Supporting Information

A remarkable regiocontrol in the palladium-catalyzed silylstannylation of fluoroalkylated alkynes –Highly regio- and stereoselective synthesis of multi-substituted fluorine-containing alkenes

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General procedures

Infrared spectra (IR) were determined in a liquid film on a NaCl plate or KBr disk method with a JASCO FT/IR-4100 typeA spectrometer. ¹H and ¹³C NMR spectra were measured with a JEOL JNM-AL400 NMR spectrometer in a chloroform-*d* (CDCl₃) solution with tetramethylsilane (Me₄Si) as an internal reference. A JEOL JNM-EX90A (84.21 MHz) FT-NMR spectrometer and a JEOL JNM-AL400 NMR spectrometer were used for determining the yields of the products with hexafluorobenzene (C₆F₆). ¹⁹F NMR (376.05 MHz) spectra were measured with a JEOL JNM-AL 400 NMR spectrometer in a chloroform-*d* (CDCl₃) solution with trichlorofluoromethane (CFCl₃) as an internal standard. High-resolution mass spectra (HRMS) were taken on a JEOL JMS-700MS spectrometer by electron impact (EI), chemical ionization (CI), and fast atom bombardment (FAB) methods.

All reactions were routinely monitored by ¹⁹F NMR spectroscopy or TLC, and carried out under an atmosphere of argon.

Materials

N,N-Dimethylformamide (DMF), triethylamine (Et₃N), and hexamethylphosphoric triamide (HMDS) were fleshly distilled from calcium hydride (CaH₂). All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use. Thin-layer chromatography (TLC) was done with Merck silica gel 60 F_{254} plates, and column chromatography was carried out using Wako gel C-200 as adsorbent.

Typical procedure for the silyIstannylation of 1-(4-chlorophenyl)-3,3,3-trifluoropropyne (Condition A): To a solution of 1-(4-chlorophenyl)-3,3,3- trifluoropropyne (0.051 g, 0.25 mmol) and Pd(PPh₃)₂Cl₂ (0.007 g, 0.00625 mmol, 2.5 mol%) in THF (2.5 mL) was added a THF solution of trimethyl(tributylstannyl)silane (0.109 g, 0.30 mmol) at room temperature. The reaction was stirred at 80 °C for 6 h. The resulting mixture was then quenched with H₂O. The reaction mixture was extracted with Et₂O three times. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in *vacuo*. The residue was chomatographed on silica gel (Hexane : EtOAc = 30 : 1) to afford the corresponding silyIstannylated products as a regioisomeric mixture of **2d** and **3d** (0.089g, 0.16 mmol, 63%).

(Z)-3,3,3-Trifluoro-1-(4-methoxyphenyl)-1-tributylstannyl-2-trimethylsilyl-1-propene (2a)

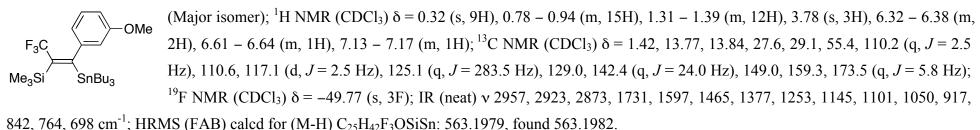
Isolated yield : 75% (Eluent of silica gel column chromatography; Hexane : EtOAc = 30 : 1. This compound was isolated as a mixture of the

regioisomers 2a and 3a.)

 $\begin{array}{c} \mathsf{M}_{a} \mathsf{S}_{i} \mathsf{S}_{n} \mathsf{B}_{u_{3}} \\ \mathsf{N}_{a} \mathsf{S}_{i} \mathsf{S}_{n} \mathsf{B}_{u_{3}} \end{array} \\ \begin{array}{c} \mathsf{M}_{a} \mathsf{M}_{a} \mathsf{O}_{a} \mathsf{I}_{a} \mathsf{I$

(Z)-3,3,3-Trifluoro-1-(3-methoxyphenyl)-1-tributylstannyl-2-trimethylsilyl-1-propene (2b)

Isolated yield : 56% (Eluent of silica gel column chromatography; Hexane only. This compound was isolated as a mixture of the regioisomers **2b** and **3b**.)



(Z)-3,3,3-Trifluoro-1-(2-methoxyphenyl)-1-tributylstannyl-2-trimethylsilyl-1-propene (2c)

Isolated yield : 61% (Eluent of silica gel column chromatography; Hexane : EtOAc = 30 : 1. This compound was isolated as a mixture of the

 $F_{3}C \longrightarrow OMe \\ Me_{3}Si \longrightarrow SnBu_{3}$ regioisomer **2c** and **3c**.) (Major isomer); ¹H NMR (CDCl₃) $\delta = 0.32$ (s, 9H), 0.68 – 0.92 (m, 15H), 1.19 – 1.38 (m, 12H), 3.74 (s, 3H), 6.67 (d, J = 7.6 Hz, 1H), 6.75 (d, J = 7.6 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H); ¹³C NMR (CDCl₃) $\delta = 1.06$, 13.4, 13.6, 27.4, 28.7, 54.9, 109.4, 120.0, 124.9 (q, J = 283.5 Hz), 124.8 (d, J = 2.5 Hz), 126.7, 136.4, 142.0 (q, J = 23.9 Hz), 153.3, 170.6 (q, J = 23.5 Hz), 124.8 (d, J = 2.5 Hz), 126.7, 136.4, 142.0 (q, J = 23.9 Hz), 153.3, 170.6 (q, J = 23.5 Hz), 124.8 (d, J = 2.5 Hz), 126.7, 136.4, 142.0 (q, J = 23.9 Hz), 153.3, 170.6 (q, J = 23.9 Hz), 153.3, 5.7 Hz); ¹⁹F NMR (CDCl₃) $\delta = -51.22$ (s, 3F); IR (neat) v 2957, 2873, 1731, 1596, 1483, 1464, 1377, 1235, 1174, 1140, 1102, 1048, 844, 805, 749 cm⁻¹.

(Z)-1-(4-Chlorophenyl)-3,3,3-trifluoro-1-tributylstannyl-2-trimethylsilyl-1-propene (2d)

Isolated yield : 63% (Eluent of silica gel column chromatography; Hexane : EtOAc = 30 : 1. This compound was isolated as a mixture of the regioisomer 2d and 3d.)

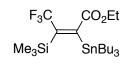
CI (Major isomer); ¹H NMR (CDCl₃) δ 0.31 (s, 9H), 0.80 – 1.45 (m, 18H), 0.85 (t, *J* = 7.39 Hz, 9H), 6.71 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (CDCl₃) d 1.3, 13.8, 13.9, 27.6, 29.2, 125.0 (q, *J* = 283.5 Hz), 125.8 – 126.1 (m, 1C), 128.0, 131.0, 143.9 (q, *J* = 24.0 Hz), 146.1, 172.5 (q, *J* = 5.7 Hz); ¹⁹F NMR (CDCl₃) δ –49.70 (s, 3F); IR (neat) v 2957, 2923, 2873, 1721, 1483, Me₃Si SnBu₃ 1252, 1233, 1184, 1142, 1097, 1015, 962 cm⁻¹.

(Z)-Ethyl 4-(3,3,3-trifluoro-1-tributylstannyl-2-trimethylsilylpropen-1-yl)benzoate (2e)

Isolated yield : 65% (Eluent of silica gel column chromatography; Hexane : EtOAc = 30 : 1. This compound was isolated as a mixture of the regioisomer 2e and 3e.)

F₃C Me₃Si SnBu₃ (Major isomer); ¹H NMR (CDCl₃) $\delta = 0.33$ (s, 9H), 0.75 – 0.95 (m, 15H), 1.10 – 1.41 (m, 15H), 4.36 (q, J = 6.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H); ¹³C NMR (CDCl₃) $\delta = 0.63$, 13.6, 13.9, 14.6, 27.6, 29.1, 61.0, 124.4 – 124.5 (m, 1C), 126.2 (q, J = 280.2 Hz), 126.4, 126.5, 128.0, 129.1, 146.5 (q, J = 28.1 Hz), 166.9, 167.6 (q, J = 6.6 Hz); ¹⁹F NMR (CDCl₃) $\delta = -49.83$ (s, 3F); IR (neat) v 2957, 2923, 2873, 1720, 1605, 1464, 1403, 1282, 1233, 1134, 1098, 1022, 951, 844, 748, 705 cm⁻¹; HRMS (FAB) calcd for (M+H) C₂₇H₄₆F₃O₂SiSn: 607.2241, found 607.2249.

(Z)-Ethyl 4,4,4-Trifluoro-2-tributylstannyl-3-trimethylsilyl-2-propenoate (2f)



Combined isolated yield : 52% (Eluent of silica gel column chromatography; Hexane : EtOAc = 10 : 1. Two regioisomers could not be separated completely, but each isomer could be partially obtained in a pure form.) (Minor isomer); ¹H NMR (CDCl₃) δ = 0.20 (s, 9H), 0.17 – 1.05 (m, 15H), 1.25 – 1.52 (m, 15H), 4.15 (q, *J* = 7.2 Hz, 2H); ¹³C NMR (CDCl₃) $\delta = 1.0, 12.2$ (q, J = 3.2 Hz), 13.6, 14.1, 27.1, 28.6, 60.5, 126.3 (q, J = 273.6 Hz), 143.8 (q, J = 28.1 Hz), 161.9 (q, J = 9.9 Hz), 172.5; ¹⁹F NMR (CDCl₃) $\delta = -58.70$ (s, 3F); IR (neat) v 2958, 2925, 2873, 1714, 1571, 1465, 1378, 1254, 1215, 1147, 1116, 1034, 924, 848, 768, 671, 630 cm⁻¹; HRMS (FAB) calcd for (M+Na) C₂₁H₄₁F₃NaO₂SiSn: 553.1748, found 553.1744.

(Z)-Ethyl 4,4,4-Trifluoro-3-tributylstannyl-2-trimethylsilyl-2-propenoate (3f)

 $F_{3}C \xrightarrow{CO_{2}Et}_{SiMe_{3}} (Major isomer); {}^{1}H NMR (CDCl_{3}) \delta = 0.24 (s, 9H), 0.90 (t, J = 7.2 Hz, 9H), 1.07 - 1.60 (m, 21H), 4.18 (q, J = 7.2 Hz, 2H); {}^{13}C NMR (CDCl_{3}) \delta = 0.6, 13.4 - 13.5 (m, 1C), 14.3, 14.8, 27.9, 29.3, 61.5, 126.3 (q, J = 278.5 Hz), 146.6 (q, J = 31.4 Hz), 157.5 (q, J = 6.6 Hz), 172.0 (q, J = 1.7 Hz); {}^{19}F NMR (CDCl_{3}) \delta = -55.98 (s, 3F); IR (neat) 2958, 2925, 2873, 1720, 1567, 1464, 1378, 1231, 1146, 1107, 1034, 991, 851, 763, 694, 670 cm^{-1}; HRMS (FAB) calcd for (M+H) C_{21}H_{42}F_{3}O_{2}SiSn: 531.1928, found 531.1927.$

Typical procedure for silyIstannylation of 1-(4-chlorophenyl)-3,3,3-trifluoropropyne (Condition B): To a solution of 1-(4-chlorophenyl)-3,3,3-trifluoropropyne (0.051 g, 0.25 mmol) and Pd(*t*-BuNC)₂Cl₂ (0.002 g, 0.00625 mmol, 2.5 mol%) in THF (2.5 mL) was added a THF solution of trimethyl(tributylstannyl)silane (0.109 g, 0.30 mmol) at room temperature. The reaction was stirred for 6 h at room temperature. The resulting mixture was then quenched with H₂O. The reaction mixture was extracted with Et₂O three times. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in *vacuo*. The residue was chomatographed on silica gel (hexane: EtOAc = 30 : 1) to afford the corresponding silylstannylated product **2** and **3** (0.128 g, 0.23 mmol, 90%).

(Z)-3,3,3-Trifluoro-1-(4-methoxyphenyl)-2-tributylstannyl-1-trimethylsilyl-1-propene (3a)

Isolated yield : 82% (Eluent of silica gel column chromatography; Hexane : EtOAc = 30 : 1. This compound was isolated as a mixture of the regioisomer 2a and 3a.)

 $\begin{array}{c} \mathsf{OMe} \\ \mathsf{(Major isomer);} \ ^1\mathrm{H} \ \mathrm{NMR} \ (\mathrm{CDCl_3}) \ \delta = 0.06 \ (\mathrm{s}, 9\mathrm{H}), \ 0.83 - 0.94 \ (\mathrm{m}, 11\mathrm{H}), \ 1.08 - 1.12 \ (\mathrm{m}, 4\mathrm{H}), \ 1.34 - 1.39 \ (\mathrm{m}, 6\mathrm{H}), \ 1.51 - 1.54 \ (\mathrm{m}, 6\mathrm{H}), \ 3.79 \ (\mathrm{s}, 3\mathrm{H}), \ 6.68 - 6.81 \ (\mathrm{m}, 4\mathrm{H}); \ ^{13}\mathrm{C} \ \mathrm{NMR} \ (\mathrm{CDCl_3}) \ \delta = 0.8, \ 13.6 \ (\mathrm{m}, 1\mathrm{C}), \ 14.0, \ 27.7, \ 29.2, \ 55.4, \ 113.4, \ 126.4 \ (\mathrm{q}, J = 280.2 \ \mathrm{Hz}), \ 127.7 \ (\mathrm{q}, J = 2.5 \ \mathrm{Hz}), \ 137.2, \ 146.5 \ (\mathrm{q}, J = 28.1 \ \mathrm{Hz}), \ 157.9, \ 168.9 \ (\mathrm{q}, J = 6.6 \ \mathrm{Hz}); \ ^{19}\mathrm{F} \ \mathrm{NMR} \ (\mathrm{CDCl_3}) \ \delta = -49.46 \ (\mathrm{s}, 3\mathrm{F}); \ \mathrm{IR} \ (\mathrm{neat}) \ 2956, \ 2923, \ 2872, \ 1606, \ 1503, \ 1464, \ 1282, \ 1236, \ 1187, \ 1137, \ 1098, \ 1039, \ 962, \ 842, \ 760, \ 618 \ \mathrm{cm}^{-1}; \ \mathrm{HRMS} \ (\mathrm{FAB}) \ \mathrm{calcd for} \ (\mathrm{M-H}) \ \mathrm{C}_{25}\mathrm{H}_{42}\mathrm{F}_{3}\mathrm{OSiSn}: \ 563.1979, \ \mathrm{found} \ 563.2133. \end{array}$

(Z)-3,3,3-Trifluoro-1-(3-methoxyphenyl)-2-tributylstannyl-1-trimethylsilyl-1-propene (3b)

Isolated yield : 87% (Eluent of silica gel column chromatography; Hexane only. This compound was isolated as a mixture of the regioisomer 2b and

 $\begin{array}{c} \textbf{3b.} \\ \textbf{F_{3}C} \\ \textbf{Bu_{3}Sn} \\ \textbf{SiMe_{3}} \end{array} \qquad \begin{array}{c} \textbf{3b.} \\ \textbf{(Major isomer); }^{1}\text{H NMR (CDCl_{3}) } \delta = 0.07 \ (\text{s}, 9\text{H}), \ 0.79 - 1.57 \ (\text{m}, 27\text{H}), \ 3.78 \ (\text{s}, 3\text{H}), \ 6.30 - 6.46 \ (\text{m}, 2\text{H}), \ 6.60 - 6.75 \ (\text{m}, 1\text{H}), \ 7.10 - 7.20 \ (\text{m}, 1\text{H}); \ ^{13}\text{C NMR (CDCl_{3}) } \delta = 0.3, \ 13.2 - 13.3 \ (\text{m}, 1\text{C}), \ 13.6, \ 27.3, \ 28.8, \ 55.1, \ 110.6, \ 112.1, \ 118.9, \ 126.3 \ (\text{q}, J = 280.2 \ \text{Hz}), \ 128.3, \ 145.4 \ (\text{q}, J = 28.1 \ \text{Hz}), \ 146.2, \ 158.8, \ 168.0 \ (\text{q}, J = 6.6 \ \text{Hz}); \ ^{19}\text{F NMR (CDCl_{3}) } \delta = -49.61 \ (\text{s}, 3\text{F}); \ \text{IR} \ (\text{neat) } 2957, \ 2923, \ 2873, \ 1730, \ 1598, \ 1464, \ 1377, \ 1284, \ 1230, \ 1137, \ 1099, \ 1051, \ 995, \ 976, \ 841, \ 770, \ 699, \ 628 \ \text{cm}^{-1}; \ \text{HRMS (FAB) calcd for (M+H)} \ C_{25}\text{H}_{44}\text{F}_{3}\text{OSiSn: } 565.2135, \ \text{found } 565.2143. \end{array}$

(Z)-3,3,3-Trifluoro-1-(2-methoxyphenyl)-2-tributylstannyl-1-trimethylsilyl-1-propene (3c)

Isolated yield : 86% (Eluent of silica gel column chromatography; Hexane : EtOAc = 30 : 1. This compound was isolated as a mixture of the regioisomer 2c and 3c.)

(Major isomer); ¹H NMR (CDCl₃) $\delta = 0.02$ (s, 9H), 0.82 – 1.60 (m, 27H), 3.74 (s, 3H), 6.70 – 6.90 (m, 3H), 7.10 – 7.20 (m, 1H); ¹³C NMR (CDCl₃) $\delta = 0.2$, 13.1 – 13.2 (m, 1C), 13.7, 27.3, 28.9, 54.9, 109.6, 119.8, 126.1 (q, J = 279.4 Hz), 126.6 – 126.7 (m, 1C), 127.0, 134.3, 145.1 (q, J = 28.9 Hz), 154.7, 165.7 (q, J = 7.4 Hz); ¹⁹F NMR (CDCl₃) $\delta = -51.16$ (s, 3F); IR (neat) v 2957, 2924, 1731, 1596, 1484, 1377, 1231, 1174, 1136, 1105, 1049, 960, 842, 751 cm⁻¹; HRMS (FAB) calcd for (M+H) C₂₅H₄₄F₃OSiSn: 565.2135, found 565.2129.

(Z)-1-(4-Chlorophenyl)-3,3,3-trifluoro-2-tributylstannyl-1-trimethylsilyl-1-propene (3d)

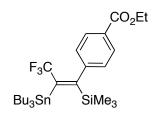
Isolated yield : 90% (Eluent of silica gel column chromatography; Hexane : EtOAc = 30 : 1. This compound was isolated as a mixture of the regioisomer 2d and 3d.)

(Major isomer); ¹H NMR (CDCl₃) δ 0.06 (s, 9H), 0.80 – 1.60 (m, 18H), 0.93 (t, *J* = 7.39 Hz, 9H), 6.78 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (CDCl₃) δ 1.1, 14.0 (q, *J* = 1.7 Hz), 14.3, 28.0, 29.5, 125.01 (q, *J* = 283.5 Hz), 126.4 (q, *J* = 2.5 Hz), 128.3, 132.1, 143.9, 147.5 (q, *J* = 28.6 Hz)

CI Hz), 167.8 (q, J = 7.2 Hz); ¹⁹F NMR (CDCl₃) δ -49.54 (s, 3F); IR (neat) v 2957, 2855, 1547, 1484, 1465, 1420, 1377, 1232, 1184, 1139, 1095, 1015, 962 cm⁻¹; HRMS (FAB) calcd for (M+Na) C₂₄H₄₀ClF₃NaSiSn: 591.1460, found 591.1459. F₃C SiMe₃

(Z)-Ethyl 4-(3,3,3-trifluoro-2-tributylstannyl-1-trimethylsilyl-1-propen-1-yl)benzoate (3e)

Isolated yield : 90% (Eluent of silica gel column chromatography; Hexane : EtOAc = 30 : 1. This compound was isolated as a mixture of the regioisomer 2e and 3e.)



