Supporting Information

Design and Synthesis of 1,2-Deoxy-pyranose Derivatives of Spliceostatin A toward Prostate Cancer Treatment

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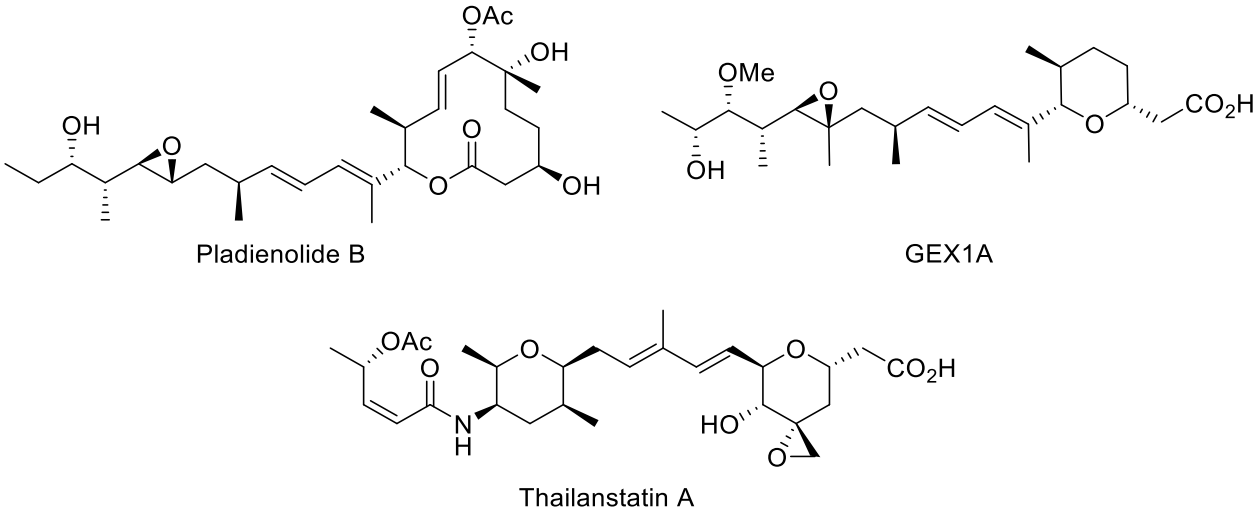
Contents

1. General Remarks

All reactions were monitored by thin-layer chromatography using silica plate. The products were purified by column chromatography over silica gel (70−230 mesh ASTM or 40−50 μm, spherical neutral). ^{1}H NMR and ^{13}C NMR were recorded at 25 °C on 300 and 75, 400 and 100, 500 and 125 MHz, respectively, and the chemical shifts are reported relative to $CDCl_3$ (^{1}H, δ = 7.26, ^{13}C, δ = 77.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (integration, multiplicity, coupling constant (Hz)). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra were performed by a mass spectrometer using an orbitrap analyzer. Optical rotations were measured on a polarimeter.

2. Structure of SF3b complex Inhibitors

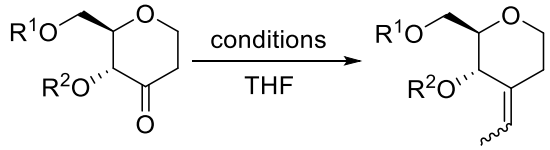


Scheme S1. Structure of Pladienolide B, GEX1A and Thailanstatin A

3. Reaction Conditions

(1) Wittig reaction of **I** and **18**

Conditions for Wittig reactions to build trisubstituted olefins (from **I** to **II** and **III,** and from **18** to **19** and **20**) are shown below. The type of base and the reaction temperature significantly affect the yields and *E* and *Z* selectivity.



II (R^1 = TBS, R^2 = TBS, *Z* isomer)
III (R^1 = TBS, R^2 = TBS, *E* isomer)
19 (R^1 = TBS, R^2 = PMB, *Z* isomer)
20 (R^1 = TBS, R^2 = PMB, *E* isomer)

I, R^1 = TBS, R^2 = TBS
18, R^1 = TBS, R^2 = PMB

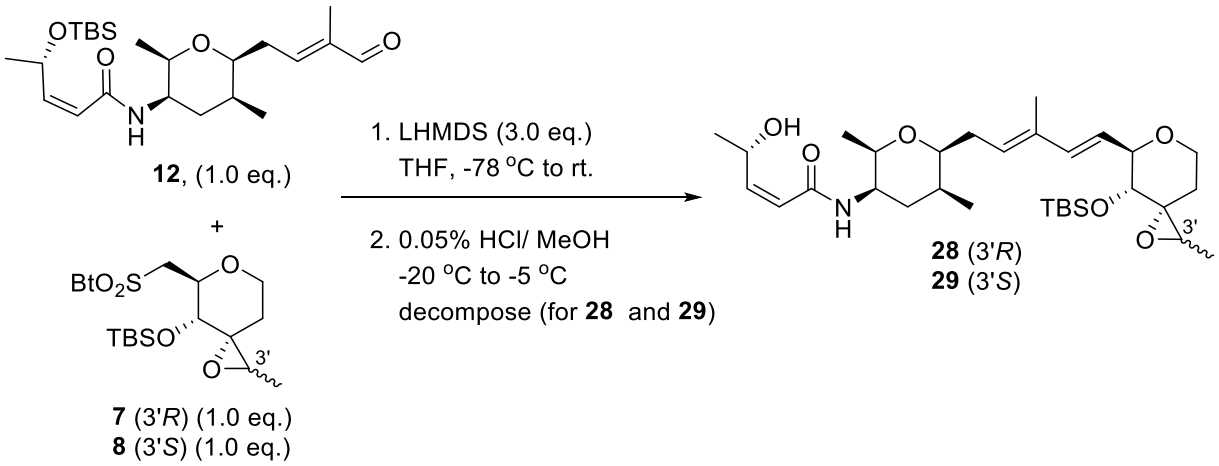
entry		reagent	Base	yield
1 2	**I**	$EtPPh_3^+Br^-$ (3.0 eq.)	^{t}BuOK (2.8 eq.)	0 °C to rt. : trace 0 °C to 40 °C : trace
3 4	**I**	$EtPPh_3^+Br^-$ (3.0 eq.)	*n*-BuLi (2.8 eq.)	0 °C to rt. : trace 0 °C to 40 °C : 55% (**II** : **III** = 5.5 : 1)[a]
5 6	**18**	$EtPPh_3^+Br^-$ (3.0 eq.)	^{t}BuOK (2.8 eq.)	0 °C to rt.: trace 0 °C to 40 °C : trace
7	**18**	**$EtPPh_3^+Br^-$ (3.0 eq.)**	***n*-BuLi (2.8 eq.)**	**93% (19 : 20 = 1 : 1) (0 °C to 40 °C)**

a, Ratio of geometric isomers were determined by H^1NMR

Scheme S2. Wittig reaction of **I** and **18**

(2)

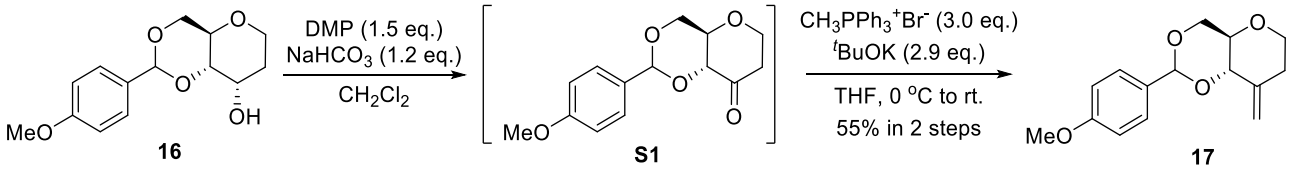
As shown below, the Julia coupling reaction with combination **12** and **7** or **8** was not successful. Introduction of a methyl group into the epoxide group could change the steric environment around the sulfonyl group.



Scheme S3. Julia Kocienski olefination of **12** and **7**, **8**

4. Experimental Procedure

Preparation and data for **16** from D-glucal : See reference 1.

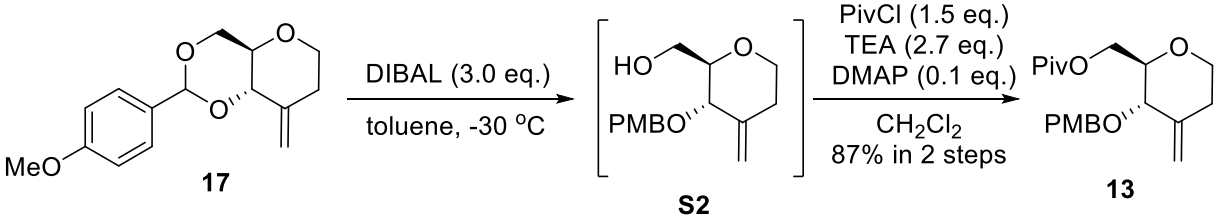


Compound 17

(Step 1): To a solution of **16** (250 mg, 0.939 mmol, 1.0 equiv.) in dry CH_2Cl_2 (10 ml) was added DMP (593 mg, 1.40 mmol, 1.5 equiv.) and $NaHCO_3$ (94.0 mg, 1.12 mmol, 1.2 equiv.) at room temperature. After stirring for 6 h, the reaction mixture was diluted with Et_2O and quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with Et_2O. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 1/1) to give the crude S**1** (231 mg, 0.874 mmol).

(Step 2): To a solution of $MePPh_3^+Br^-$ (934 mg, 2.61 mmol, 3.0 equiv.) in dry THF (13 ml) was added ^{t}BuOK (285 g, 2.54 mmol, 2.9 equiv.) at 0 °C. After stirring for 10 min, a solution of **S1** (231 mg, 0.874 mmol, 1.0 equiv.) in THF (5.0 ml) was then added via syringe, and then the reaction mixture was warmed to room temperature. After stirring for 20 min, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **17** (135 mg, 0.514 mmol, 55% in 2 steps) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.46 (2H, d, *J* = 8.7 Hz), 6.90 (2H, d, *J* = 8.7 Hz), 5.61 (1H, s), 5.09 (1H, d, *J* = 1.8 Hz), 4.89 (1H, d, *J* = 1.8 Hz), 4.89 (1H, d, *J* = 1.8 Hz), 4.26 (1H, dd, *J* = 10.6, 5.0 Hz), 4.04 (1H, dd, *J* = 10.6, 4.6 Hz), 4.01 (1H, d, *J* = 9.2 Hz), 3.81 (3H, s), 3.74 (1H, dd, *J* = 10.3,10.3 Hz), 3.53 (1H, ddd, *J* = 12.4, 10.5, 2.8 Hz), 3.31 (1H, ddd, *J* = 9.2, 9.2, 5.0 Hz), 2.53 (1H, ddd, *J* = 14.2, 13.7, 6.0 Hz), 2.36 (1H, ddd, *J* = 14.2, 1.8, 1.8 Hz). **^{13}C-NMR**; 35.0, 55.2, 69.1, 69.3, 74.8, 80.2, 101.3, 105.8, 113.5, 127.5, 130.2, 142.0, 160.0; **HRMS** (MALDI-TOF) *m/z* 263.1279 (calcd for $C_{15}H_{19}O_4$ [M], 263.1278). $[\alpha]^{23}_D$ = +37.9 (c 0.34, $CHCl_3$).

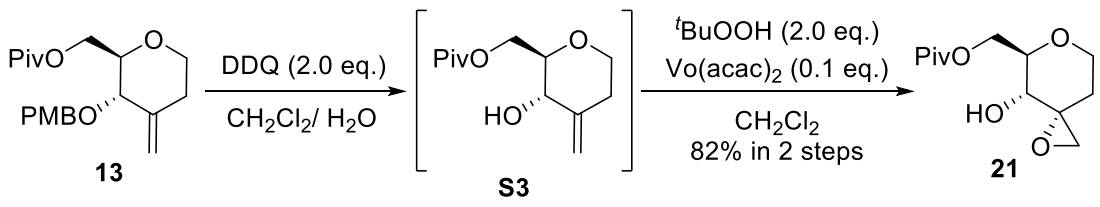


Compound 13

(Step 1): To a solution of **17** (3.00 g, 11.4 mmol, 1.0 equiv.) in dry toluene (110 ml) was added DIBAL (1M toluene solution) (34 ml, 34.0 mmol, 3.0 equiv.) at -30 °C. After stirring for 6.5 h, the reaction mixture was quenched with MeOH and saturated potassium sodium tartrate aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude S**2** (2.89 g, 10.9 mmol).

(Step 2): To a solution of S**2** (2.89 g, 10.9 mmol, 1.0 equiv.) in dry CH_2Cl_2 (50 ml) were added PivCl (2.0 ml, 16.4 mmol, 1.5 equiv.), TEA (4.0 ml, 28.9 mmol, 2.7 equiv.) and DMAP (133 mg, 1.09 mmol, 0.1 equiv.) at room temperature. After stirring for 2 h, the reaction mixture was quenched with H_2O. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **13** (3.47 g, 9.96 mmol, 87%) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.28 (2H, d, *J* = 8.7 Hz), 6.88 (2H, d, *J* = 8.7 Hz), 5.11 (1H, d, *J* = 0.9 Hz), 4.94 (1H, d, *J* = 0.9 Hz), 4.63 (1H, d, *J* = 10.8 Hz), 4.39 (1H, d, *J* = 10.8 Hz), 4.35 (1H, dd, *J* = 11.9, 2.7 Hz), 4.25 (1H, dd, *J* = 11.9, 5.0 Hz), 3.99 (1H, m), 3.80 (3H, s), 3.79 (1H, m), 3.43-3.37 (2H, m), 2.40-2.29 (2H, m), 1.21 (9H, s). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; 27.1, 35.1, 38.8, 55.2, 63.4, 68.5, 72.5, 79.9, 107.2, 113.8, 113.9, 129.6, 129.8, 143.9, 159.3, 178.2. **HRMS** (MALDI-TOF) *m/z* 371.1829 (calcd for $C_{20}H_{28}O_5Na$ $[M+Na]^+$, 371.1826). $[\alpha]^{23}_D$ = +130.9 (c 0.09, $CHCl_3$).

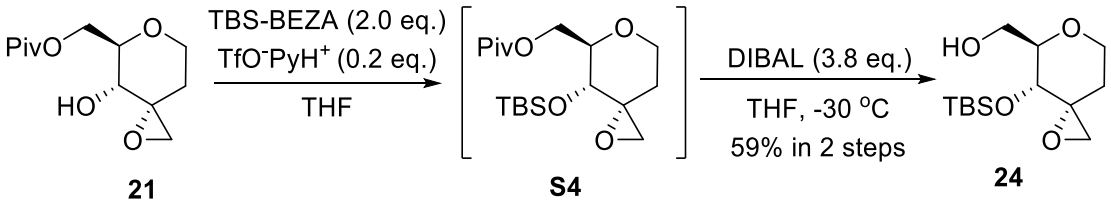


Compound 21

(Step 1): To a solution of **13** (3.47 g, 9.96 mmol, 1.0 equiv.) in CH_2Cl_2/ H_2O (10 : 1, 100 ml) was added DDQ (4.52 g, 19.9 mmol, 2.0 equiv.) at room temperature. After stirring for 14 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 3/1) to give the crude **S3**.

(Step 2): To a solution of **S3** in dry CH_2Cl_2 (97 ml) were added ^{t}BuOOH (5.5 M in decane solution) (3.5 ml, 19.4 mmol, 2.0 equiv.) and $VO(acac)_2$ (257 mg, 0.969 mmol, 0.1 equiv.) at room temperature. After stirring for 4 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 2/1) to give **21** (2.01 g, 8.23 mmol, 82% in 2 steps) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 4.41 (1H, dd, *J* = 11.9, 4.1 Hz), 4.31 (1H, dd, *J* = 11.9, 5.0 Hz), 3.98 (1H, dd, *J* = 10.5, 4.6 Hz), 3.74-3.63 (2H, m), 3.43 (1H, ddd, *J* = 7.4, 5.0, 2.3 Hz), 3.15 (1H, d, *J* = 4.4 Hz), 2.65 (1H, d, *J* = 4.4 Hz), 2.32 (1H, m), 1.99 (1H, d, *J* = 10.5 Hz), 1.40 (1H, m), 1.23 (9H, s).**^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; 27.1, 32.9, 38.8, 49.5, 58.3, 63.9, 64.8, 65.0, 78.9, 178.6. **HRMS** (MALDI-TOF) *m/z* 267.1203 (calcd for $C_{12}H_{20}O_5Na$ $[M+Na]^+$, 267.1204). $[\alpha]^{23}_D$ = +30.2 (c 0.19, $CHCl_3$).



21 **S4** **24**

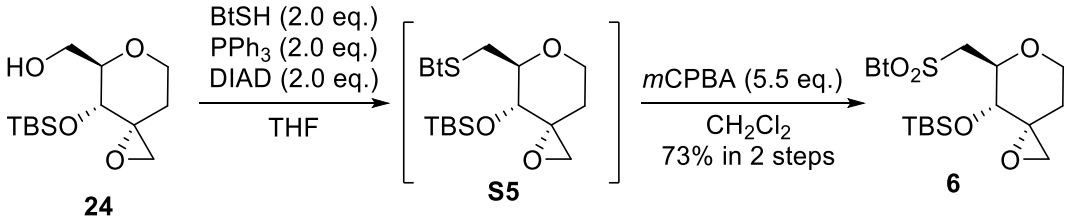
Compound 24

(Step 1): To a solution of **21** (857 mg, 3.51 mmol, 1.0 equiv.) in dry THF (8.0 ml) was added TBS-BEZA (2.19 g, 7.03 mmol, 2.0 equiv.) and TfO^-PyH^+ (174 mg, 0.759 mmol, 0.2 equiv.) at room temperature. After stirring for 15 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 10/1 to 5/1) to give the crude **S4** (1.01 g, 2.82 mmol).

(Step 2): To a solution of **S4** (1.01 g, 2.82 mmol, 1.0 equiv.) in dry THF (15 ml) was added DIBAL (1M toluene solution) (10.7 ml, 10.7 mmol, 3.8 equiv.) at -30 °C. After stirring for 4 h, the reaction mixture was quenched with MeOH and saturated potassium sodium tartrate aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure.

The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 3/1 to 2/1) to give **24** (567 mg, 2.07 mmol, 59% in 2 steps) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 3.96 (1H, ddd, *J* = 11.4, 5.5, 1.4 Hz), 3.84 (1H, d, *J* = 9.2 Hz), 3.84-3.74 (2H, m), 3.64 (1H, ddd, *J* = 7.4, 6.9, 5.0 Hz), 3.54(1H, ddd, *J* = 7.4, 5.0, 2.8 Hz), 3.06 (1H, d, *J* = 5.0 Hz), 2.59 (1H, d, *J* = 5.0 Hz), 2.22 (1H, ddd, *J* = 13.7, 12.4, 5.5 Hz), 1.94 (1H, t, *J* = 6.4 Hz), 1.34 (1H, ddd, *J* = 13.7, 2.3, 1.4 Hz), 0.89 (9H, s), 0.11 (3H, s), 0.06 (3H, s). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; -4.76, -4.57, 18.0, 25.7, 33.9, 50.1, 59.3, 62.0, 65.1, 66.2, 79.9. **HRMS** (MALDI-TOF) *m/z* 297.1493 (calcd for $C_{13}H_{26}O_4SiNa$ $[M+Na]^+$, 297.1493). $[\alpha]^{23}_D$ = +68.2 (c 0.15, $CHCl_3$).



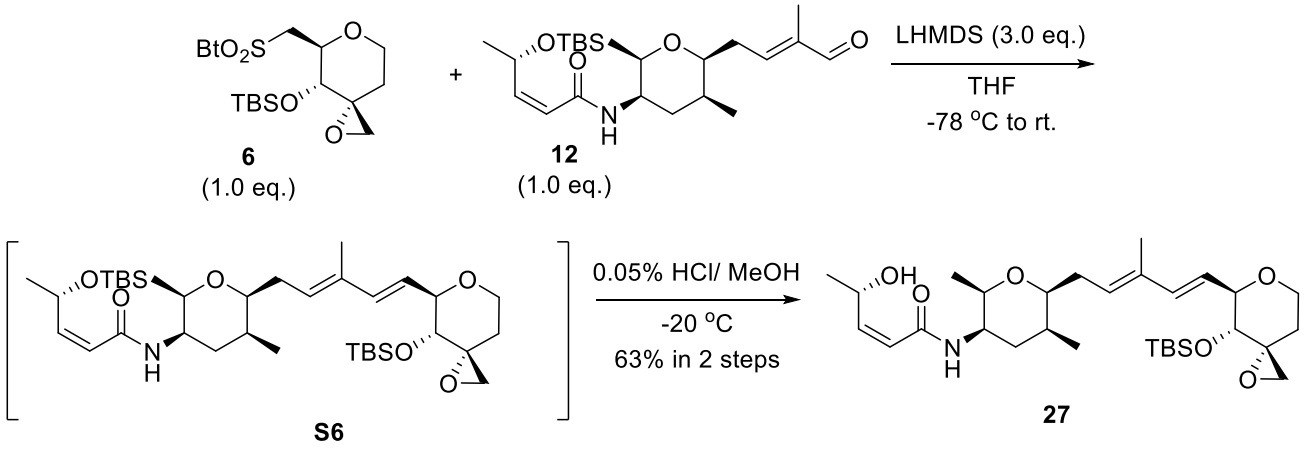
Compound 6

(Step 1): To a solution of **27** (214 mg, 0.780 mmol, 1.0 equiv.) in dry THF (5.2 ml) was added BtSH (260 mg, 1.55 mmol, 2.0 equiv.), PPh_3 (409 mg, 1.56 mmol, 2.0 equiv.) and DIAD (0.3 ml, 1.56 mmol, 2.0 equiv.) at 0°C, and then the reaction mixture was warmed to room temperature. After stirring for 2 h, the reaction mixture was quenched with H_2O. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 20/1 to 10/1) to give the crude **S5**.

(Step 2): To a solution of above **S5** in dry CH_2Cl_2 (3.2 ml) was added *m*-CPBA (740 mg, 4.29 mmol, 5.5 equiv.) at room temperature. After stirring for 18 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 3/1) to give **6** (250 mg, 0.569 mmol, 73% in 2 steps) as a white solid (mp 150-152 °C).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 8.20 (1H, dd, *J* = 7.8, 0.9 Hz), 8.00 (1H, dd, *J* = 7.8, 1.8 Hz), 7.64-7.55 (2H, m), 4.17 (1H, ddd, *J* = 10.1, 8.7, 2.3 Hz), 3.83 (1H, ddd, *J* = 14.6, 2.3 Hz), 3.73 (1H, ddd, *J* = 14.6, 10.1 Hz), 3.67 (1H, d, *J* = 8.7 Hz), 3.66 (1H, m), 3.56 (1H, ddd, *J* = 11.4, 6.0, 2.1 Hz), 3.00 (1H, d, *J* = 4.8 Hz), 2.57 (1H, d, *J* = 4.8 Hz), 2.06 (1H, ddd, *J* = 14.0, 11.9, 6.0 Hz), 1.31 (1H, ddd, *J* = 14.0, 2.3, 2.1 Hz), 0.90 (9H, s), 0.12 (3H, s), 0.06 (3H, s). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ; -4.5, -4.2, 17.9, 25.6, 33.2, 50.2, 56.9, 58.6, 64.9, 69.0, 75.2, 122.2, 125.3, 127.3, 127.8, 136.8, 152.5, 170.0. **HRMS** (MALDI-TOF) *m/z* 478.1147 (calcd for $C_{20}H_{29}NO_5SiNaS_2$ $[M+Na]^+$, 478.1149). $[\alpha]^{23}_D$ = +24.9 (c 0.19, $CHCl_3$).

Preparation and data for **12** : See reference 2.

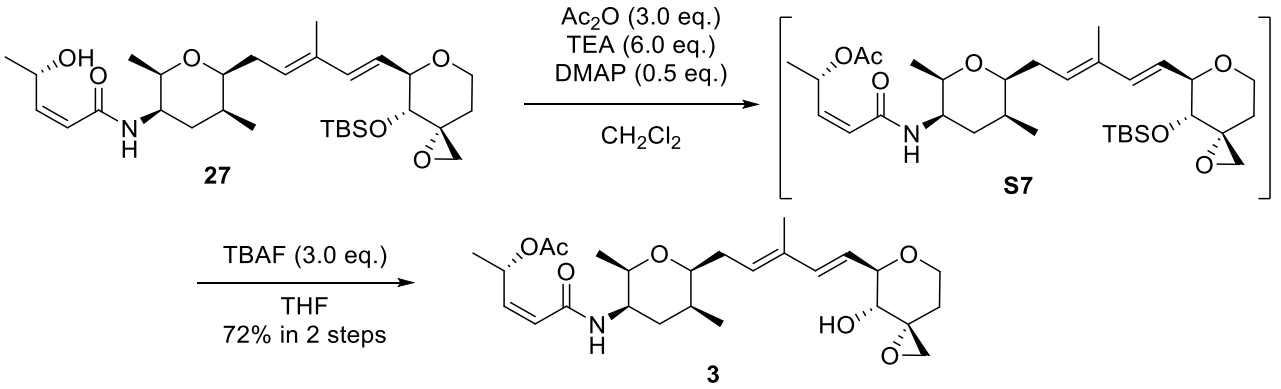


Compound 27

(Step 1): To a solution of **6** (99.0 mg, 0.234 mmol, 1.0 equiv.) and **12** (107 mg, 0.243 mmol, 1.0 equiv.) in dry THF (1.5 ml) was added LHMDS (1M THF solution) (0.7 ml, 0.700 mmol, 3.0 equiv.) at -78 °C for 10 min. Then, the reaction mixture was warm to room temperature. After stirring for 18 h, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/ EtOAc = 5/1) to give the crude **S6** (136 mg, 0.205 mmol).

(Step 2): To **S6** (136 mg, 0.205 mmol) was added 0.05% HCl/ MeOH (1.5 ml) at -20 °C. After stirring for 13 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/1) to give **27** (81.6 mg, 0.148 mmol, 63% in 2 steps) as a colorless amorphous solid.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.20 (1H, d, *J* = 15.6 Hz), 6.18 (1H, dd, *J* = 11.9, 5.5 Hz), 5.90 (1H, d, *J* = 8.7 Hz), 5.71 (1H, d, *J* = 11.9 Hz), 5.57 (1H, d, *J* = 4.6 Hz), 5.53 (1H, dd, *J* = 15.6, 7.3 Hz), 5.45 (1H, t, *J* = 6.6 Hz), 4.77 (1H, m), 4.01-3.93 (3H, m), 3.79 (1H, m), 3.65 (2H, d, *J* = 8.7 Hz), 3.53 (1H, m), 3.06 (1H, d, *J* = 5.0 Hz), 2.60 (1H, d, *J* = 5.0 Hz), 2.37 (1H, m), 2.28-2.20 (2H, m), 1.94 (1H, m), 1.79-1.73 (2H, m), 1.75 (3H, s), 1.37 (1H, m), 1.35 (3H, d, *J* = 6.9 Hz), 1.13 (3H, d, *J* = 6.4 Hz), 1.00 (3H, d, *J* = 6.8 Hz), 0.84 (9H, s), 0.02 (3H, s), -0.03 (3H, s), **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; -4.4, -4.2, 12.5, 15.1, 17.8, 18.0, 22.7, 25.7, 28.8, 31.8, 34.0, 35.7, 47.5, 50.3, 59.4, 64.5, 65.0, 70.4, 75.8, 80.9, 81.5, 122.5, 124.5, 128.6, 134.5, 138.2, 150.7, 166.1. **HRMS** (MALDI-TOF) *m/z* 572.3382 (calcd for $C_{30}H_{51}NO_6SiNa$ $[M+Na]^+$, 572.3378). $[\alpha]^{23}_D$ = +14.3 (c 0.03, $CHCl_3$).



