General Procedures and Methods.

NMR spectra were recorded on a Bruker DMX 500, AM 500, or AM 400 spectrometer. Chemical shifts are reported in parts per million (ppm). For ^{1}H NMR spectra, the central residual solvent peak (methanol, DMSO and chloroform) was used as the internal reference (3.30, 2.49 and 7.25 ppm) while the central solvent peak as the reference (49.0, 39.5 and 77.0 ppm, respectively) for ^{13}C NMR spectra. Fast atom bombardment (FAB) mass spectra were obtained with 3-nitrobenzyl alcohol or glycerol as the matrix. In order to save space, spectroscopic data is reported only selected compounds. Analytical thin layer chromatography (TLC) was performed with E. Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on E. Merck kieselgel 60 (230-400) mesh silica gel. Preparative thin layer chromatography (PTLC) separations were performed on E. Merck pre-coated plates, silica gel 60F-254, layer thickness 0.50 mm. Reagents and solvents are commercial grade and were used as supplied, with the following exceptions. Benzene, ether, and THF were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from phosphorus pentoxide, and toluene was distilled from sodium. All reactions were conducted under an argon or nitrogen atmosphere. Reaction vessels were flame-dried or oven-dried and allowed to cool under an inert atmosphere.

A correlation of the ^{13}C NMR characteristics of the C.5-C.10 portion of oasomycin B with the ^{13}C NMR database created was conducted with the following operations.

Step 1. Carbon Chemical Shifts of Propionate Portion in Compounds **1** and **2** Estimated by the Schaller Program.

Carbon	**1**	Carbon	**2**
C.4	35.7	*C.10*	35.7
C.5	70.6	*C.9*	70.7
C.6	40.1	*C.8*	40.2
C.7	74.6	*C.7*	75.0
C.8	37.3	*C.6*	35.2
C.9	24.1	*C.5*	31.3
C.11	8.0	*C.49*	8.0
C.12	13.9	*C.48*	14.3

See text for carbon number.

Step 2. Calculation of Increments.

	Increments ($\delta_1 - \delta_2$)
C.4 - *C.10*	0.0
C.5 - *C.9*	-0.1
C.6 - *C.8*	-0.1
C.7 - *C.7*	-0.4
C.8 - *C.6*	+2.1
C.9 - *C.5*	-7.2
C.11 - *C49*	0.0
C.12 - *C48*	-0.4

Step 3. Adjustment of ^{13}C NMR Data Reported for Natural Product by Calculated Increments.

Carbon Position in Oasomycin B	Reported Chemical Shift of Oasomycin B[a]	Increments ($\delta_1 - \delta_2$)	Adjusted Chemical Shift
10	32.1	0.0	32.1
9	72.0	-0.1	71.9
8	41.4	-0.1	41.3
7	74.6	-0.4	74.2
6	34.3	+2.1	36.4
5	32.9	-7.2	25.7
49	11.2	0.0	11.2
48	12.2	-0.4	11.8

[a] See ref 2 in text of this paper.

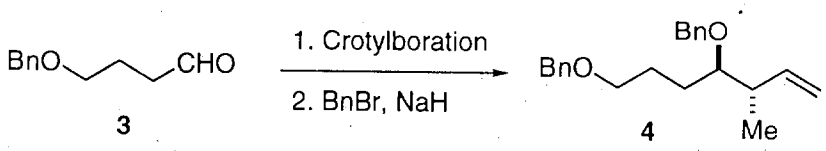
Step 4. Difference[b] between Adjusted Carbon Chemical Shifts of Oasomycin B and Those of Each of 1a~h (100MHz, $(CD_3)_2SO$).[c]

		Chemical Shift Difference $\Delta\delta = (\delta_{1a\sim h}) - (\delta_{oasomycin\ B})$							
Osaomycin B	Databse	1 a	1 b	1 c	1 d	1 e	1 f	1 g	1 h
10	4	+2.1	+2.7	+2.3	+2.5	-0.6	+1.2	-0.3	+2.1
9	5	-2.2	+0.2	-2.2	+1.8	-0.2	0.0	-0.3	+0.6
8	6	-1.5	-2.2	-2.8	-2.8	+0.3	-1.4	+0.1	-2.1
7	7	-1.0	+1.4	+2.8	+2.9	+0.3	-1.3	+3.2	-1.3
6	8	-0.2	+0.1	+0.4	+0.7	0.0	+0.5	+0.3	+0.8
5	9	+1.1	+0.2	-3.1	-1.4	+1.2	-0.3	-4.3	-0.7
49	11	-1.1	-3.1	-0.6	-4.4	0.0	-0.9	+0.3	-1.4
48	12	+0.6	+2.3	+4.7	+3.5	+0.2	+3.3	+5.1	+3.3

[b] See Figure 3. in text of this paper.

