

# Supporting Information

## **Precision Synthesis of Poly(*N*-hexylpyrrole) and its Diblock Copolymer with Poly(*p*-phenylene) via Catalyst-Transfer Polycondensation**

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## Experimental.

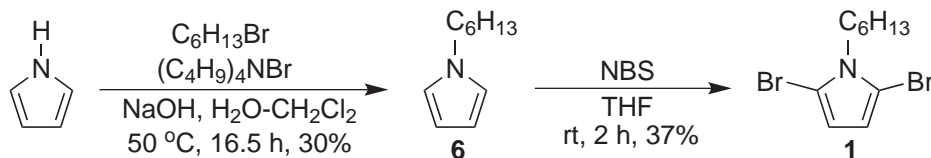
### General.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on JEOL ECA-500 and ECA-600 spectrometers, and internal standards of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were tetramethylsilane (0.00 ppm) and midpoint of  $\text{CDCl}_3$  (77.0 ppm), respectively. Conversion of monomer was determined by analytical GC performed on a Shimadzu GC-14B gas chromatograph equipped with a Shimadzu fused silica capillary column CBP1-W12-100 (12 m length, 0.53 mm i.d.) and a FID detector, and analyses of conversion were carried out with naphthalene as an internal standard. The  $M_n$  and  $M_w/M_n$  values of polymers were measured with a TOSOH HLC-8120 gel-permeation chromatography (GPC) unit (eluent: tetrahydrofuran (THF), calibration: polystyrene standards) using two TSK-gel columns ( $2 \times$  Multipore H<sub>XL</sub>-M) and a UV detector at 40 °C. MALDI-TOF mass spectra were recorded on a Shimadzu/Krotos Axima CFR in the linear mode using a laser ( $\lambda = 337$  nm). GC Mass spectra were obtained on a Shimadzu GCMS-QP5050A gas chromatograph mass spectrometer with a Frontier Laboratories Ultra ALLOY capillary column UA<sup>+</sup>-1(HT)-15M-0.1F. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with a specified solvent. Commercially available (Kanto) dehydrated dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), THF (stabilizer-free), and acetone were used as dry solvents. Isopropylmagnesium chloride (2.0 M solution in THF, Aldrich), [1,3-bis(diphenylphosphino)propane]dichloronickel(II) ( $\text{Ni}(\text{dppp})\text{Cl}_2$ , Aldrich), [1,1'-bis(diphenylphosphino)ferrocene]dichloronickel(II) ( $\text{Ni}(\text{dppf})\text{Cl}_2$ , Aldrich), and [1,2-bis(diphenylphosphino)ethane]dichloronickel(II) ( $\text{Ni}(\text{dppe})\text{Cl}_2$ , Aldrich) were used as received. Naphthalene, which was used as an internal standard for GC analysis, was purified by recrystallization from EtOH.

### Synthesis of 2,5-Dibromo-1-Hexylpyrrole (1).

This compound was synthesized by the procedure as shown in Scheme S1 according to a modified procedure in the literature.<sup>1</sup>

**Scheme S1**

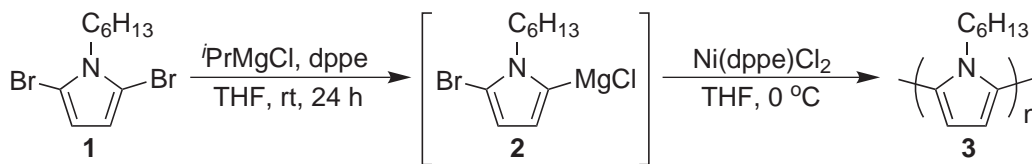


**Preparation of 1-hexylpyrrole (6).** To a stirred mixture of tetrabutylammonium bromide (80.8 g, 0.25 mol), 1-bromohexane (39 mL, 0.28 mol), and pyrrole (17 mL, 0.25 mol) in  $\text{CH}_2\text{Cl}_2$  (250 mL) at  $0\text{ }^\circ\text{C}$  was added 50% aqueous NaOH (250 mL) dropwise. After the addition, the reaction mixture was refluxed for 22 h under an argon atmosphere. The mixture was cooled to room temperature, and extracted with toluene (three times). The combined organic extracts were washed with water (once), 1 mol/L hydrochloric acid (three times) and brine (once), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The crude product was purified by distillation ( $46.0\text{ }^\circ\text{C}/0.6\text{ mmHg}$ ), followed by silica gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{hexane} = 1/10$ ) to afford **6** (16.2 g, 43%) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.65 (t,  $J = 2.3\text{ Hz}$ , 2 H), 6.13 (t,  $J = 2.3\text{ Hz}$ , 2 H), 3.86 (t,  $J = 7.2\text{ Hz}$ , 2 H), 1.75 (quint,  $J = 6.9\text{ Hz}$ , 2 H), 1.36–1.21 (m, 6 H), 0.88 (t,  $J = 6.6\text{ Hz}$ , 3 H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  120.4, 107.7, 49.6, 31.5, 31.4, 26.4, 22.5, 14.0; IR (neat) 3101, 2956, 2929, 2859, 1543, 1499, 1466, 1377, 1282, 1088, 1064, 719,  $457\text{ cm}^{-1}$ ; EIMS  $m/z$  (relative intensity) 151 (36,  $\text{M}^+$ ), 81 (100).

**Preparation of 2,5-dibromo-1-hexylpyrrole (1).** A solution of **6** (6.00 g, 40 mmol) in THF (150 mL) was stirred at  $-78\text{ }^\circ\text{C}$  under an argon atmosphere, and *N*-bromosuccinimide (NBS, 15.5 g, 87 mmol) was added. The mixture was stirred at  $-78\text{ }^\circ\text{C}$  for 2 h and concentrated under reduced pressure. Diethyl ether was added to the residue, and the mixture was filtered. The filtrate was washed with 10% aqueous NaOH (twice), water (once) and brine (once), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. Purification of the crude product by distillation ( $71.5\text{ }^\circ\text{C}/0.16\text{ mmHg}$ ) gave **1** (4.56 g, 37%) as a colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.16 (s, 2 H), 3.95 (t,  $J = 7.7\text{ Hz}$ , 2 H), 1.67 (quint,  $J = 7.7\text{ Hz}$ , 2 H), 1.38–1.28 (m, 6 H), 0.89 (t,  $J = 6.9\text{ Hz}$ , 3 H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  111.6, 100.6, 47.3, 31.3, 30.2, 26.1, 22.5, 14.0; IR (neat) 3132, 2930, 2858, 1637, 1516, 1458, 1421, 1377, 1281, 1107, 904,  $741\text{ cm}^{-1}$ ; EIMS  $m/z$  (relative intensity) 311 (26,  $\text{M}^+$  containing two  $^{81}\text{Br}$ ), 309 (50,  $\text{M}^+$  containing one  $^{81}\text{Br}$  and one  $^{79}\text{Br}$ ), 307 (27,  $\text{M}^+$  containing two  $^{79}\text{Br}$ ), 120 (100).

## Polymerization of **1**.

**Scheme S2**

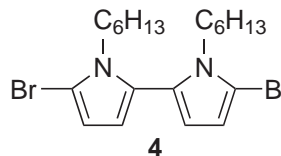


**General procedure.** All glass apparatuses were dried prior to use. Addition of reagents into the reaction flask and withdrawing a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock with a stream of nitrogen. A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure, and then cooled to room temperature under a nitrogen atmosphere. Monomer precursor **1** (312 mg, 1.01 mmol), dppe (11.7 mg, 0.0294 mmol, 2.9 mol %) and naphthalene (used as an internal standard for GC analysis, 42 mg, 0.33 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Into the flask was added dry THF (5.0 mL) via a syringe, and the mixture was stirred at 0 °C. *i*-PrMgCl (2.0 M solution in THF, 0.48 mL, 0.96 mmol) was added via a syringe, and the mixture was stirred at room temperature for 24 h (conversion of **1** = 80%). Then, the mixture was cooled to 0 °C, and a suspension of Ni(dppe)Cl<sub>2</sub> (13.5 mg, 0.0256 mmol, 2.5 mol %) in THF (5.0 mL) was added via a syringe. After the reaction mixture was stirred at 0 °C for 9 h (conversion of **2** = 82%), 5 mol/L hydrochloric acid was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was washed with saturated aqueous NaHCO<sub>3</sub> and water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to give a crude product (241 mg, *M<sub>n</sub>* = 6800, *M<sub>w</sub>*/*M<sub>n</sub>* = 1.09). The crude was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub>, and the solution was poured into CH<sub>3</sub>OH (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH = 1/100) with vigorous stirring to remove the low-molecular-weight compounds. The precipitated polymer was collected and dried under reduced pressure to give **3** as a dark red-brown oil (91 mg, 60%, *M<sub>n</sub>* = 7110, *M<sub>w</sub>*/*M<sub>n</sub>* = 1.09). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.29 (br s, 2 H), 3.80–3.62 (br m, 2 H), 1.44–1.37 (br m, 2 H), 1.18 (quint, *J* = 7.2 Hz, 2 H), 1.12–1.00 (m, 4 H), 0.81 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 125.6, 110.8, 45.1, 31.3, 26.4, 22.5, 13.9.

