Electronic Supplementary Information

Palladium-Catalyzed Carboboration of Alkynes Using Chloroborane and Organozirconium Reagents

Masaki Daini and Michinori Suginome*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Contents

1. General

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury vx400, Gemini-2000, or JEOL JNM-A500 spectrometer at ambient temperature. ^{1}H NMR data are reported as follows: chemical

shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, dt = double triplet, m = multiplet), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C NMR spectra were obtained with complete proton decoupling. Signals for the boron-bound carbon atoms were not detectable due to the quadrupolar coupling. High-resolution mass spectra were recorded on a JEOL JMS-SX102A (EI) spectrometer. Column chromatography was performed with Ultra Pure Silca Gel 230-400 mesh (SILICYCLE). Toluene was dried and deoxygenized using an alumina/catalyst column system (GlassContour Co.). Pinacol (TCI), trimethylphosphine (Strem), tricyclohexylphosphine (Aldrich), triphenylphosphine (Wako), tri(*t*-butyl)phosphine (Kanto), Cp_2ZrHCl (TCI) and Cp_2ZrCl_2 (TCI) were used as received from the commercial sources. TsOH was used after dehydration of *p*-toluene sulfonic acid monohydride (TCI). PdCp(allyl)[1] and chloroboranes[2] (**1a-1f**) were prepared according to the literature methods.

2. Experimental Procedures

2.1. Procedures for the Preparation of Organozirconium reagents

2.1.1. General Procedure for the Preparation of Alkenylzirconium Reagents

A mixture of Cp_2ZrHCl (77.4 mg, 0.30 mmol) and alkyne (0.30 mmol) in dichloromethane (300 μL) was stirred at room temperature for 3 h. Evaporation of the solvent in vacuo left an alkenylzirconium reagent as a solid, which was used in the following carboboration reaction without further purification.

2.1.2. Representative Procedure for Preparation of Arylzirconium Reagents

Preparation of 4-methoxyphenylzirconium reagents: A solution of 4-bromo anisole (56.2 mg, 0.30 mmol) in THF (0.20 mL) was cooled to –78 °C. To the solution was added *n*-BuLi (0.19 mL, 1.6 M hexane solution) dropwise at –78 °C. The reaction mixture was stirred for 1 h at -78 °C and further 30 min at room temperature to generate 4-methoxyphenyllithium. In a second flask, a suspension of Cp_2ZrCl_2 (116.9 mg, 0.40 mmol) in THF(0.20 mL) was cooled

(1) Shriver, D. F. *Inorg. Synth.* **1979**, *19*, 220.

(2) Ramaiah, K., Seunghoon, S., Isabelle, G., and T. V. RajanBabu *J. O. C.*, **2004**, *69*, 7157.

to –78 °C. To the suspension, the aryllithium solution was added dropwise at –78 °C. The reaction mixture was stirred for 2 h at –78 °C and further 30 min at room temperature. Evaporation of the solvent in vacuo left 4-$MeOC_6H_4ZrClCp_2$ as a solid, which was used in the carboboration reaction without further purification.

2.2. Procedures for the Carboboration Reactions

2.2.1. General procedure for Alkenylboration Using Alkenylzirconium Reagents (Table 2)

PdCp(π-allyl) (0.010 mmol) and PMe_3 (0.020 mmol) were dissolved in toluene (0.05 mL). To the catalyst solution were added chloroborane **1a** (0.20 mmol), 4-octyne **2a** (2.0 mmol), and hexen-1-yldicyclopentadienylzirconium chloride **3a** (0.30 mmol), which was dissolved in toluene (0.05 mL). The mixture was heated at 120 °C for 12 h under a nitrogen atmosphere. After removal of the solvent in vacuo, pinacol (2.0 mmol), THF (0.30 mL), and TsOH (0.60 mmol) were added, and the mixture was stirred for 3 h at room temperature. The mixture was passed through a pad of Florisil®, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexane : AcOEt = 20 : 1), affording *cis*-alkenylboration product **5aaa** in 89% yield.

2.2.2. General procedure for the determination of ^{1}H NMR yields of 4 (Table 1)

PdCp(π-allyl) (2.1 mg, 0.010 mmol) and PMe_3 (2.1 μl, 0.020 mmol) were dissolved in toluene (0.05 mL). To the catalyst solution were added chloroborane **1a** (26.5 mg, 0.20 mmol), 4-octyne **2a** (220.4 mg, 2.0 mmol), hexen-1-yldicyclopentadienylzirconium chloride **3a** (0.30 mmol), and dibenzylether (internal standard, 5.0 μL, 0.025 mmol) which was dissolved in toluene (0.05 mL). The mixture was heated at 120 °C for 12 h under a nitrogen atmosphere. The reaction mixture was then cooled to room temperature and subjected to ^{1}H NMR. Reaction yields of **4aaa** were determined on the basis of the ^{1}H NMR measurement.

2.2.3. General procedure for Arylboration Using Arylzirconium Reagents (Table 3)

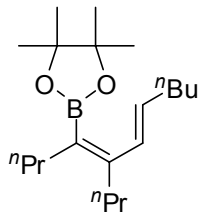
PdCp(π-allyl) (0.010 mmol) and PMe_3 (0.020 mmol) were dissolved in toluene (0.05 mL). To the catalyst solution were added chloroborane **1a** (0.20 mmol), 4-octyne **2a** (2.0 mmol), and phenyldicyclopentadienylzirconium chloride **6a** (0.30 mmol), which was dissolved in toluene (0.05 mL). The mixture was heated at 120 °C for 12 h under a nitrogen atmosphere.

After removal of the solvent in vacuo, pinacol (2.0 mmol), THF (0.30 mL), and TsOH (0.60 mmol) were added, and the mixture was stirred for 3 h at room temperature. The mixture was passed through a pad of Florisil, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexane : AcOEt = 20 : 1), affording *cis*-arylboration product **7aaa** in 92% yield.

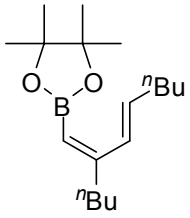
2.3 Procedure for the Suzuki-Miyaura coupling reaction of 5aa with *p*-tolyl bromide

$Pd(P^tBu_3)_2$ (1.0 mg, 0.002 mmol) were dissolved in dioxane (0.50 mL). To the catalyst solution were added compound **5aaa** (32.0 mg, 0.10 mmol), *p*-bromotoluene (17.1 mg, 0.10 mmol), and NaOH aq (60 μL, 5.0 N). The mixture was stirred at 60 °C for 5 h and cooled to room temperature. To the reaction mixture was added water, and the organic layer was extracted with CH_2Cl_2 3 times. The organic layer was washed with water and dried over magnesium sulfate. The crude product was purified by column chromatography on silica gel (hexane/AcOEt = 100/1) to give corresponding product (27.1 mg, 95%).

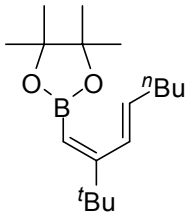
3. Spectral data for new compounds



(4*E*,6*E*)-5-Propyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,6-undecadiene (5aaa): ^{1}H NMR ($CDCl_3$) δ0.89-0.96 (m, 9H), 1.31 (s, 12H), 1.32-1.45 (m, 8H), 2.08-2.12 (m, 2H), 2.17-2.20 (m, 2H), 2.23-2.27 (m, 2H), 5.71 (dt, *J* = 15.6 and 6.6 Hz), 6.63 (dt, *J* = 15.6 and 1.4 Hz), ^{13}C NMR ($CDCl_3$) δ14.0, 14.4, 14.7, 22.3, 22.8, 23.6, 24.8, 30.5, 31.5, 32.8, 33.5, 83.0, 129.9, 132.0, 149.4, ^{11}B NMR ($CDCl_3$) δ31.3, HRMS(EI) calcd. for $C_{20}H_{37}BO_2$ (M^+): 320.2887 Found: 320.2899.

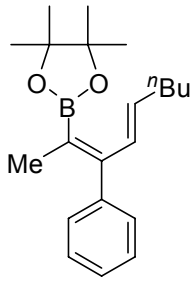


(1*Z*,3*E*)-2-Butyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-octadiene (5aba): ^{1}H NMR ($CDCl_3$) δ0.89-0.94 (m, 6H), 1.31 (s, 12H), 1.31-1.51 (m, 8H), 2.17 (dt, *J* = 6.4 and 6.6 Hz, 2H), 2.30 (t, *J* = 7.6 Hz, 2H), 5.19 (s, 1H), 5.90 (dt, *J* = 16.0 and 6.6 Hz, 1H), 6.94 (d, *J* = 16.0 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ13.9, 14.0, 22.3, 22.7, 24.9, 31.1, 31.3, 32.7, 35.2, 82.8, 130.5, 133.4, 160.1, ^{11}B NMR ($CDCl_3$) δ29.7, HRMS(EI) calcd. for $C_{18}H_{33}BO_2$ (M^+): 292.2574 Found: 292.2575.

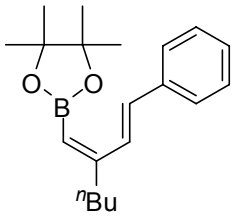


(1*Z*,3*E*)-2-*t*-Butyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-octadiene (5aca): ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.2 Hz, 3H), 1.07 (s, 9H), 1.26 (s, 12H), 1.30-1.45 (m, 4H), 2.09 (dt, *J* = 6.0 and 6.5 Hz, 2H), 5.16 (s, 1H), 5.66 (dt, *J* = 15.2 and 6.5 Hz, 1H), 6.20 (d, *J* = 15.2 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ14.0, 22.3, 24.8, 29.5, 31.3, 32.7, 37.0, 82.8, 129.2, 134.9,

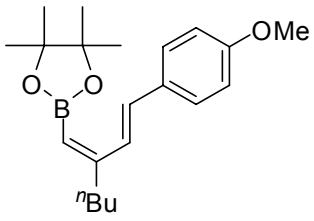
168.7, ^{11}B NMR ($CDCl_3$) δ31.4, HRMS(EI) calcd. for $C_{18}H_{33}BO_2$ (M^+): 292.2574 Found: 292.2572.



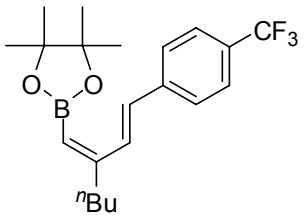
(2*Z*,4*E*)-3-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,4-nonadiene (5ada): ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.2 Hz, 3H), 1.29 (s, 12H), 1.33-1.47 (m, 4H), 1.79 (s, 3H), 2.14-2.20 (m, 2H), 5.91 (dt, *J* = 15.2 and 6.5 Hz, 1H), 6.67 (d, *J* = 15.2 Hz, 1H), 7.10-7.12 (m, 2H), 7.16-7.20 (m, 1H), 7.27-7.31 (m, 2H), ^{13}C NMR ($CDCl_3$) δ14.0, 16.1, 22.3, 24.7, 31.3, 32.8, 83.4, 125.6, 127.8, 129.0, 132.7, 132.8, 143.4, 146.2, ^{11}B NMR ($CDCl_3$) δ30.7, HRMS(EI) calcd. for $C_{21}H_{31}BO_2$ (M^+): 326.2417 Found: 326.2419.



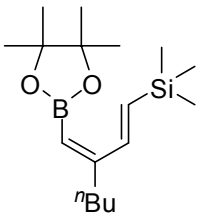
(1*Z*,3*E*)-2-Butyl-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-butadiene (5abb): ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J = 7.4 Hz, 3H), 1.31 (s, 12H), 1.33-1.47 (m, 4H), 2.39 (t, *J* = 7.4 Hz, 2H), 5.50 (s, 1H), 6.75 (d, *J* = 16.4 Hz, 1H), 7.48-7.55 (m, 5H), 7.68 (d, *J* = 16.4 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ14.4, 23.6, 24.8, 30.2, 31.9, 82.2, 126.1, 128.3, 131.2, 133.4, 137.5, 141.0, 151.2, ^{11}B NMR ($CDCl_3$) δ31.4, Anal. calcd. for $C_{20}H_{29}BO_2$: C, 76.93; H, 9.36. Found: C, 77.02; H, 9.54.



