# $Bi(OTf)_3$ as Novel and Efficient Catalyst for the Stereoselective Synthesis of *C*-Pseudoglycals

J. S. Yadav,* B. V. S. Reddy, K. Srinivasa Reddy, L. Chandraiah, V. Sunitha

Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad–500 007, India
Fax +91(40)27160512; E-mail: yadav@iict.res.in

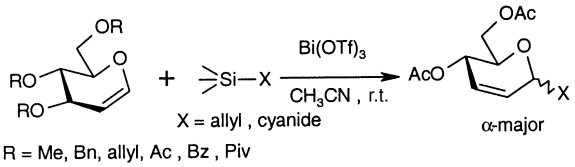
*Received 26 April 2004; revised 23 June 2004*

**Abstract:** D-Glycals undergo smoothly allylic rearrangement with allyltrimethylsilane and trimethylsilyl cyanide in the presence of catalytic amount of bismuth triflate to afford the corresponding 2,3-unsaturated allyl glycosides and glycosyl cyanides in excellent yields with high α-selectivity.

**Key words:** bismuth reagents, glycals, pseudoglycals, *C*-glycosides

*C*-Glycosides are versatile chiral intermediates for the synthesis of many biologically active macromolecules such as palytoxin, spongistatin, halichondrin and many others.[1] In addition, *C*-glycosides are potential inhibitors of carbohydrate processing enzymes and they are stable analogs of glycals involved in important intra- and intercellular processes.[2] In particular, allyl glycosides are attractive due to the presence of a terminal double bond that can be easily converted into other chiral molecules and carbohydrate derivatives.[3] Among these *C*-glycosides, glycosyl cyanides are used as chiral intermediates for the synthesis of naturally occurring *C*-nucleoside antibiotics.[4] Lewis acids such as titanium tetrachloride, boron trifluoride etherate and TMSOTf are required for the *C*-glycosilation of glycals with carbon nucleophiles.[5] Other reagents including montmorillonite K10, DDQ and lanthanide triflates are also reported to effect this transformation.[6,7] High catalytic activity, low toxicity, moisture and air tolerance and their recyclability make use of lanthanide triflates attractive alternatives to conventional Lewis acids. However, unfortunately lanthanide triflates are rather expensive and thus their use in large-scale synthesis is limited. Therefore, cheaper and efficient catalysts are desirable for glycosidation reactions. In this direction, bismuth triflate has evolved as remarkable Lewis acid catalyst for effecting various organic transformations.[8] Compared to lanthanide triflates, bismuth triflate is an inexpensive and easy to prepare even on multi-gram scale in laboratory from commercially available bismuth oxide and triflic acid.[9]

In this report, we wish to highlight our results on bismuth triflate catalyzed *C*-glycosilation of glycals with carbon nucleophiles (Scheme 1).



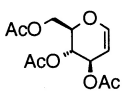
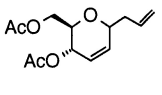
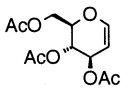
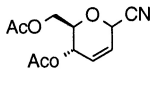
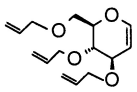
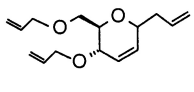
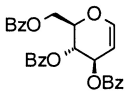
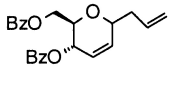
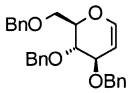
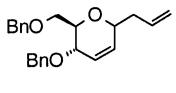
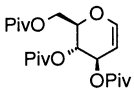
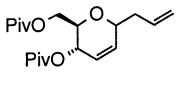
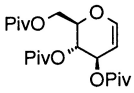
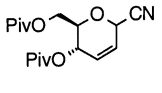
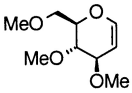
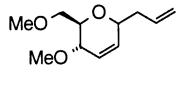
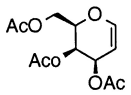
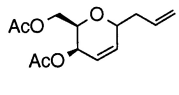
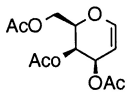
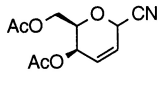

