Supporting Information

A Radical-Based Approach for the Construction of the Tetracyclic Structure of Resiniferatoxin

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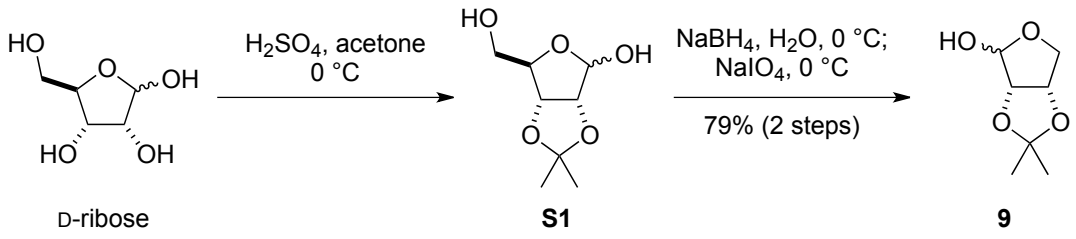
General: All reactions sensitive to air or moisture were carried out under argon atmosphere in dry solvents under anhydrous conditions, unless otherwise noted. THF, CH_2Cl_2, DMF and Et_2O were purified by Glass Contour solvent dispensing system (Nikko Hansen & Co., Ltd., Osaka, Japan). All other reagents were used as supplied. Analytical thin-layer chromatography (TLC) was performed using E. Merck Silica gel 60 F254 pre-coated plates. Flash chromatography was performed using 40-50 μm Silica-gel 60N (Kanto Chemical Co., Inc.), 40-63 μm Silica-gel 60 (Merck) or 32-53 μm Silica-gel BW-300 (Fuji Silysia Chemical Ltd.). Melting points were measured on Yanaco MP-J3 micro melting point apparatus, and are uncorrected. Optical rotations were measured on JASCO DIP-1000 Digital Polarimeter at room temperature using the sodium D line. Infrared (IR) spectra were recorded on JASCO FT/IR-4100 spectrometer. ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-ECX-500, JNM-ECA-500, or JNM-ECS-400 spectrometer. Chemical shifts were reported in ppm on the δ scale relative to $CHCl_3$ (δ = 7.26 for ^1H NMR), $CDCl_3$ (δ = 77.0 for ^{13}C NMR), C_6D_5H (δ = 7.16 for ^1H NMR), C_6D_6 (δ = 128.0 for ^{13}C NMR), CD_2HOD (δ = 3.31 for ^1H NMR) and CD_3OD (δ = 49.0 for ^{13}C NMR) as internal references. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broaden peak. The numbering of compounds corresponds to that of natural product. High resolution mass spectra were measured on BRUKER DALTONICS microTOF II or JEOL JMS-T100LP instrument.

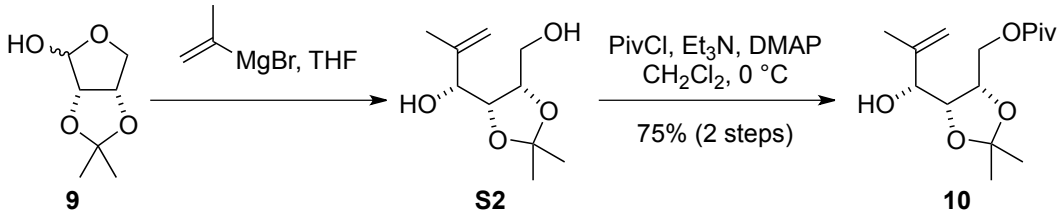


D-ribose **S1** **9**

Lactol 9. Concentrated H_2SO_4 (88 μL, 1.7 mmol) was added to a solution of D-ribose (5.00 g, 33.3 mmol) in acetone (130 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h, and was neutralized by addition of solid $Ca(OH)_2$ (2 g). The insoluble salts were removed by passing the mixture through a pad of Celite. The filter cake was washed with acetone (100 mL), and the filtrate was concentrated to afford crude **S1** (6.75 g), which was used for the next reaction without further purification.

The above crude **S1** was dissolved in H_2O (130 mL), and the solution was cooled to 0 °C. $NaBH_4$ (2.14 g, 56.6 mmol) in H_2O (90 mL) was added to the solution. The reaction mixture was stirred at 0 °C for 30 min, and then the pH of the reaction mixture

was adjusted to 6 by adding AcOH. $NaIO_4$ (6.28 g, 29.3 mmol) was added to the mixture, and the combined mixture was stirred at 0 °C for 80 min. Then, the reaction mixture was concentrated. The residue was partitioned between EtOAc (100 mL) and H_2O (50 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (150 mL ×3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Merck silica gel 60 g, hexane/Et_2O 2:1 to 0:1) to afford lactol **9** (4.23 g, 26.4 mmol) in 79% yield over 2 steps. All the spectral data were identical with those reported previously.[S1]



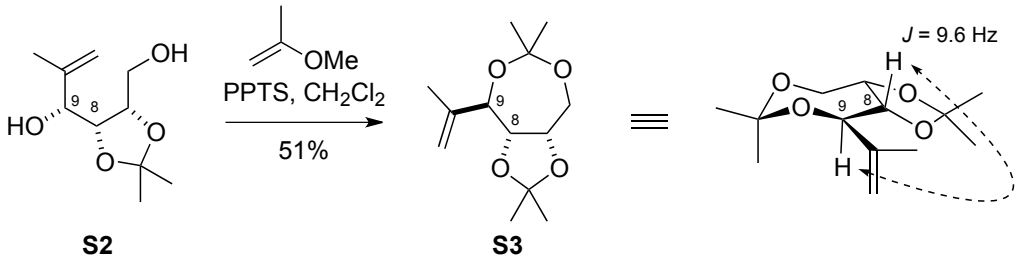
9 **S2** **10**

Pivaloate 10. A solution of lactol **9** (15.6 g, 97.5 mmol) in THF (160 mL) was cooled to 0°C. Isopropenylmagnesium bromide (0.5 M solution in THF, 500 mL, 250 mmol) was added by an addition funnel over 40 min to the solution, and the reaction mixture was stirred at 0°C for 1 h. The mixture was poured into saturated aqueous NH_4Cl (500 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (300 mL ×3). The combined organic layers were washed with brine (300 mL), dried over Na_2SO_4, filtered, and concentrated. The crude mixture was passed through a short pad of silica gel (Kanto silica gel, 200 g) with EtOAc (500 mL). The filtrate was concentrated to afford crude diol **S2**, which was used for the next reaction without further purification.

PivCl (14 mL, 110 mmol) was added to a mixture of the above crude diol **S2**, Et_3N (33 mL, 240 mmol) and DMAP (1.19 g, 9.74 mmol) in CH_2Cl_2 (330 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3 min, and was poured into H_2O (300 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (200 mL ×3). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (100 mL ×3) and brine (200 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Kanto silica gel 500 g, hexane/EtOAc 30:1 to 3:1) to afford pivaloate **10** (20.8 g, 72.7 mmol) in 75% yield over 2 steps: white

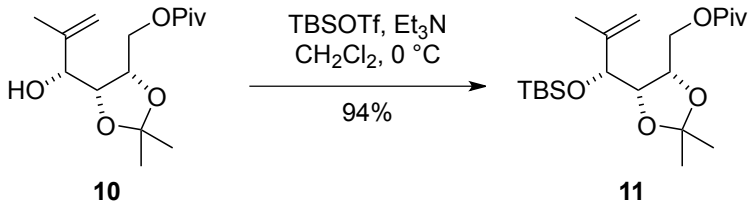
S1. a) T. Hudlicky, H. Luna, J. D. Price, F. Rulin, *J. Org. Chem.* **1990**, *55*, 4683-4687; b) H. Kotsuki, A. Miyazaki, M. Ochi, *Tetrahedron Lett.* **1991**, *32*, 4503-4504.

crystal; m.p. 62-63 °C; $[\alpha]_D^{19}$ -0.27 (*c* 1.00, $CHCl_3$): IR (neat) ν_{max} 3503, 2980, 1711, 1458, 1370, 1289, 1215, 1170, 1081, 1046 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.19 (3H, s, acetonide), 1.22 (9H, s, $COC(CH_3)_3$), 1.39 (3H, s, acetonide), 1.72 (3H, s, H18), 3.94 (1H, br d, *J* = 9.2 Hz, H9), 4.02 (1H, dd, *J* = 9.2, 6.0 Hz, H8), 4.38 (1H, ddd, *J* = 7.8, 6.0, 3.7 Hz, H14), 4.49 (1H, dd, *J* = 11.9, 7.8 Hz, H13a), 4.58 (1H, dd, *J* = 11.9, 3.7 Hz, H13b), 4.84 (1H, s, $C{=}CH_AH_B$), 4.96 (1H, s, $C{=}CH_AH_B$); ^{13}C NMR (100 MHz, C_6D_6) δ 17.8, 25.5, 27.3, 28.0, 38.8, 63.8, 73.8, 76.2, 77.8, 108.9, 113.7, 145.7, 177.9; HRMS (ESI) calcd for $C_{15}H_{26}O_5Na$, 309.1672 ($M+Na^+$), found 309.1678.



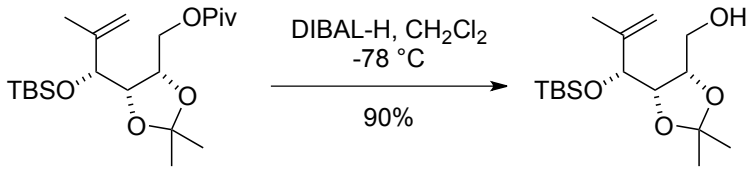
S2 **S3**

***Determination of the C9 stereochemistry*: Acetonide S3**. PPTS (9.6 mg, 38 μmol) was added to a solution of diol **S2** (16 mg, 79 μmol) in CH_2Cl_2 (0.8 mL) and 2-methoxy-1-propene (36 μL, 0.38 mmol) at room temperature. The reaction mixture was stirred at room temperature for 5 min, and was quenched with saturated aqueous $NaHCO_3$ (1.5 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (1 mL ×3). The combined organic layers were washed with brine (2 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified twice by flash chromatography (1^{st}: Kanto silica gel 2 g, hexane/EtOAc 20:1 to 1:1; 2^{nd}: Kanto silica gel 1 g, CH_2Cl_2/EtOAc 1:0 to 0:1) to afford **S3** (9.8 mg, 40 μmol) in 51% yield: colorless oil; $[\alpha]_D^{19}$ +37 (*c* 0.49, $CHCl_3$); IR (neat) ν_{max} 2989, 1380, 1217, 1163, 1085, 1049 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.21 (3H, s, acetonide), 1.27 (3H, s, acetonide), 1.33 (3H, s, acetonide), 1.50 (3H, s, acetonide), 1.87 (3H, s, H18), 3.62 (1H, dd, *J* = 14.2, 1.4 Hz, H13a), 3.71 (1H, dt, *J* = 5.5, 1.8 Hz, H14), 3.85 (1H, dd, *J* = 14.2, 1.8 Hz, H13b), 3.89 (1H, dd, *J* = 9.6, 5.5 Hz, H8), 4.40 (1H, d, *J* = 9.6 Hz, H9), 5.00 (1H, t, *J* = 1.8 Hz, $C{=}CH_AH_B$), 5.15 (1H, s, $C{=}CH_AH_B$); ^{13}C NMR (100 MHz, C_6D_6) δ 18.8, 23.9, 25.0, 26.0, 28.7, 58.7, 73.5, 77.2, 78.0, 101.3, 108.2, 114.0, 143.9; HRMS (ESI) calcd for $C_{13}H_{22}O_4Na$, 265.1410 ($M+Na^+$), found 265.1399.



10 **11**

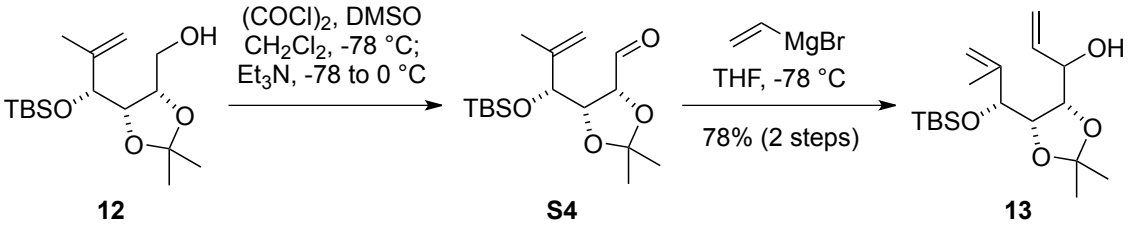
TBS ether 11. A solution of pivaloate **10** (18.9 g, 66.1 mmol) in CH_2Cl_2 (220 mL) was cooled to 0 °C, and then Et_3N (18.4 mL, 132 mmol) and TBSOTf (15.6 mL, 66.0 mmol) were successively added. The reaction mixture was stirred at 0 °C for 10 min, and was poured into H_2O (200 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (200 mL ×3). The combined organic layers were washed with H_2O (200 mL) and brine (200 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Merck silica gel 600 g, hexane/EtOAc 50:1 to 5:1) to afford TBS ether **11** (24.9 g, 62.1 mmol) in 94% yield: colorless oil; $[\alpha]_D^{21}$ -30 (*c* 1.00, $CHCl_3$); IR (neat) ν_{max} 2957, 2932, 2859, 1732, 1462, 1371, 1254, 1160, 1086 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.05 (3H, s, C*H*$_3$ of TBS), 0.16 (3H, s, C*H*$_3$ of TBS), 0.96 (9H, s, *t*-Bu of TBS), 1.22 (9H, s, COC(C*H*$_3$)$_3$), 1.23 (3H, s, acetonide), 1.45 (3H, s, acetonide), 1.69 (3H, s, H18), 4.12 (1H, dd, *J* = 8.2, 6.0 Hz, H8), 4.26 (1H, d, *J* = 8.2 Hz, H9), 4.38 (1H, ddd, *J* = 8.2, 6.0, 2.3 Hz, H14), 4.47 (1H, dd, *J* = 11.9, 8.2 Hz, H13a), 4.59 (1H, *J* = 11.9, 2.3 Hz, H13b), 4.85 (1H, t, *J* = 1.4 Hz, C=C*H*$_A$H$_B$), 4.99 (1H, s, C=CH$_A$*H*$_B$); ^{13}C NMR (100 MHz, C_6D_6) δ -5.2, -4.0, 17.2, 18.3, 25.6, 26.0, 27.4, 28.0, 38.8, 64.4, 75.5, 76.0, 77.7, 108.8, 115.0, 145.1, 177.9; HRMS (ESI) calcd for $C_{21}H_{40}O_5SiNa$, 423.2537 ($M+Na^+$), found 423.2525.



11 **12**

Alcohol 12. DIBAL-H (1.0 M in hexane, 124 mL, 124 mmol) was added dropwise to a solution of **11** (24.9 g, 62.2 mmol) in CH_2Cl_2 (210 mL) -78 °C. The reaction mixture was stirred at -78 °C for 45 min, and was poured into a mixture of EtOAc and saturated aqueous Rochelle's salt (300 mL, 1:1). The mixture was stirred at room temperature for 12 h. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (200 mL ×3). The combined organic layers was washed with H_2O (200 mL ×2) and brine (200 mL), dried over Na_2SO_4, filtered, and concentrated. The crude residue was combined with another batch of alcohol **12** that was synthesized from **11**

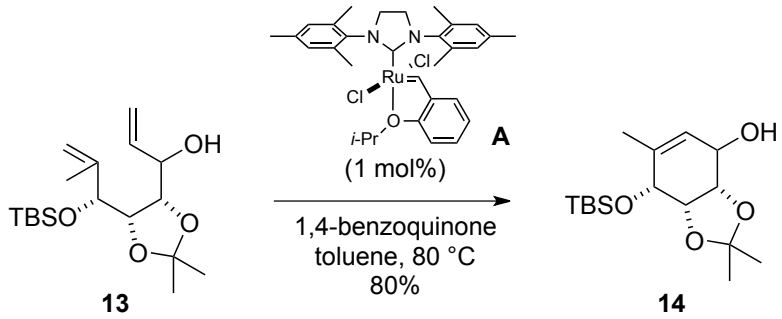
(32.0 g, 79.8 mmol) by the same procedure described above. The combined crude was purified by recrystallization from Et_2O/hexane to afford **12** (27.8g, 87.7 mmol) in 62% yield as a white needle. The mother liquid was concentrated and purified by flash chromatography (Merck silica gel 600 g, hexane/EtOAc 50:1 to 5:1) to afford **12** (12.4 g, 39.2 mmol) in 28% yield. The combined yield of the reactions was 90%: m.p. 54-56 °C; $[\alpha]_D^{19}$ -19 (*c* 1.00, $CHCl_3$); IR (neat) ν_{max} 3488, 2954, 2932, 2858, 1463, 1371, 1253, 1220, 1078 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.05 (3H, s, C*H*$_3$ of TBS), 0.10 (3H, s, C*H*$_3$ of TBS), 0.94 (9H, s, *t*-Bu of TBS), 1.23 (3H, s, acetonide), 1.39 (3H, s, acetonide), 1.67 (3H, s, H18), 2.32 (1H, ddd, *J* = 7.8, 6.0, 6.0 Hz, O*H*), 3.85 (1H, dd, *J* = 11.4, 6.0 Hz, H13a), 3.91 (1H, ddd, *J* = 11.4, 7.8, 4.6 Hz, H13b), 4.10 (1H, dd, *J* = 8.2, 6.4 Hz, H8), 4.23 (1H, ddd, *J* = 6.4, 6.0, 4.6 Hz, H14), 4.35 (1H, d, *J* = 8.2 Hz, H9), 4.83 (1H, m, C=C*H*$_A$H$_B$), 5.00 (1H, s, C=CH$_A$*H*$_B$); ^{13}C NMR (100 MHz, C_6D_6) δ -5.1, -4.1, 17.4, 18.3, 25.5, 26.0, 28.0, 61.7, 75.4, 77.8, 78.5, 108.2, 114.9, 145.1; HRMS (ESI) calcd for $C_{16}H_{32}O_4SiNa$, 339.1962 ($M+Na^+$), found 339.1974.



Diene 13. DMSO (1.1 mL, 16 mmol) in CH_2Cl_2 (16 mL) was added dropwise to a solution of $(COCl)_2$ (540 μL, 6.4 mmol) in CH_2Cl_2 (40 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 10 min. To the mixture was added a solution of alcohol **12** (1.01 g, 3.19 mmol) in CH_2Cl_2 (8 mL). The resultant mixture was stirred at -78 °C for 1 h, and then Et_3N (3.1 mL, 22 mmol) was added at -78 °C. The reaction mixture was allowed to warm to 0 °C, stirred for 1 h, and was quenched with H_2O (80 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (50 mL ×3). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered, and concentrated to afford crude aldehyde **S4**, which was used for the next reaction without further purification.

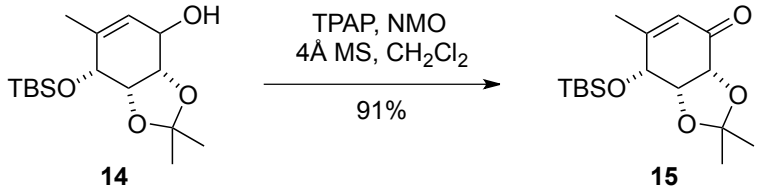
Vinylmagnesium bromide (1.0 M in THF, 4.0 mL, 4.0 mmol) was added dropwise to the above crude aldehyde **S4** in THF (44 mL) at -78 °C. The reaction mixture was stirred at -78 °C for 10 min, and was quenched with saturated aqueous NH_4Cl (50 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (30 mL ×3). The combined organic layers were washed with brine (60 mL), dried over

Na_2SO_4, filtered, and concentrated. The crude residue was purified by flash chromatography (Merck silica gel 20 g, hexane/EtOAc 30:1 to 2:1) to afford diene **13** (854 mg, 2.49 mmol) in 78% yield over 2 steps: crystal: m.p. 48-51 °C; $[\alpha]_D^{20}$ -29 (*c* 1.01, $CHCl_3$); IR (neat) ν_{max} 3567, 3486, 2954, 2931, 2858, 1462, 1372, 1253, 1069 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.07 (3H, s, C*H*$_3$ of TBS), 0.14 (3H, s, C*H*$_3$ of TBS), 0.90 (9H, s, *t*-Bu of TBS), 1.36 (3H, s, acetonide), 1.52 (3H, s, acetonide), 1.78 (3H, s, H18), 2.85 (1H, d, *J* = 6.8 Hz, O*H*), 4.09 (1H, dd, *J* = 7.0, 1.4 Hz, H9), 4.25 (1H, dd, *J* = 7.0, 7.0 Hz, H8), 4.43 (1H, m, H13), 4.61 (1H, d, *J* = 7.0 Hz, H14), 5.01 (1H, d, *J* = 1.4 Hz, C=C*H*$_A$H$_B$), 5.13 (1H, s, C=CH$_A$*H*$_B$), 5.18 (1H, ddd, *J* = 10.5, 1.6, 1.6 Hz, CH=C*H*$_A$H$_B$), 5.30 (1H, ddd, *J* = 17.4, 1.6, 1.6 Hz, CH=CH$_A$*H*$_B$), 5.93 (1H, ddd, *J* = 17.4, 10.5, 5.5 Hz, H12); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.3, -4.3, 17.6, 18.2, 24.6, 25.8, 26.5, 70.0, 75.0, 77.2, 79.4, 108.1, 114.9, 115.2, 138.6, 144.1; HRMS (ESI) calcd for $C_{18}H_{34}O_4SiNa$, 365.2119 ($M+Na^+$), found 365.2108.



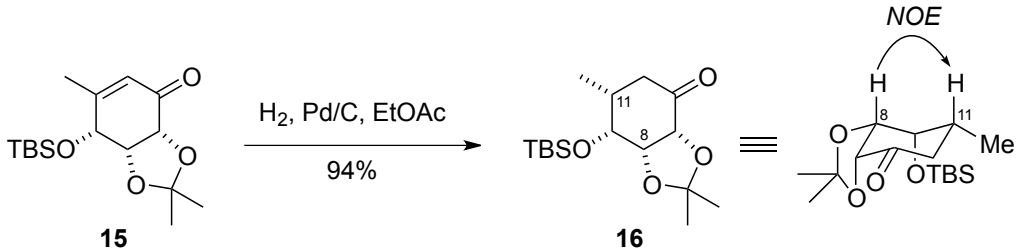
Allyl alcohol 14. A mixture of diene **13** (4.38 g, 12.8 mmol) and 1,4-benzoquinone (28 mg, 260 μmol) in toluene (210 mL) was heated to 80 °C. Hoveyda-Grubbs 2nd generation catalyst **A** (80 mg, 130 μmol) in toluene (50 mL) was added by an addition funnel over 5.5 h, and the resultant mixture was stirred at 80 °C for further 3 h. The reaction mixture was passed through a short pad of silica gel (Merck silica gel) and the filter cake was washed with a mixture of CH_2Cl_2 and acetone (2:1). The filtrate was concentrated, and the residue was purified by flash chromatography (Merck silica gel 100 g, hexane/EtOAc 20:1 to 2:1) to afford allyl alcohol **14** (3.20 g, 10.3 mmol) in 80% yield as a green oil. The green color was attributed to the residual ruthenium catalyst although the isolated compound was sufficiently pure from the ^1H NMR. The product was isolated as a single diastereomer, however the stereochemistry at the C13 position was not determined: $[\alpha]_D^{29}$ -51 (*c* 1.00, $CHCl_3$); IR (neat) ν_{max} 3453, 2931, 2857, 1378, 1254, 1209, 1135, 1066 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (3H, s, C*H*$_3$ of TBS), 0.10 (3H, s, C*H*$_3$ of TBS), 0.90 (9H, s, *t*-Bu of TBS), 1.33 (3H, s, acetonide), 1.43 (3H,

s, acetonide), 1.81 (3H, s, H18), 2.09 (1H, br s, O*H*), 4.21 (1H, dd, *J* = 7.8, 4.6 Hz, H14), 4.30 (1H, dd, *J* = 7.8, 3.6 Hz, H8), 4.39 (1H, d, *J* = 3.6 Hz, H9), 4.45 (1H, m, H13), 5.59 (1H, m, H12); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.7, -4.5, 18.2, 20.3, 24.6, 25.8, 26.4, 69.2, 69.6, 76.9, 80.0, 109.7, 125.5, 140.9; HRMS (ESI) calcd for $C_{16}H_{30}O_4SiNa$, 337.1806 ($M+Na^+$), found 337.1791.



14 **15**

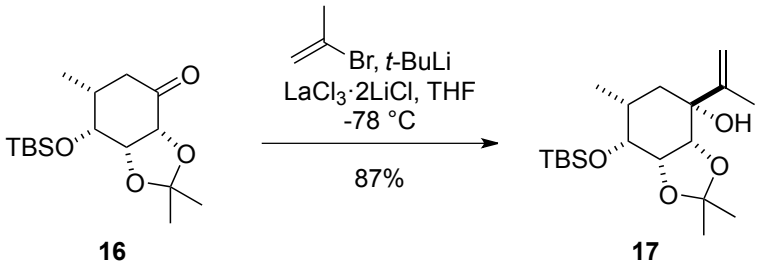
Enone 15. TPAP (107 mg, 304 μmol) was added to a mixture of **14** (1.87 g, 5.95 mmol), NMO (1.04 g, 8.92 mmol) and 4Å MS (3 g, activated by drying in oven at 120 °C for 3 h) in CH_2Cl_2 (60 mL) at room temperature. The resultant suspension was stirred at room temperature for 1 h, and was filtered through a pad of Celite with a mixture of CH_2Cl_2/acetone (200 mL, 5:1). The filtrate was concentrated, and the residue was passed through a pad of silica gel (Kanto silica gel 100 g, CH_2Cl_2/acetone 5:1) to remove the residual ruthenium catalyst. The fractions containing the product were collected and concentrated. The concentrate was further purified by flash chromatography (Merck silica gel 30 g, hexane/Et_2O 5:1 to 1:2) to afford enone **15** (1.70 g, 5.45 mmol) in 91% yield: colorless oil: $[\alpha]_D^{24}$ -40 (*c* 0.94, $CHCl_3$); IR (neat) ν_{max} 2931, 2857, 1675, 1379, 1234, 1135, 1102, 1065 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.18 (3H, s, C*H*$_3$ of TBS), 0.19 (3H, s, C*H*$_3$ of TBS), 0.96 (9H, s, *t*-Bu of TBS), 1.36 (3H, s, acetonide), 1.38 (3H, s, acetonide), 2.05 (3H, m, H18), 4.25 (1H, d, *J* = 4.6 Hz, H14), 4.59 (1H, dd, *J* = 4.6, 4.6 Hz, H8), 4.74 (1H, m, H9), 5.93 (1H, m, H12); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.7, -4.5, 18.3, 21.0, 25.7, 25.9, 27.5, 69.1, 76.0, 77.1, 110.6, 124.5, 162.6, 195.5; HRMS (ESI) calcd for $C_{16}H_{28}O_4SiNa$, 335.1649 ($M+Na^+$), found 335.1640.



15 **16**

Ketone 16. A solution of enone **15** (1.70 g, 5.44 mmol) and Pd/C (10 wt% Pd on

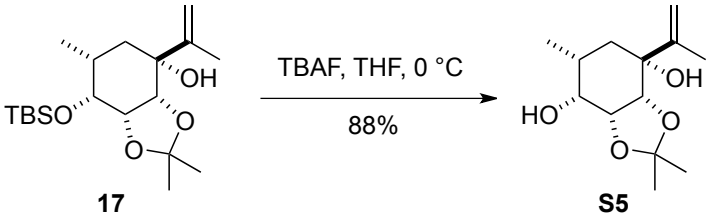
carbon, 170 mg) in EtOAc (27 mL) was exposed to H_2 atmosphere (1 atm), and was stirred at room temperature for 30 min. Then, the reaction mixture was passed through a pad of Celite. The filter cake was washed with EtOAc (100 mL), and the filtrate was concentrated to afford keone **16** (1.60 g, 5.09 mmol) in 94% yield, which was used in the next reaction without further purification: white crystal; m.p. 102-104 °C; $[\alpha]_D^{25}$ -0.017 (*c* 1.07, $CHCl_3$); IR (neat) ν_{max} 2928, 1726, 1460, 1377, 1257, 1167, 1107 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.04 (3H, s, C*H*$_3$ of TBS), 0.06 (3H, s, C*H*$_3$ of TBS), 0.85 (9H, *t*-Bu of TBS), 1.07 (3H, d, *J* = 6.4 Hz, H18), 1.34 (3H, s, acetonide), 1.51 (3H, s, acetonide), 2.07 (1H, dd, *J* = 17.0, 10.1 Hz, H12a), 2.16-2.22 (1H, m, H11), 2.37 (1H, dd, *J* = 17.0, 7.4 Hz, H12b), 3.99 (1H, d, *J* = 3.7 Hz, H9), 4.36 (1H, d, *J* = 9.6 Hz, H14), 4.48 (1H, dd, *J* = 9.6, 3.7 Hz, H8); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.7, -3.7, 18.1, 18.6, 24.2, 25.8, 26.0, 31.3, 40.1, 70.1, 77.2, 78.4, 110.1, 205.9; HRMS (ESI) calcd for $C_{16}H_{30}O_4SiNa$, 337.1806 ($M+Na^+$), found 337.1811.



16 **17**

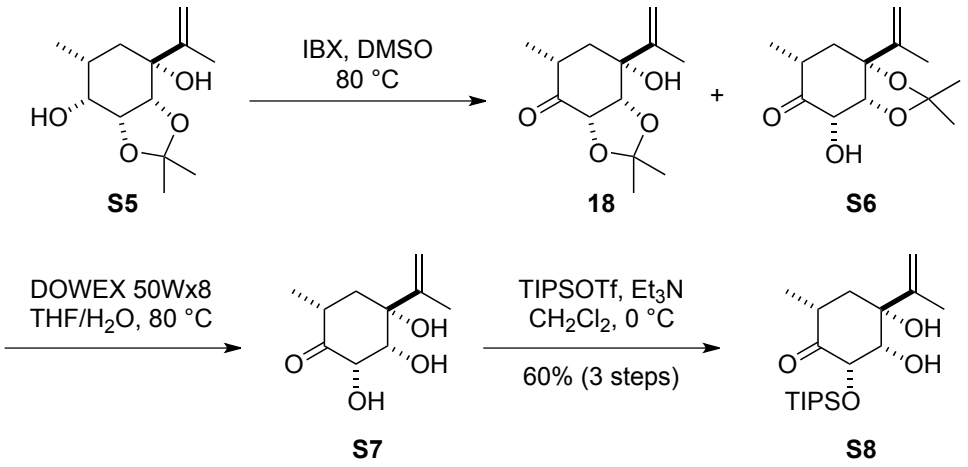
Alcohol 16. A oven-dried 3-neck round-bottom flask was charged with 2-bromopropene (2.6 mL, 29 mmol) and THF (80 mL), and the solution was cooled to -78 °C. *t*-BuLi (1.65 M solution in pentane, 37 mL, 61 mmol) was added dropwise by an addition funnel, and the resultant canary yellow solution was stirred at -78 °C for 30 min. The mixture was then treated with $LaCl_3$·2LiCl (0.6 M solution in THF, 50 mL, 30 mmol). The resultant burgundy mixture was further stirred at -78 °C for 30 min, and a solution of alcohol **16** (4.75 g, 15.1 mmol) in THF (20 mL) was added dropwise via cannula. The reaction mixture was stirred at -78 °C for 30 min, and was poured into a stirring mixture of saturated aqueous NH_4Cl (200 mL) and EtOAc (60 mL). The mixture was filtered through a pad of Celite with EtOAc (80 mL). The aqueous phase was separated and extracted with EtOAc (100 mL ×3). The combined organic layers were washed with brine (150 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Merck silica gel 200 g, hexane/EtOAc 100:1 to 1:1) to afford alcohol **17** (4.71 g, 13.2 mmol) in 87% yield: crystal; m.p. 57-60 °C; $[\alpha]_D^{28}$ -31 (*c* 0.83, $CHCl_3$); IR (neat) ν_{max} 3417, 2929, 2360, 1366, 1255,

1039 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.13 (3H, s, C*H*$_3$ of TBS), 0.17 (3H, s, C*H*$_3$ of TBS), 0.94 (9H, s, *t*-Bu of TBS), 1.05 (3H, d, *J* = 6.8 Hz, H18), 1.36 (3H, s, acetonide), 1.54 (3H, s, acetonide), 1.57 (1H, dd, *J* = 14.6, 10.5 Hz, H12a), 1.64-1.71 (1H, m, H11), 1.82 (3H, s, H17), 2.00 (1H, dd, *J* = 14.6, 7.8 Hz, H12b), 4.12 (1H, dd, *J* = 5.0, 1.8 Hz, H9), 4.18 (1H, d, *J* = 8.2 Hz, H14), 4.23 (1H, dd, *J* = 8.2, 5.0 Hz, H8), 4.72 (1H, s, O*H*), 4.93 (1H, m, H16a), 5.17 (1H, m, H16b); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.9, -4.2, 18.4, 19.1, 19.6, 25.2, 25.9, 26.2, 30.6, 40.3, 71.1, 73.3, 75.6, 77.2, 109.7, 111.5, 147.7; HRMS (ESI) calcd for $C_{19}H_{36}O_4SiNa$, 379.2275 ($M+Na^+$), found 379.2256.



17 **S5**

Diol S5. TBAF (1.0 M in THF, 45 mL, 45 mmol) was added to a solution of alcohol **17** (7.76 g, 21.7 mmol) in THF (70 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min, and was quenched with saturated aqueous NH_4Cl (70 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (20 mL ×3). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Merck silica gel 120 g, hexane/EtOAc 5:1 to 1:2) to afford diol **S5** (4.65 g, 19.2 mmol) in 88% yield: crystal; m.p. 113-117 °C; $[\alpha]_D^{24}$ -53 (*c* 1.04, $CHCl_3$); IR (neat) ν_{max} 3387, 2928, 1455, 1382, 1261, 1212, 1162 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 1.09 (3H, d, *J* = 6.8 Hz, H18), 1.39 (3H, s, acetonide), 1.53 (3H, s, acetonide), 1.53 (1H, dd, *J* = 14.6, 9.6 Hz, H12a), 1.65-1.75 (1H, m, H11), 1.82 (3H, s, H17), 1.88 (1H, dd, *J* = 14.6, 8.2 Hz, H12b), 3.84 (1H, dd, *J* = 5.5, 2.3 Hz, H9), 4.30 (1H, dd, *J* = 8.2, 5.5 Hz, H8), 4.38 (1H, d, *J* = 8.2 Hz, H14), 4.90 (1H, m, H16a), 5.09 (1H, s, H16b); ^{13}C NMR (100 MHz, CD_3OD) δ 19.0, 19.5, 24.7, 26.2, 31.1, 38.7, 70.5, 75.6, 77.1, 77.3, 110.0, 111.9, 149.5; HRMS (ESI) calcd for $C_{13}H_{22}O_4Na$, 265.1410 ($M+Na^+$), found 265.1419.

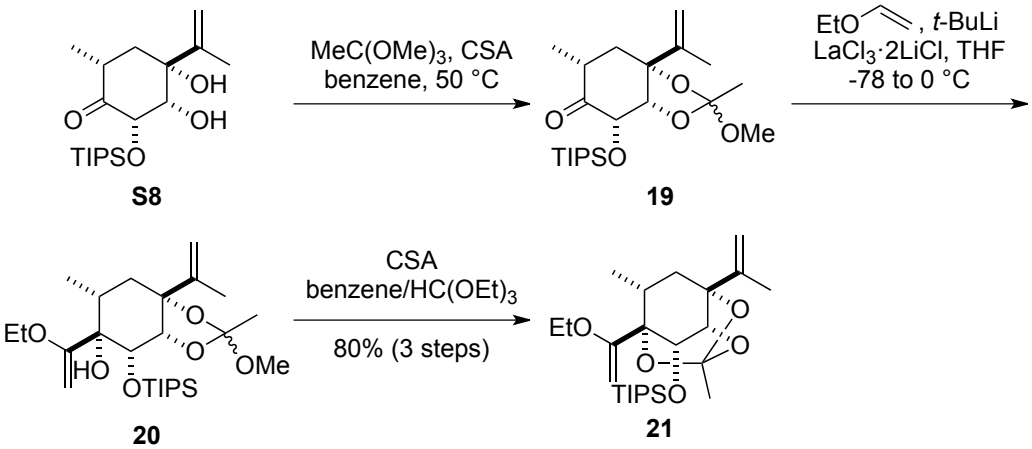


TIPS ether S8. IBX (3.87 g, 13.8 mmol) was added to a solution of diol **S5** (2.23 g, 9.21 mmol) in DMSO (61 mL) was added. The reaction mixture was stirred at 80 °C for 30 min, cooled to room temperature, and then quenched with saturated aqueous $NaHCO_3$ (50 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (30 mL ×3). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Merck silica gel) to afford an inseparable mixture of ketones **18** and **S6** (2.09 g, 8.70 mmol), which was used for the next reaction without further purification.

DOWEX 50W×8 (200-400 mesh, 10.5 g) was added to a solution of the above mixture of ketones **18** and **S6** in THF/H_2O (87 mL, 3:1). The reaction mixture was stirred at 80 °C for 12 h, and was cooled to room temperature. The resin was removed by the filtration through a pad of Celite with acetone (200 mL). The filtrate was concentrated to afford crude triol **S7**, which was used for the next reaction without further purification. For a characterization, a small amount of triol **S7** was purified by flash chromatography (Merck silica gel, hexane/EtOAc 1:1 to 1:3): $[\alpha]_D^{24}$ -4.3 (*c* 1.74, $CHCl_3$); IR (neat) ν_{max} 3400, 2971, 2933, 1726, 1450, 1129, 1027 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.10 (3H, d, *J* = 6.4 Hz, H18), 1.96 (3H, s, H17), 2.01 (1H, dd, *J* = 14.2 Hz, H12a), 2.32 (1H, ddd, *J* = 14.2, 6.4, 2.3 Hz, H12b), 2.50 (1H, ddq, *J* = 14.2, 6.4, 6.4 Hz, H11), 2.88 (1H, s, O*H*), 3.41 (1H, d, *J* = 2.3 Hz, O*H*), 3.93 (1H, d, *J* = 4.1 Hz, O*H*), 4.22 (1H, m, H8), 4.43 (1H, m, H14), 5.24 (1H, s, H16a), 5.31 (1H, s, H16b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 18.8, 38.7, 39.3, 73.9, 74.5, 76.8, 114.8, 144.0, 210.7; HRMS (ESI) calcd for $C_{10}H_{16}O_4Na$, 223.0941 ($M+Na^+$), found 223.0945.

