Lipid A and Related Compounds. XXIV.[1] Efficient Synthesis of Several Lipid as *via* Common Disaccharide Intermediates

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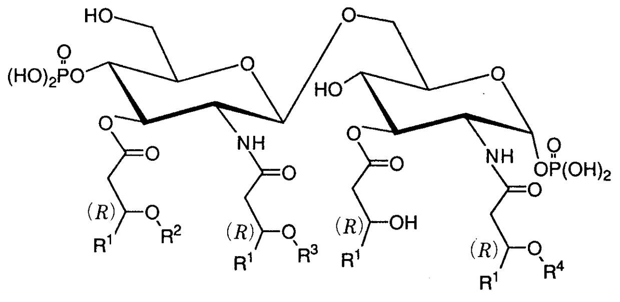
We describe the development of new common disaccharide intermediates bearing two amino and six hydroxyl groups that are chemically differentiated, and their application to syntheses of several lipid As.

Keywords total synthesis; *Proteus mirabilis* lipid A; *Salmonella* mutant lipid A; disaccharide intermediate; chemical differentiation

Lipid A is responsible for the expression of many biological activities of the lipopolysaccharide (LPS) of gram-negative bacteria, *e.g.*, endotoxicity, adjuvanticity, antitumor activity and so on.[2] Lipid A consists of a $\beta(1\rightarrow6)$-linked D-glucosamine disaccharide moiety which carries phosphate residues at positions 1 and 4′ as well as amide-bound and ester-bound D-3-hydroxy and/or acyloxy fatty acids as indicated in Chart 1.[3]



1a: $R^1 = CH_3(CH_2)_{10}$-, $R^2 = R^3 = R^4 = H$
(*Salmonella* mutant)

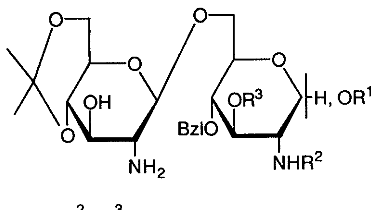
1b: $R^1 = CH_3(CH_2)_{10}$-, $R^2 = CH_3(CH_2)_{12}CO$-, $R^3 = CH_3(CH_2)_{10}CO$-, $R^4 = H$
(*Escherichia coli*)

1c: $R^1 = CH_3(CH_2)_{10}$-, $R^2 = CH_3(CH_2)_{12}CO$-, $R^3 = CH_3(CH_2)_{10}CO$-, $R^4 = CH_3(CH_2)_{14}CO$-
(*Salmonella minnesota*)

1d: $R^1 = CH_3(CH_2)_{10}$-, $R^2 = CH_3(CH_2)_{12}CO$-, $R^3 = CH_3(CH_2)_{12}CO$-, $R^4 = H$
(*Proteus mirabilis*)

1e: $R^1 = CH_3(CH_2)_{10}$-, $R^2 = CH_3(CH_2)_{12}CO$-, $R^3 = CH_3(CH_2)_{12}CO$-, $R^4 = CH_3(CH_2)_{14}CO$-
(*Proteus mirabilis*)

Chart 1



2a: R^1 = allyl (β), $R^2 = R^3$ = TCBOC

2b: R^1 = allyl (α), $R^2 = R^3$ = TCBOC

2c: R^1 = allyl (α), R^2 = TCEC, R^3 = TCBOC

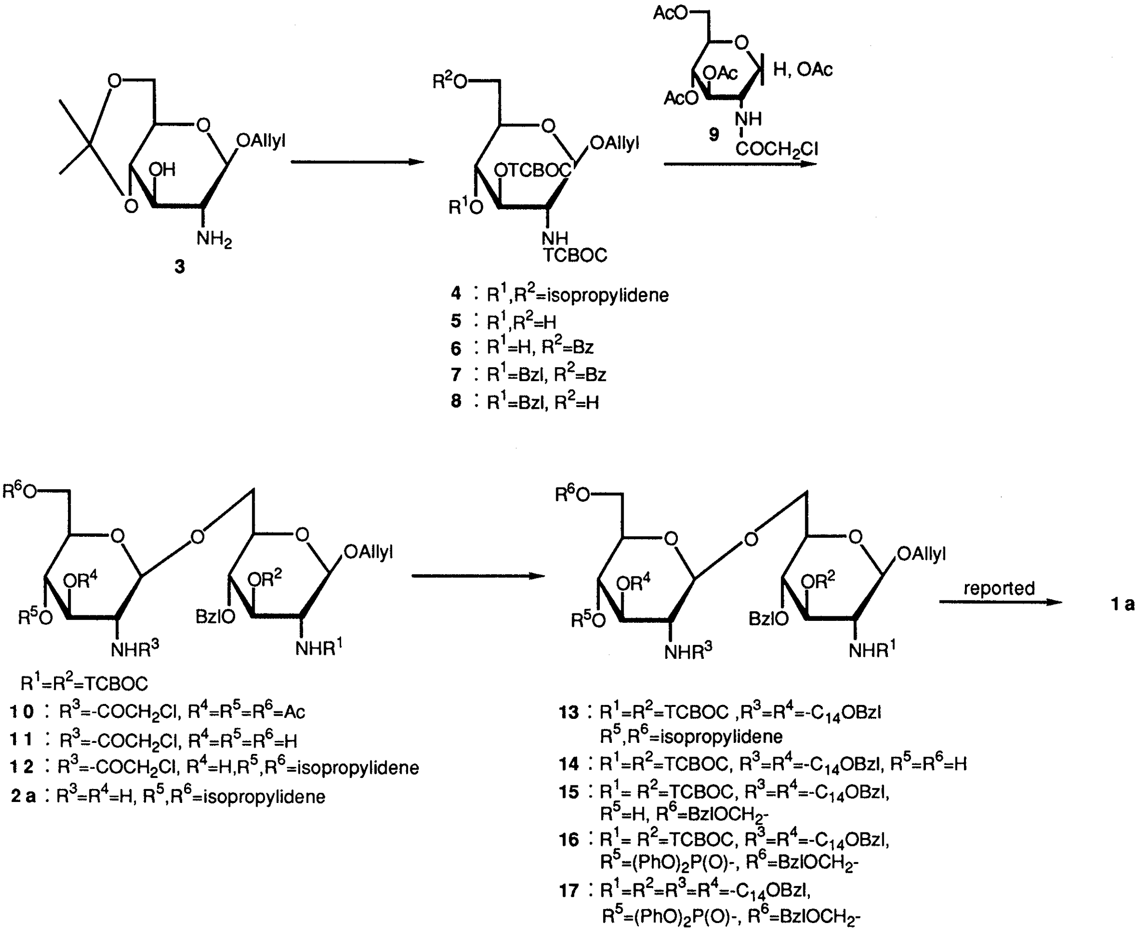
allyl: $CH_2=CHCH_2$-, TCEC : Cl_3CCH_2OCO-, TCBOC : $Cl_3CC(CH_3)_2OCO$-

Chart 2

Recently, Shiba's group has synthesized the biologically active constituents of LPS from *Salmonella* mutant (**1a**),[4] *Escherichia coli* (**1b**),[5] and *Salmonella minnesota* (**1c**)[6] by means of an elegant two-fragment condensation method. In this paper, we describe the development of the new common disaccharide intermediates **2a**,[7] **2b**,[8] **2c** bearing two amino and six hydroxyl groups that are chemically differentiated, and their application to syntheses of several lipid As.

We first describe the formal synthesis of *Salmonella* mutant lipid A (**1a**) *via* **2a** from the previously reported key intermediate[9] of lipid X, allyl 2-amino-2-deoxy-4,6-isopropylidene-β-D-glucopyranoside (**3**). The amino alcohol **3** was treated with 2,2,2-trichloro-*tert*-butoxycarbonyl chloride (TCBOC-Cl) in pyridine containing a catalytic amount of 4-dimethylaminopyridine (DMAP) to afford the diacylate **4** in 95% yield. The isopropylidene group of **4** was removed by treatment with 90% aqueous AcOH to afford the diol **5** in 90% yield and the primary alcohol of **5** was selectively protected with benzoyl chloride in pyridine–tetrahydrofuran (THF) to give the 6-*O*-benzoylated compound **6** in 75% yield. The remaining hydroxyl group of **6** was benzylated with benzyl 2,2,2-trichloroacetimidate in the presence of a catalytic amount of trifluoromethanesulfonic acid in CH_2Cl_2 to afford compound **7** in 49% yield, then the benzoyl group of **7** was removed with NH_4OH–MeOH (1 : 10) to give the reducing unit **8** in 74% yield. The neighboring group supported glycosylation of **8** with the suitably protected glycosyl donor **9** by using anhydrous $FeCl_3$, 1,1,3,3-tetramethylurea (TMU), and Molecular Sieves 4A (MS4A) in CH_2Cl_2[10] to give stereoselectively, as expected, the $\beta(1\rightarrow6)$-disaccharide **10** in 72% yield as a single isomer. The β-configuration of the newly formed glycosidic linkage was confirmed by the coupling constant value (8.0 Hz) of the signal due to the anomeric protons in the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **10**. The disaccharide **10** was deacetylated with NH_4OH–MeOH (1 : 10) to give the triol **11** in 86% yield, then **11** was converted into the 4′,6′-*O*-isopropylidene derivative **12** with 2,2-dimethoxypropane in the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) in dimethylformamide (DMF) in 71% yield. Selective removal of the N-chloroacetyl group of **12** was carried out with thiourea and diisopropylethylamine in THF to give the common key intermediate **2a** in 92% yield.

The common key intermediate **2a** thus obtained was applied for the formal synthesis of *Salmonella* mutant lipid A as follows. The free amino and hydroxyl groups of **2a** were acylated with optically active (*R*)-3-benzyloxytetra-



Ac: CH_3CO-, Bz: C_6H_5CO-, Bzl: $C_6H_5CH_2$-, allyl: CH_2=CH-CH_2-, TCBOC: $Cl_3CC(CH_3)_2OCO$-, C_{14}OBzl: $CH_3(CH_2)_{10}$CH(BzlO)CH_2CO- ((*R*))

Chart 3

decanoic acid in the presence of dicyclohexylcarbodiimide (DCC) and a catalytic amount of DMAP in CH_2Cl_2 to give the diacylate **13** in 87% yield. Hydrolysis of the isopropylidene group of **13** with 90% AcOH gave the diol **14** in 94% yield. The 6′-*O*-hydroxyl group was selectively protected with benzyloxymethyl chloride and TMU in CH_2Cl_2, then the 4′-*O*-hydroxyl group was phosphorylated with diphenylphosphorochloridate in the presence of pyridine and DMAP in CH_2Cl_2 to afford the phosphorylated compound **16** in 55% yield. Replacement of the TCBOC group with an acyl group was carried out as follows. Treatment of **16** with activated Zn-dust in acetic acid at room temperature followed by acylation of free amino and hydroxyl groups with (*R*)-3-benzyloxytetradecanoic acid and DCC–DMAP in CH_2Cl_2 gave the fully protected compound **17** in 52% yield. Compound **17** is the intermediate for *Salmonella* mutant lipid A synthesis as reported by Shiba's group.[4] Accordingly we proved the availability of **2a** as a common key intermediate for the construction of lipid As.

Next, we describe a short preparation of the new disaccharide intermediate **2b** as a synthetic equivalent of **2a** and its application to the total synthesis of *Proteus mirabilis* lipid A (**1e**) as shown in Chart 4.

The selective protection of the amino group of D-glucosamine hydrochloride with TCBOC-Cl afforded the carbamate compound **18** in 87% yield. The glycosylation of **18** in 2% dry HCl in allyl alcohol at 100 °C gave the α-allyl glycoside **19** in 62% yield and its β-anomer in 7% yield. The configuration at C-1 of **19** was assigned as α on the basis of ^{1}H-NMR data (δ 4.89 with J=2.6 Hz for H-1). The α-glycoside **19** was then converted into the 4,6-*O*-isopropylidene derivative **20** with 2,2-dimethoxypropane in the presence of *p*-TsOH in DMF in 82% yield. Acylation of the free hydroxyl group of **20** with TCBOC-Cl in pyridine and DMAP gave **21** in 94% yield. Subsequently, cleavage of the isopropylidene group of **21**, followed by selective protection as the benzoyl ester, benzylation of the remaining hydroxyl group, and debenzoylation of **24** led to **25** in good overall yield. Coupling of the glycosyl donor **9** and the glycosyl acceptor **25** was achieved with $FeCl_3$ and TMU to give a sole disaccharide **26**, whose configuration of the glycosidic linkage at C-1′ was assigned as β from ^{13}C-NMR data (δ 100.2 with $^1J_{CH}$=161 Hz for C-1′). After cleavage of the acetyl group of **26**, 4′,6′-*O*-isopropylidenation of the resulting triol **27** and then deprotection of the chloroacetyl group of **28** were successively carried out by the same procedure as described for **2a**. The successful approach to the total synthesis of **1e** *via* **2b** is described below.

