Enantiomerically Pure α,β-Unsaturated Five-Membered-Ring Aldehydes by Ring Contraction of Epoxyhexopyranosides

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A series of epoxyhexopyranosides, variously substituted in the 6-position, were each transformed by ring contraction into a single, enantiomerically pure, α,β-unsaturated furanosidic aldehyde. Similar ring contraction of a *C*-propylglycosidic analog of one of the epoxyhexopyranosides gave a mixture of two diastereomeric aldehydes. This finding supports the previously suggested mechanism of the reaction and indicates that *O*-glycosidic epoxypyranosides also rearrange into two aldehydes, one of which is unstable.

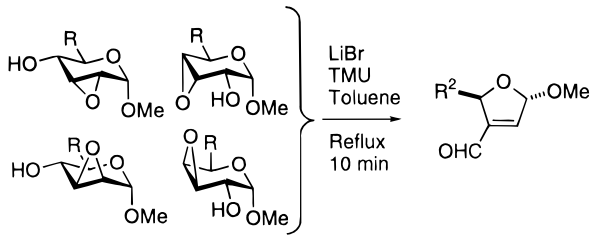
Introduction

Ring contraction of epoxycyclohexanes and epoxycyclohexanols provides cyclopentane- and cyclopentenecarboxaldehydes, respectively.[1−4] The latter have been used as starting materials for the syntheses of a number of terpenes.[5] Similarly, epoxypyranosides give α,β-unsaturated furanosidic aldehydes,[6,7] which were used for the synthesis of enantiomerically pure tetrahydrofuran-based natural products, including several lignans.[8] The mechanism of the ring contraction has been investigated using deuterium-labeled epoxy alcohols.[4,6,7]

Epoxycyclohexanols[3,4] normally give high yields (>80%) of the ring-contracted aldehydes as isomeric mixtures that are difficult to separate into the individual aldehydes. In contrast, epoxypyranosides give only a single aldehyde that is easily purified, but the yields are modest (∼25−60%).[6,7] However, different stereo- and regioisomers of the epoxypyranosides provide the same aldehyde (cf. Scheme 1), which makes it possible to use readily available mixtures of sugar epoxides for the ring contraction. It should also be noted that the methyl *O*-glycosidic aldehydes can undergo a 1,4-elimination of methanol, thus providing a route to substituted furan-3-aldehydes.[6,7] Ring contractions have also been performed with pyranosidic sulfonyl esters, which gave some furanosidic saturated and α,β-unsaturated aldehydes.[9,10]

In order to investigate the generality of the formation of a single stable aldehyde from epoxypyranosides, we submitted a number of these compounds to ring contraction (Scheme 2). A *C*-glycoside analog of one of the *O*-glycosidic epoxypyranosides was also synthesized and ring-contracted, which gave a mixture of two isomeric aldehydes (Scheme 4). This experiment provided an explanation for the fortuitous formation of a single aldehyde in most ring contractions of *O*-glycosidic epoxypyranosides.

Scheme 1



Results and Discussion

I. Ring Contraction of Methyl Epoxyhexopyranosides. Treatment of the epoxy alcohols[11,12] **1**−**6** with LiBr and tetramethylurea (TMU) in refluxing toluene for 10 min resulted in ring contraction and dehydration, which produced the α,β-unsaturated aldehydes **10**−**15** in 57−38% yield (Scheme 2). Only one aldehyde could be isolated from each reaction mixture, except for **15**, which contained approximately 3% of an isomeric aldehyde (**15a**). The latter was not obtained in pure form, but its ^{1}H NMR spectrum (mixture of **15** and **15a**) was consistent with a structure corresponding to the unstable aldehyde depicted in Scheme 3. The chromatographic isolation of **10**−**15** on silica gel was simple since they all had a higher R_f value than the byproducts.

Sulfone epoxide **7** gave the aldehyde **16** in only 9% yield, and the sulfone epoxides **8** and **9** gave no aldehyde product at all. Compound **8** was recovered (75%) after standard treatment with LiBr/TMU, and compound **9** was only consumed after prolonged reaction in the presence of additional LiBr. It seems as if the sulfone group competes with the epoxide oxygen for lithium ion, thus interfering with bromide ion attack on the epoxide carbon and consequently reducing the amount of the bromohydrin intermediate available for ring contraction. A simplified reaction mechanism is depicted in Scheme 3; for a full discussion, see refs 4, 6, and 7.

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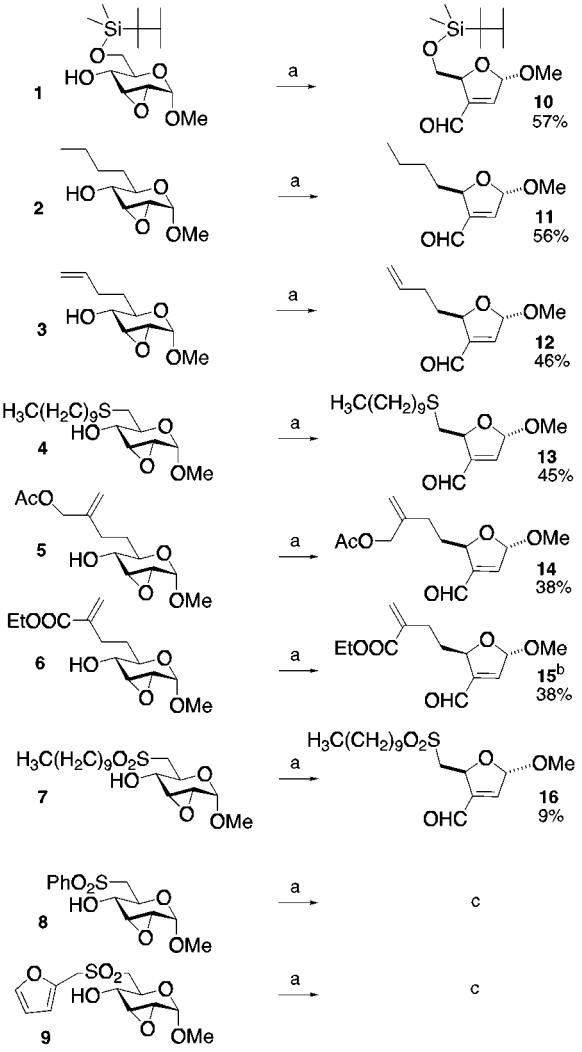
Scheme 2[a]

