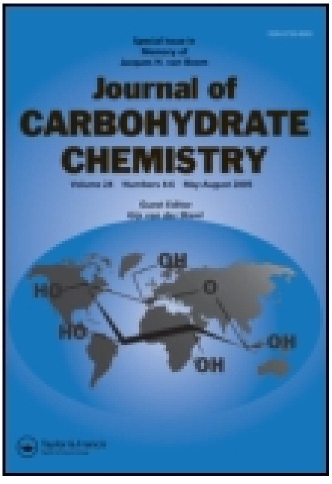

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lcar20

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Published online: 27 Feb 2008.

To cite this article: Adél Medgyes , István Bajza , Erzsébet Farkas , Vince Pozsgay & András Lipták (2000) Synthetic Studies Towards the O-Specific Polysaccharide of Shigella Sonnei , Journal of Carbohydrate Chemistry, 19:3, 285-310, DOI: 10.1080/07328300008544079

To link to this article: http://dx.doi.org/10.1080/07328300008544079

J. CARBOHYDRATE CHEMISTRY, 19(3), 285–310 (2000)

SYNTHETIC STUDIES TOWARDS THE *O*-SPECIFIC POLYSACCHARIDE OF *SHIGELLA SONNEI*†

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Received August 18, 1999 - Final Form January 3, 2000

ABSTRACT

Synthetic routes are described to zwitter-ionic disaccharides that are diastereoisomerically related to frame-shifted repeating units of the title polysaccharide that contains 2-acetamido-4-amino-2,4,6-trideoxy-D-galactose and 2-acetamido-2-deoxy-L-altruronic acid. The intermediates corresponding to the trideoxygalactose residue feature acylamino functions at C-2 and an azido group at C-4. Best results were obtained with *N*-phthaloyl- and *N*-trichloroacetyl-protected derivatives. The intermediates corresponding to the uronic acid residue were either a D-altruronic acid-derived acceptor or a D-altrose-derived donor in which C-6 was oxidized after disaccharide formation.

INTRODUCTION

Shigellae are among the most common causative organisms of dysentery, an acute inflammatory disease of the lower intestines. Because of their resistance to most available

† Dedicated to Professor Pierre Sinaÿ on his first birthday in the third millenium.

antibiotics, prevention might be an alternative to treatment to combat this disease. An essential virulence factor of *Shigella* strains is the *O*-specific polysaccharide (O-SP) component of their lipopolysaccharides.[1] Robbins and co-workers suggested that a critical level of serum IgG antibodies to the O-SP of enteric bacteria may confer immunity to infection by the homologous organism.[2-4] It appeared to us that such antibodies may be induced by protein conjugates of oligosaccharide fragments of the O-SPs. Our long-term goal is to prepare protein conjugates of synthetic oligosaccharide fragments of the O-SP of *Sh. sonnei* for the evaluation of their immunogenicity.

The O-SP of *Sh. sonnei* is built up of a disaccharide repeating unit (Figure 1) consisting of the rare monosaccharides 2-acetamido-4-amino-2,4,6-trideoxy-D-galactose (A) and 2-acetamido-2-deoxy-L-altruronic acid (B).[5-7]

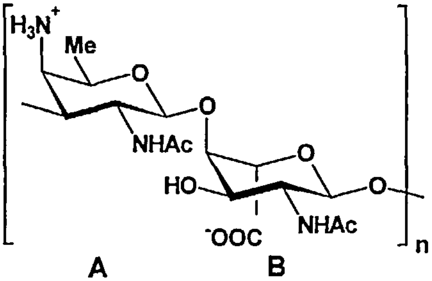


Figure 1. The repeating unit of the polysaccharide

The starting material in our published approach to the L-AltNAcA moiety is L-glucose.[8] The high price of this compound ($ 30/g, Sigma) requires careful optimization of each step in the synthetic sequence. For the optimization experiments we used D-glucose to keep expenses at a minimum. In this report we describe synthetic studies towards the diastereomer analogues of the AB and BA disaccharides. In these analogues, AB(D) and B(D)A, the AltNAcA moiety has the unnatural D configuration. Because the success of the synthetic plan is crucially influenced by the *N*-protecting groups, several intermediates were designed and synthesized that only differ in the identity of the protecting groups at the C-2 amino groups.

RESULTS AND DISCUSSION

Glycosyl Donors Related to the Trideoxygalactose Moiety

Precursor to glycosyl donors **3**-**5** was the amino derivative **2** obtained upon treatment of thioglycoside[8] **1** with ethylenediamine[9] (Figure 2). Reaction of **2** with tetrachlorophthalic anhydride,[10] trichloroacetyl chloride,[11] and 2,2,2-trichloroethylchloroformate,[12] respectively, afforded donors **3**-**5** in acceptable to good yields. Glycosyl trichloroacetimidate **7** was prepared from the hemiacetal **6** that was obtained by NBS-mediated hydrolysis[13] of thioglycoside **1**. We note, that attempted conversion of thioglycosides **4** and **5** to the corresponding glycosyl trichloroacetimidates failed due to the formation of several by-products in attempted hydrolysis of thioglycoside linkage by NBS, NIS, NIS/TfOH, or MeOTf in wet dichloromethane.

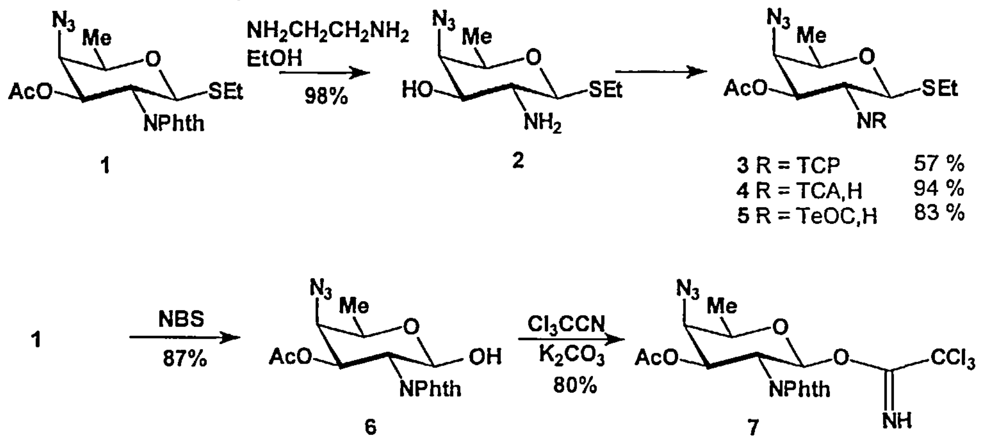


Figure 2. Preparation of glycosyl donors

Glycosyl Acceptors Related to the Altruronic Acid Moiety*

Common precursor in the syntheses of glycosyl acceptors corresponding to the uronic acid moiety was methyl glycoside **9** that was prepared in analogy to the corresponding L-enantiomer, by azide opening of the epoxide ring in compound **8**.[8] Treatment of **9** with $LiAlH_4$ afforded the amine **10** from which the *N*-phthalimido (**11**), *N*-

*These intermediates are shown as if they assumed $^4C_1$ conformation. This is done for the purpose of convenience, only. The actual conformation of these intermediates has not been determined.

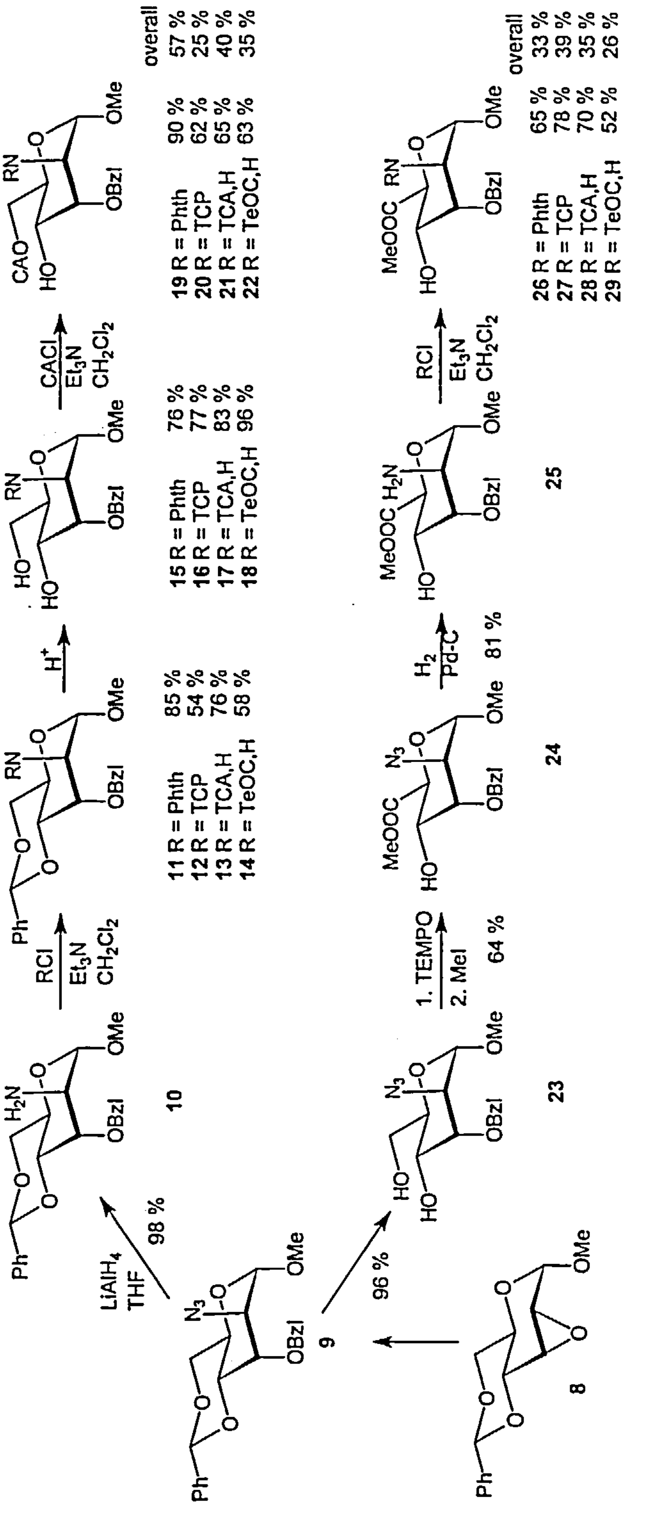


Figure 3. Synthesis of glycosyl acceptors

tetrachlorophthalimido (**12**), *N*-trichloroacetyl (**13**), and *N*-2,2,2-trichloroethoxycarbonyl derivatives (**14**) were prepared by conventional procedures. Acid-catalyzed hydrolytic removal of the benzylidene group from compounds **11-14** afforded the diols **15-18** that were regioselectively acylated at O-6 with a limiting amount of monochloroacetyl chloride to afford the partially protected derivatives **19-22**.

