Synthesis of Fucosyl Saccharides under Neutral Conditions in Solutions of Lithium Perchlorate in Dichloromethane

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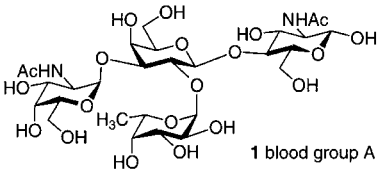
Abstract: Trisaccharides embodying the Fuc–α-(1-2)-Gal or the Fuc–α-(1-2)-Glc substructure can be built up under neutral conditions by glycosylation of selectively deprotected glycosyl acceptor disaccharides with 2,3,4-tri-*O*-benzyl fucosyl fluoride in 0.07 M solutions of $LiClO_4$ in CH_2Cl_2. The glucosyl and the galactosyl trisaccharides, which are stereoisomers of the carbohydrate determinant of the human blood group H, are obtained in high yield and with complete α-selectivity. The glycosyl acceptor disaccharides with a deblocked 2-OH group in the saccharide unit are obtained by treatment of the respective 1,2-anhydro carbohydrates with glycosyl acceptors in 0.07 M $LiClO_4/CH_2Cl_2$.

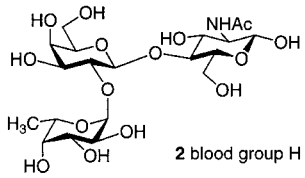
Keywords: blood group determinants · fucose · glycosides · glycosylations · oligosaccharides

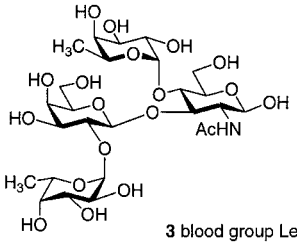
Introduction

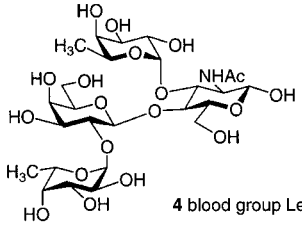
Oligosaccharides play an important role in numerous biological processes;[1] for this reason the development of new synthetic methods for the construction of tailor-made glycosides,[2] which could, for instance, be used to study biological phenomena, is of great interest to synthetic and to medicinal chemistry.[3] Within the class of biologically relevant *O*-glycosides, oligosaccharides that embody one or several fucose residues are of particular interest. For instance, the characteristic oligosaccharide determinants of the human A (**1**) and H blood groups (**2**) and the Lewis^b (**3**) and Lewis^{y,4} (**4**) determinants contain a Fuc–α-(1-2)-Gal saccharide unit (Scheme 1). The construction of fucosyl glycosides[2, 3, 16–20] is often substantially hampered by their high sensitivity to acid, in particular if the fucosyl donor is protected with a benzyl group.[4] It is, therefore, highly desirable to develop methods for the chemical snythesis of *O*-fucosides that can proceed under very mild conditions and without the use of promoters like strong Lewis acids. We have recently reported[5] that in solutions of $LiClO_4$ in organic media[6] various glycosyl donors, including fucose derivatives,[5d] are activated under neutral conditions and participate in glycosylations with various glycosyl acceptors.

In this paper we report on the application of this method for the construction of fucosyl trisaccharides that embody the









Scheme 1. Structure of the characteristic carbohydrate determinants of the human A-, H-, Le^b- and Le^{y,4} blood groups.

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0947-6539/98/0403-0494 $ 17.50+.50/0

characteristic Fuc–α-(1-2)-Gal substructure found in the blood group determinants shown in Scheme 1.

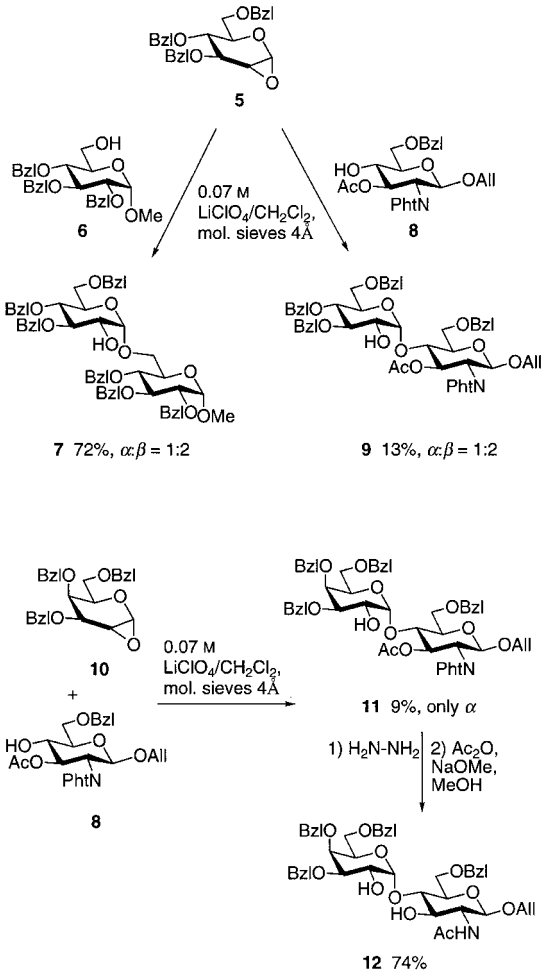
Results and Discussion

For the synthesis of oligosaccharides with a α-Fuc-(1-2) unit, glycosyl acceptors with a selectively deprotected 2-OH group are needed. The respective acceptors employed in this study were built up by means of 1,2-anhydro carbohydrates, that is, the anhydro glucopyranose **5**[7] and the anhydro galactopyranose **10**,[8] which were recently employed by Danishefsky et al.[9] in several oligosaccharide syntheses.

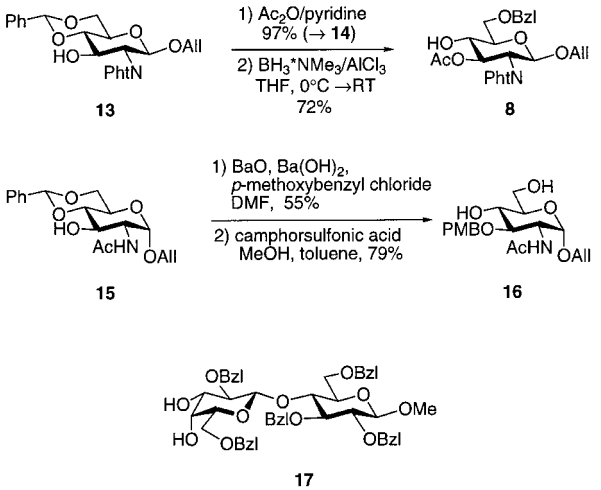
Since glycosylations using these epoxides, in general, are promoted by Lewis acids, we reasoned that these anhydro pyranoses might also be activated in solutions of $LiClO_4$ in organic media. In order to investigate this notion, we treated **5** with the glucose derivative **6** in 1M $LiClO_4$ in CH_2Cl_2. Gratifyingly, the desired disaccharide **7** was formed in 60% yield. Part of the inorganic salt remained undissolved in this heterogeneous reaction mixture so the reaction was repeated with only 2 equiv of $LiClO_4$ present (0.07M solution). Under these homogeneous conditions the yield was raised to 72% and the stereoselectivity remained unchanged (Scheme 2).

Subsequently, the same trend was also observed in other glycoside syntheses in this medium,[10] and therefore all further glycosylations were carried out in 0.07M $LiClO_4$/CH_2Cl_2. Encouraged by these results, we treated **5** with the glucosamine-derived glycosyl acceptor **8**, which carries a less reactive secondary hydroxyl group. Compound **8** was built up from **13**[11] by acetylation of the 3-OH group ($\rightarrow$**14**; see the Experimental Section) and subsequent regioselective opening of the benzylidene acetal present in the acetate **14** in high yield (Scheme 3).

In the reactions with **8** glycoside **9** was formed in only 13% yield (Scheme 2). In addition, the 1,2-anhydro galactose **10** reacted with **8** to deliver the selectively deprotected disaccharide **11** in only 9% yield (Scheme 2). In order to determine whether these unfavorable results represent an inherent limitation of the glycosylation in $LiClO_4/CH_2Cl_2$, we repeated the reaction of **10** and **8** to give **11** in the presence of $ZnCl_2$ in THF or ether and in the presence of zinc triflate as Lewis acid,



Scheme 2. Activation of the 1,2-anhydro pyranoses **5** and **10** in 0.07M $LiClO_4/CH_2Cl_2$.



Scheme 3. Synthesis of the glycosyl acceptors **8**, **16**, and **17**.

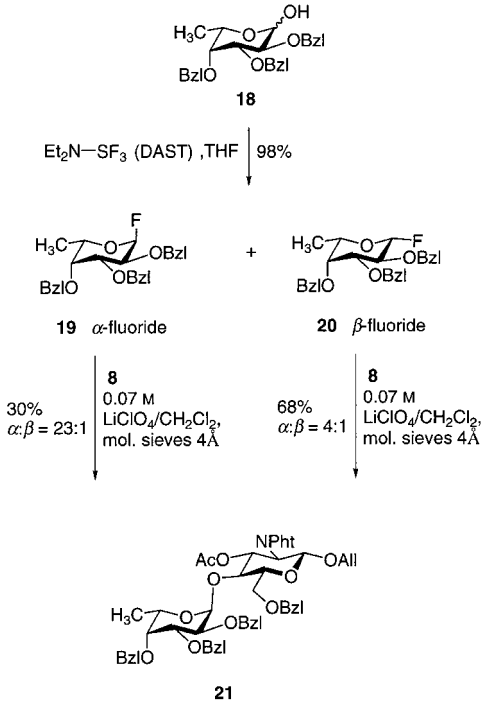
as recommended.[7, 9] However, even under these conditions the disaccharide **11** was obtained in only 5–11% yield as the pure α-anomer. Obviously, **10**, in general, shows only a limited reactivity towards glycosyl acceptors carrying less reactive secondary alcohols, like **8**. The finding that **11** is formed exclusively as the α-anomer and, for **7** and **9**, that α,β mixtures

Abstract in German: *Trisaccharide, die die Substrukturen Fuc–α-(1-2)-Gal oder Fuc–α-(1-2)-Glc enthalten, können unter neutralen Bedingungen durch Glycosylierungen mit selektiv entschützten Disacchariden als Glycosylacceptoren und 2,3,4-Tri-O-benzylfucosylfluorid als Glycosyldonor in 0.07M Lösungen von $LiClO_4$ in CH_2Cl_2 synthetisiert werden. Die Glycosyl- und Galactosyltrisaccharide, die Stereoisomere der Kohlenhydratdeterminante des menschlichen Blutgruppenantigens H sind, werden in hoher Ausbeute und ausschließlich α-konfiguriert erhalten. Die Synthese der Glycosylacceptordisaccharide mit einer 2-OH-Gruppe gelingt durch den Einsatz des entsprechenden 1,2-Anhydrokohlenhydrats mit Glycosylacceptoren in 0.07M $LiClO_4/CH_2Cl_2$.*

are obtained is remarkable, since in the $ZnCl_2$-mediated glycosylations with **5** exclusively β-glycosides were observed.[7] (However, van Boom et al.[12] also obtained α,β mixtures.) We currently have no explanation for this unexpected selectivity. A possible subsequent anomerization of the product under the reaction conditions could, however, be excluded. Compound **11** does not anomerize in the reaction medium even after several days.

