

Supporting Information

Monoprotected Benzenediboronic Acid Esters: New Divalent Cross-Coupling Modules for Convenient Synthesis of Boron-Substituted Oligoarenes

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5. Copies of ^1H and ^{13}C NMR charts for the new compounds

1. General

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury vx400, or a JEOL JNM-A500 spectrometer at ambient temperature. ^1H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, and br = broad), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). ^{11}B NMR chemical shifts are reported in ppm downfield from $\text{BF}_3\cdot\text{OEt}_2$. All ^{13}C NMR spectra were obtained with complete proton decoupling. High-resolution mass spectra were recorded on a JEOL JMS-HX110A (FAB) spectrometer. IR spectra were recorded on a FTIR SHIMADZU DR-8000 spectrometer. Column chromatography was performed with Ultra Pure Silica Gel (40-63 μm) (Silicycle).

2. Materials

Dioxane (Wako) was distilled from benzophenone ketyl. DMSO (Nacalai) was distilled from CaH_2 . 1,8-Diaminonaphthalene (Aldrich), 2-bromophenylboronic acid (Aldrich), 3-bromophenylboronic acid (Aldrich), 4-bromophenylboronic acid (Aldrich), bis(pinacolato)diboron (Boron Molecular), tricyclohexyl phosphine (Aldrich), (2-biphenyl)dicyclohexylphosphine (Strem), potassium acetate (Kanto), sodium hydroxide (Nacalai), cesium fluoride (Wako), iodobenzene (Wako), 4-iodoanisole (Aldrich), 1-iodo-4-nitrobenzene (Aldrich), 4-bromotoluene (Wako), 4-bromofluorobenzene (Wako), 2,6-dimethylbromobenzene (Wako), 1-bromonaphthalene (Wako), 2-bromopyridine (Wako), 2-

bromothiophene (Wako), 1-chloro-4-nitrobenzene (Aldrich), 4-chlorotoluene (Kanto), 2,4-dibromophenol (TCI), 3-hexylthiophene (TCI), 4-bromoacetophenone (Aldrich), 2-bromotoluene (Wako), 4-bromoanisole (Aldrich), 2,4,6-tribromophenol (TCI), hydrochloric acid (Wako), and THF (Wako) were used as received from the commercial sources. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium, bis(dibenzylideneacetone)palladium, bis(tri-*t*-butylphosphine)palladium,¹ palladium acetate, 1,1'-bis(diphenylphosphino)ferrocene, and bromophenylboronamide **1**² were prepared according to the literature methods.

3. Experimental Procedures

3.1 Synthesis of Differentially Protected Benzenediboronic Acid Derivatives 2

Preparation of 2,3-Dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (*p*-2) (Scheme 2):

Under a nitrogen atmosphere, a mixture of 4-bromophenylboronamide *p*-1 (3.50 g, 10.8 mmol), bis(pinacolato)diboron (3.03 g, 11.9 mmol), potassium acetate (3.18 g, 32.4 mmol), and PdCl₂(dppf) (237 mg, 0.324 mmol) in DMSO (67 mL) was heated at 80 °C for 17 h. After cooling to room temperature, water was added to the mixture. After extraction with CHCl₃, the organic layer was washed with brine and dried over magnesium sulfate. The solvent was evaporated under vacuum. The crude product was purified by flash chromatography (hexane/CH₂Cl₂ = 1:1) and recrystallization (CH₂Cl₂–hexane), giving the title compound *p*-2 (3.25 g, 81%).

Preparation of 2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (*m*-2) (Scheme 2):

According to a procedure similar to that for *p*-2, *m*-2 (133 mg, 77%) was prepared from 3-bromophenylboronamide *m*-1 (150 mg, 0.47 mmol), bis(pinacolato)diboron (130 mg, 0.51 mmol), potassium acetate (68.3 mg, 0.70 mmol), Pd(dba)₂ (8.0 mg, 0.014 mmol), and PCy₃ (9.4 mg, 0.033 mmol) in dioxane (3.1 mL) at 100 °C for 24 h. The compound *m*-2 was isolated by column chromatography on silica gel (hexane/CH₂Cl₂ = 1:1).

Preparation of 2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (*o*-2) (Scheme 2):

According to a procedure similar to that for *p*-2, *o*-2 (5.55 g, 75%) was prepared from 2-bromophenylboronamide *m*-1 (6.48 g, 20.0 mmol), bis(pinacolato)diboron (5.59 g, 22.0 mmol), potassium acetate (5.89 g, 60.0 mmol), and PdCl₂(dppf) (439 mg, 0.60 mmol) in DMSO (100 mL) at 100 °C for 12 h. The compound *o*-2 was isolated by column chromatography on silica gel (hexane/EtOAc = 9:1).

3.2 Suzuki-Miyaura Coupling Reaction of Aryl Halides with Differentially Protected Benzenediboronic Acid Derivatives 2

General procedure for the Suzuki-Miyaura coupling reaction of aryl bromides and iodides with benzenediboronic acid derivatives 2 in a 0.14 mmol Scale (Table 1, entry 5; Table 2, entries 2-5, 7, 8, 10, and 11; Scheme 3).

¹ C. Dai, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 2719 -2724.

² H. Noguchi, K. Hojo, M. Sugimoto, *J. Am. Chem. Soc.* **2007**, *129*, 758 -759.

Under a nitrogen atmosphere in a glove box, masked arylboronamide **2** (0.135 mmol), aryl halides (0.135 mmol), Pd[P(*t*-Bu)₃]₂ (1.4 mg, 0.0027 mmol), NaOH aq. (5 N, 82 μ L, 0.41 mmol), and dioxane (0.82 mL) were taken in a Schlenk tube. The tube was taken out from the box, and the mixture was stirred at 60 °C for 4 h under a nitrogen atmosphere. To the mixture was added water at room temperature, and the organic material was extracted with CHCl₃. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (hexane/CH₂Cl₂ = 4:1) to afford corresponding coupling products **3**.

General procedure for the Suzuki-Miyaura coupling reaction of aryl halides with benzenediboronic acid derivatives **2 in a 1.0 mmol Scale (Table 2, entries 1, 6, and 12).**

To a dried two-neck flask under a nitrogen atmosphere, masked arylboronamide **2** (1.0 mmol), aryl halides (1.0 mmol), Pd[P(*t*-Bu)₃]₂ (3.0 mM in dioxane, 6.7 mL, 0.020 mmol), NaOH aq. (5 N, 0.6 mL, 3.0 mmol), and dioxane (0.82 mL) were added. The mixture was stirred at 60 °C for 4 h under a nitrogen atmosphere. To the mixture was added water at room temperature, and the organic material was extracted with CHCl₃. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (hexane/CH₂Cl₂ = 4:1) to afford corresponding coupling products **3**.

Procedure for the Suzuki-Miyaura coupling reaction of *p*-chlorotoluene with benzenediboronic acid derivatives *p*-2** (Table 1, entry 8).**

Under a nitrogen atmosphere in a glove box, masked arylboronamide *p*-**2** (50 mg, 0.14 mmol), *p*-chlorotoluene (16 μ L, 0.14 mmol), Pd[P(*t*-Bu)₃]₂ (2.1 mg, 0.0041 mmol), NaOH aq. (5 N, 82 μ L, 0.41 mmol), and dioxane (0.82 mL) were taken in a Schlenk tube. The tube was taken out from the box, and the mixture was stirred at 80 °C for 24 h. To the mixture was added water at room temperature, and the organic material was extracted with CHCl₃. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (hexane/CH₂Cl₂ = 3:1), to afford a coupling product **3a**.

Procedure for the Suzuki-Miyaura coupling reaction of *p*-tolyl trifluoromethanesulfonate with benzenediboronic acid derivatives *p*-2** (Table 1, entry 10).**

Under a nitrogen atmosphere in a glove box, masked arylboronamide *p*-**2** (50 mg, 0.14 mmol), *p*-tolyl trifluoromethanesulfonate (24 mg, 0.14 mmol), Pd(OAc)₂ (0.61 mg, 0.0027 mmol), PCy₂(2-biphenyl) (1.1 mg, 0.0032 mmol), NaOH aq. (5 N, 82 μ L, 0.41 mmol), and dioxane (0.82 mL) were taken in a Schlenk tube. The tube was taken out from the box, and the mixture was stirred at 60 °C for 4 h. To the mixture was added water, and the organic material was extracted with CHCl₃. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The crude product was purified by silica gel column chromatography (hexane/CH₂Cl₂ = 3:1), to afford a coupling product **3a**.

Procedure for the Suzuki-Miyaura coupling reaction of 1-chloro-4-nitrobenzene with benzenediboronic acid derivatives *p*-2** (Table 2, entry 9).**

According to a similar procedure to that for the reaction of *p*-chlorotoluene, compound **3d** was prepared from masked arylboronamide *p*-**2** (50 mg, 0.14 mmol), 1-chloro-4-nitrobenzene (21 mg, 0.14 mmol), Pd[P(*t*-Bu)₃]₂ (1.4 mg, 0.0027 mmol), and NaOH aq. (5 N, 82 μ L, 0.41

mmol) in dioxane (0.82 mL). The crude product was purified by silica gel column chromatography (hexane/CH₂Cl₂ = 2:3).

Procedure for the Suzuki-Miyaura coupling reaction of *p*-bromotoluene with benzenediboronic acid derivatives *o*-2 (Table 2, entries 13-16).

According to a similar procedure to that for the reaction of aryl bromides and iodides, a mixture of masked arylboronamide *o*-2 (50 mg, 0.14 mmol), aryl bromides (0.14 mmol), K₃PO₄ (86 mg, 0.41 mmol), and Pd[P(*t*-Bu)₃]₂ (1.4 mg, 0.0027 mmol), water (0.082 mL) in dioxane (0.82 mL) was stirred at 60 °C for 4 h and cooled to room temperature. To the mixture was added water, and the organic material was extracted with CHCl₃. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The crude product was purified by silica gel column chromatography (hexane/CH₂Cl₂ = 3:1), to afford corresponding coupling products 3.

Procedure for the Suzuki-Miyaura coupling reaction of aryl dibromides with benzenediboronic acid derivatives *p*-2 (Scheme 4).

Under a nitrogen atmosphere in a glove box, masked arylboronamide *p*-2 (0.135 mmol), aryl dibromides 4, 6, or 8 (0.068 mmol), Pd[P(*t*-Bu)₃]₂ (1.4 mg, 0.0027 mmol), NaOH aq (5 N, 0.41 mmol), and dioxane (0.82 mL) were taken in a Schlenk tube. The mixture was stirred at 60 °C for 4 h and cooled to room temperature. To the mixture was added water, and extraction with CHCl₃. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The crude product was purified by column chromatography (hexane/CH₂Cl₂ = 2:1) or filtration, to afford corresponding coupling products.

Procedure for the Suzuki-Miyaura coupling reaction of aryl tribromides with benzenediboronic acid derivatives *p*-2 (Scheme 4).

Under a nitrogen atmosphere, a mixture of the masked arylboronamide *p*-2 (0.135 mmol), aryl tribromides 10a or 10b (0.045 mmol), Pd[P(*t*-Bu)₃]₂ (1.4 mg, 0.0027 mmol), NaOH aq (5 N, 0.41 mmol) in dioxane (0.82 mL) was added. The reaction mixture was stirred at 60 °C for 4 h and cooled to room temperature. To the mixture was added water, and the organic material was extracted with CHCl₃. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The crude product was purified by recrystallization (CH₂Cl₂-hexane) or column chromatography (hexane/CH₂Cl₂ = 1:1), to afford coupling products 11a and 11b.

3.3 Deprotection of the 1,8-Diaminonaphthalene Group

Preparation of boronic acid 12 via deprotection (Scheme 5).

To a solution of 3r (35 mg, 0.10 mmol) in THF (0.7 mL) under air was added HCl aq (5 N, 0.060 mL, 0.30 mmol) at room temperature. The mixture was stirred at room temperature for 4 h. To the mixture was added HCl aq (2 N), and the organic material was extracted with Et₂O. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The material (22 mg, 99% yield) was essentially pure by ¹H NMR determination (see below).

Preparation of boronic acid 13 via deprotection (Scheme 5).

To a solution of 5b (76 mg, 0.10 mmol) in THF (2.6 mL) under air, was added HCl aq (5 N, 0.120 mL, 0.60 mmol) at room temperature. The mixture was stirred at room temperature for 8 h. To the mixture was added HCl aq (2 N), and the organic material was extracted with Et₂O. The organic layer was dried over magnesium sulfate and the solvent was evaporated

under vacuum. The material (50 mg, 97%) was essentially pure by ^1H NMR determination (see below).

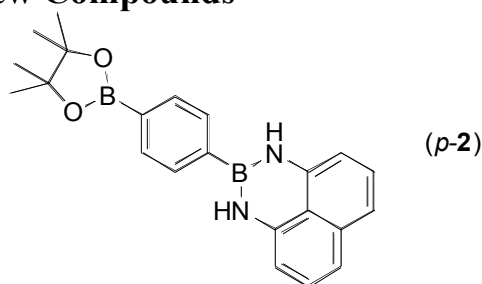
Preparation of boronic acid **14** via deprotection (Scheme 5).

To a solution of **9** (33 mg, 0.050 mmol) in THF (1.3 mL) under air was added HCl aq. (5 N, 0.120 mL, 0.60 mmol) at room temperature. The mixture was stirred at room temperature for 8 h. To the mixture was added HCl aq (2 N), and the organic material was extracted with Et₂O. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The material (16 mg, 98%) was essentially pure by ^1H NMR determination (see below).

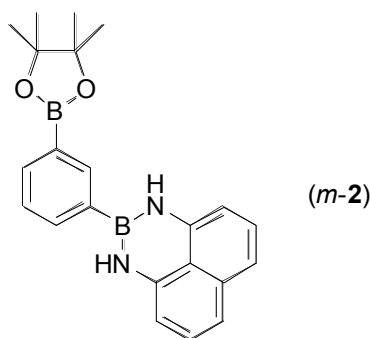
Preparation of boronic acid **15** via deprotection (Scheme 5).

To a solution of **11b** (100 mg, 0.11 mmol) in THF (4.4 mL) under air was added HCl aq. (5 N, 0.40 mL, 2.0 mmol) at room temperature. The mixture was stirred at room temperature for 8 h. To the mixture was added HCl aq (2 N), and the organic material was extracted with Et₂O. The organic layer was dried over magnesium sulfate and the solvent was evaporated under vacuum. The material (57 mg, 96%) was essentially pure by ^1H NMR determination (see below).

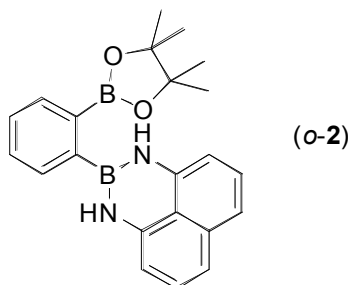
4. Spectral Data for New Compounds



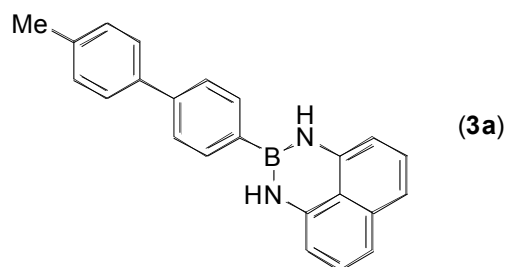
2,3-Dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (*p*-2): mp 218.6–223.2 °C; ^1H NMR (CDCl₃) δ 1.38 (s, 12H), 6.06 (brs, 2H), 6.43 (dd, J = 7.2 Hz, 1.2 Hz, 2H), 7.06 (dd, J = 8.4 Hz, 1.2 Hz, 2H), 7.14 (dd, J = 8.4 Hz, 7.2 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, CDCl₃) δ 24.9, 83.9, 106.1, 117.9, 119.9, 127.6, 130.6, 134.4, 136.3, 141.0. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl₃) δ 30.4. IR (KBr) 3424, 3374, 1599, 1358, 1093 cm⁻¹. HRMS (FAB) m/z calcd for C₂₂H₂₄B₂N₂O₂ (M⁺): 370.2024, found: 370.2034. Anal. Calcd for C₂₂H₂₄B₂N₂O₂: C, 71.40; H, 6.54; N, 7.57. Found: C, 71.21; H, 6.59; N, 7.56.



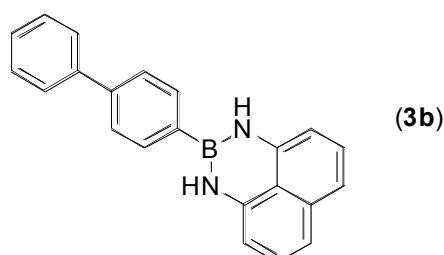
2,3-Dihydro-1H-Naphtho[1,8-de]-1,3,2-Diazaborinyl-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (*m*-2): mp 216.4–219.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.40 (s, 12H), 6.12 (brs, 2H), 6.43 (dd, $J = 7.2$ Hz, 1.2 Hz, 2H), 7.05 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H), 7.14 (dd, $J = 8.4$ Hz, 7.2 Hz, 2H), 7.46 (t, $J = 7.6$ Hz, 1 H), 7.75 (dt, $J = 7.6$ Hz, 1.6 Hz, 1H), 7.93 (dt, $J = 7.6$ Hz, 1.6 Hz, 2H), 8.08–8.10 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 24.9, 84.0, 106.0, 117.7, 119.9, 127.6, 134.3, 136.3, 136.8, 137.8, 141.3. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 31.0. IR (KBr) 3418, 3376, 1603, 1362, 1140 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{22}\text{H}_{24}^{10}\text{B}^{11}\text{B N}_2\text{O}_2$ (M^+): 369.2065, found: 369.2068. Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{B}_2\text{N}_2\text{O}_2$: C, 71.40; H, 6.54; N, 7.57. Found: C, 71.68; H, 6.58; N, 7.62.



2,3-Dihydro-1H-Naphtho[1,8-de]-1,3,2-Diazaborinyl-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (*o*-2): mp 134.5–136.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.35 (s, 12H), 6.34 (dd, $J = 7.2$ Hz, 1.2 Hz, 2H), 6.40 (brs, 2H), 7.03 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H), 7.13 (dd, $J = 8.4$ Hz, 7.2 Hz, 2H), 7.40–7.50 (m, 2H), 7.62–7.66 (m, 1H), 7.80–7.84 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 24.8, 84.2, 105.5, 117.2, 119.9, 127.6, 128.6, 130.1, 132.2, 135.1, 136.4, 141.7. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 31.5. IR (KBr) 3378, 3362, 1601, 1341, 1140 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{22}\text{H}_{24}^{10}\text{B}^{11}\text{B N}_2\text{O}_2$ (M^+): 369.2065, found: 369.2068. Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{B}_2\text{N}_2\text{O}_2$: C, 71.40; H, 6.54; N, 7.57. Found: C, 71.11; H, 6.56; N, 7.38.

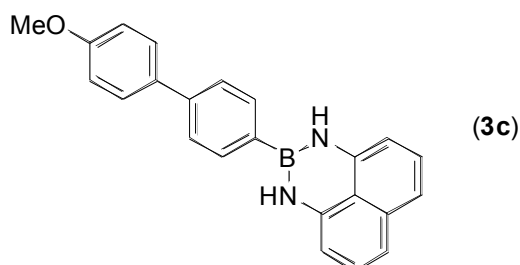


4-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-4'-methyl-1,1'-biphenyl (3a): ² 99% (45 mg). Anal. Calcd for $\text{C}_{23}\text{H}_{19}\text{BN}_2$: C, 82.65; H, 5.73; N, 8.38. Found: C, 82.49; H, 5.91; N, 8.24.

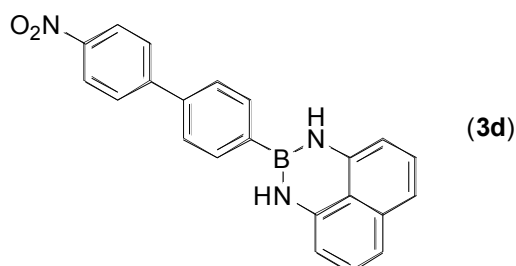


4-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-1,1'-biphenyl (3b): 92% (40 mg). mp 200.7–204.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.08 (brs, 2H), 6.45 (dd, $J = 7.4$ Hz, 0.8 Hz, 2H), 7.07 (dd, $J = 8.4$ Hz, 0.8 Hz, 2H), 7.16 (dd, $J = 8.4$ Hz, 7.4 Hz, 2H), 7.38 (tt, $J = 7.2$

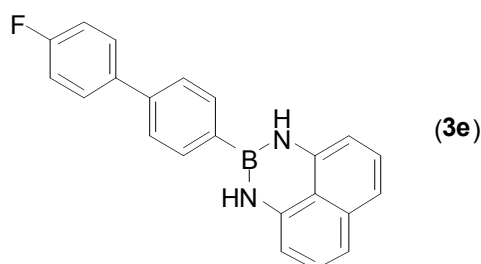
Hz, 1.2Hz, 1H), 7.45-7.50 (m, 2H), 7.61-7.66 (m, 2H), 7.66-7.70 (m, 2H), 7.72-7.75 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 106.0, 117.9, 119.9, 126.9, 127.1, 127.6, 128.8, 131.9, 136.4, 140.7, 141.02, 141.04, 143.0. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 29.9. IR (KBr) 3428, 3413, 1599, 1410, 1086 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{22}\text{H}_{17}\text{BN}_2$ (M^+): 320.1485, found: 320.1481. Anal. Calcd for $\text{C}_{22}\text{H}_{17}\text{BN}_2$: C, 82.52; H, 5.35; N, 8.75. Found: C, 82.27; H, 5.57; N, 8.80.



4-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-4'-methoxyl-1,1'-biphenyl (3c): 92% (44 mg). mp 234.8–237.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 3.88 (s, 3H), 6.07 (brs, 2H), 6.44 (dd, J = 7.2 Hz, 1.2 Hz, 2H), 6.98-7.03 (m, 2H), 7.06 (dd, J = 8.4 Hz, 1.2 Hz, 2H), 7.15 (dd, J = 8.4 Hz, 7.2 Hz, 2H), 7.56-7.61 (m, 2H), 7.62-7.66 (m, 2H), 7.69-7.73 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 55.4, 106.0, 114.3, 117.8, 119.8, 126.4, 127.6, 128.2, 131.9, 133.2, 136.3, 141.1, 142.6, 159.4. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 29.3. IR (KBr) 3424, 1607, 1408, 1086 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{BN}_2\text{O}$ (M^+): 350.1590, found: 350.1589.

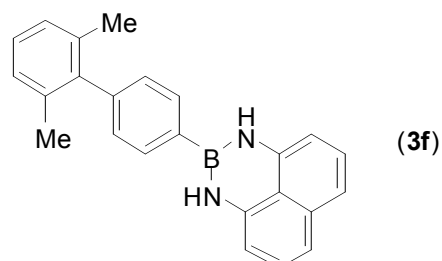


4-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-4'-nitro-1,1'-biphenyl (3d): The title compound **3d** (44 mg, 88%) was isolated by recrystallization (CH_2Cl_2 -hexane). mp 281.4–284.9 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 6.07 (brs, 2H), 6.45 (dd, J = 7.2 Hz, 1.2 Hz, 2H), 7.08 (dd, J = 8.2 Hz, 1.2 Hz, 2H), 7.16 (dd, J = 8.2 Hz, 7.2 Hz, 2H), 7.69-7.73 (m, 2H), 7.77-7.81 (m, 4H), 8.31-8.35 (m, 2H). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 105.7, 116.3, 119.7, 124.1, 126.4, 127.6, 127.9, 133.5, 135.9, 139.0, 142.3, 146.4, 146.8. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 28.5. IR (KBr) 3407, 1601, 1339, 1088 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{22}\text{H}_{16}\text{BN}_3\text{O}_2$ (M^+): 365.1336, found: 365.1335.

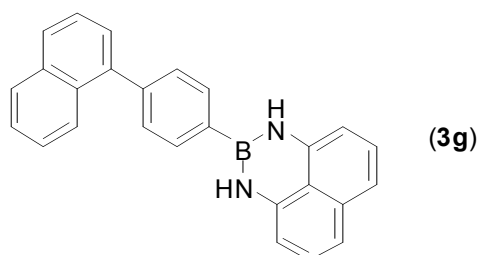


4-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-4'-fluoro-1,1'-biphenyl (3e): 99% (45 mg). mp 212.6–215.1 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 6.07 (brs, 2H), 6.44 (dd, J =

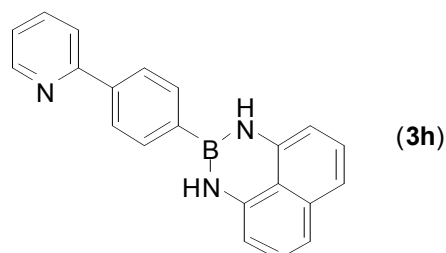
7.2 Hz, 1.2 Hz, 2H), 7.07 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H), 7.13-7.19 (m, 4H), 7.57-7.65 (m, 4H), 7.70-7.74 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 106.1, 115.7 (d, $^2J_{\text{CF}} = 21.4$ Hz), 117.9, 119.8, 126.8, 127.6, 128.7 (d, $^3J_{\text{CF}} = 8.5$ Hz), 132.0, 136.4, 136.8 (d, $^4J_{\text{CF}} = 2.6$ Hz), 141.0, 142.0, 162.7 (d, $^1J_{\text{CF}} = 247$ Hz). The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 29.2. IR (KBr) 3440, 1597, 1408, 1086 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{22}\text{H}_{16}\text{BFN}_2$ (M^+): 338.1391, found: 338.1398.



4-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-2',6'-dimethyl-1,1'-biphenyl (3f): 93% (44 mg). mp 161.2–164.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.06 (s, 6H), 6.10 (brs, 2H), 6.44 (dd, $J = 7.2$ Hz, 1.2 Hz, 2H), 7.07 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H), 7.11-7.21 (m, 5H), 7.22-7.26 (m, 2H), 7.70-7.74 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 20.8, 106.0, 117.8, 119.8, 127.2, 127.3, 127.6, 129.0, 131.6, 135.9, 136.4, 141.1, 141.5, 143.3. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 29.5. IR (KBr) 3412, 1599, 1408, 1086 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{24}\text{H}_{21}\text{BN}_2$ (M^+): 348.1798, found: 348.1800.

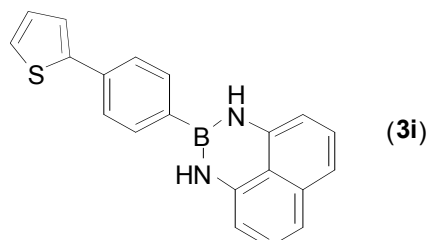


4-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-4'-naphthyl-1,1'-biphenyl (3g): 87% (44 mg). mp 209.4–212.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.13 (brs, 2H), 6.47 (dd, $J = 7.2$ Hz, 1.2 Hz, 2H), 7.08 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H), 7.17 (dd, $J = 8.4$ Hz, 7.2 Hz, 2H), 7.43-7.48 (m, 2H), 7.49-7.57 (m, 2H), 7.58-7.62 (m, 2H), 7.77-7.81 (m, 2H), 7.87-7.95 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 106.1, 117.9, 119.9, 125.4, 125.8, 125.9, 126.1, 126.9, 127.6, 127.9, 128.3, 129.9, 131.4, 131.5, 133.8, 136.4, 139.8, 141.1, 142.8. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 29.5. IR (KBr) 3418, 1599, 1410, 1084 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{26}\text{H}_{19}\text{BN}_2$ (M^+): 370.1641, found: 370.1645.