TIPSOTf (4.7 mL, 18 mmol) were added to a solution of the above crude **S7** and Et_3N (4.8 mL, 35 mmol) in CH_2Cl_2 (44 mL) at 0 °C. The reaction mixture was stirred at

0 °C for 3 h, and was quenched with H_2O (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL ×3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Merck silica gel 100 g, hexane/EtOAc 6:1 to 4:1) to afford TIPS ether **S8** (1.98 g, 5.56 mmol) in 60% yield over 3 steps: white solid: m.p. 46-47 °C; $[\alpha]_D^{24}$ -16 (*c* 0.51 $CHCl_3$); IR (neat) ν_{max} 3463, 2943, 2868, 1739, 1464, 1165, 1011 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04-1.17 (24H, m, H18, (Si(C*H*(CH_3)$_2$)$_3$), 1.95 (1H, dd, *J* = 13.3, 13.3 Hz, H12a), 1.97 (3H, s, H17), 2.29 (1H, ddd, *J* = 13.3, 5.9, 1.8 Hz, H12b), 2.35 (1H, dqd, *J* = 13.3, 6.4, 5.9 Hz, H11), 2.76 (1H, s, O*H*), 2.90 (1H, s, O*H*), 4.36 (1H, br s, H8), 4.43 (1H, d, *J* = 3.2 Hz, H14), 5.25 (1H, d, *J* = 0.9 Hz, H16a), 5.27 (1H, s, H16b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 13.9, 17.9, 19.0, 38.8, 39.7, 74.0, 75.8, 78.5, 114.6, 144.3, 208.2; HRMS (ESI) calcd for $C_{19}H_{36}O_4SiNa$, 379.2275 ($M+Na^+$), found 379.2282.

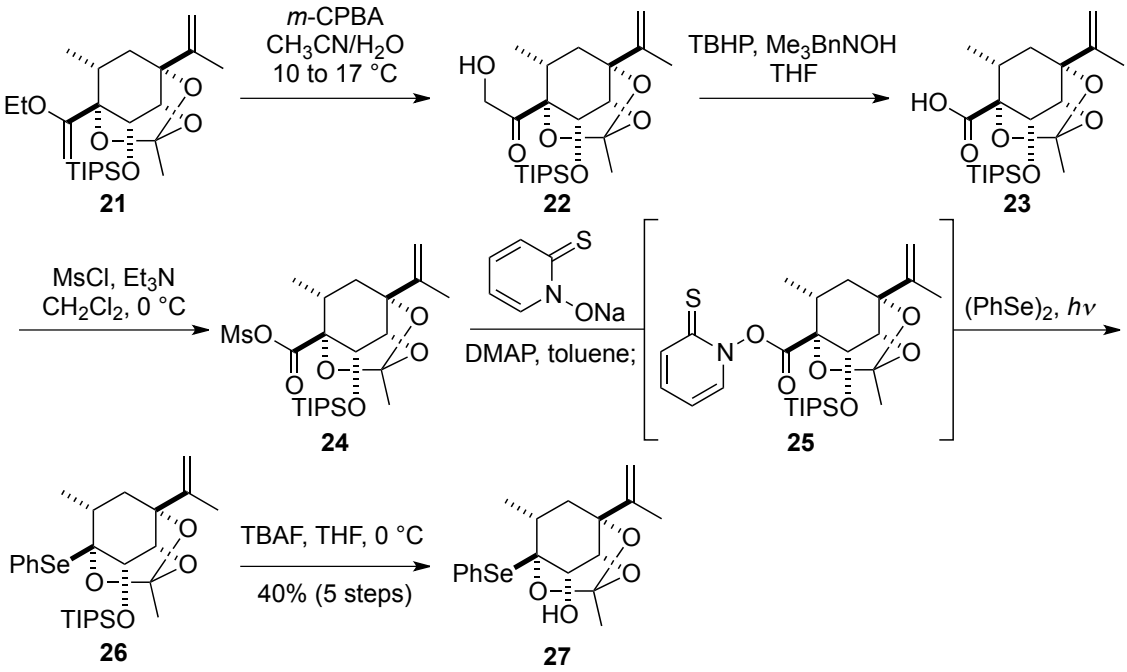


Orthoester 21. (+)-CSA (97 mg, 420 μmol) was added to a solution of TIPS ether **S8** (1.49 g, 4.17 mmol) and trimethyl orthoacetate (3.8 mL, 30 mmol) in benzene (42 mL). The mixture was heated to 50 °C for 30 min, and was allowed to cool to room temperature. Then, saturated aqueous $NaHCO_3$ (40 mL) was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc (30 mL ×3). The combined organic layers were washed with brine (40 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was azeotropically dried with toluene to afford a 8.3 : 1 diastereomixture of crude **19**, which was used for the next reaction without further purification.

A oven-dried 3-neck round-bottom flask was charged with ethyl vinyl ether (2.8 mL, 29 mmol) and THF (33 mL), and the solution was cooled to -78 °C. After *t*-BuLi (1.65 M solution in pentane, 13 mL, 21 mmol) was injected dropwise into the flask, the dry

ice-acetone bath was replaced with an ice bath and the reaction flask was allowed to warm to 0 °C. The canary yellow solution turned colorless after stirred at 0 °C for 15 min. The resultant colorless solution was cooled to -78 °C, and was treated with $LaCl_3 \cdot 2LiCl$ (0.6 M solution in THF, 35 mL, 21 mmol). The resultant amber-colored solution was further stirred at -78 °C for 15 min, then a solution of the above crude **19** in THF (9 mL) was added dropwise via cannula. The mixture was stirred at -78 °C for 10 min and at 0 °C for 5 min, and was poured into a stirring mixture of saturated aqueous NH_4Cl (50 mL) and EtOAc (20 mL). The white precipitate was filtered through a pad of Celite with EtOAc (200 mL). The filtrate was concentrated to ca.100 mL. The aqueous phase was separated and extracted with EtOAc (30 mL ×3). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated to afford crude alcohol **20** (1.6 g), which was used for the next reaction without further purification.

(+)-CSA (97 mg, 420 μmol) was added to a solution of the above crude alcohol **20** in a mixture of benzene and triethyl orthoformate (42 mL, 5:1). The reaction mixture was stirred at room temperature for 30 min. Saturated aqueous $NaHCO_3$ (60 mL) was added to the mixture, and the organic layer was separated. The aqueous layer was extracted with EtOAc (40 mL ×3). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Kanto silica gel 50 g, hexane/EtOAc 20:1) to afford orthoester **21** (1.52 g, 3.36 mmol) in 80% yield over 3 steps: colorless oil: $[\alpha]_D^{24}$ +87 (*c* 0.96, MeOH); IR (neat) ν_{max} 2941, 2867, 1402, 1302, 1158, 1107 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.10-1.15 (3H, m, SiC*H*$(CH_3)_2$ x 3), 1.11 (3H, t, *J* = 7.3 Hz, CH_2CH_3), 1.17 (9H, d, *J* = 6.4 Hz, SiCH(C*H*$_3$) x 3), 1.21 (9H, d, *J* = 6.4 Hz, SiCH(C*H*$_3$) x 3), 1.29 (3H, d, *J* = 7.3 Hz, H18), 1.63 (1H, d, *J* = 14.6 Hz, H12a), 1.71 (3H, br s, H17), 1.78 (3H, s, CC*H*$_3$), 1.83 (1H, dd, *J* = 14.6, 9.2 Hz, H12b), 2.48 (1H, dq, *J* = 9.2, 7.3 Hz, H11), 3.43 (1H, dq, *J* = 9.6, 7.3 Hz, $CH_AH_BCH_3$), 3.57 (1H, dq, *J* = 9.6, 7.3 Hz, $CH_AH_BCH_3$), 4.00 (1H, d, *J* = 3.2 Hz, H8), 4.18 (1H, d, *J* = 1.4 Hz, (EtO)C=CH_AH_B), 4.42 (1H, d, *J* = 3.2 Hz, H14), 4.84 (1H, d, *J* = 1.4 Hz, H16a), 4.85 (1H, d, *J* = 1.4 Hz, (EtO)C=CH_AH_B), 5.14 (1H, d, *J* = 1.4 Hz, H16b); ^{13}C NMR (100 MHz, C_6D_6) δ 13.4, 14.5, 17.7, 18.4, 18.5, 19.2, 21.5, 33.0, 33.6, 62.7, 67.4, 80.4, 82.1, 83.9, 85.4, 110.9, 118.5, 146.7, 160.1; HRMS (ESI) calcd for $C_{25}H_{44}O_5SiNa$, 475.2850 ($M+Na^+$), found 475.2878.



O,Se-Acetal 27. *m*-CPBA (75% purity, 283 mg, 1.23 mmol) was added to a solution of **21** (1.11 g, 2.46 mmol) in a mixture of CH_3CN/H_2O (35 mL, 2:1) at 10 °C. The equal amount of *m*-CPBA was added to the reaction mixture at 10 °C in every 20 min twice. Once TLC indicated the disappearance of **21**, the reaction temperature was carefully raised to 15~17 °C. After completion of the reaction was indicated on TLC, saturated aqueous $NaHCO_3$ (5 mL) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (10 mL ×3). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL ×2), saturated aqueous NH_4Cl (10 mL ×2), saturated aqueous $NaHCO_3$ (10 mL), and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated to afford crude hydroxyketone **22**, which was used for the next reaction without further purification. For a characterization, a small amount of hydroxyketone **22** was purified by flash chromatography (Fuji Silysia silica gel, hexane/EtOAc 10:1): white crystal m.p. 58-60 °C; $[\alpha]_D^{24}$ +108 (*c* 0.78, MeOH); IR (neat) ν_{max} 3535, 2944, 2867, 1718, 1461, 1400, 1305, 1263, 1154, 1077 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.92 (3H, d, *J* = 7.3 Hz, H18), 0.96-1.04 (3H, m, SiC*H*$(CH_3)_2$ x 3), 1.07 (9H, d, *J* = 6.9 Hz, SiCH(C*H*$_3$) x 3), 1.10 (9H, d, *J* = 6.9 Hz, SiCH(C*H*$_3$) x 3), 1.42 (1H, d, *J* = 14.6 Hz, H12a), 1.60 (3H, s, H17), 1.62 (3H, s, CC*H*$_3$), 1.68 (1H, dd, *J* = 14.6, 9.2 Hz, H12b), 2.51 (1H, dq, *J* = 9.2, 7.3 Hz, H11), 3.14 (1H, t, *J* = 4.6, O*H*), 3.90 (1H, d, *J* = 3.2 Hz, H14), 4.28 (1H, d, *J* = 3.2 Hz, H8), 4.57 (1H, dd, *J* = 21.1, 4.6 Hz, COC*H*$_A$H$_B$OH), 4.79 (1H, s, H16a), 4.86 (1H, dd, *J* = 21.1, 4.6 Hz, COCH$_A$*H*$_B$OH), 5.03 (1H, s, H16b); ^{13}C NMR (100 MHz, C_6D_6) δ 13.0, 17.8, 18.0, 18.1, 19.0, 20.9, 33.1,

35.4, 69.0, 69.2, 79.8, 86.1, 88.0, 111.3, 118.5, 145.7, 212.9; HRMS (ESI) calcd for $C_{23}H_{40}O_6SiNa$, 463.2486 ($M+Na^+$), found 463.2476.

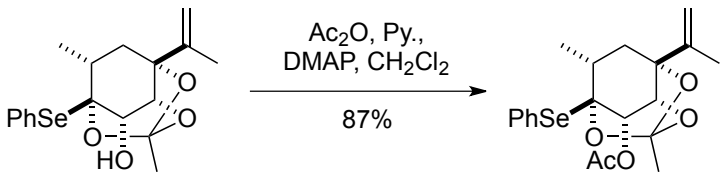
Me_3BnNOH (40% in MeOH, 4.5 mL, 9.9 mmol) and TBHP (70% in H_2O, 1.2 mL, 8.7 mmol) were successively added to a solution of crude hydroxyketone **22** in THF (7.4 mL) at 0 °C. The reaction mixture was stirred at 0 °C for for 10 min, and was allowed to warm to room temperature. After 1.5 h, solid NH_4Cl (2.63 g) and H_2O (1 mL) were added to the reaction mixture. The suspension was stirred for 20 min, then Na_2SO_4 was added. The insoluble salts were filtered through a pad of Celite with EtOAc (200 mL). The filtrate was concentrated, and the resultant residue was diluted with EtOAc (10 mL). White precipitate formation was observed. The precipitate was removed by passing the mixture through a pad of Celite with EtOAc (200 mL) and acetone (100 mL). The filtrate was concentrated. Toluene (30 mL) was added to the concentrate, and excess TBHP was removed azeotropically under reduced pressure twice to afford crude carboxylic acid **23**, which was used for the next reaction without further purification.

MsCl (0.38 mL, 4.9 mmol) was added to a solution of the above crude carboxylic acid **23** and Et_3N (3.4 mL, 2.5 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min, and was quenched with saturated aqueous $NaHCO_3$ (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL ×3). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated to afford crude mesylate **24**, which was used for the next reaction without further purification.

2-mercaptopyridine *N*-oxide sodium salt (733 mg, 4.92 mmol) and DMAP (60 mg, 0.49 mmol) were successively added to a solution of the above crude mesylate **24** in toluene (25 mL) at room temperature. The reaction flask was wrapped with aluminum foil, and the mixture was stirred at room temperature for 1 h. [HRMS (ESI) of Barton ester **25**, calcd for $C_{27}H_{41}NO_6SSiNa$, 558.2316 ($M+Na^+$), found 558.2327] Then, $(PhSe)_2$ (1.53 g, 4.92 mmol) was added to the reaction mixture. The aluminum foil was removed, and the reaction mixture was stirred under photo irradiation (a medium pressure mercury lamp, 100 W) at room temperature for 30 min. Saturated aqueous $NaHCO_3$ (10 mL) was added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted with EtOAc (10 mL ×3). The combined organic layer was washed with H_2O (10 mL ×2) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated to afford crude O,Se-acetal **26**, which was used for the next reaction without purification. For a characterization, a small amount of O,Se-acetal **26**

was purified by flash chromatography (Kanto silica gel, hexane/EtOAc 20:1 to 5:1): colorless oil; $[\alpha]_D^{24}$ +88 (*c* 0.61, MeOH); IR (neat) ν_{max} 2942, 2867, 1463, 1400, 1154, 1069 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.16-1.22 (21H, m, Si(C*H*(CH_3)$_2$)$_3$), 1.28 (3H, d, *J* = 6.9 Hz, H18), 1.48 (1H, d, *J* = 14.2 Hz, H12a), 1.63 (3H, s, H17), 1.67 (3H, s, CC*H*$_3$), 1.67 (1H, dd, *J* = 14.2, 8.7 Hz, H12b), 2.11 (1H, dq, *J* = 8.7, 6.9 Hz, H11), 3.89 (1H, d, *J* = 2.7 Hz, H8), 4.45 (1H, d, *J* = 2.7 Hz, H14), 4.80 (1H, m, H16a), 5.03 (1H, s, H16b), 7.03-7.07 (3H, m, aromatic), 7.86-7.88 (2H, m, aromatic); ^{13}C NMR (100 MHz, C_6D_6) δ 13.6, 18.5, 18.6, 19.0, 19.2, 21.0, 34.8, 39.3, 70.7, 80.7, 85.3, 92.0, 111.2, 119.5, 128.7, 130.6, 136.5, 146.0; HRMS (ESI) calcd for $C_{27}H_{42}O_4SeSiNa$, 561.1910 ($M+Na^+$), found 561.1904.

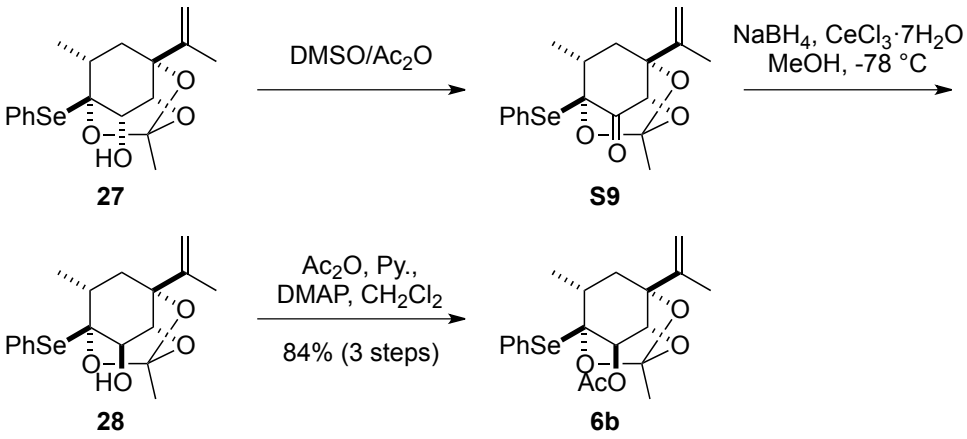
TBAF (1.0 M solution in THF, 3.0 mL, 3.0 mmol) was added to a solution of the above crude **26** in THF (25 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min, and was quenched with saturated aqueous NH_4Cl (10 mL). The mixture was extracted with EtOAc (10 mL ×3). The combined organic layers were washed with H_2O (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Kanto silica gel 30 g, hexane/EtOAc 10:1 to 5:1) to afford O,Se-acetal **27** (373 mg, 0.980 mmol) in 40% yield over 5 steps: yellow oil; $[\alpha]_D^{24}$ +95.7 (*c* 1.45, MeOH); IR (neat) ν_{max} 3467, 2934, 1438, 1398, 1302, 1170, 1124, 1102, 1070 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.25 (1H, dd, *J* = 14.6, 8.7 Hz, H12a), 1.43 (1H, d, *J* = 14.6 Hz, H12b), 1.43 (3H, s, H17), 1.50 (3H, d, *J* = 7.3 Hz, H18), 1.60 (3H, s, CC*H*$_3$), 1.88 (1H, dq, *J* = 8.7, 7.3 Hz, H11), 3.14 (1H, dd, *J* = 10.0, 3.2 Hz, H8), 3.21 (1H, m, O*H*), 4.15 (1H, dd, *J* = 3.2, 1.4 Hz, H14), 4.71 (1H, m, H16a), 4.85 (1H, s, H16b), 7.00-7.06 (3H, m, aromatic), 7.86-7.89 (2H, m, aromatic): ^{13}C NMR (100 MHz, C_6D_6) δ 18.7, 18.8, 20.8, 33.7, 36.7, 67.0, 80.4, 85.5, 93.6, 111.2, 119.5, 129.1, 138.4, 145.5. Two peaks overlap with solvent peak; HRMS (ESI), calcd for $C_{18}H_{22}O_4SeNa$, 405.0576 ($M+Na^+$), found 405.0580.



27 **6a**

Acetate 6a. Ac_2O (95 μL, 1.0 mmol), pyridine (0.33 mL, 4.0 mmol), and DMAP (2.5 mg, 0.20 μmol) were successively added to a solution of O,Se-acetal **27** (38 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) at room temperature. The mixture was stirred at room

temperature for 24 h, and was quenched with saturated aqueous $NaHCO_3$ (5 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (5 mL ×3). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Kanto silica gel 10 g, hexane/EtOAc 20:1) to afford acetate **6a** (37 mg, 87 μmol) in 87% yield: colorless oil; $[\alpha]_D^{25}$ +88.0 (*c* 1.43, MeOH); IR (neat) ν_{max} 2977, 2936, 1735, 1439, 1401, 1376, 1239, 1100 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.46 (3H, d, *J* = 6.8 Hz, H18), 1.47-1.49 (2H, m, H12), 1.48 (3H, s, H17), 1.65 (3H, s, CC*H*$_3$), 1.78 (3H, s, Ac), 1.87 (1H, m, H11), 4.41 (1H, d, *J* = 3.6 Hz, H14), 4.72 (1H, m, H16a), 4.89 (1H, d, *J* = 3.6 Hz, H8), 4.90 (1H, s, H16b), 7.10-7.04 (3H, m, aromatic), 7.74-7.77 (2H, m, aromatic); ^{13}C NMR (100 MHz, C_6D_6) δ 18.8, 18.9, 20.7, 20.9, 34.0, 37.3, 69.7, 78.4, 85.5, 88.9, 111.6, 119.9, 128.6, 129.0, 129.4, 137.0, 145.3, 170.2; HRMS (ESI) calcd for $C_{20}H_{24}O_5SeNa$, 447.0681 ($M+Na^+$), found 447.0673.

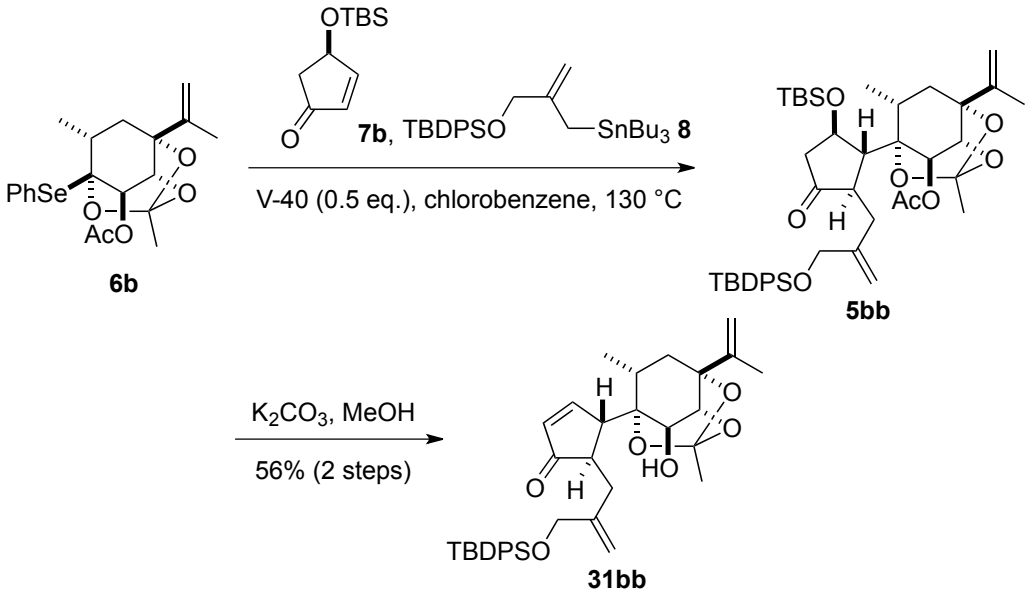


Acetate 6b. A solution of O,Se-acetal **27** (373 mg, 0.980 mmol) in DMSO/Ac_2O (9.8 mL, 4:1) was stirred at 35 °C for 2 h. Then, the reaction mixture was cooled to 0 °C, and was quenched with saturated aqueous $NaHCO_3$ (15 mL). EtOAc (10 mL) was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with H_2O (10 mL ×2) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated to afford crude ketone **S9**, which was used for the next reaction without purification.

$CeCl_3·7H_2O$ (728 mg, 1.95 mmol) and $NaBH_4$ (74 mg, 2.0 mmol) were successively added to a solution of the above crude ketone **S9** in MeOH (14 mL) at -78 °C. The reaction mixture was stirred for 10 min at -78 °C, and was quenched with saturated aqueous NH_4Cl (10 mL). EtOAc (5 mL) was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc (10 mL × 3). The combined

organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated to afford crude alcohol **28**, which was used for the next reaction without purification. For a characterization, a small amount of alcohol **28** was purified by flash chromatography (Kanto silica gel, hexane/EtOAc 20:1 to 5:1): white solid; m.p. 99-101 °C; $[\alpha]_D^{24}$ +47 (*c* 0.36, MeOH); IR (neat); ν_{max} 3490, 2928, 1441, 1398, 1298, 1109, 1073, 1038 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.53 (3H, d, *J* = 7.3 Hz, H18), 1.58 (1H, d, *J* = 13.7 Hz, H12a), 1.61 (3H, s, H17), 1.64 (3H, s, CC*H*$_3$), 1.79 (1H, br s, O*H*), 2.26 (1H, dq, *J* = 9.2, 7.3H, H11), 2.53 (1H, dd, *J* = 13.7, 9.2 Hz, H12b), 3.83 (1H, br s, H8), 4.03 (1H, d, *J* = 2.3 Hz, H14), 4.80 (1H, m, H16a), 5.11 (1H, m, H16b), 7.01-7.07 (3H, m, aromatic), 7.66-7.69 (2H, m, aromatic); ^{13}C NMR (100 MHz, C_6D_6) δ 18.9, 20.2, 20.4, 34.1, 34.4, 69.5, 78.1, 84.9, 92.6, 111.1, 119.6, 127.4, 128.8, 128.9, 137.1, 146.2; HRMS (ESI) calcd for $C_{18}H_{22}O_4SeNa$, 405.0576 ($M+Na^+$), found 405.0573.

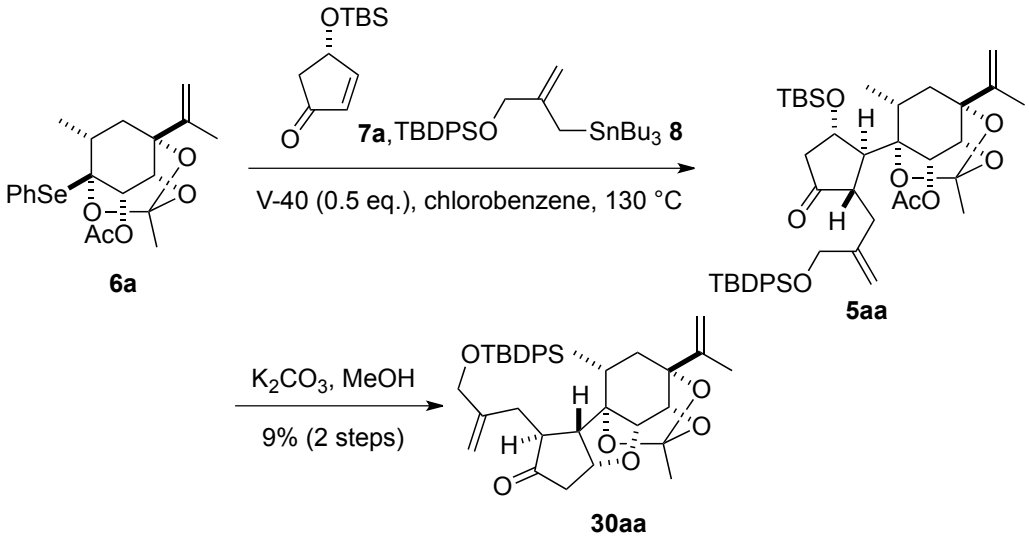
Ac_2O (0.46 mL, 4.9 mmol), pyridine (1.6 mL, 20 mmol) and DMAP (24 mg, 0.20 mmol) were successively added to a solution of the above crude alcohol **28** in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 12 h, and was quenched with saturated aqueous $NaHCO_3$ (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL ×3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Kanto silica gel 20 g, hexane/EtOAc 20:1 to 10:1) to afford acetate **6b** (350 mg, 0.83 mmol) in 84% over 3 steps: colorless oil; $[\alpha]_D^{22}$ +4.4 (*c* 0.39, MeOH); IR (neat) ν_{max} 2969, 2934, 1750, 1440, 1399, 1373, 1223, 1064 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.59 (3H, s, H17), 1.66 (3H, d, *J* = 6.9 Hz, H18), 1.70 (3H, s, CC*H*$_3$), 1.73 (3H, s, Ac), 1.74 (1H, d, *J* = 12.4 Hz, H12a), 2.33 (1H, dd, *J* = 12.4, 9.2 Hz, H12b), 2.36 (1H, dq, *J* = 9.2, 6.9 Hz, H11), 4.20 (1H, d, *J* = 2.3 Hz, H14), 4.85 (1H, m, H16a), 5.11 (1H, s, H16b), 5.50 (1H, d, *J* = 2.3 Hz, H8), 7.13-7.18 (3H, m, aromatic), 7.92-7.95 (2H, m, aromatic); ^{13}C NMR (100 MHz, C_6D_6) δ 18.7, 20.0, 20.1, 20.4, 34.4, 34.8, 70.4, 76.9, 84.6, 88.3, 111.3, 119.7, 127.0, 128.8, 129.2, 138.2, 145.8, 168.4; HRMS (ESI) calcd for $C_{20}H_{24}O_5SeNa$, 447.0681 ($M+Na^+$), found 447.0677.



***General procedure A*: Compound 31bb**. A two-neck round-bottomed flask equipped with a reflux condenser was charged with **6b** (49 mg, 115 μmol), **7b** (123 mg, 580 μmol), V-40 (7 mg, 29 μmol) and chlorobenzene (0.8 mL). A separate pear-shaped flask was charged with **8** (348 mg, 580 μmol), V-40 (7 mg, 29 μmol) and chlorobenzene (0.4 mL). Both solutions were degassed by freeze-thaw procedure (x3). The latter solution was added to the refluxing former mixture by a syringe pump over 30 min, and then the reaction mixture was concentrated to afford crude **5bb**, which was used for the next reaction without purification.

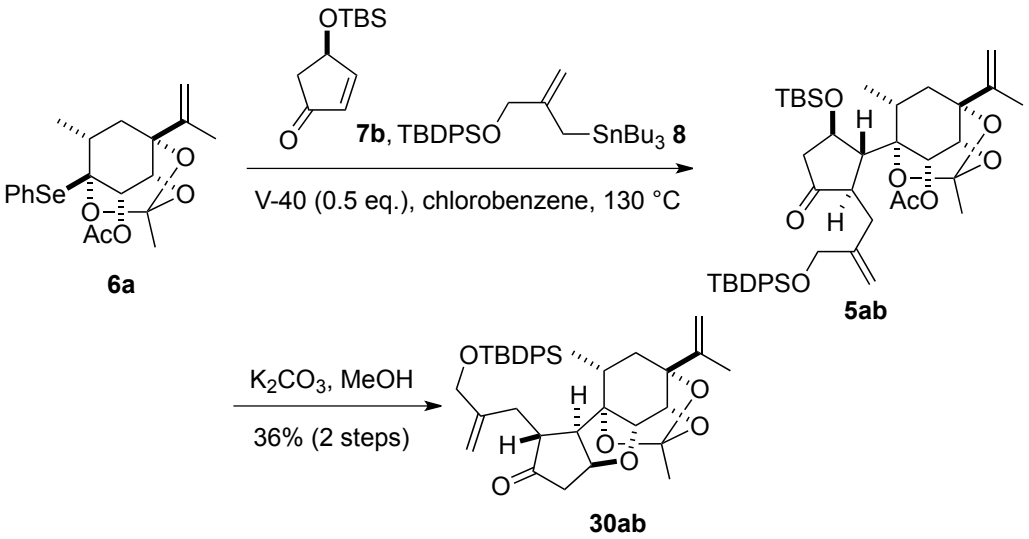
A mixture of the above crude **5bb** and K_2CO_3 (14 mg, 100 μmol) in MeOH (2.3 mL) was stirred at room temperature for 3 h. Upon completion of the reaction indicated by ESI-MS, the reaction was quenched with saturated aqueous NH_4Cl (10 mL). The aqueous layer was extracted with EtOAc (10 mL ×3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (a column consecutively packed with Kanto silica gel 20 g and 10% (w/w) KF contained Kanto silica gel 7 g, hexane/EtOAc 10:1 to 5:1) to afford **31bb** (40 mg, 65 μmol) in 56% yield over 2 steps: colorless oil; $[\alpha]_D^{22}$ +131 (*c* 0.54, MeOH); IR (neat) ν_{max} 3432, 2931, 2855, 1693, 1399, 1110 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.17 (9H, s, *t*-Bu of TBDPS), 1.23 (3H, d, *J* = 7.3 Hz, H18), 1.64 (1H, d, *J* = 13.7 Hz, H12a), 1.71 (3H, s, H17), 1.72 (3H, s, CC*H*$_3$), 2.14 (1H, dq, *J* = 9.2, 7.3 Hz, H11), 2.24 (1H, dd, *J* = 15.1, 4.6 Hz, H5a), 2.43 (1H, dd, *J* = 15.1, 6.0 Hz, H5b), 2.54 (1H, dd, *J* = 13.7, 9.2 Hz, H12b), 3.03 (2H, m, H4 and 10), 3.54 (1H, m, H8), 3.73 (1H, m, H14), 4.09 (1H, d, *J* = 14.6 Hz, H20a), 4.24 (1H, d, *J* = 14.6 Hz,

H20b), 4.89 (2H, m, H7a and 16a), 5.21 (1H, s, H16b), 5.38 (1H, s, H7b), 5.97 (1H, d, *J* = 5.5 Hz, H2), 7.22-7.24 (6H, m, aromatic), 7.46 (1H, dd, *J* = 5.5, 2.3 Hz, H1), 7.76-7.79 (4H, m, aromatic); ^{13}C NMR (100 MHz, C_6D_6) δ 18.5, 19.1, 19.5, 20.9, 27.0, 30.3, 35.01, 35.04, 45.8, 52.3, 66.4, 68.2, 78.9, 82.4, 84.7, 110.9, 112.0, 118.5, 130.0, 133.79, 133.82, 134.5, 135.87, 135.89, 145.1, 146.8, 166.8, 211.7. Two peaks overlap with solvent peak; HRMS (ESI) calcd for $C_{37}H_{46}O_6SiNa$, 637.2956 ($M+Na^+$), found 637.2982.

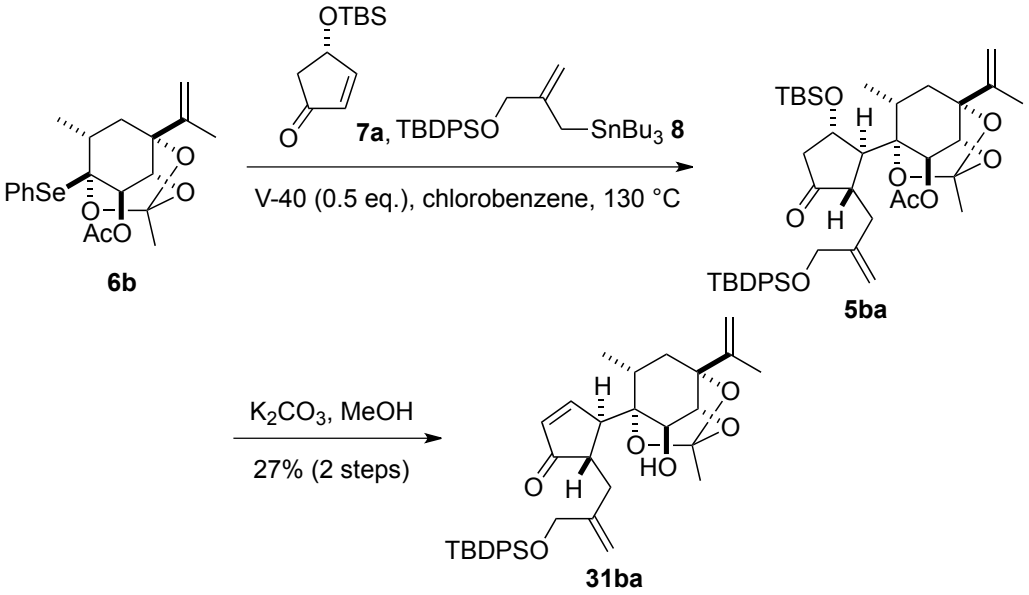


Compound 30aa. According to the general procedure A, **30aa** (1.4 mg, 2.3 μmol) was synthesized from **6a** (11 mg, 26 μmol) in 9% yield over 2 steps by using **7a** (27 mg, 0.13 mmol), **8** (76 mg, 0.13 mmol), V-40 (3.0 mg, 12 μmol), chlorobenzene (0.26 mL), K_2CO_3 (1.8 mg, 13 μmol), and MeOH (1.3 mL). The crude reside was purified by flash chromatography (a column consecutively packed with Kanto silica gel 5 g and 10% (w/w) KF contained Kanto silica gel 3 g, hexane/EtOAc 10:1 to 5:1): colorless oil; $[\alpha]_D^{24}$ +12 (*c* 0.10, MeOH); IR (neat) ν_{max} 2926, 2855, 1740, 1402, 1110 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 1.00 (3H, d, *J* = 7.3 Hz, H18), 1.19 (9H, s, *t*-Bu of TBDPS), 1.31-1.41 (2H, m, H11 and 12a), 1.52 (3H, s, H17), 1.58 (3H, s, CCH_3), 1.52-1.60 (1H, m, H12b), 1.75 (1H, dd, *J* = 14.2, 10.5 Hz, H5a), 2.21 (1H, d, *J* = 8.7 Hz, H10), 2.30 (1H, dd, *J* = 14.2, 5.0 Hz, H5b), 2.45 (1H, dd, *J* = 19.2, 8.7 Hz, H2a), 2.84 (1H, dd, *J* = 19.2, 5.0 Hz, H2b), 2.88 (1H, d, *J* = 10.5, 5.0 Hz, H4), 3.21 (1H, d, *J* = 3.2 Hz, H8), 4.09 (1H, d, *J* = 14.2 Hz, H20a), 4.19 (1H, d, *J* = 14.2 Hz, H20b), 4.23 (1H, d, *J* = 3.2 Hz, H14), 4.69 (1H, td, *J* = 8.7, 5.0 Hz, H1), 4.76 (1H, s, H16a), 4.84 (1H, s, H7a), 4.98 (1H, s, H16b), 5.38 (1H, s, H7b), 7.21-7.25 (6H, m, aromatic), 7.76-7.81 (4H, m, aromatic); ^{13}C NMR (100 MHz, C_6D_6) δ 18.1, 18.8, 19.5, 20.8, 27.0, 34.7, 35.7, 36.4,

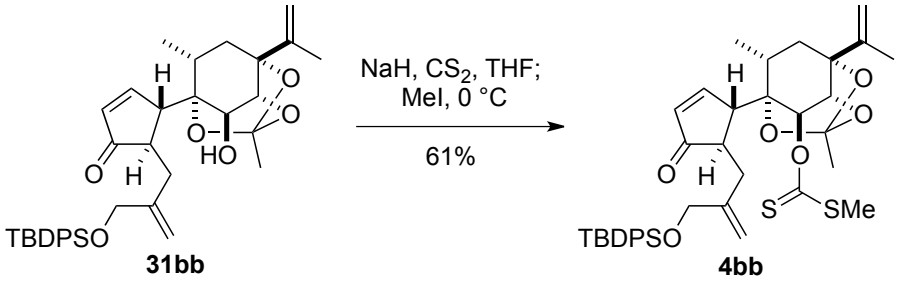
44.2, 47.9, 55.0, 66.2, 76.0, 79.1, 81.6, 82.8, 86.4, 111.0, 111.9, 118.4, 130.09, 130.13, 133.7, 133.8, 135.91, 135.94, 145.7, 146.0, 214.6. Two peaks overlap with solvent peak; HRMS (ESI) calcd for $C_{37}H_{46}O_6SiNa$, 637.2956 ($M+Na^+$), found 637.2957.



