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Synthesis of α- and β-Glycosyl Asparagine Ethylene Isosteres (*C*-Glycosyl Asparagines) via Sugar Acetylenes and Garner Aldehyde Coupling

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Supporting Information

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3,7-Anhydro-4,5,6,8-tetra-*O*-benzyl-1,2-dideoxy-D-*glycero*-D-*ido*-oct-1-ynitol (11). The acetate **5** (400 mg, 0.69 mmol) was treated with tributylstannyl(trimethylsilyl)acetylene (575 mg, 1.38 mmol) as described for the preparation of **7** to give, after the same workup and purification, **8** (278 mg, 65%) as a syrup; $[\alpha]_D$ = +21.7 (*c* 1.8, $CHCl_3$). ^{1}H NMR: δ 7.42-7.15 (m, 20 H, 4 Ph), 4.99 and 4.83 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.85 and 4.52 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.85 (d, 1 H, $J_{3,4}$ = 5.5 Hz, H-3), 4.71 (s, 2 H, PhCH_2), 4.64 and 4.51 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.01 (ddd, 1 H, $J_{6,7}$ = 9.0, $J_{7,8a}$ = 3.5, $J_{7,8b}$ = 2.0 Hz, H-7), 3.94 (dd, 1 H, $J_{4,5}$ = 9.5, $J_{5,6}$ = 9.0 Hz, H-5), 3.79 (dd, 1 H, $J_{8a,8b}$ = 11.0 Hz, H-8a), 3.68 (dd, 1 H, H-8b), 3.66 (d, 1 H, H-6), 3.64 (dd, 1 H, H-5), 0.25 (s, 9 H, $SiMe_3$). MALDI-TOF MS: 644.3 (M^+ + Na), 660.6 (M^+ + K). Anal. Calcd. for $C_{39}H_{44}O_5Si$: C, 75.44; H, 7.14. Found: C, 75.42; H, 7.13.

The compound **8** (250 mg, 0.40 mmol) was desilylated as described for the preparation of **10** to afford, after filtration through a short column of silica gel (2 x 10 cm, d x h) with 9:1 cyclohexane-AcOEt, **11** (222 mg, 99%) as a syrup; $[\alpha]_D$ = +44.1 (*c* 1.5, $CHCl_3$); lit.[34] $[\alpha]_D$ = +46.7 (*c* 1.7, $CHCl_3$). ^{1}H NMR: δ 7.40-7.11 (m, 20 H, 4 Ph), 5.02 and 4.85 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.85 and 4.50 (2 d, 2 H, *J* = 10.7 Hz, PhCH_2), 4.78 and 4.72 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.76 (dd, 1 H, $J_{1,3}$ = 2.2, $J_{3,4}$ = 5.5 Hz, H-3), 4.63 and 4.50 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.01 (ddd, 1 H, $J_{6,7}$ = 10.0, $J_{7,8a}$ = 3.5, $J_{7,8b}$ = 2.0 Hz, H-7), 3.98 (dd, 1 H, $J_{4,5}$ = 9.3, $J_{5,6}$ = 9.3 Hz, H-5), 3.76 (dd, 1 H, $J_{8a,8b}$ = 11.0 Hz, H-8a), 3.68 (dd, 1 H, $J_{7,8b}$ = 2.0 Hz, H-8b), 3.65 (dd, 1 h, H-4), 3.64 (dd, 1 H, H-

6), 2.62 (d, 1 H, H-1). MALDI-TOF MS: 572.4 (M^+ + Na), 588.5 (M^+ + K). Anal. Calcd. for $C_{36}H_{36}O_5$: C, 78.80; H, 6.61. Found: C, 78.90; H, 6.58.

3,7-Anhydro-4,5,6,8-tetra-*O*-benzyl-1,2-dideoxy-D-*glycero*-D-*talo*-oct-1-ynitol (12). The acetate **6** (2.00 g, 3.40 mmol) was treated with tributylstannyl(trimethylsilyl)acetylene (2.87 g, 6.80 mmol) as described for the preparation of **7** to give, after column chromatography on silica gel (10:1 cyclohexane-AcOEt), syrupy **9** (1.89 g, 90%) slightly contaminated by tin-containing byproducts. ^{1}H NMR selected data: δ 7.58-7.18 (m, 8 H, 4 Ph), 5.08 and 5.06 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.89 and 4.64 (2 d, 2 H, J = 10.5 Hz, PhCH_2), 4.65 (s, 2 H, PhCH_2), 4.64 and 4.55 (2 d, 2 H, J = 11.0 Hz, PhCH_2), 3.55 (dd, 1 H, $J_{4,5}$ = 3.0, $J_{5,6}$ = 9.0 Hz, H-5), 3.46 (m, 1 H, H-7), 0.20 (s, 9 H, $SiMe_3$).

The compound **9** (1.60 g, 2.61 mmol) was desilylated as described for the preparation of **10** to afford, after column chromatography on silica gel (9:1 cyclohexane-AcOEt), **12** (1.42 g, 95%) as a syrup; $[\alpha]_D$ = +23.1 (*c* 1.0, $CHCl_3$); lit.[7b] $[\alpha]_D$ = +23.5 (*c* 0.9, $CHCl_3$). ^{1}H NMR: δ 7.43-7.17 (m, 20 H, 4 Ph), 4.91 and 4.54 (2 d, 2 H, J = 10.5 Hz, PhCH_2), 4.85 (dd, 1 H, $J_{1,3}$ = 2.3, $J_{3,4}$ = 2.3 Hz, H-3), 4.79 and 4.69 (2 d, 2 H, J = 12.3 Hz, PhCH_2), 4.69 and 4.57 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.66 and 4.61 (2 d, 2 H, J = 11.2 Hz, PhCH_2), 4.07 (m, 1 H), 4.02-3.97 (m, 2 H), 3.86 (d, 1 H, $J_{4,5}$ = 2.7 Hz, H-4), 3.83-3.73 (m, 2 H), 2.53 (d, 1 H, H-1). MALDI-TOF MS: 572.5 (M^+ + Na), 588.8 (M^+ + K). Anal. Calcd. for $C_{36}H_{36}O_5$: C, 78.80; H, 6.61. Found: C, 78.87; H, 6.53.

4-Azido-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-1-*C*-(trimethylsilyl)-D-*gluco*-oct-1-yn-3-ulopyranose (17). Treatment of **14** (1.00 g, 2.11 mmol) as described for the preparation of **16** gave syrupy **17** (1.18 g, 98%) as a 1.5:1 mixture of anomers ~95% pure by ^{1}H NMR analysis. This product was used for the following step without further purification. ^{1}H NMR selected data: ^{1}H NMR: δ 7.40-7.16 (m, 15, 3 Ph), 4.93 and 4.85 (2 d, 0.8 H, J = 10.7 Hz, PhCH_2), 4.91 and 4.83 (2 d, 1.2 H, J = 10.9 Hz, PhCH_2), 4.64 and 4.55 (2 d, 0.8 H, J = 12.0 Hz, PhCH_2), 4.63 and 4.54 (2 d, 1.2 H, J = 12.0 Hz, PhCH_2), 4.01 (ddd, 0.6 H, $J_{4,5}$ = 10.0, $J_{5,6a}$ = 2.2, $J_{5,6b}$ = 4.0 Hz, H-5), 3.20 (s, 0.6 H, OH), 0.25 and 0.23 (2 s, 9 H, $SiMe_3$).

4-Azido-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-1-*C*-(trimethylsilyl)-D-*manno*-oct-1-yn-3-ulopyranose (18). Treatment of **15** (3.64 g, 7.71 mmol) as described for the preparation of **16** gave **18** (4.34 g, 99%) as a 1:1 mixture of anomers ~90% pure by ^{1}H NMR analysis. This product was used for the following step without further purification. ^{1}H NMR selected data: ^{1}H NMR: δ 7.41-7.17 (m, 15, 3 Ph), 4.63 and 4.57 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 3.00 (s, 0.5 H, OH). MALDI-TOF MS: 596.2 (M^+ + Na), 612.3 (M^+ + K).

3,7-Anhydro-4-azido-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-D-*glycero*-D-*gulo*-oct-1-ynitol (20). Deoxygenation of ketose **17** (1.26 g, 2.20 mmol), as described for the preparation of **19** gave, after column chromatography on silica gel (15:1 cyclohexane-AcOEt), 3,7-anhydro-4-azido-5,6,8-tri-*O*-

benzyl-1,2,4-trideoxy-1-*C*-(trimethylsilyl)-D-*glycero*-D-*gulo*-oct-1-ynitol (1.14 g, 93%) as a syrup; $[\alpha]_D$ = +6.5 (*c* 1.4, $CHCl_3$). ^1H NMR: 7.40-7.10 (m, 15 H, 3 Ph), 4.92 and 4.84 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.82 and 4.54 (2 d, 2 H, *J* = 10.5 Hz, PhCH_2), 4.64 and 4.54 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 3.94 (d, 1 H, $J_{3,4}$ = 10.0 Hz, H-3), 3.75 (dd, 1 H, $J_{7,8a}$ = 2.0, $J_{8a,8b}$ = 11.0 Hz, H-8a), 3.71 (dd, 1 H, $J_{7,8b}$ = 4.0 Hz, H-8b), 3.66 (dd, 1 H, $J_{5,6}$ = 9.0, $J_{6,7}$ = 9.5 Hz, H-6), 3.56 (dd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4), 3.42 (ddd, 1 H, H-7), 3.38 (dd, 1 H, H-5), 0.23 (s, 9 H, $SiMe_3$). Anal. Calcd. for $C_{32}H_{37}N_3O_4Si$: C, 69.15; H, 6.72; N, 7.56. Found: C, 68.99; H, 6.73; N, 7.59.

This compound (1.00 g, 1.80 mmol) was desilylated as described for the preparation of **10** to give, after column chromatography on silica gel (15:1 cyclohexane-AcOEt), **20** (0.78 g, 90%) as a syrup; $[\alpha]_D$ = -18.3 (*c* 1.8, $CHCl_3$). ^1H NMR: δ 7.43-7.18 (m, 15 H, 3 Ph), 4.93 and 4.87 (2 d, 2 H, *J* = 10.5 Hz, PhCH_2), 4.83 and 4.58 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.64 and 4.55 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 3.92 (dd, 1 H, $J_{1,3}$ = 2.2, $J_{3,4}$ = 10.0 Hz, H-3), 3.76 (dd, 1 H, $J_{7,8a}$ = 2.5, $J_{8a,8b}$ = 10.0 Hz, H-8a), 3.73 (dd, 1 H, $J_{7,8b}$ = 2.0 Hz, H-8b), 3.69 (dd, 1 H, $J_{5,6}$ = 9.0, $J_{6,7}$ = 9.0 Hz, H-6), 3.58 (dd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4), 3.46 (dd, 1 H, H-5), 3.44 (ddd, 1 H, H-7), 2.62 (d, 1 H, H-1). Anal. Calcd. for $C_{29}H_{29}N_3O_4$: C, 72.02; H, 6.06; N, 8.69. Found: C, 72.00; H, 6.04; N, 8.73.