Compounds **7** and **11** were subsequently employed as glycosyl acceptors in the fucosylation reactions (vide infra). In addition, in order to address the issue of regioselectivity and the scope of the method, **11** was further converted into the disaccharide **12**. The latter embodies two secondary hydroxyl groups, both of which might participate in glycoside synthesis with an appropriate fucosyl donor. In addition, the *p*-methoxybenzyl-protected *N*-acetylglucosamine derivative **16**, embodying a deblocked OH group in the less accessible 4-position and a primary hydroxyl group in the 6-position, was investigated for this purpose (vide infra). Compound **16** was readily obtained from **15** by *O*-benzylation employing BaO/$Ba(OH)_2$ as base and subsequent selective cleavage of the benzylidene acetal in methanol/toluene in the presence of 0.1 equiv of 10-camphorsulfonic acid[13] (Scheme 3). Furthermore, the lactose derivative **17**,[14] which carries two secondary alcohols, served as glycosyl acceptor in fucosylation reactions.

Our preliminary investigations concerning the use of various fucosyl donors for glycosylations in $LiClO_4$/solvent mixtures had revealed that fucosyl fluorides are particularly suitable donors for glycoside formation in these media.[5a] Therefore, the use of the α- and β-configured benzyl-protected fucosyl fluorides **19** and **20** was investigated first, employing the glucosamine derivative **8** as acceptor (Scheme 4).

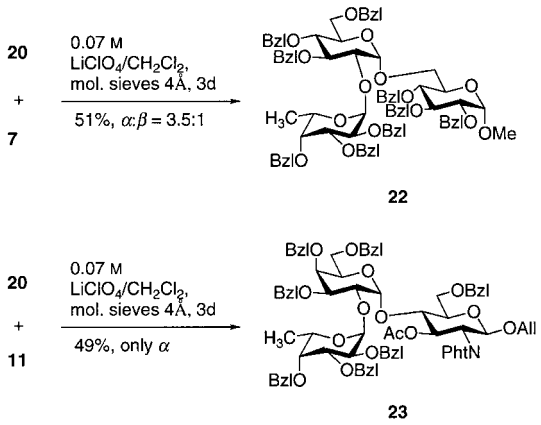


Scheme 4. Synthesis of the fucosyl donors **19** and **20** and activation in 0.07 M $LiClO_4/CH_2Cl_2$.

Compounds **19** and **20** are readily obtained[15] from 2,3,4-tri-*O*-benzyl fucose **18** by treatment with diethylaminosulfur trifluoride (DAST) as a 1:1 mixture and are easily separated by flash chromatography.

The disaccharide **21** is formed on treatment of **19** or **20** with **8**. From the reaction with the β-fluoride **20** the glycoside **21** is obtained in 68% yield and with an $\alpha:\beta$ ratio of 4:1; with the α-anomer **19** the yield is much lower but the stereoselectivity is improved (Scheme 4). The reaction is best carried out in 0.07 M solutions of $LiClO_4$ in CH_2Cl_2 (vide supra), and in order to obtain a high yield, 2–2.5 equiv of the fucosyl donor should be employed. As was already observed for other benzyl-protected glycosyl donors,[5] in particular glycosyl iodides, in this reaction medium the β-configured halogenose is significantly more reactive than the analogous α-anomer. Therefore, the subsequent fucosylations were carried out employing the β-fucosyl fluoride **20** wherever possible.

The 1-6-linked glucosyl disaccharide **7** (the α-anomer) reacted smoothly with the β-fluoride **20** in 0.07 M $LiClO_4/CH_2Cl_2$ to give the trisaccharide **22** in appreciable yield and with an $\alpha:\beta$ ratio of 3.5:1 (Scheme 5). Similarly, the galactosyl



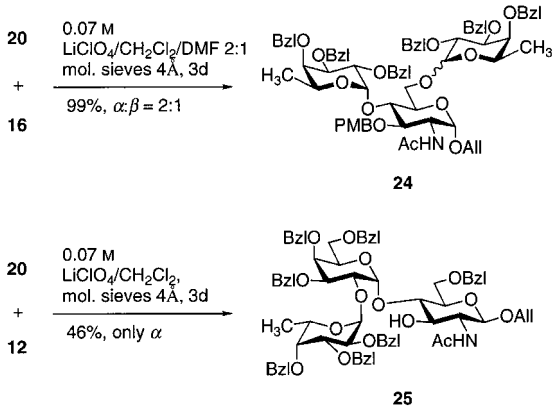
Scheme 5. Activation of the fucosyl donor **20** in 0.07 M $LiClO_4/CH_2Cl_2$ to give the fucosides **22** and **23**.

disaccharide **11** underwent the glycosylation reaction to deliver the fucosyl trisaccharide in nearly the same yield with exclusive formation of the α-anomer **23** (Scheme 5). Both results demonstrate that, under the reaction conditions employed, the reactivity of the fucosyl fluoride is high enough to glycosylate the sterically congested secondary hydroxyl groups present in **7** and **11**.

The issue of regioselectivity is addressed in the reactions with the monosaccharide **16** and the disaccharide **12**, both of which contain two hydroxyl groups (Scheme 6).

If the monosaccharide acceptor **16** is treated with three equivalents of the fucosyl fluoride **20** in a 0.07 M solution of $LiClO_4$ in CH_2Cl_2/DMF 2:1 the trisaccharide **24** is formed in quantitative yield (the DMF is needed to dissolve the glycosyl acceptor **16**). Whereas the glycosidic bond to the 6-OH group was formed with an $\alpha:\beta$ ratio of 2:1, the second fucose was introduced exclusively as the α-anomer, probably for steric reasons. A selective glycosylation of one of the two OH-groups was not observed and could not be effected by

0947-6539/98/0403-0496 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 3



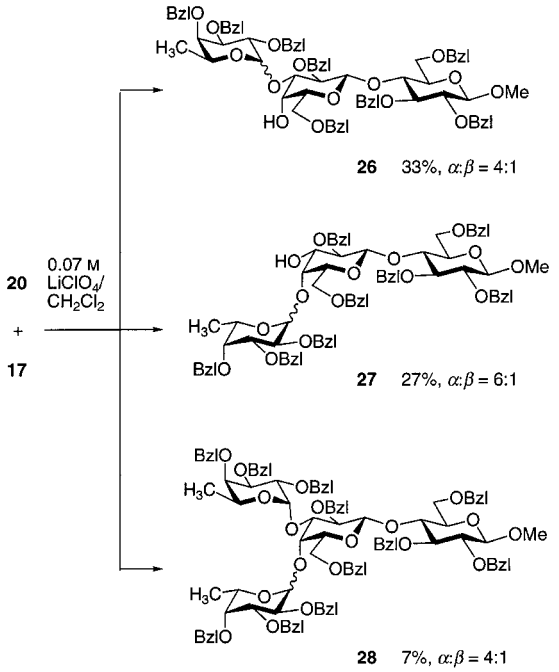
Scheme 6. Activation of the fucosyl donor **20** in 0.07 M $LiClO_4/CH_2Cl_2$ to give the fucosides **24** and **25**.

employing less glycosyl donor. On the other hand, **12** was converted regio- and stereoselectively into the trisaccharide **25** in appreciable yield. In this case, the second hydroxyl group is obviously not reactive enough to yield a bis-fucosylated tetrasaccharide.

Finally, the lactose derivative **17** was subjected to the glycosylation reactions. Only 1.5 equivalents of a 2:1 mixture of the α- and β-fucosyl fluorides **19** and **20** were used in order to allow for a regioselective glycosylation. However, the fucose was attached to the 3b- and the 4b-position of the terminal galactose residue of **17** in nearly equal amounts (Scheme 7). Obviously the reactivity of the fucosyl fluorides under these conditions is too high to allow for a differentiation between the two deprotected hydroxyl groups. In addition to the two trisaccharides **26** and **27** thus obtained, the tetrasaccharide **28** was also formed, albeit in low yield (Scheme 7).

The results recorded for the use of $LiClO_4/CH_2Cl_2$ as reaction medium for fucosylations compare favorably with those from several of the established procedures currently in use for the construction of fucosyl saccharides. For instance, the generation of Fuc-α-(1–2)-Gal linkages via fucosyl thioglycosides was described as proceeding with yields of 50–65 %,[16] and the activation of fucosyl phosphites, for example, with TMS triflate shows comparable or less advantageous results.[17] Also the activation of fucosyl fluorides according to the Mukaiyama method ($AgClO_4/SnCl_2$) delivers the desired glycosides with yields comparable with those obtained in the $LiClO_4$ method (see, for example, ref. [18]). Although better results can often be obtained with fucosyl bromides,[19] for their activation heavy metal salts, for example, Hg salts, must be applied as promoters. This disadvantage is clearly overcome by using $LiClO_4$/solvent mixtures as reaction medium. Notably, glycosylations with fucosyl trichloroacetimidates according to Schmidt et al.[20] consistently give higher yields than the method described in this paper. However, although in some of the reactions with these glycosyl donors as few as 0.05 equiv of the promoting reagent TMS triflate could be employed, in other cases up to 0.3 equiv must be applied. Under the conditions of the fucoside syntheses described above the use of such a strong Lewis acid is rendered unnecessary so that no undesired acid mediated cleavage of the glycosidic bonds has to be feared.

