Supporting Information

Palladium-catalysed *cis*- and *trans*-silaboration of terminal alkynes: complementary access to stereo-defined trisubstituted alkenes

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Contents

1. General

All palladium-catalyzed reactions were performed in a drybox or using Schlenk technique under an atmosphere of nitrogen or argon with magnetic stirring. Column chromatography was performed with Ultra Pure Silica Gel (SILICYCLE, pH 7.0, 40-63 μm, 60Å). ^{1}H NMR spectra were recorded on a Varian Mercury-400 (400.44 MHz) spectrometer. ^{13}C NMR spectra were recorded on a JEOL JNM-A500 (125.65 MHz) spectrometer. ^{11}B NMR spectra were recorded on a Varian Mercury-400 (128.48 MHz) spectrometer. Chemical shifts were reported in ppm downfield from tetramethylsilane (^{1}H and ^{13}C) or BF_3•OEt_2 (^{11}B). IR spectra were recorded on a SHIMADZU FTIR-8100 spectrometer. Elemental analyses were performed by Elemental Analysis Center of Kyoto University. High resolution mass spectra were recorded on a JEOL JMS-MS700 spectrometer.

2. Materials

Toluene and tetrahydrofuran (THF) were dried and degassed by The Ultimate Solvent System (GlassContour). Silylboranes **1**,[1] (η^3-C_3H_5)PdCl(PPh_3),[2] and Pd(dba)$_2$[3] were synthesized by the method reported previously. Alkynes **2a**, **2c**, **2h** (TCI), **2b**, **2f-g**, and **2j** (Aldrich) were purchased and distilled prior to use. Silylated alkynes **2d-e** were prepared by silylation of 1-butyn-4-ol and 1-pentyn-5-ol (TCI), resprctively.[4] Ethynylcyclohexane (**2i**) was prepared from 2-cyclohexyl-1,1-dibromoethene by Corey's method.[5] Pyridine, *i*-PrOH, and Me_3SiCl were purchased and distilled prior to use. Triphenylphosphine (Wako), Pd(OAc)$_2$ (Mitsuwa), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-PHOS) (STREM), and Bu_4NF (1.0 M solution in THF, TCI) were used as received from commercial sources. Potassium phosphate *n*-hydrate (nacalai) was purified by sublimation.

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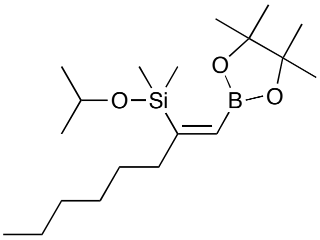
(1) T. Ohmura, K. Masuda, H. Furukawa and M. Suginome, *Organometallics* 2007, **26**, 1291.
(2) P. Kisanga and R. A. Widenhoefer, *J. Am. Chem. Soc.* 2000, **122**, 10017.
(3) T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet and J. A. Ibers, *J. Organomet. Chem.* 1974, **65**, 253.
(4) E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.* 1972, **94**, 6190.
(5) E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.* 1972, 243.

3. Palladium-Catalyzed Reaction of 1 with 1-Octyne (2a) (Scheme 1)

To a toluene solution of (η^3-C_3H_5)PdCl(PPh_3) (1.8 mg, 4.0 μmol) were added **2a** (0.40-0.48 mmol) and **1** (0.38-0.49 mmol), and then the resulting mixture was stirred at room temperature. After 1 h, pyridine (57 mg, 0.72 mmol) and *i*-PrOH (36 mg, 0.60 mmol) were added to the solution. Resulting mixture was stirred at room temperature for 96 h. GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio of **3a** formed. Bulb-to-bulb distillation (90 °C/0.6 mmHg) of the mixture afforded pure **3a**.

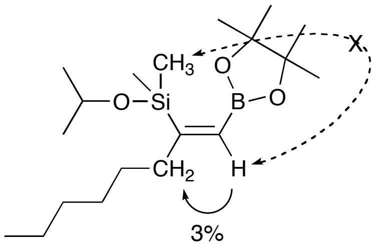
When the reaction carried out using **2a** (53 mg, 0.48 mmol) and **1** (84 mg, 0.38 mmol), (*Z*)-**3a** was formed in 91% yield (123 mg) with excellent *Z* slelctivity (*Z*:*E* = > 99:1). On the other hand, the reaction of **2a** (45 mg, 0.41 mmol) with **1** (108 mg, 0.49 mmol) gave (*E*)-**3a** in 85% yield (123 mg) with high *E* selectivity (*Z*:*E* = 11:89).

(Z)-2-(Isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-ene [(Z)-3a]

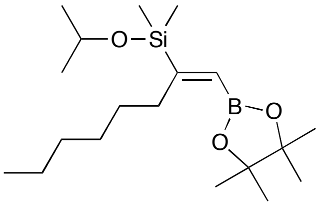


(*Z*)-**3a**

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (t, *J* = 1.2 Hz, 1H), 4.03 (septet, *J* = 6.0 Hz, 1H), 2.27 (dt, *J* = 7.6, 1.2 Hz, 2H), 1.35-1.42 (m, 2H), 1.24-1.35 (m, 6H), 1.27 (s, 12H), 1.15 (d, *J* = 6.0 Hz, 6H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.29 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 83.1, 64.8, 41.9, 31.8, 29.7, 29.3, 25.8, 24.9, 22.6, 14.1, 0.4. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.5. IR (neat): 1588 (C=C) cm^{-1}. Anal. Calcd for $C_{19}H_{39}BO_3Si$: C, 64.39; H, 11.09. Found: C, 64.51; H, 11.11. The stereochemistry was assigned by NOE experiments. The NOE was observed between the vinylic proton (δ 6.04 ppm) and the allylic protons (δ 2.27 ppm), whereas no NOE between the vinylic proton (δ 6.04 ppm) and the Si–CH_3 (δ 0.29 ppm) was observed. These results indicate that the double bond of the compound has *Z* geometry.

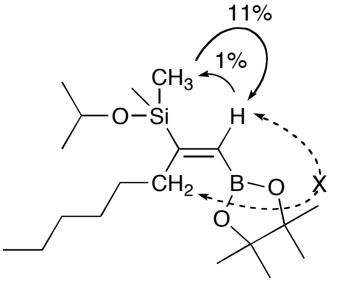


(*E*)-2-(Isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-ene [(*E*)-3a]



(*E*)-**3a**

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.93 (s, 1H), 3.97 (septet, *J* = 6.0 Hz, 1H), 2.46-2.51 (m, 2H), 1.23-1.45 (m, 8H), 1.28 (s, 12H), 1.14 (d, *J* = 6.0 Hz, 6H), 0.90 (t, *J* = 6.8 Hz, 3H), 0.19 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 169.5, 82.8, 65.1, 34.4, 31.7, 31.2, 29.6, 25.7, 24.8, 22.6, 14.1, -1.3. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, CDCl$_3$) δ 29.3. IR (neat): 1593 (C=C) cm^{-1}. HRMS (CI) *m/z* calcd for $C_{19}H_{39}BO_3Si$ (M$^+$): 354.2762, found: 354.2764. The stereochemistry was assigned by NOE experiments. The NOE was observed between the vinylic proton (δ 5.93 ppm) and the Si–CH$_3$ (δ 0.19 ppm), whereas no NOE between the vinylic proton (δ 6.04 ppm) and the allylic protons (δ 2.46-2.51 ppm) was observed. These results indicate that the double bond of the compound has *E* geometry.



4. Tracing of the Reaction of 1 with 2a (Scheme 2)

To a toluene solution (0.2 ml) of (η^3-C_3H_5)PdCl(PPh_3) (1.8 mg, 4.0 μmol) were added **2a** (0.40-0.48 mmol) and **1** (0.38-0.49 mmol), and then the resulting mixture was stirred at room temperature. After 1 h, the crude reaction mixture was analyzed by GC and ^{1}H NMR, indicating selective formation of (*Z*)-**4a**.[6] Pyridine (57 mg, 0.72 mmol) and *i*-PrOH (36 mg, 0.60 mmol) were added to the solution, and resulting mixture was stirred at room temperature. GC analysis of the reaction indicated that slow isomerization occurred when the reaction was carried out with excess of **1**.

5. Palladium-Catalyzed *cis*- and *trans*-Silaboration of Terminal Alkynes 2 (Table 1)

***General Procedure for cis-Silaboration*:** To a toluene solution (0.2 ml) of (η^3-C_3H_5)PdCl(PPh_3) (1.8 mg, 4.0 μmol) were added **2** (0.48 mmol) and **1** (88 mg, 0.40 mmol), and then the resulting mixture was stirred at room temperature. After 1 h, pyridine (57 mg, 0.72 mmol) and *i*-PrOH (36 mg, 0.60 mmol) were added to the solution. The resulting mixture was stirred at room temperature for 1 h. GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio of **3** formed. Bulb-to-bulb distillation of the mixture afforded pure **3**.

***General Procedure for trans-Silaboration*:** To a toluene solution (0.2 ml) of (η^3-C_3H_5)PdCl(PPh_3) (3.6 mg, 8.0 μmol) were added **2** (0.40 mmol) and **1** (106 mg, 0.48 mmol), and then the resulting mixture was stirred at room temperature. After 1 h, pyridine (57 mg, 0.72 mmol) and *i*-PrOH (36 mg, 0.60 mmol) were added to the solution. The resulting mixture was stirred at 50 °C for 24 h. GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio of **3** formed. Bulb-to-bulb distillation of the mixture afforded pure **3**. The *Z*/*E* isomers were separable by column chromatography on silica gel.

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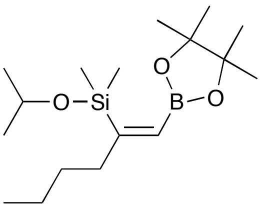
(6) T. Ohmura, K. Masuda and M. Suginome, *J. Am. Chem. Soc.*, 2008, **130**, 1526.

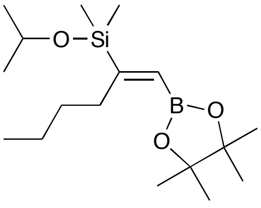
(*Z*)-2-(Isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-ene [(*Z*)-3b, entry 2]



(*Z*)-**3b**

According to the general procedure for *cis*-silaboration, **1** (99 mg, 0.45 mmol) was reacted with **2b** (46 mg, 0.56 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as > 99:1. The product **3b** (137 mg, 93%) was isolated by bulb-to-bulb distillation (85 °C/0.6 mmHg). (*Z*)-**3b:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (t, J = 1.2 Hz, 1H), 4.04 (septet, J = 6.0 Hz, 1H), 2.28 (dt, J = 7.6, 1.2 Hz, 2H), 1.31-1.43 (m, 4H), 1.27 (s, 12H), 1.16 (d, J = 6.0 Hz, 6H), 0.90 (t, J = 6.8 Hz, 3H), 0.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 83.2, 64.8, 41.6, 31.9, 25.8, 24.9, 22.7, 14.0, 0.4. The boron-bound carbon was not detected due to quadrupolar relaxation. IR (neat): 1586 (C=C) cm^{-1}. Anal. Calcd for $C_{17}H_{35}BO_3Si$: C, 62.56; H, 10.81. Found: C, 62.74; H, 11.06.

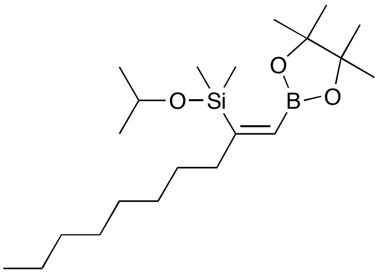
(*E*)-2-(Isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-ene [(*E*)-3b, entry 2]



(*E*)-**3b**

According to the general procedure for *trans*-silaboration, **1** (103 mg, 0.47 mmol) was reacted with **2b** (30 mg, 0.36 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as 11:89. The product **3b** (102 mg, 92%) was isolated by bulb-to-bulb distillation (85 °C/0.6 mmHg). (*E*)-**3b:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (s, 1H), 3.96 (septet, J = 6.0 Hz, 1H), 2.49 (t, J = 7.6 Hz, 2H), 1.30-1.43 (m, 4H), 1.27 (s, 12H), 1.13 (d, J = 6.0 Hz, 6H), 0.90 (t, J = 6.8 Hz, 3H), 0.18 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 82.8, 65.1, 34.1, 33.4, 25.7, 24.8, 23.0, 13.9, -1.3. The boron-bound carbon was not detected due to quadrupolar relaxation. IR (neat): 1593 (C=C) cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{17}H_{35}BO_3Si$ (M^+): 326.2449, found: 326.2438.

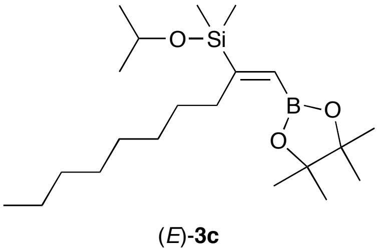
(*Z*)-2-(Isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-1-ene [(*Z*)-3c, entry 3]



(*Z*)-**3c**

According to the general procedure for *cis*-silaboration, **1** (85 mg, 0.38 mmol) was reacted with **2c** (65 mg, 0.47 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as > 99:1. The product **3c** (134 mg, 91%) was isolated by bulb-to-bulb distillation (95 °C/0.6 mmHg). (*Z*)-**3c:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (t, J = 1.2 Hz, 1H), 4.03 (septet, J = 6.0 Hz, 1H), 2.25-2.30 (m, 2H), 1.35-1.45 (m, 2H), 1.20-1.35 (m, 10H), 1.27 (s, 12H), 1.16 (d, J = 6.0 Hz, 6H), 0.89 (t, J = 7,2 Hz, 3H), 0.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 83.1, 64.8, 41.9, 31.9, 29.7, 29.6, 29.5, 29.3, 25.8, 24.9, 22.7, 14.1, 0.4. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.7. IR (neat): 1586 (C=C) cm^{-1}. Anal. Calcd for $C_{21}H_{43}BO_3Si$: C, 65.95; H, 11.33. Found: C, 65.77; H, 11.39.

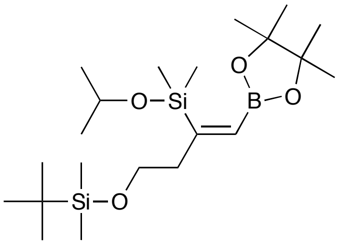
(*E*)-2-(Isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-1-ene [(*E*)-3c, entry 3]



(*E*)-**3c**

According to the general procedure for *trans*-silaboration, **1** (106 mg, 0.48 mmol) was reacted with **2c** (58 mg, 0.42 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as 8:92. The product **3c** (147 mg, 91%) was isolated by bulb-to-bulb distillation (95 °C/0.6 mmHg). (*E*)-**3c:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (s, 1H), 3.96 (septet, J = 6.0 Hz, 1H), 2.45-2.50 (m, 2H), 1.23-1.44 (m, 12H), 1.27 (s, 12H), 1.13 (d, J = 6.0 Hz, 6H), 0.88 (t, J = 6.8 Hz, 3H), 0.18 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.5, 82.8, 65.1, 34.4, 31.9, 31.3, 30.0, 29.4, 29.3, 25.7, 24.9, 22.7, 14.1, -1.3. The boron-bound carbon was not detected due to quadrupolar relaxation. IR (neat): 1593 (C=C) cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{21}H_{42}BO_3Si$ (M-H$^+$): 381.2996, found: 381.3000.

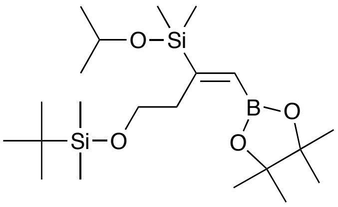
(*Z*)-4-(*tert*-Butyldimethylsilyloxy)-2-(isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-ene [(*Z*)-3d, entry 4]



(*Z*)-**3d**

According to the general procedure for *cis*-silaboration, **1** (81 mg, 0.37 mmol) was reacted with **2d** (86 mg, 0.47 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as > 99:1. The product **3d** (141 mg, 90%) was isolated by bulb-to-bulb distillation (110 °C/0.6 mmHg). (*Z*)-**3d:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (t, J = 1.2 Hz, 1H), 4.03 (septet, J = 6.0 Hz, 1H), 3.61-3.66 (m, 2H), 2.54 (dt, J = 7.6, 1.2 Hz, 2H), 1.27 (s, 12H), 1.17 (d, J = 6.0 Hz, 6H), 0.89 (s, 9H), 0.30 (s, 6H), 0.06 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 83.3, 64.9, 63.5, 44.7, 26.0, 25.8, 24.9, 18.4, 0.3, -5.2. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.2. IR (neat): 1590 (C=C) cm^{-1}. Anal. Calcd for $C_{21}H_{45}BO_4Si_2$: C, 58.85; H, 10.58. Found: C, 58.64; H, 10.72.

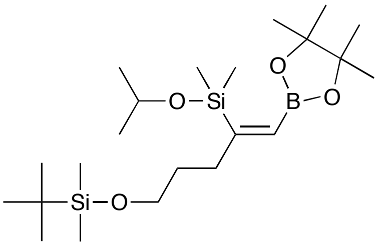
(*E*)-4-(*tert*-Butyldimethylsilyloxy)-2-(isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-ene [(*E*)-3d, entry 4]



(*E*)-**3d**

According to the general procedure for *trans*-silaboration, **1** (103 mg, 0.47 mmol) was reacted with **2d** (67 mg, 0.37 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as 9:91. The product **3d** (129 mg, 82%) was isolated by bulb-to-bulb distillation (110 °C/0.6 mmHg). (*E*)-**3d:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (s, 1H), 3.97 (septet, J = 6.0 Hz, 1H), 3.58-3.63 (m, 2H), 2.73-2.78 (m, 2H), 1.27 (s, 12H), 1.13 (d, J = 6.0 Hz, 6H), 0.90 (s, 9H), 0.19 (s, 6H), 0.06 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 83.0, 65.1, 63.8, 37.8, 26.1, 25.7, 24.8, 18.4, -1.5, -5.1. The boron-bound carbon was not detected due to quadrupolar relaxation. IR (neat): 1595 (C=C) cm^{-1}. HRMS (FAB) *m*/*z* calcd for $C_{21}H_{44}BO_4Si_2$ (M-H$^+$): 427.2871, found: 427.2865.

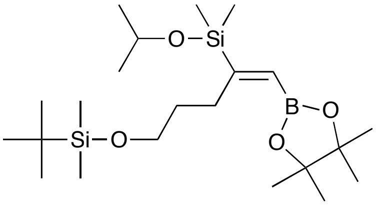
(*Z*)-5-(*tert*-Butyldimethylsilyloxy)-2-(isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-ene [(*Z*)-3e, entry 5]



(*Z*)-**3e**

According to the general procedure for *cis*-silaboration, **1** (88 mg, 0.40 mmol) was reacted with **2e** (95 mg, 0.49 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as > 99:1. The product **3e** (124 mg, 81%) was isolated by bulb-to-bulb distillation (110 °C/0.6 mmHg). (*Z*)-**3e:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (t, J = 1.2 Hz, 1H), 4.03 (septet, J = 6.0 Hz, 1H), 3.61 (t, J = 6.4 Hz, 2H), 2.30-2.35 (m, 2H), 1.60-1.68 (m, 2H), 1.27 (s, 12H), 1.16 (d, J = 6.0 Hz, 6H), 0.90 (s, 9H), 0.30 (s, 6H), 0.05 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 168.1, 83.2, 64.8, 63.1, 37.9, 32.8, 26.0, 25.8, 24.9, 18.3, 0.4, -5.3. The boron-bound carbon was not detected due to quadrupolar relaxation. IR (neat): 1588 (C=C) cm^{-1}. Anal. Calcd for $C_{22}H_{47}BO_4Si_2$: C, 59.70; H, 10.70. Found: C, 59.41; H, 10.98.