3,7-Anhydro-4-azido-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-D-*glycero*-D-*galacto*-oct-1-ynitol (21). Deoxygenation of ketose **18** (3.30 g, 5.78 mmol) as described for the preparation of **19** gave, after column cromatography on silica gel (9:1 cyclohexane-AcOEt), a 17:1 mixture of 3,7-anhydro-4-azido-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-1-*C*-(trimethylsilyl)-D-*glycero*-D-*galacto*- and-D-*talo*-oct-1-ynitol (2.82 g, 88%) as a syrup. A sample of pure β-*C*-mannopyranoside derivative was obtained by column cromatography on silica gel with 10:1 cyclohexane-AcOEt; $[\alpha]_D$ = -36.4 (*c* 1.8, $CHCl_3$). ^1H NMR: 7.40-7.10 (m, 15 H, 3 Ph), 4.87 and 4.52 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.79 and 4.73 (2 d, 2 H, *J* = 10.5 Hz, PhCH_2), 4.65 and 4.57 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.23 (d, 1 H, $J_{3,4}$ = 1.5 Hz, H-3), 3.99 (dd, 1 H, $J_{4,5}$ = 3.5 Hz, H-4), 3.78 (dd, 1 H, $J_{5,6}$ = 9.0, $J_{6,7}$ = 9.5 Hz, H-6), 3.72 (dd, 1 H, $J_{7,8a}$ = 2.0, $J_{8a,8b}$ = 5.3 Hz, H-8a), 3.71 (dd, 1 H, $J_{7,8b}$ = 4.8 Hz, H-8b), 3.68 (dd, 1 H, H-5), 3.40 (ddd, 1 H, H-7), 0.22 (s, 9 H, $SiMe_3$). Anal. Calcd. for $C_{32}H_{37}N_3O_4Si$: C, 69.15; H, 6.72; N, 7.56. Found: C, 69.10; H, 6.79; N, 7.58.

Desilylation of the mixture of α,β-*C*-mannopyranoside derivatives (2.65 g, 4.70 mmol) as described for the preparation of **10** gave, after column cromatography on silica gel with 8:1 cyclohexane-AcOEt, first **30** (126 mg, 5%) as a syrup. Eluted second was **21** (2.14 g, 94%) as a white solid; mp 91 °C (cyclohexane); $[\alpha]_D$ = -32.8 (*c* 1.4, $CHCl_3$). ^1H NMR: δ 7.42-7.16 (m, 15 H, 3 Ph), 4.87 and 4.54 (2 d, 2 H, *J* = 10.5 Hz, PhCH_2), 4.80 and 4.74 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.65 and 4.56 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.22 (dd, 1 H, $J_{1,3}$ = 2.0, $J_{3,4}$ = 1.8 Hz, H-3), 3.96 (dd, 1 H, $J_{4,5}$ = 3.5 Hz, H-4), 3.83 (dd, 1 H, $J_{5,6}$ = 9.0, $J_{6,7}$ = 9.5 Hz, H-6), 3.73 (dd, 1 H, $J_{7,8a}$ = 2.3, $J_{8a,8b}$ = 11.0 Hz, H-8a), 3.72 (dd, 1 H, $J_{4,5}$ = 3.5 Hz, H-5), 3.71 (dd, 1 H, $J_{7,8b}$ = 4.5 Hz, H-8b), 3.42 (ddd, 1 H, H-7), 2.60 (d, 1 H, H-1). MALDI-TOF MS: 507.5 (M^+ + Na), 523.4 (M^+ + K). Anal. Calcd. for $C_{29}H_{29}N_3O_4$: C, 72.02; H, 6.06; N, 8.69. Found: C, 72.35; H, 6.18; N, 8.70.

3,7-Anhydro-4-azido-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-D-*glycero*-L-*gluco*-oct-1-ynitol (28). Desilylation of **25** (1.30 g, 2.34 mmol) as described for the preparation of **10** gave, after column chromatography on silica gel (8:1 cyclohexane-AcOEt), **28** (1.13 g, 99%) as a white solid; mp 100-103 °C (cyclohexane); $[\alpha]_D$ = +54.2 (*c* 1.1, $CHCl_3$). ^1H NMR: δ 7.45-7.23 (m, 15 H, 3 Ph), 4.90 and 4.55 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.84 (dd, 1 H, $J_{1,3}$ = 2.0, $J_{3,4}$ = 5.8 Hz, H-3), 4.79 and 4.74 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.53 and 4.44 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.14 (dd, 1 H, $J_{4,5}$ = 10.1 Hz, H-4), 4.13 (ddd, 1 H, $J_{6,7}$ = 1.0, $J_{7,8a}$ = 7.0, $J_{7,8b}$ = 6.2 Hz, H-7), 4.05 (dd, 1 H, $J_{5,6}$ = 2.6 Hz, H-6), 3.89 (dd, 1 H, H-5), 3.61 (dd, 1 H, $J_{8a,8b}$ = 9.2 Hz, H-8a), 3.57 (dd, 1 H, H-8b), 2.58 (d, 1 H, H-1). Anal. Calcd. for $C_{29}H_{29}N_3O_4$: C, 72.02; H, 6.06; N, 8.69. Found: C, 72.10; H, 6.00; N, 8.73.

3,7-Anhydro-4-azido-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-D-*glycero*-D-*ido*-oct-1-ynitol (29). Desilylation of **26** (556 mg, 1.04 mmol) as described for the preparation of **10** gave, after column chromatography on silica gel (12:1 cyclohexane-AcOEt), syrupy **29** (502 mg, 99%); $[\alpha]_D$ = +23.0 (*c* 2.0, $CHCl_3$). ^1H NMR: δ 7.41-7.18 (m, 15 H, 3 Ph), 4.93 (s, 2 H, PhCH_2), 4.85 (dd, 1 H, $J_{1,3}$ = 2.0, $J_{3,4}$ = 5.5 Hz, H-3), 4.82 and 4.56 (2 d, 2 H, *J* = 10.5 Hz, PhCH_2), 4.65 and 4.53 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.03 (ddd, 1 H, $J_{6,7}$ = 9.5, $J_{7,8a}$ = 3.5, $J_{7,8b}$ = 2.0 Hz, H-7), 3.94 (dd, 1 H, $J_{4,5}$ = 10.0, $J_{5,6}$ = 9.0 Hz, H-5), 3.80 (d, 1 H, $J_{8a,8b}$ = 11.0 Hz, H-8a), 3.74 (dd, 1 H, H-6), 3.71 (dd, 1 H, H-8b), 3.68 (dd, 1 H, H-4), 2.64 (d, 1 H, H-1). Anal. Calcd. for $C_{29}H_{29}N_3O_4$: C, 72.02; H, 6.06; N, 8.69. Found: C, 72.00; H, 6.10; N, 8.58.

3,7-Anhydro-4-azido-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-D-*glycero*-D-*talo*-oct-1-ynitol (30). Desilylation of **27** (281 mg, 0.51 mmol) as described for the preparation of **10** gave, after column chromatography on silica gel (10:1 cyclohexane-AcOEt), syrupy **30** (246 mg, 99%); $[\alpha]_D$ = +40.7 (*c* 1.1, $CHCl_3$). ^1H NMR: δ 7.43-7.17 (m, 15 H, 3 Ph), 4.86 and 4.53 (2 d, 2 H, *J* = 10.5 Hz, PhCH_2), 4.78 (s, 2 H, PhCH_2), 4.75 (dd, 1 H, $J_{1,3}$ = 2.5, $J_{3,4}$ = 2.0 Hz, H-3), 4.68 and 4.54 (2 d, 2 H, *J* = 12.5 Hz, PhCH_2), 4.20 (dd, 1 H, $J_{4,5}$ = 4.5, $J_{5,6}$ = 8.5 Hz, H-5), 3.97 (dd, 1 H, H-4), 3.96 (ddd, 1 H, $J_{6,7}$ = 9.5, $J_{7,8a}$ = 4.0, $J_{7,8b}$ = 2.0 Hz, H-7), 3.90 (dd, 1 H, H-6), 3.77 (dd, 1 H, $J_{8a,8b}$ = 11.0 Hz, H-8a), 3.70 (dd, 1 H, H-8b), 2.58 (d, 1 H, H-1). Anal. Calcd. for $C_{29}H_{29}N_3O_4$: C, 72.02; H, 6.06; N, 8.69. Found: C, 72.10; H, 6.00; N, 8.73.

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,4,5-trideoxy-1,2-*N*,*O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*arabino*-D-*manno*- and -D-*altro*-undec-4-ynitol (36). The *C*-glucoside **2** (1.10 g, 2.00 mmol) was treated with butyllithium (1.37 mL, 2.19 mmol, of a 1.6 M solution in hexane) and the aldehyde **34** (0.60 g, 2.60 mmol) as described for the preparation of **35**. The residue was eluted from a column of silica gel with cyclohexane-AcOEt (from 5:1 to 3:1) to afford first unreacted **2** (0.11 g, 10%). Eluted second was syrupy **36** as a ~10:1 mixture of diastereomers (1.07 g, 68%). ^1H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.38-7.18 (m, 20 H, 4 Ph), 5.30 (d, 1 H, *J* = 6.0 Hz, OH), 4.98 and 4.78 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.83 and 4.76 (2

d, 2 H, J = 11.5 Hz, PhCH_2), 4.74 and 4.58 (2 d, 2 H, J = 11.0 Hz, PhCH_2), 4.56 and 4.50 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.17 (dd, 1 H, $J_{3,6}$ = 1.8, $J_{6,7}$ = 9.3 Hz, H-6), 4.06 (dd, 1 H, $J_{1a,1b}$ = 12.5, $J_{1a,2}$ = 5.5 Hz, H-1a), 3.91 (dd, 1 H, $J_{1b,2}$ = 6.5 Hz, H-1b), 3.71 (dd, 1 H, $J_{10,11a}$ = 1.8, $J_{11a,11b}$ = 11.0 Hz, H-11a), 3.64 (dd, 1 H, $J_{10,11b}$ = 4.5 Hz, H-11b), 1.48 and 1.42 (2 s, 6 H, 2 Me), 1.44 (s, 9 H, *t*-Bu). MALDI-TOF MS: 802.2 (M^+ + Na), 818.3 (M^+ + K). Anal. Calcd. For $C_{47}H_{55}NO_9$: C, 72.56; H, 7.13; N, 1.80. Found: C, 72.60; H, 7.20; N, 1.75.

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,4,5-trideoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*arabino*-L-*galacto*- and -L-*gulo*-undec-4-ynitol (37). The *C*-mannoside **3** (616 mg, 1.12 mmol) was treated with butyllithium (0.77 mL, 1.23 mmol, of a 1.6 M solution in hexane) and the aldehyde **34** (419 mg, 1.83 mmol) as described for the preparation of **28**. The residue was eluted from a column of silica gel with cyclohexane-AcOEt (from 6:1 to 3:1) to afford first unreacted **3** (215 mg, 35%). Eluted second was syrupy **37** as a ~6:1 mixture of diastereomers (479 mg, 55%). ^{1}H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.48-7.20 (m, 20 H, 4 Ph), 4.93 and 4.84 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.73 and 4.62 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.57 and 4.89 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.38 (dd, 1 H, $J_{3,6}$ = 1.0, $J_{6,7}$ = 3.0 Hz, H-6), 3.68 (dd, 1 H, $J_{10,11a}$ = 2.3, $J_{11a,11b}$ = 11.0 Hz, H-11a), 3.65 (dd, 1 H, $J_{10,11b}$ = 4.5 Hz, H-11b), 1.50 and 1.43 (2 s, 6 H, 2 Me), 1.42 (s, 9 H, *t*-Bu). MALDI-TOF MS: 802.3 (M^+ + Na), 818.3 (M^+ + K). Anal. Calcd. for $C_{47}H_{55}NO_9$: C, 72.56; H, 7.13; N, 1.80. Found: C, 72.50; H, 7.15; N, 1.83.

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,4,5-trideoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*lyxo*-D-*ido*- and -D-*talo*-undec-4-ynitol (38). The *C*-galactoside **10** (240 mg, 0.44 mmol) was treated with butyllithium (0.30 mL, 0.48 mmol, of a 1.6 M solution in hexane) and the aldehyde **34** (380 mg, 1.66 mmol) as described for the preparation of **35**. The residue was eluted from a column of silica gel with cyclohexane-AcOEt (from 10:1 to 5:1) to afford first unreacted **10** (96 mg, 40%). Eluted second was syrupy **38** as a ~1:1 mixture of diastereomers (198 mg, 58%). ^{1}H NMR (DMSO-d6, 120 °C) selected data: δ 7.41-7.25 (m, 20 H, 4 Ph), 5.21-5.18 (m, 1 H, OH), 4.90-4.42 (m, 10 H), 4.20-3.83 (m, 9 H), 1.50 and 1.49 (2 s, 6 H, 2 Me), 1.42 (s, 9 H, *t*-Bu). MALDI-TOF MS: 802.8 (M^+ + Na), 818.2 (M^+ + K). Anal. Calcd. for $C_{47}H_{55}NO_9$: C, 72.56; H, 7.13; N, 1.80. Found: C, 72.40; H, 7.30; N, 1.69.

