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Total syntheses of aminomethyl-C-dideoxyglycopyranosides and their quinamides

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Abstract—Lewis acid promoted cyclization of homoallylic alcohol **1** with acetal **2** gave 4-chloro-2-phthalimidomethyl-6-methyltetrahydropyrans. Their dehydrochlorination produced two regioisomeric dihydropyrans. Subsequent *cis*- and *trans*-dihydroxylation gave four racemic dihydroxy-6-methyl-2-phthalimidomethyl tetrahydropyrans. They were deprotected and *N*-acylated with a chiral quinic acid lactone, producing a library of four diastereomeric mixtures of novel C-pseudodisaccharides, which were separable after derivatization.
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C-Glycosides, chemically and enzymatically stable analogues of carbohydrates, may compete in cell surface adhesion, inhibit carbohydrate-processing enzymes and interfere in the biosynthesis of specific cell surface carbohydrates, and are therefore potential therapeutic agents against HIV and other infections, against cancer, diabetes and other metabolic disorders.[1–3] C-Glycopyranosides with an aminomethyl group on the anomeric carbon may be potent inhibitors for glycosidases.[3] C-Glycosides are building blocks of polyether antibiotics and toxins.[1] The great majority of methods developed for the synthesis of C-glycosides[1,2] start from natural sugars, mostly D-glucose, D-mannose and D-galactose, which are commercially available in multigram quantities.[4] Other D-monosaccharides and all L-monosaccharides are very expensive and available only on a milligram scale.[4] Moreover, D-gulose, D-altrose and D-idose exist in appreciable proportions as their 1,6-anhydrides with essentially different chemical behavior.[5] Here we report the total syntheses of partially functionalized β-C-glycopyranosides, related to 2,4- and 4,6-dideoxyhexoses, found as cardiac glycosides.[6,7] These C-glycosides are tetrahydropyrans, obtained from homoallylic alcohols and acetals by a Lewis acid promoted cyclization, followed by dehydrohalogenation and subsequent double bond functionalization. (Some parts of this work have been reported previously[8]). A subsequent use of these building blocks for the syntheses of di- and oligosaccharide mimics is illustrated by their quinoylation. Quinic acid is an important structural component in a number of naturally occurring biologically active compounds which exhibit HIV-integrase inhibition,[9] as well as hypocholesterolemic,[10] hepatoprotective[11] and antioxidative activities.[12] Commercially available quinic acid is an attractive starting material for syntheses of shikimic acid and other chiral compounds, such as carbasugars.[13] A combination of racemic aminomethyl C-glycosides with chiral quinic acid may directly yield biologically active chiral compounds.

Acid-catalyzed reactions between homoallylic alcohols and aldehydes or acetals have been used before for the preparation of 2,6-disubstituted di- and tetrahydropyran derivatives.[8,14] We chose an expandable two-component scheme of cyclization with a possibility of various functional groups in readily available starting compounds. Use of phthalimido derivatives allowed for syntheses of (protected) aminomethyl C-glycopyranosides (Scheme 1).

Cyclizations of this type furnish exclusively *cis*-2,6-disubstituted tetrahydropyrans[8,14] corresponding to the β-configuration of the projected C-glycopyranosides. Most C-glycoside syntheses provide α-products.[2] The new stereocenter C(6) is entirely determined by the configuration of the existing stereocenter in the homoallylic alcohol. Chiral homoallylic alcohols would give enantiomerically pure tetrahydropyrans, and finally C-glycosides, while we obtained racemic aminomethyl C-glycosides, subsequently acylated with the chiral lactone of quinic acid (Scheme 1), and sepa-

