

# Palladium-Catalyzed Cyanation of Porphyrins Utilizing Cyanoethylzinc Bromide As an Efficient Cyanide Ion Source

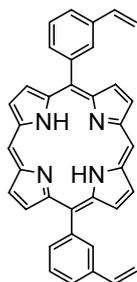
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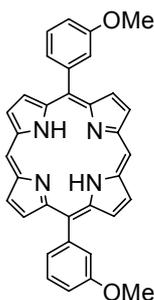
## Supporting Information

**General.** All palladium-catalyzed cyanation reactions were carried out under an argon atmosphere in oven-dried glassware following standard Schlenk techniques. Tetrahydrofuran (THF) and dioxane were distilled under argon from sodium benzophenone ketyl. Kanto Kagaku Silica Gel 60 (spherical) and Merck kiesel-gel 60 F<sub>254</sub> were employed for silica gel column and thin layer chromatographies, respectively. Cyanoethylzinc bromide (0.5M THF solution) and Pd<sub>2</sub>(dba)<sub>3</sub> were purchased from Aldrich Chemical Co. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a JEOL JNM-EX270, JNM-AL300, and JNM-AL400 spectrometer. The chemical shifts were reported in ppm relative to CHCl<sub>3</sub> (δ = 7.26) or dioxane (δ = 3.53) for <sup>1</sup>H-NMR and relative to the central resonance of CDCl<sub>3</sub> (δ = 77.0) or dioxane-d<sub>8</sub> (δ = 66.5) for <sup>13</sup>C-NMR. IR spectra were recorded on a JASCO FT/IR-7000 spectrophotometer. The mass spectroscopic data were obtained on a JEOL JNM-DX302 spectrometer.

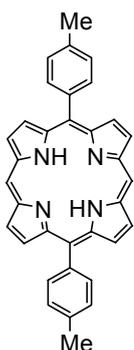
**General Procedure for Synthesis of 5,15-Diarylporphyrins.** 5,15-Diphenylporphyrin<sup>1</sup> and other diarylporphyrins are prepared according to the method described in literature.<sup>1</sup> A mixture of dipyrromethane<sup>2</sup> (15.5 mmol) and aldehyde (15.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 L) was purged with nitrogen. Trifluoroacetic acid (10 mmol) was added dropwise via a syringe, and the flask was shielded from light with aluminum foil. The solution was stirred under a nitrogen atmosphere at room temperature for 3 h. The reaction was quenched by the addition of DDQ (20 mmol), and the solution was stirred for an additional 30 min. The mixture was neutralized with triethylamine (15 mL), and then directly poured on top of a silica gel column packed with CH<sub>2</sub>Cl<sub>2</sub>. The column was eluted with CH<sub>2</sub>Cl<sub>2</sub>. The fractions containing product were collected and concentrated under a reduced pressure. The residue was washed several times with hexane, and recrystallized from a mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub> to give the pure compound.



**5,15-Bis(3-vinylphenyl)porphyrin.** Yield: 53%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  10.32 (s, 2H), 9.40 (d,  $J = 4.6$  Hz, 4H), 9.10 (d,  $J = 4.6$  Hz, 4H), 8.33 (s, 2H), 8.17 (d,  $J = 7.5$  Hz, 2H), 7.88 (d,  $J = 7.9$  Hz, 2H), 7.77 (t,  $J = \text{Hz}$ , 2H), 7.04 (dd,  $J = 11.0$  and 17.5 Hz, 2H), 6.01 (d,  $J = 17.5$  Hz, 2H), 5.44 (d,  $J = 11.0$  Hz, 2H),  $-3.10$  (s, 2H). HRMS-FAB $^+$  ( $[\text{M}+\text{H}]^+$ ): Calcd for  $\text{C}_{36}\text{H}_{27}\text{N}_4$  515.2236; found: 515.2238.



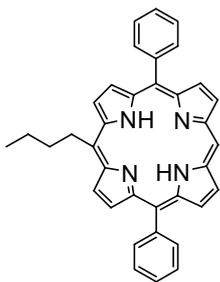
**5,15-Bis(3-methoxyphenyl)porphyrin.** Yield: 33%. Neither  $^1\text{H-NMR}$  nor  $^{13}\text{C-NMR}$  data are available owing to the poor solubility of the compound. HRMS-FAB $^+$  ( $[\text{M}+\text{H}]^+$ ): Calcd for  $\text{C}_{34}\text{H}_{27}\text{N}_4\text{O}_2$  523.2134; found: 523.2124.



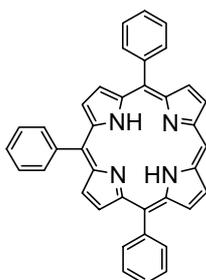
**5,15-Di-*p*-tolylporphyrin.** Yield: 44%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  10.30 (s, 2H), 9.39 (d,  $J = 4.6$  Hz, 4H), 9.11 (d,  $J = 4.6$  Hz, 4H), 8.17 (d,  $J = 7.9$  Hz, 4H), 7.62 (d,  $J = 7.9$  Hz, 4H), 2.74 (s, 6H),  $-3.09$  (s, 2H). HRMS-FAB $^+$  ( $[\text{M}+\text{H}]^+$ ): Calcd for  $\text{C}_{34}\text{H}_{27}\text{N}_4$  491.2236; found: 491.2239.

### General Procedure for Preparation of *meso*-Alkyl- and Phenyl-Substituted Porphyrins.

*meso*-Alkyl and phenyl-substituted porphyrins were prepared according to the method described in literature.<sup>3</sup> A flask equipped with a magnetic stirring bar and a septum was charged with 5,15-diphenylporphyrin (1 mmol). After flashing with dry Ar, 400 mL of anhydrous THF was added, and the solution was chilled to  $-78^\circ\text{C}$ . *n*-BuLi (1.0M in cyclohexane–*n*-hexane, 7.5 mL) or PhLi (1.05 M in cyclohexane–ether, 7.5 mmol) was added dropwise to this solution. The mixture was stirred for 30 min at this temperature, and then allowed to warm to room temperature for 2 h. The reaction was quenched by the addition of water (9 mL), and then DDQ (5.3 mmol) was added. After stirring for 30 min, the mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (400 mL), washed with brine, dried ( $\text{MgSO}_4$ ), and concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/THF 15:1) followed by recrystallization from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  gave the pure compound.

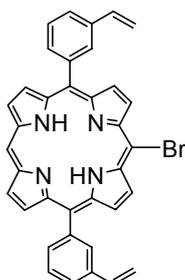


**10-*n*-Butyl-5,15-diphenylporphyrin.** Yield: 38%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 10.10 (s, 1H), 9.55 (d, *J* = 4.8 Hz, 2H), 9.27 (d, *J* = 4.6 Hz, 2H), 8.98 (d, *J* = 4.6 Hz, 2H), 8.96 (d, *J* = 4.4 Hz, 2H), 8.26–8.22 (m, 4H), 7.84–7.75 (m, 6H), 5.09 (t, *J* = 8.0 Hz, 2H), 2.61–2.51 (m, 2H), 1.90–1.77 (m, 2H), 1.14 (t, *J* = 7.3 Hz, 3H), –2.97 (s, 2H). HRMS-FAB<sup>+</sup> ([M+H]<sup>+</sup>): Calcd for C<sub>36</sub>H<sub>31</sub>N<sub>4</sub> 519.2549; found: 519.2544.

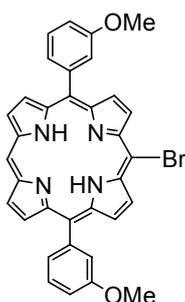


**5,10,15-Triphenylporphyrin.** Yield: 57%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 10.23 (s, 1H), 9.35 (d, *J* = 4.6 Hz, 2H), 9.02 (d, *J* = 4.6 Hz, 2H), 8.91–8.86 (m, 4H), 8.26–8.18 (m, 6H), 7.81–7.71 (m, 9H), –2.99 (s, 2H). HRMS-FAB<sup>+</sup> ([M+H]<sup>+</sup>): Calcd for C<sub>38</sub>H<sub>27</sub>N<sub>4</sub> 539.2236; found: 539.2229.

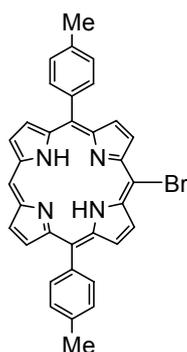
**General Procedure for Preparation of *meso*-mono-Bromoporphyrins.** 5-Bromo-10,20-diphenylporphyrin **1a**,<sup>4</sup> β-bromo-tetraphenylporphyrin **8**,<sup>1</sup> and other *meso*-mono-bromoporphyrins were prepared according to the method described in literature.<sup>4</sup> To a solution of 5,15-diarylporphyrin (1 mmol) in CHCl<sub>3</sub> (600 mL) was added NBS (1 mmol) at room temperature. After stirring for 1 h, the solution was concentrated in vacuo. Column chromatography on silica gel (*n*-hexane/toluene 5:1) followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane gave the pure compound.



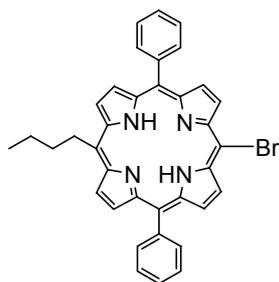
**10-Bromo-5,15-bis(3-vinylphenyl)porphyrin 1b.** Yield: 52%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 10.17 (s, 1H), 9.75 (d, *J* = 5.0 Hz, 2H), 9.29 (d, *J* = 4.8 Hz, 2H), 8.98 (d, *J* = 4.6 Hz, 2H), 8.97 (d, *J* = 4.8 Hz, 2H), 8.26 (s, 2H), 8.11 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 2H), 7.02 (dd, *J* = 11.0 and 17.6 Hz, 2H), 5.99 (d, *J* = 17.6 Hz, 2H), 5.45 (d, *J* = 11 Hz, 2H), –2.99 (s, 2H). HRMS-FAB<sup>+</sup> ([M+H]<sup>+</sup>): Calcd for C<sub>36</sub>H<sub>26</sub>BrN<sub>4</sub> 593.1341; found: 593.1347.



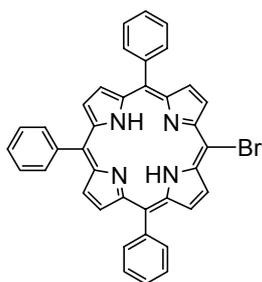
**10-Bromo-5,15-bis(3-methoxyphenyl)porphyrin 1c.** Yield: 46%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): δ 10.15 (s, 1H), 9.74 (d, *J* = 5.0 Hz, 2H), 9.27 (d, *J* = 4.8 Hz, 2H), 9.01 (d, *J* = 4.6 Hz, 2H), 9.01 (d, *J* = 5.0 Hz, 2H), 7.83–7.78 (m, 4H), 7.69 (t, *J* = 7.8 Hz, 2H), 7.39–7.35 (m, 2H), 4.02 (s, 6H), –2.99 (s, 2H). HRMS-FAB<sup>+</sup> ([M+H]<sup>+</sup>): Calcd for C<sub>34</sub>H<sub>26</sub>BrN<sub>4</sub>O<sub>2</sub> 601.1239; found: 601.1237.



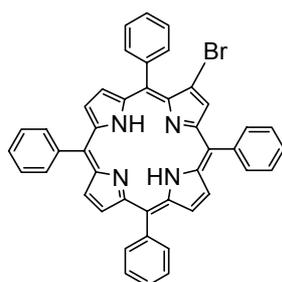
**10-Bromo-5,15-di-*p*-tolylporphyrin 1d.** Yield: 48%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  10.15 (s, 1H), 9.74 (d,  $J = 4.8$  Hz, 2H), 9.27 (d,  $J = 4.8$  Hz, 2H), 8.99 (d,  $J = 4.8$  Hz, 2H), 8.98 (d,  $J = 4.8$  Hz, 2H), 8.10 (br. d,  $J = 7.9$  Hz, 4H), 7.60 (d,  $J = 7.7$  Hz, 4H), 2.74 (s, 6H),  $-2.98$  (s, 2H). HRMS-FAB $^+$  ( $[\text{M}+\text{H}]^+$ ): Calcd for  $\text{C}_{34}\text{H}_{26}\text{BrN}_4$  569.1341; found: 569.1342.



**5-Bromo-15-*n*-butyl-10,20-diphenylporphyrin 1e.** Yield: 83%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  9.60 (d,  $J = 4.8$  Hz, 2H), 9.42 (d,  $J = 4.9$  Hz, 2H), 8.86 (d,  $J = 4.6$  Hz, 2H), 8.85 (d,  $J = 4.4$  Hz, 2H), 8.20-8.17 (m, 4H), 7.84-7.73 (m, 6H), 4.93 (t,  $J = 8.0$  Hz, 2H), 2.55-2.45 (m, 2H), 1.86-1.73 (m, 2H), 1.12 (t,  $J = 7.3$  Hz, 3H),  $-2.69$  (s, 2H). HRMS-FAB $^+$  ( $[\text{M}+\text{H}]^+$ ): Calcd for  $\text{C}_{36}\text{H}_{30}\text{BrN}_4$  597.1654; found: 597.1660.

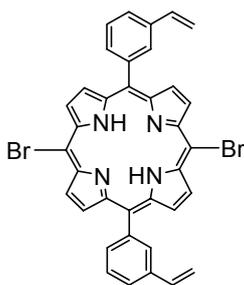


**5-Bromo-10,15,20-triphenylporphyrin 1f.** Yield: 67%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  9.67 (d,  $J = 5.0$  Hz, 2H), 8.91 (d,  $J = 5.0$  Hz, 2H), 8.81 (s, 4H), 8.22-8.18 (m, 6H), 7.84-7.71 (m, 9H),  $-2.71$  (s, 2H). HRMS-FAB $^+$  ( $[\text{M}+\text{H}]^+$ ): Calcd for  $\text{C}_{38}\text{H}_{26}\text{BrN}_4$  617.1341; found: 617.1349.

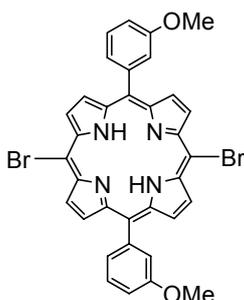


**7-Bromo-5,10,15,20-tetraphenylporphyrin 8.**<sup>1</sup> Yield: 40%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300MHz):  $\delta$  8.92-8.75 (m, 7H), 8.22-7.81 (m, 8H), 7.81-7.28 (m, 12H),  $-2.84$  (s, 2H). HRMS-FAB $^+$  ( $[\text{M}+\text{H}]^+$ ): Calcd for  $\text{C}_{44}\text{H}_{30}\text{BrN}_4$  693.1654; found: 693.1658.

