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# Stereoselective synthesis of a blood group A type glycopeptide present in human blood mucin

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**Abstract**

*N,N*-Dimethyl-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1 → 3)-*O*-[(α-L-fucopyranosyl)-(1 → 2)]-*O*-(β-D-galactopyranosyl)-(1 → 3)-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1 → 3)-L-serine, a core I glycotetraosyl peptide structure and a predominant substructure in complex glycan–glycoproteins present in human blood group A ovarian mucin, was synthesized for the first time. The title compound was synthetically accomplished via the following key manoeuvres: regio- and stereo-controlled construction of the α-GalNAc-(1 → 3)-Gal synthon, stereoselective glycosylation generating a α-$GalN_3$-(1 → 3)-Ser glycopeptide synthon and α-selective fucosylation towards an acceptor which was derived from glycosylation of the latter two synthons. An alternative route to that of the latter, to synthesize a fully protected equivalent of the title compound, involving the coupling of a α-GalNAc-(1 → 3)-β-Gal-(1 → 3)-$GalN_3X$ synthon to an aglycon serine derivative, is described herein.

*Keywords:* Human blood group A ovarian mucin; Core I glycotetraosyl serine; α-Stereocontrol and C-3 regiocontrol; Allyl–Fmoc protective group combination; α-Fucosylation

## 1. Introduction

In recent years the availability of synthetic oligosaccharide determinants either by chemical [1] or enzymatic [2] means has had an important impact on many aspects of

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medical practice such as in the production of monoclonal [3] and polyclonal antibodies [4] for tumour therapy [5]. A common characteristic of mucin-type determinants from various organs and species is the microheterogeneous nature of their carbohydrate chains. In particular Bush and co-workers have studied blood group oligosaccharides of the A and H type which vary in size from three to ten sugar residues and which were isolated by HPLC from natural sources [6–10]. Complex oligosaccharide alditols such as **1** and a tetrasaccharide bearing a *N*-acetyl-D-galactosaminitol residue at the reducing end of structure **2** are released by alkaline borohydride reductive-cleavage ( $\beta$-elimination) [11] of blood group A ovarian cyst mucin glycoproteins [9].

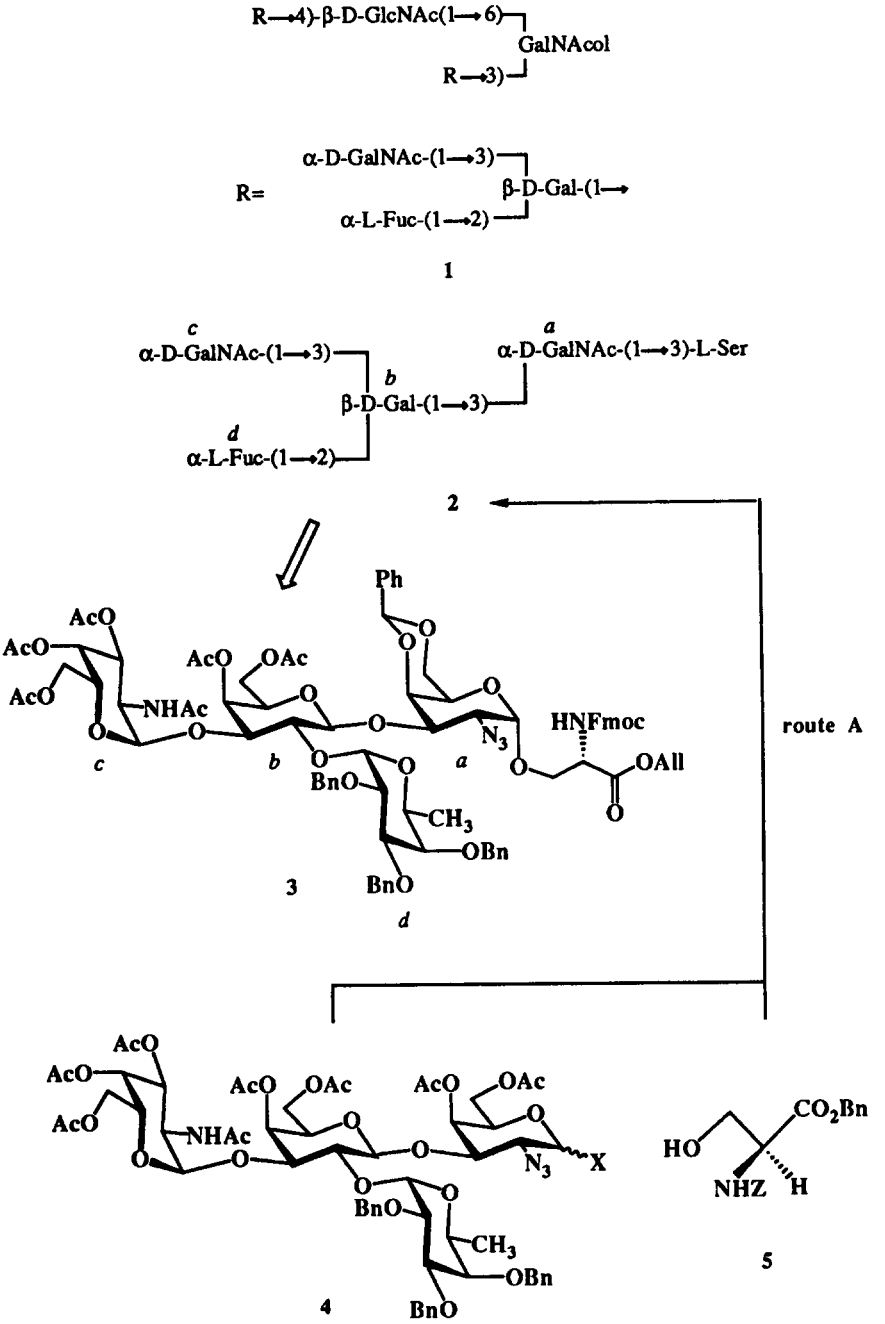
As part of our current investigations on the synthesis of glycopeptide fragments of glycophorin [12] and for the purpose of supplying structurally well defined compounds as models for natural mucin glycopeptides, structure **2** (Scheme 1) was designed as a target molecule bearing L-serine as the hypothetical linkage to the peptide backbone on the mucin cell surface. Similarly in designing alditol **1** linked in the $\alpha$-D-configuration to L-serine as a target molecule [13], it is to be noted that it differs from the glycopeptide **2** by possessing two blood group A determinant trisaccharide composite units $\alpha$-D-GalNAc-(1 → 3)-[$\alpha$-L-Fuc-(1 → 2)-]-$\beta$-D-Gal and is classified as a core II structure [14]; further classification becomes necessary since structure **1** is a $\beta$-D-Gal-(1 → 4)-D-GlcNAc containing oligosaccharide thus is said to have the type 2 structure [15].

Hitherto, synthetic studies towards blood group A active oligosaccharides which are void of an O-linked amino acid have been reported by several workers. Lemieux and Driguez achieved the full synthesis of a terminal portion of the glycoserine **2**, $\alpha$-L-Fuc-(1 → 2)-[$\alpha$-D-GalNAc-(1 → 3)]-D-Gal-(1 → 3) [16] and Paulsen and Kolar, by initially constructing the type 2 H substance trisaccharide, $\alpha$-L-Fuc-(1 → 2)-$\beta$-D-Gal-(1 → 4)-D-GlcNAc, went on to accomplish the synthesis of type 2 A and B blood group active tetrasaccharides [17]. The present report describes the stereoselective synthesis of a core I [14] glycotetraosyl serine **2**.

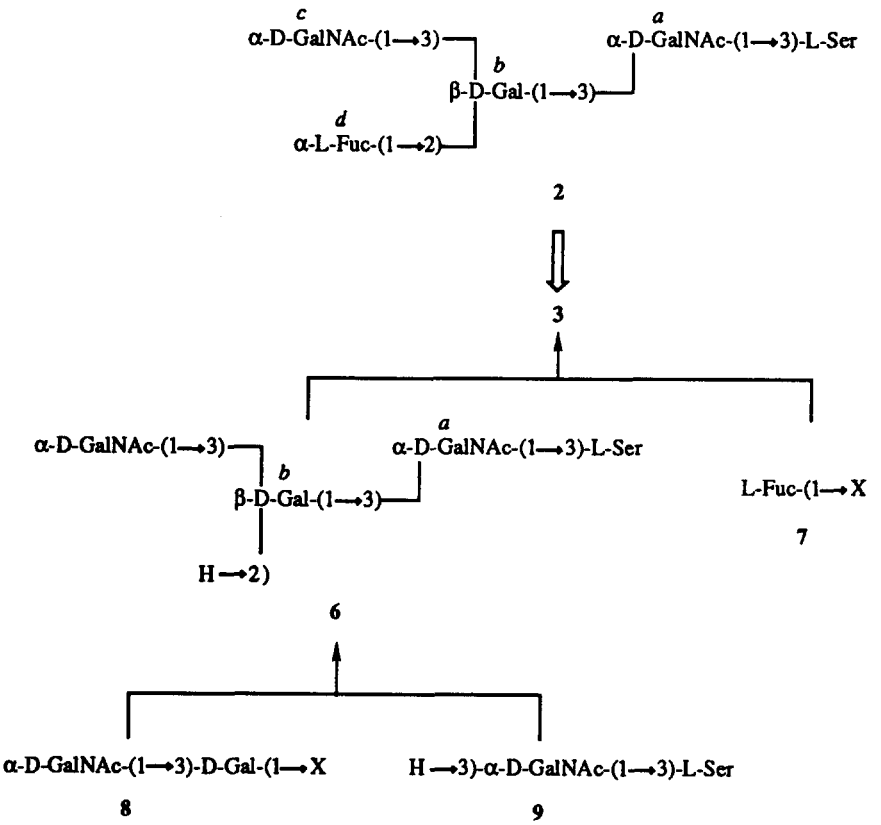
## 2. Results and discussion

The suitability of synthon **3** as the key design unit in route B (*vide infra*) can be ascribed to two features. Firstly the utility of the allyl-Fmoc temporary protective group combination for elongation of the peptide chain has been demonstrated in our laboratory [12] and elsewhere [18], while part of this work is to demonstrate its suitability as permanent protective groups for the synthesis of target **2**. Secondly it was known to us, based on a synthetic study of synthon **4**, that the normally acid-sensitive fucosyl glycoside would be resistant to acid hydrolysis of the temporary benzylidene protective group. Thus synthon **3** allows for sugar elaboration at the O-6a position, a prerequisite for the synthesis of highly branched structures such as **1** [13].

Initially our approach to synthesizing target **2** was that of route A (Scheme 1), whereby closely following the work of Paulsen and Kolar [17] we were able to access synthon **4**. However, the unsuccessful attempts in this laboratory to couple either an imidate or fluoride donor of the tetrasaccharide **4** to the protected L-serine acceptor **5** may have been disadvantaged by a limited choice of promoter systems at the time. In


R→4)-β-D-GlcNAc(1→6)
GalNAcol
R→3)
R=
α-D-GalNAc-(1→3)
β-D-Gal-(1→
α-L-Fuc-(1→2)
1
c
α-D-GalNAc-(1→3)
a
α-D-GalNAc-(1→3)-L-Ser
b
β-D-Gal-(1→3)
d
α-L-Fuc-(1→2)
2
route A
AcO
NHAc
OAc
Ph
HNFmoc
OAll
BnO
CH3
OBn
3
4
5
HO
CO2Bn
NHZ
H
X

Scheme 1.

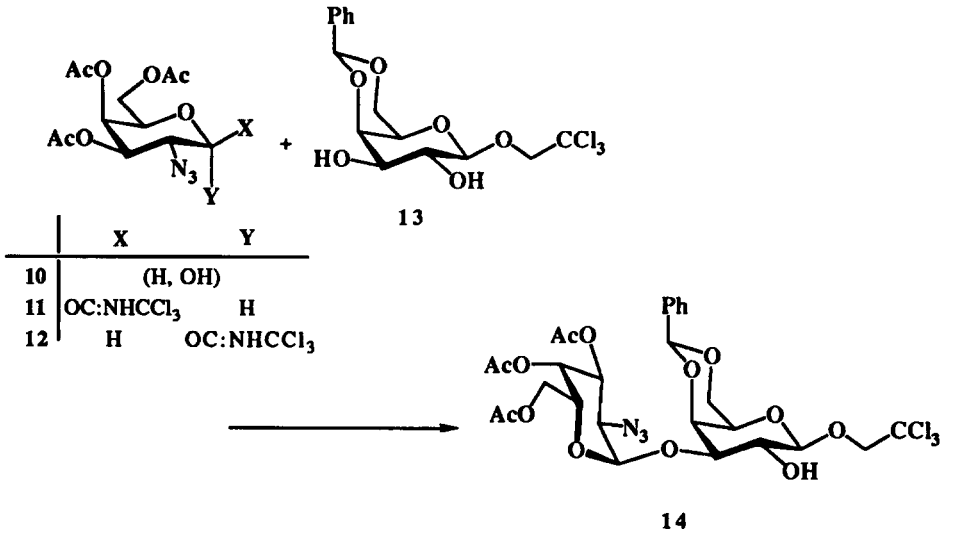



**Route B Retrosynthetic Plan**

Scheme 2.

conducting experiments on the glycosylation of a fluoride donor of **4** and an acceptor **5**, we were restricted to using the silver perchlorate–stannous chloride catalyst system and other Lewis acid variants. The highly fluorophilic metallocene type promotors devised by Suzuki et al. [19] was a later development for such glycosylations. Recently it has been claimed that use of silver trifluoromethanesulfonate gives improvements in the efficiency of the trichloroacetimidate method [20].

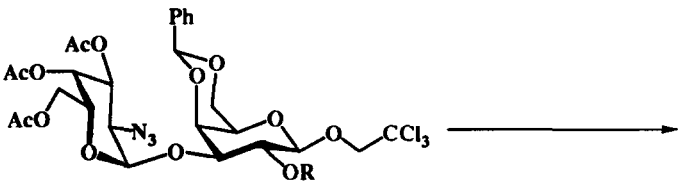
In considering the approach of route B (Scheme 2) however, it should be noted that efficient and stereoselective syntheses of protected analogues of synthons **8** [21] and **9** [12] had been cited in the literature. With the synthetic utility of synthon **3** (*vide supra*), therefore, we opted for this route as the synthetic strategy for target **2**. To generate synthon **8** a glycosylation was required which would be both efficient in terms of $\alpha$-stereocontrol and C-3 regiocontrol. Various coupling conditions were investigated as an attempt to attain this requirement, and imidate **11** (Scheme 3) proved to be the donor



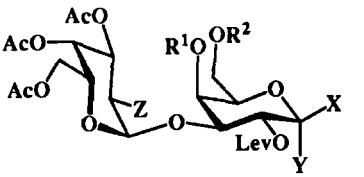

Scheme 3.

of choice. The hemiacetal **10**, prepared in four steps from D-galactose in an overall yield of 21%, was converted to the kinetic $\beta$-imidate **11** predominantly by employing trichloroacetonitrile and potassium carbonate as base in dichloromethane at 0°C, according to the procedure of Schmidt and Grundler [22]. Glycosylation of the diol **13** (prepared in three steps from peracetylated $\beta$-D-galactose in 62% overall yield [16]) with the $\beta$-imidate **11** in the presence of $Me_3SiOSO_2CF_3$ [21] in $CH_2Cl_2$ proceeded smoothly with full regioselectivity to obtain the $\alpha$-3-*O*-glycoside **14** (77%), which was treated with levulinic anhydride [23] and DMAP in pyridine to give 86% of **16** (Scheme 4). Presumably the stereocontrol attained in this glycosylation is attributable to a $S_N2$ displacement derived from the $\beta$-imidate **11** since under the same conditions except employing the $\alpha$-imidate **12** (obtainable from **10** using $CCl_3CN$–DBU, $CH_2Cl_2$, −20–0°C), glycosylation of **13** proceeded only in 19% yield to afford **14**. The other major product isolated was a complex mixture of presumably the three other possible glycosidic isomers according to proton spectral data. The newly formed $\alpha$-(1 → 3) linkage in **14** ($\delta_{H\text{-}1b}$ 5.243, *J* 3.4 Hz; $\delta_{H\text{-}2a}$ 4.008) was assigned by the synthetic sequence and confirmed by the $^1H$ NMR data of the corresponding acetate **15** ($\delta_{H\text{-}1b}$ 4.970, *J* 3.4 Hz; $\delta_{H\text{-}2a}$ 5.701).

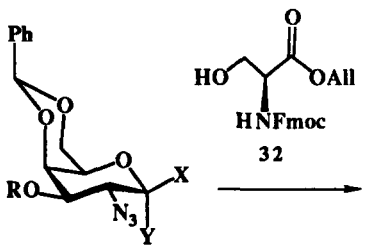
The efficacy of the trichloroacetimidate method was to be attested again in glycosylation of synthons **8** and **9**. Firstly, however, in order to furnish the trichloroacetimidate **22**, two different synthetic manoeuvres were carried out which are described as follows. Azido reduction of **16** slowly proceeded over a period of 4.5 days with thioacetic acetic [24] in dichloromethane to produce **17** (76%, $\delta_{H\text{-}2b}$ 4.545, ddd). Conversion to the pentaacetate **18** was performed quantitatively in the one-pot by treatment with 80% aqueous trifluoroacetic acid in dichloromethane to cleave the benzylidene group and subsequent acetylation with acetic anhydride and DMAP in pyridine. The alternative



14 R=H
15 R=Ac
16 R=Lev



| | $R^1$ | $R^2$ | X | Y | Z |
|---|---|---|---|---|---|
| 17 | -(PhCH)- | | $OCH_2CCl_3$ | H | NHAc |
| 18 | Ac | Ac | $OCH_2CCl_3$ | H | NHAc |
| 19 | H | H | $OCH_2CCl_3$ | H | $N_3$ |
| 20 | Ac | Ac | $OCH_2CCl_3$ | H | $N_3$ |
| 21 | Ac | Ac | -(OH, H)- | | NHAc |
| 22 | Ac | Ac | H | OC:NHCCl$_3$ | NHAc |



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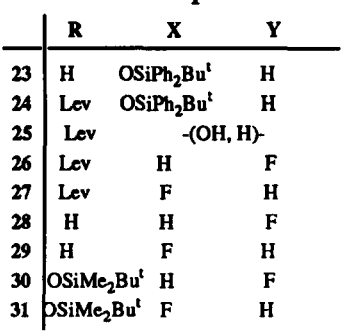
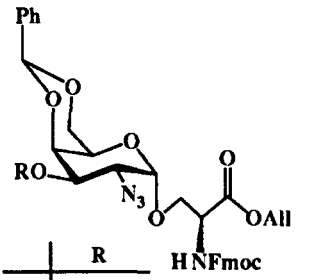
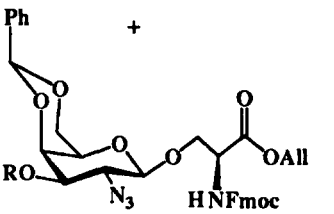


| | R | X | Y |
|---|---|---|---|
| 23 | H | $OSiPh_2Bu^t$ | H |
| 24 | Lev | $OSiPh_2Bu^t$ | H |
| 25 | Lev | -(OH, H)- | |
| 26 | Lev | H | F |
| 27 | Lev | F | H |
| 28 | H | H | F |
| 29 | H | F | H |
| 30 | $OSiMe_2Bu^t$ | H | F |
| 31 | $OSiMe_2Bu^t$ | F | H |



| | R |
|---|---|
| 33 | Lev |
| 35 | $SiMe_2Bu^t$ |
| 37 | H |



| | R |
|---|---|
| 34 | Lev |
| 36 | $SiMe_2Bu^t$ |

Scheme 4.