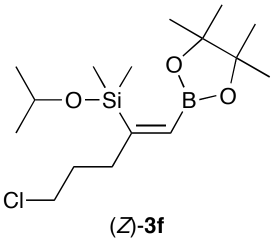
(*E*)-5-(*tert*-Butyldimethylsilyloxy)-2-(isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-ene [(*E*)-3e, entry 5]



(*E*)-**3e**

According to the general procedure for *trans*-silaboration, **1** (105 mg, 0.48 mmol) was reacted with **2e** (77 mg, 0.39 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as 7:93. The product **3e** (121 mg, 82%) was isolated by bulb-to-bulb distillation (110 °C/0.6 mmHg). (*E*)-**3e:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.94 (s, 1H), 3.96 (septet, J = 6.0 Hz, 1H), 3.62 (t, J = 6.8 Hz, 2H), 2.47-2.52 (m, 2H), 1.58-1.66 (m, 2H), 1.26 (s, 12H), 1.13 (d, J = 6.0 Hz, 6H), 0.89 (s, 9H), 0.19 (s, 6H), 0.05 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 169.0, 82.9, 65.1, 63.8, 34.4, 30.8, 26.0, 25.7, 24.9, 18.4, -1.3, -5.2. The boron-bound carbon was not detected due to quadrupolar relaxation. IR (neat): 1593 (C=C) cm^{-1}. HRMS (CI) *m*/*z* calcd for $C_{22}H_{46}BO_4Si_2$ (M-H$^+$): 441.3028, found: 441.3026.

(Z)-5-Chloro-2-(isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-ene [(*Z*)-3f, entry 6]

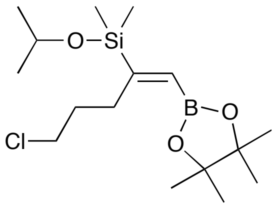


(*Z*)-**3f**

According to the general procedure for *cis*-silaboration, **1** (84 mg, 0.38 mmol) was reacted with **2f** (48 mg, 0.47 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as > 99:1. The product **3f** (125 mg, 94%) was isolated by bulb-to-bulb distillation (80 °C/0.6 mmHg). (*Z*)-**3f:** ^{1}H NMR

(400 MHz, $CDCl_3$) δ 6.06 (t, J = 1.2 Hz, 1H), 4.04 (septet, J = 6.0 Hz, 1H), 3.52 (t, J = 7.2 Hz, 2H), 2.43 (dt, J = 7.2, 1.2 Hz, 2H), 1.91 (quintet, J = 7.2 Hz, 2H), 1.27 (s, 12H), 1.16 (d, J = 6.0 Hz, 6H), 0.31 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 83.3, 64.9, 44.8, 38.9, 32.4, 25.8, 24.9, 0.3. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6. IR (neat): 1588 (C=C) cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{16}H_{32}BClO_3Si$ (M^+): 346.1902, found: 346.1889. This compound is unstable at room temperature in high concentration.

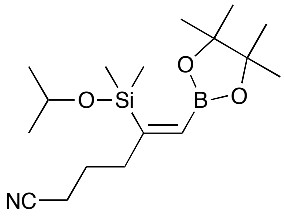
(*E*)-5-Chloro-2-(isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-ene [(*E*)-3f, entry 6]



(*E*)-**3f**

According to the general procedure for *trans*-silaboration, **1** (120 mg, 0.54 mmol) was reacted with **2f** (49 mg, 0.47 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as 11:89. The product **3f** (138 mg, 84%) was isolated by bulb-to-bulb distillation (80 °C/0.6 mmHg). (*E*)-**3f:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (s, 1H), 3.97 (septet, J = 6.0 Hz, 1H), 3.54 (t, J = 7.2 Hz, 2H), 2.58-2.63 (m, 2H), 1.85-1.93 (m, 2H), 1.27 (s, 12H), 1.13 (d, J = 6.0 Hz, 6H), 0.19 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 83.1, 65.2, 45.2, 33.9, 31.7, 25.7, 24.9, -1.4. The boron-bound carbon was not detected due to quadrupolar relaxation. IR (neat): 1593 (C=C) cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{16}H_{32}BClO_3Si$ (M^+): 346.1902, found: 346.1903.

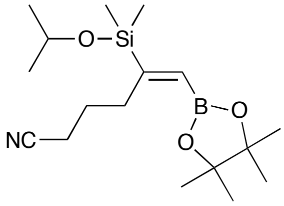
(*Z*)-5-(Isopropoxydimethylsilyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enenitrile [(*Z*)-3g, entry 7]



(*Z*)-**3g**

According to the general procedure for *cis*-silaboration, **1** (85 mg, 0.39 mmol) was reacted with **2g** (43 mg, 0.46 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as > 99:1. The product **3g** (114 mg, 87%) was isolated by bulb-to-bulb distillation (90 °C/0.6 mmHg). (*Z*)-**3g:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.04 (t, J = 1.2 Hz, 1H), 4.02 (septet, J = 6.0 Hz, 1H), 2.42 (dt, J = 7.2, 1.2 Hz, 2H), 2.30 (t, J = 7.2 Hz, 2H), 1.80 (quintet, J = 7.2 Hz, 2H), 1.26 (s, 12H), 1.15 (d, J = 6.0 Hz, 6H), 0.29 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 166.4, 119.8, 83.4, 64.9, 40.7, 25.8, 25.2, 24.9, 16.6, 0.3. The boron-bound carbon was not detected due to quadrupolar relaxation. IR (neat): 2247 (CN), 1588 (C=C) cm^{-1}. Anal. Calcd for $C_{17}H_{32}BNO_3Si$: C, 60.53; H, 9.56; N, 4.15. Found: C, 60.30; H, 9.47; N, 4.21.

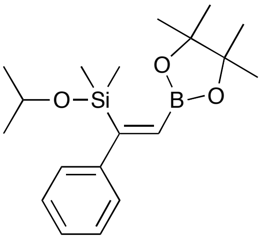
(*E*)-5-(Isopropoxydimethylsilyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enenitrile [(*E*)-3g, entry 7]



(*E*)-**3g**

According to the general procedure for *trans*-silaboration, **1** (105 mg, 0.48 mmol) was reacted with **2g** (36 mg, 0.39 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as 7:93. The product **3g** (106 mg, 81%) was isolated by bulb-to-bulb distillation (90 °C/0.6 mmHg). (*E*)-**3g:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.00 (s, 1H), 3.98 (septet, J = 6.0 Hz, 1H), 2.59-2.63 (m, 2H), 2.34 (t, J = 7.2 Hz, 2H), 1.80 (quintet, J = 7.6 Hz, 2H), 1.28 (s, 12H), 1.14 (d, J = 6.0 Hz, 6H), 0.19 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 167.1, 120.0, 83.2, 65.3, 33.1, 26.4, 25.8, 24.9, 16.9, -1.4. The boron-bound carbon was not detected due to quadrupolar relaxation. IR (neat): 2247 (CN), 1593 (C=C) cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{17}H_{32}BNO_3Si$ (M^+): 337.2245, found: 337.2255.

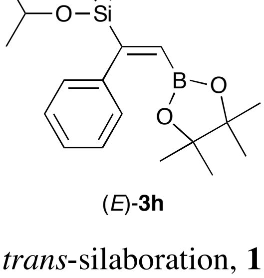
(*Z*)-1-(Isopropoxydimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenylethene [(*Z*)-3h, entry 8]



(*Z*)-**3h**

According to the general procedure for *cis*-silaboration, **1** (80 mg, 0.36 mmol) was reacted with **2h** (48 mg, 0.47 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as > 99:1. The product **3h** (109 mg, 87%) was isolated by bulb-to-bulb distillation (100 °C/0.6 mmHg). (*Z*)-**3h:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.29 (m, 2H), 7.16-7.21 (m, 3H), 6.24 (s, 1H), 3.96 (septet, J = 6.0 Hz, 1H), 1.32 (s, 12H), 1.01 (d, J = 6.0 Hz, 6H), 0.35 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 148.3, 127.7, 126.7, 126.1, 83.6, 65.4, 25.4, 25.0, 0.9. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.8. IR (neat): 1576 (C=C) cm^{-1}. Anal. Calcd for $C_{19}H_{31}BO_3Si$: C, 65.89; H, 9.02. Found: C, 65.64; H, 8.98.

(*E*)-1-(Isopropoxydimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenylethene [(*E*)-3h, entry 8]

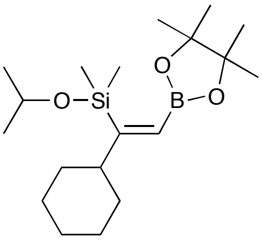


(*E*)-**3h**

According to the general procedure for *trans*-silaboration, **1** (104 mg, 0.47 mmol) was reacted with **2h** (38 mg, 0.38 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as 62:38. The product **3h** (104 mg, 80%) was isolated by bulb-to-bulb distillation (110 °C/0.6 mmHg). (*E*)-**3h:** ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.11-7.27 (m, 5H), 6.25 (s, 1H), 3.97 (septet, J = 6.0 Hz, 1H), 1.09 (s, 12H), 1.08 (d, J = 6.0 Hz, 6H), 0.20 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 144.3, 127.5, 127.4, 126.0, 83.2, 65.4, 25.6, 24.6, -1.3. The boron-bound carbon was not detected due to quadrupolar relaxation. IR (neat): 1586 (C=C) cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{19}H_{32}BO_3Si$ (M+H$^+$): 347.2214, found: 347.2223.

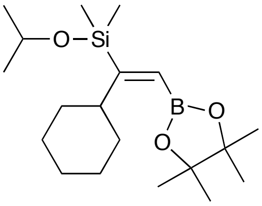
(*Z*)-1-(Isopropoxydimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-cyclohexylethene [(*Z*)-3i, entry 9]



(*Z*)-**3i**

According to the general procedure for *cis*-silaboration, **1** (82 mg, 0.37 mmol) was reacted with **2i** (52 mg, 0.48 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as > 99:1. The product **3i** (118 mg, 90%) was isolated by bulb-to-bulb distillation (100 °C/0.6 mmHg). (*Z*)-**3i:** ^1H NMR (400 MHz, $CDCl_3$) δ 6.04 (d, J = 1.2 Hz, 1H), 4.03 (septet, J = 6.0 Hz, 1H), 2.34-2.41 (m, 1H), 1.66-1.77 (m, 4H), 1.23-1.35 (m, 2H), 1.27 (s, 12H), 1.09-1.20 (m, 4H), 1.16 (d, J = 6.0 Hz, 6H), 0.29 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 83.2, 64.9, 45.2, 32.9, 27.0, 26.5, 25.8, 24.9, 0.7. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.1. IR (neat): 1586 (C=C) cm^{-1}. Anal. Calcd for $C_{19}H_{37}BO_3Si$: C, 64.76; H, 10.58. Found: C, 64.74; H, 10.52.

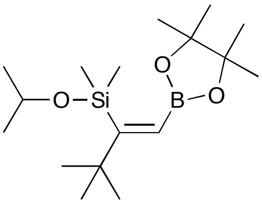
(*E*)-1-(Isopropoxydimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-cyclohexylethene [(*E*)-3i, entry 9]



(*E*)-**3i**

According to the general procedure for *trans*-silaboration, **1** (107 mg, 0.48 mmol) was reacted with **2i** (45 mg, 0.41 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as 67:33. The product **3i** (129 mg, 91%) was isolated by bulb-to-bulb distillation (100 °C/0.6 mmHg). (*E*)-**3i:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (s, 1H), 3.99 (septet, J = 6.0 Hz, 1H), 2.78 (tt, J = 12.0, 4.0 Hz, 1H), 1.43-1.77 (m, 6H), 1.28 (s, 12H), 1.10-1.34 (m, 4H), 1.14 (d, J = 6.0 Hz, 6H), 0.21 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 83.0, 65.0, 45.8, 33.1, 26.9, 26.1, 25.8, 24.8, 0.4. The boron-bound carbon was not detected due to quadrupolar relaxation. HRMS (FAB) *m*/*z* calcd for $C_{19}H_{38}BO_3Si$ (M+H^{+}): 353.2683, found: 353.2678.

(*Z*)-2-(Isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3-dimethylbut-1-ene [(*Z*)-3j, entry 10]

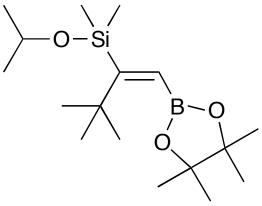


(*Z*)-**3j**

According to the general procedure for *cis*-silaboration, **1** (80 mg, 0.36 mmol) was reacted with **2j** (37 mg, 0.46 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as > 99:1. The product **3j** (103 mg, 87%) was isolated by bulb-to-bulb distillation (80 °C/0.6 mmHg). (*Z*)-**3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 1H), 4.05 (septet, J = 6.0 Hz, 1H), 1.29 (s, 12H), 1.18 (d, J = 6.0 Hz, 6H), 1.15 (s, 9H), 0.34 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.2, 83.3, 64.9, 40.1, 29.6, 25.8, 25.0, 2.1. The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ

30.5. IR (neat): 1574 (C=C) cm^{-1}. Anal. Calcd for $C_{17}H_{35}BO_3Si$: C, 62.56; H, 10.81. Found: C, 62.49; H, 10.94.

(*E*)-2-(Isopropoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3-dimethylbut-1-ene [(*E*)-3j, entry 10]



(*E*)-**3j**

According to the general procedure for *trrans*-silaboration, **1** (107 mg, 0.49 mmol) was reacted with **2j** (34 mg, 0.41 mmol). GC analysis of the crude reaction mixture indicated the *Z*/*E* ratio as 90:10. The product **3j** (102 mg, 76%) was isolated by bulb-to-bulb distillation (80 °C/0.6 mmHg). The minor isomer (*E*)-**3j** was separated by column chromatography on silica gel (hexane:Et_2O = 20:1). (*E*)-**3j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (s, 1H), 3.99 (septet, J = 6.0 Hz, 1H), 1.29 (s, 12H), 1.20 (s, 9H), 1.14 (d, J = 6.0 Hz, 6H), 0.23 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 83.4, 65.0, 38.6, 31.1, 25.8, 24.8, 1.4. The boron-bound carbon was not detected due to quadrupolar relaxation. IR (neat): 1593 (C=C) cm^{-1}. HRMS (FAB) *m/z* calcd for $C_{17}H_{34}BO_3Si$ (M-H$^+$): 325.2370, found: 325.2374.

6. Isomerization of (*Z*)-3a to (*E*)-3a (Table 2)

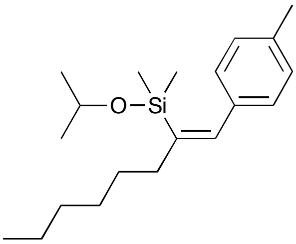
Isomerization of (*Z*)-3a to (*E*)-3a under the conditions shown in entry 1: To a toluene (0.10 mL) solution of (η^3-C_3H_5)PdCl(PPh_3) (1.8 mg, 4 μmol) were added (*Z*)-**3a** (*Z* 100%, 68 mg, 0.19 mmol), **1** (9.0 mg, 0.041 mmol), *i*-PrOH (3.1 mg, 0.051 mmol), pyridine (5.0 mg, 0.063 mmol), and tridecane (35 mg, internal standard) in this order. The mixture was then heated to 50 °C and stirred for 24 h at the temperature. The resulting reaction mixture was analyzed by GC.

The experiments under the conditions shown in entries 2-7 were carried out according to the procedure described above.

7. A Synthetic Application to Stereoselective Preparation of 1,2-Diarylalk-1-enes (Scheme 3)

General Procedure for Suzuki-Miyaura Coupling of (*Z*)- and (*E*)-3a with Aryl Iodides: To a mixture of $Pd(OAc)_2$ (1.8 mg, 8 μmol), S-PHOS (3.9 mg, 9.6 μmol), K_3PO_4 (170 mg, 0.80 mmol), H_2O (50 mg, 2.8 mmol) in toluene (0.40 mL) was added Ar-I (0.44 mmol) and **3a** (0.40 mmol). The resulting mixture was heated to 100 °C and stirred for 5 h at the temperature. After cooling to room temperature, the mixture was filtrated through a pad of Celite and the resulting solution was dried over anhydrous $MgSO_4$. The coupling products, 2-silyl-1-aryloct-1-enes, were isolated by bulb-to-bulb distillation.

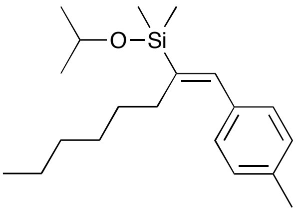
(*Z*)-2-(Isopropoxydimethylsilyl)-1-(4-methylphenyl)oct-1-ene [(*Z*)-5]



(*Z*)-**5**

According to the general procedure, (*Z*)-**3a** (126 mg, 0.35 mmol) was reacted with 4-iodotoluene (81 mg, 0.37 mmol). The product **5** (91 mg, 80%, *E*:*Z* = > 99:1) was isolated by bulb-to-bulb distillation (120 °C/0.6 mmHg). (*Z*)-**5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.0 Hz, 2H), 7.11 (s, 1H), 7.08 (d, J = 8.0 Hz, 2H), 3.96 (septet, J = 6.0 Hz, 1H), 2.33 (s, 3H), 2.27 (dt, J = 7.6, 1.2 Hz, 2H), 1.42-1,51 (m, 2H), 1.24-1.40 (m, 6H), 1.12 (d, J = 6.0 Hz, 6H), 0.90 (t, J = 6.8 Hz, 3H), 0.03 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 142.4, 137.1, 136.4, 128.7, 128.4, 65.0, 39.0, 31.8, 30.7, 29.2, 25.6, 22.7, 21.2, 14.1, 0.3. Anal. Calcd for $C_{20}H_{34}OSi$: C, 75.40; H, 10.76. Found: C, 75.47; H, 10.47.

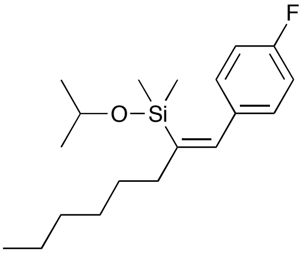
(*E*)-2-(Isopropoxydimethylsilyl)-1-(4-methylphenyl)oct-1-ene [(*E*)-5]



(*E*)-**5**

According to the general procedure, (*E*)-**3a** (129 mg, 0.36 mmol, *Z*:*E* = 11:89) was reacted with 4-iodotoluene (85 mg, 0.39 mmol). The product **5** (87 mg, 76%, *Z*:*E* = 14:86) was isolated by bulb-to-bulb distillation (120 °C/0.6 mmHg). (*E*)-**5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.20 (m, 4H), 6.82 (s, 1H), 4.40 (septet, J = 6.0 Hz, 1H), 2.32-2.39 (m, 2H), 2.35 (s, 3H), 1.42-1.52 (m, 2H), 1.22-1.37 (m, 6H), 1.18 (d, J = 6.0 Hz, 6H), 0.88 (t, J = 7.2 Hz, 3H), 0.27 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 138.7, 136.4, 135.4, 128.8, 128.7, 65.1, 31.6, 30.3, 29.8, 25.78, 25.75, 22.6, 21.2, 14.1, -1.0. Anal. Calcd for $C_{20}H_{34}OSi$: C, 75.40; H, 10.76. Found: C, 75.66; H, 10.89.

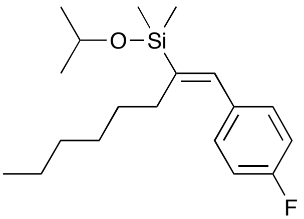
(*Z*)-1-(4-Fluorophenyl)-2-(isopropoxydimethylsilyl)oct-1-ene [(*Z*)-7]



(*Z*)-**7**

According to the general procedure, (*Z*)-**3a** (132 mg, 0.37 mmol) was reacted with 4-fluoroiodobenzene (94 mg, 0.42 mmol). The product **7** (98 mg, 82%, *E*:*Z* = > 99:1) was isolated by bulb-to-bulb distillation (130 °C/0.6 mmHg). (*Z*)-**7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.35 (m, 2H), 7.08 (s, 1H), 6.90-7.00 (m, 2H), 3.95 (septet, J = 6.0 Hz, 1H), 2.27 (dt, J = 7.6, 1.2 Hz, 2H), 1.40-1.51 (m, 2H), 1.25-1.40 (m, 6H), 1.11 (d, J = 6.0 Hz, 6H), 0.90 (t, J = 6.8 Hz, 3H), 0.02 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 ($^1J_{CF}$ = 245.1 Hz), 143.6, 141.6, 136.1 ($^4J_{CF}$ = 3.4 Hz), 130.4 ($^3J_{CF}$ = 7.7 Hz), 114.5 ($^2J_{CF}$ = 21.4 Hz), 65.1, 38.8, 31.8, 30.6, 29.2, 25.6, 22.7, 14.1, 0.2. Anal. Calcd for $C_{19}H_{31}FOSi$: C, 70.75; H, 9.69. Found: C, 70.67; H, 9.55.

