Supporting Information

Silylboranes Bearing Dialkylamino Groups on Silicon as Silylene Equivalents: Palladium-Catalyzed Regioselective Synthesis of 2,4-Disubstituted Siloles

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Contents

1. General

All palladium-catalyzed reactions and bromination by NBS 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 Varian Mercury-400 (400.44 MHz) or JEOL JNM-A500 (500.00 MHz) spectrometers. ^{13}C NMR spectra were recorded on Varian GEMINI-2000 (75.45 MHz), JEOL JNM-A500 (125.65 MHz), or JEOL JNM-A600 (150.92 MHz) spectrometers. ^{11}B NMR spectra were recorded on a Varian Mercury-400 (128.48 MHz) spectrometer. ^{29}Si NMR spectra were recorded on a JEOL JNM-A400 (79.30 MHz) spectrometer. Chemical shifts were reported in ppm downfield from tetramethylsilane (^{1}H, ^{13}C, and ^{29}Si) or BF_3•OEt_2 (^{11}B). For ^{13}C NMR, a number of equivalent carbons are shown in parenthesis. Elemental analyses were performed by Elemental Analysis Center of Kyoto University. High resolution mass spectra were recorded on a JEOL JMS-MS700 spectrometer. UV-visible spectra were recorded on a JASCO V-550. Fluorescence spectra were recorded on a HORIBA JOBIN YVON FluoroMax-3.

2. Materials

Toluene was dried and degassed by The Ultimate Solvent System (GlassContour). Silylboranes **1**,[1] **2**-**4**,[2] CpPd(η^3-C_3H_5)[3] and Pd(dba)$_2$[4] were synthesized by the method reported previously. Alkynes **5a**, **5b** (TCI), **5d** (Aldrich), and **5e** (Wako) were purchased and distilled prior to use. **5c** was prepared by silylation of 1-butyn-4-ol (TCI).[5] Aryl alkynes **5f**, **5i**, and **5l** were prepared via Sonogashira coupling of aryl bromide with trimethylsilylacetylene followed by protodesilylation.[6] **5h** was synthesized by *N*-

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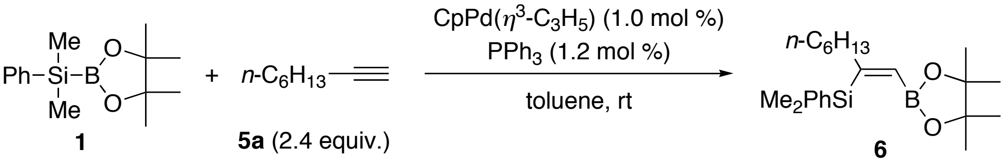
(1) Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647.
(2) Ohmura, T.; Masuda, K.; Furukawa, H.; Suginome, M. *Organometallics* **2007**, *26*, 1291.
(3) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220.
(4) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.
(5) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.
(6) (a) Flatt, A. K.; Yao, Y.; Maya, F.; Tour, J. M. *J. Org. Chem.* **2004**, *69*, 1752. (b) Serwinski, P. R.; Lahti, P. M. *Org. Lett.* **2003**, *5*, 2099.

methylation of 4-ethynylaniline (Wako).[7] **5g**, **5j**, and **5k** was prepared from 2-aryl-1,1-dibromoethene by Corey's method.[8] PPh_3, NBS (Wako), **12**, **13** (STREM), and P(*t*-Bu)$_3$ (Kanto) were used as received from commercial sources. Tributyl(phenylethynyl)stannane and tributyl(4-methoxyphenylethynyl)stannane were synthesized by the reaction of the corresponding (arylalkynyl)lithium with tributyltin chloride.

3. Palladium-Catalyzed Reaction of Silylboranes 1-4 with 1-Octyne (5a) (Table 1)

General Procedure: Triphenylphosphine (1.3 mg, 4.8 μmol) and CpPd(η^3-C_3H_5) (0.85 mg, 4.0 μmol) were dissolved in toluene (200 μL) in a screw-capped vial and the mixture was stirred at room temperature for 5 min. To the mixture was added 1-octyne (**5a**, 106 mg, 0.96 mmol) and silylborane (0.40 mmol) in this order, and then the resulting mixture was reacted at room temperature with stirring. The reaction was monitored by GC. After the reaction was completed (0.2-70 h), the volatile materials were evaporated. The product was isolated by bulb-to-bulb distillation or silica gel column chromatography.

Reaction of 1 with 5a (entry 1)



According to the general procedure, **5a** (106 mg, 0.97 mmol) was reacted with **1** (106 mg, 0.49 mmol). It took 70 h to consumption of 1. The yield of **6** was determined as 99% by GC analysis (tridecane as internal standard). The compound may be purified by silica gel column chromatography. ***(Z)*-2-(Dimethylphenylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-ene (6)**[9]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.54 (m, 2H), 7.28-7.31 (m, 3H), 6.19 (t, J = 1.2 Hz, 1H), 2.23 (dt, J = 7.8, 1.2 Hz,

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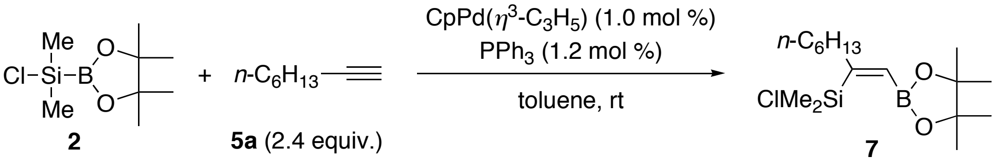
(7) Nguyen, N.-H.; Apriletti, J. W.; Baxter, J. D.; Scanlan, T. S. *J. Am. Chem. Soc.* **2005**, *127*, 4599.
(8) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 243.
(9) Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun.* **1996**, 2777.

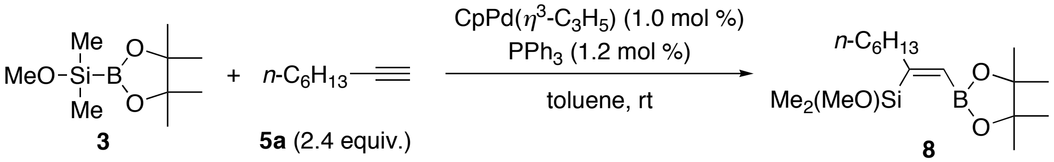
2H), 1.20-1.39 (m, 8H), 1.08 (s, 12H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.46 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 140.5, 134.0 (2C), 128.3, 127.3 (2C), 83.0 (2C), 42.6, 31.7, 29.6, 29.1, 24.6 (4C), 22.5, 14.1, -0.9 (2C). The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.6.

Reaction of 2 with 5a (entry 2)



According to the general procedure, **5a** (107 mg, 0.97 mmol) was reacted with **2** (90 mg, 0.41 mmol) for 15 min. Bulb-to-bulb distillation (170 °C/0.3 mmHg) of the crude mixture afforded **7** in 92% yield (124 mg). **(*Z*)-2-(Chlorodimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-ene (7):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (t, *J* = 1.2 Hz, 1H), 2.37 (dt, *J* = 7.6, 1.2 Hz, 2H), 1.36-1.44 (m, 2H), 1.26-1.33 (m, 6H), 1.28 (s, 12H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.63 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 83.6 (2C), 42.0, 31.7, 29.7, 29.1, 24.9 (4C), 22.6, 14.1, 4.3 (2C). The boron-bound carbon was not detected due to quadrupolar relaxation. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.2. HRMS (CI) *m/z* calcd for $C_{16}H_{33}BClO_2Si$ (MH^+): 331.2031, found: 331.2029.

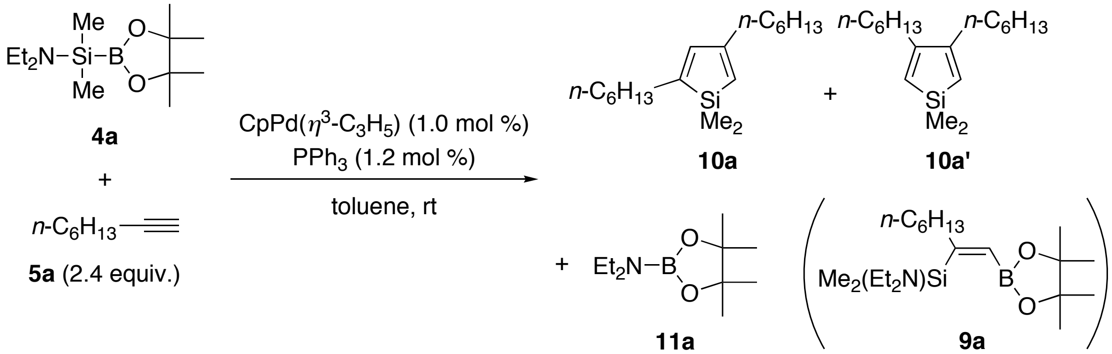
Reaction of 3 with 5a (entry 3)



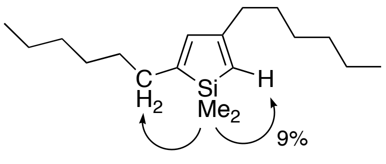
According to the general procedure, **5a** (105 mg, 0.96 mmol) was reacted with **3** (87 mg, 0.40 mmol) for 4 h. Bulb-to-bulb distillation (180-200 °C/1.0 mmHg) of the crude mixture afforded **8** in 80% yield (106 mg). **(*Z*)-2-(Methoxydimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-ene (8):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (t, *J* = 1.2 Hz, 1H), 3.43 (s, 3H), 2.23 (dt, *J* = 7.6, 1.2 Hz, 2H), 1.34-1.44 (m, 2H), 1.28 (s, 12H), 1.26-1.34 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.29 (s, 6H). ^{13}C NMR

(75 MHz, $CDCl_3$) δ 166.1, 131.5 (br, *C*-B), 83.2 (2C), 50.4, 41.0, 31.7, 29.5, 29.2, 24.9 (4C), 22.6, 14.1, -1.0 (2C). ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.7. Anal. Calcd for $C_{17}H_{35}BO_3Si$: C, 62.56; H, 10.81. Found: C, 62.77; H, 10.53.

Reaction of 4a with 5a (entry 4)



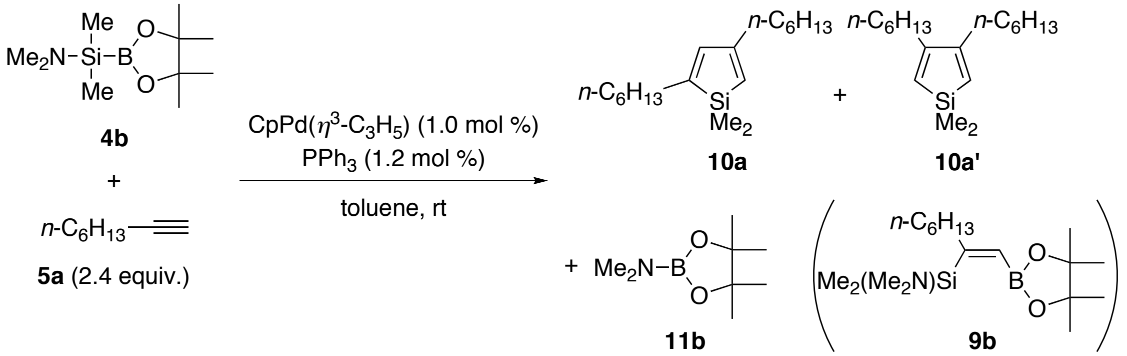
According to the general procedure, **5a** (106 mg, 0.96 mmol) was reacted with **4a** (104 mg, 0.40 mmol) for 80 min. ^{1}H NMR analysis of crude products indicated formation of **10** (**10a**:**10a’** = 77:23) and **11a**, whereas no formation of **9a** was observed (see below for preparation and characterization of **9a**). Bulb-to-bulb distillation (180 °C/2.5 mmHg) afforded **10** in 79% yield (89 mg) as mixture of two regioisomers. Isolation of **11a** (45 mg, 56%) was also performed by bulb-to-bulb distillation (90 °C/2.5 mmHg). **2,4-Dihexyl-1,1-dimethylsilole (10a):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (q, *J* = 1.6 Hz, 1H), 5.40 (q, *J* = 1.6 Hz, 1H), 2.20-2.30 (m, 4H), 1.41-1.52 (m, 4H), 1.22-1.36 (m, 12H), 0.87-0.91 (m, 6H), 0.18 (s,6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 150.0, 141.5, 119.6, 36.1, 32.7, 31.77, 31.76, 29.6, 29.3, 29.1, 27.6, 22.7, 22.6, 14.12, 14.09, -4.3 (2C, H_3C-Si). ^{29}Si NMR (79 MHz, $CDCl_3$) δ 3.8. HRMS (EI) *m*/*z* calcd for $C_{18}H_{34}Si$ (M^+): 278.2430, found: 278.2423. The structure of **10a** was also confirmed by the results of NOE experiments as follows.



10a

3,4-Dihexyl-1,1-dimethylsilole (10a')[10]**:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.64 (t, J =0.8 Hz, 2H), 2.20-2.30 (m, 4H), 1.41-1.52 (m, 4H), 1.22-1.36 (m, 12H), 0.87-0.91 (m, 6H), 0.15 (s, 6H). **2-Diethylamino-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11a)**[11]**:** ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 3.07 (q, J = 6.8 Hz, 4H), 1.13 (s, 12H), 1.05 (t, J = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, C$_6$D$_6$) δ 81.8 (2C), 40.1 (2C), 24.8 (4C), 15.9 (2C). ^{11}B NMR (128 MHz, C$_6$D$_6$) δ 23.5.

Reaction of 4b with 5a (entry 5)



According to the general procedure, **5a** (107 mg, 0.97 mmol) was reacted with **4b** (104 mg, 0.45 mmol) in C$_6$D$_6$ for 1.5 h. ^{1}H NMR analysis of crude products indicated formation of **10** (55%, dibenzyl ether as internal standard, **10a**:**10a'** = 69:31) and **11b** (77%), whereas no formation of **9b** was observed. **2-Dimethylamino-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11b):** ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 2.62 (s, 6H), 1.10 (s, 12H). ^{13}C NMR (126 MHz, C$_6$D$_6$) δ 82.1 (2C), 36.5 (2C), 24.9 (4C). ^{11}B NMR (128 MHz, C$_6$D$_6$) δ 23.4.

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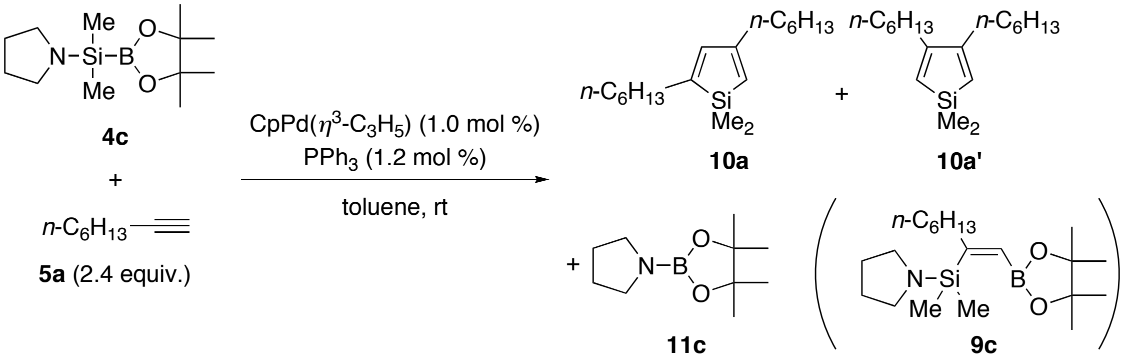
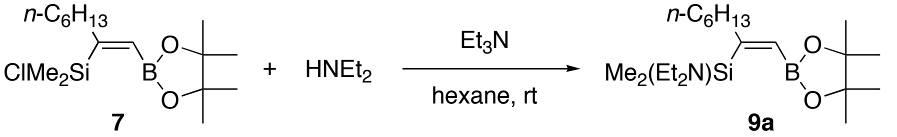
(10) Ikenaga, K.; Hiramatsu, K.; Nasaka, N.; Matsumoto, S. *J. Org. Chem.* **1993**, *58*, 5045.
(11) Suginome, M.; Uehlin, L.; Murakami, M. *J. Am. Chem. Soc.* **2004**, *126*, 13196.

Reaction of 4c with 5a (entry 6)



According to the general procedure, **5a** (106 mg, 0.96 mmol) was reacted with **4c** (101 mg, 0.40 mmol) in C_6D_6 for 1.5 h. ^{1}H NMR analysis of crude products indicated formation of **10** (69%, dibenzyl ether as internal standard, **10a**:**10a'** = 75:25) and **11c** (82%), whereas no formation of **9c** was observed. **2-N-Pyrrolidino-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11c):** ^{1}H NMR (400 MHz, C_6D_6) δ 3.26-3.30 (m, 4H), 1.42-1.46 (m, 4H), 1.16 (s, 12H). ^{13}C NMR (126 MHz, C_6D_6) δ 81.9, 46.0, 26.6, 25.0. ^{11}B NMR (128 MHz, C_6D_6) δ 22.8.

4. Preparation and Characterization of 9a (eq S1)

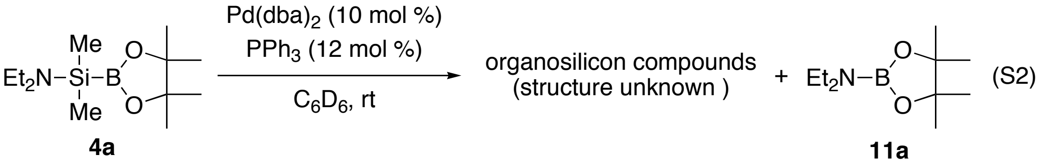


(S1)

To obtain characterization data, **9a** was prepared from **7**. To a mixture of **7** (0.69 g, 2.1 mmol) and Et_3N (0.27 g, 2.5 mmol) in hexane was added $HNEt_2$ (0.17 g, 2.4 mmol) at room temperature. The resulting mixture was stirred at room temperature for 3 days. Precipitates were filtrate off and volatiles were removed in vacuo. The crude mixture was treated with Et_3N (0.27 g, 2.5 mmol) and $HNEt_2$ (0.17 g, 2.4 mmol) in hexane, again. After stirring at room temperature for 24 h, precipitates were filtrate off and volatiles were removed in vacuo. Bulb-to-bulb distillation (220 °C/5.0 mmHg) of the residues afforded **9a** in 66% yield (0.50 g). **(*Z*)-2-(Diethylaminodimethylsilyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-1-ene (9a):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (t, J = 1.6 Hz, 1H), 2.81 (q, J =

7.2 Hz, 4H), 2.16-2.20 (m, 2H), 1.27 (s, 12H), 1.23-1.42 (m, 8H), 0.97 (t, J = 7.2 Hz, 6H), 0.88 (t, J = 6.8 Hz, 3H), 0.23 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 83.0 (2C), 41.4, 40.5 (2C), 31.8, 29.6, 29.4, 25.0 (4C), 22.6, 15.7 (2C), 14.1, 0.0 (2C). The boron-bound carbon was not detected due to quadrupolar relaxation. Anal. Calcd for $C_{20}H_{42}BNO_2Si$: C, 65.37; H, 11.52; N, 3.81. Found: C, 65.28; H, 11.30; N, 3.54.

