CHCl₃ was added to **4b** under argon and the mixture was stirred at room temperature for 2 h. After the mixture was diluted by CHCl₃ it was washed with saturated aqueous Na₂S₂O₃ solution. The aqueous layer was extracted with CHCl₃ twice. The combined organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure. ¹H NMR spectrum of this product exhibited signals assigned to **4b**, **4c** and **4d** from which the relative ratio was determined (Figure S1). Mass spectrum (LDI-TOF) also exhibited molecular ion peak at *m/z* 731.04 corresponding to C₄₀H₄₄BrI⁺.

amount of 4b used / mg (μmol)	amount of IBr used / mg (μmol)	amount and ratio of products 4b , 4c and 4d obtained / mg
4.3 (5.5)	0.57 (2.7)	3.9; 4b : 4c : 4d = 1 : 0.1 : 0.5
18.6 (23.9)	4.2 (0.73)	16.5; 4b : 4c : 4d = 1 : 0.7 : 1.3
40.0 (51.4)	12.8 (61.7)	34.3; 4b : 4c : 4d = 1 : 2.6 : 2

The ratio of **4b**, **4c** and **4d** was estimated from the integrated area of signals at δ 8.53 (**4b**), 8.64 (**4c**) and 8.62 (**4d**) in the ¹H NMR spectrum.

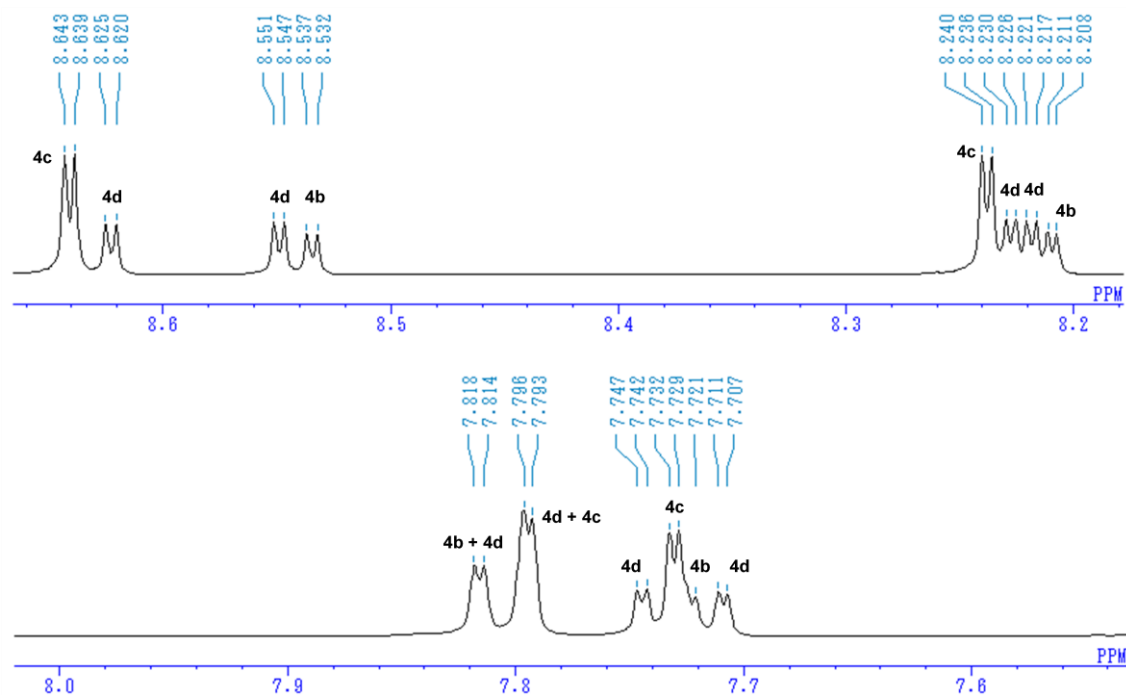


Fig. S1 ¹H NMR spectrum of a mixture of **4b**, **4c** and **4d**

4. UV-vis spectra of **2d** in various solvents

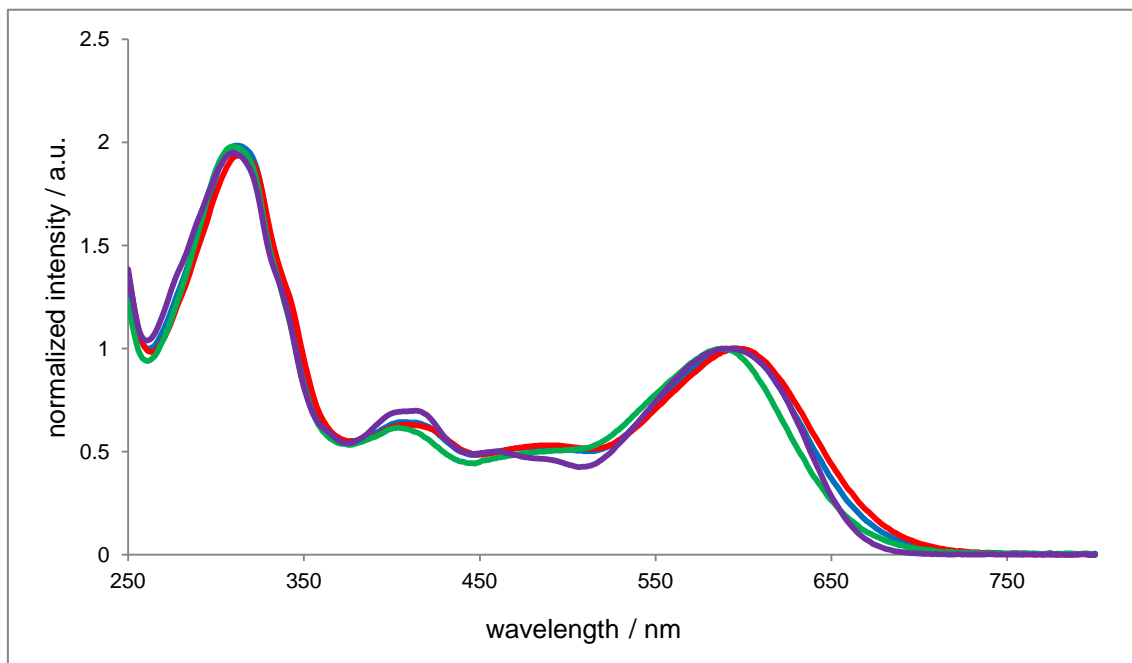


Fig. 2 UV-vis absorption spectra of **2d** in CH_2Cl_2 (red), cyclohexane (purple), THF (blue) and CH_3CN (green)

5. Fluorescence spectra of **2a** and **2b**

Compounds **2a** and **2b** exhibited fluorescence emission at 619 nm ($\lambda_{\text{ex}} = 545$ nm, $\Phi = 0.05$) and 649 nm ($\lambda_{\text{ex}} = 500$ nm, $\Phi = 0.05$), respectively, whereas **2c** and **2d** did not. Measurements were performed with 5.36×10^{-6} M solution for **2a** and 8.73×10^{-6} M solution for **2b** under air without degassing. Quantum yields were determined relative to rohdamine B in EtOH ($\Phi = 0.70$).⁶

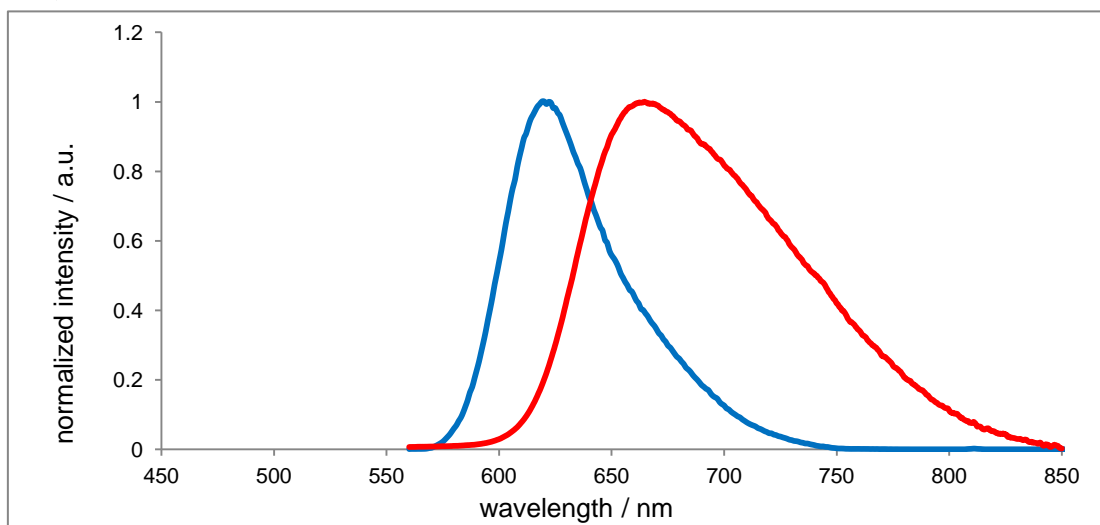
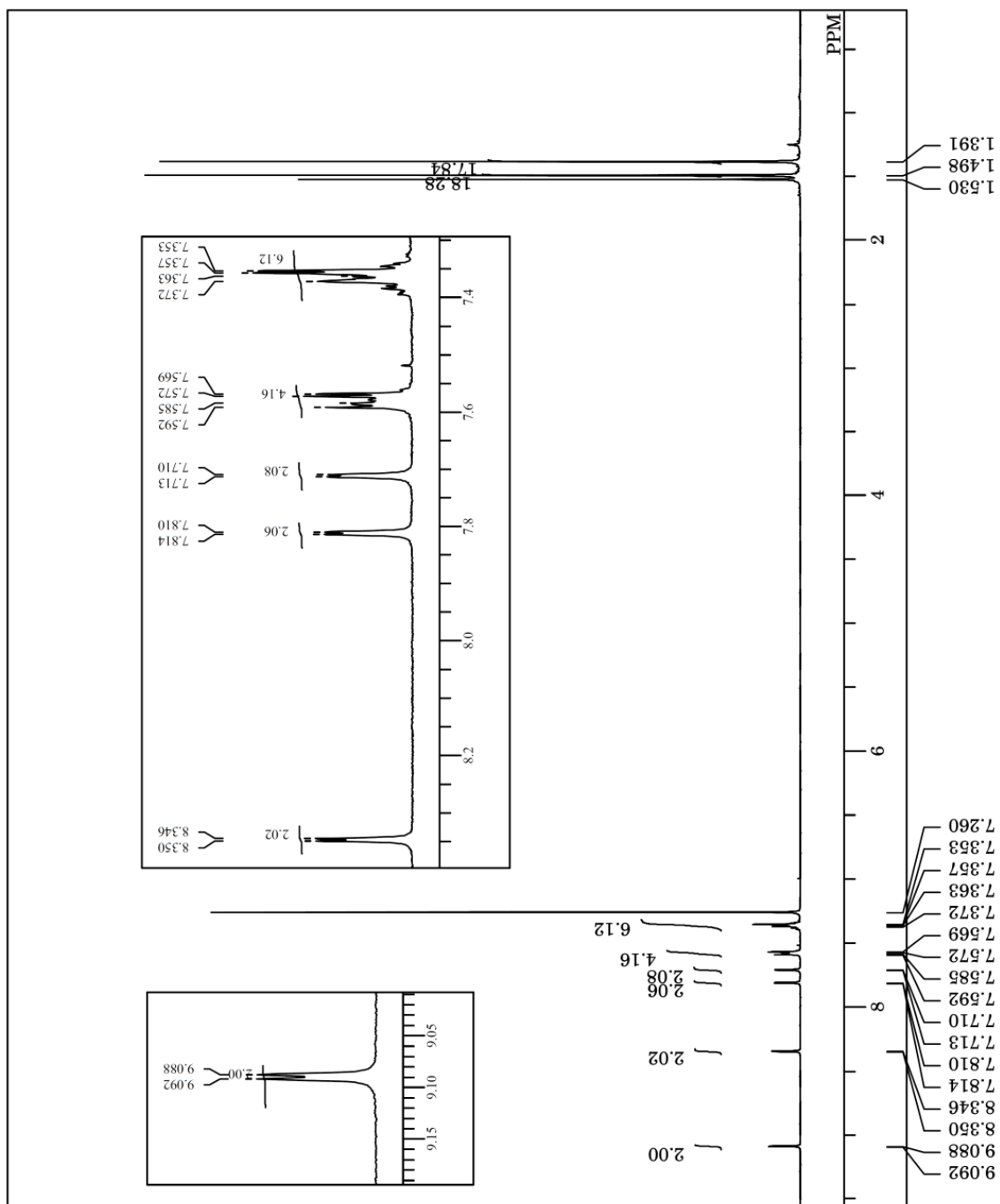


