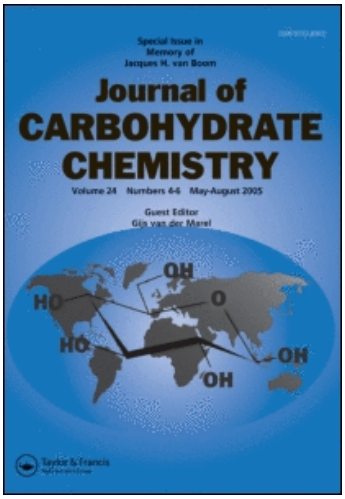

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Preparation of S- and N-Linked Glycosylated Amino Acid Building Blocks for Solid-phase Glycopeptide Library Synthesis

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A general route for the preparation of 1,2-*trans*-linked S-glycosylated amino acid building blocks by a Lewis-acid-promoted condensation of peracetylated glycosyl donors and N^{α}-Fmoc-Cys-OH, in good overall yield, is described. In addition, a short and time-efficient route was applied for the synthesis of N-glycosylated amino acid building blocks in good overall yields by coupling unprotected glycosylamines and N^{α}-Fmoc-Asp(OH)-O^{t}Bu using TBTU activation.

Keywords Glycosylated amino acid, S-Glycosidic linkage, N-Glycosidic linkage, Glycopeptide

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In memory of Professor Jacques H. van Boom.
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INTRODUCTION

Interactions between membrane glycoconjugates and carbohydrate-binding proteins are highly important in mediating intercellular recognition processes. Typical examples of these processes are cell–cell recognition, cell growth regulation, cancer cell metastasis, and viral, bacterial, and parasitical infections.[1,2] Fundamental interaction studies to understand at a molecular level, and possibly to intervene with these processes, are hampered by the low accessibility of complex carbohydrates. It has been shown that the complete glycan is not involved in the interaction with the receptor. Essentially, only the residues at the nonreducing end of the glycan that are in close contact with the external environment are important for the interaction. This allows the use of simplified structures containing a carbohydrate epitope attached to a scaffold as mimics of complex glycans in interaction studies.

Previously, glycopeptides, built up from relatively small peptide backbones decorated with one or more O-linked monosaccharides, have been successfully used as mimics of complex oligosaccharides. These compounds can be generated in library format via a combinatorial approach.[3,4] However, a common disadvantage of O-glycopeptides is the low stability of the O-glycosidic linkage toward glycan-degrading enzymes and acidic conditions. Replacing the O-glycosidic linkage by an N- (amide) or S-glycosidic linkage greatly enhances the stability of these compounds toward biodegradation and acidic conditions.

The most frequently implemented method for the generation of "one-bead-one-compound" (glyco)peptide libraries[5,6] is the split-and-mix method.[7,8] In this method, glycosylated amino acids are used in the stepwise assembly of glycopeptides on the solid support. To facilitate the synthesis of S- and N-glycopeptide libraries via this methodology, easy access to S- and N-glycosylated amino acid building blocks is a prerequisite. Different approaches for the preparation of protected S-glycosylated amino acids have been reported, including Koenigs-Knorr[9] and Lewis-acid catalyzed glycosylation reactions,[10] as well as the use of diverse glycosyl donors, such as glycosyl fluorides,[11] trichloroacetimidates,[12] and isothiouronium salts.[13] Furthermore, the synthesis of unprotected S-glycosylated amino acids on solid support has been described.[14] N-Glycosylated amino acids have been prepared by coupling a glycosylamine to an array of aspartic acid derivatives and using a variety of coupling agents, such as dicyclohexyl carbodiimide (DCC), benzatriazole-1-yl-oxy-*tris*-(dimethylamino)-phosphoniumhexafluorophosphate (BOP), and 2-(1H-benzotriazole-1–yl)-1,1,3,3-tetramethyluronium tetrafluoroborate (TBTU).[15–18] In these protocols, the glycosylamine is usually prepared by the catalytic reduction of a properly protected glycosyl azide[7,16,19] or by the treatment of unprotected monosaccharides with ammonium hydrogencarbonate.[17,18,20] Additionally, N-glycosylated amino acids have been prepared via isothiocyanates or

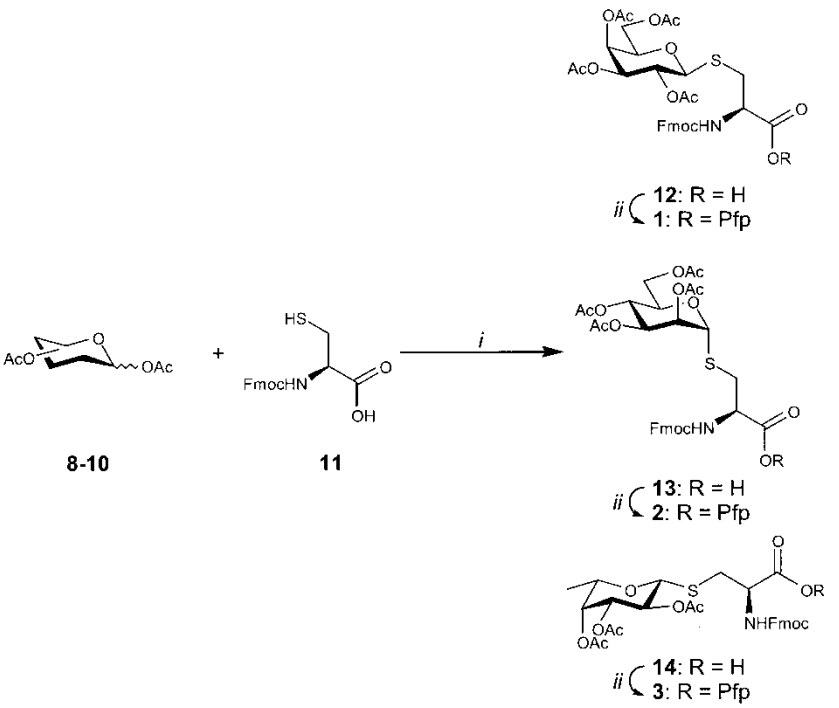
pentenyl glycosides.[21–25] All approaches described so far for the synthesis of S- and N-glycosylated amino acids resulted in reasonable to good yields; however, in general, the preparation of the used glycosyl donors is time consuming and requires multiple steps.