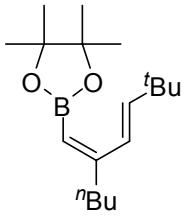
(1*Z*,3*E*)-2-Butyl-4-(4-methoxyphenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-butadiene (5abc): ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 7.5 Hz, 3H), 1.31 (s, 12H), 1.35-1.41 (m, 2H), 1.45-1.51 (m, 2H), 2.41 (t, *J* = 7.4 Hz, 2H), 3.71 (s, 3H), 5.52 (s, 1H), 6.70 (d, *J* = 16.5 Hz, 1H), 7.50-7.62 (m, 4H), 7.83 (d, *J* = 16.5 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ14.1, 21.8, 24.6, 30.3, 31.1, 34.8, 56.2, 82.8, 124.0, 124.1, 124.3, 141.0, 151.2, 160.2, ^{11}B NMR ($CDCl_3$) δ31.1, Anal. calcd. for $C_{21}H_{31}BO_3$: C, 73.69; H, 9.13. Found: C, 73.42; H, 9.41.



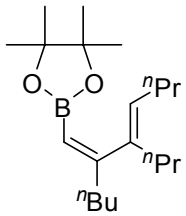
(1*Z*,3*E*)-2-Butyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4-trifluoromethylphenyl)-1,3-butadiene (5abd): ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.2 Hz, 3H), 1.33 (s, 12H), 1.36-1.41 (m, 2H), 1.47-1.54 (m, 2H), 2.43 (t, *J* = 7.6 Hz, 2H), 5.48 (s, 1H), 6.71 (d, *J* = 16.2 Hz, 1H), 7.53-7.60 (m, 4H), 7.89 (d, *J* = 16.2 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ14.0, 22.7, 25.0, 31.0, 34.7, 83.1, 125.2 (q, *J* = 270 Hz), 125.5 (q, *J* = 4.2 Hz), 126.8, 128.3 (q, *J* = 32.7 Hz), 128.51, 128.52, 132.3, 158.9, ^{11}B NMR ($CDCl_3$) δ31.2, HRMS(EI) calcd. for $C_{21}H_{28}BF_3O_2$ (M^+): 380.2134 Found: 380.2132.



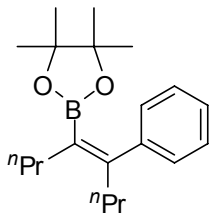
(1*Z*,3*E*)-2-Butyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-trimethylsilyl-1,3-butadiene (5abe): ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9H), 0.90 (t, J = 7.2 Hz, 3H), 1.29 (s, 12H), 1.31-1.48 (m, 4H), 2.27-2.35 (m, 2H), 5.38 (s, 1H), 6.05 (d, *J* = 19.2 Hz, 1H), 7.50 (d, *J* = 19.2 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ-1.30, 14.0, 22.7, 24.9, 30.9, 33.9, 82.9, 131.2, 144.5, 160.5, ^{11}B NMR ($CDCl_3$) δ28.5, HRMS(EI) calcd. for $C_{17}H_{33}BO_2Si$ (M^+): 308.2343 Found: 308.2343.



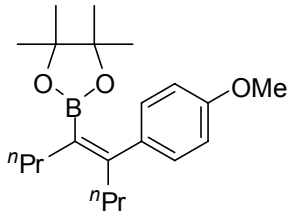
(1*Z*,3*E*)-2-Butyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-*t*-butyl-1,3-butadiene (5abf): ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 7.4 Hz, 3H), 1.07 (s, 9H), 1.28 (s, 12H), 1.31-1.49 (m, 4H), 2.30 (t, *J* = 7.8 Hz, 2H), 5.22 (s, 1H), 5.88 (d, *J* = 6.5 and 16.4 Hz, 1H), 6.96 (d, *J* = 16.4 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ14.1, 23.6, 24.8, 29.5, 32.4, 33.9, 42.6, 82.8, 127.8, 132.7, 150.3, ^{11}B NMR ($CDCl_3$) δ29.8, Anal. calcd. for $C_{18}H_{33}BO_2$: C, 73.97; H, 11.38. Found: C, 74.07; H, 11.54.



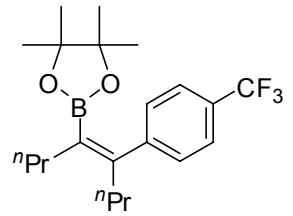
(1*Z*,3*E*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-butyl-3-propyl-1,3-heptadiene (5abg): ^{1}H NMR ($CDCl_3$) δ 0.85-0.91 (m, 3H), 1.16 (s, 12H), 1.26-1.44 (m, 6H), 2.10-2.17 (m, 6H), 2.30 (t, *J* = 7.8 Hz, 2H), 5.35 (s, 1H), 6.07-6.11 (m, 1H), ^{13}C NMR ($CDCl_3$) δ13.9, 14.0, 14.5, 21.3, 23.3, 23.5, 24.8, 29.7, 30.8, 32.7, 40.7, 82.8, 131.6, 146.5, 158.2, ^{11}B NMR ($CDCl_3$) δ30.5, Anal. calcd. for $C_{20}H_{37}BO_2$: C, 74.99; H, 11.64. Found: C, 74.88; H, 11.40.



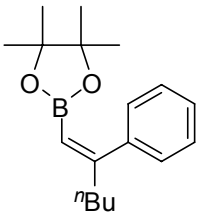
(*E*)-4-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-octene (7aaa): ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 7.5 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H), 1.02 (s, 12H), 1.23-1.28 (m, 2H), 1.42-1.47 (m, 2H), 2.24-2.27 (m, 2H), 2.40-2.43 (m, 2H), 7.18-7.24 (m, 5H), ^{13}C NMR ($CDCl_3$) δ14.0, 14.4, 21.2, 23.3, 24.5, 32.5, 35.3, 82.9, 126.4, 127.6, 128.5, 145.2, 150.9, ^{11}B NMR ($CDCl_3$) δ31.0, HRMS(EI) calcd. for $C_{20}H_{31}BO_2$ (M^+): 314.2417 Found: 314.2415.



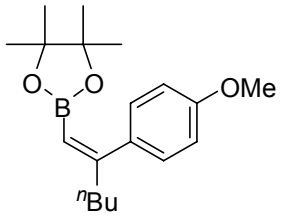
(*E*)-4-(4-Methoxy)phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-octene (7aab): ^{1}H NMR ($CDCl_3$) δ0.83 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.4 Hz, 3H), 1.04 (s, 12H), 1.21-1.28 (m, 2H), 1.40-1.45 (m, 2H), 2.23-2.28 (m, 2H), 2.39-2.43 (m, 2H), 3.73 (s, 3H), 7.33 (d, J = 7.4 Hz, 2H), 7.54 (d, J = 7.4 Hz, 2H), ^{13}C NMR ($CDCl_3$) δ14.0, 14.4, 21.2, 23.1, 24.7, 32.3, 35.9, 56.2, 82.8, 126.1, 127.3, 128.8, 150.6, 161.2, ^{11}B NMR ($CDCl_3$) δ31.1, Anal. calcd. for $C_{21}H_{33}BO_3$: C, 73.26; H, 9.66. Found: C, 73.40; H, 9.88.



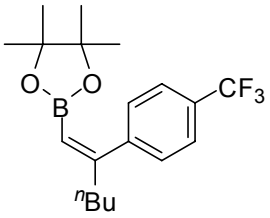
(*E*)-4-(4-Trifluoromethyl)phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-octene (7aac): ^{1}H NMR ($CDCl_3$) δ 0.84 (t, J = 7.2 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H), 1.01 (s, 12H), 1.21-1.27 (m, 2H), 1.41-1.47 (m, 2H), 2.25-2.29 (m, 2H), 2.40-2.44 (m, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 7.8 Hz, 2H), ^{13}C NMR ($CDCl_3$) δ14.0, 14.4, 21.1, 23.2, 24.5, 33.5, 35.2, 83.0, 124.4 (q, J = 272 Hz), 124.5 (q, J = 3.3 Hz), 128.6 (q, J = 32.2 Hz), 128.9, 149.0, 150.0, ^{11}B NMR ($CDCl_3$) δ31.5, HRMS(EI) calcd. for $C_{20}H_{30}BF_3O_2$ (M^+): 382.2291 Found: 382.2288.



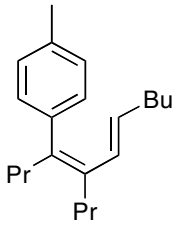
(*E*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-phenyl-1-hexene (7aba): ^{1}H NMR ($CDCl_3$) δ0.88 (t, J = 7.4 Hz, 3H), 1.10 (s, 12H), 1.26-1.33 (m, 2H), 1.36-1.42 (m, 2H), 2.23-2.27 (m, 2H), 5.36 (s, 1H), 7.16-7.22 (m, 5H), ^{13}C NMR ($CDCl_3$) δ14.0, 23.5, 24.9, 31.1, 35.8, 82.8, 126.3, 127.7, 128.3, 145.3, 151.9, ^{11}B NMR ($CDCl_3$) δ30.6, Anal. calcd. for $C_{18}H_{27}BO_2$: C, 75.53; H, 9.51. Found: C, 75.58; H, 9.24.



(*E*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-methoxy)phenyl-1-hexene (7abb): ^{1}H NMR ($CDCl_3$) δ0.90 (t, J = 7.5 Hz, 3H), 1.04 (s, 12H), 1.21-1.29 (m, 2H), 1.39-1.46 (m, 2H), 2.21-2.25 (m, 2H), 3.68 (s, 3H), 5.31 (s, 1H), 7.30 (d, J = 7.6 Hz, 2H), 7.48 (d, J = 7.6 Hz, 2H), ^{13}C NMR ($CDCl_3$) δ14.0, 23.1, 24.7, 32.3, 35.8, 56.0, 82.6, 126.2, 127.0, 129.1, 150.7, 160.2, ^{11}B NMR ($CDCl_3$) δ30.0, Anal. calcd. for $C_{19}H_{29}BO_3$: C, 72.16; H, 9.24. Found: C, 72.41; H, 9.44.



(*E*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(4-trifluoromethyl)phenyl-1-hexene (7abc): ^{1}H NMR ($CDCl_3$) δ0.86 (t, J = 7.6 Hz, 3H), 1.01 (s, 12H), 1.26-1.33 (m, 2H), 1.41-1.46 (m, 2H), 2.26-2.30 (m, 2H), 5.36 (s, 1H), 7.33 (d, J = 7.5 Hz, 2H), 7.49 (d, J = 7.5 Hz, 2H), ^{13}C NMR ($CDCl_3$) δ14.1, 23.3, 24.8, 31.3, 34.3, 82.8, 124.1 (q, J = 270 Hz), 125.3 (q, J = 3.2 Hz), 128.2 (q, J = 33.0 Hz), 128.8, 130.3, 151.7, ^{11}B NMR ($CDCl_3$) δ30.7, Anal. calcd. for $C_{19}H_{26}BF_3O_2$: C, 64.43; H, 7.40. Found: C, 64.20; H, 7.11.