(*E*)-1-(4-Fluorophenyl)-2-(isopropoxydimethylsilyl)oct-1-ene [(*E*)-7]

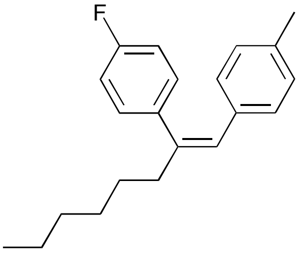


(*E*)-**7**

According to the general procedure, (*E*)-**3a** (132 mg, 0.37 mmol, *Z*:*E* = 11:89) was reacted with 4-fluoroiodobenzene (93 mg, 0.42 mmol). The product **7** (88 mg, 74%, *Z*:*E* = 10:90) was bulb-to-bulb distillation (130 °C/0.6 mmHg). (*E*)-**7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.26 (m, 2H), 6.98-7.05 (m, 2H), 6.80 (s, 1H), 4.04 (septet, J = 6.0 Hz, 1H), 2.30-2.35 (m, 2H), 1.40-1.48 (m, 2H), 1.21-1.34 (m, 6H), 1.18 (d, J = 6.0 Hz, 6H), 0.87 (t, J = 6.8 Hz, 3H), 0.27 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5 ($^1J_{CF}$ = 246.0 Hz), 144.1, 137.6, 134.4 ($^4J_{CF}$ = 3.4 Hz), 130.2 ($^3J_{CF}$ = 7.7 Hz), 115.0 ($^2J_{CF}$ = 21.4 Hz), 65.1, 31.5, 30.1, 29.73, 29.71, 25.8, 22.6, 14.0, -1.1. Anal. Calcd for $C_{19}H_{31}FOSi$: C, 70.75; H, 9.69. Found: C, 70.72; H, 9.90.

General Procedure for Hiyama Coupling of 1-Aryl-2-silyloct-1-enes 5 and 7 with Aryl Iodides: To a THF (0.40 mL) of solution of $Pd(dba)_2$ (5.8 mg, 10 μmol) were added Bu_4NF (1.0 M solution in THF, 0.30 mL, 0.30 mmol), Ar-I (0.22 mmol) and **5** or **7** (0.20 mmol). The resulting mixture was heated to 50 °C and stirred for 3 h at the temperature. After cooling to room temperature, water was added to the mixture and the organic layer was extracted with Et_2O. The extracts were dried over anhydrate $MgSO_4$ and concentrated by rotary evaporator. The coupling products, 1,2-diaryloct-1-enes, were isolated by column chromatography on silica gel.

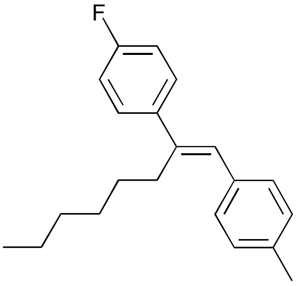
(*Z*)-2-(4-Fluorophenyl)-1-(4-methylphenyl)oct-1-ene [(*Z*)-6]



(*Z*)-**6**

According to the general procedure, (*Z*)-**5** (77 mg, 0.24 mmol) was reacted with 4-fluoroiodobenzene (63 mg, 0.28 mmol). The product **6** (47 mg, 66%, *E*:*Z* = > 99:1) was isolated by column chromatography on silica gel (eluent: hexane). (*Z*)-**6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-7.14 (m, 2H), 6.94-7.01 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.39 (s, 1H), 2.44 (t, *J* = 6.8 Hz, 2H), 2.24 (s, 3H), 1.20-1.45 (m, 8H), 0,87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7 ($^1J_{CF}$ = 245.0 Hz), 141.5, 137.4 ($^4J_{CF}$ = 3.4 Hz), 135.8, 134.5, 130.2 ($^3J_{CF}$ = 7.7 Hz), 128.8, 128.6, 126.4, 115.4 ($^2J_{CF}$ = 20.5 Hz), 40.6, 31.7, 28.8, 27.9, 22.6, 21.0, 14.1. HRMS (EI) *m*/*z* calcd for $C_{21}H_{25}F$ (M^+): 296.1940, found: 296.1941.

(*E*)-2-(4-Fluorophenyl)-1-(4-methylphenyl)oct-1-ene [(*E*)-6]

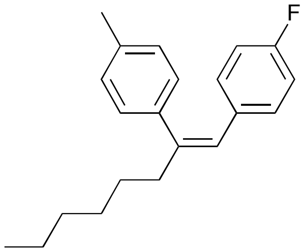


(*E*)-**6**

According to the general procedure, (*E*)-**5** (74 mg, 0.23 mmol, *Z*:*E* = 14:86) was reacted with 4-fluoroiodobenzene (59 mg, 0.25 mmol). The product **6** (66 mg, 66%, *Z*:*E* = 10:90) was isolated by column chromatography on silica gel (eluent: hexane). (*E*)-**6**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.44 (m, 2H), 7.15-7.23 (m, 4H), 7.00-7.08 (m, 2H), 6.60 (s, 1H), 2.63-2.68 (m, 2H), 2.37 (s, 3H), 1.15-1.45 (m, 8H), 0.84 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.0 ($^1J_{CF}$ = 245.1 Hz), 141.7, 139.3

($^4J_{CF}$ = 3.4 Hz), 136.3, 135.2, 129.0, 128.6, 128.1 ($^3J_{CF}$ = 7.7 Hz), 128.0, 115.1 ($^2J_{CF}$ = 21.4 Hz), 31.5, 30.3, 29.3, 28.6, 22.6, 21.2, 14.0. HRMS (EI) *m/z* calcd for $C_{21}H_{25}F$ (M^+): 296.1940, found: 296.1942.

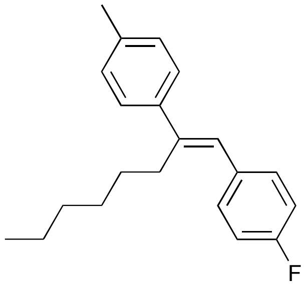
(*Z*)-1-(4-Fluorophenyl)-2-(4-methylphenyl)oct-1-ene [(*Z*)-8]



(*Z*)-**8**

According to the general procedure, (*Z*)-**7** (41 mg, 0.13 mmol) was reacted with 4-iodotoluene (30 mg, 0.14 mmol). The product **8** (26 mg, 70%, *E*:*Z* = > 99:1) was isolated by column chromatography on silica gel (eluent: hexane). (*Z*)-**8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07-7.13 (m, 2H), 6.98-7.04 (m, 2H), 6.84-6.91 (m, 2H), 6.73-6.80 (m, 2H), 6.35 (s, 1H), 2.42-2.47 (m, 2H), 2.35 (s, 3H), 1.20-1.43 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0 ($^1J_{CF}$ = 245.0 Hz), 143.4, 138.1, 136.5, 133.8 ($^4J_{CF}$ = 3.4 Hz), 130.4 ($^3J_{CF}$ = 7.7 Hz), 129.2, 128.4, 124.6, 114.6 ($^2J_{CF}$ = 21.4 Hz), 40.6, 31.7, 28.9, 27.9, 22.6, 21.2, 14.1. HRMS (EI) *m/z* calcd for $C_{21}H_{25}F$ (M^+): 296.1940, found: 296.1938.

(*E*)-1-(4-Fluorophenyl)-2-(4-methylphenyl)oct-1-ene [(*E*)-8]



(*E*)-**8**

According to the general procedure, (*E*)-**7** (82 mg, 0.26 mmol, *Z*:*E* = 10:90) was reacted with 4-iodotoluene (62 mg, 0.29 mmol). The product **8** (50 mg, 67%, *Z*:*E* = 9:91) was isolated by column chromatography on silica gel (eluent: hexane). (*E*)-**8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.37 (m, 2H), 7.23-7.29 (m, 2H), 7.15-7.20 (m, 2H), 7.01-7.08 (m, 2H), 6.62 (s, 1H), 2.61-2.66 (m, 2H), 2.38 (s, 3H), 1.15-1.45 (m, 8H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4 ($^1J_{CF}$ = 245.0 Hz), 143.3, 140.0, 136.9, 134.5 ($^4J_{CF}$ = 3.4 Hz), 130.3 ($^2J_{CF}$ = 7.7 Hz), 129.1, 126.4, 126.2, 115.0 ($^2J_{CF}$ = 21.2 Hz), 31.5, 30.1, 29.3, 28.7, 22.6, 21.1, 14.0. HRMS (EI) *m*/*z* calcd for $C_{21}H_{25}F$ (M^+): 296.1940, found: 296.1939.

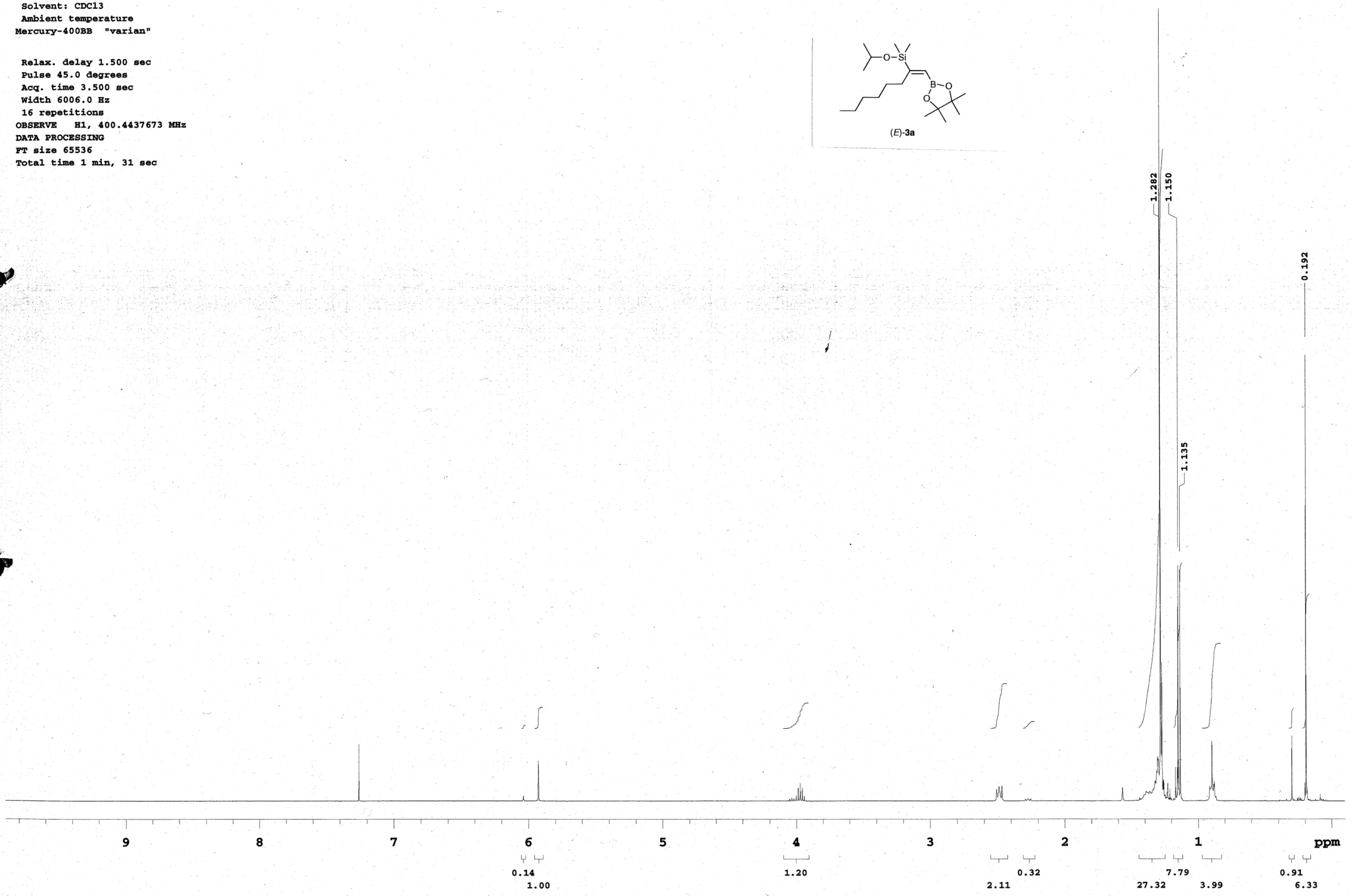
8. ^{1}H and ^{13}C NMR spectra of the compounds that do not have elemental analysis data

^{1}H and ^{13}C NMR spectra of (*E*)-**3a**-**j**, **6**, and **8** are shown in following pages.

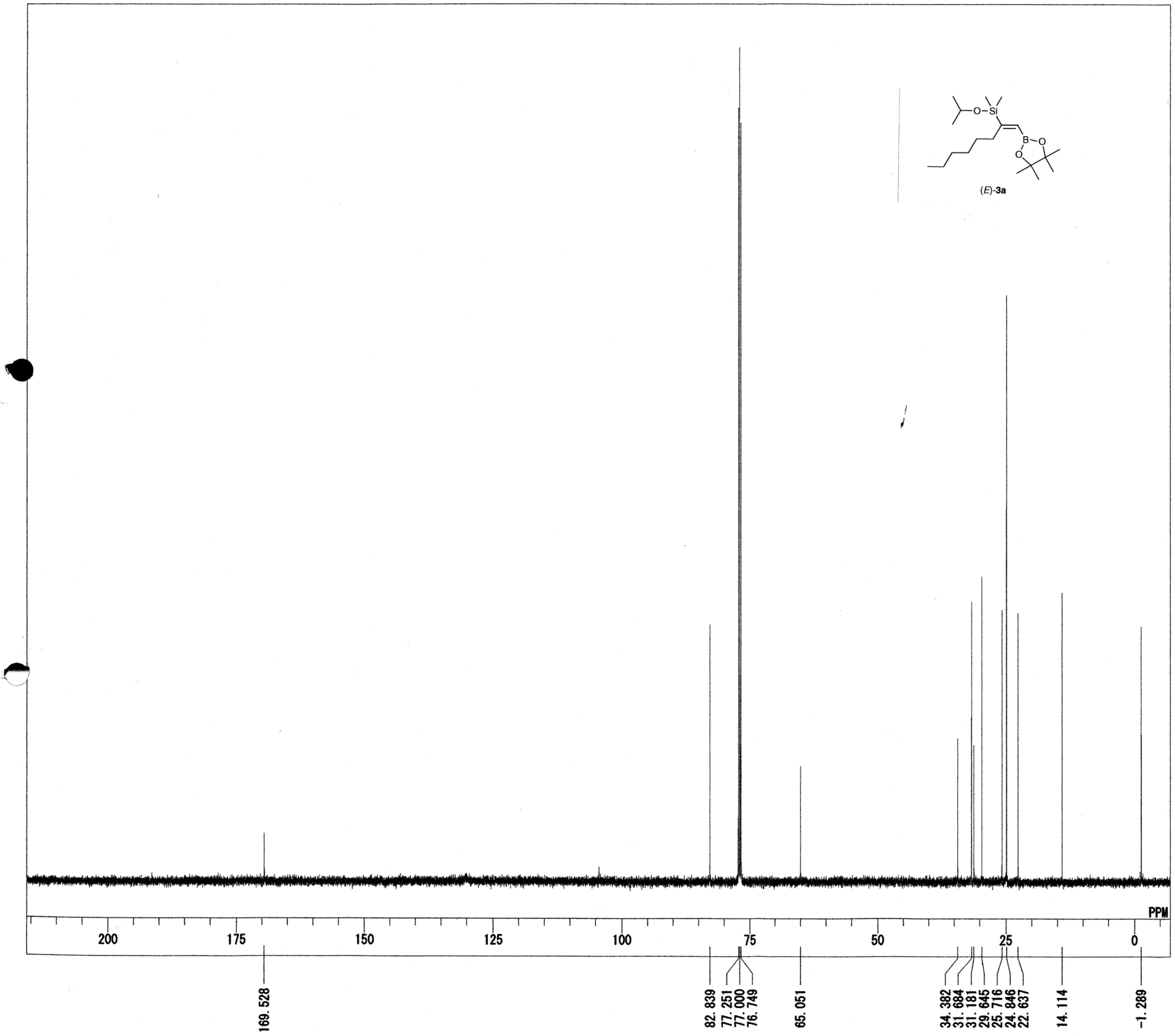
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
16 repetitions
OBSERVE H1, 400.4437673 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec


(E)-3a

C:¥WINALPHA¥DATA¥Suginome¥Oshima¥KO137-BCM.ALS



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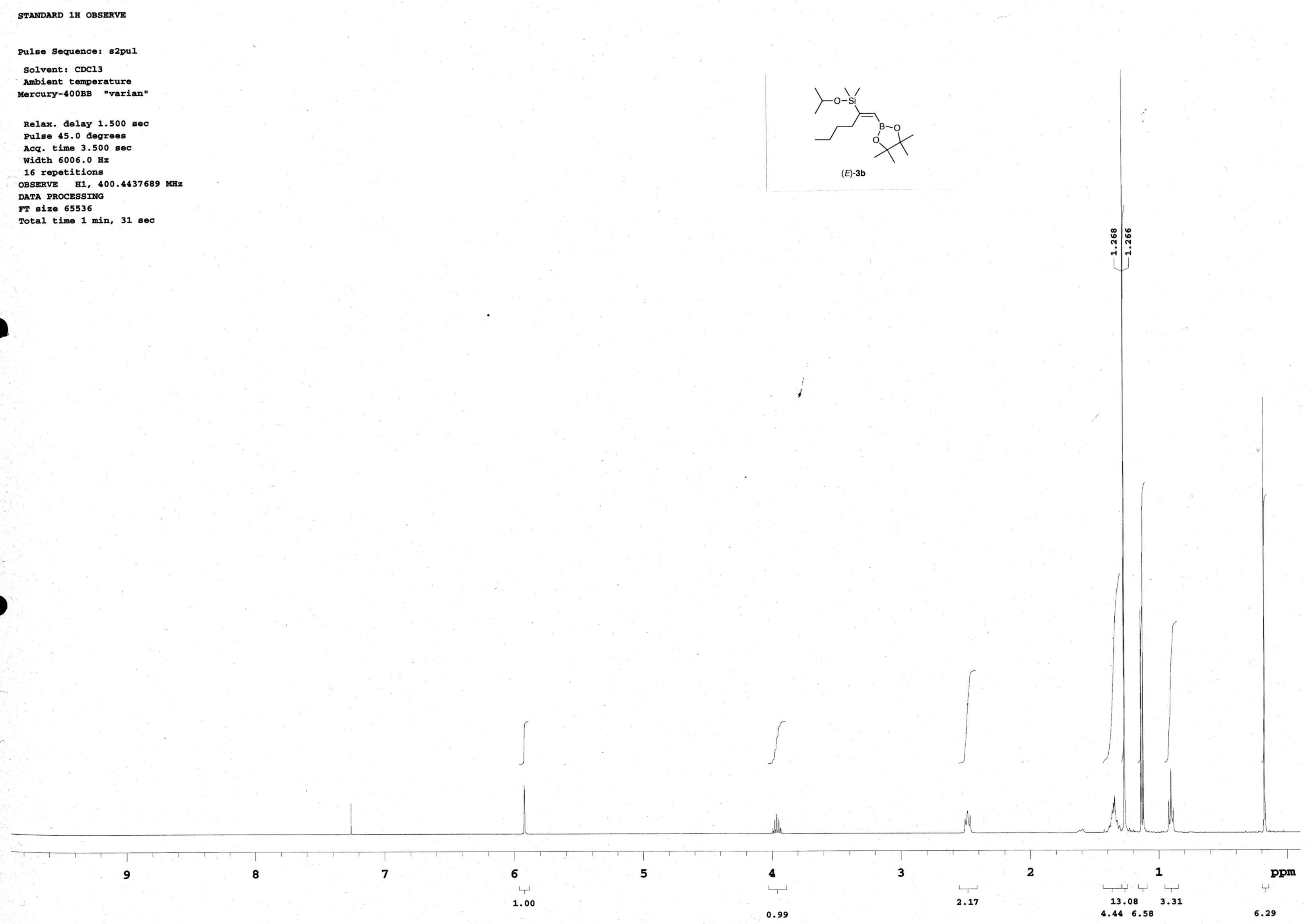
COMNT
DATIM  Tue Jan 16 20:43:50 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        32768
FREQU     28011.20 Hz
SCANS         1921
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         22.5 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.19 Hz
RGAIN           34
```



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STANDARD 1H OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
Mercury-400BB  "varian"

 Relax. delay 1.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6006.0 Hz
 16 repetitions
OBSERVE   H1, 400.4437689 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec
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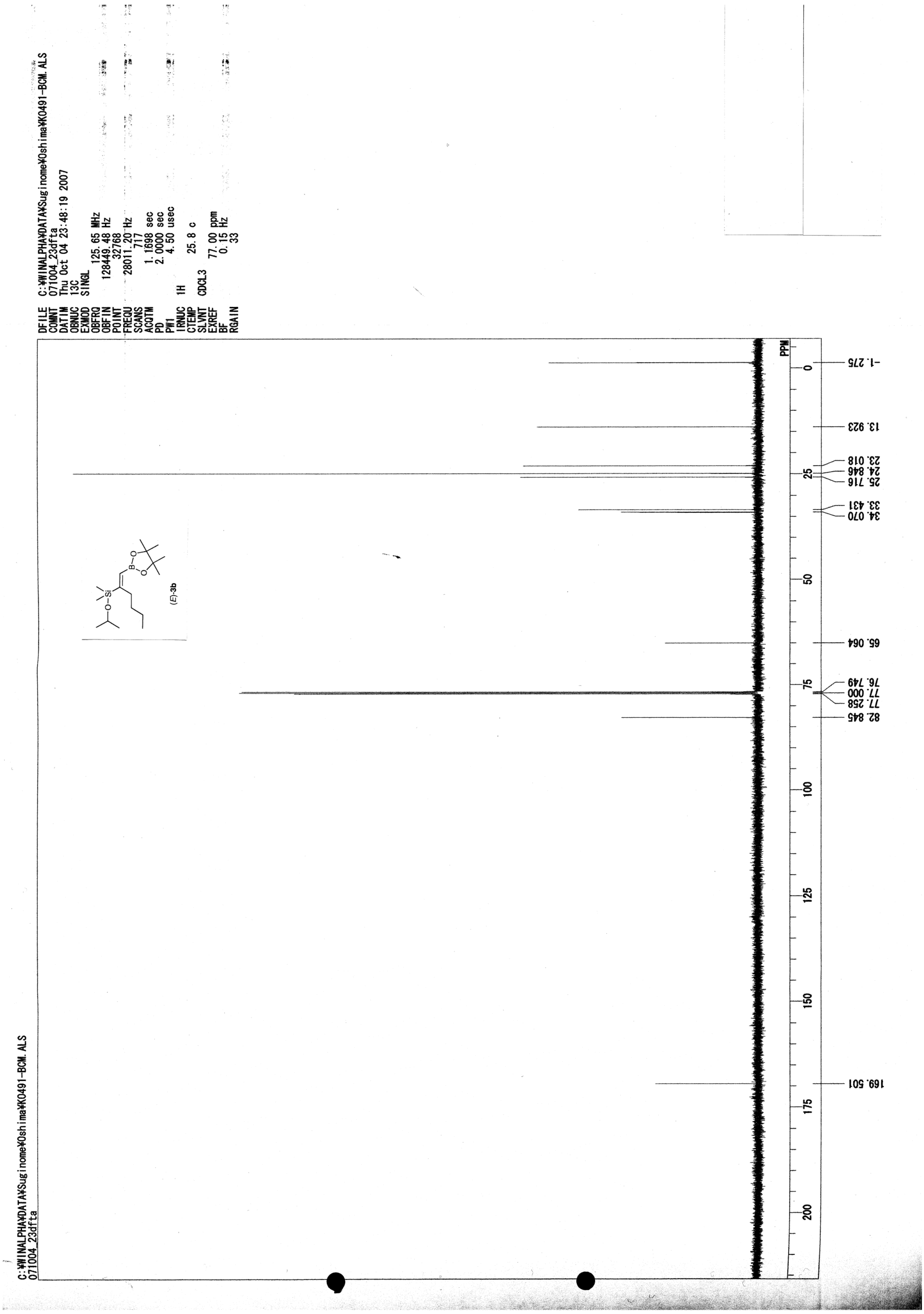
(*E*)-3b



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DATIM   Thu Oct 04 23:48:19 2007
OBNUC   13C
EXMOD   SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        32768
FREQU     28011.20 Hz
SCANS          717
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC   1H
CTEMP         25.8 c
SLVNT   CDCL3
EXREF        77.00 ppm
BF            0.15 Hz
RGAIN           33
```

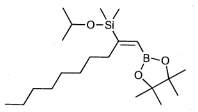
C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0491-BCM.ALS
071004_23dfta

(E)-3b

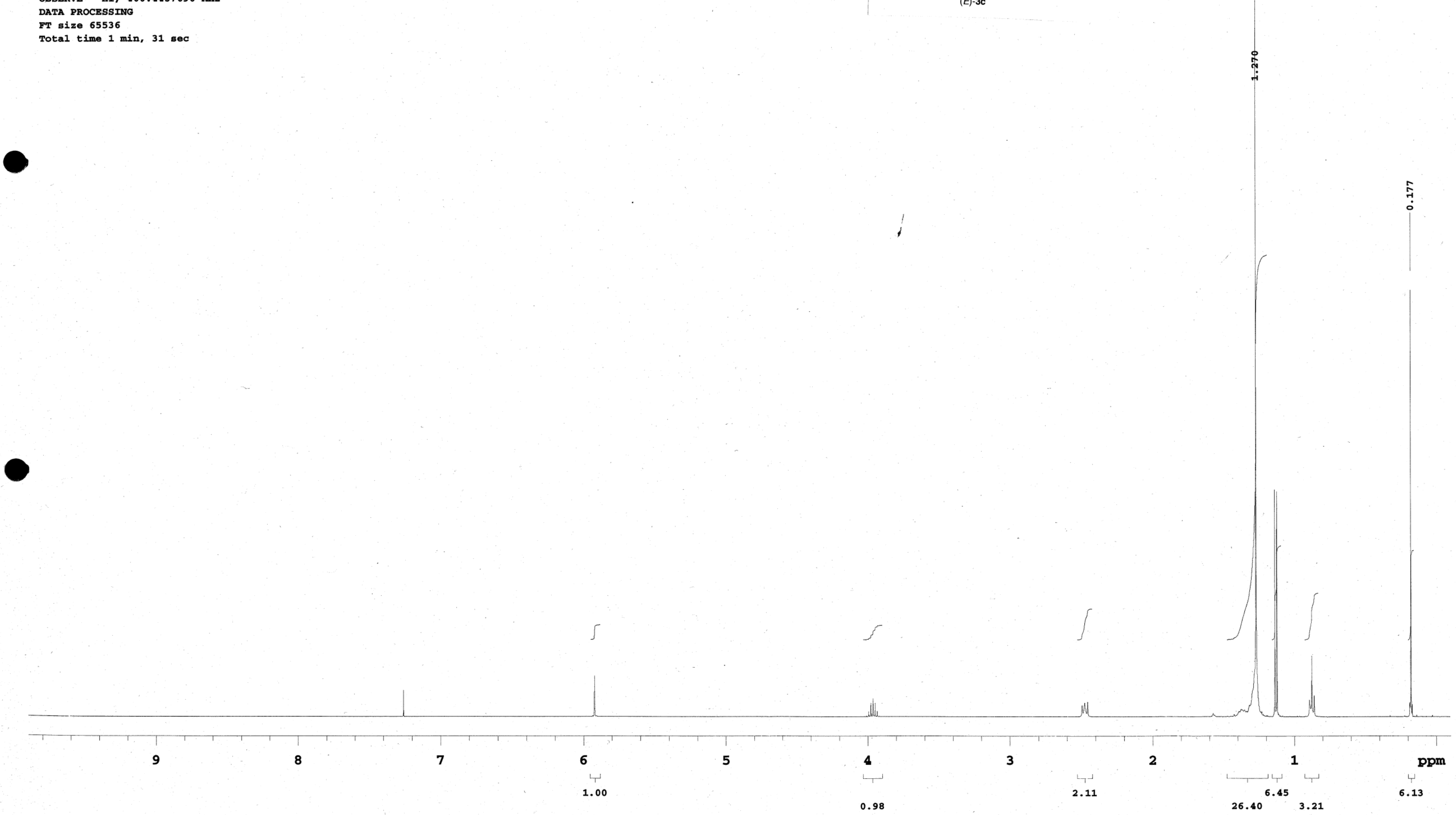
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

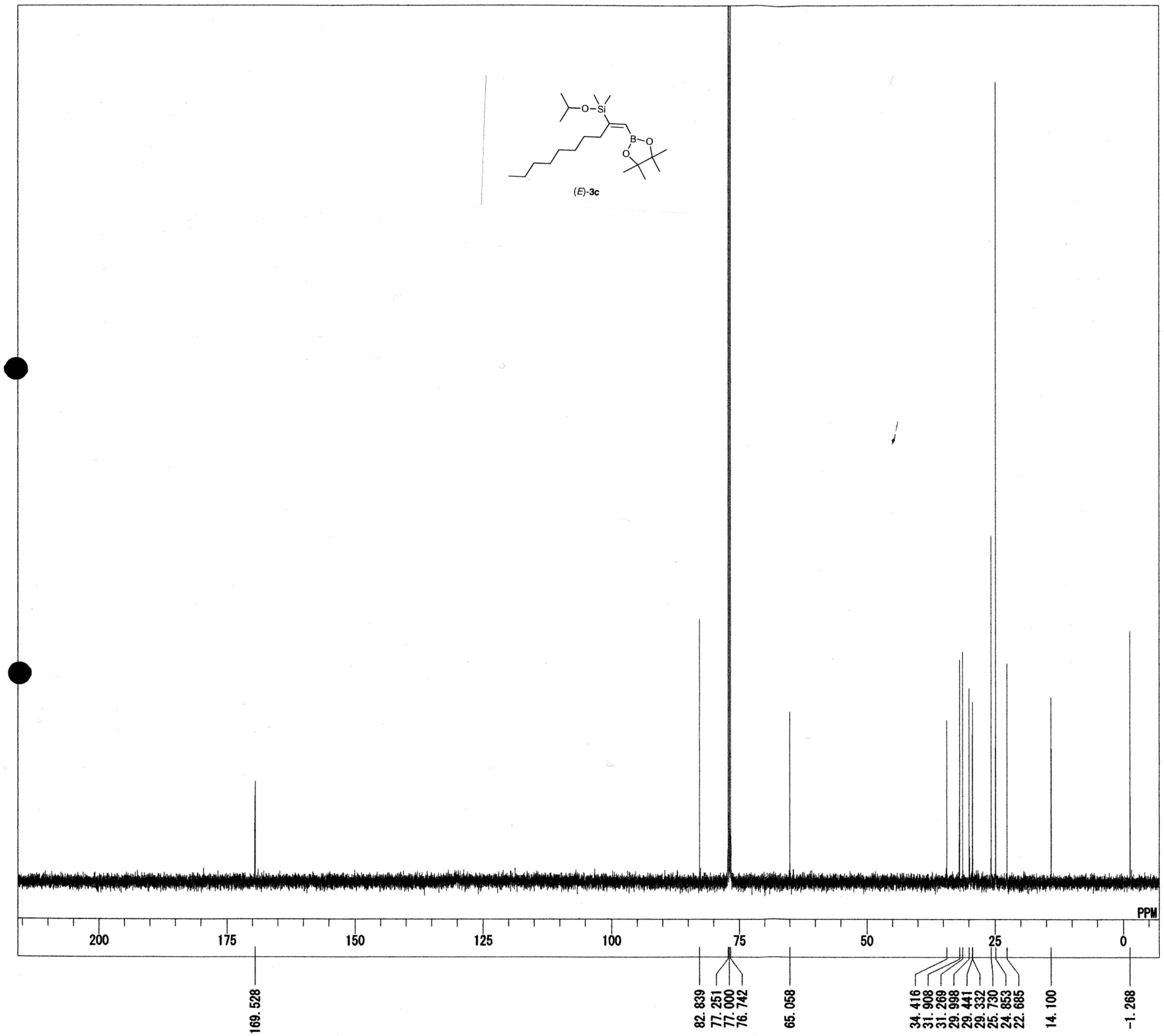
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
16 repetitions
OBSERVE H1, 400.4437690 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec



(*E*)-3c



C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0498-BCM.ALS



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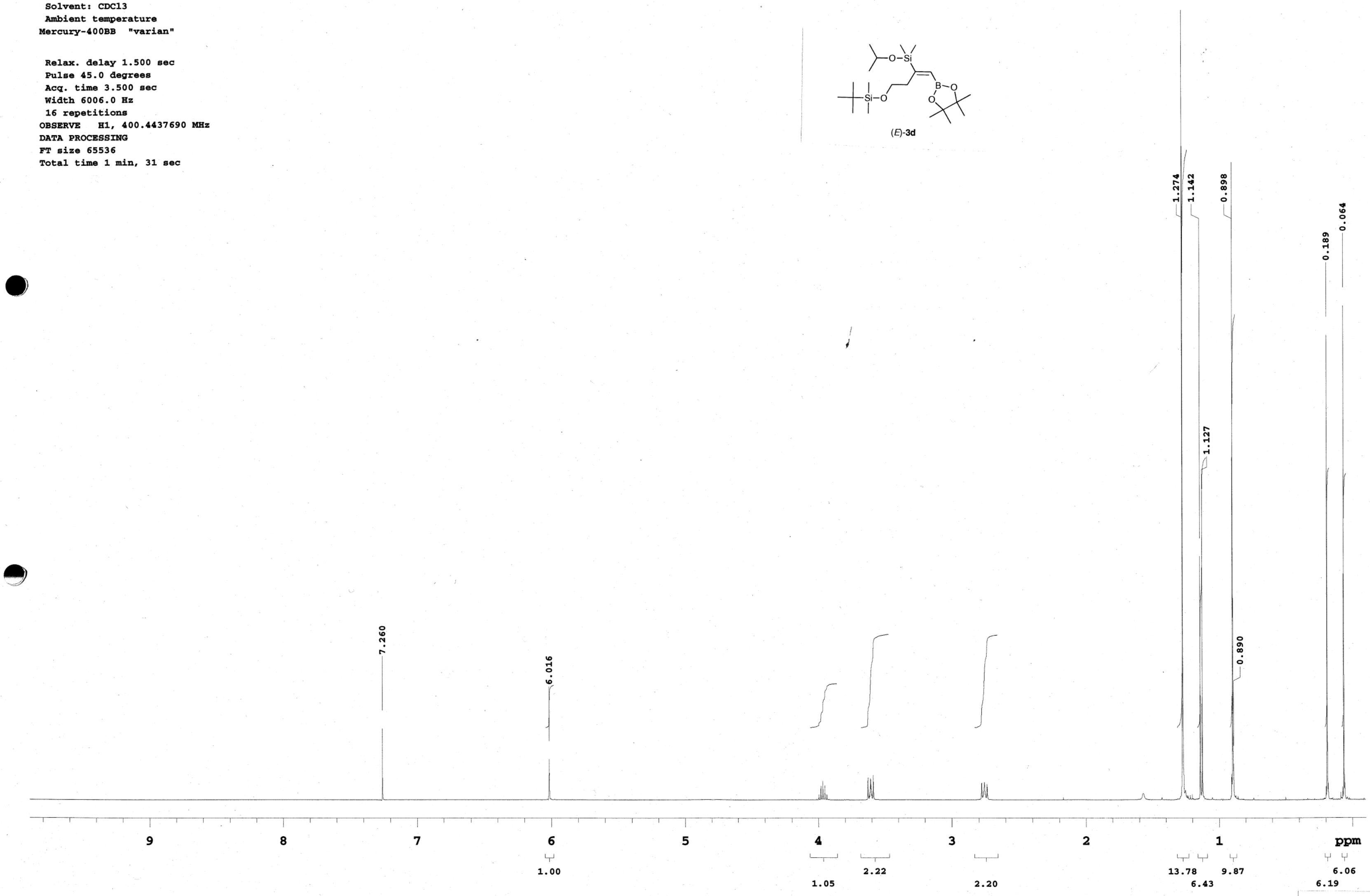
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0498-BCM.ALS
COMNT
DATIM  Fri Oct 12 13:42:17 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        32768
FREQU     28011.20 Hz
SCANS          713
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         26.2 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.43 Hz
RGAIN           35
```

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

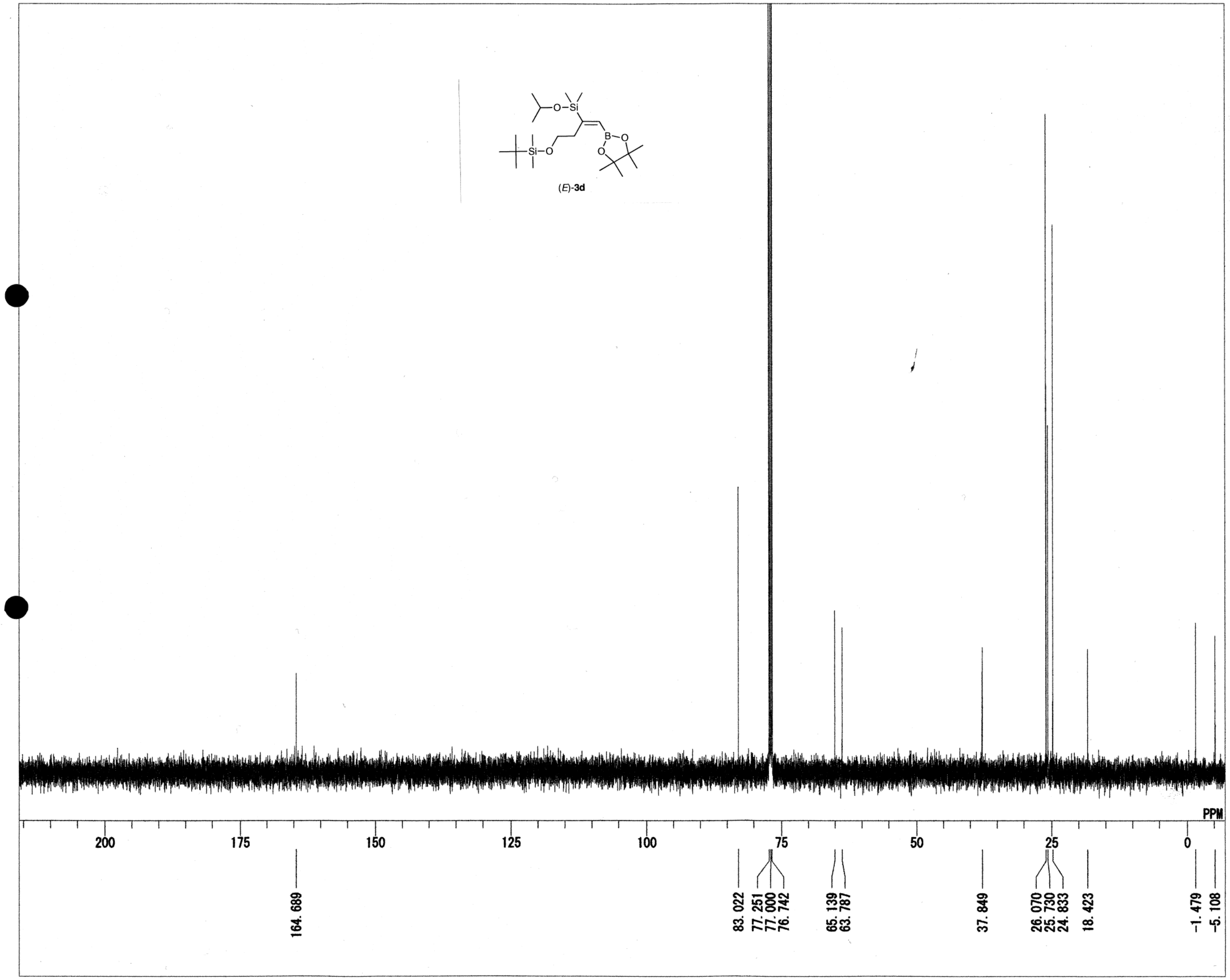
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
16 repetitions
OBSERVE H1, 400.4437690 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec



(E)-3d

C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0452c-BCM.ALS



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DFILE  C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0452c-B
COMNT
DATIM  Wed Sep 26 22:34:00 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        32768
FREQU     28011.20 Hz
SCANS         1753
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         26.0 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.15 Hz
RGAIN           35
```
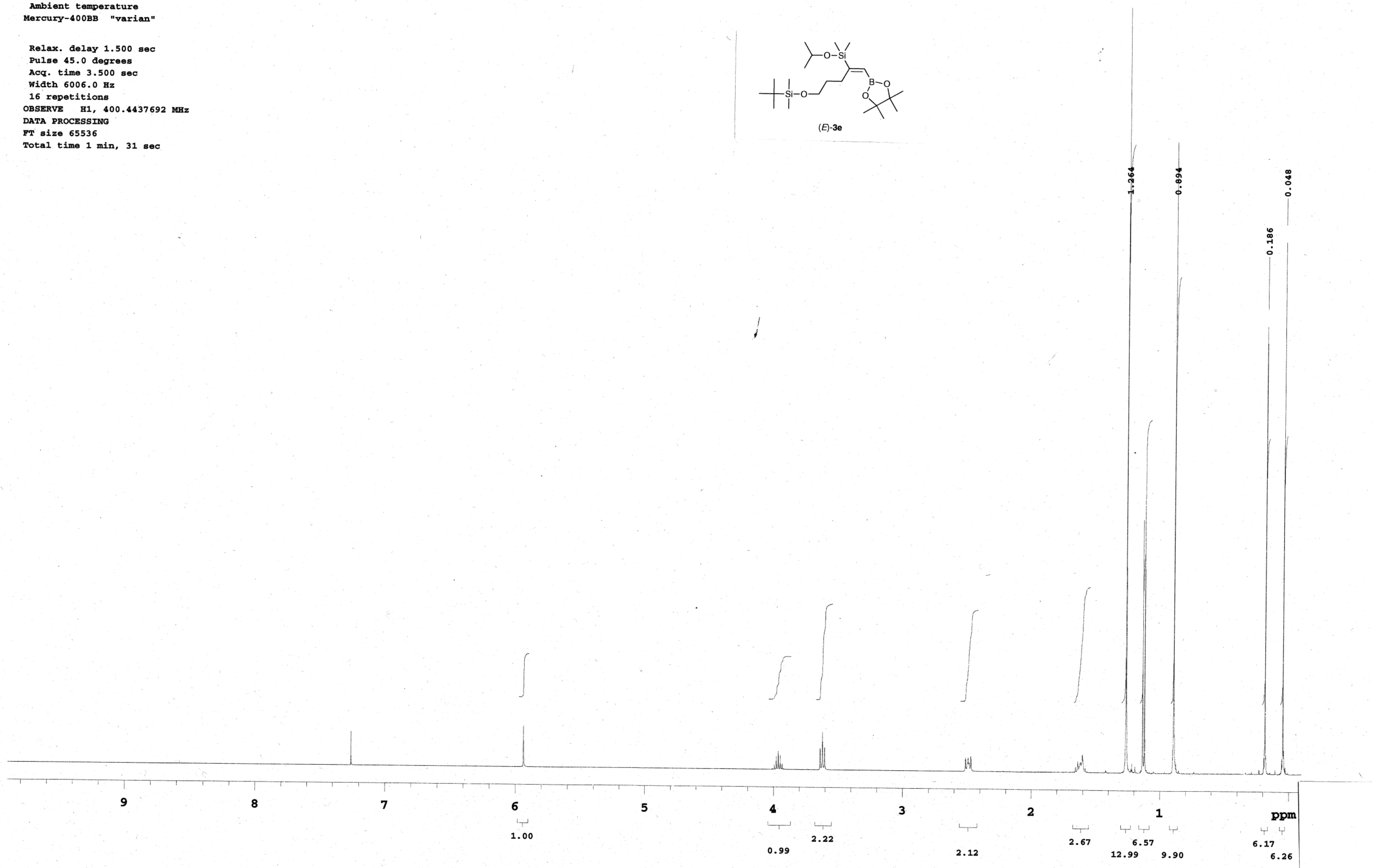
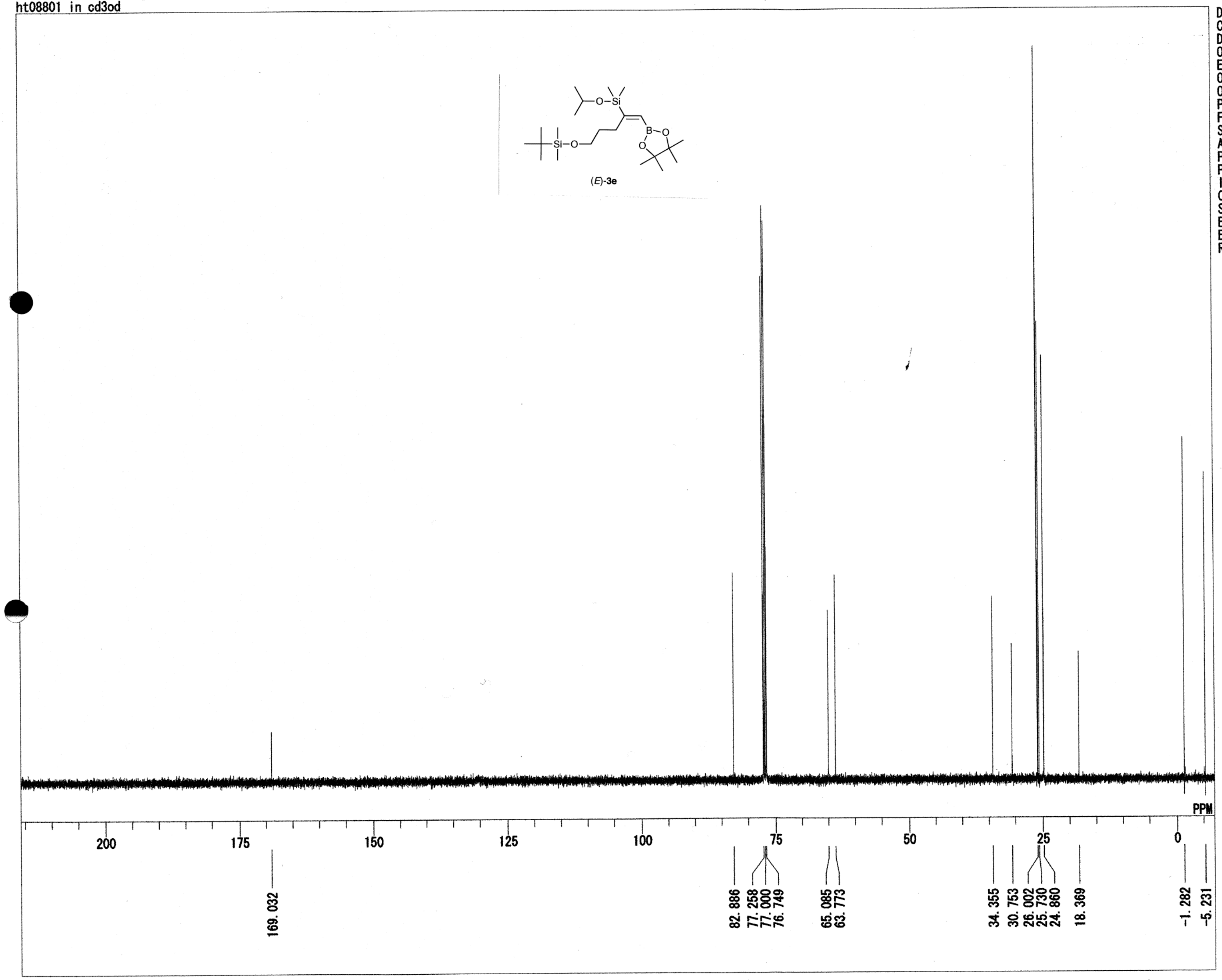