5. Reaction of 4a with Catalytic Amount of a Pd/PPh_3 Complex in the Absence of Alkyne (eq S2 and Table S1)



Silylborane **4a** (50 mg, 0.20 mmol) was reacted with $Pd(dba)_2$ (12 mg, 0.020 mmol) and PPh_3 (6.3 mg, 0.024 mmol) in C_6D_6 (0.2 mL) containing dibenzyl ether as an internal standard. The reaction mixture was stirred at room temperature and analyzed by ^{1}H NMR and GCMS. After 48 h, the ^{1}H NMR spectrum of the reaction mixture showed more than 10 new Si–CH_3 signals in the region of -1.0–0.6 ppm. Although GCMS analysis was carried out for assignment of these products, we could only detect dodecamethylcyclohexasilane,[12] which was formed as a very minor product (<1%). The assignment was on the basis of the ^{1}H NMR (δ 0.22 ppm in C_6D_6) and GCMS fragment pattern [EI m/z 348 (M^+, 100), 275 (25), 259 (33), 201 (50)]. On the other hand, efficient formation of aminoborane **11a** was observed in the reaction. The time course of the reaction is shown in Table S1 (see next page). Under the reaction conditions, **4a** was slowly consumed (89% conversion after 48 h) and **11a** was formed in high yield (84% yield after 48 h).

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(12) Authentic sample was prepared by the method reported. Laguerre, M.; Dunogues, J.; Calas, R. *J. Chem. Soc., Chem. Commun.* **1978**, 272.

Table S1. Palladium-Catalyzed Conversion of Silylborane **4a** to Aminoborane **11a** Under the Conditions Shown in Equation S2

entry	time (h)	conversion of **4a** (%)[a]	yield of **11a** (%)[a]
1	0.3	55	52
2	10	74	70
3	48	89	84

[a] Determined by ^{1}H NMR analysis using dibenzyl ether as an internal standard.

6. Screening of Ligand and Palladium Precursor (Table S2 and S3)

Table S2. Screening of Ligand

$$\mathbf{4a} \quad + \quad \underset{\text{(2.4 equiv.)}}{\mathbf{5a}} \quad \xrightarrow[\text{toluene, rt}]{\substack{\text{CpPd}(\eta_3\text{-}C_3H_5)\ \text{(1.0 mol \%)} \\ \text{ligand (1.2 mol \%)}}} \quad \mathbf{10a} + \mathbf{10a'}$$

entry	ligand	yield (%)[a]	**10a**:**10a'**
1	PPh_3	79[b]	77:23
2	$PCyPh_2$	90	80:20
3	PCy_2Ph	89	82:18
4	PCy_3	80	77:23
5	P^tBu_3	75	68:32
6	PPh_2(2-biphenyl)	84	86:14
7	PCy_2(2-biphenyl)	86	88:12
8	P^tBu_2(2-biphenyl)	73[b]	90:10

[a] GC yield. [b] Isolated yield.

Table S3. Screening of Catalyst Precursor

$$\mathbf{4a} \quad + \quad \underset{\text{(2.4 equiv.)}}{\mathbf{5c}} \quad \xrightarrow[\text{toluene, rt}]{\substack{\text{Pd precursor (1.0 mol \%)} \\ PPh_3\ \text{(1.2 mol \%)}}} \quad \mathbf{10c}$$

entry	Pd precursor	GC yield after 2 h (%)	GC yield after 12 h (%)	ratio
1	$Pd(dba)_2$	87	90	74:26
2	$Pd(OAc)_2$	10	89	79:21
3	$PdCl_2(CH_3CN)_2$	46	92	76:24

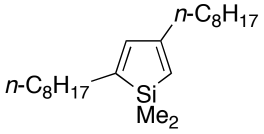
Screening of ligand on palladium catalyst was carried out for reaction of **4a** with **5a** (Table S2). A phosphine (4.8 μmol) and CpPd(η^3-C_3H_5) (0.85 mg, 4.0 μmol) were dissolved in toluene (200 μL) in a screw-capped vial and the mixture was stirred at room temperature for 5 min. To the mixture was added **5a** (106 mg, 0.96 mmol) and **4a** (103 mg, 0.40 mmol) in this order, and then the resulting mixture was reacted at room temperature with stirring. The yield of silole obtained was determined by GC analysis using tridecane as internal standard.

Screening of palladium precursor was carried out for reaction of **4a** with **5c** (Table S3). Triphenylphosphine (0.63 mg, 2.4 μmol) and a palladium precursor (2.0 μmol) were dissolved in toluene (100 μL) in a screw-capped vial and the mixture was stirred at room temperature for 5 min. To the mixture was added **5c** (88 mg, 0.48 mmol), **4a** (51 mg, 0.20 mmol) and tridecane (internal standard) in this order, and then the resulting mixture was reacted at room temperature with stirring. GC analysis was performed after 2 and 12 h to determine the yield of **10c**.

7. Regioselective Synthesis of 2,4-Disubstituted Siloles via Palladium-Catalyzed Reaction of 4a with Terminal Alkynes under Optimized Conditions (Table 2)

***Typical Procedure is given for the synthesis of 10a (entry 1)*:** A phosphine **12** (1.4 mg, 4.8 μmol) and Pd(dba)$_2$ (2.3 mg, 4.0 μmol) were dissolved in toluene (200 μL) in a screw-capped vial and the mixture was stirred at room temperature for 5 min. To the mixture was added **5a** (108 mg, 0.96 mmol) and **4a** (102 mg, 0.40 mmol) in this order, and then the resulting mixture was reacted at room temperature with stirring. The reaction was monitored by GC. After the reaction was completed (20 h), the volatile materials were evaporated. ^{1}H NMR analysis of crude products indicated the ratio of regioisomer as 90:10. The product **10a** (82 mg, 74%) was isolated by column chromatography on silica gel (hexane, R_f = 0.86).

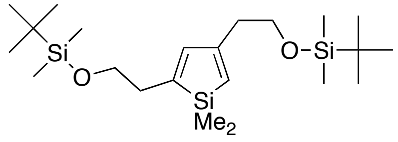
1,1-Dimethyl-2,4-dioctylsilole (10b, entry 2)



10b

According to the typical procedure, **5b** (134 mg, 0.97 mmol) was reacted with **4a** (102 mg, 0.40 mmol) for 22 h in the presence of Pd/**12** catalyst. ^{1}H NMR analysis of crude products indicated the ratio of regioisomer as 96:4. The product **10b** (94 mg, 71%) was isolated by column chromatography on silica gel (hexane, R_f = 0.81). **10b:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.33 (q, J = 1.6 Hz, 1H), 5.40 (q, J = 1.6 Hz, 1H), 2.28 (dt, J = 7.6, 1.6 Hz, 2H), 2.23 (dt, J = 7.6, 1.6 Hz, 2H), 1.42-1.52 (m, 4H), 1.22-1.36 (m, 20H), 0.89 (t, J = 6.8 Hz, 6H), 0.18 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 160.7, 150.0, 141.5, 119.6, 36.1, 32.7, 31.91, 31.90, 31.6, 29.68, 29.66, 29.50, 29.49, 29.39, 29.32, 29.28, 27.7, 22.68, 22.67, 14.1, -4.3 (2C). HRMS (EI) m/z calcd for $C_{22}H_{42}Si$ (M$^+$): 334.3056, found: 334.3054.

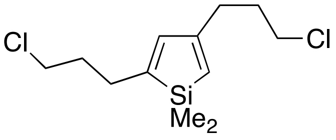
2,4-Bis[2-(*tert*-butyldimethylsilyloxy)ethyl]-1,1-dimethylsilole (10c, entry 3)



10c

According to the typical procedure, **5c** (178 mg, 0.97 mmol) was reacted with **4a** (103 mg, 0.40 mmol) for 22 h in the presence of Pd/**12** catalyst. ^{1}H NMR analysis of crude products indicated the ratio of regioisomer as 93:7. The product **10c** (141 mg, 83%) was isolated by column chromatography on silica gel (hexane, $R_f = 0.24$). **10c:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.42 (q, J = 1.6 Hz, 1H), 5.49 (q, J = 1.6 Hz, 1H), 3.76 (t, J = 6.8 Hz, 2H), 3.67 (t, J = 7.2 Hz, 2H), 2.52 (dt, J = 7.2, 1.6 Hz, 2H), 2.48 (dt, J = 6.8, 1.6 Hz, 2H), 0.91 (s, 9H), 0.89 (s, 9H), 0.18 (s, 6H), 0.08 (s, 6H), 0.05 (s, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 156.6, 145.3, 143.5, 123.1, 63.3, 62.3, 39.5, 36.5, 26.03 (3C), 25.97 (3C), 18.5, 18.4, -4.7 (2C), -5.16 (2C), -5.23 (2C). Anal. Calcd for $C_{22}H_{46}O_2Si_3$: C, 61.90; H, 10.86. Found: C, 61.63; H, 10.63.

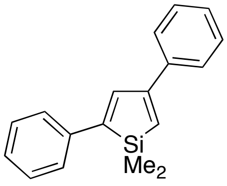
2,4-Bis(3-chloropropyl)-1,1-dimethylsilole (10d, entry 4)



10d

According to the typical procedure, **5d** (100 mg, 0.97 mmol) was reacted with **4a** (100 mg, 0.39 mmol) for 24 h in the presence of Pd/**13** catalyst. ^{1}H NMR analysis of crude products indicated the ratio of regioisomer as 91:9. The product **10d** (80 mg, 78%) was isolated by column chromatography on silica gel (hexane:Et$_2$O = 40:1, $R_f = 0.28$). **10d:** ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.38 (q, J = 1.6 Hz, 1H), 5.50 (q, J = 1.6 Hz, 1H), 3.55 (t, J = 6.8 Hz, 2H), 3.54 (t, J = 6.8 Hz, 2H), 2.45 (dt, J = 7.6, 1.6 Hz, 2H), 2.40 (dt, J = 7.6, 1.6 Hz, 2H), 1.89-2.05 (m, 4H), 0.20 (s, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 158.1, 148.3, 142.1, 121.5, 44.7, 44.5, 32.9, 32.3, 30.5, 29.5, -4.6 (2C). HRMS (CI) m/z calcd for $C_{12}H_{21}Cl_2Si$ (MH$^+$): 263.0790, found: 263.0786. Characteristic ^{1}H NMR chemical shifts of the regioisomer, 3,4-di(3-chloropropyl)-1,1-dimethylsilole, are as follows: ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.70 (t, J = 1.2 Hz, 2H), 3.61 (t, J = 6.4 Hz, 4H), 0.16 (s, 6H).

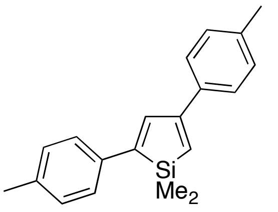
1,1-dimethyl-2,4-diphenylsilole (10e, entry 5)



10e

According to the typical procedure, **5e** (249 mg, 2.4 mmol) was reacted with **4a** (259 mg, 1.0 mmol) for 5 h in the presence of Pd/PPh_3 catalyst. ^{1}H NMR analysis of crude products indicated the ratio of regioisomer as 95:5. The product **10e** (242 mg, 92%) was isolated by column chromatography on silica gel (hexane:Et_2O = 40:1, R_f = 0.24). **10e:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.65 (m, 2H), 7.61 (d, J = 1.6 Hz, 1H), 7.46-7.49 (m, 2H), 7.31-7.42 (m, 6H), 6.32 (d, J = 1.6 Hz, 1H), 0.45 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 147.2, 139.3, 139.0, 138.9, 128.7 (2C), 128.4 (2C), 128.0, 127.0, 126.5 (2C), 126.0 (2C), 125.2, -3.7 (2C). Anal. Calcd for $C_{18}H_{18}Si$: C, 82.38; H, 6.91. Found: C, 82.15; H, 7.00.

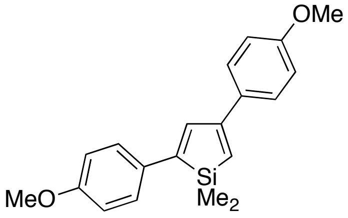
1,1-dimethyl-2,4-bis(4-methylphenyl)silole (10f, entry 6)



10f

According to the typical procedure, **5f** (114 mg, 0.98 mmol) was reacted with **4a** (103 mg, 0.40 mmol) for 3 h in the presence of Pd/PPh_3 catalyst. ^{1}H NMR analysis of crude products indicated the ratio of regioisomer as 95:5. The product **10f** (111 mg, 96%) was isolated by column chromatography on silica gel (hexane:Et_2O = 40:1, R_f = 0.30). **10f:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 1.7 Hz, 1H), 7.56 (d, J = 7.9 Hz, 2H), 7.41 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 6.27 (d, J = 1.7 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 0.44 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 146.9, 138.1, 137.8, 136.8, 136.5, 136.3, 129.4 (2C), 129.1 (2C), 126.4 (2C), 125.9 (2C), 123.5, 21.21, 21.20, -3.6 (2C). HRMS (EI) *m/z* calcd for $C_{20}H_{22}Si$ (M^+): 290.1491, found: 290.1504.

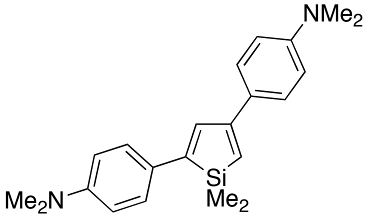
2,4-Bis(4-methoxyphenyl)-l,1-dimethylsilole (10g, entry 7)



10g

According to the typical procedure, **5g** (126 mg, 0.96 mmol) was reacted with **4a** (102 mg, 0.40 mmol) for 24 h in the presence of Pd/PPh_3 catalyst. ^1H NMR analysis of crude products indicated the ratio of regioisomer as 96:4. The product **10g** (122 mg, 96%) was isolated by column chromatography on silica gel (hexane:AcOEt = 40:1, $R_f = 0.24$). **10g:** ^1H NMR (400 MHz, $CDCl_3$) δ 7.58-7.63 (m, 2H), 7.51 (d, $J = 1.6$ Hz, 1H), 7.42-7.47 (m, 2H), 6.89-6.95 (m, 4H), 6.16 (d, $J = 1.6$ Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 0.44 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 158.8, 156.2, 146.5, 136.8, 132.0, 131.8, 127.6 (2C), 127.3 (2C), 121.5, 114.1 (2C), 113.7 (2C), 55.2 (2C), -3.5 (2C). HRMS (EI) *m/z* calcd for $C_{20}H_{22}O_2Si$ (M^+): 322.1389, found: 322.1403.

1,1-Dimethyl-2,4-bis(4-dimethylaminophenyl)silole (10h, entry 8)

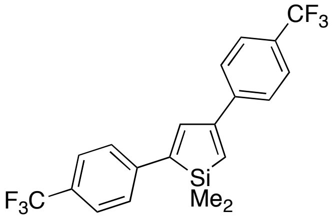


10h

According to the typical procedure, **5h** (137 mg, 0.95 mmol) was reacted with **4a** (105 mg, 0.41 mmol) for 48 h in the presence of Pd/PPh_3 catalyst. ^1H NMR analysis of crude products indicated the ratio of regioisomer as 88:12. The yield of **10h** was determined as 80% by ^1H NMR analysis (dibenzyl ether as internal standard), because of instability against column chromatography. **10h:** ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, $J = 8.8$ Hz, 2H), 7.50 (d, $J = 1.6$ Hz, 1H), 7.41 (d, $J = 8.8$ Hz, 2H), 6.74 (d, $J = 8.8$ Hz, 2H), 6.73 (d, $J = 8.8$ Hz, 2H), 6.02 (d, $J = 1.6$ Hz, 1H), 3.00 (s, 6H), 2.98 (s, 6H), 0.41 (s, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 156.7, 150.2, 149.6, 146.4, 134.8, 127.4 (2C), 127.0 (2C), 117.8, 112.6 (2C), 112.1 (2C), 40.5 (2C), 40.4 (2C), -3.2 (2C). Two carbons were not identified by the analysis of crude mixture. HRMS (EI) *m/z* calcd for $C_{22}H_{28}N_2Si$ (M$^+$): 348.2022, found: 308.2016.

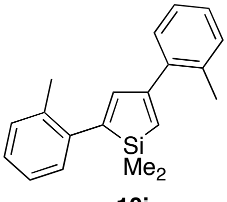
1,1-Dimethyl-2,4-bis(4-trifluoromethylphenyl)silole (10i, entry 9)



10i

According to the typical procedure, **5i** (163 mg, 0.96 mmol) was reacted with **4a** (103 mg, 0.40 mmol) for 22 h in the presence of Pd/PPh$_3$ catalyst. ^{1}H NMR analysis of crude products indicated the ratio of regioisomer as 94:6. The product **10i** (116 mg, 73%) was isolated as white solid (m.p. 75 °C) by column chromatography on silica gel (hexane, $R_f = 0.25$). **10i:** ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.60-7.63 (m, 3H), 7.55 (d, J = 8.3 Hz, 2H), 6.49 (d, J = 1.7 Hz, 1H), 0.46 (s, 6H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 155.4, 146.7, 142.3, 140.4, 130.0 (q, $^2J_{CF}$ = 33 Hz), 129.0, 128.9 (q, $^2J_{CF}$ = 32 Hz), 128.1, 126.5 (2C), 126.3 (2C), 125.7 (q, $^3J_{CF}$ = 4 Hz, 2C), 125.5 (q, $^3J_{CF}$ = 4 Hz, 2C), 124.3 (q, $^1J_{CF}$ = 271 Hz), 124.2 (q, $^1J_{CF}$ = 272 Hz), -4.0 (2C). HRMS (EI) *m/z* calcd for $C_{20}H_{16}F_6Si$ (M$^+$): 398.0925, found: 398.0912.

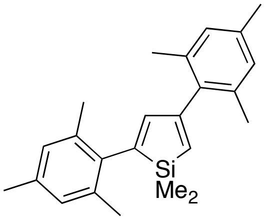
1,1-Dimethyl-2,4-bis(2-methylphenyl)silole (10j, entry 10)



10j

According to the typical procedure, **5j** (112 mg, 0.96 mmol) was reacted with **4a** (102 mg, 0.40 mmol) for 4 h in the presence of Pd/PPh$_3$ as catalyst. ^{1}H NMR analysis of crude products indicated the ratio of regioisomer as 95:5. The product **10j** (89 mg, 78%) was isolated by column chromatography on silica gel (hexane:AcOEt = 50:1, R_f = 0.28). **10j:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.32 (m, 1H), 7.20-7.25 (m, 4H), 7.10-7.18 (m, 3H), 6.84 (d, J = 1.7 Hz, 1H), 5.99 (d, J = 1.7 Hz, 1H), 2.38 (s, 3H), 2.36 (s, 3H), 0.39 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 147.5, 145.1, 141.3, 140.4, 135.0, 134.8, 130.4, 130.3, 128.2, 128.0, 127.9, 127.4, 126.0, 125.7, 125.5, 21.3, 20.5, -4.1 (2C). HRMS (EI) m/z calcd for $C_{20}H_{22}Si$ (M^+): 290.1491, found: 290.1486.