In an alternative sequence, the benzylidene acetal **9** was routinely converted to the diol **23**. Next, the primary carbon atom was selectively oxidized with the TEMPO/NaOCl reagent[14] followed by treatment with MeI to afford the uronate **24**. Catalytic reduction of the azido group provided the amine **25** which was conventionally *N*-acylated to afford glycosyl acceptors **26-29** (Figure 3).

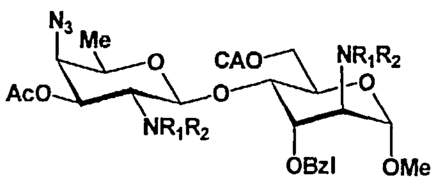
Synthesis of AB(D) Disaccharide

Having readied glycosyl donors (**1, 3-5, 7**) and glycosyl acceptors (**19-22, 26-29**), we next investigated the effects of the *N*-protecting groups and the structure of the acceptor moieties on the outcome of glycosylation. The arbitrary criterium for pairing of the donor and the acceptor moieties was the identity of the *N*-protecting groups. In the glycosylation reactions (Table 1) the donors were used in a slight excess (1.2 equiv). Other conditions for the glycosylation reactions are to be found in the Experimental Part.

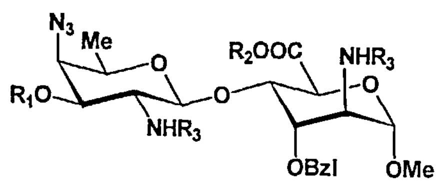
Table 1. Results of the glycosylation reactions

Item	Donor	Acceptor	Activator	Disaccharide	Yield (%)
1	**1**	**19**	NIS/TfOH	**30**	33
2	**1**	**26**	NIS/TfOH	No glycosylation	
3	**3**	**20**	NIS/TfOH	**31**	53
4	**3**	**27**	NIS/TfOH	No glycosylation	
5	**4**	**21**	NIS/TfOH	**32**	24
6	**4**	**28**	NIS/TfOH	**33**	62
7	**5**	**22**	NIS/TfOH	No glycosylation	
8	**5**	**29**	NIS/TfOH	No glycosylation	
9	**7**	**19**	TMSOTf	**30**	73

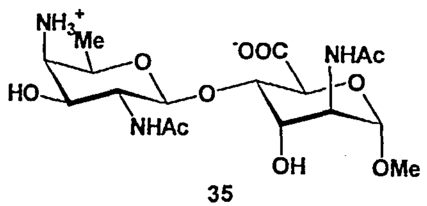
The results presented in Table 1 demonstrate that the nature of the *N*-protecting group had a significant effect on the yields of the glycosidation reactions. The best yield was obtained when the *N*-phthalyl-protected derivatives **7** and **19** were coupled under Schmidt-conditions[15] (item 9). Combination of the *N*-TCA-protected partners **4** and **28** also gave the disaccharide in an acceptable yield (item 6). Couplings between the *N*-phthalyl-protected derivatives **1** and **19** or between the two *N*-TCP-protected partners **3** and **20** under NIS/TfOH activation[16] proceeded in moderate yield. As expected, the reactivity of the uronic acid derivatives towards thioglycosides was poor (items 2, 4, 8). As an exception to this observation, glycosylation of the uronic acid derivative **28** with the donor **4** afforded a higher yield (item 6), than glycosylation of the chloroacetate **21** with the same donor (item 5). Surprisingly, the *N*-TeOC protection turned out to be unsuitable for the synthesis of the targeted disaccharide (items 7 and 8).



30 R_1,R_2 = Phth
31 R_1,R_2 = TCP
32 R_1 = TCA, R_2 = H



33 R_1 = Ac, R_2 = Me, R_3 = TCA
34 R_1,R_2 = H, R_3 = Ac



35

Figure 4.

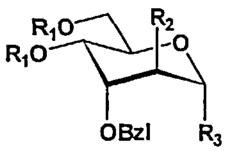
Considering the glycosylation yields (Table 1) and the subsequent transformations that are necessary at the disaccharide level we have selected the route conducive to disaccharide **33** for further evaluation focusing on the efficiency of protecting group removal. This was performed in two steps. First, we subjected compound **33** to basic hydrolysis to cleave the ester moiety and to remove the *N*-TCA and *O*-acetyl groups. *N*-Acetylation of the intermediate so obtained afforded compound **34** in 62 % overall yield. We note, that attempted transformation of the TCA groups to acetyls under reductive conditions[11] failed to proceed in an acceptable yield. Next, the *O*-benzyl group was removed by hydrogenolysis and the azido group was simultaneously reduced to give the targeted disaccharide **35** in 78 % yield.

Synthesis of the B(D)A Disaccharide

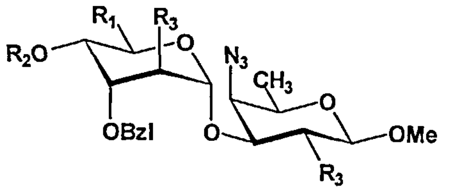
Our initial approach to the BA disaccharide called for a *N*-trichloroacetyl-protected donor corresponding to the ester **28**. However, numerous attempts to convert **28** to either a glycosyl acetate by acetolysis or to a glycosyl chloride by treatment with dichloromethyl methyl ether[17] proved to be abortive. In an alternative approach we decided to fashion the carboxyl after the assembly of an altrose→trideoxygalactose disaccharide. Thus, compound **23** was converted to ethylthio glycoside **37** through acetolysis (→**36**) followed by Lewis-acid catalyzed thioglycoside formation. Catalytic reduction of the N_3 function and consecutive amide formation yielded **38**. Following NIS/TfOH promoted glycosylation of methyl 4-azido-2,4,6-trideoxy-2-trichloroacetamido-β-D-galactopyranoside[8] with **38** then gave disaccharide **39** in 84 % yield. Deacetylation of **39** provided the diol **40** which was oxidized at the primary carbon atom to afford **41** using phase-transfer-catalyzed TEMPO-mediated reaction.[18,19] In this case we were able to isolate the free acid without converting it to the methyl ester. Deprotection of **41** was carried out as described for **33** to give the free disaccharide **43** in 40 % yield (Figure 5).

CONCLUSION

In summary, we have developed synthetic strategies to disaccharides **35** and **43** that are diastereomers of frame-shifted disaccharide repeating units of the *O*-specific polysaccharide of *Shigella sonnei*. We have used the D-enantiomer of the altruronic acid instead of the natural L-counterpart since it was readily synthesized from inexpensive D-glucose. Minding that there may be substantial differences in glycosylation of two enantiomers of an acceptor protected with a bulky *N*-phthalimido group,[20] we have also prepared derivatives having other *N*-protecting groups (trichloroacetamido, 2,2,2-



	R1	R2	R3
36	Ac	N_3	OAc
37	Ac	N_3	SEt
38	Ac	NHTCA	SEt



	R1	R2	R3
39	CH_2OAc	Ac	NHTCA
40	CH_2OH	H	NHTCA
41	COOH	H	NHTCA
42	COOH	H	NHAc

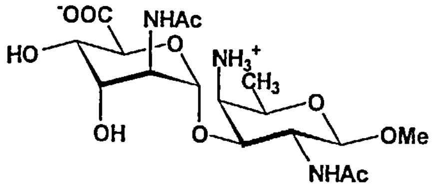


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Figure 5.

trichloroethoxycarbonyl). The best results could be obtained in the condensation reactions of the *N*-phthalyl- (**7** and **19**) and *N*-trichloroacetyl-protected derivatives (**4** and **28**).

EXPERIMENTAL

General methods. Optical rotations were measured at rt with a Perkin-Elmer 241 automatic polarimeter in $CHCl_3$. Melting points were determined on a Kofler apparatus and are uncorrected. TLC was performed on Kieselgel 60 F_{254} (Merck) with detection by charring with 50 % aqueous sulfuric acid. Column chromatography was performed on Silica gel 60 (Merck 0.063-0.200 mm). The ^{1}H (200, 360 and 500 MHz) and ^{13}C NMR (50.3, 90.54, 125.76 MHz) spectra were recorded with Bruker WP-200 SY, Bruker AM-360 and Bruker DRX-500 spectrometers in $CDCl_3$ solutions, except when stated otherwise. Internal references: TMS (0.000 ppm for ^{1}H), $CDCl_3$ (77.00 ppm for ^{13}C). Elemental analyses were performed at the analytical laboratories in Debrecen. Abbreviations: Ac = acetyl, Bzl = benzyl, CA = chloroacetyl, Et = ethyl, Me = methyl, Ph

= phenyl, Phth = phthaloyl, TeOC = 2,2,2-trichloroethoxycarbonyl, TCA = trichloroacetyl, TCP = tetrachlorophthaloyl.

Ethyl 2-Amino-4-azido-2,4,6-trideoxy-1-thio-β-D-galactopyranoside (2). A solution of compound[8] **1** (1.9 g, 4.7 mmol) and ethylenediamine (5 mL) in EtOH (20 mL) was stirred under reflux for 3 h. The solution was concentrated and the residue was purified by chromatography (CH_2Cl_2/MeOH, 9:1) to yield **2** (1.36 g, 98 %) as a colourless syrup: $[\alpha]_D$ -12.5° (*c* 0.9); ^{1}H NMR δ 4.15 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 3.69 (dd, 1H, $J_{3,4}$ = 3.5 Hz, $J_{4,5}$ = 1.5 Hz, H-4), 3.68 (dq, 1H, $J_{5,6}$ = 6.5 Hz, H-5), 3.62 (dd, 1H, $J_{2,3}$ = 9.5 Hz, H-3), 2.89 (t, 1H, H-2), 2.72 (m, 2H, SCH_2CH_3), 1.29, (t, 3H, SCH_2CH_3), 2.32 (bs, 3H, NH_2, OH), 1.36 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6); ^{13}C NMR δ 87.4 (C-1), 75.6, 73.6 (C-4, C-5), 65.2 (C-3), 53.1 (C-2), 24.0 (SCH_2CH_3), 17.9 (C-6), 15.1 (SCH_2CH_3).

Anal. Calcd for $C_8H_{16}N_4O_2S$ (232.30): C, 41.36; H, 6.94. Found: C, 41.30; H, 6.91.