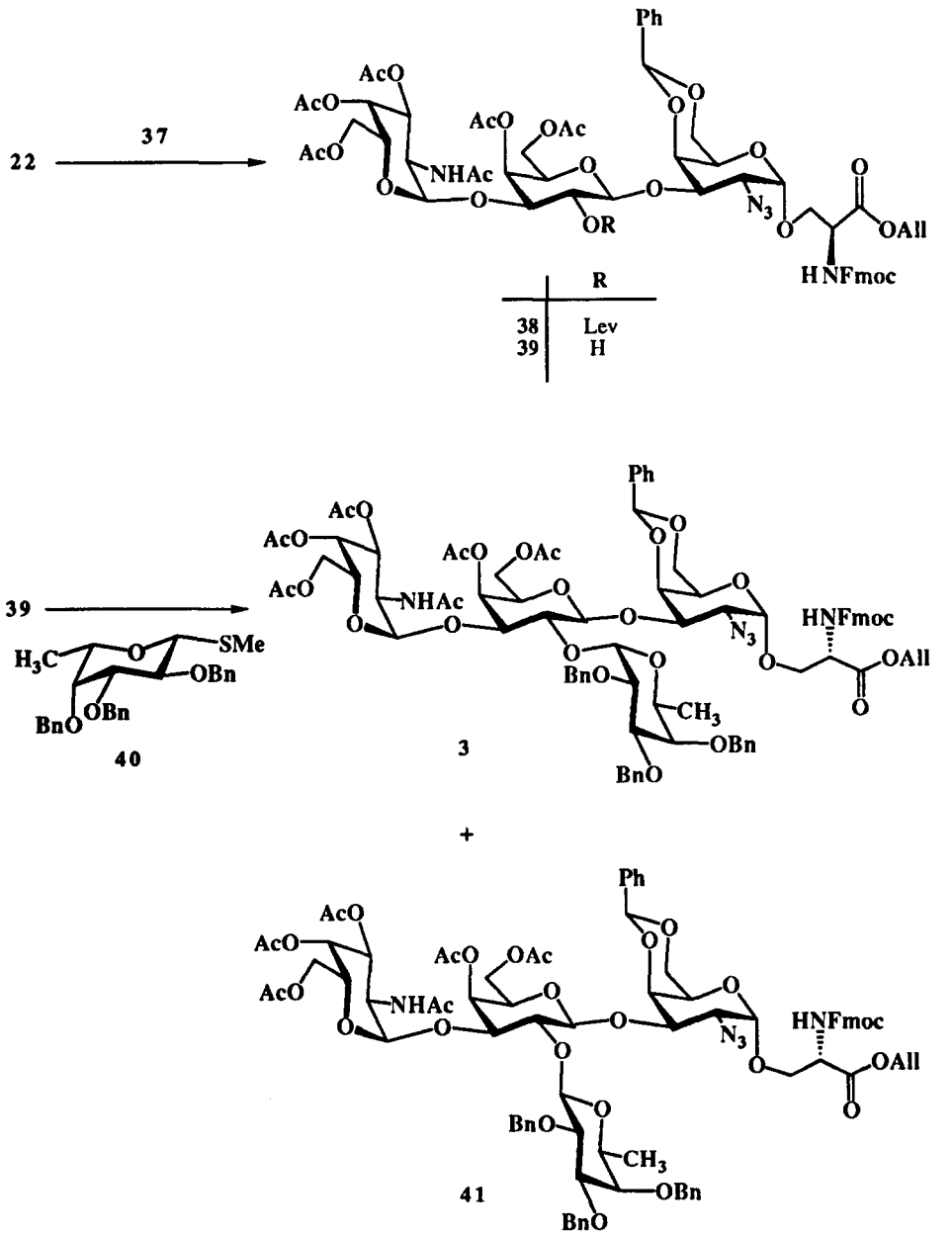
route was essentially performing the latter exchange of a benzylidene group for two acetate groups prior to azido reduction. Thus **16** was converted into the diol **19** (84%) with 80% aqueous acetic acid at 60°C, then **19** was acetylated using acetic anhydride

and pyridine to give **20** in 96% yield. Reduction of **20** to a free amine using propanedithiol, triethylamine in methanol [25], then acetylation with acetic anhydride and pyridine afforded compound **18** (65%). Reductive cleavage of the trichloroethyl ether group of **18** using zinc powder in THF–acetic acid [16] under the influence of ultrasound produced a 4:1 mixture of hemiacetal **21** (76.3%, $\delta_{C\text{-}1b}$ 96.26, $\delta_{C\text{-}1a\beta}$ 96.21, $\delta_{C\text{-}1a\alpha}$ 90.4). Subsequent treatment with $CCl_3CN$ and DBU in dichloromethane gave the $\alpha$-trichloroacetimidate **22** (99%, $\delta_H$ 8.683, s, $OCNHCCl_3$; $\delta_{H\text{-}1a}$ 6.585, d, $J$ 3.7 Hz).

For the synthesis of the acceptor corresponding to synthon **8**, the choice of a suitable donor would be a putative 2-amino-2-deoxy-D-galactose synthon, which carries an azido group as the latent amino function and a C-3 protective group compatible with both the donor reactivity and the allyl–Fmoc protective group combination. Thus synthons **26**, **27**, **30**, and **31** were chosen and obtained as follows. The known silylated **23** [12] was levulinoylated (→ **24**, 91%), desilylation with tetrabutylammonium fluoride–acetic acid in tetrahydrofuran [26] gave **25** (82%), which on treatment with diethylaminosulfur trifluoride [27] in THF, generated the easily separable fluoride anomers **26** and **27** in 53 and 47% yields, respectively. The $\alpha$-fluoride **26** was coupled with the L-serine derivative **32** [18], employing $Cp_2ZrCl_2$–silver perchlorate as a promoter [19] in dichloromethane to give the $\alpha$-glycoside **33** (46%, $\delta_{H\text{-}1}$ 5.033, $J$ 3.0 Hz; $\delta_{C\text{-}1}$ 99.9) and the $\beta$ isomer **34** (28%, $\delta_{C\text{-}1}$ 102.3). Use of the $\beta$-fluoride **27** in this glycosylation reaction gave a similar stereoselectivity of the $\alpha$-product **33** and its $\beta$ isomer **34** in 52 and 21% yields, respectively. The levulinoyl ester of **26** was selectively removed without hydrolysis of the anomeric fluoride by $NH_2NH_2$AcOH, 1:5 toluene–ethanol to give **28** in 99% yield. Silylation of **28** with *tert*-butylchlorodimethylsilane, imidazole, and DMAP in DMF, furnished the desired donor **30** in 91% yield. The corresponding conversions were carried out on the $\beta$-precursor **27**, thus delevulinoylation (→ **29**, 93%), then silylation gave the 3-*O*-silylated $\beta$-fluoride **31** (96%). As expected a silyl ether rather than a levulinoyl ester at the C-3 position of the fluoride donor induced a greater glycosylation efficiency in the $Cp_2ZrCl_2$–$AgClO_4$ promoted glycosylation of **30** (or **31**) with **32** mediated in $CH_2Cl_2$, affording **35** ($\delta_{H\text{-}1}$ 4.964, $J$ 3.4 Hz; $\delta_{C\text{-}1}$ 100.3; 85% from **30**, 86% from **31**) and **36** ($\delta_{H\text{-}1}$ 4.404, $J$ 7.6 Hz; 8% from **30**, 11% from **31**). To generate the requisite acceptor **37**, either compound **33** was mildly delevulinoylated (→ **37**, 93%, hydrazine acetate in 1:5 toluene–ethanol [28]), or compound **35** was desilylated (→ **37**, 72%) using neutral conditions ($NH_4F$, MeOH [29]).

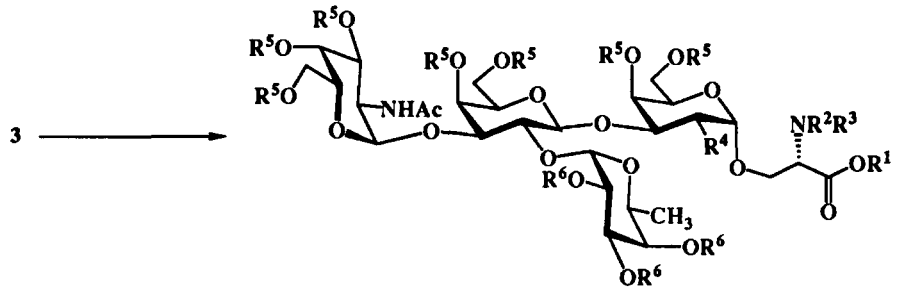
Having the disaccharide imidate **22** at our disposal and with 2-azido-$\alpha$-D-galactosyl serine derivative **37** as a synthetic equivalent of the synthon **9**, we proceeded with the crucial glycosylation of compound **22** and **37** in the presence of $Me_3SiOSO_2CF_3$–$CH_2Cl_2$ at −20°C (Scheme 5). By virtue of the neighbouring group participation of the C-2 levulinoyl group in compound **22**, the glycotriosylated $\alpha$-serine **38** (58%, $\delta_{C\text{-}1b}$ 102.10, $J_{C\text{-}H}$ 159.9 Hz) was the sole glycosylation product formed, which was subsequently converted to the acceptor **39** by delevulinoylation in the usual manner in 98% yield.

An initial attempt of coupling thioglycoside **40** [30] to acceptor **39** using methyl triflate as a promoter in ethereal solvent [10:1 $Et_2O$–$(CH_2Cl)_2$] at −20°C generated the $\alpha$-fucosylated product; however, such conditions were unyielding in terms of stereocontrol and coupling efficiency, viz., yields of compound **3** and the $\beta$ isomer **41** were 39 and 24%, respectively. However, when the promoter system $AgOSO_2CF_3$–$CuBr_2$–

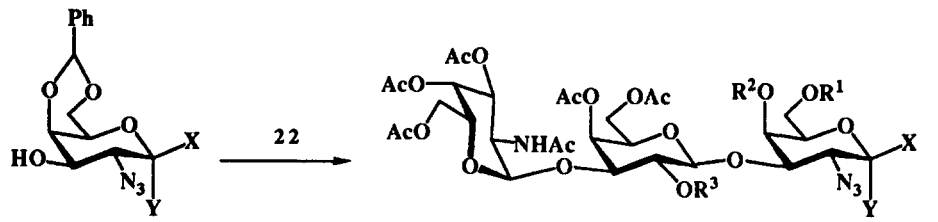



Scheme 5.

$^{n}Bu_4NBr$ [31] in 16:16:1.8 equivalents, respectively, was used to couple donor **40** to acceptor **39** (**40** was reacted with **39** in 10:1 equivalents, respectively) in 5:1 $(CH_2Cl)_2$–toluene at room temperature, it generated **3** and the $\beta$ isomer **41** in 58 and 14% yields,



| | R¹ | R² | R³ | R⁴ | R⁵ | R⁶ |
|---|---|---|---|---|---|---|
| 42 | All | H | Fmoc | $N_3$ | Ac | Bn |
| 43 | All | H | Fmoc | NHAc | Ac | Bn |
| 44 | H | H | Fmoc | NHAc | Ac | Bn |
| 45 | H | H | H | NHAc | H | Bn |
| 46 | H | Me | Me | NHAc | H | H |



| | X | Y |
|---|---|---|
| 47 | OAll | H |
| 48 | H | $OC_6H_4OMe$ |

| | X | Y | R¹ | R² | R³ |
|---|---|---|---|---|---|
| 49 | OAll | H | -(PhCH)- | | Lev |
| 50 | H | $OC_6H_4OMe$ | -(PhCH)- | | Lev |
| 51 | OAll | H | -(PhCH)- | | H |
| 52 | OAll | H | -(PhCH)- | | Ac |
| 53 | OAll | H | Ac | Ac | Lev |
| 54 | -(OH,H)- | | Ac | Ac | Lev |
| 55 | H | Br | Ac | Ac | Lev |

Scheme 6.

respectively. Discrimination of fucosyl proton signals against protons of other sugar units in compounds **3** and **41** were made possible by conducting $^1$H NMR homonuclear Hartman–Hahn experiments [32]. Thus **3** had a doublet at $\delta$ 5.438 ($J$ 3.7 Hz) corresponding to H-1d and **41** possessed a corresponding doublet at $\delta$ 4.773 ($J$ 7.7 Hz).

Since construction of the requisite tetraosyl serine unit **3** was accomplished, we proceeded with the deblocking of this fully protected derivative. Heating compound **3** in the presence of 80% aqueous acetic acid at 60°C cleaved the benzylidene group and acetylation in the usual manner afforded **42** in 87% yield (Scheme 6). Reduction of the azido group of **42** and subsequent acetylation of the corresponding amino compound to

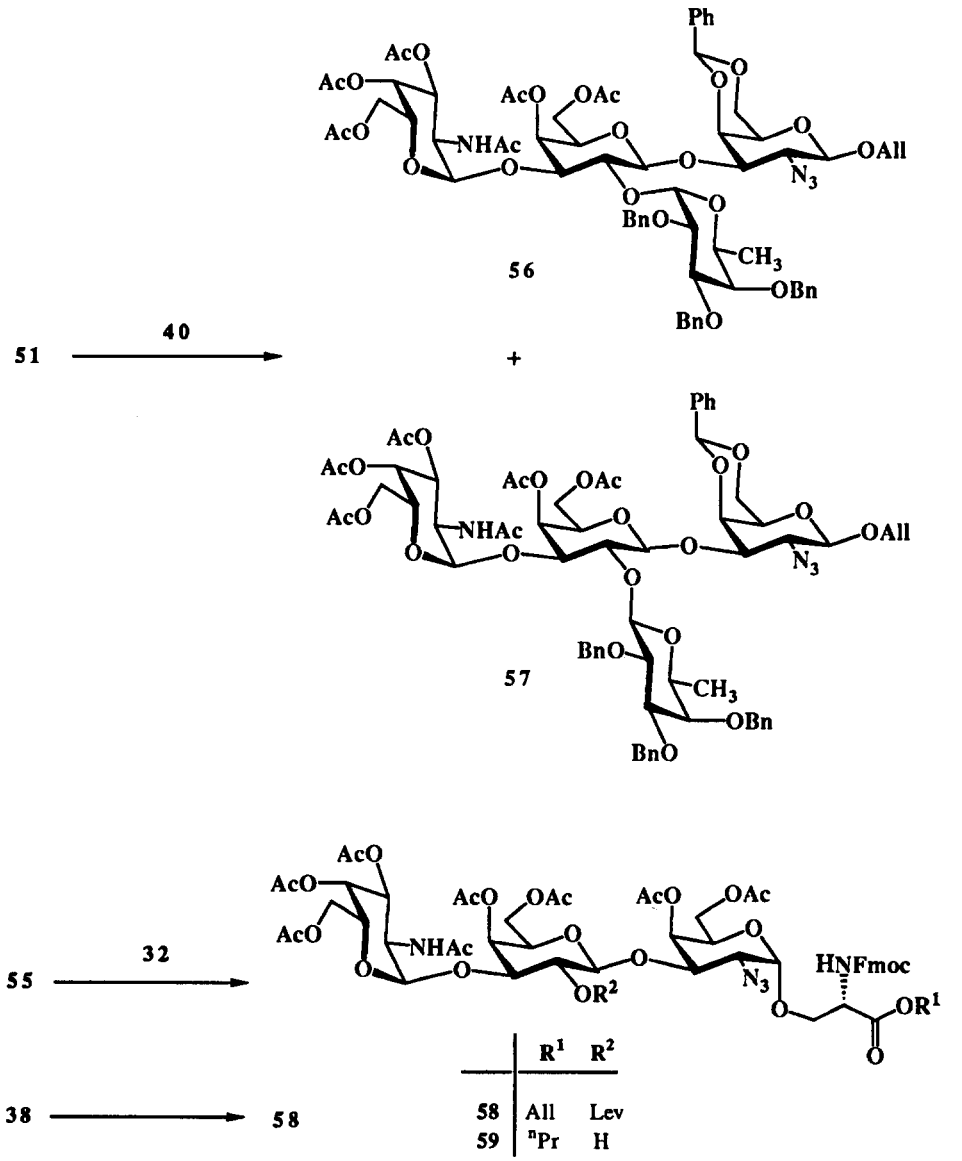
generate the diacetamide **43** was achieved in 97% yield in a one-pot reaction using thioacetic acid–pyridine–$CH_2Cl_2$. A $Pd[PPh_3]_4$–PhNHMe-mediated deallylation [18] of **43** in THF produced the free acid (→ **44**, 74%), which upon treatment with N NaOH–MeOH, underwent a facile tandem deacetylation–Fmoc carbamate cleavage affording **45** in 95% yield. In a model reaction, the β-fucosyl analogue of **45** was fully hydrogenolyzed employing 10% Pd–C, 12:3:2 EtOAc–EtOH–$H_2O$ [33] to produce the β-fucosyl analogue of **2** [1]; however, such conditions were unyielding in the case of converting **45** to **2**. Hydrogenolysis of **45** using 20% $Pd(OH)_2$–C as the catalyst in 80% aqueous methanol completely deblocked the fucosyl unit after 5 days; however, concomitant dimethylation of the free amino terminus, perhaps due to the presence of a trace amount [34] of HCHO in the reaction medium, was also observed to give compound **46**. The $^1$H NMR spectrum of **46** confirmed its structure when compared with the NMR data reported for the related alditol isolated from a natural source [9].

The final stage of this work was to investigate other possible synthetic routes towards producing a protected tetraosyl serine derivative (compound **42**, for example) as an alternative to the routes A and B discussed hitherto. In particular the introduction of the serine aglycon at a later stage of synthesis but prior to fucosylation would be one such approach. Thus $BF_3 \cdot Et_2O$-promoted glycosylation of **22** with **47** in dichloroethane according to the method of Schmidt [35] afforded the trisaccharide **49** ($\delta_{H\text{-}1b}$ 4.788, d, $J$ 7.9 Hz) with high efficiency (93% yield). However, interestingly, a similar trisaccharide **50** ($\delta_{H\text{-}1b}$ 4.830, d, $J$ 7.9 Hz) could be synthesized from acceptor **48**, again with trichloroacetimidate **22** using Schmidt methodology, but with a significantly lower yield (28%). Then delevulinoylation of **49** using hydrazine acetate in DMF (→ **51**, 84%) and subsequent conventional acetylation (→ **52**, 96%) confirmed this trisaccharide structure ($\delta_{H\text{-}1b}$ 4.753, d, $J$ 7.9 Hz).