In the context of our studies focused on an understanding of the interaction between glycan mimics (synthetic glycopeptides) and plant and animal lectins, here, two short and generally applicable routes are described for the preparation of galactosylated, mannosylated, and fucosylated amino acids with a 1,2-*trans*-thioglycosidic linkage or a β-N-glycosidic linkage in overall yields, comparable to those reported in literature.

RESULTS AND DISCUSSION

Synthesis of D-Galactosylated, D-Mannosylated, and L-Fucosylated L-Cysteine

N^{α}-fluoren-9-ylmethoxycarbonyl-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-L-cysteine-*O*-pentafluorophenyl ester (**1**), N^{α}-fluoren-9-ylmethoxycarbonyl-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-L-cysteine-*O*-pentafluorophenyl ester (**2**), and N^{α}-fluoren-9-ylmethoxycarbonyl-*S*-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-L-cysteine-*O*-pentafluorophenyl ester (**3**) (Sch. 1) were prepared in a two-step reaction sequence from the appropriate peracetylated glycosyl donor and N^{α}-Fmoc-Cys-OH (**11**). Initial attempts to couple either peracetylated D-galactose or 2,3,4,6-tetra-*O*-acetyl-α/β-D-galactopyranosyl trichloroacetimidate to **11**, using trimethylsilyl triflate-activation (3 equiv. and 0.1 equiv., respectively), resulted in low yields. Coupling of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide to **11**, using $Hg(CN)_2$ activation, showed no product formation. Previously, the coupling of peracetylated D-galactose to **11** (1.2 equiv.) using tin(IV) chloride as the activator yielded 59% of **12**.[10] This procedure was slightly modified, and 2 equiv. of the appropriate peracetylated donors D-galactopyranose (**8**), D-mannopyranose (**9**), and L-fucopyranose (**10**) were each coupled with acceptor **11** in the presence of tin(IV) chloride (2.6 equiv.) to afford **12**, **13**, and **14** in 75%, 63%, and 69% yield, respectively. It may be clear that the use of an excess of donor, the least expensive starting compound, resulted in a higher yield than previously reported for glycosylated amino acid building block **12**. Compounds **12**–**14** could be converted into their corresponding pentafluorophenyl ester derivatives by treatment with pentafluorophenyl trifluoroacetate and pyridine in DMF[26] to afford glycosylated amino acid building blocks **1** in 67% yield and **2** and **3** in quantitative yield.

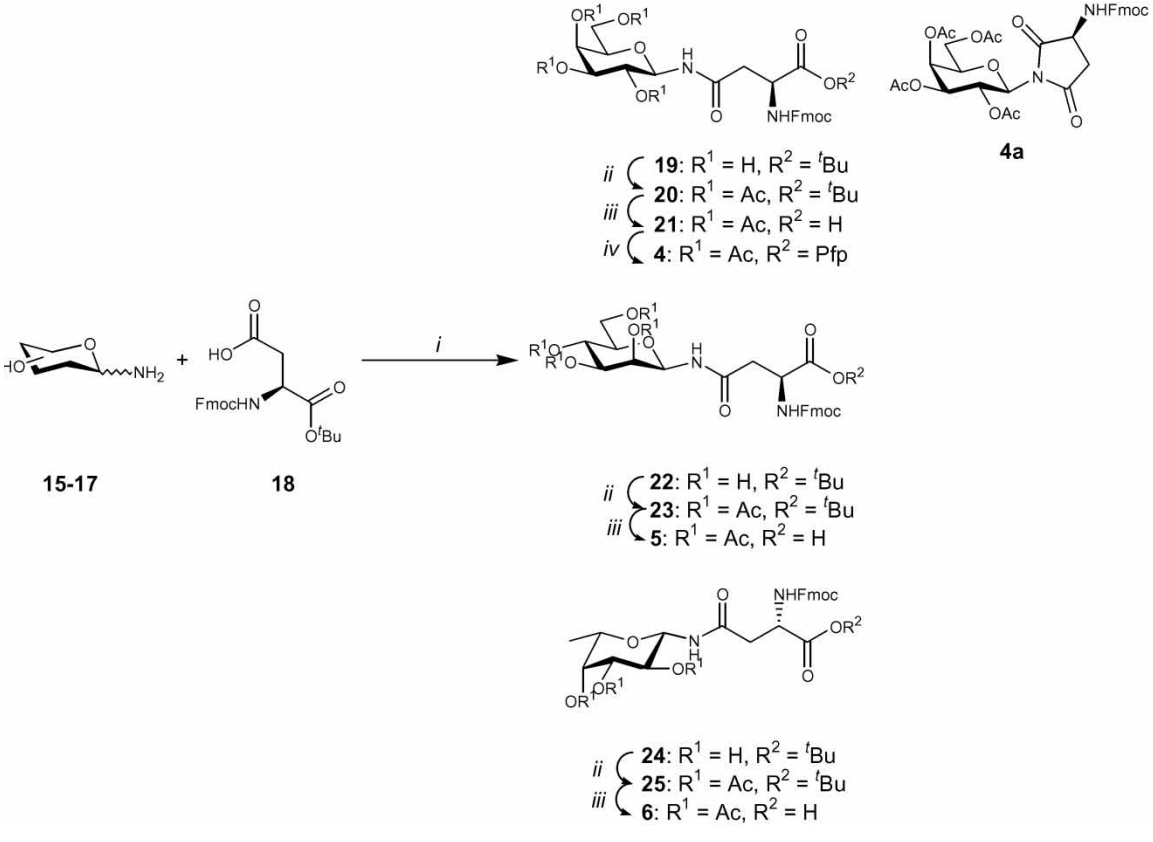


Scheme 1: *i*: $SnCl_4$, CH_2Cl_2; *ii*: $PfpO(CO)CF_3$, pyridine, DMF.

Synthesis of D-Galactosylated, D-Mannosylated, and L-Fucosylated L-Asparagine

N^{α}-fluoren-9-ylmethoxycarbonyl-N^{γ}-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-L-asparagine-*O*-pentafluorophenyl ester (**4**), N^{α}-fluoren-9-ylmethoxycarbonyl-N^{γ}-(2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl)-L-asparagine (**5**), and N^{α}-fluoren-9-ylmethoxycarbonyl-N^{γ}-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-L-asparagine (**6**) (Sch. 2) were synthesized from unprotected glycosylamines and commercially available N^{α}-Fmoc-Asp-O^{t}Bu (**18**). The D-galactopyranosyl (**15**), D-mannopyranosyl (**16**), and L-fucopyranosyl (**17**) amines were prepared from their corresponding unprotected saccharides by treatment with ammonium hydrogencarbonate.[27] Due to their labile nature, the glycosylamines were directly used for their coupling with **18**, using TBTU/*N*-hydroxybenzotriazole·H_2O (HOBt) activation, to afford **19**, **22**, and **24**, respectively. All three compounds were directly acetylated using acetic anhydride in pyridine, yielding **20**, **23**, and **25**, respectively. Subsequent removal of the *tert*-butyl groups under acidic conditions afforded compounds **21**, **5**, and **6**, respectively, in 56%, 35%, and 73% overall yield.