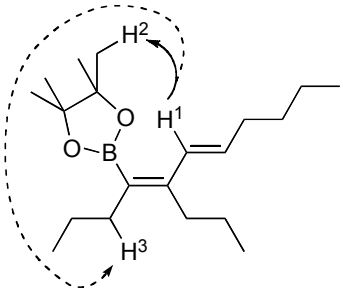
(4*Z*,6*E*)-4-Phenyl-5-propyl-4,6-undecadiene (8): ^{1}H NMR ($CDCl_3$) δ0.82-0.86 (m, 6H), 0.99 (t, J = 7.6 Hz, 3H), 1.20-1.30 (m, 6H), 1.46-1.52 (m, 2H), 1.92-1.97 (m, 2H), 2.31-2.39 (m, 4H), 2.36 (s, 3H), 5.57 (dt, J = 7.0 and 15.6 Hz, 1H), 5.90 (dt, J = 1.2 and 15.6 Hz, 1H), 6.98-7.01 (m, 2H), 7.12 (dd, J = 0.8 and 8.4 Hz, 2H), ^{13}C NMR ($CDCl_3$) δ13.9, 14.1, 14.5,

21.2, 21.7, 22.2, 22.8, 30.4, 31.9, 32.9, 36.8, 128.4, 128.5, 129.4, 129.9, 133.5, 135.4, 139.0, 140.1, HRMS(EI) calcd. for $C_{21}H_{32}$ (M^+): 284.2504 Found: 284.2501.

4. Summary of the nOe experiments

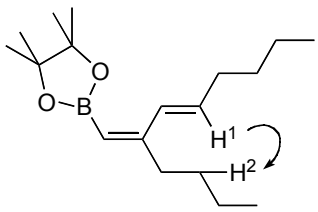
NOe experiments were carried out for the stereochemical assignment of the products. The curved arrows indicate the observed nOe, and the dotted arrows indicate the protons between which no nOe was observed. Only selected nOes are shown.

Compound 5aaa. NOe was observed for the protons H^1 and H^2, on the other hand, no nOe was observed for the protons H^1 and H^3, strongly indicating that *cis*-addition had taken place.



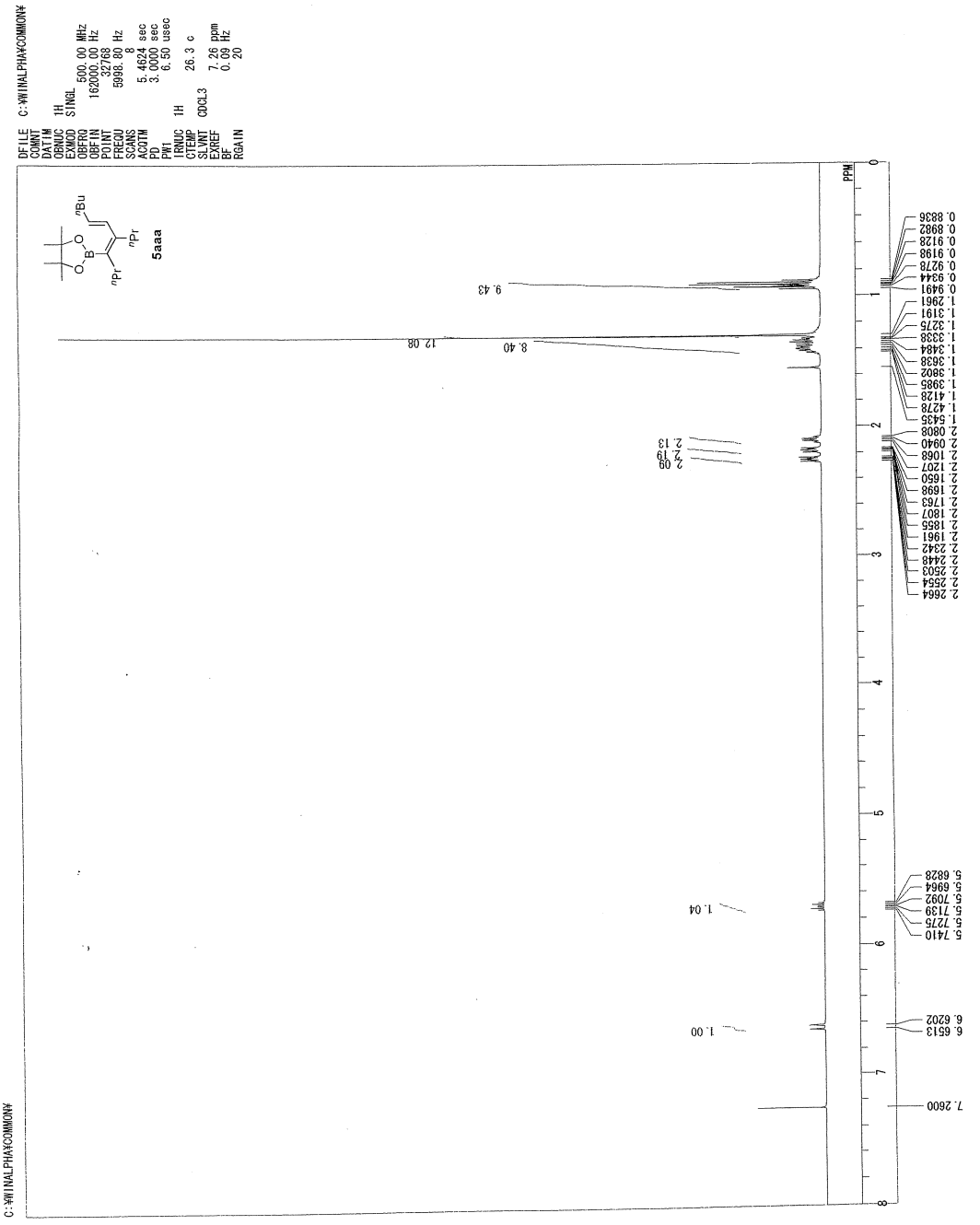
5aaa

Compound 5aba. NOe was observed for the protons H^1 and H^2, strongly indicating that the boron atom was attached to the terminal position.

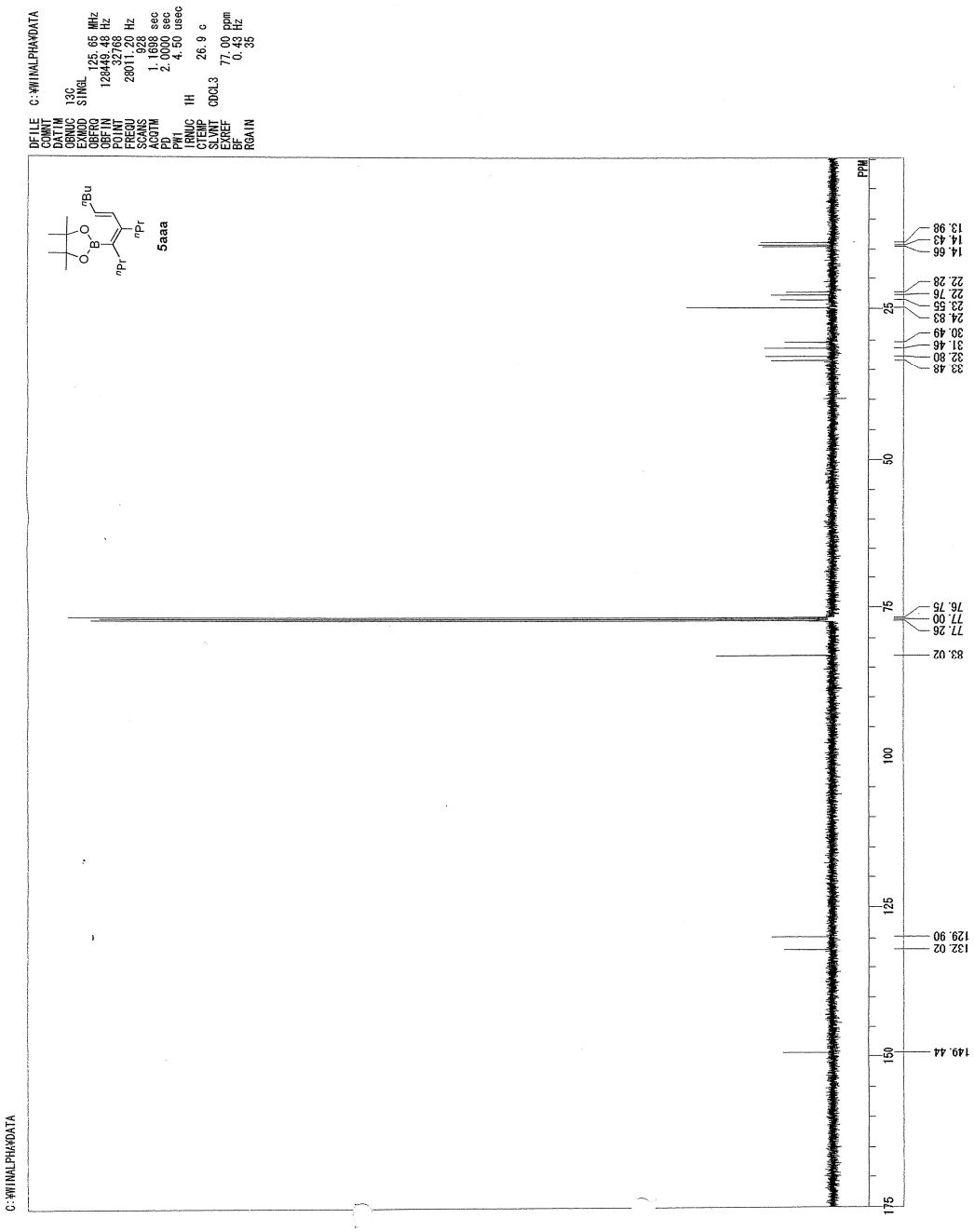


5aba

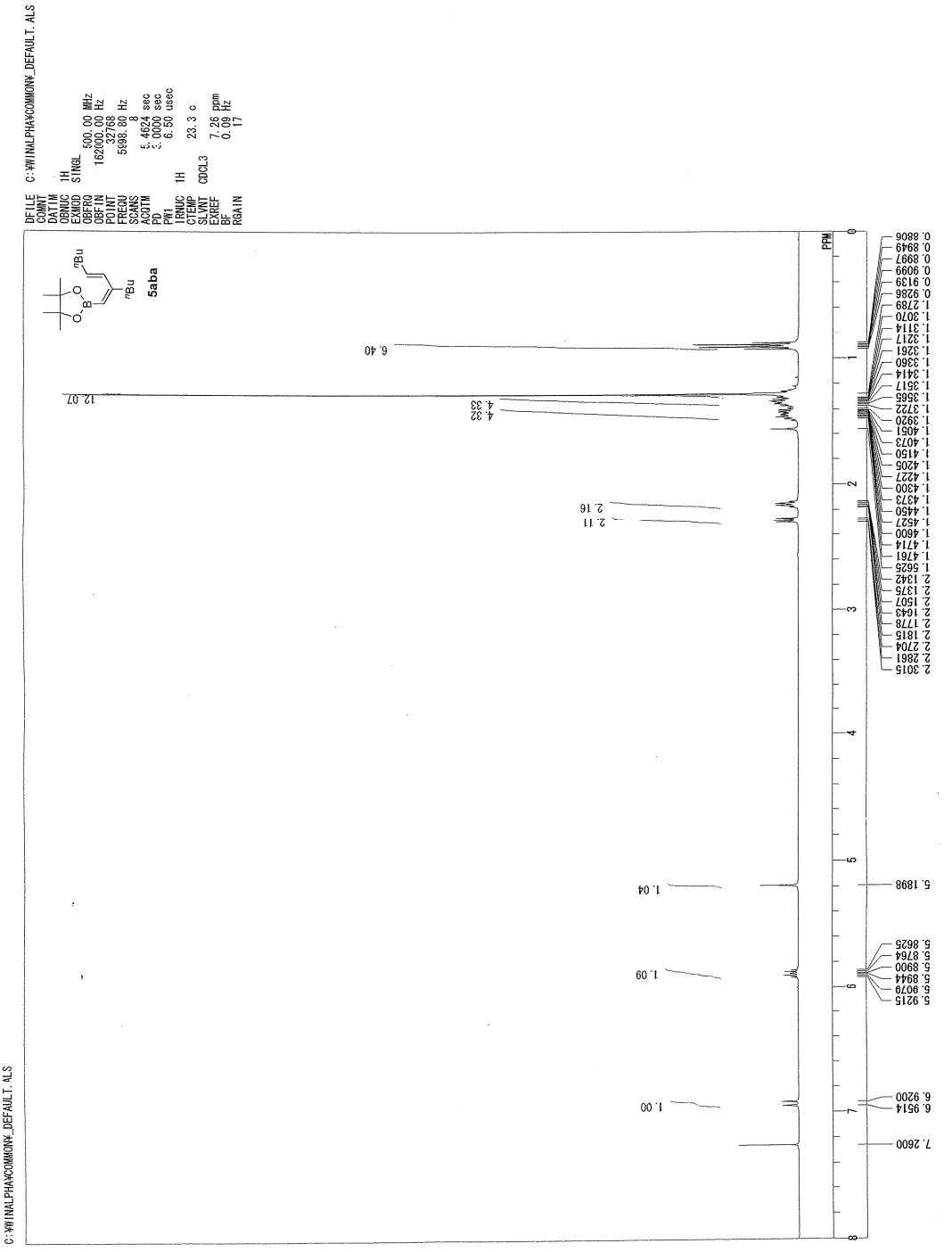
5. Copies of ^{1}H and ^{13}C NMR charts for new compounds



