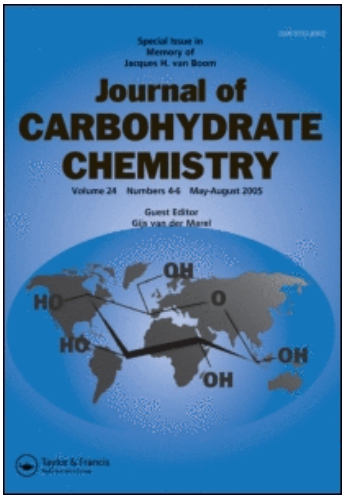

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Synthesis of Ganglioside Mimics for Binding Studies with Myelin-Associated Glycoprotein (MAG)

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Glycosylation of 3-*O*-unprotected 2-azido-2-deoxy-galactopyranoside (compound **5**) with O-(2,3-di-*O*-acyl-4,6-*O*-benzylidene-D-galactopyranosyl) trichloroacetimidates (compounds **4A**, **B**) as glycosyl donors afforded β (1–3)-linked disaccharides (**9A**, **B**) in high yield. Removal of the 2,3-*O*-acyl groups and selective 3-*O*-alkylation with α-benzyloxycarbonyl-alkyl triflates furnished the protected target molecules, which could be readily transformed into the desired ganglioside mimics.

Keywords Carbohydrate mimics, Glycosidation, *O*-Alkylation, Trifluoromethanesulfonates, MAG, Inhibition

INTRODUCTION

Damage of the central nervous system of higher vertebrates generally leads to persistent functional deficits. The first myelin protein that was characterized as an inhibitor of the required axonal neurite outgrowth after such events was myelin-associated glycoprotein (MAG).[1–3] MAG is a member of the "sialic acid-binding immunoglobulin-like lectin" (Siglec) family and binds to neurons in a sialic acid-dependent manner.[4] As neurite outgrowth inhibition is abolished either by desialylation of the neurons by sialidase or by including small sialic acid-bearing sugars to the cell cultures,[4] it has been assumed that MAG mediates neurite outgrowth inhibition by the interaction with gangliosides (sialic acid-containing glycosphingolipids),[5] which are the major

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Dedicated to the memory of late Professor Jacques H. van Boom.
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glycans on the surface of nerve cells and the major sialic acid-containing glycoconjugates in the brain.[6,7] Studies with these structurally diverse compounds led in binding studies to the conclusion that GQ1bα (Fig. 1, **A**) and the structurally derived GD1a (lacking Neu5Ac residues d and h) and GT1b (lacking Neu5Ac residue h) bind with high specificity and affinity to MAG.[8]

As concluded from these studies, the Neu5Acα(2–3)Galβ(1–3)GalNAc (Sch. 1, **B**) or the Neu5Acα(2–3)Galβ(1–3)[Neu5Acα(2–6)]GalNAc terminus (Sch. 1, **C**) is important to mediate neurite outgrowth inhibition.[8,9] Further investigations on the contribution of substructures of **B** and **C** led to further important features for MAG binding: the neuraminic acid moiety g, and particularly its carboxylate group, and the carboxylate group of neuraminic acid residue h are decisive for binding, and modifications at the functional groups of the Neu5Ac residues can also strongly influence the binding event.[5–12]

Because of the generally low binding affinity of carbohydrate epitopes to protein receptors and the observed poor bioavailability of carbohydrates,[13,14] carbohydrate mimics have been successfully employed to replace the natural structures.[13,15] For instance, the Neu5Ac residue has been substituted by mimics in the selectin research,[16] in the search for anti-influenza agents,[17] and in sialyltransferase inhibition studies.[18] In some studies, the α-anomerically linked Neu5Ac residue has been replaced by α-hydroxycarbonyl-alkyl residues.[16,19–21] Hence we have designed target compounds **1** and **2** (Sch. 1)

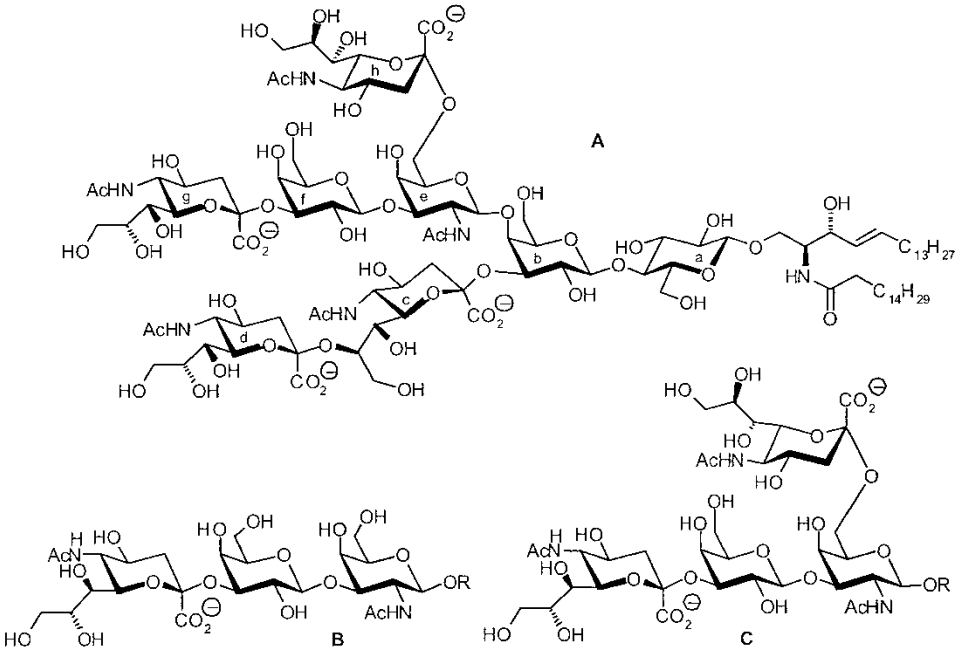
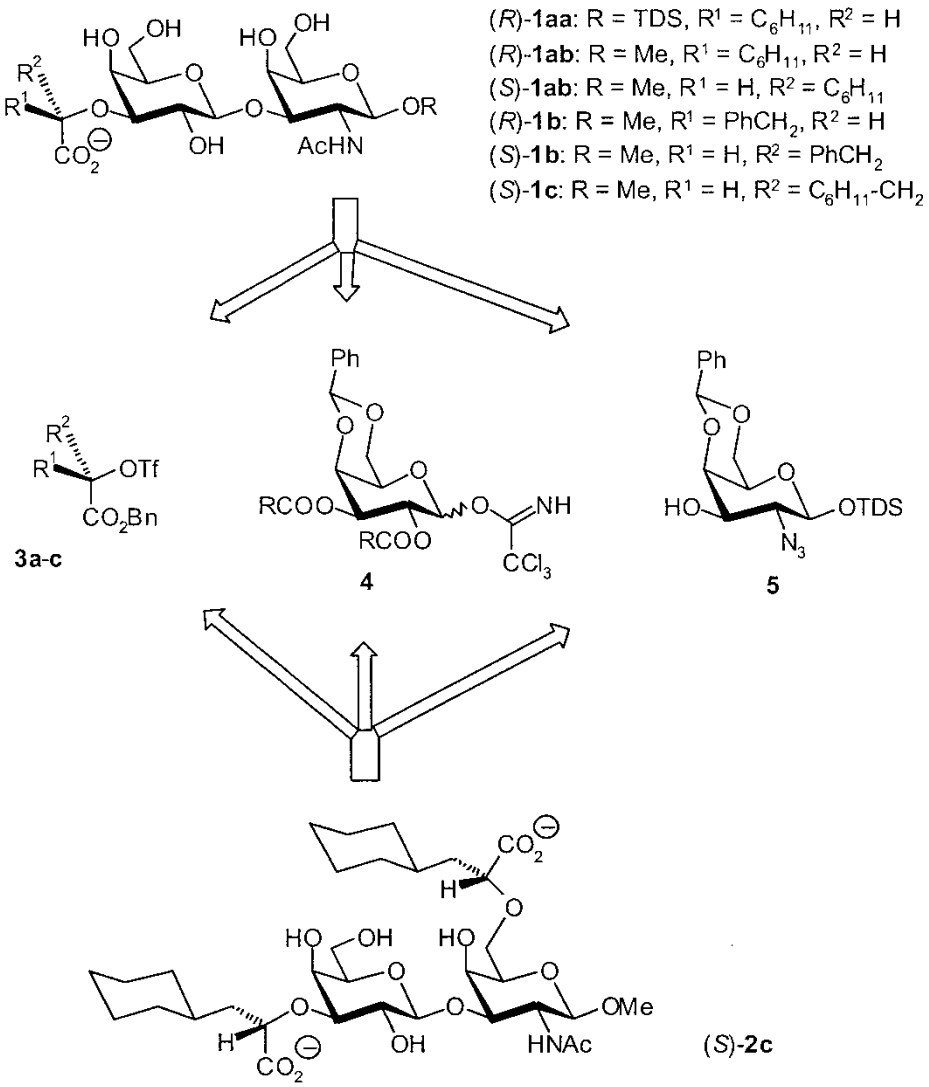


Figure 1: Structure of GQ1bα (**A**) and constituents **B** and **C**.



Scheme 1: Target molecules (*R*)-**1aa**, -**1ab**, -**1b** and (*S*)-**1ab**, -**1b**, -**1c** and disconnection into building blocks **3**–**5**.

in which the Neu5Ac residues are replaced by hexahydromandelic acid (**1aa**, **1ab**), phenyllactic acid (**1b**), and cyclohexyllactic acid (**1c**, **2c**).[22]

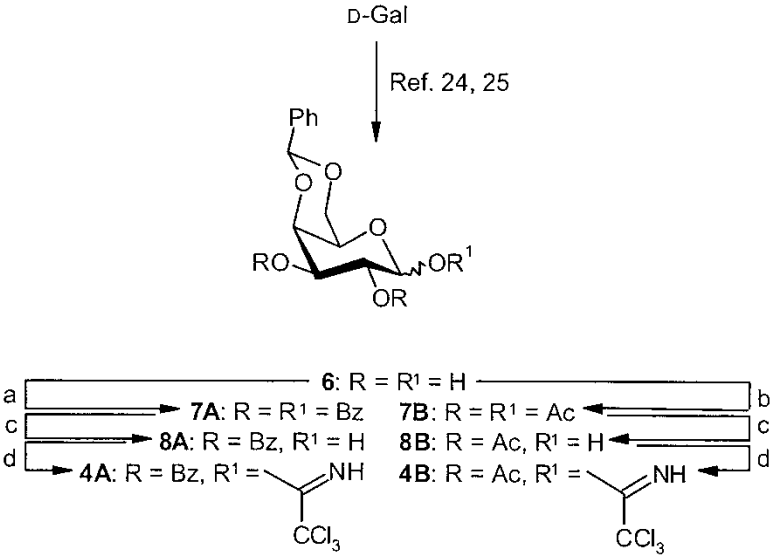
RESULTS AND DISCUSSION

The disconnection of the target molecules **1** and **2** leads to building blocks **4** and **5**, which are typical precursors for the construction of the Galβ(1–3)GalNAc

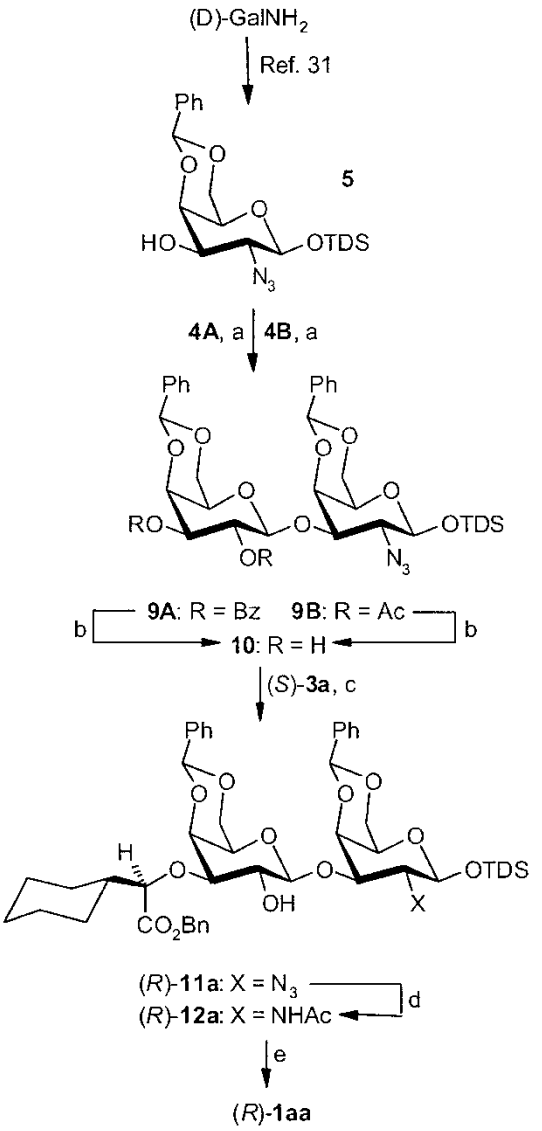
moiety, and to triflates **3a**–**c**. Triflates of this type were successfully employed by us for the construction of structurally related muramic acids[23] and later by others also in the synthesis of sLe^X mimetics.[16] The S_N2 mechanism of the reaction with sugar hydroxy groups could be ascertained.[23]

The synthesis of glycosyl donors **4A**, **B** (Sch. 2) followed essentially published procedures. Readily available 4,6-*O*-benzylidene-D-galactose (**6**)[24,25] was benzoylated or acetylated under standard conditions (→ **7A**,[26] **7B**[27]); regioselective 1-*O*-deacylation with hydrazinium acetate in DMF (→ **8A**,[28] **8B**[28–30]), and then treatment with trichloroacetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base afforded trichloroacetimidates **4A** and **4B**,[29,30] respectively, in high overall yields.

Glycosylation of known 3-*O*-unprotected acceptor **5**[31] (Sch. 3) with **4A** or **4B** in dichloromethane and trimethylsilyl trifluoro methanesulfonate (TMSOTf) as catalyst furnished disaccharides **9A** and **9B**, respectively, in very high yields. From the NMR coupling constants (1′-H: $J_{1',2'} \approx 8$ Hz) the $\beta(1-3)$-linkage could be assigned. Treatment of **9A**, **B** with NaOMe in methanol[32] led to 2′,3′-*O*-unprotected derivative **10**. For the regioselective 3′-*O*-alkylation of **10** with trifluoromethanesulfonate (*S*)-**3a**, which was readily obtained from benzyl (*S*)-hexahydromandelate,[33] dibutyltin oxide treatment in refluxing toluene was peRformed[34] and then (*S*)-**3a** was added, thus leading to (*R*)-**11a** in 47% yield. In addition, under loss of benzylalcohol, concomitant lactone formation with the 2′-hydroxy group occurred, thus



Scheme 2: Synthesis of glycosyl donors **4A** and **4B**. *Reagents and conditions*: (a) BzCl, pyr, DMAP (96%); (b) Ac_2O, Pyr (82%); (c) $N_2H_4 \cdot HOAc$, DMF (70%); (d) CCl_3-CN, DBU, CH_2Cl_2 (**4A**: 97%; **4B**: 94%).



Scheme 3: Synthesis of target molecule (*R*)-**1aa**. *Reagents and conditions*: (a) TMSOTf, CH_2Cl_2 (**9A**: 83%; **9B**: 89%); (b) NaOMe, $MeOH/CH_2Cl_2$ (70% from **9A**; 88% from **9B**); (c) Bu_2SnO, toluene; (*S*)-**3a**, CsF, DME (47% + lactone 24%); (d) propane-1,3-dithiol, pyr/H_2O, NEt_3; Ac_2O (90%); (e) Pd/C, H_2, $MeOH/HCO_2H$ (43%).

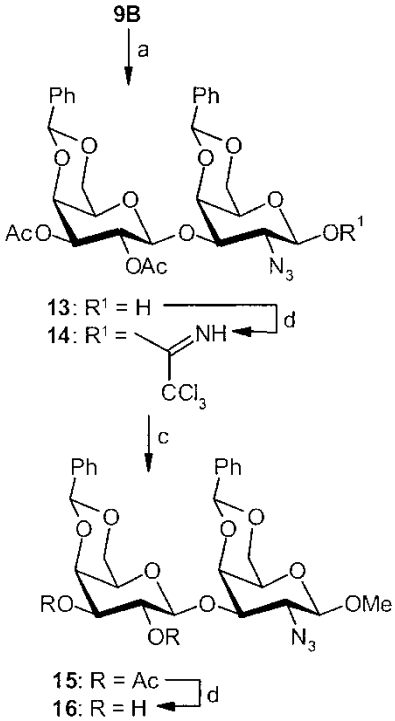
leading also to isolation of the lactone in 24% yield; the lactone could be transformed with alcoholate into the desired product. Azide group reduction in (*R*)-**11a** with propane-1,3-dithiol in pyridine/water in the presence of triethylamine[35] led to the amino compound from which, on acetylation with acetic anhydride, the acetylamino derivative (*R*)-**12a** was obtained. Hydrogenolytic

O-debenzylation and *O*-debenzylidenation with palladium on carbon (Pd/C)as catalyst gave target molecule (*R*)-**1aa**, which could be characterized by NMR and MS data (^{13}C NMR, δ 78.5, C-3; 81.8, C-3′).

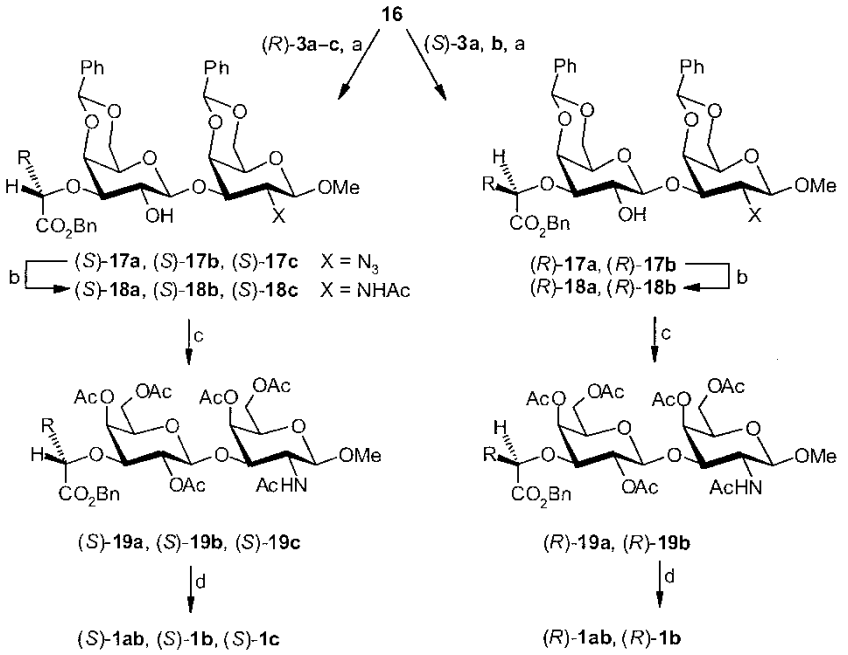
For the synthesis of target molecules (*R*)- and (*S*)-**1ab**, (*R*)- and (*S*)-**1b**, and (*S*)-**1c**, disaccharide **9B** was selectively desilylated by treatment with HF•pyridine complex in pyridine (→ **13**, Sch. 4).

Reaction with trichloroacetonitrile in dichloromethane in the presence of DBU as base afforded known trichloroacetimidate **14** in high yield;[36] **14** is a useful glycosyl donor in ganglioside synthesis. Here, reaction with methanol and tin(II) trifluoromethanesulfonate as catalyst in acetonitrile as solvent (use of the nitrile effect)[37] was carried out affording the desired β-glycoside **15** in good yield; no α-glycoside was found. Treatment of **15** with NaOMe in methanol[32] afforded the desired 2′,3′-*O*-unprotected disaccharide **16** in high overall yield.

Reaction of **16** with dibutyltin oxide in refluxing toluene[34] and then with the (*R*)-configurated trifluoromethanesulfonates **3a**–**c** or the (*S*)-configurated trifluoromethanesufonates **3a**, **b** afforded exclusively the 3′-*O*-alkylated derivatives (*S*)-**17a**–**c** and (*R*)-**17a**, **b**, respectively, in mainly very good yields (Sch. 5).