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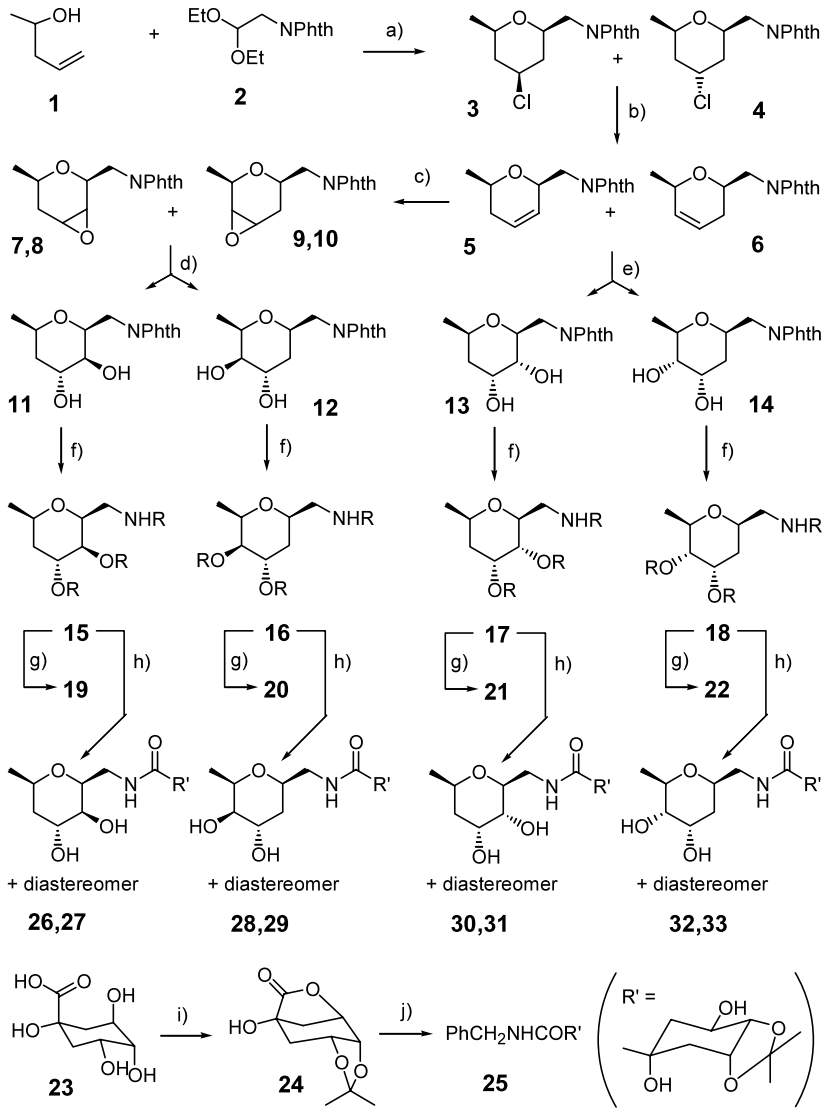


Scheme 1. Synthesis of aminomethyl-C-glycosides (**3**–**10**: stereoisomeric mixtures; **11**–**22**: racemic mixtures; Phth = phthaloyl). (a) $SnCl_4$, CH_2Cl_2, −55°C, 82%; (b) DBU, LiCl, Py, reflux, 79%; (c) urea–H_2O_2, TFAA, 93%; (d) TFAA, H_2O/THF, 60°C, 74%; (e) OsO_4, NMO, 64%; (f) (1) Me_2NH, MeOH, H_2O, (2) H_2SO_4, H_2O, (3) NH_4OH, 80–86% (**15**–**18**: R = H); (g) Ac_2O, DMAP, Py, 51–85% (**19**–**22**: R = Ac); (h) **24**, DMA, 70°C, 58–77%; (i) acetone, *p*-TsOH, reflux, 86%; (j) $BnNH_2$, DMA, 55°C, 72%.

rated as derivatives of diastereomeric quinamides (Scheme 2).

The starting materials **1** and **2** were prepared as described earlier.[15] Acid promoted cyclization of these compounds at −55°C in CH_2Cl_2 solution with $SnCl_4$ (Scheme 1) gave chlorotetrahydropyrans **3** and **4** (5:1, separable by column chromatography).[†] The alkenes **5**, **6** were obtained as a 2:1 mixture (by NMR) by heating of the mixture **3**, **4** with DBU in pyridine in presence of LiCl, which facilitated isomerization of equatorial into axial halogen, more suitable for elimination. Epoxidation of the alkene mixture with urea–H_2O_2 complex in the presence of CF_3COOH[16] produced an epoxide mixture **7**–**10** (93%), which was difficult to separate. However, the well known tendency of epoxides to open *trans*-diaxially,[17] allowed for direct synthesis of a two-component *trans*-diol mixture **11**, **12**, separated by column chromatography (51 and 23%, respectively).[‡] After *cis*-dihydroxylation (OsO_4/NMO) of the mixture **5**,**6**, only compounds **13** and **14** were isolated by column chromatography (SiO_2, CH_2Cl_2/*i*PrOH 20/1; 45 and 19%, respectively).[§] This stereoselectivity is worth of additional investigation.

