CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600832

Extended Applications of Di-*tert*-butylsilylene-Directed α-Predominant Galactosylation Compatible with C2-Participating Groups toward the Assembly of Various Glycosides

Akihiro Imamura,[b] Akiyoshi Kimura,[b] Hiromune Ando,*[a] Hideharu Ishida,[b] and Makoto Kiso*[b]

Abstract: The high versatility of di-*tert*-butylsilylene(DTBS)-directed α-predominant galactosylation have been extended to the construction of difficult glycan sequences. First, to investigate the compatibility of the α-predominant reaction with various glycosylation systems a variety of 4,6-*O*-DTBS-tethered galactosaminyl or galactosyl donors were synthesized efficiently, which have C2-participating groups with a wide variety of leaving groups such as alkylsulfenyl, halide, trichloroacetimidate groups. The results of the detailed examination of the glycosylation reaction using the glycosyl donors showed the wide scope of the 4,6-DTBS-directed α-galactosylation. In the next step, the stereoselective construction of α-GalN-Ser/Thr sequences was examined by employing the DTBS-directed glycosylation. As a result, various types of serine and threonine derivatives were glycosylated α-selectively, producing α-GalN-Ser/Thr sequences in high yields. Moreover, the DTBS-directed galactosylation was successfully applied for the synthesis of α-tetrasaccharyl-Ser segment of glycophorin A.

Keywords: carbohydrates · glycosylation · neighboring-group effect · oligosaccharides

Introduction

α-Gal-type linkages are ubiquitously found in natural oligosaccharides such as globoseries and isogloboseries glycolipids (Galα(1→4)Gal sequence) and mucin-type glycoproteins (GalNHAcα(1→)Ser/Thr core sequences). These oligosaccharides are involved in a variety of important biological processes[1] such as recognition of toxin receptors, the innate immune response, malignant alteration. These biological profiles are spurring efforts toward the synthesis of α-galactosyl glycan sequences.[2]

α-Gal-type linkages can be established using the anomeric effect, often with the aid of the etheral solvent effect.[2c] To minimize β-isomer formation, C2 hydroxyl or amino group protection is limited to the nonparticipating mode. Therefore, despite the elaborate procedure, the synthesis of 2-azido-galactosyl donors became a part of the standard protocol to generate α-galactosaminyl linkages.[2a] However, the anomeric selectivity and yield of conventional glycosylation varies greatly depending on the structures of the coupling partners; therefore difficult separation procedures are occasionally required. In particular, this drawback causes the drastic decrease in the overall yield of the α-galactosaminyl glycan synthesis. In this context, Schmidt and co-worker have described the nitroglycal-based approach toward the synthesis of various mucin-type O-glycans to circumvent the arduous preparation of the 2-azido-galactosyl donor.[3] Very recently, Boons and co-workers have developed a novel general method toward 1,2-*cis* glycosides synthesized by the neighboring-group participation of the (1*S*)-phenyl-2-(phenylsulfanyl)ethyl group at the C2-hydroxyl position.[4]

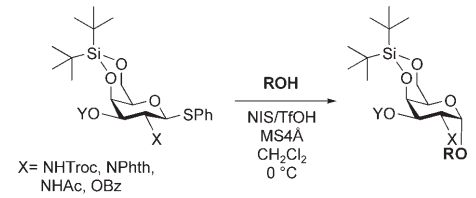
Previously, we reported that the phenylthio glycoside of 4,6-di-*tert*-butylsilylene(DTBS)-protected galactose performs

[a] Dr. H. Ando
Division of Instrumental Analysis
Life Science Research Center, Gifu University
1-1 Yanagido, Gifu-shi, Gifu 501-1193 (Japan)
Fax: (+81) 58-293-2617
E-mail: hando@cc.gifu-u.ac.jp

[b] Dr. A. Imamura, A. Kimura, Prof. H. Ishida, Prof. M. Kiso
Department of Applied Bioorganic Chemistry
Faculty of Applied Biological Sciences, Gifu University and CREST
Japan Science and Technology Corporation (JST)
1-1 Yanagido, Gifu-shi, Gifu 501-1193 (Japan)
Fax: (+81) 58-293-2916
E-mail: kiso@cc.gifu-u.ac.jp

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

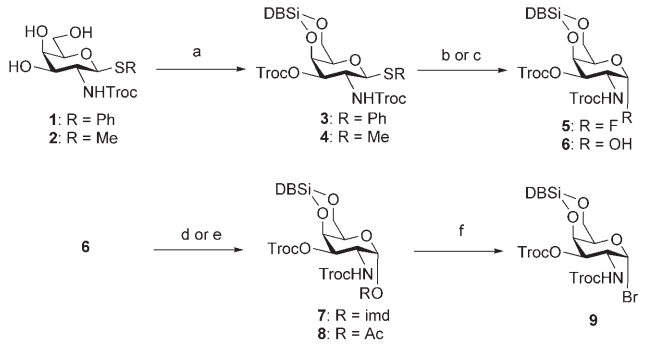
α-selective glycosidation despite the presence of participating groups at the C2 position (Scheme 1).[5] In this study, we demonstrate that the new glycosylation method is a comprehensive and powerful method for the synthesis of α-galactosyl and galactosaminyl glycans.



Scheme 1. Di-*tert*-butylsilylene-directed α-galactosylation. Troc = 2,2,2-trichloroethoxycarbonyl, Phth = phthaloyl, Bz = benzoyl, NIS = *N*-iodosuccinimide, TfOH = trifluoromethanesulfonic acid, and MS = molecular sieves.

Results and Discussion

Among the compatible protecting groups of the C2-amino group, 2,2,2-trichloroethoxycarbonyl (Troc) was selected because of its easy introduction and chemoselective cleavage. For C2 hydroxyl protection, a conventional benzoyl group was used. The installation of the DTBS group on the 4,6-hydroxyl groups of the galactosides proceeded almost quantitatively. As exemplified in Scheme 2, the thioglycosides of



Scheme 2. a) i) DTBS(OTf)$_2$/pyr, RT, 3 min; ii) subsequent addition of TrocCl, 30 min, 93% (**3**) and 54% (**4**); b) **3**, DAST, NBS/CH_2Cl_2, −15 °C, 5 h, 88%; c) **3**, NBS/aq. acetone, RT, 30 min, 83%; d) **6**, CCl_3CN, DBU, CH_2Cl_2, 0 °C, 30 min, 70%; e) **6**, Ac_2O, pyr, RT, 1 h, 94%; f) **8**, 25% HBr in AcOH, CH_2Cl_2, RT, 2 h, 86%. DB = di-*tert*-butyl, DTBS(OTf)$_2$ = di-*tert*-butylsilyl bis(trifluoromethanesulfonate), DAST = (diethylamino)sulfur trifluoride, NBS = *N*-bromosuccinimide, DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene.

N-Troc-protected galactosamine **1** and **2**, which were easily prepared from galactosamine hydrochloride **1**,[5b] successively reacted with DTBS(OTf)$_2$[6] and 2,2,2-trichloroethyl chloroformate (TrocCl) in pyridine to produce 4,6-DTBS-protected **3** and **4** in almost quantitative yield, respectively. Further, the phenylsulfenyl group of **3** could be successfully replaced with fluoride by action of *N*-bromosuccinimide (NBS) and (diethylamino)sulfur trifluoride (DAST), yielding **5** in 88% yield. The anomeric arrangement of **5** was exclusively α, as indicated by the ^{1}H NMR spectrum (δ 5.76; d, $J_{1,F}$ = 52.9 Hz), probably a result of the DTBS effect during the fluorination. For the synthesis of other glycosyl donors, compound **3** was subsequently hemiacetalized by NBS in aqueous acetone to produce **6**. Then, the C1 hydroxyl in **6** was transformed into trichloroacetimidate to form **7**,[7] or acetylated to yield acetoxy derivative **8**, which, upon the treatment with 25% HBr solution in acetic acid, afforded galactosaminyl bromide **9** with again predominant α-stereochemistry. Other types of glycosyl donors, namely, **10**–**12**[8] and **13**[5b] were also prepared in high yields. These compounds were used with various coupling partners, namely, compounds **14**–**22** (Figures 1 and 2).

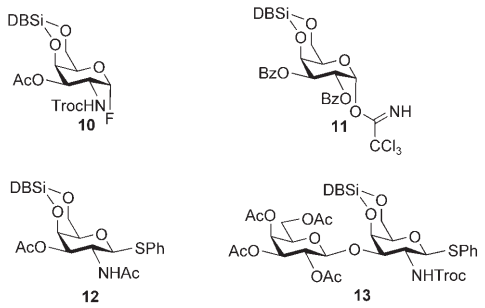


Figure 1. DTBS-bridged galactosyl donors used in this study. Bz = benzoyl.

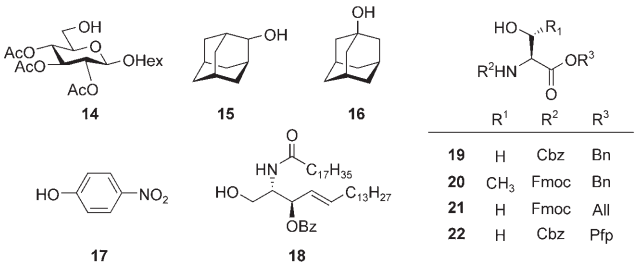
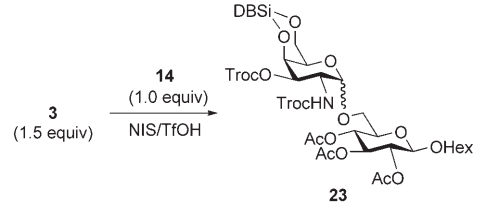


Figure 2. Various glycosyl acceptors used in this study. Hex = *n*-hexyl, Cbz = benzyloxycarbonyl, Fmoc = 9-fluorenylmethoxycarbonyl, All = allyl, Pfp = pentafluorophenyl.

