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Synthesis of selected aminodeoxy analogs of globotriosylceramide

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Abstract

Four aminodeoxy analogs of globotriosylceramide (6″-, 4″-, 2″-, and 6′-aminodeoxy) were synthesized by glycosylation of 3-*O*-benzoylated azidosphingosine with the corresponding aminodeoxy-globotriose trichloroacetimidate, followed by reduction of the azido group, N-acylation with 1-adamantaneacetic acid, and removal of the protecting groups.

Keywords: Globotriosylceramide aminodeoxy analogs

1. Introduction

In the previous paper [1], we described the synthesis of some aglycon analogs of globotriosylceramide [Gal-α-(1→4)Gal-β-(1→4)Glc-β-(1→Cer), Gb3], including the adamantylceramide analog **1** (Fig. 1). Compound **1** was originally obtained [2] by hydrolysis of the amide group of Gb3 followed by N-acylation with 1-adamantaneacetic acid. This semisynthetic compound was found to be an efficient inhibitor of verotoxin binding [2]. We have also reported the synthesis of four aminodeoxy analogs of Gb3 [3]. Computer docking of Gb3 and verotoxin b subunit revealed a close proximity between some hydroxyl groups of Gb3 to carboxyl groups in the b subunit [4], indicating that exchange of these hydroxyl groups for amino groups might give salt bridges in the molecular complex. As an attempt to increase the inhibitory power, combination of the adamantylceramide aglycon with aminodeoxy saccharides furnished compounds **2–5** as a novel set of Gb3 analogs (Fig. 1). We now report the synthesis of **2–5**.

The exploitation of **2–5** as inhibitors of globotriose-binding proteins will be reported in due course.

2. Results and discussion

Synthesis of compounds **2–5**.—The known [3] azido-functionalized 2-(trimethylsilyl)ethyl (Me_3SiEt) globotriosides **6a–d** were each O-debenzoylated with methanolic sodium methoxide and the purified products were hydrogenated under slightly acidic conditions (H_2, Pd–C, EtOH, 0.1 M HCl) in order both to remove the *O*-benzyl protecting groups and reduce the azido groups to amino groups. The crude amines were dissolved in methanol containing a small amount of triethylamine, and the slightly basic mixtures were treated with

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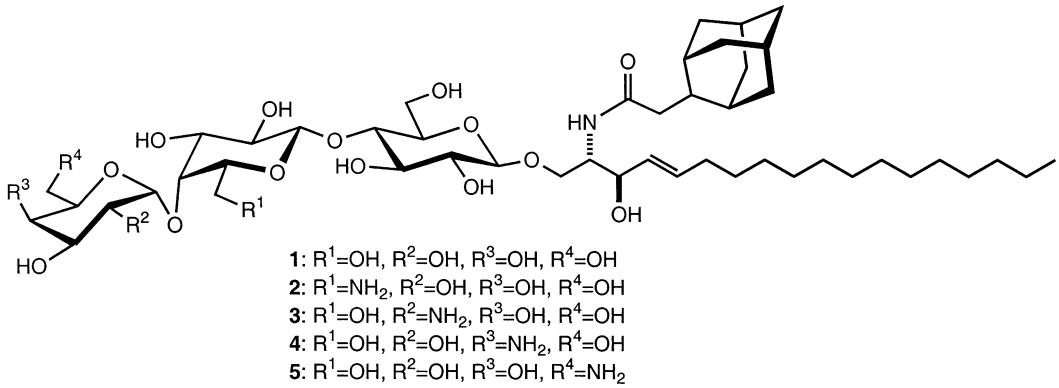


Fig. 1. Inhibition of globotriose-binding proteins.

CF_3COSEt [5] to yield the corresponding crude *N*-trifluoroacetyl derivatives. Treatment with acetic anhydride in pyridine and chromatography of the crude materials then furnished **7a–d** (Scheme 1) in 54–67% overall yields over four reaction steps.

Compounds **7a–d** were each treated with CF_3COOH in CH_2Cl_2 for 40 min, and chromatography of the crude materials yielded the hemiacetals **8a–d** (Scheme 1) in 81–95% yields.

Treatment of **8a–d** with Cl_3CCN in dichloromethane [6] in the presence of diazabicycloundecane (DBU), and chromatography of the crude materials gave the trichloroacetimidates **9a–d** (Scheme 1) in 73–83% yields. Compounds **9a–d** were somewhat labile under the acidic conditions of silica chromatography. Consequently, a small amount of triethylamine was added to the eluent, which permitted purification to a degree of $> 90\%$.

Glycosylation of 3-*O*-benzoylated azidosphingosine [7] was performed by treatment with compounds **9a–d** and $BF_3{\cdot}OEt_2$ in dry dichloromethane. Chromatography of the crude materials gave the azidosphingosinyl Gb3 derivatives **10a–d** (Scheme 2) in 63–65% yields.

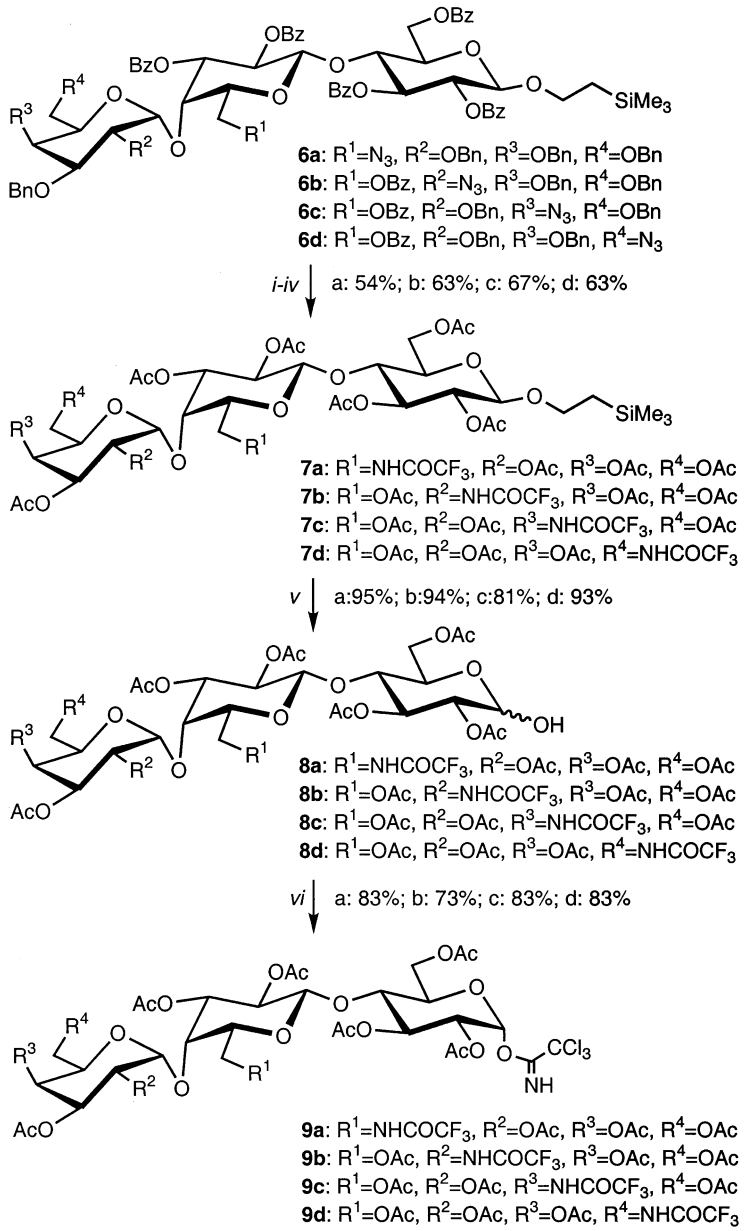
The azido groups of **10a–d** were reduced by treatment with hydrogen sulfide in pyridine–water mixture. The crude amines were dissolved in dichloromethane and acylated with 1-adamantaneacetic acid in the presence of *N*-(3 - dimethylaminopropyl) - *N′* - ethylcarbodiimide (EDC). Chromatography of the crude materials gave the N-adamantaneacetyl-Gb3 derivatives **11a–d** (Scheme 2) in 75–87% yields.

The *N*-trifluoroacetyl, *O*-acetyl and *O*-benzoyl protecting groups of **11a–d** were removed by treatment with aqueous sodium hydroxide in methanol, and the crude materials were chromatographed on a reverse phase (C18) column, using a water–methanol gradient, which furnished the globotriosylceramide analogs **2–5** (Scheme 2 and Fig. 1) in 73–84% yields (purity $> 90\%$). Attempted chromatography on silica gel was unsuccessful. The polarity profiles of **2–5** made it difficult to obtain high-quality ^1H NMR spectra, probably due to micelle formation.

