BASE-ASSISTED MIGRATION OF TRIMETHYLSILYL GROUP FROM CARBON TO OXYGEN IN γ-TRIMETHYLSILYL-γ,δ-UNSATURATED ALCOHOLS, γ-TRIMETHYLSILYL-γ,δ-EPOXY ALCOHOLS, AND β-TRIMETHYLSILYL-β,γ-EPOXY ALCOHOLS TO THE CORRESPONDING SILYL ETHERS†

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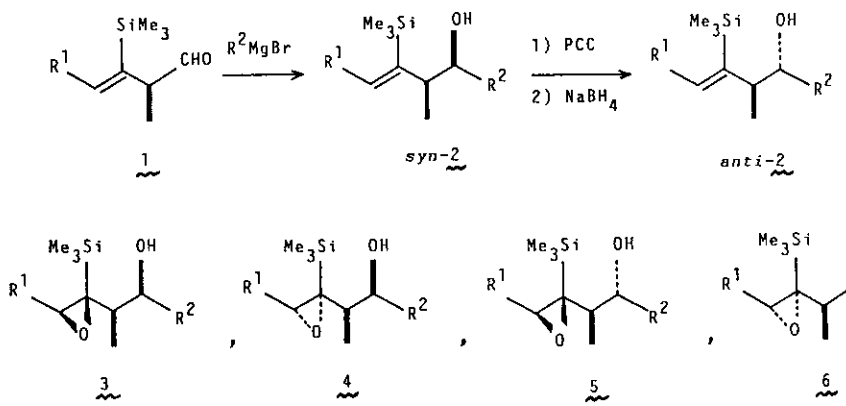
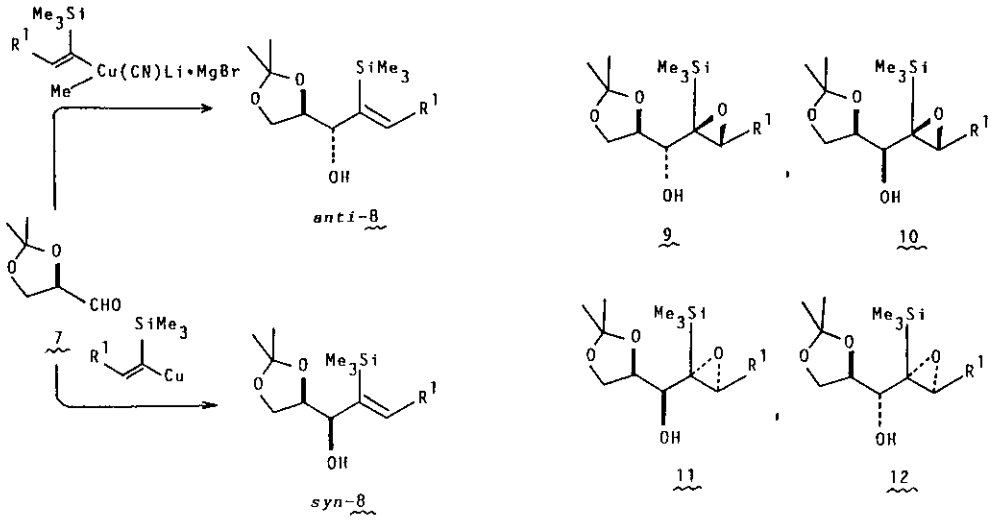
Abstract —Treatment of γ-trimethylsilyl-γ,δ-unsaturated alcohols 2, γ-trimethylsilyl-γ,δ-epoxy alcohols 3-6, and β-trimethylsilyl-β,γ-epoxy alcohols 9-12 with NaH in HMPA or t-BuOK in THF brought about facile migration of $SiMe_3$ group from carbon to oxygen to produce the corresponding silyl ethers in high yields.

Recently, we have reported a highly stereoselective synthesis of syn and anti diastereoisomers of the homoallylic alcohols 2 from the aldehydes 1[1] and the allylic alcohols 8 from the glyceraldehyde acetonide 7[2] by the procedures shown in Scheme 1 and 2, respectively, where the addition of nucleophiles to 1 and 7 proceeds highly diastereoselectively. The alcohols 2 and 8 thus prepared



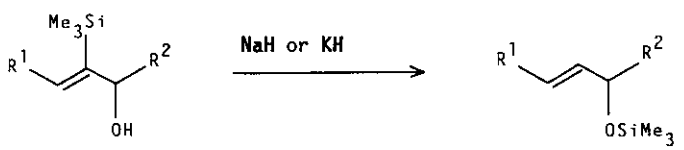
Scheme 1

†Dedicated to Professor Gilbert Stork on the occasion of his 65th birthday.