From the synthetic study of route A, it was realised at this juncture that, compared to our previous encounter of $MeOSO_2CF_3$-promoted fucosylation towards the trisaccharide serine acceptor **39**, coupling of methyl thiofucoside **40** to acceptor **51** using methyl triflate as promoter proceeded with a higher stereoselectivity, furnishing the α-fucosylated tetrasaccharide **56** ($\delta_{H\text{-}2d}$ 4.118, dd, $J$ 4.0 Hz, $J$ 10.1 Hz) and the β isomer **57** ($\delta_{H\text{-}1d}$ 4.649, d, $J$ 7.3 Hz) in 72 and 8%, respectively (Scheme 7). A tentative explanation for the improvement in stereoselectivity of the latter fucosylation over the former one may be that the steric constraint against the α-face of the approaching fucosyl donor from the acceptor **39** during $MeOSO_2CF_3$-promoted fucosylation may be greater than that of acceptor **51**.

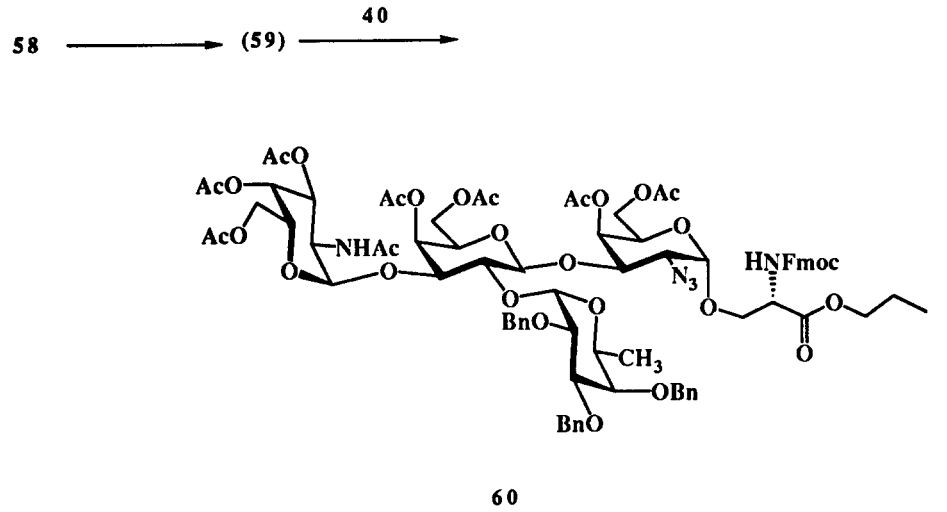
Now with the trisaccharide **49** in hand, to complete the synthesis of **42** we proceeded with the following synthetic steps. Replacement of the benzylidene group of **49** with diacetate protection was quantitatively carried out in the usual manner to afford **53**. Conversion of **53** into bromide **55** was carried out via quantitative deallylation to give the hemiacetal **54** ($PdCl_2$, NaOAc, 95% AcOH–$H_2O$ [36]), then treatment with $CBr_4$,

[1] The structure of the β-fucosyl isomer was elucidated by comparison of its $^1$H NMR spectral data with that of the alditol equivalent of **2** given in [9]. In any case the spectrum showed complete disappearance of all aromatic signals.




Scheme 7.

HMPT, and THF [37], 0–25°C, gave **55**. Due to the inherent instability of the glycosyl bromide, purification by silica gel chromatography caused significant loss of this material. Thus, instead crude **55** was directly coupled to the serine derivative **32** in the presence of $Ag_2CO_3$–$AgClO_4$ [38] in toluene–$CH_2Cl_2$ at room temperature to give **58** ($\delta_{H\text{-}1a}$ 4.916, d, $J$ 3.4 Hz) in 12.3% overall yield from compound **53**. As a means of confirming **38**, the latter quantitatively underwent debenzylidenation and subsequent




60

Scheme 8.

acetylation in the usual manner to afford a sample that was spectroscopically identical in all respects to a sample of **58** which had been derived from **55**. Delevulinoylation of **58** (Scheme 8) in the usual manner afforded acceptor **59**, and $AgOSO_2CF_3$–$CuBr_2$–$^nBu_4NBr$-promoted coupling of thiofucoside **40** to **59**, according to the previous procedure, yielded in 39% yield from **59**, the glycotetraosyl serine **60** ($\delta_{H\text{-}1d}$ 5.439, d, $J$ 3.7 Hz). Compound **60** had, however, undergone full saturation of the allylic double bond presumably during levulinoyl deprotection that required a longer subjection to hydrazine acetate. Nevertheless, confirmation that a serine propyl ester analogue of **42**, compound **60**, had been obtained came from NMR spectral data, whereby the resonances and splitting patterns of H-3a, H-4a, H-4b, H-1c, H-4c, H-4d, and H-1d were virtually the same for both **42** and **60**.

In conclusion, the $^1H$ NMR spectrum of **3** confirmed the structure when compared with that reported for the related alditol isolated from human blood A ovarian mucin [9]. Further support that **58** was the structure as assigned was provided by arriving at the latter via either intermediates **38** or **55**, and subsequently the tetraosyl serine derivative **60** was derived from **55**. Moreover, **3** was synthesized, in the main part of this work, in a stereocontrolled manner utilizing the synthons **8** and **9**.

## 3. Experimental

*General.*—Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with a Jasco DIP-370 polarimeter, for solutions in $CHCl_3$, unless noted otherwise. Silica gel chromatography was performed on Wako Gel C-300 (200–300 mesh), unless indicated otherwise. Thin-layer chromatography (TLC), high-performance (HP)TLC, and preparative TLC

were performed on Silica Gel 60 $F_{254}$ (E. Merck). NMR spectra were recorded with Jeol GX500 [$^1$H (500 MHz)], Jeol JNM-EX270 [$^1$H (270 MHz)], or FX90Q [$^{13}$C (22.50 MHz)] spectrometers. The values of $\delta_C$ and $\delta_H$ are recorded in ppm downfield from the signal for internal $Me_4Si$, for solutions in $CDCl_3$, unless stated otherwise, and for solutions in $D_2O$, in ppm downfield from the signal for $Me_4Si$, by reference to internal $Me_2CO$ (2.225 ppm). FAB-mass spectra were obtained with a Jeol HX 110 (HF) mass spectrometer, using *m*-nitrobenzylalcohol as the matrix. Molecular sieves were purchased from Nakarai Chemicals. Peroxide impurities in tetrahydrofuran were removed by passing it down a column of basic alumina, dried by refluxing over calcium hydride under nitrogen, and distilled prior to immediate use. Dichloromethane and dichloroethane were dried by refluxing over $P_2O_5$, distilled and then stored over 4A molecular sieves. Anhydrous pyridine was obtained by refluxing in the presence of barium oxide, fractionally distilling under a dry atmosphere, and storing over KOH pellets. All other reagents were used, unless noted otherwise, as commercially received. Yields given in glycosylation experiments are based on consumption of either donor or acceptor, whichever was the limiting material, unless stated otherwise.

*2,2,2-Trichloroethyl 4,6-O-benzylidene-β-D-galactopyranoside* (**13**).—2,2,2-Trichloroethyl-β-D-galactopyranoside [25] **10** (3.91g, 12.55 mmol), suspended in acetonitrile (60 mL), was dissolved upon addition of benzaldehyde dimethylacetal (4.20g, 27.6 mmol) at room temperature. After addition of *p*-toluenesulfonic acid monohydrate (*p*-TsOH · $H_2O$, 115 mg), the solution was left to stir for 1 h at 20°C, and then it was neutralized with $Et_3N$ (pH 8–9) and concentrated in vacuo. The residue was extracted with EtOAc, and the extract was washed with water, brine, and dried ($MgSO_4$). Reconcentrating in vacuo, the product was recrystallized from toluene, concentrating the mother liquor and then trituration with petroleum ether gave a further crop of product. The total yield was 4.86 g (97%); mp 134–135°C (prism, toluene); $[\alpha]_D$ −39.8° (*c* 0.50), $R_f$ 0.23 in 1:1 EtOAc–toluene. NMR data: $\delta_H$ 7.51–7.36 (m, 5 H, Ph), 5.570 (s, 1 H, PhCH), 4.621 (d, 1 H, *J* 7.6 Hz, H-1), 4.517, and 4.190 (2d, 2 H, *J* 11.2 Hz, $CH_2CCl_3$), 4.344 (dd, 1 H, *J* 1.6, 12.5 Hz, H-6), 4.239 (dd, 1 H, *J* 1.0, 3.8 Hz, H-4), 4.104 (dd, 1 H, *J* 1.9, 12.7 Hz, H-6′), 3.896 (dd, 1 H, *J* 7.6, 9.5 Hz, H-2), 3.740 (dd, 1 H, *J* 3.9, 9.5 Hz, H-3) 3.525 (d, 1 H, *J* 1.3 Hz, H-5), 2.599 (br s, 2 H, OH). Anal. Calcd for $C_{15}H_{17}Cl_3O_6$: C, 45.08; H, 4.29. Found: C, 45.19; H, 4.21.

*2,2,2-Trichloroethyl O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-(1 → 3)-4,6-O-benzylidene-β-D-galactopyranoside* (**14**).—A mixture of compound **13** (1.50 g, 3.75 mmol), the β-imidate **11** (2.07 g, 4.36 mmol), and powdered 4A molecular sieves (1.20 g) in $CH_2Cl_2$ (5 mL) at room temperature was stirred for 30 min under Ar. The mixture was cooled to −20°C, a solution of $Me_3SiOSO_2CF_3$ (28.5 μL, 157 μmol) in 8 mL of $CH_2Cl_2$ was added, and the mixture was left to stir for 3 h at −20°C. The mixture was neutralized with satd aq $NaHCO_3$, diluted with $CHCl_3$, and filtered through a bed of Celite. The filtrate was successively washed with aq $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated to give a residue that was chromatographed on silica gel in 1:1 EtOAc–hexane to give 2.06 g, 77.0% of product **14** (based on **13**), which was recrystallized from $Et_2O$–petroleum ether; mp 108–109°C; $[\alpha]_D^{18}$ +72.7° (*c* 1.22); $R_f$ 0.17 in 1:1 hexane–EtOAc. NMR data: $\delta_H$ 7.53–7.33 (m, 5 H, Ph), 5.587 (s, 1 H, PhCH), 5.476 (dd, 1 H, *J* 3.0 Hz, H-4b) 5.444 (dd, 1 H, *J* 11.0 Hz, H-3b), 5.243 (d, 1

H, *J* 3.4 Hz, H-1b), 4.633 (d, 1 H, *J* 7.6 Hz, H-1a) 4.500 and 4.185 (2 d, 2 H, $J_{gem}$ 11.9 Hz, $CH_2CCl_3$), 4.370 (dd, 1 H, *J* 12.5 Hz, H-6a), 4.331 (d, 1 H, *J* 3.4 Hz, H-4a), 4.17–4.06 (m, 3 H, H-5b, H-6b, and H-6'b), 4.008 (dd, 1 H, *J* 11.3 Hz, H-2a), 3.810 (dd, 1 H, *J* 9.5 Hz, H-3a), 3.632 (dd, 1 H, *J* 3.7, 11.0 Hz, H-2b), 3.490 (br d, 1 H, *J* 0.9 Hz, H-5a), 2.957 (br s, 1 H, OH) 2.134, 2.050, 2.040 (3 s, 9 H, 3Ac). Anal. Calcd for $C_{27}H_{32}Cl_3N_3O_{13}$: C, 45.49; H, 4.52; N, 5.89. Found: C, 45.20; H, 4.57; N, 6.20.

*2,2,2-Trichloroethyl* O-*(3,4,6-tri*-O-*acetyl-2-azido-2-deoxy-α*-D-*galactopyranosyl)-(1 → 3)-2*-O-*acetyl-4,6*-O-*benzylidene-β*-D-*galactopyranoside* (**15**).—Compound **14** (13 mg, 0.018 mmol) was dissolved in pyridine (0.8 mL) and $Ac_2O$ (0.6 mL). The solution was stirred for 24 h at room temperature and then coevaporated with toluene in vacuo. The residue was chromatographed over silica gel in 40:30:1 EtOAc–hexane–$Et_3N$, to give **15** (13.3 mg, 97%); $[\alpha]_{D17}$ +83.3° (*c* 0.30); $R_f$ 0.30 (4:3 EtOAc–hexane). NMR data: $\delta_H$ ($C_6D_6$) 7.74–7.72 and 7.20–7.13 (m, 5 H, Ph), 5.701 (dd, 1 H, *J* 7.9, 10.1 Hz, H-2a), 5.662 (dd, 1 H, *J* 3.4, 11.3 Hz, H-3b), 5.612 (d, 1 H, *J* 3.1 Hz, H-4b), 5.341 (s, 1 H, PhCH), 4.970 (d, 1 H, *J* 3.4 Hz, H-1b), 4.508 (d, 1 H, *J* 7.9 Hz, H-1a), 4.245 and 4.020 (2 d, 2 H, *J* 11.9 Hz, $CH_2CCl_3$), 3.859 (d, 1 H, *J* 3.1 Hz, H-4a), 3.693 (dd, 1 H, *J* 3.4, 11.3 Hz, H-2b), 3.589 (dd, 1 H, *J* 3.7, 10.1 Hz, H-3a), 1.971, 1.723, 1.721, and 1.649 (4 s, 12 H, 4 Ac). Anal. Calcd for $C_{29}H_{34}Cl_3N_3O_{14}$: C, 46.14; H, 4.50; N, 5.57. Found: C, 46.52; H, 4.52; N, 5.24.

*2,2,2-Trichloroethyl* O-*(3,4,6-tri*-O-*acetyl-2-azido-2-deoxy-α*-D-*galactopyranosyl)-(1 → 3)-4,6*-O-*benzylidene-2*-O-*levulinoyl-β*-D-*galactopyranoside* (**16**).—A pre-dried sample of compound **14** (4.55 g, 6.38 mmol) was dissolved in dry pyridine (24 mL) and levulinic anhydride (3.41 g, 21.7 mmol) and DMAP (45 mg) were added, and the solution was stirred for 48 h at ambient temperature under Ar. Evaporation of the solution gave a residue that was chromatographed on silica gel with 60:40:1 EtOAc–hexane–$Et_3N$ to give **16** (4.42g, 85.5%); mp 182–183°C (recrystallized from EtOAc–hexane); $[\alpha]_D^{20}$ +72.5° (*c* 0.73); $R_f$ 0.27 (4:3 EtOAc–hexane). NMR data: $\delta_H$ 7.57–7.33 (m, 5 H, Ph), 5.602 (br s, 2 H, PhCH and H-4b), 5.473 (dd, 1 H, *J* 7.9, 10.0 Hz, H-2a), 5.332 (dd, 1 H, *J* 3.4, 11.3 Hz, H-3b), 5.208 (d, 1 H, *J* 3.7 Hz, H-1b), 4.819 (d, 1 H, *J* 7.9 Hz, H-1a), 4.486 (t, 1 H, *J* 6.4 Hz, H-5b), 4.407 and 4.196 (2 d, 2 H, $J_{gem}$ 12.2 Hz, $CH_2CCl_3$), 3.983 (dd, 1 H, *J* 3.4, 10.0 Hz, H-3a) 3.554 (dd, 1 H, *J* 3.7, 11.3 Hz, H-2b), 3.526 (br s, 1 H, H-5a), 2.98–2.93, 2.72–2.60, and 2.53–2.48 (m, 4 H, $CH_2CH_2$ of Lev), 2.196, 2.132, 2.039, and 2.007 (4 s, 12 H, 3 Ac and $COCH_3$ of Lev). Anal. Calcd for $C_{32}H_{38}Cl_3N_3O_{15}$: C, 47.39; H, 4.72; N, 5.18. Found: C, 47.16; H, 4.70; 5.09.

*2,2,2-Trichloroethyl* O-*(2-acetamido-3,4,6-tri*-O-*acetyl-2-deoxy-α*-D-*galactopyranosyl)-(1 → 3)-4,6*-O-*benzylidene-2*-O-*levulinoyl-β*-D-*galactopyranoside* (**17**).—Azido compound **16** (4.60g, 5.67 mmol) was dissolved in $CH_2Cl_2$ (15 mL), freshly distilled thioacetic acid (32.7 mL) was added, and the solution was left to stir for 4 days at ambient temperature. The solution was then reduced to a syrup by coevaporation with toluene in vacuo. Column chromatography of the syrup over silica gel (300 g) in 20:18:1:1 toluene–EtOAc–MeOH–$Et_3N$, afforded **17** (3.99 g, 85%); mp 225–226°C (recrystallized from 1:10 EtOAc–petroleum ether); $[\alpha]_D^{19}$ +61.4° (*c* 0.50); $R_f$ 0.17 (20:20:1 toluene–EtOAc–MeOH). NMR data: $\delta_H$ 7.49–7.35 (m, 5 H, Ph), 5.741 (d, 1 H, *J* 9.5 Hz, NHAc), 5.548 (d, 1 H, *J* 3.3 Hz, H-4b), 5.488 (s, 1 H, PhCH), 5.455 (dd,

1 H, *J* 8.0, 10.0 Hz, H-2a), 5.101 (d, 1 H, *J* 4.0 Hz, H-1b), 4.842 (d, 1 H, *J* 8.0 Hz, H-1a), 4.545 (ddd, 1 H, *J* 3.7, 9.5, 11.0 Hz, H-2b), 4.439 and 4.216 (2 d, 2 H, $J_{gem}$ 12.4 Hz, $CH_2CCl_3$), 4.106 (dd, 1 H, *J* 1.5, 12.4 Hz, H-6a), 3.964 (dd, 1 H, *J* 3.3, 10.0 Hz, H-3a), 3.518 (br s, 1 H, H-5a), 3.06–2.96 and 2.77–2.67 (2 m, 2 H, $CH_2CH_2$ of Lev), 2.63–2.57 and 2.49–2.44 (2 dt, 2 H, $J_{vic}$ 5.5 Hz, $CH_2CH_2$ of Lev), 2.175, 2.153, 2.036, 1.916, 1.825 (5 s, 15 H, 4 Ac, $COCH_3$ of Lev and NHAc). Anal. Calcd for $C_{34}H_{42}Cl_3NO_{16} \cdot H_2O$: C, 48.33; H, 5.25; N, 2.00. Found: C, 48.60; H, 5.03; N, 1.74.