Compound 30ab. According to the general procedure A, **30ab** (7.6 mg, 12 μmol) was synthesized from **6a** (15 mg, 34 μmol) in 36% yield over 2 steps by using **7b** (36 mg, 0.17 mmol), **8** (102 mg, 0.17 mmol), V-40 (4.2 mg, 17 μmol), chlorobenzene (0.68 mL), K_2CO_3 (2.4 mg, 17 μmol), and MeOH (1.7 mL). The crude reside was purified by flash chromatography (a column consecutively packed with Kanto silica gel 8 g and 10% (w/w) KF contained Kanto silica gel 4 g, hexane/EtOAc 10:1 to 5:1): colorless oil; $[\alpha]_D^{20}$ +23 (*c* 0.30, MeOH); IR (neat) ν_{max} 2928, 2855, 1743, 1430, 1399, 1296, 1108 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.14 (3H, d, *J* = 6.4 Hz, H18), 1.18 (9H, s, *t*-Bu of TBDPS), 1.42-1.53 (3H, m, H11 and 12), 1.59 (3H, s, H17), 1.69 (1H, m, H4), 1.76 (3H, s, CCH_3), 1.77 (1H, dd, *J* = 18.8, 5.0 Hz, H2a), 2.05 (1H, dd, *J* = 14.5, 6.9 Hz, H5a), 2.23 (1H, dd, *J* = 9.6, 5.0 Hz, H10), 2.46 (1H, d, *J* = 14.5 Hz, H5b), 2.47 (1H, d, *J* = 18.8 Hz, H2b), 3.01 (1H, d, *J* = 2.8 Hz, H8), 4.01 (1H, d, *J* = 14.7 Hz, H20a), 4.22 (1H, d, *J* = 2.8 Hz, H14), 4.26 (1H, d, *J* = 14.7 Hz, H20b), 4.83 (1H, br s, H16a), 4.85 (1H, t, *J* = 5.0 Hz, H1), 4.96 (1H, s, H7a), 5.08 (1H, s, H16b), 5.51 (1H, s, H7b), 7.18-7.23 (6H, m, aromatic), 7.76-7.79 (4H, m, aromatic); ^{13}C NMR (100 MHz, C_6D_6) δ 18.7, 19.1, 19.5, 21.3, 27.0, 31.7, 33.4, 35.2, 44.7, 46.4, 52.2, 66.7, 75.6, 76.6, 82.2, 86.0, 86.8, 110.9, 112.7, 118.1, 130.1, 133.66, 133.74, 135.8, 135.9, 144.9, 146.2, 216.3. Two peaks overlap with solvent peak; HRMS (ESI) calcd for $C_{37}H_{46}O_6SiNa$, 637.2956 ($M+Na^+$), found 637.2955.

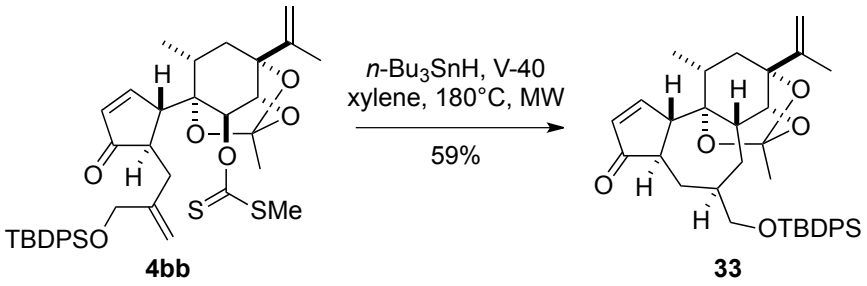


Compound 31ba. According to the general procedure A, **31ba** (10 mg, 16 μmol) was synthesized from **6b** (26 mg, 61 μmol) in 27% yield over 2 steps by using **7a** (64 mg, 0.30 mmol), **8** (181 mg, 0.30 mmol), V-40 (7.5 mg, 30 μmol), chlorobenzene (1.5 mL), K_2CO_3 (4.2 mg, 30 μmol), and MeOH (3.0 mL). The crude reside was purified by flash chromatography (a column consecutively packed with Kanto silica gel 10 g and 10% (w/w) KF contained Kanto silica gel 5 g, hexane/EtOAc 10:1 to 5:1): colorless oil; $[\alpha]_D^{20}$ -44 (*c* 0.18, MeOH); IR (neat) ν_{max} 3445, 2931, 2857, 1692, 1399, 1298, 1110 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.19 (9H, s, *t*-Bu of TBDPS), 1.17 (3H, d, *J* = 8.2 Hz, H18), 1.56 (3H, s, CC*H*$_3$), 1.64 (1H, d, *J* = 13.7 Hz, H12a), 1.71 (3H, s, H17), 2.06 (1H, m, H11), 2.43-2.60 (4H, m, H12b, 4 and 5), 2.99 (1H, br s, H10), 3.32 (1H, m, H8), 3.82 (1H, d, *J* = 7.7 Hz, H14), 4.21 (1H, d, *J* = 14.6 Hz, H20a), 4.29 (1H, d, *J* = 14.6 Hz, H20b), 4.88 (1H, m, H16a), 5.02 (1H, s, H7a), 5.20 (1H, s, H16b), 5.47 (1H, s, H7b), 5.77 (1H, dd, *J* = 5.9, 2.3 Hz, H2), 7.07 (1H, m, H1), 7.22-7.24 (6H, m, aromatic), 7.78-7.82 (4H, m, aromatic); ^{13}C NMR (100 MHz, C_6D_6) δ 18.5, 19.1, 19.5, 20.6, 27.1, 30.1, 34.9, 35.0, 46.3, 51.5, 66.6, 66.8, 78.6, 82.7, 84.7, 110.9, 111.9, 118.4, 127.9, 128.1, 130.0, 132.3, 134.0, 135.91, 135.93, 146.2, 146.8, 164.1, 210.4; HRMS (ESI) calcd for $C_{37}H_{46}O_6SiNa$, 637.2956 ($M+Na^+$), found 637.2984.



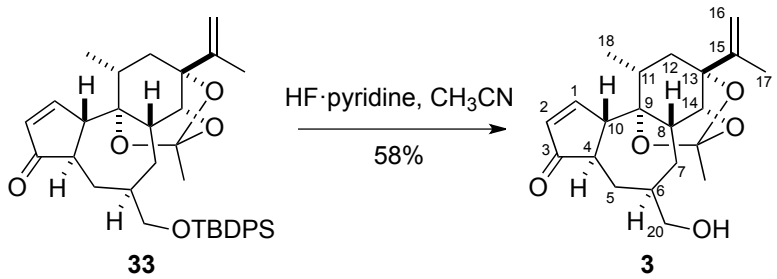
31bb **4bb**

Xanthate 4bb. CS_2 (5.0 μL, 83 μmol) and NaH (50-70% in oil, 3.5 mg, ca. 88 μmol) were successively added to a solution of **31bb** (27 mg, 44 μmol) in THF (2.2 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 10 min, and then MeI (5.0 μL, 80 μmol) was added. The mixture was allowed to warm to room temperature and stirred for further 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL). The mixture was extracted with EtOAc (5 mL ×3). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Kanto silica gel 15 g, hexane/EtOAc 20:1) to afford xanthate **4bb** (19 mg, 27 μmol) in 61% yield: yellow oil; $[\alpha]_D^{20}$ +137 (*c* 0.38, MeOH); IR (neat) ν_{max} 2962, 2932, 2857, 1712, 1400, 1198, 1108 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 1.19 (9H, s, *t*-Bu of TBDPS), 1.25 (3H, d, *J* = 7.3 Hz, H18), 1.58 (3H, s, H17), 1.69 (3H, s, CCH_3), 1.70 (1H, d, *J* = 14.2 Hz, H12a), 1.97 (3H, s, $C(=S)SCH_3$), 2.20 (1H, dq, *J* = 9.2, 7.3 Hz, H11), 2.23 (1H, dd, *J* = 14.7, 6.9 Hz, H5a), 2.35 (1H, dd, *J* = 14.2, 9.2 Hz, H12b), 2.43 (1H, dd, *J* = 14.7, 5.9 Hz, H5b), 2.59 (1H, dd, *J* = 6.9, 5.9 Hz, H4), 2.98 (1H, br s, H10), 4.17 (1H, d, *J* = 14.7 Hz, H20a), 4.35 (1H, d, *J* = 14.7 Hz, H20b), 4.53 (1H, m, H14), 4.81 (1H, m, H16a), 4.93 (1H, s, H7a), 5.14 (1H, m, H16b), 5.41 (1H, m, H7b), 5.91 (1H, s, H8), 5.96 (1H, dd, *J* = 5.9, 1.8 Hz, H2), 7.21-7.24 (6H, m, aromatic), 7.28 (1H, dd, *J* = 5.9, 2.8 Hz, H1), 7.77-7.80 (4H, m, aromatic); ^{13}C NMR (100 MHz, C_6D_6) δ 18.6, 18.9, 19.2, 19.5, 20.5, 27.0, 31.3, 35.1, 35.8, 45.2, 52.2, 66.5, 75.1, 77.3, 81.8, 84.5, 111.4, 112.1, 119.0, 128.5, 130.0, 133.85, 133.95, 135.4, 135.9, 145.2, 145.8, 163.1, 207.9, 214.1. Two peaks overlap with solvent peak; HRMS (ESI) calcd for $C_{39}H_{48}O_6S_2SiNa$, 727.2544 ($M+Na^+$), found 727.2551.



4bb **33**

Compound 33. A flask was charged with xanthate **4bb** (60 mg, 85 μmol), *n*-Bu_3SnH (115 μL, 428 μmol) and V-40 (10 mg, 43 μmol) and degassed xylene (10 mL). The mixture was heated under microwave irradiation at 180 °C for 5 min. The reaction mixture was then concentrated, and the residue was purified by flash chromatography (a column consecutively packed with Kanto silica gel 8 g and 10% (w/w) KF contained Kanto silica gel 3 g, hexane/EtOAc 5:1) to afford **33** (30 mg, 50 μmol) in 59% yield: colorless oil; $[\alpha]_D^{19}$ +120 (*c* 0.17, MeOH); IR (neat) ν_{max} 3007, 2934, 2858, 1708, 1399, 1296, 1108 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.80 (1H, ddd, *J* = 13.7, 13.7, 8.7 Hz, H5a), 1.16-1.19 (1H, m, H8), 1.17 (9H, s, *t*-Bu of TBDPS), 1.18 (3H, d, *J* = 6.9 Hz, H18), 1.45-1.55 (2H, m, H7a and 11), 1.55 (3H, s, CC*H*$_3$), 1.56 (1H, d, *J* = 14.2 Hz, H12a), 1.69 (3H, s, H17), 1.72 (1H, dd, *J* = 14.2, 8.2 Hz, H12b), 2.03 (1H, br dd, *J* = 10.6, 4.1 Hz, H7b), 2.07 (1H, m, H10), 2.46 (1H, m, H6), 2.55 (1H, ddd, *J* = 13.7, 4.6, 4.6 Hz, H5b), 3.03 (1H, ddd, *J* = 13.7, 4.6, 4.6 Hz, H4), 3.47 (1H, dd, *J* = 10.1, 8.2 Hz, H20a), 3.59 (1H, dd, *J* = 10.1, 6.0 Hz, H20b), 4.00 (1H, d, *J* = 2.3 Hz, H14), 4.85 (1H, t, *J* = 1.8 Hz, H16a), 5.03 (1H, s, H16b), 5.96 (1H, dd, *J* = 6.0, 2.8 Hz, H2), 7.09 (1H, dd, *J* = 6.0, 1.8 Hz, H1), 7.22-7.28 (6H, m, aromatic), 7.78-7.81 (4H, m, aromatic); ^{13}C NMR (100 MHz, C_6D_6) δ 18.9, 19.5, 20.9, 21.4, 27.1, 31.4, 33.3, 35.4, 36.8, 37.1, 38.8, 46.2, 56.7, 69.1, 77.8, 84.0, 84.7, 110.7, 118.4, 129.99, 130.03, 133.1, 134.1, 134.3, 135.97, 136.04, 147.2, 160.3, 207.6. Two peaks overlap with solvent peak; HRMS (ESI) calcd for $C_{37}H_{46}O_5SiNa$, 621.3007 ($M+Na^+$), found 621.3012.



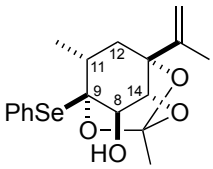
33 **3**

Compound 3. A plastic test tube was charged with **33** (6.8 mg, 11 μmol) and CH_3CN (1.1 mL). HF·pyridine (ca. 70% HF, 20 μL, 770 μmol for HF) was added to the

solution at 0 °C. While the mixture was stirred at room temperature for 2 h, additional HF·pyridine (100 μL) was added three times every 30 min. The reaction mixture was carefully quenched with saturated aqueous $NaHCO_3$ (10 mL). The mixture was extracted with EtOAc (5 mL ×3). The combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (Kanto silica gel 10 g, hexane/EtOAc 5:1) to afford **3** (2.3 mg, 6.4 μmol) in 58% yield: colorless oil; $[\alpha]_D^{21}$ + 130 (*c* 0.21, MeOH); IR (neat) ν_{max} 3418, 2934, 1705, 1449, 1400, 1295, 1132 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.74 (1H, ddd, *J* = 13.8, 13.8, 10.1 Hz, H5a), 1.12 (1H, m, H8), 1.15 (3H, d, *J* = 6.9 Hz, H18), 1.30 (1H, m, H7a), 1.48 (1H, dq, *J* = 8.2, 6.9 Hz, H11), 1.52 (1H, d, *J* = 14.2 Hz, H12a), 1.53 (3H, s, CC*H*$_3$), 1.63 (3H, s, H17), 1.67 (1H, dd, *J* = 14.2, 8.2 Hz, H12b), 1.92 (1H, dd, *J* = 15.1, 2.3 Hz, H7b), 2.12-2.20 (2H, m, H6 and 10), 2.51 (1H, ddd, *J* = 13.8, 4.1, 4.1 Hz, H5b), 3.05 (1H, ddd, *J* = 13.8, 4.1, 4.1 Hz, H4), 3.11-3.17 (1H, m, H20a), 3.19-3.24 (1H, m, H20b), 3.94 (1H, s, H14), 4.83 (1H, t, *J* = 1.8 Hz, H16a), 4.99 (1H, s, H16b), 5.98 (1H, dd, *J* = 6.0, 2.8 Hz, H2), 7.08 (1H, d, *J* = 6.0 Hz, H1); ^{13}C NMR (100 MHz, C_6D_6) δ 18.9, 20.7, 21.4, 31.9, 33.8, 35.1, 36.9, 37.4, 38.9, 46.4, 56.5, 68.2, 77.8, 83.9, 84.7, 110.7, 118.3, 133.0, 147.1, 160.4, 207.7; HRMS (ESI) calcd for $C_{21}H_{28}O_5Na$, 383.1829 ($M+Na^+$), found 383.1835.

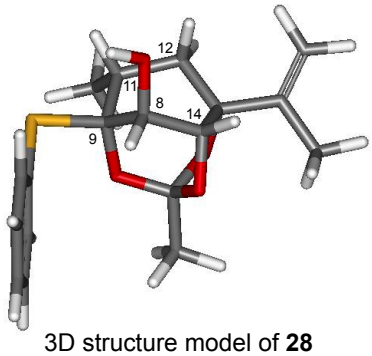
Molecular modeling

The 3D structure of **28**, in which Se atom was replaced with S atom, was built by the molecular mechanics simulation using a 1000-steps of mixed torsional/low-mode sampling conformational search and PRCG energy minimization with MM3* (MacroModel 9.9).[S2]



28

≡



3D structure model of **28**
(Se Atom was replaced with S atom)

S2. (a) *MacroModel version 9.9*; Schrodinger, LLC, New York, NY; (b) F. Mohamadi, N. G. J. Richards, W. C. Guida, R. Liskamp, M. Lipton, C. Caufield, G. Chang, T. Hendrickson, W. C. Still, *J. Comput. Chem.* **1990**, *11*, 440-467.

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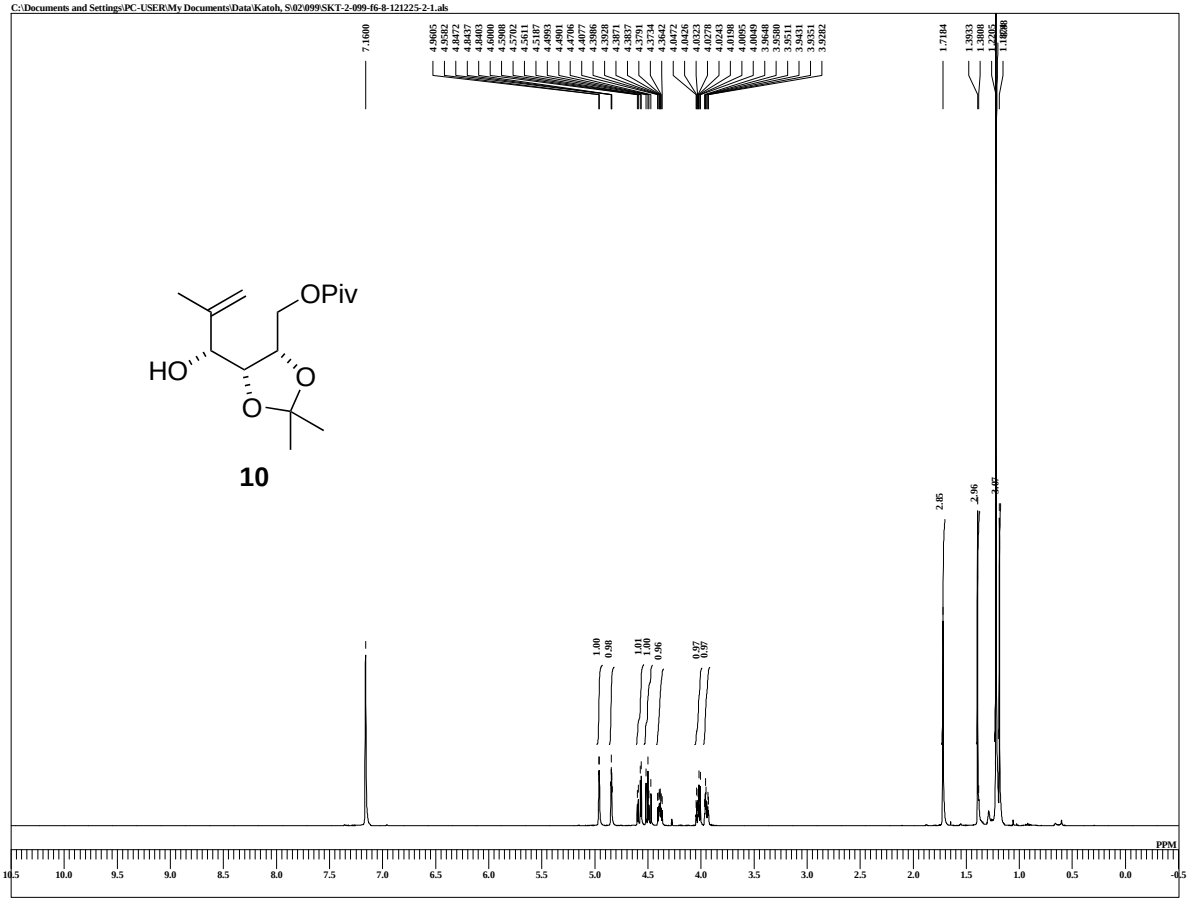

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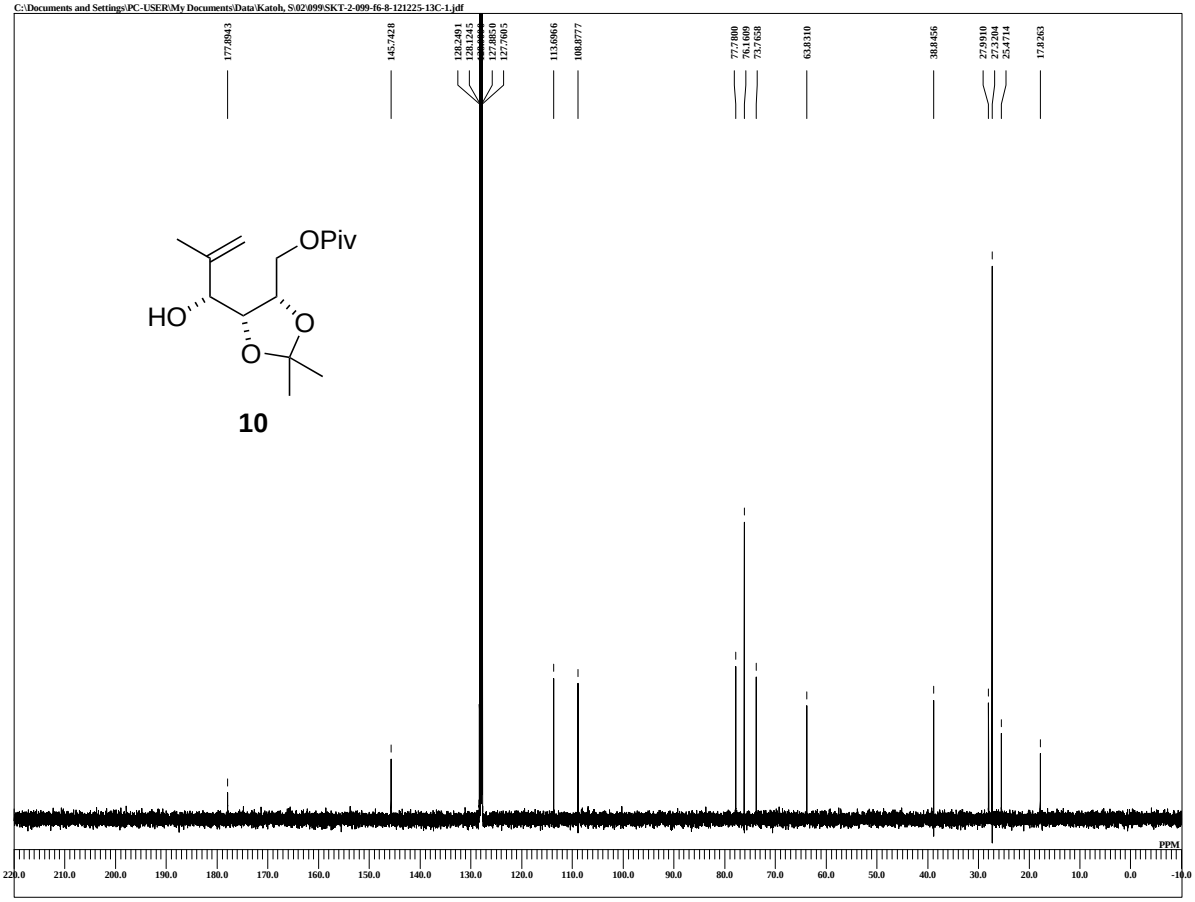

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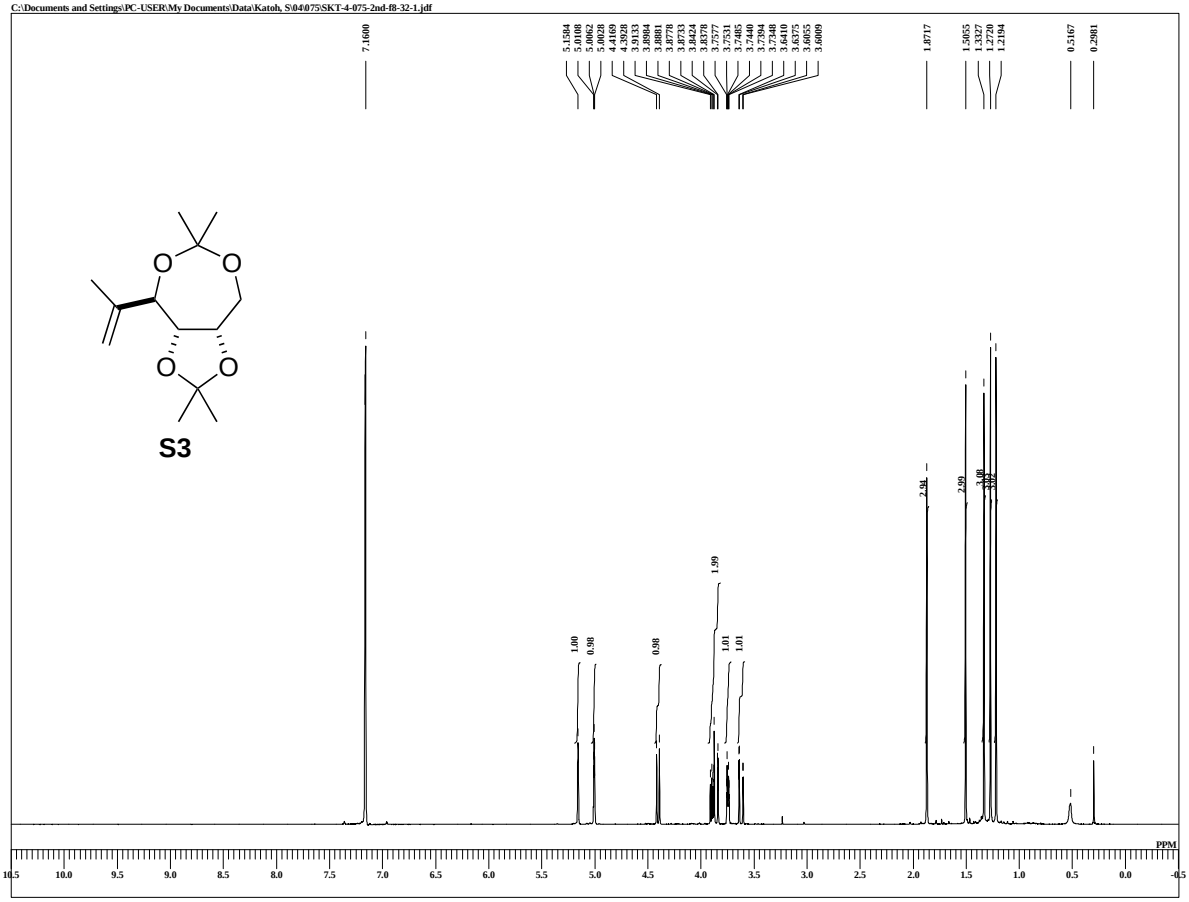

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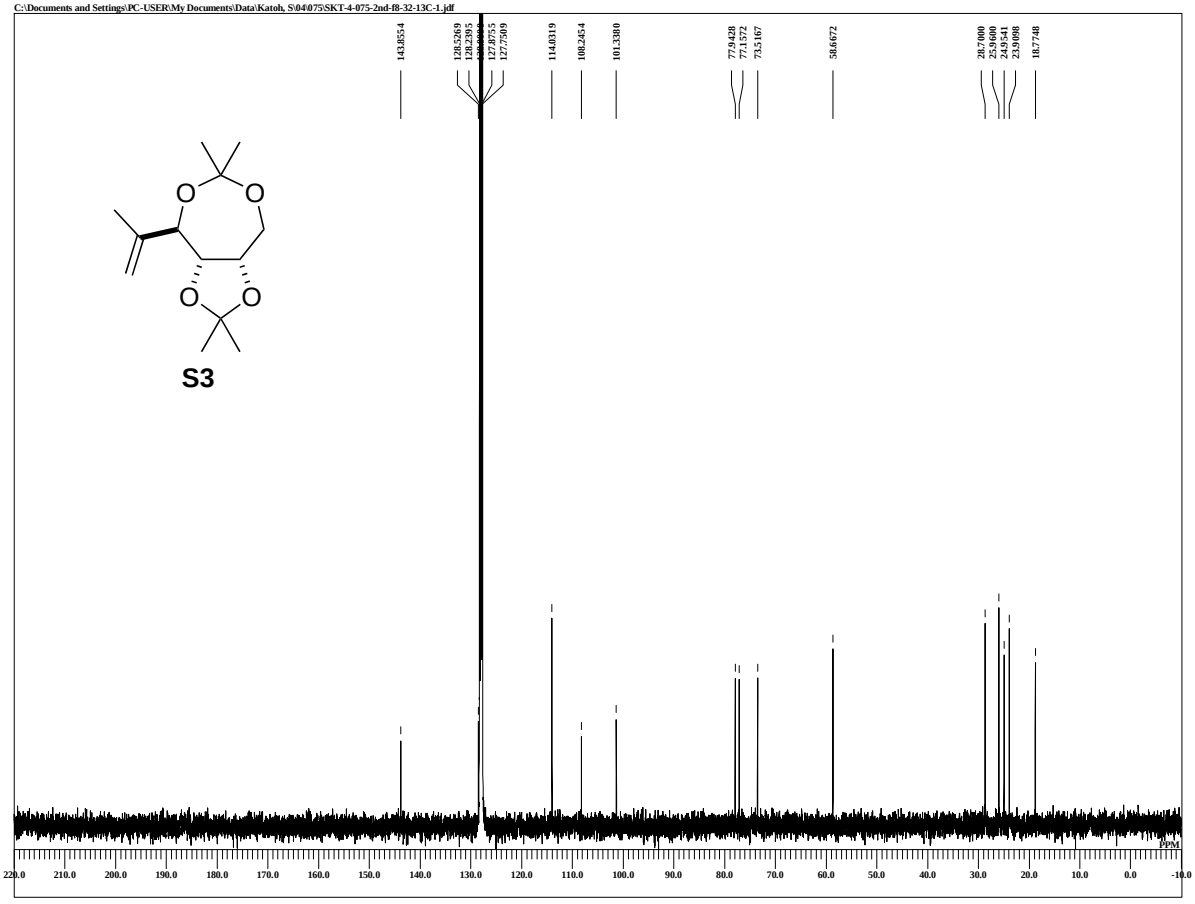

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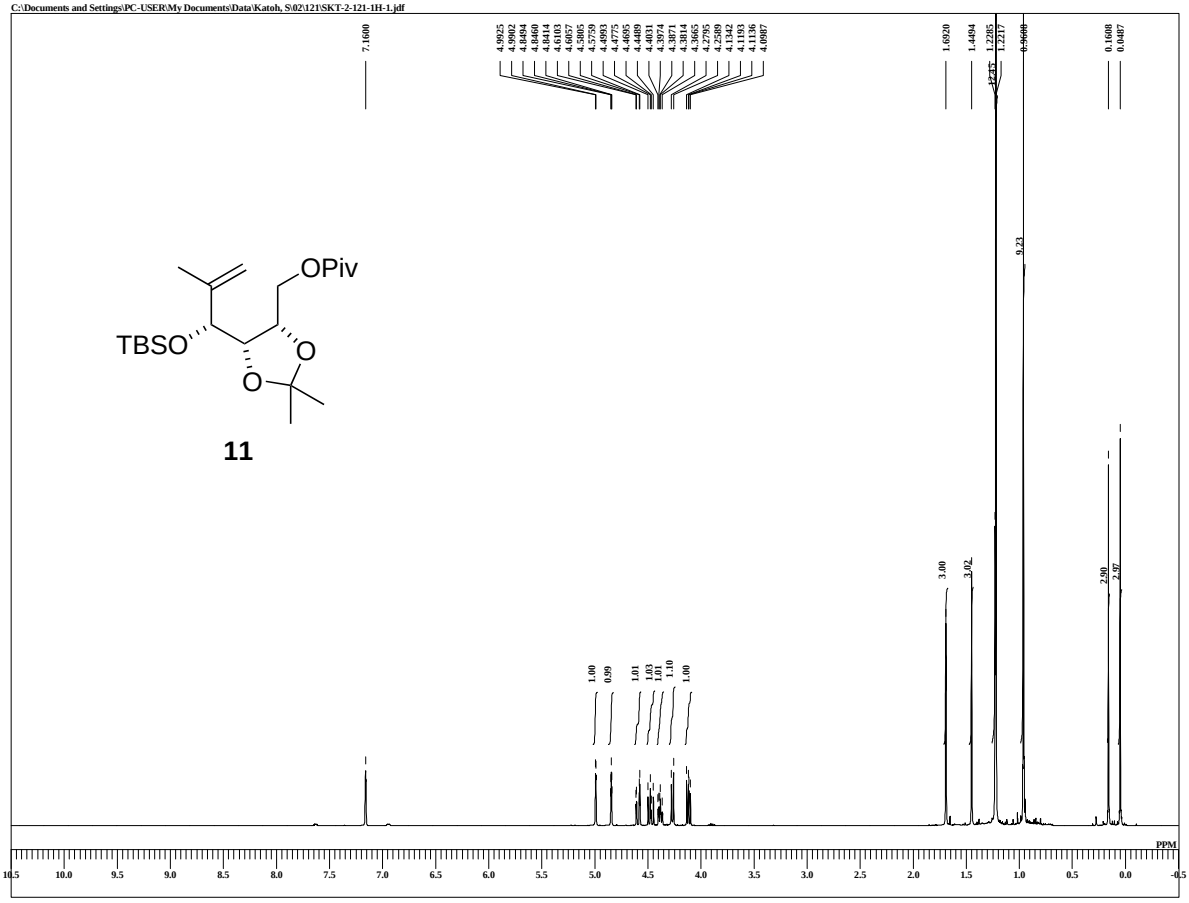


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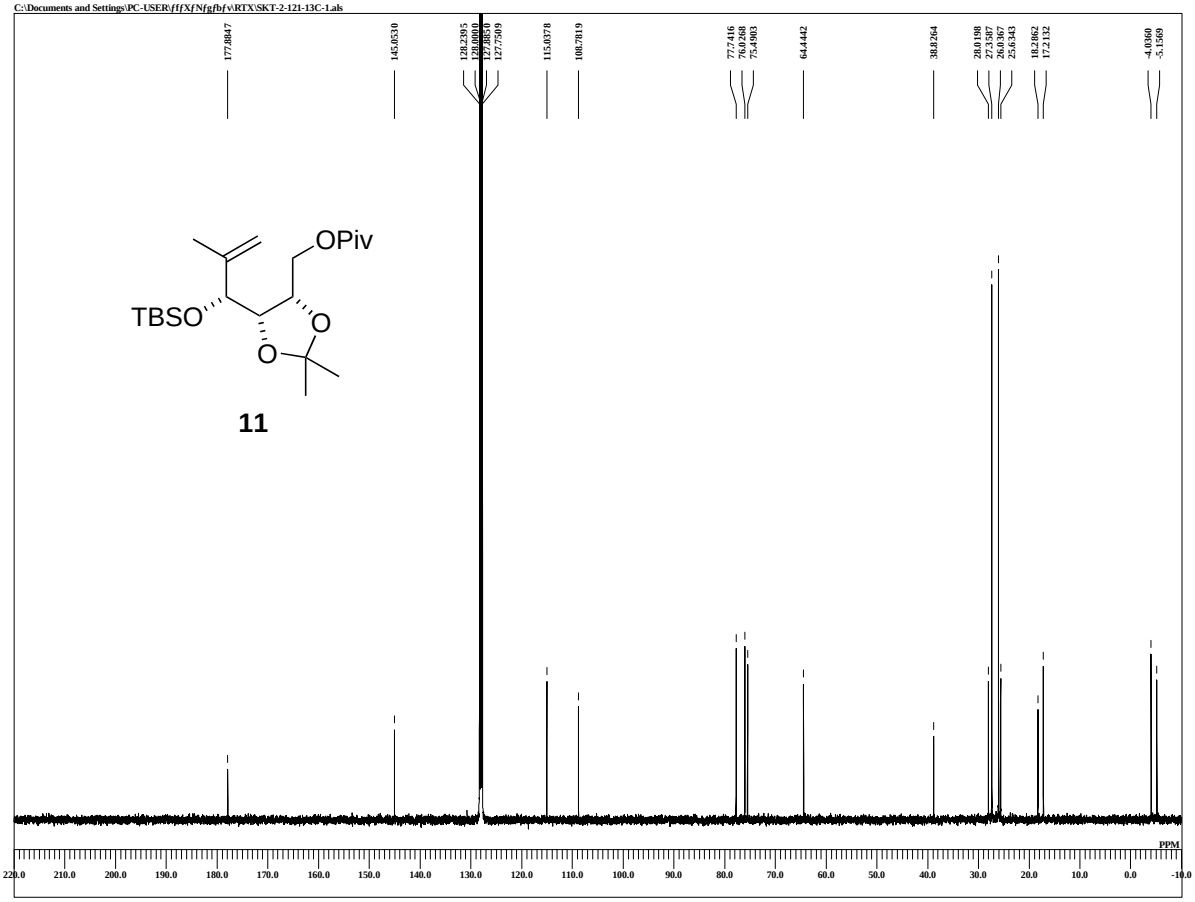