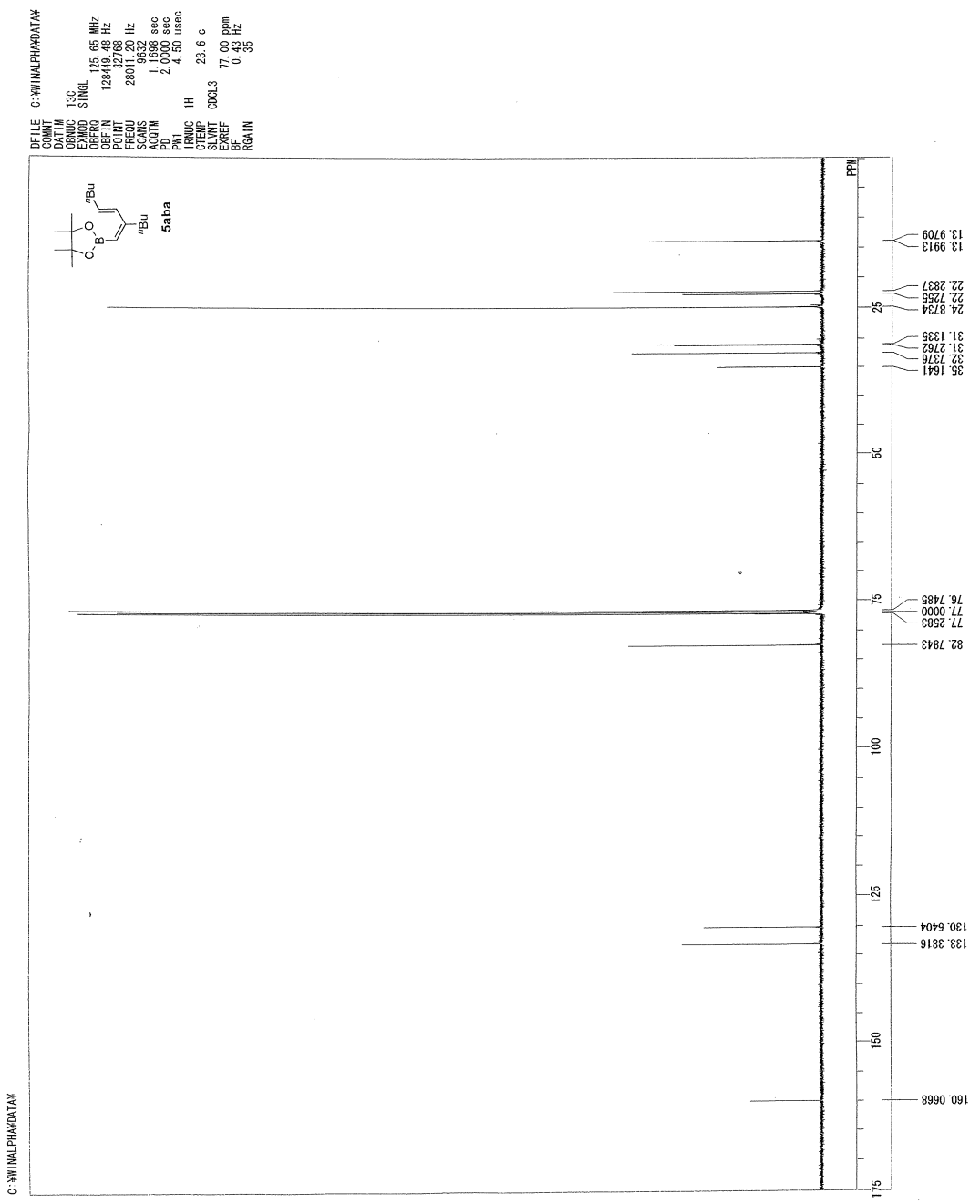
^{1}H NMR of Compound **5aaa** (entry 1 in Table 2)



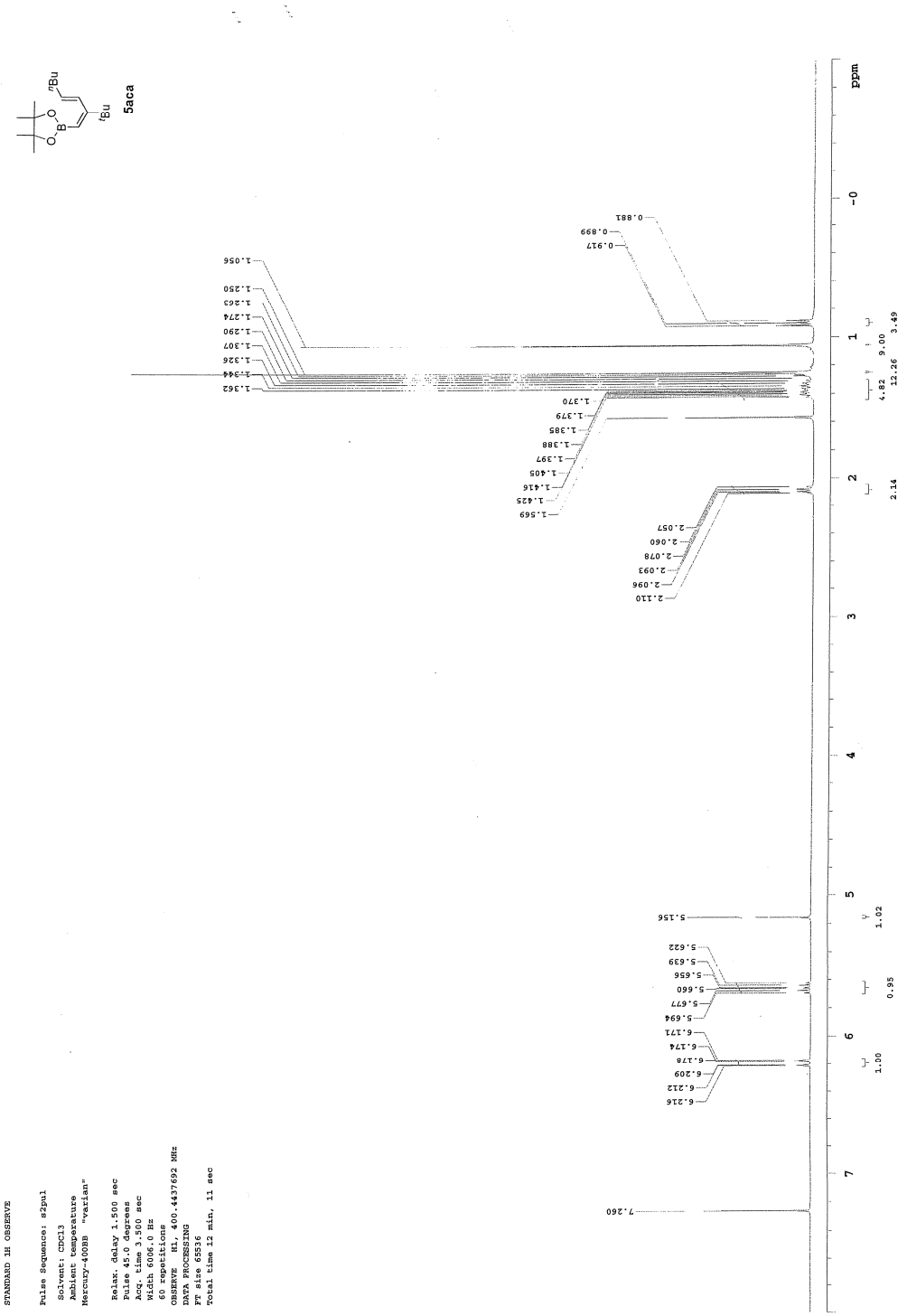
^{13}C NMR of Compound **5aaa** (entry 1 in Table 2)



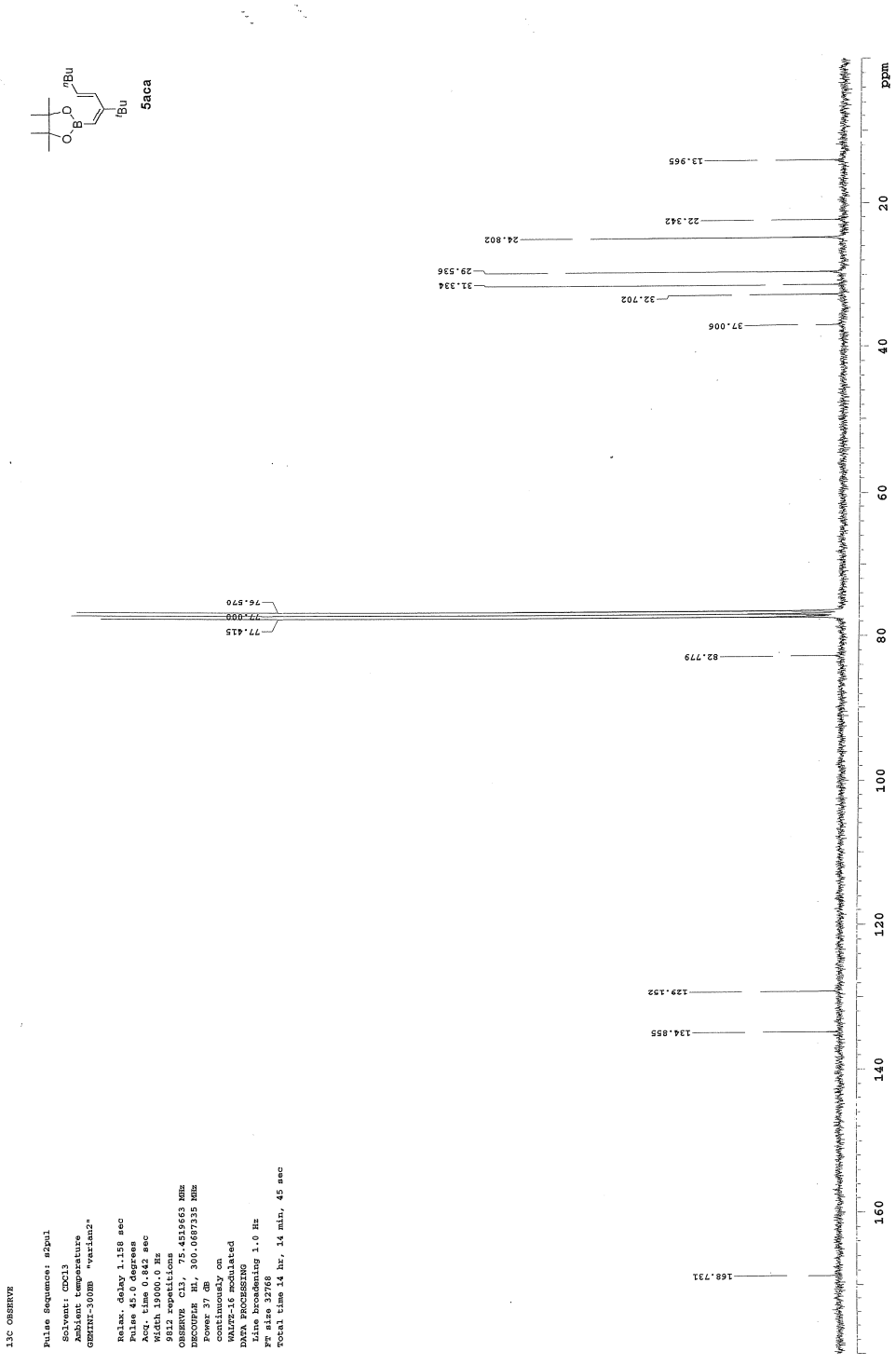
^{1}H NMR of Compound **5aba** (entry 2 in Table 2)



