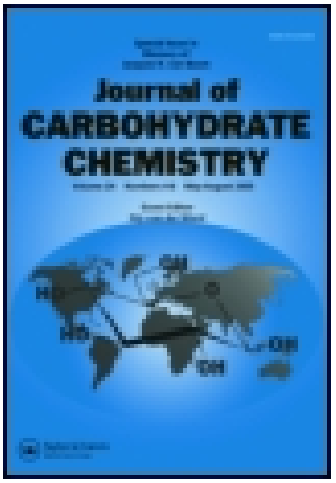

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Synthesis of Lewis a and Lewis X Pentasaccharides Based on N-Trichloroethoxycarbonyl Protection

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SYNTHESIS OF LEWIS A AND LEWIS X PENTASACCHARIDES BASED ON *N*-TRICHLOROETHOXYCARBONYL PROTECTION[1]

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ABSTRACT

Thexyldimethylsilyl 4,6-*O*-benzylidene-2-deoxy-2-trichloroethoxycarbonylamino-β-D-glucopyranoside (**4**), having the 3-hydroxy group unprotected, is a versatile starting material for the synthesis of glucosamine containing oligosaccharides. Thus, reaction with galactosyl donor **5** or fucosyl donor **6** afforded the desired β(1-3)- and α(1-3)-linked disaccharides **7** and **8**, respectively, in high yields. Reductive opening of the benzylidene moieties in **7** and **8** gave access to the 4-hydroxy groups in **9** and **10**. Ensuing fucosylation of **9** or galactosylation of **10** led to Lewis A (Le^a) and Lewis X (Le^x) trisaccharide building blocks **13** and **14**, respectively. Their transformation into glycosyl donors **19** and **20** and subsequent reaction with 3b-*O*-unprotected lactose derivative **23** as acceptor furnished the Le^a- and Le^x pentasaccharide precursors **24** and **25**. Exchange of the *N*-trichloroethoxycarbonyl group for an *N*-acetyl group and removal of the *O*-benzyl and *O*-acetyl protective groups afforded the desired Le^a- and Le^x-pentasaccharides **1** and **2**.

INTRODUCTION

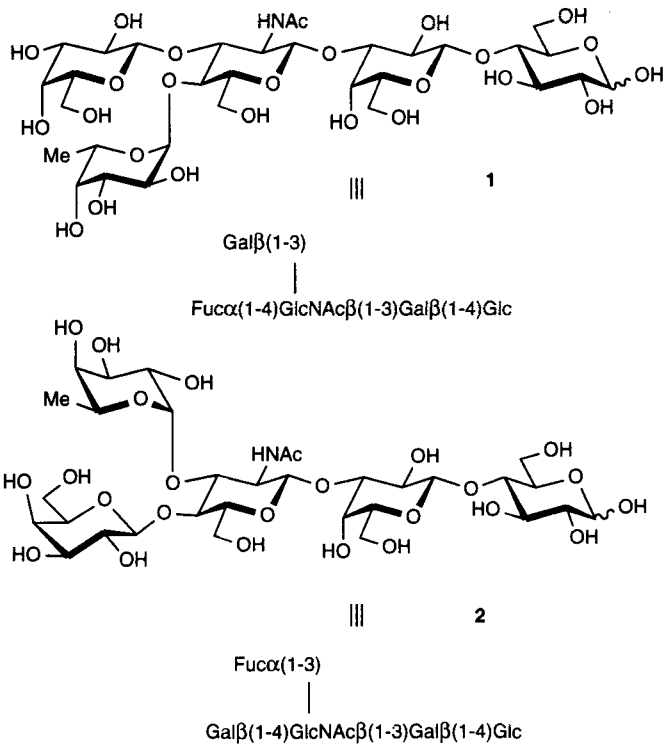
An important constituent of various glycoconjugates is D-glucosamine which is mainly found as its *N*-acetyl derivative in a β-glycosidic linkage.[2] Glycoside bond formation with donors derived from *N*-acetylglucosamine (GlcNAc) occurs generally via neighboring group participation to give a 1,3-oxazolinium intermediate,[3] which due to its stability exhibits only weak glycosyl donor properties. Therefore, various alternatives have been investigated having, for instance, a phthalimido,[2,3] a tetrachloro-phthalimido,[4,5] an *N,N*-diacetylamino,[6] or an *N,N*-dithiasuccinylimido group[7] in the 2-position, thus supporting formation of the β-anomer; yet, because of the strong

electron withdrawing character of the *N*-substituents, they also exhibit increased glycosyl donor properties. The 2-azido group has also gained wide use in this regard.[2,3,8-10] However, all these groups exhibit some disadvantages which have been recently discussed in detail.[11,12] Therefore, we resorted to the *N*-trichloroethoxycarbonyl (Teoc) group, which, as has been shown,[12-14] can be readily introduced into glucosamine. This group is also compatible with trichloroacetimidate attachment and activation, thus readily leading to powerful glycosyl donors.[12,14] In order to further study the usefulness of this group both in a glycosyl acceptor and in a glycosyl donor situation, we selected the synthesis of Lewis A (Le^a) and Lewis X (Le^x) pentasaccharides **1** and **2** (Scheme 1) in which *N*-acetylglucosamine possesses in terms of strategy a central role.[15] Both compounds are important epitopes which are found in various tissue and also as constituents of human milk oligosaccharides.

RESULTS AND DISCUSSION

Following a previous successful strategy for the construction of Le^a and Le^x epitopes,[9] first attachment of either the galactosyl or the fucosyl residue to the 3-hydroxy group of the glucosamine moiety and then attachment of either the fucosyl or the galactosyl residue, respectively, to the 4-hydroxy group of the disaccharides obtained in the first glycosylation reaction was envisaged. Ensuing ligation of the two trisaccharides thus obtained to the lactose moiety would conclude the pentasaccharide syntheses.

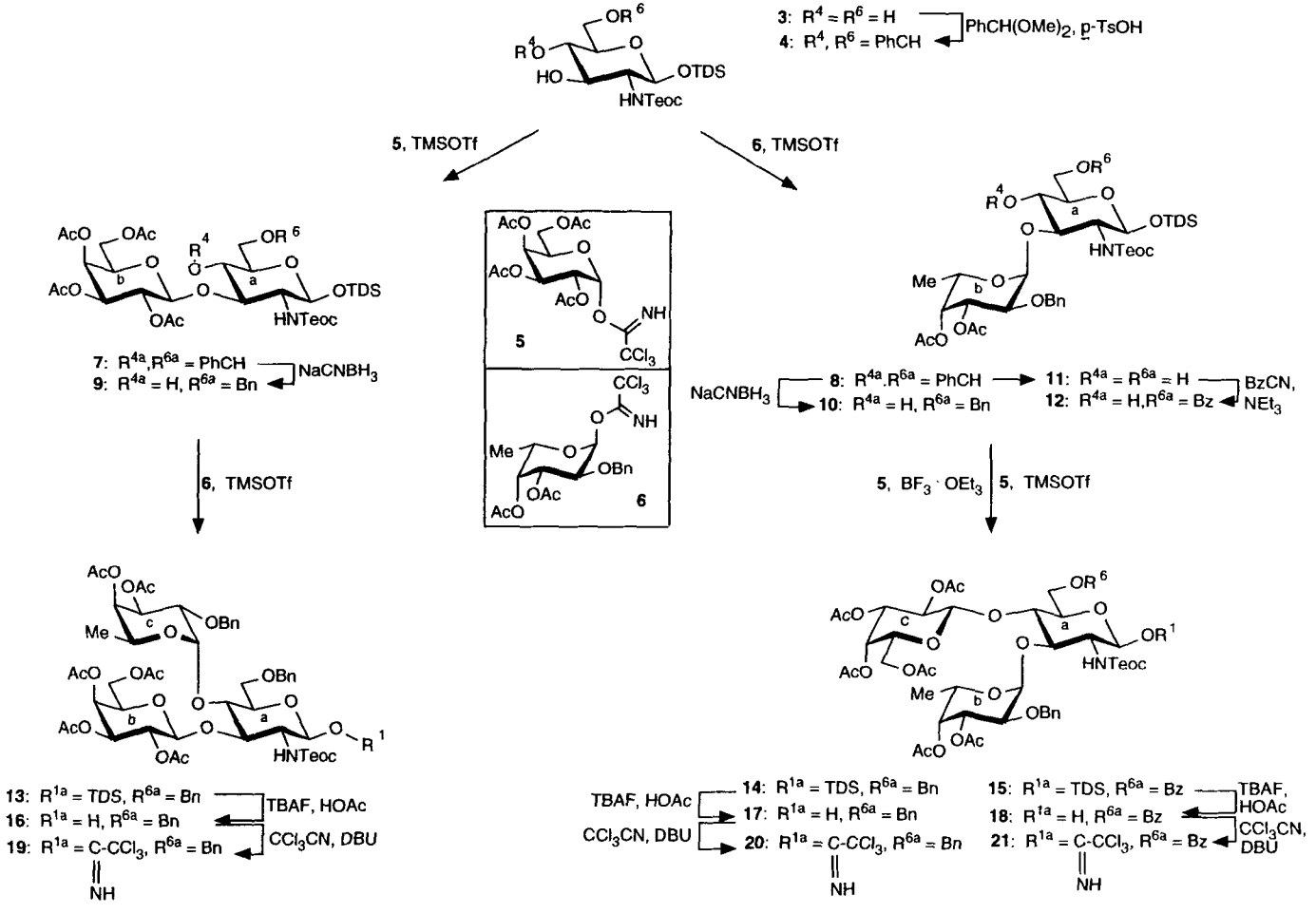
To this aim, D-glucosamine was transformed into known *N*-Teoc protected thexyldimethylsilyl (TDS) derivative **3** (Scheme 2).[12] In order to block glycosylation reaction at the 4- and 6-position, 4,6-*O*-benzylidenation with benzaldehyde dimethyl acetal was performed providing the desired starting material **4** in good yield. For the galactosylation, known galactosyl donor **5**[16] was selected. Reaction of **5** with **4** in dichloromethane as solvent at room temperature in the presence of 0.01 equivalents of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as catalyst gave the desired β(1-3)-linked disaccharide **7** in very high yield. All structural assignments are essentially based on ^1H NMR data (**7**, H-1b: δ 4.65, $J_{1,2}$ = 8.0 Hz). For the fucosylation of **4**, known fucosyl donor **6**[15,17] was chosen because the nonparticipating 2-*O*-benzyl group admits formation of the thermodynamically more stable α-linkage and the 3,4-di-*O*-acetyl groups provide the required acid stability of the glycosidic bond throughout the synthesis of the target molecules. Reaction of **6** with acceptor **4** in dichloromethane with 0.003 equivalents of TMSOTf as catalyst afforded, as expected, the α(1-3)-linked disaccharide **8** in very high yield (**8**, H-1b: δ 5.09, $J_{1,2}$ = 3.6 Hz). Obviously, *N*-Teoc groups do not interfere with trichloroacetimidate based glycosylation reactions. Regioselective reductive opening of the benzylidene groups in **7** and **8** with sodium cyanoborohydride in



Scheme 1

the presence of HCl in ether[18] gave the desired 4a-*O*-unprotected 6a-*O*-benzyl-protected disaccharides **9** and **10** in yields of 87% and 63%, respectively. Fucosylation of **9** with trichloroacetimidate **6** under inverse procedure[19] conditions gave the desired Le^a-trisaccharide building block **13** in 90% yield. (**13**, H-1c: δ 5.17, $J_{1,2}$ = 3.5 Hz). For the galactosylation of **10** with galactosyl donor **5**, boron trifluoride-ether proved to be a good catalyst, thus affording the desired Le^x-trisaccharide building block **14** in nearly quantitative yield (**14**, H-1c: δ 4.65, $J_{1,2}$ = 8.9 Hz).

