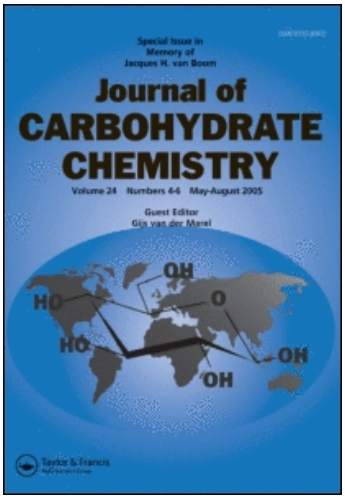


Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Novel Synthetic Approaches to Manβ1-4GLCNAc and Le^x Units from *N*-Acetyllactosamine

Ken-ichi Sato[a]; Hiroshi Seki[a]; Akira Yoshitomo[a]; Hiroshi Nanaumi[a]; Yoshimitsu Takai[a]; Yoshiharu Ishido[b]

[a] Laboratory of Organic Chemistry, Faculty of Engineering, Kanagawa University, Yokohama, Japan [b] Laboratory of Pharmaceutical Chemistry, School of Pharmacy, Tokyo University of Pharmacy and Life Science, Tokyo, Japan

To cite this Article Sato, Ken-ichi , Seki, Hiroshi , Yoshitomo, Akira , Nanaumi, Hiroshi , Takai, Yoshimitsu and Ishido, Yoshiharu(1998) 'Novel Synthetic Approaches to Manβ1-4GLCNAc and Le^x Units from *N*-Acetyllactosamine', Journal of Carbohydrate Chemistry, 17: 4, 703 — 727

To link to this Article: DOI: 10.1080/07328309808002347

URL: http://dx.doi.org/10.1080/07328309808002347

J. CARBOHYDRATE CHEMISTRY, 17(4&5), 703-727 (1998)

NOVEL SYNTHETIC APPROACHES TO MANβ1-4GLCNAc AND Le^x UNITS FROM *N*-ACETYLLACTOSAMINE[1]

Ken-ichi Sato,* Hiroshi Seki, Akira Yoshitomo, Hiroshi Nanaumi,
Yoshimitsu Takai and Yoshiharu Ishido†

Laboratory of Organic Chemistry, Faculty of Engineering, Kanagawa University,
Rokkakubashi, Kanagawa-ku, Yokohama, Japan 221

†Laboratory of Pharmaceutical Chemistry, School of Pharmacy,
Tokyo University of Pharmacy and Life Science,
1432-1 Horinouchi, Hachioji, Tokyo, Japan 192-03

Final Form February 24, 1998

ABSTRACT

Regioselective protection of *N*-acetyllactosamine with triphenylmethyl (trityl) and pivaloyl groups afforded the corresponding 3, 2', 4'-tri- and 2',4'-dihydroxyl derivatives in a few steps, respectively; these derivatives were used efficiently for the syntheses of the title compounds from *N*-acetyllactosamine in 46% (7 steps) and 19% (8 steps) overall yields, respectively.

INTRODUCTION

N-Acetyllactosamine (**1**, Galβ1-4GlcNAc) is one of the important components commonly occurring in oligosaccharides, and is biologically essential and of interest from the mechanistic viewpoint of structural biology such as intermolecular recognition in living systems. Hitherto, *N*-acetyllactosamine has been merely available by chemical synthesis from monosaccharides,[2] and from lactal.[3] Recently, an efficient synthesis of **1** has been established through the enzymatic trans-β-D-galactopyranosylation from lactose to the 4-position of 2-acetamido-2-deoxy-β-D-glucopyranose,[4] and **1** is now easily available. Therefore, the authors undertook the present investigation on the chemical syntheses of the title oligosaccharides by the use of **1** as the starting material, which was expected to show

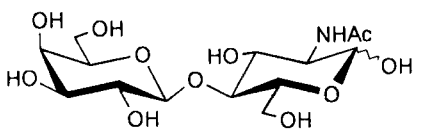
unique regioselectivity on the introduction of protecting groups, and enable us to develop a novel strategy in the synthesis of *N*-acetyllactosamine-derived oligosaccharides. The results thus obtained will be described in full herein.

RESULTS AND DISCUSSION

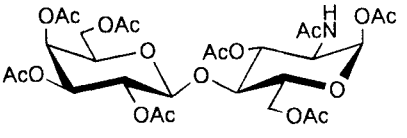
Regioselective Protection of Allyl O-(β-D-Galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (**4**): Compound **1** was converted into **4**, by way of *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose (**2**) and the oxazoline intermediate (**3**).[5] The resulting **4** was then subjected to regioselective triphenylmethylation and pivaloylation reactions under controlled conditions. (Figure 1)

Triphenylmethylation of methyl β-D-galactopyranoside with the bis(tributyltin) oxide [$(Bu_3Sn)_2O$] - triphenylmethyl chloride (TrCl) system has been reported by Ogawa *et al.*[6] to give the corresponding 2,6-di-*O*-triphenylmethyl derivative in 72% yield. This approach was of interest to us in connection with triphenylmethylation of **4**, which was thus treated with $(Bu_3Sn)_2O$ (2.25 equiv) and TrCl (4.5 equiv) in toluene to give 6,3',6'-tri-*O*-triphenylmethyl derivative **5** and 6,2',6'-tri-*O*-triphenylmethyl derivative in 58 and 14% yields (ca. 4:1), respectively. Their structures were confirmed by formation of the corresponding 3,2',4'-triacetate **6** and 3,3',4'-triacetate in quantitative yields on acetylation in the usual manner. The formation of **5** likely reflects the steric effect of 2-acetamido-2-deoxy-D-glucopyranos-4-yl moiety on the 2'-position of **4**.

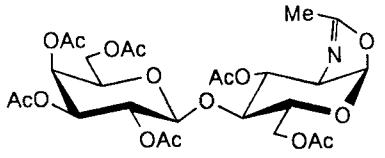
In view of the bulkiness of the pivaloyl group, moreover, regioselective pivaloylation of **4** was performed by treatment with $(Bu_3Sn)_2O$ (5.0 equiv) and pivaloyl chloride (7.0 equiv) in 1:1 acetonitrile-benzene, to give the corresponding 6,3',6'-tri-*O*-pivaloyl derivative **7** in 56% yield as the main product along with three by-products. The more polar by-product (based on **7**) seems to be di-*O*-pivaloyl derivative and two less polar products seem to be tri- and tetra-*O*-pivaloyl products. ^1H NMR data of one of the less polar products is identical with that of 3,6,3',6'-tetra-*O*-pivaloyl derivative **8**. The ratio of the by-products was ca. 1:1:3 in order of the polarity (less → more) on TLC. On the other hand, it was interesting to have found that pivaloylation of **4** with pivaloyl chloride (5.0 equiv) in a mixture of dichloromethane - pyridine at 0 °C gave **8** in 60% yield. Compound **8** was also expected to be one of the most useful intermediates for the synthesis of Manβ1-4GlcNAc unit **10** in view of the efficient chemical conversion of β-D-galactopyranosides 2,4-bis(triflate) into the corresponding β-D-mannopyranosides by way of simultaneous inversion reactions at both the 2- and 4- positions.[7]



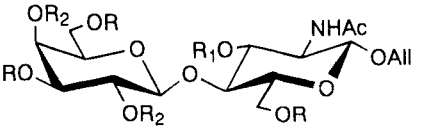
1



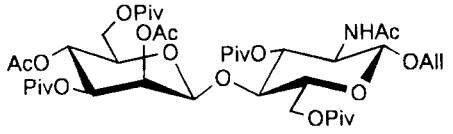
2



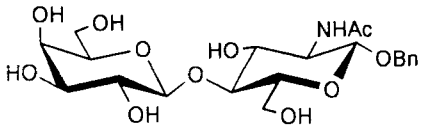
3



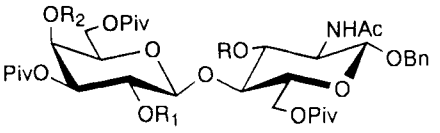
4 R = R_1 = R_2 = H
5 R = Tr, R_1 = R_2 = H
6 R = Tr, R_1 = R_2 = Ac
7 R = Piv, R_1 = R_2 = H
8 R = R_1 = Piv, R_2 = H
9 R = R_1 = Piv, R_2 = Tf



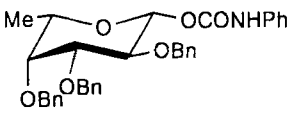
10



11



12 R = R_1 = R_2 = H
13 R = Troc R_1 = R_2 = H
14 R = H R_1 = R_2 = Ac
15 R = Fuc R_1 = R_2 = Ac



16

Ac : acetyl
All : allyl
Bn : benzyl
Piv : pivaloyl
Tf : trifluoromethanesulfonyl
Troc : 2,2,2-trichloroethoxycarbonyl

Figure 1

Similar to **4**, the bis(tributyltin) oxide-mediated regioselective pivaloylation reaction of the corresponding benzyl β-D-lactosaminide **11** resulted in the formation of 6,3',6'-tri-*O*-pivaloyl derivative **12** in 73% yield. Compound **12**, on treatment with 2,2,2-trichloroethoxycarbonyl chloride (TrocCl) in dichloromethane - pyridine at 0 °C, gave the corresponding 3-*O*-Troc derivative **13** in 70% yield. Compound **13** obtained here is a potential candidate as the substrate for the 3-*O*-L-fucopyranosylation reaction to give the Le^x unit.

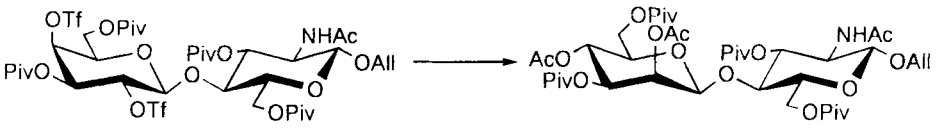
Incidentally, the above experiments provided us with insight into the reactivity order of the secondary hydroxyl groups of **4** as 3'-OH > 3-OH > 2'-OH, 4'-OH, although that reported for those of β-D-lactoside derivative in a benzoylation reaction was 3'-OH > 2-OH > 2'-OH, 4'-OH > 3-OH.[8] Moreover, these products, bearing free hydroxyl groups at 2'- and 4'- or 3-, 2'-, and 4'- positions are potentially practical material for the synthesis of Manβ1-4GlcNAc and Le^x units, respectively.

Efficient Chemical Conversion of ***1*** *into Manβ1-4GlcNAc*: In view of the occurrence of a β-D-mannopyranosidic structure in tumor-associated oligosaccharides,[9] construction of the β-D-mannopyranosidic linkage at the 4-position of 2-acetamido-2-deoxy-D-glucopyranose (GlcNAc) has been investigated through a variety of multi-step methodologies involving oxidation-reduction,[10-19] intramolecular aglycon delivery,[20-25] S_N2 reaction at *C*-2-position,[26-29] direct glycosylation by the use of mannosyl halide,[30] mannosyl sulfoxide,[31] or mannosyl 1,2-*O*-stannylene acetal,[32] and glycosidase-catalyzed transglycosylation.[33,34] Further elaboration of this construction is now feasible on the basis of our present results.

On the other hand, the formation of **8** in the regioselective pivaloylation as described above prompted us to explore its possibility in chemical conversion of its 4-*O*-β-D-galactopyranosyl moiety into the β-D-mannopyranoside structure by the simultaneous S_N2 reaction at both the 2'- and 4'-positions. This strategy starting from **1** seems to provide us an alternative efficient synthetic approach to Manβ1-4GlcNAc.

Compound **8** was first converted into the corresponding 2',4'-bis(triflate) quantitatively by treatment with trifluoromethanesulfonic anhydride (2.1 equiv) in the presence of pyridine in dichloromethane at 0 °C. Compound **9** was then subjected to the simultaneous nucleophilic substitution reaction at both 2'- and 4'- positions with cesium acetate or tetrabutylammonium acetate; the results thus obtained are summarized in Table 1. Among the reactions as seen from Entry 1, cesium acetate (6.0 equiv) gave allyl *O*- (2,4-di-*O*-acetyl-3, 6-di-*O*-pivaloyl-β-D-mannopyranosyl)-(1→ 4)-2-acetamido-2-deoxy-3, 6-di-*O*-pivaloyl-β-D-glucopyranoside (**10**) (93% yield) when the reaction was conducted in combination with 18-crown-6 (6.0 equiv) in toluene[35] under reflux for 1 h. Moreover, it was of interest that ultrasound irradiation by the use of an ordinary sonicator (reaction time: 12 h) facilitated the reaction to give a competitive yield of **10** (92%) even at room temperature (Entry 2). A comparative experiment using tetra-butylammonium acetate[27] was confirmed to give **10** in 43% yield (Entry 7).