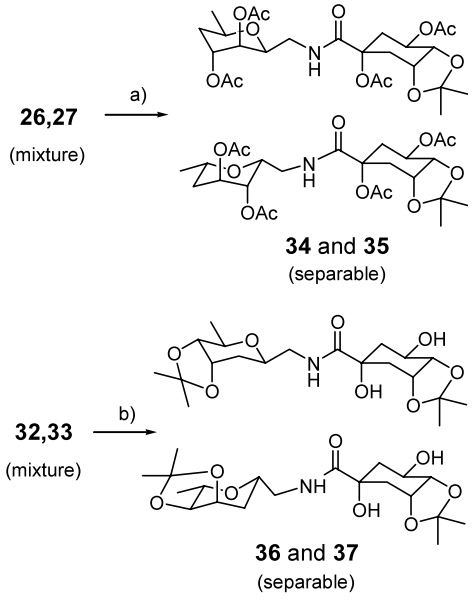
Thus, we obtained a series of four racemic phthalimido-protected aminomethyl C-dideoxyglycopyranosides **11**–**14**, which produced with Me_2NH aq.[18] the dimethylammonium salts of phthalamic acids. They were hydrolyzed after evaporation of excess Me_2NH by heating with aq. H_2SO_4 (70°C), followed by extraction

[†] Cpd **3**: mp 146–148°C; cpd **4**: mp 121–122°C.

[‡] Cpd **11**: mp 187–188°C; cpd **12**: mp 162–164°C.

[§] Cpd **13**: mp 190–191°C; cpd **14**: mp 193–195°C.

of phthalic acid with CH_2Cl_2 and Et_2O. Neutralization by NH_3 aq. and subsequent evaporation followed by column chromatography (SiO_2; CH_2Cl_2/MeOH/NH_3 aq. = 49/49/2) gave compounds **15**–**18** (80–86%), characterized and analyzed as their *N*-acetyl- and/or *N*,*O*-triacetyl derivatives,[¶] and used as building blocks for pseudodisaccharide syntheses. Acylation of benzylamine with the isopropylidenated γ-lactone of quinic acid **24**[19] provided us with ^{1}H NMR chemical shifts and coupling constants for the quinoyl part of compound **25**. Similarly we converted racemic C-glycosides **15**–**18** into their quinamides **26**–**33** (i.e. into diastereomeric C-pseudodisaccharides; Scheme 1).[‖]



Scheme 2. Separation of diastereomeric mixtures of quinamides as isopropilidene-tetra-*O*-acetyl or diisopropilidene derivatives. (a) Ac_2O, DMAP, Py; (b) 2-methoxypropene, *p*-TsOH, DMF.[20]

Generally, separation of diastereomeric pairs **26**–**33** could only be achieved via their derivatives (Scheme 2). Thus, the *trans*-dihydroxy aminomethyl C-glycosides **26**,**27** were separated as their *O*-acetyl derivatives by flash chromatography (SiO_2, EtOAc/hexane, 5/1) to produce **34** (or **35**) (7%), **35** (or **34**) (28%), and **34**+**35** (32%).[**] Quinamides **32**,**33** were isopropylidenated, and the mixture **36**,**37** was enriched with one of the stereoisomers (9:1) by column chromatography (SiO_2, CH_2Cl_2/*i*PrOH 20/1).[††]

All isolated compounds gave satisfactory elemental analyses, and MS, IR, ^{1}H and ^{13}C NMR data.

[¶] Cpd **19**: mp 142–144°C; cpd **20**: mp 143–144°C; cpd **21**: mp 152–154°C; cpd **22**: oil.