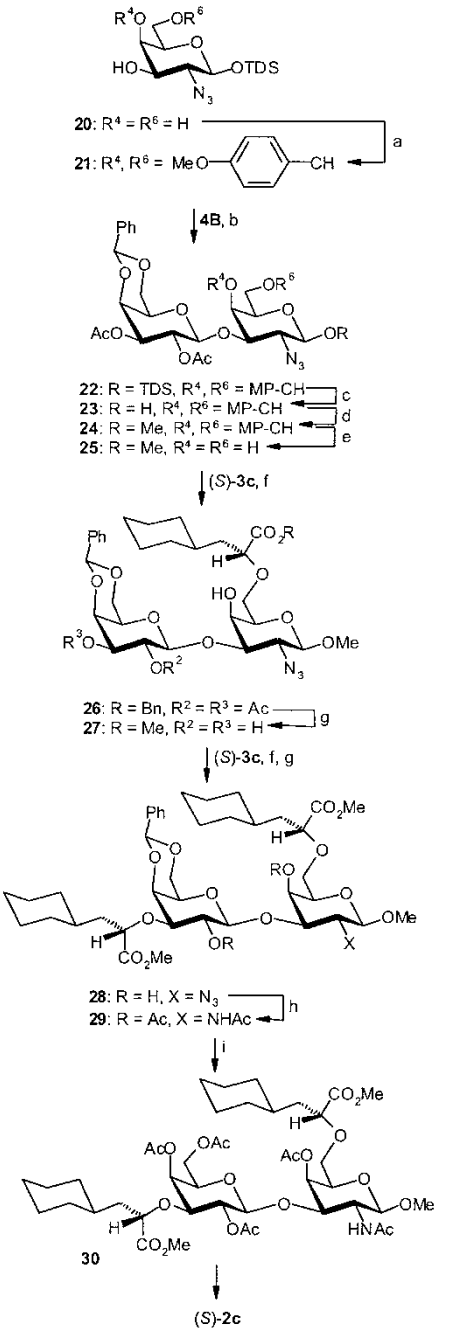
Scheme 4: Synthesis of acceptor **16**. *Reagents and conditions*: (a) HF · pyr, pyr (71%); (b) CCl_3–CN, DBU, CH_2Cl_2 (95%); (c) MeOH, $Sn(OTf)_2$, MeCN (59%); (d) NaOMe, $MeOH/CH_2Cl_2$ (88%).



Scheme 5: Synthesis of target molecules **1ab**, **1b**, and **1c**. R=C_6H_{11}, **a**; R=$PhCH_2$, **b**; R=C_6H_{11}–CH_2, **c**. *Reagents and conditions*: (a) Bu_2SnO, toluene; (*R*)-**3a-c**/(*S*)-**3a**, **b**, CsF, DME ((*S*)-**17a**: 59%; (*S*)**17b**: 73%; (*S*)-**17c**: 49% + lactone: 28%; (*R*)-**17a**: 80%; (*R*)-**17b**: 62%); (b) propane-1,3-dithiol, NEt_3, pyr H_2O; Ac_2O, pyr ((*S*)-**18a**: 83%; (*S*)-**18b**: 54%; (*S*)-**18c**: 75%; (*R*)-**18a**: 84%; (*R*)-**18b**: 43%); (c) EtSH, *p*-TsOH, CH2Cl2/MeOH; Ac2O, pyr ((*S*)-**19a**: 50%; (*S*)-**19b**: 53%; (*S*)-**19c**: 72%; (*R*)-**19a**: 28%; (*R*)-**19b**: 69%); (d) Pd/C, H_2, MeOH; NaOMe ((*S*)-**1ab**: 69%; (*S*)-**1b**: 86%; (*S*)-**1c**: 87%; (*R*)-**1ab**: 55%; (*R*)-**1b**: 90%).

Only the transformation of **16** with (*R*)-**3c** led also to lactone formation with the 2′-hydroxy group (yield: 28%). The connections in compounds (*S*)-**17a–c** and (R)-**17a**, **b** are again supported by the NMR and MS data (^{13}C NMR: $\delta \sim 77.5$, *C*-3; ~ 80.5, *C*-3′). Azide group reduction with propane-1,3-dithiol in the presence of triethylamine in pyridine/water[35] and then *N*-acetylation with acetic anhydride in pyridine afforded acetylamino derivatives (*S*)-**18a–c** and (*R*)-**18a**, **b**. Next the *O*-benzylidene groups were removed with ethylmercaptan in dichloromethane/methanol in the presence of p toluenesulfonic acid as catalyst;[38] ensuing per-*O*-acetylation furnished (*S*)-**19a–c** and (*R*)-**19a**, **b**. Hydrogenolytic *O*-debenzylation with Pd/C as catalyst and then treatment with NaOMe in methanol afforded the desired target compounds (*S*)-**1ab**, (*S*)-**1b**, (*S*)-**1c**, (*R*)-**1ab**, and (*R*)-**1b**.

For the synthesis of (*S*)-**2c** as mimetic of substructure **C** of GQ1bα (Fig. 1 and Sch. 1), a strategy was chosen that enables attachment of different Neu5Ac mimetics at the GalNAc residue and at the Gal residue. To this end, azidogalactoside **20** (Sch. 6), readily available from galactosamine via the same procedure as described for **5**,[31] was treated with 4-methoxybenzylidene



Scheme 6: Synthesis of target molecule (*S*)-**3a**. *Reagents and conditions*: (a) MeO–C_6H_4–$CH(OMe)_2$, *p*-TsOH, DMF (36%); (b) TMSOTf, CH_2Cl_2 (66%); (c) HF·pyr, pyr (59%); (d) CCl_3–CN, DBU, CH_2Cl_2; $Sn(OTf)_2$, MeOH CH_3CN (64%); (e) TFA/H_2O, CH_2Cl_2 (90%); (f) Bu_2SnO, toluene; (*S*)-**3c**, CsF, DME (85%); (g) NaOMe, MeOH (78%); (h) propane-1,3-dithiol, NEt_3, pyr, H_2O; Ac_2O, pyr (77%); (i) Et-SH, *p*-TsOH, CH_2Cl_2; Ac_2O, pyr (79%); (j) NaOMe, MeOH; LiOH, H_2O, MeOH (51%).

dimethylacetal in the presence of p-TsOH to afford the 4,6-*O*-(4-methoxybenylidene)-protected compound **21**. Glycosylation with galactosyl donor **4B** in the presence of TMSOTf as catalyst afforded the desired β-linked disaccharide **22** (^{1}H NMR: $J_{1',2'} = 7.9$ Hz). 1-*O*-Desilylation ($\rightarrow$ **23**), transformation into the trichloroacetimidate, and reaction with methanol, as described for **15**, afforded methyl glycoside **24**. Treatment with aqueous trifluoroacetic acid (TFA) led to selective removal of the 4-methoxybenzylidene group, thus furnishing 4,6-*O*-unprotected disaccharide **25** in high yield. Treatment of **25** with dibutyltin oxide in refluxing toluene and then with (*R*)-**3c** as alkylating agent in DME in the presence of CsF furnished selectively 6-*O*-alkylated compound **26**. Removal of the 2′,3′-*O*-acetyl group under Zemplén conditions[32] led also to transformation of the benzyl to the methyl ester **27**; following alkylation with (*R*)-**3c** under the above described conditions afforded protected target molecule **28**. Azide group reduction and acetylation with acetic anhydride in pyridine led to acetylamino derivative **29**. The 4′,6′-*O*-benzylidene group was removed with ethylmercaptan in the presence of p-TsOH as catalyst; ensuing acetylation gave compound **30**. De-*O*-acetylation under Zemplén conditions[32] and then methyl ester hydrolysis with LiOH in aqueous methanol led to liberation of target molecule (*S*)-**2c**.

All compounds could be characterized by NMR and MS data. The biologic evaluation of these compounds is under investigation.

In conclusion, mimics of the important ganglioside constituent Neu5Acα(2−3)Galβ(1−3)GalNAcβ(1-OR) could be readily obtained. The 3b-*O*-linked Neu5Ac residue was replaced by α-hydroxycarbonyl-alkyl groups, which could be attached via the corresponding trifluoromethanesulfonates as alkylating agents.

EXPERIMENTAL

General Procedures

Solvents were dried according to the standard procedures. NMR spectroscopic measurements were performed at 22°C with Bruker DRX600 and BrukerAC250 Cryospec instruments. TMS or the resonances of the deuterated solvents were used as internal standard. $CDCl_3$ ($\delta = 7.24$ ppm) was used as external standard; 85% of phosphoric acid was used as external standard for ^{31}P spectra. MALDI mass spectra were recorded with a Kratos Kompact Maldi II spectrometer; 2,5-dihydroxybenzoic acid (DHB) or *p*-nitroaniline and NaI were used as matrices for positive mode measurements, and trihydroxyacetophenone (THAP) was used as a matrix for negative mode measurements. Optical rotations were measured with a Perkin Elmer polarimeter 241/MS in a 1-dm cell at 22°C. Thin layer chromatography (TLC) was performed on Merck

silica gel 60 F_{254} plastic plates. Compounds were visualized by treatment with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (20 g) and $Ce(SO_4)_2$ (0.4 g) in 10% sulphuric acid (400 mL). Flash chromatography was peR$_f$ormed on J. T Baker silica gel 60 (0.040–0.063 mm) at a pressure of 0.3 bar.

Benzyl (*R*)-2-Trifluormethane sulfonyloxy-cyclohexylacetate ((*R*)-3a). Benzyl (*R*)-2-Hydroxy-cycloheylacetate. A solution of (*R*)-hexahydromandelic acid (10.0 g, 63.2 mmol) in MeOH/H_2O (9 : 1, 125 mL) was neutralized with Cs_2CO_3 (20%). Then the solvent was removed in vacuo and the residue was coevaporated with DMF (130 mL). The white salt was dissolved in dry DMF (65 mL) under argon and cooled to 0°C. Within 10 min benzyl bromide (6.76 mL, 9.73 g, 56.9 mmol) was added dropwise, then stirred for 2 hr at 0°C and for 14 hr at rt. After removal of the solvent the residue was dissolved in Et_2O (950 mL) and washed with H_2O (950 mL). The organic phase was washed with 1 M $NaHCO_3$ (3 × 320 mL) and with saturated NaCl (3 × 320 mL), and then dried over $MgSO_4$. Removal of the solvent furnished **3** (13.6 g, 54.9 mmol, 97%) as yellow oil; further purification was not required. TLC (toluene/ethyl acetate 12 : 1): $R_f = 0.48$. $[a]_D = +5.5$ (c = 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.14–1.74 (m, 11H, C_6H_{11}), 2.67 (d, $J_{H,OH} = 6.3$ Hz, 1H, OH), 4.06 (dd, $J_{H,OH} = 6.3$, $J_{vic} = 3.5$ Hz, 1H, C*H*C$_6$H$_{11}$), 5.22 (s, 2H, CH_2Ph), 7.35–7.38 (m, 5H, Ph). $C_{15}H_{20}O_3$ (248.3) Calcd.: C: 72.55, H: 8.12. Found: C: 72.27, H: 8.33.

(*R*)-3a. To a solution of **3** (13.2 g, 53.0 mmol) in dry CH_2Cl_2 (105 mL) under argon was added 2,6-lutidine (8.00 mL, 7.38 g, 68.9 mmol) and then cooled to −78°C. After 5 min Tf_2O (10.1 mL, 17.3 g, 61.2 mmol) was added. After 30 min at −78°C the reaction mixture was warmed to rt over a period of 1.5 hr and after further 45 min diluted with CH_2Cl_2 (1000 mL)and washed with H_2O (750 mL). The aqueous phase was then reextracted with CH_2Cl_2 (2 × 250 mL), the combined organic phases dried over $MgSO_4$, and the solvents removed in vacuo. The residue was dissolved in CH_2Cl_2/petroleum ether (1 : 1) and filtered over silica gel. Removal of the solvent furnished (*R*)-**3a** (19.4 g, 50.9 mmol, 96%) as orange oil, which could be used without further purification. TLC (petroleum ether/CH_2Cl_2 20 : 1): $R_f = 0.67$. $[a]_D = +34$ (c = 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.16–2.13 (m, 11H, C_6H_{11}), 4.96 (d, $J_{vic} = 4.3$ Hz, 1H, C*H*C$_6$H$_{11}$), 5.26 (s, 2H, CH_2Ph), 7.34–7.37 (m, 5H, Ph). $C_{16}H_{19}F_3O_5S$ (380.4) Calcd.: C: 50.52, H: 5.03. Found: C: 50.27, H: 5.04.

Benzyl (*S*)-2-Trifluormethansulfonyloxy-cyclohexylacetate ((*S*)-3a). Benzyl (*S*)-2-Hydroxy-cyclohexylacetate. A solution of (*S*)-hexahydromandelic acid (10.0 g, 63.2 mmol) in MeOH/H_2O (9 : 1, 125 mL) was neutralized with Cs_2CO_3 (20%). The solvent was removed in vacuo and the residue was coevaporated with DMF (130 mL).

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1,2,3-Tri-*O*-benzoyl-4,6-*O*-benzylidene-a/ß-D-galactopyranose (7A). A solution of **6** (2.76 g, 10.3 mmol) and pyridine (75 mL) was cooled to 4°C in ice/water. Then benzoyl chloride (4.21 mL, 5.10 g, 36.3 mmol) was added dropwise and also a pinch of DMAP. After 3 d at rt the solvent was removed in vacuo and the residue coevaporated twice with toluene.

Purification by flash chromatography (petroleum ether/ethyl acetate 2 : 1 to 1 : 1) furnished **7A** (5.08 g, 8.75 mmol, 85%) as colorless foam. The physical data are identical with the literature.[26]

2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-a/ß-D-galactopyranose (8A). A solution of **7A** (5.60 g, 9.65 mmol) and $N_2H_4 \cdot HOAc$ (1.33 g, 14.4 mmol) in dry DMF (30 mL) under argon was stirred for 3 hr at 45°C and then diluted with H_2O (3 × 50 mL) and extracted with ethyl acetate (100 mL). The aqueous phase was reextracted with ethyl acetate (2 × 50 mL), the combined organic

phases dried over $MgSO_4$, and the solvent removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate 9 : 1) furnished **8A** (1.31 g, 2.75 mmol, 29%) as colorless foam. The physical data are identical with the literature.[28]

***O*-(2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-a-D-galactopyranosyl) trichloracetimidate (4A).** To a solution of **8A** (1.84 g, 3.86 mmol) and dry CH_2Cl_2 (30 mL) under argon was added CCl_3CN (4.25 mL, 6.12 g, 43.3 mmol). After addition of DBU (5 drops) the reaction mixture was stirred for 45 min at rt, and then concentrated to approximately 5 mL. Purification by flash chromatography (petroleum ether/ethyl acetate 1 : 1 + 1% Et_3N) furnished **4A** (2.13 g, 3.43 mmol, 89%) as colorless foam. TLC (toluene/ethyl acetate 3 : 1): $R_f = 0.74$. $[a]_D = +159$(c = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ4.14 (d, $J_{6,6} = 11.6$ Hz, 1H, 6′-H), 4.17 (s,1H, 5-H), 4.41 (d, $J_{6,6} = 11.6$ Hz, 1H, 6-H), 4.77 (d, $J_{3,4} = 3.3$ Hz, 1H, 4-H), 5.60 (s, 1H, C*H*Ph), 5.85–6.09 (2dd, 2H, 2-H, 3-H), 6.88 (d, $J_{1,2} = 3.4$ Hz, 1H, 1-H), 7.32–8.03 (m, 15H, 3Ph), 8.59 (s, 1H, N*H*). MALDI-MS (positive mode, DHB): $[M + Na]^+$, $m/z = 642.1$; found: $m/z = 642.8$, $[M + K]^+$, $m/z = 658.2$; found: $m/z = 658.8$.

Thexyldimethylsilyl 2-Azido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside (5).[31] To a solution of thexyldimethylsilyl 2-azido-2-deoxy-β-D-galactopyranoside6 (10.0 g, 28.8 mmol) in dry DMF (250 mL) under argon was added benzaldehyde dimethylacetal (11.9 mL, 12.1 g, 79.5 mmol). Then p-TsOH (120 mg, 0.62 mmol) was added and stirred for 5 hr at 50°C. After cooling to rt the reaction mixture was neutralized with Et_3N (1.00 mL) and the solvent removed in high vacuo at 40°C. Purification by flash chromatography (petroleum ether/ethyl acetate 1 : 1) furnished **20** (7.86 g, 18.0 mmol, 63%) as colorless oil. The physical data are identical with the literature.[31]

Thexyldimethylsilyl *O*-(2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene -ß-D-galactopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside (9A). A solution of **4A** (1.10 g, 1.77 mmol) and **5** (670 mg, 1.54 mmol) in dry CH_2Cl_2 (75 mL) under argon was cooled to 0°C. After addition of TMSOTf (0.1 N, 0.77 mL, 0.05 eq.) the reaction mixture was stirred for 1 hr at rt, then neutralized with Et_3N (0.30 mL) and the solvent removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate 9 : 1) furnished **9A** (1.14 g, 1.27 mmol, 83%) as colorless foam. TLC (toluene/ethyl acetate 3 : 1): $R_f = 0.37$. $[a]_D = +45$ (c = 1,$CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ 0.17 (2 × s, 6H, Si(CH_3)$_2$), 0.85 (m, 12H, C(CH_3)),1.64 (m, 1H, C(CH$_3$)$_2$*H*), 3.34 (s, 1H, 5-H), 3.63 (m, 2H, 2-H, 3-H), 3.71 (s, 1H, 5′-H), 4.01(dd, $J_{5,6} = 1.5$, $J_{6,6} = 12.3$ Hz, 1H, 6-H), 4.18 (m, 2H, 6′-H, 6-H), 4.33 (d, $J_{3,4} = 2.1$ Hz, 1H, 4-H), 4.38 (dd, $J_{5,6} = 1.2$, $J_{6,6} = 12.5$ Hz, 1H, 6′-H), 4.53 (d, $J_{1,2} = 7.3$ Hz, 1H, 1-H), 4.61 (d, $J_{3,4} = 3.6$ Hz, 1H, 4′-H), 5.17 (d, $J_{1,2} = 8.0$ Hz, 1H, 1′-H), 5.36

(dd, $J_{3,4} = 3.6$, $J_{2,3} = 10.4$ Hz, 1H, 3′-H), 5.55 (s, 2H, 2C*H*Ph), 5.88 (dd, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, 1H, 2′-H), 7.18–8.02 (m, 20H, 4Ph). MALDI-MS (positive mode, DHB): $[M + Na]^+$, $m/z = 916.4$; found: $m/z = 917.0$,$[M + K]^+$, $m/z = 932.5$; found: $m/z = 932.7$. $C_{48}H_{55}N_3O_{12}Si$ (894.1) Calcd.: C: 64.48, H: 6.20, N: 4.70. Found: C: 63.92, H: 6.28, N: 4.62.

Thexyldimethylsilyl *O*-(2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-ß-D-galactopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside (9B). A solution of **4B** (4.72 g, 9.50 mmol) and **5** (3.77 g, 8.65 mmol) in dry CH_2Cl_2 (100 mL) under argon was cooled to 0°C. After addition of TMSOTf (0.1 N, 4.00 mL, 0.05 eq) the reaction mixture was stirred for 1 hr at 0°C, then neutralized with Et_3N (3.50 mL) and the solvent removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate 5 : 1) furnished **9B** (5.93 g, 7.70 mmol, 89%) as colorless foam. TLC (toluene/ethyl acetate 1 : 1): $R_f = 0.59$. $[a]_D = +45$ (c = 1,$CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.20 + 0.21 (2 × s, 6H, Si(C*H*$_3$)2), 0.89–0.91 (m,12H, C(C*H*$_3$)), 1.64–1.74 (m, 1H, C(CH$_3$)$_2$*H*), 2.06 + 2.07 (2 × s, 6H, 2 × COC*H*$_3$), 3.34 (s,1H, 5-H), 3.51–3.57 (m, 2H, 3-H, 5′-H), 3.71 (dd, $J_{1,2} = 7.5$, $J_{2,3} = 9.6$ Hz, 1H, 2-H), 3.99–4.33(m, 5H, 4-H, 6-H, 6-H, 6′-H, 6′-H), 4.38 (d, $J_{3,4} = 3.6$ Hz, 1H, 4′-H), 4.52 (d, $J_{1,2} = 7.5$ Hz, 1H,1-H), 4.88 (d, $J_{1,2} = 7.9$ Hz, 1H, 1′-H), 4.97 (dd, $J_{2,3} = 10.4$, $J_{3,4} = 3.6$ Hz, 1H, 3′-H), 5.42 (dd, $J_{1,2} = 7.9$, $J_{2,3} = 10.4$ Hz, 1H, 2′-H), 5.51 + 5.56 (2 × s, 2H, 2 × C*H*Ph), 7.32–7.57 (m, 10H, Ar). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 792.3$; found: $m/z = 792.2$, $[M + K]^+$, $m/z = 792.3$; found: $m/z = 792.2$. $C_{38}H_{51}N_3O_{12}Si$ (769.9) Calcd.: C: 59.28, H: 6.68, N: 5.46. Found: C: 59.17, H: 6.84, N: 5.69.