Although the free acids **21**, **5**, and **6** are useful building blocks, the pentafluorophenyl derivatives may also be of interest, because these activated esters



Scheme 2

can be directly applied for peptide couplings, using 3,4-dihydro-3-hydroxy-4-oxo-1,2,3-benzotriazine (DHBT) as the catalyst. To demonstrate this, **21** was treated with pentafluorophenyl trifluoroacetate and pyridine[26] to obtain building block **4** in 56% yield, however, together with a significant amount of a byproduct. The MALDI-TOF mass spectrum indicated a mass of 689.375 $[M + Na]^+$. The disappearance of the anomeric NH-signal in the ^1H NMR spectrum and the change of the $J_{\alpha,\beta}$-coupling pattern suggested the formation of a succinimide **4a**. Nucleophilic attack of the amide nitrogen on the β-carboxyl function of aspartic acid during the formation of the pentafluorophenyl ester under alkaline conditions leads to succinimide formation. A similar cyclization reaction has been reported previously.[28,29] It could be of interest to explore succinimides as possible glycosylated amino acid building blocks in glycopeptide synthesis.

It should be noted that pentafluorophenyl ester derivatives of glycosylated asparagine building blocks have previously been prepared by coupling of a 2,3,4,6-tetra-*O*-acetyl-β-D-mannosylamine and acid chloride N^{α}-Fmoc-Asp(Cl)-O^{t}Bu in reasonable overall yield over six reaction steps.[20] This synthesis route avoids succinimide formation; however, more steps are required to prepare the glycosylated amino acid. Recently, galactosylated amino acid **21** and mannosylated amino acid **5** have been prepared in an eight-step reaction sequence using 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl azide and 2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl azide as the key intermediates.[16] The protocol described in this paper for the preparation of glycosylated asparagine derivatives turned out to be shorter and more time efficient than the published methods.

In summary, 1,2-*trans*-S-linked glycosylated amino acid building blocks have been synthesized in good overall yields. Furthermore, N-glycosylated amino acid building blocks could be obtained in good overall yields via a short and time-efficient route. The prepared S- and N-glycosylated amino acid building blocks **1**–**6** have been used for the preparation of *in vivo* stable glycopeptide libraries, as will be published elsewhere.

EXPERIMENTAL

General Methods

All solvents and reagents were of reagent grade and were used without further purification. The reactions were monitored by TLC on Silica Gel 60 F_{254} (Merck); after examination under UV light, the compounds were visualized by heating with orcinol (2 mg mL^{-1}) in 20% (v/v) methanolic H_2SO_4. In the work-up procedures of reaction mixtures, organic solutions were washed with appropriate amounts of the indicated aqueous solutions, and then dried over Na_2SO_4, and concentrated under reduced pressure at 30 to 50°C on a

water bath. Column chromatography was performed on Silica Gel 60 (Merck, 0.040–0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded at 300 K with a Bruker AMX 500 spectrometer; the values for δ_H are given in ppm relative to the signal for internal Me_4Si ($\delta_H = 0$, $CDCl_3$) and the values for δ_C are given in ppm relative to the signal for $CDCl_3$ ($\delta_C = 77.1$, $CDCl_3$). Two-dimensional ^{1}H-^{1}H TOCSY (mixing times 7 and 100 ms) and ^{1}H-^{13}C correlated HSQC-spectra were recorded at 300 K with a Bruker AMX 500 spectrometer. Exact masses were measured by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) using a Voyager-DE Pro (Applied Biosystems) instrument in the reflector mode at a resolution of 5000 FWHM. α-Cyano-4-hydroxycinnamic acid was used as a matrix. A mixture of peptides (Peptide calibration Mix4 [Proteomix] 500–3500 Da, LaserBio Labs) was added as the internal standard.

***N*$^\alpha$-fluoren-9-ylmethoxycarbonyl-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-L-cysteine (12).** Compound **11** was quantitatively obtained from commercially available N^α-Fmoc-Cys(Trt)-OH via treatment with trifluoroacetic acid/CH_2Cl_2/H_2O/triisopropylsilane (6 : 4 : 0.5 : 0.5, v/v). A solution of peracetylated D-galactose (**8**; 262 mg, 0.67 mmol) and N^α-fluoren-9-ylmethoxycarbonyl-L-cysteine (**11**; 115 mg, 0.34 mmol) in dry CH_2Cl_2 (10 mL) was stirred at rt, then $SnCl_4$ (102 μL, 0.87 mmol) was added, and the mixture was stirred overnight. After dilution with CH_2Cl_2, the mixture was washed with 1 M aq. HCl and H_2O, dried, filtered, and concentrated. Column chromatography (8 : 2 CH_2Cl_2/acetone → 95 : 5 CH_2Cl_2/MeOH) of the residue yielded **12**, isolated as a white solid (131 mg, 75%). TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.50$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.99$, 2.03, 2.07, and 2.15 (4 s, each 3H, 4 COC*H*$_3$), 3.26 (m, 2H, H-β1 and H-β2), 3.75 (t, 1H, H-5), 3.99 (dd, 1H, $J_{5,6b} = 6.6$ Hz, $J_{6a,6b} = 11.6$ Hz, H-6b), 4.24 (t, 1H, $J_{CH,CH2} = 6.7$ Hz, Fmoc-C*H*), 4.29 (dd, 1H, $J_{5,6a} = 5.8$ Hz, H-6a), 4.42 (bt, 1H, Fmoc-CH*H*), 4.50 (m, 2H, H-1 and Fmoc-C*H*H), 4.64 (m, 1H, H-α), 5.02 (dd, 1H, $J_{2,3} = 10.1$ Hz, $J_{3,4} = 3.1$ Hz, H-3), 5.19 (t, 1H, H-2), 5.41 (d, 1H, H-4), 6.00 (d, 1H, $J_{NH,\alpha} = 7.0$ Hz, N*H*), 7.54 (m, 8H, Fmoc-Ar*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 20.5$ (CO*C*H$_3$), 34.0 (C-β), 46.9 (Fmoc-*C*H), 53.6 (C-α), 61.7 (C-6), 66.8 (C-2), 67.2 (Fmoc-*C*H2 and C-4), 71.6 (C-3), 74.6 (C-5), 85.8 (C-1), 120.0, 124.9, 127.0, and 127.8 (Fmoc Ar*C*). High-resolution MS data of $C_{32}H_{35}NO_{13}S$ (M, 673.183): $[M + Na]^+$ found 696.305; calcd 696.173.