The free amino and hydroxyl groups of **2b** were simulta-

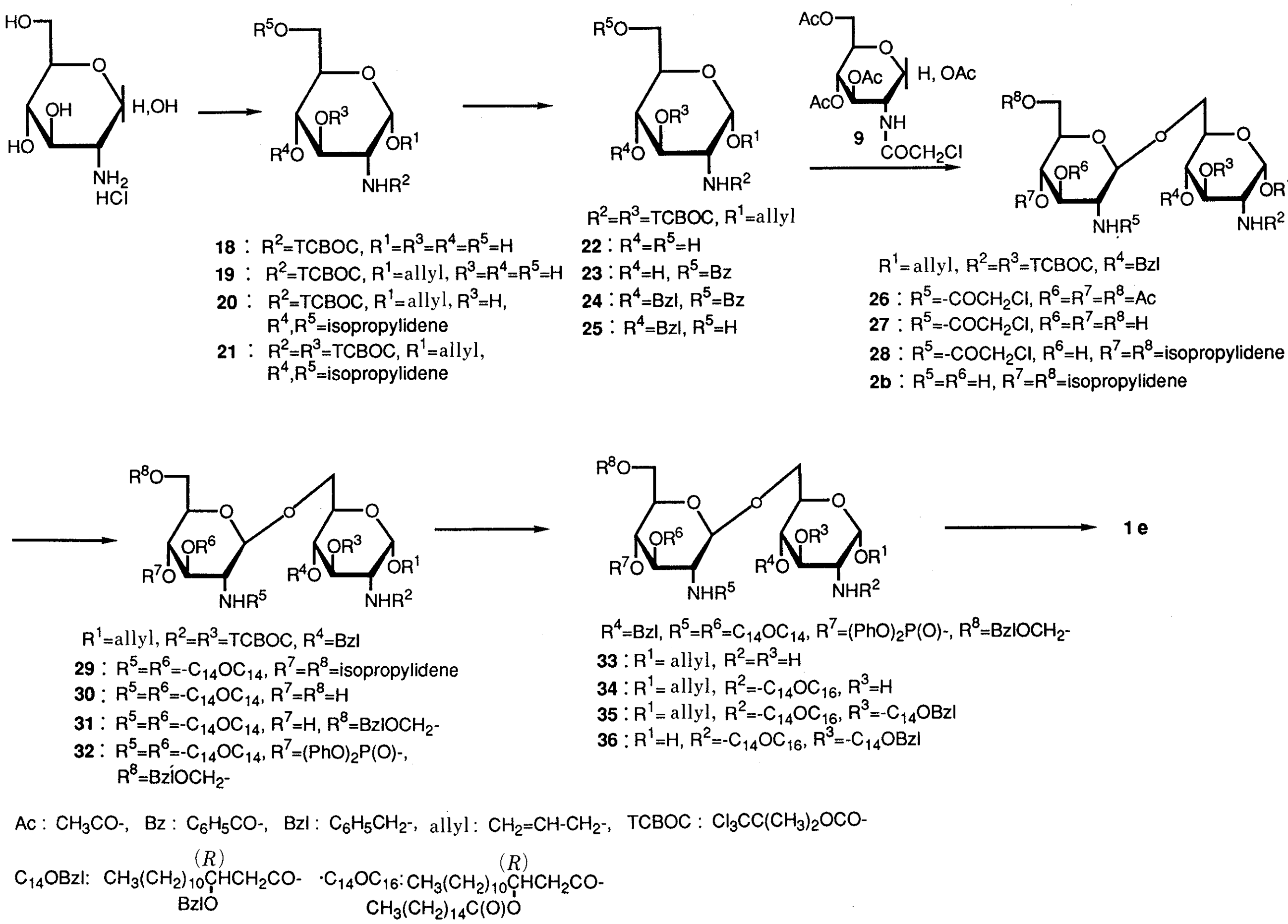


Chart 4

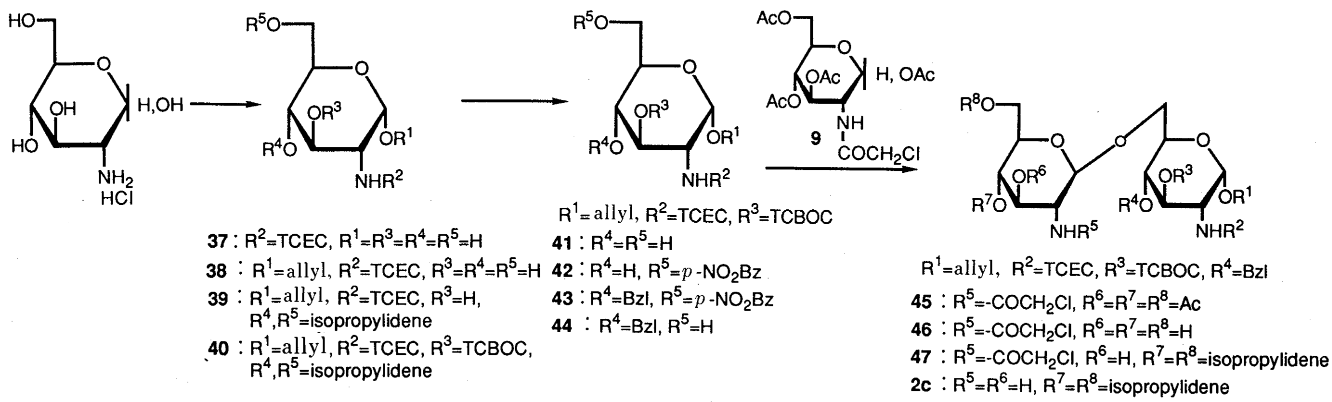


Chart 5

neously acylated with (*R*)-3-tetradecanoyloxytetradecanoic acid in the presence of DCC and a catalytic amount of DMAP in CH_2Cl_2 to give the diacylate **29** in 73% yield. Removal of the isopropylidene group of **29** with 90% acetic acid afforded the diol **30** in 75% yield. The 6′-*O*-hydroxyl group was selectively protected with benzyloxymethyl chloride and TMU in CH_2Cl_2 to give the benzyloxymethyl compound **31** in 63% yield. Then the phosphorylation of **31** with diphenylphosphoryl chloride in the presence of pyridine–DMAP in CH_2Cl_2 gave **32** in 76% yield. Treatment of **32** with Zn-dust in acetic acid gave the amino alcohol compound **33** in 89% yield. Then the free amino group of **33** was acylated with (*R*)-3-hexadecanoyloxytetradecanoic acid and DCC in CH_2Cl_2 to give the triacylated compound **34** in 67% yield. The remaining hydroxyl group of **34** was acylated with (*R*)-3-benzyloxytetradecanoic acid and DCC–DMAP in CH_2Cl_2 to give **35** in 72% yield. Selective removal of the glycosidic allyl group was followed by isomerization with iridium complex,[11] then the resultant 1-propenyl glycoside was treated with iodine[12] in aqueous THF to give **36** in 87% yield. α-Configuration of the hydroxyl group at C-1 of **36** was assigned on the basis of ^{13}C-NMR data (C-1 signal at δ 91.3 with $^{1}J_{CH}=173$ Hz). The glycosidic hydroxyl group of **36** was phosphorylated with *n*-BuLi and dibenzylphosphoryl chloride in THF at $-70\,°C$[13] and the product was immediately hydrogenolyzed. Stepwise removal of the benzyl group with Pd–C, H_2 and then phenyl esters of the 4′-*O*-phosphate group with PtO_2, H_2 afforded the final product **1e** in 10% yield from **36** after isolation by means of a silica gel column ($CHCl_3$–MeOH–H_2O–Et_3N, 20:5:1:0.05) and then acidic precipitation, and lyophilization from dioxane. The molecular weight of **1e** was confirmed by positive ion fast atom bombardment (FAB)-mass spectrometry, which showed an $(M+H+NEt_3)^+$ ion at *m*/*z* 2164.7, and an $(M+NEt_3+Na)^+$ ion at *m*/*z* 2186.8. Compound **1e** possesses a variety of biological activities of lipid A.[14] An improved synthesis of the key intermediate **2c** was developed as indicated in Chart 5. That is, the amino group of **37** was protected by a 2,2,2-trichloroethoxycarbonyl (TCEC) group in place of the expensive TCBOC group, and the protection of the 6-*O*-hydroxyl group of **41** was carried out with a *p*-nitrobenzoyl group. The overall yield of **2c** was 22.2% from D-glucosamine HCl in 12 steps, in contrast with the synthesis of **2b** in 5.0% yield from D-glucosamine HCl in 12 steps.

In this way, we have developed methods for the chemoselective protection and deprotection of the glucosamine, and demonstrated the utility of the new methodology for the efficient synthesis of lipid As, using key disaccharide intermediates.

Experimental

All melting points are uncorrected. ^{1}H-NMR spectra (90 MHz) and ^{13}C-NMR spectra (22.5 MHz) were taken on a JEOL JNM-FX90Q NMR spectrometer with tetramethylsilane (in $CDCl_3$) as an internal standard, and the chemical shifts are given in δ values. The abbreviations of signal patterns are as follows: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a JASCO A-202 infrared spectrophotometer. Optical rotations were determined with a JASCO DIP-140 digital polarimeter.

Column chromatography was carried out on silica gel (Kiesel gel-60, 70—230 mesh, Merck). Thin-layer chromatography (TLC) on Kiesel gel 60-F_{254} (Merck) was used to monitor the reaction and to ascertain the purity of the reaction products. The spots were visualized by spraying with aqueous sulfuric acid and then heating.

Allyl 2-Deoxy-4,6-*O*-isopropylidene-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-*O*-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (4) A solution of TCBOC-Cl (2.88 g, 12 mmol) in dry CH_2Cl_2 (2 ml) was added to a stirred solution of allyl 2-amino-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (**3**) (1.04 g, 4.0 mmol), prepared as previously described in the literature,[9] and DMAP (49 mg, 0.40 mmol) in dry pyridine (20 ml) at 0 °C under nitrogen. The mixture was stirred for 12 h at room temperature, then the insoluble materials were filtered off and the filtrate was evaporated. The residue was chromatographed on silica gel with $CHCl_3$–isopropyl ether (IPE) (20:1) to give **4** (2.56 g, 96%), mp 85—87 °C. $[\alpha]_D^{21}$ $-18.1°$ ($c=1.00$, $CHCl_3$). IR (KBr): 3404 (NH), 1761 (carbonate), 1732 (carbamate), 858 cm^{-1} (Me_2C). ^{1}H-NMR ($CDCl_3$) δ: 1.39, 1.47 (each 3H, s, Me_2C), 1.91 (12H, s, $Cl_3CCMe_2\times2$), 4.77 (1H, d, $J=8.1$ Hz, H-1), 5.62—6.14 (1H, m, $-CH_2=$). *Anal.* Calcd for $C_{22}H_{31}Cl_6NO_9$: C, 39.66; H, 4.69; N, 1.80. Found: C, 40.17; H, 4.76; N, 2.06.

Allyl 2-Deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (5) A solution of **4** (1.21 g, 1.82 mmol) in 90% aqueous AcOH (12 ml) was heated at 90 °C for 15 min. The mixture was cooled and the solvent was evaporated off *in vacuo*. The residue was chromatographed on silica gel with $CHCl_3$–MeOH (15:1) to give **5** (1.03 g, 90%) as prisms, mp 106 °C. $[\alpha]_D^{21}$ $-10.7°$ ($c=1.00$, $CHCl_3$). IR (KBr): 3376 (OH, NH), 1760 (carbonate), 1725 cm^{-1} (carbamate). ^{1}H-NMR ($CDCl_3$) δ: 1.90 (12H, s, $Cl_3CCMe_2\times2$), 4.70 (1H, d, $J=7.9$ Hz, H-1), 5.64—6.15 (1H, m, $-CH=$). *Anal.* Calcd for $C_{19}H_{27}Cl_6NO_9$: C, 36.45; H, 4.35; N, 2.24. Found: C, 36.18; H, 4.26; N, 2.22.

Allyl 6-*O*-Benzoyl-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (6) Benzoyl chloride (0.343 g, 2.44 mmol) was added to a stirred solution of **5** (1.02 g, 1.63 mmol) and pyridine (0.387 g, 4.89 mmol) in dry THF (15 ml) at 0 °C under nitrogen. The mixture was stirred for 2 h at 0 °C with addition of benzoyl chloride (0.343 g, 2.44 mmol) after 5 h at 0 °C, and then a small amount of water (1.0 ml) was added. The organic layer was dried and evaporated. After removal of the solvent, the residue was chromatographed on silica gel with $CHCl_3$–IPE (20:1) to give **6** (0.892 g, 75%) as white prisms, mp 84 °C. $[\alpha]_D^{23}$ $-9.97°$ ($c=1.00$, $CHCl_3$). IR (KBr): 3404 (NH, OH), 1756 (carbonate), 1723 (carbamate, ester), 710 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.91 (12H, s, $Cl_3CCMe_2\times2$), 5.66—6.14 (1H, m, $-CH=$), 7.33—8.18 (5H, m, Ph). *Anal.* Calcd for $C_{26}H_{31}Cl_6NO_{10}$: C, 42.76; H, 4.28; N, 1.92. Found: C, 43.07; H, 4.37; N, 1.92.