[‖] The azeotropically dried (PhMe) aminodiol **15**, **16**, **17**, or **18** (1.4 g, 8.4 mmol) with **24** (1.8 g, 8.4 mmol) in 1 ml of DMA was heated with stirring at 70°C for 48 h, and was kept at rt for 48 h. DMA was evaporated in vacuo. The residual yellow oil was analyzed by TLC and was chromatographed (CH_2Cl_2:MeOH:NH_4OH = 95:16:2) to give, respectively, **26**/**27** (58%; oil), **28**/**29** (70%; oil), **30**/**31** (64%; colorless cryst.), or **32**/**33** (77%; oil). One of the diastereomers **30** or **31** crystallized from *i*PrOH (16%): mp 201–202°C; $[\alpha]_D^{25} = -69$ (*c* 0.9, MeOH). IR (KBr): 3580, 3500, 3380, 2900, 2450, 1640, 1530, 1200, 900 cm^{-1}. ^{1}H NMR (CD_3OD): δ 1.12 (d, 3H, J = 6.3 Hz, CH_3^A), 1.28 (s, 3H, CH_3^B), 1.45 (ddd, 1H, J = 14.2, 11.5, 2.8 Hz, H-5a^A), 1.52 (s, 3H, CH-3^B), 1.61 (br s, 1H, OH), 1.80 (ddd, 1H, J = 14.2, 3.2, 2.4 Hz, H-5e^A), 2.09 (m, 2H, H-2a^B, H-6a^B), 2.26 (dd, 1H, J = 15.5, 5.6 Hz, H-6e^B), 2.43 (dd, 1H, J = 15.5, 2.5 Hz, H-2e^B), 3.17 (dd, 1H, J = 9.7, 3.1 Hz, H-3^A), 3.28 (ddd, 1H, J = 14.6, 4.8, 3.0 Hz, CH_2N^A), 3.51 (br s, 1H, OH), 3.71 (dd, 1H, J = 9.7, 3 Hz, H-2^A), 3.87 (dd, 1H, J = 14.6, 3.0 Hz, CH_2N^A), 3.90 (m, 1H, H-5^B), 3.92 (m, 1H, J = 11.5, 6.3, 2.4 Hz, H-6^A), 4.14 (m, 1H, J = 3.2, 3.1, 2.8 Hz, H-4^A), 4.16 (m, 1H, J = 6.6, 3.6 Hz, H-4^B), 4.28 (br s, 1H, OH), 3.5, 2.5 Hz, H-3^B), 7.49 (t, 1H, J = 4.8, 3.0 Hz, NH). ^{13}C NMR ($CDCl_3$): δ 21.46, 25.92, 28.49, 35.71, 40.26, 41.08, 42.23, 68.43, 68.63, 69.01, 70.67, 74.92, 75.05, 75.75, 81.34, 109.70, 178.38. Anal. $C_{17}H_{29}NO_8$ (375.42). Calcd (%): C, 54.39; H, 7.79; N, 3.73. Found (%): C, 54.20; H, 7.42; N, 4.02.