Ethyl 3-*O*-Acetyl-4-azido-2,4,6-trideoxy-2-tetrachlorophthalimido-1-thio-β-D-galactopyranoside (3). To a solution of amine **2** (100 mg, 0.43 mmol) in dry CH_2Cl_2 was added tetrachlorophthalic anhydride (123 mg, 0.47 mmol) at 0 °C. After 15 min, the mixture was concentrated. Pyridine (5 mL) and Ac_2O (2 mL) were added and stirring was continued overnight. The solution was concentrated and the brownish syrup was purified by column chromatography (hexane/acetone, 8:2) to yield **3** (132 mg, 57 %) as a white powder: $[\alpha]_D$ -32.7° (*c* 0.84); ^{1}H NMR δ 5.73 (dd, 1H, $J_{2,3}$ = 10.6 Hz, $J_{3,4}$ = 3.7 Hz, H-3), 5.21 (d, 1H, $J_{1,2}$ = 10.6 Hz, H-1), 4.57 (t, 1H, H-2), 3.92 (d, 1H, H-4), 3.83 (dd, 1H, $J_{5,6}$ = 6.3 Hz, H-5), 2.61 (m, 2H, SCH_2CH_3), 1.14 (t, 3H, SCH_2CH_3), 1.95 (s, 3H, CH_3CO), 1.32 (d, 3H, H-6) (m, 2H, SCH_2CH_3), (t, 3H, SCH_2CH_3); ^{13}C NMR δ 170.3 (CH_3CO), 163.5 and 162.7 (C=O of TCP), 140.8, 130.1 and 127.0 (TCP), 80.3 (C-1), 73.5, 71.3 (C-4, C-5), 63.6 (C-3), 50.8 (C-2), 23.9 (SCH_2CH_3), 20.6 (CH_3CO), 17.9 (C-6), 14.8 (SCH_2CH_3).

Anal. Calcd for $C_{18}H_{16}Cl_4N_4O_5S$ (542.22): C, 39.87; H, 2.97. Found: C, 39.79; H, 2.90.

Ethyl 3-*O*-Acetyl-4-azido-2,4,6-trideoxy-1-thio-2-trichloroacetamido-β-D-galactopyranoside (4). To a solution of amine **2** (100 mg, 0.43 mmol) in dry CH_2Cl_2 (10 mL) were added triethylamine (100 μL) and trichloroacetyl chloride (53 μL, 0.47 mmol) at 0 °C. Stirring was continued for 20 min, followed by addition of pyridine (5 mL) and Ac_2O (2 mL). After 2 h the mixture was concentrated. Column chromatographic purification of the residue (hexane/EtOAc, 8:2) yielded pure 4 (171 mg, 94 %) as a white foam: $[\alpha]_D$ -52.05° (*c* 0.43); ^{1}H NMR δ 6.64 (bd, 1H, $J_{2,NH}$ = 9.5 Hz, NH), 5.37 (dd, 1H, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 3.5 Hz, H-3), 4.63 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 4.24 (ddd, 1H, $J_{2,NH}$ = 9.5 Hz, H-2), 3.85 (dd, 1H, $J_{4,5}$ = 1.5 Hz, H-4), 3.79 (dq, 1H, $J_{5,6}$ = 6.5 Hz, H-5), 2.74 (m, 2H, SCH_2CH_3), 2.13 (s, 3H, CH_3CO), 1.37 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6), 1.26 (t, 3H, SCH_2CH_3); ^{13}C NMR δ 161.8 (Cl_3CCO), 83.3 (C-1), 73.6, 73.0 (C-4, C-5), 63.6 (C-3), 51.5 (C-2), 23.9 (SCH_2CH_3), 20.5 (CH_3CO), 17.7 (C-6), 14.8 (SCH_2CH_3).

Anal. Calcd for $C_{12}H_{17}Cl_3N_4O_4S$ (419.71): C, 34.34; H, 4.08. Found: C, 34.40; H, 4.10.

Ethyl 3-*O*-Acetyl-4-azido-2,4,6-trideoxy-1-thio-2-(2,2,2-trichloroethoxy carbonylamino)-β-D-galactopyranoside (5). To a stirred solution of amine **2** (100 mg, 0.43 mmol) in dry CH_2Cl_2 (10 mL) were added triethylamine (100 μL) and 2,2,2-trichloroethyl chloroformate (65 μL, 0.47 mmol) at 0 °C. After 15 min, pyridine (5 mL) and Ac_2O (2 mL) were added and stirring was continued for an additional 2 h. The mixture was concentrated. The residue was purified by column chromatography (hexane/EtOAc, 8:2) to yield pure **5** (161 mg, 83 %) as a white powder: $[\alpha]_D$ -41.6° (*c* 0.33); ^{1}H NMR δ 5.25 (dd, 1H, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 3 Hz, H-3), 5.05 (bd, 1H, NH), 4.80 and 4.69 (bd, 2x1H, Cl_3CCH_2), 4.56 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 3.97 (ddd, 1H, $J_{2,NH}$ = 10.0 Hz, H-2), 3.83 (dd, 1H, $J_{4,5}$ = 1.0 Hz, H-4), 3.75 (bd, 1H, $J_{5,6}$ = 6.0 Hz, H-5), 2.73 (m, 2H, SCH_2CH_3), 2.12 (s, 3H, CH_3CO), 1.35 (d, 3H, $J_{5,6}$ = 6 Hz, H-6), 1.26 (t, 3H, SCH_2CH_3); ^{13}C NMR δ 170.5 (CH_3CO), 154.0 (Cl_3CCH_2OCO), 83.9 (C-1), 74.5 (Cl_3CCH_2), 73.4, 73.3 (C-4, C-5), 63.6 (C-3), 51.3 (C-2), 23.8 (SCH_2CH_3), 20.6 (CH_3CO), 17.7 (C-6), 14.7 (SCH_2CH_3).

Anal. Calcd for $C_{13}H_{19}Cl_3N_4O_5S$ (449.74): C, 34.72; H, 4.26. Found: C, 34.68; H, 4.19.

3-*O*-Acetyl-4-azido-2,4,6-trideoxy-2-phthalimido-β-D-galactopyranosyl trichloroacetimidate (7). To a chilled solution of **1** (260 mg, 0.64 mmol) in a 9:1 mixture of acetone/water (10 mL) *N*-bromosuccinimide (170 mg, 0.96 mmol) was added portionwise. After 20 min the reaction mixture was concentrated until turbidity and the residue diluted with EtOAc (100 mL). Extractive work-up followed by chromatography (CH_2Cl_2/EtOAc, 9:1) yielded pure 3-*O*-acetyl-4-azido-2,4,6-trideoxy-2-phthalimido-D-galactopyranose (**6**) (200 mg, 87 %) as a colourless syrup. $[\alpha]_D$ –6.1° (*c* 1.04). To a solution of **6** (136 mg, 0.36 mmol) in dry CH_2Cl_2 (5 mL) trichloroacetonitrile (400 μL) and K_2CO_3 (500 mg) were added. The suspension was stirred at rt for 3h. Inorganic salts were removed by filtration, the cake was washed with CH_2Cl_2 (2 x 10 mL) and the filtrate was concentrated to yield **7** (146 mg, 80 %) as a white foam which was used in glycosylation reactions without any purification.

Methyl 2-Amino-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-altropyranoside (10). To a stirred solution of **9** (4.0 g, 10 mmol) in dry tetrahydrofuran (60 mL), $LiAlH_4$ (800 mg, 20 mmol) was added and stirring was continued for 1.5 h. The excess of the hydride was decomposed by addition of EtOAc (200 mL) and water, then the solution was extracted with brine (2 x 100 mL) the organic layer was separated, dried, and concentrated to yield crude **10** (3.68 g, 98 %) which was used in the next steps without further purification.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-α-D-altropyranoside (11). To an ice cold solution of crude **10** (370 mg, 0.99 mmol) and triethylamine (1.6 mL) in dry CH_2Cl_2 (10 mL), a solution of 2-methoxycarbonylbenzoyl chloride [prepared from 270 mg (1.1 mmol) of phthalic acid monomethyl ester and 3 mL of thionyl chloride] in dry CH_2Cl_2 (2 mL) was added dropwise. The mixture was stirred for 16 h at rt, then concentrated. Extractive work-up of the residue followed by column chromatography (hexane/EtOAc, 8:2 then 7:3) yielded pure **11** (430 mg, 85 %) as a white foam: $[\alpha]_D$ –4° (*c* 0.99); ^{1}H NMR δ 7.80, 7.45 and 7.10 (3m, 14H, aromatic), 5.62 (s, 1H, PhC*H*), 4.98 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1), 4.77 (t, 1H, $J_{2,3}$ = 3.0 Hz, H-2), 4.47 (m, 2H, H-6, H-6'), 4.38 (dd, 1H, $J_{3,4}$ = 3.0, $J_{4,5}$ = 10.0 Hz, H-4), 3.99 (t, 1H, H-3), 3.39 (s, 3H, OC*H*$_3$); ^{13}C NMR δ 167.5 (C=O), 101.9 (PhCH), 98.2 (C-1), 76.5, 73.7, 72.6 (Ph*C*H$_2$), 69.8 (C-6), 59.2, 55.4, 54.6.

Anal. Calcd for $C_{29}H_{27}NO_7$ (501.54): C, 69.45; H, 5.43. Found: C, 69.41; H, 5.42.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-tetrachlorophthalimido-α-D-altropyranoside (12). To a stirred solution of crude **10** (510 mg, 1.37 mmol) in CH_2Cl_2 (10 mL) was added tetrachlorophthalic anhydride (432 mg, 1.5 mmol). After 30 min diisopropylethylamine (1 mL) was added. The mixture was stirred under reflux for 4 h followed by concentration. Column chormatographic purification (hexane/EtOAc, 9:1) of the residual syrup afforded **12** (470 mg, 54 %): $[\alpha]_D$ −90° (*c* 0.88); ^{1}H NMR δ 7.3 (m, 10H, aromatic), 5.63 (s, 1H, PhC*H*), 4.98 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1), 4.81, 4.65 (2d, 2H, PhCH_2), 4.69 (t, 1H, $J_{2,3}$ = 4.5 Hz, H-2), 4.43 (m, 2H, H-5, H-6′), 4.29 (dd, 1H, $J_{3,4}$ = 4.5, $J_{4,5}$ = 10.0 Hz, H-4), 4.06 (t, 1H, H-3), 3.84 (t, 1H, $J_{5,6}$ = $J_{6,6'}$ = 12.0 Hz, H-6), 3.36 (s, 3H, OCH_3).