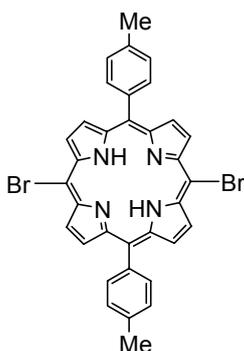
**General Procedure for Preparation of *meso*-Dibromoporphyrins.** 5,15-Dibromo-10,20-diphenylporphyrin<sup>1</sup> and other *meso*-dibromoporphyrins were prepared according to the method described in literature.<sup>1</sup> To a solution of 5,15-diarylporphyrin (1 mmol) in  $\text{CHCl}_3$  (250 mL) was added pyridine (1 mL) and NBS (2.2 mmol) at  $0^\circ\text{C}$ . After stirring at the same temperature for 30 min, the solution was concentrated in vacuo. The resulting residue was washed several times with methanol and pumped dry to afford the pure compound.



**5,15-Dibromo-10,20-bis(3-vinylphenyl)porphyrin 6b.** Yield: 89%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300MHz):  $\delta$  9.61 (d,  $J = 4.8$  Hz, 4H), 8.86 (d,  $J = 4.8$  Hz, 4H), 8.20 (s, 2H), 8.05 (d,  $J = 7.2$  Hz, 2H), 7.87 (br d,  $J = 7.9$  Hz, 2H), 7.73 (br t,  $J = 7.6$  Hz, 2H), 7.00 (dd,  $J = 11.0$  and 17.5 Hz, 2H), 5.98 (d,  $J = 17.5$  Hz, 2H), 5.44 (d,  $J = 11.0$  Hz, 2H),  $-2.72$  (s, 2H). HRMS-FAB $^+$  ( $[\text{M}+\text{H}]^+$ ): Calcd for  $\text{C}_{36}\text{H}_{25}\text{Br}_2\text{N}_4$  671.0446; found: 671.0449.



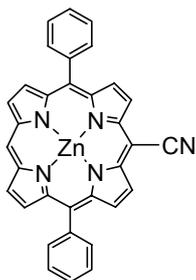
**5,15-Dibromo-10,20-bis(3-methoxyphenyl)porphyrin 6c.** Yield: 92%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300MHz):  $\delta$  9.60 (d,  $J = 4.8$  Hz, 4H), 8.88 (d,  $J = 4.8$  Hz, 4H), 7.77-7.72 (m, 4H), 7.66 (t,  $J = 7.9$  Hz, 2H), 7.38-7.34 (m, 2H), 4.01 (s, 6H),  $-2.74$  (s, 2H). HRMS-FAB $^+$  ( $[\text{M}+\text{H}]^+$ ): Calcd for  $\text{C}_{34}\text{H}_{25}\text{Br}_2\text{N}_4\text{O}_2$  679.0344; found: 679.0341.



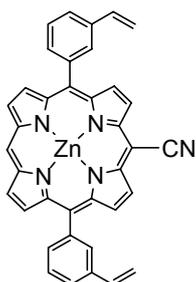
**5,15-Dibromo-10,20-di-p-tolylporphyrin 6d.** Yield: > 99%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300MHz):  $\delta$  9.60 (d,  $J = 4.8$  Hz, 4H), 8.86 (d,  $J = 4.8$  Hz, 4H), 8.04 (d,  $J = 7.9$  Hz, 4H), 7.58 (d,  $J = 7.9$  Hz, 4H), 2.73 (s, 6H),  $-2.72$  (s, 2H). HRMS-FAB $^+$  ( $[\text{M}+\text{H}]^+$ ): Calcd for  $\text{C}_{34}\text{H}_{25}\text{Br}_2\text{N}_4$  647.0446; found: 647.0440.

**General Procedure for the Palladium-Catalyzed Cyanation of Bromoporphyrins.** An oven-dried 25 ml sealable Schlenk flask equipped with a magnetic stirring bar was charged with a *meso*-bromoporphyrin **1** or  $\beta$ -bromoporphyrin **8** (0.05 mmol),  $\text{Pd}_2(\text{dba})_3$  (5.2mg, 0.005mmol), and triphenylphosphine (2.6mg, 0.01mmol). The reaction vessel was evacuated and flushed with argon (three times), and then absolute dioxane (10 ml) was added. To the solution was added 2-cyanoethylzinc bromide **2** (0.5 M in THF, 0.25 mmol, 5 equiv) at room temperature. The mixture was heated under argon at 95 °C for 0.5–2.5h, and then allowed to reach room temperature. The reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (10 ml), and washed with aqueous  $\text{NH}_4\text{Cl}$  and brine. The organic layer was dried over anhydrous  $\text{MgSO}_4$ , and concentrated in vacuo. The residue was charged on top of a silica gel column packed with *n*-hexane/THF (15:1), and the column was eluted with *n*-hexane/THF (15:1). The fractions containing product were collected and concentrated under a reduced pressure. The resulting crude product was washed several times with hexane, and recrystallized from  $\text{CH}_2\text{Cl}_2$ /*n*-hexane to give the pure compound.

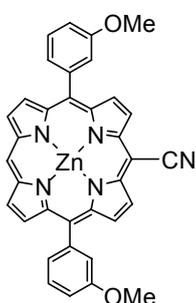
A similar procedure was used to prepare *meso*-dicyano porphyrins, using *meso*-dibromo porphyrin **6** (0.05 mmol),  $\text{Pd}_2(\text{dba})_3$  (5.2mg, 0.005mmol), triphenylphosphine (2.6mg, 0.01mmol) and 10 equiv of 2-cyanoethylzinc bromide **2** (0.5 M in THF, 0.5 mmol).



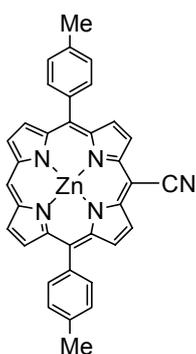
**[5-Cyano-10,15-diphenyl porphinato]zinc(II) 3a.**  $^1\text{H-NMR}$  (dioxane- $d_8$ , 300MHz):  $\delta$  10.36 (s, 1H), 9.68 (d,  $J = 4.6$  Hz, 2H), 9.40 (d,  $J = 4.4$  Hz, 2H), 9.07 (d,  $J = 4.6$  Hz, 2H), 8.95 (d,  $J = 4.4$  Hz, 2H), 8.24-8.21 (m, 4H), 7.84–7.80 (m, 6H).  $^{13}\text{C-NMR}$  (dioxane- $d_8$ , 100MHz):  $\delta$  151.9, 151.7, 150.6, 149.6, 142.9, 135.1, 134.7, 133.1, 132.8, 130.7, 128.3, 127.2, 123.0, 122.8, 110.7, 85.8. IR (KBr): 2232, 1524, 1439, 1311, 1214, 1067, 994, 936, 864, 787, 750, 729, 700  $\text{cm}^{-1}$ . HRMS-EI ( $[\text{M}]^+$ ): Calcd for  $\text{C}_{33}\text{H}_{19}\text{N}_5\text{Zn}$  549.0932; found: 549.0938.



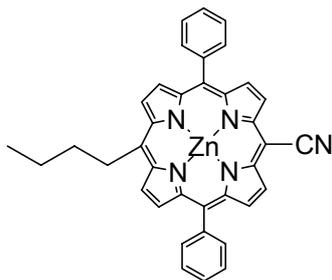
**[5-Cyano-10,20-bis(3-vinyl-phenyl)porphinato]zinc(II) 3b.**  $^1\text{H-NMR}$  (dioxane- $d_8$ , 300 MHz):  $\delta$  10.37 (s, 1H), 9.69 (d,  $J = 4.6$  Hz, 2H), 9.41 (d,  $J = 4.6$  Hz, 2H), 9.10 (d,  $J = 4.8$  Hz, 2H), 8.98 (d,  $J = 4.6$  Hz, 2H), 8.27 (br. d,  $J = 1.7$  Hz, 2H), 8.09 (d,  $J = 7.3$  Hz, 2H), 7.95 (d,  $J = 7.9$  Hz, 2H), 7.78 (t,  $J = \text{Hz}$ , 2H), 7.07 (dd,  $J = 11.0$  and 17.8 Hz, 2H), 6.06 (d,  $J = 17.8$  Hz, 2H), 5.45 (d,  $J = 11.0$  Hz, 2H).  $^{13}\text{C-NMR}$  ( $\text{C}_4\text{D}_8\text{O}_2$ , 100 MHz):  $\delta$  151.9, 151.7, 150.5, 149.6, 143.1, 137.5, 136.7, 134.8, 134.7, 133.1, 133.0, 132.8, 130.8, 127.4, 125.9, 122.8, 122.7, 115.2, 110.6, 85.9. IR (KBr): 2232, 1597, 1551, 1524, 1388, 1313, 1216, 1065, 996, 944, 917, 864, 789, 735, 712  $\text{cm}^{-1}$ . HRMS-EI ( $[\text{M}]^+$ ): Calcd for  $\text{C}_{37}\text{H}_{23}\text{N}_5\text{Zn}$  601.1245; found: 601.1252.



**[5-Cyano-10,20-Bis(3-methoxyphenyl)porphinato]zinc(II) 3c.**  $^1\text{H-NMR}$  (dioxane- $d_8$ , 300 MHz):  $\delta$  10.35 (s, 1H), 9.67 (d,  $J = 4.6$  Hz, 2H), 9.39 (d,  $J = 4.4$  Hz, 2H), 9.12 (d,  $J = 4.8$  Hz, 2H), 9.00 (d,  $J = 4.4$  Hz, 2H), 7.78-7.76 (m, 4H), 7.69 (t,  $J = 8.0$  Hz, 2H), 7.42–7.39 (m, 2H), 4.01 (s, 6H).  $^{13}\text{C-NMR}$  ( $\text{C}_4\text{D}_8\text{O}_2$ , 100MHz):  $\delta$  158.8, 151.9, 151.6, 150.4, 149.6, 144.1, 134.7, 133.0, 132.8, 130.7, 128.1, 128.0, 122.8, 121.4, 113.8, 110.6, 85.8, 55.5. IR (KBr): 2214, 1599, 1524, 1483, 1462, 1431, 1388, 1315, 1288, 1214, 1152, 1065, 1050, 996, 944, 924, 864, 787, 735, 698  $\text{cm}^{-1}$ . HRMS-EI ( $[\text{M}]^+$ ): Calcd for  $\text{C}_{35}\text{H}_{23}\text{N}_5\text{O}_2\text{Zn}$  609.1143; found: 609.1144.

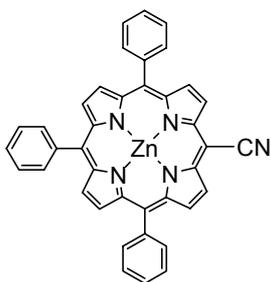


**[5-Cyano-10,20-Di-*p*-tolylporphinato]zinc(II) 3d.**  $^1\text{H-NMR}$  (dioxane- $d_8$ , 400 MHz):  $\delta$  10.34 (s, 1H), 9.67 (d,  $J = 4.9$  Hz, 2H), 9.39 (d,  $J = 4.6$  Hz, 2H), 9.08 (d,  $J = 4.6$  Hz, 2H), 8.96 (d,  $J = 4.4$  Hz, 2H), 8.10 (d,  $J = 7.8$  Hz, 2H), 7.63 (d,  $J = 8.1$  Hz, 2H), 2.73 (s, 6H).  $^{13}\text{C-NMR}$  ( $\text{C}_4\text{D}_8\text{O}_2$ , 100 MHz):  $\delta$  151.8, 150.7, 149.5, 140.0, 137.9, 135.0, 134.7, 132.9, 132.8, 130.6, 127.9, 123.0, 122.8, 110.5, 85.7, 21.5. IR (KBr): 2232, 1549, 1524, 1508, 1388, 1309, 1214, 1183, 1064, 996, 936, 864, 791, 735, 708  $\text{cm}^{-1}$ . HRMS-EI ( $[\text{M}]^+$ ): Calcd for  $\text{C}_{35}\text{H}_{23}\text{N}_5\text{Zn}$  577.1245; found: 577.1243.

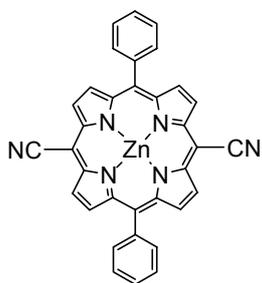


**[5-*n*-Butyl-15-cyano-10,20-diphenylporphinato]zinc(II) 3e.**

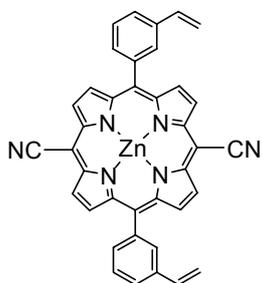
$^1\text{H-NMR}$  (dioxane- $d_8$ , 400 MHz):  $\delta$  9.59 (d,  $J = 4.6$  Hz, 2H), 9.54 (d,  $J = 4.6$  Hz, 2H), 8.94 (d,  $J = 4.6$  Hz, 2H), 8.82 (d,  $J = 4.6$  Hz, 2H), 8.19–8.16 (m, 4H), 7.84–7.77 (m, 6H), 5.10 (t,  $J = 7.6$  Hz, 2H), 2.50–2.42 (m, 2H), 1.83–1.74 (m, 2H), 1.09 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C-NMR}$  ( $\text{C}_4\text{D}_8\text{O}_2$ , 100 MHz):  $\delta$  152.5, 151.1, 150.2, 150.0, 143.1, 134.9, 134.7, 132.4, 130.4, 130.1, 128.2, 127.4, 127.2, 123.1, 122.7, 84.8, 42.3, 36.0, 24.1, 14.5. IR (KBr): 2218, 1599, 1555, 1526, 1441, 1348, 1319, 1247, 1214, 1073, 990, 934, 793, 752, 702, 661  $\text{cm}^{-1}$ . HRMS-EI ( $[\text{M}]^+$ ): Calcd for  $\text{C}_{37}\text{H}_{27}\text{N}_5\text{Zn}$  605.1558; found: 605.1555.



