Supporting Information

Palladium-Catalyzed Silylene-1,3-Diene [4+1] Cycloaddition with Use of (Aminosilyl)boronic Esters as Synthetic Equivalents of Silylene

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Contents

1. General Remarks

All 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 Varian Mercury-400 (400.44 MHz) or JEOL-JNM-500 (500.00 MHz) spectrometers. ^{13}C NMR spectra were recorded on a JEOL-JNM-500 (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 (for ^{1}H, ^{13}C) and $Et_2O \cdot BF_3$ (for ^{11}B). Elemental analyses were performed by Elemental Analysis Center of Kyoto University. High resolution mass spectra were recorded on JEOL JMS-MS700 or JMS-SX102A spectrometers. UV-visible spectra were recorded on a JASCO V-550. Fluorescence spectra were recorded on a JASCO FP-6300.

2. Experimental Procedures

2.1 Materials

Toluene was dried and degassed by The Ultimate Solvent System (GlassContour). Benzene-d_6 was dried with CaH_2 and distilled. Silylboronic esters **1a-c** and **5** were prepared as reported procedure.[1] Dienes **2a**[2], **2b**[3], **2d**[4], **2f**[5], **2h**[6], **2j**[6], **2l**[7], **2m**[8], (*E*,*E*)-**2p**[9], and (*E*,*Z*)-**2p**[10] were prepared as reported procedures. Dienes **2e** was similarly prepared as known procedure.[11] Dienes **2c**, **2g**, **2k**, and **2q** were purchased from TCI and distilled and degassed prior to use. Synthesis of **2i** and its analogues was described later (see section 2.7.1). Diene **2n** was prepared as describes bellow. 1,3-Butadiene (**2o**) was purchased from TCI and used without further purification. PPh_3 (Wako), PPh_2Me (Strem), *p*-chloranil (TCI), and DDQ (TCI) were used as received. $Pd(dba)_2$ was

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1 Ohmura, T.; Masuda, K.; Furukawa, H.; Suginome, M. *Organometallics* **2007**, *26*, 1291.
2 Negishi, E.; Takahashi, T.; Baba, S.; Van. Horn, David E.; Okukado, M. *J. Am. Chem. Soc.* **1987**, *109*, 2393.
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8 Nguyet Anh Le; Jones, Maitland, Jr.; Bickelhaupt, Friedrich; De Wolf, Willem H. *J. Am. Chem. Soc.* **1989**, *111*, 8491.
9 Zweifel, G.; Miller R. L. *J. Am. Chem. Soc.* **1970**, *92*, 6678.
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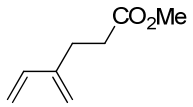
11 Stevens M. Sparks, Chun P. Chow, Liang Zhu, and Kenneth, J. Shea *J. Org. Chem.* **2004**, *69*, 3025.

prepared from $PdCl_2$ (Tanaka Kikinzoku Kogyo, Guaranteed Grade) as reported procedure.[12]

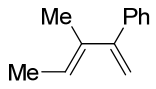
Methyl 3-methylene-1-hexenoate (**2e**)



2e

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.37 (dd, J = 18.0, 11.0 Hz, 1H), 5.25 (d, J = 18.0 Hz, 1H), 5.09 (d, J = 11.0 Hz, 1H), 5.04 (s, 1H), 5.01 (s, 1H), 3.68 (s, 3H), 2.50-2.58 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.6, 144.6, 138.3, 116.1, 113.5, 51.6, 32.8, 26.4; Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63: Found. C, 68.34; H, 8.81.

(*E*)- 3-Methyl-2-phenyl-1,3-pentadiene (**2n**)[13]



2n

To a solution of (*E*)-2-bromo-2-butene (Aldrich, 1.1 g, 8.2 mmol) and $NiCl_2$(dppp)[14] (100 mg, 0.16 mmol) in THF (5 mL) was added a THF solution of α-(bromomagnesio)styrene, which was prepared from α-bromostyrene (Aldrich, 2.2 g, 12 mmol) and magnesium (Nacalai, 580 mg, 24 mg-atom) in THF (15 mL), and the mixture stirred and heated to reflux for 2 h. The flask was cooled to room temperature, and the reaction mixture was quenched with water (50 mL) and 2N HCl (20 mL). The mixture was extracted with Et_2O (30 mL, twice). The extracts was dried over $MgSO_4$ and concentrated by rotary evaporator. The crude oil was purified by bulb-to-bulb distillation (150 °C/ 90 mmHg) to afford **2n** (0.85 g, 66%) as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.35 (m, 5H), 5.46 (q, J = 7.0 Hz, 1H), 5.19 (d, J = 1.5 Hz, 1H), 5.01 (d, J = 1.5 Hz, 1H), 1.84 (s, 3H), 1.70 (d, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.7, 142.0, 136.1, 128.6, 127.8, 127.0, 126.3, 111.6, 14.4, 14.1.

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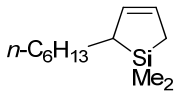
[12] Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.
[13] An alternate route to **2n**, see Nakayama, J.; Machida, H.; Saito, R.; Akimoto, K.; Hosono, M. *Chem. Lett*. **1985**, 1173.
[14] Van Heck, G. R.; Horrocks, Jr. W. D. *Inorg. Chem*. **1966**, *5*, 1968.

2.2 Palladium-Catalyzed Reaction of Silylboronic Ester 1 with Diene 2a (Table 1)

General Procedure

To a solution of $Pd(dba)_2$ (0.30 μmol), ligand (0, 0.36, 0.72, or 1.44 μmol), Bn_2O (30 mg, internal standard) and **2a** (0.33 mmol) in C_6D_6 (0.15 mL) was added **1** (0.30 mmol). The mixture was stirred for 3 h at room temperature. To determine the yield of **3a**, the reaction mixture was then analyzed by GC. The yield of **4**[15] was estimated by ^{1}H NMR.

1,1-Dimethyl-2-hexyl-1-silacyclopent-3-ene (**3a**)



3a

The best result (entry 2 in Table 1) was obtained by the following procedure, which was almost identical that described above. $Pd(dba)_2$ (2.3 mg, 4.0 μmol) and PPh_2Me (0.96 mg, 4.8 μmol) were dissolved in toluene (200 μL) and the mixture was stirred for 5 min at room temperature. 1,3-Decadiene (**2a**) (53 mg, 0.38 mmol) and silylboronic ester **1a** (111 mg, 0.43 mmol) were added to the mixture, and the resulting mixture was stirred at room temperature for 14 h. Bulb-to-bulb distillation (100 °C/3.0 mmHg) of the crude products gave **3a** as colorless liquid (47 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74-5.83 (m, 2H), 1.49-1.55 (m, 1H), 1.22-1.46 (m, 12H), 0.90 (t, J = 7.0 Hz, 3H), 0.19 (s, 3H), 0.09 (s, 3H); ^{13}C NMR($CDCl_3$, 125 MHz) δ 137.1, 129.1, 31.9, 31.2, 30.6, 30.2, 29.5, 22.7, 18.0, 14.1, -1.9, -5.0; HRMS (EI) Calcd for $C_{12}H_{24}Si$ (M^+): *m/z* 196.1647; Found 196.1648.

Additional Note: The Pd/PPh_3 catalyst, which showed the best results for reaction of terminal alkynes with **1a**,[15] afforded 17% of **3a** with 36% of **4a** (entry 1, Table 1). The remainder is unreacted **1a** and **2a**. The efficiency of the silylene equivalent formation seems to depend on the unsaturated hydrocarbons used, probably because coordination of the substrates to palladium plays an important role in the catalytic cycle.

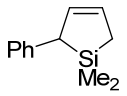
[15] Ohmura, T.; Masuda, K.; Suginome, M. *J. Am. Chem. Soc.* **2008**, *130*, 1526.

2.3 Palladium-Catalyzed Reaction of Silylboronic Esters 1a and 5 with Dienes 2 (Table 2)

General Procedures

Procedure A: To a solution of $Pd(dba)_2$ (2.3 mg, 0.40 μmol), $PMePh_2$ (1.0 mg, 0.48 μmol), and 1,3-Diene **2** (0.44-0.68 mmol) in toluene (0.2 mL) was added silylboronic esters **1a** or **5** (0.40 mmol), and the mixture was stirred for several hours at room temperature (for **1a**) or 50 °C (for **5**). After the reaction, the crude product was purified by silica gel column chromatography. ***Procedure B***: To a solution of $Pd(dba)_2$ (2.3 mg, 0.40 μmol), $PMePh_2$ (1.0 mg, 0.48 μmol), and 1,3-Diene **2** (0.40 mmol) in toluene (0.2 mL) was added silylboronic ester **1a** (0.44 mmol), and the mixture was stirred for several hours at room temperature. After the reaction, the crude product was purified by silica gel column chromatography. The procedure B was useful when the separation of the product and starting diene **2** was difficult, because remaining silylboronic ester could be easily removed through silica gel column chromatography.

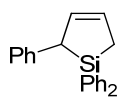
1,1-Dimethyl-2-phenyl-1-silacyclopent-3-ene (3b, entry 1)



3b

According to the *Procedure B*, **2b** (257 mg, 2.0 mmol) was reacted with **1a** (569 mg, 2.2 mmol) for 5 h. Purification of the products by chromatography on silica gel (eluent: hexane, R_f = 0.60) afforded **3b** as a colorless liquid (343 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.27 (m, 2H), 7.04-7.10 (m, 1H), 6.97-7.02 (m, 2H), 6.10 (ddt, J = 6.8, 3.6, 2.0 Hz, 1H), 5.91 (ddt, J = 6.8, 3.6, 2.0 Hz, 1H), 3.08-3.11 (m, 1H), 1.45 (ddt, J = 18.0, 3.6, 2.0 Hz, 1H), 1.38 (ddt, J = 18.0, 3.6, 2.0 Hz, 1H), 0.27 (s, 3H), -0.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.0, 134.3, 132.1, 128.3, 126.4, 124.1, 39.5, 17.8, -2.2, -4.4; Anal. Calcd. for $C_{12}H_{16}Si$: C, 76.53; H, 8.56: Found: C, 76.82; H, 8.62.

1,1,2-Triphenyl-1-silacyclopent-3-ene (6b, entry 2)

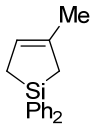


6b

According to the *Procedure A*, **2b** (64 mg, 0.49 mmol) was reacted with **5** (173 mg, 0.45 mmol) at 50 °C for 18 h. Chromatography on silica gel (eluent: hexane/Et_2O = 50/1, R_f = 0.25) afforded **6b** as a colorless

liquid (109 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.67 (m, 2H), 7.38-7.47 (m, 3H), 7.20-7.26 (m, 1H), 7.05-7.14 (m, 6H), 6.91-7.00 (m, 3H), 6.27-6.33 (m, 1H), 6.03-6.10 (m, 1H), 3.73 (br s, 1H), 2.14 (ddt, J = 18.4, 3.2, 2.0 Hz, 1H), 1.92 (ddt, J = 18.4, 3.2, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.6, 135.5, 135.3, 135.1, 134.8, 132.4, 131.7, 129.7, 129.2, 128.04, 128.03, 127.3, 127.1, 124.3, 39.2, 16.3; Anal. Calcd. for $C_{22}H_{20}Si$: C, 84.56; H, 6.45: Found: C, 84.83; H, 6.51.

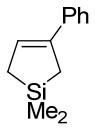
3-Methyl-1,1-diphenyl-1-silacyclopent-3-ene (6c, entry 3)[16]



6c

According to the *Procedure A*, **2c** (47 mg, 0.69 mmol) was reacted with **5** (153 mg, 0.40 mmol) at 50 °C for 3 h. Chromatography on silica gel (eluent: hexane, R_f = 0.40) afforded **6c** as a colorless liquid (82 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.59 (m, 4H), 7.34-7.43 (m, 6H), 5.64-5.67 (m, 1H), 1.85 (s, 3H+2H), 1.78 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.1, 136.2, 134.7, 129.4, 127.9, 124.7, 22.6, 21.7, 17.6; Anal. Calcd. for $C_{17}H_{18}Si$: C, 81.54; H, 7.25: Found: C, 81.79; H, 7.21.

1,1-Dimethyl-3-phenyl-1-silacyclopent-3-ene (3d, entry 4)

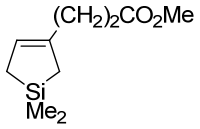


3d

According to the *Procedure A*, **2d** (72 mg, 0.55 mmol) was reacted with **1a** (102 mg, 0.40 mmol) for 24 h. Chromatography on silica gel (eluent: hexane, R_f = 0.57) afforded **3d** as a colorless liquid (63 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.52 (m, 2H), 7.29-7.34 (m, 2H), 7.19-7.24 (m, 1H), 6.38 (tt, J = 3.6, 1.8 Hz, 1H), 1.71 (q, J = 1.8 Hz, 2H), 1.55 (dt, J = 3.6, 1.8 Hz, 2H), 0.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.6, 140.8, 128.1, 127.2, 126.6, 125.6, 19.4, 19.3, -1.8; HRMS (EI) *m/z* Calcd for $C_{12}H_{16}Si$ (M^+): 188.1021, Found: 188.1021. Anal. Calcd. for $C_{12}H_{16}Si$: C, 76.53; H, 8.56: Found: C, 76.32; H, 8.62.

[16] Rieke, R. D.; Xiong, H. *J. Org. Chem.* **1991**, *56*, 3109.

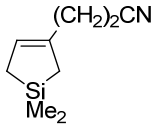
3-(2-Methoxycarbonylethyl)-1,1-dimethyl-1-silacyclopent-3-ene (3e, entry 5)



3e

According to the *Procedure A*, **2e** (63 mg, 0.49 mmol) was reacted with **1a** (105 mg, 0.41 mmol) for 21 h. Chromatography on silica gel (eluent: hexane/Et_2O = 10/1, R_f = 0.34) afforded **3e** as a colorless liquid (62 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (tt, J = 3.2, 1.6 Hz, 1H), 3.66 (s, 3H), 2.35-2.47 (m, 4H), 1.27 (dt, J = 3.2, 1.6 Hz, 2H), 1.19-1.22 (m, 2H), 0.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 174.0, 142.0, 124.9, 51.4, 32.7, 31.8, 20.3, 18.3, -1.9; Anal. Calcd. for $C_{10}H_{18}O_2Si$: C, 60.56; H, 9.15: Found. C, 60.42; H, 9.10.

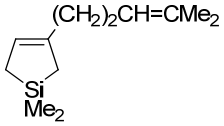
3-(2-Cyanoethyl)-1,1-dimethyl-1-silacyclopent-3-ene (3f, entry 6)



3f

According to the *Procedure A*, **2f** (51 mg, 0.48 mmol) was reacted with **1a** (104 mg, 0.40 mmol) for 2 h. Chromatography on silica gel (eluent: hexane/Et_2O = 5/1, R_f = 0.36) afforded **3f** as a colorless liquid (47 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (tt, J = 3.2, 1.6 Hz, 1H), 2.38-2.49 (m, 4H), 1.33 (dt, J = 3.2, 1.6 Hz, 2H), 1.19-1.23 (m, 2H), 0.18 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.6, 127.3, 119.7, 32.1, 19.9, 18.3, 15.9, -1.9; HRMS (EI) *m/z* Calcd for $C_9H_{15}NSi$ (M^+): 165.0974, Found: 165.0970.