[**] Cpd **34** (or **35**): oil, $[\alpha]_D^{25} = -51.5$ (*c* 1.65, CCl_4). IR (neat): 3400, 1760, 1680, 1550, 1380, 1250 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.13 (d, J = 6.0 Hz, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.59 (dt, J = 14.8, 2.2 Hz, 1H, H-5e^A), 1.60 (dd, J = 13.2, 12.1 Hz, 1H, H-2a^B), 1.70 (ddd, J = 14.6, 11.5, 3.3 Hz, 1H, H-5a^A), 2.02 (s, 3H, $COCH_3$), 2.06 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$), 2.16 (ddd, J = 13.5, 4.4, 2.5 Hz, 1H, H-2e^B), 2.46 (dd, J = 16.5, 4.4 Hz, 1H, H-6a^B), 2.52 (ddd, J = 14.8, 11.3, 4.4 Hz, 1H, CH_2N^A), 2.92 (ddd, J = 16.8, 2.5, 2.5 Hz, 1H, H-6e^B), 3.68 (m, 2H, CH_2N^A, H-2^A), 3.79 (m, 1H, H-6^A), 3.97 (dd, J = 8.0, 5.8 Hz, 1H, H-4^B), 4.37 (m, J = 4.7, 2.5 Hz, 1H, H-5^B), 4.52 (d, J = 3.0 Hz, 1H, H-3^A), 4.86 (q, J = 3.0 Hz, 1H, H-4^A), 5.25 (ddd, J = 12.1, 7.7, 4.7 Hz, 1H, H-3^B), 6.58 (dd, J = 7.7, 4.4 Hz, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.89, 21.09, 21.13, 21.29, 25.90, 28.13, 28.17, 33.09, 36.81, 38.36, 65.45, 67.01, 68.74, 70.68, 71.34, 73.17, 76.62, 80.40, 109.11, 169.75, 169.90, 170.04, 171.21, 171.32. Anal. $C_{25}H_{37}NO_{12}$ (543.57). Calcd (%): C, 55.24; H, 6.86; N, 2.58. Found (%): C, 55.03; H, 7.02; N, 2.53. MS: m/z calcd for $C_{25}H_{38}NO_{12}$ (M+1) 544.24, found 544.3. Cpd **35** (or **34**): oil, $[\alpha]_D^{25} = -16.73$ (*c* 1.15, CCl_4). IR (neat): 3200, 2780, 1740, 1680, 1440, 1260, 900 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.19 (d, J = 6.0 Hz, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.73 (m, 2H, H-5a^A, H-5e^A), 2.00 (dd, J = 14.3, 11.5, 1H, H-2a^B), 2.08 (s, 3H, $COCH_3$), 2.12 (s, 3H, $COCH_3$), 2.13 (s, 3H, $COCH_3$), 2.15 (s, 3H, $COCH_3$), 2.26 (dd, J = 16.2, 4.9 Hz, 1H, H-6a^B), 2.36 (ddd, J = 14.0, 4.4, 2.2 Hz, H-2e^B), 2.71 (ddd, J = 16.2, 2.5, 2.5 Hz, 1H, H-6e^B), 2.97 (ddd, J = 13.7, 7.7, 6.0 Hz, CH_2N^A), 3.47 (ddd, J = 13.5, 6.6, 6.6 Hz, 1H, CH_2N^A), 3.76 (t, J = 7.7 Hz, 1H, H-2^A), 3.81 (m, 1H, H-6^A), 4.10 (dd, J = 7.7, 5.8 Hz, 1H, H-4^B), 4.42 (dt, J = 4.7, 2.8, 2.8 Hz, 1H, H-5^B), 4.64 (d, J = 3.3 Hz, 1H, H-3^A), 4.93 (q, J = 3.0 Hz, 1H, H-4^A), 5.16 (ddd, J = 11.8, 7.7, 4.4 Hz, 1H, H-3^B), 6.52 (t, J = 6.3 Hz, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 20.88, 21.12, 21.16, 21.23, 21.30, 25.63, 27.93, 31.62, 33.12, 34.08, 38.95, 65.94, 67.15, 68.64, 70.43, 71.79, 72.70, 76.42, 80.49, 109.06, 169.54, 169.58, 170.02, 170.71, 171.15. Anal. $C_{25}H_{37}NO_{12}$ (543.57). Calcd (%): C, 55.24; H, 6.86; N, 2.58. Found (%): C, 55.41; H, 7.11; N, 2.71. MS: m/z calcd for $C_{25}H_{38}NO_{12}$ (M+1) 544.24, found 544.3.

[††] For the predominant diastereomer **36** or **37**: ^{1}H NMR ($CDCl_3$): δ 1.24 (d, J = 6.3 Hz, 3H, CH_3^A), 1.36 (s, 6H, 2C(CH_3)$_2$), 1.48 (s, 1H, CCH_3), 1.52 (s, 1H, CCH_3), 1.70 (ddd, 1H, J = 15.4, 11.8, 4.1 Hz, H-3a^A), 2.06 (m, 3H, H-2a^B,6a^B,3e^A), 2.28 (ddd, 1H, J = 15.1, 5.2, 1.7 Hz, H-6e^B), 2.46 (dd, 1H, J = 15.7, 2.5 Hz, H-2e^B), 3.12 (ddd, 1H, J = 13.5, 7.7, 4.4 Hz, CH_2N^A), 3.40 (m, 2H, H-5^A, OH-1), 3.58 (m, 2H, H-6^A, CH_2N^A), 3.72 (m, 1H, H-2^A), 3.84 (br d, J = 2.2 Hz, 1H, H-5^B), 4.18 (ddd, 1H, J = 6.9, 3.0, 1.4 Hz, H-4^A), 4.36 (ddd, 1H, J = 4.4, 4.4, 1.9 Hz, H-4^B), 4.59 (m, 1H, J = 6.3, 2.8 Hz, H-3^B), 4.72 (s, 1H, OH-3), 7.34 (t, 1H, J = 5.77 Hz, NHCO). ^{13}C NMR ($CDCl_3$): δ 18.65, 24.28, 26.25, 26.95, 28.27, 30.41, 34.36, 36.96, 43.28, 65.67, 71.17, 71.63, 71.93, 72.70, 73.91, 75.78, 76.84, 108.47, 108.80, 176.29. MS: m/z calcd for $C_{20}H_{34}NO_8$ (M+1) 416.23, found 416.2.