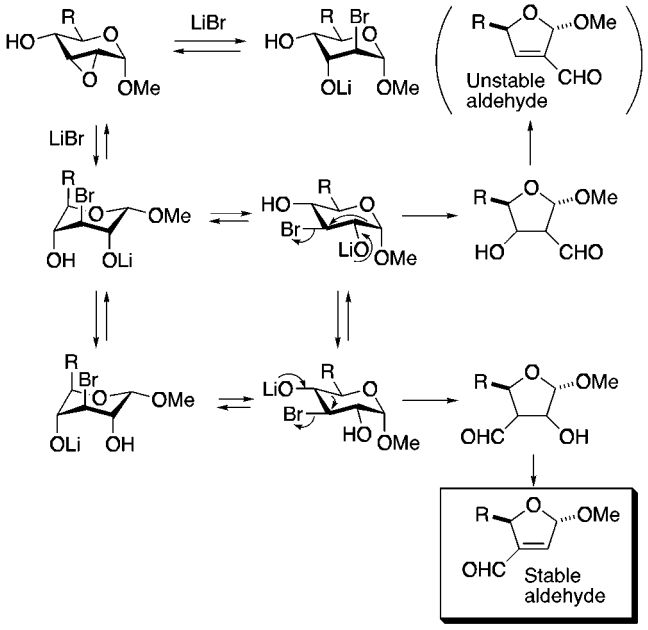


[a] (a) LiBr, TMU, toluene, reflux, 10 min; (b) 3% of the isomer **15a** (see Experimental Section) was also formed; (c) no aldehyde was obtained.

The ease of preparation and the purity of the aldehydes shown in Scheme 2 makes the ring contraction a useful preparative procedure. However, it is disturbing not knowing the reasons for the modest yields obtained. On the basis of mechanistic investigations with deuterated epoxycyclohexanols[4] and epoxypyranosides,[6,7] we expect that not only the isolated aldehyde is formed in the ring contraction but also its isomer (cf. the unstable aldehyde of Scheme 3). A very limited number of α,β-unsaturated aldehydes carrying an $(RO)_2CH$ group in the α-position is known. They are generally difficult to prepare, and more importantly, they are prone to undergo elimination of alcohol from the acetal moiety, as well as polymerization.[13] Such side reactions would explain the limited yield of isolated aldehydes (Scheme 2), as well as the absence of isomers (except for **15a**).

II. Synthesis and Ring Contraction of *C*-Glycosidic Epoxy Alcohols. In order to investigate the importance of the methoxy group for the formation of

Scheme 3[a]



[a] Simplified mechanistic scheme; for a full account, see refs 4, 6, and 7.

byproducts, the *C*-epoxyglycoside analogs **24** and **25** were prepared and submitted to ring contraction (Scheme 4).

Allyl *C*-glycoside **17**[14] was hydrogenated to give the *C*-propyl analog **18** (95%). Deacetylation of **18** with methanolic MeONa, followed by acetalization with α,α-dimethoxytoluene gave the 4,6-*O*-benzylidene acetal **19** (88%). Treatment of **19** with *p*-TsCl−K_2CO_3−NaOH−DMSO in toluene[15] gave the corresponding ditosylate, which was treated, without purification, with the two-phase system H_2O−toluene−NaOH−Bu_4NHSO_4−MeO-CH_2CH_2OH−DMSO to give the epoxide **20** (18%). In an attempt to raise the yield, **19** was tosylated in pyridine, which gave a mixture of the two corresponding monotosylates. Treatment of the mixture with methanolic MeONa gave the epoxides **21** (65%) and **20** (25%). The benzylidene group of **20** and **21** was removed by hydrogenolysis over several days, which gave **22** (74%) and **23** (75%), respectively. Silylation of **22** with dimethylhexylchlorosilane gave the epoxy alcohol **24** (16%) after 3 days. The low yield was probably due to migration of the silyl group from O-6 to O-4, followed by silylation of O-6, since a significant amount of disilylated material was also obtained. Silylation of **23** under the same conditions gave, after 18 h, epoxy alcohol **25** (61%), as well as some disilylated material. The sluggishness of the epoxidation, hydrogenolysis, and silylation reactions was unexpected, since the *O*-glycoside analogs reacted readily under the same conditions.[7,15]

Ring contraction (LiBr, TMU) of the epoxy alcohols **24** and **25** gave mixtures of the two aldehydes **26** and **27**, together with the ketone **28**. No other products could be identified. The ketone was probably formed via a 1,2-hydride shift followed by loss of water. Such hydride shifts were observed in the rearrangement of epoxycyclohexanols described previously.[4] The total product yield in the rearrangement of **24** and **25** was lower than expected from the TLC analysis. It might in part be due

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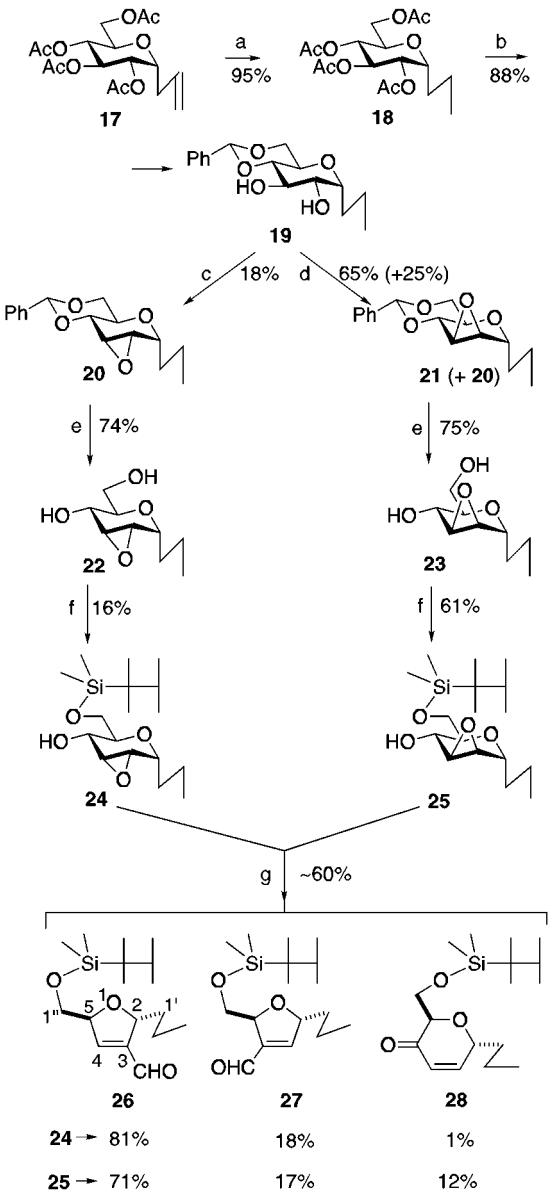
Scheme 4[a]