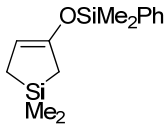
1,1-Dimethyl-3-(4-methyl-3-penten-1-yl)-1-silacyclopent-3-ene (3g, entry 7)



3g

According to the *Procedure A*, **2g** (88 mg, 0.65 mmol) was reacted with **1a** (103 mg, 0.40 mmol) for 20 h. Chromatography on silica gel (eluent: hexane, R_f = 0.75) afforded **3g** as a colorless liquid (55 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47-5.53 (m, 1H), 5.06-5.13 (m, 1H), 2.04-2.14 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H), 1.28 (dt, J = 3.2, 1.6 Hz, 2H), 1.20-1.23 (m, 2H), 0.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.9, 131.1, 124.6, 124.0, 36.7, 26.4, 25.7, 20.4, 18.3, 17.7, -1.8; Anal. Calcd. for $C_{12}H_{22}Si$: C, 74.14; H, 11.41. Found: C, 74.12; H, 11.47.

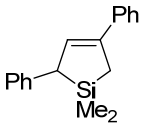
1,1-Dimethyl-3-(dimethylphenylsilyloxy)-1-silacyclopent-3-ene (3h, entry 8)



3h

According to the *Procedure B*, **2h** (206 mg, 1.0 mmol) was reacted with **1a** (269 mg, 1.1 mmol) for 4 h. Chromatography on silica gel (eluent: hexane, R_f = 0.42) afforded **3h** as a colorless liquid (218 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.62 (m, 2H), 7.34-7.41 (m, 3H), 4.89 (tt, J = 3.2, 1.6 Hz, 1H), 1.33 (q, J = 1.6 Hz, 2H), 1.21 (dt, J = 3.2, 1.6 Hz, 2H), 0.44 (s, 6H), 0.14 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.8, 138.0, 133.4, 129.6, 127.8, 106.5, 21.4, 14.8, -0.9, -1.6; Anal. Calcd. for $C_{14}H_{22}OSi_2$: C, 64.06; H, 8.45. Found: C, 64.10; H, 8.54.

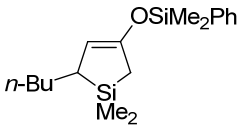
1,1-Dimethyl-2,4-Diphenyl-1-silacyclopent-3-ene (3i, entry 9)



3i

According to the *Procedure B*, **2i** (207 mg, 1.0 mmol) was reacted with **1a** (279 mg, 1.1 mmol) for 3 h. Chromatography on silica gel (eluent: hexane/Et_2O = 40/1, R_f = 0.50) afforded **3i** as a colorless liquid (251 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.61 (m, 2H), 7.33-7.38 (m, 3H), 7.23-7.28 (m, 2H), 7.07-7.12 (m, 1H), 7.03-7.05 (m, 2H), 6.42 (dt, J = 2.8, 1.8 Hz, 1H), 3.32-3.35 (m, 1H), 1.87 (dt, J = 17.6, 1.8 Hz, 1H), 1.80 (dt, J =17.6, 1.8 Hz, 1H), 0.35 (s, 3H), -0.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.9, 142.7, 140.2, 130.3, 128.3, 128.2, 127.1, 126.4, 125.8, 124.3, 40.6, 19.3, -2.1, -4.2; Anal. Calcd. for $C_{18}H_{20}Si$: C, 81.76; H, 7.62. Found: C, 81.54; H, 7.44.

2-Butyl-1,1-dimethyl-3-(dimethylphenylsilyloxy)-1-silacyclopent-3-ene (3j, entry 10)

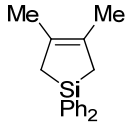


3j

According to the *Procedure B*, **2j** (101 mg, 0.38 mmol) was reacted with **1a** (110 mg, 0.43 mmol) for 15 h. Chromatography on silica gel (eluent: hexane/Et_2O = 20/1, R_f = 0.63) afforded **3j** as a colorless liquid (113 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.63 (m, 2H), 7.35-7.42 (m, 3H), 4.88 (dt, J = 3.6, 1.2 Hz,

1H), 1.44-1.50 (m, 1H), 1.34 (t, J = 1.2 Hz, 2H), 1.12-1.36 (m, 6H), 0.87 (t, J = 7.2 Hz, 3H), 0.45 (s, 6H), 0.12 (s, 3H), 0.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.7, 137.9, 133.4, 129.6, 127.7, 112.8, 32.2, 31.7, 27.6, 22.8, 21.5, 14.1, -0.9, -1.0, -1.6, -4.7; Anal. Calcd. for $C_{18}H_{30}OSi_2$: C, 67.86; H, 9.49. Found: C, 67.96; H, 9.51.

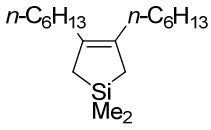
3,4-Dimethyl-1,1-diphenyl-1-silacyclopent-3-ene (6k, entry 11)[17]



6k

According to the *Procedure A*, **2k** (51 mg, 0.62 mmol) was reacted with **5** (149 mg, 0.39 mmol) at 50 °C for 12 h. Chromatography on silica gel (eluent: hexane, R_f = 0.35) afforded **6k** as a colorless liquid (81 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.62 (m, 4H), 7.34-7.44 (m, 6H), 1.88 (s, 4H), 1.79 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.4, 134.7, 130.7, 129.3, 127.9, 24.2, 19.3.

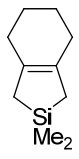
3,4-Dihexyl-1,1-dimethyl-1-silacyclopent-3-ene (3l, entry 12)



3l

According to the *Procedure A*, **2l** (99 mg, 0.45 mmol) was reacted with **1a** (103 mg, 0.40 mmol) for 3 h. Chromatography on silica gel (eluent: hexane, R_f = 0.86) afforded **3l** as a colorless liquid (94 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (t, J = 7.6 Hz, 4H), 1.20-1.39 (m, 20H), 0.89 (t, J = 6.8 Hz, 6H), 0.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.1, 32.8, 31.9, 29.3, 28.2, 22.7, 22.3, 14.1, -2.1; Anal. Calcd. for $C_{18}H_{36}Si$: C, 77.06; H, 12.93. Found: C, 77.20; H, 13.20.

2,3,4,5,6,7-Hexahydro-2,2-dimethyl-1*H*-2-silaindene (3m, entry 13)



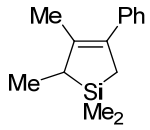
3m

According to the *Procedure A*, **2m** (50 mg, 0.55 mmol) was reacted with **1a** (102 mg, 0.40 mmol) for

[17] Wu, T. C.; Xiong, H.; Rieke,R. D. *J. Org. Chem.* **1990**, *55*, 5045.

6 h. Chromatography on silica gel (eluent: hexane, R_f = 0.81) afforded **3m** as a colorless liquid (55 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (m, 4H), 1.55-1.64 (m, 4H), 1.23-1.27 (m, 4H), 0.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 133.0, 31.2, 23.9, 23.6, -1.7; HRMS (EI) *m/z* Calcd for $C_{10}H_{17}Si$ ($[M-H]^+$): 165.1100; Found: 165.1099.

1,1,2,3-Tetramethyl-4-phenyl-1-silacyclopent-3-ene (3n, entry 14)



3n

According to the *Procedure B*, **2n** (63 mg, 0.40 mmol) was reacted with **1a** (115 mg, 0.45 mmol) for 20 h. Chromatography on silica gel (eluent: hexane, R_f = 0.68) afforded **3n** as a colorless liquid (74 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.33 (m, 2H), 7.15-7.23 (m, 3H), 1.71-1.74 (m, 3H), 1.64-1.69 (m, 2H), 1.57-1.62 (m, 1H), 1.11 (d, J = 8.0 Hz, 3H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.7, 139.4, 134.7, 128.2, 127.7, 125.7, 29.6, 23.9, 16.8, 13.9, -2.6, -5.0; HRMS (EI) *m/z* Calcd for $C_{14}H_{20}Si$ (M^+): 216.1334; Found: 216.1335.

The corresponding *Z* isomer of **2n** did not react under the identical reaction conditions.

2.4 Reaction of 1,3-Butadiene (2o) with 5 (eq 1)

1,1-Diphenyl-1-silacyclopent-3-ene (6o)[18]

6o

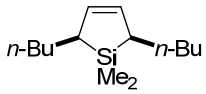
$Pd(dba)_2$ (2.3 mg, 4.0 μmol), PPh_2Me (0.96 mg, 4.8 μmol), and **5** (160 mg, 0.42 mmol) were placed in a glass tube having PTFE stopcock (J. Young). The mixture was dissolved in toluene (1.0 mL), and the resultant solution was stirred for 5 min at room temperature. 1,3-Butadiene gas (**2o**) (22.4 mL, 1.0 mmol) was passed through the solution via a disposable syringe equipped with stainless needle. The tube was sealed by the stopcock and the reaction mixture was stirred for 15 h at 50 °C. Purification of the product by chromatography

[18] Mignani, S.; Damour, D.; Bastart, J.-P.; Manuel, G. *Synth. Commun*. **1995**, *25*, 3855.

on silicagel (eluent: hexane/Et_2O = 20/1, R_f = 0.75) afforded **6o** as a colorless liquid (83 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.60 (m, 4H), 7.34-7.44 (m, 6H), 6.04 (s, 2H), 1.85 (d, J = 1.2 Hz, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.8, 134.7, 131.0, 129.5, 127.9, 16.8; HRMS (EI) *m/z* Calcd for $C_{16}H_{16}Si$ (M^+): 236.1021; Found: 236.1022

2.5 Reaction of 2p with 1a (eqs 2 and 3)

***cis*-2,5-Dibutyl-1,1-dimethyl-1-silacyclopent-3-ene (*cis*-3p, eq 2)**



cis-**3p**

$Pd(dba)_2$ (4.6 mg, 8.0 μmol) and PPh_2Me (1.9 mg, 9.6 μmol) were dissolved in toluene (200 μL) and the mixture was stirred for 5 min at room temperature. To a mixture was added (*E,E*)-**2p** (*EE:EZ* = 99:1, 68 mg, 0.41 mmol) and **1a** (155 mg, 0.60 mmol) in this order, and the mixture was stirred at room temperature for 24 h. ^{1}H NMR analysis of the crude reaction mixture indicated formation of **3p** with the *cis:tran*s ratio of 99:1. Purification of the products by chromatography on silica gel (eluent: hexane, R_f = 0.85) afforded *cis*-**3p** as a colorless liquid (84 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69 (s, 2H), 1.52 (t, J = 7.0 Hz, 2H), 1.22-1.47 (m, 12H), 0.89 (t, J = 7.0 Hz, 6H), 0.19 (s, 3H), 0.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.1, 32.4, 31.2, 31.1, 22.9, 14.1, -1.7, -8.4; Anal. Calcd. for $C_{14}H_{28}Si$: C, 74.91; H, 12.57. Found: C, 74.89; H, 12.77. Unequivalent methyl groups on the silicon atom indicate the *cis* structure. The stereochemistry was also confirmed by an nOe experiments.

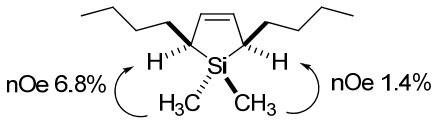
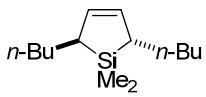


Figure S1. nOe experiment of *cis*-**3p** in $CDCl_3$

***trans*-2,5-Dibutyl-1,1-dimethyl-1-silacyclopent-3-ene (*trans*-3p, eq 3)**



trans-**3p**

$Pd(dba)_2$ (6.9 mg, 12 μmol) and PPh_2Me (2.9 mg, 14 μmol) were dissolved in toluene (200 μL) and the mixture was stirred for 5 min at room temperature. To a mixture was added (*E,Z*)-**2p** (*EE:EZ* = 2:98, 68 mg,

0.41 mmol) and **1a** (155 mg, 0.60 mmol) in this order, and the mixture was stirred at room temperature for 10 h. ^{1}H NMR analysis of the crude reaction mixture indicated formation of **3p** with the *cis:tran*s ratio of 3:97. Purification of the products by chromatography on silica gel (eluent: hexane, R_f = 0.85) afforded *trans*-**3p** as a colorless liquid (78 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (d, J = 1.2 Hz, 2H), 1.49-1.55 (m, 2H), 1.22-1.46 (m, 12H), 0.89 (t, J = 7.2 Hz, 6H), 0.09 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.5, 32.4, 30.9, 30.3, 22.9, 14.1, -4.6; Anal. Calcd. for $C_{14}H_{28}Si$: C, 74.91; H, 12.57. Found: C, 75.01; H, 12.79. Equivalent methyl groups on the silicon atom indicate the *trans* structure. The stereochemistry was also confirmed by an nOe experiments.

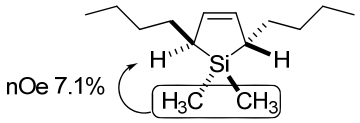


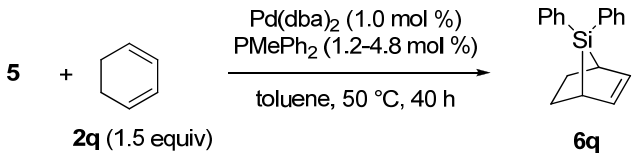
Figure S2. nOe experiment of *trans*-**3p** in $CDCl_3$

2.6 Reaction of 1,3-Cyclohexadiene (2q) with 5 (eq 4)

Optimization of the reaction conditions (Table S1).

Reaction of **2q** with **5** gave **6q** in only 22% yield under the conditions used for other dienes (entry 1). We found that the reaction took place more efficiently by the palladium catalyst having two or more phosphine ligand (entries 2 and 3).

Table S1. Optimization of Reaction Conditions



entry	P/Pd	yield (%)[a]
1[b]	1.2	22
2	2.4	80
3	4.8	95 (88)[c]

[a] GC yield. [b] 2.0 equiv of **2q** was used. [c] Isolated yield.

7,7-Diphenyl-7-silabicyclo[2.2.1]hept-2-ene (6q)

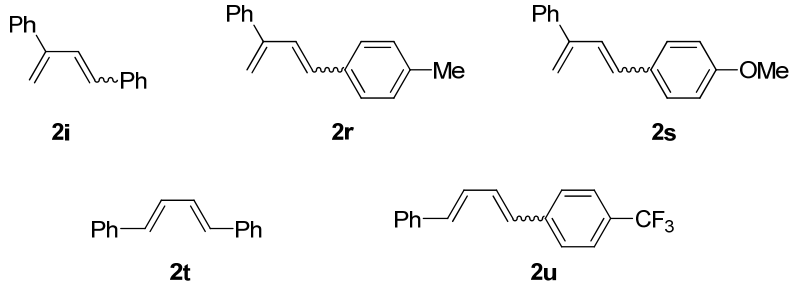
In the presence of $Pd(dba)_2$ (2.3 mg, 4.0 μmol) and $PMePh_2$ (3.8 mg, 19 μmol), **2q** (49 mg, 0.61 mmol) was reacted with **5** (147 mg, 0.39 mmol) in toluene (0.2 mL) at 50 °C for 40 h. Purification of the products by chromatography on silica gel (eluent: hexane/Et_2O = 10/1, R_f = 0.72) afforded **6q** as a white solid (90 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.56 (m, 4H), 7.31-7.40 (m, 4H), 7.22-7.27 (m, 2H), 6.43 (dd, J = 4.2, 3.2 Hz, 2H), 2.43-2.49 (m, 2H), 1.98-2.06 (m, 2H), 1.38-1.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.0, 136.4, 134.1, 133.9, 133.0, 129.40, 129.37, 128.1, 127.4, 28.9, 25.2; Anal. Calcd. for $C_{18}H_{18}Si$: C, 82.38; H, 6.91. Found: C, 82.17; H, 7.00.