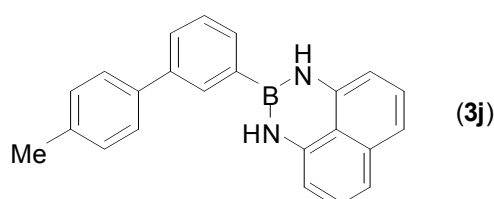


4-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-(2-pyridyl)benzene (3h): 96% (46 mg). mp 176.2–178.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.09 (brs, 2H), 6.45 (dd, $J = 7.2$ Hz,

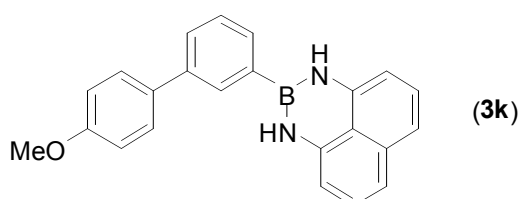
1.2 Hz, 2H), 7.07 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H), 7.16 (dd, $J = 8.4$ Hz, 7.2 Hz, 2H), 7.27-7.30 (m, 1H), 7.75-7.81 (m, 4H), 8.06-8.10 (m, 2H), 8.73 (dt, $J = 4.8$ Hz, 1.6 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 106.1, 117.8, 119.9, 120.7, 122.40, 122.41, 126.6, 127.6, 131.9, 136.3, 136.8, 141.0, 149.8, 157.0. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 29.7. IR (KBr) 3440, 3416, 1599, 1410, 1086 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{BN}_3$ (M^+): 321.1437, found: 321.1433. Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{BN}_3$: C, 78.53; H, 5.02; N, 13.08. Found: C, 78.37; H, 5.11; N, 12.96.



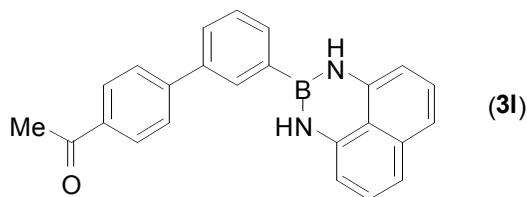
4-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-(2-thiophenyl)benzene (3i): 98% (43 mg). mp 212.4–215.2 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 6.05 (brs, 2H), 6.44 (dd, $J = 7.2$ Hz, 1.2 Hz, 2H), 7.06 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H), 7.10-7.18 (m, 3H), 7.33 (dd, $J = 5.2$ Hz, 1.2 Hz, 1H), 7.40 (dd, $J = 3.6$ Hz, 1.2 Hz, 1H), 7.64-7.71 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 106.1, 117.9, 119.8, 123.5, 125.3, 125.5, 127.6, 128.1, 132.0, 136.1, 136.3, 141.0, 144.0. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 29.1. IR (KBr) 3416, 1597, 1408, 1086 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{20}\text{H}_{15}^{10}\text{BN}_2\text{S}$ (M^+): 325.1085, found: 325.1082.



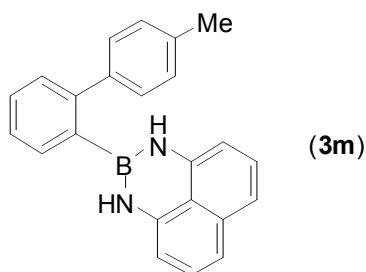
3-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-4'-methyl-1,1'-biphenyl (3j): 94% (42 mg).



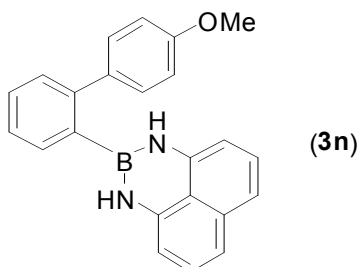
3-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-4'-methoxyl-1,1'-biphenyl (3k): 94% (45 mg). mp 151.5–153.0 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 3.88 (s, 3H), 6.08 (brs, 2H), 6.44 (dd, $J = 7.2$ Hz, 0.8 Hz, 2H), 7.00-7.04 (m, 2H), 7.07 (dd, $J = 8.4$ Hz, 0.8 Hz, 2H), 7.15 (dd, $J = 8.4$ Hz, 7.2 Hz, 2H), 7.50 (t, $J = 7.6$ Hz, 1H), 7.56-7.60 (m, 3H), 7.65 (dt, $J = 7.6$ Hz, 1.6 Hz, 1H), 7.79-7.81 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 55.4, 106.0, 114.3, 117.9, 119.9, 127.6, 128.3, 128.65, 128.72, 129.7, 129.9, 133.7, 136.3, 140.8, 141.0, 159.3. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 29.5. IR (KBr) 3420, 1601, 1406, 1082 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{BN}_2\text{O}$ (M^+): 350.1591, found: 350.1603.



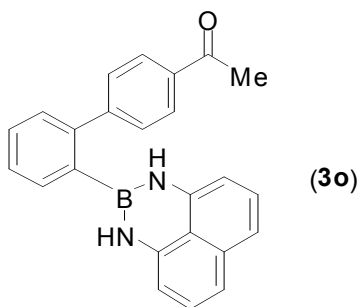
3-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-4'-acetyl-1,1'-biphenyl (3l): 93% (45 mg). mp 222.4–225.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.67 (s, 3H), 6.09 (brs, 2H), 6.45 (dd, $J = 7.2$ Hz, 1.2 Hz, 2H), 7.08 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H), 7.16 (dd, $J = 8.4$ Hz, 7.2 Hz, 2H), 7.53–7.59 (m, 1H), 7.67–7.76 (m, 4H), 7.86–7.88 (m, 1H), 8.07 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 26.7, 106.1, 118.0, 119.9, 127.4, 127.6, 128.9, 129.0, 129.1, 130.4, 131.3, 136.0, 136.3, 139.8, 140.9, 145.7, 197.8. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 29.5. IR (KBr) 3387, 1667, 1597, 1410, 1088 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{24}\text{H}_{19}\text{BN}_2\text{O}$ (M^+): 362.1590, found: 362.1592.



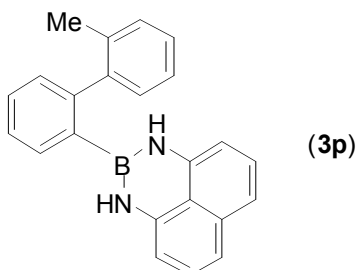
2-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-4'-methyl-1,1'-biphenyl (3m): ² 96% (44 mg).



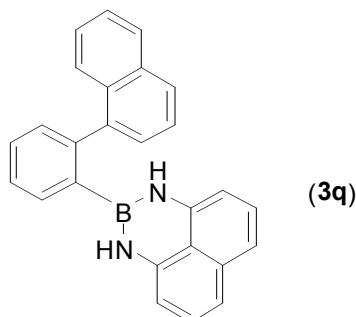
2-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-4'-methoxyl-1,1'-biphenyl (3n): 94% (45 mg). mp 133.4–136.1 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.83 (s, 3H), 5.52 (brs, 2H), 6.15 (d, $J = 7.2$ Hz, 2H), 6.91–6.95 (m, 2H), 7.00 (d, $J = 8.0$ Hz, 2H), 7.06 (t, $J = 8.0$ Hz, 2H), 7.36–7.42 (m, 4H), 7.47 (t, $J = 7.2$ Hz, 1H), 7.64 (d, $J = 7.2$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 55.3, 105.8, 113.8, 117.5, 119.4, 126.5, 127.5, 129.3, 129.6, 130.1, 132.8, 135.0, 136.2, 141.1, 145.9, 159.1. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 30.9. IR (KBr) 3399, 1599, 1410, 1082 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{BN}_2\text{O}$ (M^+): 350.1591, found: 350.1594.



2-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-4'-acetyl-1,1'-biphenyl (3o): 99% (49 mg). mp 223.0–224.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.61 (s, 3H), 5.50 (brs, 2H), 6.14 (dd, $J = 7.2$ Hz, 1.2 Hz, 2H), 7.01 (dd, $J = 8.4$ Hz, 1.2 Hz, 2H), 7.06 (dd, $J = 8.4$ Hz, 7.2 Hz, 2H), 7.43–7.49 (m, 2H), 7.50–7.54 (m, 1H), 7.59 (d, $J = 8.8$ Hz, 2H), 7.66–7.70 (m, 1H), 7.99 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 26.7, 105.9, 117.8, 119.5, 127.5, 127.6, 128.5, 129.2, 129.3, 129.8, 133.0, 135.9, 136.2, 140.8, 144.7, 147.4, 197.8. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 30.5. IR (KBr) 3418, 3366, 1655, 1601, 1410, 1078 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{24}\text{H}_{19}\text{BN}_2\text{O}$ (M^+): 362.1590, found: 362.1593.

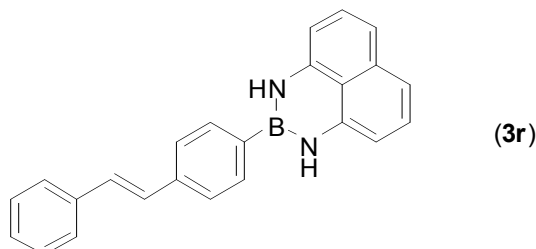


2-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-2'-methyl-1,1'-biphenyl (3p): 99% (45 mg). mp 111.2–112.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.13 (s, 3H), 5.43 (brs, 2H), 6.22 (dd, $J = 7.2$ Hz, 0.8 Hz, 2H), 6.95 (d, $J = 8.4$ Hz, 2H), 7.03 (dd, $J = 8.4$ Hz, 7.2 Hz, 2H), 7.24–7.38 (m, 5H), 7.43 (td, $J = 7.6$ Hz, 1.6 Hz, 1H), 7.50 (td, $J = 7.6$ Hz, 1.6 Hz, 1H), 7.71 (dd, $J = 7.6$ Hz, 1.6 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 20.2, 105.7, 117.3, 119.4, 125.8, 126.8, 127.5, 127.8, 129.3, 129.5, 129.8, 130.2, 132.2, 135.9, 136.1, 141.1, 142.7, 146.4. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 29.4. IR (KBr) 3416, 1597, 1404, 1082 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{BN}_2$ (M^+): 334.1641, found: 334.1638.

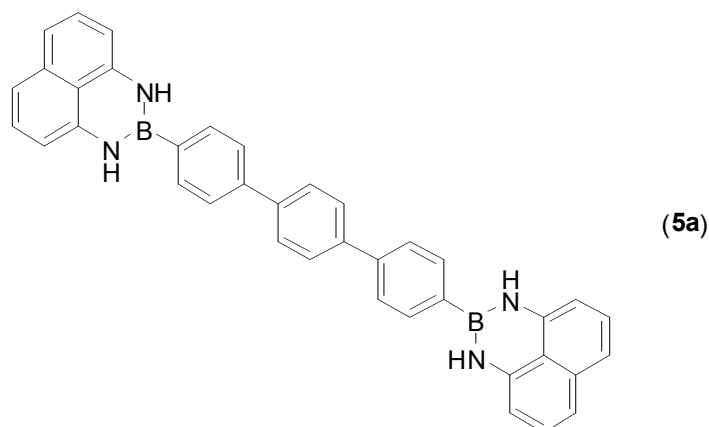


1-{2-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)phenyl}naphthalene (3q): 94% (45 mg). mp 137.9–140.7 °C; ^1H NMR (400 MHz, CDCl_3) δ 5.36 (brs, 2H), 5.85 (d, $J = 7.2$ Hz, 2H), 6.88 (d, $J = 8.0$ Hz, 2H), 6.95 (dd, $J = 8.0$ Hz, 7.2 Hz, 2H), 7.39–7.45 (m, 3H), 7.47–7.58 (m, 4H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 6.8$ Hz, 1H), 7.89–7.95 (m, 2H). ^{13}C NMR

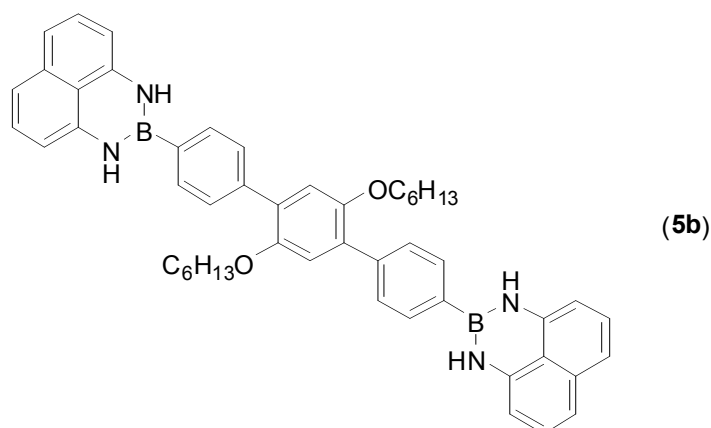
(125 MHz, CDCl₃) δ 105.5, 117.2, 119.3, 125.2, 125.9, 126.1, 126.5, 126.8, 127.2, 127.4, 128.0, 128.3, 129.4, 130.6, 132.37, 132.42, 133.4, 136.0, 140.8, 140.9, 144.7. The boron-bound carbon was not detected due to quadrupolar relaxation. ¹¹B NMR (128 MHz, CDCl₃) δ 29.3. IR (KBr) 3416, 1599, 1410, 1076 cm⁻¹. HRMS (FAB) m/z calcd for C₂₆H₂₀BN₂ (MH⁺): 371.1720, found: 371.1721.



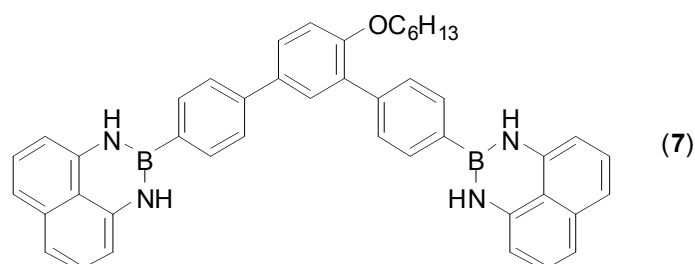
4-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-(2-phenylethyl)benzene (3r): 90% (42 mg). mp 213.5–216.4 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.05 (brs, 2H), 6.35 (dd, J = 7.2 Hz, 0.8 Hz, 2H), 7.06 (dd, J = 8.4 Hz, 0.8 Hz, 2H), 7.12–7.20 (m, 4H), 7.26–7.31 (m, 1H), 7.36–7.42 (m, 2H), 7.53–7.57 (m, 2H), 7.57–7.61 (m, 2H), 7.63–7.67 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 106.0, 117.8, 119.8, 126.3, 126.6, 127.6, 127.9, 128.3, 128.7, 129.6, 131.9, 136.4, 137.1, 139.2, 141.0. The boron-bound carbon was not detected due to quadrupolar relaxation. ¹¹B NMR (128 MHz, CDCl₃) δ 29.2. IR (KBr) 3422, 1601, 1406, 1086 cm⁻¹. HRMS (FAB) m/z calcd for C₂₄H₁₉BN₂ (M⁺): 346.1641, found: 346.1631.



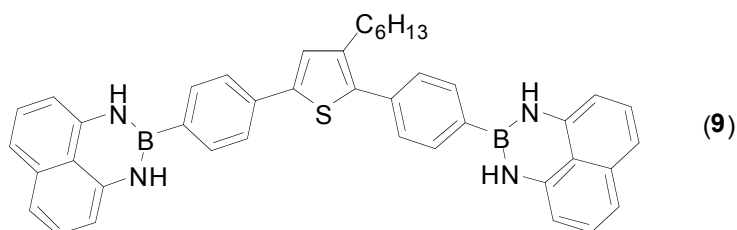
4,4''-Bis(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-1,1':4',1''-terphenyl (5a): The title compound **5a** (30 mg, 80%) was filtrated and washed by H₂O and CHCl₃. mp >300 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.61 (dd, J = 7.6 Hz, 0.8 Hz, 4H), 6.91 (dd, J = 8.0 Hz, 0.8 Hz, 4H), 7.07–7.12 (m, 4H), 7.82 (d, J = 8.4 Hz, 4H), 7.88 (s, 4H), 8.06 (d, J = 8.4 Hz, 4H), 8.34 (brs, 4H). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 105.7, 116.2, 119.7, 125.7, 127.3, 127.6, 133.4, 135.9, 139.1, 140.9, 142.3. The boron-bound carbon was not detected due to quadrupolar relaxation. ¹¹B NMR (128 MHz, DMSO-*d*₆) δ 29.0. IR (KBr) 3407, 1597, 1406, 1084 cm⁻¹. HRMS (FAB) m/z calcd for C₃₈H₂₈B₂N₄ (M⁺): 562.2500, found: 562.2473.



2',5'-Bis(hexyloxy)-4,4''-bis(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-1,1':4',1''-terphenyl (5b): 99% (51 mg). mp 212.8–216.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.89 (t, J = 6.8 Hz, 6H), 1.25–1.35 (m, 8H), 1.36–1.44 (m, 4H), 1.68–1.76 (m, 4H), 3.96 (t, J = 6.4 Hz, 4H), 6.09 (brs, 4H), 6.45 (dd, J = 7.2 Hz, 0.8 Hz, 4H), 7.03 (s, 2H), 7.06–7.09 (m, 4H), 7.14–7.19 (m, 4H), 7.68–7.74 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3) δ 14.0, 22.6, 25.7, 29.3, 31.4, 69.6, 106.0, 116.2, 117.8, 119.8, 127.6, 129.3, 130.6, 131.1, 136.3, 140.3, 141.1, 150.3. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 29.2. IR (KBr) 3433, 3418, 1605, 1410, 1086 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{50}\text{H}_{51}^{10}\text{B}^{11}\text{BN}_4\text{O}_2$ (M^+): 760.4234, found: 760.4233.

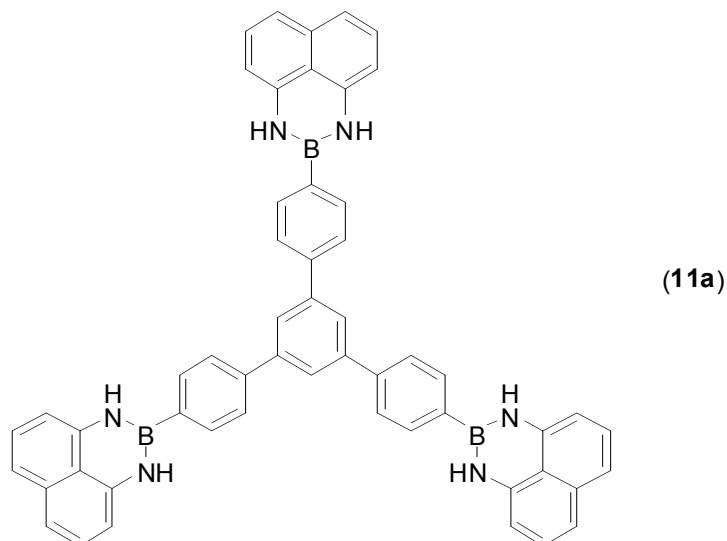


4'-Hexyloxy-4,4''-bis(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-1,1':3',1''-terphenyl (7): 93% (42 mg). mp 113.4–116.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.82–0.95 (m, 3H), 1.30–1.35 (m, 4H), 1.38–1.50 (m, 2H), 1.72–1.84 (m, 2H), 4.05 (t, J = 6.4 Hz, 2H), 6.08 (brs, 2H), 6.10 (brs, 2H), 6.45 (d, J = 7.2 Hz, 4H), 7.05–7.11 (m, 5H), 7.13–7.19 (m, 4H), 7.59–7.78 (m, 10H). ^{13}C NMR (125 MHz, CDCl_3) δ 14.0, 22.6, 25.7, 29.1, 31.4, 68.6, 106.01, 106.02, 112.8, 117.80, 117.82, 119.8, 119.9, 126.5, 127.4, 127.6, 129.47, 129.54, 130.8, 131.1, 132.0, 133.2, 136.4, 140.5, 141.06, 141.12, 142.5, 155.9. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 30.0. IR (KBr) 3416, 3387, 1597, 1410, 1086 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{44}\text{H}_{40}^{10}\text{B}_2\text{N}_4\text{O}$ (M^+): 660.3461, found: 660.3475.

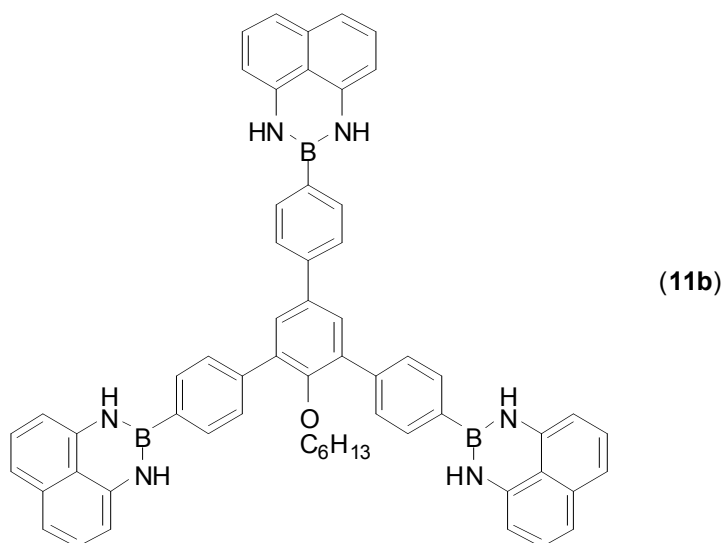


4-Hexyl-1,5-bis(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)thiophene (9): 99% (43 mg). mp 105.6–108.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.90 (t, J = 7.2 Hz, 3H), 1.27–1.32 (m, 4H), 1.33–1.40 (m, 2H), 1.67–1.73 (m, 2H), 2.73 (t, J = 8.0 Hz, 2H), 6.06 (brs, 2H),

6.08 (brs, 2H), 6.45 (d, $J = 7.2$ Hz, 4H), 7.05-7.09 (m, 4H), 7.13-7.19 (m, 4H), 7.31 (s, 1H), 7.54-7.59 (m, 2H), 7.64-7.73 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 22.6, 29.0, 29.2, 29.7, 31.0, 31.6, 106.05, 106.07, 117.85, 117.89, 119.83, 119.85, 125.1, 126.3, 127.61, 127.62, 128.8, 131.7, 132.0, 136.0, 136.3, 136.4, 137.5, 140.3, 141.0, 142.1. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl_3) δ 30.5. IR (KBr) 3416, 1599, 1406, 1086 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{42}\text{H}_{38}^{10}\text{B}^{11}\text{BN}_4\text{S}$ (M^+): 651.3039, found: 651.3030.

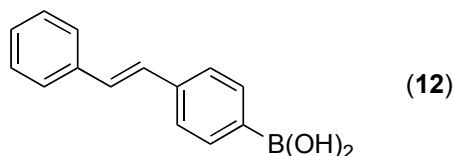


5'-[4-(2,3-Dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)phenyl]-4,4''-bis(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-1,1':3',1''-terphenyl (11a): The title compound **11a** (31 mg, 85%) was isolated by recrystallization (CH_2Cl_2 -hexane). mp >300 $^\circ\text{C}$; ^1H NMR (400 MHz, DMSO-d_6) δ 6.63 (d, $J = 7.6$ Hz, 6H), 6.91 (d, $J = 8.4$ Hz, 6H), 7.07-7.13 (m, 6H), 7.90 (d, $J = 8.0$ Hz, 6H), 8.05 (s, 3H), 8.10 (d, $J = 8.0$ Hz, 6H), 8.34 (brs, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 105.6, 116.2, 119.7, 124.8, 126.5, 127.7, 133.4, 135.9, 141.59, 141.63, 142.4. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, DMSO-d_6) δ 29.6. IR (KBr) 3416, 1599, 1410, 1084 cm^{-1} . HRMS (FAB) m/z calcd for $\text{C}_{54}\text{H}_{39}\text{B}_3\text{N}_6$ (M^+): 804.3515, found: 804.3515.

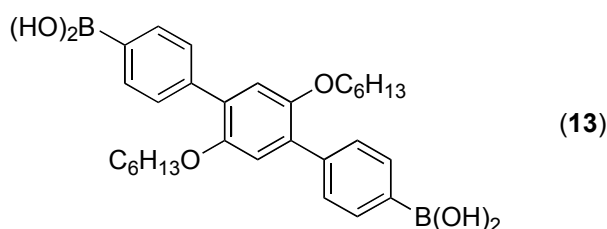


2'-Hexyloxy-5'-[4-(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)phenyl]-4,4''-bis(2,3-dihydro-1H-naphtho[1,8-de]-1,3,2-diazaborinyl)-1,1':3',1''-terphenyl (11b): The

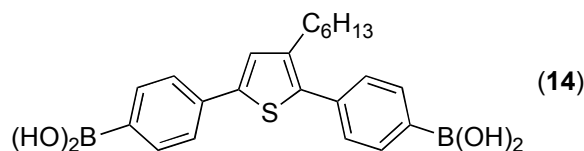
title compound **11b** (38 mg, 94%) was isolated by column chromatography (hexane/CH₂Cl₂ = 1:1). mp 160.5–163.2 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.79 (t, *J* = 7.2 Hz, 3H), 0.94–0.98 (m, 4H), 1.08–1.16 (m, 2H), 1.20–1.26 (m, 2H), 3.30 (t, *J* = 6.4 Hz, 2H), 6.08 (brs, 2H), 6.11 (brs, 4H), 6.42–6.48 (m, 6H), 7.05–7.11 (m, 6H), 7.13–7.19 (m, 6H), 7.66 (s, 2H), 7.73–7.81 (m, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 14.0, 22.6, 25.4, 29.8, 31.3, 73.6, 106.0, 106.1, 117.8, 119.84, 119.85, 126.8, 127.62, 127.64, 129.1, 129.37, 129.38, 131.3, 132.0, 136.27, 136.34, 136.4, 136.7, 140.7, 141.00, 141.05, 142.1, 154.1. The boron-bound carbon was not detected due to quadrupolar relaxation. ¹¹B NMR (128 MHz, CDCl₃) δ 29.1. IR (KBr) 3416, 1599, 1408, 1084 cm⁻¹. HRMS (FAB) *m/z* calcd for C₆₀H₅₁¹⁰B₂¹¹BN₆O (M⁺): 902.4480, found: 902.4488.



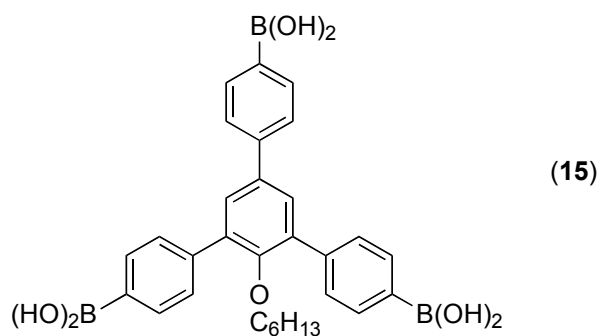
4-[4-(boronylphenyl)]-(2-phenylethyl)benzene (12): 99% (22 mg). ¹H NMR (400 MHz, DMSO-d₆) δ 7.25 (d, *J* = 16.4 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 16.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 8.05 (brs, 2H). ¹³C NMR (125 MHz, DMSO-d₆) δ 125.5, 126.5, 127.7, 128.4, 128.7, 128.9, 134.5, 137.0, 138.5. The boron-bound carbon was not detected due to quadrupolar relaxation. ¹¹B NMR (128 MHz, DMSO-d₆) δ 31.5.



2',5'-bis(hexyloxy)-4,4''-bis[4-(boronylphenyl)]-1,1':4',1''-terphenyl (13): 97% (50 mg). ¹H NMR (400 MHz, DMSO-d₆) δ 0.83 (t, *J* = 6.8 Hz, 6H), 1.20–1.28 (m, 4H), 1.30–1.36 (m, 4H), 1.60 (quin, *J* = 7.2 Hz, 4H), 3.95 (t, *J* = 6.0 Hz, 4H), 7.02 (s, 2H), 7.55 (d, *J* = 8.0 Hz, 4H), 7.83 (d, *J* = 8.0 Hz, 4H), 8.06 (brs, 4H). ¹³C NMR (125 MHz, DMSO-d₆) δ 13.8, 22.1, 25.2, 28.7, 30.8, 68.6, 115.6, 128.2, 130.0, 133.7, 139.5, 149.7. The boron-bound carbon was not detected due to quadrupolar relaxation. ¹¹B NMR (128 MHz, DMSO-d₆) δ 30.9.