[a] (a) H_2, Pd/C, EtOAc/toluene 1:1, 5 h, 22 °C; (b) MeONa/MeOH, 3 h, 22 °C, then $(MeO)_2CHC_6H_5$, *p*-TsOH, MeCN, 24 h, 22 °C; (c) *p*-TsCl, K_2CO_3, NaOH, toluene/DMSO, 22:1, 22 h, 22 → 55 °C, then $MeOCH_2CH_2OH$, Bu_4NHSO_4, 28 h, 22 °C (→ ditosylate), then 50% aqueous NaOH, Bu_4NHSO_4, DMSO, $MeOCH_2CH_2OH$, toluene, 8.7 d, 22 °C → reflux; (d) *p*-TsCl, pyridine, 24 h, 60 °C, then MeONa/MeOH, 96 h, 22 °C; (e) H_2, Pd/C, EtOAc/THF 1:3, 6 d (**20**) and 10 d (**23**), 22 °C; (f) $Me_2CHMe_2CMe_2SiCl$, pyridine, 72 h (**24**) and 18 h (**25**), 22 °C; (g) LiBr, TMU, toluene, reflux, 10 min.

to losses in the workup, since the products are quite volatile.

The aldehydes **26** and **27** could not be separated by preparative column chromatography. Attempted separation with HPLC, both on SiO_2 and C_8 columns, was equally unsuccessful. Similar difficulties would probably have arisen with the *O*-glycosidic aldehydes of Scheme 2, if the unstable isomeric aldehyde (cf. Scheme 3) had not been destroyed in the rearrangement reaction. This was corroborated by unsuccessful attempts to separate **15** from its isomer **15a**.

Aldehyde **26** was obtained, by preparative GC, in acceptable purity (90−95%) for structure determination by NMR ($^1H-^1H$ NOESY and $^1H-^{13}C$ long-range HETCOR). Thus, H-4 showed a strong NOE with CHO, H-5, H-1″, Me_2Si, and Me_2CH, but not with H-2 and H-1′ (for numbering, see Scheme 4). In addition, the long-range HETCOR experiment showed couplings between C-2 and CHO, and between C-4 and H-1″. The NMR spectra of **27** (in a mixture with **26**) were fully consistent with the given structure. The observation that aldehyde **26** was formed from the *C*-glycosidic epoxy alcohol **24** indicates that an isomer of **10** was probably also formed in the reaction of the analogous *O*-glycosidic epoxy alcohol **1**, but it was destroyed during the reaction, thus greatly simplifying the isolation of **10**.

Experimental Section

^1H NMR spectra were recorded (23 °C) at 400 or 300 MHz proton frequency, using $CDCl_3$ or C_6D_6 as solvent and $CHCl_3$ (δ 7.26 ppm) or C_6D_5H (δ 7.30 ppm) as internal standards. ^{13}C NMR spectra were recorded at 100 or 75 MHz carbon frequency, using the same solvents and internal standards (δ 77.0 and 128.0 ppm, respectively) as above. The compounds described below with signal assignments were investigated by 2D NMR experiments. LiBr was dried under reduced pressure (0.1 mmHg) at 120 °C for 2−12 h. Tetramethylurea (TMU) was distilled and kept over 4 Å molecular sieves. TLC analyses were performed with Merck SiO_2 60 F_{254} precoated aluminum sheets with visualization by UV light, by I_2, or by charring with anisaldehyde in ethanolic sulfuric acid.[16] Preparative column chromatography was performed with Matrex SiO_2 60 (35−70 mm) unless otherwise stated. Compounds **1**,[7] **3**,[12] **4**,[11] **5**,[12] **6**,[12] **7**,[11] **8**,[11] **9**,[11] **10**,[7] and **17**[14] have been described.

Methyl 2,3-Anhydro-6-deoxy-6-propyl-α-D-allopyranoside (2). Methyl 2,3-anhydro-4-benzoyl-6-deoxy-6-(prop-2-en-1-yl)-α-D-allopyranoside[17] (378 mg, 1.24 mmol) was dissolved in EtOAc (30 mL), and the mixture was hydrogenated (H_2, 1 atm, Pd/C, 74 mg) for 15 h. The catalyst was filtered off (Celite), and the solvent was removed. The crude product was dissolved in MeOH (10 mL) and debenzoylated by treatment with methanolic NaOMe (0.25 mL, 0.5 M) for 20 h. The mixture was neutralized with SiO_2 and concentrated. The residue was chromatographed (heptane/EtOAc, 1:1) to give **2** (198 mg, 79%) as an oil: $[\alpha]^{23}_D$ +167 (*c* 0.9, $CHCl_3$); ^1H NMR data (C_6D_6) δ 4.57 (d, 1 H, J = 2.7 Hz), 3.79 (dt, 1 H, J = 2.3, 9.1 Hz), 3.49 (br dd, 1 H, J = 8.6, 9.1 Hz), 3.35 (s, 3 H), 3.14 (dd, 1 H, J = 2.8, 4.1 Hz), 3.12 (dd, 1 H, J = 1.5, 4.1 Hz), 2.01 (m, 1 H), 1.94 (br d, 1 H, J = 8.9 Hz), 1.70 (m, 1 H), 1.34−1.60 (m, 4 H), 1.04 (t, 3 H, J = 7.1 Hz); ^{13}C NMR data ($CDCl_3$) δ 94.5, 69.9, 68.7, 56.0, 55.7, 54.1, 31.1, 27.9, 22.5, 14.0; HRMS calcd for $C_{10}H_{22}O_4N$ (M + NH_4) 220.1549, found 220.1552.

General Procedure for Ring Contraction of the Epoxy Alcohols 1−9, 24, and 25. The epoxy alcohol was dissolved in dry toluene, and dry LiBr and dry TMU were added under stirring (magnet). The mixture was refluxed for 10 min and then cooled to room temperature. TLC analysis showed a UV-active aldehyde spot with an R_f value 2−3 times greater than the R_f values of the byproducts (the TLC plates were developed by the anisaldehyde/H_2SO_4 reagent[16]). The mixture was added to a short (10−15 cm) SiO_2 column and chromatographed to give pure **10**−**16** and **26** + **27**. The eluent was chosen to give an R_f value of approximately 0.3 for the aldehyde product. The ring contractions that produced aldehydes in less than 20% yield generally appeared as brown−black mixtures, whereas reaction mixtures giving more than 20% yield were less colored; mixtures giving **10**−**13** and **26** + **27** had a weak yellow color.