2.7 Synthesis of 2,4- and 2,5-Diarylsiloles from 1,3-Dienes (Scheme 1)

2.7.1 Preparation of 1,3- and 1,4-Diaryl-1,3-butadienes 2i and 2r-u

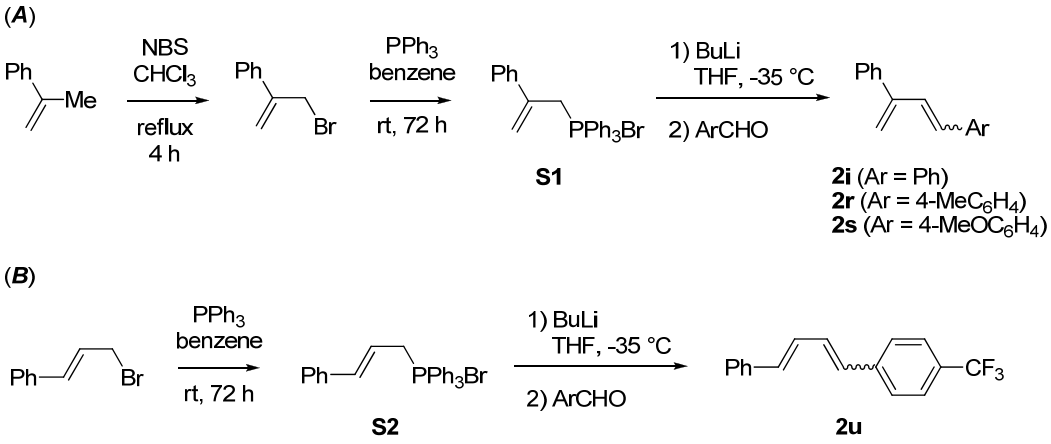
Dienes used in Scheme 1 are numbered as **2r-u** (Chart S1).

Chart S1.



Dienes **2i**, **2r**, and **2s** were prepared from α-methylstyrene (nacalai) according to the reported procedure (Scheme S1-A).[19] Diene **2u** was prepared from cinnamyl bromide (TCI) via the similar reactions (Scheme S1-B).[19] 1,4-Diphenyl-1,3-butadiene (**2t**) was purchased from Aldrich and used as received.

Scheme S1. Preparation of **2** via Wittig Reaction



Synthesis of 2i

Bromination of α-Methylstyrene

To a solution of α-methylstyrene (25 mL, 192 mmol) in $CHCl_3$ (30 mL) was added *N*-bromosuccinimide (NBS, 39 g, 220 mmol), and the mixture was heated to reflux for 4 h. After cooling the reaction mixture to room temperature, insoluble succinimide was removed by filtration. The filtrate was

[19] Mulzer, J.; Brüntrup, G.; Kühl, U.; Hartz, G. *Chem. Ber.* **1982**, *115*, 3453.

concentrated and distilled under the reduced pressure (72-80 ^{o}C/0.8 mmHg) to afford the α-(bromomethyl)styrene (30 g, 80%). This compound is irritant substance for eyes.

Preparation of Phosphomium Salt S1

To a solution of α-(bromomethyl)styrene (30 g, 153 mmol) in benzene (100 mL) was added PPh_3 (26 g, 99 mmol), and the mixture was stirred for 72 h at room temperature. The mixture was then filtrated and the filtered cake was washed with benzene twice. The crude cake was recrystallized from CH_2Cl_2/Et_2O to afford the phosphonium salt **S1** as a white solid (35.4 g, 78%).

Diene Formation via Wittig Reaction

A suspension of the phosphonium salt **S1** (15 g, 33 mmol) in THF (300 mL) was cooled to -35 ^{o}C by dry ice/CH_3CN bath. BuLi (1.57 M, 20.8 mL) was added dropwise to the mixture. After stirring for 30 min at that temperature, freshly distilled benzaldehyde (3.5 g, 33 mmol) in THF (10 mL) was added dropwise to the mixture. After the addition, the resulting mixture was allowed to react at room temperature for 2 h. The volatile materials were removed by rotary evaporator. Hexane was added to the residue to extract products. Insoluble solid was removed by filtration. The crude products were purified by column chromatography on silica gel (eluent: hexane, R_f = 0.5) to afford **2i** as a colorless liquid (5.3 g, 79%). GC and NMR analyses indicated that the product was a mixture of stereoisomer (*E/Z* = 45/55).

Synthesis of 2r, 2s, and 2u

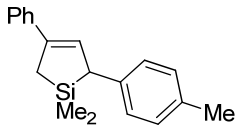
According to the procedure described above, **2r** was synthesized by the reaction of **S1** (10 g, 23 mmol) with *p*-tolualdehyde (Wako, 2.7 g, 22 mmol). Diene **2r** was obtained as a colorless liquid (3.1 g, 63%, *E/Z* = 50/50) after purification by column chromatography on silica gel (eluent: hexane, R_f = 0.29).

According to the procedure described above, **2s** was synthesized by the reaction of **S1** (5.5 g, 12 mmol) with *p*-anisaldehyde (TCI, 1.9 g, 14 mmol). Diene **2s** was obtained as a colorless liquid (1.6 g, 56%, *E/Z* = 41/59) after purification by column chromatography on silica gel (eluent: hexane/Et_2O =40/1, R_f = 0.30).

According to the procedure described above, **2u** was synthesized by the reaction of **S2** (9.5 g, 21 mmol) with *p*-trifluoromethylbenzaldehyde (TCI, 3.5 g, 20 mmol). Diene **2u** was obtained as a yellow solid (2.5 g, 45%, *EE/EZ* = 21/79) after purification by column chromatography on silica gel (eluent: hexane/Et_2O =10/1, R_f = 0.70).

2.7.2 Palladium-Catalyzed Reaction of Diene 2 with Silylboronic Ester 1a

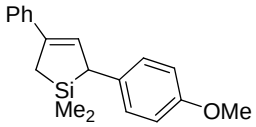
1,1-Dimethyl-2-(4-methylphenyl)-4-phenyl-1-silacyclopent-3-ene (3r)



3r

According to the *Procedure B*, **2r** (214 mg, 0.97 mmol) was reacted with **1a** (268 mg, 1.0 mmol) for 3 h. Chromatography on silica gel (eluent: hexane/Et_2O = 40/1, R_f = 0.43) afforded **3r** as a colorless liquid (241 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 7.24-7.28 (m, 1H), 7.06 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.40-6.44 (m, 1H), 3.30 (br s, 1H), 2.31 (s, 3H), 1.86 (dt, J = 17.2, 1.6 Hz, 1H), 1.78 (dt, J = 17.2, 1.6 Hz, 1H), 0.33 (s, 3H), -0.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.4, 140.7, 140.3, 133.6, 130.6, 129.0, 128.2, 127.0, 126.3, 125.8, 40.1, 20.9, 19.3, -2.1, -4.2; Anal. Calcd. for $C_{19}H_{22}Si$: C, 81.95; H, 7.96. Found: C, 81.70; H, 7.78.

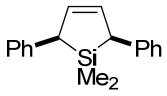
2-(4-Methoxyphenyl)-1,1-dimethyl-4-phenyl-1-silacyclopent-3-ene (3s)



3s

According to the *Procedure B*, **2s** (229 mg, 0.97 mmol) was reacted with **1a** (268 mg, 1.1 mmol) for 3 h. Chromatography on silica gel (eluent: hexane/Et_2O = 40/1, R_f = 0.13) afforded **3s** as a colorless liquid (252 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 2H), 7.32-7.38 (m, 2H), 7.23-7.28 (m, 1H), 6.95 (d, J = 6.8 Hz, 2H), 6.81 (d, J = 6.8 Hz, 2H), 6.40 (dt, J = 3.2, 1.6 Hz, 1H), 3.78 (s, 3H), 3.25-3.28 (m, 1H), 1.86 (dt, J = 17.2, 1.6 Hz, 1H), 1.78 (dt, J = 17.2, 1.6 Hz, 1H), 0.33 (s, 3H), -0.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.8, 142.4, 140.3, 135.9, 130.7, 128.2, 127.2, 127.0, 125.8, 113.8, 55.3, 39.5, 19.3, -2.1, -4.1; HRMS (EI) *m/z* Calcd for $C_{19}H_{22}OSi$ (M^+): 294.1440. Found: 294.1441.

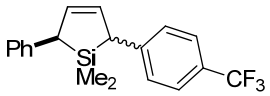
***cis*-1,1-Dimethyl-2,5-diphenyl-1-silacyclopent-3-ene (3t)**[20]



3t

$Pd(dba)_2$ (4.6 mg, 8.0 μmol) and PPh_2Me (1.9 mg, 9.6 μmol) were dissolved in toluene (400 μL) and the mixture was stirred for 5 min at room temperature. To a mixture was added **2t** (*EE* 100%, 83 mg, 0.40 mmol) and **1a** (159 mg, 0.62 mmol), and the mixture was stirred for 24 h at room temperature. Chromatography on silica gel (eluent: hexane/Et_2O = 35/1, R_f = 0.52) afforded **3t** as a colorless liquid (100 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.29 (m, 4H), 7.03-7.13 (m, 6H), 6.12 (s, 2H), 3.28 (s, 2H), 0.41 (s, 3H), -0.67 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 143.4, 135.0, 128.3, 126.4, 124.3, 39.9, -2.8, -6.8; HRMS (EI) *m/z* Calcd for $C_{18}H_{20}Si$ (M^+): 264.1334. Found: 264.1342.

2-(4-Trifuluoromethylphenyl)-1,1-dimethyl-5-phenyl-1-silacyclopent-3-ene (3u)



3u

$Pd(dba)_2$ (6.9 mg, 12 μmol) and PPh_2Me (2.9 mg, 14 μmol) were dissolved in toluene (400 μL) and the mixture was stirred for 5 min at room temperature. To a mixture was added **2u** (*EE:EZ*=21:79, 117 mg, 0.44 mmol) and **1a** (175 mg, 0.68 mmol), and the mixture was stirred for 12 h at 50 °C. Chromatography on silica gel (eluent: hexane/Et_2O = 35/1, R_f = 0.51) afforded **3u** as a colorless liquid (130 mg, 88%). The product was a mixture of *cis* and *trans* isomers (22:78). ^{1}H NMR of *trans* isomer (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.4 Hz, 2H), 7.24-7.28 (m, 3H), 7.01-7.17 (m, 4H), 6.22-6.25 (m, 1H), 6.15-6.18 (m, 1H), 3.36-3.39 (m, 1H), 3.29-3.32 (m, 1H), -0.15 (s, 3H), -0.17 (s, 3H); Some characteristic signals of *cis* isomer δ 6.07-6.11 (m, 1H), 3.34-3.36 (m, 1H), 0.42 (s, 3H), -0.67 (s, 3H); ^{13}C NMR was omitted for the complexity due to the mixture of *cis/trans* isomer and C-F remote coupling. HRMS (EI) *m/z* Calcd for $C_{19}H_{19}F_3Si$ (M^+): 332.1208. Found: 332.1200.

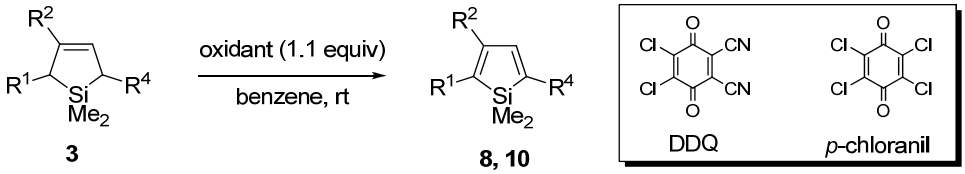
[20] Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1989**, *54*, 3247.

2.7.3 Conversion of 2,4- and 2,5-Diaryl-1-silacyclopent-3-enes to 2,4- and 2,5-Diarylsiloles

Dehydrogenation of several silacyclopent-3-enes **3** was examined (Table S2). Reaction of diaryl-substituted **3r** with DDQ or *p*-chloranil in benzene at room temperature gave diarylsilole **8** in good ^{1}H NMR yield (entries 1 and 2). However, the isolated yield of **8** was rather low due to decomposition of **8** via reaction with acidic hydroquinone derivatives (entry 2). Treatment of the reaction mixture with Et_3N was found essential for isolation of the silole: **8** was obtained in 98% isolated yield after purification by column chromatography on silica gel (entry 3).

A 2,5-diphenylsilacycloprop-3-ene (**3t**) was less reactive than 2,4-diarylsubstituted **3r**: no silole formation was observed by *p*-chloranil (entry 6), whereas reaction with DDQ afforded silole **10** in 78% yield (entry 7). No dehydrogenation proceeded in reaction of 2,5-dibutyl-substituted *trans*-**3p** with DDQ (entry 8), indicating the conversion was applicable to the aryl-substituted substrates.

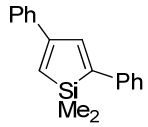
Table S2. Dehydrogenation of Silacyclopent-3-enes [a]



entry	dihydrosilole	oxidant	time (h)	work-up	yield (%)[b]
1	**3r** (R^1 = H, R^2 = Ph, R^4 = 4-MeC_6H_4)	DDQ	1	none	64 (**8**)
2	**3r**	*p*-chloranil	1	none	99 (25)[c] (**8**)
3	**3r**	*p*-chloranil	1	Et_3N[d]	98 [c] (**8**)
4	**3r**	benzoquinone	1	none	18[e] (**8**)
5	**3r**	anthraquinone	1	none	0 (**8**)
6	**3t** (R^1 = Ph, R^2 = H, R^4 = Ph)	*p*-chloranil	12	none	0 (**10**)
7	**3t**	DDQ	12	Et_3N[d]	78 [c] (**10**)
8	*trans*-**3p** (R^1 = *n*-Bu, R^2 = H, R^4 = *n*-Bu)	DDQ	12	none	0

[a] **3** (0.30 mmol) was reacted with oxidant (0.33 mmol) in benzene (6.0 mL) at room temperature. [b] NMR yield. [c] Isolated yield. [d] 2.4 equiv of Et_3N was added after the reaction. [e] Conversion of **3r**.

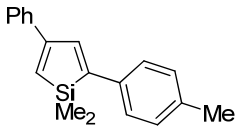
1,1-Dimethyl-2,4-diphenylsilole (7) [21]



7

Typical procedure was given for the synthesis of **7**. To a solution of **3i** (119 mg, 0.45 mmol) in benzene (9.0 mL) under an atmosphere of argon was added *p*-chloranil (122 mg, 0.50 mmol) at one portion. The mixture was stirred for 1 h at room temperature. NEt_3 (126 mg, 1.2 mmol) was added, and the mixture was stirred for 10 min. Resulting suspension was purified by column chromatography on silica gel (hexane/ether = 30/1, R_f = 0.43) to afford the silole **7** (115 mg, 97%) as colorless liquid. ^{1}H NMR (400 MHz, C_6D_6) δ 7.63 (d, J = 2.0 Hz, 1H), 7.55-7.58 (m, 2H), 7.44-7.48 (m, 2H), 7.18-7.25 (m, 4H), 7.09-7.15 (m, 2H), 6.28 (d, J = 2.0 Hz, 1H), 0.33 (s, 6H); ^{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(125 MHz, C_6D_6) δ 157.5, 147.7, 139.7, 139.5, 139.4, 129.0, 128.7, 128.3, 127.4, 126.9, 126.5, 125.2, -3.7; ^{13}C NMR(125 MHz, $CDCl_3$) δ 156.7, 147.2, 139.3, 139.0, 138.9, 128.7, 128.4, 128.0, 127.0, 126.5,126.0, 125.2, -3.7; HRMS (EI) *m/z* Calcd for $C_{18}H_{18}Si$ (M^+): 262.1178. Found: 262.1180.

