Supporting Information

Symmetry-Driven Synthesis of 9-Demethyl-10,15-dideoxyryanodol

Daisuke Urabe, Masanori Nagatomo, Koji Hagiwara, Kengo Masuda and Masayuki Inoue*

Graduate School of Pharmaceutical Sciences
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
Fax: (+81)3-5841-0568
E-mail: inoue@mol.f.u-tokyo.ac.jp

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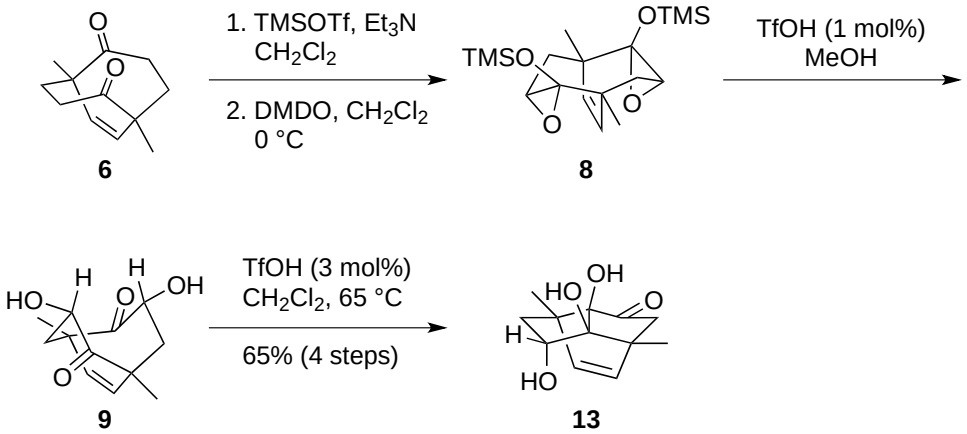
1. Experimental

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 50-60 μm Silica Gel 60 (Kanto Chemical Co., Inc.). Melting points were measured on a Yanaco MP-S3 micro melting point apparatus or a Yanaco MP-J3 micro melting point apparatus, and are uncorrected. 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 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. High resolution mass spectra were measured on Bruker microTOFII or JEOL JMS-T100LP. The numbering corresponds to those of 9-demethyl-10,15-dideoxyryanodol (**1**).



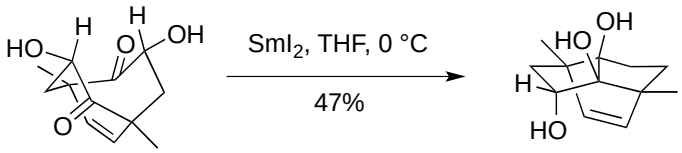
Epoxide 8. TMSOTf (12 mL, 66 mmol) was added to a mixture of ketone **6** (4.09 g, 21.3 mmol) and Et_3N (18 mL, 130 mmol) in CH_2Cl_2 (200 mL) at room temperature. The reaction mixture was stirred for 1.5 h at room temperature, and successively diluted with hexane and saturated aqueous $NaHCO_3$. The resultant mixture was extracted with hexane (200 mL x3). The combined organic layers were washed with brine (200 mL), dried over Na_2SO_4, filtered and

concentrated to afford the crude TMS enol ether, which was used for the next reaction without further purification.

DMDO (71 mM in acetone, 600 mL, 43 mmol) was added to a solution of the above crude TMS enol ether in CH_2Cl_2 (200 mL) at 0 °C. The reaction mixture was stirred for 10 min at 0 °C, and concentrated to afford crude epoxide **8**, which was used for the next reaction without further purification.

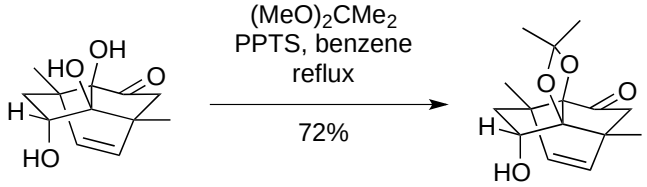
α-Hydroxy ketone 9. TfOH (19 μL, 0.21 μmol) was added to a solution of the above crude epoxide **8** in MeOH (200 mL) at room temperature. The reaction mixture was stirred for 2 h at room temperature, and concentrated to afford crude α-hydroxy ketone **9**, which was used for the next reaction without further purification. For a characterization, a small amount of **9** was purified by flash chromatography on silica gel (hexane/EtOAc 2:1): colorless crystal; m.p. 133 °C; IR (neat) ν_{max} 3450, 1699, 1081, 923 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.35 (6H, s, C*H*$_3$ x 2), 1.95 (2H, dd, *J* = 14.9, 10.3 Hz, C*H*$_A$H$_B$ x 2), 2.58 (2H, dd, *J* = 14.9, 8.6 Hz, CH$_A$*H*$_B$ x 2), 3.59 (2 H, br s, O*H* x 2), 4.79 (2H, dd, *J* = 10.3, 8.6 Hz, C*H*OH x 2), 5.68 (2H, s, C*H*=C x 2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.8, 46.5, 48.0, 75.1, 137.1, 206.9; HRMS (ESI) calcd for $C_{12}H_{16}O_4Na$ 247.0946 ($M+Na^+$), found 247.0944.

Triol 13. TfOH (19 μL, 0.21 μmol) was added to a solution of the above crude α-hydroxy ketone **9** in CH_2Cl_2 (430 mL) at room temperature. The reaction mixture was stirred for 9 h at 65 °C in a sealed tube, and additional TfOH (19 μL, 0.21 μmol) was added. After the reaction mixture was stirred for further 24 h, TfOH (19 μL, 0.21 μmol) was added again. The reaction mixture was stirred for further 15 h and concentrated. The residue was purified by flash chromatography on silica gel (90 g, hexane/EtOAc 3:1 to 1:1 to 1:2) to afford triol **13** (3.12 g, 13.9 mmol) in 65% yield over 4 steps: colorless solid; m.p. 170 °C; IR (neat) ν_{max} 3443, 2559, 1742, 1104 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) δ 0.97 (3H, s, C*H*$_3$), 1.36 (3H, s, C*H*$_3$), 1.67 (1H, dd, *J* = 13.2, 1.2 Hz, C*H*$_A$H$_B$CHOH), 2.22 (1H, d, *J* = 17.2 Hz, C*H*$_A$H$_B$CO), 2.48 (1H, dd, *J* = 13.2, 9.8 Hz, CH$_A$*H*$_B$CHOH), 2.57 (1H, d, *J* = 17.2 Hz, CH$_A$*H*$_B$CO), 4.38 (1H, dd, *J* = 9.8, 1.2 Hz, C*H*OH), 5.45 (1H, d, *J* = 9.2 Hz, C*H*$_A$=CH$_B$), 5.65 (1H, d, *J* = 9.2 Hz, CH$_A$=C*H*$_B$); ^{13}C NMR (125 MHz, CD_3OD) δ 18.1, 18.6, 46.8, 51.0, 52.1, 56.7, 80.7, 92.6, 92.9, 134.2, 136.7, 217.6; HRMS (ESI) calcd for $C_{12}H_{16}O_4Na$ 247.0946 ($M+Na^+$), found 247.0943.



9 **11**

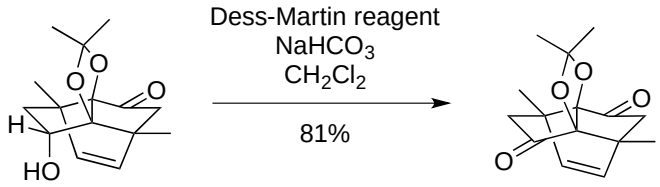
Triol 11. SmI_2 (0.1M in THF, 1.4 mL, 140 μmol) was added to a solution of α-hydroxy ketone **9** (7.6 mg, 34 μmol) in THF (1.2 mL) at 0 °C. The reaction mixture was stirred for 5 min at 0 °C, and then 0.5 M HCl solution was added. The resultant solution was extracted with EtOAc (x3), and the combined organic layers were washed with saturated aqueous $Na_2S_2O_3$ and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 5:1 to 3:1) to afford triol **11** (3.3 mg, 16 μmol) in 47% yield: white solid; m.p. 149 °C; IR (neat) ν_{max} 3476, 3499, 2930, 1457, 1278, 1110, 1019 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.99 (3H, s, C*H*$_3$), 1.21 (3H, s, C*H*$_3$), 1.41-1.52 (2H, m, C*H*$_A$H$_B$C*H*$_A$H$_B$), 1.58 (1H, d, *J* = 13.2 Hz, C*H*$_A$H$_B$CHOH), 1.90 (1H, br s, O*H*), 2.40 (1H, br s, O*H*), 2.82 (1H, br, s, O*H*), 2.01-2.12 (2H, m, CH$_A$*H*$_B$CH$_A$*H*$_B$), 2.54 (1H, dd, *J* = 13.2, 9.2 Hz, CH$_A$*H*$_B$CHOH), 4.26 (1H, d, *J* = 9.2 Hz, CH$_2$C*H*OH), 5.49 (1H, d, *J* = 9.2 Hz, C*H*$_A$=CH$_B$), 5.51 (1H, d, *J* = 9.2 Hz, CH$_A$=C*H*$_B$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.2, 18.8, 29.5, 40.5, 50.2, 50.5, 50.8, 81.0, 90.9, 91.4, 133.7, 135.8; HRMS (ESI) calcd for $C_{12}H_{18}O_3Na$ 233.1154 ($M+Na^+$), found 233.1144.



13 **14**

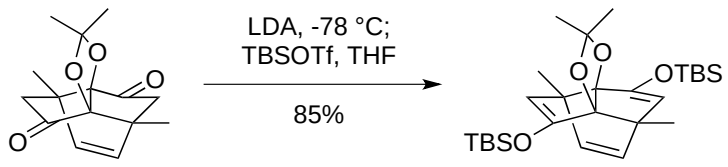
Acetonide 14. A solution of triol **13** (3.12 g, 13.9 mmol), PPTS (3.49 g, 13.9 mmol) in a mixture of 2,2-dimethoxypropane (140 mL) in benzene (140 mL) was refluxed for 3.5 days. After addition of MeOH (100 mL), the resultant solution was concentrated. The procedure was repeated three times. The resultant residue was purified by flash chromatography on silica gel (150 g, hexane/EtOAc 5:1 to 3:1 to 1:1) to afford acetonide **14** (2.65 g, 10.0 mmol) in 72% yield: colorless solid; m.p. 90 °C; IR (neat) ν_{max} 3494, 2993, 1750, 1068, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.12 (3H, s, C*H*$_3$), 1.34 (3H, s, C*H*$_3$), 1.46 (3H, s, C*H*$_3$), 1.50 (3H, s, C*H*$_3$), 1.74 (1H, d, *J* = 13.7 Hz, C*H*$_A$H$_B$CHOH), 2.03 (1H, br d, *J* = 8.0 Hz, O*H*), 2.38 (1H, d, *J* = 17.2 Hz, C*H*$_A$H$_B$CO), 2.71 (1H, dd, *J* = 13.7,

9.2 Hz, CH_AH_BCHOH), 2.77 (1H, d, J = 17.2 Hz, CH_AH_BCO), 4.39 (1H, br dd, J = 9.2, 8.0 Hz, C*H*OH), 5.61 (1H, d, J = 9.8 Hz, CH_A=CH_B), 5.84 (1H, d, J = 9.2 Hz, CH_A=CH_B); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.7, 17.7, 28.0, 28.1, 45.3, 49.7, 52.0, 56.5, 78.7, 96.9, 100.3, 115.4, 135.0, 137.4, 214.7; HRMS (ESI) calcd for $C_{15}H_{20}O_4Na$ 287.1259 ($M+Na^+$), found 287.1253.



14 **5**

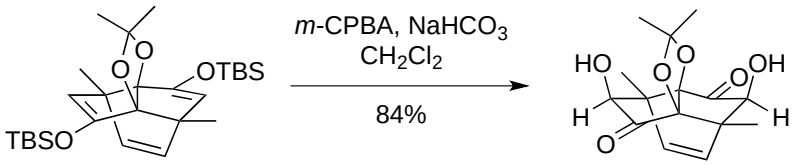
Ketone 5. Dess-Martin periodinane (6.40 g, 15.1 mmol) was added to a suspension of acetonide **14** (2.65 g, 10.0 mmol) in CH_2Cl_2 (100 mL) at room temperature. The reaction mixture was stirred for 80 min at room temperature, and saturated aqueous $Na_2S_2O_3$ (50 mL) and $NaHCO_3$ (50 mL) were successively added. The resultant mixture was extracted with EtOAc (100 mL x2), and the combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica gel (50 g, hexane/EtOAc 5:1) to afford ketone **5** (2.12 g, 8.09 mmol) in 81% yield: colorless solid; m.p. 179 °C; IR (neat) ν_{max} 2931, 1750, 1075 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (6H, s, CH_3 x 2), 1.40 (6H, s, CH_3 x 2), 2.48 (2H, d, J = 17.2 Hz, CH_AH$_B$ x 2), 2.83 (2H, d, J = 17.2 Hz, CH_AH_B x 2), 5.68 (2H, s, C*H*=C x 2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.4, 27.5, 44.9, 55.0, 94.6, 116.9, 135.4, 212.3; HRMS (ESI) calcd for $C_{15}H_{18}O_4Na$ 285.1103 ($M+Na^+$), found 285.1098.



5 **15**

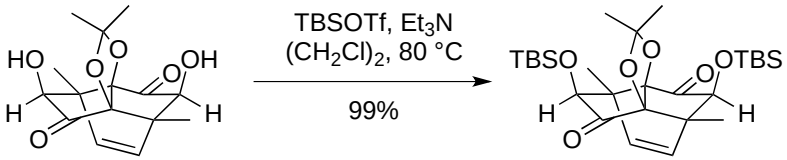
TBS-enol ether 15. *n*-BuLi (1.6 M in hexane, 11 mL, 18 mmol) was added to a solution of *i*-Pr_2NH (2.5 μL, 18 mmol) in THF (10 mL) at -78 °C. The mixture was stirred for 30 min at 0 °C, and cooled to -78 °C. A solution of ketone **5** (465 mg, 1.77 μmol) in THF (8 mL) was added to the mixture via cannula. The reaction mixture was stirred for further 30 min at -78 °C, and then TBSOTf (2.0 mL, 8.7 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for further 1 h, and then saturated aqueous NH_4Cl (15

mL) was added. The resultant mixture was extracted with Et_2O (20 mL x3), and 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 on silica gel (Fujisilysia BW-300, 50 g, hexane/EtOAc 1:0 to 70:1 to 30:1) to afford TBS-enol ether **15** (733 mg, 1.50 mmol) in 85% yield: pale yellow solid; m.p. 182-183 °C; IR (neat) ν_{max} 2935, 1624, 1319, 1247, 1138 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.11 (6H, s, C*H*$_3$ of TBS x 2), 0.15 (6H, s, C*H*$_3$ of TBS x 2), 0.98 (18H, s, *t*-Bu of TBS x 2), 1.31 (6H, s, C*H*$_3$ x 2), 1.73 (6H, s, C*H*$_3$ x 2), 5.06 (2H, s, C*H*=COTBS x 2), 5.92 (2H, s, C*H*=C x 2); ^{13}C NMR (100 MHz, C_6D_6) δ -4.7, -4.3, 17.2, 18.1, 25.7, 28.5, 48.3, 102.6, 115.1, 119.1, 141.5, 149.3; HRMS (ESI) calcd for $C_{27}H_{46}O_4Si_2Na$ 513.2832 ($M+Na^+$), found 513.2831.



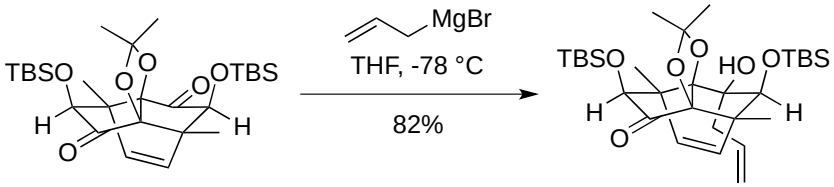
15 **16**

α-Hydroxy ketone 16. A solution of *m*-CPBA (purified by washing with pH 7 phosphate buffer and drying in vacuo, 1.0 g, 5.8 mmol) was added to a mixture of TBS enol ether **15** (733 mg, 1.50 mmol) and $NaHCO_3$ (1.3 g, 15 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The reaction mixture was stirred for 1.5 h at room temperature, and saturated aqueous $Na_2S_2O_3$ (15 mL) was added. The resultant mixture was extracted with EtOAc (50 mL x3), and the combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (50 g, hexane/EtOAc 3:1 to 0:1) to afford α-hydroxy ketone **16** (369 mg, 1.26 mmol) in 84% yield: colorless solid; m.p. 220 °C; IR (neat) ν_{max} 3416, 2996, 1745, 1445, 1379, 1220, 1078 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) δ 1.33 (6H, s, C*H*$_3$ x 2), 1.39 (6H, s, C*H*$_3$ x 2), 3.65 (2H, s, C*H*OH x 2), 5.67 (2H, s, C*H*=C x 2); ^{13}C NMR (125 MHz, CD_3OD) δ 12.1, 27.9, 51.2, 83.1, 95.9, 118.9, 136.6, 216.0; HRMS (ESI) calcd for $C_{15}H_{18}O_6Na$ 317.1001 ($M+Na^+$), found 317.1003.



16 **4**

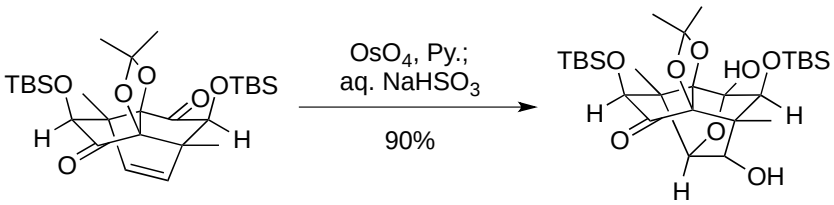
TBS-ether 4. TBSOTf (700 μL, 3.1 mmol) was added to a mixture of α-hydroxy ketone **16** (90 mg, 310 μmol) and Et_3N (860 μL, 6.1 mmol) in $(CH_2Cl)_2$ (3.1 mL) at room temperature. The reaction mixture was stirred for 4 h at 80 °C, and then cooled to 0 °C. Saturated aqueous NH_4Cl (3 mL) was added, and the resultant mixture was concentrated to remove $(CH_2Cl)_2$. The aqueous solution was extracted with EtOAc (3 mL x3), and the combined organic layers were washed with brine (3 mL), dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (10 g; hexane/EtOAc 20:1) to afford TBS-ether **4** (160 mg, 306 μmol) in 99% yield: colorless solid; m.p. 150-152 °C; IR (neat) ν_{max} 2931, 1765, 1257, 1102 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.09 (6H, s, C*H*$_3$ of TBS x 2), 0.10 (6H, s, C*H*$_3$ of TBS x 2), 0.88 (18H, s, *t*-Bu of TBS x 2), 1.33 (6H, s, C*H*$_3$ x 2), 1.39 (6H, s, C*H*$_3$ x 2), 3.64 (2H, s, C*H*OTBS x 2), 5.57 (2H, s, C*H*=C x 2); ^{13}C NMR (125 MHz, $CDCl_3$) δ –5.5, –4.6, 12.3, 18.2, 25.6, 27.6, 50.7, 82.1, 94.2, 117.9, 135.5, 213.8; HRMS (ESI) calcd for $C_{27}H_{46}O_6Si_2Na$ 545.2731 ($M+Na^+$), found 545.2714.



4 **17**

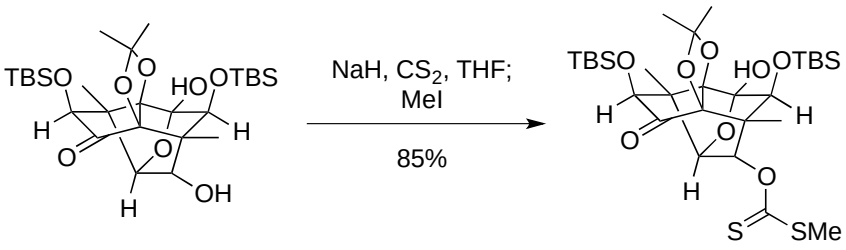
Allyl alcohol 17. Allyl magnesium bromide (1.0 M in Et_2O, 180 μL, 180 μmol) was added to a solution of **4** (4.7 mg, 9.0 μmol) in THF (0.9 mL) at -78 °C. The reaction mixture was stirred for 1 h at -78 °C, and then saturated aqueous NH_4Cl (5 mL) was added. The resultant mixture was stirred at room temperature, and extracted with CH_2Cl_2 (3 mL x3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (2 g, hexane/EtOAc 30:1 to 10:1) to afford allyl alcohol **17** (4.2 mg, 7.4 μmol) in 82% yield: colorless oil; IR (neat) ν_{max} 3469, 2936, 1755, 1464, 1373, 1255, 1097 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.10 (9H, s, C*H*$_3$ of TBS x 3), 0.11 (3H, s, C*H*$_3$ of TBS), 0.90 (9H, s, *t*-Bu of TBS), 0.94 (9H, s, *t*-Bu of TBS), 1.17 (3H, s, C*H*$_3$), 1.42 (3H, s, C*H*$_3$), 1.46 (3H, s, C*H*$_3$), 1.67 (3H,

s, C*H*$_3$), 2.34 (1H, dd, *J* = 13.5, 10.0 Hz, CH$_2$=CHC*H*$_A$H$_B$), 2.92 (1H, ddt, *J* = 13.5, 5.0, 1.5 Hz, CH$_2$=CHCH$_A$*H*$_B$), 3.51 (1H, s, C*H*(OTBS)CO), 3.54 (1H, s, O*H*), 3.79 (1H, s, C*H*(OTBS)COH), 5.06 (1H, br d, *J* = 17.5 Hz, C*H*$_A$H$_B$=CH), 5.09 (1H, dt, J = 10.0, 1.5 Hz, CH$_A$*H*$_B$=CH), 5.33 (1H, d, *J* = 9.0 Hz, CH=C*H*CC(OTBS)C(OH)), 5.65 (1H, d, *J* = 9.0 Hz, C*H*=CHCC(OTBS)C(OH)), 5.95 (1H, dtd, *J* = 17.5, 10.0, 5.0 Hz, CH$_2$=C*H*CH$_A$H$_B$); ^{13}C NMR (100 MHz, CDCl$_3$) δ –5.3, –4.6, –4.1, –3.7, 14.0, 14.5, 18.3, 18.4, 25.8, 25.9, 27.7, 29.4, 47.3, 51.2, 51.6, 79.0, 82.3, 83.7, 96.8, 98.3, 117.3, 117.7, 132.5, 136.1, 138.0, 217.5; HRMS (ESI) calcd for $C_{30}H_{52}O_6Si_2Na$ 587.3195 (M+Na$^+$), found 587.3205.



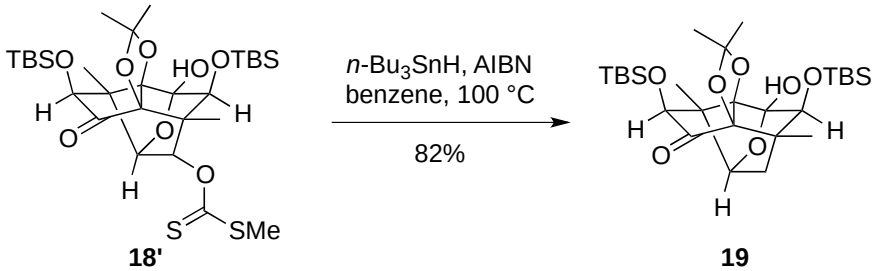
4 **18**

Hemiacetal 18. OsO_4 (609 mg, 2.40 mmol) was added to a solution of TBS-ether **4** (501 mg, 958 μmol) in pyridine (9.6 mL) at room temperature. The reaction mixture was stirred for 5 h at room temperature, and then saturated aqueous $NaHSO_3$ (20 mL) was added. The resultant mixture was diluted with EtOAc (20 mL) and stirred for further 17 h. The solution was extracted with EtOAc (20 mL x3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (15 g, hexane/EtOAc 3:1) to afford hemiacetal **18** (480 mg,862 μmol) in 90% yield: colorless solid; m.p. 223-225 °C; IR (neat) ν_{max} 3457, 2931, 1759, 1643, 1252 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.09 (3H, s, C*H*$_3$ of TBS), 0.11 (3H, s, C*H*$_3$ of TBS), 0.12 (3H, s, C*H*$_3$ of TBS), 0.13 (3H, s, C*H*$_3$ of TBS), 0.87 (9H, s, *t*-Bu of TBS), 0.90 (9H, s, *t*-Bu of TBS), 1.17 (3H, s, C*H*$_3$), 1.31 (3H, s, C*H*$_3$), 1.38 (3H, s, C*H*$_3$), 1.56 (3H, s, C*H*$_3$), 2.58 (1H, br s, O*H*), 3.34 (1H, br s, C*H*OH), 3.65 (1H, br s, O*H*), 3.72 (1H, s, C*H*OTBSCO), 3.86 (1H, d, *J* = 1.2 Hz, C*H*OCOH), 4.15 (1H, s, C*H*OTBSCOH); ^{13}C NMR (125 MHz, CDCl$_3$) δ –5.5, –5.2, –4.6, –4.4, 10.1, 12.3, 18.3, 18.6, 25.6, 25.9, 27.6, 27.7, 50.8, 55.1, 73.4, 75.7, 81.1, 83.4, 96.9, 97.1, 105.3, 121.2, 215.2; HRMS (ESI) calcd for $C_{27}H_{48}O_8Si_2Na$ 579.2785 (M+Na$^+$), found 579.2792.



18 **18'**

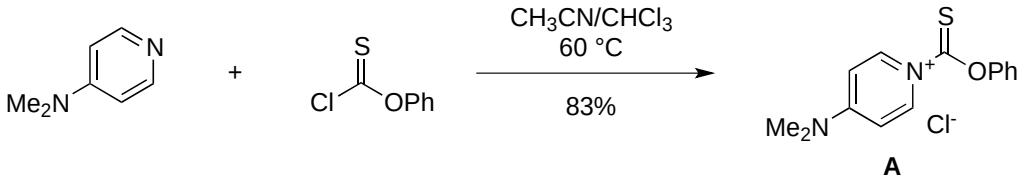
Xanthate 18'. NaH in mineral oil (>60%) was washed with hexane and dried in vacuo before use. The purified NaH (119 mg, 5.17 mmol) and CS_2 (600 μL, 9.9 mmol) were successively added to a solution of the hemiacetal **18** (554 mg, 995 μmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred for 30 min at room temperature, and then MeI (930 μL, 15.0 mmol) was added. The reaction mixture was stirred for further 30 min at room temperature, and cooled to 0 °C. Saturated aqueous NH_4Cl (20 mL) was added, and the resultant mixture was extracted with Et_2O (20 mL x3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (20 g, hexane/EtOAc 20:1 to 10:1) to afford xanthate **18'** (550 mg, 850 μmol) in 85% yield: pale yellow solid; m.p. 77-78 °C; IR (neat) ν_{max} 3487, 2930, 1762, 1252, 1072 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.12 (3H, s, C*H*$_3$ of TBS), 0.14 (3H, s, C*H*$_3$ of TBS), 0.15 (3H, s, C*H*$_3$ of TBS), 0.16 (3H, s, C*H*$_3$ of TBS), 0.89 (9H, s, *t*-Bu of TBS), 0.92 (9H, s, *t*-Bu of TBS), 1.14 (3H, s, C*H*$_3$), 1.33 (3H, s, C*H*$_3$), 1.40 (3H, s, C*H*$_3$), 1.59 (3H, s, C*H*$_3$), 2.58 (3H, s, SC*H*$_3$), 3.57 (1H, s, O*H*), 3.89 (1H, s, C*H*OTBSCO), 4.20 (1H, d, *J* = 1.2 Hz, C*H*OCOH), 4.39 (1H, s, C*H*OTBSCOH), 5.34 (1H, d, *J* = 1.2 Hz, C*H*OCSSCH$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ –5.5, –5.2, –4.6, –4.4, 10.1, 12.1, 18.3, 18.6, 18.9, 25.6, 25.9, 27.6, 27.7, 51.9, 54.3, 75.4, 80.5, 81.7, 81.9, 96.7, 97.3, 104.9, 121.4, 214.7, 215.3; HRMS (ESI) calcd for $C_{29}H_{50}O_8S_2Si_2Na$ 669.2383 ($M+Na^+$), found 669.2393.



18' **19**

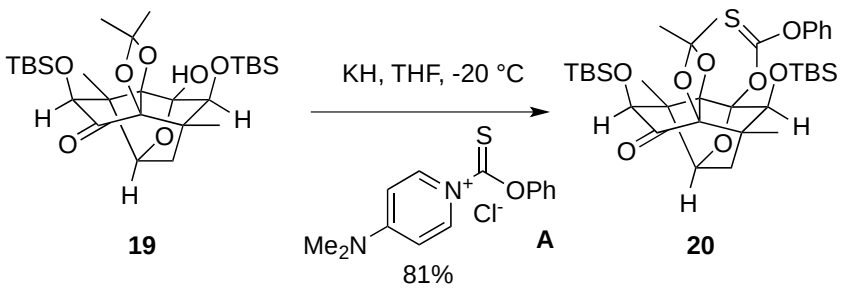
Hemiacetal 19. A mixture of the xanthate **18'** (550 mg, 850 μmol), *n*-Bu_3SnH (1.8 mL, 6.8 mmol) and AIBN (42 mg, 260 μmol) in benzene (85 mL) was

degassed by a freeze-thaw procedure (x3). The reaction mixture was stirred for 3 h at reflux temperature, cooled to room temperature, and concentrated. The residue was purified by flash column chromatography on 10% (w/w) KF contained silica gel (15 g, hexane/EtOAc 20:1 to 10:1) to afford hemiacetal **19** (375 mg, 693 μmol) in 82% yield: colorless solid; m.p. 145-146 °C; IR (neat) ν_{max} 3487, 2931, 1759, 1461, 1251 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.09 (3H, s, C*H*$_3$ of TBS), 0.11 (3H, s, C*H*$_3$ of TBS), 0.12 (3H, s, C*H*$_3$ of TBS), 0.14 (3H, s, C*H*$_3$ of TBS), 0.89 (9H, s, *t*-Bu of TBS), 0.91 (9H, s, *t*-Bu of TBS), 1.12 (3H, s, C*H*$_3$), 1.27 (1H, dd, *J* = 15.1, 1.4 Hz, C*H*$_A$H$_B$), 1.32 (3H, s, C*H*$_3$), 1.40 (3H, s, C*H*$_3$), 1.57 (3H, s, C*H*$_3$), 1.77 (1H, dd, *J* = 15.1, 3.2 Hz, CH$_A$*H*$_B$), 3.50 (1H, s, O*H*), 3.67 (1H, s, C*H*OTBS), 3.85 (1H, s, C*H*OTBS), 3.94 (1H, dd, *J* = 3.2, 1.4 Hz, C*H*OCH$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ –5.4, –5.2, –4.5, –4.3, 12.5, 13.4, 18.3, 18.6, 25.6, 25.9, 27.6, 27.7, 38.4, 49.4, 54.3, 76.2, 79.2, 86.2, 97.6, 97.9, 104.9, 119.7, 215.8; HRMS (ESI) calcd for $C_{27}H_{48}O_7Si_2Na$ 563.2836 ($M+Na^+$), found 563.2857.