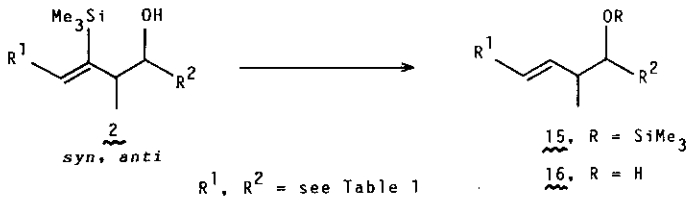
Scheme 2

can be converted selectively into the four possible stereoisomers of γ-trimethysilyl-γ,δ-epoxy alcohols 3-6[3] and β-trimethylsilyl-β,γ-epoxy alcohols 9-12,[2] respectively. In these reactions, the presence of $SiMe_3$ group is crucial for obtaining the high diastereoselectivity. For utilization of these products for synthesis of acyclic natural compounds such as macrolide antibiotics and sugars, it was needed to protodesilylate the silyl alcohols 2, 3-6, 8, and 9-12. Previously, we reported that 1,3-migration of $SiMe_3$ group from carbon to oxygen occurs readily to yield the allyl silyl ethers 14 when β-trimethylsilylallylic alcohols 13 are treated with NaH in HMPA or KH in THF.[4] We now found that this reaction conditions are also effective for protodesilylation of the present compounds.[5,6]



Protodesilylation of γ-trimethylsilyl-γ,δ-unsaturated alcohols 2

The results of the reaction of various alcohols 2 with NaH (1 equiv) in HMPA-THF (2 : 3) at 30 °C are summarized in Table 1. It can be seen from the Table that various alcohols 2 can be readily protodesilylated in high yields irrespective of the substituents R^1 and R^2 and the stereochemistry of 2. The



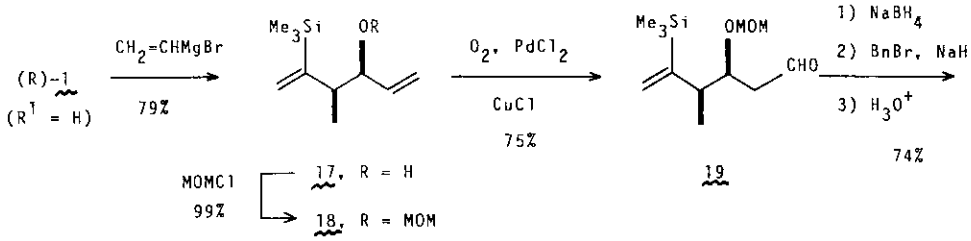
protodesilylation proceeded with retention of configuration which was confirmed by the large coupling constant (ca. 15 Hz) between olefinic protons in ^{1}H NMR spectra of 16c (entries 5 and 6). Although we isolated the products as the alcohols 16, TLC analysis indicated that the initial products of the reaction are the silyl ethers 15.

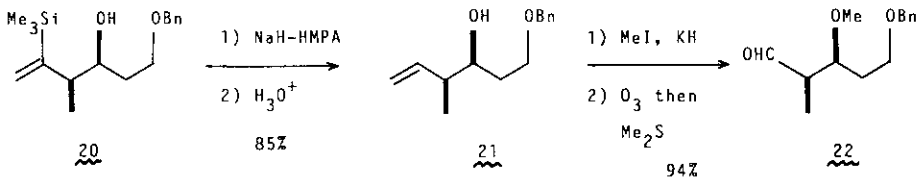
Table 1. Protodesilylation of the alcohols 2[a]

entry	substrate 2				yield (%)[b]
		stereo-chemistry	R^1	R^2	16
1	a	syn	H	Et	86
2	a	anti	H	Et	90
3	b	syn	H	Ph	90
4	b	anti	H	Ph	93
5	c	syn	n-Bu	Me	85
6	c	anti	n-Bu	Me	93

a) NaH (1 equiv) in HMPA-THF (2 : 3) at 30 °C for 2 h followed by acidic work-up. b) Isolated yields after purification by silica gel chromatography.