3. Experimental

General experimental procedures and methods were as described previously [3]. The compounds **1** [1] and **6a–d** [3] have been reported.

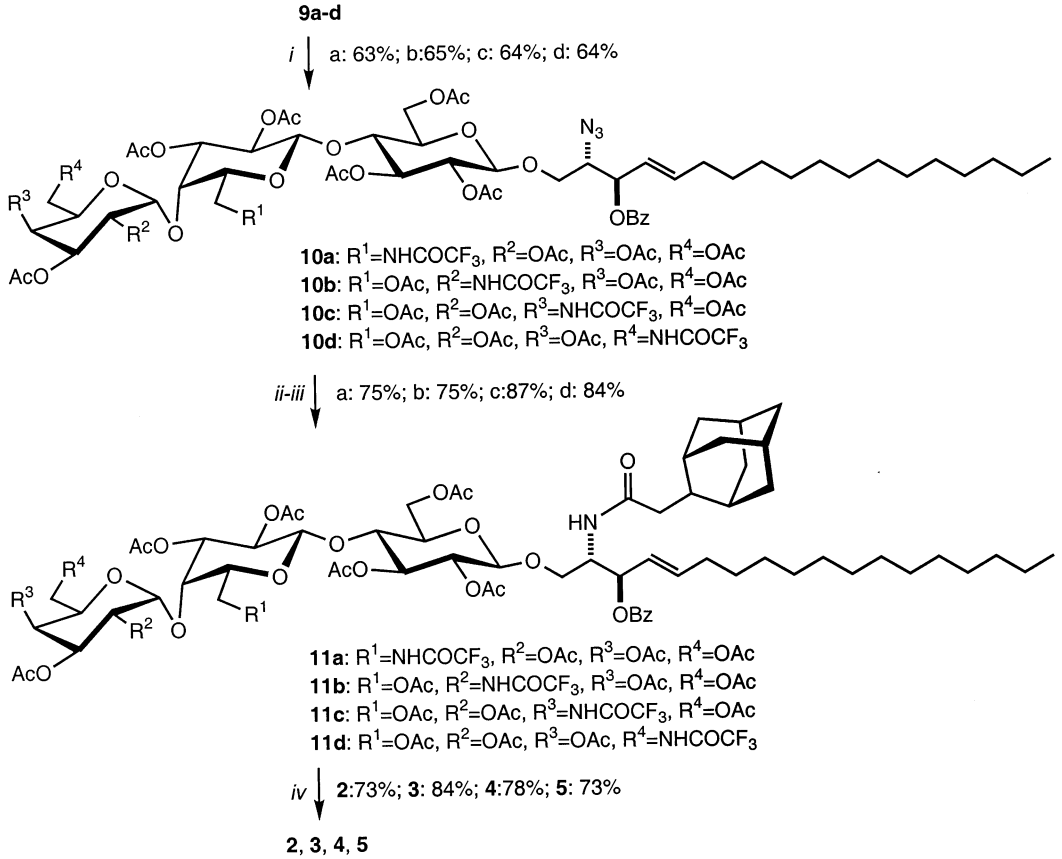
*(2*S*,3*R*,4*E*)-2-(1-Adamantaneacetamido)-3-hydroxy-octadec-4-enyl (α-*D*-galactopyranosyl)-(1→4)-(6-amino-6-deoxy-β-*D*-galactopyranosyl)-(1→4)-β-*D*-glucopyranoside* (**2**).—Compound **11a** (5.5 mg, 0.004 mmol) was dissolved in MeOH (5 mL), aq NaOH (1 M, 0.5 mL) was added, and the mixture was stirred at room temperature (rt) for 18 h. The reaction mixture was neutralized with Duolite C436 (H^+) resin, filtered, and concd. The residue was chromatographed on a reverse-phase column (Varian Mega Bond Elut C18 (water–MeOH 1:0 → 8:2 → 6:4 → 4:6 → 2:8 →



Scheme 1. (i) NaOMe, MeOH, 22 °C, 14–18 h; (ii) H_2, Pd–C, EtOH, 0.1 M HCl, 22 °C, 14–18 h; (iii) CF_3COSEt, MeOH, Et_3N, 0 °C, 6 h; (iv) Ac_2O, pyridine, 22 °C, 16 h; (v) CF_3COOH, CH_2Cl_2, 22 °C, 40 min; (vi) Cl_3CCN, CH_2Cl_2, DBU, 0 °C, 1 h.

0:1, 6 mL of each) to give **2** (2.5 mg, 73%); $[\alpha]_D^{22}$ +20° (*c* 0.1, MeOH); ^{1}H NMR (3:1 CD_3OD–D_2O): δ (assignments of aglycon protons are shown in italic) 5.69–5.78 (m, 1 H, H-5), 5.45 (br dd, 1 H, *J* 7.7, 15.4 Hz, H-4), 4.46, 4.34 (br d, 1 H each, *J* 7.9 and 7.6 Hz, H-1,1′), 4.27 (br t, 1 H, *J* 6.2 Hz, H-5″), 3.10–4.22 (m), 0.8–2.20 (m, 46 H); HRMS Anal. Calcd for $C_{48}H_{84}O_{17}N_2Na$ [M + Na]: 983.5668. Found: 983.5658.

*(2*S*,3*R*,4*E*)-2-(1-Adamantaneacetamido)-3-hydroxy-octadec-4-enyl (2-amino-2-deoxy-α-*D*-galactopyranosyl)-(1→4)-(β-*D*-galactopyranosyl)-(1→4)-β-*D*-glucopyranoside* (**3**).— Compound **11b** (10 mg, 0.007 mmol) was treated essentially as described in the preparation of **2**, thus yielding **3** (5.2 mg, 84%); $[\alpha]_D^{22}$ +10° (*c* 0.3, MeOH); ^{1}H NMR (3:1 CD_3OD–D_2O): δ (assignments of aglycon protons are shown in italic) 5.65–5.77 (m, 1 H, H-5), 5.46 (dd, 1 H, *J* 7.8, 15.3 Hz, H-4), 3.10–4.47 (m), 0.80–2.20 (m, 46 H); HRMS Anal. Calcd for $C_{48}H_{84}O_{17}N_2Na$ [M + Na]: 983.5668. Found: 983.5692.



Scheme 2. (i) (2*S*,3*R*,4*E*)-2-azido-3-(benzoyloxy)-4-octadecen-1-ol, BF_3OEt_2, CH_2Cl_2, 22 °C, 1.5 h; (ii) H_2S, pyridine, H_2O, 0 °C, 1 h → 22 °C, 44 h; (iii) adamantaneacetic acid, EDC, CH_2Cl_2, 22 °C, 16 h; (iv) NaOH, H_2O, MeOH, 22 °C, 18 h.

*(2*S,*3*R,*4*E*)-2-(1-Adamantaneacetamido)-3-hydroxy-octadec-4-enyl (4-amino-4-deoxy-α-*D*-galactopyranosyl)-(1→4)-(β-*D*-galactopyranosyl)-(1→4)-β-*D*-glucopyranoside* (**4**).—Compound **11c** (11 mg, 0.007 mmol) was treated essentially as described in the preparation of **2**, thus yielding **4** (5.4 mg, 78%); $[\alpha]_D^{22}$ + 17° (*c* 0.5, MeOH); ^{1}H NMR (3:1 CD_3OD–D_2O): δ (assignments of aglycon protons are shown in italic) 5.63–5.76 (m, 1 H, H-5), 5.42–5.51 (m, 1 H, H-4), 4.31 (br d, 1 H, *J* 7.9 Hz, H-1′ or H-1), 3.10–4.45 (m), 0.80–2.20 (m, 46 H); HRMS Anal. Calcd for $C_{48}H_{84}O_{17}N_2Na$ [M + Na]: 983.5668. Found: 983.5652.