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,4,5-trideoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*arabino*-D-*ido*- and -D-*talo*-undec-4-ynitol (39). The *C*-glucoside **11** (745 mg, 1.36 mmol) was treated with butyllithium (0.94 mL, 1.50 mmol, of a 1.6 M solution in hexane) and the aldehyde **34** (0.93 g, 4.04 mmol) as described for the preparation of **35**. The residue was eluted from a column of silica gel with cyclohexane-AcOEt (from 5:1 to 3:1) to afford first unreacted **11** (260 mg, 35%). Eluted second was syrupy **39** as a ~10:1 mixture of diastereomers (720 mg, 68%). ^{1}H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.40-7.20 (m, 20 H, 4 Ph), 5.27-5.25 (m, 1 H, OH), 4.96 (dd, 1 H, $J_{3,6}$ = 1.5, $J_{6,7}$ = 5.5 Hz, H-6), 4.88 and 4.75 (2 d,

2 H, J = 11.5 Hz, PhCH_2), 4.77 and 4.58 (2 d, 2 H, J = 11.0 Hz, PhCH_2), 4.72 and 4.64 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.54 and 4.48 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.13 (dd, 1 H, $J_{1a,1b}$ = 12.0, $J_{1a,2}$ = 7.0 Hz, H-1a), 3.95-3.89 (m, 3 H, H-1b, H-2, H-10), 3.84 (dd, 1 H, $J_{7,8}$ = 9.3, $J_{8,9}$ = 9.3 Hz, H-8), 3.61 (dd, 1 H, H-7), 3.46 (dd, 1 H, $J_{9,10}$ = 9.5 Hz, H-9), 1.51 and 1.46 (2 s, 6 H, 2 Me), 1.44 (s, 9 H, *t*-Bu). MALDI-TOF MS: 802.3 (M^+ + Na), 818.4 (M^+ + K). Anal. Calcd. for $C_{47}H_{55}NO_9$: C, 72.56; H, 7.13; N, 1.80. Found: C, 72.43; H, 7.20; N, 1.83.

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,4,5-trideoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*arabino*-L-*gluco*- and -L-*allo*-undec-4-ynitol (40). The *C*-mannoside **12** (671 mg, 1.22 mmol) was treated with butyllithium (0.84 mL, 1.34 mmol, of a 1.6 M solution in hexane) and the aldehyde **34** (419 mg, 1.83 mmol) as described for the preparation of **35**. The residue was eluted from a column of silica gel with cyclohexane-AcOEt (from 6:1 to 3:1) to afford first unreacted **12** (309 mg, 46%). Eluted second was syrupy **40** as a ~1:1 mixture of diastereomers (426 mg, 45%). ^{1}H NMR (DMSO-d6, 120 °C) selected data of one isomer: δ 7.40-7.20 (m, 20 H, 4 Ph), 5.29 (d, 1 H, J = 6.3 Hz, OH), 4.84 (dd, 1 H, $J_{3,6}$ = $J_{6,7}$ = 2.0 Hz, H-6), 4.78 and 4.67 (2 d, 2 H, J = 11.3 Hz, PhCH_2), 4.66 (s, 2 H, PhCH_2), 4.64 and 4.48 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.01 (dd, 1 H, $J_{1a,1b}$ = 8.5, $J_{1a,2}$ = 3.0 Hz, H-1a), 3.81 (dd, 1 H, $J_{8,9}$ = 9.5, $J_{9,10}$ = 9.0 Hz, H-9), 3.72 (dd, 1 H, $J_{10,11a}$ = 4.0, $J_{11a,11b}$ = 11.0 Hz, H-11a), 3.68 (dd, 1 H, $J_{10,11b}$ = 2.5 Hz, H-11b), 1.52 and 1.45 (2 s, 6 H, 2 Me), 1.44 (s, 9 H, *t*-Bu). MALDI-TOF MS: 802.4 (M^+ + Na), 818.4 (M^+ + K). Anal. Calcd. for $C_{47}H_{55}NO_9$: C, 72.56; H, 7.13; N, 1.80. Found: C, 72.48; H, 7.20; N, 1.89.

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,3,4,5-tetradeoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-undecitol (42). The alkyne **36** (475 mg, 0.61 mmol) was hydrogenated as described for the preparation of **3-hydroxy-41** to give, after column chromatography on silica gel (2.5:1 cyclohexane-AcOEt), syrupy **3-hydroxy-42** (410 mg, 86%) as a ~10:1 mixture of diastereomers. ^{1}H NMR (DMSO-d6, 140 °C) selected data of the main isomer: δ 7.38-7.22 (m, 20 H, 4 Ph), 4.82 (s, 2 H, PhCH_2), 4.79 and 4.62 (2 d, 2 H, J = 10.7 Hz, PhCH_2), 4.75 and 4.69 (2 d, 2 H, J = 11.3 Hz, PhCH_2), 4.57 and 4.52 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.00 (dd, 1 H, $J_{1a,1b}$ = 8.5, $J_{1a,2}$ = 2.3 Hz, H-1a), 3.83 (dd, 1 H, $J_{1b,2}$ = 6.0 Hz, H-1b), 3.75 (dd, 1 H, $J_{2,3}$ = 5.3 Hz, H-2), 3.71 (m, 2 H), 3.68 (dd, 1 H, $J_{10,11a}$ = 2.0, $J_{11a,11b}$ = 11.0 Hz, H-11a), 3.65 (dd, 1 H, $J_{10,11b}$ = 4.0 Hz, H-11b), 3.51 (dd, 1 H), 3.46 (ddd, 1 H, $J_{9,10}$ = 9.5 Hz, H-10), 3.32-3.26 (m, 2 H), 2.80 (m, 1 H, OH), 1.92 and 1.42 (2 s, 6 H, 2 Me), 1.41 (s, 9 H, *t*-Bu). MALDI-TOF MS: 806.2 (M^+ + Na), 822.0 (M^+ + K). Anal. Calcd. For $C_{47}H_{59}NO_9$: C, 72.19; H, 7.61; N, 1.79. Found: C, 72.23; H, 7.56; N, 1.83.

The alcohol **3-hydroxy-42** (300 mg, 0.38 mmol) was deoxygenated as described for the preparation of **41** to give, after column chromatography on silica gel (10:1 cyclohexane-AcOEt), **42** (185 mg, 63%) as a syrup; $[\alpha]_D$ = +6.1 (*c* 0.9, $CHCl_3$); lit.[15d] $[\alpha]_D$ = +6.2 (*c* 1.0, $CHCl_3$). The ^{1}H NMR spectrum of compound **42** was identical to that of the product prepared by another route.[15d]

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,3,4,5-tetradeoxy-1,2-*N*,*O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*gluco*-undecitol (43). The alkyne **37** (394 mg, 0.51 mmol) was hydrogenated as described for the preparation of **3-hydroxy-41** to give, after column chromatography on silica gel (3:1 cyclohexane-AcOEt), syrupy **3-hydroxy-43** (378 mg, 95%) as a ~6:1 mixture of diastereomers. ^{1}H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.48-7.20 (m, 20 H, 4 Ph), 5.26-5.24 (m, 1 H, OH), 4.92 and 4.81 (2 d, 2 H, J = 11.0 Hz, PhCH_2), 4.75 and 4.52 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.72 (s, 2 H, PhCH_2), 4.53 and 4.48 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 3.72 (dd, 1 H, $J_{10,11a}$ = 2.5, $J_{11a,11b}$ = 11.0 Hz, H-11a), 3.70 (dd, 1 H, $J_{10,11b}$ = 4.5 Hz, H-11b), 1.50 and 1.43 (2 s, 6 H, 2 Me), 1.41 (s, 9 H, *t*-Bu). MALDI-TOF MS: 806.3 (M^+ + Na), 822.6 (M^+ + K). Anal. Calcd. for $C_{47}H_{59}NO_9$: C, 72.19; H, 7.61; N, 1.79. Found: C, 72.10; H, 7.55; N, 1.85.

The alcohol **3-hydroxy-43** (180 mg, 0.23 mmol) was deoxygenated as described for the preparation of **41** to give, after column chromatography on silica gel (from 20:1 to 4:1 cyclohexane-AcOEt), **43** (139 mg, 79%) as a syrup; $[\alpha]_D$ = +7.3 (*c* 1.5, $CHCl_3$); lit.[15d] $[\alpha]_D$ = +7.1 (*c* 1.0, $CHCl_3$). The ^{1}H NMR spectrum of compound **43** was identical to that of the product prepared by another route.[15d]

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,3,4,5-tetradeoxy-1,2-*N*,*O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*threo*-L-*gulo*-undecitol (44). The alkyne **38** (195 mg, 0.25 mmol) was hydrogenated as described for the preparation of **3-hydroxy-41** to give, after column chromatography on silica gel (4:1 cyclohexane-AcOEt), syrupy **3-hydroxy-44** (168 mg, 86%) as a ~1:1 mixture of diastereomers. ^{1}H NMR (DMSO-d6, 60 °C) selected data: δ 7.41-7.24 (m, 20 H, 4 Ph), 4.78 and 4.58 (2 d, 2 H, J = 11.8 Hz, PhCH_2), 4.72 and 4.66 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.66 and 4.59 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.55 and 4.47 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 3.90 (dd, 1 H, $J_{8,9}$ = 3.0, $J_{9,10}$ = 0.5 Hz, H-9), 3.87 (ddd, 1 H, $J_{10,11a}$ = 7.5, $J_{10,11b}$ = 4.5 Hz, H-10), 3.82 (dd, 1 H, $J_{11a,11b}$ = 10.5 Hz, H-11a), 3.73 (dd, 1 H, $J_{7,8}$ = 7.5 Hz, H-8), 3.60 (dd, 1 H, H-11b), 1.59 and 1.56 (2 s, 6 H, 2 Me), 1.49 (s, 9 H, *t*-Bu). MALDI-TOF MS: 806.2 (M^+ + Na), 821.7 (M^+ + K). Anal. Calcd. for $C_{47}H_{59}NO_9$: C, 72.19; H, 7.61; N, 1.79. Found: C, 72.10; H, 7.72; N, 1.74.

The alcohol **3-hydroxy-44** (100 mg, 0.13 mmol) was deoxygenated as described for the preparation of **41** to give, after column chromatography on silica gel (from 20:1 to 4:1 cyclohexane-AcOEt), **44** (71 mg, 73%) as a syrup; $[\alpha]_D$ = +33.9 (*c* 0.5, $CHCl_3$). ^{1}H NMR (DMSO-d6, 120 °C) selected data: δ 7.39-7.25 (m, 20 H, 4 Ph), 4.72 and 4.59 (2 d, 2 H, J = 10.5 Hz, PhCH_2), 4.70 (s, 2 H, PhCH_2), 4.63 and 4.59 (2 d, 2 H, J = 10.7 Hz, PhCH_2), 4.52 and 4.42 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 3.99 (dd, 1 H, $J_{8,9}$ = 3.0, $J_{9,10}$ = 0.5 Hz, H-9), 3.79 (ddd, 1 H, $J_{10,11a}$ = 4.0, $J_{10,11b}$ = 7.0 Hz, H-10), 3.67 (dd, 1 H, $J_{11a,11b}$ = 11.0 Hz, H-11a), 3.64 (dd, 1 H, H-11b), 1.48 and 1.44 (2 s, 6 H, 2 Me), 1.43 (s, 9 H, *t*-Bu). MALDI-TOF MS: 789.6 (M^+ + Na), 805.6 (M^+ + K). Anal. Calcd. for $C_{47}H_{59}NO_8$: C, 73.70; H, 7.76; N, 1.83. Found: C, 73.80; H, 7.65; N, 1.77.