Thexyldimethylsilyl *O*-(4,6-*O*-Benzylidene-β-D-galactopyranosyl)-(1→3)-2-azido-4,6-*O*benzylidene-2-deoxy-β-D-galactopyranoside (10). To a solution of **9A** (1.16 g, 1.30 mmol) in dry MeOH/CH_2Cl_2 (1 : 1, 30 mL) under argon was added NaOMe (0.2 N, 0.50 mL). After 20 hr at rt the reaction mixture was neutralized with ion exchange resin IR 120 (H^+-Form) and the solvent removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate 2 : 1 to 1 : 1) furnished **10** (315 mg, 0.46 mmol, 35%) as colorless foam. TLC (toluene/ethyl acetate 1 : 1): $R_f = 0.16$. $[a]_D = +5.8$ (c = 0.57, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.22 (2 × s, 6H, Si(C*H*$_3$)$_2$), 0.91 (m, 12H, C(C*H*$_3$)), 1.69 (m, 1H, C(CH$_3$)$_2$*H*), 2.50 + 2.71 (m, 2H, 2 × O*H*), 3.36 (s, 1H, 5-H), 3.47 (s, 1H, 5′-H), 3.57 (dd, $J_{2,3} = 10.6$, $J_{3,4} = 3.5$ Hz, 1H, 3-H), 3.71 (s, 1H, 3′-H), 3.79–3.81 (m, 2H, 2′-H, 2-H), 4.02 (dd, $J_{6,6} = 12.3$, $J_{5,6} = 1.6$ Hz, 1H, 6-H), 4.09 (dd, $J_{6,6} = 12.3$, $J_{5,6} = 1.7$ Hz, 1H, 6′-H), 4.20 (d, $J_{3,4} = 3.9$ Hz, 1H, 4′-H), 4.25 (dd, $J_{6,6} = 12.3$, $J_{5,6} = 1.6$ Hz, 1H, 6-H), 4.29 (dd, $J_{6,6} = 12.3$, $J_{5,6} = 1.7$ Hz, 1H, 6′-H), 4.33 (d, $J_{3,4} = 3.5$ Hz,1H, 4-H), 4.57 (d, $J_{1,2} = 7.6$ Hz, 1H, 1-H), 4.59 (d, $J_{1,2} = 7.7$ Hz, 1H, 1′-H), 5.55 (s, 1H, C*H*Ph), 5.56 (s, 1H, C*H*Ph), 7.34–7.55 (m, 10H, 2Ph). ^{13}C NMR (150.9 MHz,

$CDCl_3$): δ 64.7 (2-C), 66.6 (5-C), 66.8 (5′-C), 69.1 (6-C), 69.2 (6′-C), 71.6 (2′-C), 72.3 (3′-C), 75.2 (4′-C), 75.4 (4-C), 77.5 (3-C), 97.3 (1-C), 101.2 (2 × *C*HPh), 104.0 (1′-C). MALDI-MS (positive mode, DHB): $[M + Na]^+$, $m/z = 708.3$; found: $m/z = 708.0$, $[M + K]^+$, $m/z = 724.4$; found: $m/z = 724.0$. $C_{34}H_{47}N_3O_{10}Si$ (685.8) Calcd.: C: 59.54, H: 6.91, N: 6.13. Found: C: 59.24, H: 6.80, N: 5.98.

Thexyldimethylsilyl *O*-(4,6-*O*-Benzylidene -3-*O*-[(R)-1-benzyloxycarbonyl-1-cyclohexylmethyl]-ß-D-galactopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside((*R*)-11a) and Thexyldimethylsilyl *O*-(4,6-*O*-Benzylidene-3-*O*-[(R)-1-carboxy-1-cyclohexylmethyl]-ß-D-galactopyranosyl-2b-lactone)-(1→3)-2-azido-4,6-*O*benzylidene-2-deoxy-ß-D-galactopyranoside (Lactone). To a mixture of **10** (261 mg, 0.38 mmol) and Bu_2SnO (113 mg, 0.45 mmol) under argon was added dry toluene (10 mL); the mixture was heated for 2 hr under reflux over molecular sieves (0.4 nm). After cooling to rt CsF (704 mg, 1.90 mmol), (*S*)-**3a** (723 mg, 1.90 mmol), and 1,2-dimethoxyethane (10 mL) were added to the pale yellow reaction mixture and stirred for 3 hr at rt, then diluted with $CHCl_3$ (40 mL) and washed with H_2O (2 × 30 mL). The aqueous phase was reextracted with$CHCl_3$ (2 × 30 ml), the combined organic phases dried over $MgSO_4$, and the solvent removed under vacuo. Purification by flash chromatography (toluene/ethyl acetate 7 : 1) furnished (*R*)-**11a** (164 mg, 0.18 mmol, 47%) as colorless, amorphous solid and **Lactone** (74 mg, 0.09 mmol, 24%) as colorless, amorphous solid.

(*R*)-**11a**. TLC (toluene/ethyl acetate 3 : 1): $R_f = 0.39$. $[\alpha]_D = +45$ (c = 0.67, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.20 + 0.23 (2 × s, 6H, Si(CH_3)$_2$), 0.90 (m, 12H, C(CH_3)), 1.02–1.75(m, 12H, CHC$_6$$H_{11}$, C(CH$_3$)$_2$$H$), 3.33–3.34 (m, 3H, 3′-H, 5-H, 5′-H), 3.57 (dd, $J_{2,3} = 10.6$, $J_{3,4} = 3.3$ Hz, 1H, 3-H), 3.82 (dd, $J_{1,2} = 7.7$, $J_{2,3} = 10.6$ Hz, 1H, 2-H), 3.88 (d, $J_{vic} = 5.4$ Hz, 1H, CHC$_6$H$_{11}$), 3.94 (dd, $J_{1,2} = 7.7$, $J_{2,3} = 8.5$ Hz, 1H, 2′-H), 4.00–4.30 (m, 6H, 4-H, 4′-H, 6-H, 6-H,6′-H, 6′-H), 4.55 (d, $J_{1,2} = 7.7$ Hz, 1H, 1-H), 4.61 (d, $J_{1,2} = 7.7$ Hz, 1H, 1′-H), 5.12 + 5.20 (2 × d, $J_{gem} = 12.1$ Hz, 2H, CO$_2$CH_2Ph), 5.50 (s, 1H, CH'Ph), 5.94 (s, 1H, CHPh), 7.31–7.53 (m, 15H, 3Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 64.7 (2-C), 66.6 (5-C, 5′-C), 68.9 (2′-C), 69.1(6-C), 69.4 (6′-C), 72.3 (4′-C), 75.3 (4-C), 76.7 (3-C), 80.3 (3′-C), 81.8 (*C*HC$_6$H$_{11}$), 97.3 (1-C), 100.7 (*C*'HPh), 101.0 (*C*HPh), 103.8 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 938.4$; found: $m/z = 938.2$, $[M + K]^+$, $m/z = 954.5$; found: $m/z = 954.1$. $C_{49}H_{65}N_3O_{12}Si$ (916.1) Calcd: C: 64.24, H: 7.15, N: 4.59. Found: C: 63.92, H: 7.45, N: 4.46.

Lactone. TLC (toluene/ethyl acetate 1 : 1): $R_f = 0.39$. $[\alpha]_D = +25$ (c = 0.36, $CHCl_3$). ^{1}H NMR(600 MHz, $CDCl_3$): δ 0.21 (2 × s, 6H, Si(CH_3)$_2$), 0.91 (m, 12H,

C(CH_3)), 1.08–1.75 (2 × m, 11H, $C_6H_{10}H$, $C(CH_3)_2H$), 1.98 (m, 1H, $C_6H_{10}H$), 3.34 (s, 1H, 5-H), 3.49 (s, 1H, 5′-H), 3.56(dd, $J_{2,3} = 10.7$, $J_{3,4} = 3.3$ Hz, 1H, 3-H), 3.66 (dd, $J_{2,3} = 9.7$, $J_{3,4} = 3.3$ Hz, 1H, 3′-H), 3.82 (dd, $J_{1,2} = 7.6$, $J_{2,3} = 10.7$ Hz, 1H, 2-H), 4.00 (dd, $J_{6,6} = 12.2$, $J_{5,6} = 1.1$ Hz, 1H, 6-H), 4.13 (dd, $J_{6,6} = 12.4$, $J_{5,6} = 1.0$ Hz, 1H, 6′-H), 4.22 (d, $J_{6,6} = 12.2$ Hz, 1H, 6-H), 4.28–4.33 (m, 4H, 6′-H, 4′-H, CHC$_6$H$_{11}$, 4-H), 4.54 (d, $J_{1,2} = 7.6$ Hz, 1H, 1-H), 4.60 (dd, $J_{1,2} = 7.9$, $J_{2,3} = 9.7$ Hz, 1H, 2′-H), 4.91 (d, $J_{1,2} = 7.9$ Hz, 1H, 1′-H), 5.53 + 5.59 (2 × s, 2H, 2 × CHPh), 7.31–7.53 (m, 10H, 2Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 64.8 (2-C), 66.7 (5-C), 66.8 (5′-C), 69.1 (6-C, 6′-C), 73.0 (3′-C), 73.3 (4′-C), 74.3 (2′-C), 75.3 (4-C), 77.1 (3-C), 81.0 (*C*HC$_6$H$_{11}$), 97.5 (1-C), 100.8 (1′-C), 100.5 + 101.8 (2 × *C*HPh). MALDI-MS (positive mode, DHB): $[M + Na]^+$, $m/z = 846.4$; found: $m/z = 846.0$.

Thexyldimethylsilyl *O*-(4,6-*O*-Benzylidene-3-*O*-[(R)-1-benzyloxycarbonyl-1-cyclohexylmethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene -2-deoxy-ß-D-galactopyranoside((*R*)-12a). To a solution of (*R*)-**11a** (150 mg, 0.16 mmol) and pyridine/H_2O (5 : 1, 9.25 mL) was added 1,3-propanedithiol (0.29 mL, 0.32 g, 2.93 mmol) and the pH value adjusted to 9–10 with Et_3N (0.3 mL). After 20 h at rt the solvent was removed in vacuo and the residue coevaporated with toluene/EtOH (5 : 1, 4 × 25 ml). The residue was dissolved in dry CH_2Cl_2 (8.00 mL) and Ac_2O (1.90 mL, 2.10 g, 20.5 mmol) added. After 6 h at rt the solvent was removed in vacuo and the crude product coevaporated with toluene (3 × 25 mL). Purification by flash chromatography (toluene/ethyl acetate 1 : 2) furnished (*R*)-**12a** (138 mg, 0.15 mmol, 90%) as colourless, amorphous solid. TLC (toluene/ethyl acetate 1 : 2): $R_f = 0.31$. MALDI-MS (positive mode, DHB): $[M + Na]^+$, $m/z = 954.5$; found: $m/z = 954.7$, $[M + K]^+$, $m/z = 970.6$; found: $m/z = 970.8$.

Thexyldimethylsilyl *O*-(3-*O*-[(R)-1-Hydroxycarbonyl-1-cyclohexylmethyl]-ß-D-galactopy ranosyl)-(1→3)-2-acetamido-2-deoxy-ß-D-galactopyranoside ((*R*)-1aa). To a solution of (*R*)-**12a** (50 mg, 54μmol) and dry MeOH (2.5 mL) was added Pd/C (10%, 15 mg) and stirred for 24 hr under H_2-atmosphere. If the starting material was not totally consumed, HCO_2H (0.10 mL) was added and the reaction mixture stirred for further 24 hr under H_2-atmosphere. The catalyst was filtered off over Celite; the reaction mixture was neutralized with NH_3 solution (1 : 100) and then concentrated under reduced pressure. Purification by flash chromatography ($CHCl_3$/MeOH/H_2O 30 : 20 : 1) furnished (*R*)-**1aa** (15 mg, 23μmol, 43%) as colorless, amorphous solid. TLC ($CHCl_3$/MeOH/H_2O 6 : 4 : 1): $R_f = 0.52$. ^{1}H NMR (600 MHz, d_6-DMSO): δ 0.07 (2 × s, 6H, Si(CH_3)$_2$), 0.76–0.81 (m, 12H, C(CH_3)), 1.07–1.73 (m, 15H, NHCOCH_3, CHC$_6H_{11}$, C(CH$_3$)$_2H$), 3.02 (d, $J_{2,3} = 9.7$ Hz, 1H, 3′-H), 3.22 + 3.28 (2 × m, 2H, 5-H, 5′-H), 3.41–3.52 (m, 5H, 2′-H, 6-H, 6-H, 6′-H, 6′-H), 3.67 (d, $J_{2,3} = 10.8$ Hz, 1H, 3-H), 3.73 (s, 1H, 4′-H), 3.77 (m, 1H, 2-H),

3.83–3.85 (m, 2H, 4-H, C*H*C_6H_{11}), 4.23 (d, $J_{1,2} = 7.6$ Hz, 1H, 1′-H), 4.52 (d, $J_{1,2} = 7.8$ Hz, 1H, 1-H), 7.55 (d, $J_{N,NH} = 9.0$ Hz, 1H, N*H*). ^{13}C NMR (150.9 MHz, d_6-DMSO): δ 52.0 (2-C), 59.9 (6-C, 6′-C), 64.5 (4′-C), 66.8 (4-C), 68.5 (2′-C),69.1 (*C*HC_6H_{11}), 74.9 + 75.0 (5-C, 5′-C), 78.5 (3-C), 81.8 (3′-C), 96.1 (1-C), 103.9 (1′-C). FAB-MS (positive mode, NBA): $[M + Na]^+$, $m/z = 688.3$; found: $m/z = 688$, $[M + 2Na\text{-}H]^+$, $m/z = 710.3$; found: $m/z = 710$, $[M + Na + K\text{-}H]^+$, $m/z = 726.4$; found: $m/z = 726$. FAB-MS (positive mode, NBA + NaI): $[M + 2Na\text{-}H]^+$, $m/z = 710.3$; found: $m/z = 710$. MALDI-MS (positive mode, DHB): $[M + Na]^+$, $m/z = 688.3$; found: $m/z = 688.6$, $[M + K]^+$, $m/z = 704.4$; found: $m/z = 704.7$.

Methyl *O*-(2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1 → 3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (15). A solution of **14**[38] (1.44 g, 186 mmol) and dry MeOH (0.18 mL, 0.14 g, 4.4 mmol) in dry CH_3CN (17.0 mL) was cooled under argon to −18°C and stirred for 2 hr at this temperature after adding $Sn(OTf)_2$-solution (0.1 N, 0.19 mL, 0.01 eq.). The reaction mixture was diluted with Et_2O (150 mL) and washed with saturated $NaHCO_3$ solution (90 mL) and H_2O (90 mL), and the organic phase was dried over $MgSO_4$. The solvent was evaporated under reduced pressure. Purification by flash chromatography (toluene/ethyl acetate 2 : 1 → 1 : 1) furnished **15** (710 mg, 1.11 mmol, 59%) as colorless foam. TLC (toluene/ethyl acetate 1 : 1): $R_f = 0.20$. $[\alpha]_D = +44$ (c = 0.92, $CHCl_2$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.05 + 2.07 (2 × s, 6H, 2 × COC*H*$_3$), 3.37 (s, 1H, 5-H), 3.54–3.64 (m, 5H, 3-H, 5′-H, OC*H*$_3$), 3.80 (dd, $J_{1,2} = 7.9$, $J_{2,3} = 10.5$ Hz, 1H, 2-H), 4.01–4.11 (m, 2H, 6-H, 6′-H), 4.18 (d, $J_{1,2} = 7.9$ Hz, 1H, 1-H), 4.27–4.38 (m, 4H, 4-H, 4′-H, 6-H, 6′-H), 4.90 (d, $J_{1,2} = 7.9$ Hz, 1H, 1′-H), 4.98 (dd, $J_{2,3} = 10.4$, $J_{3,4} = 3.6$ Hz, 1H, 3′-H), 5.43 (dd, $J_{1,2} = 7.9$, $J_{2,3} = 10.4$ Hz, 1H, 2′-H), 5.51 + 5.57 (2 × s, 2H, 2 × C*H*Ph), 7.29–7.56 (m, 10H, Ar). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 664.2$; found: $m/z = 664.2$, $[M + K]^+$, $m/z = 680.3$; gef.: $m/z = 680.1$. $C_{31}H_{35}N_3O_{12}$ (641.6) Calcd.: C: 58.03, H: 5.50, N: 6.55. Found: C: 58.09, H: 5.32, N: 7.13.

Methyl *O*-(4,6-*O*-Benzylidene-β-D-galactopyranosyl)-(1 → 3)-2-azido-4,6-*O*-benzylidene -2-deoxy-β-D-galactopyranoside (16). To a solution of **15** (710 mg, 1.11 mmol) and dry MeOH/CH_2Cl_2 (1 : 1, 40 mL) was added NaOMe solution (1.2 M, 1.50 mL) under argon. After18 hr at rt the solution was neutralized with ion exchange resin IR 120 (H^+-Form) and the solvent removed under reduced pressure. Purification by flash chromatography (toluene/acetone 1 : 1) furnished **16** as colorless amorphous solid. TLC (toluene/acetone 1 : 1):$R_f = 0.42$. $[a]_D = -98$ (c = 0.11, $CHCl_3$). ^{1}H NMR (600 MHz, d_6-DMSO): δ 3.36 (m, 1H, 2′-H), 3.47–3.51 (m, 5H, 3-b, 5-H, OC*H*$_3$), 3.57–3.61 (m, 2H, 2-H, 5′-H), 3.70 (dd, $J_{2,3} = 10.5$, $J_{3,4} = 3.0$ Hz, 1H, 3-H), 4.06–4.08 (m, 5H, 4′-H, 6-H, 6-H, 6′-H, 6′-H), 4.30 (d, $J_{3,4} = 3.0$ Hz,

1H,4-H), 4.36 (d, $J_{1,2} = 8.0$ Hz, 1H, 1-H), 4.47 (d, $J_{1,2} = 7.7$ Hz, 1H, 1′-H), 4.90 (d, $J_{H,OH} = 6.0$ Hz,1H, 3′-OH), 5.04 (d, $J_{H,OH} = 4.5$ Hz, 1H, 2′-OH), 5.56 + 5.63 (2 × s, 2H, 2 × C*H*Ph), 7.31–7.47(m, 10H, 2Ph). ^{13}C NMR (150.9 MHz, d_6-DMSO): δ 56.3 (O*C*H$_3$), 62.8 (2-C), 65.8 + 66.2 (5-C, 5′-C), 68.1 + 68.6 (6-C, 6′-C), 69.8 (2′-C), 71.7 (3′-C), 74.8 (4-C), 75.9 (4′-C), 76.9 (3-C), 99.5 + 99.8 (2 × *C*HPh), 102.0 (1-C), 104.7 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 580.2$; found: $m/z = 580.2$, $[M + K]^+$, $m/z = 596.3$; found: $m/z = 596.1$. $C_{27}H_{31}N_3O_{10}$ (557.6) Calcd.: C: 58.16, H: 5.60, N: 7.54. Found: C: 57.48, H: 5.94, N: 7.53.