*(2*S,*3*R,*4*E*)-2-(1-Adamantaneacetamido)-3-hydroxy-octadec-4-enyl (6-amino-6-deoxy-α-*D*-galactopyranosyl)-(1→4)-(β-*D*-galactopyranosyl)-(1→4)-β-*D*-glucopyranoside* (**5**).—Compound **11d** (18 mg, 0.012 mmol) was treated essentially as described in the preparation of **2**, which gave **5** (8 mg, 73%); $[\alpha]_D^{22}$ + 4° (*c* 0.5, MeOH); ^{1}H NMR (3:1 CD_3OD–D_2O): δ (assignments of aglycon protons are shown in italic) 7.90 (m, 1 H, NHCO), 5.66–5.78 (m, 1 H, H-5), 5.45 (br dd, 1 H, *J* 7.6, 15.1 Hz, H-4), 4.44, 4.34 (br d, 1 H each, *J* 7.6 and 7.8 Hz, H-1,1′), 3.20–4.35 (m), 2.73–2.89 (m, 2 H), 0.80–2.20 (m, 46 H); HRMS Anal. Calcd for $C_{48}H_{84}O_{17}N_2Na$ [M + Na]: 983.5668. Found: 983.5686.

*2-(Trimethylsilyl)ethyl (2,3,4,6-tetra-*O*-acetyl-α-*D*-galactopyranosyl)-(1→4)-(2,3-di-*O*-acetyl-6-deoxy-6-trifluoroacetamido-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside* (**7a**).—Compound **6a** [3] (200 mg, 0.132 mmol) was treated with 0.5 M methanolic NaOMe for 18 h and the reaction mixture was neutralized with Duolite C436 (H^+) resin, filtered, and concentrated. The residue was chromatographed (SiO_2, 20:10:3 toluene–EtOAc–MeOH) and the product was dissolved in a mixture of EtOH (10 mL) and 0.1 M aqueous HCl (1.1 mL) and hydrogenated (Pd–C, H_2, 1 atm) for 14 h. The reaction mixture was filtered through Celite

and concentrated. The residue was dissolved in MeOH (10 mL) and Et_3N (0.05 mL), cooled to 0 °C, and CF_3COSEt (0.06 mL, 0.47 mmol) was added. The mixture was stirred under N_2 while slowly allowed to attain rt. After 6 h, toluene (5 mL) was added and the mixture was concd. The residue was treated with a 1:1 mixture of Ac_2O and pyridine (10 mL) for 16 h and the mixture was co-concd with toluene. The residue was chromatographed (1:1 EtOAc–heptane) to give **7a** (77 mg, 54%); $[\alpha]_D^{22}$ +59° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.64 (br d, 1 H, *J* 5.4 Hz, NH), 5.54 (br d, 1 H, *J* 3.2 Hz, H-4″), 5.34 (dd, 1 H, *J* 3.3, 11.0 Hz, H-3″), 5.23 (dd, 1 H, *J* 3.4, 11.0 Hz, H-2″), 5.16 (br t, 1 H, *J* 8.2 Hz, H-3), 5.10 (dd, 1 H, *J* 7.5, 10.5 Hz, H-2′), 4.97 (d, 1 H, *J* 3.4 Hz, H-1″), 4.94 (dd, 1 H, *J* 7.1, 8.2 Hz, H-2), 4.74 (dd, 1 H, *J* 2.6, 10.5 Hz, H-3′), 4.60 (d, 1 H, *J* 7.4 Hz, H-1′), 4.53 (d, 1 H, *J* 6.9 Hz, H-1), 4.49–4.55 (m, 1 H, H-6), 4.47 (br t, 1 H, *J* 7.1 Hz, H-5″), 4.18 (dd, 1 H, *J* 8.2, 10.8 Hz, H-6″), 4.04–4.14 (m, 3 H, H-4′,6″,6), 3.88–4.00 (m, 2 H, H-4 and OCH_2CH_2Si), 3.84 (ddd, 1 H, *J* 2.0, 8.7, 14.0 Hz, H-6′), 3.65–3.77 (m, 2 H, H-5,5′), 3.47–3.62 (m, 2 H, H-6′ and OCH_2CH_2Si), 2.14, 2.10, 2.09, 2.07, 2.06, 2.05, 1.98 (7 s, 27 H, OAc), 0.84–1.03 (m, 2 H, CH_2Si), 0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 171.12, 171.10, 171.0, 170.9, 170.6, 170.5, 170.4, 170.2, 169.4, 158.3 (q), 116.2 (q), 100.6, 100.5, 100.2, 78.4, 76.1, 73.8, 72.8, 72.7, 72.1, 69.14, 69.12, 68.3, 68.0, 67.5, 63.2, 61.0, 41.2, 21.4, 21.3, 21.25, 21.20, 21.19, 21.12, 21.06, 21.04, 20.97, 18.3, −1.0; HRMS Anal. Calcd for $C_{43}H_{62}O_{25}F_3NSiNa$ [M + Na]: 1100.3230. Found: 1100.3198.

*2-(Trimethylsilyl)ethyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-α-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside* (**7b**).—Compound **6b** [3] (220 mg, 0.144 mmol) was treated essentially as described in the preparation of **7a**, thus yielding **7b** (97 mg, 63%); $[\alpha]_D^{22}$ +28° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.55 (d, 1 H, *J* 8.5 Hz, NH), 5.56 (br d, 1 H, *J* 2.9 Hz, H-4″), 5.36 (dd, 1 H, *J* 3.1, 11.6 Hz, H-3″), 5.23 (t, 1 H, *J* 9.2 Hz, H-3), 5.13 (dd, 1 H, *J* 7.5, 10.9 Hz, H-2′), 5.06 (d, 1 H, *J* 3.5 Hz, H-1″), 4.83–4.90 (m, 2 H, H-3′,2), 4.57 (d, 1 H, *J* 7.5 Hz, H-1'), 4.55–4.62 (m, 2 H, incl. H-2″), 4.52 (br t, 1 H, *J* 6.5 Hz, H-5″), 4.47 (d, 1 H, *J* 8.0 Hz, H-1), 4.43 (dd, 1 H, *J* 6.0, 11.2 Hz), 4.04–4.17 (m, 3 H), 4.05 (d, 1 H, *J* 2.0 Hz, H-4′), 3.87–3.98 (m, 2 H), 3.76–3.83 (m, 2 H, incl. H-4), 3.64–3.70 (m, 1 H), 3.57 (dt, 1 H, *J* 6.5, 9.8 Hz, OCH_2CH_2Si), 2.16, 2.08, 2.07, 2.055, 2.050, 2.04, 2.025, 2.00 (8 s, 27 H, OAc), 0.84–1.01 (m, 2 H, CH_2Si), 0.00 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 171.4, 171.2, 170.74, 170.69, 170.6, 170.5, 170.4, 170.0, 169.5, 158.1 (q), 116.0 (q), 100.5, 100.2, 99.2, 75.3, 73.0, 72.9, 72.6, 72.1, 69.7, 67.9, 67.7, 67.6, 67.2, 63.2, 60.8, 60.6, 50.1, 21.27, 21.25, 21.17, 21.16, 21.10, 20.98, 20.97, 20.93, 18.3, −1.0; HRMS calcd for $C_{43}H_{62}O_{25}F_3NSiNa$ [M + Na]: 1100.3230, found 1100.3250.

*2-(Trimethylsilyl)ethyl (2,3,6-tri-*O*-acetyl-4-deoxy-4-trifluoroacetamido-α-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside* (**7c**).—Compound **6c** [3] (165 mg, 0.11 mmol) was treated essentially as described in the preparation of **7a**, thus yielding **7c** (112 mg, 67%); $[\alpha]_D^{21}$ +29° (c 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 6.75 (d, 1 H, *J* 9.2 Hz, NH), 5.38 (dd, 1 H, *J* 4.2, 11.1 Hz, H-3″), 5.20 (t, 1 H, *J* 9.1 Hz, H-3), 5.08 (dd, 1 H, *J* 7.7, 10.9 Hz, H-2′), 5.00 (d, 1 H, *J* 3.8 Hz, H-1″), 4.93 (dd, 1 H, *J* 3.8, 11.1 Hz, H-2″), 4.88 (dd, 1 H, *J* 8.0, 9.4 Hz, H-2), 4.82–4.89 (m, 1 H, H-4″), 4.69 (dd, 1 H, *J* 2.5, 10.9 Hz, H-3′), 4.60–4.65 (m, 1 H, H-5″), 4.53 (d, 1 H, *J* 7.7 Hz, H-1′), 4.50 (d, 1 H, *J* 7.9 Hz, H-1), 4.46 (dd, 1 H, *J* 2.0, 11.4 Hz, H-6), 4.42 (dd, 1 H, *J* 6.4, 11.0 Hz, H-6′), 4.24 (dd, 1 H, *J* 7.3, 11.6 Hz, H-6″), 4.18 (dd, 1 H, *J* 4.3, 11.7 Hz, H-6″), 4.15 (dd, 1 H, *J* 6.9, 11.0 Hz, H-6′), 4.11 (dd, 1 H, *J* 5.5, 11.8 Hz, H-6), 4.06 (br d, 1 H, *J* 2.3 Hz, H-4′), 3.95 (dt, 1 H, *J* 5.7, 9.8 Hz, OCH_2CH_2Si), 3.75–3.83 (m, 2 H, H-4,5′), 3.64 (ddd, 1 H, *J* 1.9, 5.4, 9.7 Hz, H-5), 3.57 (dt, 1 H, *J* 6.8, 9.8 Hz, OCH_2CH_2Si), 2.11, 2.090, 2.086, 2.075, 2.062, 2.059, 2.036, 2.00 (8 s, 27 H, OAc), 0.84–1.01 (m, 2 H, CH_2Si), 0.00 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 171.2, 171.1, 170.92, 170.90, 170.6, 170.14, 170.11, 169.4, 158.2 (q), 116.1 (q), 101.4, 100.3, 99.9, 78.1, 77.0, 73.8, 73.4, 72.8, 72.3, 72.1, 69.2, 69.15, 67.9, 67.7, 66.4,