***N*$^\alpha$-fluoren-9-ylmethoxycarbonyl-*S*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-L-cysteine-*O*-pentafluorophenyl ester (1).** Pentafluorophenyl trifluoroacetate (154 μL, 0.90 mmol) and pyridine (72.7 μL, 0.90 mmol) were added to a solution of **12** (575 mg, 0.85 mmol) in dry DMF (5 mL). After 1.5 hr, an additional portion of pentafluorophenyl trifluoroacetate (154 μL, 0.90 mmol) and pyridine (72.7 μL, 0.90 mmol) were added. After 0.5 hr, TLC showed a complete conversion of the starting compound into a higher moving

spot. The solution was co-concentrated with toluene, and column chromatography (99 : 1 → 95 : 5 → 9 : 1 CH_2Cl_2/EtOAc) of the residue afforded **1**, isolated as a white foam (473 mg, 67%). TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.75$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.89$, 2.01, 2.08, and 2.11 (4 s, each 3H, 4 COCH_3), 3.17 (dd, 1H, $J_{\alpha,\beta2} = 7.6$ Hz, $J_{\beta1,\beta2} = 14.8$ Hz, H-β2), 3.43 (dd, 1H, $J_{\alpha,\beta1} = 3.4$ Hz, H-β1), 3.75 (t, 1H, H-5), 4.03 (m, 2H, H-6a and H-6b), 4.26 (t, 1H, $J_{CH,CH2} = 6.4$ Hz, Fmoc-C*H*), 4.43 (d, 2H, $J_{1,2} = 9.9$ Hz, H-1 and Fmoc-CH*H*), 4.66 (dd, 1H, $J_{CH2,CH2} = 10.9$ Hz, Fmoc-C*H*H), 4.82 (m, 1H, H-α), 5.04 (dd, 1H, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 2.6$ Hz, H-3), 5.26 (t, 1H, H-2), 5.39 (d, 1H, H-4), 6.21 (d, 1H, $J_{NH,\alpha} = 7.5$ Hz, N*H*), 7.54 (m, 8H, Fmoc-Ar*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 20.5$, 20.7, and 20.8 (CO*C*H$_3$), 31.4 (C-β), 47.1 (Fmoc-*C*H), 54.7 (C-α), 61.7 (C-6), 66.4 (C-2), 67.0 (Fmoc-*C*H$_2$ and C-4), 71.7 (C-3), 75.2 (C-5), 83.4 (C-1), 120.4, 125.1, 127.4, and 128.0 (Fmoc-Ar*C*). High-resolution MS data of $C_{38}H_{34}F_5NO_{13}S$ (M, 839.167): $[M + Na]^+$ found 862.159; calcd 862.157.

***N*$^{\alpha}$-fluoren-9-ylmethoxycarbonyl-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-L-cysteine (13).** Compound **13** was prepared from peracetylated D-mannopyranose (**9**; 151.9 mg, 0.39 mmol) and **11** (66.8 mg, 0.19 mmol) as described for **12**. The product was purified by column chromatography (8 : 2 CH_2Cl_2/acetone → 95 : 5 CH_2Cl_2/MeOH → 9 : 1 CH_2Cl_2/MeOH + 1% HOAc) to yield **13**, isolated as a white solid (81 mg, 63%). TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.35$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.00$, 2.05, 2.06, and 2.15 (4 s, each 3H, 4 COCH_3), 3.18 (dd, 1H, $J_{\alpha,\beta1} = 2.1$ Hz, $J_{\beta1,\beta2} = 14.7$ Hz, H-β1), 3.31 (dd, 1H, $J_{\alpha,\beta2} = 4.5$ Hz, H-β2), 4.22 (m, 4H, Fmoc-C*H*, Fmoc-CH*H*, H-6a, and H-6b), 4.32 (m, 1H, H-5), 4.42 (m, 1H, Fmoc-C*H*H), 4.79 (m, 1H, H-α), 5.19 (dd, 1H, $J_{2,3} = 2.6$ Hz, $J_{3,4} = 9.8$ Hz, H-3), 5.30 (m, 2H, H-4 and H-1), 5.35 (bs, 1H, H-2), 6.10 (d, 1H, $J_{NH,\alpha} = 8.1$ Hz, N*H*), 7.54 (m, 8H, Fmoc-Ar*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 20.8$ and 21.1 (CO*C*H$_3$), 36.0 (C-β), 47.4 (Fmoc-*C*H), 54.0 (C-α), 62.6 (C-6), 66.6 (C-4), 67.7 (Fmoc-*C*H$_2$), 69.7 (C-3), 70.1 (C-5), 71.6 (C-2), 84.6 (C-1, $J_{C\text{-}1,H\text{-}1} = 169$ Hz), 120.2, 125.3, 127.6, and 128.0 (Fmoc-Ar*C*). High-resolution MS data of $C_{32}H_{35}NO_{13}S$ (M, 673.183): $[M + Na]^+$ found 696.308; calcd 696.173.

***N*$^{\alpha}$-fluoren-9-ylmethoxycarbonyl-*S*-(2,3,4,6–tetra-*O*-acetyl-α-D-mannopyranosyl)-L-cysteine-*O*-pentafluorophenyl ester (2).** Compound **2** was prepared from **13** (81.2 mg, 0.12 mmol) as described for **1**. Column chromatography (99 : 1 → 95 : 5 → 9 : 1 CH_2Cl_2/EtOAc) afforded **2**, isolated as a white foam (99.3 mg, quantitative). TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.95$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.97$, 2.01, 2.07, and 2.16 (4 s, each 3H, 4 COCH_3), 3.24 (dd, 1H, $J_{\alpha,\beta1} = 3.2$ Hz, $J_{\beta1,\beta2} = 15.0$ Hz, H-β1), 3.51 (dd, 1H, $J_{\alpha,\beta2} = 5.5$ Hz, H-β2), 4.15 (dd, 1H, $J_{5,6} = 7.2$ Hz, $J_{6a,6b} = 12.4$ Hz, H-6b), 4.24 (m, 2H, Fmoc-C*H* and H-6a), 4.32 (t, 1H, H-5), 4.46 (m, 2H, Fmoc-CH_2), 5.16 (m, 2H, H-3 and H-α), 5.30 (m, 2H, H-1 and H-4), 5.43 (bs, 1H, H-2), 6.37