Practically the same result was obtained when instead of the 6a-*O*-benzyl group, a 6a-*O*-benzoyl group was introduced into the glucosamine residue of the disaccharide leading to the Le^x-trisaccharide building block. For instance, trifluoroacetic acid catalyzed removal of the 4,6-*O*-benzylidene group in **8** afforded 4,6-*O*-unprotected disaccharide **11** which could be selectively benzoylated at the 6-hydroxy group with benzoyl cyanide/NEt_3 to afford 4a-*O*-unprotected disaccharide **12** in good yield. Galactosylation of **12** with trichloroacetimidate **5** in the presence of TMSOTf as catalyst



Scheme 2

afforded Le^x-trisaccharide building block **15** in practically quantitative yield (**15**, H-1c: δ 4.60, $J_{1,2}$ = 8.1 Hz).

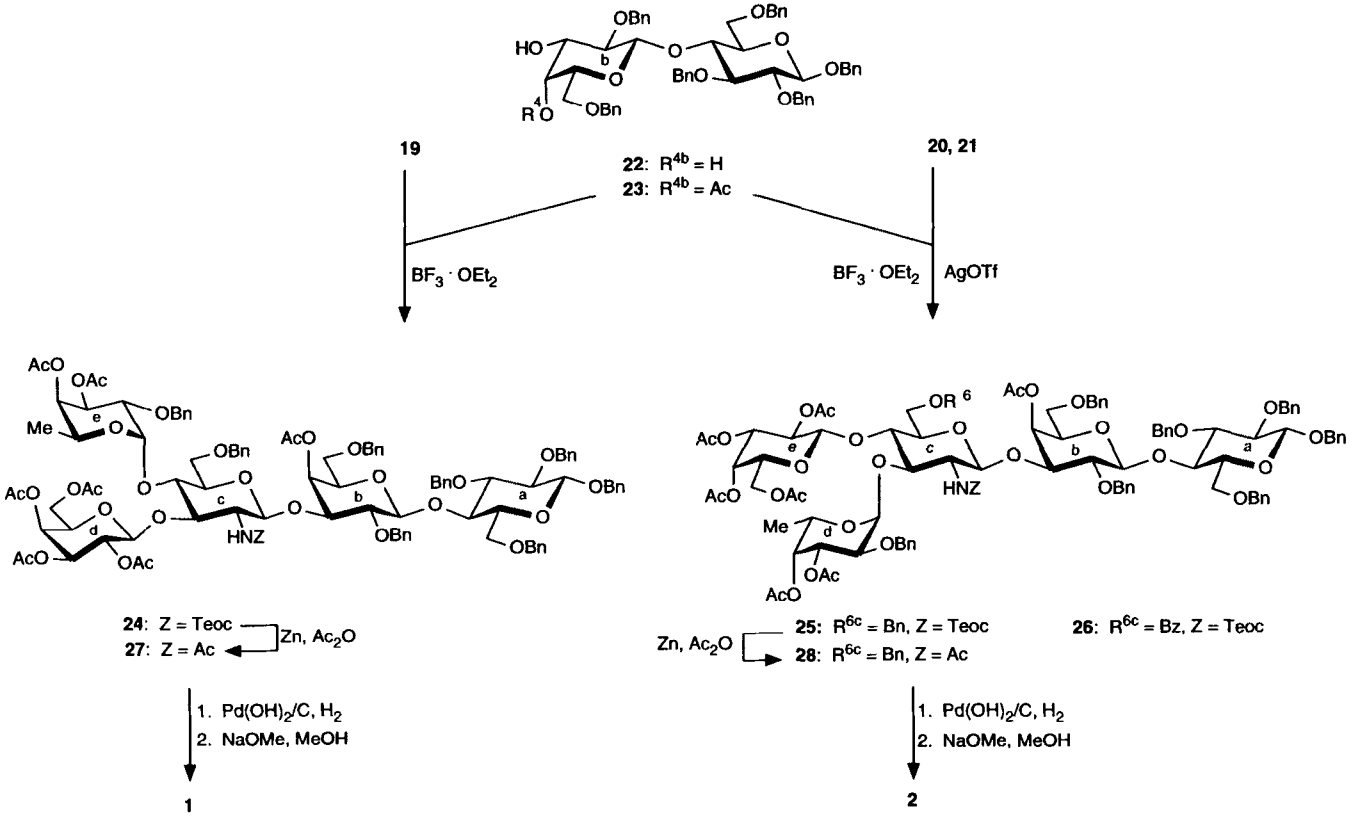
Transformation of trisaccharides **13-15** into donors could be performed by a standard protocol without affecting the *N*-Teoc groups; with tetrabutylammonium fluoride (TBAF) in the presence of acetic acid the corresponding 1a-*O*-unprotected trisaccharides **16-18** were obtained as anomeric mixtures (only the β-isomer is drawn) in high yields. Ensuing treatment with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base afforded the corresponding trichloroacetimidates **19-21** again as anomeric mixtures. **19-21** were immediately used for the ligation with the lactose moiety. As acceptor, 3b-*O*-unprotected lactose derivative **23** was chosen (Scheme 3), which could be readily obtained from the corresponding 3b,4b-*O*-unprotected derivative **22**[20] by treatment with methyl orthoacetate and then with acetic acid.[20] Due to the presence of the 4b-*O*-acetyl group, **23** does not exhibit high acceptor properties at the 3b-hydroxy group; yet, reaction with donor **19** in dichloromethane as solvent in the presence of boron trifluoride-ether as catalyst furnished the desired pentasaccharide **24** in 60% yield (**24**, H-1c: δ 4.38, $J_{1,2}$ > 8 Hz). Similar results were obtained for the reactions of **20** and **21** with **17**, furnishing the desired pentasaccharides **25** (H-1c: δ 5.02, $J_{1,2}$ = 6.9 Hz) and **26** (H-1c: δ 5.05, $J_{1,2}$ = 10.4 Hz), respectively.

Removal of the protective groups was quite straightforward. Replacement of the *N*-Teoc group by the acetyl group, for instance in pentasaccharides **24** and **25** could be carried out with zinc in acetic anhydride in a one-pot procedure, as previously described,[12] yielding the corresponding pentasaccharides **27** and **28**, respectively. The remaining protective groups in **27** and **28** were removed by hydrogenolysis in the presence of palladium on carbon as catalyst (*O*-benzyl) and then by using Zemplén conditions (*O*-acetyl),[22] thus providing the unprotected Le^a-pentasaccharide **1** and the Le^x-pentasaccharide **2**, respectively, in high overall yields. The anomeric protons of both compounds could be assigned by 600 MHz NMR spectroscopy, thus confirming the configurations at the anomeric centers.

In conclusion, *N*-Teoc-protected glucosamine can be readily transformed into glycosyl acceptor and glycosyl donor moieties which are useful building blocks for the construction of complex oligosaccharides.

EXPERIMENTAL

Solvents were purified in the usual way, the petroleum ether (PE) used has a boiling range of 35-65 °C. ^{1}H NMR spectra: Bruker AC-250 (250 MHz) and Bruker DRX (600 MHz): some chemical shifts and coupling constants were obtained from



Scheme 3

COSY spectra. Flash Chromatography: Silica gel 60 (Baker; 30-60 μm). Thin-layer chromatography (TLC): foil plates, silica gel 60 F_{254} (Merck; layer thickness 0.2 mm). Elemental analyses: Heraeus CHN-O-Rapid. Optical rotations: Perkin-Elmer polarimeter 241 MC; 1 dm cell, temp. 20 °C.

Thexyldimethylsilyl 4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (4). To a solution of **3**[12] (11.07 g, 22.3 mmol) in CH_3CN (200 mL) were added benzaldehyde dimethyl acetal (26.76 mmol, 4 mL) and *p*-toluenesulfonic acid (0.424 g, 2.23 mmol). After 2 h the solution was neutralized with Et_3N and then concentrated under reduced pressure. H_2O (200 mL) and AcOEt (200 mL) were added to the residue and the aqueous phase was extracted with AcOEt (3 × 150 mL). The combined organic phases were dried with Na_2SO_4, filtered and concentrated under reduced pressure. Flash chromatography (9:1 toluene/ethyl acetate) yielded **4** (10.1 g, 78%) as a colorless foam; TLC (9:1 toluol/ethyl acetate): R_f = 0.37; $[\alpha]_D$ = -33.1° (*c* 1.175, chloroform). ^1H NMR (250 MHz, $CDCl_3$) δ 0.2, 0.1 [2 s, 6H, -Si$(CH_3)_2$], 0.85 [s, 6H, -C$(CH_3)_2$)], 0.86, 0.89 [2 d, 6H, -CH$(CH_3)_2$], 1.63 [m, 1H, -CH$(CH_3)_2$], 3.35 (m, 1H, H-2), 3.39 (ddd, $J_{5,6}$ = 4.8 Hz, $J_{5,4}$ = 9.5 Hz, $J_{5,6'}$ = 10.4 Hz, 1H, H-5), 3.52 (dd, $J_{2,3}$ = 9 Hz, $J_{3,4}$ = 9 Hz, 1H, H-3), 3.72 (dd, $J_{6,6'}$ = 10.4 Hz, $J_{6',6}$ = 10.4 Hz, 1H, H-6), 3.87 (dd, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, 1H, H-4), 4.26 (dd, $J_{6',5}$ = 4.8 Hz, $J_{6,6'}$ = 10.4 Hz, 1H, H-6'), 4.69 (2 d, 2H, -CH_2CCl_3), 4.87 (d, $J_{1,2}$ = 7.9 Hz, 1H, H-1), 5.12 (d, $J_{NH,2}$ = 8.6 Hz, 1H, -N*H*), 5.49 (s, 1H, -C*H*Ph), 7.6-7.1 (m, 5H, aromatics).

Anal. Calcd for $C_{24}H_{36}Cl_3NO_7Si$ (583.6): C, 49.39; H, 6.22; N, 2.40. Found: C, 49.73; H, 6.04; N, 2.05; MS (MALDI): (M+Na^+) 608.

Thexyldimethylsilyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-deoxy-2 - (2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (7). To a solution of **1** (3.53 g, 6.04 mmol) and **5**[16] (3.19 g, 6.65 mmol) in dry CH_2Cl_2 (60 mL) was added, at room temperature, a 0.01 M solution of TMSOTf (6.04 mL, 0.0604 mmol) in CH_2Cl_2. After 10 min Et_3N was added for neutralization and the solution was evaporated under reduced pressure. Flash chromatography (4:1 petroleum ether/ethyl acetate) yielded **7** (5.13 g, 93%) as a colorless foam; TLC (4:1 petroleum ether/ethyl acetate): R_f = 0.28; $[\alpha]_D$ = -11.8° (*c* 1.36, $CHCl_3$). ^1H NMR (250 MHz, chloroform) δ 0.09, 0.11 [2 s, 6H, -Si$(CH_3)_2$], 0.78 [s, 6H, -C$(CH_3)_2$], 0.81, 0.83 [2 d, 6H, -CH$(CH_3)_2$], 1.55 [m, 1H, -CH$(CH_3)_2$], 1.91, 2.00, 2.10 (3 s, 12H, CH_3), 3.23 (ddd, 1H, H-2a), 3.46 (ddd, 1H, H-5a), 3.62 (ddd, 1H, H-5b), 3.70 (dd, $J_{4,3}$ = $J_{4,5}$ = 9 Hz, 1H, H-4a), 3.77 (dd, $J_{6,6'}$ = $J_{6,5}$ = 10 Hz, 1H, H-6a), 3.84 (dd, 1H, H-6b), 4.03 (dd, $J_{6,6'}$ = 10.8 Hz, $J_{6,5}$ = 8.0 Hz, 1H, H-6b), 4.25 (dd, $J_{6',6}$ = 10 Hz, $J_{6',5}$ = 4.9 Hz, 1H, H-6'a), 4.31 (dd, $J_{3,4}$ = $J_{3,2}$ = 9.0 Hz, 1H, H-3a), 4.65 (d, $J_{1,2}$ = 8 Hz, 1H, H-1b), 4.66 (2 d, 2H, -CH_2CCl_3), 4.89 (dd, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 3.4 Hz, 1H, H-3b), 5.02 (d, $J_{1,2}$ = 7.8 Hz, 1H,

H-1a), 5.15 (db, 1H, -N*H*), 5.17 (dd, $J_{2,3}$ = 10.3 Hz, $J_{2,1}$ = 8 Hz, 1H, H-2b), 5.27 (db, J = 3.2 Hz, 1H, H-4b), 5.51 (s, 1H, -C*H*Ph), 7.6-7.1 (m, 5H, aromatics).

Anal. Calcd for $C_{38}H_{54}Cl_3NO_{16}Si$ (913.8):C, 49.90; H, 5.90; N, 1.50. Found: C, 49.60; H, 6.05; N, 1.34; MS (MALDI): (M+Na^+) 937.

Thexyldimethylsilyl *O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-4,6-*O*-benzylidene -2-deoxy-2- (2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (8). To a solution of **4** (7.9 g, 13.53 mmol) and **6**[15,17] (15.6 g, 32.5 mmol) in dry CH_2Cl_2 (280 mL) was added a 0.01 M solution of TMSOTf (0.1353 mmol, 13.53 mL) in CH_2Cl_2. After 5 min the solution was neutralized with Et_3N and the solvent evaporated under reduced pressure. Flash chromatography (4:1 petroleum ether/ethyl acetate) yielded **8** (10.8 g, 88%) as a colorless foam; TLC (4:1 petroleum ether/ethyl acetate): R_f = 0.25; $[\alpha]_D$ = -80.6° (*c* 1.01, chloroform). ^1H NMR (250 MHz, $CDCl_3$) 0.05, 0.08 [2 s, 6H, -Si$(CH_3)_2$], 0.51 (d, 3H, -CH_3-b), 0.90 [s, 6H, C$(CH_3)_2$], 0.91, 0.92 [2 d, 6H, CH$(CH_3)_2$], 1.54 [m, 1H, CH$(CH_3)_2$], 1.93, 2.05 (2 s, 6H, CH_3), 3.10 (ddd, 1H, H-2a), 3.5 (ddd, 1H, H-5a), 3.54 (dd, $J_{4,5}$ = 9.3 Hz, $J_{4,3}$ = 10.3 Hz, 1H, H-4a), 3.73 (dd, $J_{6,6'}$ = $J_{6,5}$ = 10.3 Hz, 1H, H-6a), 3.80 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H-2b), 4.27 (qd, 1H, H-5b), 4.29 (dd, 1H, H-6'a), 4.31 (dd, 1H, H-3a), 4.46 (d, $J_{H,H'}$ = 11.8 Hz, 1H, -CH_2CCl_3), 4.66 (2 s, 2H, -OPh), 4.82 (d, $J_{H',H}$ = 11.8 Hz, 1H, -CH_2CCl_3), 5.08 (dd, 1H, H-4b), 5.13 (d, $J_{1,2}$ = 7.8 Hz, 1H, H-1a), 5.09 (d, 1H, H-1b), 5.2 (db, 1H, -NH), 5.28 (dd, $J_{3,4}$ = 3.2 Hz, $J_{3,2}$ = 10.5 Hz, 1H, H-3b), 5.48 (s, 1H, -OPh), 7.5-7.26 (m, 5H, aromatics)

Anal. Calcd for $C_{41}H_{56}Cl_3NO_{13}Si$ (904): C, 54.47; H, 6.24; N, 1.55. Found: C, 53.75; H, 6.19; N, 1.39; MS (MALDI-TOF): (M+Na^+) 927.

Thexyldimethylsilyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (9). To a solution of **7** (20.3 g, 22.2 mmol) in dry THF (200 mL) were added $NaCNBH_3$ (4.58 g, 66.6 mmol) and dropwise a solution of HCl in dry Et_2O until the pH remained acidic (~ 2 h). Then a saturated solution of $NaHCO_3$ was added for neutralization. The aqueous phase was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic phases were dried with Na_2SO_4, filtered, and the solvent evaporated under reduced pressure. Flash chromatography (3:1 petroleum ether/ethyl acetate) yielded **9** (17.7 g, 87%) as a colorless foam; TLC (4:1 petroleum ether/ethyl acetate): R_f = 0.40; $[\alpha]_D$ = + 92.5° (*c* 1.12, chloroform). ^1H NMR (250 MHz, $CDCl_3$) 0.08, 0.13 [2 s, 6H, -Si$(CH_3)_2$], 0.80 [s, 6H, -C$(CH_3)_2$], 0.81, 0.82 [2 d, 6H, -CH$(CH_3)_2$], 1.55 [m, 1H, -CH$(CH_3)_2$], 1.92, 1.98, 2.05, 2.10 (4 s, 12H, CH_3), 2.97 (ddd, 1H, H-2a), 3.48 (dd, 1H, H-5a), 3.64 (dd, $J_{6,6'}$ = 10.8 Hz, $J_{6,5}$ = 5.5 Hz, 1H, H-6a), 3.80 (dd, $J_{6',6}$ = 10.8 Hz, $J_{6'5}$ < 1 Hz, 1H, H-6'a), 3.94 (dd, 1H, H-4a), 3.97 (ddd, 1H, H-5b), 4.09 (dd, 2H, H-6b), 4.21 (dd, 1H, H-3a), 4.54 (d, $J_{1,2}$ = 8.3 Hz, 1H, H-1b), 4.57 (s, 2H, -CH_2Ph), 4.66-4.67 (2 d, 2H, -CH_2CCl_3), 4.94 (dd, $J_{3,4}$ =

3 Hz, $J_{3,2}$ = 10.4 Hz, 1H, H-3b), 3.93 (d, $J_{1,2}$ = 8.3 Hz, 1H, 1a-H), 5.10 (db, 1H, -NH), 5.25 (dd, $J_{2,3}$ = 10.4 Hz, $J_{2,1}$ = 8.3 Hz, 1H, H-2b), 5.34 (dd, $J_{4,3}$ = 3 Hz, $J_{4,5}$ < 1 Hz, 1H, H-4b), 7.15-7.35 (m, 5H, aromatics).

Anal. Calcd for $C_{38}H_{56}Cl_3NO_{16}Si$ (915.8); MS (MALDI-TOF): (M + Na^+) = 940.

Thexyldimethylsilyl *O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzyl-2-deoxy-2- (2,2,2-trichloroethoxycarbonylamino) -β-D-glucopyranoside (10). To a solution of **8** (8.30 g, 9.18 mmol) in dry THF (100 mL) were added $NaCNBH_3$ (6.3 g, 91.8 mmol) and dropwise a solution of HCl in dry Et_2O until the pH remained acidic (~ 2 h). Then a saturated solution of $NaHCO_3$ was added for neutralization. The aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were dried with Na_2SO_4, filtered, and the solvent evaporated under reduced pressure. Flash chromatography (3:1 petroleum ether/ethyl acetate) yielded **10** (5.24 g, 63%) as a colorless foam; TLC (3:1 petroleum ether/ethyl acetate): R_f = 0.35; $[\alpha]_D$ = - 41.95° (*c* 1.84, chloroform). ^1H NMR (250 MHz, $CDCl_3$) 0.02, 0.07 [2 s, 6H, -$Si(CH_3)_2$], 0.71 [s, 6H, -$C(CH_3)_2$], 0.72-0.73 [2 d, 6H, -$CH(CH_3)_2$], 1.03 (d, $J_{Me,5}$ = 6.9 Hz, 3H, Me-b), 1.53 [m, 1H, -$CH(CH_3)_2$], 1.89, 2.04 (2 s, 6H, CH_3), 2.60 (s, 1H, -OH), 3.1 (m, 1H, H-2a), 3.40 (dd, 1H, H-4a), 3.48 (dd, 1H, H-5a), 3.61 (dd, 1H, H-6a), 3.62 (dd, 1H, H-6'a), 3.80 (dd, $J_{2,1}$ = 3.1 Hz, $J_{2,3}$ = 8.8 Hz, 1H, H-2b), 3.85 (m, 1H, H-3a), 4.32 (m, $J_{5,Me}$ = 6.9 Hz, 1H, H-5b), 4.47 (s, 2H, -CH_2Ph), 4.5 (d, $J_{1,2}$ = 8.2 Hz, 1H, H-1a), 4.53 (2 d, 2H, -CH_2CCl_3), 4.58 (s, 2H, -CH_2Ph), 4.83 (db, 1H, -NH), 5.03 (d, $J_{1,2}$ = 3.1 Hz, 1H, H-1b), 5.20 (dd, $J_{4,3}$ = 3.4 Hz, $J_{4,5}$ < 1 Hz, 1H, H-4b), 5.22 (dd, $J_{3,4}$ = 3.4 Hz, $J_{3,2}$ = 8.8 Hz, 1H, H-3b), 7.15-7.31 (m, 10 H, aromatics).