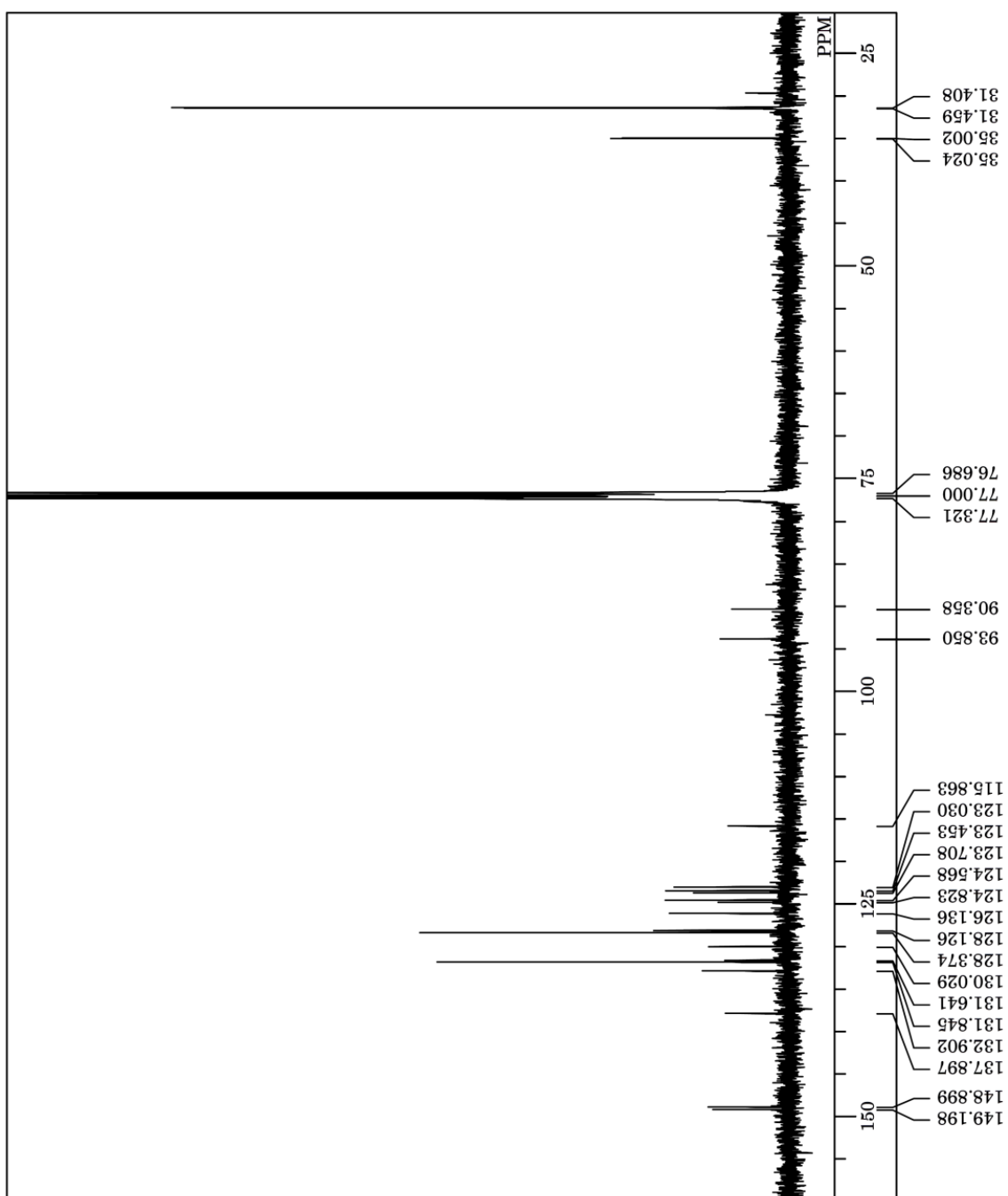
Fig. S3 Fluorescence spectra of **2a** (blue) and **2b** (red) recorded in CH_2Cl_2