(d, 1H, $J_{NH,\alpha} = 9.2$ Hz, N*H*), 7.54 (m, 8H, Fmoc-Ar*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 20.8$ and 21.1 (CO*C*H$_3$), 36.8 (C-β), 47.4 (Fmoc-*C*H), 54.4 (C-α), 62.6 (C-6), 66.2 (C-4), 67.7 (Fmoc-*C*H$_2$), 69.3 (C-3), 70.5 (C-5), 71.6 (C-2), 85.3 (C-1), 120.6, 125.3, 127.2, and 128.0 (Fmoc-Ar*C*). High-resolution MS data of $C_{38}H_{34}F_5NO_{13}S$ (M, 839.167): $[M + Na]^+$ found 862.166; calcd 862.157.

***N*$^{\alpha}$-fluoren-9-ylmethoxycarbonyl-*S*-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-L-cysteine (14).** Compound **14** was prepared from peracetylated L-fucopyranose (**10**; 550.7 mg, 1.66 mmol) and **11** (474.2 mg, 1.38 mmol) according to the procedure described for **12**. Column chromatography (7 : 3 CH_2Cl_2/acetone → 95 : 5 CH_2Cl_2/MeOH → 9 : 1 CH_2Cl_2/MeOH + 1% HOAc) afforded **14**, isolated as an off-white foam (582 mg, 69%). TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.78$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.93$ (d, 3H, $J_{5,6} = 6.3$ Hz, H-6), 2.00, 2.06, and 2.14 (3 s, each 3H, 3 COC*H*$_3$), 2.79 (dd, 1H, $J_{\alpha,\beta1} = 3.8$ Hz, $J_{\beta1,\beta2} = 15.0$ Hz, H-β1), 3.35 (m, 2H, H-5 and H-β2), 4.15 (d, 1H, $J_{1,2} = 9.9$ Hz, H-1), 4.21 (t, 1H, $J_{CH,CH2} = 5.5$ Hz, Fmoc-C*H*), 4.54 (dd, 1H, $J_{CH2,CH2} = 11.0$ Hz, Fmoc-CH*H*), 4.66 (m, 1H, H-α), 4.77 (m, 1H, Fmoc-C*H*H), 4.98 (dd, 1H, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 2.8$ Hz, H-3), 5.12 (m, 2H, H-2 and H-4), 6.17 (d, 1H, $J_{NH,\alpha} = 7.3$ Hz, N*H*), 7.54 (m, 8H, Fmoc-Ar*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 15.9$ (C-6), 20.6 (CO*C*H$_3$), 34.1 (C-β), 47.5 (Fmoc-*C*H), 54.1 (C-α), 66.2 (Fmoc-*C*H$_2$), 67.2 (C-4), 70.1 (C-2), 72.1 (C-3), 73.6 (C-5), 85.0 (C-1, $J_{C\text{-}1,H\text{-}1} = 156$ Hz), 120.2, 125.1, 127.2, and 128.0 (Fmoc-Ar*C*). High-resolution MS data of $C_{30}H_{33}NO_{11}S$ (M, 613.198): $[M + Na]^+$ found 638.376; calcd 638.167.

***N*$^{\alpha}$-fluoren-9-ylmethoxycarbonyl-*S*-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-L-cysteine-*O*-pentafluorophenyl ester (3).** Compound **3** was prepared from **14** (80.6 mg, 0.13 mmol) as described for **1**. Column chromatography (99 : 1 → 95 : 5 → 9 : 1 CH_2Cl_2/EtOAc) afforded **3**, isolated as a white foam (102 mg, quantitative). TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.95$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.88$ (d, 3H, $J_{5,6} = 6.4$ Hz, H-6), 2.01, 2.07, and 2.13 (3 s, each 3H, 3 COC*H*$_3$), 2.89 (dd, 1H, $J_{\alpha,\beta1} = 3.8$ Hz, $J_{\beta1,\beta2} = 15.0$ Hz, H-β1), 3.32 (q, 1H, H-5), 3.39 (dd, 1H, $J_{\alpha,\beta2} = 5.7$ Hz, H-β2), 4.10 (d, 1H, $J_{1,2} = 10.1$ Hz, H-1), 4.21 (t, 1H, Fmoc-C*H*), 4.58 (dd, 1H, $J_{CH,CH2} = 5.1$ Hz, $J_{CH2,CH2} = 11.0$ Hz, Fmoc-CH*H*), 4.85 (dd, 1H, $J_{CH,CH2} = 5.7$ Hz, Fmoc-C*H*H), 4.97 (m, 2H, H-3 and H-α), 5.12 (m, 2H, H-2 and H-4), 6.37 (d, 1H, $J_{NH,\alpha} = 8.4$ Hz, N*H*), 7.54 (m, 8H, Fmoc-Ar*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 15.8$ (C-6), 20.7 (CO*C*H$_3$), 34.6 (C-β), 47.7 (Fmoc-*C*H), 54.6 (C-α), 65.9 (Fmoc-*C*H$_2$), 67.3 (C-4), 70.0 (C-2), 72.0 (C-3), 73.5 (C-5), 85.1 (C-1), 120.3, 125.2, 127.3, and 128.1 (Fmoc-Ar*C*). High-resolution MS data of $C_{36}H_{32}F_5NO_{11}S$ (M, 781.162): $[M + Na]^+$ found 804.150; calcd 804.151.