1,1-Dimethyl-2-(4-methylphenyl)-4-phenylsilole (**8**)

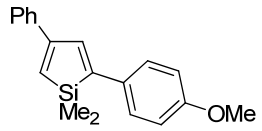


8

Silacyclopent-3-ene **3r** (83 mg, 0.30 mmol) was reacted with *p*-chloranil (82 mg, 0.33 mmol) in benzene (6.0 mL). After treatment with Et_3N (71 mg, 0.70 mmol), the product was purified by column chromatography on silica gel (hexane/ether = 40/1, R_f = 0.43) to afford the silole **8** (80 mg, 98%) as pale yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.67 (m, 2H), 7.59 (d, J = 2.0 Hz, 1H), 7.39-7.43 (m, 4H), 7.32-7.36 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.31 (d, J = 2.0 Hz, 1H), 2.38 (s, 3H), 0.45 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.8, 147.0, 139.3, 137.9, 136.9, 136.2, 129.4, 128.4, 128.0, 126.4, 126.0, 124.7, 21.2, -3.6; HRMS (EI) *m/z* Calcd for $C_{19}H_{20}Si$ (M^+): 276.1334. Found: 276.1312.

[21] Ohmura, T.; Masuda, K.; Suginome, M. *J. Am. Chem. Soc.* **2008**, *130*, 1526.

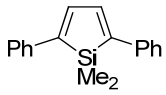
2-(4-Methoxyphenyl)-1,1-dimethyl-4-phenylsilole (9)



9

Silacyclopent-3-ene **3s** (102 mg, 0.35 mmol) was reacted with *p*-chloranil (94 mg, 0.38 mmol) in benzene (6.0 mL). After treatment with Et_3N (82 mg, 0.81 mmol), the product was purified by column chromatography on silica gel (hexane/ether = 20/1, R_f = 0.33) to afford the silole **9** (100 mg, 99%) as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.65 (m, 2H), 7.50 (d, J = 1.8 Hz, 1H), 7.36-7.44 (m, 4H), 7.29-7.35 (m, 1H), 6.88-6.93 (m, 2H), 6.25 (d, J = 1.8 Hz, 1H), 3.84 (s, 3H), 0.42 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.8, 156.9, 146.9, 139.4, 136.7, 131.8, 128.4, 127.9, 127.6, 126.0, 124.0, 114.1, 55.2, -3.6; HRMS (EI) *m/z* Calcd for $C_{19}H_{20}OSi$ (M^+): 292.1283; Found 292.1284.

1,1-Dimethyl-2,5-diphenylsilole (10) [22]

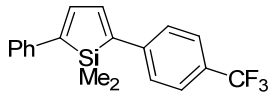


10

Silacyclopent-3-ene **3t** (78 mg, 0.30 mmol) was reacted with DDQ (80 mg, 0.35 mmol) in benzene (3 mL). The mixture was stirred for 12 h at room temperature. NEt_3 (95.6 mg, 0.94 mmol) was added, and the mixture was stirred for 10 min. Resulting suspension was purified by column chromatography on silica gel (hexane/ether = 20/1, R_f = 0.59) to afford the silole **10** (61 mg, 78%) as yellow crystal (m.p. 108.0-110.0 °C, lit. 133 °C[21]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.47 (m, 4H), 7.32-7.38 (m, 4H), 7.31 (s, 2H), 7.20-7.25 (m, 2H), 0.54 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 144.8, 138.8, 137.9, 128.7, 126.9, 126.2, -2.8; HRMS (EI) *m/z* Calcd for $C_{18}H_{18}Si$ (M^+): 262.1178. Found: 262.1182.

[22] Katkevics, M.; Yamaguchi, S.; Toshimitsu, A.; Tamao, K. *Organometallics* **1998**, *17*, 5796.

2-(4-Trifluoromethylphenyl)-1,1-dimethyl-5-phenylsilole (11)



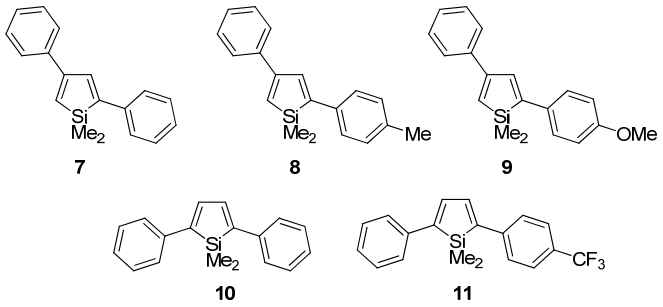
11

Silacyclopent-3-ene **3u** (125 mg, 0.38 mmol) was reacted with DDQ (106 mg, 0.47 mmol) in benzene (4.0 mL) for 12 h. After treatment with Et_3N (102 mg, 1.0 mmol), the product was purified by column chromatography on silica gel (hexane/ether = 10/1, R_f = 0.58) to afford the silole **11** (90 mg, 72%) as yellow crystal (m.p. 89.5-91.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.30-7.40 (m, 4H), 7.23-7.29 (m, 1H), 0.55 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.4, 143.3, 142.4 (q, $^4J_{CF}$ = 1.3 Hz), 140.3, 138.4, 137.5, 128.8, 128.4 (q, $^2J_{CF}$ = 32.5 Hz), 127.3, 126.3, 126.2, 125.7 (q, $^3J_{CF}$ = 3.8 Hz), 124.3 (q, $^1J_{CF}$ = 271.8 Hz), -3.0; HRMS (EI) *m/z* Calcd for $C_{19}H_{17}F_3Si$ (M^+): 330.1052. Found: 330.1051.

2.7.4 Photophysical Properties of Diarylsiloles 7-11

UV-visible spectra and fluorescence spectra were measured in $CHCl_3$ (nacalai, specially prepared reagent grade).

Table S3. Photophysical properties of siloles



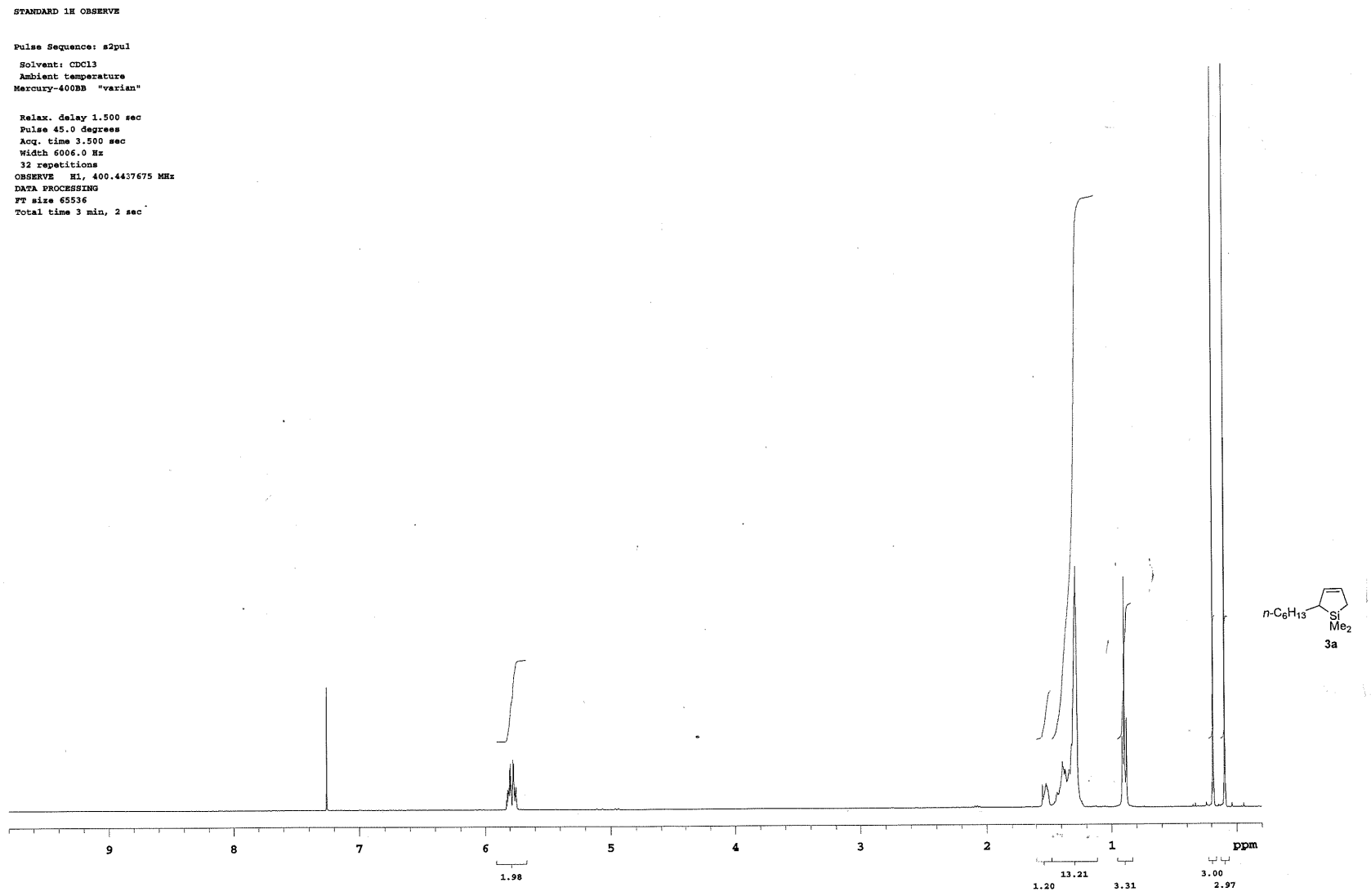
7 **8** **9** **10** **11**

silole	absorption		emission [a]		stokes shift/nm
	λ_{max}/nm	log ε	λ_{max}/nm	Φ [b]	
7	338	3.30	452	0.13	114
8	342	3.69	392	0.00040	48
9	352	3.98	406	0.010	54
10	375	4.34	480	0.27	93
10 lit.[c]	376	4.24	463	0.29	87
11	379	4.30	452	0.015	99

[a] Excited at λ_{max} of absorption. [b] Quantum yield was determined with reference to quinine sulfate in 0.1 N H_2SO_4 and anthracene in EtOH. [c] Katkevics, M.; Yamaguchi, S.; Toshimitsu, A.; Tamao, K. *Organometallics* **1998**, *17*, 5796.

3 Copies of ^{1}H, and ^{13}C NMR Spectra of all new compounds that do not have elemental analysis data

^{1}H, and ^{13}C NMR spectra of **3a**, **3f**, **3m**, **3n**, **3r**, **8**, **9**, and **11** are shown in following pages. ^{1}H NMR spectra of **3u** (*cis:trans* = 22:78) is also provided.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Width 6006.0 Hz
32 repetitions
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Total time 3 min, 2 sec
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8
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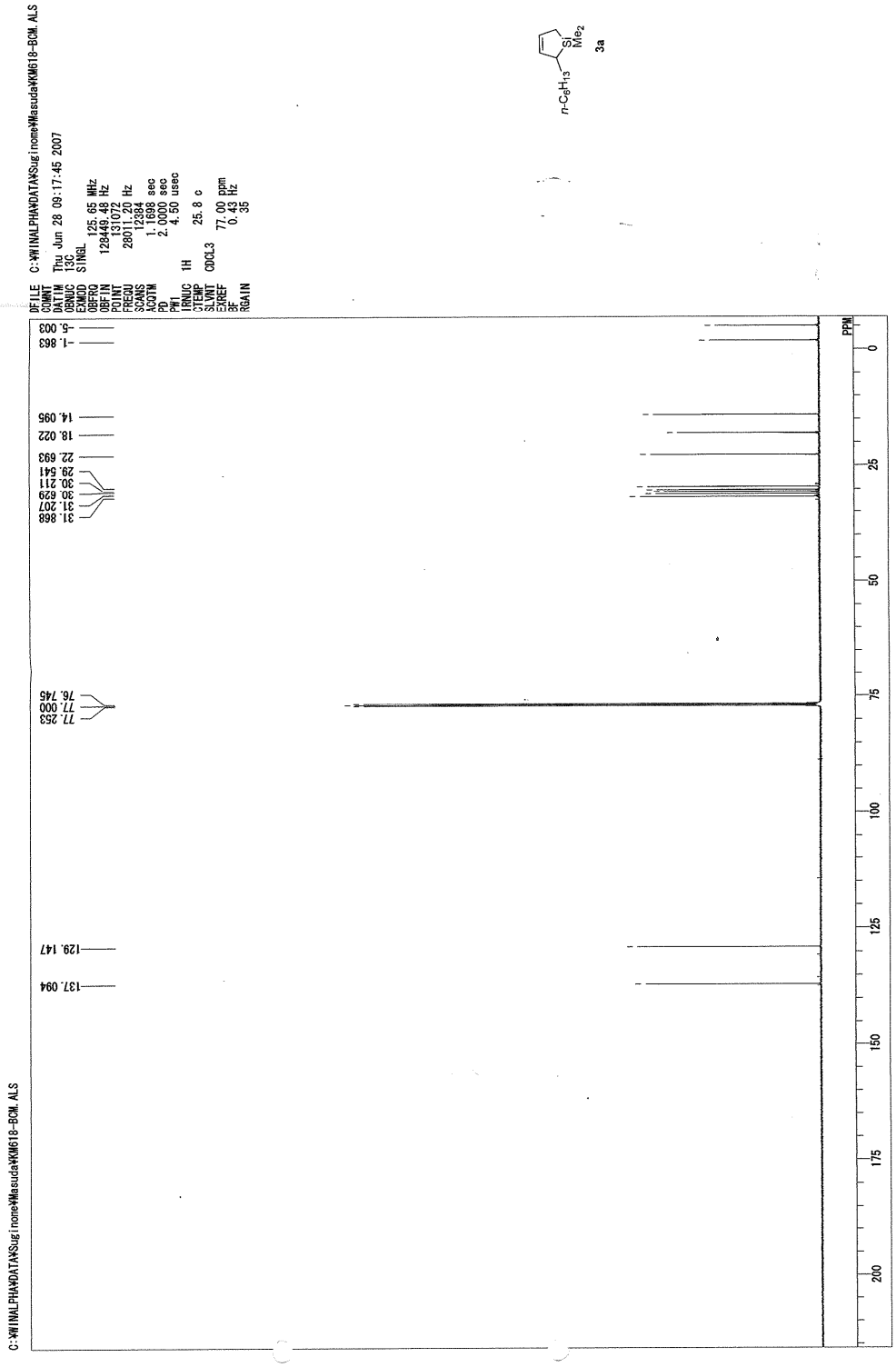
2.97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OBFIN 131072
POINT 28011.20 Hz
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ACQTM 2.0000 sec
PD 4.50 usec
PW1
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CTEMP 25.8 c
SLVNT CDCL3 77.00 ppm
SFREF 0.43 Hz
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75
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125
150
175
200
n-C6H13
SiMe2
3a