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
16 repetitions
OBSERVE H1, 400.4437692 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec



C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0512-BCM.ALS
ht08801 in cd3od



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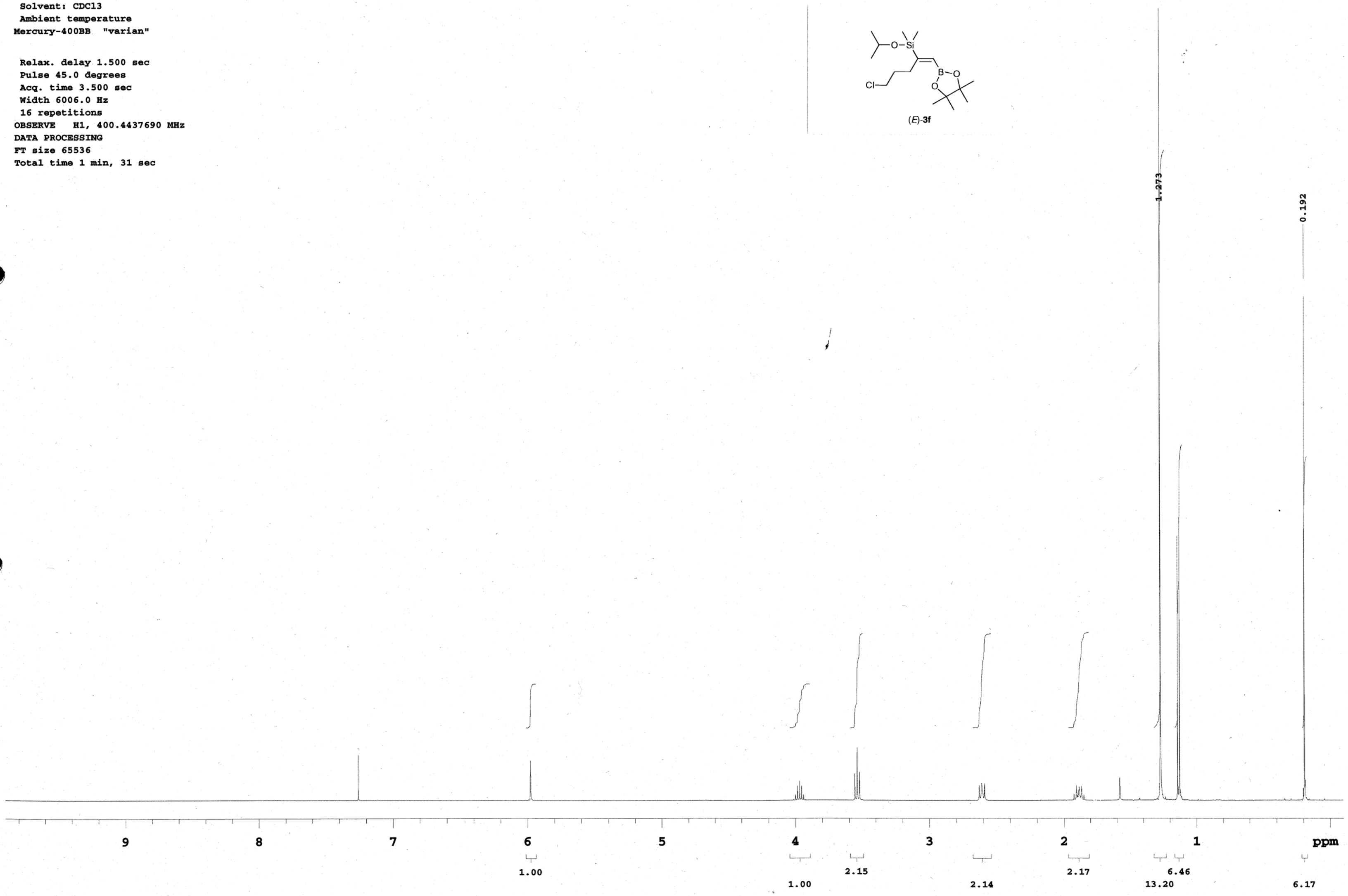
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0512-BC
COMNT  ht08801 in cd3od
DATIM  Fri Oct 19 12:19:57 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        32768
FREQU     28011.20 Hz
SCANS          938
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         25.6 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.15 Hz
RGAIN           35
```

STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
16 repetitions
OBSERVE H1, 400.4437690 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec



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C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0513-BCM.ALS
ht08801 in cd3od
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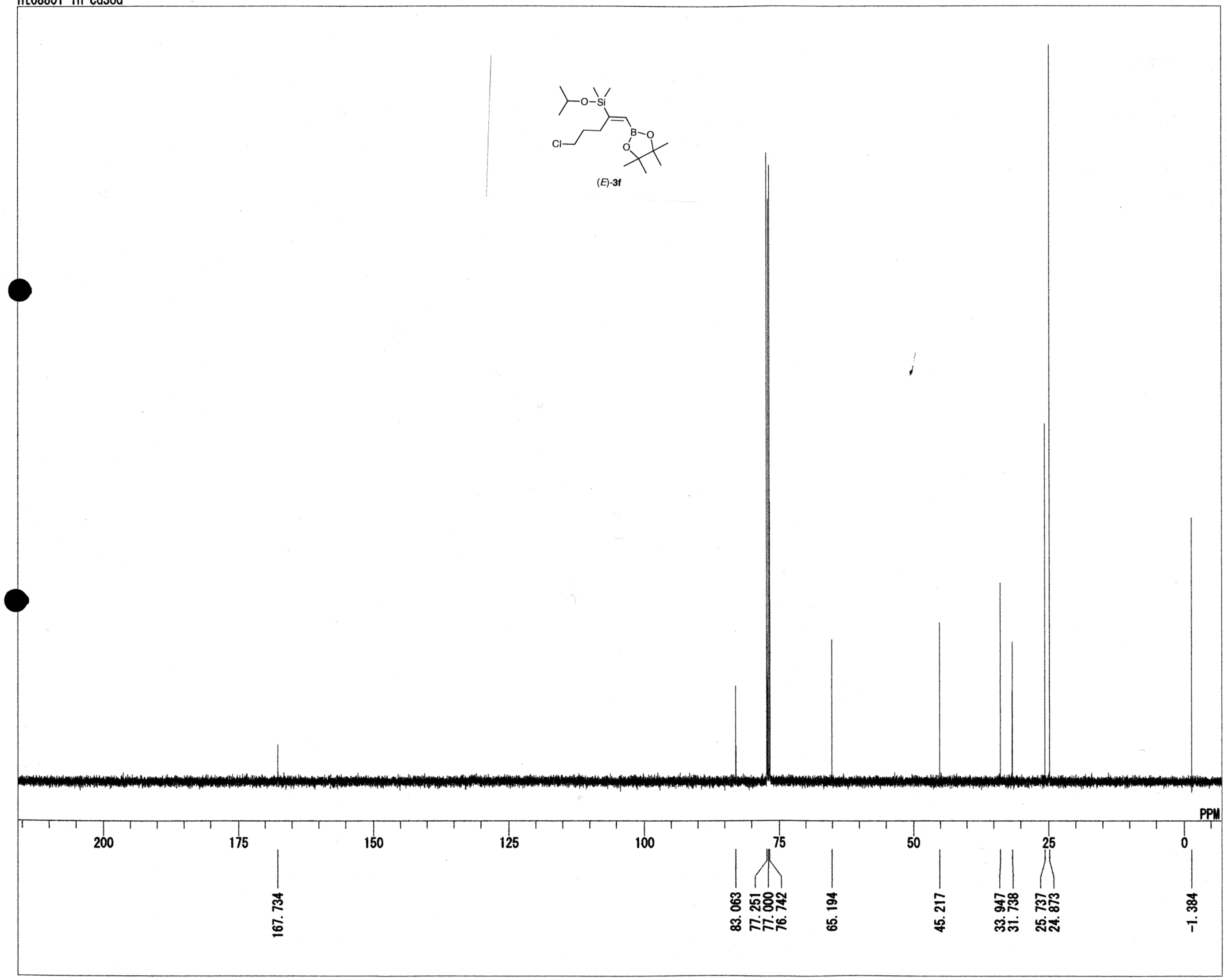

(E)-3f

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DFILE  C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0513-BC
COMNT  ht08801 in cd3od
DATIM  Wed Oct 17 23:28:27 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ        125.65 MHz
OBFIN     128449.48 Hz
POINT         32768
FREQU      28011.20 Hz
SCANS           917
ACQTM        1.1698 sec
PD           2.0000 sec
PW1            4.50 usec
IRNUC  1H
CTEMP          25.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.15 Hz
RGAIN            35
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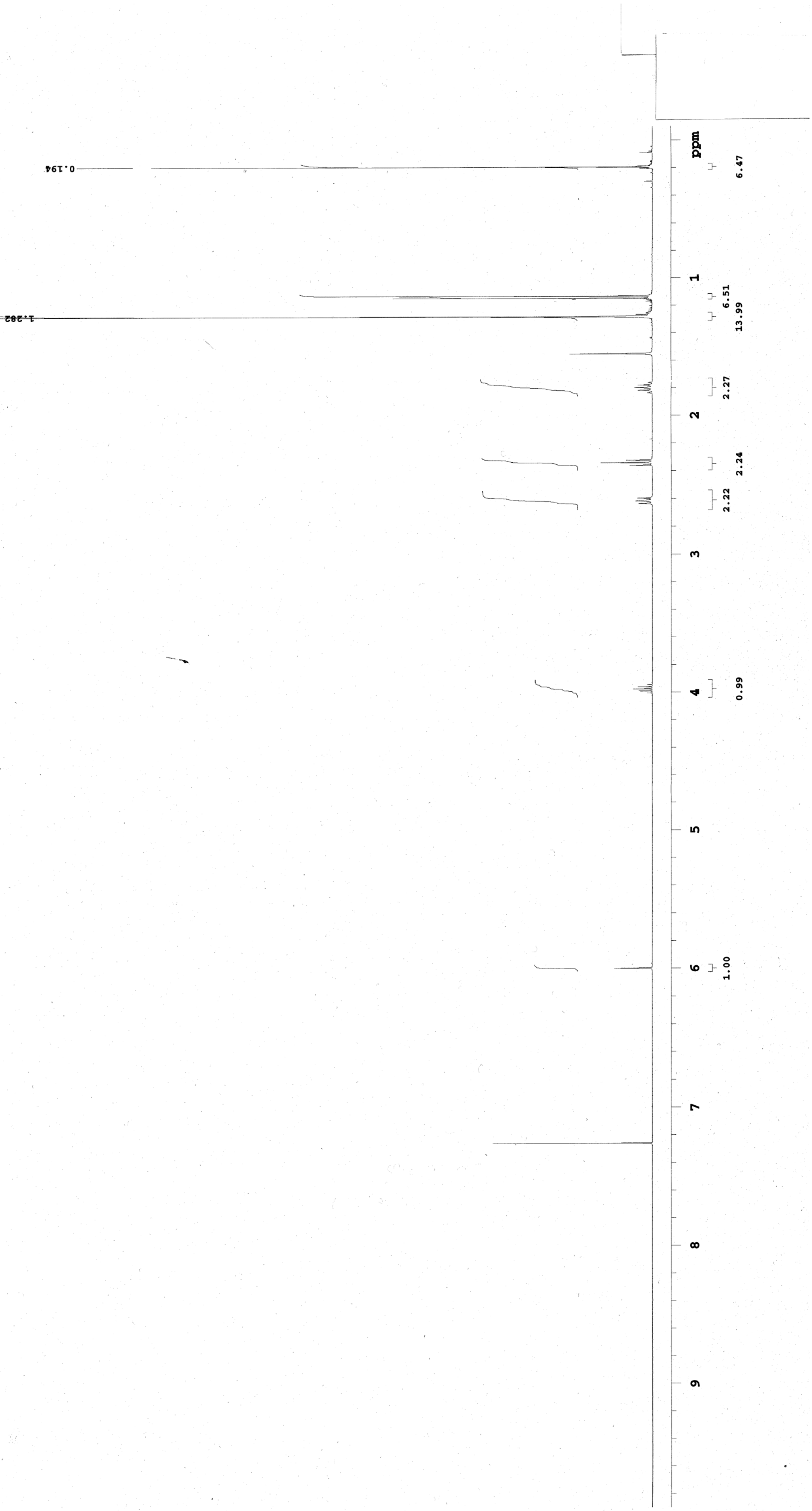
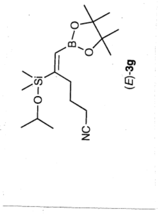




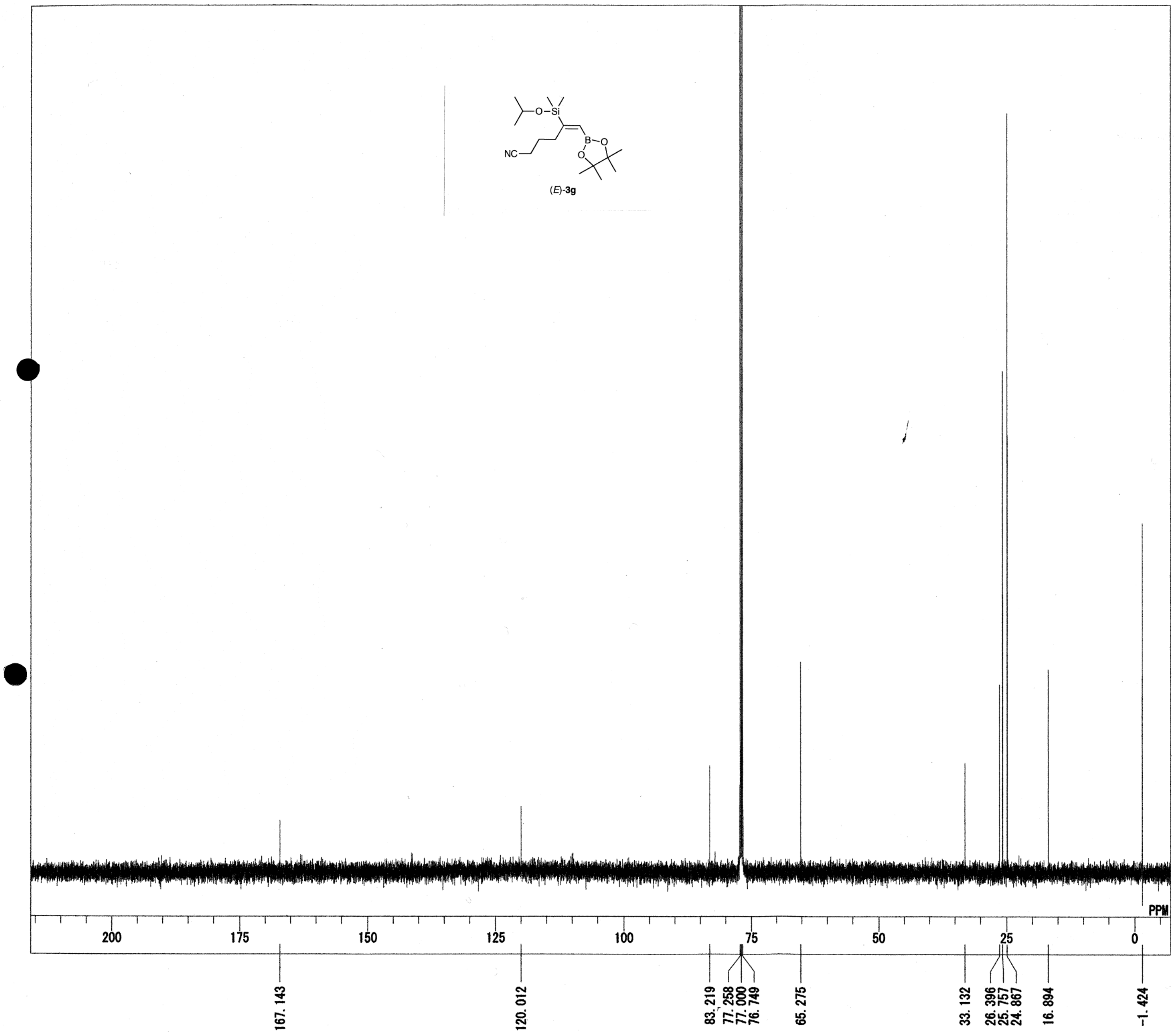
(E)-3g

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
16 repetitions
OBSERVE H1, 400.4437690 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec

```
C:¥WINALPHA¥DATA¥Suginome¥Oshima¥KO496-BCM.ALS
```



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DFILE   C:¥WINALPHA¥DATA¥Suginome¥Oshima¥KO496-BCM.ALS
COMNT
DATIM   Sat Oct 13 00:33:28 2007
OBNUC   13C
EXMOD   SINGL
OBFRQ         125.65 MHz
OBFIN      128449.48 Hz
POINT          32768
FREQU       28011.20 Hz
SCANS           4893
ACQTM         1.1698 sec
PD            2.0000 sec
PW1             4.50 usec
IRNUC   1H
CTEMP           25.6 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.09 Hz
RGAIN             35
```
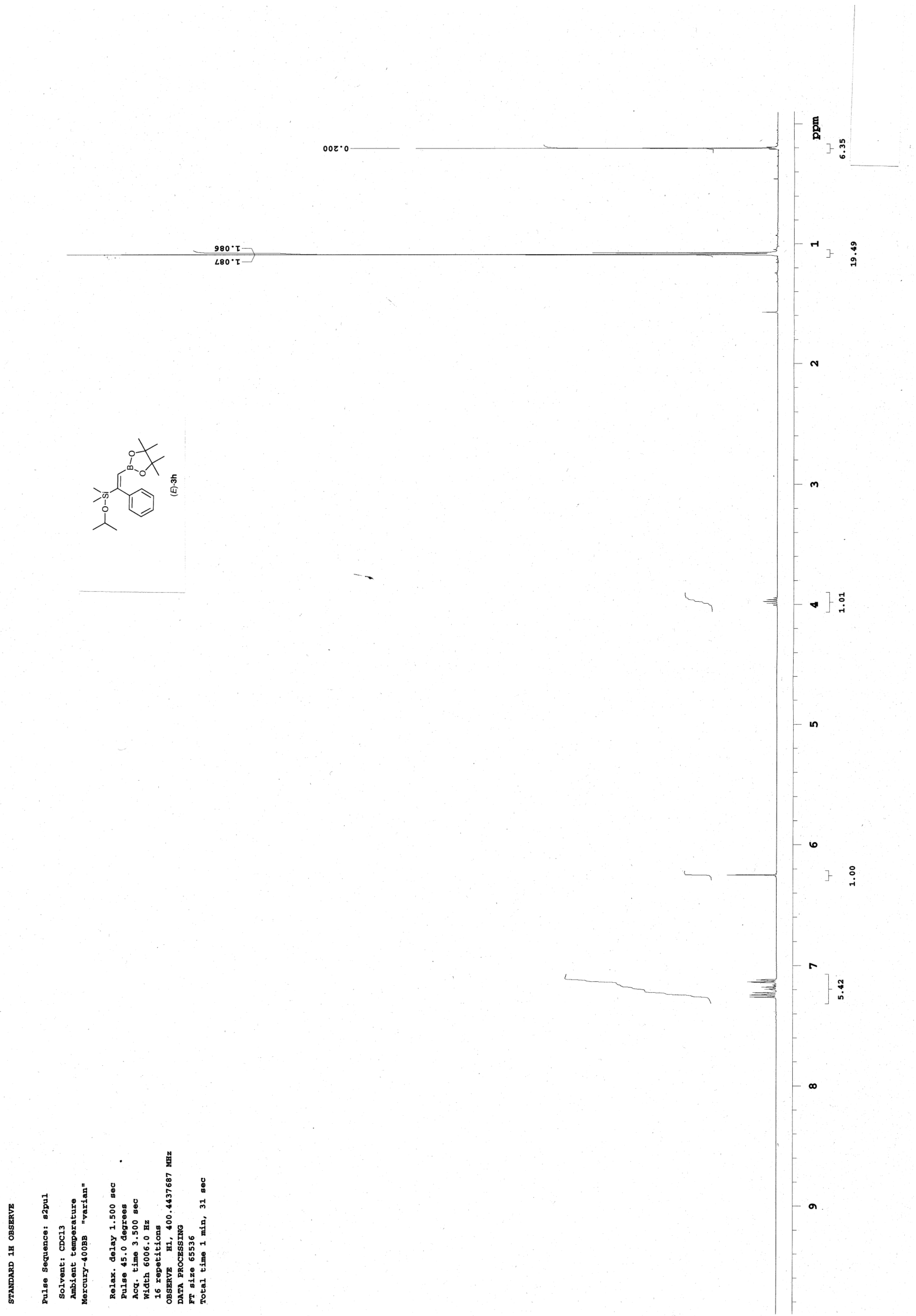



(E)-3h

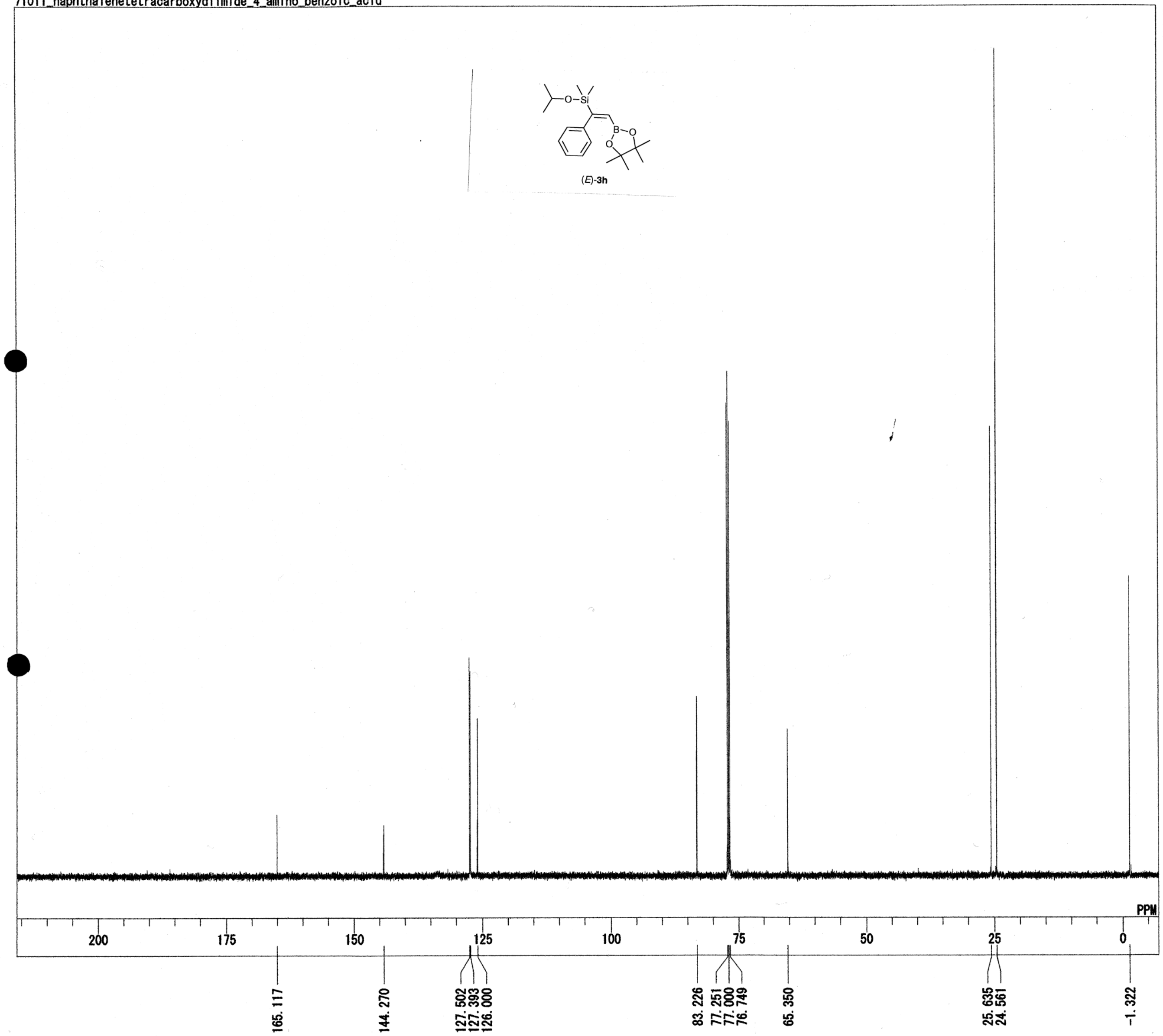
STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
16 repetitions
OBSERVE H1, 400.4437687 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec

C:¥WINALPHA¥DATA¥Suginome¥Oshima¥KO492-BCM.ALS
71011_naphthalenetetracarboxydiimide_4_amino_benzoic_acid



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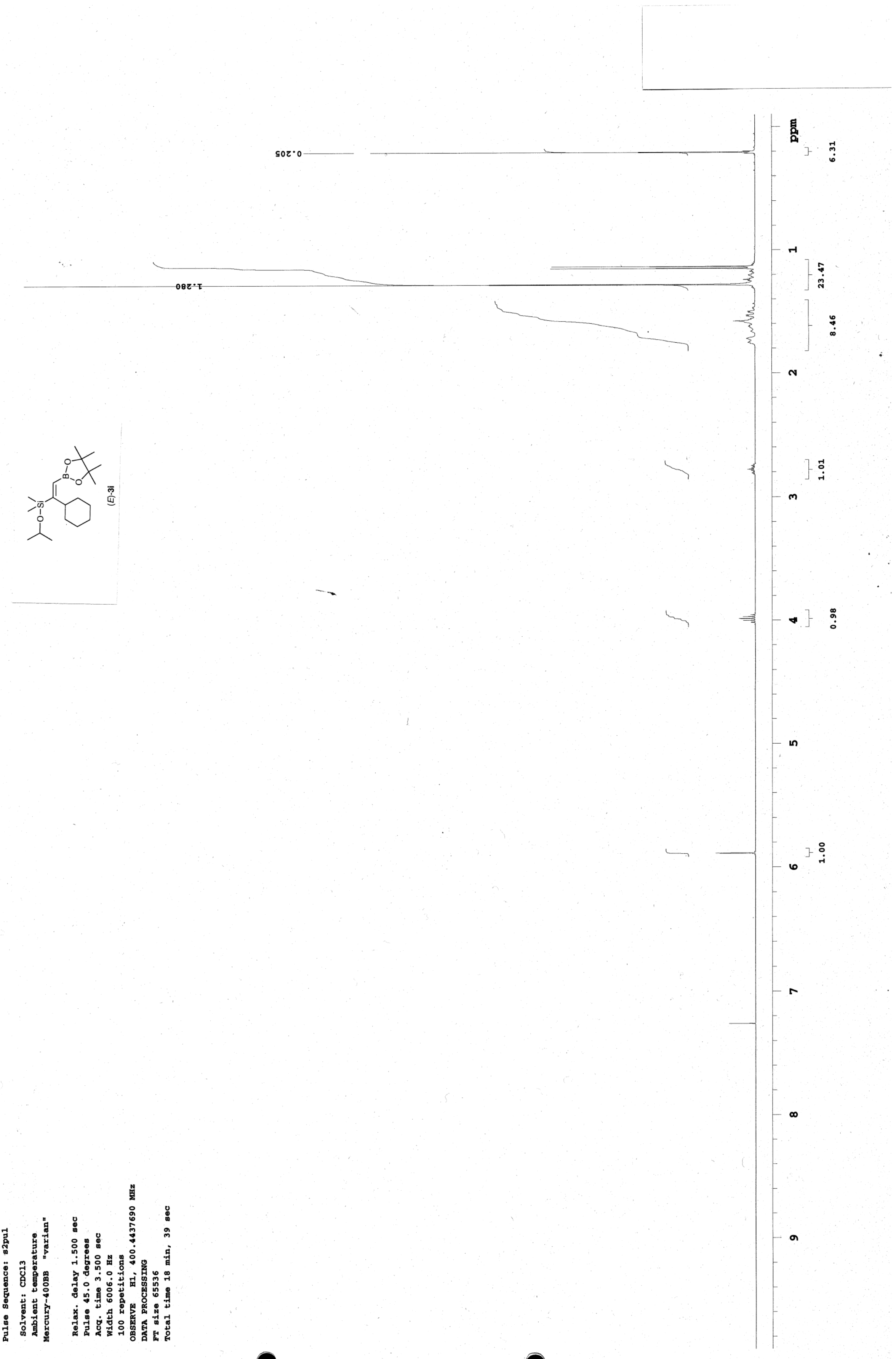
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Oshima¥KO492-BCM.ALS
COMNT  71011_naphthalenetetracarboxydiimide_4_amino_be
DATIM  Thu Oct 11 16:44:48 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        32768
FREQU     28011.20 Hz
SCANS          925
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         26.7 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.43 Hz
RGAIN           35
```

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
100 repetitions
OBSERVE H1, 400.4437690 MHz
DATA PROCESSING
FT size 65536
Total time 18 min, 39 sec



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C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0483-BCM.ALS
71011_naphthalenetetracarboxydiimide_4_amino_benzoic_acid
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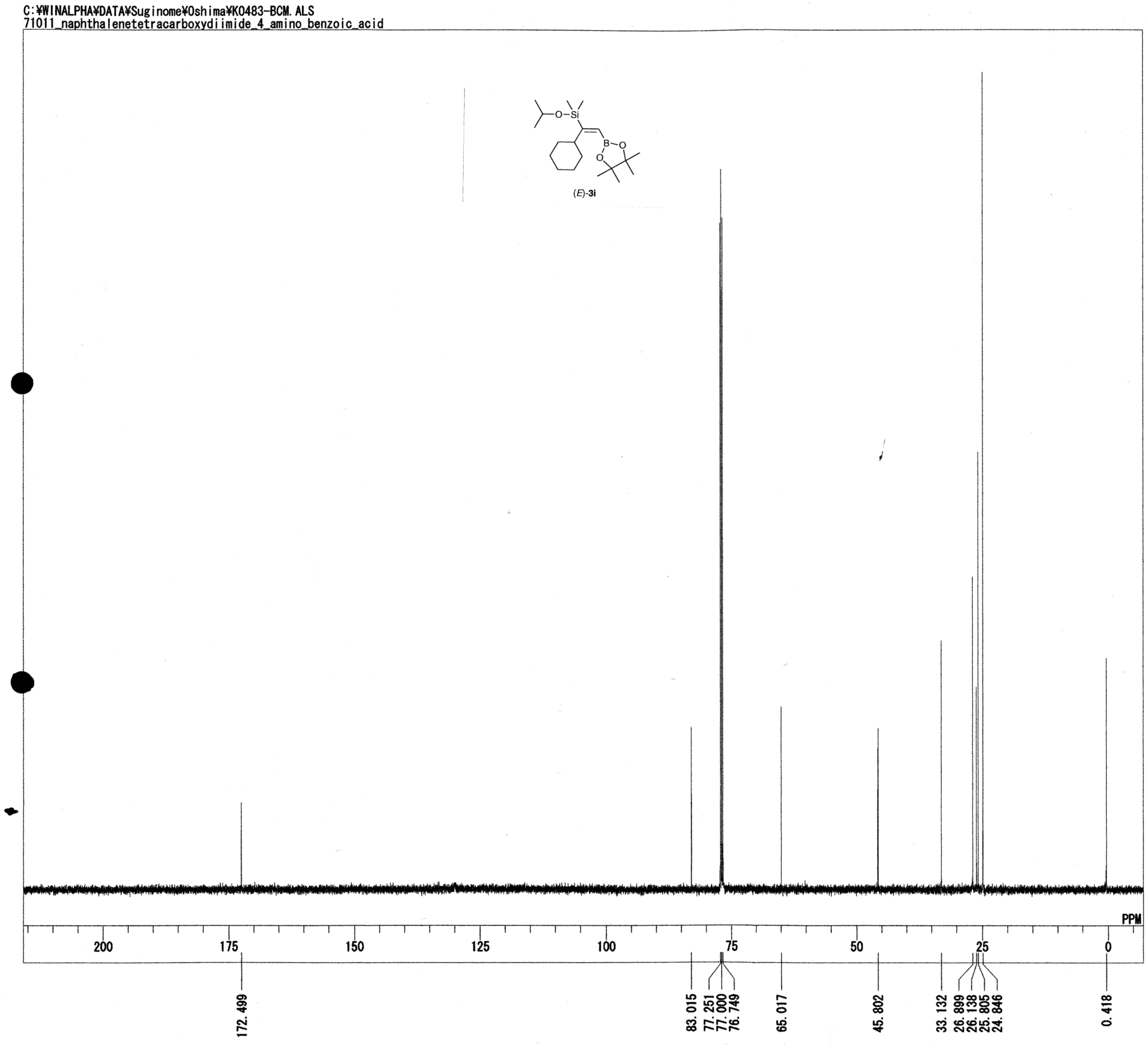

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DFILE  C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0483-BCM.ALS
COMNT  71011_naphthalenetetracarboxydiimide_4_amino_be
DATIM  Thu Oct 11 15:41:49 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        32768
FREQU     28011.20 Hz
SCANS         1181
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         26.5 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.43 Hz
RGAIN           35
```
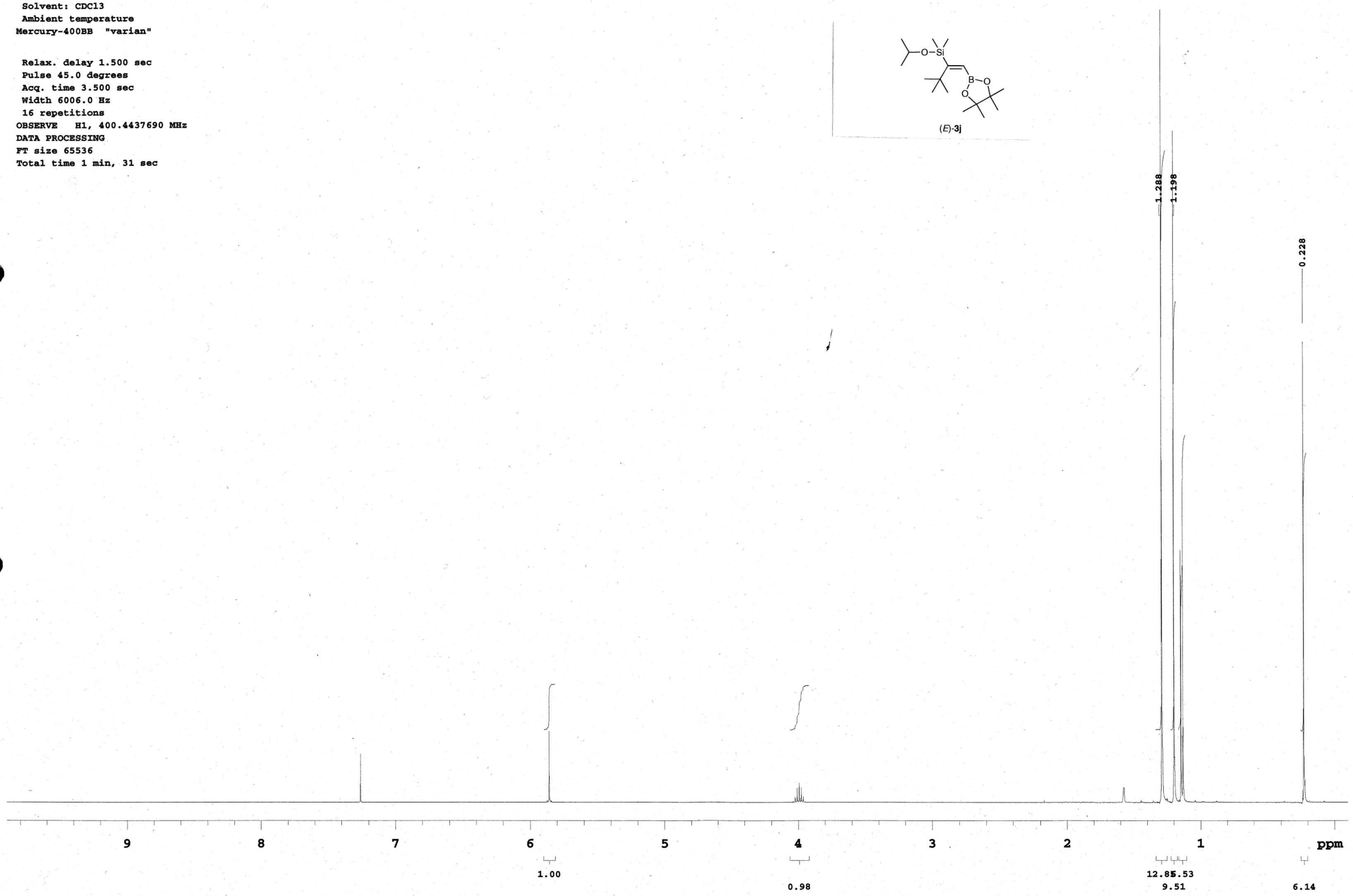
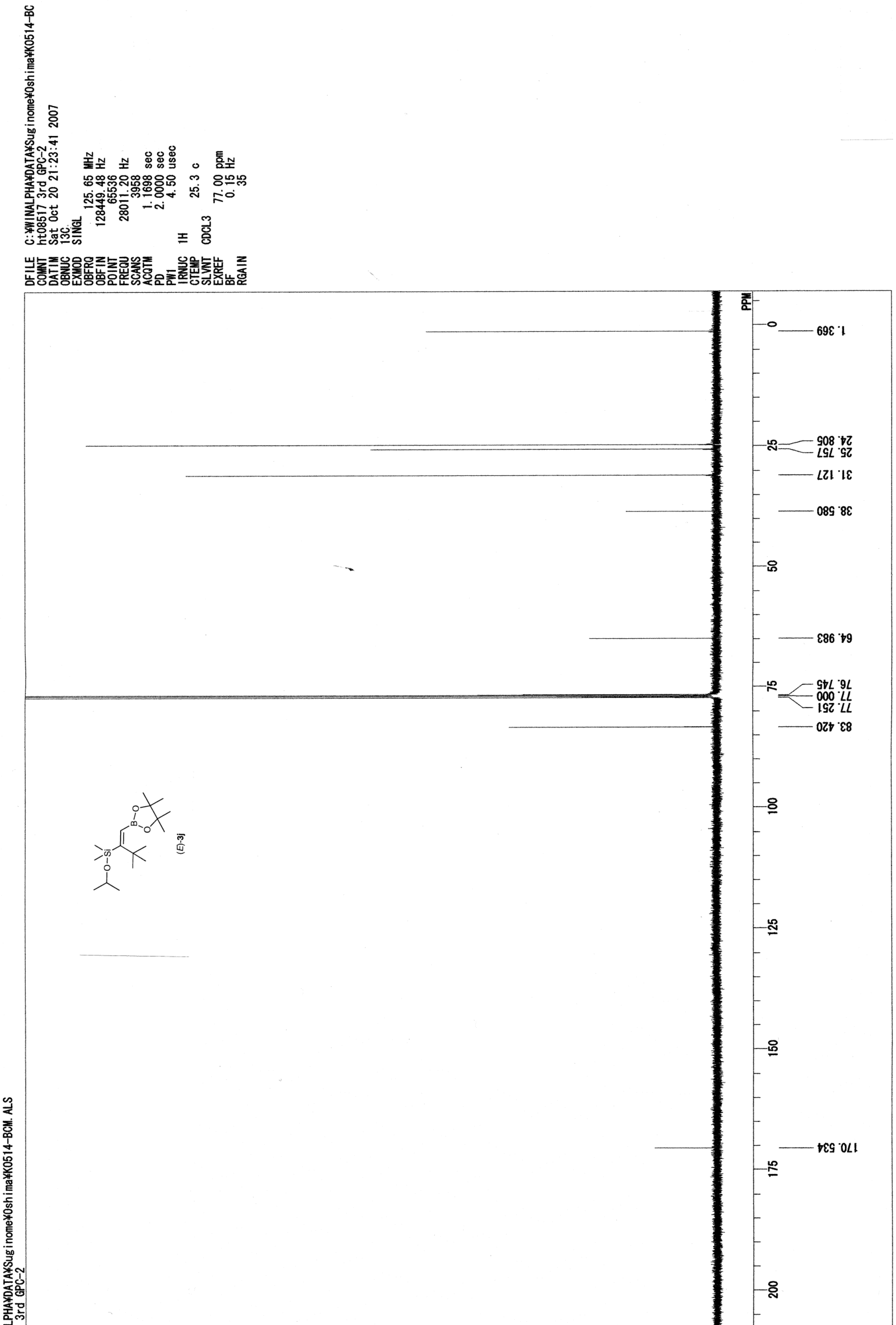