**[5-Cyano-10,15,20-triphenylporphinato]zinc(II) 3f.**  $^1\text{H-NMR}$  (dioxane- $d_8$ , 400 MHz):  $\delta$  9.62 (d,  $J = 4.6$  Hz, 2H), 9.01 (d,  $J = 4.6$  Hz, 2H), 8.79 (d,  $J = 4.6$  Hz, 2H), 8.77 (d,  $J = 4.6$  Hz, 2H), 8.20–8.15 (m, 6H), 7.80–7.75 (m, 9H).  $^{13}\text{C-NMR}$  ( $\text{C}_4\text{D}_8\text{O}_2$ , 100 MHz):  $\delta$  152.3, 151.6, 150.6, 149.8, 143.2, 142.9, 135.0, 134.8, 133.1, 132.2, 130.7, 128.3, 128.3, 127.2, 127.1, 126.2, 123.6, 122.7, 85.6. IR (KBr): 2214, 2190, 1599, 1553, 1526, 1441, 1346, 1309, 1212, 1180, 1073, 1006, 936, 797, 756, 725, 704  $\text{cm}^{-1}$ . HRMS-EI ( $[\text{M}]^+$ ): Calcd for  $\text{C}_{39}\text{H}_{23}\text{N}_5\text{Zn}$  625.1245; found: 625.1244.

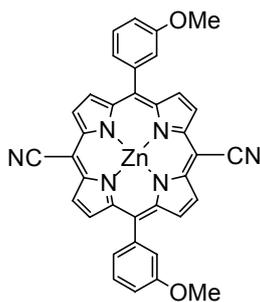


**[5,15-Dicyano-10,20-diphenylporphinato]zinc(II) 7a.**  $^1\text{H-NMR}$  (dioxane- $d_8$ , 300 MHz):  $\delta$  9.72 (d,  $J = 4.8$  Hz, 4H), 9.04 (d,  $J = 4.6$  Hz, 4H), 8.22–8.19 (m, 4H), 7.87–7.80 (m, 6H).  $^{13}\text{C-NMR}$  ( $\text{C}_4\text{D}_8\text{O}_2$ , 125 MHz):  $\delta$  153.3, 152.5, 143.2, 136.2, 136.0, 132.9, 129.7, 128.5, 126.0, 123.0, 90.7. IR (KBr): 2206, 1537, 1499, 1444, 1348, 1319, 1212, 1075, 998, 932, 832, 799, 754, 741, 712, 702, 665  $\text{cm}^{-1}$ . HRMS-EI ( $[\text{M}]^+$ ): Calcd for  $\text{C}_{34}\text{H}_{18}\text{N}_6\text{Zn}$  574.0884; found: 574.0892.

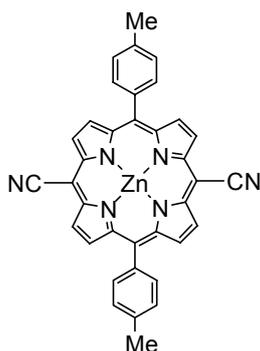


**[5,15-Dicyano-10,20-bis(3-vinylphenyl)porphinato]zinc(II) 7b.**

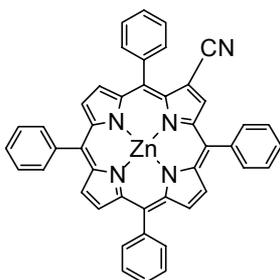
$^1\text{H-NMR}$  (dioxane- $d_8$ , 300 MHz):  $\delta$  9.72 (d,  $J = 4.8$  Hz, 4H), 9.08 (d,  $J = 4.6$  Hz, 4H), 8.25 (br. d,  $J = 1.5$  Hz, 2H), 8.07 (d,  $J = 7.3$  Hz, 2H), 7.98 (d,  $J = 7.9$  Hz, 2H), 7.80 (t,  $J = 7.6$  Hz, 2H), 7.07 (dd,  $J = 11.0$  and  $17.6$  Hz, 2H), 6.07 (d,  $J = 17.6$  Hz, 2H), 5.48 (d,  $J = 11.0$  Hz, 2H).  $^{13}\text{C-NMR}$  ( $\text{C}_4\text{D}_8\text{O}_2$ , 100 MHz):  $\delta$  152.1, 151.4, 142.4, 137.3, 136.9, 134.9, 134.7, 133.0, 131.8, 127.6, 126.3, 124.7, 121.9, 115.5, 89.7. IR (KBr): 2216, 1599, 1537, 1499, 1417, 1348, 1317, 1274, 1209, 1071, 1004, 932, 920, 833, 791, 743, 710, 663  $\text{cm}^{-1}$ . HRMS-EI ( $[\text{M}]^+$ ): Calcd for  $\text{C}_{38}\text{H}_{22}\text{N}_6\text{Zn}$  626.1197; found: 626.1198.



**[5,15-Dicyano-10,20-bis(3-methoxyphenyl)porphinato]zinc(II) 7c.**  $^1\text{H-NMR}$  (dioxane- $d_8$ , 300 MHz):  $\delta$  9.71 (d,  $J = 4.8$  Hz, 4H), 9.10 (d,  $J = 4.6$  Hz, 4H), 7.77–7.69 (m, 6H), 7.45–7.41 (m, 2H), 4.02 (s, 6H).  $^{13}\text{C-NMR}$  ( $\text{C}_4\text{D}_8\text{O}_2$ , 100 MHz):  $\delta$  158.8, 152.1, 151.4, 143.3, 134.9, 131.7, 128.2, 124.6, 121.9, 121.6, 114.0, 89.7, 55.6. IR (KBr): 2208, 1601, 1537, 1487, 1462, 1419, 1350, 1319, 1286, 1265, 1209, 1176, 1073, 1046, 1002, 932, 791, 741, 710  $\text{cm}^{-1}$ . HRMS-EI ( $[\text{M}]^+$ ): Calcd for  $\text{C}_{36}\text{H}_{22}\text{N}_6\text{O}_2\text{Zn}$  634.1096; found: 634.1100.



**[5,15-Dicyano-10,20-di-p-tolylporphinato]zinc(II) 7d.**  $^1\text{H-NMR}$  (dioxane- $d_8$ , 400MHz):  $\delta$  9.66 (d,  $J = 4.6$  Hz, 4H), 9.07 (d,  $J = 4.6$  Hz, 4H), 8.11 (br d,  $J = 7.8$  Hz, 4H), 7.67 (d,  $J = 7.6$  Hz, 4H), 2.75 (s, 6H).  $^{13}\text{C-NMR}$  ( $\text{C}_4\text{D}_8\text{O}$ , 100MHz):  $\delta$  151.7, 150.6, 138.7, 137.7, 134.3, 133.9, 130.3, 127.3, 124.3, 121.4, 88.7, 20.7. IR (KBr): 2210, 1537, 1499, 1419, 1350, 1317, 1212, 1073, 998, 930, 791, 743, 710, 507  $\text{cm}^{-1}$ . HRMS-EI ( $[\text{M}]^+$ ): Calcd for  $\text{C}_{36}\text{H}_{22}\text{N}_6\text{Zn}$  602.1197; found: 602.1190.



**[2-Cyano-5,10,15,20-tetraphenylporphinato]zinc(II) 9.**  $^1\text{H-NMR}$  (dioxane- $d_8$ , 400 MHz):  $\delta$  9.33 (s, 1H), 8.74–8.66 (m, 6H), 8.10–7.99 (m, 8H), 7.77–7.62 (m, 12H).  $^{13}\text{C-NMR}$  ( $\text{C}_4\text{D}_8\text{O}_2$ , 100 MHz):  $\delta$  152.2, 151.9, 151.8, 151.5, 151.0, 150.1, 146.3, 146.2, 143.4, 143.3, 142.9, 141.8, 141.4, 135.1, 135.0, 134.5, 133.8, 133.2, 133.0, 132.5, 129.5, 128.4, 128.1, 127.4, 127.2, 127.1, 123.0, 121.7, 121.4, 115.4, 113.3. IR (KBr): 2232, 1599, 1522, 1489, 1441, 1340, 1193, 1158, 1073, 1006, 799, 752, 723, 700  $\text{cm}^{-1}$ . HRMS-FAB $^+$  ( $[\text{M}+\text{H}]^+$ ): Calcd for  $\text{C}_{45}\text{H}_{28}\text{N}_5\text{Zn}$  702.1636; found: 702.1635.

## References

1. DiMugno, S. G.; Lin, V. S. -Y.; Therien, J. M. *J. Org. Chem.* **1993**, *58*, 5983–5993.
2. Wang, Q. M.; Bruce, D. W. *Synlett*, **1995**, 1267–1268.
3. (a) Kalisch, W. W.; Senge, M. O. *Angew. Chem. Int. Ed.* **1998**, *37*, 1107–1109. (b) Senge, M. O.; Bischoff, I.; *Eur. J. Org. Chem.* **2001**, 1735-1751.
4. Arnold, D. P.; Bott, R. C.; Eldridge, H.; Elms, F. M.; Smith, G.; Zojaji, M. *Aust. J. Chem.* **1997**, *50*, 495–503.