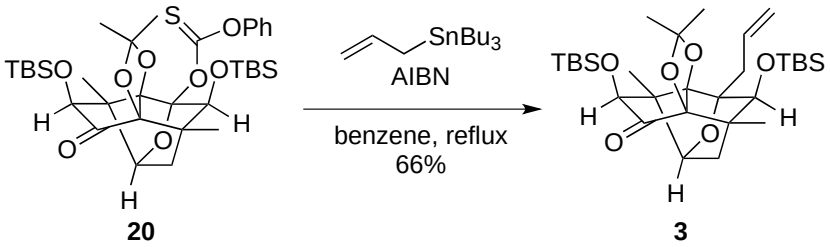


A

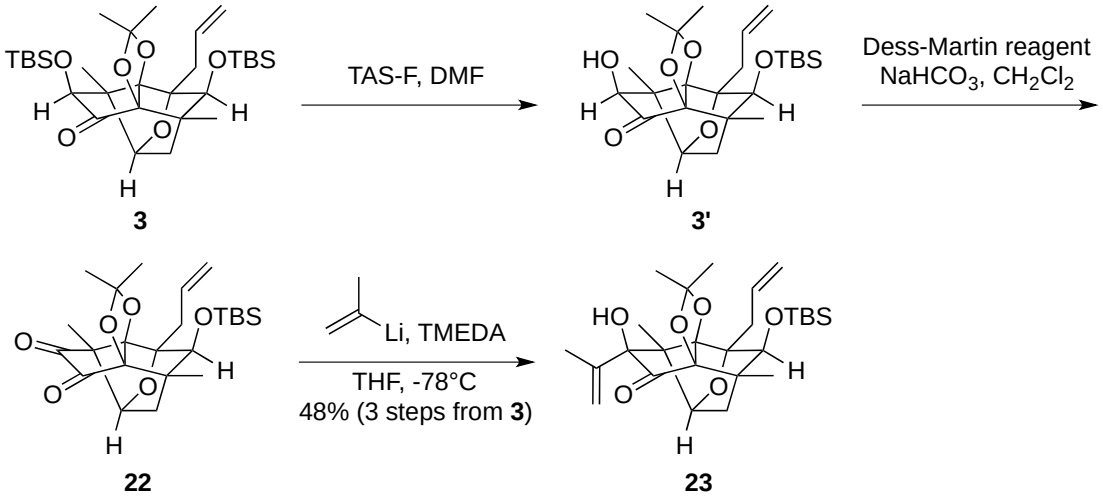
Pyridinium salt A. *O*-Phenyl chlorothionoformate (5.0 mL, 36 mmol) was added to a solution of DMAP (4.4 g, 36 mmol) in MeCN (36 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h at room temperature, and then $CHCl_3$ (36 mL) was added. The reaction mixture was heated 60 °C until the solid was dissolved. The resultant solution was cooled to room temperature, and Et_2O (36 mL) was added to crystallize pyridinium salt **A**. The solid was filtered with Et_2O (10 mL), and the filtrate was concentrated to afford pyridinium salt **A** (8.8 g, 30 mmol) in 83% yield: yellow solid; m.p. 199-200 °C; IR (neat) ν_{max} 3428, 3073, 1651, 1493, 1371, 1261, 1183 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.61 (6H, s, NC*H*$_3$ x 2), 7.17 (2H, d, *J* = 7.8 Hz, OC=C*H* x 2), 7.38 (1H, t, *J* = 7.8 Hz, OC=CH-CH=C*H*), 7.49 (2H, *t*, J = 7.8 Hz, OC=CH-C*H* x 2), 7.60 (2H, d, *J* = 8.7 Hz, C*H*=CH-N^+=C x 2), 9.12 (2H, d, *J* = 8.7 Hz, CH=C*H*-N^+=C x 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.1, 108.9, 121.1, 127.6, 129.9, 137.1, 153.0, 158.2, 183.1; HRMS (ESI) calcd for $C_{14}H_{15}N_2OS$ 259.0900 (M^+) , found 259.0900.



Thiocarbonate 20. KH in mineral oil (>30%) was washed with hexane and dried in vacuo. The purified KH (695 mg, 17.3 mmol) was added to a solution of hemiacetal **19** (375 mg, 693 μmol) in THF (23 mL) at -78 °C. The mixture was stirred for 20 min at -78 °C, and then freshly prepared pyridinium salt **A** (2.0 g, 6.9 mmol) was added. The reaction mixture was allowed to warm to -20 °C and stirred for 19 h. The reaction was quenched with AcOH (1.5 mL). The resultant mixture was neutralized with saturated aqueous $NaHCO_3$ (15 mL), and extracted with Et_2O (20 mL x3). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (30 g, hexane/EtOAc 20:1 to 10:1) to afford thiocarbonate **20** (379 mg, 560 μmol) in 81% yield: pale yellow amorphous; IR (neat) ν_{max} 2932, 2858, 1761, 1461, 1286, 1120, 1053 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.13 (3H, s, C*H*$_3$ of TBS), 0.15 (6H, s, C*H*$_3$ of TBS x 2), 0.22 (3H, s, C*H*$_3$ of TBS), 0.88 (9H, s, *t*-Bu of TBS), 0.95 (9H, s, *t*-Bu of TBS), 1.22 (3H, s, C*H*$_3$), 1.30 (1H, br d, *J* = 15.6 Hz, C*H*$_A$H$_B$), 1.40 (3H, s, C*H*$_3$), 1.42 (3H, s, C*H*$_3$), 1.64 (3H, s, C*H*$_3$), 1.90 (1H, dd, *J* = 15.6, 3.6 Hz, CH$_A$*H*$_B$), 3.70 (1H, s, C*H*OTBSCO), 4.14 (1H, d, *J* = 3.6 Hz, C*H*OCH$_2$), 4.65 (1H, s, C*H*OTBSCCOSOPh), 7.15 (2H, m, aromatic), 7.29 (1H, m, aromatic), 7.42 (2H, m, aromatic); ^{13}C NMR (125 MHz, $CDCl_3$) δ -5.5, -4.8, -4.5, -3.2, 13.1, 14.3, 18.3, 19.0, 25.6, 26.7, 27.5, 27.8, 38.2, 49.6, 53.8, 76.1, 80.8, 85.4, 97.1, 99.6, 108.8, 119.9, 122.0, 126.6, 129.5, 153.2, 190.0, 215.2; HRMS (ESI) calcd for $C_{34}H_{52}O_8SSi_2Na$ 699.2819 ($M+Na^+$), found 699.2800.



Compound 3. A solution of thiocarbonate **20** (67 mg, 99 μmol), allyltributyltin (460 μL, 1.5 mmol), and AIBN (3 mg, 20 μmol) in benzene (2.0 mL) was degassed by freeze-thaw procedure (x3). The reaction mixture was stirred for 3 h at reflux temperature, cooled to room temperature, and concentrated. The residue was purified by flash chromatography on 10% (w/w) KF contained silica gel (15 g, hexane/EtOAc 30:1 to 15:1) to afford **3** with a small amount of impurity. The mixture was further purified by flash chromatography on 10% (w/w) KF contained silica gel (7 g, hexane/CH_2Cl_2 2:1 to 1:1) to afford **3** (37 mg, 66 μmol) in 66% yield: colorless oil; IR (neat) ν_{max} 2931, 2858, 1759, 1461, 1250, 1111 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.09 (3H, s, C*H*$_3$ of TBS), 0.10 (3H, s, C*H*$_3$ of TBS), 0.12 (3H, s, C*H*$_3$ of TBS), 0.14 (3H, s, C*H*$_3$ of TBS), 0.89 (9H, s, *t*-Bu of TBS), 0.92 (9H, s, *t*-Bu of TBS), 1.11 (3H, s, C*H*$_3$), 1.29 (1H, d, *J* = 15.1 Hz, CHOC*H*$_A$H$_B$), 1.29 (3H, s, C*H*$_3$), 1.37 (3H, s, C*H*$_3$), 1.56 (3H, s, C*H*$_3$), 1.78 (1H, dd, *J* = 15.1, 3.2 Hz, CHOCH$_A$*H*$_B$), 2.40 (1H, br dd, *J* = 14.2, 8.7 Hz, CC*H*$_A$H$_B$CH=CH$_2$), 2.61 (1H, br dd, *J* = 14.2, 9.2 Hz, CCH$_A$*H*$_B$CH=CH$_2$), 3.66 (1H, s, C*H*OTBS), 3.81 (1H, br d, *J* = 3.2 Hz, C*H*OCH$_2$), 3.86 (1H, s, C*H*OTBS), 5.14 (1H, br d, *J* = 10.5 Hz, CH$_2$CH=C*H*$_A$H$_B$), 5.15 (1H, br d, *J* = 17.8 Hz, CH$_2$CH=CH$_A$*H*$_B$), 5.95 (1H, dddd, *J* = 17.8, 10.5, 9.2, 8.7 Hz, CH$_2$C*H*=CH$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.5, -4.5, -4.3, -3.9, 13.2, 14.3, 18.3, 18.4, 25.7, 26.1, 27.9 (two peaks), 34.8, 38.7, 49.9, 55.6, 76.3, 80.5, 88.7, 89.6, 99.2, 101.4, 117.7, 118.2, 134.2, 216.9; HRMS (ESI) calcd for $C_{30}H_{52}O_6Si_2Na$ 587.3200 ($M+Na^+$), found 587.3223.

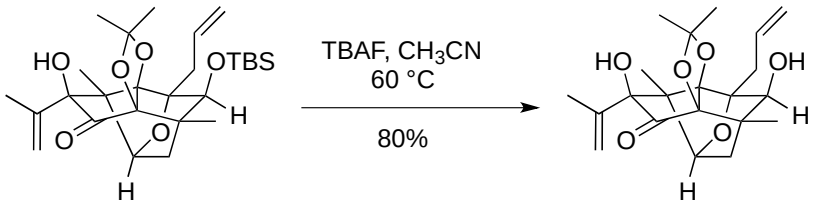


α-Hydroxy ketone 3'. A solution of **3** (84 mg, 149 μmol) in DMF (1.5 mL) was degassed by freeze-thaw procedure (x3), and cooled to 0 °C. A solution of TAS-F (61 mg, 222 μmol) in DMF (1.5 m), degassed by freeze-thaw procedure (x3), was added to the solution via cannula. Then the reaction mixture was stirred for 40 min at room temperature, and cooled to 0 °C. Saturated aqueous NH_4Cl (3 mL) was added, and the resultant mixture was extracted with EtOAc (5 mL x3). The combined organic layers were washed with water (10 mL x2) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated. The residue was filtered through a short pad of silica gel (3 g, hexane/EtOAc 1:1), and the filtrate was concentrated to afford crude α-hydroxy ketone **3'** (64 mg), which was used for the next reaction without further purification.

Diketone 22. Dess-Martin periodinane (188 mg, 443 μmol) was added to a suspension of the above crude α-hydroxy ketone **3'** (64 mg) and $NaHCO_3$ (187 mg, 2.25 mmol) in CH_2Cl_2 (3.0 mL) at 0 °C. The reaction mixture was stirred for 50 min at 0 °C, and saturated aqueous $Na_2S_2O_3$ (3 mL) was added. The resultant mixture was extracted with Et_2O (5 mL x3), and the combined organic layers were washed with saturated aqueous Na_2CO_3 (10 mL x3) and brine (10 mL), dried over Na_2SO_4, filtered and concentrated to afford crude diketone **22** (69 mg) as pale red oil, which was used for the next reaction without further purification.

Ally alcohol 23. *t*-BuLi (1.65 M in *n*-pentane, 3.6 mL, 5.9 mmol) was added to a solution of 2-bromopropene (260 μL, 2.9 mmol) in THF (12 mL) at -78 °C. The mixture was stirred for 20 min at -78 °C, and then TMEDA (440 μL, 2.9 mmol) was added. The mixture was stirred for 10 min, and then a solution of the above crude diketone **22** (69 mg) in THF (3 mL) was added at -78 °C via cannula. The reaction mixture was stirred for 50 min at -78 °C, and then saturated aqueous NH_4Cl (10 mL) was added. The resultant mixture was extracted with EtOAc (15

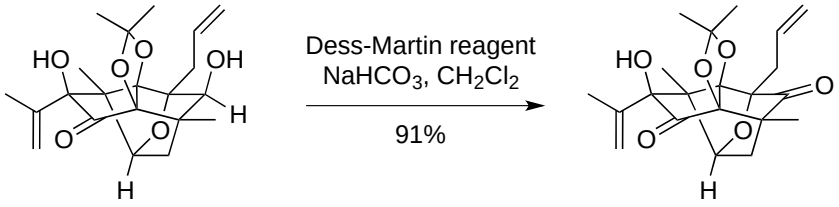
mL x3), and the combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (3 g, hexane/EtOAc 10:1 to 5:1) to afford allyl alcohol **23** (35 mg, 71 μmol) in 48% yield over 3 steps: colorless solid; m.p. 148-149 °C; IR (neat) ν_{max} 3376, 2934, 2858, 1750, 1249, 1110 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.10 (3H, s, C*H*$_3$ of TBS), 0.11 (3H, s, C*H*$_3$ of TBS), 0.93 (9H, s, *t*-Bu of TBS), 1.13 (3H, s, C*H*$_3$), 1.44 (3H, s, C*H*$_3$), 1.48 (3H, s, C*H*$_3$), 1.61 (3H, s, C*H*$_3$), 1.71 (1H, dd, *J* = 15.1, 3.2 Hz, CHOC*H*$_A$H$_B$), 1.78 (1H, dd, *J* = 15.1, 1.4 Hz, CHOCH$_A$*H*$_B$), 1.91 (3H, s, C*H*$_3$C), 2.48 (1H, br dd, *J* = 15.1, 7.4 Hz, C*H*$_A$H$_B$CH=CH$_2$), 2.51 (1H, s, O*H*), 2.62 (1H, br dd, *J* = 15.1, 7.3 Hz, CH$_A$*H*$_B$CH=CH$_2$), 3.87 (1H, s, C*H*OTBS), 3.88 (1H, dd, *J* = 3.2, 1.4 Hz, C*H*OCH$_2$), 5.09 (1H, s, CH$_3$C=C*H*$_A$H$_B$), 5.13 (1H, br s, CH$_3$C=CH$_A$*H*$_B$), 5.15 (1H, br d, *J* = 11.0 Hz, CH$_2$CH=C*H*$_A$H$_B$), 5.16 (1H, d, *J* = 16.9 Hz, CH$_2$CH=CH$_A$*H*$_B$), 5.95 (1H, dddd, *J* = 16.9, 11.0, 7.4, 7.3 Hz, CH$_2$C*H*=CH$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.2, -3.8, 12.7, 14.7, 18.5, 20.4, 26.2, 27.8, 28.3, 34.7, 39.0, 50.6, 58.4, 79.8, 82.0, 89.0, 89.1, 98.8, 101.2, 117.9, 118.0, 118.5, 133.7, 140.6, 215.9; HRMS (ESI) calcd for $C_{27}H_{42}O_6SiNa$ 513.2648 ($M+Na^+$), found 513.2643.



23 **23'**

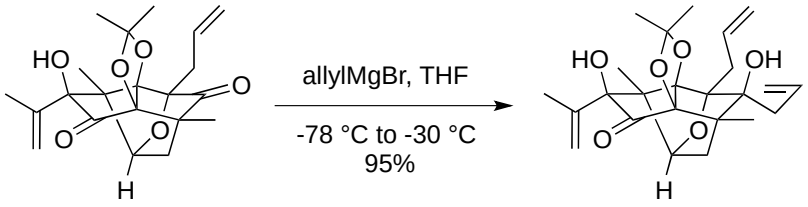
Diene 23'. TBAF (1.0 M in THF, 1.7 mL, 1.7 mmol) was added to a solution of allyl alcohol **23** (55 mg, 110 μmol) in MeCN (5.6 mL) at room temperature. The reaction mixture was stirred for 2 h at 60 °C, and then cooled to room temperature. The mixture was filtered through a short pad of silica gel (3 g) with a mixture of hexane/EtOAc (1:1). The filtrate was concentrated, and the residue was purified by flash column chromatography on silica gel (3 g, hexane/EtOAc 3:1) to afford diene **23'** (33 mg, 88 μmol) in 80% yield: colorless solid; m.p. 203-204 °C; IR (neat) ν_{max} 3443, 2930, 1741, 1456, 1385, 1204, 1085 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (3H, s, C*H*$_3$), 1.47 (3H, s, C*H*$_3$), 1.53 (3H, s, C*H*$_3$), 1.64 (3H, s, C*H*$_3$), 1.76 (1H, dd, *J* = 15.1, 3.2 Hz, CHOC*H*$_A$H$_B$), 1.83 (1H, dd, *J* = 15.1, 1.4 Hz, CHOCH$_A$*H*$_B$), 1.91 (3H, s, C*H*$_3$C=CH$_2$), 2.39 (1H, br s, O*H*), 2.42 (1H, dd, *J* = 14.6, 7.8 Hz, C*H*$_A$H$_B$CH=CH$_2$), 2.78 (1H, br dd, *J* = 14.6, 6.4 Hz, CH$_A$*H*$_B$CH=CH$_2$), 3.16 (1H, d, *J* = 11.0 Hz, C*H*OH), 3.72 (1H, d, J = 11.0 Hz,

CHO*H*), 3.91 (1H, dd, *J* = 3.2, 1.4 Hz, C*H*OCH$_2$), 5.10 (1H, br s, CH$_3$C=C*H*$_A$H$_B$), 5.15 (1H, br s, CH$_3$C=CH$_A$*H*$_B$), 5.16 (1H, br d, *J* = 11.0 Hz, CH$_2$CH=C*H*$_A$H$_B$), 5.22 (1H, dq, *J* = 17.4, 1.4 Hz, CH$_2$CH=CH$_A$*H*$_B$), 5.97 (1H, dddd, *J* = 17.4, 11.0, 7.8, 6.4 Hz, CH$_2$C*H*=CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 12.6, 13.3, 20.2, 27.5, 28.1, 34.9, 38.6, 49.3, 58.0, 79.8, 81.8, 86.4, 88.8, 98.8, 100.9, 118.1, 118.2, 118.3, 133.3, 140.5, 214.0; HRMS (ESI) calcd for C$_{21}$H$_{28}$O$_6$Na 399.1784 (M+Na$^+$), found 399.1769.



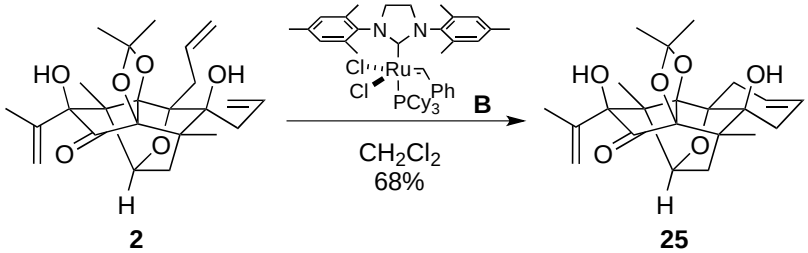
23' **24**

Diketone 24. Dess-Martin periodinane (190 mg, 448 μmol) was added to a suspension of **23'** (33 mg, 88 μmol) and NaHCO$_3$ (226 mg, 2.69 mmol) in CH$_2$Cl$_2$ (3.0 mL) at 0 °C. The reaction mixture was stirred for 12 h at 0 °C, and saturated aqueous Na$_2$S$_2$O$_3$ (4 mL) was added. The resultant mixture was extracted with Et$_2$O (7 mL x3), and the combined organic layers were washed with saturated aqueous Na$_2$CO$_3$ (10 mL x3) and brine (10 mL), dried over Na$_2$SO$_4$, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (3 g, hexane/EtOAc 3:1) to afford diketone **24** (30 mg, 80 μmol) in 91% yield: colorless solid; m.p. 180-182 °C; IR (neat) ν_{max} 3456, 2988, 1765, 1745 1379, 1214 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.16 (3H, s, C*H*$_3$), 1.39 (3H, s, C*H*$_3$), 1.47 (3H, s, C*H*$_3$), 1.59 (3H, s, C*H*$_3$), 1.96 (3H, d, *J* = 0.9 Hz, C*H*$_3$C=CH$_2$), 2.14 (2H, d, *J* = 2.3 Hz, CHOC*H*$_2$), 2.42 (1H, dd, *J* = 15.1, 7.3 Hz, C*H*$_A$H$_B$CH=CH$_2$), 2.54 (1H, s, O*H*), 2.67 (1H, ddt, *J* = 15.1, 7.3, 1.4 Hz, CH$_A$*H*$_B$CH=CH$_2$), 4.05 (1H, t, *J* = 2.3 Hz, C*H*OCH$_2$), 5.11 (1H, br s, CH$_3$C=C*H*$_A$H$_B$), 5.16-5.24 (3H, m, CH$_3$C=CH$_A$*H*$_B$, CH$_2$CH=C*H*$_2$), 6.05 (1H, ddt, J = 14.6, 10.1 Hz, CH$_2$C*H*=CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 11.2, 13.1, 20.2, 27.3, 28.9, 31.9, 43.1, 55.8, 56.7, 80.1, 80.5, 82.6, 91.2, 95.5, 118.3, 118.7, 118.8, 131.9, 139.9, 206.2, 214.0; HRMS (ESI) calcd for C$_{21}$H$_{26}$O$_6$Na 397.1627 (M+Na$^+$), found 397.1608.



24 **2**

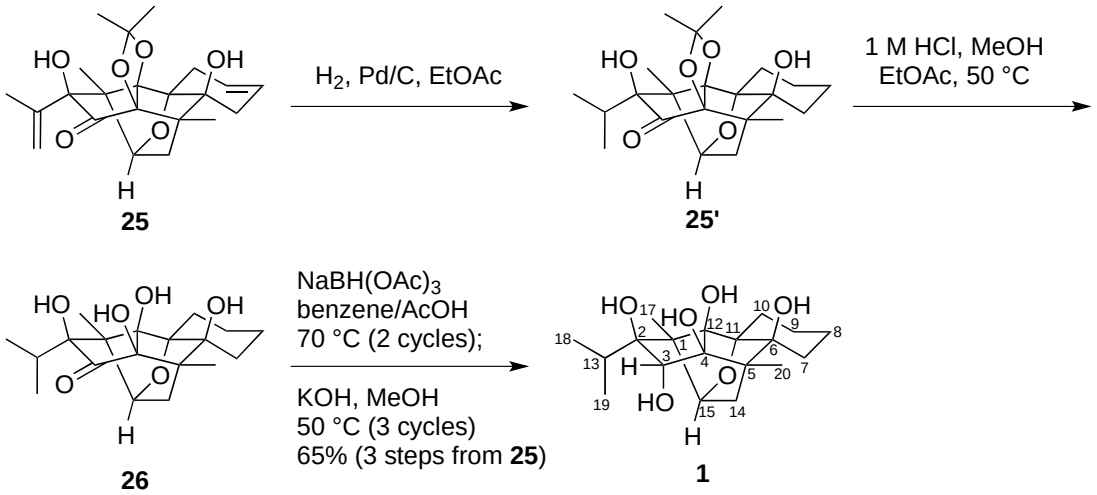
Triene 2. Allyl magnesium bromide (1.0 M in Et_2O, 1.6 mL, 1.6 mmol) was added to a solution of diketone **24** (30 mg, 80 μmol) in THF (4.0 mL) at -78 °C. The reaction mixture was allowed to warm to -30 °C, and stirred for 30 min. Saturated aqueous NH_4Cl (5 mL) was added at -30 °C. The resultant mixture was stirred at room temperature, and extracted with Et_2O (7 mL x3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (3 g, hexane/EtOAc 4:1) to afford triene **2** (32 mg, 77 μmol) in 95% yield: colorless solid; m.p. 138-140 °C; IR (neat) ν_{max} 3490, 3075, 2958, 1751 1381, 1205, 1121 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.15 (3H, s, C*H*$_3$), 1.47 (3H, s, C*H*$_3$), 1.50 (3H, s, C*H*$_3$), 1.62 (1H, d, *J* = 15.6 Hz, CHOC*H*$_A$H$_B$), 1.65 (3H, s, C*H*$_3$), 1.92 (3H, s, C*H*$_3$C=CH$_2$), 2.00 (1H, dd, *J* = 15.6, 3.6 Hz, CHOCH$_A$*H*$_B$), 2.37 (1H, s, O*H*), 2.56-2.66 (3H, m, C*H*$_A$H$_B$CH=CH$_2$ x 2, CH$_A$*H*$_B$-CH=CH$_2$), 2.71 (1H, br dd, *J* = 15.6, 6.4 Hz, CH$_A$*H*$_B$CH=CH$_2$), 3.92 (1H, d, *J* = 3.6 Hz, C*H*OCH$_2$), 4.23 (1H, br s, O*H*), 5.02-5.19 (6H, m, CH$_3$C=C*H*$_2$, CH$_2$CH=C*H*$_2$ x 2), 5.93-6.09 (2H, m, CH$_2$C*H*=CH$_2$ x 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5, 12.8, 20.4, 27.6, 27.9, 33.1, 35.4, 36.6, 51.5, 57.3, 79.6, 81.3, 86.0, 90.1, 98.5, 100.6, 116.6, 117.9, 118.3, 118.4, 134.1, 134.6, 140.4, 214.3; HRMS (ESI) calcd for $C_{24}H_{32}O_6Na$ 439.2097 ($M+Na^+$), found 439.2074.



2 **25**

Compound 25. A mixture of triene **2** (32 mg, 77 μmol) and Grubbs' 2nd catalyst **B** (32 mg, 38 μmol) in CH_2Cl_2 (25 mL) was stirred for 2.5 h at room temperature. After additional Grubbs' 2nd catalyst (6.5 mg, 7.6 μmol) was added, the reaction was stirred for further 1 h at same temperature. The mixture was filtered through a short pad of silica gel (1 g, hexane/EtOAc 1:1), and the filtrate was concentrated.

The residue was purified by flash column chromatography on silica gel (3 g, hexane/EtOAc 5:1 to 2:1) to afford **25** (20 mg, 52 μmol) in 68% yield: colorless solid; m.p. 243-245 °C; IR (neat) ν_{max} 3462, 3370, 3027, 2995, 1750, 1459, 1383, 1217 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (3H, s, C*H*$_3$), 1.49 (3H, s, C*H*$_3$), 1.53 (3H, s, C*H*$_3$), 1.66 (3H, s, C*H*$_3$), 1.69 (1H, d, *J* = 15.6 Hz, CHOC*H*$_A$H$_B$), 1.91 (3H, s, C*H*$_3$C=CH$_2$), 1.96 (1H, br d, *J* = 17.8 Hz, CCH=CHC*H*$_A$H$_B$), 1.99 (1H, dd, *J* = 15.6, 3.6 Hz, CHOCH$_A$*H*$_B$), 2.19 (1H, br d, *J* = 16.5 Hz, C*H*$_A$H$_B$CH=CHC), 2.44 (1H, br s, O*H*), 2.63 (1H, br d, *J* = 16.5 Hz, CH$_A$*H*$_B$CH=CHC), 2.79 (1H, br d, *J* = 17.8 Hz, CCH=CHCH$_A$*H*$_B$), 3.85 (1H, d, *J* = 3.6 Hz, C*H*OCH$_2$), 4.40 (1H, d, *J* = 2.7 Hz, O*H*), 5.13 (1H, br s, CH$_3$C=C*H*$_A$H$_B$), 5.15 (1H, br s, CH$_3$C=CH$_A$*H*$_B$), 5.68-5.78 (2H, m, C*H*=C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 12.6, 20.2, 27.6, 28.1, 29.4, 31.6, 36.2, 51.3, 57.9, 78.9, 81.3, 82.5, 86.4, 98.7, 100.5, 118.2, 119.0, 123.9 (two peaks), 140.3, 214.5; HRMS (ESI) calcd for $C_{22}H_{28}O_6Na$ 411.1784 ($M+Na^+$), found 411.1777.



Compound 25'. A suspension of **25** (14 mg, 36 μmol) and 5% Pd/C (29 mg) in EtOAc (3.7 mL) was exposed to H_2 atmosphere (1 atm). Then, the reaction mixture was stirred under H_2 atmosphere for 11 h at room temperature. The resultant mixture was filtered through a pad of Celite with EtOAc. The filtrate was concentrated to afford crude **25'** (14 mg), which was used for the next reaction without further purification.

Tetraol 26. HCl solution (1.0 M in EtOAc, 2.5 mL) was added to a solution of the above crude **25'** (14 mg) in MeOH (1.2 mL) at room temperature. The reaction mixture was stirred for 2.5 h at 50 °C, cooled to room temperature and then quenched with solid $NaHCO_3$ (ca. 500 mg). The resultant mixture was filtered through a short pad of silica gel (3 g, EtOAc/MeOH 10:1). The filtrate

was concentrated to afford crude tetraol **26** (14 mg), which was used for the next reaction without further purification.