***N*$^{\alpha}$-fluoren-9-ylmethoxycarbonyl-*N*$^{\gamma}$-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-L-asparagine-*O*-*tert*-butyl ester (20).** A solution of N^{α}-fluoren-9-ylmethoxycarbonyl-L-aspartic acid-*O*-*tert*-butyl ester (**18**; 2.00 g, 4.86 mmol), TBTU (4.68 g, 14.6 mmol), and *N,N*-diisopropylethylamine (0.64 mL, 3.65 mmol) in dry DMF (20 mL) was added to 1-amino-D-galactopyranose (**15**; 3.48 g, 19.4 mmol),[27] and the mixture was stirred overnight. After co-concentration with toluene, a solution of the residue in CH_2Cl_2 was washed with H_2O, dried, and concentrated to obtain glycosylated amino acid intermediate **19** as a white foam (1.86 g, 67%). TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.28$. A solution of **19** (1.86 g, 3.25 mmol) in 1 : 1 pyridine/Ac_2O (30 mL) was stirred overnight, then co-concentrated with toluene. Column chromatography (85 : 15 → 75 : 25 CH_2Cl_2/EtOAc) of the residue afforded **20**, isolated as a white foam (2.04 g, 85%). TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.56$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.45$ (s, 9H, C(C*H*$_3$)$_3$), 2.00, 2.02, 2.08, and 2.13 (4 s, each 3H, 4 COC*H*$_3$), 2.68 (dd, 1H, $J_{\alpha,\beta1} = 3.8$ Hz, $J_{\beta1,\beta2} = 16.3$ Hz, H-β1), 2.86 (dd, 1H, $J_{\alpha,\beta2} = 4.1$ Hz, H-β2), 4.01 (t, 1H, H-5), 4.09 (m, 2H, H-6a and H-6b), 4.23 (t, 1H, $J_{CH,CH2} = 7.2$ Hz, Fmoc-C*H*), 4.32 (t, 1H, Fmoc-CH*H*), 4.43 (dd, 1H, $J_{CH2,CH2} = 10.1$ Hz, Fmoc-C*H*H), 4.51 (m, 1H, H-α), 5.13 (t, 1H, $J_{2,3} = 10.1$ Hz, H-2), 5.14 (dd, 1H, $J_{3,4} = 2.3$ Hz, H-3), 5.21 (t, 1H, $J_{1,NH} = J_{1,2} = 8.9$ Hz, H-1), 5.43 (d, 1H, H-4), 5.92 (d, 1H, $J_{NH,\alpha} = 8.6$ Hz, N$^{\alpha}$*H*), 6.38 (d, 1H, N$^{\gamma}$*H*), 7.54 (m, 8H, Fmoc-Ar*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 20.5$ (CO*C*H$_3$), 28.1 (C(*C*H$_3$)$_3$), 38.1 (C-β), 47.4 (Fmoc-*C*H), 50.6 (C-α), 60.9 (C-6), 67.4 (Fmoc-*C*H$_2$), 67.4 (C-4), 68.6 (C-2), 70.9 (C-3), 72.7 (C-5), 78.5 (C-1), 120.2, 125.5, 127.2, and 127.8 (Fmoc-Ar*C*). High-resolution MS data of $C_{37}H_{44}N_2O_{14}$ (M, 740.279): $[M + Na]^+$ found 763.263; calcd 763.269.

***N*$^{\alpha}$-fluoren-9-ylmethoxycarbonyl-*N*$^{\gamma}$-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-L-asparagine (21).** A solution of **20** (2.04 g, 2.75 mmol) in 95% aq. TFA (20 mL) was stirred for 1 hr, after which the mixture was co-concentrated with toluene, EtOH, and CH_2Cl_2. Column chromatography (9:1 CH_2Cl_2/MeOH + 1% HOAc) of the residue yielded **21**, isolated as a white foam (1.85 g, 98%). TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.14$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.00$, 2.04, 2.05, and 2.15 (4 s, each 3H, 4 COC*H*$_3$), 2.80 (dd, 1H, $J_{\alpha,\beta2} = 4.4$ Hz, $J_{\beta1,\beta2} = 16.5$ Hz, H-β2), 2.92 (dd, 1H, $J_{\alpha,\beta1} = 2.5$ Hz, H-β1), 4.12 (m, 4H, Fmoc-C*H*, H-5, H-6a, and H-6b), 4.22 (t, 1H, $J_{CH,CH2} = 7.2$ Hz, Fmoc-CH*H*), 4.39 (t, 1H, Fmoc-C*H*H), 4.59 (m, 1H, H-α), 5.13 (m, 2H, H-2 and H-3), 5.32 (t, 1H, $J_{1,NH} = J_{1,2} = 9.2$ Hz, H-1), 5.50 (d, 1H, $J_{3,4} = 2.5$ Hz, H-4), 6.24 (bd, 1H, N$^{\alpha}$*H*), 6.51 (d, 1H, N$^{\gamma}$*H*), 7.54 (m, 8H, Fmoc-Ar*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 20.5$ (CO*C*H$_3$), 37.5 (C-β), 46.9 (Fmoc-*C*H), 50.0 (C-α), 60.9 (C-6), 67.0 (C-4), 67.4 (Fmoc-*C*H$_2$), 68.6 (C-2), 70.7 (C-3), 72.1 (C-5), 78.3 (C-1), 120.0, 125.1, 127.0, and 127.8 (Fmoc-Ar*C*). High-resolution MS data of $C_{33}H_{36}N_2O_{14}$ (M, 684.217): $[M + Na]^+$ found 707.199; calcd 707.206.

***N*$^{\alpha}$-fluoren-9-ylmethoxycarbonyl-*N*$^{\gamma}$-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-L-asparagine-*O*-pentafluorophenyl ester (4).** Compound **4** was prepared from **21** (101 mg, 0.15 mmol) as described for **1**. Column chromatography (9 : 1 CH_2Cl_2/MeOH) of the residue yielded **4** (69.4 mg, 56%) and succinimide **4a**, both isolated as a white solid. TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.74$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.00$, 2.04, 2.15, and 2.20 (4 s, each 3H, 4 COC*H*$_3$), 2.87 (dd, 1H, $J_{\alpha,\beta1} = 3.8$ Hz, $J_{\beta1,\beta2} = 17.0$ Hz, H-β1), 3.07 (dd, 1H, $J_{\alpha,\beta2} = 4.2$ Hz, H-β2), 4.03 (t, 1H, $J_{5,6} = 6.6$ Hz, H-5), 4.12 (m, 2H, H-6a and H-6b), 4.24 (t, 1H, $J_{CH,CH2} = 7.0$ Hz, Fmoc-C*H*), 4.38 (dd, 1H, $J_{CH2,CH2} = 10.5$ Hz, Fmoc-CH*H*), 4.50 (dd, 1H, Fmoc-C*H*H), 5.01 (m, 1H, H-α), 5.10 (t, 1H, $J_{1,2} = J_{2,3} = 10.1$ Hz, H-2), 5.15 (dd, 1H, $J_{3,4} = 3.4$ Hz, H-3), 5.24 (t, 1H, $J_{1,NH} = 9.0$ Hz, H-1), 5.45 (d, 1H, H-4), 6.18 (d, 1H, $J^{\alpha}_{NH} = 11.0$ Hz, Nα*H*), 6.45 (d, 1H, N$^{\gamma}$*H*), 7.54 (m, 8H, Fmoc-Ar*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 20.5$, 20.6, and 20.7 (CO*C*H$_3$), 37.7 (C-β), 47.1 (Fmoc-*C*H), 50.2 (C-α), 61.1 (C-6), 67.1 (C-4), 67.6 (Fmoc-*C*H$_2$), 68.3 (C-2), 70.6 (C-3), 72.5 (C-5), 78.6 (C-1, $J_{C\text{-}1,H\text{-}1} = 153$ Hz), 120.1, 125.1, 127.1, and 127.8 (Fmoc-Ar*C*). High-resolution MS data of $C_{39}H_{35}N_2O_{14}$ (M, 850.201): $[M + Na]^+$ found 873.338; calcd 873.191.