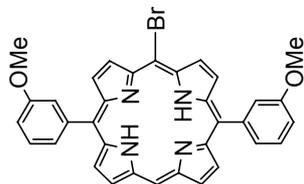
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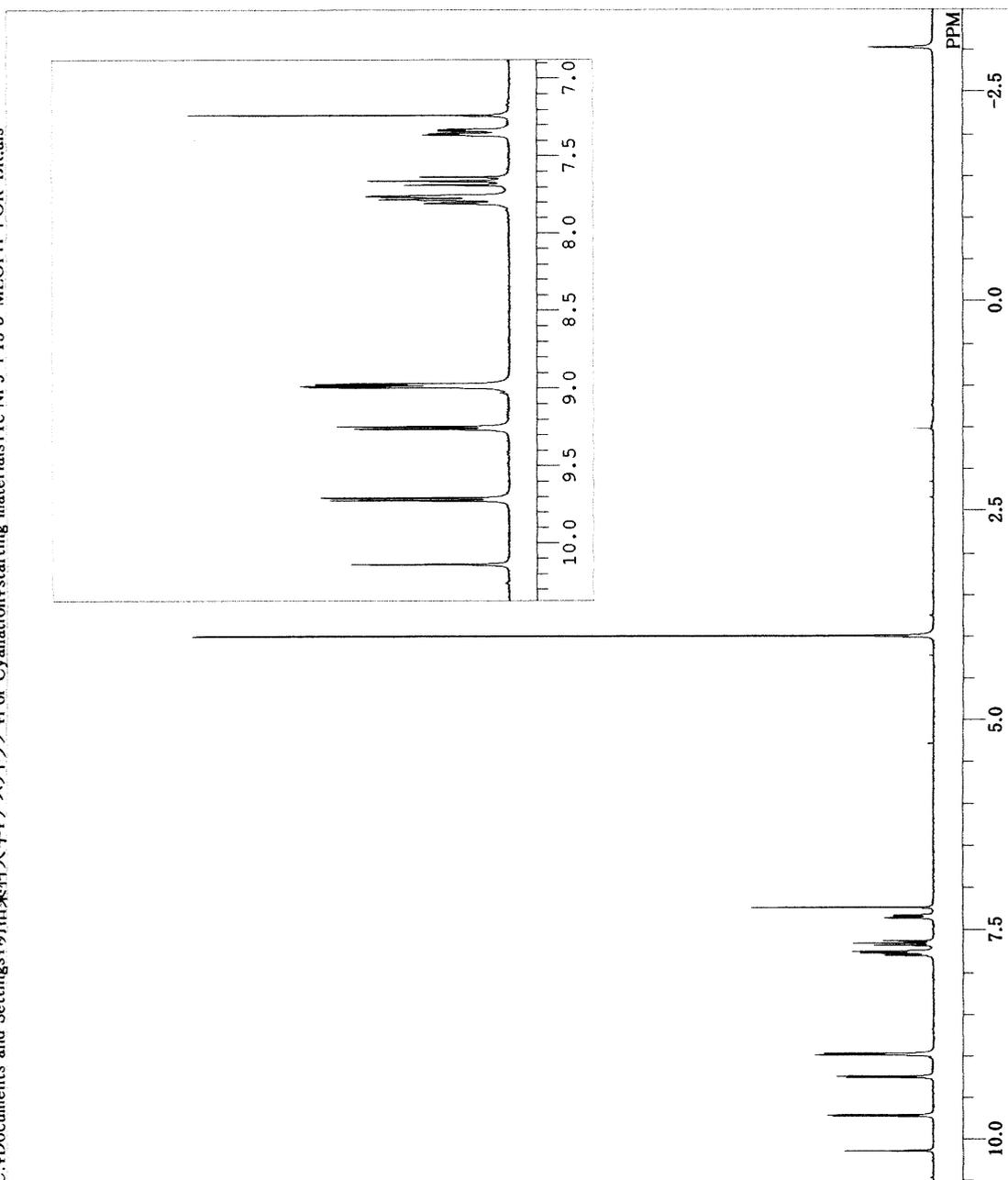
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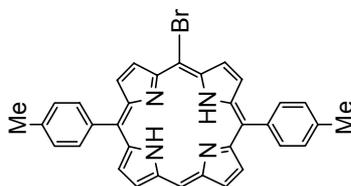
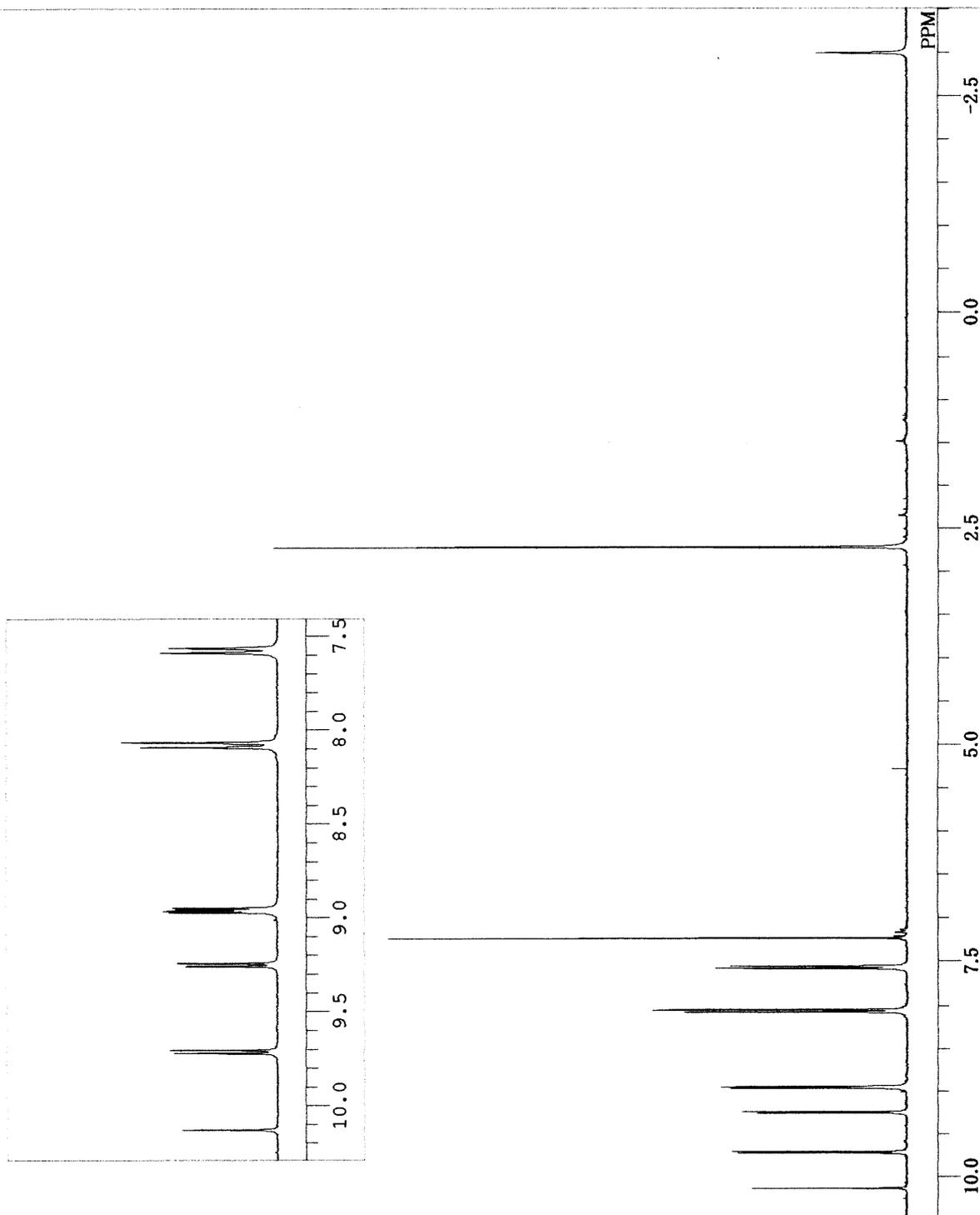
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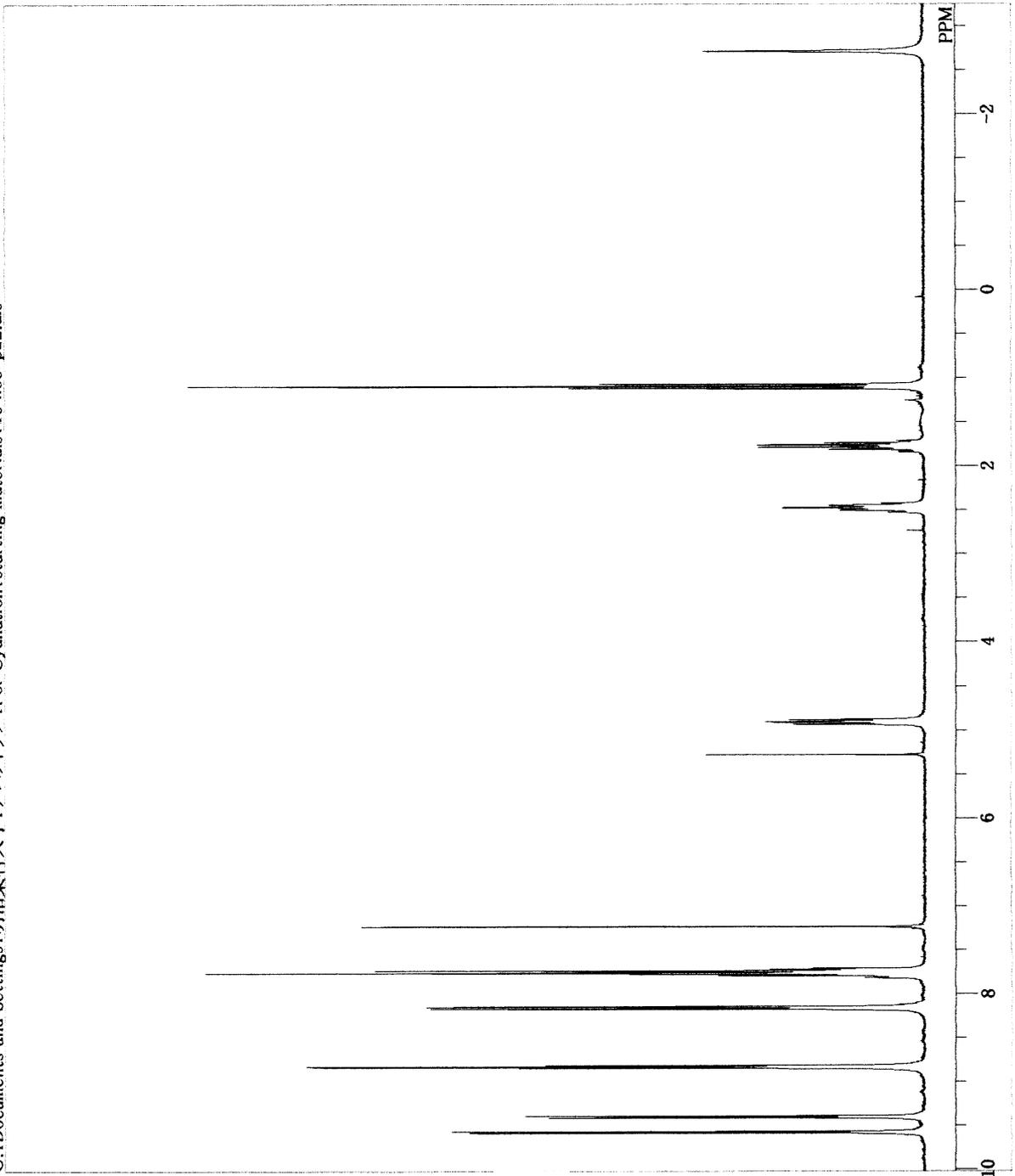
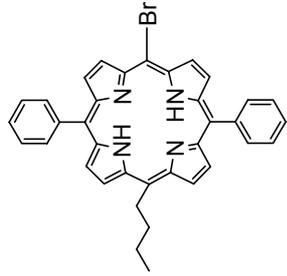
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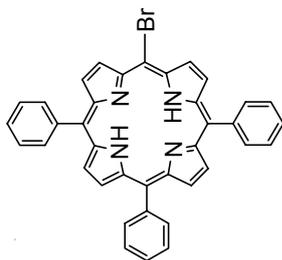


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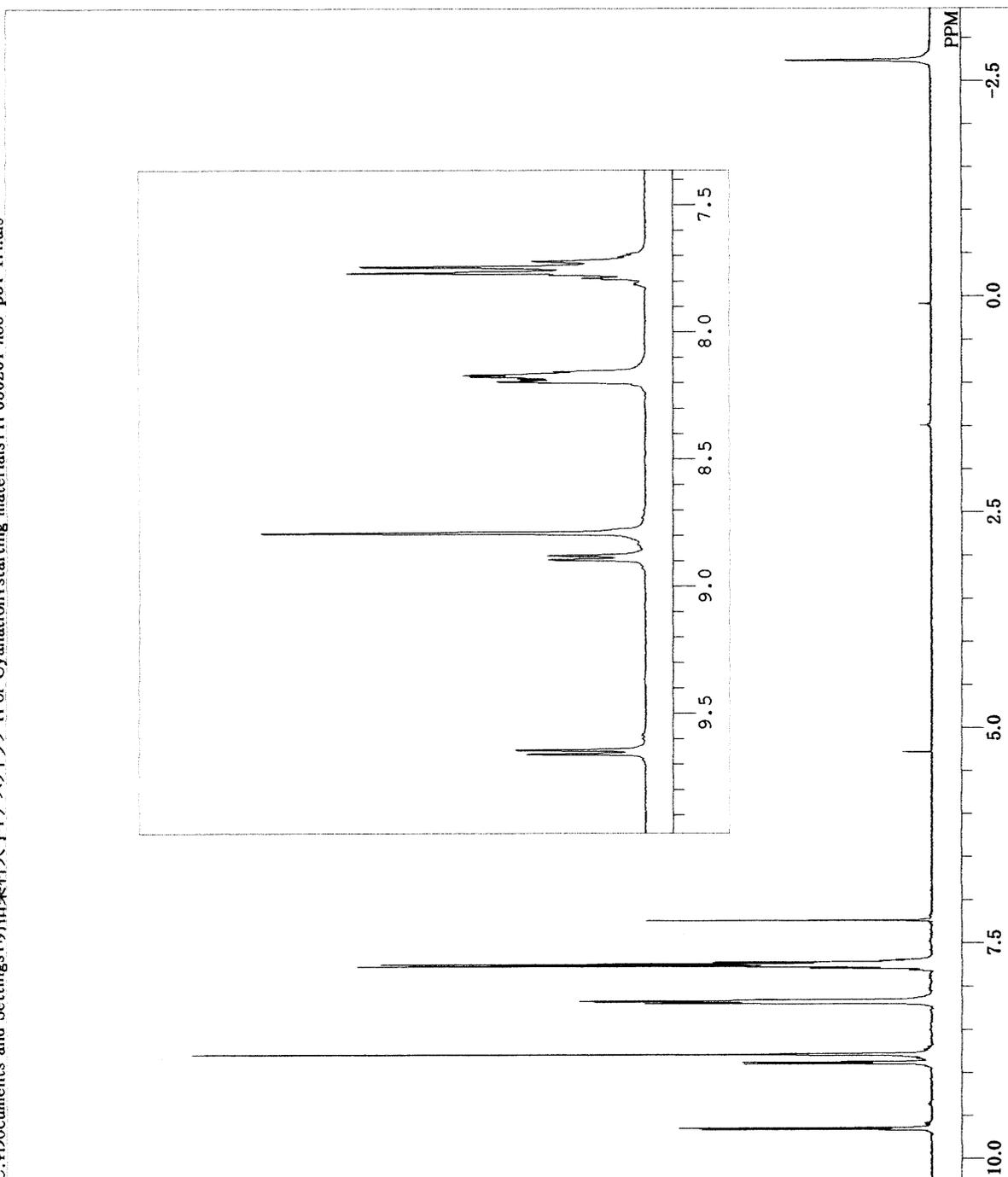
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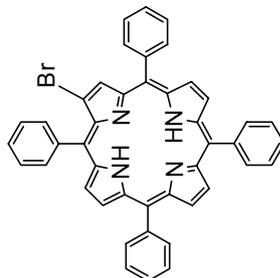
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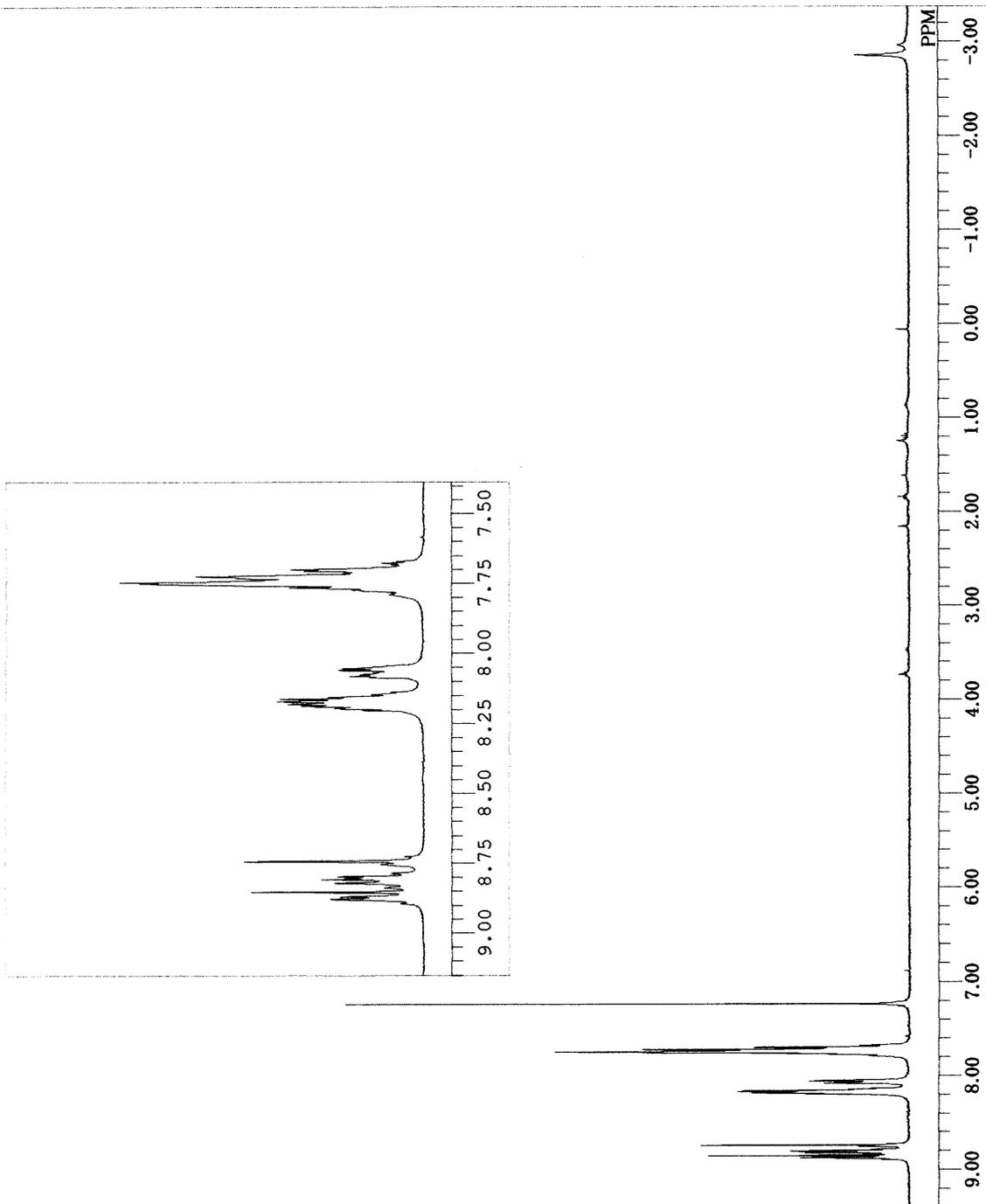
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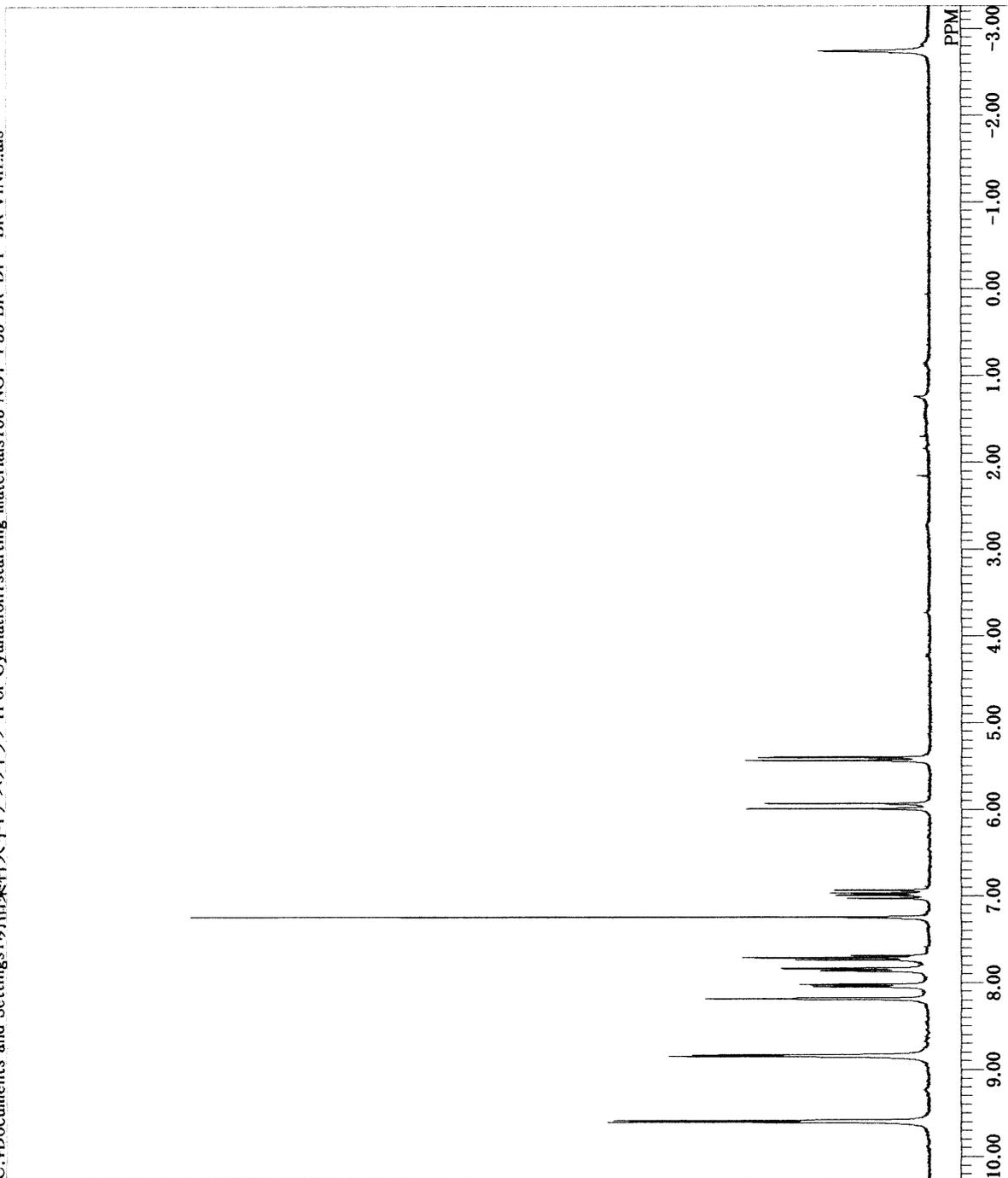
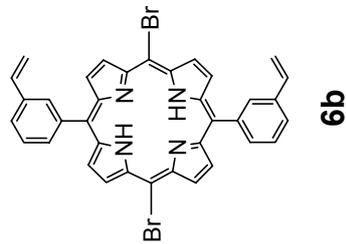