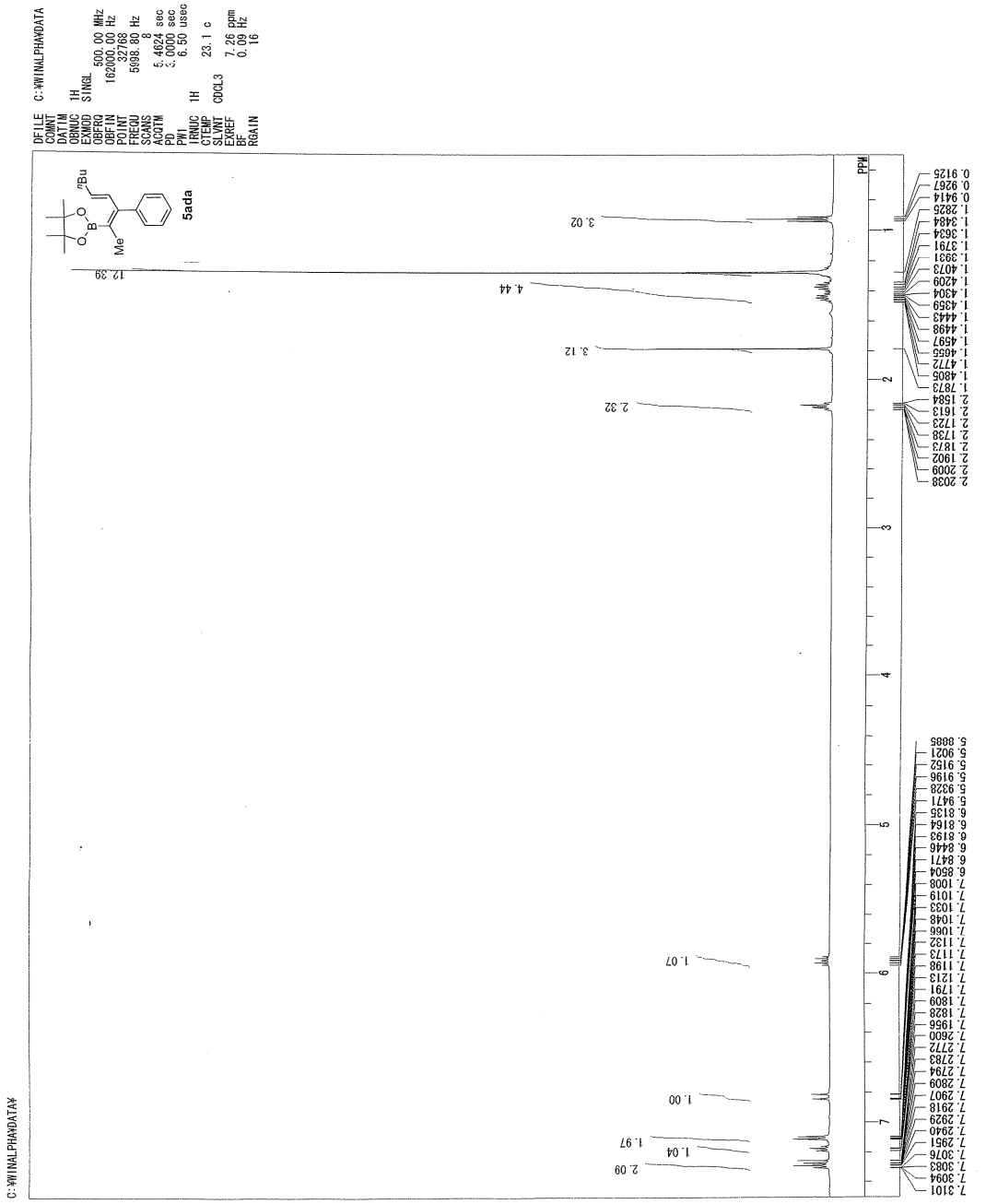
^{13}C NMR of Compound **5aba** (entry 2 in Table 2)



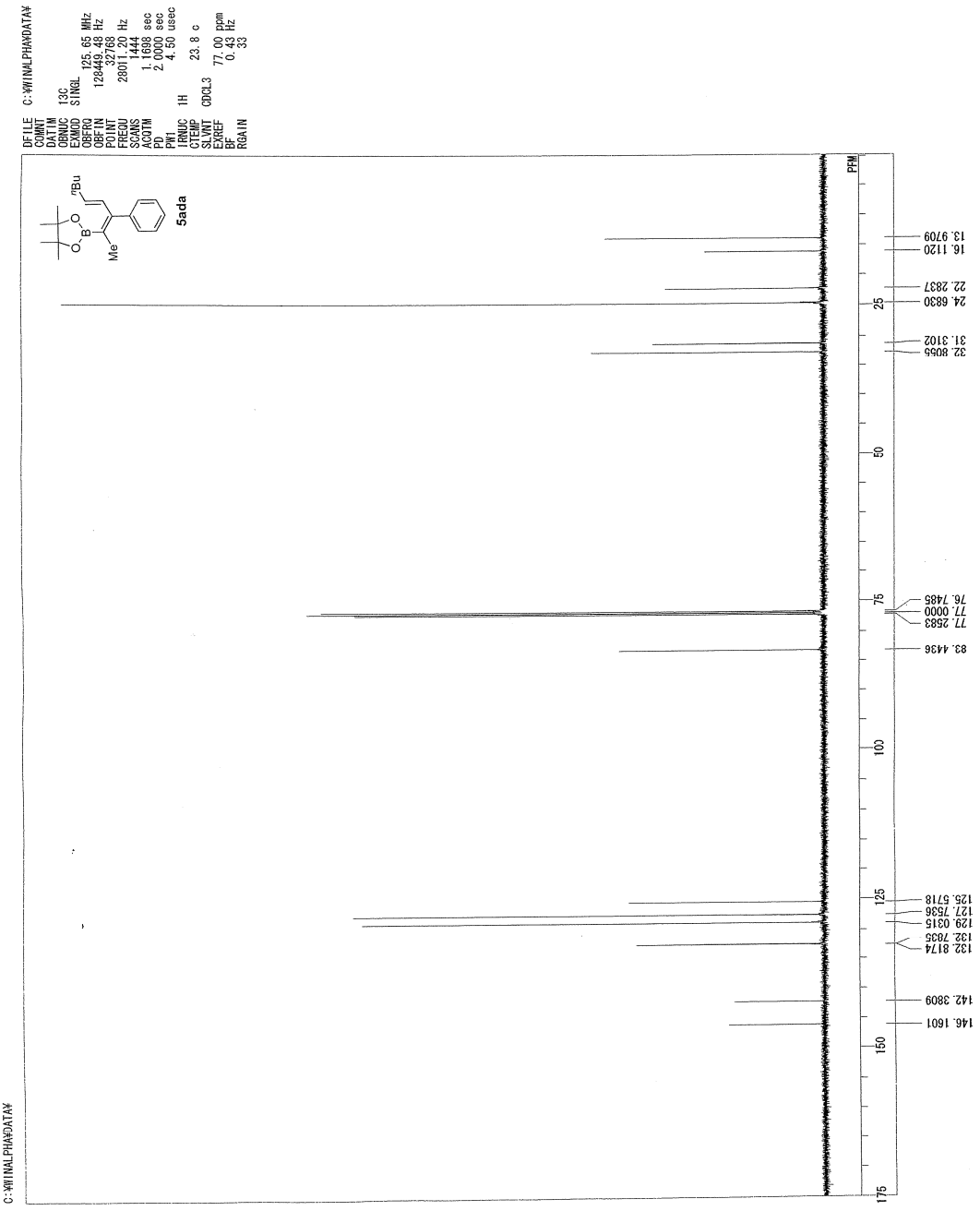
^{1}H NMR of Compound **5aca** (entry 3 in Table 2)



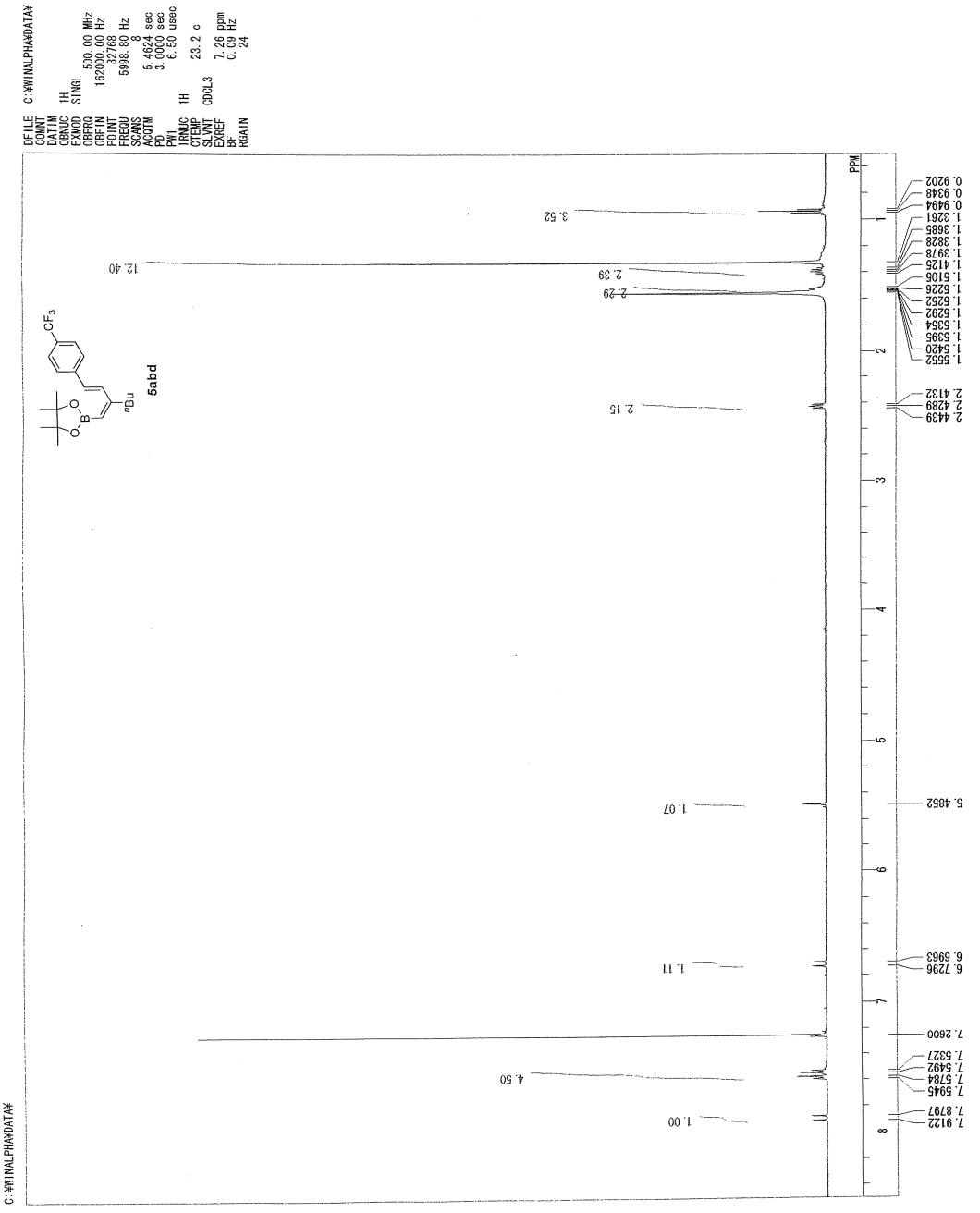
^{13}C NMR of Compound **5aca** (entry 3 in Table 2)