In conclusion, fucosyl glycosides can be built up under mild, neutral conditions and without the need for a further promoting reagent in 0.07 M $LiClO_4$ in CH_2Cl_2. Less reactive hydroxyl groups are also glycosylated with satisfactory results under these conditions. The method opens up new opportunities for the construction of biologically relevant oligosaccharides, for instance, the fucosyl trisaccharides **23** and **25**, which are stereoisomers of the characteristic carbohydrate determinant of the human blood group H.



Scheme 7. Activation of the fucosyl donor **20** in 0.07 M $LiClO_4/CH_2Cl_2$ to give the fucosides **26**, **27**, and **28**.

Experimental Section

General: All melting points were recorded on a Büchi melting point apparatus and are uncorrected. Proton and carbon NMR spectra were measured on a Bruker AM-400 or a Bruker DRX-500 spectrometer. Chemical shifts are expressed downfield relative to tetramethylsilane as an internal standard. Specific optical rotation values were determined on a Perkin–Elmer polarimeter 241. Mass spectra were obtained with a Finnigan MAT90 spectrometer or a PerSeptive Biosystems Voyager® spectrometer. Elemental analyses were performed on an Elementar CHN-Rapid analyzer. For thin-layer chromatography (TLC) Macherey–Nagel silica gel ALUGRAM® SIL G/UV254 layers were used. Flash chromatography was performed with Baker silica gel (40–60 mm). $LiClO_4$ was obtained from Acros as a >99 % pure solid. It was dried extensively in vacuo at 150 °C prior to use.

The carbohydrates **5**,[7] **6**,[21] **10**,[8] **17**,[14] **18**,[22] **19**, and **20**[15] were prepared as described in the literature.

Allyl-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (14): To a solution of **13**[11] (224 mg, 0.5 mmol) in pyridine (4 mL) acetic anhydride (0.5 mL) was added. After stirring for 18 h at room temperature, the mixture was poured into ice water and the mixture was extracted twice with chloroform (10 mL). The solution was concentrated in vacuo to give a colorless solid from which traces of pyridine and acetic anhydride were removed by coevaporation in vacuo with toluene, yielding **14** (247 mg, 97 %) as a colorless solid. M.p. 171 °C; R_f: 0.49 (ethyl acetate/hexane 1/2); $[\alpha]_D^{22} = -9.5$ ($c = 1$ in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.90$ (s, 3H, C(O)OCH_3), 3.75 (dd, $J_{5,6'} = 4.5$ Hz, $J_{5,6} = J_{4,5} =$

9.3 Hz, 1H, 5-H), 3.82 (dd, $J_{3,4}=J_{4,5}=9.3$ Hz, 1H, 4-H), 3.87 (dd, $J_{5,6}=$ 9.3 Hz, $J_{6,6'}=10.3$ Hz, 1H, 6-H), 4.05 (dd, $J_{vic}=6.2$ Hz, $J_{gem}=12.9$ Hz, 1H, OCH_2CH=CH$_2$), 4.29 (dd, $J_{vic}=5.1$ Hz, $J_{gem}=12.9$ Hz, 1H, OCH_2CH=CH$_2$), 4.33 (dd, $J_{1,2}=8.5$ Hz, $J_{2,3}=10.1$ Hz, 1H, 2-H), 4.42 (dd, $J_{5,6'}=4.5$ Hz, $J_{6,6'}=10.3$ Hz, 1H, 6′-H), 5.06 (d, $J_{cis}=10.4$ Hz, 1H, OCH$_2$CH=CH_2), 5.15 (dd, $J_{gem}=1.3$ Hz, $J_{trans}=17.2$ Hz, 1H, OCH$_2$CH=CH_2), 5.48 (d, $J_{1,2}=8.5$ Hz, 1H, 1-H), 5.55 (s, 1H, C*H*-Ph), 5.65–5.75 (m, 1H, OCH$_2$C*H*=CH$_2$), 5.90 (dd, $J_{3,4}=9.3$ Hz, $J_{2,3}=10.1$ Hz, 1H, 3-H), 7.26–7.87 (m, 9H, Ph-*H*); MS (FAB): $m/z=480$ $[M+H]^+$; $C_{26}H_{25}NO_8$: calcd C 65.13, H 5.26, N 2.92; found C 64.89, H 5.32, N 2.44.

Allyl-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (**8**): First $BH_3\cdot NMe_3$ (90 mg, 1.2 mmol) and then freshly pulverized $AlCl_3$ (163 mg, 1.2 mmol) were added to an ice-cold mixture of **14** (100 mg, 0.2 mmol), molecular sieves 4 Å (657 mg), and THF (3 mL) under N_2. The mixture was stirred at 0 °C for 30 min and at room temperature for 2 h, and was then diluted with diethyl ether (10 mL). Ice water and 2 N aqueous HCl (0.5 mL) were added, and the mixture was filtered through Celite. The filtrate was extracted several times with chloroform (20 mL each), the combined extracts were washed with saturated brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography (toluene/acetone 4/1) to afford 72 mg (72 %) of **8** as a colorless oil. R_f: 0.47 (toluene/acetone 5/1); $[\alpha]_D^{22}=-3.3$ ($c=1$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.91$ (s, 3H, C(O)OCH_3), 3.14 (d, $J_{4,OH}=4.2$ Hz, 1H, 4-OH), 3.73–3.85 (m, 4H, 4-H, 5-H, 6-H, 6′-H), 4.05 (ddt, $^4J=1.1$ Hz, $J_{vic}=6.2$ Hz, $J_{gem}=13.0$ Hz, 1H, OCH_2CH=CH$_2$), 4.25–4.30 (m, 2H, 2-H, OCH_2CH=CH$_2$), 4.62 (d, $J_{gem}=12.0$ Hz, 1H, OCH_2Ph), 4.66 (d, $J_{gem}=12.0$ Hz, 1H, OCH_2Ph), 5.04 (dd, $J_{gem}=1.3$ Hz, $J_{cis}=10.4$ Hz, 1H, OCH$_2$CH=CH_2), 5.12 (dd, $J_{gem}=1.3$ Hz, $J_{trans}=17.2$ Hz, 1H, OCH$_2$CH=CH_2), 5.42 (d, $J_{1,2}=8.5$ Hz, 1H, 1-H), 5.67 (dd, $J_{3,4}=8.6$ Hz, $J_{2,3}=10.7$ Hz, 1H, 3-H), 5.68–5.76 (m, 1H, OCH$_2$C*H*=CH$_2$), 7.27–7.37 (m, 5H, Ph-*H*), 7.71 (m, 2H, Ph-*H*), 7.84 (m, 2H, Ph-*H*); $C_{26}H_{27}NO_8$: calcd C 64.86, H 5.65, N 2.91; found C 64.80, H 5.62, N 2.43.

Allyl-2-acetamido-2-deoxy-3-*O*-*p*-methoxybenzyl-*α*-D-glucopyranoside (**16**): *p*-Methoxybenzyl chloride (0.18 mL, 1.3 mmol) was added to a suspension of **15**[23] (196 mg, 0.56 mmol), BaO (494 mg, 3.2 mmol), and $Ba(OH)_2\cdot 8H_2O$ (144 mg, 0.5 mmol) in DMF (4.2 mL). After stirring for 7 d, the mixture was diluted with chloroform (50 mL) and acetic acid (50 %) (5.4 mL) and the organic layer extracted twice with a solution of $NaHCO_3$ and then with water. After evaporation of the solvent flash chromatography on silica gel using ethyl acetate/hexane (3/2) yielded 144 mg (55 %) of the *p*-methoxybenzyl ether. The colorless solid was dissolved in a solution of (±)-10-camphorsulfonic acid (11.7 mg, 0.05 mmol) in toluene/methanol 1:3 (4.7 mL). The solution was stirred at room temperature for 24 h, and then concentrated in vacuo. Flash chromatography on silica gel with dichloromethane/methanol (20/1) afforded **16** (149 mg, 79 %), a colorless solid. M.p. 141 °C; R_f: 0.46 (dichloromethane/methanol 10/1); $[\alpha]_D^{22}=+109.8$ ($c=1$ in methanol); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.93$ (s, 3H, C(O)OCH_3), 3.52 (dd, $J_{4,5}=$ 8.9 Hz, $J_{3,4}=9.7$ Hz, 1H, 4-H), 3.62–3.68 (m, 2H, 3-H, 5-H), 3.71 (dd, $J_{5,6}=5.6$ Hz, $J_{6,6'}=11.8$ Hz, 1H, 6-H), 3.77 (s, 3H, OCH_3), 3.82 (dd, $J_{5,6'}=$ 2.3 Hz, $J_{6,6'}=11.8$ Hz, 1H, 6′-H), 4.01 (ddt, $^4J=1.3$ Hz, $J_{vic}=6.2$ Hz, $J_{gem}=$ 13.1 Hz, 1H, OCH_2CH=CH$_2$), 4.05 (dd, $J_{1,2}=3.6$ Hz, $J_{2,3}=10.7$ Hz, 1H, 2-H), 4.22 (ddt, $^4J=1.5$ Hz, $J_{vic}=5.2$ Hz, $J_{gem}=13.1$ Hz, 1H, OCH_2CH=CH$_2$), 4.78 (d, $J_{1,2}=3.6$ Hz, 1H, 1-H), 4.80 (d, $J_{gem}=10.8$ Hz, 1H, OCH_2Ar), 4.99 (d, $J_{gem}=10.8$ Hz, 1H, OCH_2Ar), 5.19 (dq, $^4J=J_{gem}=1.4$ Hz, $J_{cis}=10.5$ Hz, 1H, OCH$_2$CH=CH_2), 5.32 (dq, $^4J=J_{gem}=1.7$ Hz, $J_{trans}=17.3$ Hz, 1H, OCH$_2$CH=CH_2), 5.91–5.99 (m, 1H, OCH$_2$C*H*=CH$_2$), 6.86 (m, 2H, Ar-*H*), 7.24 (m, 2H, Ar-*H*); MS (FAB): $m/z=382$ $[M+H]^+$; $C_{19}H_{27}NO_7$: calcd C 59.83, H 7.13, N 3.67; found C 59.72, H 6.98, N 3.01.

General procedure for glycosylation with the 1,2-anhydro carbohydrates 5 and 10: A solution of the glycosyl acceptor **6** or **8** (0.6 mmol) in dichloromethane (2 mL) was added to a mixture of the glycosyl donor **5** or **10** (0.3 mmol), $LiClO_4$ (64 mg, 0.6 mmol), powdered molecular sieves 4 Å (500 mg), and dichloromethane (6 mL). After stirring for 3 d at room temperature under argon the reaction mixture was diluted with dichloromethane (25 mL), filtered, and washed with water. The organic layer was dried with Na_2SO_4 and concentrated in vacuo. The glycoside was isolated from the remaining residue by flash chromatography using ethyl acetate/hexane mixtures as eluent.