*2,2,2-Trichloroethyl O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-galactopyranosyl)-(1 → 3)-4,6-di-O-acetyl-2-O-levulinoyl-β-D-galactopyranoside* (**18**).—Compound **17** (116 mg, 140 μmol) was dissolved in $CH_2Cl_2$ (0.5 mL). At 0°C, aq 80% $CF_3COOH$ (4.8 mL) was added, the mixture was stirred for 2 h at 0°C and then overnight at room temperature. Coevaporation of the trifluoroacetic acid by addition of toluene, followed by neutralization at 0°C with $Et_3N$ and concentration in vacuo, gave a dark syrup. To the latter was added acetic anhydride (20 mL), pyridine (20 mL), and DMAP (5 mg), the solution was stirred at room temperature for 12 h, then diluted with EtOAc–$Et_2O$, washed with water, aq $NaHCO_3$ and brine, dried ($Na_2SO_4$), and concentrated in vacuo. Flash chromatography of the residue on silica gel (130 g) in 10:10:1 toluene–EtOAc–MeOH furnished **18** (122 mg, quant); $[\alpha]_D^{18}$ +36.7° (*c* 0.40); $R_f$ 0.20 in 20:20:1 EtOAc–toluene–MeOH. NMR data: $\delta_H$ 6.015 (d, 1 H, *J* 9.5 Hz, NH), 5.522 and 5.432 (2 d, 2 H, *J* 2.1 and 2.4 Hz, H-4a and H-4b), 5.263 (dd, 1 H, *J* 7.6, 10.0 Hz, H-2a), 5.102 (d, 1 H, *J* 4.0 Hz, H-1b), 5.090 (dd, 1 H, *J* 3.2, 11.5 Hz, H-3b), 4.767 (d, 1 H, *J* 7.6 Hz, H-1a), 4.613 (ddd, 1 H, *J* 3.7, 9.8, 11.3 Hz, H-2b), 4.388 and 4.167 (2 d, 2 H, *J* 11.9 and 12.2 Hz, $CH_2Cl_3$), 4.042 (dd, 1 H, *J* 6.4, 11.0 Hz, H-6a), 3.976 (dd, 1 H, *J* 3.4, 10.0 Hz, H-3a), 3.888 (dt, 1 H, *J* 0.9, 6.7 Hz, H-5a), 2.952, 2.664, and 2.510 (3 m, 4 H, $CH_2CH_2$ of Lev), 2.189, 2.165, 2.153, 2.060, 2.030, 1.965, and 1.956 (7 s, 21 H, 6 Ac and $COCH_3$ of Lev). Anal. Calcd for $C_{31}H_{42}Cl_3NO_{18}$: C, 45.24; H, 5.14; N, 1.70. Found: C, 44.88; H, 5.13; N, 1.68.

*2,2,2-Trichloroethyl O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-(1 → 3)-2-O-levulinoyl-β-D-galactopyranoside* (**19**).—Compound **16** (4.34 g, 5.35 mmol) was dissolved in AcOH (64 mL) and $H_2O$ (16 mL). The solution was stirred for 5 h at 60°C and evaporated in vacuo. The residue was chromatographed on silica gel in 4:1 EtOAc–hexane, to give **19** (3.25 g, 84%); $[\alpha]_D^{17}$ +41.3° (*c* 0.15); $R_f$ 0.42 in 4:1 EtOAc–hexane. NMR data: $\delta_H$ 5.601 (d, 1 H, *J* 3.4 Hz, H-4b), 5.332 (dd, 1 H, *J* 7.9, 9.8 Hz, H-2a), 5.302 (dd, 1 H, *J* 3.4, 11.0 Hz, H-3b), 5.080 (d, 1 H, *J* 3.7 Hz, H-1b), 4.746 (d, 1 H, *J* 7.9 Hz, H-1a), 4.506 (t, 1 H, *J* 6.3 Hz, H-5b), 4.387 and 4.182 (2 d, 2 H, *J* 12.2 Hz, $CH_2CCl_3$), 4.204 (dd, 1 H, *J* 6.7, 11.3 Hz, H-6b), 4.142 (d, 1 H, *J* 3.4 Hz, H-4a), 4.118 (dd, 1 H, *J* 5.8, 11.3 Hz, H-6b), 4.026 (dd, 1 H, *J* 6.4, 11.6 Hz, H-6′a), 3.958 (dd, 1 H, *J* 3.7, 11.0 Hz, H-2b), 3.910 (dd, 1 H, *J* 5.2, 11.6 Hz, H-6a), 3.867 (dd, 1 H, *J* 3.4, 9.8 Hz, H-3a), 3.624 (t, 1 H, *J* 5.8 Hz, H-5a), 2.962, 2.720, 2.594, and 2.473 (4 m, 4 H, $CH_2CH_2$ of Lev), 2.203, 2.161, 2.035, 2.034 (4s, 12 H, 3 Ac and $COCH_3$ of Lev). Anal. Calcd for $C_{25}H_{34}Cl_3N_3O_{15}$: C, 41.54; H, 4.74; N, 5.81. Found: C, 41.45; H, 4.72; N, 5.65.

*2,2,2-Trichloroethyl O-(3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-(1 → 3)-4,6-di-O-acetyl-2-O-levulinoyl-β-D-galactopyranoside* (**20**).—Compound **19** (2.09 g, 2.89 mmol) was dissolved in pyridine (40 mL) and $Ac_2O$ (25 mL). The solution was

stirred for 12 h at room temperature and evaporated in vacuo. The residue was chromatographed on silica gel in 3:2 toluene–EtOAc, to give **20** (2.24g, 96%); mp 149–150°C (MeOH); $[\alpha]_D^{18}$ +59.7° (*c* 0.72); $R_f$ 0.36 in 3:2 toluene–EtOAc. NMR data: $\delta_H$ 5.609 and 5.547 (2 d, 2 H, *J* 3.1 and 3.4 Hz, H-4a and H-4b), 5.331 (dd, 1 H, *J* 7.9, 10.1 Hz, H-2a), 5.220 (d, 1 H, *J* 3.7 Hz, H-1b), 5.200 (dd, 1 H, *J* 3.7, 11.0 Hz, H-3b), 4.773 (d, 1 H, *J* 7.9 Hz, H-1a), 4.441 (t, 1 H, *J* 6.3 Hz, H-5b), 4.394 and 4.168 (2 d, 2 H, *J* 12.2 Hz, $CH_2Cl_3$), 3.993 (dd, 1 H, *J* 3.4, 10.1 Hz, H-3a), 3.894 (t, 1 H, *J* 6.7 Hz, H-5a), 3.655 (dd, 1 H, *J* 3.7, 11.0 Hz, H-2b), 3.002, 2.641, and 2.485 (3 m, 4 H, $CH_2CH_2$ of Lev), 2.203, 2.203, 2.147, 2.085, 2.041, 2.013 (6 s, 18 H, 5 Ac and $COCH_3$ of Lev). Anal. Calcd for $C_{29}H_{38}Cl_3N_3O_{17}$: C, 43.16; H, 4.75; N, 5.21. Found: C, 42.97; H, 4.70; N, 5.18.

O-*(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-galactopyranosyl)-(1 → 3)-4,6-di-*O*-acetyl-2-*O*-levulinoyl-β-*D*-galactopyranose* (**21**).—To a stirred solution of **20** (95.9 mg, 116 μmol) in freshly distilled THF (3.2 mL) and AcOH (1.3 mL) at room temperature was added zinc powder (384 mg, 5.87 mmol, prior to use, washed with 2 N HCl, water, EtOH, and $Et_2O$, then dried in vacuo). The suspension was sonicated for 12 h, filtered through Celite, and the filtrate was evaporated in vacuo. The residue was extracted with EtOAc, washed with aq $NaHCO_3$ and brine, dried ($Na_2SO_4$), and evaporated in vacuo. Flash chromatography of the residue on silica gel (10 g) in 10:10:2 toluene–EtOAc–MeOH) afforded **21** (61.2 mg, 76.3%); $[\alpha]_D^{18}$ +86.9° (*c* 1.88); $R_f$ 0.32 and 0.28 in 10:10:2 toluene–EtOAc–MeOH. NMR data: $\delta_H$ 5.999 (d, 0.25 H, *J* 9.5 Hz, βNH), 5.892 (d, 0.75 H, *J* 9.8 Hz, αNH), 5.114 (d, 1 H, *J* 3.7 Hz, H-1b), 5.090 (d, 0.75 H, *J* 3.4 Hz, αH-1a), 4.672 (br d, 0.25 H, βH-1a), 4.629 (ddd, 1 H, *J* 3.4, 9.5, 11.3 Hz, H-2b), 2.828 (t, 2 H, OCOC$H_2$CH$_2$ of Lev), 2.580 (m, 2 H, OCOCH$_2$C$H_2$ of Lev), 2.189, 2.176, 2.158, 2.064, 2.048, 1.971, and 1.971 (7 s, 21 × 0.75 H, αAc and α$COCH_3$ of Lev); $\delta_C$ 96.3 (C-1b), 96.0 (C-1aβ), 90.4 (C-1aα). Anal. Calcd for $C_{29}H_{41}NO_{18}$: C, 50.36; H, 5.98; N, 2.03. Found: C, 50.19; H, 6.04; N, 2.02.

O-*(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-galactopyranosyl)-(1 → 3)-4,6-di-*O*-acetyl-2-*O*-levulinoyl-α-*D*-galactopyranosyl trichloroacetimidate* (**22**).—A mixture of **21** (193 mg, 280 μmol) and $CCl_3CN$ (138 μL, 1.41 mmol) in $CH_2Cl_2$ (2.3 mL) was cooled to 0°C with stirring under Ar, DBU (10.2 μL, 0.069 mmol) was added and stirring was continued at 0°C for 12 h. The mixture was directly chromatographed over silica gel (10 g) in 20:20:3 EtOAc–toluene–MeOH to give **22** (232 mg, 99.2%); $[\alpha]_D^{18}$ +104.6° (*c* 1.85); $R_f$ 0.36 in 20:20:3 EtOAc–toluene–MeOH. NMR data: $\delta_H$ 8.683 (s, 1 H, OCNHCCl$_3$), 6.585 (d, 1 H, *J* 3.7 Hz, H-1a), 5.886 (d, 1 H, *J* 9.8 Hz, NHAc), 5.538 and 5.419 (2 d, 2 H, *J* 2.8 and 2.2 Hz, H-4a and H-4b), 5.339 (dd, 1 H, *J* 3.7, 10.4 Hz, H-2a), 5.122 (d, 1 H, *J* 3.4 Hz, H-1b), 5.097 (dd, 1 H, *J* 3.4, 11.6 Hz, H-3b), 4.646 (ddd, 1 H, *J* 3.4, 9.8, 11.6 Hz, H-2b), 2.84, 2.72, 2.58, 2.47 (4 m, 4 H, $CH_2CH_2$ of Lev), 2.204, 2.162, 2.157, 2.020, 2.014, 1.980, and 1.974 (7 s, 21 H, 6Ac and $CH_3CO$ of Lev). Anal. Calcd for $C_{31}H_{41}Cl_3N_2O_8$; C, 44.54; H, 4.94; N, 3.35. Found: C, 44.58; H, 4.81; N, 3.09.

tert-*Butyldiphenylsilyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-levulinoyl-β-*D*-galactopyranoside* (**24**).—To a solution of **23** (2.28 g, 4.29 mmol) in pyridine (4 mL) was added a solution of levulinic anhydride [2.29 g, 14.57 mmol, dissolved in pyridine (12 mL)]. After addition of DMAP (30 mg), the solution was stirred for 12 h at room

temperature under Ar, the solution was then concentrated in vacuo and purified by flash chromatography on silica gel (200 g) in 7:3 hexane–EtOAc affording **24** (2.42 g, 3.89 mmol, 90.7%); $[\alpha]_D^{20}$ +32.0° (*c* 0.50); $R_f$ 0.30 in 7:3 hexane–EtOAc. NMR data: $\delta_H$ 7.80–7.70 (m, 2 H, Ph), 7.54–7.25 (m, 15 H, Ph), 5.435 (s, 1 H, PhCH), 4.612 (dd, 1 H, *J* 3.4, 10.7 Hz, H-3), 4.490 (d, 1 H, *J* 7.6 Hz, H-1), 4.164 (dd, 1 H, *J* 0.9, 3.7 Hz, H-4), 3.97--3.91 (m, 2 H, H-2, H-6b), 3.824 (dd, 1 H, *J* 1.8, 12.2 Hz, H-6′), 3.012 (d, 1 H, *J* 1.2 Hz, H-5), 2.75–2.72 and 2.65–2.62 (m, 4 H, $CH_2CH_2$ of Lev), 2.086 (s, 3 H, $CH_3CO$ of Lev), 1.134 (s, 9 H, $CH_3$ of $^t$Bu). Anal. Calcd for $C_{34}H_{39}N_3O_7Si$; C, 64.84; H, 6.24; N, 6.67. Found: C, 64.68; H, 6.22; N, 6.52.

*2-Azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-levulinoyl-*D*-galactopyranose* (**25**).—To a stirred mixture of **24** (2.26 g, 3.64 mmol) and AcOH (2.1 mL, 37.0 mmol) in tetrahydrofuran (50 mL) was added 1.0 M $^n$Bu$_4$NF–tetrahydrofuran (14.9 mL, 14.9 mmol) at 0°C. Stirring was continued with the temperature rising from 0°C to room temperature overnight. The mixture was then concentrated in vacuo, the residue was extracted with 1:1 ether–EtOAc, and the extract was washed with water, aq $NaHCO_3$ and brine, dried ($Na_2SO_4$), and concentrated in vacuo. Column chromatography of the residue on silica gel (200 g) with 3:2 toluene–EtOAc gave **25** (1.24 g, 81.4%); $[\alpha]_D^{23}$ +119.0° (*c* 0.5); $R_f$ 0.31 (3:2 toluene–EtOAc). NMR data: $\delta_H$ 7.70–7.18 (m, 5 H, Ph), 5.536 and 5.532 (2s, 1 H, $\alpha$ and $\beta$ PhC*H*), 5.465 (d, 0.83 H, *J* 3.3 Hz, $\alpha$H-1), 5.375 (dd, 0.83 H, *J* 3.4, 10.7 Hz, $\alpha$H-3), 4.769 (dd, 0.17 H, *J* 3.7, 11.0 Hz, $\beta$H-3), 4.632 (d, 0.17 H, *J* 7.9 Hz, $\beta$H-1), 4.436 (d, 0.83 H, *J* 2.4 Hz, $\alpha$H-4), 4.32–4.29 (m, 0.17 H, $\beta$H-4), 4.225 (dd, 1 H, *J* 1.5, 12.8 Hz, H-6), 4.054 (dd, 1 H, *J* 1.8, 10.4 Hz, H-6′), 4.006 (dd, 0.83 H, *J* 3.0, 10.7 Hz, $\alpha$H-2), 3.976 (d, 0.83 H, *J* 0.9 Hz, $\alpha$H-5), 3.856 (dd, 0.17 H, *J* 7.9, 10.7 Hz, $\beta$H-2), 2.78--2.66 (m, 4 H, C$H_2$C$H_2$ of Lev), 2.116 and 2.112 (2s, 3 H, $\alpha$ and $\beta CH_3CO$ of Lev). Anal. Calcd for $C_{18}H_{21}N_3O_7$: C, 55.24; H, 5.40; N, 10.74. Found: C, 55.35; H, 5.74; N, 10.81.

*2-Azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-levulinoyl-α-*D*-galactopyranosyl fluoride* **26** *and 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-levulinoyl-β-*D*-galactopyranosyl fluoride* **27**.—To a stirred solution of **25** (1.15 g, 2.75 mmol) in dry dichloromethane (20 mL) at 0°C was added diethylaminosulfur trifluoride (0.58 mL, 4.40 mmol). The mixture was stirred at room temperature for 30 min, MeOH (0.5 mL) was added, and the mixture was concentrated in vacuo. The residue was extracted with 1:1 ether–EtOAc, and the extract was washed with water and brine, dried ($Na_2SO_4$), and concentrated in vacuo. Column chromatography of the crude product on silica gel (100 g) with 7:3 toluene–EtOAc gave **26** (507 mg, 46.9%) and **27** (582 mg, 53.0%).

Compound **26** had $[\alpha]_D^{20}$ −136.4° (*c* 0.25); $R_f$ 0.43 (7:3 toluene–EtOAc). NMR data: $\delta_H$ 7.51–7.26 (m, 5 H, Ph), 5.804 (dd, 1 H, *J* 2.4, 52.8 Hz, H-1), 5.558 (s, 1 H, PhC*H*), 5.314 (dd, 1 H, *J* 3.4, 11.3 Hz, H-3), 4.498 (d, 1 H, *J* 2.4 Hz, H-4), 4.309 (dd, 1 H, *J* 1.5, 12.8 Hz, H-6), 4.064 (dd, 1 H, *J* 1.5, 9.4 Hz, H-6′), 4.041 (ddd, 1 H, *J* 2.4, 11.0, 52.8 Hz, H-2), 3.970 (br s, 1 H, H-5), 2.79–2.66 (m, 4 H, C$H_2$C$H_2$ of Lev), 2.123 (s, 3 H, $CH_3CO$ of Lev). Anal. Calcd for $C_{18}H_{20}FN_3O_6$; C, 54.96; H, 5.12; N, 10.68. Found: C, 55.06; H, 5.10; N, 10.30.

Compound **27** had $[\alpha]_D^{20}$ +133.2° (*c* 0.25), $R_f$ 0.30 (7:3 toluene–EtOAc). NMR data: $\delta_H$ 7.53–7.38 (m, 5 H, Ph) 5.535 (s, 1 H, PhC*H*), 5.127 (dd, 1 H, *J* 7.6, 52.5 Hz, H-1), 4.795 (ddd, 1 H, *J* 0.9, 3.4 and 11.0 Hz, H-3), 4.363 (dd, 1 H, *J* 1.8, 12.8 Hz,

H-6), 4.338 (t, 1 H, *J* 2.4 Hz, H-4), 4.08–4.02 (m, 2 H, H-2 and H-6′), 3.580 (br s, 1 H, H-5), 2.77–2.62 (m, 4 H, $CH_2CH_2$ of Lev), 2.110 (s, 3 H, $CH_3CO$ of Lev). Anal. Calcd for $C_{18}H_{20}FN_3O_6$; C, 54.96; H, 5.12; N, 10.68. Found: C, 54.78; H, 5.07; N, 10.51.

*2-Azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl fluoride* (**28**).—The α-fluoride **26** (1.40 g, 3.56 mmol) was dissolved in dry toluene (14 mL). To this solution, with stirring, was added dry ethanol (56 mL), followed by an addition of freshly prepared hydrazine acetate (1.64 g, 17.8 mmol) under Ar at room temperature. Stirring was continued for a further 30 min, diluted with EtOAc, washed with aq $NaHCO_3$, brine and dried ($Na_2SO_4$), concentrated in vacuo and purified by flash chromatography in 9:1 $CHCl_3$–THF, affording **28** (1.04 g, 99.9%); $[\alpha]_D^{25}$ +37.9° (*c* 0.73); $R_f$ 0.46 (9:1 $CHCl_3$–THF). NMR data: $\delta_H$ 7.50–7.39 (m, 5 H, Ph), 5.752 (dd, 1 H, *J* 2.4, 52.5 Hz, H-1), 5.603 (s, 1 H, PhC*H*), 4.360 (dd, 1 H, *J* 1.2, 3.6 Hz, H-4), 4.335 (dd, 1 H, *J* 1.8, 13.1 Hz, H-6), 4.099 (dd, 1 H, *J* 1.5, 12.8 Hz, H-6′), 3.964 (s, 1 H, H-5), 3.741 (m, 1 H, H-3), 3.685 (ddd, 1 H, *J* 2.4, 10.4, 25.6 Hz, H-2), 2.554 (br d, 1 H, *J* 10.0 Hz, OH). Anal. Calcd for $C_{13}H_{14}FN_3O_4$: C, 52.88; H, 4.78; N, 14.23. Found C, 53.19; H, 5.18; N, 13.99.