Anal. Calcd for $C_{29}H_{23}Cl_4NO_7$ (639.32): C, 54.48; H, 3.63. Found: C, 54.38; H, 3.63.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-trichloroacetamido-α-D-altropyranoside (13). To a chilled solution of **10** (520 mg, 1.4 mmol) in dry CH_2Cl_2 (10 mL) containing triethylamine (500 μL, 3.8 mmol) was added trichloroacetyl chloride (166 μL, 1.54 mmol) and the stirring was continued for 1 h. The mixture was diluted with CH_2Cl_2 (200 mL). Extractive work-up followed by column chromatographic purification of the residue (hexane/EtOAc, 8:2) yielded pure **13** (550 mg, 76 %): $[\alpha]_D$ +48.2° (*c* 0.26); ^{1}H NMR δ 7.40 (m, 5H, aromatic), 7.25 (bd, 1H, $J_{2,NH}$ = 8.5 Hz, NH), 5.58 (s, 1H, PhC*H*), 4.87 and 4.81 (2d, 2H, PhCH_2), 4.65 (s, 1H, H-1), 4.51 (m, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 5.0 Hz, $J_{5,6'}$ = 10.0 Hz, H-5), 4.42 (dd, 1H, $J_{2,NH}$ = 8.5 Hz, $J_{2,3}$ = 2.5 Hz, H-2), 4.34 (dd, 1H, H-5), 4.42 (dd, 1H, $J_{2,NH}$ = 8.5 Hz, H-2), 4.34 (dd, 1H, H-6), 3.94 (dd, 1H, $J_{3,4}$ = 3.0 Hz, H-3), 3.77 (t, 1H, H-6′), 3.67 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 3.45 (s, 3H, OCH_3); ^{13}C NMR δ 161.2 (C=O), 102.4 (PhCH), 100.2 (C-1), 77.2, 73.2, 58.6 (C-3, C-4, C-5), 72.6 (Ph*C*H_2), 69.1 (C-6), 55.9 (C-2), 52.5 (O*C*H_3).

Anal. Calcd for $C_{23}H_{24}Cl_3NO_6$ (516.81): C, 53.45; H, 4.68. Found: C, 53.40; H, 4.67.

Methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-α-D-altropyranoside (14). To a stirred solution of amine **10** (400 mg, 1.08 mmol) in dry CH_2Cl_2 (10 mL) were added triethylamine (500 μL), and 2,2,2-trichloroethyl chloroformate (164 μL, 1.2 mmol) at 0 °C and stirring was continued for 1 h. After work-up and purification 340 mg (58 %) of pure **14** was isolated: $[\alpha]_D$ +26.4° (*c* 0.3); ^{1}H NMR δ 7.35 (m, 10H, aromatic), 5.57 (s, 1H, PhC*H*), 5.22 (d, 1H, $J_{2,NH}$ = 8.5 Hz, NH), 4.83 (d, 2H, Cl_3CCH_2), 4.76 and 4.68 (2d, 2H, PhCH_2), 4.63 (s, 1H, H-1), 4.47 (dt, 1H, $J_{4,5} = J_{5,6} = 10.0$ Hz, $J_{5,6'} = 5.0$ Hz, H-5), 4.34 (dd, 1H, $J_{6,6'} = 10.0$ Hz, H-6), 4.24 (dd, 1H, $J_{2,NH} = 8.5$ Hz, $J_{2,3} = 2.5$ Hz, H-2), 3.93 (t, 1H, $J_{3,4} = 3.0$ Hz, H-3), 3.75 (dd, 1H, H-4), 3.74 (t, 1H, H-6′), 3.43 (s, 3H, OC*H*$_3$); ^{13}C NMR δ 153.5 (C=O), 102.4 (PhCH), 100.9 (C-1), 76.9, 73.9, 58.5 (C-3, C-4, C-5), 74.8 (CCl_3CH_2OCO), 72.4 ($PhCH_2$), 69.3 (C-6), 55.8 (C-2), 52.5 (OCH_3).

Anal. Calcd for $C_{24}H_{26}Cl_3NO_7$ (546.83): C, 52.72; H, 4.79. Found: C, 52.69; H, 4.77.

Methyl 3-*O*-Benzyl-2-deoxy-2-phthalimido-α-D-altropyranoside (15). To a solution of **11** (800 mg, 1.6 mmol) in CH_2Cl_2 (20 mL) were added trifluoroacetic acid (1 mL) and water (0.5 mL) at rt. After 30 min, the mixture was concentrated. Toluene (10 mL) was added to and evaporated from the residue twice. Column chromatography of the residual syrup (hexane/acetone, 6:4) yielded pure **15** (500 mg, 76 %) as a colourless oil: $[\alpha]_D$ −11° (*c* 1.05); ^{1}H NMR δ 7.75 (m, 4H, Phth), 7.02 (bs. 5H, aromatic), 4.18 (d, 1H, $J_{1,2} = 6.0$ Hz, H-1), 4.6 and 4.35 (2d, 2H, PhC*H*$_2$), 4.57 (dd, 1H, $J_{2,3} = 10.5$ Hz, H-2), 4.23 (bt, 1H, $J_{3,4} = J_{4,5} = 4.4$ Hz, H-4), 4.11 (m,1H, H-5), 3.89 (bs, 2H, H-6, H-6'), 3.38 (s, 3H, OC*H*$_3$), 3.05 and 2.73 (2bs, 2x1H, OH).

Anal. Calcd for $C_{22}H_{23}NO_7$ (413.43): C, 63.92; H, 5.61. Found: C, 63.89; H, 5.60.

Methyl 3-*O*-Benzyl-2-deoxy-2-tetrachlorophthalimido-α-D-altropyranoside (16). Prepared from 12 (450 mg, 0.7 mmol) as described above for the preparation of compound 15. Chromatographic purification (CH_2Cl_2/acetone, 8:2) resulted in pure 16 (300 mg, 77 %): ^{1}H NMR δ 7.25 (m, 5H, aromatic), 4.52 (d, 1H, $J_{1,2} = 5$ Hz, H-1), 4.61, 4.42 (2d, 2H, PhC*H*$_2$), 4.29 (t, 1H, $J_{2,3} = 4.5$ Hz, H-2), 4.13 (m, 3H, H-5, H-6, H-6), 4.02 (t, 1H, H-3), 3.33 (s, 3H, OC*H*$_3$). ^{13}C NMR δ (DMSO-*d*$_6$) 163.0 (C=O), 97.1 (C-1), 77.5, 72.8, 63.9 (C-3, C-4, C-5), 70.2 ($PhCH_2$), 60.9 (C-6), 54.8 (C-2), 52.5 (OCH_3).

Anal. Calcd for $C_{22}H_{19}Cl_4NO_7$ (551.21): C, 47.94; H, 3.47. Found: C, 47.95; H, 3.46.

Methyl 3-*O*-Benzyl-2-deoxy-2-trichloroacetamido-α-D-altropyranoside (17). Prepared from **13** (980 mg, 1.9 mmol) as described above for the preparation of compound **15**. Chromatographic purification (CH_2Cl_2/acetone, 8:2) yielded pure **17** (675 mg, 83 %): $[\alpha]_D$ +84.2° (*c* 0.98); ^{1}H NMR δ 7.35 (m, 5H, aromatic), 6.87 (bd, 1H, $J_{2,NH} = 8.5$ Hz, NH), 4.93 and 4.56 (d, 2H, PhC*H*$_2$), 4.69 (s, 1H, H-1), 4.47 (dd, 1H,

$J_{2,3}$ = 3.0 Hz, H-2), 3.98 (m, 1H, H-5), 3.87 (m, 3H, H-3, H-6, H-6′), 3.69 (bd, 1H, H-4), 3.44 (s, 3H, OCH_3), 2.52 (bs, 1H, OH), 1.9 (bs, 1H, OH); ^{13}C NMR δ 99.4 (C-1), 74.6, 68.7, 64.4 (C-3, C-4, C-5), 71.8 (PhCH_2), 62.5 (C-6), 55.8 (C-2), 50.1 (OCH_3).

Anal. Calcd for $C_{16}H_{20}Cl_3NO_6$ (428.70): C, 44.83; H, 4.70. Found: C, 44.80; H, 4.71.

Methyl 3-*O*-Benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-altropyranoside (18). Prepared from **14** (320 mg, 0.59 mmol) as described above for the preparation of compound **15**. Chromatographic purification (CH_2Cl_2/acetone, 8:2) afforded pure **18** (270 mg, 96 %): $[\alpha]_D$ +80.3° (*c* 0.93); ^{1}H NMR δ 7.35 (m, 5H, aromatic), 5.60 (d, 1H, $J_{2,NH}$ = 8.5 Hz, NH), 4.91 and 4.51 (2d, 2H, PhCH_2), 4.77 and 4.71 (2d, 2x1H, Cl_3CCH_2), 4.65 (s, 1H, H-1), 4.31 (dd, 1H, $J_{2,NH}$ = 8.5 Hz, $J_{2,3}$ = 2.5 Hz, H-2), 3.85 (m, 5H, H-3, H-4, H-5, H-6, H-6′), 3.40 (s, 3H, OCH_3), 2.58 and 2.24 (d, and bs, 2x1H, 2 x O*H*); ^{13}C NMR δ 153,9 (Cl_3CCH_2OCO), 100.2 (C-1), 75.5, 68.5, 64.0 (C-3, C-4, C-5), 74.7 (Cl_3CCH_2), 71.5 (PhCH_2), 62.5 (C-6), 55.6 (C-2), 49.9 (OCH_3).

Anal. Calcd for $C_{17}H_{22}Cl_3NO_7$ (458.72): C, 44.51; H, 4.83. Found: C, 44.52; H, 4.9.

Methyl 3-*O*-Benzyl-6-*O*-chloroacetyl-2-deoxy-2-phthalimido-α-D-altro-pyranoside (19). To a solution of **15** (3.44 g, 8.2 mmol) and triethylamine (2.7 mL) in dry CH_2Cl_2 (60 mL), was added chloroacetyl chloride (780 μL, 9.8 mmol) at -40 °C and the mixture was stirred at -40 °C for 30 min. The mixture was diluted with CH_2Cl_2 (200 mL) and after extractive work-up the crude syrup was chromatographed (hexane/EtOAc, 6:4) to yield pure **19** (3.60 g, 90 %): $[\alpha]_D$ –13° (*c* 0.99); ^{1}H NMR δ 7.80 (m, 4H, Phth), 7.10 (m. 5H, aromatic), 5.17 (d, 1H, $J_{1,2}$ = 7.0 Hz, H-1), 4.45 (m, 4H, H-2, H-3, H-6, H-6'), 4.26 (dd, 1H, H-5), 4.15 (s, 2H, ClCH_2), 4.06 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 4.5 Hz, H-4), 3.34 (s, 3H, OCH_3), 2.87 (bs, 1H, O*H*).

Anal. Calcd for $C_{24}H_{24}ClNO_8$ (489.91): C, 58.84; H, 4.94. Found: C, 58.83; H, 4.91.