Succinimide **4a:** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.00$, 2.01, 2.04, and 2.20 (4 s, each 3H, 4 COC*H*$_3$), 2.69 (dd, 1H, $J_{\alpha,\beta1} = 4.6$ Hz, $J_{\beta1,\beta2} = 18.2$ Hz, H-β1), 3.14 (dd, 1H, $J_{\alpha,\beta2} = 9.2$ Hz, H-β2), 4.01 (t, 1H, $J_{5,6a} = 6.1$ Hz, H-5), 4.09 (dd, 1H, $J_{6a,6b} = 11.5$ Hz, H-6a), 4.17 (dd, 1H, $J_{5,6b} = 6.3$ Hz, H-6b), 4.23 (m, 2H, Fmoc-C*H* and Fmoc-CH*H*), 4.38 (m, 2H, H-α and Fmoc-C*H*H), 5.09 (dd, 1H, $J_{2,3} = 10.1$ Hz, $J_{3,4} = 3.1$ Hz, H-3), 5.31 (bd, 1H, H-1), 5.45 (d, 1H, H-4), 5.57 (bd, 1H, N$^{\alpha}$*H*), 6.04 (bt, 1H, H-2), 7.54 (m, 8H, Fmoc-Ar*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 20.5$ (CO*C*H$_3$), 35.7 (C-β), 46.9 (Fmoc-*C*H), 49.6 (C-α), 61.3 (C-6), 65.4 (C-2), 66.6 (C-4), 67.4 (Fmoc-*C*H$_2$), 71.5 (C-3), 73.4 (C-5), 78.5 (C-1, $J_{C\text{-}1,H\text{-}1} = 156$ Hz), 120.0, 124.9, 127.0, and 127.8 (Fmoc-Ar*C*). High-resolution MS data of $C_{33}H_{34}N_2O_{13}$ (M, 666.214): $[M + Na]^+$ found 689.375; calcd 689.196.

***N*$^{\alpha}$-fluoren-9-ylmethoxycarbonyl-*N*$^{\gamma}$-(2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl)-L-asparagine-*O*-*tert*-butyl ester (23).** Glycosylated amino acid intermediate **22** was prepared in 35% yield (69.4 mg) from 1-amino-D-mannopyranose (**16**; 500 mg, 2.78 mmol) and **18** (143 mg, 0.35 mmol) as described for **19**. TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.30$. Compound **23** was prepared from **22** (100 mg, 0.17 mmol) as described for **20**. Column chromatography (9 : 1 CH_2Cl_2/acetone → 9 : 1 CH_2Cl_2/MeOH) yielded **23**, isolated as a white foam (129.4 mg, quantitative). TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.75$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.47$ (s, 9H, C(C*H*$_3$)$_3$), 1.98, 2.03, 2.04, and 2.24 (4 s, each 3H, 4 COC*H*$_3$), 2.75 (dd, 1H, H-β1), 2.89 (dd, 1H, H-β2), 3.75 (m, 1H, H-5), 4.03 (d, 1H, H-6a), 4.22 (t, 1H, $J_{CH,CH2} = 7.2$ Hz, Fmoc-C*H*), 4.31 (dd, 1H, $J_{5,6b} = 5.1$ Hz, $J_{6a,6b} = 12.5$ Hz, H-6b), 4.39 (m, 3H, H-α and

Fmoc-CH_2), 5.10 (dd, 1H, $J_{2,3} = 2.6$ Hz, $J_{3,4} = 10.1$ Hz, H-3), 5.23 (t, 1H, $J_{4,5} = 10.1$ Hz, H-4), 5.37 (d, 1H, H-2), 5.53 (d, 1H, $J_{1,NH} = 8.9$ Hz, H-1), 5.88 (d, 1H, $J_{NH,\alpha} = 7.2$ Hz, N$^{\alpha}H$), 6.48 (d, 1H, N$^{\gamma}H$), 7.54 (m, 8H, Fmoc-ArH). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 20.8$ and 21.1 (COCH_3), 28.2 (C(CH_3)$_3$), 38.8 (C-β), 47.4 (Fmoc-CH), 51.5 (C-α), 62.6 (C-6), 65.6 (C-4), 67.7 (Fmoc-CH_2), 70.5 (C-2), 72.0 (C-3), 74.8 (C-5), 76.3 (C-1, $J_{C\text{-}1,H\text{-}1} = 154$ Hz), 120.6, 125.7, 128.0, and 128.4 (Fmoc-ArC). High-resolution MS data of $C_{37}H_{44}N_2O_{14}$ (M, 740.279): $[M + Na]^+$ found 763.474; calcd 763.269.