9-demethyl-10,15-dideoxyryanodol (1). $NaBH(OAc)_3$ (157 mg, 741 μmol) was added to a solution of the above crude tetraol **26** (14 mg) in a mixture of benzene (3.4 mL) and AcOH (0.34 mL). The reaction mixture was stirred for 3 h at 70 °C, and cooled to room temperature. MeOH (5 mL) was added, and the resultant mixture was concentrated to remove trimethyl borate azeotropically (x3). The resultant residue was filtered through a short pad silica gel (1 g, EtOAc/MeOH 10:1) and the filtrate was concentrated. The ESI-MS analysis indicated that the crude material contained a mixture of tetraol **26** and the borate of **1**. Thus, the crude mixture was again subjected to the reduction with $NaBH(OAc)_3$ (79 mg, 373 μmol) in a mixture of benzene (3.4 mL) and AcOH (0.34 mL) for 11 h at 70 °C. The same work up procedure of the reaction mixture as described above afforded the borate of **1**. A mixture of KOH (42 mg, 750 μmol) and the crude borate of **1** in a mixture of EtOH (1.9 mL) and H_2O (0.2 mL) was stirred for 21 h at 70 °C, and cooled to room temperature. The reaction mixture was neutralized with AcOH (0.1 mL) and concentrated. The resultant mixture was filtered through a short pad of silica gel (1 g, EtOAc/MeOH 10:1), and the filtrate was concentrated to afford a mixture of **1** and the borate. The hydrolysis procedure was repeated twice to completely convert the borate to **1**. The crude **1** was purified by flash column chromatography on silica gel (1 g, $CHCl_3$/MeOH 20:1 to 10:1) by using a vial made of soda-lime glassware and a flask made of quartz glassware for fraction collection to afford 9-demethyl-10,15-dideoxyryanodol (**1**) (8.5 mg, 24 μmol) in 65% yield over 3 steps: colorless solid; m.p. 220-221 °C; IR (neat) ν_{max} 3408, 2927, 2858, 1405, 1384, 1045 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 0.96 (3H, d, *J* = 6.8 Hz, H18), 0.99 (3H, d, *J* = 6.4 Hz, H19), 1.10 (3H, s, H20), 1.22 (3H, s, H17), 1.27-1.37 (1H, m, H7eq), 1.37-1.43 (1H, m, H10eq), 1.43-1.55 (2H, m, H8eq and H9eq), 1.59-1.75 (2H, m, H8ax and H9ax), 1.72 (1H, dd, *J* = 14.2, 3.7 Hz, H14a), 1.98 (1H, td, *J* = 13.2, 5.5 Hz, H10ax), 2.06 (1H, td, *J* = 12.8, 5.0 Hz, H7ax), 2.12 (1H, qq, *J* = 6.8, 6.4 Hz, H13), 2.24 (1H, dd, *J* = 14.2, 1.4 Hz, H14b), 3.80 (1H, dd, *J* = 3.7, 1.4 Hz, H15), 4.16 (1H, s, H3); ^{13}C NMR (100 MHz, CD_3OD) δ 13.2, 15.7, 18.9, 19.7, 20.4, 21.7, 26.5, 27.4, 30.7, 36.5, 51.2, 65.0, 80.5, 84.3, 84.7, 87.9, 92.1, 92.7, 95.6; HRMS (ESI) calcd for $C_{19}H_{30}O_6Na$ 377.1940 ($M+Na^+$), found 377.1938.

Toxicity to Houseflies[S1]

Ryanodine was purchased from Wako Pure Chemical Industries (Japan), and ryanodol was prepared according to the literature procedure.[2]

A filter paper of a diameter of 5.5 cm was spread on the bottom of a polyethylene cup of a diameter of 5.5 cm. A solution of varied amounts of ryanodine, ryanodol or 9-demethyl-10,15-dideoxyryanodol (**1**) in acetone (X ppm, 0.7 ml) was added dropwise onto the filter paper, and the filter paper was dried. Sucrose (30 mg) in water (0.7 mL) was applied to the filter paper as a bait. Then, five female imagoes of house flies (*Musca domestica*) were released into the polyethylene cup, and the cup was sealed with a lid. After 2 days, the number of surviving house flies was counted, and the death rate of the house flies was calculated. LD_{100} of ryanodine, ryanodol and **1** were determined to be 15.6 ppm, 200 ppm and >200 ppm, respectively.

(S1) Toxicity of ryanodine and ryanodol to house flies has been known. See for examples: (a) Waterhouse, A. L.; Pessah, I. N.; Francini, A. O.; Casida, J. E. *J. Med. Chem.* **1987**, *30*, 710-716. (b) Jefferies, P. R.; Toia, R. F.; Brannigan, B.; Pessah, I.; Casida, J. E. *J. Agric. Food. Chem.* **1992**, *40*, 142-146. (c) Jefferies, P. R.; Yu, P.; Casida, J. E. *Pestic. Sci.* **1997**, *51*, 33-38.

(S2) Kelly, R. B.; Whittingham, D. J.; Wiesner, K. *Can. J. Chem.* **1951**, *29*, 905-910.

single_pulse

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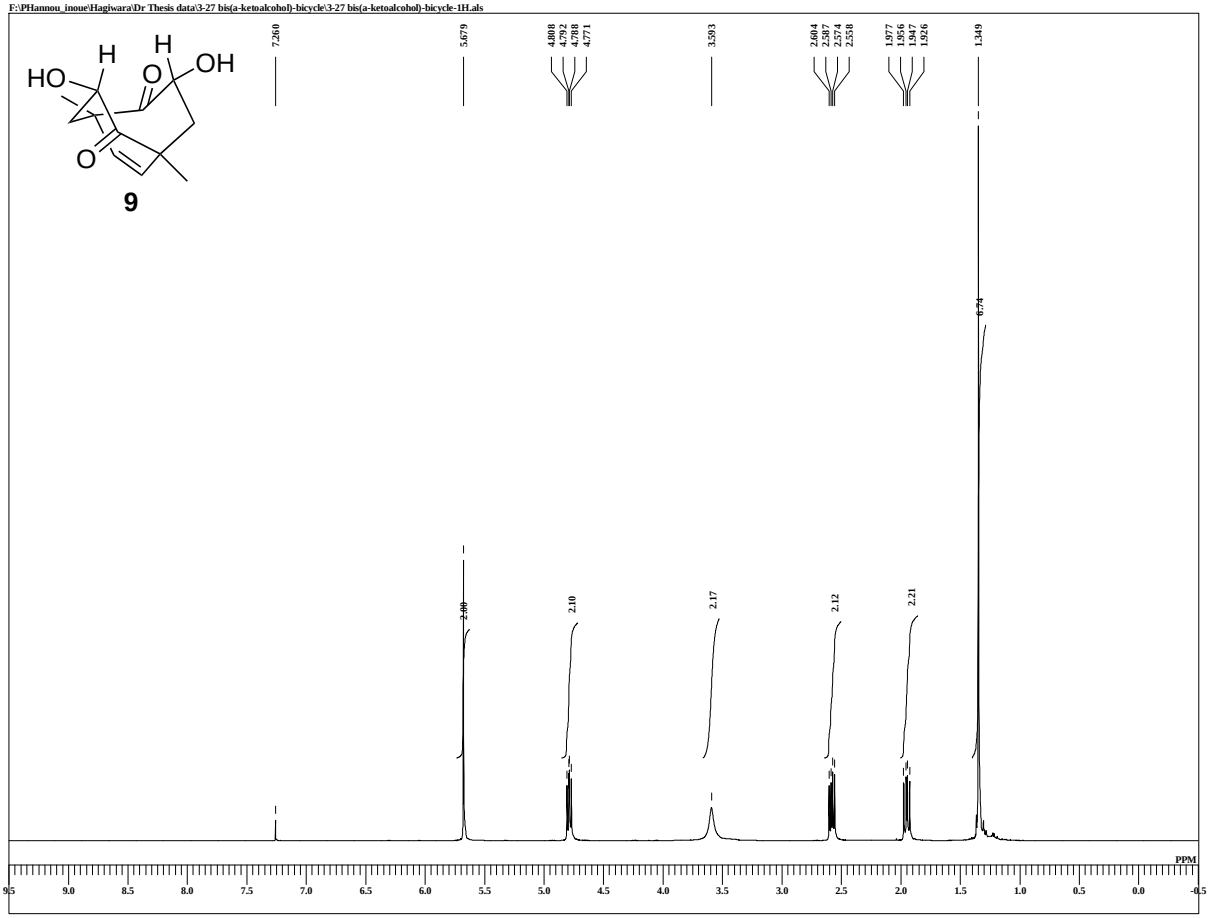

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OBFIN	9.64 Hz
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IWT	1.0000 sec
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SPO	13107
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DUMMY	1
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FLT	38000 Hz
DELAY	13.16 usec
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PD	1.5000 sec
SCANS	8
ADBIT	16
RGAIN	38
BF	0.01 Hz
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T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse.ex2
EXPCM	
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IFR	495.13 MHz
IRSET	4.38 KHz
IRFIN	9.64 Hz
IRRPW	118 usec
IRATN	79
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LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	19.5 c
SLVNT	CDCL3
EXREF	7.26 ppm

single pulse decoupled gated NOE

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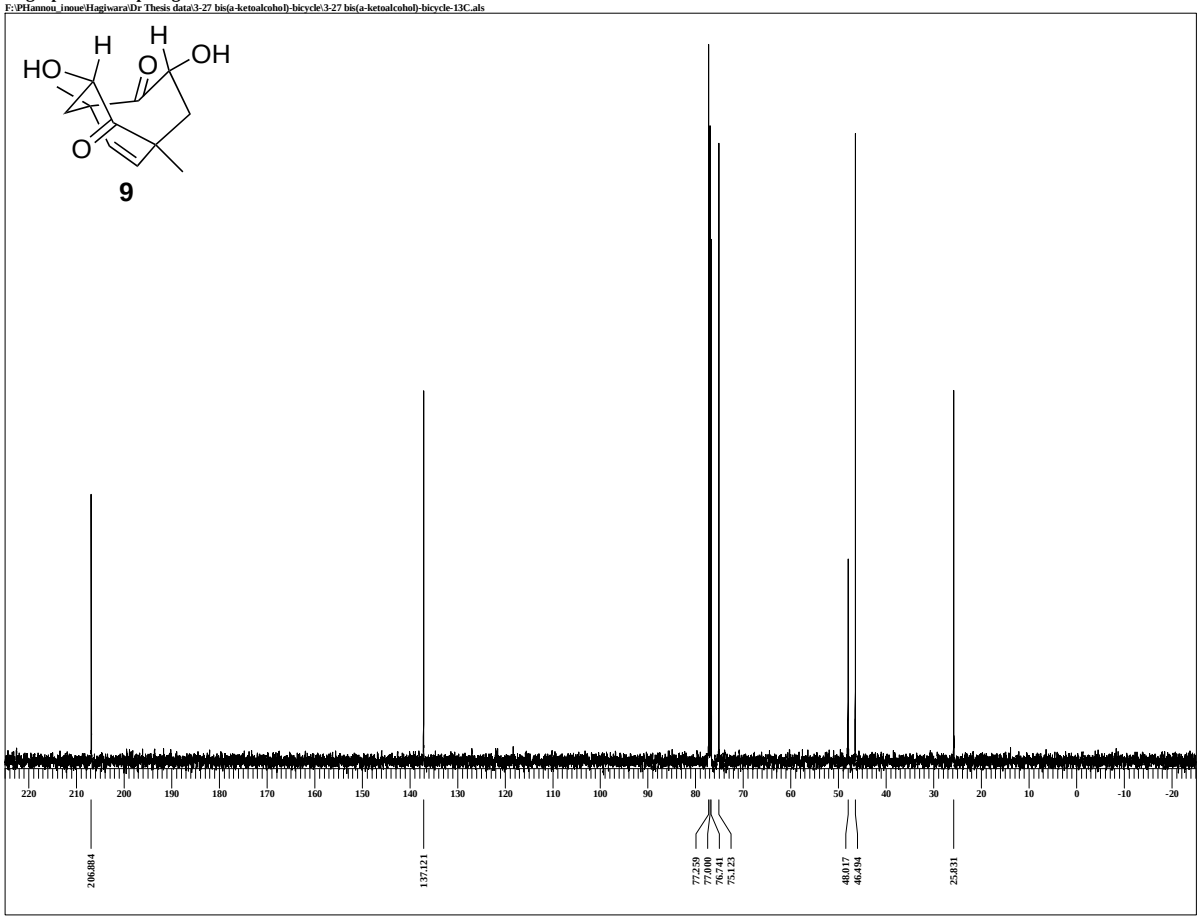

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IWT	1.0000 sec
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SPO	26214
TIMES	8
DUMMY	4
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FLT	157000 Hz
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PD	5.0000 sec
SCANS	8
ADBIT	16
RGAIN	60
BF	0.01 Hz
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T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse_dec
EXPCM	
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IFR	495.13 MHz
IRSET	4.38 KHz
IRFIN	9.64 Hz
IRRPW	50 usec
IRATN	79
DFILE	3-27 bis(a-ketoalcohol)-bi
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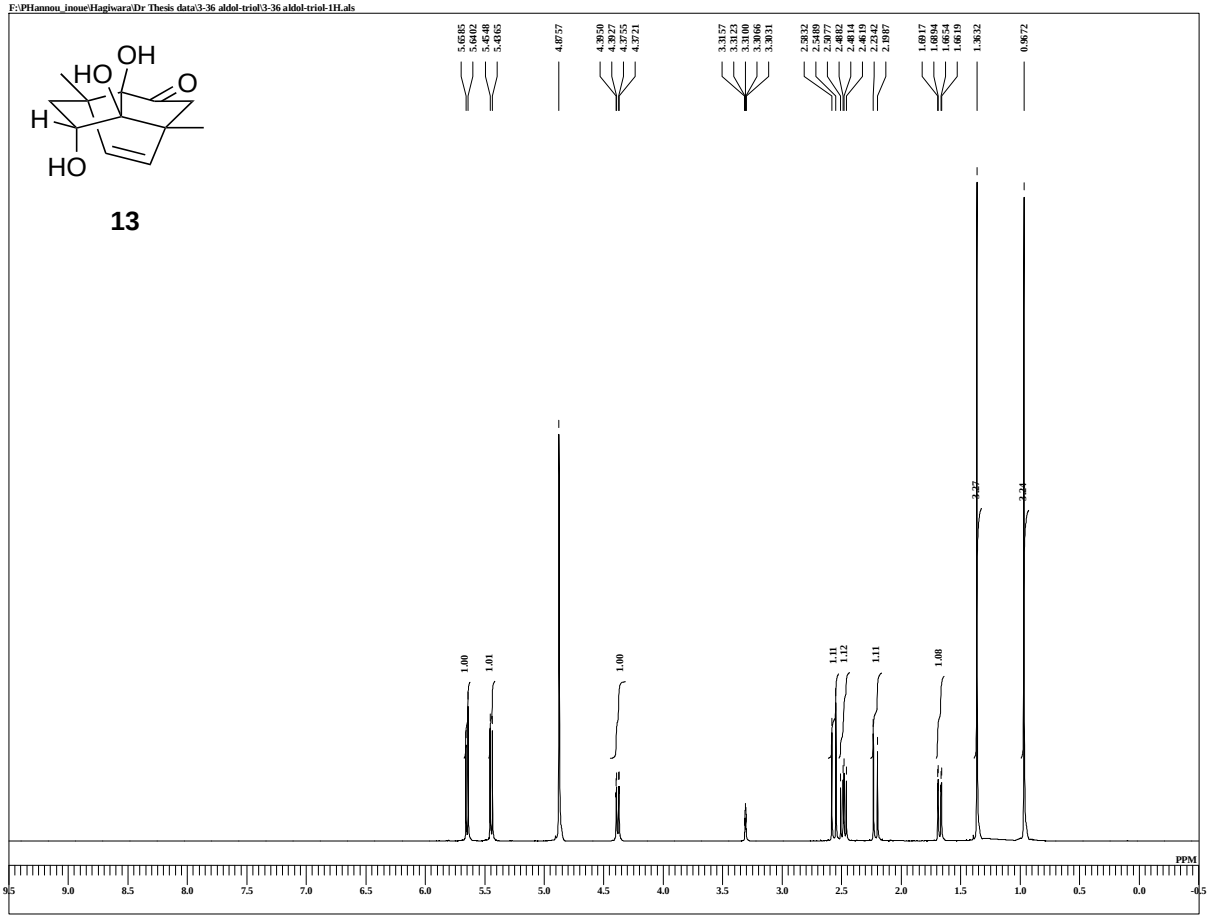
LKSET	-601.50 KHz
LKFIN	-1.8 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	77.00 ppm

single_pulse

F:\PHannou_inoue\Hagiwara\Dr Thesis data\3-36 aldol-triol\3-36 aldol-triol-1H.als



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OBFRQ 490.15 MHz
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OBFIN 7.60 Hz
PW1 8.55 usec
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PREDL 0.00000 msec
IWT 1.0000 sec
POINT 13107
SPO 13107
TIMES 8
DUMMY 1
FREQU 7352.83 Hz
FLT 37000 Hz
DELAY 13.52 usec
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PD 2.0000 sec
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ADBIT 16
RGAIN 30
BF 0.01 Hz
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T2 0.00
T3 90.00
T4 100.00
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EXPCM
IRNUC 1H
IFR 490.15 MHz
IRSET 9.16 KHz
IRFIN 7.60 Hz
IRRPW 118 usec
IRATN 79
DFILE 3-36 aldol-triol-1H.als
SF
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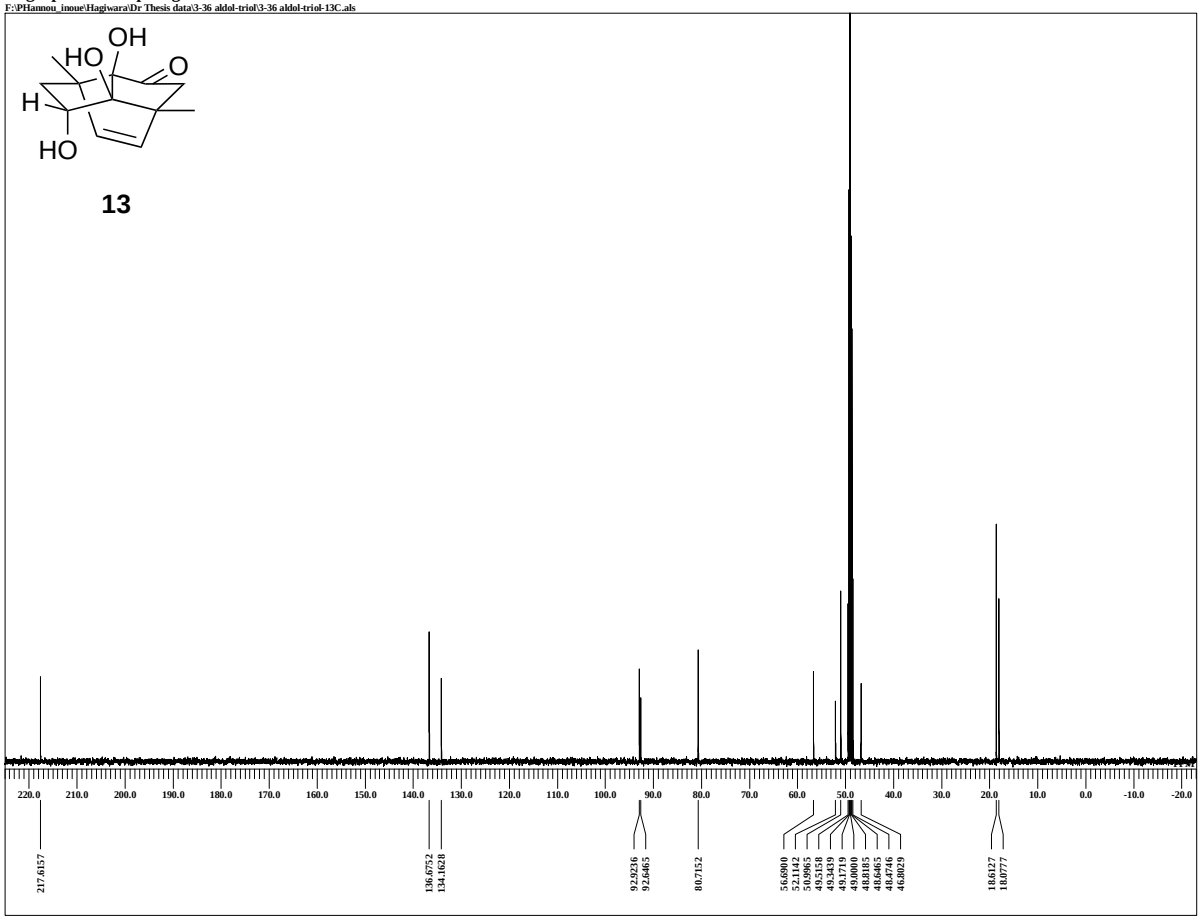
LKFIN 36.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.2 c
SLVNT CD3OD
EXREF 3.31 ppm

single pulse decoupled gated NOE

F:\PHannou_inoue\Hagiwara\Dr Thesis data\3-36 aldol-triol\3-36 aldol-triol-13C.als



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OBSET 2.31 KHz
OBFIN 6.71 Hz
PW1 3.20 usec
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PREDL 0.00000 msec
IWT 1.0000 sec
POINT 26214
SPO 26214
TIMES 8
DUMMY 4
FREQU 30863.73 Hz
FLT 155000 Hz
DELAY 21.06 usec
ACQTM 0.8493 sec
PD 5.0000 sec
SCANS 8
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 490.15 MHz
IRSET 9.16 KHz
IRFIN 7.60 Hz
IRRPW 92 usec
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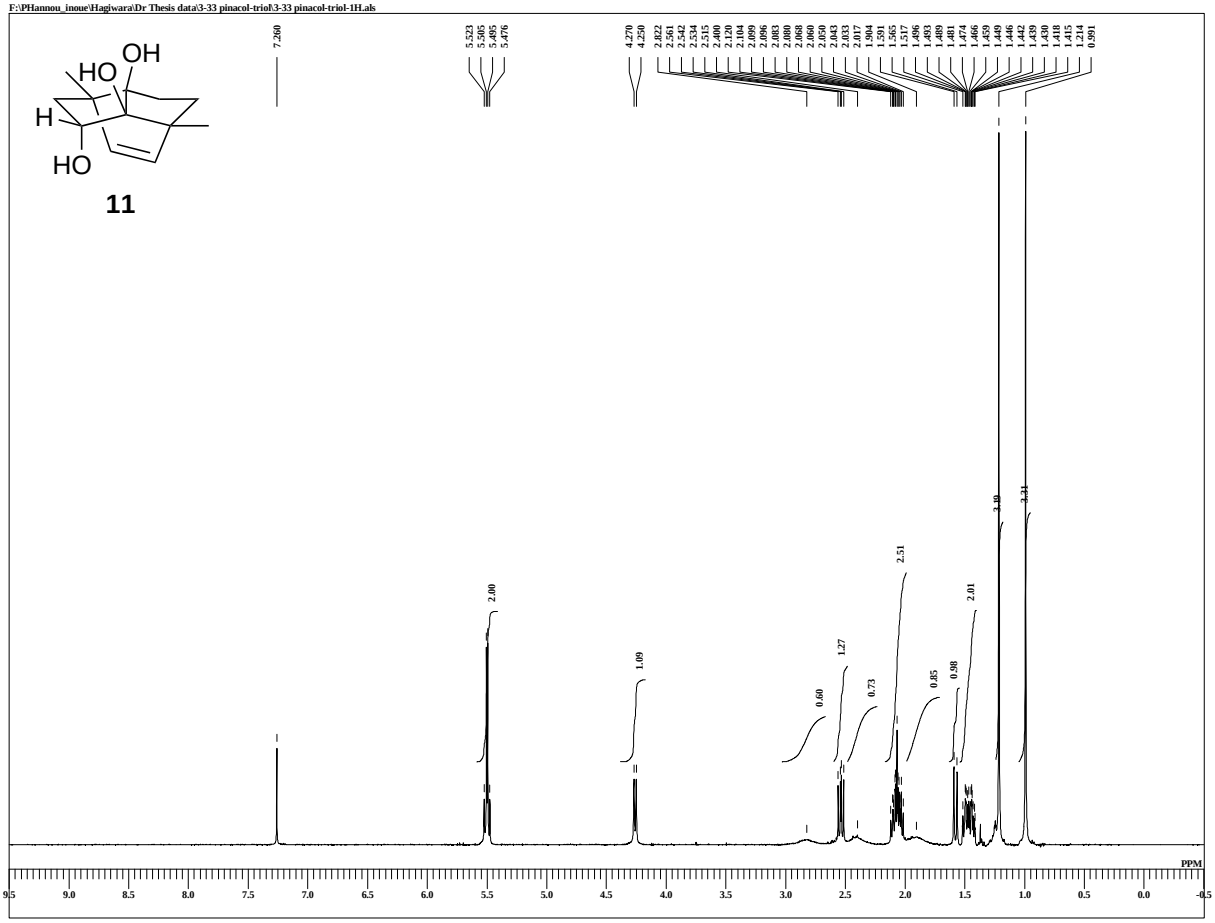
DFILE 3-36 aldol-triol-13C.als
SF
LKSET 70.00 KHz
LKFIN 36.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.6 c
SLVNT CD3OD
EXREF 49.00 ppm

single_pulse

F:\PHannou_inoue\Hagiwara\Dr Thesis data\3-33 pinacol-triol\3-33 pinacol-triol-1H.als



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PW1 6.20 usec
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PREDL 0.00000 msec
IWT 1.0000 sec
POINT 13107
SPO 13107
TIMES 8
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FREQU 7429.31 Hz
FLT 38000 Hz
DELAY 13.16 usec
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PD 1.5000 sec
SCANS 8
ADBIT 16
RGAIN 50
BF 0.01 Hz
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T2 0.00
T3 100.00
T4 100.00
EXMOD single_pulse.ex2
EXPCM
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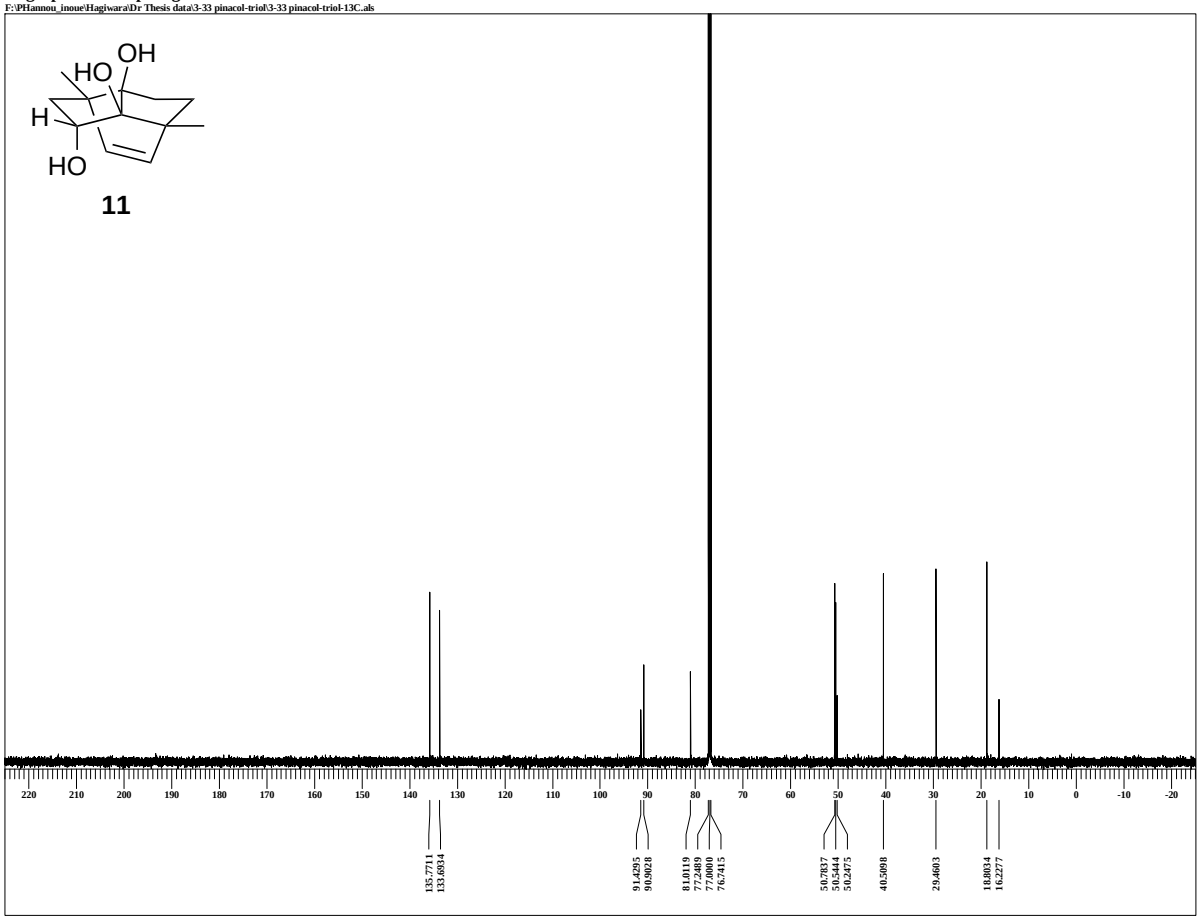
IFR 495.13 MHz
IRSET 4.38 KHz
IRFIN 9.64 Hz
IRRPW 50 usec
IRATN 79
DFILE 3-33 pinacol-triol-1H.als
SF
LKSET -601.50 KHz
LKFIN -1.8 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 19.3 c
SLVNT CDCL3
EXREF 7.26 ppm

single pulse decoupled gated NOE

F:\PHannou_inoue\Hagiwara\Dr Thesis data\3-33 pinacol-triol\3-33 pinacol-triol-13C.als