Methyl 3-*O*-Benzyl-6-*O*-chloroacetyl-2-deoxy-2-tetrachlorophthalimido-α-D-altropyranoside (20). To a solution of **16** (300 mg, 0.54 mmol) in dry pyridine (10 mL) was added chloroacetyl chloride (51 μL, 0.65 mmol) at -50 °C. After 1 h stirring the mixture was concentrated and the crude syrup was purified by chromatography (hexane/EtOAc, 7:3) to yield **20** (210 mg, 62 %): $[\alpha]_D$ -43.7° (*c* 0.35); ^{1}H NMR 7.10 (m. 5H, aromatic), 4.77 (d, 1H, $J_{1,2}$ = 6.0 Hz, H-1), 4.35 (m, 4H, H-2, H-3, H-6, H-6'), 4.26 (dd, 1H, H-5), 4.15 (s, 2H, ClCH_2), 4.06 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 4.5 Hz, H-4), 3.34 (s, 3H, OCH_3), 2.87 (bs, 1H, O*H*). ^{13}C NMR δ 167.1 (ClCH$_2$CO), 163.2 (C=O), 97.6 (C-1), 73.2, 72.9, 65.9 (C-3, C-4, C-5), 72.8 (PhCH$_2$), 65.5 (C-6), 55.7 (C-2), 52.4 (OCH$_3$), 40.7 (ClCH$_2$).

Anal. Calcd for $C_{24}H_{20}Cl_5NO_8$ (627.69): C, 45.92; H, 3.21. Found: C, 45.90; H, 3.20.

Methyl 3-*O*-Benzyl-6-*O*-chloroacetyl-2-deoxy-2-trichloroacetamido-α-D-altropyranoside (21). Prepared from **17** (600 mg, 1.4 mmol) as described above for the preparation of compound **19**. Chromatographic purification (hexane/EtOAc, 7:3) resulted in pure **21** (460 mg, 65 %): $[\alpha]_D$ +78.1° (*c* 0.54); ^{1}H NMR δ 7.4 (m, 5H, aromatic), 6.77 (d, 1H, $J_{2,NH}$ = 8.5 Hz, NH), 4.93, 4.56 (2d, 2H, PhCH_2), 4.69 (s, 1H, H-1), 4.55 (dd, 1H, $J_{5,6}$ = 2.0 Hz, $J_{6,6'}$ = 12.0 Hz, H-6), 4.48 (dd, 1H, $J_{2,3}$ = 3.0 Hz, H-2), 4.43 (dd, 1H, $J_{5,6'}$ = 5.5 Hz, H-6'), 4.16 (m, 1H, $J_{4,5}$ = 9.5 Hz, H-5), 4.09 (s, 2H, ClCH_2), 3.88 (t, 1H, $J_{3,4}$ = 3.0 Hz, H-3), 3.68 (bd, 1H, H-4), 3.43 (s, 3H, OCH_3), 2.53 (bs, 1H, O*H*); ^{13}C NMR δ 161.5 (Cl$_3$CCO), 99.3 (C-1), 74.2, 66.9, 63.8 (C-3, C-4, C-5), 71.8 (PhCH$_2$), 64.9 (C-6), 55.9 (C-2), 49.9 (OCH$_3$), 40.7 (ClCH$_2$).

Anal. Calcd for $C_{18}H_{21}Cl_4NO_7$ (505.18): C, 42.80; H, 4.19. Found: C, 42.79; H, 4.17.

Methyl 3-*O*-Benzyl-6-*O*-chloroacetyl-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-α-D-altropyranoside (22). Prepared from **18** (260 mg, 0.57 mmol) as described above for the preparation of compound **19**. Purification (hexane/EtOAc, 8:2) resulted in **22** (190 mg, 63 %): $[\alpha]_D$ +69.5° (*c* 0.14); ^{1}H NMR δ 7.4 (m, 5H, aromatic), 5.24 (d, 1H, $J_{2,NH}$ = 9.0 Hz, NH), 4.91, 4.52 (2d, 2H, PhCH_2), 4.75 (d, 2H, Cl$_3$CCH_2), 4.54 (dd, 1H, $J_{6,6'}$ = 12.0 Hz, $J_{5,6}$ = 2.0 Hz, H-6), 4.42 (dd, 1H, $J_{5,6'}$ = 6.0 Hz, J-6'), 4.31 (dd, 1H, $J_{2,3}$ = 2.5 Hz, H-2), 4.1 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, H-5), 4.1 (s, 2H, ClCH_2), 3.83 (bt, 1H, $J_{3,4}$ = 3.0 Hz, H-3), 3.68 (bm, 1H, H-4), 3.41 (s, 3H, OCH_3), 2.53 (bd, 1H, O*H*); ^{13}C NMR δ 167.1 (ClCH$_2$CO), 153.7 (Cl$_3$CCH$_2$OCO), 99.9 (C-1), 95.2 (Cl$_3$CCH$_2$), 75.0, 66.8, 63.7

(C-3, C-4, C-5), 74.7 (Cl_3CCH_2), 71.5 (PhCH_2), 65.2 (C-6), 55.7 (C-2), 49.7 (OCH_3), 40.8 (ClCH_2).

Anal. Calcd for $C_{19}H_{23}Cl_4NO_8$ (535.21): C, 42.64; H, 4.33. Found: C, 42.60; H, 4.32.

Methyl 2-Azido-3-*O*-benzyl-2-deoxy-α-D-altropyranoside (23). To a stirred solution of 9[8] (4.0 g, 10.06 mmol) in CH_2Cl_2 (50 mL) were added trifluoroacetic acid (5 mL) and water (1 mL) at rt. After 30 min the reaction mixture was concentrated then co-concentrated with toluene (2 x 20 mL) and the crude syrup was purified by chromatography (CH_2Cl_2/acetone, 8:2) to yield pure **23** (3.01 g, 96 %): $[\alpha]_D$ +75.2° (*c* 0.58); ^1H NMR δ 7.10 (m, 5H, aromatic), 4.98 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1), 4.77 (t, 1H, $J_{2,3}$ = 3.0 Hz, H-2), 4.47 (m, 2H, H-6, H-6'), 4.38 (dd, 1H, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 10.0 Hz, H-4), 3.99 (t, 1H, H-3), 3.39 (s, 2H, OCH_3); ^{13}C NMR δ 98.2 (C-1), 76.5, 73.7, 72.6 (PhCH_2), 69.8 (C-6), 59.2, 55.4, 54.6.

Anal. Calcd for $C_{14}H_{19}N_3O_5$ (309.32): C, 54.36; H, 6.19. Found: C, 54.12; H, 6.10.

Methyl (Methyl 2-azido-3-*O*-benzyl-2-deoxy-α-D-altropyranosid)uronate (24). The diol **23** (3.0 g, 9.7 mmol), KBr (300 mg) and TEMPO (60 mg) in sat. aq. $NaHCO_3$ (50 mL) was cooled to 0 °C and NaOCl solution (70 mL) was added dropwise to the vigorously stirred suspension. The mixture was allowed to warm up to rt and stirring was continued for 1 day when the solution become clear. The mixture was concentrated and co-concentrated with toluene (2 x 20 mL). The resulting white powder was suspended in *N,N*-dimethylformamide (15 mL), chilled and methyl iodide (6 mL) was added to the mixture and stirred for overnight. CH_2Cl_2 was added, the inorganic salts were removed by extractive work-up, the crude syrup was purified by chromatography (CH_2Cl_2/EtOAc, 8:2) to yield **24** (2.08 g, 64 %): $[\alpha]_D$ +67.2° (*c* 0.34); ^1H NMR δ 7.10 (m, 5H, aromatic), 4.98 (d, 1H, $J_{1,2}$ = 3 Hz, H-1), 4.77 (t, 1H, $J_{2,3}$ = 3 Hz, H-2), 4.47 (m, 2H, H-6, H-6'), 4.38 (dd, 1H, $J_{3,4}$ = 3 Hz, $J_{4,5}$ = 10 Hz, H-4), 3.99 (t, 1H, H-3), 3.39 (s, 3H, OCH_3); ^{13}C NMR δ 98.2 (C-1), 76.5, 73.7, 72.6 (PhCH_2), 59.2, 55.4, 54.6.

Anal. Calcd for $C_{15}H_{19}N_3O_6$ (337.33): C, 53.41; H, 5.68. Found: C, 53.39; H, 5.66.

Methyl (Methyl 2-amino-3-*O*-benzyl-2-deoxy-α-D-altropyranosid)uronate (25). To a solution of the azide **24** (2.0 g, 5.9 mmol) in MeOH (100 mL) were added pyridine (500 mL) and Pd-C (10%, 50 mg) and the mixture was vigorously stirred under H_2-atmosphere for 2 h. The catalyst was filtered off, the cake was washed with MeOH and the combined filtrates were concentrated. The crude syrup (1.76 g) was used for the next steps without purification.

Methyl (Methyl 3-*O*-benzyl-2-deoxy-2-phthalimido-α-D-altropyranosid) uronate (26). To a solution of the amine **25** (100 mg, 0.32 mmol) and triethylamine (100 μL) in dry CH_2Cl_2 (10 mL) 2-methoxycarbonyl benzoyl chloride (0.38 mmol) was added at rt. The mixture was refluxed for overnight then concentrated and the resulting crude syrup was chromatographed (CH_2Cl_2/EtOAc, 95:5) to yield **26** (92 mg, 65%): ^{1}H NMR δ 7.73, 7.03 (2m, 2x5H, aromatic), 5.32 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1), 4.77 (d, 1H, $J_{4,5}$ = 2.5 Hz, H-5), 4.61, 4.36 (2d, 2H, PhCH_2), 4.56 (t, 1H, $J_{3,4}$ = 3.0 Hz, H-4), 4.50 (dd, 1H, $J_{2,3}$ = 11.0 Hz, H-2), 4.32 (dd, 1H, H-3), 3.86 (s, 3H, COOCH_3), 3.43 (OCH_3), 2.88 (bs, 1H, OH); ^{13}C NMR δ 169.5 (*C*OOCH$_3$), 167.9 (C=O), 97.3 (C-1), 74.9, 72.7, 66.4 (C-3, C-4, C-5), 71.7 (Ph*C*H$_2$), 56.3 (COO*C*H$_3$), 52.5 (C-2), 51.4 (O*C*H$_3$).

Anal. Calcd for $C_{23}H_{23}NO_8$ (441.44): C, 62.58; H, 5.25. Found: C, 62.55; H, 5.24.