6. ^1H NMR and ^{13}C NMR spectra for 2a-f, 3b, 4b-c, 5 and 6

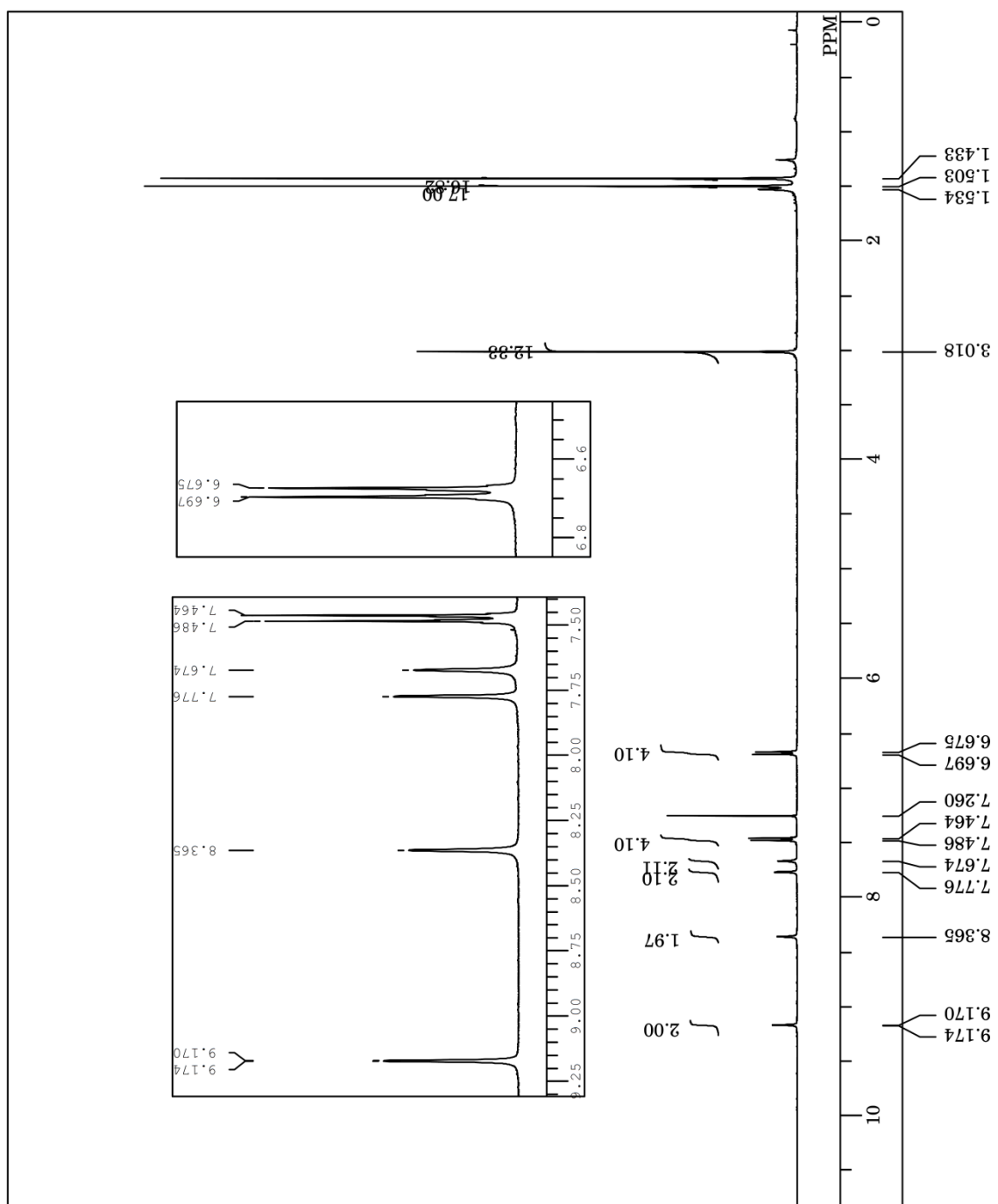
^1H NMR spectrum of 2a



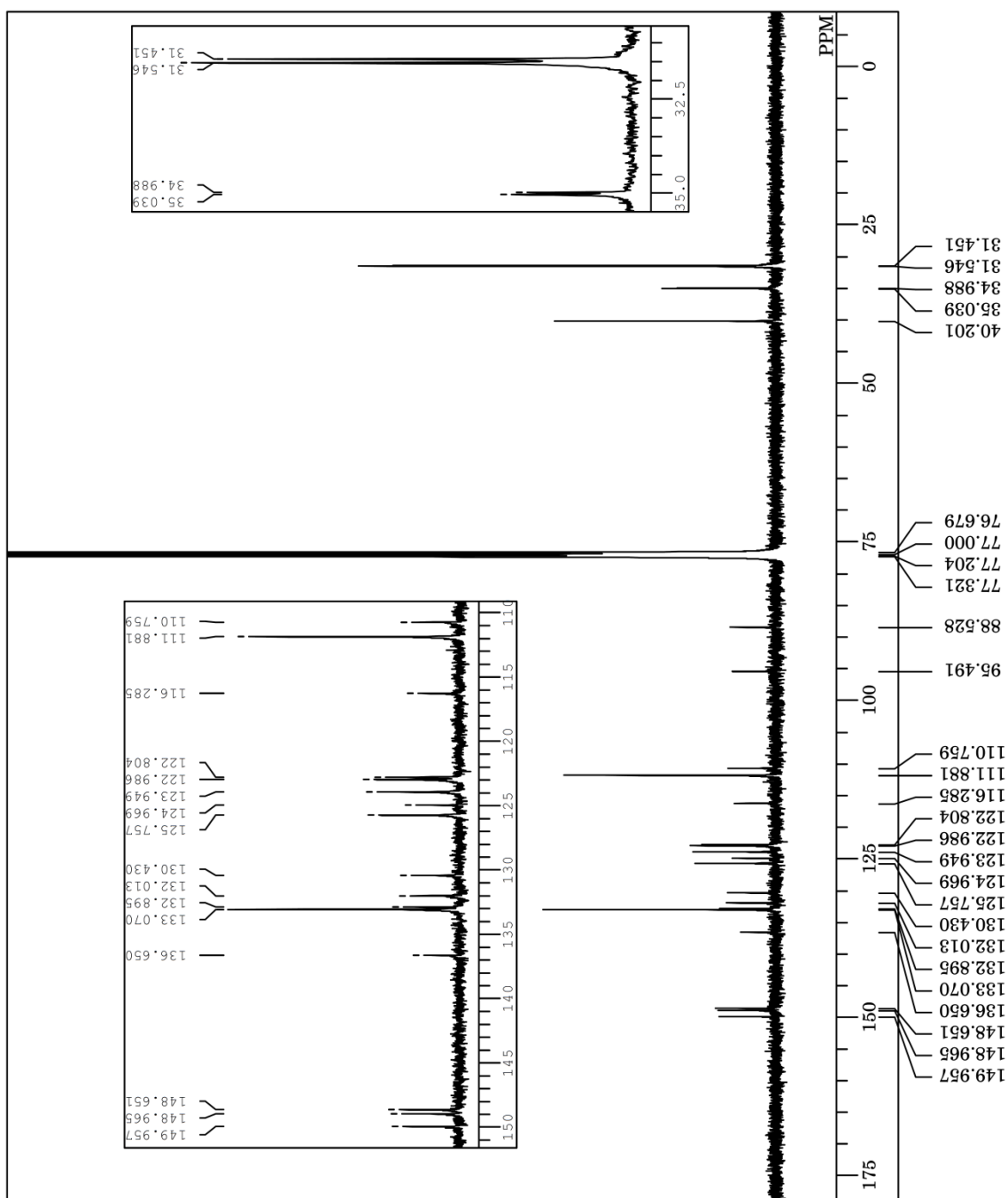
^{13}C NMR spectrum of **2a**



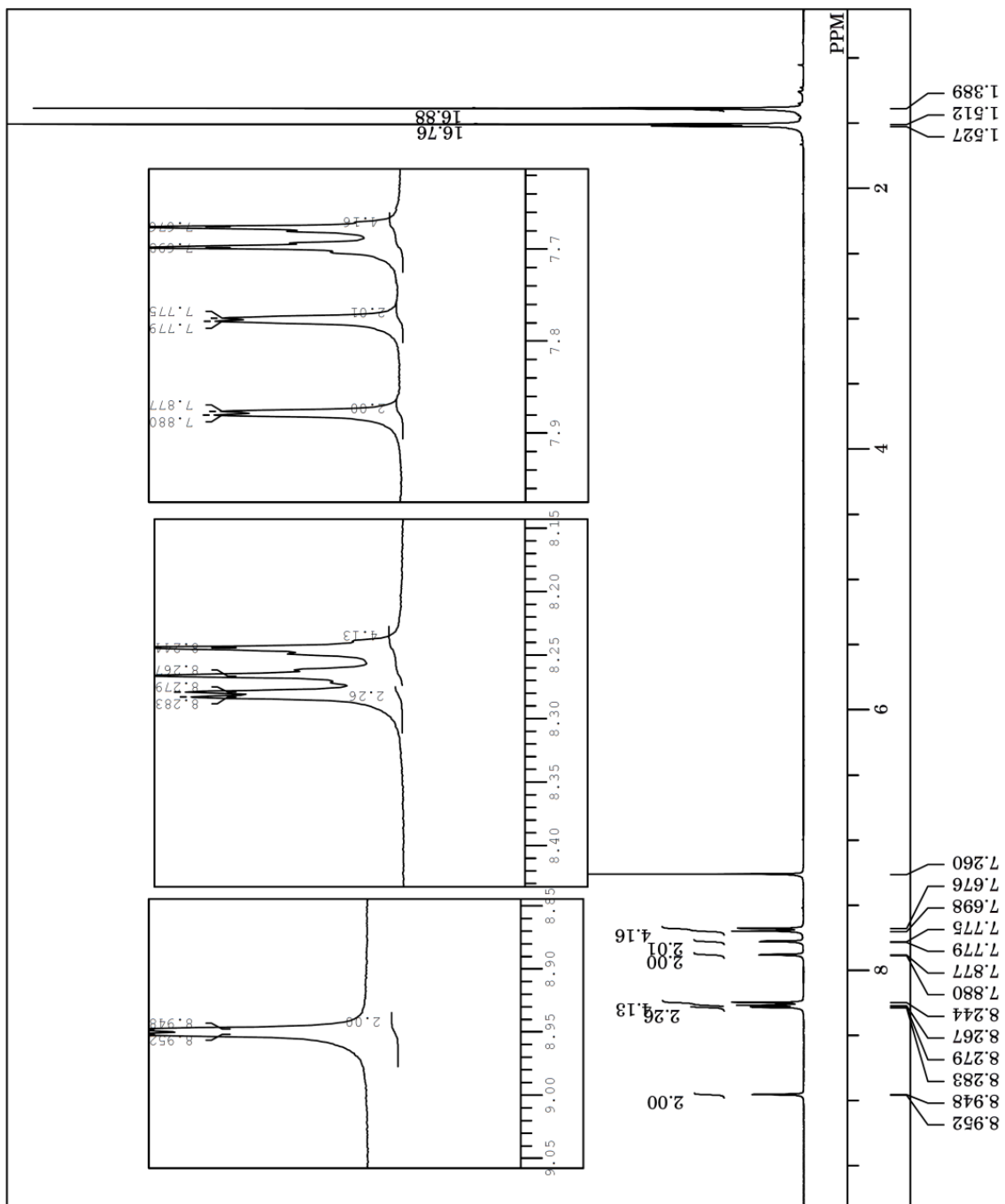
^1H NMR spectrum of **2b**



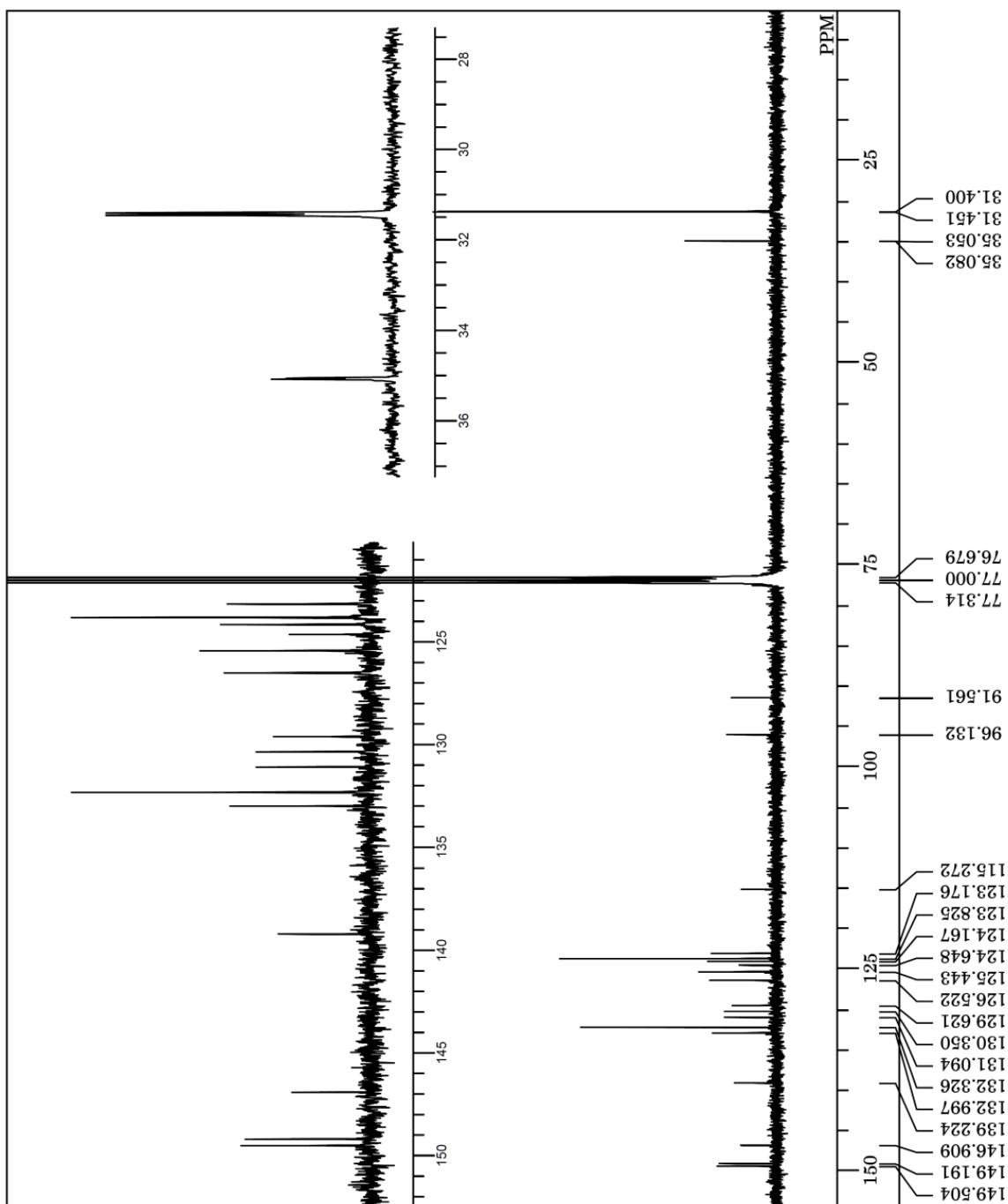
^{13}C NMR spectrum of **2b**



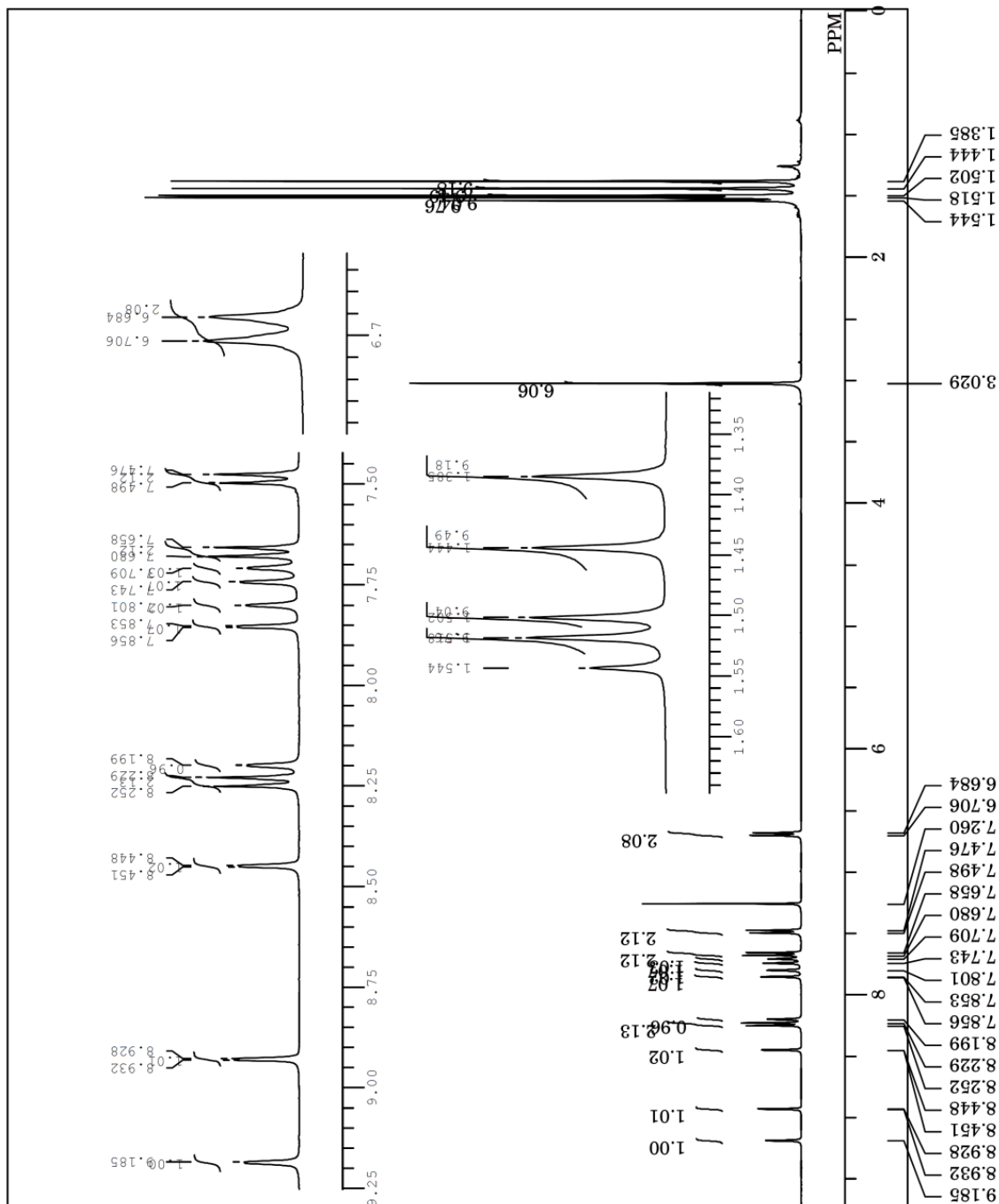
¹H NMR spectrum of **2c**



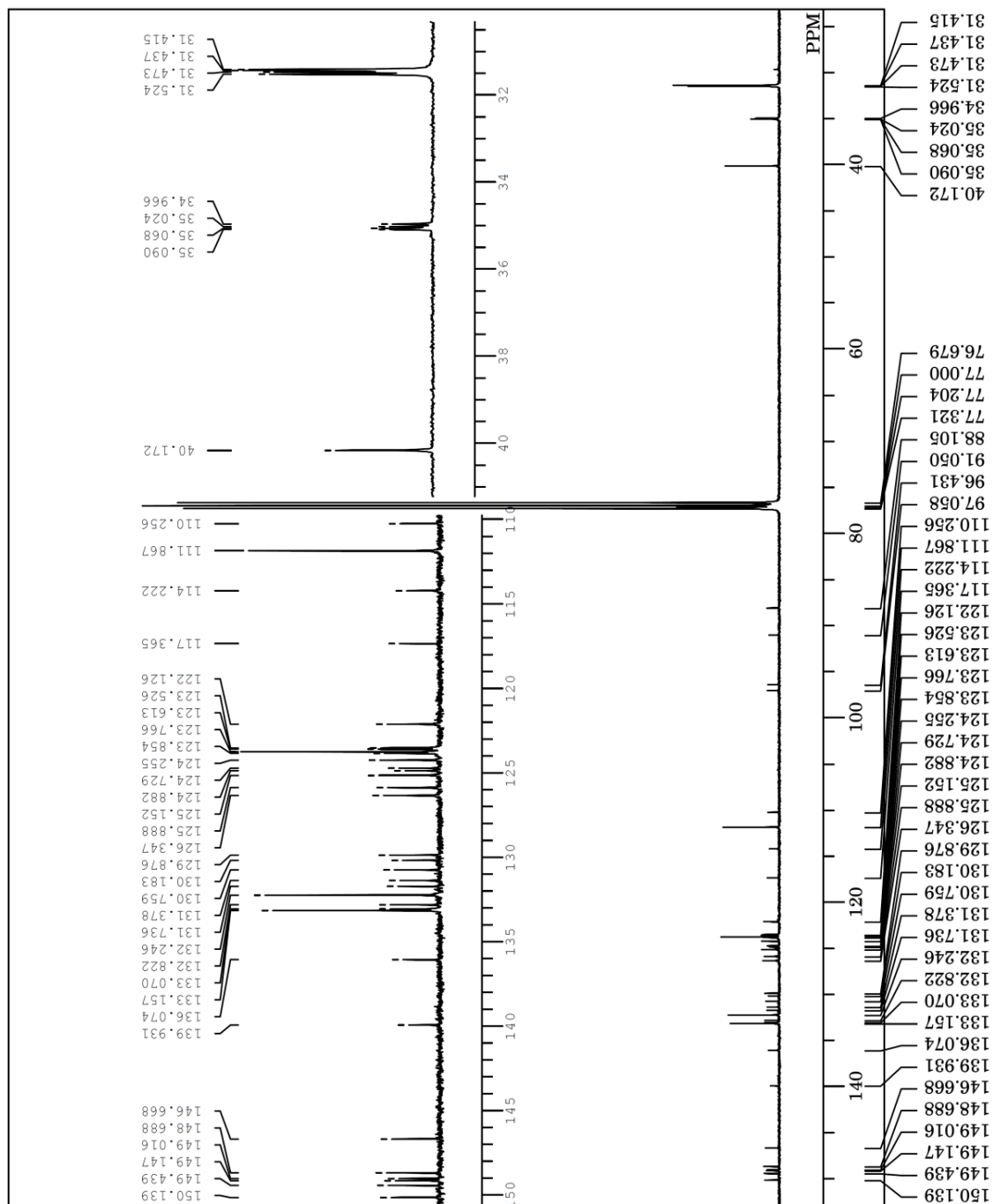
^{13}C NMR spectrum of **2c**



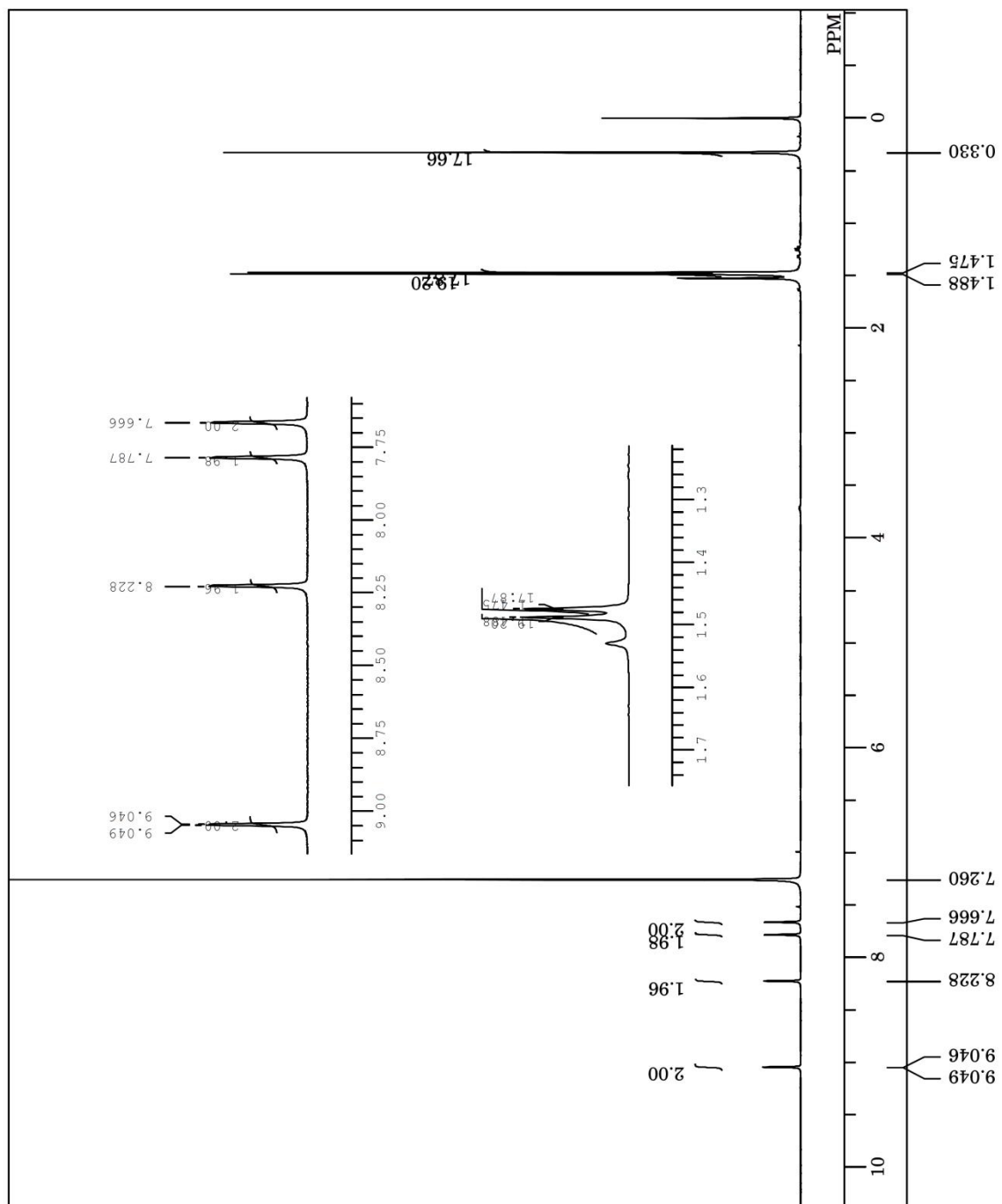
^1H NMR spectrum of **2d**



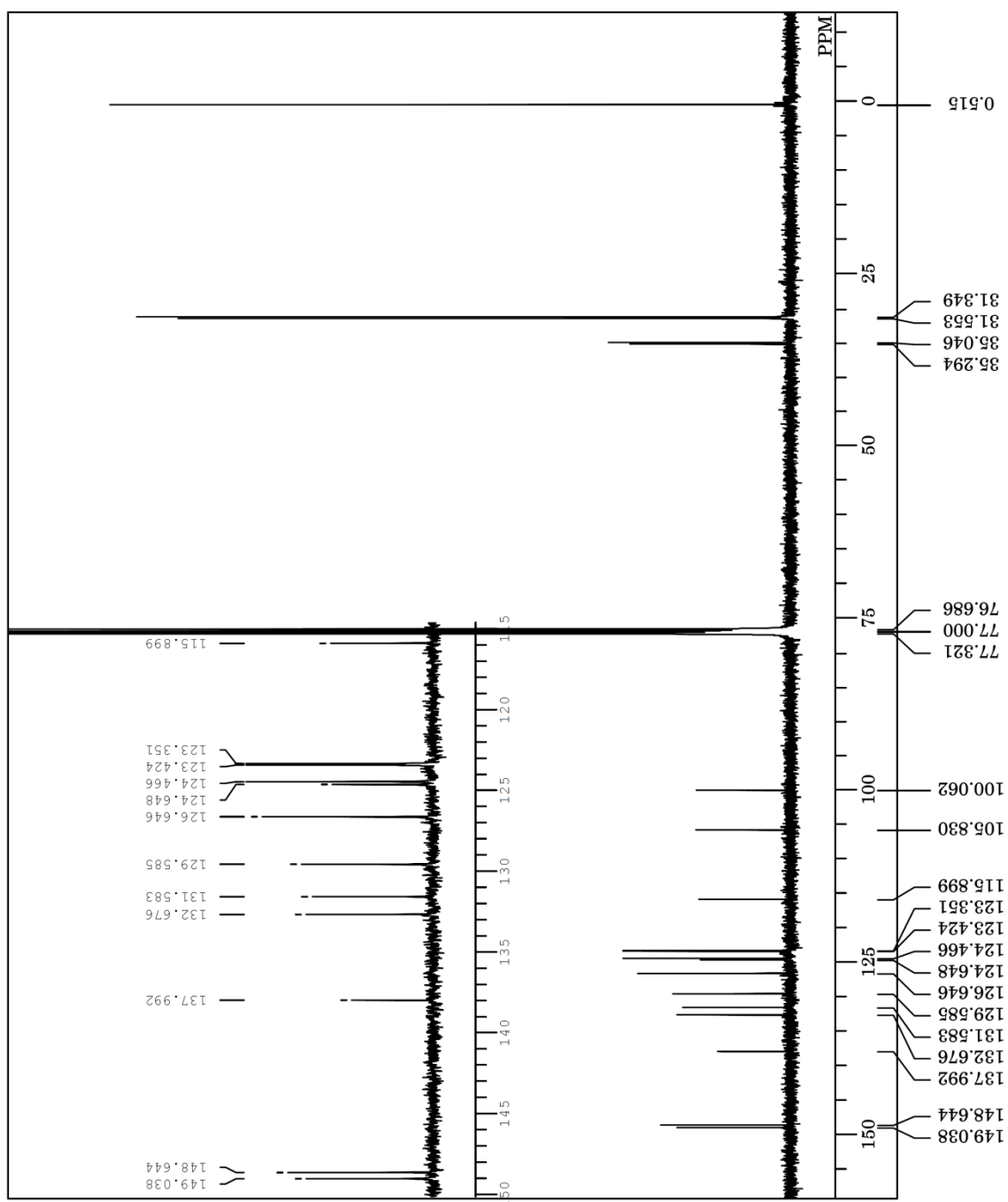
^{13}C NMR spectrum of **2d**



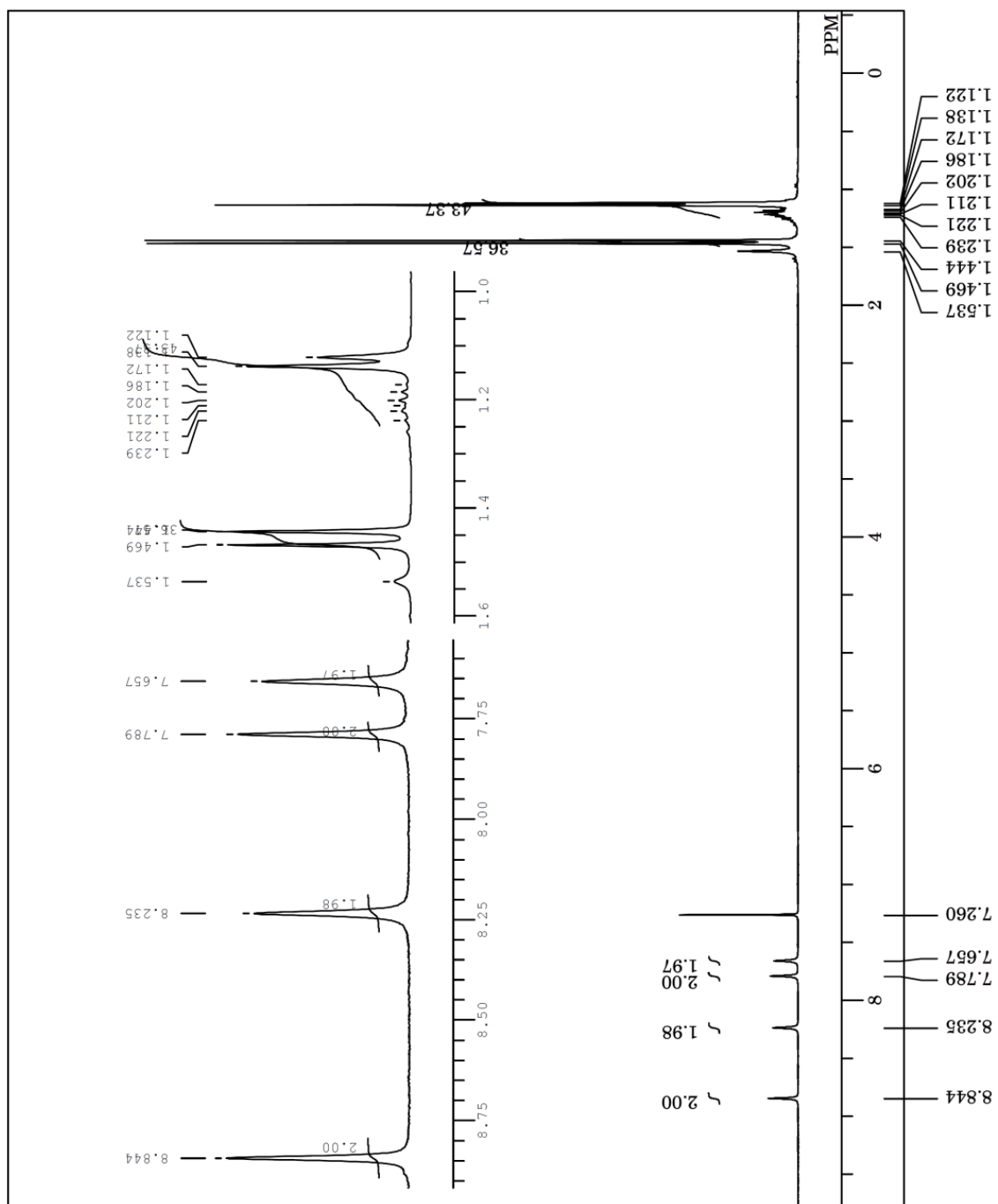
^1H NMR spectrum of **2e**



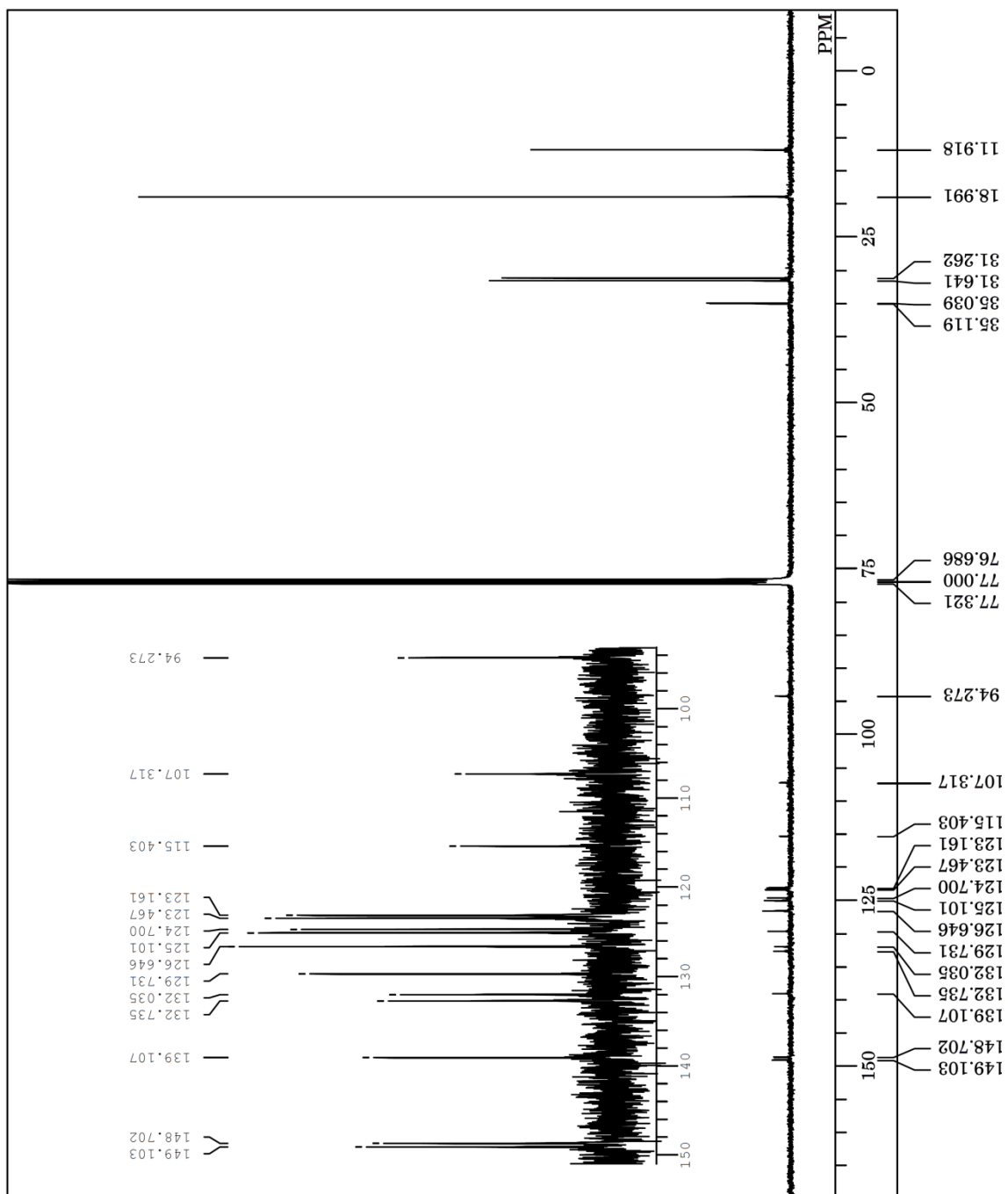
^{13}C NMR spectrum of **2e**



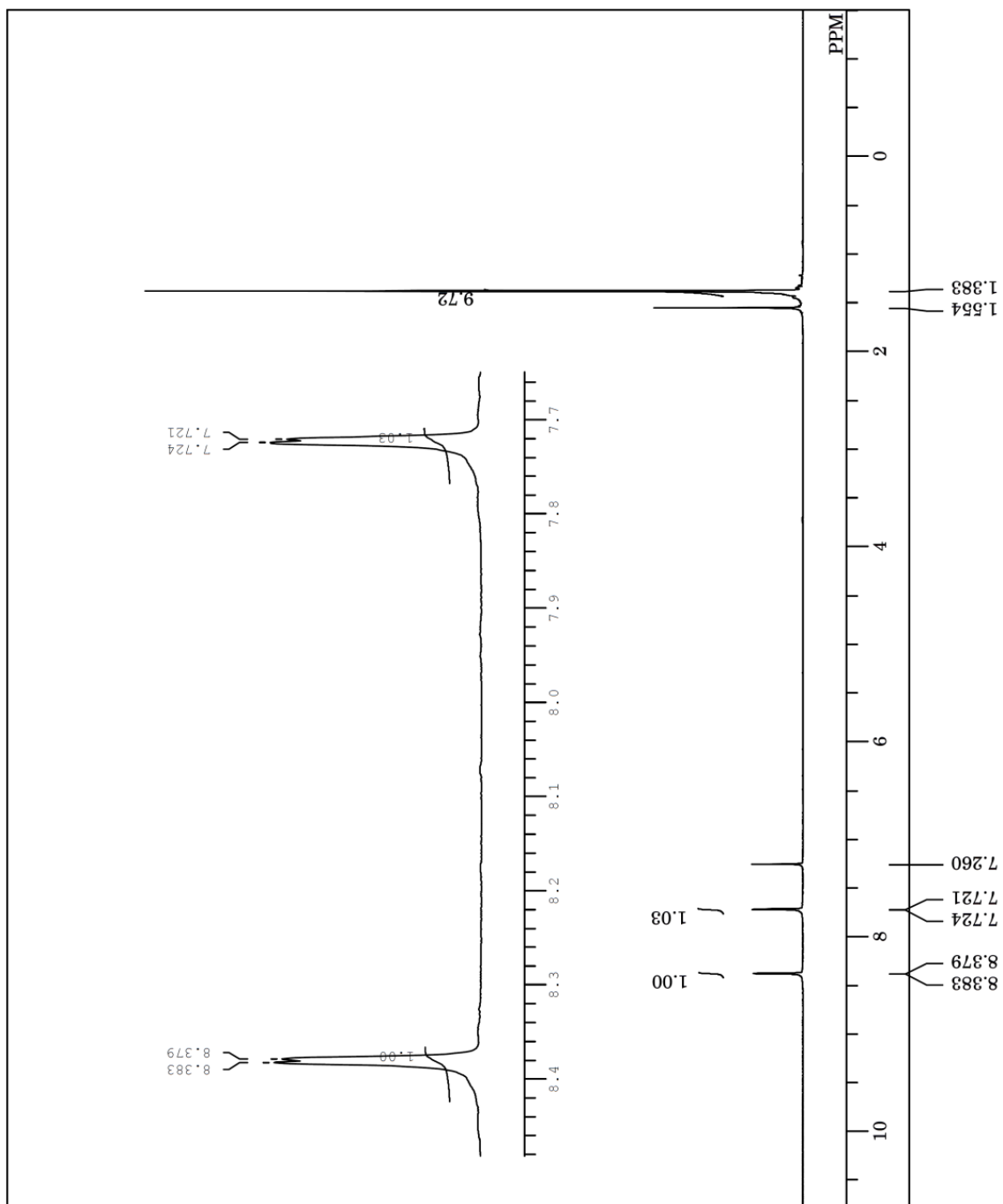