62.8, 61.8, 61.7, 50.5, 21.4, 21.3, 21.22, 21.15, 21.12, 21.07, 21.0, 20.9, 18.3, −1.0; HRMS Anal. Calcd for $C_{43}H_{62}O_{25}F_3NSiNa$ [M + Na]: 1100.3230. Found: 1100.3247.

2-(Trimethylsilyl)ethyl (2,3,4-tri-O-acetyl-6-deoxy-6-trifluoroacetamido-α-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**7d**).—Compound **6d** [3] (51 mg, 0.033 mmol) was treated essentially as described in the preparation of **7a**, thus yielding **7d** (22.5 mg, 63%); $[\alpha]_D^{22}$ +49° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.40–7.48 (m, 1 H, NH), 5.45 (bd, 1 H, *J* 3.4 Hz, H-4″), 5.39 (dd, 1 H, *J* 3.4, 10.9 Hz, H-3″), 5.20 (t, 1 H, *J* 9.2 Hz, H-3), 5.15 (dd, 1 H, *J* 3.5, 10.9 Hz, H-2″), 5.12 (dd, 1 H, *J* 7.7, 11.1 Hz, H-2′), 5.02 (d, 1 H, *J* 3.5 Hz, H-1″), 4.91 (dd, 1 H, *J* 8.0, 9.5 Hz, H-2), 4.72 (dd, 1 H, *J* 2.2, 11.1 Hz, H-3′), 4.54 (d, 1 H, *J* 7.7 Hz, H-1′), 4.50 (d, 1 H, *J* 7.9 Hz, H-1), 4.39–4.51 (m, 3 H, H-5″,6′,6), 4.18 (dd, 1 H, *J* 6.8, 11.1 Hz, H-6′), 4.14 (dd, 1 H, *J* 5.4, 11.8 Hz, H-6), 4.03 (br d, 1 H, *J* 2.1 Hz, H-4′), 3.97 (dt, 1 H, *J* 5.7, 10.2 Hz, OCH_2CH_2Si), 3.76–3.86 (m, 3 H, H-4,5′,6″), 3.66 (ddd, 1 H, *J* 1.9, 5.3, 9.8 Hz, H-5), 3.58 (dt, 1 H, *J* 6.7, 9.9 Hz, OCH_2CH_2Si), 3.39 (br dt, 1 H, *J* 5.3, 13.5 Hz, H-6″), 2.20, 2.13, 2.11, 2.10, 2.095, 2.075, 2.06, 2.045, 1.99 (9 s, 27 H, OAc), 0.83–1.02 (m, 2 H, CH_2Si), 0.02 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 171.00, 170.97, 170.94, 170.8, 170.6, 170.4, 170.13, 170.10, 100.97, 100.5, 99.8, 77.6, 76.8, 73.6, 73.4, 73.0, 72.3, 72.1, 69.6, 69.4, 68.1, 68.0, 67.4, 62.7, 62.1, 39.0, 21.4, 21.3, 21.21, 21.19, 21.1, 18.3, −1.0; HRMS Anal. Calcd for $C_{43}H_{62}O_{25}F_3NSiNa$ [M + Na]: 1100.3230. Found: 1100.3210.

(2,3,4,6-Tetra-O-acetyl-α-D-galactopyranosyl)-(1→4)-(2,3-di-O-acetyl-6-deoxy-6-trifluoroacetamido-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranose (**8a**).—Compound **7a** (47 mg, 0.044 mmol) was dissolved in a mixture of CH_2Cl_2 (1 mL) and trifluoroacetic acid (2 mL) and stirred at rt for 40 min, then co-concd with *n*-propyl acetate (5 mL) and toluene (2 × 5 mL) [8]. The residue was chromatographed (3:1 EtOAc–heptane) to give **8a** (40.3 mg, 95%); HRMS Anal. Calcd for $C_{38}H_{50}O_{25}F_3NNa$ [M + Na]: 1000.2522. Found: 1000.2504.

(3,4,6-Tri-O-acetyl-2-deoxy-2-trifluoroacetamido-α-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranose (**8b**).—Compound **7b** (55 mg, 0.051 mmol) was treated essentially as described in the preparation of **8a**, thus yielding **8b** (47.1 mg, 94%); HRMS Anal. Calcd for $C_{38}H_{50}O_{25}F_3NNa$ [M + Na]: 1000.2522. Found: 1000.2526.

(2,3,6-Tri-O-acetyl-4-deoxy-4-trifluoroacetamido-α-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranose (**8c**).—Compound **7c** (90 mg, 0.083) was treated essentially as described in the preparation of **8a**, thus yielding **8c** (66 mg, 81%); HRMS Anal. Calcd for $C_{38}H_{50}O_{25}F_3NNa$ [M + Na]: 1000.2522. Found: 1000.2508.

(2,3,4-Tri-O-acetyl-6-deoxy-6-trifluoroacetamido-α-D-galactopyranosyl)-(1→4)-(2,3,6-tri-O-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-β-D-glucopyranose (**8d**).—Compound **7d** (54 mg, 0.05 mmol) was treated essentially as described in the preparation of **8a**, thus yielding **8d** (45.8 mg, 93%); HRMS Anal. Calcd for $C_{38}H_{50}O_{25}F_3NNa$ [M + Na]: 1000.2522. Found: 1000.2504.

(2,3,4,6-Tetra-O-acetyl-α-D-galactopyranosyl)-(1→4)-(2,3-di-O-acetyl-6-deoxy-6-trifluoroacetamido-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-α-D-glucopyranosyl trichloroacetimidate (**9a**).—Compound **8a** (64 mg, 0.065 mmol) was dissolved in a mixture of CH_2Cl_2 (3 mL) and Cl_3CCN (0.20 mL, 2 mmol) and cooled to 0 °C under N_2. Diazabicycloundecane (DBU, 0.020 mL, 0.13 mmol) was added and after 1 h the reaction mixture was concd. The residue was chromatographed (1:1 EtOAc–heptane, 3% Et_3N) to give **9a** (61 mg, 83%; purity: ~90%). ^1H NMR ($CDCl_3$): δ 8.66 (s, 1 H, =NH), 7.64 (br d, 1 H, *J* 5.7 Hz, NHCO), 6.49 (d, 1 H, *J* 4.1 Hz, H-1), 5.54 (br d, 1 H, *J* 3.1 Hz, H-4″), 5.44 (br t, 1 H, *J* 8.0 Hz, H-3), 5.35 (dd, 1 H, *J* 3.3, 11.0 Hz, H-3″), 5.29 (dd, 1 H, *J* 4.2, 8.4 Hz, H-2), 5.24 (dd, 1 H, *J* 3.4, 11.0 Hz, H-2″), 5.13 (dd, 1 H, *J* 7.5, 10.5 Hz, H-2′), 4.98 (d, 1 H, *J* 3.3 Hz, H-1″), 4.77 (dd, 1 H, *J* 2.7, 10.4 Hz, H-3′), 4.64 (d, 1 H, *J* 7.5 Hz, H-1′), 4.40–4.51 (m, 2 H, incl. H-5″), 4.05–4.24 (m, 5 H, incl. H-4′,5), 3.92–4.01 (m, 1 H, H-4), 3.72–3.89 (m,

2 H), 3.47–3.61 (m, 1 H), 2.15, 2.13, 2.115, 2.10, 2.09, 2.075, 2.070, 2.06, 1.99 (9 s, 27 H, OAc); ^{13}C NMR ($CDCl_3$): δ 171.1, 171.0, 170.9, 170.8, 170.54, 170.48, 170.2, 169.5, 161.1, 158.2 (q), 116.2 (q), 101.4, 100.2, 93.3, 78.4, 76.0, 73.6, 72.9, 71.4, 69.2, 69.1, 68.9, 68.3, 68.0, 67.4, 62.4, 60.9, 41.0, 21.33, 21.26, 21.2, 21.13, 21.07, 21.03, 21.00; HRMS Anal. Calcd for $C_{40}H_{50}O_{25}N_2Cl_3F_3Na$ [M + Na]: 1143.1618. Found: 1143.1611.