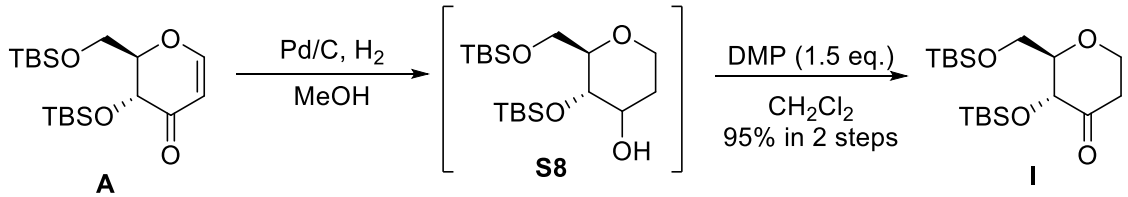
Compound 3

(Step 1): To a solution of **27** (158 mg, 0.288 mmol, 1.0 equiv.) in dry CH_2Cl_2 (3.0 ml) was added TEA (200 µl, 1.64 mmol, 6.0 equiv.), DMAP (18.0 mg, 0.144. mmol, 0.5 equiv.) then Ac_2O (90 µl, 0.862 mmol, 3.0 equiv.) at room temperature. After stirring for 3.5 h, the reaction mixture was quenched with H_2O. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 5/1) to give the crude **S7** (165 mg, 0.278 mmol).

(Step 2): To a solution of **S7** (165 mg, 0.278 mmol) in dry THF (1.0 ml) was added TBAF (1M THF solution) (0.85 ml, 0.85 mmol, 3.0 equiv.) at room temperature. After stirring for 1.5 h, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/2) to give **3** (99.0 mg, 0.207 mmol, 72% in 2 steps) as a white solid (mp 72-75 °C).

^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 6.39 (1H, d, *J* = 15.8 Hz), 6.25 (1H, m), 6.00 (1H, d, *J* = 8.9 Hz), 5.89 (1H, dd, *J* = 11.7, 8.1 Hz), 5.70 (1H, dd, *J* = 11.7, 1.2 Hz), 5.64 (1H, dd, *J* = 15.8, 6.0 Hz), 5.50 (1H, t, *J* = 7.0 Hz), 4.01 (1H, dd, *J* = 11.5, 6.0 Hz), 3.93 (1H, m), 3.79-3.71 (2H, m), 3.65 (1H, dq, *J* = 6.3, 2.0 Hz), 3.63 (1H, m), 3.51 (1H, dt, *J* = 7.2, 2.9 Hz), 3.15 (1H, d, *J* = 4.6 Hz), 2.65 (1H, d, *J* = 4.6 Hz), 2.41-2.31 (2H, m), 2.23 (1H, m), 2.03 (3H, s), 1.98-1.89 (2H, m), 1.80-1.74 (2H, m), 1.77 (3H, s), 1.42 (1H, m), 1.38 (3H, d, *J* = 6.6 Hz), 1.14 (3H, d, *J* = 6.3 Hz), 1.01 (3H, d, *J* = 7.2 Hz). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; 12.6, 15.1, 17.8, 20.0, 21.2, 28.9, 31.9, 33.2, 35.8, 47.1, 49.7, 58.5, 64.9, 68.7, 68.9, 75.9, 80.8, 81.3, 122.5, 124.1, 129.1, 134.6, 138.0, 143.6, 164.8, 170.4. **HRMS** (MALDI-TOF) *m/z* 500.2618 (calcd for $C_{26}H_{39}NO_7Na$ $[M+Na]^+$, 500.2619). $[\alpha]^{23}_D$ = -11.0 (c 0.03, $CHCl_3$).

Preparation and data for **A** from D-glucal : See reference 3.

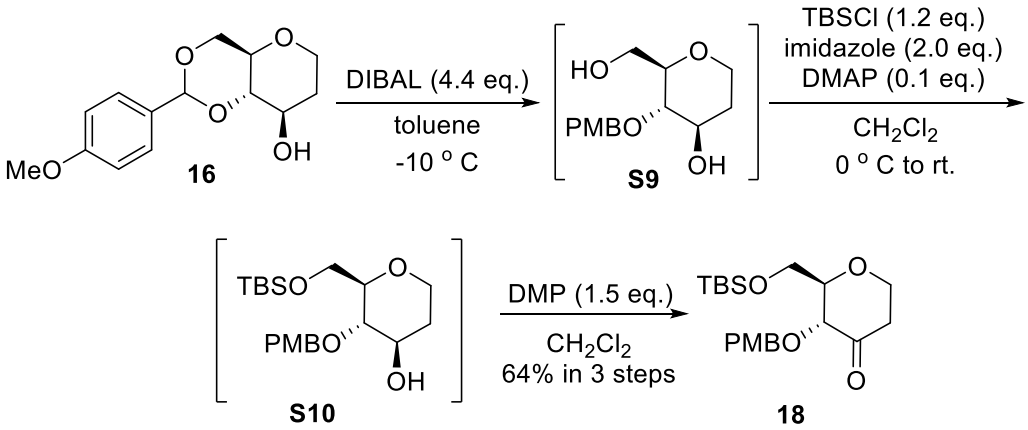


Compound I

(Step 1): To a solution of **A** (1.13 g, 2.99 mmol, 1.0 equiv.) in dry MeOH (30 ml) was added 10% Pd/C (110 mg, 10% *w/w*) at room temperature. After stirring for 9 h, the reaction mixture was filtered with celite and washed with AcOEt to give the crude **S8**.

(Step 2): To a solution of **S8** in dry CH_2Cl_2 (30 ml) was added DMP (1.90 g, 4.48 mmol, 1.2 equiv.) at room temperature. After stirring for 1 h, the reaction mixture was diluted with Et_2O and quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with Et_2O. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a silica gel column (*n*-hexane/EtOAc = 10/1) to give **xx** (1.18 g, 3.15 mmol, 95% in 2 steps) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 4.26-4.20 (2H, m), 3.93 (1H, dd, *J* = 11.3, 1.7 Hz), 3.85 (1H, dd, *J* = 11.3, 4.1 Hz), 3.61 (1H, m), 3.40 (1H, ddd, *J* = 9.3, 3.8, 1.7 Hz), 2.65 (1H, m), 2.41 (1H, m), 0.91 (9H, s), 0.90 (9H, s), 0.17 (3H, s), 0.09 (3H, s), 0.08 (3H, s), 0.03 (3H, s).**^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; -5.7, -5.3, -5.0, -4.3, 18.4, 18.5, 25.8, 25.9, 42.1, 62.9, 66.8, 75.1, 84.3, 206.5. **HRMS** (APCA) *m/z* 375.2381 (calcd for $C_{18}H_{39}O_4Si_2$ [M+H], 375.2387). $[\alpha]^{23}_D$ = +62.2 (c 0.75, $CHCl_3$).



Compound 18

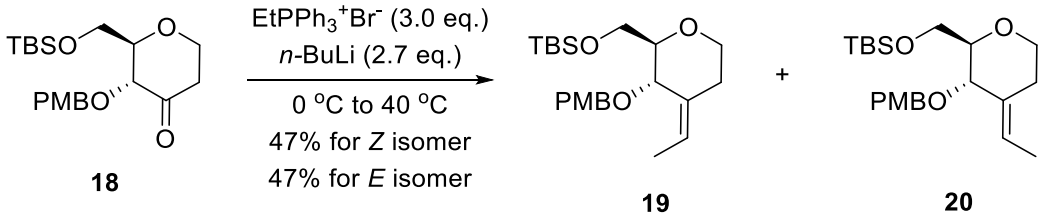
(Step 1): To a solution of **16** (600 mg, 2.25 mmol, 1.0 equiv.) in dry toluene (22 ml) was added DIBAL (1M toluene solution) (10.0 ml, 10.0 mmol, 4.4 equiv.) at -10 °C. After stirring for 6 h, the reaction mixture was quenched with MeOH and saturated potassium sodium tartrate aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude **S9**.

(Step 2): To a solution of crude **S9** in dry CH_2Cl_2 (12 ml) were added imidazole (306 mg, 4.5 mmol, 2.0 equiv.), DMAP (29.2 mg, 0.239 mmol, 0.1 equiv.) at 0℃. After stirring for 10 min, TBSCl (405 mg, 2.69 mmol, 1.2 equiv.) was then added, and then the reaction mixture was warmed to room temperature. After stirring for 1 h, the reaction

mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by short silica gel column chromatography (*n*-hexane/EtOAc = 2/1) to give crude **S10** (560 mg, 1.46 mmol) as a colorless oil.

(Step 3): To a solution of crude **S10** (560 mg, 1.46 mmol, 1.0 equiv.) in dry CH_2Cl_2 (10 ml) was added DMP (929 mg, 2.19 mmol, 1.5 equiv.) at room temperature. After stirring for 2 h, the reaction mixture was diluted with Et_2O and quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with Et_2O. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a silica gel column (*n*-hexane/EtOAc = 5/1) to give **18** (550 mg, 1.45 mmol, 64% in 3 steps) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.31 (2H, d, *J* = 8.6 Hz), 6.87 (2H, d, *J* = 8.6 Hz), 4.82 (1H, d, *J* = 10.7 Hz), 4.43 (1H, d, *J* = 10.7 Hz), 4.25 (1H, ddd, *J* = 11.2, 9.3, 1.1 Hz), 4.10 (1H, d, *J* = 9.3 Hz), 3.90-3.82 (2H, m), 3.80 (3H, s), 3.62 (1H, ddd, *J* = 12.4, 11.2, 2.4 Hz), 3.49 (1H, ddd, *J* = 8.7, 3.5, 2.1 Hz), 2.69 (1H, m), 2.44 (1H, m), 0.91 (9H, s), 0.09 (6H, s).**^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; -5.4, -5.2, 18.4, 25.9, 42.5, 55.2, 62.7, 66.9, 73.1, 79.5, 82.8, 113.7, 129.7, 129.8, 159.3, 206.6. **HRMS** (MALDI-TOF) *m/z* 403.1910 (calcd for $C_{20}H_{32}O_5NaSi$ $[M+Na]^+$, 403.1911). $[\alpha]^{23}_D$ = +94.6 (c 0.29, $CHCl_3$).



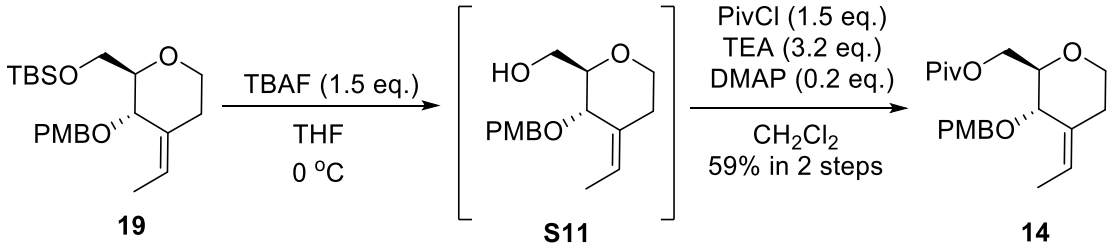
Compound 19 and **20**

To a solution of $EtPPh_3^+Br^-$ (1138 mg, 3.07 mmol, 3.0 equiv.) in dry THF (10 ml) was added *n*-BuLi (2.76 M hexane solution) (1.0 ml, 2.76 mmol, 2.7 equiv.) at 0 °C. After stirring for 10 min, a solution of **18** (390 mg, 1.02 mmol, 1.0 equiv.) in THF (5.0 ml) was then added via syringe, and then the reaction mixture was warmed to 40 °C. After stirring for 2 h, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/0 to 10/1 to 5/1) to give **19** (*Z* isomer) (190 mg, 0.48 mmol, 47%) and **20** (*E* isomer) (190 mg, 0.48 mmol, 47%) as a colorless oil respectively.

19 (*Z* isomer)**: ^{1}H-NMR** ($CDCl_3$, 400 MHz) δ: 7.27 (2H, d, *J* = 8.7 Hz), 6.85 (2H, d, *J* = 8.7 Hz), 5.64 (1H, dq, *J* = 6.9, 1.8 Hz), 4.56 (1H, d, *J* = 11.9 Hz), 4.34 (1H, m), 4.30 (1H, d, *J* = 11.9 Hz), 3.96 (1H, ddd, *J* = 7.8, 5.5, 1.8 Hz), 3.83-3.77 (1H, m), 3.80 (3H, s), 3.66-3.62 (2H, m), 3.59 (1H, m), 2.73 (1H, m), 1.91 (1H, m), 1.58 (3H, dd, *J* = 6.9, 1.8 Hz), 0.89 (9H, s), 0.02 (3H, s), 0.01 (3H, s). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ; -5.6, -5.5, 12.8, 18.0, 25.7, 32.3,

55.2, 60.7, 64.2, 69.0, 70.5, 78.3, 113.7, 124.4, 129.1, 130.8, 131.4, 159.0. **HRMS** (MALDI-TOF) *m/z* 415.2274 (calcd for $C_{22}H_{36}O_4NaSi$ $[M+Na]^+$, 415.2275). $[\alpha]^{23}_D$ = -8.19 (c 0.20, $CHCl_3$).

20 (*E* isomer)**: ^{1}H-NMR** ($CDCl_3$, 400 MHz) δ: 7.27 (2H, d, *J* = 8.5 Hz), 6.87 (2H, d, *J* = 8.5 Hz), 5.59 (1H, q, *J* = 6.7 Hz), 4.56 (1H, d, *J* = 11.0 Hz), 4.39 (1H, d, *J* = 11.0 Hz), 3.88 (1H, m), 3.80 (3H, s), 3.76 (1H, d, *J* = 4.1 Hz), 3.79-3.74 (2H, m), 3.45 (1H, dt, *J* = 10.3, 3.2 Hz), 3.35 (1H, dt, *J* = 7.3, 4.1 Hz), 2.53 (1H, dt, *J* = 14.2, 3.4 Hz), 2.12 (1H, ddd, *J* = 14.2, 10.3, 5.0 Hz), 1.66 (3H, d, *J* = 6.7 Hz), 0.89 (9H, s), 0.06 (6H, s). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ; -5.3, -5.2, 12.5, 18.3, 25.9, 27.7, 55.2, 62.8, 65.5, 71.6, 77.5, 81.9, 113.7, 117.0, 129.4, 130.6, 133.9, 159.1. **HRMS** (MALDI-TOF) *m/z* 415.2275 (calcd for $C_{22}H_{36}O_4NaSi$ $[M+Na]^+$, 415.2275). $[\alpha]^{23}_D$ = +67.4 (c 0.17, $CHCl_3$).

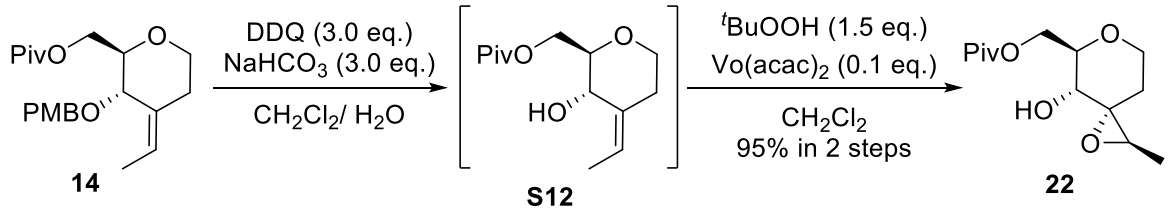


Compound 14

(Step 1): To a solution of **19** (1.85 g, 4.71 mmol, 1.0 equiv.) in dry THF (23 ml) was added TBAF (1M THF solution) (7.0 ml, 7.00 mmol, 1.5 equiv.) at 0 °C. After stirring for 2 h, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 1/1 to 1/2) to give the crude **S11** (1.17 g, 4.20 mmol).

(Step 2): To a solution of **S11** (1.17 g, 4.20 mmol, 1.0 equiv.) in dry CH_2Cl_2 (35 ml) were added TEA (1.33 g, 13.1 mmol, 3.2 equiv.) and DMAP (54.0 mg, 0.44 mmol, 0.1 equiv.) and then PivCl (790 mg, 6.55 mmol, 1.5 equiv.) at room temperature. After stirring for 1 h, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **14** (1.01 g, 2.79 mmol, 59% in 2 steps) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 7.26 (2H, d, *J* = 8.7 Hz), 6.86 (2H, d, *J* = 8.7 Hz), 5.67 (1H, q, *J* = 6.4 Hz), 4.58 (1H, d, *J* = 11.9 Hz), 4.26 (1H, d, *J* = 11.9 Hz), 4.21-4.01 (4H, m), 3.83 (1H, m), 3.80 (3H, s), 3.66 (1H, dt, *J* = 11.0, 3.2 Hz), 2.75 (1H, m), 1.94 (1H, m), 1.55 (3H, d, *J* = 6.4 Hz), 1.13 (9H, s), **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; 12.5, 26.9, 32.2, 38.5, 55.1, 61.1, 63.9, 68.9, 70.4, 75.5, 113.6, 124.5, 129.1, 130.3, 130.9, 160.0, 177.9. **HRMS** (MALDI-TOF) *m/z* 385.1980 (calcd for $C_{21}H_{30}O_5Na$ $[M+Na]^+$, 385.1986). $[\alpha]^{23}_D$ = +21.9 (c 0.28, $CHCl_3$).

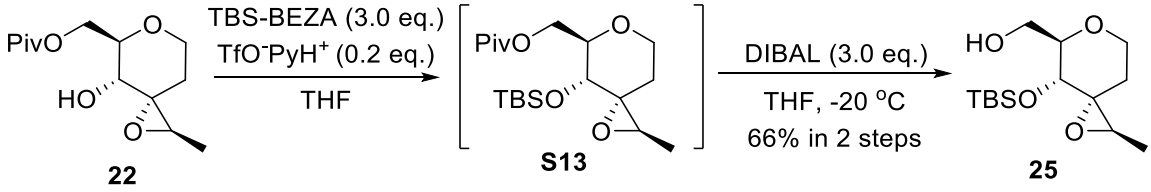


Compound 22

(Step 1): To a solution of **14** (1.47 g, 4.06 mmol, 1.0 equiv.) in CH_2Cl_2/ H_2O (10 : 1, 40 ml) was added DDQ (2.76 mg, 12.2 mmol, 3.0 equiv.) and $NaHCO_3$ (1.02 g, 12.1 mmol, 3.0 equiv.) at room temperature. After stirring for 2 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 5/1 to 3/1) to give the crude **S12**.

(Step 2): To a solution of **S12** in dry CH_2Cl_2 (40 ml) were added ^{t}BuOOH (5.5 M in decane solution) (1.1 ml, 6.05 mmol, 1.5 equiv.) and $Vo(acac)_2$ (103 mg, 0.39 mmol, 0.1 equiv.) at room temperature. After stirring for 4 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 2/1) to give **22** (996 mg, 3.86 mmol, 95% in 2 steps) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 4.41 (1H, dd, *J* = 11.9, 5.3 Hz), 4.31 (1H, dd, *J* = 11.9, 2.1 Hz), 3.92 (1H, ddd, *J* = 10.2, 5.3, 2.1 Hz), 3.76 (1H, t, *J* = 10.2 Hz), 3.64 (1H, dt, *J* = 12.2, 2.3 Hz), 3.44 (1H, m), 2.92 (1H, q, *J* = 6.0 Hz), 2.18 (1H, ddd, *J* = 14.2, 12.2, 5.5 Hz), 2.05 (1H, d, *J* = 10.2 Hz), 1.55 (3H, d, *J* = 6.0 Hz), 1.34 (1H, m), 1.22 (9H, s), **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; 13.4, 27.0, 33.9, 38.6, 60.7, 61.3, 63.5, 64.3, 64.7, 79.1, 178.3. **HRMS** (MALDI-TOF) *m/z* 281.1359 (calcd for $C_{13}H_{22}O_5Na$ $[M+Na]^+$, 281.1359). $[\alpha]^{23}_D$ = +21.1 (c 0.32, $CHCl_3$).

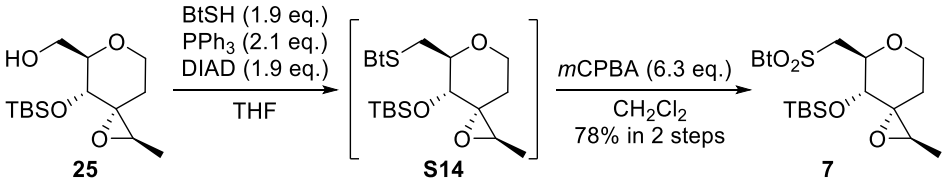


Compound 25

(Step 1): To a solution of **22** (422 mg, 1.63 mmol, 1.0 equiv.) in dry THF (8.0 ml) was added TBS-BEZA (1.52 g, 4.88 mmol, 3.0 equiv.) and TfO^-PyH^+ (75.6 mg, 0.33 mmol, 0.2 equiv.) at room temperature. After stirring for 6 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 10/1) to give the crude **S13** (424 mg, 1.14 mmol).

(Step 2): To a solution of **S13** (424 mg, 1.14 mmol, 1.0 equiv.) in dry THF (11 ml) was added DIBAL (1M toluene solution) (3.4 ml, 3.40 mmol, 3.0 equiv.) at -20 °C. After stirring for 3 h, the reaction mixture was quenched with saturated potassium sodium tartrate aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 2/1) to give **25** (310 mg, 1.07 mmol, 66% in 2 steps) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 3.97-3.87 (2H, m), 3.87-3.76 (2H, m), 3.55-3.45 (2H, m), 2.96 (1H, q, *J* = 5.5 Hz), 2.64 (1H, ddd, *J* = 11.9, 11.9, 5.9 Hz), 1.85 (1H, dd, *J* = 8.7, 2.3 Hz), 1.32 (3H, d, *J* = 5.5 Hz), 1.01 (1H, m), 0.92 (9H, s), 0.12 (3H, s), 0.09 (3H, s). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; -4.9, -4.5, 14.5, 18.1, 25.8, 30.0, 58.9, 60.5, 61.1, 61.2, 68.3, 81.4. **HRMS** (MALDI-TOF) *m/z* 311.1643 (calcd for $C_{14}H_{28}O_4NaSi$ $[M+Na]^+$, 311.1649). $[\alpha]^{23}_D$ = +25.4 (c 0.14, $CHCl_3$).



Compound 7

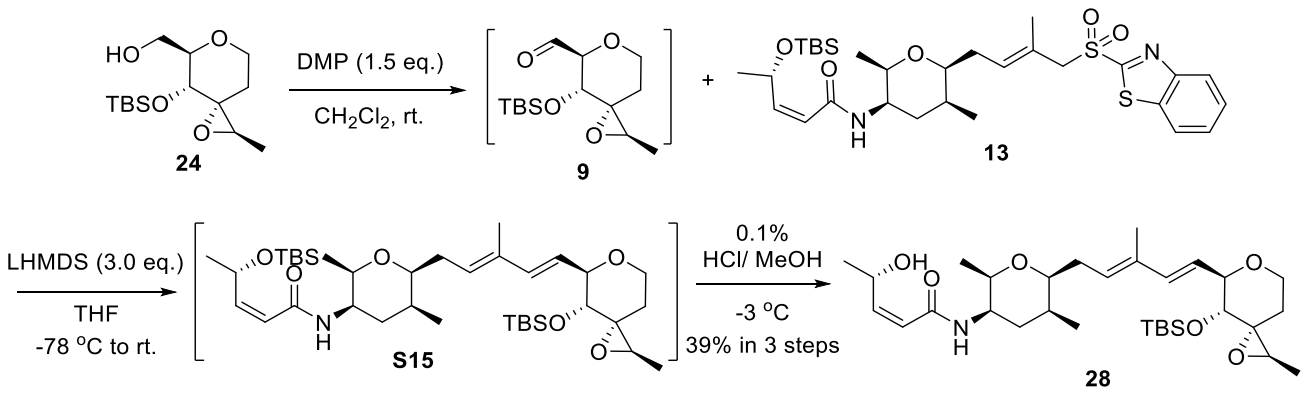
(Step 1): To a solution of **25** (30.7 mg, 0.106 mmol, 1.0 equiv.) in dry THF (1.0 ml) was added BtSH (34.4 mg, 0.206 mmol, 1.9 equiv.), PPh_3 (57.2 mg, 0.218 mmol, 2.1 equiv.) and DIAD (40 µl, 0.198 mmol, 1.9 equiv.) at room temperature. After stirring for 2 h, the reaction mixture was quenched with H_2O. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 8/1) to give the crude **S14**.

(Step 2): To a solution of above **S14** in dry CH_2Cl_2 (2.0 ml) was added *m*-CPBA (115 mg, 0.666 mmol, 6.3 equiv.) at room temperature. After stirring for 15 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 5/1) to give **7** (39.0 mg, 0.083 mmol, 78% in 2 steps) as a colorless amorphous solid.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 8.20 (1H, d, *J* = 7.8 Hz), 8.01 (1H, d, *J* = 7.8 Hz), 7.67-7.58 (2H, m), 4.52 (1H, dd, *J* = 6.4, 6.4 Hz), 4.08 (1H, dd, *J* = 14.7, 7.8 Hz), 3.60 (1H, m Hz), 3.55 (1H, m Hz), 3.53 (1H, m Hz), 3.43 (1H, dd, *J* = 14.7, 5.5 Hz), 3.00 (1H, q, *J* = 5.8 Hz), 2.57 (1H, m), 1.43 (3H, d, *J* = 5.8 Hz), 0.9 (9H, s), 0.88 (1H, m), 0.911 (3H, s), 0.09 (3H, s). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ; -4.9, -4.6, 14.9, 18.1, 25.7, 29.5, 53.3, 60.2, 60.4, 61.2, 69.9, 74.8, 122.4, 125.3, 127.7, 128.1, 136.8, 152.5, 165.8. **HRMS** (MALDI-TOF) *m/z* 492.1307 (calcd for

$C_{21}H_{31}NO_5NaSiS_2$ $[M+Na]^+$, 492.1305). $[\alpha]^{23}_D$ = -10.2 (c 0.18, $CHCl_3$).

Preparation and data for **13** : See reference 4.



Compound 28

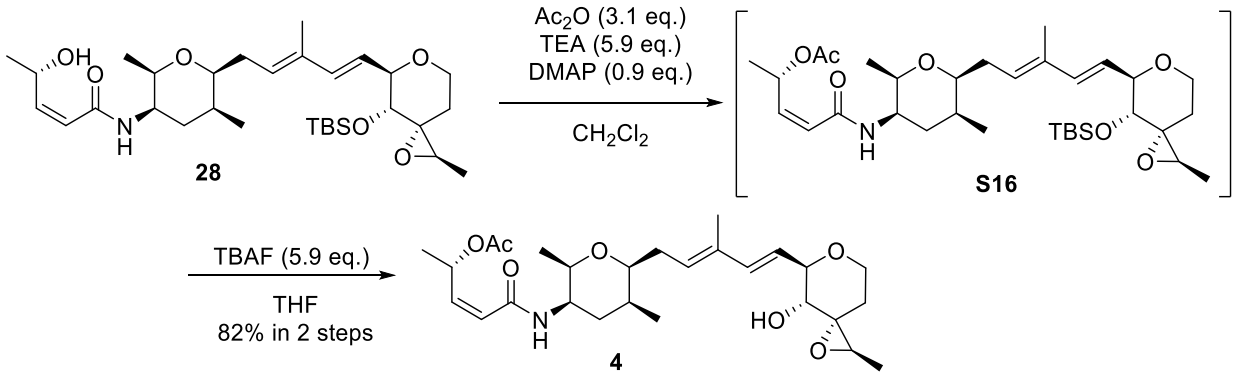
(Step 1): To a solution of **24** (30.3 mg, 0.105 mmol, 1.0 equiv.) in dry CH_2Cl_2 (1.0 ml) was added DMP (66.5 mg, 0.157 mmol, 1.5 equiv.) at room temperature. After stirring for 1 h, the reaction mixture was diluted with Et_2O and quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with Et_2O. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude **9** (29.2 mg, 0.101 mmol).