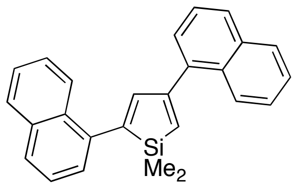
1,1-Dimethyl-2,4-bis(2,4,6-trimethylphenyl)silole (10k, entry 11)



10k

According to the typical procedure, **5k** (139 mg, 0.97 mmol) was reacted with **4a** (102 mg, 0.40 mmol) for 20 h in the presence of Pd/PPh_3 catalyst. ^{1}H NMR analysis of crude products indicated the ratio of regioisomer as 97:3. The product **10k** (110 mg, 80%) was isolated by column chromatography on silica gel (hexane, R_f = 0.24). **10k:** ^{1}H NMR (400 MHz, C_6D_6) δ 6.86 (s, 2H), 6.84 (s, 2H), 6.31 (d, J = 1.8 Hz, 1H), 5.86 (d, J = 1.8 Hz, 1H), 2.30 (s, 6H), 2.25 (s, 6H), 2.21 (s, 3H), 2.20 (s, 3H), 0.27 (s, 6H). ^{13}C NMR (126 MHz, C_6D_6) δ 158.5, 149.0, 146.4, 139.2, 137.8, 136.1, 134.8, 134.6 (2C), 134.5 (2C), 128.51 (2C), 128.48 (2C), 127.5, 21.1, 21.03 (2C), 21.01, 20.5 (2C), -3.3 (2C). Anal. Calcd for $C_{24}H_{30}Si$: C, 83.17; H, 8.72. Found: C, 83.46; H, 8.87.

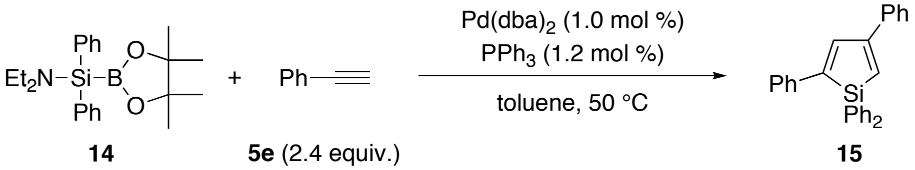
1,1-Dimethyl-2,4-di(1-naphthalenyl)silole (10l, entry 12)



10l

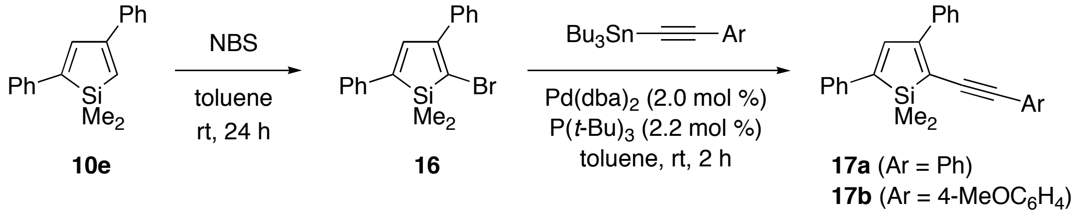
According to the typical procedure, **5l** (148 mg, 0.97 mmol) was reacted with **4a** (103 mg, 0.30 mmol) for 24 h in the presence of Pd/PPh_3 catalyst. ^{1}H NMR analysis of crude products indicated the ratio of regioisomer as 99:1. The product **10l** (109 mg, 75%) was isolated by column chromatography on silica gel (hexane:AcOEt = 10:1, R_f = 0.41). **10l:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.20 (m, 2H), 7.85-7.91 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.44-7.53 (m, 6H), 7.32 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.16 (d, *J* = 1.8 Hz, 1H), 6.32 (d, *J* = 1.8 Hz, 1H), 0.48 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 146.81, 146.75, 139.6, 139.3, 134.0, 133.8, 131.7, 130.7, 129.9, 128.4, 128.3, 128.0, 126.5, 126.3, 126.0, 125.9, 125.8, 125.7, 125.6, 125.5, 125.4, 125.2, 124.4, -4.0 (2C). HRMS (EI) *m/z* calcd for $C_{26}H_{22}Si$ (M^+): 362.1491, found: 362.1485.

8. Palladium-Catalyzed Reaction of 14 with 5e (eq 1)

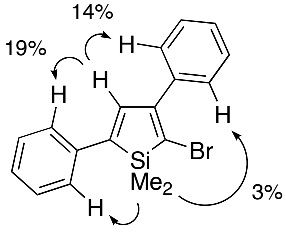


Triphenylphosphine (1.3 mg, 4.8 μmol) and $Pd(dba)_2$ (2.3 mg, 4.0 μmol) were dissolved in toluene (200 μL) in a screw-capped vial and the mixture was stirred at room temperature for 5 min. To the mixture was added **5e** (98 mg, 0.96 mmol) and **14** (159 mg, 0.42 mmol) in this order, and then the resulting mixture was reacted at 50 °C with stirring. The reaction was monitored by GC. After the reaction was completed (18 h), the volatile materials were evaporated. The ratio of regio isomers was determined as 92:8 by ^{1}H NMR analysis of the crude mixture. Isolation of the product was performed by silica gel column chromatography (hexane:Et_2O = 20:1, R_f = 0.22) to afford **15** in 70% yield (112 mg). **1,1,2,4-tetraphenylsilole (15):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 2.0 Hz, 1H), 7.67-7.72 (m, 4H), 7.16-7.49 (m, 16H), 6.60 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 145.2, 141.5 (2C), 138.9, 138.8, 135.7 (4C), 131.9, 130.1 (2C), 128.6 (2C), 128.5 (2C), 128.4 (4C), 128.2, 127.3, 127.0 (2C), 126.1 (2C), 123.0. HRMS (EI) *m/z* calcd for $C_{28}H_{22}Si$ (M^+): 386.1491, found: 386.1495.

9. Site-selective Functionalization of 10e (Scheme 1)



Bromination of 10e: Fleshly prepared **10e** (89 mg, 0.34 mmol) was dissolved in toluene (1.0 mL), and the solution was treated with *N*-bromosuccinimide (63 mg, 0.35 mmol) at room temperature with stirring. After 24 h, volatile materials were removed and the residue was mixed with pentane (ca. 2.0 mL). The white suspension was filtrated through short pad of Celite® (No. 535) to remove succinimide and residual NBS. Concentration of the filtrate afforded **16** as colorless liquid, which was used for next reaction without purification. The compound **16** could be purified by HPLC [column: Cica-MERCK LiChrosorb CN (25 mm x 250 mm); eluent: hexane], despite low yield because of partial decomposition during chromatography. The yield of this bromination reaction was estimated at 85% by GC analysis of another batch, in which tridecane was used as internal standard. **2-Bromo-1,1-dimethyl-3,5-diphenylsilole (16):** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57-7.60 (m, 2H), 7.32-7.47 (m, 7H), 7.29 (s, 1H), 7.23-7.28 (m, 1H), 0.50 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 151.9, 144.4, 141.3, 138.4, 137.6, 128.9 (2C), 128.2 (2C), 128.1, 127.9 (2C), 127.3, 126.2 (2C), 121.9, -4.7. HRMS (EI) *m/z* calcd for $C_{18}H_{17}BrSi$ (M^+): 340.0283, found: 340.0292. The structure of **16** was assigned based on the results of NOE experiments as follows.



16

Migita-Kosugi-Stille coupling of 16:[13] To a mixture of Pd(dba)$_2$ (3.9 mg, 6.7 μmol), P(*t*-Bu)$_3$ (1.6 mg, 8.0 μmol), toluene (1.0 mL), and fleshly prepared **16** was added (phenylethynyl)tributylstannane (140 mg, 0.36 mmol), and then the resulting mixture was stirred at room temperature. After 2 h, the solution was diluted with Et$_2$O (2.0 mL) and treated with KF (310 mg). The resulting suspension was filtrated by passing through short column of silica gel. After removal of volatile materials, the crude products were purified by chromatography on silica gel (hexane:Et$_2$O = 40:1, R_f = 0.20) to give **17a** (95 mg, 78% from **10e**). **1,1-Dimethyl-3,5-diphenyl-2-(phenylethynyl)silole (17a):** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93-7.96 (m, 2H), 7.64 (s, 1H), 7.28-7.51 (m, 13H), 0.58 (s, 6H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 156.9, 145.5, 140.8, 138.4, 138.1, 131.4 (2C), 128.9 (2C), 128.4, 128.3 (2C), 128.1 (2C), 127.66 (2C), 127.65, 127.4, 126.6 (2C), 124.7, 119.9, 100.2, 90.0, -4.0 (2C). HRMS (EI) *m/z* calcd for $C_{26}H_{22}Si$ (M$^+$): 362.1491, found: 362.1493.

Migita-Kosugi-Stille coupling of **16** (0.52 mmol based on **10e** used) with [(4-methoxyphenyl)ethynyl]tributylstannane (276 mg, 0.66 mmol) was carried out applying similar procedure described above. The silole **17b** (107 mg, 52% from **10e**) was isolated as bright yellow solid (m.p. 125 °C) by chromatography on silica gel (hexane:Et$_2$O = 40:1, R_f = 0.20). **2-[(4-Methoxyphenyl)ethynyl]-1,1-dimethyl-3,5-diphenylsilole (17b):** ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91-7.93 (m, 2H), 7.62 (s, 1H), 7.44-7.48 (m, 4H), 7.33-7.38 (m, 5H), 7.24-7.27 (m, 1H), 6.83-6.87 (m, 2H), 3.83 (s, 3H), 0.55 (s, 6H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 159.3, 156.0, 144.9, 141.0, 138.6, 138.2, 132.9 (2C), 128.8 (2C), 128.2, 128.1 (2C), 127.6 (2C), 127.3, 126.5 (2C), 120.4, 117.0, 114.0 (2C), 100.5, 88.9, 55.3, -4.0 (2C). Anal. Calcd for $C_{27}H_{24}OSi$: C, 82.61; H, 6.16. Found: C, 82.66; H, 6.22.

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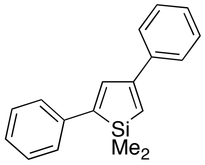
[13] Littke, A. F.; Schwarz, L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6343.

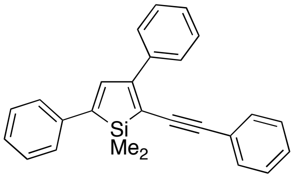
10. Photophysical measurement of **10e**, **17a**, and **17b**

UV-visible absorption spectra and fluorescence spectra of **10e**, **17a**, and **17b** were measured, and quantum yields were determined. All measurements were carried out in chloroform (nacalai, specially prepared reagent for fluorescence spectroscopy). The spectra are shown in Figures S1 and S2 (see next page), and summary of their data is shown in Table S4.

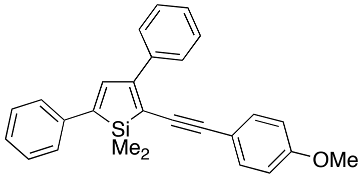
Table S4. Summary of UV-vis Absorption and Fluorescence Spectral Data for **10e**, **17a**, and **17b**



10e



17a



17b

	UV-vis[a]		fluorescence[a]	
silole	$\lambda_{\max}$ [nm]	ε	$\lambda_{\max}$ [nm]	Φ_f[b]
10e	338	2.0×10^3	452	0.13
17a	403	2.5×10^3	456	0.069
17b	420	2.2×10^4	516	0.015

[a] In $CHCl_3$. [b] Determined with reference to quinine sulfate in 0.1 M H_2SO_4 (exited at 366 nm).

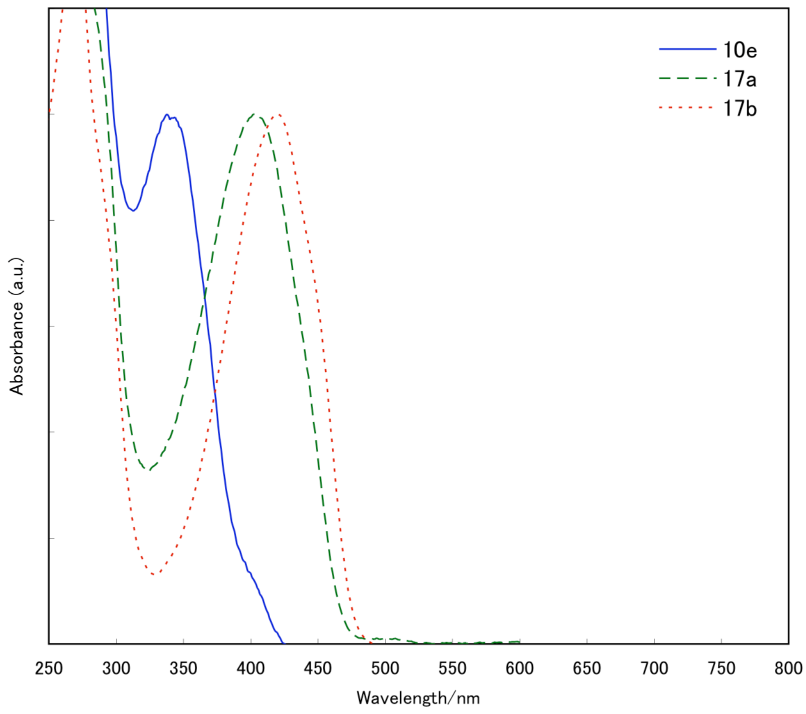


Figure S1. UV-vis Absorption Spectra in $CHCl_3$ for **10a** (solid blue line), **17a** (dashed green line), and **17b** (dotted red line)

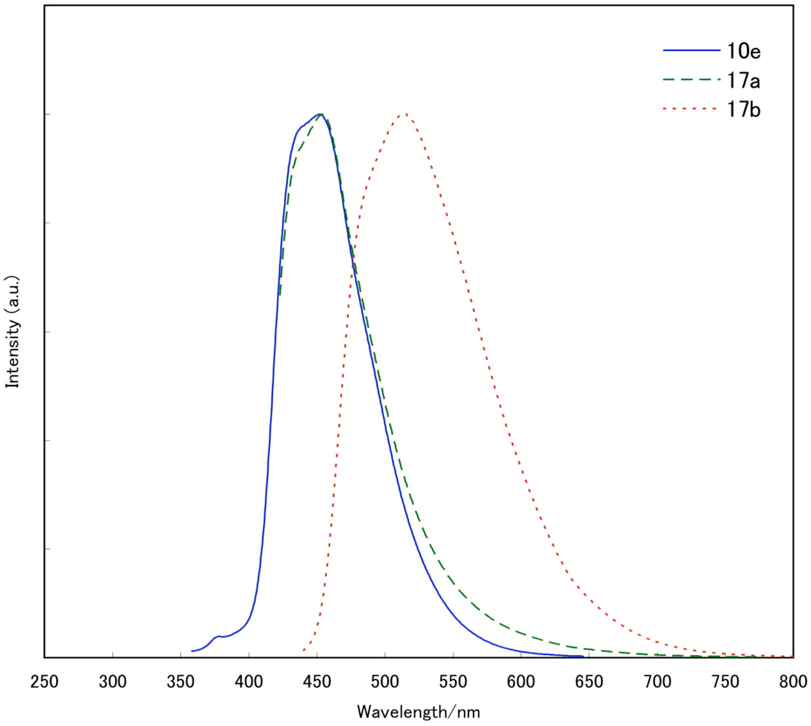


Figure S2. Fluorescence Spectra in $CHCl_3$ for **10a** (solid blue line), **17a** (dashed green line), and **17b** (dotted red line)

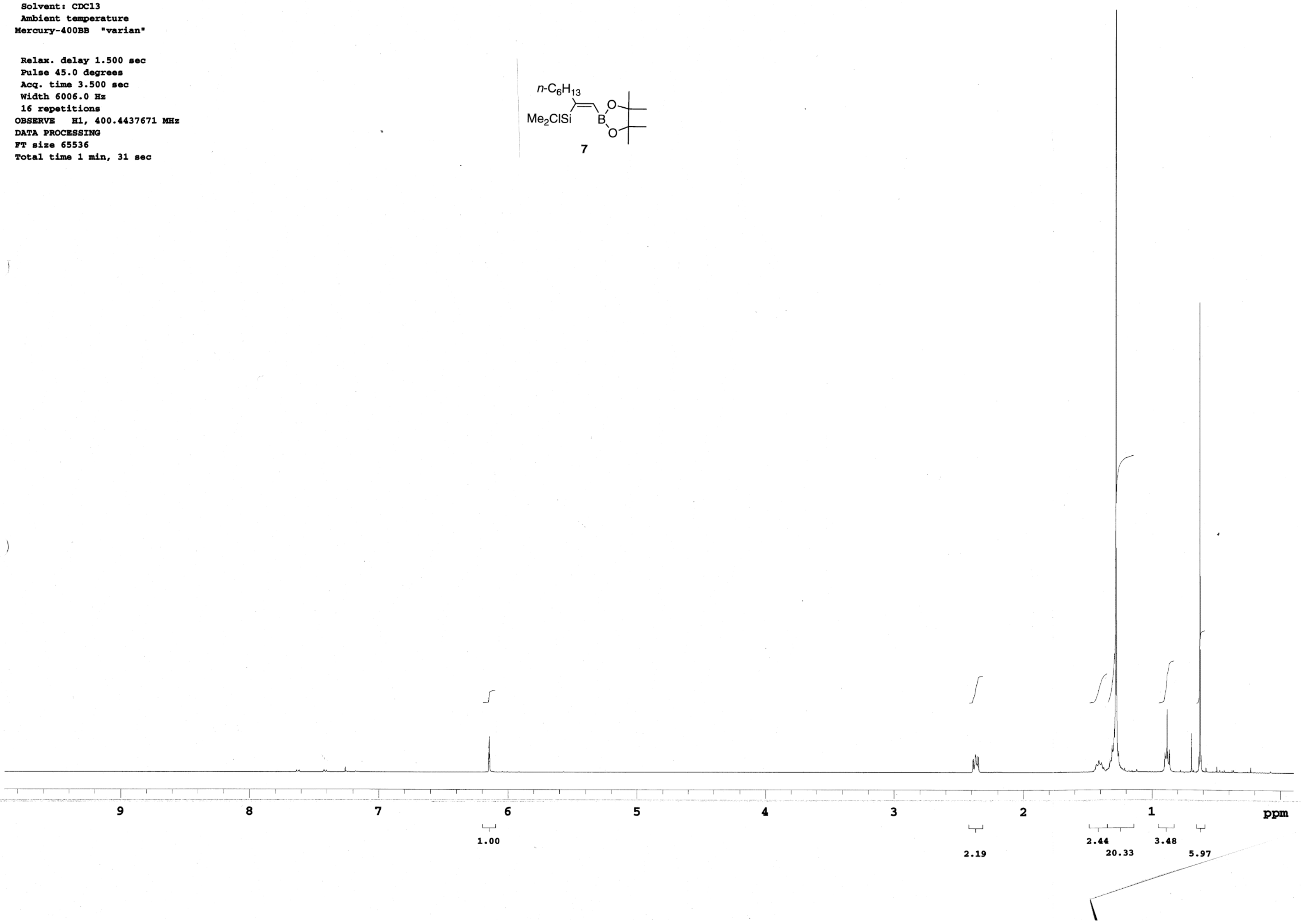
11. ^{1}H and ^{13}C NMR spectra of the compounds that do not have elemental analysis data

^{1}H and ^{13}C NMR spectra of **7**, **10a**, **10b**, **10d**, **10f**, **10g**, **10i**, **10j**, **10l**, **15**, **16** and **17a** are shown in following pages. NMR spectra of **10h**, unstable compound for isolation, are not provided because of difficulty to obtain pure sample.