KM692

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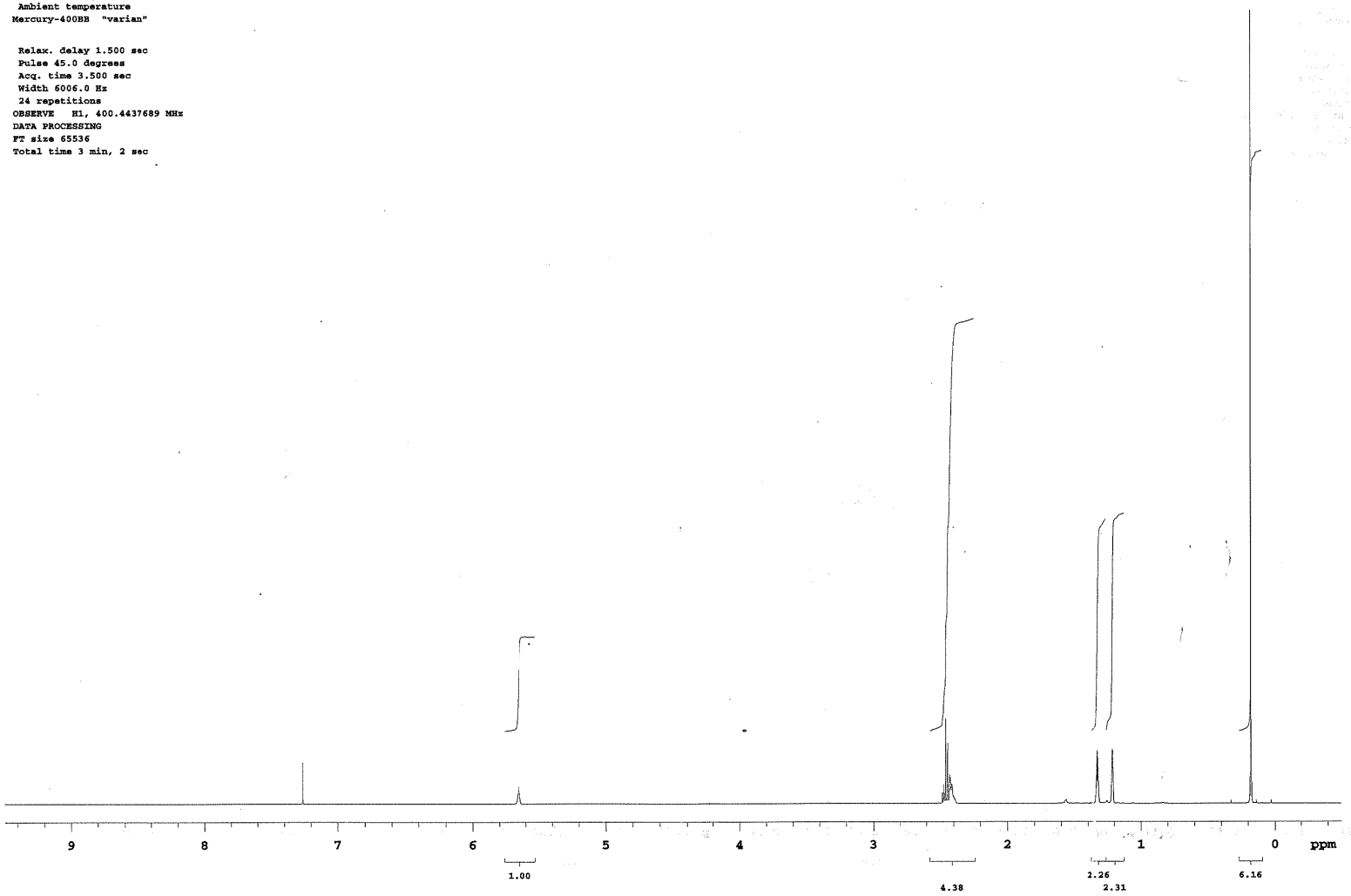
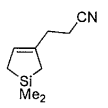
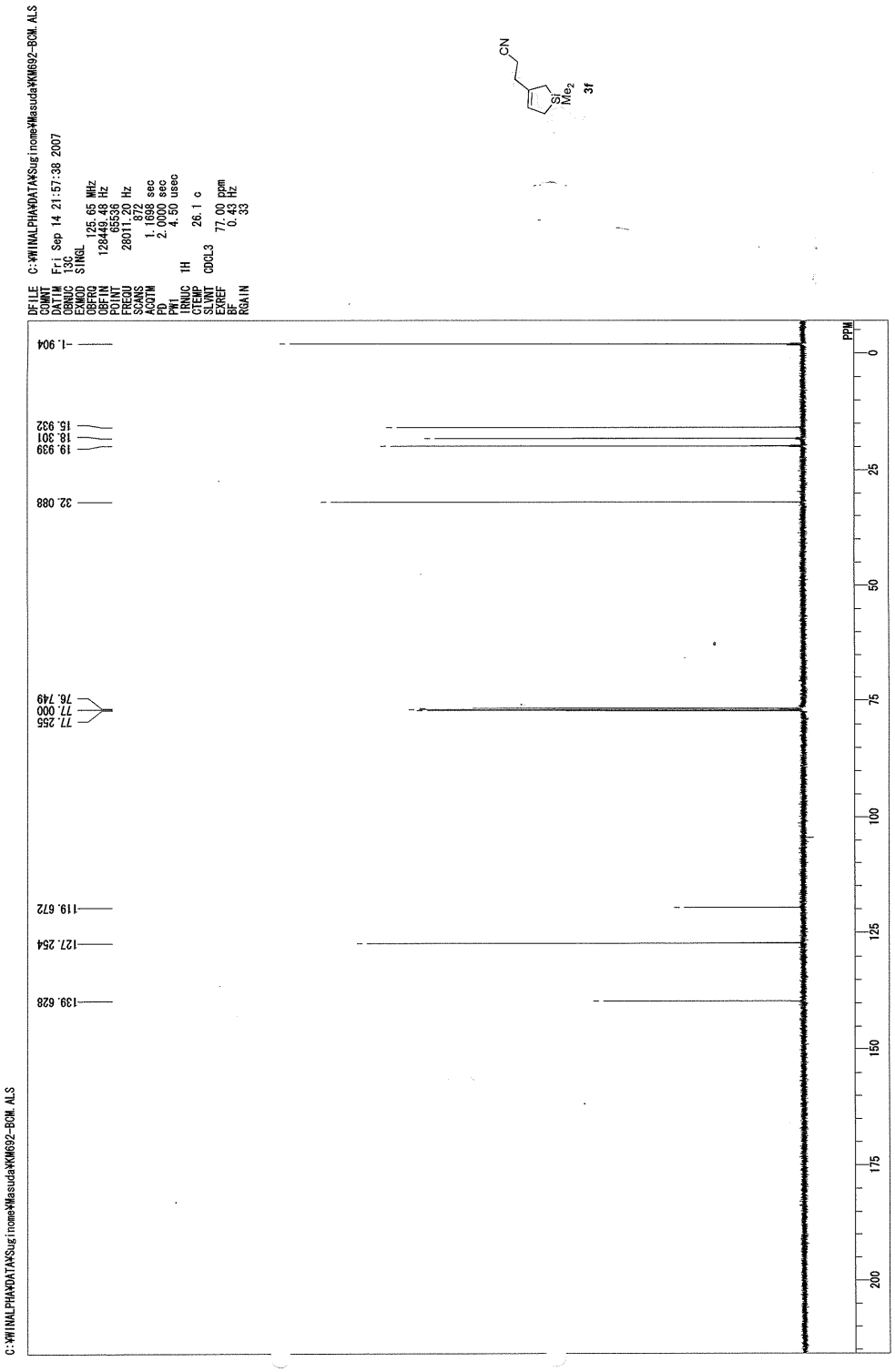




3f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EXREF 0.43 Hz
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3f
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18.301
19.939
32.088
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PPM
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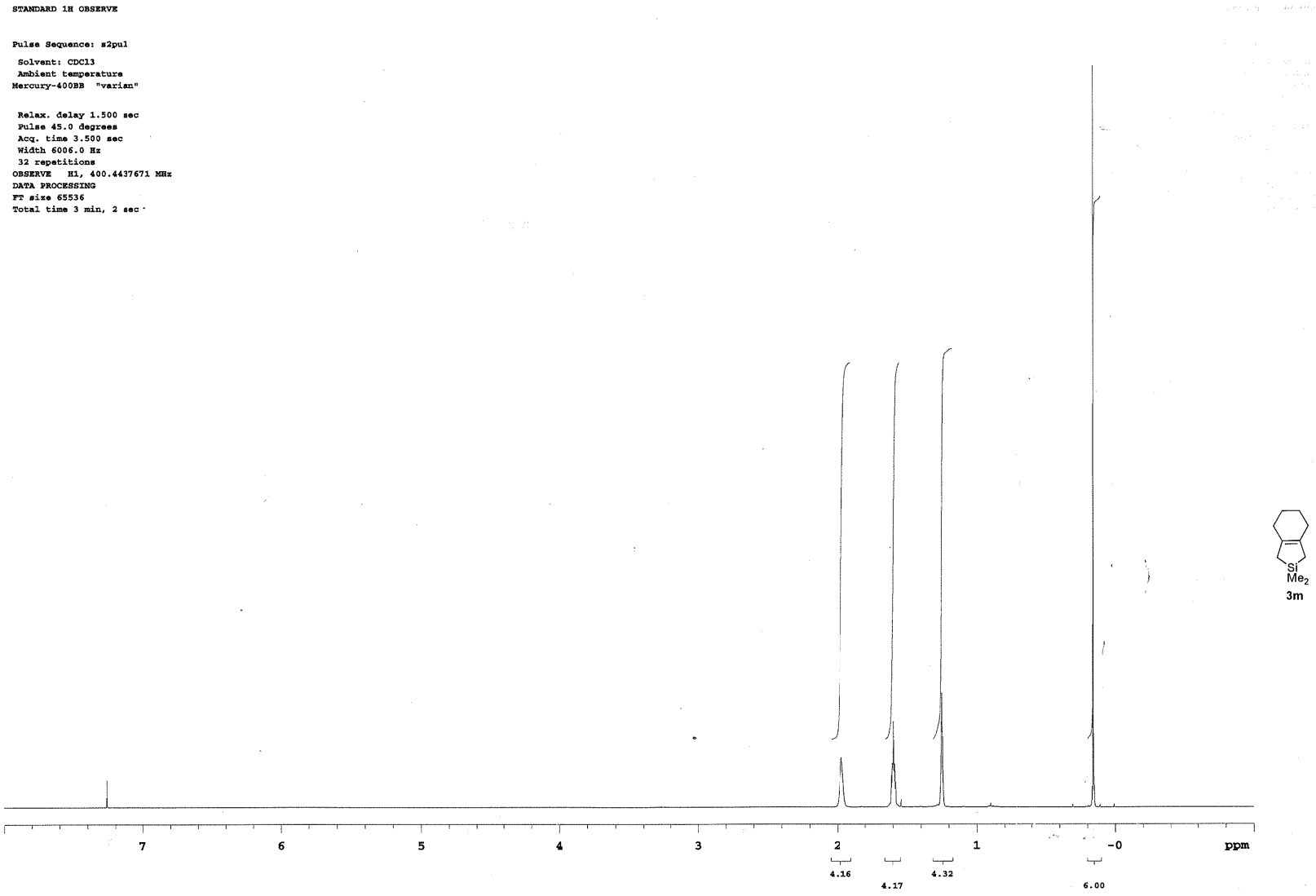
125
150
175
200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Pulse 45.0 degrees
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Width 6006.0 Hz
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OBSERVE H1, 400.4437671 MHz
DATA PROCESSING
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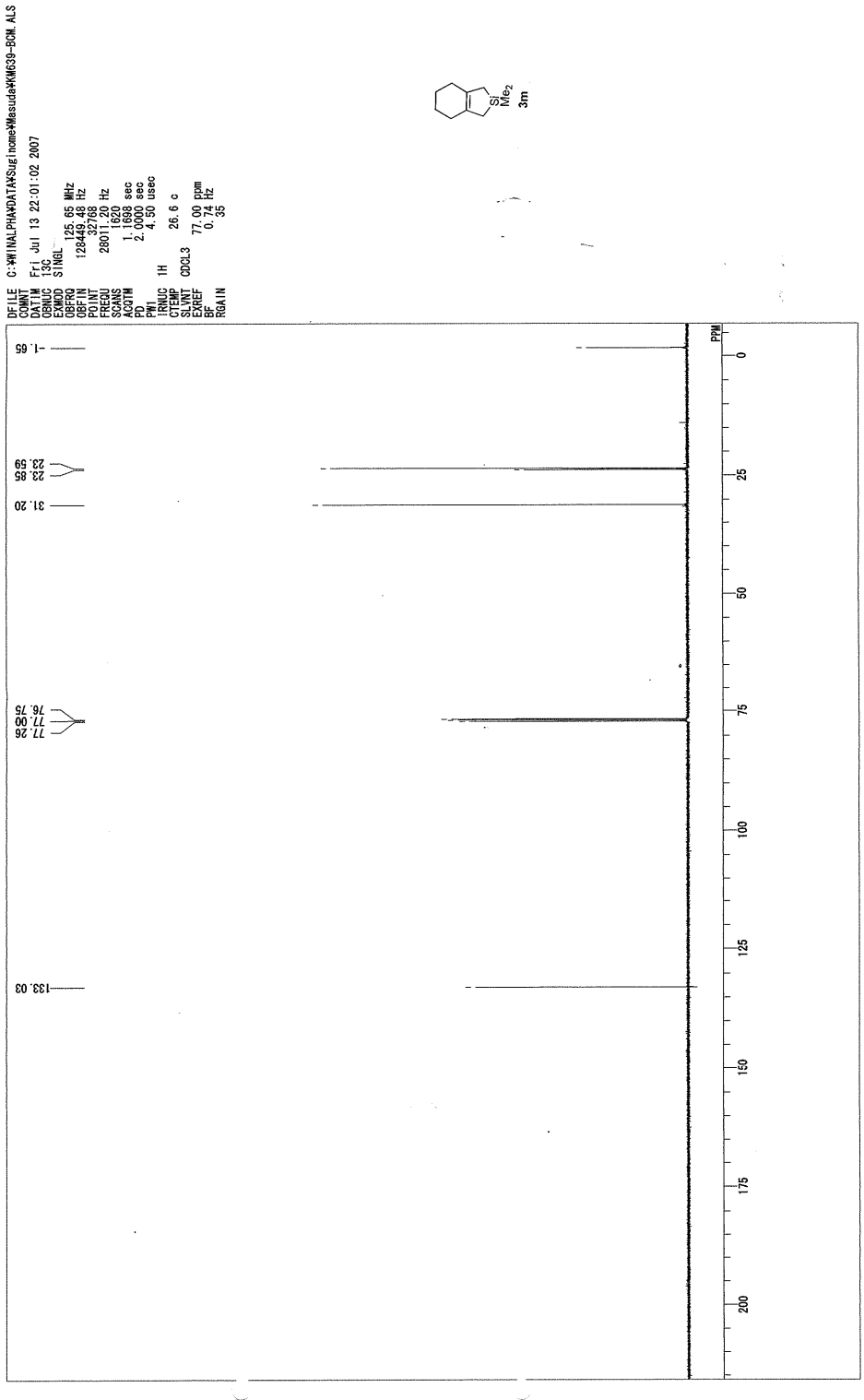
3m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CTEMP 26.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.74 Hz
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Me2
3m
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23.59
23.85
31.20
76.75
77.00
77.26
133.03
PPM
0
25
50
75
100
125
150
175
200