**Scheme 1**

Thus, treatment of 3,4,6-tri-*O*-acetyl-D-glucal with allyltrimethylsilane in the presence of 2 mol% $Bi(OTf)_3$ in MeCN at ambient temperature resulted in the formation of 2,3-unsaturated allyl glycoside in 95% yield with high α-selectivity. In a similar fashion, various derivatives of D-glucal react smoothly with allyltrimethylsilane to give the corresponding allyl *C*-pseudoglycals in excellent yields. These results prompted us to investigate the *C*-glycosylation reactions with trimethylsilyl cyanide to produce glycosyl cyanides. 3,4,6-Trisubstituted-D-glucal derivatives reacted smoothly with TMSCN in the presence of bismuth triflate to afford the corresponding glycosyl cyanides in high yields. D-Galactal also underwent allylic rearrangement with carbon nucleophiles under bismuth triflate catalysis to afford the corresponding pseudoglycal *C*-glycosides. This method is applicable for both ester and ether derivatives of D-glucal. There are several advantages in the use of bismuth triflate as catalyst for this transformation, which include high yields of products, cleaner reaction profiles, short reaction times, operational simplicity and high α-selectivity. All products were characterized by $^1H$, $^{13}C$ NMR and IR spectra and also by comparison with authentic samples.[10] The ratio of α and β-isomers was determined by $^1H$ NMR spectrum of crude product. The spectroscopic data of the products was identical with the data reported in the literature. The scope and generality of this method is illustrated with respect to various glycals and silylated carbon nucleophiles and the results are presented in the Table 1.

In summary, bismuth triflate is proved to be a remarkable and highly efficient catalyst for the activation of glycals under mild conditions. The use of inexpensive and readily accessible bismuth triflate together with high yields and good stereoselectivity makes it useful and attractive alternative to the more expensive lanthanide triflates or stoichiometric conventional Lewis acids promoted *C*-glycosidation procedures.

**SYNTHESIS** 2004, No. 15, pp 2523–2526
Advanced online publication: 19.08.2004
DOI: 10.1055/s-2004-831187; Art ID: Z08204SS

**Table 1** $Bi(OTf)_3$-Catalyzed Syntheses of *C*-Pseudoglycals from Glycols

| Entry | Substrate (**1**) | Product (**3**) | Time (min) | Yield (%)[a] | Ratio (α:β)[b] |
|---|---|---|---|---|---|
| **a** |  |  | 15 | 95 | 9.5:1 |
| **b** |  |  | 20 | 92 | 7:3 |
| **c** |  |  | 10 | 89 | 10:1 |
| **d** |  |  | 20 | 95 | 9.5:1 |
| **e** |  |  | 10 | 88 | 10:1 |
| **f** |  |  | 20 | 92 | 9.5:1 |
| **g** |  |  | 25 | 90 | 6:4 |
| **h** |  |  | 10 | 89 | 9.5:1 |
| **i** |  |  | 15 | 91 | 9:1 |
| **j** |  |  | 25 | 87 | 7:3 |

[a] Isolated yields as pure products after purification.
[b] Anomeric ratio was determined on the basis of the integrated ratios of the anomeric hydrogens in $^1$H NMR spectroscopy.

Melting points were recorded on Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. $^1$H NMR spectra were recorded on Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. CHN analyses were recorded on a Vario EL analyzer. The optical rotations were measured on a Jasco Dip 360 Digital polarimeter.

### Stereoselective Synthesis of *C*-Pseudoglycals; General Procedure

A mixture of D-glucal or D-galactal derivative (2 mmol) and allyltrimethylsilane or cyanotrimethylsilane (2.5 mmol) and bismuth triflate (2 mol%) in MeCN (10 mL) was stirred at ambient temperature for an appropriate time. After complete conversion, as indicated by TLC, the reaction mixture was diluted with water (10 mL) and extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over anhyd $Na_2SO_4$ and purified by column chromatography on silica gel (Merck, 100–200 mesh, EtOAc–hexane, 2:8) to afford pure glycoside.

### 3-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-1-propene (3a)

Liquid; $[\alpha]_D^{25}$ +79.9 (*c* = 1.0, $CHCl_3$).