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

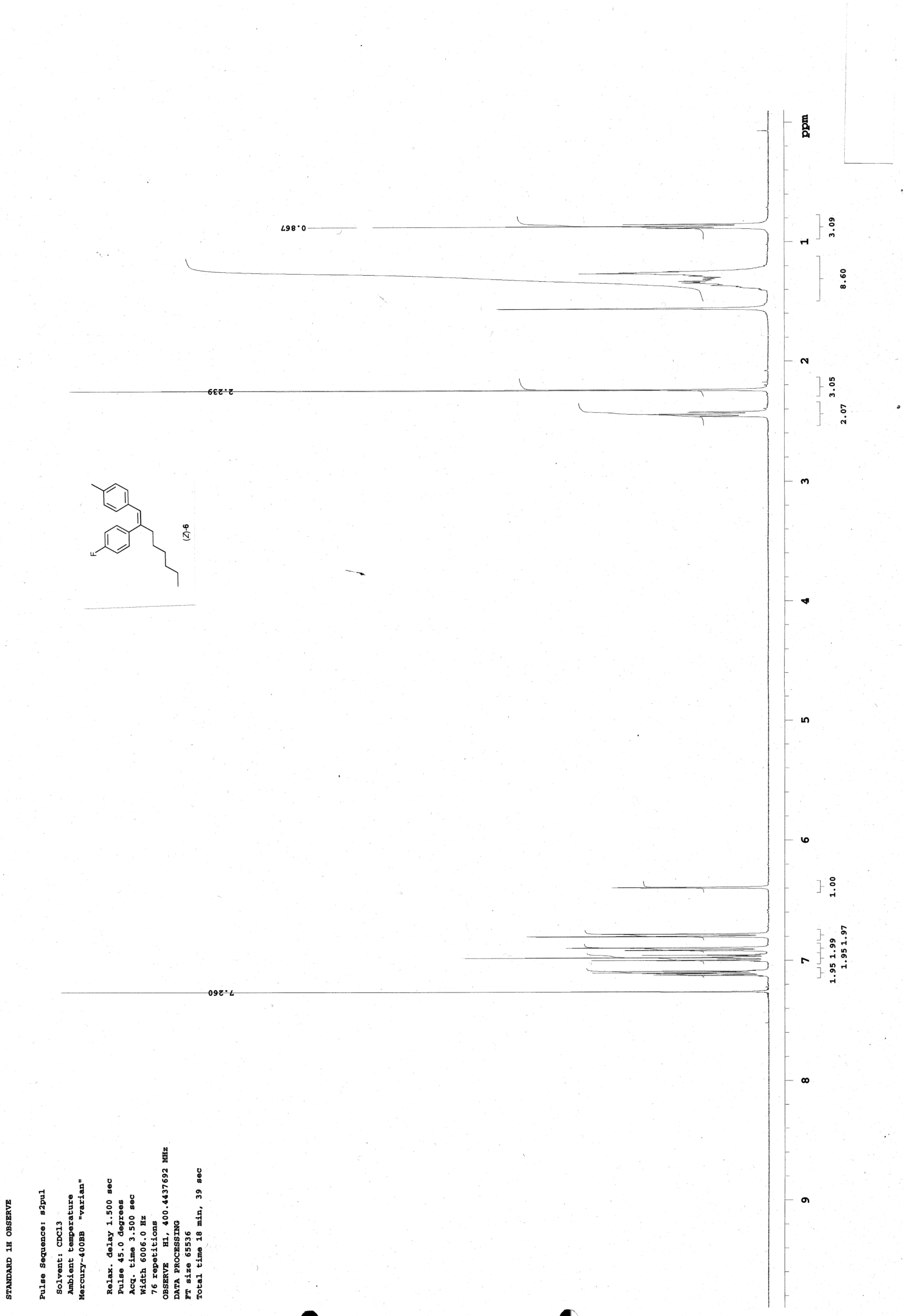
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
16 repetitions
OBSERVE H1, 400.4437690 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec





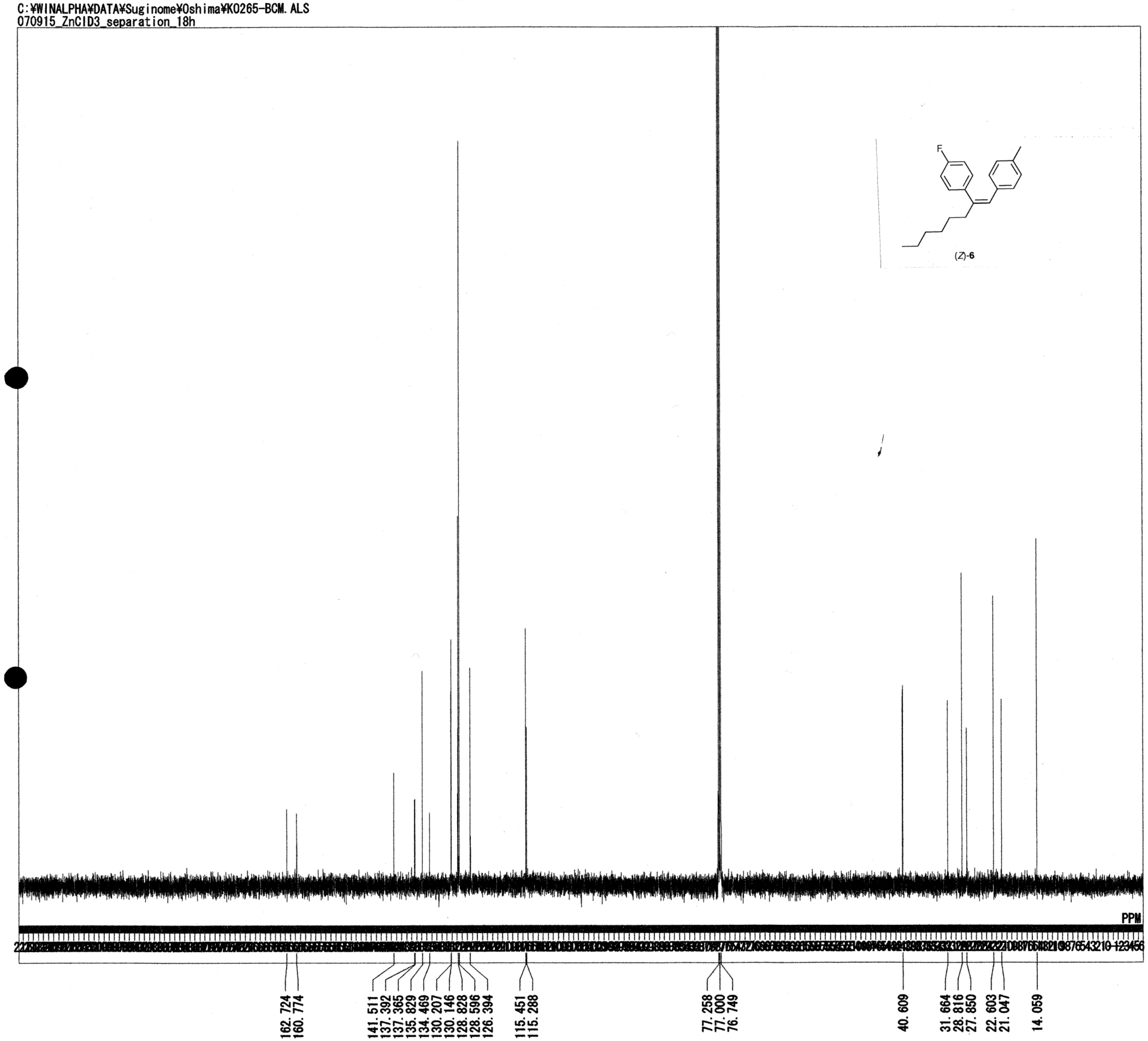
```
DFILE   C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0514-BC
COMNT   ht08517 3rd GPC-2
DATIM   Sat Oct 20 21:23:41 2007
OBNUC   13C
EXMOD   SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        65536
FREQU     28011.20 Hz
SCANS         3958
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC   1H
CTEMP         25.3 c
SLVNT   CDCL3
EXREF        77.00 ppm
BF            0.15 Hz
RGAIN           35
```

```
C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0514-BCM.ALS
ht08517 3rd GPC-2
```

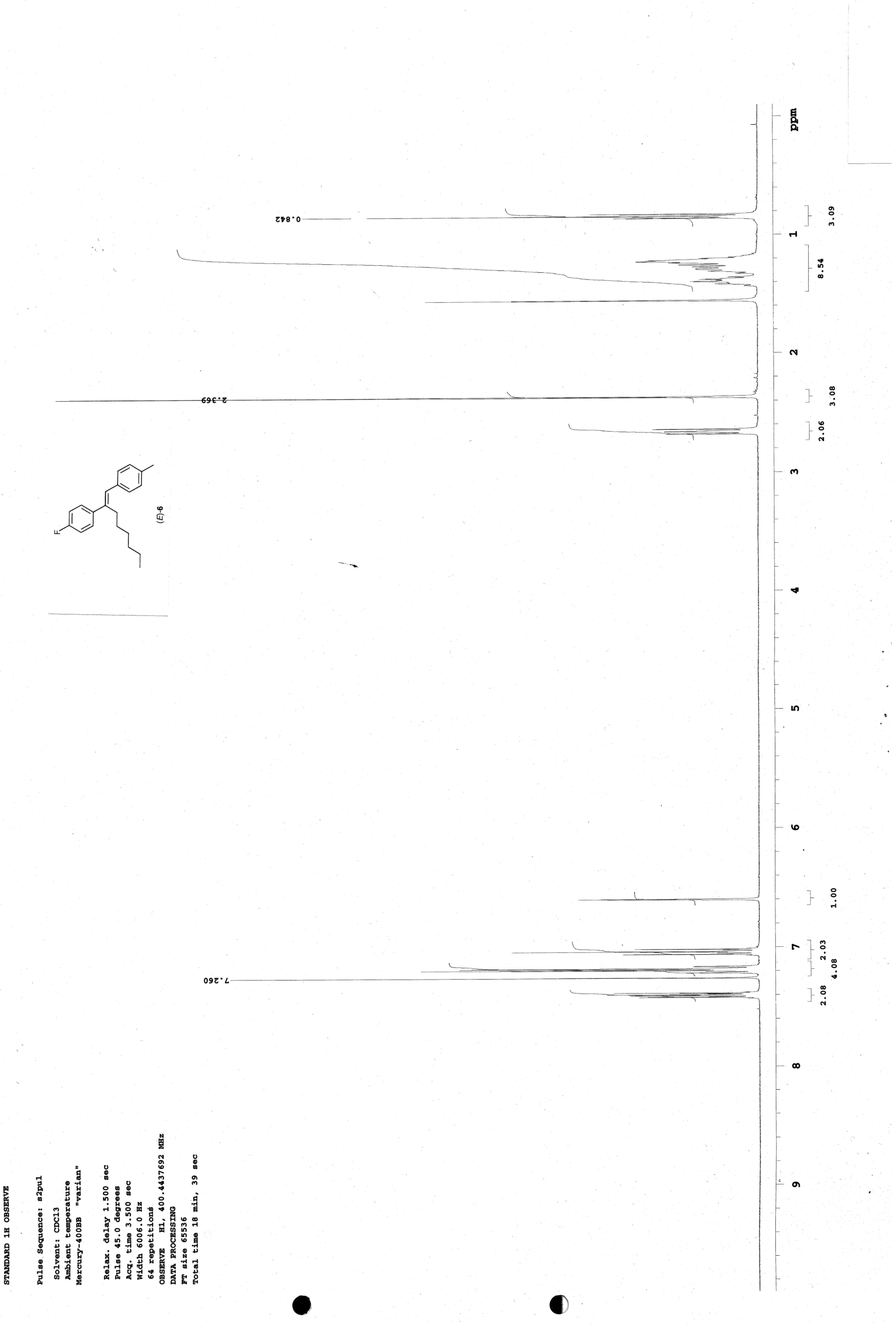


```
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
76 repetitions
OBSERVE   H1, 400.4437692 MHz
DATA PROCESSING
FT size 65536
Total time 18 min, 39 sec
```