Methyl-*O*-(3,4,6-tri-*O*-benzyl-*α*/*β*-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (**7**): colorless oil; yield 72 %; anomeric ratio $\alpha:\beta=1:2$.

α-Anomer: R_f: 0.14 (ethyl acetate/hexane 1/2); $[\alpha]_D^{22}=+74.1$ ($c=1$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=2.16$ (d, $J_{2,OH}=7.7$ Hz, 1H, 2-OH), 3.35 (s, 3H, OCH_3), 3.46–3.54 (m, 3H, 6′b-H, 2a-H, 4a-H), 3.58–3.78 (m, 7H, 5a-H, 2b-H-6b-H, 6a-H), 3.92 (dd, $J_{5,6'}=4.4$ Hz, $J_{6,6'}=11.2$ Hz, 1H, 6′a-H), 3.99 (dd, $J_{2,3}=J_{3,4}=9.2$ Hz, 1H, 3a-H), 4.42–4.57 (m, 4H, OCH_2Ph), 4.60 (d, $J_{1,2}=3.4$ Hz, 1H, 1a-H), 4.66 (d, $J_{gem}=12.0$ Hz, 1H, OCH_2Ph), 4.76–4.82 (m, 4H, OCH_2Ph), 4.90–4.93 (m, 3H, 1b-H, OCH_2Ph (2)), 4.99 (d, $J_{gem}=10.9$ Hz, 1H, OCH_2Ph), 7.13–7.37 (m, 30H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=55.26$ (1C, CH_3, O*C*H$_3$), 67.01 (1C, CH_2, C-6a), 68.31 (1C, CH_2, C-6b), 69.56 (1C, CH, C-5a), 70.78 (1C, CH, C-5b), 73.19 (1C, CH, C-4b), 73.33–75.79 (6C, CH_2, O*C*H$_2$Ph), 77.17 (1C, CH, C-3b), 77.68 (1C, CH, C-4a), 80.12 (1C, CH, C-2a), 82.05 (1C, CH, C-3a), 83.17 (1C, CH, C-2b), 97.89 (1C, CH, C-1a), 99.21 (1C, CH, C-1b), 127.35–128.47 (30C, Ph-*C*H), 137.89–138.66 (6C, C_{ipso}); $C_{55}H_{60}O_{11}\cdot 1H_2O$: calcd C 72.19, H 6.82; found C 71.99, H 6.74.

β-Anomer: R_f: 0.52 (ethyl acetate/hexane 1/2), $[\alpha]_D^{22}=+12.3$ ($c=1$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=2.47$ (s, 1H, 2-OH), 3.37 (s, 3H, OCH_3), 3.45–3.56 (m, 6H, 2a-H, 4a-H, 2b-H-5b-H), 3.66–3.71 (m, 3H, 6b-H, 6a-H, 6′a-H), 3.80–3.84 (m, 1H, 5a-H), 3.99 (dd, $J_{2,3}=J_{3,4}=$ 9.3 Hz, 1H, 3a-H), 4.14 (dd, $J_{5,6'}=1.6$ Hz, $J_{6,6'}=10.9$ Hz, 1H, 6′b-H), 4.22 (d, $J_{1,2}=6.8$ Hz, 1H, 1b-H), 4.50–4.67 (m, 6H, OCH_2Ph (5), 1a-H), 4.77–4.99 (m, 7H, OCH_2Ph), 7.16–7.36 (m, 30H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=55.28$ (1C, CH_3, O*C*H$_3$), 68.78 (1C, CH_2, C-6b), 68.96 (1C, CH_2, C-6a), 69.82 (1C, CH, C-5a), 73.37, 73.44 (2C, CH2, O*C*H$_2$Ph), 74.48 (1C, CH, C-5b), 75.05, 75.08 (3C, CH_2, O*C*H$_2$Ph), 75.33 (1C, CH, C-3b), 75.76 (1C, CH_2, O*C*H$_2$Ph), 77.49 (1C, CH, C-4a), 78.03 (1C, CH, C-2b), 79.72 (1C, CH, C-4b), 81.99 (1C, CH, C-3a), 84.46 (1C, CH, C-2a), 98.09 (1C, CH, C-1a), 103.48 (1C, CH, C-1b), 127.57–128.42 (30C, Ph-*C*H), 138.07–138.63 (6C, C_{ipso}); $C_{55}H_{60}O_{11}$: calcd C 73.64, H 6.74; found C 73.29, H 6.84.

Allyl-*O*-(3,4,6-tri-*O*-benzyl-*α*/*β*-D-glucopyranosyl)-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (**9**): colorless oil; yield 13 %; anomeric ratio $\alpha:\beta=1:2$; R_f: 0.38 (diethyl ether/hexane 2/1); MS (FAB): $m/z=937$ $[M+Na]^+$; $C_{53}H_{55}NO_{13}$.

β-Anomer: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.83$ (s, 3H, C(O)CH_3), 2.79 (d, $J_{2,OH}=1.6$ Hz, 1H, 2-OH), 3.28 (dt, $J_{5,6}=J_{5,6'}=2.7$ Hz, $J_{4,5}=9.8$ Hz, 1H, 5b-H), 3.39–3.46 (m, 2H, 2b-H, 3b-H), 3.60 (dd, $J_{2,3}=J_{3,4}=9.8$ Hz, 1H, 3b-H), 3.66 (d, $J_{5,6}=J_{5,6'}=2.7$ Hz, 2H, 6b-H, 6′b-H), 3.73 (m, 1H, 5a-H), 3.81 (dd, $J_{5,6'}=2.5$ Hz, $J_{6,6'}=11.3$ Hz, 1H, 6′a-H), 3.96 (dd, $J_{5,6}=3.4$ Hz, $J_{6,6'}=$ 11.3 Hz, 1H, 6a-H), 4.02–4.08 (m, 2H, OCH_2CH=CH$_2$, 4a-H), 4.25–4.33 (m, 3H, 1b-H ($J_{1,2}=7.3$ Hz), OCH_2CH=CH$_2$, 2a-H), 4.39–4.89 (m, 8H, OCH_2Ph), 5.04 (dd, $J_{gem}=1.2$ Hz, $J_{cis}=10.3$ Hz, 1H, OCH$_2$CH=CH_2), 5.11 (dd, $J_{gem}=1.6$ Hz, $J_{trans}=17.2$ Hz, 1H, OCH$_2$CH=CH_2), 5.37 (d, $J_{1,2}=$ 8.6 Hz, 1H, 1a-H), 5.68–5.75 (m, 1H, OCH$_2$C*H*=CH$_2$), 5.77 (dd, $J_{3,4}=$ 10.8 Hz, $J_{2,3}=8.6$ Hz, 1H, 3a-H), 7.09–7.86 (m, 24H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=20.52$ (1C, CH_3, C(O)*C*H$_3$), 54.91 (1C, CH, C-2a), 68.24 (1C, CH_2, C-6a), 68.70 (1C, CH_2, C-6b), 70.03 (1C, CH_2, OCH$_2$CH=CH$_2$), 71.28 (1C, CH, C-3a), 73.24–73.60 (3C, CH_2, O*C*H$_2$Ph), 74.44 (1C, CH, C-5a), 74.84 (2C, CH, C-5b, C-3b), 74.92 (1C, CH_2, O*C*H$_2$Ph), 76.33 (1C, CH, C-4a), 77.11 (1C, CH, C-4b), 84.40 (1C, CH, C-2b), 97.33 (1C, CH, C-1a), 102.91 (1C, CH, C-1b), 117.47 (1C, CH_2, OCH$_2$CH=CH$_2$), 123.5 (2C, CH, Ph-*C*H (Pht)), 127.60–128.49 (20C, CH, Ph-*C*H), 131.51 (2C, C_{ipso} (Pht)), 133.58 (1C, CH, OCH$_2$C*H*=CH$_2$), 134.16 (2C, CH, Ph-*C*H (Pht)), 137.62–138.73 (4C, C_{ipso}), 167.85 (2C, C(O) (Pht)), 170.39 (1C, C(O)).

Characteristic signals for the α-anomer: ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=20.68$ (1C, CH_3, C(O)*C*H$_3$), 97.33 (1C, CH, C-1a), 97.14 (1C, CH, C-1b).

Allyl-*O*-(3,4,6-tri-*O*-benzyl-*α*-D-galactopyranosyl)-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (**11**): Colorless oil; yield 9 %; only α; R_f: 0.66 (ethyl acetate/hexane 1/2); $[\alpha]_D^{22}=+58.3$ ($c=2$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.85$ (s, 3H, C(O)CH_3), 1.98 (s, 1H, 2-OH), 3.50–3.54 (m, 3H, 3b-H, 6b-H, 6′b-H), 3.76–3.86 (m, 4H, 5a-H, 5b-H, 6a-H, 6′a-H), 3.90–3.94 (m, 2H, 4b-H, 4a-H), 3.96–4.11 (m, 2H, 2b-H, OCH_2CH=CH$_2$), 4.23 (dd, $J_{1,2}=8.5$ Hz, $J_{2,3}=10.8$ Hz, 1H, 2a-H), 4.27 (ddt, $^4J=1.4$ Hz, $J_{vic}=5.0$ Hz, $J_{gem}=12.8$ Hz, 1H, OCH_2CH=CH$_2$), 4.37–4.67 (m, 7H, OCH_2Ph), 4.85 (d, $J_{gem}=11.4$ Hz, 1H, OCH_2Ph), 5.05 (dd, $J_{gem}=1.3$ Hz, $J_{cis}=10.4$ Hz, 1H, OCH$_2$CH=CH_2),

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5.12 (dd, $J_{gem}=1.6$ Hz, $J_{trans}=17.2$ Hz, 1H, $OCH_2CH{=}CH_2$), 5.16 (d, $J_{1,2}=3.8$ Hz, 1H, 1b-H), 5.44 (d, $J_{1,2}=8.5$ Hz, 1H, 1a-H), 5.70–5.77 (m, 2H, $OCH_2CH{=}CH_2$, 3a-H ($J_{3,4}=8.5$ Hz, $J_{2,3}=10.8$ Hz)), 7.15–7.83 (m, 24H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=20.69$ (1C, CH_3, $C(O)CH_3$), 55.03 (1C, CH, C-2a), 68.65 (1C, CH_2, C-6b), 69.47 (1C, CH_2, C-6a), 70.06 (1C, CH_2, $OCH_2CH{=}CH_2$), 70.63 (1C, CH, C-4a), 72.52, 73.21 (2C, CH_2, OCH_2Ph), 73.58 (2C, CH, C-3a, CH_2, OCH_2Ph), 73.90 (1C, CH, C-4b), 74.69 (2C, CH_2, OCH_2Ph, CH, C-5a), 76.78 (1C, CH, C-5b), 79.23 (1C, CH, C-3a), 96.86 (1C, CH, C-1a), 100.99 (1C, CH, C-1b), 117.55 (1C, CH_2, $OCH_2CH{=}CH_2$), 123.46 (2C, CH, Ph-*C*H (Pht)), 127.46–128.49 (20C, CH, Ph-*C*H), 131.49 (2C, C_{ipso} (Pht)), 133.59 (1C, CH, $OCH_2CH{=}CH_2$), 134.19 (2C, CH, Ph-*C*H (Pht)), 137.86–138.40 (4C, C_{ipso}), 170.82 (1C, C(O)); MS (FAB): $m/z=937$ $[M+Na]^+$; $C_{53}H_{55}NO_{13}$.