^1H NMR spectrum of **2f**



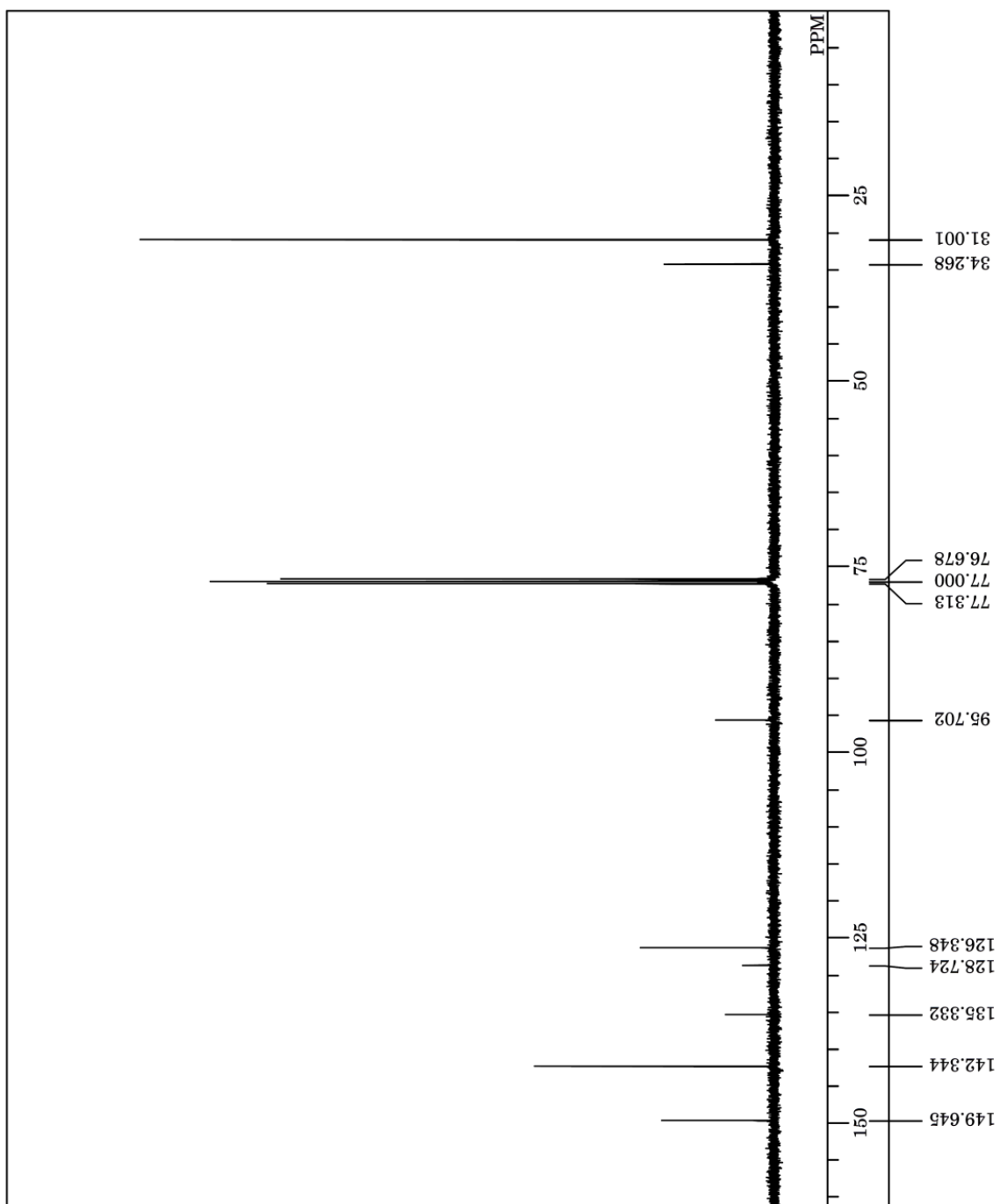
^{13}C NMR spectrum of **2f**



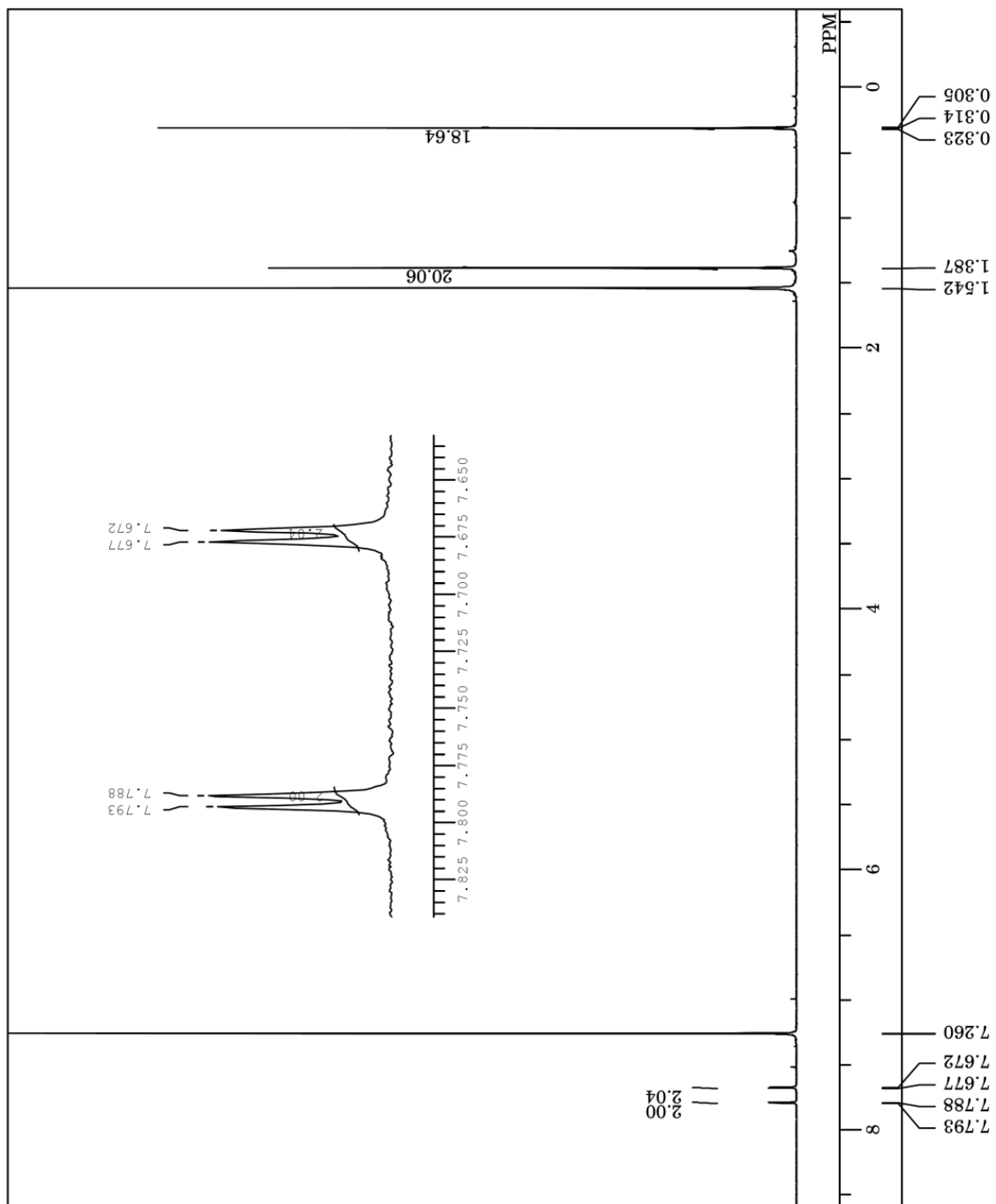
^1H NMR spectrum of **6**



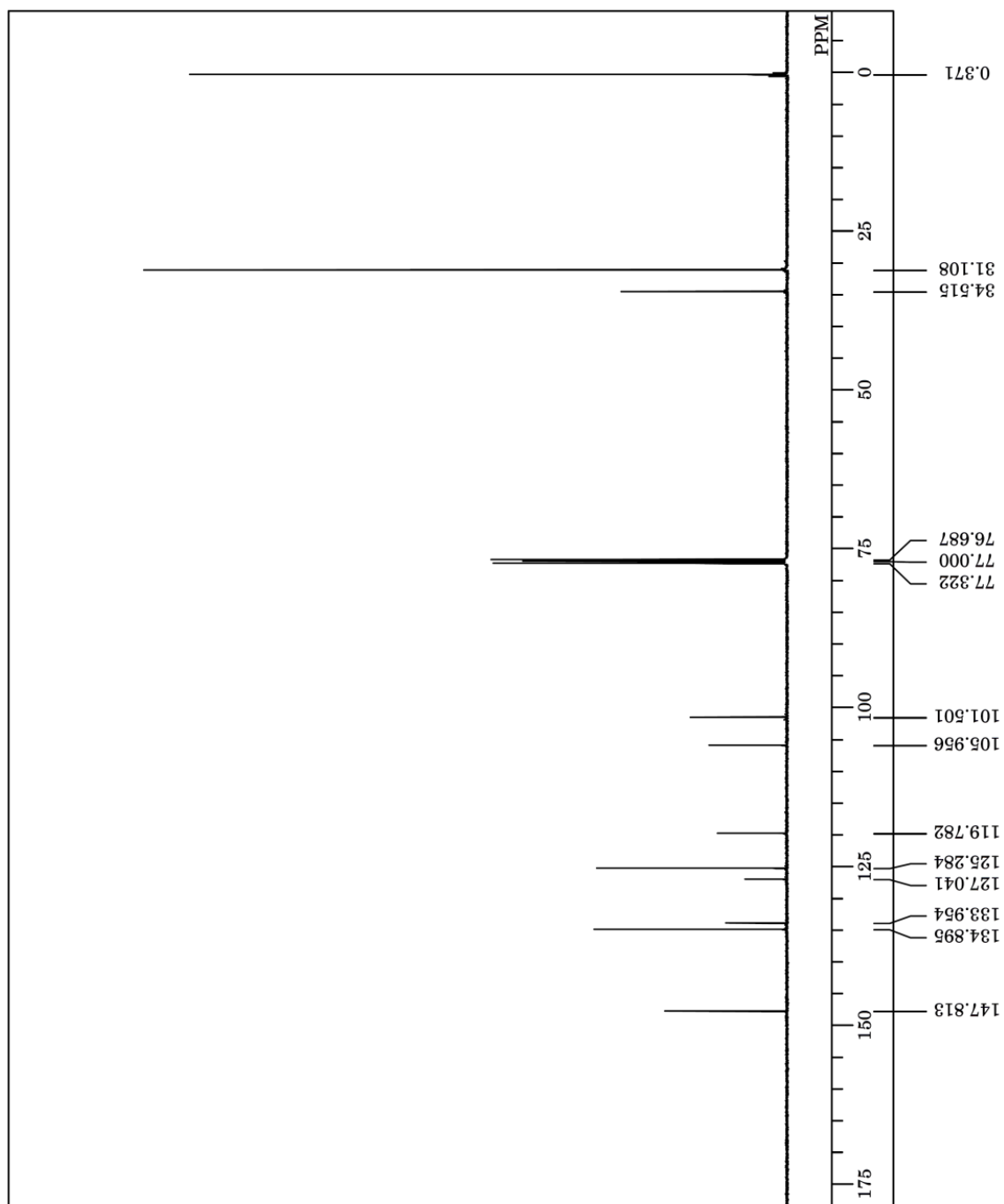
^{13}C NMR spectrum of **6**



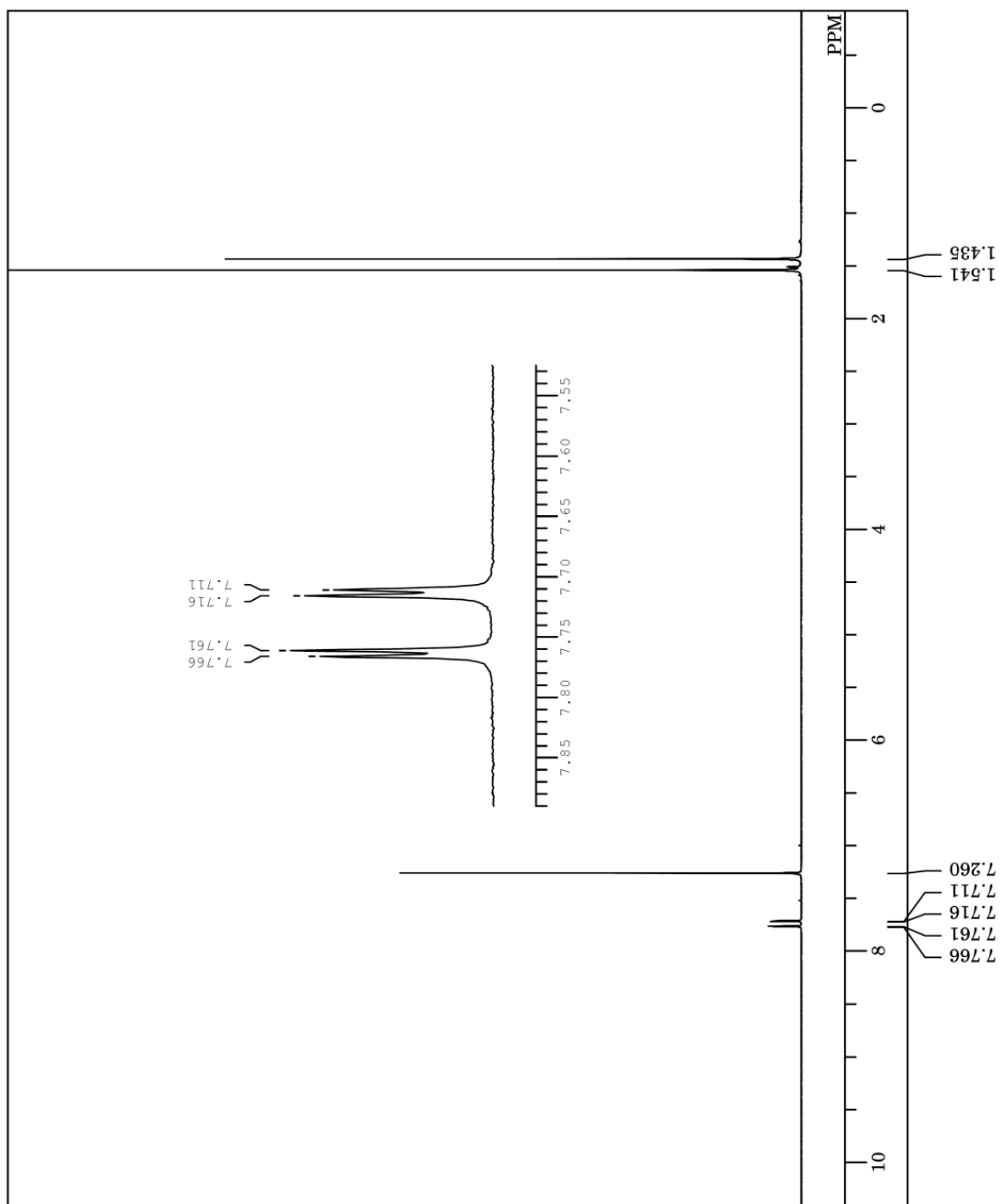
^1H NMR spectrum of **7**



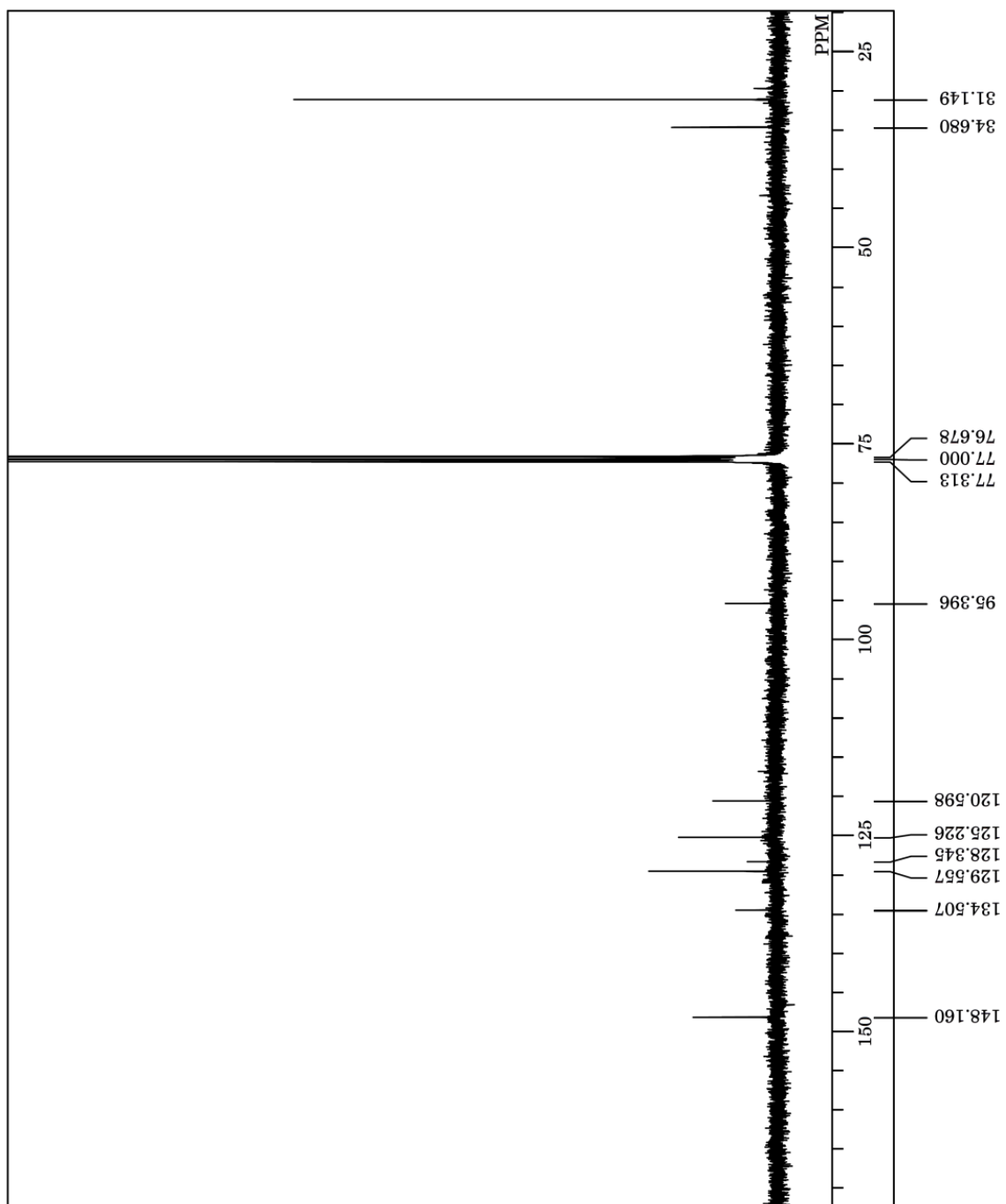
^{13}C NMR spectrum of **7**



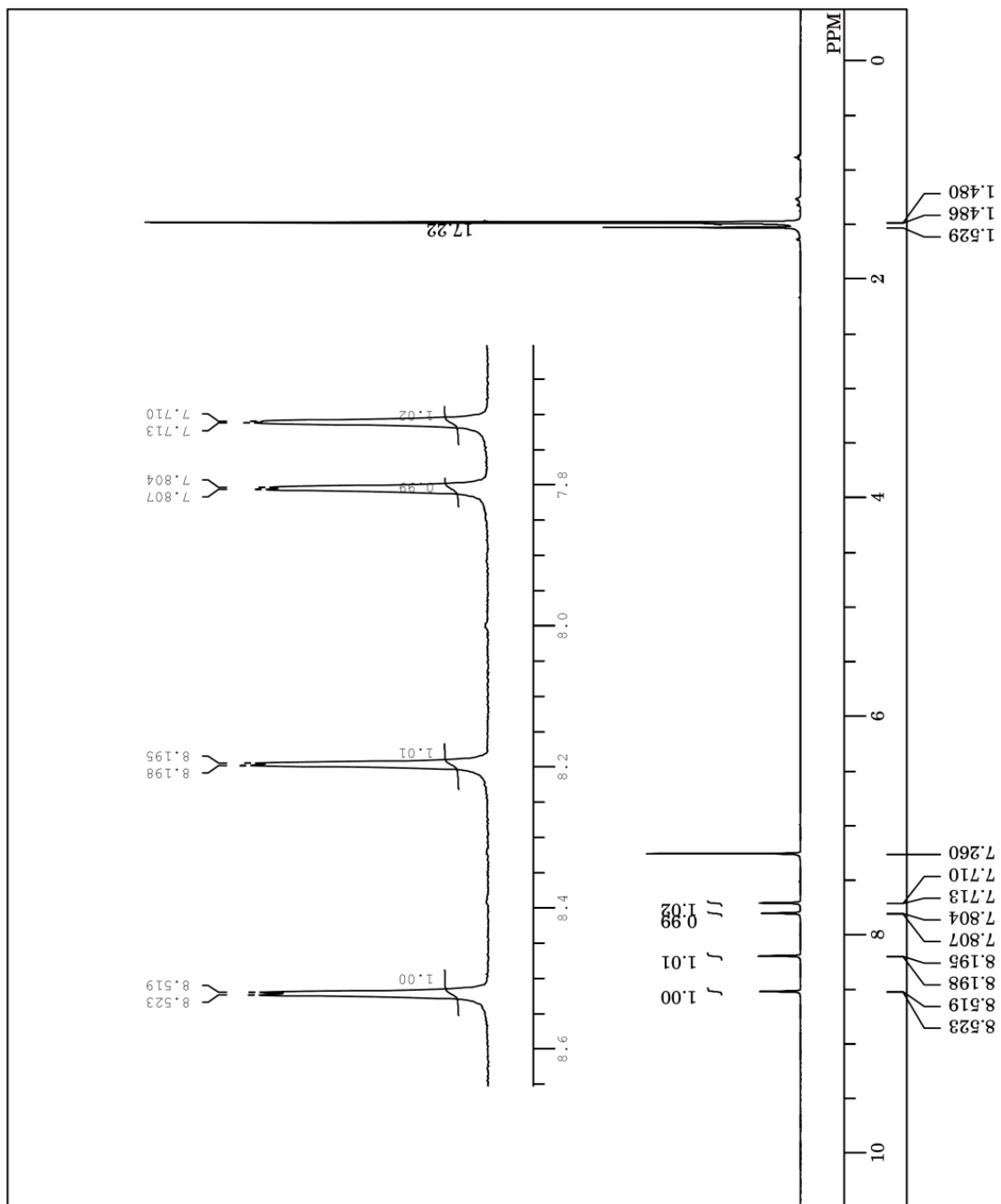
^1H NMR spectrum of **3b**



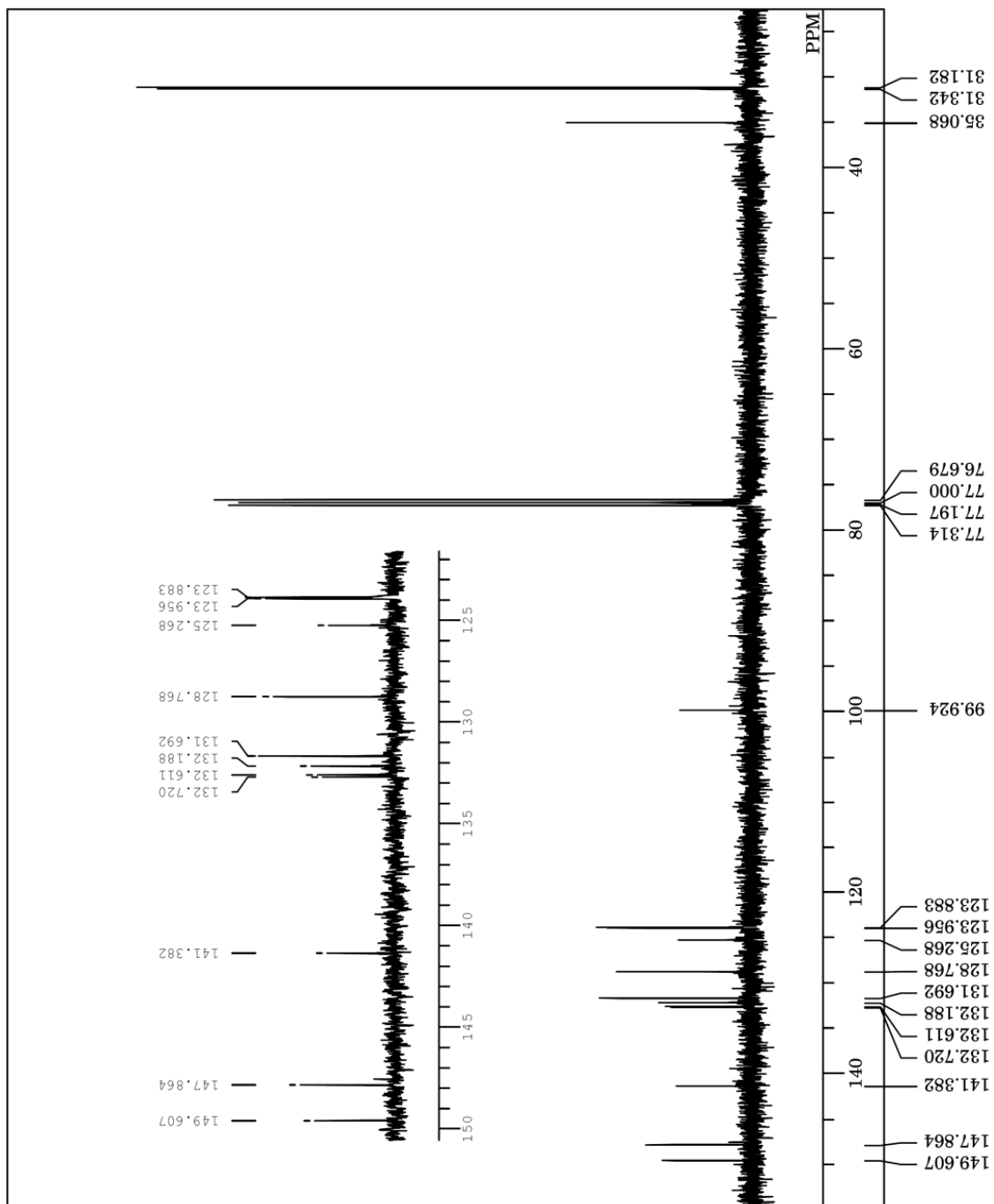
^{13}C NMR spectra of **3b**



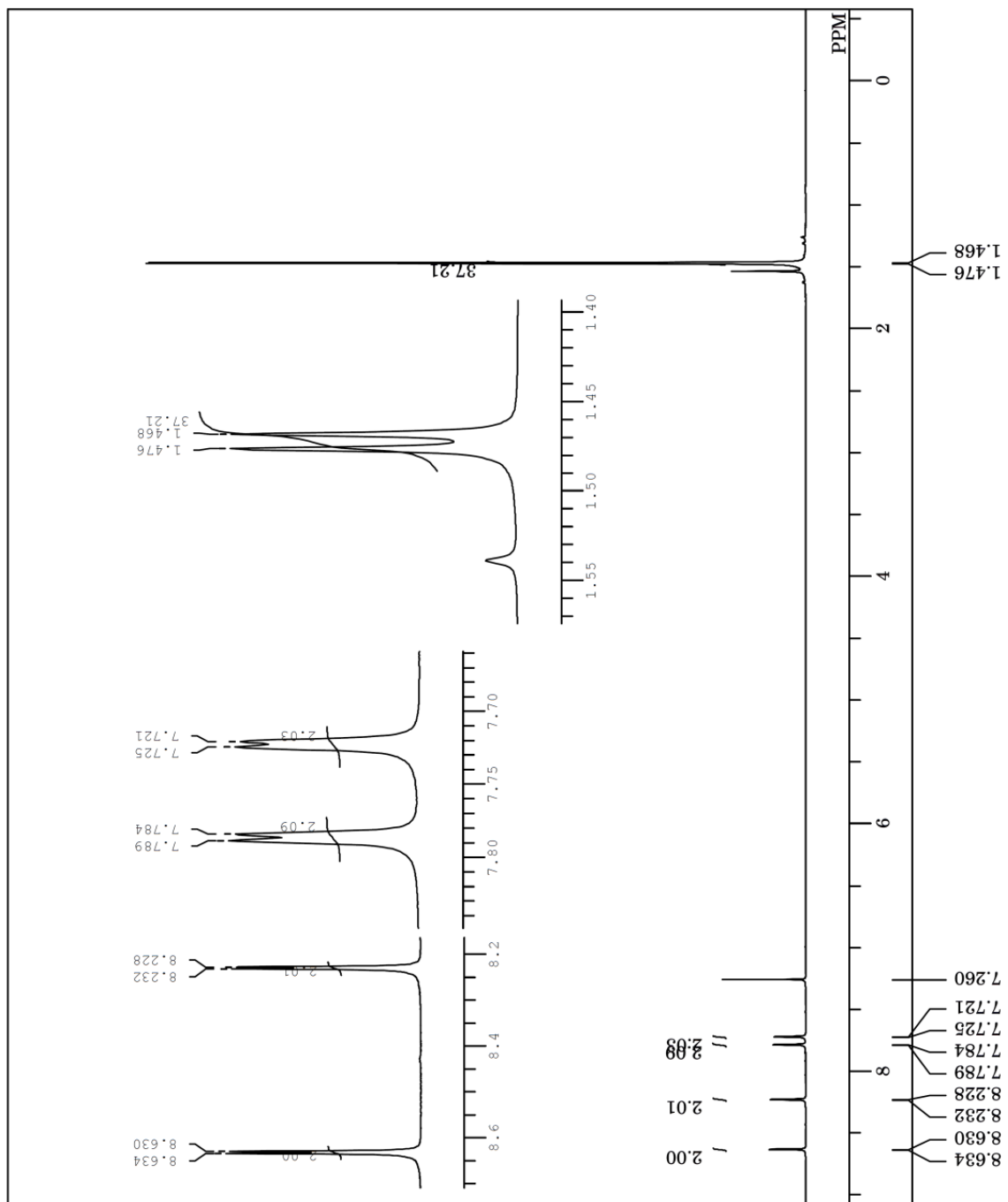
^1H NMR spectrum of **4b**



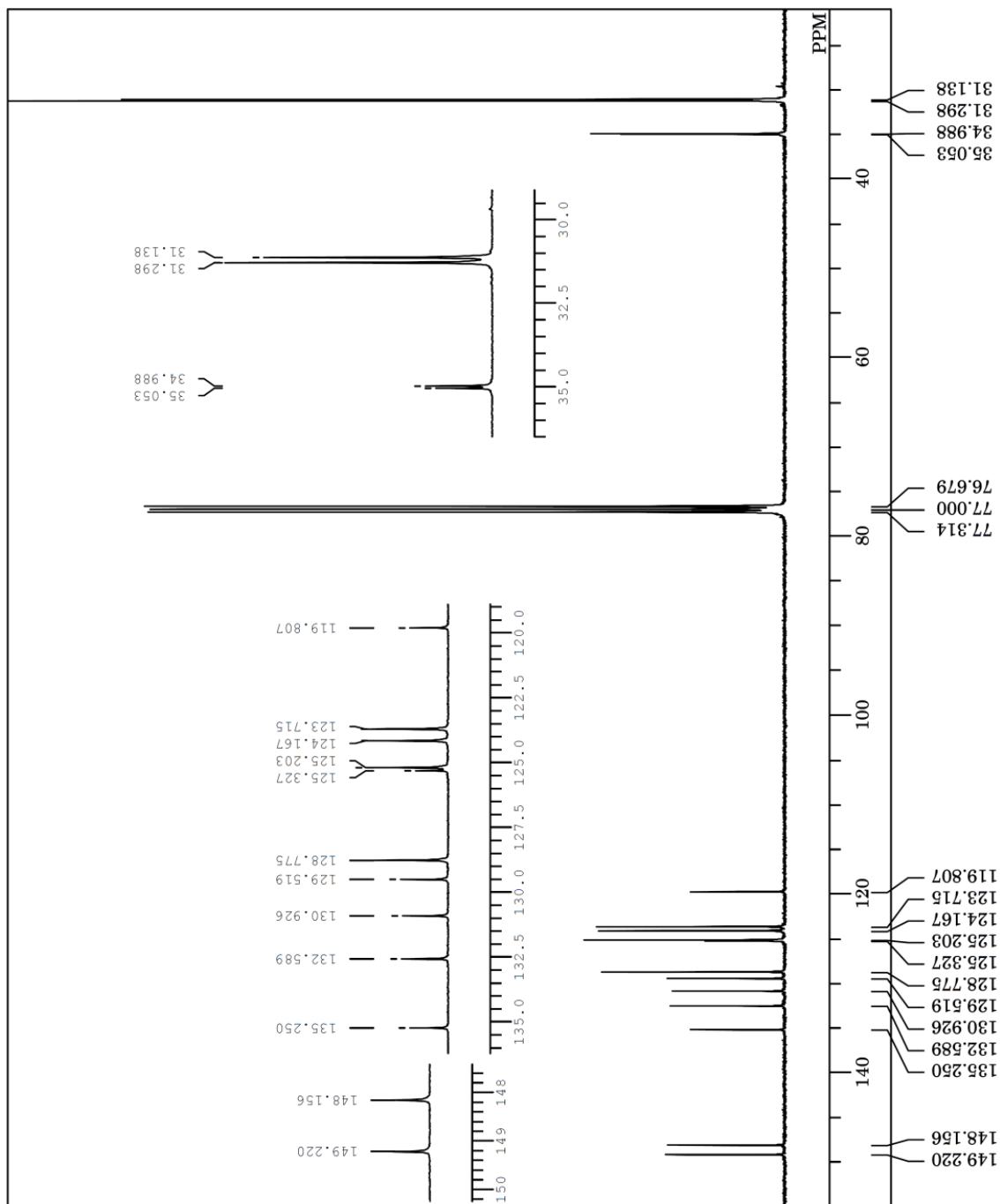
^{13}C NMR spectra of **4b**



^1H NMR spectrum of **4c**



^{13}C NMR spectrum of **4c**



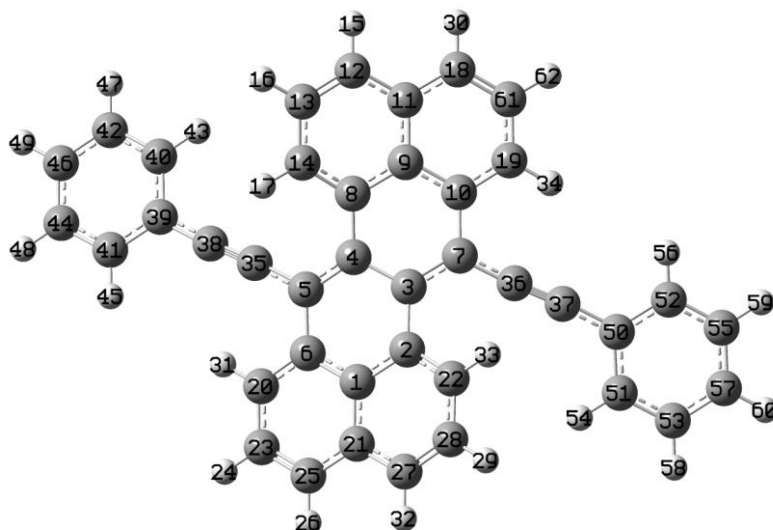
7. Cartesian coordinates for optimized geometry of zethrene derivatives