$^1$H NMR ($CDCl_3$): δ = 2.08 (s, 6 H), 2.25 (ddd, *J* = 5.5, 8.7, 14.5 Hz, 1 H), 2.40 (ddd, *J* = 6.5, 7.8, 14.7 Hz, 1 H), 3.75 (ddd, *J* = 3.5, 6.5, 10.0 Hz, 1 H), 4.15 (dd, *J* = 3.5, 12.0 Hz, 1 H), 4.20 (dd, *J* = 6.5, 12.0 Hz, 1 H), 4.35 (ddd, *J* = 2.5, 5.0, 8.7 Hz, 1 H), 5.05 (dd, *J* = 1.7, 17.3 Hz, 1 H), 5.08 (dd, *J* = 1.8, 17.3, Hz, 1 H), 5.20 (dd, *J* = 2.4, 10.0 Hz, 1 H), 5.75 (dd, *J* = 2.4, 10.5 Hz, 1 H), 5.80 (dd, *J* = 2.5, 10.5 Hz, 1 H), 5.95 (ddt, *J* = 6.8, 10.3, 17.3 Hz, 1 H).

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$; α-isomer): δ = 20.5, 20.8, 37.7, 62.8, 64.9, 69.8, 71.3, 117.4, 123.5, 132.5, 134.0, 169.7, 170.2.

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$; β-isomer): δ = 20.5, 20.8, 39.8, 63.7, 65.4, 73.9, 74.2, 117.4, 125.0, 132.2, 133.5, 169.7, 170.4.

### 4,6-Di-*O*-acetyl 2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl Cyanide (3b)

α-Isomer: Solid; mp 81.5 °C; $[\alpha]_D^{25}$ –14.8 (*c* = 1.0, $CHCl_3$).

β-Isomer: Liquid; $[\alpha]_D^{25}$ 214° (*c* = 1.0, $CHCl_3$).

IR (neat): 2950, 2362, 1732, 1436, 1371, 1221, 1108, 1046, 890, 769 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 2.15 (s, 3 H), 2.25 (s, 3 H), 4.05 (dt, *J* = 4.0, 9.0 Hz, 1 H), 4.25 (dd, *J* = 4.0, 11.8 Hz, 2 H), 5.10 (dt, *J* = 3.5, 2.5 Hz, 1 H), 5.35 (dq, *J* = 2.5, 9.0 Hz, 1 H), 5.90 (dt, *J* = 3.5, 10.5 Hz, 1 H), 6.05 (dt, *J* = 2.5, 10.5 Hz, 1 H).

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$; α-isomer): δ = 20.5, 20.6, 62.0, 62.4, 63.5, 71.8, 115.5, 123.4, 129.4, 169.8, 169.9.

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$; β-isomer): δ = 20.5, 20.6, 62.3, 62.7, 63.3, 74.2, 115.3, 124.0, 128.5, 169.8, 169.9.

### 3-(4,6-Di-*O*-allyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-1-propene (3c)

Liquid; $[\alpha]_D^{25}$ +36.5 (*c* = 1.0, $CHCl_3$).

$^1$H NMR ($CDCl_3$): δ = 2.25 (ddd, *J* = 5.5, 8.5, 14.3 Hz, 1 H), 2.45 (ddd, *J* = 6.0, 7.5, 14.3 Hz, 1 H), 3.60 (dd, *J* = 4.0, 12.0 Hz, 2 H), 3.65 (ddd, *J* = 3.5, 6.5, 9.8 Hz, 1 H), 3.93 (dd, *J* = 3.5, 12.0 Hz, 1 H), 4.05 (m, 4 H), 4.20 (dt, *J* = 1.8, 6.0, 8.5 Hz, 1 H), 5.10 (dd, *J* = 1.3, 17.3 Hz, 3 H), 5.20 (dd, *J* = 1.5, 17.3 Hz, 3 H), 5.80–6.0 (m, 5 H).

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$): δ = 37.9, 62.6, 65.6, 70.2, 71.3, 71.9, 72.5, 117.3, 126.0, 128.0, 130.3, 130.5, 134.2, 134.3, 134.5.

Anal. Calcd for $C_{15}H_{22}O_3$ (250.34): C, 71.97; H, 8.86. Found: C, 71.3; H, 8.28.

### 3-(4,6-Di-*O*-benzoyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-1-propene (3d)

Solid; mp 74–76 °C; $[\alpha]_D^{25}$ +105.1 (*c* = 1.0, $CHCl_3$).