As summarized in Table 1, we have explored the versatility of the DTBS-directed α-galactosylation with a special focus on α-galactosaminyl bond formation. First, the silylene-bridged glycosyl donor **3** reacted with glucosyl acceptor **14** in various solvents affected by NIS/TfOH[9] (entries 1–5). As a result, the α-selectivity of this DTBS-directed coupling was found to be independent of solvent effects; thus, in all cases the α-anomer **23** was stereoselectively produced in 84% to 100% *de*. Notably even the glycosidation in CH_3CN[10] exclusively yielded the α-glycoside (23%, 100% *de*).

Next, in Table 2, various leaving groups such as the methylsulfenyl,[9,11] fluoride,[12,13] and trichloroacetimidate[14] groups were examined. The glycosyl donors **3**–**7** were treated with 2-adamantanol (**15**). All stereochemical outcomes in entries 1–7 were predominantly α with sufficiently high

Table 1. Glycosidation of galactosyl donor **3** with glucosyl acceptor **14** under various condition.



Entry	Solvent	T [°C]	t [h]	Yield (α/β)[a] [%]
1[b]	CH_2Cl_2	0	0.5	96:3
2	*n*-hexane	RT	8.0	58:3
3	PhMe	0	0.5	91:7
4	CH_3NO_2	0	0.5	93:6
5	CH_3CN	0→40	22	23:0

[a] Isolated yield. [b] ref. [5a]. Hex = *n*-hexyl

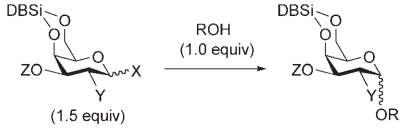
yields ranging from 68 to 91%. The results reveal the broad compatibility of DTBS-directed coupling with various leaving groups and promoters. Moreover, the results of entries 4–7 where α-fluoride or α-imidate donors were used ruled out the possibility that the α-anomeric selectivity of the DTBS-directed reaction is attributed to the stereoconversion of the β-glycosyl donor via S_N2-like mechanism. Interestingly, in contrast to these results, when insoluble silver silicate[15] was selected as a promoter for the glycosyl bromide donor **9**, the glycosylation predominantly produced the corresponding β-anomeric outcome **25** at 77% yield (entry 8). For entry 9, the smallest alkyl alcohol, that is, methanol was α-selectively glycosylated with **3**. In addition, tertiary alcohol **16** and aryl alcohol **17**[16] functioned as α-predominant coupling partners, thus producing the corresponding galactosides **27** and **28** in high yields (entries 10 and 11). At the final stage of this study, we attempted to directly α-galactosylate the hindered 1-hydroxyl of the ceramide fragment **18** with the 2,3-benzoylated galactosyl donor **11**. This reaction resulted in the successful synthesis of biologically-important α-Gal-Cer frame **29** in a relatively high yield (entry 12).[17]

In accordance with the above-mentioned results, the DTBS galactosyl donors have also been successfully used in the efficient synthesis of α-galactosaminyl Ser/Thr sequences (Table 3). Thus, various types of Ser derivatives, namely, **19**, **21**, and **22** as well as Thr derivative **20** were α-selectively galactosylated by the GalNTroc donors **3** and **7** in high yields (entries 1–3). The 2-acetamido-galactosyl donor **12** also served as an α-selective glycosylation unit to produce an α-GalNAc-Ser linkage in a moderate yield (entry 4). In entry 5, we found that the glycosidation of the Gal-GalN-Troc disaccharide donor **13** with Ser derivative **22** yielded the T-antigen structure **34** in 88% yield.

Moreover, the DTBS-containing trisaccharide **35**[8] was applied to the coupling of the Fmoc-Ser derivative **36** (Scheme 3). Fortunately, this coupling also confirmed our expectations by producing a Neu5Acα(2→3)Galβ(1→3)GalNα(1→)Ser sequence **37** as a single α-isomer in high yield. Further, to establish an α-sialyl branch on the C6 of the GalN residue, the 4,6-DTBS group was cleaved by the action of the fluoride anion released from *n*-tributylammonium hydrogenfluoride (TBAHF)[18] without affecting the Fmoc moiety. The resulting 4,6-diol glycan **38** was then sialylated with the previously obtained *N*-Troc sialyl donor **39**[19] to afford the tetrasaccharide **40** in 88% yield. Finally, the Troc groups within **40** were chemoselectively replaced by acetyl groups to produce glycophorin A glycan frame **41**.[20]

In summary, we have described the broad application of the DTBS-directed glycosylation for use in the synthesis of various α-galactosyl glycosides. As exemplified by the high α-selectivity and high-yielding synthesis of biologically significant α-Gal-Cer and glycophorin A glycan frames, this approach will greatly improve the efficiency of the general strategy toward the synthesis of α-galactosyl glycan structures.

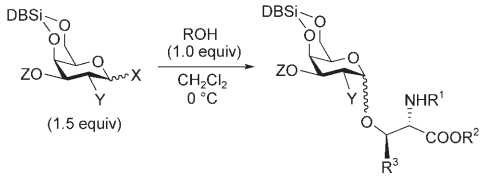
Table 2. Examination of various leaving groups in DTBS-directed galactosylation.



Entry	Donor	ROH	Promoter	T [°C]	t [h]	Product	Yield (α/β)[a] [%]
1	**3**	**15**	NIS/TfOH	0	0.5	**24**	91:7
2	**3**	**15**	DMTST[b]	0	21	**24**	83:15
3	**4**	**15**	NIS/TfOH	0	0.5	**24**	87:11
4	**5**	**15**	$SnCl_2$/$AgClO_4$[c]	0	1.5	**24**	82:0
5	**5**	**15**	Cp_2HfCl_2/AgOTf[d]	−20	0.5	**24**	71:0
6	**7**	**15**	TMSOTf	0	0.5	**24**	91:8
7	**7**	**15**	$BF_3{\cdot}OEt_2$	0	0.5	**24**	68:9
8	**9**	**15**	Ag-silicate[e]	−20	2.0	**25**	6:77
9	**3**	MeOH	NIS/TfOH	0	4.0	**26**	90:9
10	**3**	**16**	NIS/TfOH	0	0.5	**27**	90:5
11	**10**	**17**	BF_3OEt_2/Et_3N[f]	0	3.0	**28**	95:0
12	**11**	**18**	TMSOTf	0	48	**29**	60:0

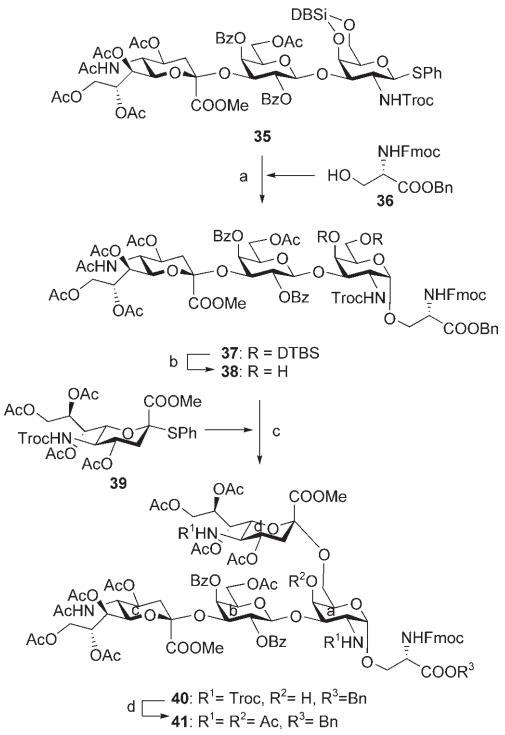
[a] Isolated yield. [b] See ref. [11]. [c] See ref. [12]. [d] See ref. [13]. [e] See ref. [15]. [f] See ref. [16]. DMTST = dimethyl(methylthio)sulfonium trifluoromethanesulfonate.

Table 3. α-Predominant formation of GalN-Ser/Thr linkages.



Entry	Donor	ROH	Promoter	t [h]	Product	Yield (α/β)[a] [%]
1	**3**	**19**	NIS/TfOH	0.5	**30**	95:2
2	**3**	**20**	NIS/TfOH	0.5	**31**	93:0
3	**7**	**21**	TMSOTf	0.5	**32**	97:0
4	**12**	**19**	NIS/TfOH	0.5	**33**	65:0
5	**13**	**22**	NIS/TfOH	1.0	**34**	88:0

[a] Isolated yield.



Scheme 3. a) NIS/TfOH, MS 4 Å, CH_2Cl_2, 0 °C, 8 h, 88 % (only α); b) TBAHF, THF, H_2O, RT, 5 h, 86 %; c) NIS/TfOH, MS 3 Å, CH_3CN, CH_2Cl_2, −35 °C, 31 h, 94 % (α/β 73:21); d) i) Zn, AcOH, 40 °C, 3 h, 68 %; ii) Ac_2O, pyr, RT, 11 h, 68 %. MS = molecular sieves, TBAHF = tri-*n*-butylammonium hydrogenfluoride.

Experimental Section

General procedures: ^{1}H and ^{13}C NMR spectra were taken by Varian INOVA 400 and 500. Chemical shifts are expressed in ppm (δ) relative to the signal of either $CHCl_3$ or Me_4Si, adjusted to δ 7.26 or 0.00 ppm, respectively. MALDI-TOF MS spectra were recorded in positive ion mode on a Bruker Autoflex with the use of α-cyano-4-hydroxycinnamic acid (CHCA) as a matrix. Molecular sieves were purchased from Wako Chemicals Inc. and dried at 300 °C for 2 h in muffle furnace prior to use. Drierite was powdered and dried at 300 °C for 6 h in muffle furnace prior to use. Solvents as reaction media were dried over molecular sieves and used without purification. TLC analysis was performed on Merck TLC (silica gel 60F_{254} on glass plate). Silica gel (80 mesh and 300 mesh) manufactured by Fuji Silysia Co. was used for flash column chromatography. Quantity of silica gel was usually estimated as 100 to 150-fold weight of sample to be charged. Solvent systems in chromatography were specified in v/v. Evaporation and condensation were carried out in vacuo.