tert-Butyl groups were replaced by hydrogen for simplicity reason.

7,14-Bis(phenylethynyl)zethrene

C₂ symmetry

SCF Done: E (RB+HF-LYP) = -1537.45034023



Standard orientation

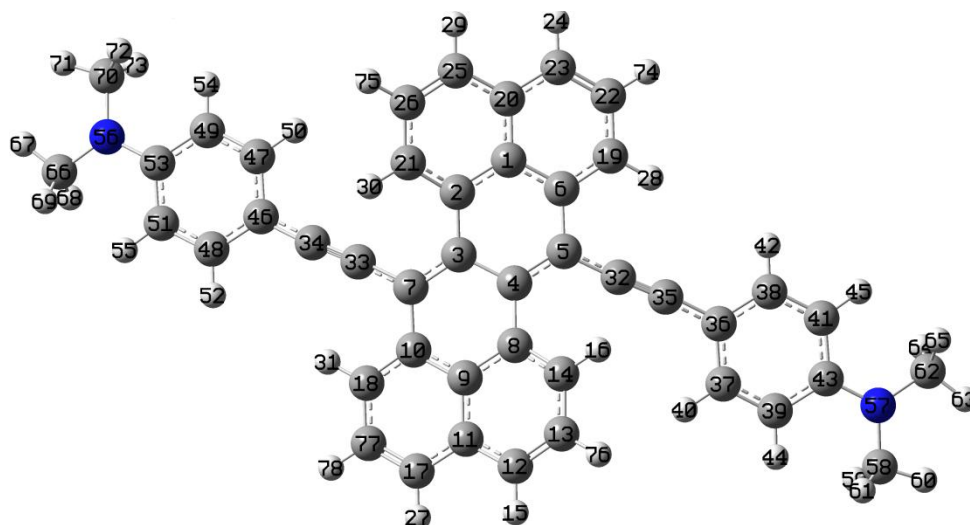
Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	2.566898	0.347557	-0.546040
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4	6	0	-0.290764	0.668960	-0.602385
5	6	0	0.527242	1.756676	-0.294601
6	6	0	1.984192	1.604915	-0.204813
7	6	0	-0.527242	-1.756676	-0.294601
8	6	0	-1.741581	0.783909	-0.821431
9	6	0	-2.566898	-0.347557	-0.546040
10	6	0	-1.984192	-1.604915	-0.204813
11	6	0	-3.991212	-0.230754	-0.630005
12	6	0	-4.557585	0.990234	-1.073481
13	6	0	-3.743613	2.040566	-1.440115
14	6	0	-2.345950	1.939894	-1.315516
15	1	0	-5.639349	1.073904	-1.143235
