2-(Phenylsulfonyl)-3-(2,6-dichlorophenyl)oxaziridines (**5d**): 86% yield; mp 97–8 °C dec; NMR ($CDCl_3$) 5.75 (s, 1 H), 7.2–8.3 (m, 8 H, Ar).

Anal. Calcd for $C_{13}H_9Cl_2NO_3S$: C, 47.28; H, 2.75. Found: C, 47.42; H, 2.80.

Aryl methyl sulfoxides **7** were purchased from Parish Chem. Co. or were prepared by oxidation of the corresponding sulfides[45] using (*E*)-2-(phenylsulfonyl)-3-phenyloxaziridine (**5b**) as previously described.[20]

Kinetic Study of the Oxidation of Me_2SO to Dimethyl Sulfone. In a 1.0-mL volumetric flask, 0.38 mmol of the appropriate oxaziridine **5** and an equilmolar amount of Me_2SO, 0.0296 g (0.38 mmol), was combined with 0.0346 g (0.019 mmol) of the diphenylmethane standard and diluted to 1.0 mL with $CDCl_3$. The solution was transferred to an NMR tube, thermostated in an oil bath at the desired temperature or in the NMR probe using an NMR variable-temperature controller. For kinetics the course of the oxidation was determined by NMR initially at 0.5 h and than at 1-h intervals at which time the reaction was quenched by cooling the NMR tube in an ice bath. The amount of dimethyl sulfone present at anyone time was determined by comparison of the integrated peak areas of the sulfone (s, 2.9 ppm) and the methylene protons of the diphenylmethane standard (s, 4.0 ppm).

The reactions were followed beyond 75% completion and the individual integrations were repeated at least four times and the results averaged. Errors in the NMR technique are estimated to be between 1–2% by Kesler.[35] All kinetic determinations were performed at least twice and the results averaged.

The second-order rate constants (k) were calculated from the slope of the line obtained by plotting the reciprocal of the concentration ($1/c$) vs. the time (t) by using a least-squares program. Errors reported are standard deviations. These results are summarized in Table I.

Kinetic Study of the Oxidation of Aryl Methyl Sulfoxides 7 to Aryl Methyl Sulfones. This studies were carried out as described above. The amount of aryl methyl sulfone **8** present at anyone time was determined by comparison of the integrated peak areas of the sulfone (s, 3.6 ppm) and the methylene protons of the diphenylmethane standard (s, 4.0 ppm). These results are summarized in Table II.

Kinetic Study of the Oxidation of Methylcyclohexene to Methylcyclohexene Oxide (10). In a 1-mL volumetric were placed 0.074 g (0.077 mmol) of 1-methylcyclohexene, an equivalent molar amount of the appropriate 2-sulfonyloxaziridine **5** or **9**, and 0.129 g (0.077 mmol) of the diphenylmethane standard. The mixture was dissolved in $CDCl_3$ and transferred to an NMR tube. In the case of oxaziridines **5e,f**, it was necessary to use 1.5 mL of $CDCl_3$ for complete solubility. The NMR tubes were heated in an oil bath at 30 °C. After the reaction mixture was heated in the NMR tube for the prescribed period of time, the reaction was quenched by cooling in an ice bath. The amount of 1-methylcyclohexene oxide (**10**) at any one time was determined by comparison of the integrated peak areas of **10** (2.8–3.0 ppm) and the methylene protons of the diphenylmethane standard (s, 4.0 ppm). These results are summarized in Table IV.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation.

Registry No. **5a**, 104393-73-9; **5b**, 63160-13-4; **5c**, 104393-74-0; **5f**, 104393-75-1; **5g**, 86428-23-1; **5i**, 63160-14-5; **5j**, 63160-15-6; **7a**, 934-72-5; **7b**, 1193-82-4; **7c**, 934-73-6; **7f**, 940-12-5; **9**, 73845-10-0; Me_2SO, 67-68-5; 1-methylcyclohexane, 591-49-1.

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An Efficient, Fully Stereocontrolled Total Synthesis of *N*-Benzoyl-L-daunosamine

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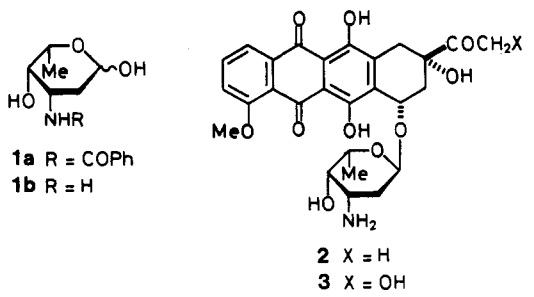
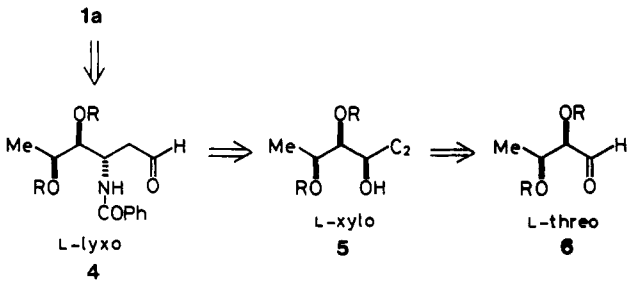
Completely stereocontrolled synthesis of *N*-benzoyl-L-daunosamine (**1a**) is described. The synthesis starts with 4-*O*-benzyl-2,3-*O*-bis(methoxymethyl)-L-threose (**12**), readily accessible from L-tartaric acid, and proceeds via the xylo alcohol **14** which is formed by an extremely high degree of chelation controlled addition of the acetal-containing Grignard reagent to **12**. The Mitsunobu reaction of **14** gives the phthalimide **15** which undergoes debenzylation followed by tosylation, iodination, and deiodination. The resulting 6-deoxyphthalimide **19** is converted to the *N*-benzoyl derivative **20**. Deprotection of **20** by treatment with BF_3·Et_2O–EtSH followed by $HgCl_2$–HgO provides *N*-benzoyl-L-daunosamine (**1a**).