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OBFRQ 124.51 MHz
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OBFIN 6.00 Hz
PW1 3.57 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 26214
SPO 26214
TIMES 2056
DUMMY 4
FREQU 31249.52 Hz
FLT 157000 Hz
DELAY 20.80 usec
ACQTM 0.8389 sec
PD 5.0000 sec
SCANS 2056
ADBIT 16
RGAIN 60
BF 0.01 Hz
T1 0.00
T2 0.00
T3 100.00
T4 100.00
EXMOD single_pulse_dec
EXPCM
IRNUC 1H
IFR 495.13 MHz
IRSET 4.38 KHz
IRFIN 9.64 Hz
IRRPW 50 usec
IRATN 79
DFILE 3-33 pinacol-triol-13C.als
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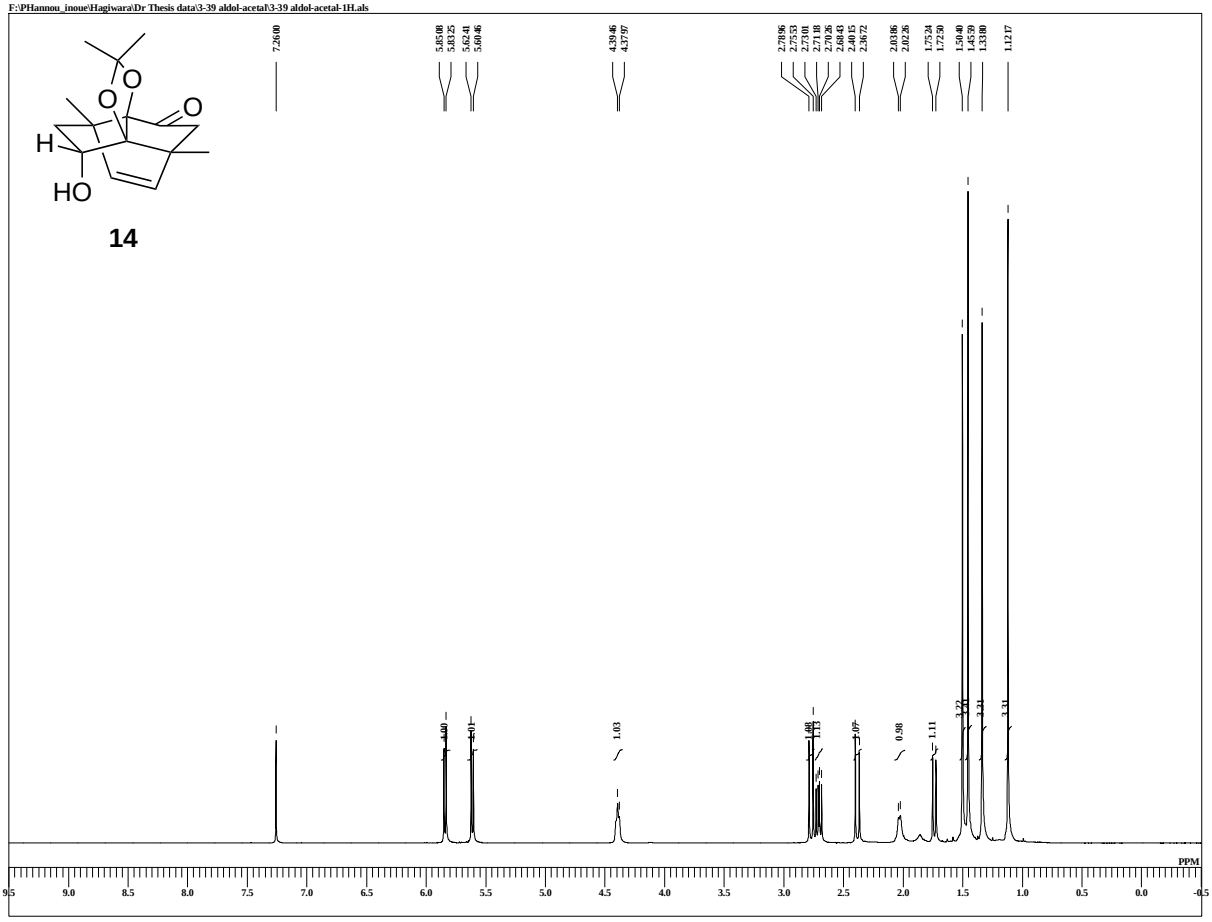
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 21.0 c
SLVNT CDCL3
EXREF 77.00 ppm

single_pulse

F:\PHannou_inoue\Hagiwara\Dr Thesis data\3-39 aldol-acetal\3-39 aldol-acetal-1H.als



14

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OBFRQ	495.13 MHz
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OBFIN	9.64 Hz
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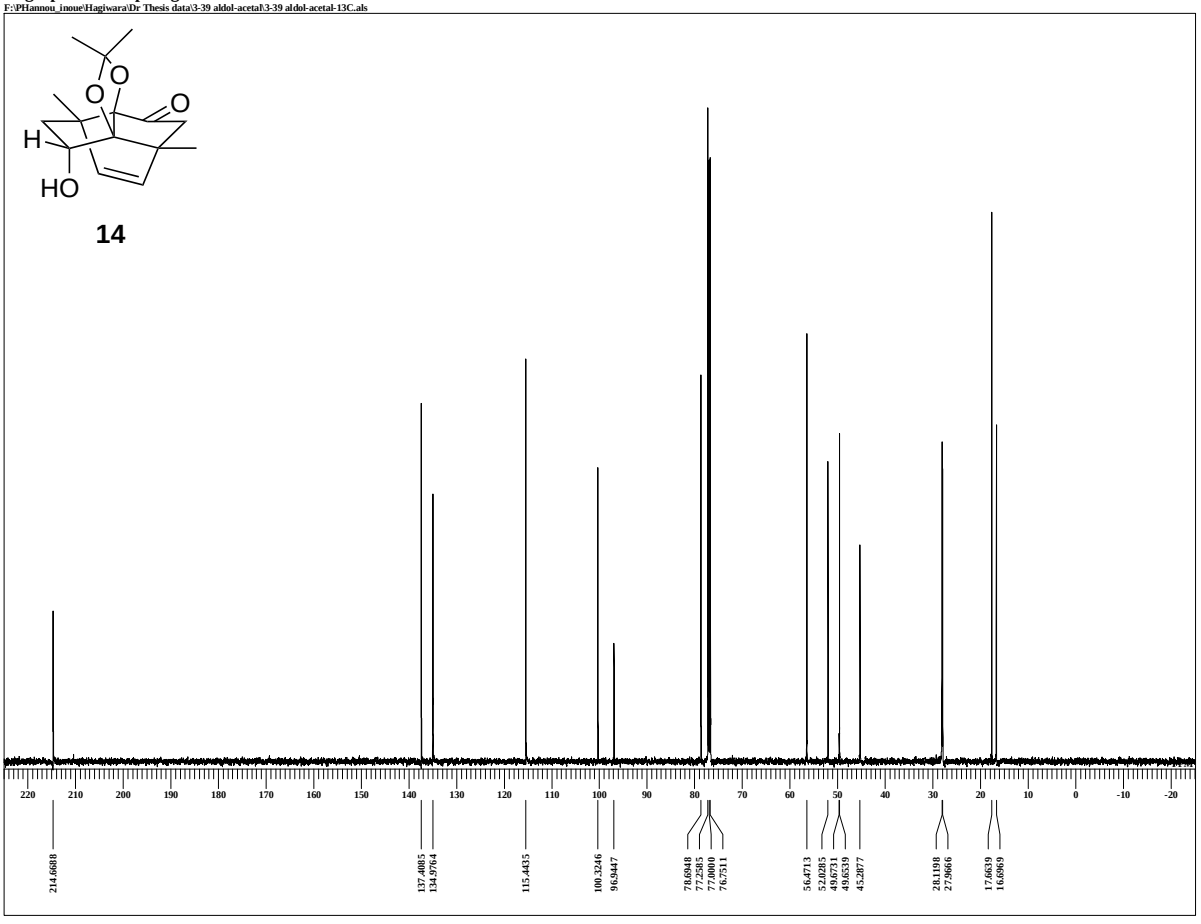
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	13107
SPO	13107
TIMES	8
DUMMY	1
FREQU	7429.31 Hz
FLT	38000 Hz
DELAY	13.16 usec
ACQTM	1.7642 sec
PD	1.5000 sec
SCANS	8
ADBIT	16
RGAIN	36
BF	0.01 Hz
T1	0.00
T2	0.00
T3	90.00
T4	100.00
EXMOD	single_pulse.ex2
EXPCM	
IRNUC	1H
IFR	495.13 MHz
IRSET	4.38 KHz
IRFIN	9.64 Hz
IRRPW	50 usec
IRATN	79
DFILE	3-39 aldol-acetal-1H.als
SF	
LKSET	-601.50 KHz
LKFIN	-1.8 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	19.7 c
SLVNT	CDCL3
EXREF	7.26 ppm

single pulse decoupled gated NOE

F:\PHannou_inoue\Hagiwara\Dr Thesis data\3-39 aldol-acetal\3-39 aldol-acetal-13C.als

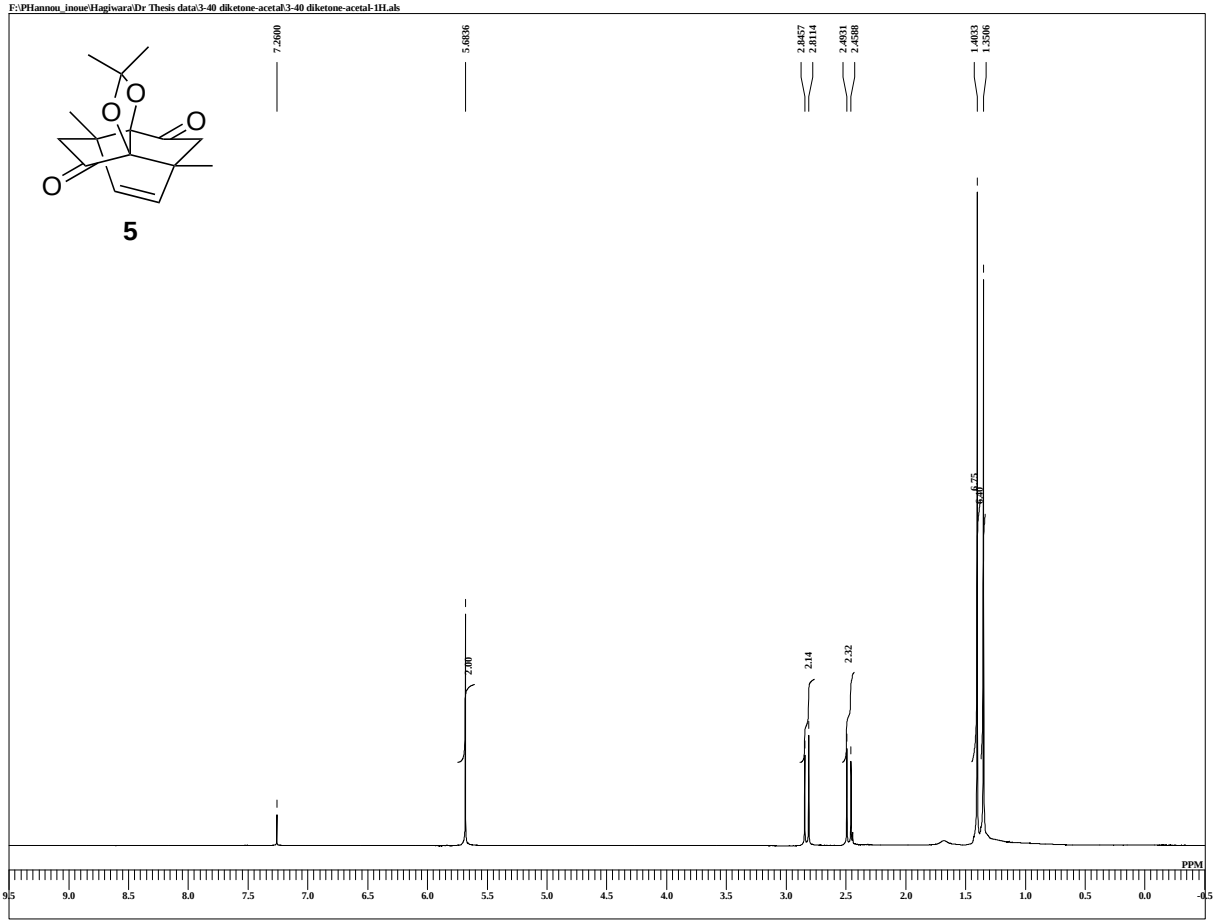


14

DFILE	3-39 aldol-acetal-13C.als
COMNT	single pulse decoupled gat
DATIM	17-07-2008 12:59:24
MENUF	
OBNUC	13C
OFR	124.51 MHz
OBFRQ	124.51 MHz
OBSET	3.45 KHz
OBFIN	6.00 Hz
PW1	3.57 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	26214
SPO	26214
TIMES	64
DUMMY	4
FREQU	31249.52 Hz
FLT	157000 Hz
DELAY	20.80 usec
ACQTM	0.8389 sec
PD	5.0000 sec
SCANS	64
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	495.13 MHz
IRSET	4.38 KHz
IRFIN	9.64 Hz
IRRPW	50 usec
IRATN	79
DFILE	3-39 aldol-acetal-13C.als
SF	
LKSET	-601.50 KHz
LKFIN	-1.8 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	21.3 c
SLVNT	CDCL3
EXREF	77.00 ppm

single_pulse

F:\PHannou_inoue\Hagiwara\Dr Thesis data\3-40 diketone-acetal\3-40 diketone-acetal-1H.als

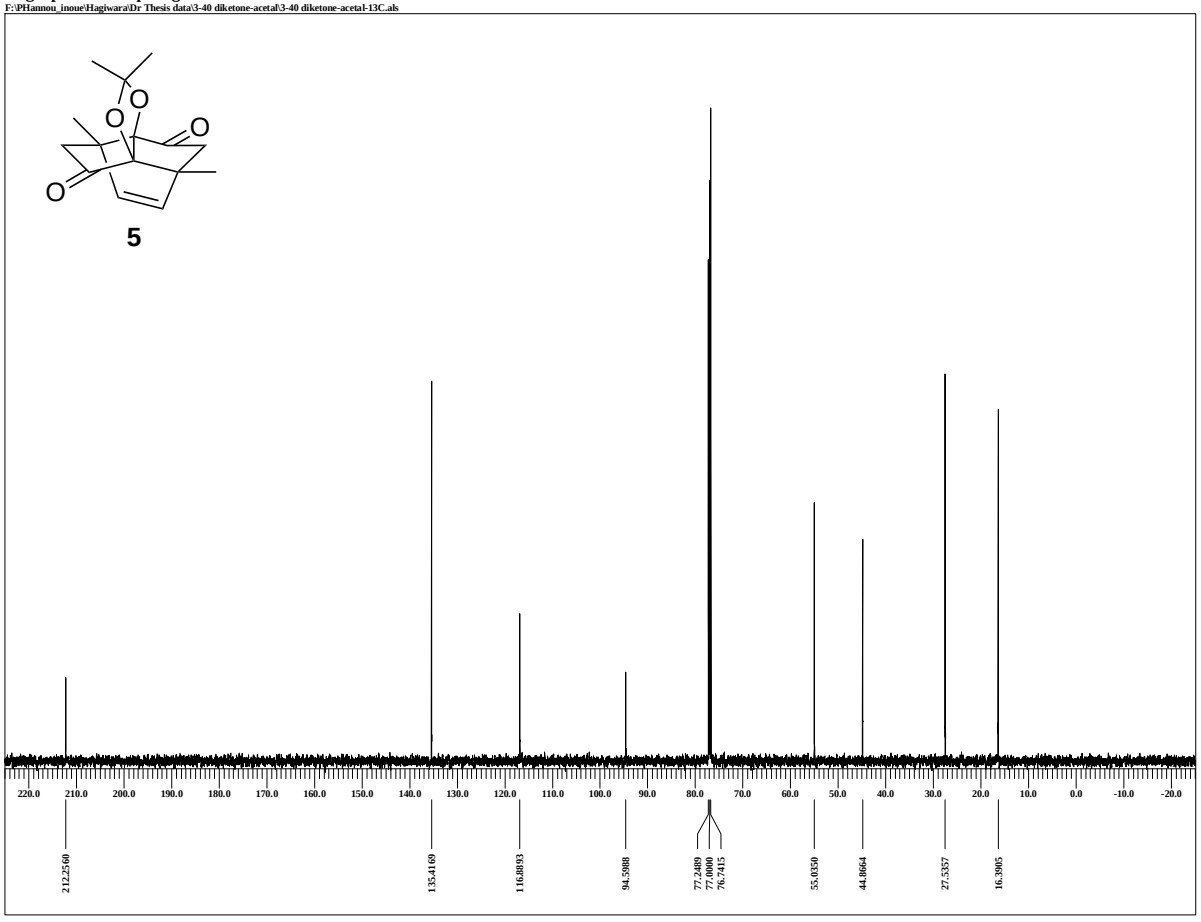


5

DFILE 3-40 diketone-acetal-1H.
COMNT single_pulse
DATIM 28-07-2008 14:01:01
MENUF
OBNUC 1H
OFR 495.13 MHz
OBFRQ 495.13 MHz
OBSET 4.38 KHz
OBFIN 9.64 Hz
PW1 6.20 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 13107
SPO 13107
TIMES 8
DUMMY 1
FREQU 7429.31 Hz
FLT 38000 Hz
DELAY 13.16 usec
ACQTM 1.7642 sec
PD 1.5000 sec
SCANS 8
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 495.13 MHz
IRSET 4.38 KHz
IRFIN 9.64 Hz
IRRPW 50 usec
IRATN 79
DFILE 3-40 diketone-acetal-1H.
SF
LKSET -601.50 KHz
LKFIN -1.8 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 19.7 c
SLVNT CDCL3
EXREF 7.26 ppm

single pulse decoupled gated NOE

F:\PHannou_inoue\Hagiwara\Dr Thesis data\3-40 diketone-acetal\3-40 diketone-acetal-13C.als

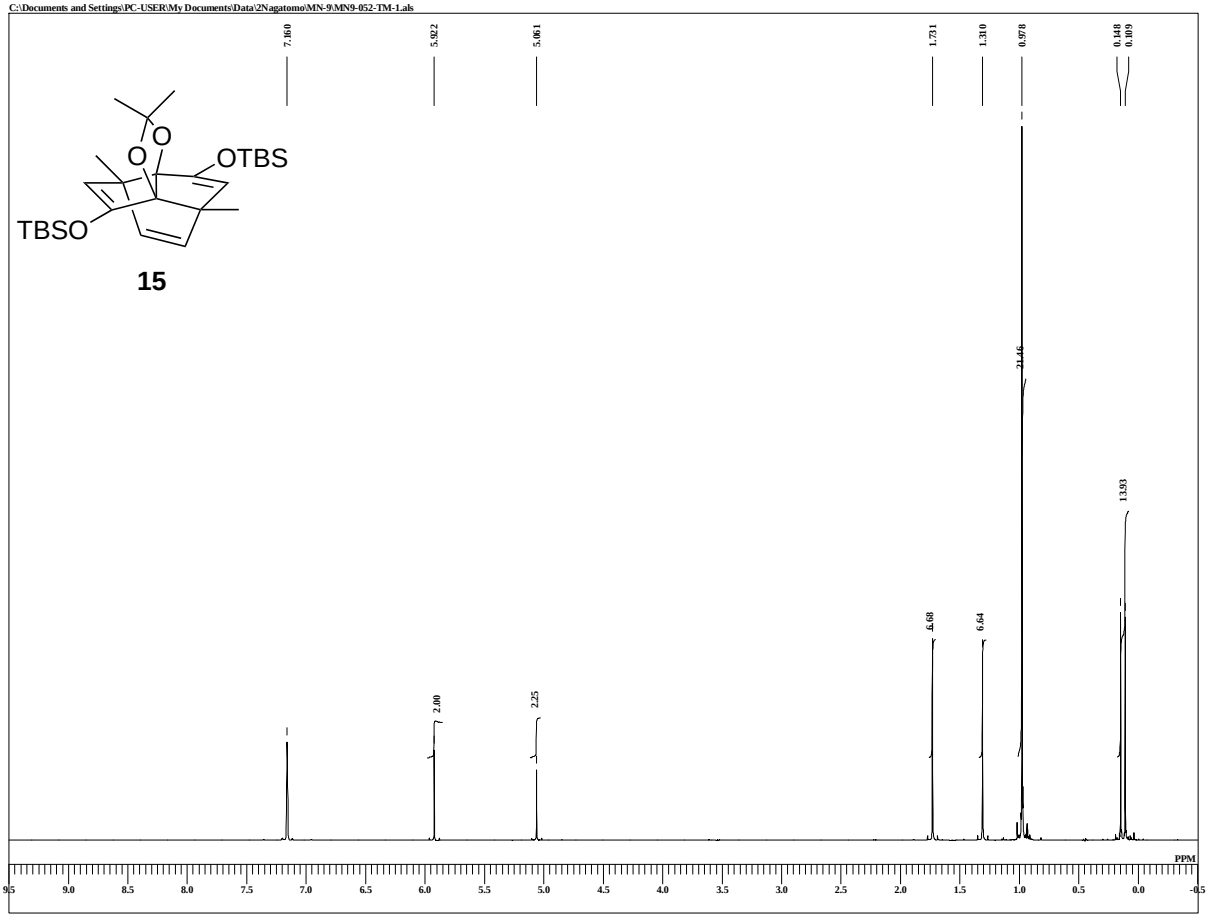


5

DFILE 3-40 diketone-acetal-13C.
COMNT single pulse decoupled gat
DATIM 28-07-2008 14:06:04
MENUF
OBNUC 13C
OFR 124.51 MHz
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
PW1 3.57 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 26214
SPO 26214
TIMES 32
DUMMY 4
FREQU 31249.52 Hz
FLT 157000 Hz
DELAY 20.80 usec
ACQTM 0.8389 sec
PD 5.0000 sec
SCANS 32
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 495.13 MHz
IRSET 4.38 KHz
IRFIN 9.64 Hz
IRRPW 50 usec
IRATN 79
DFILE 3-40 diketone-acetal-13C.
SF
LKSET -601.50 KHz
LKFIN -1.8 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 21.0 c
SLVNT CDCL3
EXREF 77.00 ppm

MN9-052-TM

C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\MN-9\MN9-052-TM-1.als

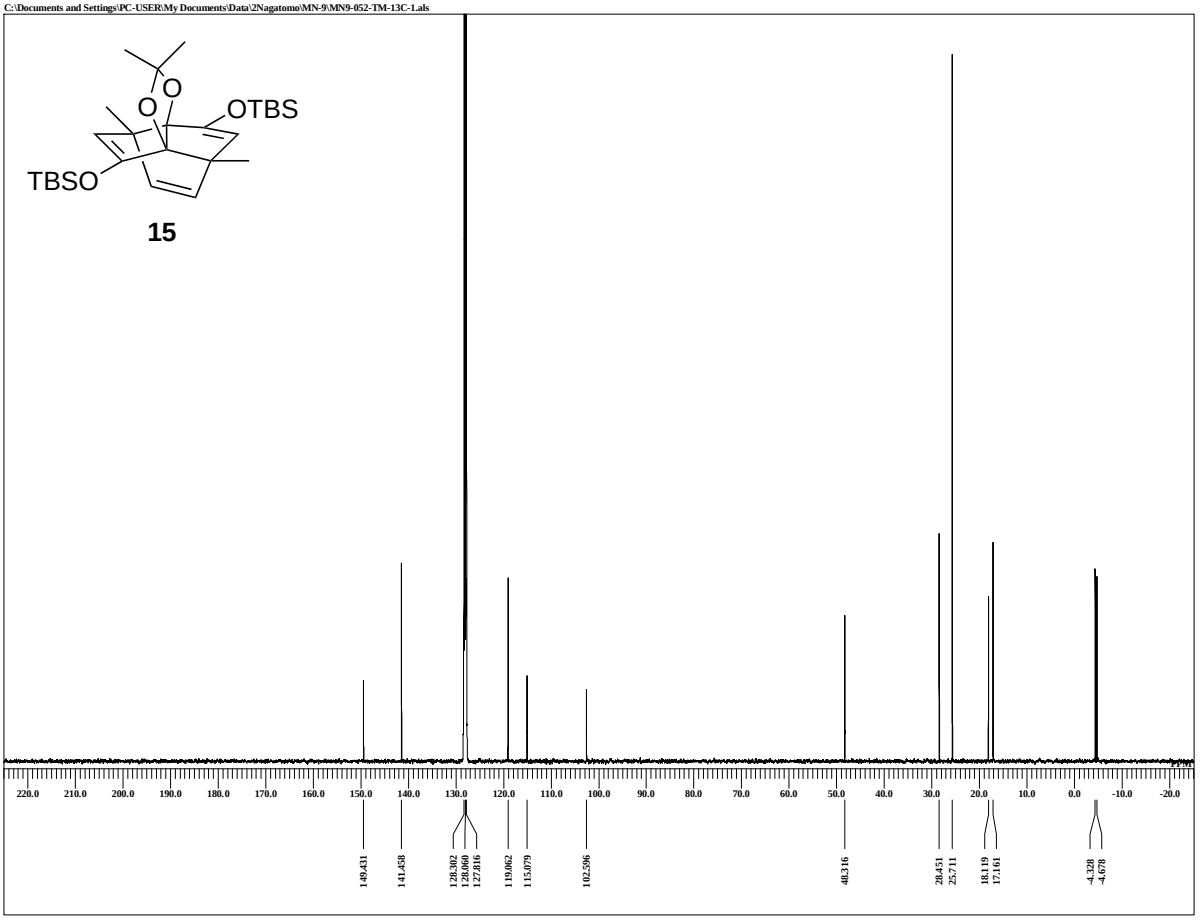


15

DFILE	MN9-052-TM-1.als
COMNT	MN9-052-TM
DATIM	21-06-2011 13:57:18
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	16
DUMMY	1
FREQU	5938.15 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	2.0000 sec
SCANS	16
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	MN9-052-TM-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

MN9-052-TM

C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\MN-9\MN9-052-TM-13C-1.als

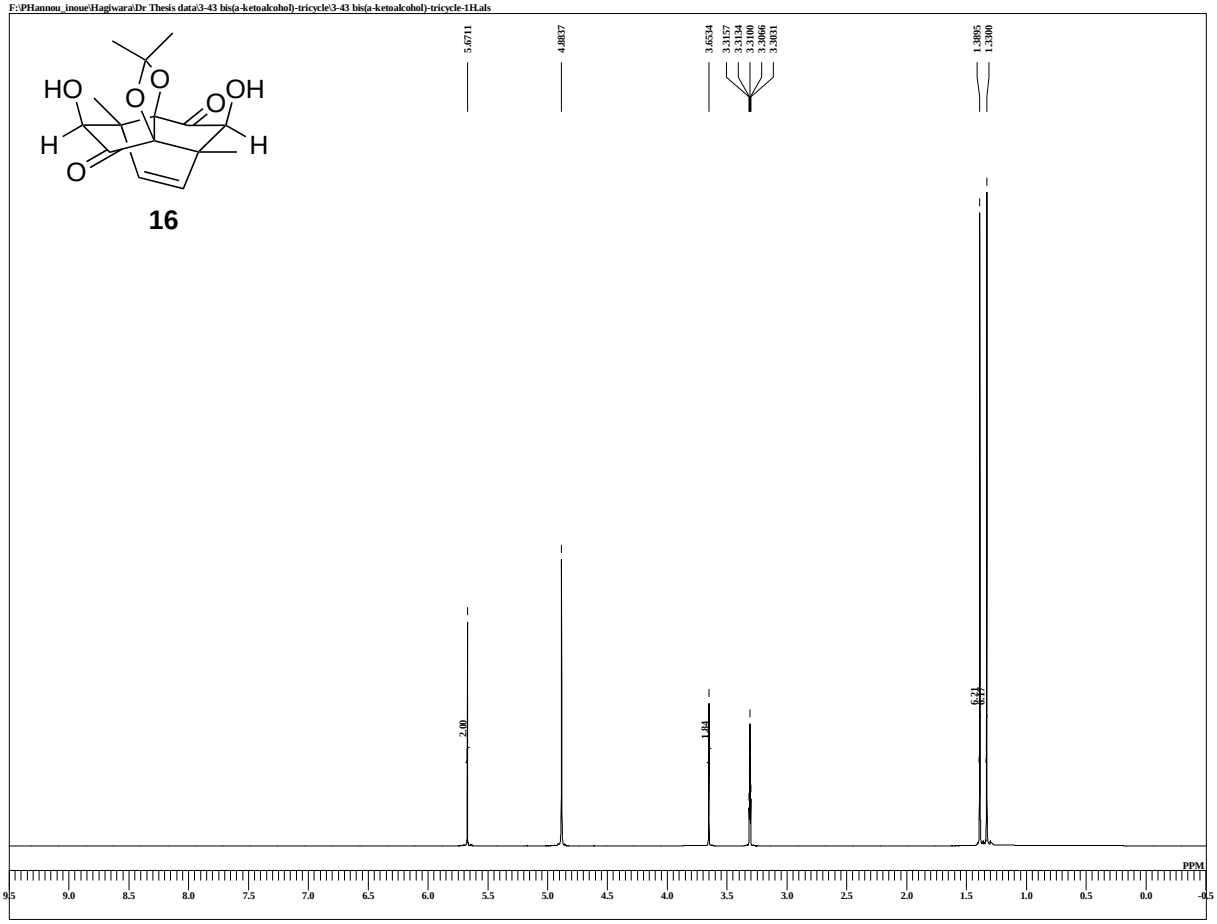


15

DFILE	MN9-052-TM-13C-1.als
COMNT	MN9-052-TM
DATIM	21-06-2011 14:07:42
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	104856
SPO	104856
TIMES	200
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	2.0000 sec
SCANS	200
ADBIT	16
RGAIN	36
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	MN9-052-TM-13C-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	24.3 c
SLVNT	C6D6
EXREF	128.06 ppm

single_pulse

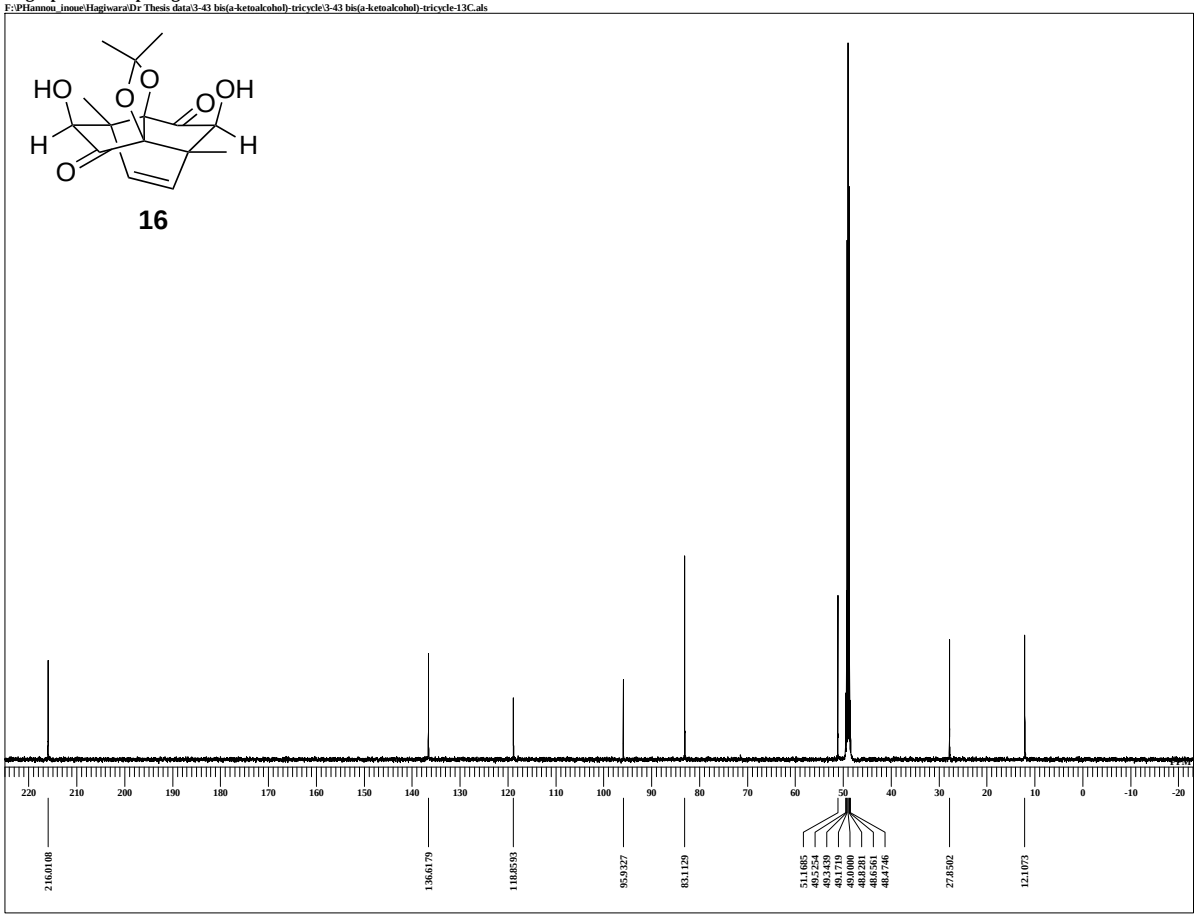
F:\PHannou_inoue\Hagiwara\Dr Thesis data\3-43 bis(a-ketoalcohol)-tricycle\3-43 bis(a-ketoalcohol)-tricycle-1H.als