16	1	0	-4.175789	2.959005	-1.828127
17	1	0	-1.733748	2.776675	-1.623376
18	6	0	-4.799655	-1.344304	-0.281436
19	6	0	-2.819440	-2.669272	0.125900
20	6	0	2.819440	2.669272	0.125900
21	6	0	3.991212	0.230754	-0.630005

22	6	0	2.345950	-1.939894	-1.315516
23	6	0	4.219345	2.532895	0.104620
24	1	0	4.840442	3.383264	0.372596
25	6	0	4.799655	1.344304	-0.281436
26	1	0	5.880986	1.243592	-0.330733
27	6	0	4.557585	-0.990234	-1.073481
28	6	0	3.743613	-2.040566	-1.440115
29	1	0	4.175789	-2.959005	-1.828127
30	1	0	-5.880986	-1.243592	-0.330733
31	1	0	2.378423	3.624908	0.385592
32	1	0	5.639349	-1.073904	-1.143235
33	1	0	1.733748	-2.776675	-1.623376
34	1	0	-2.378423	-3.624908	0.385592
35	6	0	0.003028	3.038668	0.014313
36	6	0	-0.003028	-3.038668	0.014313
37	6	0	0.373357	-4.150689	0.344112
38	6	0	-0.373357	4.150689	0.344112
39	6	0	-0.906561	5.419882	0.703067
40	6	0	-2.297798	5.578141	0.879576
41	6	0	-0.066673	6.537571	0.886653
42	6	0	-2.825907	6.818300	1.225600
43	1	0	-2.946767	4.718216	0.744733
44	6	0	-0.604971	7.773370	1.232965
45	1	0	1.004704	6.423239	0.752241
46	6	0	-1.984192	7.919609	1.403721
47	1	0	-3.898932	6.926275	1.359633
48	1	0	0.053977	8.626385	1.370938
49	1	0	-2.400352	8.885756	1.675520
50	6	0	0.906561	-5.419882	0.703067
51	6	0	2.297798	-5.578141	0.879576
52	6	0	0.066673	-6.537571	0.886653
53	6	0	2.825907	-6.818300	1.225600
54	1	0	2.946767	-4.718216	0.744733
55	6	0	0.604971	-7.773370	1.232965
56	1	0	-1.004704	-6.423239	0.752241
57	6	0	1.984192	-7.919609	1.403721
58	1	0	3.898932	-6.926275	1.359633
59	1	0	-0.053977	-8.626385	1.370938
60	1	0	2.400352	-8.885756	1.675520
61	6	0	-4.219345	-2.532895	0.104620
62	1	0	-4.840442	-3.383264	0.372596