(Major isomer); ¹H NMR (CDCl₃) $\delta = 0.06$ (s, 9H), 0.80 – 1.60 (m, 30H), 4.36 (q, J = 7.2 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃) $\delta = 1.4$, 14.2 – 14.3 (m 1C), 14.6, 15.3, 28.3, 29.8, 61.8, 125.2 (d, J = 2.5 Hz), 126.9 (q, J = 280.2 Hz), 127.1 – 127.2 (m, 1C), 129.8, 147.3 (q, J = 28.9 Hz), 151.1, 167.6, 168.3 (q, J = 6.9 Hz); ¹⁹F NMR (CDCl₃) $\delta = -49.65$ (s, 3F); IR (neat) 2957, 2924, 2873, 1719, 1605, 1464, 1403, 1282, 1251, 1232, 1175, 1139, 1097, 1021, 951, 844, 749, 705, 618 cm⁻¹; HRMS (FAB) calcd for (M+H) C₂₇H₄₆F₃O₂SiSn: 607.2241, found 607.2241.

(Z)-1-(4-Chlorophenyl)-4,4,4-Trifluoro-2-tributylstannyl-3-trimethylsilyl-2-buten-1-ol (2h)

Isolated yield : 25%. (Eluent of silica gel column chromatography; Hexane : Benzene = 3 : 1.)

HO F_3C Me_3Si $SnBu_3$ (Minor isomer); ¹H NMR (CDCl₃) $\delta = 0.26$ (s, 9H), 0.58 – 0.75 (m, 6H), 0.76 (t, J = 7.2 Hz, 9H), 1.10 – 1.27 (m, 12H), 2.42 (d, J = 4.0 Hz, 1H), 5.79 (s, 1H), 7.14 – 7.25 (m, 4H); ¹³C NMR (CDCl₃) $\delta = 1.0$, 13.2, 14.3, 27.1, 28.5, 74.6 – 74.7 (m, 1C), 124.8 (q, J = 284.1 Hz), 127.8, 132.8, 138.9, 142.0 (q, J = 24.8 Hz), 162.5, 177.4 (q, J = 4.1 Hz); ¹⁹F NMR (CDCl₃) $\delta = -49.96$ (s, 3F); IR (neat) 3610, 3466, 2957, 2923, 2872, 1726, 1671, 1597, 1538, 1491, 1464, 1400, 1377, 1254, 1222, 1141, 1106, 1015, 961, 920, 840, 801, 767 cm⁻¹.

(Z)-1-(4-Chlorophenyl)-4,4,4-trifluoro-3-tributylstannyl-2-trimethylsilyl-2-buten-1-ol (3h)

Isolated yield : 69%. (Eluent of silica gel column chromatography; Hexane : Benzene = 3 : 1.)

(Major isomer); ¹H NMR (CDCl₃) $\delta = 0.0$ (s, 9H), 0.93 (t, J = 7.4 Hz, 9H), 1.05 – 1.55 (m, 18H), 2.27 (d, J = 4.8 Hz, 1H), 5.94 (s, 1H), 7.24 – 7.31

 $\begin{array}{c} \text{HO} \\ \text{F}_{3}\text{C} \\ \text{Bu}_{3}\text{Sn} \\ \text{SiMe}_{3} \end{array} \xrightarrow{\text{HO}} \text{Cl} \\ \begin{array}{c} \text{(m, 4H);} \ ^{13}\text{C} \ \text{NMR} \ (\text{CDCl}_{3}) \ \delta = 2.2, \ 13.3, \ 13.5, \ 27.0, \ 28.7, \ 74.2, \ 126.1 \ (q, J = 281.0 \ \text{Hz}), \ 127.3, \ 127.7, \ 132.4, \ 139.6, \ 146.5 \ (q, J = 28.1 \ \text{Hz}), \ 168.8 \ (q, J = 6.6 \ \text{Hz}); \ ^{19}\text{F} \ \text{NMR} \ (\text{CDCl}_{3}) \ \delta = -48.20 \ (s, \ 3F); \ \text{IR} \ (\text{neat}) \ 3619, \ 3484, \ 2957, \ 2924, \ 2873, \ 1714, \ 1490, \ 1464, \ 1400, \ 1249, \ 1215, \ 1133, \ 1102, \ 1071, \ 1015, \ 961, \ 848, \ 806, \ 764, \ 723 \ \text{cm}^{-1}; \ \text{HRMS} \ (\text{FAB}) \ \text{calcd} \end{array}$

for (M+Na) C₂₅H₄₂ClF₃NaOSiSn: 621.1565, found 621.1572.

(Z)-1,1,1-Trifluoro-6-phenyl-3-tributylstannyl-2-trimethylsilyl-2,5-hexadien-4-ol (2i)

Isolated yield : 23%. (Eluent of silica gel column chromatography; Hexane : Benzene = 2 : 1.)

¹H NMR (CDCl₃) $\delta = 0.30$ (s, 9H), 0.84 (t, J = 7.2 Hz, 9H), 0.90 – 1.55 (m, 18H), 2.17 (d, J = 4.0 Hz, 1H), 5.49 (s, 1H), 6.17 (dd, J = 16.0, 4.0 Hz, HO F₃C Me₃Si SnBu₃ HO Me₃Si SnBu₃ SnBu₃ = 0.30 (s, 9H), 0.84 (t, J = 7.2 Hz, 9H), 0.90 – 1.55 (m, 18H), 2.17 (d, J = 4.0 Hz, 1H), 5.49 (s, 1H), 6.17 (dd, J = 16.0, 4.0 Hz, 1H), 7.24 – 7.38 (m, 5H); ¹³C NMR (CDCl₃) $\delta = 1.3$, 13.6, 15.1, 27.5, 29.0, 75.3, 125.2 (q, J = 283.5 Hz), 126.5, 127.7, 128.5, 129.5, 131.3, 136.7, 141.0 (q, J = 24.8 Hz), 178.1 (q, J = 4.1 Hz); ¹⁹F NMR (CDCl₃) $\delta = -49.89$ (s, 3F); IR (neat) 3454, 3027, 2956, 2854, 1725, 1600, 1538, 1495, 1464, 1421, 1376, 1222, 1140, 1106, 1020, 964, 899, 843, 770, 748, 693, 633 cm⁻¹; HRMS (FAB) calcd for (M+Na) C₂₇H₄₅F₃NaOSiSn: 613.2112, found 613.2120.

(Z)-1,1,1-Trifluoro-6-phenyl-2-tributylstannyl-3-trimethylsilyl-2,5-hexadien-4-ol (3i)

Isolated yield : 52%. (Eluent of silica gel column chromatography; Hexane : Benzene = 2 : 1.)

1600, 1537, 1464, 1377, 1249, 1216, 1132, 1103, 964, 843, 746, 693, 640 cm⁻¹; HRMS (FAB) calcd for (M+Na) C₂₇H₄₅F₃NaOSiSn: 613.2112, found 613.2110.

(Z)-1,1,1-Trifluoro-3-tributhylstannyl-2-trimethylsilyl-2-decen-4-ol (2j)

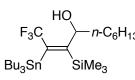
Isolated yield : 30%. (Eluent of silica gel column chromatography; Hexane : EtOAc = 30 : 1.)

¹H NMR (CDCl₃) $\delta = 0.25$ (s, 9H), 0.80 – 1.15 (m, 18H), 1.25 – 1.55 (m, 22H), 1.91 (d, J = 3.6 Hz, 1H), 4.68 (s, 1H); ¹³C NMR (CDCl₃) $\delta = 1.4$, 13.6,

HO F_3C $n-C_6H_{13}$ Me₃Si SnBu₃ HO r_3C $n-C_6H_{13}$ Hz; ¹⁹F NMR (CDCl₃) $\delta = -49.94$ (s, 3F); IR (neat) 3622, 3477, 2956, 2923, 2856, 1537, 1464, 1377, 1253, 1221, 1141, 1103, 1035, 960, 902, 840, 769 cm⁻¹.

(Z)-1,1,1-Trifluoro-2-tributylstannyl-3-trimethylsilyl-2-decen-4-ol (3j)

Isolated yield : 35%. (Eluent of silica gel column chromatography; Hexane : EtOAc = 30 : 1.)



¹H NMR (CDCl₃) $\delta = 0.27$ (s, 9H), 0.88 – 1.06 (m, 18H), 1.28 – 1.55 (m, 22H), 1.69 (d, J = 4.0 Hz, 1H), 4.75 (s, 1H); ¹³C -*n*-C₆H₁₃ NMR (CDCl₃) $\delta = 3.9$, 14.3, 14.5, 14.8, 23.3, 27.0, 27.6, 29.5, 29.9, 32.5, 36.8, 76.6 – 76.7 (m, 1C), 127.3 (q, J = 281.0 Hz), 145.0 (q, J = 28.1 Hz), 173.2 (q, J = 5.8 Hz); ¹⁹F NMR (CDCl₃) $\delta = -48.44$ (s, 3F); IR (neat) 3626, 3477, 2957, 2925, 2857, 1464, 1377, 1250, 1216, 1101, 1036, 960, 843, 765 cm⁻¹.

(Z)-1,1,1-Trifluoro-4-Methoxymethoxy-3-tributylstannyl-2-trimethylsilyl-2-decene (2k)

Isolated yield : 49%. (Eluent of silica gel column chromatography; Hexane : Benzene = 5 : 1.)

 $\begin{array}{l} \text{MOMO} \\ \text{F}_{3}\text{C} \\ \text{Me}_{3}\text{Si} \\ \text{SnBu}_{3} \end{array} \stackrel{1}{\text{H NMR (CDCl}_{3})} \delta = 0.25 \text{ (s, 9H), 0.90 (t, } J = 7.4 \text{ Hz, 9H), 0.87 - 1.03 (m, 9H), 1.28 - 1.54 (m, 22H), 3.36 (s, 3H), 4.40 - 4.45 (m, 2H), 4.55 - 4.65 (m, 1H); {}^{13}\text{C NMR (CDCl}_{3}) \delta = 1.5, 13.6, 14.1, 15.0, 22.6, 25.7, 27.5, 29.0, 29.1, 31.8, 34.6, 55.8, 80.5 - 80.6 (m, 1C), 94.5, 125.2 (q, } J = 283.5 \text{ Hz}), 141.1 (q, J = 24.8 \text{ Hz}), 180.1 (q, J = 4.1 \text{ Hz}); {}^{19}\text{F NMR (CDCl}_{3}) \delta = -50.07 (s, 3F); IR (neat) 2956, 2926, 2856, 1731, 1537, 1464, 1377, 1253, 1223, 1464, 1377, 1253, 1223, 1142, 1108, 1016, 924, 840, 769 \text{ cm}^{-1}; HRMS (FAB) calcd for (M+Na) C_{27}H_{55}F_{3}NaO_{2}SiSn; 639.2843, found 639.2844. \end{array}$

(Z)-1,1,1-Trifluoro-4-methoxymethoxy-2-tributylstannyl-3-trimethylsilyl-2-decene (3k)

Isolated yield : 36%. (Eluent of silica gel column chromatography; Hexane : Benzene = 5 : 1.)

 $\begin{array}{l} {}^{\text{MOMO}}_{\text{F}_{3}\text{C}} & -n\text{-}C_{6}\text{H}_{13} \\ \text{Bu}_{3}\text{Sn} & \text{SiMe}_{3} \end{array} \right) \overset{1}{\text{H NMR (CDCl}_{3}) \ \delta = 0.23 \ (\text{s}, 9\text{H}), \ 0.87 \ (\text{t}, J = 7.4 \ \text{Hz}, 9\text{H}), \ 0.86 - 1.05 \ (\text{m}, 8\text{H}), \ 1.25 - 1.50 \ (\text{m}, 22\text{H}), \ 1.70 - 1.76 \ (\text{m}, 1\text{H}), \ 3.37 \ (\text{s}, 3\text{H}), \ 4.40 - 4.50 \ (\text{m}, 2\text{H}), \ 4.60 - 4.68 \ (\text{m}, 1\text{H}); \ ^{13}\text{C NMR (CDCl}_{3}) \ \delta = 3.2, \ 13.9, \ 14.2, \ 14.4, \ 22.9, \ 26.6, \ 27.6, \ 29.2, \ 29.4, \ 32.2, \ 35.4, \ 56.0, \ 80.5, \ 94.9, \ 126.7 \ (\text{q}, J = 280.2 \ \text{Hz}), \ 146.2 \ (\text{q}, J = 29.0 \ \text{Hz}), \ 171.0 \ (\text{q}, J = 5.0 \ \text{Hz}); \ ^{19}\text{F NMR (CDCl}_{3}) \ \delta = -48.74 \ (\text{s}, 3\text{F}); \ \text{IR (neat) } 2956, \ 2926, \ 2856, \ 1732, \ 1537, \ 1464, \ 1378, \ 1249, \ 1216, \ 1107, \ 1022, \ 960, \ 924, \ 843, \ 764 \ (\text{m}) \ \text{cm}^{-1}; \end{array} \right)$

HRMS (FAB) calcd for (M+Na) C₂₇H₅₅F₃NaO₂SiSn: 639.2843, found 639.2844.

Procedure for silylstannylation of 4-methoxymethoxy-1,1,1-trifluorodecyne (Condition B): To a solution of 4-methoxymethoxy-1,1,1-trifluorodecyne (0.063 g, 0.25 mmol) and Pd(*t*-BuNC)₂Cl₂ (0.002 g, 0.00625 mmol, 2.5 mol%) in THF (2.5 mL) was added a THF solution of dimethylphenyl(tributylstannyl)silane (0.128 g, 0.30 mmol) at room temperature. The reaction was stirred for 6 h at room temperature. The resulting mixture was then quenched with H₂O. The reaction mixture was extracted with Et₂O three times. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in *vacuo*. Purification of the residue oil by flash chromatography five times, and concentrated in *vacuo*. The residue was chomatographed on silica gel (hexane: EtOAc = 30 : 1) to afford the corresponding silylstannylated product **21** and **31** (0.106 g, 0.15 mmol, 62%).

(Z)-2-Dimethylphenylsilyl-1,1,1-trifluoro-4-methoxymethoxy-3-tributylstannyl-2-decene (2k)

Isolated yield : 28%. (Eluent of silica gel column chromatography; Hexane : Benzene = 3 : 1.)

 $MOMO = \frac{1}{1000} = \frac{1}{1000$

(Z)-3-Dimethylphenylsilyl-1,1,1-trifluoro-4-methoxymethoxy-2-tributylstannyl-2-decene (3k)

Isolated yield : 34%. (Eluent of silica gel column chromatography; Hexane : Benzene = 3 : 1.)

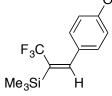
823, 820, 729, 702 cm⁻¹; HRMS (FAB) calcd for (M-H) C₃₂H₅₆F₃O₂SiSn: 677.3024, found 677.3027.

Destannylation of (*Z*)-3,3,3-trifluoro-1-(4-methoxyphenyl)-1-tributylstannyl-2-trimethylsilyl-1-propene (2a) and : (*Z*)-3,3,3-trifluoro-1-(4-methoxyphenyl)-2-tributylstannyl-1-trimethylsilyl-1-propene (3a): To a solution of the isomeric mixture of 2a and 3a (0.113 g, 0.20 mmol, 2a : 3a = 22 ; 78) in MeOH (2 mL) was added PPTS (1.0 mL, 6.0 mmol) at room temperature. The reaction was stirred for 52 h at the reflux temperature. The resulting mixture was neutralized with NaHCO₃ aq. (20 mL of sat. and 10 mL of water) and extracted with Et₂O (2×30 mL). The combined organic layers were dried over anhydride Na₂SO₄ and concentrated in *vacuo*. The residue was chomatographed on silica gel (Hexane: EtOAc = 5 : 1) to afford the products 5a and 6a (0.052g, 0.19 mmol, 95%).

5a or 6a could not be isolated in a pure form. They were obtained as a regioisomeric mixture in a ratio of 19:81.

(E)-3,3,3-Trifluoro-1-(4-methoxyphenyl)-2-trimethylsilyl-1-propene (5a) (Only observed peaks are shown.)

OMe (Minor isomer); ¹H NMR (CDCl₃) $\delta = 0.26$ (s, 9H), 3.83 (s, 3H); ¹⁹F NMR (CDCl₃) $\delta = -53.04$ (s, 3F).



(E)-3,3,3-Trifluoro-1-(4-methoxyphenyl)-1-trimethylsilyl-1-propene (6a)

OMe (Major isomer); ¹H NMR (CDCl₃) $\delta = 0.12$ (s, 9H), 3.81 (s, 3H), 5.99 (q, J = 7.6 Hz, 1H), 6.87 – 6.89 (m, 4H); ¹³C NMR (CDCl₃) $\delta = -2.0, 55.4, 113.7, 113.8, 122.5$ (q, J = 274.4 Hz), 126.0 (q, J = 31.4 Hz), 127.5 – 127.6 (m, 1C), 147.3 (q, J = 7.4 Hz), 158.5; ¹⁹F NMR (CDCl₃) $\delta = -57.71$ (d, J = 7.6 Hz, 3F); IR (neat) 2959, 2839, 1729, 1606, 1509, 1351, 1285, 1190, 1136, 1037, 951, 924, 844, 758, 697 cm⁻¹; HRMS (FAB) calcd for (M+) C₁₃H₁₇F₃OSi: 274.1001, found 274.1000.

Typical procedure for the Stille coupling reaction of vinylstannane 2k with iodobenzene: To a solution of Pd(PPh₃)₄ (0.032 g, 0.028 mmol, 10 mol%) in toluene (3.0 mL) were added silylstannylated adduct **2k** (0.169 g, 0.25 mmol), CuI (0.010 g, 0.052 mmol), and iodobenzene (0.042 mL,

0.375 mmol), and then the reaction mixture was heated to 80 °C. After stirred at 80 °C for 24 h, the reaction was quenched with NH₄Cl. The reaction mixture was extracted with Et₂O three times. The combined organic layers were dried over anhydrous Na₂SO₄ and filtered and stirred with 20% of aqueous KF (10 mL) for 30 min before being dried and concentrated. The residue was chomatographed on silica gel (Hexane: EtOAc = 10 : 1) to afford (*Z*)-1,1,1-trifluoro-4-methoxymethoxy-2-phenyl-3-trimethylsilyl-2-decene (7k).