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, 400.4437671 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 31 sec

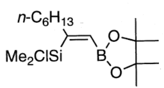


7

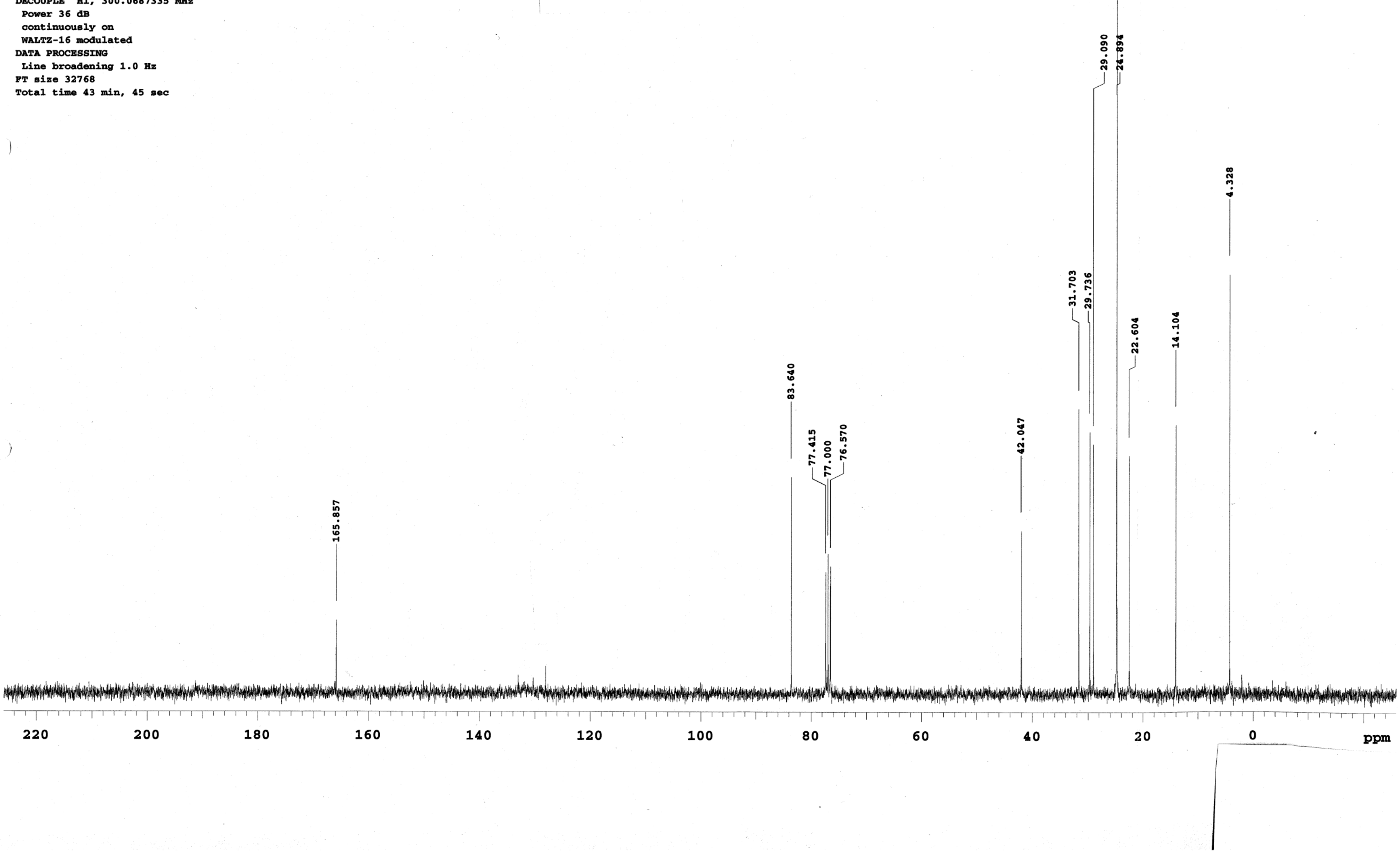
13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
GEMINI-300BB "varian2"

Relax. delay 1.158 sec
Pulse 45.0 degrees
Acq. time 0.842 sec
Width 19000.0 Hz
400 repetitions
OBSERVE C13, 75.4519651 MHz
DECOUPLE H1, 300.0687335 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 43 min, 45 sec



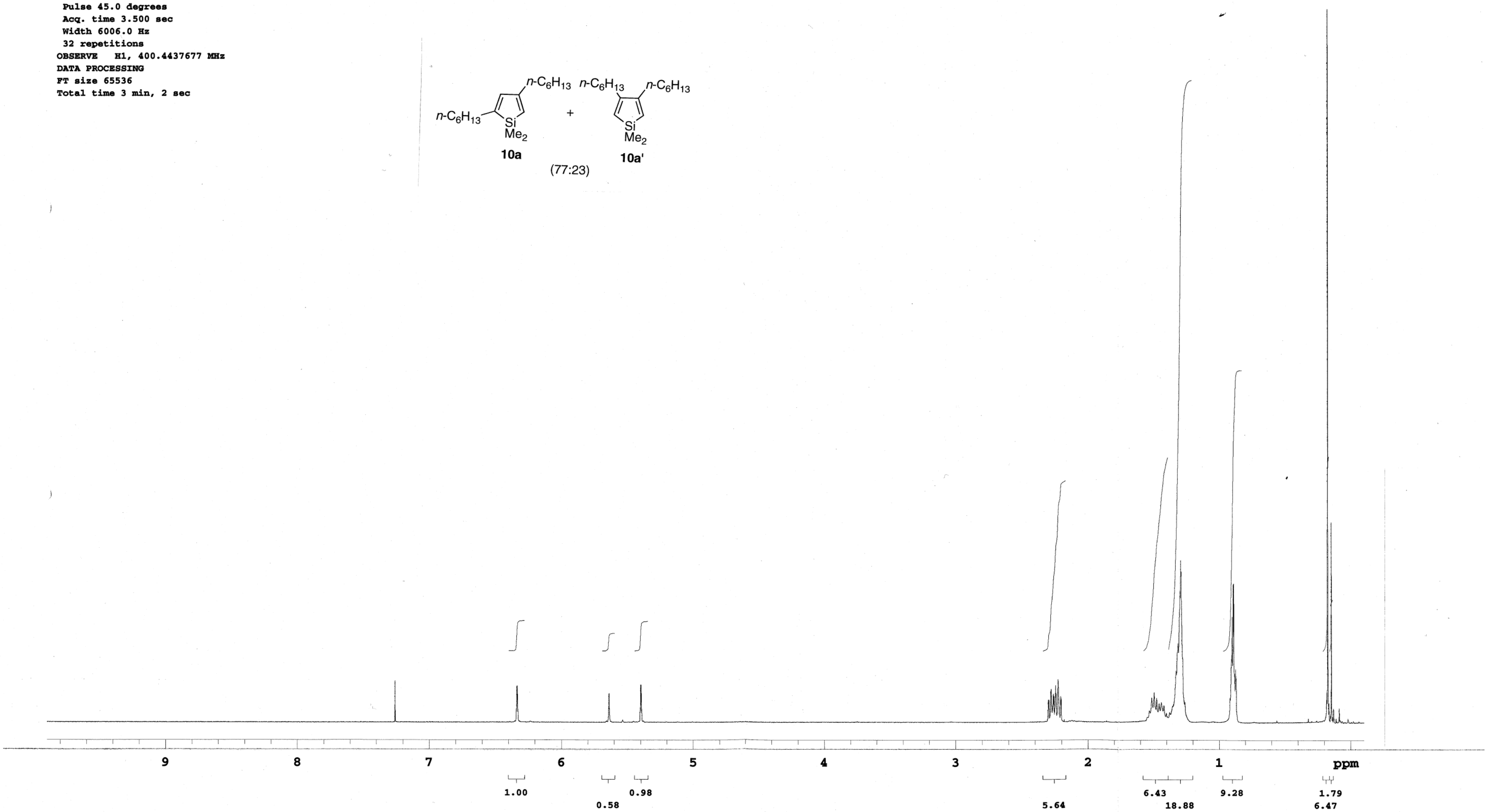
7



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
32 repetitions
OBSERVE H1, 400.4437677 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 2 sec



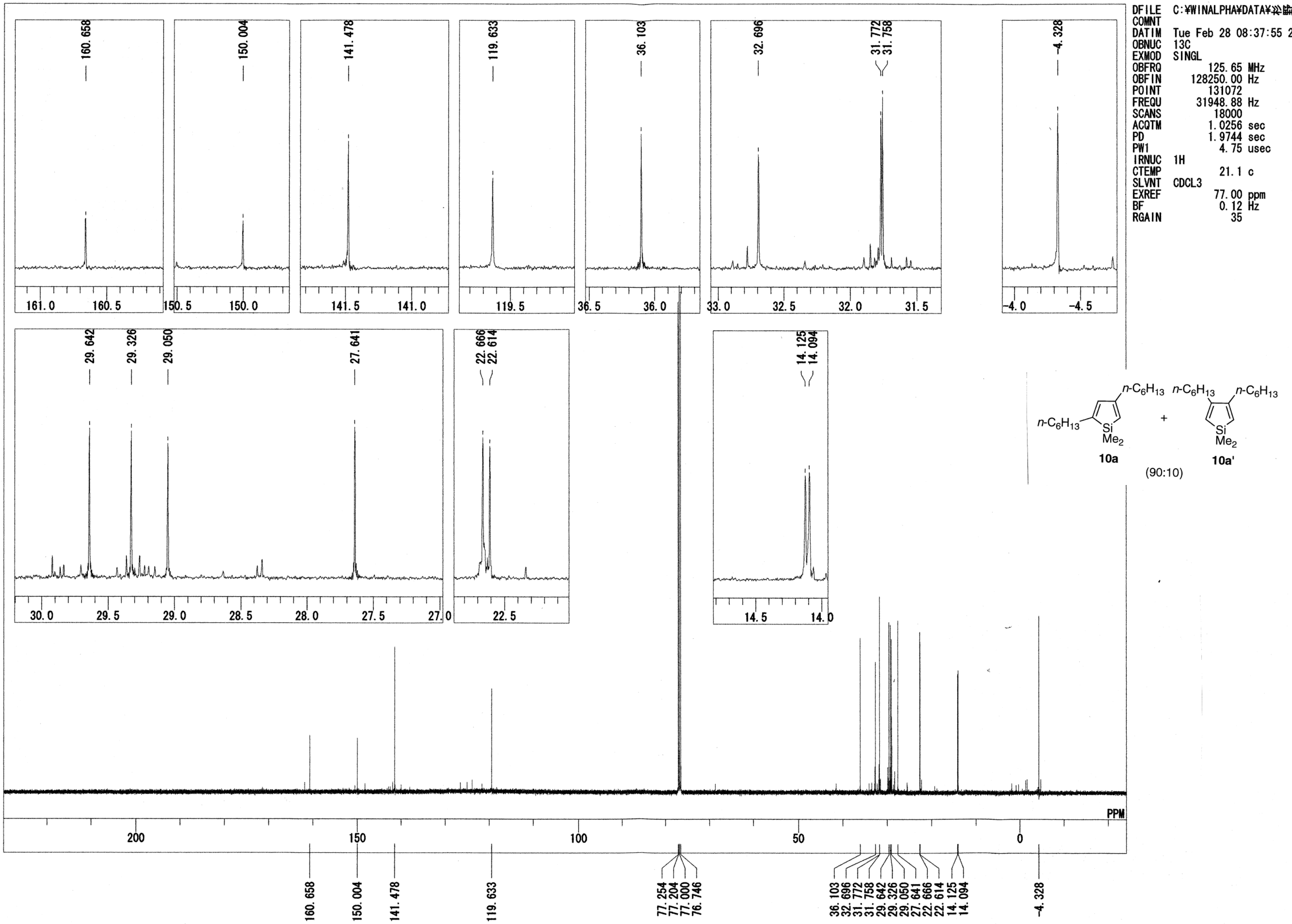
10a

+

10a'

(77:23)

C:¥WINALPHA¥DATA¥尖臨皿韭（野田）¥masuda-km227-BCM.ALS



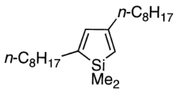
```
DFILE   C:¥WINALPHA¥DATA¥尖臨皿
COMNT
DATIM   Tue Feb 28 08:37:55 200
OBNUC   13C
EXMOD   SINGL
OBFRQ         125.65 MHz
OBFIN      128250.00 Hz
POINT         131072
FREQU       31948.88 Hz
SCANS          18000
ACQTM         1.0256 sec
PD            1.9744 sec
PW1             4.75 usec
IRNUC   1H
CTEMP           21.1 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             35
```

KM411

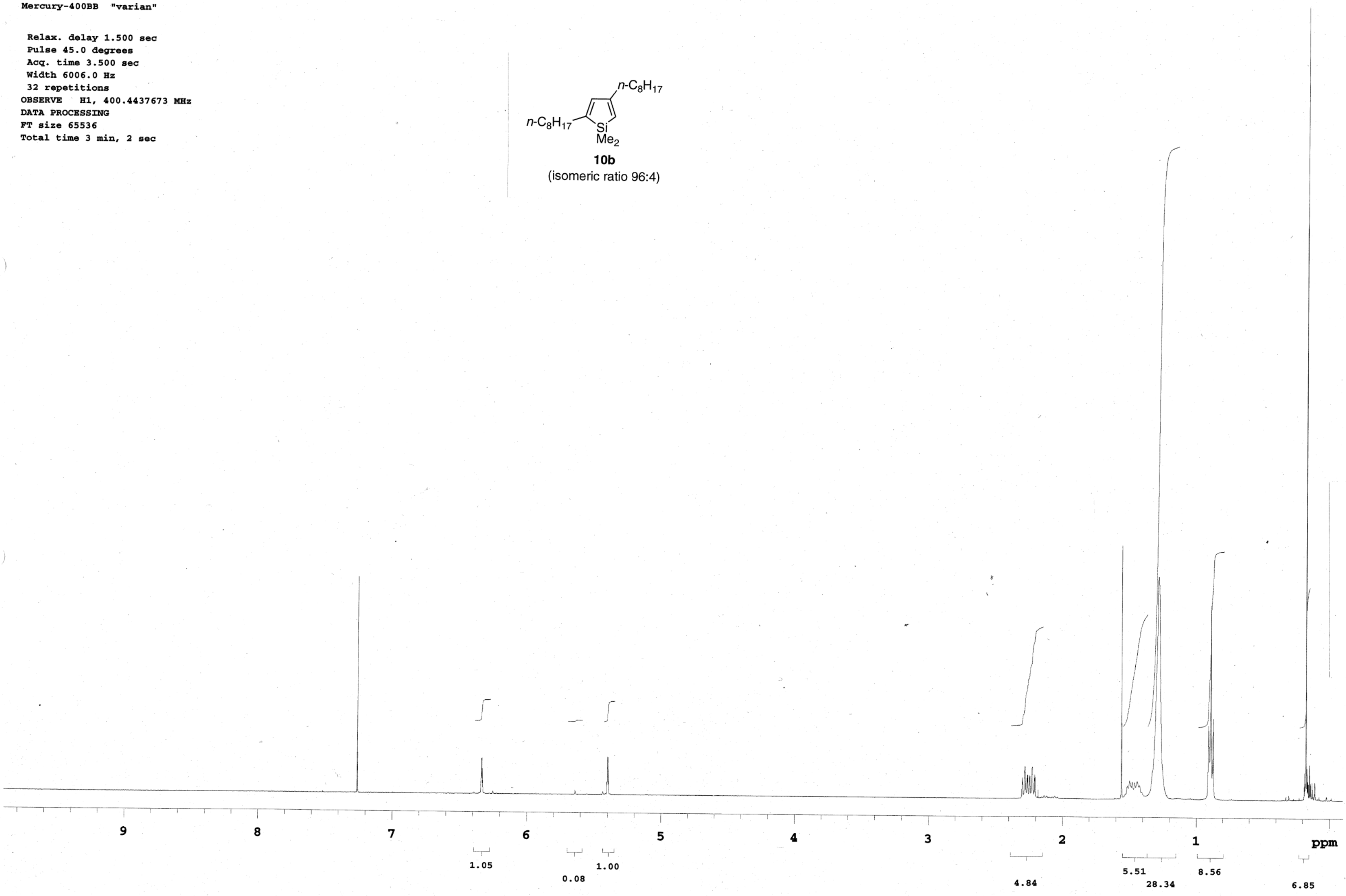
Pulse Sequence: s2pul

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

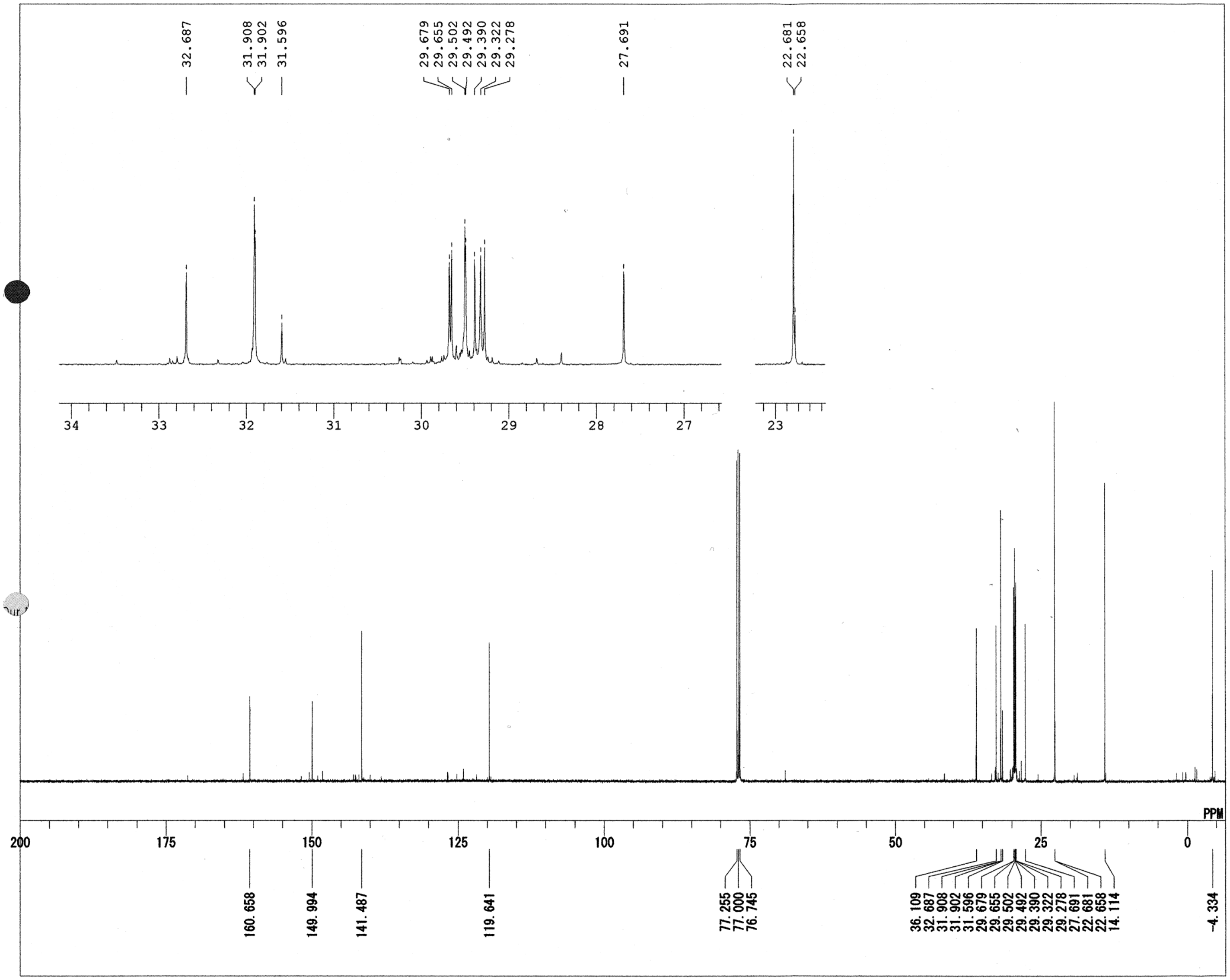
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 400.4437673 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 2 sec