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,3,4,5-tetradeoxy-1,2-*N*,*O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*gulo*-undecitol (45). The alkyne **39** (640 mg, 0.80 mmol) was

hydrogenated as described for the preparation of **3-hydroxy-41** to give, after column chromatography on silica gel (7:3 cyclohexane-AcOEt), syrupy **3-hydroxy-45** (539 mg, 86%) as a ~10:1 mixture of diastereomers. ^{1}H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.40-7.20 (m, 20 H, 4 Ph), 4.83 and 4.73 (2 d, 2 H, J = 11.0 Hz, PhCH_2), 4.73 and 4.56 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.65 (s, 2 H, PhCH_2), 4.54 and 4.48 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 3.48 (dd, 1 H, $J_{8,9} = J_{9,10}$ = 9.2 Hz, H-9), 1.49 and 1.45 (2 s, 6 H, 2 Me), 1.43 (s, 9 H, *t*-Bu). MALDI-TOF MS: 806.4 (M^+ + Na), 821.9 (M^+ + K). Anal. Calcd. for $C_{47}H_{59}NO_9$: C, 72.19; H, 7.61; N, 1.79. Found: C, 72.20; H, 7.68; N, 1.82.

The alcohol **3-hydroxy-45** (447 mg, 0.57 mmol) was deoxygenated as described for the preparation of **41** to give, after column chromatography on silica gel (from 10:1 to 5:1 cyclohexane-AcOEt), **45** (349 mg, 80%) as a syrup; $[\alpha]_D$ = +37.1 (*c* 1.7, $CHCl_3$). ^{1}H NMR (DMSO-d6, 120 °C): δ 7.40-7.22 (m, 20 H, 4 Ph), 4.83 and 4.73 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.74 and 4.56 (2 d, 2 H, J = 10.7 Hz, PhCH_2), 4.67 and 4.62 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.54 and 4.49 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 3.99 (ddd, 1 H, $J_{5a,6}$ = 9.0, $J_{5b,6} = J_{6,7}$ = 5.0 Hz, H-6), 3.88 (dd, 1 H, $J_{1a,1b}$ = 9.0, $J_{1a,2}$ = 2.5 Hz, H-1a), 3.79 (dd, 1 H, $J_{7,8}$ = 8.5, $J_{8,9}$ = 8.0 Hz, H-8), 3.79-3.74 (m, 1 H, H-2), 3.68-3.60 (m, 5 H), 3.45 (dd, 1 H, $J_{8,9} = J_{9,10}$ = 8.0 Hz, H-9), 1.80-1.54 (m, 6 H), 1.50 and 1.43 (2 s, 6 H, 2 Me), 1.44 (s, 9 H, *t*-Bu). MALDI-TOF MS: 789.9 (M^+ + Na), 805.8 (M^+ + K). Anal. Calcd. for $C_{47}H_{59}NO_8$: C, 73.70; H, 7.76; N, 1.83. Found: C, 73.85; H, 7.75; N, 1.78.

6,10-Anhydro-7,8,9,11-tetra-*O*-benzyl-2,3,4,5-tetradeoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*allo*-undecitol (46). The alkyne **40** (382 mg, 0.49 mmol) was hydrogenated as described for the preparation of **3-hydroxy-41** to give, after column chromatography on silica gel (2:1 cyclohexane-AcOEt), syrupy **3-hydroxy-46** (355 mg, 93%) as a ~1:1 mixture of diastereomers. ^{1}H NMR (DMSO-d6, 120 °C) selected data: δ 7.40-7.20 (m, 20 H, 4 Ph), 5.20 (d, 1 H, J = 6.3 Hz, OH), 4.71 and 4.68 (2 d, 2 H, J = 11.0 Hz, PhCH_2), 4.65 and 4.54 (2 d, 2 H, J = 11.0 Hz, PhCH_2), 4.60 and 4.55 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.52 and 4.48 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.20 (dd, 1 H, $J_{10,11a}$ = 4.0, $J_{11a,11b}$ = 10.7 Hz, H-11a), 4.22 (dd, 1 H, $J_{10,11b}$ = 2.7 Hz, H-11b), 1.48 and 1.25 (2 s, 6 H, 2 Me), 1.24 (s, 9 H, *t*-Bu). MALDI-TOF MS: 806.4 (M^+ + Na), 822.3 (M^+ + K). Anal. Calcd. for $C_{47}H_{59}NO_9$: C, 72.19; H, 7.61; N, 1.79. Found: C, 72.19; H, 7.65; N, 1.73.

The alcohol **3-hydroxy-46** (226 mg, 0.29 mmol) was deoxygenated as described for the preparation of **41** to give, after column chromatography on silica gel (from 20:1 to 2:1 cyclohexane-AcOEt), **46** (176 mg, 80%) as a syrup; $[\alpha]_D$ = + 13.2 (*c* 2.1, $CHCl_3$). ^{1}H NMR (DMSO-d6, 120 °C) selected data: δ 7.40-7.20 (m, 20 H, 4 Ph), 4.68 and 4.56 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.64-4.59 (m, 3 H), 4.58 (s, 2 H, PhCH_2), 3.92-3.63 (m, 9 H), 1.72-1.51 (m, 6 H), 1.49 and 1.24 (2 s, 6 H, 2 Me), 1.23 (s, 9 H, *t*-Bu). MALDI-TOF MS: 790.4 (M^+ + Na), 806.3 (M^+ + K). Anal. Calcd. for $C_{47}H_{59}NO_8$: C, 73.70; H, 7.76; N, 1.83. Found: C, 73.75; H, 7.69; N, 1.88.

4-Acetamido-3,7-anhydro-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-D-*glycero*-D-*gulo*-oct-1-ynitol (58). Treatment of **20** (596 mg, 1.23 mmol) as described for the preparation of **57** gave, after column cromatography on silica gel (20:1 CH_2Cl_2-acetone), **58** (536 mg, 87%) as a white solid; mp 198-199 °C (cyclohexane-AcOEt); $[\alpha]_D$ = +43.0 (*c* 1.0, $CHCl_3$). ^1H NMR: δ 7.40-7.18 (m, 15 H, 3 Ph), 5.37 (d, 1 H, $J_{4,NH}$ = 8.0 Hz, NH), 4.88 and 4.67 (2 d, 2 H, *J* = 11.5 Hz, PhCH_2), 4.82 and 4.59 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.65 and 4.56 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.44 (dd, 1 H, $J_{1,3}$ = 2.0, $J_{3,4}$ = 10.2 Hz, H-3), 3.96 (dd, 1 H, $J_{5,6}$ = 9.0, $J_{6,7}$ = 10.0 Hz, H-6), 3.77 (dd, 1 H, $J_{7,8a}$ = 2.5, $J_{8a,8b}$ = 10.5 Hz, H-8a), 3.74 (dd, 1 H, $J_{7,8b}$ = 2.5 Hz, H-8b), 3.70 (ddd, 1 H, $J_{4,5}$ = 9.0 Hz, H-4), 3.68 (dd, 1 H, H-5), 3.53 (ddd, 1 H, H-7), 2.46 (d, 1 H, H-1), 1.88 (s, 3 H, Ac). MALDI-TOF MS: 523.5 (M^+ + Na), 539.7 (M^+ + K). Anal. Calcd. for $C_{31}H_{33}NO_5$: C, 74.51; H, 6.67; N, 2.80. Found: C, 74.44; H, 6.69; N, 2.73.

4-Acetamido-3,7-anhydro-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-D-*glycero*-D-*galacto*-oct-1-ynitol (59). Treatment of **21** (380 mg, 0.78 mmol) as described for the preparation of **57** gave, after column cromatography on silica gel (1:1 cyclohexane-AcOEt), **59** (366 mg, 93%) as a syrup; $[\alpha]_D$ = -44.5 (*c* 1.5, $CHCl_3$). ^1H NMR: δ 7.42-7.18 (m, 15 H, 3 Ph), 5.89 (d, 1 H, $J_{4,NH}$ = 10.0 Hz, NH), 4.93 (ddd, 1 H, $J_{3,4}$ = $J_{4,5}$ = 2.5 Hz, H-4), 4.92 and 4.50 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.91 and 4.47 (2 d, 2 H, *J* = 10.5 Hz, PhCH_2), 4.63 and 4.54 (2 d, 2 H, *J* = 11.8 Hz, PhCH_2), 4.29 (dd, 1 H, $J_{1,3}$ = 2.3 Hz, H-3), 3.77-3.72 (m, 3 H), 3.69 (dd, 1 H, $J_{5,6}$ = 8.5, $J_{6,7}$ = 9.0 Hz, H-6), 3.48-3.42 (m, 1 H, H-7), 2.51 (d, 1 H, H-1), 2.12 (s, 3 H, Ac). Anal. Calcd. for $C_{31}H_{33}NO_5$: C, 74.51; H, 6.67; N, 2.80. Found: C, 74.59; H, 6.71; N, 2.71.

4-Acetamido-3,7-anhydro-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-D-*glycero*-L-*gluco*-oct-1-ynitol (60). Treatment of **28** (1.00 g, 2.07 mmol) as described for the preparation of **57** gave, after column cromatography on silica gel (1:1 cyclohexane-AcOEt), **60** (0.94 g, 91%) as a white solid; mp 143-145 °C (cyclohexane); $[\alpha]_D$ = +95.9 (*c* 0.9, $CHCl_3$). ^1H NMR: δ 7.40-7.22 (m, 15 H, 3 Ph), 5.06 (d, 1 H, $J_{4,NH}$ = 8.0 Hz, NH), 5.04 (dd, 1 H, $J_{1,3}$ = 2.0, $J_{3,4}$ = 5.5 Hz, H-3), 4.93 and 4.61 (2 d, 2 H, *J* = 11.5 Hz, PhCH_2), 4.77 and 4.43 (2 d, 2 H, *J* = 12.3 Hz, PhCH_2), 4.60 (ddd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4), 4.53 and 4.46 (2 d, 2 H, *J* = 11.5 Hz, PhCH_2), 4.16-4.06 (m, 2 H), 3.69-3.57 (m, 3 H), 2.41 (d, 1 H, H-1), 1.90 (s, 3 H, Ac). MALDI-TOF MS: 523.5 (M^+ + Na), 539.8 (M^+ + K). Anal. Calcd. for $C_{31}H_{33}NO_5$: C, 74.51; H, 6.67; N, 2.80. Found: C, 74.49; H, 6.63; N, 2.83.

4-Acetamido-3,7-anhydro-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-D-*glycero*-D-*ido*-oct-1-ynitol (61). Treatment of **29** (469 mg, 0.96 mmol) as described for the preparation of **57** gave, after column cromatography on silica gel (1:1 cyclohexane-AcOEt), **61** (407 g, 85%) as a white solid; mp 109 °C (cyclohexane); $[\alpha]_D$ = +110.9 (*c* 1.2, $CHCl_3$). ^1H NMR: δ 7.43-7.22 (m, 15 H, 3 Ph), 4.97 (d, 1 H, $J_{4,NH}$ = 8.5 Hz, NH), 4.90 and 4.67 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.89 (dd, 1 H, $J_{1,3}$ = 2.0, $J_{3,4}$ = 5.5 Hz, H-3), 4.83 and 4.60 (2 d, 2 H, *J* = 10.8 Hz, PhCH_2), 4.67 and 4.56 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.20 (ddd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4), 3.98 (ddd, 1 H, $J_{6,7}$ = 9.5, $J_{7,8a}$ = 4.0, $J_{7,8b}$ = 2.0 Hz,

H-7), 3.81 (dd, 1 H, $J_{8a,8b}$ = 11.0 Hz, H-8a), 3.79-3.71 (m, 2 H), 3.71 (dd, 1 H, H-8b), 2.51 (dd, 1 H, H-1), 1.79 (s, 3 H, Ac). MALDI-TOF MS: 523.5 (M^+ + Na), 539.8 (M^+ + K). Anal. Calcd. for $C_{31}H_{33}NO_5$: C, 74.51; H, 6.67; N, 2.80. Found: C, 74.49; H, 6.63; N, 2.83.