(−)-(2*S*,5*S*)-2-[[[Dimethyl(1,1,2-trimethylpropyl)-silyl]oxy]methyl]-5-methoxy-2,5-dihydrofuran-3-carbaldehyde (10). Epoxy alcohol **1**[7] (145 mg, 0.45 mmol), toluene (4 mL), LiBr (69 mg, 0.79 mmol), and TMU (0.128 mL, 1.07 mmol) were treated according to the general procedure. The

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mixture was chromatographed (heptane/EtOAc, 4:1) to give **10** (78 mg, 57%); $[\alpha]_D$ and NMR data were as reported.[7]

(−)-(2*R*,5*S*)-2-Butyl-5-methoxy-2,5-dihydrofuran-3-carbaldehyde (11). Epoxy alcohol **2** (171 mg, 0.84 mmol), toluene (8 mL), LiBr (124 mg, 1.43 mmol), and TMU (0.240 mL, 2.00 mmol) were treated according to the general procedure. The mixture was chromatographed (heptane/EtOAc, 4:1) to give **11** (87 mg, 56%): $[\alpha]^{23}_D$ −19 (*c* 2.3, $CHCl_3$); ^{1}H NMR data ($CDCl_3$) δ 9.90 (s, 1 H), 6.66 (dd, 1 H, J = 1.6, 1.8 Hz), 5.88 (dd, 1 H, J = 1.3, 4.2 Hz), 5.14 (m, 1 H), 3.43 (s, 3 H), 1.92 (dddd, 1 H, J = 3.2, 4.8, 10.9, 13.8 Hz), 1.59 (m, 1 H), 1.38−1.21 (m, 4 H), 0.89 (t, 3 H, J = 7.1 Hz); ^{13}C NMR data ($CDCl_3$) δ 187.7, 148.6, 142.3, 107.7, 83.8, 55.2, 33.5, 27.2, 23.0, 14.4; HRMS calcd for $C_{10}H_{17}O_3$ (M + H) 185.1178, found 185.1178.

(−)-(2*R*,5*S*)-2-(But-3-en-1-yl)-5-methoxy-2,5-dihydrofuran-3-carbaldehyde (12). Epoxy alcohol **3**[12] (180 mg, 0.90 mmol), toluene (8 mL), LiBr (132 mg, 1.51 mmol), and TMU (0.250 mL, 2.08 mmol) were treated according to the general procedure. The mixture was chromatographed (heptane/EtOAc, 4:1) to give **12** (75 mg, 46%): $[\alpha]^{23}_D$ −26 (*c* 2.0, $CHCl_3$); ^{1}H NMR data ($CDCl_3$) δ 9.90 (s, 1 H, CHO), 6.67 (dd, 1 H, J = 1.4, 2.0 Hz, H-4), 5.89 (dd, 1 H, J = 1.3, 4.2 Hz, H-5), 5.81 (dddd, 1 H, J = 5.9, 6.7, 10.4, 17.1 Hz, H-3′), 5.16 (dddd, 1 H, J = 2.2, 4.3, 6.6, 9.2 Hz, H-2), 5.02 (ddd, 1 H, J = 1.6, 3.3, 17.1 Hz, H-4′), 4.96 (dddd, 1 H, J = 1.2, 1.8, 3.3, 10.2 Hz, H-4′), 3.43 (s, 3 H, OMe), 2.18−2.00 (m, 3 H, H-1′ and 2′), 1.72−1.61 (m, 1 H, H-1′); ^{13}C NMR data ($CDCl_3$): δ 187.7 (CHO), 148.4 (C-3), 142.4 (C-4), 138.3 (C-3′), 115.4 (C-4′), 107.7 (C-5), 83.2 (C-2), 55.2 (OMe), 32.9 (C-1′), 29.3 (C-2′); HRMS calcd for $C_{10}H_{15}O_3$ (M + H) 183.1021, found 183.0985.

(+)-(2*S*,5*S*)-2-[(Decylthio)methyl]-5-methoxy-2,5-dihydrofuran-3-carbaldehyde (13). Epoxy alcohol **4**[11] (504 mg, 1.51 mmol), toluene (12 mL), LiBr (215 mg, 2.47 mmol), and TMU (0.425 mL, 3.54 mmol) were treated according to the general procedure. The mixture was chromatographed (heptane/EtOAc, 6:1) to give **13** (215 mg, 45%) as an oil: $[\alpha]^{23}_D$ +4.2 (*c* 1.3, $CHCl_3$); ^{1}H NMR data ($CDCl_3$) δ 9.91 (d, 1 H, J = 0.3 Hz), 6.77 (ddd, 1 H, J = 0.3, 1.3, 1.8 Hz), 5.95 (dd, 1 H, J = 1.3, 4.1 Hz), 5.38 (dddd, 1 H, J = 2.0, 2.9, 4.1, 5.0 Hz), 3.45 (s, 3 H), 3.13 (ddd, 1 H, J = 0.4, 3.2, 13.9 Hz), 2.89 (dd, 1 H, J = 4.9, 13.9 Hz), 2.53 (t, 2 H, J = 7.5 Hz), 1.56 (m, 2 H), 1.40−1.24 (m, 14 H), 0.89 (t, 3 H, J = 6.7 Hz); ^{13}C NMR data ($CDCl_3$) δ 187.5, 146.7, 143.1, 108.3, 83.5, 55.5, 36.0, 33.9, 32.3, 30.2, 30.0, 29.9, 29.8, 29.7, 29.6, 29.3, 14.5; HRMS calcd for $C_{17}H_{30}O_3S$ (M^+) 314.1916, found 314.1906.

(−)-(2*R*,5*S*)-2-[3-(Acetoxymethyl)but-3-en-1-yl]-5-methoxy-2,5-dihydrofuran-3-carbaldehyde (14). Epoxy alcohol **5**[12] (237 mg, 0.87 mmol), toluene (8 mL), LiBr (123 mg, 1.42 mmol), and TMU (0.250 mL, 2.08 mmol) were treated according to the general procedure. The mixture was chromatographed (heptane/EtOAc, 3:1) to give **14** (85 mg, 38%): $[\alpha]^{23}_D$ −18 (*c* 0.9, $CHCl_3$); ^{1}H NMR data ($CDCl_3$) δ 9.90 (d, 1 H, J = 0.3 Hz, CHO), 6.68 (dd, 1 H, J = 1.3, 2.1 Hz, H-4), 5.88 (dd, 1 H, J = 1.3, 4.2 Hz, H-5), 5.14 (m, 1 H, H-2), 5.04 (dd, 1 H, J = 0.8, 1.2 Hz, H-4′), 4.96 (t, 1 H, J = 0.6 Hz, H-4′), 4.53, 4.50 (AB q, 2 H, J = 14.3 Hz, CH_2OAc), 3.42 (s, 3 H, OMe), 2.17−2.04 (m, 3 H, H-1′ and 2′), 2.09 (s, 3 H, Ac), 1.77−1.65 (m, 1 H, H-1′); ^{13}C NMR data ($CDCl_3$) δ 187.6 (CHO), 171.2 (Ac), 148.2 (C-3), 143.5 (C-3′), 142.5 (C-4), 113.2 (C-4′), 107.7 (C-5), 83.1 (C-2), 67.3 (CH_2OAc), 55.2 (OMe), 31.8 (C-1′), 28.7 (C-2′), 21.4 (Ac); HRMS calcd for $C_{13}H_{18}O_5$ (M^+) 254.1154, found 254.1153.