Methyl (Methyl 3-*O*-benzyl-2-deoxy-2-tetrachlorophthalimido-α-D-altropyranosid)uronate (27). To a solution of the amine **25** (100 mg, 0.32 mmol) in 2,2-dichloroethane (10 mL) tetrachlorophthalic anhydride (105 mg, 0.34 mmol) was added and the mixture was stirred for 15 min at rt. Diisopropylethylamine (500 μL) was added and the mixture was refluxed for overnight, then concentrated and purified by chromatography (CH_2Cl_2/EtOAc, 95:5) to yield pure **27** (144 mg, 78 %): ^{1}H NMR δ 7.0 (m, 5H, aromatic), 5.26 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1), 4.78 (d, 1H, $J_{4,5}$ = 2.0 Hz, H-5), 4.70, 4.27 (2d, 2H, PhCH_2), 4.58 (dd, 1H, $J_{3,4}$ = 3.0 Hz, H-4), 4.45 (dd, 1H, $J_{2,3}$ = 11.0 Hz, H-2), 4.24 (dd, 1H, H-3), 3.88 (s, 3H, COOCH_3), 3.42 (s, 3H, OCH_3), 2.78 (bs, 1H, O*H*); ^{13}C NMR δ 169.3 (*C*OOCH$_3$), 163.0 (C=O), 96.7 (C-1), 75.0, 73.4, 66. 7 (C-3, C-4, C-5), 72.4 (Ph*C*H$_2$), 56.4 (COO*C*H$_3$), 52.7 (C-2), 52.2 (O*C*H$_3$).

Anal. Calcd for $C_{23}H_{19}Cl_4NO_8$ (579.22): C, 47.69; H, 3.31. Found: C, 47.68; H, 3.32.

Methyl (Methyl 3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-altropyranosid)uronate (28). To a solution of amine **25** (480 mg, 1.54 mmol) in dry CH_2Cl_2 (10 mL), were added triethylamine (500 μL) and trichloroacetyl chloride (190 μL, 1.7 mmol) at 0 °C, and the mixture was stirred for 1 h then concentrated and purified by chromatography (CH_2Cl_2/EtOAc, 98:2) to yield pure **28** (488 mg, 70 %) as a colourless syrup: ^{1}H NMR δ 7.35 (m, 5H, aromatic), 6.93 (d, 1H, $J_{2,NH}$ = 8.5 Hz, NH), 4.85, 4.60 (2d, 2H, PhCH_2), 4.82 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1), 4.56 (d, 1H, $J_{4,5}$ = 8.0 Hz, H-5), 4.33 (m, 1H, $J_{3,4}$ = 4.0 Hz, $J_{4,OH}$ = 8.0 Hz, H-4), 4.01 (bm, 1H, H-2), 3.92 (t, 1H, $J_{2,3}$ = 4. Hz, H-3), 3.81 (s, 3H, COOCH_3), 3.47 (s, 3H, OCH_3), 2.72 (bd, 1H, OH); ^{13}C NMR δ 170.1 (*C*OOCH$_3$), 161.8 (C=O), 99.3 (C-1), 74.3, 69.8, 65.9 (C-3, C-4, C-5), 71.9 (Ph*C*H$_2$), 56.4 (COO*C*H$_3$), 52.6 (C-2), 50.9 (O*C*H$_3$).

Anal. Calcd for $C_{17}H_{20}Cl_3NO_7$ (456.71): C, 44.71; H, 4.41. Found: C, 44.72; H, 4.43.

Methyl [Methyl 3-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-altropyranosid]uronate (29). Prepared from **25** (525 mg, 1.7 mmol) as described above for the preparation of compound **28** to yield after chromatography (CH_2Cl_2/EtOAc, 98:2) **29** (430 mg, 52 %) as a colourless syrup: ^{1}H NMR δ 7.35 (m, 5H, aromatic), 5.65 (d, 1H, $J_{2,NH}$ = 8.5 Hz, NH), 4.84, 4.56 (2d, 2H, PhCH_2), 4.73 (d, 1H, $J_{1,2}$ = 2.0 Hz, H-1), 4.72 (s, 2H, Cl_3CCH_2), 4.50 (d, 1H, $J_{4,5}$ = 8.5 Hz, H-5), 4.21 (m, 1H, H-4), 4.03 (bs, 1H, H-2), 3.84 (t, 1H, $J_{2,3}$ = 4.0 Hz, $J_{3,4}$ = 4.0 Hz, H-3), 3.79 (s, 3H, COOCH_3), 3.43 (s, 3H, OCH_3), 2.77 (bd, 1H, O*H*); ^{13}C NMR δ 170.4 (*C*OOCH$_3$), 153.9 (Cl_3CCH_2O*C*O), 100.1 (C-1), 95.2 (Cl_3*C*CH$_2$), 75.2, 69.4, 65.6 (C-3, C-4, C-5), 74.6 (Cl_3C*C*H$_2$), 71.6 (Ph*C*H$_2$), 56.1 (COO*C*H$_3$), 52.5 (C-2), 50.2 (O*C*H$_3$).

Anal. Calcd for $C_{18}H_{22}Cl_3NO_8$ (486.73): C, 44.42; H, 4.56. Found: C, 44.42; H, 4.53.

General method for the glycosylation reactions with thioethyl glycosides

The solution of the acceptor (0.1 mmol) and the donor (0.11 mmol) in dry CH_2Cl_2 (1 mL) and 4 A molecular sieves (pellets) were stirred for 30 min at rt, then cooled to -40 °C. Solution of *N*-iodosuccinimide (0.13 mmol) and triflic acid (0.013 mmol) in dry CH_2Cl_2 (1 mL, containing 10% of dry tetrahydrofuran) was added dropwise to the solution. After 20 min triethylamine (100 μL) was added, the reaction mixture was diluted with CH_2Cl_2 (20 mL), and after extractive work-up the crude syrup was purified by chromatography.

Methyl (3-*O*-Acetyl-4-azido-2,4,6-trideoxy-2-phthalimido-β-D-galactopyranosyl)-(1→4)-3-*O*-benzyl-6-*O*-chloroacetyl-2-deoxy-2-phthalimido-α-D-altropyranoside (30). *Glycosylation with thioglycoside*: Prepared from ethyl 3-*O*-acetyl-4-azido-2,4,6-trideoxy-2-phthalimido-1-thio-β-D-galactopyranoside[8] (1) and **19** as described above. The crude mixture was purified by chromatography to yield pure **30** (30 mg, 33 %) as a colourless syrup.

Glycosylation with trichloroacetimidate: To a solution of the acceptor **19** (300 mg, 0.66 mmol) and the donor **7** (440 mg, 0.86 mmol) in dry CH_2Cl_2 (6 mL) was added molecular sieves (4 A, 200 mg) and the mixture was stirred for 30 min, then cooled to –50 °C and a solution of trimethylsilyl trifluoromethanesulfonate (50 μL in 500 μL of dry CH_2Cl_2) was injected. After 15 min triethylamine (200 μL) was added, the mixture was diluted with CH_2Cl_2 and after an extractive work-up chromatographed (CH_2Cl_2/EtOAc, 97:3) to yield pure **30** (400 mg, 73 %): $[\alpha]_D$ –93.1° (*c* 1.03); ^{1}H NMR δ 7.75 (m, 8H, aromatic), 7.11 (m, 5H, aromatic), 5.83 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, $J_{3',4'}$ = 3.5 Hz, H-3'), 5.42 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.89 (d, 1H, $J_{1,2}$ = 6.0 Hz, H-1), 4.70 (dd, 1H, H-2'), 4.43 (dd, 1H, $J_{2,3}$ = 8.0 Hz, H-2), 4.38 (dd, 1H, $J_{3,4}$ = 3.5 Hz, $J_{4,5}$ = 4.5 Hz, H-4), 4.29 (dd, 1H, H-3), 4.10 (s, 2H, ClCH_2), 3.92 (m, 1H, H-5'), 2.90 (s, 3H, OCH_3), 2.00 (s, 3H, CH_3CO), 1.33 (d, 3H, $J_{CH3,5'}$ = 6 Hz, H-6'); ^{13}C NMR δ 170.2 (ClCH$_2$CO), 167.7, 166.9 (C=O), 98.2 and 96.9 (C-1 and C-1'), 72.5, 71.8, 71.2 (PhCH$_2$), 70.69, 70.3, 69.4, 65.1 (C-6), 63.2, 54.8 (O*C*H$_3$), 52.5 and 51.1 (C-2 and C-2'), 40.7 (Cl*C*H$_2$), 20.4 (*C*H$_3$CO), 17.3 (C-6).

Anal. Calcd for $C_{40}H_{38}ClN_5O_{13}$ (832.22): C, 57.73; H, 4.60. Found: C, 56.99; H, 4.53.

Methyl (3-*O*-Acetyl-4-azido-2,4,6-trideoxy-2-tetrachlorophthalimido-β-D-galactopyranosyl)-(1→4)-3-*O*-benzyl-6-*O*-chloroacetyl-2-deoxy-2-tetrachlorophthalimido-α-D-altropyranoside (31). Prepared from **3** and **20** as described above and purified by chromatography (hexane/EtOAc, 75:25) to yield pure **31** (56 mg, 53 %) as a colourless syrup: $[\alpha]_D$ –53.8° (*c* 0.33); ^{1}H NMR δ 7.4 (m, 5H, aromatic), 5.77 (dd, 1H, $J_{2',3'}$ = 11.1, $J_{3',4'}$ = 3.8 Hz, H-3'), 5.45 (d, 1H, $J_{1',2'}$ = 8.3 Hz, H-1'), 4.92 (d, 1H, $J_{1,2}$ = 6.9

Hz, H-1), 4.72 (dd, 1H, H-2'), 4.08 and 4.1 (2s, 2H, ClCH_2), 4.0 (dd, 1H, $J_{4',5'}$ = 1.0 Hz, H-4'), 3.92 (bd, 1H, $J_{5',6'}$ = 6.3 Hz, H-5'), 3.03 (s, 3H, OCH_3), 2.05 (s, 3H, CH_3CO), 1.39 (d, 3H, $J_{5',6'}$ = 6.3 Hz, H-6'); ^{13}C NMR δ 170.2 (CH_3*C*O), 97.9 (C-1), 94.8 (C-1'), 71.4 (Ph*C*H_2), 71.1 (C-3'), 64.2 (C-6), 63.2 (C-4'), 55.7 (O*C*H_3), 52.7 (C-2), 51.5 (C-2'), 40.6 (Cl*C*H_2), 20.5 (*C*H_3CO), 17.4 (C-6').

Anal. Calcd for $C_{39}H_{30}Cl_8N_5O_{13}$ (1060.32): C, 44.18; H, 2.85. Found: C, 43.99; H, 2.87.