(Step 2): To a solution of **9** (29.2 mg, 0.102 mmol, 1.0 equiv.) and **13** (60.3 mg, 0.099 mmol, 1.0 equiv.) in dry THF (1.0 ml) was added LHMDS (1M THF solution) (0.30 ml, 0.300 mmol, 3.0 equiv.) at -78 °C. After 30 min, the solution was warm to room temperature and stirred for 15 h. The reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 3/1) to give the crude S**15**.

(Step 3): To **S15** was added 0.1% HCl/ MeOH (2.0 ml) at -3 °C. After stirring for 21 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/1 to 4/6) to give **28** (23.1 mg, 0.041 mmol, 39% in 3 steps) as a colorless amorphous solid.

^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 6.30 (1H, d, *J* = 15.8 Hz), 6.17 (1H, dd, *J* = 12.1, 5.5 Hz), 5.93 (1H, d, *J* = 9.2 Hz), 5.71 (1H, dd, *J* = 12.1, 1.8 Hz), 5.62 (1H, dd, *J* = 15.8, 6.9 Hz), 5.54 (1H, d, *J* = 4.6 Hz), 5.50 (1H, t, *J* = 6.6 Hz), 4.78 (1H, m), 4.37 (1H, d, *J* = 6.9 Hz), 3.93 (1H, m), 3.90-3.83 (2H, m), 3.67 (1H, dq, *J* = 6.3, 2.3 Hz), 3.54 (1H, dt, *J* = 7.2, 2.6 Hz), 3.47 (1H, m), 2.95 (1H, q, *J* = 5.7 Hz), 2.66 (1H, m), 2.39 (1H, m), 2.24 (1H, m), 1.95 (2H, t, *J* = 3.5 Hz), 1.83-1.74 (2H, m), 1.76 (3H, s), 1.34 (3H, d, *J* = 6.9 Hz), 1.30 (3H, d, *J* = 5.7 Hz), 1.14 (3H, d, *J* = 6.3 Hz), 1.01 (3H, d, *J* = 7.5 Hz), 0.92 (9H, s), 0.12 (3H, s), 0.08 (3H, s). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; -4.8, -4.5, 12.7,

15.1, 15.2, 17.8, 18.2, 22.7, 25.8, 28.9, 30.5, 31.9, 35.7, 47.4, 60.5, 61.2, 61.2, 64.6, 71.8, 75.9, 80.8, 81.5, 121.1, 122.5, 129.2, 134.4, 138.1, 150.7, 166.1. **HRMS** (MALDI-TOF) *m/z* 586.3534 (calcd for $C_{31}H_{53}NO_6SiNa$ $[M+Na]^+$, 586.3534). $[\alpha]^{23}_D$ = +33.1 (c 0.15, $CHCl_3$).

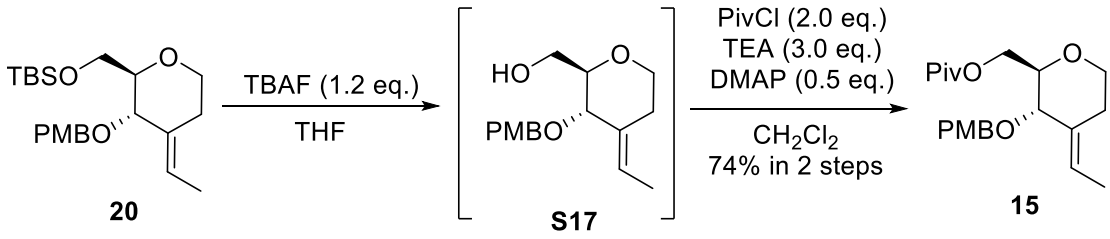


Compound 4

(Step 1): To a solution of **28** (12.2 mg, 0.022 mmol, 1.0 equiv.) in dry CH_2Cl_2 (1.0 ml) was added TEA (15 µl, 0.129 mmol, 5.9 equiv.), DMAP (2.5 mg, 0.020 mmol, 0.9 equiv.) then Ac_2O (7 µl mg, 0.068 mmol, 3.1 equiv.) at room temperature. After stirring for 1 h, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 1/1) to give the crude **S16** (13.2 mg, 0.021 mmol).

(Step 2): To a solution of **S16** (13.2 mg, 0.022 mmol, 1.0 equiv.) in dry THF (1.0 ml) was added TBAF (1M THF solution) (130 µl, 0.130 mmol, 5.9 equiv.) at room temperature. After stirring for 1 h, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/2) to give **4** (8.7 mg, 0.018 mmol, 82% in 2 steps) as a white solid (mp 96-99 ^oC).

^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 6.39 (1H, d, *J* = 16.1 Hz), 6.28 (1H, m), 6.02 (1H, d, *J* = 9.2 Hz), 5.89 (1H, dd, *J* = 11.5, 7.5 Hz), 5.75-5.67 (2H, m), 5.50 (1H, t, *J* = 7.2 Hz), 3.97-3.90 (2H, m), 3.81 (1H, m), 3.71 (1H, dt, *J* = 11.5, 2.9 Hz), 3.68-3.62 (2H, m), 3.51 (1H, dt, *J* = 6.9, 2.9 Hz), 2.93 (1H, q, *J* = 6.3 Hz), 2.38 (1H, m), 2.21 (1H, m), 2.14 (1H, m), 2.04 (3H, s), 1.98-1.89 (3H, m), 1.79-1.77 (1H, m), 1.77 (3H, s), 1.53 (3H, d, *J* = 6.3 Hz), 1.44 (1H, m), 1.38 (3H, d, *J* = 6.3 Hz), 1.14 (3H, d, *J* = 6.3 Hz), 1.00 (3H, d, *J* = 7.5 Hz). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; 12.6, 13.7, 15.0, 17.8, 20.0, 21.2, 28.9, 31.9, 34.1, 35.8, 47.1, 60.9, 61.6, 64.2, 68.6, 68.9, 75.9, 80.8, 81.5, 122.5, 123.8, 129.1, 134.6, 138.2, 143.6, 164.9, 170.4. **HRMS** (MALDI-TOF) *m/z* 514.2775 (calcd for $C_{27}H_{41}NO_7Na$ $[M+Na]^+$, 514.2775). $[\alpha]^{23}_D$ = -33.1 (c 0.02, $CHCl_3$).

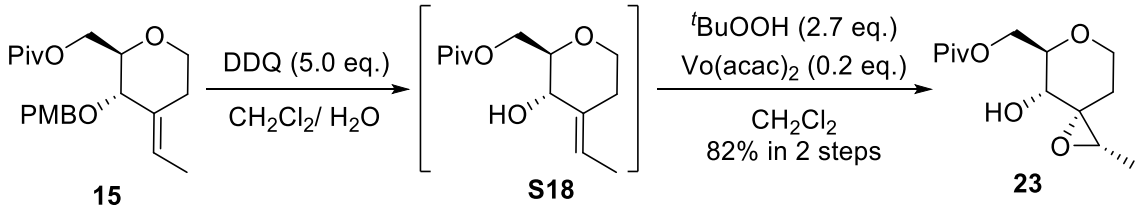


Compound 15

(Step 1): To a solution of **20** (2.45 g, 6.24 mmol, 1.0 equiv.) in dry THF (35 ml) was added TBAF (1M THF solution) (7.5 ml, 7.50 mmol, 1.2 equiv.) at room temperature. After stirring for 12 h, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 1/1) to give the crude S**17** (1.40 g, 5.03 mmol).

(Step 2): To a solution of S**17** (1.40 g, 5.03 mmol, 1.0 equiv.) in dry CH_2Cl_2 (20 ml) were added PivCl (1.24 g, 10.3 mmol, 2.0 equiv.), TEA (1.53 g, 15.1 mmol, 3.0 equiv.) and DMAP (309 mg, 2.53 mmol, 0.5 equiv.) at room temperature. After stirring for 3 h, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 10/1) to give **16** (1.68 g, 4.63 mmol, 74% in 2 steps) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.26 (2H, d, *J* = 8.7 Hz), 6.88 (2H, d, *J* = 8.7 Hz), 5.61 (1H, q, *J* = 6.9 Hz), 4.57 (1H, d, *J* = 11.0 Hz), 4.33 (1H, d, *J* = 11.0 Hz), 4.30-4.20 (2H, m), 3.91 (1H, m), 3.80 (3H, s), 3.69 (1H, m), 3.50 (1H, m), 3.44 (1H, dt, *J* = 10.5, 3.2 Hz), 2.57 (1H, m), 2.12 (1H, m), 1.67 (3H, d, *J* = 6.9 Hz), 1.19 (9H, s).**^{13}C-NMR** ($CDCl_3$, 100 MHz) δ; 12.5, 27.2, 27.8, 38.8, 55.2, 63.3, 66.8, 71.7, 77.6, 79.3, 113.8, 117.1, 129.5, 130.0, 133.4, 159.2, 178.2. **HRMS** (MALDI-TOF) *m/z* 385.1980 (calcd for $C_{21}H_{30}O_5Na$ $[M+Na]^+$, 385.1986). $[\alpha]^{23}_D$ = +86.6 (c 0.20, $CHCl_3$).

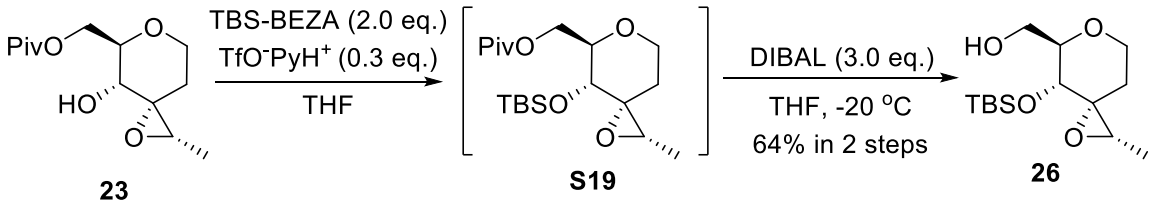


Compound 23

(Step 1): To a solution of **15** (2.40 g, 6.62 mmol, 1.0 equiv.) in CH_2Cl_2/ H_2O (10 : 1, 150 ml) was added DDQ (7.51 g, 33.1 mmol, 5.0 equiv.) at room temperature. After stirring for 12 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 3/1) to give the crude S**18**.

(Step 2): To a solution of S**18** in dry CH_2Cl_2 (60 ml) were added ^{t}BuOOH (5.5M in decane solution) (3.2 ml, 17.6 mmol, 2.7 equiv.) and Vo(acac)$_2$ (311 mg, 1.17 mmol, 0.2 equiv.) at room temperature. After stirring for 1 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 2/1) to give **23** (1.41 g, 5.46 mmol, 82% in 2 steps) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 4.40 (1H, dd, *J* = 11.9, 2.3 Hz), 4.30 (1H, dd, *J* = 11.9, 5.0 Hz), 4.02 (1H, ddd, *J* = 10.1, 5.5, 1.4 Hz), 3.69-3.57 (2H, m), 3.43 (1H, q, *J* = 6.0 Hz), 3.42-3.30 (2H, m), 2.09 (1H, m), 1.98 (1H, d, *J* = 10.6 Hz), 1.55 (3H, m), 1.23 (9H, s). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ; 12.6, 27.1, 28.6, 38.9, 54.4, 61.7, 64.1, 65.1, 65.3, 78.6, 178.7. **HRMS** (MALDI-TOF) *m/z* 281.1359 (calcd for $C_{13}H_{22}O_5Na$ $[M+Na]^+$, 281.1359). $[\alpha]^{23}_D$ = +10.9 (c 0.10, $CHCl_3$).

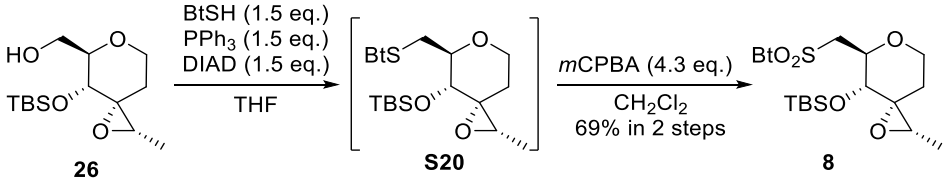


Compound 26

(Step 1): To a solution of **26** (810 mg, 3.14 mmol, 1.0 equiv.) in dry THF (8.0 ml) was added TBS-BEZA (1955 mg, 6.28 mmol, 2.0 equiv.) and TfO^-PyH^+ (185 mg, 0.807 mmol, 0.3 equiv.) at room temperature. After stirring for 12 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 7/1) to give the crude **S19** (910 mg, 2.44 mmol).

(Step 2): To a solution of **S19** (910 mg, 2.44 mmol, 1.0 equiv.) in dry THF (24 ml) was added DIBAL (1M toluene solution) (7.3 ml, 7.30 mmol, 3.0 equiv.) at -20 °C. After stirring for 1 h, the reaction mixture was quenched with saturated potassium sodium tartrate aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 2/1) to give **26** (577 mg, 2.00 mmol, 64% in 2 steps) as a colorless oil.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 4.00 (1H, ddd, *J* = 11.0, 5.5, 1.8 Hz), 3.79 (1H, m), 3.75 (1H, d, *J* = 4.1 Hz), 3.72 (1H, m), 3.63 (1H, m), 3.53 (1H, ddd, *J* = 8.7, 50., 2.7 Hz), 3.34 (1H, q, *J* = 5.5 Hz), 1.97 (1H, m), 1.94 (1H, t, *J* = 6.4 Hz), 1.50 (1H, m), 1.27 (3H, d, *J* = 5.5 Hz), 0.90 (9H, s), 0.11 (3H, s), 0.05 (3H, s). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ; -4.8, -4.7, 12.8, 18.0, 25.7, 29.6, 54.6, 62.1, 62.8, 65.0, 67.2, 79.5. **HRMS** (MALDI-TOF) *m/z* 311.1645 (calcd for $C_{14}H_{28}O_4SiNa$ $[M+Na]^+$, 311.1649). $[\alpha]^{23}_D$ = +59.0 (c 0.19, $CHCl_3$).

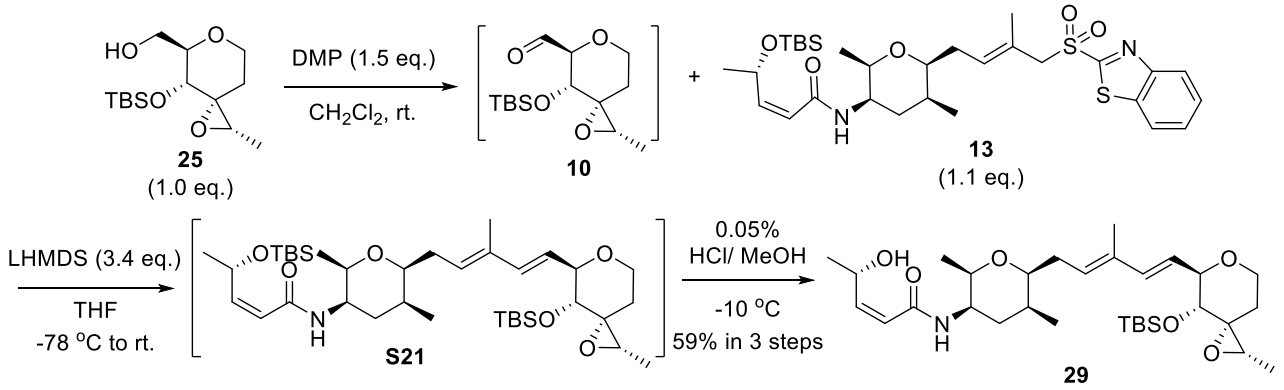


Compound 8

(Step 1): To a solution of **26** (150 mg, 0.520 mmol, 1.0 equiv.) in dry THF (3.5 ml) was added BtSH (131 mg, 0.783 mmol, 1.5 equiv.), PPh_3 (205 mg, 0.782 mmol, 1.5 equiv.) and DIAD (0.15 ml, 0.78 mmol, 1.5 equiv.) at room temperature. After stirring for 2 h, the reaction mixture was quenched with H_2O. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 7/1) to give the crude **S20**.

(Step 2): To a solution of above **S20** in dry CH_2Cl_2 (2.0 ml) was added *m*-CPBA (382 mg, 2.21 mmol, 4.3 equiv.) at room temperature. After stirring for 2 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 3/1) to give **8** (170 mg, 0.361 mmol, 69% in 2 steps) as a white solid (mp 145-148 ^oC).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 8.20 (1H, d, *J* = 8.1 Hz), 8.00 (1H, d, *J* = 8.1 Hz), 7.64-7.55 (2H, m), 4.15 (1H, m), 3.82 (1H, dd, *J* = 14.7, 2.3 Hz), 3.72 (1H, dd, *J* = 14.7, 10.1 Hz), 3.61-3.56 (2H, m), 3.56 (1H, d, *J* = 8.7 Hz), 3.26 (1H, q, *J* = 5.8 Hz), 1.84 (1H, m), 1.44 (1H, m), 1.23 (3H, d, *J* = 5.8 Hz), 0.90 (9H, s), 0.11 (3H, s), 0.04 (3H, s). **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ; -4.5, -4.2, 12.7, 18.0, 25.6, 29.0, 54.9, 57.0, 62.1, 64.9, 69.9, 74.8, 122.2, 125.4, 127.4, 127.8, 136.9, 152.5, 167.0. **HRMS** (MALDI-TOF) *m/z* 492.1311 (calcd for $C_{21}H_{31}NO_5NaSiS_2$ $[M+Na]^+$, 492.1305). $[\alpha]^{23}_D$ = +5.95 (c 0.20, $CHCl_3$).



Compound 29

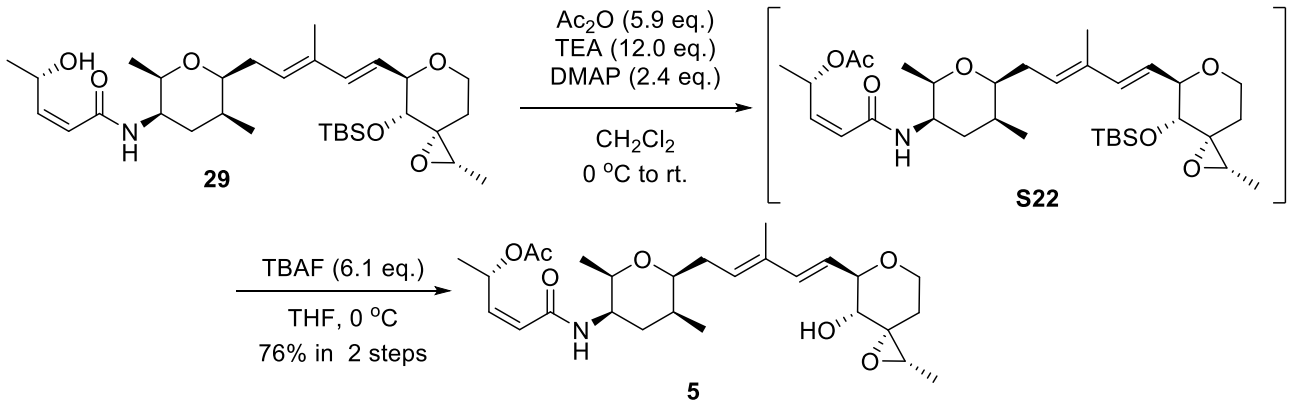
(Step 1): To a solution of **25** (33.5 mg, 0.116 mmol, 1.0 equiv.) in dry CH_2Cl_2 (1.1 ml) was added DMP (76.0 mg,

0.179 mmol, 1.5 equiv.) at room temperature. After stirring for 2 h, the reaction mixture was diluted with Et_2O and quenched with saturated $NaHCO_3$ aq and saturated $Na_2S_2O_3$ aq. The organic compounds were extracted with Et_2O. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude **10**.

(Step 2): To a solution of **13** (75.1 mg, 0.124 mmol, 1.1 equiv.) and **10** in dry THF (1.2 ml) was added LHMDS (1M THF solution) (0.4 ml, 0.400 mmol, 3.4 equiv.) at -78 °C. After 30 min, the solution was warm to room temperature and stirred for 23 h. The reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 3/1) to give the crude S**21**.

(Step 3): To S**21** was added 0.05% HCl/ MeOH (3.0 ml) at -10 °C. After stirring for 12 h, the reaction mixture was quenched with saturated $NaHCO_3$ aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/1) to give **29** (38.2 mg, 0.068 mmol, 59% in 3 steps) as a colorless amorphous solid.

^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 6.29 (1H, d, *J* = 15.8 Hz), 6.17 (1H, dd, *J* = 12.1, 5.2 Hz), 5.93 (1H, d, *J* = 9.2 Hz), 5.70 (1H, dd, *J* = 12.1, 1.7 Hz), 5.58 (1H, d, *J* = 4.6 Hz), 5.52 (1H, dd, *J* = 15.8, 6.9 Hz), 5.44 (1H, t, *J* = 7.2 Hz), 4.77 (1H, m), 4.02-3.90 (3H, m), 3.75 (1H, dt, *J* = 12.1, 2.3 Hz), 3.65 (1H, m), 3.55 (1H, d, *J* = 8.6 Hz), 3.52 (1H, m), 3.33 (1H, q, *J* = 5.6 Hz), 2.37 (1H, m), 2.24 (1H, m), 1.99 (1H, m), 1.93 (2H, m), 1.76 (1H, m), 1.74 (3H, s), 1.52 (1H, m), 1.34 (3H, d, *J* = 6.3 Hz), 1.26 (3H, d, *J* = 5.6 Hz), 1.12 (3H, d, *J* = 6.3 Hz), 0.98 (3H, d, *J* = 7.5 Hz), 0.84 (9H, s), 0.003 (3H, s), -0.041 (3H, s). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; -4.5, -4.2, 12.5, 12.9, 15.1, 17.8, 18.0, 22.7, 25.7, 28.8, 29.7, 31.9, 35.7, 47.5, 54.9, 62.9, 64.6, 64.9, 71.3, 75.8, 80.9, 81.0, 122.5, 124.5, 128.5, 134.5, 138.0, 150.7, 166.1.**HRMS** (MALDI-TOF) *m/z* 586.3535 (calcd for $C_{31}H_{53}NO_6SiNa$ $[M+Na]^+$, 586.3534). $[\alpha]^{23}_D$ = +5.94 (c 0.09, $CHCl_3$).



Compound 5

(Step 1): To a solution of **29** (38.2 mg, 0.068 mmol, 1.0 equiv.) in dry CH_2Cl_2 (2.0 ml) was added TEA (82.3 mg, 0.813 mmol, 12.0 equiv.), DMAP (20.2 mg, 0.165 mmol, 2.4 equiv.) then Ac_2O (38 µl, 0.402 mmol, 5.9 equiv.) at 0 ℃ and the gradually warm to room temperature. After stirring for 1 h, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with CH_2Cl_2. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was passed through a short silica gel column (*n*-hexane/EtOAc = 3/1) to give the crude **S22** (34.5 mg, 0.057 mmol).

(Step 2): To a solution of crude **S22** (34.5 mg, 0.057 mmol, 1.0 equiv.) in dry THF (3.0 ml) was added TBAF (1M THF solution) (0.35 ml, 0.350 mmol, 6.1 equiv.) at 0 ºC. After stirring for 12 h, the reaction mixture was quenched with saturated NH_4Cl aq. The organic compounds were extracted with EtOAc. The organic layers were combined, and the solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/2) to give **5** (25.8 mg, 0.052 mmol, 76% in 2 steps) as a white solid (mp 92-95 ºC).

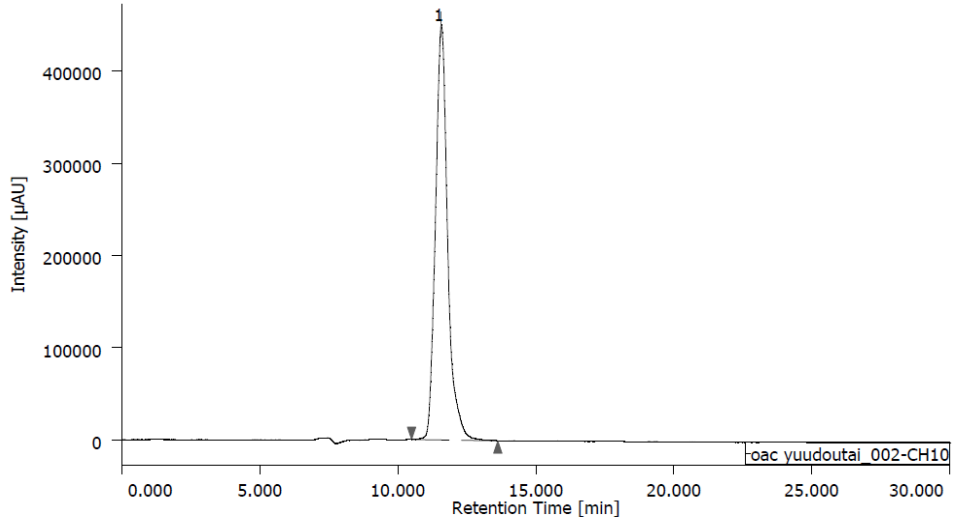
^{1}H-NMR ($CDCl_3$, 500 MHz) δ: 6.38 (1H, d, *J* = 15.5 Hz), 6.25 (1H, m), 6.01 (1H, d, *J* = 9.2 Hz), 5.88 (1H, dd, *J* = 10.1, 6.7 Hz), 5.71 (1H, m), 5.68 (1H, m), 5.49 (1H, t, *J* = 6.9 Hz), 4.04 (1H, d, *J* = 11.5, 4.6 Hz), 3.92 (1H, m), 373-3.68 (2H, m), 3.65 (1H, m), 3.54-3.49 (2H, m), 3.43 (1H, q, *J* = 5.7 Hz), 2.38 (1H, m), 2.22 (1H, m), 2.12 (1H, m), 2.03 (3H, s), 1.98-1.89 (2H, m), 1.79 (1H, m), 1.77 (3H, s), 1.71 (1H, d, *J* = 10.3 Hz), 1.57 (1H, m), 1.38 (3H, d, *J* = 6.9 Hz), 1.30 (3H, d, *J* = 5.7 Hz), 1.13 (3H, d, *J* = 6.3 Hz), 1.00 (3H, d, *J* = 7.5 Hz). **^{13}C-NMR** ($CDCl_3$, 125 MHz) δ; 12.6, 12.7, 15.0, 17.8, 20.0, 21.2, 28.8, 28.9, 31.9, 35.8, 47.1, 54.4, 61.9, 64.9, 68.9, 69.2, 75.9, 80.8, 80.9, 122.5, 124.3, 129.0, 134.6, 137.9, 143.6, 164.8, 170.3. **HRMS** (MALDI-TOF) *m/z* 514.2772 (calcd for $C_{27}H_{41}NO_7Na$ $[M+Na]^+$, 514.2775). $[\alpha]^{23}_D$ = -37.9 (c 0.02, $CHCl_3$).

5. Analytical RP-HPLC

HPLC purity determination of compound **3, 4** and **5** was performed on a reversed CEL (Mightysil RP-18 GP 250-10).