KM1336KD

Pulse Sequence: s2pul

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

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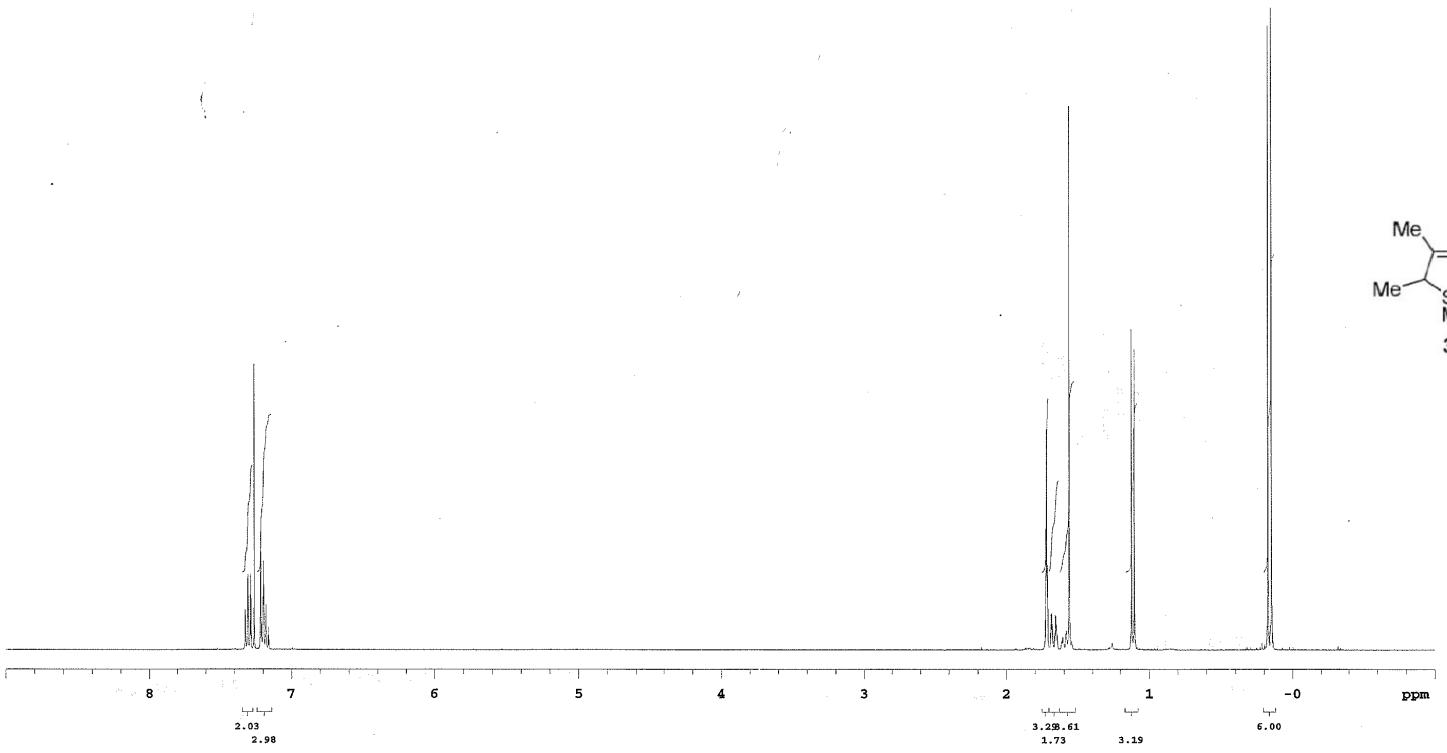
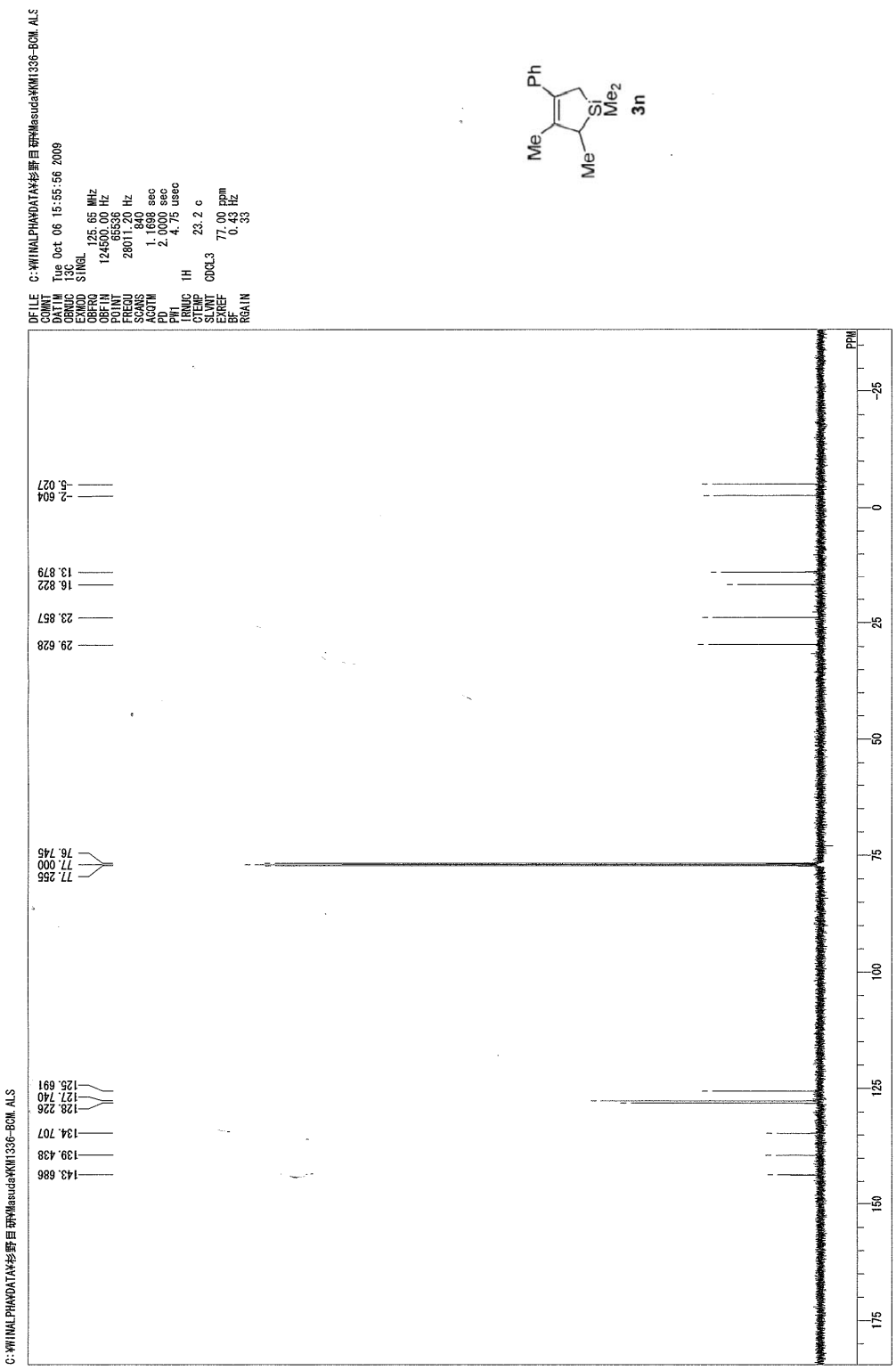


3n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OBFIN 124500.00 Hz
POINT 65536
FREQU 28011.20 Hz
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EXREF 0.43 Hz
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77.000
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Ph
Si
Me2
Me
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KM1037C

Pulse Sequence: s2pul

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Ambient temperature
Mercury-400BB "varian"

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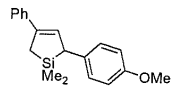
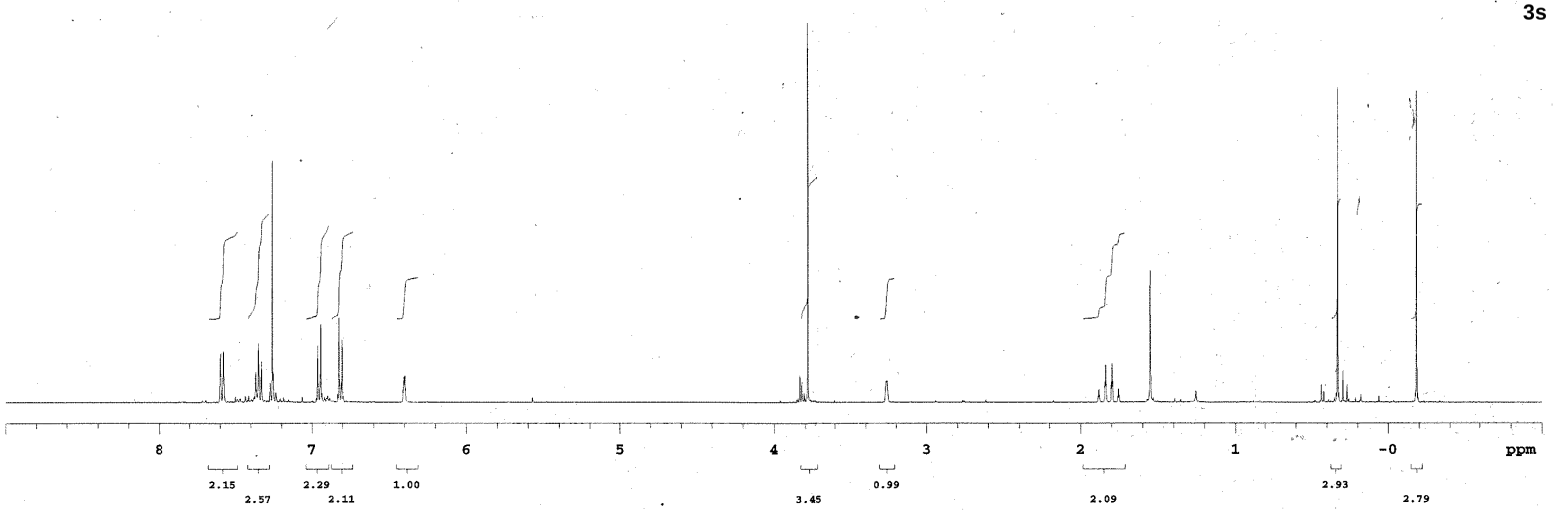
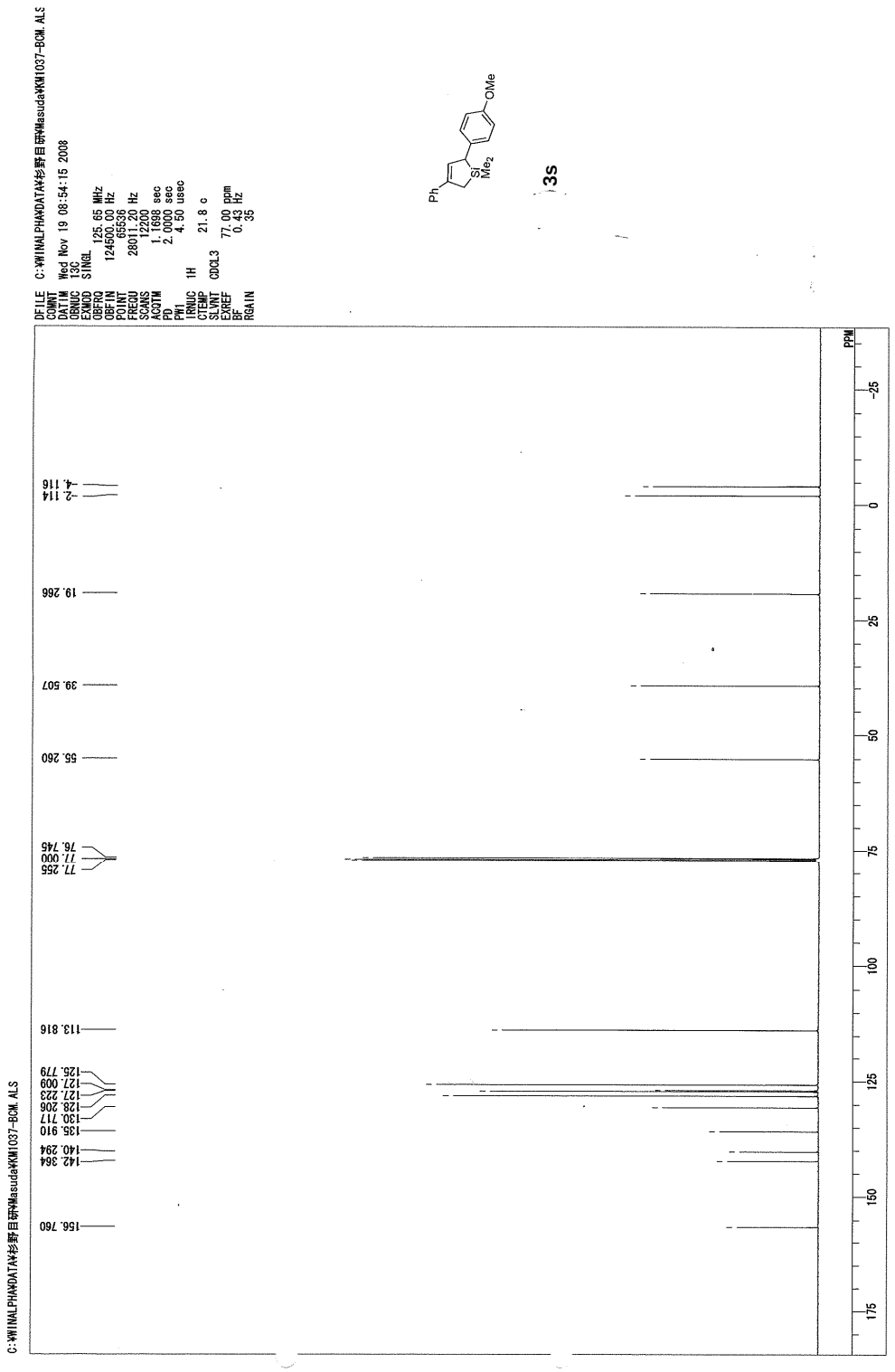
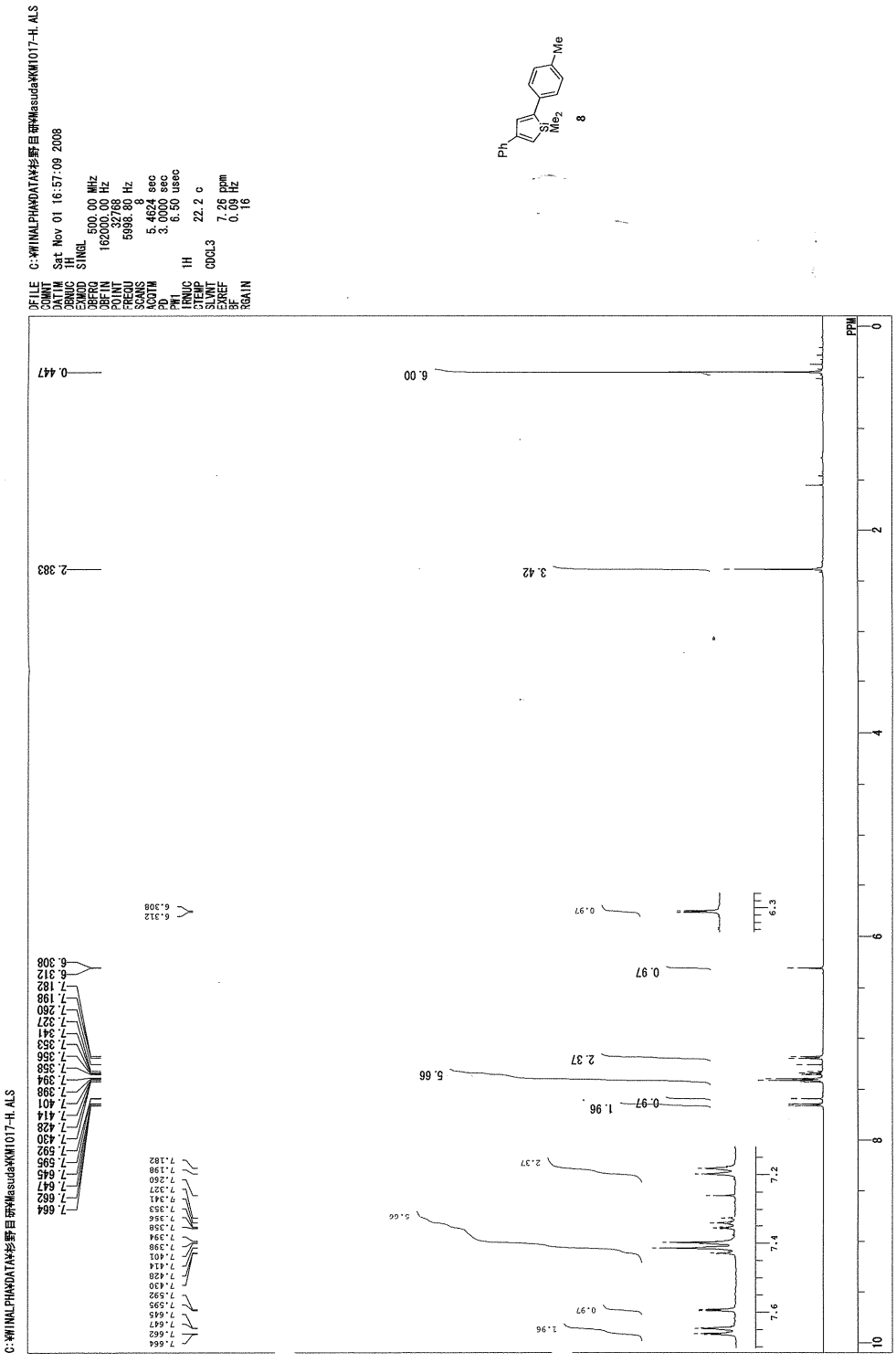
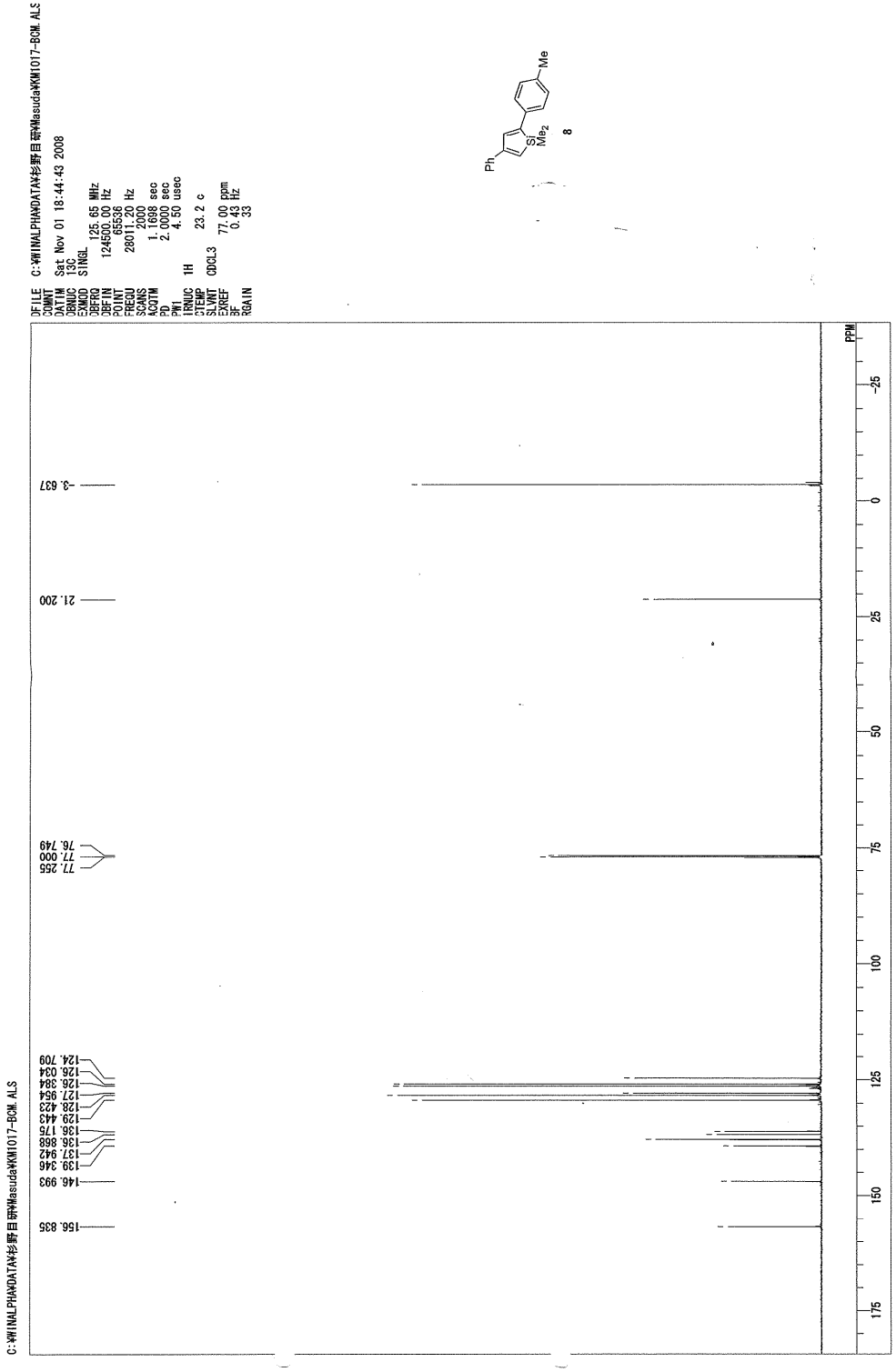