Methyl (3-*O*-Acetyl-4-azido-2,4,6-trideoxy-2-trichloroacetamido-β-D-galacto-pyranosyl)-(1→4)-3-*O*-benzyl-6-*O*-chloroacetyl-2-deoxy-2-trichloroacetamido-α-D-altropyranoside (32). Prepared from **4** and **21** as described above and purified by chromatography (CH_2Cl_2/EtOAc, 85:15) to yield pure **32** (21 mg, 24 %) as a colourless syrup: $[\alpha]_D$ –9.2° (*c* 0.1); ^{1}H NMR δ 7.3 (m, 5H, aromatic), 6.81 (d, 1H, $J_{NH,2}$ = 7.9 Hz, NH), 6.61 (d, 1H, $J_{NH,2}$ = 8.5 Hz, NH), 5.37 (dd, $J_{2',3'}$ = 10.8, $J_{3',4'}$ = 3.9 Hz, H-3'), 4.81 (d, 1H, $J_{1',2'}$ = 8.2 Hz, H-1'), 4.59 (s, 1H, H-1), 4.38 (bs, 2H, PhCH_2), 4.07 (d, 2H, ClCH_2), 3.35 (s, 3H, OCH_3), 2.25 (s, 3H, CH_3CO), 1.19 (d, 3H, $J_{5',6'}$ = 6.9 Hz, H-6'); ^{13}C NMR δ 161.9 (Cl_3*C*CO), 128.3, 127.9 and 127.5 (aromatic), 100.6 (C-1'), 99.9 (C-1), 75.3, 75.4, 73.2, 72.9, 71.1, 69.6, 65.2, 64.2, 63.1, 56.1, 53.4, 52.3, 40.9 (Cl*C*H_2), 20.4 (*C*H_3CO), 17.2 (C-6').

Anal. Calcd $C_{39}H_{30}Cl_7N_5O_{13}$ (1024.86): C, 45.71; H, 2.95. Found: C, 45.40; H, 3.00.

Methyl (3-*O*-Acetyl-4-azido-2,4,6-trideoxy-2-trichloroacetamido-β-D-galacto-pyranosyl)-(1→4)-(methyl 3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-altropyra-nosid)uronate (33). Prepared from **4** and **28** as described above and purified by chromatography (CH_2Cl_2/EtOAc, 85:15) to yield pure **33** (50 mg, 62 %) as a colourless syrup: $[\alpha]_D$ –34.6° (*c* 0.4); ^{1}H NMR δ 7.4 (m, 5H, aromatic), 6.87 (d, 1H, $J_{2',NH}$ = 8.0 Hz, NH), 6.76 (d, 1H, $J_{2,NH}$ = 7.6 Hz, NH), 5.54 (dd, 1H, $J_{2',3'}$ = 11.1, $J_{3',4'}$ = 3.8 Hz, H-3'), 4.99 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.89 (d, 1H, $J_{1,2}$ = 4.8 Hz, H-1), 4.60 (d, 1H, $J_{4,5}$ = 5.9 Hz, H-5), 4.33 (dd, 1H, $J_{3,4}$ = 3.1, H-4), 4.07 (dd, 1H, $J_{2,3}$ = 7.3, H-3), 3.99 (m, 1H, H-2), 3.90 (m, 1H, H-2'), 3.86 (d, 1H, H-4'), 3.80 (d, 1H, $J_{5',6'}$ = 6.3 Hz, H-5'), 3.46 (s, 3H, OCH_3), 2.11 (s, 3H, CH_3CO), 1.31 (d, 3H, $J_{5',6'}$ = 6.3 Hz, H-6'); ^{13}C NMR δ 170.2 (CH_3*C*O), 169.7 (*C*OOCH_3), 161.9 and 161. 6 (Cl_3*C*CO), 99.1 (C-1), 98.7(C-1'), 93.3

(Cl_3C), 73.7 (C-3), 72.6 ($PhCH_2$), 72.0 (C-4), 71.1 (C-3'), 70.3 (C-5), 69.6 (C-5'), 63.2 (C-4'), 56.5 (OCH_3), 53.5 (C-2), 53.2 (C-2'), 52.8 ($COOCH_3$), 20.4 (CH_3CO), 17.3 (C-6').

Anal. Calcd for $C_{27}H_{31}Cl_6N_5O_{11}$ (814.29): C, 39.83; H, 3.84. Found: C, 39.9; H, 3.80.

Methyl (4-Azido-2-acetamido-2,4,6-trideoxy-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3-*O*-benzyl-2-deoxy-α-D-altropyranosid)uronic acid (34). To a solution of **33** (100 mg, 0.12 mmol) in MeOH(3 mL) was added solution of NaOH (1M, 1 mL) and the mixture was stirred for 3 days at rt. The mixture was then concentrated, the crude solid was dissolved in MeOH (3 mL) and Ac_2O (600 μL) was added at 0 °C. The stirring was continued for 1 h, then the mixture was concentrated and purified by chromatography (CH_2Cl_2/MeOH/H_2O, 7:3:0.5) to yield pure **34** (42 mg, 62 %) as a colourless glass: $[\alpha]_D$ –22.7° (*c* 0.35, MeOH); ^{1}H NMR δ 7.3 (m, 5H, aromatic), 4.7 and 4.58 (2d, 2H, $PhCH_2$), 4.7 (2d, 1-1H, $J_{1,2}$ = 5.0 Hz, $J_{1',2'}$ = 8.5 Hz, H-1, H-1'), 4.61 (d, 1H, $J_{4,5}$ = 6.0 Hz, H-5), 4.32 (dd, 1H, $J_{3,4}$ = 3.0 Hz, H-4), 4.14 (dd, $J_{2',3'}$ = 10.7 Hz, $J_{3',4'}$ = 3.5 Hz, H-3'), 4.08 (dd, 1H, $J_{3,4}$ = 3.0 Hz, H-2), 3.80 (dd, $J_{2,3}$ = 7.0 Hz, H-3), 3.72 (m, 2H, H-4', H-5'), 3.63 (dd, 1H, H-2'), 3.40 (s, 3H, OCH_3), 1.97 and 1.92 (2s, 2x3H, CH_3CO), 1.30 (d, 3H, 6.4 Hz, H-6'); ^{13}C NMR δ 174.3, 173.1, 171.4, 139.7, 129.3, 129.2, 101.4, 76.3, 74.3, 72.7, 72.2, 71.2, 70.8, 67.8, 56.3, 55.3, 52.2, 23.3, 22.7, 17.6.

Anal. Calcd for $C_{24}H_{33}O_{10}N_5$ (551.55): C, 52.26; H, 6.03. Found: C, 52.22; H, 6.00.

Methyl (2-Acetamido-4-amino-2,4,6-trideoxy-β-D-galactopyranosyl)-(1→4)-(2-acetamido-2-deoxy-α-D-altropyranosid)uronic acid (35). To a solution of **34** (40 mg, 0.07 mmol) in MeOH (3 mL) was added a solution of HCl (1M, 0.5 mL) and $Pd(OH)_2$ (10 mg), and the mixture was stirred vigorously under H_2 for 1 day, then was concentrated under vacuum and purified by chromatography (CH_2Cl_2/MeOH/H_2O, 5:5:0.5) to yield pure **35** (24 mg, 78 %) as a colourless glass: $[\alpha]_D$ +11.76° (*c* 0.12, H_2O); ^{1}H NMR δ 4.74 (d, 1H, $J_{1',2'}$ = 7.2 Hz, H-1'), 4.61 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 3.99 (d, 1H, $J_{2',3'}$ = 10.2, $J_{3',4'}$ = 3.9 Hz, H-3'), 3.94 (dd, $J_{2',3'}$ = 9.6 Hz, H-2'), 3.82 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 3.71 (dd, $J_{3,4}$ = 2.95 Hz, H-3), 3.40 (dd, $J_{4',5'}$ = 1.2 Hz, H-4'), 3.47 (s, 3H, OCH_3), 2.05 and 2.01 (2s, 2x3H, CH_3CONH), 1.31 (d, 3H, $J_{5',6'}$ = 6.89 Hz, H-6'); ^{13}C

NMR δ 100.0, 99.84 (C-1, C-1'), 74.57, 70.55, 67.76, 67.58 and 67.31 (C-3, C-3', C-4, C-4' and C-5), 56.23, 53.22, 51.94 and 51.53 (C-5', C-2, C-2' and O*C*H_3), 22.24 and 22.02 (CH_3*C*ONH), 15.66 (C-6').

Anal. Calcd for $C_{17}H_{29}O_{10}N_2$ (421.42): C, 48.45; H, 6.94. Found: C, 48.39; H, 6.88.

1,4,6-Tri-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α,β-D-altropyranose (36). To a solution of **23** (1 g, 3.2 mmol) in Ac_2O (50 mL) was added H_2SO_4 (200 μL dissolved in 1 mL of Ac_2O) at 0 °C and the stirring was continued for 3h. The mixture was poured on ice cold solution of $NaHCO_3$, extracted with CH_2Cl_2, the organic layer was washed with $NaHCO_3$ solution until neutral, dried and concentrated. The crude syrup was passed through a short column of silica (CH_2Cl_2/EtOAc, 95:5) to yield pure **36** (1.2 g, 89 %) as a colourless syrup: $[\alpha]_D$ -74.7° (*c* 0.54); ^{1}H NMR 7.3 (m, 5H, aromatic), 6.15 (d, $J_{1,2}$ = 2.5 Hz, H-1α), 5.80 (d, $J_{1,2}$ = 4.3 Hz, H-1β), 5.15 (dd, $J_{3,4}$ = 3.1, $J_{4,5}$ = 6.2 Hz, H-4α), 5.07 (dd, $J_{3,4}$ = 3.1, $J_{4,5}$ = 6.8 Hz, H-4β), 4.56 (m, PhC*H_2*), 4.28 (m, H-5), 2.03, 2.02 and 1.98 (3s, C*H_3*CO); ^{13}C NMR 91.9 (C-1β), 91.4 (C-1α), 74.3, 73.5, 73.2, 72.7, 72.5, 70.2, 65.9 (Ph*C*H_2), 62.6 and 62.3 (C-6α,β), 59.8 and 59.5 (C-2α,β), 20.9 and 20.8 (*C*H_3CO).

Anal. Calcd for $C_{19}H_{23}N_3O_8$ (421.41): C, 54.15; H, 5.50. Found: C, 54.12; H, 5.54.

Ethyl 4,6-Di-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-α,β-D-altro-pyranoside (37). To an ice cold solution of **36** (2 g, 4.8 mmol) in dry CH_2Cl_2 (20 mL) were added EtSH (5 mmol) and $SnCl_4$ (4.8 mmol) and the mixture was stirred at 0 °C for 1h. The mixture was diluted with CH_2Cl_2, washed until neutral with $NaHCO_3$ solution, dried, concentrated and chromatographed (hexane/EtOAc, 8:2) to yield **37** (1.5 g, 75 % overall) as α and β mixture: **37**β $[\alpha]_D$ + 17.20° (*c* 0.33) and **37**α $[\alpha]_D$ +94.87° (*c* 0.67); ^{13}C NMR 170.5 and 169.7 (C=O), 82.6 (C-1), 74.3 (C-5), 72.6 and 67.5 (C-3,4), 66.2 (C-6), 62.3 (Ph*C*H_2), 61.6 (C-2), 26.6 (S*C*H_2CH_3), 20.7 and 20.6 (*C*H_3CO), 14.9 (SCH_2*C*H_3).