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References

1. *Carbohydrate Mimics*; Chapleur, Y., Ed.; Wiley-VCH: Weinheim, 1998.
2. (a) Levy, D. E.; Tang, C. *The Chemistry of C-Glycosides*; Pergamon: Oxford, 1995; (b) Postema, M. H. D. *C-Glycoside Synthesis*; CRC Press: London, 1995.
3. Schmidt, R. R.; Dietrich, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1328–1329.
4. SIGMA Catalogue, 2002–2003.
5. Collins, P. M.; Ferrier, R. J. *Monosaccharides*: *Their Chemistry and Their Roles in Natural Products*; Wiley: New York, 1995.
6. Hoffmann, B. F.; Bigger, J. T. In *The Pharmacological Basis of Therapeutics*, 8th ed.; Gilman, A. G.; Rall, T. W.; Nies, A. S.; Taylor, P., Eds.; Pergamon Press: New York, 1990; pp. 814–839.
7. Thomas, R.; Gray, P.; Andrews, J. *Adv. Drug Res.* **1990**, *19*, 312–562.
8. (a) Gross, P. H. *Carbohydr. Polym.* **1998**, *37*, 215–217; (b) Samoshin, V. V.; Gremyachinskiy, D. E.; Gross, P. H. *Mendeleev Commun.* **1999**, 53; (c) Gremyachinskiy, D. E.; Samoshin, V. V.; Gross, P. H. *Glycobiology* **2001**, *11*, 908; (d) Gremyachinskiy, D. E. Ph.D. Dissertation, University of the Pacific, Stockton, CA, 2002.
9. (a) Robinson, E.; Reinecke, M.; Abdel-Malek, S.; Jia, Q.; Chow, S. *Proc. Nat. Acad. Sci. USA* **1996**, *93*, 6326–6331; (b) Robinson, E.; Cordeiro, M.; Abdel-Malek, S.; Jia, Q.; Chow, S.; Reinecke, M.; Mitchell, W. *Mol. Pharmacol.* **1996**, *50*, 846–855; (c) Neamati, N.; Hong, H.; Sunder, S.; Milne, G.; Pommier, Y. *Mol. Pharmacol.* **1997**, *52*, 1041–1055.
10. Montini, M.; Levoni, P.; Ongaro, A.; Pagani, G. *Arzneim-Forsch. Drug. Res.* **1975**, *25*, 1311–1314.
11. Adzet, T.; Camarasa, J.; Laguna, J. *J. Nat. Prod.* **1987**, *50*, 612–617.
12. (a) Gebhardt, R.; Fausel, M. *Toxicol. In Vitro* **1997**, *11*, 669–672; (b) Basnet, P.; Matsushige, K.; Hase, K.; Kadota, S.; Namba, T. *Biol. Pharm. Bull.* **1996**, *19*, 655–657; (c) Slanina, J.; Taborska, E.; Bochorakova, H.; Slaninova, I.; Humpa, O.; Robinson, E.; Schram, K. *Tetrahedron Lett.* **2001**, *42*, 3383–3385.
13. (a) Frank, M.; Miethchen, R. *Carbohydr. Res.* **1998**, *313*, 49–53; (b) Barco, A.; Benetti, S.; De Risi, C.; Marchetti, P.; Pollini, G.; Zanirato, V. *Tetrahedron: Asymmetry* **1997**, *8*, 3515–3545; (c) Hanessian, S.; Beaulieu, P.; Dube, D. *Tetrahedron Lett.* **1986**, *27*, 5071–5074; (d) Jiang, S.; Singh, G. *Tetrahedron* **1998**, *54*, 4697–4753; (e) Carballido, M.; Luis, C.; Gonzales, C. *Tetrahedron Lett.* **2001**, *42*, 3973–3976; (f) Hanessian, S.; Huynh, H. K.; Reddy, G. V.; Duthaler, R. O.; Katopodis, A.; Streiff, M. B.; Kinzy, W.; Oehrlein, R. *Tetrahedron* **2001**, *57*, 3281–3290.