Methyl *O*-(4,6-Benzylidene -3-*O*-[(R)-1-benzyloxycarbonyl-1-cyclohexylmethyl]-β-D-galactosylpyranosyl)-(1 → 3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside ((*R*)-17a). To a solution of **16** (116 mg, 0.21 mmol) and Bu_2SnO (66 mg, 0.26 mmol) was added dry toluene under argon and then heated for 1.5 hr under reflux over molecular sieves (0.4 nm). After cooling to rt CsF (402 mg, 1.04 mmol), (*S*)-**3a** (306 mg, 1.04 mmol) and 1,2-dimethoxyethane (4.00 mL) were added to the pale yellow reaction mixture and stirred for 2 hr at rt. Then it was diluted with $CHCl_3$ (30 mL) and washed with H_2O (2 × 20 mL). The aqueous phase was reextracted with $CHCl_3$ (2 × 20 mL), the combined organic phases dried over $MgSO_4$, and the solvent removed in vacuo. Purification by flash chromatography (toluene/acetone 2 : 1) furnished (*R*)-**17a** (131 mg, 0.17 mmol, 80%) as colorless amorphous solid. TLC (toluene/acetone 1 : 1): $R_f = 0.30$. $[a]_D = +39$ (c = 0.31, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.80–1.65 (m, 11H, C_6H11), 3.33 (m, 2H, 3-b, 5-H), 3.37 (s, 1H, 5′-H), 3.58(s, 3H, OC*H*$_3$), 3.64 (dd, $J_{2,3} = 10.5$, $J_{3,4} = 3.3$ Hz, 1H, 3-H), 3.88–4.05 (m, 5H, 2-H, 2′-H, 6-H,6′-H, C*H*C_6H_{11}), 4.12 (d, $J_{3,4} = 3.1$ Hz, 1H, 4′-H), 4.20 (d, $J_{1,2} = 8.0$ Hz, 1H, 1-H), 4.29–4.34(m, 3H, 4-H, 6-H, 6′-H), 4.62 (d, $J_{1,2} = 7.7$ Hz, 1H, 1′-H), 5.13 + 5.20 (2 × d, $J_{gem} = 12.1$ Hz, 2H, CO_2CH_2Ph), 5.49 + 5.55 (2 × s, 2H, 2 × C*H*Ph), 7.26–7.48 (m, 15H, 3Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 56.9 (O*C*H$_3$), 61.9 (2-C), 66.5 + 66.7 (5-C, 5′-C), 68.8 (2′-C), 68.9 + 69.2 (6-C, 6′-C), 72.2 (4′-C), 75.3 (4-C), 76.9 (3-C), 80.5 (3′-C), 81.6 (*C*HC_6H_{11}), 100.7 + 101.0 (2 × *C*HPh), 103.3 (1-C), 104.0 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 810.3$; found: $m/z = 810.4$, $[M + K]^+$, $m/z = 826.4$; found: $m/z = 826.4$. $C_{42}H_{49}N_3O_{12}$ (787.9) Calcd.: C: 64.03, H: 6.27, N: 5.33. Found: C: 64.03, H: 6.60, N: 5.44.

Methyl *O*-(4,6-*O*-Benzylidene-3-*O*-[(S)-1-benzyloxycarbonyl-1-cyclohexylmethyl]-β-D-galactopyranosyl)-(1 → 3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside ((*S*)-17a). As described for (*R*)-**17a** from **16** (125 mg, 0.22 mmol), Bu_2SnO (60 mg, 0.25 mmol), CsF (440 mg, 1.14 mmol), and (*R*)-**3a** (434 mg, 1.14 mmol), after flash chromatography (toluene/acetone 5 : 1) 102 mg (0.13 mmol, 59%) of (*S*)-**17a** were obtained as colorless oil. TLC

(toluene/acetone 1 : 1): $R_f = 0.42$. $[a]_D = -15$ (c = 0.40, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 0.80–1.81 (m, 11H, C_6H_{11}), 2.54 (d, $J_{H,OH} = 1.9$ Hz, 1H, OH), 3.29 (s, 1H, 5-H), 3.37–3.38 (m, 2H, 3′-H, 5′-H), 3.58–3.60 (m, 4H, 3-H, OCH_3), 3.85 (dd, $J_{1,2} = 8.2$, $J_{2,3} = 10.4$ Hz, 1H, 2-H), 4.00 (m, 3H, 2′-H, 6-H, 6′-H), 4.18–4.23 (m, 4H, 1-H, 4′-H, 6-H, CHC_6H_{11}),4.30–4.34 (m, 2H, 4-H, 6′-H), 4.52 (d, $J_{1,2} = 7.6$ Hz, 1H, 1′-H), 5.07 (2 × s, 2H, CO_2CH_2Ph), 5.42 + 5.54 (2 × s, 2H, 2 × $CHPh$), 7.31–7.52 (m, 15H, 3Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 57.1 (OCH_3), 62.0 (2-C), 66.8 + 66.9 (5-C, 5′-C), 68.9 + 69.0 (6-C, 6′-C), 71.2 (2′-C), 74.9 (4′-C), 75.4 (4-C), 77.5 (3-C), 79.3 (3′-C), 84.2 (CHC_6H_{11}), 100.6 + 101.1 (2 × $CHPh$), 103.3 (1-C), 104.3 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 810.3$; found: $m/z = 810.4$, $[M + K]^+$, $m/z = 826.4$; found: $m/z = 826.4$. $C_{42}H_{49}N_3O_{12}$ (787.9) Calcd.: C: 64.03, H:6.27, N: 5.33. Found: C: 64.25, H: 6.17, N: 5.50.

Methyl *O*-(4,6-*O*-Benzylidene-3-*O*-[(S)-1-benzyloxycarbonyl-2-phenylethyl]-ß-D-galactopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside ((*S*)-17b). As described for (*R*)-**17a** from **16** (125 mg, 0.22 mmol), Bu_2SnO (60 mg, 0.25 mmol), CsF (440 mg, 1.14 mmol), (*R*)-**3b**[33] (434 mg, 1.14 mmol), and 1,2-dimethoxyethane (1.50 mL), after flash chromatography (toluene/acetone 5 : 1) 127 mg (0.16 mmol, 73%) of (*S*)-**17b** were obtained as colorless oil. TLC (toluene/acetone 1 : 1): $R_f = 0.40$. $[a]_D = -4.0$ (c = 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 3.06 (dd, $J_{vic} = 8.0$, $J_{gem} = 13.9$ Hz, 1H, CHC*H*HPh), 3.11 (dd, $J_{vic} =$ Hz, $J_{gem} = 13.9$ Hz, 1H, CHCH*H*Ph), 3.30 + 3.36 (2 × s, 2H, 5-H, 5′-H), 3.46 (dd, $J_{2,3} = 9.7$, $J_{3,4} = 3.3$ Hz, 1H, 3′-H), 3.55–3.58 (m, 4H, 3-H, OCH_3), 3.82–3.90 (m, 2H, 2-H, 2′-H), 3.95–4.01 (m, 2H, 6-H, 6′-H), 4.18–4.21 (m, 3H, 1-H, 4′-H, 6′-H), 4.29–4.31 (m, 2H, 4-H, 6-H), 4.47 (d, $J_{1,2} = 7.7$ Hz, 1′-H), 4.75 (m, 1H, C*H*CHHPh), 5.05–5.09 (2 × d, 2H, $J_{gem} = 12.1$ Hz, CO_2CH_2Ph), 5.43 + 5.53 (2 × s, 2H, 2 × $CHPh$), 7.19–7.52 (m, 20H, 4Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 39.1 ($CHCH_2Ph$), 56.9 (OCH_3), 61.9 (2-C), 66.6 (5-C), 66.8 (5′-C),68.9 (6′-C), 69.0 (6-C), 71.1 (2′-C), 74.9 (4′-C), 75.3 (4-C), 77.7 (3-C), 79.1 (3′-C), 80.2 ($CHCH_2Ph$), 100.5 + 101.1 (2 × $CHPh$), 103.1 (1-C), 104.1 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 818.3$; found: $m/z = 818.1$, $[M + K]^+$, $m/z = 834.4$; found: $m/z = 834.3$. $C_{43}H_{45}N_3O_{12}$ (795.8) Calcd.: C: 64.90, H: 5.70, N: 5.28. Found: C: 64.27, H: 5.88, N: 5.23.

Methyl *O*-(4,6-*O*-Benzylidene-3-*O*-[(R)-1-benzyloxycarbonyl-2-phenylethyl]-ß-D-galactopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside ((*R*)-17b). As described for (*R*)-**17a** from **16** (90 mg, 0.16 mmol), Bu_2SnO (43 mg, 0.18 mmol), CsF (317 mg, 0.82 mmol), (*S*)-**3b**[33] (318 mg, 0.82 mmol), and 1,2-dimethoxyethane (1.50 mL), after flash chromatography (toluene/acetone 3 : 1) 79 mg (0.10 mmol, 62%) of (*R*)-**17b** were obtained as colorless amorphous solid. TLC (toluene/acetone 1 : 1): $R_f = 0.28$. $[a]_D = +20$

(c = 0.64, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 2.97 (dd, $J_{vic} = 9.5$, $J_{gem} = 14.0$ Hz, 1H, CHC*H*HPh), 3.09 (dd, $J_{vic} = 3.2$, $J_{gem} = 14.0$ Hz, 1H, CHCH*H*Ph), 3.19 (s, 1H, 5-H), 3.26 (dd, $J_{2,3} = 9.6$, $J_{3,4} = 3.2$ Hz, 1H, 3′-H), 3.35 (s, 1H, 5′-H), 3.57–3.60 (m, 5H, 3-H, 4′-H, OCH_3), 3.89–4.32 (m, 9H, 1-H, 2-H, 2′-H, 4-H, 6-H, 6′-H, C*H*CHHPh), 4.56 (d, $J_{1,2} = 7.6$ Hz, 1H, 1′-H), 5.09 (d, $J_{gem} = 12.1$ Hz, 1H, CO_2C*H*HPh), 5.20 (d, $J_{gem} = 12.1$ Hz, 1H, CO_2CH*H*Ph), 5.19 + 5.54 (2 × s, 2H, 2 × C*H*Ph), 7.09–7.43 (m, 20H, 4Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 39.4 (CH*C*H_2Ph), 56.9 (O*C*H_3), 62.0 (2-C), 66.4 + 66.7 (5-C, 5′-C), 68.9–69.0 (2′-C, 6-C, 6′-C), 72.9 (4′-C), 75.3 (4-C), 77.2 (3-C), 80.3 (*C*HCH$_2$Ph), 81.8 (3′-C), 100.6 + 100.9 (2 × *C*HPh), 103.2 (1-C), 103.9 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 818.3$; found: $m/z = 818.1$, $[M + K]^+$, $m/z = 834.4$; found: $m/z = 834.3$. $C_{43}H_{45}N_3O_{12}$ (795.8) Calcd.: C: 64.90, H: 5.70, N: 5.28. Found: C: 64.41, H: 5.28, N: 5.38.

Methyl *O*-(4,6-*O*-Benzylidene-3-*O*-[(S)-1-benzyloxycarbonyl-2-cyclohexylethyl]-ß-D-galactopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside ((*S*)-17c) and Methyl *O*-(4,6-*O*-benzylidene-3-*O*-[(S)-1-carboxy-2-cyclohexylethyl]-ß-D-galactopyranosyl-2b-lactone)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside (Lactone). To a solution of **16** (240 mg, 0.44 mmol) and Bu_2SnO (115 mg, 0.48 mmol) was added dry toluene (6.00 mL) under argon and the reaction mixture heated for 1.5 hr under reflux over molecular sieves (0.4 nm). After cooling CsF (850 mg, 2.19 mmol), (*R*)-**3c**[39] (850 mg, 2.19 mmol), and 1,2-dimethoxyethane (3.00 mL) were added to the pale yellow solution and stirred for 1.25 hr at rt. The reaction mixture was then diluted with $CHCl_3$ (40 mL) and washed with H_2O (2 × 25 mL). The aqueous phase was then reextracted with $CHCl_3$ (2 × 20 mL), the combined organic phases dried over $MgSO_4$, and the solvent removed in vacuo. Purification by flash chromatography (toluene/acetone 4 : 1) furnished (*S*)-**17c** (173 mg, 0.22 mmol, 49%) as colorless oil and **Lactone** (93 mg, 0.13 mmol, 28%). TLC (toluene/acetone 1 : 1): $R_f = 0.51$ ((*S*)-**17c**); $R_f = 0.26$ (**Lactone**). (*S*)-**17c**): $[a]_D = -3.2$ (c = 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 0.81–1.69 (m, 13H, C$H_2C_6H_{11}$), 3.30 (s, 1H, 5′-H),3,38 (s, 1H, 5-H), 3.45 (dd, $J_{2,3} = 9.8$, $J_{3,4} = 3.0$ Hz, 1H, 3′-H), 3.58–3.61 (m, 4H, 3-H, OCH_3), 3.87 (dd, $J_{1,2} = 8.1$, $J_{2,3} = 10.5$ Hz, 1H, 2-H), 3.97–4.02 (m, 3H, 2′-H, 6-H, 6′-H), 4.20–4.24 (m,3H, 1-H, 4′-H, 6′-H), 4.30 (d, $J_{6,6} = 12.6$ Hz, 1H, 6-H), 4.34 (d, $J_{3,4} = 3.1$ Hz, 1H, 4-H), 4.51(d, $J_{1,2} = 7.6$ Hz, 1H, 1′-H), 4.62 (dd, $J_{vic} = 3.9$, $J_{vic} = 9.1$ Hz, 1H, C*H*CH$_2$), 5.06 + 5.16 (2 × d, $J_{gem} = 12.2$ Hz, 2H, CO_2CH_2Ph), 5.47 + 5.55 (2 × s, 2H, 2 × C*H*Ph), 7.30–7.52 (m, 15H, 3Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 57.0 (O*C*H_3), 62.1 (2-C), 66.7 (5-C), 67.0 (5′-C), 68.9 (6-C), 69.0 (6′-C), 71.3 (2′-C), 75.2 (4′-C), 75.4 (4-C), 77.6 (3-C), 77.9 (*C*HCH$_2$), 78.7 (3′-C), 100.6 + 101.2 (2 × *C*HPh), 103.2 (1-C), 104.5 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 824.4$;

found: $m/z = 824.5$, $[M + K]^+$, $m/z = 840.5$; found: $m/z = 840.4$. $C_{43}H_{51}N_3O_{12}$ (801.9) Calcd.: C: 64.41, H: 6.41, N: 5.24. Found: C: 63.67, H: 6.35, N: 5.20.

Methyl *O*-(2-*O*-acetyl-4,6-*O*-Benzylidene-3-*O*-[(S)-1-benzyloxycarbonyl-1-cyclohexylmethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside ((*S*)-18a). To a solution of (*S*)-**17a** (38 mg, 48μmol) in pyridine/H_2O (5 : 1, 2.80 mL) was added 1,3-propanedithiol (0.10 mL, 0.11 g, 1.00 mmol) and the pH value adjusted with Et_3N (0.10 mL) to 9–10. After 3.75 hr at rt the solvent was removed in vacuo and the residue coevaporated with toluene (4 × 15 mL). The residue was then dissolved in pyridine (3.00 mL) and Ac_2O (0.90 mL, 1.00 g, 9.7 mmol) was added. After 48 hr at rt the solvent was evaporated in vacuo and the crude product coevaporated with toluene (3 × 10 mL). Purification by flash chromatography (toluene/acetone 2 : 1 to 1 : 2) furnished (*S*)-**18a** (34 mg, 40μmol, 83%) as colorless amorphous solid. TLC (toluene/acetone 2 : 1): $R_f = 0.14$. $[a]_D = -8.0$ (c = 0.30, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 1.02–1.74 (m, 11H, C_6H_{11}), 1.97 (s, 3H, $NHCOCH_3$), 2.03 (s, 3H, OAc), 3.26 (s, 1H, 5′-H), 3.40–3.44 (m, 2H, 3′-H, 5-H), 3.49 (s, 3H, OCH_3), 3.62 (m, 1H, 2-H), 3.77 (d, $J_{vic} = 6.2$ Hz, 1H, CHC_6H_{11}), 3.88 (d, $J_{6,6} = 11.5$ Hz, 1H, 6′-H), 4.03 (d, $J_{6,6} = 12.3$ Hz, 1H, 6-H), 4.14–4.16 (m, 2H, 4′-H, 6′-H), 4.29 (d, $J_{6,6} = 12.3$ Hz, 1H, 6-H), 4.37 (d, $J_{3,4} = 3.0$ Hz, 1H, 4-H), 4.51 (dd, $J_{2,3} = 11.2$, $J_{3,4} = 3.0$ Hz, 1H, 3-H), 4.70 (d, $J_{1,2} = 7.9$ Hz, 1H, 1′-H), 4.79 (d, $J_{1,2} = 8.2$ Hz, 1H, 1-H), 5.07 (s, 2H, CO_2CH_2Ph), 5.27 (dd, $J_{1,2} = 7.9$, $J_{2,3} = 9.3$ Hz, 1H, 2′-H), 5.32 + 5.53 (2 × s, 2H, 2 × $CHPh$), 5.83 (d, $J_{H,NH} = 6.3$ Hz, 1H, NH), 7.27–7.54 (m, 15H, 3Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 53.4 (2-C),56.6 (OCH_3), 66.5 (CO_2CH_2Ph), 66.7 (5-C, 5′-C), 69.1 (6′-C), 69.3 (6-C) 71.5 (2′-C), 74.2 (3-C), 74.6 (4′-C), 75.8 (4-C), 79.1 (3′-C), 85.6 (CHC_6H_{11}) 100.6 (1′-C), 100.8 (2 × $CHPh$),100.9 (1-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 868.4$; found: $m/z = 867.7$,$[M + K]^+$, $m/z = 884.4$; found: $m/z = 883.6$. $C_{46}H_{55}NO_{14} \cdot 0.5H_2O$ (854.9) Calcd.: C: 64.63, H:6.60, N: 1.64. Found: C: 64.36, H: 6.83, N: 1.81.

Methyl *O*-(2-*O*-Acetyl-4,6-*O*-benzylidene-3-*O*-[(R)-1-benzyloxycarbonyl-1-cyclohexylmethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-ß-D-alactopyranoside((*R*)-18a). To a solution of (*R*)-**17a** (32 mg, 41 μmol) in pyridine/H_2O (5:1, 2.35 mL) was added 1,3-propanedithiol (0.07 mL, 0.08 g, 0.71 mmol) and the pH value adjusted with Et_3N (0.10 mL) to 9–10. After 3.5 hr at rt the solvent was removed in vacuo andthe residue coevaporated with toluene (4 × 15 mL), dissolved in pyridine (2.50 mL) and Ac_2O(0.75 mL, 0.82 g, 8.1 mmol) was added. After 48 hr at rt the solvent was removed in vacuo and the crude product was coevaporated with toluene (3 × 15 mL). Purification by flash chromatography (toluene/acetone 3:2) furnished (*R*)-**18a** (29 mg, 34 μmol, 84%) as colorless amorphous solid. TLC (toluene/acetone 1:1): $R_f = 0.36$. $[a]_D = +62$ (c = 0.45, $CHCl_3$). 1H

NMR (600 MHz, $CDCl_3$): $\delta = 1.02-1.71$ (m, 11H, C_6H_{11}), 1.95 (s, 3H, $NHCOCH_3$), 2.00 (s, 3H, OAc),3.34 (s, 1H, 5′-H), 3.40 (s, 1H, 5-H), 3.50–3.52 (m, 4H, 3′-H, OCH_3), 3.60 (m, 1H, 2-H), 3.85(d, $J_{vic} = 5.3$ Hz, 1H, CHC_6H_{11}), 4.00–4.02 (m, 2H, 6-H, 6′-H), 4.15 (dd, $J_{3,4} = 3.0$, $J_{4,5} < 1$ Hz,1H, 4′-H), 4.22–4.27 (m, 2H, 6-H, 6′-H), 4.35 (dd, $J_{3,4} = 3.0$, $J_{4,5} < 1$ Hz, 1H, 4-H), 4.49 (dd, $J_{2,3} = 11.0$, $J_{3,4} = 3.0$ Hz, 1H, 3-H), 4.71 (d, $J_{1,2} = 8.0$ Hz, 1H, 1′-H), 4.82 (d, $J_{1,2} = 8.2$ Hz, 1H, 1-H), 5.06–5.13 (2 × d, $J_{gem} = 12.2$ Hz, 2H, CO_2CH_2Ph), 5.21 (dd, $J_{1,2} = 8.0$, $J_{2,3} = 8.8$ Hz, 1H, 2′-H), 5.46 + 5.51 (2 × s, 2H, 2 x CHPh), 5.92 (d, $J_{H,NH} = 6.2$ Hz, 1H, NH), 7.25–7.51 (m, 15H, 3Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 53.4 (2-C), 56.7 (OCH_3), 66.2 (5′-C), 66.4(CO_2CH_2Ph), 66.6 (5-C), 69.2 (6-C, 6′-C), 69.7 (2′-C), 71.5 (4′-C), 74.4 (3-C), 75.9 (4-C),77.0 (3′-C), 79.8 (CHC_6H_{11}) 100.5 (1′-C), 100.6 + 100.7 (CHPh), 100.8 (1-C). MALDI-MS(positive mode, CHCA): $[M + Na]^+$, $m/z = 868.4$; found: $m/z = 867.7$, $[M + K]^+$, $m/z = 884.4$; found: $m/z = 883.6$. $C_{46}H_{55}NO_{14}$ (845.9) Calcd.: C: 65.31, H: 6.55, N: 1.66. Found: C: 64.92,H: 6.78, N: 1.68.