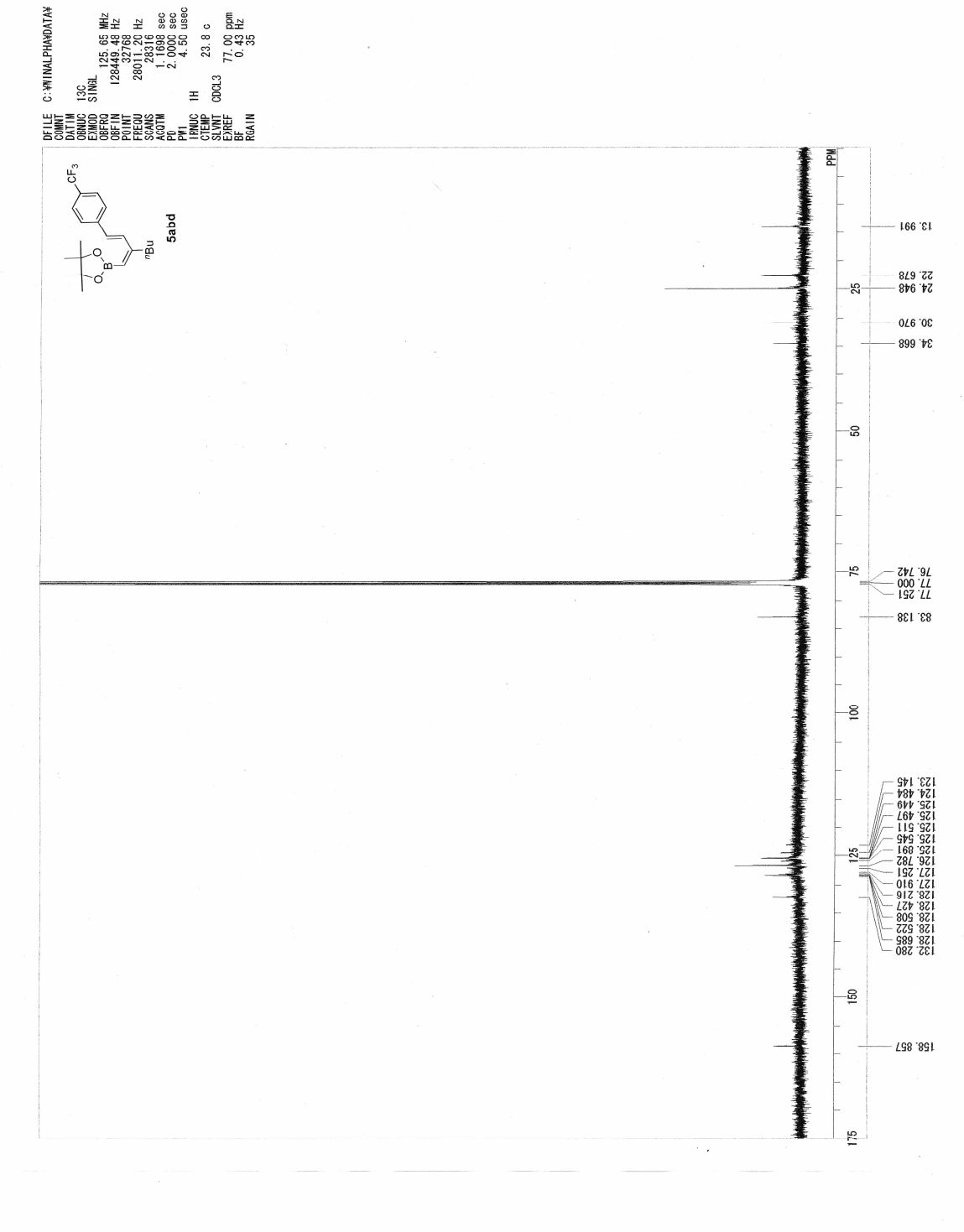
^{1}H NMR of Compound **5ada** (entry 4 in Table 2)



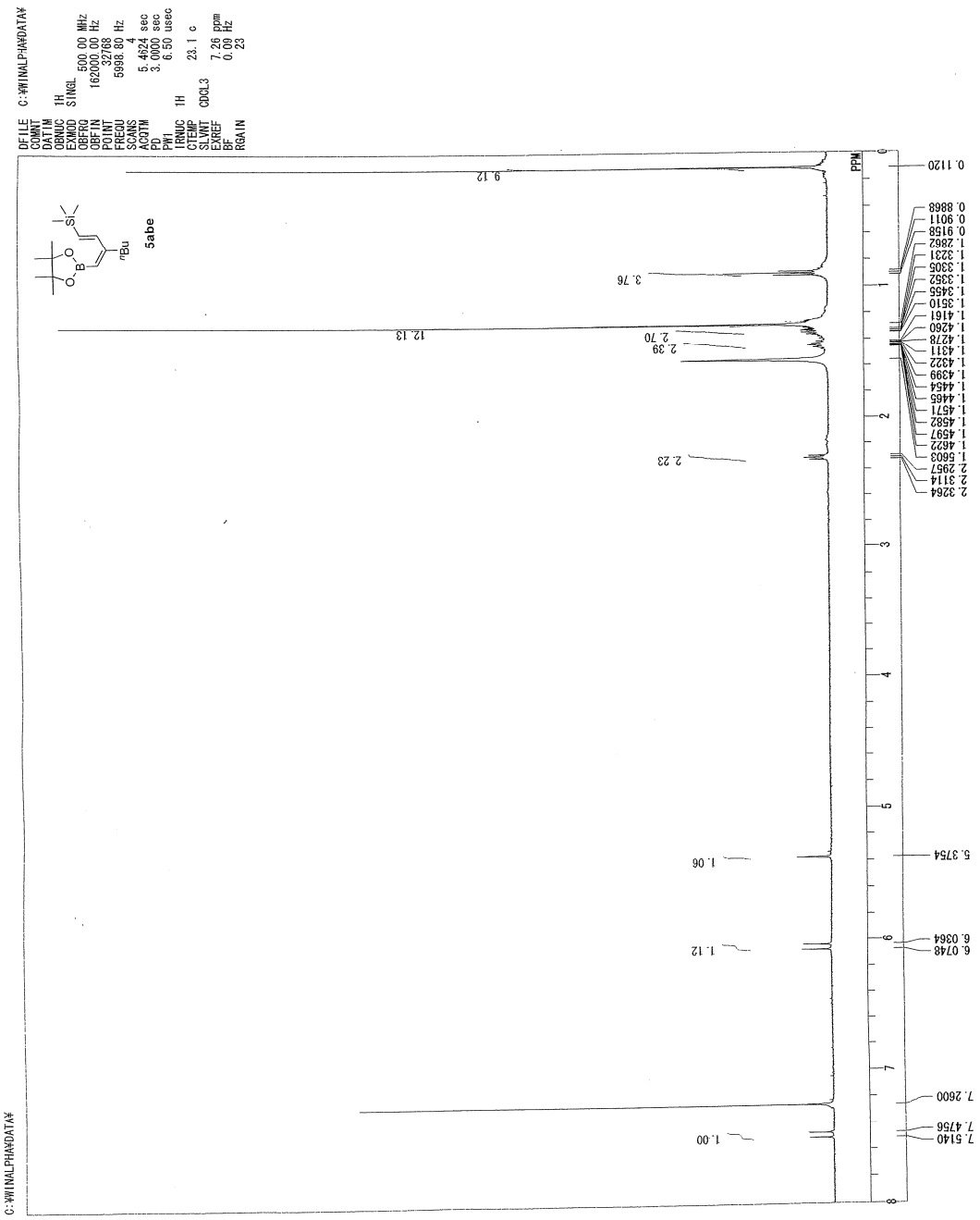
^{13}C NMR of Compound **5ada** (entry 4 in Table 2)



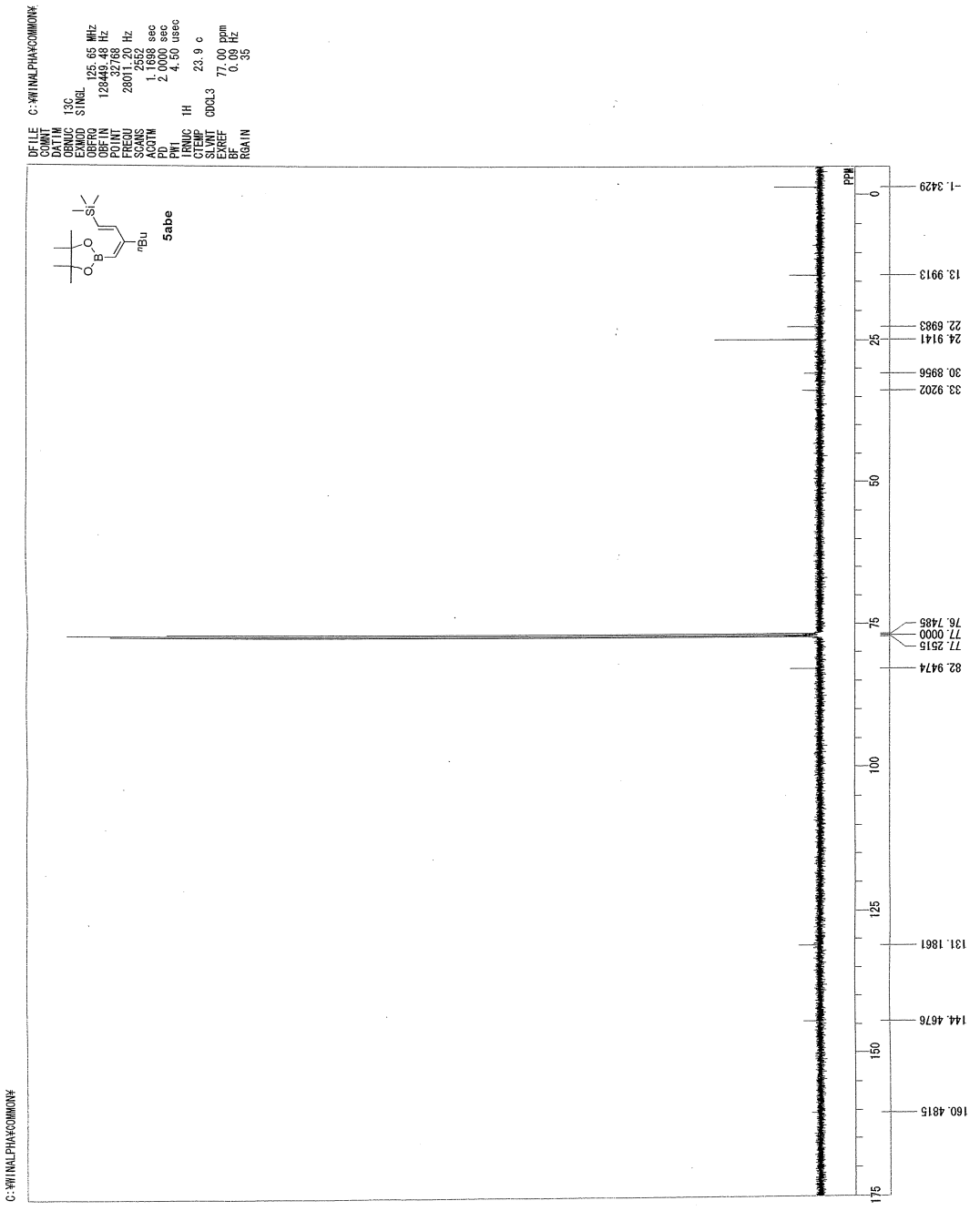
^{1}H NMR of Compound **5abd** (entry 7 in Table 2)