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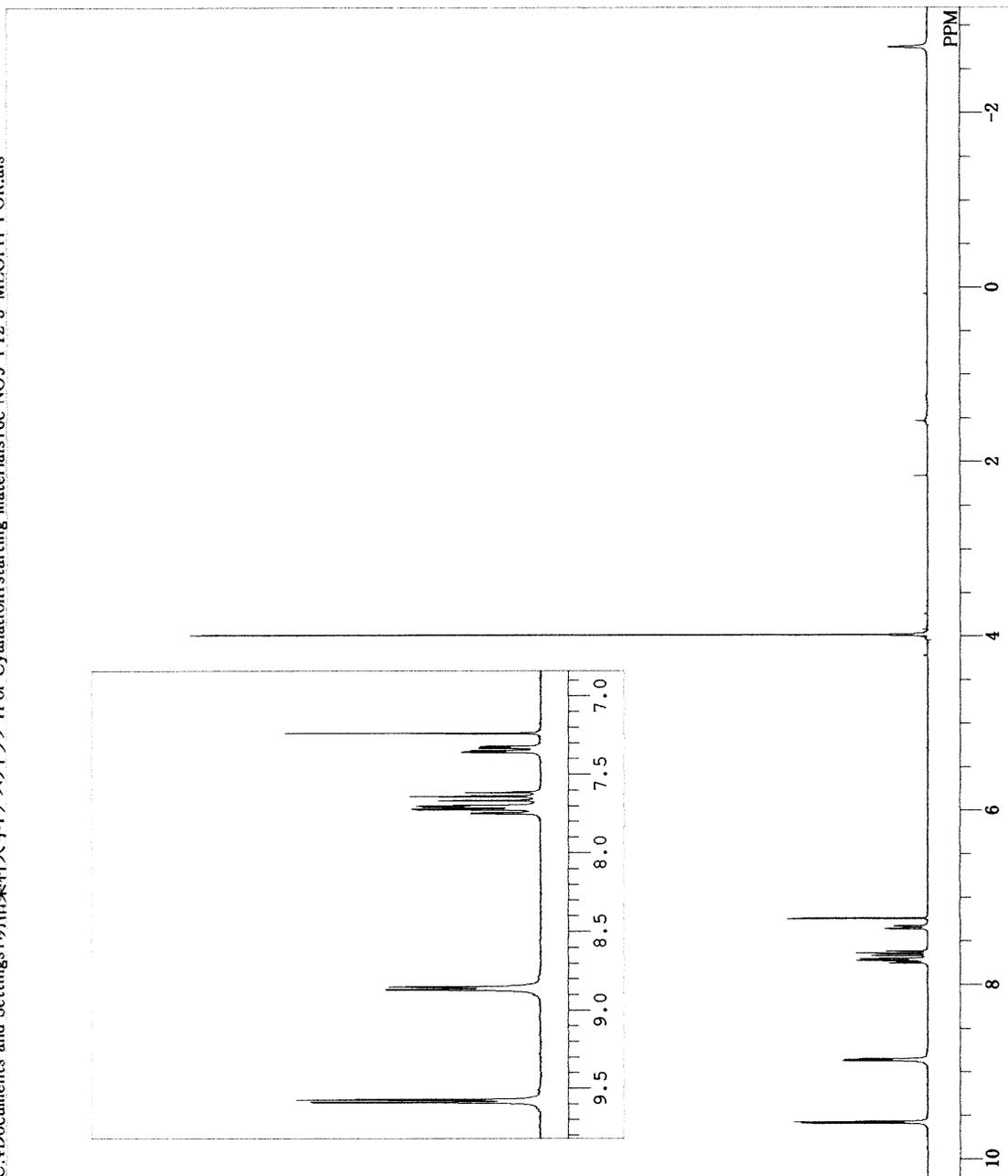
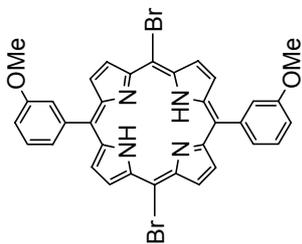
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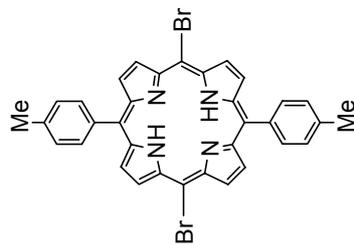
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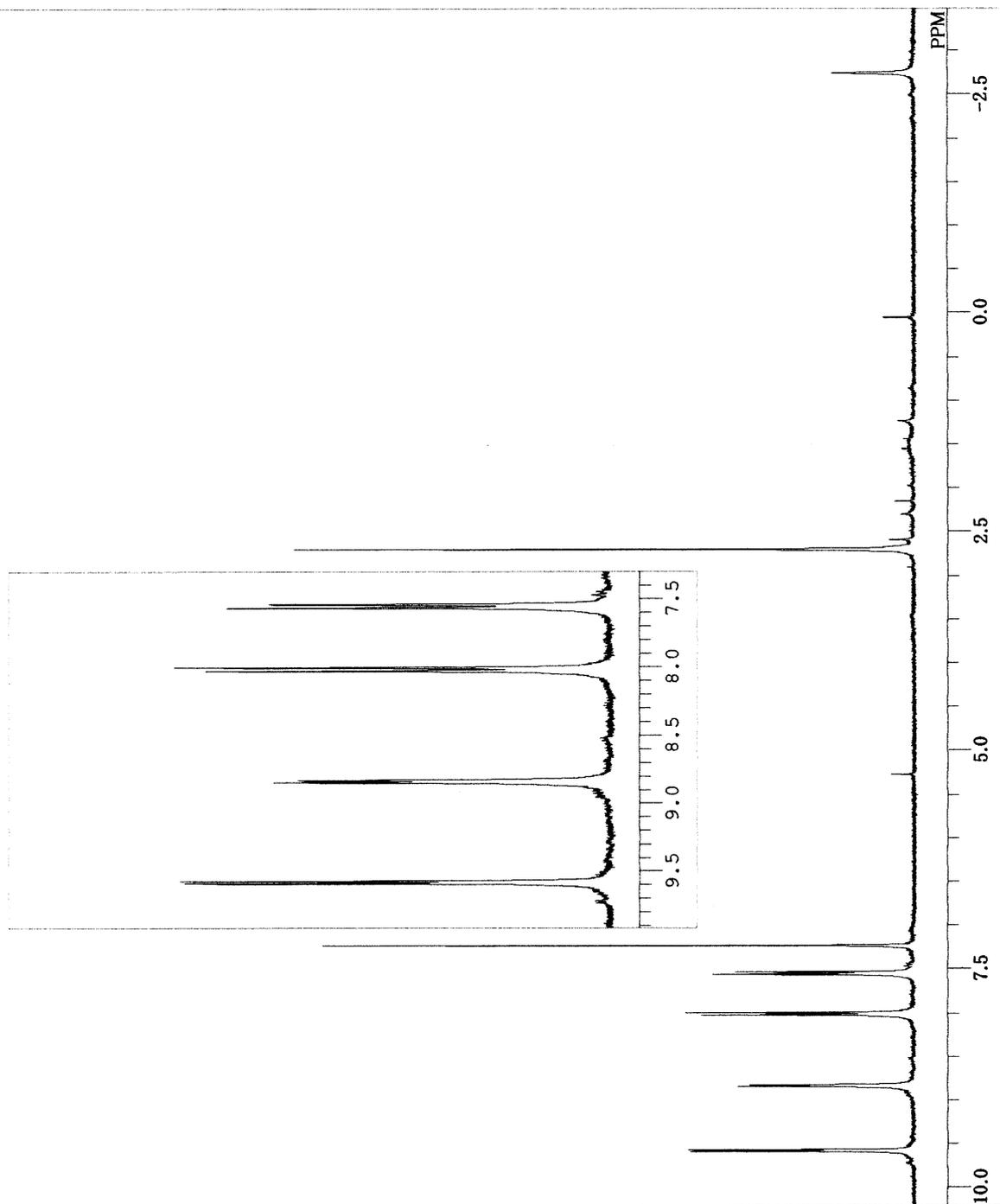


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 OBNUC  
 EXMOD  
 OBFRQ  
 OBSET  
 OBFIN  
 POINT  
 FREQU  
 SCANS  
 ACQTM  
 PD  
 PW1  
 IRNUC  
 CTEMP  
 SLVNT  
 EXREF  
 BF  
 RGAIN

6d NO9-P30 BR-POR-BR P  
 Fri Nov 26 16:54:13 2004  
 1H  
 NON  
 300.40 MHz  
 130.00 KHz  
 1150.00 Hz  
 32768  
 6013.20 Hz  
 16  
 5.493 sec  
 1.5510 sec  
 5.30 usec  
 1H  
 26.3 c  
 CDCL3  
 7.24 ppm  
 0.12 Hz  
 25