Anal. Calcd for $C_{41}H_{58}Cl_3NO_{13}Si$ (906); MS (MALDI-TOF): (M + Na^+) = 930.

Thexyldimethylsilyl *O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-deoxy-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (11). To a solution of **8** (1.027 g, 1.14 mmol) in CH_2Cl_2 (12 mL) was added, at 0 °C, a 60% solution of TFA (2.1 mL). When the TLC showed that the reaction was completed a saturated solution of $NaHCO_3$ (10 mL) was added. The aqueous phase was extracted with CH_2Cl_2, the combined organic phases were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Flash chromatography (1:1 petroleum ether/ethyl acetate) yielded **11** (0.552 g, 60%) as a colorless foam; TLC (1:1 petroleum ether/ethyl acetate): R_f = 0.38; $[\alpha]_D$ = -41.9° (*c* 0.94, chloroform). ^1H NMR (250 MHz, $CDCl_3$) δ 0.08, 0.12 [2 s, 6H, -$Si(CH_3)_2$], 0.80 [s, 6H, -$SiC(CH_3)_2$], 0.82, 0.84 [2 d, 6H, -$C(CH_3)_2$], 1.11 (d, $J_{Me,5}$ = 6.5 Hz, 3H, Me-b), 1.57 [m, 1H, -$CH(CH_3)_2$], 1.94, 2.10 (2 s, 6H, CH_3), 3.15 (m, 1H, H-2a), 3.37 (m, 1H, H-5a), 3.48 (dd, $J_{4,3}$ = $J_{4,5}$ = 8.4 Hz, 1H, H-4a), 3.66 (dd, $J_{6,6'}$ = 7.3 Hz, $J_{6,5}$ = 5 Hz, 1H, H-6a), 3.81 (dd, 1H, H-6'a), 3.82 (dd, 1H, H-3a),

3.83 (dd, 1H, H-2b), 4.33 (q, $J_{5,Me}$ = 6.5 Hz, $J_{5,4}$ < 1 Hz, 1H, H-5b), 4.44 (d, $J_{H,H'}$ = 11 Hz, 1H, -CH_2Bn), 4.53 (d, $J_{H',H}$ = 11 Hz, 1H, -CH_2Bn), 4.6 (2 d, 2H, -CH_2CCl_3), 4.65 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1a), 5.05 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1b), 5.23 (db, 1H, -NH), 5.14 (dd, 1H, H-3b), 5.27 (dd, 1H, H-4b), 7.28-7.35 (m, 5H, aromatics).

Anal. Calcd for $C_{31}H_{50}Cl_3NO_{15}Si{\cdot}H_2O$ (828): C, 44.97; H, 6.33; N, 1.69. Found: C, 44.75; H, 5.97; N, 2.32; MS (MALDI-TOF): (M + Na^+) = 833.

Thexyldimethylsilyl *O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-6-*O*-benzoyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (12). To a solution of **11** (0.520 g, 0.642 mmol) in CH_3CN (6 mL) and Et_3N (179 μL, 1.28 mmol) was added, at 0 °C, a solution of benzoyl cyanide (0.0926 g, 0.706 mmol) in CH_3CN (7 mL). After 10 min MeOH (5 mL) was added and the mixture stirred for 10 min. Then the solvent was evaporated under reduced pressure. Flash chromatography (7:3 petroleum ether/ethyl acetate) yielded **12** (0.520 g, 88%) as a colorless foam; TLC (1:1 petroleum ether/ethyl acetate): R_f = 0.43; $[\alpha]_D$ = -41.8° (c 1.28, chloroform). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.03, 0.04 [2 s, 6H, -$Si(CH_3)_2$], 0.73 [s, 6H, -$SiC(CH_3)_2$], 0.80-0.81 [2 d, 6H, $CH(CH_3)_2$], 1.09 (d, $J_{Me,5}$ = 6.4 Hz, 3H, Me-b), 1.52 [m, 1H, $CH(CH_3)_2$], 1.93, 2.10 (2 s, 6H, CH_3), 3.16 (m, 1H, 2a-H), 3.44 (dd, $J_{4,5}$ = $J_{4,3}$ = 9.3 Hz, 1H, 4a-H), 3.62 (ddd, 1H, 5a-H), 3.86 (dd, 1H, 2b-H), 3.95 (dd, 1H, 3a-H), 4.36 (m, $J_{5,Me}$ = 6.4 Hz, $J_{5,4}$ < 1 Hz, 1H, H-5b), 4.48 (dd, $J_{6,6'}$ = 12 Hz, $J_{6,5}$ = 6.5 Hz, 1H, H-6a), 4.49 (d, $J_{H,H'}$ = 12 Hz, 1H, -CH_2Ph), 4.58 (dd, 1H, H-6'a), 4.63 (2 d, 2H, -CH_2Ph), 4.65 (2 d, 2H, -CH_2CCl_3), 4.96 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1a), 4.99 (d, $J_{1,2}$ = 3.2 Hz, 1H, H-1b), 5.25 (dd, 1H, H-3b), 5.27 (dd, 1H, H-4b), 5.30 (db, 1H, -NH), 7.2-8.05 (m, 10 H, aromatics).

Anal. Calcd for $C_{41}H_{56}Cl_3NO_{14}Si$ (919.9); MS (MALDI-TOF): (M + Na^+) = 944.

Thexyldimethylsilyl *O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→4)-[2,3,4,6-tetra-*O*-acetyl-β-D- galactopyranosyl- (1→3)] -6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (13). To a solution of **9** (7.14 g, 7.79 mmol) and a solution of TMSOTf (0.01 M in CH_2Cl_2, 77.9 μL, 0.078 mmol) in dry CH_2Cl_2 (60 mL) was added slowly, 0 °C, a solution of **6**[14,16] (15.01 g, 31.18 mmol) in CH_2Cl_2 (100 mL). When the addition was completed, after 5 min Et_3N was added for neutralization. Then the solvent was evaporated under reduced pressure. Flash chromatography (9:1 toluene/acetone) yielded **13** (8.66 g, 90%) as a colorless foam; TLC (9:1 toluene/acetone): R_f = 0.25; $[\alpha]_D$ = -52.4° (*c* 1.035, chloroform). ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.06, 0.12 [2 s, 6H, -$Si(CH_3)_2$], 0.79 [2 s, 6H, -$C(CH_3)_2$], 0.81-0.83 [2 d, 6H, -$CH(CH_3)_2$], 1.20 (d, $J_{Me,5}$ = 6.6 Hz, 3H, Me-c), 1.91, 1.92, 2.03, 2.05, 2.10, 2.14 (6 s, 18H, CH_3), 3.33-5.33 [m, 27 H, H,H-COSY: 3.33 (ddd, $J_{5,4}$ = 8.6

Hz, $J_{5,6} = J_{5,6'} < 1$ Hz, 1H, H-5a), 3.53 (d, $J_{6,6'} = 11.2$ Hz, $J_{6,5} < 1$ Hz, 1H, H-6a), 3.65 (m, 1H, H-2a), 3.81 (m, 1H, H-5b), 3.82 (d, $J_{6',6} = 11.2$ Hz, $J_{6'5} < 1$ Hz, 1H, H-6a), 3.86 (dd, $J_{2,1} = 3.5$ Hz, $J_{2,3} = 10.7$ Hz, 1H, H-2c), 3.88 (dd, $J_{3,4} = J_{3,2} = 9.2$ Hz, 1H, H-3a), 3.94 (dd, $J_{4,3} = 9.2$ Hz, $J_{4,5} = 8.6$ Hz, 1H, H-4a), 4.22 (dd, $J_{6,6'} = 11.2$ Hz, $J_{6,5} = 8.4$ Hz, 1H, H-6b), 4.43 (dd, $J_{6'6} = 11.2$ Hz, $J_{6'5} = 11.7$ Hz, 1H, H-6'b), 4.46 (d, $J_{H,H'} = 12.2$ Hz, 1H, $-CH_2Ph$), 4.51 (d, $J_{H',H} = 12.2$ Hz, 1H, $-CH_2Ph$), 4.51 (d, $J_{H',H} = 12.2$ Hz, 1H, $-CH_2Ph$), 4.51 (d, $J_{H,H'} = 12.2$ Hz, 1H, $-CH_2Ph$), 4.51 (d, $J_{1,2} > 6.1$ Hz, 1H, H-1a), 4.56 (d, $J_{H,H'} = 12.2$ Hz, 1H, $-CH_2Ph$), 4.57 (d, $J_{H',H} = 12.2$ Hz, 1H, $-CH_2Ph$), 4.79 (d, $J_{H',H} = 12.2$ Hz, 1H, $-CH_2Ph$), 4.81 (d, $J_{1,2} = 8.1$ Hz, 1H, H-1b), 4.85 (dd, $J_{3,4} = 3.2$ Hz, $J_{3,2} = 10.3$ Hz, 1H, H-3b), 4.97 (m, 1H, H-5c), 4.99 (db, 1 H, -NH), 5.05 (dd, $J_{2,3} = 10.3$ Hz, $J_{2,1} = 8.1$ Hz, 1H, H-2b), 5.17 (d, $J_{1,2} = 3.5$ Hz, 1H, H-1c), 5.18 (dd, $J_{3,2} = 10.7$ Hz, $J_{3,4} = 3$ Hz, 1H, H-3c), 5.32 (dd, $J_{4,3} = 3.4$ Hz, 1H, H-4c), 5.33 (dd, $J_{4,3} = 3.2$ Hz, 1H, H-4b)], 7.23-7.33 (m, 10H, aromatics).

Anal. Calcd for $C_{55}H_{76}Cl_3NO_{22}Si \cdot H_2O$ (1254): C, 52.68; H, 6.27; N, 1.12. Found: C, 51.96; H, 5.96; N, 1.71; MS (MALDI-TOF): $(M + Na^+) = 1259$.

Thexyldimethylsilyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-[(3,4-di-*O*- acetyl- 2-*O*- benzyl -α-L- fucopyranosyl) - (1→3)] -6-*O*- benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (14). To a solution of **10** (5.24 g, 5.78 mmol) and **5**[16] (5.5 g, 11.6 mmol) in dry CH_2Cl_2 (60 mL) was added $BF_3 \cdot Et_2O$ (0.1 M solution, 1.156 mmol, 11.56 mL) in CH_2Cl_2. After 5 min the solution was neutralized with Et_3N and the solvent evaporated under reduced pressure. Flash chromatography (6:4 petroleum ether/ethyl acetate) yielded **14** (7.00 g, 98%) as a colorless foam; TLC (6:4 petroleum ether/ethyl acetate): $R_f = 0.25$; $[\alpha]_D = -36.7°$ (*c* 1.01, chloroform). ^1H NMR (600 MHz, $CDCl_3$): δ 0.04, 0.11 [2 s, 6H, $-Si(CH_3)_2$], 0.77, 0.78 [2 s, 6H, $-C(CH_3)_2$], 0.81, 0.82 [2 d, 6H, $-CH(CH_3)$], 1.15 (d, $J_{Me,5} = 6.5$ Hz, 3H, Me-b), 1.53 [m, 1H, $-CH(CH_3)_2$], 1.92, 1.93, 1.95, 2.01, 2.09, 2.12 (6 s, 18H, CH_3), 2.94 (m, 1H, H-2a), 3.33-5.29 [m, 25H, H,H-COSY: 3.33 (d, $J_{5,4} = 9.5$ Hz, $J_{5,6} = J_{5,6'} < 1$ Hz, 1H, H-5a), 3.59 (dd, $J_{5,6} = J_{5,6'} = 7.0$ Hz, $J_{5,4} < 1$ Hz, 1H, H-5c), 3.62 (dd, $J_{6,6'} = 12.6$ Hz, $J_{6,5} = J_{6',5} < 1$ Hz, 1H, H-6a), 3.74 (dd, $J_{6',6} = 11.3$ Hz, $J_{6',5} = 2.7$ Hz, 1H, H-6'a), 3.82 (dd, $J_{2,3} = 10.6$ Hz, $J_{2,1} = 3.7$ Hz, 1H, H-2b), 3.95 (dd, $J_{4,3} = J_{4,5} = 9.5$ Hz, 1H, H-4a), 4.21 (dd, $J_{3,2} = J_{3,4} = 9.5$ Hz, 1H, H-3a), 4.23 (dd, $J_{6,6'} = 11.5$ Hz, $J_{6,5} = 7.5$ Hz, 1H, H-6c), 4.34 (dd, $J_{6,6'} = 11.5$ Hz, $J_{6',5} = 6.3$ Hz, 1H, H-6'c), 4.47 (dd, $J_{H,H'} = 12.5$ Hz, 1H, $-CH_2-$), 4.49 (d, $J_{H,H'} = 12.5$ Hz, 1H, $-CH_2-$), 4.63 (d, $J_{H,H'} = 12.5$ Hz, 1H, $-CH_2-$), 4.65 (d, $J_{1,2} = 8.9$ Hz, 1H, H-1c), 4.68 (d, $J_{H',H} = 12.5$ Hz, 1H, $-CH_2-$), 4.71 (d, $J_{H',H} = 12.5$ Hz, 1H, $-CH_2-$), 4.72 (d, $J_{H',H} = 12.5$ Hz, 1H, $-CH_2-$), 4.80 (dd, $J_{3,2} = 10.4$ Hz, $J_{3,4} = 3.6$ Hz, 1H, H-3c), 4.94 (m, 1H, H-5b), 4.98 (dd, $J_{2,1} = 8.9$ Hz, $J_{2,3} = 10.4$ Hz, 1H, H-2c), 4.99 (db, 1 H, -NH), 5.05 (d, $J_{1,2} = 7.5$ Hz, 1H, H-1a), 5.16 (d, $J_{1,2} = 3.7$ Hz, 1H, H-1b),

5.19 (dd, $J_{3,4}$ = 3.4 Hz, $J_{3,2}$ = 10.6 Hz, 1H, H-3b), 5.29 (dd, $J_{4,3}$ = 3.6 Hz, $J_{4,5}$ < 1 Hz, 1H, H-4c), 5.29 (dd, $J_{4,3}$ = 3.4 Hz, $J_{4,5}$ = 7.0 Hz, 1H, H-4b)], 7.23-7.36 (m, 10 H, aromatics).

Anal. Calcd for $C_{55}H_{76}Cl_3NO_{22}Si$ (1236); MS (MALDI-TOF): (M + Na^+) = 1260.

Thexyldimethylsilyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl -2-*O*- benzyl -α-L- fucopyranosyl) - (1→3)] -6-*O*-benzoyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (15). To a solution of **12** (0.914 g, 0.994 mmol) and **5**[16] (0.953 g, 1.988 mmol) in dry CH_2Cl_2 (10 mL) was added a solution of TMSOTf in CH_2Cl_2 (0.1 M, 0.0497 mmol, 497 μL). After 5 min the solution was neutralized with Et_3N and the solvent evaporated under reduced pressure. Flash chromatography (7:3 petroleum ether/ethyl acetate) yielded **15** (1.21 g, 98%) as a colorless foam; TLC (1:1 petroleum ether/ethyl acetate): R_f = 0.56; $[\alpha]_D$ = -23.2° (*c* 1.00, chloroform). ^1H NMR (600 MHz, $CDCl_3$): δ 0.07, 0.02 [2 s, 6H, -Si$(CH_3)_2$], 0.72 [2 s, 6H, -C$(CH_3)_2$], 0.76, 0.77 [2 d, 6H, CH$(CH_3)_2$], 1.19 (d, $J_{Me,5}$ = 6.5 Hz, 3H, Me-b), 1.50 [m, 1 H, -CH$(CH_3)_2$], 1.93, 1.94, 2.02, 2.06, 2.10, 2.14 (6 s, 18H, CH_3), 2.98 (m, 1H, H-2a), 3.64-5.35 [m, 33H, H,H-COSY: 3.64 (m, 1H, H-5a), 3.75 (dd, $J_{5,4}$ < 1 Hz, $J_{5,6}$ = $J_{5,6'}$ = 6.5 Hz, 1H, H-5c), 3.86 (dd, $J_{2,1}$ = 3.6 Hz, $J_{2,3}$ = 12 Hz, 1H, H-2b), 3.88 (dd, $J_{4,3}$ = 9.4 Hz, $J_{4,5}$ = 12 Hz, 1H, H-4a), 4.25 (m, 1H, H-6c), 4.26 (m, 1H, H-6a), 4.30 (dd, $J_{3,2}$ = $J_{3,4}$ = 9.4 Hz, 1H, H-3a), 4.45 (dd, $J_{6',6}$ = 12 Hz, $J_{6',5}$ = 6.5 Hz, 1H, H- 6'c), 4.52 (d, $J_{H,H'}$ = 11.9 Hz, 1H, -CH_2), 4.60 (d, $J_{1,2}$ = 8.1 Hz, 1H, H-1c), 4.67 (d, 2 H, -CH_2), 4.68 (d, 2 H, -CH_2), 4.74 (d, $J_{H',H}$ = 11.9 Hz, 1H, -CH_2), 4.87 (dd, $J_{6',6}$ = 10.3 Hz, $J_{6',5}$ < 1 Hz, 1H, H-6'a), 4.91 (dd, $J_{3,4}$ = 3.9 Hz, $J_{3,2}$ = 10.4 Hz, 1H, H-3c), 4.93 (m, 1H, H-5b), 5.08 (db, 1H, -NH), 5.10 (d, 1H, H-1a), 5.10 (dd, 1H, H-2c), 5.20 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1b), 5.22 (dd, $J_{3,2}$ = 12 Hz, $J_{3,4}$ = 3.3 Hz, 1H, H-3b), 5.33 (dd, $J_{4,3}$ = 3.3 Hz, $J_{4,5}$ < 1 Hz, 1H, H-4b), 5.35 (dd, $J_{4,5}$ < 1 Hz, $J_{4,3}$ = 3.9 Hz, 1H, H-4c)], 7.24-8.00 (m, 10 H, aromatics).

Anal. Calcd for $C_{55}H_{74}Cl_3NO_{23}Si{\cdot}4H_2O$ (1322): C, 49.92; H, 6.20; N, 1.05; Found: C, 49.61; H, 5.73; N, 1.60; MS (MALDI-TOF): (M + Na^+) = 1274.

***O*-(3,4-di-*O*-acetyl -2-*O*- benzyl -α- L- fucopyranosyl)-(1→4)-[(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→3)]-6-*O*-benzyl -2- deoxy-2- (2,2,2-trichloroethoxy-carbonyl-amino)-β-D-glucopyranose (16).** To a solution of **13** (7.54 g, 6.1 mmol) in THF (60 mL) was added AcOH (30.5 mmol, 1.5 mL) and a solution of Bu_4NF in THF (1 M, 7.3 mmol, 1.7 mL). The solution was stirred for 8 d, then brine (30 mL) was added and the aqueous phase was extracted with AcOEt (3 × 50 mL). The combined organic phases were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Flash

chromatography (1:1 petroleum ether/ethyl acetate) yielded **16** (6.2 g, 93%) as a colorless foam; TLC (1:1 petroleum ether/ethyl acetate): $R_f = 0.35$.

Anal. Calcd for $C_{47}H_{58}Cl_3NO_{22} \cdot H_2O$ (1112): C, 50.76; H, 5.44; N, 1.26; Found: C, 50.76; H, 5.43; N: 1.18.

***O*-(2,3,4,6-tetra-*O*-acetyl-β-D- galactopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L- fucopyranosyl)- (1→3)] -6-*O*- benzyl-2- deoxy-2- (2,2,2-trichloroethoxy-carbonylamino)-β-D-glucopyranose (17)**. To a solution of **14** (0.782 g, 0.632 mmol) in THF (6 mL) was added AcOH (1.896 mmol, 108.3 μL) and a solution of Bu_4NF in THF (1 M, 0.758 mmol, 758 μL). The solution was stirred for 8 d, then brine was added (3 mL) and the aqueous phase was extracted with AcOEt (3 × 5 mL). The combined organic phases were dried with Na_2SO_4, filtered and concentrated under reduced pressure. Flash chromatography (1:1 petroleum ether/ethyl acetate) yielded **17** (0.552 g, 80%) as a colorless foam; TLC (1:1 petroleum ether/ethyl acetate): $R_f = 0.37$.

Anal. Calcd for $C_{47}H_{58}Cl_3NO_{22} \cdot H_2O$ (1112): C, 50.76; H, 5.44; N, 1.26. Found: C, 50.32; H, 5.34; N, 1.65.

***O*-(2,3,4,6-tetra-*O*-acetyl-β-D- galactopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L- fucopyranosyl-) (1→3)] -6-*O*-benzoyl- 2-deoxy-2- (2,2,2-trichloroethoxy-carbonylamino) -β-D-glucopyranose (18)**. To a solution of **15** (1.096 g, 0.877 mmol) in THF (9 mL) was added AcOH (4.385 mmol, 250.8 μL) and a solution of Bu_4NF in THF (1 M, 1.05 mmol, 1.05 μL). The solution was stirred for 8 d, then brine was added (5 mL) and the aqueous phase was extracted with AcOEt (3 × 10 mL). The combined organic phases were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. Flash chromatography (1:1 petroleum ether/ethyl acetate) yielded **18** (0.87 g, 90%) as a colorless foam; TLC (1:1 petroleum ether/ethyl acetate): $R_f = 0.28$.

Anal. Calcd for $C_{47}H_{56}O_{23}Cl_3$ (1108): C, 50.95; H, 5.09; N, 1.26. Found: C, 51.36; H, 5.26; N, 1.32; - MS (MALDI-TOF): $(M + Na^+) = 1132$.