L-Daunosamine (**1b**),[1] which is important as the amino sugar moiety of anthracycline antitumor agents daunorubicin (**2**) and adriamycin (**3**), has been the object of intense synthetic study because it contributes significantly to reduce its toxity and to improve upon its potency and efficiency, and several successful syntheses of optically active L-daunosamine have been described.[2,3] Traditionary, most



Scheme I



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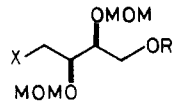
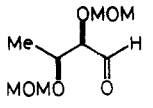
0022-3263/86/1951-4245$01.50/0

of such syntheses were based on the use of carbohydrate precursors.[4] More recently, major synthetic efforts have focused on approaches starting with nonsugar substrates.[5] We report here a completely stereocontrolled synthesis of *N*-benzoyl-L-daunosamine (**1a**) in optically pure state based on an extremely high degree of chelation-controlled nucleophilic addition of the acetal-containing Grignard reagent to the acyclic substrate **12**. Our synthesis provides a facile new entry to the elaboration of L-daunosamine involving no diastereomeric separation problem in the entire sequence.

Our strategy for the synthesis of **1a** is shown in Scheme I which began with introducing the C_2 unit with a suitable functionality and a new asymmetric center to the L-*threo* synthon **6**, affording the L-*xylo* framework as in **5**. Thus, mesylation of the L-threitol derivative **7**, prepared from the nonsugar chiral pool [(*R*,*R*)-tartaric acid],[6] and subsequent reduction of the resulting product **8** with $LiAlH_4$ gave **9**. Debenzylation of **9** (H_2, Pd/C, MeOH) produced



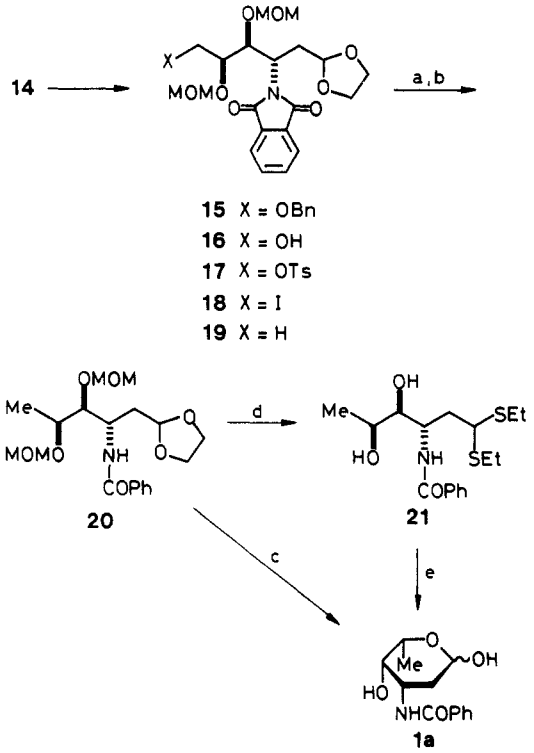
7 X = OH; R = Bn
8 X = OMs; R = Bn
9 X = H; R = Bn
10 X = R = H



11

10, which was then converted to the L-*threo* aldehyde **11** by Swern oxidation.[7] This product obtained, however, proved to be unstable under the basic conditions and partly decomposed on standing at room temperature for several days. We thus turned attention to the L-threose derivative **12** as a more efficient chiral substrate derived from **7**.[6]

Scheme II[a]



15 X = OBn
16 X = OH
17 X = OTs
18 X = I
19 X = H

20

21

1a

[a] (a) (from **19**) $(NH_2)_2 \cdot H_2O$, EtOH; (b) PhCOCl, aqueous Na_2CO_3, CH_2Cl_2; (c) method A: CF_3CO_2H, THF; method B: BCl_3, CH_2Cl_2; method C: Me_2BBr, CH_2Cl_2; (d) $BF_3 \cdot OEt_2$, EtSH; (e) $HgCl_2$, HgO, MeCN.

Our initial attempts at the diastereoselective formation of the *xylo* alcohol **13a** based on the Reformatsky reaction of **12** resulted in the formation of a 55:45 mixture of the *xylo*/*lyxo* (or *lyxo*/*xylo*) isomers **13a** and **13b** (or **13b** and **13a**).[8] The complete diastereoselectivity in the desired sense was achieved successfully by the Grignard reaction of **12** with [(1,3-dioxolan-2-yl)methyl]magnesium bromide.[9,10] By this procedure the desired *xylo* adduct **14** was obtained in 70% yield as a single isomer, as judged by both 400-MHz ^1H and 100.6-MHz ^{13}C NMR spectra. Syn stereo induction realized with **12** is in agreement with the prediction based on the cyclic α-chelation model.[6a,11,12] The high level of stereoselectivity of the Grignard addition in this case is assumed to depend on the nucleophile used because other Grignard additions of the same substrate **12** with ordinal alkyl- and arylmagnesium halides under similar conditions have proved to provide less diastereoselectivity (ranging from 77:23 to 78.:22 in favor of syn isomers).[6a,12] In the latter cases, however, it has been indicated that the steric demand of the nucleophile is not an important factor since no significant differences of diastereoselectivity have been observed among these

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(7) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

(8) These diastereomers are chromatographically separable (see Experimental Section), but the assignment of the stereostructure to each isomer has not been made.

(9) When this Grignard reaction was carried out by using bromoacetaldehyde diethyl acetal instead of 2-(bromomethyl)-1,3-dioxolane, it resulted in the recovery of the starting material **12**.

(10) For recent examples of cyclic acetal containing Grignard reagents, see: (a) Forbes, C. P.; Wenteler, G. L.; Wiechers, A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2353. (b) Abbott, R. E.; Spencer, T. A. *J. Org. Chem.* **1980**, *45*, 5398. (c) Bal, S. A.; Marfat, A.; Helquist, P. *Ibid.* **1982**, *47*, 5045. (d) Paquette, L. A.; Leone-Bay, A. *J. Am. Chem. Soc.* **1983**, *105*, 7352 and also see: ref 14.

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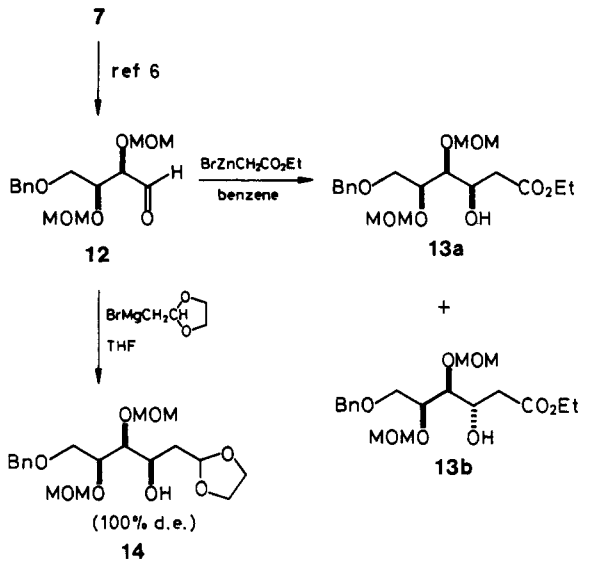
(12) Iida, H.; Yamazaki, N.; Kibayashi, C. *J. Org. Chem.* **1986**, *51*, 3769.