*(3,4,6-Tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-*α*-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-*β*-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-*α*-*D*-glucopyranosyl trichloroacetimidate* (**9b**).—Compound **8b** (45 mg, 0.046 mmol) was treated essentially as described in the preparation of **9a**, thus yielding **9b** (37 mg, 73%); $[\alpha]_D^{22}$ +62° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.67 (s, 1 H, =NH), 7.43 (d, 1 H, *J* 8.4 Hz, NHCO), 6.49 (d, 1 H, *J* 3.8 Hz, H-1), 5.54–5.62 (m, 2 H, H-4″,3), 5.36 (dd, 1 H, *J* 3.1, 11.6 Hz, H-3″), 5.15 (dd, 1 H, *J* 7.5, 10.7 Hz, H-2′), 5.09 (d, 1 H, *J* 3.9 Hz, H-1″), 5.06 (dd, 1 H, *J* 3.8, 9.9 Hz, H-2), 4.87 (dd, 1 H, *J* 2.5, 10.8 Hz, H-3′), 4.63 (d, 1 H, *J* 7.6 Hz, H-1′), 4.44–4.65 (m, 4 H, incl. H-2″), 4.05–4.24 (m, 4 H), 4.05 (d, 1 H, *J* 2.2 Hz, H-4′), 3.80–3.96 (m, 3 H, incl. H-4), 2.17, 2.09, 2.085, 2.080, 2.06, 2.05, 2.015 (7 s, 27 H, OAc); ^{13}C NMR ($CDCl_3$): δ 171.4, 171.2, 170.8, 170.7, 170.6, 170.5, 170.4, 169.9, 169.4, 161.4, 100.8, 99.3, 93.3, 76.6, 75.3, 72.8, 71.9, 71.4, 70.7, 69.8, 69.6, 67.8, 67.7, 67.2, 62.6, 60.7, 60.4, 50.4, 21.31, 21.27, 21.22, 21.11, 21.00, 20.98, 20.95, 20.9; HRMS Anal. Calcd for $C_{40}H_{50}O_{25}N_2Cl_3F_3Na$ [M + Na]: 1143.1618. Found: 1143.1606.

*(2,3,6-Tri-*O*-acetyl-4-deoxy-4-trifluoroacetamido-*α*-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-*β*-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-*α*-*D*-glucopyranosyl trichloroacetimidate* (**9c**).—Compound **8c** (65 mg, 0.066 mmol) was treated essentially as described in the preparation of **9a**, thus yielding **9c** (61 mg, 83%); $[\alpha]_D^{22}$ +197° (*c* 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.07 (s, 1 H, =NH), 6.60 (br d, 1 H, *J* 9.0 Hz, NHCO), 6.50 (d, 1 H, *J* 3.7 Hz, H-1), 5.58 (t, 1 H, *J* 9.6 Hz, H-3), 5.41 (dd, 1 H, *J* 4.1, 11.2 Hz, H-3″), 5.07–5.14 (m, 2 H, H-2′,2), 5.05 (d, 1 H, *J* 3.8 Hz, H-1″), 4.93 (dd, 1 H, *J* 3.7, 11.2 Hz, H-2″), 4.86 (br dd, 1 H, *J* 3.7, 9.2 Hz, H-4″), 4.73 (dd, 1 H, *J* 2.3, 10.8 Hz, H-3′), 4.62–4.67 (m, 1 H), 4.57 (d, 1 H, *J* 7.8 Hz, H-1′), 4.45–4.52 (m, 2 H), 4.11–4.31 (m, 6 H, incl. H-5), 4.04 (br d, 1 H, *J* 2.2 Hz, H-4′), 3.89 (t, 1 H, *J* 9.2 Hz, H-4), 3.80 (t, 1 H, *J* 6.9 Hz), 2.12, 2.110, 2.105, 2.100, 2.08, 2.065, 2.055, 2.025, 2.02 (9 s, 27 H, OAc); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.9, 170.8, 170.6, 170.1, 169.4, 161.4, 158.3 (q), 116.1 (q), 101.5, 99.9, 93.3, 78.1, 76.5, 73.4, 72.1, 71.3, 70.33, 70.26, 69.3, 67.7, 66.4, 62.1, 61.7, 61.6, 50.6, 21.4, 21.3, 21.21, 21.15, 21.1, 21.0; HRMS Anal. Calcd for $C_{40}H_{50}O_{25}N_2Cl_3F_3Na$ [M + Na]: 1143.1618. Found: 1143.1611.

*(2,3,4-Tri-*O*-acetyl-6-deoxy-6-trifluoroacetamido-*α*-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-*β*-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-*α*-*D*-glucopyranosyl trichloroacetimidate* (**9d**).—Compound **8d** (45 mg, 0.046 mmol) was treated essentially as described in the preparation of **9a**, thus yielding **9d** (42.9 mg, 83%; purity: >90%). ^{1}H NMR ($CDCl_3$): δ 8.67 (s, 1 H, =NH), 7.35–7.44 (m, 1 H, NHCO), 6.50 (d, 1 H, *J* 3.8 Hz, H-1), 5.55 (t, 1 H, *J* 9.7 Hz, H-3), 5.45 (br d, 1 H, *J* 3.2 Hz, H-4″), 5.39 (dd, 1 H, *J* 3.4, 10.9 Hz, H-3″), 5.10–5.18 (m, 2 H, H-2′,2″), 5.08 (dd, 1 H, *J* 3.8, 10.2 Hz, H-2), 5.03 (d, 1 H, *J* 3.5 Hz, H-1″), 4.71 (dd, 1 H, *J* 2.0, 11.1 Hz, H-3′), 4.56 (d, 1 H, *J* 7.7 Hz, H-1′), 4.37–4.53 (m, 3 H, incl. H-5″), 4.10–4.24 (m, 3 H), 4.04 (br d, 1 H, *J* 1.9 Hz, H-4′), 3.76–3.91 (m, 3 H, incl. H-4,6″), 2.19, 2.12, 2.105, 2.100, 2.07, 2.06, 2.02, 1.99 (8 s, 27 H, OAc); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.9, 170.8, 170.6, 170.1, 170.0, 161.4, 158.0 (q), 116.0 (q), 101.2, 99.8, 93.3, 77.6, 76.3, 73.6, 72.4, 71.4, 70.2, 70.0, 69.5, 69.4, 68.2, 68.1, 67.4, 62.04, 61.99, 39.1, 21.4, 21.3, 21.2, 21.11, 21.06, 20.9; HRMS Anal. Calcd for $C_{40}H_{50}O_{25}N_2Cl_3F_3Na$ [M + Na]: 1143.1618. Found: 1143.1621.

*(2*S*,3*R*,4*E*)-2-Azido-3-benzoyloxyoctadec-4-enyl (2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-(1→4)-(2,3-di-*O*-acetyl-6-deoxy-6-trifluoroacetamido-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside* (**10a**).—Compound **9a** (6.5 mg, 0.006 mmol) and (2*S*,3*R*,4*E*)-2-azido-3-(benzoyloxy)-4-octadecen-1-ol [7] (5 mg, 0.012 mmol) were dissolved in dry CH_2Cl_2 (3 mL). Molecular sieves