4-Acetamido-3,7-anhydro-5,6,8-tri-*O*-benzyl-1,2,4-trideoxy-D-*glycero*-D-*talo*-oct-1-ynitol (62). Treatment of **30** (150 mg, 0.31 mmol) as described for the preparation of **57** gave, after column cromatography on silica gel (1:1 cyclohexane-AcOEt), **62** (139 mg, 90%) as a syrup; $[\alpha]_D$ = +28.8 (*c* 1.2, $CHCl_3$). ^1H NMR: δ 7.40-7.18 (m, 15 H, 3 Ph), 5.98 (d, 1 H, $J_{4,NH}$ = 8.5 Hz, NH), 4.89 and 4.53 (2 d, 2 H, *J* = 10.6 Hz, PhCH_2), 4.82 (dd, 1 H, $J_{1,3}$ = 2.3, $J_{3,4}$ = 2.0 Hz, H-3), 4.78 and 4.48 (2 d, 2 H, *J* = 10.9 Hz, PhCH_2), 4.76 (ddd, 1 H, $J_{4,5}$ = 4.5 Hz, H-4), 4.66 and 4.50 (2 d, 2 H, *J* = 11.8 Hz, PhCH_2), 4.21 (dd, 1 H, $J_{5,6}$ = 9.5 Hz, H-5), 4.01 (ddd, 1 H, $J_{6,7}$ = 9.5, $J_{7,8a}$ = 3.2, $J_{7,8b}$ = 2.0 Hz, H-7), 3.84 (dd, 1 H, $J_{8a,8b}$ = 10.6 Hz, H-8a), 3.72 (dd, 1 H, H-6), 3.70 (dd, 1 H, H-8b), 2.61 (d, 1 H, H-1), 2.04 (s, 3 H, Ac). MALDI-TOF MS: 523.6 (M^+ + Na), 539.7 (M^+ + K). Anal. Calcd. for $C_{31}H_{33}NO_5$: C, 74.51; H, 6.67; N, 2.80. Found: C, 74.56; H, 6.70; N, 2.70.

7-Acetamido-6,10-anhydro-8,9,11-tri-*O*-benzyl-2,4,5,7-tetradeoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*arabino*-D-*manno*- and -D-*altro*-undec-4-ynitol (64). The *C*-glucoside **58** (421 mg, 0.84 mmol) was treated with the aldehyde **34** (580 mg, 2.53 mmol) as described for the preparation of **63**. The residue was eluted from a column of silica gel with CH_2Cl_2-acetone (from 9:1 to 5:1) to afford first unreacted **58** (42 mg, 10%). Eluted second was syrupy **64** as a ~5:1 mixture of diastereomers (538 mg, 88%). ^1H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.55-7.48 (m, 1 H, OH), 7.38-7.20 (m, 15 H, 3 Ph), 5.00-4.90 (m, 1 H, NH), 4.74 and 4.57 (2 d, 2 H, *J* = 11.5 Hz, PhCH_2), 4.70 (s, 2 H, PhCH_2), 4.68-4.65 (m, 1 H, H-3), 4.57 and 4.50 (2 d, 2 H, *J* = 11.5 Hz, PhCH_2), 4.20 (dd, 1 H, $J_{3,6}$ = 1.5, $J_{6,7}$ = 9.5 Hz, H-6), 4.06 (dd, 1 H, $J_{1a,1b}$ = 8.5, $J_{1a,2}$ = 3.5 Hz, H-1a), 3.95 (dd, 1 H, $J_{1b,2}$ = 7.0 Hz, H-1b), 3.90-3.84 (m, 1 H, H-2), 1.85 (s, 3 H, Ac), 1.44 (s, 9 H, *t*-Bu). MALDI-TOF MS: 752.8 (M^+ + Na), 768.9 (M^+ + K). Anal. Calcd. for $C_{42}H_{52}N_2O_9$: C, 69.21; H, 7.19; N, 3.84. Found: C, 69.19; H, 7.24; N, 3.90.

7-Acetamido-6,10-anhydro-8,9,11-tri-*O*-benzyl-2,4,5,7-tetradeoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*arabino*-L-*galacto*- and -L-*gulo*-undec-4-ynitol (65). The *C*-mannoside **59** (400 mg, 0.80 mmol) was treated with the aldehyde **34** (550 mg, 2.40 mmol) as described for the preparation of **63**. The residue was eluted from a column of silica gel with AcOEt-cyclohexane (from 1:1 to 3:1) to afford first unreacted **59** (44 mg, 11%). Eluted second was syrupy **65** as a ~8:1 mixture of diastereomers (512 mg, 88%). ^1H NMR (DMSO-d6, 120 °C) data of the main isomer: δ 7.38-7.18 (m, 15 H, 3 Ph), 5.08 (d, 1 H, $J_{7,NH}$ = 6.0 Hz, NH), 4.77 and 4.46 (2 d, 2 H, *J* = 11.5 Hz, PhCH_2), 4.72 and 4.45 (2 d, 2 H, *J* = 11.5 Hz, PhCH_2), 4.71-4.64 (m, 2 H), 4.55 and 4.50 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.44 (dd, 1 H, $J_{3,6}$ = 2.0, $J_{6,7}$ = 3.5 Hz, H-6), 4.06 (dd, 1 H, $J_{1a,1b}$ = 9.0, $J_{1a,2}$ = 3.5 Hz, H-1a), 3.97 (dd, 1 H, $J_{1b,2}$ = 7.0 Hz, H-1b), 3.86 (ddd, 1 H, $J_{2,3}$ = 9.0

Hz, H-2), 3.79 (ddd, 1 H, $J_{7,8}$ = 4.5 Hz, H-7), 3.72 (dd, 1 H, $J_{10,11a}$ = 2.0, $J_{11a,11b}$ = 11.0 Hz, H-11a), 3.70 (dd, 1 H, $J_{8,9}$ = 9.0 Hz, H-8), 3.65 (dd, 1 H, $J_{10,11b}$ = 5.3 Hz, H-11b), 3.54 (dd, 1 H, $J_{9,10}$ = 9.5 Hz, H-9), 3.52 (ddd, 1 H, H-10), 1.98 (s, 3 H, Ac), 1.49 and 1.45 (2 s, 6 H, 2 Me), 1, 44 (s, 9 H, *t*-Bu). MALDI-TOF MS: 753.3 (M^+ + Na), 769.6 (M^+ + K). Anal. Calcd. for $C_{42}H_{52}N_2O_9$: C, 69.21; H, 7.19; N, 3.84. Found: C, 69.32; H, 7.23; N, 3.79.

7-Acetamido-6,10-anhydro-8,9,11-tri-*O*-benzyl-2,4,5,7-tetradeoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*lyxo*-D-*ido*- and -D-*talo*-undec-4-ynitol (66). The *C*-galactoside **60** (1.00 g, 2.07 mmol) was treated with the aldehyde **34** (1.42 g, 6.21 mmol) as described for the preparation of **63**. The residue was eluted from a column of silica gel with cyclohexane-AcOEt (from 1.5:1 to 1:1) to afford first unreacted **60** (430 mg, 43%). Eluted second was syrupy **66** as a ~20:1 mixture of diastereomers (783 mg, 52%). ^{1}H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.42-7.22 (m, 15 H, 3 Ph), 7.50-7.41 (m, 1 H, NH), 5.19-5.14 (m, 1 H, OH), 4.78 and 4.53 (2 d, 2 H, *J* = 11.2 Hz, PhCH_2), 4.78 and 4.68 (2 d, 2 H, *J* = 11.0 Hz, PhCH_2), 4.75-4.69 (m, 1 H, H-6), 4.53 and 4.48 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.40-4.30 (m, 1 H, H-2), 4.16 (dd, 1 H, $J_{1a,1b}$ = 11.5, $J_{1a,2}$ = 6.5 Hz, H-1a), 4.12 (dd, 1 H, $J_{1b,2}$ = 4.5 Hz, H-1b), 4.00 (dd, 1 H, $J_{8,9}$ = 2.5, $J_{9,10}$ = 0.5 Hz, H-9), 3.78 (dd, 1 H, $J_{7,8}$ = 10.5 Hz, H-8), 3.64 (dd, 1 H, $J_{10,11a}$ = 6.0, $J_{11a,11b}$ = 10.0 Hz, H-11a), 3.55 (dd, 1 H, $J_{10,11b}$ = 6.5 Hz, H-11b), 1.91 (s, 3 H, Ac), 1.53 and 1.49 (2 s, 6 H, 2 Me), 1.47 (s, 9 H, *t*-Bu). MALDI-TOF MS: 752.5 (M^+ + Na), 768.7 (M^+ + K). Anal. Calcd. for $C_{42}H_{52}N_2O_9$: C, 69.21; H, 7.19; N, 3.84. Found: C, 69.18; H, 7.23; N, 3.79.

7-Acetamido-6,10-anhydro-8,9,11-tri-*O*-benzyl-2,4,5,7-tetradeoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*arabino*-D-*ido*- and -D-*talo*-undec-4-ynitol (67). The *C*-glucoside **61** (317 mg, 0.64 mmol) was treated with the aldehyde **34** (436 mg, 1.92 mmol) as described for the preparation of **63**. The residue was eluted from a column of silica gel with CH_2Cl_2-acetone (from 30:1 to 1:1) to afford first unreacted **61** (95 mg, 30%). Eluted second was syrupy **67** as a ~20:1 mixture of diastereomers (298 mg, 64%). ^{1}H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.39-7.22 (m, 15 H, 3 Ph), 7.10-6.98 (m, 1 H, NH), 5.12-5.08 (m, 1 H, OH), 4.79 and 4.76 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 4.74 and 4.63 (2 d, 2 H, *J* = 11.3 Hz, PhCH_2), 4.57 and 4.40 (2 d, 2 H, *J* = 12.0 Hz, PhCH_2), 3.82 (dd, 1 H, $J_{8,9}$ = 8.0, $J_{9,10}$ = 9.0 Hz, H-9), 3.56 (dd, 1 H, $J_{7,8}$ = 8.0 Hz, H-8), 1.95 (s, 3 H, Ac), 1.54 and 1.49 (2 s, 6 H, 2 Me), 1.48 (s, 9 H, *t*-Bu). MALDI-TOF MS: 752.4 (M^+ + Na), 768.6 (M^+ + K). Anal. Calcd. for $C_{42}H_{52}N_2O_9$: C, 69.21; H, 7.19; N, 3.84. Found: C, 69.19; H, 7.11; N, 3.70.

7-Acetamido-6,10-anhydro-8,9,11-tri-*O*-benzyl-2,4,5,7-tetradeoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*arabino*-L-*gluco*- and -L-*allo*-undec-4-ynitol (68). The *C*-mannoside **62** (300 mg, 0.60 mmol) was treated with the aldehyde **34** (412 mg, 1.80 mmol) as described for the preparation of **63**. The residue was eluted from a column of silica gel with CH_2Cl_2-acetone (from 10:1 to 2:1) to afford first unreacted **62** (90 mg, 30%). Eluted second was

syrupy **68** as a ~5:1 mixture of diastereomers (262 mg, 60%). ^{1}H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.50-7.41 (m, 1 H, NH), 7.38-7.24 (m, 15 H, 3 Ph), 4.80 and 4.50 (2 d, 2 H, J = 11.0 Hz, PhCH_2), 4.66 (s, 2 H, PhCH_2), 4.60-4.41 (m, 4 H), 4.11-3.70 (m, 9 H), 1.97 (s, 3 H, Ac), 1.50 and 1.42 (2 s, 6 H, 2 Me), 1.43 (s, 9 H, *t*-Bu). Anal. Calcd. for $C_{42}H_{52}N_2O_9$: C, 69.21; H, 7.19; N, 3.84. Found: C, 69.23; H, 7.12; N, 3.73.