Methyl *O*-(2-*O*-Acetyl-4,6-*O*-benzylidene-3-*O*-[(S)-1-benzyloxycarbonyl-2-phenylethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside((*S*)-18b). To a solution of (*S*)-**17b** (127 mg, 0.16 mmol) in pyridine/H_2O(5:1, 9.25 mL) was added 1,3-propanedithiol (0.30 mL, 0.33 g, 3.00 mmol) and the pH valueadjusted with Et_3N (0.30 mL) to 9–10. After 3.75 hr at rt the solvent was removed in vacuo and the residue coevaporated with toluene (3 × 15 mL). The residue was dissolved in pyridine (10.0 mL) and Ac_2O (2.70 mL, 3.00 g, 29 mmol) was added. After 20 hr at rt the solvent wasremoved in vacuo and the residue coevaporated with toluene (3 × 10 mL). Purification by flash chromatography (toluene/acetone 3:1) furnished (*S*)-**18b** (74 mg, 0.09 mmol, 54%) as colorless amorphous solid. TLC (toluene/acetone 1:1): $R_f = 0.49$. $[a]_D = +18$ (c = 1, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.76 (s, 3H, $NHCOCH_3$), 1.93 (s, 3H, $COCH_3$), 2.99–3.01(m, 2H, $CHCH_2$), 3.15–3.59 (m, 8H, 2-H, 3-H, 3′-H, 5-H, 5′-H, OCH_3), 3.86–4.53 (m, 7H, 4-H, 4′-H, 6-H, 6-H, 6′-H, 6′-H, $CHCH_2$), 4.63 (d, $J_{1,2} = 7.8$ Hz, 1H, 1-H), 4.84 (d, $J_{1,2} = 8.3$ Hz,1H, 1′-H), 5.03 (s, 2H, OCH_2Ph), 5.21 (dd, $J_{1,2} = 8.3$, $J_{2,3} = 9.2$ Hz, 1H, 2′-H), 5.34 + 5.52 (2 × s, 2H, 2 × CHPh), 5.82 + 5.94 (2 × d, $J_{H,NH} = 6.8$ Hz, 1H, NH), 7.16–7.51 (m, 20H, Ar). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 876.3$; found: $m/z = 876.5$, $[M + K]^+$,$m/z = 892.4$; found: $m/z = 892.5$. $C_{47}H_{51}NO_{14}$ (879.9). Calcd.: C: 64.16, H: 5.84, N: 1.59.Found: C: 64.65, H: 6.34, N: 1.70.

Methyl *O*-(2-*O*-Acetyl-4,6-*O*-benzylidene-3-*O*-[(R)-1-benzyloxycarbonyl-2-phenylethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside((*R*)-18b). To a solution of (*R*)-**17b** (79 mg, 0.10 mmol) in pyridine/H_2O (5:1, 5.60 mL) was added 1,3-propandithiol (0.20 mL, 0.22 g, 2.00 mmol) and the pH value adjusted with Et_3N (0.20 mL) to

9–10. After 4 hr at rt the solvent was removed in vacuo and the residue was coevaporated with toluene (3 × 10 mL). The residue was dissolved in pyridine (6.00 mL) and Ac_2O (1.80 mL, 2.00 g, 19.5 mmol) was added. After 19 hr at rt the solvent removed in vacuo and the residue was coevaporated with toluene (3 × 10 mL). Purification by flash chromatography (toluene/acetone 3:1 to 2:1) furnished (*R*)-**18b** (36 mg, 0.04 mmol, 43%) as colorless amorphous solid. TLC (toluene/acetone 1:1): $R_f = 0.44$. $[a]_D = +66$ ($c = 0.46$, $CHCl_3$). ^{1}H NMR (600 MHz, d_6-DMSO): δ 1.78 (s, 3H, NHCOCH_3), 1.88 (s, 3H,COCH_3), 2.92 (m, 2H, CHCH_2), 3.34 (s, 3H, OCH_3), 3.49 (s, 1H, 5′-H), 3.53 (s, 1H, 5-H), 3.71 (dd, $J_{2,3} = 10.1$, $J_{3,4} = 3.2$ Hz, 1H, 3′-H), 3.82 (bs, 2H, 2-H, 3-H), 4.00–4.14 (m, 4H, 6-H,6-H, 6′-H, 6′-H), 4.24 (d, $J_{3,4} = 2.7$ Hz, 1H, 4′-H), 4.31 (s, 1H, 4-H), 4.35 (bs, 1H, 1-H), 4.49 (m, 1H, C*H*CH$_2$), 4.59 (d, $J_{1,2} = 8.1$ Hz, 1H, 1′-H), 4.89 (dd, $J_{1,2} = 8.1$, $J_{2,3} = 10.1$ Hz, 1H, 2′-H), 5.04 (s, 2H, OCH_2Ph), 5.49 + 5.59 (2 × s, 2H, 2 × C*H*Ph), 7.13–7.46 (m, 20H, Ar), 7.66(d, $J_{H,NH} = 6.8$ Hz, 1H, N*H*). ^{13}C NMR (150.9 MHz, d_6-DMSO): δ 38.5 (CH*C*H$_2$), 49.8 (2-C), 65.5 (5′-C), 65.7 (5-C, O*C*H$_2$Ph), 68.3 (6-C, 6′-C), 68.9 (2′-C), 71.8 (4′-C), 74.6 (4-C),76.8 (*C*HCH$_2$), 77.2 (3-C), 77.3 (3′-C), 99.4 (*C*HPh), 99.5 (*C*HPh), 101.0 (1′-C), 101.3 (1-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 876.3$; found: $m/z = 876.5$, $[M + K]^+$, $m/z = 892.4$; found: $m/z = 892.5$. $C_{47}H_{51}NO_{14}$ (879.9) Calcd.: C: 64.16, H: 5.84, N: 1.59. Found: C: 64.78, H: 6.28, N: 1.43.

Methyl *O*-(2-*O*-Acetyl-4,6-*O*-benzylidene-3-*O*-[(S)-1-benzyloxycarbonyl-2-cyclohexylethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4,6-*O*-benzylidene-2-deoxy-ß-D-galactopyranoside((*S*)-18c). To a solution of (*S*)-**17c** (130 mg, 0.16 mmol) in pyridine/H_2O (5:1, 8.75 mL) was added 1,3-propanedithiol (0.29 mL, 0.32 g, 2.94 mmol) and the pH value adjusted with Et_3N (0.25 mL) to 9–10. After 4.5 hr at rt the solvent was removed in vacuo and the residue was coevaporated with toluene (3 × 25 mL). The residue was dissolved in pyridine (10.0 mL) and Ac_2O (3.00 mL, 3.28 g, 32.4 mmol) was added. After 16 hr at rt the solvent was removed in vacuo and the residue was coevaporated with toluene (3 × 20 mL). Purification by flash chromatography (toluene/acetone 4:1 to 2:1) furnished (*S*)-**18c** (105 mg, 0.12 mmol, 75%) as colorless amorphous solid. TLC (toluene/acetone 1:1): $R_f = 0.50$. $[a]_D = +4.6$ ($c = 1$,$CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.84–1.67 (m, 13H, CH_2C6H_{11}), 1.97 (s, 3H,NHCOCH_3), 2.04 (s, 3H, OAc), 3.29 (s, 1H, 5′-H), 3.40–3.53 (m, 5H, 3′-H, 5-H, OCH_3), 3.64 (m, 1H, 2-H), 3.89 (d, $J_{6,6} = 11.5$ Hz, 1H, 6′-H), 4.01 (d, $J_{6,6} = 11.8$ Hz, 1H, 6-H), 4.11 (dd, $J_{vic} = 4.9$, $J_{vic} = 8.0$ Hz, 1H, C*H*CH$_2$), 4.16–4.18 (m, 2H, 4′-H, 6′-H), 4.27 (d, $J_{6,6} = 11.8$ Hz, 1H, 6-H), 4.35 (d, $J_{3,4} = 3.0$ Hz, 1H, 4-H), 4.50 (dd, $J_{2,3} = 11.2$, $J_{3,4} = 3.0$ Hz, 1H, 3-H), 4.71 (d, $J_{1,2} = 7.9$ Hz, 1H, 1′-H), 4.77 (d, $J_{1,2} = 8.4$ Hz, 1H, 1-H), 5.08 (s, 2H, CO_2CH_2Ph), 5.25 (dd, $J_{1,2} = 7.9$, $J_{2,3} = 9.4$ Hz, 1H, 2′-H), 5.34 + 5.53 (2 × s, 2H, 2 × C*H*Ph), 6.02 (bs, 1H, N*H*), 7.27-7.53(m, 15H, 3Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 53.2 (2-C), 56.6 (O*C*H$_3$), 66.6 (5-C, 5′-C,CO_2CH_2Ph),

69.0 (6′-C), 69.2 (6-C), 71.3 (2′-C), 74.2 (3-C), 74.4 (4′-C), 75.8 (4-C), 78.6 (*C*HCH$_2$), 78.7 (3′-C), 100.6 (*C*HPh, 1′-C), 100.7 (*C*HPh), 100.8 (1-C). $C_{47}H_{57}NO_{14} \cdot 2.5$ H_2O(905.0) Calcd.: C: 62.38, H: 6.91, N: 1.55. Found: C: 62.41, H: 7.03, N: 1.30.

Methyl *O*-(2,4,6-Tri-*O*-acetyl-3-*O*-[(S)-1-benzyloxycarbonyl-1-cyclohexylmethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-ß-D-galactopyranoside((*S*)-19a). To a solution of (*S*)-**18a** (83 mg, 98 μmol) in dry CH_2Cl_2/MeOH (1:1, 4.60 mL)under argon was added EtSH (75 μL, 64 mg, 0.97 mmol). After adding p-TsOH (2.0 mg, 9μmol) the reaction mixture was stirred at rt for 15 hr, then neutralized with Et_3N (0.10 mL) and the solvent removed in vacuo. The residue was dissolved in pyridine (5.00 mL) and Ac_2O(2.50 mL, 2.75 g, 27.5 mmol) was added. After 24 hr at rt the solvents were removed in vacuo andthe residue coevaporated with toluene (3 × 20 mL). Purification by flash chromatography(toluene/acetone 4:1) furnished (*S*)-**18a** (41 mg, 49 μmol, 50%) as colorless amorphoussolid. TLC (toluene/acetone 1:1): $R_f = 0.48$. $[a]_D = +15$ (c = 0.55, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.01–1.68 (m, 11H, C6H_{11}), 1.99 (s, 3H, NHCOCH_3), 2.06–2.09 (5 × s,15H, 5 × OAc), 3.27 (m, 1H, 2-H), 3.45 (dd, $J_{2,3} = 9.9$, $J_{3,4} = 3.1$ Hz, 1H, 3′-H), 3.50 (s, 3H,OCH_3), 3.62 (m, 1H, 5′-H), 3.82–3.86 (m, 2H, 5-H, C*H*C_6H_{11}), 3.94 (dd, $J_{5,6} = 6.6$, $J_{6,6} = 11.4$Hz, 1H, 6′-H), 4.04 (dd, $J_{5,6} = 7.2$, $J_{6,6} = 11.6$ Hz, 1H, 6-H), 4.10 (dd, $J_{5,6} = 5.8$, $J_{6,6} = 11.4$ Hz, 1H, 6′-H), 4.17 (dd, $J_{5,6} = 5.3$, $J_{6,6} = 11.6$ Hz, 1H, 6-H), 4.45 (d, $J_{1,2} = 7.9$ Hz, 1H, 1′-H), 4.63 (dd, $J_{2,3} = 10.7$, $J_{3,4} = 2.9$ Hz, 1H, 3-H), 4.98 (d, $J_{1,2} = 8.2$ Hz, 1H, 1-H), 5.11-5.15 (m, 2H, 2′-H, CO_2C*H*HPh), 5.20 (d, $J_{gem} = 12.1$ Hz, 1H, CO_2C*H*HPh), 5.40 (d, $J_{3,4} = 2.9$ Hz, 1H, 4-H), 5.46 (d, $J_{3,4} = 3.1$ Hz, 1H, 4′-H), 5.65 (d, $J_{H,NH} = 6.7$ Hz, 1H, N*H*), 7.35–7.38 (m, 5H, C6H_5).^{13}C NMR (150.9 MHz, $CDCl_3$): δ 55.3 (2-C), 57.0 (OCH_3), 61.9 (6′-C), 62.6 (6-C), 67.0(CO_2*C*HHPh), 68.0 (4′-C), 68.1 (4-C), 71.3 (5-C), 71.6 (5′-C), 71.8 (2′-C), 74.5 (3-C), 77.4 (3′-C), 84.1 (*C*HC_6H_{11}), 99.8 (1-C), 100.0 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 860.3$; found: $m/z = 859.9$. $C_{40}H_{55}NO_{18}$ (837.9) Calcd.: C: 57.34, H: 6.62, N:1.67. Found: C: 57.12, H: 7.09, N: 1.43.

Methyl *O*-(2,4,6-Tri-*O*-acetyl-3-*O*-[(R)-1-benzyloxycarbonyl-1-cyclohexylmethyl]-ß-Dgalactopyranosyl)-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-ß-D-galactopyranoside((*R*)-19a). To a solution of (*R*)-**18a** (27 mg, 32 μmol) in dry CH_2Cl_2/MeOH (1:1, 1.50 mL) was added EtSH (24 μL, 21 mg, 0.32 mmol). After adding p-TsOH (1.0 mg, 5 μmol) the reaction mixture was stirred at rt for 20 hr, then neutralized with Et_3N (0.20 mL) and the solvent removed in vacuo. The residue was dissolved in pyridine (3.00 mL) and Ac_2O (1.50 mL, 1.65 g, 16.5 mmol) was added. After 48 hr at rt the solvents were removed in vacuo and the residue was coevaporated with toluene (3 × 20 mL). Purification by flash chromatography (toluene/acetone 4:1 to 3:1)

furnished (*R*)-**19a** (7 mg, 8.4 μmol, 26%) as colorless amorphous solid. TLC (toluene/acetone 1:1): $R_f = 0.50$. $[a]_D = +17$ ($c = 0.24$, $CHCl_3$). 1HNMR (600 MHz, $CDCl_3$): δ0.98–1.66 (m, 11H, C_6H_{11}), 1.97 (s, 3H, NHCOCH_3), 2.05–2.10 (5 × s, 15H, 5 × OAc), 3.23 (m, 1H, 2-H), 3.44 (dd, $J_{2,3} = 9.9$, $J_{3,4} = 3.1$ Hz, 1H, 3′-H), 3.52 (s,3H, OCH_3), 3.66 (m, 1H, 5′-H), 3.87 (m, 1H, 5-H), 3.94–3.98 (m, 2H, 6′-H, CHC$_6$H$_{11}$), 4.05–4.09 (m, 1H, 6-H), 4.11–4.20 (m, 2H, 6-H, 6′-H), 4.53 (d, $J_{1,2} = 8.0$ Hz, 1′-H), 4.70 (dd, $J_{2,3} = 10.8$, $J_{3,4} = 3.2$ Hz, 1H, 3-H), 5.08 (m, 2H, 1-H, 2′-H), 5.14 + 5.19 (2 × d, $J_{gem} = 12.2$ Hz, 2H,CO_2CHHPh), 5.37 (d, $J_{3,4} = 3.1$ Hz, 1H, 4′-H), 5.45 (d, $J_{3,4} = 2.8$ Hz, 1H, 4-H), 5.67 (d, $J_{H,NH} = 5.9$ Hz, 1H, NH), 7.36–7.41 (m, 5H, C6H5). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 55.70 (2-C),57.5 (OCH$_3$), 61.7 (6′-C), 62.8 (6-C), 64.7 (4′-C), 66.7 (CO_2CHHPh), 67.5 (4-C), 70.5 (2′-C),71.3 (5-C), 71.4 (5′-C), 74.7 (3-C), 76.3 (3′-C), 79.6 (CHC$_6$H$_{11}$), 99.5 (1′-C), 100.0 (1-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 860.3$; found: $m/z = 859.9$. $C_{40}H_{55}NO_{18}$ (837.9) Calcd.: C: 57.34, H: 6.62, N: 1.67. Found: C: 56.81, H: 7.11, N: 1.68.

Methyl *O*-(2,4,6-Tri-*O*-acetyl-3-*O*-[(S)-1-benzyloxycarbonyl-2-phenylethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-ß-D-galactopyranoside ((*S*)-19b). To a solution of (*S*)-**18b** (61 mg, 71 μmol) in dry CH_2Cl_2/MeOH (1:1, 3.35 mL) was added EtSH (55 μl, 47 mg, 0.73 mmol) under argon. After adding p-TsOH (1.5 mg, 7 μmol) the reaction mixture was stirred for 15 hr at rt, then neutralized with Et_3N (0.05 mL) and the solvent removed in vacuo. The residue was dissolved in pyridine (4.00 mL) and Ac_2O (2.00 mL, 2.20 g, 22 mmol) was added. After 18 hr at rt the solvents were removed in vacuo and the residue was coevaporated with toluene (3 × 20 mL). Purification by flash chromatography (toluene/acetone 4:1 to 3:1) furnished (*S*)-**19b** (32 mg, 37 μmol, 53%) as colorless amorphous solid. TLC (toluene/acetone 1:1): $R_f = 0.46$. $[a]_D = +21$ ($c = 0.48$, $CHCl_3$). 1HNMR (600 MHz, $CDCl_3$): δ 1.80 (s, 3H, NHCOCH_3), 1.95 (s, 3H, OAc), 2.06–2.10 (4 × s, 12H, 4 × OAc), 2.94 (dd, $J_{vic} = 7.0$, $J_{gem} = 11.0$ Hz, 1H, CHCHHPh), 2.97 (dd, $J_{vic} = 5.2$, $J_{gem} = 11.0$ Hz, 1H, CHCHHPh), 3.22 (m, 1H, 2-H), 3.49–3.53 (m, 4H, 3′-H, OCH_3), 3.61 (m, 1H, 5′-H), 3.83 (m, 1H, 5-H), 3.94 (dd, $J_{5,6} = 6.6$, $J_{6,6} = 11.4$ Hz, 1H, 6′-H), 4.01–4.08 (m, 2H, 6-H,6′-H), 4.16 (dd, $J_{5,6} = 5.2$, $J_{6,6} = 11.7$ Hz, 1H, 6-H), 4.24 (dd, $J_{vic} = 5.2$, $J_{vic} = 7.0$ Hz, 1H, CHCHHPh), 4.40 (d, $J_{1,2} = 8.0$ Hz, 1H, 1′-H), 4.61 (dd, $J_{2,3} = 10.7$, $J_{3,4} = 3.0$ Hz, 1H, 3-H), 4.96 (d, $J_{1,2} = 8.2$ Hz, 1H, 1-H), 5.04 (dd, $J_{1,2} = 8.0$, $J_{2,3} = 9.6$ Hz, 1H, 2′-H), 5.07 + 5.11 (2 × d, $J_{gem} = 12.0$ Hz, 2H, CO_2CHHPh), 5.37 (d, $J_{3,4} = 3.0$ Hz, 1H, 4-H), 5.46 (d, $J_{3,4} = 2.6$ Hz, 1H, 4′-H), 5.62 (d, $J_{H,NH} = 6.8$ Hz, 1H, NH), 7.08–7.36 (m, 10H, Ar). ^{13}C NMR (150.9 MHz,$CDCl_3$): δ 39.0 (CHCHHPh), 55.4 (2-C), 57.2 (OCH3), 61.8 (6′-C), 62.8 (6-C), 68.0 (4′-C), 68.3 (4-C), 71.2 (5-C), 71.4 (5′-C), 71.6 (2′-C), 74.7 (3-C), 77.4 (3′-C), 80.8 (*C*HCHHPh), 100.0 (1-C), 100.4 (1′-C). MALDI-MS

(positive mode, CHCA): $[M + Na]^+$, $m/z = 868.3$;found: $m/z = 867.8$, $[M + K]^+$, $m/z = 884.4$; found: $m/z = 883.8$. $C_{40}H_{55}NO_{18}$ (837.9) Calcd.: C: 58.22, H: 6.08, N: 1.66. Found: C: 58.09, H: 6.64, N: 1.59.