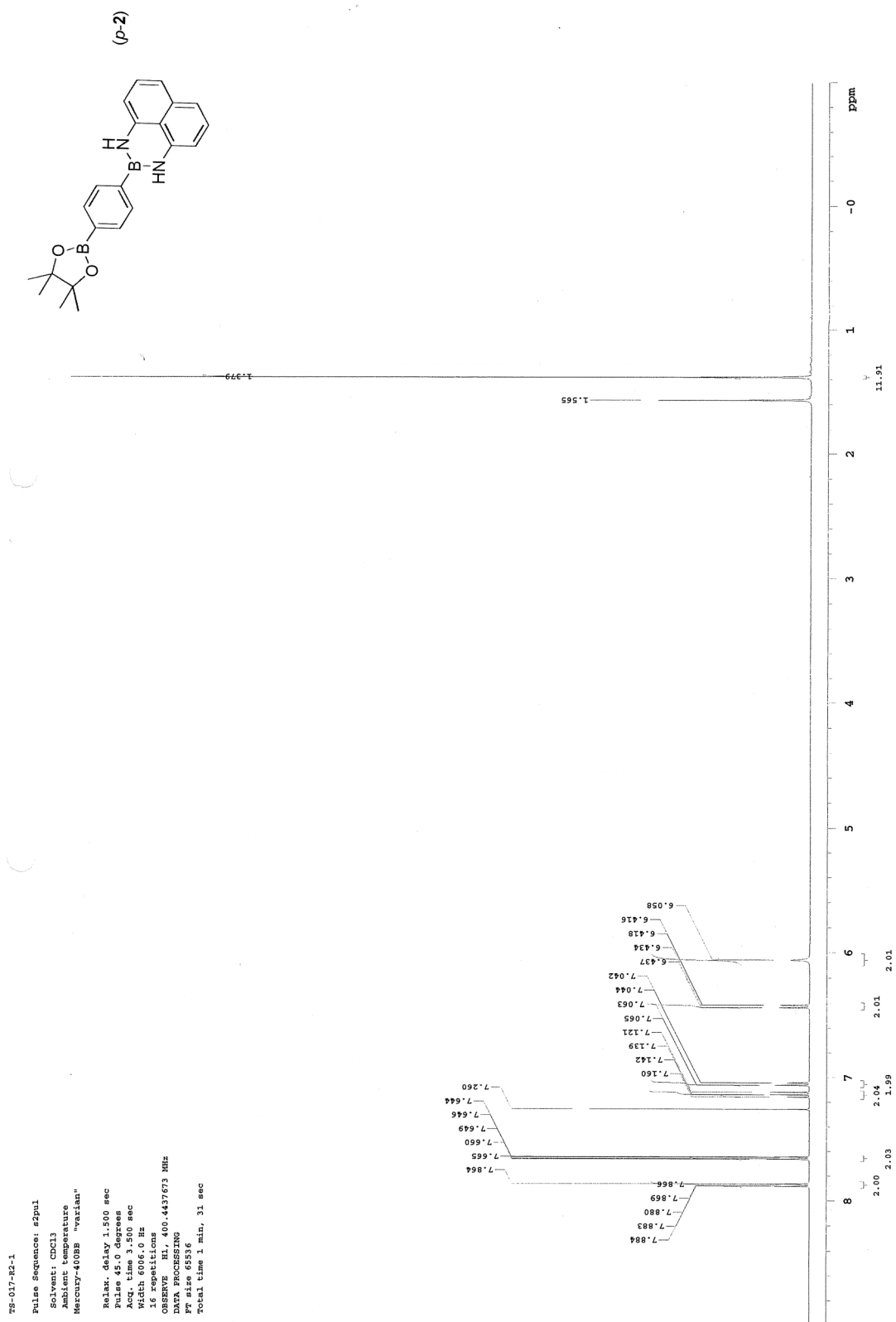


4-hexyl-1,5-bis[4-(boronylphenyl)]thiophene (14): 98% (19 mg). ¹H NMR (400 MHz, DMSO-d₆) δ 0.82 (t, *J* = 7.2 Hz, 3H), 1.19–1.30 (m, 6H), 1.61 (quintet, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 8.10 (brs, 2H), 8.14 (brs, 2H). ¹³C NMR (125 MHz, DMSO-d₆) δ 13.9, 22.0, 28.4, 28.5, 30.1, 30.9, 123.9, 126.7, 127.6, 134.6, 134.9, 135.4, 136.8, 139.9, 141.4. The boron-bound carbon was not detected due to quadrupolar relaxation. ¹¹B NMR (128 MHz, DMSO-d₆) δ 31.4.



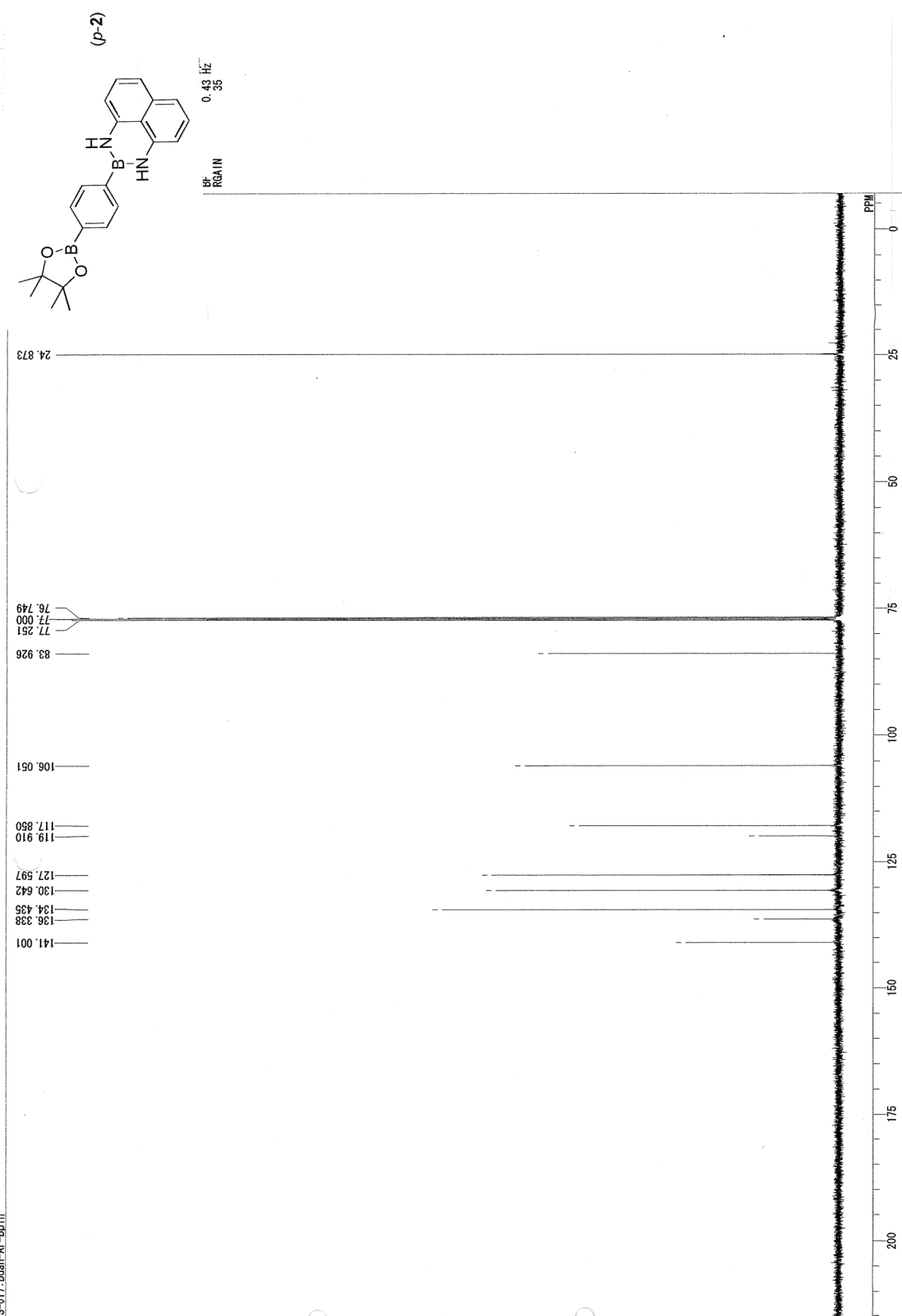
2'-Hexyloxy-5'-[4-(boronylphenyl)]-4,4''-bisboronyl-1,1':3',1''-terphenyl (15): 96% (57 mg). ^1H NMR (400 MHz, DMSO- d_6) δ 0.71 (t, $J = 7.2$ Hz, 3H), 0.77-0.85 (m, 2H), 0.85-0.92 (m, 2H), 1.01 (quintet, $J = 7.2$ Hz, 2H), 1.07-1.13 (m, 2H), 3.17 (t, $J = 6.0$ Hz, 2H), 7.60-7.65 (m, 6H), 7.72 (s, 1H), 7.74 (s, 1H), 7.86-7.92 (m, 6H), 8.06 (brs, 6H) ^{13}C NMR (125 MHz, DMSO- d_6) δ 13.9, 22.0, 24.9, 29.2, 30.7, 72.6, 125.8, 128.3, 128.4, 134.0, 134.8, 136.1, 136.3, 139.9, 141.0, 153.5. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, DMSO- d_6) δ 30.6.

5. Copies of ^1H and ^{13}C NMR charts for new compounds

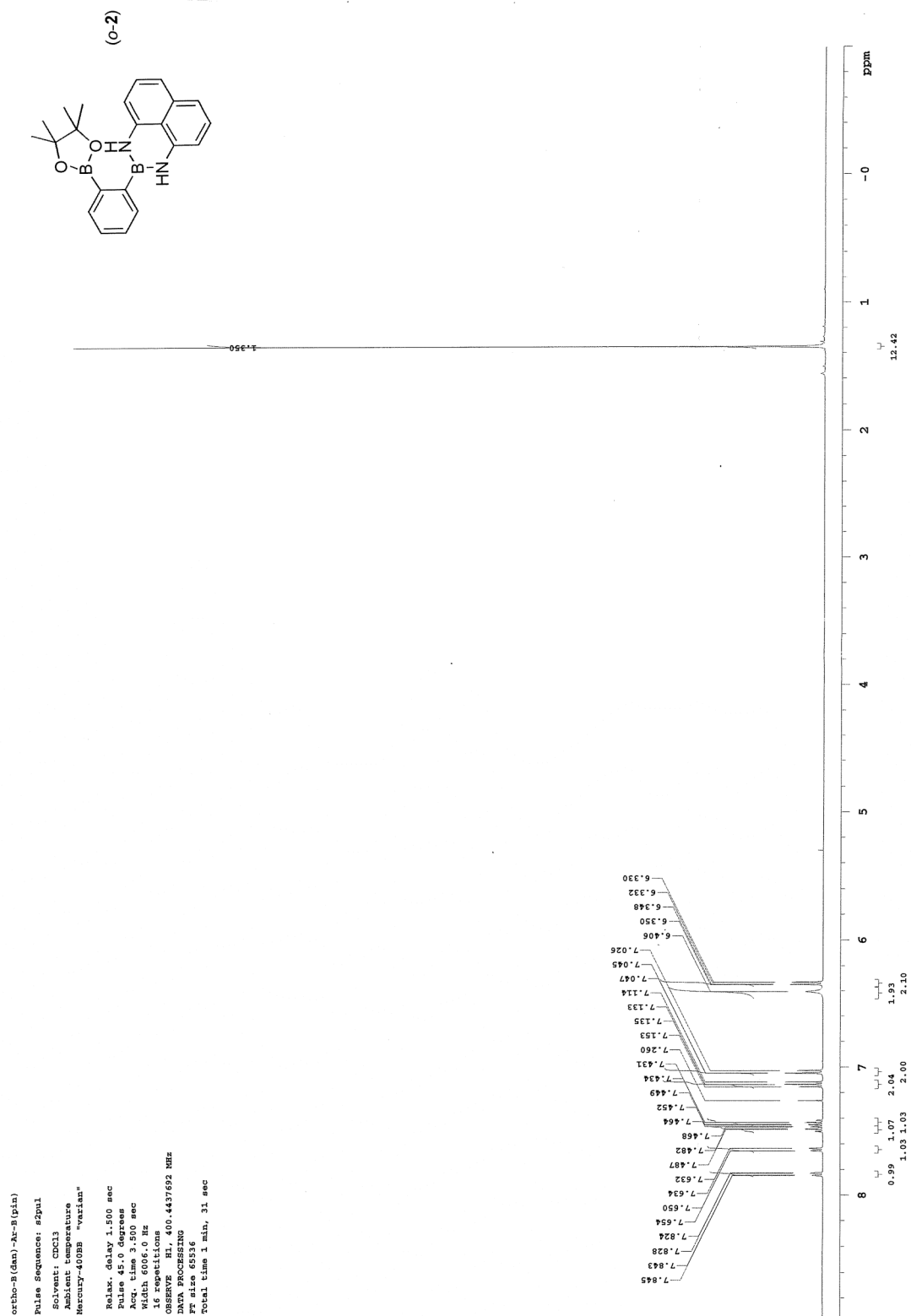


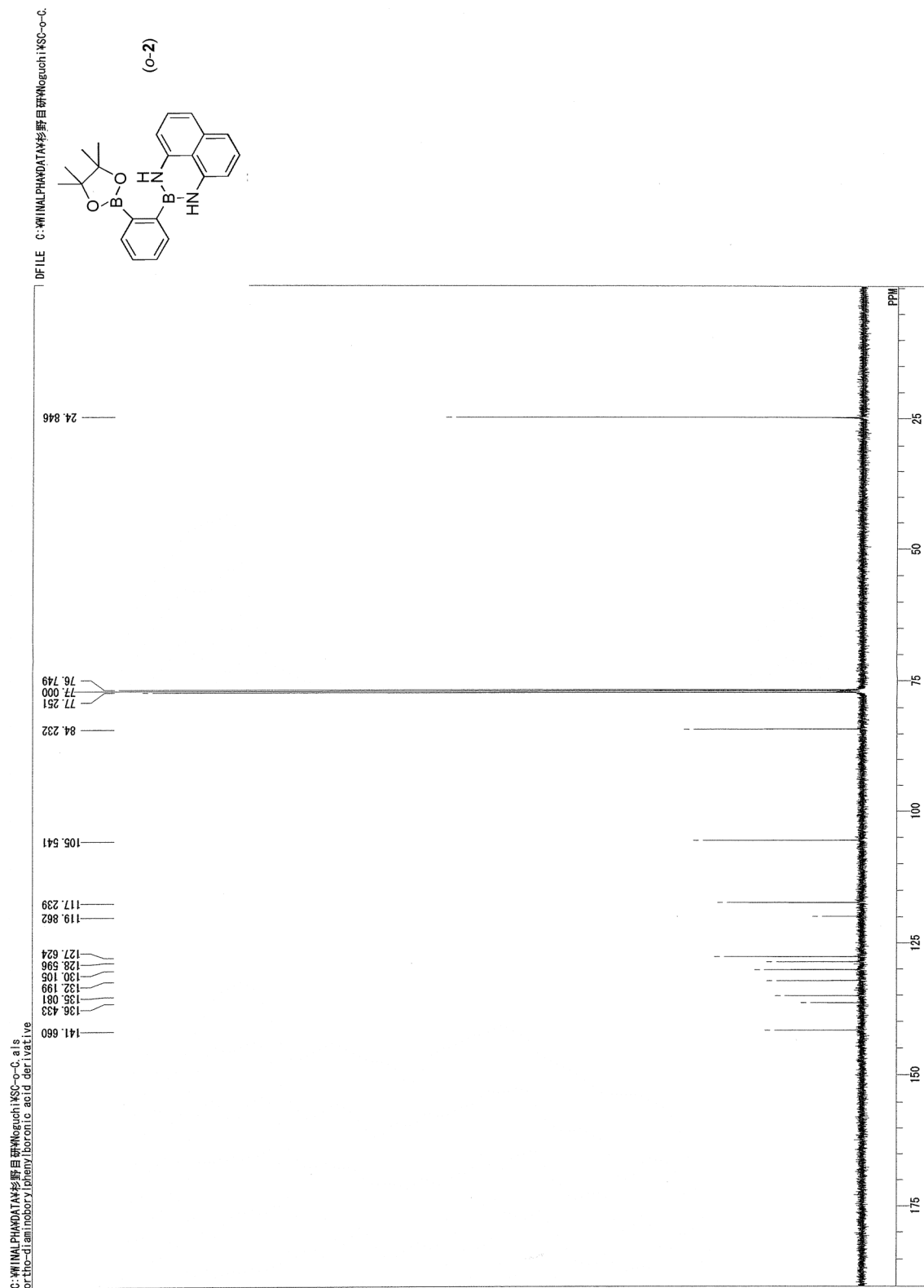
^1H NMR of Compound **p-2**

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TS-017: Bdm-Ar-Bp.in



^{13}C NMR of Compound *p-2*

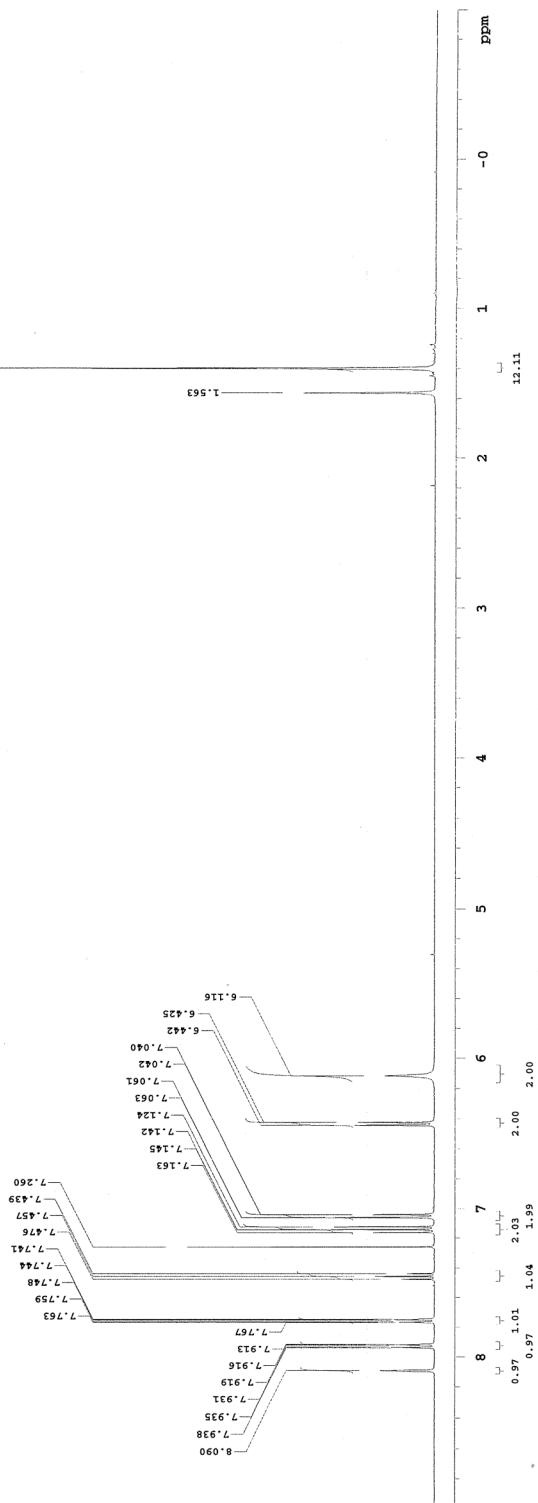
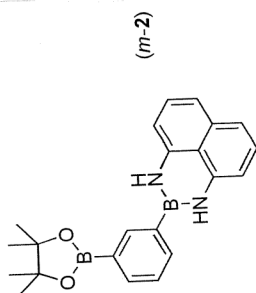


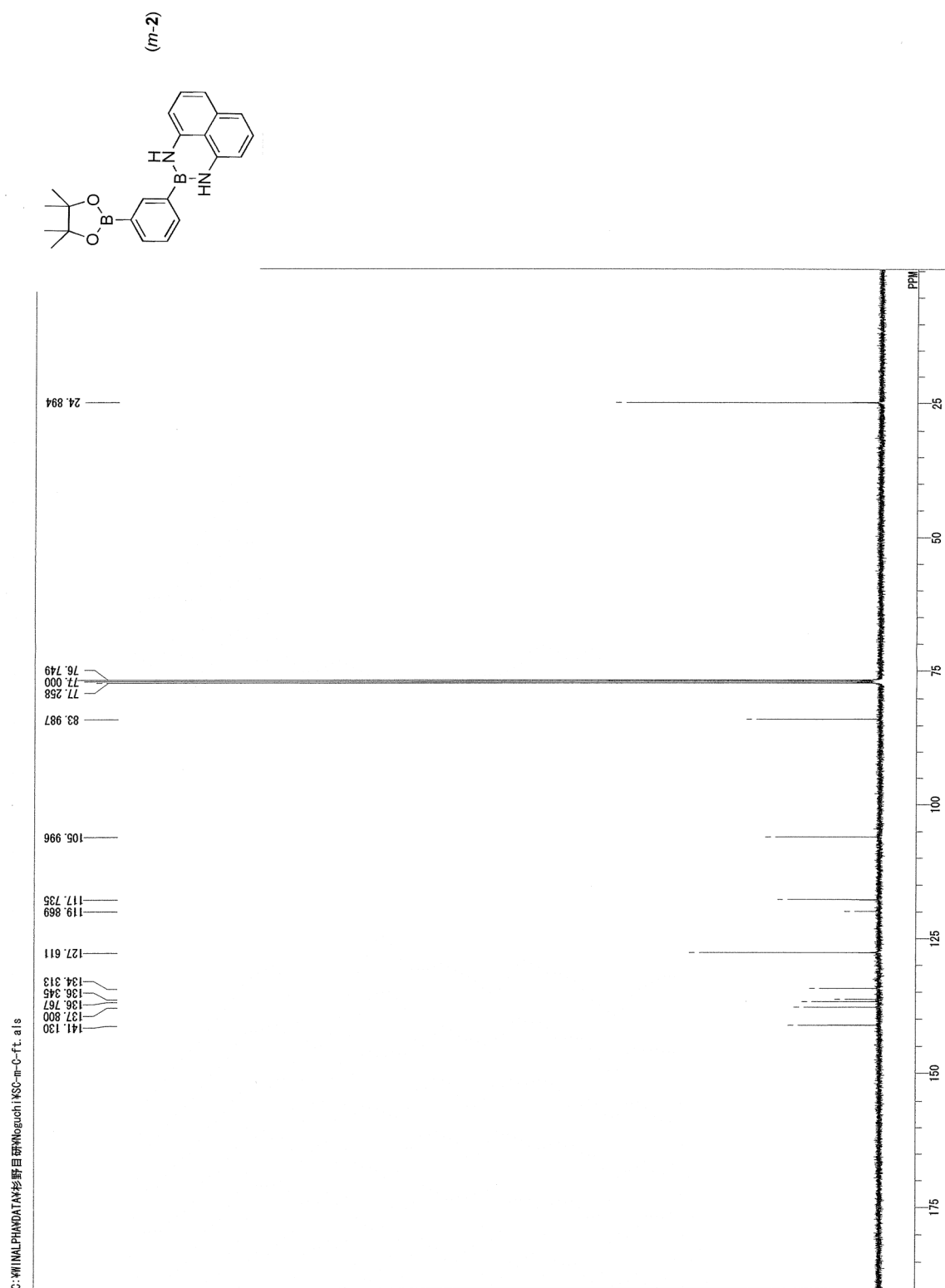


¹³C NMR of Compound **o-2**

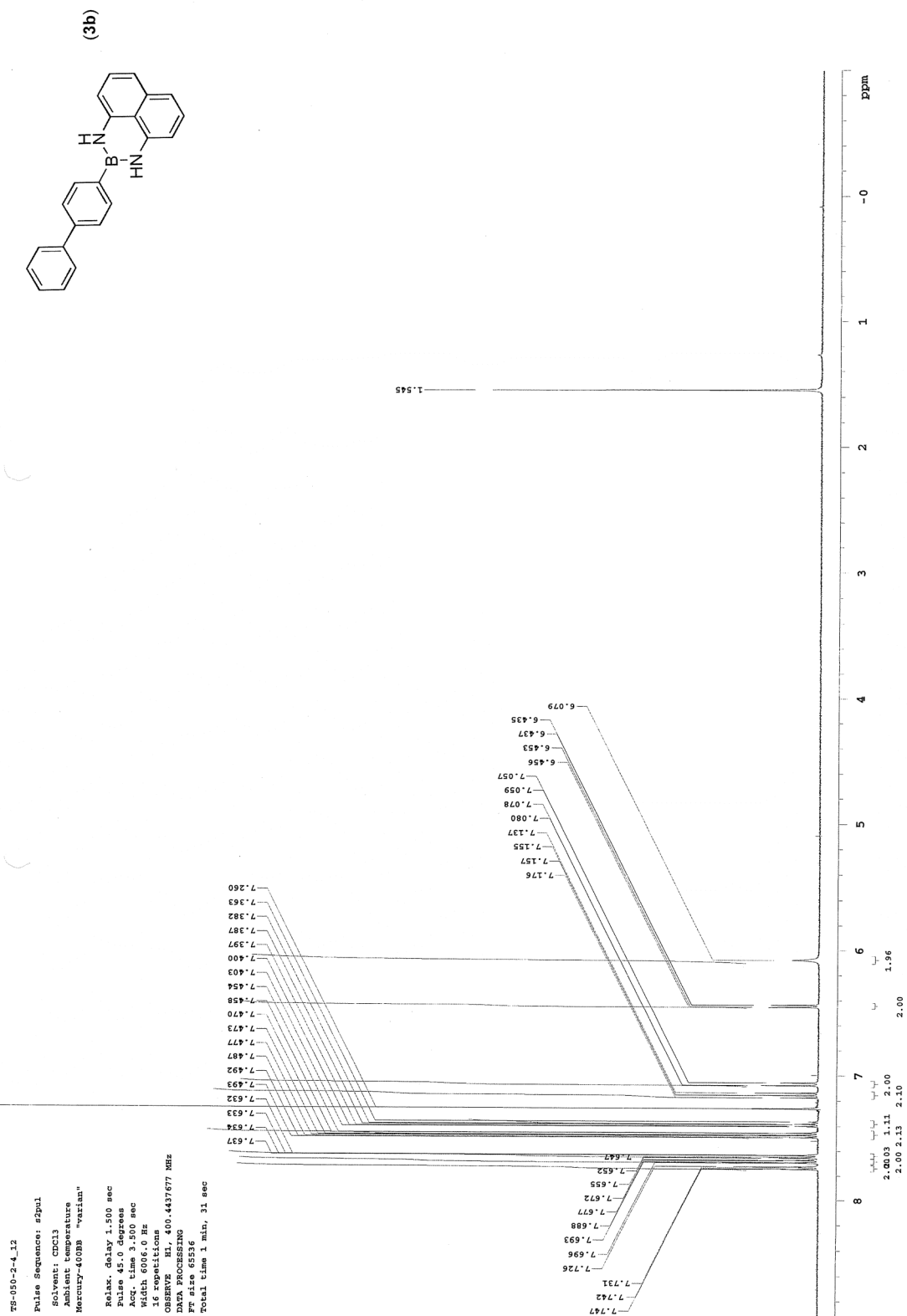
TS-084-11

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 Pulse 15.000 sec
 Acq. time 3.500 sec
 Width 6006.0 Hz
 16 repetitions
 OBSERVE H1, 400.4437675 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 31 sec