### Isolation of 5,5'-dibromo-1,1'-dihexyl-2,2'-bipyrrole (**4**) as an oligomeric byproduct.

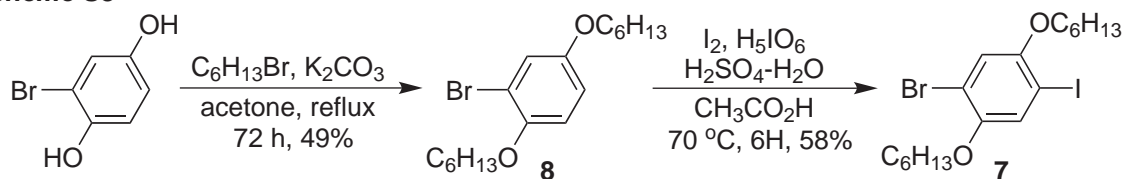
Polymerization of **1** in the absence of additional dppe was carried out by treatment of **1** (309 mg, 1.00 mmol) with *i*-PrMgCl (2.0 M solution in THF, 0.48 mL, 0.96 mmol) in THF (5.0 mL) at room temperature for 24 h (conversion of **1** = 83%), followed by treatment with Ni(dppe)Cl<sub>2</sub> (5.6 mg, 0.0106 mmol, 1.1 mol %, suspension in 5.0 mL of THF) at 0 °C for 37 h (conversion of **2** = 94%). After the reaction mixture was quenched with 5 mol/L

hydrochloric acid and extracted with CH<sub>2</sub>Cl<sub>2</sub> as mentioned above, the crude product containing the polypyrrole ( $M_n = 14500$  and  $M_w/M_n = 1.20$ ) was separated with silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexane = 1/20), followed by preparative HPLC to afford **4** as a yellow oil (31.5 mg, 14%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.21 (d,  $J = 3.7$  Hz, 2 H), 6.16 (d,  $J = 3.7$  Hz, 2 H), 3.71 (t,  $J = 7.7$  Hz, 4 H), 1.55 (quint,  $J = 7.4$  Hz, 4 H), 1.30–1.17 (m, 12 H), 0.85 (t,  $J = 7.2$  Hz, 6 H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  125.1, 112.3, 110.2, 102.4, 45.9, 31.2, 30.9, 26.1, 22.4, 13.9; IR (neat) 2955, 2930, 2858, 1494, 1458, 1415, 1367, 1272, 1211, 754 cm<sup>-1</sup>; EIMS  $m/z$  (relative intensity) 460 (50, M<sup>+</sup> containing two <sup>81</sup>Br), 458 (100, M<sup>+</sup> containing one <sup>81</sup>Br and one <sup>79</sup>Br), 456 (51, M<sup>+</sup> containing two <sup>79</sup>Br).



### Synthesis of 1-Bromo-2,5-Dihexyloxy-4-Iodobenzene (**7**).

**Scheme S3**



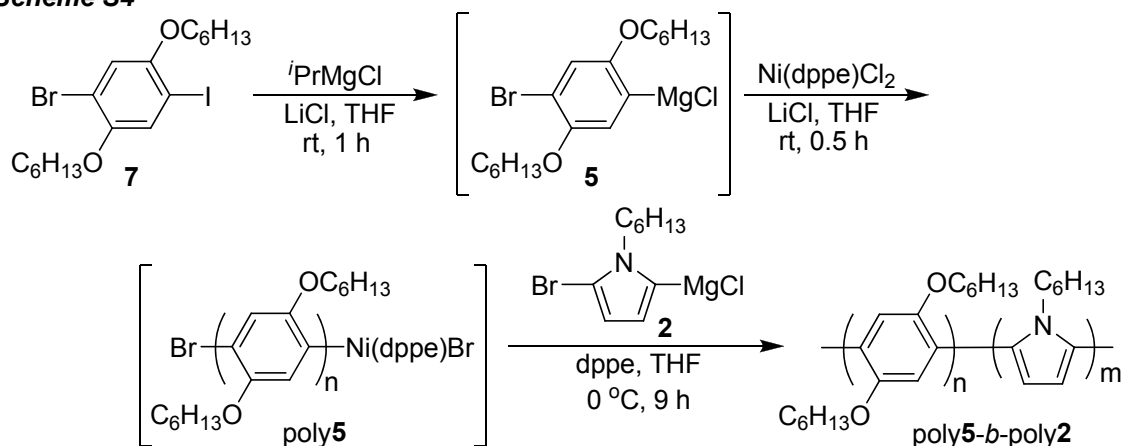
**Preparation of 1-bromo-2,5-dihexyloxybenzene (**8**).** A mixture of bromohydroquinone (10.02 g, 53.0 mmol), 1-bromohexane (19.56 g, 119 mmol) and ground K<sub>2</sub>CO<sub>3</sub> (25.57 g, 185 mmol) in acetone (130 mL) was refluxed for 72 h and cooled to room temperature, and water was added. After the mixture was extracted with Et<sub>2</sub>O, the organic layer was washed with 10% aqueous NaOH and water, and dried over anhydrous MgSO<sub>4</sub>. Purification with silica gel column chromatography (CHCl<sub>3</sub>/hexane = 1/4) afforded **8** (9.30 g, 49%) as a colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.11 (d,  $J = 2.9$  Hz, 1 H), 6.82 (d,  $J = 9.2$  Hz, 1 H), 6.78 (dd,  $J = 2.9$  and 8.9 Hz, 1 H), 3.95 (t,  $J = 6.6$  Hz, 2 H), 3.88 (t,  $J = 6.6$  Hz, 2 H), 1.80 (quint,  $J = 7.4$  Hz, 2 H), 1.74 (quint,  $J = 7.2$  Hz, 2 H), 1.51–1.41 (m, 4 H), 1.37–1.31 (m, 8 H), 0.91 (t,  $J = 6.9$  Hz, 6 H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  153.6, 149.7, 119.4, 114.7, 114.4, 112.7, 70.2, 68.8, 31.5, 29.2, 25.7, 22.6, 14.0; IR (neat) 2931, 2859, 1495, 1468, 1272, 1037, 841, 791 cm<sup>-1</sup>.

**Preparation of 1-bromo-2,5-dihexyloxy-4-iodobenzene (**7**).** A mixture of **8** (7.16 g, 20.0 mmol), I<sub>2</sub> (2.54 g, 10.0 mmol), H<sub>5</sub>IO<sub>6</sub> (1.31 g, 5.7 mmol), acetic acid (16.6 mL), 97% H<sub>2</sub>SO<sub>4</sub> (0.5 mL) and water (3.3 mL) was refluxed for 6 h. After the mixture was cooled to room temperature, 10% aqueous NaOH was added, and the mixture was extracted with Et<sub>2</sub>O. The organic layer was washed with 10% aqueous NaOH, 10% aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and

water, and dried over  $\text{MgSO}_4$ . Purification with silica gel column chromatography (hexane), followed by recrystallization from methanol-THF gave **7** (5.57 g, 58%) as colorless needles (mp 45.2–46.0 °C).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (s, 1 H), 6.98 (s, 1 H), 3.95–3.92 (m, 4 H), 1.83–1.77 (m, 4 H), 1.53–1.45 (m, 4 H), 1.39–1.31 (m, 8 H), 0.93–0.89 (m, 6 H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  152.5, 150.4, 124.2, 117.0, 112.5, 84.8, 70.34, 70.28, 31.5, 31.4, 29.09, 29.06, 25.7, 25.6, 22.6, 14.02, 14.01; IR (neat) 2939, 2922, 1489, 1455, 1354, 1213, 1124, 850, 742, 726, 527  $\text{cm}^{-1}$ .