Allyl 6-*O*-Benzoyl-4-*O*-benzyl-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (7) Trifluoromethanesulfonic acid (0.123 g, 0.82 mmol) was added to a stirred solution of **5** (2.00 g, 2.73 mmol) and benzyl 2,2,2-trichloroacetimidate (1.38 g, 5.46 mmol) in dry CH_2Cl_2 (30 ml) at 0 °C under nitrogen. After 12 h at room temperature, the reaction mixture was washed with saturated aqueous $NaHCO_3$, dried and concentrated. The residue was subjected to column chromatography on silica gel with $CHCl_3$–IPE (50:1) to give **7** (1.08 g, 49%), as white prisms, mp 69 °C. $[\alpha]_D^{23}$ $+9.73°$ ($c=1.04$, $CHCl_3$). IR (KBr): 3420 (NH), 1759 (carbonate), 1730 (carbamate, ester), 712, 700 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.91 (12H, s, $Cl_3CCMe_2\times2$), 5.64—6.11 (1H, m, $-CH=$), 7.24 (5H, s, $PhCH_2$), 7.40—8.14 (5H, m, PhCO). *Anal.* Calcd for $C_{33}H_{37}Cl_6NO_{10}$: C, 48.32; H, 4.55; N, 1.71. Found: C, 48.08; H, 4.60; N, 1.70.

Allyl 4-*O*-Benzyl-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (8) Compound **6** (0.470 g, 0.58 mmol) was dissolved in a solution (20 ml) of NH_4OH–MeOH (1:10). The solution was stirred at room temperature for 48 h, then the solvent was evaporated off *in vacuo*. The residue was chromatographed on silica gel with $CHCl_3$–IPE (10:1) to give **8** (0.488 g, 74%), as white prisms, mp 75—77 °C. $[\alpha]_D^{24}$ $-9.98°$ ($c=1.04$, $CHCl_3$). IR (KBr): 3412 (NH, OH), 1759 (carbonate), 1729 (carbamate), 698 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.90 (12H, s, $Cl_3CCMe_2\times2$), 4.68 (2H, s, $PhCH_2$), 5.64—6.13 (1H, m, $-CH=$), 7.29 (5H, s, $PhCH_2$). *Anal.* Calcd for $C_{26}H_{33}Cl_6NO_9$: C, 43.60; H, 4.64; N, 1.96. Found: C, 43.84; H, 4.66; N, 1.89.

Allyl 4-*O*-Benzyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-chloroacetylamino-2-deoxy-β-D-glucopyranosyl)-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (10) A mixture of **8** (0.323 g, 0.46 mmol), 1,3,4,6-tetra-*O*-acetyl-2-chloroacetamido-2-deoxy-β-D-glucopyranose (**9**) (0.109 g, 0.92 mmol), TMU (0.390 g, 0.92 mmol) and pulverized MS 4A (1 g) in dry CH_2Cl_2 (10 ml) was stirred for 1 h, and anhydrous $FeCl_3$ (0.180 g, 1.1 mmol) was added at room temperature under nitrogen. After 24 h at room temperature, the same amounts of $FeCl_3$ and TMU were again added. Since the donor **9** was still present, more reagents (equivalent to the previous amounts) were added and stirring was continued for 24 h. The mixture was then poured into ice-cold, aqueous $NaHCO_3$. After the addition of $CHCl_3$ and mixing, the organic layer was filtered through Celite, and the filtrate and washings were combined, washed with saturated aqueous $NaHCO_3$ and then water, dried and concentrated. The crude product was purified by column chromatography with $CHCl_3$–acetone (30:1) to give **10** (0.351 g, 72%) as white prisms, mp 100—102 °C. $[\alpha]_D^{21}$ $-6.97°$ ($c=1.13$, $CHCl_3$). IR (KBr): 3320 (NH), 1757 (carbonate, carbamate), 1657 (amide), 697 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.84, 1.88 (12H, s, $Cl_3CCMe_2\times2$), 2.03 (9H, s, $AcO\times3$), 3.92 (2H, s, $ClCH_2CO$), 4.62 (2H, s, $PhCH_2$), 4.83 (1H, d, $J=8.0$ Hz, H-1′), 5.63—6.12 (1H, m, $-CH=$), 6.76 (1H, d, $J=9.3$ Hz, $NHCOCH_2Cl$), 7.28 (5H, s, $PhCH_2$). *Anal.* Calcd for $C_{40}H_{51}Cl_7NO_{17}$: C, 44.48; H, 4.76; N, 2.59. Found: C, 44.36; H, 4.81; N, 2.46.

Allyl 4-*O*-Benzyl-6-*O*-(2-chloroacetylamino-2-deoxy-β-D-glucopyranosyl)-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (11) Compound **9** (0.300 g, 0.28 mmol) was dissolved in a solution of NH_4OH–MeOH (1:10) (3.0 ml). The mixture was stirred for 15 h at room temperature and concentrated *in vacuo*. The residue was chromatographed on silica gel with $CHCl_3$–MeOH (10:1) to give **11** (0.227 g, 86%) as a white powder, mp 174—175 °C. $[\alpha]_D^{24}$ $-21.6°$ ($c=1.00$, $CHCl_3$). IR (KBr): 3372 br (NH, OH), 1762 (carbonate), 1740 (carbamate), 1683 (amide), 700 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.83, 1.89 (12H, s, $Cl_3CCMe_2\times2$), 4.05 (2H, s,

$ClCH_2CO$), 4.70 (2H, s, $PhCH_2$), 5.70—6.20 (1H, m, –CH=), 6.74 (1H, d, J=9.3 Hz, $NHCOCH_2Cl$), 7.33 (5H, s, Ph). *Anal.* Calcd for $C_{34}H_{45}Cl_7N_2O_{14}\cdot H_2O$: C, 42.02; H, 4.87; N, 2.88. Found: C, 42.11; H, 4.68; N, 2.79.

Allyl 4-*O*-Benzyl-6-*O*-(2-chloroacetylamino-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (12) *p*-TsOH (0.012 g, 0.07 mmol) was added to a stirred solution of **11** (0.225 g, 0.24 mmol) and 2,2-dimethoxypropane (0.075 g, 0.72 mmol) in DMF (2.0 ml) at room temperature under nitrogen. After 5 h, the reaction mixture was neutralized with ion exchange resin (Amberlite IRA-400) (0.282 g, 1.04 mg eq.) and then the resin was removed by filtration. The filtrate was evaporated to dryness and the residue was chromatographed on silica gel with $CHCl_3$–acetone (10 : 1) to give **12** (0.166 g, 71%) as white prisms, mp 126—128 °C. $[\alpha]_D^{26}$ −23.7° (c=0.27, $CHCl_3$). IR (KBr): 3400 br (NH, OH), 1761 (carbonate), 1737 (carbamate), 1673 (amide), 855 (Me_2C), 700 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.43, 1.52 (each 3H, s, Me_2C), 1.83, 1.88 (12H, s, $Cl_3CCMe_2\times 2$), 3.99 (2H, s, $ClCH_2CO$), 4.61 (2H, s, $PhCH_2$), 5.68—6.18 (1H, m, –CH=), 6.75 (1H, d, J=9.0 Hz, $NHCOCH_2Cl$), 7.22 (5H, s, Ph). *Anal.* Calcd for $C_{37}H_{49}Cl_7N_2O_{14}$: C, 44.71; H, 4.79; N, 2.82. Found: C, 44.45; H, 4.92; N, 2.88.

Allyl 4-*O*-Benzyl-6-*O*-(2-amino-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (2a) A mixture of **12** (0.766 g, 0.77 mmol), thiourea (0.293 g, 3.85 mmol), diisopropylethylamine (0.498 g, 3.85 mmol), and pulverized MS 4A (1 g) was stirred at 55 °C for 12 h under nitrogen. The resulting suspension was filtered through Celite and the filtrate was concentrated *in vacuo*. The residue was subjected to silica gel chromatography with $CHCl_3$–MeOH (40 : 1) to give **2a** (0.648 g, 92%) as reddish prisms, mp 119—121 °C. $[\alpha]_D^{21}$ −20.0° (c=1.17, $CHCl_3$). IR (KBr): 3372 br (NH, OH), 1761 (carbonate), 1738 (carbamate), 854 (Me_2C), 700 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.43, 1.50 (each 3H, s, Me_2C), 1.84, 1.89 (12H, s, $Cl_3CCMe_2\times 2$), 4.65, 4.69 (each 1H, d, J=11.2 Hz, $PhC\underline{H}_2$), 5.65—6.11 (1H, m, –CH=), 7.29 (5H, s, Ph). *Anal.* Calcd for $C_{35}H_{48}Cl_7N_2O_{13}$: C, 45.82; H, 5.27; N, 3.05. Found: C, 45.57; H, 5.30; N, 3.05.

Allyl 4-*O*-Benzyl-6-*O*-[3-*O*-[(*R*)-3-benzyloxytetradecanoyl]-2-[(*R*)-3-benzyloxytetradecanoylamino]-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranosyl]-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (13) DCC (0.481 g, 2.3 mmol) was added to a stirred solution of **2a** (0.648 g, 0.71 mmol), (*R*)-3-benzyloxytetradecanoic acid (0.709 g, 2.1 mmol), and DMAP (0.009 g, 0.07 mmol) in dry CH_2Cl_2 (10 ml) at 0 °C under nitrogen. The mixture was stirred for 6 h at 0 °C, then at room temperature for 12 h. The resulting suspension was filtered through Celite and evaporated. The residue was chromatographed on silica gel with $CHCl_3$–IPE (10 : 1) to give **13** (0.948 g, 87%) as white prisms, mp 95—97 °C. $[\alpha]_D^{27}$ −13.0° (c=0.64, $CHCl_3$). IR (KBr): 3328 (NH), 1761 (carbonate), 1738 (carbamate), 1651 (amide), 859 (Me_2C), 700 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (6H, t, J=5.8 Hz, $-(CH_2)_{10}C\underline{H}_3\times 2$), 1.25 (40H, br s, $-(C\underline{H}_2)_{10}CH_3\times 2$), 1.33, 1.38 (each 3H, s, Me_2C), 1.84, 1.88 (12H, s, $Cl_3CCMe_2\times 2$), 2.27 (2H, d, J=4.7 Hz, $NCOCH_2$), 2.48 (2H, d, J=5.6 Hz, $OCOCH_2$), 4.50 (4H, br s, $PhCH_2\times 2$), 4.58 (2H, br s, 4-position $PhCH_2$), 5.62—6.04 (1H, m, –CH=), 6.27 (1H, d, J=9.5 Hz, $NHCOCH_2$), 7.27, 7.31, 7.34 (15H, s, Ph × 3). *Anal.* Calcd for $C_{77}H_{112}Cl_6N_2O_{17}$: C, 59.65; H, 7.28; N, 1.81. Found: C, 59.37; H, 7.21; N, 1.76.

Allyl 4-*O*-Benzyl-6-*O*-[3-*O*-[(*R*)-3-benzyloxytetradecanoyl]-2-[(*R*)-3-benzyloxytetradecanoylamino]-2-deoxy-β-D-glucopyranosyl]-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (14) A solution of **13** (0.412 g, 0.27 mmol) in 90% aqueous AcOH (5.0 ml) was heated at 90 °C for 15 min. After cooling, the solvent was evaporated off *in vacuo*. The residue was subjected to silica gel chromatography with $CHCl_3$–MeOH (20 : 1) to give **14** (0.376 g, 94%) as white prisms, mp 65—67 °C. $[\alpha]_D^{20}$ −13.3° (c=1.09, $CHCl_3$). IR (KBr): 3406 br (NH, OH), 1758 (carbonate), 1742 (carbamate, ester), 1664 (amide), 696 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (6H, t, J=5.5 Hz, $-(CH_2)_{10}C\underline{H}_3\times 2$), 1.25 (40H, br s, $-(C\underline{H}_2)_{10}CH_3\times 2$), 1.84, 1.88 (each 6H, s, $Cl_3CCMe_2\times 2$), 2.28 (2H, d, J=5.4 Hz, $NCOCH_3$), 2.56 (2H, d, J=4.9 Hz, $OCOCH_2$), 4.50 (4H, br s, $PhCH_2\times 2$), 4.62 (2H, br s, 4-position $PhCH_2$), 5.62—6.11 (1H, m, –CH=), 6.29 (1H, d, J=9.5 Hz, $NHCOCH_2$), 7.28, 7.30, 7.33 (15H, s, Ph × 3). *Anal.* Calcd for $C_{74}H_{108}Cl_6N_2O_{17}$: C, 58.85; H, 7.21; N, 1.85. Found: C, 58.80; H, 7.19; N, 1.93.