DFILE 3-43 bis(a-ketoalcohol)-t
COMNT single_pulse
DATIM 08-10-2008 14:06:17
MENUF
OBNUC 1H
OFR 490.15 MHz
OBFRQ 490.15 MHz
OBSET 9.16 KHz
OBFIN 7.60 Hz
PW1 8.55 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 13107
SPO 13107
TIMES 8
DUMMY 1
FREQU 7352.83 Hz
FLT 37000 Hz
DELAY 13.52 usec
ACQTM 1.7826 sec
PD 1.5000 sec
SCANS 8
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 490.15 MHz
IRSET 9.16 KHz
IRFIN 7.60 Hz
IRRPW 118 usec
IRATN 79
DFILE 3-43 bis(a-ketoalcohol)-t
SF
LKSET 70.00 KHz
LKFIN 36.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.8 c
SLVNT CD3OD
EXREF 3.31 ppm

single pulse decoupled gated NOE

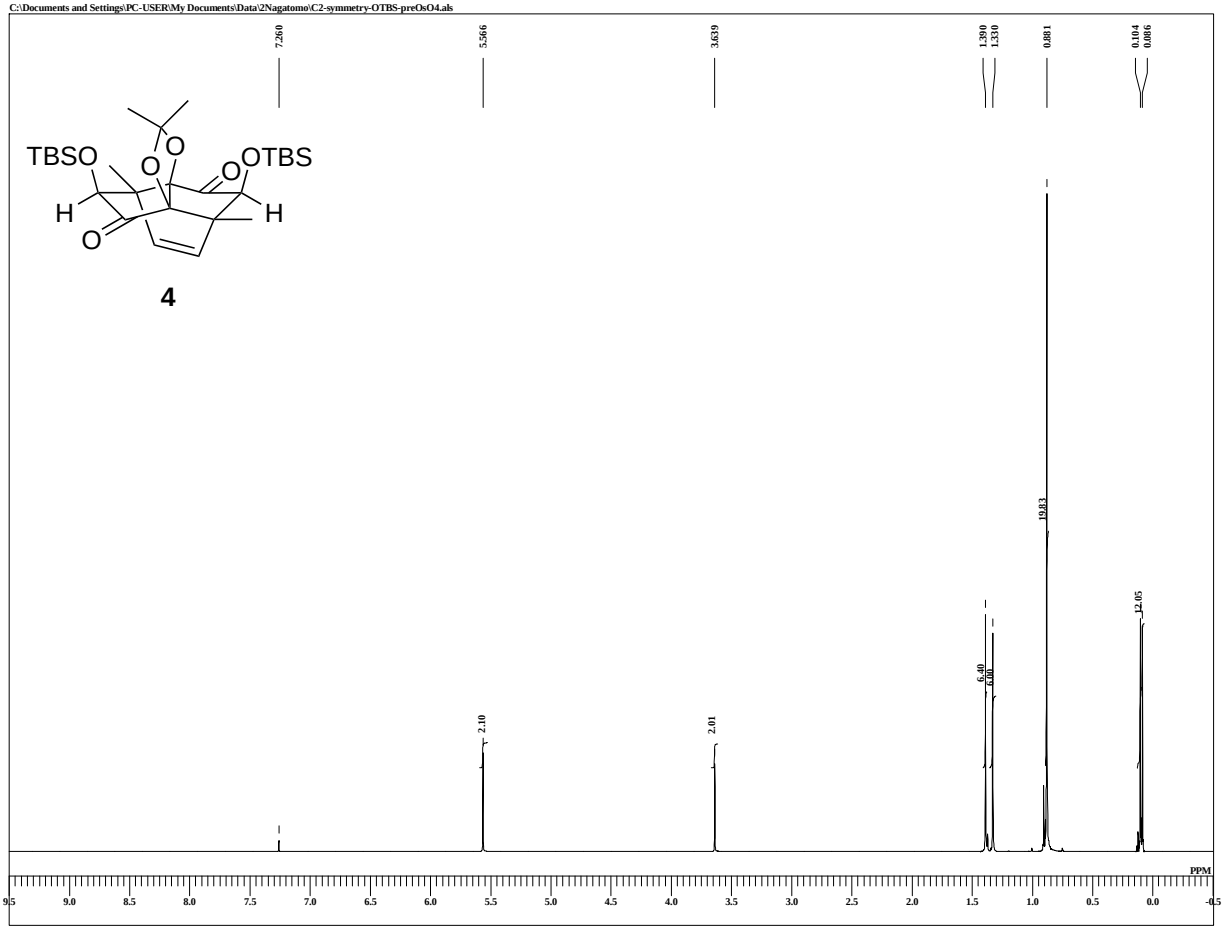
F:\PHannou_inoue\Hagiwara\Dr Thesis data\3-43 bis(a-ketoalcohol)-tricycle\3-43 bis(a-ketoalcohol)-tricycle-13C.als



DFILE 3-43 bis(a-ketoalcohol)-tr
COMNT single pulse decoupled gat
DATIM 12-09-2008 10:57:44
MENUF
OBNUC 13C
OFR 123.26 MHz
OBFRQ 123.26 MHz
OBSET 2.31 KHz
OBFIN 6.71 Hz
PW1 3.20 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 26214
SPO 26214
TIMES 32
DUMMY 4
FREQU 30863.73 Hz
FLT 155000 Hz
DELAY 21.06 usec
ACQTM 0.8493 sec
PD 5.0000 sec
SCANS 32
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 490.15 MHz
IRSET 9.16 KHz
IRFIN 7.60 Hz
IRRPW 92 usec
IRATN 79
DFILE 3-43 bis(a-ketoalcohol)-tr
SF
LKSET 70.00 KHz
LKFIN 36.6 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.8 c
SLVNT CD3OD
EXREF 49.00 ppm

C2-symmetry-OTBS-preOsO4

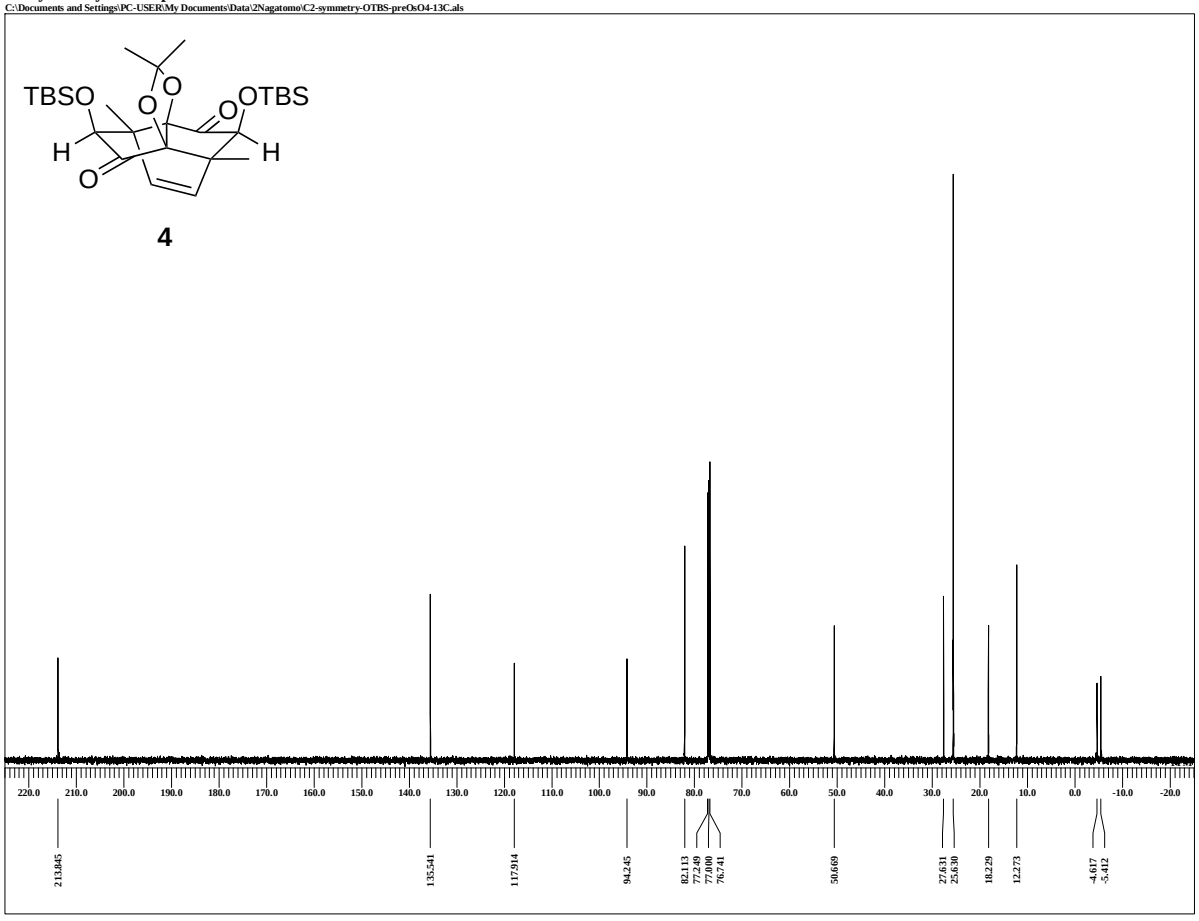
C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\C2-symmetry-OTBS-preOsO4.als



DFILE C2-symmetry-OTBS-p
COMNT C2-symmetry-OTBS-p
DATIM 28-10-2009 10:44:43
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 msec
IWT 1.0000 sec
POINT 13107
SPO 13107
TIMES 8
DUMMY 1
FREQU 7429.31 Hz
FLT 38000 Hz
DELAY 13.16 usec
ACQTM 1.7642 sec
PD 5.0000 sec
SCANS 8
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 495.13 MHz
IRSET 4.38 KHz
IRFIN 9.64 Hz
IRRPW 92 usec
IRATN 79
DFILE C2-symmetry-OTBS-p
SF
LKSET -601.50 KHz
LKFIN -1.8 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 24.1 c
SLVNT CDCL3
EXREF 7.26 ppm

C2-symmetry-OTBS-preOsO4

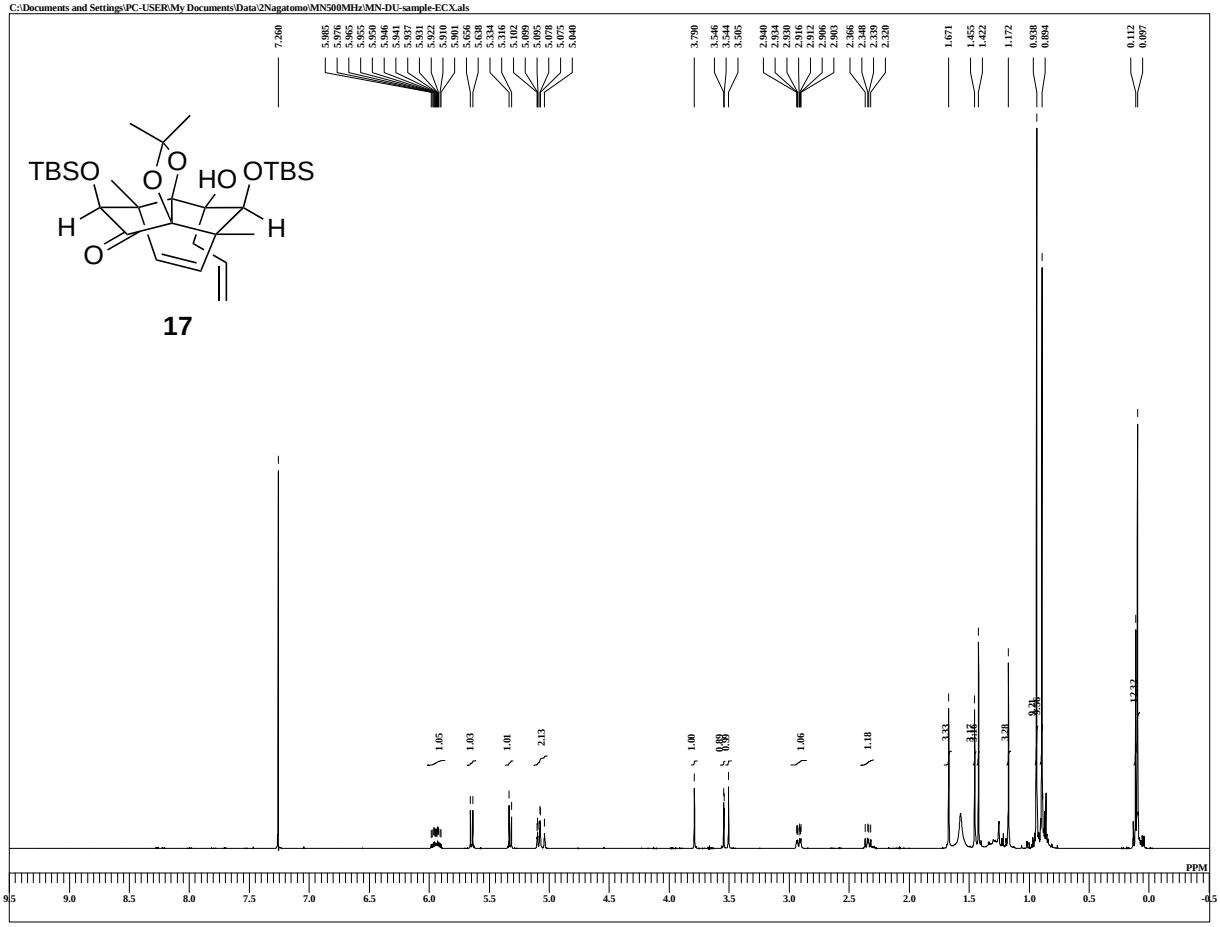
C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\C2-symmetry-OTBS-preOsO4-13C.als



DFILE C2-symmetry-OTBS-preO
COMNT C2-symmetry-OTBS-preO
DATIM 28-10-2009 10:52:35
MENUF
OBNUC 13C
OFR 124.51 MHz
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
PW1 3.25 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 26214
SPO 26214
TIMES 160
DUMMY 4
FREQU 31249.52 Hz
FLT 157000 Hz
DELAY 20.80 usec
ACQTM 0.8389 sec
PD 2.0000 sec
SCANS 160
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 5.37 KHz
IRFIN 9.90 Hz
IRRPW 92 usec
IRATN 79
DFILE C2-symmetry-OTBS-preO
SF
LKSET 748.40 KHz
LKFIN 98.2 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 24.5 c
SLVNT CDCL3
EXREF 77.00 ppm

MN-DU-sample-ECX

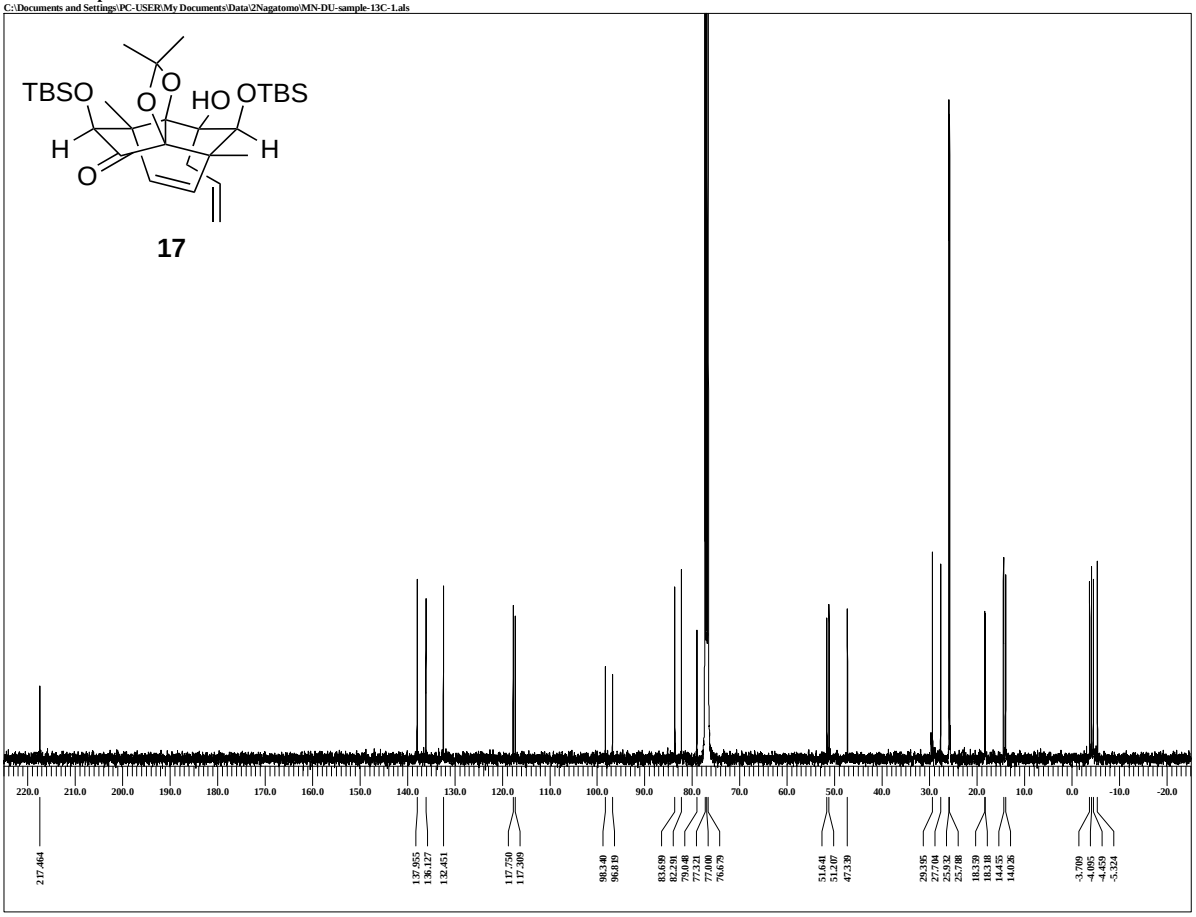
C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\MN500MHz\MN-DU-sample-ECX.als




```
DFILE    MN-DU-sample-ECX.al
COMNT    MN-DU-sample-ECX
DATIM    03-09-2012 11:31:45
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 msec
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       2.0000 sec
SCANS    64
ADBIT    16
RGAIN    50
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    MN-DU-sample-ECX.al
SF
LKSET    -601.50 KHz
LKFIN    -1.8 Hz
LKLEV    0
LGAIN    0
LKPHS    0
LKSIG    0
CSPED    0 Hz
FILDC
FILDF
CTEMP    23.4 c
SLVNT    CDCL3
EXREF    7.26 ppm
```

MN-DU-sample-13C

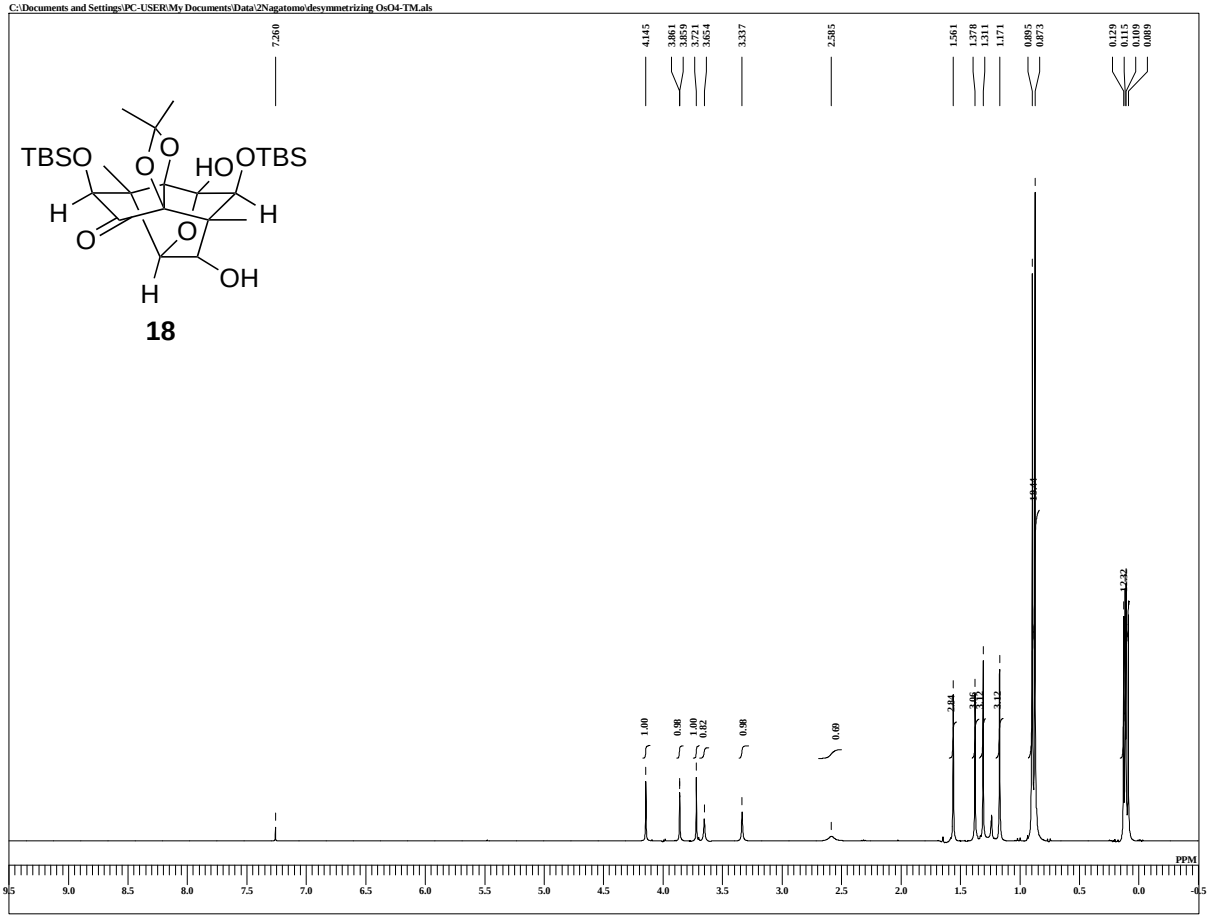
C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\MN-DU-sample-13C-1.als




```
DFILE    MN-DU-sample-13C-1.als
COMNT    MN-DU-sample-13C
DATIM    04-09-2012 09:11:39
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    104856
SPO      104856
TIMES    13926
DUMMY    4
FREQU    24999.62 Hz
FLT      125000 Hz
DELAY    20.50 usec
ACQTM    1.0486 sec
PD       2.0000 sec
SCANS    13926
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    MN-DU-sample-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    23.4 c
SLVNT    CDCL3
EXREF    77.00 ppm
```

desymmetrizing OsO4-TM

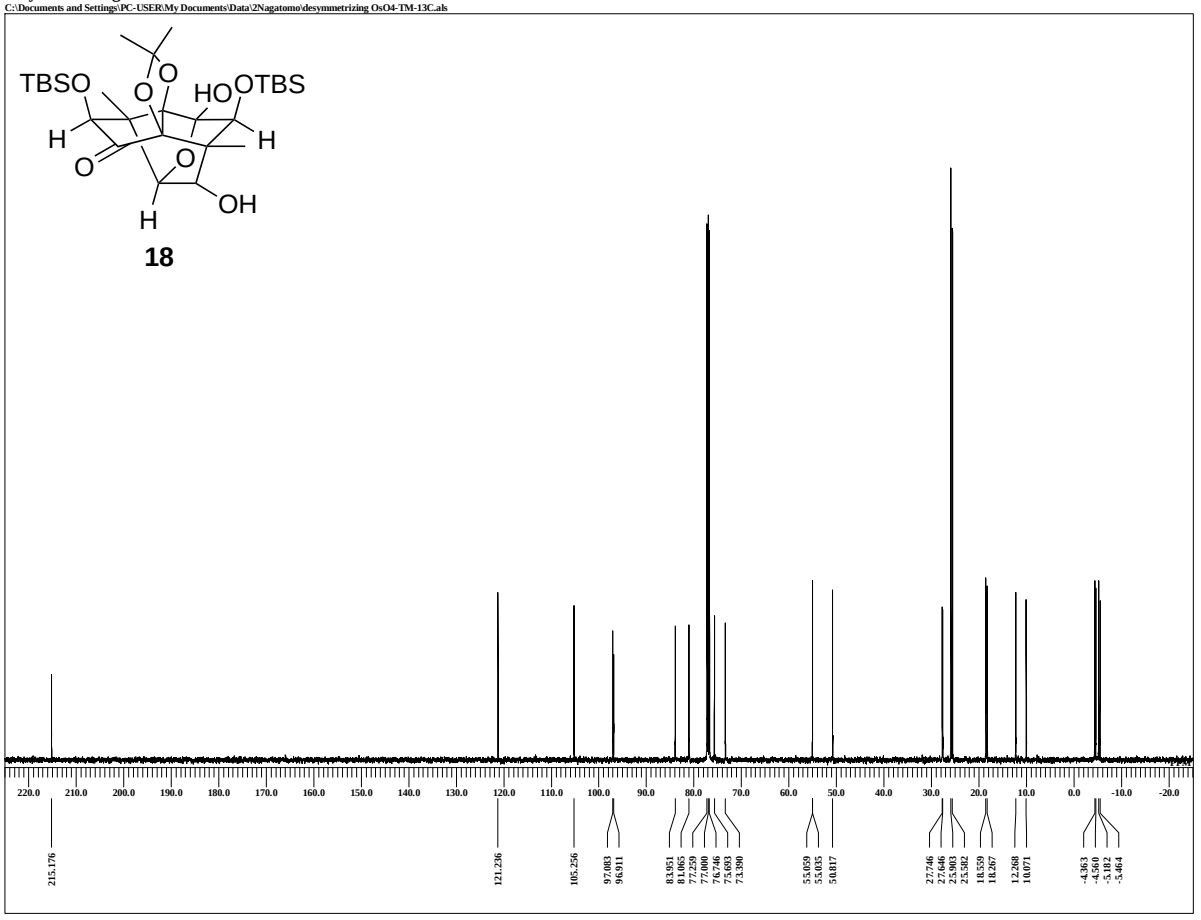
C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\desymmetrizing OsO4-TM.als




```
DFILE     desymmetrizing OsO4-TM
COMNT     desymmetrizing OsO4-TM
DATIM     28-10-2009 13:26:03
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 msec
IWT       1.0000 sec
POINT     13107
SPO       13107
TIMES     8
DUMMY     1
FREQU     7429.31 Hz
FLT       38000 Hz
DELAY     13.16 usec
ACQTM     1.7642 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       495.13 MHz
IRSET     4.38 KHz
IRFIN     9.64 Hz
IRRPW     118 usec
IRATN     79
DFILE     desymmetrizing OsO4-TM
SF
LKSET     -601.50 KHz
LKFIN     -1.8 Hz
LKLEV     0
LGAIN     0
LKPHS     0
LKSIG     0
CSPED     0 Hz
FILDC
FILDF
CTEMP     24.1 c
SLVNT     CDCL3
EXREF     7.26 ppm
```

desymmetrizing OsO4-TM

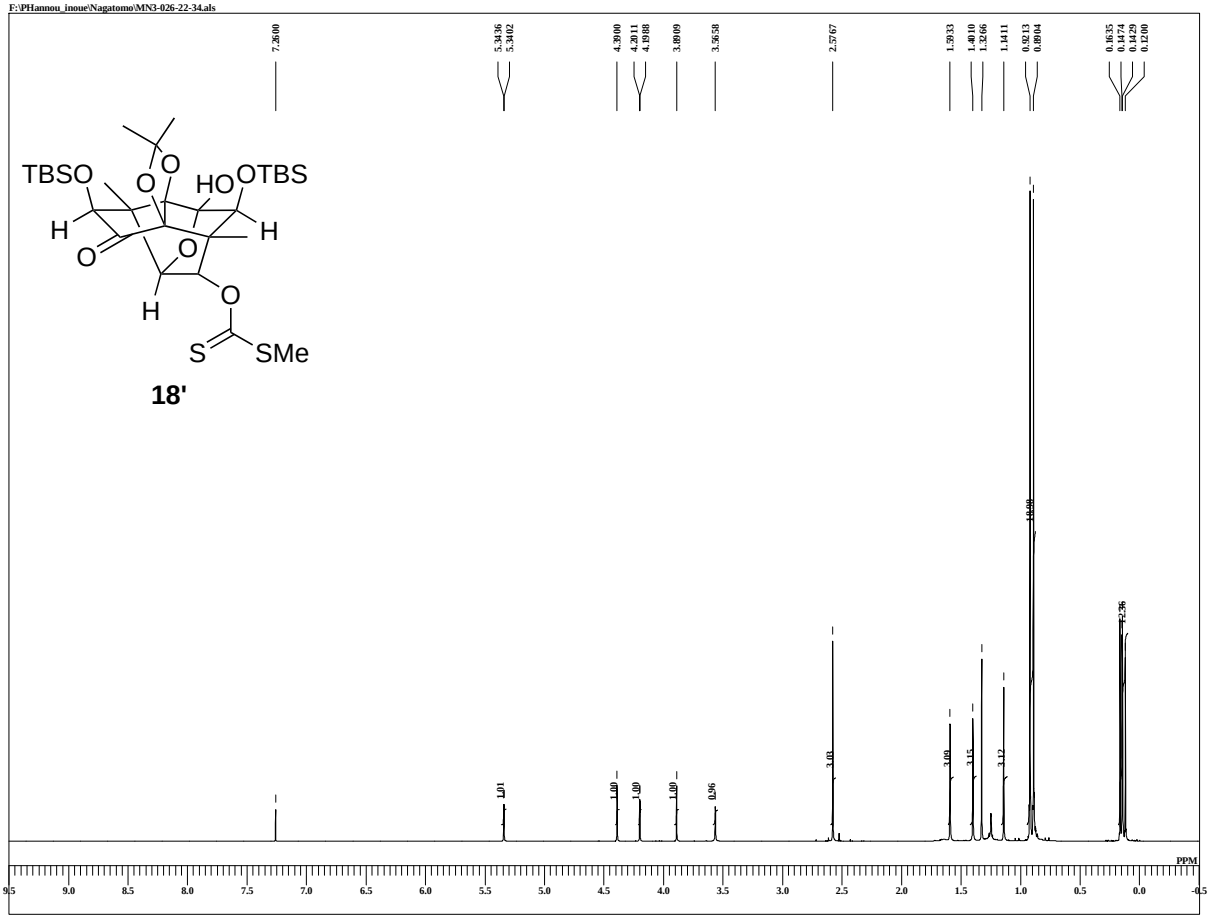
C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\desymmetrizing OsO4-TM-13C.als




```
DFILE     desymmetrizing OsO4-TM
COMNT     desymmetrizing OsO4-TM
DATIM     28-10-2009 13:37:08
MENUF
OBNUC     13C
OFR       124.51 MHz
OBFRQ     124.51 MHz
OBSET     3.45 KHz
OBFIN     6.00 Hz
PW1       3.25 usec
DEADT     0.00 usec
PREDL     0.00000 msec
IWT       1.0000 sec
POINT     52428
SPO       52428
TIMES     80
DUMMY     4
FREQU     31249.52 Hz
FLT       157000 Hz
DELAY     20.00 usec
ACQTM     0.8389 sec
PD        7.0000 sec
SCANS     80
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     desymmetrizing OsO4-TM
SF
LKSET     -601.50 KHz
LKFIN     -1.8 Hz
LKLEV     0
LGAIN     0
LKPHS     0
LKSIG     0
CSPED     0 Hz
FILDC
FILDF
CTEMP     24.6 c
SLVNT     CDCL3
EXREF     77.00 ppm
```