We applied this protodesilylation reaction in the synthesis of the C(25)-C(29) segment of rifamycin S[7] 22 (Scheme 3). Addition reaction of the aldehyde (R)-1 (R^1 = H, >95% e.e.)[1b] with CH_2=CHMgBr followed by protection of the resulting alcohol 17 with MOMCl afforded 18 with >99% diastereoselectivity in 77% yield. The regioselective introduction of hydroxyl group to one of the



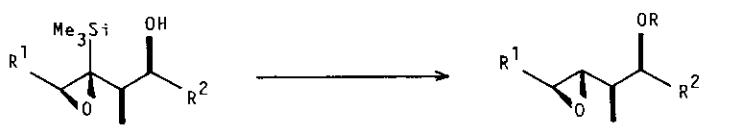


Scheme 3

olefinic moieties of 18 was effectively realized by Wacker oxidation.[8] Thus, oxidation of 18 with oxygen in the presence of $PdCl_2$ (0.1 equiv) and CuCl (1 equiv) (room temperature, 24 h) resulted in the exclusive production of the aldehyde 19 in 75% yield. It is noteworthy that no methyl ketone derivative was obtained in the present reaction. The aldehyde 19 was changed to the silyl alcohol 20 by reduction with $NaBH_4$ followed by benzylation and deprotection of MOM ether group (74% yield from 19). Treatment of 20 with NaH in HMPA yielded the alcohol 21 after hydrolysis in 85% yield. From 21, the aldehyde 22 was synthesized by O-methylation followed by ozonolysis (94%). The ^1H NMR spectrum and the optical rotation of 22 were in accord with the data reported by Masamune[9] ($[\alpha]_D^{25}$ -54.1° (c 1.33, $CHCl_3$); lit. 9, $[\alpha]_D^{25}$ -54.5° (c 3.17, $CHCl_3$)).

Protodesilylation of γ-trimethylsilyl-γ,δ-epoxy and β-trimethylsilyl-β,γ-epoxy alcohols

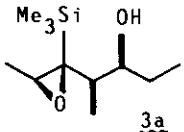
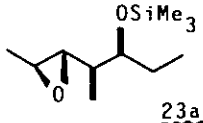
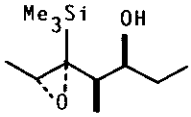
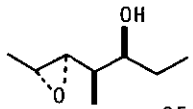
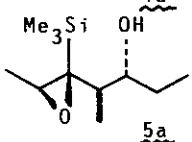
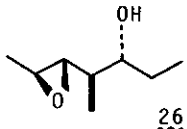
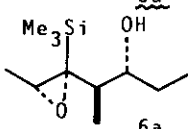
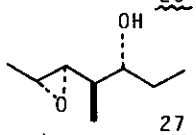
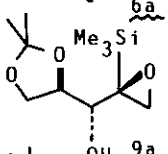
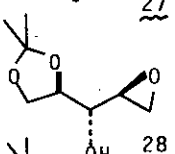
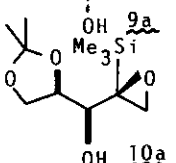
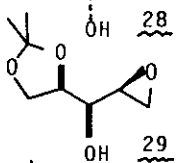
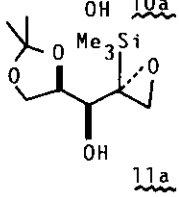
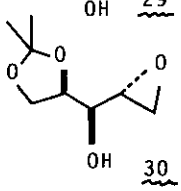
Treatment of γ-trimethylsilyl-γ,δ-epoxy alcohols 3-6 with NaH in HMPA



3
a: R^1 = Me, R^2 = Et

23, R = SiMe
24, R = H

Table 2. Protodesilylation of the alcohols 3-6 and 9-11 with t-BuOK[a]