Allyl 4-*O*-Benzyl-6-*O*-[6-*O*-benzyloxymethyl-3-*O*-[(*R*)-3-benzyloxytetradecanoyl]-2-[(*R*)-3-benzyloxytetradecanoylamino]-2-deoxy-β-D-glucopyranosyl]-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (15) Benzyloxymethyl chloride (0.279 g, 1.78 mmol) was added to a stirred solution of **14** (0.538 g, 0.36 mmol), and TMU (0.207 g, 1.80 mmol), in dry CH_2Cl_2 (7.0 ml) at 0 °C under nitrogen. After 20 h at room temperature, the reaction mixture was washed with saturated aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel with $CHCl_3$–acetone (10 : 1) to give **15** (0.424 g, 73%) as white prisms, mp 87—89 °C. $[\alpha]_D^{21}$ −11.5° (c=0.61, $CHCl_3$). IR (KBr): 3408 br (NH, OH), 1758 (carbonate), 1742 (carbamate, ester), 1653 (amide), 715, 698 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (6H, t, J=5.6 Hz, $-(CH_2)_{10}C\underline{H}_3\times 2$), 1.25 (40H, br s, $-(C\underline{H}_2)_{10}CH_3\times 2$), 1.84, 1.88 (each 6H, s, $Cl_3CCMe_2\times 2$), 2.28 (2H, d, J=5.2 Hz, $NCOCH_2$), 2.56 (2H, d, J=6.6 Hz, $OCOCH_2$), 4.51 (4H, br s, $PhCH_2\times 2$), 4.57 (4H, br s, 4,6′-position $PhCH_2\times 2$), 4.74 (2H, s, $OC\underline{H}_2OCH_2Ph$), 5.62—6.07 (1H, m, –CH=), 6.25 (1H, d, J=8.5 Hz, $NHCOCH_2$), 7.29, 7.32, 7.33 (20H, s, Ph × 4). *Anal.* Calcd for $C_{82}H_{116}Cl_6N_2O_{18}\cdot H_2O$: C, 59.74; H, 7.21; N, 1.70. Found: C, 59.63; H, 6.97; N, 1.73.

Allyl 4-*O*-Benzyl-6-*O*-[6-*O*-benzyloxymethyl-3-*O*-[(*R*)-3-benzyloxytetradecanoyl]-2-[(*R*)-3-benzyloxytetradecanoylamino]-2-deoxy-4-*O*-diphenylphosphono-β-D-glucopyranosyl]-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-β-D-glucopyranoside (16) Diphenylphosphorochloridate (0.211 g, 0.75 mmol) was added to a stirred solution of **15** (0.250 g, 0.15 mmol), pyridine (0.059 g, 0.75 mmol) and DMAP (0.092 g, 0.75 mmol) at 0 °C under nitrogen. After 3 h at room temperature, the reaction mixture was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and evaporated to dryness. The residue was chromatographed on silica gel with $CHCl_3$–acetone (30 : 1) to give **16** (0.211 g, 76%) as white prisms, mp 53—55 °C. $[\alpha]_D^{21}$ −4.72° (c=1.09, $CHCl_3$). IR (KBr): 3420 (NH), 1754 (carbonate), 1742 (carbamate, ester), 1670 (amide), 1215 (P=O), 958 (P–O–Ph), 695 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (6H, t, J=5.4 Hz, $-(CH_2)_{10}C\underline{H}_3\times 2$), 1.24 (40H, br s, $-(C\underline{H}_2)_{10}CH_3\times 2$), 2.13 (2H, d, J=6.1 Hz, $NCOCH_2$), 2.43 (2H, d, J=6.6 Hz, $OCOCH_2$), 4.52 (8H, br s, $PhCH_2\times 4$), 4.63 (2H, s, $OC\underline{H}_2OCH_2Ph$), 5.57—5.96 (1H, m, –CH=), 6.09 (1H, d, J=9.0 Hz, $NHCOCH_2$), 7.19, 7.25, 7.34 (30H, s, Ph × 6). *Anal.* Calcd for $C_{94}H_{125}Cl_6N_2O_{21}P$: C, 60.61; H, 6.76; N, 1.50. Found: C, 60.61; H, 6.76; N, 1.29.

Allyl 4-*O*-Benzyl-6-*O*-[6-*O*-benzyloxymethyl-3-*O*-[(*R*)-3-benzyloxytetradecanoyl]-2-[(*R*)-3-benzyloxytetradecanoylamino]-2-deoxy-4-*O*-diphenylphosphono-β-D-glucopyranosyl]-2-deoxy-3-*O*-[(*R*)-3-benzyloxytetradecanoyl]-2-[(*R*)-3-benzyloxytetradecanoylamino]-β-D-glucopyranoside (17) Zinc powder (0.252 g, 3.9 mmol) was added to a stirred solution of **16** (0.120 g, 0.064 mmol) in AcOH (3.0 ml) and the mixture was stirred at room temperature for 12 h. After removal of the insoluble materials by filtration, the solvent was evaporated off *in vacuo*. The residue was again dissolved in CH_2Cl_2 (3.0 ml), and the solution was washed with saturated aqueous $NaHCO_3$, dried and concentrated. The residue was dissolved in dry CH_2Cl_2 (1.0 ml). To this solution, (*R*)-3-benzyloxytetradecanoic acid (0.048 g, 0.14 mmol) and DMAP (0.009 g, 0.07 mmol) were added, and then DCC (0.029 g, 0.14 mmol) was added at 0 °C and the whole was stirred for 5 h at the same temperature. After being stirring at room temperature for 12 h, the resulting suspension was filtered off and the filtrate was concentrated. The residue was dissolved in ethyl acetate (2.0 ml), the insoluble materials were filtered off, and the filtrate was evaporated *in vacuo*. After removal of the solvent, the residue was subjected to silica gel chromatography with $CHCl_3$–ether (10 : 1) to give **17** (0.070 g, 52%) as white prisms, mp 50—53 °C. $[\alpha]_D^{19}$ −1.67° (c=1.29, $CHCl_3$). IR (KBr): 3312 (NH), 1750, 1727 (ester), 1662 (amide), 1220 (P=O), 958 (P–O–Ph), 710, 697 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (12H, t, J=5.6 Hz, $-(CH_2)_{10}C\underline{H}_3\times 4$), 1.25 (80H, br s, $-(C\underline{H}_2)_{10}CH_3\times 4$), 1.98—2.62 (8H, m, $COCH_2\times 4$), 4.50 (12H, br s, $PhCH_2\times 6$), 4.62 (2H, s, $OC\underline{H}_2OCH_2Ph$), 5.52—5.90 (1H, m, –CH=), 7.18, 7.25, 7.26, 7.32 (40H, s, Ph × 8). *Anal.* Calcd for $C_{126}H_{179}N_2O_{21}P\cdot 4H_2O$: C, 70.04; H, 8.72; N, 1.30. Found: C, 70.02; H, 8.53; N, 1.34.

2-Deoxy-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-D-glucopyranose (18) A solution of TCBOC-Cl (21.6 g, 90.0 mmol) in ether (100 ml) was added portionwise to a stirred solution of D-glucosamine hydrochloride (19.4 g, 90.0 mmol) and $NaHCO_3$ (15.1 g, 180 mmol) in water (400 ml) at 0 °C for 1 h. The mixture was stirred for overnight at room temperature. The colorless precipitate was collected by filtration, and washed with ether to give **18** (29.8 g, 86.7%), mp 141—144 °C. $[\alpha]_D^{24}$ +37.0° (c=1.00, MeOH). *Anal.* Calcd for $C_{11}H_{18}Cl_3NO_7\cdot 1/2H_2O$: C, 33.74; H, 4.89; N, 3.58. Found: C, 33.75; H, 5.02; N, 3.29.

Allyl 2-Deoxy-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-α-D-gluco-

pyranoside (19) Compound **18** (23.2 g, 60.7 mmol) was heated with stirring at 100 °C in allyl alcohol (150 ml) containing 2% (w/v) dry HCl for 1.5 h. The mixture was cooled and the solvent was evaporated off *in vacuo*. The residue was chromatographed on silica gel with $CHCl_3$–MeOH (15 : 1) to give **5**α (15.8 g, 61.7%) and **5**β (1.86 g, 7.25%). **5**α: mp 143—146 °C. $[\alpha]_D^{25}$ +91.7° (c=1.00, MeOH). IR (KBr): 3424 (NH, OH), 1743 (carbamate), 1640 cm^{-1} (allyl). ^1H-NMR (acetone-d_6) δ: 1.89 (6H, s, Cl_3CCMe_2), 4.89 (1H, d, J=2.6 Hz, H-1), 5.02—5.54 (2H, m, $=CH_2$), 5.68—6.17 (1H, m, =CH–), 6.32 (1H, d, J=6.9 Hz, NH). ^{13}C-NMR (acetone-d_6) δ: 21.9, 22.1 (q, CH_3), 55.7 (t, O$\underline{C}H_2CH=$), 88.3 (s, $Cl_3C\underline{C}Me_2$), 97.5 (d, C-1), 107.6 (s, CCl_3), 116.9 (t, $=CH_2$), 135.3 (d, =CH–), 155.6 (s, NHCO). *Anal.* Calcd for $C_{14}H_{22}Cl_3NO_7$: C, 39.78; H, 5.25; N, 3.31. Found: C, 39.91; H, 5.26; N, 3.20.

Allyl 2-Deoxy-4,6-*O*-isopropylidene-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-α-D-glucopyranoside (20) 2,2-Dimethoxypropane (3.44 g, 33 mmol) and *p*-TsOH (0.48 g, 2.8 mmol) were added to a solution of compound **19** (4.67 g, 11.0 mmol) in DMF (50 ml) at room temperature. After 5 h, ethyl acetate–water (7 : 30) (925 ml) was added, and the mixture was neutralized by addition of 10% aqueous NaOH (25 ml). The organic layer was washed with brine, and dried over $MgSO_4$. After evaporation, the residue was chromatographed on silica gel with $CHCl_3$–acetone (15 : 1) to give **20** (4.17 g, 81.9%), mp 129—131 °C. $[\alpha]_D^{21}$ +63.9° (c=1.34, $CHCl_3$). IR (KBr): 3480 (NH, OH), 1748 (carbamate), 1640 (allyl), 858 cm^{-1} (Me_2C). ^1H-NMR ($CDCl_3$) δ: 1.44, 1.52 (6H, s, Me_2C), 1.92 (6H, s, Cl_3CCMe_2), 4.88 (1H, d, J=1.3 Hz, H-1), 5.11—5.44 (3H, m, $=CH_2$, H-3), 5.65—6.15 (1H, m, =CH–). ^{13}C-NMR ($CDCl_3$) δ: 19.2, 29.1 (q, Me_2C), 21.7 (q, $Cl_3CC\underline{Me}_2$), 55.6 (t, O$\underline{C}H_2CH=$), 88.6 (s, $NHCO_2\underline{C}$), 97.1 (d, C-1), 99.9 (s, $Me_2\underline{C}$), 106.4 (s, $NHCO_2C\underline{C}Cl_3$), 118.1 (t, $=CH_2$), 133.4 (d, =CH–), 154.4 (s, $NHCO_2$). *Anal.* Calcd for $C_{17}H_{26}Cl_3NO_7$: C, 44.12; H, 5.66; N, 3.03. Found: C, 44.37; H, 5.73; N, 2.88.

Allyl 2-Deoxy-4,6-*O*-isopropylidene-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-α-D-glucopyranoside (21) A solution of TCBOC-Cl (9.0 g, 37.6 mmol) in dry CH_2Cl_2 (30 ml) was added to a stirred solution of **20** (11.6 g, 25.1 mmol) and DMAP (0.61 g, 5.0 mmol) in dry pyridine (60 ml) at 0 °C under nitrogen. The mixture was stirred for 12 h at room temperature, then the insoluble materials were filtered off and the filtrate was evaporated. The residue was chromatographed on silica gel with $CHCl_3$–IPE (20 : 1) to give **21** (15.7 g, 93.8%), mp 65—67 °C. $[\alpha]_D^{21}$ +50.4° (c=1.01, $CHCl_3$). IR (KBr): 3360 (NH), 1760 (carbonate), 1740 (carbamate), 1655 (allyl), 859 cm^{-1} (Me_2C). ^1H-NMR ($CDCl_3$) δ: 1.40, 1.48 (6H, s, Me_2C), 1.89 (12H, s, $Cl_3CCMe_2 \times 2$), 4.88 (1H, d, J=3.6 Hz, H-1), 5.65—6.12 (1H, m, =CH–). ^{13}C-NMR ($CDCl_3$) δ: 19.1, 29.0 (q, Me_2C), 21.2, 21.6, 21.7 (q, $Cl_3CC\underline{Me}_2$), 54.1 (t, O$\underline{C}H_2CH=$), 88.5 (s, $NHCO_2\underline{C}$), 90.2 (s, $OCO_2\underline{C}$), 97.1 (d, C-1), 99.9 (s, $Me_2\underline{C}$), 105.5 (s, $OCO_2C\underline{C}Cl_3$), 106.3 (s, $NHCO_2C\underline{C}Cl_3$), 118.2 (t, $=CH_2$), 133.4 (d, =CH–), 152.4 (s, OCO_2), 153.4 (s, $NHCO_2$). *Anal.* Calcd for $C_{22}H_{31}Cl_6NO_9$: C, 39.66; H, 4.69; N, 2.10. Found: C, 39.64; H, 4.61; N, 2.05.