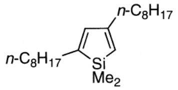
10b
(isomeric ratio 96:4)



C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM411-BCM.ALS



```
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM411-BC
COMNT
DATIM  Fri Nov 17 09:07:08 2006
OBNUC  13C
EXMOD  SINGL
OBFRQ        125.65 MHz
OBFIN     128449.48 Hz
POINT         65536
FREQU      28011.20 Hz
SCANS         11317
ACQTM        1.1698 sec
PD           2.0000 sec
PW1            4.50 usec
IRNUC  1H
CTEMP          23.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.42 Hz
RGAIN            35
```

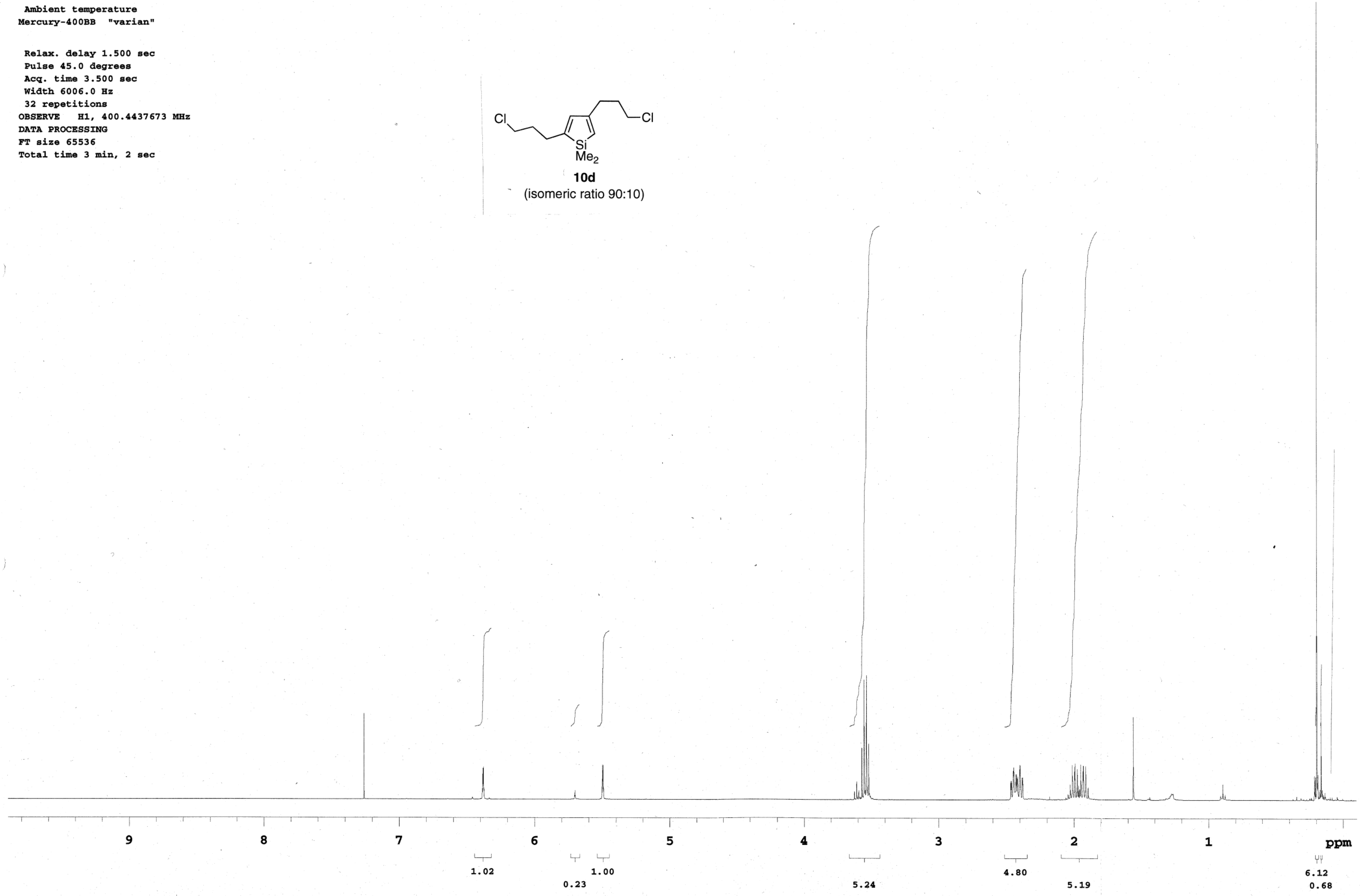


10b
(isomeric ratio 96:4)

STANDARD 1H OBSERVE

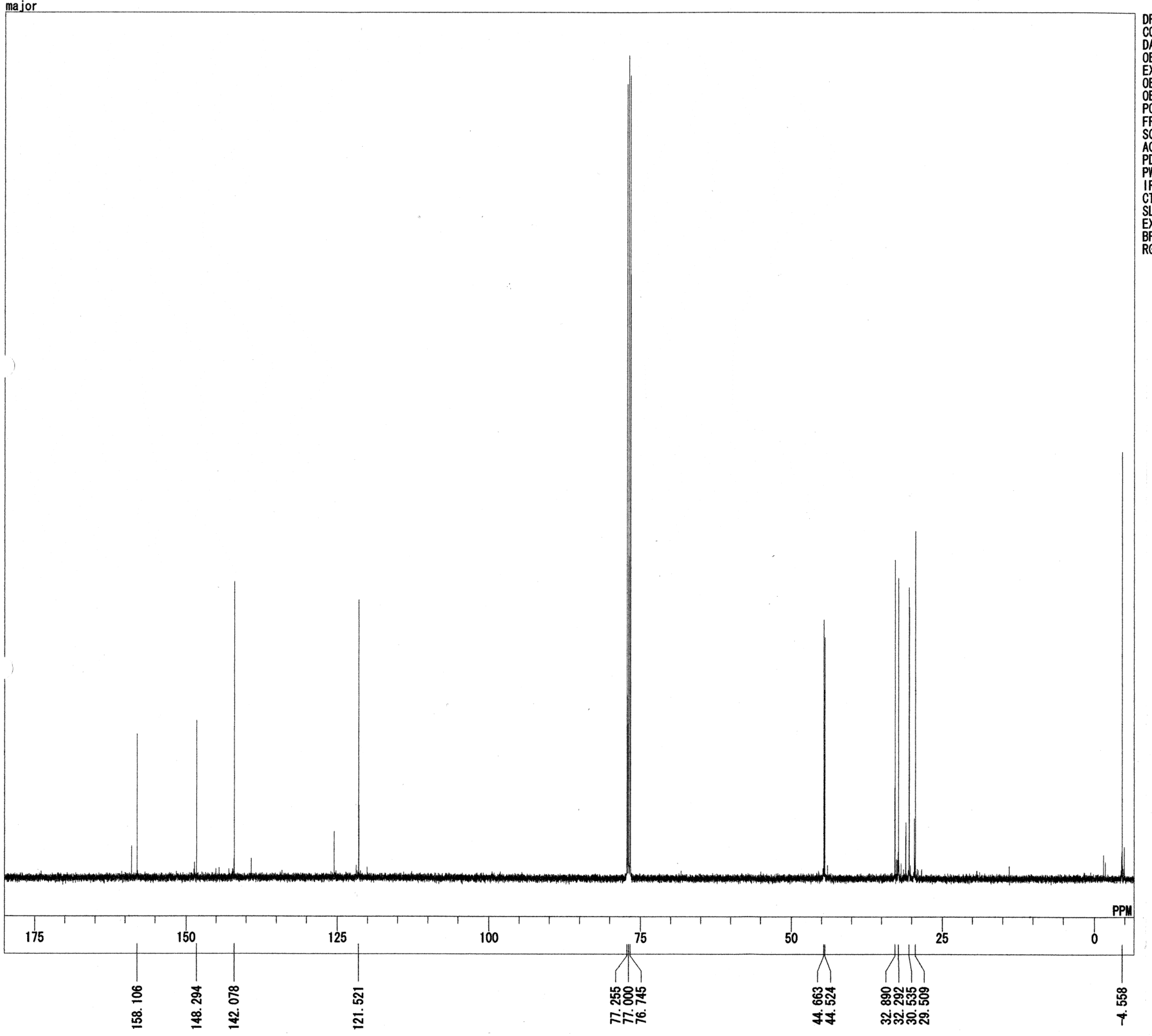
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 400.4437673 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 2 sec



10d
(isomeric ratio 90:10)

C:¥WINALPHA¥DATA¥[illegible]¥[illegible]¥KM363-BCM.ALS
major



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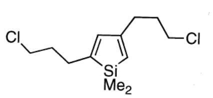
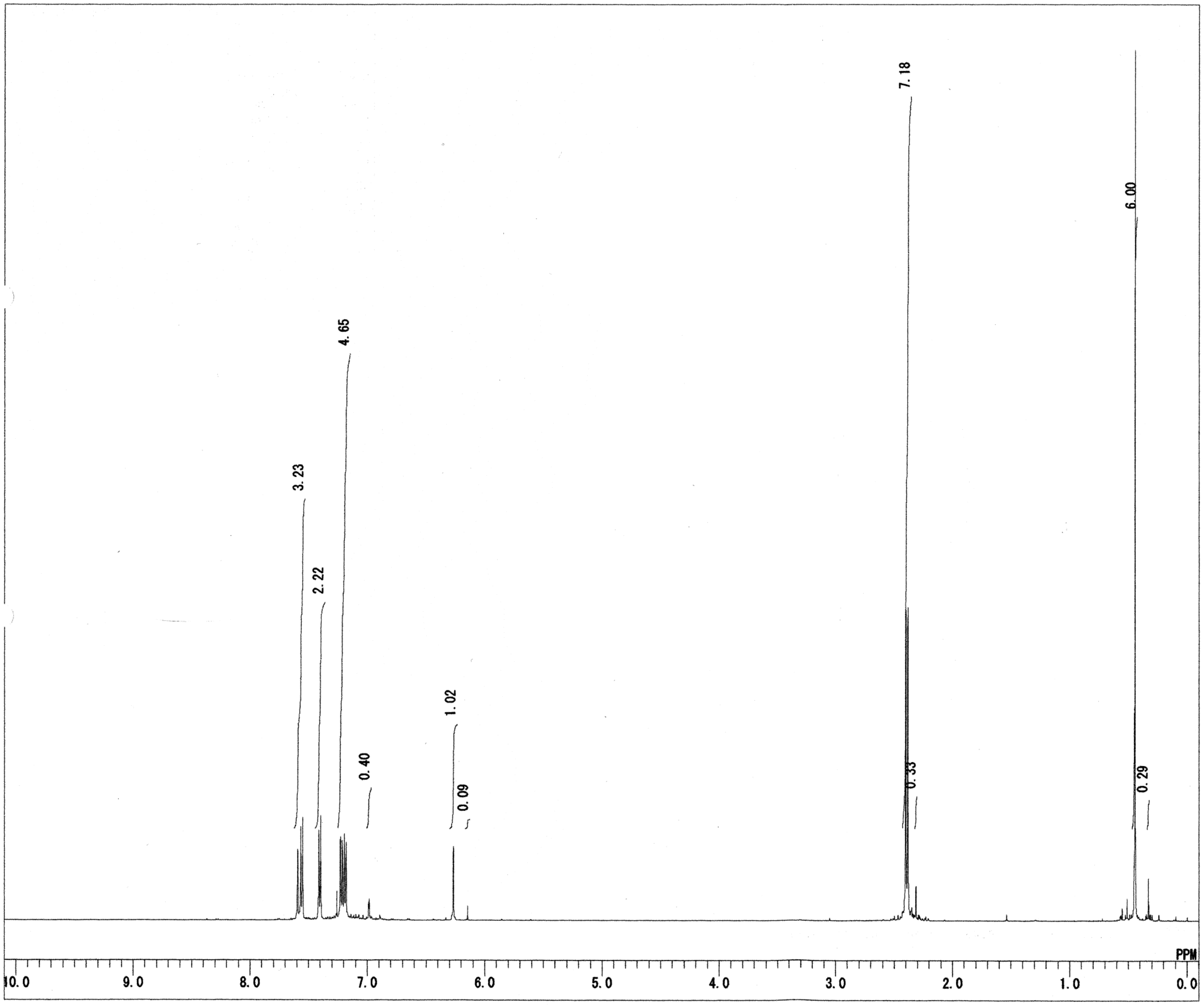
DFILE  C:¥WINALPHA¥DATA¥[illegible]¥[illegible]¥KM363-BCM.ALS
COMNT  major
DATIM  Thu Sep 07 21:47:32 2006
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        65536
FREQU     28011.20 Hz
SCANS         2000
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         24.6 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.43 Hz
RGAIN           35
```

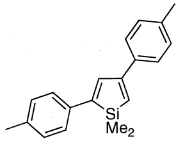


10d
(isomeric ratio 90:10)

C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM520-H.ALS



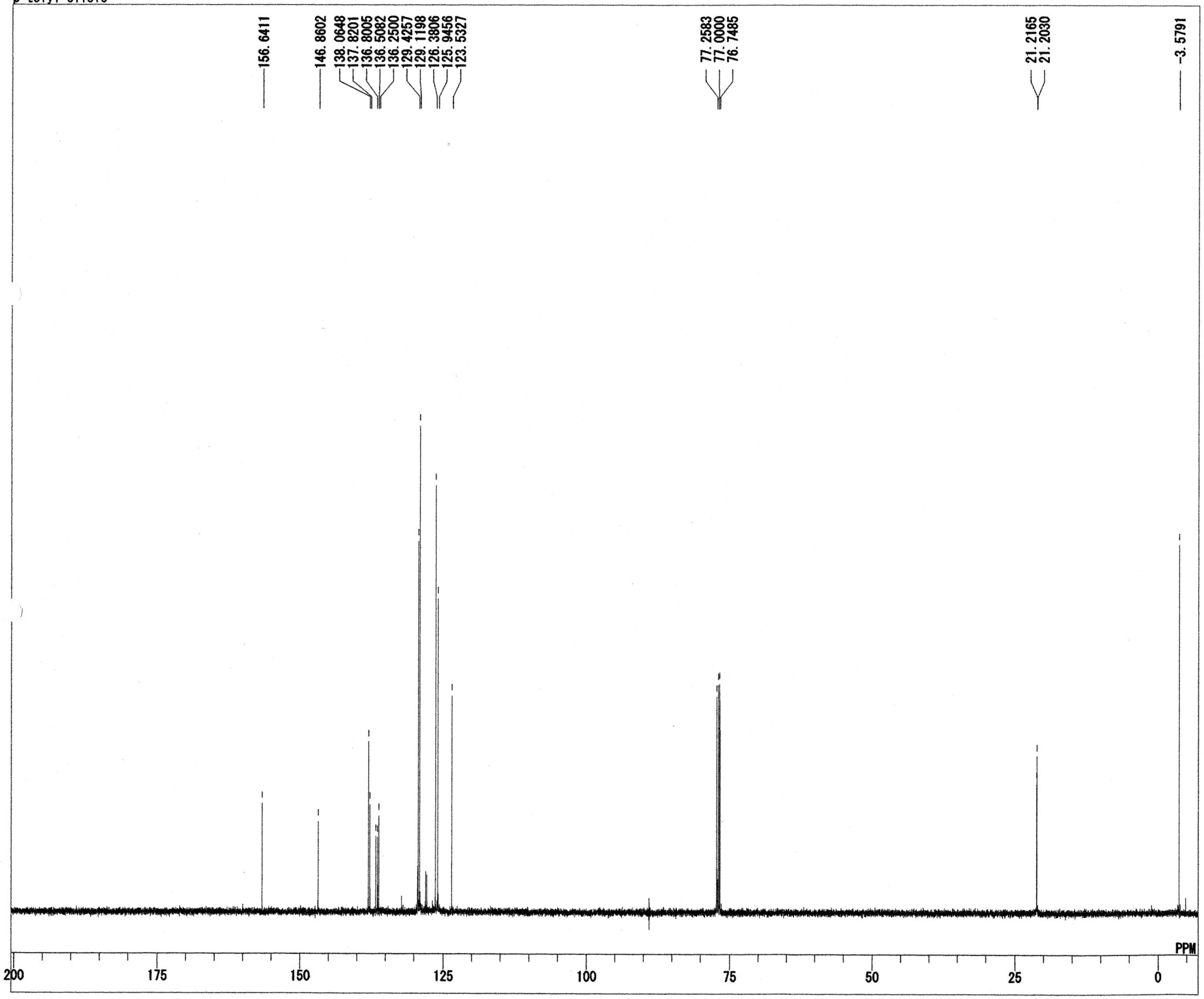
```
DFILE   C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM520-H.ALS
COMNT
DATIM   Thu Apr 12 16:06:29 2007
OBNUC   1H
EXMOD   SINGL
OBFRQ        500.00 MHz
OBFIN     162000.00 Hz
POINT         32768
FREQU       5998.80 Hz
SCANS             8
ACQTM        5.4624 sec
PD           3.0000 sec
PW1            6.50 usec
IRNUC   1H
CTEMP          22.0 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.15 Hz
RGAIN            16
```



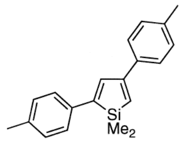
10f

(isomeric ratio 96:4)

C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM520-BCM.ALS
p-tolyl-silole