7-Acetamido-6,10-anhydro-8,9,11-tri-*O*-benzyl-2,3,4,5,7-pentadeoxy-1,2-*N*,*O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*threo*-L-*galacto*-undecitol (69). The alkyne **63** (300 mg, 0.41 mmol) was hydrogenated as described for the preparation of **3-hydroxy-41** to give, after column chromatography on silica gel (1:1 cyclohexane-AcOEt), syrupy **3-hydroxy-69** (241 mg, 80%) as a ~8:1 mixture of diastereomers. ^{1}H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.40-7.20 (m, 15 H, 3 Ph), 5.03 (d, 1 H, $J_{7,NH}$ = 6.0 Hz, NH), 4.81 and 4.54 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.71 and 4.58 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.52 and 4.47 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 3.98 (dd, 1 H, $J_{8,9}$ = 2.0, $J_{9,10}$ = 0.5 Hz, H-9), 3.97 (dd, 1 H, $J_{7,8}$ = 8.9 Hz, H-8), 3.82 (dd, 1 H, $J_{1a,1b}$ = 8.5, $J_{1a,2}$ = 6.2 Hz, H-1a), 3.29 (ddd, 1 H, $J_{5a,6}$ = 3.0, $J_{5b,6}$ = 6.5, $J_{6,7}$ = 10.0 Hz, H-6), 1.80 (s, 3 H, Ac), 1.65-1.45 (m, 4 H), 1.49 and 1.45 (2 s, 6 H, 2 Me), 1.43 (s, 9 H, *t*-Bu). MALDI-TOF MS: 756.7 (M^+ + Na), 772.6 (M^+ + K). Anal. Calcd. for $C_{42}H_{56}N_2O_9$: C, 68.82; H, 7.70; N, 3.82. Found: C, 68.89; H, 7.62; N, 3.78.

The alcohol **3-hydroxy-69** (385 mg, 0.53 mmol) was deoxygenated as described for the preparation of **41** to give, after column chromatography on silica gel (from 80:1 to 10:1 CH_2Cl_2-acetone), **69** (309 mg, 82%) as a syrup; $[\alpha]_D$ = +27.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (DMSO-d6, 120 °C): δ 7.40-7.20 (m, 15 H, 3 Ph), 4.81 and 4.53 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.71 and 4.58 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.53 and 4.47 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 3.98 (dd, 1 H, $J_{8,9}$ = 2.5, $J_{9,10}$ = 0.5 Hz, H-9), 3.92 (d, 1 H, $J_{7,NH}$ = 6.5 Hz, NH), 3.89 (dd, 1 H, $J_{1a,1b}$ = 8.5, $J_{1a,2}$ = 6.0 Hz, H-1a), 3.77-3.70 (m, 1 H, H-2), 3.65 (dd, 1 H, $J_{1b,2}$ = 2.0 Hz, H-1b), 3.62-3.52 (m, 5 H), 3.27 (ddd, 1 H, $J_{5a,6}$ = 2.5, $J_{5b,6}$ = 7.5, $J_{6,7}$ = 9.5 Hz, H-6), 1.80 (s, 3 H, Ac), 1.70-1.20 (m, 6 H), 1.49 and 1.43 (2 s, 6 H, 2 Me), 1.43 (s, 9 H, *t*-Bu). MALDI-TOF MS: 740.8 (M^+ + Na), 757.3 (M^+ + K). Anal. Calcd. for $C_{42}H_{56}N_2O_8$: C, 70.36; H, 7.87; N, 3.90. Found: C, 70.95; H, 7.52; N, 3.95.

7-Acetamido-6,10-anhydro-8,9,11-tri-*O*-benzyl-2,3,4,5,7-pentadeoxy-1,2-*N*,*O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-undecitol (70). The alkyne **64** (531 mg, 0.73 mmol) was hydrogenated as described for the preparation of **3-hydroxy-41** to give, after column chromatography on silica gel (6:1 CH_2Cl_2-acetone), syrupy **3-hydroxy-70** (518 mg, 97%) as a ~5:1 mixture of diastereomers. ^{1}H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.54-7.48 (m, 1 H, NH), 7.38-7.20 (m, 15 H, 3 Ph), 4.74 and 4.59 (2 d, 2 H, J = 11.0 Hz, PhCH_2), 4.73 and 4.68 (2 d, 2 H, J = 10.5 Hz, PhCH_2), 4.64-4.58 (m, 1 H, OH), 4.57 and 4.52 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 3.91 (dd, 1 H, $J_{1a,1b}$ = 8.5, $J_{1a,2}$ = 2.5 Hz, H-1a), 3.80-3.62 (m, 6 H), 3.50-3.24 (m, 4 H), 1.82 (s, 3 H, Ac), 1.74-1.52 (m, 4 H), 1.49 and 1.41 (2 s, 6 H, 2 Me), 1.44 (s, 9 H, *t*-Bu).

MALDI-TOF MS: 756.4 (M^+ + Na), 772.6 (M^+ + K). Anal. Calcd. for $C_{42}H_{56}N_2O_9$: C, 68.82; H, 7.70; N, 3.82. Found: C, 68.55; H, 7.90; N, 3.85.

The alcohol **3-hydroxy-70** (354 mg, 0.48 mmol) was deoxygenated as described for the preparation of **41** to give, after column chromatography on silica gel (from 80:1 to 2:1 CH_2Cl_2-acetone), **70** (319 mg, 92%) as a syrup; $[\alpha]_D$ = +28.4 (*c* 1.1, $CHCl_3$). ^1H NMR (DMSO-d6, 120 °C): δ 7.53-7.46 (m, 1 H, NH), 7.38-7.20 (m, 15 H, 3 Ph), 4.74 and 4.58 (2 d, 2 H, J = 11.0 Hz, PhCH_2), 4.72 and 4.68 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.56 and 4.51 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.12-4.07 (m, 1 H), 3.99 (dd, 1 H, $J_{1a,1b}$ = 8.5, $J_{1a,2}$ = 2.5 Hz, H-1a), 3.83 (dd, 1 H, $J_{1b,2}$ = 6.0 Hz, H-1b), 3.75-3.60 (m, 5 H), 3.50-3.26 (m, 3 H), 1.81 (s, 3 H, Ac), 1.65-1.50 (m, 6 H), 1.50 and 1.46 (2 s, 6 H, 2 Me), 1.44 (s, 9 H, *t*-Bu). MALDI-TOF MS: 741.0 (M^+ + Na), 756.2 (M^+ + K). Anal. Calcd. for $C_{42}H_{56}N_2O_8$: C, 70.36; H, 7.87; N, 3.90. Found: C, 70.43; H, 7.80; N, 3.80.

7-Acetamido-6,10-anhydro-8,9,11-tri-*O*-benzyl-2,3,4,5,7-pentadeoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*gluco*-*undecitol* (71). The alkyne **65** (510 mg, 0.70 mmol) was hydrogenated as described for the preparation of **3-hydroxy-41** to give, after column chromatography on silica gel (4:1 AcOEt-cyclohexane), syrupy **3-hydroxy-71** (466 mg, 91%) as a ~8:1 mixture of diastereomers. ^1H NMR (DMSO-d6, 100 °C) selected data of the main isomer: δ 7.38-7.21 (m, 15 H, 3 Ph), 7.10-7.04 (m, 1 H, OH), 4.79 and 4.42 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.72 and 4.50 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.52 (s, 2 H, PhCH_2), 4.32 (d, 1 H, $J_{7,NH}$ = 6.0 Hz, NH), 3.97 (dd, 1 H, $J_{1a,1b}$ = 8.5, $J_{1a,2}$ = 2.3 Hz, H-1a), 3.83 (dd, 1 H, $J_{1b,2}$ = 6.3 Hz, H-1b), 3.72 (dd, 1 H, $J_{10,11a}$ = 2.5, $J_{11a,11b}$ = 11.0 Hz, H-11a), 3.65 (dd, 1 H, $J_{10,11b}$ = 6.0 Hz, H-11b), 3.54 (dd, 1 H, $J_{8,9}$ = 9.5, $J_{9,10}$ = 9.0 Hz, H-9), 3.40 (ddd, 1 H, H-10), 1.97 (s, 3 H, Ac), 1.52-1.47 (m, 4 H), 1.44 and 1.42 (2 s, 6 H, 2 Me), 1.41 (s, 9 H, *t*-Bu). MALDI-TOF MS: 757.2 (M^+ + Na), 773.3 (M^+ + K). Anal. Calcd. for $C_{42}H_{56}N_2O_9$: C, 68.82; H, 7.70; N, 3.82. Found: C, 68.71; H, 7.61; N, 3.89.

The alcohol **3-hydroxy-71** (462 mg, 0.63 mmol) was deoxygenated as described for the preparation of **41** to give, after column chromatography on silica gel (from 80:1 to 4:1 CH_2Cl_2-acetone), **71** (384 mg, 85%) as a syrup; $[\alpha]_D$ = -8.61 (*c* 0.7, $CHCl_3$). ^1H NMR (DMSO-d6, 120 °C): δ 7.57-7.21 (m, 15 H, 3 Ph), 7.00 (d, 1 H, $J_{7,NH}$ = 8.0 Hz, NH), 4.79 and 4.51 (2 d, 2 H, J = 11.0 Hz, PhCH_2), 4.72 and 4.43 (2 d, 2 H, J = 11.3 Hz, PhCH_2), 4.61-4.52 (m, 1 H), 4.54 (s, 2 H, PhCH_2), 3.90 (dd, 1 H, $J_{1a,1b}$ = 8.5, $J_{1a,2}$ = 6.0 Hz, H-1a), 3.74 (dd, 1 H, $J_{10,11a}$ = 2.5, $J_{11a,11b}$ = 11.0 Hz, H-11a), 3.72-3.64 (m, 4 H), 3.54 (dd, 1 H, $J_{8,9}$ = 9.3, $J_{9,10}$ = 9.3 Hz, H-9), 3.47-3.40 (m, 2 H), 1.98 (s, 3 H, Ac), 1.75-1.50 (m, 6 H), 1.52 and 1.46 (2 s, 6 H, 2 Me), 1.44 (s, 9 H, *t*-Bu). MALDI-TOF MS: 740.6 (M^+ + Na), 756.7 (M^+ + K). Anal. Calcd. for $C_{42}H_{56}N_2O_8$: C, 70.36; H, 7.87; N, 3.90. Found: C, 70.27; H, 7.92; N, 3.93.

7-Acetamido-6,10-anhydro-8,9,11-tri-*O*-benzyl-2,3,4,5,7-pentadeoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*threo*-L-*gulo*-undecitol (72). The alkyne **66** (200 mg, 0.27 mmol) was hydrogenated as described for the preparation of **3-hydroxy-41** to give, after column

chromatography on silica gel (from 1:1 to 2:1 AcOEt-cyclohexane), syrupy **3-hydroxy-72** (168 mg, 85%) as a ~20:1 mixture of diastereomers. ^{1}H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.39-7.23 (m, 15 H, 3 Ph), 4.68 and 4.64 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.63 and 4.53 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.53 and 4.48 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.19-3.62 (m, 13 H), 1.83 (s, 3 H, NAc), 1.62-1.45 (m, 4 H), 1.43 and 1.41 (2 s, 6 H, 2 Me), 1.41 (s, 9 H, *t*-Bu). MALDI-TOF MS: 756.3 (M^+ + Na), 772.5 (M^+ + K). Anal. Calcd. for $C_{42}H_{56}N_2O_9$: C, 68.82; H, 7.70; N, 3.82. Found: C, 68.90; H, 7.60; N, 3.85.