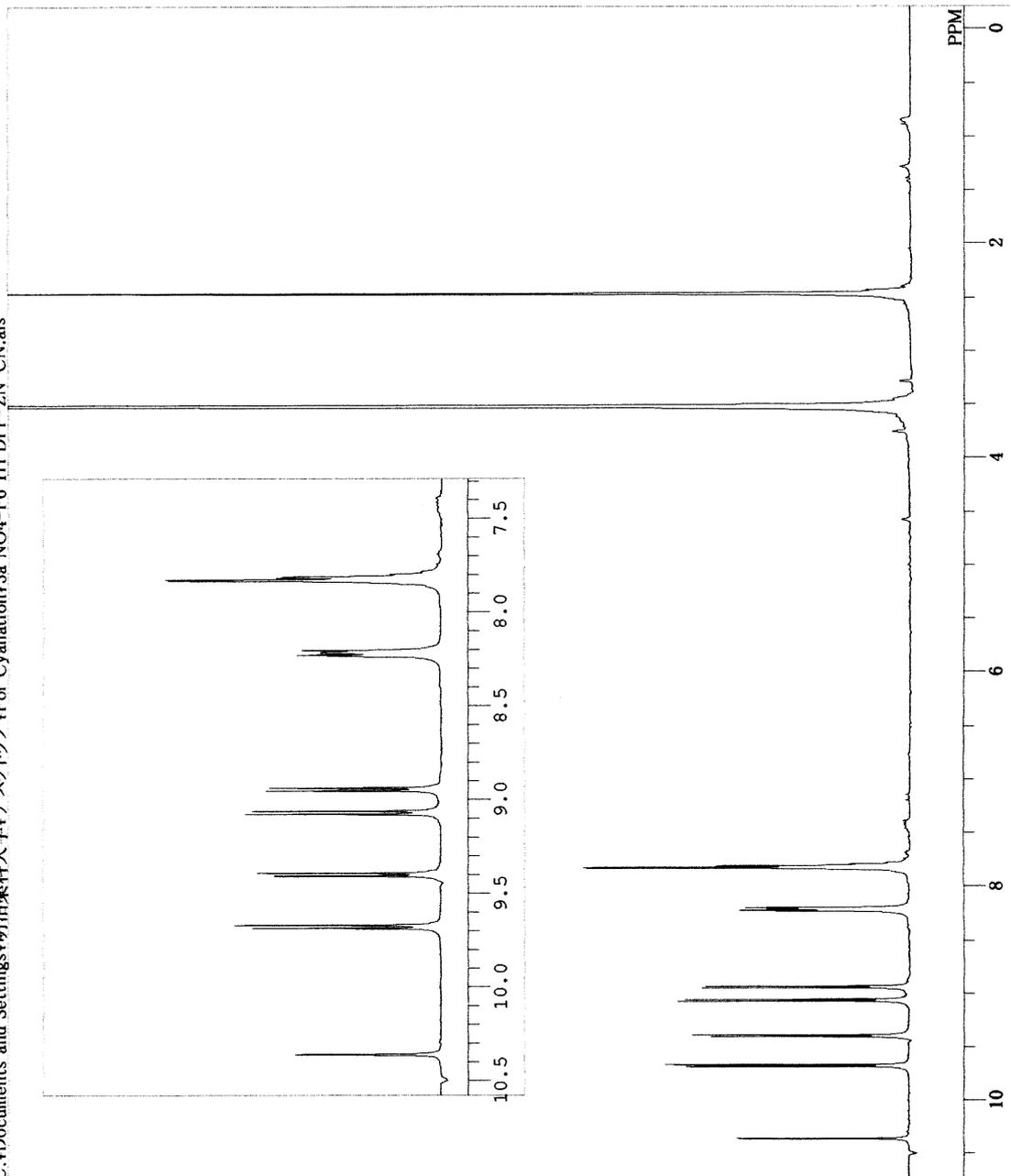
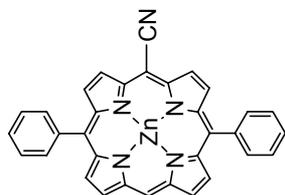
6d



C:\Documents and Settings\明治薬科大\学生\デスクリップ\3a\_NO4-P6 1H DPP-ZN-CN.als

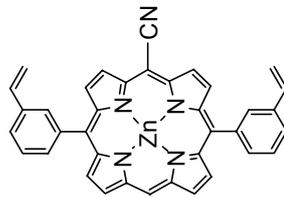
3a\_NO4-P6 1H DPP-ZN-CN  
Thu Nov 20 20:33:01 2003  
IH  
NON  
300.40 MHz  
130.00 KHz  
1150.00 Hz  
32768  
6013.20 Hz  
5.493 sec  
1.5510 sec  
5.30 usec  
5.493 sec  
1.5510 sec  
5.30 usec  
IH  
C4D8O2  
27.6 c  
3.53 ppm  
0.09 Hz  
18

DFILE  
COMNT  
DATIM  
OBNUC  
EXMOD  
OBFRQ  
OBSET  
OBFIN  
POINT  
FREQU  
SCANS  
ACQTM  
PD  
PW1  
IRNUC  
CTEMP  
SLVNT  
EXREF  
BF  
RGAIN

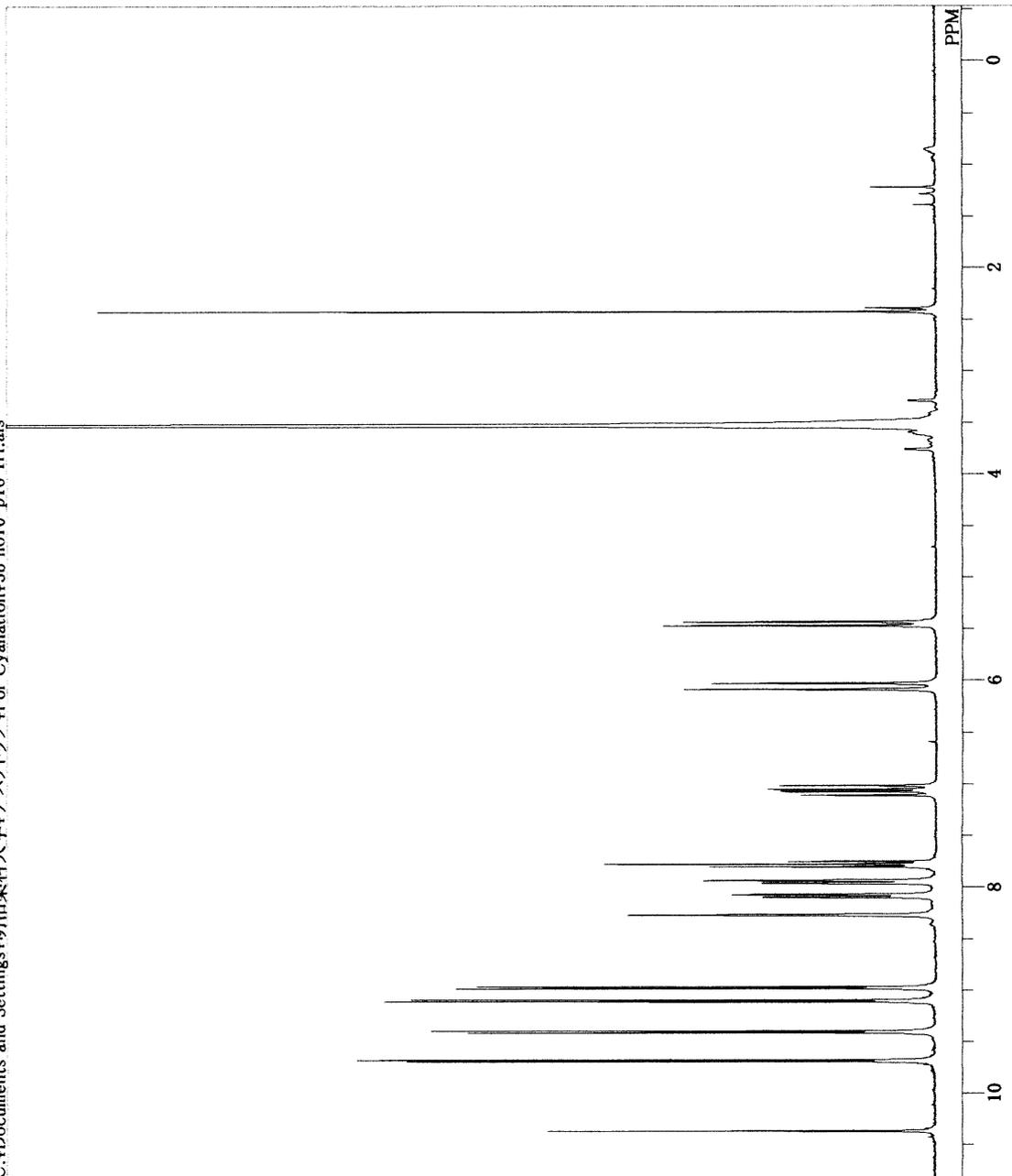


DFILE  
COMNT  
DATIM  
OBNUC  
EXMOD  
OBFREQ  
OBSET  
OBFIN  
POINT  
FREQU  
SCANS  
ACQTM  
PD  
PW1  
IRNUC  
CTEMP  
SLVNT  
EXREF  
BF  
RGAIN

3b no10-p16 1H.als  
Mon Dec 27 16:12:43 2004  
1H  
NON  
300.40 MHz  
130.00 KHz  
1150.00 Hz  
32768  
6013.20 Hz  
32  
5.4493 sec  
1.5510 sec  
5.30 usec  
1H 25.8 c  
C4D8O2  
3.53 ppm  
0.09 Hz  
18



3b

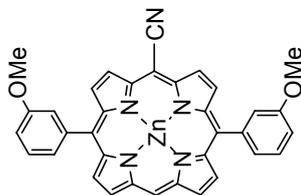


DFILE  
COMNT  
DATIM  
OBNUC  
EXMOD  
OBFRQ  
OBSET  
OBFIN  
POINT  
FREQU  
SCANS  
ACQTM  
PD  
PW1  
IRNUC  
SLVNT  
EXREF  
BF  
RGAIN

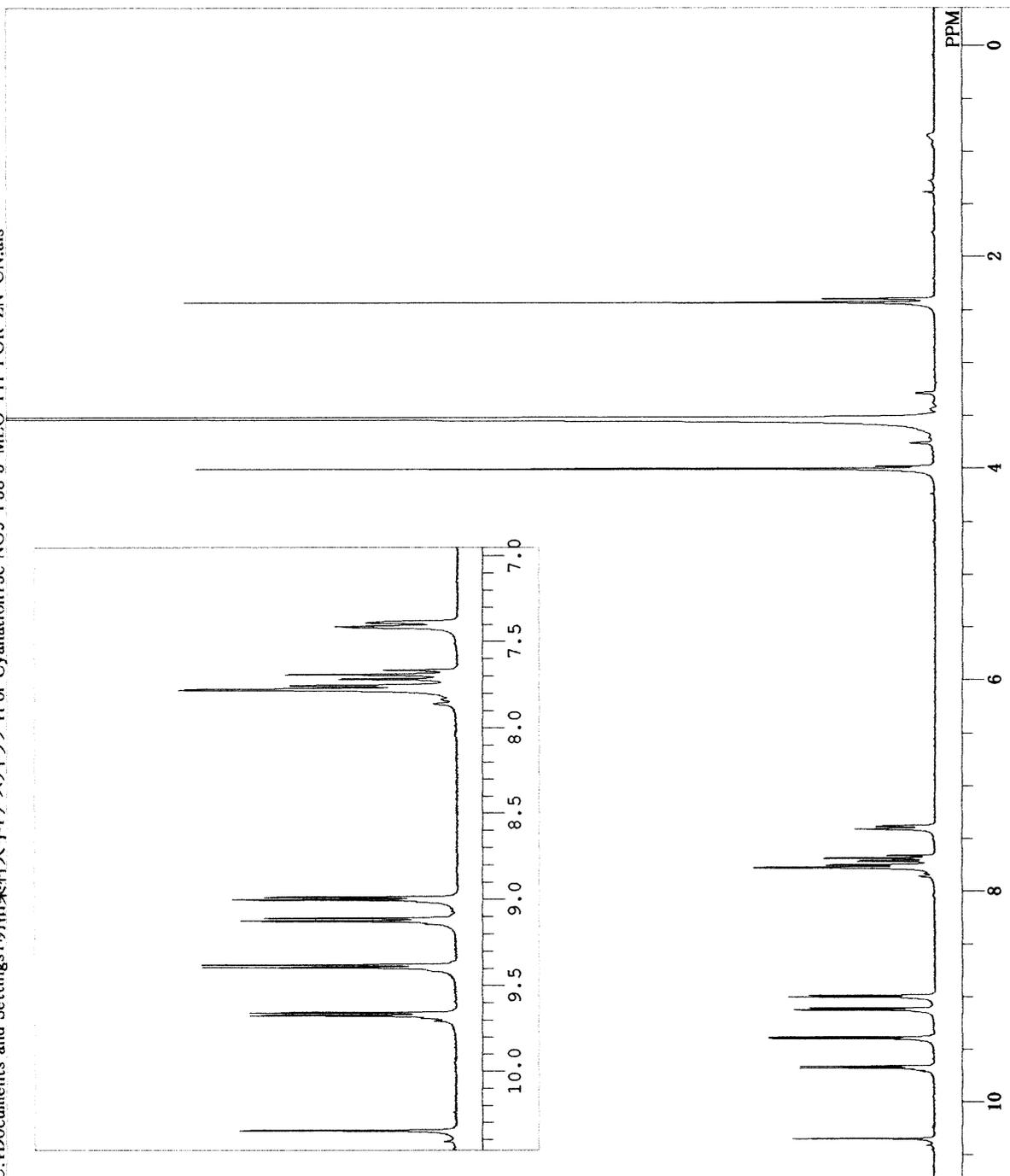
3c NO9-P38 3-MEO-PH-POR

Sat Dec 18 15:01:43 2004

1H  
NON  
300.40 MHz  
130.00 KHz  
1150.00 Hz  
32768  
6013.20 Hz  
32  
5.4493 sec  
1.5510 sec  
5.30 usec  
1H  
26.7 c  
C4D8O2  
3.53 ppm  
0.09 Hz  
18