***O*-(3,4-di-*O*-acetyl -2-*O*- benzyl -α-L- fucopyranosyl) -(1→4)-[(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→3)]-6- *O*-benzyl- 2-deoxy-2- (2,2,2-trichloroethoxy-carbonylamino)-β-D-glucopyranosyl trichloroacetimidate (19)**. To a solution of **16** (2.73 g, 2.49 mmol) in CH_2Cl_2 (9 mL) was added CCl_3CN (24.95 mmol, 2.5 mL) and DBU (0.0498 mmol, 7 μL). After 5 min the solution was concentrated under reduced pressure. Flash chromatography (1:1:0.01 petroleum ether/ethyl acetate/Et_3N) yielded **14** (3.02 g, 98%) as a colorless foam; TLC (1:1 petroleum ether/ethyl acetate): $R_f = 0.47$.

***O*-(2,3,4,6-tetra-*O*-acetyl-β-D- galactopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L- fucopyranosyl)- (1→3)] -6-*O* -benzyl- 2-deoxy- 2- (2,2,2-trichloroethoxy-carbonylamino)-β-D-glucopyranosyl trichloroacetimidate (20)**. To a solution of **17** (5.11 g, 4.67 mmol) in CH_2Cl_2 (16 mL) was added CCl_3CN (46.7 mmol, 4.7 mL) and

DBU (0.0934 mmol, 13.9 μL). After 10 min the solution was concentrated under reduced pressure. Flash chromatography (1:1:0.01 petroleum ether/ethyl acetate/Et_3N) yielded **20** (3.46 g, 60%) as a colorless foam; TLC (1:1 petroleum ether/ethyl acetate): $R_f = 0.45$.

***O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)- [(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl) -(1→3)] -6-*O*- benzoyl-2-deoxy- 2- (2,2,2-trichloroethoxy-carbonylamino)-β-D-glucopyranosyl trichloroacetimidate (21).** To a solution of **18** (0.874 g, 0.789 mmol) in CH_2Cl_2 (8 mL) was added CCl_3CN (7.89 mmol, 791 μL) and DBU (0.0158 mmol, 2.4 μL). After 10 min the solution was concentrated under reduced pressure. Flash chromatography (1:1:0.01 petroleum ether/ethyl acetate/Et_3N) yielded **21** (0.888 g, 90%) as a colorless foam; TLC (1:1 petroleum ether/ethyl acetate): $R_f = 0.38$.

Benzyl *O*-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (23). To a solution of **22**[20] (10.7 g, 11.42 mmol), in CH_3CN (110 mL), was added $MeC(OMe)_3$ (3.5 mL) and a catalytic quantity of PTS. After 10 min a solution of 80% AcOH (165 mL) was added and stirred for 15 min. Then the solution was neutralized with a solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic phase was dried with Na_2SO_4, filtered and concentrated under reduced pressure. Flash chromatography (7:3 petroleum ether/ethyl acetate) yielded **23** (9.51 g, 90%) as a colorless oil; TLC (1:1 petroleum ether/ethyl acetate): $R_f = 0.53$; $[\alpha]_D = -10.7$ (*c* 1.145 chloroform). ^1H NMR (600 MHz, $CDCl_3$): δ 2.02 (s, 3H, CH_3), 3.33 (2 dd, 2H, H-6,6'b), 3.36 (m, 1 H, H-5a), 3.40 (dd, $J_{2,1} = 7.9$ Hz, $J_{2,3} = 9.4$ Hz, 1H, H-2b), 3.49 (dd, 1H, H-2a), 3.51 (m, 1H, H-5b), 3.56 (dd, $J_{3,2} = J_{3,4} = 9.1$ Hz, 1H, H-3a), 3.63 (dd, $J_{3,2} = 9.4$ Hz, $J_{3,4} = 3.4$ Hz, 1H, H-3b), 3.74 (dd, $J_{6,5} = 1.1$ Hz, $J_{6,6'} = 9.7$ Hz, 1H, H-6a), 3.80 (dd, $J_{6'6} = 9.7$ Hz, $J_{6',5} = 4.1$ Hz, 1H, H-6'a), 4.02 (dd, $J_{4,5} = J_{4,3} = 9.1$ Hz, 1H, H-4a), 4.24 (d, J = 12 Hz, 1H, $-CH_2Ph$), 4.43 (d, 1H, $-CH_2Ph$), 4.46 (d, 1H, $-CH_2Ph$), 4.47 (d, 1H, H-1b), 4.48 (d, 1H, H-1a), 4.61, 4.65, 4.66, 4.73, 4.77, 4.78, 4.90, 4.94, 4.96 (9 d, 9H, $-CH_2Ph$), 5.32 (dd, $J_{4,5} < 1$ Hz, $J_{4,3} = 2.9$ Hz, 1H, H-4b), 7.17-7.37 (m, 30 H, aromatics).

Anal. Calcd for $C_{56}H_{60}O_{12} \cdot H_2O$ (943): C, 71.32; H, 6.63. Found: C, 71.19; H, 6.12; MS (MALDI-TOF): $(M + Na^+) = 948$.

Benzyl *O*-(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl)-(1→4)-[(2,3,4,6-tetra -*O*- acetyl -β-D- galactopyranosyl) -(1→3)] -[6-*O*-benzyl -2- deoxy -2- (2,2,2-trichloroethoxy -carbonylamino) -β-D -glucopyranosyl] -(1→3) -(4-*O*-acetyl -2,6 -di- *O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (24). To a solution of **19** (0.407 g, 0.328 mmol) and **23** (0.313 g, 0.239 mmol) in dry CH_2Cl_2 (4 mL) was added $BF_3 \cdot Et_2O$ until the reaction was completed. Then the solution was neutralized with Et_3N and the solvent evaporated under reduced pressure. Flash chromatography (7:3 petroleum ether/ethyl acetate) yielded **24** (0.286 g, 60%) as a colorless foam; TLC (6:4 petroleum ether/ethyl acetate): $R_f = 0.30$; $[\alpha]_D = -32.2$ (*c* 1.055

chloroform). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.19 (d, $J_{Me,5}$ = 6.4 Hz, 3H, Me-e), 1.93, 1.95, 1.97, 1.98, 2.09, 2.10, 2.15 (7 s, 21H, CH_3), 3.20-5.60 [m, 52H, H,H-COSY: 3.24 (dd, 1H, H-3c), 3.26 (m, 1H, H-5c), 3.32 (m, 1H, H-5a), 3.35 (dd, 1H, H-6b), 3.35 (dd, 1H, H-6'b), 3.47 (dd, 1H, H-2b), 3.47 (dd, 1H, H-2a), 3.50 (m, 1H, H-5b), 3.51 (dd, $J_{3,4}$ = 3.1 Hz, 1H, H-3b), 3.56 (dd, 1H, H-3a), 3.61 (m, 1H, H-2c), 3.63 (d, $J_{6'6}$ = 11.2 Hz, 1H, H-6'c), 3.69 (dd, $J_{6,5}$ < 1 Hz, 1H, H-6a), 3.76 (ddd, 1H, H-5d), 3.80 (dd, 1H, H-6'a), 3.85 (dd, 1H, H-6'c), 3.87 (dd, 1H, H-4c), 3.89 (dd, 1H, H-2e), 3.90 (db, 1H, -NH), 4.07 (dd, 1H, H-4a), 4.25 (d, 1H, H-6'd), 4.28 (d, $J_{H,H'}$ = 12.1 Hz, 1H, -CHPh), 4.32 (d, $J_{1,2}$ = 7.1 Hz, 1H, H-1d), 4.36 (d, 1H, H-1b), 4.38 (d, J > 8 Hz, 1H, H-1c), 4.40 (d, $J_{H,H'}$ = 12.5 Hz, 1H, -CHPh), 4.45 (d, 1H, H-1a), 4.46 (d, $J_{H',H}$ = 12.5 Hz, 1H, -CHPh), 4.51 (dd, 1H, H-6d), 4.57 (d, 1H, -CHPh), 4.60 (2 d, 2H, $-CH_2$), 4.63 (d, 1H, $-CH_2$), 4.64 (d, 1H, -CHPh), 4.73 (d, 1H, -CH), 4.75 (d, 1H, -CH), 4.76 (d, 1H, -CH), 4.84 (dd, 1H, H-3dH), 4.90 (d, $J_{H,H'}$ = 11.3 Hz, 1H, -CH), 4.91 (d, 1H, $-CH_2$), 4.91 (m, 1H, H-5e), 4.96 (d, $J_{H',H}$ = 11.3 Hz, 1H, -CH), 4.99 (dd, 1H, H-2d), 5.17 (dd, 1H, H-3e), 5.24 (d, $J_{1,2}$ = 3.2 Hz, 1H, H-1e), 5.33 (dd, $J_{4,5}$ < 1 Hz, 1H, H-4e), 5.35 (dd, $J_{4,5}$ < 1 Hz, 1H, H-4d), 5.42 (dd, $J_{4,5}$ < 1 Hz, 1H, H-4b)], 7.15-7.40 (m, 40 H, aromatics).

Anal. Calcd for $C_{103}H_{116}Cl_3NO_{33}\cdot 3\ H_2O$ (2055): C, 60.15; H, 5.74; N, 0.68. Found: C, 59.90; H, 5.85; N, 0.77; MS (MALDI-TOF): (M + Na^+) = 2024.

Benzyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-(3,4-di-*O*-acetyl -2-*O*- benzyl-α-L- fucopyranosyl) -(1→3)]-[6 -*O*-benzyl -2-deoxy- 2- (2,2,2-trichloroethoxycarbonylamino) -β-D- glucopyranosyl] - (1→3) - (4-*O*- acetyl -2,6- di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (25). To a solution of **20** (0.305 g, 0.246 mmol) and **23** (0.235 g, 0.22 mmol) in dry CH_2Cl_2 (3 mL) was added $BF_3\cdot Et_2O$ until the reaction was completed. Then the solution was neutralized with Et_3N and the solvent evaporated under reduced pressure. Flash chromatography (9:1 toluene/acetone) yielded **25** (0.264 g, 60%) as a colorless foam; TLC (6:4 petroleum ether/ethyl acetate): R_f = 0.35; $[\alpha]_D$ = -27.5° (*c* 0.895, chloroform). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.15 (d, $J_{Me,5}$ = 6.5 Hz, 3H, Me-d), 1.89, 1.93, 1.94, 2.00, 2.02, 2.09, 2.12 (7 s, 21H, CH_3), 3.25-5.45 [m, 52H, H,H-COSY: 3.23 (db, $J_{5,4}$ = 9.4 Hz, 1H, H-5a), 3.28 (m, 1H, H-2c), 3.29 (m, 1H, H-5c), 3.32 (d, $J_{6,5}$ < 1 Hz, 1H, H-6b), 3.32 (2d, $J_{6,5}$ < 1 Hz, 1H, H-6,6'b), 3.44 (dd, 1H, H-2a), 3.47 (m, 1H, H-5b), 3.50 (dd, 1H, H-3a), 3.51 (dd, 1H, H-2b), 3.60 (dd, 1H, H-5e), 3.64 (dd, 1H, H-6a), 3.66 (dd, $J_{3,4}$ = 3 Hz, 1H, H-3b), 3.69 (d, 1H, H-6c), 3.69 (d, 1H, H-6'c), 3.71 (dd, 1H, H-6'a), 3.79 (dd, $J_{2,1}$ = 3.2 Hz, $J_{2,3}$ = 10.3 Hz, 1H, H-2d), 3.89 (dd, 1H, H-3c), 3.99 (dd, 1H, H-4a), 4.09 (d, $J_{H,H'}$ = 12.1 Hz, 1H, $-CH_2Ph$), 4.09 (dd, $J_{4,5}$ = $J_{4,3}$ = 10.8 Hz, 1H, H-4c), 4.23 (dd, 1H, H-6e), 4.25 (d, $J_{H,H'}$ = 11.7 Hz, 1H, $-CH_2Ph$), 4.3c (d, 1H, $-CH_2Ph$), 4.41 (d, $J_{H',H}$ = 11.7 Hz, 1H, $-CH_2Ph$), 4.41 (d, 1H, $-CH_2Ph$), 4.42 (d, 1H, H-1a), 4.42 (d, 1H,