$^1$H NMR ($CDCl_3$): δ = 2.30 (ddd, *J* = 5.5, 8.7, 14.3 Hz, 1 H), 2.53 (ddd, *J* = 6.0, 7.8, 14.3 Hz, 1 H), 4.31 (ddd, *J* = 3.5, 6.5, 9.8 Hz, 1 H), 4.39 (dd, *J* = 3.5, 12.0 Hz, 1 H), 4.52 (dq, *J* = 4.0, 11.8 Hz, 2 H), 5.08 (dd, *J* = 1.3, 17.3 Hz, 1 H), 5.15 (dd, *J* = 1.7, 17.3 Hz, 1 H), 5.48 (ddd, *J* = 2.1, 5.8, 8.5 Hz, 1 H), 5.88 (ddt, *J* = 7.3, 10.3, 17.2 Hz, 1 H), 5.97 (dt, *J* = 2.1, 2.4, 10.3 Hz, 1 H), 6.01 (dt, *J* = 1.2, 2.1, 10.3 Hz, 1 H), 7.45–7.55 (m, 6 H), 8.05–8.15 (m, 4 H).

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$): δ = 37.8, 63.7, 65.8, 69.9, 71.3, 117.6, 123.7, 128.2, 128.3, 129.7, 129.7, 129.7, 133.0, 133.1, 133.2, 134.0, 165.9, 166.3.

**3-(4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-1-propene (3e)**
Liquid; $[\alpha]_D^{25}$ +40.1 (*c* = 1.5, $CHCl_3$).

$^1$H NMR ($CDCl_3$): δ = 2.25 (ddd, *J* = 5.7, 8.5, 14.3 Hz, 1 H), 2.45 (ddd, *J* = 6.0, 7.5, 14.3 Hz, 1 H), 3.65 (dq, *J* = 4.0, 12.0 Hz, 2 H), 3.78 (ddd, *J* = 3.5, 6.5, 9.8 Hz, 1 H), 3.97 (dd, *J* = 3.5, 12.0 Hz, 1 H), 4.20 (dt, *J* = 2.0, 6.0, 8.5 Hz, 1 H), 4.50 (dd, *J* = 8.5, 14.7 Hz, 2 H), 4.58 (dd, *J* = 6.5, 14.7 Hz, 2 H), 5.05 (dd, *J* = 1.3, 17.3 Hz, 1 H), 5.10 (dd, *J* = 1.5, 17.3 Hz, 1 H), 5.79 (ddt, *J* = 7.3, 10.3, 17.2 Hz, 1 H), 5.83 (dt, *J* = 2.0, 2.4, 10.3 Hz, 1 H), 5.85 (dt, *J* = 1.2, 2.0, 10.3 Hz, 1 H), 7.23–7.35 (m, 10 H).

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$): δ = 38.0, 69.3, 69.9, 70.7, 71.4, 71.9, 73.2, 96.1, 117.1, 125.7, 127.3, 127.4, 127.5, 127.7, 128.1, 128.2, 130.9, 134.4, 138.2.

**3-(4,6-Di-*O*-pivolyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-1-propene (3f)**
Liquid; $[\alpha]_D^{25}$ +82.2 (*c* = 1.0, $CHCl_3$).

$^1$H NMR ($CDCl_3$): δ = 1.20 (s, 18 H), 2.30 (ddd, *J* = 5.5, 8.7, 14.2 Hz, 1 H), 2.45 (ddd, *J* = 6.0, 7.9 14.2 Hz, 1 H), 3.97 (ddd, *J* = 3.3, 6.5, 9.8 Hz, 1 H), 4.18 (dd, *J* = 3.3, 12.0 Hz, 2 H), 4.28 (dd, *J* = 6.2, 12.0 Hz, 1 H), 5.07 (ddd, *J* = 2.4, 5.5, 8.7 Hz, 1 H), 5.10 (dd, *J* = 1.3, 17.2 Hz, 1 H), 5.13 (dd, *J* = 1.5, 17.2 Hz, 1 H), 5.78 (dt, *J* = 2.4, 10.5 Hz, 1 H), 5.85 (ddt, *J* = 7.0, 10.3, 17.2 Hz, 1 H), 5.91 (dt, *J* = 2.3, 10.5 Hz, 1 H).

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$): δ = 27.0, 27.1, 38.0, 38.7, 38.8, 62.9, 64.7, 70.4, 71.2, 117.3, 123.9, 132.7, 134.1, 177.8, 178.1.

**4,6-Di-*O*-pivolyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl Cyanide (3g)**
Liquid; $[\alpha]_D^{25}$ +36.8 (*c* = 1.45, $CHCl_3$).