## Synthesis of Diblock Copolymer

**Scheme S4**

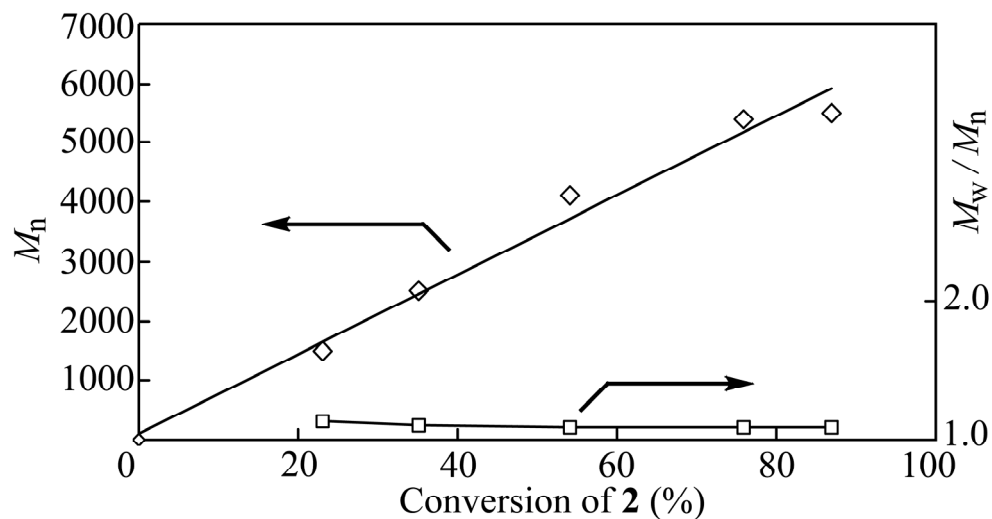


A round-bottomed flask equipped with a three-way stopcock containing lithium chloride (45 mg, 1.1 mmol) was heated under reduced pressure, and then cooled to room temperature under a nitrogen atmosphere. 1-Bromo-2,5-dihexyloxy-4-iodobenzene (**7**) (496 mg, 1.03 mmol) and naphthalene (used as an internal standard for GC analysis, 43.0 mg, 0.335 mmol) were placed in the flask, and the atmosphere in the flask was replaced with nitrogen. Into the flask was added THF (5.0 mL) via a syringe, and the mixture was stirred at 0 °C. Isopropylmagnesium chloride (2.0 M solution in THF, 0.48 mL, 0.96 mmol) was added via a syringe, and the mixture was stirred at room temperature for 1 h (conversion of **7** = 88%). To the mixture was added a suspension of  $\text{Ni}(\text{dppe})\text{Cl}_2$  (13.2 mg, 0.025 mmol, 2.5 mol %) in THF (5.0 mL) via a syringe, and then the mixture was stirred at room temperature for 0.5 h (conversion of **5** = 93%, poly5:  $M_n$  = 11300 and  $M_w/M_n$  = 1.13). After the reaction mixture was cooled to 0 °C, a THF solution of **2** containing dppe and naphthalene, which had been prepared by treatment of **1** (310 mg, 1.00 mmol) in THF (5.0 mL) with isopropylmagnesium chloride (2.0 M solution in THF, 0.48 mL, 0.96 mmol) in the presence of dppe (10.0 mg, 0.0251 mmol) and naphthalene (43.2 mg, 0.337 mmol) at

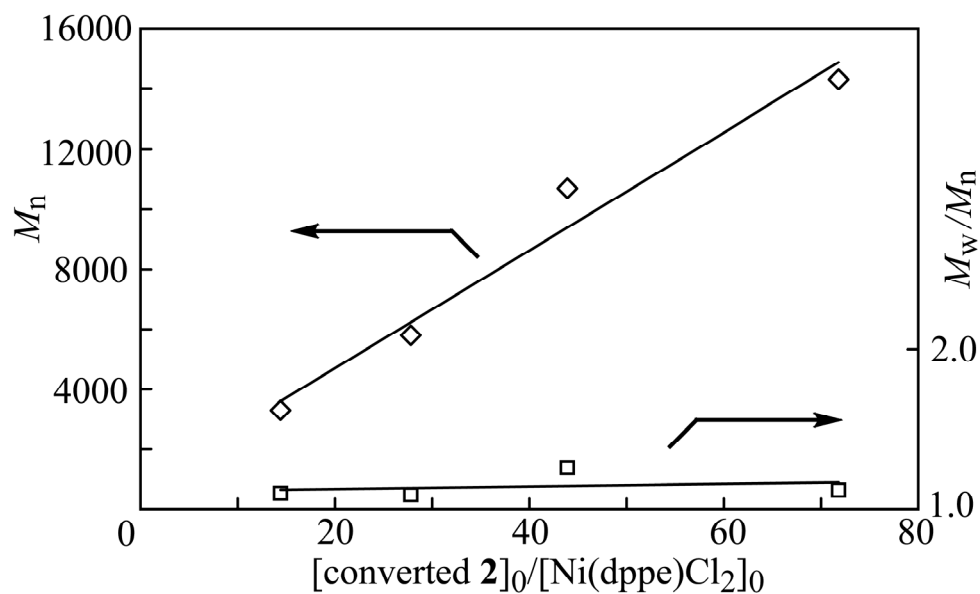
room temperature for 24 h as described above (conversion of **1** = 85%), was added to the solution of poly**5**, and the solution was stirred at 0 °C for 9 h. Then 5 mol/L hydrochloric acid was added, and the mixture was extracted with CHCl<sub>3</sub>. The combined organic layer was washed with saturated aqueous NaHCO<sub>3</sub> and water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to give a crude product (770 mg,  $M_n = 11300$ ,  $M_w/M_n = 1.13$ ). The crude was dissolved in a small amount of CHCl<sub>3</sub>, and the solution was poured into CH<sub>3</sub>OH (CHCl<sub>3</sub>/CH<sub>3</sub>OH = 1/100) with vigorous stirring. The precipitated polymer was collected and dried under reduced pressure to give poly**5-*b***-poly**2** as an orange viscous solid (223 mg, 51%,  $M_n = 16400$ ,  $M_w/M_n = 1.16$ ). The integral ratios of <sup>1</sup>H NMR spectrum indicated that the block copolymer contained the *p*-phenylene and pyrrole units by a ratio of 61.5/38.5. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.19–6.93 (m, 2n H), 6.39–6.17 (m, 2m H), 4.08–3.84 (m, 4n H), 3.84–3.55 (m, 2m H), 1.89–1.57 (m, 4n H), 1.52–1.15 (m, 12n + 4m H), 1.15–0.96 (m, 4m H), 0.96–0.68 (m, 6n + 3m H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  150.1, 127.5, 125.6, 117.3, 110.8, 69.5, 45.1, 31.6, 31.3, 29.5, 26.5, 25.8, 22.6, 22.5, 14.0, 13.9.

## References

- (1) Brockmann, T.; Tour, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 4437.