(−)-(2*R*,5*S*)-2-[3-(Ethoxycarbonyl)but-3-en-1-yl]-5-methoxy-2,5-dihydrofuran-3-carbaldehyde (15) and (−)-(2*S*,5*R*)-5-[3-(Ethoxycarbonyl)but-3-en-1-yl]-2-methoxy-2,5-dihydrofuran-3-carbaldehyde (15a). Epoxy alcohol **6**[12] (58 mg, 0.21 mmol), toluene (2.5 mL), LiBr (31 mg, 0.35 mmol), and TMU (0.060 mL, 0.50 mmol) were treated according to the general procedure. The mixture was chromatographed (heptane/EtOAc, 1:1) to give **15**, containing 3% of its isomer **15a** (20 mg, 38%); $[\alpha]_D^{23}$ −16 (*c* 2.0, $CDCl_3$). Compound **15**: ^{1}H NMR data ($CDCl_3$) δ 9.91 (s, 1 H), 6.68 (dd, 1 H, J = 1.3, 2.0 Hz), 6.15 (m, 1 H), 5.89 (dd, 1 H, J = 1.3, 4.1 Hz), 5.54 (dd, 1 H, J = 1.4, 2.8 Hz), 5.17 (m, 1 H), 4.20 (q, 2 H, J = 7.1 Hz), 3.43 (s, 3 H), 2.34 (dd, 2 H, J = 7.5, 8.0 Hz), 2.13 (m, 1 H), 1.77 (m, 1 H), 1.31 (t, 3 H, J = 7.1 Hz); ^{13}C NMR data ($CDCl_3$) δ 187.2, 167.1, 147.7, 142.1, 140.1, 124.7, 107.4, 82.6, 60.7, 54.9, 31.9, 26.9, 14.2; HRMS calcd for $C_{13}H_{19}O_5$ (M + H) 255.1232, found 255.1216. Compound **15a**: ^{1}H NMR data ($CDCl_3$) δ 9.90 (d, 1 H, J = <1 Hz), 6.67 (dd, 1 H, J = 1.5, 3.0 Hz), 6.18 (d, 1 H, J = 1.5 Hz), 5.87 (dd, 1 H, J = 1.2, 4.2 Hz), 5.49 (m, 1 H), 5.14 (m, 1 H), 4.18 (q, 2 H, J = 7.1 Hz), 1.30 (t, 3 H, J = 7.1 Hz).

(+)-(2*S*,5*S*)-2-[(Decylsulfonyl)methyl]-5-methoxy-2,5-dihydrofuran-3-carbaldehyde (16). Epoxy alcohol **7**[11] (272 mg, 0.75 mmol), toluene (6 mL), LiBr (110 mg, 1.26 mmol), and TMU (0.215 mL, 1.79 mmol) were treated according to the general procedure. The mixture was chromatographed (heptane/EtOAc, 1:1 → 0:1) to give **16** (23 mg, 9%), which crystallized upon standing: mp 54−56 °C; $[\alpha]^{23}_D$ +46 (*c* 1.4, $CHCl_3$); ^{1}H NMR data ($CDCl_3$): δ 9.92 (d, 1 H, J = 0.4 Hz, CHO), 6.79 (dd, 1 H, J = 1.3, 2.3 Hz, H-4), 5.96 (dd, 1 H, J = 1.3, 4.0 Hz, H-5), 5.53 (dddt, 1 H, J = 0.4, 2.3, 4.0, 8.7 Hz, H-2), 3.66 (dd, 1 H, J = 2.3, 14.9 Hz, H-1′), 3.46 (s, 3 H, OMe), 3.16 (dd, 1 H, J = 8.7, 14.9 Hz, H-1′), 3.12 (dd, 2 H, J = 7.9, 8.3 Hz, H-3′), 1.94−1.76 (m, 2 H, H-4′), 1.48−1.41 (m, 2 H, H-5′), 1.35−1.27 (m, 12 H), 0.89 (t, 3 H, J = 6.7 Hz, H-12′); ^{13}C NMR data ($CDCl_3$) δ 186.6, 145.1, 142.1, 108.1, 78.2, 55.4, 55.1, 31.8, 29.5, 29.3, 29.1, 28.5, 22.7, 21.9, 14.1; HRMS calcd for $C_{17}H_{30}O_5S$ (M^+) 346.1814, found 346.1800.

***C*-Propyl 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranoside (18).** Compound **17**[14] (112 mg, 0.30 mmol) was dissolved in EtOAc/toluene (10 mL, 1:1) and the mixture was hydrogenated (H_2, 1 atm, Pd/C, 10 mg). After 5 h, the catalyst was filtered off (Celite), and the solvent was removed. The residue was chromatographed (SiO_2, heptane/EtOAc, 3:1), and the crude material was crystallized from ether by addition of heptane to give pure **18** (107 mg, 95%): mp 132−133 °C; $[\alpha]^{23}_D$ +70 (*c* 0.8, $CHCl_3$); ^{1}H NMR data ($CDCl_3$) δ 5.33 (t, 1 H, J = 9.2 Hz, H-3), 5.08 (dd, 1 H, J = 5.8, 9.6 Hz, H-2), 4.99 (dd, 1 H, J = 9.0, 9.4 Hz, H-4), 4.25 (dd, 1 H, J = 5.2, 12.1 Hz, H-6), 4.19 (ddd, 1 H, J = 3.3, 5.8, 11.5 Hz, H-1), 4.08 (dd, 1 H, J = 2.6, 12.1 Hz, H-6), 3.82 (ddd, 1 H, J = 2.6, 5.2, 9.3 Hz, H-5), 2.10, 2.06, 2.043, 2.036 (4s, 3 H each, Ac), 1.78 (m, 1 H, H-1′), 1.51−1.42 (m, 2 H, H-1′,2′), 1.33 (m, 1 H, H-2′), 0.97 (t, 3 H, J = 7.2 Hz, H-3′); ^{13}C NMR data ($CDCl_3$) δ 171.1, 170.6, 170.1, 170.0, 72.9, 70.9, 69.4, 68.9, 62.8, 27.7, 21.2, 21.09, 21.06, 18.6, 14.2; HRMS calcd for $C_{17}H_{27}O_9$ (M + H) 375.1655, found 375.1656.