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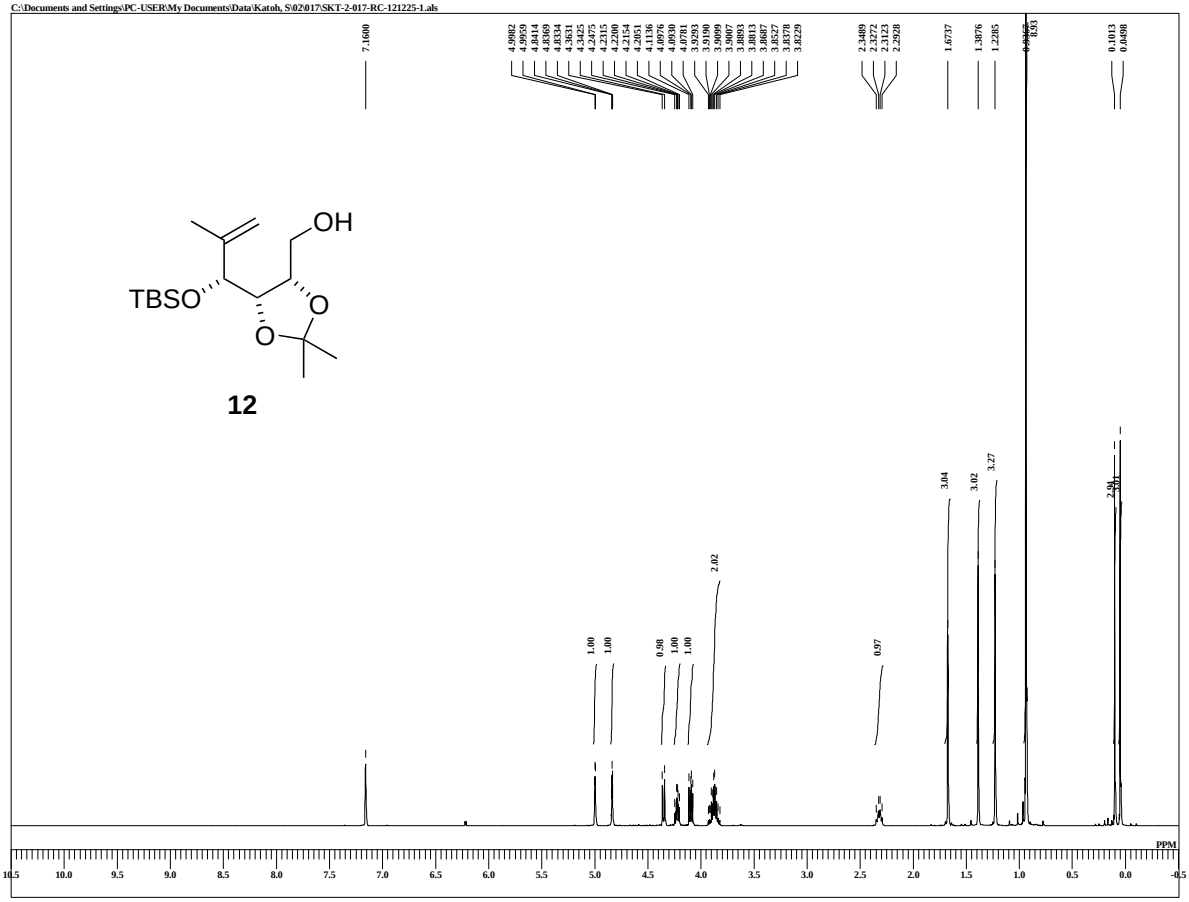

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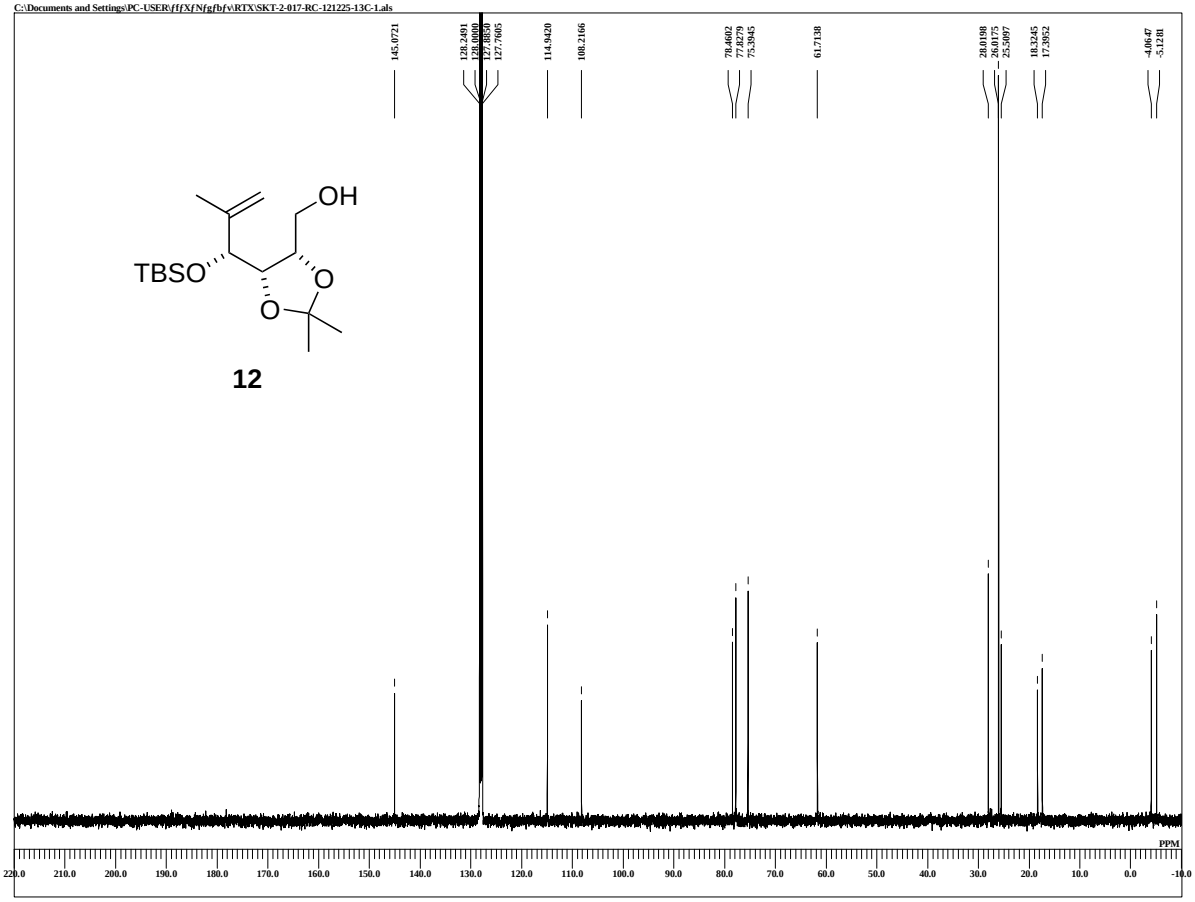

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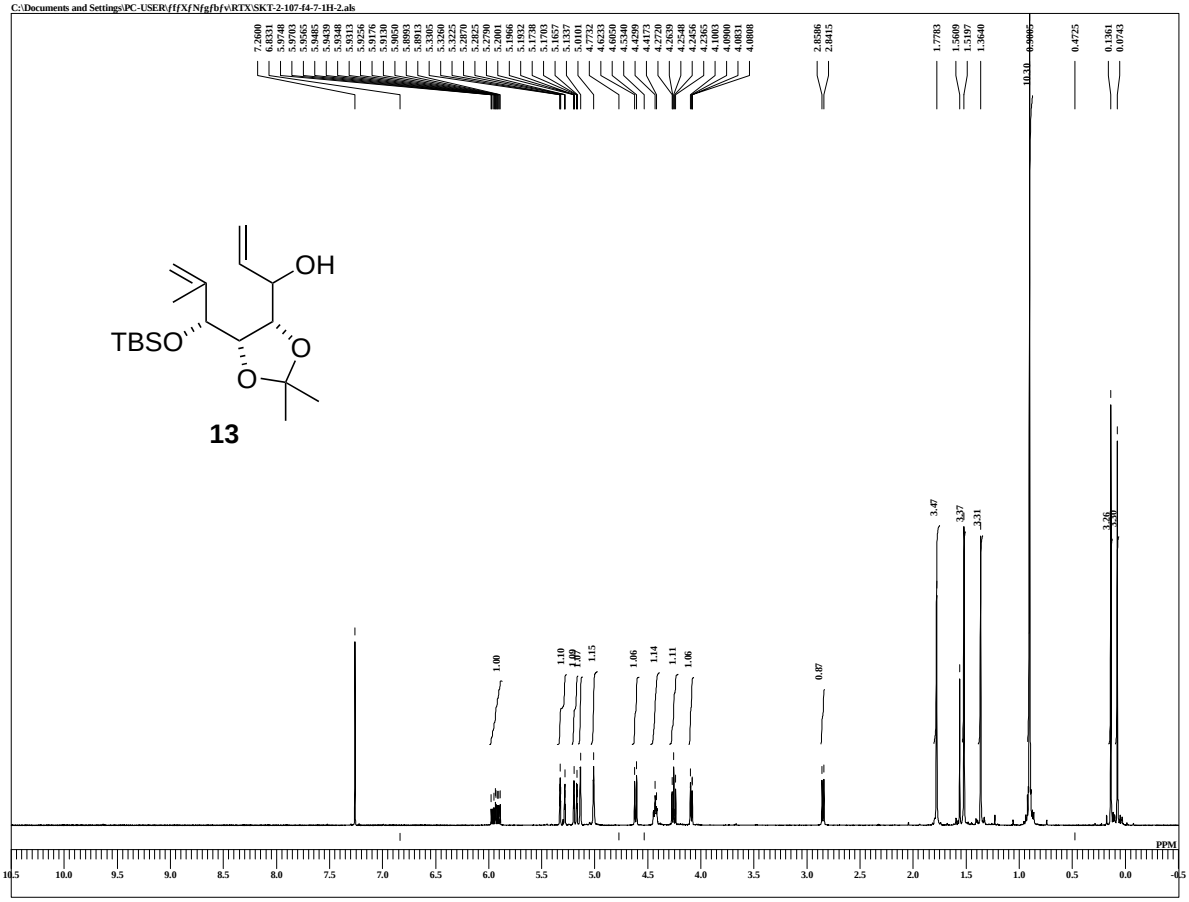
OBFIN 0.98 Hz
PW1 3.25 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 26214
SPO 26214
TIMES 57
DUMMY 4
FREQU 24999.62 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 2.0000 sec
SCANS 57
ADBIT 16
RGAIN 60
BF 1.00 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse_dec
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE SKT-2-017-RC-121225-13
SF
LKSET 13.20 KHz
LKFIN 69.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.6 c
SLVNT C6D6
EXREF 128.00 ppm

SKT-2-107-f4-7-1H

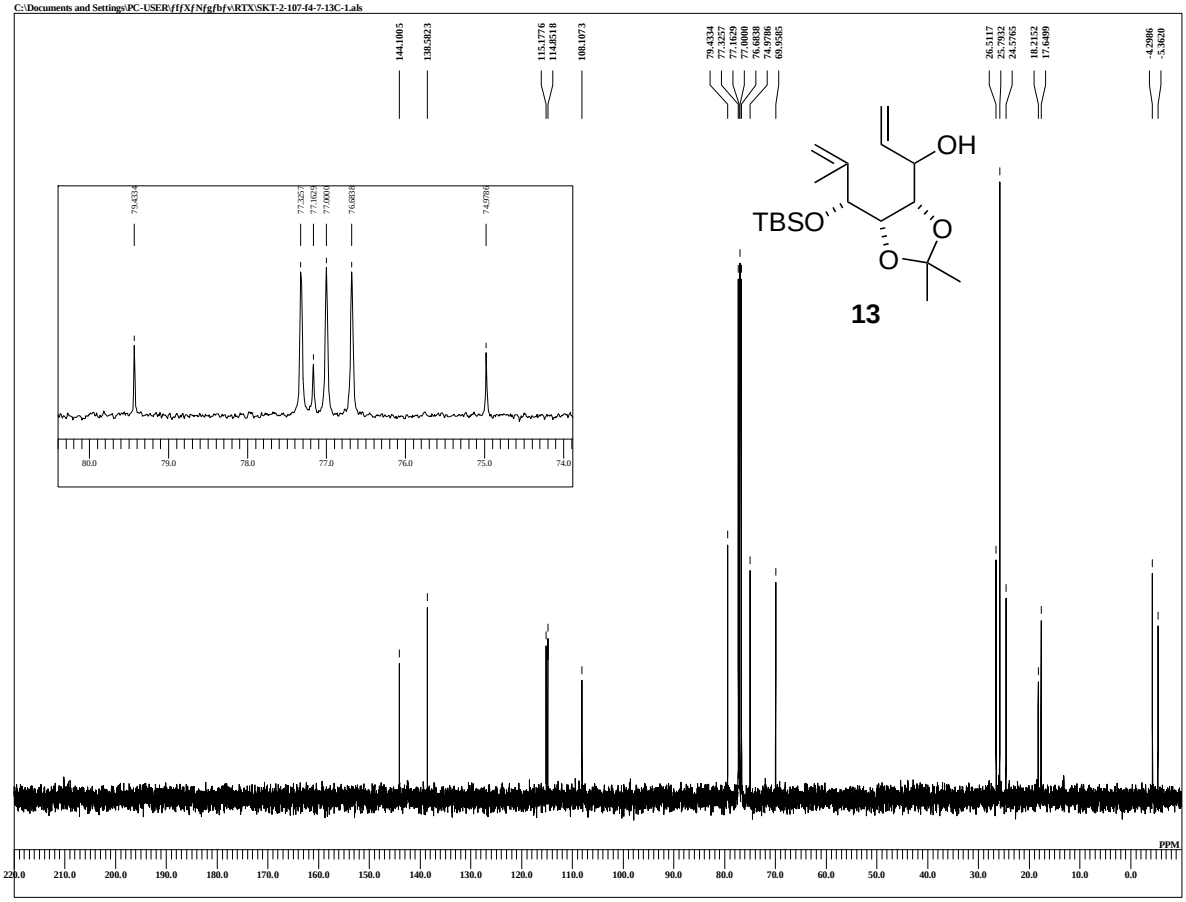
C:\Documents and Settings\PC-USER\ffXfNfgfbfv\RTX\SKT-2-107-f4-7-1H-2.als




```
DFILE     SKT-2-107-f4-7-1H-2.als
COMNT     SKT-2-107-f4-7-1H
DATIM     03-03-2012 16:05:06
MENUF
OBNUC     1H
OFR       395.88 MHz
OBFRQ     395.88 MHz
OBSET     6.28 KHz
OBFIN     0.87 Hz
PW1       6.62 usec
DEADT     0.00 usec
PREDL     0.00000 msec
IWT       1.0000 sec
POINT     16384
SPO       16384
TIMES     8
DUMMY     1
FREQU     7422.80 Hz
FLT       30000 Hz
DELAY     16.68 usec
ACQTM     2.2073 sec
PD        5.0000 sec
SCANS     8
ADBIT     16
RGAIN     40
BF        0.01 Hz
T1        0.00
T2        0.00
T3        90.00
T4        100.00
EXMOD     single_pulse.ex2
EXPCM
IRNUC     1H
IFR       395.88 MHz
IRSET     6.28 KHz
IRFIN     0.87 Hz
IRRPW     115 usec
IRATN     79
DFILE     SKT-2-107-f4-7-1H-2.als
SF
LKSET     13.20 KHz
LKFIN     75.7 Hz
LKLEV     0
LGAIN     0
LKPHS     0
LKSIG     0
CSPED     0 Hz
FILDC
FILDF
CTEMP     22.7 c
SLVNT     CDCL3
EXREF     7.26 ppm
```

SKT-2-107-f4-7-13C

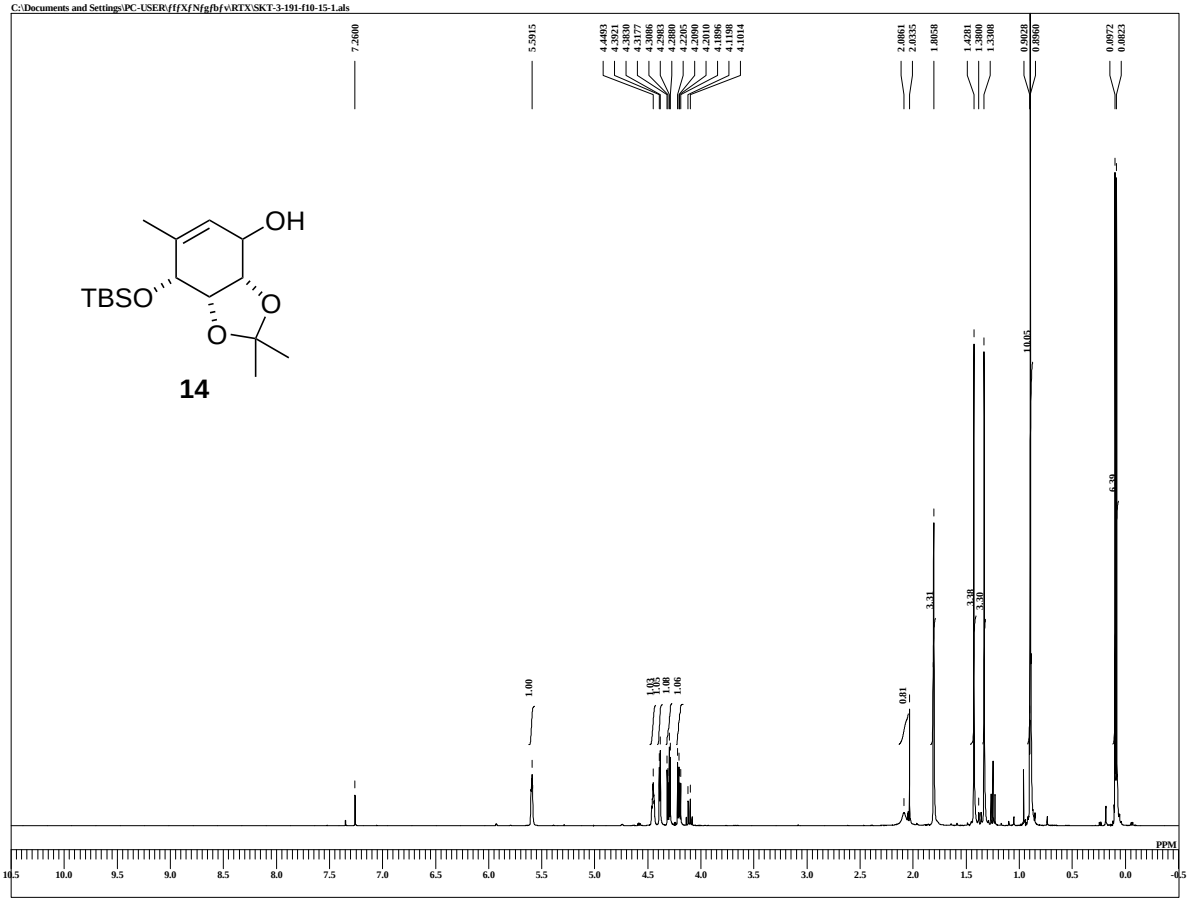
C:\Documents and Settings\PC-USER\ffXfNfgfbfv\RTX\SKT-2-107-f4-7-13C-1.als




```
DFILE     SKT-2-107-f4-7-13C-1.als
COMNT     SKT-2-107-f4-7-13C
DATIM     05-03-2012 16:22:15
MENUF
OBNUC     13C
OFR       99.55 MHz
OBFRQ     99.55 MHz
OBSET     5.13 KHz
OBFIN     0.98 Hz
PW1       2.92 usec
DEADT     0.00 usec
PREDL     0.00000 msec
IWT       1.0000 sec
POINT     32768
SPO       32768
TIMES     38
DUMMY     4
FREQU     31250.00 Hz
FLT       125000 Hz
DELAY     20.50 usec
ACQTM     1.0486 sec
PD        2.0000 sec
SCANS     38
ADBIT     16
RGAIN     60
BF        1.00 Hz
T1        0.00
T2        0.00
T3        90.00
T4        100.00
EXMOD     single_pulse_dec
EXPCM
IRNUC     1H
IFR       395.88 MHz
IRSET     6.28 KHz
IRFIN     0.87 Hz
IRRPW     115 usec
IRATN     79
DFILE     SKT-2-107-f4-7-13C-1.als
SF
LKSET     13.20 KHz
LKFIN     75.7 Hz
LKLEV     0
LGAIN     0
LKPHS     0
LKSIG     0
CSPED     0 Hz
FILDC
FILDF
CTEMP     22.7 c
SLVNT     CDCL3
EXREF     77.00 ppm
```

SKT-3-191-f10-15

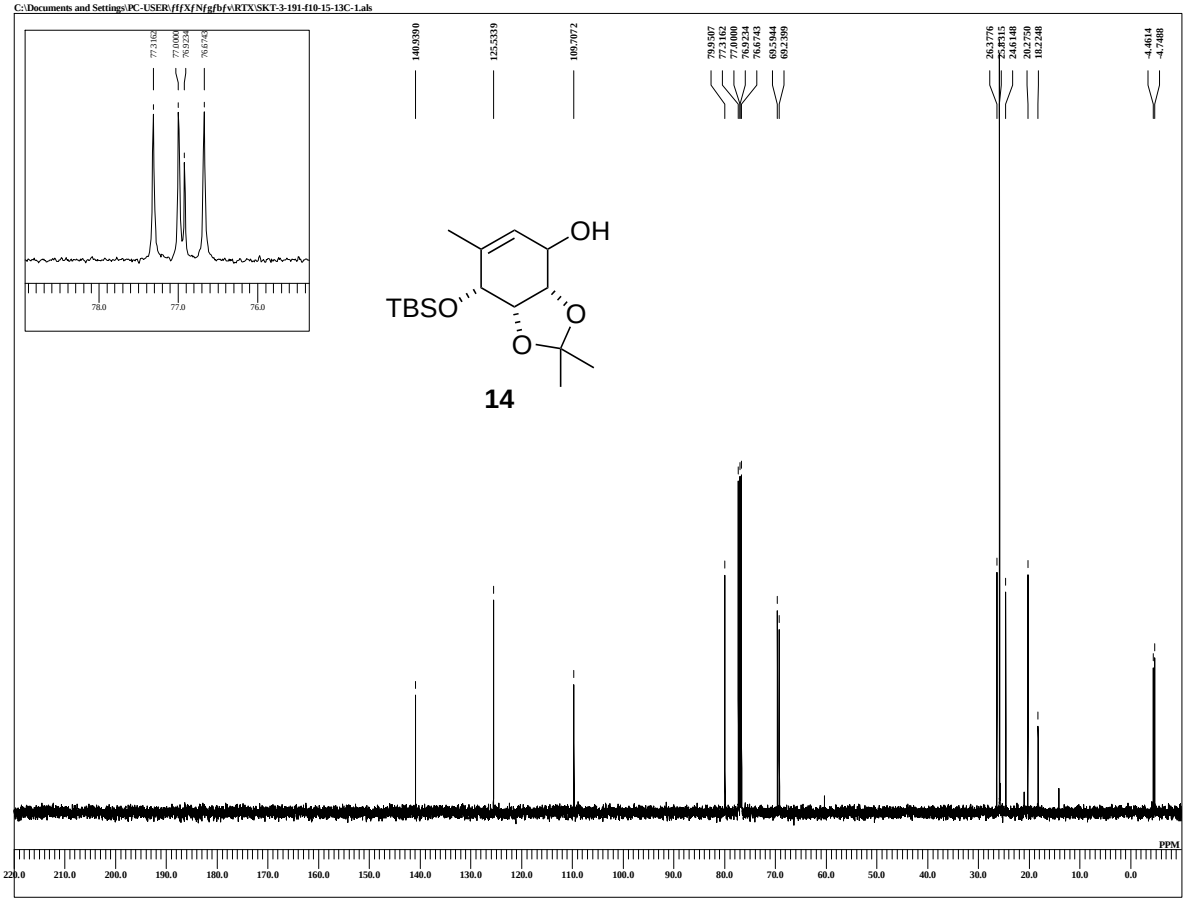
C:\Documents and Settings\PC-USER\ffXfNfgfbfv\RTX\SKT-3-191-f10-15-1.als



DFILE SKT-3-191-f10-15-1.als
COMNT SKT-3-191-f10-15
DATIM 13-09-2012 21:27:13
MENUF
OBNUC 1H
OFR 395.88 MHz
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
PW1 6.38 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 16384
SPO 16384
TIMES 8
DUMMY 1
FREQU 7422.80 Hz
FLT 30000 Hz
DELAY 16.68 usec
ACQTM 2.2073 sec
PD 1.5000 sec
SCANS 8
ADBIT 16
RGAIN 26
BF 0.01 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse.ex2
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE SKT-3-191-f10-15-1.als
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 24.2 c
SLVNT CDCL3
EXREF 7.26 ppm

SKT-3-191-f10-15-13C

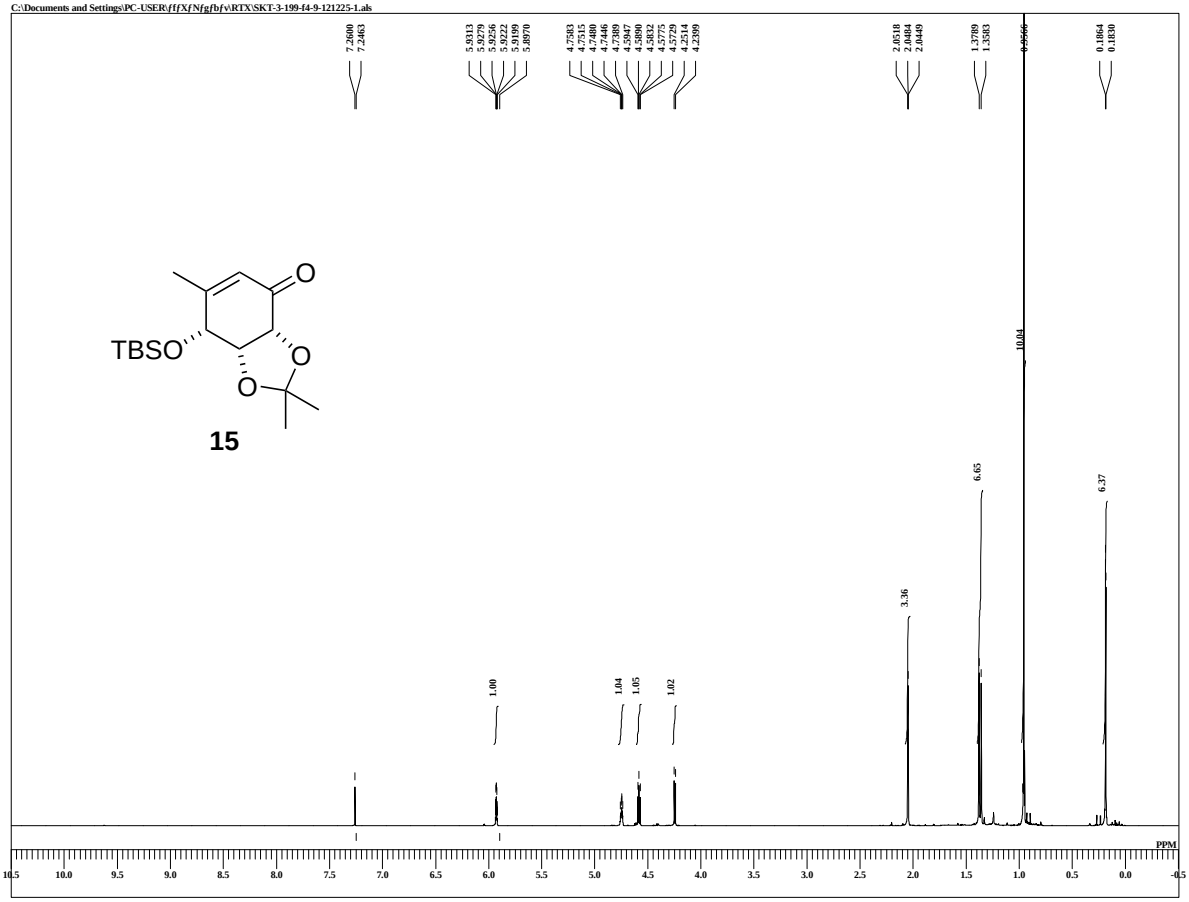
C:\Documents and Settings\PC-USER\ffXfNfgfbfv\RTX\SKT-3-191-f10-15-13C-1.als



DFILE SKT-3-191-f10-15-13C-1.
COMNT SKT-3-191-f10-15-13C
DATIM 13-09-2012 21:31:49
MENUF
OBNUC 13C
OFR 99.55 MHz
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
PW1 3.25 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 32768
SPO 32768
TIMES 69
DUMMY 4
FREQU 31250.00 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 2.0000 sec
SCANS 69
ADBIT 16
RGAIN 60
BF 1.00 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse_dec
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE SKT-3-191-f10-15-13C-1.
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 24.4 c
SLVNT CDCL3
EXREF 77.00 ppm

SKT-3-199-f4-9-121225

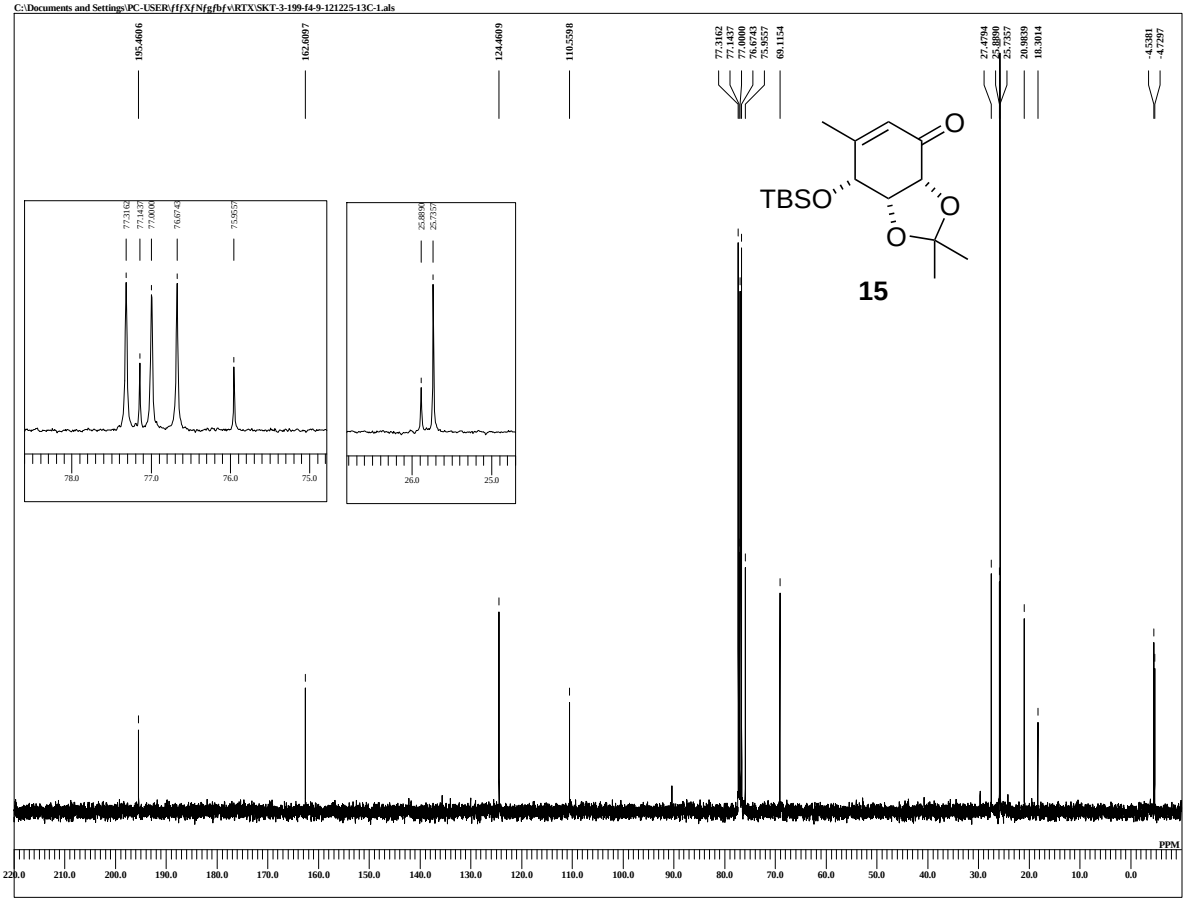
C:\Documents and Settings\PC-USER\ffXfNfgfbfv\RTX\SKT-3-199-f4-9-121225-1.als



DFILE SKT-3-199-f4-9-121225-1
COMNT SKT-3-199-f4-9-121225
DATIM 25-12-2012 13:52:06
MENUF
OBNUC 1H
OFR 395.88 MHz
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
PW1 6.38 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 16384
SPO 16384
TIMES 8
DUMMY 1
FREQU 7422.80 Hz
FLT 30000 Hz
DELAY 16.68 usec
ACQTM 2.2073 sec
PD 5.0000 sec
SCANS 8
ADBIT 16
RGAIN 30
BF 0.01 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse.ex2
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE SKT-3-199-f4-9-121225-1
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.4 c
SLVNT CDCL3
EXREF 7.26 ppm

SKT-3-199-f4-9-121225-13C

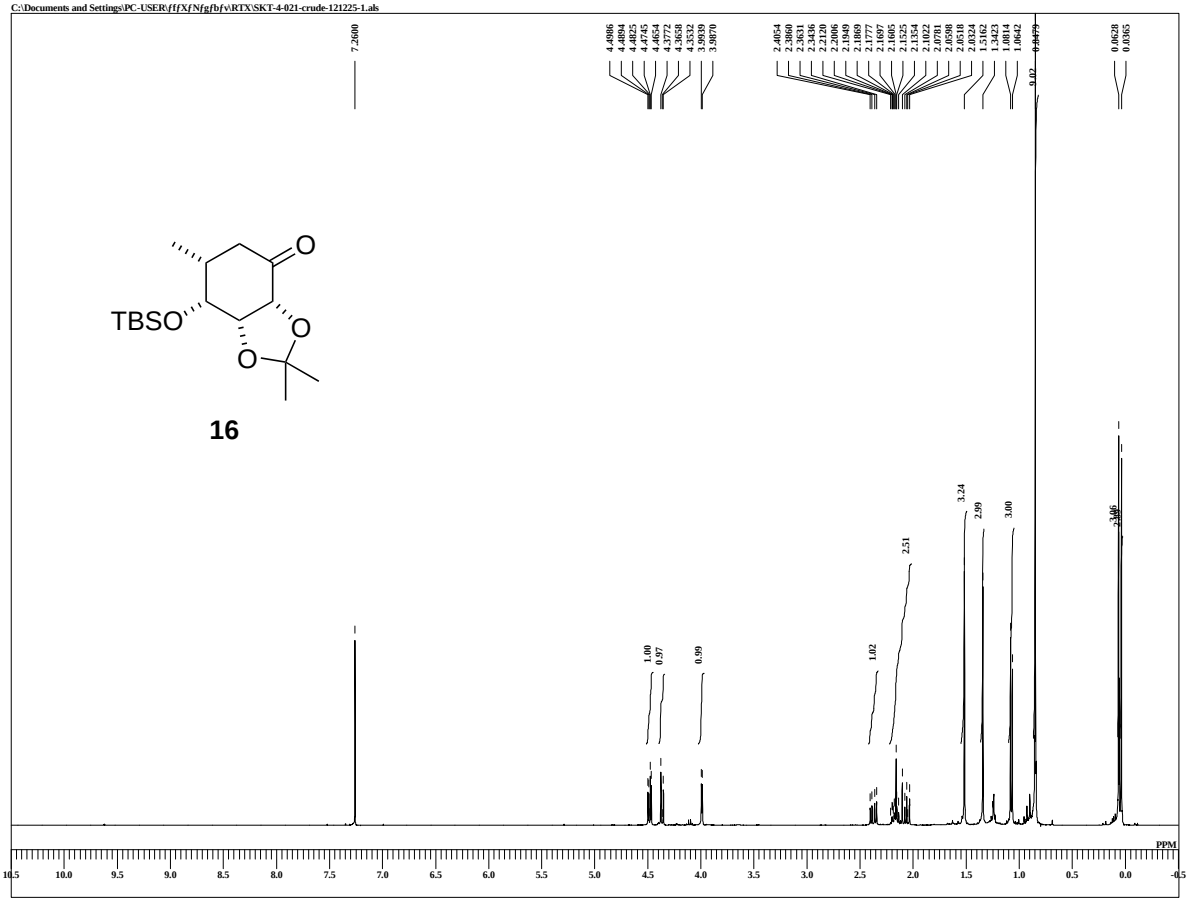
C:\Documents and Settings\PC-USER\ffXfNfgfbfv\RTX\SKT-3-199-f4-9-121225-13C-1.als



DFILE SKT-3-199-f4-9-121225-1
COMNT SKT-3-199-f4-9-121225-1
DATIM 25-12-2012 13:59:22
MENUF
OBNUC 13C
OFR 99.55 MHz
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
PW1 3.25 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 32768
SPO 32768
TIMES 112
DUMMY 4
FREQU 31250.00 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 2.0000 sec
SCANS 112
ADBIT 16
RGAIN 60
BF 1.00 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse_dec
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE SKT-3-199-f4-9-121225-1
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.6 c
SLVNT CDCL3
EXREF 77.00 ppm