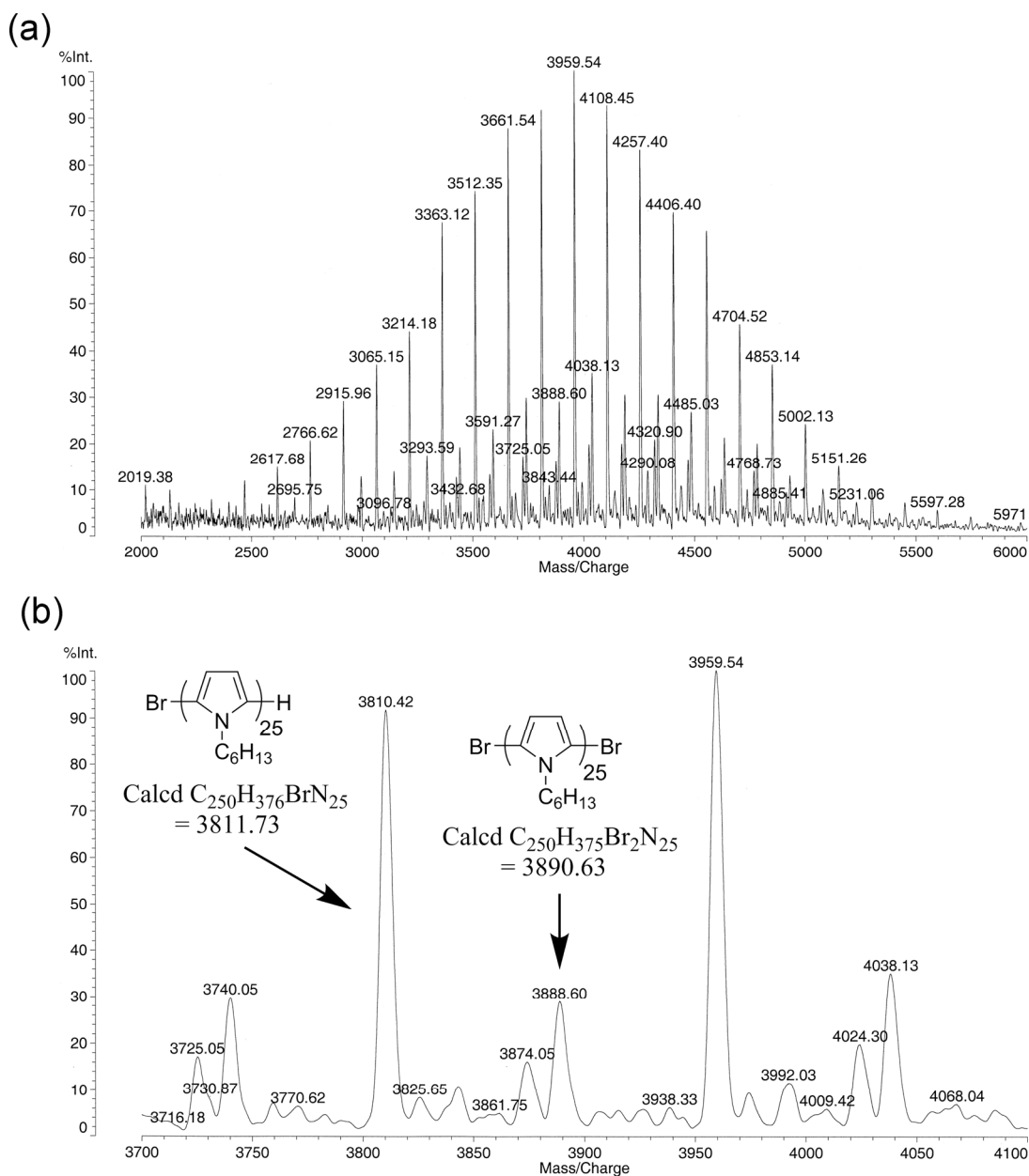


**Figure S1.**  $M_n$  and  $M_w/M_n$  values of **3** as a function of monomer conversion. The polymerization of **2** was carried out with 2.5 mol % of Ni(dppe)Cl<sub>2</sub> in the presence of 2.5 mol % of dppe in THF at 0 °C.



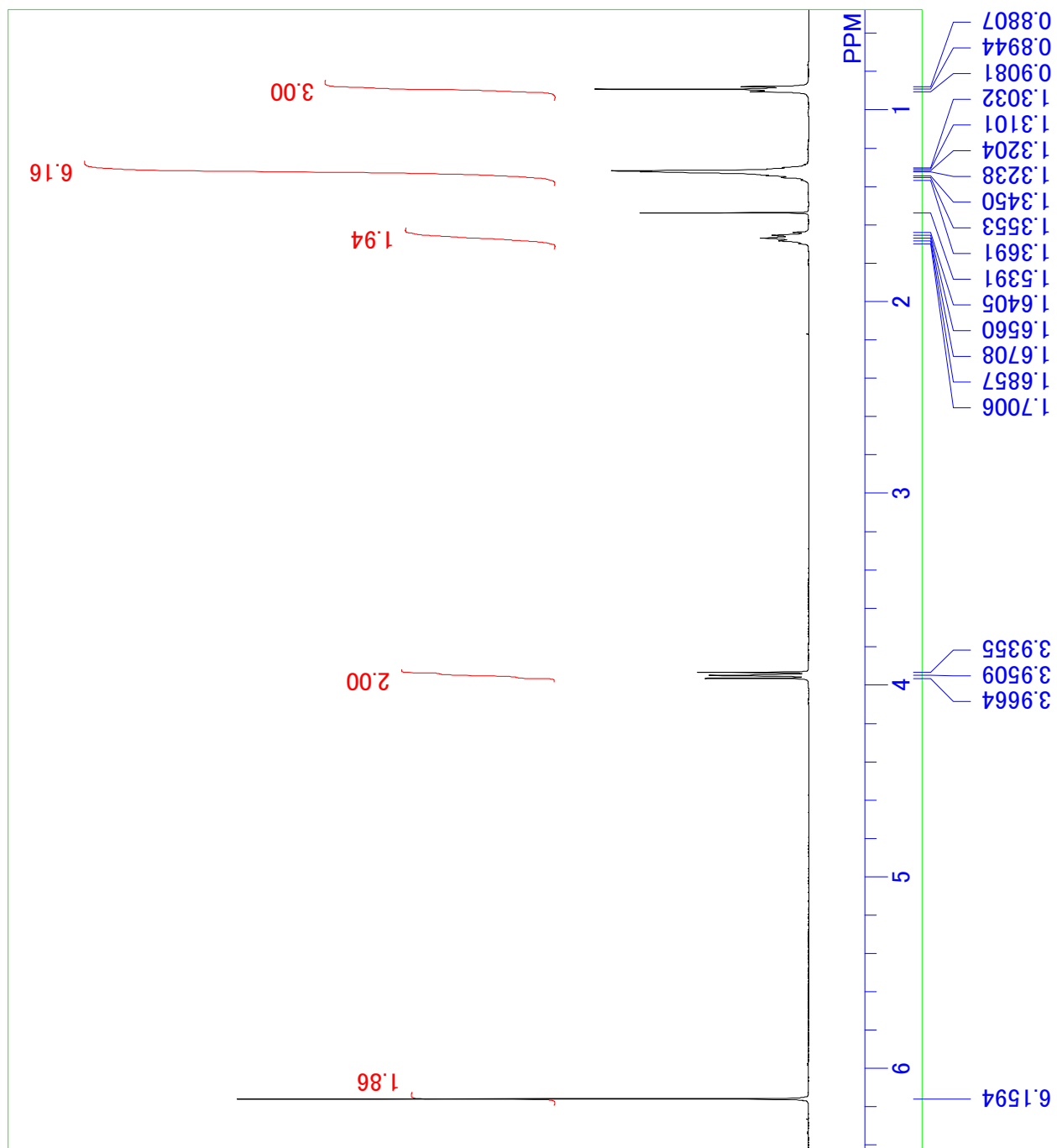
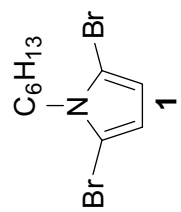
**Figure S2.**  $M_n$  and  $M_w/M_n$  values of **3** as a function of the feed ratio of **2** to Ni(dppe)Cl<sub>2</sub>. The polymerization of **2** was carried out with Ni(dppe)Cl<sub>2</sub> in the presence of 1.0 equiv of dppe to Ni(dppe)Cl<sub>2</sub> in THF at 0 °C.