Anal. Calcd for $C_{19}H_{25}N_3SO_6$ (423.48): C, 53.89; H, 5.95. Found: C, 53.9; H, 5.86.

Ethyl 4,6-Di-*O*-acetyl-3-*O*-benzyl-2-deoxy-1-thio-2-trichloroacetamido-α,β-D-altropyranoside (38). A solution of **36** (450 mg, 1.06 mmol) in EtOAc (30 mL) containing PtO_2 catalyst (50 mg) was stirred vigorously under H_2 for 2h. The mixture was cooled to 0 °C, Et_3N (443 μL, 3.18 mmol) and trichloroacetyl chloride (130 μL, 1.2

mmol) were added and the stirring was continued for an additional 1 h. The catalyst was filtered off, the filtrate was extracted with water, dried, concentrated and chromatographed (hexane/EtOAc, 8:2) to yield pure **38** (350 mg, 62 %) as a colourless oil: $[\alpha]_D$ +87.46° (*c* 0.44); ^{1}H NMR 7.3 (m, 5H, aromatic), 6.95 (d, 1H, $J_{2,NH}$ = 7.9 Hz, NH), 5.12 (bs, 1H, H-1), 4.87 (dd, 1H, $J_{4,5}$ = 9.8, $J_{3,4}$ = 3.3 Hz, H-4), 4.73 and 4.47 (2d, 2H, PhC*H*$_2$), 4.72 (bm, 1H, H-2), 4.34 (m, 1H, $J_{5,6}$ = 2.6, $J_{5,6}$ = 4.6 Hz, H-5), 4.29 (dd, 1H, $J_{6,6'}$ = 12.5 Hz, H-6), 4.03 (dd, 1H, H-6'), 3.96 (t, 1H, $J_{2,3}$ = 3.6 Hz, H-3), 2.58 (m, 2H, SC*H*$_2$CH$_3$), 2.0 and 1.88 (2s, 2x3H, C*H*$_3$CO), 1.24 (t, 3H, SCH$_2$C*H*$_3$). ^{13}C NMR 170.5 and 169.6 (CH$_3$*C*O), 161.1 (Cl$_3$*C*CONH), 83.2 (C-1), 72.5 (C-5), 72.2 and 66.1 (C-3,4), 65.9 (C-6), 62.4 (Ph*C*H$_2$), 53.2 (C-2), 27.4 (S*C*H$_2$CH$_3$), 20.63 (*C*H$_3$CO), 15.1 (SCH$_2$*C*H$_3$).

Anal. Calcd for $C_{21}H_{26}NCl_3SO_7$ (542.86): C, 46.46; H, 4.83. Found: C, 46.38; H, 4.86.

Methyl (4,6-Di-*O*-acetyl-3-*O*-benzyl-2-deoxy-2-trichloroacetamido-α-D-altropyranosyl)-(1→3)-4-azido-2,4,6-trideoxy-2-trichloroacetamido-β-D-galactopyranoside (39). A solution of the glycosyl donor **38** (170 mg, 0.32 mmol) and methyl 4-azido-2,4,6-trideoxy-2-trichloroacetamido-β-D-galactopyranoside (90 mg, 0.26 mmol) in dry acetonitrile (1.5 mL) containing freshly fused molecular sieves (4 A) was stirred for 20 min at -30 °C, then a mixture of NIS (110 mg, 0.38 mmol) and TfOH (5 μL) in dry acetonitrile (600 μL) was added dropwise. After 15 min trimethylamine (200 μL) was added, then the mixture was diluted with CH$_2$Cl$_2$, extracted with Na$_2$S$_2$O$_3$ solution, dried, concentrated and chromatographed (CH$_2$Cl$_2$/acetone, 9:1) to yield pure **39** (180 mg, 84 %) as a colourless syrup: $[\alpha]_D$ -82.7° (*c* 0.5); ^{1}H NMR 7.25 (m, 5H, aromatic), 6.90 and 6.75 (2d, 1-1H, $J_{NH,2}$ = $J_{NH,2'}$ = 7.2 Hz, NH), 5.23 (d, 1H, $J_{1',2'}$ = 4.0 Hz, H-1'), 5.07 (dd, 1H, $J_{4',5'}$ = 6.56, $J_{3',4'}$ = 3.6 Hz, H-4'), 4.75 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 3.78 (dd, 1H, $J_{4,5}$ = 1, $J_{3,4}$ = 3.6 Hz, H-4), 3.62 (m, 1H, H-5), 3.49 (m, 1H, $J_{2,3}$ = 10.8 Hz, H-2), 3.41 (s, 3H, OC*H*$_3$), 2.03 and 1.96 (2s, 2x3H, C*H*$_3$CO), 1.29 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6); ^{13}C NMR 170.6 and 169.8 (CH$_3$*C*O), 161.9 (Cl$_3$*C*CONH), 99.7 (C-1), 95.02 (C-1'), 74.3 (C-3), 72.2, 71.8, 69.1 (C-5',3',4'), 66.01 (C-4), 62.1 (C-6'), 61.7 (Ph*C*H$_2$), 56.9 and 55.0 (C-2,2'), 53.1 (O*C*H$_3$), 20.7 (*C*H$_3$CO), 17.5 (C-6).

Anal. Calcd for $C_{28}H_{33}O_{11}N_5Cl_6$ (828.31): C, 40.60; H, 4.02. Found: C, 40.51; H, 4.00.

Methyl (3-*O*-Benzyl-2-deoxy-2-trichloroacetamido-α-D-altropyranosyl)-(1→3)-4-azido-2,4,6-trideoxy-2-trichloroacetamido-β-D-galactopyranoside (40). To a stirred, ice cold solution of **39** (100 mg, 0.12 mmol) in MeOH (10 mL) was added acetyl chloride (100 μL) and the stirring was continued at rt for 1 day. The solution was concentrated and chromatographed (CH_2Cl_2/acetone, 8:2) to yield pure **40** (60 mg, 69 %) as a colourless syrup: $[\alpha]_D$ +63.56° (*c* 0.3); ^{1}H NMR 7.30 (m, 5H, aromatic), 5.0 (d, 1H, $J_{1',2'}$ = 1.3 Hz, H-1'), 4.61 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 3.40 (s, 3H, OCH_3), 1.40 (d, 1H, H-6); ^{13}C 162.3 (NHCO), 100.2 (C-1), 93.9 (C-1'), 73.9, 72.6, 71.6, 69.5, 68.8, 62.9 (C-4), 60.7 and 60.6 (C-6' and CH_2Ph), 56.7 and 53.9 (C-2,2'), 50.3 (OMe), 17.2 (CH_3).

Anal. Calcd for $C_{24}H_{24}O_8N_5Cl_6$ (723.20): C, 39.86; H, 3.34. Found: C, 39.79; H, 3.34.

Methyl [(3-*O*-Benzyl-2-deoxy-2-trichloroacetamido-α-D-altropyranosyl) uronic acid)]-(1→3)-4-azido-2,4,6-trideoxy-2-trichloroacetamido-β-D-galactopyranoside (41). To a solution of diol **40** (80 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) were added TEMPO (5 mg), KBr (3 mg), tetraethylammonium chloride (3 mg) and sat. aq. $NaHCO_3$ (5 mL) and then cooled to 0 °C. A solution of NaOCl (5 mL) was added dropwise to the vigorously stirred solution at 0 °C and the stirring was continued for 30 min. The mixture was acidified by addition of 1M HCl solution, then extracted with CH_2Cl_2 (3 x 10 mL), the combined organic phases were washed until neutral with water, dried and concentrated. Chromatography (CH_2Cl_2/acetone, 7:3) yielded pure **41** (52 mg, 70 %): $[\alpha]_D$+19.89° (*c* 0.15); ^{1}H NMR 7.3 (m, 5H, aromatic), 5.3 (d, 1H, 7.4 Hz, H-1'), 4.46 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.34 (dd, 1H, $J_{3,4}$ = 3.7, $J_{2,3}$ = 11.0 Hz, H-3), 3.45 (s, 3H, OCH_3), 1.33 (d, 3H, $J_{5,6}$ = 6.1 Hz, H-6); ^{13}C NMR 103.6 and 97.5 (C-1, C-1'), 78.3, 77.3, 76.4, 72.3, 71.2, 67.5, 63.9, 57.3 and 54.5 (C-2,2'), 54.1 (OCH_3, 17.7 (C-6).

Anal. Calcd for $C_{24}H_{22}O_9N_5Cl_6$ (737.18): C, 39.10; H, 3.01. Found: C, 39.01; H, 3.06.

Methyl [(2-Acetamido-2-deoxy-α-D-altropyranosyl)uronic acid]-(1→3)-2-acetamido-4-amino-2,4,6-trideoxy-β-D-galactopyranoside (43). Compound **41** (45 mg, 0.06 mmol) was deprotected as described earlier (for compounds **34, 35**) to yield after chromatography (CH_2Cl_2/MeOH/H_2O, 6:4:0.3) pure **43** (11 mg, 40 %) as a colourless glass: $[\alpha]_D$ − 10.85° (*c* 0.11, H_2O); ^{1}H NMR (D_2O) 4.91 (d, 1H, $J_{1',2'}$ = 6.5 Hz, H-1'), 4.46 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1), 4.37 (d, 1H, $J_{4',5'}$ = 4.0 Hz, H-5'), 4.27 (t, 1H, $J_{4',5'}$ = 4.0 Hz, H-4'), 4.04 (dd, 1H, $J_{1',2'}$ = 6.5 Hz, $J_{2',3'}$ = 9.0 Hz, H-2'), 3.99 (bd,1H, $J_{5,6}$ = 6.0 Hz, H-5), 3.92 (dd, 1H, $J_{1,2}$ = 8.5 Hz, $J_{2,3}$ = 11 Hz H-2), 3.77 (dd, 1H, $J_{2',3'}$ = 9.0 Hz, $J_{3',4'}$ = 3.0 Hz, H-3'), 3.55 (OCH_3), 2.07 and 2.09 (2s, 2x3H, CH_3CONH), 1.35 (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6); ^{13}C NMR 105.0 (C-1), 101.2 (C-1'), 78.3 (C-5'), 71.6 (C-4'), 71.3 (C-5'), 71.0 (C-3'), 60.0 (OCH_3), 54.4 (C-2'), 52.6 (C-2), 25.0 (2xCH_3CONH), 18.2 (C-6).

ACKNOWLEDGEMENT

This work was supported by an International Research Scholar's award from the Howard Hughes Medical Institute. The Hungarian Scientific Research Fund OTKA F19482 and the Mizutani Foundation also supported these investigations. Generous support from Bolyai Postdoctoral Scholarship to I. Bajza is also acknowledged.

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