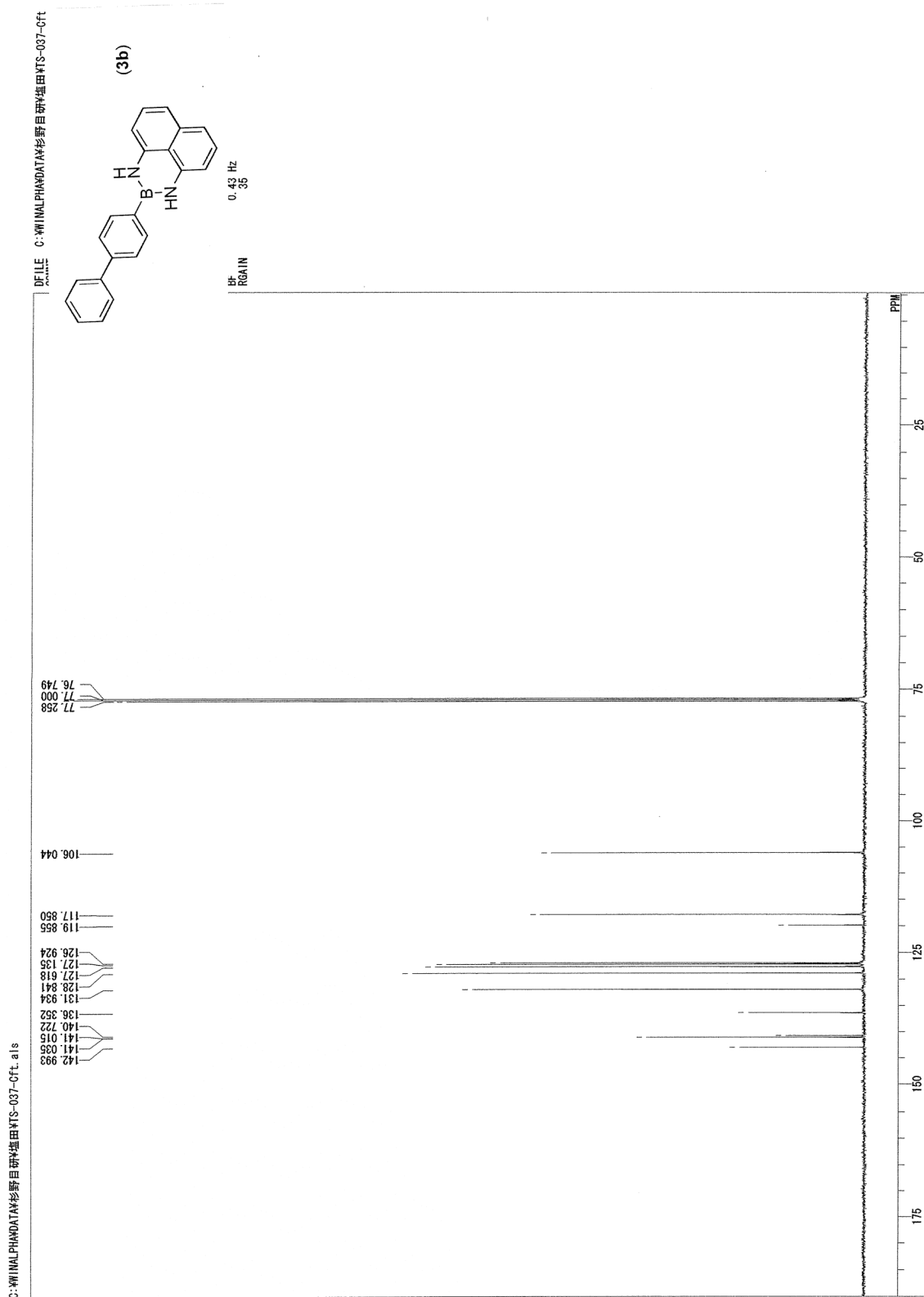




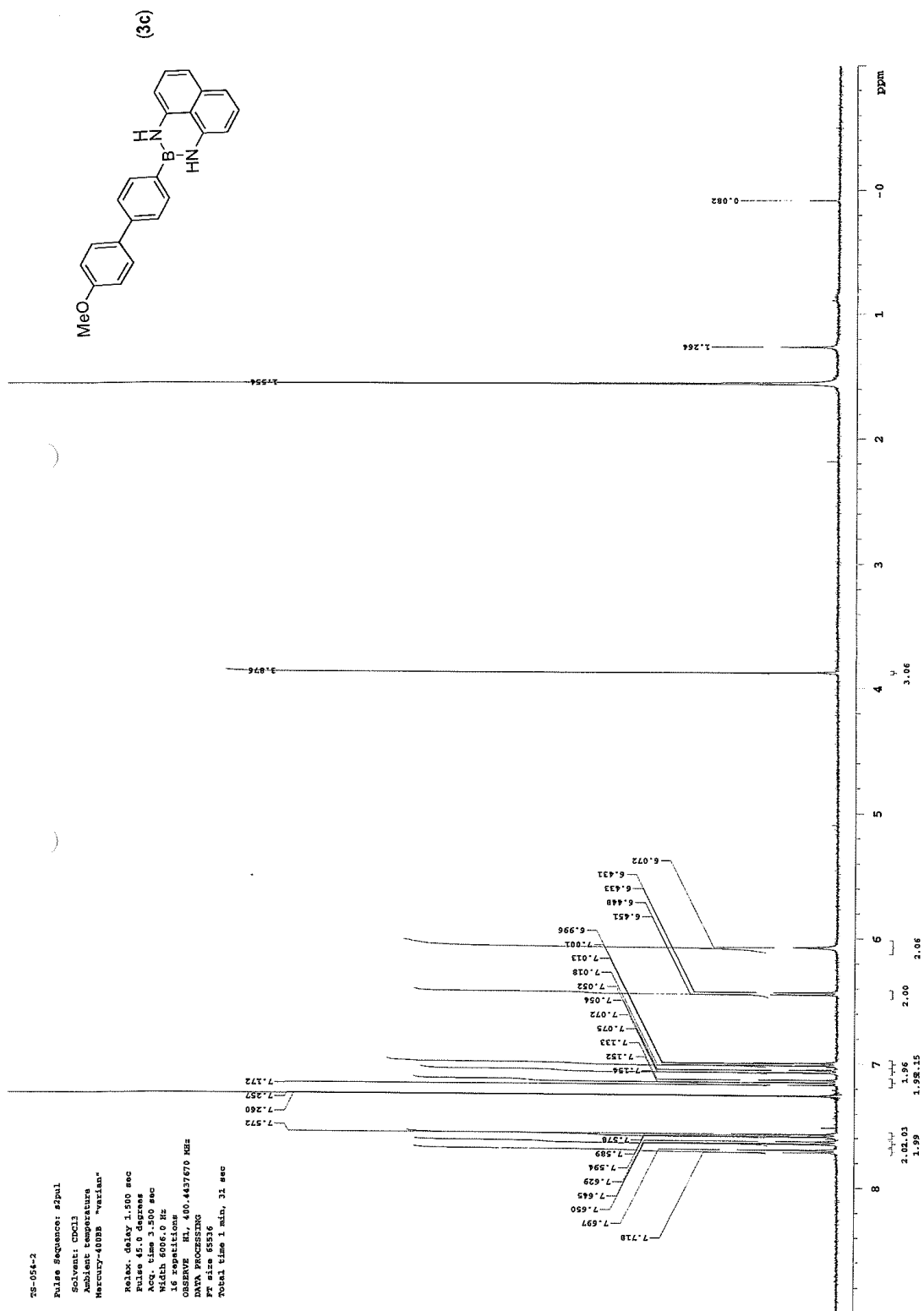
¹³C NMR of Compound o-2



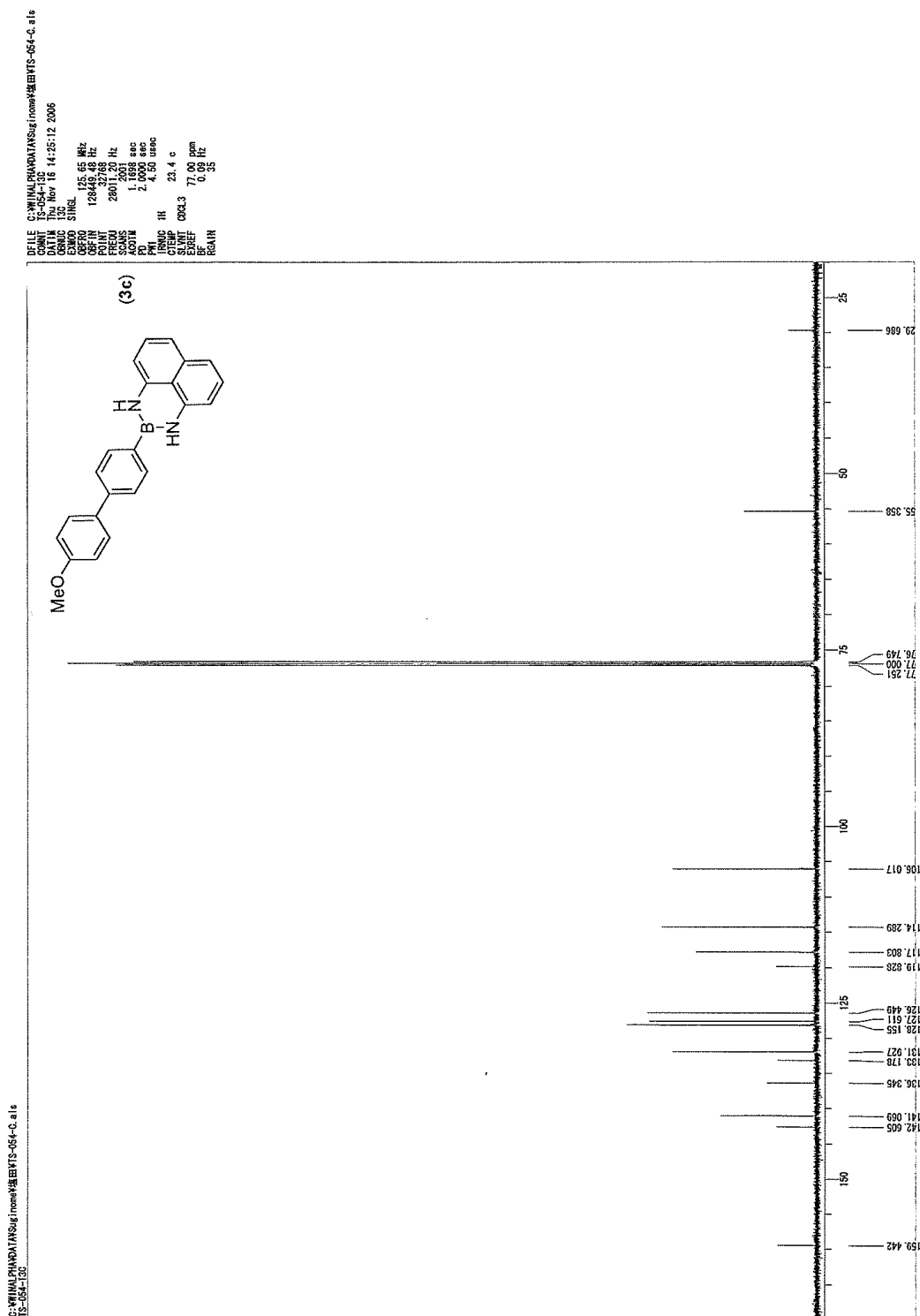
¹H NMR of Compound 3b



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



¹H NMR of Compound **3c**



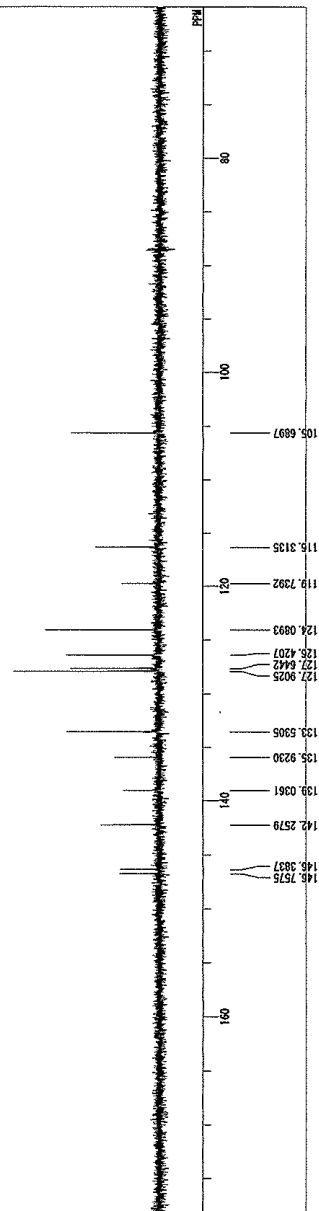
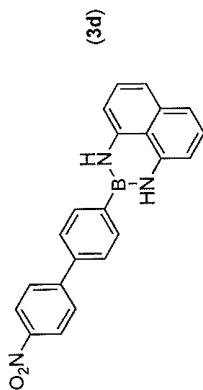
^{13}C NMR of Compound 3c



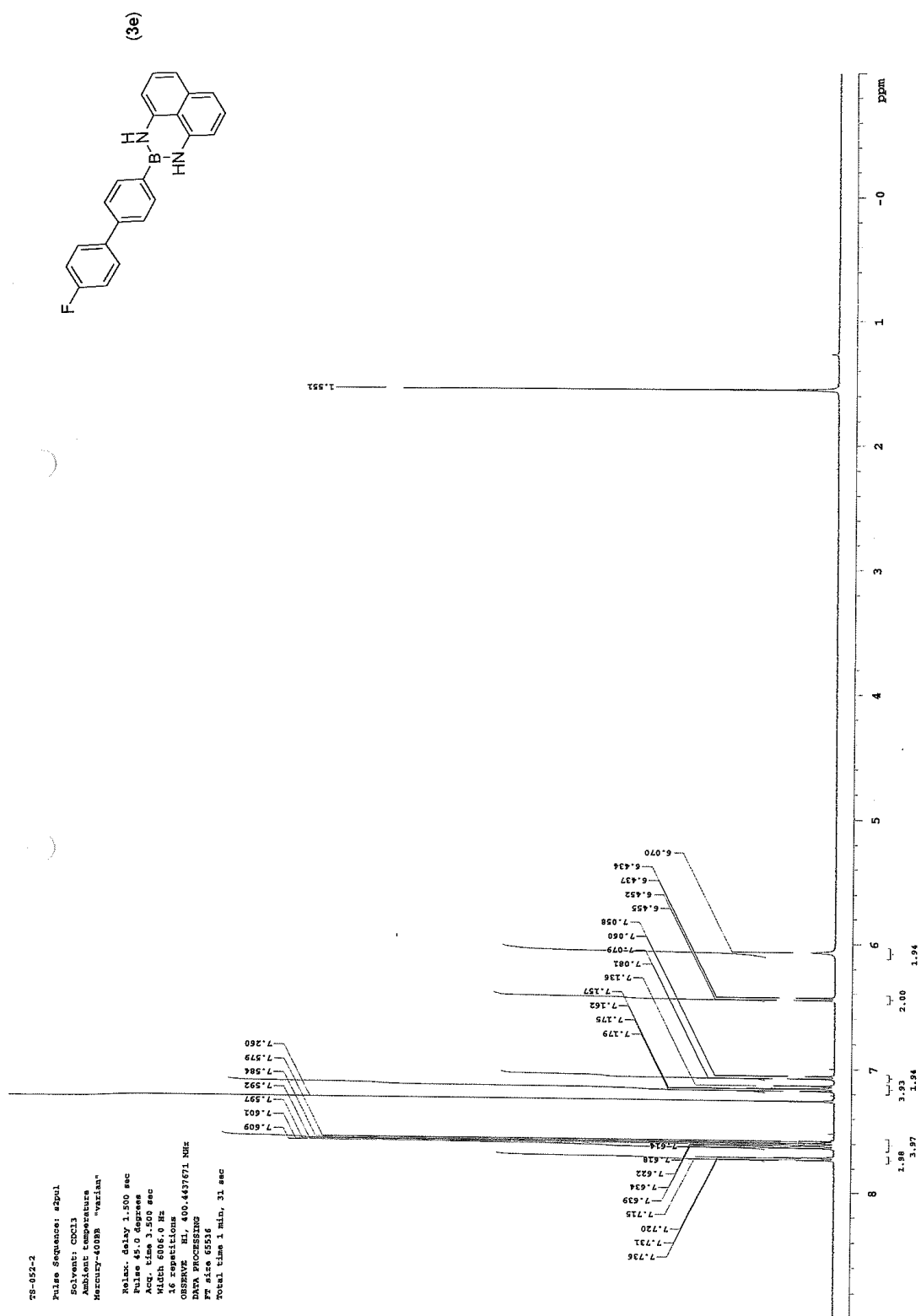
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 DATE 05 Apr 21 11:52:51 2007
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 P3 38.50
 P4 0.45
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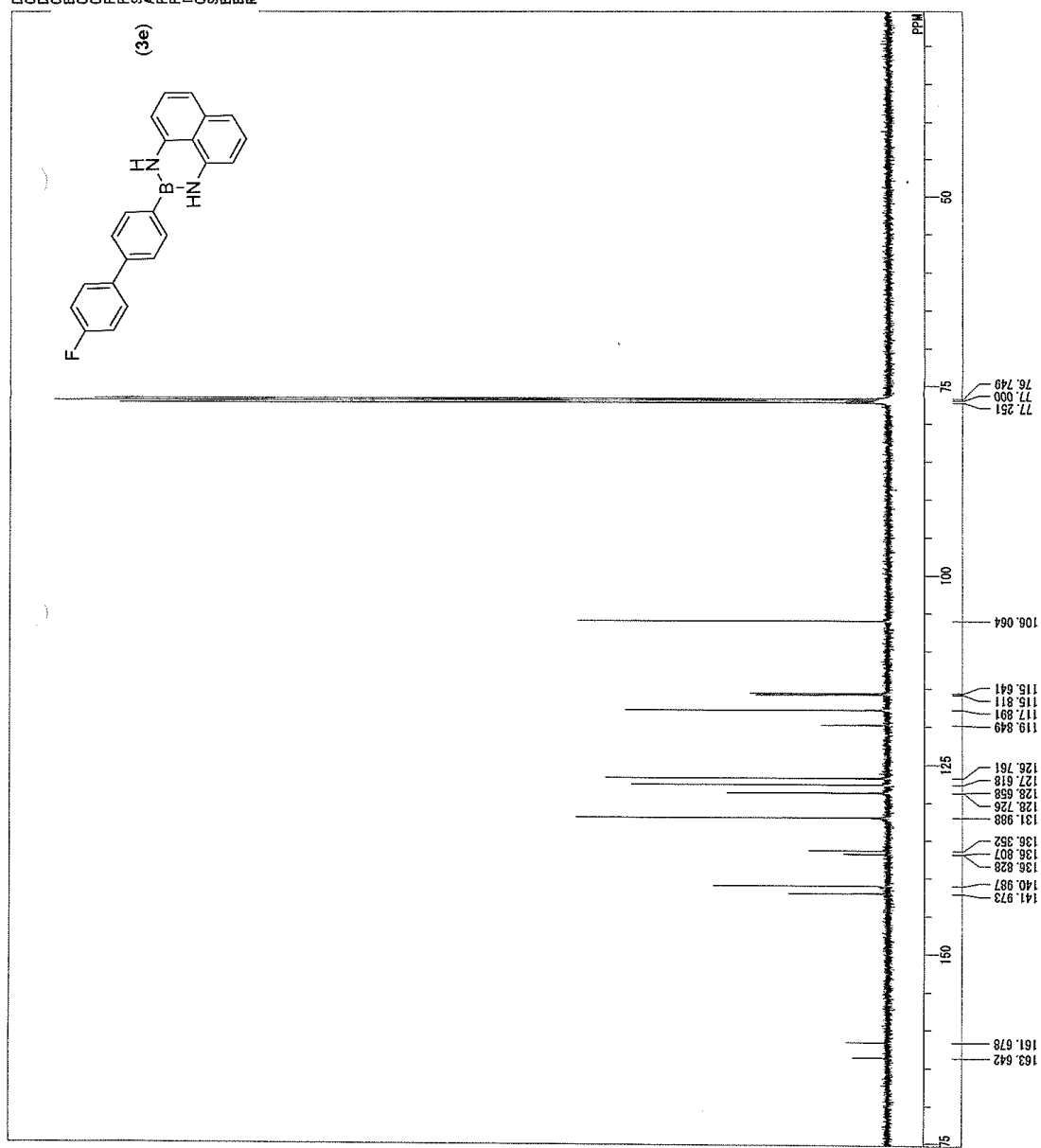


¹³C NMR of Compound **3d**

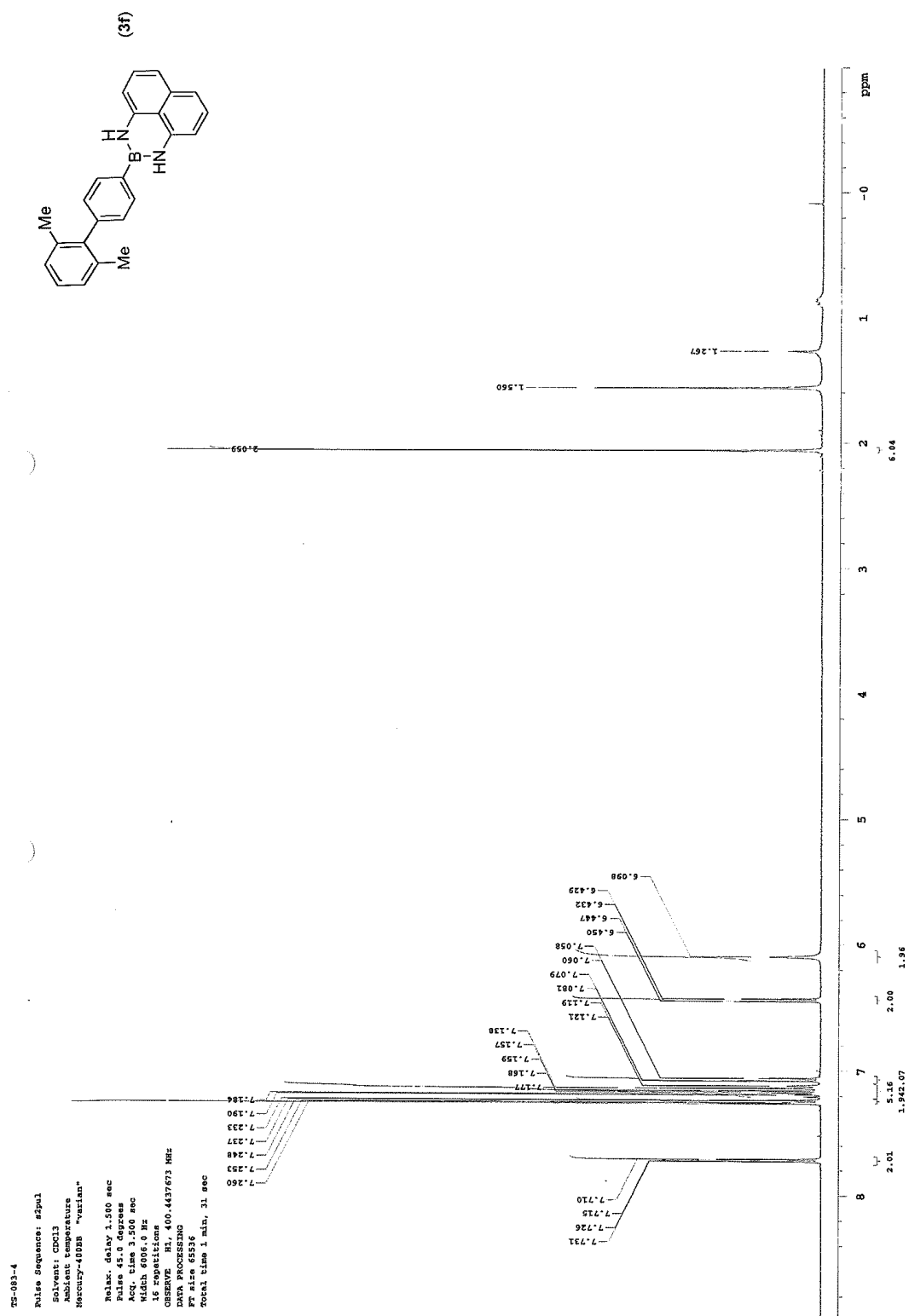


¹H NMR of Compound 3e

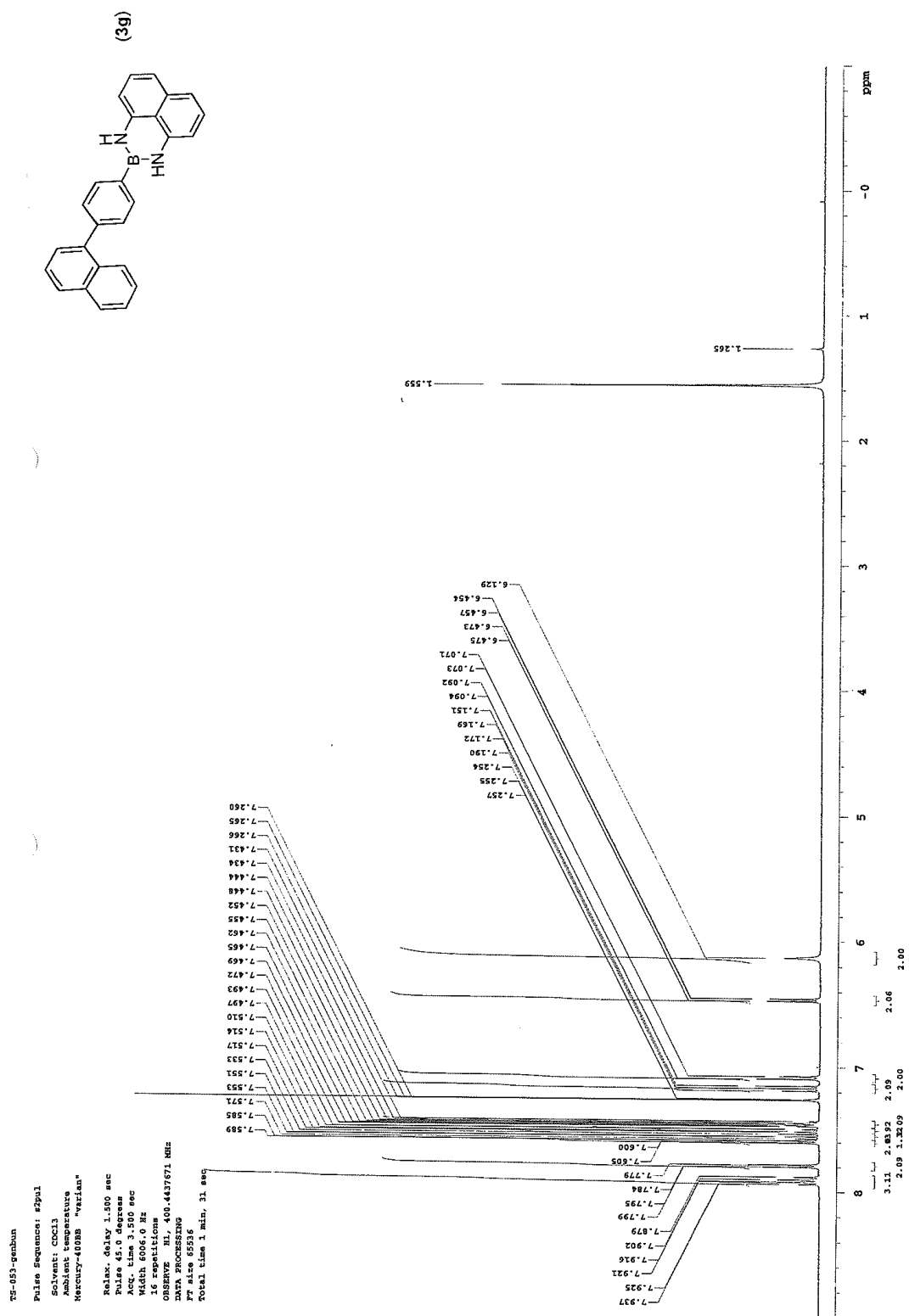
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 ACQTM 1.5000 sec
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 TRNG 24.8 c
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 SLYNT 0.43 Hz
 SREF 35
 RGAIN