The efficiency of the ultrasound irradiation observed in the chemical conversion of **9** into **10** (Entry 2 in Table 1) led us to investigate the potential effect of protecting groups on the neighboring hydroxyl groups at the 3- and 6- positions by the use of benzyl 3,6-di-*O*-allyl- (**22**), -pivaloyl- (**23**), -benzyl- (**24**), and -allyloxycarbonyl- (**25**) β-D-



9 10

Table 1. Effects of reaction conditions on S_N2 reaction of **9** into **10**[a]

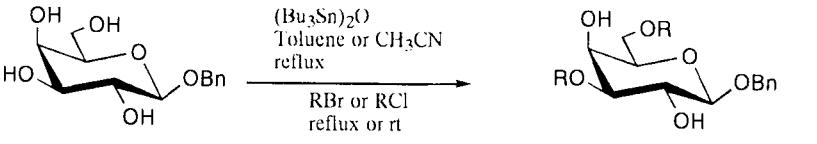
Entry	Acetate	Additive	Solvent	Temp	Time (h)	Yield (%)
1	CsOAc	18-crown-6	Toluene	reflux	1	93
2	CsOAc	18-crown-6	Toluene	rt[b]	12	92
3	CsOAc	18-crown-6	DMF	rt	10	59
4	CsOAc	18-crown-6	DMSO	rt	10	62
5	CsOAc	——	DMF	rt	24	36
6	CsOAc	——	DMSO	rt	24	39
7	*n*-Bu_4NOAc	——	Toluene	rt	24	43

a. The reaction was carried out under following conditions : **9** 0.13 - 0.16 mmol ; Acetate 5.6 - 6.3 equiv ; Additive 5.7 - 6.0 equiv ; Solvent 5.0 - 6.0 mL.
b. Under ultrasonication in a water bath.

galactopyranosides 2,4-bis(triflates) (Scheme 1) toward the S_N2 reaction with cesium acetate; the results thus obtained are summarized in Table 2. The protection with acyl groups (Entry 2,4), in contrast with that with ether-type groups (Entry 1,3), is likely to accelerate the S_N2 reaction judging from the yields of the resulting 2,4-diacetates **26** (69% yield), **27** (88% yield), **28** (62% yield), and **29** (89% yield). In particular, the reactions of **22** and **24** were not completed after 12 h judging from their TLC, and thus they were further continued under reflux for another 12 h. Monitoring these reactions by TLC demonstrated the practical advantage of ultrasound irradiation over conventional reflux conditions giving rise to a rather neat profile on TLC.

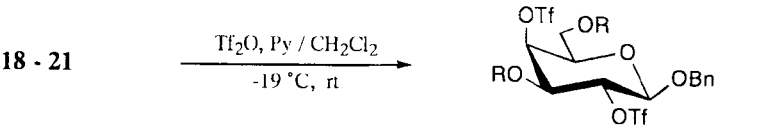
Synthesis of a Tumor Associated Antigen Lewis X (Le^x): The Le^x unit {Galβ(1→4)[Fucα(1→3)]GlcNAc} has been well known as a prominent tumor-associated antigen[36] and an interesting target in synthetic carbohydrate chemistry.[37-50]

Compound **13**, which was obtained by the reaction of **12** with TrocCl, was converted into the corresponding 2',4'-diacetate by treatment with acetic anhydride in pyridine in the usual manner, and the diacetate was then treated with zinc powder in aqueous acetic acid to give benzyl *O*-(2,4-di-*O*-acetyl-3,6-di-*O*-pivaloyl-β-D-galacto-pyranosyl)-(1→4)-2-acetamido-2-deoxy-6-*O*-pivaloyl-β-D-glucopyranoside (**14**) in 96% overall yield from **13**. In the present study, for the first time, 3-*O*-L-fucopyranosylation of



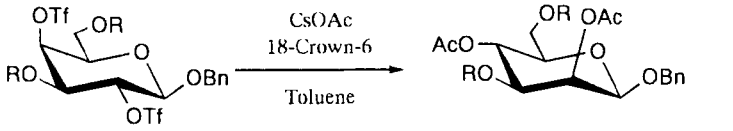
17

18 R = All y. 72%
19 R = Piv y. 86%
20 R = Bn y. 76%
21 R = CO_2All y. 81%



22 R = All y. quant.
23 R = Piv y. 98%
24 R = Bn y. quant.
25 R = CO_2All y. quant.

Scheme 1



22 - 25 **26 - 29**

Table 2. Simultaneous S_N2 reactions of 2,4-bis(triflates) **22** - **25** into **26** - **29**[a]

Entry	Substrate	Temp	Time (h)	Product	Yield (%)
1	**22** R = All	rt → reflux	24[b]	**26**	69
2	**23** R = Piv	rt	12[c]	**27**	88
3	**24** R = Bn	rt → reflux	24[b]	**28**	62
4	**25** R = CO_2All	rt	12[c]	**29**	89

a. The reaction was carried out under following conditions : Substrate 0.16 - 1.35 mmol ; CsOAc 2.8 - 3.0 equiv ; 18-crown-6 2.8 - 3.2 equiv ; toluene 10 - 20mL.
b. Under ultrasonication in a water bath for 12 h, then reflux for 12 h.
c. Under ultrasonication in a water bath.

14 was performed by the use of 2,3,4-tri-*O*-benzyl-1-*O*-(phenylcarbamoyl)-*β*-L-fucopyranose (**16**; α/β = 1:3; 1.2 equiv) in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) in dichloromethane at 0 °C. The glycosylation of **14** with **16** is mechanistically characterized by the concomitant formation of **15** and *N*-phenylcarbamic acid, latter of which is easily decomposed into carbon dioxide and aniline; the aniline thus formed reacts with the acidic catalyst and loses its nucleophilicity by the formation of anilinium triflate.[52a] This is in contrast with the reaction of an alcohol with a 1-*O*-phenyloxycarbonyl sugar derivative as a glycosylating agent, which gives a phenyl glycoside as the by-product in addition to an objective alkyl glycoside.[51, 52b] This approach was found to give the 3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl) derivative of **14** (**15**) in 58% yield, as expected.[53] Although formation of the corresponding *β*-L-fucopyranosyl derivative was deduced *via* TLC of the resulting mixture, another smaller product spot with higher polarity but very close to that from **15**, was observed. However, separation of the minor product in pure form from **15** was impossible in spite of repeated chromatography.

EXPERIMENTAL

General Methods. All melting points were determined using a Yanagimoto apparatus and are uncorrected. Solvents were evaporated under reduced pressure at a bath temperature not exceeding 40 °C. Optical rotations were measured in a 0.5 dm tube with a JASCO DIP-140 polarimeter. ^{1}H NMR spectra were recorded in chloroform-*d* unless otherwise stated, with a JEOL FX-200, JEOL EX-270, or JEOL A-500 spectrometer. IR spectra were recorded with a Hitachi 270-30 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C or 2400 II elemental analyzer. The chemical shifts, coupling constants, and IR frequencies were recorded in *δ*, Hz, and cm^{-1} units, respectively. Column chromatography was performed on silica gel (Silica gel 60, 70 - 230 mesh, Merck) unless otherwise stated. Thin-layer chromatography (TLC) on silica gel (Silica gel 60F254, Merck) was used to monitor the reactions and to certify the purity of the reaction products.

***O*-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl)- (1 → 4) -2-acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranose (2).** A mixture of **1** (500 mg, 1.31 mmol), acetic anhydride (6.0 mL) , and 4-dimethylaminopyridine (30 mg) in pyridine (8.0 mL), was stirred at room temperature for 18 h. The reaction mixture was diluted with chloroform, washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated to give a residue, which was purified on a column of silica gel

(Wakogel C-300) with hexane/ethyl acetate (1:3 v/v) to afford **2** (861 mg, 97%): mp 222 - 223 °C (ethanol-hexane); IR 1758 cm^{-1} (C=O), 1677 cm^{-1} (amido); $[\alpha]_D^{26}$ + 62 ° (*c* 1.2, $CHCl_3$); ^1H NMR (FX-200) δ 6.10 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.69 (d, 1H, $J_{2,NH}$ = 9.3 Hz, NH), 5.36 (d, 1H, $J_{3',4'}$ = 3.7 Hz, $J_{4',5'}$ = 0 Hz, H-4'), 5.23 (dd, 1H, $J_{2,3}$ = 11.5 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 5.13 (dd, 1H, $J_{1',2'}$ = 7.8 Hz, $J_{2',3'}$ = 10.5 Hz, H-2'), 4.97 (dd, 1H, H-3'), 4.53 (d, 1H, H-1'), 4.38 (ddd, 1H, H-2), 4.44-4.04 (m, 4H, H-6a, H-6b, H-6'a, H-6'b), 3.93-3.87 (m, 3H, H-4, H-5, H-5'), 2.19, 2.16, 2.12, 2.10, 2.07, 1.97, 1.94 (each s, 7 x 3H, 7 x OAc), 1.94 (s, 3H, NAc).

Anal. Calcd for $C_{28}H_{39}NO_{18}$: C, 49.63; H, 5.80; N, 2.07. Found: C, 49.46; H, 5.78; N, 1.96.

***O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)- (1→ 4) -2-methyl-(3,6-di-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-2-oxazoline (3).** To a solution of **2** (1.34 g, 1.98 mmol) in 1,2-dichloroethane (23 mL), trimethylsilyl trifluoromethanesulfonate (0.40 mL) was added at 0 °C, and kept at 50 °C for 5 h. The reaction mixture was neutralized with triethylamine at room temperature and concentrated to give a residue, which was purified on a column of silica gel (Wakogel C-300) with hexane/ethyl acetate/triethylamine (100:200:1 v/v/v) to afford **3** (1.05 g, 86%): amorphous powder; IR 1746 cm^{-1} (C=O), 1536 cm^{-1} (C=N); $[\alpha]_D^{20}$ +17.0 ° (*c* 1.1, $CHCl_3$); ^1H NMR (FX-200) δ 5.92 (d, 1H, $J_{1,2}$ = 7.3 Hz, H-1), 5.66 (d, 1H, $J_{2,3}$ = 2.2 Hz, $J_{3,4}$ = 0 Hz, H-3), 5.38 (d, 1H, $J_{3',4'}$ = 3.2 Hz, $J_{4',5'}$ = 0 Hz, H-4'), 5.19 (dd, 1H, $J_{1',2'}$ = 8.1 Hz, $J_{2',3'}$ = 10.3 Hz, H-2'), 5.01 (dd, 1H, H-3'), 4.65 (d, 1H, H-1'), 4.24-4.02 (m, 5H, H-2, H-6a, H-6b, H-6'a, H-6'b), 3.96 (dd, 1H, $J_{5',6'a} = J_{5',6'b}$ = 6.8 Hz, H-5'), 3.66 (d, 1H, $J_{4,5}$ = 9.3 Hz, H-4), 3.53 (m, 1H, H-5), 2.17, 2.12, 2.10, 2.05, 2.04, 1.96 (each s, 6 x 3H, 6 x OAc), 1.71 (s, 3H, Me).

Anal. Calcd for $C_{26}H_{35}NO_{16}$: C, 50.56; H, 5.71; N, 2.27. Found: C, 50.23; H, 5.80; N, 2.21.

Allyl *O*-(β-D-Galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (4). To a stirred solution of allyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside[5] (200 mg, 0.315 mmol) in MeOH (30 mL), NaOMe/MeOH (Na, 90 mg/MeOH, 5.0 mL) was added dropwise, and kept at room temperature until the disappearance of the starting compound (for 3 h). The reaction mixture was neutralized with Dowex 50W-X8 (H^+), then the resin was filtered off, and the filtrate was concentrated to give **4** (133 mg, quant.): mp 269 - 270 °C (ethanol-hexane); $[\alpha]_D^{24}$ - 35.0 ° (*c* 0.3, MeOH); IR 3268 cm^{-1} (OH), 1653 cm^{-1} (amido C =O); ^1H NMR in D_2O (FX-200) δ 5.28 - 5.11 (m, 1H, -CH_2-CH=CH_2), 4.65 - 4.54 (m, 2H, CH_2-CH=CH_2), 3.90 and 3.76 (each d, 2 x 1H, $J_{1,2}$

$=J_{1',2'}$ = 7.6 Hz, H-1 and H-1'), 3.67 - 3.41 (m, 2H, -C*H*$_2$-CH=CH$_2$), 3.33 - 2.79 (m, 12H, H-2 - H-6b, H-2' - H-6b'), 1.34 (s, 3H, NAc).

Anal. Calcd for $C_{17}H_{29}NO_{11}$: C, 48.22; H, 6.90; N, 3.31. Found: C, 48.28; H, 6.82; N, 3.29.

Allyl *O*-(2,4-Di-*O*-acetyl-3,6-di-*O*-triphenylmethyl-β-D-galacto-pyranosyl)-(1→4)-2-acetamido-3-*O*-acetyl-2-deoxy-6-*O*-triphenylmethyl-β-D-glucopyranoside (6). A mixture of **4** (210 mg, 0.496 mmol) and bis(tributyltin) oxide (664 mg, 2.24 equiv) in toluene was refluxed for 6 h by the use of a Dean-Stark apparatus (with Molecular Sieves 4A). To this reaction mixture, triphenylchloromethane (620 mg, 4.48 equiv) was added at room temperature, and the reaction mixture was stirred at 60 °C for 46 h, then concentrated to give syrupy crude allyl *O*-(3,6-di-*O*-triphenylmethyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-6-*O*-triphenylmethyl-β-D-glucopyranoside (**5**) and its 6,2',6'-tri-*O*-triphenylmethyl derivative. The crude mixture was converted into the corresponding acetyl derivatives (acetylated with acetic anhydride-pyridine, quantitative yields) for purification. The crude acetylated products were purified on a column of silica gel (Wakogel C-300) with benzene/acetone (3:1 v/v) to afford **6** (367 mg, 58%) and its 6,2',6'-tri-*O*-triphenylmethyl derivative (88 mg, 14%): syrup; $[\alpha]_D^{24}$ - 74.1 ° (*c* 0.6, $CHCl_3$); IR 1755 cm^{-1} (C=O), 1677 cm^{-1} (amido C=O); ^1H NMR (FX-200) δ 7.39 - 7.07 (m, 9 x 5H, 3 x Tr), 5.94 - 5.87 (m, 1H, -CH$_2$-C*H*=CH$_2$), 5.40 - 5.37 (m, 2H, NH and H-4'), 5.30 - 5.18 (m, 2H, -CH$_2$-CH=C*H*$_2$), 5.20 - 5.12 (dd, 1H, H-2'), 4.54 (dd, 1H, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 4.40 - 4.36 (m, 1H, -C*H*$_2$-CH=CH$_2$), 4.25 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1), 4.19 (dd, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 4.15 (d, 1H, $J_{1',2'}$ = 7.6 Hz, H-1'), 4.15 - 4.08 (m, 2H, H-2 and -C*H*$_2$-CH=CH$_2$), 3.62 - 3.59 (dd, 1H, H-3'), 3.55 (dd, 1H, $J_{5,6b}$ = 1.9 Hz, $J_{6a,6b}$ = 10.7 Hz, H-6b), 3.47 (dd, 1H, $J_{5',6'a}$ = 5.8 Hz, $J_{6'a,6'b}$ = 8.3Hz, H-6'a), 3.35 (dd, 1H, $J_{5',6'b}$ = 5.3 Hz, H-6'b), 3.30 (dd, 1H, $J_{5,6a}$ = 2.1Hz, H-6a), 2.94 - 2.89 (m, 1H, H-5'), 2.73 - 2.67 (m, 1H, H-5), 2.16 (each s, 3 x 3H, 3 x OAc), 1.93 (s, 3H, NAc).