Phenyl 2-deoxy-4,6-*O*-di-*tert*-butylsilylene-1-thio-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-β-D-galactopyranoside (3): Di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (2.20 mL, 6.15 mmol) was added at 0 °C under argon atmosphere to a solution of compound **1** (2.50 g, 5.59 mmol) in pyridine (110 mL), and the mixture was stirred for 3 min at ambient temperature. After the complete consumption of the starting material was confirmed on TLC analysis ($CHCl_3$/MeOH 10:1), 2,2,2-trichloroethyl chloroformate (1.15 mL, 8.39 mmol) was added and stirred for 30 min (TLC monitoring: EtOAc/hexane 1:3). The reaction mixture was coevaporated with toluene and extracted with $CHCl_3$. The organic phase was washed with 2 M HCl, H_2O, satd. aq. Na_2CO_3 and brine, dried (Na_2SO_4) and concentrated. The residue was purified by chromatography on silica gel (EtOAc/hexane 1:6) to give **3** (3.05 g, 93 %). $[\alpha]_D = +27.7°$ (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 8.05 (d, 1H, $J_{2,NH}$ = 9.3 Hz, NH), 7.40–7.24 (m, 5H, Ph), 5.50 (d, 1H, $J_{1,2}$ = 10.5 Hz, H-1), 5.03, 4.90 (2d, 2H, J_{gem} = 12.3 Hz, OCH_2CCl_3), 4.85 (q, 2H, J_{gem} = 12.3 Hz, OCH_2CCl_3), 4.82 (dd, 1H, $J_{2,3}$ = 10.5, $J_{3,4}$ = 2.9 Hz, H-3), 4.74 (d, 1H, H-4), 4.24 (dd, 1H, J_{gem} = 12.5 Hz, H-6), 4.10 (q, 1H, H-2), 4.07 (dd, 1H, H-6′), 3.83 (s, 1H, H-5), 1.04, 0.96 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 152.7, 134.7, 129.1, 129.1, 126.6, 96.1, 94.8, 86.0, 78.2, 76.0, 73.3, 68.9, 66.6, 66.3, 49.4, 27.4, 27.2, 22.7, 20.2; MALDI MS: *m*/*z*: calcd for $C_{26}H_{35}Cl_6NO_8SSiNa$: 781.98; found: 781.95 $[M+Na]^+$.

Methyl 2-deoxy-4,6-*O*-di-*tert*-butylsilylene-1-thio-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-β-D-galactopyranoside (4): Di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (1.32 mL, 3.62 mmol) was added at 0 °C under argon atmosphere to a solution of compound **2** (1.16 g, 3.02 mmol) in pyridine (15 mL), and the mixture was stirred for 3 min at ambient temperature. After the complete consumption of the starting material was confirmed on TLC analysis ($CHCl_3$/MeOH 10:1), 2,2,2-trichloroethyl chloroformate (1.25 mL, 9.06 mmol) was added and stirred for 30 min (TLC: EtOAc/hexane 1:3). The reaction mixture was coevaporated with toluene and extracted with $CHCl_3$. The organic phase was washed with 2 M HCl, H_2O, satd. aq. Na_2CO_3 and brine, dried (Na_2SO_4) and concentrated. The residue was purified by chromatography on silica gel (EtOAc/hexane 1:5) to give **4** (1.13 g, 54 %). $[\alpha]_D = +33.3°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, [D_6]DMSO): δ = 7.93 (d, 1H, NH), 4.97, 4.82 (2d, 2H, OCH_2CCl_3), 4.75 (dd, 1H, $J_{2,3}$ = 10.3, $J_{3,4}$ = 2.9 Hz, H-3), 4.72 (d, 1H, H-4), 4.53 (d, 1H, $J_{1,2}$ = 10.3 Hz, H-1), 4.25 (dd, 1H, J_{gem} = 12.5 Hz, H-6), 4.07 (dd, 1H, H-6′), 4.01 (q, 1H, H-2), 3.71 (s, 1H, H-5), 2.12 (s, 3H, Me), 1.02, 0.95 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 154.3, 152.8, 96.1, 94.8, 84.4, 79.2, 78.4, 76.1, 74.0, 73.3, 68.9, 66.6, 49.3, 27.4, 27.3, 23.0, 20.2, 12.5; MALDI MS: *m*/*z*: calcd for $C_{21}H_{33}Cl_6NO_8SSiNa$: 719.97; found: 720.04 $[M+Na]^+$.

2-Deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-α-D-galactopyranosyl fluoride (5): (Diethylamino)sulfur trifluoride (260 μL, 1.97 mmol) and *N*-bromosuccinimide (303 mg, 1.7 mmol) at −15 °C under argon atmosphere were added to a solution of compound **3** (1.00 g, 1.31 mmol) in CH_2Cl_2 (13 mL) and the mixture was stirred for 5 h (TLC: EtOAc/hexane 1:3). The reaction mixture was diluted with $CHCl_3$ and satd. aq. $NaHCO_3$ was added with ice. The mixture was stirred for 5 min vigorously. The organic layer was washed with water and dried over Na_2SO_4. After concentration, the resulted residue was subjected to column chromatography on silica gel (EtOAc/hexane 1:8) to give **5** (778 mg, 88 %). $[\alpha]_D = +86.0°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 8.38 (d, 1H, NH), 5.76 (d, 1H, $J_{1,F}$ = 52.9 Hz, H-1), 5.08, 4.94 (2d, 2H, OCH_2CCl_3), 4.90 (dd, 1H, H-3), 4.85 (m, 2H, OCH_2CCl_3), 4.82 (d, 1H, H-4), 4.30 (m, 2H, H-2, H-6), 4.09 (s, 1H, H-5), 1.01, 0.97 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 154.7, 152.6, 107.7, 105.5, 95.9, 94.8, 76.0, 73.8, 73.7, 68.7, 68.7, 68.5, 65.9, 48.5, 48.3, 27.2, 27.0, 22.7, 20.3; MALDI MS: *m*/*z*: calcd for $C_{20}H_{30}Cl_6FNO_8SSiNa$: 691.97; found: 691.95 $[M+Na]^+$.

2-Deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-α-D-galactopyranose (6): *N*-Bromosuccinimide (2.33 g, 13.1 mmol) was added at ambient temperature to a solution of compound **3** (2.00 g, 2.62 mmol) in acetone (44 mL)/water (9 mL), and the stirring was continued for 30 min until TLC analysis (EtOAc/hexane 1:3) indicated the completion of the reaction. The reaction mixture was concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane 1:5) to give **6** (1.45 g, 83 %). ^{1}H NMR (500 MHz, $CDCl_3$): mixture of rotamers **6a** and **6b** (**a**/**b** 3:1); **6a**: δ = 5.42 (d, 1H, $J_{1,2}$ = 2.9 Hz, H-1), 5.03 (d, 1H, NH), 4.86 (dd, 1H, $J_{2,3}$ = 11.0, $J_{3,4}$ = 2.6 Hz, H-3), 4.84, 4.70 (2d, 2H, OCH_2CCl_3), 4.77 (d, 1H, H-4), 4.58 (td, 1H, H-2), 4.23 (m, 2H, H-6, H-6′), 4.01 (s, 1H, H-5), 2.92 (s, 1H, OH), 1.08, 1.03 (2s, 18H, 2 *t*Bu); **6b**: δ 5.41 (d, 1H, $J_{1,2}$ = 2.9 Hz, H-1), 5.29 (d, 1H, NH), 4.95 (dd, 1H, $J_{2,3}$ = 11.0, $J_{3,4}$ = 2.6 Hz, H-3), 4.84, 4.70 (2d, 2H, OCH_2CCl_3), 4.77 (dd, 1H, H-4), 4.58 (td, 1H, H-2), 4.32 (d, 1H, H-6), 4.17 (d, 1H, H-6′), 4.01 (s, 1H, H-5), 2.86 (s, 1H, OH), 1.08, 1.03 (2s, 18H, 2 *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.4, 154.0, 95.4, 94.4, 92.6, 75.8, 74.7, 70.2, 67.3, 67.0, 49.7, 49.2, 27.6, 27.5, 27.4, 23.4, 20.8; MALDI MS: *m*/*z*: calcd for $C_{20}H_{31}Cl_6NO_9SiNa$: 689.97; found: 689.97 $[M+Na]^+$.

2-Deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-α-D-galactopyranosyl trichloroacetimidate (7): Trichloroacetonitrile (1.0 mL, 10.4 mmol) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (93.7 μL, 0.63 mmol) were added at 0 °C to a solution of compound **6** (350 mg, 0.52 mmol) in CH_2Cl_2 (5.2 mL), and the mixture was stirred for 30 min at ambient temperature (TLC: EtOAc/hexane 1:3). The reaction mixture was evaporated. The residue was purified with column chromatography on silica gel (EtOAc/hexane 1:2) to give **7** (293 mg, 70 %). ^{1}H NMR (500 MHz, $CDCl_3$); mixture of rotamers **7a** and **7b** (**a**/**b** 4:1); **7a**: δ = 8.75 (s, 1H, C=NH), 6.25 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 5.14 (d, 1H, NH), 4.99 (dd, 1H, $J_{2,3}$ = 11.5, $J_{3,4}$ = 3.0 Hz, H-3), 4.80 (m, 5H, H-2, 2 OCH_2CCl_3), 4.75 (d, 1H, H-4), 4.26 (m, 2H, H-6, H-6′), 3.96 (s, 1H, H-5), 1.10, 1.04 (2s, 18H, 2 *t*Bu); **7b**: δ = 8.79 (s, 1H, C=NH), 6.50 (d, 1H, $J_{1,2}$ = 2.9 Hz, H-1), 4.93 (d, 1H, NH), 4.99 (dd, 1H, $J_{2,3}$ = 11.5, $J_{3,4}$ = 3.0 Hz, H-3), 4.80 (m, 5H, H-2, 2 OCH_2CCl_3), 4.75 (d, 1H, H-4), 4.26 (m, 2H, H-6, H-6′), 3.96 (s, 1H, H-5), 1.10, 1.04 (2s, 18H, 2 *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.4, 154.1, 154.0, 96.1, 95.2, 94.1, 90.9, 75.2, 74.6, 69.8, 69.5, 66.5, 49.3, 48.9, 31.6, 27.5, 27.2, 23.3, 21.0, 20.7; MALDI MS: *m*/*z*: calcd for $C_{22}H_{31}Cl_9N_2O_9SiK$: 848.86; found: 848.96 $[M+K]^+$.