SKT-4-021-crude-121225

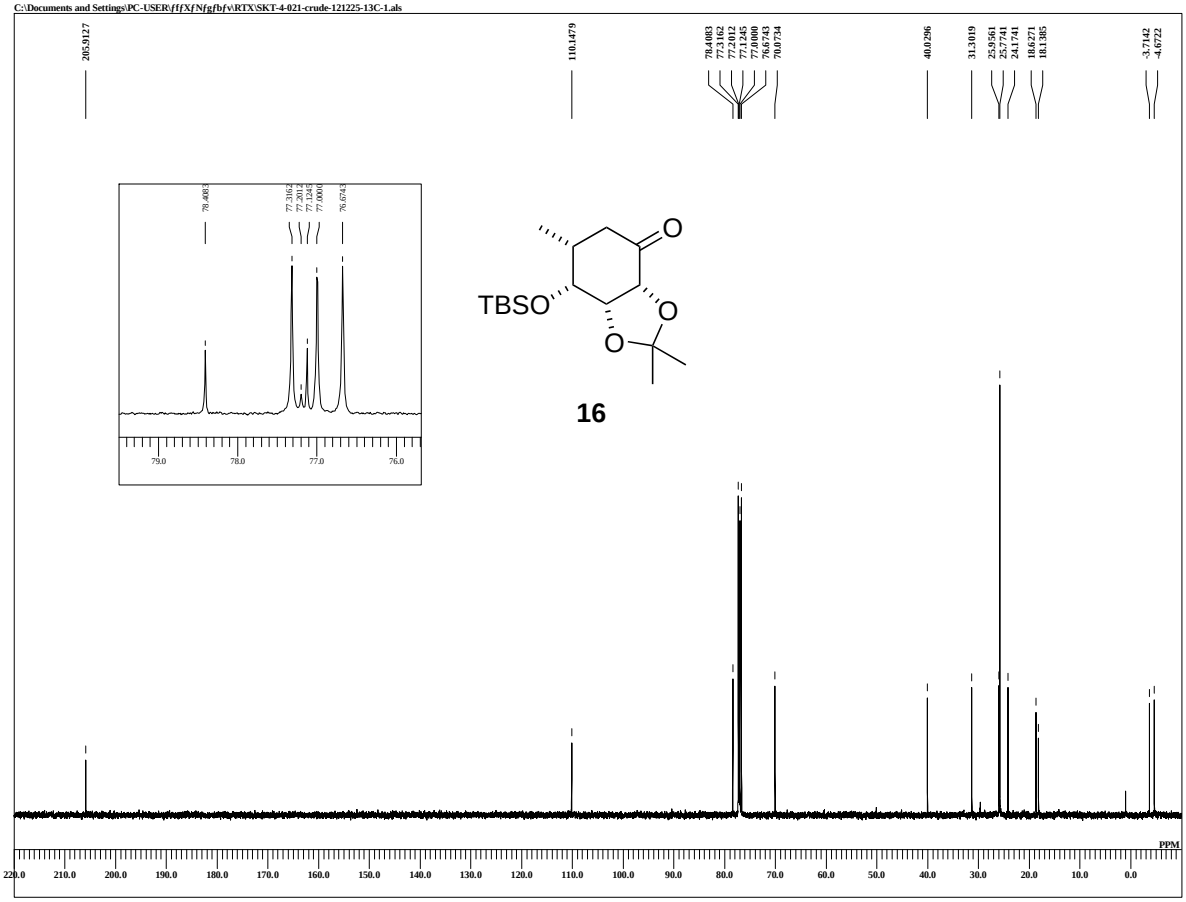
C:\Documents and Settings\PC-USER\ffXfNfgfbfv\RTX\SKT-4-021-crude-121225-1.als



DFILE SKT-4-021-crude-121225-
COMNT SKT-4-021-crude-121225
DATIM 25-12-2012 18:00:12
MENUF
OBNUC 1H
OFR 395.88 MHz
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
PW1 6.38 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 16384
SPO 16384
TIMES 8
DUMMY 1
FREQU 7422.80 Hz
FLT 30000 Hz
DELAY 16.68 usec
ACQTM 2.2073 sec
PD 5.0000 sec
SCANS 8
ADBIT 16
RGAIN 30
BF 0.01 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse.ex2
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE SKT-4-021-crude-121225-
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.5 c
SLVNT CDCL3
EXREF 7.26 ppm

SKT-4-021-crude-121225-13C

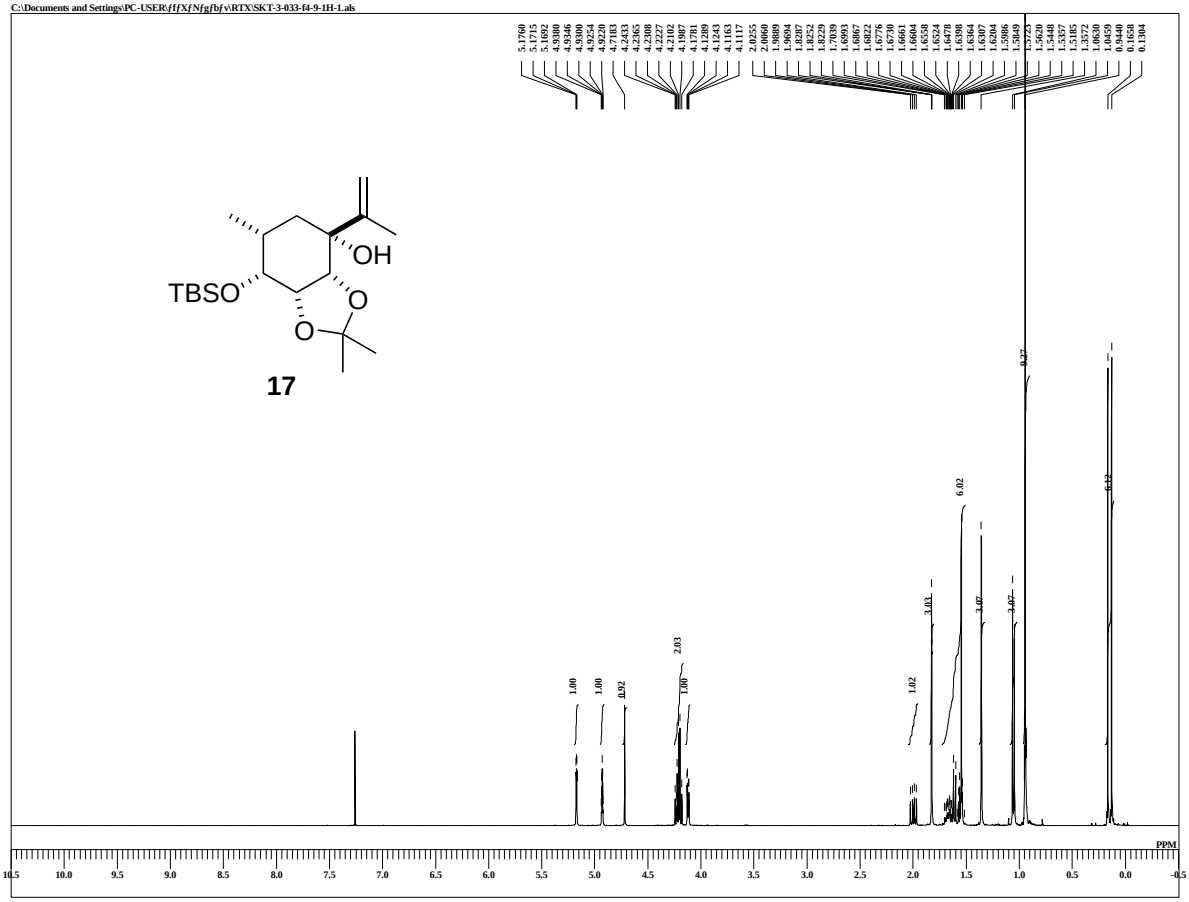
C:\Documents and Settings\PC-USER\ffXfNfgfbfv\RTX\SKT-4-021-crude-121225-13C-1.als



DFILE SKT-4-021-crude-121225-
COMNT SKT-4-021-crude-121225-
DATIM 25-12-2012 18:14:35
MENUF
OBNUC 13C
OFR 99.55 MHz
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
PW1 3.25 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 32768
SPO 32768
TIMES 248
DUMMY 4
FREQU 31250.00 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 2.0000 sec
SCANS 248
ADBIT 16
RGAIN 60
BF 1.00 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse_dec
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE SKT-4-021-crude-121225-
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.00 ppm

SKT-3-033-f4-9-1H

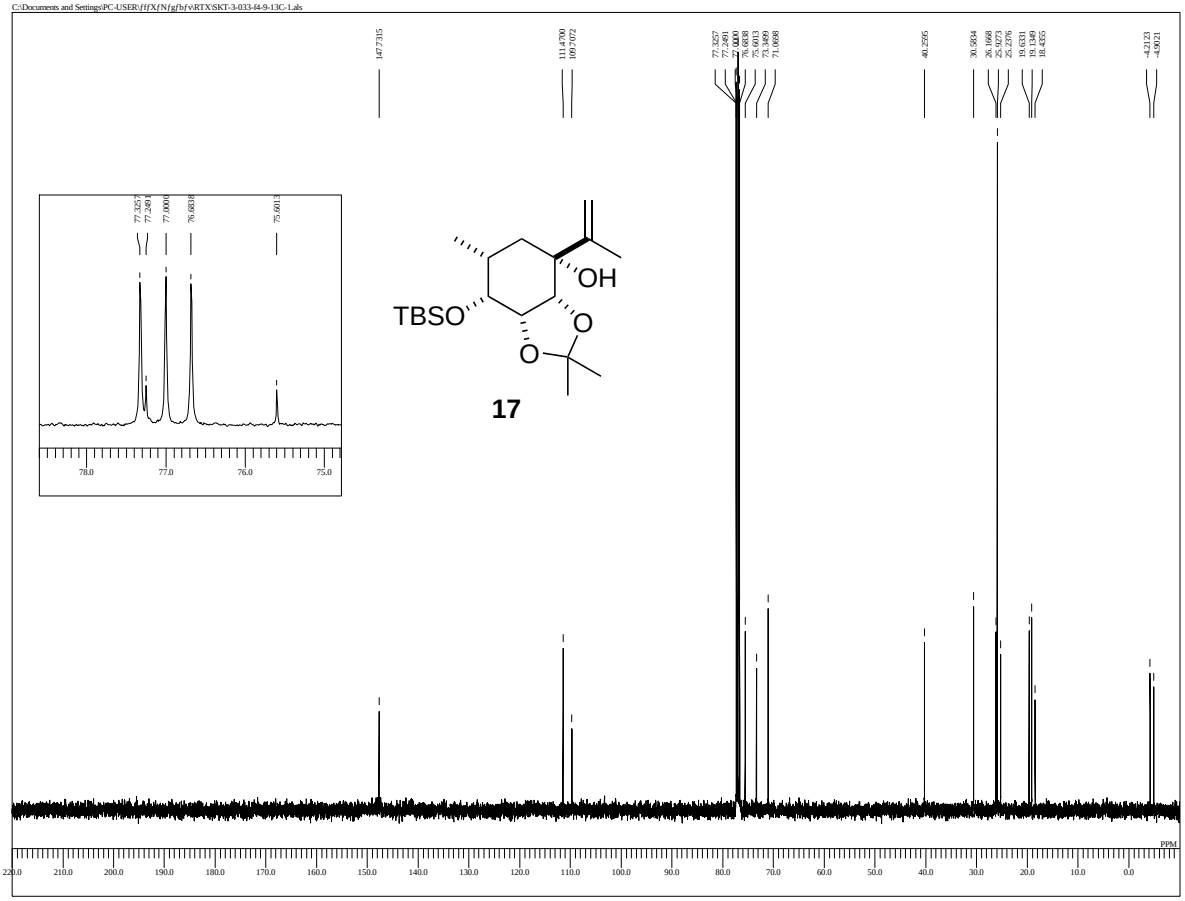
C:\Documents and Settings\PC-USER\ffXfNfgfbf\vRTX\SKT-3-033-f4-9-1H-1.als



DFILE	SKT-3-033-f4-9-1H-1.als
COMNT	SKT-3-033-f4-9-1H
DATIM	19-07-2012 18:23:45
MENUF	
OBNUC	1H
OFR	395.88 MHz
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
PW1	6.38 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	16384
SPO	16384
TIMES	8
DUMMY	1
FREQU	7422.80 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	5.0000 sec
SCANS	8
ADBIT	16
RGAIN	32
BF	0.01 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse.ex2
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	SKT-3-033-f4-9-1H-1.als
SF	
LKSET	13.20 KHz
LKFIN	75.7 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	23.9 c
SLVNT	CDCL3
EXREF	7.26 ppm

SKT-3-033-f4-9-13C

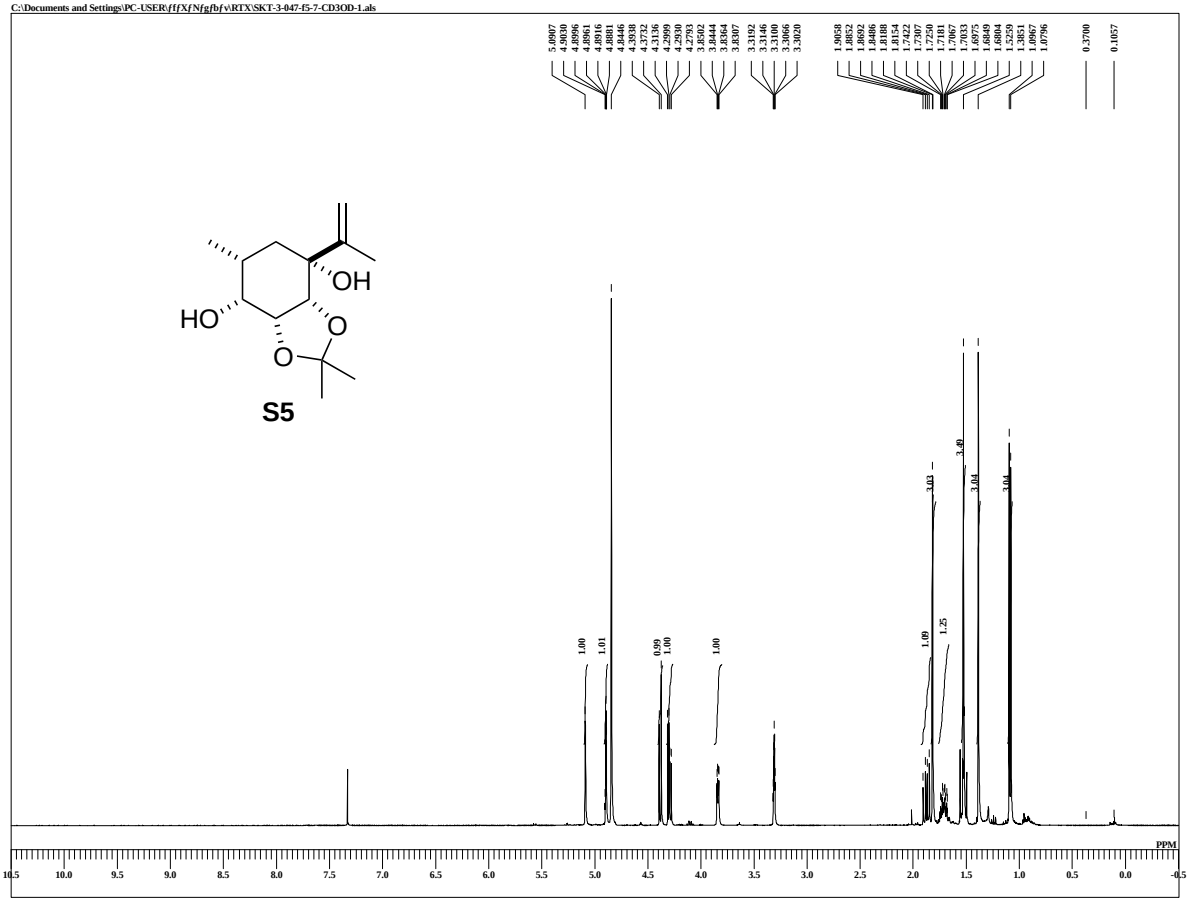
C:\Documents and Settings\PC-USER\ffXfNfgfbf\vRTX\SKT-3-033-f4-9-13C-1.als



DFILE	SKT-3-033-f4-9-13C-1.als
COMNT	SKT-3-033-f4-9-13C
DATIM	19-07-2012 18:35:25
MENUF	
OBNUC	13C
OFR	99.55 MHz
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
PW1	3.25 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	26214
SPO	26214
TIMES	202
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	2.0000 sec
SCANS	202
ADBIT	16
RGAIN	60
BF	1.00 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse_dec
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	SKT-3-033-f4-9-13C-1.als
SF	
LKSET	13.20 KHz
LKFIN	75.7 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	77.00 ppm

SKT-3-047-f5-7

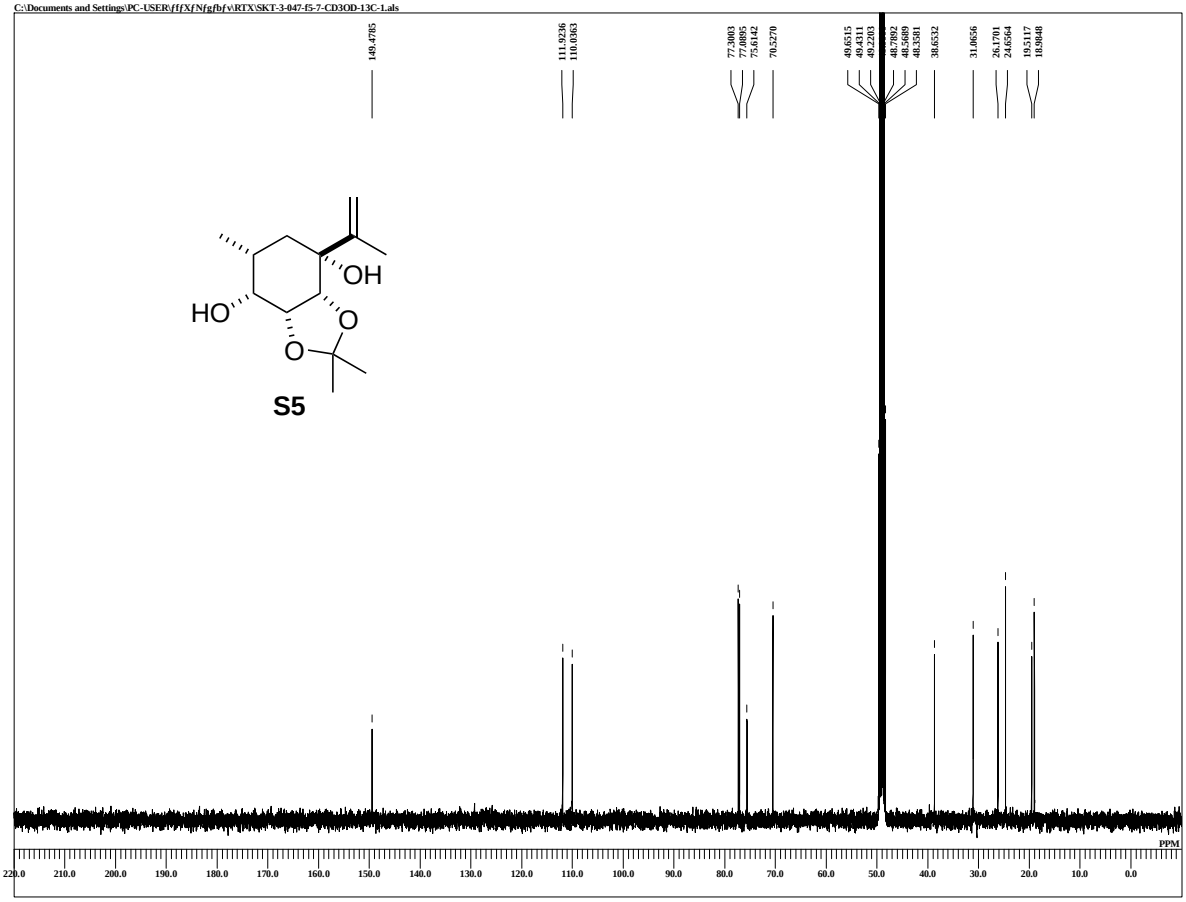
C:\Documents and Settings\PC-USER\ffXfNfgfbfv\RTX\SKT-3-047-f5-7-CD3OD-1.als



DFILE	SKT-3-047-f5-7-CD3OD-1
COMNT	SKT-3-047-f5-7
DATIM	03-10-2012 20:28:49
MENUF	
OBNUC	1H
OFR	395.88 MHz
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
PW1	6.38 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	16384
SPO	16384
TIMES	8
DUMMY	1
FREQU	7422.80 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	5.0000 sec
SCANS	8
ADBIT	16
RGAIN	30
BF	0.01 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse.ex2
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	SKT-3-047-f5-7-CD3OD-1
SF	
LKSET	13.00 KHz
LKFIN	35.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	24.8 c
SLVNT	CD3OD
EXREF	3.31 ppm

SKT-3-047-f5-7-13C

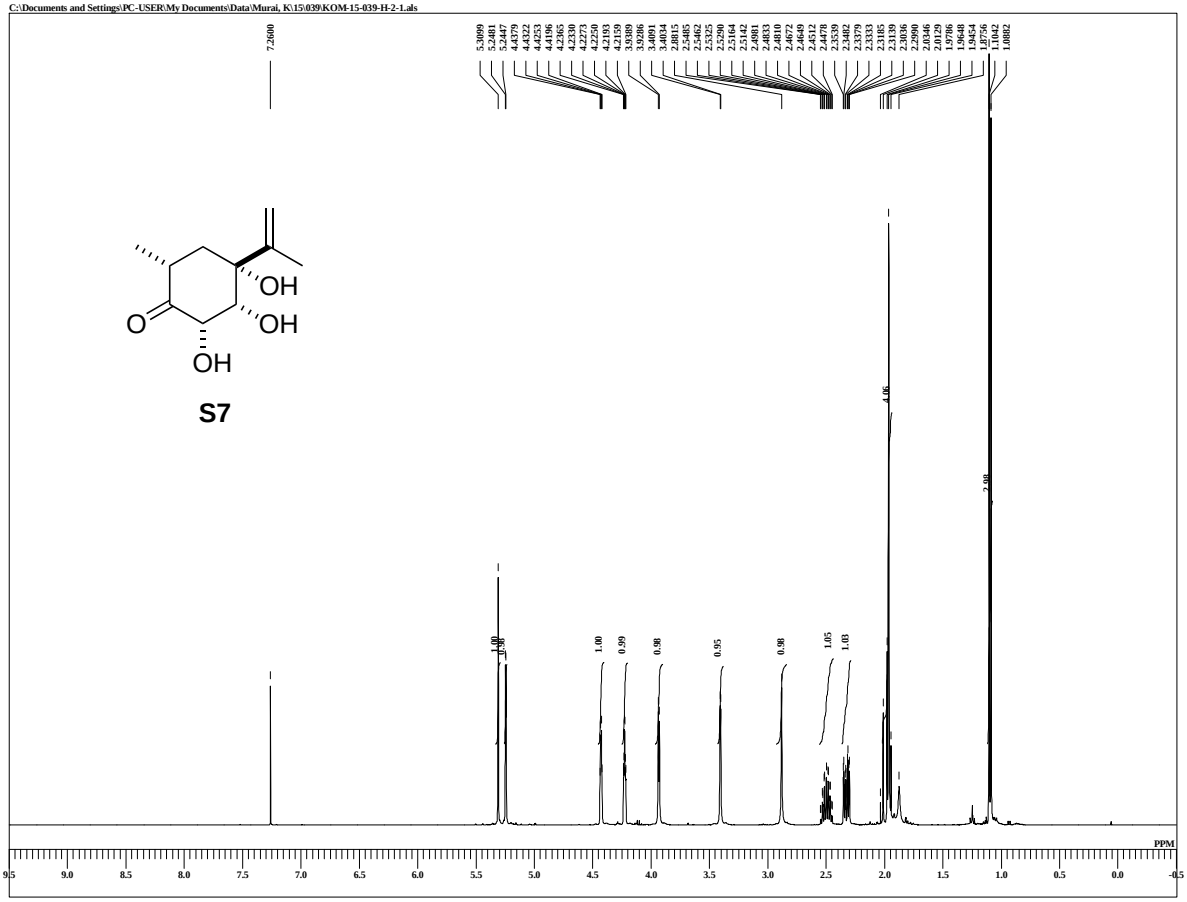
C:\Documents and Settings\PC-USER\ffXfNfgfbfv\RTX\SKT-3-047-f5-7-CD3OD-13C-1.als



DFILE	SKT-3-047-f5-7-CD3OD-1
COMNT	SKT-3-047-f5-7-13C
DATIM	03-10-2012 20:35:47
MENUF	
OBNUC	13C
OFR	99.55 MHz
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
PW1	3.25 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	32768
SPO	32768
TIMES	117
DUMMY	4
FREQU	31250.00 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	2.0000 sec
SCANS	117
ADBIT	16
RGAIN	60
BF	1.00 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse_dec
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	SKT-3-047-f5-7-CD3OD-1
SF	
LKSET	13.00 KHz
LKFIN	35.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	25.0 c
SLVNT	CD3OD
EXREF	49.00 ppm

KOM-15-039-H-2

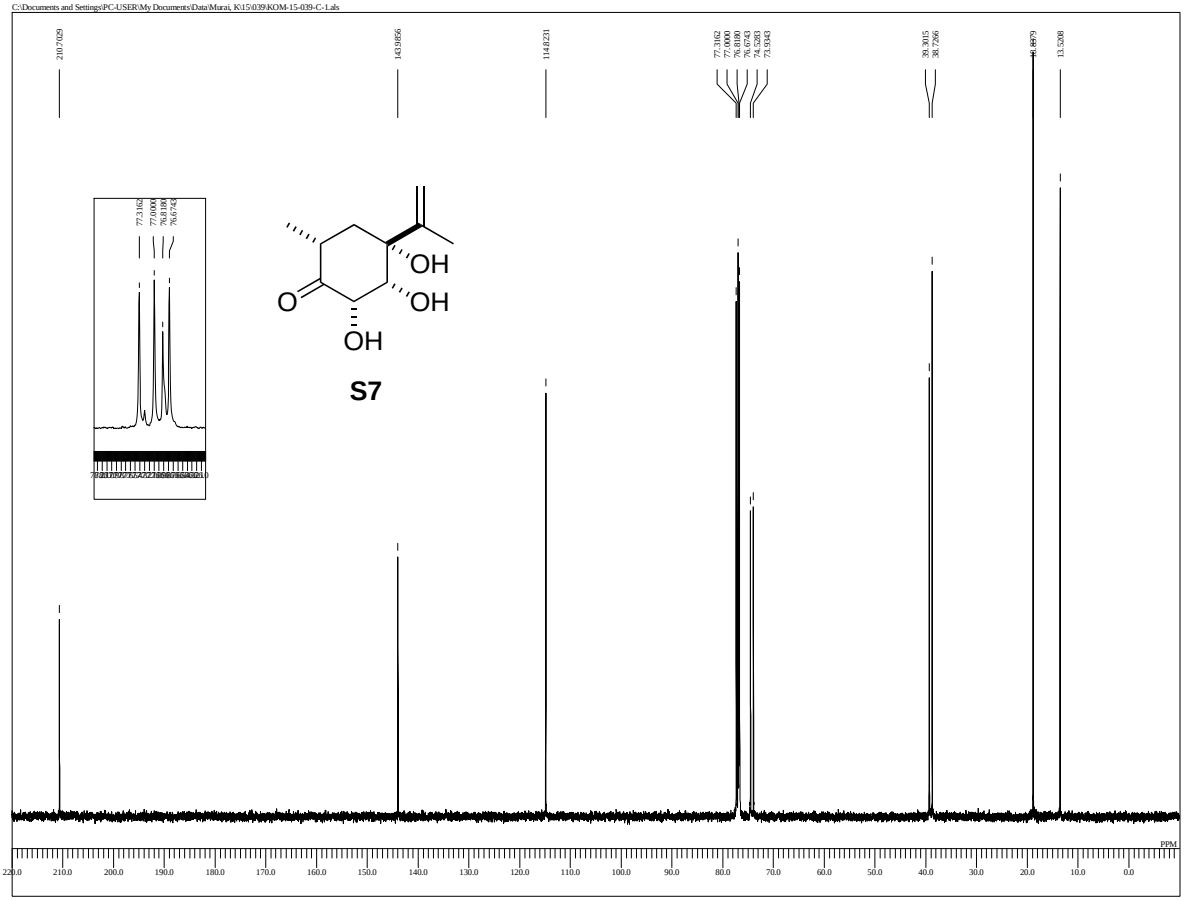
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\039\KOM-15-039-H-2-1.als



DFILE	KOM-15-039-H-2-1.als
COMNT	KOM-15-039-H-2
DATIM	31-08-2012 17:06:45
MENUF	
OBNUC	1H
OFR	395.88 MHz
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
PW1	6.38 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	13107
SPO	13107
TIMES	16
DUMMY	1
FREQU	5938.15 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	5.0000 sec
SCANS	16
ADBIT	16
RGAIN	34
BF	0.01 Hz
T1	0.00
T2	0.00
T3	100.00
T4	100.00
EXMOD	single_pulse.ex2
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-15-039-H-2-1.als
SF	
LKSET	13.20 KHz
LKFIN	75.7 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	7.26 ppm

KOM-15-039-C

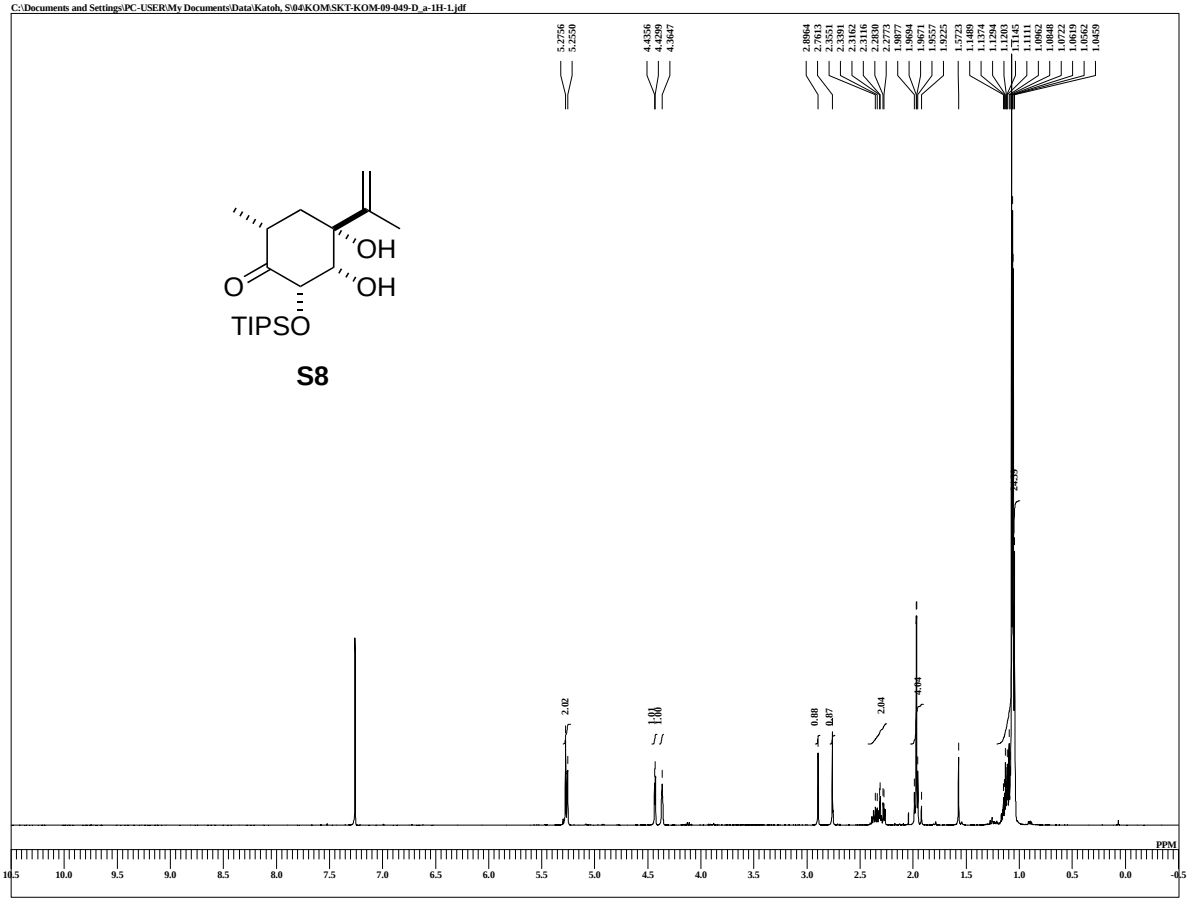
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\039\KOM-15-039-C-1.als



DFILE	KOM-15-039-C-1.als
COMNT	KOM-15-039-C
DATIM	27-07-2012 09:16:24
MENUF	
OBNUC	13C
OFR	99.55 MHz
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
PW1	3.25 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	26214
SPO	26214
TIMES	500
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	2.0000 sec
SCANS	500
ADBIT	16
RGAIN	58
BF	1.00 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse_dec
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-15-039-C-1.als
SF	
LKSET	13.20 KHz
LKFIN	75.7 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	22.4 c
SLVNT	CDCL3
EXREF	77.00 ppm

SKT-KOM-09-049-D_a

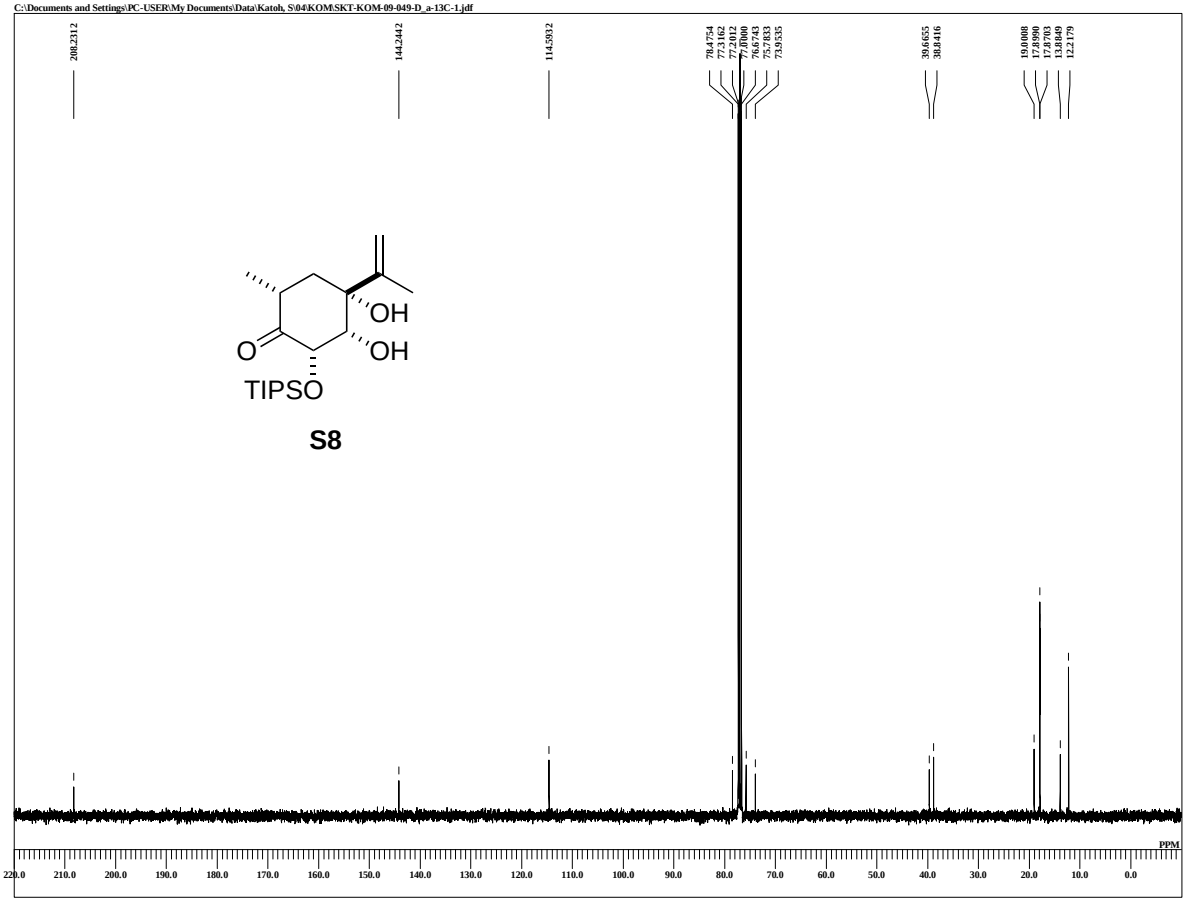
C:\Documents and Settings\PC-USER\My Documents\Data\Katoh, S\04\KOM\SKT-KOM-09-049-D_a-1H-1.jdf



DFILE SKT-KOM-09-049-D_a-1
COMNT SKT-KOM-09-049-D_a
DATIM 04-01-2013 17:11:52
MENUF
OBNUC 1H
OFR 395.88 MHz
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
PW1 6.38 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 16384
SPO 16384
TIMES 8
DUMMY 1
FREQU 7422.80 Hz
FLT 30000 Hz
DELAY 16.68 usec
ACQTM 2.2073 sec
PD 5.0000 sec
SCANS 8
ADBIT 16
RGAIN 40
BF 0.01 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse.ex2
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE SKT-KOM-09-049-D_a-1
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.5 c
SLVNT CDCL3
EXREF 7.26 ppm

SKT-KOM-09-049-D-a

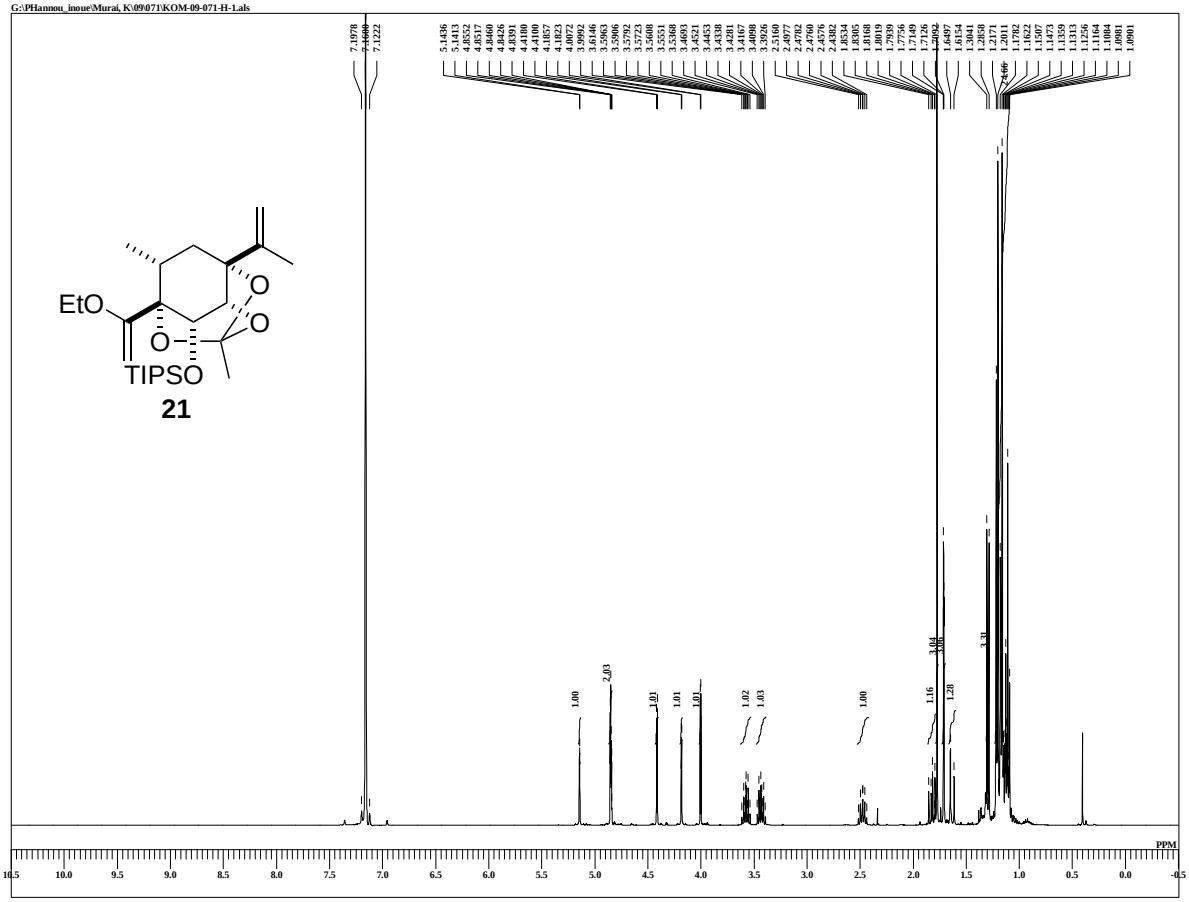
C:\Documents and Settings\PC-USER\My Documents\Data\Katoh, S\04\KOM\SKT-KOM-09-049-D_a-13C-1.jdf