(Z)-1,1,1-Trifluoro-4-methoxymethoxy-3-phenyl-2-trimethylsilyl-2-decene (7k)

¹⁹F NMR yield : 88%, Isolated yield : 86%, ¹H NMR (CDCl₃) $\delta = -0.20$ (s, 9H), 0.85 (t, J = 7.2 Hz, 3H), 1.23 – 1.45 (m, 10H), 3.40 (s, 3H), 4.58 (d, J = 6.6 Hz, 1H), 4.78 (d, J = 6.6 Hz, 1H), 4.85 – 4.90 (m, 1H), 7.04 – 7.05 (m, 1H), 7.06 – 7.16 (m, 1H), 7.29 – 7.36 (m, 3H); ¹³C NMR (CDCl₃) $\delta = 0.4$, MOMO F_3^{C} $n - C_6^{H_{13}}$ 13.9, 22.5, 25.8, 28.9, 31.7, 34.1, 55.7, 76.1, 94.5, 126.2 (q, J = 277.8 Hz), 127.4, 127.6, 128.1, 129.8, 129.9, 132.8 (q, J = 277.2 Hz), 138.5, 162.9 (q, J = 5.2 Hz); ¹⁹F NMR (CDCl₃) $\delta = -49.64$ (s, 3F); IR (neat) 2930, 2859, 1730, 1586, 1467, 1378, 1244, 1137, 1113, 1025, 921, 846, 769, 703 cm⁻¹; HRMS (FAB) calcd for (M+Na) C₂₁H₃₃F₃NaO₂Si: 425.2100, found 425.2095.

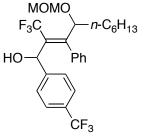
(E)-1,1,1-Trifluoro-4-methoxymethoxy-2-phenyl-3-trimethylsilyl-2-decene (8k)

 $\begin{array}{l} {}^{19}\text{F NMR yield : 91\%, Isolated yield : 91\%, }^{1}\text{H NMR (CDCl_3) } \delta = -0.17 \text{ (s, 9H), } 0.91 \text{ (t, } J = 6.8 \text{ Hz, 3H), } 1.20 - 1.40 \text{ (m, 9H), } \\ {}^{19}\text{F NMR yield : 91\%, Isolated yield : 91\%, }^{1}\text{H NMR (CDCl_3) } \delta = -0.17 \text{ (s, 9H), } 0.91 \text{ (t, } J = 6.8 \text{ Hz, 3H), } 1.20 - 1.40 \text{ (m, 9H), } \\ {}^{1.75 - 1.90 \text{ (m, 1H), } 3.43 \text{ (s, 3H), } 4.56 \text{ (d, } J = 6.8 \text{ Hz, 1H), } 4.68 \text{ (d, } J = 6.8 \text{ Hz, 1H), } 4.80 - 4.90 \text{ (m, 1H), } 7.15 - 7.16 \text{ (m, 2H), } \\ {}^{7.33 - 7.35 \text{ (m, 3H); }^{13}\text{C NMR (CDCl_3) } \delta = 2.1, 14.1, 22.6, 26.3, 29.1, 31.8, 35.5, 55.8, 78.0, 95.0 - 95.1 \text{ (m, 1C), } 122.7 \text{ (q, } J = 279.4 \text{ Hz), } 127.8, 127.9, 128.4, 130.5, 130.6, 136.0 140.6 \text{ (q, } J = 28.9 \text{ Hz), } 154.9; \\ {}^{19}\text{F NMR (CDCl_3) } \delta = -55.48 \text{ (s, 3F); IR } \\ \\ \text{(neat) } 2955, 2930, 2859, 1729, 1467, 1380, 1290, 1249, 1200, 1164, 1117, 1024, 923, 844, 765, 704, 671 \text{ cm}^{-1}; \text{ HRMS (FAB) calcd for (M+Na) } \\ {}^{C_{21}H_{33}F_3NaO_2Si; 425.2100, \text{ found } 425.2105. \end{array}$

The coupling reaction of (*Z*)-2-trimethysilyl-1,1,1-trifluoro-4-methoxymethoxy-3-phenyl-2-decene (7k) with 4-trifluoromethylbenzaldehyde: To a solution of 7k (0.162 g, 0.40 mmol) in NMP (1.0 mL) were added 4-trifluoromethylbenzaldehyde (0.082 mL, 0.60 mmol), TBAF (0.04 mL, 20 mol%), and Zn(OTf)₂ (0.218g, 0.60 mmol), and then the reaction mixture was heated to 80 °C. After stirred at 80 °C for 24 h, the reaction was quenched with coleded NH₄Cl. The reaction mixture was extracted with Et_2O five times. The combined organic layers were dried over anhydride Na₂SO₄ and concentrated in *vacuo*. The residue was chomatographed on silica gel (Hexane: EtOAc = 5 : 1) to afford the product **9k** (0.080g, 0.158 mmol, 39% isolated yield, 54% ¹⁹F NMR yield).

(Z)-4-Methoxymethoxy-3-phenyl-2-trifluoromethyl-1-(4-trifluoromethylphenyl)-2-decen-1-ol (9k)

¹⁹F NMR yield : 54%, Isolated yield : 39%, (Major isomer : 21%, Minor isomaer : 18%), Diastereomeric ratio = 54: 46 (The diastereomers could be separted by silica gel column chromatography.)



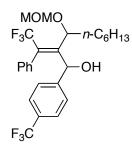
³ Major isomer (Less polar); ¹H NMR (CDCl₃) $\delta = 0.87$ (t, J = 6.8 Hz, 3H), 1.20 - 1.56 (m, 10H), 2.25 (d, J = 8.0 Hz, 1H), 3.44 (s, 3H), 4.70 (d, J = 21.2 Hz, 1H), 4.89 (d, J = 6.8 Hz, 2H), 4.85 – 4.95 (m, 1H), 5.35 (d, J = 8.4 Hz, 1H), 7.20 – 7.25 (m, 2H), 7.36 – 7.43 (m, 5H), 7.58 (d, J = 8.4 Hz, 2H); ¹³C NMR (CDCl₃) $\delta = 14.0$, 22.6, 25.7, 28.9, 31.7, 33.7, 56.0, 71.6, 75.1, 95.1, 123.8 (q, J = 278.8 Hz), 124.1 (q, J = 271.4 Hz), 125.1, 125.31, 125.34, 125.38, 128.21, 128.29, 128.34, 128.45, 129.0, 129.5 (q, J = 32.2 Hz), 130.9 (q, J = 26.4 Hz), 135.3, 144.7, 153.3 (q, J = 3.3 Hz) (All aromatic carbons were detected.); ¹⁹F NMR (CDCl₃) $\delta = -52.03$ (s, 3F), -63.00 (s, 3F); IR (neat) 3448, 2931, 2859, 1726, 1413, 1327, 1258, 1122,

1067, 1027, 707 cm⁻¹; HRMS (FAB) calcd for (M+Na) C₂₆H₃₀F₆NaO₃: 527.1997, found 527.2001.

Minor isomer (More polar); ¹H NMR (CDCl₃) $\delta = 0.89$ (t, J = 6.8 Hz, 3H), 1.20 - 1.75 (m, 10H), 2.20 - 2.30 (m, 1H), 3.41 (s, 3H), 4.61 (d, J = 6.8 Hz, 1H), 4.88 (d, J = 6.8 Hz, 1H), 4.93 - 4.95 (m, 1H), 5.31 (s, 1H), 7.00 - 7.20 (m, 2H), 7.30 - 7.50 (m, 5H), 7.55 - 7.65 (m, 2H); ¹³C NMR (CDCl₃) $\delta = 14.0, 22.6, 25.9, 28.9, 31.8, 34.3, 56.0, 71.5, 74.5, 94.6, 123.8$ (q, J = 278.5 Hz), 124.0 (q, J = 261.9 Hz), 125.2, 125.31, 125.35, 125.38, 127.8, 128.1, 128.3, 128.6, 128.8, 129.5 (q, J = 32.5 Hz), 130.9 (q, J = 26.4 Hz), 135.1, 145.0, 153.1 (q, J = 3.2 Hz) (All aromatic carbons were detected.); ¹⁹F NMR (CDCl₃) $\delta = -51.96$ (s, 3F), -63.01 (s, 3F); IR (neat) 3436, 2931, 2859, 1728, 1620, 1327, 1257, 1223, 1067, 1017, 921, 706 cm⁻¹; HRMS (FAB) calcd for (M+Na) C₂₆H₃₀F₆NaO₃: 527.1997, found 527.1993.

(Z)-1-(4-Trifluoromethylphenyl)-3-methoxymethoxy-2-(2,2,2-trifluoro-1-phenyl-1-ethylidene)-1-nonanol (10k)

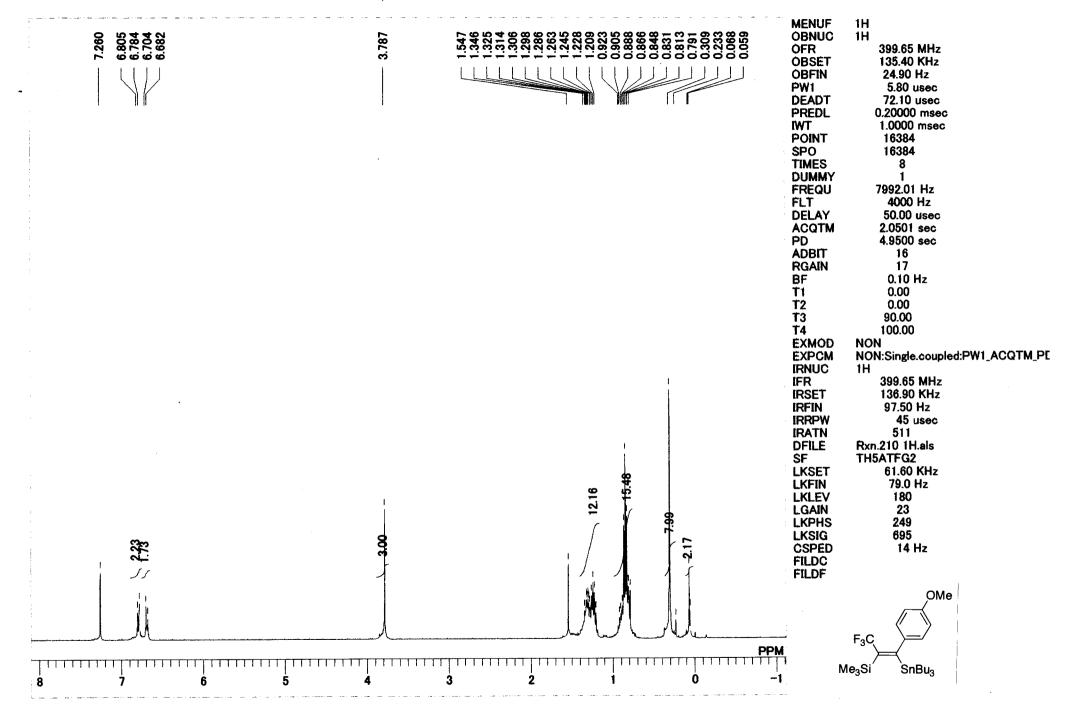
 19 F NMR yield : 28%, Isolated yield : 15%, Diastereomeric ratio = 100: 0



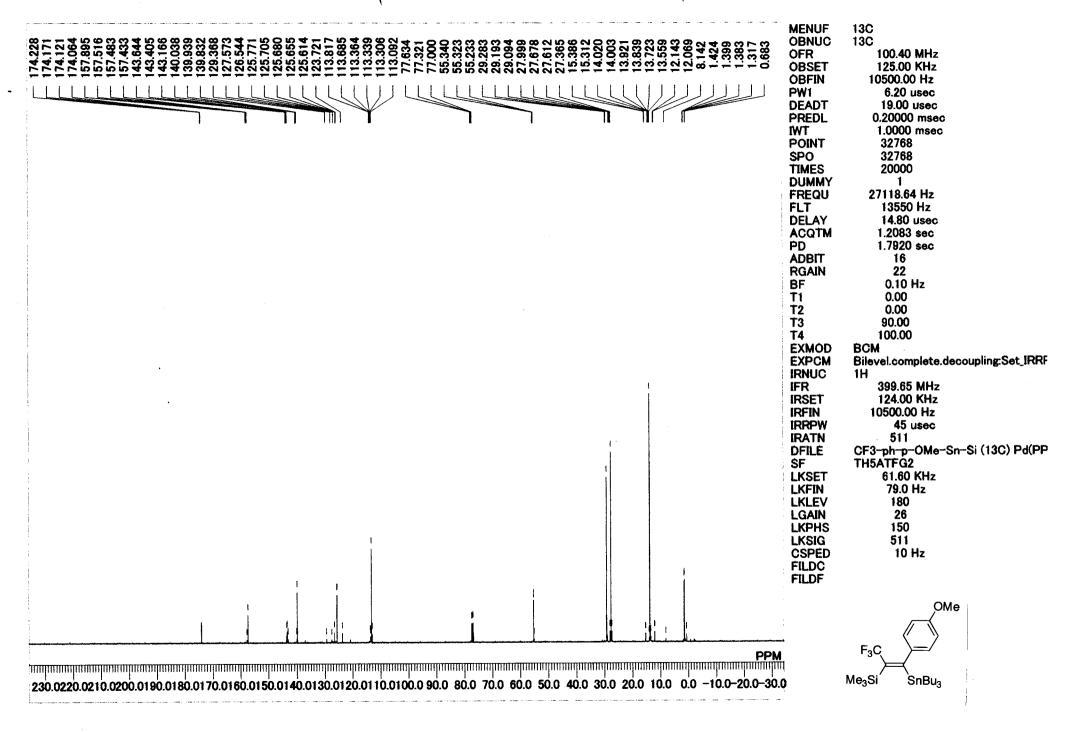
¹H NMR (CDCl₃) $\delta = 0.85$ (t, J = 7.0 Hz, 3H), 1.00 – 1.50 (m, 10H), 3.49 (s, 3H), 4.68 (d, J = 6.4 Hz, 1H), 4.88 – 4.94 (m, 1H), 5.50 (s, 1H), 7.12 – 7.61 (m, 10H); ¹³C NMR (CDCl₃) $\delta = 14.0$, 22.5, 26.2, 28.8, 31.5, 35.9, 56.3, 72.7, 78.8, 96.5, 121.4 (q, J = 271.2 Hz), 123.2 (q, J = 276.1 Hz), 124.8 (q, J = 3.3 Hz), 125.8, 126.6, 126.9, 128.4, 128.6, 128.8, 129.1 (q, J = 33.1 Hz), 129.5, 129.6, 133.2 (q, J = 30.3 Hz), 133.5 (q, J = 1.7 Hz), 146.6, 148.3 (q, J = 2.5 Hz) (All aromatic carbons were detected.);¹⁹F NMR (CDCl₃) $\delta = -55.13$ (s, 3F), -63.00 (s, 3F); IR (neat) 3440, 2958, 2931, 2859, 1724, 1467, 1327, 1164, 1122, 1067, 1017, 764, 705 cm⁻¹; HRMS (FAB) calcd for (M+Na) C₂₆H₃₀F₆NaO₃: 527.1997, found

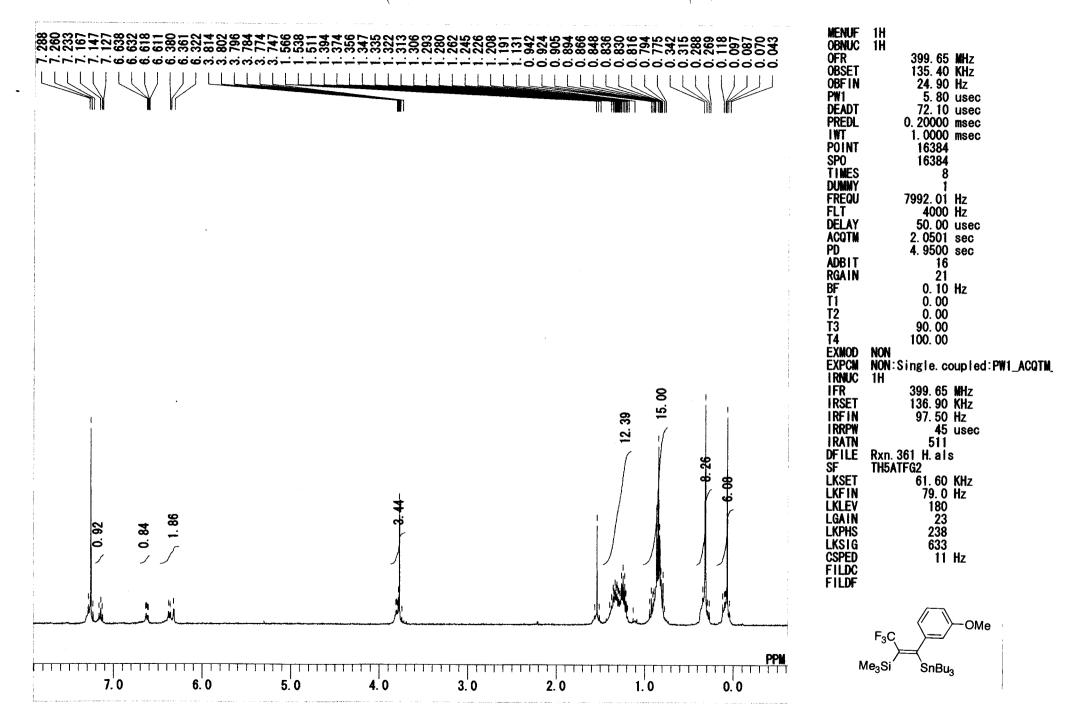
527.2001.