Anal. Calcd for $C_{80}H_{77}NO_{14}$: C, 75.27; H, 6.08; N, 1.10. Found: C, 75.72; H, 6.23; N, 1.39.

Allyl *O*-(3,4-Di-*O*-acetyl-2,6-di-*O*-triphenylmethyl-β-D-galacto-pyranosyl)-(1→4)-2-acetamido-3-*O*-acetyl-2-deoxy-6-*O*-triphenylmethyl-β-D-glucopyranoside: ^1H NMR (FX-200) δ 7.39-7.07 (m, 9 x 5H, 3 x Tr), 5.94-5.87 (m, 1H, -CH$_2$-C*H*=CH$_2$), 5.37 (d, 1H, $J_{2,NH}$ = 9.1 Hz, NH), 5.30-5.18 (m, 3H, -CH$_2$-CH=C*H*$_2$ and H-4'), 4.73 (dd, 1H, $J_{2',3'}$ = 10.7 Hz, $J_{3',4'}$ = 2.7 Hz, H-3'), 4.57 (dd, 1H, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 4.40-4.36 (m, 1H, -C*H*$_2$-CH=CH$_2$), 4.29 (d, 1H, $J_{1',2'}$ = 7.6 Hz, H-1'), 4.28-4.21 (m, 2H, H-2 and H-4), 4.15-

4.08 (m, 2H, H-1 and -C*H*$_2$-CH=CH$_2$), 3.59-3.51 (m, 2H, H-6a and H-6'a), 3.39-3.28 (m, 2H, H-6b and H-6'b), 2.94-2.87 (m, 2H, H-2' and H-5'), 2.73-2.67 (m, 1H, H-5), 2.16 (each s, 3 x 3H, 3 x OAc), 1.93 (s, 3H, NAc).

Allyl *O*-(3,6-Di-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-6-*O*-pivaloyl-β-D-glucopyranoside (7). A mixture of **4** (40 mg, 0.094 mmol) and bis(tributyltin) oxide (0.24 mL, 5.0 equiv) in a mixed solvent of acetonitrile/benzene (1:1 v/v, 6.0 mL) was refluxed by the use of a Dean-Stark apparatus with Molecular Sieves 4A for 3 h. To this reaction mixture, pivaloyl chloride (0.08 mL, 7.0 equiv) was added at room temperature, and the reaction mixture was heated at 90 °C for 19 h. The reaction mixture was concentrated to give a residue, which was purified on a column of silica gel (Wakogel C-300) with hexane/ethyl acetate (1:5 v/v) to afford **7** (36 mg, 56%): syrup; $[\alpha]_D^{26}$ + 23.1 ° (*c* 0.9, CHCl3); IR 1722 cm^{-1} (C=O), 1659 cm^{-1} (amido C=O); ^{1}H NMR (A-500) δ 5.98 (d, 1H, $J_{2,\ NH}$ = 7.3 Hz, NH), 5.88 (m, 1H, -CH$_2$-C*H*=CH$_2$), 5.28 - 5.17 (m, 2H, -CH$_2$-CH=C*H*$_2$), 4.81 (dd, 1H, $J_{2',\ 3'}$ = 10.1 Hz, $J_{3',\ 4'}$ = 3.1 Hz, H-3'), 4.70 (d, 1H, $J_{1,\ 2}$ = 8.2 Hz, H-1), 4.68 (bs, 1H, 3-OH), 4.60 (dd, 1H, H-6a), 4.38 (d, 1H, $J_{1',\ 2'}$ = 7.9 Hz, H-1'), 4.31 and 4.07 (each m, 2 x 1H, -C*H*$_2$-CH=CH$_2$), 4.31 (dd, 1H, $J_{6'a,6'b}$ = 11.0 Hz, H-6'a), 4.28 (dd, 1H, H-6'b), 4.18 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, $J_{5,\ 6b}$ = 6.1 Hz , H-6b), 3.99 (dd, 1H, $J_{4',OH}$ = 4.6 Hz, H-4'), 3.97 (dd, 1H, H-3), 3.93 (ddd, 1H, H-2'), 3.83 (dd, 1H, $J_{5',6'a}$ = $J_{5',6'b}$ = 6.1 Hz, H-5'), 3.75 (d, 1H, $J_{2',\ OH}$ = 4.3 Hz, 2'-OH), 3.61 (ddd, 1H, $J_{5,6a}$ = 1.2 Hz, H-5), 3.48 (ddd, 1H, $J_{2,\ 3}$ = 10.1 Hz, H-2), 3.42 (dd, 1H, $J_{3,\ 4}$ = $J_{4,\ 5}$ = 8.9 Hz, H-4), 2.84 (d, 1H, 4'-OH), 1.26, 1.21, and 1.20 (each s, 3 x 9H, 3 x OPiv).

Anal. Calcd for $C_{32}H_{53}NO_{14}$: C, 56.87; H, 7.91; N, 2.07. Found: C, 56.54; H, 7.93; N, 1.80.

Allyl *O*-(2,4-Di-*O*-acetyl-3,6-di-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3-*O*-acetyl-2-deoxy-6-*O*-pivaloyl-β-D-glucopyranoside (7a). The structure of **7** was confirmed from its acetyl derivative **7a** (acetylation with acetic anhydride-pyridine, quantitative yield): Syrup; $[\alpha]_D^{26}$ - 17.1 ° (*c* 1.1, CHCl$_3$); IR 1734 cm^{-1} (C=O), 1671 cm^{-1} (amido C=O); ^{1}H NMR (A-500) δ 5.84 (m, 1H, -CH$_2$-C*H*=CH$_2$), 5.59 (d, 1H, $J_{2,\ NH}$ = 9.5 Hz, NH), 5.41 (dd, 1H, $J_{3',\ 4'}$ = 3.7 Hz, $J_{4',\ 5'}$ = 0.9 Hz, H-4'), 5.27 - 5.17 (m, 2H, -CH$_2$-CH=C*H*$_2$), 5.17 (dd, 1H, H-2'), 5.07 (dd, 1H, $J_{2,\ 3}$ = 9.5 Hz, $J_{3,\ 4}$ = 8.2 Hz, H-3), 4.94 (dd, 1H, $J_{2',\ 3'}$ = 10.4 Hz, H-3'), 4.53 (dd, 1H, $J_{6a,\ 6b}$ =11.9 Hz, $J_{5,\ 6a}$ = 3.1 Hz, H-6a), 4. 49 (d, 1H, $J_{1,\ 2}$ = 7.3 Hz, H-1), 4.48 (d, 1H, $J_{1',\ 2'}$ = 7.9 Hz, H-1'), 4.29 and 4.03 (each m, 2 x 1H, -C*H*$_2$-CH=CH$_2$), 4.13 (dd, 1H, $J_{6'a,\ 6'b}$ = 11.0 Hz, H-6'a), 4.10 (dd, 1H, $J_{6a,\ 6b}$ = $J_{5,\ 6b}$ = 5.5 Hz, H-6b), 4.05 (dd, 1H, H-6'b), 4.02 (ddd, 1H, H-2), 3.89 (ddd, 1H, $J_{5',\ 6'a}$ = $J_{5',\ 6'b}$ = 6.7 Hz, H-5'), 3.74 (dd, 1H, $J_{4,\ 5}$ = 8.2 Hz, H-4), 3.63 (ddd, 1H, H-5), 2.13, 2.08, and

2.03 (each s, 3 x 3H, 3 x OAc), 1.97 (s, 3H, NAc), 1.24, 1.19, and 1.10 (each s, 3 x 9H, 3 x OPiv).

Anal. Calcd for $C_{38}H_{59}NO_{17}$: C, 56.92; H, 7.42; N, 1.75. Found: C, 56.89; H, 7.42; N, 1.44.

Allyl *O*-(3,6-Di-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-3,6-di-*O*-pivaloyl-β-D-glucopyranoside (8). To a solution of **4** (310 mg, 0.732 mmol) in pyridine (3.0 mL) was added dropwise a solution of pivaloyl chloride (479 μL, 5.4 equiv) in dichloromethane (1.0 mL) at 0 °C with stirring. The reaction mixture was stirred for 12 h at room temperature, then diluted with chloroform, and washed with aqueous sodium hydrogen carbonate and water. The organic layer was dried over anhydrous magnesium sulfate, concentrated under reduced pressure to give a residue, which was purified on a column of silica gel (Wakogel C-300) with hexane/ethyl acetate (1:2 v/v) to afford **8** (334 mg, 60%): mp 106 - 108 °C (ethanol-hexane); $[\alpha]_D^{24}$ + 15.2 ° (*c* 0.9, $CHCl_3$); IR 3395 cm^{-1} (OH) and 1725 cm^{-1} (C=O), 1668 cm^{-1} (amido C=O); ^1H NMR (FX-200) δ 5.91 (d, 1H, $J_{2,NH}$ = 9.2 Hz, NH), 5.88 - 5.80 (m, 1H, -CH_2-C*H*=CH_2), 5.30-5.14 (m, 2H, -CH_2-CH=C*H*$_2$), 5.14 (dd, 1H, $J_{2,3}$ = 9.8 Hz, $J_{3,4}$ = 8.9 Hz, H-3), 4.76 (dd, 1H, $J_{2',3'}$ = 10.1 Hz, $J_{3',4'}$ = 3.4 Hz, H-3'), 4.69 (dd, 1H, $J_{6'a,6'b}$ = 2.4 Hz, $J_{5',6'a}$ = 11.9 Hz, H-6'a), 4.50 (d, 1H, $J_{1',2'}$ = 7.6 Hz, H-1'), 4.32 - 4.27 (m, 2H, H-6a and -C*H*$_2$CH=CH_2), 4.25 - 4.16 (m, 2H, H-6'b and H-6b), 4.09 - 4.03 (m, 2H, H-2 and -C*H*$_2$CH=CH_2), 3.93 (d, 1H, H-4'), 3.88 (dd, 1H, $J_{4,5}$ = 9.2 Hz, H-4), 3.78 (dd, 1H, H-2'), 3.71 - 3.68 (m, 2H, H-5 and H-5'), 3.11 (bs, 1H, 2'-OH), 2.35 (bs, 1H, 4'-OH), 1.92 (s, 3H, NAc), 1.23, 1.22, and 1.20 (each s, 4 x 9H, 4 x OPiv).

Anal. Calcd for $C_{37}H_{61}NO_{15}$: C, 58.48; H, 8.09; N, 1.84. Found: C, 58.96; H, 8.32; N, 1.69.

Allyl *O*-[3,6-Di-*O*-pivaloyl-2,4-bis(*O*-trifluoromethylsulfonyl)-β-D-galactopyranosyl]-(1→4)-2-acetamido-2-deoxy-3,6-di-*O*-pivaloyl-β-D-glucopyranoside (9). A solution of trifluoromethanesulfonic anhydride (700 μL, 10.8 equiv) in dichloromethane (2.0 mL) was added dropwise to a mixed solution (dichloromethane, 2.0 mL and pyridine, 613 μL, 19.2 equiv) at -15 ~ -18 °C with stirring, and kept for 5 min. To the reaction mixture, a solution of **8** (300 mg, 0.395 mmol) in dichloromethane (5.0 mL) was added dropwise at - 18 °C and kept for 6 h. The reaction mixture was diluted with dichloromethane, washed with an aqueous solution saturated with sodium hydrogen carbonate, 1% hydrochloric acid, and then cold water. The organic solution was dried over magnesium sulfate, filtered, and concentrated to give **9** (404 mg, quant.): mp 148 - 149 °C (ethanol-hexane); $[\alpha]_D^{24}$ - 8.9 ° (*c* 0.8, $CHCl_3$); IR 1743 cm^{-1}

(C=O), 1668 cm^{-1} (amido C=O); ^1H NMR (FX-200) δ 5.87 - 5.79 (m, 1H, -CH_2-C*H*=CH_2), 5.71 (d, 1H, $J_{2,\ NH}$ = 9.4 Hz, NH), 5.30 (d, 1H, $J_{3',\ 4'}$ = 2.8 Hz, H-4'), 5.27 - 5.16 (m, 2H, -CH_2-CH=C*H*$_2$), 5.17 - 5.15 (m, 1H, H-3'), 5.03 (dd, 1H, $J_{2,\ 3}$ = 10.2 Hz, $J_{3,\ 4}$ = 9.0 Hz, H-3), 4.81 - 4.78 (m, 2H, H-1' and H-2), 4.51 (dd, 1H, $J_{5,\ 6b}$ = 2.1 Hz, $J_{6a,\ 6b}$ = 12.2 Hz, H-6b), 4.46 (d, 1H, $J_{1,\ 2}$ = 7.9 Hz, H-1), 4.38 (dd, 1H, $J_{5',\ 6'a}$ = 6.4 Hz, $J_{6'a,\ 6'b}$ = 11.3 Hz, H-6'a), 4.35 - 4.26 (m, 1H, -C*H*$_2$-CH=CH_2), 4.15 - 4.09 (m, 2H, H-2 and H-6a), 4.07 - 4.03 (m, 3H, H-5', H-6'b, -C*H*$_2$-CH=CH_2), 4.00 (dd, 1H, $J_{4,\ 5}$ = 8.8 Hz, H-4), 3.97 - 3.94 (m, 1H, H-6'a), 3.63- 3.60 (m, 1H, H-5), 1.92 (s, 3H, NAc), 1.28, 1.27, 1.22, and 1.18 (each s, 4 x 9H, 4 x OPiv).