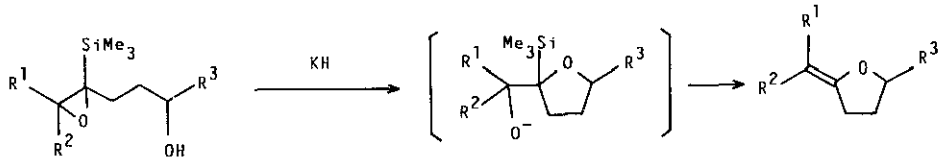
entry	substrate	conditions	product	yield (%)[b]
1	 3a	A	 23a	86[c,d]
2	 4a	B	 25	87
3	 5a	B	 26	91
4	 6a	B	 27	92
5	 9a	B	 28	80
6	 10a	B	 29	83
7	 11a	B	 30	94

a) Conditions A: t-BuOK (1 equiv) in THF at 0 °C for 5-10 min; conditions B: t-BuOK (1 equiv) and n-Bu_4NF (1-1.3 equiv) in THF at 0 °C for 5-10 min. b) Isolated yields after purification by silica gel chromatography. c) When 3a was treated with t-BuOK and n-Bu_4NF (conditions B), the alcohol 24a was isolated in 95% yield. d) The silyl ether 23a was also obtained by using NaH (1.2 equiv) in HMPA at 30 °C for 15 min in 92% yield.

or t-BuOK in THF also resulted in facile 1,4-migration of $SiMe_3$ group to give the corresponding silyl ethers essentially quantitatively. The results are summarized in Table 2. The reaction proceeded with retention of configuration which was confirmed by a small coupling constant (2 Hz) between epoxy protons, a characteristic value for trans epoxide,[10] in ^1H NMR spectra of the products.

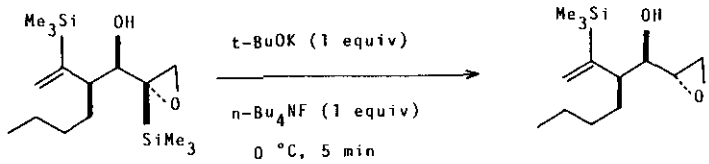
Similarly, when the β-trimethylsilyl-β,γ-epoxy alcohols 9-12 were treated with t-BuOK in THF, 1,3-migration of $SiMe_3$ group occurred readily to afford the corresponding alcohols (entries 5-7 in Table 2). Thus, combination of the highly stereoselective addition reaction of 1-trimethylsilylvinylorganocopper compounds with glyceraldehyde acetonide 7[2] with the present protodesilylation reaction provides a convenient and practical method for preparation of key intermediates for the synthesis of alditols.[11]

In connection with our findings, it is noteworthy that the alcohols 31 which have 1-trimethylsilylepoxy moiety at γ-position has been reported to undergo intramolecular epoxide ring opening reaction on treatment with KH in THF to afford the furans 33 via the intermediates 32.[12] In the cases of the alcohols 3-6 and 9-12, however, such epoxide ring opening products were not detected by TLC and NMR analysis.



31 32 33

It has been shown that base-assisted migration of $SiMe_3$ group from carbon to oxygen proceeded readily in the alcohols containing 1-trimethylsilylvinyl or 1-trimethylsilylepoxy moieties at α or β position. Finally, we wish to show that it is also possible to carry out the selective protodesilylation of alcohols which contain both silylvinyl and silylepoxy moieties. Thus, treatment of 34 with t-BuOK and n-Bu_4NF in THF caused 1,3-migration of $SiMe_3$ group from epoxy carbon to oxygen selectively to afford 35 as the sole product (88% yield). From 35, blastmycinone was synthesized as reported in the preliminary communication.[5]



34 96% 35

EXPERIMENTAL

^{1}H NMR spectra were recorded on a HITACHI R-40, whereas ^{13}C NMR spectra were recorded on a JEOL FX-90Q. Chemical shifts are reported as δ values in ppm with tetramethylsilane as an internal standard (δ =0). Coupling constants (J) are given in herz. Signals in the ^{1}H NMR spectra are characterized as s (singlet), d (doublet), t (triplet), q (quartet), qi (quintet), m (multiplet), and bs (broad singlet). Optical rotations were determined in a 20-ml cell with 5-cm path length on a YANACO OR-50 polarimeter. For thin-layer chromatography (TLC) analysis precoated silica gel plates (Merk 60 F_{254}, 0.2 mm) were used.