Grignard reagents (methyl, *n*-propyl, and aryl). Thus, the exclusive formation of **14** is probably due to the incorporation of the acetal oxygen(s) in the nucleophile which contributes to stabilize the cyclic transition state. Enhancement of the syn selectivity in the nucleophilic reaction with organometallics based on such "acetal oxygen effect" has been realized in a few cases.[13,14]

The Mitsunobu reaction of **14** with phthalimide gave **15** in 94% yield with complete stereo inversion, which was then hydrogenated to form the alcohol **16** in 82% yield (Scheme II). The tosylate **17** derived from **16** was converted to the iodide **18** with NaI in refluxed methyl ethyl ketone in 95% overall yield from **16**. Hydrogenolysis (H_2, Pd/C, MeOH) of **18** in the presence of triethylamine gave **19** in 89% yield, which was then transformed into the benzamide **20** in 81% yield by treatment with hydrazine hydrate followed by benzoylation.

Both alcohol and aldehyde protecting groups were cleaved by treating **20** with trifluoroacetic acid with aqueous THF as the cosolvent to give in 57% yield *N*-benzoyl-L-daunosamine (**1a**), having physical and spectral data identical with those reported in literature.[15] In an effort to improve the cleavage of the MOM ether and cyclic acetal, we studied the reaction with some boron reagents possessing a good oxygenophilic character. Thus **20** was treated with boron trichloride in dichloromethane at −78 °C and then quenched with $NaHCO_3$; however, only a modest yield (51%) of **1a** was realized. A similar result was obtained (54% yield) when dimethylboron bromide (Me_2BBr)[16] was applied to **20** under similar conditions as described above. Remarkable improvement could be achieved by employing a combination of boron trifluoride etherate ($BF_3{\cdot}Et_2O$) and a soft nucleophile such as ethanethiol[17] at room temperature for 30 min. Thus **20** was subjected to the cleavage of MOM ether and acetal more cleanly, accompanied by in situ dithioacetalization to afford **21** in 92% yield. The deprotection of the resulting dithioacetal **21** by treatment with $HgCl_2$ (2 equiv) and HgO (1 equiv) in aqueous acetonitrile at room temperature resulted in the formation of **1a** in 92% yield. Thus our synthesis leads to *N*-benzoyl-L-daunosamine (**1a**) in ten steps from the L-threose synthon **12** in an overall isolated yield of 30.9%.

Experimental Section

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 400 and 100.6 MHz, respectively. Mass spectra were obtained at an ionizing potential of 70 eV. Optical rotations were measured at the sodium D line in a 1-dm cell at the designated concentration in g per 100 mL. TLC was run on Wako precoated silica gel 70 FM plates. Column chromatography refers to flash chromatography on Merck silica gel 60 (230–400 mesh).

4-*O*-Benzyl-2,3-*O*-bis(methoxymethyl)-1-*O*-(methylsulfonyl)-L-threitol (8). To a stirred and cooled (0 °C) solution of 1-*O*-benzyl-2,3-*O*-bis(methoxymethyl)-L-threitol (**7**)[6] (5.0 g, 16.6 mmol) and triethylamine (2.5 g, 24.7 mmol) in CH_2Cl_2 (20 mL) was added methanesulfonyl chloride (2.1 g, 18.3 mmol) over a period of 5 min. The mixture was stirred at 0 °C for 30 min and ether (200 mL) was added to the reaction mixture. The resulting precipitation of the salt was filtered off and the filtrate was evaporated to dryness. The residue was chromatographed on a silica gel column with hexane ethyl-acetate (2:1, v/v) to give **8** (6.1 g, 97%) as a colorless oil: $[\alpha]^{26}_D$ −8.5° (*c* 2.63, MeOH); ^1H NMR ($CDCl_3$) δ $CHCl_3$ 2.96 (3 H, s), 3.357 (3 H, s), 3.358 (3 H, s), 3.63 (1 H, q, *J* = 10.1 Hz), 3.64 (1 H, q, *J* = 10.1 Hz), 3.90 (1 H, q, *J* = 4.8 Hz), 4.04 (1 H, dt, *J* = 6.3, 4.4 Hz), 4.30 (1 H, dd, *J* = 10.6, 6.3 Hz), 4.42 (1 H, dd, *J* = 10.6, 4.2 Hz), 4.51 (1 H, $^1/_2$ AB q, *J* = 11.3 Hz), 4.52 (1 H, $^1/_2$ AB q, *J* = 11.3 Hz), 4.68 (1 H, $^1/_2$ AB q, *J* = 6.9 Hz), 4.69 (2 H, s), 4.74 (1 H, $^1/_2$ AB q, *J* = 6.9 Hz), 7.23–7.36 (5 H, m); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 37.2, 55.7, 55.9, 68.8, 69.0, 73.4, 75.5, 75.6, 96.9, 97.3, 127.7, 128.3, 137.7; mass spectrum, *m/e* 347 ($M^+ - CH_3O$, 30), 341 (22), 315 (50), 303 (26), 302 (30), 301 (100), 255 (58), 225 (100), 211 (40), 195 (28), 181 (28), 179 (28), 161 (28), 91 (81).