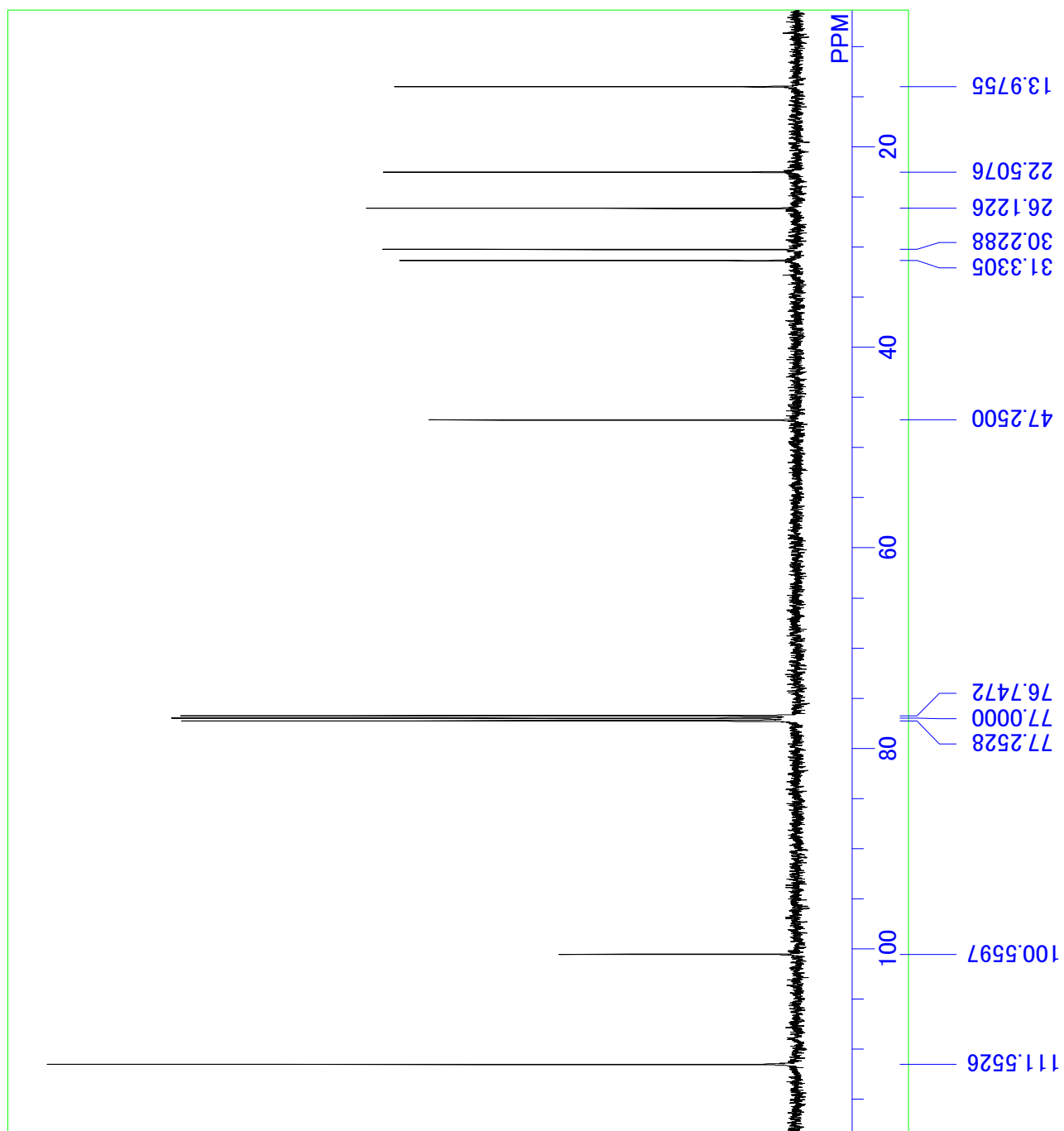
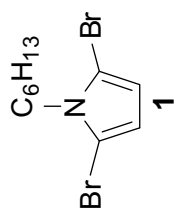


**Figure S3.** (a) Whole and (b) expanded spectra of MALDI-TOF mass analysis. The polymerization was carried out by treatment of **1** with isopropylmagnesium chloride (0.95 equiv) in the presence of dppe (2.5 mol %) in THF at room temperature for 24 h, followed by treatment with Ni(dppe)Cl<sub>2</sub> (2.5 mol %) at 0 °C for 8 h (GPC:  $M_n = 5900$ ,  $M_w/M_n = 1.06$ ).

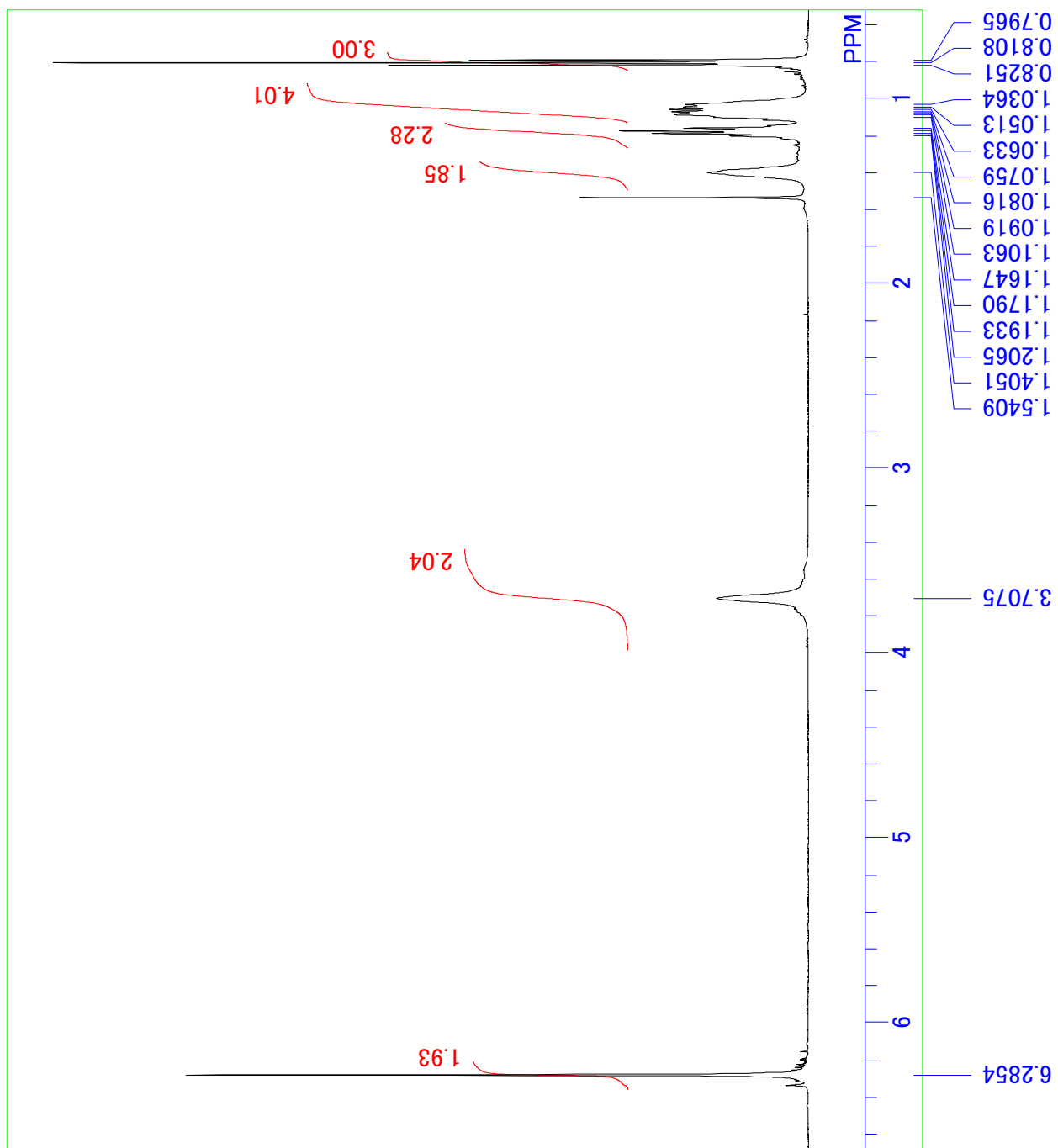
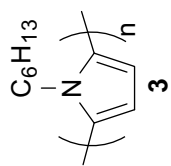
$^1\text{H}$  NMR  
( $\text{CDCl}_3$ , 500 MHz)