¹³C NMR of Compound 3e

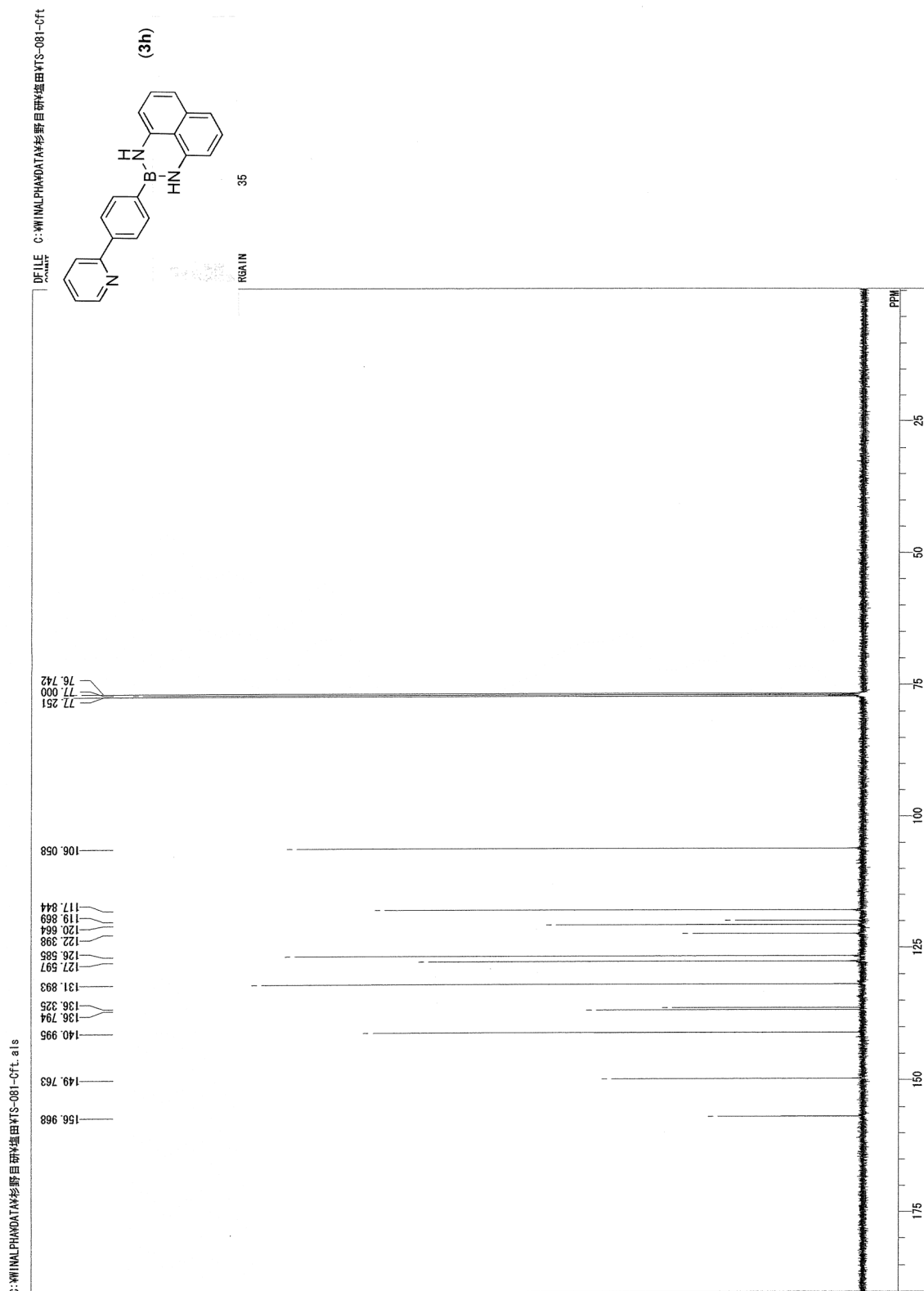


¹H NMR of Compound 3f

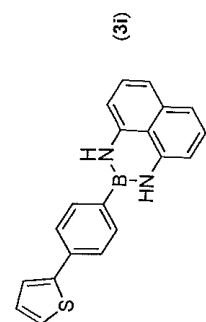


¹H NMR of Compound 3g

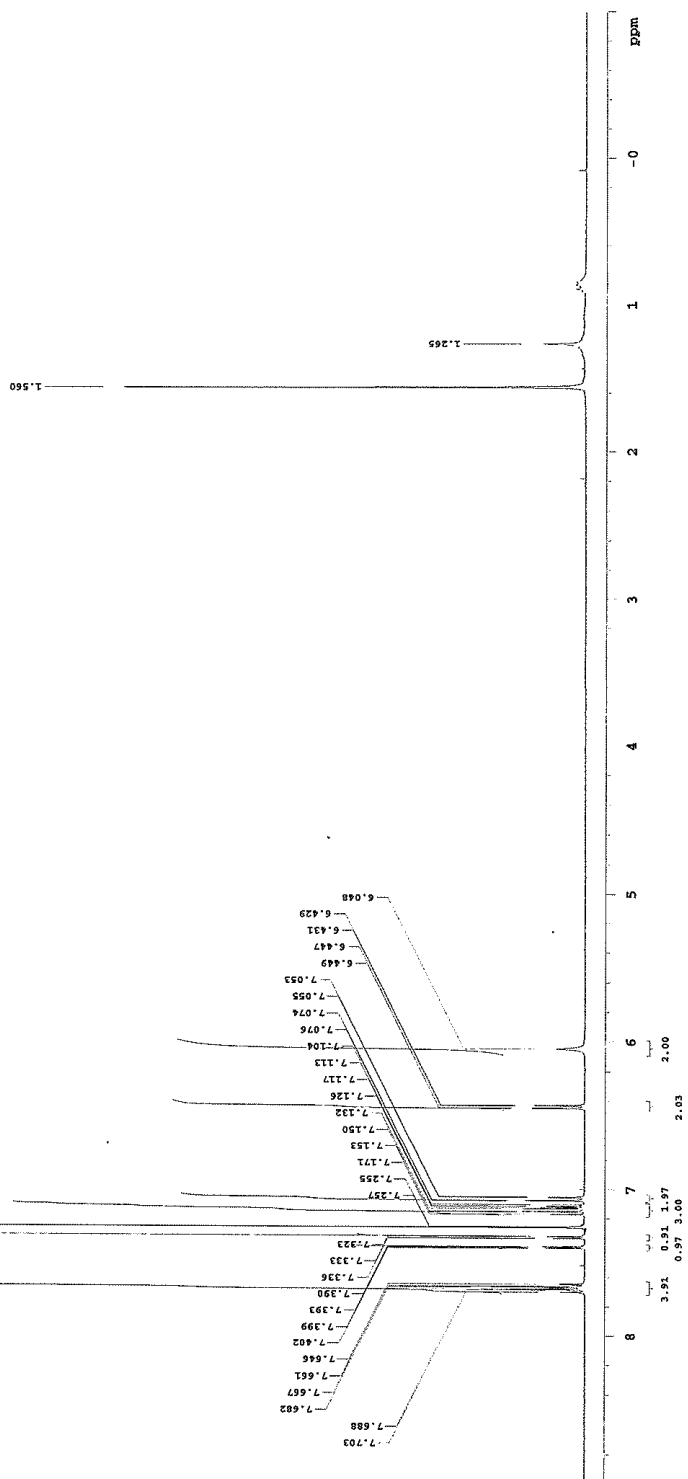


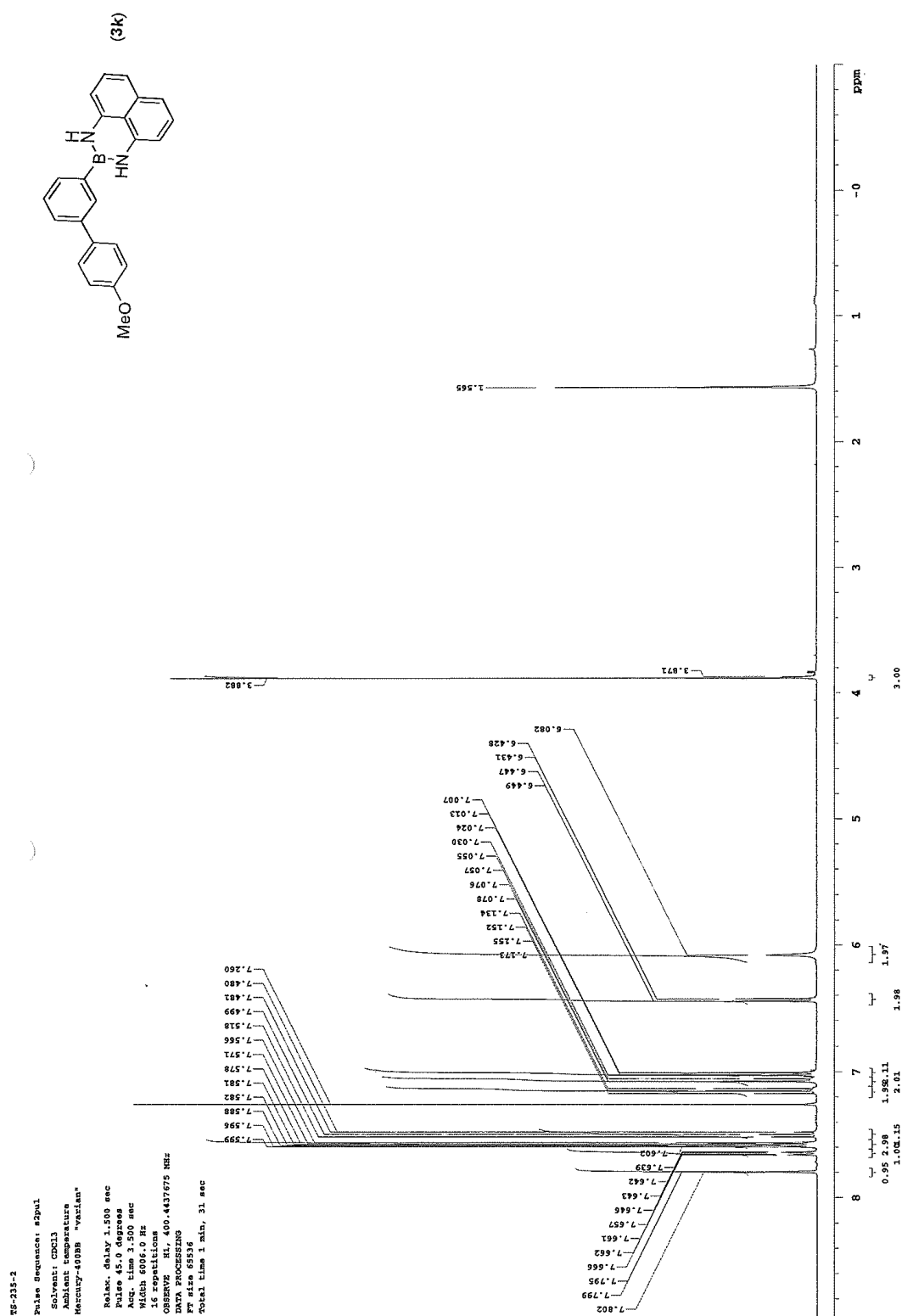


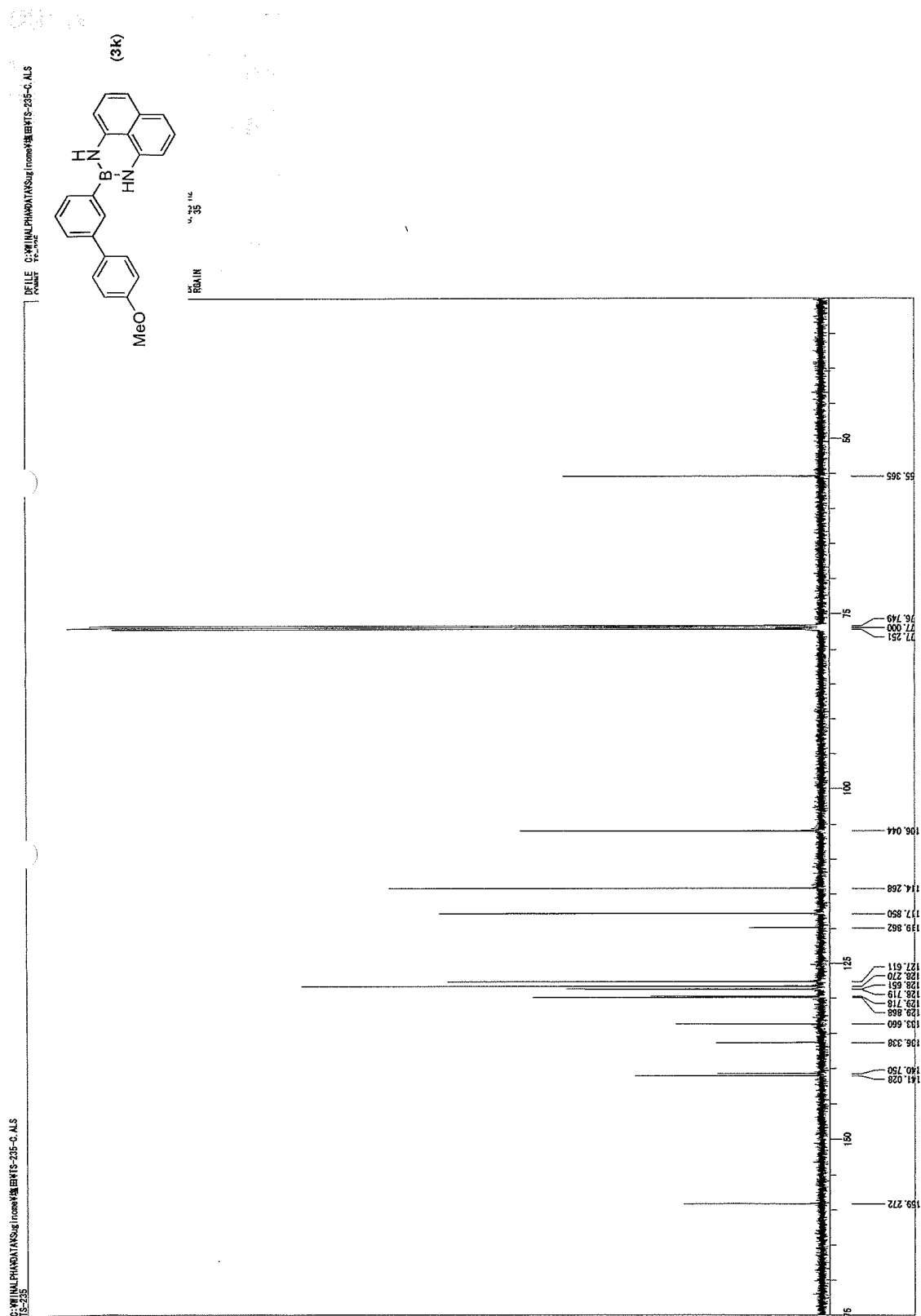
^{13}C NMR of Compound **3h**

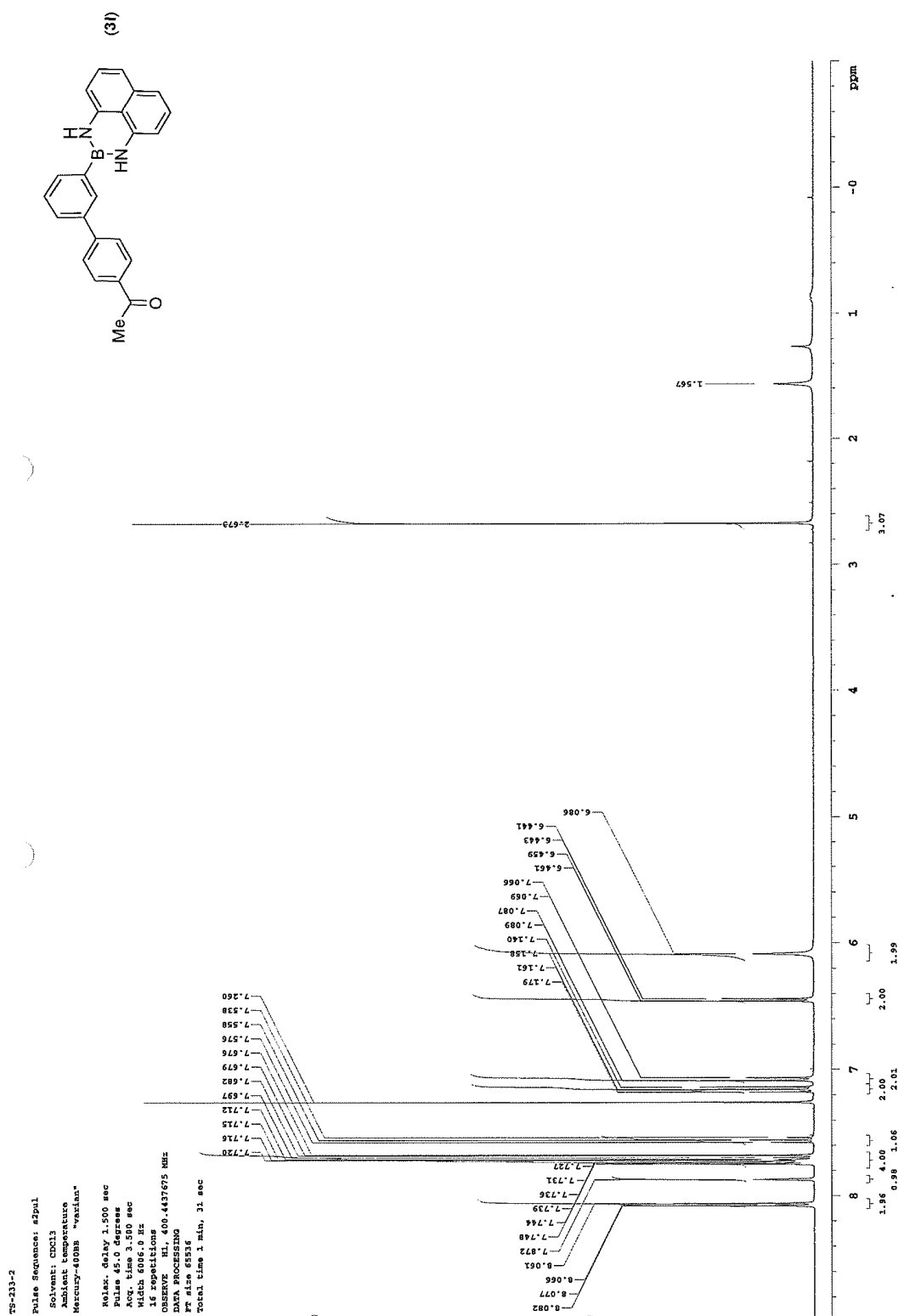


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 Pulse: 45.0 degrees
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 FT size: 65536
 DATA PROCESSING
 Total time: 1 min, 31 sec





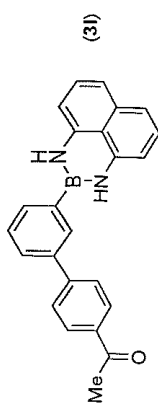




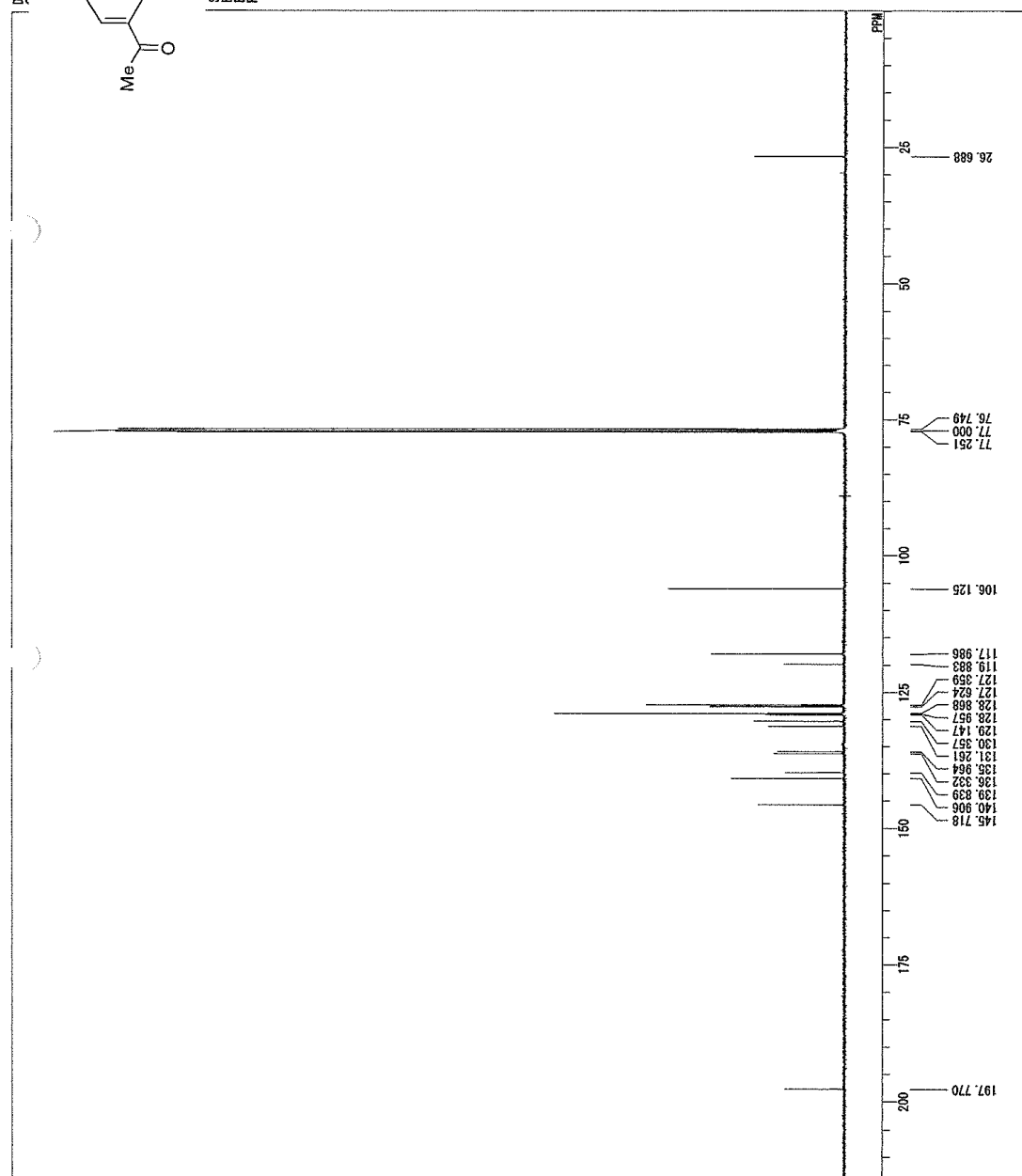
¹H NMR of Compound 31

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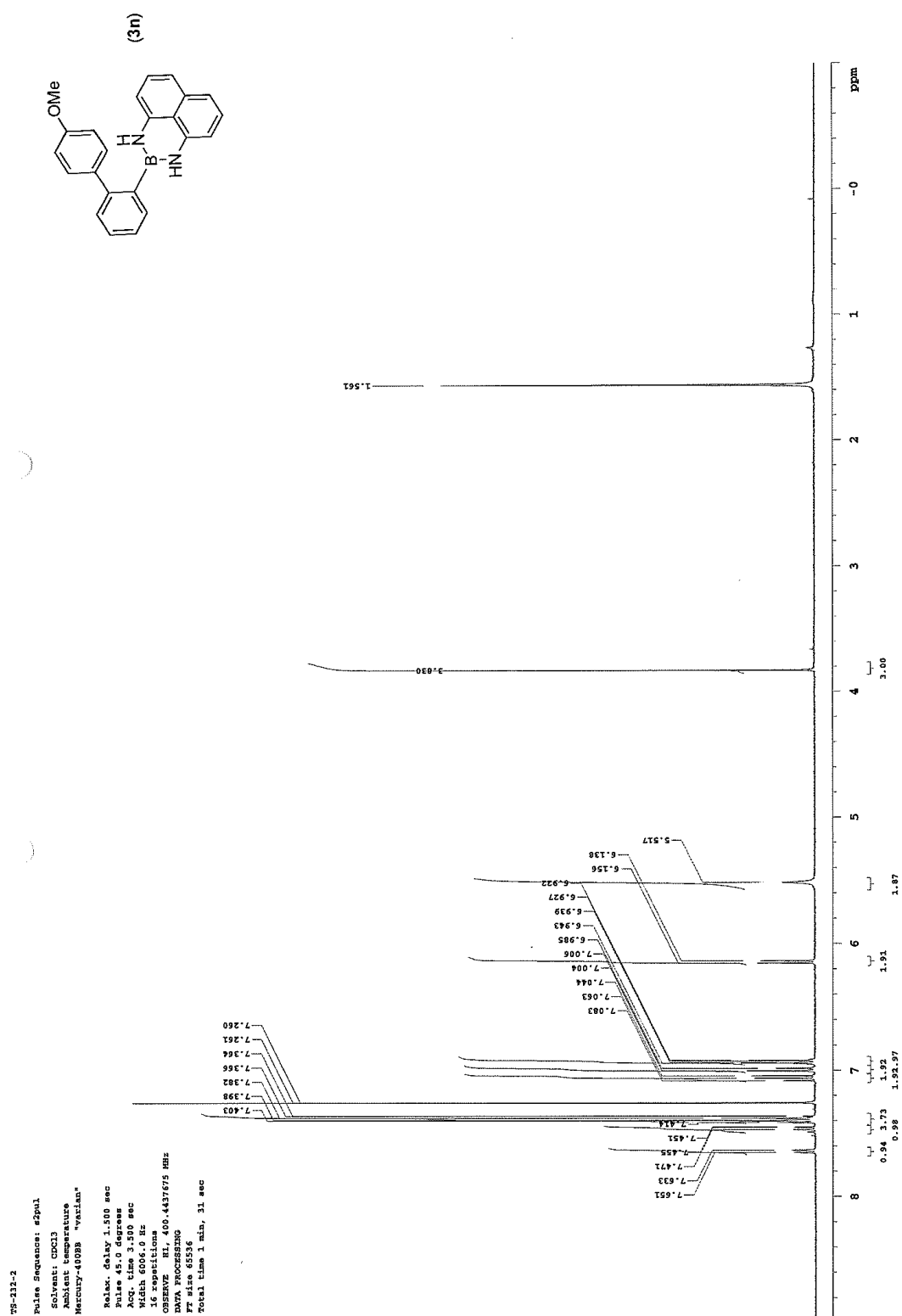
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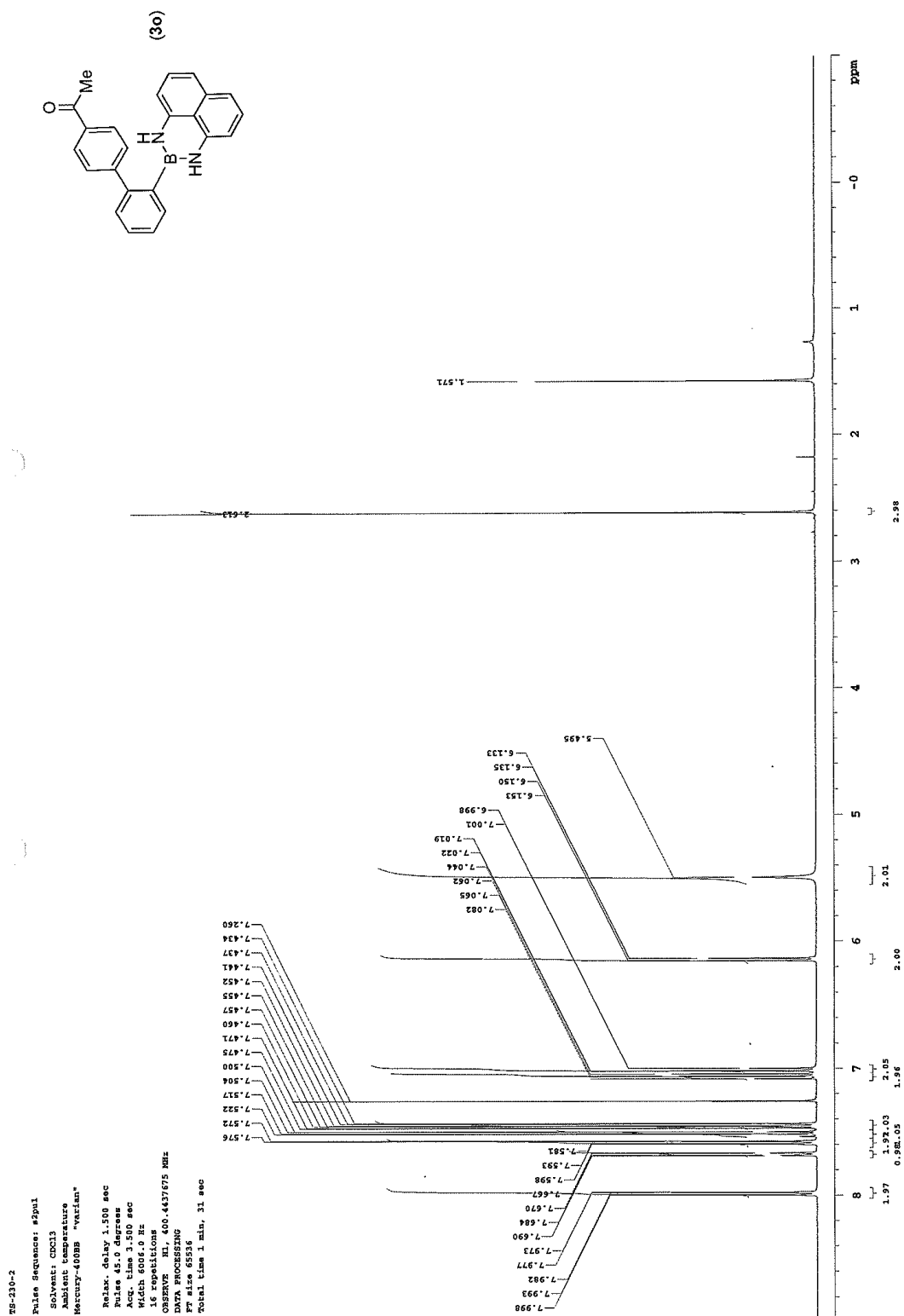
¹³C NMR of Compound **31**