Acetyl 2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-α-D-galactopyranoside (8): Acetic anhydride (1.5 mL) was added at 0 °C to a solution of compound **6** (1.00 g, 1.49 mmol) in pyridine (1.5 mL), and the stirring was continued for 1 h at ambient temperature (TLC: EtOAc/hexane 1:3). The reaction mixture was coevaporated with toluene and extracted with EtOAc. The organic phase was washed with 2 M HCl, H_2O, satd. aq. Na_2CO_3 and brine, dried (Na_2SO_4) and concentrated. The residue was purified by chromatography on silica gel (EtOAc/hexane 1:5) to give **8** (1.01 g, 94 %). ^{1}H NMR (500 MHz, $CDCl_3$): mixture of rotamers **8a** and **8b** (**a**/**b** 3:1); **8a**: δ = 6.31 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 5.05 (d, 1H, NH), 4.94 (dd, 1H, $J_{2,3}$ = 11.4, $J_{3,4}$ = 2.9 Hz, H-3), 4.78 (m, 6H, H-2, H-4, 2 OCH_2CCl_3), 4.23 (2d, 2H, H-6, H-6′), 3.83 (s, 1H, H-5), 2.17 (s, 3H, Ac), 1.09, 1.03 (2s, 18H, 2 *t*Bu); **8b**: δ 6.35 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 5.02 (d, 1H, NH), 4.88 (dd, 1H, $J_{2,3}$ = 7.0, $J_{3,4}$ = 2.9 Hz, H-3), 4.78 (m, 6H, H-2, H-4, 2 OCH_2CCl_3), 4.23 (m, 2H, H-6, H-6′), 3.83 (s, 1H, H-5), 2.16 (s, 3H, Ac), 1.09, 1.03 (2s, 18H, 2 *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.0, 154.1, 96.3, 94.8, 94.2, 91.7, 75.3, 74.7, 70.1, 69.3, 66.6, 48.6, 48.2, 27.5, 23.3, 21.0, 20.8; MALDI MS: *m*/*z*: calcd for $C_{22}H_{33}Cl_6NO_{10}SiNa$: 731.99; found: 731.95 $[M+Na]^+$.

2-Deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-α-D-galactopyranosyl bromide (9): 25 % HBr solution in acetic acid (182 μL, 0.56 mmol) was added at 0 °C to a solution of compound **8** (200 mg, 0.28 mmol) in CH_2Cl_2 (1.4 mL), and the mixture was stirred for 2 h at ambient temperature (TLC: EtOAc/hexane 1:3). The reaction mixture was extracted with $CHCl_3$. The organic phase was washed with satd. aq. Na_2CO_3 and brine, dried (Na_2SO_4) and concentrated. The residue was purified chromatography on silica gel (EtOAc/hexane 1:20) to give **9** (177 mg, 86 %). $[\alpha]_D$ = +131.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.70 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 5.12 (d, 1H, NH), 4.99 (dd, 1H, $J_{2,3}$ = 10.9, $J_{3,4}$ = 2.3 Hz, H-3), 4.79 (m, 5H, H-4, 2 OCH_2CCl_3), 4.67 (td, 1H, $J_{2,NH}$ = 9.7 Hz, H-2), 4.07 (s, 1H, H-5), 1.07, 1.04 (2s, 18H, 2 *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.0, 153.9, 95.1, 94.8, 94.1, 75.8, 74.8, 72.3, 69.2, 66.2, 50.7, 29.7, 27.4, 27.1, 23.3, 21.0, 20.8.

2-Adamantyl 2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-α-D-galactopyranoside (24): *With glycosyl donor **3***: Molecular sieves 4 Å (140 mg) was added under argon atmosphere to a solution of **3** (120 mg, 157 μmol) and **15** (16 mg, 105 μmol) in CH_2Cl_2 (2.6 mL). The mixture was stirred at room temperature for 2 h. To the mixture was added dimethyl(methylthio)sulfonium triflate (DMTST, 48 %) (338 mg, 629 μmol) at 0 °C, and the stirring was continued for 21 h at 0 °C. The reaction was monitored by TLC ($PhCH_3$/EtOAc 50:1). The precipitate was filtered off and washed with $CHCl_3$. The filtrate and washings were combined, and the solution was successively washed with satd. aq. Na_2CO_3 and brine, dried and concentrated. Purification by column chromatography ($PhCH_3$/EtOAc 130:1) gave **24** (70 mg, 83 %) and its β-isomer (13 mg, 15 %).

*With glycosyl donor **5***: Molecular sieves 4 Å (170 mg) under argon atmosphere was added to a solution of **5** (150 mg, 223 μmol) and **15** (22 mg, 144 μmol) in CH_2Cl_2 (3.7 mL). The mixture was stirred at room temperature for 1 h. To the mixture were added $SnCl_2$ (42 mg, 223 μmol) and $AgClO_4$ (55 mg, 267 μmol) at 0 °C, and the stirring was continued for 16 h at 0 °C. The precipitate was filtered off and washed with $CHCl_3$. The filtrate and washings were combined, and the solution was successively washed with satd. aq. $NaHCO_3$ and brine, dried (Na_2SO_4) and concentrated. Purification by column chromatography ($PhCH_3$/EtOAc 130:1) gave **22** (93 mg, 78 %) and its β-isomer (12 mg, 10 %).

*With glycosyl donor **7***: Molecular sieves 4 Å (AW300) (170 mg) was added under argon atmosphere to a solution of **7** (150 mg, 184 μmol) and **15** (19 mg, 124 μmol) in CH_2Cl_2 (3.1 mL). To the mixture was added trimethylsilyl trifluoromethanesulfonate (TMSOTf) (0.67 μL, 3.68 μmol) at 0 °C, and the stirring was continued for 1 h at 0 °C. A similar work-up and purification as mentioned above gave **24** (91 mg, 91 %) and its β-isomer (8 mg, 8 %). $[\alpha]_D$ = +95.0° (*c* 1.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.15 (d, 1H, NH), 5.11 (dd, 1H, $J_{2,3}$ = 11.2, $J_{3,4}$ = 2.7 Hz, H-3), 5.10 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.85, 4.75 (2d, 2H, J_{gem} = 11.4 Hz, OCH_2CCl_3), 4.77, 4.70 (2d, 2H, J_{gem} = 11.9 Hz, OCH_2CCl_3), 4.75 (d, 1H, $J_{3,4}$ = 2.7 Hz, H-4), 4.57 (td, 1H, $J_{1,2}$ = 3.6, $J_{2,3}$ = 11.2 Hz, H-2^{GalN}), 4.28, 4.16 (2dd, 2H, J_{gem} = 12.8 Hz, H-6, 6′), 3.83 (s, 1H, H-5), 3.80 (t, 1H, H-2^{adamantane}), 2.07–1.54 (m, 14H, adamantane), 1.08, 1.02 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 154.1, 95.9, 80.1, 79.8, 76.9, 76.8, 76.5, 76.3, 75.2, 74.6, 70.1, 70.0, 67.5, 67.0, 49.3, 37.3, 36.7, 36.3, 33.6, 32.0, 31.8, 30.8, 27.6, 27.4, 27.3, 27.1, 23.4, 20.8; MALDI MS: *m*/*z*: calcd for $C_{30}H_{45}Cl_6NO_9SiNa$: 824.08; found: 824.16 $[M+Na]^+$.

2-Adamantyl 2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-β-D-galactopyranoside (25): Molecular sieves 4 Å (180 mg) under argon atmosphere was added to a solution of **9** (21 mg, 137 μmol) and Ag-silicate (180 mg) in CH_2Cl_2 (2.1 mL). The suspension was stirred for 1 h at room temperature. To the suspension was added the solution of **15** (150 mg, 205 μmol) in CH_2Cl_2 (1.3 mL) at −20 °C dropwise, and the stirring was continued for 1 h at −20 °C. The reaction was monitored by TLC (EtOAc/hexane 1:4). The reaction mixture was diluted with $CHCl_3$ and filtered through Celite. The filtrate and washings were combined and concentrated. Purification by column chromatography ($PhCH_3$/EtOAc 130:1) gave **25** (85 mg, 77 %) and **24** (7 mg, 6 %). $[\alpha]_D$ = +22.0° (*c* 1.7, $CHCl_3$); ^{1}H NMR (500 MHz, [D$_6$]DMSO) δ = 7.80 (d, 1H, NH), 5.04, 4.93 (2d, 2H, J_{gem} = 12.5 Hz, OCH_2CCl_3), 4.77 (q, 2H, J_{gem} = 12.5 Hz, OCH_2CCl_3), 4.72 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 4.64 (d, 1H, H-4), 4.61 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.22, 4.04 (2dd, 2H, J_{gem} = 11.2 Hz, H-6, 6′), 3.94 (pseudo q, 1H, $J_{1,2}$ = 8.0 Hz, H-2), 3.74 (brt, 1H, adamantane), 3.62 (s, 1H, H-5), 2.00–1.22 (m, 14H, adamantane), 1.02, 0.95 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 154.3, 152.9, 98.9, 96.1, 94.9, 79.8, 79.1, 77.6, 75.9, 73.6, 73.3, 69.4, 68.9, 66.6, 55.5, 50.9, 36.9, 35.9, 35.6, 32.9, 30.9, 30.8, 30.6, 29.0, 27.4, 27.1, 26.7, 26.5, 22.7, 20.4; MALDI MS: *m*/*z*: calcd for $C_{30}H_{45}Cl_6NO_9SiNa$: 824.08; found: 824.24 $[M+Na]^+$.