***C*-Propyl 4,6-*O*-Benzylidene-α-D-glucopyranoside (19).** Compound **18** (59 mg, 0.16 mmol) was dissolved in MeOH (2 mL), and methanolic NaOMe (0.015 mL, 0.5 M) was added. After 3 h, SiO_2 (ca 0.5 g) was added, and the mixture was filtered (Celite) and concentrated. The residue was suspended in a mixture of CH_3CN (2.0 mL, freshly distilled) and α,α-dimethoxytoluene (0.10 mL, 0.67 mmol). *p*-TsOH (catalytic amount) was added, and the mixture was stirred for 24 h. The acid was neutralized by passing the reaction mixture through a short pad of Al_2O_3 (basic, grade II). The solvent was removed to give **19** (41 mg, 88%), which crystallized upon standing: mp 195−197 °C; $[\alpha]^{23}_D$ +51 (*c* 0.6, $CHCl_3$); ^{1}H NMR data ($CDCl_3$) δ 7.51 (m, 2 H, Ph), 7.39 (m, 3 H, Ph), 5.55 (s, 1 H, PhCH), 4.28 (dd, 1 H, J = 4.6, 10.1 Hz, H-6), 4.10 (m, 1 H, H-1), 3.90 (m, 2 H, H-2,3), 3.71 (t, 1 H, J = 10.1 Hz, H-6), 3.62 (dt, 1 H, J = 4.6, 9.7 Hz, H-5), 3.47 (t, 1 H, J = 9.3 Hz, H-4), 2.65 (d, 1 H, J = 1.8 Hz, OH), 2.44 (d, 1 H, J = 2.4 Hz, OH), 1.71 (m, 2 H, H-1′), 1.53 (m, 1 H, H-2′), 1.36 (m, 1 H, H-2′), 0.99 (t, 3 H, J = 7.3 Hz, H-3′); ^{13}C NMR data ($CDCl_3$) δ 137.5, 129.8, 128.8, 126.7, 102.4, 82.6, 76.8, 72.8, 72.1, 69.9, 63.7, 27.0, 19.0, 14.3; HRMS calcd for $C_{16}H_{23}O_5$ (M + H) 295.1545, found 295.1549.

***C*-Propyl 4,6-*O*-Benzylidene-2,3-anhydro-α-D-allopyranoside (20).** Compound **19** (243 mg, 0.82 mmol) was dissolved in toluene (9 mL), and K_2CO_3 (1.32 g, 9.55 mmol), powdered NaOH (480 mg, 12.0 mmol), 4-toluenesulfonyl chloride (409 mg, 2.14 mmol), and DMSO (0.40 mL) were added. The mixture was stirred at room temperature for 12 h and at 55 °C for 10 h and then cooled to room temperature. 2-Methoxyethanol (0.45 mL, 5.70 mmol) and tetrabutylammonium hydrogen sulfate (76.2 mg, 0.22 mmol) were added, and the stirring was continued for 28 h at room temperature. The mixture was poured into water/toluene (50 mL, 1:1), and the organic phase was washed with water (3 × 10 mL), dried (Na_2-

SO_4), and concentrated to give a crude ditosylate (497 mg). Attempts to purify the ditosylate on silica were unsuccessful. The crude ditosylate (396 mg, approx. 0.66 mmol) was dissolved in a mixture of toluene (7 mL), DMSO (0.35 mL) and 2-methoxyethanol (0.15 mL), and aqueous sodium hydroxide (2 mL, 50%) and tetrabutylammonium hydrogen sulfate (76.2 mg) were added. The reaction mixture was stirred at room temperature for 8 days, then refluxed for 17 h, and treated as in the preparation of the mixture of **21** and **20** below. The crude product was chromatographed (SiO_2, heptane/EtOAc, 4:1) to give **20** (34 mg, 18%): mp 90−92 °C; $[\alpha]^{23}_D$ +40 (*c* 0.9, $CHCl_3$); ^{1}H NMR data ($CDCl_3$) δ 7.53 (m, 2 H, Ph), 7.36−7.40 (m, 3 H, Ph), 5.58 (s, 1 H, PhCH), 4.20 (ddd, 1 H, J = 0.7, 4.9, 10.2 Hz, H-6), 4.07 (ddd, 1 H, J = 3.2, 5.8, 8.6 Hz, H-1), 4.01 (dd, 1 H, J = 1.2, 9.0 Hz, H-4), 3.85 (ddd, 1 H, J = 4.9, 9.0, 10.2 Hz, H-5), 3.65 (t, 1 H, J = 10.2 Hz, H-6), 3.58 (br d, 1 H, J = 4.6 Hz, H-3), 3.40 (dd, 1 H, J = 3.2, 4.6 Hz, H-2), 1.83 (m, 1 H, H-1′), 1.70 (m, 1 H, H-1′), 1.40−1.55 (m, 2 H, H-2′), 1.00 (t, 3 H, J = 7.3 Hz, H-3′); ^{13}C NMR data ($CDCl_3$) δ 137.7, 129.6, 128.8, 126.7, 103.1, 78.8, 71.4, 69.8, 61.4, 56.1, 52.2, 32.3, 19.2, 14.4; HRMS calcd for $C_{16}H_{21}O_4$ (M + H) 277.1440; found 277.1444.

***C*-Propyl 4,6-*O*-Benzylidene-2,3-anhydro-α-D-mannopyranoside (21) and *C*-Propyl 4,6-*O*-Benzylidene-2,3-anhydro-α-D-allopyranoside (20).** Compound **19** (769 mg, 2.61 mmol) was dissolved in dry pyridine (75 mL), and 4-toluenesulfonyl chloride (1030 mg, 5.40 mmol) was added. The mixture was left at room temperature for 1 h, then heated at 60 °C for 24 h, and cooled to room temperature. The solvent was removed by coevaporation with two portions of toluene, the residue was partitioned between ether and water, and the aqueous phase was extracted with ether (5 × 50 mL). The extract was dried (Na_2SO_4), filtered, and concentrated. The syrupy residue was chromatographed (SiO_2, heptane/EtOAc, 3:1) to give a regioisomeric mixture of monotosylates (971 mg, 83%). Part of the mixture (237 mg, 0.53 mmol) was dissolved in MeOH (5 mL), and methanolic NaOMe (2 mL, 0.5 M) was added under stirring. An additional portion of methanolic NaOMe (0.5 mL) was added after 3 days, and the stirring was continued for 24 h. CH_2Cl_2 (25 mL) was added, and the mixture was washed with water (3 × 5 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (heptane/EtOAc, 3:1) to give **20** (25 mg, 25%) and **21** (95 mg, 65%). Both **20** and **21** crystallized upon standing. Compound **21**: mp 113−115 °C; $[\alpha]^{23}_D$ +28 (*c* 0.8, $CHCl_3$); ^{1}H NMR data ($CDCl_3$) δ 7.52 (m, 2 H, Ph), 7.39 (m, 3 H, Ph), 5.60 (s, 1 H, PhCH), 4.25 (dd, 1 H, J = 4.7, 10.4 Hz, H-6), 4.18 (dd, 1 H, J = 4.4, 10.1 Hz, H-1), 3.72 (d, 1 H, J = 10.4 Hz, H-6), 3.68 (d, 1 H, J = 9.6 Hz, H-4), 3.50 (d, 1 H, J = 3.8 Hz, H-3), 3.35 (dt, 1 H, J = 4.7, 9.8 Hz, H-5), 3.07 (d, 1 H, J = 3.8 Hz, H-2), 1.85−1.94 (m, 1 H, H-1′), 1.44−1.61 (m, 3 H, H-1′,2′), 1.01 (t, 3 H, J = 7.2 Hz, H-3′); ^{13}C NMR data ($CDCl_3$) δ 137.6, 129.7, 128.8, 126.6, 102.7, 76.2, 72.8, 70.3, 63.3, 54.5, 53.2, 32.2, 19.5, 14.2; HRMS calcd for $C_{16}H_{21}O_4$ (M + H) 277.1440, found 277.1437.