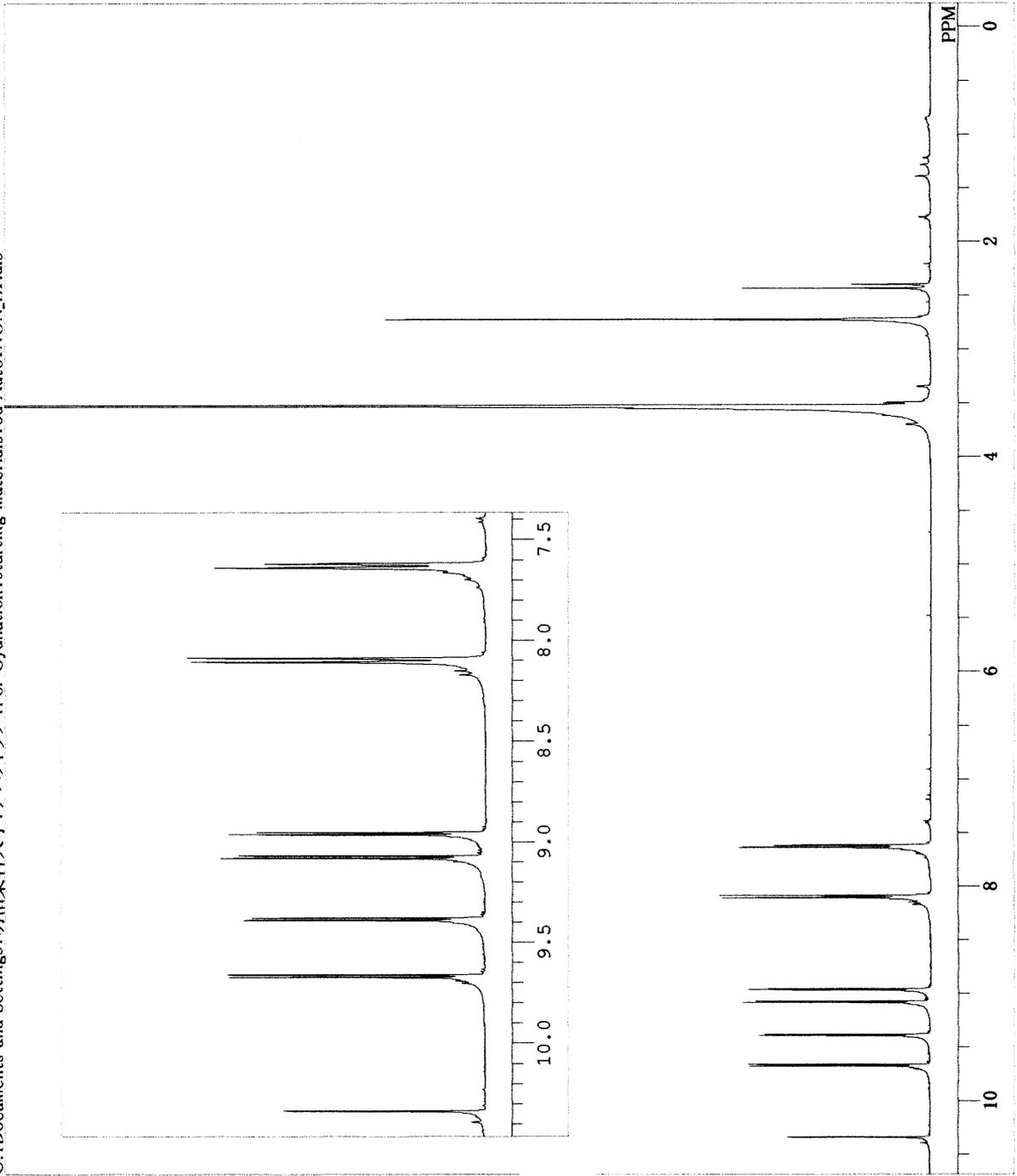
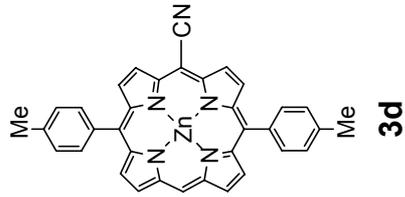


**3c**

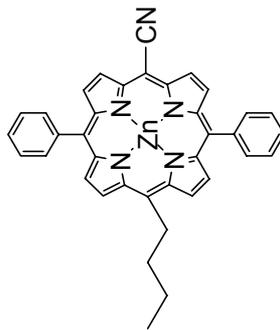


DFILE  
COMNT  
DATIM  
OBNUC  
EXMOD  
OBFRQ  
OBSET  
OBFIN  
POINT  
FREQU  
SCANS  
ACQTM  
PD  
PW1  
IRNUC  
CTEMP  
SLVNT  
EXREF  
BF  
RGAIN

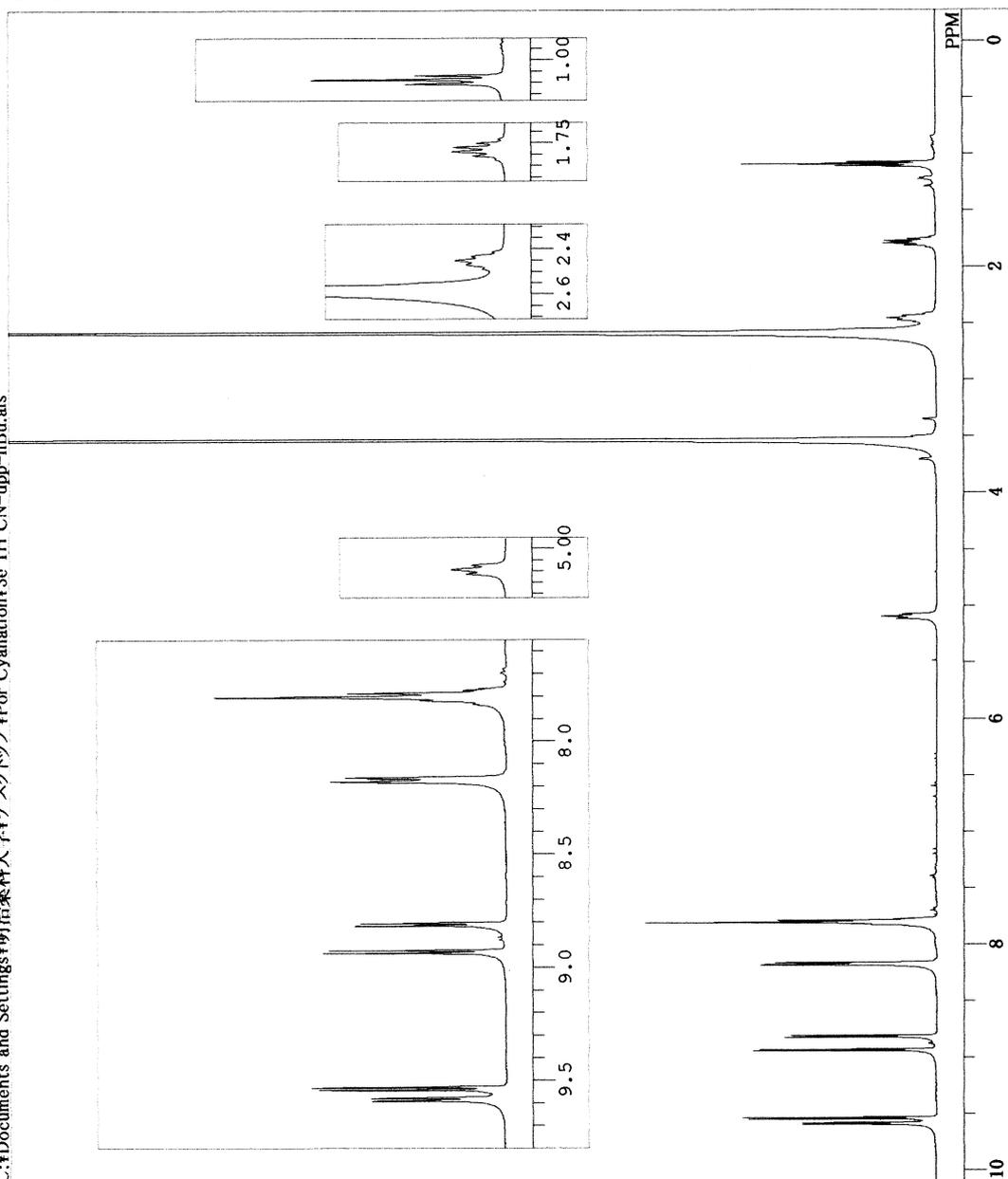
3d Auto1NON\_E1.als  
Fri Dec 24 20:09:57 2004  
IH  
NON  
399.65 MHz  
124.00 KHz  
10500.00 Hz  
32768  
8000.00 Hz  
4.0960 sec  
2.9010 sec  
5.70 usec  
IH  
24.2 c  
C4D8O  
3.53 ppm  
0.09 Hz  
15



3e 1H CN-dpp-nBu.als  
 Tue Jul 27 19:13:09 2004  
 1H  
 NON 399.65 MHz  
 124.00 KHz  
 10500.00 Hz  
 32768  
 7993.60 Hz  
 240  
 4.0993 sec  
 2.9010 sec  
 5.70 usec  
 1H 24.8 c  
 C4D8O 3.53 ppm  
 0.12 Hz  
 13  
 DFIL  
 COMNT  
 DATIM  
 OBNUC  
 EXMOD  
 OBFRQ  
 OBSRT  
 OBFIN  
 POINT  
 FREQU  
 SCANS  
 ACQTM  
 PD  
 PWI  
 IRNUC  
 CTEMP  
 SLVNT  
 EXREF  
 BF  
 RGAIN



3e



3f no7-p2 1H CN-dpp-Zn-P

Fri Sep 03 14:17:59 2004

1H  
NON

399.65 MHz

124.00 KHz

10500.00 Hz

32768

7993.60 Hz

32

4.0993 sec

2.9010 sec

5.70 usec

1H

25.9 c

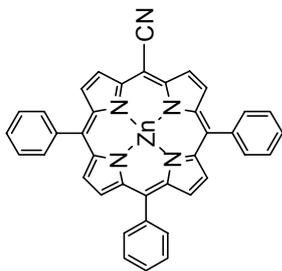
C4D8O

3.53 ppm

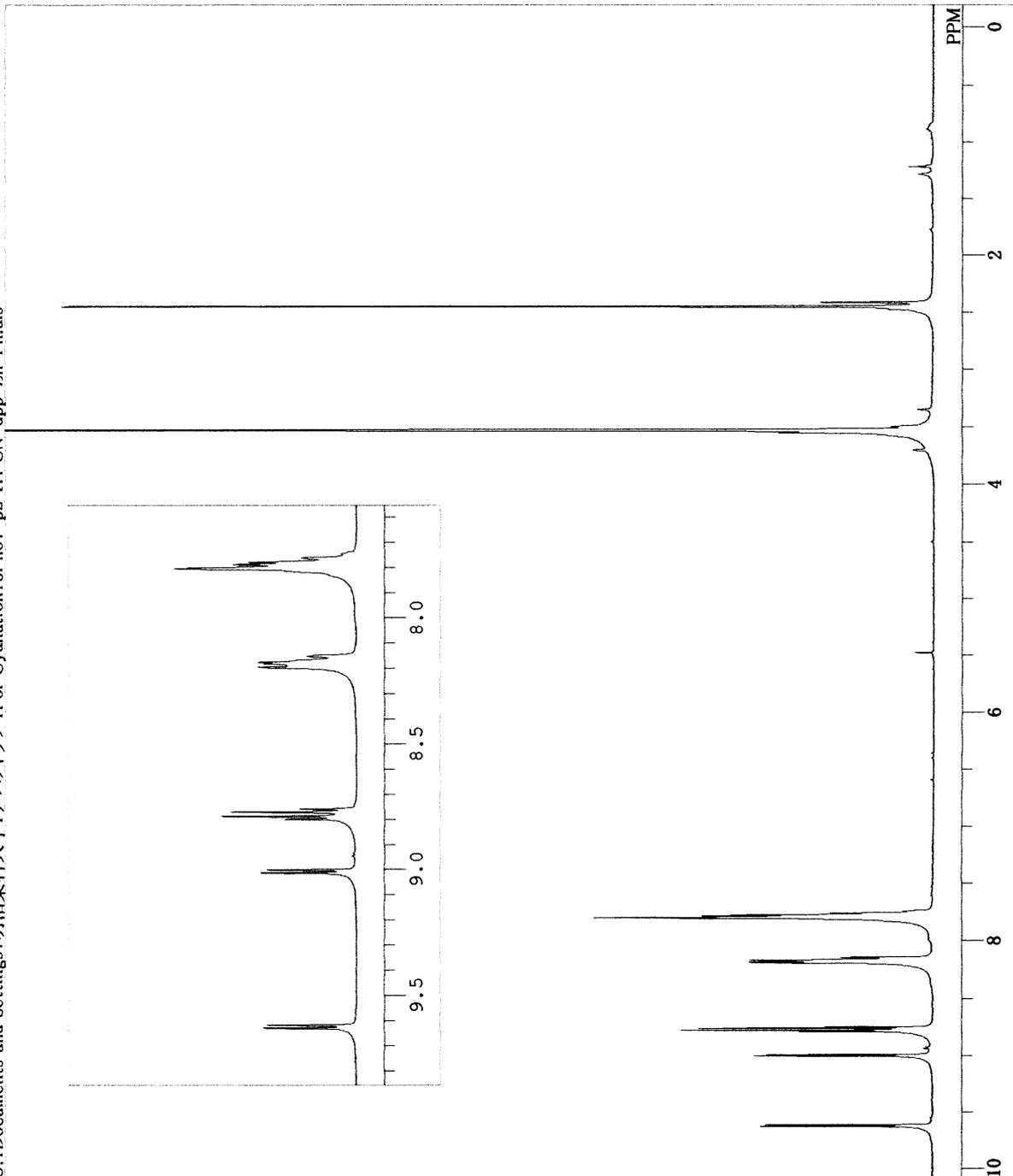
0.12 Hz

16

DFILE  
COMNT  
DATIM  
OBNUC  
EXMOD  
OBFRQ  
OBSET  
OBFIN  
POINT  
FREQU  
SCANS  
ACQTM  
PD  
PWI  
IRNUC  
CTEMP  
SLVNT  
EXREF  
BF  
RGAIN



3f



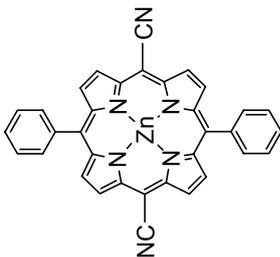
DFILE  
COMNT  
DATIM  
OBNUC  
EXMOD  
OBFRQ  
OBSET  
OBFIN  
POINT  
FREQU  
SCANS  
ACQTM  
PD  
PW1  
IRNUC  
CTEMP  
SLVNT  
EXREF  
BF  
RGAIN