¹H NMR of Compound **3n**

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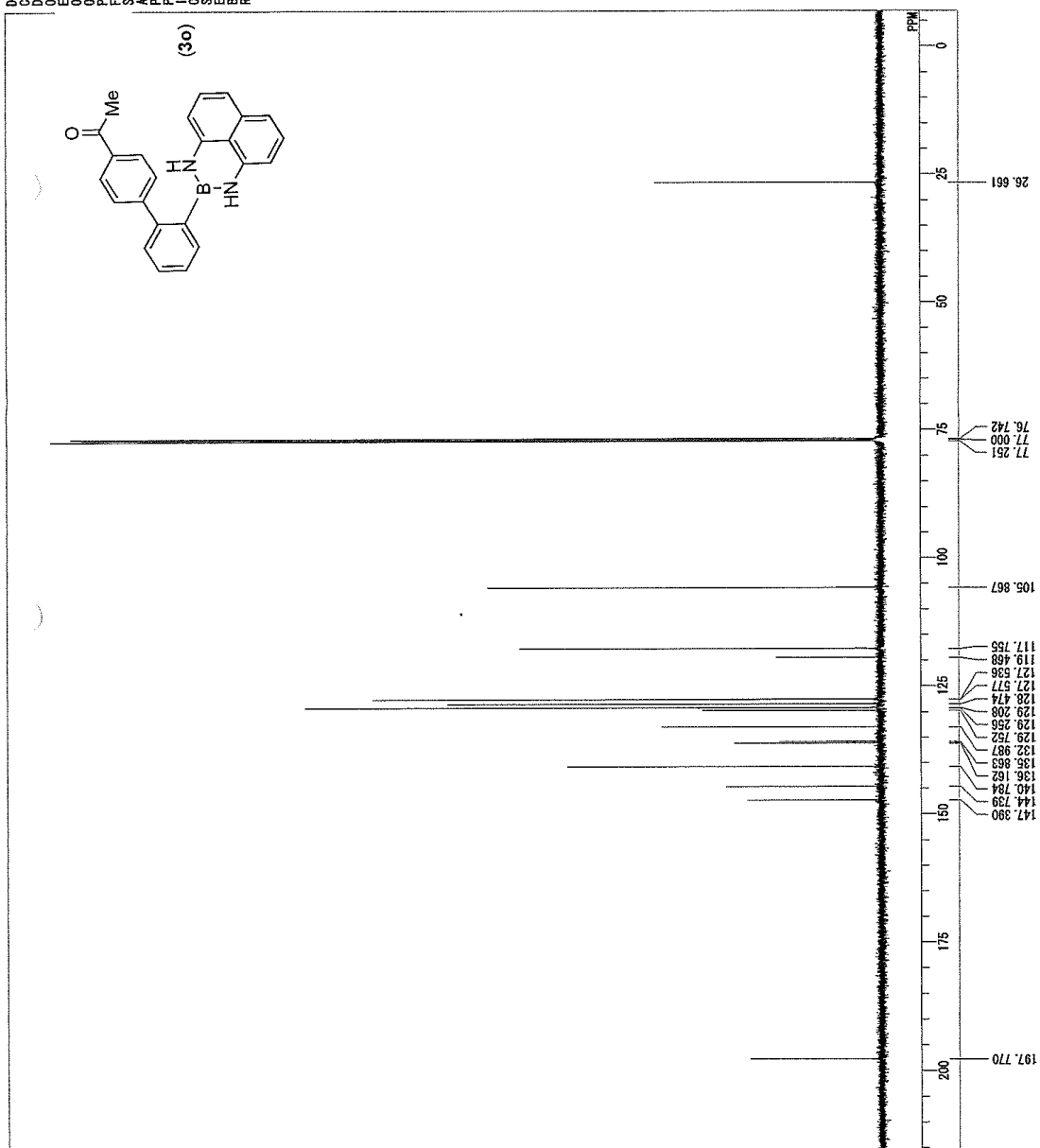
¹H NMR of Compound **3o**

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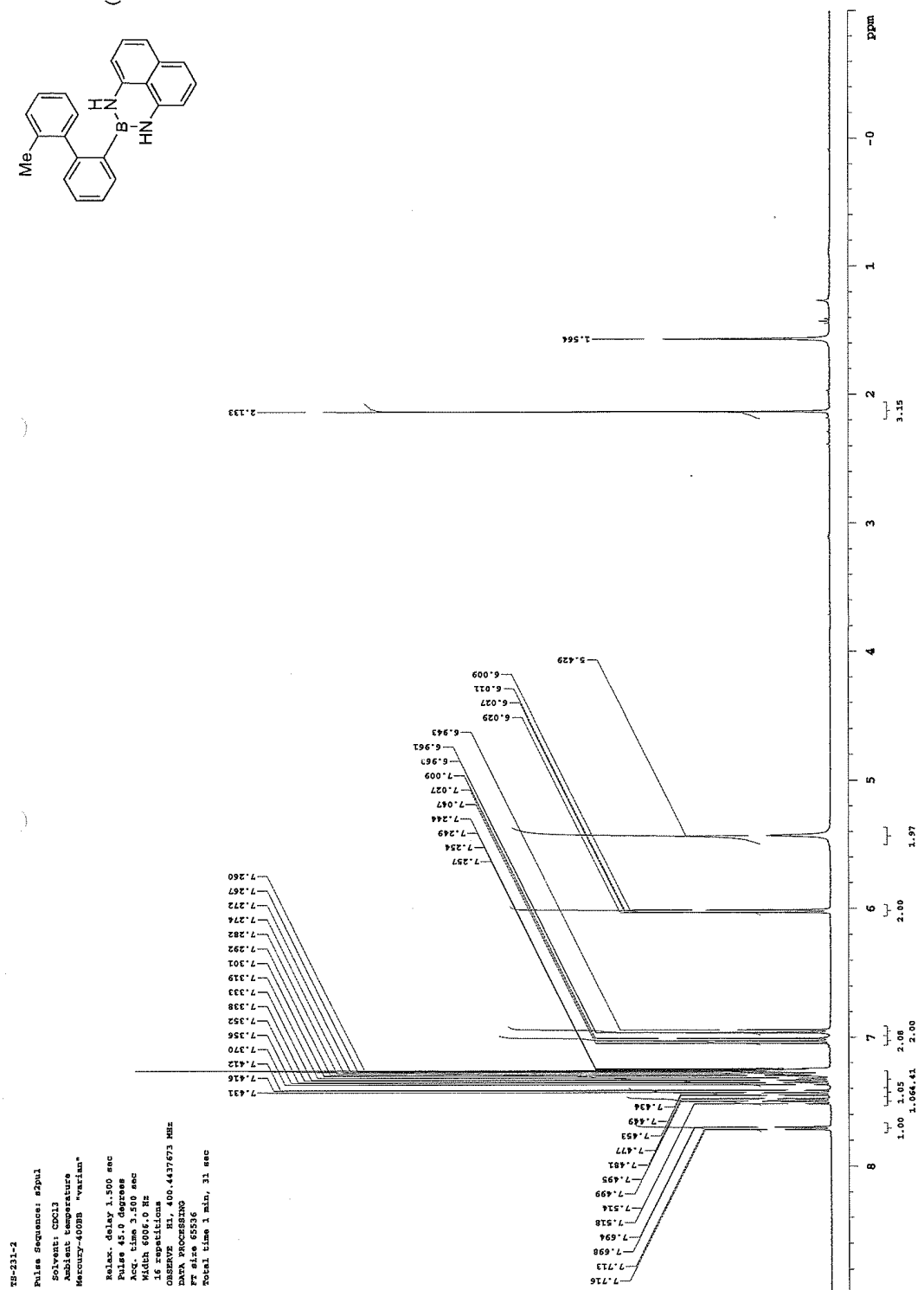
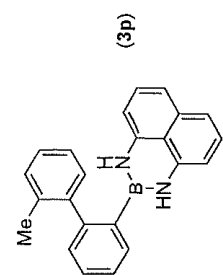
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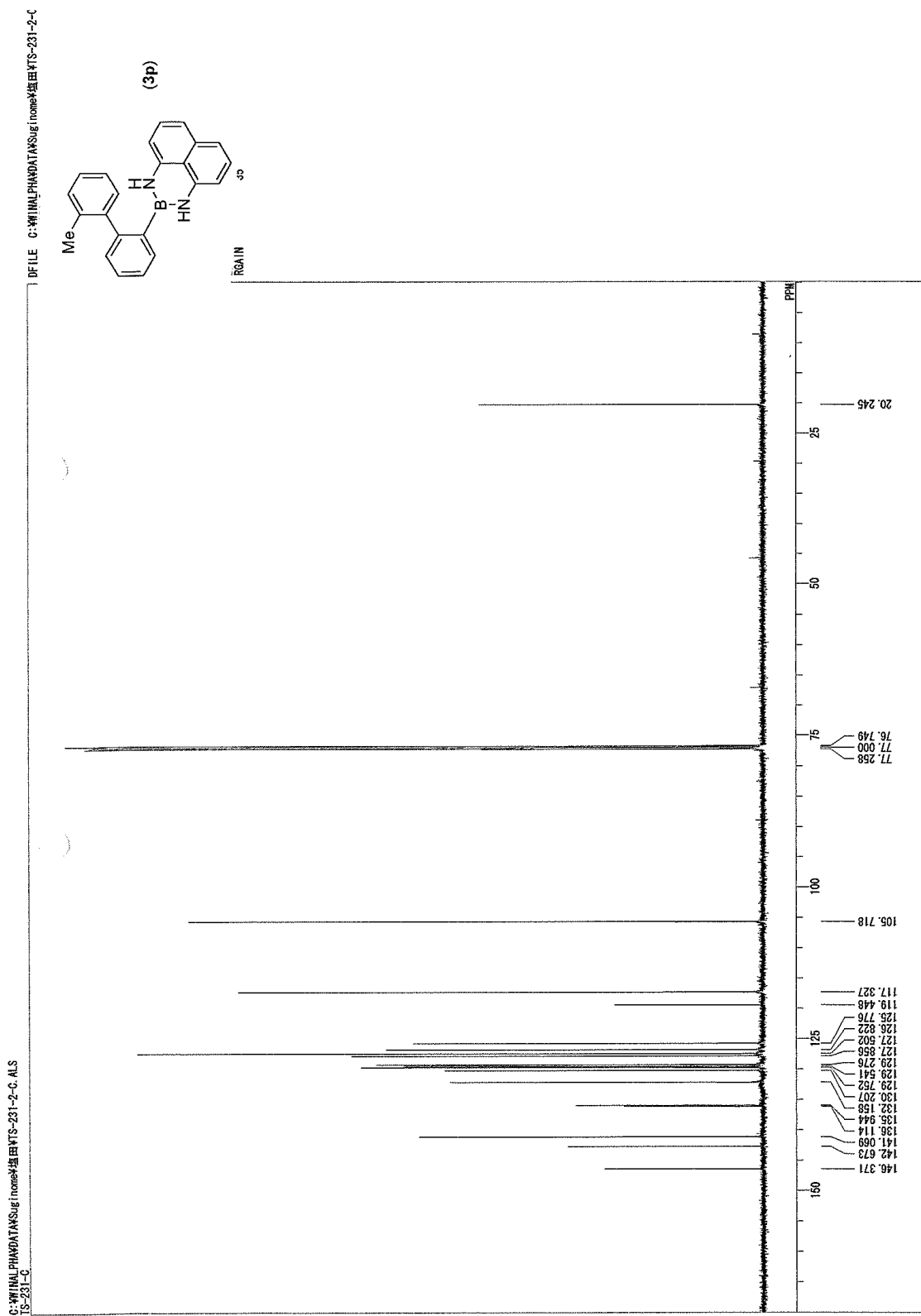
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 ORFQ 128448.48 Hz
 PULP 32778 Hz
 FREQ 28017260 Hz
 SCANS 1
 ACQTM 1.1688 sec
 PD 2.0000 sec
 PM 4.50 usec
 PM 23.2 °
 CTEMP 000.3
 SREF 77.00 ppm
 RF 0.43 Hz
 RGAIN 35



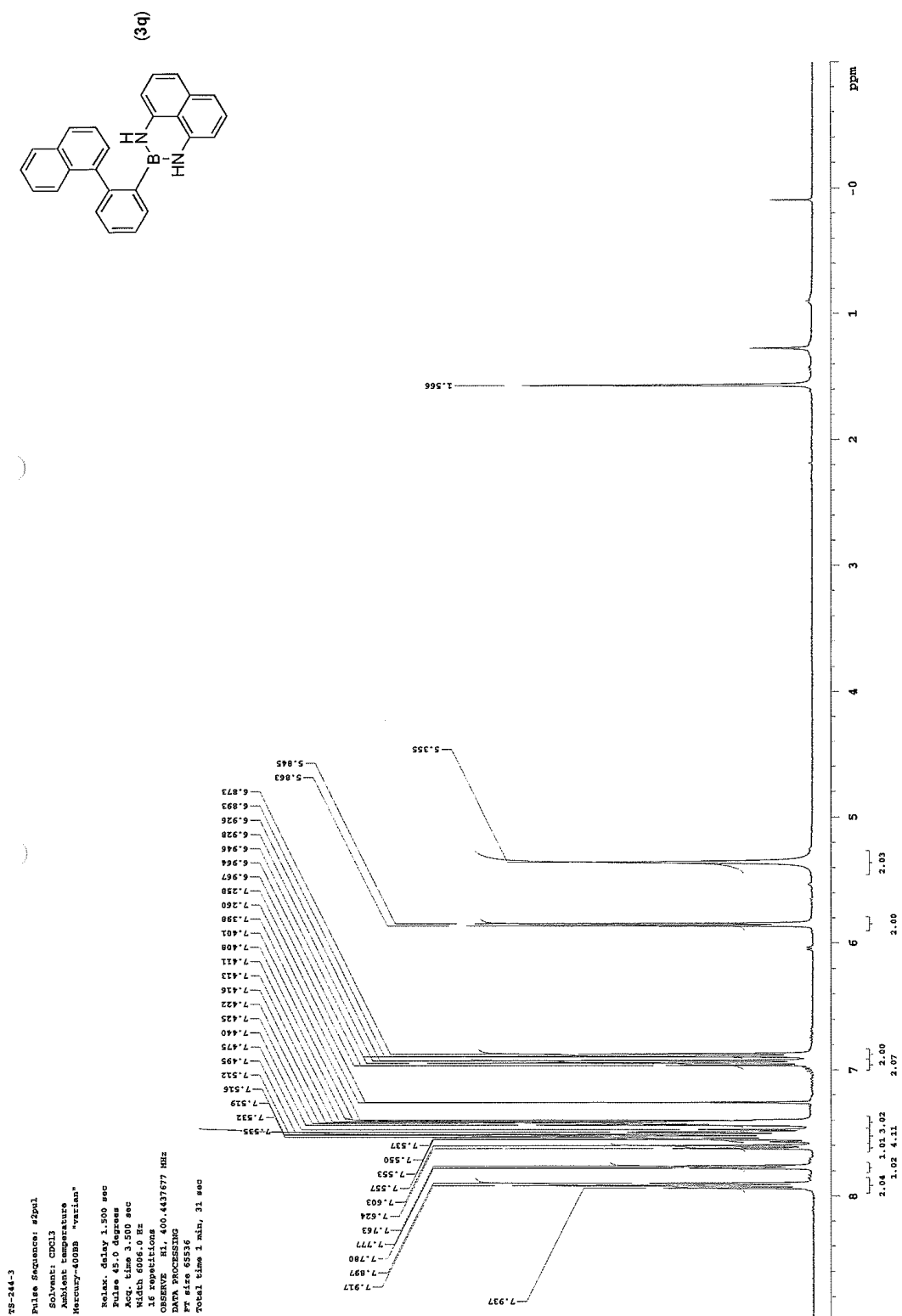
¹³C NMR of Compound 3o



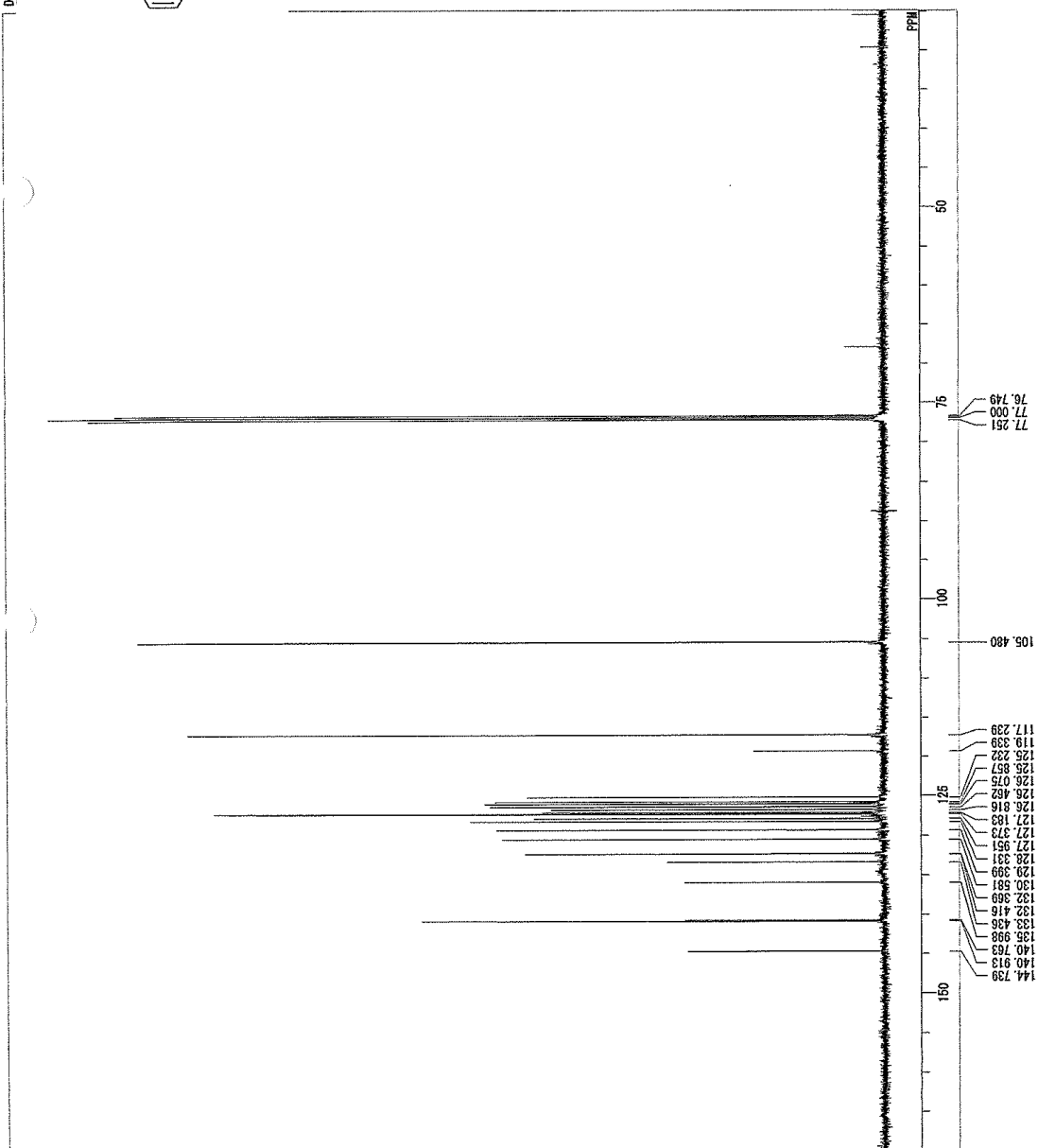
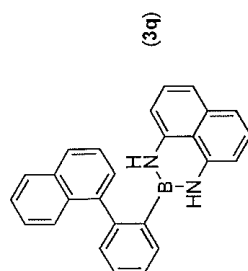
^1H NMR of Compound 3p