[c] For the details of DMSO ^{13}C NMR database, see Table 5 in supporting infomation of the preceding paper.

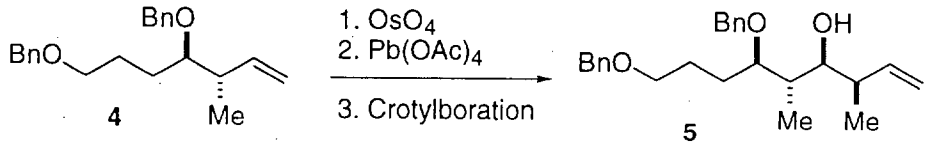
Experimental Procedures for the Synthesis Summarized in Scheme 1.



To a stirred mixture of potassium *tert*-butoxide (4.2 g, 34.2 mmol), THF (35 mL), and *trans*-2-butene (3.8 g, 69 mmol), *n*-BuLi in THF (2.5 M, 34.2 mmol) was added at -78 °C. After complete addition of *n*-BuLi, the mixture was stirred at -45 °C for 10 min. The resulting solution was recooled to -78 °C, and to it was added dropwise (-)-methoxydiisopinocampheylborane in ether (1 M, 41.0 mmol). After the reaction mixture was stirred at -78 °C for 30 min, boron trifluoride etherate (5.8 mL, 45.8 mmol) was added dropwise. Then the aldehyde **3** (6.56 g, 34.2 mmol) in

ether (7 mL) was added dropwise at -78 °C. The mixture was now stirred at -78 °C for 3 h and then treated with 3 N NaOH (50 mL, 150.4 mmol) and H_2O_2 (30%, 25 mL), and the resulting mixture was stirred overnight. The organic layer was separated and the aqueous layer was extracted with ether (100 mL x 2). The organic layers were combined, and dried ($MgSO_4$). After removal of the solvent, the residue was used for the next step without further purification.

To a crude alcohol (21.0 g, 140 mmol) and tetrabutylammonium iodide (5.2 g, 14.0 mmol) in DMF (280 mL) was added NaH (60% in mineral oil, 8.4 g, 210 mmol) at 0 °C. The mixture was stirred for 30 min. To the stirred mixture was added benzyl bromide (19.0 mL, 154 mmol) at 0 °C. The mixture was stirred and warmed to rt overnight. To the mixture was added saturated aqueous $Na_2S_2O_3$ (250 mL). The mixture was extracted with ether (300 mL x 2). The organic layers were combined, and dried ($MgSO_4$). After removal of ether, DMF was further removed by rotary evaporator under high vacuum to give the crude desired benzyl ether **4**.

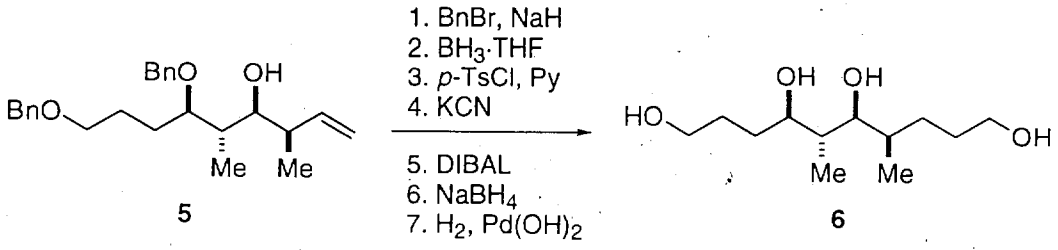


The crude benzyl ether **4** (31 mmol) in a mixture of acetone (320 mL) and H_2O (40 mL) was treated with OsO_4 (0.3 M in toluene, 2.1 mL, 0.62 mmol) and 4-methylmorpholine *N*-oxide (7.2 g, 62 mmol) at rt. The reaction mixture was stirred at rt overnight. To the mixture was added saturated aqueous $Na_2S_2O_3$ solution (200 mL), and stirred for 1 h. The organic layer was separated and the aqueous layer was extracted with ether (200 mL x 2). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. At this stage, the crude material was separated by column chromatography over SiO_2 (Hex/EtOAc 3:1 then 1:2) to provide the pure diol.