3s




C:¥WINALPHA¥DATA¥杉野目研¥Masuda¥KM1037-BGM.ALS
DFILE C:¥WINALPHA¥DATA¥杉野目研¥Masuda¥KM1037-BGM.ALS
COMNT
DATIM Wed Nov 19 08:54:15 2008
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBFIN 124500.00 Hz
POINT 65536
FREQU 28011.20 Hz
SCANS 1120
ACQTM 1.1693 sec
PD 2.0000 sec
PW1 4.50 usec
IRNUC 1H
OTEMP 21.8 c
SLVNT CDCL3 77.00 ppm
EXREF 0.43 Hz
BF 35
RGAIN
Ph
Si
Me2
OMe
3s
-4.116
-2.114
19.266
39.507
55.260
76.745
77.000
77.255
113.816
125.779
127.009
127.223
128.206
130.717
135.910
140.294
142.364
156.760
PPM
-25
0
25
50
75
100
125
150
175

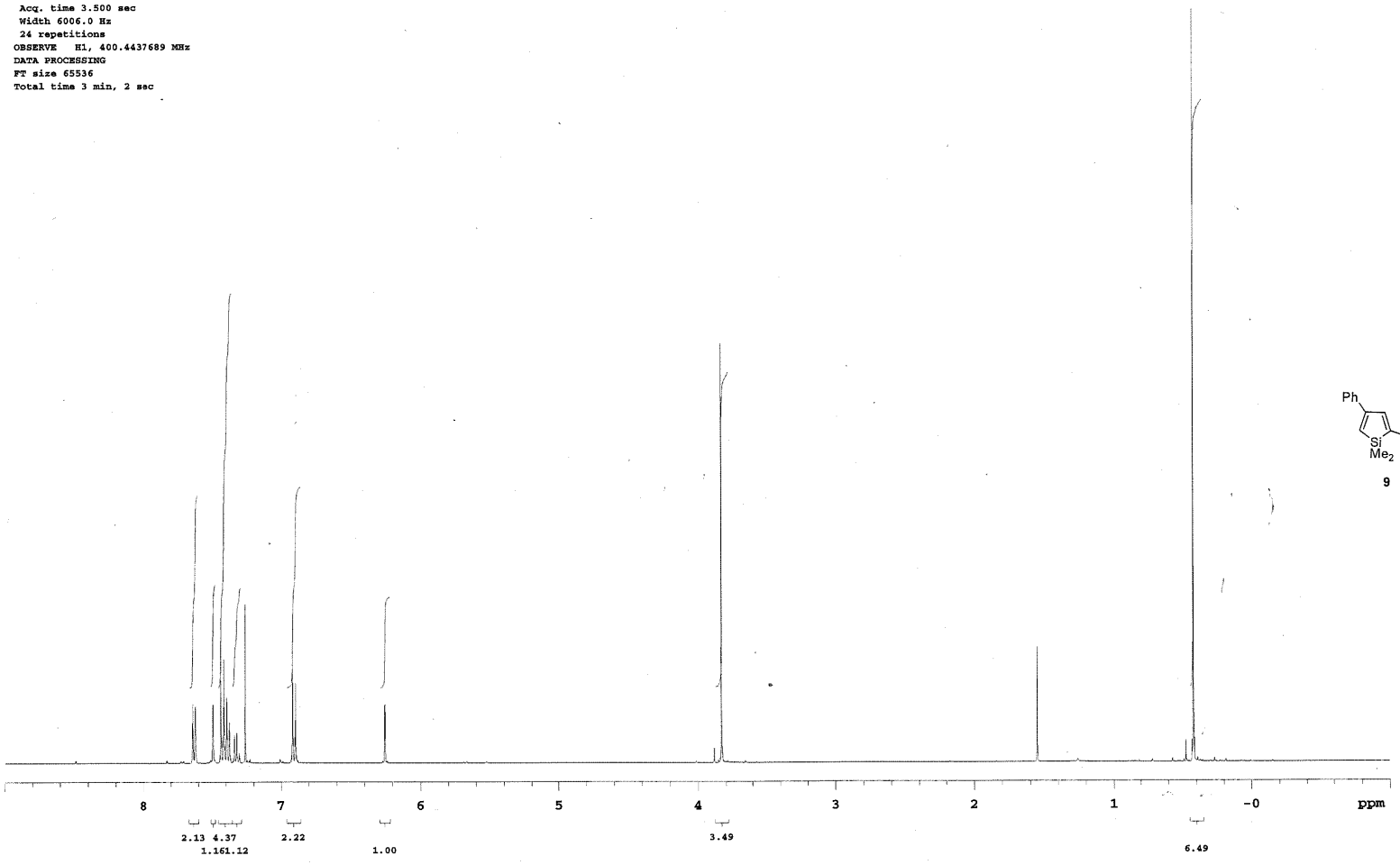

C:¥WINALPHA¥DATA¥杉野目 研¥Masuda¥KM1017-H. ALS
C:¥WINALPHA¥DATA¥杉野目 研¥Masuda¥KM1017-H. ALS
Sat Nov 01 16:57:09 2008
1H
SINGL
500.00 MHz
162000.00 Hz
32768
5998.80 Hz
8
5.4624 sec
3.0000 sec
6.50 usec
1H
22.2 c
CDCL3
7.26 ppm
0.09 Hz
16
Ph
Si
Me2
Me
8
PPM

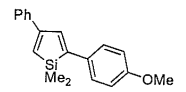

C:¥NMRALPHA¥DATA¥杉野目研¥Masuda¥KM1017-BOM.ALS
DFILE C:¥NMRALPHA¥DATA¥杉野目研¥Masuda¥KM1017-BOM.ALS
COMNT
DATIM Sat Nov 01 18:44:43 2008
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBFIN 124500.00 Hz
POINT 65536
FREQU 28011.20 Hz
SCANS 2600
ACQTM 1.6998 sec
PD 2.0000 sec
PW1 4.50 usec
IRNUC 1H
CTEMP 23.2 c
SLVNT CDCL3 77.00 ppm
EXREF 0.43 Hz
BF 33
RGAIN
-3.637
21.200
77.255
77.000
76.749
124.709
126.034
126.384
127.954
128.423
129.443
136.175
136.868
137.942
139.346
146.993
156.835
PPM
25
0
-25
50
75
100
125
150
175
Ph
Si
Me2
Me
8

KM1045C

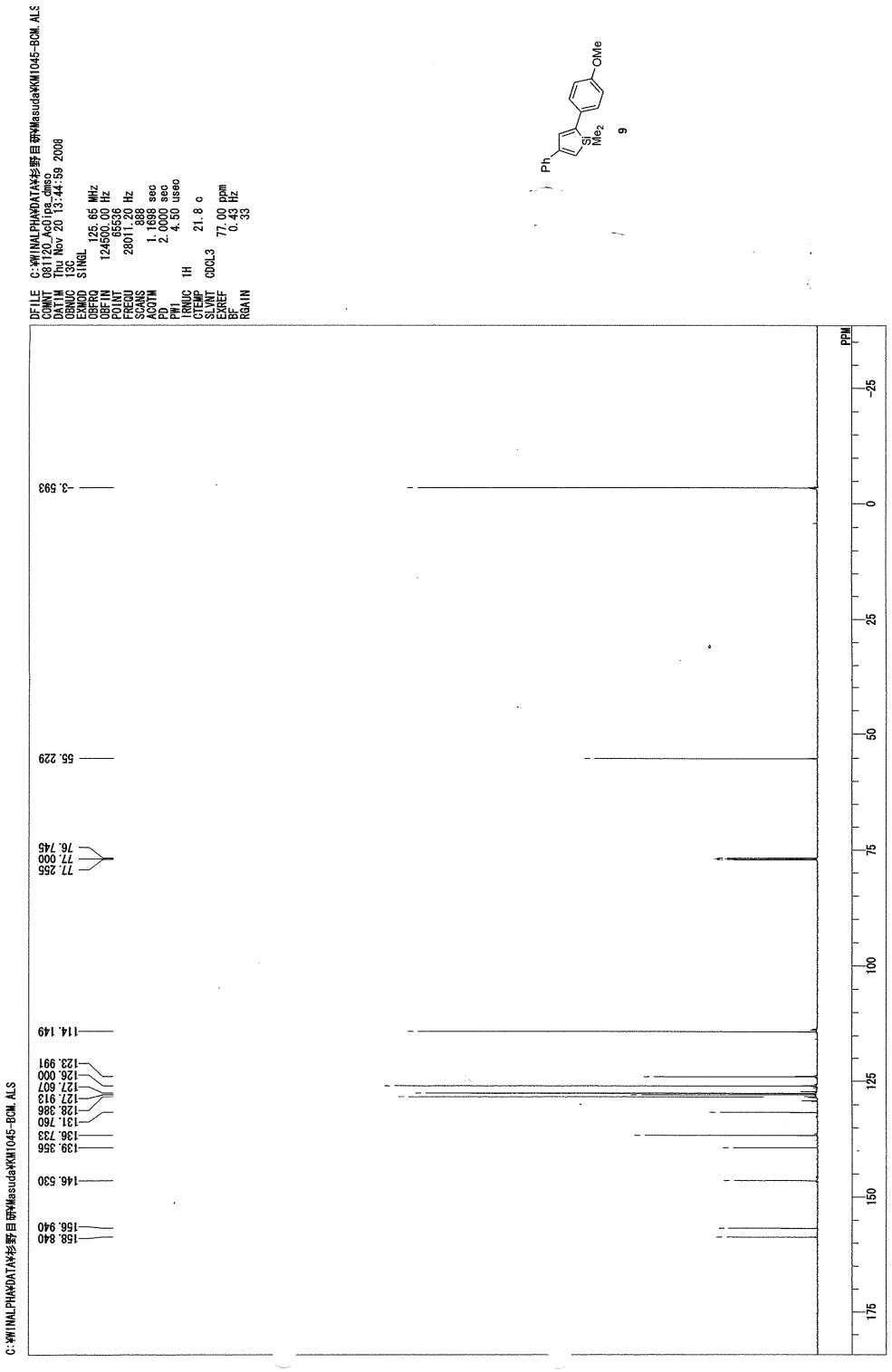
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "varian"