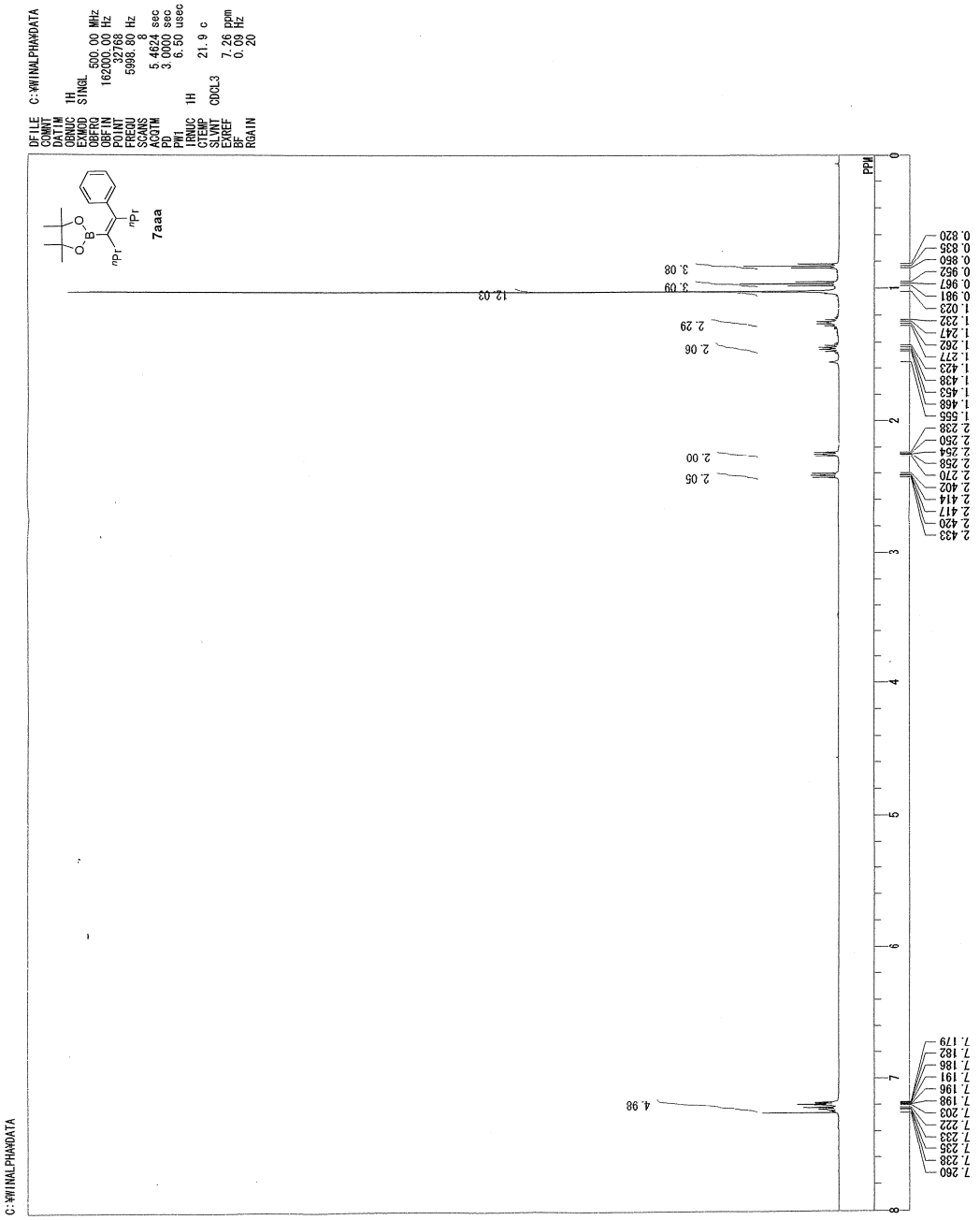
^{13}C NMR of Compound **5abd** (entry 7 in Table 2)



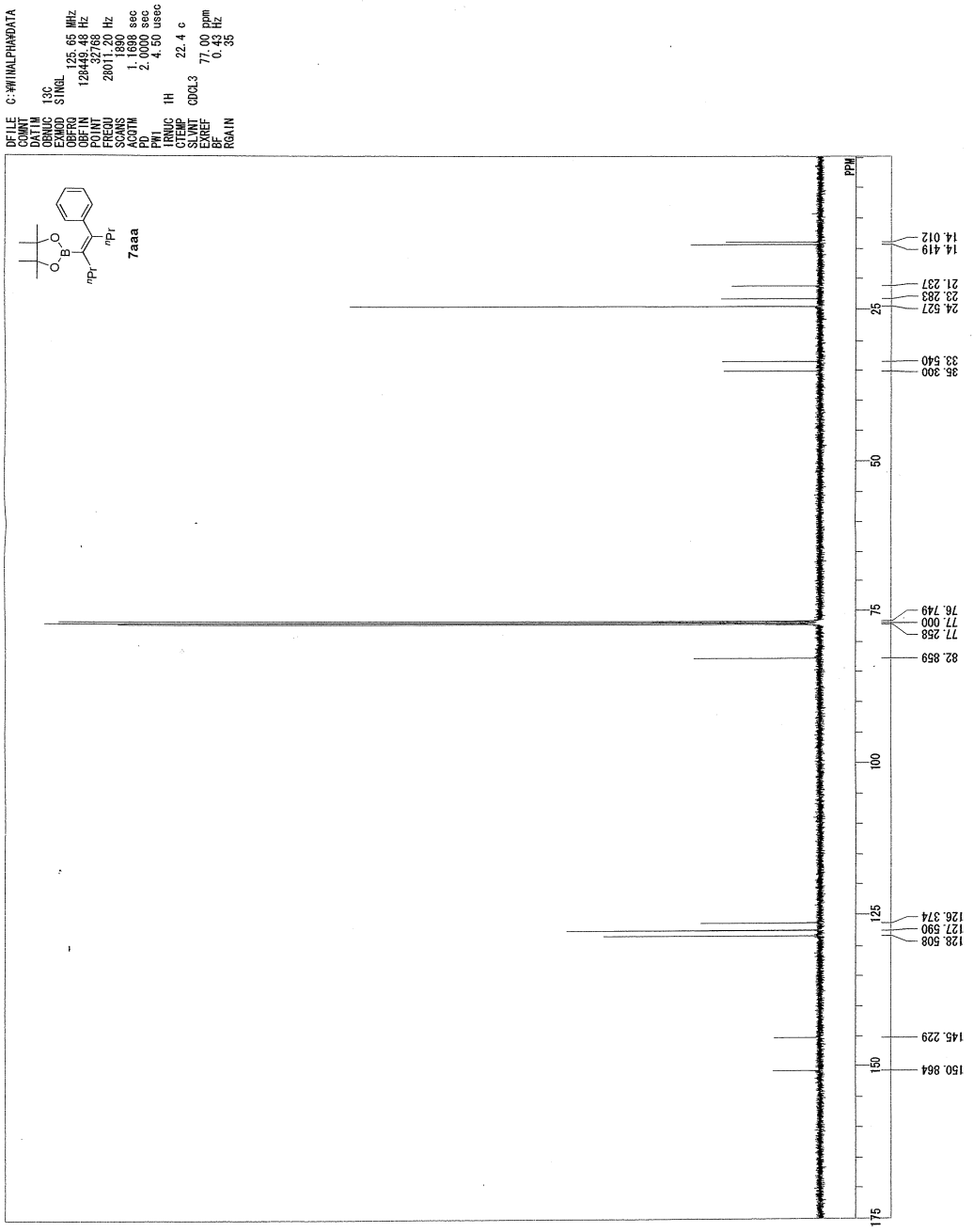
^{1}H NMR of Compound **5abe** (entry 8 in Table 2)



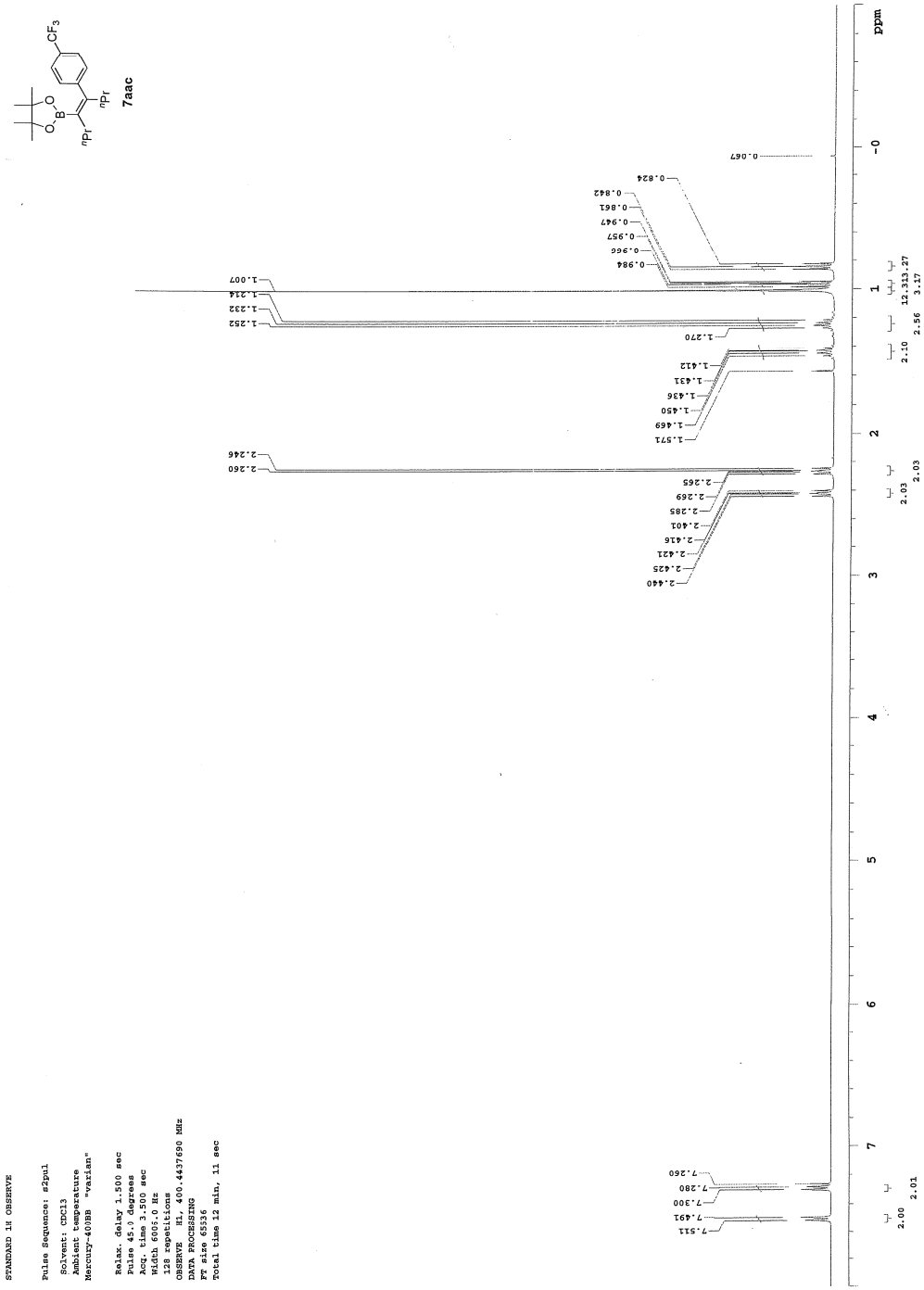
^{13}C NMR of Compound **5abe** (entry 8 in Table 2)