```
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM520-BCM.ALS
COMNT  p-tolyl-silole
DATIM  Thu Apr 12 16:36:45 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT        32768
FREQU     28011.20 Hz
SCANS          501
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         22.8 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.43 Hz
RGAIN           33
```



10f

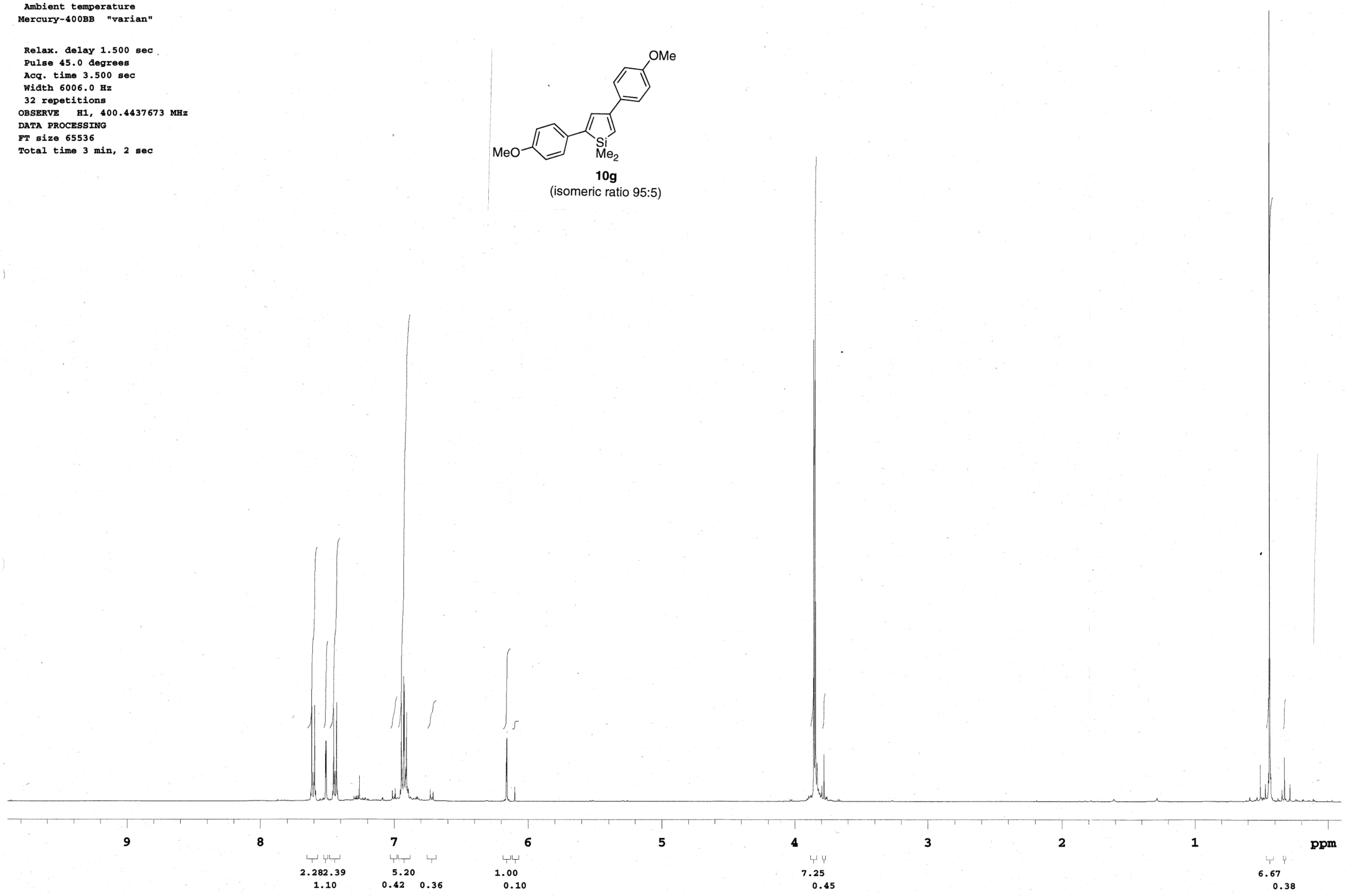
(isomeric ratio 96:4)

KM506column

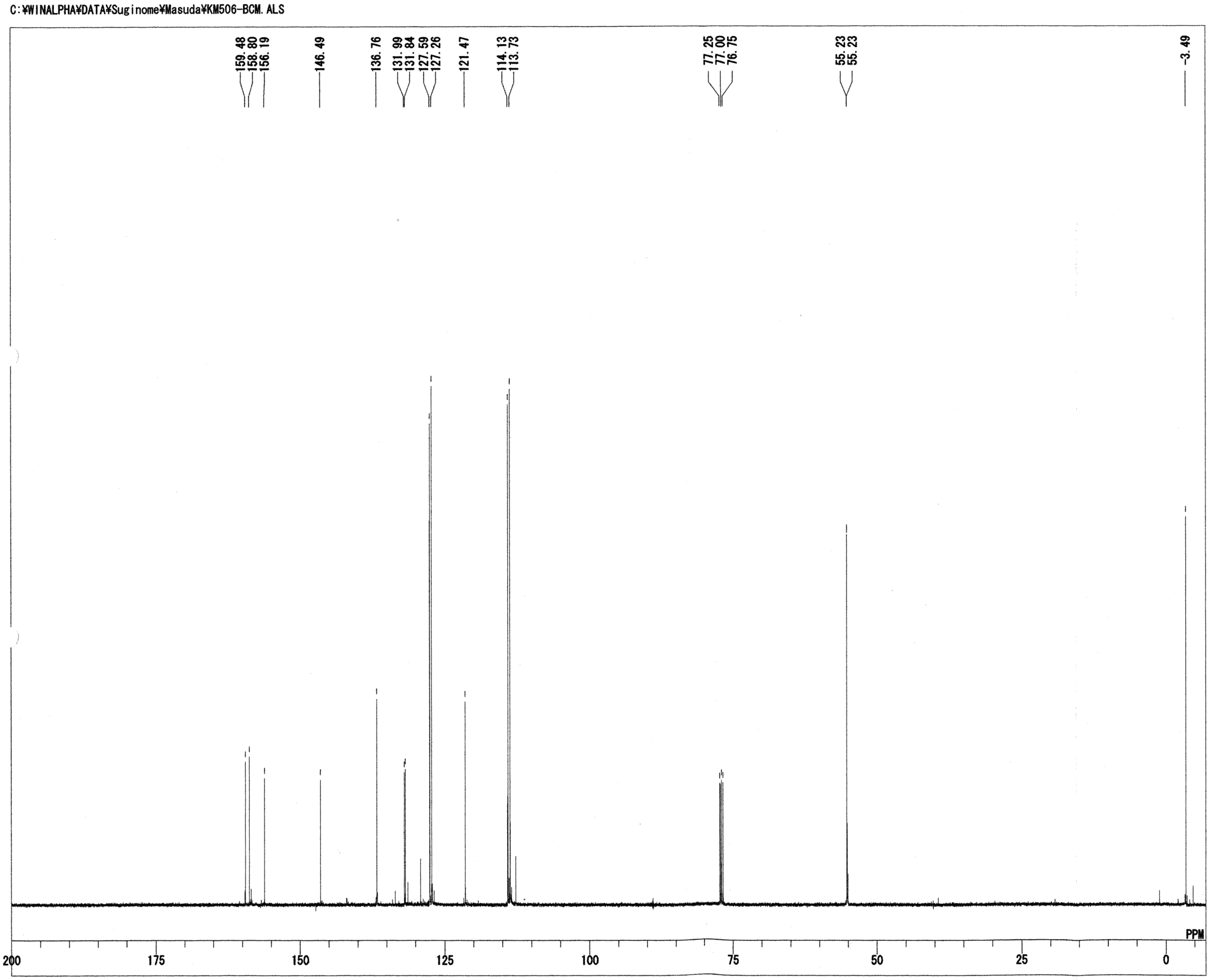
Pulse Sequence: s2pul

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

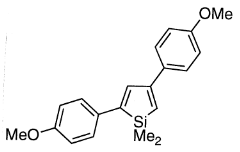
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 400.4437673 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 2 sec



10g
(isomeric ratio 95:5)



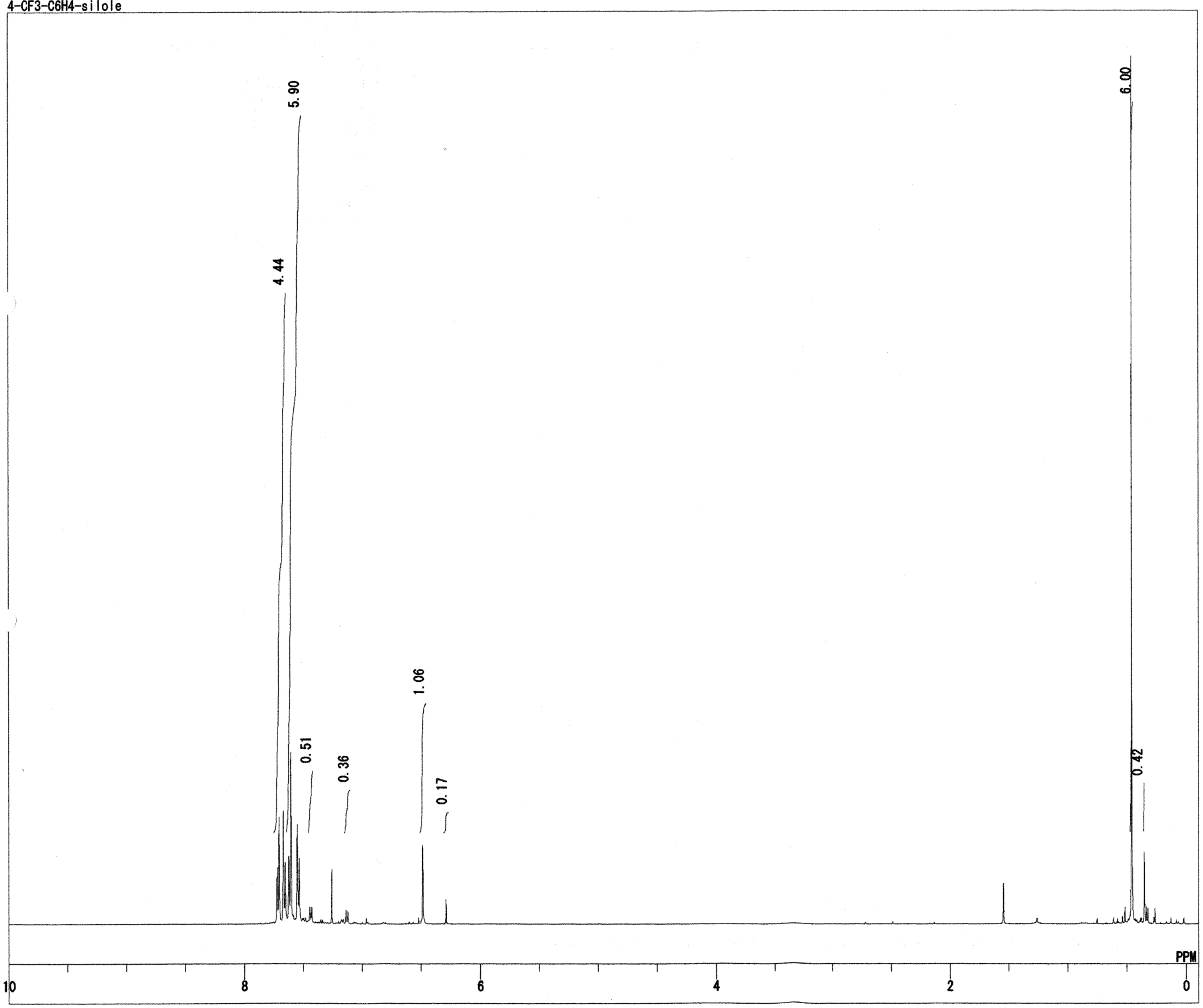
```
DFILE   C:¥WINALPHA¥DATA¥Suginor
COMNT
DATIM   Wed Apr 04 17:43:13 200
OBNUC   13C
EXMOD   SINGL
OBFRQ        125.65 MHz
OBFIN     128449.48 Hz
POINT        262144
FREQU      28011.20 Hz
SCANS           700
ACQTM        1.1698 sec
PD           2.0000 sec
PW1            4.50 usec
IRNUC   1H
CTEMP          22.7 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             0.42 Hz
RGAIN            35
```



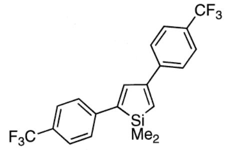
10g

(isomeric ratio 95:5)

C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM515-H-ft.als
4-CF3-C6H4-silole

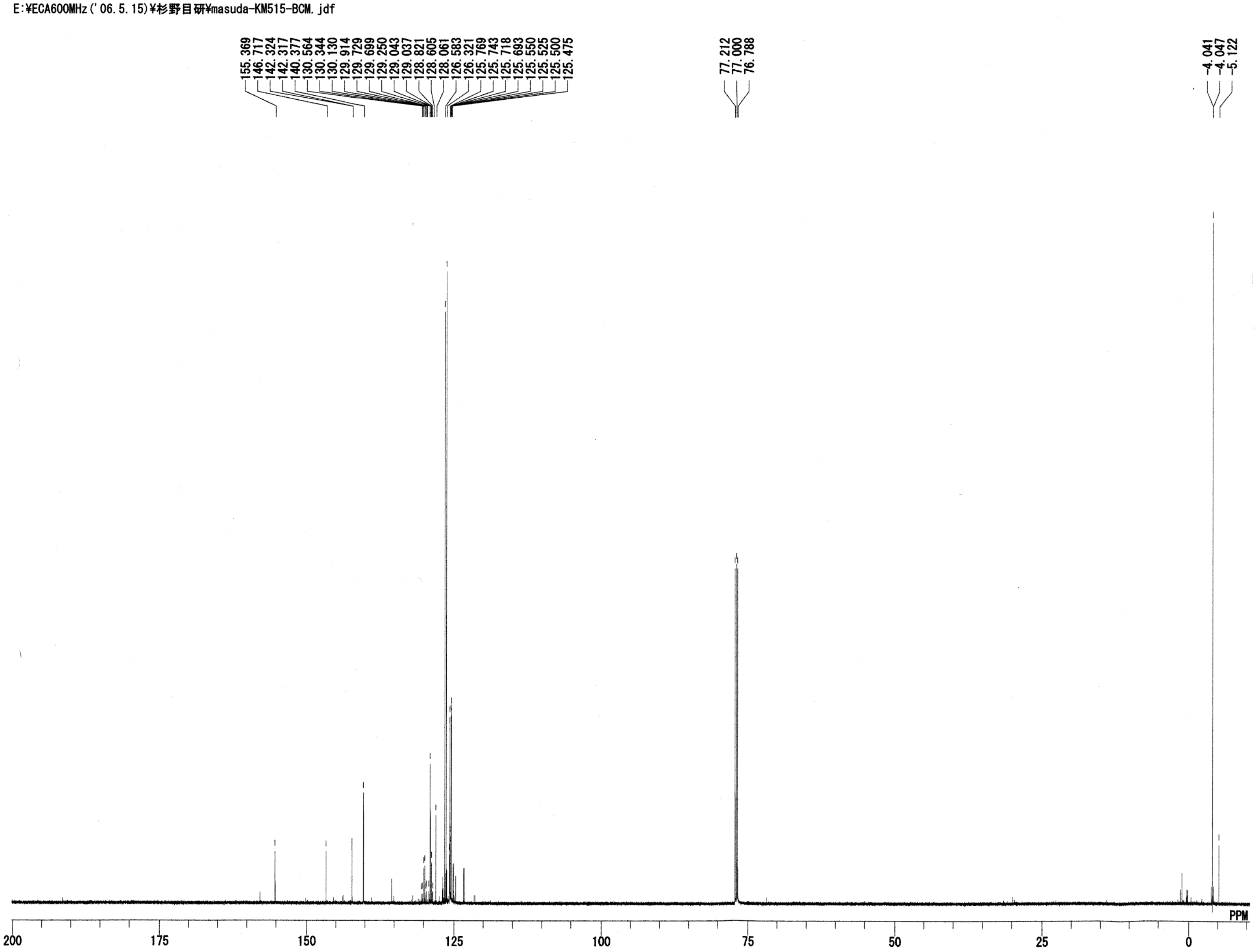


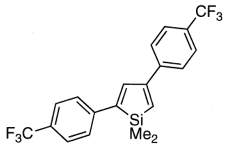
```
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM515-H-ft.als
COMNT  4-CF3-C6H4-silole
DATIM  Sat Apr 07 12:56:08 2007
OBNUC  1H
EXMOD  SINGL
OBFRQ       500.00 MHz
OBFIN    162000.00 Hz
POINT        32768
FREQU      5998.80 Hz
SCANS            8
ACQTM       5.4624 sec
PD          3.0000 sec
PW1           6.50 usec
IRNUC  1H
CTEMP         21.6 c
SLVNT  CDCL3
EXREF         7.26 ppm
BF            0.42 Hz
RGAIN           17
```



10i

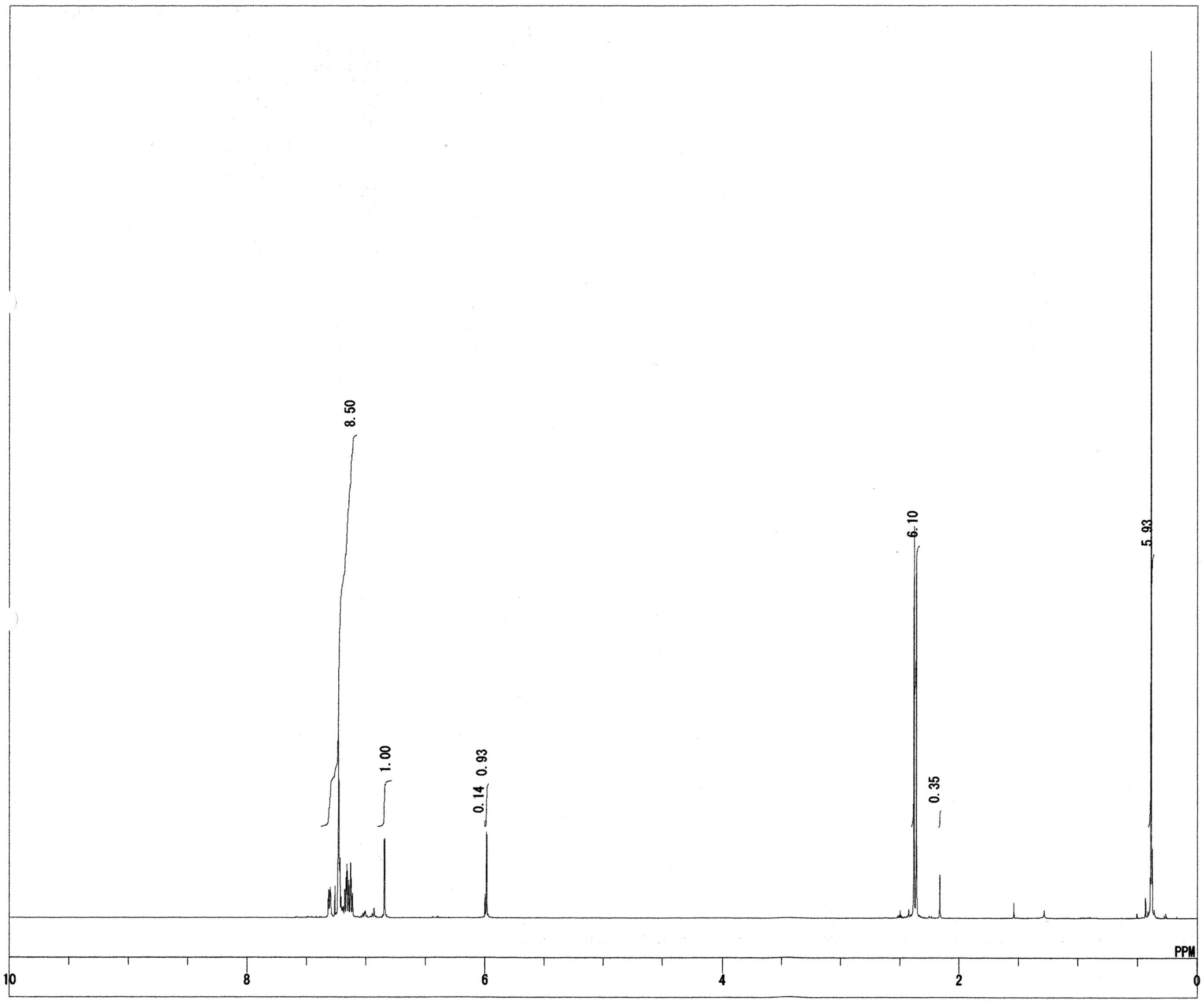
(isomeric ratio 93:7)



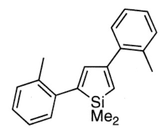


10i
(isomeric ratio 93:7)

C:¥WINALPHA¥DATA¥Suginome¥Masuda¥tolylsilole-H.ALS

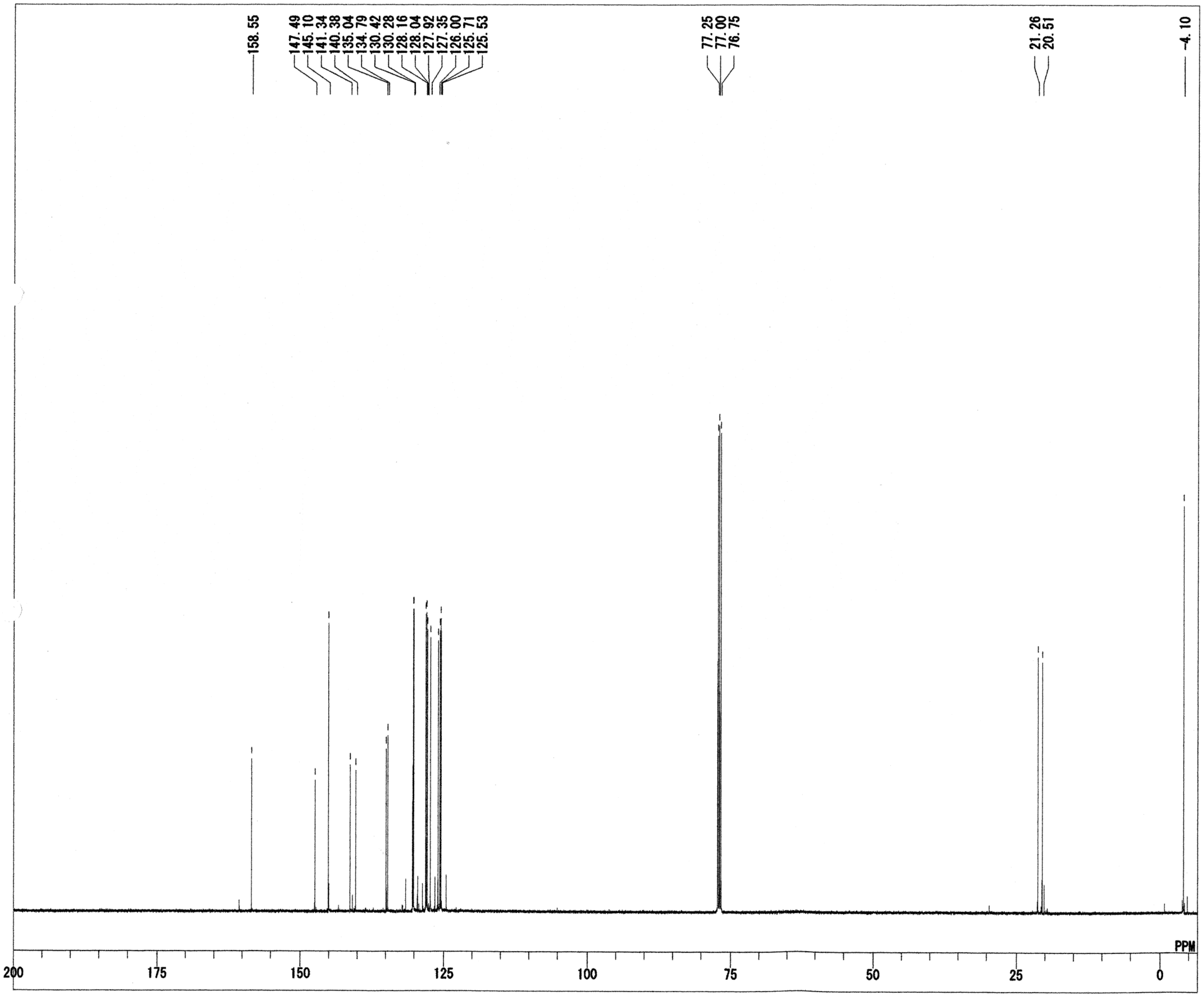