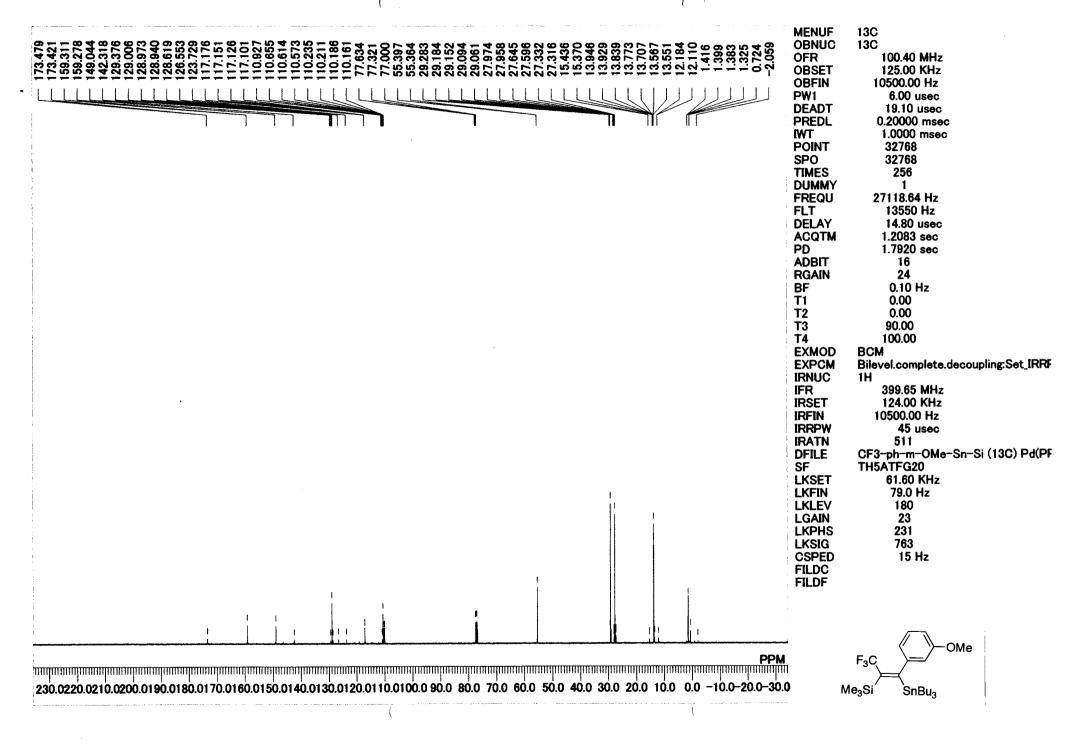
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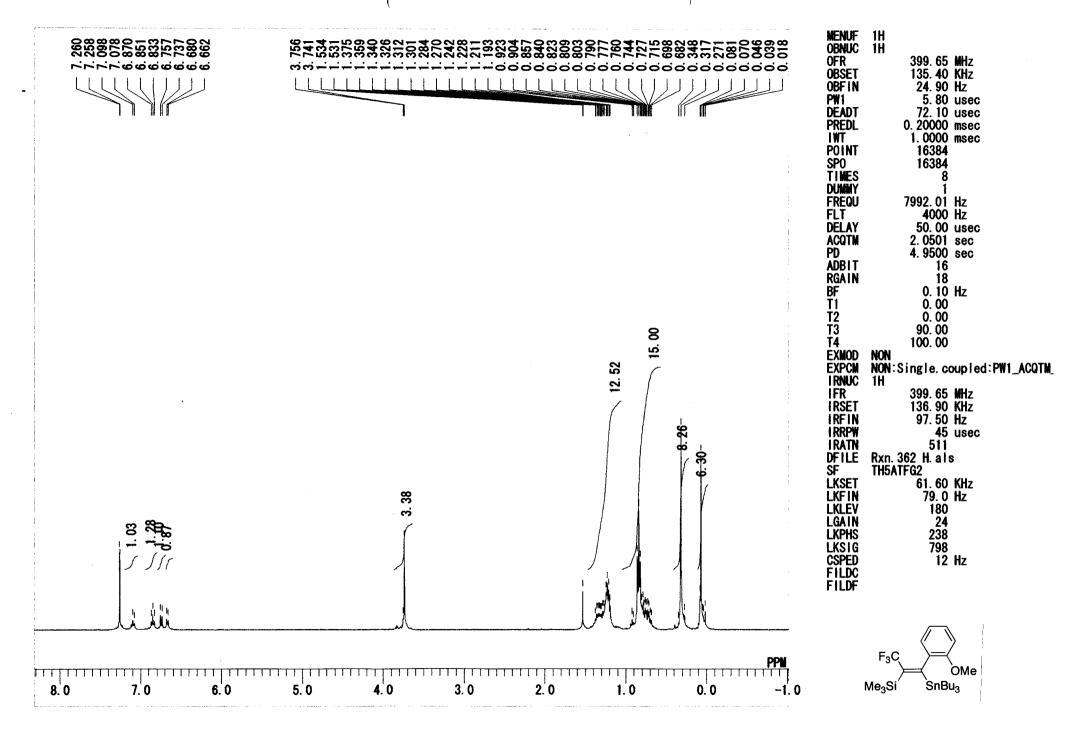


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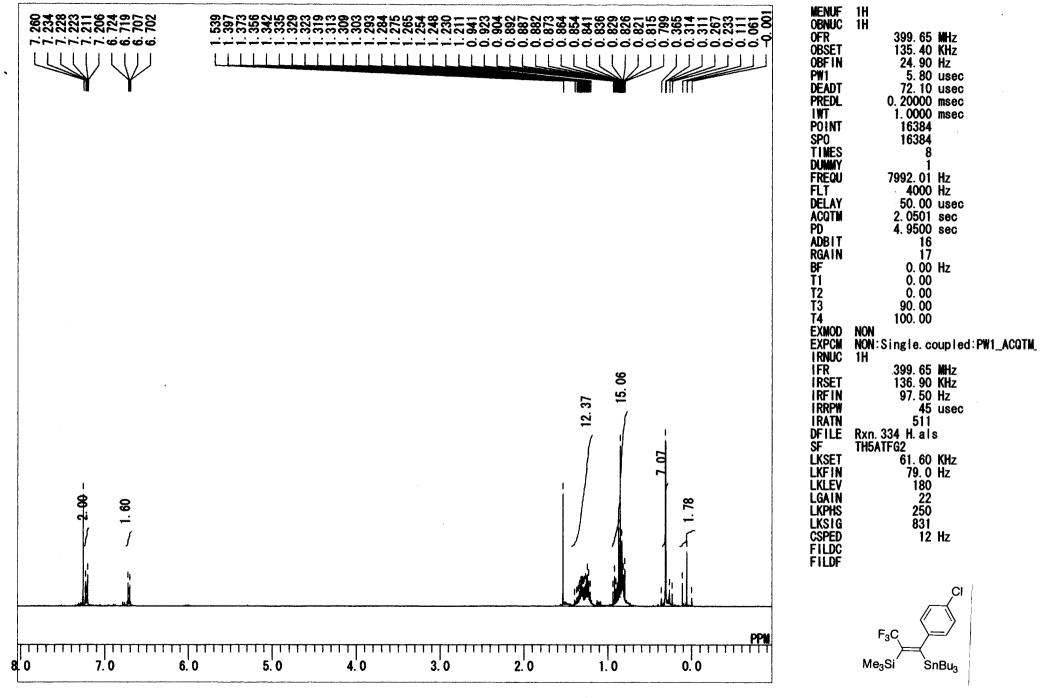




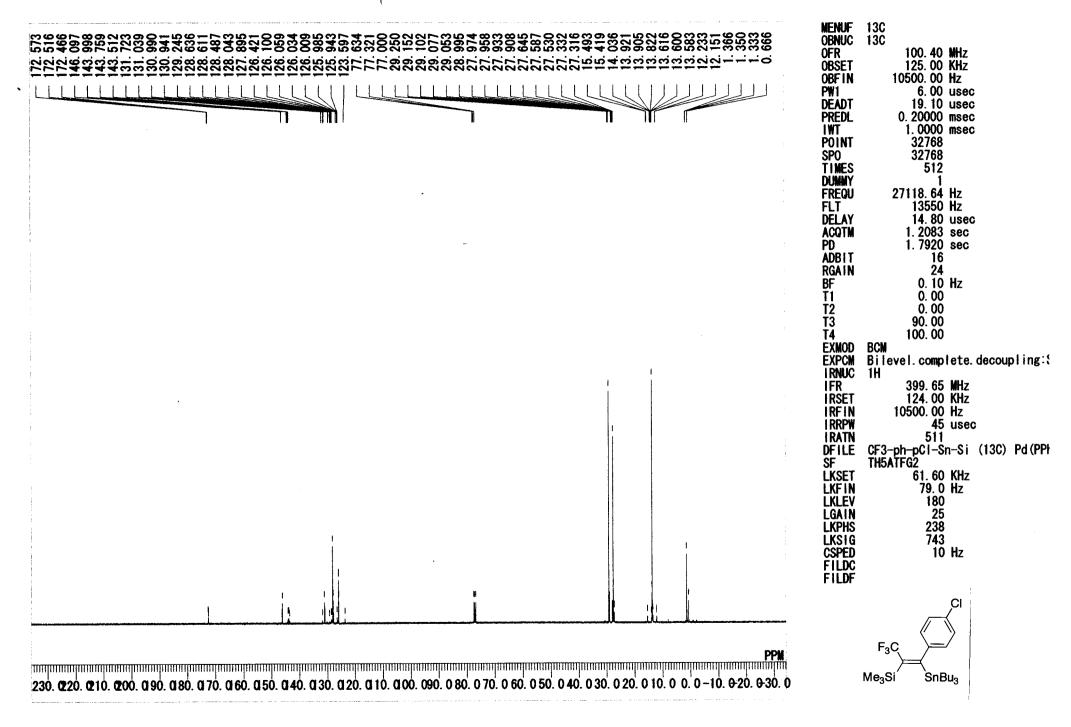


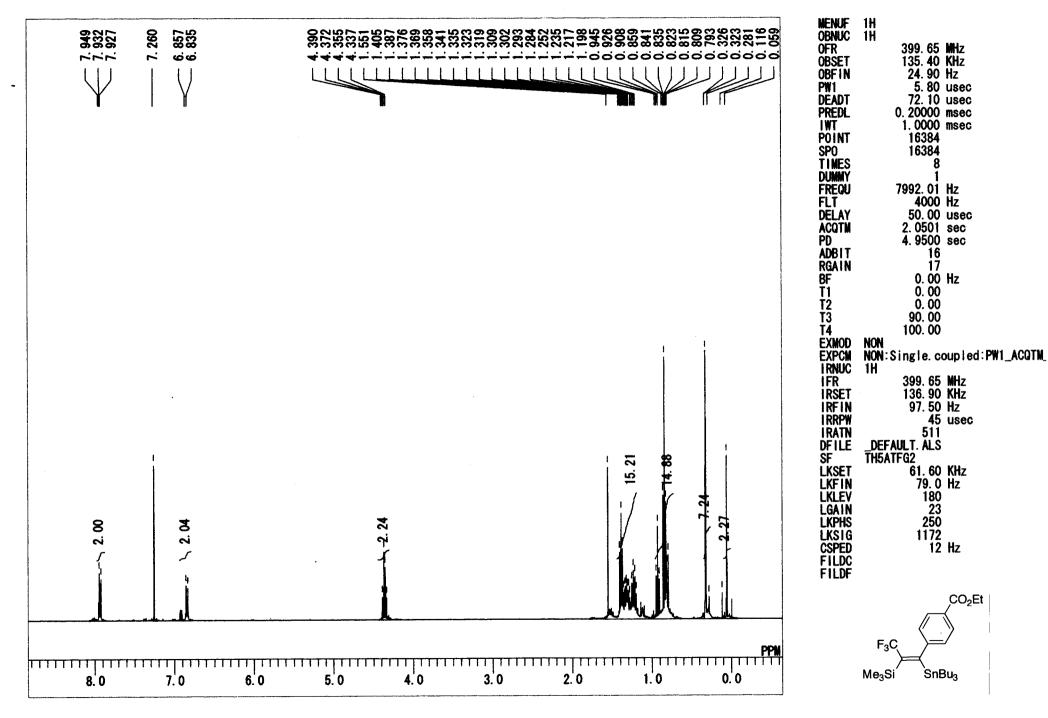
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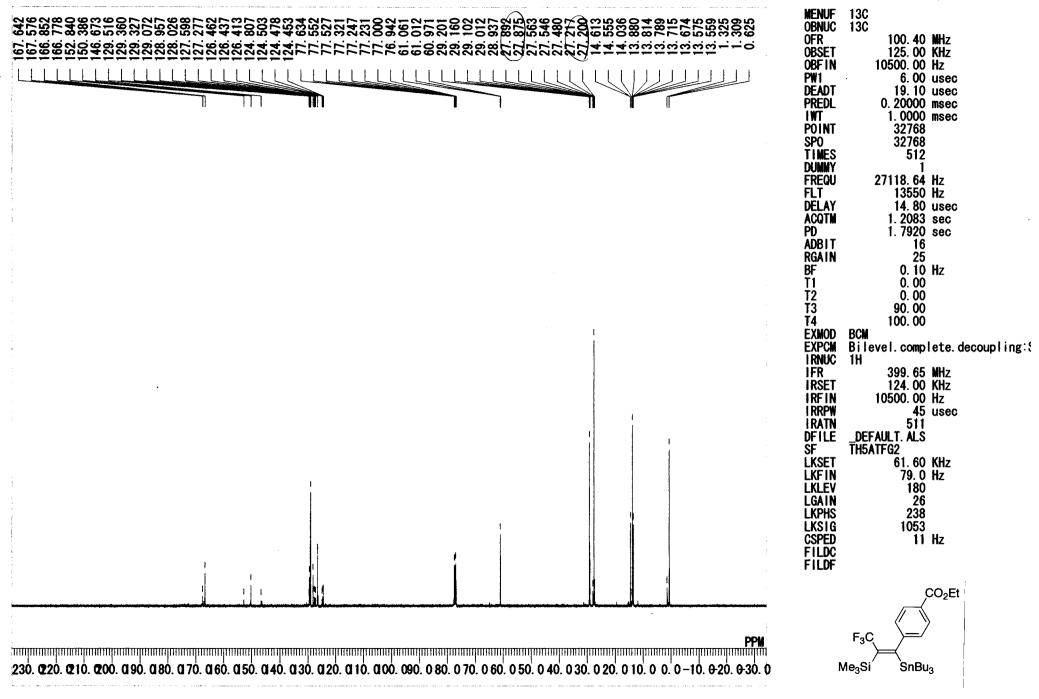
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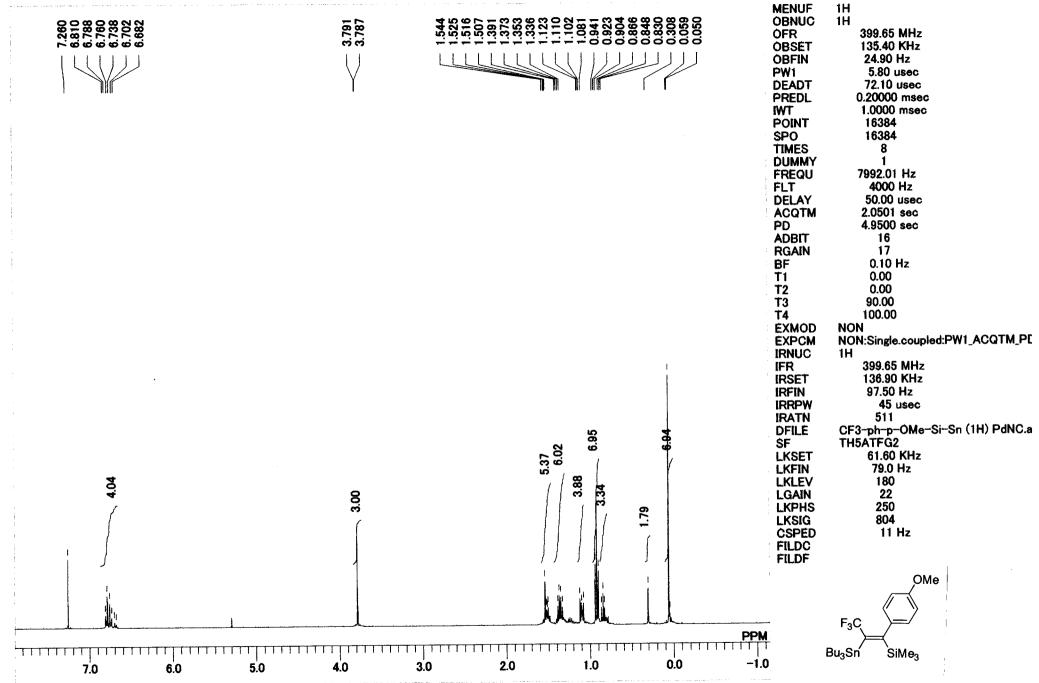
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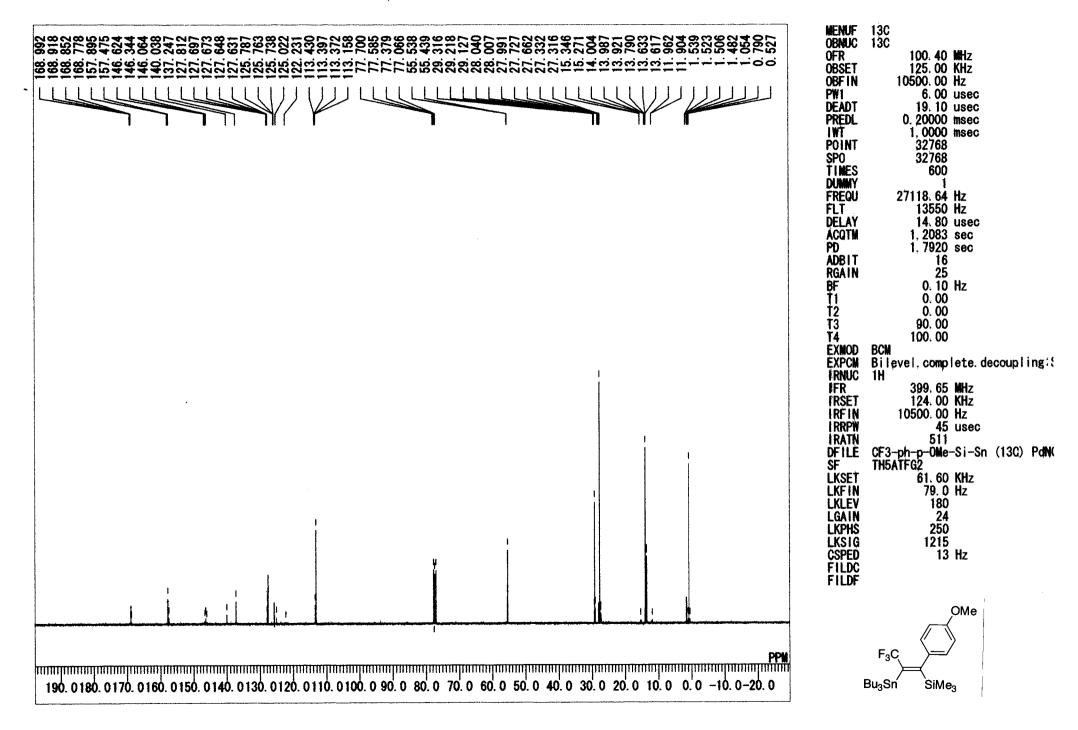
			MENUF OBNUC OFR OBSET OBFIN PW1 DEADT PREDL IWT POINT SPO TIMES DUMMY FREQU FLT DELAY ACQTM PD ADBIT RGAIN BF T1 T2 T3 T4 EXMOD EXPCM IRNUC IFR IRSET	1H 1H 1399.65 MHz 135.40 KHz 24.90 Hz 5.80 usec 72.10 usec 0.20000 msec 16384 16384 8 1 7992.01 Hz 4000 Hz 50.00 usec 2.0501 sec 4.9500 sec 16 19 0.10 Hz 0.00 0.00 90.00 100.00 NON NON:Single.coupled:PW1_ACQTM_PE 1H 399.65 MHz 136.90 KHz 97.50 Hz 45 usec 511 5.27 shita H CF3-Sn-Si-COOEt Pd(TH5ATFG2 61.60 KHz 79.0 Hz 180 24 238 884 13 Hz
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0	8.0 7.0 6.0	5.0 4.0 3.0		Bu ₃ Sn SiMe ₃

	NENUF 13C NENUF 100.40 M NENUF <	Hz Hz ec sec nsec isec isec ec ec ec
	IRNUC 1H IFR 399.65 M IRSET 124.00 K IRFIN 10500.00 IRRPW 45 us IRATN 511	Hz Hz ec CF3-Sn-Si-COOEt Pd(Hz
	F ₃ C C	D ₂ Et