Methyl *O*-(2,4,6-Tri-*O*-acetyl-3-*O*-[(R)-1-methoxycarbonyl-2-phenylethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-ß-D-galactopyranoside ((*R*)-19b). To a solution of (*R*)-**18b** (27 mg, 32 μmol) in dry CH_2Cl_2/MeOH (1:1, 1.50 mL) under argon was added EtSH (24 μL, 21 mg, 0.32 mmol). After adding p-TsOH (1.0 mg, 5 μmol) the reaction mixture was stirred for 4 hr at rt, then neutralized with Et_3N (0.05 mL) and the solvent evaporated in vacuo. The residue was dissolved in pyridine (3.00 mL) and Ac_2O (1.50 mL,1.65 g, 16.5 mmol) was added. After 72 h at rt the solvents were removed in vacuo and the residue coevaporated with toluene (3 × 20 mL). Purification by flash chromatography (toluene/acetone 4:1 to 2:1) furnished (*R*)-**19b** (17 mg, 22 μmol, 69%) as colorless amorphous solid. TLC (toluene/acetone 1:1): $R_f = 0.33$. $[a]_D = +40$ (c = 0.33, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 1.97 (s, 3H, NHCOCH_3), 2.04–2.12 (5 × s, 15H, 5 × OAc), 2.85–2.91 (m, 2H, CHC*HH*Ph), 3.22–3.25 (m, 1H, 2-H), 3.49–3.51 (m, 4H, 3′-H, 1-OCH_3), 3.63 (s, 3H, CO_2CH_3), 3.73 (m, 1H, 5′-H), 3.86 (m, 1H, 5-H), 4.00–4.17 (m, 4H, 6-H, 6-H, 6′-H, 6′-H), 4.36 (m, 1H, C*H*CHHPh), 4.55 (d, $J_{1,2} = 8.0$ Hz, 1H, 1′-H), 4.70 (dd, $J_{2,3} = 10.7$, $J_{3,4} = 3.1$ Hz, 1H, 3-H), 5.05 (d, $J_{1,2} = 8.3$ Hz, 1H, 1-H), 5.09 (dd, $J_{1,2} = 8.0$, $J_{2,3} = 9.5$ Hz, 1H, 2′-H), 5.33 (d, $J_{3,4} = 2.5$ Hz, 1H, 4′-H), 5.43 (d, $J_{3,4} = 3.1$ Hz, 1H, 4-H), 5.67 (d, $J_{H,NH} = 6.8$ Hz,1H, N*H*), 7.12–7.27 (m, 5H, Ar). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 39.3 (CH*C*HHPh), 51.7(CO_2*C*H3), 55.5 (2-C), 57.2 (1-O*C*H3), 61.4 (6′-C), 62.4 (6-C), 64.6 (4′-C), 67.5 (4-C), 70.2 (2′-C), 70.9 (5′-C), 71.1 (5-C), 74.6 (3-C), 76.3 (3′-C), 76.5 (*C*HCHHPh), 99.5 (1′-C), 99.9 (1-C). $C_{35}H_{47}NO_{18}$ (769.7) Calcd.: C: 54.61, H: 6.15, N: 1.82. Found: C: 54.51, H: 6.62, N: 1.90.

Methyl *O*-(2,4,6-Tri-*O*-acetyl-3-*O*-[(S)-1-benzyloxycarbonyl-2-cyclohexylethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-ß-D-galactopyranoside((*S*)-**19c**). To a solution of (*S*)-**18c** (70 mg, 81 μmol) in dry CH_2Cl_2/MeOH (1:1, 3.80 mL)under argon was added EtSH (62 μL, 53 mg, 0.80 mmol). After adding p-TsOH (2.0 mg, 9 μmol) the reaction mixture was stirred for 24 hr at rt, then neutralized with Et_3N (0.15 mL) and the solvent removed in vacuo. The residue was dissolved in pyridine (5.00 mL) and Ac_2O (2.50 mL, 2.75 g, 27.5 mmol) was added. After 72 hr at rt the solvents were removed in vacuo and the residue coevaporated with toluene (3 × 20 mL). Purification by flash chromatography (toluene/acetone 4:1 to 3:1) furnished (*S*)-**19c** (50 mg, 59 μmol, 72%) as colorless amorphous solid. TLC (toluene/acetone 1:1): $R_f = 0.55$. $[a]_D = +8.7$ (c = 0.38, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 0.82–1.65 (m, 13H, CH_2C6H_{11}), 1.99 (s, 3H, NHCOCH_3), 2.05–2.11 (5 × s, 15H, 5 × OAc), 3.28 (m, 1H, 2-H), 3.48–3.50 (m, 4H, 3′-H, OCH_3), 3.63 (m, 1H,

5′-H), 3.85 (m, 1H, 5-H), 3.95 (dd, $J_{5,6} = 6.6$, $J_{6,6} = 11.4$ Hz, 1H, 6′-H), 4.03–4.11 (m, 3H, 6-H, 6′-H, C*H*CH_2), 4.16 (dd, $J_{5,6} = 5.3$, $J_{6,6} = 11.6$ Hz, 1H, 6-H), 4.45 (d, $J_{1,2} = 7.9$ Hz, 1H, 1′-H), 4.64 (dd, $J_{2,3} = 10.7$, $J_{3,4} = 2.9$ Hz, 1H, 3-H), 4.97 (d, $J_{1,2} = 8.2$ Hz, 1H, 1-H), 5.07–5.13 (m, 2H, 2′-H, CO_2C*H*HPh), 5.19 (d, $J_{gem} = 12.1$ Hz, 1H, CO_2CH*H*Ph), 5.39 (d, $J_{3,4} = 2.9$ Hz, 1H, 4-H), 5.45 (d, $J_{3,4} = 2.7$ Hz, 1H, 4′-H), 5.66 (d, $J_{H,NH} = 6.8$ Hz, 1H, N*H*), 7.32–7.38 (m, 5H, C_6H_5). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 55.4 (2-C), 57.1 (O*C*H3), 61.9 (6′-C), 62.6 (6-C), 68.0 (4′-C), 68.1 (4-C), 71.2 (5-C), 71.5 (5′-C), 71.8 (2′-C), 74.6 (3-C), 77.3 (3′-C), 78.0 (*C*HCH_2), 100.0 (1-C), 100.2 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 874.4$; found: $m/z = 874.3$, $[M + K]^+$, $m/z = 890.5$; found: $m/z = 890.2$.

Methyl *O*-(3-*O*-[Triethylammonium-(S)-1-cyclohexylmethyl-1-carboxylate]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-ß-D-galactopyranoside ((*S*)-1ab). To a solution of (*S*)-**19a** (22 mg, 26 μmol) in MeOH (3.00 mL) was added Pd/C (10 mg) and the reaction mixture was stirred for 10 h under H_2 atmosphere. The catalyst was filtered off, the solvent removed in vacuo, and the residue diluted in dry MeOH (3.00 mL). Then NaOMe-solution (0.1 N, 0.20 mL) was added and the reaction mixture stirred for 48 hr at rt. After neutralization with ion exchange resin IR 120 (H^+-Form) the solvent was removed in vacuo. Purification by flash chromatography ($CHCl_3$/MeOH/Et_3N 60:40:1) furnished (*S*)-**1ab** (9.7 mg, 18 μmol, 69%) as colorless amorphous solid. TLC ($CHCl_3$/MeOH/H_2O 60:40:1): $R_f = 0.32$. ^{1}H NMR (600 MHz, D_2O): δ 0.99–1.18 + 1.47–1.62 (2 × m, 20H, C_6H_{11}, N(CH_2CH_3)$_3$), 1.89 (s, 3H, NHCOC*H*$_3$), 3.08 (q, 6H, N(C*H*$_2$CH$_3$)$_3$), 3.26 (dd, $J_{2,3} = 9.6$, $J_{3,4} = 3.0$ Hz, 1H, 3′-H), 3.39 (s, 3H, OC*H*$_3$), 3.49–3.53 (m, 2H, 2′-H, 5′-H), 3.57–3.74 (m, 7H, 3-H, 5-H, 6-H, 6-H, 6′-H, 6′-H, C*H*C_6H_{11}), 3.83 (d, $J_{3,4} = 3.0$ Hz, 1H, 4′-H), 3.89 (dd, $J_{1,2} = 8.8$, $J_{2,3} = 10.6$ Hz, 1H, 2-H), 4.07 (d, $J_{3,4} = 2.7$ Hz, 1H, 4-H), 4.31 (m, 2H, 1-H, 1′-H). ^{13}C NMR (150.9 MHz, D_2O): δ 50.6 (2-C), 56.5 (O*C*H3). 60.7 (6-C, 6′-C), 66.0 (4′-C), 67.6 (4-C), 69.7 (2′-C), 74.2 (5′-C), 74.4 (5-C), 80.3 (3-C), 82.3 (3′-C), 84.7 (*C*HC_6H_{11}), 101.8 (1-C), 104.5 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 560.2$; found: $m/z = 560.1$, $[M + K]^+$, $m/z = 576.3$; found: $m/z = 576.1$, $[M - H + Na + K]^+$, $m/z = 598.3$; found: $m/z = 598.1$.

Methyl *O*-(3-*O*-[Triethylammonium-(R)-1-cyclohexylmethyl-1-carboxylate]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-ß-D-galactopyranoside ((*R*)-1ab). To a solution of (*R*)-**19a** (4.5 mg, 5.4 μmol) in MeOH (1.00 mL) was added Pd/C (5 mg) and the reaction mixture was stirred for 2 hr under H_2 atmosphere. The catalyst was filtered off, the solvent removed in vacuo, and the residue diluted in dry MeOH (1.00 mL). Then NaOMe-solution (0.1 N, 0.10 mL) was added and the reaction mixture stirred for 4 hr at rt. After neutralization with ion exchange resin IR 120 (H^+-Form) the

solvent was removed in vacuo. Purification by flash chromatography ($CHCl_3$/MeOH/Et_3N 60:40:1) furnished (*R*)-**1ab** (1.9 mg, 3.0 μmol, 55%) as colorless amorphous solid. TLC ($CHCl_3$/MeOH/H_2O 60:40:1): $R_f = 0.37$. ^1H NMR (600 MHz, D_2O): δ 0.99–1.61 (m, 20H, C_6H_{11}, $N(CH_2CH_3)_3$), 1.90 (s, 3H, $NHCOCH_3$), 3.08(q, 6H, $N(CH_2CH_3)_3$), 3.21 (dd, $J_{2,3} = 10.0$, $J_{3,4} = 3.1$ Hz, 1H, 3′-H), 3.39 (s, 3H, OCH_3), 3.48 (m, 2H, 2′-H, 5′-H), 3.58–3.70 (m, 6H, 5-H, 6-H, 6-H, 6′-H, 6′-H, CHC_6H_{11}), 3.76 (dd, $J_{2,3} = 10.8$, $J_{3,4} = 2.8$ Hz, 1H, 3-H), 3.87–3.92 (m, 2H, 2-H, 4′-H), 4.06 (d, $J_{3,4} = 2.8$ Hz, 1H, 4-H), 4.32–4.35 (m, 2H, 1-H, 1′-H). ^{13}C NMR (150.9 MHz, D_2O): δ 51.1 (2-C), 57.2 ($OCH3$), 61.1 (6-C, 6′-C), 65.7 (4′-C), 68.0 (4-C), 69.5 (2′-C), 74.9 (5-C), 75.6 (5′-C), 80.3 (3-C), 81.1(3′-C), 85.4 (CHC_6H_{11}), 102.5 (1-C), 105.2 (1′-C). MALDI-MS (positive mode, CHCA):$[M + Na]^+$, $m/z = 560.2$; found: $m/z = 560.1$, $[M + K]^+$, $m/z = 576.3$; found: $m/z = 576.1$, $[M - H + Na + K]^+$, $m/z = 598.3$; found: $m/z = 598.1$.

Methyl *O*-(3-*O*-[Triethylammonium-(S)-2-phenylethyl-1-carboxylate]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-ß-D-galactopyranoside ((*S*)-1b). To a solution of (*S*)-**19b** (15 mg, 18 μmol) in MeOH (3.00 mL) was added Pd/C (10 mg) and the reaction mixture was stirred for 20 hr under H_2 atmosphere. The catalyst was filtered off, the solvent removed in vacuo and the residue diluted in dry MeOH (3.00 mL). Then NaOMe-solution (0.1 N, 0.20 mL) was added and the reaction mixture stirred for 10 hr at rt. After neutralization with ion exchange resin IR 120 (H^+-Form) the solvent was removed in vacuo. Purification by flash chromatography ($CHCl_3$/MeOH/Et_3N 60:40:1) furnished (*S*)-**1b** (8.3 mg, 15 μmol, 86%) as colorless amorphous solid. TLC ($CHCl_3$/MeOH/H_2O 6:4:1): $R_f = 0.31$. ^1H NMR (600 MHz, D_2O): δ 1.15 (t, 9H, $N(CH_2CH_3)_3$), 1.86 (s, 3H, $NHCOCH_3$), 2.87 (dd, $J_{vic} = 8.3$, $J_{gem} = 14.0$ Hz, 1H, CHCH*H*), 3.02 (dd, $J_{vic} = 4.7$, $J_{gem} = 14.0$ Hz, 1H, CHCH*H*), 3.02 (q, 6H,$N(CH_2CH_3)_3$), 3.17 (dd, $J_{2,3} = 9.6$, $J_{3,4} = 2.8$ Hz, 1H, 3′-H), 3.38–3.47 (m, 5H, 2′-H, 5′-H, $-OCH_3$), 3.55–3.70 (m, 6H, 3-H, 5-H, 6-H, 6-H, 6′-H, 6′-H), 3.81 (d, $J_{3,4} = 2.8$ Hz, 1H, 4′-H), 3.86 (dd, $J_{1,2} = 8.6$, $J_{2,3} = 10.7$ Hz, 1H, 2-H), 4.03 (d, $J_{3,4} = 2.6$ Hz, 1H, 4-H), 4.09 (dd, $J_{vic} = 4.7$, $J_{vic} = 8.3$ Hz, 1H, C*H*CHH), 4.23 (d, $J_{1,2} = 7.9$ Hz, 1H, 1′-H), 4.30 (d, $J_{1,2} = 8.6$ Hz, 1H, 1-H), 7.18–7.26 (m, 5H, Ar). ^{13}C NMR (150.9 MHz, D_2O): δ 38.6 (CH*C*HH), 50.4 (2-C), 56.5 (OCH_3), 60.5 (6-C, 6′-C), 65.7 (4′-C), 67.4 (4-C), 69.3 (2′-C), 73.9 (5′-C), 74.3 (5-C), 80.0 (3-C), 81.2 (*C*HCHH), 81.9 (3′-C), 101.7 (1-C), 104.1 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 568.2$; found: $m/z = 568.3$, $[M + K]^+$, $m/z = 584.3$; found: $m/z = 584.2$, $[M - H + 2Na]^+$, $m/z = 590.2$; found: $m/z = 590.3$, $[M - H + Na + K]^+$, $m/z = 606.3$; found: $m/z = 606.3$.

Methyl *O*-(3-*O*-[Triethylammonium-(R)-2-phenylethyl-1-carboxylate]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-ß-D-galactopyranoside ((*R*)-1b). To a solution of (*R*)-**19b** (8 mg, 10 μmol) in dry MeOH (1.00 mL)

was added NaOMe-solution (0.1 N, 0.20 mL) and the reaction mixture was stirred for 12 hr at rt. Then LiOH-solution (1 N, 0.10 mL) was added and the reaction mixture stirred for further 7 hr at rt. After neutralization with ion exchange resin IR 120 (H^+-Form) the solvent was removed in vacuo. Purification by flash chromatography ($CHCl_3$/MeOH/Et_3N 60:40:1) furnished (*R*)-**1b** (5.8 mg, 9 μmol, 90%) as colorless amorphous solid. TLC ($CHCl_3$/MeOH/H_2O 60:40:1): $R_f = 0.37$. ^1H NMR (600 MHz, D_2O): δ 1.16 (t, 9H, $N(CH_2CH_3)_3$), 1.89 (s, 3H, $NHCOCH_3$), 2.77 (dd, $J_{vic} = 9.2$, $J_{gem} = 14.0$ Hz, 1H, CHCH*H*), 3.02–3.30 (m, 7H, CHCHH, $N(CH_2CH_3)_3$), 3.21 (dd, $J_{2,3} = 9.7$, $J_{3,4} = 2.9$ Hz, 1H, 3′-H), 3.36–3.46 (m, 7H, 2′-H, 4′-H, 5′-H, 6′-H, OCH_3), 3.50–3.69 (m, 2H, 5-H, 6′-H), 3.62–3.69 (m, 2H, 6-H, 6-H), 3.72 (dd, $J_{2,3} = 10.9$, $J_{3,4} = 2.6$ Hz, 1H, 3-H), 3.86 (dd, $J_{1,2} = 8.6$, $J_{2,3} = 10.9$ Hz, 1H, 2-H), 4.02 (d, $J_{3,4} = 2.6$ Hz, 1H, 4-H), 4.08 (dd, $J_{vic} = 4.2$, $J_{vic} = 9.2$Hz, 1H, C*H*CHH), 4.28 (d, $J_{1,2} = 7.8$ Hz, 1H, 1′-H), 4.31 (d, $J_{1,2} = 8.6$ Hz, 1H, 1-H). ^{13}C NMR (150.9 MHz, D_2O): δ 38.8 (CH*C*HH), 50.7 (2-C), 56.7 (OCH_3), 60.6 (6-C, 6′-C), 65.4 (4′-C), 67.3 (4-C), 68.9 (2′-C), 74.4 (5-C, 5′-C), 79.8 (3-C), 80.5 (3′-C), 81.2 (*C*HCHH), 101.8 (1-C), 104.2 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 568.2$; found: $m/z = 568.3$, $[M + K]^+$, $m/z = 584.3$; found: $m/z = 584.2$, $[M - H + 2Na]^+$, $m/z = 590.2$; found: $m/z = 590.3$, $[M - H + Na + K]^+$, $m/z = 606.3$; found: $m/z = 606.3$.

Methyl *O*-(3-*O*-[Triethylammonium-(S)-2-cyclohexylethyl-1-carboxylate]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-ß-D-galactopyranoside ((*S*)-1c). To a solution of (*S*)-**19c** (18 mg, 21 μmol) in MeOH (3.00 mL) was added Pd/C (10 mg) and the reaction mixture was stirred for 16 hr under H_2 atmosphere. The catalyst was filtered off, the solvent removed in vacuo and the residue diluted in dry MeOH (3.00 mL). Then NaOMe-solution (0.1, 0.20 mL) was added and the reaction mixture stirred for 24 hr at rt. After neutralization with ion exchange resin IR 120 (H^+-Form) the solvent was removed in vacuo. Purification by flash chromatography ($CHCl_3$/MeOH/Et_3N 60:40:1) furnished (*S*)-**1c** (10.1 mg, 18.3 μmol, 87%) as colorless amorphous solid. TLC ($CHCl_3$/MeOH/H_2O 60:40:1): $R_f = 0.39$. ^1H NMR (600 MHz, D_2O): δ 0.77–0.85, 1.02–1.70, 1.42–1.55, 1.66–1.68 (4 × m, 22H, CH_2C6H_{11}, $N(CH_2CH_3)_3$), 1.89 (s, 3H, $NHCOCH_3$), 3.08 (q, 6H, $N(CH_2CH_3)_3$), 3.27 (dd, $J_{2,3} = 9.6$, $J_{3,4} = 2.7$ Hz, 1H, 3′-H), 3.39 (s, 3H, OCH_3), 3.47–3.51 (m, 2H, 2′-H, 5′-H), 3.57–3.72 (m, 6H, 3-H, 5-H, 6-H, 6-H, 6′-H, 6′-H), 3.83 (d, $J_{3,4} = 2.7$ Hz, 1H, 4′-H), 3.89 (dd, $J_{1,2} = 8.7$, $J_{2,3} = 10.6$ Hz, 1H, 2-H), 3.98 (dd, $J = 3.2$, $J = 8.9$ Hz, 1H, $CHCH_2$), 4.08 (d, $J_{3,4} = 2.7$ Hz, 1H, 4-H), 4.30–4.32 (m, 2H, 1-H, 1′-H). ^{13}C NMR (150.9 MHz, D_2O): δ 50.5 (2-C), 56.3 (OCH3), 60.5 (6-C, 6′-C), 66.1 (4′-C), 67.6 (4-C), 69.4 (2′-C), 73.9 (5′-C), 74.3 (5-C), 78.3 ($CHCH_2$), 80.1 (3-C), 82.1 (3′-C), 101.5 (1-C), 104.5 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 574.3$; found: $m/z = 574.2$, $[M + K]^+$, $m/z = 590.4$; found: $m/z = 590.2$.