Allyl 2-Deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-α-D-glucopyranoside (22) Compound **22** was obtained by a procedure similar to that described for **5**, and was recrystallized from IPE in 83% yield, mp 74—77 °C. $[\alpha]_D^{24}$ +55.3° (c=1.00, $CHCl_3$). IR (KBr): 3440 br (NH, OH), 1757 (carbonate), 1740 (carbamate), 1650 cm^{-1} (allyl). ^1H-NMR ($CDCl_3$) δ: 1.89, 1.93 (12H, s, $Cl_3CCMe_2 \times 2$), 4.91 (1H, d, J=3.7 Hz, H-1), 5.12—5.44 (2H, m, $=CH_2$), 5.65—6.15 (1H, m, =CH–). ^{13}C-NMR ($CDCl_3$) δ: 21.3, 21.6, 21.7 (q, $Cl_3CC\underline{Me}_2$), 53.6 (t, O$\underline{C}H_2CH=$), 88.5 (s, $NHCO_2\underline{C}$), 90.5 (s, $OCO_2\underline{C}$), 96.7 (d, C-1), 105.4 (s, $OCO_2C\underline{C}Cl_3$), 106.3 (s, $NHCO_2C\underline{C}Cl_3$), 118.1 (t, $=CH_2$), 133.3 (d, =CH–), 152.8 (s, OCO_2), 153.4 (s, $NHCO_2$). *Anal.* Calcd for $C_{19}H_{27}Cl_6NO_9$: C, 36.45; H, 4.35; N, 2.24. Found: C, 35.99; H, 4.25; N, 2.13.

Allyl 6-*O*-Benzoyl-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-α-D-glucopyranoside (23) Compound **23** was obtained by a procedure similar to that described for **6**, and was chromatographed on silica gel with $CHCl_3$–IPE (10 : 1); 77% yield, mp 69—70 °C. $[\alpha]_D^{21}$ +52.0° (c=1.01, $CHCl_3$). IR (KBr): 3440 (NH, OH), 1758 (carbonate), 1740 (carbamate), 1648 (allyl), 710 cm^{-1} (Ph). ^1H-NMR ($CDCl_3$) δ: 1.89, 1.93 (12H, s, $Cl_3CCMe_2 \times 2$), 4.93 (1H, d, J=3.4 Hz, H-1), 5.12—5.42 (2H, m, $=CH_2$), 5.67—6.14 (1H, m, =CH–), 7.32—8.11 (5H, m, PhCO). ^{13}C-NMR ($CDCl_3$) δ: 21.3, 21.6, 21.7 (q, $Cl_3CC\underline{Me}_2$), 53.7 (t, O$\underline{C}H_2CH=$), 88.9 (s, $NHCO_2\underline{C}$), 90.5 (s, $OCO_2\underline{C}$), 96.8 (d, C-1), 105.4 (s, $OCO_2C\underline{C}Cl_3$), 107.0 (s, $NHCO_2C\underline{C}Cl_3$), 118.2 (t, $=CH_2$), 128.5, 130.0 (d, Ph), 133.3 (d, =CH–), 152.9 (s, OCO_2), 153.5 (s, $NHCO_2$), 166.9 (s, OCOPh). *Anal.* Calcd for $C_{26}H_{31}Cl_6NO_{10}$: C, 42.76; H, 4.28; N, 1.92. Found: C, 42.31; H, 4.28; N, 1.94.

Allyl 6-*O*-Benzoyl-4-*O*-benzyl-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-α-D-glucopyranoside (24) Compound **24** was obtained by a procedure similar to that described for **7**, and was chromatographed on silica gel with $CHCl_3$–IPE (50 : 1); 83% yield, mp 50—51 °C. $[\alpha]_D^{19}$ +49.7° (c=0.30, $CHCl_3$). IR (KBr): 3432 (NH), 1756 (carbonate), 1723 (carbamate), 1650 (allyl), 711, 697 cm^{-1} (Ph). ^1H-NMR ($CDCl_3$) δ: 1.90 (12H, s, $Cl_3CCMe_2 \times 2$), 4.58, 4.78 (each 1H, d, J=10.7 Hz, CH_2Ph), 4.92 (1H, d, J=3.4 Hz, H-1), 5.65—6.13 (1H, m, =CH–), 7.25 (5H, s, $PhCH_2$), 7.30—8.08 (5H, m, PhCO). ^{13}C-NMR ($CDCl_3$) δ: 21.1, 21.6, 21.7 (q, $Cl_3CC\underline{Me}_2$), 53.8 (t, O$\underline{C}H_2CH=$), 88.5 (s, $NHCO_2\underline{C}$), 90.3 (s, $OCO_2\underline{C}$), 96.7 (d, C-1), 105.4 (s, $OCO_2C\underline{C}Cl_3$), 106.3 (s, $NHCO_2C\underline{C}Cl_3$), 118.2 (t, $=CH_2$), 128.1, 128.4, 129.6 (d, Ph), 133.1 (s, Ph), 133.1 (d, =CH–), 152.4 (s, OCO_2), 153.5 (s, $NHCO_2$), 166.0 (s, OCOPh). *Anal.* Calcd for $C_{33}H_{37}Cl_6NO_{10}$: C, 48.32; H, 4.55; N, 1.71. Found: C, 48.68; H, 5.10; N, 1.64.

Allyl 4-*O*-Benzyl-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butyloxycarbonylamino)-α-D-glucopyranoside (25) Compound **25** was obtained by a procedure similar to that described for **8**, and was chromatographed on silica gel with $CHCl_3$–IPE (10 : 1); 57% yield, mp 41 °C. $[\alpha]_D^{21}$ +53.8° (c=1.06, $CHCl_3$). IR (KBr): 3448 (NH, OH), 1758 (carbonate), 1740 (carbamate), 1650 (allyl), 715, 697 cm^{-1} (Ph). ^1H-NMR ($CDCl_3$) δ: 1.90 (12H, s, $Cl_3CCMe_2 \times 2$), 4.69, 4.72 (each 1H, d, J=10.7 Hz, CH_2Ph), 4.90 (1H, d, J=3.4 Hz, H-1), 5.65—6.12 (1H, m, =CH–), 7.31 (5H, s, $PhCH_2$). ^{13}C-NMR ($CDCl_3$) δ: 21.1, 21.6 (q, $Cl_3CC\underline{Me}_2$), 53.9 (t, O$\underline{C}H_2CH=$), 88.4 (s, $NHCO_2\underline{C}$), 90.3 (s, $OCO_2\underline{C}$), 96.6 (d, C-1), 105.4 (s, $OCO_2C\underline{C}Cl_3$), 106.3 (s, $NHCO_2C\underline{C}Cl_3$), 118.0 (t, $=CH_2$), 127.5, 128.5 (d, Ph), 133.2 (d, =CH–), 137.5 (s, Ph), 152.5 (s, OCO_2), 153.6 (s, $NHCO_2$). *Anal.* Calcd for $C_{26}H_{33}Cl_6NO_9$: C, 43.60; H, 4.64; N, 1.94. Found: C, 43.39; H, 4.66; N, 1.99.

Allyl 4-*O*-Benzyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-chloroacetylamino-2-deoxy-β-D-glucopyranosyl)-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-α-D-glucopyranoside (26) Compound **26** was obtained by a procedure similar to that described for **10**, and was chromatographed on silica gel with $CHCl_3$–acetone (20 : 1); 80% yield, mp 102—104 °C. $[\alpha]_D^{20}$ +32.8° (c=1.41, $CHCl_3$). IR (KBr): 3444 (NH), 1753 (carbonyl), 1690 (amide), 696 cm^{-1} (Ph). ^1H-NMR ($CDCl_3$) δ: 1.89 (12H, s, $Cl_3CCMe_2 \times 2$), 2.04, 2.05 (9H, s, $CH_3CO \times 3$), 3.92 (2H, s, $NCOCH_2Cl$), 4.61, 4.67 (each 1H, d, J=11.7 Hz, CH_2Ph), 5.65—6.12 (1H, m, =CH–), 6.71 (1H, d, J=8.3 Hz, $NHCOCH_2Cl$), 7.35 (5H, s, $PhCH_2$). ^{13}C-NMR ($CDCl_3$) δ: 20.6 (q, CH_3CO), 21.1, 21.5, 21.6 (q, $Cl_3CC\underline{Me}_2$), 42.4 (t, Cl$\underline{C}H_2CO$), 53.5 (t, O$\underline{C}H_2CH=$), 88.4 (s, $NHCO_2\underline{C}$), 90.2 (s, $OCO_2\underline{C}$), 96.4 (d, C-1), 100.2 (C-1′), 105.3 (s, $OCO_2C\underline{C}Cl_3$), 106.3 (s, $NHCO_2C\underline{C}Cl_3$), 118.0 (t, $=CH_2$), 127.7, 128.0, 128.5 (d, Ph), 133.2 (d, =CH–), 137.5 (s, Ph), 152.3 (s, OCO_2), 153.3 (s, $NHCO_2$), 166.3 (s, NH$\underline{C}OCH_2Cl$), 169.3, 170.6 (s, CH_3CO). *Anal.* Calcd for $C_{40}H_{51}Cl_7N_2O_{17}$: C, 44.48; H, 4.76; N, 2.59. Found: C, 44.40; H, 4.57; N, 2.59.

Allyl 4-*O*-Benzyl-6-*O*-(2-chloroacetylamino-2-deoxy-β-D-glucopyranosyl)-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-α-D-glucopyranoside (27) Compound **27** was obtained by a procedure similar to that described for **11**, and was chromatographed on silica gel with $CHCl_3$–MeOH (10 : 1); 76% yield, mp 153—154 °C. $[\alpha]_D^{27}$ +31.6° (c=1.00, $CHCl_3$). IR (KBr): 3440 br (NH, OH), 1757, 1734 (carbonyl), 1677 (amide), 696 cm^{-1} (Ph). ^1H-NMR (acetone-d_6) δ: 1.89 (12H, s, $Cl_3CCMe_2 \times 2$), 4.06 (2H, s, $NCOCH_2Cl$), 4.71 (2H, s, CH_2Ph), 5.74—6.11 (1H, m, =CH–), 6.21 (1H, d, J=10.1 Hz, $NHCOCH_2Cl$), 7.32 (5H, s, $PhCH_2$). ^{13}C-NMR (acetone-d_6) δ: 21.4, 21.9, 22.0 (q, $Cl_3CC\underline{Me}_2$), 43.5 (t, Cl$\underline{C}H_2CO$), 54.5 (t, O$\underline{C}H_2CH=$), 88.6 (s, $NHCO_2\underline{C}$), 90.5 (s, $OCO_2\underline{C}$), 97.4 (d, C-1), 101.9 (C-1′), 106.4 (s, $OCO_2C\underline{C}Cl_3$), 107.3 (s, $NHCO_2C\underline{C}Cl_3$), 117.4 (t, $=CH_2$), 126.8, 129.0 (d, Ph), 134.9 (d, =CH–), 139.2 (s, Ph), 153.1 (s, OCO_2), 154.5 (s, $NHCO_2$), 167.2 (s, NH$\underline{C}OCH_2Cl$). *Anal.* Calcd for $C_{34}H_{45}Cl_7N_2O_{14} \cdot 1/2H_2O$: C, 42.41; H, 4.81; N, 2.91. Found: C, 42.32; H, 4.68; N, 3.03.

Allyl 4-*O*-Benzyl-6-*O*-(2-chloroacetylamino-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-α-D-glucopyranoside (28) Compound **28** was obtained by a procedure similar to that described for **12**, and was chromatographed on silica gel with $CHCl_3$–acetone (10 : 1); 69% yield, mp 117—118 °C. $[\alpha]_D^{20}$ +17.7° (c=0.550, $CHCl_3$). IR (KBr): 3480 (NH, OH), 1756, 1729 (carbonyl), 1669 (amide), 855 (Me_2C), 696 cm^{-1} (Ph). ^1H-NMR ($CDCl_3$) δ: 1.44, 1.52 (each 3H, s, Me_2C), 1.85, 1.88 (12H, s, $Cl_3CCMe_2 \times 2$), 3.98 (2H, s, $NCOCH_2Cl$), 4.61, 4.68 (each 1H, d, J=10.7 Hz, CH_2Ph), 4.89 (1H, d, J=3.7 Hz, H-1), 5.64—6.13 (1H, m, =CH–), 6.89 (1H, d, J=7.1 Hz, $NHCOCH_2Cl$), 7.30 (5H, s, $PhCH_2$).

^{13}C-NMR ($CDCl_3$) δ: 19.1, 29.0 (q, $\underline{Me_2}$C), 21.6, 22.2 (q, $Cl_3CC\underline{Me_2}$), 42.6 (t, Cl$\underline{C}H_2$CO), 53.7 (t, O$\underline{C}H_2$CH=), 88.5 (s, $NHCO_2\underline{C}$), 90.3 (s, $OCO_2\underline{C}$), 97.0 (d, C-1), 99.9 (s, $Me_2\underline{C}$), 100.6 (d, C-1′), 105.4 (s, $OCO_2C\underline{C}Cl_3$), 106.4 (s, $NHCO_2C\underline{C}Cl_3$), 128.0, 128.5 (d, Ph), 137.6 (s, Ph), 152.4 (s, OCO_2), 153.4 (s, $NHCO_2$), 167.0 (s, $NHCOCH_2Cl$). *Anal.* Calcd for $C_{37}H_{49}Cl_7N_2O_{14}$: C, 44.71; H, 4.97; N, 2.82. Found: C, 44.60; H, 4.91; N, 2.76.