7a NO5-P31 1H BR-DPP-BI

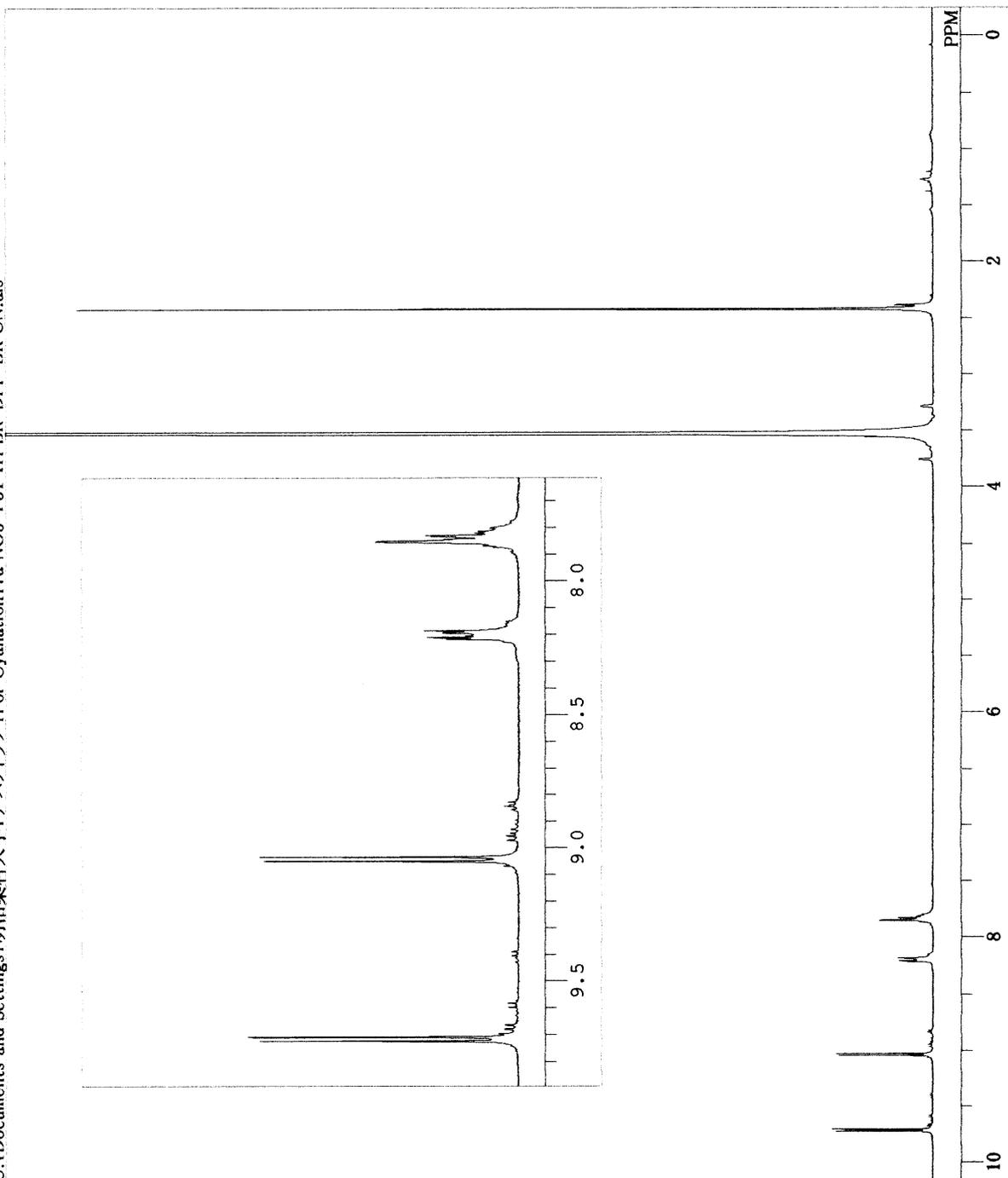
Wed Apr 07 13:41:17 2004

1H  
NON  
300.40 MHz  
130.00 KHz  
1150.00 Hz  
32768  
6013.20 Hz  
100  
5.4493 sec  
1.5510 sec  
5.30 usec

1H  
C4D8O2  
26.1 c  
3.53 ppm  
0.12 Hz  
19



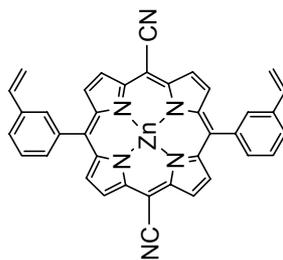
7a



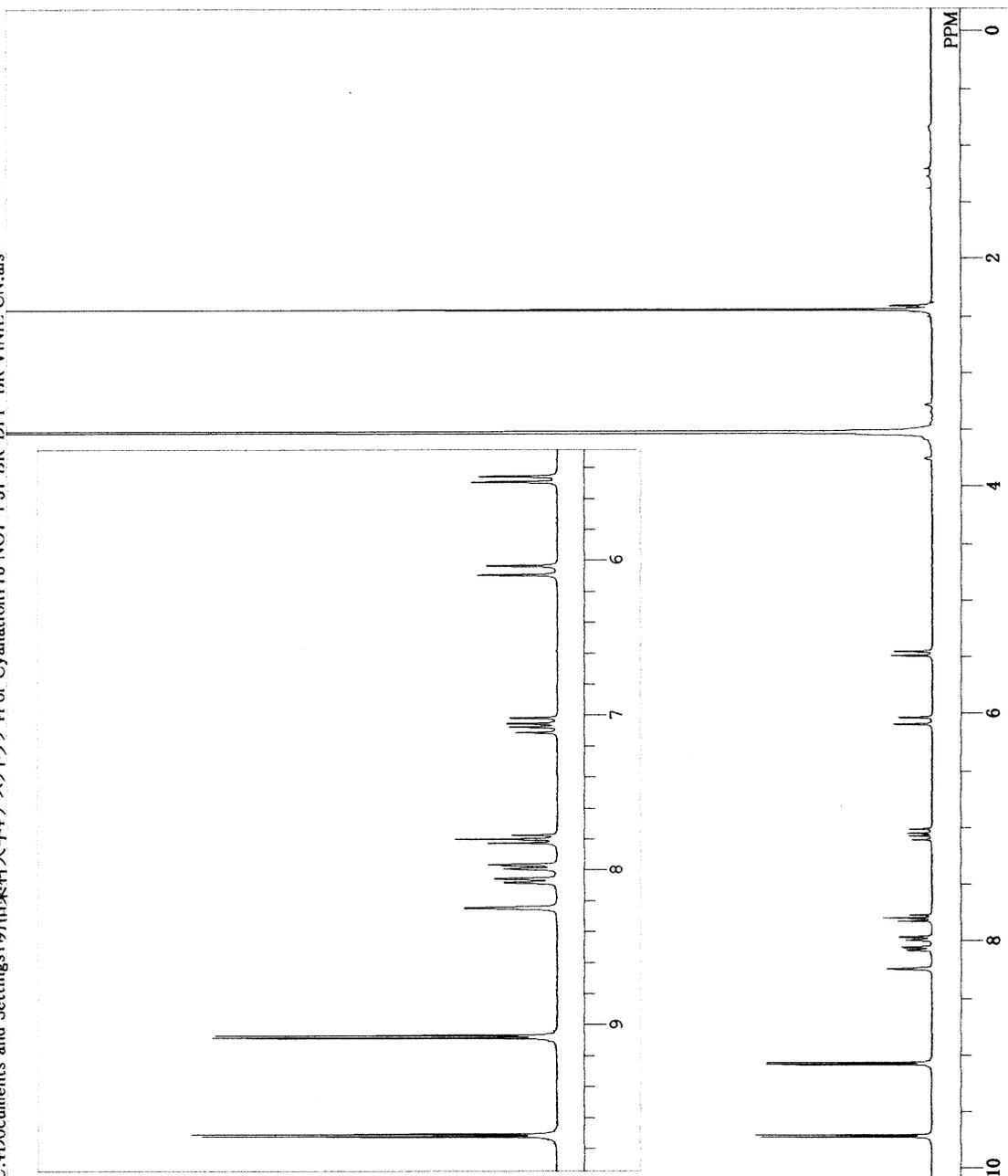
7b NO7-P37 BR-DPP-BR V

DEILE  
COMINT  
DATIM  
OBNUC  
EXMOD  
OBFREQ  
OBSEF  
OBFIN  
POINT  
FREQU  
SCANS  
ACQTM  
PD  
PW1  
IRNUC  
CTEMP  
SLVNT  
EXREF  
BF  
RGAIN

1H  
NON  
300.40 MHz  
130.00 KHz  
1150.00 Hz  
32768  
6013.20 Hz  
32  
5.4493 sec  
1.5510 sec  
5.30 usec  
1H  
26.2 c  
C4D8O2  
3.53 ppm  
0.09 Hz  
16

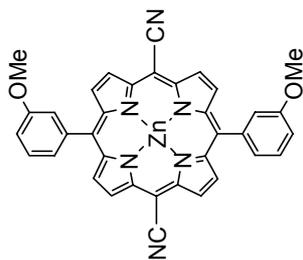
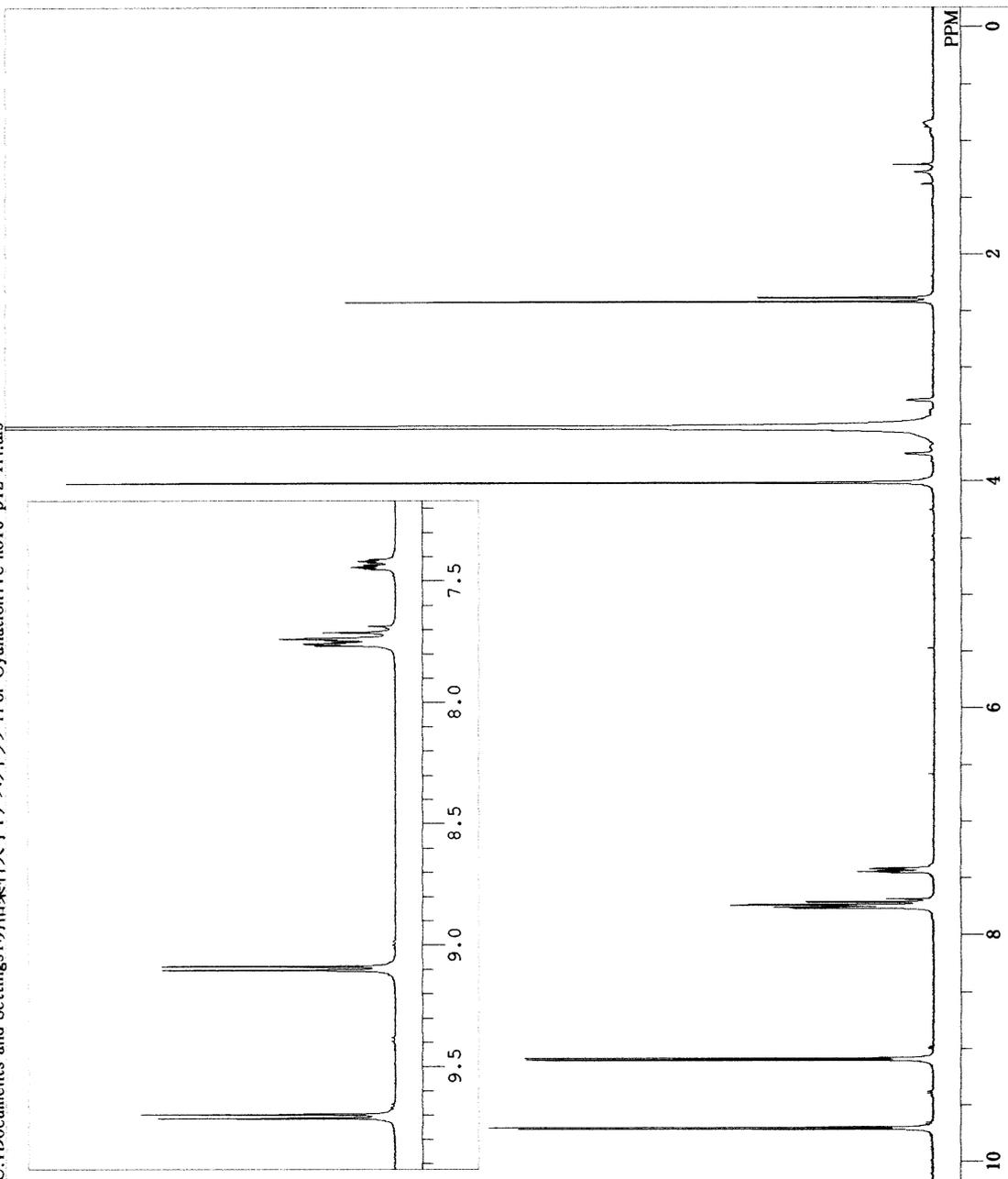


7b



DFILE  
COMNT  
DATIM  
OBNUC  
EXMOD  
OBFRQ  
OBSET  
OBFIN  
POINT  
FREQU  
SCANS  
ACQTM  
PD  
PWI  
IRNUC  
CTEMP  
SLVNT  
EXREF  
BF  
RGAIN

7c no10-p12 1H.als  
Mon Dec 27 16:25:57 2004  
1H  
NON  
300.40 MHz  
130.00 KHz  
1150.00 Hz  
32768  
6013.20 Hz  
5.493 sec  
1.5510 sec  
5.30 usec  
1H  
25.9 c  
C4D8O2  
3.53 ppm  
0.09 Hz  
18



7c

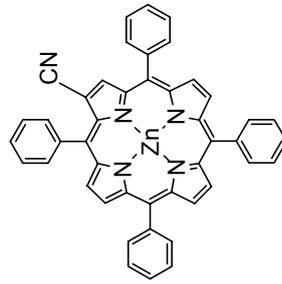


no6-p1 tpp-br CN

C:\Documents and Settings\明治薬科大学\Desktop\材料学\9 AutoINON\_EI.als

DFILE  
COMNT  
DATIM  
OBNUC  
EXMOD  
OBFRQ  
OBSET  
OBFIN  
POINT  
FREQU  
SCANS  
ACQTM  
PD  
PW1  
IRNUC  
CTEMP  
SLVNT  
EXREF  
BF  
RGAIN

9 AutoINON\_EI.als  
no6-p1 tpp-br CN  
Fri Apr 23 17:43:25 2004  
1H  
NON  
399.65 MHz  
124.00 KHz  
10500.00 Hz  
32768  
8000.00 Hz  
256  
4.0960 sec  
2.9010 sec  
5.70 usec  
1H  
24.5 c  
C4D8O  
3.53 ppm  
0.09 Hz  
16



9