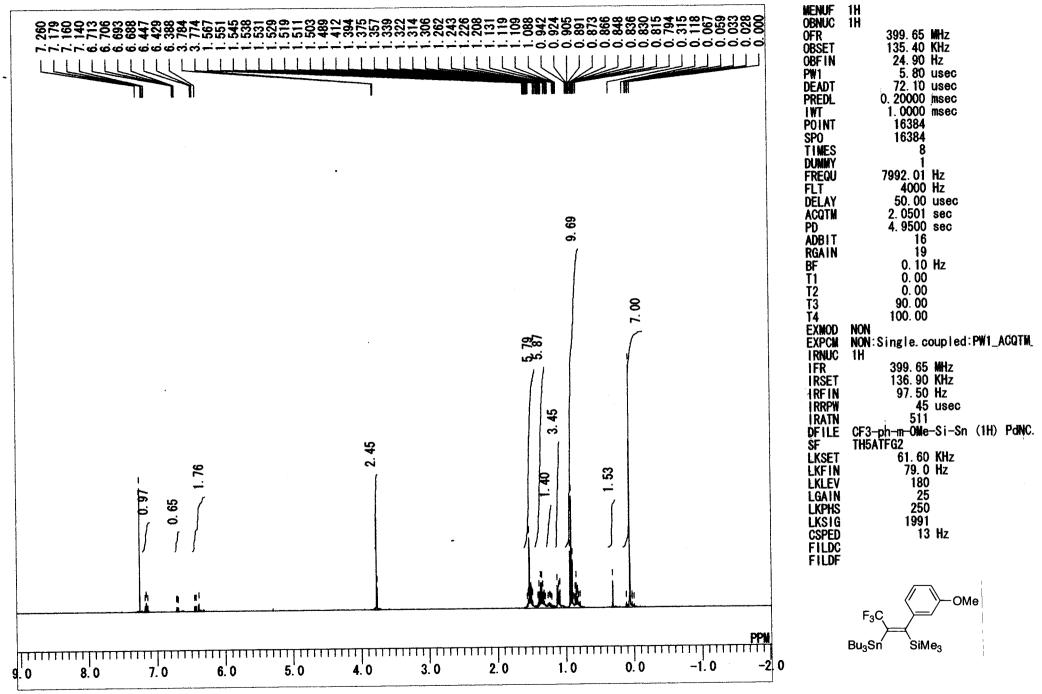
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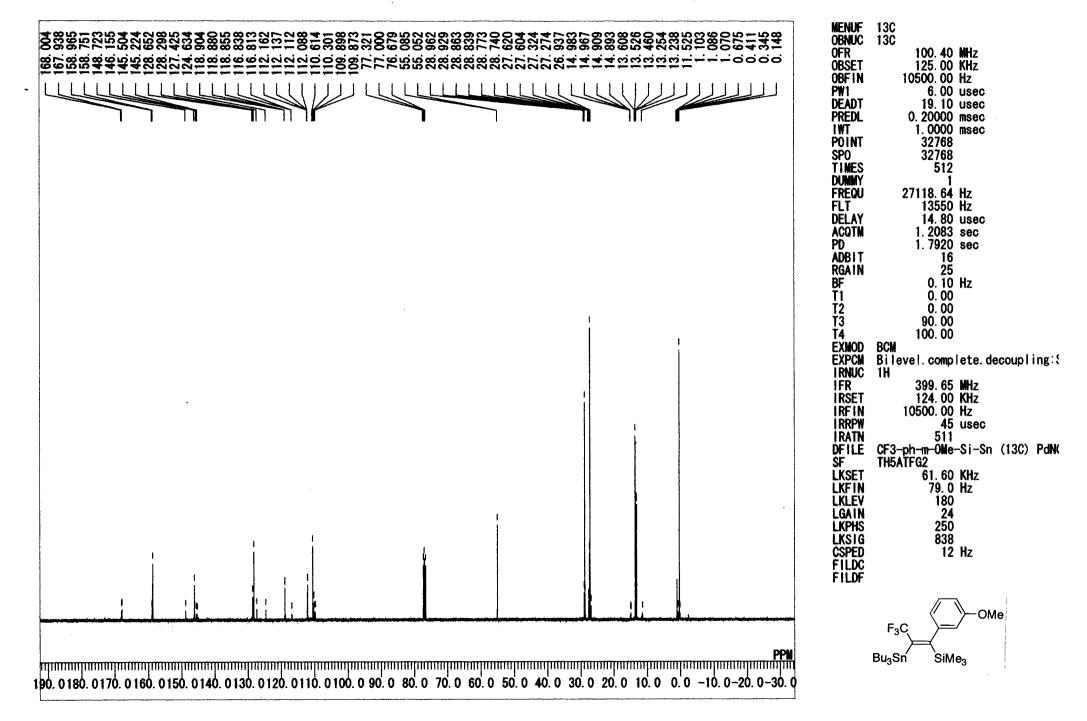


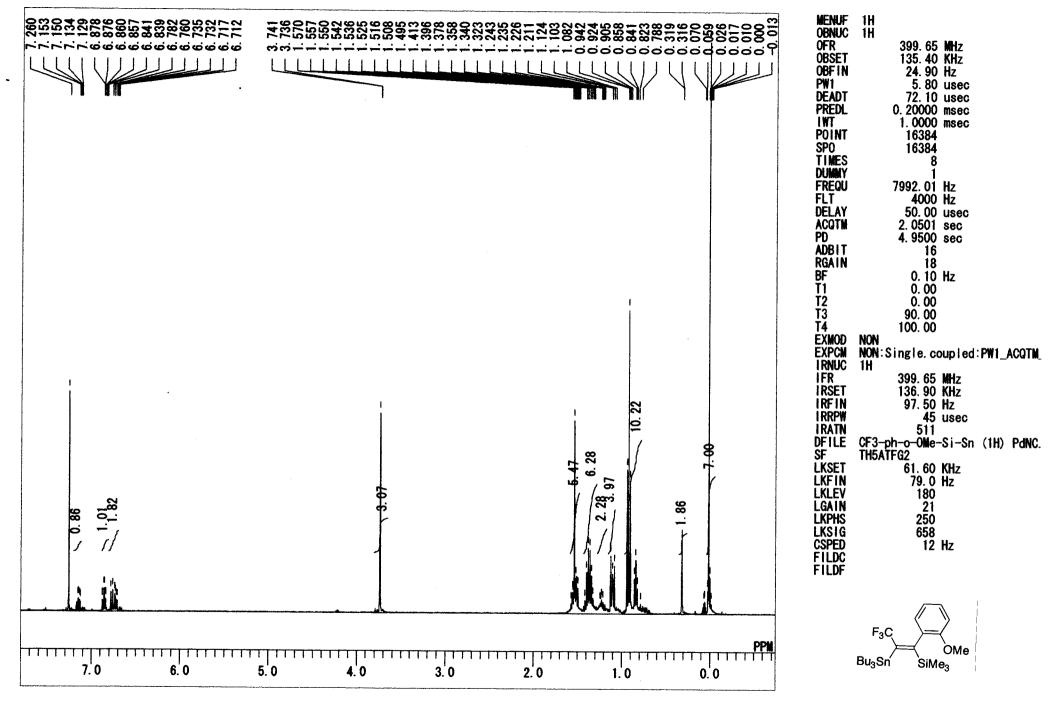




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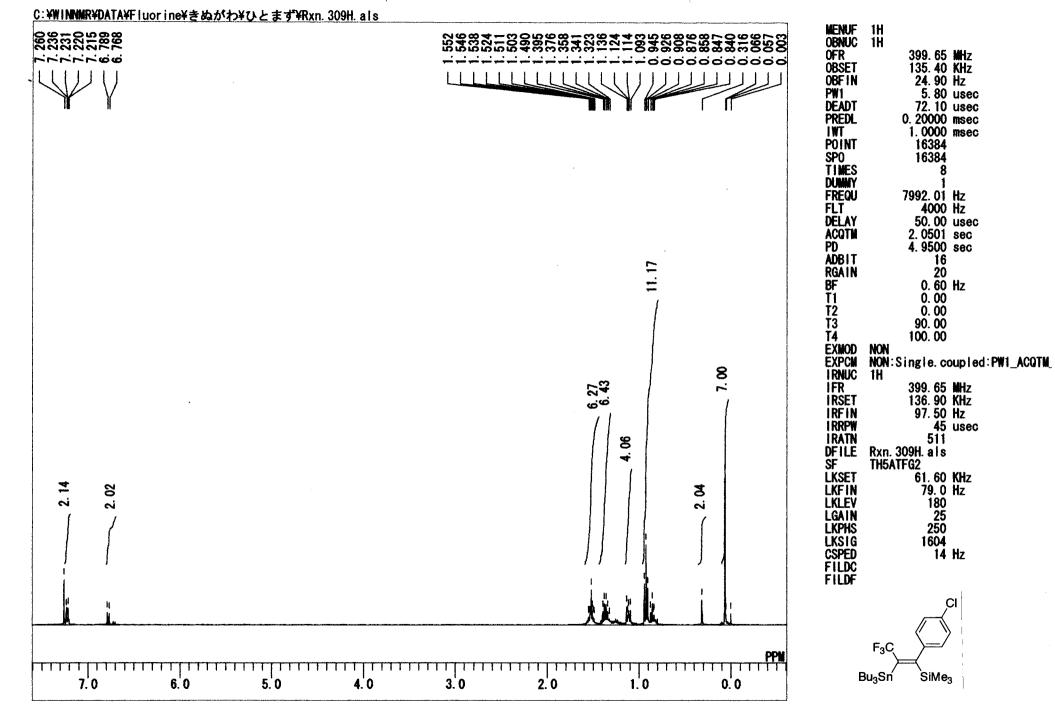
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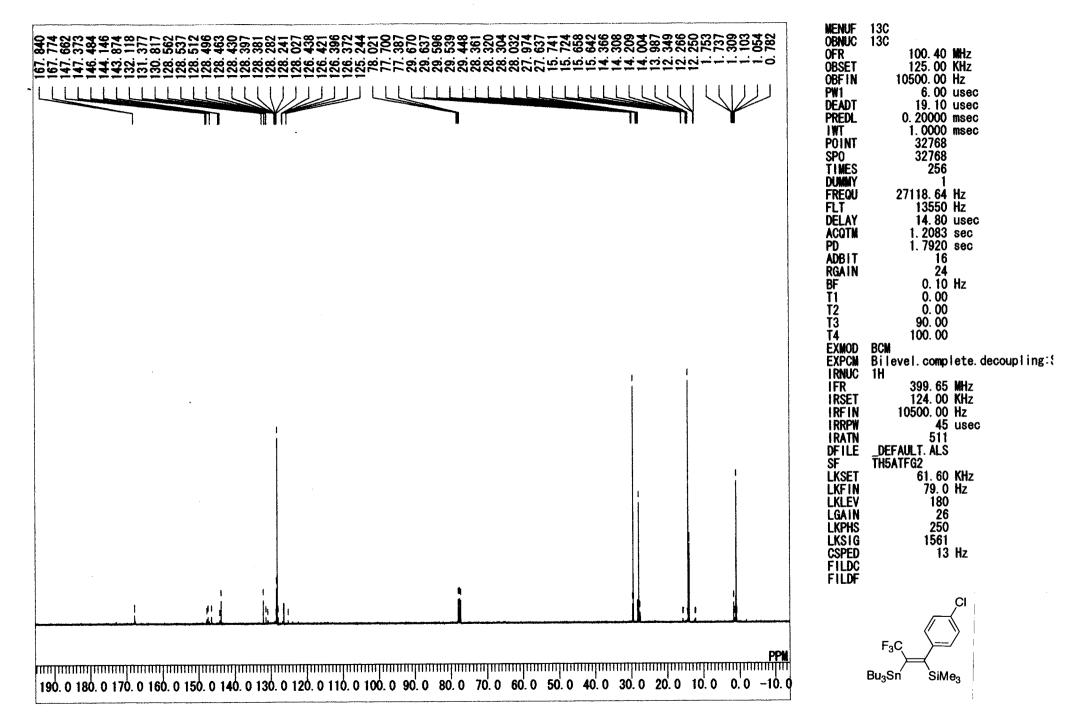
	124.774 124.733 124.733 124.733 124.733 123.507 123.507 109.593 112.779 109.593 109.593 109.593 109.546 109.546 17.321 77.600 54.661 54.661		OBSET OBFIN PW1 DEADT PREDL IWT POINT SPO TIMES DUMMY FREQU FLT DELAY ACQTM PD ADBIT RGAIN BF T1 T2	125.00 KHz 10500.00 Hz 6.20 usec 19.00 usec 0.20000 msec 32768 32768 20000 1 27118.64 Hz 13550 Hz 14.80 usec 1.2083 sec 1.7920 sec 16 24 0.10 Hz 0.00 0.00 0.00
			T3 T4 EXMOD EXPCM IRNUC IFR IRSET IRFIN IRRPW IRATN DFILE SF LKSET LKFIN LKLEV LGAIN LKPHS LKSIG CSPED FILDC FILDF	90.00 100.00 BCM Bilevel.complete.decoupling:Set_IRRI 1H 399.65 MHz 124.00 KHz 10500.00 Hz 45 usec 511 _DEFAULT.ALS TH5ATFG2 61.60 KHz 79.0 Hz 180 24 150 311 13 Hz
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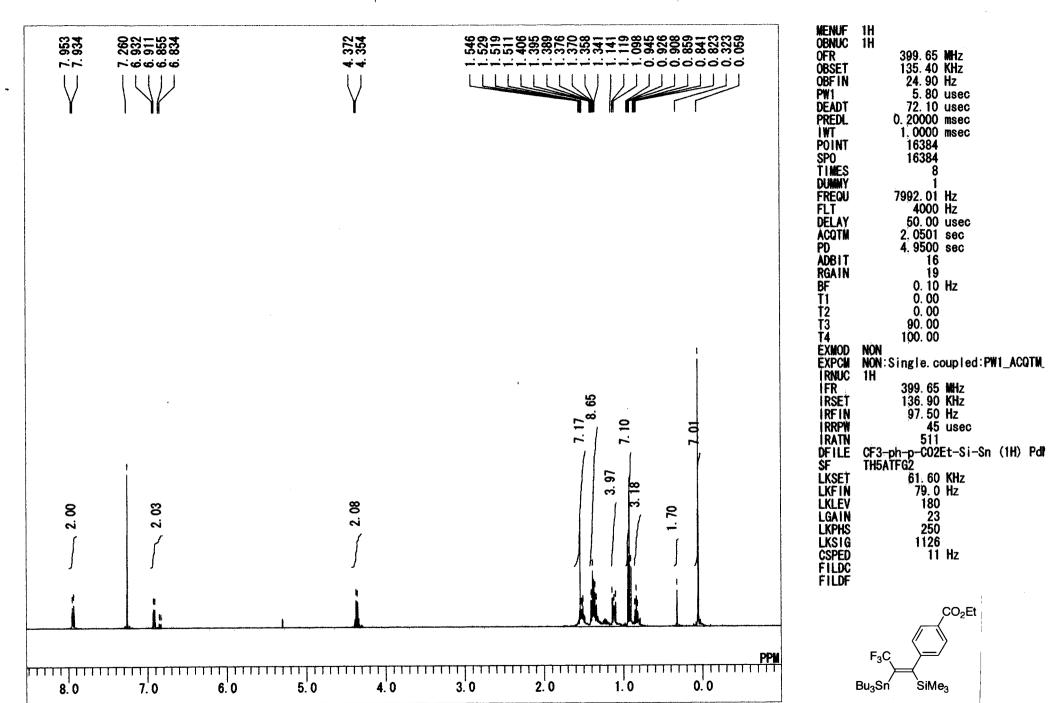
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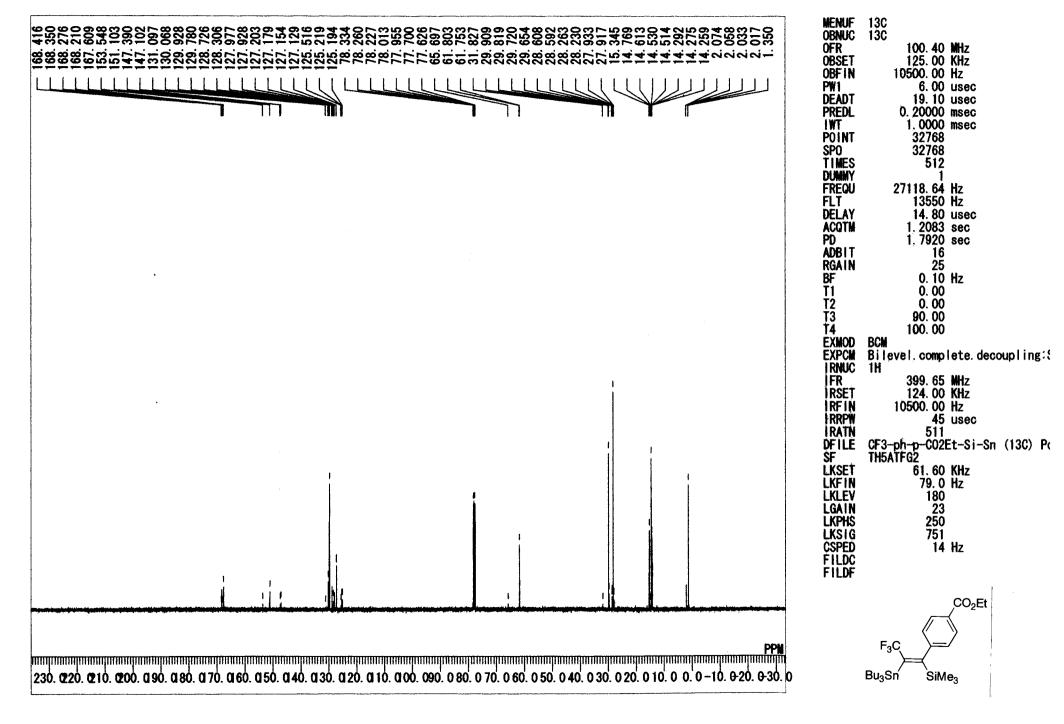
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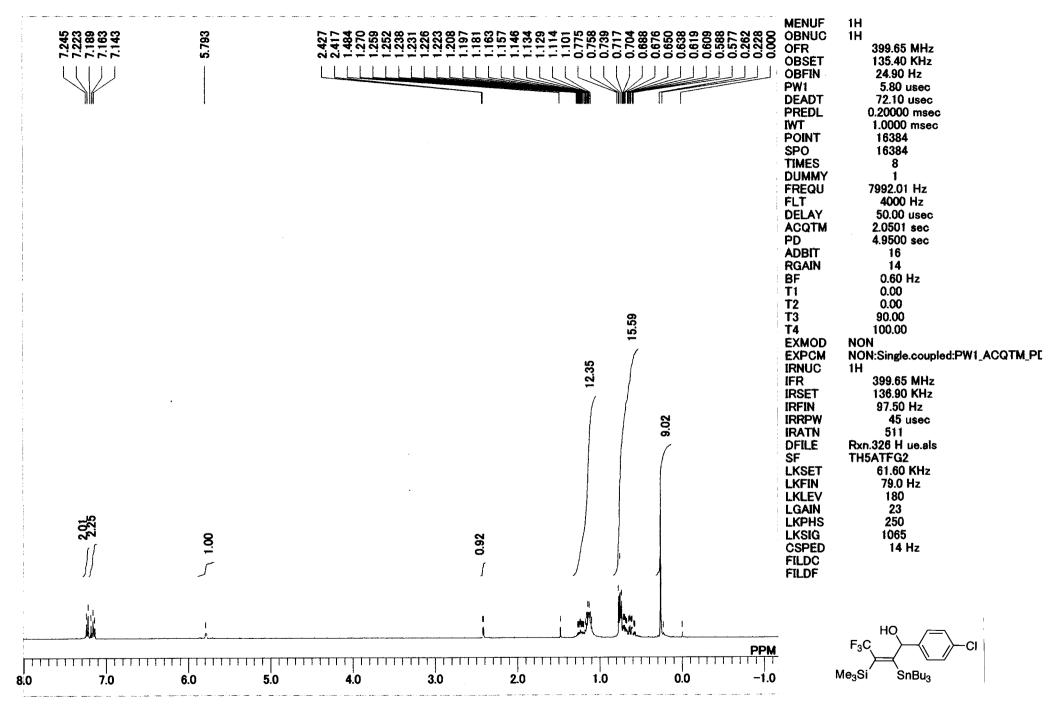
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry This journal is © The Royal Society of Chemistry 2013