MN3-026-22-34

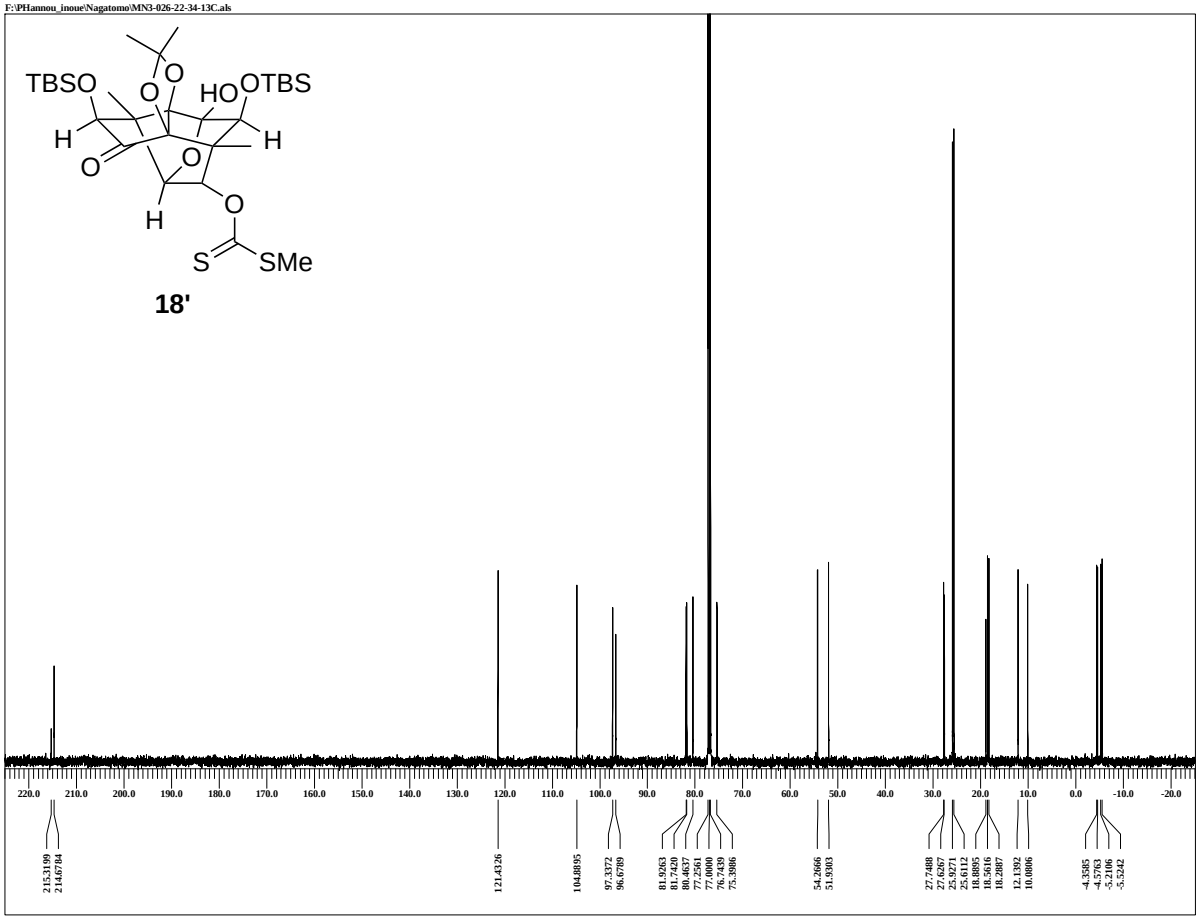
F:\PHannou_inoue\Nagatomo\MN3-026-22-34.als



DFILE MN3-026-22-34.als
COMNT MN3-026-22-34
DATIM 29-10-2009 16:04:18
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 msec
IWT 1.0000 sec
POINT 13107
SPO 13107
TIMES 16
DUMMY 1
FREQU 7429.31 Hz
FLT 38000 Hz
DELAY 13.16 usec
ACQTM 1.7642 sec
PD 5.0000 sec
SCANS 16
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 495.13 MHz
IRSET 4.38 KHz
IRFIN 9.64 Hz
IRRPW 92 usec
IRATN 79
DFILE MN3-026-22-34.als
SF
LKSET -601.50 KHz
LKFIN -1.8 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 23.9 c
SLVNT CDCL3
EXREF 7.26 ppm

MN3-026-22-34

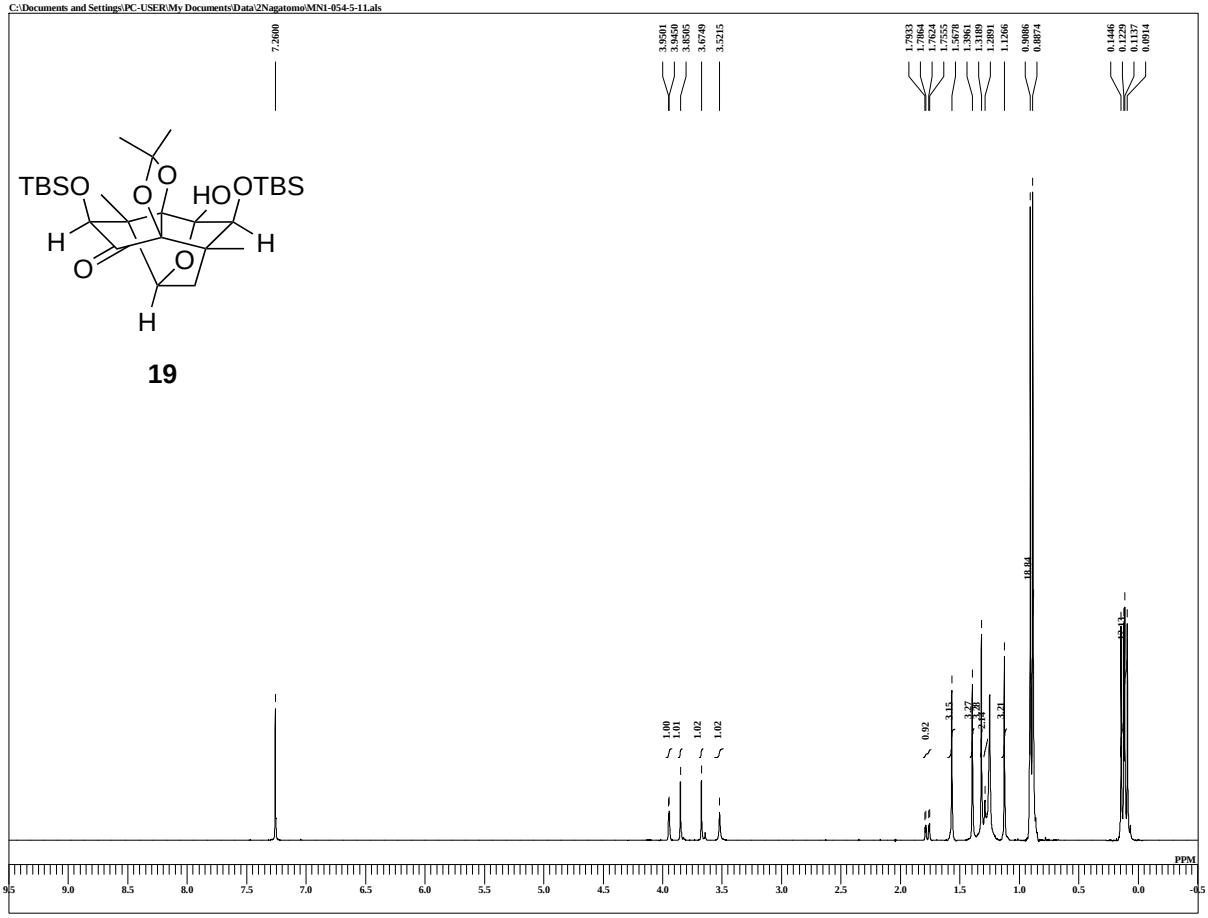
F:\PHannou_inoue\Nagatomo\MN3-026-22-34-13C.als



DFILE MN3-026-22-34-13C.als
COMNT MN3-026-22-34
DATIM 29-10-2009 16:17:60
MENUF
OBNUC 13C
OFR 124.51 MHz
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
PW1 3.25 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 104856
SPO 104856
TIMES 100
DUMMY 4
FREQU 31249.52 Hz
FLT 157000 Hz
DELAY 20.80 usec
ACQTM 0.8389 sec
PD 7.0000 sec
SCANS 100
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 MN3-026-22-34-13C.als
SF
LKSET -601.50 KHz
LKFIN -1.8 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 24.4 c
SLVNT CDCL3
EXREF 77.00 ppm

MN1-054-5-11

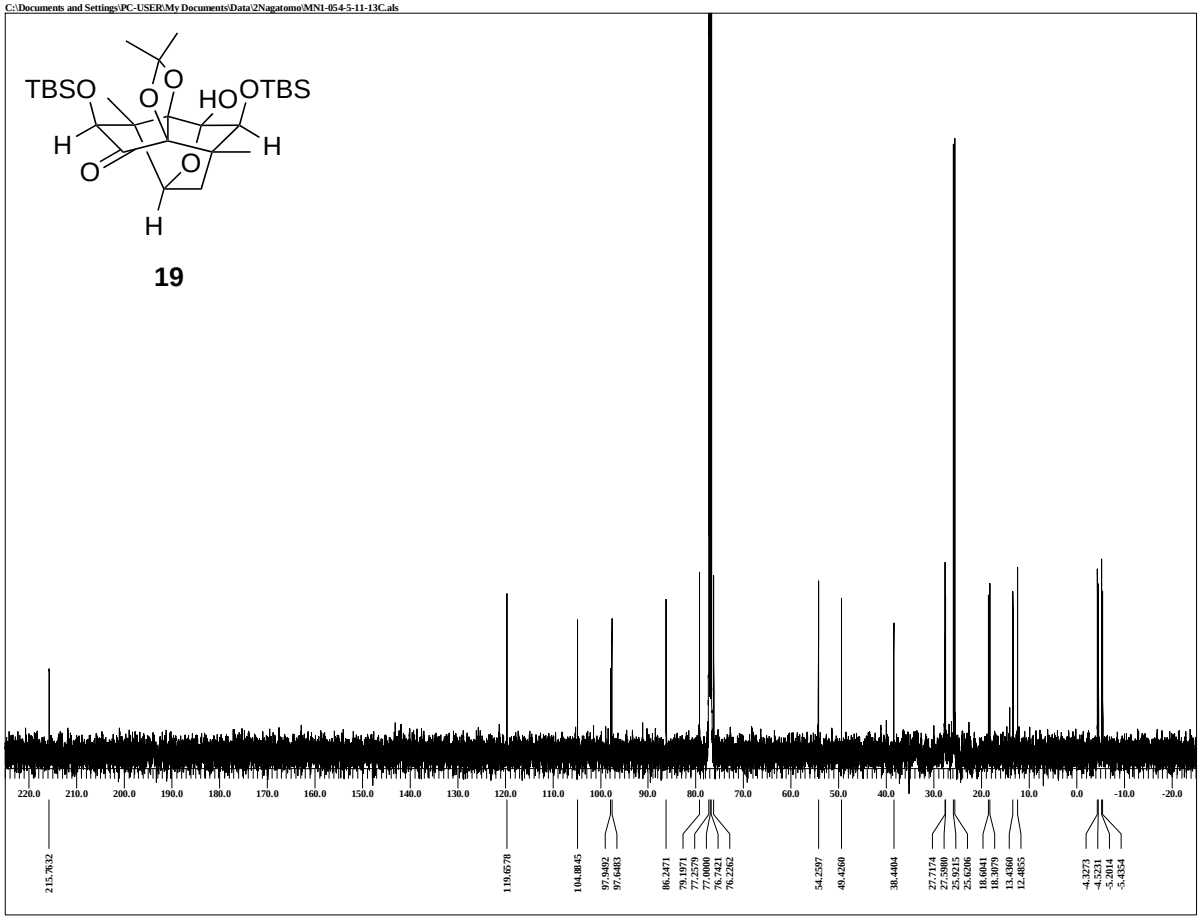
C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\MN1-054-5-11.als



DFILE MN1-054-5-11.als
COMNT MN1-054-5-11
DATIM 27-05-2009 10:19:19
MENUF
OBNUC 1H
OFR 490.15 MHz
OBFRQ 490.15 MHz
OBSET 9.16 KHz
OBFIN 7.60 Hz
PW1 8.55 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 26214
SPO 26214
TIMES 32
DUMMY 1
FREQU 7352.83 Hz
FLT 37000 Hz
DELAY 13.52 usec
ACQTM 1.7826 sec
PD 5.0000 sec
SCANS 32
ADBIT 16
RGAIN 50
BF 0.01 Hz
T1 0.00
T2 0.00
T3 90.00
T4 100.00
EXMOD single_pulse.ex2
EXPCM
IRNUC 1H
IFR 490.15 MHz
IRSET 9.16 KHz
IRFIN 7.60 Hz
IRRPW 92 usec
IRATN 79
DFILE MN1-054-5-11.als
SF
LKSET 70.30 KHz
LKFIN 32.5 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 20.7 c
SLVNT CDCL3
EXREF 7.26 ppm

MN1-054-5-11

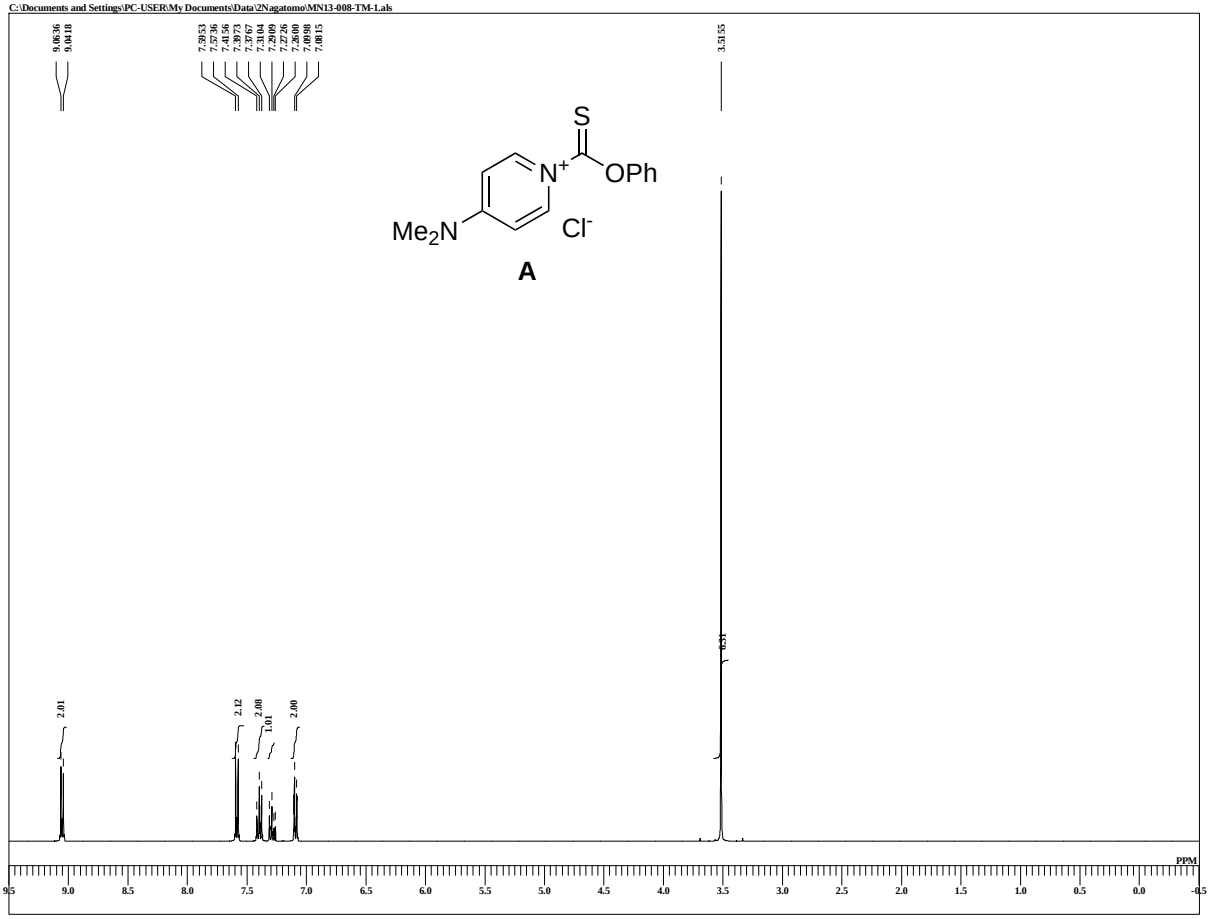
C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\MN1-054-5-11-13C.als



DFILE MN1-054-5-11-13C.als
COMNT MN1-054-5-11
DATIM 27-05-2009 11:15:49
MENUF
OBNUC 13C
OFR 123.26 MHz
OBFRQ 123.26 MHz
OBSET 2.31 KHz
OBFIN 6.71 Hz
PW1 3.20 usec
DEADT 0.00 usec
PREDL 0.00000 msec
IWT 1.0000 sec
POINT 52428
SPO 52428
TIMES 500
DUMMY 4
FREQU 30863.73 Hz
FLT 155000 Hz
DELAY 21.06 usec
ACQTM 0.8493 sec
PD 5.0000 sec
SCANS 500
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 490.15 MHz
IRSET 9.16 KHz
IRFIN 7.60 Hz
IRRPW 92 usec
IRATN 79
DFILE MN1-054-5-11-13C.als
SF
LKSET 70.30 KHz
LKFIN 32.5 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 21.8 c
SLVNT CDCL3
EXREF 77.00 ppm

MN13-008-TM

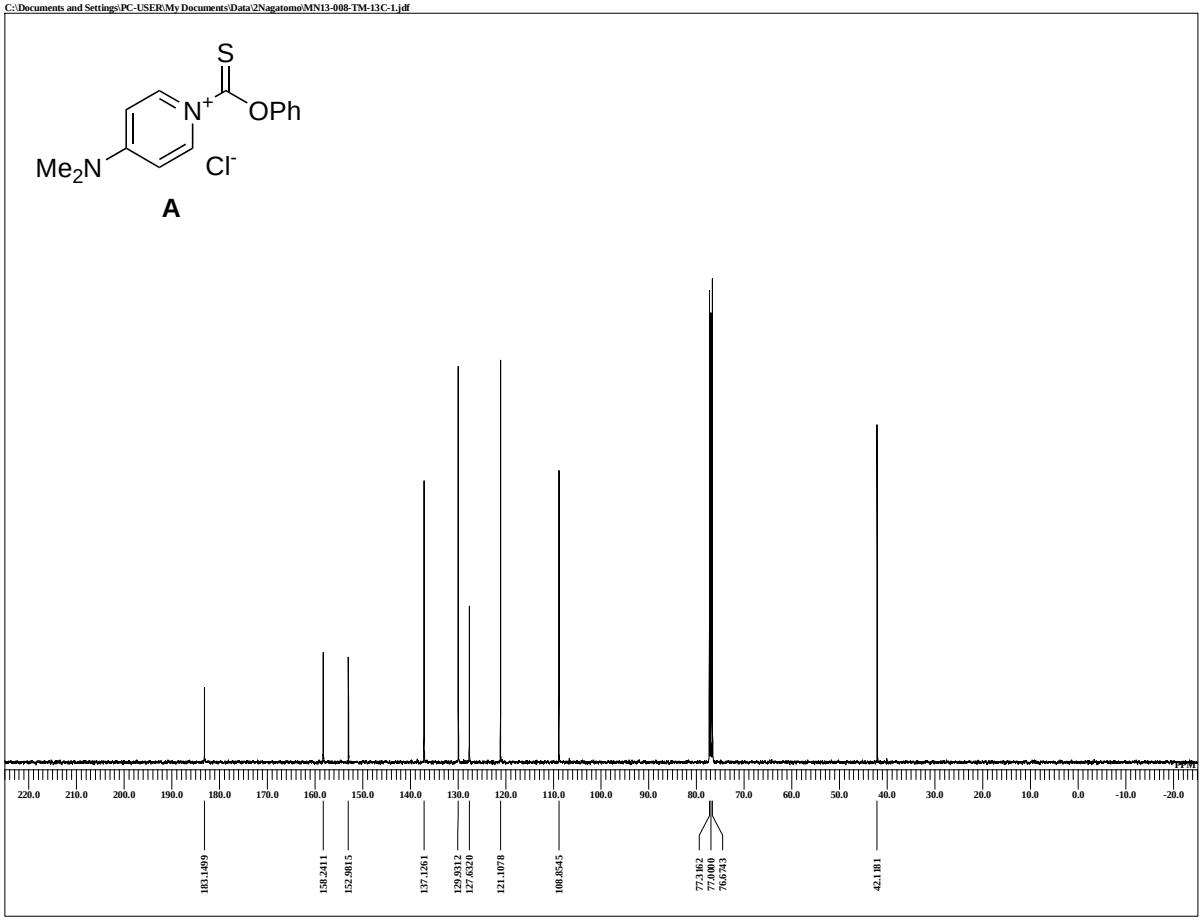
C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\MN13-008-TM-1.als



DFILE MN13-008-TM-1.als
COMNT MN13-008-TM
DATIM 30-05-2012 16:49:30
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 2.0000 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 MN13-008-TM-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 24.8 c
SLVNT CDCL3
EXREF 7.26 ppm

MN13-008-TM

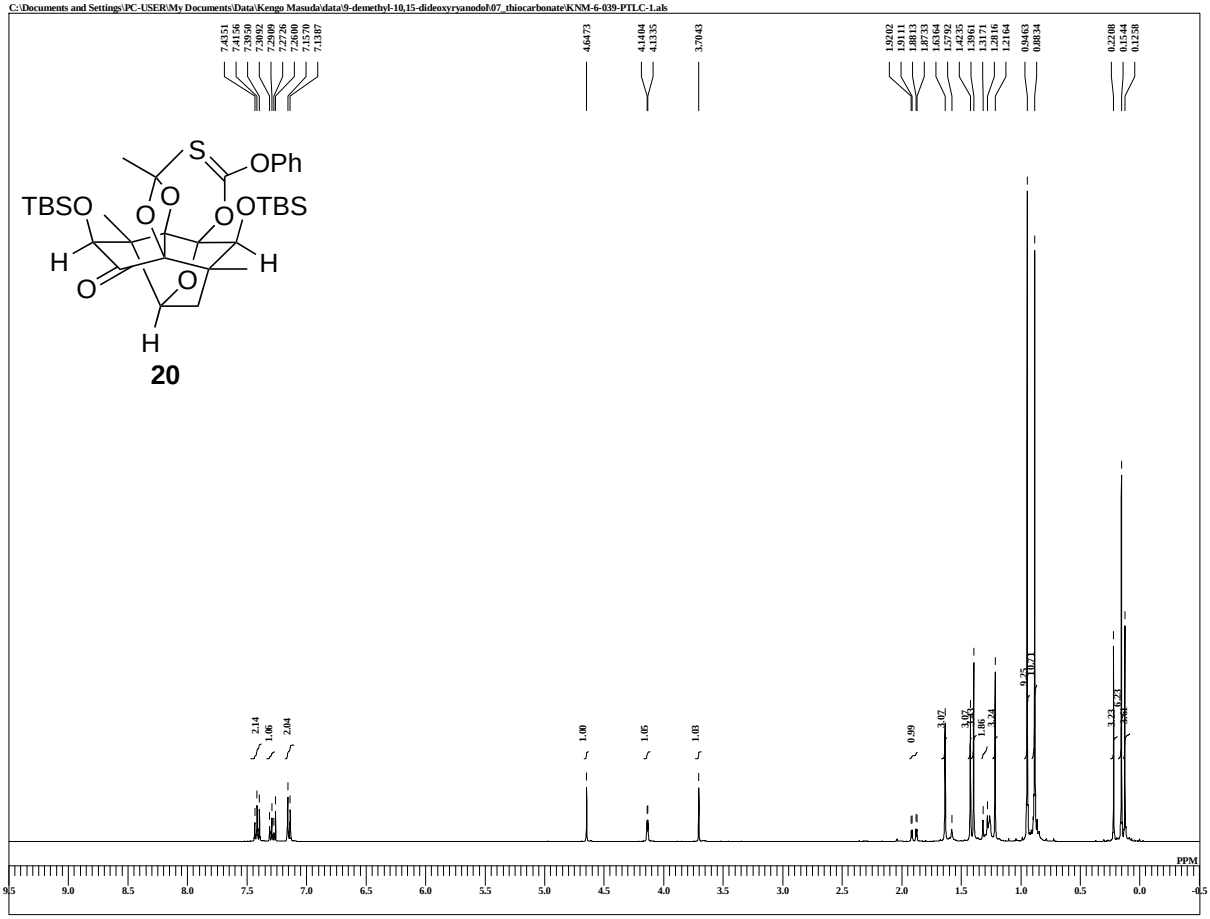
C:\Documents and Settings\PC-USER\My Documents\Data\2Nagatomo\MN13-008-TM-13C-1.jdf



DFILE MN13-008-TM-13C-1.jdf
COMNT MN13-008-TM
DATIM 30-05-2012 17:05:02
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 301
DUMMY 4
FREQU 31250.00 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 2.0000 sec
SCANS 301
ADBIT 16
RGAIN 30
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 MN13-008-TM-13C-1.jdf
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 24.9 c
SLVNT CDCL3
EXREF 77.00 ppm

KNM-6-039-PTLC

C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\07_thiocarbonate\KNM-6-039-PTLC-1.als