IR (neat): 2950, 1755, 1748, 1652, 1438, 1370, 1225, 1108, 1040, 1010, 980, 920 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 1.25 (s, 18 H), 4.05 (dt, *J* = 3.8, 9.0 Hz, 1 H), 4.25 (dd, *J* = 12.0 Hz, 2 H), 5.10 (dt, *J* = 3.5, 2.5 Hz, 1 H), 5.35 (dq, *J* = 2.5, 9.0 Hz, 1 H), 5.90 (dt, *J* = 3.5, 10.5 Hz, 1 H), 6.05 (dt, *J* = 2.5, 10.5 Hz, 1 H).

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$): δ = 27.0, 27.2, 38.0, 38.6, 63.5, 64.0, 72.3, 74.6, 115.8, 123.9, 124.0, 177.8, 178.1.

**3-(4,6-Di-*O*-methyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-1-propene (3h)**
Liquid; $[\alpha]_D^{25}$ +34.5 (*c* = 3.0, $CHCl_3$).

$^1$H NMR ($CDCl_3$): δ = 2.25 (ddd, *J* = 5.7, 8.5, 14.3 Hz, 1 H), 2.45 (ddd, *J* = 6.0, 7.5, 14.3 Hz, 1 H), 3.40 (s, 6 H), 3.53–3.65 (m, 4 H), 4.20 (dt, *J* = 2.0, 6.0, 8.3 Hz, 1 H), 5.05 (dd, *J* = 1.5, 17.3 Hz, 1 H), 5.10 (dd, *J* = 1.5, 17.3 Hz, 1 H), 5.79–5.98 (m, 3 H).

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$): δ = 37.9, 56.0, 58.9, 70.7, 71.4, 71.7, 72.0, 124.8, 125.4, 130.9, 133.6.

Anal. Calcd for $C_{11}H_{18}O_3$ (198.26): C, 66.64; H, 9.15. Found: C, 66.05; H, 9.87.

**3-(4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranosyl)-1-propene (3i)**
Liquid; $[\alpha]_D^{25}$ –293 (*c* = 1.0, $CHCl_3$).

$^1$H NMR ($CDCl_3$): δ = 2.07 (s, 3 H), 2.15 (s, 3 H), 2.24 (ddd, *J* = 5.6, 8.5, 14.3 Hz, 1 H), 2.43 (ddd, *J* = 6.3, 7.7, 14.5 Hz, 1 H), 4.09 (ddd, *J* = 3.5, 6.3, 10.3 Hz, 1 H), 4.18 (dd, *J* = 3.5, 12.0 Hz, 1 H), 4.20 (dd, *J* = 6.3, 12.0 Hz, 1 H), 4.33 (ddd, *J* = 2.5, 5.0, 8.5 Hz, 1 H), 5.03 (dd, *J* = 1.7, 17.3 Hz, 1 H), 5.10 (dd, *J* = 1.8, 17.3 Hz, 1 H), 5.15 (dd, *J* = 2.4, 10.0 Hz, 1 H), 5.80 (ddt, *J* = 6.8, 10.3, 17.3 Hz, 1 H), 5.95 (dd, *J* = 2.5, 10.3 Hz, 1 H), 6.03 (dd, *J* = 2.4, 10.3 Hz, 1 H).

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$): δ = 20.7, 20.8, 36.8, 62.8, 63.7, 68.0, 72.1, 117.5, 122.0, 133.8, 134.7, 170.3, 170.5.

Anal. Calcd for $C_{13}H_{18}O_5$ (254.28): C, 61.41; H, 7.13. Found: C, 61.05; H, 7.65.

**4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-threo-hex-2-enopyranosyl Cyanide (3j)**
Solid; mp 115 °C $[\alpha]_D^{25}$ –353 (*c* = 1.0, $CHCl_3$).

IR (neat): 2927, 2359, 1746, 1436, 1372, 1228, 1048, 1010, 915, 765 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 2.08 (s, 6 H), 4.19 (dt, *J* = 4.0, 9.0 Hz, 1 H), 4.25 (dd, *J* = 4.0, 11.8 Hz, 2 H), 5.15 (dd, *J* = 2.5, 9.0 Hz, 2 H), 6.05 (dd, *J* = 3.5, 10.3 Hz, 1 H), 6.25 (dd, *J* = 2.5, 10.3 Hz, 1 H).

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$; α-isomer): δ = 20.5, 20.6, 62.0, 62.4, 63.5, 71.8, 115.5, 123.4, 129.4, 169.8, 169.9.