Anal. Calcd for $C_{39}H_{59}F_6NO_{19}S_2$: C, 45.74; H, 5.81; N, 1.37. Found: C, 46.10; H, 5.72; N, 1.34.

Allyl *O*-(2,4-Di-*O*-acetyl-3,6-di-*O*-pivaloyl-β-D-mannopyranosyl)-(1→4)-2-acetamido-2-deoxy-3,6-di-*O*-pivaloyl-β-D-glucopyranoside (10). A mixture of **9** (150 mg, 0.146 mmol), cesium acetate (170 mg, 6.07 equiv), and 18-crown-6 (233 mg, 6.04 equiv) in toluene (6.0 mL) was refluxed for 1 h (Entry 1 in Table 1). The reaction mixture was concentrated under reduced pressure to give a residue, which was purified on a column of silica gel (Wakogel C-300) with benzene/acetone (5:1 v/v) to afford **10** (115 mg, 93%): mp 102 - 104 °C (ethanol-hexane); $[\alpha]_D^{24}$ - 28.2° (*c* 0.6, $CHCl_3$); IR 1737 cm^{-1} (C=O), 1668 cm^{-1} (amido C=O); ^1H NMR (FX-200) δ 5.87 - 5.79 (m, 1H, -CH_2-C*H*=CH_2), 5.50 (d, 1H, $J_{2,\ NH}$ = 9.5 Hz, NH), 5.42 (dd, 1H, $J_{2',\ 3'}$ = 3.7 Hz, $J_{1',\ 2'}$ = 0 Hz, H-2'), 5.26 - 5.17 (m, 2H, -CH_2-CH=C*H*$_2$), 5.19 (dd, 1H, $J_{3',\ 4'}$ = 9.7 Hz, $J_{4',\ 5'}$ = 9.7 Hz, H-4'), 5.09 (dd, 1H, $J_{3,\ 4}$ = 8.5 Hz, $J_{2,\ 3}$ = 9.5 Hz, H-3), 4.97 (dd, 1H, H-3'), 4.69 (s, 1H, H-1'), 4.49 (dd, 1H, H-6a), 4.47 (d, 1H, $J_{1,\ 2}$ = 7.3 Hz, H-1), 4.30 - 4.26 (m, 1H, -C*H*$_2$-CH=CH_2), 4.20 (dd, 1H, $J_{6'a,\ 6'b}$ = 11.9 Hz, $J_{5',\ 6'a}$ = 2.5 Hz, H-6'a), 4.15 (dd, 1H, H-6b), 4.12 (dd, 1H, H-6'b), 4.06 - 3.98 (m, 2H, -C*H*$_2$-CH=CH_2 and H-2), 3.90 (dd, 1H, $J_{4,\ 5}$ = 8.8 Hz, H-4), 3.70 - 3.64 (m, 2H, H-5 and H-5'), 2.08, 2.02, and 1.92 (each s, 3 x 3H, 2 x OAc, 1 x NAc), 1.25, 1.24, 1.21, and 1.11 (each s, 4 x 9H, 4 x OPiv).

Anal. Calcd for $C_{41}H_{65}NO_{17}$: C, 58.35; H, 7.76; N, 1.66. Found: C, 58.06; H, 7.59; N, 1.71.

Examinations of the reaction conditions for acetoxylation of 9 (Table 1). A mixture of **9** (150 mg, 0.146 mmol), cesium acetate (170 mg, 6.07 equiv), and 18-crown-6 (233 mg, 6.04 equiv) in toluene (6.0 mL) was stirred under ultrasonication for 12 h. It was then treated in a similar manner as mentioned above to give **10** in 92% yield. (Entry 2) A mixture of **9** (155 mg, 0.151 mmol), cesium acetate (176 mg, 6.07 equiv), and 18-crown-6 (241 mg, 6.04 equiv) in *N,N*-dimethylformamide (DMF, 5.0 mL) was stirred for 10 h. It was then treated in a similar manner as mentioned

above to give **10** in 59% yield. (Entry 3) A mixture of **9** (150 mg, 0.146 mmol), cesium acetate (156 mg, 5.57 equiv), and 18-crown-6 (233 mg, 6.04 equiv) in dimethyl sulfoxide (DMSO, 5.0 mL) was stirred for 10 h. It was then treated in a similar manner as mentioned above to give **10** in 62% yield. (Entry 4) A mixture of **9** (138 mg, 0.134 mmol) and cesium acetate (161 mg, 6.26 equiv) in DMF (5.0 mL) was stirred for 24 h. It was then treated in a similar manner as mentioned above to give **10** in 36% yield. (Entry 5) A mixture of **9** (163 mg, 0.159 mmol) and cesium acetate (185 mg, 6.06 equiv) in DMSO (5.0 mL) was stirred for 24 h. It was then treated in a similar manner as mentioned above to give **10** in 39% yield. (Entry 6) A mixture of **9** (152 mg, 0.148 mmol), tetrabutylammonium acetate (250 mg, 5.60 equiv), and 18-crown-6 (221 mg, 5.66 equiv) in toluene (6.0 mL) was stirred for 24 h. It was then treated in a similar manner as mentioned above to give **10** in 43% yield (Entry 7).

Benzyl *O*-(β-D-Galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (11). A mixture of **3** (1.93 g, 3.1 mmol), benzyl alcohol (1.6 mL, 5.0 equiv), and a catalytic amount of pyridinium *p*-toluenesulfonate (ca. 50 mg) in 1,2-dichloroethane was refluxed for 1.5 h. The reaction mixture was neutralized with pyridine at room temperature and concentrated to give a residue, which was purified on a column of silica gel (Wakogel C-300) with hexane/ethyl acetate (1:8 v/v) to afford benzyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (2.05 g, 91%): amorphous powder; $[\alpha]_D^{25}$ - 37.0 ° (*c* 1.1, $CHCl_3$); IR 1746 cm^{-1} (C=O), 1671 cm^{-1} (amido C=O); ^1H NMR (A-500) δ 7.41 - 7.28 (m, 5H, Ph), 5.51 (d, 1H, $J_{2,\ NH}$ = 9.6 Hz, NH), 5.35 (d, 1H, $J_{3',\ 4'}$ = 3.3 Hz, H-4'), 5.10 (dd, 1H, $J_{1',\ 2'}$ = 7.9 Hz, $J_{2',\ 3'}$ = 10.2 Hz, H-2'), 5.00 (dd, 1H, $J_{2,\ 3}$ = 9.6 Hz, $J_{3,\ 4}$ = 8.2 Hz, H-3), 4.96 (dd, 1H, H-3'), 4.86 and 4.56 (ABq, 2H, $J_{A,\ B}$ = 12.2 Hz, -CH_2-Ph), 4.53 (dd,1H, $J_{5,\ 6b}$ = 2.9 Hz, $J_{6a,\ 6b}$ = 11.6 Hz, H-6b), 4.50 (d, 1H, H-1'), 4.42 (d, 1H, $J_{1,\ 2}$ = 7.9 Hz, H-1), 4.19 - 4.09 (m, 4H, H-2, H-6'a, H 6'b, and H-6a), 3.69 (ddd, 1H, H-5'), 3.81 (dd, 1H, $J_{4,\ 5}$ = 8.2 Hz, H-4), 3.59 (ddd, 1H, H-5), 2.14, 2.06, 2.05, 1.97, and 1.94 (each s, 7 x 3H, 6 x OAc and 1 x NAc).

Anal. Calcd for $C_{33}H_{43}NO_{17}$: C. 54.61; H, 5.97; N, 1.93. Found: C, 54.50; H, 6.01; N, 2.04.

The hexa-*O*-acetylated derivative of **11** was stirred with a catalytic amount of sodium methoxide in methanol (ca. pH 9) at room temperature for 30 min, the solution was neutralized with ion exchange resin Dowex 50W-X8 (H^+), filtered, and concentrated to give **11** (1.33 g, quant.), which was used for the next step without further purification.

Benzyl *O*-(3,6-Di-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-6-*O*-pivaloyl-β-D-glucopyranoside (12). A mixture of **11** (100 mg, 0.211 mmol) and bis(tributyltin) oxide (378 mg, 3.0 equiv) in a mixed solvent of

benzene/actonitrile (1:1 v/v, 15.0 mL) was refluxed by the use of a Dean-Stark apparatus and Molecular Sieves 4A for 3 h, then pivaloyl chloride (183 μL, 7.1 equiv) was added at room temperature. The reaction mixture was again heated at 90 °C for 24 h and concentrated to give a residue, which was purified on a column of silica gel (Wakogel C-300) with hexane/ethyl acetate (1:5 v/v) to afford **12** (112 mg, 73%): mp 133 - 134 °C (ethanol-hexane); $[\alpha]_D^{25}$ + 2.4 ° (*c* 1.0, $CHCl_3$); IR 3490 cm^{-1} (OH), 1728 cm^{-1} (C=O), 1662 cm^{-1} (amido C=O); ^1H NMR (A-500) δ 7.36 - 7.28 (m, 5H, Ph), 6.00 (d, 1H, $J_{2, NH}$ = 7.3 Hz, NH), 4.87 and 4.54 (ABq, 2H, $J_{A, B}$ = 12.8 Hz, -CH_2-Ph), 4.81 (dd, 1H, $J_{2', 3'}$ = 10.3 Hz, $J_{3', 4'}$ = 3.3 Hz, H-3'), 4.68 (d, 1H, $J_{1, 2}$ = 6.5 Hz, H-1), 4.65 (bs, 1H, 3-OH), 4.62 (dd, 1H, $J_{5, 6b}$ = 1.6 Hz, $J_{6a, 6b}$ = 11.9 Hz, H-6b), 4.38 (d, 1H, $J_{1', 2'}$ = 7.9 Hz, H-1'), 4.30 (dd, 1H, $J_{5', 6'a}$ = 7.7 Hz, $J_{6'a, 6'b}$ = 11.6 Hz, H-6'a), 4.27 (dd, 1H, $J_{5', 6'b}$ = 5.4 Hz, H-6'b), 4.22 (dd, 1H, $J_{5, 6a}$ = 6.1 Hz, H-6a), 3.99 (dd, 1H, H-4'), 3.93 (dd, 1H, H-2'), 3.91 (dd, 1H, $J_{2, 3}$ = 10.4 Hz, $J_{3, 4}$ = 8.9 Hz, H-3), 3.83 (bs, 1H, 2'-OH), 3.83 (dd, 1H, H-5'), 3.63 (ddd, 1H, $J_{4, 5}$ = 8.9 Hz, H-5), 3.57 (ddd, 1H, H-2), 3.45 (dd, 1H, H-4), 3.03 (bs, 1H, 4'-OH), 1.95 (s, 3H, NAc), 1.25, 1.22, and 1.19 (each s, 3 x 9H, 3 x OPiv).

Anal. Calcd for $C_{36}H_{55}NO_{14}$: C, 59.57; H, 7.64; N, 1.93. Found: C, 59.40; H, 7.58; N, 1.96.

The structure of **12** was further confirmed by derivation into its acetyl derivative. Downfield shifts of H-3, H-2', and H-4' were observed. ^1H NMR (A-500) δ 7.36 - 7.17 (m, 5H, Ph), 5.46 (d, 1H, $J_{2, NH}$ = 9.2 Hz, NH), 5.40 (dd, 1H, $J_{3', 4'}$ = 3.7 Hz, H-4'), 5.15 (dd, 1H, $J_{1', 2'}$ = 7.9 Hz, $J_{2', 3'}$ = 10.3 Hz, H-2'), 5.00 (dd, 1H, $J_{2, 3}$ = 10.8 Hz, $J_{3, 4}$ = 8.2 Hz, H-3), 4.94 (dd, 1H, H-3'), 4.85 and 4.56 (ABq, 2H, $J_{A, B}$ = 12.8 Hz, -CH_2-Ph), 4.56 (dd, 1H, $J_{5, 6b}$ = 2.4 Hz, $J_{6a, 6b}$ = 11.3 Hz, H-6b), 4.48 (d, 1H, H-1'), 4.43 (d, 1H, $J_{1, 2}$ = 7.9 Hz, H-1), 4.13 (dd, 1H, $J_{5', 6'b}$ = 6.4 Hz, $J_{6'a, 6'b}$ = 11.3 Hz, H-6'b), 4.11 (dd, 1H, $J_{5, 6a}$ = 5.2 Hz, H-6a), 4.08 (ddd, 1H, H-2), 4.04 (dd, 1H, $J_{5', 6'a}$ = 7.0 Hz, H-6'a), 3.88 (ddd, 1H, H-5'), 3.75 (dd, 1H, $J_{4, 5}$ = 8.2 Hz, H-4), 3.60 (ddd, 1H, H-5), 2.12, 2.06, 2.02, and 1.93 (each s, 4 x 3H, 3 x OAc and 1 x NAc), 1.26, 1.19, and 1.19 (each s, 3 x 9H, 3 x OPiv).