Compound **3**

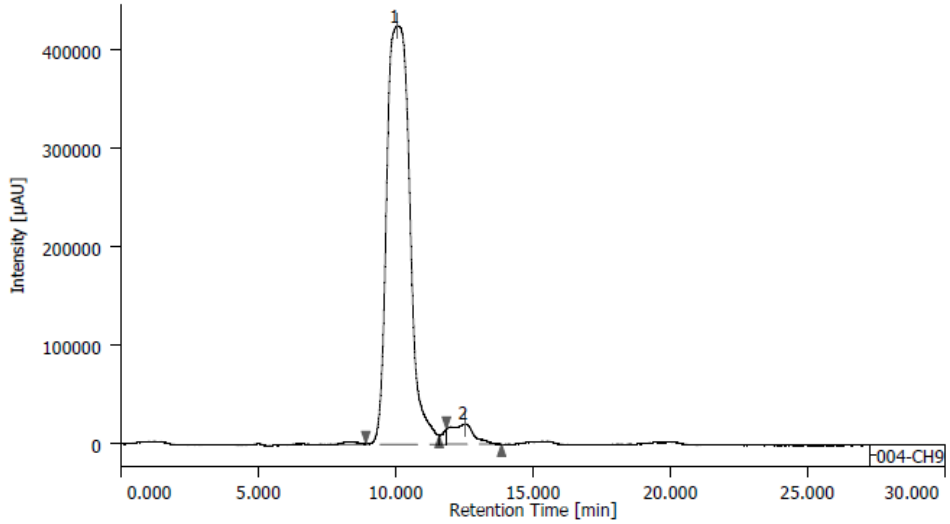
Purity is > 95%. Condition : eluting with acetonitrile and water (70 : 30, 0.2 ml/ min) over 30 min. UV detection (λ = 254 nm)



#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	11.573	13852229	100.000

Compound **4**

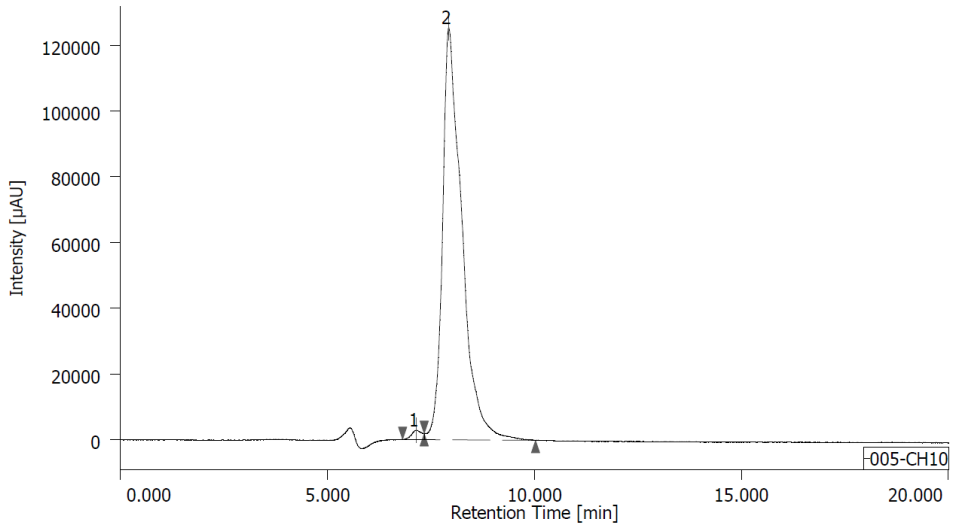
Purity is > 95%. Condition : eluting with acetonitrile and water (60 : 40, 0.4 ml/ min) over 30 min. UV detection (λ = 210 nm)



#	peak_name	tR [min]	area [μV·sec]	area%
1	Unknown	10.053	24798136	95.348
2	Unknown	12.547	1209819	4.652

Compound **5**

Purity is > 95%. Condition : eluting with acetonitrile and water (80 : 20, 0.3 ml/ min) over 20 min. UV detection (λ = 210 nm)



#	peak_name	tR [min]	area [µV·sec]	area%
1	Unknown	7.147	49160	1.193
2	Unknown	7.933	4072958	98.807

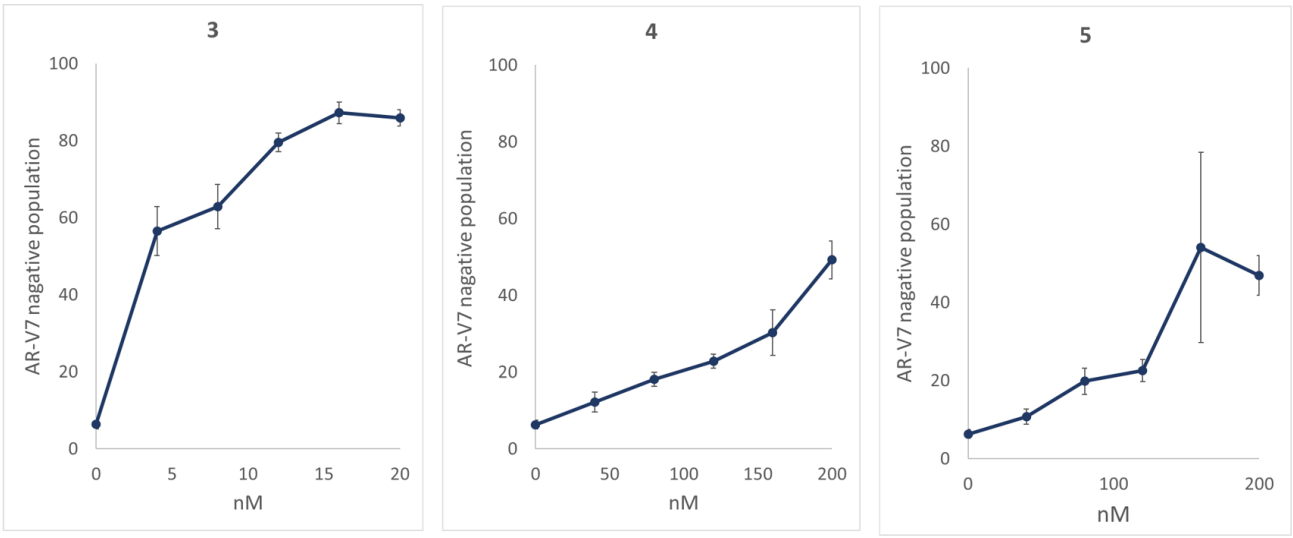
6. Biological Assay

Method

AR-V7-GFP splicing assay. AR-V7-GFP CWR22Rv1 cell was previously established and cultured as previously described[5]. GFP signals can be used for quantitative examination of AR-V7 splicing in this system. After three days of treatment, GFP expression was measured by FACSAria II (BD Biosciences) as previously described. IC_{50} was calculated using approximate curves[5].

In vivo toxicity test. Animal experiments were approved by the Osaka University Animal Experiments committee and were performed following the guidelines. Spliceostain A or its derivatives (**3-5**) were intraperitoneally injected into eight to ten-week-old C57BL/6 male mice with 300 µl PBS containing 10% DMSO three times on every other day. Body weight was measured on every other day.

AR-V7-GFP expression assay for **3, 4, 5**



7. Reference

1) Catino, A. J.; Sherlock, A.; Shieh, P.; Wzorek, J. S.; Evans, D. A. *Org. Lett*. **2013**, *15*, 3330-3333.

2) Yoshikawa, Y.; Ishibashi, A.; Murai, K.; Kaneda, Y.; Nimura, K.; Arisawa, M. *Tetrahedron Lett*. 10.1016/j.tetlet.2019.151313.

3) Fujiwara, T.; Hayashi, M. *J. Org. Chem*. **2008**, *73*, 9161-9163.

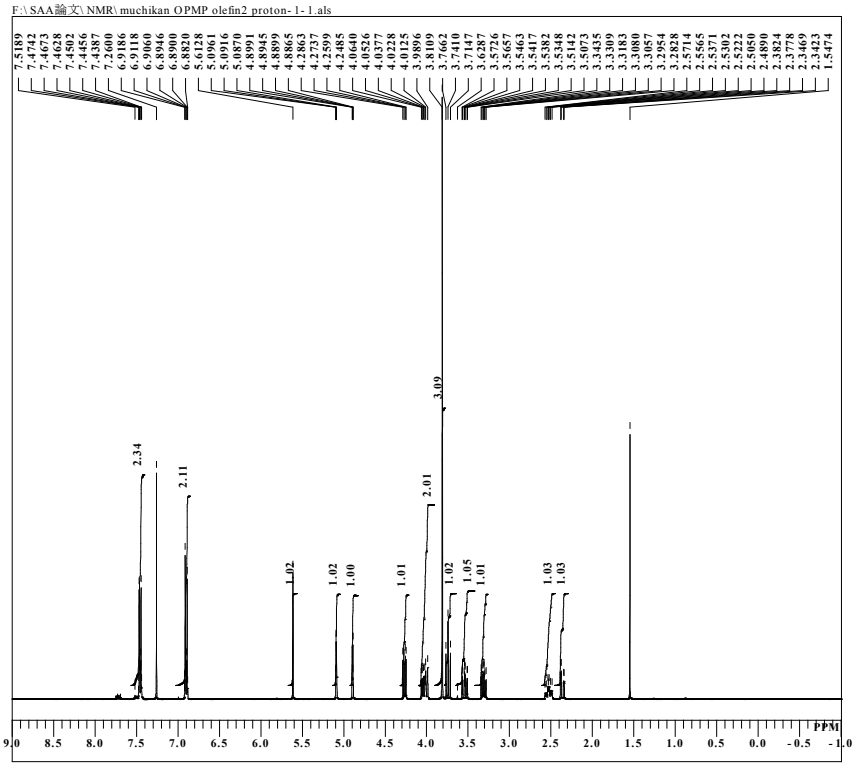
4) Motoyoshi, H.; Horigome, M.; Watanabe, H.; Kitahara, T. *Tetrahedron* **2006**, *62*, 1378−1389

5) N. Kawamura, K. Nimura, K. Saga, A. Ishibashi, K. Kitamura, H. Nagano, Y. Yoshikawa, K. Ishida, N. Nonomura, M. Arisawa, J. Luo and Y. Kaneda, *Can. Res.* **2019**, *79*, 5204-5217.

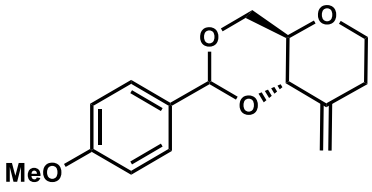
8. NMR Spectra

single_pulse

F:\ SAA論文\ NMR\ muchikan OPMP olefin2 proton- 1- 1.als



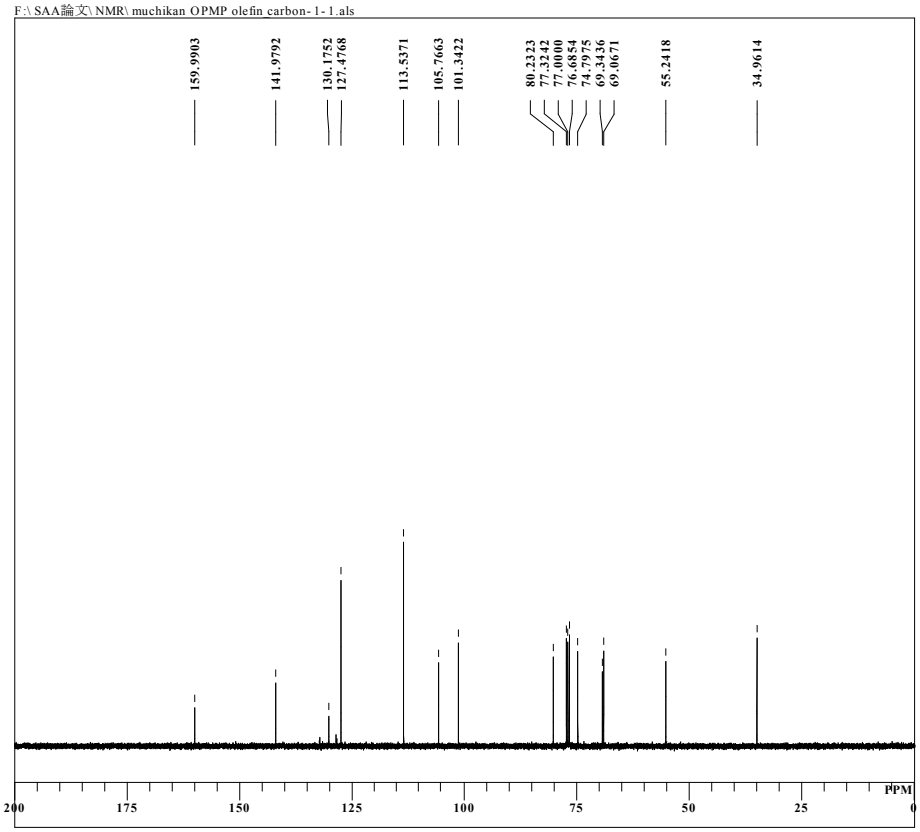
DFILE	muchikan OPMP olefin2_proton- 1- 1.als
COMNT	single_pulse
DATIM	2019- 07- 24 16:54:59
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	5
ACQTM	2.1837 sec
PD	10.0000 sec
PW1	7.25 usec
IRNUC	1H
CTEMP	22.6 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	48



17
55% in 2 steps

single pulse decoupled gated NOE

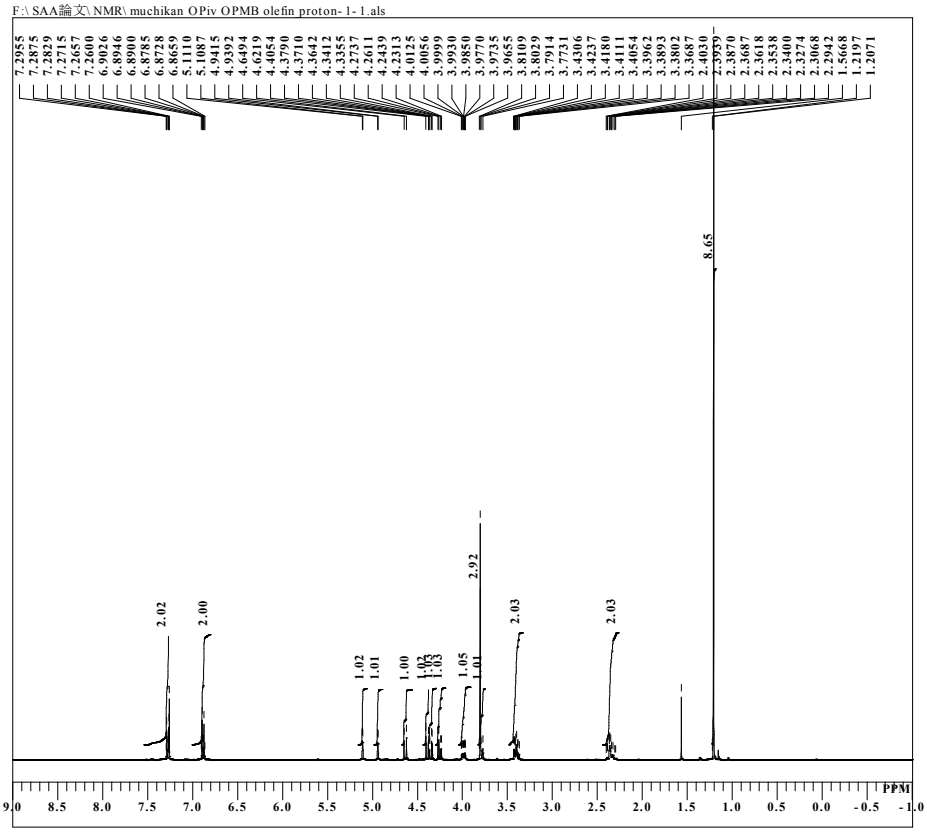
F:\ SAA論文\ NMR\ muchikan OPMP olefin carbon- 1- 1.als



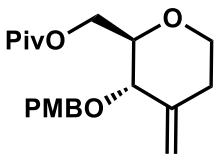
DFILE	muchikan OPMP olefin_carbon- 1- 1.als
COMNT	single pulse decoupled gated NOE
DATIM	2019- 07- 24 17:42:03
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	176
ACQTM	1.0433 sec
PD	1.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

single_pulse

F:\ SAA論文\ NMR\ muchikan OPiv OPMB olefin proton-1-1.als



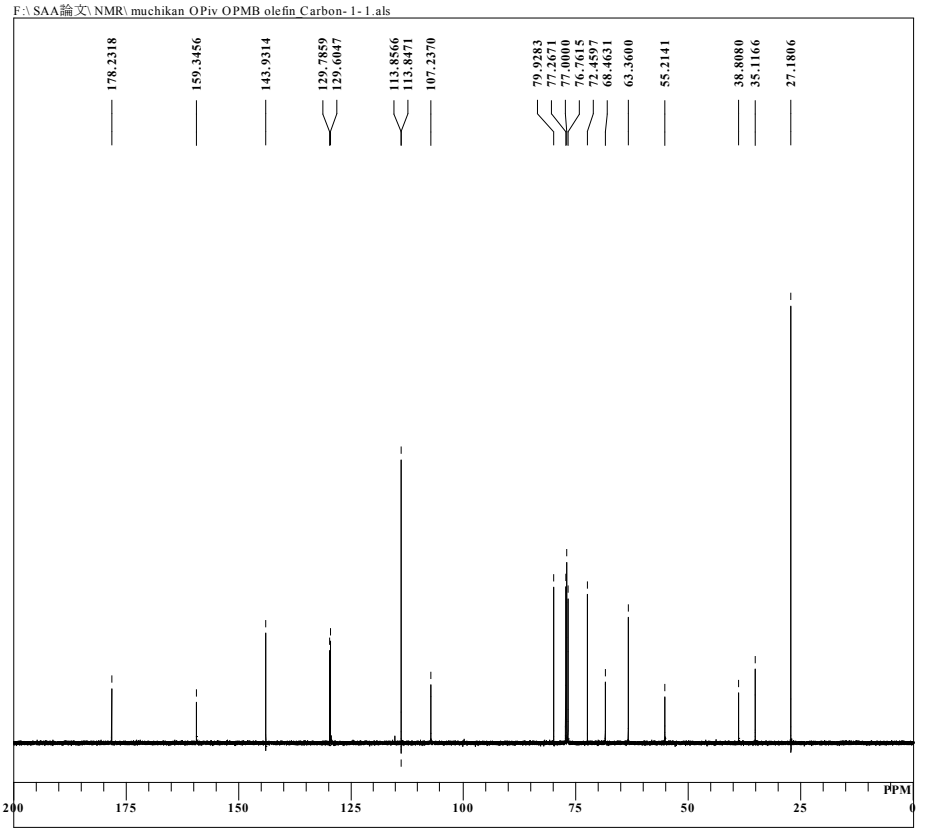
DFILE	muchikan OPiv OPMB olefin_proton-1-
COMNT	single_pulse
DATIM	2019-05-20 15:13:09
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	11
ACQTM	2.1837 sec
PD	1.0000 sec
PW1	7.25 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	46



13
87% in 2 steps

single pulse decoupled gated NOE

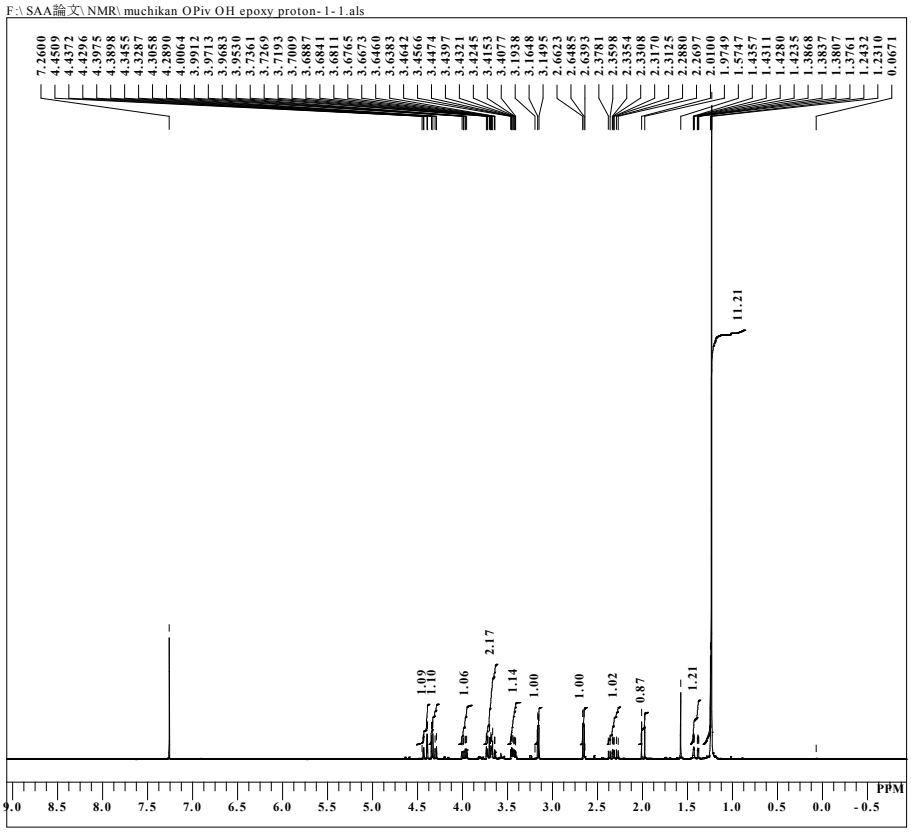
F:\ SAA論文\ NMR\ muchikan OPiv OPMB olefin Carbon-1-1.als



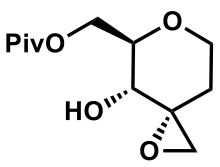
DFILE	muchikan OPiv OPMB olefin_Carbon-1
COMNT	single pulse decoupled gated NOE
DATIM	2019-05-20 14:58:39
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	87
ACQTM	0.8336 sec
PD	3.0000 sec
PW1	3.27 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

single_pulse

F:\ SAA論文\ NMR\ muchikan OPiv OH epoxy proton-1-1.als

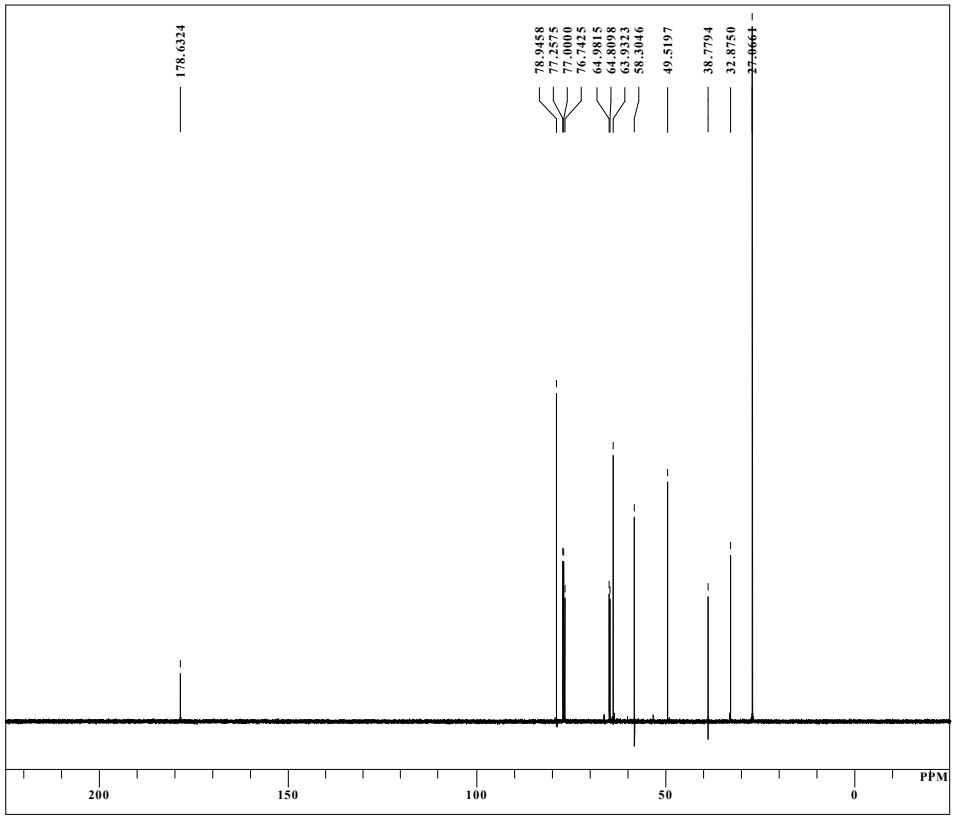


DFILE	muchikan OPiv OH epoxy_proton-1-1.
COMNT	single_pulse
DATIM	2019-05-22 12:10:26
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	6016.85 Hz
SCANS	13
ACQTM	2.1784 sec
PD	1.0000 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	19.7 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



21
82% in 2 steps

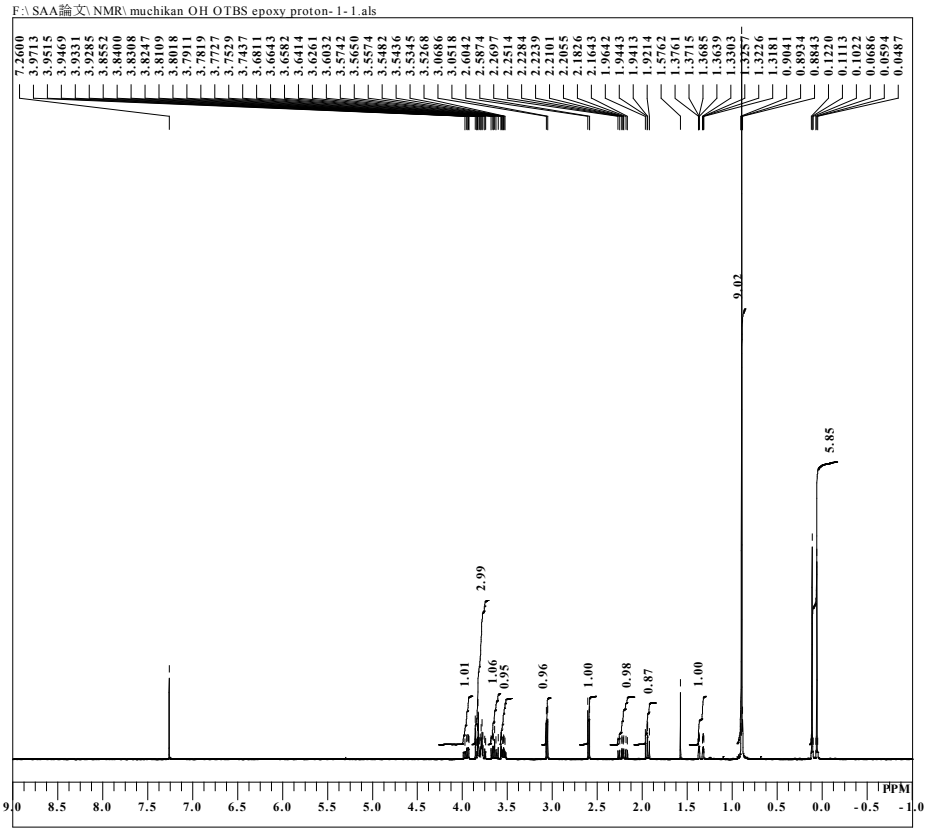
single pulse decoupled gated NOE



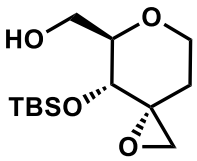
DFILE	muchikan OPiv OH epoxy_Carbon-2-
COMNT	single pulse decoupled gated NOE
DATIM	2019-05-22 14:11:07
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	122
ACQTM	0.8336 sec
PD	2.5000 sec
PW1	3.27 usec
IRNUC	1H
CTEMP	20.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	58

single_pulse

F:\ SAA論文\ NMR\ muchikan OH OTBS epoxy proton-1-1.als



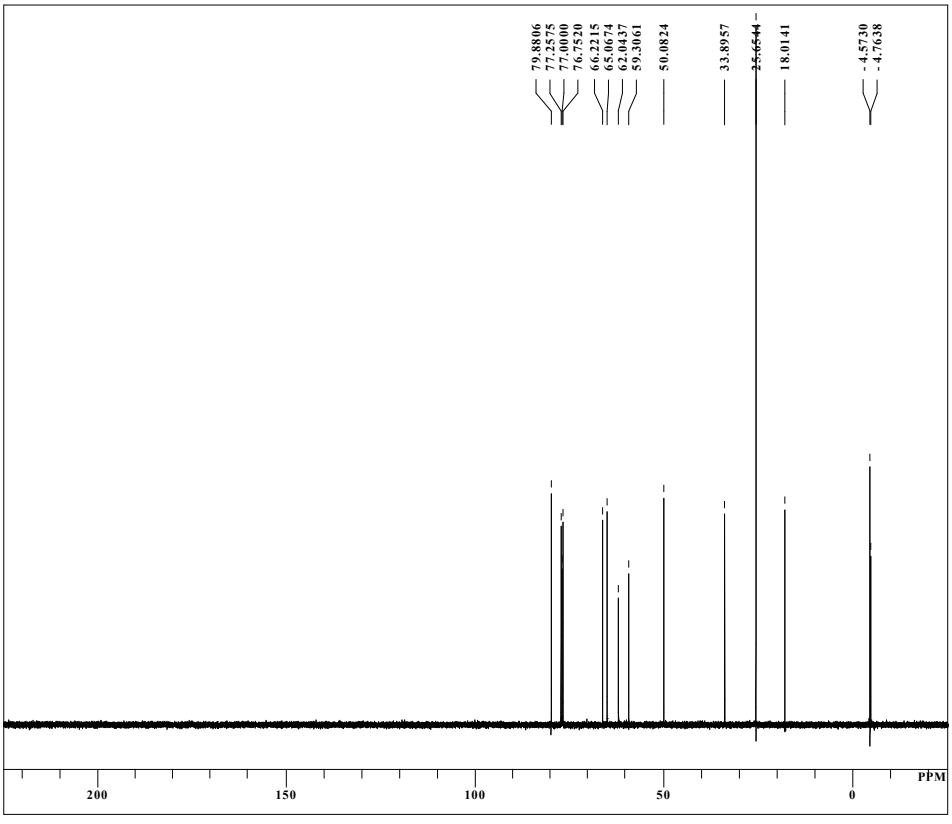
DFILE	muchikan OH OTBS epoxy_proton-1-1
COMNT	single_pulse
DATIM	2019-05-23 15:42:23
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	6016.85 Hz
SCANS	16
ACQTM	2.1784 sec
PD	1.0000 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	20.1 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	38