*2-Azido-4,6-O-benzylidene-2-deoxy-β-D-galactopyranosyl fluoride* (**29**).—Reaction of the β-fluoride **27** (1.02 g, 2.58 mmol) was carried out with hydrazine acetate (1.19 g, 12.9 mmol) in 4:1 EtOH–toluene (50 mL) as described in the preparation of **28** to afford **29** (790 mg, 93.4%); $[\alpha]_D^{23}$ +40.6° (*c* 0.5); $R_f$ 0.30 (9:1 $CHCl_3$–THF). NMR data: $\delta_H$ 7.52–7.50 (m, 2 H, H-2 and H-6 Ph of PhCH), 7.410–7.259 (m, 3 H, H-3,4 and 5 Ph of PhCH), 5.588 (s, 1 H, PhC*H*), 5.060 (dd, 1 H, *J* 7.6, 52.2 Hz, H-1), 4.393 (dd, 1 H, *J* 1.5, 12.5 Hz, H-6), 4.213 (m, 1 H, H-4), 4.103 (dt, 1 H, *J* 1.8, 3.7, 12.8 Hz, H-6′), 3.750 (ddd, 1 H, *J* 7.6, 10.4, 11.9 Hz, H-2), 3.574 (br s, 1 H, H-5), 2.614 (br d, 1 H, *J* 8.2 Hz, OH). Anal. Calcd for $C_{13}H_{14}FN_3O_4$: C, 52.88; H, 4.78; N, 14.23. Found: C, 53.04; H, 4.87; N, 13.83.

*2-Azido-4,6-O-benzylidene-3-O-tert-butyldimethylsilyl-2-deoxy-α-D-galactopyranosyl fluoride* (**30**).—The α-fluoride **28** (1.16 g, 3.56 mmol) was dissolved in DMF (7.4 mL), under Ar at room temperature, *tert*-butylchlorodimethylsilane (723 mg, 4.80 mmol), imidazole (701 mg, 10.3 mmol), and DMAP (10 mg) were added in that order to the stirred fluoride solution. The solution was left to stir overnight at room temperature, diluted with EtOAc–$Et_2O$, washed with water, brine, and dried ($Na_2SO_4$). Evaporation to a syrup in vacuo and flash chromatography on silica gel (12 g) in 9:1 toluene–THF gave **30** (1.44 g, 91.4%); $[\alpha]_D^{26}$ +99.2° (*c* 2.62, $CHCl_3$); $R_f$ 0.51 (9:1 $CHCl_3$–THF). NMR data: $\delta_H$ 7.50–7.34 (m, 5 H, Ph), 5.730 (dd, 1 H, *J* 2.4, 53.1 Hz, H-1), 5.543 (s, 1 H, PhC*H*), 4.309 (dd, 1 H, *J* 1.5, 12.8 Hz, H-6′), 3.877 (s, 1 H, H-5), 3.868 (ddd, 1 H, *J* 2.4, 9.5, 25.9 Hz, H-2), 0.926 (s, 9 H, $CH_3$ of $^tBu$), 0.184, 0.148 (2 s, 6 H, 2 $CH_3$ of TBDMS). Anal. Calcd for $C_{19}H_{28}FN_3O_4Si$: C, 55.72; H, 6.89; N, 10.26. Found: C, 55.54; H, 6.90; N, 10.06.

*2-Azido-4,6-O-benzylidene-3-O-tert-butyldimethylsilyl-2-deoxy-β-D-galactopyranosyl fluoride* (**31**).—Compound **29** (719 mg, 2.20 mmol) was dissolved in DMF (4.4 mL) and treated with *tert*-butylchlorodimethylsilane (431 mg, 2.86 mmol), imidazole (418 mg, 6.14 mmol), and DMAP (10 mg) in the manner as described in the preparation of **30** to produce **31** (932 mg, 96.1%); $[\alpha]_D$ +23.6° (*c* 0.50); $R_f$ 0.51 (3:1 toluene–EtOAc).

NMR data: $\delta_H$ 7.53–7.36 (m, 5 H, Ph), 5.541 (s, 1 H, PhCH), 5.058 (dd, 1 H, *J* 7.6, 52.8 Hz, H-1), 4.392 (dd, 1 H, *J* 1.5, 12.5 Hz, H-6), 4.080 (dt, 1 H, *J* 1.5, 12.8 Hz, H-6′), 4.022 (t, 1 H, *J* 2.4 Hz, H-4), 3.826 (ddd, 1H, *J* 2.4, 7.6, 10.0 Hz, H-2), 3.644 (ddd, 1 H, *J* 0.9, 3.7, 4.6 Hz, H-3), 3.489 (br s, 1 H, H-5), 0.926 (s, 9 H, $CH_3$ of $^t$Bu), 0.167, 0.130 (2s, 6 H, $2CH_3$ of TBDMS). Anal. Calcd for $C_{19}H_{28}FN_3O_4Si$: C, 55.72; H, 6.89; N, 10.26. Found: C, 55.87; H, 6.98; N, 9.96.

*Allyl* N-*(9-fluorenylmethoxycarbonyl)-[*O-*(2-azido-4,6-*O-*benzylidene-2-deoxy-3-*O-*levulinoyl-α-*D-*galactopyranosyl)-(1 → 3)]-*L-*serine* (**33**) *and allyl* N-*(9-fluorenylmethoxycarbonyl)-*O-*(2-azido-4,6-*O-*benzylidene-2-deoxy-3-*O-*levulinoyl-β-*D-*galactopyranosyl)-(1 → 3)-*L-*serine* (**34**).—*(a) By coupling of* **26** *and* **32**. A mixture of $Cp_2ZrCl_2$ (121 mg, 414 μmol), $AgClO_4$ (172 mg, 830 μmol), and well-dried powdered 4A molecular sieves (1.2g) in dry $CH_2Cl_2$ (4 mL) was stirred at room temperature for 1 h. A solution of **26** (87.2 mg, 207 μmol) and **32** (177.8 mg, 484 μmol) in dry $CH_2Cl_2$ (6 mL) was added to the cooled suspension (−20°C). Monitoring the reaction after 1 h by TLC indicated only partial conversion. Further addition of $Cp_2ZrCl_2$ (60.5 mg, 207 μmol), $AgClO_4$ (86.0 mg, 415 μmol), and continued stirring at −20 to 5°C gave further conversion to **33** by TLC after 3 h. A final addition of the promotor salts, $Cp_2ZrCl_2$ (60.5 mg, 207 μmol) and $AgClO_4$ (86.0 mg, 415 μmol), resulted in complete disappearance of the fluoride **26** after 18 h at room temperature. The reaction was then quenched with aq $NaHCO_3$, diluted with $CHCl_3$, filtered through Celite, washed with water, aq $NaHCO_3$ and brine, dried ($Na_2SO_4$), and concentrated in vacuo. The residue was purified firstly by gel-permeation chromatography on Bio-beads S-X8 (80 mL) with toluene, followed by preparative TLC to afford **33** (71.0 mg, 46.3%) and **34** (43.5 mg, 28.3%).

*(b) By coupling of* **27** *and* **32**. To the reaction flask containing 4A molecular sieves (600 mg) under Ar was added $Cp_2ZrCl_2$ (52 mg, 178 μmol) and $AgClO_4$ (74 mg, 357 μmol), followed by addition of $CH_2Cl_2$ (2 mL) at room temperature. The suspension was stirred for 30 min, then cooled to −20°C, and a solution of **27** (50 mg, 118 μmol) and **32** (217.9 mg, 593 μmol) in $CH_2Cl_2$ (4 mL) was added. After 18 h with the temperature rising from −20°C to room temperature, fluoride **27** still remained. Thus, another 1.5 equic of $Cp_2ZrCl_2$ and 3.0 equiv of $AgClO_4$ were added to the mixture at −20°C and stirred for a further 18 h. Workup and purification was carried out as described above to produce **33** (45.5 mg, 51.8%) and **34** (18.6 mg, 21.2%).

Compound **33** had $[\alpha]_D^{23}$ +168.0° (*c* 0.25); $R_f$ 0.38 (3:1 toluene–EtOAc). NMR data: $\delta_H$ 7.76–7.42 (m, 13 H, Ar), 5.98–5.90 (m, 1 H, $CH_2CH{:}CH_2$), 5.873 (d, 1 H, *J* 4.0 Hz, NH), 5.506 (s, 1 H, PhCH), 5.365 (d, 1 H, $J_{trans}$ 17.0 Hz, $CH_2CH{:}CH_2$), 5.292 (dd, 1 H, $J_{cis}$ 10.4 Hz, $CH_2CH{:}CH_2$), 5.260 (d, 1 H, H-3), 5.033 (d, 1 H, *J* 3.0 Hz, H-1), 4.706 (d, 2 H, *J* 5.5 Hz, $CH_2CH{:}CH_2$), 4.581 (m, 1 H, Serα-H), 4.423 (d, 2 H, *J* 3.7 Hz, $CH_2OCONH$ and H-4), 4.359 (t, 1 H, *J* 7.3 Hz, $CH_2OCONH$), 4.250 (t, 1 H, *J* 7.2 Hz, $CHAr_2$), 4.208 and 3.936 (2 d, 2 H, *J* 13.0 Hz, H-6, 6′), 4.155 and 4.034 (2 dd, 2 H, *J* 2.8, 11.0 Hz, Serβ H), 3.903 (dd, 1 H, *J* 3.4, 11.3 Hz, H-2), 3.759 (br s, 1 H, H-5), 2.77–2.75 (m, 2 H, $CH_2CH_2$ of Lev), 2.69–2.64 (m, 2 H, $CH_2CH_2$ of Lev), 2.116 (s, 3 H, $CH_3CO$). $\delta_C$ 169.4 ($CO_2CH_2$ of Fmoc), 155.9 (NHCO), 143.8 (C-9a of Fmoc), 141.3 (C-4a of Fmoc), 125.2, 125.1 (C-4b of Fmoc), 119.4 ($Ar_2CCH_2OCO$), 100.7 (PhCH), 99.9 (C-1), 73.2, 69.9, 69.7, 69.1, 67.4, 66.6, 63.1, 57.1, 54.6, 47.0, 37.9,

29.7, and 28.1 ($CH_2CH_2$ of Lev). Anal. Calcd for $C_{39}H_{40}N_4O_{11} \cdot H_2O$: C, 61.74; H, 5.58; N, 7.38. Found: C, 62.12; H, 5.41; N, 6.99.

Compound **34** had $[\alpha]_D$ +29.0° (*c* 0.70); $R_f$ 0.21 (3:1 toluene–EtOAc). NMR data: $\delta_H$ 7.752 (d, 4 H, *J* 7.6 Hz, Ar of Fmoc), 7.610 (t, 2 H, *J* 6.7 Hz, Ar of Fmoc), 5.909 (d, 1 H, *J* 7.0 Hz, NH), 5.491 (s, 1 H, PhC*H*), 5.340 (d, 1 H, $J_{trans}$ 17.4 Hz, $CH_2CH{:}CH_2$), 5.205 (dd, 1 H, $J_{gem}$ 1.2 Hz, $J_{cis}$ 10.7 Hz, $CH_2CH{:}CH_2$), 4.718 (m, 2 H, $CH_2CH{:}CH_2$), 4.610 (m, 1 H, α-Ser), 4.243 (t, 1 H, *J* 7.6 Hz, $CHAr_2$), 2.80–2.75 (m, 2 H, $CH_2CH_2$ of Lev), 2.70–2.62 (m, 2 H, $CH_2CH_2$ of Lev), 2.105 (s, 3 H, $CH_3CO$); $\delta_C$ 169.3 ($COOCH_2$), 156.0 (NHCO), 143.7 (C-9a of Fmoc), 125.0 (C-4b), 119.0 ($Ar_2CCH_2$), 102.3 (C-1), 100.9 (PhCH), 29.7, 28.0 ($CH_2CH_2$ of Lev). Anal. Calcd for $C_{39}H_{40}N_4O_{11}$: C, 63.23; H, 5.44; N, 7.56. Found: C, 63.96; H, 5.61; N, 7.02.

*Allyl* N-*(9-fluorenylmethoxycarbonyl)-{*O-*[2-azido-4,6-*O-*benzylidene-3-*O-tert-*butyldimethylsilyl-α-*D-*galactopyranosyl]-(1 → 3)}-*L-*serine* (**35**) *and allyl* N-*(9-fluorenylmethoxycarbonyl)-{*O-*[2-azido-4,6-*O-*benzylidene-3-*O-tert-*butyldimethylsilyl-β-*D-*galactopyranosyl]-(1 → 3)}-*L-*serine* (**36**).—*(a) By coupling* **30** *and* **32**. A mixture of $Cp_2ZrCl_2$ (1.38g, 4.71 mmol), $AgClO_4$ (981 mg, 4.73 mmol), and well-dried powdered 4A molecular sieves (23.8 g) in dry $CH_2Cl_2$ (80 mL) was stirred at room temperature for 30 min under Ar. The temperature was then lowered to −25°C, **30** (1.38 g, 3.13 mmol) and **32** (1.20 g, 3.27 mmol) in dry $CH_2Cl_2$ (120 mL) were added and stirred for 10 h from −20°C to room temperature. After quenching with aq $NaHCO_3$, the mixture was diluted with EtOAc, filtered through Celite, washed with water, brine, and dried ($Na_2SO_4$). Evaporation in vacuo gave a residue which was purified by gel-permeation chromatography on Bio-Beads S-X8 (3 L) with 4:1 toluene–EtOAc. The appropriate pooled fractions were evaporated to a syrup in vacuo and chromatographed on silica gel (175 g) in 3:1 toluene–EtOAc to give **35** (2.10 g, 85.3%) and **36** (205 mg, 8.3%).

*(b) By coupling* **31** *and* **32**. Reaction of the β-fluoride **31** (901 mg, 2.04 mmol) and **32** (800 mg, 2.18 mmol) was carried out with $Cp_2ZrCl_2$ (929 mg, 3.18 mmol), $AgClO_4$ (644 mg, 3.10 mmol), and 4A molecular sieves (17.8 g) in $CH_2Cl_2$ (138 mL), as described above, to afford **35** (1.38g, 85.8%) and **36** (170 mg, 10.6%).

Compound **35** had $[\alpha]_D^{25}$ +72.0° (*c* 1.54); $R_f$ 0.51 (4:1 toluene–EtOAc). NMR data: $\delta_H$ 7.77–7.32 (m, 13 H, Ar), 5.97–5.90 (m, 2 H, NH and $CH_2CH{:}CH_2$), 5.509 (s, 1 H, PhC*H*), 5.359 (d, 1 H, $J_{trans}$ 17.4 Hz, $CH_2CH{:}CH_2$), 5.278 (dd, 1 H, $J_{gem}$ 0.9 Hz, $J_{cis}$ 10.4 Hz, $CH_2CH{:}CH_2$), 4.964 (d, 1 H, *J* 3.4 Hz, H-1), 4.470 (dd, 1 H, *J* 7.3, 10.7 Hz, H-3), 4.354 (dd, 1 H, *J* 7.3, 10.4 Hz, H-4), 4.238 (br t, 2 H, *J* 7.3 Hz, $CHAr_2$), 4.171 (dd, 1 H, *J* 3.7, 7.6 Hz, H-6′), 4.090 (d, 1 H, *J* 3.0 Hz, H-6), 3.732 (dd, 1 H, *J* 3.4, 10.0 Hz, H-2), 3.702 (s, 1 H, H-5), 0.934 (s, 9 H, $CH_3$ of $^t$Bu), 0.179 and 0.145 (2 s, 6 H, 2 $CH_3$ of TBDMS). $\delta_C$ (68 MHz) 100.54 (Ph*C*H), 100.36 (C-1). Anal. Calcd for $C_{40}H_{48}N_4O_{11}Si \cdot 1.5H_2O$: C, 58.89; H, 6.30; N, 6.86. Found: C, 58.90; H, 5.92; N, 6.30.

Compound **36** had $[\alpha]_D^{25}$ 21.9° (*c* 0.465); $R_f$ 0.34 (4:1 toluene–EtOAc). NMR data: $\delta_H$ 7.75–7.52 (m, 8 H, Ar), 5.974 (d, 1 H, *J* 8.5 Hz, NHSer), 5.94–5.87 (m, 1 H, $CH_2CH{:}CH_2$), 5.522 (s, 1 H, PhCH), 5.329 (dd, 1 H, $J_{gem}$ 1.2 Hz, $J_{trans}$ 17.4 Hz, $CH_2CH{:}CH_2$), 5.192 (dd, 1 H, $J_{gem}$ 1.2 Hz, $J_{cis}$ 10.4 Hz, $CH_2CH{:}CH_2$), 4.689 (br t, 2 H, *J* 1.5, 7.3 Hz, $CH_2CH{:}CH_2$), 4.598–4.575 (m, 1 H, Ser$\alpha$H), 4.433 (dd, 1 H, *J* 2.7, 10.0 Hz, Ser$\beta$H), 4.404 (d, 1 H, *J* 7.6 Hz, H-1), 4.383 (d, 1 H, *J* 7.3 Hz, Ser$\beta$H),

4.314 (dd, 1 H, *J* 1.5, 12.5 Hz, H-6), 4.264 (br t, 1 H, *J* 7.9 Hz, $CHAr_2$), 4.043 (dd, 1 H, *J* 1.5, 12.5 Hz, H-6'), 3.982 (d, 1 H, *J* 3.0 Hz, H-4), 3.892 (dd, 1 H, *J* 3.0, 10.0 Hz, H-2), 3.580 (dd, 1 H, *J* 3.7, 10.0 Hz, H-3), 3.354 (s, 1 H, H-5), 0.926 (s, 9 H, $CH_3$ of $^t$Bu), 0.162 and 0.117 (2 s, 6 H, 2 $CH_3$ of TBDMS). Anal. Calcd for $C_{40}H_{48}N_4O_{11}Si$: C, 60.90; H, 6.13; N, 7.10. Found: C, 60.73; H, 6.20; N, 6.40.

*Allyl* N-*(9-fluorenylmethoxycarbonyl)-[*O-*(2-azido-4,6-*O*-benzylidene-2-deoxy-α-*D*-galactopyranosyl)-(1 → 3)]-*L*-serine* (**37**).—*(a) By deprotection of* **33** . Compound **33** (302 mg, 408 μmol) was dissolved in toluene (6.0 mL). EtOH (30 mL) was added, the solution was stirred under Ar at room temperature, and hydrazine acetate was added (188 mg, 2.04 mmol). The reaction was complete after 20 min at room temperature. The mixture was then diluted with EtOAc, coevaporated in vacuo, and directly purified by flash chromatography over silica gel (30 g) in 10:1 $CHCl_3$–THF to afford **37** (243 mg, 92.7%).