Allyl 4-*O*-Benzyl-6-*O*-(2-amino-2-deoxy-4,6-*O*-isopropylidene-*β*-D-glucopyranosyl)-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-*α*-D-glucopyranoside (2b) Compound **2b** was obtained by a procedure similar to that described for **2a**, and was chromatographed on silica gel with $CHCl_3$–MeOH (40 : 1); 95% yield, mp 88—89 °C. $[\alpha]_D^{20}$ +23.1° (*c*=0.308, $CHCl_3$). IR (KBr): 3424, 3384 (NH, OH), 1757 (carbonate), 1734 (carbamate), 853 (Me_2C), 696 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.43, 1.49 (each 3H, s, Me_2C), 1.85, 1.89 (12H, s, Cl_3CCMe_2 × 2), 4.68, 4.72 (each 1H, d, *J*=11.0 Hz, CH_2Ph), 4.91 (1H, d, *J*=3.6 Hz, H-1), 5.66—6.13 (1H, m, =CH–), 7.30 (5H, s, $PhCH_2$). ^{13}C-NMR ($CDCl_3$) δ: 19.1, 29.0 (q, $\underline{Me_2}$C), 21.1, 21.6 (q, $Cl_3CC\underline{Me_2}$), 53.6 (t, O$\underline{C}H_2$CH=), 88.4 (s, $NHCO_2\underline{C}$), 90.2 (s, $OCO_2\underline{C}$), 96.6 (d, C-1), 99.8 (s, $Me_2\underline{C}$), 104.8 (d, C-1′), 105.3 (s, $OCO_2C\underline{C}Cl_3$), 127.7, 128.0, 128.5 (d, Ph), 133.2 (d, =CH), 137.6 (s, Ph), 152.4 (s, OCO_2), 153.4 (s, $NHCO_2$). *Anal.* Calcd for $C_{35}H_{48}Cl_6N_2O_{13}$: C, 45.82; H, 5.27; N, 3.05. Found: C, 45.25; H, 5.08; N, 2.92.

Allyl 4-*O*-Benzyl-2-deoxy-6-*O*-[2-deoxy-4,6-*O*-isopropylidene-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-*β*-D-glucopyranosyl]-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-*α*-D-glucopyranoside (29) DCC (0.155 g, 0.75 mmol) was added to a stirred solution of **2b** (0.223 g, 0.25 mmol), (*R*)-3-tetradecanoyloxytetradecanoic acid (0.341 g, 0.75 mmol) and DMAP (0.031 g, 0.25 mmol) in dry CH_2Cl_2 (5.0 ml) at 0 °C under nitrogen. The mixture was stirred for 4 h at 0 °C, then at room temperature for 12 h. The resulting suspension was filtered through Celite and evaporated. The residue was chromatographed on silica gel with $CHCl_3$–IPE (50 : 1) to give **29** (0.32 g, 73%), mp 132—134 °C. $[\alpha]_D^{19}$ +11.8° (*c*=1.41, $CHCl_3$). IR (KBr): 3392, 3300 (NH), 1759 (carbonate), 1743 (ester), 1721 (carbamate), 1655 (amide), 857 (acetonide), 751, 698 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 0.87 (12H, t, *J*=5.4 Hz, $(CH_2)_nC\underline{H}_3$ × 4), 1.25 (88H, br s, $(CH_2)_n$), 1.35, 1.44 (each 3H, s, Me_2C), 1.84, 1.88 (each 6H, s, Cl_3CCMe_2), 2.15—2.40 (6H, m, $OCOCH_2$), 4.67, 4.71 (each 1H, d, *J*=10.6 Hz, CH_2Ph), 4.87 (1H, d, *J*=3.7 Hz, H-1), 5.01—5.40 (3H, m, =CH_2, H-1′), 5.56—6.15 (2H, m, =CH–, NH), 7.29 (5H, s, Ph). *Anal.* Calcd for $C_{91}H_{152}Cl_6N_2O_{19}$: C, 59.83; H, 8.61; N, 1.53. Found: C, 59.41; H, 8.10; N, 1.64.

Allyl 4-*O*-Benzyl-2-deoxy-6-*O*-[2-deoxy-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-*β*-D-glucopyranosyl]-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-*α*-D-glucopyranoside (30) A solution of **29** (0.32 g, 0.18 mmol) in 90% aqueous AcOH (40 ml) was heated at 85—90 °C for 15 min. After removal of the solvent, the residue was chromatographed on silica gel with $CHCl_3$–acetone (20 : 1) to give **30** (0.23 g, 75%), mp 88—90 °C. $[\alpha]_D^{20}$ +15.1° (*c*=0.68, $CHCl_3$) IR (KBr): 3296 (NH, OH), 1759 (carbonate), 1736 (ester), 1719 (carbamate), 1653 (amide), 751, 698 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (12H, t, *J*=5.4 Hz, $(CH_2)_nC\underline{H}_3$ × 4), 1.26 (88H, br s, $(CH_2)_n$), 1.86, 1.89 (each 6H, s, Cl_3CCMe_2), 2.16—2.50 (6H, m, $OCOCH_2$), 2.50—2.63 (2H, m, $NHCOCH_2$), 4.70, 4.72 (each 1H, d, *J*=11.0 Hz, CH_2Ph), 4.88 (1H, d, *J*=3.4 Hz, H-1), 4.81—5.42 (3H, m, =CH_2, H-1′), 5.60—6.16 (2H, m, =CH–, NH), 7.30 (5H, s, Ph). *Anal.* Calcd for $C_{88}H_{148}Cl_6N_2O_{19}$: C, 60.37; H, 8.52; N, 1.60. Found: C, 60.46; H, 8.42; N, 1.78.

Allyl 4-*O*-Benzyl-6-*O*-[6-*O*-benzyloxymethyl-2-deoxy-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-*β*-D-glucopyranosyl]-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-*α*-D-glucopyranoside (31) Benzyloxymethyl chloride (0.454 g, 2.90 mmol) was added to a stirred solution of **30** (2.50 g, 1.45 mmol) and TMU (0.337 g, 2.90 mmol) in dry CH_2Cl_2 (30 ml) at 0 °C under nitrogen. After 20 h at room temperature, the reaction mixture was successively washed with saturated aqueous $NaHCO_3$ and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel with $CHCl_3$–ether (20 : 1) to give **31** (1.67 g, 62.5%), mp 94—96 °C. $[\alpha]_D^{20}$ +14.6° (*c*=1.28, $CHCl_3$). IR (KBr): 3376, 3280 (NH, OH), 1759 (carbonate), 1739 (ester), 1718 (carbamate), 1652 (amide), 740, 696 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (12H, t, *J*=5.6 Hz, $(CH_2)_nC\underline{H}_3$ × 4), 1.26 (88H, br s, $(CH_2)_n$), 1.84, 1.88 (each 6H, s, Cl_3CCMe_2), 2.21—2.37 (6H, m, $OCOCH_2$), 2.51—2.64 (2H, m, $NHCOCH_2$), 4.59—4.87 (7H, m, H-1, CH_2Ph at 4-*O*-position, CH_2OCH_2Ph at 6′-*O*-position), 4.93—5.41 (3H, m, =CH_2, H-1′), 5.62—6.13 (2H, m, =CH–, NH), 7.28, 7.32 (10H, s, Ph). *Anal.* Calcd for $C_{96}H_{154}Cl_6N_2O_{19}$: C, 61.63; H, 8.40; N, 1.50. Found: C, 61.56; H, 8.34; N, 1.56.

Allyl 4-*O*-Benzyl-6-*O*-[6-*O*-benzyloxymethyl-2-deoxy-4-*O*-diphenylphosphono-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-*β*-D-glucopyranosyl]-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloro-*tert*-butoxycarbonylamino)-*α*-D-glucopyranoside (32) Diphenylphosphorochloridate (1.26 g, 4.5 mmol) was added to a stirred solution of **31** (1.66 g, 0.90 mmol), pyridine (0.356 g, 4.5 mmol) and DMAP (0.55 g, 4.5 mmol) at 0 °C under nitrogen, and then the mixture was stirred for 12 h at room temperature. The reaction mixture was washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was chromatographed on silica gel with $CHCl_3$–IPE (20 : 1) to give **32** (1.42 g, 76%), syrup. $[\alpha]_D^{20}$ +20.8° (*c*=0.74, $CHCl_3$). IR (KBr): 3356 (NH), 1758 (carbonate), 1745 (ester, carbamate), 1652 (amide), 1270 (P=O), 962 (P–O–Ph), 690 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (12H, t, *J*=5.5 Hz, $(CH_2)_nC\underline{H}_3$ × 4), 1.25 (88H, br s, $(CH_2)_n$), 1.88 (12H, br s, Cl_3CCMe_2), 2.07—2.68 (8H, m, $OCOCH_2$, $NHCOCH_2$), 4.46—4.77 (6H, m, CH_2Ph at 4-*O*-position, CH_2OCH_2Ph at 6′-*O*-position), 4.85 (1H, d, *J*=3.7 Hz, H-1), 4.93—5.38 (3H, m, =CH_2, H-1′), 5.51—6.06 (2H, m, =CH–, NH), 6.39 (1H, br d, *J*=7.3 Hz, NH), 7.06—7.36 (20H, m, Ph). *Anal.* Calcd for $C_{108}H_{163}Cl_6N_2O_{22}P$: C, 62.21; H, 7.88; N, 1.34. Found: C, 61.92; H, 8.02; N, 1.50.

Allyl 4-*O*-Benzyl-6-*O*-[6-*O*-benzyloxymethyl-2-deoxy-4-*O*-diphenylphosphono-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-*β*-D-glucopyranosyl]-2-deoxy-*α*-D-glucopyranoside (33) Zinc powder (0.44 g, 6.8 mmol) was added to a stirred solution of **32** (1.42 g, 0.68 mmol) in AcOH (25 ml) and the mixture was stirred at room temperature for 12 h. After removal of the insoluble materials by filtration, the solvent was evaporated off *in vacuo*. The residue was again dissolved in CH_2Cl_2 (30 ml), and the solution was washed with saturated aqueous $NaHCO_3$ and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel with $CHCl_3$–MeOH (20 : 1) to give **33** (1.01 g, 88.5%) as a syrup. $[\alpha]_D^{23}$ +22.9° (*c*=0.68, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.87 (12H, t, *J*=5.7 Hz, $(CH_2)_nC\underline{H}_3$ × 4), 1.25 (88H, br s, $(CH_2)_n$), 2.11—2.47 (8H, m, $OCOCH_2$, $NHCOCH_2$), 4.42—4.86 (6H, m, CH_2Ph at 4-*O*-position, CH_2OCH_2Ph at 6′-*O*-position), 4.94—5.24 (3H, m, =CH_2, H-1′), 5.38—6.04 (1H, m, =CH–), 6.14 (1H, br d, *J*=7.8 Hz, NH), 6.99—7.44 (20H, m, Ph).

Allyl 4-*O*-Benzyl-6-*O*-[6-*O*-benzyloxymethyl-2-deoxy-4-*O*-diphenylphosphono-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-*β*-D-glucopyranosyl]-2-deoxy-2-[(*R*)-3-hexadecanoyloxytetradecanoylamino]-*α*-D-glucopyranoside (34) DCC (0.240 g, 1.14 mmol) was added to a stirred solution of **33** (0.96 g, 0.57 mmol) and (*R*)-3-hexadecanoyloxytetradecanoic acid (0.55 g, 1.14 mmol) in dry CH_2Cl_2 (30 ml) at 0 °C under nitrogen. The mixture was stirred for 4 h at 0 °C, then at room temperature for 12 h. The resulting suspension was filtered through Celite and the filtrate was evaporated *in vacuo*. The residue was chromatographed on silica gel with $CHCl_3$–acetone (20 : 1) to give **34** (0.83 g, 67%), mp 53—55 °C. $[\alpha]_D^{23}$ +15.0° (*c*=0.57, $CHCl_3$). IR (KBr): 3428, 3420 (NH, OH), 1735 (ester), 1665 (amide), 1289 (P=O), 954 (P–O–Ph), 750, 730, 690 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (18H, t, *J*=5.7 Hz, $(CH_2)_nC\underline{H}_3$ × 4), 1.25 (136H, br s, $(CH_2)_n$), 2.07—2.52 (12H, m, $OCOCH_2$, $NHCOCH_2$), 4.46—4.86 (6H, m, CH_2Ph at 4-*O*-position, CH_2OCH_2Ph at 6′-*O*-position), 4.89—5.27 (3H, m, =CH_2, H-1′), 5.39—6.11 (1H, m, =CH–), 6.18 (1H, br d, *J*=7.1 Hz, NH), 7.06—7.39 (20H, m, Ph). *Anal.* Calcd for $C_{128}H_{211}N_2O_{22}P$: C, 70.55; H, 9.85; N, 1.29. Found: C, 70.12; H, 9.74; N, 1.51.