24

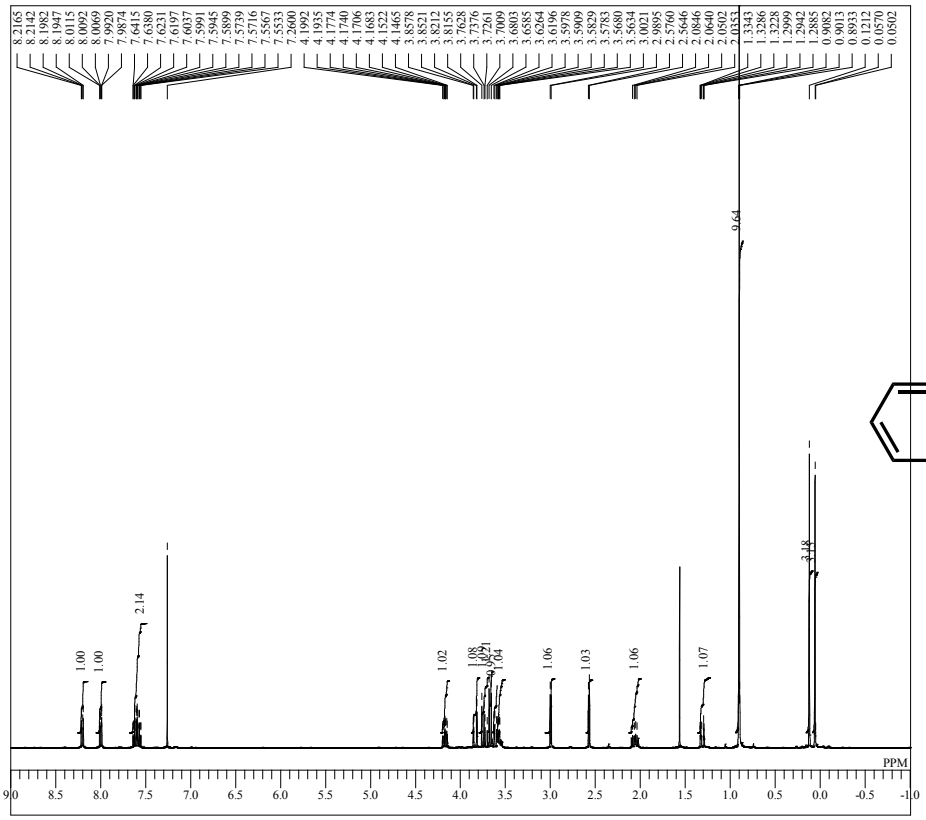
59% in 2 steps

single pulse decoupled gated NOE

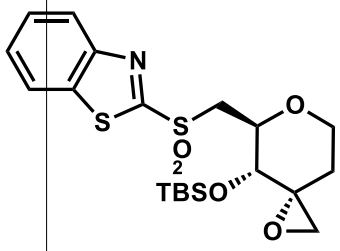


DFILE	muchikan OH OTBS epoxy_Carbon-1
COMNT	single pulse decoupled gated NOE
DATIM	2019-05-23 15:20:28
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	76
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.27 usec
IRNUC	1H
CTEMP	20.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

single_pulse

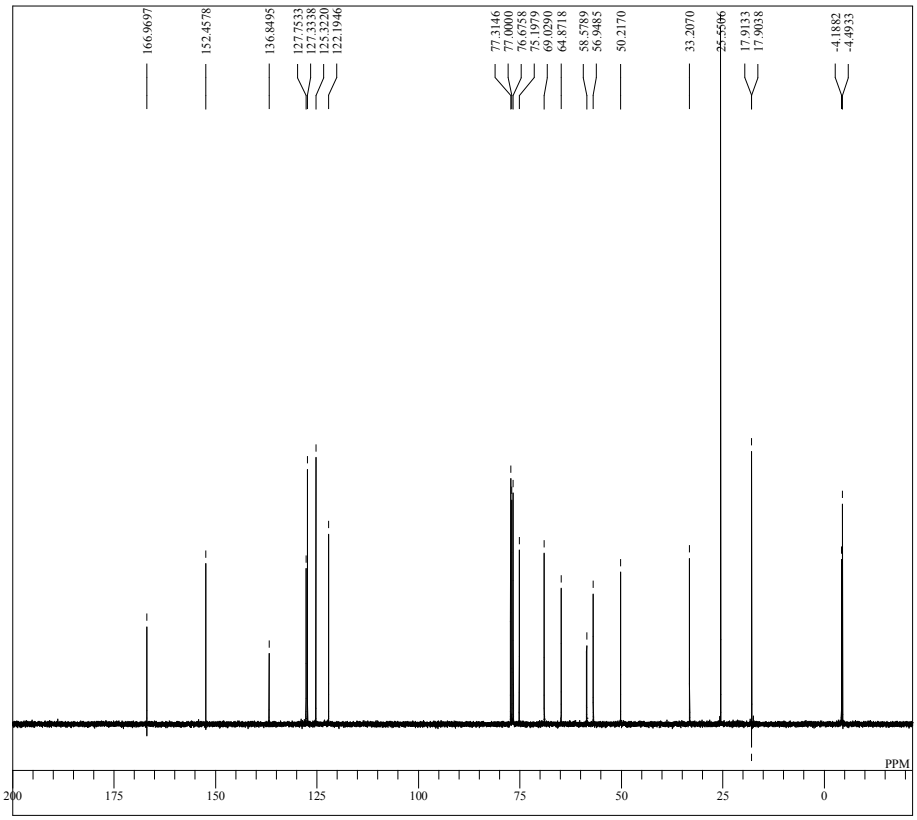


DFILE muchikan SO2Bt_proton-1-1.als
COMNT single_pulse
DATIM 2019-07-30 15:04:14
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 12
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 7.25 usec
IRNUC 1H
CTEMP 23.1 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 46



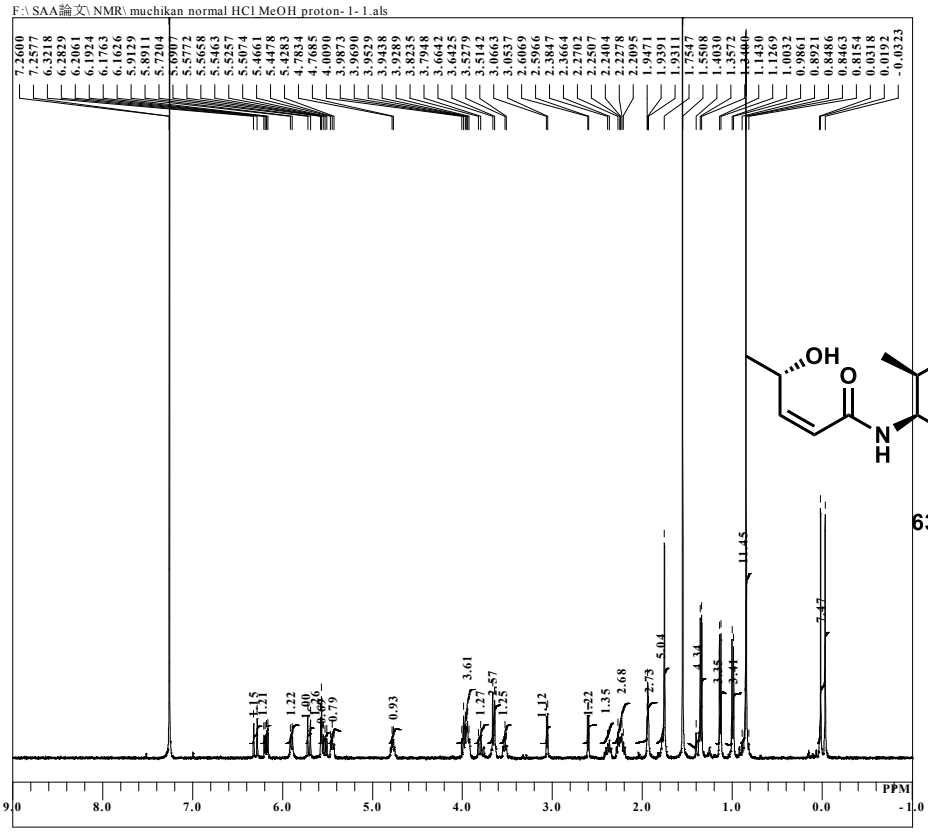
6
73% in 2 steps

single pulse decoupled gated NOE

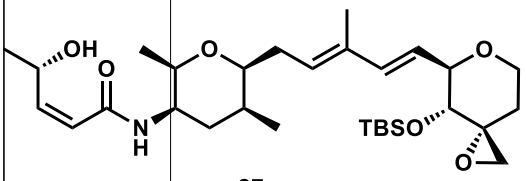


DFILE muchikan SO2Bt_carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-07-30 15:25:04
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 372
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 23.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

single_pulse

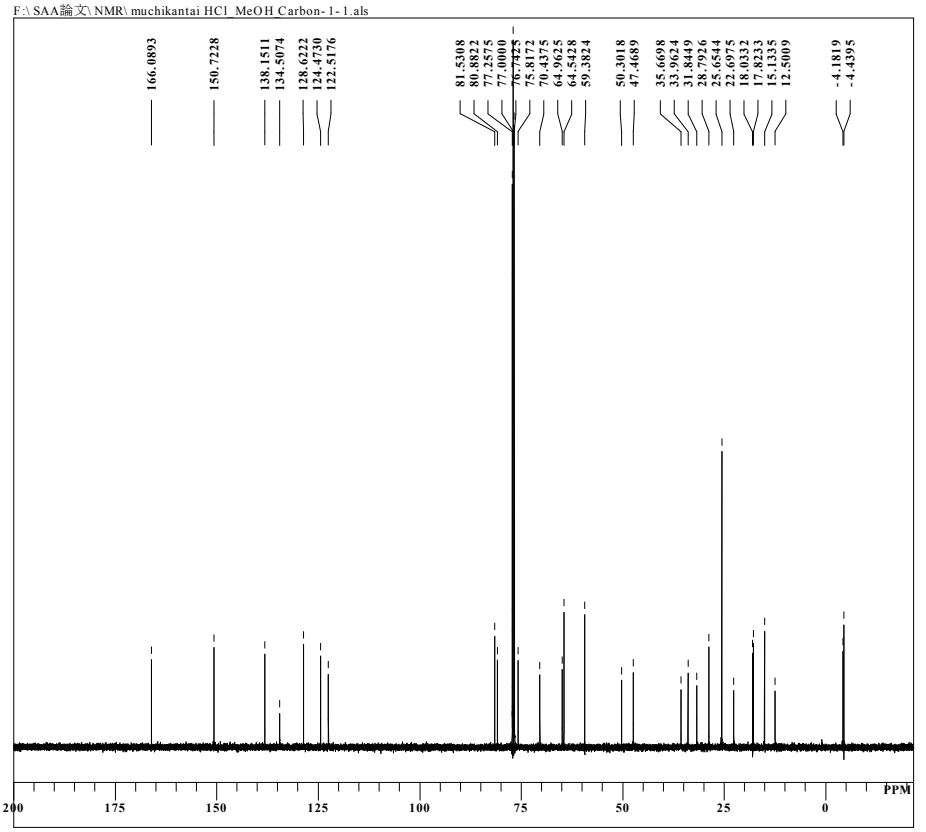


DFILE	muchikan normal HCl_MeOH_proton-1-
COMNT	single_pulse
DATIM	2019-06-13 15:26:00
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	16
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	7.25 usec
IRNUC	1H
CTEMP	21.8 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	54



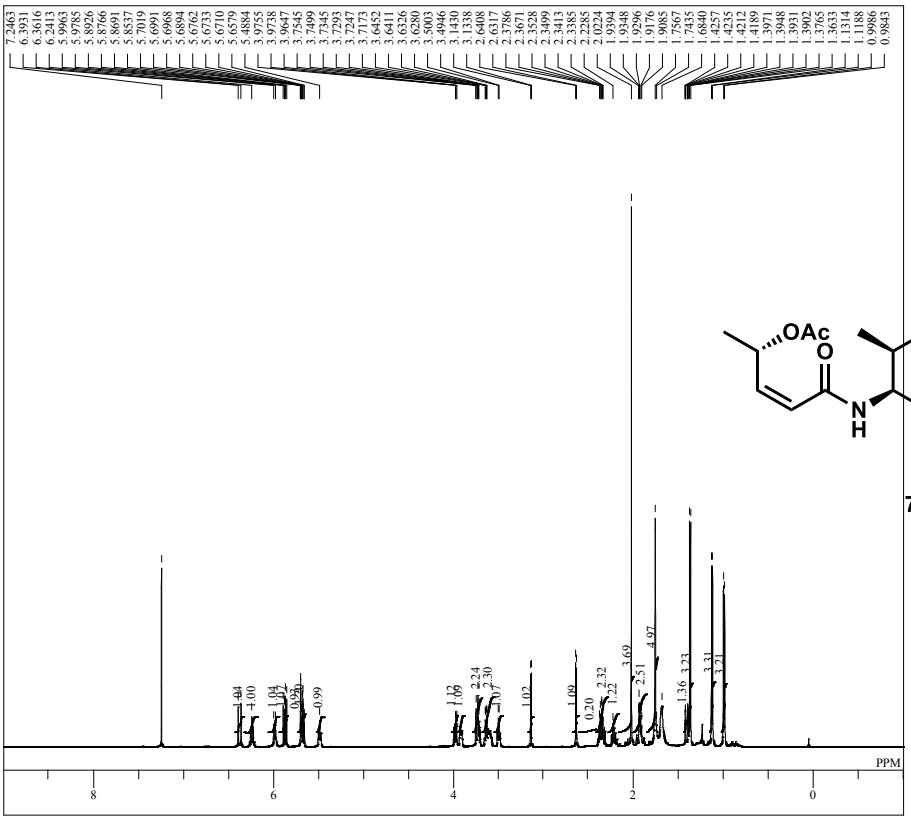
27
63% in 2 steps

single pulse decoupled gated NOE

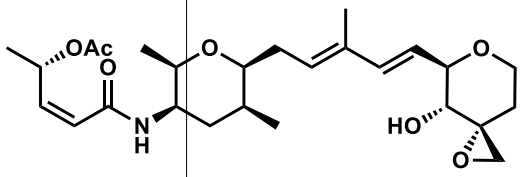


DFILE	muchikantai HCl_MeOH_Carbon-1-1.a
COMNT	single pulse decoupled gated NOE
DATIM	2019-06-13 15:49:31
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	1052
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.27 usec
IRNUC	1H
CTEMP	20.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

single_pulse

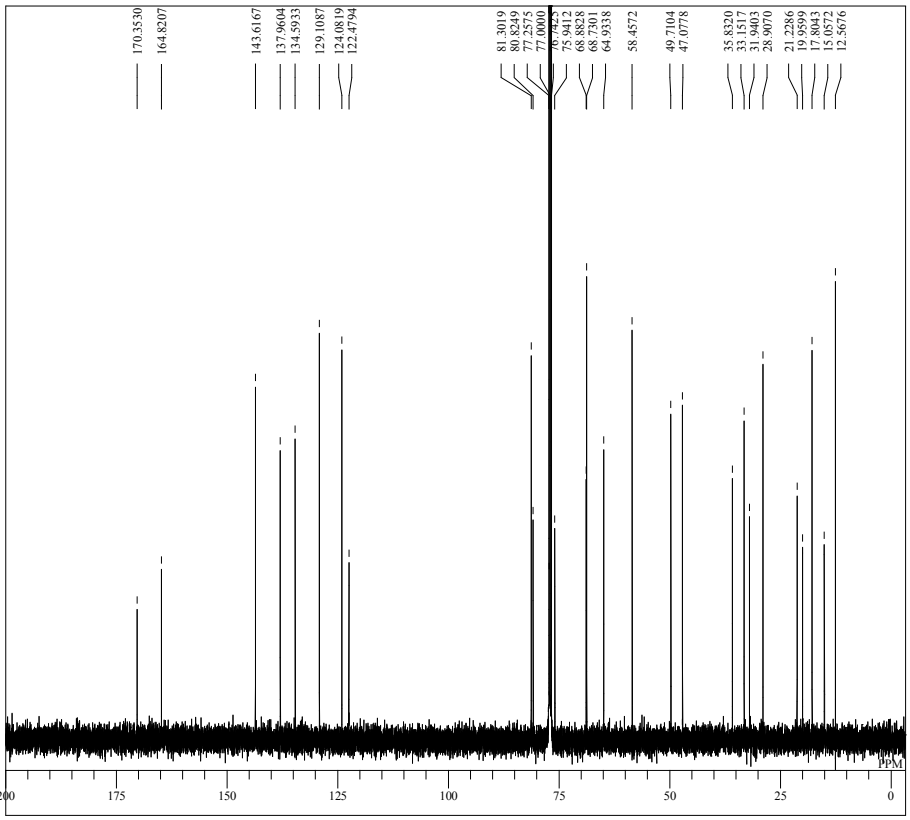


DFILE muchikan OAc yuudoutai_proton-1-1.als
COMNT single_pulse
DATIM 2019-09-04 21:13:03
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 26214
FREQU 7507.51 Hz
SCANS 9
ACQTM 3.4918 sec
PD 2.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 44



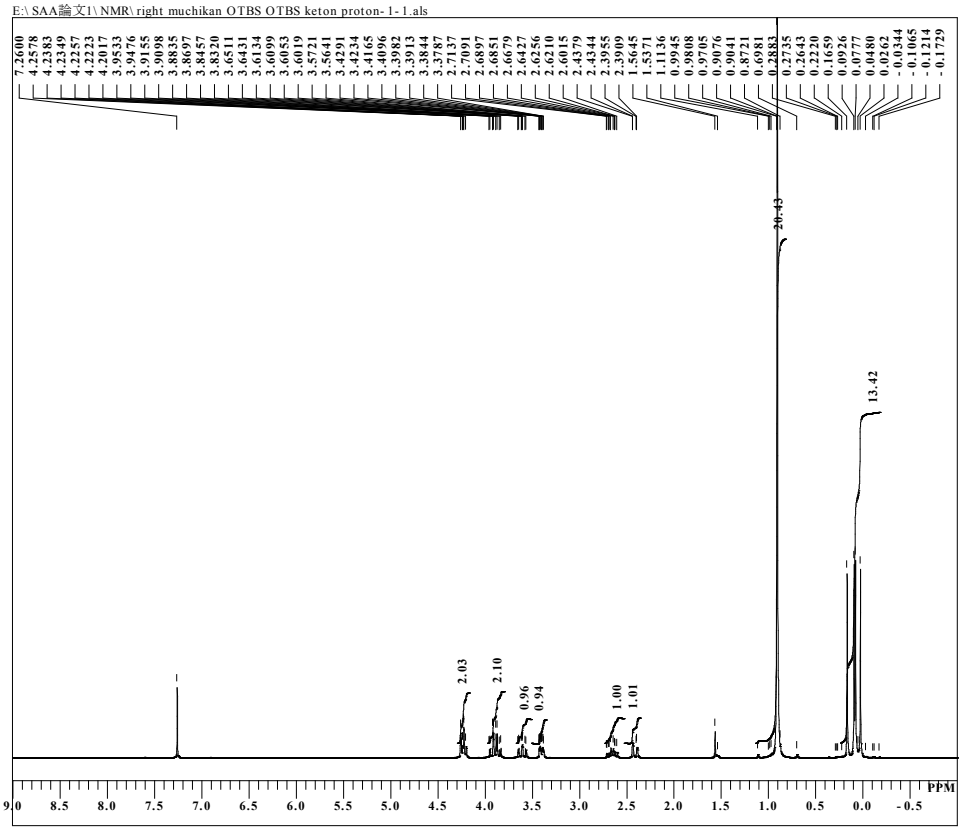
3
72% in 2 steps

single pulse decoupled gated NOE

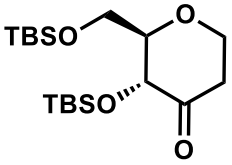


DFILE muchikan OAc yuudoutai_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-09-04 19:39:35
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 2898
ACQTM 0.8336 sec
PD 1.0000 sec
PW1 3.27 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 50

single_pulse



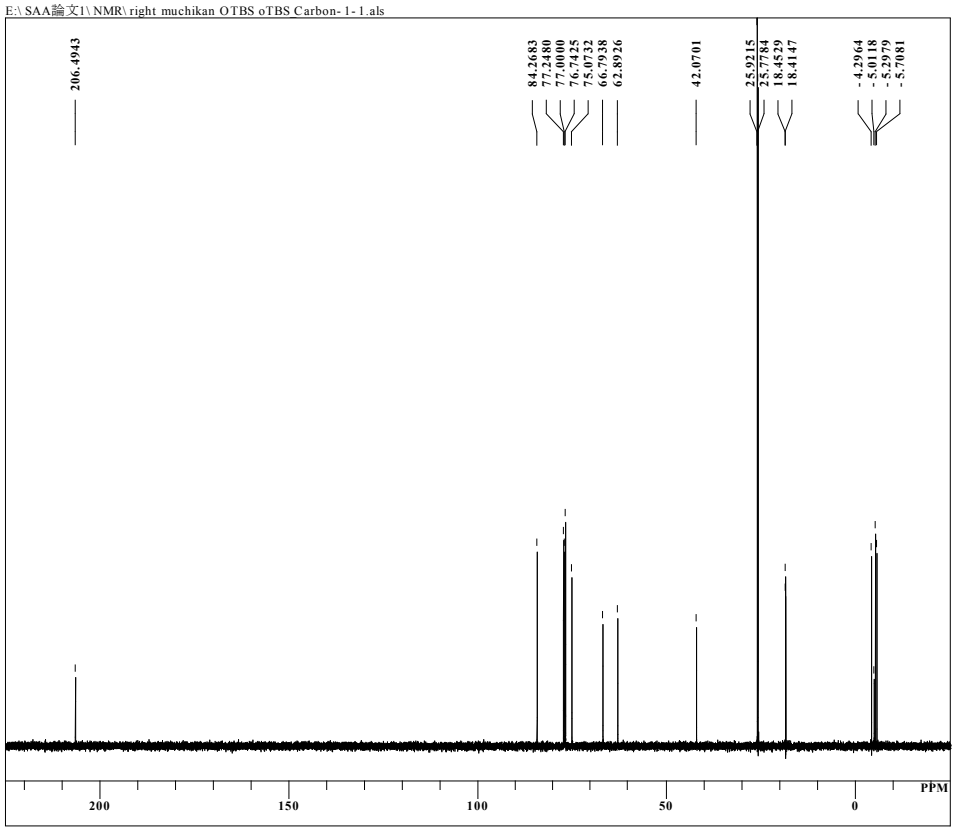
DFILE	right muchikan OTBS OTBS keton_pr
COMNT	single_pulse
DATIM	2020- 02- 04 22:00:52
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	4508.57 Hz
SCANS	12
ACQTM	2.9072 sec
PD	2.0000 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	17.8 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