*(b) By deprotection of* **35**. To a solution of **35** (47.4 mg, 60.1 μmol) in MeOH (2.0 mL) was added ammonium fluoride (30.6 mg, 828 μmol, 13.8 equiv). The mixture was stirred at 60°C for 10 h, then at room temperature for 12 h, and finally again at 60°C for 3 h. The solvent was evaporated in vacuo, and the residue was then directly purified by preparative TLC (10:1 toluene–THF) to afford **37** (28.0 mg, 72.5%).

Compound **37** had $[\alpha]_D^{21}$ +97.2° (*c* 0.36); $R_f$ 0.46 (10:1 $CHCl_3$–THF). NMR data: $\delta_H$ 7.78–7.33 (m, 13 H, Ar), 5.98–5.90 (m, 1 H, $CH_2CH$:$CH_2$), 5.831 (d, 1 H, *J* 7.7 Hz, NH), 5.540 (s, 1 H, PhC*H*), 5.365 (d, 1 H, $J_{trans}$ 17.2 Hz, $CH_2CH$:C$H_2$), 5.293 (dd, 1 H, $J_{gem}$ 0.7 Hz, $J_{cis}$ 9.9 Hz, $CH_2CH$:C$H_2$), 4.573 (m, 1 H, Ser$\alpha$H), 4.467 (dd, 2 H, *J* 7.0, 10.3 Hz, C$H_2$OCONH), 4.348 (dd, 1 H, *J* 7.3, 10.0 Hz, C*H*$Ar_2$), 4.036 (dd, 1 H, *J* 2.2, 10.2 Hz, Ser$\beta$H), 3.948 (d, 1 H, *J* 12.4 Hz, H-6), 3.556 (dd, 1 H, *J* 3.3, 10.6 Hz, H-2), 2.417 (br s, 1 H, OH). Anal. Calcd for $C_{34}H_{34}N_4O_9 \cdot H_2O$: C, 61.81; H, 5.49; N, 8.48. Found: C, 61.24; H, 5.29; N, 7.83.

*Allyl* N-*(9-fluorenylmethoxycarbonyl)-{*O-*[*O-*(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*-galactopyranosyl)-(1 → 3)-*O*-(4.6-di-*O*-acetyl-2-*O*-levulinoyl-β-*D*-galactopyranosyl)-(1 → 3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-*D*-galactopyranosyl]-(1 → 3)}-*L*-serine* (**38**).—A mixture of **22** (45.4 mg, 54.3 μmol), **37** (45.4 mg, 70.6 μmol), and 4A molecular sieves (103 mg) in $CH_2Cl_2$ (2.1 mL) was stirred at room temperature for 30 min under Ar, then cooled to −20°C. To this mixture, a solution of $Me_3SiOSO_2CF_3$ (3.14 μL, 17.4 μmol, 0.32 equiv) in $CH_2Cl_2$ (0.4 mL) was added dropwise and stirring was continued for 16 h with the temperature rising to 10°C. The mixture was diluted with EtOAc, quenched with aq $NaHCO_3$, stirred for 5 min, filtered through Celite, and the filtrate was washed with brine and dried ($Na_2SO_4$). Evaporation of the solvent in vacuo gave a residue that was purified firstly by gel-permeation chromatography on Bio-Beads S-X4 (80 mL) in toluene, then by preparative TLC (1:1 toluene–THF) to afford **38** (53.6 mg, 57.6% based on acceptor **37**), hemiacetal **21** (5.7 mg), and recovered acceptor **37** (17.1 mg).

Compound **38** had $[\alpha]_D^{20}$ +101.3° (*c* 0.30); $R_f$ 0.44 (1:1 toluene–THF). NMR data: $\delta_H$ 7.78–7.30 (m, 13 H, Ar), 5.997 (d, 1 H, *J* 9.9 Hz, NHAc), 5.930 (m, 1 H, $CH_2CH$:$CH_2$), 5.888 (d, 1 H, *J* 8.4 Hz, NH of Ser), 5.522 (s, 1 H, PhC*H*), 5.514 (d, 1 H, *J* 3.4 Hz, H-4b), 5.392 (d, 1 H, *J* 7.6 Hz, H-4c), 5.367 (d, 1 H, $J_{trans}$ 17.2 Hz, $CH_2CH$:C$H_2$), 5.292 (d, 1 H, $J_{cis}$ 10.6 Hz, $CH_2CH$:C$H_2$), 5.208 (dd, 1 H, *J* 7.7, 9.9

Hz, H-2b), 5.078 (d, 1 H, *J* 3.7 Hz, H-1c), 5.005 (m, 2 H, H-1a and H-3c), 4.699 (d, 1 H, *J* 7.9 Hz, H-1b), 4.598 (ddd, 1 H, *J* 1.8, 3.7, 9.8 Hz, H-2c), 4.350 (d, 2 H, *J* 2.9 Hz, $CH_2CH{:}CH_2$), 4.132 and 4.043 (2 d, 2 H, *J* 6.4 and 6.1 Hz, Ser$\beta$H), 3.698 (br s, 1 H, H-5a), 2.88–2.83 and 2.69–2.53 (m, 4 H, $CH_2CH_2$ of Lev), 2.172, 2.149, 2.123, 2.034, 2.010, 1.959, and 1.949 (7 s, 21 H, 7 Ac). $\delta_C$ 171.9, 170.43, 170.36, 170.30, 170.2, 170.0 ($CH_3CO$), 169.5 ($CO_2CH_2$ of Fmoc), 155.9 (NHCO), 143.7, 143.6 (C-9a of Fmoc), 141.35, 141.32 (C-4a of Fmoc), 131.3 ($CH_2CH{:}CH_2$), 128.9, 128.3, 128.1, 127.9, 127.8, 126.0, 120.13, 120.08 (Ar of Fmoc and PhCH), 125.07, 124.98 (C-4b of Fmoc), 102.1 (C-1b), 100.5 (PhCH), 100.1 (C-1a), 96.2 (C-1c), 75.5 ($CH_2CH{:}CH_2$), 70.4 (C-2b), 67.72, 67.64 (C-4b, C-3c), 65.49 (C-4c), 63.6 (C-5a), 61.3 (Ser$\beta$C), 54.6, 47.4 (C-2c), 37.5 ($CH_2CH_2$ of Lev), 29.7, 23.1, 20.80, 20.78, 20.70, 20.68 ($CH_3CO$). Anal. Calcd for $C_{63}H_{73}N_5O_{26} \cdot 2H_2O$: C, 55.96; H, 5.74; N, 5.18. Found: C, 56.34; H, 5.71; N, 4.80.

*Allyl* N-*(9-fluorenylmethoxycarbonyl)*-O-*{[*O-*(2-acetamido-3,4,6-tri-*O-*acetyl-2-deoxy-α-*D-*galactopyranosyl)-(1 → 3)-*O-*(4,6-di-*O-*acetyl-β-*D-*galactopyranosyl)-(1 → 3)-2-azido-4,6-*O-*benzylidene-2-deoxy-α-*D-*galactopyranosyl]-(1 → 3)}-*L-*serine* (**39**).—Compound **38** (154 mg, 117 $\mu$mol) was reacted in the manner as described for **28** by using hydrazine acetate (54.0 mg, 586 $\mu$mol), toluene (1.7 mL), and EtOH (8.66 mL) to afford the desired compound **39** (140 mg, 97.8%); $[\alpha]_D^{22}$ +53.3° (*c* 0.12); $R_f$ 0.50 (20:20:3 toluene–EtOAc–MeOH). NMR data: $\delta_H$ 7.78–7.31 (m, 13 H, Ar), 6.137 (d, 1 H, *J* 10.0 Hz, NH of Ser), 5.95–5.91 (m, 1 H, $CH_2CH{:}CH_2$), 5.862 (m, 1 H, NHAc), 5.536 (s, 1 H, PhCH), 5.359 (d, 1 H, *J* 3.0 Hz, H-1c), 5.357 (d, 1 H, $J_{trans}$ 17.4 Hz, $CH_2CH{:}CH_2$), 5.290 (d, 1 H, $J_{cis}$ 10.7 Hz, $CH_2CH{:}CH_2$), 5.040 (d, 1 H, *J* 3.0 Hz, H-1c), 5.029 (dd, 1 H, *J* 3.3, 11.3 Hz, H-3c), 4.982 (d, 1 H, *J* 3.7 Hz, H-1a), 4.705 (d, 2 H, *J* 5.8 Hz, $CH_2CH{:}CH_2$), 4.662 (ddd, 1 H, *J* 3.7, 11.6, 13.7 Hz, H-2c), 4.528 (dd, 1 H, *J* 2.4, 7.3 Hz, H-2b), 4.365 (d, 2 H, *J* 3.0 Hz, $CH_2OCONH$), 3.173 (br s, 1 H, OH), 2.172, 2.159, 2.029, 2.018, 2.012, 1.991 (6 s, 18 H, 6 Ac). Anal. Calcd for $C_{58}H_{67}N_5O_{24}$: C, 57.18; H, 5.54; N, 5.74. Found C, 57.56; H, 5.70; N, 5.63.

*Allyl* N-*(9-fluorenylmethoxycarbonyl)*-O-*{*O-*[*O-*(2-acetamido-3,4,6-tri-*O-*acetyl-2-deoxy-α-*D-*galactopyranosyl)-(1 → 3)-*O-*{[2,3,4-tri-*O-*benzyl-α-*L-*fucopyranosyl]-(1 → 2)}-*O-*(4,6-di-*O-*acetyl-β-*D-*galactopyranosyl)-(1 → 3)-2-azido-4,6-*O-*benzylidene-deoxy-α-*D-*galactopyranosyl]-(1 → 3)}-*L-*serine* (**3**) *and allyl* N-*(9-fluorenylmethoxycarbonyl)*-*{*O-*[*O-*(2-acetamido-3,4,6-tri-*O-*acetyl-2-deoxy-α-*D-*galactopyranosyl)-(1 → 3)-*O-*{[2,3,4-tri-*O-*benzyl-β-*L-*fucopyranosyl]-(1 → 2)}-*O-*(4,6-di-*O-*acetyl-β-*D-*galactopyranosyl)-(1 → 3)-2-azido-4,6-*O-*benzylidene-deoxy-α-*D-*galactopyranosyl]-(1 → 3)}-*L-*serine* (**41**).—To a mixture of $CuBr_2$ (27.5 mg, 123 $\mu$mol,), $^nBu_4NBr$ (4.40 mg, 13.6 mmol), $AgOSO_2CF_3$ (31.6 mg, 123 $\mu$mol), and 4A molecular sieves (136 mg), which had been stirred in dry 5:1 1,2-dichloroethane–toluene (0.7 mL) for 30 min at room temperature, was injected in one portion, a solution of **40** (38.1 mg, 82.0 $\mu$mol, 10.8 equiv), and **39** (9.20 mg, 7.55 $\mu$mol), in dry 5:1 1,2-dichloroethane–toluene (0.7 mL) under Ar at room temperature. Stirring was continued for 12 h; thereafter, a further portion of $AgOSO_2CF_3$ (15.8 mg, 61.5 $\mu$mol) was added, and after 18 h the mixture was diluted with EtOAc, quenched with aq $NaHCO_3$, and filtered through a Celite bed that had been prewashed with aq $NaHCO_3$. The filtrate was washed with brine, dried ( $mgSO_4$), and evaporated to a residue in vacuo. Gel-permeation chromatography on Bio-Beads S-X3 in toluene

(40 mL) gave a crude $\alpha,\beta$-product mixture that was further purified by preparative TLC (1:1 toluene–THF) to give **3** (7.1 mg, 57.5%) and the corresponding $\beta$-product **41** (1.8 mg, 14.5%).

Compound **3** had $[\alpha]_D^{23}$ +51.6° (*c* 0.54); $R_f$ 0.50 (1:1 toluene–THF). NMR data: $\delta_H$ 7.78–7.21 (m, 28 H, Ar), 5.94–5.91 (m, 1 H, $CH_2CH$:$CH_2$), 5.88–5.85 (m, 1 H, NHAc), 5.646 (d, 1 H, *J* 9.2 Hz, NH of Ser), 5.557 (s, 1 H, PhCH), 5.438 (d, 1 H, *J* 3.7 Hz, H-1d), 5.390 (m, 1 H, H-4b), 5.158 (d, 1 H, *J* 3.7 Hz, H-1c), 5.050 (br s, 1 H, H-4c), 4.913 (dd, 1 H, *J* 2.9, 11.7 Hz, H-3c), 4.834 (dd, 2 H, *J* 11.5, 42.5 Hz, $PhCH_2$), 4.702 (m, 1 H, H-1b), 4.560 (ddd, 1 H, *J* 3.7, 9.5, 11.4 Hz, H-2c), 4.490 (dd, 1 H, *J* 3.7, 10.6 Hz, H-2a), 4.447 (dd, 1 H, *J* 5.9 Hz, H-5d), 4.170 (m, 1 H, H-2d/H-3d), 4.081 (dd, 1 H, *J* 7.3, 9.5 Hz, H-2b), 3.716 (s, 1 H, H-5a), 3.604 (br s, 1 H, H-4d), 2.096, 2.063, 1.997, 1.965, 1.935, 1.917 (6 s, 18 H, $CH_3CO$ of OAc and NHAc), 0.992 (d, 3 H, $CH_3$ of Fuc). $\delta_C$ 169.6 ($COOCH_2$ of Fmoc), 128.3, 128.2, 128.0, 127.9 (Ar of Fmoc and PhCH), 127.44, 127.40 (Ph of $PhCH_2$), 126.1 and 120.1 (Ar of Fmoc), 76.0 ($PhCH_2$), 70.6 (C-2b), 67.8 (C-4c), 23.1, 20.7 ($CH_3CO$ of Ac). FABMS (positive-ion): *m/z* 1634 ($M^+ + 1$).

Compound **41** had $[\alpha]_D^{23}$ +4.6° (*c* 0.25); $R_f$ 0.30 (1:1 toluene–THF). NMR data: $\delta_H$ 7.76–7.22 (m, 28 H, Ar), 5.870 (m, 1 H, $CH_2CH$:$CH_2$), 5.676 (d, 1 H, *J* 9.5 Hz, NH of Ser/NHAc), 5.492 (m, 1 H, H-4), 5.401 (s, 1 H, PhCH), 5.335 (dd, 1 H, $J_{gem}$ 3.3 Hz, $J_{trans}$ 16.5 Hz, $CH_2CH$:$CH_2$), 5.299 (dd, 1 H, $J_{cis}$ 9.9 Hz, $CH_2CH$:$CH_2$), 4.973 (d, 1 H, *J* 3.3 Hz, H-1c), 4.773 (d, 1 H, *J* 7.7 Hz, H-1d), 3.656 (t, 1 H, *J* 9.2 Hz, H-2d), 3.384 (m, 1 H, H-4d), 3.243 (d, 1 H, *J* 8.8 Hz, H-3d), 3.132 (dq, 1 H, *J* 5.5 Hz, H-5d), 2.147, 2.139, 2.000, 1.988, 1.923, 1.811 (6 s, 18 H, 6 Ac), 1.010 (d, 3 H, *J* 6.2 Hz, Fuc-$CH_3$). FABMS (positive-ion): *m/z* 1656 ($M^+ + Na$).

*Allyl* N-*(9-fluorenylmethoxycarbonyl)-{*O-*{*O-*(2-acetamido-3,4,6-tri-*O-*acetyl-2-deoxy-α-*D-*galactopyranosyl)-(1 → 3)-[*O-*(2,3,4-tri-*O-*benzyl-α-*L-*fucopyranosyl)-(1 → 2)]-*O-*(4,6-di-*O-*acetyl-β-*D-*galactopyranosyl)-(1 → 3)-4,6-di-*O-*acetyl-2-azido-2-deoxy-α-*D-*galactopyranosyl}-(1 → 3)}-*L-*serine* (**42**).—Compound **3** (5.9 mg, 3.60 μmol) was stirred in aq 80% AcOH (400 μL) for 7 h at 60°C, diluted with EtOAc, washed with aq $NaHCO_3$, dried ($Na_2SO_4$), and evaporated in vacuo. This residue was directly acetylated by adding acetic anhydride (140 μL), pyridine (122 μL), and DMAP (0.1 mg), stirring for 12 h at room temperature. Coevaporation in vacuo with toluene and purification by preparative TLC (1:1 toluene–THF) gave **42** (5.10 mg, 87.0%). Compound **42** had $[\alpha]_D^{26}$ +41.8° (*c* 0.055); $R_f$ 0.47 (1:1 toluene–THF). NMR data: $\delta_H$ 7.77–7.40 (t, 8 H, Ar of Fmoc), 5.938 (m, 1 H, $CH_2CH$:$CH_2$), 5.914 (d, 1 H, *J* 8.6 Hz, NHAc), 5.724 (d, 1 H, *J* 9.5 Hz, NH of Ser), 5.570 (d, 1 H, *J* 3.0 Hz, H-4a), 5.440 (d, 1 H *J* 3.7 Hz, H-1d), 5.360 (br s, 1 H, H-4b), 5.305 (2 d, 2 H, $J_{cis}$ 10.4 Hz, $CH_2CH$:$CH_2$), 5.175 (d, 1 H, *J* 3.7 Hz, H-1c), 5.050 (br s, 1 H, H-4c), 4.954 and 4.817 (dd, 2 H, *J* 11.9 Hz, 69.0 Hz, $PhCH_2$), 4.680 and 4.582 (dd, 2 H, *J* 11.9, 49.1 Hz, $PhCH_2$), 4.372 (m, 1 H, H-2a), 3.761 (br s, 1 H, H-4d), 3.741 (s, 1 H, H-5a), 3.363 (dd, 1 H, *J* 3.7, 11.0 Hz, H-3a), 2.113, 2.090, 2.076, 2.025, 2.022, 2.011, 1.972, 1.940, (8 s, 24 H, Ac). FABMS (positive-ion): *m/z* 1630. ($M^+ + 1$).