***C*-Propyl 2,3-Anhydro-α-D-allopyranoside (22).** Compound **20** (149 mg, 0.54 mmol) was dissolved in THF/EtOH (4.5 mL, 3:1), and the mixture was hydrogenated (H_2, 1 atm, Pd/C, 38 mg). The reaction was monitored by TLC (heptane/EtOAc, 2:1). The starting material was consumed after 6 days, and the catalyst was filtered off (Celite). The solvent was removed, and the residue was chromatographed (toluene/EtOAc, 1:1 → 0:1) to give **22** (75 mg, 74%) as an oil: $[\alpha]^{23}_D$ +26 (*c* 1.6, $CHCl_3$); ^{1}H NMR data ($CDCl_3$) δ 4.03 (ddd, 1 H, J = 3.5, 6.0, 9.0 Hz, H-1), 3.95 (br t, 1 H, J = 7.9 Hz, H-4), 3.76, 3.71 (br ABq, 2 H, J = 11.7 Hz, H-6), 3.52 (dd, 1 H, J = 1.8, 4.5 Hz, H-3), 3.47 (dd, 1 H, J = 3.6, 4.5 Hz, H-2), 3.43 (m, 1 H, H-5), 3.26 (d, 1 H, J = 8.2 Hz, OH-4), 2.69 (m, 1 H, OH-6), 1.77−1.68 (m, 1 H, H-1′), 1.65−1.56 (m, 1 H, H-1′), 1.51−1.35 (m, 2 H, H-2′), 0.96 (t, 3 H, J = 7.3 Hz, H-3′); ^{13}C NMR data ($CDCl_3$) δ 70.5, 70.4, 66.5, 62.9, 58.5, 55.5, 31.5, 19.2, 14.4; HRMS calcd for $C_9H_{17}O_4$ (M + H) 189.1127, found 189.1127.

***C*-Propyl 2,3-Anhydro-α-D-mannopyranoside (23).** Compound **21** (571 mg, 2.07 mmol) was dissolved in THF/EtOH (13.5 mL, 3:1), and the mixture was hydrogenated (H_2, 1 atm, Pd/C, 102 mg). The reaction was monitored by TLC (heptane/EtOAc, 2:1). The starting material was consumed after 10 days, and the catalyst was filtered off (Celite). The solvent was removed, and the residue was chromatographed (toluene/EtOAc, 1:1 → 0:1) to give **23** (293 mg, 75%), which crystallized from an ether/heptane mixture: mp 75−78 °C; $[\alpha]^{23}_D$ +5.3 (*c* 1.4, $CDCl_3$); ^{1}H NMR data ($CDCl_3$) δ 4.11 (dd, 1 H, J = 4.3, 10.0 Hz, H-1), 3.84 (br d, 1 H, J = 8.8 Hz, H-4), 3.74 (m, 2 H, H-6), 3.50 (br d, 1 H, J = 2.3 Hz, OH), 3.31 (d, 1 H, J = 3.8 Hz, H-2 or 3), 3.21 (ddd, 1 H, J = 4.3, 4.5, 9.0 Hz, H-5), 3.06 (d, 1 H, J = 3.8 Hz, H-2 or 3), 2.70 (br s, 1 H, OH), 1.84 (m, 1 H, H-1′), 1.40−1.55 (m, 3 H, H-1′,2′), 0.98 (t, 3 H, J = 7.2 Hz, H-3′); ^{13}C NMR data ($CDCl_3$) δ 71.3, 70.2, 63.5, 63.2, 56.1, 53.3, 31.3, 19.4, 14.3; HRMS calcd for $C_9H_{17}O_4$ (M + H) 189.1127, found 189.1123.

***C*-Propyl 2,3-Anhydro-6-*O*-[dimethyl(1,1,2-trimethylpropyl)silyl]-α-D-allopyranoside (24).** Compound **22** (67 mg, 0.36 mmol) was dissolved in dry pyridine (5 mL), and dimethyl(1,1,2-trimethylpropyl)chlorosilane (0.085 mL, 0.43 mmol) was added at room temperature under stirring. After 2 days, a second portion of dimethyl(1,1,2-trimethylpropyl-)chlorosilane (0.007 mL, 0.03 mmol) was added, and the mixture was stirred at −18 °C overnight. TLC (toluene/EtOAc, 1:1) showed that **22** had been consumed. MeOH (1 drop) and toluene (3 × 10 mL) were added, and the solvents were removed. The syrupy residue was dissolved in ether (75 mL), and the organic phase was washed with water (3 × 5 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (CH_2Cl_2/EtOAc, 100:1 → 10:1) to give **24** (19 mg, 16%) as a syrup: $[\alpha]^{23}_D$ −3.2 (*c* 1.6, $CHCl_3$); ^{1}H NMR data ($CDCl_3$) δ 4.00 (ddd, 1 H, J = 3.4, 5.8, 8.9 Hz, H-1), 3.93 (ddd, 1 H, J = 2.1, 5.2, 7.7 Hz, H-4), 3.76 (dd, 1 H, J = 5.3, 10.2 Hz, H-6), 3.67 (dd, 1 H, J = 6.3, 10.2 Hz, H-6), 3.51 (dd, 1 H, J = 2.1, 4.4 Hz, H-3), 3.47 (dt, 1 H, J = 5.8, 8.2 Hz, H-5), 3.43 (dd, 1 H, J = 3.4, 4.4 Hz, H-2), 3.00 (br d, 1 H, J = 5.2 Hz, OH-4), 1.73 (m, 1 H, H-1′), 1.63 (m, 2 H, H-1′ and Me_2CH), 1.45 (m, 2 H, H-2′), 0.97 (t, 3 H, J = 7.3 Hz, H-3′), 0.87 (d, 6 H, J = 6.9 Hz, Me_2CH), 0.85 (s, 6 H, Me_2C), 0.13 (s, 6 H, Me_2Si); ^{13}C NMR data ($CDCl_3$) δ 70.2, 69.7, 69.2, 65.5, 57.7, 54.8, 34.5, 31.6, 25.5, 20.7, 20.6, 19.1, 18.9, 18.8, 14.4, −3.1, −3.2; HRMS calcd for $C_{17}H_{35}O_4Si$ (M + H) 331.2305, found 331.2307.