Thexyldimethylsilyl 2-Azido-2-deoxy-4,6-*O*-(4-methoxybenzylidene)-ß-D-galactopyranoside(21). To a solution of **20**[31] (1.00 g, 2.88 mmol) in dry DMF (25 mL) under argon was added anisaldehyde dimethylacetal (1.35 mL, 1.45 g, 7.95 mmol) and p-TsOH (50 mg) and then stirred for 90 min at 55°C. The reaction mixture was neutralized with Et_3N (1.00 mL) and evaporated to dryness. Purification by flash chromatography (PE/EA 5:1 to 1:1) furnished **21** (479 mg, 1.03 mmol, 36%) as colorless oil. TLC (PE/EE 1:1): $R_f = 0.46$. $[a]_D = -4.4$ (c = 0.50, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ 0.21 + 0.23 (2 × s, 6H, Si(CH_3)$_2$), 0.91–0.93 (m, 12H, C(CH_3)), 1.65–1.73 (m, 1H, C(CH_3)$_2$*H*), 2.56 (d, $J_{H,OH} = 9.3$ Hz, 1H, 3-O*H*), 3.38 (m, 1H, 5-H), 3.47–3.51 (m, 2H, 2-H, 3-H), 3.81 (s, 3H, OCH_3), 4.03 (dd, $J_{5,6} = 1.9$, $J_{6,6} = 12.4$ Hz, 1H, 6-H), 4.12 (m, 1H, 4-H), 4.25 (dd, $J_{5,6} = 1.5$, $J_{6,6} = 12.4$ Hz, 1H, 6′-H), 4.53 (d, $J_{1,2} = 7.4$ Hz, 1H, 1-H), 5.50 (s, 1H, C*H*Ar), 6.88–6.94 + 7.10–7.45 (2 × m, 4H, Ar).$C_{22}H_{35}N_3O_6Si$ (465.6) Calcd.: C: 56.75, H: 7.58, N: 9.02. Found: C: 57.11, H: 7.18, N: 8.68.

Thexyldimethylsilyl *O*-(2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-ß-D-galactopyranosyl)-(1→3)-2-azido-2-deoxy-4,6-*O*-(4-methoxybenzylidene)-ß-D-galactopyranoside (22). A solution of **4B** (2.53 g, 5.10 mmol) and **21** (1.90 g, 4.08 mmol) in dry CH_2Cl_2 (40.0 mL) under argon was cooled to 0°C. After adding TMSOTf-solution (0.1 N, 0.83 mL, 0.02 eq.) the reaction mixture was stirred for 1 hr at 0°C, then neutralized with Et_3N (1.00 mL) and the solvent removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate 5:1 to 3:1) furnished **22** (2.14 g, 2.68 mmol, 66%) as colorless foam. TLC (toluene/acetone 3:1): $R_f = 0.59$. $[\alpha]_D = +27$ (c = 1, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ 0.20 + 0.21 (2 × s, 6H, Si(CH_3)$_2$), 0.89–0.93 (m, 12H, C(CH_3)), 1.65–1.71 (m, 1H, C(CH_3)$_2$*H*), 2.06 + 2.07 (2 × s, 6H, COCH_3), 3.32(s, 1H, 5-H), 3.49–3.55 (m, 2H, 3-H, 5′-H), 3.71 (dd, $J_{1,2} = 7.6$, $J_{2,3} = 10.5$ Hz, 1H, 2-H), 3.79(s, 3H, ArOCH_3), 3.97–4.11 (m, 2H, 6-H, 6′-H), 4.19–4.33 (m, 3H, 4-H, 6-H, 6′-H), 4.38 (d, $J_{3,4} = 3.6$ Hz, 1H, 4′-H), 4.51 (d, $J_{1,2} = 7.6$ Hz, 1H, 1-H), 4.87 (d, $J_{1,2} = 7.9$ Hz, 1H, 1′-H), 4.97 (dd, $J_{2,3} = 10.4$, $J_{3,4} = 3.6$ Hz, 1H, 3′-H), 5.41 (dd, $J_{1,2} = 7.9$, $J_{2,3} = 10.4$ Hz, 1H, 2′-H), 5.51 (s, 2H, 2 × C*H*Ar), 6.83–7.54 (m, 9H, Ar). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 822.3$; found: $m/z = 822.3$, $[M + K]^+$, $m/z = 838.4$; found: $m/z = 838.3$.

***O*-(2,3-Di-*O*-acetyl-4,6-*O*-benzyliden-ß-D-galactopyranosyl)-(1→3)-2-azido-2-deoxy-4,6-*O*-(4-methoxybenzylidene)-a/ß-D-galactopyranose (23).** To a solution of **22** (2.10 g, 2.63 mmol) in pyridine (20.0 mL) was added HF pyridine (4.00 mL). After 21 hr at rt the reaction mixture was neutralized with saturated $NaHCO_3$-solution and the solvent removed in vacuo. The residue was suspended in CH_2Cl_2 and adsorbed on silica gel. Purification by flash chromatography (toluene/acetone 3:1) furnished **23** (1.01 g, 1.54 mmol, 59%)

as colourless amorphous solid. TLC (toluene/acetone 3:1): $R_f = 0.30$, 0.20. $[a]_D = +104$ ($c = 1$, $CHCl_3$/MeOH 10:1). ^1H NMR (600 MHz, d_6-DMSO): δ 1.98–2.00 (m, 6H, 2 × COCH_3), 3.38–3.55 (m, 3/2H, 2a-H, 2ß-H, 5-H), 3.65–3.82 (m, 5H, 3ß-H, 5-H, 5′-H, OCH_3), 3.99–4.18 (m, 9/2H, 3a-H, 6-H, 6-H, 6′-H, 6′-H), 4.34 (d, $J_{3,4} = 3.3$ Hz, 1/2H, 4ß-H), 4.39 (d, $J_{3,4} = 2.8$ Hz, 1H, 4′-H), 4.51–4.54 (m, 1H, 1ß-H, 4a-H), 4.90 + 4.99 (2 × m, 1H, 1′-H), 5.07–5.10 (m, 1H, 2′-H), 5.13–5.15 (m, 1H, 3′-H), 5.26 (m, 1/2H, 1a-H), 5.52 + 5.62 (2 × s, 2H, 2 × C*H*Ph), 6.74–7.47 (m, 10H, Ar, O*H*). ^{13}C NMR (150.9 MHz, d_6-DMSO): δ 20.3, 20.5, 55.0, 58.8, 61.9, 64.0, 65.5, 65.7, 68.3, 68.5, 68.7, 71.0, 71.2, 73.1, 74.3, 75.2, 75.6, 78.8, 91.9, 95.4, 99.6, 99.7, 101.1, 113.1, 126.2, 126.3, 127.5, 127.8, 128.1, 128.9, 130.7, 138.3, 159.2, 169.0, 169.8. MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 680.2$; found: $m/z = 680.3$, $[M + K]^+$, $m/z = 696.3$; found: $m/z = 696.3$. $C_{31}H_{35}N_3O_{13}$ (657.6) Calcd.: C: 56.62, H: 5.36, N: 6.39. Found: C: 56.84, H: 5.14, N: 6.57.

Methyl *O*-(2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-ß-D-galactopyranosyl)-(1→3)-2-azido-2-deoxy-4,6-*O*-(4-methoxybenzyliden)-ß-D-galactopyranoside (24). To a solution of **23** (1.01 g, 1.54 mmol) in dry CH_2Cl_2 (15.0 mL) under argon was added CCl_3CN (2.50 mL, 3.60 g, 25.5 mmol), then DBU (0.20 mL), and the reaction mixture stirred for 4 hr at rt. It was then concentrated to 4 mL and purified by flash chromatography (toluene/acetone 3:1 + 1% Et_3N).The residue (1.17 g, 1.46 mmol) was dissolved in dry MeOH (0.17 mL, 0.13 g, 4.2 mmol) and dry CH_3CN (14.0 mL) and cooled to −18 °C. After adding $Sn(OTf)_2$-solution (0.1 N, 0.17 mL, 0.01 eq.) it was stirred for 45 min at −18 °C, then diluted with Et_2O (125 mL) and washed with saturated $NaHCO_3$-solution (80 mL) and H_2O (80 mL). The organic phase was dried over $MgSO_4$ and the solvent removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate 2:1 to 1:1) furnished **24** (660 mg, 0.98 mmol, 64%) as colourless amorphous solid. TLC (toluene/ethyl acetate 1:1): $R_f = 0.27$. $[a]_D = +58$ ($c = 1$, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ 2.04 + 2.07 (2 × s, 6H, 2 × OAc), 3.35 (s, 1H, 5-H), 3.54–3.60 (m, 5H, 3-H, 5′-H, OCH_3), 3.75–3.80 (m, 4H, 2-H, OCH_3), 4.02 (d, $J_{6,6} = 12.3$ Hz, 1H, 6-H), 4.08 (d, $J_{6,6} = 12.3$ Hz, 1H, 6′-H), 4.17 (d, $J_{1,2} = 8.0$ Hz, 1H, 1-H), 4.28–4.31 (m, 3H, 4-H, 6-H, 6′-H), 4.37 (d, $J_{3,4} = 3.3$ Hz, 1H, 4′-H), 4.88 (d, $J_{1,2} = 8.0$ Hz, 1H, 1′-H), 4.98 (dd, $J_{2,3} = 10.3$, $J_{3,4} = 3.3$ Hz, 1H, 3′-H), 5.41 (dd, $J_{1,2} = 8.0$, $J_{2,3} = 10.3$ Hz, 1H, 2′-H), 5.51 (2 × s, 2H, C*H*Ph, C*H*$C_6H_4OCH_3$), 6.82 + 7.34–7.51 (m, 9H, Ph, $C_6H_4OCH_3$). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 55.4 + 57.1 (2 × O*C*H_3), 62.6 (2-C), 66.7 (5′-C), 66.9 (5-C), 68.9 (2′-C), 69.0 (6-C), 69.1(6′-C), 72.3 (3′-C), 73.5 (4′-C), 75.2 (4-C), 77.4 (3-C), 100.8 + 101.3 (2 × *C*HPh), 101.7 (1′-C), 103.3 (1-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 694.4$; found: $m/z = 693.6$, $[M + K]^+$, $m/z = 710.3$; found: $m/z = 709.5$. $C_{32}H_{37}N_3O_{13}$ (671.7) Calcd.: C: 57.22, H: 5.55, N: 6.26. Found: C: 57.42, H: 5.36, N: 6.34.

Methyl *O*-(2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-ß-D-galactopyranosyl)-(1→3)-2-azido-2-deoxy-ß-D-galactopyranoside (25). To a solution of **24** (660 mg, 0.98 mmol) in CH_2Cl_2 (66 mL) was added 60% TFA (1.21 mL). After 15 min at rt the reaction mixture was washed with saturated NaHCO3-solution (10.0 mL) and saturated NaCl-solution (20.0 mL), the organicphase was dried over $MgSO_4$, and the solvent was removed in vacuo. Purification by flash chromatography (toluene/acetone 2:1 to 1:1) furnished **25** (491 mg, 0.89 mmol, 90%) as colorless foam. TLC (toluene/acetone 1:1): $R_f = 0.41$. $[a]_D = +49$ (c = 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.09 + 2.10 (2 × s, 6H, 2 × OAc), 2.40 + 3.05 (2 × bs, 2H, 2 × O*H*), 3.40 (dd, $J_{2,3} = 10.1$, $J_{3,4} = 3.1$ Hz, 1H, 3-H), 3.45 (m, 1H, 5-H), 3.56–3.62 (m, 5H, 2-H, 5′-H, OCH_3), 3.79 + 3.90 (2 × m, 2H, 6-H, 6-H), 4.06–4.08 (m, 2H, 4-H, 6′-H), 4.15 (d, $J_{1,2} = 8.0$ Hz, 1H, 1-H), 4.27 (d, $J_{6,6} = 12.5$ Hz, 1H, 6′-H), 4.38 (d, $J_{3,4} = 3.3$ Hz, 4′-H), 4.75 (d, $J_{1,2} = 8.0$Hz, 1H, 1′-H), 4.99 (dd, $J_{2,3} = 10.4$, $J_{3,4} = 3.3$ Hz, 1H, 3′-H), 5.41 (dd, $J_{1,2} = 8.0$, $J_{2,3} = 10.4$ Hz, 2′-H), 5.51 (s, 1H, C*H*Ph), 7.37–7.51 (m, 5H, Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 57.2 (O*C*H$_3$), 62.4 (6-C), 62.8 (2-C), 66.7 (5′-C), 68.2 (4-C), 68.7 (2′-C), 69.0 (6′-C), 71.7 (3′-C), 73.3 (4′-C), 74.2 (5-C), 81.0 (3-C), 101.1 (*C*HPh), 102.3 (1′-C), 103.3 (1-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 576.2$; found: $m/z = 575.8$, $[M + K]^+$, $m/z = 592.3$; found: $m/z = 591.8$. $C_{24}H_{31}N_3O_{12}$ (553.5) Calcd.: C: 52.08, H: 5.65, N: 7.59. Found: C: 52.55, H: 5.73, N: 7.06.

Methyl *O*-(2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-ß-D-galactopyranosyl)-(1→3)-2-azido-3-*O*-[(S)-1-benzyloxycarbonyl-2-cyclohexylethyl]-2-deoxy-ß-D-galactopyranoside (26). A solution of **25** (197 mg, 0.36 mmol) and Bu_2SnO (96 mg, 0.40 mmol) in dry toluene (5.00 mL) was heated for 2.25 hr under reflux over molecular sieves (0.4 nm). After cooling to rt CsF (270 mg, 1.78 mmol), (*R*)-**3c** (702 mg, 1.78 mmol), and 1,2-dimethoxyethane (2.50 mL) were added to the pale yellow solution, which was stirred for 2.25 hr. The reaction mixture was diluted with $CHCl_3$ (40 mL) and washed with H_2O (2 × 20 mL). The aqueous phase was reextracted with $CHCl_3$ (2 × 20 mL), the combined organic phases dried over $MgSO_4$, and the solvents removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate 9:1 to 5:1) furnished **26** (205 mg, 0.26 mmol, 72%) as colorless oil. TLC (toluene/ethyl acetate 1:1): $R_f = 0.20$. $[a]_D = -13$ (c = 0.40, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.88–1.68 (m, 13H, CH_2C$_6$H$_{11}$), 2.09 (2 × s, 6H, 2 × OAc), 2.60–2.75 (bs, 1H, 4-OH), 3.38 (dd, $J_{2,3} = 10.1$, $J_{3,4} = 3.1$ Hz, 1H, 3-H), 3.55–3.82 (m, 8H, 2-H, 5-H, 5′-H, 6-H, 6-H, OCH_3), 4.02–4.07 (m, 3H, 4-H, 6′-H, C*H*CH$_2$), 4.13 (d, $J_{1,2} = 8.0$ Hz, 1H, 1-H), 4.32 (d, $J_{6,6} = 12.1$ Hz, 1H, 6′-H), 4.39 (d, $J_{3,4} = 3.4$ Hz, 1H, 4′-H), 4.73 (d, $J_{1,2} = 7.9$ Hz, 1H, 1′-H), 4.98 (dd, $J_{2,3} = 10.4$, $J_{3,4} = 3.4$ Hz, 3′-H), 5.11 + 5.18 (2 × d, $J_{gem} = 12.2$ Hz, 2H, CO$_2$CH_2Ph), 5.43 (dd, $J_{1,2} = 7.9$, $J_{2,3} = 10.4$ Hz, 1H, 2′-H), 5.50 (s, 1H, C*H*Ph), 7.33–7.51 (m, 10H, Ar). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 56.9

(OCH_3), 62.8 (2-C), 66.8 (5′-C), 68.0 (4-C), 68.7 (2′-C), 68.9 (6′-C), 70.1 (6-C), 72.0 (3′-C), 73.4 (4′-C), 73.8 (5-C), 77.9 ($CHCH_2$), 81.2 (3-C), 101.0 ($CHPh$), 102.3 (1′-C), 103.1 (1-C). $C_{40}H_{51}N_3O_{14} \cdot 2H_2O$ (833.9) Calcd.: C: 57.62, H: 6.65, N: 5.04. Found: C: 57.94, H: 6.51, N: 4.35.

Methyl *O*-(4,6-*O*-Benzylidene-ß-D-galactopyranosyl)-(1→3)-2-azido-6-*O*-[(S)-2-cyclohexyl-1-methoxycarbonyl-ethyl]-2-deoxy-ß-D-galactopyranoside (27). To a solution of **26** (185 mg, 0.23 mmol) in dry MeOH (7.50 mL) under argon was added NaOMe-solution (0.2 M, 0.20 mL). After 40 hr at rt the reaction mixture was neutralized with ion exchange resin IR 120 (H^+-Form) and the solvent removed in vacuo. Purification by flash chromatography (toluene/acetone 4:1) furnished **27** (116 mg, 0.18 mmol, 78%) as colourless foam. TLC (toluene/acetone 2:1): $R_f = 0.29$. $[a]_D = -33$ ($c = 1$, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ 0.91–1.79 (m, 13H, CH_2C6H_{11}), 2.58 (d, $J_{H,OH} = 8.2$ Hz, 1H, O*H*), 2.88 + 3.15 (2 × s, 2H, 2 × O*H*), 3.52–4.35 (m, 20H, 1-H, 2-H, 2′-H, 3-H, 3′-H, 4-H, 4′-H, 5-H, 5′-H, 6-H, 6-H, 6′-H, 6′-H, $CHCH_2$, 2 × OCH_3), 4.51 (d, $J_{1,2} = 7.5$ Hz, 1H, 1′-H), 5.56 (s, 1H, C*H*Ph), 7.36–7.52 (m, 5H, Ph). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 660.3$; found: $m/z = 659.8$, $[M + K]^+$, $m/z = 676.4$; found: $m/z = 675.8$. $C_{30}H_{43}N_3O_{12}$ (637.7) Calcd.: C: 56.51, H: 6.80, N: 6.59. Found: C: 56.86, H: 6.87, N: 6.60.

Methyl *O*-(4,6-*O*-Benzylidene-3-*O*-[(S)-2-cyclohexyl-1-methoxycarbonyl-ethyl]-ß-D-galactopyranosyl)-(1→3)-2-azido-6-*O*-[(S)-2-cyclohexyl-1-methoxycarbonyl-ethyl]-2-deoxy-ß-D-galactopyranoside (28). A solution of **27** (94 mg, 0.15 mmol) and Bu_2SnO (40 mg, 0.17 mmol) in dry toluene (3.00 mL) was heated under reflux over molecular sieves (0.4 nm). After cooling CsF (112 mg, 0.74 mmol), (*R*)-**3c** (291 mg, 0.74 mmol), and 1,2-dimethoxyethane (1.50 mL) were added to the pale yellow solution and then stirred for 8 hr at rt. The reaction mixture was diluted with $CHCl_3$ (50 mL) and washed with H_2O (2 × 25 mL). The aqueous phase was reextracted with $CHCl_3$ (2 × 20 mL), the combined organic phases dried over $MgSO_4$, and the solvent removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate 5:1) furnished the coupling product as a mixture of benzylester and lactone (R_f (toluene/ethyl acetate 4:1) = 0.53, 0.47). This was diluted in dry MeOH (5.00 mL)and NaOMe-solution (0.1 N, 0.10 mL) added. After 12 hr at rt the reaction mixture was neutralized with ion exchange resin IR 120 (H^+-Form) and the solvent removed in vacuo. Purification by flash chromatography (toluene/ethyl acetate 5:1 to 3:1) furnished **28** (40 mg, 0.05 mmol, 34%) as colorless amorphous solid. TLC (toluene/acetone 4:1): $R_f = 0.55$. ^1H NMR (600 MHz, $CDCl_3$): δ 0.82–1.81 (m, 26H, 2 × CH_2C6H_{11}), 2.68 (bs, 1H, 2′-O*H*), 2.95 (bs, 1H, 4-O*H*), 3.44 (s, 1H, 5′-H), 3.48–3.51 (m, 2H, 3-H, 3′-H), 3.56 (s, 3H, 1-OCH_3), 3.61–3.66 (m, 5H, 5-H, 6-H, CO_2CH_3), 3.71–3.74 (m, 4H, 2-H, CO_2CH_3), 3.80 (dd, $J_{5,6} = 4.3$, $J_{6,6} = 9.7$ Hz, 1H, 6-H), 3.99

(dd, $J_{vic} = 2.8$, $J_{gem} = 9.2$ Hz, 6-C*H*CH_2), 4.04–4.10 (m, 3H, 2′-H, 4-H, 6′-H), 4.17 (d, $J_{1,2} = 8.0$ Hz, 1H, 1-H), 4.26 (d, $J_{6,6} = 12.4$ Hz, 1H, 6′-H), 4.37 (d, $J_{3,4} = 2.8$ Hz, 1H, 4′-H), 4.44 (d, $J_{1,2} = 7.6$ Hz, 1H, 1′-H), 4.57 (dd, $J_{vic} = 3.4$, $J_{gem} = 9.5$ Hz, 1H, 3′-C*H*CH_2), 5.55 (s, 1H, C*H*Ph), 7.32–7.52 (m, 5H, C_6H_5). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 52.1 + 52.3 (2 × CO_2*C*H3), 57.0 (1-O*C*H3), 62.5 (2-C), 67.7 (5′-C), 68.0 (4-C), 69.2 (6′-C), 70.1 (6-C), 71.6 (2′-C), 73.7 (5-C), 75.3 (4′-C), 77.8 (2 × *C*HCH_2), 79.1 (3′-C), 82.4 (3-C), 101.1 (*C*HPh), 103.1 (1-C), 104.9 (1′-C).