Methyl 2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-α-D-galactopyranoside (26): Molecular sieves 3 Å (500 mg) was added to a solution of compound **3** (100 mg, 131 μmol) and MeOH (10.6 μL, 262 μmol) in CH_2Cl_2 (1.3 mL). The suspension was stirred for 1 h and cooled to 0 °C. To the mixture were added *N*-iodosuccinimide (NIS) (59 mg, 262 μmol) and trifluoromethanesulfonic acid (TfOH) (2.3 μL, 26.2 μmol), and the stirring was continued for 4 h. The termination of reaction was confirmed by TLC (EtOAc/hexane 1:3). The reaction mixture was filtered through Celite. The combined filtrate and washings were extracted with $CHCl_3$, and the organic layer was washed with satd. aq. Na_2CO_3, satd. aq. $Na_2S_2O_3$ and brine, dried over Na_2SO_4 and concentrated. The residue was purified with column chromatography on silica gel (EtOAc/hexane 1:30) to give **26** (72 mg, 90 %) and the corresponding β-isomer (16 mg, 9 %). $[\alpha]_D$ = +85.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.22 (d, 1H, NH), 4.80 (m, 4H, H-1, H-3, OCH_2CCl_3), 4.58 (td, 1H, $J_{1,2}$ = 3.7, $J_{2,3}$ = $J_{2,NH}$ = 10.6 Hz, H-2), 4.24 (2d, 2H, H-6, H-6′), 3.73 (s, 1H, H-5), 3.41 (s, 3H, OMe), 1.09, 1.03 (2s, 18H, 2 *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.0, 154.7, 99.8, 96.2, 95.1, 75.4, 70.8, 68.0, 67.7, 56.4, 50.3, 49.8, 28.3,

28.1, 24.1, 21.5; MALDI MS: *m/z*: calcd for $C_{21}H_{33}Cl_6NO_9Si$: 703.99; found: 704.00 $[M+Na]^+$; β-isomer: $[\alpha]_D = +26.5°$ (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, 1H, NH), 4.97–4.81 (4d, 4H, 2 OCH_2CCl_3), 4.72 (dd, 1H, H-3), 4.65 (d, 1H, H-4), 4.41 (d, $J_{1,2}$ = 8.0 Hz, H-1), 4.17 (2d, 2H, H-6, H-6′), 3.89 (q, 1H, $J_{2,3} = J_{2,NH}$ = 10.8 Hz, H-2), 3.66 (s, 1H, H-5), 3.37 (s, 3H, OMe), 1.01, 0.95 (2s, 18H, 2 *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.0, 153.6, 100.8, 94.3, 70.8, 69.4, 67.0, 57.0, 52.3, 29.7, 27.4, 27.4, 23.3, 20.7; MALDI MS: *m/z*: calcd for $C_{21}H_{33}Cl_6NO_9SiNa$: 703.99; found: 703.93 $[M+Na]^+$.

1-Adamantyl 2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-α-D-galactopyranoside (27): Molecular sieves 4 Å (170 mg) was added to a solution of compound **3** (150 mg, 196 μmol) and compound **16** (20 mg, 131 μmol) in CH_2Cl_2 (3.3 mL). The suspension was stirred for 1 h and cooled to 0 °C. To the mixture were added NIS (88 mg, 392 μmol) and TfOH (3.4 μL, 13.1 μmol), and the stirring was continued for 30 min. A similar work-up and purification by silica gel column chromatography (EtOAc/hexane 1:30) as described for **26** gave **27** (95 mg, 90 %) and the corresponding β-isomer (10 mg, 5 %). $[\alpha]_D = +85.5°$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 5.33 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 5.07 (d, 1H, $J_{2,NH}$ = 9.7 Hz, NH), 4.85, 4.72 (2d, 2H, J_{gem} = 12.1 Hz, OCH_2CCl_3), 4.83 (dd, 1H, $J_{2,3}$ = 11.4, $J_{3,4}$ = 3.2 Hz, H-3), 4.77, 4.70 (2d, 2H, J_{gem} = 12.0 Hz, OCH_2CCl_3), 4.75 (d, 1H, H-4), 4.50 (td, 1H, $J_{1,2}$ = 3.4, $J_{2,3}$ = 11.4, $J_{2,NH}$ = 9.7 Hz, H-2), 4.28, 4.11 (2d, 2H, J_{gem} = 12.8 Hz, H-6, H-6′), 3.92 (s, 1H, H-5), 2.16–1.56 (m, 15H, adamantane), 1.08, 1.02 (2s, 18H, 2 *t*Bu); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 156.0, 155.8, 97.3, 96.2, 93.0, 92.8, 76.3, 71.9, 68.9, 68.8, 62.2, 51.3, 51.0, 44.2, 37.9, 32.4, 29.4, 29.1, 25.1, 22.9, 22.5, 16.0; MALDI MS: *m/z*: calcd for $C_{30}H_{45}Cl_6NO_9SiNa$: 824.08; found: 824.08 $[M+Na]^+$; β-isomer: $[\alpha]_D = +23.5°$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, [D$_6$]DMSO): δ = 7.69 (d, 1H, NH), 5.15, 4.92 (2d, 2H, J_{gem} = 11.9 Hz, OCH_2CCl_3), 4.85, 4.80 (2d, 2H, J_{gem} = 12.3 Hz, OCH_2CCl_3), 4.77 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.75 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 4.63 (d, 1H, H-4), 4.23, 4.00 (2d, 2H, J_{gem} = 11.4 Hz, H-6, H-6′), 3.78 (pseudo q, 1H, H-2), 3.60 (s, 1H, H-5), 2.05–1.50 (m, 15H, adamantane), 1.02, 0.94 (2s, 18H, 2 *t*Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.1, 152.8, 96.3, 94.8, 93.7, 79.1, 77.6, 75.9, 73.9, 73.2, 69.3, 68.7, 66.9, 51.0, 41.1, 38.0, 29.9, 27.4, 27.1, 22.7, 20.3; MALDI MS: *m/z*: calcd for $C_{30}H_{45}Cl_6NO_9SiNa$: 824.09; found: 824.08 $[M+Na]^+$.

***p*-Nitrophenyl 3-*O*-acetyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-α-D-galactopyranoside (28)**: Molecular sieves 4 Å (700 mg) was added under argon atmosphere to a solution of compound **10** (583 mg, 1.08 mmol) and **17** (100 mg, 721 μmol) in CH_2Cl_2 (18 mL). The suspension was stirred for 1 h and cooled to 0 °C. To the mixture were added triethylamine (75 μL, 541 μmol) and $BF_3{\cdot}Et_2O$ complex (340 μL, 2.70 mmol) and stirring was continued for 3 h at 0 °C. The termination of reaction was confirmed by TLC (EtOAc/hexane 1:3). To the reaction mixture, satd. aq. $NaHCO_3$ was added. The mixture was extracted with $CHCl_3$. The organic phase was washed with H_2O and brine, dried (Na_2SO_4) and concentrated. The residue was purified with column chromatography on silica gel (EtOAc/$PhCH_3$ 1:50) to give **28** (450 mg, 95 %). $[\alpha]_D = +180.0°$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.21, 7.20 (2d, 4H, Ar), 5.80 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1), 5.35 (d, 1H, $J_{2,NH}$ = 9.8 Hz, NH), 5.22 (dd, 1H, $J_{2,3}$ = 10.9, $J_{3,4}$ = 2.5 Hz, H-3), 4.84, 4.63 (2d, 2H, J_{gem} = 12.0 Hz, OCH_2CCl_3), 4.73 (td, 1H, H-2), 4.69 (d, 1H, H-4), 4.22, 4.09 (2dd, 2H, J_{gem} = 12.8 Hz, H-6, 6′), 3.79 (s, 1H, H-5), 2.15 (s, 3H, Ac), 1.12, 1.04 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.3, 160.8, 154.3, 142.9, 125.8, 116.3, 96.8, 95.2, 74.5, 70.3, 70.0, 68.6, 66.5, 48.9, 27.4, 27.1, 23.2, 20.8, 20.7; MALDI MS: *m/z*: calcd for $C_{25}H_{35}Cl_3N_2O_{10}SiNa$: 679.10; found: 679.48 $[M+Na]^+$.

2,3-Di-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-α-D-galactopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol (29): Molecular sieves 4 Å AW-300 (200 mg) was added to a solution of compound **11** (240 mg, 357 μmol) and compound **18** (80 mg, 119 μmol) in CH_2Cl_2 (3.0 mL). The suspension was stirred for 1 h and cooled to 0 °C. To the mixture was added TMSOTf (1.2 μL, 7.16 μmol) and the stirring was continued for 48 h. The termination of reaction was confirmed by TLC (EtOAc/hexane 1:5). The reaction mixture was filtered through Celite. The combined filtrate and washings were extracted with $CHCl_3$, and the organic layer was washed with satd. aq. Na_2CO_3 and brine, dried over Na_2SO_4 and concentrated. The residue was purified with column chromatography on silica gel (EtOAc/$PhCH_3$ 1:100) to give **29** (83 mg, 59 %). $[\alpha]_D = +96.5°$ (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 8.02–7.33 (m, 15H, 3 Ph), 5.78 (d, 1H, NH), 5.76 (dd, 1H, $J_{1,2}$ = 3.7, $J_{2,3}$ = 10.4 Hz, H-2^{GalN}), 5.74 (m, 1H, $J_{5,6}$ = 6.8 Hz, H-5^{Cer}), 5.56 (dd, 1H, $J_{3,4}$ = 3.1 Hz, H-3^{GalN}), 5.49 (m, 2H, H-3^{Cer}, H-4^{Cer}), 5.28 (d, 1H, H-1^{GalN}), 4.88 (d, 1H, H-4^{GalN}), 4.50 (m, 1H, $J_{1,2}$ = 4.6 Hz, H-2^{Cer}), 4.28, 4.19 (2dd, 2H, J_{gem} = 12.6 Hz, H-6^{GalN}, H-6′^{GalN}), 3.92 (s, 1H, H-5^{GalN}), 3.84 (dd, 1H, J_{gem} = 10.7 Hz, H-1′^{Cer}), 3.70 (dd, 1H, J_{gem} = 10.7 Hz, H-1^{Cer}), 2.10 (m, 2H, NHCOCH_2CH$_2$), 1.98 (q, 2H, $J_{5,6}$ = 6.8 Hz, H-6^{Cer}, H-6′^{Cer}), 1.57 (m, 2H, NHCOCH$_2$CH_2), 1.24 (m, 52H, CH_2), 1.11, 0.96 (2s, 18H, 2 *t*Bu), 0.88 (t, 6H, 2 CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.7, 166.2, 166.0, 165.2, 137.5, 133.2, 133.1, 133.0, 129.9, 129.8, 129.7, 129.7, 129.6, 129.4, 129.0, 128.4, 128.3, 128.3, 128.2, 124.6, 97.9, 74.4, 71.1, 70.9, 68.5, 67.7, 67.4, 66.8, 51.2, 36.9, 32.3, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.2, 28.9, 27.5, 27.2, 25.8, 23.3, 22.7, 20.7, 14.1; MALDI MS: *m/z*: calcd for $C_{71}H_{109}NO_{11}SiNa$: 1202.77; found: 1202.96 $[M+Na]^+$.