I

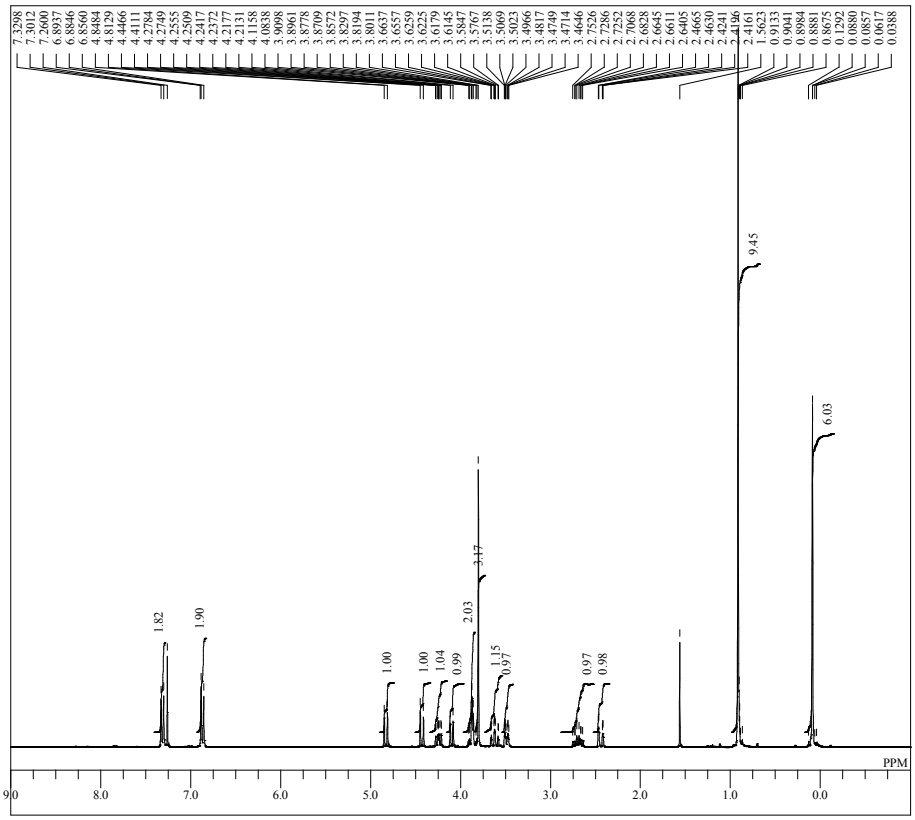
95% in 2 steps

single pulse decoupled gated NOE

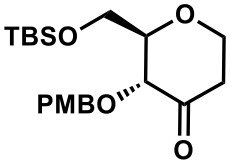


DFILE	right muchikan OTBS oTBS_Carbon- 1
COMNT	single pulse decoupled gated NOE
DATIM	2020- 02- 04 21:53:45
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	62
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.27 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

single_pulse

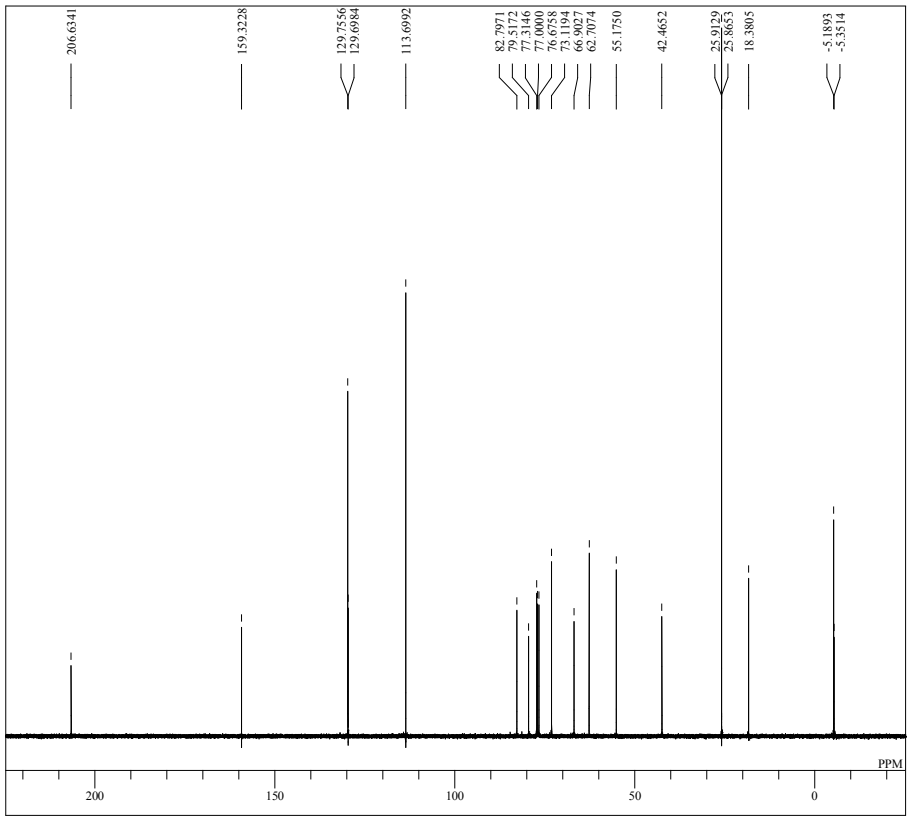


DFILE right muchikan OTBS OPMB keton_proton-1-1.als
COMNT single_pulse
DATIM 2019-07-26 14:24:51
OBNUC 1H
EXMOD proton.jxp
OBFRQ 300.53 MHz
OBSET 1.15 KHz
OBFIN 8.57 Hz
POINT 13107
FREQU 4508.57 Hz
SCANS 12
ACQTM 2.9072 sec
PD 1.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 42



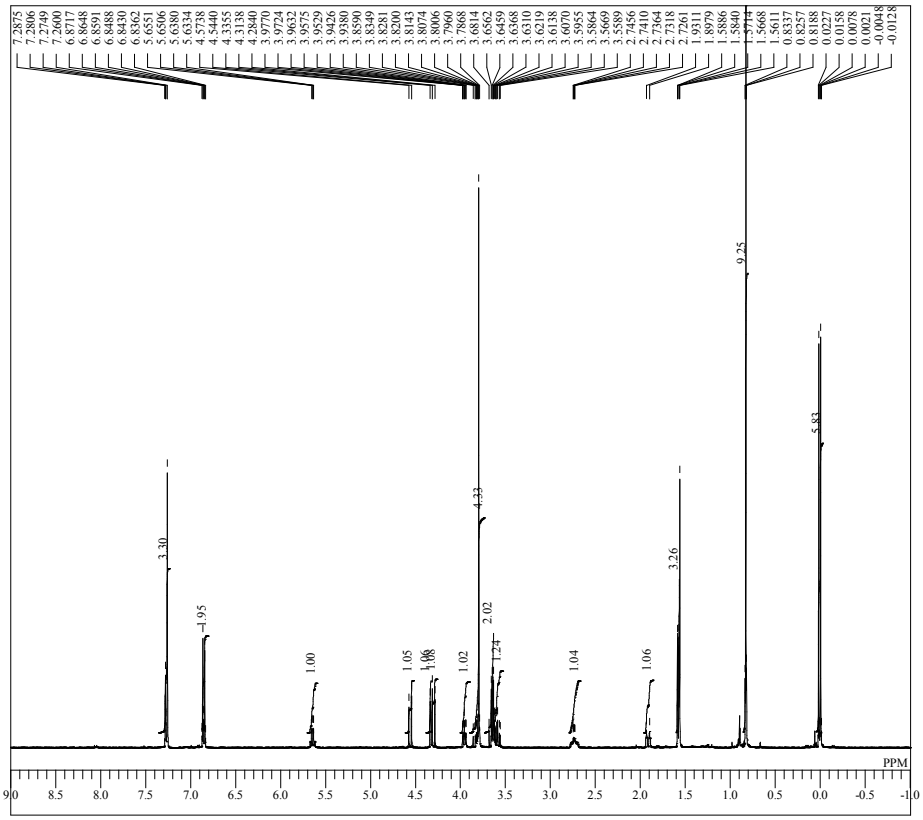
18
64% in 3 steps

single pulse decoupled gated NOE

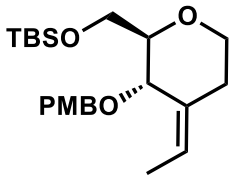


DFILE right muchikan OTBS OPMB keton_carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-07-26 15:33:22
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 448
ACQTM 1.0433 sec
PD 1.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 23.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

single_pulse

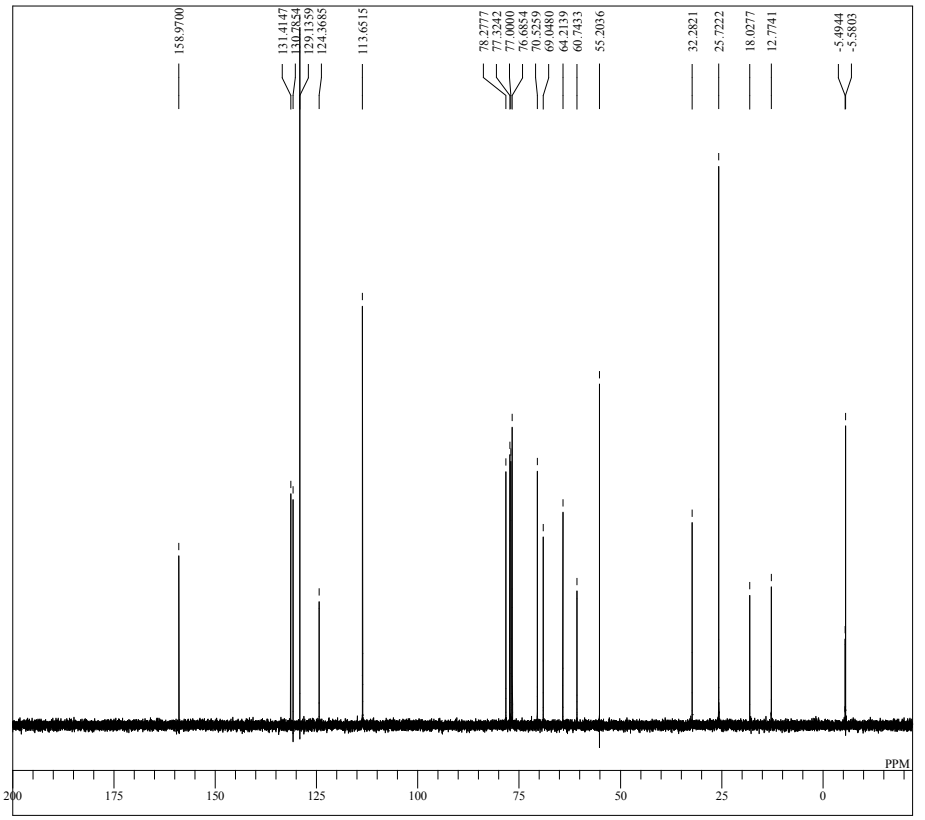


DFILE right muchikan OTBS OPMB etylolrfin shita_proton
COMNT single_pulse
DATIM 2019-07-27 17:43:37
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 8
ACQTM 2.1837 sec
PD 1.0000 sec
PW1 7.25 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 46



19
47%

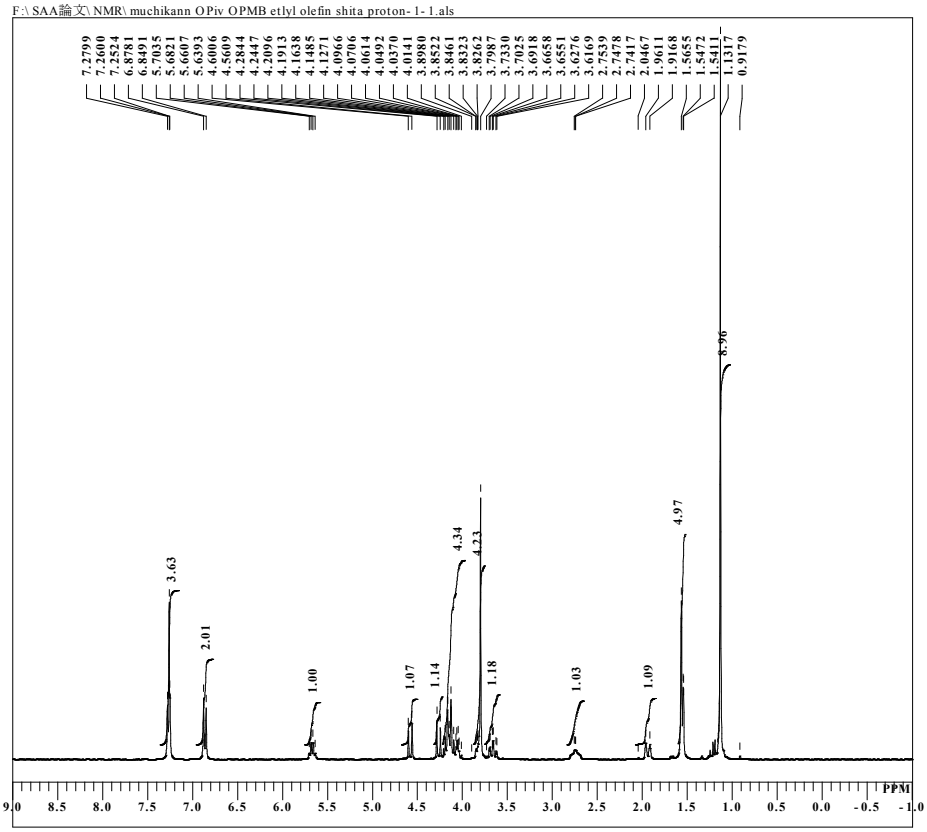
single pulse decoupled gated NOE



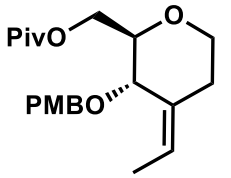
DFILE right muchikan OPMB OTBS etylolrfin shita_carbon
COMNT single pulse decoupled gated NOE
DATIM 2019-07-27 18:00:47
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 196
ACQTM 1.0433 sec
PD 1.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 22.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

single_pulse

F:\ SAA論文\ NMR\ muchikann OPiv OPMB etlyl olefin shita proton-1-1.als



DFILE	muchikann OPiv OPMB etlyl olefin shit
COMNT	single_pulse
DATIM	2019-05-29 13:31:09
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	6016.85 Hz
SCANS	20
ACQTM	2.1784 sec
PD	1.0000 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	20.4 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	1.20 Hz
RGAIN	40

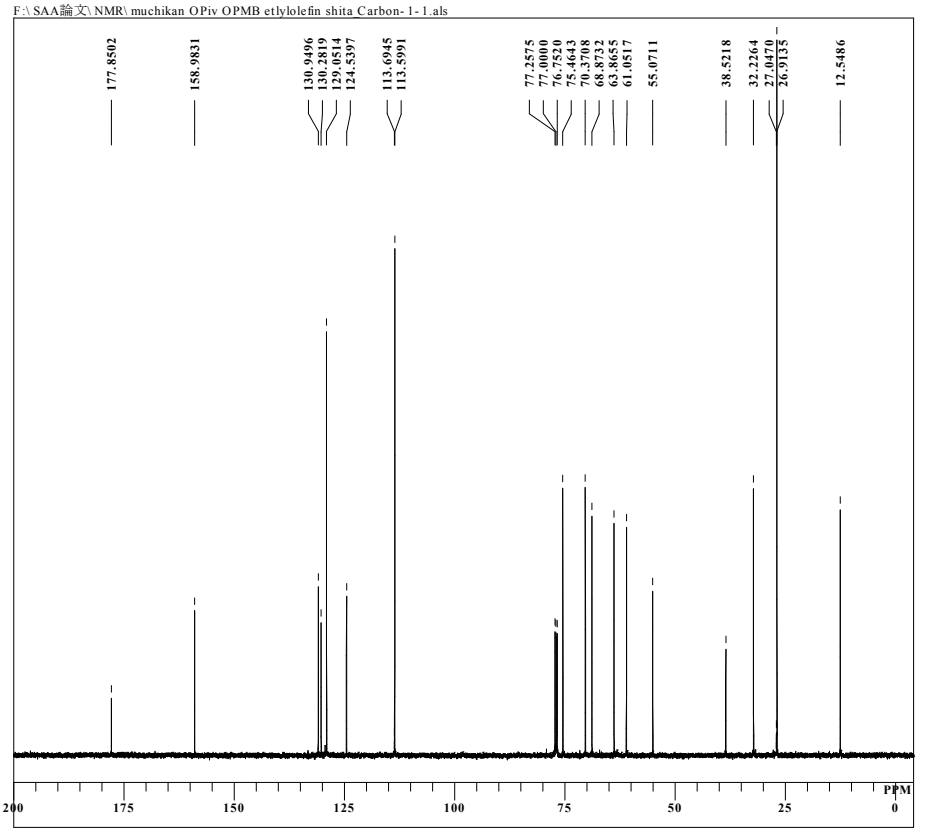


14

59% in 2 steps

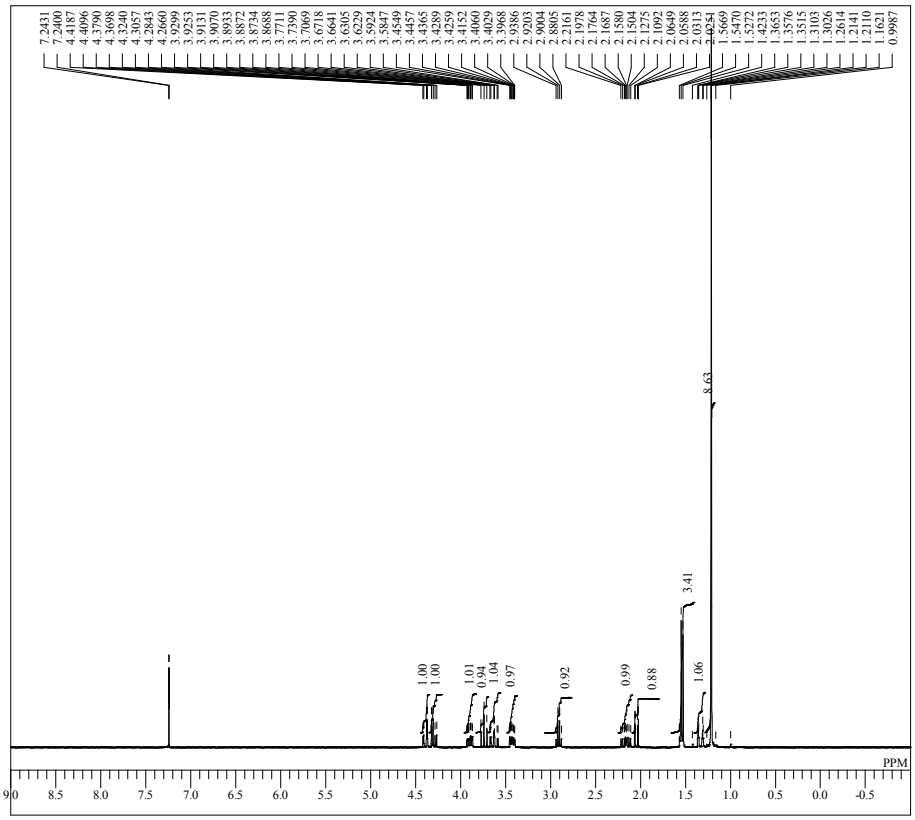
single pulse decoupled gated NOE

F:\ SAA論文\ NMR\ muchikan OPiv OPMB etlylolefin shita Carbon-1-1.als

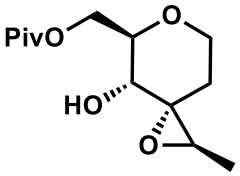


DFILE	muchikan OPiv OPMB etlylolefin shita_
COMNT	single pulse decoupled gated NOE
DATIM	2019-05-29 13:41:32
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	76
ACQTM	0.8336 sec
PD	2.0000 sec
PW1	3.27 usec
IRNUC	1H
CTEMP	20.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.20 Hz
RGAIN	58

single_pulse



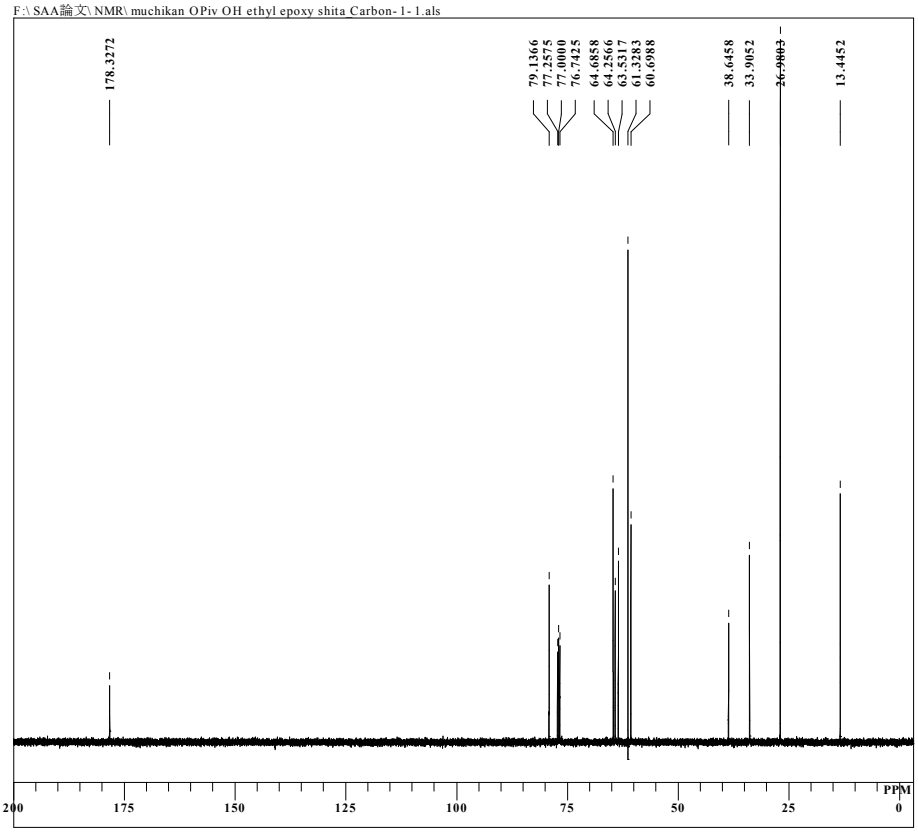
DFILE muchikan OPiv OH ethylolefin shita_proton-1-1.als
COMNT single_pulse
DATIM 2019-05-30 18:21:44
OBNUC 1H
EXMOD proton.jxp
OBFRQ 300.53 MHz
OBSET 1.15 KHz
OBFIN 8.57 Hz
POINT 13107
FREQU 6016.85 Hz
SCANS 16
ACQTM 2.1784 sec
PD 1.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 40



22
95% in 2 steps

single pulse decoupled gated NOE

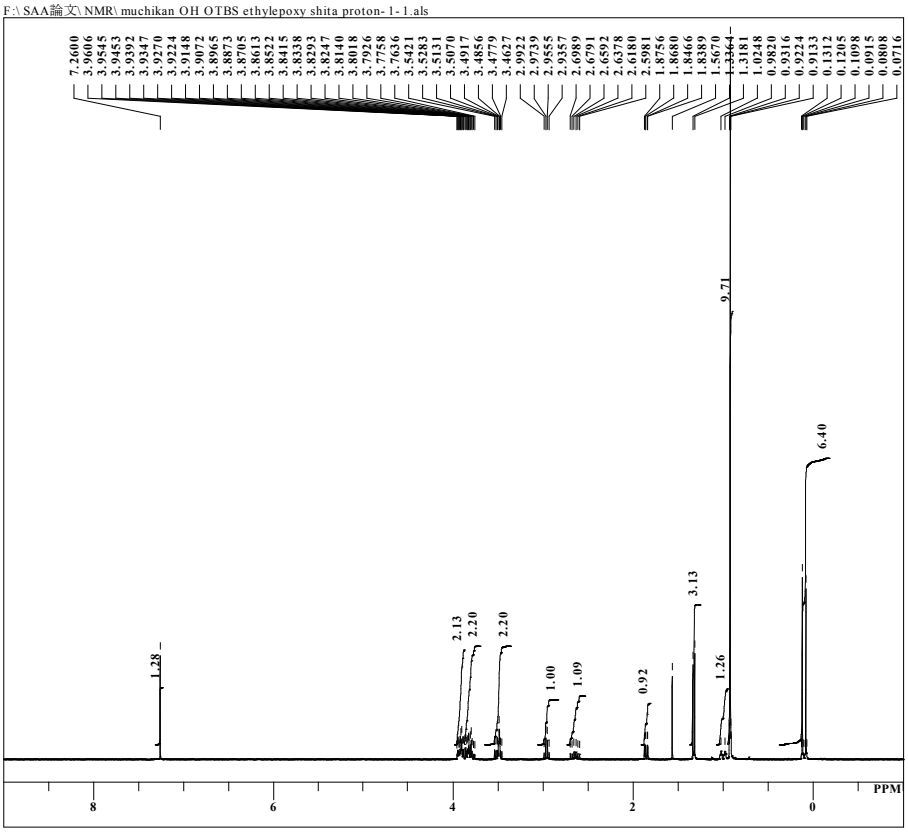
F:\ SAA論文\ NMR\ muchikan OPiv OH ethyl epoxy shita Carbon-1-1.als



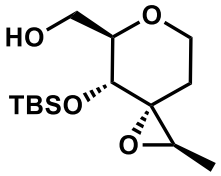
DFILE muchikan OPiv OH ethyl epoxy shita_C
COMNT single pulse decoupled gated NOE
DATIM 2019-05-30 20:21:51
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 43
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.27 usec
IRNUC 1H
CTEMP 20.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

single_pulse

F:\ SAA論文\ NMR\ muchikan OH OTBS ethylepoxy shita proton-1-1.als

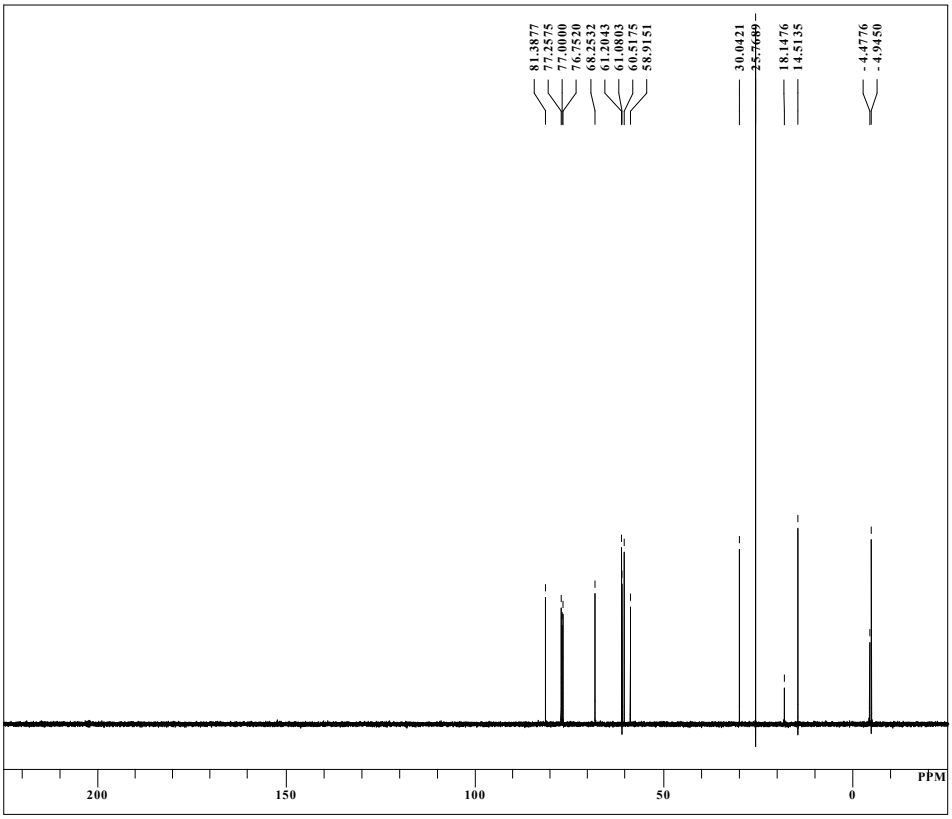


DFILE	muchikan OH OTBS ethylepoxy shita_p
COMNT	single_pulse
DATIM	2019-05-31 21:44:56
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	6016.85 Hz
SCANS	13
ACQTM	2.1784 sec
PD	1.0000 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	20.6 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