***C*-Propyl 2,3-Anhydro-6-*O*-[dimethyl(1,1,2-trimethylpropyl)silyl]-α-D-mannopyranoside (25).** Compound **23** (266 mg, 1.41 mmol) was dissolved in dry pyridine (20 mL), and dimethyl(1,1,2-trimethylpropyl)chlorosilane (0.335 mL, 1.70 mmol) was added at room temperature under stirring. After 18 h, TLC (toluene/EtOAc, 1:1) showed that **23** had been consumed. MeOH (1 drop) and toluene (3 × 25 mL) were added, and the solvents were removed. The syrupy residue was dissolved in ether (200 mL), and the organic phase was washed with water (3 × 20 mL), dried (Na_2SO_4), and concentrated. The residue was chromatographed (CH_2Cl_2/EtOAc, 10:1) to give **25** (285 mg, 61%) as a syrup [chromatography with heptane/EtOAc, 4:1, gave a mixture of **25** and the isomer silylated in the 4-position (407 mg, 10:1)]. Compound **25**: $[\alpha]^{23}_D$ −19 (*c* 0.9, $CHCl_3$); ^{1}HNMR data ($CDCl_3$) δ 4.08 (dd, 1 H, J = 4.4, 10.2 Hz, H-1), 3.81 (dd, 1 H, J = 5.3, 9.5 Hz, H-6), 3.76 (dd, 1 H, J = 1.3, 8.6 Hz, H-4), 3.57 (dd, 1 H, J = 9.0, 9.5 Hz, H-6), 3.28 (d, 1 H, J = 1.7 Hz, OH-4), 3.26 (d, 1 H, J = 3.9 Hz, H-2 or −3), 3.23 (m, 1 H, H-5), 3.03 (d, 1 H, J = 3.8 Hz, H-2 or −3), 1.85 (m, 1 H, H-1′), 1.61 (heptet, 1 H, J = 6.9 Hz, Me_2CH), 1.39−1.56 (m, 3 H, H-1′,2′), 0.98 (t, 3 H, J = 7.1 Hz, H-3′), 0.88 (d, 6 H, J = 6.8 Hz, Me_2CH), 0.86 (s, 6 H, Me_2C), 0.14 (s, 6 H, Me_2Si); ^{13}C NMR data ($CDCl_3$) δ 71.3, 68.7, 67.6, 66.6, 55.1, 53.0, 34.5, 31.3, 25.6, 20.7, 20.5, 19.4, 18.9, 18.8, 14.2, −3.2, −3.3; HRMS calcd for $C_{17}H_{35}O_4Si$ (M + H) 331.2305, found 331.2312.

(2*R*,5*S*)-2-Propyl-5-[[[Dimethyl(1,1,2-trimethylpropyl)-silyl]oxy]methyl]-2,5-dihydrofuran-3-carbaldehyde (26). (a) Epoxy alcohol **24** (16.3 mg, 0.049 mmol), toluene (0.8 mL), LiBr (8.1 mg, 0.093 mmol), and TMU (0.015 mL, 0.125 mmol) were treated according to the general procedure. The mixture was chromatographed (heptane/EtOAc, 10:1) to give a mixture (81:18:1 according to ^{1}H-NMR and GC−MS analysis: DB-Wax 30 m capillary column, 100 °C for 3 min, then 3 °C/min) of **26**, **27**, and **28** (9.3 mg, 61%).

(b) Epoxy alcohol **25** (201 mg, 0.61 mmol), toluene (6 mL), LiBr (99 mg, 1.14 mmol), and TMU (0.200 mL, 1.67 mmol)

were treated according to the general procedure. The mixture was chromatographed (heptane/EtOAc, 10:1) to give a mixture (71:17:12 according to ^{1}H-NMR and GC−MS analysis) of **26**, **27**, and **28** (114 mg, 60%). A sample of **26** (90−95% purity) was obtained by preparative GC (6 m OV-351 column with inner diameter 4 mm; column temperature 175 °C; injector temperature 225 °C; detector temperature 210 °C; injected volume of **26** dissolved in ether: 0.150 mL, 100 mg/mL; elution time 225−230 min). Compounds **27** and **28** were not obtained pure enough for full structural analysis; ^{1}H NMR and HRMS of the crude material was consistent with the structures given. Compound **26**: ^{1}H NMR data ($CDCl_3$) δ 9.83 (s, 1 H, CHO), 6.90 (t, 1 H, J = 1.7 Hz, H-4), 5.11 (dddd, 1 H, J = 1.7, 4.2, 5.7, 6.3 Hz, H-2), 5.01 (dddd, 1 H, J = 1.7, 3.5, 5.1, 8.8 Hz, H-5), 3.81 (dd, 1 H, J = 4.2, 10.2 Hz, CH_2OSi), 3.64 (dd, 1 H, J = 6.3, 10.2 Hz, CH_2OSi), 1.83 (m, 1 H, $OCHCH_2CH_2$), 1.66−1.54 (m, 2 H, $OCHCH_2CH_2$, Me_2CH), 1.45−1.33 (m, 2 H, $OCHCH_2CH_2$), 0.93 (t, 3 H, J = 7.3 Hz, CH_2CH_3), 0.87 (d, 6 H, J = 6.8 Hz, Me_2CH), 0.84 (s, 6 H, Me_2C), 0.10 (s, 6 H, Me_2Si); ^{13}C NMR data ($CDCl_3$) δ 187.4 (CHO), 148.5 (C-4), 146.1 (C-3), 86.1 (C-5), 84.5 (C-2), 65.4 (C-1″), 36.8 (C-1′), 34.6 (Me_2CH), 25.5 (Me_2C), 20.7, 18.9, 18.6, 14.4 (C-3′), −3.1 (Me_2Si); HRMS calcd for $C_{17}H_{33}O_3Si$ (M + H): 313.2199, found 313.2186.

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Supporting Information Available: ^{1}H NMR spectra for all title compounds described in the Experimental Section (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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