*Allyl* N-*(9-fluorenylmethoxycarbonyl)-{*O-*{*O-*(2-acetamido-3,4,6-tri-*O-*acetyl-2-deoxy-α-*D-*galactopyranosyl)-(1 → 3)-[*O-*(2,3,4 tri-*O-*benzyl-α-*L-*fucopyranosyl)-(1 → 2)]-*O-*(4,6-di-*O-*acetyl-β-*D-*galactopyranosyl)-(1 → 3)-2-acetamido-4,6-di-*O-*acetyl-2-deoxy-*

*α*-D-*galactopyranosyl}-(1 → 3)}*-L-*serine* (**43**).—To a solution of the azide **42** (24.6 mg, 15.1 μmol) in dry pyridine (400 μL) was added freshly distilled thioacetic acid (790 μL). The mixture was stirred at room temperature for 12 h in the dark. Concentration in vacuo and column chromatography of the residue on silica gel (2.5g) in 20:20:3 toluene–EtOAc–MeOH and further purification by preparative TLC (1:1 THF–toluene) yielded **43** (23.3 mg, 94.4%); $[\alpha]_D^{25}$ +82.1° (*c* 0.145); $R_f$ 0.36 (1:1 THF–toluene). NMR data: $\delta_H$ 7.76–7.21 (m, 23 H, Ar) 5.85–5.80 (m, 1 H, $CH_2CH$:$CH_2$), 5.697 (m, 1 H, NH of Ser), 5.522 (dd, 2 H, *J* 2.1 Hz, H-4a), 5.362 (d, 1 H, *J* 2.1 Hz, H-4b), 5.347 (d, 1 H, *J* 3.0 Hz, H-1d), 5.234 (dd, 1 H, $J_{gem}$ 1.2 Hz, $J_{cis}$ 10.4 Hz, $CH_2CH$:$CH_2$), 5.192 (d, 1 H, *J* 3.7 Hz, H-1c), 4.858 (dd, 2 H, *J* 10.7 Hz, 98.3 Hz, $PhCH_2$), 4.799 (dd, 2 H, *J* 12.5 Hz, 102.5 Hz, $PhCH_2$), 4.223 (ddd, 1 H, *J* 5.2, 11.3, 16.5 Hz, H-2a), 3.993 (t, 1 H, *J* 6.7 Hz, $CHAr_2$), 2.158 (s, 6 H, 2 Ac), 2.139, 2.121, 2.095, 2.033, 2.095, 1.901, 1.887 (7 s, 21 H, 7 Ac), 1.241 (t, 3 H, $CH_3$ of Fuc). FABMS (positive-ion): *m*/*z* 1648 ($M^+$ + 1), 1670 ($M^+$ + Na).

N-*(9-Fluorenylmethoxycarbonyl)*-O-*{2-(*O-*acetamido-3,4,6-tri*-O-*acetyl-2-deoxy-α*-D-*galactopyranosyl)-(1 → 3)-[*O-*(2,3,4-tri*-O-*benzyl-α*-L-*fucopyranosyl)-(1 → 2)]*-O-*(4,6-di*-O-*acetyl-β*-D-*galactopyranosyl)-(1 → 3)-2-acetamido-4,6-di*-O-*acetyl-2-deoxy-α*-D-*galactopyranosyl}-(1 → 3)*-L-*serine* (**44**).—A mixture of the allyl ester **43** (5.4 mg, 3.30 μmol), $Pd[PPh_3]_4$ (3.8 mg, 3.30 μmol), and freshly distilled *N*-methylaniline (33.0 μL, 305 μmol) in freshly distilled THF (250 μL) was stirred at room temperature under Ar in the dark for 3 days. The solution was diluted with EtOAc, washed with 2 N HCl, brine, and dried ($Na_2SO_4$). Evaporation of the solvents in vacuo gave a residue that was purified by preparative TLC (190:5:5 $CHCl_3$–AcOH–MeOH), yielding **44** (3.9 mg, 73.6%); $[\alpha]_D^{27}$ +32.8° (*c* 0.09, $CHCl_3$); $R_f$ 0.27 (190:5:5 $CHCl_3$–AcOH–MeOH). NMR data: $\delta_H$ 7.73–7.24 (m, 23 H, Ar), 5.577 (m, 1 H, NHAc), 5. 516 (d, 1 H, *J* 2.2 Hz, NH of Ser), 5.349 and 5.343 (2 s, 2 H, H-4a and H-4c), 5.236 (d, 1 H, *J* 3.0 Hz, H-1d), 5.213 (d, 1 H, *J* 3.3 Hz, H-1a), 5.185 (d, 1 H, *J* 3.4 Hz, H-1c), 4.792 (dd, 2 H, *J* 12.2, 138.5 Hz, $PhCH_2$), 4.424 (d, 1 H, *J* 7.0 Hz, H-1b), 4.160 (t, 1 H, *J* 6.4 Hz, $CHAr_2$), 3.100 (br s, 1 H, COOH), 2.154, 2.133, 2.105, 2.082, 2.051, 2.031, 1.992, 1.897, 1.877 (9 s, 27 H, 9 Ac), 1.206 (d, 3 H, *J* 6.1 Hz, $CH_3$ of Fuc). FABMS (positive-ion): *m*/*z* 1606 ($M^+$ + 1), 1629 ($M^+$ + Na), 1645 ($M^+$ + K).

O-*{*O-*2-Acetamido-2-deoxy-α*-D-*galactopyranosyl-(1 → 3)-[*O-*(2,3,4-tri*-O-*benzyl-α*-L-*fucopyranosyl-(1 → 2)]*-O-*β*-D-*galactopyranosyl-(1 → 3)-2-acetamido-2-deoxy-α*-D-*galactopyranosyl}-(1 → 3)*-L-*serine* (**45**).—Compound **44** (5.1 mg, 3.17 μmol) was dissolved in MeOH (4.0 mL), 1 N NaOH (400 mL) was added to the solution, with stirring at room temperature for 20 min. The mixture was neutralized with Amberlyst 15 ($H^+$), filtered, and evaporated in vacuo. Chromatography of the crude product on a Sephadex LH-20 column in MeOH gave **45** (3.3 mg, 95.3%); $[\alpha]_D^{27}$ +41.2° (*c* 0.16, MeOH); $R_f$ 0.47 (1:2:1 $^n$BuOH–EtOH–$H_2O$). NMR data (270 MHz): $\delta_H$ ($CD_3OD$) 7.83–7.26 (m, 15 H, Ar), 2.002, 1.889 (2 s, 6 H, Ac), 0.921 (d, 3 H, *J* 14.2 Hz, $CH_3$ of Fuc). FABMS (positive-ion): *m*/*z* 1090 ($M^+$ + 1), 1112 ($M^+$ + Na).

N,N-*Dimethyl*-O-*{2-acetamido-2-deoxy-α*-D-*galactopyranosyl-(1 → 3)-[*O-*α*-L-*fucopyranosyl-(1 → 2)]*-O-*β*-D-*galactopyranosyl-(1 → 3)-2-acetamido-2-deoxy-α*-D-*galactopyranosyl}-(1 → 3)*-L-*serine* (**46**).—Compound **45** (3.9 mg, 3.58 μmol) was rapidly stirred in a suspension of 20% $Pd(OH)_2$–C (7.0 mg) in aq 80% MeOH (700 mL) under

$H_2$ at room temperature for 5 days, then filtered through a Chromato-disc (0.45 μm). Preparative TLC (5:5:1 $CHCl_3$–MeOH–$H_2O$), then Sephadex chromatograhy (LH-20, aq 80% MeOH), gave fractions of **46** that were pooled and concentrated in vacuo. Finally lyophilization gave **46** (2.7 mg, 89.0%); $[\alpha]_D^{26}$ +55.7° (*c* 0.07, $H_2O$); $R_f$ 0.21 (1:2:1 $^n$BuOH–EtOH–$H_2O$). NMR data (600 MHz): $\delta_H$ ($D_2O$, $(CH_3)_2CO$) 5.295 (d, 1 H, *J* 4.0 Hz, H-1d), 5.207 (d, 1 H, *J* 4.0 Hz, H-1c), 4.926 (d, 1 H, J 3.7 Hz, H-1a), 4.713 (d, 1 H, *J* 7.3 Hz, H-1b), 4.316 (q, 1 H, *J* 7.0 Hz, H-5d), 4.269 (dd, 1 H, *J* 4.0, 11.0 Hz, H-2c), 4.198 (dd, 1 H, *J* 3.3, 11.0 Hz, H-4b), 4.147 (dd, 1 H, *J* 4.6 Hz, H-5c), 4.127 (dd, 1 H, *J* 11.3 Hz, H-3a), 4.019 (m, 2 H, H-3b, H-4c), 3.953 (dd, 1 H, *J* 3.3, 7.3 Hz, H-3c), 3.925 (dd, 1 H, *J* 7.3, 9.8 Hz, H-2b), 3.822 (m, 2 H, H-2d and H-3d), 3.694 (d, 1 H, *J* 3.0 Hz, H-5b), 3.656 (dd, 2 H, *J* 4.2 Hz, H-6a and H-6′a), 3.620 (dd, 1 H, *J* 3.4, 10.4 Hz, H-4a), 3.591 (t, 1 H, Ser$\alpha$H), 2.710 (s, 6 H, $N(CH_3)_2$), 2.085, 2.068 (2 s, 6 H, Ac), 1.222 (d, 3 H, *J* 6.7 Hz, H-6d). FABMS (positive-ion): *m/z* 848 ($M^+ + 1$), 871 ($M^+ + Na$); (negative-ion) *m/z* 847 ($M^-$).

*Allyl* O-*(2-acetamido-3,4,6-tri*-O-*acetyl-2-deoxy-α*-D-*galactopyranosyl)-(1 → 3)*-O-*(4,6-di*-O-*acetyl-2*-O-*levulinoyl-β*-D-*galactopyranosyl)-(1 → 3)-2-azido-4,6*-O-*benzylidene-2-deoxy-β*-D-*galactopyranoside* (**49**).—To a stirred mixture of compound **47** (54.7 mg, 164 μmol) and powdered molecular sieves AW-300 (232 mg) in 1,2-dichloroethane (1.0 mL) maintained at −15°C under Ar, was added a solution of compound **22** (114 mg, 136 μmol) in 1,2-dichloroethane (1.0 mL), followed by $BF_3 \cdot Et_2O$ (20.2 μL, 164 μmol). After stirring for 1.5 h at −15°C, the mixture was neutralized with $Et_3N$ (24 μL), and diluted with $CHCl_3$ and filtered through Celite. The filtrate was successively washed with aq $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated in vacuo. The residue was subjected to gel-permeation chromatography on Bio-Beads S-X8 in toluene (80 mL). Crystallization from MeOH gave **49** (127 mg, 92.8%); mp 188–189°C (MeOH); $[\alpha]_D^{20}$ +61.8° (*c* 0.23); $R_f$ 0.24 (4:3 toluene–THF). NMR data: $\delta_H$ 7.54–7.35 (m, 5 H, Ph), 6.140 (d, 1 H, *J* 9.5 Hz, NH), 5.949 (m, 1 H, $CH_2CH$:$CH_2$), 5.560 (s, 1 H, PhC*H*), 5.527 (d, 1 H, *J* 2.1 Hz, H-4c), 5.417 (d, 1 H, *J* 2.8 Hz, H-4b), 5.337 (dd, 1 H, $J_{gem}$ 1.5 Hz, $J_{cis}$ 10.4 Hz, $CH_2CH$:C$H_2$), 5.226 (dd, 1 H, $J_{gem}$ 1.5 Hz, $J_{trans}$ 17.1 Hz, $CH_2CH$:C$H_2$), 5.202 (dd, 1 H, *J* 7.9, 10.0 Hz, H-2b), 5.084 (d, 1 H, *J* 3.7 Hz, H-1c), 5.028 (dd, 1 H, *J* 3.4, 11.6 Hz, H-3c), 4.788 (d, 1 H, *J* 7.9 Hz, H-1b), 4.599 (ddd, 1 H, *J* 3.7, 9.8, 11.6 Hz, H-2c), 4.466 and 4.440 (2 dt, 1 H, C$H_2$CH:$CH_2$), 4.363 (d, 1 H, *J* 8.2 Hz, H-1a), 4.275 (t, 1 H, *J* 6.4 Hz, H-5c), 4.226 (d, 1 H, *J* 3.4 Hz, H-4a), 3.925 (d, 1 H, *J* 3.7, 10.4 Hz, H-3b), 3.907 (dd, 1 H, *J* 7.9 and 10.7 Hz, H-2a), 3.824 (t, 1 H, *J* 7.0 Hz, H-5b), 3.487 (dd, 1 H, *J* 3.7, 10.4 Hz, H-3a), 3.379 (br d, 1 H, *J* 0.6 Hz, H-5a), 2.884, 2.659 and 2.543 (3 m, 4 H, $CH_2CH_2$ of Lev), 2.174, 2.148, 2.129, 2.057, 2.042, 1.958, and 1.938 (7 s, 21 H, 7 Ac). Anal. Calcd for $C_{45}H_{58}N_4O_{22}$: C, 53.68; H, 5.81; N, 5.56. Found: C, 53.32; H, 5.79; N, 5.52.

p-*Methoxyphenyl* O-*(2-acetamido-3,4,6-tri*-O-*acetyl-2-deoxy-α*-D-*galactopyranosyl-(1 → 3)-(4,6-di*-O-*acetyl-2*-O-*levulinoyl-β*-D-*galactopyranosyl)-(1 → 3)-(2-azido-4,6*-O-*benzylidene-2-deoxy-α*-D-*galactopyranoside* (**50**).—Reaction of the α-imidate **22** (70.3 mg, 84.0 μmol) in $(CH_2Cl)_2$ (1.0 mL) with acceptor **48** (40.9 mg, 101.1 μmol) in $(CH_2Cl)_2$ (1.0 mL) in the presence of $BF_3 \cdot Et_2O$ (12.4 μL, 101.1 μmol) and molecular sieves AW-300 (230 mg) was carried out as described in the preparation of **49** to yield **50** (25.4 mg, 28.0%), along with **22** (8.4 mg, 12.0% recovered from the imidate starting

material), **21** (9.2 mg), and **48** (45.4 mg, 65.0% based on starting material) as recovered compounds. Compound **50** had $[\alpha]_D^{23}$ +133° (*c* 0.06); $R_f$ 0.31 (4:3 toluene–THF). NMR data: $\delta_H$ 7.55–6.83 (m, 9 H, Ar), 6.159 (d, 1 H, *J* 9.8 Hz, NHAc), 5.618 (d, 1 H, *J* 3.4 Hz, H-1a), 5.591 (s, 1 H, PhC*H*), 5.548 (d, 1 H, *J* 2.2 Hz, H-4c), 5.462 (d, 1 H, *J* 2.4 Hz, H-4b), 5.269 (dd, 1 H, *J* 7.9, 10.4 Hz, H-2b), 5.115 (d, 1 H, *J* 3.7 Hz, H-1c), 5.042 (dd, 1 H, *J* 3.0, 11.6 Hz, H-3c), 4.830 (d, 1 H, *J* 7.9 Hz, H-1b), 4.614 (ddd, 1 H, *J* 3.7, 9.8, 11.6 Hz, H-2c), 4.456 (d, 1 H, *J* 3.0 Hz, H-4a), 4.335 (dd, 1 H, *J* 3.4, 11.0 Hz, H-2a), 3.913 (t, 1 H, *J* 6.1 Hz, H-5b), 3.854 (br s, 1 H, H-5a), 3.781 (s, 3 H, OC$H_3$), 2.93–2.56 (3 m, 4 H, $CH_2CH_2$ of Lev), 2.188, 2.155, 2.129, 2.067, 2.048, 1.960, 1.944 (7 s, 21 H, 7 Ac). Anal. Calcd for $C_{49}H_{60}N_4O_{23} \cdot H_2O$: C, 53.94; H, 5.73; N, 5.13. Found: C, 53.90; H, 5.69; N, 4.62.

*Allyl* O-*(2-acetamido-3,4,6-tri*-O-*acetyl-2-deoxy-α*-D-*galactopyranosyl)-(1 → 3)*-O-*(4,6-di*-O-*acetyl-β*-D-*galactopyranosyl)-(1 → 3)-2-azido-4,6*-O-*benzylidene-2-deoxy-β*-D-*galactopyranoside* (**51**).—Compound **50** (38.0 mg, 35.4 μmol) was dissolved in DMF (0.3 mL), and hydrazine acetate (4.52 mg, 49.0 μmol) was added. The mixture was stirred for 1 h at room temperature, diluted with EtOAc (20 mL), and washed twice with aq NaCl. The EtOAc layer was dried ($MgSO_4$), and evaporated in vacuo. The residue was chromatographed on silica gel in 30:40:1 THF–toluene–$Et_3N$, to give **51** (29.0 mg, 84.0%); $[\alpha]_D^{20}$ +33.1° (*c* 0.61); $R_f$ 0.37 in 3:4 THF--toluene. NMR data: $\delta_H$ 7.57–7.34 (m, 5 H, Ar), 6.121 (d, 1 H, *J* 10.1 Hz, NH), 5.960 (m, 1 H, $CH_2CH$:$CH_2$), 5.565 (s, 1 H, PhC*H*), 5.37–5.33 (m, 3 H, H-4b, H-4c, $CH_2CH$:C$H_2$), 5.240 (m, 1 H, $CH_2CH$:C$H_2$), 5.042 (dd, 1 H, *J* 3.4, 11.3 Hz, H-3c), 4.992 (d, 1 H, *J* 3.7 Hz, H-1c), 4.652 (ddd, 1 H, *J* 3.7, 10.1, 11.3 Hz, H-2c), 4.604 (d, 1 H, *J* 7.3 Hz, H-1b), 4.383 (d, 1 H, *J* 7.9 Hz, H-1a), 4.33 and 4.06 (2 m, 2 H, C$H_2$CH:$CH_2$), 4.239 (d, 1 H, *J* 3.4 Hz, H-4a), 3.907 (dd, 1 H, *J* 7.9, 10.4 Hz, H-2a), 3.703 (m, 1 H, H-2b), 3.543 (dd, 1 H, *J* 3.4, 10.4 Hz, H-3a), 3.391 (br s, 1 H, H-5a), 2.211, 2.152, 2.051, 2.009, 2.004, and 1.985 (6 s, 18 H, 6 Ac). Anal. Calcd for $C_{40}H_{52}N_4O_{20}$: C, 52.86; H, 5.77; N, 6.16. Found: C, 52.58; H, 5.88; N, 6.01.

*Allyl* O-*(2-acetamido-3,4,6-tri*-O-*acetyl-2-deoxy-α*-D-*galactopyranosyl)-(1 → 3)*-O-*(2,4,6-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1 → 3)-2-azido-4,6*-O-*benzylidene-2-deoxy-β*-D-*galactopyranoside* (**52**).—Compound **51** (15.0 mg, 17.0 mmol) was dissolved in pyridine (1.0 mL) and $Ac_2O$ (0.8 mL). The mixture was stirred for 6 h at room temperature, and evaporated in vacuo. The residue was chromatographed on silica gel in 30:40:1 THF–toluene–$Et_3N$, to give **52** (15.0 mg, 96.0%); $[\alpha]_D^{20}$ +16.4° (*c* 0.22); $R_f$ 0.27 in 3:4 THF–toluene. NMR data: $\delta_H$ 7.54–7.30 (m, 5 H, Ph), 6.239 (d, 1 H, *J* 9.8 Hz, NH), 5.950 (m, 1 H, $CH_2CH$:$CH_2$), 5.554 (s, 1 H, PhC*H*), 5.37–5.32 (m, 2 H, H-4b, H-4c, $CH_2CH$:C$H_2$), 5.220 (m, 1 H, $CH_2CH$:C$H_2$), 5.181 (dd, 1 H, *J* 7.9, 10.1 Hz, H-2b), 5.031 (d, 1 H, *J* 3.4 Hz, H-1c), 4.917 (dd, 1 H, *J* 3.1, 11.6 Hz, H-3c), 4.753 (d, 1 H, *J* 7.9 Hz, H-1b), 4.569 (ddd, 1 H, *J* 3.4, 9.8, 11.6 Hz, H-2c), 4.440 and 4.341 (2 m, 2 H, C$H_2$CH:$CH_2$), 4.354 (d, 1 H, *J* 8.2 Hz, H-1a), 3.468 (dd, 1 H, *J* 3.4, 10.7 Hz, H-3a), 3.374 (br d, 1 H, *J* 0.9 Hz, H-5a), 2.222, 2.131, 2.044, 2.040, 1.990, and 1.978 (7 s, 21 H, 7 Ac). Anal. Calcd for $C_{42}H_{54}N_4O_{21}$: C, 53.05; H, 5.72; N, 5.89. Found: C, 52.86; H, 5.56; N, 5.61.