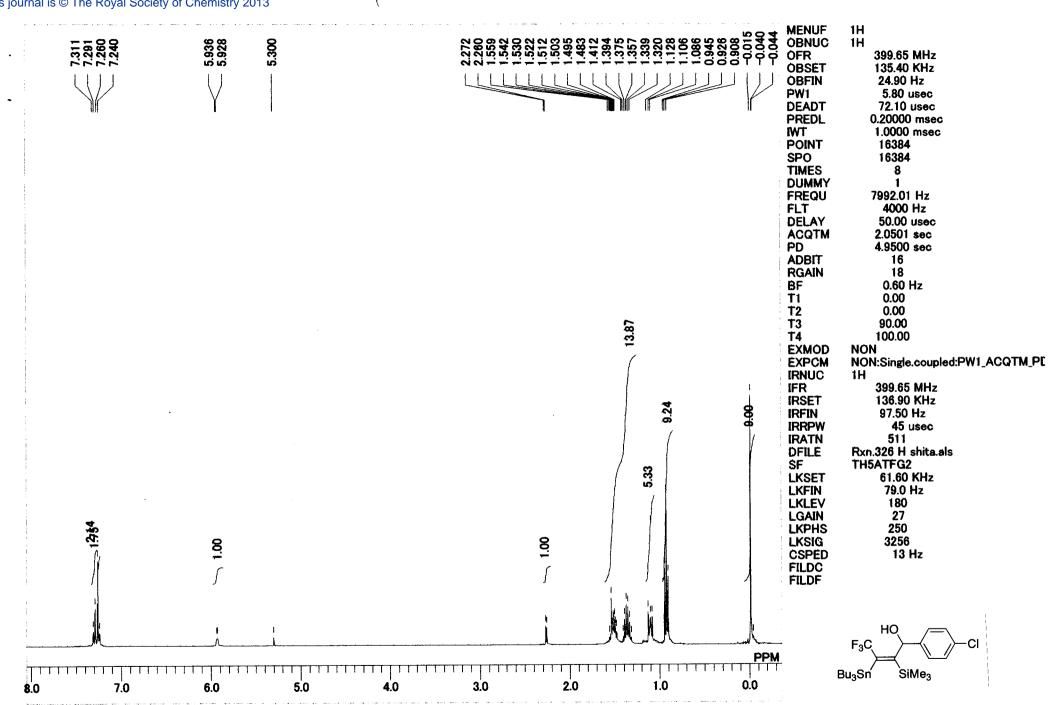




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	I I I I I I I I I I I I I I I I I I I		PW1 DEADT PREDL IWT POINT SPO TIMES DUMMY FREQU FLT DELAY ACQTM PD ADBIT RGAIN BF T1 T2	6.00 usec 19.10 usec 0.20000 msec 1.0000 msec 32768 32768 256 1 27118.64 Hz 13550 Hz 14.80 usec 1.2083 sec 1.7920 sec 16 23 0.10 Hz 0.00 0.00
			T3 T4 EXMOD EXPCM IRNUC IFR IRSET IRFIN IRRPW IRATN DFILE SF LKSET LKFIN LKLEV LGAIN LKPHS LKSIG CSPED FILDC FILDF	90.00 100.00 BCM Bilevel.complete.decoupling:Set 1H 399.65 MHz 124.00 KHz 10500.00 Hz 45 usec 511 CF3-ph-p-CI-OH-Si-Sn ue.als TH5ATFG20 61.60 KHz 79.0 Hz 180 25 231 971 13 Hz

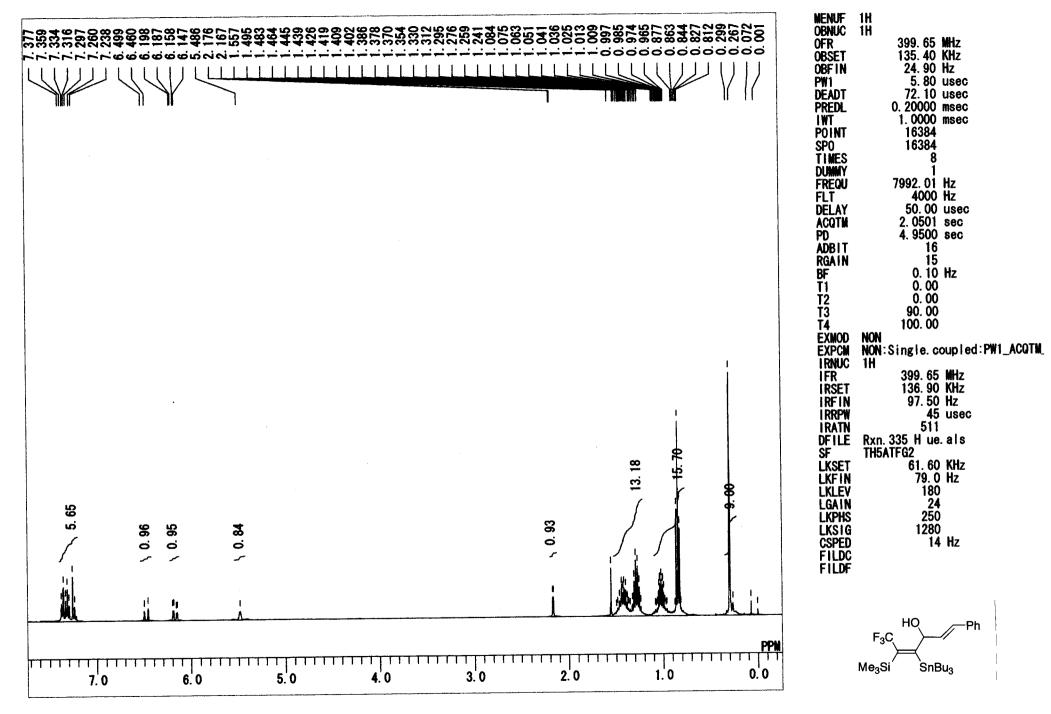
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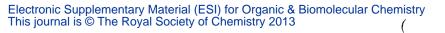


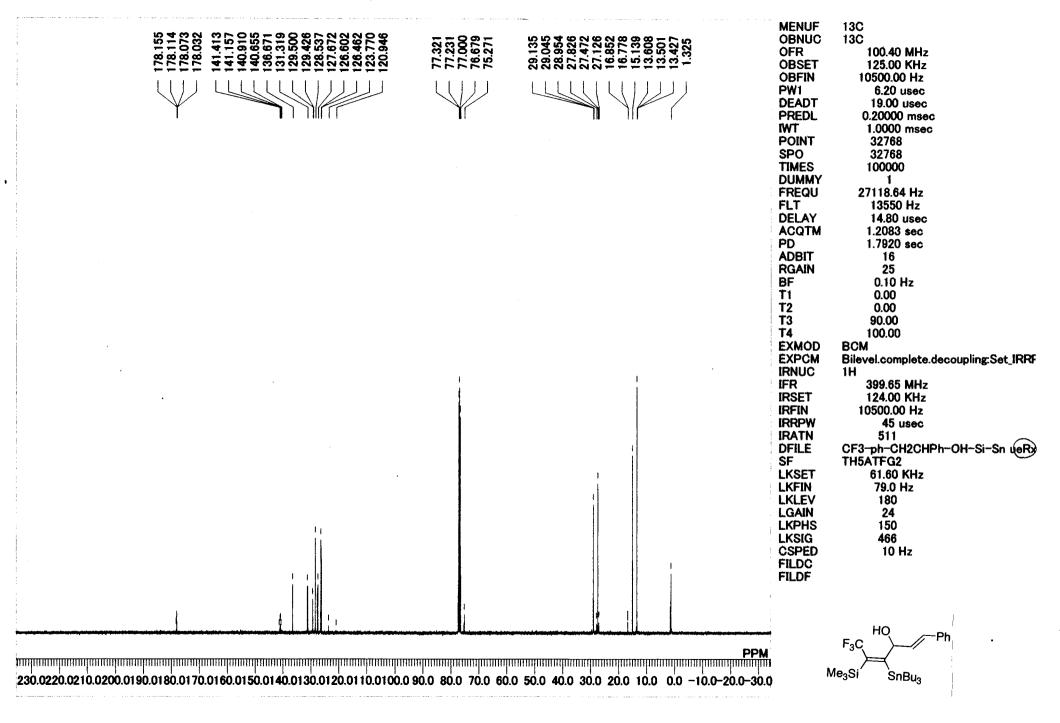
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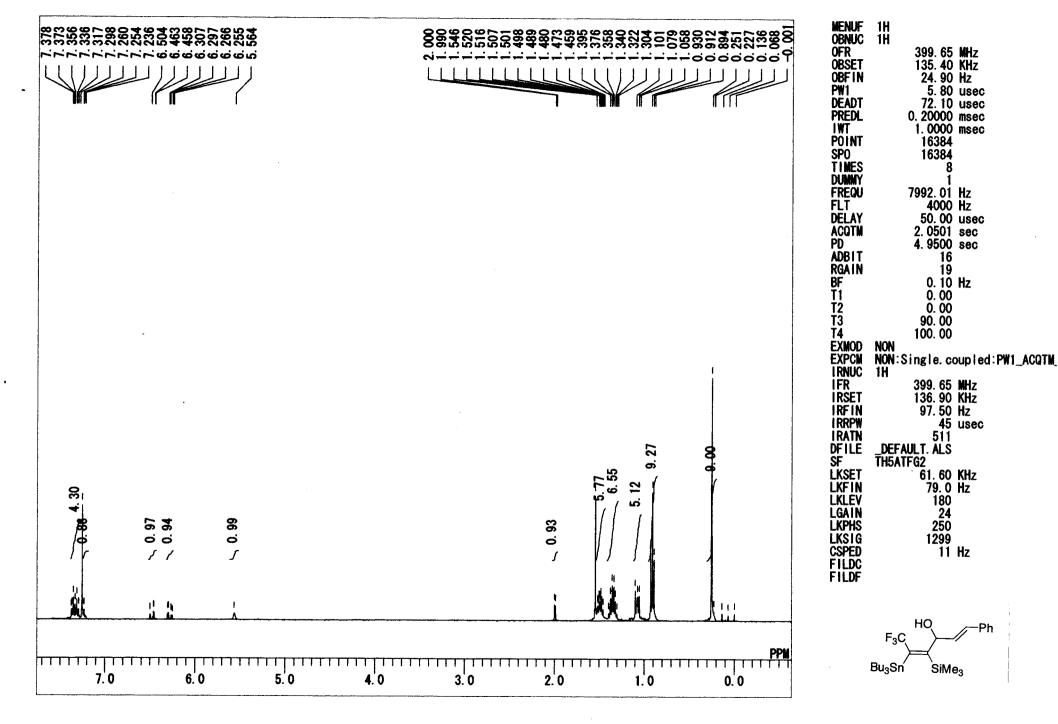
			OBFIN PW1 DEADT PREDL IWT POINT SPO TIMES DUMMY FREQU FLT DELAY ACQTM PD ADBIT RGAIN BF T1 T2 T3 T4	10500.00 Hz 6.00 usec 19.10 usec 0.20000 msec 32768 32768 256 1 27118.64 Hz 13550 Hz 14.80 usec 1.2083 sec 1.7920 sec 16 22 0.10 Hz 0.00 0.00 90.00 100.00
			EXMOD EXPCM IRNUC IFR IRSET IRFIN IRRPW IRATN DFILE SF LKSET LKSET LKFIN LKLEV LGAIN LKPHS LKSIG CSPED FILDC FILDF	BCM Bilevel.complete.decoupling: 1H 399.65 MHz 124.00 KHz 10500.00 Hz 45 usec 511 _DEFAULT.ALS TH5ATFG20 61.60 KHz 79.0 Hz 180 24 231 605 10 Hz
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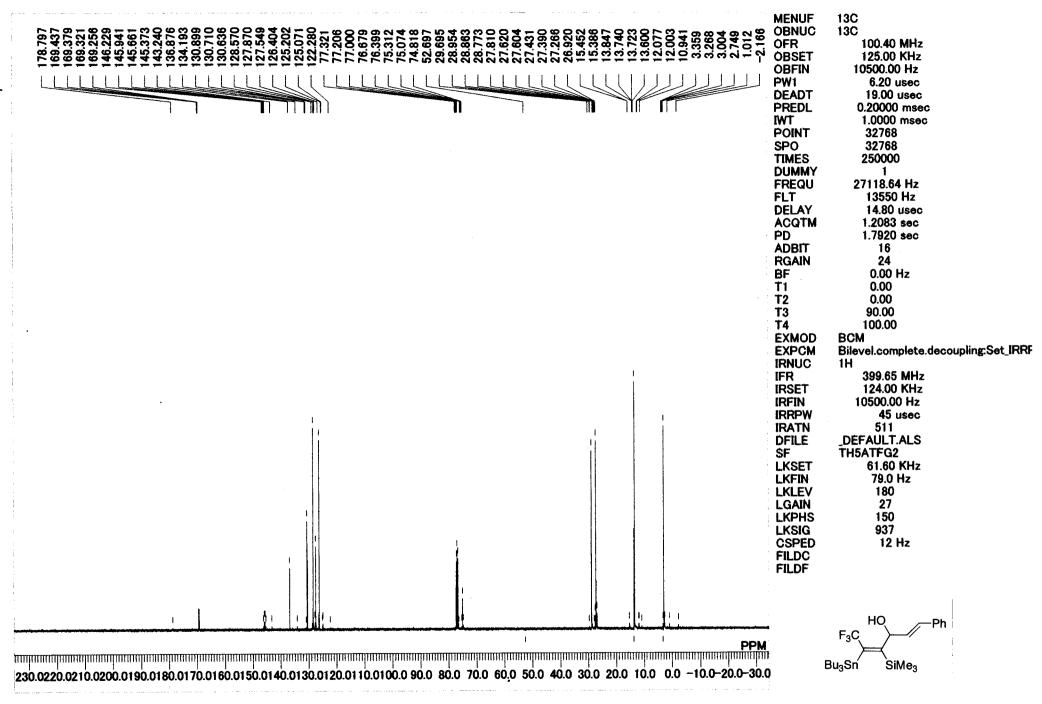
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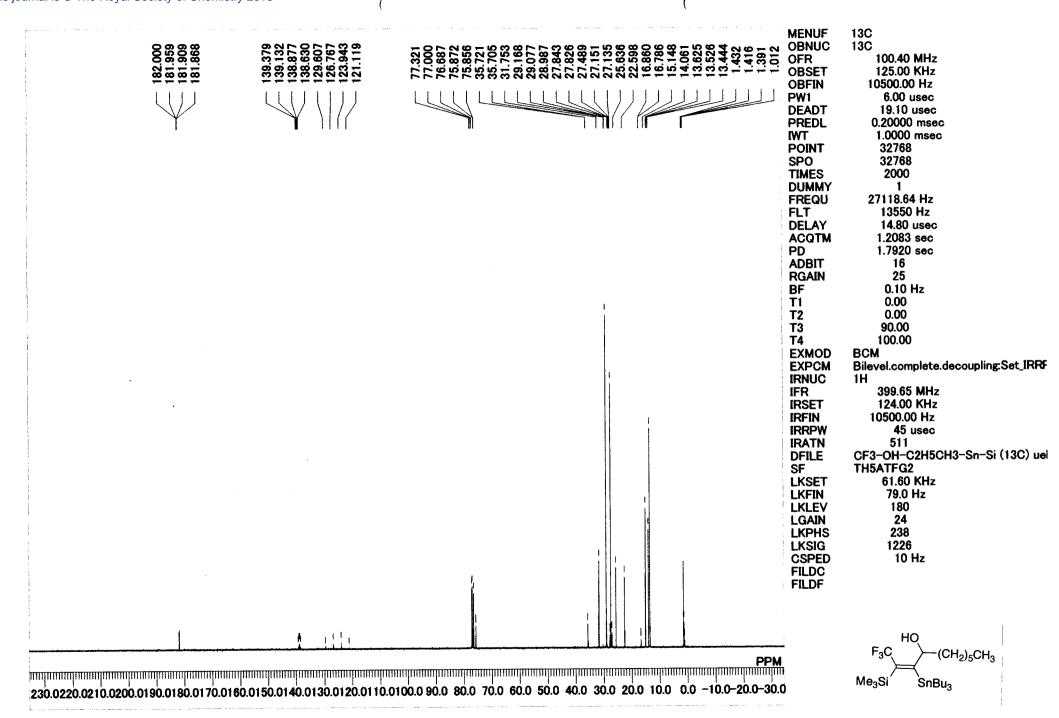




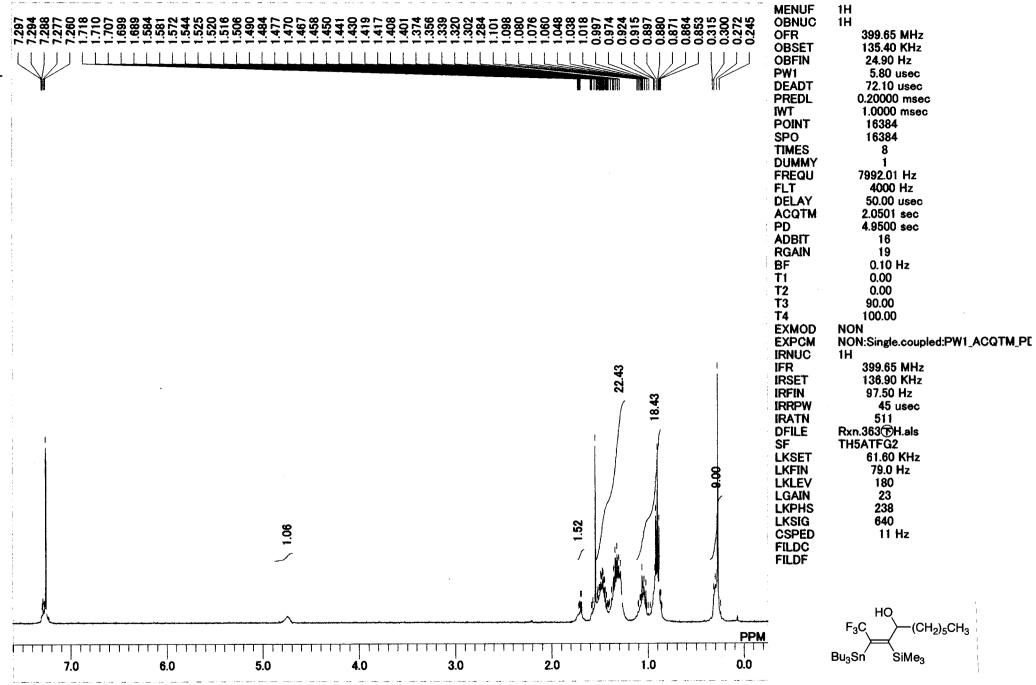




	MENUF OBNUC OFR OBSET OBFIN PW1 DEADT PREDL IWT POINT SPO TIMES DUMMY FREQU FLT DELAY ACQTM PD ADBIT RGAIN BF T1 T2 T3 T4 EXMOD EXPCM IRNUC IFR IRSET IRFIN IRRPW IRATN DFILE SF LKSET LKSET LKSET	1H 1H 399.65 MHz 135.40 KHz 24.90 Hz 5.80 usec 72.10 usec 0.20000 msec 1.0000 msec 16384 16384 8 1 7992.01 Hz 4000 Hz 50.00 usec 2.0501 sec 4.9500 sec 16 19 0.10 Hz 0.00 90.00 100.00 NON NON:Single.coupled:PW1_ACQTM_PC 1H 399.65 MHz 136.90 KHz 97.50 Hz 45 usec 511 Rxn.363 @H.als TH5ATFG2 61.60 KHz 79.0 Hz 180
160	LKLEV LGAIN LKPHS LKSIG CSPED FILDC FILDF	180 24 238 807 13 Hz
PPI 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0	Mi T	$\begin{array}{c} HO \\ F_3C \\ HO \\ HO \\ HO \\ HO \\ Si \\ SnBu_3 \\ \end{array}$