Allyl 4-*O*-Benzyl-6-*O*-[6-*O*-benzyloxymethyl-2-deoxy-4-*O*-diphenylphosphono-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-*β*-D-glucopyranosyl]-2-deoxy-3-*O*-[(*R*)-3-benzyloxytetradecanoyl]-2-[(*R*)-3-hexadecanoyloxytetradecanoylamino]-*α*-D-glucopyranoside (35) DCC (0.16 g, 0.76 mmol) was added to a stirred solution of **34** (0.83 g, 0.38 mmol), (*R*)-3-benzyloxytetradecanoic acid (0.25 g, 0.76 mmol), DMAP (0.023 g, 0.19 mmol) in dry CH_2Cl_2 (25 ml) at 0 °C under nitrogen. The mixture was stirred for 5 h at 0 °C, then at room temperature for 12 h. The resulting suspension was filtered through Celite and the filtrate was evaporated off *in vacuo*. The residue was chromatographed on silica gel with $CHCl_3$–acetone (40 :1) to give **35** (0.72 g, 77%), mp 48—49 °C. $[\alpha]_D^{23}$ +18.9° (*c*=2.18, $CHCl_3$). IR (KBr): 3316 (NH), 1738 (ester), 1664 (amide), 1291 (P=O), 958 (P–O–Ph), 731, 639 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (21H, t, *J*=6.8 Hz, $(CH_2)_n$-$C\underline{H}_3$ × 7), 1.25 (156H, br s, $(CH_2)_n$), 1.97—2.53 (14H, m, $OCOCH_2$ × 5,

$NHCOCH_2 \times 2$), 4.46—4.89 (8H, m, CH_2Ph at 4-*O*-position, CH_2Ph at 3′-*O*-position, CH_2OCH_2Ph at 6′-*O*-position), 5.10—5.29 (3H, m, $=CH_2$, H-1′), 5.38—6.02 (1H, m, $=CH$–), 6.32 (1H, br d, $J=7.3$ Hz, NH), 6.97—7.41 (25H, m, Ph). ^{13}C-NMR ($CDCl_3$) δ: 94.8 (t, –OCH_2O–), 96.3 (d, C-1), 100.0 (d, C-1′). *Anal.* Calcd for $C_{149}H_{243}N_2O_{24}P$: C, 72.23; H, 9.89; N, 1.13. Found: C, 71.78; H, 9.69; N, 1.20.

4-*O*-Benzyl-6-*O*-[6-*O*-benzyloxymethyl-2-deoxy-4-*O*-diphenylphosphono-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-*β*-D-glucopyranosyl]-2-deoxy-3-*O*-[(*R*)-3-benzyloxytetradecanoyl]-2-[(*R*)-3-hexadecanoyloxytetradecanoylamino]-*α*-D-glucopyranose (36) Bis(methyldiphenylphosphine)cycloocta-1,5-diene iridium(I) hexafluorophosphate $[C_8H_{12}Ir(PMePh_2)_2]PF_4$ (3.8 mg, 4.5×10^{-6} mol) was added to a stirred solution of **35** (0.224 g, 9.0×10^{-5} mol) in peroxide-free THF (8.0 ml) (freshly distilled from sodium-benzophenone). The stirred solution was degassed, placed under dry and oxygen-free nitrogen, and degassed once more. The catalyst was activated by hydrogen, during which operation the slightlly red suspension became colorless. To effect isomerization, the solution was degassed once more, placed under dry and oxygen-free nitrogen and heated at 50 °C for 2 h. To this solution, water (0.8 ml) and then iodine (46 mg, 1.8×10^{-4} mol) and pyridine (28 mg, 3.6×10^{-4} mol) were added, and the mixture was stirred at room temperature for 15 min. After removal of the solvent, the residue was chromatographed on silica gel with $CHCl_3$–acetone (20 : 1) to give **36** (190 mg, 87%) as a syrup. $[\alpha]_D^{22}$ +12.6° (c=0.89, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.25 (156H, br s, $(CH_2)_n$), 2.06—2.61 (14H, m, $OCOCH_2 \times 5$, $NHCOCH_2 \times 2$), 4.47—4.82 (8H, m, CH_2Ph at 4-*O*-position, CH_2Ph at 3′-*O*-position, CH_2OCH_2Ph at 6′-*O*-position), 5.96 (1H, br d, $J=8.1$ Hz, NH), 6.50 (1H, br d, $J=6.8$ Hz, NH), 7.11—7.36 (25H, m, Ph). ^{13}C-NMR ($CDCl_3$) δ: 91.3 (d, C-1), 94.9 (t, –OCH_2O–), 99.0 (d, C-1′).

***Proteus mirabilis* Lipid A (1e)** *n*-BuLi (1.6 mol in *n*-hexane) (0.654 ml, 8.7×10^{-5} mol) was added to a stirred solution of **36** (180 mg, 8.7×10^{-5} mol) in dry THF (6.0 ml) at −70 °C under dry nitrogen. After 3 min, dibenzylphosphorochloridate (32 mg, 1.13×10^{-4} mol) in dry THF (0.5 ml) was added and the mixture was stirred for a further 10 min. The whole mixture was immediately subjected to hydrogenolysis over Pd-black (100 mg) at 40—45 °C under slight pressure for 20 h, the reaction being monitored by TLC developed with $CHCl_3$–MeOH (10 : 1). The catalyst was filtered off and Adams' platinum catalyst (50 mg) was added to the filtrate. Hydrogenolysis was continued at 40—45 °C for 20 h, when TLC with $CHCl_3$–MeOH–H_2O–Et_3N (20 : 5 : 1 : 0.05) showed the reaction to be complete. The catalyst was filtered off and the filtrate was concentrated to dryness. The residue was purified on a column (10 ml) of silica gel with $CHCl_3$–MeOH–H_2O–Et_3N (20 : 5 : 1 : 0.05) followed by treatment with aqueous 0.1 N HCl at 0 °C, then lyophilization from dioxane to give the desired compound (**1e**), mp 60—62 °C. $[\alpha]_D^{23}$ +3.64° (c=0.22, $CHCl_3$). *Anal.* Calcd for $C_{112}H_{212}N_2O_{26}P$: C, 65.15; H, 10.35; N, 1.36. Found: C, 64.96; H, 9.98; N, 1.52. Positive ion FAB-mass spectrometry (triethanol amine, m/z 2164.7 $(M+H+NEt_3)^+$, m/z 2186.8 $(M+NEt_3+Na)^+$.

Allyl 2-Deoxy-4,6-*O*-isopropylidene-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-*O*-(2,2,2-trichloroethoxycarbonylamino)-*α*-D-glucopyranoside (40) Compound **40** was prepared from **39**[5] by a procedure similar to that described for **4**, and was chromatographed on silica gel with $CHCl_3$–IPE (20 : 1); 97.3% yield, mp 168—170 °C. $[\alpha]_D^{20}$ +62.2° (c=0.99, $CHCl_3$). IR (KBr): 3456 (NH), 1750 (carbonate), 1739 (carbamate), 1654 (allyl), 864 (Me_2C). ^{1}H-NMR ($CDCl_3$) δ: 1.40, 1.49 (6H, s, Me_2C), 1.91 (6H, s, Cl_3CCMe_2), 4.71 (2H, s, Cl_3CCH_2), 4.90 (1H, d, $J=3.7$ Hz, H-1), 5.19—5.38 (2H, m, $=CH_2$), 5.66—6.15 (1H, m, $=CH$). ^{13}C-NMR ($CDCl_3$) δ: 19.07, 28.99 (q, $\underline{Me_2}C$), 21.18 (q, $Cl_3CC\underline{Me_2}$), 54.51 (t, $O\underline{C}H_2CH=$), 90.27 (s, OCO_2C), 97.04 (d, C-1), 99.91 (s, $Me_2\underline{C}$), 108.02 (s, $OCO_2CC(Me)_2\underline{C}Cl_3$), 118.33 (t, $=CH_2$), 133.01 (d, $=CH$), 152.36 (s, OCO_2), 155.03 (s, $NHCO_2$). *Anal.* Calcd for $C_{20}H_{27}Cl_6NO_9$: C, 37.68; H, 4.26; N, 2.19. Found: C, 37.80; H, 4.05; N, 2.15.

Allyl 2-Deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-*α*-D-glucopyranoside (41) Compound **41** was obtained by a procedure similar to that described for **5** and was chromatographed on silica gel with $CHCl_3$–acetone (10 : 1); 97.0% yield, mp 196—198 °C. $[\alpha]_D^{20}$ +57.4° (c=1.00, $CHCl_3$). IR (KBr): 3448 (OH), 3364 (NH), 1759 (carbonate), 1737 (carbamate), 1650 cm^{-1} (allyl). ^{1}H-NMR ($CDCl_3$) δ: 1.93 (6H, s, Cl_3CCMe_2), 4.69 (2H, s, Cl_3CCH_2), 4.92 (1H, d, $J=3.4$ Hz, H-1), 5.15—5.41 (2H, m, $=CH_2$), 5.75—6.17 (1H, m, $=CH$). ^{13}C-NMR ($CDCl_3$) δ: 21.40 (q, $Cl_3CC\underline{Me_2}$), 54.83 (t, $O\underline{C}H_2CH=$), 90.64 (s, $OCO_2\underline{C}$), 97.09 (d, C-1), 110.75 (s, $OCO_2CC(Me)_2\underline{C}Cl_3$), 118.01 (t, $=CH_2$), 134.15 (d, $=CH$), 155.38 (s, OCO_2), 155.50 (s, $NHCO_2$). *Anal.* Calcd for $C_{17}H_{23}Cl_6NO_9$: C, 34.14; H, 3.88; N, 2.34. Found: C, 33.60; H, 3.73; N, 2.22.

Allyl 2-Deoxy-6-*O*-(*p*-nitrobenzoyl)-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-*α*-D-glucopyranoside (42) A solution of *p*-nitrobenzoyl chloride (5.57 g, 30 mmol) in CH_2Cl_2 (20 ml) was added to an ice-cooled solution of **41** (12.0 g, 20 mmol) and pyridine (4.75 g, 60 mmol) in CH_2Cl_2 (200 ml). The mixture was stirred at 0 °C for 1 h. The brine (50 ml) was added and the mixture was stirred at room temperature. The organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel with $CHCl_3$–acetone (20 : 1) to give **42** (13.99 g, 93.6%), mp 121—123 °C. $[\alpha]_D^{20}$ +47.2° (c=1.00, $CHCl_3$). IR (KBr): 3532 (OH), 3452 (NH), 1757 (carbonate), 1744 (carbamate), 1719 (ester), 1655 (allyl), 717 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.91 (6H, s, Cl_3CCMe_2), 4.69 (2H, s, Cl_3CCH_2), 4.95 (1H, d, $J=3.9$ Hz, H-1), 5.19—5.44 (2H, m, $=CH_2$), 5.69—6.18 (1H, m, $=CH$), 8.15—8.39 (4H, m, Ph). ^{13}C-NMR ($CDCl_3$) δ: 21.29 (q, $Cl_3CC\underline{Me_2}$), 54.13 (t, $O\underline{C}H_2CH=$), 90.64 (s, $OCO_2\underline{C}$), 96.60 (d, C-1), 105.27 (s, CCl_3), 118.44 (t, $=CH_2$), 123.64 (d, *p*-NO_2Ph), 133.01 (d, $=CH$), 135.02 (s, *p*-NO_2Ph), 150.78 (s, $PhCO_2$), 152.84 (s, OCO_2), 154.14 (s, $NHCO_2$). *Anal.* Calcd for $C_{24}H_{26}Cl_6N_2O_{12}$: C, 38.58; H, 3.51; N, 3.75. Found: C, 38.45; H, 3.35; N, 3.65.

Allyl 4-*O*-Benzyl-2-deoxy-6-*O*-(*p*-nitrobenzoyl)-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-*α*-D-glucopyranoside (43) Compound **43** was obtained by a procedure similar to that described for **7** and was chromatographed on silica gel with $CHCl_3$–IPE (100 : 1); 86.1% yield, mp 159—161 °C. $[\alpha]_D^{23}$ +68.6° (c=1.00, $CHCl_3$). IR (KBr): 3444 (NH), 1745 (carbonate, carbamate, ester), 1655 (allyl), 718, 697 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.93 (6H, s, Cl_3CCMe_2), 4.68 (2H, s, Cl_3CCH_2), 4.94 (1H, d, $J=3.7$ Hz, H-1), 5.11—5.47 (2H, m, $=CH_2$), 5.70—6.13 (1H, m, $=CH$), 7.31 (5H, s, $PhCH_2$), 8.07—8.37 (4H, m, *p*-NO_2Ph). ^{13}C-NMR ($CDCl_3$) δ: 21.07 (q, $Cl_3CC\underline{Me_2}$), 54.29 (t, $O\underline{C}H_2CH=$), 90.53 (s, $OCO_2\underline{C}$), 96.49 (d, C-1), 105.30 (s, CCl_3), 118.44 (t, $=CH_2$), 123.58 (d, *p*-NO_2Ph), 128.52 (d, $PhCH_2$), 132.96 (d, $=CH$), 135.02 (s, *p*-NO_2Ph), 136.91 (s, $PhCH_2$), 150.38 (s, $PhCO_2$), 152.41 (s, OCO_2), 154.14 (s, $NHCO_2$). *Anal.* Calcd for $C_{31}H_{32}Cl_6N_2O_{12}$: C, 44.47; H, 3.85; N, 3.35. Found: C, 44.80; H, 3.83; N, 3.34.