```
DFILE   C:¥WINALPHA¥DATA¥Suginome¥Masuda¥tolylsilole-H.
COMNT
DATIM   Tue Apr 18 23:44:19 2006
OBNUC   1H
EXMOD   SINGL
OBFRQ         500.00 MHz
OBFIN      162000.00 Hz
POINT          32768
FREQU        5998.80 Hz
SCANS              8
ACQTM         5.4624 sec
PD            3.0000 sec
PW1             6.50 usec
IRNUC   1H
CTEMP           21.2 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.15 Hz
RGAIN             16
```

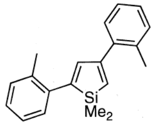


10j
(isomeric ratio 93:7)

C:¥WINALPHA¥DATA¥Suginome¥Masuda¥tolylsilole-BCM.ALS



```
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Masuda¥tolylsilole-BC
COMNT
DATIM  Wed Apr 19 08:42:45 2006
OBNUC  13C
EXMOD  SINGL
OBFRQ       125.65 MHz
OBFIN    128449.48 Hz
POINT       131072
FREQU     28011.20 Hz
SCANS        10000
ACQTM       1.1698 sec
PD          2.0000 sec
PW1           4.50 usec
IRNUC  1H
CTEMP         21.7 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            0.42 Hz
RGAIN           35
```

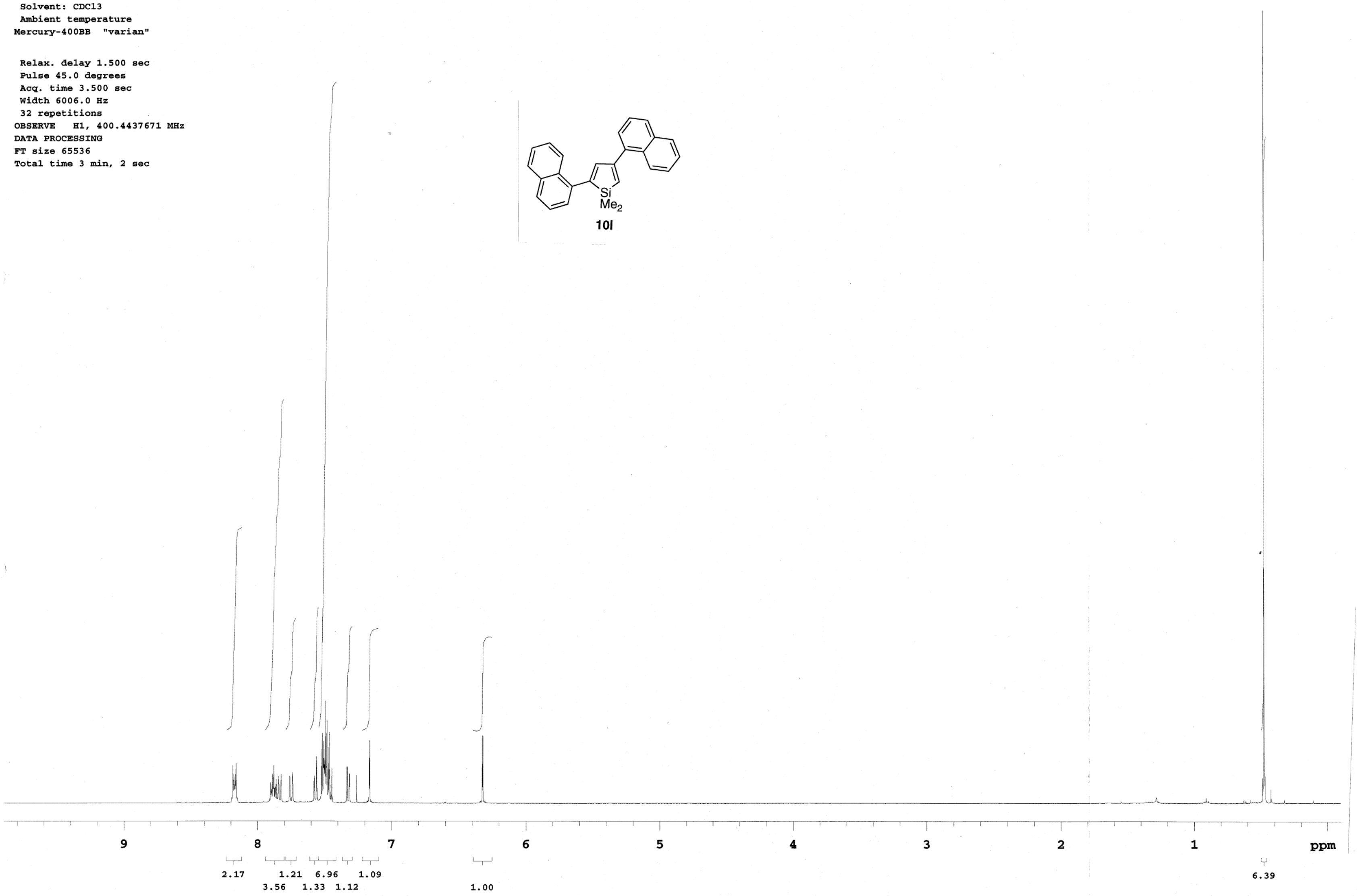


10j
(isomeric ratio 93:7)

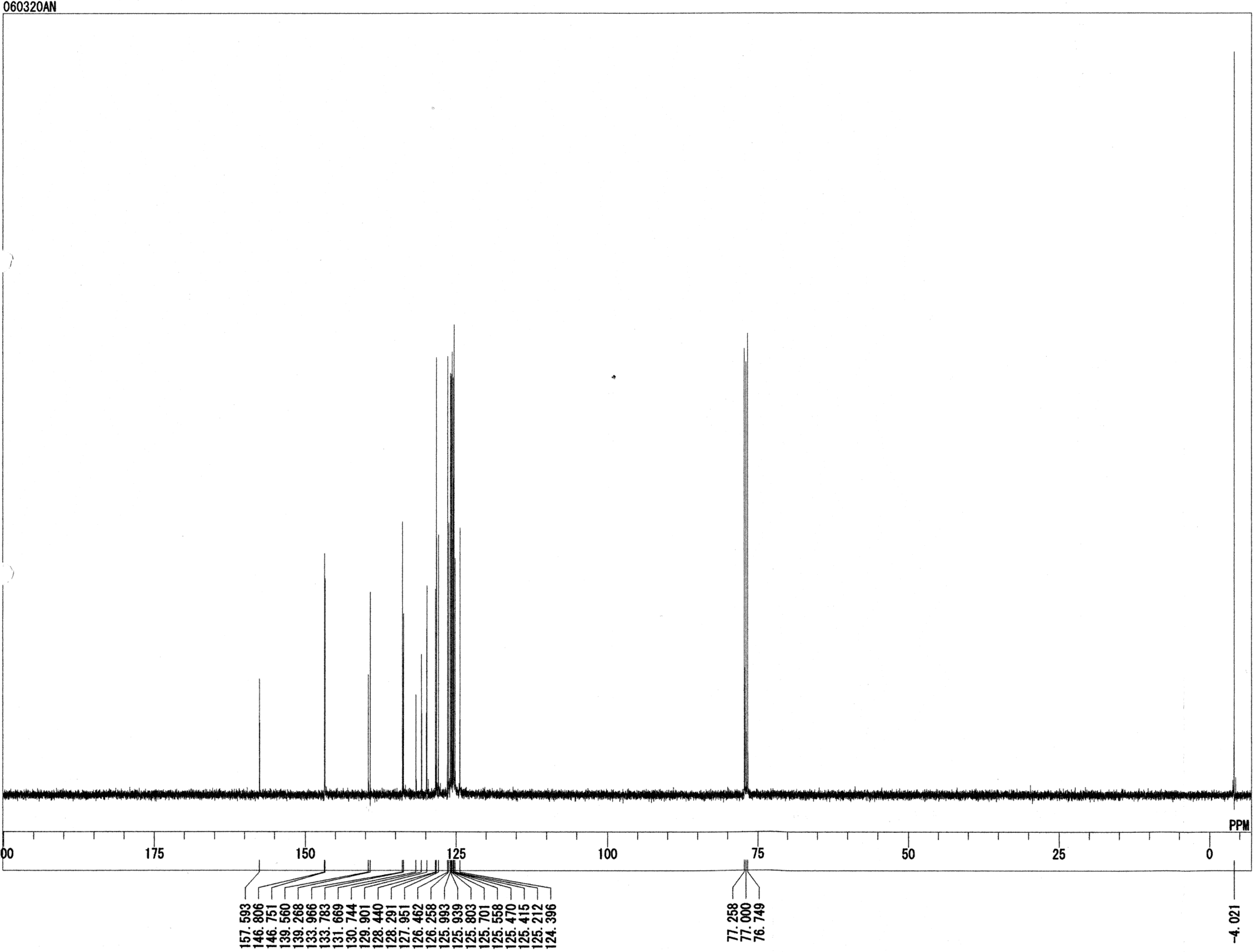
STANDARD 1H OBSERVE

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

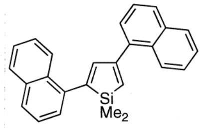
 Relax. delay 1.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6006.0 Hz
 32 repetitions
OBSERVE   H1, 400.4437671 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 2 sec



```
C:¥WINALPHA¥DATA¥杉野目研¥増田¥KM258-BCM.ALS
060320AN
```

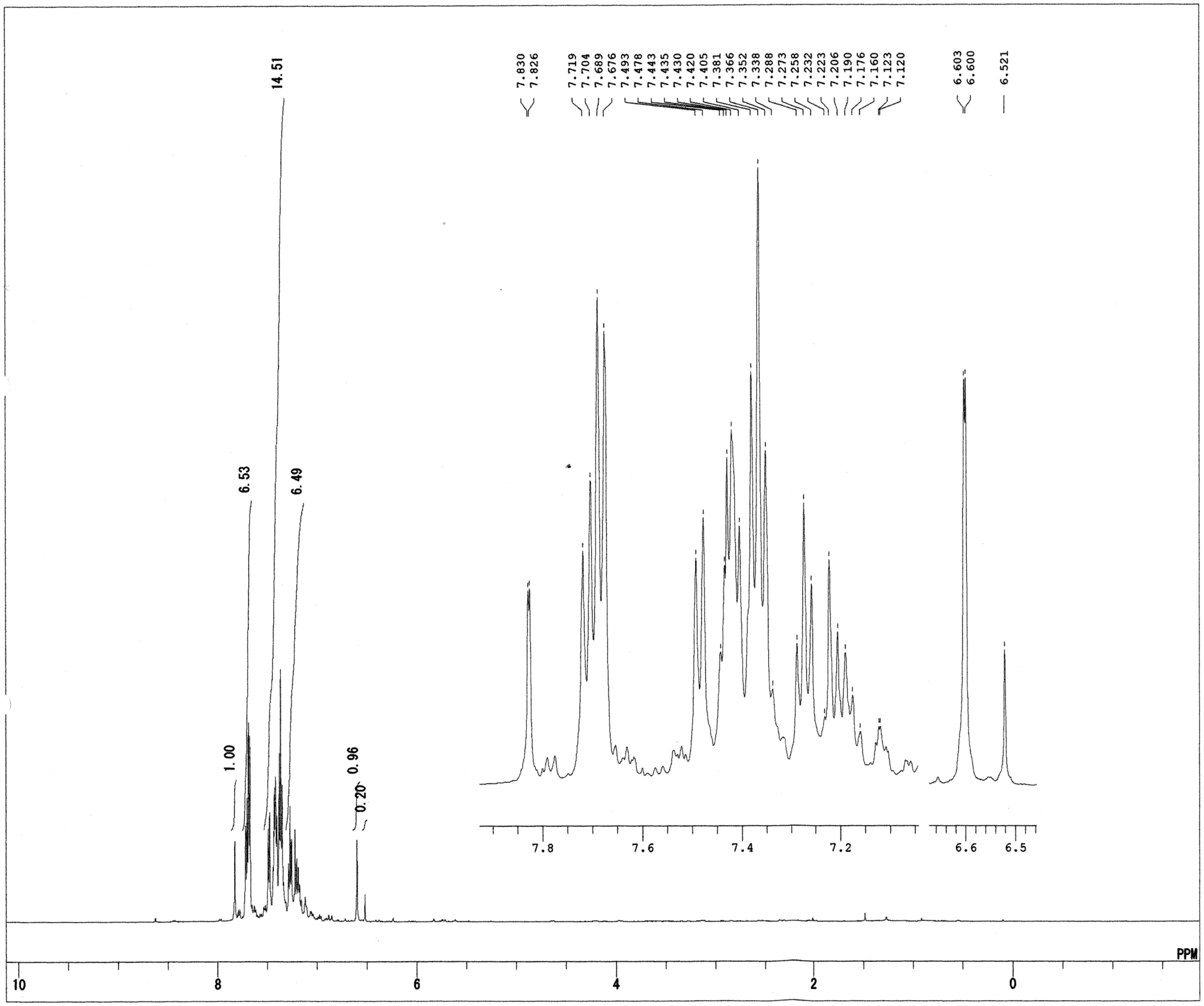


```
DFILE  C:¥WINALPHA¥DATA¥杉野目研¥増田¥KM25
COMNT  060320AN
DATIM  Thu Mar 23 16:25:35 2006
OBNUC  13C
EXMOD  SINGL
OBFRQ        125.65 MHz
OBFIN     128449.48 Hz
POINT         32768
FREQU      28011.20 Hz
SCANS          1200
ACQTM        1.1698 sec
PD           2.0000 sec
PW1            4.50 usec
IRNUC  1H
CTEMP          22.0 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.15 Hz
RGAIN            35
```

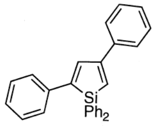


10l

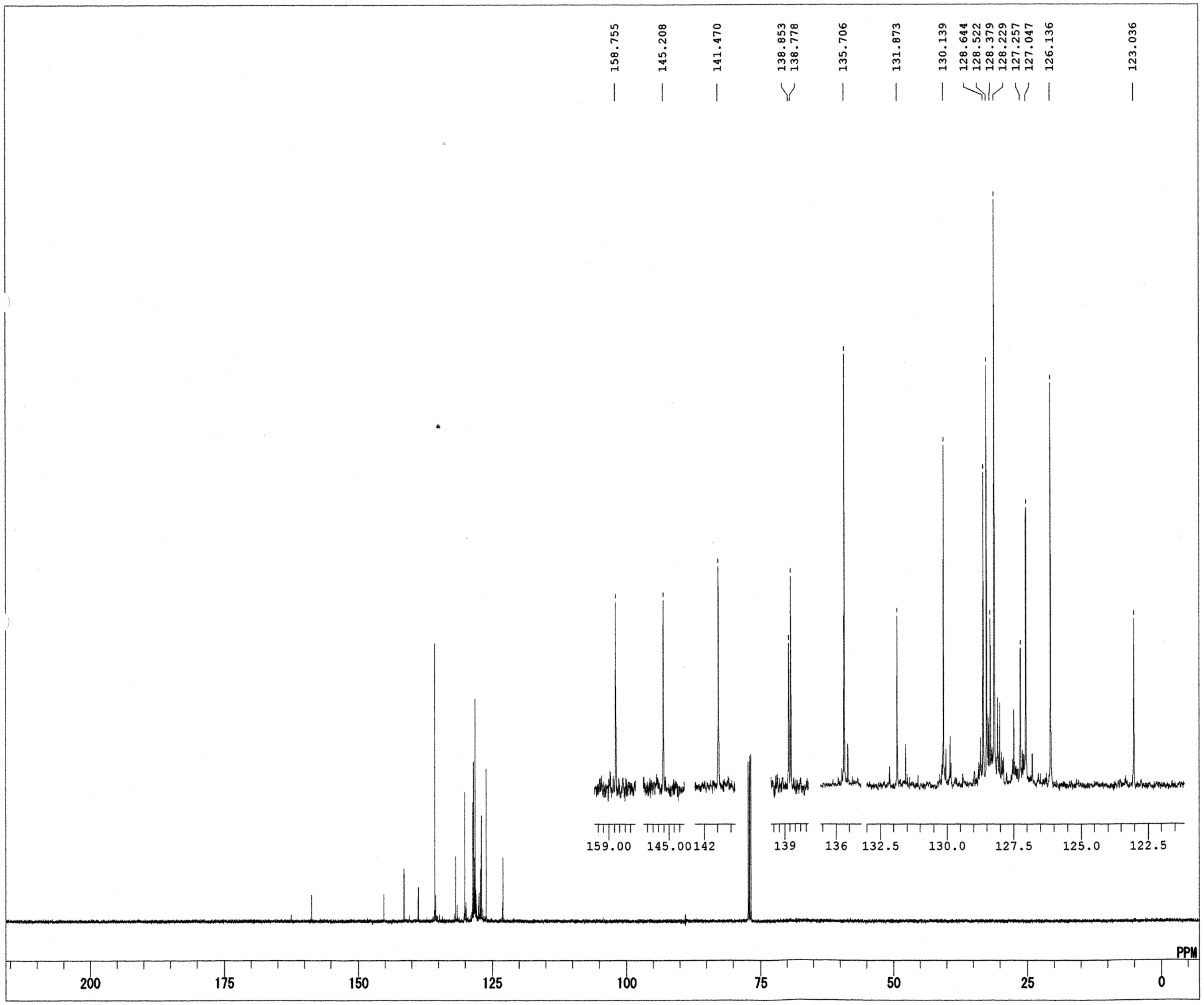
C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM522-H. ALS



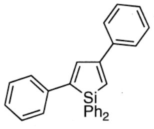
```
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM522-H. ALS
COMNT
DATIM  Thu Apr 12 23:37:53 2007
OBNUC  1H
EXMOD  SINGL
OBFRQ      500.00 MHz
OBFIN   162000.00 Hz
POINT       32768
FREQU     5998.80 Hz
SCANS           8
ACQTM      5.4624 sec
PD         3.0000 sec
PW1          6.50 usec
IRNUC  1H
CTEMP        21.8 c
SLVNT  CDCL3
EXREF        7.83 ppm
BF           0.90 Hz
RGAIN          15
```



15
(isomeric ratio 91:9)