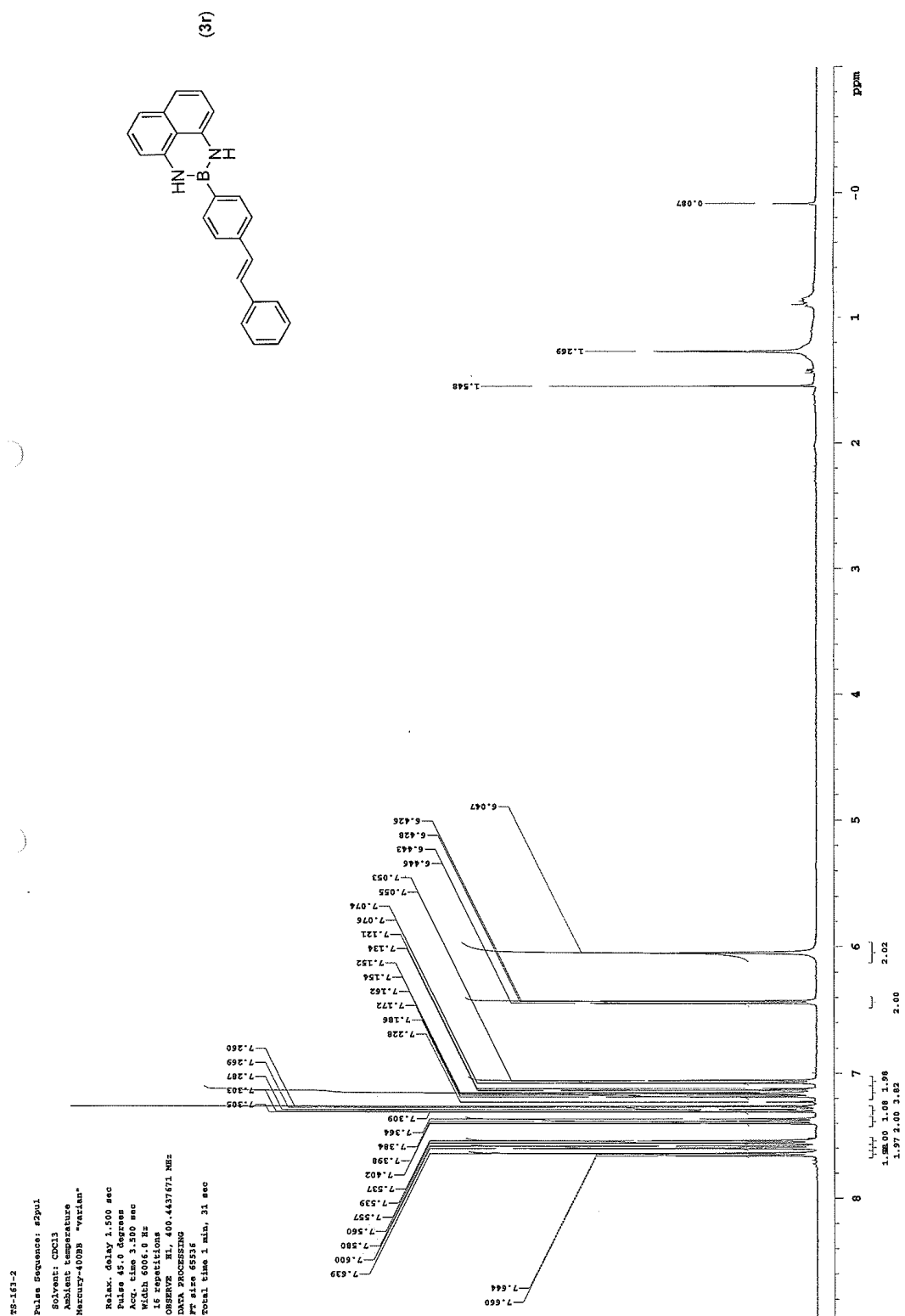
^{13}C NMR of Compound **3p**



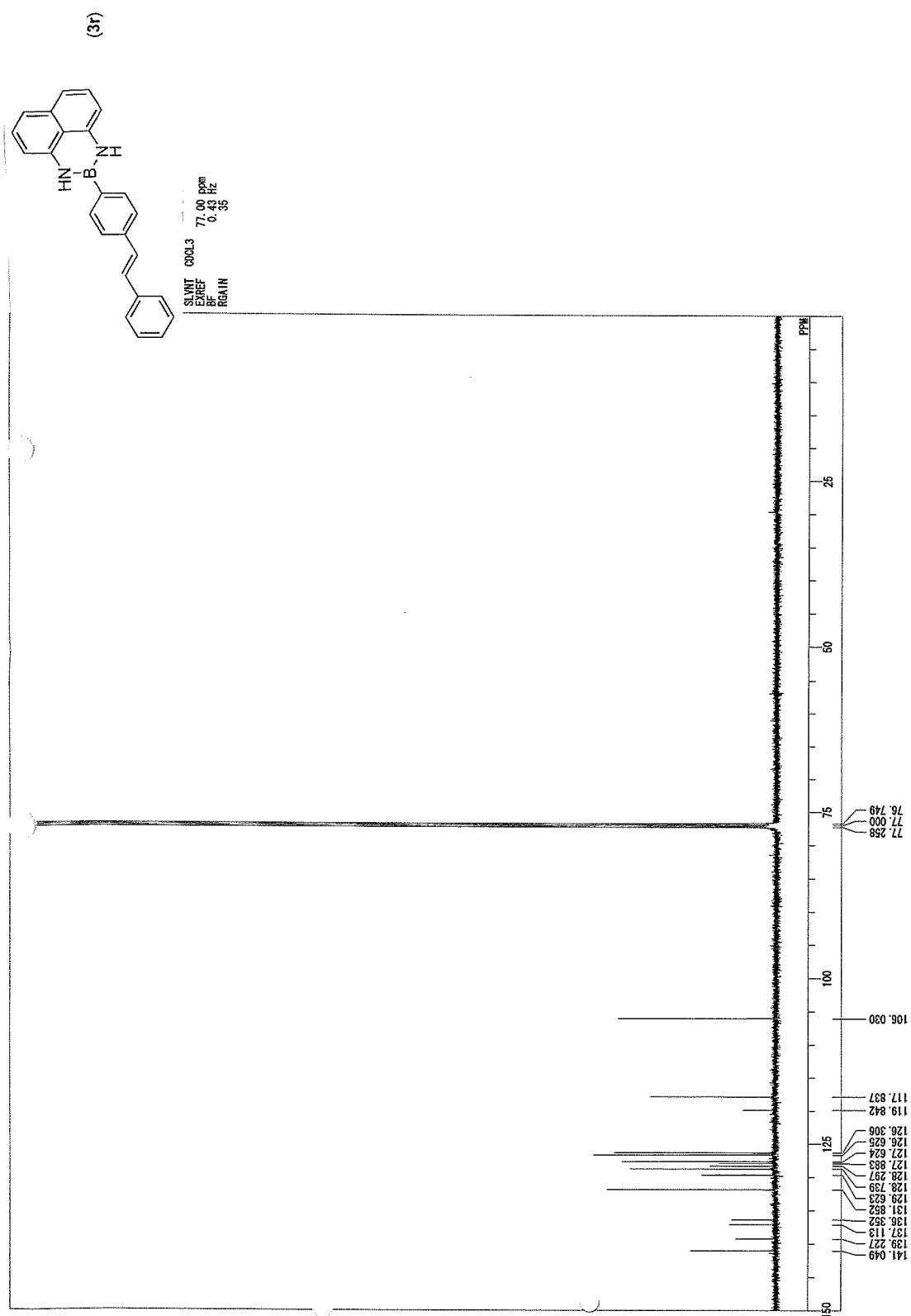
¹H NMR of Compound 3q



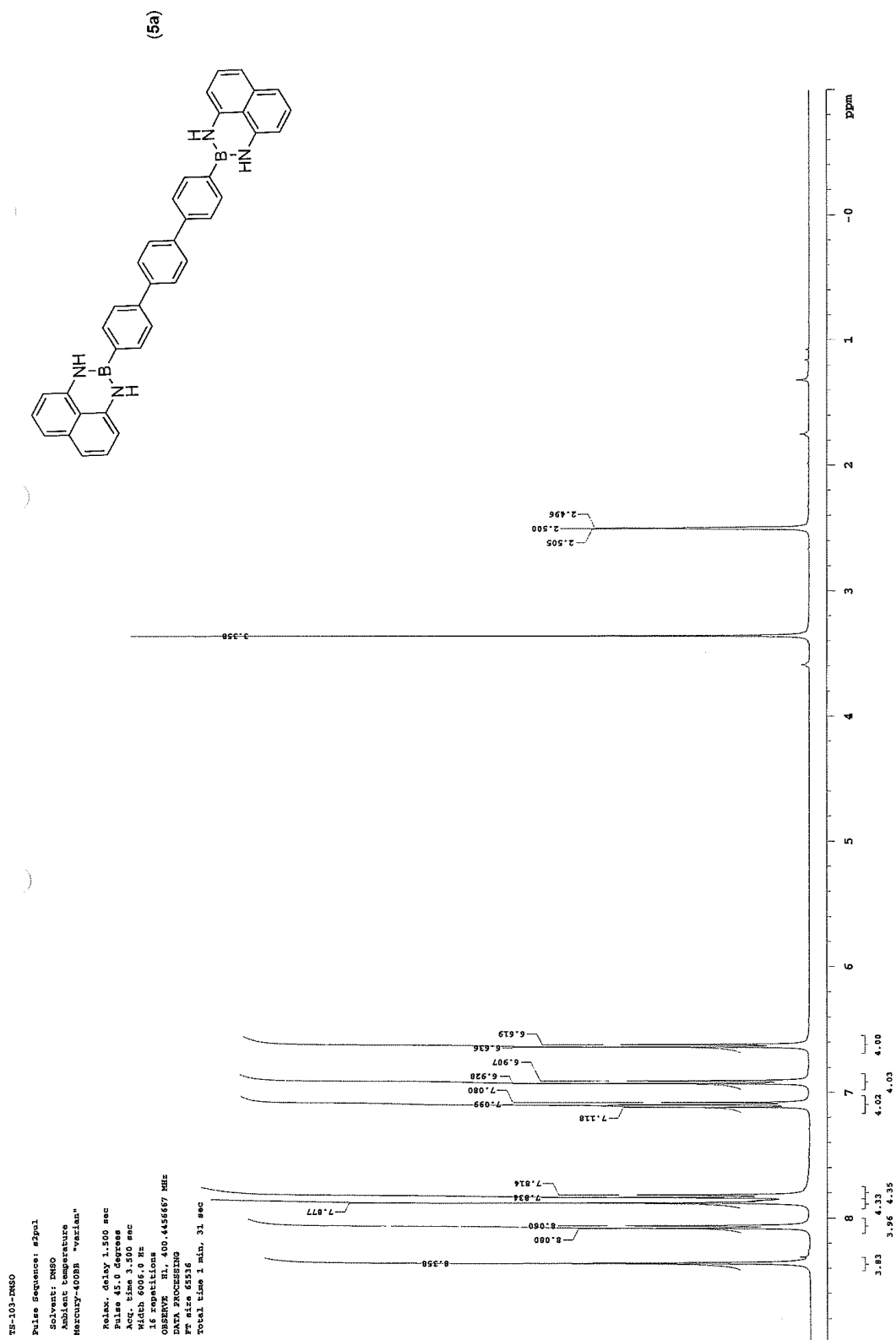
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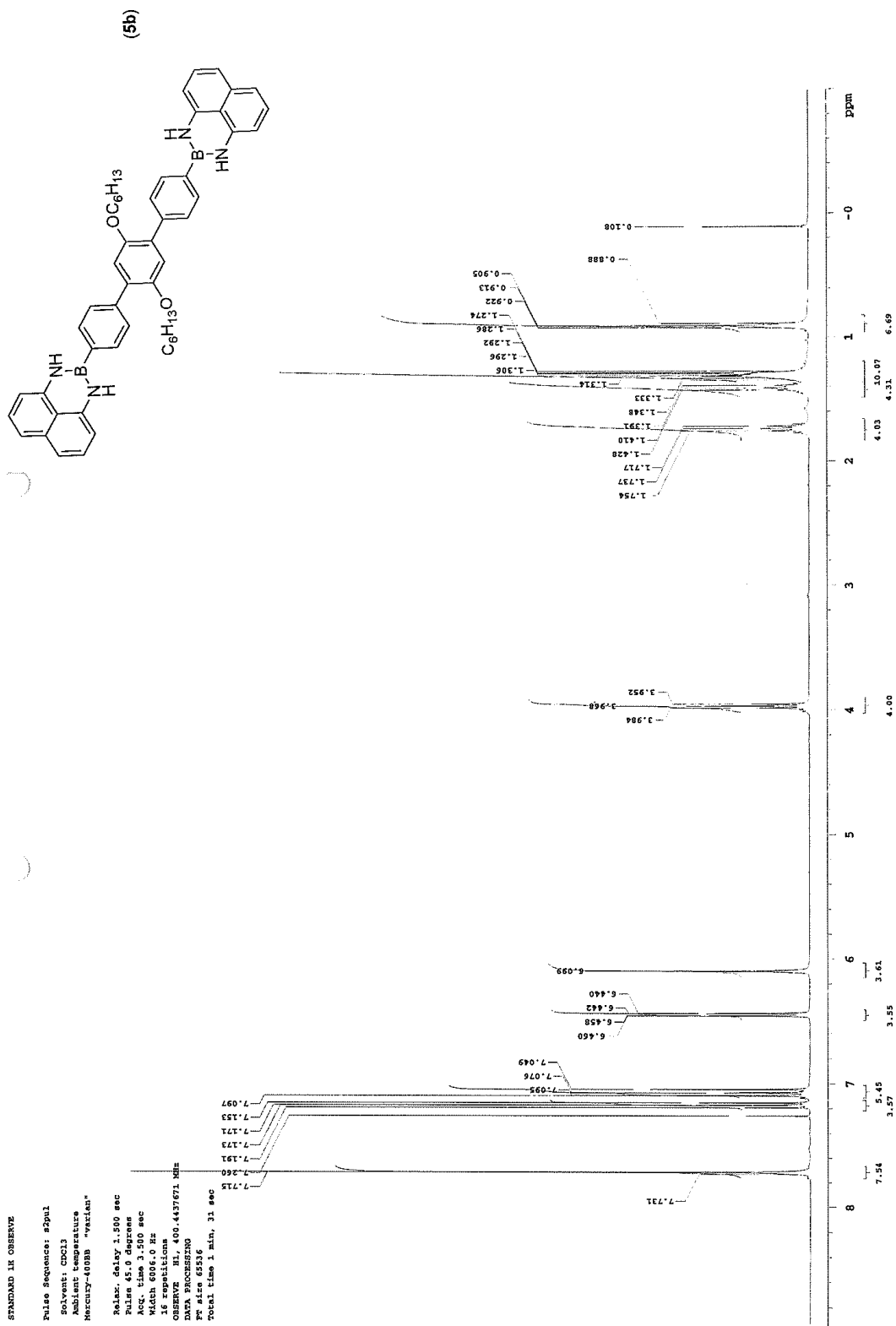
¹H NMR of Compound **3r**



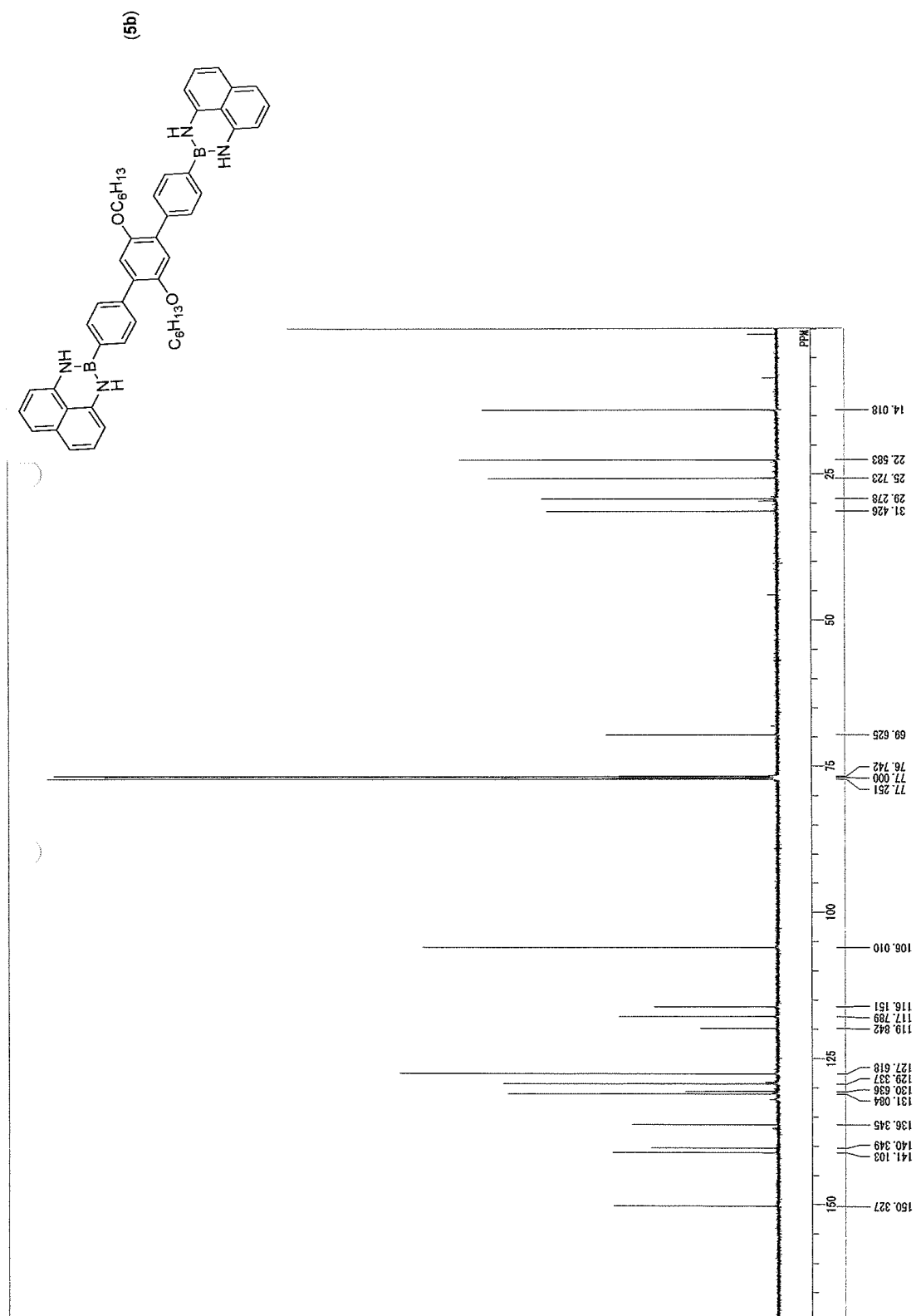
^{13}C NMR of Compound **3r**



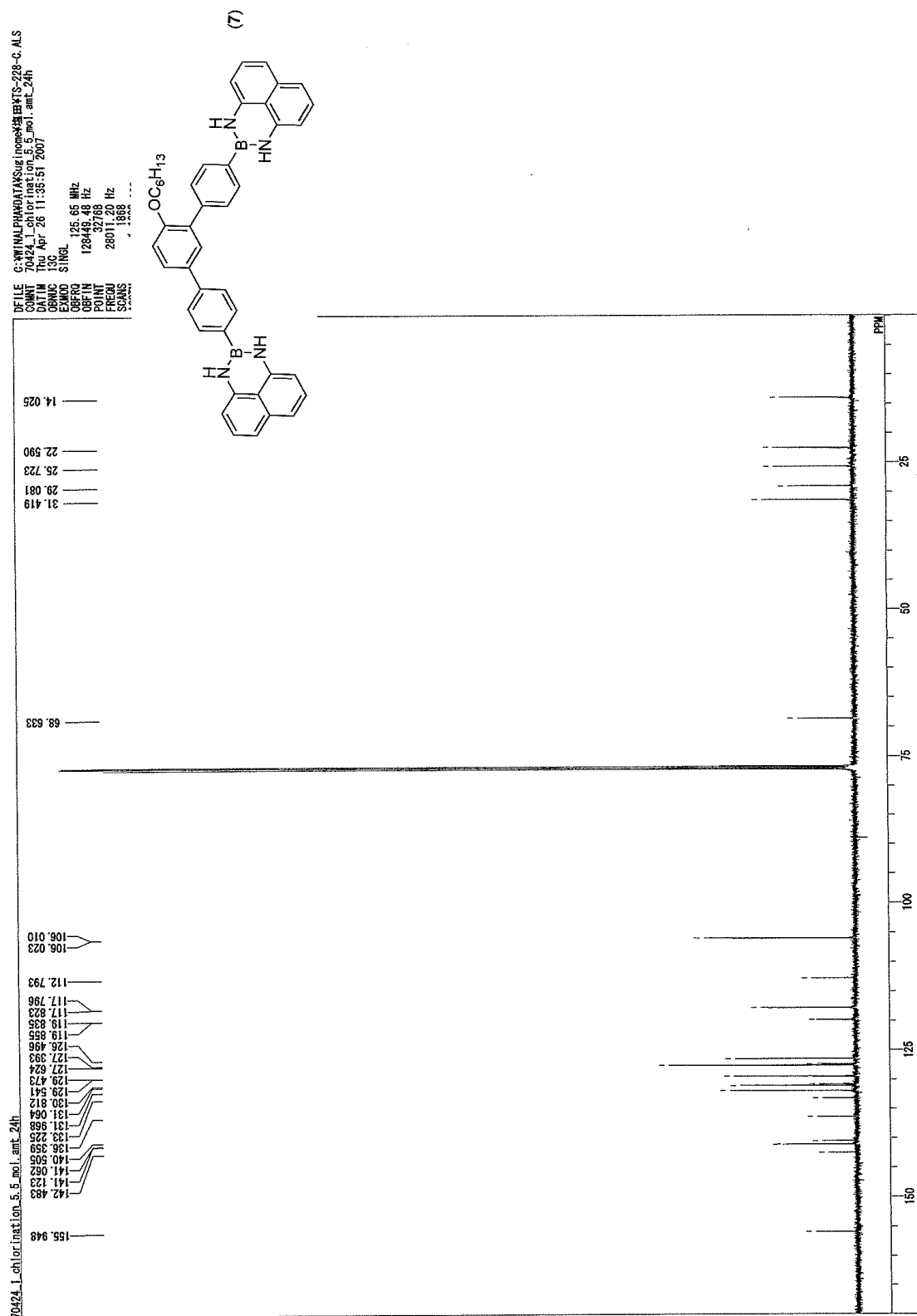
^1H NMR of Compound **5a**



¹H NMR of Compound 5b

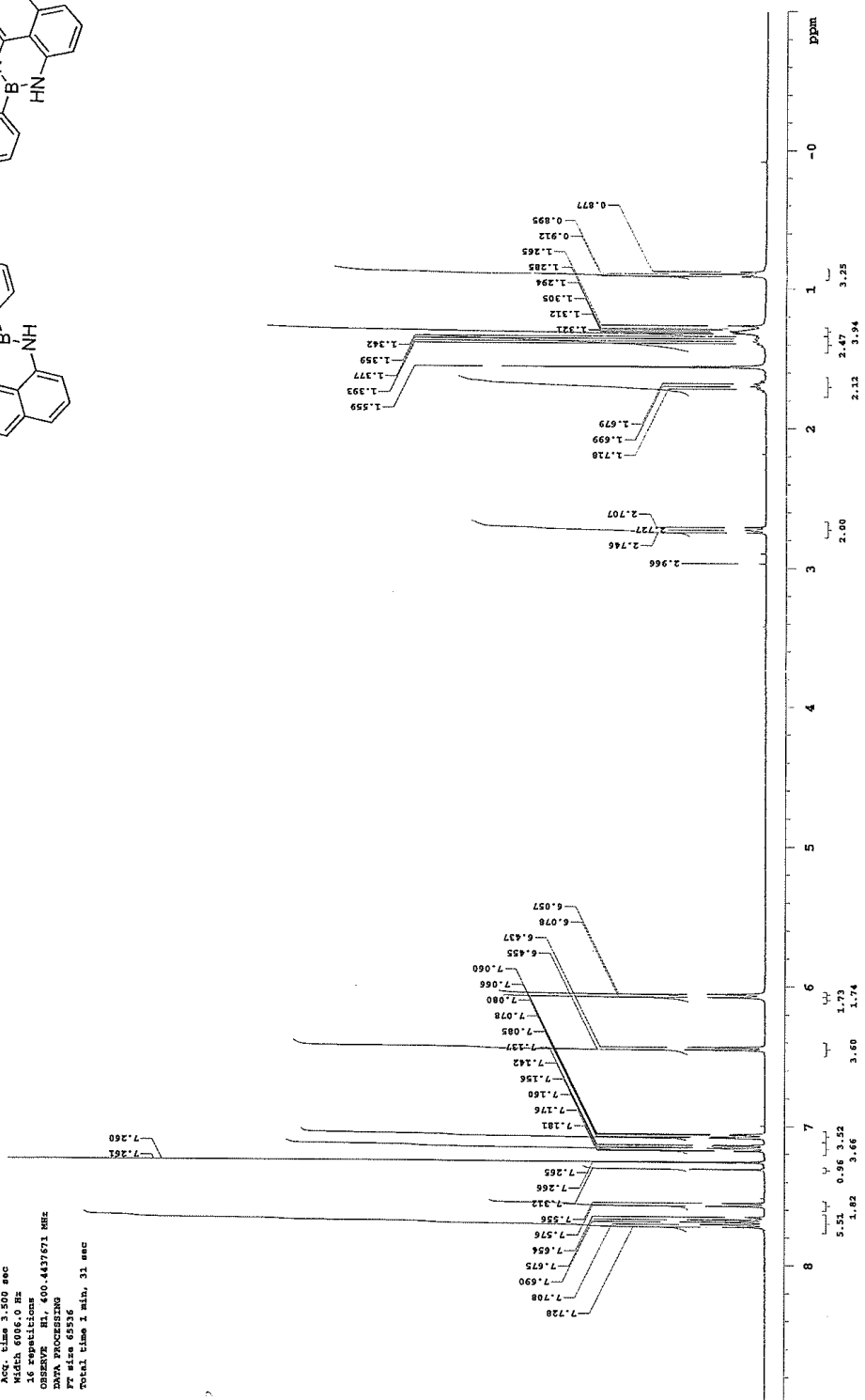
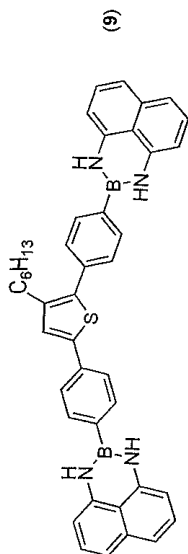


^{13}C NMR of Compound 5b

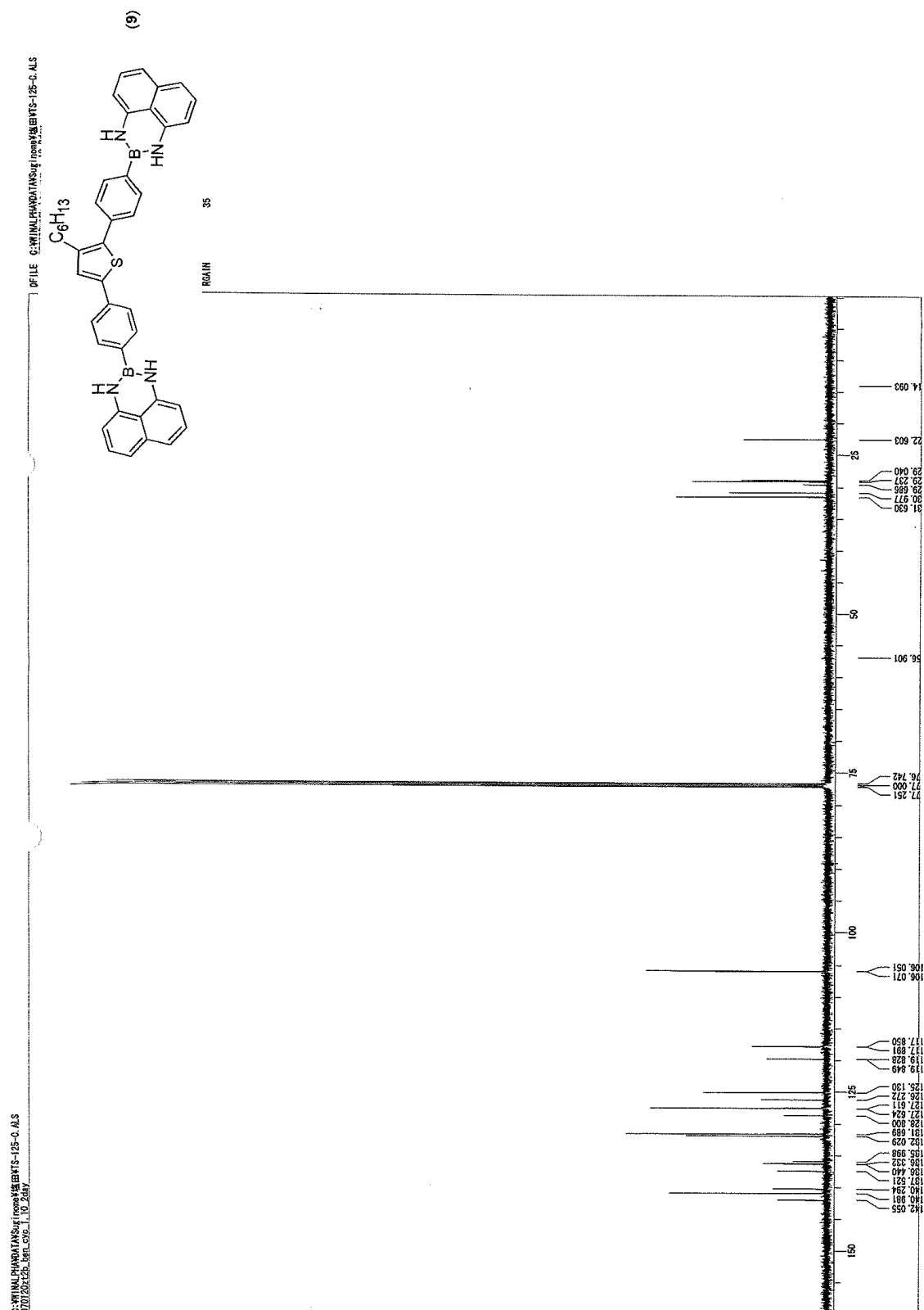


¹³C NMR of Compound 7

TS-125-2
 Pulse Sequence: zgpg30
 Solvent: CDCl3
 Ambient temperature
 Nucleus: 13C
 Relax: Delay 1.500 sec
 Pulse 15.0 degrees
 Relax 1.500 sec
 Width 6006.0 Hz
 16 repetitions
 OBSERVE H1, 400.4437671 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min. 31 sec



¹H NMR of Compound 9

 ^{13}C NMR of Compound **9**

(11a)

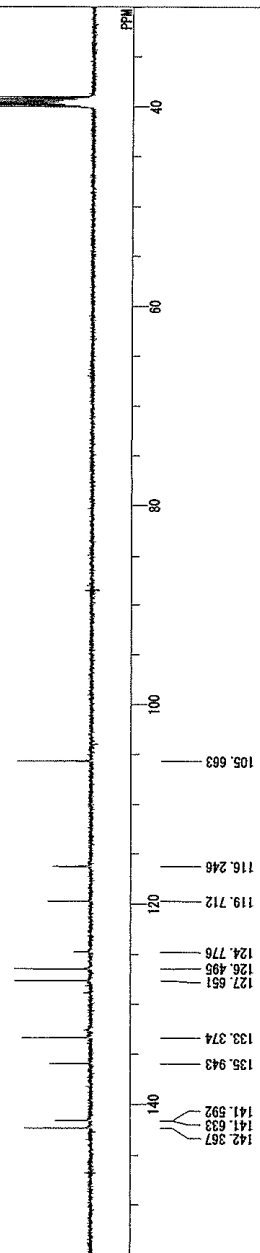
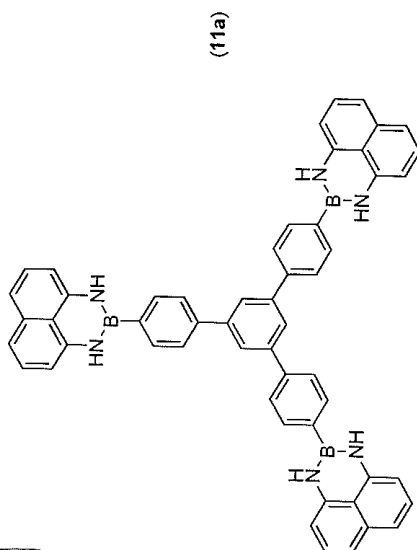