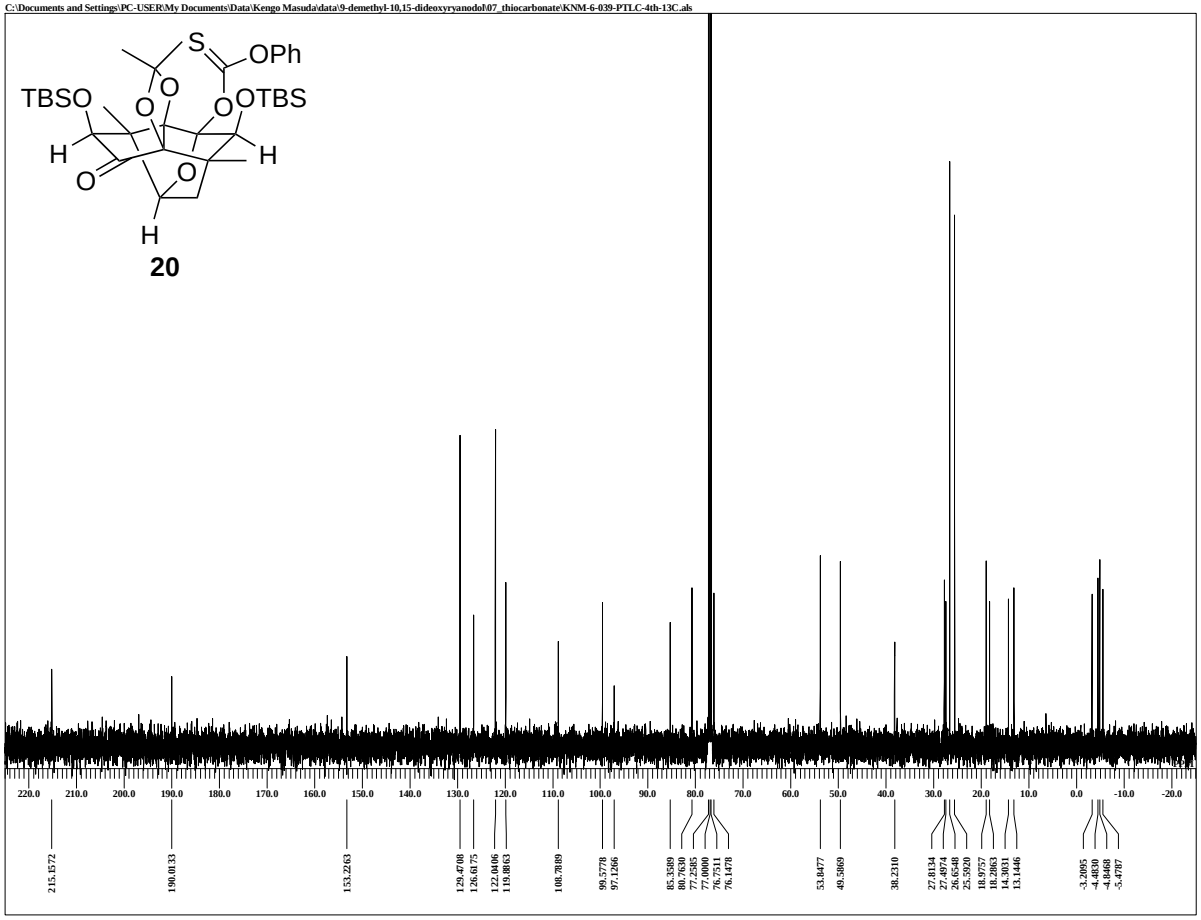


20

DFILE KNM-6-039-PTLC-1.als
COMNT KNM-6-039-PTLC
DATIM 01-09-2012 17:38:26
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 8
DUMMY 1
FREQU 5938.15 Hz
FLT 30000 Hz
DELAY 16.68 usec
ACQTM 2.2073 sec
PD 2.0000 sec
SCANS 8
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 KNM-6-039-PTLC-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 24.4 c
SLVNT CDCL3
EXREF 7.26 ppm

KNM-6-039-PTLC-4th-13C

C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\07_thiocarbonate\KNM-6-039-PTLC-4th-13C.als

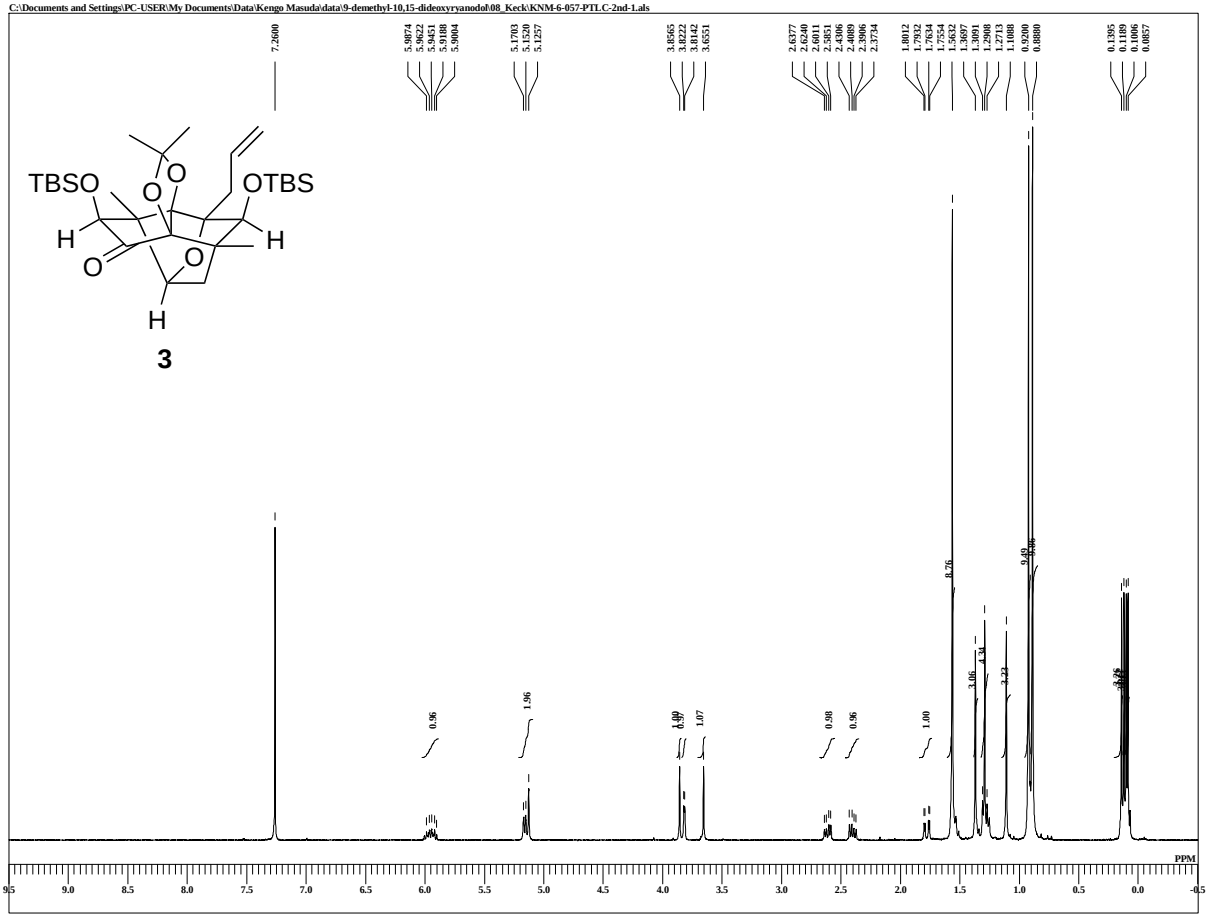


20

DFILE KNM-6-039-PTLC-4th-13
COMNT KNM-6-039-PTLC-4th-13
DATIM 04-09-2012 14:14:12
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 26214
SPO 26214
TIMES 61
DUMMY 4
FREQU 31249.52 Hz
FLT 157000 Hz
DELAY 20.80 usec
ACQTM 0.8389 sec
PD 5.0000 sec
SCANS 61
ADBIT 16
RGAIN 50
BF 1.00 Hz
T1 0.00
T2 0.00
T3 100.00
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 KNM-6-039-PTLC-4th-13
SF
LKSET 748.40 KHz
LKFIN 98.2 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 23.9 c
SLVNT CDCL3
EXREF 77.00 ppm

KNM-6-057-PTLC-2nd

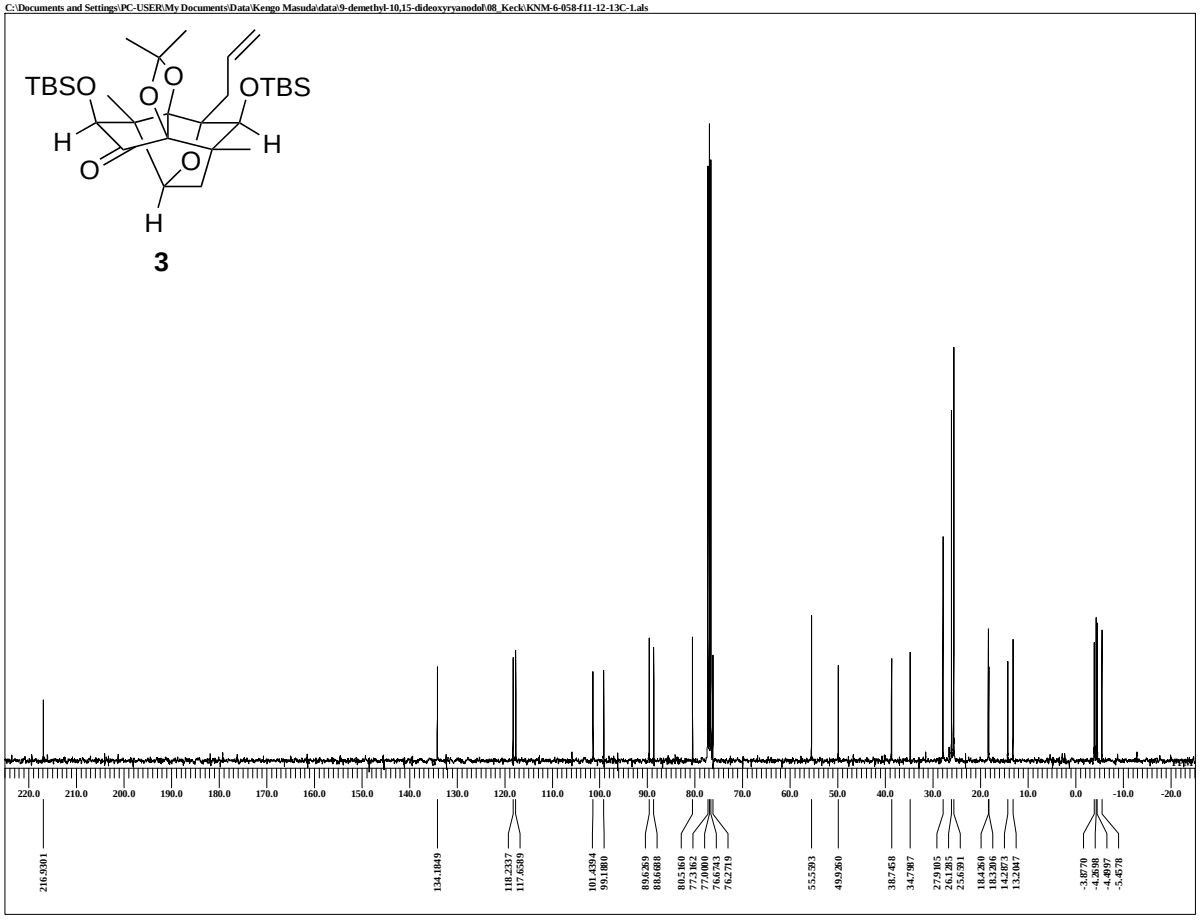
C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\08_Keck\KNM-6-057-PTLC-2nd-1.als



DFILE KNM-6-057-PTLC-2nd-1.
COMNT KNM-6-057-PTLC-2nd
DATIM 10-09-2012 11:39:02
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 2.0000 sec
SCANS 16
ADBIT 16
RGAIN 46
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 1 usec
IRATN 10
DFILE KNM-6-057-PTLC-2nd-1.
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 21.0 c
SLVNT CDCL3
EXREF 7.26 ppm

KNM-6-058-f11-12-13C

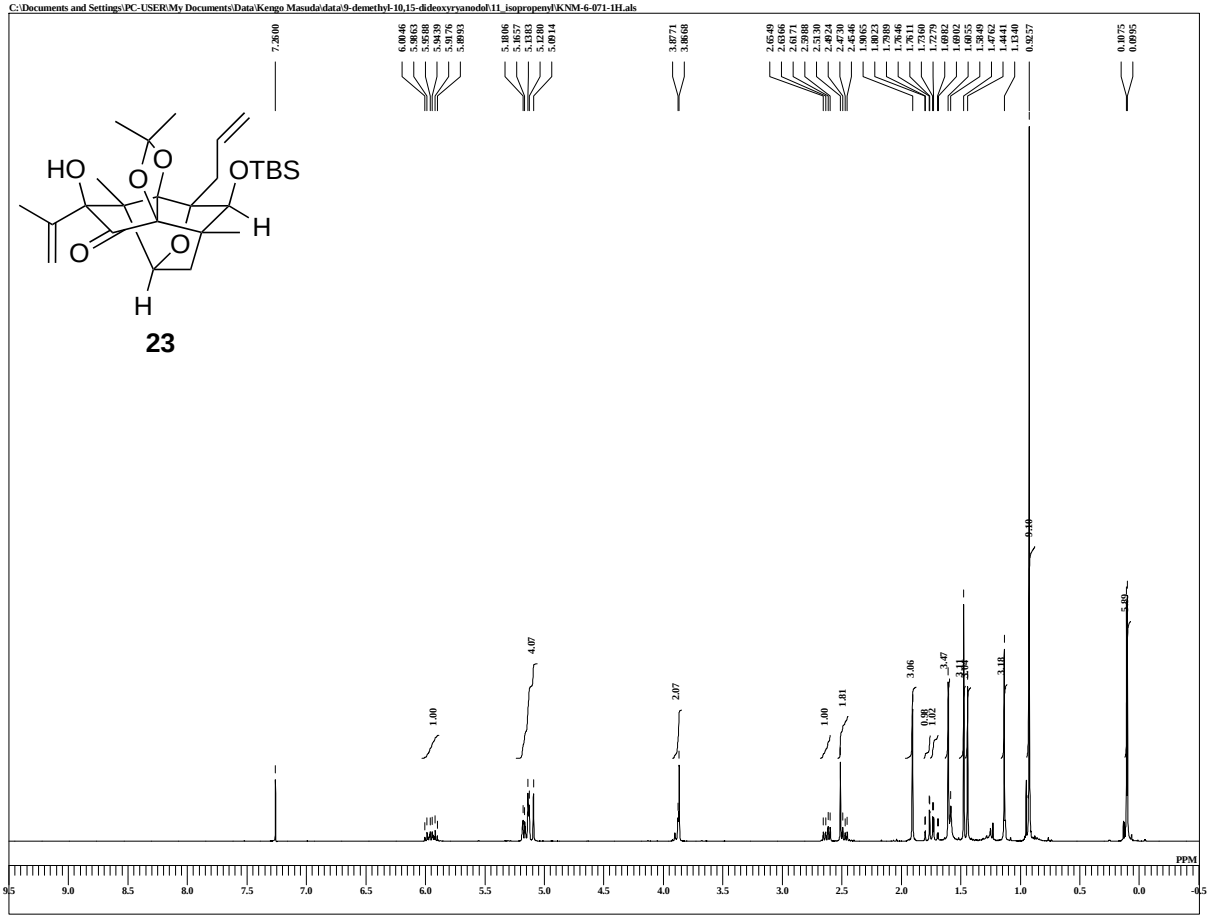
C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\08_Keck\KNM-6-058-f11-12-13C-1.als



DFILE KNM-6-058-f11-12-13C-1
COMNT KNM-6-058-f11-12-13C
DATIM 11-09-2012 10:03:12
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 60
DUMMY 4
FREQU 24999.62 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 5.0000 sec
SCANS 60
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 KNM-6-058-f11-12-13C-1
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 23.1 c
SLVNT CDCL3
EXREF 77.00 ppm

KNM-6-071-1H

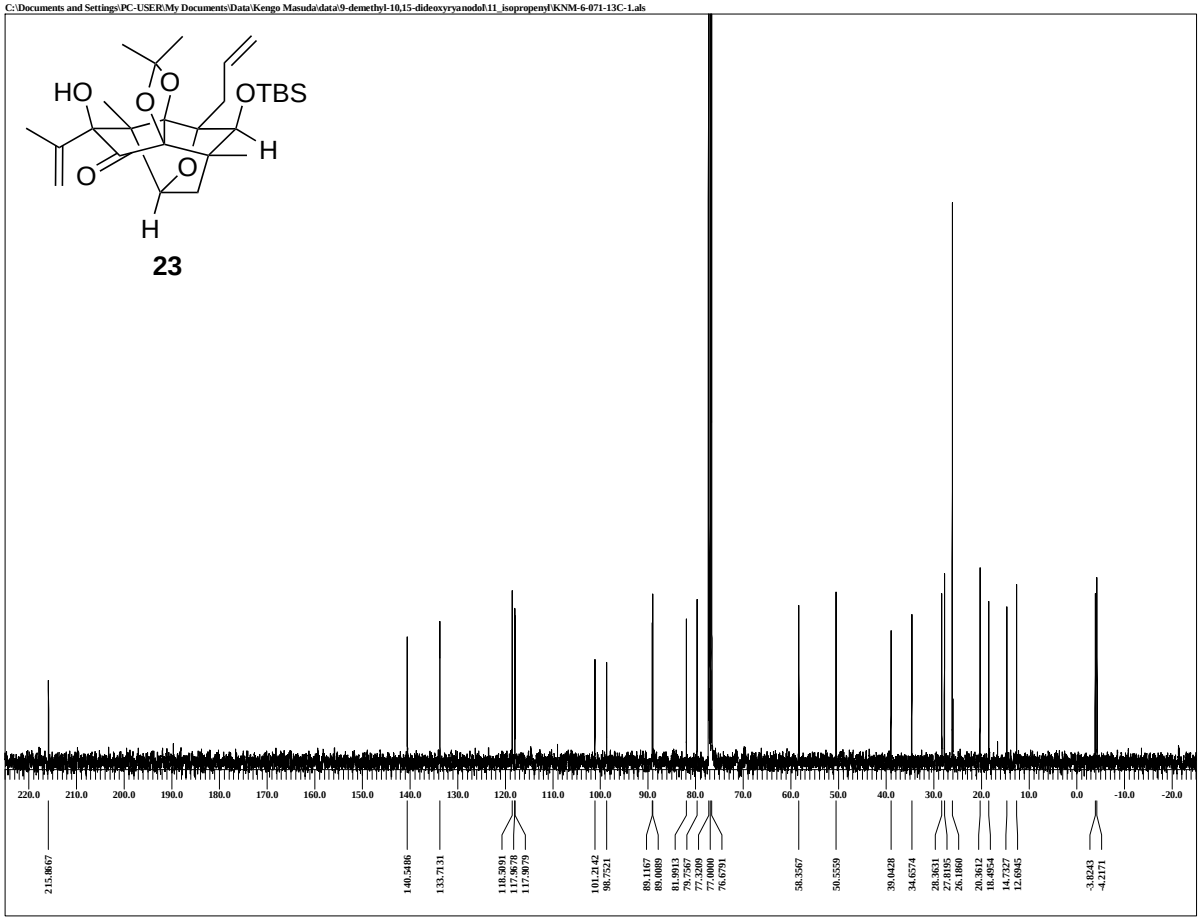
C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\11_isopropenyl\KNM-6-071-1H.als



DFILE KNM-6-071-1H.als
COMNT KNM-6-071-1H
DATIM 12-09-2012 11:50:11
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 8
DUMMY 1
FREQU 5938.15 Hz
FLT 30000 Hz
DELAY 16.68 usec
ACQTM 2.2073 sec
PD 2.0000 sec
SCANS 8
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 KNM-6-071-1H.als
SF
LKSET 13.20 KHz
LKFIN 75.7 Hz
LKLEV 0
LGAIN 0
LKPHS 0
LKSIG 0
CSPED 0 Hz
FILDC
FILDF
CTEMP 23.5 c
SLVNT CDCL3
EXREF 7.26 ppm

KNM-6-071-13C

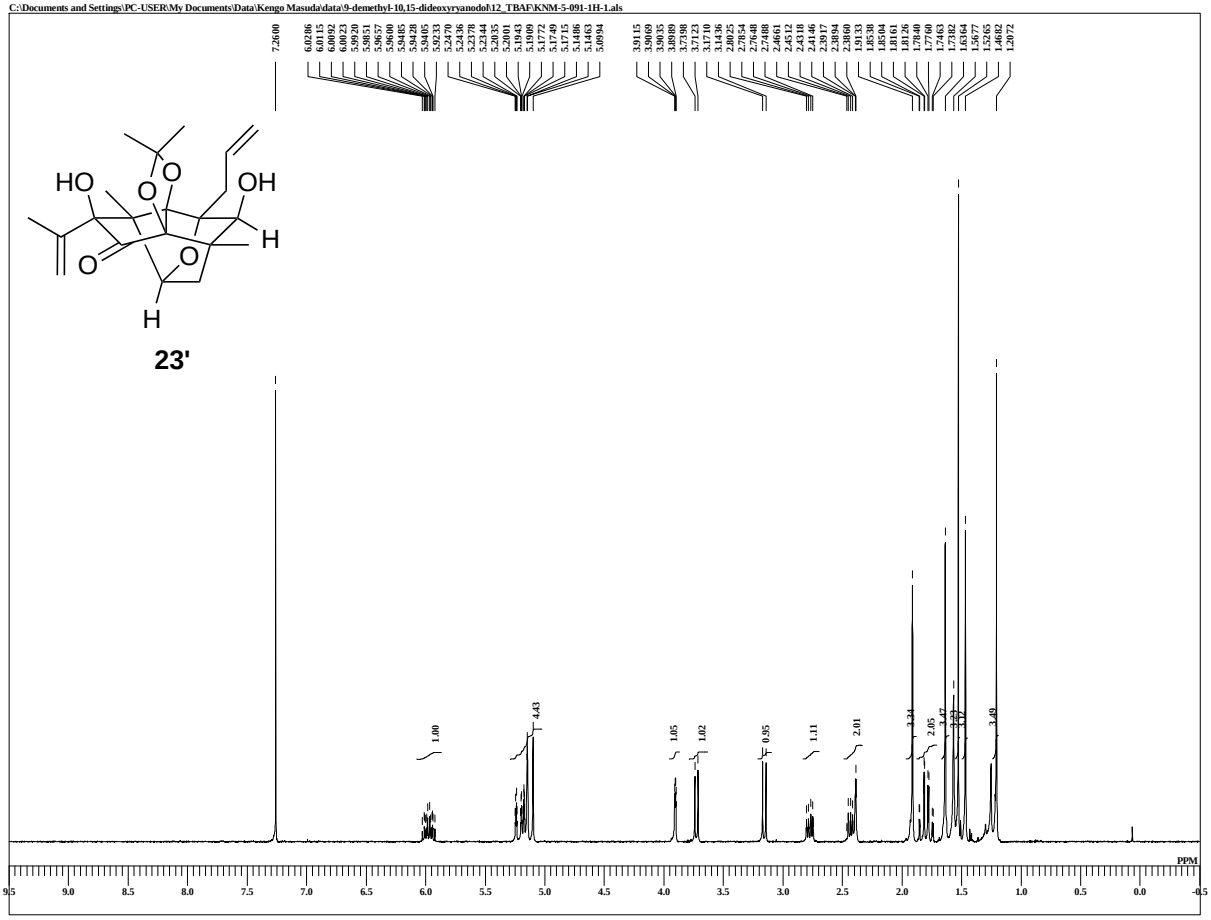
C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\11_isopropenyl\KNM-6-071-13C-1.als



DFILE KNM-6-071-13C-1.als
COMNT KNM-6-071-13C
DATIM 12-09-2012 12:02:09
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 104856
SPO 104856
TIMES 99
DUMMY 4
FREQU 24999.62 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 5.0000 sec
SCANS 99
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 KNM-6-071-13C-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 23.8 c
SLVNT CDCL3
EXREF 77.00 ppm

KNM-5-091-1H

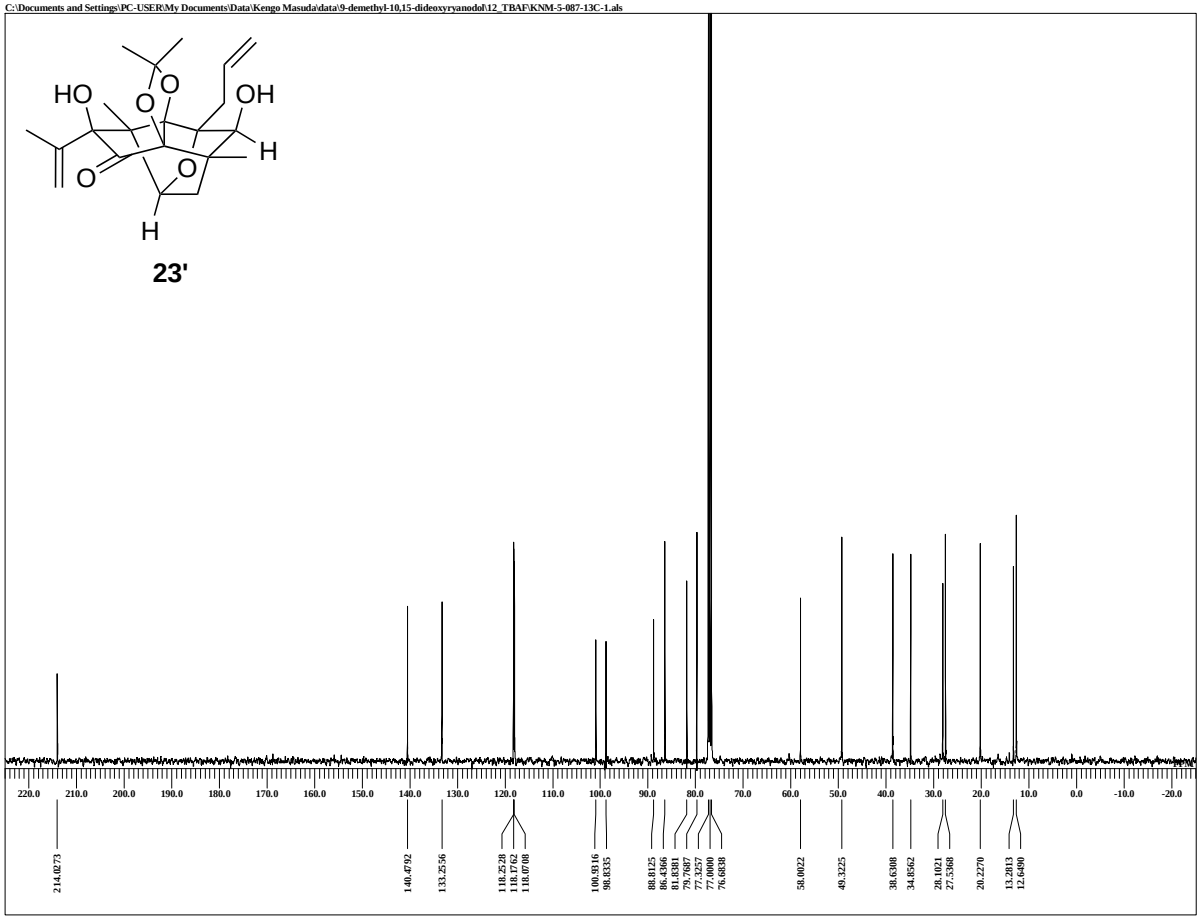
C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\12_TBAF\KNM-5-091-1H-1.als



DFILE KNM-5-091-1H-1.als
COMNT KNM-5-091-1H
DATIM 20-06-2012 20:15:33
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 8
DUMMY 1
FREQU 5938.15 Hz
FLT 30000 Hz
DELAY 16.68 usec
ACQTM 2.2073 sec
PD 2.0000 sec
SCANS 8
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 395.88 MHz
IRSET 6.28 KHz
IRFIN 0.87 Hz
IRRPW 115 usec
IRATN 79
DFILE KNM-5-091-1H-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 24.6 c
SLVNT CDCL3
EXREF 7.26 ppm

KNM-5-087-13C

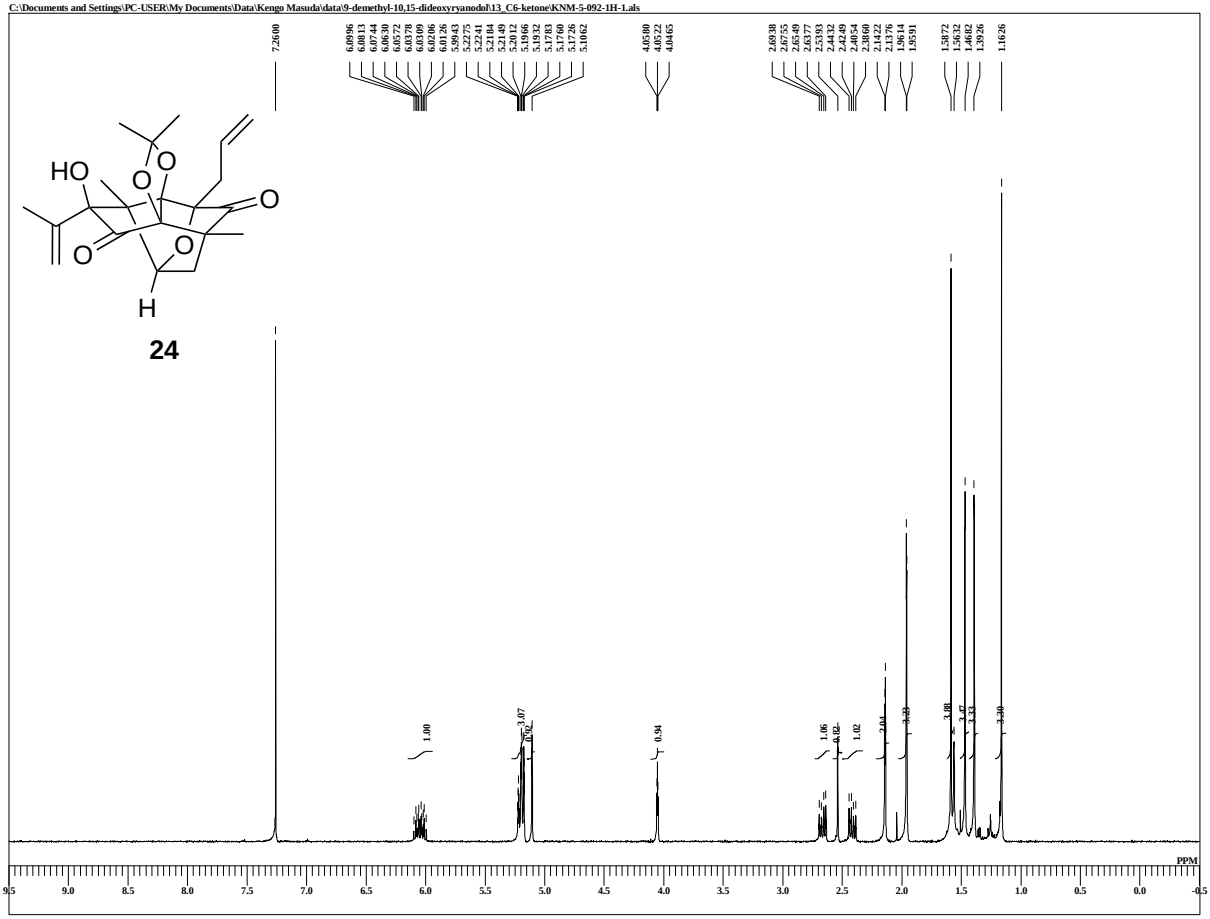
C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\12_TBAF\KNM-5-087-13C-1.als