(2*S*,3*S*)-1-(Benzyloxy)-2,3-bis[(methoxymethyl)oxy]butane (9). To a stirred cold (0 °C) slurry of $LiAlH_4$ (320 mg, 8.42 mmol) in 20 mL of THF–ether (1:1, v/v) was added dropwise a solution of **8** (1.59 g, 4.20 mmol) in 20 mL of THF–ether (1:1, v/v). After heating for 9 h, the mixture was cooled to 0 °C and quenched with water (1 mL). The resulting mixture was filtered through a Celite pad, the Celite was rinsed with ether, and the combined fractions were dried ($MgSO_4$). After removal of the solvent, the residue was chromatographed on a silica gel column with hexane–ethyl acetate (4:1, v/v) to give **9** (861 mg, 72%) as a colorless oil: $[\alpha]^{26}_D$ +2.4° (*c* 3.70, MeOH); ^1H NMR ($CDCl_3$) δ $CHCl_3$ 1.21 (3 H, d, *J* = 6.5 Hz), 3.36 (3 H, s), 3.39 (3 H, s), 3.60 (1 H, dd, *J* = 9.6, 5.7 Hz), 3.68 (1 H, dd, *J* = 9.6, 4.5 Hz), 3.72 (1 H, dt, *J* = 5.8, 4.3 Hz), 3.93 (1 H, qd, *J* = 6.5, 4.1 Hz), 4.52 (1 H, $^1/_2$ AB q, *J* = 12.0 Hz), 4.55 (1 H, $^1/_2$ AB q, *J* = 12.0 Hz), 4.66 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.69 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.71 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.81 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 7.25–7.38 (5 H, m); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 16.6, 55.5, 55.8, 70.1, 73.0, 73.5, 79.2, 95.9, 97.1, 127.7, 128.4, 138.2; mass spectrum, *m/e* 253 ($M^+ - CH_3O$, 2), 239 (15), 207 (70), 167 (100); mass spectrum (isobutane CI), *m/e* 253 ($M^+ - CH_3O$, 5), 207 (30), 167 (15), 131 (100).

(2*S*,3*S*)-2,3-Bis[(methoxymethyl)oxy]-1-butanol (10). A solution of **9** (695 mg, 2.44 mmol) in methanol (10 mL) was hydrogenated in the presence of 10% Pd/C (695 mg) at 1 atm for 2 h. The catalyst was removed by filtration and washed with methanol. The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel with hexane–ethyl acetate (2:1, v/v) to give **10** (438 mg, 92%) as a colorless oil: $[\alpha]^{26}_D$ −4.9° (*c* 2.78, MeOH); ^1H NMR ($CDCl_3$) δ $CHCl_3$ 1.17 (3 H, d, *J* = 6.5 Hz), 3.00 (1 H, dd, *J* = 7.9, 4.7 Hz), 3.34 (3 H, s), 3.39 (3 H, s), 3.51 (1 H, dt, *J* = 6.5, 4.2 Hz), 3.60–3.76 (2 H, m), 3.85 (1 H, qd, *J* = 6.5, 4.4 Hz), 4.60 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.65 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.67 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.74 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 16.1, 55.6, 55.8, 62.5, 73.4, 83.3, 95.6, 97.6; mass spectrum, *m/e* 163 ($M^+ - CH_3O$, 6), 131 (100), 101 (20), 89 (30), 88 (42).

(2*R*,3*S*)-2,3-Bis[(methoxymethyl)oxy]-1-butanal (11). To a stirred −78 °C solution of oxalyl chloride (470 mg, 3.7 mmol) in CH_2Cl_2 (5 mL) was added dropwise a solution of Me_2SO (577 mg, 7.4 mmol) in CH_2Cl_2 (5 mL) over a period of 5 min, and the

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mixture was stirred for another 15 min at −78 °C. To this mixture was added dropwise a solution of **10** (360 mg, 1.85 mmol) in CH_2Cl_2 (5 mL), and stirring was continued at −78 °C. After 1 h, triethylamine (1.12 g, 11.1 mmol) was added to the reaction mixture and the reaction was allowed to warm to ambient temperature. After addition of water (5 mL) the mixture was stirred for 15 min, extracted with CH_2Cl_2 (3 × 30 mL), washed with brine, and the extract was dried ($MgSO_4$). Removal of the solvent left an oil which was chromatographed on silica gel with hexane–ethyl acetate (4:1, v/v) to give **11** (270 mg, 76%) as a colorless oil: $[\alpha]^{26}_D$ +38.9° (*c* 2.62, MeOH); ^1H NMR ($CDCl_3$) δ $CHCl_3$ 1.31 (3 H, d, *J* = 6.4 Hz), 3.33 (3 H, s), 3.45 (3 H, s), 3.93 (1 H, dd, *J* = 3.5, 1.2 Hz), 4.19 (1 H, qd, *J* = 6.5, 3.5 Hz), 4.60 (1 H, $^1/_2$ AB q, *J* = 7.0 Hz), 4.70 (1 H, $^1/_2$ AB q, *J* = 7.0 Hz), 4.76 (1 H, $^1/_2$ AB q, *J* = 6.9 Hz), 4.81 (1 H, $^1/_2$ AB q, *J* = 6.9 Hz), 9.75 (1 H, d, *J* = 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 16.4, 55.8, 56.3, 72.8, 84.7, 95.4, 97.5, 202.6.

Reformatsky Reaction of 4-*O*-Benzyl-2,3-*O*-bis(methoxymethyl)-L-threose (12). A mixture of ethyl monobromoacetate (684 mg, 4.10 mmol) and **12**[6] (814 mg, 2.73 mmol) in benzene (1.5 mL) was added with use of a syringe through a septum to a stirred suspension of Zn (99.9%) powder (268 mg, 4.10 mmol) in benzene (1 mL) at 80 °C under a nitrogen atmosphere. After ca. 5 min, the exothermic reaction occurred to give a greenish yellow solution, which was heated at 80 °C for another 25 min with stirring. After cooling to 0 °C, to this stirred mixture were added water (0.5 mL) then ether (50 mL). The resulting mixture was filtered through a Celite pad, the Celite was rinsed with ether (50 mL), and the filtrate was washed with saturated brine and dried ($MgSO_4$). Removal of the solvent in vacuo and purification by chromatography on silica gel with hexane–ethyl acetate (3:1, v/v → 2:1, v/v) gave a diastereomeric mixture of the hydroxy esters **13a** and **13b** (867 mg, 82%) as a colorless oil. These isomers were shown to be in a 55:45 ratio by ^1H NMR analysis and subjected to a second chromatographic separation to give the major isomer as a less polar component and the minor isomer as a more polar component.