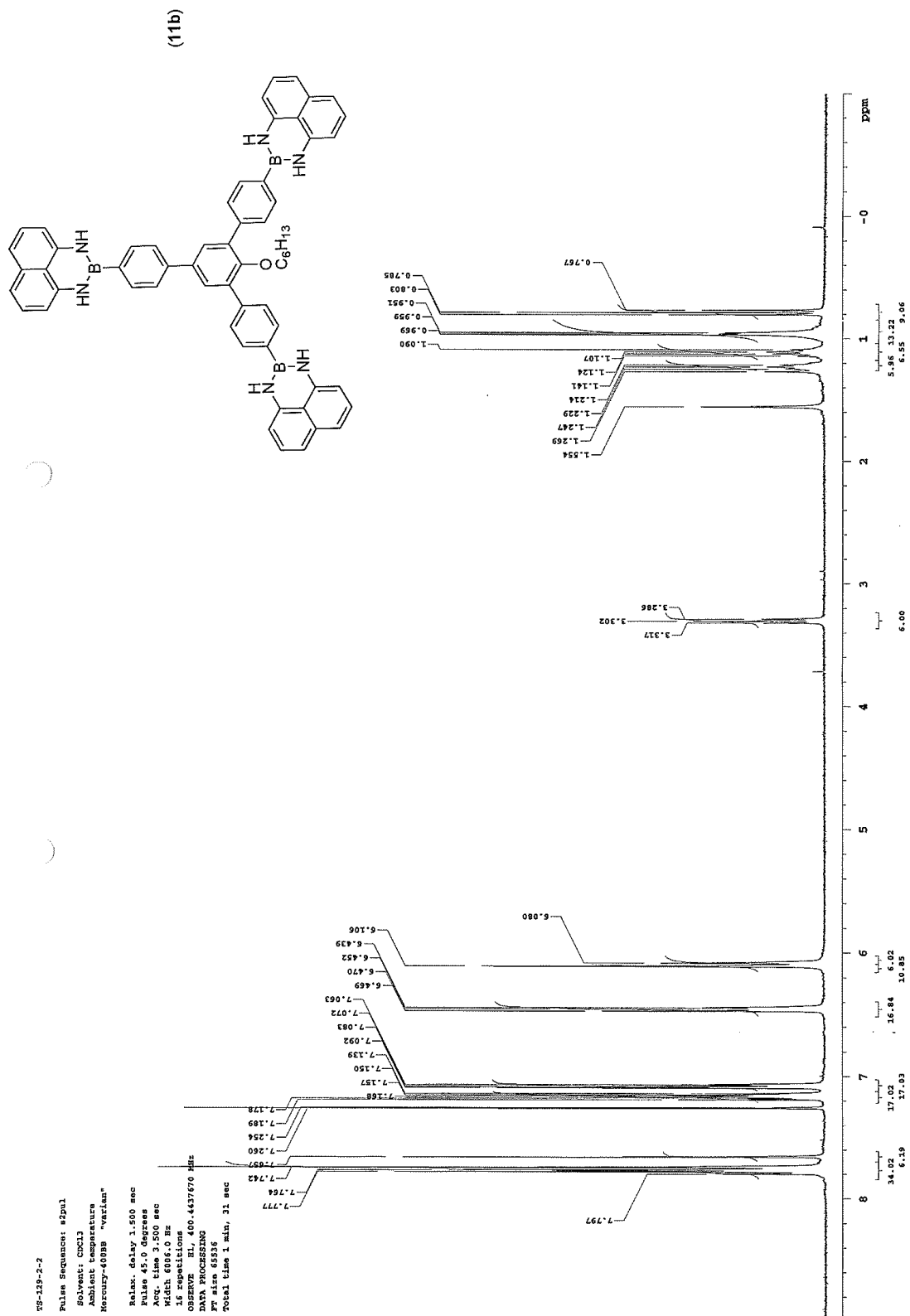
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TS-186-DMSO
Tue Apr 24 21:07:11 2007
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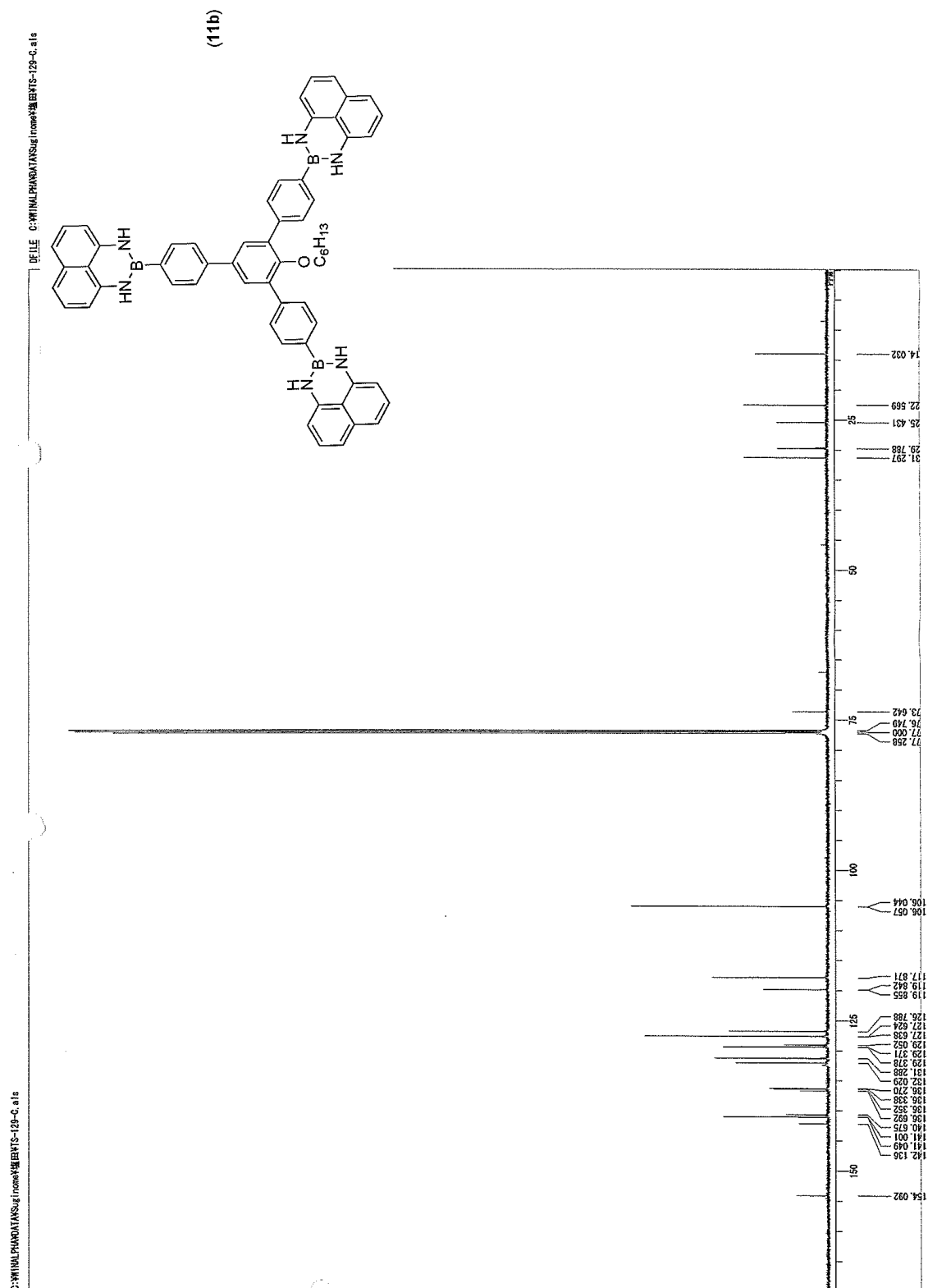
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EXMOD	13C
EXMID	SINGL
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OFBFI	128449.48 Hz
POINT	32768
FREQU	28011.20 Hz
SCANS	1636
ACQIM	1.1698 sec
PD	2.0000 sec
PRTI	4.50 usec
IRUAC	23.2 C
SLVMT	DMSO
TEMP	39.50 ppm
EAREF	0.43 Hz
BF	33
RGAIN	33

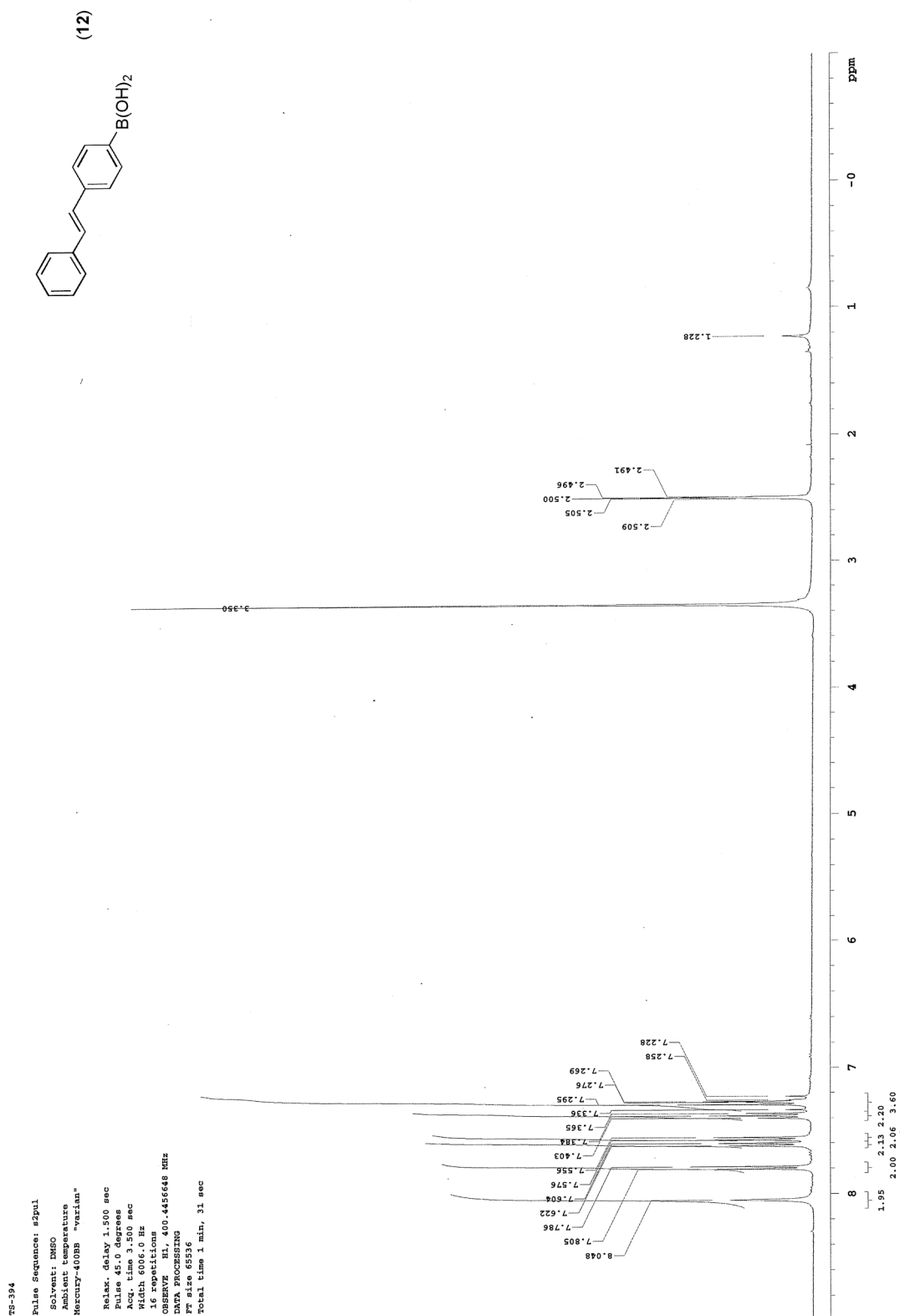
 ^{13}C NMR of Compound **11a**



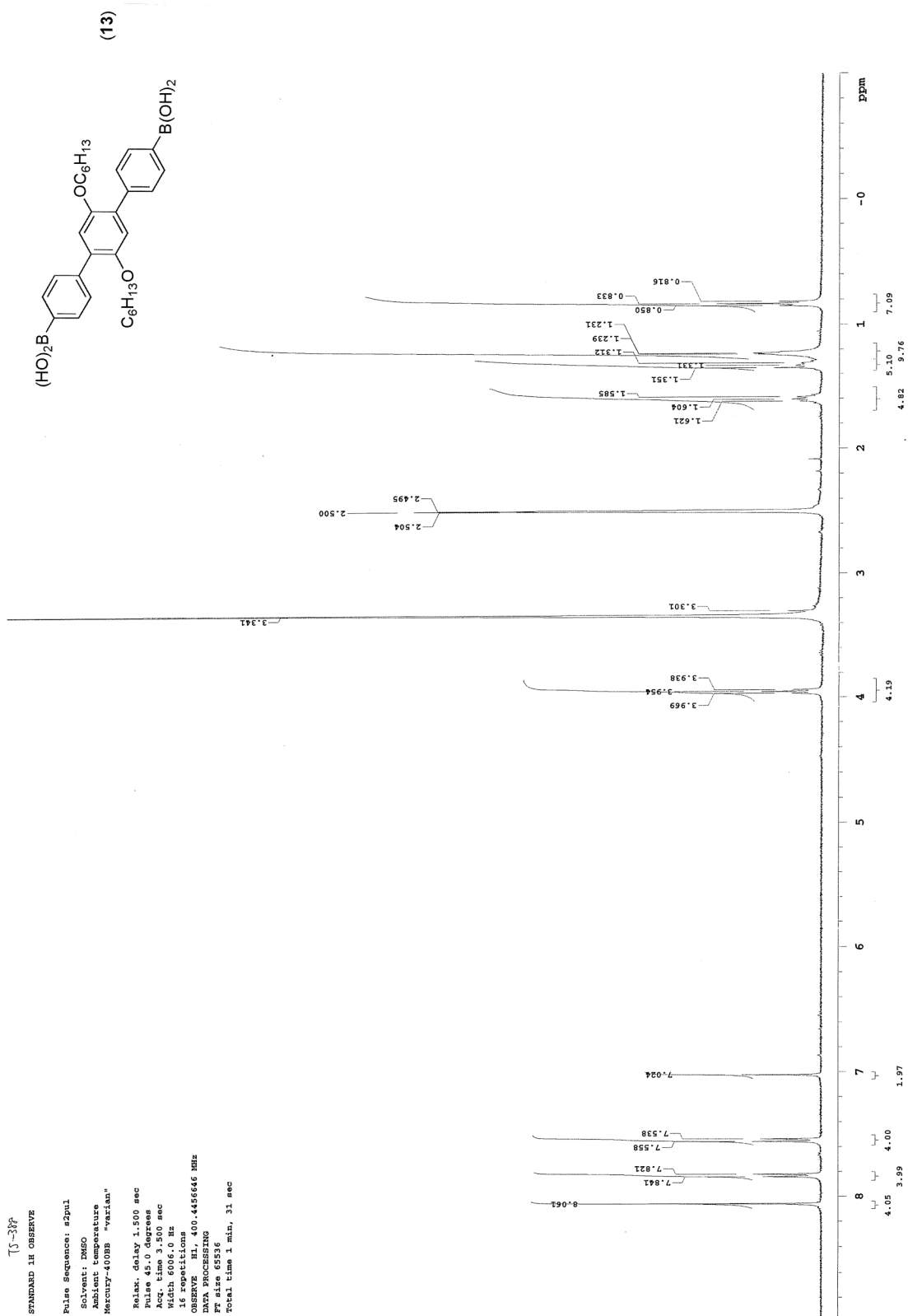
¹H NMR of Compound 11b



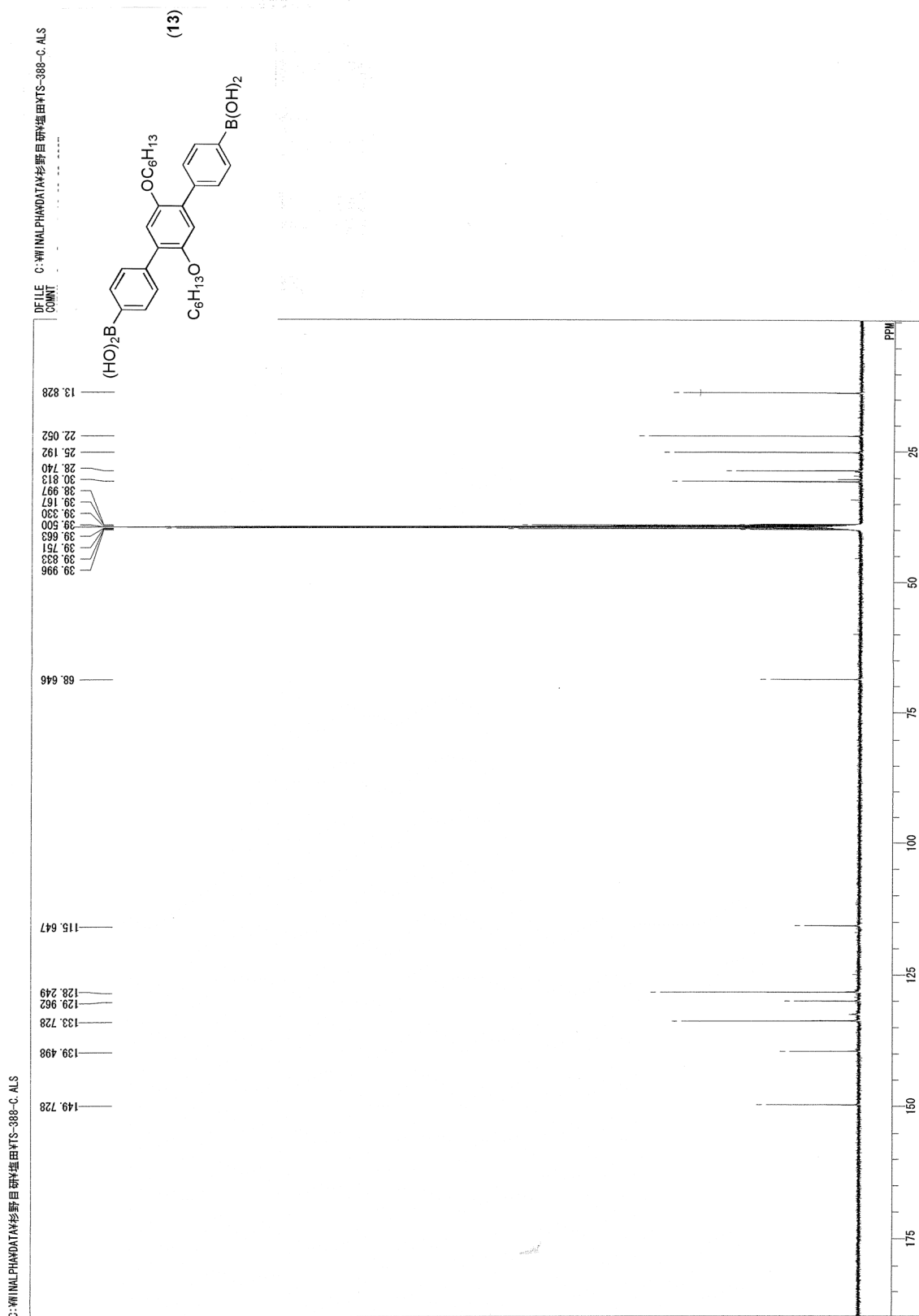
¹³C NMR of Compound 11b



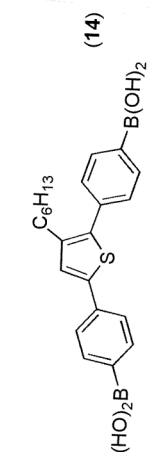
¹H NMR of Compound 12



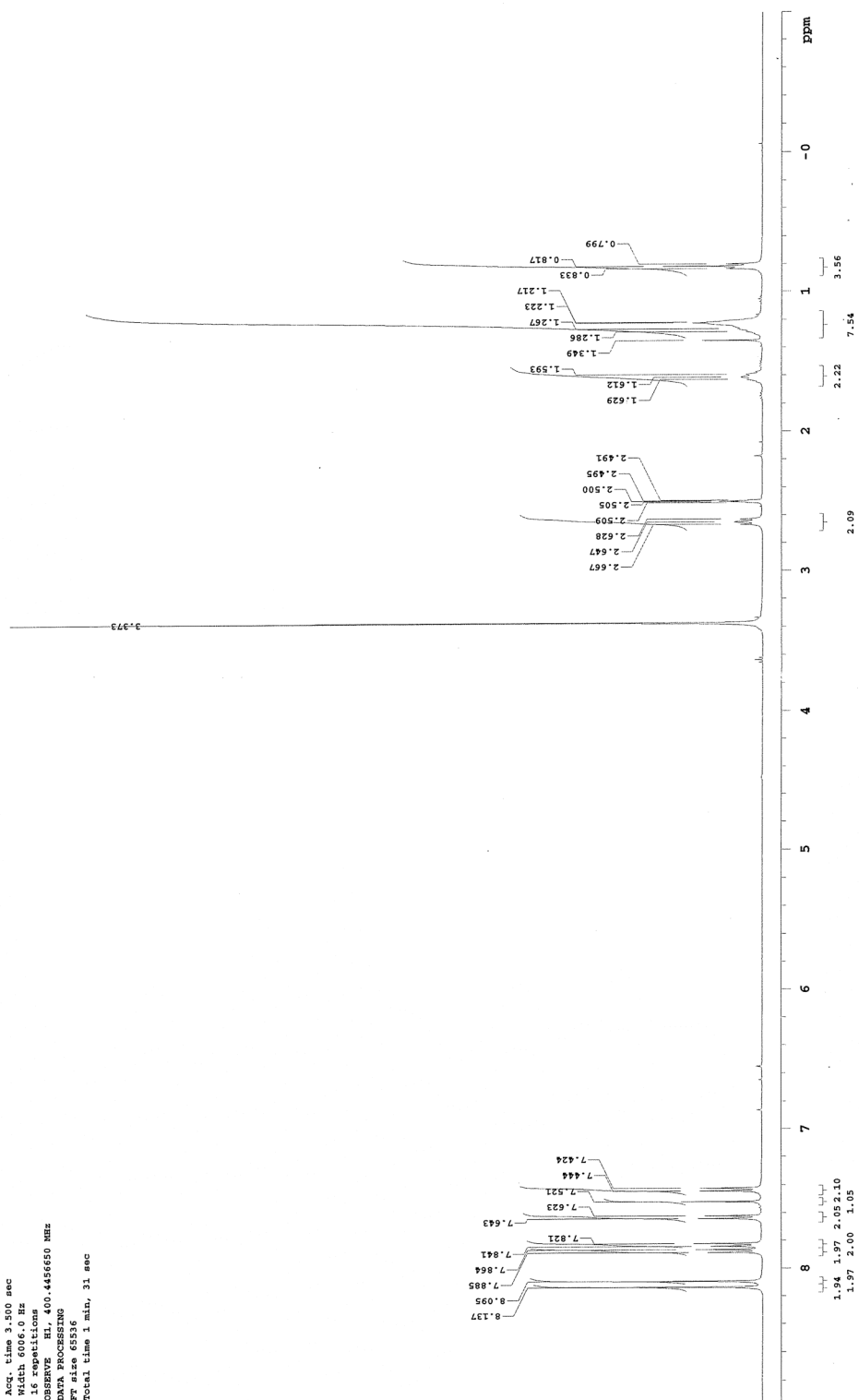
¹H NMR of Compound 13



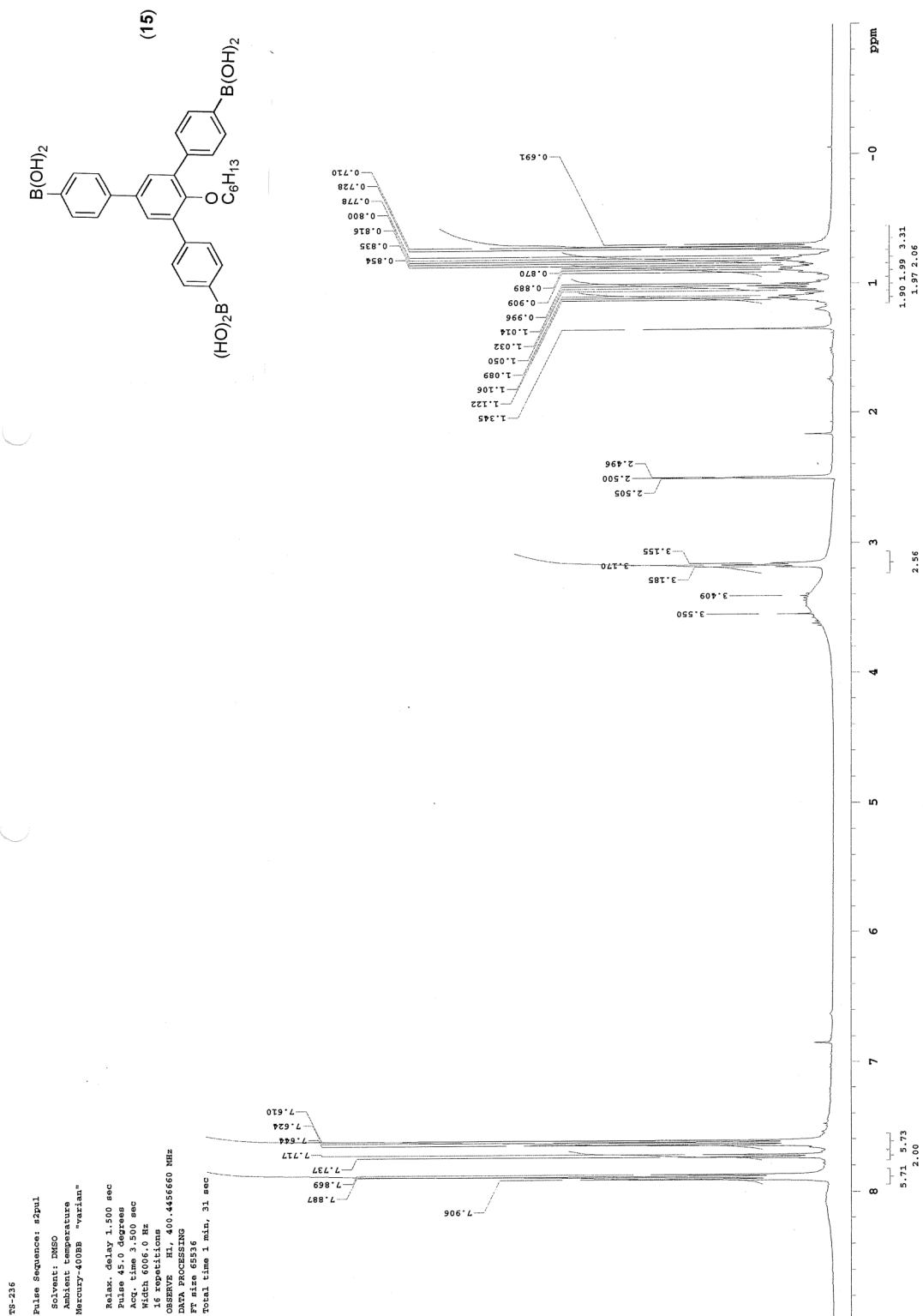
¹³C NMR of Compound 13



TS-392
 Pulse Sequence: zgpg30
 Solvent: DMSO
 Ambient temperature
 Mercury-400SB "varian"
 Relax. Delay 1.500 sec
 Pulse 45.0 degrees
 Width 10.000 sec
 Width 10.000 sec
 Width 10.000 sec
 16 repetitions
 OBSERVE H1, 400.445650 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min, 31 sec

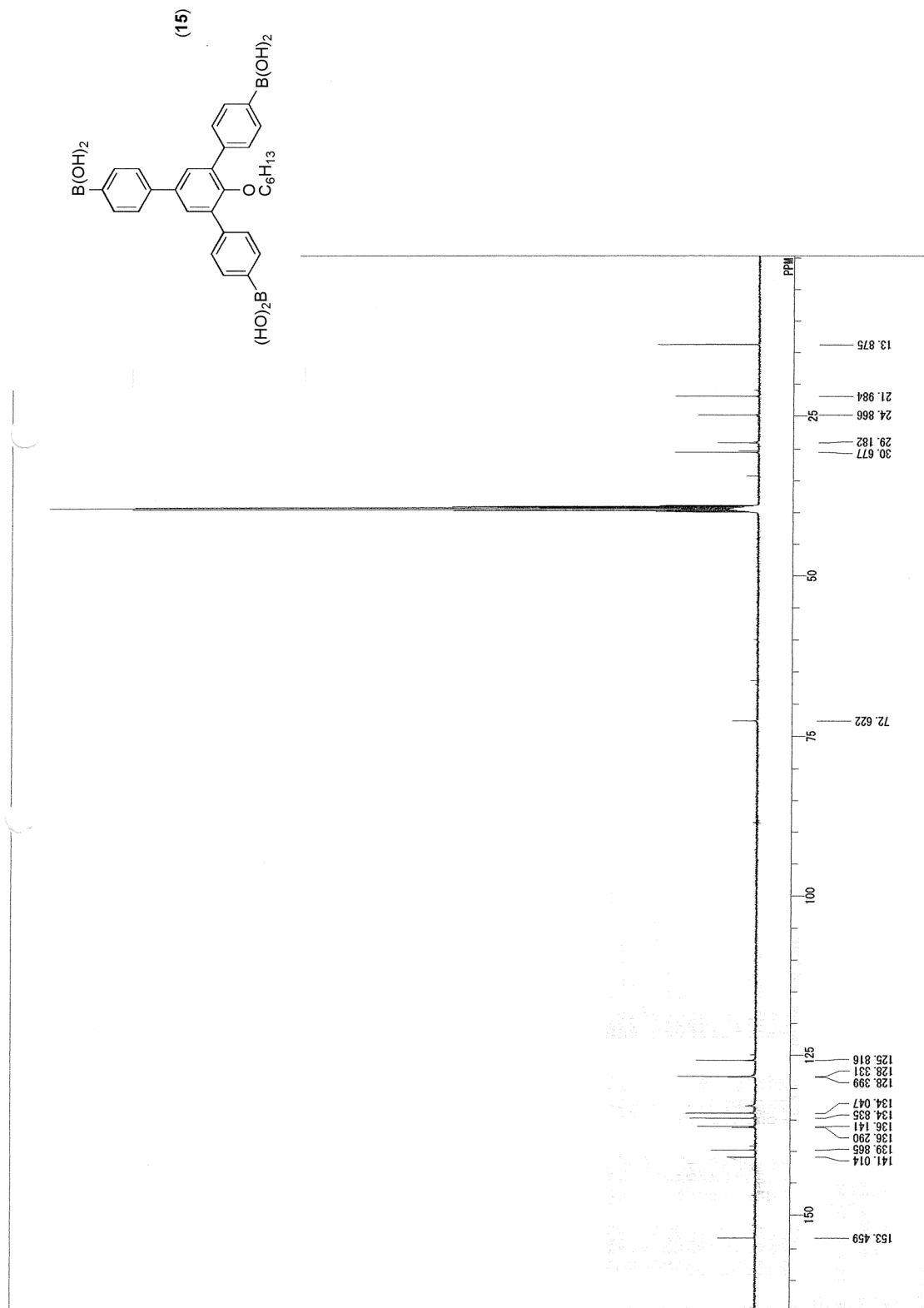


¹H NMR of Compound 14



^1H NMR of Compound 15

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¹³C NMR of Compound 15