To the diol (3.5 g, 9.8 mmol) in benzene (150 mL) was added lead(IV) acetate (5.3 g, 11.8 mmol) at rt. The mixture was stirred for 2 h at rt. To the mixture was then added saturated aqueous $NaHCO_3$ (150 mL). The organic layer was separated and the aqueous layer was extracted with ether (150 mL x 2). After removal of the solvent, the desired aldehyde (3.2 g, 52% overall from the aldehyde **3**) was used directly for the next step without any further purification.

To a stirred mixture of potassium *tert*-butoxide (1.2 g, 9.8 mmol), THF (10 mL), and *cis*-2-butene (1.1 g, 19.6 mmol), *n*-BuLi in THF (2.5 M, 9.8 mmol) was added at -78 °C. After complete addition of *n*-BuLi, the mixture was stirred at -45 °C for 10 min. The resulting solution was recooled to -78 °C, and to it was added dropwise (-)-methoxydiisopinocampheylborane in ether (1 M, 11.8 mmol). After the reaction mixture was stirred at -78 °C for 30 min, boron trifluoride

etherate (1.7 mL, 13.1 mmol) was added dropwise. Then the aldehyde (3.2 g, 9.8 mmol) in ether (3 mL) was added dropwise at -78 °C. The mixture was stirred at the same temperature for 3 h and then treated with 3 N NaOH (15 mL) and H_2O_2 (30%, 10 mL), and the resulting mixture was stirred overnight. The organic layer was separated and the aqueous layer was extracted with ether (40 mL x 2). The organic layers were combined, and dried ($MgSO_4$).



5 6

To a crude alcohol **5** (5.0 g, 33.3 mmol) and tetrabutylammonium iodide (1.3 g, 3.33 mmol) in DMF (67 mL) was added NaH (60% mineral oil, 4.0 g, 100 mmol) at 0 °C. The mixture was stirred for 30 min. To the stirred mixture was added benzyl bromide (7.9 mL, 66.7 mmol) at 0 °C. The mixture was stirred and warmed to rt overnight. To the mixture was added saturated aqueous $Na_2S_2O_3$ (200 mL). The mixture was extracted with ether (250 mL x 2). The organic layers were combined, and dried ($MgSO_4$). After removal of ether, DMF was further removed by rotary evaporator under high vacuum to give the desired benzyl ether.

To the above crude benzyl ether (2.2 g, 4.66 mmol) in THF (20 mL) was added BH_3·THF (1 M, 19.1 mmol) at 0 °C. The reaction solution was stirred at 0 °C for 8 h, and then treated with NaOH (3 N, 30 mL) and H_2O_2 (30 mL) for 1.5 h at 0 °C. The aqueous layer was extracted with ether (100 mL x 2). The organic layers were combined, dried ($MgSO_4$), filtered and evaporated. The residue was purified by column chromatography on SiO_2 (Hex/EtOAc 2:1) to provide the pure alcohol (1.75 g, overall 43% from the aldehyde).

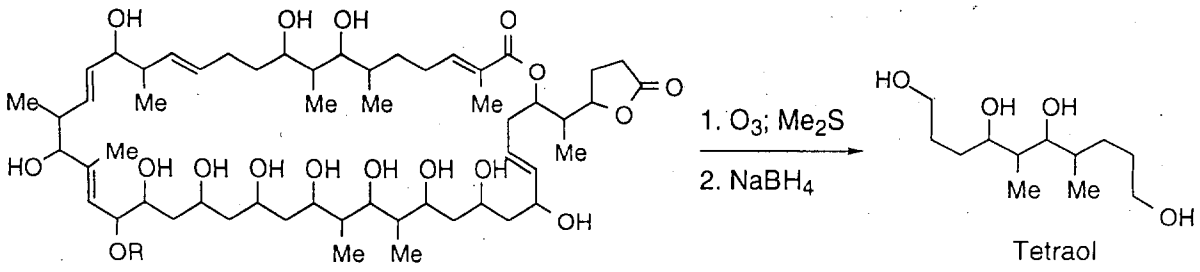
To the alcohol (310 mg, 0.63 mmol) dissolved in CH_2Cl_2 (3 mL) and pyridine (3 mL) was added *p*-TsCl (180 mg, 0.95 mmol) in one portion at 0 °C. The reaction mixture was stirred and allowed to warm to rt overnight. After the reaction was completed, saturated aqueous $NaHCO_3$ (20 mL) was added to the reaction mixture. The aqueous layer was extracted with ether (20 mL x 2). The combined organic layers were dried ($MgSO_4$), filtered and evaporated.