DFILE SKT-KOM-09-049-D_a-1
COMNT SKT-KOM-09-049-D-a
DATIM 04-01-2013 17:37:30
MENUF
OBNUC 13C
OFR 99.55 MHz
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
PW1 3.25 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 32768
SPO 32768
TIMES 486
DUMMY 4
FREQU 31250.00 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 2.0000 sec
SCANS 486
ADBIT 16
RGAIN 60
BF 1.00 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse_dec
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE SKT-KOM-09-049-D_a-1
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.4 c
SLVNT CDCL3
EXREF 77.00 ppm

KOM-09-071-H

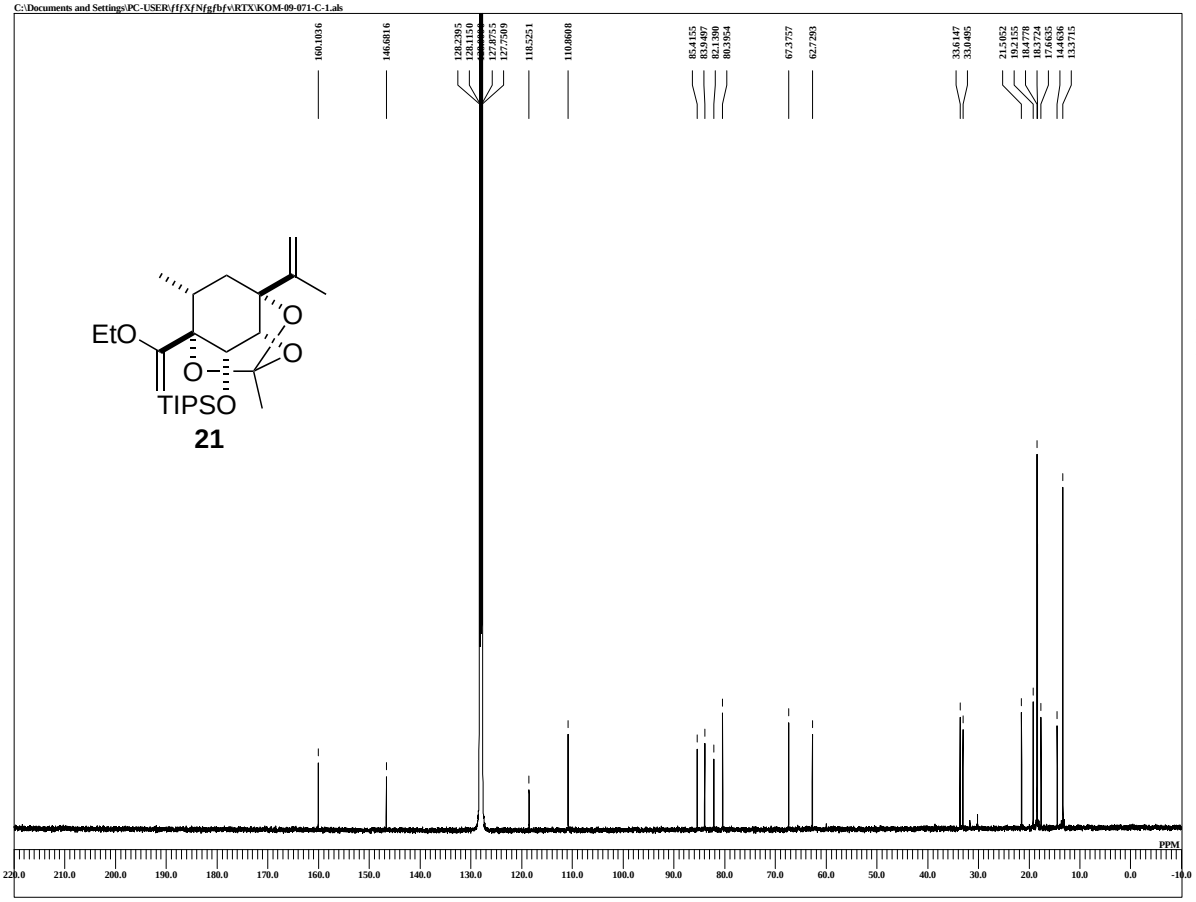
G:\PHannou_inoue\Murai, K\09071\KOM-09-071-H-1.als




```
DFILE   KOM-09-071-H-1.als
COMNT   KOM-09-071-H
DATIM   07-02-2011 21:49:24
MENUF
OBNUC   1H
OFR     395.88 MHz
OBFRQ   395.88 MHz
OBSET   6.28 KHz
OBFIN   0.87 Hz
PW1     6.50 usec
DEADT   0.00 usec
PREDL   0.00000 msec
IWT     1.0000 sec
POINT   13107
SPO     13107
TIMES   32
DUMMY   1
FREQU   5938.15 Hz
FLT     30000 Hz
DELAY   16.68 usec
ACQTM   2.2073 sec
PD      5.0000 sec
SCANS   32
ADBIT   16
RGAIN   40
BF      0.01 Hz
T1      0.00
T2      0.00
T3      90.00
T4      100.00
EXMOD   single_pulse.ex2
EXPCM
IRNUC   1H
IFR     395.88 MHz
IRSET   6.28 KHz
IRFIN   0.87 Hz
IRRPW   115 usec
IRATN   79
DFILE   KOM-09-071-H-1.als
SF
LKSET   13.20 KHz
LKFIN   69.6 Hz
LKLEV   0
LGAIN   0
LKPHS   0
LKSIG   0
CSPED   0 Hz
FILDC
FILDF
CTEMP   20.8 c
SLVNT   C6D6
EXREF   7.16 ppm
```

KOM-09-071-C

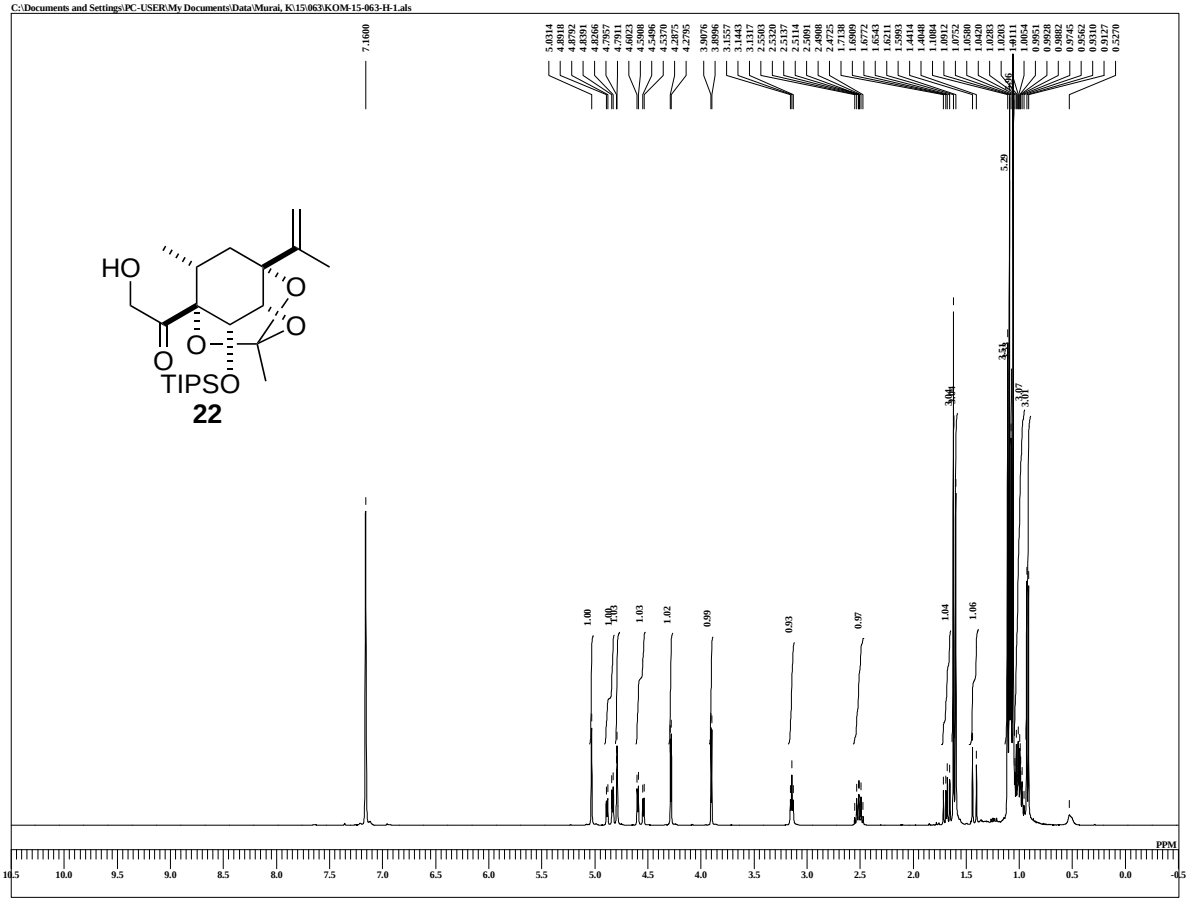
C:\Documents and Settings\PC-USER\ffXfNfgfbf\RTX\KOM-09-071-C-1.als




```
DFILE   KOM-09-071-C-1.als
COMNT   KOM-09-071-C
DATIM   08-02-2011 07:46:29
MENUF
OBNUC   13C
OFR     99.55 MHz
OBFRQ   99.55 MHz
OBSET   5.13 KHz
OBFIN   0.98 Hz
PW1     3.33 usec
DEADT   0.00 usec
PREDL   0.00000 msec
IWT     1.0000 sec
POINT   32768
SPO     32768
TIMES   7000
DUMMY   4
FREQU   31250.00 Hz
FLT     125000 Hz
DELAY   20.50 usec
ACQTM   1.0486 sec
PD      2.0000 sec
SCANS   7000
ADBIT   16
RGAIN   60
BF      1.00 Hz
T1      0.00
T2      0.00
T3      90.00
T4      100.00
EXMOD   single_pulse_dec
EXPCM
IRNUC   1H
IFR     395.88 MHz
IRSET   6.28 KHz
IRFIN   0.87 Hz
IRRPW   115 usec
IRATN   79
DFILE   KOM-09-071-C-1.als
SF
LKSET   13.20 KHz
LKFIN   69.6 Hz
LKLEV   0
LGAIN   0
LKPHS   0
LKSIG   0
CSPED   0 Hz
FILDC
FILDF
CTEMP   21.5 c
SLVNT   C6D6
EXREF   128.00 ppm
```

KOM-15-063-H

C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\063\KOM-15-063-H-1.als




```
DFILE    KOM-15-063-H-1.als
COMNT    KOM-15-063-H
DATIM    20-08-2012 22:08:33
MENUF
OBNUC    1H
OFR      395.88 MHz
OBFRQ    395.88 MHz
OBSET    6.28 KHz
OBFIN    0.87 Hz
PW1      6.38 usec
DEADT    0.00 usec
PREDL    0.00000 msec
IWT      1.0000 sec
POINT    13107
SPO      13107
TIMES    32
DUMMY    1
FREQU    5938.15 Hz
FLT      30000 Hz
DELAY    16.68 usec
ACQTM    2.2073 sec
PD       5.0000 sec
SCANS    32
ADBIT    16
RGAIN    30
BF       0.01 Hz
T1       0.00
T2       0.00
T3       100.00
T4       100.00
EXMOD    single_pulse.ex2
EXPCM
IRNUC    1H
IFR      395.88 MHz
IRSET    6.28 KHz
IRFIN    0.87 Hz
IRRPW    115 usec
IRATN    79
DFILE    KOM-15-063-H-1.als
SF
LKSET    13.20 KHz
LKFIN    69.6 Hz
LKLEV    0
LGAIN    0
LKPHS    0
LKSIG    0
CSPED    0 Hz
FILDC
FILDF
CTEMP    23.3 c
SLVNT    C6D6
EXREF    7.16 ppm
```

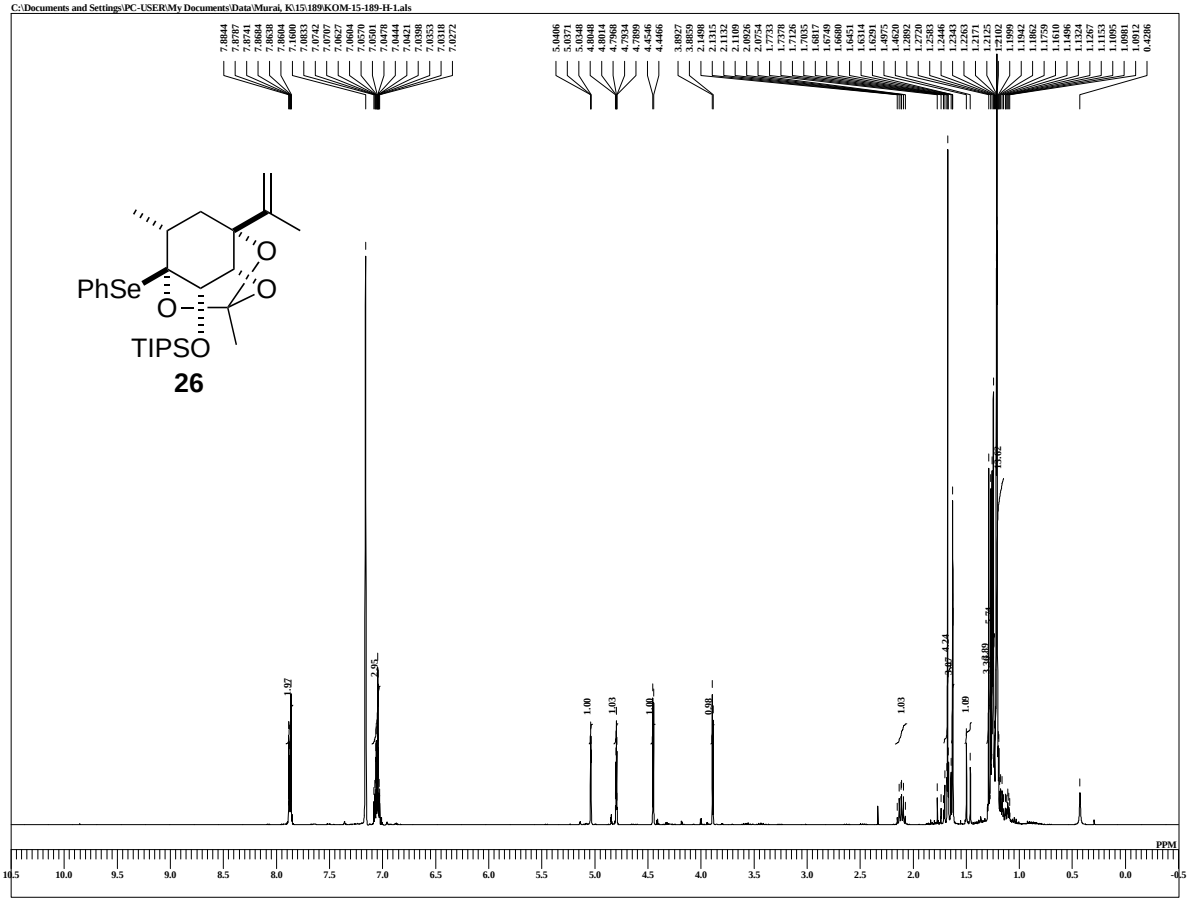
KOM-15-063-C

C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\063\KOM-15-063-C-1.als


```
DFILE    KOM-15-063-C-1.als
COMNT    KOM-15-063-C
DATIM    21-08-2012 07:32:39
MENUF
OBNUC    13C
OFR      99.55 MHz
OBFRQ    99.55 MHz
OBSET    5.13 KHz
OBFIN    0.98 Hz
PW1      3.25 usec
DEADT    0.00 usec
PREDL    0.00000 msec
IWT      1.0000 sec
POINT    52428
SPO      52428
TIMES    4000
DUMMY    4
FREQU    24999.62 Hz
FLT      125000 Hz
DELAY    20.50 usec
ACQTM    1.0486 sec
PD       2.0000 sec
SCANS    4000
ADBIT    16
RGAIN    60
BF       1.00 Hz
T1       0.00
T2       0.00
T3       100.00
T4       100.00
EXMOD    single_pulse_dec
EXPCM
IRNUC    1H
IFR      395.88 MHz
IRSET    6.28 KHz
IRFIN    0.87 Hz
IRRPW    115 usec
IRATN    79
DFILE    KOM-15-063-C-1.als
SF
LKSET    13.20 KHz
LKFIN    69.6 Hz
LKLEV    0
LGAIN    0
LKPHS    0
LKSIG    0
CSPED    0 Hz
FILDC
FILDF
CTEMP    23.0 c
SLVNT    C6D6
EXREF    128.00 ppm
```

KOM-15-189-H

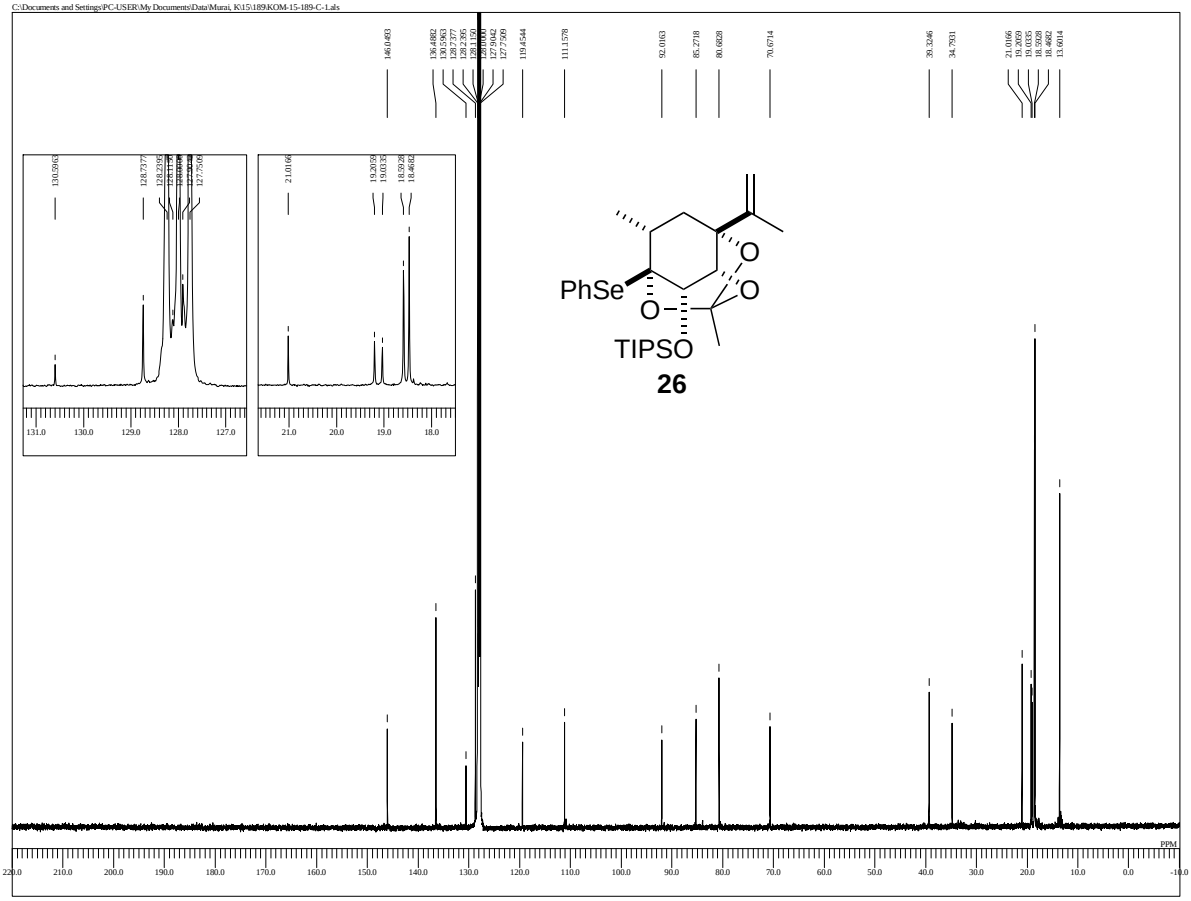
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\189\KOM-15-189-H-1.als



DFILE KOM-15-189-H-1.als
COMNT KOM-15-189-H
DATIM 30-10-2012 21:50:54
MENUF
OBNUC 1H
OFR 395.88 MHz
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
PW1 6.38 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 13107
SPO 13107
TIMES 32
DUMMY 1
FREQU 5938.15 Hz
FLT 30000 Hz
DELAY 16.68 usec
ACQTM 2.2073 sec
PD 5.0000 sec
SCANS 32
ADBIT 16
RGAIN 36
BF 0.01 Hz
T1 0.00
T2 0.00
T3 100.00
T4 100.00
EXMOD single_pulse.ex2
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE KOM-15-189-H-1.als
SF
LKSET 13.20 KHz
LKFIN 69.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 23.4 c
SLVNT C6D6
EXREF 7.16 ppm

KOM-15-189-C

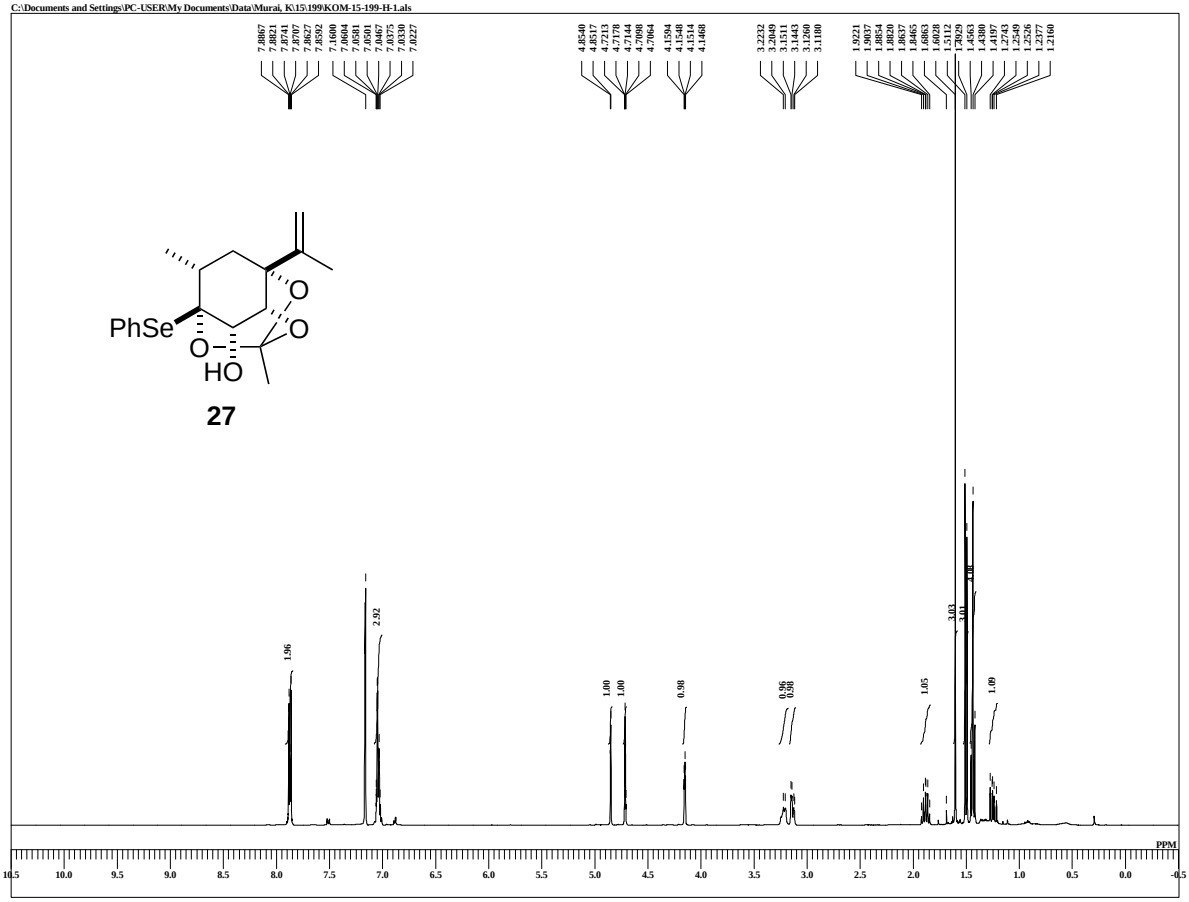
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\189\KOM-15-189-C-1.als



DFILE KOM-15-189-C-1.als
COMNT KOM-15-189-C
DATIM 31-10-2012 05:15:42
MENUF
OBNUC 13C
OFR 99.55 MHz
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
PW1 3.25 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 26214
SPO 26214
TIMES 4000
DUMMY 4
FREQU 24999.62 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 2.0000 sec
SCANS 4000
ADBIT 16
RGAIN 60
BF 1.00 Hz
T1 0.00
T2 0.00
T3 100.00
T4 100.00
EXMOD single_pulse_dec
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE KOM-15-189-C-1.als
SF
LKSET 13.20 KHz
LKFIN 69.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 22.8 c
SLVNT C6D6
EXREF 128.00 ppm

KOM-15-199-H

C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\199\KOM-15-199-H-1.als



DFILE KOM-15-199-H-1.als
COMNT KOM-15-199-H
DATIM 18-10-2012 22:29:39
MENUF
OBNUC 1H
OFR 395.88 MHz
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
PW1 6.38 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 13107
SPO 13107
TIMES 32
DUMMY 1
FREQU 5938.15 Hz
FLT 30000 Hz
DELAY 16.68 usec
ACQTM 2.2073 sec
PD 5.0000 sec
SCANS 32
ADBIT 16
RGAIN 30
BF 0.01 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse.ex2
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE KOM-15-199-H-1.als
SF
LKSET 13.20 KHz
LKFIN 69.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 23.9 c
SLVNT C6D6
EXREF 7.16 ppm

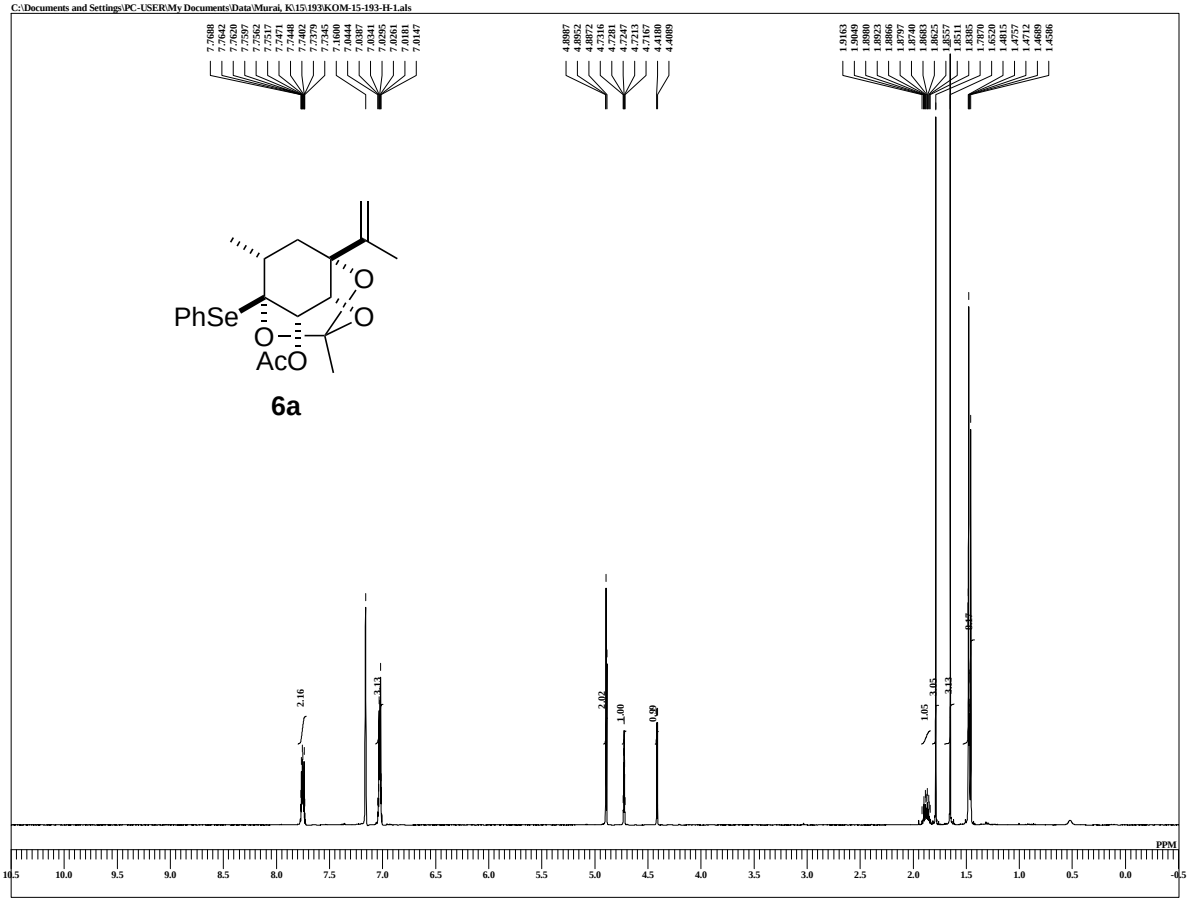
KOM-15-199-C

C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\199\KOM-15-199-C-1.als

DFILE KOM-15-199-C-1.als
COMNT KOM-15-199-C
DATIM 19-10-2012 05:03:39
MENUF
OBNUC 13C
OFR 99.55 MHz
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
PW1 3.25 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 26214
SPO 26214
TIMES 3000
DUMMY 4
FREQU 24999.62 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 2.0000 sec
SCANS 3000
ADBIT 16
RGAIN 60
BF 0.01 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse_dec
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE KOM-15-199-C-1.als
SF
LKSET 13.20 KHz
LKFIN 69.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 22.8 c
SLVNT C6D6
EXREF 128.00 ppm

KOM-15-193-H

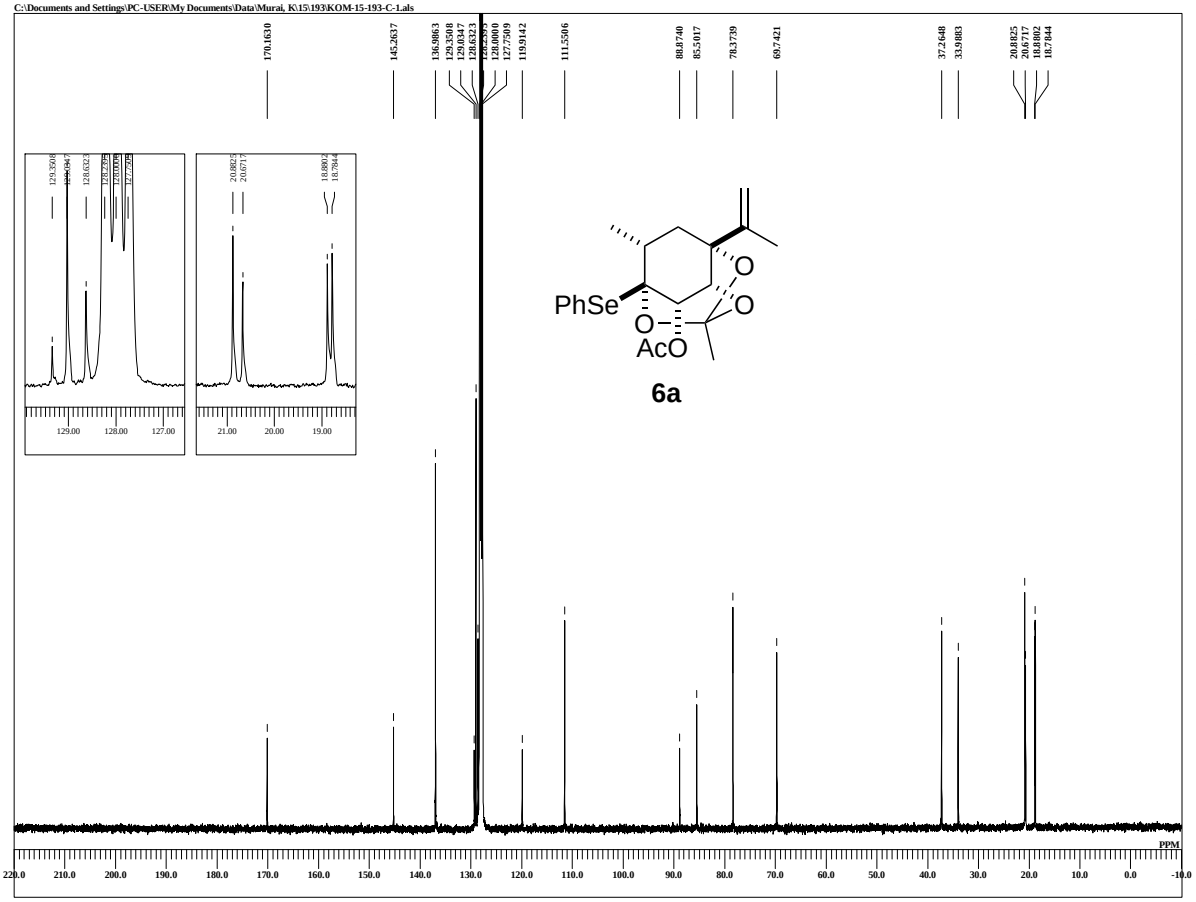
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\193\KOM-15-193-H-1.als



DFILE KOM-15-193-H-1.als
COMNT KOM-15-193-H
DATIM 17-10-2012 09:48:47
MENUF
OBNUC 1H
OFR 395.88 MHz
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
PW1 6.38 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 13107
SPO 13107
TIMES 16
DUMMY 1
FREQU 5938.15 Hz
FLT 30000 Hz
DELAY 16.68 usec
ACQTM 2.2073 sec
PD 5.0000 sec
SCANS 16
ADBIT 16
RGAIN 34
BF 0.01 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse.ex2
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE KOM-15-193-H-1.als
SF
LKSET 13.20 KHz
LKFIN 69.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 23.0 c
SLVNT C6D6
EXREF 7.16 ppm

KOM-15-193-C

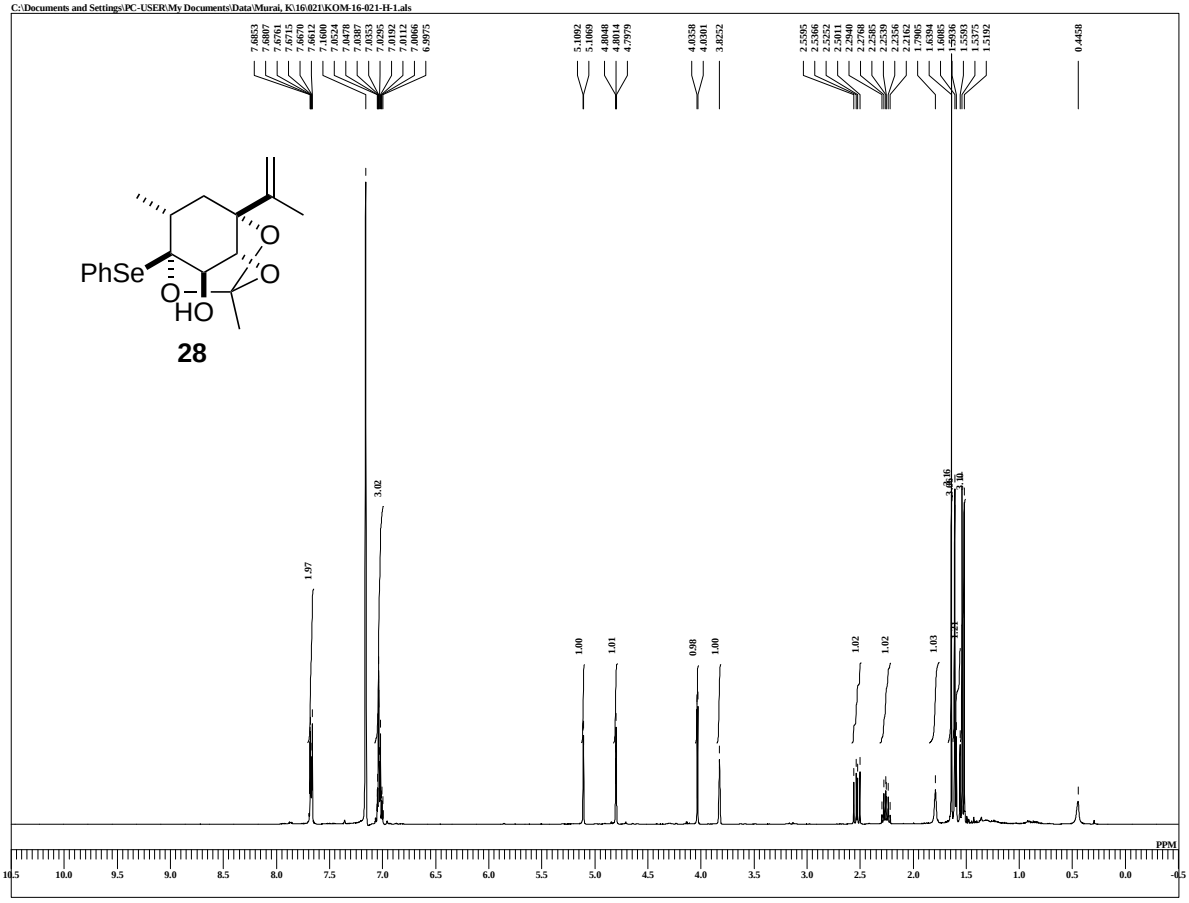
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\193\KOM-15-193-C-1.als