General procedure for the protodesilylation of γ-trimethylsilyl-γ,δ-unsaturated alcohols 2. A solution of the syn alcohol 2a (64 mg, 0.34 mmol) and NaH (16 mg, 50% in oil, 0.34 mmol) in HMPA (1 ml) and THF (1.5 ml) was stirred at 30 °C for 2 h after which time TLC examination showed complete consumption of the starting alcohol 2a and the appearence of only one spot corresponding to the silyl ether 15a (R_f 0.9, hexane : Et_2O = 4 : 1; 2a, R_f 0.4). The mixture was poured into 3N HCl (3 ml) and extracted with hexane-Et_2O (1 : 1, 2 X 10 ml). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give an oil which was purified by silica gel chromatography to afford the syn product 16a (31 mg) in 86% yield. The ^{1}H NMR spectrum of the syn product 16a was identical in all respects with the data described in the literature.[13]

In a similar way, anti-2a, syn- and anti-2b, syn- and anti-2c were protodesilylated to give the corresponding alcohols 16a-c. The ^{1}H NMR spectra of the products 16a,b were identical in all respects with the data reported in the literatures.[13] The ^{1}H NMR ($CDCl_3$) spectra of syn- and anti-16c were as follows. syn-16c: δ 0.90 (t, J = 6, 3H), 0.96 (t, J = 6.5, 3H), 1.05 (d, J = 6.3, 3H), 1.16-1.53 (m, 4H), 1.86-2.28 (m, 4H), 3.51 (qi, J = 6.2, 1H), 5.27 (dd, J = 7, 15, 1H), 5.42 (dt, J = 15, 5, 1H); anti-16c: δ 0.88 (t, J = 6, 3H),

0.93 (t, J = 6, 3H), 1.06 (d, J = 6, 3H), 1.18-1.48 (m, 4H), 1.74-2.14 (m, 4H), 3.42 (qi, J = 6.2, 1H), 5.27 (dd, J = 7, 15, 1H), 5.44 (dt, J = 15, 6, 1H).

Preparation of the MOM ether 18. To a solution of (R)-1 (R^1 = H) (1.4 g, 9.0 mmol, >95% e.e.) in Et_2O (30 ml) was added CH_2=CHMgBr (35 ml, 0.52 M in THF, 18 mmol) at -78 °C and the solution was stirred at -78 °C for 1 h. After addition of sat NH_4Cl (40 ml), the mixture was allowed to warm to room temperature and extracted with hexane (3 X 15 ml). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give an oil which was purified by chromatography on silica gel to give the syn addition product 17 (1.3 g, 79%): ^{1}H NMR (CCl_4 + D_2O) δ 0.05 (s, 9H), 1.01 (d, J = 7.3 Hz, 3H), 2.36 (qi, J = 7.3 Hz, 1H), 3.90-4.13 (m, 1H,), 4.91-5.35 (m, 2H), 5.47 and 5.68 (2d, J = 2.4, 2H), 5.61-6.05 (m, 1H); ^{13}C NMR ($CDCl_3$) δ -1.2, 14.8, 43.7, 74.5, 114.4, 125.2, 139.9, 154.9; $[\alpha]_D^{25}$ -39.3° (c 0.956, $CHCl_3$).

A solution of 17 (1.25 g, 6.8 mmol), i-Pr_2NEt (6 ml, 34 mmol), and chloromethyl methyl ether (1.6 ml, 20 mmol) in CH_2Cl_2 (10 ml) was stirred at room temperature for 5 h and sat NH_4Cl (10 ml) was added. The mixture was extracted with hexane (3 X 10 ml). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give an oil which was purified by column chromatography on silica gel to afford the MOM ether 18 (1.53 g, 99%): ^{1}H NMR (CCl_4) δ 0.05 (s, 9H), 1.07 (d, J = 6.7 Hz, 3H), 2.43 (dq, J =6.9, 6.7, 1H), 3.27 (s, 3H), 3.89 (t, J = 6.9, 1H), 4.37 and 4.59 (2d, J = 6.7, 2H), 4.94-5.25 (m, 2H), 5.37-5.79 (m, 1H), 5.45 and 5.66 (2d, J = 2.9, 2H); $[\alpha]_D^{25}$ +54.3° (c 1.02, $CHCl_3$).