AW-300 (100 mg) were added, the mixture was stirred for 20 min, and $BF_3{\cdot}OEt_2$ (0.0012 mL, 0.01 mmol) was added. The reaction mixture was stirred at rt for 1.5 h, filtered through Celite, washed with a saturated aqueous $NaHCO_3$, dried, and concd. The residue was chromatographed (1:1 EtOAc–heptane) to give **10a** (5 mg, 63%); $[\alpha]_D^{22}$ +44° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ (assignments of aglycon protons are shown in italic) 8.04–8.08 (m, 2 H, Ar–H), 7.56–7.63 (m, 2 H, NH and Ar–H), 7.44–7.50 (m, 2 H, Ar–H), 5.94 (dt, 1 H, *J* 6.8, 15.0 Hz, H-5), 5.63 (dd, 1 H, *J* 4.1, 8.1 Hz, H-3), 5.51–5.60 (m, 3 H, incl. H-4″, H-4), 5.35 (dd, 1 H, *J* 3.3, 11.1 Hz, H-3″), 5.24 (dd, 1 H, *J* 3.4, 11.1 Hz, H-2″), 5.21 (t, 1 H, *J* 7.6 Hz, H-3), 5.11 (dd, 1 H, *J* 7.5, 10. 5 Hz, H-2′), 4.95–5.01 (m, 2 H, H-1″, H-2), 4.75 (dd, 1 H, *J* 2.7, 10.5 Hz, H-3′), 4.61 (2 d, 1 H each, *J* 6.2, 7.5 Hz, H-1,1′), 4.43–4.52 (m, 2 H, incl. H-5″), 4.19 (dd, 1 H, *J* 8.2, 10.8 Hz), 4.07–4.14 (m, 2 H, incl. H-4), 4.04 (dd, 1 H, *J* 5.8, 12.0 Hz), 3.87–4.00 (m, 3 H, H-1, H-2, H-4), 3.84 (dq, 1 H, *J* 2.2, 14.1 Hz), 3.67–3.77 (m, 2 H), 3.62 (dd, 1 H, *J* 3.4, 10.1 Hz, H-1), 3.48–3.58 (m, 1 H), 2.15, 2.13, 2.12, 2.10, 2.07, 2.065, 2.055, 2.03, 1.995 (9 s, 27 H, OAc), 1.20–1.45 (m, 24 H,CH_2), 0.89 (t, 3 H, *J* 6.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 171.2, 171.0, 170.9, 170.6, 170.4, 170.3, 169.4, 165.5, 139.4, 133.7, 130.3, 130.2, 128.9, 123.1, 101.0, 100.9, 100.2, 78.5, 75.9, 75.0, 73.8, 73.3, 72.8, 72.7, 71.8, 69.2, 69.1, 68.9, 68.3, 68.0, 67.5, 63.9, 62.9, 60.9, 41.3, 32.8, 32.4, 30.1, 30.0, 29.83, 29.79, 29.6, 29.1, 23.1, 21.3, 21.2, 21.12, 21.08, 21.05, 20.96, 14.6; HRMS Anal. Calcd for $C_{63}H_{87}O_{27}F_3N_4Na$ [M + Na]: 1411.5407. Found: 1411.5432.

*(2*S,*3*R,*4*E*)-2-Azido-3-benzoyloxyoctadec-4-enyl (3,4,6-tri*-O-*acetyl-2-deoxy-2-trifluoroacetamido-α-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri*-O-*acetyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri*-O-*acetyl-β-*D*-glucopyranoside* (**10b**).—Compound **9b** (20 mg, 0.018 mmol) was treated essentially as described in the preparation of **10a**, thus yielding **10b** (16.3 mg, 65%); $[\alpha]_D^{22}$ +13° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ (assignments of aglycon protons are shown in italic) 8.03–8.08 (m, 2 H, Ar-H), 7.55–7.62 (m, 1 H, Ar–H), 7.43–7.50 (m, 3 H, Ar–H, NH), 5.93 (dt, 1 H, *J* 6.7, 14.9 Hz, H-5), 5.51–5.64 (m, 3 H, H-4″,4,3), 5.36 (dd, 1 H, *J* 3.1, 11.6 Hz, H-3″), 5.24 (t, 1 H, *J* 9.0 Hz, H-3), 5.14 (dd, 1 H, *J* 7.5, 10.8 Hz, H-2′), 5.07 (d, 1 H, *J* 3.5 Hz, H-1″), 4.93 (br t, 1 H, *J* 8.5 Hz, H-2), 4.87 (dd, 1 H, *J* 2.5, 10.8 Hz, H-3′), 4.49–4.63 (m, 5 H, incl. H-1,1′,2″,5″), 4.44 (dd, 1 H, *J* 5.9, 11.1 Hz), 4.01–4.19 (m, 4 H, incl. H-4′), 3.77–3.97 (m, 5 H, incl. H-4), 3.66–3.73 (m, 1 H), 3.60 (dd, 1 H, *J* 5.7, 10.3 Hz), 2.17, 2.085, 2.080, 2.06, 2.045, 2.03, 2.015 (7 s, 27 H, OAc), 1.21–1.43 (m, 24 H,CH_2), 0.89 (t, 3 H, *J* 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 171.3, 171.2, 170.74, 170.69, 170.65, 170.47, 170.4, 170.0, 169.5, 165.5, 139.5, 133.7, 130.3, 130.2, 128.9, 123.1, 100.6, 100.5, 99.2, 77.0, 75.3, 75.1, 73.2, 72.9, 72.7, 72.3, 72.1, 69.6, 68.7, 67.8, 67.7, 67.2, 63.9, 63.0, 60.7, 60.6, 50.2, 32.8, 32.4, 30.1, 30.0, 29.83, 29.79, 29.6, 29.1, 23.1, 21.3, 21.2, 21.1, 21.0, 14.6; HRMS Anal. Calcd for $C_{63}H_{87}O_{27}F_3N_4Na$ [M + Na]: 1411.5407. Found: 1411.5449.

*(2*S,*3*R,*4*E*)-2-Azido-3-benzoyloxyoctadec-4-enyl (2,3,6-tri*-O-*acetyl-4-deoxy-4-trifluoroacetamido-α-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri*-O-*acetyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri*-O-*acetyl-β-*D*-glucopyranoside* (**10c**).—Compound **9c** (17 mg, 0.015 mmol) was treated essentially as described in the preparation of **10a**, thus yielding **10c** (13.5 mg, 64%); $[\alpha]_D^{22}$ +14° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ (assignments of aglycon protons are shown in italic) 8.03–8.08 (m, 2 H, Ar–H), 7.55–7.62 (m, 1 H, Ar–H), 7.43–7.50 (m, 2 H, Ar–H), 6.65 (d, 1 H, *J* 9.2 Hz, NH), 5.93 (dt, 1 H, *J* 6.8, 15.0 Hz, H-5), 5.51–5.64 (m, 2 H, H-3,4), 5.39 (dd, 1 H, *J* 4.1, 11.1 Hz, H-3″), 5.21 (t, 1 H, *J* 8.9 Hz, H-3), 5.09 (dd, 1 H, *J* 7.8, 10.9 Hz, H-2′), 5.02 (d, 1 H, *J* 3.8 Hz, H-1″), 4.90–4.97 (m, 2 H, H-2,2″), 4.85 (br dd, 1 H, *J* 2.9, 9.0 Hz, H-4″), 4.71 (dd, 1 H, *J* 2.4, 10.9 Hz, H-3′), 4.60–4.66 (m, 1 H, H-5″), 4.55 (d, 2 H, *J* 7.7 Hz, H-1,1′), 4.40–4.50 (m, 2 H), 4.01–4.29 (m, 5 H, incl. H-4′,6″), 3.75–3.97 (m, 4 H, incl. H-2), 3.66 (ddd, 1 H, *J* 2.0, 5.4, 9.8 Hz), 3.59 (dd, 1 H, *J* 5.8, 10.3 Hz), 2.015, 2.045, 2.055, 2.07, 2.09, 2.10 (6 s, 27 H, OAc), 1.20–1.45 (m, 24 H, CH_2), 0.89 (t, 3 H, *J* 6.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 171.1, 171.0, 170.9, 170.8, 170.6, 170.2, 170.09, 170.08, 169.5, 165.5, 139.5,

133.7, 130.3, 130.2, 128.9, 123.1, 101.5, 100.7, 99.9, 78.1, 76.8, 75.1, 73.7, 73.3, 73.0, 72.1, 72.0, 69.21, 69.15, 68.8, 67.7, 66.3, 63.9, 62.5, 61.8, 61.7, 50.5, 32.8, 32.4, 30.11, 30.09, 30.08, 30.02, 29.83, 29.78, 29.6, 29.1, 23.1, 21.4, 21.2, 21.13, 21.07, 20.99, 20.96, 20.9, 14.6; HRMS Anal. Calcd for $C_{63}H_{87}O_{27}F_3N_4Na$ [M + Na]: 1411.5407. Found: 1411.5370.