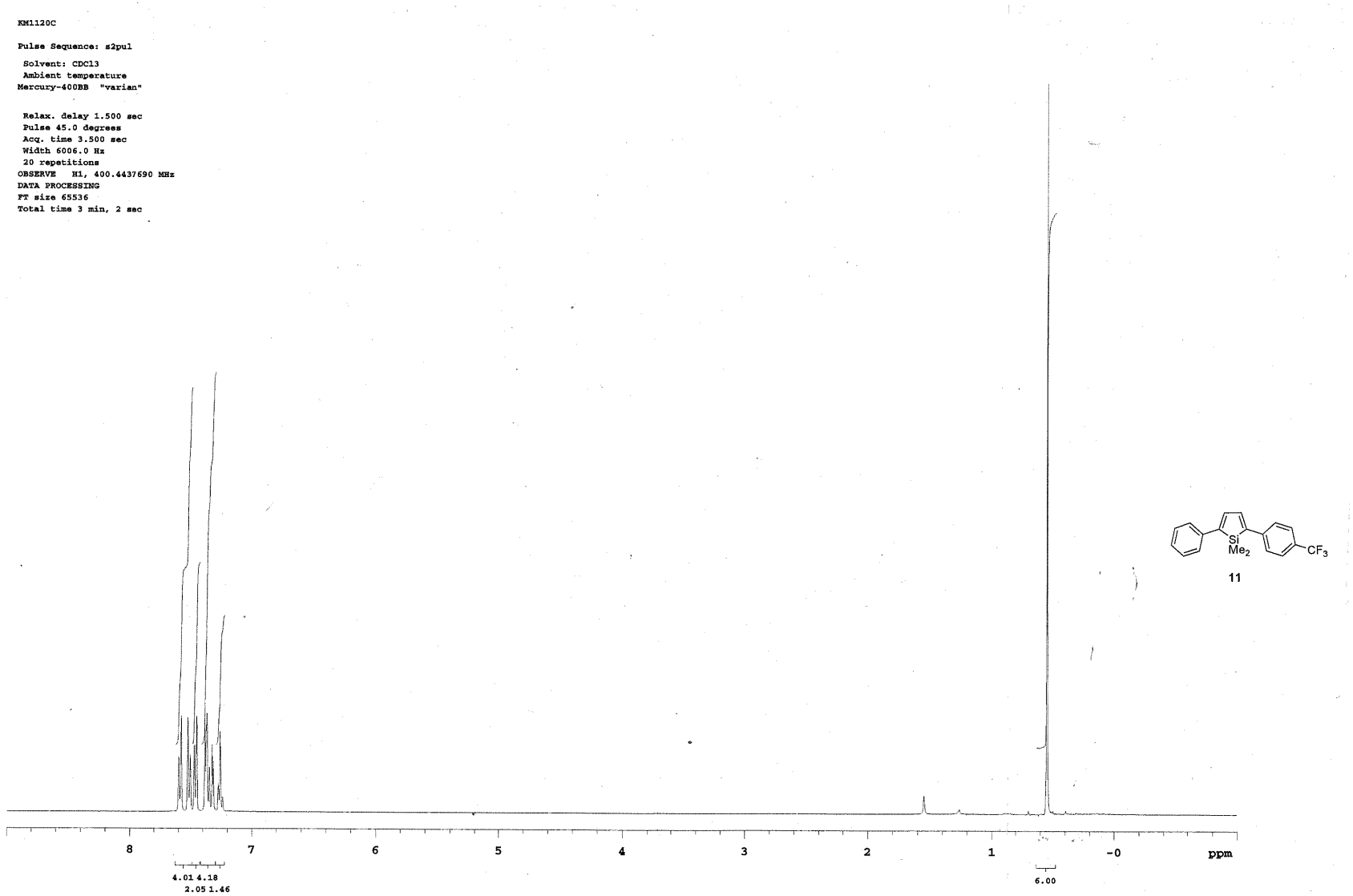
Relax. delay 1.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6006.0 Hz
24 repetitions
OBSERVE H1, 400.4437689 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 2 sec

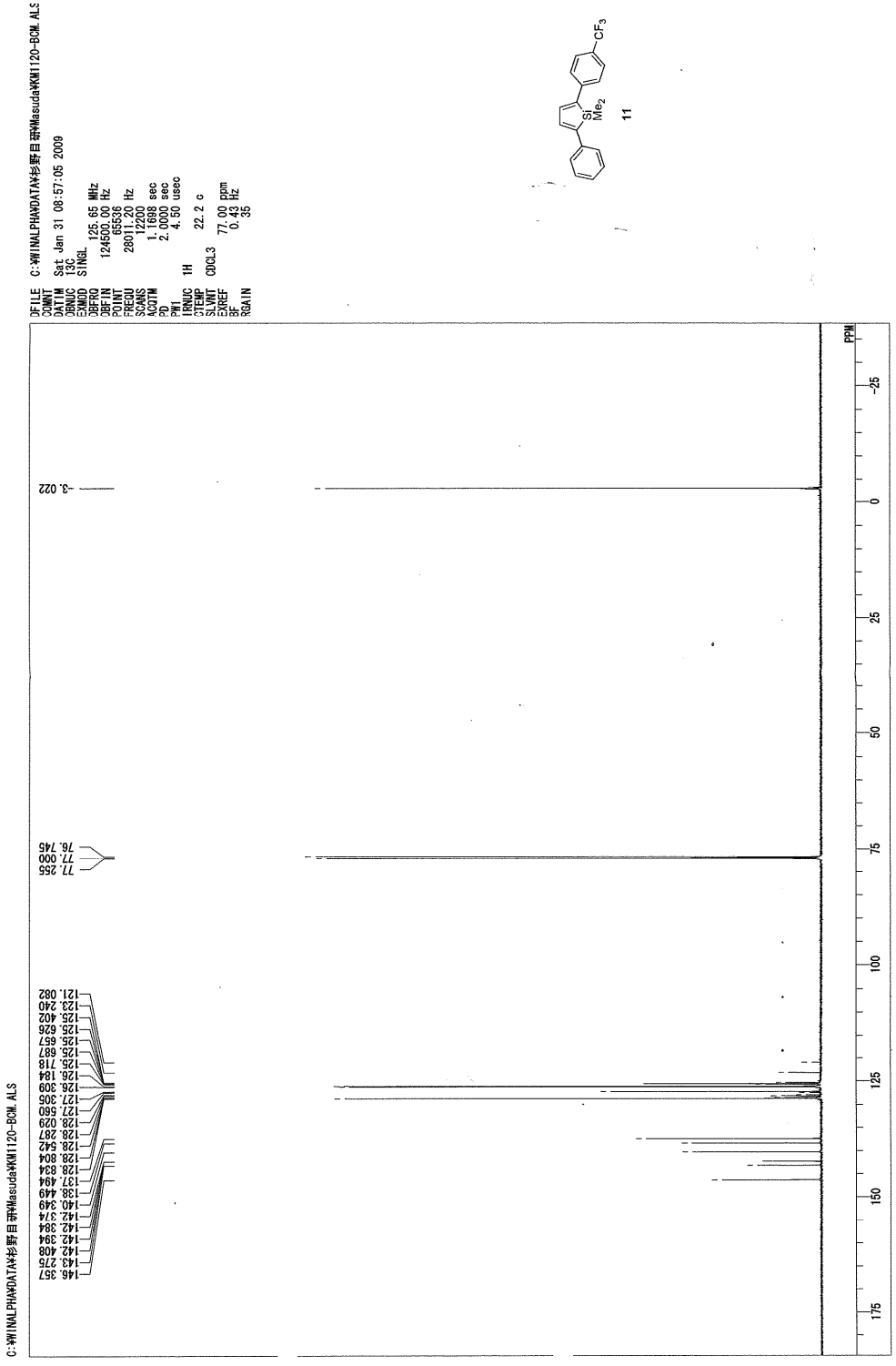


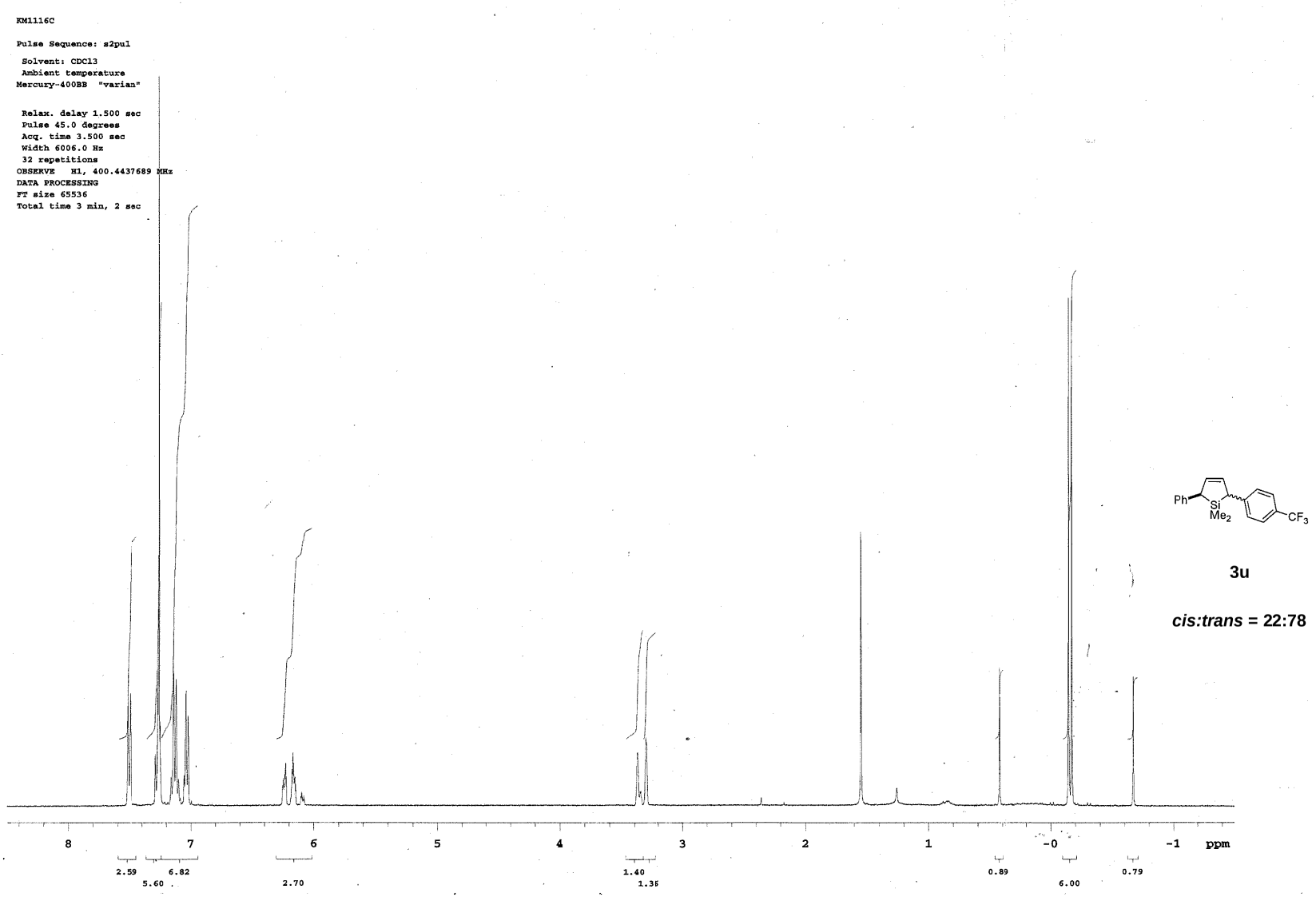


9


C:¥WINALPHADATA¥杉野目研¥Masuda¥KM1045-BCM.ALS
DFILE C:¥WINALPHADATA¥杉野目研¥Masuda¥KM1045-BCM.ALS
COMNT 081120_Acdlpa_dmso
DATIM Thu Nov 20 13:44:59 2008
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBFIN 124500.00 Hz
POINT 65536
FREQU 28011.20 Hz
SCANS 888
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 33
-3.593
55.229
76.745
77.000
77.255
114.149
123.991
126.000
127.607
127.913
128.386
131.760
136.733
139.356
146.530
156.940
158.840
PPM
-25
0
25
50
75
100
125
150
175
Ph
Si
Me2
OMe
9


KM1120C
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
20 repetitions
OBSERVE H1, 400.4437690 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 2 sec
8
7
6
5
4
3
2
1
-0
ppm
4.01 4.18
2.05 1.46
6.00
Si
Me2
CF3
11


C:¥WINALPHA¥DATA¥杉野目研¥Masuda¥KM1120-BOM.ALS
C:¥WINALPHA¥DATA¥杉野目研¥Masuda¥KM1120-BOM.ALS
DFILE
COMNT
DATIM Sat Jan 31 08:57:05 2009
OBNUC 13C
EXMOD SINGL
OBFRQ 125.65 MHz
OBFIN 1245600.00 Hz
POINT 65536
FREQU 28011.20 Hz
SCANS 1200
ACQTM 1.1698 sec
PD 2.0000 sec
PW1 4.50 usec
IRNUC 1H
OTEMP 22.2 c
SLVNT CDCL3 77.00 ppm
EXREF 0.43 Hz
BF 35
RGAIN
-3.022
76.745
77.000
77.255
121.082
123.240
125.402
125.626
125.657
125.687
125.718
126.184
126.309
127.305
127.560
128.029
128.287
128.542
128.804
128.834
137.494
138.449
140.349
142.374
142.384
142.394
142.408
142.278
146.357
PPM
175
150
125
100
75
50
25
0
-25
CF3
Si
Me2
11



3u

***cis*:*trans* = 22:78**