Allyl-*O*-(3,4,6-tri-*O*-benzyl-*α*-D-galactopyranosyl)-(1→4)-2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (**12**): A mixture of **11** (95 mg, 0.1 mmol), $CaSO_4$ (Drierite) (1.1 g, 8 mmol), ethanol (8 mL), and hydrazine monohydrate (0.4 mL, 7 mmol) was heated to reflux for 2 h. After dilution with acetone (20 mL) and filtration the solution was evaporated under reduced pressure. The resulting syrup was thoroughly dried in vacuo, dissolved in a 0.7 M solution of $NaOCH_3$ in methanol (0.14 mL), and the solution was treated with acetic anhydride (0.12 mL, 1.3 mmol). The mixture was kept for 15 h at room temperature, treated again with acetic anhydride (0.12 mL, 1.3 mmol), and stirred for four additional hours. Evaporation of traces of solvent and codistillation with toluene left a syrup that was purified by flash chromatography on silica gel with chloroform/methanol 20/1 as eluent, yielding **12** as a colorless oil (60 mg, 74%). R_f: 0.21 (chloroform/methanol 50/1); $[\alpha]_D^{22}=+25.0$ ($c=0.5$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=2.02$ (s, 3H, $C(O)CH_3$), 3.37 (ddd, $J_{1,2}=8.1$ Hz, $J_{2,NH}=5.4$ Hz, $J_{2,3}=10.1$ Hz, 1H, 2a-H), 3.48 (m, 3H, 5a-H, 6′a-H, 6′b-H), 3.63 (dd, $J_{3,4}=J_{4,5}=9.3$ Hz, 1H, 4a-H), 3.71–3.81 (m, 3H, 3b-H, 6a-H, 6b-H), 3.94 (d, $J_{3,4}=1.4$ Hz, 1H, 4b-H), 4.00–4.09 (m, 3H, 3a-H, 5b-H, $OCH_2CH{=}CH_2$), 4.21 (dd, $J_{1,2}=3.6$ Hz, $J_{2,3}=10.1$ Hz, 1H, 2b-H), 4.34 (dd, $J_{vic}=5.2$ Hz, $J_{gem}=12.7$ Hz, 1H, $OCH_2CH{=}CH_2$), 4.39–4.56 (m, 5H, OCH_2Ph), 4.68 (d, $J_{1,2}=8.1$ Hz, 1H, 1a-H), 4.72 (s, 2H, OCH_2Ph), 4.88 (d, $J_{gem}=11.5$ Hz, 1H, OCH_2Ph), 5.18 (d, $J_{1,2}=3.6$ Hz, 1H, 1b-H), 5.20 (dd, $J_{gem}=1.0$ Hz, $J_{cis}=11.4$ Hz, 1H, $OCH_2CH{=}CH_2$), 5.27 (dd, $J_{gem}=1.4$ Hz, $J_{trans}=17.2$ Hz, 1H, $OCH_2CH{=}CH_2$), 5.81 (d, $J_{2,NH}=5.4$ Hz, 1H, NH), 5.86–5.93 (m, 1H, $OCH_2CH{=}CH_2$), 7.22–7.46 (m, 20H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=23.64$ (1C, CH_3, $C(O)CH_3$), 58.09 (1C, CH, C-2a), 69.07 (1C, CH_2, C-6a), 69.30 (1C, CH2, C-6b), 69.82 (1C, CH_2, $OCH_2CH{=}CH_2$), 69.98 (1C, CH, C-2b), 70.78 (1C, CH, 5b-H), 72.70–73.53 (3C, CH_2, OCH_2Ph), 73.68 (1C, CH, C-3a), 74.20 (1C, CH, C-4b), 74.64 (1C, CH_2, OCH_2Ph), 74.78 (1C, CH, C-5a), 79.47 (1C, CH, C-3b), 81.75 (1C, CH, C-4a), 98.98 (1C, CH, C-1a), 102.21 (1C, CH, C-1b), 118.07 (1C, CH_2, $OCH_2CH{=}CH_2$), 127.42–128.49 (20C, CH, Ph-*C*H), 133.64 (1C, CH, $OCH_2CH{=}CH_2$), 137.83–138.46 (4C, C_{ipso}), 171.89 (1C, C(O)); MS (FAB): $m/z=784$ $[M+H]^+$; $C_{45}H_{53}NO_{11}$.

General procedure for glycosylation with the fucosyl fluorides 19 and 20: A solution of the glycosyl donor **19** or **20** (190 mg, 0.43 mmol) in dichloromethane (5 mL) was added to a mixture of the glycosyl acceptor (0.29 mmol), $LiClO_4$ (92 mg, 0.8 mmol), powdered molecular sieves 4 Å (730 mg), CsF (98 mg, 0.65 mmol), and dichloromethane (6.9 mL). After stirring for 3 d at room temperature under argon the reaction mixture was diluted with dichloromethane (25 mL), filtered, and extracted with water (10 mL). The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The glycoside was isolated from the remaining residue by flash chromatography with ethyl acetate/hexane mixtures as eluents.

Allyl-*O*-(2,3,4-tri-*O*-benzyl-*α*/*β*-L-fucopyranosyl)-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (**21**): Yield 30% (with **19**); anomeric ratio $\alpha:\beta=23:1$; yield 68% (with **20**); anomeric ratio $\alpha:\beta=4:1$.

α-Anomer: Colorless oil; R_f: 0.47 (ethyl acetate/hexane 1/2); $[\alpha]_D^{22}=-26.6$ ($c=1$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.98$ (d, $J_{5,6}=6.5$ Hz, 3H, 6b-CH_3), 1.84 (s, 3H, OCH_3), 3.59 (d, $J_{3,4}=1.4$ Hz, 1H, 4b-H), 3.66–3.77 (m, 3H, 5a-H, 6a-H, 4a-H), 3.81–3.85 (m, 2H, 5b-H, 3b-H), 3.96 (dd, $J_{1,2}=3.5$ Hz, $J_{2,3}=10.2$ Hz, 1H, 2b-H), 4.04–4.07 (m, 2H, 6′a-H, $OCH_2CH{=}CH_2$), 4.20 (dd, $J_{1,2}=8.5$ Hz, $J_{2,3}=10.6$ Hz, 1H, 2a-H), 4.27 (dd, $J_{vic}=5.1$ Hz, $J_{gem}=12.9$ Hz, 1H, $OCH_2CH{=}CH_2$), 4.33–4.92 (m, 8H, OCH_2Ph), 4.94 (d, $J_{1,2}=3.5$ Hz, 1H, 1b-H), 5.04 (dd, $J_{gem}=1.3$ Hz, $J_{cis}=10.5$ Hz, 1H, $OCH_2CH{=}CH_2$), 5.13 (dd, $J_{gem}=1.5$ Hz, $J_{trans}=17.2$ Hz, 1H, $OCH_2CH{=}CH_2$), 5.41 (d, $J_{1,2}=8.5$ Hz, 1H, 1a-H), 5.64 (d, $J_{3,4}=8.1$ Hz, $J_{2,3}=10.6$ Hz, 1H, 3a-H), 5.70–5.78 (m, 1H, $OCH_2CH{=}CH_2$), 7.22–7.82 (m, 24H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=16.28$ (1C, CH_3, C-6b), 20.91 (1C, CH3, $C(O)CH_3$), 55.07 (1C, CH, C-2a), 67.71 (1C, CH, C-5b), 69.49 (1C, CH_2, C-6a), 70.01 (1C, CH_2, $OCH_2CH{=}CH_2$), 72.83 (1C, CH_2, OCH_2Ph), 73.15 (1C, CH, C-3a), 73.85, 74.94, 75.03 (3C, CH_2, OCH_2Ph), 76.61 (1C, CH, C-5a), 77.30 (1C, CH, C-2b), 77.67 (1C, CH, C-4b), 78.34 (1C, CH, C-4a), 79.01 (1C, CH, C-3b), 96.81 (1C, CH, C-1a), 100.49 (1C, CH, C-1b), 117.52 (1C, CH_2, $OCH_2CH{=}CH_2$), 123.41 (2C, CH, *C*H-Ph (Pht)), 127.35–128.47 (20C, CH, *C*H-Ph), 131.41, 131.69 (2C, C_{ipso} (Pht)), 133.61 (1C, CH, $OCH_2CH{=}CH_2$), 134.00, 134.19 (2C, CH, *C*H-Ph (Pht)), 138.44, 138.49, 138.60, 138.64 (4C, C_{ipso}), 167.63, 168.14 (2C, C(O) (Pht)), 170.79 (1C, *C*(O)); $C_{53}H_{55}NO_{12}\cdot 0.5\,H_2O$: calcd C 70.18, H 6.22, N 1.54; found C 70.24, H 6.22, N 0.99.