***N*-Benzyloxycarbonyl-*O*-[2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-α-D-galactopyranosyl]-L-serine benzyl ester (30)**: Molecular sieves 4 Å (400 mg) was added to a solution of compound **3** (277 mg, 364 μmol) and **19** (100 mg, 303 μmol) in CH_2Cl_2 (6.6 mL). The suspension was stirred for 1 h and cooled to 0 °C. To the mixture were added NIS (163 mg, 728 μmol) and TfOH (6.4 μL, 72.8 μmol) and stirring was continued for 0.5 h. The termination of reaction was confirmed by TLC (EtOAc/hexane 1:2). A similar work-up as described for **26** and purification by silica gel column chromatography (EtOAc/hexane 1:5) gave **30** (283 mg, 95 %) and the corresponding β-isomer (7 mg, 2 %). $[\alpha]_D = +68.2°$ (*c* 2.9, $CHCl_3$); ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 7.86 (d, 1H, NH^{Ser}), 7.71 (d, 1H, $J_{2,NH}$ = 9.0 Hz, NH^{GalN}), 7.38–7.31 (m, 10H, 2 Ph), 5.12 (2 d, 2H, J_{gem} = 12.4 Hz, OCH_2), 5.10, 5.05 (2 d, 2H, J_{gem} = 12.2 Hz, OCH_2), 5.04, 4.92 (2 d, 2H, OCH_2), 4.91, 4.65 (2 d, 2H, J_{gem} = 12.2 Hz, OCH_2), 4.87 (dd, 1H, $J_{2,3}$ = 11.2, $J_{3,4}$ = 2.4 Hz, H-3), 4.83 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 4.65 (d, 1H, $J_{3,4}$ = 2.4 Hz, H-4), 4.49 (m, 1H, CH^{Ser}), 4.26 (td, 1H, H-2), 4.11, 3.97 (2 dd, 2H, J_{gem} = 12.2 Hz, H-6, 6′), 3.82 (m, 2H, CH_2^{Ser}), 3.78 (s, 1H, H-5), 1.00, 0.95 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 169.9, 156.1, 154.4, 152.8, 136.6, 135.6, 128.4, 128.3, 128.1, 127.9, 127.8, 127.3, 98.2, 95.9, 94.8, 79.1, 75.9, 74.9, 73.6, 69.3, 67.3, 66.6, 66.3, 65.8, 54.2, 48.5, 27.2, 27.1, 22.7, 20.3, 0.0; MALDI MS: *m/z*: calcd for $C_{38}H_{48}Cl_6N_2O_{13}SiNa$: 1001.09; found: 1001.08 $[M+Na]^+$; β-isomer: $[\alpha]_D = -28.3°$ (*c* 0.3, $CHCl_3$); ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 7.87 (d, 1H, $J_{2,NH}$ = 9.0 Hz, NH^{GalN}), 7.39–7.30 (m, 10H, 2 Ph), 7.20 (d, 1H, NH^{Ser}), 5.11 (q, 2H, J_{gem} = 12.6 Hz, OCH_2), 5.07, 5.02 (2 d, 2H, J_{gem} = 12.6 Hz, OCH_2), 5.02, 4.92 (2 d, 2H, J_{gem} = 12.4 Hz, OCH_2), 4.80, 4.65 (2 d, 2H, J_{gem} = 12.4 Hz, OCH_2), 4.74 (dd, 1H, $J_{2,3}$ = 10.9, $J_{3,4}$ = 2.9 Hz, H-3), 4.64 (d, 1H, H-4), 4.56 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1), 4.38 (m, 1H, CH^{Ser}), 4.24, 4.06 (2 dd, 2H, J_{gem} = 10.4 Hz, H-6, 6′), 4.04, 3.82 (2 dd, 2H, J_{gem} = 10.4 Hz, CH_2^{Ser}), 3.89 (q, 1H, H-2), 3.64 (s, 1H, H-5), 0.96, 0.94 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.5, 156.0, 153.9, 153.5, 136.1, 135.2, 128.6, 128.5, 128.4, 128.3, 128.1, 99.8, 96.2, 94.2, 92.7, 77.2, 74.3, 70.8, 69.3, 67.5, 67.1, 66.7, 54.2, 52.0, 29.6, 27.4, 27.3, 23.2, 20.6, 0.0; MALDI MS: *m/z*: calcd for $C_{38}H_{48}Cl_6N_2O_{13}SiNa$: 1001.09; found: 1001.09 $[M+Na]^+$.

***N*-(9-Fluorenylmethoxycarbonyl)-*O*-[2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-α-D-galactopyranosyl]-L-threonine benzyl ester (31)**: $[\alpha]_D = +72.0°$ (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 7.57 (d, 1H, NH), 7.52 (m, 14H, NH^{Thr}, Ph), 5.08 (q, 2H, OCH_2CCl_3), 4.98 (q, 2H, PhCH_2), 4.84 (dd, 1H, H-3), 4.81 (q, 2H, OCH_2CCl_3), 4.80 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.69 (d, 1H, H-4), 4.52 (dd, 2H, CH_2 of Fmoc), 4.36 (dd, 1H, CH^{Thr}), 4.26 (m, 3H, CH of Fmoc, CH_2^{Thr}), 4.25 (m, 1H, $J_{1,2}$ = 3.7 Hz, H-2), 4.11 (2 d, 2H, H-6, H-6′), 3.83 (s, 1H, H-5), 1.01, 0.98 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 170.7, 170.5, 157.5, 155.2, 153.6, 144.5, 144.3, 141.5, 141.4, 136.3, 129.6, 129.1, 129.0, 128.9, 128.8, 128.3, 128.2, 127.8, 126.0, 125.6, 120.9, 120.8, 96.7, 95.5, 79.9, 76.7, 75.9, 74.6, 74.4, 70.2, 67.4, 67.2, 66.9, 66.2, 59.3, 47.5, 28.0, 27.9, 27.8, 23.5, 21.7, 21.0, 19.3; MALDI MS: *m/z*: calcd for $C_{46}H_{54}Cl_6N_2O_{13}SiNa$: 1103.14; found: 1103.04 $[M+Na]^+$.

***N*-(9-Fluorenylmethoxycarbonyl)-*O*-[2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-3-*O*-(2,2,2-trichloroethoxycarbonyl)-α-D-galactopyranosyl]-L-serine allyl ester (32)**: Molecular sieves 4 Å (AW-300) (200 mg) was added to a solution of compound **7** (154 mg, 189 μmol) and **21** (46 mg, 126 μmol) in CH_2Cl_2 (3.1 mL). The suspension was stirred for 1 h. To the mixture were added TMSOTf (0.68 μL, 3.78 μmol) and stirring was continued for 0.5 h. The termination of reaction was confirmed by TLC (EtOAc/hexane 1:3). A similar work-up and purification as described for **29** gave **32** (125 mg, 97%). $[\alpha]_D = +81.1°$ (*c* 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$); mixture of rotamers **32a** and **32b** (**a**/**b** 2.3:1), **32a**: δ = 7.77–7.26 (m, 8H, Ph), 5.93 (m, 2H, CH_2CH=CH_2, NH^{Ser}), 5.37, 5.31 (2 d, 2H, CH_2CH=CH_2), 5.22 (d, 1H, $J_{2,NH}$ = 10.0 Hz, NH^{GalN}), 4.94 (d, 1H, $J_{1,2}$ = 2.6 Hz, H-1), 4.83, 4.71 (2 d, 2H, J_{gem} = 11.9 Hz, OCH_2CCl_3), 4.82 (m, 1H, H-3), 4.80, 4.59 (2 d, 2H, J_{gem} = 11.9 Hz, OCH_2CCl_3), 4.73 (d, 1H, $J_{3,4}$ = 2.1 Hz, H-4), 4.70 (d, 2H, CH_2CH=CH_2), 4.65 (s, 1H, CH^{Ser}), 4.57 (td, 1H, $J_{1,2}$ = 2.6, $J_{2,NH}$ = 10.0 Hz, H-2), 4.47–4.35 (2 m, 2H, J_{gem} = 10.4, J = 7.0 Hz, CH_2 of Fmoc), 4.22 (t, 1H, J = 7.0 Hz, CH of Fmoc), 4.18–4.09 (m, 2H, H-6, 6′), 3.99 (br s, 2H, CH_2^{Ser}), 3.74 (s, 1H, H-5), 1.07, 1.00 (2s, 18H, 2 *t*Bu); **32b**: δ = 7.77–7.26 (m, 8H, Ph), 6.01 (d, 1H, NH^{Ser}), 5.93 (m, 1H, CH_2CH=CH_2), 5.37, 5.31 (2 d, 2H, CH_2CH=CH_2), 5.13 (d, 1H, $J_{2,NH}$ = 10.0 Hz, NH^{GalN}), 4.98 (d, 1H, $J_{1,2}$ = 2.6 Hz, H-1), 4.83, 4.71 (2 d, 2H, J_{gem} = 11.9 Hz, OCH_2CCl_3), 4.82 (m, 1H, H-3), 4.80, 4.59 (2 d, 2H, J_{gem} = 11.9 Hz, OCH_2CCl_3), 4.73 (d, 1H, $J_{3,4}$ = 2.1 Hz, H-4), 4.70 (d, 2H, CH_2CH=CH_2), 4.65 (s, 1H, CH^{Ser}), 4.57 (td, 1H, $J_{1,2}$ = 2.6, $J_{2,NH}$ = 10.0 Hz, H-2), 4.47–4.35 (2 m, 2H, CH_2 of Fmoc), 4.22 (t, 1H, CH of Fmoc), 4.18–4.09 (m, 2H, H-6, 6′), 3.99 (br s, 2H, CH_2^{Ser}), 3.74 (s, 1H, H-5), 1.03, 1.00 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.6, 155.7, 154.1, 153.7, 143.6, 143.5, 141.2, 131.0, 127.7, 127.0, 127.0, 124.99, 124.9, 120.0, 119.8, 99.1, 95.3, 94.2, 77.2, 76.8, 75.7, 74.9, 74.5, 69.7, 69.6, 67.7, 67.3, 66.6, 66.5, 54.3, 49.3, 48.8, 46.9, 27.4, 27.2, 23.2, 20.6, 0.0; MALDI MS: *m*/*z*: calcd for $C_{41}H_{50}Cl_6N_2O_{13}SiNa$: 1039.11; found: 1039.20 $[M+Na]^+$.