$^{13}$C NMR ($^1$H-decoupled, $CDCl_3$; β-*isomer*): δ = 20.5, 20.6, 62.3, 62.7, 63.3, 74.2, 115.3, 124.0, 128.5, 169.8, 169.9.

Anal. Calcd for $C_{11}H_{13}NO_5$ (239.23): C, 55.23; H, 5.48, N, 5.86. Found: C, 55.61; H, 5.50, N, 5.37.

## Acknowledgements

BVS, KSR, LC and VS thank CSIR, New Delhi for the award of fellowships.

## References

(1) (a) Lewis, M. D.; Cha, J. K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976. (b) Paterson, L.; Keown, L. E. *Tetrahedron Lett.* **1997**, *38*, 5727. (c) Horita, K.; Sakkurai, Y.; Nagasawa, M.; Hacliya, S.; Yonemistu, O. *Synlett* **1994**, 43.

(2) (a) Weatherman, R. V.; Mortell, K. H.; Chervenak, M.; Kiessling, L. L.; Toone, E. *J. Biochem.* **1996**, *35*, 3619. (b) Levy, D. E.; Tan, C. *The Chemistry of C-Glycosides*; Pergamon Press: Oxford, **1995**.

(3) (a) Du, Y.; Linhardt, R. J. *Tetrahedron* **1998**, *54*, 9913. (b) Nicolaou, K. C.; Duggan, M. E.; Hwang, C. K.; Somers, P. K. *J. Chem. Soc., Chem. Commun.* **1985**, 1359. (c) Wincott, F. E.; Danishefsky, S. J.; Schutte, G. *Tetrahedron Lett.* **1987**, *28*, 4951. (d) Andersen, L.; Mikkelsen, L. M.; Beau, J. M.; Skrydstrup, T. *Synlett* **1998**, 1393. (e) Mazeas, D.; Skrydstrup, T.; Beau, J. M. *Angew. Chem., Int. Ed. Engl.* **1995**, 909.

(4) (a) Suhadolnik, R. J. *Nucleoside Antibiotics*; Wiley-Interscience: New York, **1970**. (b) Hanessian, S. C. *Total Synthesis of Natural Products: The Chiron Approach*; Pergamon Press: Oxford, **1984**.

(5) (a) Danishefsky, S. J.; Keerwin, J. F. *J. Org. Chem.* **1982**, *47*, 3803. (b) De Raadt, A.; Griegl, H.; Klempic, N.; Stutz, A. E. *J. Org. Chem.* **1993**, *58*, 3179. (c) De LasHeras, F. G.; Felix, A. S.; Ferdanzandez-Risa, P. *Tetrahedron* **1983**, *39*, 1617. (d) Kunz, H.; Weibmuller, J.; Muller, B. *Tetrahedron Lett.* **1984**, *25*, 3571.

(6) (a) Dawe, R. D.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1981**, 1180. (b) Toshima, K.; Ishizuka, T.; Matsuo, G.; Nakata, M. *Chem. Lett.* **1993**, 2013. (c) Toshima, K.; Miyamito, N.; Matsuo, G.; Nakata, M.; Matsumura, S. *Chem. Commun.* **1996**, 1379.

(7) (a) Hayashi, M.; Kawabata, H.; Inoue, K. *Carbohydr. Res.* **2000**, *325*, 68. (b) Takhi, M.; Adel, A.-H. A. R.; Schimdt, R. R. *Tetrahedron Lett.* **2001**, *42*, 4053. (c) Yadav, J. S.; Reddy, B. V. S.; Chand, P. K. *Tetrahedron Lett.* **2001**, *42*, 4057.
(8) Leonard, M. N.; Wieland, L. C.; Mohan, R. S. *Tetrahedron* **2002**, *58*, 8373.
(9) Repichet, S.; Zwick, A.; Vendier, L.; Le Roux, C.; Dubac, J. *Tetrahedron Lett.* **2002**, *43*, 993.
(10) (a) Macro-Conlelles, J. L.; Farnandez, C.; Gomez, A.; Martin-Leon, N. *Tetrahedron Lett.* **1990**, *31*, 1467. (b) Ichikawa, Y.; Isobe, M.; Konobe, M.; Goto, T. *Carbohydr. Res.* **1987**, *171*, 193. (c) Hosokawa, S.; Krischbaum, B.; Isobe, M. *Tetrahedron Lett.* **1998**, *39*, 1917.