β-Anomer: Colorless oil; R_f: 0.39 (ethyl acetate/hexane 1/2); $[\alpha]_D^{22}=+2.2$ ($c=0.5$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.15$ (d, $J_{5,6}=6.3$ Hz, 3H, 6b-CH_3), 1.78 (s, 3H, OCH_3), 3.38 (dd, $J_{3,4}=2.8$ Hz, $J_{2,3}=9.7$ Hz, 1H, 3b-H), 3.42 (q, $J_{5,6}=6.3$ Hz, 1H, 5b-H), 3.54 (d, $J_{3,4}=2.8$ Hz, 1H, 4b-H), 3.65–3.70 (m, 2H, 2b-H, 6a-H), 3.78 (ddd, $J_{5,6'}=1.7$ Hz, $J_{4,5}=J_{5,6}=9.7$ Hz, 1H, 5a-H), 3.85 (dd, $J_{4,5}=J_{3,4}=9.7$ Hz, 1H, 4a-H), 4.08 (dd, $J_{vic}=6.3$ Hz, $J_{gem}=12.9$ Hz, 1H, $OCH_2CH{=}CH_2$), 4.12 (dd, $J_{5,6'}=1.7$ Hz, $J_{6,6'}=11.2$ Hz, 1H, 6′a-H), 4.22 (dd, $J_{1,2}=8.4$ Hz, $J_{2,3}=10.8$ Hz, 1H, 2a-H), 4.30 (dd, $J_{vic}=5.1$ Hz, $J_{gem}=12.9$ Hz, 1H, $OCH_2CH{=}CH_2$), 4.43 (d, $J_{1,2}=7.7$ Hz, 1H, 1b-H), 4.57–4.73 (m, 7H, OCH_2Ph), 4.95 (d, $J_{gem}=11.7$ Hz, 1H, OCH_2Ph), 5.05 (dd, $J_{gem}=0.9$ Hz, $J_{cis}=10.4$ Hz, 1H, $OCH_2CH{=}CH_2$), 5.14 (dd, $J_{gem}=1.4$ Hz, $J_{trans}=17.2$ Hz, 1H, $OCH_2CH{=}CH_2$), 5.50 (d, $J_{1,2}=8.4$ Hz, 1H, 1a-H), 5.73–5.80 (m, 2H, 3a-H, $OCH_2CH{=}CH_2$), 7.15–7.88 (m, 24H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=16.70$ (1C, CH_3, C-6b), 20.59 (1C, CH_3, $C(O)CH_3$), 55.28 (1C, CH, C-2a), 69.70 (1C, CH_2, C-6a), 70.12 (1C, CH_2, $OCH_2CH{=}CH2$), 70.42 (1C, CH, C-5b), 72.92, 73.31 (2C, CH_2, OCH_2Ph), 73.47 (1C, CH, C-3a), 74.58 (1C, CH, C-5a), 74.67 (1C, CH_2, OCH_2Ph), 75.24 (1C, CH, C-4a), 75.28 (1C, CH_2, OCH_2Ph), 76.45 (1C, CH, C-4b), 78.89 (1C, CH, C-2b), 82.62 (1C, CH, C-3a), 96.84 (1C, CH, C-1a), 104.18 (1C, CH, C-1b), 117.54 (1C, CH_2, $OCH_2CH{=}CH_2$), 123.36 (2C, CH, *C*H-Ph (Pht)), 127.26–128.52 (20C, CH, *C*H-Ph), 131.46, 131.78 (2C, C_{ipso} (Pht)), 133.65 (1C, CH, $OCH_2CH{=}CH_2$), 133.90, 134.18 (2C, CH, *C*H-Ph (Pht)), 138.41, 138.65, 138.69, 138.73 (4C, C_{ipso}), 167.75, 168.05 (2C, C(O) (Pht)), 170.21 (1C, *C*(O)); $C_{53}H_{55}NO_{12}\cdot 2\,H_2O$: calcd C 68.15, H 6.36, N 1.49; found C 68.01, H 6.07, N 0.85.

Methyl-(2,3,4-tri-*O*-benzyl-*α*/*β*-L-fucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (**22**): yield 51%; anomeric ratio $\alpha:\beta=3.5:1$.

α-Anomer: Colorless oil; R_f: 0.50 (ethyl acetate/hexane 1/3); $[\alpha]_D^{22}=+12.4$ ($c=1.2$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=0.96$ (d, $J_{5,6}=6.5$ Hz, 3H, 6c-CH_3), 3.27 (s, 3H, OCH_3), 3.32–3.63 (m, 8H, 2c-H, 4c-H, 6b-H, 4b-H, 6′b-H, 6a-H, 2a-H, 4a-H), 3.69–3.72 (m, 1H, 5b-H), 3.74–3.81 (m, 2H, 5a-H, 6′a-H), 3.91 (dd, $J_{2,3}=J_{3,4}=9.3$ Hz, 1H, 3c-H), 3.95–3.98 (m, 2H, 3a-H, 3b-H), 4.02 (dd, $J_{2,3}=10.2$ Hz, $J_{1,2}=3.4$ Hz, 1H, 2b-H), 4.07 (q, $J_{5,6}=6.5$ Hz, 1H, 5c-H), 4.38 (d, $J_{gem}=12.2$ Hz, 1H, OCH_2Ph), 4.40 (d, $J_{gem}=10.9$ Hz, 1H, OCH_2Ph), 4.48 (d, $J_{1,2}=3.6$ Hz, 1H, 1a-H), 4.53–4.85 (m, 12H, OCH_2Ph), 4.92–4.96 (m, 3H, OCH_2Ph), 4.98 (d, $J_{1,2}=3.0$ Hz, 1H, 1c-H), 4.99 (d, $J_{1,2}=3.5$ Hz, 1H, 1b-H), 5.13 (d, $J_{gem}=11.6$ Hz, 1H, OCH_2Ph), 7.01–7.38 (m, 45H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=16.89$ (1C, CH_3, C-6c), 54.90 (1C, CH_3, OCH_3), 66.32 (1C, CH_2, C-6a), 66.80 (1C, CH, C-5c), 68.39 (1C, CH_2, C-6b), 69.65 (1C, CH, C-5a), 69.97 (1C, CH, C-5b), 72.91–75.85 (9C, CH_2, OCH_2Ph), 75.90 (1C, CH, C-2b), 77.43 (1C, CH, C-4b), 77.68 (1C, CH, C-2c), 77.99 (1C, CH, C-4c), 79.24 (1C, CH, C-3b), 80.37 (1C, CH, C-3c), 80.47 (1C, CH, C-2a), 82.20 (1C, CH, C-4a), 82.38 (1C, CH, C-3a), 97.58 (1C, CH, C-1a), 98.53 (1C, CH, C-1b), 100.77 (1C, CH, C-1c), 127.05–128.46 (45C, CH, *C*H-Ar), 137.99–139.24 (9C, C_{ipso}); $C_{82}H_{88}O_{15}$: calcd C 74.98, H 6.75; found C 75.96, H 6.89.

β-Anomer: Colorless oil; R_f: 0.25 (ethyl acetate/hexane 1/3); $[\alpha]_D^{22}=+15.6$ ($c=1$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.13$ (d, $J_{5,6}=6.3$ Hz, 3H, 6c-CH_3), 3.24 (s, 3H, OCH_3), 3.38 (q, $J_{5,6}=6.1$ Hz, 1H, 5c-H), 3.43–3.48 (m, 2H, 3c-H, 2a-H), 3.51–3.55 (m, 3H, 4c-H, 4a-H, 6a-H), 3.60–3.67 (m, 3H, 6′a-H, 6b-H, 4b-H), 3.75 (m, 2H, 5b-H, 5a-H), 3.79–3.86 (m, 2H, 6′b-H, 2c-H), 3.92 (dd, $J_{2,3}=J_{3,4}=9.2$ Hz, 1H, 3a-H), 3.99 (dd, $J_{3,4}=8.6$ Hz, $J_{2,3}=9.5$ Hz, 1H, 3b-H), 4.04 (dd, $J_{1,2}=3.2$ Hz, $J_{2,3}=9.5$ Hz, 1H, 2b-H), 4.34 (d, $J_{gem}=12.3$ Hz, 1H, OCH_2Ph), 4.37 (d, $J_{1,2}=3.2$ Hz, 1H, 1a-H), 4.38 (d, $J_{gem}=10.6$ Hz, 1H, OCH_2Ph), 4.47 (d, $J_{gem}=12.1$ Hz, 1H, OCH_2Ph), 4.50 (d, $J_{1,2}=7.6$ Hz, 1H, 1c-H), 4.52–4.75 (m, 10H, OCH_2Ph), 4.84–5.41 (m, 6H, 1b-H, OCH_2Ph (5)), 7.08–7.38 (m, 45H, Ph-*H*); ^{13}C

NMR (125.7 MHz, $CDCl_3$): $\delta = 16.88$ (1C, CH_3, C-6c), 55.00 (1C, CH_3, OCH_3), 66.38 (1C, CH_2, C-6b), 68.31 (1C, CH_2, C-6a), 69.60, 70.10, 70.52 (3C, CH), 73.18 – 75.60 (9C, CH_2, OCH_2Ph), 76.75, 77.00, 77.26, 77.71 (4C, CH), 79.24, 80.28, 80.87, 82.26, 82.63 (5C, CH), 96.82 (1C, CH, C-1a), 97.58 (1C, CH, C-1b), 101.98 (1C, CH, C1-c), 127.23 – 128.46 (45C, CH, *C*H-Ph), 137.98 – 139.14 (9C, C_{ipso}); MS (MALDI): $m/z = 1337$ $[M+Na]^+$; $C_{82}H_{88}O_{15}$.