Preparation of the aldehyde 19. A solution of $PdCl_2$ (194 mg, 0.66 mmol) and CuCl (653 mg, 2.0 mmol) in DMF (8 ml, aqueous 90% solution) was stirred at room temperature for 2 h under oxygen atmosphere. The MOM ether 18 (1.5 g, 6.6 mmol) in DMF (3 ml, aqueous 90% solution) was added to the solution. After 24 h under oxygen atmosphere, the solution was poured into sat NH_4Cl (10 ml) and 3N HCl (10 ml), and the mixture was extracted with hexane-Et_2O (3 : 1, 4 X 20 ml). The combined extracts were washed with sat $NaHCO_3$ (10 ml) and brine (10 ml), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the aldehyde 19 (1.2 g, 75%): ^{1}H NMR (CCl_4) δ 0.08 (s, 9H), 1.05 (d, J = 7.3, 3H), 2.33-2.56 (m, 2H), 3.25 (s, 3H), 3.96 (dt, J = 8.2, 5.1, 1H), 4.57 (s, 2H), 5.46 and 5.66 (2d, J =

2.4, 2H), 9.69 (t, J = 2.4, 1H).

Conversion of 19 into the alcohol 20. To an ice-cooled solution of 19 (1.2 g, 4.9 mmol) in MeOH (10 ml) was added $NaBH_4$ (91 mg, 2.4 mmol). After the resulting mixture was stirred for 30 min, AcOH (0.58 ml, 9.6 mmol), sat $NaHCO_3$ (15 ml), and hexane (15 ml) were added. The product was extracted with hexane (4 X 15 ml). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to leave an oil which was purified by column chromatography on silica gel to give the corresponding alcohol (1.16 g, 96%): ^{1}H NMR (CCl_4) δ 0.07 (s, 9H), 1.01 (d, J = 7.3, 3H), 1.30-1.92 (m, 2H), 2.38 (qi, J = 7.3, 1H), 2.75 (bs, 1H), 3.35 (s, 3H), 3.46-3.80 (m, 3H), 4.58 (s, 2H), 5.42 and 5.64 (2d, J = 2.4, 2H); ^{13}C NMR ($CDCl_3$) δ -1.0, 17.6, 36.0, 43.3, 56.0, 59.4, 80.3, 98.1, 125.3, 154.8; $[\alpha]_D^{25}$ -80.9° (c 1.10, $CHCl_3$).

To a suspension of an oil free KH (180 mg, 4.5 mmol) in THF (12 ml) was added the above alcohol (0.92 g, 3.7 mmol) dissolved in THF (4 ml) at 0 °C. After 20 min of stirring, benzyl bromide (0.48 ml, 4.1 mmol) was added. Stirring was continued for an additional 1 h and sat $NaHCO_3$ (15 ml) was added. The mixture was extracted with hexane (3 X 20 ml). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give an oil which was purified by column chromatography on silica gel to afford the benzyl ether (1.0 g, 80%): ^{1}H NMR (CCl_4) δ 0.06 (s, 9H), 1.03 (d, J = 7.3 Hz, 3H), 1.28-1.97 (m, 2H), 2.40 (qi, J = 7.3, 1H), 3.17 (s, 3H), 3.37-3.76 (m, 3H), 4.42 and 4.52 (2s, 4H), 5.42 and 5.55 (2d, J = 2.4, 2H), 7.27 (s, 5H); ^{13}C NMR ($CDCl_3$) δ -1.0, 17.1, 33.8, 43.0, 55.7, 67.1, 72.8, 78.9, 97.1, 125.2, 127.3, 127.5, 128.1, 138.5, 154.7; $[\alpha]_D^{25}$ -35.9° (c 0.846, $CHCl_3$).

A solution of the resulting benzyl ether (1.0 g, 3.0 mmol) in a mixture of MeOH (10 ml), H_2O (2 ml), and conc HCl (2 ml) was stirred at room temperature for 12 h and poured into sat $NaHCO_3$ (20 ml). The mixture was extracted with hexane (4 X 15 ml). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to leave an oil which was purified by column chromatography on silica gel to give 20 (0.84 g, 97%): ^{1}H NMR (CCl_4 + D_2O) δ 0.06 (s, 9H), 1.02 (d, J = 7.3, 3H), 1.44-1.73 (m, 2H), 2.27 (qi, J = 7.3, 1H), 3.46-3.78 (m, 3H), 4.44 (s, 2H), 5.41 and 5.61 (2d, J = 2.4, 2H), 7.24 (s, 5H); $[\alpha]_D^{25}$ -9.5° (c 1.14, $CHCl_3$).