H-1b), 4.42 (dd, 1H, H-6'e), 4.42 (d, 1H, -CH_2Ph), 4.42 (d, 1H, -CH_2Ph), 4.52 (d, 1H, -CH_2Ph), 4.55 (d, 1H, -CH_2Ph), 4.56 (d, 1H, H-1e), 4.64 (d, 1H, -CH_2), 4.67 (d, 1H, -CH_2), 4.69 (d, 1H, CH_2), 4.70 (d, 1H, CH_2), 4.71 (d, 1H, CH_2), 4.73 (dd, 1H, H-3e), 4.77 (d, $J_{H,H'}$ = 12 Hz, 1H, CH_2), 4.87 (d, 1H, CH_2), 4.91 (m, 1H, H-5d), 4.93 (db, 1H, -NH), 4.94 (dd, 1H, H-2e), 4.96 (d, 1H, CH_2), 5.02 (d, $J_{1,2}$ = 6.9 Hz, 1H, H-1c), 5.18 (d, $J_{1,2}$ = 3.2 Hz, 1H, H-1d), 5.19 (dd, $J_{3,2}$ = 10.3 Hz, $J_{3,4}$ = 3.3 Hz, 1H, H-3d), 5.27 (dd, 1H, H-4d), 5.28 (dd, 1H, H-4e), 5.45 (db, 1H, H-4b)], 7.22-7.34 (m, 40H, aromatics).

Anal. Calcd for $C_{103}H_{116}Cl_3NO_{33}$ (2001.4): C, 61.83; H, 5.84; N, 0.70. Found: C, 61.87; H, 5.91; N, 1.15; MS (MALDI-TOF): (M + Na^+) = 2025.

Benzyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl - 2 - *O* - benzyl - α - L -fucopyranosyl)-(1→3)] - [6-*O*-benzoyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino) -β-D - glucopyranosyl] - (1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (26). To a solution of **21** (0.462 g, 0.369 mmol) and **23** (0.352 g, 0.336 mmol) in dry CH_2Cl_2 (1 mL) was added BF_3·Et_2O until the reaction was completed. Then the solution was neutralized with Et_3N and the solvent evaporated under reduced pressure. Flash chromatography (7:3 petroleum ether/ethyl acetate) yielded **26** (0.359 g, 53%) as a colorless foam; TLC (1:1 petroleum ether/ethyl acetate): R_f = 0.45; $[\alpha]_D$ = -26.8° (*c* 0.964, chloroform); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.19 (d, $J_{Me,5}$ = 6.3 Hz, 3H, Me-d), 1.90, 1.91, 1.93, 1.99, 2.08, 2.09, 2.13 (7 s, 21H, CH_3), 3.21-5.36 [m, 50H, H,H-COSY: 3.21 (m, 1H, H-5a), 3.26 (2 dd, $J_{6,5}$ < 1 Hz, $J_{6',5}$ < 1 Hz, 2H, H-6,6'b), 3.27 (m, 1H, H-2c), 3.42 (dd, $J_{2,3}$ = 9.3 Hz, 1H, H-2a), 3.43 (m, 1H, H-5b), 3.46 (dd, 1H, H-2b), 3.48 (dd, $J_{3,2}$ = 9.3 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H-3a), 3.56 (m, 1H, H-5c), 3.60 (d, $J_{6,6'}$ = 10.5 Hz, 1H, H-6a), 3.64 (dd, $J_{3,4}$ = 3.3 Hz, $J_{3,2}$ = 9.8 Hz, 1H, H-3b), 3.67 (dd, $J_{6,6'}$ = 10.5 Hz, $J_{6,5}$ = 3.7 Hz, 1H, H-6'a), 3.70 (m, 1H, H-5e), 3.82 (dd, $J_{2,3}$ = 10.6 Hz, $J_{2,1}$ = 3.5 Hz, 1H, H-2d), 3.95 (dd, $J_{4,3}$ = $J_{4,5}$ = 9.3 Hz, 1H, H-4a), 4.02 (dd, 1H, H-3c), 4.03 (dd, 1H, H-4c, 4.20 (d, $J_{H,H'}$ = 12 Hz, 1H, -CH_2-), 4.22 (dd, $J_{6,6'}$ = 11.4 Hz, $J_{6,5}$ = 8.2 Hz, 1H, H-6e), 4.33 (dd, $J_{6',6}$ = 11.8 Hz, $J_{6',5}$ = 4.2 Hz, 1H, H- 6'c), 4.36 (d, $J_{H,H'}$ = 12 Hz, 1H, -CH_2-), 4.39 (d, 1H, H-1b), 4.41 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1a), 4.46 (dd, $J_{6',6}$ = 11.4 Hz, $J_{6',5}$ = 6 Hz, 1H, H-6'e), 4.55 (d, 1H, -CH_2-), 4.55 (d, 1H, -CH_2-), 4.57 (d, 1H, -CH_2-), 4.59 (d, $J_{1,2}$ = 11.7 Hz, 1H, H-1e), 4.63 (d, 1H, -CH_2-), 4.63 (d, 1H, -CH_2-), 4.66 (d, 1H, -CH_2), 4.66 (d, 1H, -CH_2-), 4.68 (d, 1H, -CH_2-), 4.69 (d, 1H, -CH_2-), 4.69 (d, 1H, -CH_2-), 4.69 (d, 1H, -CH_2-), 4.84 (dd, 1H, H-6c), 4.86 (d, 1H, -CH_2-), 4.87 (dd, 1H, H-3e), 4.88 (d, 1H, -CH_2-), 4.91 (m, 1H, H-5d), 4.95 (d, 1H, -CH_2-), 5.00 (db, 1H, -NH), 5.09 (dd, $J_{1,2}$ = 10.4 Hz, 1H, H-1c), 5.09 (dd, 1H, H-2e), 5.19 (d, 1H, H-1d), 5.22 (dd, $J_{3,4}$ = 3.2 Hz, $J_{3,2}$ = 10.6 Hz, 1H, H-3d), 5.31 (dd, $J_{4,3}$ = 3.2 Hz, 1H, H-4d), 5.33 (dd, 1H, H-4e), 5.36 (dd, 1H, H-4b)], 7.0-7.2 (m, 38 H, aromatics), 8.1 (m, 2 H, aromatics).

Anal. Calcd for $C_{103}H_{114}Cl_3NO_{34}\cdot 4\ H_2O$ (2087): C, 59.28; H, 5.89; N, 0.67. Found: C, 59.28; H, 5.89; N, 0.60; MS (MALDI-TOF): (M + Na^+) = 2039.

Benzyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-[(3,4-di-*O*-acetyl-2-*O*-benzyl-α-L-fucopyranosyl) - (1→3)] -(2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→3)-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (27). A solution of **24** (0.227 g, 0.113 mmol) in THF - acetic anhydride - acetic acid (8 : 3: 1) was treated with activated zinc powder (activation with 2% $CuSO_4$ in water for 5 min). The mixture was stirred for 12 h at room temp. and then it was filtered and washed with THF. The solvent was evaporated under redued pressure. Flash chromatography (4:6 petroleum ether/ethyl acetate) yielded **27** (0.129 g, 61%) as a colorless foam; TLC (1:1 petroleum ether/ethyl acetate): R_f = 0.23; $[\alpha]_D$ = -35° (*c* 1.025, chloroform); ^1H NMR (600 MHz, $CDCl_3$): δ 1.22 (d, $J_{Me,5}$ = 6.6 Hz, 3H, Me-e), 1.96, 1.97, 2.05, 2.09, 2.14, 2.17 (6 s, 24H, CH_3), 3.32-5.44 [m, 50H, H,H-COSY: 3.32 (m, 1H, H-5a), 3.35 (2 dd, 2H, H-6,6'b), 3.47 (dd, 1H, H-2b), 3.48 (dd, 1H, H-2a), 3.48 (m, 1H, H-5c), 3.50 (m, 1H, H-5b), 3.55 (dd, 1H, H-3a), 3.57 (dd, $J_{3,4}$ = 3.1 Hz, $J_{3,2}$ = 6.5 Hz, 1H, H-3b), 3.68 (dd, $J_{6,6'}$ = $J_{6,5}$ = 9.7 Hz, 1H, H-6c), 3.69 (dd, $J_{6,6'}$ = $J_{6,5}$ = 9.7 Hz, 1H, H-6a), 3.76 (dd, 1H, H-3c), 3.78 (dd, 1H, H-6'a), 3.83 (m, 1H, H-5d), 3.87 (dd, 1H, H-6'c), 3.90 (2 dd, 2H, H-2c, H-2e), 3.97 (dd, $J_{4,3}$ = $J_{4,5}$ = 9.1 Hz, 1H, H-4c), 4.04 (dd, $J_{4,3}$ = $J_{4,5}$ = 9.3 Hz, 1H, H-4a), 4.28 (dd, $J_{6,6'}$ = 11.2 Hz, $J_{6,5}$ = 7.6 Hz, 1H, H-6d), 4.29 (d, J = 11.9 Hz, 1H, $-CH_2Ph$), 4.41 (d, J = 11.9 Hz, 1H, $-CH_2Ph$), 4.42 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1b), 4.44 (d, J = 11.9 Hz, 1H, $-CH_2Ph$), 4.47 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1a), 4.50 (dd, 1H, H-6'd), 4.51 (d, 1H, $-CH_2Ph$), 4.54 (d, 1H, $-CH_2Ph$), 4.55 (d, 1H, $-CH_2Ph$), 4.58 (d, 1H, H-1d), 4.62 (d, 1H, H-1c), 4.62 (d,·1H, $-CH_2Ph$), 4.63 (d, 1H, $-CH_2Ph$), 4.64 (d, 1H, $-CH_2Ph$), 4.67 (d, J = 11.9 Hz, 1 H, $-CH_2Ph$), 4.74 (d, J = 10.9 Hz, 1 H, $-CH_2Ph$), 4.75 (d, J = 10.7 Hz, 1 H, $-CH_2Ph$), 4.86 (db, 1 H, -NH), 4.88 (dd, 1 H, 3d-H), 4.9 (m, 1 H, 5e-H), 4.91 (2 d, 1 H, $-CH_2Ph$), 4.96 (d, J = 10.7 Hz, 1 H, $-CH_2Ph$), 4.93 (d, 1 H, $-CH_2Ph$), 5.06 (dd, J = 8.3 Hz, J = 10.4 Hz, 1 H, 2d-H), 5.21 (dd, $J_{3,4}$ = 3.2 Hz, $J_{3,2}$ = 10.7 Hz, 1 H, 3e-H), 5.23 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1e-H), 5.34 (dd, 1 H, 4e-H), 5.39 (dd, 1 H, 4d-H), 5.44 (dd, 1 H, 4b-H)], 7.31-7.38 (m, 40 H, aromatics).