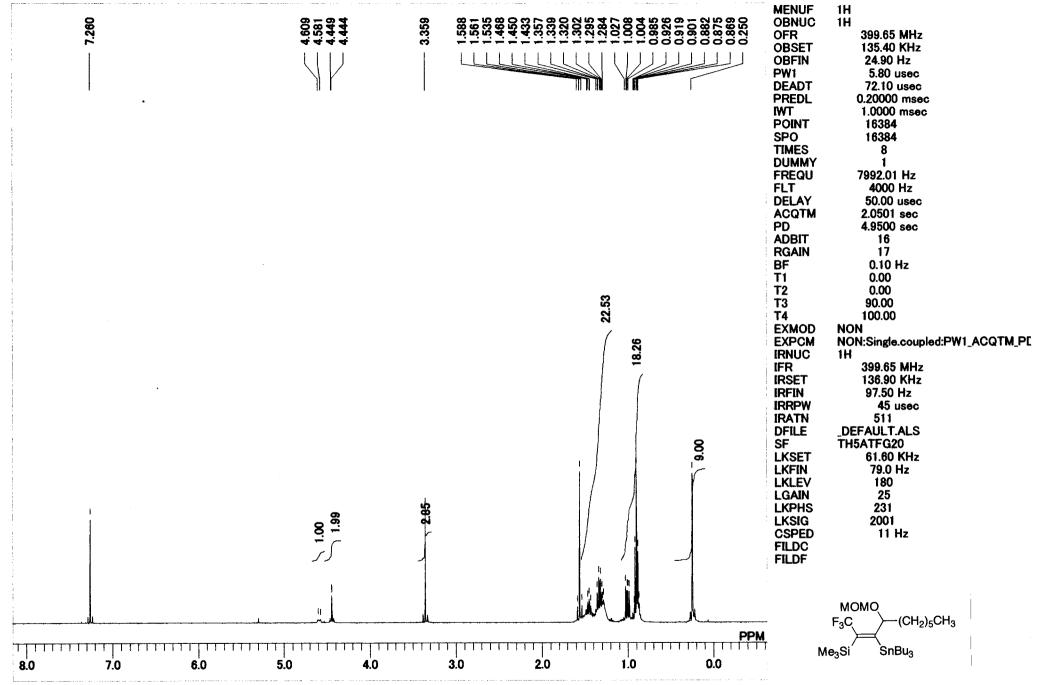


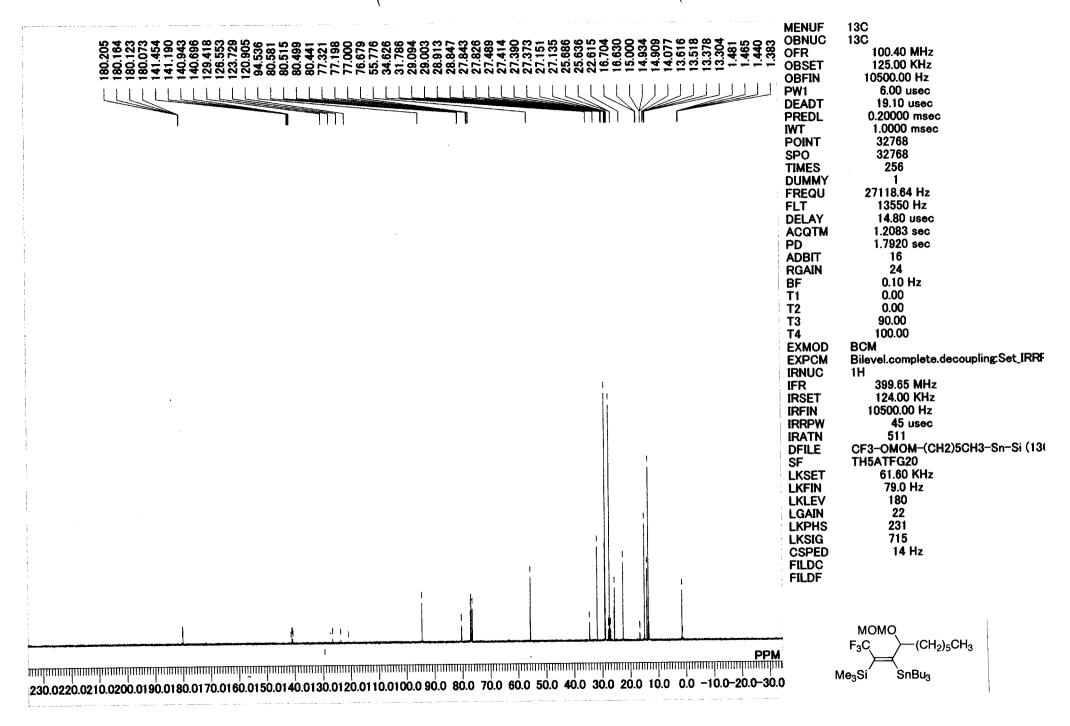
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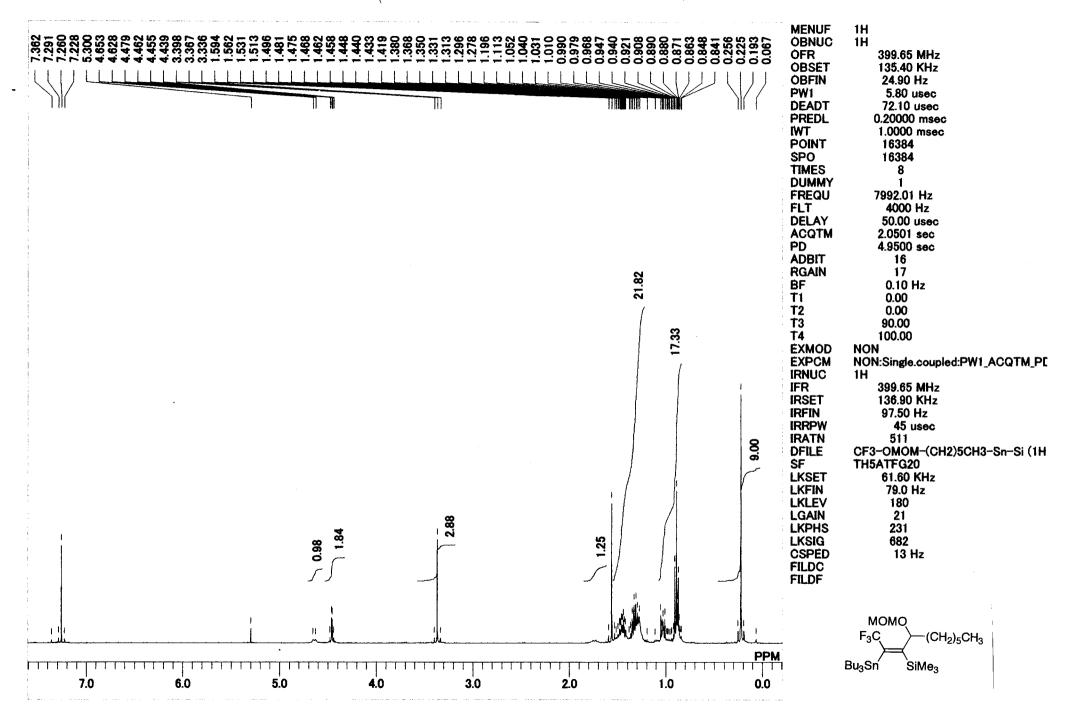


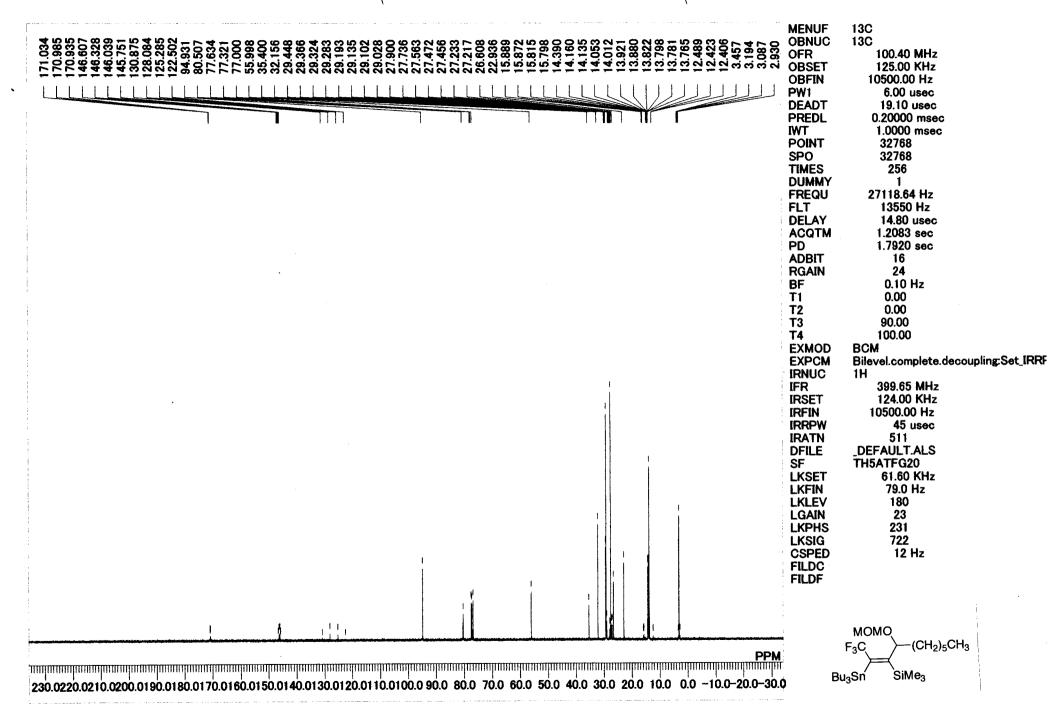
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		OBFIN PW1 DEADT PREDL IWT POINT SPO TIMES DUMMY FREQU FLT DELAY ACQTM PD ADBIT RGAIN BF	10500.00 Hz 6.00 usec 19.10 usec 0.20000 msec 32768 32768 20000 1 27118.64 Hz 13550 Hz 14.80 usec 1.2083 sec 1.7920 sec 16 24 0.10 Hz
		T1 T2 T3 T4 EXMOD EXPCM IRNUC IFR IRSET IRFIN IRFIN IRATN DFILE SF LKSET LKSET LKFIN LKLEV LGAIN LKPHS LKSIG CSPED FILDC FILDF	0.00 0.00 90.00 100.00 BCM Bilevel.complete.decoupling:Set_IRF 1H 399.65 MHz 124.00 KHz 10500.00 Hz 45 usec 511 _DEFAULT.ALS TH5ATFG2 61.60 KHz 79.0 Hz 180 23 238 1022 12 Hz
			HO F₃C、









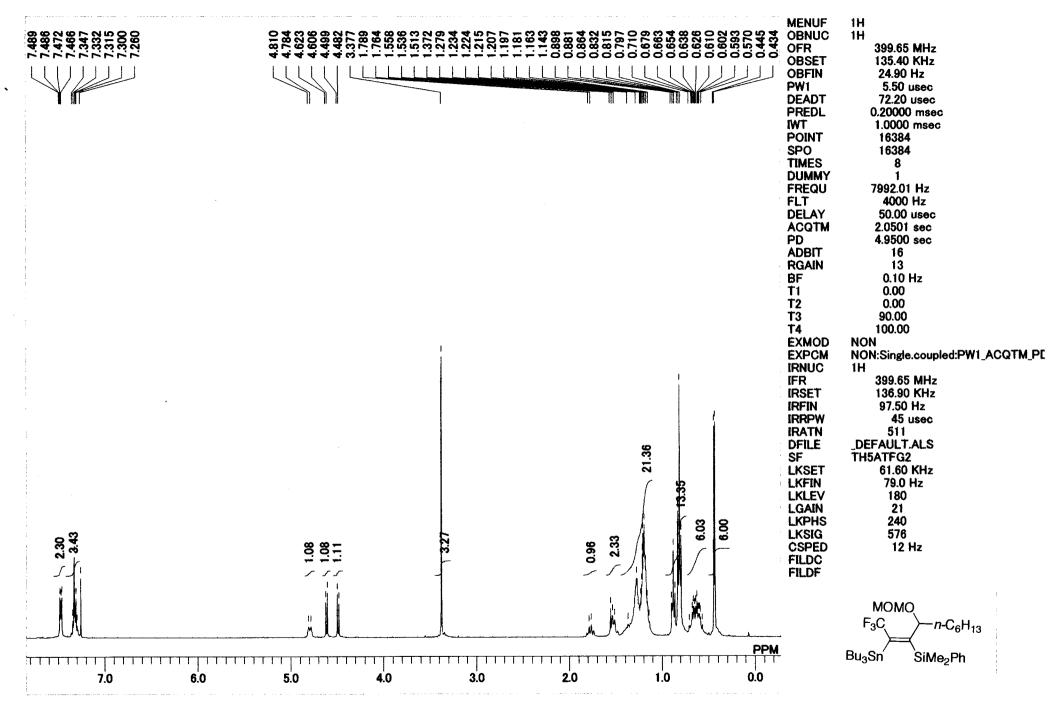
			OBSEI OBFIN PW1 DEADT PREDL IWT POINT SPO TIMES DUMMY FREQU FLT DELAY ACQTM PD ADBIT RGAIN BF T1 T2 T3 T4 EXMOD EXPCM	1H 1H 399.65 MHz 135.40 KHz 24.90 Hz 5.50 usec 72.20 usec 0.20000 msec 1.0000 msec 16384 16384 8 1 7992.01 Hz 4000 Hz 50.00 usec 2.0501 sec 4.9500 sec 16 12 0.10 Hz 0.00 90.00 100.00 NON NON NON:Single.coupled:PW1_ACQTM_PE
 0.69	2.87	2327	IRNUC IFR IRSET IRFIN IRRPW IRATN DFILE SF LKSET LKSET LKFIN LKLEV LGAIN LKPHS LKSIG CSPED FILDF	1H 399.65 MHz 136.90 KHz 97.50 Hz 45 usec 511 DEFAULT.ALS TH5ATFG2 61.60 KHz 79.0 Hz 180 22 240 743 14 Hz MOMO $F_{3}C$ $n-C_{6}H_{13}$

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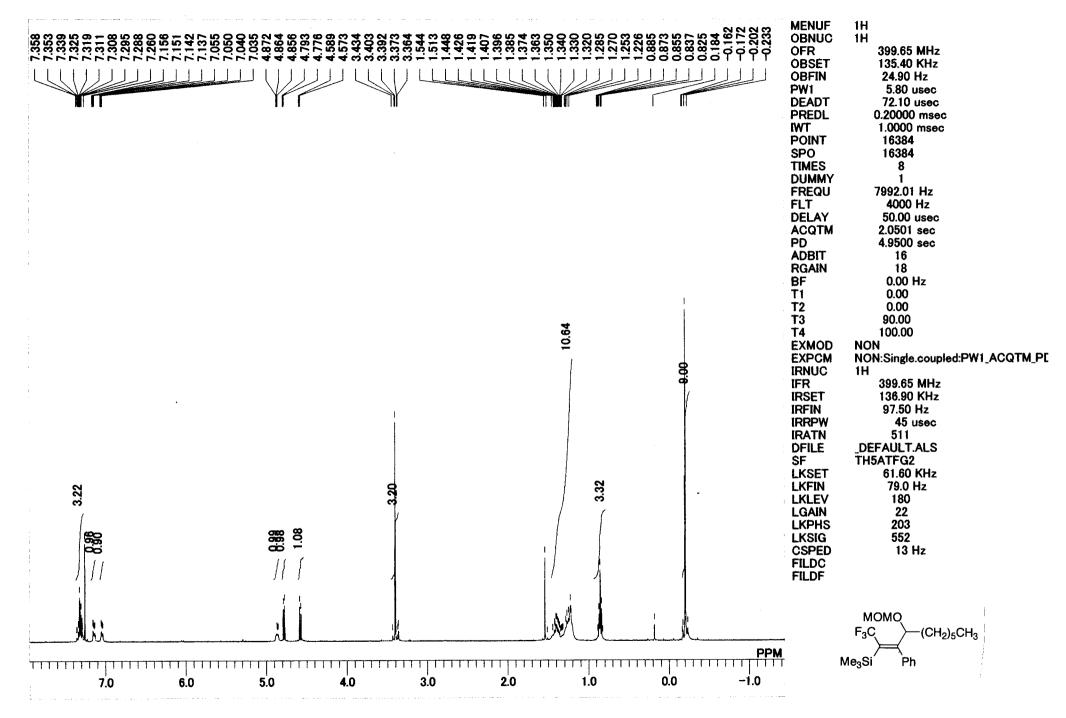
SF TH5ATFG2 LKSET 61.60 KHz LKFIN 79.0 Hz LKLEV 180 LGAIN 22 LKPHS 240 LKSIG 578 CSPED 13 Hz FILDF	ng:Set_IRRF
$\frac{1}{PPM}$	13