Methyl *O*-(2-*O*-Acetyl-4,6-*O*-benzylidene-3-*O*-[(S)-2-cyclohexyl-1-methoxycarbonylethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4-*O*-acetyl-6-*O*-[(S)-2-cyclohexyl-1-methoxycarbonyl-ethyl]-2-deoxy-ß-D-galactopyranoside (29). To a solution of **28** (30 mg, 37 μmol) in pyridine/H_2O (5:1, 2.15 mL) was added 1,3-propanedithiol (0.07 mL, 0.08 g, 0.71 mmol) and the pH value adjusted with Et_3N (0.05 mL) to 9–10. After 4 hr at rt the solvent was removed in vacuo and the residue coevaporated with toluene (3 × 15 mL). The residue was dissolved in pyridine (2.50 mL) and Ac_2O (0.75 mL, 0.82 g, 8.1 mmol) added. After 72 hr at rt the solvent was removed in vacuo and the residue coevaporated with toluene (3 × 15 mL). Purification by flash chromatography (toluene/acetone 4:1 to 2:1) furnished **29** (26 mg, 29μmol, 77%) as colorless amorphous solid. TLC (toluene/acetone 1:1): $R_f = 0.57$. $[a]_D = -31$ (c = 0.26, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.85–1.75 (m, 26H, 2 × C$H_2C_6H_{11}$), 2.00 (s, 3H, NHCOCH_3), 2.08 + 2.10 (2 × s, 6H, 2 × OAc), 3.30–3.33 (m, 3H, 2-H, 5′-H, 6-H), 3.49 (dd, $J_{2,3} = 9.9$, $J_{3,4} = 3.3$ Hz, 1H, 3′-H), 3.53 (s, 3H, OCH_3), 3.59 + 3.72 (2 × s, 6H, 2 × CO_2CH_3), 3.78 (m, 1H, 6-H), 3.86 (d, $J_{5,6} = 6.8$ Hz, 1H, 5-H), 3.94 (m, 2H, 6′-H, C*H*CH_2), 4.08 (m, 1H, C*H*CH_2), 4.25 (d, $J_{6,6} = 12.2$ Hz, 1H, 6′-H), 4.31 (d, $J_{3,4} = 2.4$ Hz, 1H, 4′-H), 4.48 (d, $J_{1,2} = 7.8$ Hz, 1H, 1′-H), 4.59 (dd, $J_{2,3} = 10.6$, $J_{3,4} = 2.7$ Hz, 1H, 3-H), 5.02 (d, $J_{1,2} = 8.3$ Hz, 1H, 1-H), 5.24 (dd, $J_{1,2} = 7.8$, $J_{2,3} = 9.9$ Hz, 1H, 2′-H), 5.28 (d, $J_{3,4} = 2.7$ Hz, 1H, 4-H), 5.46 (s, 1H, C*H*Ph), 5.74 (bs, 1H, N*H*), 7.33–7.51 (m, 5H, Ph). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 51.9 (2 × CO_2*C*H3), 55.3 (2-C), 57.2 (O*C*H3), 66.7 (5′-C), 68.6 (6′-C), 68.7 (4-C), 70.3 (6-C),71.0 (2′-C), 73.4 (5-C), 74.3 (4′-C), 75.5 (3-C), 77.6 + 78.0 (2 × *C*HCH_2), 78.8 (3′-C), 99.8 (1-C), 100.1 (1′-C), 100.9 (*C*HPh). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 928.4$; found: $m/z = 927.7$, $[M + K]^+$, $m/z = 944.5$; found: $m/z = 943.7$. $C_{46}H_{67}NO_{17} \cdot 1.5\ H_2O$ (933.0) Calcd.: C: 59.22, H: 7.45, N: 1.50. Found: C: 59.17, H: 7.30, N: 1.52.

Methyl *O*-(2,4,6-Tri-*O*-acetyl-3-*O*-[(S)-2-cyclohexyl-1-methoxycarbonyl-ethyl]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-4-*O*-acetyl-6-*O*-[(S)-2-cyclohexyl-1-methoxycarbonyl-ethyl]-2-deoxy-ß-D-galactopyranoside (30). To a solution of **29** (19 mg, 21 μmol) in dry CH_2Cl_2 (1.00 mL) under argon

was added EtSH (7.5 μL, 6.4 mg, 0.10 mmol). After adding p-TsOH (0.5 mg, 2.4 μmol) the reaction mixture was stirred for 4 hr at rt, then neutralized with Et_3N (0.10 mL) and the solvent removed in vacuo. The residue was dissolved in pyridine (2.00 mL) and Ac_2O (1.00 mL, 1.10 g, 10.8 mmol) was added. After 24 hr at rt thesolvent was removed in vacuo and the residue coevaporated with toluene (3 × 20 mL). Purification by flash chromatography (toluene/acetone 4:1) furnished **30** (15 mg, 17 μmol, 79%) as colorless amorphous solid. TLC (toluene/acetone 1:1): $R_f = 0.56$. $[a]_D = +4.5$ (c = 0.40, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.85–1.70 (m, 26H, 2 × CH_2C6H_{11}), 1.99 (s, 3H, NHCOCH_3), 2.08–2.10 (4 × s, 12H, 4 × OAc), 3.27–3.33 (m, 2H, 2-H, 6-H), 3.49–3.53 (m, 4H, 3′-H, OCH_3), 3.71–3.75 (m, 8H, 5′-H, 6-H, 2 × CO_2CH_3), 3.86 (m, 1H, 5-H), 3.94–3.98 (m, 2H, 6′-H, CHCH_2), 4.03 (dd, $J_{vic} = 5.5$, $J_{vic} = 7.1$ Hz, 1H, CH'CH_2), 4.11 (dd, $J_{5,6} = 6.2$, $J_{6,6} = 11.3$ Hz, 1H, 6′-H), 4.49 (d, $J_{1,2} = 7.9$ Hz, 1H, 1′-H), 4.63 (dd, $J_{2,3} = 10.8$, $J_{3,4} = 3.0$ Hz, 1H, 3-H), 4.99 (d, $J_{1,2} = 8.3$ Hz, 1H, 1-H), 5.11 (dd, $J_{1,2} = 7.9$, $J_{2,3} = 9.6$ Hz, 1H, 2′-H), 5.34 (d, $J_{3,4} = 3.0$ Hz, 1H, 4-H), 5.47 (d, $J_{3,4} = 2.7$ Hz, 1H, 4′-H), 5.64 (d, $J_{H,NH} = 6.7$ Hz, 1H, NH). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 51.9 (2 × CO_2C3), 55.4 (2-C), 57.1 (1-OC3), 61.8 (6′-C), 67.8 (4′-C), 68.7 (4-C), 70.0 (6-C), 71.4 (5′-C), 71.7 (2′-C), 73.3 (5-C), 74.9 (3-C), 77.4 (3′-C), 77.5 (CHCH_2), 77.9 (C′HCH_2), 99.8 (1-C), 100.0 (1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 924.4$; found: $m/z = 923.8$, $[M + K]^+$, $m/z = 940.5$; found: $m/z = 939.8$. $C_{43}H_{67}NO_{19}$ (902.0) Calcd.: C: 57.26, H: 7.49, N: 1.55. Found: C: 56.86, H: 7.61, N: 1.25.

Methyl *O*-(3-*O*-[Triethylammonium-(S)-2-cyclohexylethyl-1-carboxylate]-ß-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-6-*O*-[triethylammonium-(S)-2-cyclohexylethyl-1-carboxylate]-ß-D-galactopyranoside ((*S*)-2c). To a solution of **30** (11 mg, 12.2 μmol) in dry MeOH (1.00 mL) was added NaOMe-solution (0.1 N, 0.20 mL) and the mixture stirred for 24 hr at rt. To the reaction mixture was added LiOH-solution (1N, 0.20 mL), then stirred for 10 d at rt, neutralized with ion exchange resin IR 120 (H^+-Form), and the solvent removed in vacuo. Purification by flash chromatography ($CHCl_3$/MeOH/H_2O 60:40:1) furnished (*S*)-**2c** (5.6 mg, 6.2 μmol, 51%) as colorless amorphous solid. RP18-DC (H_2O/CH_3CN 2:1): $R_f = 0.42$. ^{1}H NMR (600 MHz, D_2O): δ 0.52–1.67 (m, 35H, 2 × CH_2C6H_{11}, N(CH_2CH_3)$_3$), 1.90 (s, 3H, NHCOCH_3), 3.08 (q, $J_{vic} = 7.3$ Hz, 6H, N(CH_2CH_3)$_3$), 3.25 (dd, $J_{2,3} = 9.5$, $J_{3,4} = 2.7$ Hz, 1H, 3′-H), 3.41 (s, 3H, OCH_3), 3.44–3.53 (m, 3H, 2′-H, 5′-H, 6-H), 3.61–3.71 (m, 5H, 3-H, 5-H, 6-H, 6′-H, 6′-H), 3.81 (d, $J_{3,4} = 2.7$ Hz, 1H, 4′-H), 3.87–3.92 (m, 3H, 2-H, 2 × CHCH_2), 4.08 (d, $J_{3,4} = 2.5$ Hz, 1H, 4-H), 4.31 (m, 2H, 1-H, 1′-H). ^{13}C NMR (150.9 MHz, D_2O): δ 51.2 (2-C), 57.3 (OC3), 61.2 (6′-C), 66.5 (4′-C), 68.4 (4-C), 69.9 (2′-C, 6-C), 73.8 (5-C), 74.5 (5′-C), 79.3 (CHCH_2), 79.7 (CHCH_2), 80.9 (3-C), 82.8 (3′-C), 102.1 + 105.0 (1-C, 1′-C). MALDI-MS (positive mode, CHCA): $[M + Na]^+$, $m/z = 728.4$; found: $m/z = 728.1$,

$[M + K]^+$, $m/z = 744.5$; found: $m/z = 744.1$, $[M - H + Na + K]^+$, $m/z = 766.5$; found: $m/z = 766.1$.

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REFERENCES

[1] Mukhopadhyay, G.; Doherty, P.; Walsh, F.S.; Crocker, P.R.; Filbin, M.T. A novel role for myelin-associated glycoprotein as an inhibitor of axonal regeneration. Neuron **1994**, *13*, 757–767.

[2] McKerracher, L.; David, S.; Jackson, D.L.; Kottis, V.; Dunn, R.J.; Braun, P.E. Identification of myelin associated glycoprotein as a major myelin-derived inhibitor of neurite growth. Neuron **1994**, *13*, 805–811.

[3] McKerracher, L. Ganglioside rafts as MAG receptors that mediate blockade of axon growth. Proc. Natl. Acad. Sci. USA **2002**, *99*, 7811–7813.

[4] DeBellard, M.-E.; Tang, S.; Mukhopadhyay, G.; Shen, Y.-J.; Filbin, M.T. Myelin-associated glycoprotein inhibits axonal regeneration from a variety of neurons via interaction with a sialoglycoprotein. Mol. Cell. NeuroSci. **1996**, *7*, 89–101.

[5] Vyas, A.A.; Patel, H.V.; Fromholt, S.E.; Heffer-Lauc, M.; Vyas, K.A.; Dang, J.; Schachner, M.; Schnaar, R.L. Gangliosides are functional nerve cell ligands for myelin-associated glycoprotein (MAG), an inhibitor of nerve regeneration. Proc. Natl. Acad. Sci. USA **2002**, *99*, 8412–8417.

[6] Tettamanti, G.; Bonali, F.; Marchesini, F.; Zambotti, V. New procedure for the extraction, purification, and fractionation of brain gangliosides. Biochim. Biophys. Acta **1973**, *296*, 160–170.

[7] Vankar, Y.D.; Schmidt, R.R. Glycosphingolipids. Chem. Soc. Rev. **2000**, *29*, 210–216.

[8] Collins, B.E.; Kiso, M.; Hasegawa, A.; Tropak, M.B.; Roder, J.C.; Crocker, P.R.; Schnaar, R.L. Binding specificities of the sialoadhesin family of I-type Lectins. Sialic acid linkage and substructure requirements for binding of myelin-associated glycoprotein, Schwann cell myelin protein, and sialoadhesin. J. Biol. Chem. **1997**, *272*, 16889–16895.

[9] Collins, B.E.; Ito, H.; Sawada, N.; Ishida, H.; Kiso, M.; Schnaar, R.L. Enhanced binding of the neural siglecs, myelin-associated glycoprotein and Schwann cell myelin protein, to Chol-1 (a -series) gangliosides and novel sulfated Chol-1 analogs. J. Biol. Chem. **1999**, *274*, 37637–37643.

[10] Strenge, K.; Schauer, R.; Bovin, N.; Hasegawa, A.; Ishida, H.; Kiso, M.; Kelm, S. Glycan specificity of myelin-associated glycoprotein and sialoadhesin deduced from interactions with synthetic oligosaccharides. Eur. J. Biochem. **1998**, *258*, 677–685.

[11] Collins, B.E.; Yang, L.J.S.; Mukhopadhyay, G.; Filbin, M.T.; Kiso, M.; Hasegawa, A.; Schnaar, R.L. Sialic acid specificity of myelin-associated glycoprotein binding. J. Biol. Chem. **1997**, *272*, 1248–1252.

[12] Kelm, S.; Brossmer, R.; Isecke, R.; Gross, H.-J.; Strenge, K.; Schauer, R. Functional groups of sialic acids involved in binding to siglecs (sialoadhesins) deduced from interactions with synthetic analogs. Eur. J. Biochem. **1998**, *255*, 663–672.

[13] (a) Sears, P.; Wong, C.-H. Kohlenhydratmimetika: ein neuer Lösungsansatz für das Problem derkohlenhydratvermittelten biologischen Erkennung. Angew. Chem. **1999**, *111*, 2447–2471; (b) Carbohydrate mimetics: a new strategy for tackling the problem of carbohydrate-mediated biological recognition. Angew. Chem. Int. Ed. **1999**, *38*, 2301–2324.

[14] Dove, A. The bittersweet promise of glycobiology. Nat. Biotechnol. **2001**, *19*, 913–917.

[15] (a) Ritter, T.K.; Wong, C.-H. Kohlenhydrate in der Antibiotikaforschung: ein neuer Ansatz zur Resistenzbekämpfung. Angew. Chem. **2001**, *113*, 3616–3641; (b) Carbohydrate-based antibiotics: a new approach to tackling the problem of resistance. Angew. Chem. Int. **2001**, *40*, 3508–3533.

[16] Bänteli, R.; Ernst, B. Synthesis of sialyl lewis x mimics. Modifications of the 6-position of galactose. Bioorg. Med. Chem. Lett. **2001**, *11*, 459–462.

[17] von Itzstein, M.; Wu, W.Y.; Kok, G.B.; Pegg, M.S.; Dyason, J.C.; Jin, B.; Phan Tho, V.; Smythe, M.L.; ;White, H.F.; Oliver, S.W.; Colman, P.M.; Varghese, J.N.; Ryan, D.M.; Woods, J.M.; Bethell, R.C.; Hotham, V.J.; Cameron, J.M.; Penn, C.R. Rational design of potent sialidase-based inhibitors of influenza virus replication. Nature **1993**, *363*, 418–423.

[18] Amann, F.; Schaub, C.; Müller, B.; Schmidt, R.R. New potent sialyltransferase inhibitors—synthesis of donor and of transition-state analogues of sialyl donor CMP-Neu5Ac. Chem. Eur. J. **1998**, *4*, 1106–1115.

[19] Müller, B.; Schaub, C.; Schmidt, R.R. Efficient sialyltransferase inhibitors based on the generation of transition-state analogues of the sialyl donor. Angew. Chem. **1998**, *110*, 3021–3024; Angew. Chem. Int. Ed. **1998**, *37*, 2893–2897.

[20] Bernardi, A.; Potenza, D.; Capelly, A.M.; Garcia-Herrero, A.; Canada, F.J.; Jimenez-Barbero, J. Second generation mimics of ganglioside GM1 oligosaccharide: a three-dimensional view of their interactions with bacterial enterotoxins by NMR and computational methods. Chem. Eur. J. **2002**, *8*, 4597–4612.

[21] Arosio, D.; Baretti, S.; Cattaldo, S.; Potenza, D.; Bernardi, A. Ganglioside GM1 mimics: lipophilic substituents improve affinity for cholera toxin. Bioorg. Med. Chem. Lett. **2003**, *13*, 3831–3834.

[22] Janssen, S. Dissertation. Universität Konstanz, 2004.

[23] Kinzy, W.; Schmidt, R.R. Muraminsäure als Glycosyldonor und –akzeptor. Liebigs Ann. Chem. **1987**, 407–415.

[24] Pacak, J.; Cerny, M. Preparation and structure of 4,6-*O*-benzylidene-D-galactopyranose. Collect. Czech. Chem. Commun. **1963**, *28*, 541–544.

[25] Duclos, R.I. The total syntheses of D-erythro-sphingosine, *N*-palmitoylsphingosine (ceramide), and glucosylceramide (cerebroside) via an azidosphingosine analog. Chem. Phys. Lipids **2001**, *111*, 111–138.

[26] Gros, E.G.; Denlofen, V. Benzylidene derivatives of D-galactose. Chem. Ind. **1962**, 1502–1503.

[27] Padron, J.I.; Morales, E.Q.; Vazquez, J.T. Alkyl galactopyranosides: rotational population dependence of the hydroxymethyl group on the aglycon and its absolute configuration and on the anomeric configuration. J. Org. Chem. **1998**, *63*, 8247–8258.

[28] Kitov, P.I.; Bindle, D.R. Mild oxidative one-pot allyl group cleavage. Org. Lett. **2001**, *3*, 2835–2838.

[29] Zimmermann, P.; Greilich, U.; Schmidt, R.R. Total synthesis of a hexaosyl ceramide glycolipid acting as a receptor for macrophage-migration inhibition factor. Tetrahedron Lett. **1990**, *31*, 1849–1852.

[30] Greilich, U.; Zimmermann, P.; Jung, K.-H.; Schmidt, R.R. Synthesis of the heptasaccharide moiety of ganglioside BGM 1. Liebigs Ann. Chem. **1993**, 859–864.

[31] Herzner, H.; Eberling, J.; Schultz, M.; Zimmer, J.; Kunz, H. Oligosaccharide synthesis via electrophile-induced activation of glycosyl-*N*-allylcarbamates. J. Carbohydr. Chem. **1998**, *17*, 759–776.

[32] Zemplén, G.; Pascu, E. Saponification of acetylated sugars and related substances. Ber. Dtsch. Chem. Ges. **1929**, *62B*, 1613–1614.

[33] Degerbeck, F.; Fransson, B.; Grehn, L.; Ragnarsson, U. Synthesis of ^{15}N-labelled chiral Boc-amino acids from triflates: enantiomers of leucine and phenylalanine. J. Chem. Soc. Perkin Trans. 1 **1993**, *1*, 11–14.

[34] Kolb, H.C.; Ernst, B. Development of tools for the design of selectin antagonists. Chem. Eur. J. **1997**, *3*, 1571–1578.

[35] (a) Bayley, H.; Standring, D.N.; Knowles, J.R. Propane-1,3-dithiol: A selective reagent for the efficient reduction of alkyl and aryl azides to amines. Tetrahedron Lett. **1978**, *19*, 3633–3634; (b) Mayer, T.G. Dissertation. Universität Konstanz, **1996**.

[36] Stauch, T.; Greilich, U.; Schmidt, R.R. Synthesis of ganglioside GM_1 via a GA_1 intermediate. Liebigs Ann. **1995**, 2101–2111.

[37] Schmidt, R.R.; Behrendt, M.; Toepfer, A. Nitriles as solvents in glycosylation reactions—highly selective β-glycoside synthesis. Synlett **1990**, 694–697.

[38] Willams, D.R.; Sit, S.-Y. Total synthesis of (+)-phyllanthocin. J. Am. Chem. Soc. **1984**, *106*, 2949–2954.

[39] Thoma, G.; Kinzy, W.; Bruns, C.; Patten, J.T.; Magnani, J.L.; Bänteli, R. Synthesis and biological evaluation of a potent E-selectin antagonist. J. Med. Chem. **1999**, *42*, 4909–4913.