***N*-Benzyloxycarbonyl-*O*-(2-acetamido-3-*O*-acetyl-2-deoxy-4,6-*O*-di-*tert*-butylsilylene-α-D-galactopyranosyl)-L-serine benzyl ester (33)**: Molecular sieves 4 Å (120 mg) was added to a solution of compound **12** (90 mg, 182 μmol) and **19** (30 mg, 91.0 μmol) in CH_2Cl_2 (2.7 mL). The suspension was stirred for 1 h and cooled to 0 °C. To the mixture were added NIS (82 mg, 364 μmol) and TfOH (3.2 μL, 36.4 μmol) and stirring was continued for 3 h. The termination of reaction was confirmed by TLC (EtOAc/hexane 2:1). A similar work-up and purification with silica gel column chromatography as described for **26** gave **33** (42 mg, 65%). $[\alpha]_D = +103.3°$ (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.81 (d, 1H, NH^{Ser}), 7.65 (d, 1H, $J_{2,NH}$ = 8.7 Hz, NH^{GalN}), 7.38–7.30 (m, 10H, 2 Ph), 5.10 (s, 2H, PhCH_2), 5.08, 5.05 (2 d, 2H, J_{gem} = 12.6 Hz, PhCH_2), 4.84 (dd, 1H, $J_{2,3}$ = 11.4, $J_{3,4}$ = 2.6 Hz, H-3), 4.75 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.52 (d, 1H, $J_{3,4}$ = 2.6 Hz, H-4), 4.44 (m, 1H, CH^{Ser}), 4.41 (td, 1H, $J_{1,2}$ = 3.6, $J_{2,3}$ = 11.4, $J_{2,NH}$ = 8.7 Hz, H-2), 4.08, 3.92 (2 dd, 2H, J_{gem} = 11.7 Hz, H-6, 6′), 3.80 (td, 2H, J_{gem} = 11.2 Hz, CH_2^{Ser}), 3.76 (s, 1H, H-5), 2.01, 1.77 (2s, 6H, 2 Ac), 1.00, 0.96 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 170.2, 169.9, 169.4, 156.1, 136.7, 135.5, 128.4, 128.3, 128.1, 127.9, 127.9, 127.9, 98.4, 70.2, 69.6, 67.3, 66.5, 66.4, 66.3, 65.7, 54.3, 45.8, 27.3, 27.1, 26.9, 22.7, 22.5, 20.7, 20.2, 1.1; MALDI MS: *m*/*z*: calcd for $C_{38}H_{48}Cl_6N_2O_{13}SiNa$: 737.18; found: 737.30 $[M+Na]^+$.

***N*-Benzyloxycarbonyl-*O*-{2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-α-D-galactopyranosyl}-L-serine pentafluorophenyl ester (34)**: Molecular sieves 4 Å (80 mg) was added to a solution of compound **13** (54 mg, 59.2 μmol) and **22** (20 mg, 49.3 μmol) in CH_2Cl_2 (1.0 mL). The suspension was stirred for 1 h and cooled to 0 °C. To the mixture were added NIS (26 mg, 118 μmol) and TfOH (1.0 μL, 11.8 μmol) and the stirring was continued for 1 h. The termination of reaction was confirmed by TLC (EtOAc/hexane 2:3). A similar work-up and purification by silica gel column chromatography (EtOAc/hexane 1:30) as described for **26** gave **34** (52 mg, 88%). $[\alpha]_D = +61.3°$ (*c* 0.46, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): mixture of rotamers **34a** and **34b** (**a**/**b** 1.4:1); **34a**: δ = 7.36–7.26 (m, 5H, Ph), 5.88 (d, 1H, NH^{Ser}), 5.36 (d, 1H, $J_{3,4}$ = 3.4 Hz, H-4^{Gal}), 5.24 (t, 1H, $J_{1,2}$ = 7.5, $J_{2,3}$ = 10.2 Hz, H-2^{Gal}), 5.16 (br s, 2H, PhCH_2), 5.11 (d, 1H, H-1^{GalN}), 5.06 (d, 1H, $J_{2,NH}$ = 7.8 Hz, NH^{GalN}), 4.98 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3^{Gal}), 4.93 (m, 1H, CH^{Ser}), 4.78 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1^{Gal}), 4.76, 4.59 (2 d, 2H, J_{gem} = 12.2 Hz, OCH_2CCl_3), 4.63 (d, 1H, $J_{3,4}$ = 2.1 Hz, H-4^{GalN}), 4.42 (td, 1H, $J_{2,3}$ = 11.3, H-2^{GalN}), 4.22–4.07 (m, 6H, H-6^{GalN}, 6′^{GalN}, 6^{Gal}, 6′^{Gal}, CH_2^{Ser}), 3.90 (t, 1H, H-5^{Gal}), 3.75 (dd, 1H, H-3^{GalN}), 3.63 (s, 1H, H-5^{GalN}), 2.13, 2.04, 2.00, 1.97 (4s, 12H, 4 Ac), 1.06, 1.05 (2s, 18H, 2 *t*Bu); **34b**: δ = 7.36–7.26 (m, 5H, Ph), 5.84 (d, 1H, NH^{Ser}), 5.37 (d, 1H, $J_{3,4}$ = 3.4 Hz, H-4^{Gal}), 5.25 (t, 1H, $J_{1,2}$ = 7.8, $J_{2,3}$ = 10.2 Hz, H-2^{Gal}), 5.17 (br s, 2H, PhCH_2), 4.98 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1^{GalN}), 4.97 (dd, 1H, H-3^{Gal}), 4.94, 4.49 (2 d, 2H, J_{gem} = 11.9 Hz, OCH_2CCl_3), 4.92 (m, 1H, CH^{Ser}), 4.71 (br s, 1H, H-4^{GalN}), 4.66 (d, 1H, $J_{2,NH}$ = 9.5 Hz, NH^{GalN}), 4.64 (d, 1H, H-1^{Gal}), 4.50 (td, 1H, $J_{2,3}$ = 11.7 Hz, H-2^{GalN}), 4.22–4.07 (m, 6H, H-6^{GalN}, 6′^{GalN}, 6^{Gal}, 6′^{Gal}, CH_2^{Ser}), 3.90 (t, 1H, H-5^{Gal}), 3.61 (s, 1H, H-5^{GalN}), 3.55 (dd, 1H, H-3^{GalN}), 2.13, 2.05, 2.00, 1.97 (4s, 12H, 4 Ac), 1.05, 1.03 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 170.1, 170.1, 169.6, 169.2, 166.7, 155.5, 154.1, 153.9, 142.1, 139.1, 136.7, 135.6, 128.6, 128.5, 128.2, 103.0, 101.5, 99.9, 99.1, 95.2, 79.1, 77.2, 76.4, 74.7, 74.6, 72.2, 71.1, 70.9, 70.8, 70.6, 69.5, 69.0, 68.8, 68.5, 67.6, 66.7, 61.4, 61.2, 54.3, 49.8, 49.6, 31.5, 29.6, 27.4, 27.2, 23.3, 22.6, 20.6, 20.5, 20.5, 14.1, 0.0; MALDI MS: *m*/*z*: calcd for $C_{48}H_{58}Cl_3F_5N_2O_{20}SiNa$: 1233.22; found: 1233.24 $[M+Na]^+$.

***N*-(9-Fluorenylmethoxycarbonyl)-*O*-[(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-(6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2-deoxy-4,6-*O*-di-*tert*-butylsilylene-2-(2,2,2-trichloroethoxycarbamoyl)-α-D-galactopyranosyl]-L-serine benzyl ester (37)**: Molecular sieves 4 Å (320 mg) was added to a solution of compound **35** (270 mg, 183 μmol) and **36** (51 mg, 122 μmol) in CH_2Cl_2 (3 mL). The suspension was stirred for 1 h and cooled to 0 °C. To the mixture were added NIS (82 mg, 366 μmol) and TfOH (3.2 μL, 36.6 μmol) and stirring was continued for 8 h. The termination of reaction was confirmed by TLC (PhCH$_3$/acetone/MeOH 10:6:1). A similar work-up and purification with silica gel column chromatography (PhCH$_3$/acetone/MeOH 90:6:1) as described for **26** gave **37** (190 mg, 88%). $[\alpha]_D = +72.0°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, [D$_6$]DMSO) δ = 7.87 (d, 1H, NH^{Ser}), 7.66 (d, 1H, NH^{Neu}), 7.61 (m, 23H, Ph), 7.17 (d, 1H, NH^{GalN}), 5.44 (m, 1H, H-8^{Neu}), 5.35 (d, 1H, H-4^{Gal}), 5.30 (q, 1H, H-2^{Gal}), 5.18 (dd, 1H, H-7^{Neu}), 5.12 (d, 1H, H-1^{Gal}), 5.10 (s, 2H, PhCH_2), 4.83 (dd, 1H, H-3^{Gal}), 4.74 (s, 1H, H-4^{GalN}), 4.71 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1^{GalN}), 4.63 (m, 1H, H-4^{Neu}), 4.53 (d, 1H, J_{gem} = 12.2 Hz, OCH_2CCl_3), 4.41 (m, 3H, CH^{Ser}, CH_2 of Fmoc), 4.25 (t, 1H, J_{gem} = 12.7 Hz, H-9^{Neu}), 4.16 (t, 1H, H-6^{Gal}), 4.07 (td, 1H, H-2^{GalN}), 4.03 (dd, 1H, H-9^{Neu}), 4.02 (m, 5H, H-3^{GalN}, H-6^{GalN}, H-5^{Gal}, H-6′^{Gal}, CH of Fmoc), 3.74 (m, 5H, H-3^{GalN}, H-6^{GalN}, H-6^{Neu}, CH_2^{Ser}), 3.73 (s, 3H, COOMe), 2.96 (d, 1H, J_{gem} = 12.2 Hz, OCH_2CCl_3), 2.19 (dd, 1H, H-3$_{eq}^{Neu}$), 1.88 (6s, 18H, 6 Ac), 1.22 (m, 1H, H-3$_{ax}^{Neu}$), 1.01, 0.92 (2s, 18H, 2 *t*Bu); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 170.4, 170.2, 170.2, 170.1, 170.0, 169.5, 169.2, 167.8, 165.0, 164.7, 156.3, 154.1, 153.0, 143.9, 141.0, 140.5, 137.5, 137.3, 135.8, 134.0, 133.5, 129.8, 129.7, 129.4, 129.1, 129.1, 129.0, 129.0, 128.8, 128.6, 128.4, 128.3, 128.0, 127.8, 127.3, 126.7, 125.5, 125.2, 125.0, 120.3, 105.1, 102.0, 100.9, 98.9, 98.0, 97.0, 96.9, 96.7, 95.9, 94.1, 86.3, 77.4, 75.4, 73.0, 72.6, 71.8, 71.2, 70.6, 70.1, 69.4, 68.7, 67.7, 67.5, 66.9, 66.4, 66.2, 65.9, 63.5, 62.0, 61.7, 59.6, 54.5, 53.6, 53.3, 52.0, 49.6, 47.6, 46.8, 39.0, 37.8, 37.3, 36.0, 27.4, 23.0, 22.9, 22.8, 22.7, 21.4, 21.2, 20.8, 20.6, 20.5, 20.4; MALDI MS: *m*/*z*: calcd for $C_{84}H_{98}Cl_3N_3O_{31}SiNa$: 1800.49; found: 1800.32 $[M+Na]^+$.