Anal. Calcd for $C_{102}H_{117}NO_{32}$ (1869); MS (MALDI-TOF): (M + Na^+) = 1892.

Benzyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-[(3,4-*O*-acetyl-2-*O*-benzyl -α-L- fucopyranosyl)-(1→3)]- (2- acetamido -6-*O*- benzyl -2- deoxy -β-D-glucopyranosyl)-(1→3)- (4-*O*-acetyl -2,6-di-*O*- benzyl-β-D- galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (28). A solution of **25** (0.195 g, 0.0975 mmol) in THF-acetic anhydride-acetic acid (8 : 3: 1) was treated with activated zinc powder (activation with 2% $CuSO_4$ in water for 5 min). The mixture was stirred for 12 h at room temp. and then it was filtered and washed with THF. The solvent was evaporated under

reduced pressure. Flash chromatography (8:2 toluene/acetone) yielded **28** (0.109 g, 60%) as a colorless foam; TLC (8:2 toluene/acetone): R_f = 0.35; $[\alpha]_D$ = -32° (*c* 1.276, chloroform); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.13 (d, $J_{Me,5}$ = 6.5 Hz, 3H, Me-d), 1.92, 1.94, 2.03, 2.04, 2.09, 2.12 (6 s, 24H, CH_3), 3.31-5.50 [m, 50H, H,H-COSY: 3.31 (2 dd, 2H, H-6,6'b), 3.32 (m, 1H, H-5a), 3.38 (m, 1H, H-5c), 3.45 (dd, 1H, H-2a), 3.46 (m, 1H, H-5b), 3.53 (m, 1H, H-2c), 3.54 (dd, 1H, H-3a), 3.55 (dd, 1H, H-2b), 3.65 (2 dd, 2H, H-6,6'c), 3.67 (dd, 1H, H-3b), 3.68 (m, 1H, H-5e), 3.72 (dd, $J_{6,6'} = J_{6,5}$ = 11 Hz, 1H, H-6a), 3.74 (dd, $J_{6',6}$ = 11 Hz, $J_{6',5}$ = 3.9 Hz, 1H, H-6'a), 3.86 (dd, $J_{2,1}$ = 4 Hz, $J_{2,3}$ = 10 Hz, 1H, H-2d), 4.00 (2 dd, 2H, H-4a, H-3c), 4.23 (d, 1H, -CH_2), 4.24 (dd, 1H, H-4c), 4.25 (dd, 1H, H-6e), 4.34 (d, J = 12 Hz, 1H, CH_2), 4.34 (d, J = 10 Hz, 1H, CH_2), 4.40 (d, 1H, CH_2), 4.44 (d, 1H, H-1b), 4.44 (d, 1H, CH_2), 4.46 (d, $J_{1,2}$ = 8.4 Hz, 1H, H-1a), 4.48 (d, $J_{1,2}$ = 9 Hz, 1H, H-1e), 4.52 (dd, 1H, H-6'e), 4.58 (d, 1H, CH_2), 4.61 (2 d, 2H, CH_2), 4.63 (d, 1H, CH_2), 4.70 (dd, $J_{3,4}$ = 3.8 Hz, 1H, H-3e), 4.72, 4.74, 4.75, 4.76 (4 d, 4H, CH_2), 4.88 (m, 1H, H-5d), 4.88 (d, 1H, CH_2), 4.92 (dd, 1H, H-2e), 4.92 (d, 1H, CH_2), 5.00 (d, J = 10.4 Hz, 1H, CH_2), 5.12 (d, $J_{1,2}$ = 6.3 Hz, H-1c), 5.20 (dd, 1H, H-3d), 5.27 (dd, 1H, H-4d), 5.30 (d, $J_{1,2}$ = 2.5 Hz, 1H, H-1d), 5.30 (dd, 1H, H-4e), 5.40 (db, 1H, -NH), 5.50 (dd, $J_{4,5} = J_{4,3}$ = 3.0 Hz, 1H, H-4b)], 7.1-7.3 (m, 40 H, aromatics).

Anal. Calcd for $C_{102}H_{117}NO_{32}$ (1869); MS (MALDI-TOF): (M + Na^+) = 1892.

***O*-(α-L-Fucopyranosyl)-(1→4)-(β-D-galactopyranosyl) -(1→3) -2-[(acetamido-2-deoxy-β-D-glucopyranosyl)-(1→3)]-(β-D-galactopyranosyl)-(1→4) -β-D-glucopyranose (1).** To a solution of **27** (0.068 g, 0.0325 mmol) in MeOH (1 mL) was added a catalytic quantity of $Pd(OH)_2$/C and the mixture was hydrogenated at 1 atm. After 1 d the solution was filtered and the solvent evaporated. The crude was submitted to the following reaction without further purification. It was dissolved in MeOH (1 mL) and a catalytic quantity of a 0.1 M solution of MeONa was added. After 24 h the solution was neutralized with ion exchange resin IR 120, H+-form. The solution was filtered and the solvent evaporated. Chromatography on amino-phase (8:2 ethanol/water) yielded **1** (0.025 g, 90%) as a colorless solid. - $C_{32}H_{55}O_{25}N$ (853.8); ^{1}H NMR (600 MHz, D_2O): δ 1.06 (d, $J_{Me,5}$ = 6.6 Hz, 3H, Me-e), 1.92 (s, 3H, CH_3), 3.16-4.91 [m, 33H, H,H-COSY: 3.16 (dd, 1H, H-2a), 3.37 (dd, $J_{2,1} = J_{2,3}$ = 8 Hz, 1H, H-2d), 3.42 (m, 1H, H-5c), 3.45 (m, 1H, H-5d), 3.49 (m, 2H, H-5a, H-2b), 3.51 (dd, 1H, H-3d), 3.52 (m, 2H, H-3a, H-4a), 3.59 (m, 1H, H-5b), 3.61 (m, 3H, H-6a, H-3b, H-6b), 3.62 (2 dd, 2H, H-6,6'd), 3.65 (dd, 1H, H-4c), 3.67 (2 dd, 2H, H-6'a, H-6'b), 3.68 (dd, 1H, H-4e), 3.69 (dd, 1H, H-2e), 3.75 (dd, 1H, H-6c), 3 77 (2 dd, 2H, H-3e, H-4d), 3.83 (dd, 1H, H-2c), 3.83 (dd, 1H, H-6'c), 3.97 (dd, 1H, H-3c), 4.03 (dd, 1H, H-4b), 4.32 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1b), 4.39 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1d), 4.55 (d, $J_{1,2}$ = 8.0 Hz, 1H, H-1a), 4.59 (d, $J_{1,2}$ = 7.9 Hz, 1H, H-1c), 4.76 (m, 1H, H-5e), 4.91 (d, $J_{1,2}$ = 3.8 Hz, 1H, H-1e).

Anal. Calcd for $C_{32}H_{55}NO_{25}$ (853.8); MS MALDI-TOF: (M+Na) (877).

***O*-(β-D-Galactopyranosyl) - (1→4) - [(α-L- fucopyranosyl) -(1→3)]-2-deoxy-2-acetamido-β-D-glucopyranosyl)-(1→3)-(β-D-galactopyranosyl-(1→4)-β-D-glucopyranose (2).** To a solution of **28** (0.058 g, 0.031 mmol) in MeOH (1 mL) was added a catalytic quantity of $Pd(OH)_2/C$ and the mixture was hydrogenated at 1 atm. After 1 day the solution was filtered and the solvent evaporated. The crude was submitted to the following reaction with further purification. It was dissolved in MeOH (1 mL) and a catalytic quantity of a 0.1 M solution of MeONa was added. After 24 h the solution was neutralized with ion exchange resin IR 120, H+-form. The solution was filtered and the solvent evaporated. Chromatography on amino-phase (8:2 ethanol/water) yielded **2** (0.024 g, 90%) as a colorless solid. ^1H NMR (600 MHz, D2O): (1.07 (d, $J_{Me,5}$ = 6.5 Hz, 3H, Me-d), 1.91 (s, 3H, CH3), 3.17-5.11 [m, 33H, H,H-COSY: 3.17 (m, 1H, H-2a), 3.39 (dd, $J_{2,1}$ = 8.1 Hz, $J_{2,3}$ = 8.5 Hz, 1H, H-2e), 3.47 (m, 1H, H-5c), 3.47 (m, 1H, H-5a), 3.47 (dd, 1H, H-2b), 3.50 (m, 1H, H-5e), 3.53 (dd, 1H, H-3a), 3.53 (dd, 1H, H-4a), 3.59 (dd, 1H, H-2d), 3.60 (m, 1H, H-5b), 3.61 (dd, 1H, H-3b), 3.62 (d, 1H, H-6e), 3.62 (d, 1H, H-6'e), 3.64 (dd, 1H, H-6a), 3.64 (dd, 1H, H-6b), 3.69 (dd, 1H, H-6'b), 3.69 (dd, 1H, H-4d), 3.70 (dd, 1H, H-6'a), 3.76 (dd, 1H, H-6c), 3.77 (dd, 1H, H-3c), 3.79 (dd, 1H, H-3d), 3.85 (dd, 1H, H-4c), 3.86 (m, 1H, H-2c), 3.86 (dd, 1H, H-6'c), 3.90 (dd, 1H, H-3e), 4.05 (dd, $J_{4,5}$ = 1 Hz, $J_{4,3}$ = 3.0 Hz, 1H, H-4b), 4.12 (dd, $J_{4,5}$ (1 Hz, $J_{4,3}$ = 2.9 Hz, 1H, H-4e), 4.33 (d, $J_{1,2}$ = 7.9 Hz, 1H, H-1b), 4.36 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1e), 4.57 (d, $J_{1,2}$ = 7.9 Hz, 1H, H-1a), 4.61 (d, 1H, H-1c), 4.74 (m, 1H, H-5d), 5.02 (d, $J_{1,2}$ = 3.9 Hz, 1H, H-1d)].

Anal. Calcd for $C_{32}H_{55}NO_{25}$ (853.8); MS MALDI-TOF: (M+Na) (877).

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