*Allyl* O-*(2-acetamido-3,4,6-tri*-O-*acetyl-2-deoxy-α*-D-*galactopyranosyl)-(1 → 3)*-O-*(4,6-di*-O-*acetyl-2*-O-*levulinoyl-β*-D-*galactopyranosyl)-(1 → 3)-2-azido-4,6-di*-O-*acetyl-*

*2-deoxy-β-D-galactopyranoside* (**53**).—Compound **49** (50.0 mg, 49.6 μmol) was stirred in aq 80% AcOH at 60°C for 4 h, then at 70°C for 30 min, diluted with EtOAc, washed with aq $NaHCO_3$ and brine, and dried ($Na_2SO_4$). Evaporation in vacuo, addition of pyridine (2.0 mL), acetic anhydride (1.5 mL) and DMAP (0.1 mg) to the resulting residue, stirring overnight at room temperature, coevaporation in the presence of toluene and gel-permeation chromatography on Bio-Beads S-X8 in toluene (160 mL) afforded **53** (49.1 mg, 98.8%); $[\alpha]_D^{24}$ +51.2° (*c* 0.57); $R_f$ 0.18 (5:4 toluene:THF). NMR data: $\delta_H$ 5.978 (d, 1 H, *J* 9.5 Hz, NH), 5.98–5.91 (m, 1 H, $CH_2CH$:$CH_2$), 5.476 (d, 1 H, *J* 1.8 Hz, H-4c), 5.364 and 5.329 (2 q, 1 H, $J_{gem}$ 1.4 Hz, $J_{trans}$ 17.0 Hz, $CH_2CH$:$CH_2$), 4.316 (d 1 H, *J* 2.7 Hz, H-4b), 5.261 and 5.240 (q, 1 H, $J_{gem}$ 1.5 Hz, $J_{cis}$ 8.5 Hz, $CH_2CH$:$CH_2$), 5.081 (dd, 1 H, *J* 7.6, 10.0 Hz, H-2b), 5.066 (d, 1 H, *J* 3.4 Hz, H-1c), 5.014 (dd, 1 H, *J* 3.0, 11.3 Hz, H-3c), 4.674 (d, 1 H, *J* 7.6 Hz, H-1b), 4.588 (ddd, 1 H, *J* 3.7, 9.8, 11.6 Hz, H-2c), 4.331 (d, 1 H, *J* 7.9 Hz, H-1a), 4.255 (t, 1 H, *J* 6.4 Hz, H-5c), 4.008 (dd, 1 H, *J* 6.1, 11.0 Hz, H-6), 3.887 (dd, 1 H, *J* 3.7, 10.4 Hz, H-3b), 3.788 (dd, 1 H, *J* 7.9, 10.4 Hz, H-2a), 3.740 (t, 1 H, *J* 5.8 Hz, H-5b), 3.525 (dd, 1 H, *J* 3.4, 10.4 Hz, H-3a), 2.87–2.56 (m, 2 H, $CH_2CH_2$ of Lev), 2.185, 2.166, 2.143, 2.094, 2.070, 2.053, 1.963, 1.954, 1.951 (9 s, 27 H, 9 Ac). Anal. Calcd for $C_{42}H_{58}N_4O_{24}$: C, 50.30; H, 5.83; N, 5.59. Found: C, 51.06; H, 5.69; N; 4.84.

O-*(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-(1 → 3)-*O*-(4,6-di-*O*-acetyl-2-*O*-levulinoyl-β-D-galactopyranosyl)-(1 → 3)-2-azido-4,6-di-*O*-acetyl-2-deoxy-D-galactopyranose* (**54**).—To the allyl glycoside **53** (48.7 mg, 48.6 μmol) in aq 95% AcOH (350 μL) containing NaOAc (19.1 mg, 233 μmol) was added $PdCl_2$ (14.6 mg, 82.6 μmol) and then acetone (30 μL). The reaction was sonicated for 30 min and stirred overnight at room temperature, diluted with EtOAc, poured into aq $NaHCO_3$, and stirred for 5 h. The organic layer was separated, the aqueous was layer extracted with EtOAc, and the combined organic layers were dried ($MgSO_4$) and evaporated in vacuo. The crude residue of **54** was further not purified (51.3 mg); $R_f$ 0.39 (5:4 THF–toluene). NMR data: $\delta_H$ 6.025 (d, 1 H, *J* 9.8 Hz, NH), 5.469 (m, 1 H, H-4c), 5.076 (d, 1 H, *J* 3.7 Hz, H-1c), 5.112 (dd, 1 H, *J* 7.9, 11.0 Hz, H-2b), 4.998 (dd, 1 H, *J* 3.0, 11.3 Hz, H-3c), 4.687 (d, 1 H, *J* 7.9 Hz, H-1b) 4.63–4.57 (m, 1 H, H-2c), 4.234 (t, 1 H, *J* 2.4 Hz, H-5c), 3.041 (br d, 1 H, *J* 2.4 Hz, OH), 2.84–2.55 (m, 4 H, $CH_2CH_2$ of Lev), 2.190, 2.174, 2.144, 2.098, 2.073, 2.053, 1.967, 1.964, 1.958 (9 s, 27 H, 9 Ac).

O-*(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-(1 → 3)-*O*-(4,6-di-*O*-acetyl-2-*O*-levulinoyl-β-D-galactopyranosyl)-(1 → 3)-2-azido-4,6-di-*O*-acetyl-2-deoxy-D-galactopyranosyl bromide* (**55**).—To a solution of the hemiacetal **54** (50.0 mg) and $CBr_4$ (172 mg, 519 mmol) in THF (1.0 mL) at 0°C was added hexamethylphosphorustriamide (HMPT, 47.2 μL, 207 μmol) under Ar. After 30 min the mixture was brought to room temperature, an additional 172 mg of $CBr_4$ and 47.2 μL of HMPT was added and the mixture was stirred for a further 2 h. Dilution with EtOAc, washing with aq $NaHCO_3$), drying ($MgSO_4$) and evaporation in vacuo gave a residue that was purified by column chromatography over silica gel (5 g) in 5:4 THF–toluene to give a crude batch of compound **55** (45.8 mg); $R_f$ 0.29 (5:4 THF–toluene).

*Allyl* O-*(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-(1 → 3)-[*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 2)]-*O*-(4,6-di-*O*-acetyl-β-D-galactopyranosyl)-(1 → 3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside* (**56**) *and allyl*

*O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-galactopyranosyl)-(1 → 3)-[O-(2,3,4-tri-O-benzyl-β-L-fucopyranosyl)-(1 → 2)]-O-(4,6-di-O-acetyl-β-D-galactopyranosyl)-(1 → 3)-2-azido-4,6-O-benzylidene-2-deoxy-β-D-galactopyranoside* (**57**).—To a stirred mixture of compund **51** (82.0 mg, 90.0 mmol), **40** (395 mg, 850 mmol), and powdered 4A molecular sieves (917 mg) in $(CH_2Cl)_2$ (0.4 mL) was added $CH_3OSO_2CF_3$ (96.0 μL, 850 mmol) at 0°C under Ar. The mixture was adjusted to room temperature, and stirring was continued for 4 h, at which time the mixture was neutralized with $Et_3N$ (96 μL), diluted with $CHCl_3$, and filtered through Celite. The filtrate was successively washed with aq $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated in vacuo. The residue was chromatographed on silica gel in 30:40:1 THF–toluene–$Et_3N$, to give **56** (86.0 mg, 72.0%) and **57** (9.60 mg, 8.0%).

Compound **56** had $[\alpha]_D^{20}$ +12.1° (*c* 0.46); $R_f$ 0.41 in 3:4 THF–toluene. NMR data: $\delta_H$ 7.48–7.22 (m, 20 H, Ar), 6.022 (m, 1 H, $CH_2CH$:$CH_2$), 5, 756 (d, 1 H, *J* 9.5 Hz, NH), 5.535 (s, 1 H, PhC*H*), 5.428 (d, 1H, *J* 4.0 Hz, H-1d), 5.402 (m, 1 H, $CH_2CH$:C$H_2$), 5.38–5.37 (m, 2 H, H-4b and H-4c), 5.283 (m, 1 H, $CH_2CH$:C$H_2$), 5.156 (d, 1 H, *J* 3.7 Hz, H-1c), 4.878 (d, 1 H, *J* 7.3 Hz, H-1b), 4.861 (dd, 1 H, *J* 3.1, 11.6 Hz, H-3c), 4.542 (ddd, 1 H, *J* 3.1, 9.5 Hz, H-2c), 4.472 (d, 1 H, *J* 7.9 Hz, H-1a), 4.118 (dd, 1 H, *J* 4.0, 10.1 Hz, H-2d), 4.034 (dd, 1 H, *J* 7.3, 9.8 Hz, H-2b), 3.935 (dd, 1 H, *J* 3.4, 9.8 Hz, H-3b), 3.887 (dd, 1 H, *J* 7.9, 10.7 Hz, H-2a), 3.743 (t, *J* 7.0 Hz, H-5b), 3.590 (dd, 1 H, *J* 3.4, 10.7 Hz, H-3a), 2.091, 2.061, 2.037, 1.980, 1.960, and 1.917 (6 s, 18 H, 6 Ac), 0.740 (d, 1 H, *J* 6.4 Hz, $CH_3$ of Fuc). Anal. Calcd for $C_{67}H_{80}N_4O_{24}$: C, 60.72; H, 6.08; N, 4.23. Found: C, 60.48; H, 5.94; N, 4.08.

Compound **57** had $[\alpha]_D^{24}$ +64.3° (*c* 0.07); $R_f$ 0.46 in 3:4 THF–toluene. NMR data: $\delta_H$ 7.48–7.24 (m, 20 H, Ar), 5.953 (m, 1 H, $CH_2CH$:$CH_2$), 5.675 (d, 1 H, *J* 9.5 Hz, NH), 5.518 and 5.320 (2 d, 2 H, *J* 2.4 and 3.1 Hz, H-4b and H-4c), 5.369 (s, 1 H, PhC*H*), 4.992 (d, 1 H, *J* 3.4 Hz, H-1c), 4.954 (d, 1 H, *J* 7.9 Hz, H-1b), 4.649 (d, 1 H, *J* 7.3 Hz, H-1d), 4.604 (ddd, 1 H, *J* 3.4, 9.5, 10.7 Hz, H-2c), 4.130 (d, 1 H, *J* 7.9 Hz, H-1a), 3.415 (dd, 1 H, *J* 3.4, 10.4 Hz, H-3a), 2.154, 2.141, 1.994, 1.982, 1.933, and 1.857 (6 s, 18 H, 6 Ac), 1.059 (d, 1 H, *J* 6.4 Hz, $CH_3$ of Fuc). Anal. Calcd for $C_{67}H_{80}N_4O_{24}$: C, 60.72; H, 6.08; N, 4.23. Found: C, 60.54; H, 6.01; N; 3.96.

*Allyl N-(9-fluorenylmethoxycarbonyl)-{O-[(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-galactopyranosyl)-(1 → 3)-O-(4,6-di-O-acetyl-2-O-levulinoyl-β-D-galactopyranosyl)-(1 → 3)-(2-azido-4,6-di-O-acetyl-2-deoxy-α-D-galactopyranosyl)]-(1 → 3)}-L-serine* (**58**).—*(a) By coupling of* **32** *and* **55**. A solution of the compound **32** (49.1 mg, 134 μmol) in 2:3 toluene–$CH_2Cl_2$ (1 mL) was stirred under Ar at room tempetrature in the dark with $Ag_2CO_3$ (13.4 mg, 48.6 μmol) and 4A molecular sieves (100 mg). After 1 h, $AgClO_4$ (1.3 mg, 6.4 μmol) was added directly, and after 20 min, a solution of the bromide **55** (45.8 mg) was added. The mixture was stirred for a further 72 h, diluted with EtOAc, filtered through Celite, washed with aq $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated in vacuo. Gel-permeation chromatography of the residue on Bio-Beads (S-X4) in toluene (100 mL), followed by preparative TLC in 2:3 THF–toluene gave **58** (7.4 mg, 12.3%, based on **53**) and presumably the corresponding β-product (0.2 mg, $R_f$ 0.46, 2:3 THF–toluene).

Compound **58** had $[\alpha]_D^{22}$ +70.5° (*c* 0.37); $R_f$ 0.44 (5:4 THF–toluene). NMR data: $\delta_H$ 7.77–7.32 (m, 8 H, Ar), 6.026 (d, 1 H, *J* 9.5 Hz, NHAc), 5.943 (d, 1 H, *J* 7.6 Hz,

SerNH), 5.97–5.90 (m, 1 H, $CH_2CH$:$CH_2$), 5.472 (d, 1 H, *J* 2.1 Hz, H-4), 5.427 (d, 1 H, *J* 3.4 Hz, H-4), 5.360 (d, 1 H, $J_{trans}$ 17.0 Hz, $CH_2CH$:$CH_2$), 5.362 (d, 1 H, *J* 3.4 Hz, H-4), 5.288 (dd, 1 H, $J_{cis}$ 10.4 Hz, $CH_2CH$:$CH_2$), 5.072 (dd, 1H, *J* 7.9, 10.4 Hz, H-2b), 5.057 (d, 1 H, *J* 3.4 Hz, H-1c), 4.999 (dd, 1 H, *J* 3.0, 11.3 Hz, H-3c), 4.916 (d, 1 H, *J* 3.4 Hz, H-1a), 4.699 (d, 2 H, *J* 5.2 Hz, $CH_2CH$:$CH_2$), 4.625 (d, 1 H, *J* 7.9 Hz, H-1b), 4.236 (br t, 3 H, $CH_2OCONH$ and H-5c), 4.002 (m, 2 H, H-3b and Ser$\beta$H), 3.802 (t, 1 H, *J* 6.4 Hz, H-5b), 3.740 (s, 1 H, H-5a), 2.86–2.59 (5 t, 4 H, $CH_2CH_2$ of Lev), 2.184, 2.164, 2.146, 2.097, 2.036, 2.028, 2.009, 1.965, 1.961 (9 s, 27 H, 9 Ac). Anal. Calcd for $C_{60}H_{73}N_3O_{28} \cdot 2H_2O$: C, 53.45; H, 5.75; N, 5.19. Found: C, 53.99; H, 5.66; N, 4.63.

*(b) By debenzylidenation and subsequent acetylation of* **38**. Compound **38** (6.1 mg, 4.63 $\mu$mol) was reacted with aq 80% AcOH (310 $\mu$L) and then acetylated using $Ac_2O$ (140 $\mu$L), pyridine (122 $\mu$L), and DMAP (0.1 mg) (according to the procedure for preparing compound **53**) to yield **58** (4.60 mg, 75.6%); $[\alpha]_D^{24}$ +52.2° (*c* 0.23). $^1$H NMR data was consistent with the data as shown above. Anal. Calcd for $C_{60}H_{70}N_5O_{28}$: C, 54.92; H, 5.60; N, 5.34. Found: C, 54.88; H, 5.66; N, 4.75.

*Propyl* N-*(9-fluorenylmethoxycarbonyl)-{*O-*{*O-*(2-acetamido-3,4,6-tri-*O-*acetyl-2-deoxy-*$\alpha$-D-*galactopyranosyl)-(1 → 3)-[*O-*(2,3,4-tri-*O-*benzyl-*$\alpha$-L-*fucopyranosyl)-(1 → 2)]-*O-*(4,6-di-*O-*acetyl-*$\beta$-D-*galactopyranosyl)-(1 → 3)-(2-azido-4,6-di-*O-*acetyl-deoxy-*$\alpha$-D-*galactopyranosyl)}-(1 → 3)}-*L-*serine* (**60**).—Compound **58** (14.6 mg, 11.2 $\mu$mol) was delevulinoylated according to the usual procedure by using hydrazine acetate (5.2 mg, 56.0 $\mu$mol) in 5:1 EtOH–toluene (1 mL); however, this experiment required an extended reaction time of 3 h to fully deblock the levulinoyl group as monitored by TLC. The mixture was diluted with EtOAc, evaporated in vacuo, and purified by silica gel chromatography to afford 7.7 mg (6.3 $\mu$mol) of **59**. The product was then reacted with donor **40** (31.8 mg, 68.4 $\mu$mol), $CuBr_2$ (23.0 mg, 103 $\mu$mol), $^n Bu_4NBr$ (3.7 mg, 11.4 $\mu$mol), $AgOSO_2CF_3$ (26.5 mg, 103 $\mu$mol), and 4A molecular sieves (200 mg) in 5:1 dichloroethane–toluene (1.2 mL) in the manner as described for the preparation of compound **3**, to yield **60** (4.0 mg, 38.7%, based on **59**). According to TLC, presumably a $\beta$-product spot appeared at $R_f$ 0.44 (1:1 toluene–THF); however, minimal quantities could not be isolated.

Compound **60** had $[\alpha]_D^{18}$ +38.0° (*c* 0.20); $R_f$ 0.41 (1:1 toluene–THF). NMR data: $\delta_H$ 7.77–7.23 (m, 23 H, Ar), 5.905 (d, 1 H, *J* 7.6 Hz, NHAc), 5.676 (d, 1 H, *J* 9.8 Hz, SerNH), 5.568 (d, 1 H, *J* 3.0 Hz, H-4a), 5.439 (d, 1H, *J* 3.7 Hz, H-1d), 5.358 (br s, 1 H, H-4b), 5.177 (d, 1 H, *J* 3.7 Hz, H-1c), 5.047 (br s, 1 H, H-4c), 4.954 and 4.819 (2 d, 2 H, $PhCH_2$), 4.668 (d, 1 H, *J* 7.9 Hz, H-1b), 4.582 (m, 1 H, H-2c), 3.760 (br s, 1 H, H-4d), 3.363 (dd, 1 H, *J* 3.4, 10.7 Hz, H-3a), 2.113, 2.092, 2.076, 2.026, 2.010, 1.972, 1.941 (7 s, 24 H), 1.941 (6 H, 8Ac), 1.712 (m, 2 H, $OCH_2CH_2CH_3$), 1.162 (d, 3 H, *J* 6.7 Hz, $CH_3$ of Fuc), 0.954 (t, 3 H, *J* 7.3 Hz, $OCH_2CH_2CH_3$). FABMS (positive-ion): *m/z* 1630 ($M^+ + 1$), 1654 ($M^+ + Na$).

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