DFILE KOM-15-193-C-1.als
COMNT KOM-15-193-C
DATIM 17-10-2012 05:01:12
MENUF
OBNUC 13C
OFR 99.55 MHz
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
PW1 3.25 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 26214
SPO 26214
TIMES 3000
DUMMY 4
FREQU 24999.62 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 2.0000 sec
SCANS 3000
ADBIT 16
RGAIN 60
BF 1.00 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse_dec
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE KOM-15-193-C-1.als
SF
LKSET 13.20 KHz
LKFIN 69.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 22.9 c
SLVNT C6D6
EXREF 128.00 ppm

KOM-16-021-H

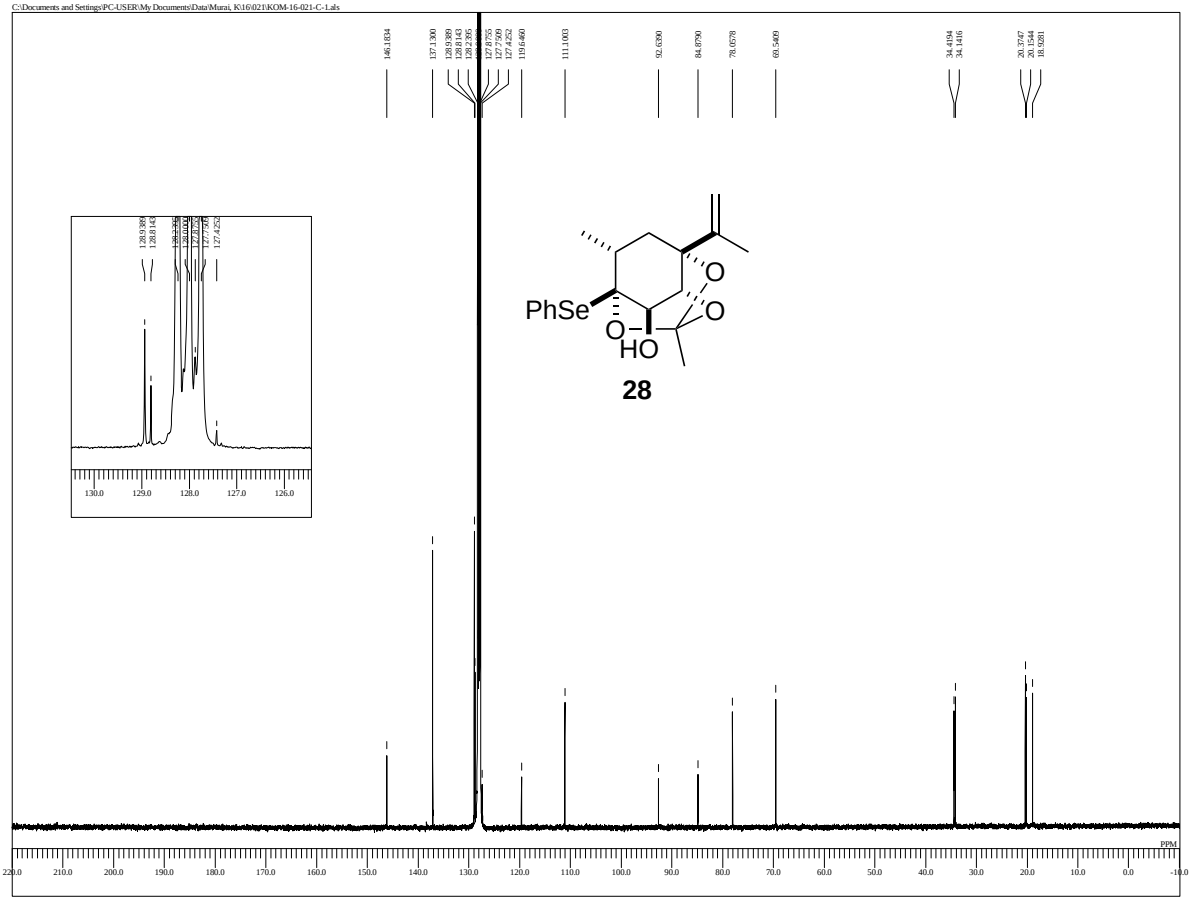
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\021\KOM-16-021-H-1.als



DFILE	KOM-16-021-H-1.als
COMNT	KOM-16-021-H
DATIM	26-10-2012 21:56:35
MENUF	
OBNUC	1H
OFR	395.88 MHz
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
PW1	6.38 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	13107
SPO	13107
TIMES	32
DUMMY	1
FREQU	5938.15 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	5.0000 sec
SCANS	32
ADBIT	16
RGAIN	40
BF	0.01 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse.ex2
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-16-021-H-1.als
SF	
LKSET	13.20 KHz
LKFIN	69.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	23.7 c
SLVNT	C6D6
EXREF	7.16 ppm

KOM-16-021-C

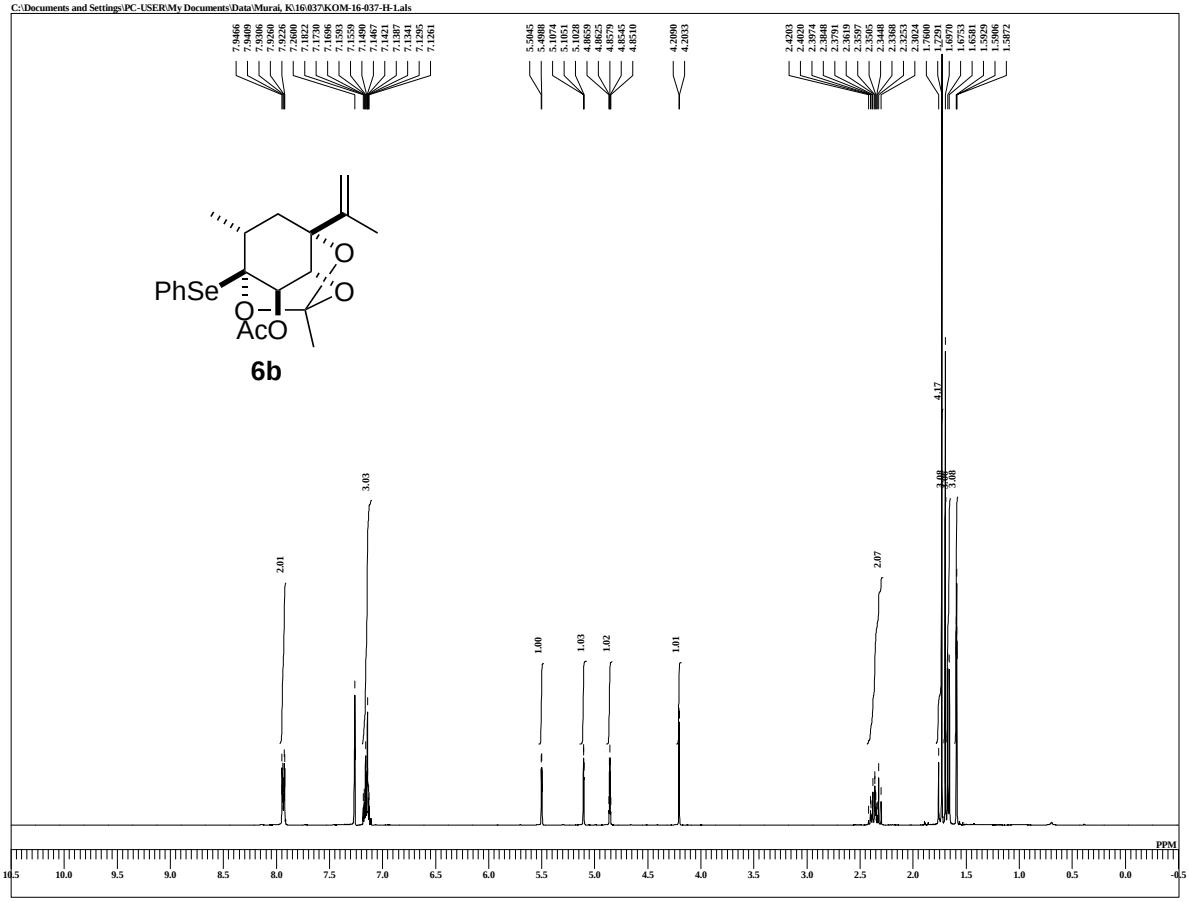
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\021\KOM-16-021-C-1.als



DFILE	KOM-16-021-C-1.als
COMNT	KOM-16-021-C
DATIM	27-10-2012 06:54:13
MENUF	
OBNUC	13C
OFR	99.55 MHz
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
PW1	3.25 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	26214
SPO	26214
TIMES	5000
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	2.0000 sec
SCANS	5000
ADBIT	16
RGAIN	60
BF	1.00 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse_dec
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-16-021-C-1.als
SF	
LKSET	13.20 KHz
LKFIN	69.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	22.5 c
SLVNT	C6D6
EXREF	128.00 ppm

KOM-16-037-H

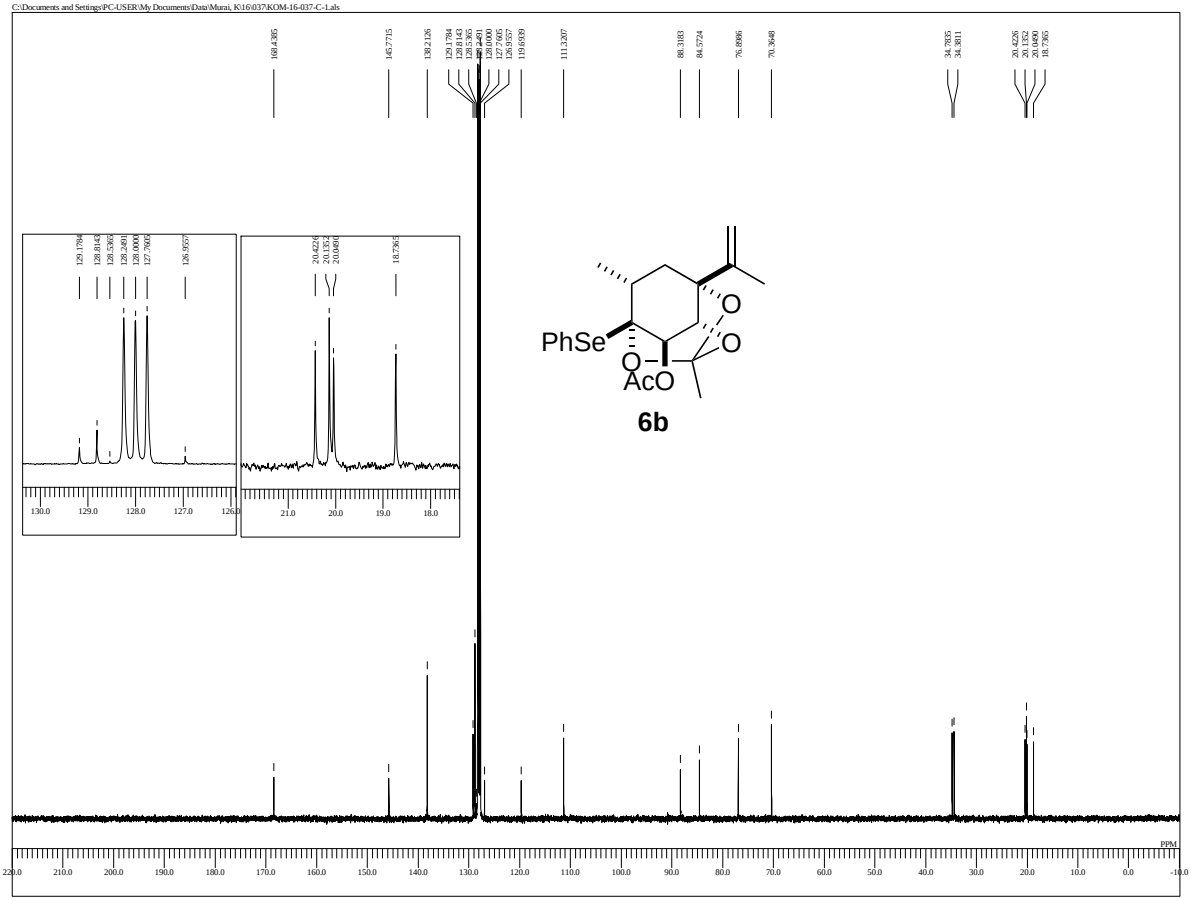
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\037\KOM-16-037-H-1.als



DFILE KOM-16-037-H-1.als
COMNT KOM-16-037-H
DATIM 31-10-2012 19:22:08
MENUF
OBNUC 1H
OFR 395.88 MHz
OBFRQ 395.88 MHz
OBSET 6.28 KHz
OBFIN 0.87 Hz
PW1 6.38 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 13107
SPO 13107
TIMES 16
DUMMY 1
FREQU 5938.15 Hz
FLT 30000 Hz
DELAY 16.68 usec
ACQTM 2.2073 sec
PD 5.0000 sec
SCANS 16
ADBIT 16
RGAIN 26
BF 0.01 Hz
T1 0.00
T2 0.00
T3 100.00
T4 100.00
EXMOD single_pulse.ex2
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE KOM-16-037-H-1.als
SF
LKSET 13.20 KHz
LKFIN 69.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 23.2 c
SLVNT C6D6
EXREF 7.26 ppm

KOM-16-037-C

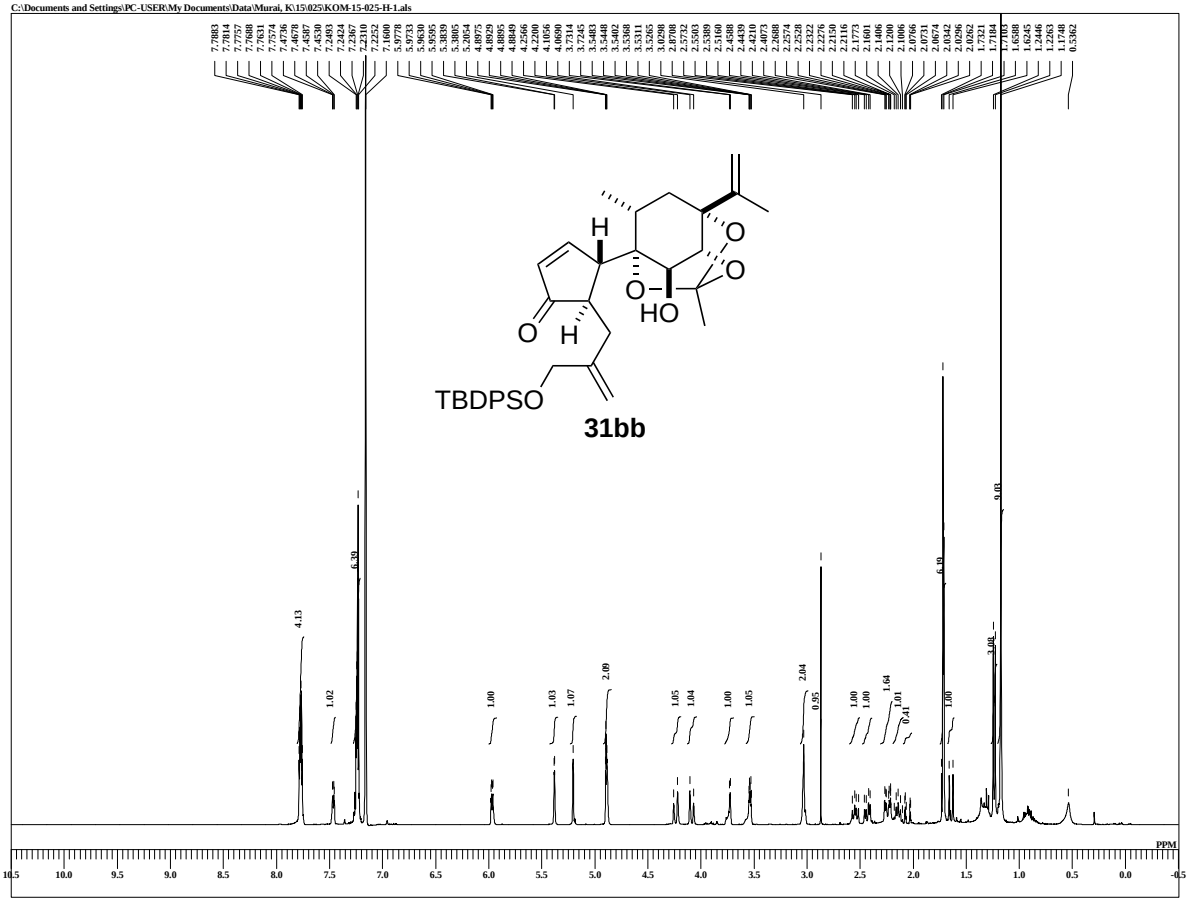
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\037\KOM-16-037-C-1.als



DFILE KOM-16-037-C-1.als
COMNT KOM-16-037-C
DATIM 31-10-2012 20:01:12
MENUF
OBNUC 13C
OFR 99.55 MHz
OBFRQ 99.55 MHz
OBSET 5.13 KHz
OBFIN 0.98 Hz
PW1 3.25 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 26214
SPO 26214
TIMES 81
DUMMY 4
FREQU 24999.62 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 2.0000 sec
SCANS 81
ADBIT 16
RGAIN 60
BF 1.00 Hz
T1 0.00
T2 0.00
T3 100.00
T4 100.00
EXMOD single_pulse_dec
EXPCM
IRNUC 1H
IFR 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE KOM-16-037-C-1.als
SF
LKSET 13.20 KHz
LKFIN 69.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 23.4 c
SLVNT C6D6
EXREF 128.00 ppm

KOM-15-025-H

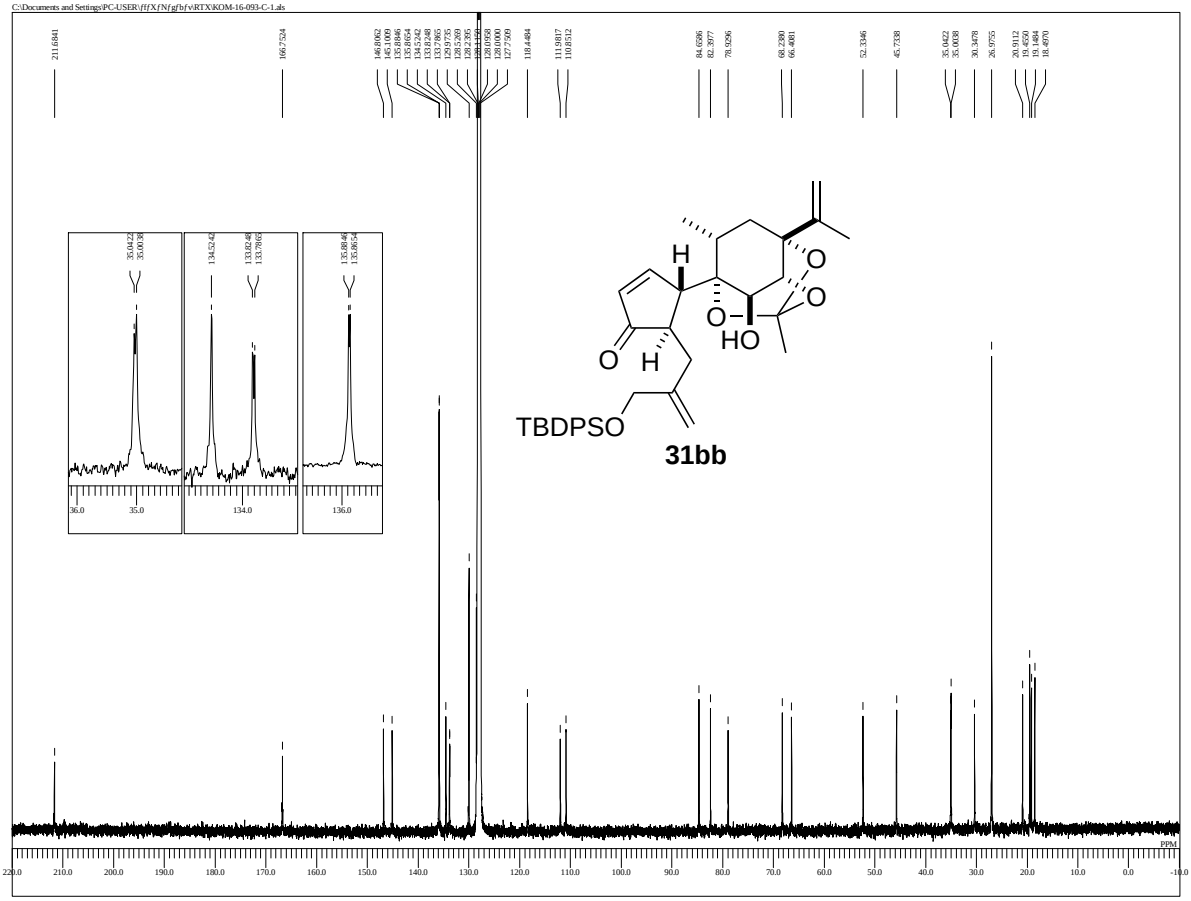
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\025\KOM-15-025-H-1.als



DFILE	KOM-15-025-H-1.als
COMNT	KOM-15-025-H
DATIM	02-07-2012 21:45:20
MENUF	
OBNUC	1H
OFR	395.88 MHz
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
PW1	6.38 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	13107
SPO	13107
TIMES	32
DUMMY	1
FREQU	5938.15 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	5.0000 sec
SCANS	32
ADBIT	16
RGAIN	36
BF	0.01 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse.ex2
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-15-025-H-1.als
SF	
LKSET	13.20 KHz
LKFIN	69.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	24.8 c
SLVNT	C6D6
EXREF	7.16 ppm

KOM-16-093-C

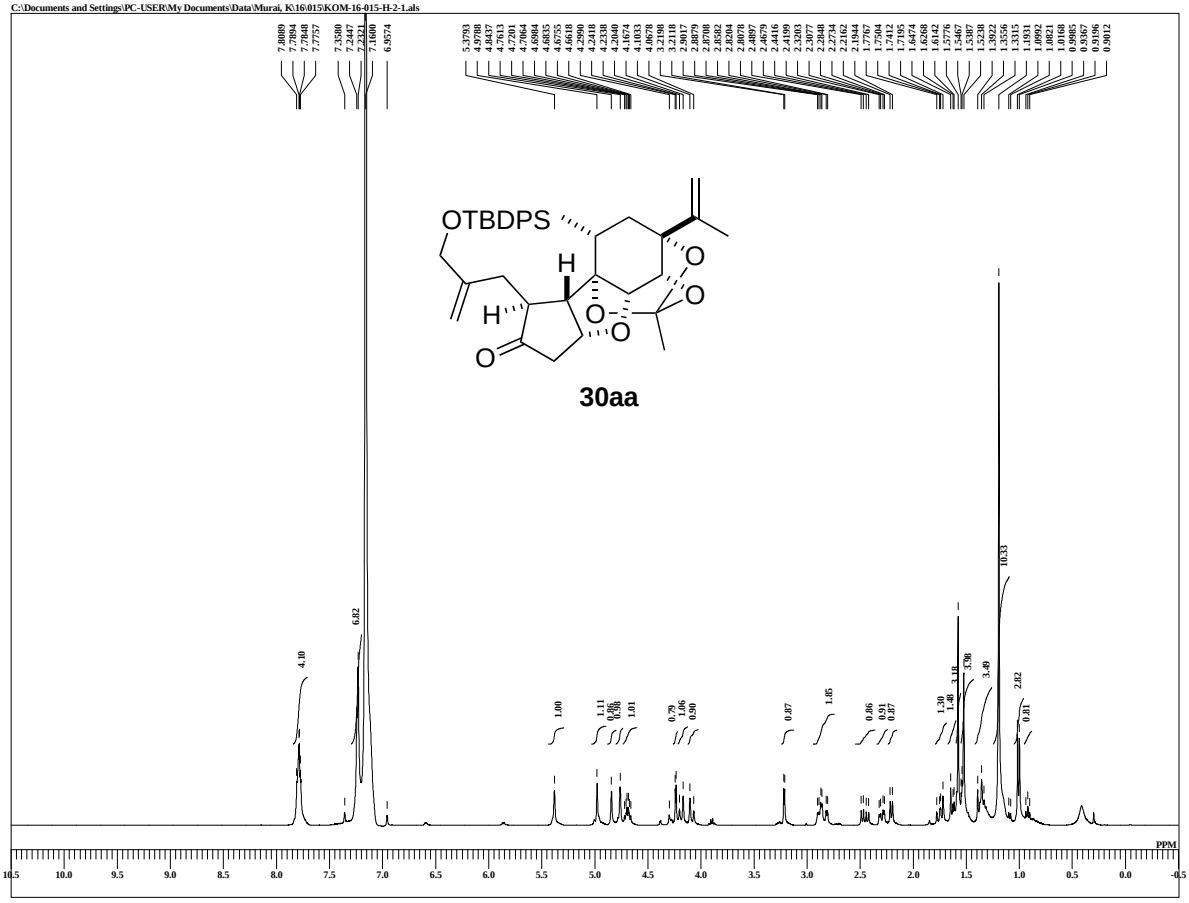
C:\Documents and Settings\PC-USER\ff\fXfNfgfbfv\RTX\KOM-16-093-C-1.als



DFILE	KOM-16-093-C-1.als
COMNT	KOM-16-093-C
DATIM	05-01-2013 14:57:09
MENUF	
OBNUC	13C
OFR	99.55 MHz
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
PW1	3.25 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	26214
SPO	26214
TIMES	3486
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	2.0000 sec
SCANS	3486
ADBIT	16
RGAIN	60
BF	1.00 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse_dec
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-16-093-C-1.als
SF	
LKSET	13.20 KHz
LKFIN	69.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	20.5 c
SLVNT	C6D6
EXREF	128.00 ppm

KOM-16-015-H-2

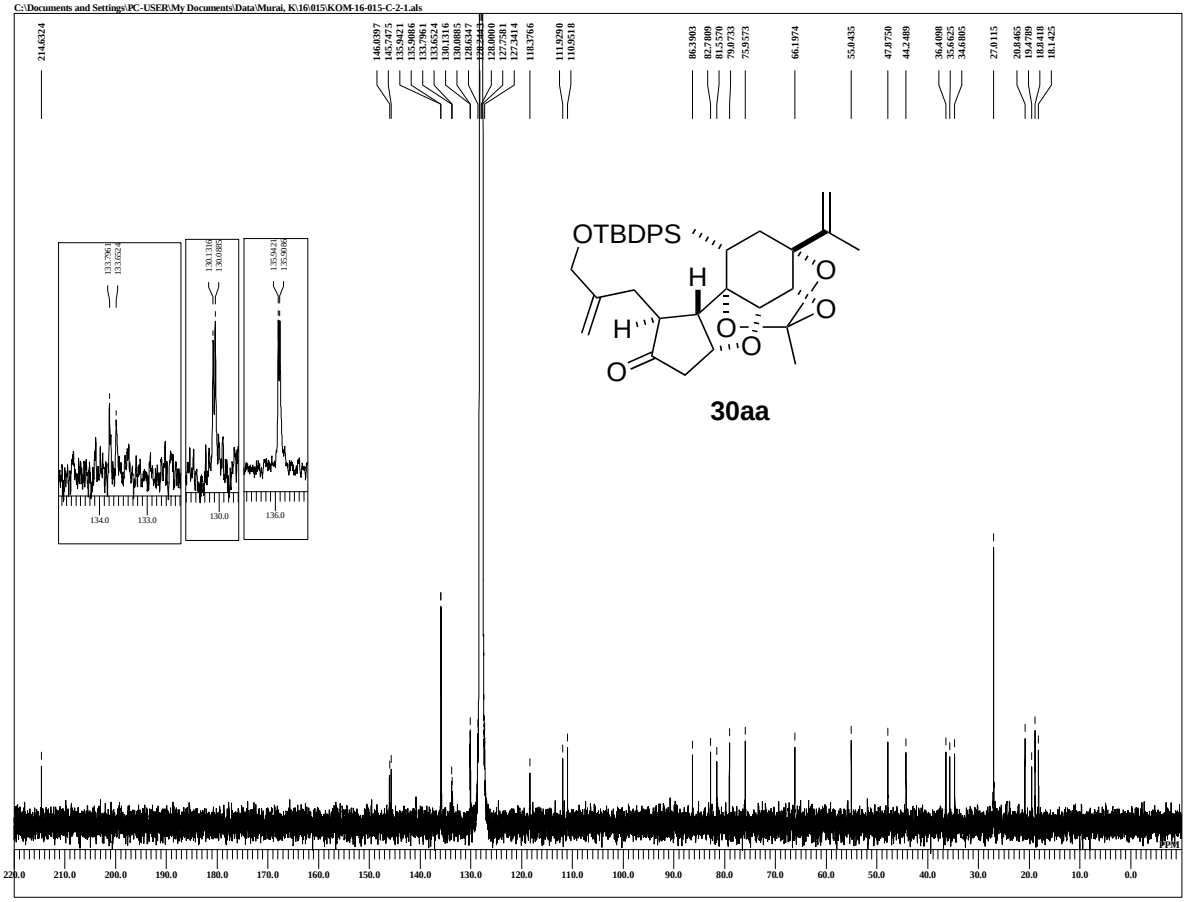
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\015\KOM-16-015-H-2-1.als



DFILE	KOM-16-015-H-2-1.als
COMNT	KOM-16-015-H-2
DATIM	05-01-2013 21:01:18
MENUF	
OBNUC	1H
OFR	395.88 MHz
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
PW1	6.38 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	13107
SPO	13107
TIMES	128
DUMMY	1
FREQU	5938.15 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	5.0000 sec
SCANS	128
ADBIT	16
RGAIN	46
BF	0.01 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse.ex2
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-16-015-H-2-1.als
SF	
LKSET	13.20 KHz
LKFIN	69.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	20.2 c
SLVNT	C6D6
EXREF	7.16 ppm

KOM-16-015-C-2

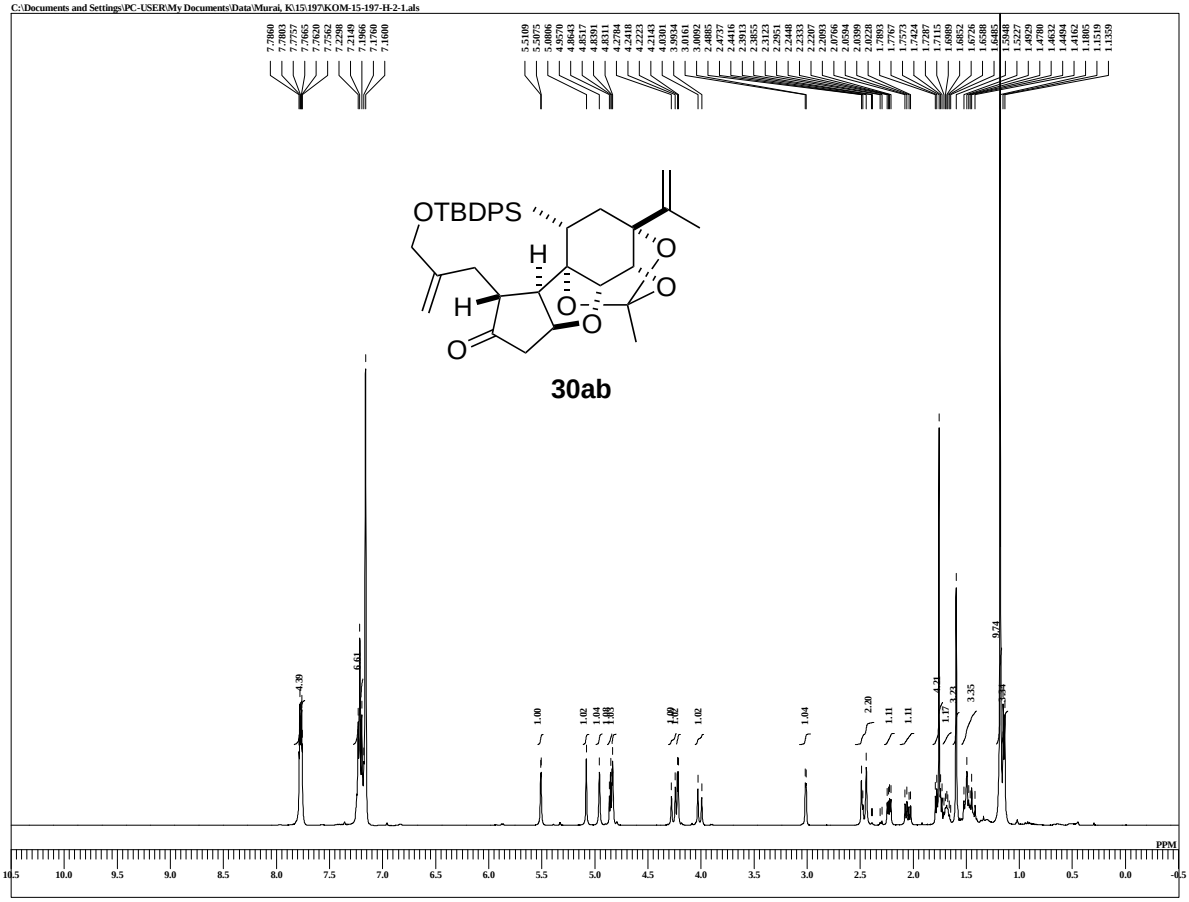
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\015\KOM-16-015-C-2-1.als



DFILE	KOM-16-015-C-2-1.als
COMNT	KOM-16-015-C-2
DATIM	06-01-2013 12:09:10
MENUF	
OBNUC	13C
OFR	99.55 MHz
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
PW1	3.25 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	104856
SPO	104856
TIMES	17855
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	2.0000 sec
SCANS	17855
ADBIT	16
RGAIN	60
BF	1.00 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse_dec
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-16-015-C-2-1.als
SF	
LKSET	13.20 KHz
LKFIN	69.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	20.1 c
SLVNT	C6D6
EXREF	128.00 ppm

KOM-15-197-H-2

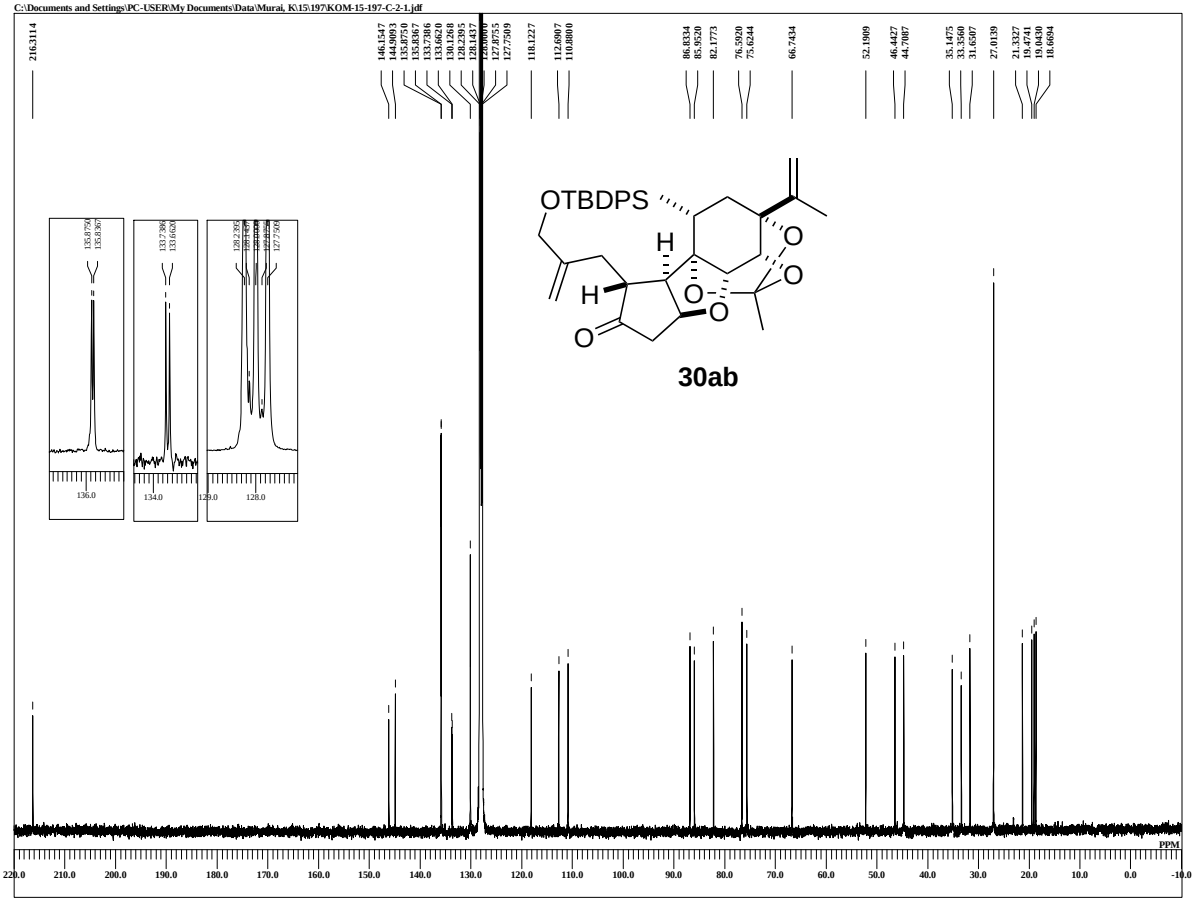
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\197\KOM-15-197-H-2-1.als




```
DFILE   KOM-15-197-H-2-1.als
COMNT   KOM-15-197-H-2
DATIM   04-01-2013 22:59:46
MENUF
OBNUC   1H
OFR     395.88 MHz
OBFRQ   395.88 MHz
OBSET   6.28 KHz
OBFIN   0.87 Hz
PW1     6.38 usec
DEADT   0.00 usec
PREDL   0.00000 msec
IWT     1.0000 sec
POINT   13107
SPO     13107
TIMES   128
DUMMY   1
FREQU   5938.15 Hz
FLT     30000 Hz
DELAY   16.68 usec
ACQTM   2.2073 sec
PD      5.0000 sec
SCANS   128
ADBIT   16
RGAIN   38
BF      0.01 Hz
T1      0.00
T2      0.00
T3      90.00
T4      100.00
EXMOD   single_pulse.ex2
EXPCM
IRNUC   1H
IFR     395.88 MHz
IRSET   6.28 KHz
IRFIN   0.87 Hz
IRRPW   115 usec
IRATN   79
DFILE   KOM-15-197-H-2-1.als
SF
LKSET   13.20 KHz
LKFIN   69.6 Hz
LKLEV   0
LGAIN   0
LKPHS   0
LKSIG   0
CSPED   0 Hz
FILDC
FILDF
CTEMP   20.1 c
SLVNT   C6D6
EXREF   7.16 ppm
```