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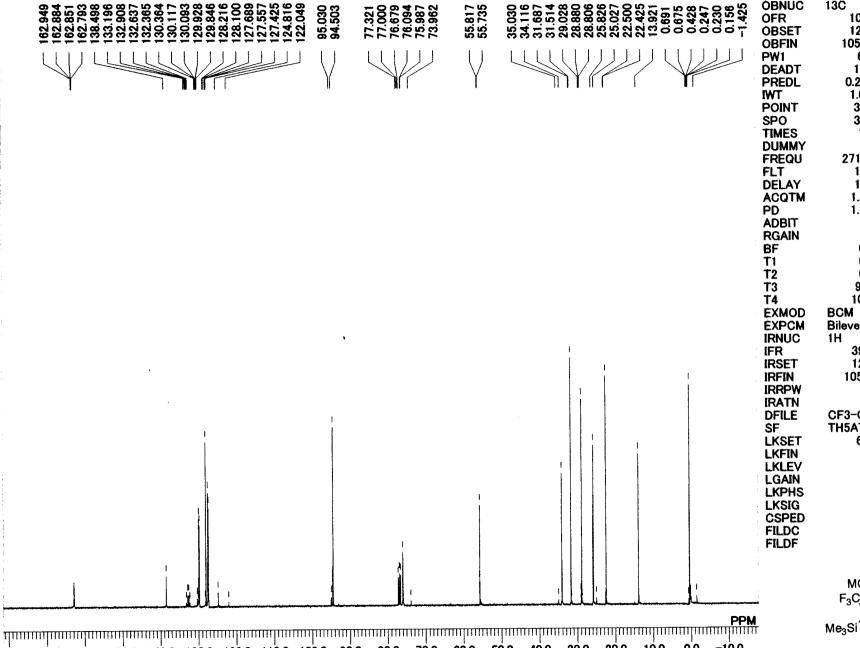
167.173	167.057	148.740 139.437 134.892 134.151	130.537	127.730	94.709	80.112	28.080 28.040 28.646 28.656 21.505 21.150 20.805 20.805	26.163	13.493	OBNUC OFR OBSET OBFIN PW1 DEADT PREDL IWT POINT SPO TIMES DUMMY FREQU FLT DELAY ACQTM PD ADBIT RGAIN BF T1 T2 T3 T3 T4	100.40 MHz 125.00 KHz 10500.00 Hz 6.20 usec 19.00 usec 0.20000 msec 1.0000 msec 32768 32768 32768 10000 1 27118.64 Hz 13550 Hz 14.80 usec 1.2083 sec 1.7920 sec 16 25 0.10 Hz 0.00 0.00 90.00 100.00	
										EXMOD EXPCM IRNUC IFR IRSET IRFIN IRRPW IRATN DFILE SF LKSET LKSET LKSET LKFIN LKLEV LGAIN LKPHS LKSIG CSPED FILDC FILDF	BCM Bilevel.complete.decoupling: 1H 399.65 MHz 124.00 KHz 10500.00 Hz 45 usec 511 CF3-OMOM-(CH2)5CH3-B TH5ATFG2 61.60 KHz 79.0 Hz 180 24 240 673 13 Hz	
		1			1						MOMO	



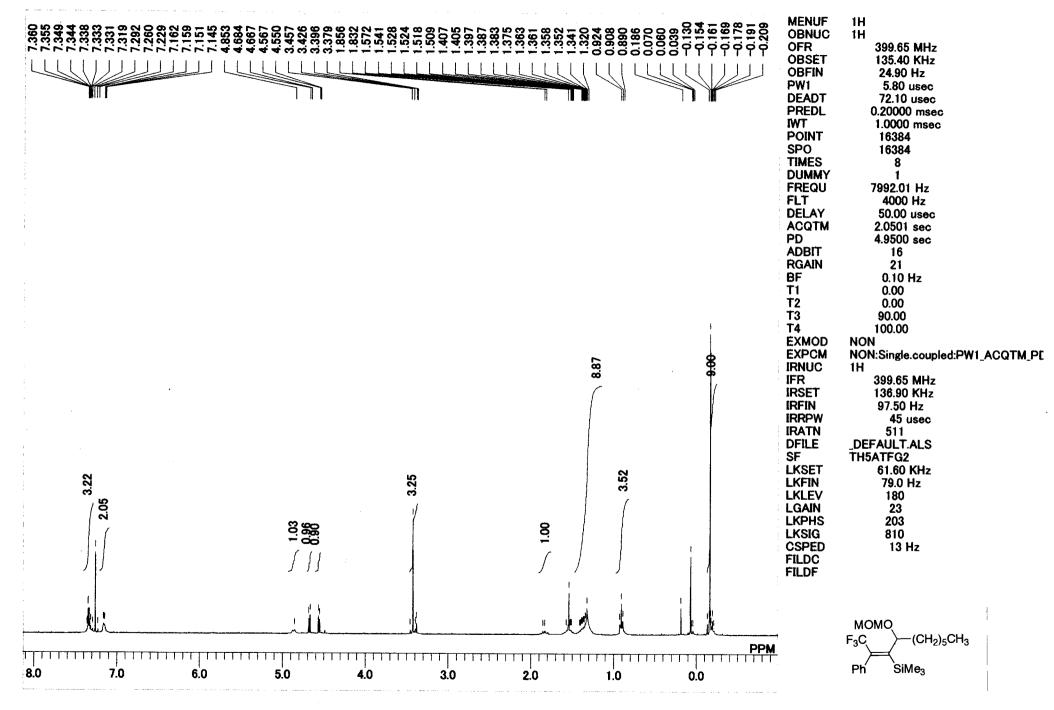


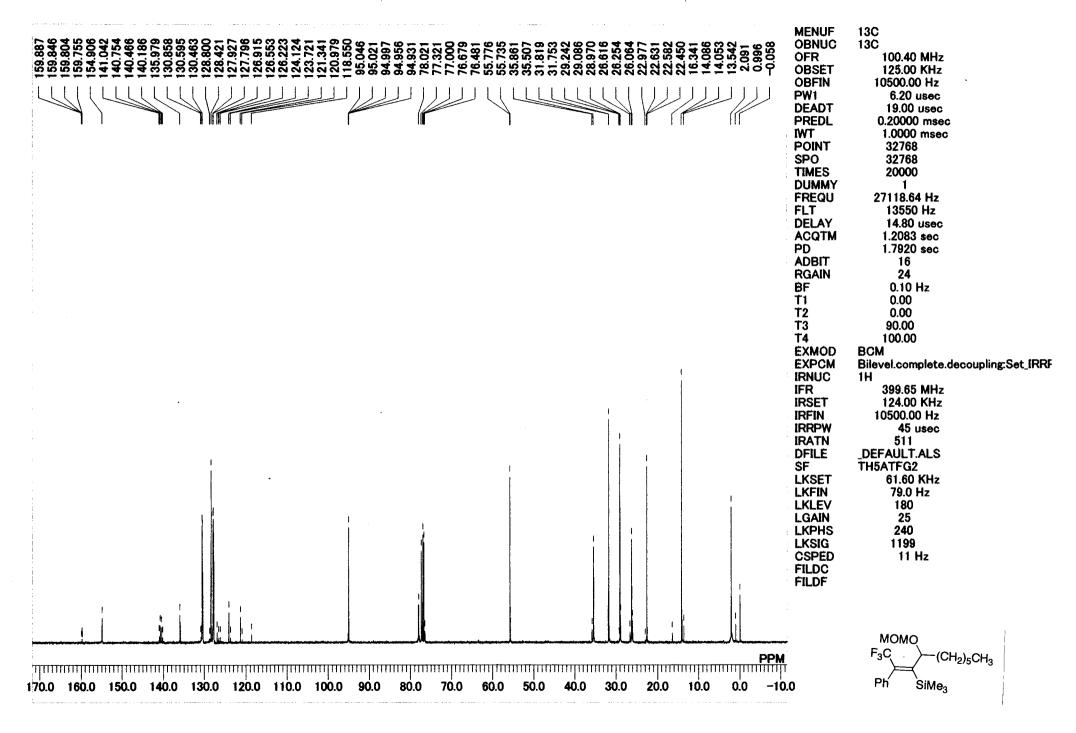


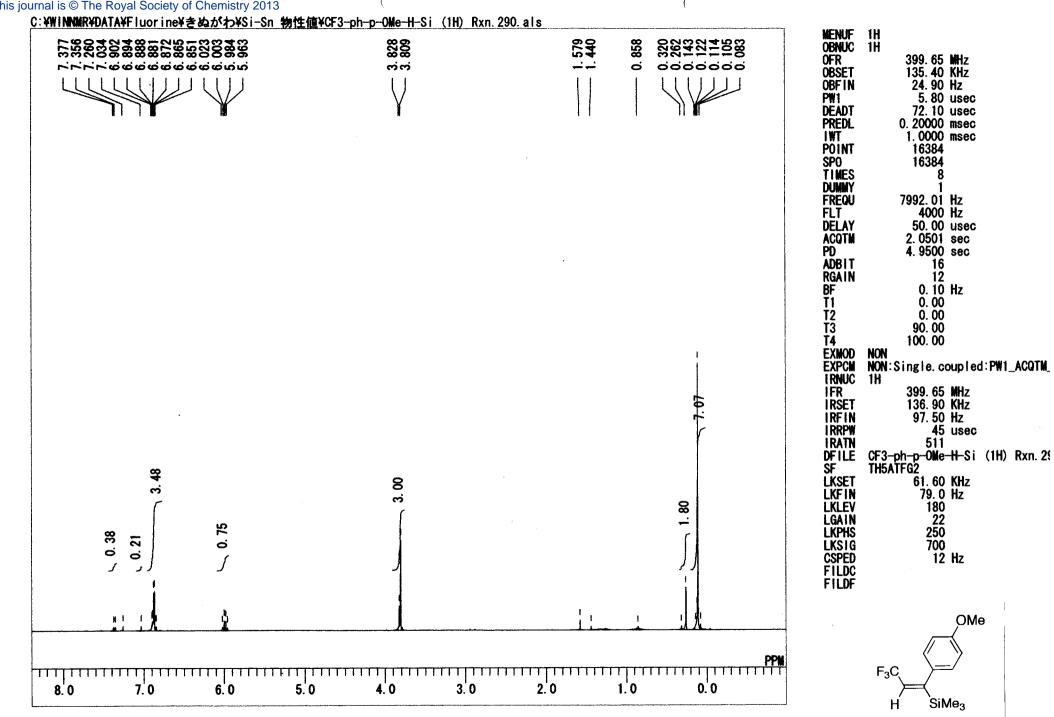
-1.425	MENUF OBNUC OFR OBSET OBFIN PW1 DEADT PREDL IWT POINT SPO TIMES DUMMY FREQU FLT DELAY ACQTM PD ADBIT RGAIN BF T1 T2 T3 T4 EXMOD EXPCM IRNUC IFR IRSET IRFIN IRATN DFILE SF LKSET LKFIN LKLEV LGAIN LKSIG CSPED FILDF	13C 13C 13C 100.40 MHz 125.00 KHz 10500.00 Hz 6.00 usec 19.10 usec 0.20000 msec 32768 32768 32768 1000 1 27118.64 Hz 13550 Hz 14.80 usec 1.2083 sec 1.7920 sec 16 23 0.10 Hz 0.00 90.00 100.00 BCM Bilevel.complete.decoupling:Set_IRRF 1H 399.65 MHz 124.00 KHz 10500.00 Hz 45 usec 511 CF3-OMOM-(CH2)5CH3-Si-ph Si: TH5ATFG2 61.60 KHz 79.0 Hz 180 28 203 490 12 Hz
PPM -10.0		$\begin{array}{c} \text{MOMO} \\ \text{F}_{3}\text{C} \\ \text{He}_{3}\text{Si} \end{array} \begin{array}{c} \text{(CH}_{2})_{5}\text{CH}_{3} \\ \text{Ph} \end{array}$



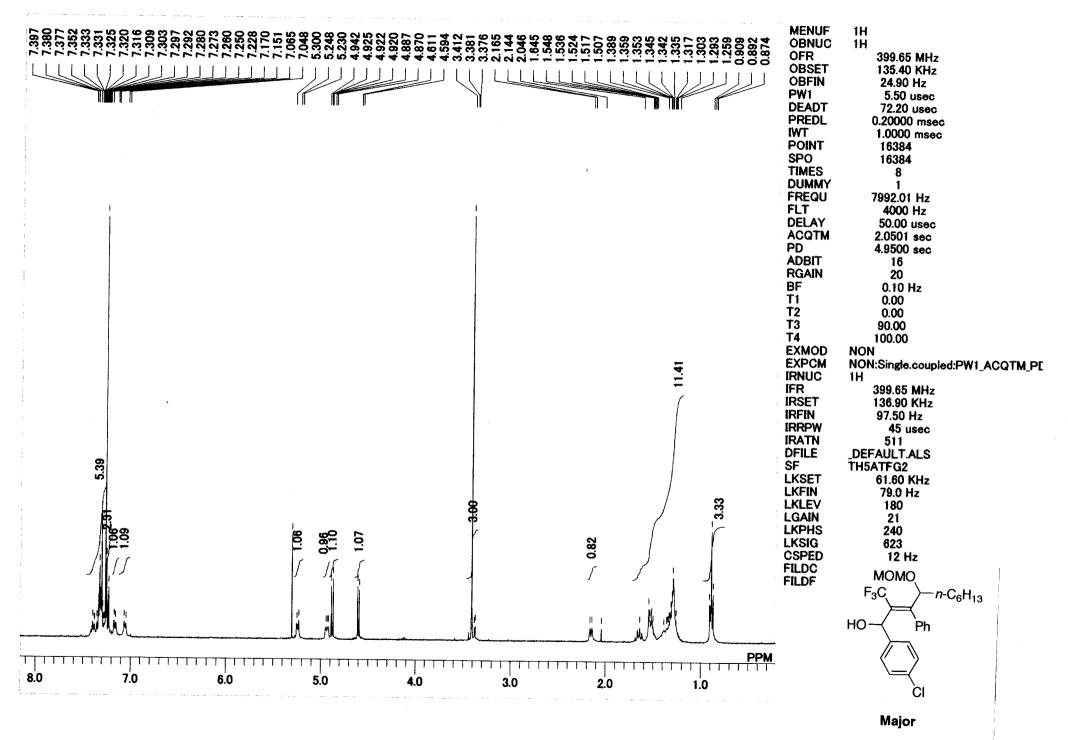
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0



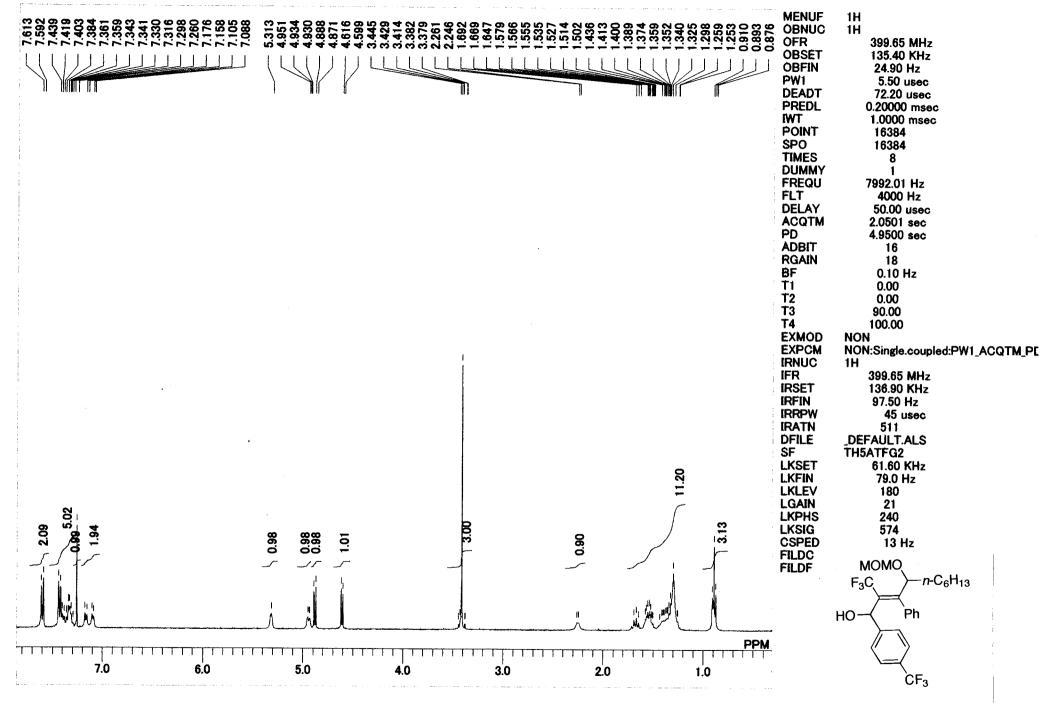




		13.863	-2026	MENUF OBNUC OFR OBSET OBFIN PW1 DEADT PREDL IWT POINT SPO TIMES DUMMY FREQU FLT DELAY ACQTM PD ADBIT RGAIN BF T1 T2 T3 T4 EXMOD EXPCM IRNUC IFR IRSET IRFIN IRRPW IRATN DFILE SF LKSET LKFIN LKSET	13C 13C 100.40 MHz 125.00 KHz 10500.00 Hz 6.20 usec 19.00 usec 0.20000 msec 1.0000 msec 32768 32768 32768 10000 1 27118.64 Hz 13550 Hz 14.80 usec 1.2083 sec 1.7920 sec 16 25 0.00 Hz 0.00 90.00 100.00 BCM Bilevel.complete.decoupling:Set_IRRF 1H 399.65 MHz 124.00 KHz 10500.00 Hz 45 usec 511 DEFAULT.ALS TH5ATFG2 61.60 KHz 79.0 Hz 180 23 240 962 12 Hz
раланириналириналириналириналириналириналириналириналириналириналириналириналириналириналириналириналириналирин 0.0220.0210.0200.0190.0180.0170.0160.0150.0140.0130.0120.0110.0100.0 90.0 80.0 70.0 6	.0. 50.0 40.0 30.0	1000 10.0	PPN PPN 0.0 -10.0-20.0-30	Π	F ₃ C H SiMe ₃



94.256	77.000 76.633 76.633 76.630 76.630 76.306 74.110 74.110	55.669	33.951	MENUF OBNUC OFR OBSET OBFIN PW1 DEADT PREDL IWT POINT SPO TIMES DUMMY FREQU FLT DELAY ACQTM PD ADBIT RGAIN BF T1 T2 T3 T4 EXMOD EXPCM IRNUC IFR	13C 13C 13C 100.40 MHz 125.00 KHz 10500.00 Hz 6.20 usec 19.00 usec 0.20000 msec 1.0000 msec 32768 32768 32768 10000 1 27118.64 Hz 13550 Hz 14.80 usec 1.2083 sec 1.7920 sec 16 25 0.10 Hz 0.00 90.00 100.00 BCM Bilevel.complete.decoupling:Set_IRRF 1H 399.65 MHz
	1 1 1		PP 11111111111111111111111111111111111	IRSET IRFIN IRRPW IRATN DFILE SF LKSET LKSET LKFIN LKEV LGAIN LKPHS LKSIG CSPED FILDC FILDF	$\begin{array}{c} 399.00 \text{ MHz} \\ 124.00 \text{ KHz} \\ 10500.00 \text{ Hz} \\ 45 \text{ usec} \\ 511 \\ \textbf{DEFAULT.ALS} \\ \textbf{TH5ATFG2} \\ 61.60 \text{ KHz} \\ 79.0 \text{ Hz} \\ 180 \\ 24 \\ 240 \\ 1218 \\ 12 \text{ Hz} \\ 12 \text{ Hz} \\ 12 \text{ Hz} \\ \textbf{MOMO} \\ \textbf{F_{3}C} \\ \textbf{F_{3}C} \\ \textbf{HO} \\ \textbf{-} $



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