*(2*S,*3*R,*4*E*)-2-Azido-3-benzoyloxyoctadec-4-enyl (2,3,4-tri*-O-*acetyl-6-deoxy-6-trifluoroacetamido-*α-D-*galactopyranosyl)-(1→4)-(2,3,6-tri*-O-*acetyl-β-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*acetyl-β-D-*glucopyranoside* (**10d**).—Compound **9d** (28 mg, 0.025 mmol) was treated essentially as described in the preparation of **10a**, thus yielding **10d** (22.5 mg, 64%); $[\alpha]_D^{22}$ +34° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (assignments of aglycon protons are shown in italic) 8.02–8.09 (m, 2 H, Ar–H), 7.55–7.62 (m, 1 H, Ar–H), 7.43–7.50 (m, 2 H, Ar–H), 7.37–7.43 (m, 1 H, H-6″ and NH), 5.93 (br dt, 1 H, *J* 6.7, 15.0 Hz, H-5), 5.61 (dd, 1 H, *J* 4.1, 8.1 Hz, H-3), 5.50–5.60 (m, 1 H, H-4), 5.45 (br d, 1 H, *J* 3.2 Hz, H-4″), 5.38 (dd, 1 H, *J* 3.4, 10.9 Hz, H-3″), 5.20 (t, 1 H, *J* 9.1 Hz, H-3), 5.08–5.17 (m, 2 H, H-2′,2″), 5.02 (d, 1 H, *J* 3.5 Hz, H-1″), 4.96 (dd, 1 H, *J* 7.7, 9.2 Hz, H-2), 4.71 (dd, 1 H, *J* 2.1, 11.1 Hz, H-3′), 4.55 (d, 1 H, *J* 7.7 Hz, H-1′), 4.54 (d, 1 H, *J* 7.7 Hz, H-1), 4.37–4.51 (m, 3 H, incl. H-5″), 4.17 (dd, 1 H, *J* 6.8, 11.2 Hz), 4.07 (dd, 1 H, *J* 5.4, 12.0 Hz), 4.03 (br d, 1 H, *J* 2.0 Hz, H-4′), 3.75–3.98 (m, 5 H, incl. H-2, and H-4,6″), 3.67 (ddd, 1 H, *J* 2.0, 5.4, 9.9 Hz, H-5 or H-5′), 3.60 (dd, 1 H, *J* 5.7, 10.3 Hz), 3.38 (br dt, 1 H, *J* 5.3, 13.6 Hz, H-6″), 2.19, 2.105, 2.09, 2.075, 2.06, 1.99 (6 s, 27 H, OAc), 1.20–1.45 (m, 24 H, CH_2), 0.89 (t, 3 H, *J* 6.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 171.03, 170.95, 170.9, 170.8, 170.6, 170.4, 170.1, 170.0, 165.5, 157.9 (q), 139.5, 133.7, 130.3, 130.2, 128.9, 123.1, 116.2 (q), 101.1, 100.8, 99.9, 76.6, 75.1, 73.4, 73.1, 72.4, 71.8, 69.5, 69.4, 68.8, 68.1, 67.4, 63.9, 62.5, 62.1, 39.0, 32.8, 32.4, 30.11, 30.09, 30.08, 30.01, 29.83, 29.78, 29.6, 29.1, 23.1, 21.4, 21.2, 21.07, 21.06, 14.6; HRMS Anal. Calcd for $C_{63}H_{87}O_{27}F_3N_4Na$ [M + Na]: 1411.5407. Found: 1411.5414.

*(2*S,*3*R,*4*E*)-2-(1-Adamantaneacetamido)-3-(benzoyloxy)-octadec-4-enyl (2,3,4,6-tetra*-O-*acetyl-α-D-galactopyranosyl)-(1→4)-(2,3-di*-O-*acetyl-6-deoxy-6-trifluoroacetamido-β-D-galactopyranosyl)-(1→4)-2,3,6-tri*-O-*acetyl-β-D-glucopyranoside* (**11a**).—Compound **10a** (7 mg, 0.005 mmol) was dissolved in a pyridine–water (6:1, 6 mL) mixture and cooled to 0 °C. H_2S was bubbled through the mixture for 1 h at 0 °C and the mixture was kept under H_2S for 44 h. Residual H_2S was removed with a stream of N_2 for 1 h, the mixture was concd with toluene, and the residue was kept under vacuum overnight. The residue was dissolved in CH_2Cl_2 (2 mL) and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide (EDC, 20 mg, 0.1 mmol) and 1-adamantaneacetic acid (20 mg, 0.1 mmol) were added. The reaction mixture was stirred at rt for 16 h and the solvent was removed. The residue was chromatographed (1:1 EtOAc–heptane) to give **11a** (5.8 mg, 75%); $[\alpha]_D^{22}$ +46° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ (assignments of aglycon protons are shown in italic) 8.00–8.05 (m, 2 H, Ar–H), 7.53–7.64 (m, 2 H, Ar–H and $NHCOCF_3$), 7.42–7.48 (m, 2 H, Ar–H), 5.90 (dt, 1 H, *J* 6.8, 15.2 Hz, H-5), 5.69 (d, 1 H, *J* 9.0 Hz, NH) 5.61 (t, 1 H, *J* 6.9 Hz, H-3), 5.53–5.56 (m, 1 H, H-4″), 5.51 (br dd, 1 H, *J* 7.3, 15.3 Hz, H-4), 5.35 (dd, 1 H, *J* 3.3, 11.0 Hz, H-3″), 5.23 (dd, 1 H, *J* 3.4, 11.0 Hz, H-2″), 5.16 (t, 1 H, *J* 7.7 Hz, H-3), 5.09 (dd, 1 H, *J* 7.5, 10.5 Hz, H-2′), 4.98 (d, 1 H, *J* 3.2 Hz, H-1″), 4.96 (dd, 1 H, *J* 6.4, 7.9 Hz, H-2), 4.74 (dd, 1 H, *J* 2.7, 10.5 Hz, H-3′), 4.58 (d, 1 H, *J* 7.3 Hz, H-1′), 4.56 (d, 1 H, *J* 6.2 Hz, H-1), 4.44–4.55 (m, 2 H, H-2 and H-5″), 4.38 (dd, 1 H, *J* 2.3, 11.9 Hz, H-6′), 4.19 (dd, 1 H, *J* 8.2, 10.8 Hz, H-6″), 4.08–4.13 (m, 2 H, incl. H-4′), 4.04 (dd, 1 H, *J* 4.2, 10.4 Hz, H-6″), 3.95 (dd, 1 H, *J* 6.0, 11.9 Hz, H-6′), 3.91 (br t, 1 H, *J* 8.2 Hz, H-4), 3.78–3.86 (m, 1 H), 3.74 (br d, 1 H, *J* 9.4 Hz), 3.61–3.69 (m, 2 H, incl. H-5′), 3.50–3.59 (m, 1 H), 1.90–2.16 (m, 32 H), 1.57–1.75 (m, 12 H), 1.20–1.40 (m, 24 H), 0.89 (t, 3 H, *J* 6.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 171.1, 170.9, 170.6, 170.2, 169.4, 165.7, 138.0, 133.5, 130.7, 130.0, 128.8, 124.9, 101.1, 100.9, 100.2, 78.4, 76.0, 74.3, 73.7, 73.3, 72.9, 72.8, 72.0, 69.2, 69.0, 68.3, 68.2, 68.0, 67.4, 63.0, 60.9, 52.3, 51.3, 48.5, 43.0, 42.7, 41.2, 37.1, 33.2, 32.8, 32.4, 30.1, 29.9, 29.8, 29.7, 29.3, 29.0, 23.1, 21.3, 21.2, 21.1, 21.0,

14.6; HRMS Anal. Calcd for $C_{75}H_{105}O_{28}F_3N_2Na$ [M + Na]: 1561.6704. Found: 1561.6681.