KOM-15-197-C-2

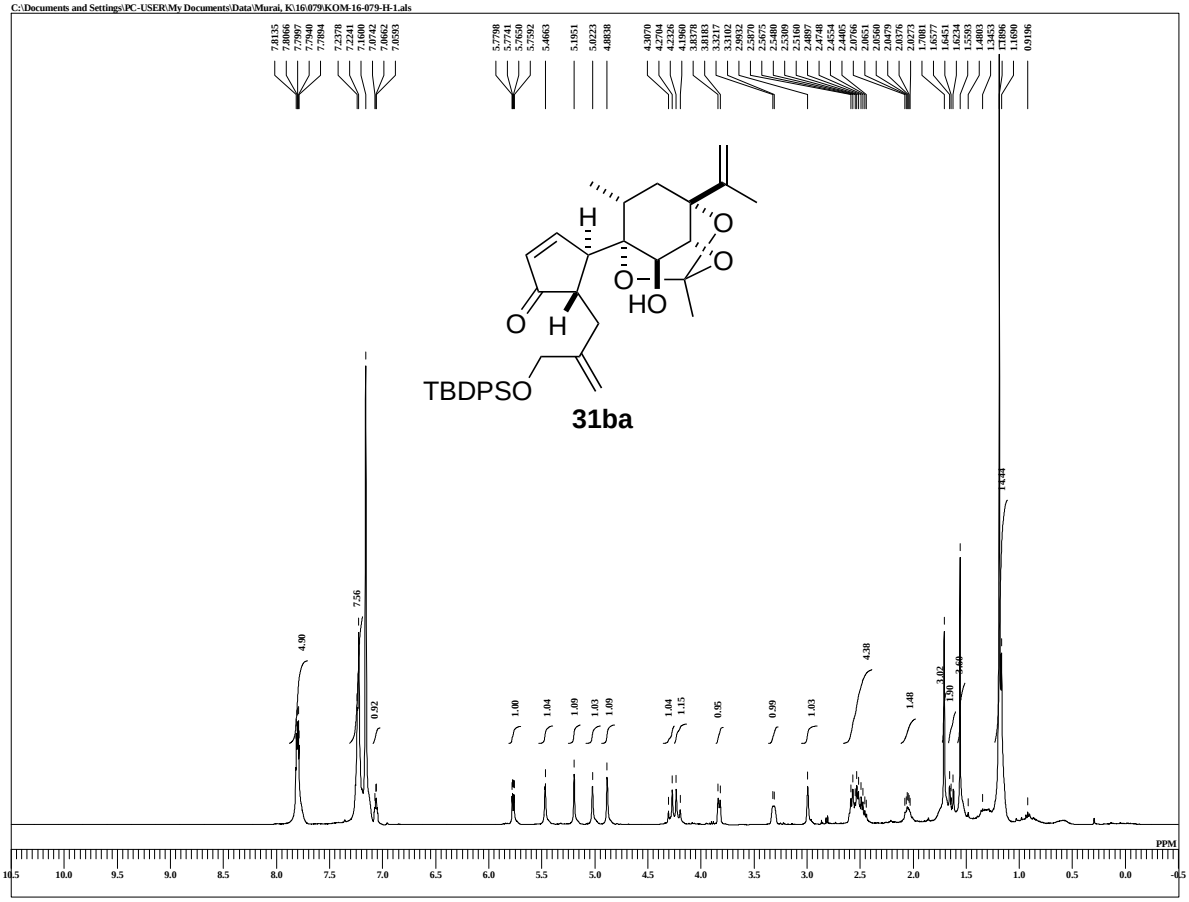
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\197\KOM-15-197-C-2-1.jdf




```
DFILE   KOM-15-197-C-2-1.jdf
COMNT   KOM-15-197-C-2
DATIM   05-01-2013 07:28:25
MENUF
OBNUC   13C
OFR     99.55 MHz
OBFRQ   99.55 MHz
OBSET   5.13 KHz
OBFIN   0.98 Hz
PW1     3.25 usec
DEADT   0.00 usec
PREDL   0.00000 msec
IWT     1.0000 sec
POINT   32768
SPO     32768
TIMES   10000
DUMMY   4
FREQU   31250.00 Hz
FLT     125000 Hz
DELAY   20.50 usec
ACQTM   1.0486 sec
PD      2.0000 sec
SCANS   10000
ADBIT   16
RGAIN   60
BF      1.00 Hz
T1      0.00
T2      0.00
T3      90.00
T4      100.00
EXMOD   single_pulse_dec
EXPCM
IRNUC   1H
IFR     395.88 MHz
IRSET   6.28 KHz
IRFIN   0.87 Hz
IRRPW   115 usec
IRATN   79
DFILE   KOM-15-197-C-2-1.jdf
SF
LKSET   13.20 KHz
LKFIN   69.6 Hz
LKLEV   0
LGAIN   0
LKPHS   0
LKSIG   0
CSPED   0 Hz
FILDC
FILDF
CTEMP   19.8 c
SLVNT   C6D6
EXREF   128.00 ppm
```

KOM-16-079-H

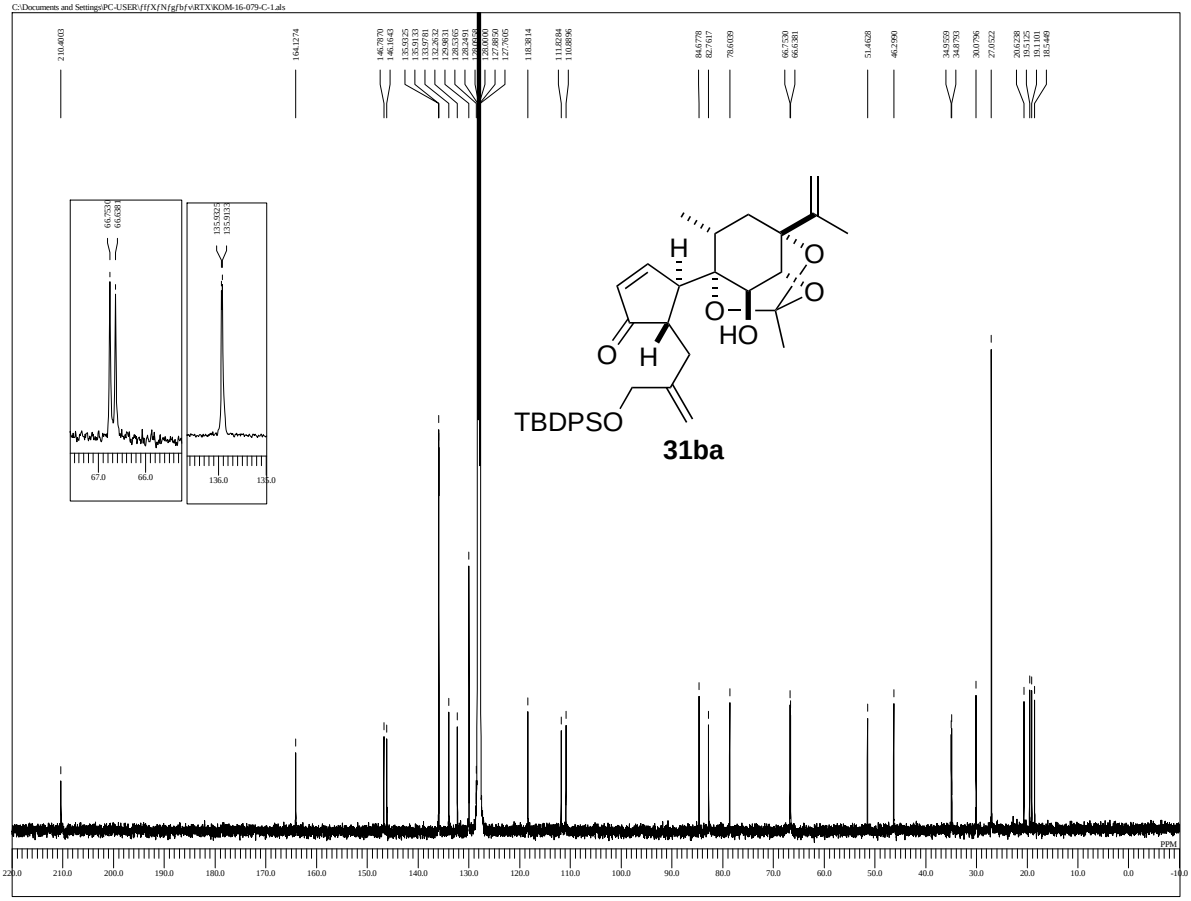
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\079\KOM-16-079-H-1.als



DFILE	KOM-16-079-H-1.als
COMNT	KOM-16-079-H
DATIM	26-11-2012 22:09:46
MENUF	
OBNUC	1H
OFR	395.88 MHz
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
PW1	6.38 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	13107
SPO	13107
TIMES	32
DUMMY	1
FREQU	5938.15 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	5.0000 sec
SCANS	32
ADBIT	16
RGAIN	38
BF	0.01 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse.ex2
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-16-079-H-1.als
SF	
LKSET	13.20 KHz
LKFIN	69.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	20.9 c
SLVNT	C6D6
EXREF	7.16 ppm

KOM-16-079-C

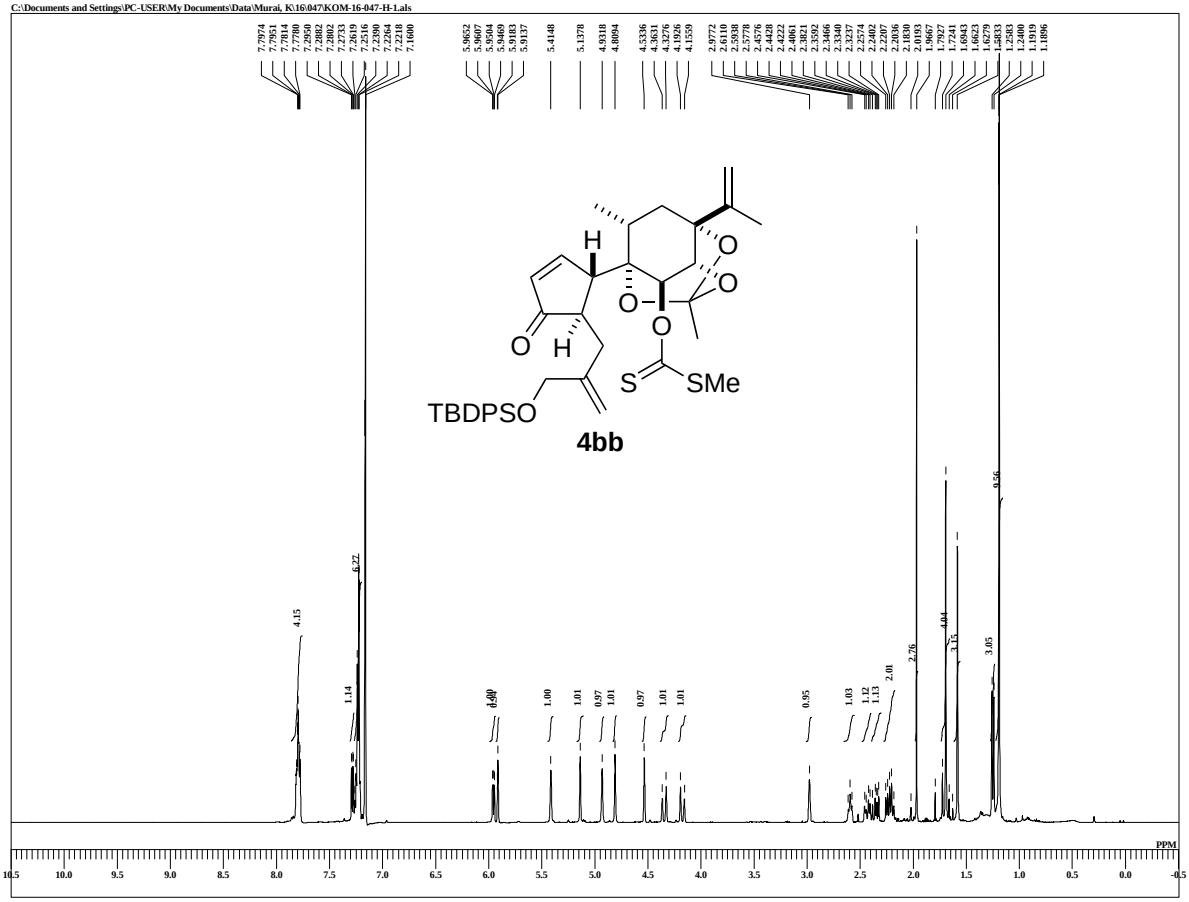
C:\Documents and Settings\PC-USER\ffXfNfgfbfvRTX\KOM-16-079-C-1.als



DFILE	KOM-16-079-C-1.als
COMNT	KOM-16-079-C
DATIM	27-11-2012 08:57:49
MENUF	
OBNUC	13C
OFR	99.55 MHz
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
PW1	3.25 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	26214
SPO	26214
TIMES	8000
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	2.0000 sec
SCANS	8000
ADBIT	16
RGAIN	60
BF	1.00 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse_dec
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-16-079-C-1.als
SF	
LKSET	13.20 KHz
LKFIN	69.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	20.5 c
SLVNT	C6D6
EXREF	128.00 ppm

KOM-16-047-H

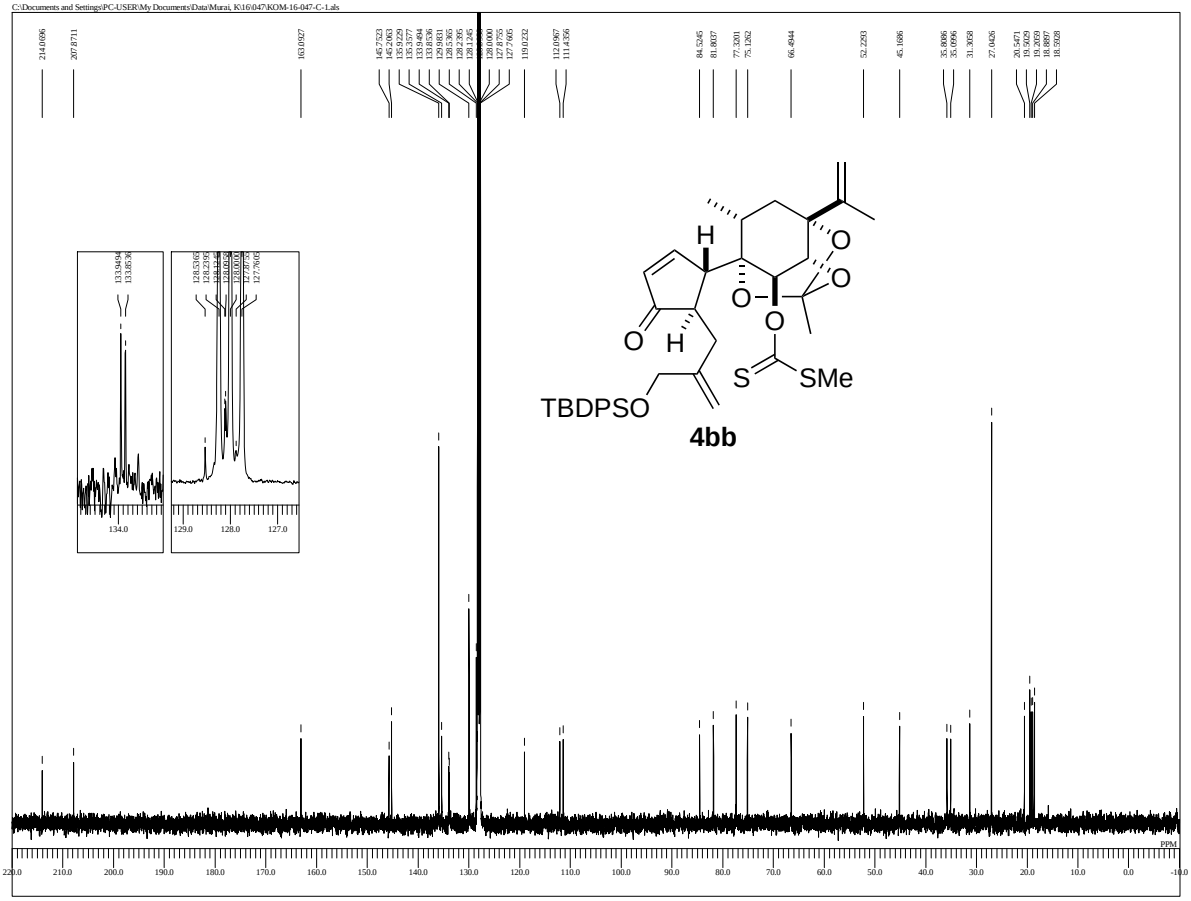
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\047\KOM-16-047-H-1.als



DFILE	KOM-16-047-H-1.als
COMNT	KOM-16-047-H
DATIM	09-11-2012 11:29:43
MENUF	
OBNUC	1H
OFR	395.88 MHz
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
PW1	6.38 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	13107
SPO	13107
TIMES	32
DUMMY	1
FREQU	5938.15 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	5.0000 sec
SCANS	32
ADBIT	16
RGAIN	30
BF	0.01 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse.ex2
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-16-047-H-1.als
SF	
LKSET	13.20 KHz
LKFIN	69.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	22.3 c
SLVNT	C6D6
EXREF	7.16 ppm

KOM-16-047-C

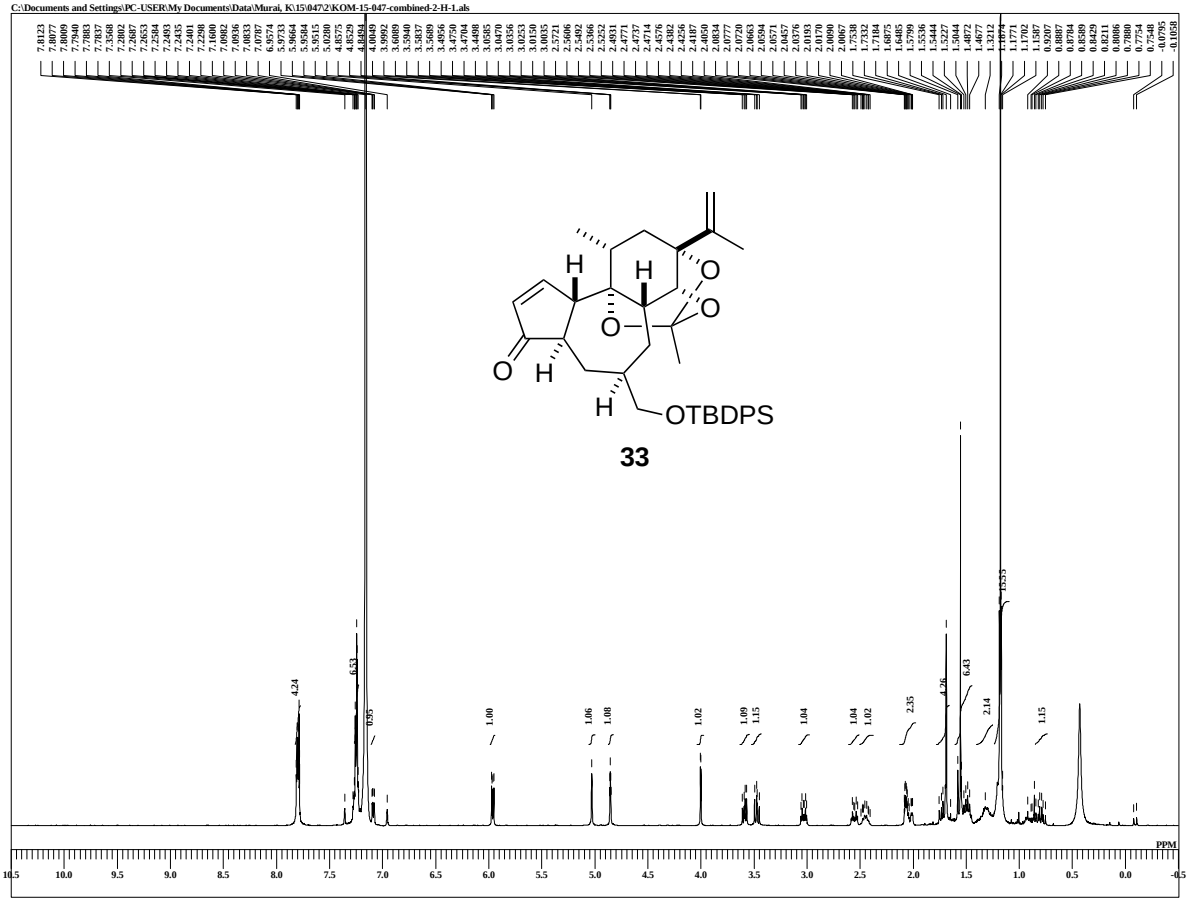
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\047\KOM-16-047-C-1.als



DFILE	KOM-16-047-C-1.als
COMNT	KOM-16-047-C
DATIM	09-11-2012 12:25:04
MENUF	
OBNUC	13C
OFR	99.55 MHz
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
PW1	3.25 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	26214
SPO	26214
TIMES	149
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	2.0000 sec
SCANS	149
ADBIT	16
RGAIN	60
BF	1.00 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse_dec
EXPCM	
IRNUC	1H
IFR	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KOM-16-047-C-1.als
SF	
LKSET	13.20 KHz
LKFIN	69.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	22.7 c
SLVNT	C6D6
EXREF	128.00 ppm

KOM-047-combined-2-H

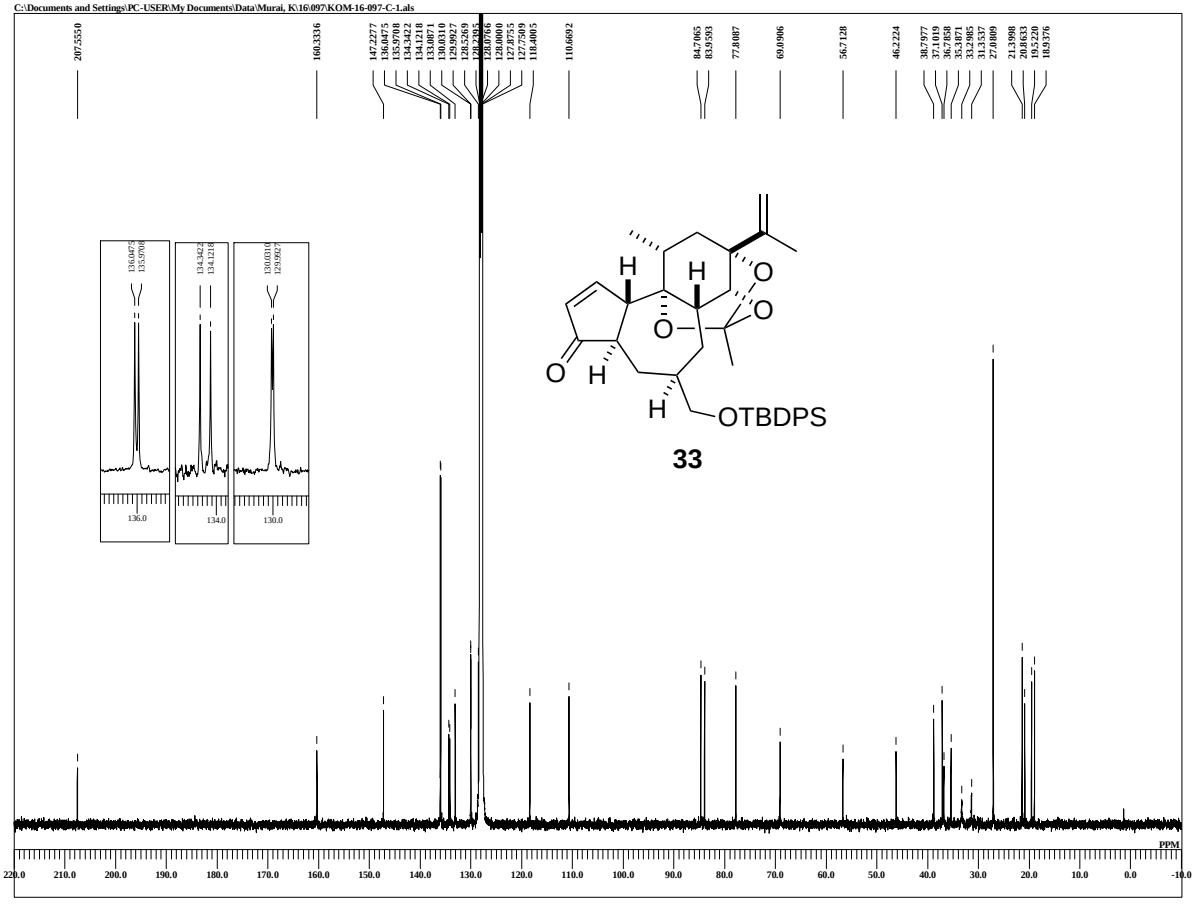
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\15\047\2\KOM-15-047-combined-2-H-1.als




```
DFILE     KOM-15-047-combined-2
COMNT     KOM-047-combined-2-H
DATIM     21-07-2012 17:58:54
MENUF
OBNUC     1H
OFR       395.88 MHz
OBFRQ     395.88 MHz
OBSET     6.28 KHz
OBFIN     0.87 Hz
PW1       6.38 usec
DEADT     0.00 usec
PREDL     0.00000 msec
IWT       1.0000 sec
POINT     13107
SPO       13107
TIMES     64
DUMMY     1
FREQU     5938.15 Hz
FLT       30000 Hz
DELAY     16.68 usec
ACQTM     2.2073 sec
PD        5.0000 sec
SCANS     64
ADBIT     16
RGAIN     46
BF        0.01 Hz
T1        0.00
T2        0.00
T3        90.00
T4        100.00
EXMOD     single_pulse.ex2
EXPCM
IRNUC     1H
IFR       395.88 MHz
IRSET     6.28 KHz
IRFIN     0.87 Hz
IRRPW     147 usec
IRATN     79
DFILE     KOM-15-047-combined-2
SF
LKSET     13.20 KHz
LKFIN     69.6 Hz
LKLEV     0
LGAIN     0
LKPHS     0
LKSIG     0
CSPED     0 Hz
FILDC
FILDF
CTEMP     23.5 c
SLVNT     C6D6
EXREF     7.16 ppm
```

KOM-16-097-C

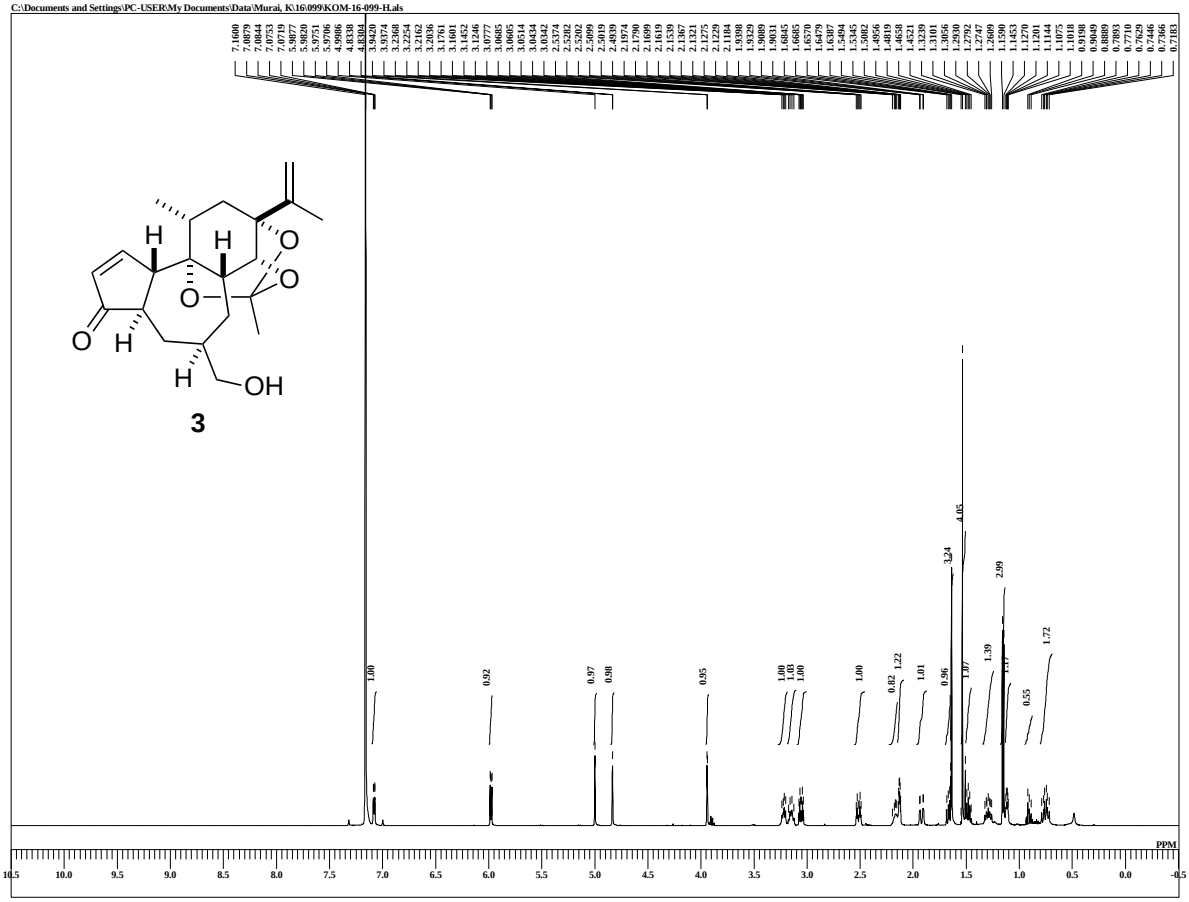
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\097\KOM-16-097-C-1.als




```
DFILE     KOM-16-097-C-1.als
COMNT     KOM-16-097-C
DATIM     07-01-2013 07:26:48
MENUF
OBNUC     13C
OFR       99.55 MHz
OBFRQ     99.55 MHz
OBSET     5.13 KHz
OBFIN     0.98 Hz
PW1       3.25 usec
DEADT     0.00 usec
PREDL     0.00000 msec
IWT       1.0000 sec
POINT     26214
SPO       26214
TIMES     12000
DUMMY     4
FREQU     24999.62 Hz
FLT       125000 Hz
DELAY     20.50 usec
ACQTM     1.0486 sec
PD        2.0000 sec
SCANS     12000
ADBIT     16
RGAIN     60
BF        1.00 Hz
T1        0.00
T2        0.00
T3        90.00
T4        100.00
EXMOD     single_pulse_dec
EXPCM
IRNUC     1H
IFR       395.88 MHz
IRSET     6.28 KHz
IRFIN     0.87 Hz
IRRPW     115 usec
IRATN     79
DFILE     KOM-16-097-C-1.als
SF
LKSET     13.20 KHz
LKFIN     69.6 Hz
LKLEV     0
LGAIN     0
LKPHS     0
LKSIG     0
CSPED     0 Hz
FILDC
FILDF
CTEMP     20.1 c
SLVNT     C6D6
EXREF     128.00 ppm
```

KOM-16-099-H

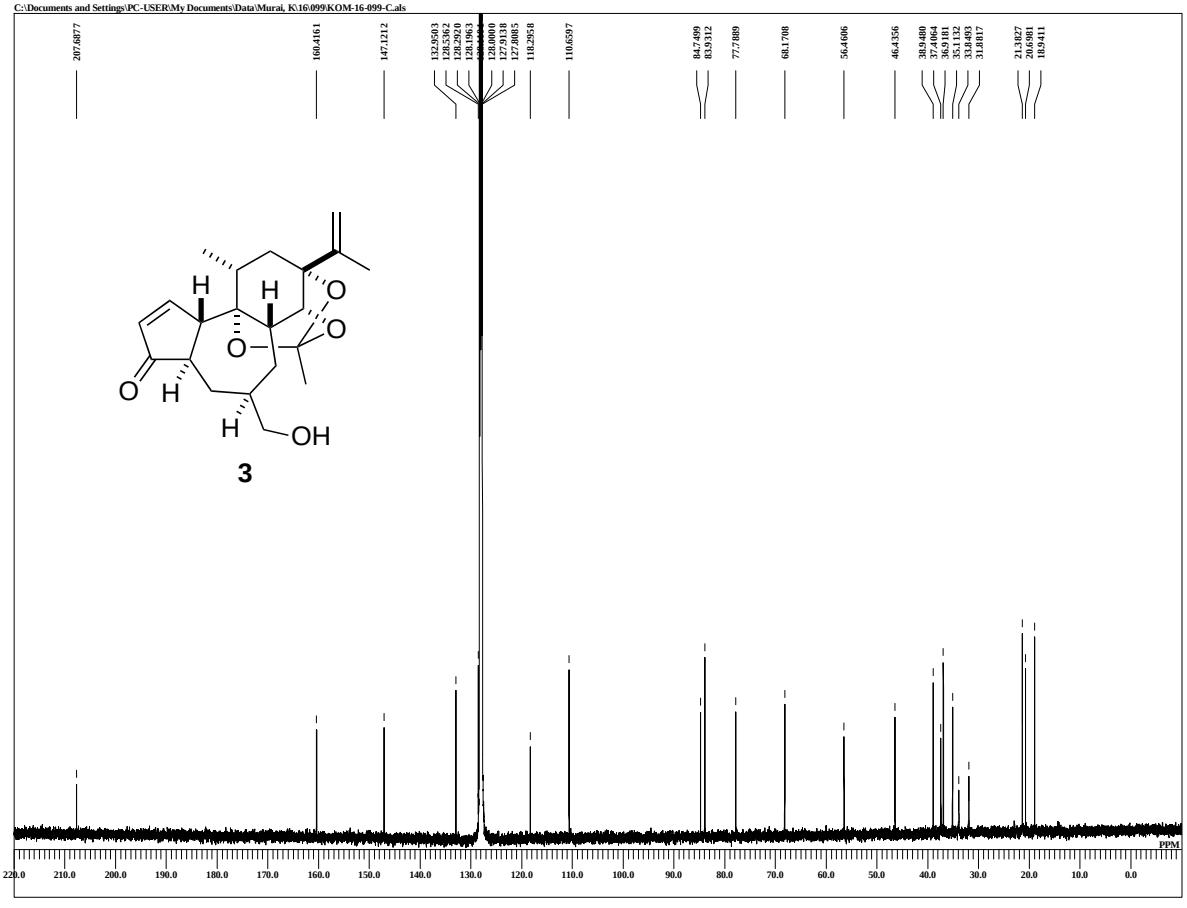
C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\099\KOM-16-099-H.als




```
DFILE   KOM-16-099-H.als
COMNT   KOM-16-099-H
DATIM   07-01-2013 01:06:39
MENUF
OBNUC   1H
OFR     495.13 MHz
OBFRQ   495.13 MHz
OBSET   4.38 KHz
OBFIN   9.64 Hz
PW1     6.00 usec
DEADT   0.00 usec
PREDL   0.00000 usec
IWT     1.0000 sec
POINT   13107
SPO     13107
TIMES   64
DUMMY   1
FREQU   7429.31 Hz
FLT     38000 Hz
DELAY   13.16 usec
ACQTM   1.7642 sec
PD      5.0000 sec
SCANS   64
ADBIT   16
RGAIN   44
BF      0.01 Hz
T1      0.00
T2      0.00
T3      90.00
T4      100.00
EXMOD   single_pulse.ex2
EXPCM
IRNUC   1H
IFR     495.13 MHz
IRSET   4.38 KHz
IRFIN   9.64 Hz
IRRPW   92 usec
IRATN   79
DFILE   KOM-16-099-H.als
SF
LKSET   748.40 KHz
LKFIN   90.6 Hz
LKLEV   0
LGAIN   0
LKPHS   0
LKSIG   0
CSPED   0 Hz
FILDC
FILDF
CTEMP   20.2 c
SLVNT   C6D6
EXREF   7.16 ppm
```

KOM-16-099-C

C:\Documents and Settings\PC-USER\My Documents\Data\Murai, K\16\099\KOM-16-099-C.als




```
DFILE   KOM-16-099-C.als
COMNT   KOM-16-099-C
DATIM   07-01-2013 09:00:23
MENUF
OBNUC   13C
OFR     124.51 MHz
OBFRQ   124.51 MHz
OBSET   3.45 KHz
OBFIN   6.00 Hz
PW1     3.70 usec
DEADT   0.00 usec
PREDL   0.00000 msec
IWT     1.0000 sec
POINT   52428
SPO     52428
TIMES   10000
DUMMY   4
FREQU   31249.52 Hz
FLT     157000 Hz
DELAY   20.80 usec
ACQTM   0.8389 sec
PD      2.0000 sec
SCANS   10000
ADBIT   16
RGAIN   50
BF      1.00 Hz
T1      0.00
T2      0.00
T3      90.00
T4      100.00
EXMOD   single_pulse_dec
EXPCM
IRNUC   1H
IFR     495.13 MHz
IRSET   4.38 KHz
IRFIN   9.64 Hz
IRRPW   92 usec
IRATN   79
DFILE   KOM-16-099-C.als
SF
LKSET   748.40 KHz
LKFIN   90.6 Hz
LKLEV   0
LGAIN   0
LKPHS   0
LKSIG   0
CSPED   0 Hz
FILDC
FILDF
CTEMP   20.7 c
SLVNT   C6D6
EXREF   128.00 ppm
```