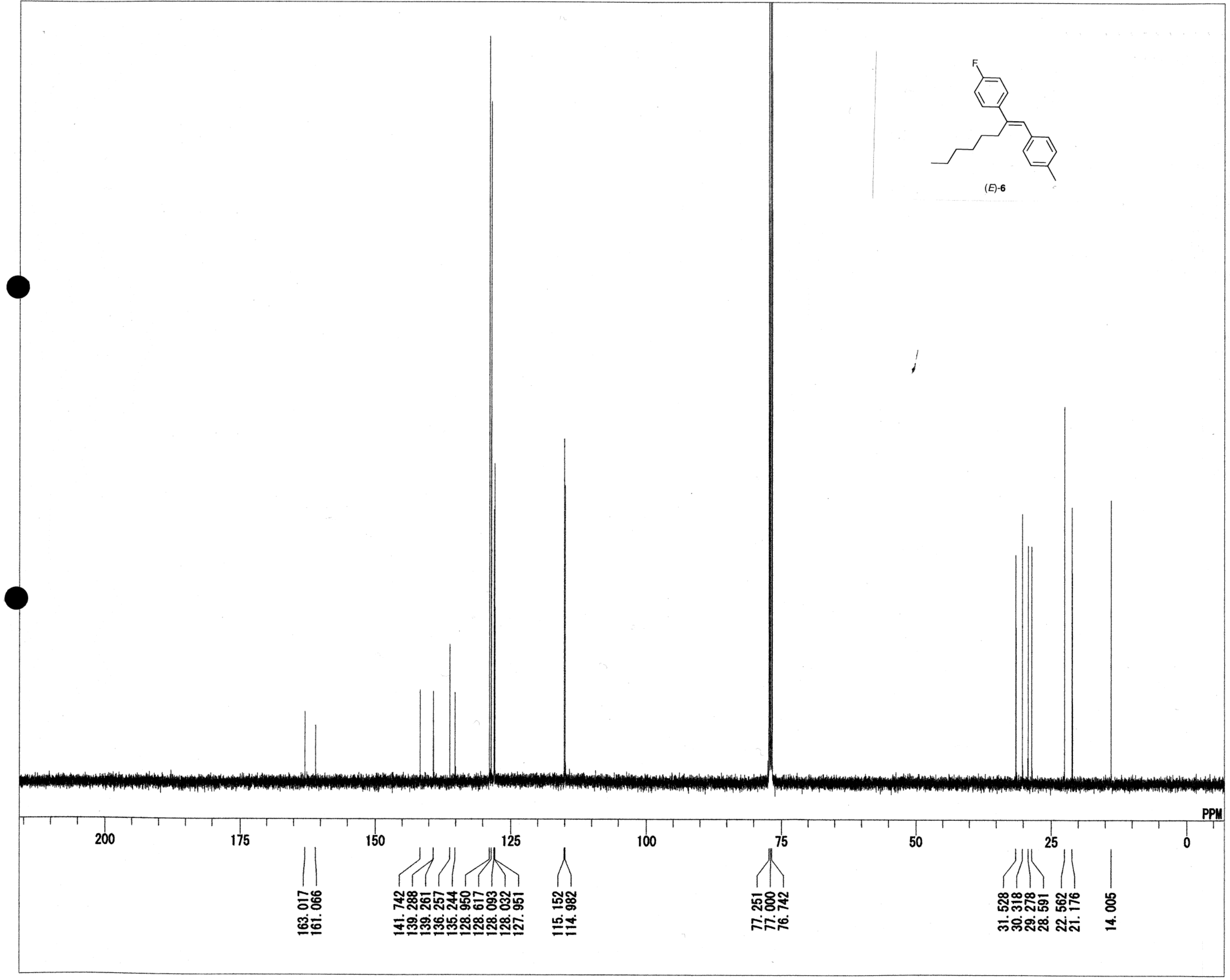
C:¥WINALPHA¥DATA¥Suginome¥Oshima¥KO265-BCM.ALS
070915_ZnClD3_separation_18h



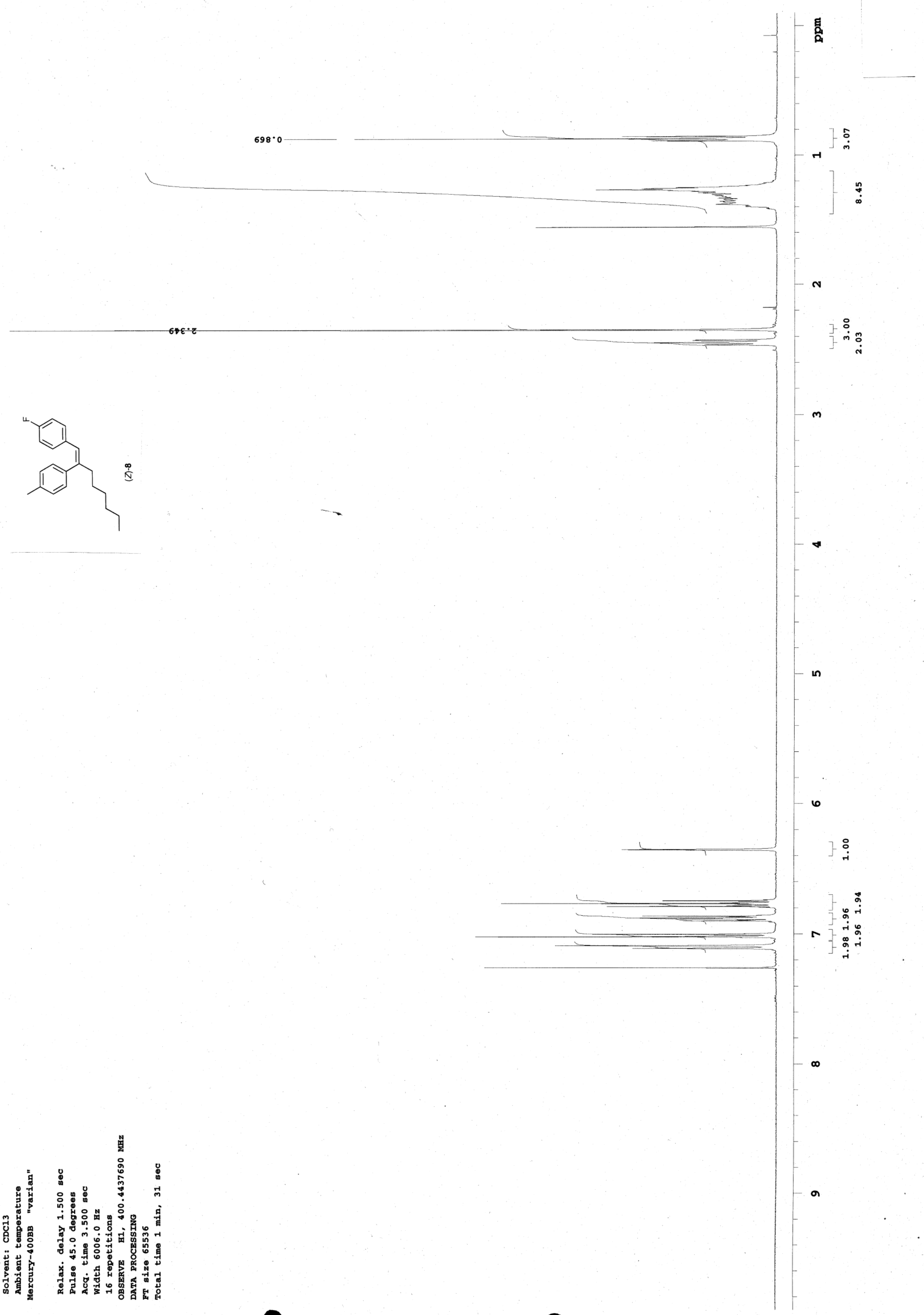
```
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Oshima¥KO265-BCM.ALS
COMNT  070915_ZnClD3_separation_18h
DATIM  Sun Sep 16 05:23:43 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        32768
FREQU     28011.20 Hz
SCANS         2065
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         26.2 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.16 Hz
RGAIN           35
```


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
64 repetitions
OBSERVE H1, 400.4437692 MHz
DATA PROCESSING
FT size 65536
Total time 18 min, 39 sec
F
(E)-6
0.842
2.369
7.260
ppm
1
2
3
4
5
6
7
8
9
3.09
8.54
3.08
2.06
1.00
2.03
4.08
2.08

```
C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0267-BCM1.ALS
071019-tt-020-2
```

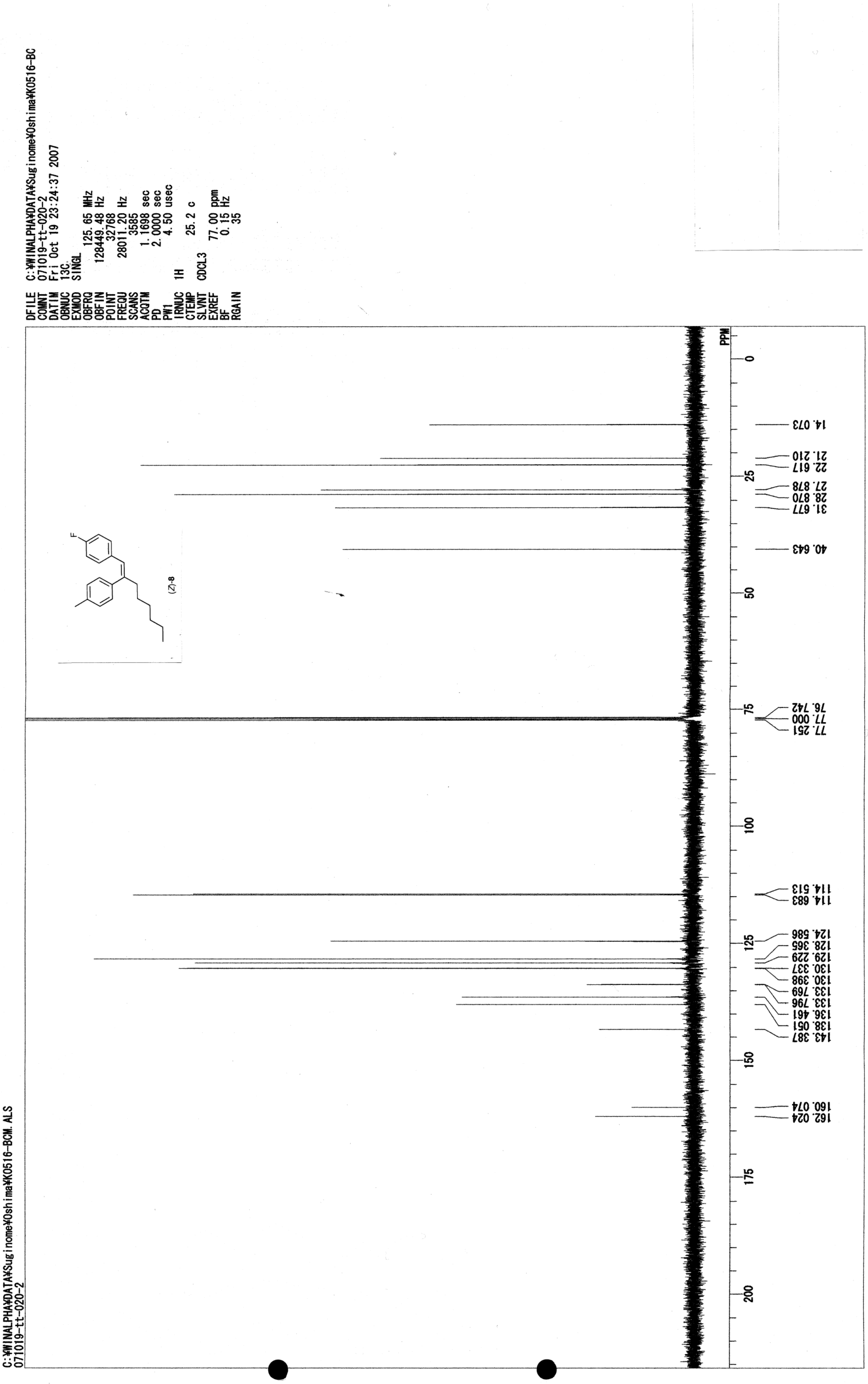


```
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0267-BC
COMNT  071019-tt-020-2
DATIM  Sat Oct 20 09:10:36 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        32768
FREQU     28011.20 Hz
SCANS        10817
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         25.1 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.15 Hz
RGAIN           35
```



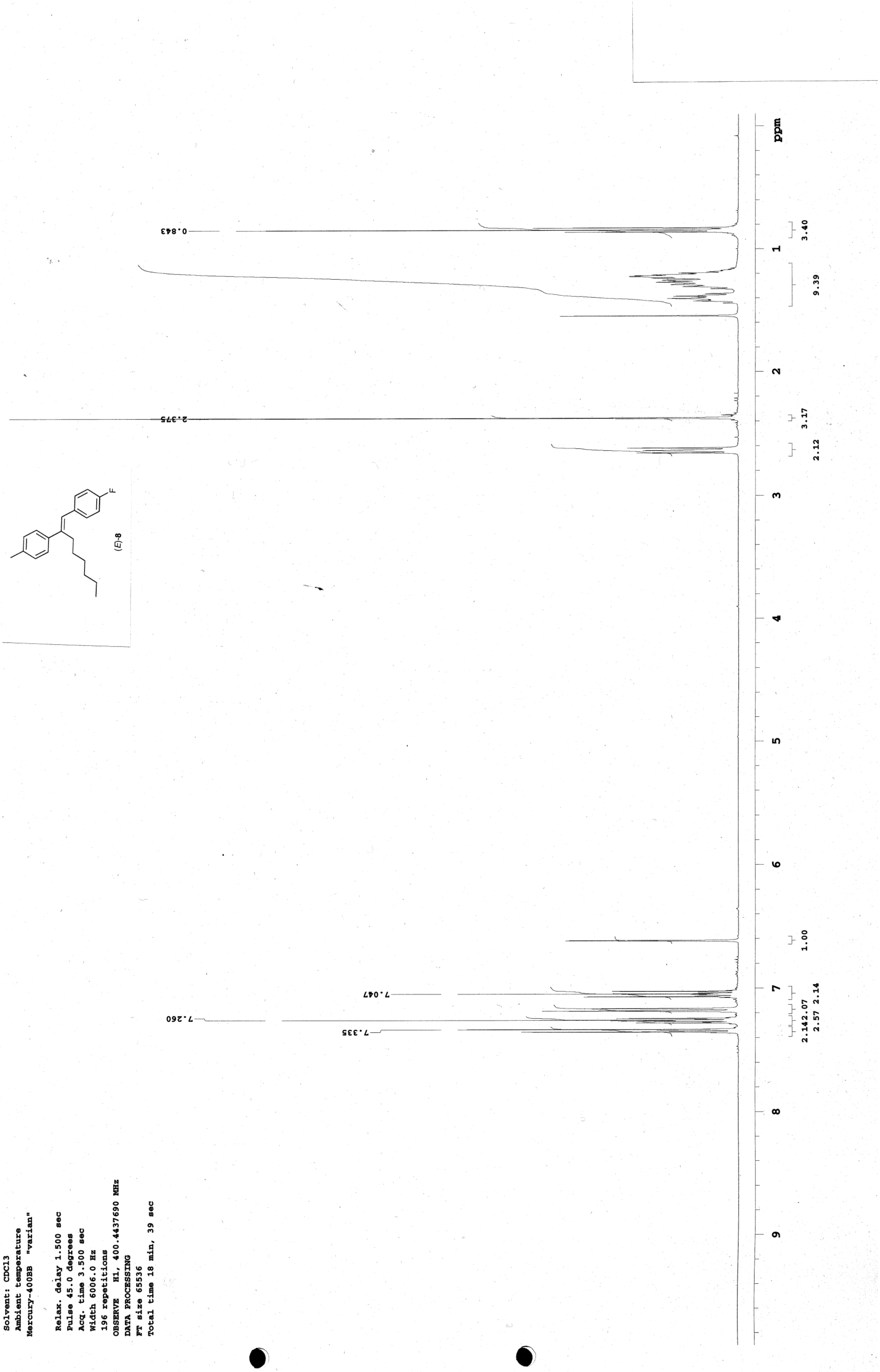
(Z)-8

```
STANDARD 1H OBSERVE

Pulse Sequence: s2pul

  Solvent: CDCl3
  Ambient temperature
Mercury-400BB  "varian"

 Relax. delay 1.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6006.0 Hz
  16 repetitions
OBSERVE   H1, 400.4437690 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec
```



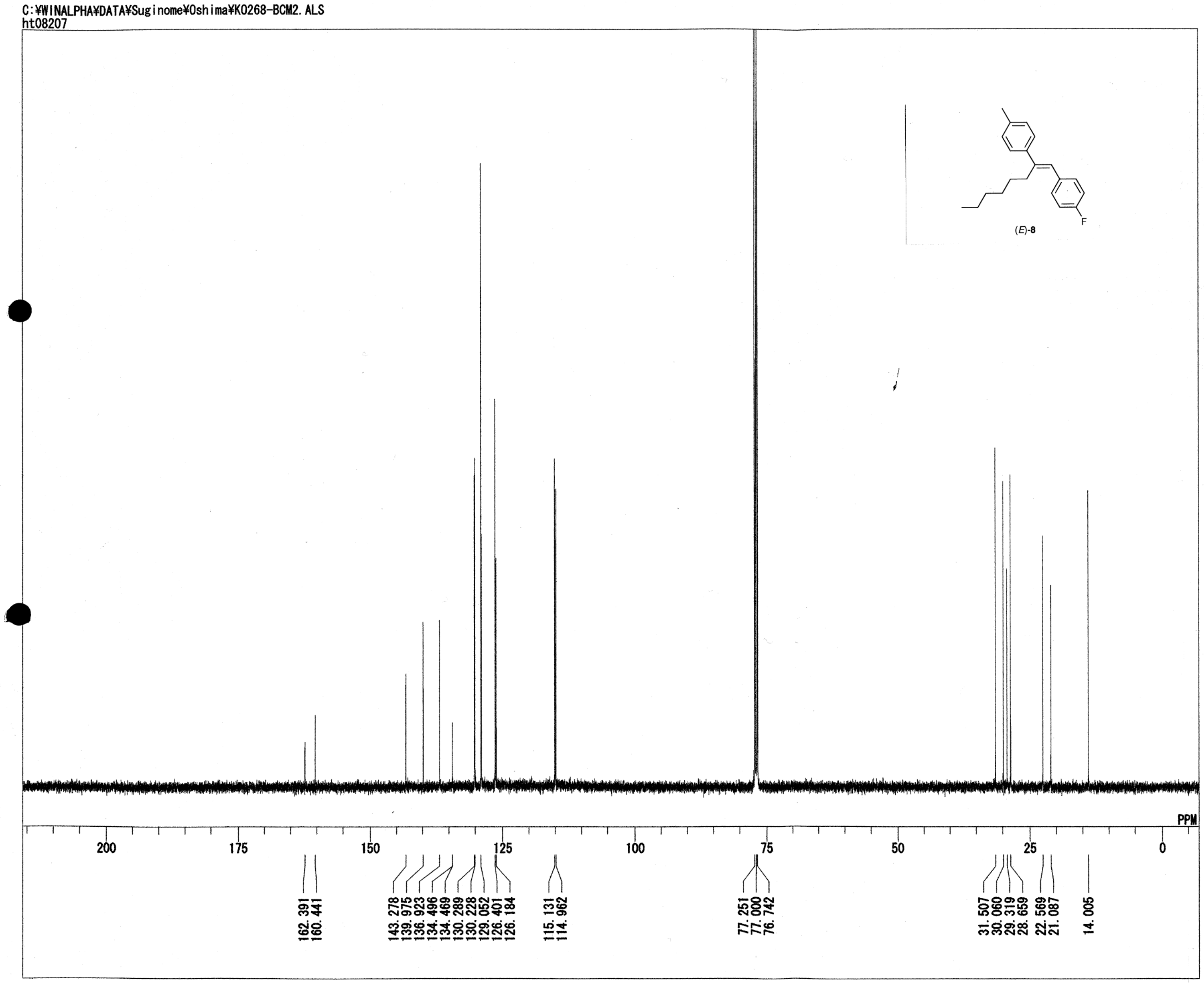
```
DFILE   C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0516-BC
COMNT   071019-tt-020-2
DATIM   Fri Oct 19 23:24:37 2007
OBNUC   13C
EXMOD   SINGL
OBFRQ        125.65 MHz
OBFIN     128449.48 Hz
POINT         32768
FREQU      28011.20 Hz
SCANS          3585
ACQTM        1.1698 sec
PD           2.0000 sec
PW1            4.50 usec
IRNUC   1H
CTEMP          25.2 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.15 Hz
RGAIN            35
```

```
C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0516-BCM.ALS
071019-tt-020-2
```



(*E*)-8

```
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
Mercury-400BB  "varian"

 Relax. delay 1.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6006.0 Hz
 196 repetitions
OBSERVE   H1, 400.4437690 MHz
DATA PROCESSING
FT size 65536
Total time 18 min, 39 sec
```



```
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Oshima¥K0268-BC
COMNT  ht08207
DATIM  Thu Oct 04 11:54:17 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        32768
FREQU     28011.20 Hz
SCANS         4130
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         26.5 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.42 Hz
RGAIN           35
```