The data for the less polar isomer follows: $[\alpha]^{29}_D$ −13.6° (*c* 1.93, MeOH); ^1H NMR ($CDCl_3$) δ $CHCl_3$ 1.23 (3 H, t, *J* = 7.1 Hz), 2.50 (1 H, dd, *J* = 15.9, 9.1 Hz), 2.71 (1 H, dd, *J* = 15.9, 3.2 Hz), 3.36 (3 H, s), 3.37 (3 H, s), 3.60–3.72 (4 H, unresolved), 4.02 (1 H, td, *J* = 5.7, 3.5 Hz), 4.12–4.22 (1 H, m, containing 2 H, q, *J* = 7.1 Hz, at δ 4.13), 4.51 (2 H, s), 4.63 (1 H, $^1/_2$ AB q, *J* = 6.7 Hz), 4.66 (1 H, $^1/_2$ AB q, *J* = 6.7 Hz), 4.70 (1 H, $^1/_2$ AB q, *J* = 6.7 Hz), 4.76 (1 H, $^1/_2$ AB q, *J* = 6.7 Hz), 7.22–7.34 (5 H, m); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 14.1, 38.1, 55.9, 56.2, 60.4, 67.8, 69.6, 73.4, 76.3, 81.4, 97.3, 98.3, 127.6, 128.3, 137.8, 172.4; mass spectrum, *m/e* 309 (M^+ − CH_3O, 5), 163 (10), 159 (10), 91 (95), 85 (50), 59 (40), 45 (70), 43 (100).

The data for the more polar isomer follows: $[\alpha]^{30}_D$ −8.6° (*c* 2.37, MeOH); ^1H NMR ($CDCl_3$) δ $CHCl_3$ 1.25 (3 H, t, *J* = 7.1 Hz), 2.58 (1 H, dd, *J* = 15.7, 8.3 Hz), 2.64 (1 H, dd, *J* = 15.7, 4.6 Hz), 3.33 (1 H, d, *J* = 4.6 Hz), 3.36 (3 H, s), 3.40 (3 H, s), 3.67 (1 H, t, *J* = 4.6 Hz), 3.69 (2 H, d, *J* = 5.0 Hz), 3.96 (1 H, q, *J* = 4.9 Hz), 4.16 (2 H, q, *J* = 7.1 Hz), 4.25 (1 H, dt, *J* = 12.8, 4.5 Hz), 4.53 (2 H, s), 4.67 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.70 (1 H, $^1/_2$ AB q, *J* = 6.7 Hz), 4.74 (1 H, $^1/_2$ AB q, *J* = 6.7 Hz), 4.77 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 7.22–7.36 (5 H, m); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 14.2, 38.6, 55.9, 56.3, 60.6, 67.6, 69.6, 73.5, 76.7, 81.2, 96.9, 98.5, 127.8, 128.4, 137.9, 172.1; mass spectrum, *m/e* 309 (M^+, 10), 163 (10), 159 (15), 91 (100), 85 (30), 59 (50), 45 (75).

6-*O*-Benzyl-2-deoxy-4,5-*O*-bis(methoxymethyl)-L-*xylo*-hexose, Ethylene Acetal (14). A solution of ((1,3-dioxolan-2-yl)methyl)magnesium bromide in THF (30 mL) was prepared from mangesium (99.5%) turnings (3.52 g, 144.1 mmol) and 2-(bromomethyl)-1,3-dioxolane (12.09 g, 72.4 mmol) by the usual Grignard technic. To this solution was added dropwise a solution of **12** (5.40 g, 18.1 mmol) in THF (20 mL) at 0 °C with stirring, and the mixture was allowed to warm to room temperature and stirred for 14 h. The reaction was quenched by addition of water (2 mL) and extracted with ether (3 × 100 mL). The combined extract was dried ($MgSO_4$) and evaporated to dryness, and the residue was purified by chromatography on a silica gel column with hexane–ethyl acetate (2:1, v/v → 1:1, v/v) to give **14** (4.90 g, 70%) as a colorless oil: $[\alpha]^{20}_D$ −5.4° (*c* 0.80, MeOH); ^1H NMR ($CDCl_3$) δ $CHCl_3$ 1.87–2.05 (2 H, m), 3.24 (1 H, d, *J* = 3.7 Hz), 3.35 (3 H, s), 3.39 (3 H, s), 3.63 (1 H, t, *J* = 4.5 Hz), 3.68 (2 H, d, *J* = 4.9 Hz, containing 1 H with sholdering), 3.80–3.89 (2 H, m), 3.91–4.00 (3 H, m), 4.08 (1 H, dt, *J* = 12.9, 3.7 Hz), 4.53 (2 H, s), 4.68 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.70 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.75 (2 H, 2 × $^1/_2$ AB q, *J* = 6.8 Hz each), 5.07 (1 H, t, *J* = 4.7 Hz), 7.21–7.39 (5 H, m); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 37.53, 55.63, 56.31, 64.71, 64.92, 67.18, 69.73, 73.45, 76.84, 81.85, 96.95, 98.51, 103.05, 127.69, 127.77, 128.39, 137.99; mass spectrum (isobutane CI), *m/e* 387 (M^+ + 1, 1), 324 (18), 323 (100), 250 (15), 249 (99), 231 (55), 201 (46), 159 (40), 91 (67). Anal. Calcd for $C_{19}H_{30}O_8$: C, 59.05; H, 7.82. Found: C, 58.95; H, 7.81.

6-*O*-Benzyl-2,3-dideoxy-4,5-*O*-bis(methoxymethyl)-3-(1,3-dioxo-2-azindan-2-yl)-L-*lyxo*-hexose, Ethylene Acetal (15). To a stirred, ice-cold solution of **14** (3.90 g, 10.09 mmol), phthalimide (3.71 g, 25.23 mmol), and triphenylphosphine (6.62 g, 25.23 mmol) in THF (40 mL) was added diethyl azodicarboxylate (4.40 g, 25.23 mmol). The mixture was allowed to warm to room temperature and stirred for 14 h. Removal of the solvent in vacuo followed by purification by chromatography on a silica gel column with hexane–ethyl acetate (3:1, v/v → 5:2, v/v) gave **15** (4.9 g, 94%) as a colorless oil: ^1H NMR ($CDCl_3$) δ $CHCl_3$ 2.31 (1 H, dt, *J* = 14.5, 3.1 Hz), 2.54 (1 H, ddd, *J* = 14.5, 11.3, 5.2 Hz), 3.24 (3 H, s), 3.41 (3 H, s), 3.61–3.89 (7 H, m), 4.41–4.63 (6 H, m), 4.76 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.78 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.87 (1 H, dd, *J* = 5.1, 3.6 Hz), 7.20–7.32 (5 H, m), 7.65–7.73 (2 H, m), 7.77–7.85 (2 H, m).