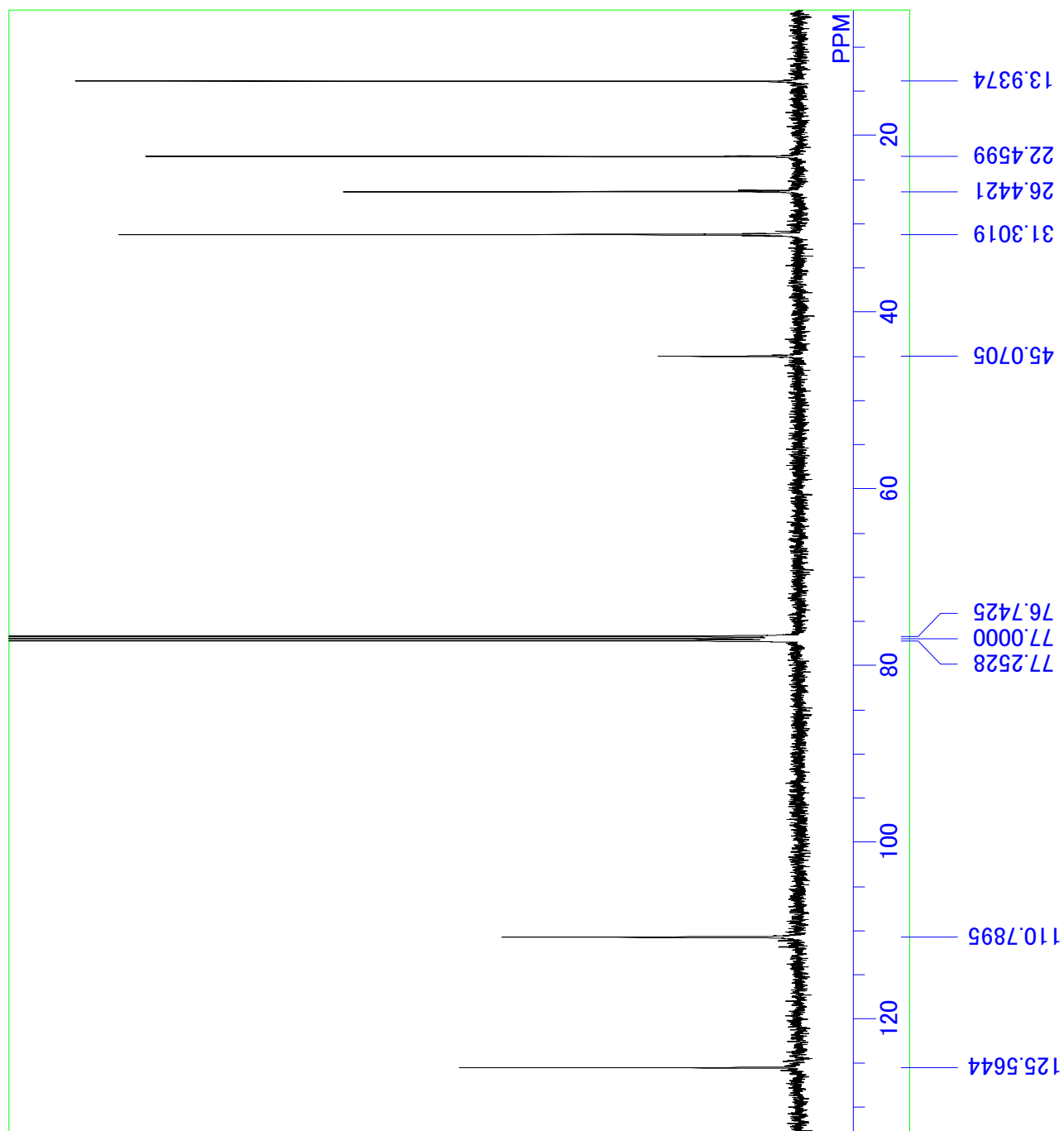
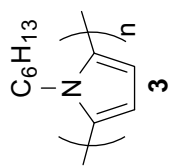
$^{13}\text{C}$  NMR  
( $\text{CDCl}_3$ , 126 MHz)

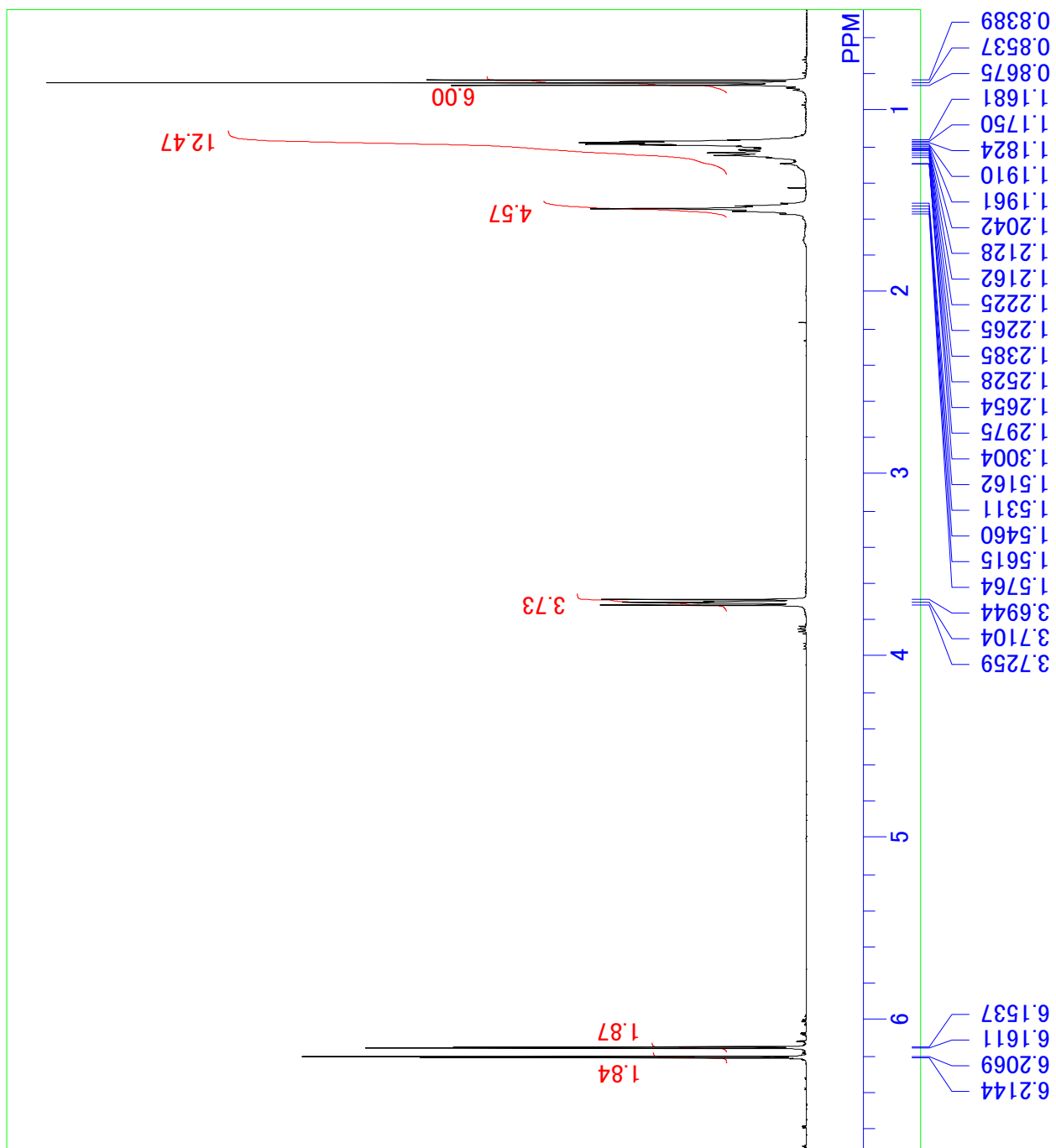
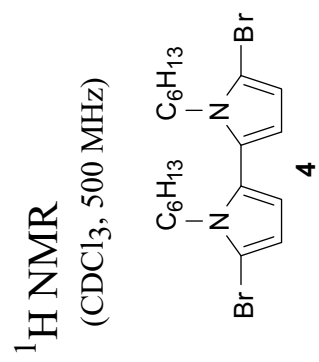