Allyl-*O*-(2,3,4-tri-*O*-benzyl-*α*-L-fucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-galactopyranosyl)-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside (23): Colorless oil; yield 49%; only α; R_f: 0.46 (ethyl acetate/hexane1/2); $[\alpha]_D^{22} = -16.7$ ($c = 1$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.01$ (d, $J_{5,6} = 6.5$ Hz, 3H, 6c-CH_3), 1.84 (s, 3H, C(O)CH_3), 3.43 – 3.51 (m, 2H, 6b-H, 6′b-H), 3.69 (brs, 1H, 4c-H), 3.72 – 3.78 (m, 3H, 5c-H, 5a-H, 6a-H), 3.82 (dd, $J_{2,3} = 10.2$ Hz, $J_{3,4} = 2.7$ Hz, 1H, 3b-H), 3.86 (brs, 1H, 4b-H), 3.96 (dd, $J_{5,6'} = 3.5$ Hz, $J_{6,6'} = 11.5$ Hz, 1H, 6′a-H), 3.98 – 4.07 (m, 3H, $OCH_2CH{=}CH_2$, 5b-H, 2c-H), 4.09 (dd, $J_{2,3} = 10.4$ Hz, $J_{3,4} = 2.5$ Hz, 1H, 3c-H), 4.21 (dd, $J_{4,5} = 9.3$ Hz, $J_{3,4} = 8.7$ Hz, 1H, 4a-H), 4.27 (ddt, $^4J = 1.3$ Hz, $J_{vic} = 5.1$ Hz, $J_{gem} = 13.0$ Hz, 1H, $OCH_2CH{=}CH_2$), 4.31 – 4.39 (m, 4H, OCH_2Ph (2), 2a-H, 2b-H), 4.41 – 4.67 (m, 9H, OCH_2Ph), 4.81 – 4.91 (m, 3H, OCH_2Ph), 5.05 (dd, $J_{gem} = 1.3$ Hz, $J_{cis} = 10.4$ Hz, 1H, $OCH_2CH{=}CH_2$), 5.13 (dq, $^4J = J_{gem} = 1.5$ Hz, $J_{trans} = 17.2$ Hz, 1H, $OCH_2CH{=}CH_2$), 5.16 (d, $J_{1,2} = 3.5$ Hz, 1H, 1b-H), 5.36 (d, $J_{1,2} = 8.5$ Hz, 1H, 1a-H), 5.41 (d, $J_{1,2} = 3.4$ Hz, 1H, 1c-H), 5.69 – 5.77 (m, 1H, $OCH_2CH{=}CH_2$), 5.87 (dd, $J_{3,4} = 8.7$ Hz, $J_{2,3} = 10.5$ Hz, 1H, 3a-H), 6.97 – 7.79 (m, 49H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 16.54$ (1C, CH_3, C-6c), 21.00 (1C, CH_3, C(O)CH_3), 55.23 (1C, CH, C-2a), 66.92 (1C, CH, C-5c), 68.39 (1C, CH_2, C-6a), 68.67 (1C, CH_2, C-6b), 69.89 (1C, CH_2, $OCH_2CH{=}CH_2$), 70.18 (1C, CH, C-2c), 71.88 (1C, CH_2, OCH_2Ph), 72.22 (1C, CH, C-2b), 72.45, 72.77 (2C, CH_2, OCH_2Ph), 72.89 (1C, CH, C-4a), 73.13 (1C, CH, C-3a), 73.23, 73.36 (2C, CH_2, OCH_2Ph), 74.17 (1C, CH, C-4b), 74.74 (1C, CH, C-5a), 74.79 (2C, CH_2, OCH_2Ph), 75.14 (1C, CH, C-5b), 77.66 (1C, CH, C-4c), 78.73 (1C, CH, C-3b), 79.07 (1C, CH, C-3c), 96.95 (1C, CH, C-1c), 97.37 (1C, CH, C-1b), 98.80 (1C, CH, C-1a), 117.48 (1C, CH_2, $OCH_2CH{=}CH_2$), 123.41 (2C, CH, *C*H-Ph (Pht)), 126.61 – 128.34 (35C, CH, *C*H-Ph), 131.49 (2C, C_{ipso}(Pht)), 133.61 (2C, CH, *C*H-Ph (Pht)), 134.08 (1C, CH, $OCH_2CH{=}CH_2$), 137.99 – 139.31 (7C, C_{ipso}), 167.70 (2C, *C*(O)(Pht)), 170.63 (1C, *C*(O)); $C_{80}H_{83}NO_{17}$: calcd C 72.22, H 6.29, N 1.05; found C 72.14, H 6.65, N 0.65.

Allyl-*O*-(2,3,4-tri-*O*-benzyl-*α*/*β*-L-fucopyranosyl)-(1→6)-[(2,3,4-tri-*O*-benzyl-*α*-L-fucopyranosyl)-(1→4)]-2-acetamido-2-deoxy-3-*O*-*p*-methoxybenzyl-*α*-D-glucopyranoside (24): Colorless oil; yield 99%; anomeric ratio $\alpha:\beta = 2:1$; R_f: 0.51 (dichloromethane/methanol 10/1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.78$ (d, $J_{5,6} = 6.4$ Hz, 3H, 6c-CH_3 (a)), 1.03 (d, $J_{5,6} = 6.5$ Hz, 3H, 6b-CH_3 (a)), 1.05 (d, $J_{5,6} = 6.4$ Hz, 3H, 6c-CH_3 (b)), 1.18 (d, $J_{5,6} = 6.5$ Hz, 3H, 6b-CH_3 (b)), 1.87 (s, 3H, NC(O)CH_3(a)), 2.04 (s, 3H, NC(O)CH_3(b)), 3.33 – 4.39 (m, 32H, [2a-H-6′a-H, 2b-H-5b-H, 2c-H-5c-H] (a), [2a-H-6′a-H, 2b-H-5b-H, 2c-H-5c-H] (b), $OCH_2CH{=}CH_2$ (4)), 3.78 (s, 3H, OCH_3 (b)), 3.81 (s, 3H, OCH_3 (a)), 4.46 – 5.30 (m, 38H, OCH_2Ph (28), $OCH_2CH{=}CH_2$ (4), [1a-H, 1b-H, 1c-H] (a), [1a-H, 1b-H, 1c-H] (b)), 5.53 (d, $J_{2,NH} = 9.7$ Hz, 1H, NH (a)), 5.66 (d, $J_{2,NH} = 8.6$ Hz, 1H, NH (b)), 5.78 – 5.86 (m, 2H, $OCH_2CH{=}CH_2$), 6.73 – 7.47 (m, 68H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 16.38$ (1C, CH_3, C-6c (b)), 16.53 (1C, CH_3, C-6c (a)), 16.58 (1C, CH_3, C-6b (a)), 16.73 (1C, CH_3, C-6b (b)), 23.39 (2C, CH_3, NC(O)CH_3), 55.17 (1C, CH_3, OCH_3 (b)), 55.19 (1C, CH_3, OCH_3 (a)), 64.67 – 80.32 (42C, CH, [C-2a-C-5a, C-2b-C-5b, C-2c-C-5c] (a), [C-2a-C-5a, C-2b-C-5b, C-2c-C-5c] (b) (24), CH_2 (C-6a (a), C-6a (b), $OCH_2CH{=}CH_2$ (a), $OCH_2CH{=}CH_2$ (b), OCH_2Ph (14)), 96.07 (1C, CH, C-1a (a)), 96.43 (1C, CH, C-1a (b)), 97.44 (1C, CH, C-1c (a)), 97.53 (2C, CH, C-1b (a + b)), 99.30 (1C, CH, C-1c (b)), 117.64, 117.69 (2C, CH_2, $OCH_2CH{=}CH_2$), 127.03 – 129.74 (68C, CH, *C*H-Ph), 133.57, 133.63 (2C, CH, $OCH_2CH{=}CH_2$), 138.19 – 138.67 (14C, C_{ipso}), 159.01, 159.05 (2C, C_{ipso} (PMB)), 169.62, 170.61 (2C, *C*(O)); $C_{73}H_{83}NO_{15} \cdot 1H_2O$: calcd C 71.14, H 6.95, N 1.13; found C 71.21, H 6.69, N 0.85.

Allyl-*O*-(2,3,4-tri-*O*-benzyl-*α*-L-fucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-galactopyranosyl)-(1→4)-2-acetamido-6-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside (25): Yellowish oil; yield 46%; only α; R_f: 0.62 (ethyl acetate/hexane 1/2); $[\alpha]_D^{22} = -12.2$ ($c = 0.55$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.05$ (d, $J_{5,6} = 6.4$ Hz, 3H, 6c-CH_3), 1.86 (s, 3H, C(O)CH_3), 3.44 – 3.53 (m, 4H, 2a-H, 5a-H, 6b-H, 6′b-H), 3.60 (brs, 1H, 4c-H), 3.65 (brs, 1H, 4a-H), 3.76 – 3.86 (m, 3H, 5c-H, 6a-H, 6′a-H), 3.95 – 4.14 (m, 7H, 3c-H, $OCH_2CH{=}CH_2$, 5b-H, 4b-H, 3a-H, 3b-H, 2c-H), 4.34 (dd, $J_{vic} = 5.1$ Hz, $J_{gem} = 12.9$ Hz, 1H, $OCH_2CH{=}CH_2$), 4.39 – 4.58 (m, 10H, OCH_2Ph (9), 2b-H), 4.68 – 4.73 (m, 3H, OCH_2Ph (2), 1a-H), 4.78 – 4.89 (m, 3H, OCH_2Ph), 5.14 (d, $J_{1,2} = 3.5$ Hz, 1H, 1b-H), 5.17 (dd, $J_{gem} = 1.2$ Hz, $J_{cis} = 10.3$ Hz, 1H, $OCH_2CH{=}CH_2$), 5.26 (dd, $J_{gem} = 1.3$ Hz, $J_{trans} = 17.4$ Hz, 1H, $OCH_2CH{=}CH_2$), 5.38 (d, $J_{2,NH} = 6.9$ Hz, 1H, NH), 5.65 (d, $J_{1,2} = 3.7$ Hz, 1H, 1c-H), 5.85 – 5.89 (m, 1H, $OCH_2CH{=}CH_2$), 7.06 – 7.37 (m, 35H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 16.54$ (1C, CH_3, C-6c), 23.56 (1C, CH_3, NC(O)CH_3), 57.32 (1C, CH, C-5a), 67.14 (1C, CH, C-5c), 68.99 (1C, CH_2, C-6a), 69.14 (1C, CH_2, C-6b), 69.56 (1C, CH_2, $OCH_2CH{=}CH_2$), 70.56 (1C, CH, C-5b), 71.37 (1C, CH_2, OCH_2Ph), 71.96 (1C, CH, C-2b), 72.94 (1C, CH, C-4b), 73.15, 73.52, 73.76 (4C, CH_2, OCH_2Ph), 74.69 (1C, CH, C-3a), 74.78 (3C, CH, C-2a, CH_2, OCH_2Ph (2)), 75.32 (1C, CH, C-2c), 77.51 (1C, CH, C-4c), 79.11 (1C, CH, C-3c), 79.77 (1C, CH, C-3b), 81.35 (1C, CH, C-4a), 97.71 (1C, CH, C-1c), 99.36 (1C, CH, C-1a), 101.20 (1C, CH, C-1b), 117.38 (1C, CH_2, $OCH_2CH{=}CH_2$), 126.47 – 128.41 (35C, CH, *C*H-Ph), 134.02 (1C, CH, $OCH_2CH{=}CH_2$), 137.83 – 139.46 (7C, C_{ipso}), 170.55 (1C, *C*(O)CH_3); $C_{72}H_{81}NO_{15}$: calcd C 72.04, H 6.80, N 1.17; found C 72.04, H 7.12, N 0.93.