Allyl 4-*O*-Benzyl-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-*α*-D-glucopyranoside (44) Compound **43** (15.0 g, 17.9 mmol) was dissolved in a solution of NH_4OH–MeOH–THF (1 : 9 : 1) (200 ml). The solution was stirred at room temperature for 4 h, then the solvent was evaporated off *in vacuo*. The residue was chromatographed on silica gel with $CHCl_3$–IPE (10 : 1) to give **44** (11.69 g, 95.0%), mp 121—123 °C. $[\alpha]_D^{23}$ +51.9° (c=0.99, $CHCl_3$). IR (KBr): 3456 (NH, OH), 1759 (carbonate), 1739 (carbamate), 1655 (allyl), 737, 698 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.89 (6H, s, Cl_3CCMe_2), 4.67 (2H, s, Cl_3CCH_2), 4.92 (1H, d, $J=3.7$ Hz, H-1), 5.16—5.39 (2H, m, $=CH_2$), 5.67—6.10 (1H, m, $=CH$), 7.31 (5H, s, $PhCH_2$). ^{13}C-NMR ($CDCl_3$) δ: 21.08 (q, $Cl_3CC\underline{Me_2}$), 54.45 (t, $O\underline{C}H_2CH=$), 90.37 (s, OCO_2C), 96.49 (d, C-1), 105.32 (s, CCl_3), 118.22 (t, $=CH_2$), 128.03, 128.46 (d, $PhCH_2$), 133.07 (d, $=CH$), 137.51 (s, $PhCH_2$), 152.57 (s, OCO_2), 154.14 (s, $NHCO_2$). *Anal.* Calcd for $C_{24}H_{29}Cl_6NO_9$: C, 41.89; H, 4.25; N, 2.04. Found: C, 41.50; H, 4.52; N, 1.97.

Allyl 4-*O*-Benzyl-2-deoxy-6-*O*-(3,4,6-tri-*O*-acetyl-2-chloroacetylamino-2-deoxy-*β*-D-glucopyranosyl)-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-*α*-D-glucopyranoside (45) Compound **45** was obtained by a procedure similar to that described for **10** and was chromatographed on silica gel with $CHCl_3$–acetone (20 : 1); 84.1% yield, mp 213—215 °C. $[\alpha]_D^{23}$ +32.9° (c=1.00, $CHCl_3$). IR (KBr): 3452 (NH), 1755 (carbonyl), 1679 (amide), 738, 698 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.88 (6H, s, Cl_3CCMe_2), 2.03, 2.05 (9H, s, $COCH_3 \times 3$), 3.92 (2H, s, $NCOCH_2Cl$), 4.67 (2H, s, Cl_3CCH_2), 4.92 (1H, d, $J=3.4$ Hz, H-1), 5.65—6.13 (1H, m, $=CH$–), 6.80 (1H, d, $J=8.6$ Hz, $NHCOCH_2Cl$), 7.31 (5H, s, $PhCH_2$). ^{13}C-NMR ($CDCl_3$) δ: 20.59 (q, $CO\underline{C}H_3$), 21.08, 21.19 (q, $Cl_3CC\underline{Me_2}$), 42.37 (t, $CO\underline{C}H_2Cl$), 54.24 (t, $O\underline{C}H_2CH=$), 88.37 (s, $NCO_2\underline{C}$), 90.37 (s, $OCO_2\underline{C}$), 96.37 (d, C-1), 100.29 (d, C-1′), 105.38 (s, CCl_3), 118.22 (t, $=CH_2$), 127.70, 128.08, 128.52 (d, $PhCH_2$), 133.12 (d, $=CH$), 137.56 (s, $PhCH_2$), 152.41 (s, OCO_2), 154.14 (s, $NHCO_2$), 166.38 (s, $NHCOCH_2$), 169.13, 170.56 (s, CH_3CO). *Anal.* Calcd for $C_{38}H_{48}Cl_7N_2O_{17}$: C, 43.35; H, 4.59; N, 2.66. Found: C, 43.11; H, 4.41; N, 2.58.

Allyl 4-*O*-Benzyl-6-*O*-(2-chloroacetylamino-2-deoxy-*β*-D-glucopyranosyl)-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-*α*-D-glucopyranoside (46) Compound **46** was obtained by a procedure similar to that described for **11** and was chromatographed on silica gel with $CHCl_3$–MeOH (10 : 1); 95.2% yield, mp 169—170 °C. $[\alpha]_D^{23}$ +23.0° (c=1.01, $CHCl_3$). IR (KBr): 3433 (NH, OH), 1755 (carbonate), 1720 (carbamate), 1672 (amide), 736, 699 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$)

δ: 1.87 (6H, s, Cl_3CCMe_2), 4.00 (2H, s, $NCOCH_2Cl$), 4.68 (2H, s, Cl_3CCH_2), 4.86 (1H, d, J=3.3 Hz, H-1), 5.72—6.25 (1H, m, =CH–), 6.71 (1H, d, J=9.5 Hz, $NHCOCH_2Cl$), 7.30 (5H, s, $PhCH_2$). ^{13}C-NMR ($CDCl_3$) δ: 21.62 (q, $Cl_3CC\underline{Me}_2$), 43.40 (t, $CO\underline{C}H_2Cl$), 55.48 (t, $O\underline{C}H_2CH=$), 88.60 (s, $NCO_2\underline{C}$), 91.18 (s, $OCO_2\underline{C}$), 97.74 (d, C-1), 102.29 (d, C-1′), 106.74 (s, CCl_3), 118.22 (t, $=CH_2$), 128.57, 128.73, 129.32 (d, $PhCH_2$), 135.02 (d, =CH), 139.41 (s, $PhCH_2$), 153.20 (s, OCO_2), 155.46 (s, $NHCO_2$), 167.15 (s, $NHCOCH_2$). *Anal.* Calcd for $C_{32}H_{42}Cl_7N_2O_{14}$: C, 41.47; H, 4.57; N, 3.02. Found: C, 40.84; H, 4.38; N, 3.03.

Allyl 4-*O*-Benzyl-6-*O*-(2-chloroacetylamino-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranoside (47) Compound **47** was obtained by a procedure similar to that described for **12** and was chromatographed on silica gel with $CHCl_3$–MeOH (10:1); 95.4% yield, mp 155—156 °C. $[\alpha]_D^{20}$ +22.8° (c=1.00, $CHCl_3$). IR (KBr): 3435 (OH), 3334 (NH), 1755 (carbonate), 1721 (carbamate), 1665 (amide), 855 (Me_2C), 738, 700 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.43, 1.50 (6H, s, Me_2C), 1.84, 1.89 (6H, s, Cl_3CCMe_2), 3.96 (2H, s, $NCOCH_2Cl$), 4.64 (2H, s, Cl_3CCH_2), 4.91 (1H, d, J=3.4 Hz, H-1), 5.64—6.12 (1H, m, =CH–), 6.71 (1H, d, J=9.5 Hz, $NHCOCH_2Cl$), 7.30 (5H, s, $PhCH_2$). ^{13}C-NMR ($CDCl_3$) δ: 19.70, 28.99 (q, $\underline{Me}_2C$), 21.02, 21.13 (q, $Cl_3CC\underline{Me}_2$), 42.59 (t, $CO\underline{C}H_2Cl$), 54.18 (t, $O\underline{C}H_2CH=$), 88.48 (s, $NCO_2\underline{C}$), 90.32 (s, $OCO_2\underline{C}$), 96.39 (d, C-1), 99.80 (s, $Me_2\underline{C}$), 100.45 (d, C-1′), 105.81 (s, CCl_3), 118.11 (t, $=CH_2$), 127.59, 127.98, 128.46 (d, $PhCH_2$), 133.12 (d, =CH), 137.56 (s, $PhCH_2$), 152.41 (s, OCO_2), 154.31 (s, $NHCO_2$), 167.03 (s, $NHCOCH_2$). *Anal.* Calcd for $C_{35}H_{46}Cl_7N_2O_{14}$: C, 43.48; H, 4.79; N, 2.90. Found: C, 43.82; H, 4.69; N, 2.89.

Allyl 6-*O*-(2-Amino-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-4-*O*-benzyl-2-deoxy-3-*O*-(2,2,2-trichloro-*tert*-butoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranoside (2c) Compound **2c** was obtained by a procedure similar to that described for **2a** and was chromatographed on silica gel with $CHCl_3$–MeOH (10:1); 84.6% yield, mp 142—143 °C. $[\alpha]_D^{20}$ +18.6° (c=1.00, $CHCl_3$). IR (KBr): 3437 (OH), 3332 (NH), 1755 (carbonate), 1724 (carbamate), 856 (Me_2C), 735, 699 cm^{-1} (Ph). ^{1}H-NMR ($CDCl_3$) δ: 1.43, 1.50 (6H, s, Me_2C), 1.86, 1.89 (6H, s, Cl_3CCMe_2), 4.66 (2H, s, Cl_3CCH_2), 4.93 (1H, d, J=3.4 Hz, H-1), 5.63—6.13 (1H, m, =CH–), 7.30 (5H, s, $PhCH_2$). ^{13}C-NMR ($CDCl_3$) δ: 19.13, 29.04 (q, $\underline{Me}_2C$), 21.02, 21.13 (q, $Cl_3CC\underline{Me}_2$), 54.18 (t, $O\underline{C}H_2CH=$), 88.48 (s, $NCO_2\underline{C}$), 90.32 (s, $OCO_2\underline{C}$), 96.39 (d, C-1), 99.75 (s, $Me_2\underline{C}$), 104.84 (d, C-1′), 105.33 (s, CCl_3), 118.17 (t, $=CH_2$), 127.65, 127.98, 128.46 (d, $PhCH_2$), 133.07 (d, =CH), 137.51 (s, $PhCH_2$), 152.41 (s, OCO_2), 154.31 (s, $NHCO_2$). *Anal.* Calcd for $C_{33}H_{45}Cl_6N_2O_{13}$: C, 44.51; H, 5.09; N, 3.15. Found: C, 44.92; H, 4.96; N, 3.33.

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References

1) Part XVII: S. Nakamoto and K. Achiwa, *Chem. Pharm. Bull.*, **36**, 202 (1988) and references cited therein; Part XVIII: T. Shimizu, T. Masuzawa, Y. Yanagihara, S. Nakamoto, H. Itoh, and K. Achiwa, *J. Pharmacobio-Dyn.*, **11**, 512 (1988); Part XVIX: K. Ikeda, S. Akamatsu, and K. Achiwa, *Carbohydr. Res.*, **189**, C1 (1989); Part XX: T. Shimizu, T. Masuzawa, Y. Yanagihara, H. Itoh, S. Nakamoto, and K. Achiwa, *Chem. Pharm. Bull.*, **37**, 2535 (1989); Part XXI: K. Ikeda, S. Akamatsu, and K. Achiwa, *Chem. Pharm. Bull.*, **38**, 279 (1990); Part XXII: T. Shimizu, Y. Ohtsuka, T. Masuzawa, Y. Yanagihara, H. Itoh, S. Nakamoto, and K. Achiwa, *Mol. Biother.*, **2**, 110 (1990); Part XXIII: K. Idegami, K. Ikeda, and K. Achiwa, *Chem. Pharm. Bull.*, **38**, 1766 (1990).
2) C. Galanos, O. Lüderitz, E. T. Rietschel, and O. Westphal, *Int. Rev. Biochem.*, **14**, 239 (1977); O. Lüderitz, C. Galanos, V. Lehmann, H. Mayer, E. T. Rietschel, and J. Wechesser, *Naturwissenschaften*, **65**, 578 (1978).
3) T. Shiba and S. Kusumoto, *Yuki Gosei Kagaku Kyokai Shi*, **42**, 507 (1984); *idem*, *Tanpakushitsu Kakusan Koso*, **31**, 353 (1986).
4) M. Imoto, H. Yoshimura, M. Yamamoto, T. Shimamoto, S. Kusumoto, and T. Shiba, *Tetrahedron Lett.*, **25**, 2667 (1984).
5) M. Imoto, H. Yoshimura, N. Sakaguchi, S. Kusumoto, and T. Shiba, *Tetrahedron Lett.*, **26**, 1545 (1985).
6) H. Yoshimura, M. Imoto, Y. Tsuji, S. Kusumoto and T. Shiba, Abstracts of Papers, 50th Annual Meeting of the Chemical Society of Japan, 1986, Part II, p. 971.
7) T. Takahashi, S. Nakamoto, K. Ikeda, and K. Achiwa, *Tetrahedron Lett.*, **27**, 1819 (1986).
8) K. Ikeda, T. Takahashi, H. Kondo, and K. Achiwa, *Chem. Pharm. Bull.*, **35**, 1311 (1987).
9) T. Takahashi, C. Shimizu, S. Nakamoto, K. Ikeda, and K. Achiwa, *Chem. Pharm. Bull.*, **33**, 1760 (1985); *idem*, *ibid.*, **35**, 1383 (1987).
10) M. Kiso and L. Anderson, *Carbohydr. Res.*, **72**, C12 (1979).
11) J. J. Oltvoort, C. A. A. van Boeckel, J. H. de Koning, and J. H. van Boom, *Synthesis*, **1981**, 305.
12) N. A. Nashed and L. Anderson, *J. Chem. Soc., Chem. Commun.*, **1982**, 1274.
13) M. Inage, H. Chaki, S. Kusumoto, and T. Shiba, *Chem. Lett.*, **1982**, 1281.
14) T. Shimizu, S. Akiyama, T. Masuzawa, Y. Yanagihara, K. Ikeda, T. Takahashi, H. Kondo, and K. Achiwa, *Microbiol. Immunol.*, **31**, 381 (1987).