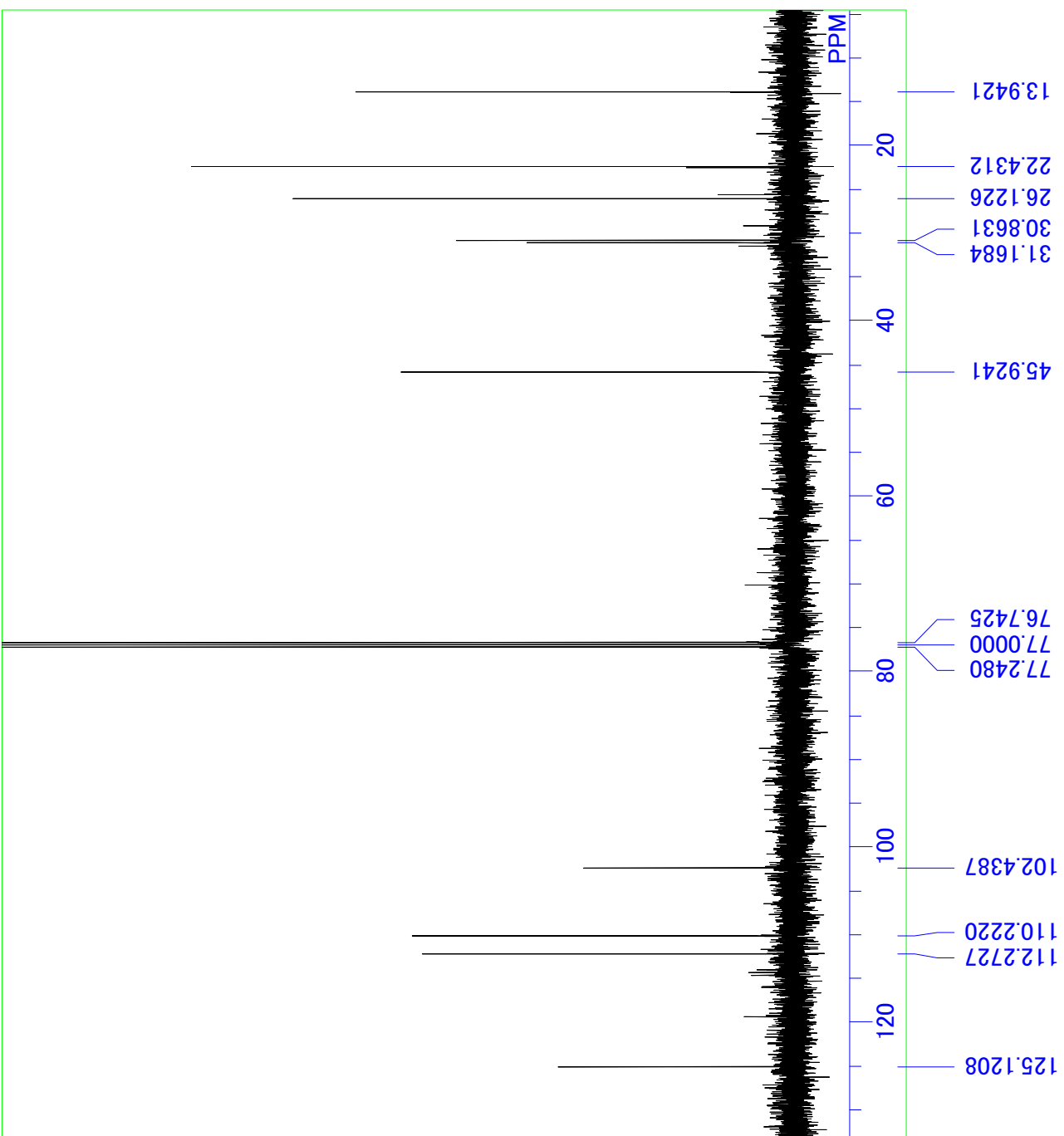
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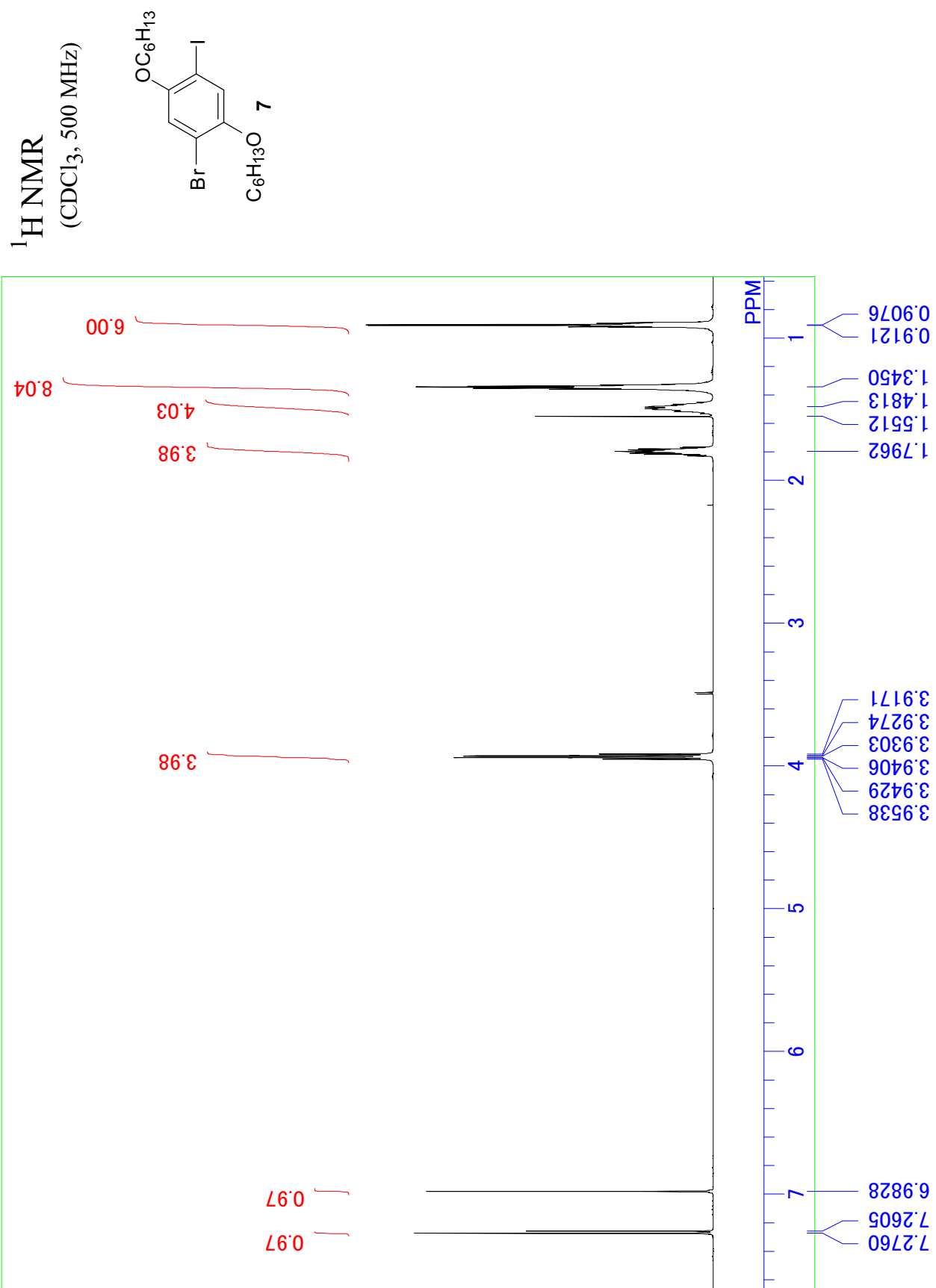


$^{13}\text{C}$  NMR  
( $\text{CDCl}_3$ , 126 MHz)