DFILE KNM-5-087-13C-1.als
COMNT KNM-5-087-13C
DATIM 19-06-2012 21:27:15
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 69
DUMMY 4
FREQU 24999.62 Hz
FLT 125000 Hz
DELAY 20.50 usec
ACQTM 1.0486 sec
PD 5.0000 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 KNM-5-087-13C-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 24.7 c
SLVNT CDCL3
EXREF 77.00 ppm

KNM-5-092-1H

C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\13_C6-ketone\KNM-5-092-1H-1.als



DFILE	KNM-5-092-1H-1.als
COMNT	KNM-5-092-1H
DATIM	21-06-2012 15:29:47
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	8
DUMMY	1
FREQU	5938.15 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	2.0000 sec
SCANS	8
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	395.88 MHz
IRSET	6.28 KHz
IRFIN	0.87 Hz
IRRPW	115 usec
IRATN	79
DFILE	KNM-5-092-1H-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	24.7 c
SLVNT	CDCL3
EXREF	7.26 ppm

KNM-5-088-13C

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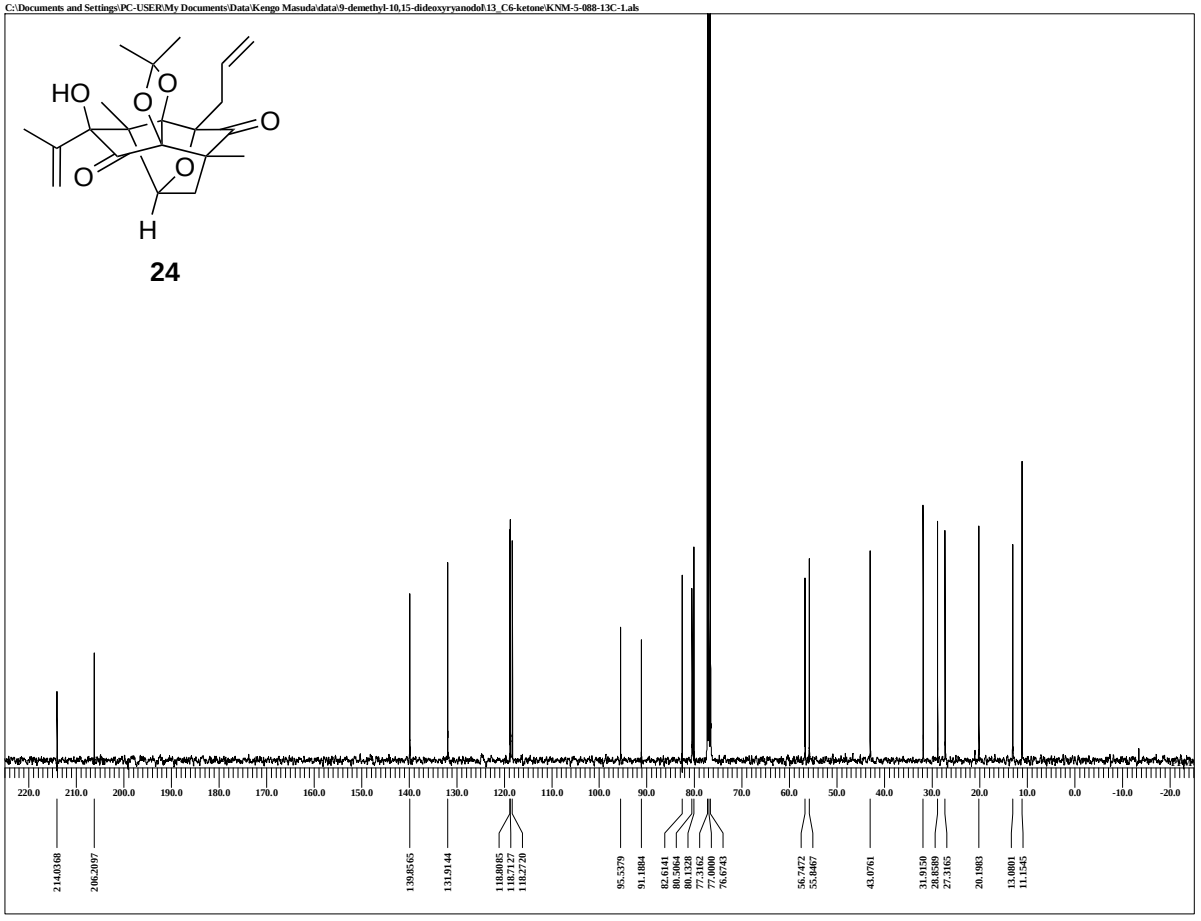
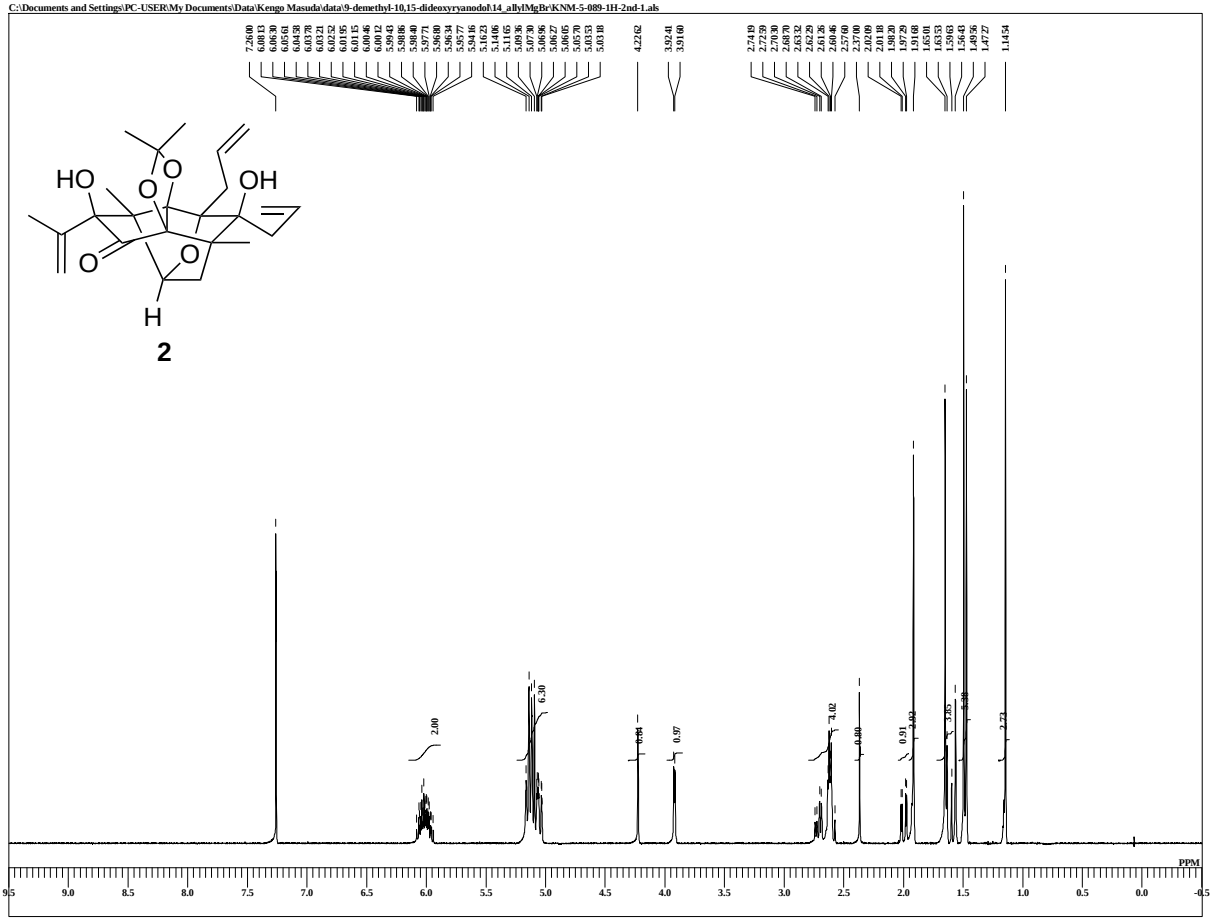


DFILE	KNM-5-088-13C-1.als
COMNT	KNM-5-088-13C
DATIM	20-06-2012 14:48:43
MENUF	
OBNUC	13C
OFR	99.55 MHz
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
PW1	3.25 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	26214
SPO	26214
TIMES	74
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	5.0000 sec
SCANS	74
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	KNM-5-088-13C-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	25.0 c
SLVNT	CDCL3
EXREF	77.00 ppm

KNM-5-092-1H

C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\14_allylMgBr\KNM-5-089-1H-2nd-1.als



DFILE	KNM-5-089-1H-2nd-1.als
COMNT	KNM-5-092-1H
DATIM	21-06-2012 15:25:06
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	13107
SPO	13107
TIMES	8
DUMMY	1
FREQU	5938.15 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	2.0000 sec
SCANS	8
ADBIT	16
RGAIN	42
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	KNM-5-089-1H-2nd-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	24.5 c
SLVNT	CDCL3
EXREF	7.26 ppm

KNM-5-091-13C

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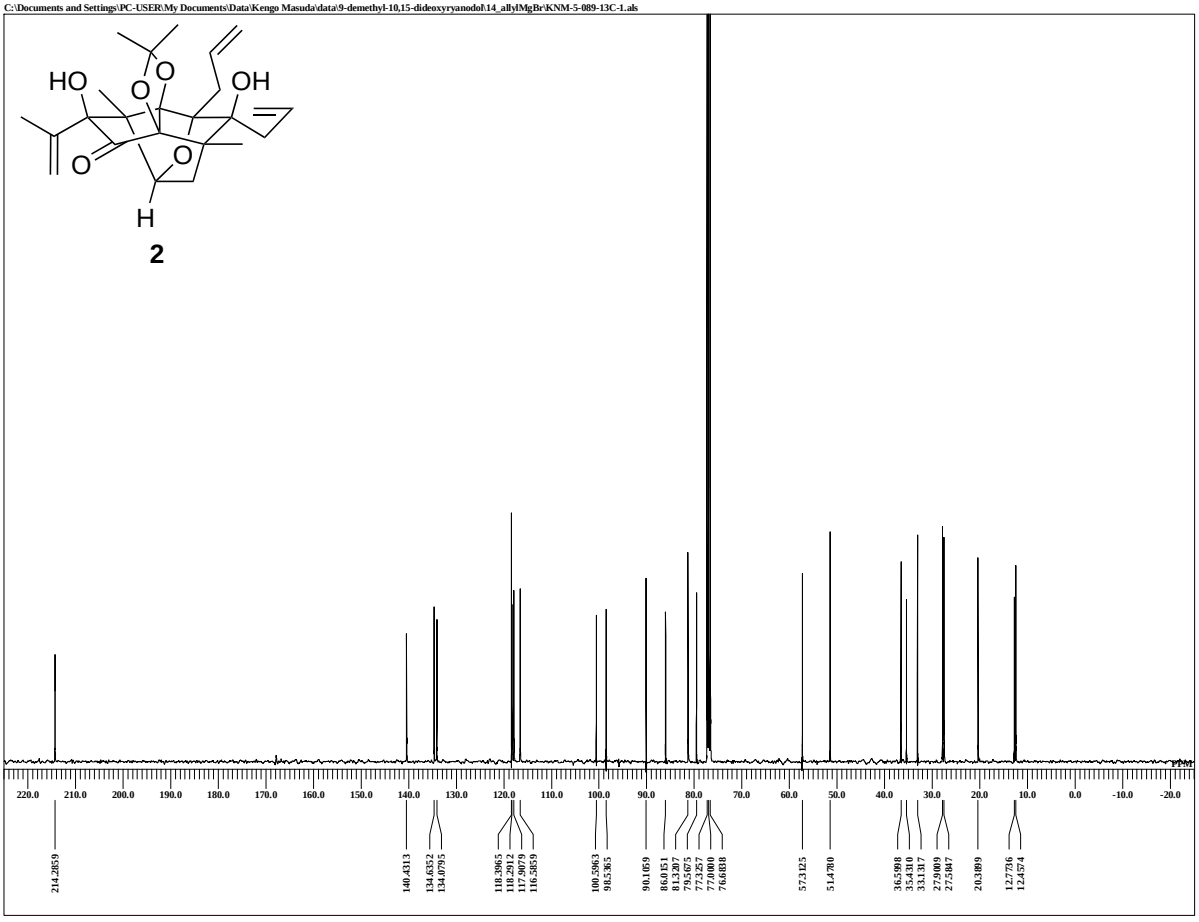
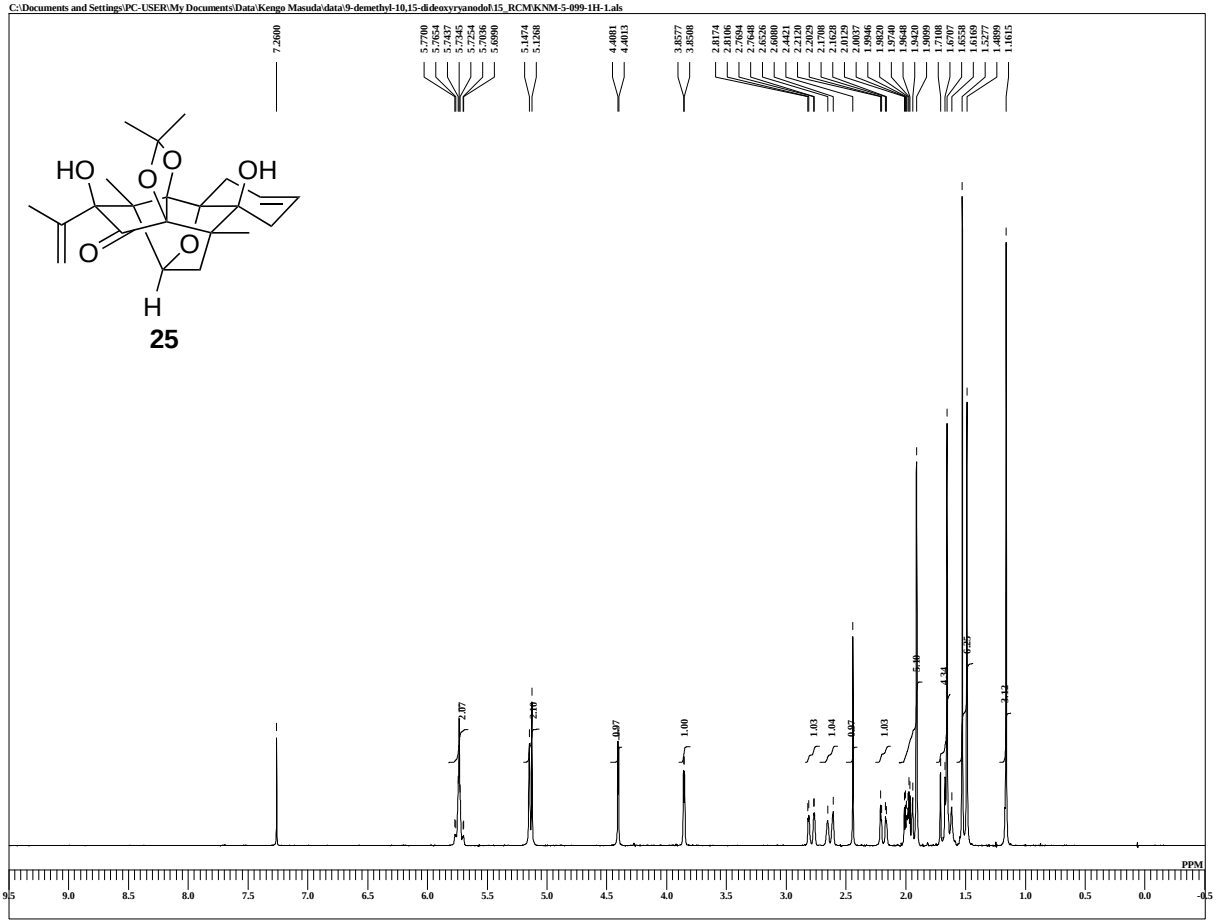


DFILE	KNM-5-089-13C-1.als
COMNT	KNM-5-091-13C
DATIM	21-06-2012 10:08:56
MENUF	
OBNUC	13C
OFR	99.55 MHz
OBFRQ	99.55 MHz
OBSET	5.13 KHz
OBFIN	0.98 Hz
PW1	3.25 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	26214
SPO	26214
TIMES	29
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	5.0000 sec
SCANS	29
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	KNM-5-089-13C-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	24.2 c
SLVNT	CDCL3
EXREF	77.00 ppm

KNM-5-099-1H

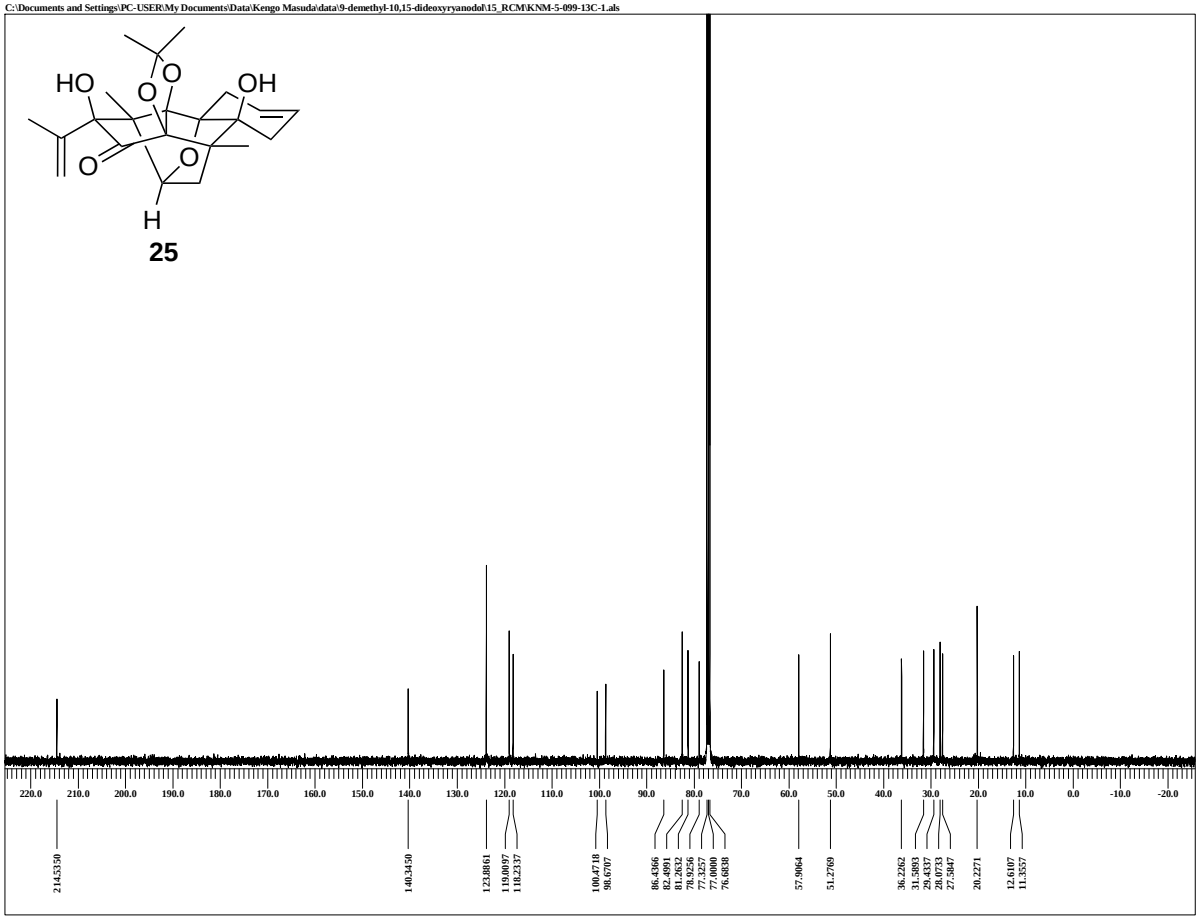
C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\15_RCM\KNM-5-099-1H-1.als



DFILE	KNM-5-099-1H-1.als
COMNT	KNM-5-099-1H
DATIM	24-06-2012 16:42:18
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	8
DUMMY	1
FREQU	5938.15 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	2.0000 sec
SCANS	8
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	KNM-5-099-1H-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	23.1 c
SLVNT	CDCL3
EXREF	7.26 ppm

KNM-5-099-13C

C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\15_RCM\KNM-5-099-13C-1.als



DFILE	KNM-5-099-13C-1.als
COMNT	KNM-5-099-13C
DATIM	24-06-2012 17:50:39
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	500
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	7.0000 sec
SCANS	500
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	KNM-5-099-13C-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	23.1 c
SLVNT	CDCL3
EXREF	77.00 ppm

KNM-5-113-1H-2

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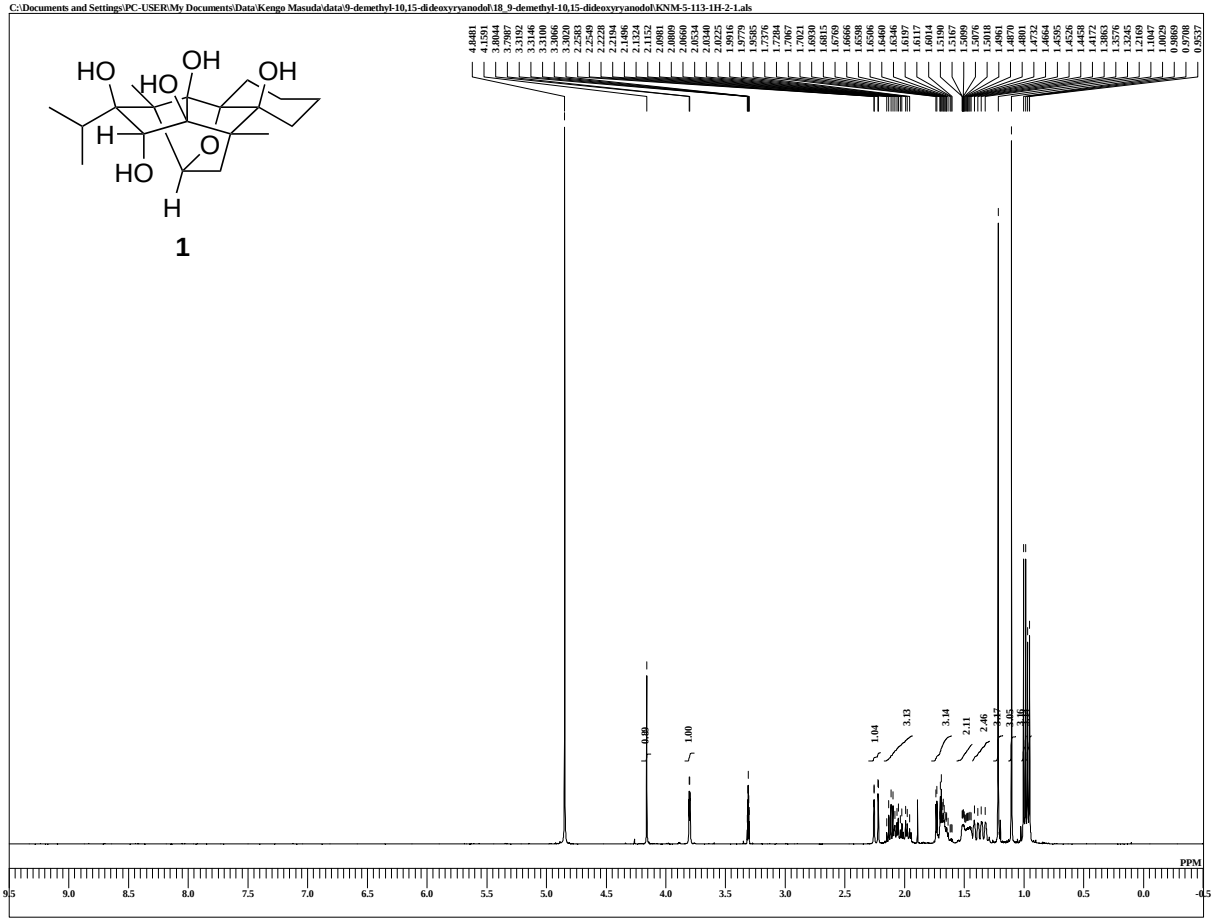
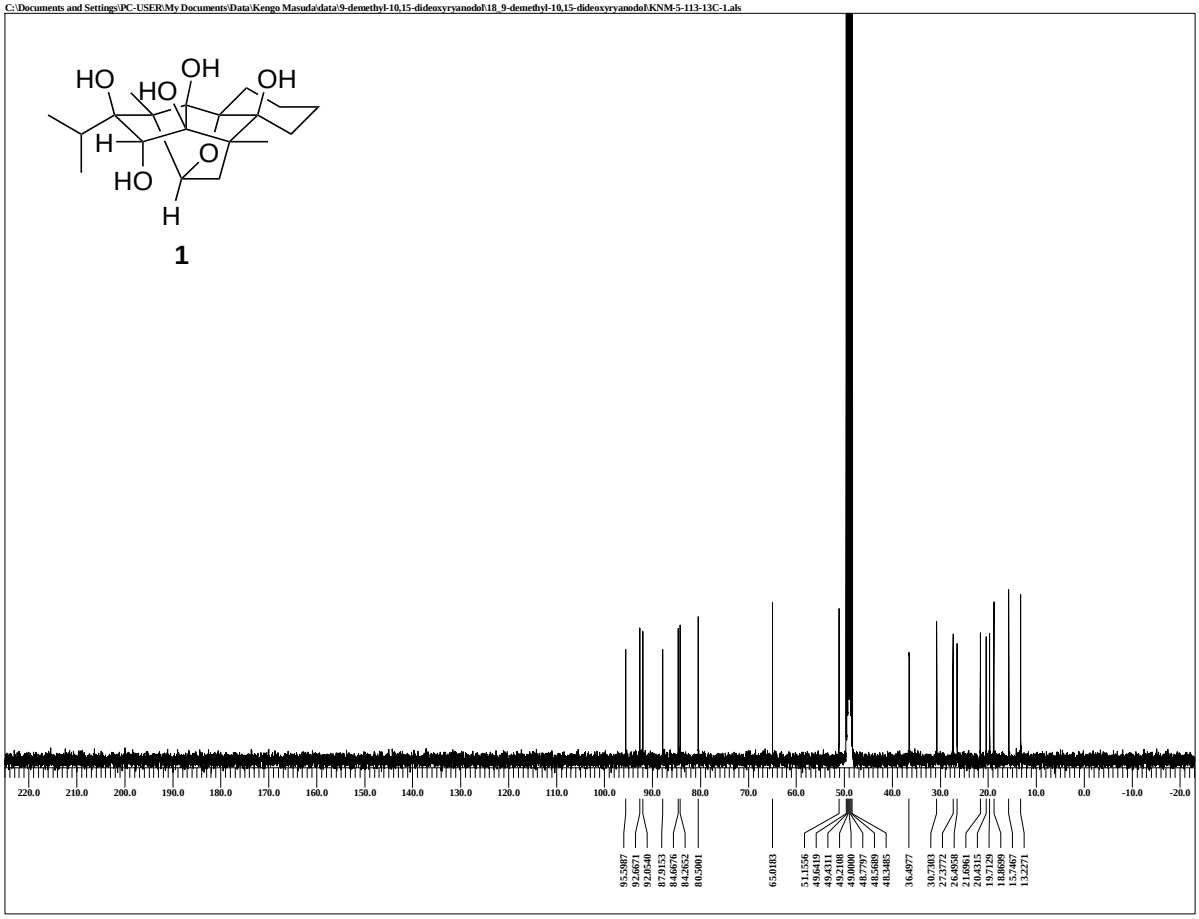


DFILE	KNM-5-113-1H-2-1.als
COMNT	KNM-5-113-1H-2
DATIM	07-07-2012 18:14:26
MENUF	
OBNUC	1H
OFR	395.88 MHz
OBFRQ	395.88 MHz
OBSET	6.28 KHz
OBFIN	0.87 Hz
PW1	6.38 usec
DEADT	0.00 usec
PREDL	0.00000 msec
IWT	1.0000 sec
POINT	13107
SPO	13107
TIMES	8
DUMMY	1
FREQU	5938.15 Hz
FLT	30000 Hz
DELAY	16.68 usec
ACQTM	2.2073 sec
PD	2.0000 sec
SCANS	8
ADBIT	16
RGAIN	42
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	KNM-5-113-1H-2-1.als
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	3.31 ppm

KNM-5-113-13C

C:\Documents and Settings\PC-USER\My Documents\Data\Kengo Masuda\data\9-demethyl-10,15-dideoxyryanodol\18_9-demethyl-10,15-dideoxyryanodol\KNM-5-113-13C-1.als



DFILE	KNM-5-113-13C-1.als
COMNT	KNM-5-113-13C
DATIM	07-07-2012 03:12:14
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	1000
DUMMY	4
FREQU	24999.62 Hz
FLT	125000 Hz
DELAY	20.50 usec
ACQTM	1.0486 sec
PD	5.0000 sec
SCANS	1000
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	KNM-5-113-13C-1.als
SF	
LKSET	13.00 KHz
LKFIN	35.6 Hz
LKLEV	0
LGAIN	0
LKPHS	0
LKSIG	0
CSPED	0 Hz
FILDC	
FILDF	
CTEMP	24.6 c
SLVNT	CD3OD
EXREF	49.00 ppm