Benzyl *O*-(3,6-Di-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-6-*O*-pivaloyl-3-*O*-(2, 2, 2-trichloroethoxycarbonyl)-β-D-glucopyranoside (13). To a solution of **12** (46 mg, 0.063 mmol) in pyridine (0.5 mL) was added dropwise a solution of 2,2,2-trichloroethyl chloroformate (10μL, 1.1 equiv) in dichloromethane (0.3 mL) at 0 °C, and the reaction mixture was kept for 30 min. The reaction mixture was quenched with MeOH and concentrated to give a residue, which was purified on a column of silica gel (Wakogel C-300) with hexane/ethyl acetate (1:1 v/v) to afford **13** (40 mg, 70 %): mp 190 - 191 °C (ethanol-hexane); $[\alpha]_D^{25}$ + 9.9 ° (*c* 1.3,

$CHCl_3$); IR 3520 cm^{-1} (OH) , 1731 cm^{-1} (C=O), 1665 cm^{-1} (amido C=O) ; ^1H NMR (A-500) δ 7.36 - 7.28 (m, 5H, Ph), 5.68 (d, 1H, $J_{2,\ NH}$ = 8.6 Hz, NH), 5.24 (dd, 1H, $J_{2,\ 3}$ = 10.7 Hz, $J_{3,\ 4}$ = 8.6 Hz, H-3), 5.02 and 4.60 (ABq, 2H, $J_{A,\ B}$ = 11.9 Hz, $-CH_2CCl_3$), 4.85 and 4.56 (ABq, 2H, $J_{A,B}$ = 12.2 Hz, CH_2Ph), 4.80 (d, 1H, $J_{1,\ 2}$ = 8.3 Hz, H-1), 4.77 (dd, 1H, $J_{2',\ 3'}$ = 10.1 Hz, $J_{3',\ 4'}$ = 3.4 Hz, H-3'), 4.69 (dd, 1H, $J_{5,\ 6b}$ = 1.8 Hz, $J_{6a,\ 6b}$ = 12.2 Hz, H-6b), 4.36 (d, 1H, $J_{1',\ 2'}$ = 7.7 Hz, H-1'), 4.28 (dd, 1H, $J_{5',\ 6'a}$ = 7.7 Hz, $J_{6'a,\ 6'b}$ = 11.3 Hz, H-6'a), 4.25 (dd, 1H, $J_{5,\ 6a}$ = 5.5 Hz, $J_{6a,\ 6b}$ = 12.2 Hz, H-6a), 4.13 (dd, 1H, $J_{5',\ 6'b}$ = 5.8 Hz, H-6'b), 3.92 (d, 1H, H-4'), 3.81 (ddd, 1H, H-2'), 3.75 (ddd, 1H, H-2), 3.75 (dd, 1H, $J_{4,\ 5}$ = 8.6 Hz, H-4), 3.70 (ddd, 1H, H-5), 3.69 (ddd, 1H, H-5'), 3.04 (d, 1H, 2'-OH), 2.29 (d, 1H, 4'-OH), 1.85 (s, 3H, NAc), 1.24 and 1.19 (each s, 3 x 9H, 3 x OPiv).

Anal. Calcd for $C_{39}H_{56}Cl_3NO_{16}$: C, 51.97; H, 6.26; N, 1.55. Found: C, 51.70; H, 6.28; N, 1.81.

Benzyl *O*-(2,4-Di-*O*-acetyl-3,6-di-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-6-*O*-pivaloyl-3-*O*-(2,2,2-trichloroethoxycarbonyl)-β-D-glucopyranoside (13a). Compound **13** was acetylated (acetic anhydride / pyridine) and worked up in the usual manner to give the corresponding acetyl derivative **13a**, in quantitative yield: syrup; $[\alpha]_D^{25}$ - 18.3 ° (*c* 1.0, $CHCl_3$); IR 1758 cm^{-1} (C=O), 1668 cm^{-1} (amido C=O); ^1H NMR (A-500) δ 7.37 - 7.28 (m, 5H, Ph), 5.51 (d, 1H, $J_{2,\ NH}$ = 8.8 Hz, NH), 5.41 (d, 1H, $J_{3',\ 4'}$ = 3.6 Hz, H-4'), 5.19 (dd, 1H, $J_{1',\ 2'}$ = 8.0 Hz, $J_{2',\ 3'}$ = 10.4 Hz, H-2'), 5.16 (dd, 1H, $J_{2,\ 3}$ = 10.1 Hz, $J_{3,\ 4}$ = 8.5 Hz, H-3), 4.97 and 4.67 (ABq, 2H, $J_{A,\ B}$ = 11.9 Hz, $-CH_2CCl_3$), 4.85 and 4.55 (ABq, 2H, $J_{A,B}$ = 11.9 Hz, $-CH_2Ph$), 4.95 (dd, 1H, H-3'), 4.72 (d, 1H, $J_{1,\ 2}$ = 7.8 Hz, H-1), 4.54 (d, 1H, H-1'), 4.52 (dd, 1H, $J_{5,\ 6b}$ = 2.5 Hz, $J_{6a,\ 6b}$ = 11.3 Hz, H-6b), 4.11 (dd, 1H, $J_{5,\ 6a}$ = 5.2 Hz, H-6a), 4.09 (dd, 1H, $J_{5',\ 6'b}$ = 6.1 Hz, $J_{6'a,\ 6'b}$ = 11.0 Hz, H-6'b), 4.02 (dd, 1H, $J_{5',\ 6'a}$ = 8.0 Hz, H-6'a), 3.90 (ddd, 1H, H-5'), 3.85 (ddd, 1H, H-2), 3.79 (dd, 1H, $J_{4,\ 5}$ = 8.5 Hz, H-4), 3.67 (ddd, 1H, H-5), 2.12, 2.04, and 1.89 (each s, 3 x 3H, 2 x OAc and 1 x NAc), 1.26, 1.17, and 1.10 (each s, 3 x 9H, 3 x OPiv).

Anal. Calcd for $C_{43}H_{60}Cl_3NO_{18}$: C, 52.42; H, 6.14; N, 1.42. Found: C, 52.29; H, 6.22; N, 1.49.

Benzyl *O*-(2,4-Di-*O*-acetyl-3,6-di-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-6-*O*-pivaloyl-β-D-glucopyranoside (14). A mixture of the above mentioned acetyl derivative **13a** (32 mg, 0.032 mmol), a catalytic amount of zinc powder, and a small amount (0.1 mL) of water in acetic acid (0.3 mL) was stirred at room temperature for 1 h. The reaction mixture was poured into chloroform, washed with saturated aqueous sodium hydrogencarbonate, then with water, dried over anhydrous magnesium sulfate, and concentrated to give **14** (25 mg, 96%): mp 158 - 160

°C (ethanol-hexane); $[\alpha]_D^{25}$ - 9.9 ° (*c* 1.0, $CHCl_3$); 3490 cm^{-1} (OH), 1737 cm^{-1} (C=O), 1668 cm^{-1} (amido C=O); ^1H NMR (A-500) δ 7.36 - 7.28 (m, 5H, Ph), 5.48 (d, 1H, $J_{2,}$ NH = 7.9 Hz, NH), 5.45 (d, 1H, $J_{3'}$, $_{4'}$ = 3.4 Hz, H-4'), 5.28 (dd, 1H, $J_{1'}$, $_{2'}$ = 7.9 Hz, $J_{2'}$, $_{3'}$ = 10.4 Hz, H-2'), 4.97 (dd, 1H, H-3'), 4.86 and 4.55 (ABq, 2H, $J_{A,\ B}$ = 12.8 Hz, -*CH*2-Ph), 4.80 (d, 1H, $J_{1,\ 2}$ = 8.2 Hz, H-1), 4.58 (d, 1H, H-1'), 4.39 (dd, 1H, $J_{5,\ 6b}$ = 1.7 Hz, $J_{6a,\ 6b}$ =11.9 Hz, H-6b), 4.14 (dd, 1H, $J_{5'}$, $_{6'b}$ = 5.8 Hz, $J_{6'a,}$ 6'b = 11.6 Hz, H-6'b), 4.13 (bs, 1H, 3-OH), 4.09 (dd, 1H, $J_{5'}$, $_{6'a}$ = 7.0 Hz, H-6'a), 4.02 (dd, 1H, $J_{5,\ 6a}$ = 5.5 Hz, H-6a), 4.02 (ddd, 1H, H-5'), 4.01 (dd, 1H, $J_{2,\ 3}$ = 11.6 Hz, $J_{3,\ 4}$ = 8.6 Hz, H-3), 3.65 (ddd, 1H, $J_{4,\ 5}$ = 8.3 Hz, H-5), 3.48 (ddd, 1H, H-2), 3.45 (dd, 1H, H-4), 2.14, 2.05, and 1.97 (each s, 3 x 3H, 2 x OAc and 1 x NAc), 1.25, 1.18, and 1.11 (each s, 3 x 9H, 3 x OPiv).

Anal. Calcd for $C_{40}H_{59}NO_{16}$: C, 59.32; H, 7.34; N, 1.73. Found: C, 59.11; H, 7.42; N, 1.93.

Benzyl *O*-(2,4-Di-*O*-acetyl-3,6-di-*O*-pivaloyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2, 3, 4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→ 3)]-2-acetamido-2-deoxy-6-*O*-pivaloyl-β-D-glucopyranoside (15). A mixture of **14** (31 mg, 0.038 mmol) , **16** (25 mg, 1.2 equiv), and Molecular Sieves 4A (20 mg) in dichloromethane (1.5 mL) was stirred for 30 min. To the reaction mixture, trimethylsilyl trifluoromethanesulfonate (9.0 μL, 1.3 equiv) was added dropwise at 0 °C, and stirred for 2 h. The reaction mixture was then neutralized with triethylamine and concentrated to give a residue, which was purified on a column of silica gel (Wakogel C-300) with toluene/acetone (4:1 v/v) to afford **15** (27 mg, 58%): mp 96 - 97 °C (ethanol-hexane); $[\alpha]_D^{25}$ - 43.5 ° (*c* 1.0, $CHCl_3$); IR 1758 cm^{-1} (C=O), 1668 cm^{-1} (amido C=O); ^1H NMR (A-500) δ 7.37 - 7.22 (m, 4 x 5H, 4 x Ph), 5.98 (d, 1H, $J_{2,\ NH}$ = 8.2 Hz, NH), 5.43 (d, 1H, $J_{3'}$, $_{4'}$ = 3.3 Hz, H-4'), 5.18 (dd, 1H, $J_{1'}$, $_{2'}$ = 7.9 Hz, $J_{2'}$, $_{3'}$ = 10.7 Hz, H-2'), 5.08 (d, 1H, $J_{1,\ 2}$ = 3.7 Hz, Fuc-H-1), 5.00 (dd, 1H, H-3'), 4.97 - 4.50 (m, 4 x 2H, 4 x -*CH*2-Ph), 4.91 (d, 1H, $J_{1,\ 2}$ = 5.2 Hz, H-1), 4.63 (dd, 1H, $J_{5,\ 6b}$ = 3.7 Hz, $J_{6a,\ 6b}$ = 11.6 Hz, H-6b), 4.51 (d, 1H, H-1'), 4.32 (dd, 1H, $J_{5,\ 6a}$ = 5.8 Hz, H-6a), 4.21 (dq, 1H, Fuc-H-5), 4.14 (dd, 1H, $J_{2,\ 3}$ = 6.4 Hz, $J_{3,\ 4}$ = 6.4 Hz, H-3), 4.08 (dd, 1H, $J_{2,\ 3}$ = 10.1 Hz, Fuc-H-2), 4.10-4.07 (m, 2H, H-6'a and H-6'b), 3.90 (dd, 1H, $J_{3,\ 4}$ = 3.1 Hz, Fuc-H-3), 3.89 (ddd, 1H, H-5'), 3.76 (ddd, 1H, H-2), 3.75 (dd, 1H, H-4), 3.63 (dd, 1H, Fuc-H-4), 2.02, 2.00, and 1.81 (each s, 3 x 3H, 2 x OAc and 1 x NAc), 1.23, 1.17, and 1.11 (each s, 3 x 9H, 3 x OPiv), 1.17 (d, 3H, Fuc-H-6).

Anal. Calcd for $C_{67}H_{87}NO_{20}$: C, 65.61, H, 7.15; N, 1.14. Found: C, 65.43; H, 7.29; N, 1.43.

2, 3, 4-Tri-*O*-benzyl-1-*O*-(phenylcarbamoyl)-β-L-fucopyranose (16). A mixture of 2,3,4-tri-*O*-benzyl-α-L-fucopyranose[54] (1.0 g, 2.3 mmol), phenyl isocyanate

(300 μL, 1.2 equiv), and 4-dimethylaminopyridine (50 mg) in dichloromethane (20 mL) was stirred at room temperature for 1 h. The reaction mixture was diluted with dichloromethane, quenched with 10% aqueous citric acid solution, washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated to give a residue, which was purified on a column of silica gel (Wakogel C-300) with hexane/ethyl acetate (4:1 v/v) to afford **16** containing some α-anomer (1.2 g, β/α = 3:1, 94%). The product was recrystallized from ethanol to give pure **16**: mp 175 - 176 °C (ethanol-hexane); $[\alpha]_D^{27}$ + 5.7 ° (*c* 0.6, *CHCl3*); *IR* 1716 cm^{-1} (C=O); ^1H *NMR (EX-270)* δ 7.37 - 7.04 (m, 4 x 5H, 4 x Ph), 6.45 (s, 1H, NH), 5.57 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 5.02 - 4.68 (m, 3 x 2H, 3 x -C*H*2-Ph), 3.96 (dd, 1H, $J_{2,3}$ = 8.2 Hz, H-2), 3.67 - 3.61 (m, 3H, H-3, H-4, and H-5), 1.19 (d, 3H, H-6).

Anal. Calcd for $C_{34}H_{35}NO_6$: C, 73.76; H, 6.37; N, 2.53. Found: C, 74.10; H, 6.27; N, 2.58.