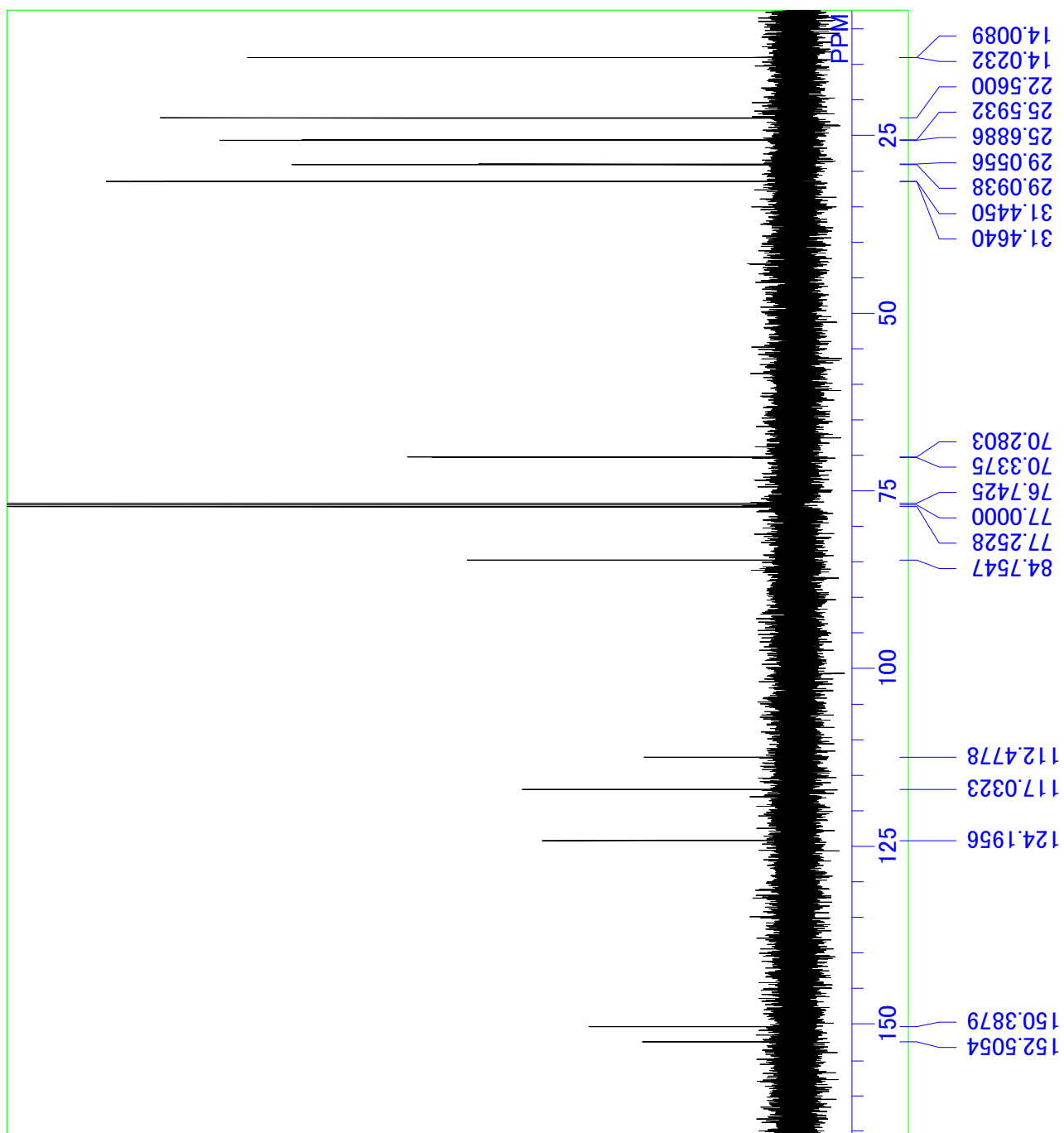
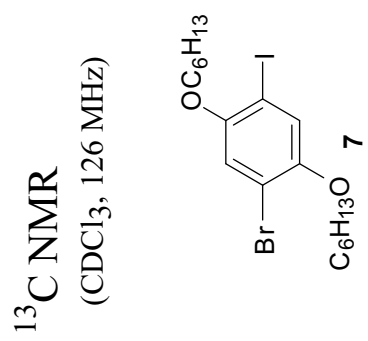


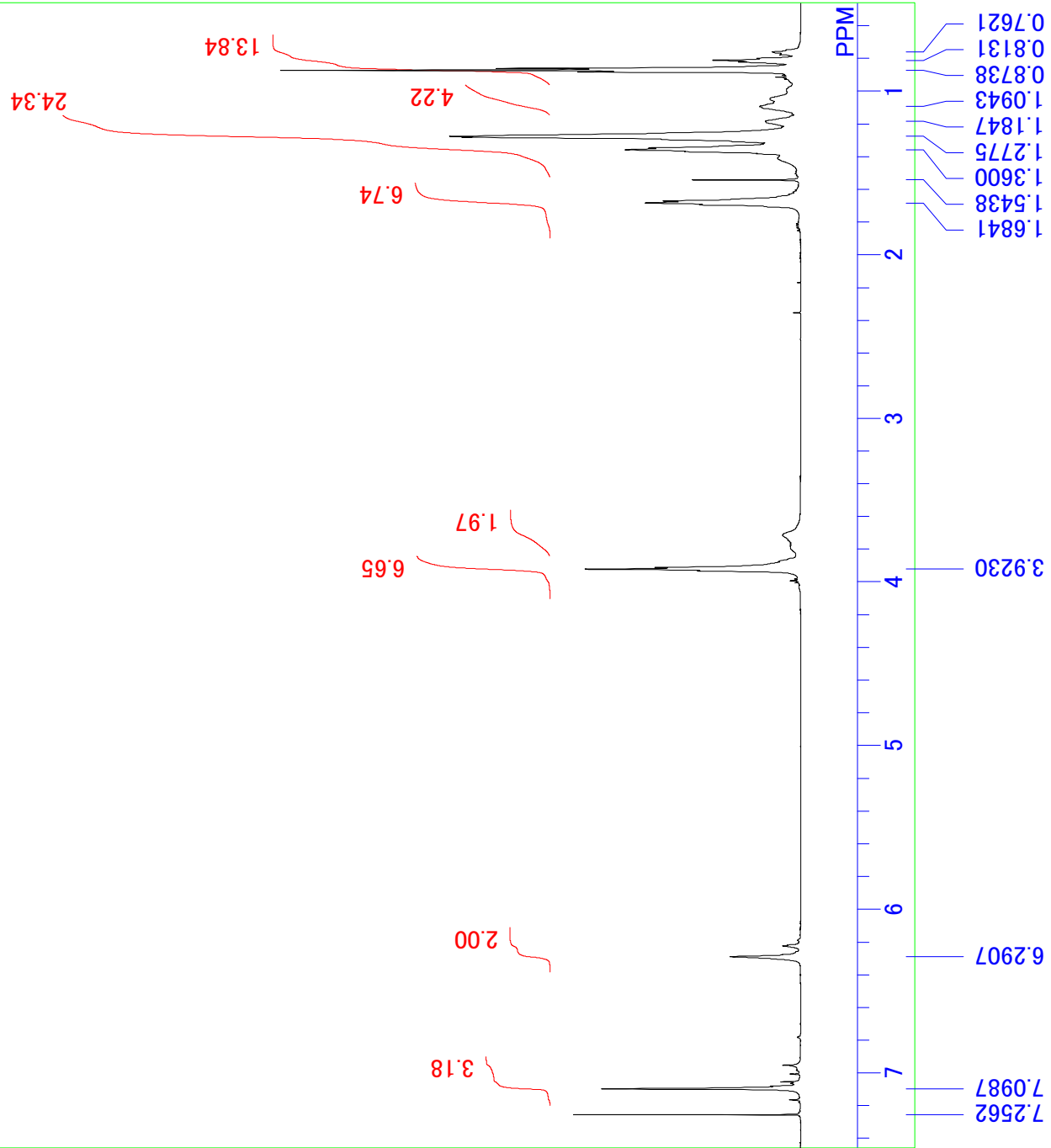












$^{13}\text{C}$  NMR(CDCl<sub>3</sub>, 151 MHz)