N^{α}-fluoren-9-ylmethoxycarbonyl-N^{γ}-(2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl)-L-asparagine (5). Compound **5** was prepared from **23** (129.4 mg, 0.17 mmol) as described for **21**. Column chromatography (9 : 1 CH_2Cl_2/MeOH + 1% HOAc) afforded **5**, isolated as a white foam (119.6 mg, quantitative). TLC: 9 : 1 CH_2Cl_2/MeOH, $R_f = 0.14$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.98$, 2.04, 2.07, and 2.22 (4 s, each 3H, 4 COCH_3), 2.77 (dd, 1H, $J_{\alpha,\beta2} = 5.4$ Hz, $J_{\beta1,\beta2} = 15.1$ Hz, H-β2), 2.95 (dd, 1H, $J_{\alpha,\beta1} = 2.6$ Hz, H-β1), 3.79 (m, 1H, H-5), 4.09 (d, 1H, H-6a), 4.22 (t, 1H, $J_{CH,CH2} = 7.3$ Hz, Fmoc-CH), 4.29 (dd, 1H, $J_{5,6b} = 5.1$ Hz, $J_{6a,6b} = 12.5$ Hz, H-6b), 4.38 (m, 2H, Fmoc-CH_2), 4.59 (m, 1H, H-α), 5.14 (dd, 1H, $J_{2,3} = 3.4$ Hz, $J_{3,4} = 10.1$ Hz, H-3), 5.24 (t, 1H, $J_{4,5} = 10.1$ Hz, H-4), 5.39 (s, 1H, H-2), 5.55 (d, 1H, $J_{1,NH} = 8.6$ Hz, H-1), 6.10 (d, 1H, $J_{NH,\alpha} = 6.9$ Hz, N$^{\alpha}H$), 6.69 (d, 1H, N$^{\gamma}H$), 7.54 (m, 8H, Fmoc-ArH). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 20.7$ and 20.9 (COCH_3), 37.9 (C-β), 47.1 (Fmoc-CH), 50.6 (C-α), 62.2 (C-6), 65.3 (C-4), 67.7 (Fmoc-CH_2), 70.0 (C-2), 71.6 (C-3), 74.5 (C-5), 76.5 (C-1), 120.3, 125.4, 127.3, and 128.1 (Fmoc-ArC). High-resolution MS data of $C_{33}H_{36}N_2O_{14}$ (M, 684.217): $[M + Na]^+$ found 707.200; calcd 707.206.

N^{α}-fluoren-9-ylmethoxycarbonyl-N^{γ}-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-L-asparagine-*O*-*tert*-butyl ester (25). Glycosylated amino acid intermediate **24** (434.5 mg, 78%) was obtained from 1-amino-L-fucopyranose (**17**; 1.0 g, 6.1 mmol) and **18** (412 mg, 1.0 mmol) as described for **19**. TLC: 9:1 CH_2Cl_2/MeOH, $R_f = 0.33$. Compound **25** was prepared from **24** (434.5 mg, 0.78 mmol) as described for **20**. Column chromatography (97:3 CH_2Cl_2/MeOH) afforded **25**, isolated as a colorless glass (533 mg, quantitative). TLC: 9:1 CH_2Cl_2/MeOH, $R_f = 0.80$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.17$ (d, 3H, $J_{5,6} = 6.4$ Hz, H-6), 1.47 (s, 9H, C(CH_3)$_3$), 1.58, 1.99, and 2.15 (3 s, each 3H, 3 COCH_3), 2.71 (dd, 1H, $J_{\alpha,\beta1} = 3.7$ Hz, $J_{\beta1,\beta2} = 15.9$ Hz, H-β1), 2.87 (dd, 1H, $J_{\alpha,\beta2} = 4.1$ Hz, H-β2), 3.90 (q, 1H, H-5), 4.24 (m, 2H, Fmoc-CH and Fmoc-CHH), 4.47 (m, 2H, Fmoc-CHH and H-α), 5.09 (m, 2H, H-2 and H-3), 5.18 (t, 1H, $J_{1,NH} = J_{1,2} = 8.9$ Hz, H-1), 5.28 (d, 1H, $J_{3,4} = 2.4$ Hz, H-4), 5.89 (d, 1H, $J_{NH,\alpha} = 7.8$ Hz, N$^{\alpha}H$), 6.35 (d, 1H, N$^{\gamma}H$), 7.54 (m, 8H, Fmoc-ArH). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 16.1$ (C-6), 20.6 (COCH_3), 27.9 (C(CH_3)$_3$), 38.4 (C-β), 47.2 (Fmoc-CH), 51.1 (C-α), 67.4 (Fmoc-CH_2), 68.5 (C-2), 70.5 (C-4), 70.9 (C-5), 71.3 (C-3), 78.3 (C-1, $J_{C\text{-}1,H\text{-}1} = 159$ Hz), 120.2, 125.2, 127.2,

and 127.8 (Fmoc-Ar*C*). High-resolution MS data of $C_{35}H_{42}N_2O_{12}$ (M, 682.274): $[M + Na]^+$ found 705.388; calcd 705.264.

***N*$^{\alpha}$-fluoren-9-ylmethoxycarbonyl-*N*$^{\gamma}$-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-L-asparagine (6).** Compound **6** was prepared from **25** (568.6 mg, 0.78 mmol) as described for **21**. Column chromatography (9:1 CH_2Cl_2/acetone → 9:1 CH_2Cl_2/MeOH → 9:1 CH_2Cl_2/MeOH + 2% HOAc) afforded **6**, isolated as a white amorphous powder (452.5 mg, 93%). TLC: 9:1 CH_2Cl_2/MeOH, $R_f = 0.29$. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.19$ (d, 1H, $J_{5,6} = 6.5$ Hz, H-6), 2.00 (s, 9H, 3 COC*H*$_3$), 2.74 (dd, 1H, $J_{\alpha,\beta2} = 6.4$ Hz, $J_{\beta1,\beta2} = 16.3$ Hz, H-β2), 2.99 (dd, 1H, $J_{\alpha,\beta1} = 2.5$ Hz, H-β1), 3.95 (q, 1H, H-5), 4.22 (t, 1H, $J_{CH,CH2} = 7.0$ Hz, Fmoc-C*H*), 4.36 (t, 1H, Fmoc-CH*H*), 4.45 (dd, 1H, Fmoc-C*H*H), 4.60 (m, 1H, H-α), 5.14 (m, 3H, H-1, H-2, and H-3), 5.28 (d, 1H, $J_{3,4} = 2.3$ Hz, H-4), 6.06 (d, 1H, $J_{NH,\alpha} = 6.6$ Hz, N$^{\alpha}$*H*), 6.84 (d, 1H, $J_{1,NH} = 8.1$ Hz, N$^{\gamma}$*H*), 7.54 (m, 8H, Fmoc-Ar*H*). ^{13}C NMR (125.76 MHz, $CDCl_3$): $\delta = 16.0$ (C-6), 20.5 (CO*C*H$_3$), 37.9 (C-β), 47.1 (Fmoc-*C*H), 50.1 (C-α), 67.5 (Fmoc-*C*H$_2$), 68.4 (C-2), 70.2 (C-4), 71.2 (C-3 and C-5), 78.6 (C-1), 120.1, 125.2, 127.1, and 127.9 (Fmoc-Ar*C*). High-resolution MS data of $C_{31}H_{34}N_2O_{12}$ (M, 626.211): $[M + Na]^+$ found 649.217; calcd 649.201.

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