2,3-Dideoxy-4,5-*O*-bis(methoxymethyl)-3-(1,3-dioxo-2-azindan-2-yl)-L-*lyxo*-hexose, Ethylene Acetal (16). A methanol solution (100 mL) of **15** (4.9 g, 9.50 mmol) including 10% Pd/C (4.9 g) was hydrogenated at atmospheric pressure for 14 h. After filtration through Celite, the filtrate was concentrated to dryness in vacuo. The residue was purified by silica gel chromatography with hexane–ethyl acetate (2:1, v/v → 1:1, v/v) to give a colorless solid which was recrystallized from $CHCl_3$–hexane to give **16** (3.2 g, 79%) as colorless pillars: mp 99–100 °C; $[\alpha]^{20}_D$ −32.7° (*c* 2.24, MeOH); ^1H NMR ($CDCl_3$) δ $CHCl_3$ 2.24 (1 H, dt, *J* = 14.4, 3.1 Hz, containing 1 H with shouldering), 2.50 (1 H, ddd, *J* = 14.4, 11.6, 5.5 Hz), 3.26 (3 H, s), 3.43 (3 H, s), 3.51 (1 H, ddd, *J* = 7.3, 4.1, 2.2 Hz), 3.59–3.80 (6 H, m), 4.37 (1 H, dd, *J* = 9.9, 2.2 Hz), 4.43 (1 H, $^1/_2$ AB q, *J* = 7.2 Hz), 4.58 (1 H, $^1/_2$ AB q, *J* = 7.2 Hz), 4.68 (1 H, ddd, *J* = 11.6, 9.9, 2.9 Hz), 4.73 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.79 (1 H, $^1/_2$ AB q, *J* = 6.8 Hz), 4.85 (1 H, dd, *J* = 5.4, 3.3 Hz), 7.68 (2 H, dd, *J* = 5.4, 3.1 Hz), 7.79 (2 H, dd, *J* = 5.4, 3.1 Hz); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 31.62, 47.25, 55.85, 56.62, 62.98, 64.53, 64.97, 77.52, 82.16, 98.50, 98.79, 103.12, 123.17, 132.03, 133.94, 166.49; mass spectrum, *m/e* 489 (M^+ + 64, 4.7), 320 (45), 288 (100), 276 (35), 246 (90), 244 (35), 226 (40), 214 (35), 73 (94); mass spectrum (isobutane CI), *m/e* 607 (2.0), 562 (1.8), 488 (1.0), 394 (10), 364 (12), 320 (70), 289 (45), 288 (100). Anal. Calcd for $C_{20}H_{27}NO_9$: C, 56.46; H, 6.40; N, 3.29. Found: C, 56.68; H, 6.50; N, 3.35.

2,3-Dideoxy-4,5-*O*-bis(methoxymethyl)-3-(1,3-dioxo-2-azindan-2-yl)-6-*O*-(*p*-tolylsulfonyl)-L-*lyxo*-hexose, Ethylene Acetal (17). To a solution of **16** (529 mg, 1.24 mmol) in pyridine (1.5 mL) at 0 °C was added *p*-toluenesulfonyl chloride (355 mg, 1.86 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 14 h. The mixture was concentrated in vacuo below 40 °C, ether (30 mL) was added to the resulting residue, and the pyridinium salt separated was filtered off. The filtrate was concentrated and the residual oil was purified by chromatography on a silica gel column with hexane–ethyl acetate (2:1, v/v) to give **17** (715 mg, 99%) as a colorless oil: $[\alpha]^{29}_D$ −5.1° (*c* 1.28, MeOH); ^1H NMR ($CDCl_3$) δ $CHCl_3$ 2.23 (1 H, dt, *J* = 14.6, 3.2 Hz), 2.40 (3 H, s), 2.51 (1 H, ddd, *J* = 14.6, 11.2, 5.0 Hz), 3.18 (3 H, s), 3.36 (3 H, s), 3.60–3.83 (4 H, m), 3.88 (1 H, ddd, *J* = 7.3, 3.9, 3.2 Hz), 4.20 (1 H, dd, *J* = 10.5, 7.8 Hz), 4.29 (1 H, dd, *J* = 10.5, 4.2 Hz), 4.34 (1 H, dd, *J* = 10.2, 3.0 Hz), 4.37 (1 H, $^1/_2$ AB q, *J* = 6.9 Hz), 4.41 (1 H, $^1/_2$ AB q, *J* = 6.9 Hz), 4.45 (1 H, td, *J* = 10.8, 2.7 Hz), 4.69 (1 H, $^1/_2$ AB q, *J* = 6.9 Hz), 4.71 (1 H, $^1/_2$ AB q, *J* = 6.9 Hz), 4.83 (1 H, dd, *J* = 4.9, 3.7 Hz), 7.28 (2 H, $^1/_2$ AB q, *J* = 8.2 Hz), 7.70 (2 H, dd, *J* = 5.5, 3.0 Hz), 7.76 (2 H, $^1/_2$ AB q, *J* = 8.2 Hz), 7.78 (2 H, dd, *J* = 5.5, 3.0 Hz); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 21.67, 31.97, 46.88, 55.93, 56.52, 64.65, 65.00, 69.33, 75.40, 75.63, 97.15, 98.35, 102.89, 123.17, 128.10, 129.81, 132.13, 132.99, 133.88, 144.71, 168.43; mass spectrum, *m/e* 503 (M^+ − 76, 0.2), 441 (4), 410 (4.5), 246 (13), 244 (10), 239 (15), 226 (23), 214

(40), 202 (22), 186 (20), 155 (25), 91 (40), 73 (100).