*(2*S*,3*R*,4*E*)-2-(1-Adamantaneacetamido)-3-(benzoyloxy)-octadec-4-enyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-α-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside* (**11b**).—Compound **10b** (16 mg, 0.012 mmol) was treated essentially as described in the preparation of **11a**, thus yielding **11b** (13.3 mg, 75%); $[\alpha]_D^{22}$ +29° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ (assignments of aglycon protons are shown in italic) 8.01–8.06 (m, 2 H, Ar–H), 7.54–7.61 (m, 1 H, Ar–H), 7.41–7.49 (m, 3 H, Ar–H and $NHCOCF_3$), 5.89 (br dt, 1 H, *J* 6.6, 15.3 Hz, H-5), 5.67 (d, 1 H, *J* 9.0 Hz, NH), 5.61 (br t, 1 H, *J* 6.8 Hz, H-3), 5.57 (br d, 1 H, *J* 2.7 Hz, H-4″), 5.50 (br dd, 1 H, *J* 7.2, 15.4 Hz, H-4), 5.36 (dd, 1 H, *J* 3.1, 11.6 Hz, H-3″), 5.23 (t, 1 H, *J* 9.1 Hz, H-3), 5.12 (dd, 1 H, *J* 7.5, 10.8 Hz, H-2′), 5.07 (d, 1 H, *J* 3.5 Hz, H-1″), 4.82–4.93 (m, 2 H, H-2,3′), 4.57 (d, 1 H, *J* 7.5 Hz, H-1′), 4.47 (d, 1 H, *J* 7.7 Hz, H-1), 4.40–4.63 (m, 5 H, incl. H-2″, H-2), 4.09–4.20 (m, 2 H), 4.05 (br d, 1 H, *J* 2.4 Hz, H-4′), 3.88–4.05 (m, 3 H), 3.79 (t, 1 H, *J* 9.3 Hz, H-4), 3.75–3.84 (m, 1 H), 3.62–3.70 (m, 2 H), 1.85–2.19 (m, 32 H), 1.56–1.76 (m, 12 H), 1.18–1.40 (m, 24 H), 0.89 (t, 3 H, *J* 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 171.3, 171.2, 170.9, 170.8, 170.7, 170.6, 170.5, 170.2, 170.1, 169.4, 165.6, 137.8, 133.5, 130.7, 130.1, 128.8, 125.0, 100.6, 100.4, 99.3, 77.3, 76.9, 75.5, 74.3, 73.2, 72.7, 72.6, 72.5, 72.1, 69.6, 68.0, 67.8, 67.7, 67.2, 63.0, 60.7, 60.6, 52.3, 51.3, 50.3, 43.0, 37.1, 33.2, 32.8, 32.4, 30.11, 30.05, 29.9, 29.8, 29.7, 29.3, 29.0, 23.1, 21.3, 21.2, 21.12, 21.08, 21.00, 20.97, 20.95, 14.6; HRMS Anal. Calcd for $C_{75}H_{105}O_{28}F_3N_2Na$ [M + Na]: 1561.6704. Found: 1561.6681.

*(2*S*,3*R*,4*E*)-2-(1-Adamantaneacetamido)-3-(benzoyloxy)-octadec-4-enyl (2,3,6-tri-*O*-acetyl-4-deoxy-4-trifluoroacetamido-α-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside* (**11c**).—Compound **10c** (13.3 mg, 0.01 mmol) was treated essentially as described in the preparation of **11a**, thus yielding **11c** (12.8 mg, 87%); $[\alpha]_D^{22}$ +24° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ (assignments of aglycon protons are shown in italic) 7.99–8.05 (m, 2 H, Ar–H), 7.54–7.60 (m, 1 H, Ar–H), 7.41–7.47 (m, 2 H, Ar–H), 6.66 (d, 1 H, *J* 9.1 Hz, $NHCOCF_3$), 5.89 (br dt, 1 H, *J* 6.7, 15.2 Hz, H-5), 5.67 (d, 1 H, *J* 9.0 Hz, NH), 5.59 (br t, 1 H, *J* 6.9 Hz, H-3), 5.50 (br dd, 1 H, *J* 7.3, 15.3 Hz, H-4), 5.38 (dd, 1 H, *J* 4.1, 11.1 Hz, H-3″), 5.19 (t, 1 H, *J* 9.1 Hz, H-3), 5.07 (dd, 1 H, *J* 7.7. 10.9 Hz, H-2′), 5.02 (d, 1 H, *J* 3.8 Hz, H-1″), 4.88–4.96 (m, 2 H, H-2,2″), 4.84 (br dd, 1 H, *J* 3.5, 9.0 Hz, H-4″), 4.70 (dd, 1 H, *J* 2.4, 10.9 Hz, H-3′), 4.59–4.65 (m, 1 H, H-5″), 4.51, 4.49 (d, 1 H each, *J* 7.5 and 7.6 Hz, H-1′ or H-1), 4.46–4.53 (m, 1 H), 4.44 (dd, 1 H, *J* 6.4, 11.1 Hz), 4.35 (br d, 1 H, *J* 12.0 Hz), 4.26 (dd, 1 H, *J* 7.4, 11.1 Hz, H-6″), 4.18 (dd, 1 H, *J* 4.1, 11.5 Hz, H-6″), 4.12 (dd, 1 H, *J* 7.1, 11.0 Hz), 3.94–4.06 (m, 3 H, incl. H-4′), 3.74–3.82 (m, 2 H, incl. H-4), 3.56–3.68 (m, 2 H), 1.85–2.13, 1.55–1.75, 1.20–1.40 (m, 68 H), 089 (t, 3 H, *J* 6.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 171.1, 171.0, 170.9, 170.8, 170.6, 170.2, 170.0, 169.5, 165.6, 137.9, 133.5, 130.7, 130.0, 128.8, 125.0, 101.4, 100.7, 99.9, 78.1, 76.8, 74.3, 73.4, 73.3, 73.0, 72.2, 72.1, 69.2, 68.0, 67.7, 66.3, 62.6, 61.7, 52.3, 51.3, 50.6, 43.0, 37.1, 33.2, 32.8, 32.4, 30.1, 29.9, 29.8, 29.7, 29.3, 29.0, 23.1, 21.4, 21.23, 21.15, 21.1, 21.0, 20.9, 14.6; HRMS Anal. Calcd for $C_{75}H_{105}O_{28}F_3N_2Na$ [M + Na]: 1561.6704. Found: 1561.6721.

*(2*S*,3*R*,4*E*)-2-(1-Adamantaneacetamido)-3-(benzoyloxy)-octadec-4-enyl (2,3,4-tri-*O*-acetyl-6-deoxy-6-trifluoroacetamido-α-*D*-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside* (**11d**).—Compound **10d** (20 mg, 0.014 mmol) was treated essentially as described in the preparation of **11a**, thus yielding **11d** (18.6 mg, 84%); $[\alpha]_D^{22}$ +45° (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ (assignments of aglycon protons are shown in italic) 7.99–8.06 (m, 2 H, Ar–H), 7.53–7.61 (m, 1 H, Ar–H), 7.39–7.48 (m, 3 H, Ar–H, $NHCOCF_3$), 5.89 (br dt, 1 H, *J* 6.6, 15.3 Hz, H-5), 5.67 (d, 1 H, *J* 9.1 Hz, NH), 5.60 (br t, 1 H, *J* 6.9 Hz, H-3), 5.45–5.54 (m, 1 H, H-4), 5.44 (br d, 1 H, *J* 3.3 Hz, H-4″), 5.38 (dd, 1 H, *J* 3.4, 10.9 Hz, H-3″), 5.18 (t, 1 H, *J* 9.2 Hz, H-3), 5.11–5.17

(m, 1 H, H-2″), 5.10 (dd, 1 H, *J* 7.7, 11.1 Hz, H-2′), 5.01 (d, 1 H, *J* 3.4 Hz, H-1″), 4.93 (dd, 1 H, *J* 7.9, 9.4 Hz, H-2), 4.70 (dd, 1 H, *J* 2.0, 11.0 Hz, H-3′), 4.51 (d, 1 H, *J* 7.8 Hz, H-1′), 4.49 (d, 1 H, *J* 7.8 Hz, H-1), 4.46–4.55 (m, 1 H, H-2), 4.32–4.46 (m, 3 H, incl. H-5″), 4.18 (dd, 1 H, *J* 6.7, 11.2 Hz, H-6″), 3.94–4.06 (m, 3 H, incl. H-4′), 3.74–3.86 (m, 3 H, incl. H-4,6″), 3.57–3.68 (m, 2 H), 3.32–3.42 (m, 1 H), 2.20–1.85 (m, 32 H), 1.55–1.75 (m, 12 H), 1.18–1.40 (m, 24 H), 0.89 (t, 3 H, *J* 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$): 171.00, 170.95, 170.9, 170.8, 170.6, 170.3, 170.1, 165.6, 157.9 (q), 138.0, 133.5, 130.7, 130.0, 128.8, 125.0, 116.2 (q), 101.0, 100.8, 99.8, 76.9, 76.5, 74.2, 73.4, 73.2, 73.1, 72.4, 72.1, 69.5, 69.4, 68.1, 68.0, 67.4, 62.5, 62.1, 52.3, 51.2, 43.0, 39.0, 37.1, 33.2, 32.8, 32.4, 30.10, 30.05, 29.9, 29.8, 29.7, 29.3, 29.0, 23.1, 21.4, 21.22, 21.19, 21.15, 21.07, 14.6; HRMS Anal. Calcd for $C_{75}H_{105}O_{28}F_3N_2Na$ [M + Na]: 1561.6704. Found: 1561.6696.

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