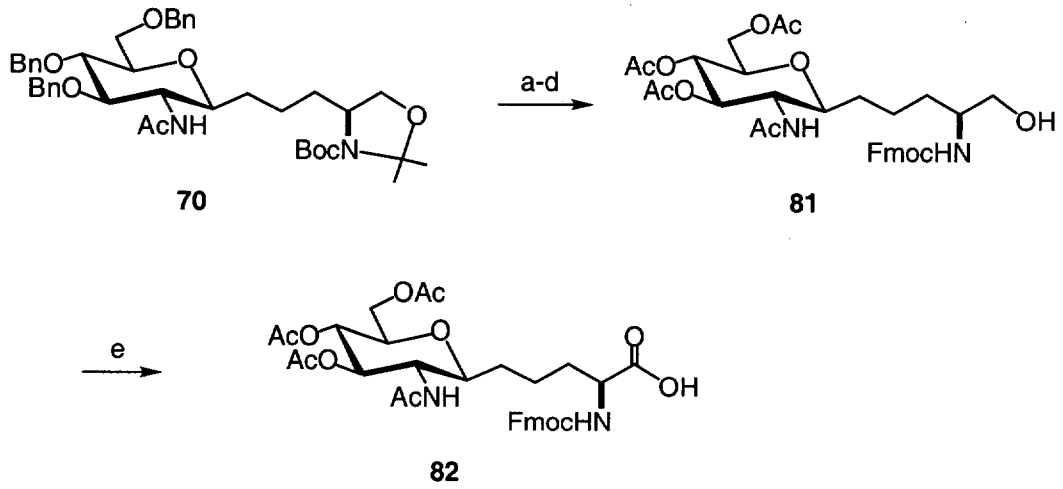
The alcohol **3-hydroxy-72** (158 mg, 0.21 mmol) was deoxygenated as described for the preparation of **41** to give, after column chromatography on silica gel (from 1:1 to 4:1 AcOEt-cyclohexane), **72** (90 mg, 60%) as a syrup; $[\alpha]_D$ = +20.1 (*c* 0.5, $CHCl_3$). ^{1}H NMR (DMSO-d6, 120 °C) selected data: δ 7.36-7.25 (m, 15 H, 3 Ph), 4.68 and 4.64 (2 d, 2 H, J = 12.0 Hz, PhCH_2), 4.65 and 4.53 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.51 (s, 2 H, PhCH_2), 3.98 (dd, 1 H, $J_{8,9}$ = 3.0, $J_{9,10}$ = 0.5 Hz, H-9), 3.94-3.85 (m, 4 H), 3.79-3.72 (m, 2 H), 3.71 (dd, 1 H, $J_{10,11a}$ = 4.0, $J_{11a,11b}$ = 11.0 Hz, H-11a), 3.64 (dd, 1 H, $J_{7,8}$ = 8.5, $J_{8,9}$ = 2.0 Hz, H-8), 1.88 (s, 3 H, Ac), 1.65-1.43 (m, 6 H), 1.49 and 1.43 (2 s, 6 H, 2 Me), 1.43 (s, 9 H, *t*-Bu). Anal. Calcd. for $C_{42}H_{56}N_2O_8$: C, 70.36; H, 7.87; N, 3.90. Found: C, 70.55; H, 7.80; N, 3.91.

7-Acetamido-6,10-anhydro-8,9,11-tri-*O*-benzyl-2,3,4,5,7-pentadeoxy-1,2-*N*,*O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*gulo*-undecitol (73). The alkyne **67** (227 mg, 0.31 mmol) was hydrogenated as described for the preparation of **3-hydroxy-41** to give, after column chromatography on silica gel (from 6:1 to 1:1 CH_2Cl_2-acetone), syrupy **3-hydroxy-73** (220 mg, 97%) as a ~20:1 mixture of diastereomers. ^{1}H NMR (DMSO-d6, 120 °C) selected data of the main isomer: δ 7.35-7.24 (m, 15 H, 3 Ph), 7.11 (d, 1 H, $J_{7,NH}$ = 8.0 Hz, NH), 4.70 and 4.64 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.64 and 4.57 (2 d, 2 H, J = 11.3 Hz, PhCH_2), 4.51 (s, 2 H, PhCH_2), 4.09-4.00 (m, 1 H, H-2), 3.98 (dd, 1 H, $J_{1a,1b}$ = 8.5, $J_{1a,2}$ = 2.1 Hz, H-1a), 3.82 (dd, 1 H, $J_{1b,2}$ = 6.5 Hz, H-1b), 2.81 (s, 3 H, Ac), 2.78-2.54 (m, 4 H), 1.43 and 1.41 (2 s, 6 H, 2 Me), 1.41 (s, 9 H, *t*-Bu). MALDI-TOF MS: 756.1 (M^+ + Na), 772.3 (M^+ + K). Anal. Calcd. for $C_{42}H_{56}N_2O_9$: C, 68.82; H, 7.70; N, 3.82. Found: C, 68.75; H, 7.58; N, 3.74.

The alcohol **3-hydroxy-73** (206 mg, 0.28 mmol) was deoxygenated as described for the preparation of **41** to give, after column chromatography on silica gel (from 50:1 to 1:1 CH_2Cl_2-acetone), **73** (156 mg, 78%) as a syrup; $[\alpha]_D$ = +19.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (DMSO-d6, 120 °C) selected data: δ 7.39-7.23 (m, 15 H, 3 Ph), 7.11 (d, 1 H, $J_{7,NH}$ = 9.0 Hz, NH), 4.69 and 4.64 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.64 and 4.57 (2 d, 2 H, J = 11.3 Hz, PhCH_2), 4.51 (s, 2 H, PhCH_2), 4.10-3.98 (m, 1 H, H-2), 3.92-3.82 (m, 3 H), 3.78-3.69 (m, 4 H), 3.65 (dd, 1 H, $J_{1a,1b}$ = 8.8, $J_{1a,2}$ = 2.0 Hz, H-1a), 3.55 (ddd, 1 H, $J_{5a,6}$ = 1.0, $J_{5b,6}$ = 5.0, $J_{6,7}$ = 5.5 Hz, H-6), 1.90 (s, 3 H, Ac), 1.70-1.51 (m, 6 H), 1.44 and 1.42 (2 s, 6 H, 2 Me), 1.41 (s, 9 H, *t*-Bu). Anal. Calcd. for $C_{42}H_{56}N_2O_8$: C, 70.36; H, 7.87; N, 3.90. Found: C, 70.40; H, 7.81; N, 3.80.

7-Acetamido-6,10-anhydro-8,9,11-tri-*O*-benzyl-2,3,4,5,7-pentadeoxy-1,2-*N,O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*allo*-undecitol (74). The alkyne **68** (244 mg, 0.34 mmol) was hydrogenated as described for the preparation of **3-hydroxy-41** to give, after column chromatography on silica gel (from 10:1 to 1:1 CH_2Cl_2-acetone), syrupy **3-hydroxy-74** (217 mg, 87%) as a ~5:1 mixture of diastereomers. ^1H NMR (DMSO-d6, 140 °C) selected data of the main isomer: δ 7.41-7.20 (m, 15 H, 3 Ph), 1.90 (s, 3 H, Ac), 1.70-1.50 (m, 4 H), 1.50 and 1.42 (2 S, 6 H, 2 Me), 1.41 (s, 9 H, *t*-Bu). MALDI-TOF MS: 756.4 (M^+ + Na), 772.6 (M^+ + K). Anal. Calcd. for $C_{42}H_{56}N_2O_9$: C, 68.82; H, 7.70; N, 3.82. Found: C, 68.95; H, 7.53; N, 3.80.

The alcohol **3-hydroxy-74** (100 mg, 0.14 mmol) was deoxygenated as described for the preparation of **41** to give, after column chromatography on silica gel (from 10:1 to 5:1 CH_2Cl_2-acetone), **74** (80 mg, 82%) as a syrup; $[\alpha]_D$ = +24.6 (*c* 0.8, $CHCl_3$). ^1H NMR (DMSO-d6, 140 °C) selected data: δ 7.38-7.14 (m, 15 H, 3 Ph), 4.66 and 4.54 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.58 and 4.51 (2 d, 2 H, J = 11.5 Hz, PhCH_2), 4.50 (s, 2 H, PhCH_2), 3.90 (dd, 1 H, $J_{1a,1b}$ = 9.0, $J_{1b,2}$ = 6.0 Hz, H-1a), 1.88 (s, 3 H, Ac), 1.74-1.52 (m, 6 H), 1.51 and 1.43 (2 s, 6 H, 2 Me), 1.42 (s, 9 H, *t*-Bu). Anal. Calcd. for $C_{42}H_{56}N_2O_8$: C, 70.36; H, 7.87; N, 3.90. Found: C, 70.39; H, 7.75; N, 3.96.

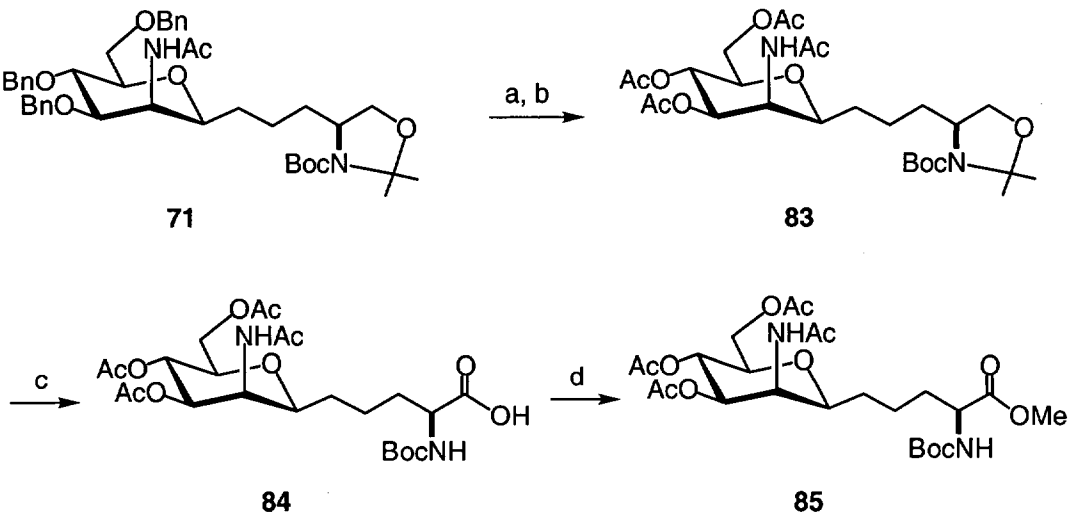


Scheme S1. Reagents and conditions: a) H_2, $Pd(OH)_2$, AcOEt-MeOH; b) Ac_2O, Py; c) TFA, CH_2Cl_2; d) FmocOSu, *i*-Pr_2EtN; e) 1 M Jones, acetone.