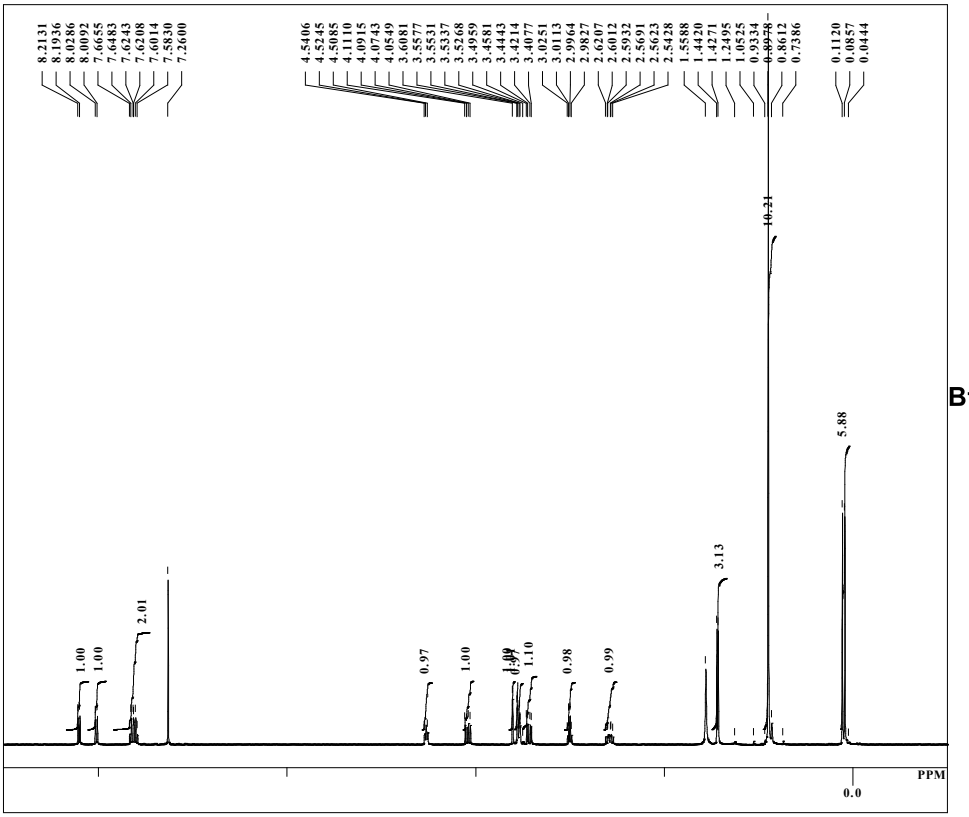
25
66% in 2 steps

single pulse decoupled gated NOE

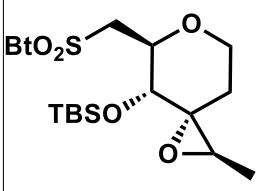


DFILE	muchikan OH OTBS ethylepoxy shita
COMNT	single pulse decoupled gated NOE
DATIM	2019-06-05 22:56:55
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	96
ACQTM	0.8336 sec
PD	1.0000 sec
PW1	3.27 usec
IRNUC	1H
CTEMP	21.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

single_pulse

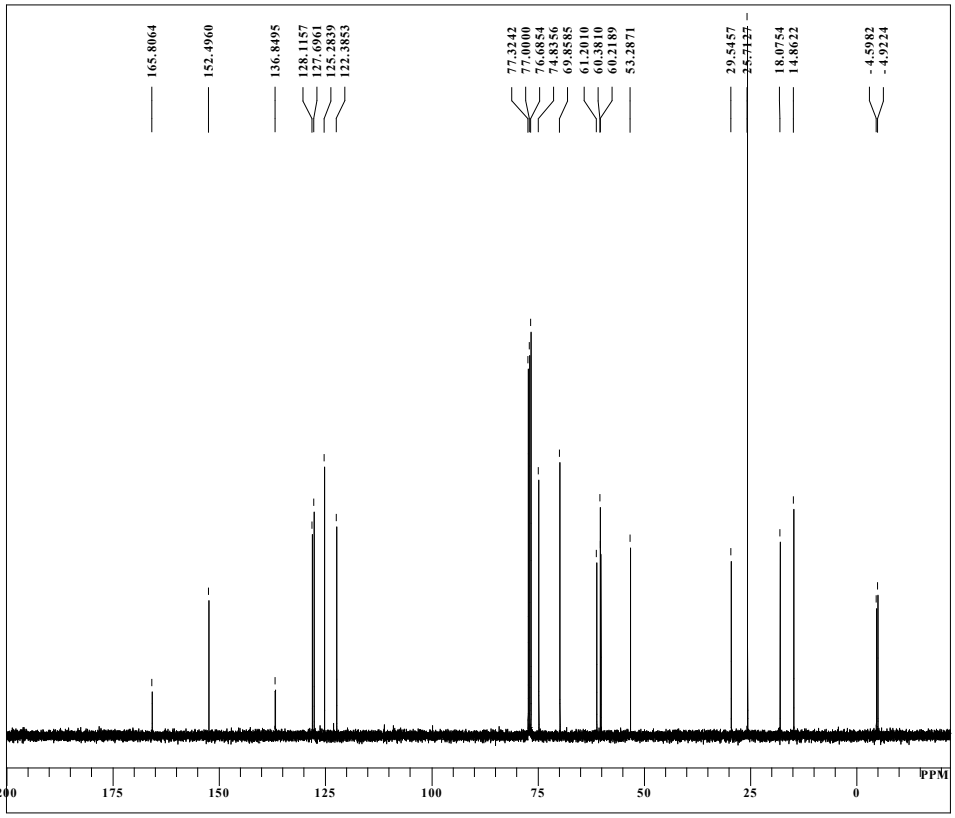


DFILE right muchikan shita SO2Bt OTBS ep
COMNT single_pulse
DATIM 2019-12-30 15:14:53
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 10
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 6.65 usec
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 40



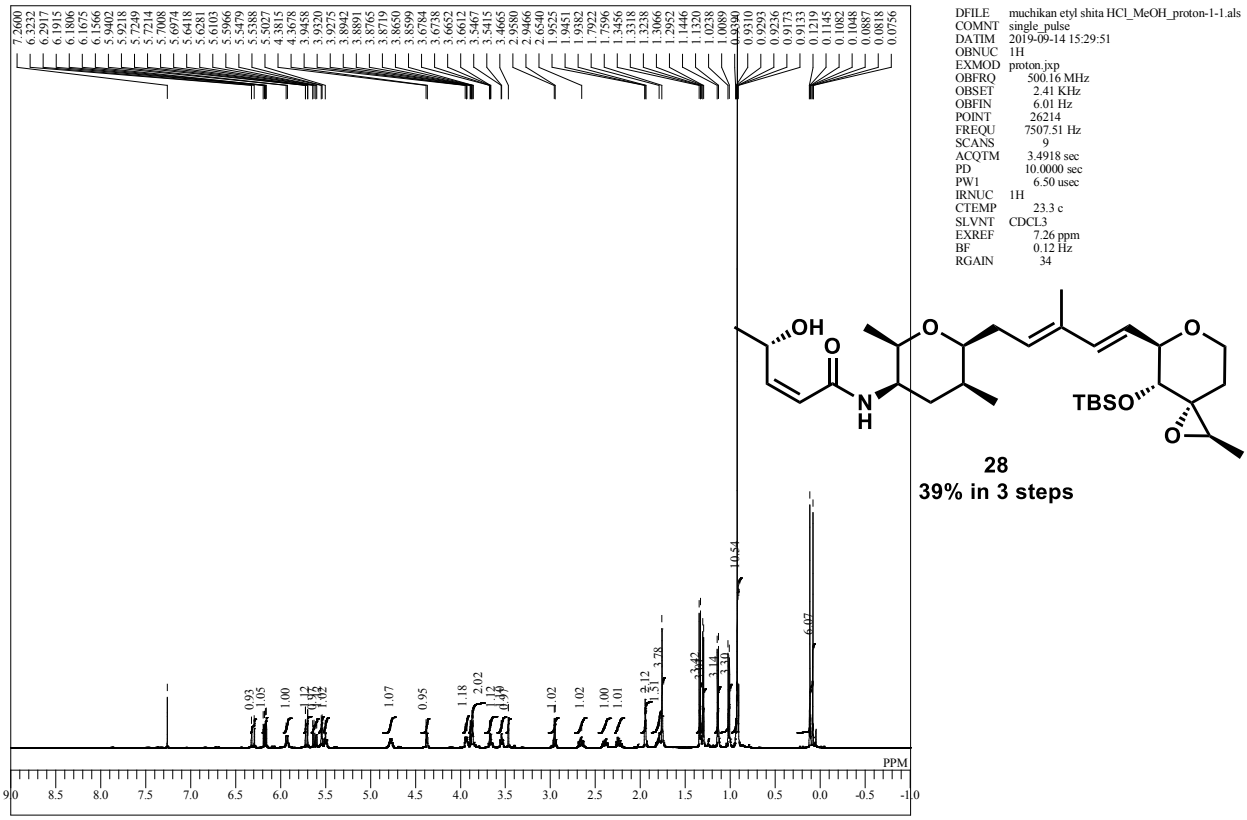
7
78% in 2 steps

single pulse decoupled gated NOE

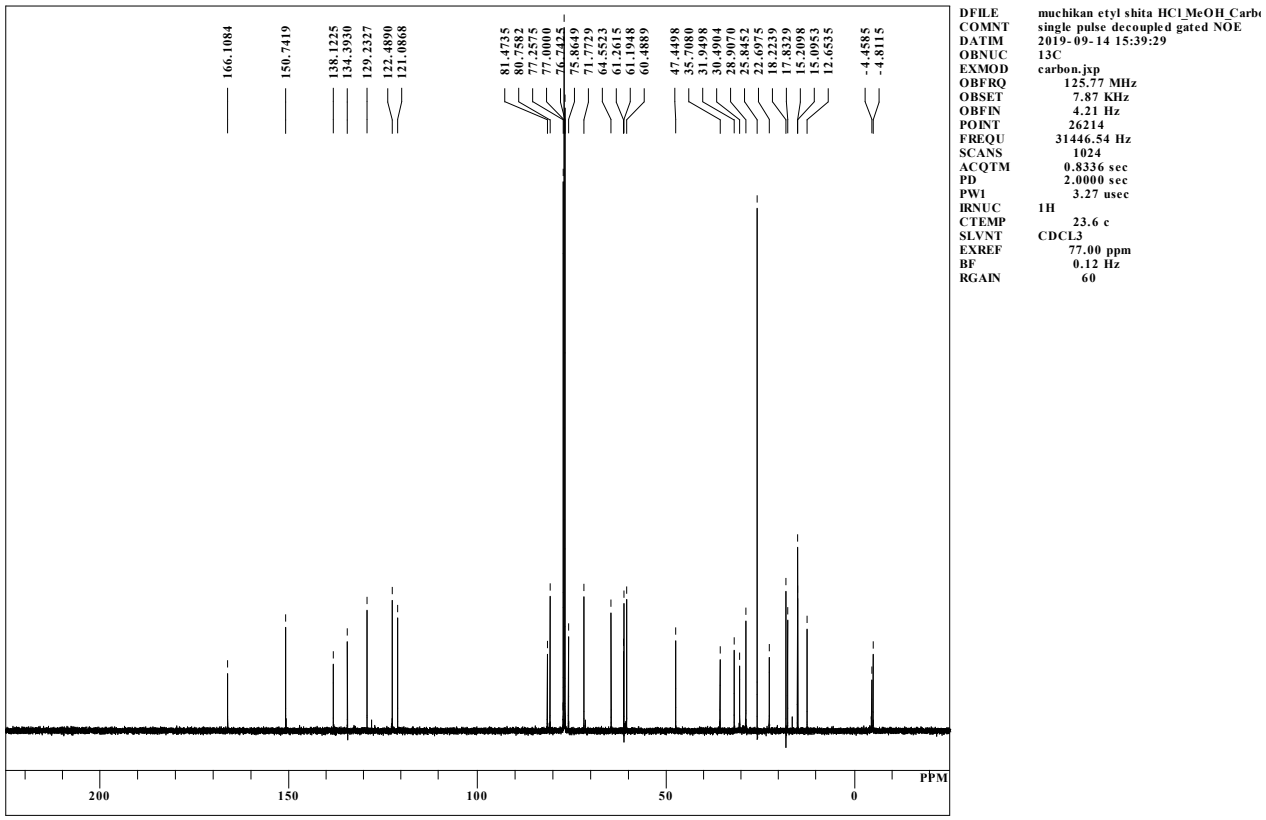


DFILE right muchikan shita SO2Bt OTBS ep
COMNT single pulse decoupled gated NOE
DATIM 2019-12-30 15:38:19
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 274
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.40 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

single_pulse

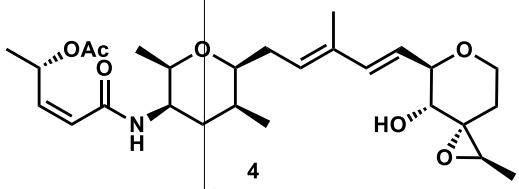


single pulse decoupled gated NOE



single_pulse

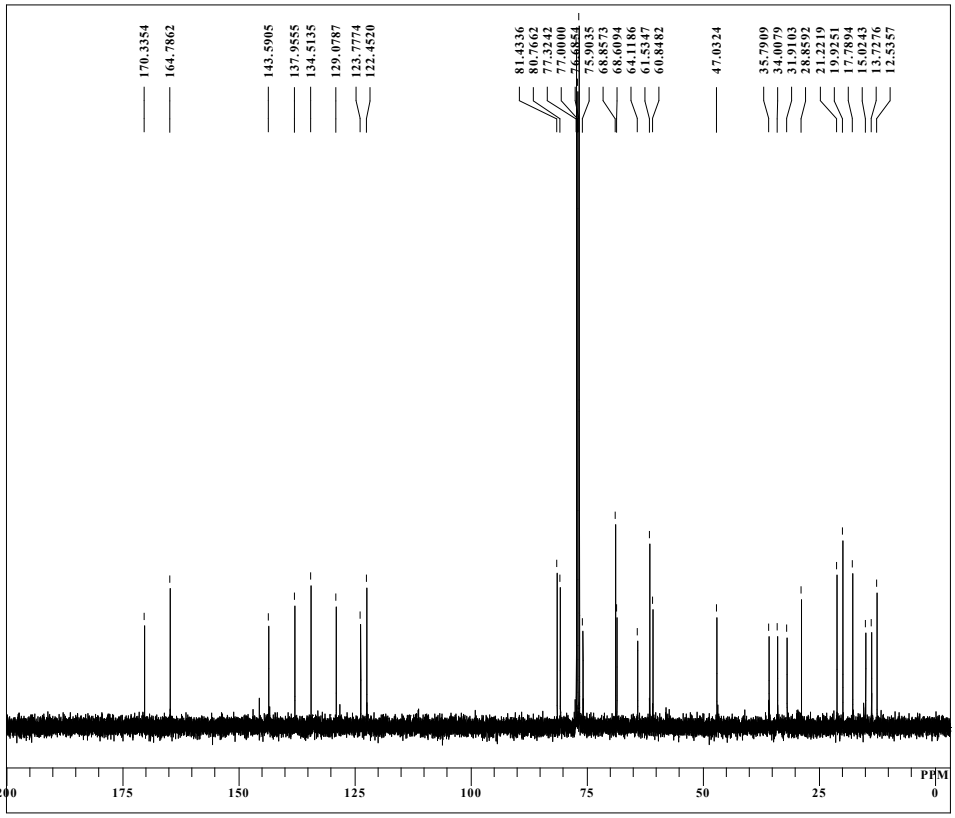
DFILE	muchikan-yuudoutai shita_proton-1-1
COMNT	single_pulse
DATIM	2019-12-30 21:05:03
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	13
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	6.65 usec
IRNUC	1H
CTEMP	19.9 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	34



4

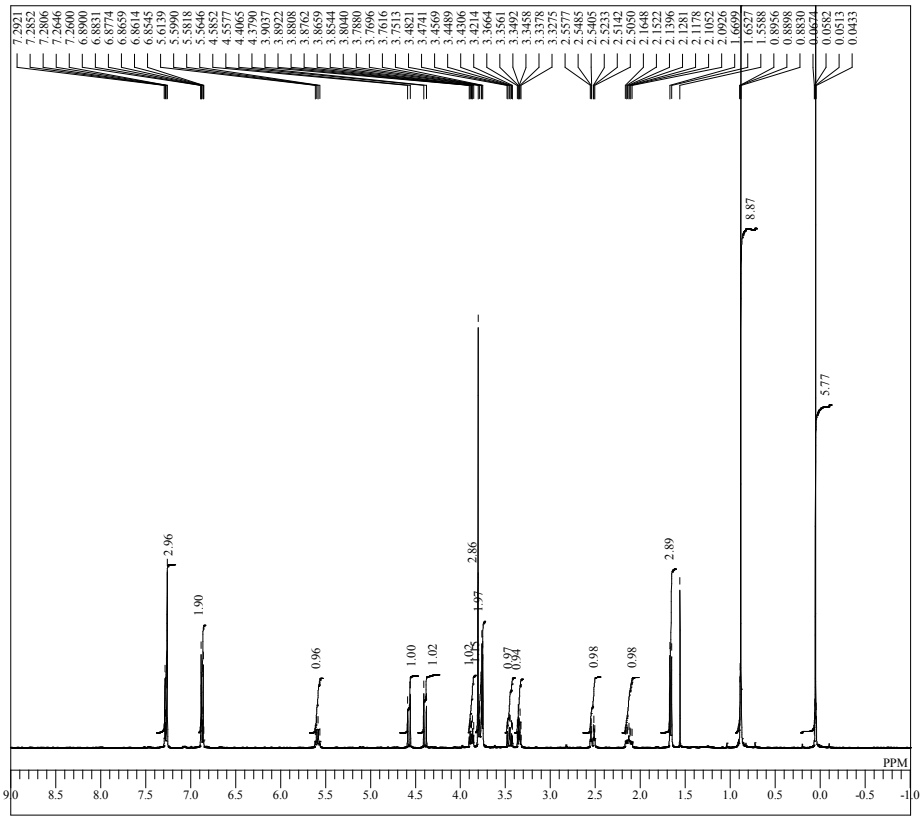
82% in 2 steps

single pulse decoupled gated NOE

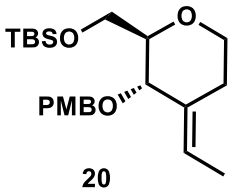


DFILE	muchikan-yuudoutai shita_carbon-1-1
COMNT	single pulse decoupled gated NOE
DATIM	2019-12-30 21:38:60
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	294
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.40 usec
IRNUC	1H
CTEMP	20.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

single_pulse

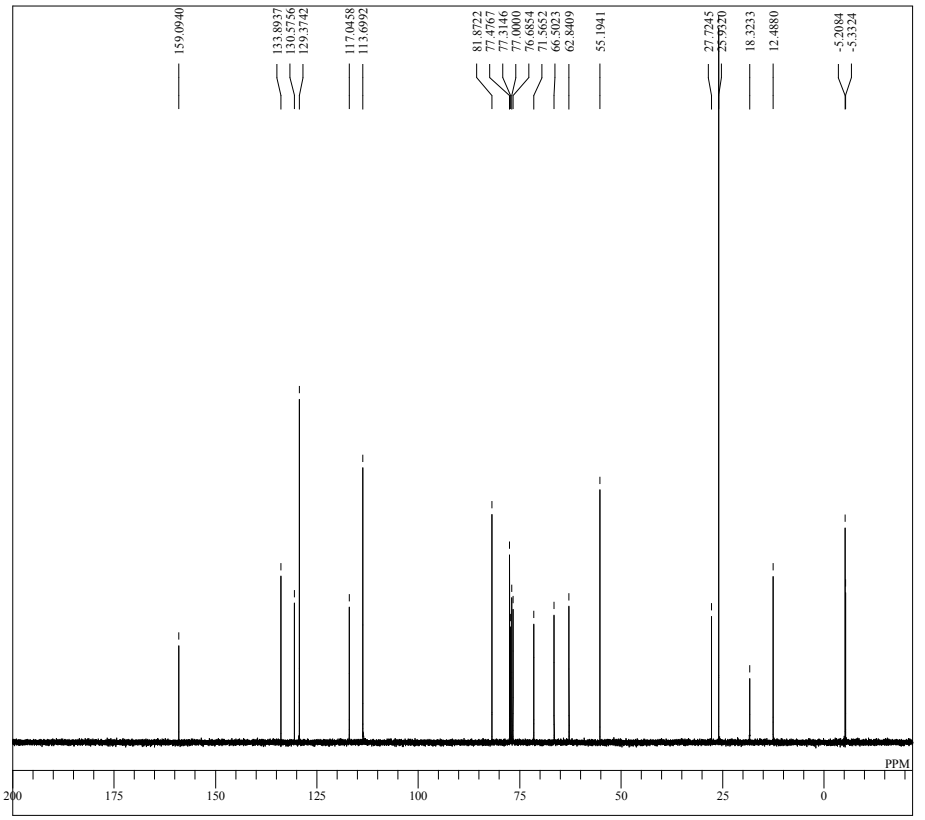


DFILE right muchikan OTBS OPMB etylolefin ue_proton-1
COMNT single_pulse
DATIM 2019-07-26 21:01:06
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 13107
FREQU 6002.40 Hz
SCANS 12
ACQTM 2.1837 sec
PD 2.0000 sec
PW1 7.25 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 44



20
47%

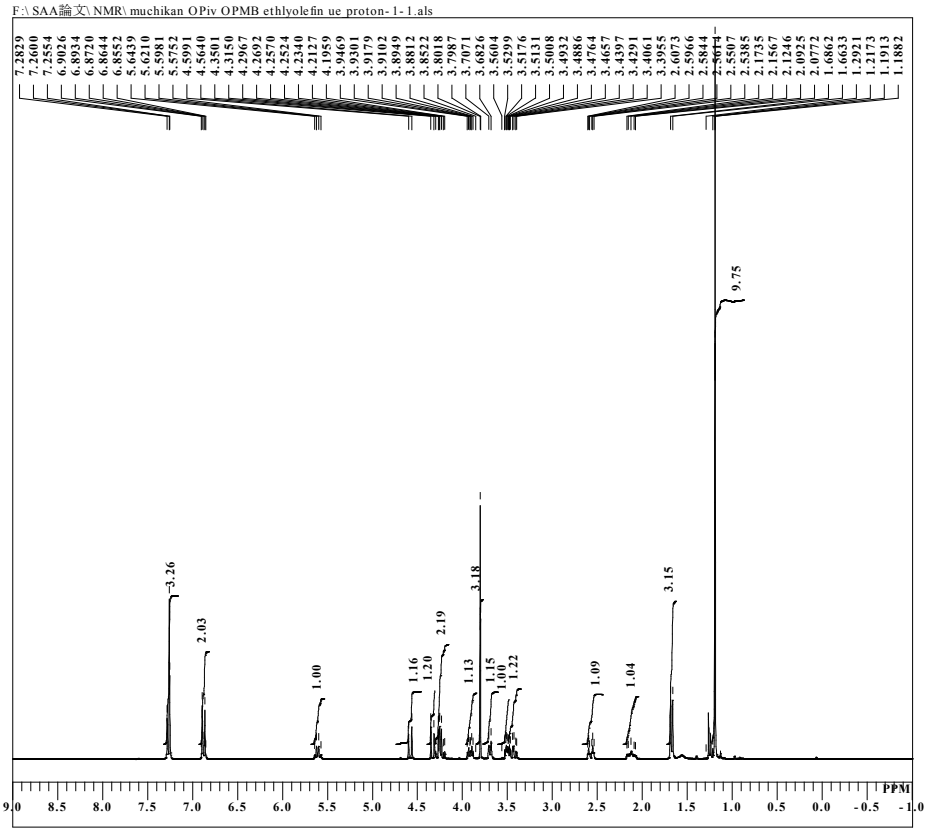
single pulse decoupled gated NOE



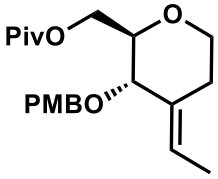
DFILE right muchikan OPMB OTBS etylolefin ue_carbon-1
COMNT single pulse decoupled gated NOE
DATIM 2019-07-26 21:28:09
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 26214
FREQU 25125.63 Hz
SCANS 160
ACQTM 1.0433 sec
PD 1.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 23.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

single_pulse

F:\ SAA論文\ NMR\ muchikan OPiv OPMB ethlyolefin ue proton-1-1.als



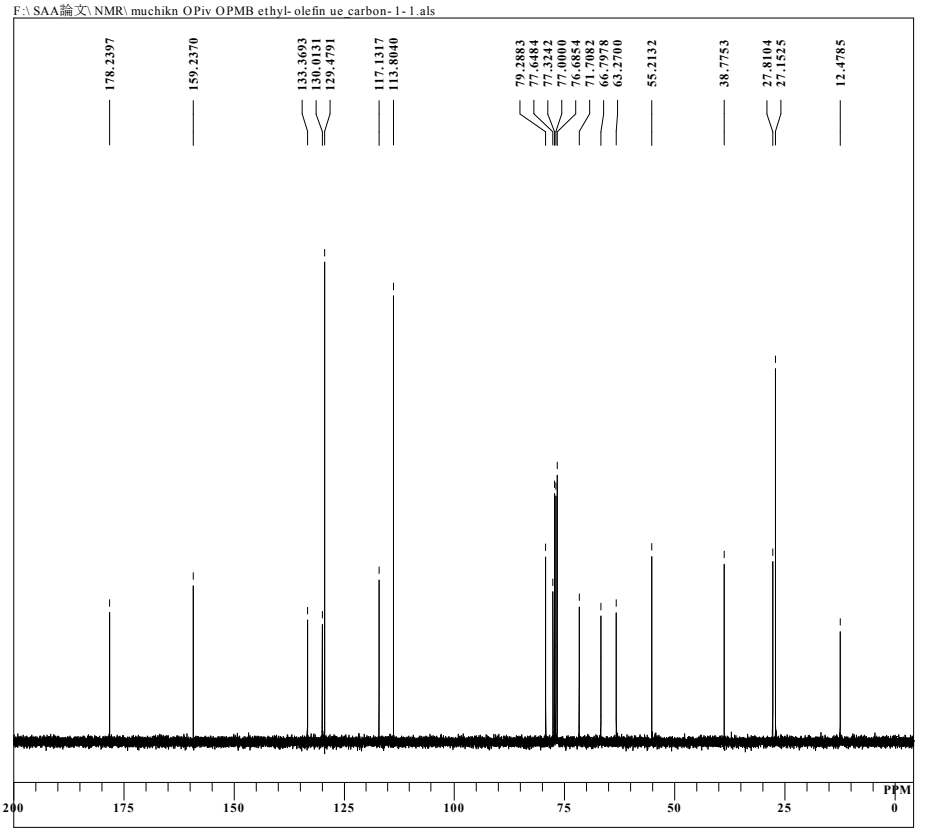
DFILE	muchikan OPiv OPMB ethlyolefin ue_p
COMNT	single_pulse
DATIM	2019-05-29 21:53:58
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	6016.85 Hz
SCANS	16
ACQTM	2.1784 sec
PD	1.0000 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	20.0 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	38