Benzyl 3,6-Di-*O*-allyl-β-D-galactopyranoside (18). A mixture of benzyl β-D-galactopyranoside (**17**)[55] (1.67 g, 6.18 mmol) and bis(tributyltin) oxide (4.7 mL, 1.5 equiv) in acetonitrile (15 mL) was refluxed by using a Dean-Stark apparatus with Molecular Sieves 4A for 12 h. To the reaction mixture, allyl bromide (3.7 mL, 6.9 equiv) and 1-methylimidazole (0.5 mL, 1.0 equiv) were added at room temperature, and the reaction mixture was refluxed for 20 h. The reaction mixture was cooled, diluted with ethyl acetate, stirred with saturated aqueous sodium hydrogencarbonate - potasium fluoride, filtered, and the layers separated. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with brine and water, dried over anhydrous magnesium sulfate, filtered, and concentrated to give a residue, which was purified on a column of silica gel with hexane/ethyl acetate (3:2 v/v) to afford **18** (1.56 g, 72%): syrup; $[\alpha]_D^{25}$ - 48.1 ° (*c* 0.9, CHCl3); ^1H NMR (FX-200) δ 7.39 - 7.26 (m, 5H, Ph), 5.98 - 5.89 (m, 2 x 1H, 2 x -CH_2-C*H*=CH_2), 5.33 - 5.21 (m, 2 x 2H, 2 x -CH_2-CH=C*H*2), 4.94 and 4.64 (ABq, 2H, $J_{A,B}$ = 11.9 Hz, -C*H*2-Ph), 4.33 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.24 - 4.07 (m, 2 x 2H, 2 x -C*H*2-CH=CH_2), 4.03 (bs, 1H, H-4), 3.80 (dd, 1H, H-2), 3.80 (dd, 1H, $J_{5,6}$ = 5.9 Hz, $J_{6,6'}$ = 9.9 Hz, H-6), 3.72 (dd, 1H, $J_{5,6'}$ = 5.8 Hz, H-6'), 3.59 (dd, 1H, H-5), 3.36 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{3,4}$ = 3.4 Hz, H-3), 2.52 (bs, 1H, 4-OH), 2.45 (bs, 1H, 2-OH).

Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.12; H, 7.48. Found: C, 64.91; H, 7.30.

Benzyl 2,4-Di-*O*-acetyl-3,6-di-*O*-allyl-β-D-galactopyranoside (18a). The structure of **18** was further confirmed by derivation into its acetyl derivative **18a**: syrup; $[\alpha]_D^{25}$ - 33.6 ° (*c* 1.3, $CHCl_3$); IR 1743 cm^{-1} (C=O); ^1H NMR (FX-200) δ 7.37 - 7.26 (5H, m, 5H, Ph), 5.95 - 5.69 (m, 2 x 1H, 2 x -CH_2-C*H*=CH_2), 5.46 (1H, dd, 1H, $J_{3,4}$ =2.3 Hz, H-4), 5.33 - 5.12 (m, 2 x 2H, 2 x -CH_2-CH=C*H*2), 5.25 (dd, 1H,

$J_{2,3}$= 10.1Hz, H-2), 4.91 and 4.62 (ABq, 2H, $J_{A,B}$ = 12.5 Hz, -CH_2-Ph), 4.44 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1), 4.15 - 3.85 (m, 2 x 2H, 2 x -CH_2-CH=CH_2), 3.70 (ddd, 1H, H-5), 3.59 (dd, 1H, $J_{5,6}$ = 6.3 Hz, $J_{6,6'}$ = 9.6 Hz, H-6), 3.51 (dd, 1H, $J_{5,6'}$ = 6.3 Hz, H-6'), 3.47 (dd, 1H, $J_{2,3}$ = 10.1 Hz, H-3), 2.15 and 2.04 (each s, 2 x 3H, 2 x OAc).

Anal. Calcd for $C_{23}H_{30}O_8$: C, 63.58; H, 6.96. Found: C, 63.51; H, 6.72.

Benzyl 3,6-Di-*O*-pivaloyl-β-D-galactopyranoside (19). A mixture of **17** (2.14 g, 7.92 mmol) and bis(tributyltin) oxide (6.0 mL, 1.5 equiv) in toluene (15 mL) was refluxed by using a Dean-Stark apparatus with Molecular Sieves 4A for 3 h. To the reaction mixture, pivaloyl chloride (2.9 mL, 3.0 equiv) was added at 0 °C, and the reaction mixture was refluxed for 24 h. The reaction mixture was cooled, diluted with ethyl acetate, stirred with saturated aqueous sodium hydrogencarbonate - potassium fluoride, filtered, and the organic layer separated. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with brine and water, dried over anhydrous magnesium sulfate, filtered, and concentrated to give a residue, which was purified on a column of silica gel with hexane/ethyl acetate (2:1 v/v) to afford **19** (2.99 g, 86%): mp 138 - 139 °C (ethanol-hexane); $[\alpha]_D^{25}$ + 22.0 ° (*c* 1.0, $CHCl_3$); IR 3452 cm^{-1} (OH), 1716 cm^{-1} (C=O); ^1H NMR (A-500) δ 7.37 - 7.29 (m, 5H, Ph), 4.93 and 4.63 (ABq, 2H, $J_{A,B}$ = 11.9 Hz, -CH_2-Ph), 4.82 (dd, 1H, $J_{2,3}$ = 10.1 Hz, $J_{3,4}$ = 3.4 Hz, H-3), 4.40 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.35 (dd, 1H, $J_{5,6}$ = 6.1 Hz, $J_{6,6'}$ = 11.6 Hz, H-6), 4.32 (dd, 1H, $J_{5,6'}$ = 6.7 Hz, H-6'), 3.96 (dd, 1H, H-4), 3.89 (ddd, 1H, $J_{2,OH}$ = 3.3 Hz, H-2), 3.74 (dd, 1H, H-5), 2.31 (d, 1H, 2-OH), 2.18 (d, 1H, $J_{4,OH}$ = 5.5 Hz, 4-OH), 1.25 and 1.22 (each s, 2 x 9H, 2 x OPiv).

Anal. Calcd for $C_{23}H_{34}O_8$: C, 62.99; H, 7.82. Found: C, 63.24; H, 8.30.

Benzyl 2,4-Di-*O*-acetyl-3,6-di-*O*-pivaloyl-β-D-galactopyranoside (19a). The structure of **19** was further confirmed by derivation into its acetyl derivative **19a**: mp 117 - 119 °C (ether-hexane); $[\alpha]_D^{25}$ - 42.8 ° (*c* 1.1, $CHCl_3$); IR 1738 cm^{-1} (C=O); ^1H NMR (FX-200) δ 7.33 - 7.27 (m, 5H, Ph), 5.42 (d, 1H, H-4), 5.33 (dd, 1H, $J_{1,2}$ = 8.1 Hz, $J_{2,3}$ = 10.3 Hz, H-2), 4.98 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 4.91 and 4.63 (ABq, 2H, $J_{A,B}$ = 12.5 Hz, -CH_2-Ph), 4.53 (d, 1H, H-1), 4.23 (dd, 1H, $J_{5,6}$ = 6.8 Hz, $J_{6,6'}$ = 11.2 Hz, H-6), 4.11 (dd, 1H, $J_{5,6'}$ = 6.6 Hz, H-6'), 3.92 (dd, 1H, H-5), 2.15 and 2.00 (each s, 2 x 3H, 2 x OAc), 1.21 and 1.11 (each s, 2 x 9H, 2 x OPiv).

Anal. Calcd for $C_{27}H_{38}O_{10}$: C, 62.05; H, 7.33. Found: C, 61.85; H, 7.45.

Benzyl 3,6-Di-*O*-benzyl-β-D-galactopyranoside (20). A mixture of **17** (606 mg, 2.24 mmol) and bis(tributyltin) oxide (1.71 mL, 1.5 equiv) in toluene (30 mL) was refluxed by using a Dean-Stark apparatus with Molecular Sieves 4A for 12 h. To the

reaction mixture, benzyl bromide (0.8 mL, 3.0 equiv) and 1-methylimidazole (0.54 mL, 3.0 equiv) were added at room temperature, and the reaction mixture was refluxed for 20 h. The reaction mixture was cooled, diluted with ethyl acetate, stirred with saturated aqueous sodium hydrogencarbonate - potassium fluoride, filtered, and the organic layer separated. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with brine and water, dried over anhydrous magnesium sulfate, filtered, and concentrated to give a residue, which was purified on a column of silica gel with hexane/ethyl acetate (2:1 v/v) to afford **20** (768 mg, 76%): syrup; $[\alpha]_D^{25}$ - 35.6 ° (*c* 1.1, $CHCl_3$); IR 3450 cm^{-1} (OH); ^1H NMR (500 MHz) δ 7.38 - 7.25 (m, 3 x 2H, $J_{A, B}$ = 12.2 Hz, -C*H*2-Ph), 4.59 (s, 2H, -C*H*2-Ph), 4.32 (d, 1H, $J_{1, 2}$ = 7.9 Hz, H-1), 4.02 (d, 1H, H-4), 3.85 (ddd, 1H, $J_{2, 3}$ = 9.2 Hz, H-2), 3.82 (dd, 1H, $J_{5, 6'}$ = 5.8 Hz, $J_{6, 6'}$ = 9.9 Hz, H-6'), 3.76 (dd, 1H, $J_{5, 6}$ = 6.1 Hz, H-6), 3.57 (dd, 1H, H-5), 3.40 (dd, 1H, $J_{3, 4}$ = 3.1 Hz, H-3), 2.50 (bs, 1H, 4-OH), 2.41 (bs, 1H, 2-OH).

Anal. Calcd for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 71.67; H, 6.54.

Benzyl 2,4-Di-*O*-acetyl-3,6-di-*O*-benzyl-β-D-galactopyranoside (20a). The structure of **20** was further confirmed by derivation into its acetyl derivative **20a**: syrup; $[\alpha]_D^{25}$ - 7.9 ° (*c* 1.2, $CHCl_3$); IR 1746 cm^{-1} (C=O); ^1H NMR (FX-270) δ 7.36 - 7.23 (m, 3 x 5H, 3 x Ph), 5.59 (dd, 1H, $J_{3, 4}$ = 3.4 Hz, $J_{4, 5}$ = 1.0 Hz, H-4), 5.18 (dd, 1H, $J_{1, 2}$ = 8.1 Hz, $J_{2, 3}$ = 10.1 Hz, H-2), 4.89 and 4.53 (ABq, 2H, $J_{A, B}$ = 11.9 Hz, -C*H*2-Ph), 4.69 and 4.37 (ABq, 2H, $J_{A, B}$ = 12.5 Hz, -C*H*2-Ph), 4.58 and 4.49 (ABq, 2H, $J_{A, B}$ = 12.2 Hz, -C*H*2-Ph), 4.39 (d, 1H, H-1), 3.71 (ddd, 1H, $J_{5, 6}$ = 5.6 Hz, $J_{5, 6'}$ = 7.1 Hz, H-5), 3.62 (dd, 1H, $J_{6, 6'}$ = 9.2 Hz, H-6), 3.55 (dd, 1H, H-6'), 3.48 (dd, 1H, H-3), 2.10 and 1.98 (each s, 2 x 3H, 2 x OAc).

Anal. Calcd for $C_{31}H_{34}O_8$: C, 69.65; H, 6.41. Found: C, 69.38; H, 6.59.

Benzyl 3,6-Bis(*O*-allyloxycarbonyl)-β-D-galactopyranoside (21). A mixture of **17** (200 mg, 0.74 mmol) and bis(tributyltin) oxide (0.57 mL, 1.5 equiv) in toluene (25 mL) was refluxed by using a Dean-Stark apparatus with Molecular Sieves 4A for 3 h. To the reaction mixture, allyl chloroformate (0.24 mL, 3.0 equiv) was added at room temperature, and the reaction mixture was stirred for 24 h. The reaction mixture was cooled, diluted with ethyl acetate, stirred with saturated aqueous sodium hydrogencarbonate - potassium fluoride, filtered, and the organic layer separated. The aqueous layer was extracted with ethyl acetate twice. The combined organic layers were washed with brine and water, dried over anhydrous magnesium sulfate, filtered, and concentrated to give a residue, which was purified on a column of silica gel with hexane/ethyl acetate (2:1 v/v) to afford **21** (251 mg, 81%): syrup; $[\alpha]_D^{25}$ - 17.3 ° (*c* 2.3, $CHCl_3$); IR 3532 cm^{-1} (OH), 1742 cm^{-1} (C=O); ^1H NMR (A-500) δ 7.37 - 7.23 (m, 5H, Ph), 6.02 - 5.87 (m, 2 x 1H, 2 x -CH_2-C*H*=CH_2), 5.42 - 5.27 (m, 2 x 2H, 2 x

-CH_2-CH=CH_2), 4.94 and 4.63 (ABq, 2H, $J_{A, B}$ = 11.5 Hz, -CH_2-Ph), 4.70 (dd, 1H, $J_{2, 3}$ = 10.2 Hz, $J_{3, 4}$ = 3.2 Hz, H-3), 4.68 - 4.62 (m, 2 x 2H, 2 x -CH_2-CH=CH_2), 4.44 (dd, 1H, $J_{6, 6'}$ = 11.2 Hz, $J_{5, 6}$ = 6.6 Hz, H-6), 4.39 (dd, 1H, $J_{5, 6'}$ = 6.3 Hz, H-6'), 4.41 (d, 1H, $J_{1, 2}$ = 7.9 Hz, H-1), 4.13 (ddd, 1H, $J_{4, 5}$ = 1.0 Hz, $J_{4, OH}$ = 5.0 Hz, H-4), 3.94 (ddd, 1H, $J_{2, OH}$ = 3.0 Hz, H-2), 3.77 (ddd, 1H, H-5), 2.48 (d, 1H, 2-OH), 2.38 (d, 1H, 4-OH).