7,14-Bis{[4-(*N,N*-dimethylamino)phenyl]ethynyl}zethrene

C_2 symmetry

SCF Done: E (RB+HF-LYP) = -1805.38815785



Standard orientation

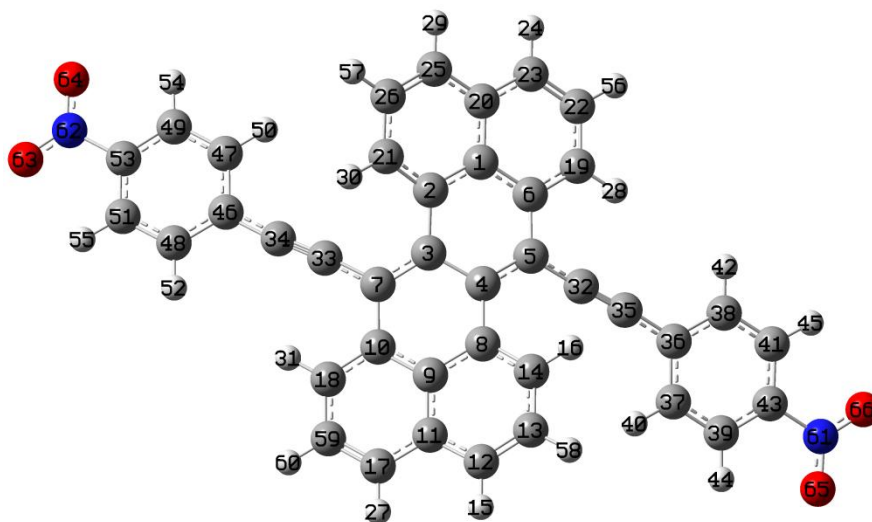
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5	6	0	-0.964317	-1.563281	-0.608477
6	6	0	-2.332656	-1.038100	-0.520004
7	6	0	0.964317	1.563281	-0.608477
8	6	0	1.479808	-1.208736	-1.128851
9	6	0	2.570422	-0.328093	-0.858232
10	6	0	2.332656	1.038100	-0.520004
11	6	0	3.916901	-0.808650	-0.942943
12	6	0	4.148658	-2.135545	-1.383157
13	6	0	3.090024	-2.940963	-1.744500
14	6	0	1.765716	-2.483594	-1.617965
15	1	0	5.172255	-2.495648	-1.453810
16	1	0	0.957663	-3.136739	-1.917824
17	6	0	4.985842	0.059656	-0.598449
18	6	0	3.415005	1.851385	-0.192220
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20	6	0	-3.916901	0.808650	-0.942943
21	6	0	-1.765716	2.483594	-1.617965
22	6	0	-4.732243	-1.358438	-0.214774
23	6	0	-4.985842	-0.059656	-0.598449
24	1	0	-6.004612	0.316814	-0.649139
25	6	0	-4.148658	2.135545	-1.383157
26	6	0	-3.090024	2.940963	-1.744500
27	1	0	6.004612	-0.316814	-0.649139
28	1	0	-3.234743	-2.888858	0.065477
29	1	0	-5.172255	2.495648	-1.453810

30	1	0	-0.957663	3.136739	-1.917824
31	1	0	3.234743	2.888858	0.065477
32	6	0	-0.796132	-2.938179	-0.306545
33	6	0	0.796132	2.938179	-0.306545
34	6	0	0.711743	4.111052	0.021169
35	6	0	-0.711743	-4.111052	0.021169
36	6	0	-0.519874	-5.468297	0.386833
37	6	0	0.778216	-6.007592	0.508328
38	6	0	-1.604686	-6.330741	0.644456
39	6	0	0.982501	-7.333085	0.858026
40	1	0	1.634066	-5.363101	0.330208
41	6	0	-1.409937	-7.657701	0.994852
42	1	0	-2.617180	-5.945090	0.567463
43	6	0	-0.107555	-8.203793	1.102521
44	1	0	2.000542	-7.693061	0.946276
45	1	0	-2.279586	-8.274334	1.187755
46	6	0	0.519874	5.468297	0.386833
47	6	0	-0.778216	6.007592	0.508328
48	6	0	1.604686	6.330741	0.644456
49	6	0	-0.982501	7.333085	0.858026
50	1	0	-1.634066	5.363101	0.330208
51	6	0	1.409937	7.657701	0.994852
52	1	0	2.617180	5.945090	0.567463
53	6	0	0.107555	8.203793	1.102521
54	1	0	-2.000542	7.693061	0.946276
55	1	0	2.279586	8.274334	1.187755
56	7	0	-0.091364	9.534678	1.427879
57	7	0	0.091364	-9.534678	1.427879
58	6	0	1.436921	10.022509	1.677986
59	1	0	1.919667	-9.518680	2.530023
60	1	0	1.395069	11.091700	1.893620
61	1	0	2.077007	-9.886290	0.797436
62	6	0	-1.038102	10.354663	1.831210
63	1	0	-0.691047	11.371417	2.023930
64	1	0	-1.529460	-9.980410	2.742934
65	1	0	-1.792898	10.406982	1.036746
66	6	0	1.038102	10.354663	1.831210
67	1	0	0.691047	11.371417	2.023930
68	1	0	1.529460	9.980410	2.742934
69	1	0	1.792898	10.406982	1.036746
70	6	0	-1.436921	10.022509	1.677986
71	1	0	-1.395069	11.091700	1.893620
72	1	0	-2.077007	9.886290	0.797436
73	1	0	-1.919667	9.518680	2.530023
74	1	0	-5.552354	-2.020530	0.050232
75	1	0	-3.269704	3.941464	2.129368
76	1	0	3.269704	-3.941464	2.129368
77	6	0	4.732243	1.358438	0.214774
78	1	0	5.552354	2.020530	0.050232

7,14-Bis[(dinitrophenyl)ethynyl]zethrene

C₂ symmetry

SCF Done: E (RB+HF-LYP) = -1946.45373662



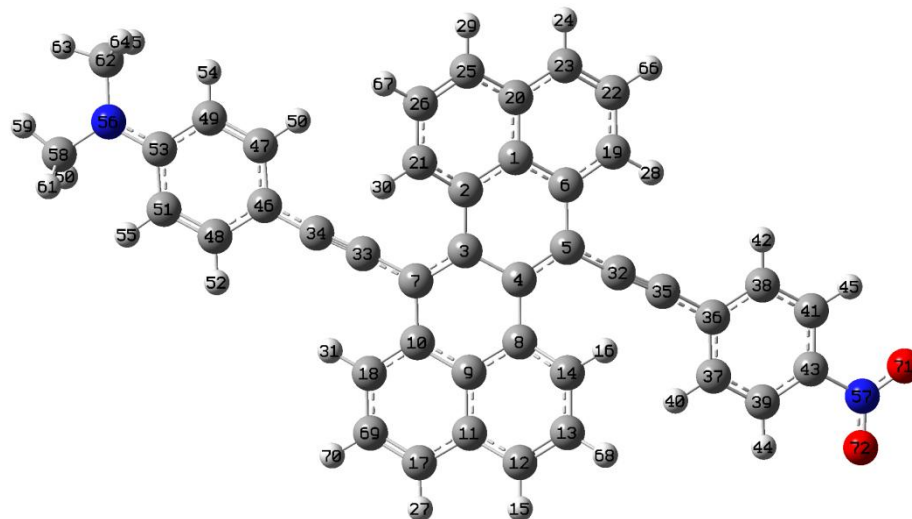
Standard orientation

Center Number	Atomic Number	Atomic Type	X	Y	Z
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2	6	0	1.217285	1.468562	-1.141619
3	6	0	0.721054	0.103077	-0.917096
4	6	0	-0.721053	-0.103069	-0.917096
5	6	0	-1.550075	0.976688	-0.603100
6	6	0	-1.018562	2.341544	-0.523113
7	6	0	1.550075	-0.976682	-0.603101
8	6	0	-1.217285	-1.468552	-1.141624
9	6	0	-0.347125	-2.566214	-0.869468
10	6	0	1.018561	-2.341539	-0.523120
11	6	0	-0.839202	-3.906808	-0.961113
12	6	0	-2.166327	-4.124228	-1.408141
13	6	0	-2.961470	-3.058298	-1.772654
14	6	0	-2.491308	-1.739065	-1.641835
15	1	0	-2.535489	-5.143810	-1.484622
16	1	0	-3.130630	-0.923641	-1.953122
17	6	0	0.017775	-4.984664	-0.616830
18	6	0	1.821603	-3.431904	-0.197167
19	6	0	-1.821605	3.431908	-0.197156
20	6	0	0.839200	3.906817	-0.961098
21	6	0	2.491307	1.739079	-1.641830
22	6	0	-1.317655	4.744728	-0.227120
23	6	0	-0.017778	4.984671	-0.616810
24	1	0	0.367108	5.999660	-0.671903
25	6	0	2.166325	4.124240	-1.408123
26	6	0	2.961469	3.058313	-1.772641

27	1	0	-0.367112	-5.999652	-0.671927
28	1	0	-2.859976	3.264062	0.065496
29	1	0	2.535487	5.143823	-1.484600
30	1	0	3.130629	0.923658	-1.953122
31	1	0	2.859974	-3.264060	0.065487
32	6	0	-2.916611	0.801472	-0.271809
33	6	0	2.916613	-0.801471	-0.271813
34	6	0	4.081086	-0.718330	0.082580
35	6	0	-4.081085	0.718328	0.082581
36	6	0	-5.432359	0.521049	0.465285
37	6	0	-5.934606	-0.790115	0.632822
38	6	0	-6.296945	1.617226	0.681790
39	6	0	-7.256257	-0.998713	0.999204
40	1	0	-5.271699	-1.634090	0.473193
41	6	0	-7.619141	1.413276	1.049379
42	1	0	-5.918458	2.626203	0.555711
43	6	0	-8.084008	0.106378	1.203150
44	1	0	-7.657484	-1.995841	1.131994
45	1	0	-8.295268	2.242127	1.218763
46	6	0	5.432358	-0.521054	0.465289
47	6	0	5.934617	0.790109	0.632796
48	6	0	6.296936	-1.617233	0.681814
49	6	0	7.256269	0.998705	0.999177
50	1	0	5.271718	1.634086	0.473143
51	6	0	7.619133	-1.413287	1.049404
52	1	0	5.918443	-2.626210	0.555752
53	6	0	8.084010	-0.106389	1.203150
54	1	0	7.657503	1.995832	1.131946
55	1	0	8.295253	-2.242139	1.218806
56	1	0	-1.971011	5.571426	0.037019
57	1	0	3.959609	3.229350	-2.166188
58	1	0	-3.959610	-3.229332	-2.166202
59	6	0	1.317652	-4.744724	-0.227137
60	1	0	1.971007	-5.571423	0.036999
61	7	0	-9.481536	-0.111983	1.591154
62	7	0	9.481538	0.111969	1.591152
63	8	0	10.188724	-0.881161	1.768286
64	8	0	9.866018	1.275765	1.716282
65	8	0	-9.866006	-1.275779	1.716309
66	8	0	-10.188730	0.881145	1.768265

7-[[4-(*N,N*-dimethylamino)phenyl]ethynyl]-14-[(nitrophenyl)ethynyl]zethrene

SCF Done: E (RB+HF-LYP) = -1875.92226890



Standard orientation

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	6	0	0.236511	2.601899	-0.832195
2	6	0	1.120035	1.514313	-1.108150
3	6	0	0.635649	0.139069	-0.904565
4	6	0	-0.804165	-0.077230	-0.901857
5	6	0	-1.646465	0.991778	-0.583624
6	6	0	-1.129191	2.361927	-0.492833
7	6	0	1.475319	-0.938174	-0.606558
8	6	0	-1.294310	-1.443259	-1.138050
9	6	0	-0.418266	-2.537962	-0.875495
10	6	0	0.946870	-2.306113	-0.532640
11	6	0	-0.903131	-3.880709	-0.975887
12	6	0	-2.229268	-4.102491	-1.423919
13	6	0	-3.029421	-3.038334	-1.782100
14	6	0	-2.565999	-1.717409	-1.641959
15	1	0	-2.592987	-5.123660	-1.506947
16	1	0	-3.209291	-0.903530	-1.948812
17	6	0	-0.039690	-4.955886	-0.640010
18	6	0	1.756410	-3.394644	-0.216202
19	6	0	-1.944651	3.440846	-0.160317
20	6	0	0.714535	3.949494	-0.910240
21	6	0	2.395923	1.804870	-1.591325
22	6	0	-1.454396	4.759036	-0.179475
23	6	0	-0.155956	5.015463	-0.562190
24	1	0	0.218640	6.034910	-0.608868
25	6	0	2.041851	4.185820	-1.346920
26	6	0	2.850707	3.130704	-1.710392
27	1	0	-0.419017	-5.972807	-0.700821

28	1	0	-2.981747	3.259938	0.098713
29	1	0	2.399791	5.210331	-1.412387
30	1	0	3.051706	0.999579	-1.893032
31	1	0	2.794431	-3.220464	0.043297
32	6	0	-3.010844	0.800869	-0.256264
33	6	0	2.846883	-0.773125	-0.296194
34	6	0	4.020341	-0.702294	0.034264
35	6	0	-4.175911	0.706850	0.095866
36	6	0	-5.524931	0.495674	0.473609
37	6	0	-6.020649	-0.821027	0.623651
38	6	0	-6.398675	1.582841	0.703883
39	6	0	-7.340953	-1.042842	0.985237
40	1	0	-5.352096	-1.658572	0.453776
41	6	0	-7.719422	1.365595	1.067126
42	1	0	-6.026521	2.595828	0.591554
43	6	0	-8.177497	0.053688	1.203363
44	1	0	-7.735522	-2.044398	1.104072
45	1	0	-8.400795	2.188048	1.246498
46	6	0	5.381102	-0.526793	0.389769
47	6	0	5.941082	0.764886	0.490025
48	6	0	6.227082	-1.622680	0.657788
49	6	0	7.270789	0.952856	0.829321
50	1	0	5.309175	1.628095	0.302844
51	6	0	7.558212	-1.444800	0.997596
52	1	0	5.824853	-2.629681	0.595852
53	6	0	8.124801	-0.148712	1.086590
54	1	0	7.649041	1.965565	0.899844
55	1	0	8.163308	-2.320924	1.197023
56	7	0	9.455090	0.033101	1.408610
57	7	0	-9.571675	-0.178412	1.586221
58	6	0	10.276042	-1.108448	1.775672
59	1	0	11.293124	-0.768131	1.976504
60	1	0	9.902448	-1.620178	2.675288
61	1	0	10.324491	-1.843777	0.962162
62	6	0	9.982771	1.375610	1.585363
63	1	0	11.048171	1.314172	1.812969
64	1	0	9.870136	1.971998	0.670781
65	1	0	9.487976	1.915697	2.406599
66	1	0	-2.117618	5.577030	0.088274
67	1	0	3.851749	3.314394	-2.091540
68	1	0	-4.026545	-3.211598	-2.177587
69	6	0	1.259622	-4.710080	-0.251929
70	1	0	1.918695	-5.534564	0.005677
71	8	0	-10.287183	0.807423	1.776264
72	8	0	-9.950564	-1.346495	1.695914

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