Protodesilylation of 20 to 21. Protodesilylation of 20 (840 mg, 2.9 mmol) was

carried out using an oil free NaH (140 mg, 5.8 mmol) in HMPA (5 ml) at room temperature for 30 min to give 21 (540 mg, 85%): ^{1}H NMR (CCl_4) δ 0.99 (d, J = 6.8, 3H), 1.47-1.77 (m, 2H), 2.15 (q, J = 6.9, 1H), 2.92 (bs, 1H), 3.37-3.74 (m, 3H), 4.43 (s, 2H), 4.85-5.13 (m, 2H), 5.74 (ddd, J = 6.9, 9.8, 18, 1H), 7.25 (s, 5H); $[\alpha]_D^{25}$ -13.2° (c 0.972, $CHCl_3$).

Conversion of 21 into the aldehyde 22. A mixture of 21 (530 mg, 2.3 mmol) and an oil free KH (136 mg, 3.4 mmol) in THF (20 ml) was stirred for 20 min and then MeI (0.18 ml, 2.7 mmol) was added to the mixture. After 30 min, sat NH_4Cl (15 ml) was added and the mixture was extracted with hexane (3 X 15 ml). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give an oil which was purified by column chromatography on silica gel to give the methyl ether (545 mg, 100%): ^{1}H NMR (CCl_4) δ 0.99 (d, J = 7.2, 3H), 1.47-1.81 (m, 2H), 2.16-2.56 (m, 1H), 3.04-3.23 (m, 1H), 3.34 (s, 3H), 3.40-3.63 (m, 2H), 4.47 (s, 2H), 4.85-5.13 (m, 2H), 5.62-6.05 (m, 1H), 7.29 (s, 5H); $[\alpha]_D^{25}$ -49.2° (c 1.32, $CHCl_3$).

A solution of the methyl ether (71 mg, 0.30 mmol) in MeOH (2 ml) and CH_2Cl_2 (2 ml) was cooled to -78 °C and ozone was passed at a rate of gentle bubbling for 20 min. Then, argon was bubbled at -78 °C for 15 min to remove off excess ozone. After addition of Me_2S (0.1 ml, 1.4 mmol), the soluiton was allowed to warm up to room temperature and then concentrated under reduced pressure. The residue was dissolved in MeOH (2 ml), and Zn (20 mg, 0.31 mmol) and AcOH (2 drops) were added. After 5 min, H_2O (3 ml) was added and the prodcut was extracted with hexane (3 X 5 ml). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give an oil which was purified by column chromatography on silica gel to give the aldehyde 22 ($[\alpha]_D^{25}$ -54.1° (c 1.33, $CHCl_3$)) whose ^{1}H NMR spectrum was identical with the data reported by Masamune ($[\alpha]_D^{25}$ -54.5° (c 3.17, $CHCl_3$)).[9]

General procedure for the protodesilylation of γ-trimethylsilyl-γ,δ-epoxy and β-trimethylsilyl-β,γ-epoxy alcohols. (1) Preparation of the silyl ethers: To a solution of 3a (430 mg, 1.99 mmol) in THF (5 ml) was added t-BuOK (250 mg, 2.1 mmol) at 0 °C. After 5 min, the solution was poured into sat NH_4Cl and the mixture was extracted with hexane (2 X 15 ml). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give an oil which was purified by silica gel chromatography to afford the silyl ether 23a (186 mg,