14. For the recent representative publications, see: (a) Cloninger, M. J.; Overman, L. E. *J. Am. Chem. Soc.* **1999**, *121*, 1092–1093; (b) Viswanathan, G. S.; Yang, J.; Li, C.-J. *Org. Lett.* **1999**, *1*, 993–995; (c) Rychnovsky, S. D.; Thomas, C. R. *Org. Lett.* **2000**, *2*, 1217–1219; (d) Yang, X.-F.; Li, C.-J. *Tetrahedron Lett.* **2000**, *41*, 1321–1325; (e) Zhang, W.-C.; Li, C.-J. *Tetrahedron* **2000**, *56*, 2403–2411; (f) Marko, I. E.; Leroy, B. *Tetrahedron Lett.* **2000**, *41*, 7225–7230; (g) Yadav, J. S.; Subba Reddy, B. V.; Mahesh Kumar, G.; Murthy, C. V. S. R. *Tetrahedron Lett.* **2001**, *42*, 89–91; (h) Rychnovsky, S. D.; Marumoto, S.; Jaber, J. J. *Org. Lett.* **2001**, *3*, 3815–3818; (i) Jaber, J. J.; Mitsui, K.; Rychnovsky, S. D. *J. Org. Chem.* **2001**, *66*, 4679–4686; (j) Crosby, S. R.; Harding, J. R.; King, C. D.; Parker, G. D.; Willis, C. L. *Org. Lett.* **2002**, *4*, 577–580; (k) Crosby, S. R.; Harding, J. R.; King, C. D.; Parker, G. D.; Willis, C. L. *Org. Lett.* **2002**, *4*, 3407–3410; (l) Cho, Y. S.; Kim, H. Y.; Cha, J. H.; Pae, A. N.; Koh, H. Y.; Choi, J. H.; Chang, M. H. *Org. Lett.* **2002**, *4*, 2025–2028; (m) Marumoto, S.; Jaber, J. J.; Vitale, J. P.; Rychnovsky, S. D. *Org. Lett.* **2002**, *4*, 3919–3922; (n) Hart, D. J.; Bennett, C. E. *Org. Lett.* **2003**, *5*, 1499–1502.
15. (a) Gremyachinskiy, D. E.; Smith, L. L.; Gross, P. H.; Samoshin, V. V. *Green Chem.* **2002**, *4*, 317–318; (b) Watanabe, G. R.; Gremyachinskiy, D. E.; Gross, P. H.; Samoshin, V. V. *J. Undergrad. Chem. Res.* **2002**, *1*, 163–167.
16. Ballini, R.; Marcantoni, E.; Petrini, M. *Tetrahedron Lett.* **1992**, *33*, 4835–4838.
17. Fuerst, A.; Plattner, P. A. *Helv. Chim. Acta* **1949**, *32*, 275–283.
18. (a) Motawia, M.; Wengel, J.; Abdel-Megid, A.; Pedersen, E. *Synthesis* **1989**, 384–387; (b) Kennedy, G.; Viziano, M.; Winders, J.; Cavallini, P.; Gevi, M.; Micheli, F.; Rodegher, P.; Seneci, P.; Zumerle, A. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1751–1754.
19. (a) Fischer, H. O. L. *Ber. Dtch. Chem. Ges.* **1921**, *54*, 775–784; (b) Trost, B.; Romero, A. *J. Org. Chem.* **1986**, *51*, 2332–2342.
20. Barbat, J.; Gelas, J.; Horton, D. *Carbohydr. Res.* **1991**, *219*, 115–121.