Anal. Calcd for $C_{21}H_{26}O_{10}$: C, 57.53; H, 5.98. Found: C, 57.61; H, 5.87.

Benzyl 2,4-Di-*O*-acetyl-3,6-bis(*O*-allyloxycarbonyl)-*β*-D-galactopyranoside (21a). The structure of **21** was further confirmed by derivation into its acetyl derivative **21a**: syrup; $[\alpha]_D^{25}$ - 22.3 ° (*c* 2.7, $CHCl_3$); IR 1746 cm^{-1} (C=O); ^1H NMR (A-500) δ 7.38 - 7.26 (m, 5H, Ph), 6.01 - 5.82 (m, 2 x 1H, 2 x -CH_2-C*H*=CH_2), 5.51 (dd, 1H, $J_{3, 4}$ = 3.6 Hz, $J_{4, 5}$ = 1.0 Hz, H-4), 5.41 - 5.24 (m, 2 x 2H, 2 x -CH_2-CH=CH_2), 5.31 (dd, 1H, $J_{1, 2}$ = 7.9 Hz, $J_{2, 3}$ = 10.6 Hz, H-2), 4.92 and 4.63 (ABq, 2H, $J_{A, B}$ = 12.5 Hz, -CH_2-Ph), 4.82 (dd, 1H, H-3), 4.66 - 4.59 (m, 2 x 2H, 2 x -CH_2-CH=CH_2), 4.51 (d, 1H, H-1), 4.30 (dd, 1H, $J_{5, 6}$ = 6.6 Hz, $J_{6,6'}$ = 11.2 Hz, H-6), 4.23 (dd, 1H, $J_{5, 6'}$ = 5.6 Hz, H-6'), 3.91 (ddd, 1H, H-5), 2.25 and 2.01 (each s, 2 x 3H, 2 x OAc).

Anal. Calcd for $C_{25}H_{30}O_{12}$: C, 57.47; H, 5.79. Found: C, 57.46; H, 5.75.

2,4-Bis(*O*-trifluoromethylsulfonyl) Derivatives of 18, 19, 20, and 21.

General Procedure: Synthesis of Benzyl 3,6-Di-*O*-pivaloyl-2,4-bis(*O*-trifluoromethylsulfonyl)-*β*-D-galactopyranoside (23). To a solution of **19** (2.21 g, 5.04 mmol) in pyridine and dichloromethane (6:1, 17.0 mL), trifluoromethanesulfonic anhydride (2.5 mL, 2.9 equiv) was added under argon at - 19 °C, and the reaction mixture was stirred at room temperature for 30 min, monitoring by TLC [hexane/ethyl acetate (2:1 v/v)]. It was then poured into a saturated aqueous sodium hydrogencarbonate solution, and separated. The aqueous layer was extracted thrice with dichloromethane. The combined organic layers were washed with brine and water, dried over anhydrous magnesium sulfate, and concentrated to give a residue, which was purified on a short column of silica gel with hexane/ethyl acetate (3:1 v/v) to afford **23** (3.47 g, 98%): mp 142 - 144 °C (ethanol-hexane); $[\alpha]_D^{25}$ - 43.5 ° (*c* 1.3, $CHCl_3$); IR 1743 cm^{-1} (C=O); ^1H NMR (EX-270) δ 7.38 - 7.31 (m, 5H, Ph), 5.29 (d, 1H, $J_{3, 4}$ = 2.6 Hz, H-4), 5.12 (dd, 1H, $J_{2, 3}$ = 10.6 Hz, H-3), 4.99 (dd, 1H, $J_{1, 2}$ = 7.6 Hz, H-2), 4.91 and 4.70 (ABq, 2H, $J_{A, B}$ = 11.2 Hz, -CH_2-Ph), 4.69 (d, 1H, H-1), 4.41 (dd, 1H, $J_{5, 6}$ = 9.6 Hz, $J_{6, 6'}$ = 14.2 Hz, H-6), 4.01 (dd, 1H, $J_{5, 6'}$ = 7.6 Hz, H-6'), 4.01 (dd, 1H, H-5), 1.28 and 1.22 (each s, 2 x 9H, 2 x OPiv).

Anal. Calcd for $C_{25}H_{32}F_6O_{12}S_2$: C, 42.73; H, 4.59. Found: C, 43.20; H, 4.52.

Benzyl 3,6-Di-*O*-allyl-2,4-bis(*O*-trifluoromethylsulfonyl)-β-D-galactopyranoside (22). In a similar manner as mentioned above, **22** was obtained in quantitative yield: syrup; $[\alpha]_D^{25}$ - 15.2 ° (*c* 1.1, $CHCl_3$); ^1H NMR (A-500) δ 7.38 - 7.26 (m, 5H, Ph), 5.99 - 5.83 (m, 2 x 1H, 2 x -CH_2-C*H*=CH_2), 5.35 - 5.23 (m, 5H, 2 x -CH_2-CH=C*H*$_2$ and H-4), 4.90 and 4.68 (ABq, 2H, $J_{A, B}$ = 11.7 Hz, -C*H*$_2$-Ph), 4.77 (dd, 1H, $J_{1, 2}$ = 7.9 Hz, $J_{2, 3}$ = 9.9 Hz, H-2), 4.57 (d, 1H, H-1), 4.30 - 3.95 (m, 2 x 2H, 2 x -C*H*$_2$ -CH=CH_2), 3.79 (dd, 1H, $J_{5, 6}$ = 7.9 Hz, $J_{6, 6'}$ = 9.5 Hz, H-6), 3.70 (dd, 1H, $J_{5, 6'}$ = 9.2 Hz, H-6'), 3.64 (dd, 1H, $J_{3, 4}$ = 3.0 Hz, H-3), 3.55 (dd, 1H, H-5).

Anal. Calcd for $C_{21}H_{24}F_6O_{10}S_2$: C, 41.04; H, 3.94. Found: C, 41.33; H, 3.99.

Benzyl 3,6-Di-*O*-benzyl-2,4-bis(*O*-trifluoromethylsulfonyl)-β-D-galactopyranoside (24). In a similar manner as mentioned above, **24** was obtained in quantitative yield: mp 88 - 89.5 °C (diethyl ether-hexane); $[\alpha]_D^{25}$ + 4.6 ° (*c* 1.0, $CHCl_3$), ^1H NMR (A-500); δ 7.40 - 7.25 (m, 3 x 5H, 3 x Ph), 5.44 (dd, 1H, $J_{3, 4}$ = 2.4 Hz, H-4), 4.86 and 4.64 (ABq, 2H, $J_{A, B}$ = 11.6 Hz, -C*H*$_2$-Ph), 4.83 and 4.55 (ABq, 2H, $J_{A, B}$ = 10.7 Hz, -C*H*$_2$-Ph), 4.81 (dd, 1H, $J_{1, 2}$ = 7.9 Hz, $J_{2, 3}$ = 9.9 Hz, H-2), 4.65 and 4.44 (ABq, 2H, $J_{A, B}$ = 11.3 Hz, -C*H*$_2$-Ph), 4.53 (d, 1H, H-1), 3.74 (dd, 1H, $J_{5, 6}$ = 6.1 Hz, $J_{6, 6'}$ = 12.5 Hz, H-6), 3.73 (dd, 1H, $J_{5, 6'}$ = 6.1 Hz, H-6'), 3.67 (dd, 1H, H-3), 3.63 (ddd, 1H, H-5).

Anal. Calcd for $C_{29}H_{28}F_6O_{10}S_2$: C, 48.74; H, 3.95. Found: C, 48.28; H, 3.83.

Benzyl 3,6-Bis(*O*-allyloxycarbonyl)-2,4-bis(*O*-trifluoromethylsulfonyl)-β-D-galactopyranoside (25). In a similar manner as mentioned above, **25** was obtained in quantitative yield: mp 49 - 51.5 °C (diethyl ether-hexane); $[\alpha]_D^{25}$ - 5.3 ° (*c* 1.7, $CHCl_3$); IR 1758 cm^{-1} (C=O); ^1H NMR (A-500) δ 7.39 - 7.34 (m, 5H, Ph), 6.00 - 5.83 (m, 2H, 2 x -CH_2-C*H*=CH_2), 5.43 - 5.32 (m, 2 x 2H, 2 x -CH_2-CH=C*H*$_2$), 5.29 (dd, 1H, $J_{3, 4}$ = 2.6 Hz, $J_{4, 5}$ = 1.0 Hz, H-4), 5.00 (dd, 1H, $J_{2, 3}$ = 8.9 Hz, $J_{3, 4}$ = 2.6 Hz, H-3), 4.92 (dd, 1H, $J_{1, 2}$ = 7.3 Hz, H-2), 4.91 - 4.73 (ABq, 2H, $J_{A, B}$ = 11.9 Hz, -C*H*$_2$-Ph), 4.64 (d, 1H, H-1), 4.42 (dd, 1H, $J_{5, 6}$ = 6.3 Hz, $J_{6, 6'}$ = 11.2 Hz, H-6), 4.22 (dd, 1H, $J_{5, 6'}$ = 6.6 Hz, H-6'), 3.99 (ddd, 1H, H-5).

Anal. Calcd for $C_{23}H_{24}F_6O_{14}S_2$: C, 39.32; H, 3.44. Found: C, 39.75; H, 3.57.

Benzyl 2,4-Di-*O*-acetyl-3,6-di-*O*-allyl-β-D-mannopyranoside (26). A mixture of **22** (832 mg, 1.35 mmol), cesium acetate (735 mg, 2.8 equiv), and 18-

crown-6 (1.15 g, 3.2 equiv) in dry toluene (20 mL) was kept for 12 h under ultrasonication in a water bath. At this time the reaction was not completed, so was refluxed further for 12 h. The reaction mixture was poured into a saturated aqueous sodium hydrogencarbonate solution and separated into two phases. The aqueous layer was extracted thrice with ethyl anhydrous magnesium sulfate, and concentrated to give a residue, which was purified on a column of silica gel with hexane/ethyl acetate (4:1 v/v) to afford **26** (406 mg, 69%): mp 119 - 121 °C (ethanol-hexane); $[\alpha]_D^{25}$ - 94.2 ° (*c* 1.4, $CHCl_3$); IR 1738 cm^{-1} (C=O); ^1H NMR (A-500) δ 7.38 - 7.26 (m, 5H, Ph), 5.95 - 5.73 (m, 2 x 1H, 2 x -CH_2-C*H*=CH_2), 5.50 (dd, 1H, $J_{2,3}$ = 3.3 Hz, H-2), 5.32 - 5.13 (m, 2 x 2H, 2 x -CH_2-CH=C*H*$_2$), 5.07 (dd, 1H, $J_{3,4} = J_{4,5}$ = 9.8 Hz, H-4), 4.89 and 4.66 (ABq, 2H, $J_{A,B}$ = 12.2 Hz, -C*H*$_2$-Ph), 4.52 (d, 1H, $J_{1,2}$ = 1.3 Hz, H-1), 4.14 - 3.85 (m, 2 x 2H, 2 x -C*H*$_2$-CH=CH_2), 3.62 (dd, 1H, $J_{5,6}$ = 6.4 Hz, $J_{6,6'}$ = 10.7 Hz, H-6), 3.58 (dd, 1H, $J_{5,6'}$ = 3.0 Hz, H-6'), 3.52 (ddd, 1H, H-5), 3.49 (dd, 1H, H-3), 2.17 and 2.05 (each s, 2 x 3H, 2 x OAc).

Anal. Calcd for $C_{23}H_{30}O_8$: C, 63.58; H, 6.96. Found: C, 63.58; H, 6.70.

Benzyl 2,4-Di-*O*-acetyl-3,6-di-*O*-pivaloyl-β-D-mannopyranoside (27). A mixture of **23** (300 mg, 0.43 mmol), cesium acetate (235 mg, 2.8 equiv), and 18-crown-6 (322 mg, 2.8 equiv) in dry toluene (10 mL) was kept for 12 h under ultrasonication in a water bath until the disappearance of **23** on TLC. The reaction mixture was poured into a saturated aqueous sodium hydrogencarbonate solution and separated into two phases. The aqueous layer was extracted thrice with ethyl acetate. The combined organic layers were washed with brine and water, dried over anhydrous magnesium sulfate, and concentrated to give a residue, which was purified on a column of silica gel with hexane/ethyl acetate (3:1 v/v) to afford **27** (196 mg, 88%): mp 138 - 139 °C (ethanol-hexane); $[\alpha]_D^{26}$ - 40.4 ° (*c* 1.0, $CHCl_3$); IR 1752 cm^{-1} (C=O); ^1H NMR (FX-200) δ 7.36 - 7.34 (m, 5H, Ph), 5.49 (dd, 1H, $J_{1,2}$ = 0.9 Hz, $J_{2,3}$ = 3.4 Hz, H-2), 5.30 (dd, 1H, $J_{3,4} = J_{4,5}$ = 10.0 Hz, H-4), 4.96 (dd, 1H, H-3), 4.88 and 4.65 (ABq, 2H, $J_{A,B}$ = 12.3 Hz, -C*H*$_2$-Ph), 4.62 (d, 1H, H-1), 4.31 (dd, 1H, $J_{5,6}$ = 2.7 Hz, $J_{6,6'}$ = 12.2 Hz, H-6), 4.18 (dd, 1H, $J_{5,6'}$ = 6.1 Hz, H-6'), 3.64 (ddd, 1H, H-5), 2.16 and 2.01 (each s, 2 x 3H, 2 x OAc), 1.26 and 1.12 (each s, 2 x 9H, 2 x OPiv).