```
DFILE  C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM522-BCM.ALS
COMNT
DATIM  Fri Apr 13 00:03:37 2007
OBNUC  13C
EXMOD  SINGL
OBFRQ      125.65 MHz
OBFIN   128449.48 Hz
POINT       32768
FREQU    28011.20 Hz
SCANS         432
ACQTM      1.1698 sec
PD         2.0000 sec
PW1          4.50 usec
IRNUC  1H
CTEMP        22.7 c
SLVNT  CDCL3
EXREF       77.00 ppm
BF           0.70 Hz
RGAIN          35
```



15

(isomeric ratio 91:9)

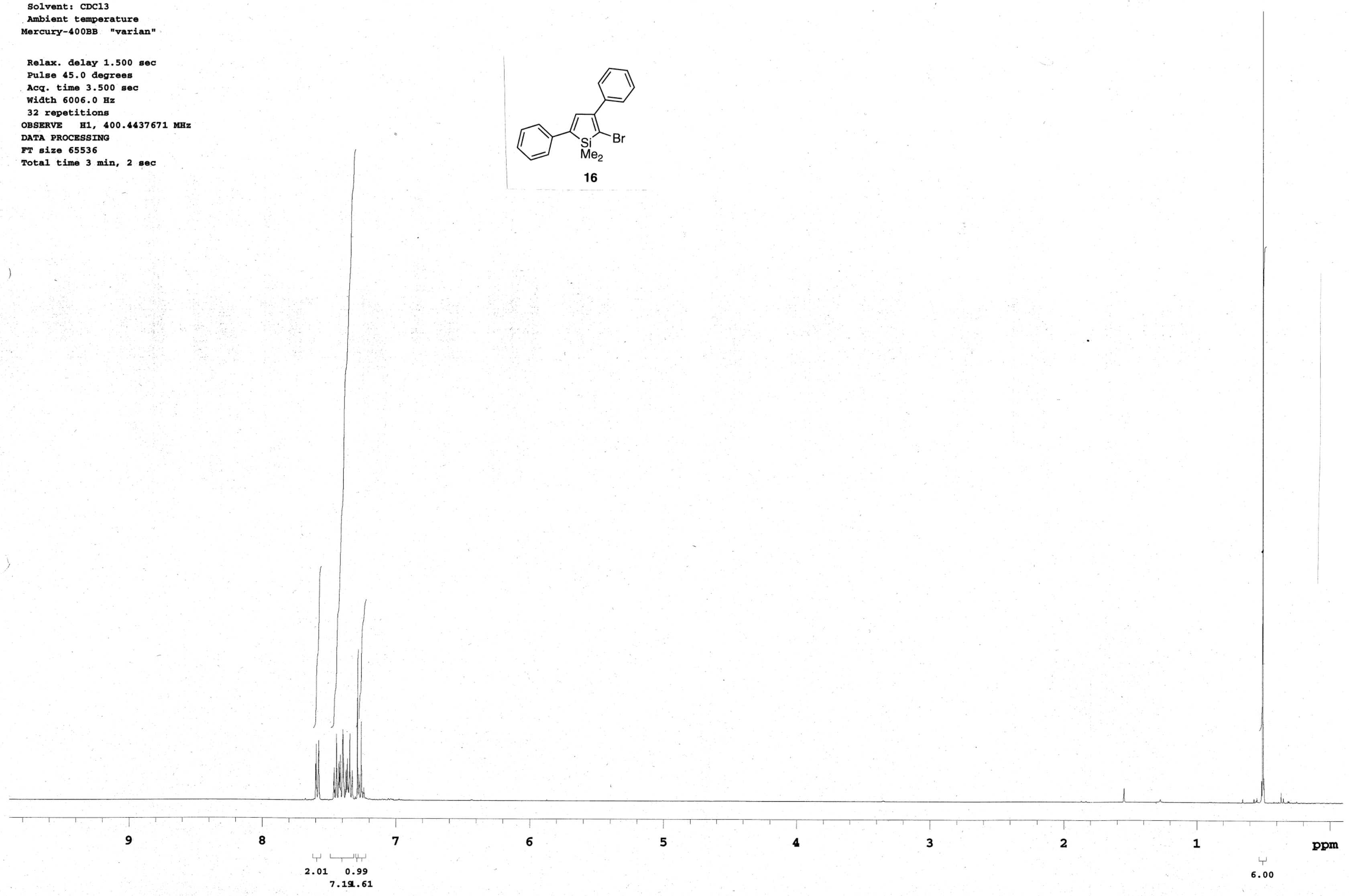
STANDARD 1H OBSERVE

Pulse Sequence: s2pul

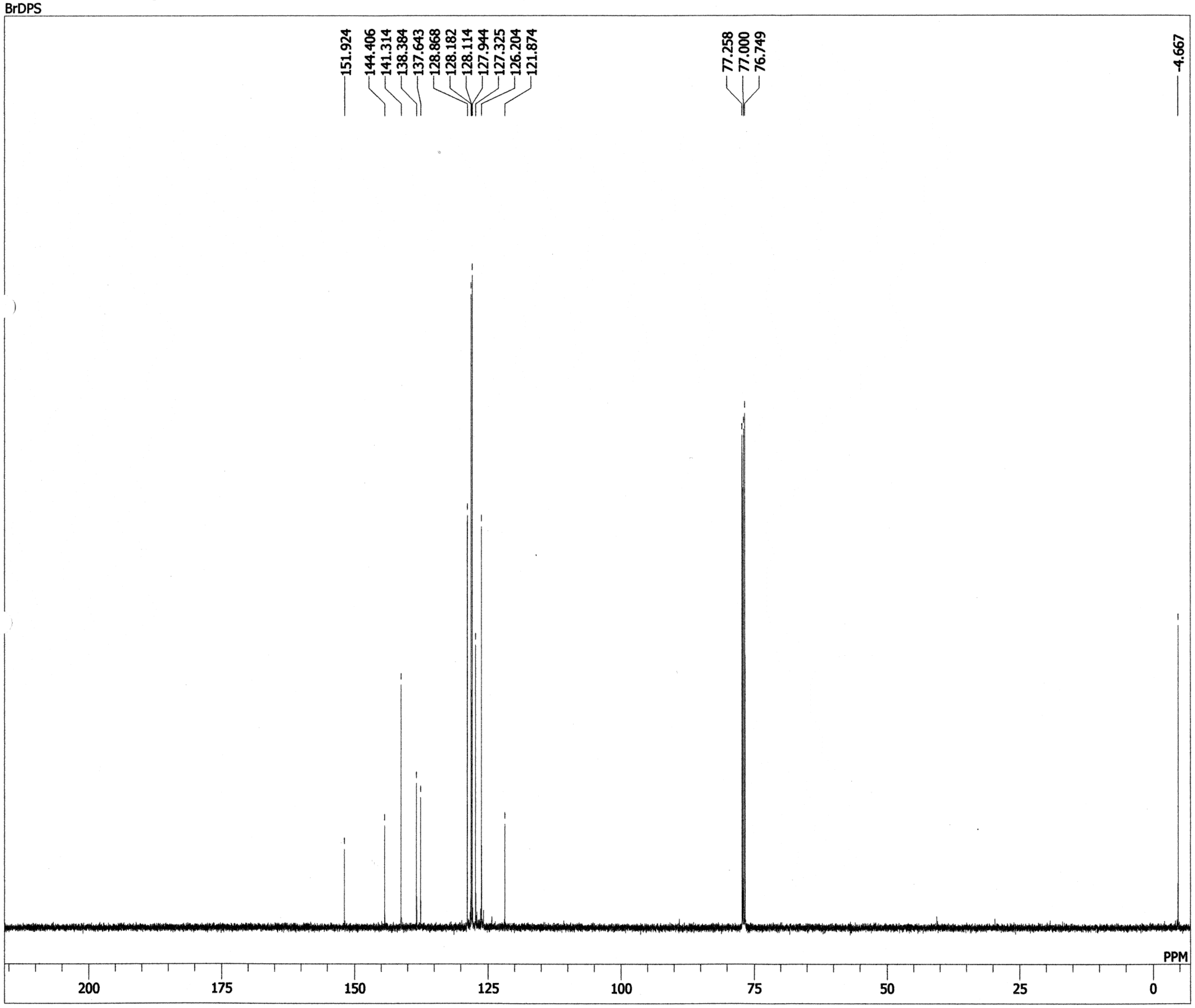
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
32 repetitions
OBSERVE H1, 400.4437671 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 2 sec

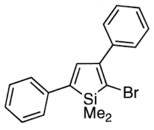
16



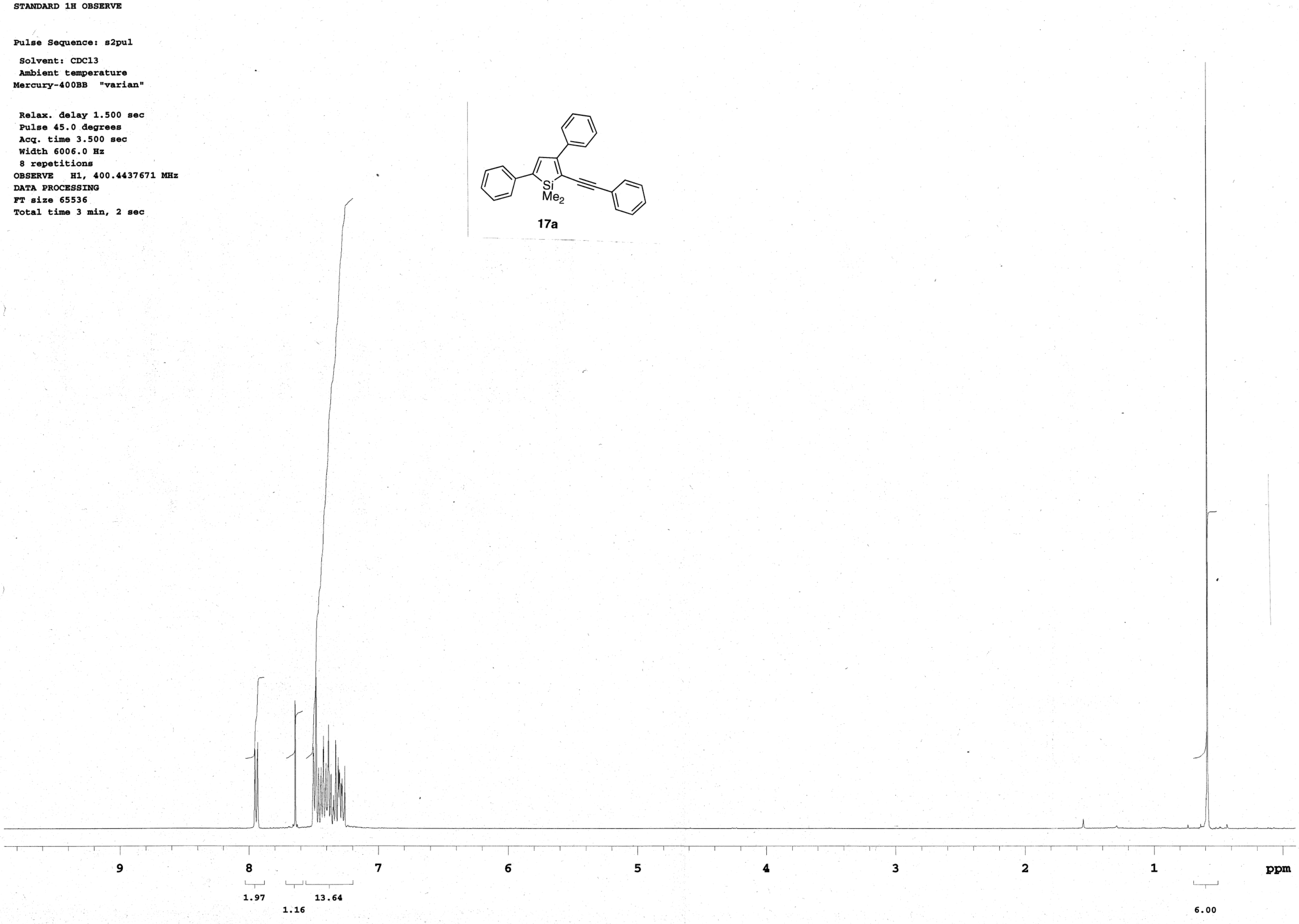
C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM466-BCM.ALS
BrDPS



DFILE	C:¥WINALPHA¥DATA¥Suginome¥Masuda¥KM466-
COMNT	BrDPS
DATIM	Sat Feb 03 14:21:32 2007
OBNUC	13C
EXMOD	SINGL
OBFRQ	125.65 MHz
OBFIN	128449.48 Hz
POINT	32768
FREQU	28011.20 Hz
SCANS	912
ACQTM	1.1698 sec
PD	2.0000 sec
PW1	4.50 usec
IRNUC	1H
CTEMP	21.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.43 Hz
RGAIN	35



16



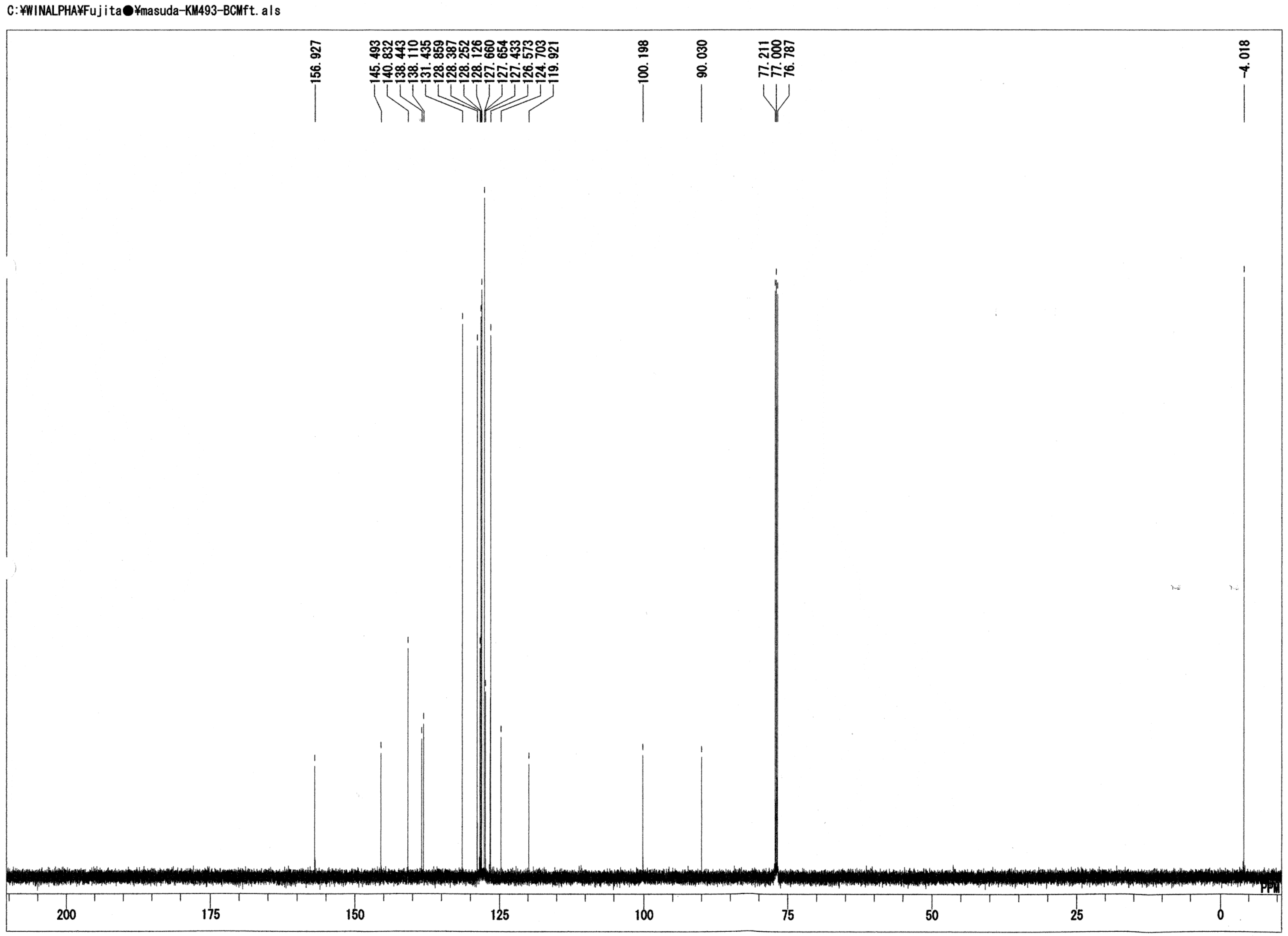
STANDARD 1H OBSERVE

Pulse Sequence: s2pul

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

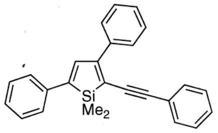
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
8 repetitions
OBSERVE H1, 400.4437671 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 2 sec

17a



```
COMNT
DATIM  14-03-2007 18:58:38
EXMOD  single_pulse_dec
EXPCM  ROESY(Rotating-frame NO
OBNUC  13C
OBFRQ        150.92 MHz
OBFIN          1.74 Hz
POINT        104856
FREQU      33332.82 Hz
ACQTM        1.5729 sec
PD           2.0000 sec
SCANS           256
DUMMY             4
PW1            3.73 usec
PW2           10.70 usec
PW3           12.00 usec
PI1        250.0000 msec
PI3         20.0000 msec
IRMOD  NON
IRNUC  1H
IRFRQ        600.17 MHz
IRSET          5.30 KHz
IRATN           511
CTEMP          23.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
RGAIN            60
RESOL          0.32 Hz
CTEMP          23.2 c
PROBE  TH5

measurement no
by  FUJITA
```



17a