The residue was separated by column chromatography on SiO_2 (Hex/EtOAc 9:1) to produce the tosylate (250 mg, 62%). To the tosylate (210 mg, 0.33 mmol) in DMSO (3 mL) was added KCN (210 mg, 3.26 mmol). The mixture was vigorously stirred and heated at 75 °C for 2.5 h. The mixture was cooled to rt, and treated with water (15 mL) and ether (15 mL). The aqueous

layer was extracted with ether (20 mL x 2). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The residue was purified by column chromatography on SiO_2 (Hex/EtOAc 4:1) to furnish the nitrile (155 mg, 96%). To the above nitrile (148 mg, 0.297 mmol) in CH_2Cl_2 (3 mL) was added dropwise diisobutylaluminum hydride (1 M, 0.445 mmol) at - 78 °C. The reaction mixture was stirred for 30 min. Excess of reagent was destroyed with ethyl acetate (5 mL) and the product was hydrolyzed by stirring with wet silica gel (5 g) for 1 h at rt. The mixture was filtered through a pad of Celite, and the filtrate was evaporated to produce the corresponding aldehyde (142 mg, 95%) in a very pure state. The above aldehyde (142 mg, 0.283 mmol) was treated with $NaBH_4$ (22 mg, 0.566 mmol) in EtOH (3 mL) for 40 min at 0 °C. After usual workup, the residue was purified by column chromatography on SiO_2 (Hex/EtOAc 3:1) to afford the corresponding alcohol (136 mg, 96%). Finally the above alcohol (124 mg, 0.246 mmol) dissolved in EtOH (3 mL) was treated with $Pd(OH)_2$ (20%, 80 mg, ca. 60% w/w) under hydrogen atmosphere at rt overnight. The mixture was filtered through a pad of Celite and washed with EtOAc. The filtrate was concentrated, and the resulting crude material was purified column chromatography on SiO_2 (ether/MeOH 9:1) to provide the tetraol **6** (57 mg, 99%). ^{13}C NMR (100MHz, CD_3OD) δ 77.70, 74.75, 63.22, 63.13, 42.79, 35.96, 31.71, 31.52, 30.13, 29.67, 12.55, 11.70; ^{1}H NMR (400MHz, CD_3OD) δ 3.82 (ddd, J = 2.2, 5.9, 9.5 Hz, 1H), 3.58 (t, J = 6.4 Hz, 2H), 3.55 (t, J = 6.8 Hz, 2H), 3.40 (dd, J = 2.0, 9.8 Hz, 1H), 1.80-1.28 (m, 10H), 0.86 (d, J = 6.8 Hz, 3H), 0.79 (d, J = 6.8 Hz, 3H).

Acetonide derived from tetraol 6: ^{13}C NMR (100MHz, C_6D_6) δ 98.05, 76.15, 74.81, 63.11, 62.85, 35.59, 33.59, 31.25, 30.69, 30.45, 30.24, 29.20, 19.69, 13.00, 11.81; ^{1}H NMR (400MHz, C_6D_6) δ 3.50 (t, J = 5.6 Hz, 2H), 3.38 (t, J =5.6 Hz, 2H), 3.30 (m, 2H), 1.69-1.30 (m, 10H), 1.46 (s, 3H), 1.27 (s, 3H), 0.93 (d, J = 6.4 Hz, 3H), 0.48 (d, J = 6.8 Hz, 3H).

Degradation of Oasomycin B



Oasomycin B: R = α-D-mannosyl

A stirred solution of oasomycin B (18.6 mg, 0.017 mmole) in MeOH (3 mL) was cooled to -78 °C. Ozone was bubbled through the reaction mixture for 30 sec. After N_2 bubbling, Me_2S (0.1 mL) was added.

The mixture was stirred for 5 min. treated with $NaBH_4$ (10 mg, 0.26 mmole) and warmed to rt. Saturated aqueous NH_4Cl was poured into the reaction mixture, and the resulting mixture was extracted with EtOAc (5 mL x 2). The combined organic layers were dried over Na_2SO_4, and evaporated *in vacuo*. The residue was purified by silica gel column chromatography (9:1 Et_2O/MeOH) to give tetraol (2.1 mg, 59%).