Anal. Calcd for $C_{27}H_{38}O_{10}$: C, 62.05; H, 7.33. Found: C, 61.82; H, 7.23.

Benzyl 2,4-Di-*O*-acetyl-3,6-di-*O*-benzyl-β-D-mannopyranoside (28). A mixture of **24** (206 mg, 0.29 mmol), cesium acetate (166 mg, 3.0 equiv), and 18-crown-6 (228 mg, 3.0 equiv) in dry toluene (20 mL) was kept for 12 h under ultrasonication in a water bath. At this time the reaction was not completed, so was refluxed for 12 h until the disappearance of **24** on TLC. The reaction mixture was poured into a saturated aqueous sodium hydrogencarbonate solution and separated into two phases. The aqueous layers were extracted thrice with ethyl acetate. The combined organic

layers were washed with brine and water, dried over anhydrous magnesium sulfate, and concentrated to give a residue, which was purified on a column of silica gel with hexane/ethyl acetate (4:1 v/v) to afford **28** (96 mg, 62%): amorphous; $[\alpha]_D^{25}$ - 95.1 ° (*c* 1.4, $CHCl_3$); IR 1744 cm^{-1} (C=O); ^1H NMR (EX-270) δ 7.32 - 7.18 (m, 3 x 5H, 3 x Ph), 5.60 (dd, 1H, $J_{2,1}$ = 0.8 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.13 (dd, 1H, $J_{3,4}$ = 9.7 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 4.90 and 4.67 (ABq, 2H, $J_{A,B}$ = 12.3 Hz, -CH_2-Ph), 4.67 and 4.37 (ABq, 2H, $J_{A,B}$ = 12.2 Hz, -CH_2-Ph), 4.55 (s, 2H, -CH_2-Ph), 4.51 (d, 1H, H-1), 3.67 (dd, 1H, $J_{5,6}$ = 6.1 Hz, $J_{6,6'}$ = 10.7 Hz, H-6), 3.62 (dd, 1H, $J_{5,6'}$ = 3.1 Hz, H-6'), 3.51 (dd, 1H, H-3), 3.50 (ddd, 1H, H-5), 2.19 and 1.92 (each s, 2 x 3H, 2 x OAc).

Anal. Calcd for $C_{31}H_{34}O_8$: C, 69.65; H, 6.41. Found: C, 69.21; H, 6.29.

Benzyl 2,3-Di-*O*-acetyl-3,6-bis(*O*-allyloxycarbonyl)-β-D-mannopyranoside (29). A reaction mixture of **25** (111 mg, 0.16 mmol), cesium acetate (91 mg, 3.0 equiv), and 18-crown-6 (125 mg, 3.0 equiv) in dry toluene (10 mL) was kept for 12 h under ultrasonication in a water bath until the disappearance of **25** on TLC. The reaction mixture was poured into a saturated aqueous sodium hydrogencarbonate solution and separated into two phases. The aqueous layer was extracted thrice with ethyl acetate. The combined organic layers were washed with brine and water, dried over anhydrous magnesium sulfate, and concentrated to give a residue, which was purified on a column of silica gel with hexane/ethyl acetate (3:1 v/v) to afford **29** (74 mg, 89%): syrup; $[\alpha]_D^{25}$ -67.4 ° (*c* 0.6, $CHCl_3$); IR 1758 cm^{-1} (C=O); ^1H NMR (FX-200) δ 7.38 - 7.28 (m, 5H, Ph), 6.02 - 5.82 (m, 2 x 1H, 2 x -CH_2-CH=CH_2), 5.56 (dd, 1H, $J_{2,3}$ = 3.3 Hz, H-2), 5.41 - 5.24 (m, 2 x 2H, 2 x -CH_2-CH=CH_2), 5.23 (dd, 1H, $J_{3,4}$ = 9.9 Hz, H-4), 4.88 and 4.64 (ABq, 2H, $J_{A,B}$ = 12.2 Hz, -CH_2-Ph), 4.83 (dd, 1H, H-3), 4.68 - 4.60 (m, 2 x 2H, 2 x -CH_2-CH=CH_2), 4.60 (d, 1H, H-1), 4.36 (dd, 1H, $J_{5,6}$ = 6.3 Hz, $J_{6,6'}$ = 11.6 Hz, H-6), 4.26 (dd, 1H, $J_{5,6'}$ = 3.6 Hz, H-6'), 3.64 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, H-5), 2.18 and 2.05 (each s, 2 x 3H, 2 x OAc).

Anal. Calcd for $C_{25}H_{30}O_{12}$: C, 57.47; H, 5.79. Found: C, 57.47; H, 5.67.

ACKNOWLEDGMENT

One of the authors (K.S.) gratefully appreciates the discussion with Professor F. W. Lichtenthaler, Institut für Organische Chemie, Technische Hochschule Darmstadt, Germany.

REFERENCES AND NOTES

1. Dedicated to the memory of Professor Akira Hasegawa.
2. J.-C. Jacqinet and P. Sinaÿ, *J. Org. Chem.*, **42**, 720 (1977).

3. J. Arnarp and J. Lönngren, *J. Chem. Soc., Perkin Trans. 1*, 2070 (1981).
4. K. Sakai, R. Katsumi, H. Ohi, T. Usui and Y. Ishido, *J. Carbohydr. Chem.*, **11**, 553 (1992).
5. T. Yoshino, K. Sato, F. Wanme, I. Takai and Y. Ishido, *Glycoconjugate J.*, **9**, 287 (1992).
6. T. Ogawa, T. Nukada and M. Matsui, *Carbohydr. Res.*, **101**, 263 (1982).
7. a) K. Sato and A. Yoshitomo, *Chem. Lett.*, 39 (1995); b) K. Sato, A. Yoshitomo and Y.Takai, *Bull. Chem. Soc. Jpn.*, **70**, 885 (1997).
8. R. S. Bhatt, L. Hough and A. C. Richardson, *Carbohydr. Res.*, **32**, C4 (1974).
9. a) K. Yamashita, K. Totani, M. Kuroki, Y. Matsuoka, I. Ueda and A. Kobata, *Cancer Res.*, **47**, 3451 (1987); b) K. Yamashita, K. Taketa, S. Nishi, K. Fukushima and T. Ohkura, *Cancer Res.*, **53**, 2970 (1993).
10. G. Ekborg, B. Lindberg and J. Lönngren, *Acta Chem. Scand.*, **26**, 3287 (1972).
11. N. K. Kochetkov, B. A. Dmitriev, N. N. Malysheva, A. Y. Chernyak, E. M. Klimov, N. E. Bayramova and V. I. Torgov, *Carbohydr. Res.*, **45**, 283 (1975).
12. M. A. E. Shaban and R. W. Jeanloz, *Carbohydr. Res.*, **52**, 103 (1976).
13. M. A. E. Shaban and R. W. Jeanloz, *Carbohydr. Res.*, **52**, 115 (1976).
14. C. D. Warren, C. Augé, M. L. Laver, S. Suzuki, D. Power and R. W. Jeanloz, *Carbohydr. Res.*, **82**, 71 (1980).
15. C. Augé, C. D. Warren, R. W. Jeanloz, M. Kiso and L. Anderson, *Carbohydr. Res.*, **82**, 85 (1980).
16. J. Kerékgyártó, J. P. Kamerling, J. B. Bouwstra, J. F. G. Vliegenthart and A. Lipták, *Carbohydr. Res.*, **186**, 51 (1989).
17. J. Kerékgyártó, J. G. M. van der Ven, J. P. Kamerling, A. Lipták and J. F. G. Vliegenthart, *Carbohydr. Res.*, **238**, 135 (1993).
18. K. K. -C. Liu and S. J. Danishefsky, *J. Org. Chem.*, **59**, 1892 (1994).
19. F. W. Lichtenthaler and T. Schneider-Adams, *J. Org. Chem.*, **59**, 6728 (1994).
20. F. Barresi and O. Hindsgaul, *J. Am. Chem. Soc.*, **113**, 9376 (1991).
21. F. Barresi and O. Hindsgaul, *Synlett*, 759 (1992).
22. G. Stork and G. Kim, *J. Am. Chem. Soc.*, **114**, 1087 (1992).
23. A. Dan, Y. Ito and T. Ogawa, *J. Org. Chem.*, **60**, 4680 (1995).
24. Y. Ito and T. Ogawa, *Angew. Chem., Int. Ed. Engl.*, **33**, 1765 (1994).
25. A. Dan, Y. Ito and T. Ogawa, *Tetrahedron Lett.*, **36**, 7487 (1995).
26. S. David, A. Malleron and C. Dini, *Carbohydr. Res.*, **188**, 193 (1989).
27. J. Alais and S. David. *Carbohydr. Res.*, **201**, 69 (1990).
28. W. Günther and H. Kunz, *Carbohydr. Res.*, **228**, 217 (1992).
29. H. Kunz and W. Günther, *Angew. Chem., Int. Ed. Engl.*, **27**, 1087 (1988).
30. H. Paulsen, R. Lebuhn and O. Lockhoff, *Carbohydr. Res.*, **103**, C7 (1982).
31. D. Crich and S. Sun, *J. Org. Chem.*, **62**, 1198 (1997).
32. G. Hodosi and P. Kovác, *J. Am. Chem. Soc.*, **119**, 2335 (1997).
33. N. Taubken, B. Sauerbrei and J. Thiem, *J. Carbohydr. Chem.*, **12**, 651 (1993).
34. T. Murata and T. Usui, *Biosci., Biotechnol., Biochem.*, **61**, 1059 (1997).
35. D. Chaplin, D. H. G. Crout, S. Bornemann, D. W. Hutchinson and R. Khan, *J. Chem. Soc., Perkin Trans. 1*, 235 (1992).
33. S. Hakomori, *Adv. Cancer Res.*, **52**, 257 (1989).
37. L. Yan and D. Kahne, *J. Am. Chem. Soc.*, **118**, 9239 (1996).
38. C.-C. Lin, M. Shimazaki, M.-P. Heck, S. Aoki, R. Wang, T. Kimura, H. Ritzen, S. Takayama, S. H. Wu, G. Weitz-Schmidt and C.-H. Wong, *J. Am. Chem. Soc.*, **118**, 6826 (1996).
39. V. Behar and S. J. Danishefsky, *Angew. Chem., Int. Ed. Engl.*, **33**, 1468 (1994).
40. R. Windmüler and R. R. Schmidt, *Tetrahedron Lett.*, **35**, 7927 (1994).
41. A. Tropfer and R. R. Schmidt, *Tetrahedron Lett.*, **33**, 5161 (1992).
42. S. Nishimura, S. Murayama, K. Kurita and H. Kuzuhara, *Chem. Lett.*, 1413 (1992).

43. K. C. Nicolaou, C. W. Hummel and Y. Iwabuchi, *J. Am. Chem. Soc.*, **114**, 3126 (1992).
44. G. E. Ball, R. A. O'Neill, J. E. Schultz, J. B. Lowe, B. W. Weston, J. O. Nagy, E. G. Brown, C. J. Hobbs and M. D. Bednarski, *J. Am. Chem. Soc.*, **114**, 5449 (1992).
45. Y. Ichikawa, Y.-C. Lin, D. P. Dumas, G.-J. Shen, E. Garcia-Junceda, M. A. Williams, R. Bayer, C. Ketcham, L. E. Walker, J. C. Paulson and C.-H. Wong, *J. Am. Chem. Soc.*, **114**, 9283 (1992).
46. R. R. Schmidt and A. Tropfer, *Tetrahedron Lett.*, **32**, 3353 (1991).
47. K. C. Nicolaou, C. W. Hummel, N. J. Bockovich and C.-H. Wong, *J. Chem. Soc., Chem. Commun.*, 870 (1991).
48. K. C. Nicolaou, T. J. Caulfield, H. Kataoka and N. A. Stylianides, *J. Am. Chem. Soc.*, **112**, 3693 (1990).
49. S. Sato, Y. Ito and T. Ogawa, *Tetrahedron Lett.*, **29**, 5267 (1988).
50. J.-C. Jacquinet and P. Sinay, *J. Chem. Soc., Perkin Trans. 1*, 314 (1979).
51. a) S. Inaba, M. Yamada, T. Yoshino, and Y. Ishido, *J. Am. Chem. Soc.*, **95**, 2062 (1973); b) Y. Yoshino, S. Inaba, A. Matsuno, T. Yoshino, and H. Umezawa, *J. Chem. Soc., Perkin Trans. 1*, 1382 (1977); c) Iimori, T. Shibazaki and S, Ikegami, *Tetrahedron Lett.*, **37**, 2267 (1996).
52. Unpublished results: a) Y. Kaneda, Y. Shibasaki, S. Koh-ga, A. Matsumoto, I. Takai and Y. Ishido, *Abstracts of XVth Japanese Carbohydrate Symposium*, pp 15 - 16, Sendai, July 29 - 30, 1993; b) I. Takai, Y. Shibasaki, N. Kataoka, Y. Kaneda and Y. Ishido, *Abstracts of XIVth Japanese Carbohydrate Symposium*, pp 15 - 16, Tokyo, July 31 - August 1, 1992.
53. Unpublished results: A coupling reaction of the 2'-hydroxy derivative of *N*-acetyllactosamine, bearing different protecting groups, with **16** (1.2 equiv) in the presence of trimethylsilyl triflate (1.2 equiv) in dichloromethane at 0 °C for 30 min gave an H-II type antigen derivative in 67% yield, and the reaction was thus extended to that of **14**. 1-*O*-phenylcarbamoyl sugar derivatives are characterized by a simple preparative procedure in excellent yields.
54. M. Dejter-Juszynski and H. M. Flowers, *Carbohydr. Res.*, **18**, 219 (1971).
55. B. Helferich and A. Porck, *Ann.*, **586**, 239 (1954).