2,3,6-Trideoxy-6-iodo-4,5-*O*-bis(methoxymethyl)-3-(1,3-dioxo-2-azindan-2-yl)-L-*lyxo*-hexose, Ethylene Acetal (18). To a solution of **17** (1.80 g, 3.11 mmol) in methyl ethyl ketone (30 mL) was added NaI (1.90 g, 12.68 mmol). The stirring mixture was refluxed for 14 h. The resulting suspension was cooled to room temperature and diluted with ether (500 mL). After filtration the filtrate was concentrated to dryness and the residue was purified by chromatography on a silica gel column with hexane–ethyl acetate (3:1, v/v → 5:2, v/v) to give **18** (1.62 g, 97%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ $CHCl_3$ 2.29 (1 H, dt, J = 14.5, 3.1 Hz), 2.56 (1 H, ddd, J = 14.5, 11.2, 5.2 Hz), 3.32 (3 H, s), 3.35 (1 H, dd, J = 10.1, 6.9 Hz), 3.47 (3 H, s), 3.50 (1 H, dd, J = 10.1, 6.6 Hz), 3.61–3.90 (5 H, m), 4.50–4.68 (4 H, m), 4.83 (2 H, apparent s), 4.88 (1 H, dd, J = 5.1, 3.4 Hz), 7.71 (2 H, dd, J = 5.4, 3.0 Hz), 7.82 (2 H, dd, J = 5.4, 3.0 Hz); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 4.26 (t), 31.80 (t), 46.95 (d), 56.44 (q), 56.55 (q), 64.68 (t), 65.05 (t), 77.31 (d), 79.74 (d), 97.89 (t), 98.83 (t), 103.11 (d), 123.29 (2 × d), 132.17 (2 × s), 133.96 (2 × d), 168.55 (2 × s).

2,3,6-Trideoxy-4,5-*O*-bis(methoxymethyl)-3-(1,3-dioxo-2-azindan-2-yl)-L-*lyxo*-hexose, Ethylene Acetal (19). A solution of **18** (455 mg, 0.850 mmol) in methanol (10 mL) containing triethylamine (129 mg, 1.275 mmol) was hydrogenated in the presence of 10% Pd/C (500 mg) at 1 atm for 20 h. The catalyst was removed by filtration and rinsed with methanol. The combined fractions were concentrated in vacuo and the residue was purified by chromatography on silica gel with hexane–ethyl acetate (5:2, v/v → 2:1, v/v) to give **19** (309 mg, 89%) as a colorless oil: $[\alpha]^{27}_D$ −35.6° (*c* 0.68, MeOH); ^{1}H NMR ($CDCl_3$) δ $CHCl_3$ 1.25 (3 H, d, J = 6.6 Hz), 2.31 (1 H, dt, J = 14.5, 3.3 Hz), 2.55 (1 H, ddd, J = 14.5, 11.4, 5.2 Hz), 3.17 (3 H, s), 3.43 (3 H, s), 3.64–3.87 (5 H, m), 4.28 (1 H, dd, J = 9.7, 2.9 Hz), 4.40 (1 H, $^1/_2$ AB q, J = 6.9 Hz), 4.42 (1 H, $^1/_2$ AB q, J = 6.9 Hz), 4.66 (1 H, ddd, J = 11.5, 9.8, 2.9 Hz), 4.76 (1 H, $^1/_2$ AB q, J = 6.8 Hz), 4.80 (1 H, $^1/_2$ AB q, J = 6.8 Hz), 4.90 (1 H, dd, J = 5.2, 3.6 Hz), 7.69 (2 H, dd, J = 5.4, 3.1 Hz), 7.81 (2 H, dd, J = 5.4, 3.1 Hz); mass spectrum, m/e 378 (M^+ − 31, 0.1), 366 (0.2), 365 (1.3), 332 (0.5), 320 (10), 288 (10), 246 (40), 226 (20), 214 (20), 160 (18), 73 (100).

3-(Benzoylamino)-2,3,6-trideoxy-4,5-*O*-bis(methoxymethyl)-L-*lyxo*-hexose, Ethylene Acetal (20). To a solution of **19** (73 mg, 0.18 mmol) in ethanol (6 mL) was added hydrazine hydrate (22 mg, 0.44 mmol), and the mixture was refluxed for 1.5 h. The reaction mixture was cooled to room temperature, diluted with ether (100 mL), and filtered. The filtrate was concentrated in vacuo to give an oily product which was disolved in CH_2Cl_2 (0.5 mL). To the stirring solution at 0 °C were added a solution of Na_2CO_3 (38 mg, 0.36 mmol) in H_2O (0.5 mL) and then dropwise a solution of benzoyl chloride (38 mg, 0.27 mmol) in CH_2Cl_2 (4 mL). The mixture was stirred at room temperature for 1 h, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$) and the solvent was evaporated. The crude product was purified by chromatography on silica gel with hexane–ethyl acetate (2:1, v/v → 1:1, v/v) to give **20** (55.2 mg, 81%) as a colorless oil: $[\alpha]^{25}_D$ −73.2° (*c* 0.81, MeOH); ^{1}H NMR ($CDCl_3$) δ $CHCl_3$ 1.29 (3 H, d, J = 6.4 Hz), 1.90 (1 H, ddd, J = 14.5, 6.1, 3.9 Hz), 2.04 (1 H, ddd, J = 14.5, 9.5, 3.4 Hz), 3.38 (3 H, s), 3.39 (3 H, s), 3.60 (1 H, dd, J = 5.9, 3.1 Hz), 3.76–3.99 (5 H, m), 4.59 (1 H, dtd, J = 8.7, 7.0, 3.6 Hz), 4.68 (1 H, $^1/_2$ AB q, J = 6.7 Hz), 4.70 (1 H, $^1/_2$ AB q, J = 6.7 Hz), 4.72 (1 H, $^1/_2$ AB q, J = 6.7 Hz), 4.80 (1 H, $^1/_2$ AB q, J = 6.7 Hz), 5.03 (1 H, dd, J = 6.1, 3.4 Hz), 7.38–7.53 (4 H, m), 7.79–7.83 (2 H, m); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 16.93 (q), 35.06 (t), 46.98 (d), 55.78 (q), 56.08 (q), 64.69 (t), 65.04 (t), 74.17 (d), 85.31 (d), 95.77 (t), 98.47 (t), 102.85 (d), 127.03 (2 × d), 128.50 (2 × d), 131.30 (d), 134.88 (s), 166.70 (s); mass spectrum, m/e 384 (M^+, 1.0), 352 (3.0), 264 (10), 220 (30), 105 (52), 73 (100); mass spectrum (isobutane CI), m/e 384 (M^+, 40), 352 (95), 308 (26), 278 (40), 264 (10), 246 (25), 220 (35), 105 (40), 73 (100).