86%): ^{1}H NMR (CCl_4) δ 0.03 (s, 9H), 0.84 (t, J = 6.9, 3H), 0.90 (d, J = 6.9 , 3H), 1.23 (d, J = 5.4, 3H), 1.02-1.66 (m, 3H), 2.36 (dd, J = 2.4, 6.6, 1H), 2.65 (dq, J = 2.4, 5.4 , 1H), 3.52 (q, J = 5.4, 1H). (2) Preparation of the alcohols: To a solution of 3a (1.19 g, 5.51 mmol) and n-Bu_4NF (1.44 g, 5.51 mmol) in THF (13 ml) was added t-BuOK (680 mg, 6.06 mmol) at 0 °C. After 10 min, the solution was poured into sat NH_4Cl and the mixture was extracted with Et_2O (2 X 50 ml). The combined extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give an oil which was chromatographed on silica gel to give the alcohol 24a (752 mg, 95%): ^{1}H NMR (CCl_4) δ 0.94 (t, J = 7.2, 3H), 0.96 (t, J = 6.3, 3H), 1.26 (d, J = 5.4, 3H), 1.12-1.68 (m, 3H), 2.52 (dd, J = 2.1, 6.4, 1H), 2.79 (dq, J = 2.1, 5.1, 1H), 3.44 (dt, J = 6.9, 5.4, 1H). ^{1}H NMR spectra and optical rotations of the other products shown in Table 2 are as follows. 25: ^{1}H NMR (CCl_4 + D_2O) δ 0.89 (d, J = 7.2, 3H), 0.90 (t, J = 7.2, 3H), 1.25 (d, J = 5.4, 3H), 1.11-1.63 (m, 3H), 2.55 (dd, J = 2.4, 7.2, 1H), 2.73 (dq, J = 2.4, 5.4, 1H), 3.49 (dt, J = 3.6, 7.2, 1H). 26: ^{1}H NMR (CCl_4) δ 0.95 (t, J = 7.5, 3H), 0.98 (d, J = 6.9, 3H), 1.28 (d, J = 5.4, 3H), 1.09-1.77 (m, 3H), 2.58 (dd, J = 2.4, 6.6, 1H), 2.84 (dq, J = 2.4, 5.4, 1H), 3.14 (bs, 1H), 3.20-3.51 (m, 1H). 27: ^{1}H NMR (CCl_4 + D_2O) δ 0.90 (d, J = 7.2, 3H), 0.93 (t, J = 7.2, 3H), 1.27 (d, J = 5.1, 3H), 1.07-1.63 (m, 3H), 2.54 (dd, J = 2.1, 7.2, 1H), 2.66 (dq, J = 2.1, 5.1, 1H), 3.43 (ddd, J = 4.5, 5.4, 6.6, 1H). 28: ^{1}H NMR (CCl_4 + D_2O) δ 1.31 and 1.39 (2s, 6H), 2.66 (dd, J = 3.8, 5.4, 1H), 2.78 (dd, J = 3.0, 5.4, 1H), 3.13 (dt, J = 3.8, 3.0, 1H), 3.63-4.30 (m, 4H); $[\alpha]_D^{25}$ -30.3° (c 0.971, $CHCl_3$). 29: ^{1}H NMR (CCl_4 + D_2O) δ 1.32 and 1.38 (2s, 6H), 2.63-2.75 (m, 2H), 2.93-3.09 (m, 1H), 3.46 (t, J = 4.2, 1H), 3.81-4.25 (m, 3H); $[\alpha]_D^{25}$ +9.6° (c 1.49, $CHCl_3$). 30: ^{1}H NMR (CCl_4 + D_2O) δ 1.34 and 1.39 (2s, 6H), 2.58-3.00 (m, 3H), 3.27 (t, J = 4.9, 1H), 3.73-4.34 (m, 3H); $[\alpha]_D^{25}$ +1.07° (c 1.12, $CHCl_3$).

Protodesilylation of 34 to 35. To a solution of 34 (0.96 g, 3.1 mmol) in THF (15 ml) was added t-BuOK (350 mg, 3.1 mmol) and n-Bu_4NF (4.7 ml, 0.66M in THF, 3.1 mmol) at 0 °C. After 5 min, sat NH_4Cl (15 ml) was added and the mixture was extracted with hexane (3 X 15 ml). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give an oil which was chromatographed on silica gel to give 35 (710 mg, 96%): ^{1}H NMR (CCl_4) δ 0.06 (s, 9H), 0.86 (t, J = 6.0, 3H), 1.06-1.80 (m, 6H), 1.90 (bs, 1H), 2.08-2.40 (m, 1H),

2.42-2.96 (m, 3H), 3.63 (dd, J = 3.0, 8.0, 1H), 5.47 and 5.56 (2d, J = 3.0, 2H); ^{13}C NMR ($CDCl_3$) δ -0.9, 13.9, 22.9, 29.5, 30.2, 43.5, 48.6, 53.6, 70.6, 126.8, 152.4; $[\alpha]_D^{25}$ -9.3° (c 1.18, $CHCl_3$).

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