7-Acetamido-8,9,11-tri-*O*-acetyl-6,10-anhydro-2,3,4,5,7-pentadeoxy-2-(9-fluorenylmethoxycarbonylamino)-D-*erythro*-L-*galacto*-undecitol (81). A vigorously stirred mixture of **70** (64 mg, 0.09 mmol), 20% $Pd(OH)_2$ on carbon (40 mg), AcOEt (2 mL), and MeOH (2 mL) was degassed under vacuum and saturated with hydrogen (by a H_2-filled balloon) three times. The suspension was stirred at room temperature for 4 h under a positive pressure of hydrogen (7 bar), then filtered through a plug of cotton and concentrated. A solution of the crude product in acetic anhydride (1

mL) and pyridine (1 mL) was kept at room temperature for 3 h, then concentrated. The residue was eluted from a column of silica gel with 2:1 AcOEt-cyclohexane to give 7-acetamido-8,9,11-tri-*O*-acetyl-6,10-anhydro-2,3,4,5,7-pentadeoxy-1,2-*N*,*O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*galacto*-undecitol (46 mg, 89%) as a syrup. ^{1}H NMR: δ 5.44 (d, 1 H, $J_{7,NH}$ = 9.0 Hz, NH), 5.09 (dd, 1 H, $J_{7,8} = J_{8,9}$ = 9.5 Hz, H-8), 5.08 (dd, 1 H, $J_{9,10}$ = 9.0 Hz, H-9), 4.25 (dd, 1 H, $J_{10,11a}$ = 5.0, $J_{11a,11b}$ = 12.0 Hz, H-11a), 4.10 (dd, 1 H, $J_{10,11b}$ = 2.0 Hz, H-11b), 4.00 (dd, 1 H, $J_{1a,1b}$ = 9.0, $J_{1a,2}$ = 3.0 Hz, H-1a), 3.93 (dd, 1 H, $J_{1b,2}$ = 6.0 Hz, H-1b), 3.80-3.73 (m, 2 H), 3.58 (ddd, 1 H, H-10), 3.26 (ddd, 1 H, $J_{5a,6}$ = 3.0, $J_{5b,6}$ = 7.5, $J_{6,7}$ = 9.2Hz, H-6), 2.12, 2.06, 2.04, and 1.96 (4 s, 12 H, 4 Ac), 1.80-1.58 (m, 6 H). MALDI-TOF MS: 596.2 (M^+ + Na), 612.2 (M^+ + K).
To a cooled (0 °C), stirred solution of the oxazolidine derivative (240 mg, 0.42 mmol) in CH_2Cl_2 (1 mL) was slowly added a solution of trifluoroacetic acid (1 mL) in CH_2Cl_2 (3 mL). The solution was stirred at 0 °C for 30 min and at rt for 30 min, then diluted with toluene (15 mL) and concentrated three times. To a stirred solution of the residue in CH_3CN (4 mL) and H_2O (4 mL) was added at rt a solution of *N*-(9-fluorenylmethoxycarbonyloxy)succinimide (FmocOSu, 184 mg, 0.55 mmol) in CH_3CN (1.5 mL) followed by the dropwise addition of *i*-Pr_2EtN (0.22 mL, 1.68 mmol) in order to mantain a basic reaction medium (pH = 8.5-9). The solution was stirred at rt for an additional 30 min, then diluted with 1 M HCl until pH = 2, and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was eluted from a column of silica gel with 1:1 CH_2Cl_2-acetone to afford **81** (208 mg, 76%) as a white solid; mp 174-176 °C (cyclohexane-AcOEt); $[\alpha]_D$ = -32.2 (*c* 1.0, $CHCl_3$). ^{1}H NMR selected data: δ 7.81-7.25 (m, 8 H, Ar), 5.41 (d, 1 H, $J_{7,NH}$ = 9.5 Hz, NH), 5.09 (dd, 1 H, $J_{7,8} = J_{8,9}$ = 9.5 Hz, H-8), 5.08 (dd, 1 H, $J_{9,10}$ = 9.0 Hz, H-9), 4.21 (dd, 1 H, *J* = 4.0, 12.0 Hz, C*H*$_2$-Fmoc), 4.12 (dd, 1 H, *J* = 2.0, 12.0 Hz, C*H*$_2$-Fmoc), 4.02 (ddd, 1 H, $J_{6,7}$ = 9.5 Hz, H-7), 3.61-3.54 (m, 1 H, H-10), 3.50 (ddd, 1 H, $J_{5a,6}$ = 9.0, $J_{5b,6}$ = 0.5 Hz, H-6), 2.09, 2.05, 2.04, and 1.96 (4 s, 12 H, 4 Ac), 1.75-1.40 (m, 6 H). MALDI-TOF MS: 678.1 (M^+ + Na), 694.2 (M^+ + K). Anal. Calcd. for $C_{34}H_{42}N_2O_{11}$: C, 62.37; H, 6.47; N, 4.28. Found: C, 62.45; H, 6.40; N, 4.36.

7-Acetamido-8,9,11-tri-*O*-acetyl-6,10-anhydro-2,3,4,5,7-pentadeoxy-2-(9-fluorenylmethoxycarbonylamino)-D-*erythro*-L-*galacto*-undeconic Acid (82). The compound **81** (105 mg, 0.16 mmol) was treated with the Jones reagent as described for the preparation of **47** to give, after trituration with Et_2O, **82** (104 mg, 98%) as a white solid; mp 179-180 °C (cyclohexane-AcOEt); $[\alpha]_D$ = -14.9 (*c* 0.9, MeOH). ^{1}H NMR selected data: δ 7.81-7.35 (m, 8 H, Ar), 5.06 (dd, 1 H, $J_{7,8} = J_{8,9}$ = 9.5 Hz, H-8), 5.02 (dd, 1 H, $J_{9,10}$ = 9.0 Hz, H-9), 4.00 (ddd, 1 H, $J_{7,NH}$ = 9.5, $J_{6,7}$ = 9.0 Hz, H-7), 3.59-3.53 (m, 1 H, H-10), 3.29 (ddd, 1 H, $J_{5a,6}$ = 1.5, $J_{5b,6}$ = 9.0 Hz, H-6), 2.02, 2.00, 1.98, and 1.96 (4 s, 12 H, 4 Ac), 1.98-1.40 (m, 6 H). MALDI-TOF MS: 692.4 (M^+ + Na), 708.4 (M^+ + K). Anal. Calcd. for $C_{34}H_{40}N_2O_{12}$: C, 61.07; H, 6.03; N, 4.19. Found: C, 61.25; H, 5.90; N, 4.30.



Scheme S2. Reagents and conditions: a) H_2, $Pd(OH)_2$, AcOEt-MeOH; b) Ac_2O, Py; c) 1 M Jones, acetone; d) CH_2N_2, Et_2O-MeOH.

7-Acetamido-8,9,11-tri-*O*-acetyl-6,10-anhydro-2,3,4,5,7-pentadeoxy-1,2-*N*,*O*-isopropylidene-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*gluco*-*undecitol* (83). Treatment of **71** (96 mg, 0.13 mmol) as described for the preparation of **81** gave **83** (76 mg, 100%) as a syrup; $[\alpha]_D$ = +1.0 (*c* 0.9, $CHCl_3$). ^1H NMR (DMSO-d6, 80 °C): δ 7.58 (d, 1 H, $J_{7,NH}$ = 9.5 Hz, NH), 5.06 (dd, 1 H, $J_{8,9}$ = 9.0, $J_{9,10}$ = 9.6 Hz, H-9), 4.99 (ddd, 1 H, $J_{5a,6}$ = 0.5, $J_{5b,6}$ = 10.0, $J_{6,7}$ = 4.5 Hz, H-6), 4.40 (ddd, 1 H, $J_{7,8}$ = 1.5 Hz, H-7), 4.15 (dd, 1 H, $J_{10,11a}$ = 7.0,$J_{11a,11b}$ = 11.5 Hz, H-11a), 4.00 (dd, 1 H, $J_{10,11b}$ = 3.0 Hz, H-11b), 3.90 (dd, 1 H, $J_{1a,1b}$ = 9.0, $J_{1a,2}$ = 5.8 Hz, H-1a), 3.78-3.72 (m, 1 H, H-2), 3.73 (ddd, 1 H, H-10), 3.69 (dd, 1 H, $J_{1b,2}$ = 3.0 Hz, H-1b), 3.64 (dd, 1 H, H-8), 2.03, 2.02, 1.94, and 1.89 (4 s, 12 H, 4 Ac), 1.68-1.50 (m, 6 H), 1.49 and 1.42 (2 s, 6 H, 2 Me), 1.43 (s, 9 H, *t*-Bu). Anal. Calcd. for $C_{27}H_{44}N_2O_{11}$: C, 56.63; H, 7.74; N, 4.89. Found: C, 56.74; H, 7.63; N, 7.70.

6,10-Anhydro-7-acetamido-8,9,11-tri-*O*-acetyl-2,3,4,5,7-pentadeoxy-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*gluco*-undeconic Acid (84). The compound **83** (33.7 mg, 0.06 mmol) was treated with the Jones reagent as described for the preparation of **47** to give **84** (32 mg, 95%) as a syrup ~95% pure by ^1H NMR analysis. ^1H NMR selected data: δ 6.20-5.73 (m, 2 H), 5.40-5.00 (m, 3 H), 4.26 (dd, 1 H, $J_{10,11a}$ = 5.0, $J_{11a,11b}$ = 11.5 Hz, H-11a), 4.08-3.56 (m, 3 H), 1.82-1.52 (m, 6 H), 1.41 (s, 9 H, *t*-Bu).

Methyl 7-Acetamido-8,9,11-tri-*O*-acetyl-6,10-anhydro-2,3,4,5,7-pentadeoxy-2-(*tert*-butoxycarbonylamino)-D-*erythro*-L-*gluco*-undeconate (85). Treatment of a solution of crude acid **84** in 1:1 Et_2O-MeOH with ethereal diazomethane at 0 °C for 5 min gave, after column chromatography on silica gel (3:1 AcOEt-cyclohexane), **85** as a syrup; $[\alpha]_D$ = -3.4 (*c* 1.1, $CHCl_3$).

^{1}H NMR: δ 5.66(d, 1 H, $J_{7,NH}$ = 9.5 Hz, NH), 5.07 (dd, 1 H, $J_{8,9}$ = 10.0, $J_{9,10}$ = 10.0 Hz, H-9), 5.08-5.00 (m, 1 H, NH), 5.00 (dd, 1 H, $J_{7,8}$ = 4.0 Hz, H-8), 4.57 (ddd, 1 H, $J_{6,7}$ = 1.4 Hz, H-7), 4.34-4.30 (m, 1 H, H-2), 4.26 (dd, 1 H, $J_{10,11a}$ = 5.5, $J_{11a,11b}$ = 12.0 Hz, H-11a), 4.05 (dd, 1 H, $J_{10,11b}$ = 2.0 Hz, H-11b), 3.75 (s, 3 H, OMe), 3.64-3.56 (m, 2 H, H-6, H-10), 2.14, 2.09, 2.07, and 2.00 (4 s, 12 H, 4 Ac), 1.80-1.43 (m, 6 H), 1.46 (s, 9 H, *t*-Bu). ^{1}H NMR (C_6D_6): δ 5.50 (d, 1 H, $J_{7,NH}$ = 10.0 Hz, NH), 5.34 (dd, 1 H, $J_{8,9}$ = 10.3, $J_{9,10}$ = 10.0 Hz, H-9), 5.11 (dd, 1 H, $J_{7,8}$ = 4.2 Hz, H-8), 5.10 (m, 1 H, NH), 4.65 (ddd, 1 H, $J_{6,7}$ = 1.4 Hz, H-7), 4.49-4.41 (m, 1 H, H-2), 4.39 (dd, 1 H, $J_{10,11a}$ = 5.0, $J_{11a,11b}$ = 12.3 Hz, H-11a), 3.96 (dd, 1 H, $J_{10,11b}$ = 2.5 Hz, H-11b), 3.27 (s, 3 H, OMe), 3.15 (ddd, 1 H, H-10), 2.91 (ddd, 1 H, $J_{5a,6}$ = 6.0, $J_{5b,6}$ = 4.5 Hz, H-6), 1.84, 1.80, 1.63, and 1.43 (4 s, 12 H, 4 Ac), 1.41 (s, 9 H, *t*-Bu), 1.40-0.95 (m, 6 H). Anal. Calcd. for $C_{25}H_{40}N_2O_{12}$: C, 53.56; H, 7.19; N, 4.99. Found: C, 53.60; H, 7.30; N, 4.95.