15
74% in 2 steps

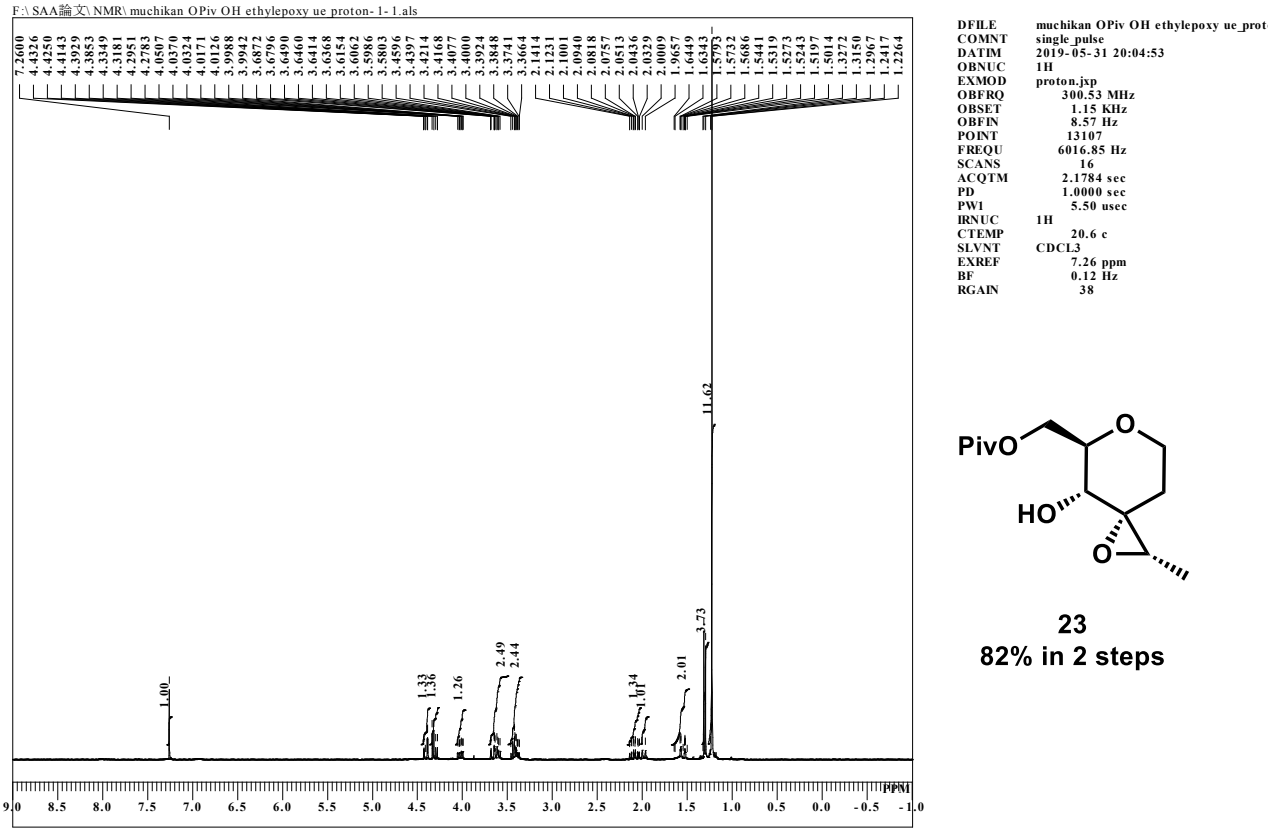
single pulse decoupled gated NOE

F:\ SAA論文\ NMR\ muchikn OPiv OPMB ethyl-olefin ue carbon-1-1.als

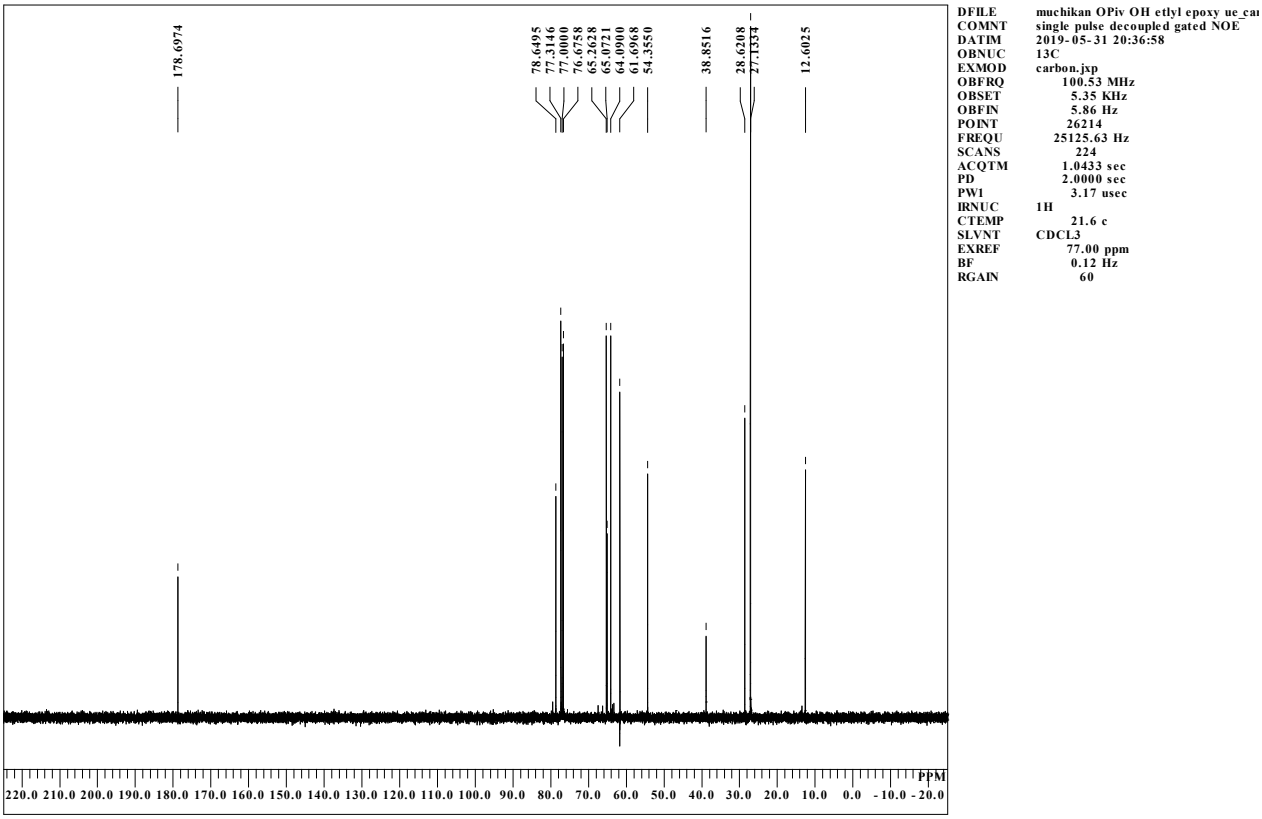


DFILE	muchikn OPiv OPMB ethyl-olefin ue_c
COMNT	single pulse decoupled gated NOE
DATIM	2019-06-10 22:52:42
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	85
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

single_pulse

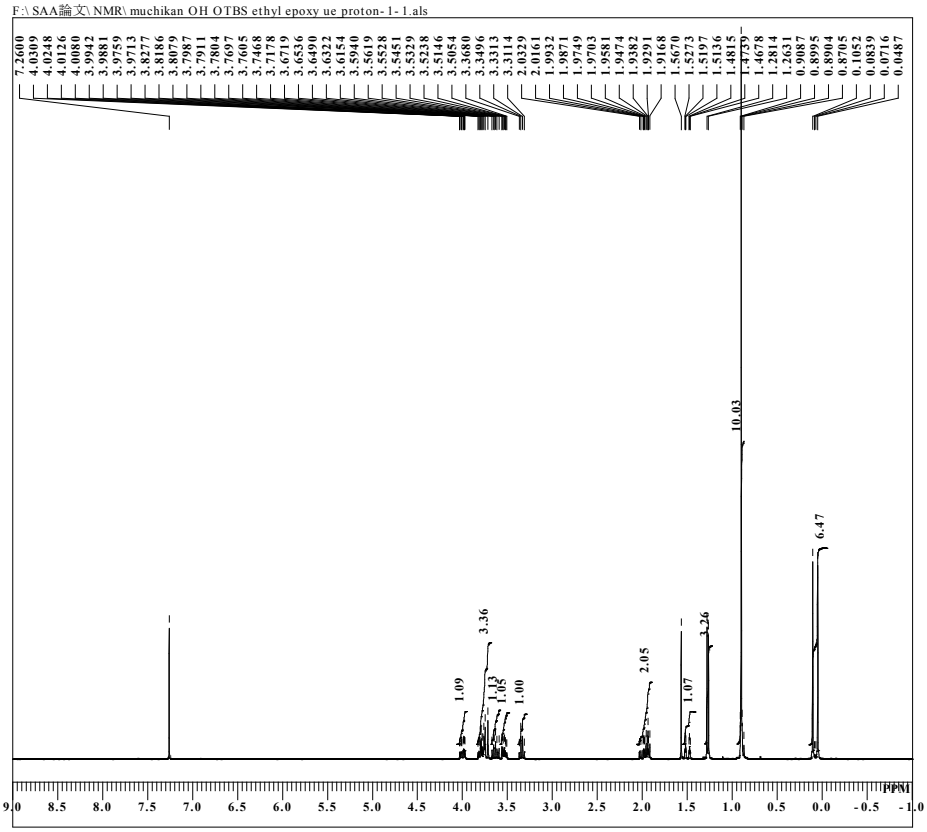


single pulse decoupled gated NOE

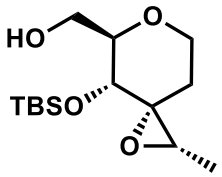


single_pulse

F:\ SAA論文\ NMR\ muchikan OH OTBS ethyl epoxy ue proton- 1- 1.als



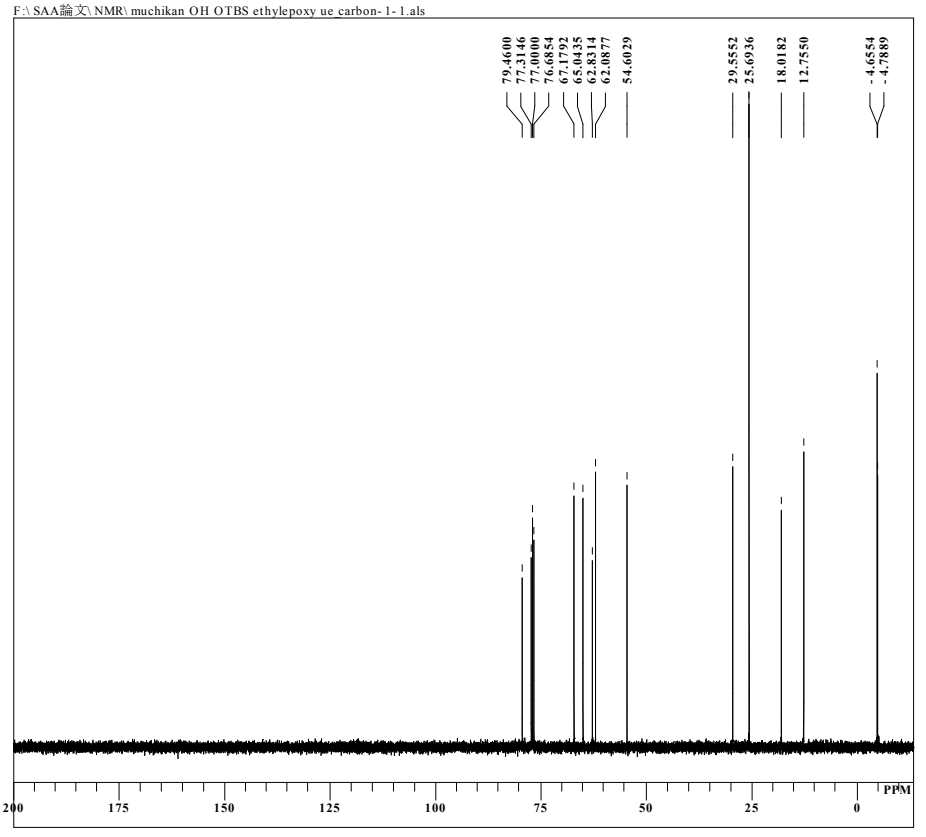
DFILE	muchikan OH OTBS ethyl epoxy ue_pr
COMNT	single_pulse
DATIM	2019-06-04 22:34:35
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	300.53 MHz
OBSET	1.15 KHz
OBFIN	8.57 Hz
POINT	13107
FREQU	6016.85 Hz
SCANS	11
ACQTM	2.1784 sec
PD	1.0000 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	21.1 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



26
64% in 2 steps

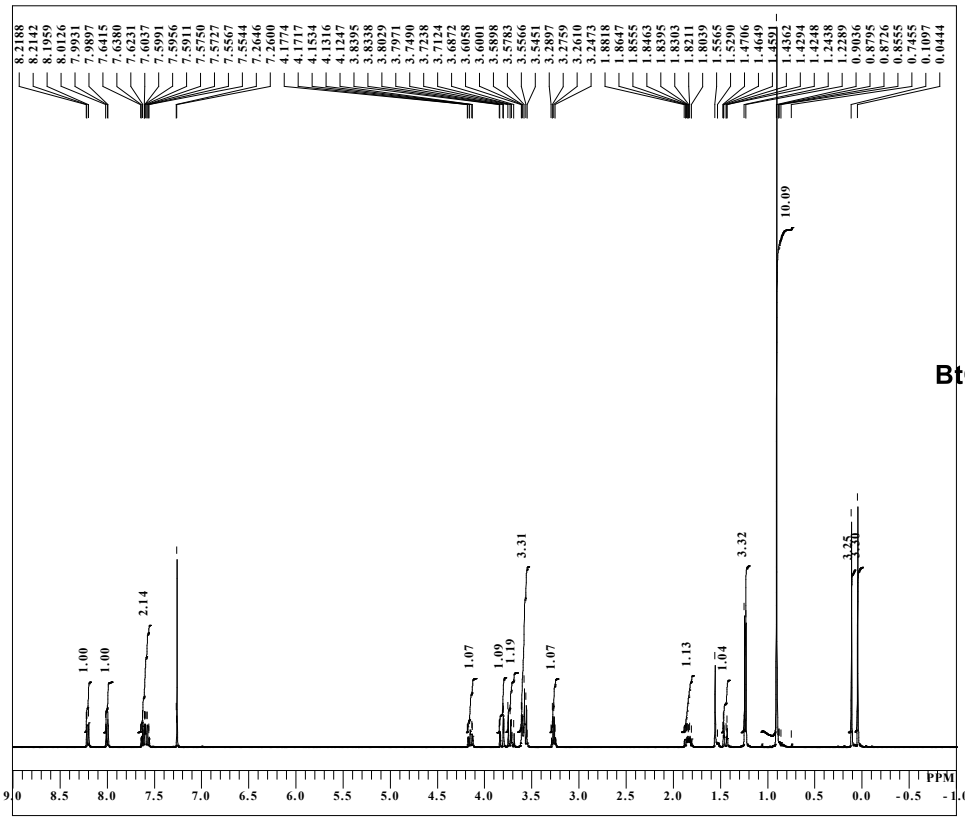
single pulse decoupled gated NOE

F:\ SAA論文\ NMR\ muchikan OH OTBS ethylepoxy ue carbon- 1- 1.als

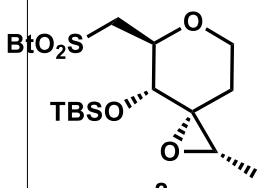


DFILE	muchikan OH OTBS ethylepoxy ue_car
COMNT	single pulse decoupled gated NOE
DATIM	2019-06-04 23:07:05
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.53 MHz
OBSET	5.35 KHz
OBFIN	5.86 Hz
POINT	26214
FREQU	25125.63 Hz
SCANS	59
ACQTM	1.0433 sec
PD	2.0000 sec
PW1	3.17 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

single_pulse



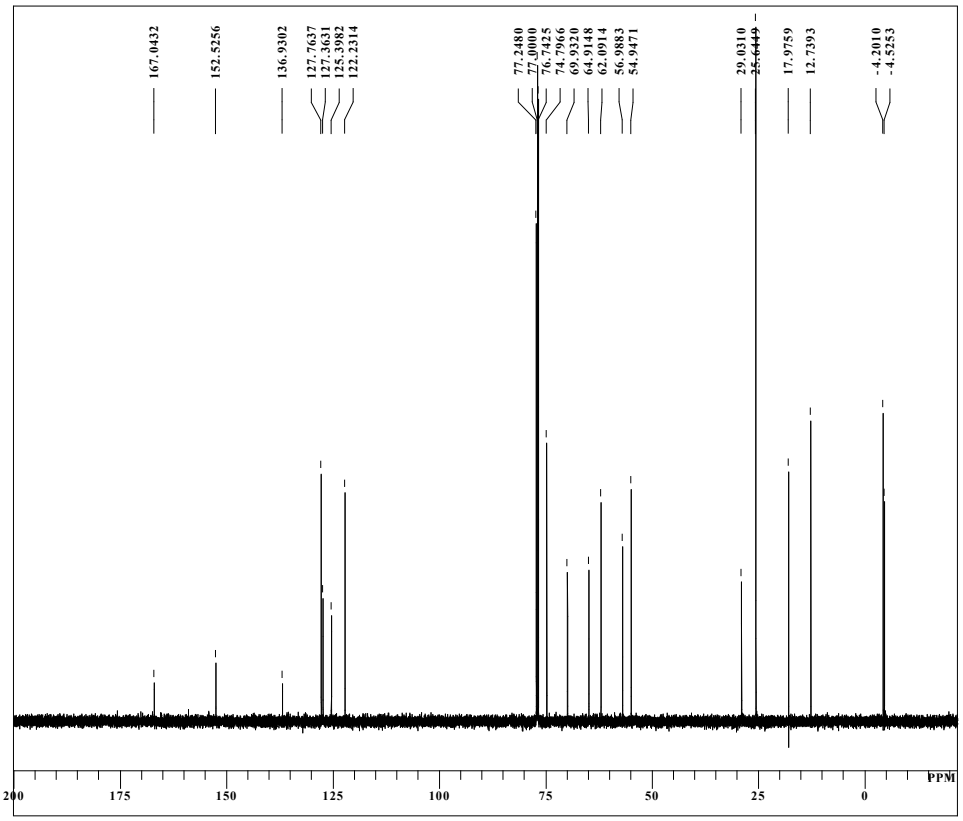
DFILE	right muchikan ue So2Bt-OTBS epox
COMNT	single_pulse
DATIM	2019-12-05 23:13:40
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	13107
FREQU	6002.40 Hz
SCANS	7
ACQTM	2.1837 sec
PD	2.0000 sec
PW1	6.65 usec
IRNUC	1H
CTEMP	20.6 c
SLVNT	CDCL3
EXREF	7.26 ppm
BF	0.12 Hz
RGAIN	40



8

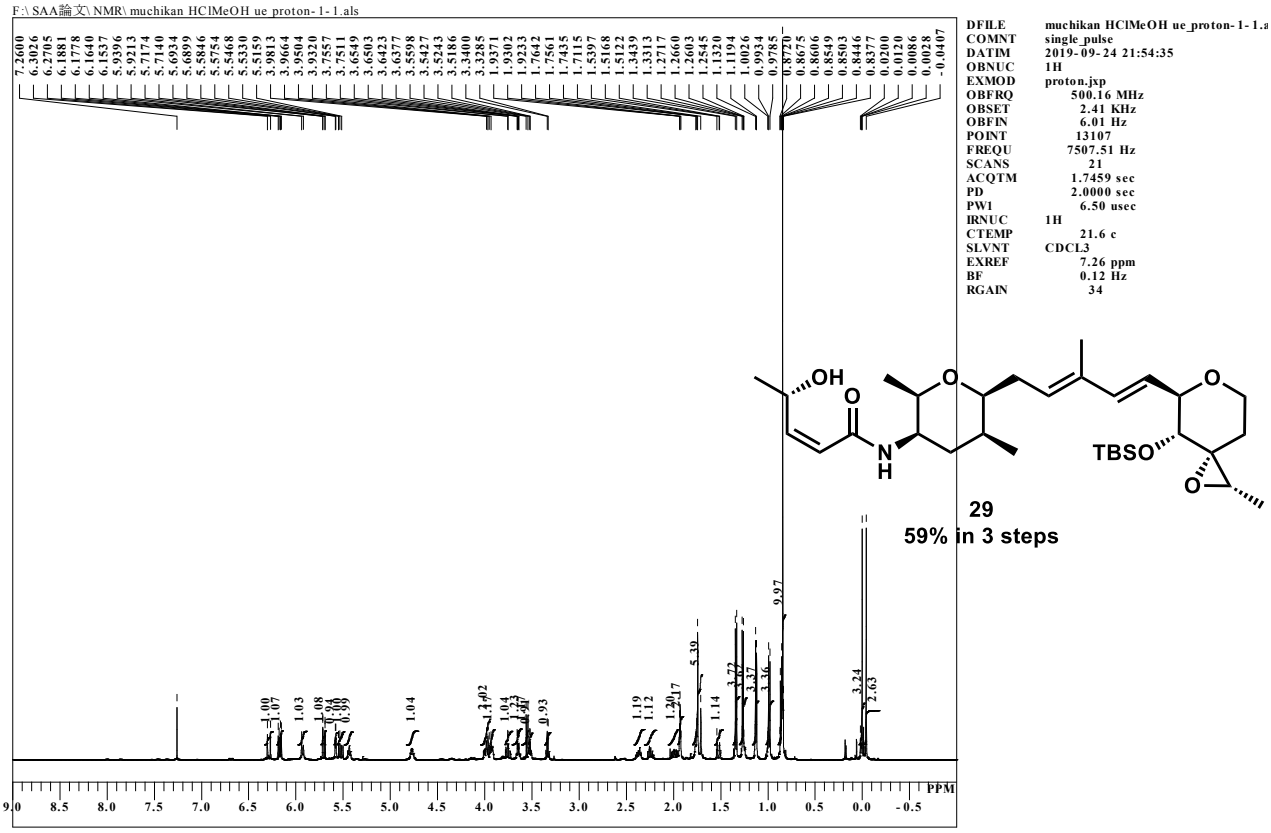
69% in 2 steps

single pulse decoupled gated NOE

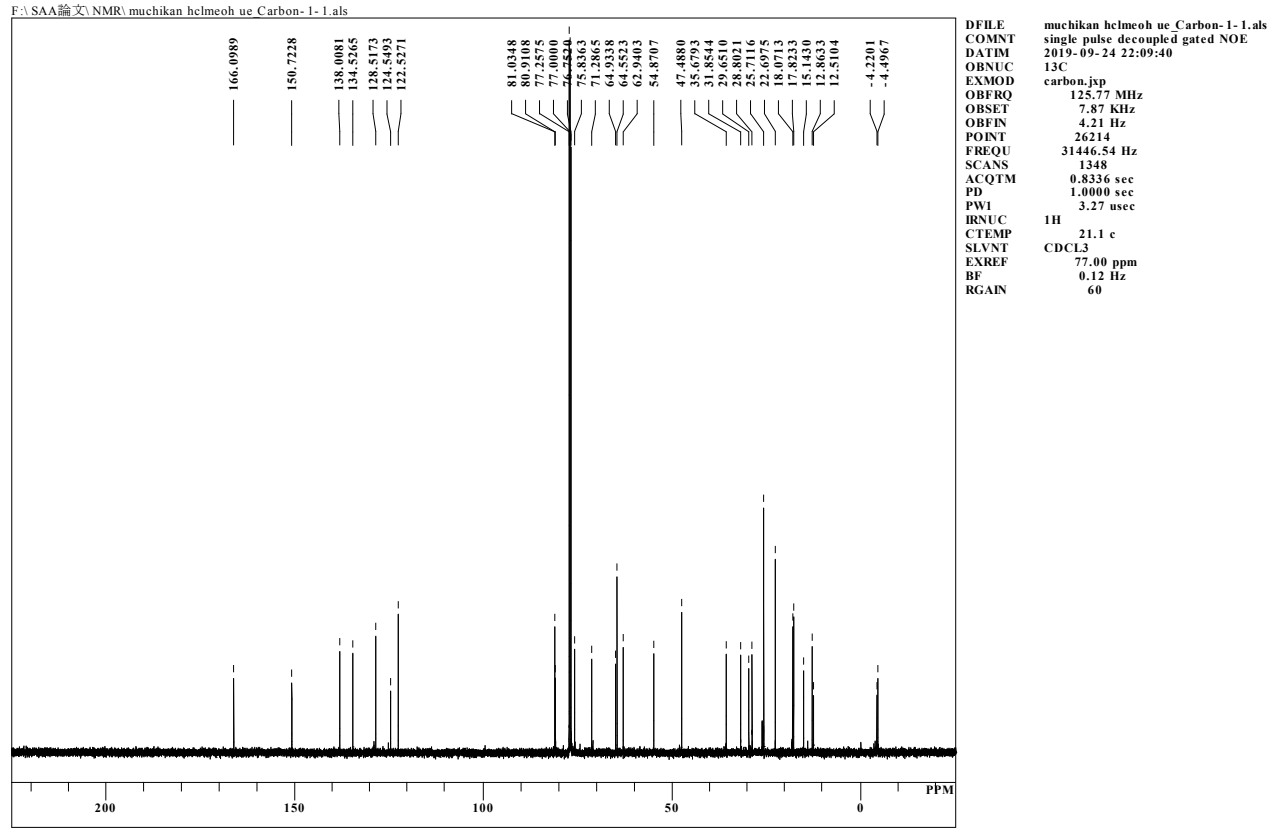


DFILE	right muchikan ue SO2Bt OTBS epox
COMNT	single pulse decoupled gated NOE
DATIM	2019-12-05 22:52:51
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	125.77 MHz
OBSET	7.87 KHz
OBFIN	4.21 Hz
POINT	26214
FREQU	31446.54 Hz
SCANS	336
ACQTM	0.8336 sec
PD	1.0000 sec
PW1	3.27 usec
IRNUC	1H
CTEMP	21.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	60

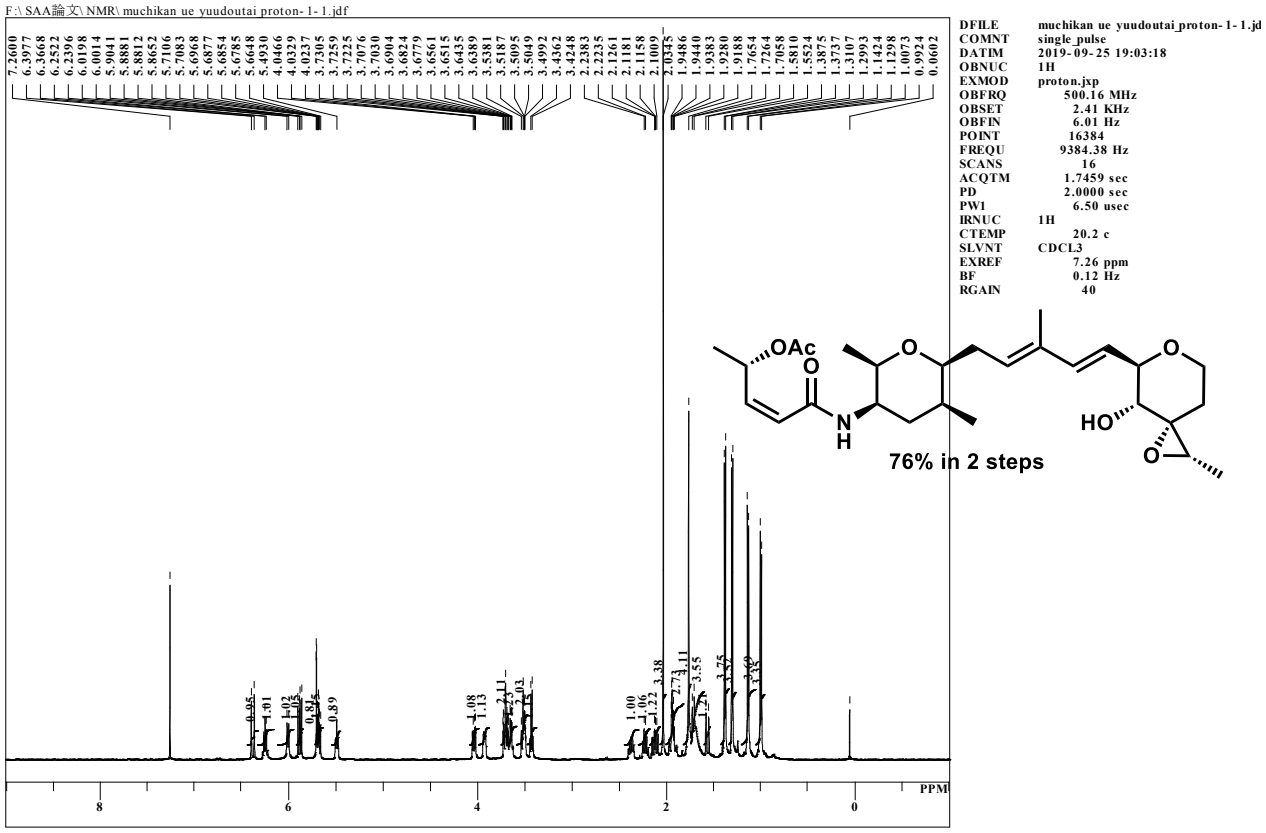
single_pulse



single pulse decoupled gated NOE



single_pulse



single pulse decoupled gated NOE