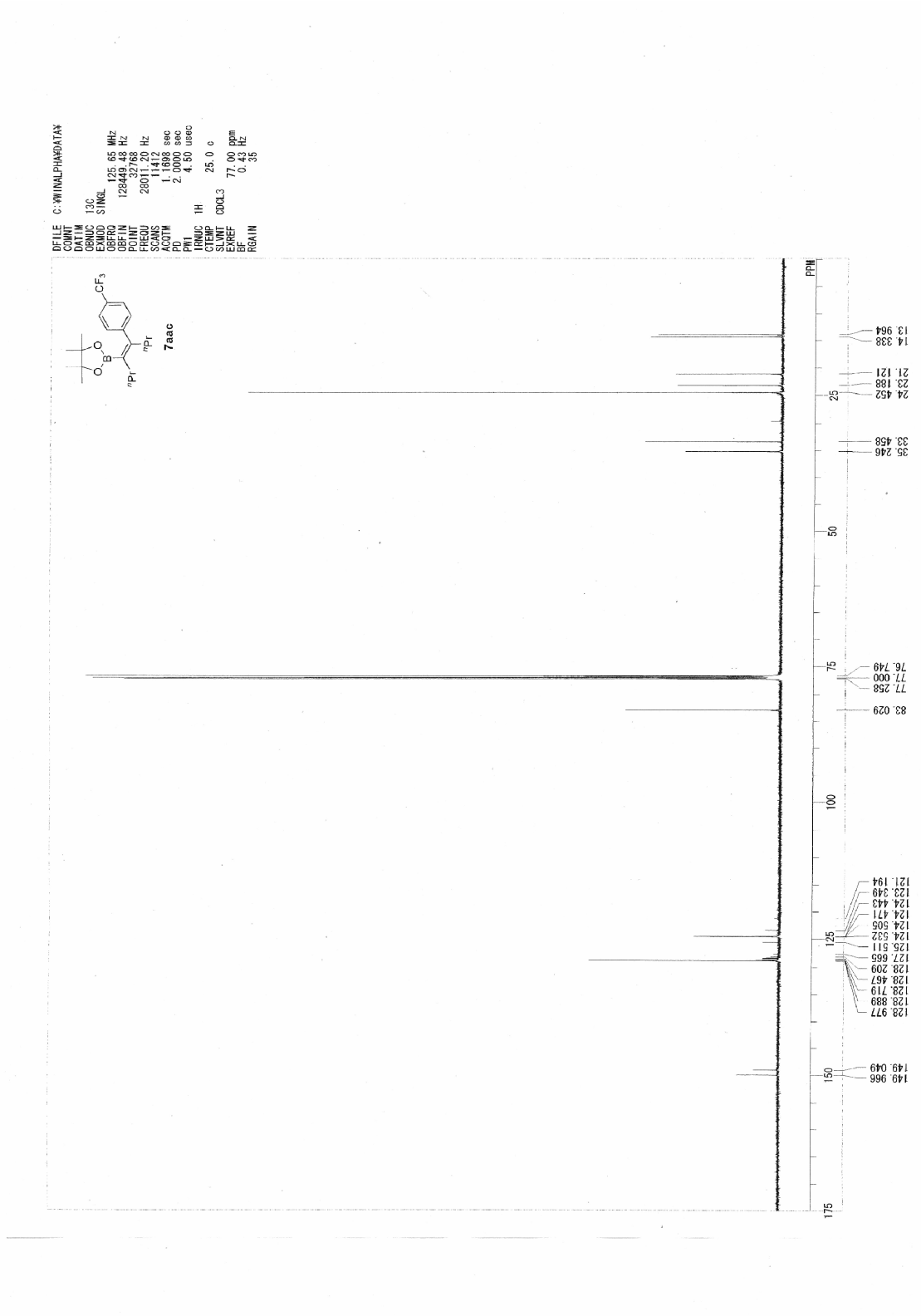
^{1}H NMR of Compound **7aaa** (entry 1 in Table 3)



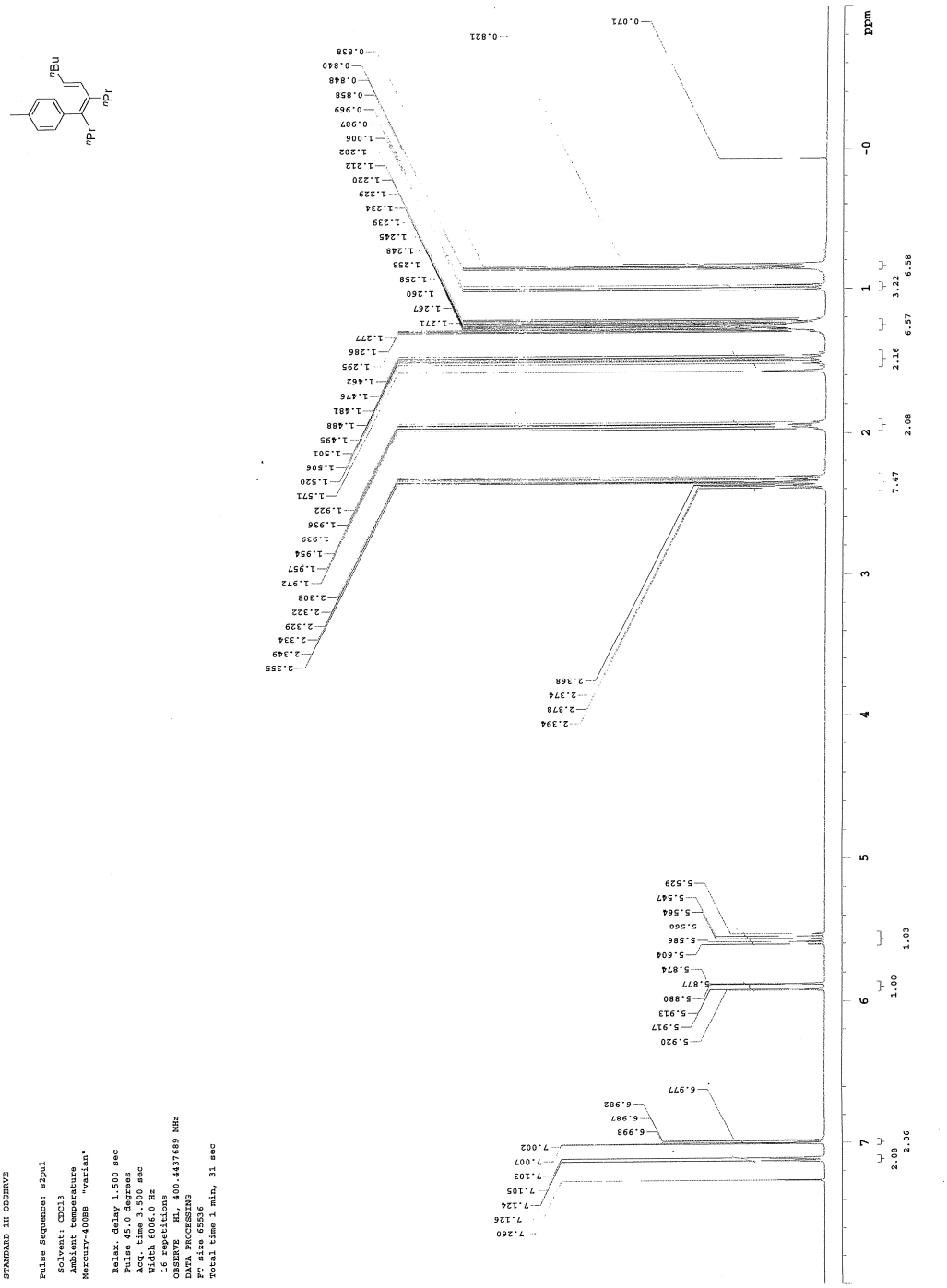
^{13}C NMR of Compound **7aaa** (entry 1 in Table 3)



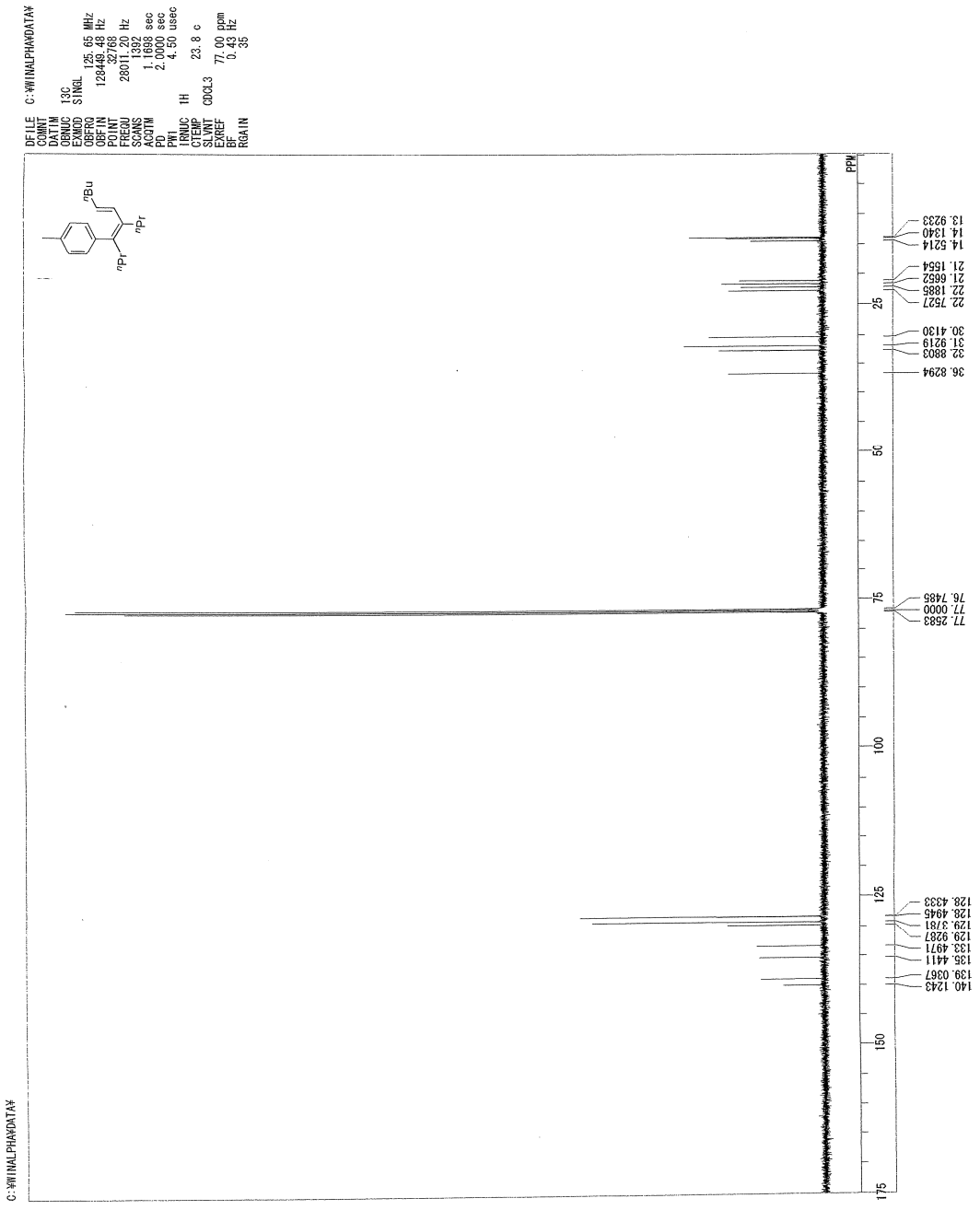
^{1}H NMR of Compound **7aac** (entry 3 in Table 3)



^{13}C NMR of Compound **7aac** (entry 3 in Table 3)



^{1}H NMR of Compound **8** (Scheme 2)



^{13}C NMR of Compound **8** (Scheme 2)