Methyl-*O*-(2,3,4-tri-*O*-benzyl-*α*/*β*-L-fucopyranosyl)-(1→3)-2,6-di-*O*-benzyl-*β*-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (26): Yield 33%; anomeric ratio $\alpha:\beta = 4:1$.

α-Anomer: Colorless oil; R_f: 0.53 (ethyl acetate/hexane 1/2); $[\alpha]_D^{22} = -32.6$ (c = 1 in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.14$ (d, $J_{5,6} = 6.5$ Hz, 3H, 6c-CH_3), 3.22 (m, 1H, 5a-H), 3.31 – 3.37 (m, 2H, 4a-H, 5b-H), 3.45 – 3.63 (m, 6H, 2b-H, 3b-H, 6b-H, 6′b-H, 6a-H, 2a-H), 3.51 (s, 3H, OCH_3), 3.68 (d, $J_{3,4} = 2.5$ Hz, 1H, 4c-H), 3.73 (dd, $J_{5,6'} = 3.9$ Hz, $J_{6,6'} = 10.9$ Hz, 1H, 6′a-H), 3.91 (d, $J_{3,4} = 2.9$ Hz, 1H, 4b-H), 3.96 (dd, $J_{2,3} = J_{3,4} = 9.6$ Hz, 1H, 3a-H), 3.99 (dd, $J_{2,3} = 10.2$ Hz, $J_{3,4} = 2.5$ Hz, 1H, 3c-H), 4.04 (dd, $J_{1,2} = 3.5$ Hz, $J_{2,3} = 10.2$ Hz, 1H, 2c-H), 4.07 (q, $J_{5,6} = 6.5$ Hz, 1H, 5c-H), 4.22 (d, $J_{1,2} = 7.8$ Hz, 1H, 1a-H), 4.32 (d, $J_{gem} = 12.1$ Hz, 1H, OCH_2Ph), 4.38 (d, $J_{gem} = 12.1$ Hz, 1H, OCH_2Ph), 4.40 (d, $J_{1,2} = 7.6$ Hz, 1H, 1b-H), 4.42 (d, $J_{gem} = 12.1$ Hz, 1H, OCH_2Ph), 4.54 – 4.97 (m, 13H, OCH_2Ph), 5.25 (d, $J_{1,2} = 3.5$ Hz, 1H, 1c-H), 7.10 – 7.39 (m, 40H, Ph-H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 16.70$ (1C, CH_3, C-6c), 56.97 (1C, CH_3, OCH_3), 67.00 (1C, CH, C-5c), 67.89 (1C, CH_2, C-6a), 68.48 (1C, CH_2, C-6b), 68.87 (1C, CH, C-4b), 72.62 (1C, CH, C-4a), 72.91 – 75.32 (8C, CH_2, OCH_2Ph), 74.38 (1C, CH, C-5a), 75.67 (1C, CH, C-2c), 76.28 (1C, CH, C-3a), 77.57 (1C, CH, C-4c), 78.99 (1C, CH, C-3c), 79.07 (1C, CH, C-3b), 79.91 (1C, CH, C-2b), 81.70 (1C, CH, C-5b), 82.85 (1C, CH, C-2a), 99.17 (1C, CH, C-1c), 102.42 (1C, CH, C-1b), 104.63 (1C, CH, C-1a), 126.87 – 128.58 (40C, CH, *C*H-Ph), 138.14 – 139.12 (8C, C_{ipso}); $C_{75}H_{82}O_{17} \cdot 1H_2O$: calcd C 72.56, H 6.81; found C 72.60, H 6.80.

β-Anomer: Colorless oil; R_f: 0.41 (ethyl acetate/hexane 1/2). Characteristic signals in ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 16.90$ (1C, CH_3, C-6c), 99.54 (1C, CH, C-1c), 102.57 (1C, CH, C-1b), 104.62 (1C, CH, C-1a); MS (FAB): $m/z = 1247$ $[M+Na]^+$; $C_{75}H_{82}O_{17}$.

Methyl-*O*-(2,3,4-tri-*O*-benzyl-*α*/*β*-L-fucopyranosyl)-(1→4)-2,6-di-*O*-benzyl-*β*-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (27): Yield 27%; anomeric ratio $\alpha:\beta = 6:1$.

α-Anomer: Colorless oil; R_f: 0.37 (ethyl acetate/hexane 1/2); $[\alpha]_D^{22} = -21.4$ ($c = 2.5$ in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.93$ (d, $J_{5,6} = 6.5$ Hz, 3H, 6c-CH_3), 3.21 (dd, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 9.2$ Hz, 1H, 2b-H), 3.31 – 3.37 (m, 3H, 2a-H, 5a-H, 5b-H), 3.39 (brs, 1H, 4c-H), 3.41 – 3.52 (m, 4H, 4a-H, 6b-H, 6′b-H, 3b-H), 3.55 (s, 3H, OCH_3), 3.67 (q, $J_{5,6} = 6.5$ Hz, 1H, 5c-H), 3.70 – 3.78 (m, 3H, 3c-H, 6a-H, 6′a-H), 3.80 (d, $J_{3,4} = 2.9$ Hz, 1H, 4b-H), 3.96 (dd, $J_{2,3} = J_{3,4} = 9.6$ Hz, 1H, 3a-H), 4.05 (dd, $J_{1,2} = 3.6$ Hz, $J_{2,3} = 10.2$ Hz, 1H, 2c-H), 4.27 (d, $J_{1,2} = 7.8$ Hz, 1H, 1a-H), 4.37 (d, $J_{1,2} = 7.8$ Hz, 1H, 1b-H), 4.39 – 4.64 (m, 11H, OCH_2Ph), 4.70 – 4.92 (m, 5H, OCH_2Ph (4), 1c-H), 5.07 (d, $J_{gem} = 11.3$ Hz, 1H, OCH_2Ph), 7.14 – 7.34 (m, 4OH, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 16.54$ (1C, CH_3, C-6c), 56.99 (1C, CH_3, OCH_3), 67.17 (1C, CH, C-5c), 68.23 (1C, CH_2, C-6a), 68.81 (1C, CH_2, C-6b), 71.97 (1C, CH_2, OCH_2Ph), 72.74 (1C, CH_2, OCH_2Ph), 73.06 (1C, CH, C-5a), 73.21, 73.47, 74.70, 74.76 (4C, CH_2, OCH_2PH), 74.84 (1C, CH, C-3b), 74.89, 74.95 (2C, CH_2, OCH_2Ph), 75.05 (1C, CH, C-5b), 76.15 (1C, CH, C-2c), 76.46 (1C, CH, C-3a), 76.51 (1C, CH, C-4c), 79.48 (1C, CH, C-3c), 80.73 (1C, CH, C-4b), 81.34 (1C, CH, C-2b), 81.47 (1C, CH, C-2a), 83.19 (1C, CH, C-4a), 101.66 (1C, CH, C-1c), 102.25 (1C, CH, C-1b), 104.59 (1C, CH, C-1a), 126.97 – 129.72 (40C, CH, *C*H-Ph), 137.05 – 139.67 (8C, C_{ipso}); $C_{75}H_{82}O_{17} \cdot 3H_2O$: calcd C 70.51, H 6.94; found C 70.93, H 6.63.

β-Anomer: Colorless oil; R_f: 0.18 (ethyl acetate/hexane 1/2). Characteristic signals in ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 16.54$ (1C, CH_3, C-6c), 103.12 (1C, CH, C-1b), 104.15 (1C, CH, C-1c), 104.49 (1C, CH, C-1a).

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Methyl-*O*-(2,3,4-tri-*O*-benzyl-α/β-L-fucopyranosyl)-(1→4)-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**28**): Yield 7%; anomeric ratio $\alpha:\beta = 4:1$.
α-Anomer: Colorless oil; R_f: 0.63 (ethyl acetate/hexane 1/2); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.99$ (d, $J_{5,6} = 6.4$ Hz, 3H, 6c-CH_3), 1.14 (d, $J_{5,6} = 6.5$ Hz, 3H, 6d-CH_3), 3.32 (dd, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 9.1$ Hz, 1H, 2a-H), 3.40–3.55 (m, 5H, 3a-H, 5a-H, 6a-H, 5b-H, 6b-H), 3.48 (s, 3H, OCH_3), 3.56 (br d, 1H, 4c-H), 3.63–3.71 (m, 4H, 3b-H, 4d-H, 6′a-H, 6′b-H), 3.77–3.89 (m, 4H, 2b-H, 3c-H, 3d-H, 5d-H), 3.93–4.08 (m, 5H, 4a-H, 4b-H, 2c-H, 2d-H, 5d-H), 4.16 (d, $J_{1,2} = 7.8$ Hz, 1H, 1a-H), 4.23–4.95 (m, 21H, OCH_2Ph (20), 1b-H [$J_{1,2} = 7.5$ Hz]), 5.05 (d, $J_{gem} = 12.3$ Hz, 1H, OCH_2Ph), 5.15 (d, $J_{gem} = 10.7$ Hz, 1H, OCH_2Ph), 5.30 (d, $J_{1,2} = 3.7$ Hz, 1H, 1d-H), 5.92 (d, $J_{1,2} = 3.8$ Hz, 1H, 1c-H), 6.98–7.41 (m, 55H, Ph-*H*); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 16.62$ (1C, CH_3, C-6c), 16.69 (1C, CH_3, C-6d), 56.98 (1C, CH_3, O*C*H_3), 66.46, 66.97 (2C, CH), 67.60 (1C, CH_2, C-6a), 68.08 (1C, CH_2, C-6b), 68.49–82.63 (25C, CH (14), CH_2, O*C*H_2Ph (11)), 95.20 (1C, CH, C-1c), 99.35 (1C, CH, C-1d), 103.14 (1C, CH, C-1b), 104.57 (1C, CH, C-1a), 125.64–129.73 (55C, CH, *C*H-Ph), 138.14–139.38 (11C, C_{ipso}). Characteristic signals for the β-anomer: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.47$ (s, 3H, OCH_3), 3.04 (m, 1H), 3.14 (m, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta = 95.20$ (1C, CH, C-1c), 103.14 (1C, CH, C-1b), 104.37 (1C, CH, C-1d), 104.57 (1C, CH, C-1a); $C_{102}H_{110}O_{19} \cdot 1H_2O \cdot 1CHCl_3$: calcd C 69.60, H 6.41; found C 69.88, H 6.51.

Acknowledgments: This research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Received: July 22, 1997 [F776]

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