3-(Benzoylamino)-4,5-*O*-bis(methoxymethyl)-2,3,6-trideoxy-L-*lyxo*-hexose, Diethyl Dithioacetal (21). To a stirred solution of **20** (262 mg, 0.681 mmol) in ethanethiol (2 mL) was added 95% BF_3·Et_2O (1.02 g, 6.83 mmol), and the mixture was stirred for 30 min at room temperature. The reaction was quenched by the addition of water (1 mL) and $CHCl_3$ (50 mL). The layers were separated and the organic phase was washed with water, dried ($MgSO_4$), and evaporated. Purification of the residue by silica gel chromatography with hexane–ethyl acetate (2:1, v/v → 1:1, v/v) followed by recrystallization from $CHCl_3$–hexane gave **21** (225 mg, 92%) as colorless needles: mp 115–116 °C; $[\alpha]^{24}_D$ −34.0° (*c* 0.17, MeOH); ^{1}H NMR ($CDCl_3$) δ $CHCl_3$ 1.23 (3 H, t, J = 7.5 Hz), 1.25 (3 H, d, J = 6.4 Hz), 1.26 (3 H, t, J = 7.4 Hz), 2.24 (1 H, ddd, J = 15.1, 9.0, 4.3 Hz), 2.42 (1 H, ddd, J = 15.1, 9.5, 3.0 Hz), 2.57–2.81 (5 H, m), 3.22 (1 H, td, J = 9.0, 1.7 Hz), 3.85 (1 H, dtd, J = 11.0, 6.4, 1.8 Hz), 3.91 (1 H, d, J = 4.3 Hz), 3.98 (1 H, dd, J = 9.5, 4.3 Hz), 4.35 (1 H, ddd, J = 17.4, 8.7, 2.9 Hz), 7.04 (1 H, d, J = 8.5 Hz), 7.41–7.58 (3 H, m), 7.79–7.85 (2 H, m); ^{13}C NMR ($CDCl_3$) δ $CDCl_3$ 14.44 (2 × q), 18.93 (q), 24.29 (t), 24.96 (t), 37.76 (t), 48.18 (d), 51.67 (d), 65.69 (d), 76.49 (d), 127.18 (2 × d), 128.83 (2 × d), 132.18 (d), 133.33 (s), 168.80 (s); mass spectrum, m/e 357 (M^+, 0.5), 328 (40), 294 (6), 266 (14), 234 (25), 164 (30), 122 (65), 105 (100), 69 (30). Anal. Calcd for $C_{17}H_{27}NO_3S_2$: C, 57.11; H, 7.61; N, 3.92. Found: C, 56.99; H, 7.66; N, 4.03.

***N*-Benzoyl-L-daunosamine (1a). (A) From the Ethylene Acetal 20 with CF_3CO_2H.** A stirred solution of **20** (107 mg, 0.278 mmol) in 5 mL of CF_3CO_2H–THF–H_2O (5:4:1, v/v) was heated at 50 °C for 10 min. The reaction mixture was poured into ice–water (2 mL) and neutralized by the addition of $NaHCO_3$. The resultant mixture was extracted with CH_2Cl_2 (3 × 30 mL) and the organic fractions were dried ($MgSO_4$). Removal of the solvent in vacuo followed by column chromatography of the residue on silica gel with benzene–acetone (1:1, v/v) gave a crystalline solid which was recrystallized from acetone–hexane to give **1a** (40 mg, 57%) as colorless prisms: mp 152–154 °C (lit.[1] mp 154–156 °C; lit.[5i] mp 151.5–153 °C); $[\alpha]^{22}_D$ −106.7° (*c* 0.22, EtOH) [lit.[1] $[\alpha]_D$ −107.5° (EtOH); lit.[5i] $[\alpha]^{26}_D$ −106° (EtOH)]; mass spectrum, m/e 252 (M^+ + 1, 1), 251 (M^+, 1), 233 (20), 215 (8), 207 (9), 206 (19), 200 (5), 190 (5), 189 (20), 188 (5), 178 (15), 177 (25), 176 (15), 148 (20), 122 (100), 106 (35), 105 (100); mass spectrum (isobutane CI), m/e 252 (M^+ + 1, 10), 250 (10), 235 (10), 234 (90), 178 (5), 123 (10), 122 (100), 113 (20), 105 (24). The ^{1}H and ^{13}C NMR spectra of this material were identical with those reported in the literature.[15]

(B) From the Ethylene Acetal 20 with BCl_3. To a cold (−78 °C), stirred solution of **20** (12 mg, 0.0312 mmol) in CH_2Cl_2 (2 mL) was added a 1 M solution of boron trichloride (0.312 μL) in CH_2Cl_2 via a micro syringe. After 1 h at −78 °C, the cold reaction mixture was poured into saturated aqueous $NaHCO_3$ (2 mL) and vigorously stirred for 10 min. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic fractions were dried ($MgSO_4$) and evaporated in vacuo. The crude product was purified by silica gel chromatography and recrystallized as described above in A to give **1a** (4 mg, 51%).

(C) From the Ethylene Acetal 20 with Me_2BBr_2. To a cold (−78 °C), sitrred solution of **20** (45 mg, 0.117 mmol) in CH_2Cl_2 (4 mL) was added a 1 M solution of dimethylboron bromide[16] (0.8 mL) in CH_2Cl_2 via syringe. The reaction was allowed to stir for 1 h at −78 °C and then worked up and purified as described above in B to give **1a** (16 mg, 54%).

(D) From the Dithioacetal 21. To a stirred solution of **21** (17.9 mg, 0.05 mmol) in 80% aqueous acetonitrile (0.5 mL) were added $HgCl_2$ (27.2 mg, 0.1 mmol) and HgO (10.8 mg, 0.05 mmol) at room temperature. The suspension was stirred at room temperature for 30 min and filtered, and the solid was washed with acetonitrile. The combined filtrates were evaporated and the residue was purified as described in A to give **1a** (11.6 mg, 92%).

Registry No. **1a**, 51996-44-2; **7**, 99891-37-9; **8**, 104487-51-6; **9**, 104465-57-8; **10**, 104465-58-9; **11**, 104465-59-0; **12**, 99878-63-4; **13a**, 104465-60-3; **13b**, 104465-61-4; **14**, 104465-62-5; **15**, 104465-63-6; **16**, 104465-64-7; **17**, 104465-65-8; **18**, 104465-66-9; **19**, 104465-67-0; **20**, 104465-68-1; **21**, 104465-69-2; ethyl bromoacetate, 105-36-2; 2-(bromoethyl)-1,3-dioxolane, 4360-63-8; phthalimide, 85-41-6.