***N*-(9-Fluorenylmethoxycarbonyl)-*O*-[(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-(6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-2-deoxy-2-(2,2,2-trichloroethoxycarbamoyl)-α-D-galactopyranosyl]-L-serine benzyl ester (38)**: A 1 M solution of *n*-tributylammonium hydrogenfluoride·1.25 H_2O (0.80 mL, 0.80 mmol) was added to a flask containing compound **37** (160 mg, 89.9 μmol), and the mixture was stirred at ambient temperature for 5 h. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH 10:1). The reaction mixture was extracted with EtOAc, and the organic layer was washed with 2 M HCl, H_2O, satd. aq. Na_2CO_3 and brine, dried over Na_2SO_4 and concentrated. The residue was purified with column chromatography on silica gel ($CHCl_3$/MeOH 70:1) to give **38** (126 mg, 86%). $[\alpha]_D = +65.5°$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (m, 23H, Ph), 6.31 (d, 1H, NH^{Ser}), 5.68 (m, 1H, H-8^{Neu}), 5.43 (t, 1H, H-2^{Gal}), 5.23 (d, 1H, H-4^{Gal}), 5.21 (dd, 1H, H-7^{Neu}), 5.14 (q, 2H, PhCH_2), 5.00 (d, 1H, NH^{Neu}), 4.95 (d, 1H, H-1^{Gal}), 4.88 (m, 2H, H-3^{Gal}, OCH_2CCl_3), 4.78 (d, 1H, $J_{1,2}$ = 2.9 Hz, H-1^{GalN}), 4.77 (m, 1H, $J_{3,4}$ =

4.4 Hz, H-4^{Neu}), 4.66 (d, 1H, NH^{GalN}), 4.59 (d, 1H, CH^{Ser}), 4.41 (m, 3H, H-9^{Neu}, CH_2 of Fmoc), 4.22 (m, 3H, H-2^{GalN}, H-6^{Gal}, CH of Fmoc), 4.11 (m, 4H, H-4^{Gal}, H-5^{Gal}, H-6′^{Gal}, CH_2^{Ser}), 4.04 (d, 1H, H-4^{GalN}), 3.88 (m, 3H, COOMe), 3.86 (m, 5H, H-6^{GalN}, H-5^{Neu}, H-9′^{Neu}, CH_2^{Ser}, OCH_2CCl_3), 3.74 (dd, 1H, H-3^{GalN}), 3.69 (m, 2H, H-5^{GalN}, H-6′^{GalN}), 3.65 (dd, 1H, H-6^{Neu}), 2.96 (s, 1H, OH-4^{GalN}), 2.46 (dd, 1H, $J_{3,4}$=4.4, J_{gem}=12.7 Hz, H-3$_{eq}^{Neu}$), 2.37 (s, 1H, OH), 1.88 (6s, 18H, 6 Ac), 1.62 (t, 1H, H-3$_{ax}^{Neu}$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.2, 170.8, 170.5, 170.2, 170.1, 170.0, 168.2, 166.0, 165.2, 156.0, 154.1, 143.7, 141.3, 135.1, 133.6, 133.4, 130.2, 130.1, 129.0, 128.8, 128.7, 128.6, 128.5, 127.8, 127.1, 125.1, 120.5, 101.0, 99.8, 96.8, 95.7, 93.0, 88.7, 78.8, 74.0, 72.0, 71.7, 71.2, 71.1, 70.6, 70.0, 69.2, 68.3, 68.0, 67.6, 67.2, 67.1, 66.8, 62.9, 62.7, 62.5, 54.7, 53.4, 50.0, 48.8, 47.1, 37.4, 37.1, 34.4, 33.1, 32.8, 31.9, 30.3, 30.1, 29.7, 29.4, 27.1, 23.1, 22.7, 21.6, 21.0, 20.7, 20.6, 20.4, 19.7, 14.2, 14.1; MALDI MS: *m*/*z*: calcd for $C_{76}H_{82}Cl_3N_3O_{31}$: 1660.39; found: 1660.25 $[M+Na]^+$.

***N*-(9-Fluorenylmethoxycarbonyl)-*O*-[{methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate-(2→3)-6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranosyl-(1→3)}-{methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-(2,2,2-trichloroethoxycarbamoyl)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate-(2→6)}-2-deoxy-2-(2,2,2-trichloroethoxycarbamoyl)-α-D-galactopyranosyl]-L-serine benzyl ester (40)**: Molecular sieves 3 Å (170 mg) was added to a solution of compound **39** (71 mg, 98.8 μmol) and **38** (108 mg, 65.9 μmol) in CH_3CN/CH_2Cl_2 (1.5/0.2 mL). The suspension was stirred for 1 h and cooled to −35 °C. To the mixture were added NIS (45 mg, 198 μmol) and TfOH (2.0 μL, 19.8 μmol) and stirring was continued for 31 h. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH/$PhCH_3$ 10:1:1). The reaction mixture was filtered through Celite. The combined filtrate and washings were extracted with $CHCl_3$, and the organic layer was washed with satd. aq. Na_2CO_3, satd. aq. $Na_2S_2O_3$ and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH/$PhCH_3$ 70:1:7) to give **40**α (108 mg, 73 %) and **40**β (32 mg, 21 %). **40**α: $[\alpha]_D$=+43.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (m, 23H, Ph), 6.11 (d, 1H, NH^{Ser}), 5.65 (m, 1H, H-8c), 5.42 (t, 1H, H-2b), 5.37 (m, 2H, H-7d, H-8d), 5.26 (d, 1H, H-4b), 5.20 (m, 1H, H-7c), 5.12 (q, 2H, PhCH_2), 5.00 (d, 1H, NHc), 4.97 (m, 3H, H-4d, NHd, OCH_2CCl_3), 4.96 (d, 1H, H-1b), 4.89 (d, 1H, OCH_2CCl_3), 4.84 (d, 1H, H-3b), 4.78 (m, 2H, H-1a, H-4c), 4.66 (m, 1H, NHa), 4.25 (t, 1H, CH^{Ser}), 4.45 (d, 1H, OCH_2CCl_3), 4.40 (d, 1H, H-9c), 4.30 (m, 5H, H-2a, H-6b, H-9d, CH_2 of Fmoc), 4.15 (m, 5H, H-5b, H-6′b, H-6d, H-9′d, CH of Fmoc), 4.04 (s, 1H, H-4a), 3.99 (m, 1H, H-6a), 3.94 (s, 1H, CH_2^{Ser}), 3.90 (m, 5H, H-3a, CH_2^{Ser}, COOMe), 3.82 (m, 3H, H-6′, H-5c, H-9′c), 3.73 (d, 1H, OCH_2CCl_3), 3.71 (s, 3H, COOMe), 3.65 (m, 2H, H-6c, H-5d), 3.58 (t, 1H, H-5a), 2.77 (s, 1H, OH-4a), 2.64 (dd, 1H, J_{gem}=12.5 Hz, H-3$_{eq}$d), 2.46 (dd, 1H, J_{gem}=12.5 Hz,H-3$_{eq}$c), 2.07 (10s, 30H, 10 Ac), 1.59 (t, 2H, J_{gem}=12.5 Hz, H-3$_{ax}$c, H-3$_{ax}$d); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1, 171.0, 170.8, 170.7, 170.7, 170.4, 170.3, 170.3, 170.2, 170.1, 169.8, 168.2, 168.1, 167.8, 165.9, 165.2, 155.9, 154.0, 143.7, 143.6, 141.2, 137.8, 135.0, 133.5, 133.4, 130.0, 129.0, 129.0, 128.8, 128.7, 128.6, 128.2, 128.1, 127.7, 127.1, 125.3, 125.2, 125.0, 120.0, 100.8, 99.1, 98.6, 96.7, 95.6, 95.4, 78.4, 74.4, 73.9, 72.1, 72.0, 71.1, 70.7, 69.2, 68.8, 68.7, 68.4, 68.2, 67.5, 67.3, 67.0, 66.8, 63.7, 62.7, 62.1, 54.4, 53.3, 52.8, 51.5, 50.0, 48.7, 47.0, 37.5, 37.3, 37.1, 32.7, 31.9, 30.0, 29.7, 29.3, 27.0, 23.1, 22.7, 21.5, 21.4, 20.9, 20.8, 20.7, 20.7, 20.5, 20.4, 19.7, 14.1; MALDI MS: *m*/*z*: calcd for $C_{97}H_{108}Cl_6N_4O_{44}Na$: 2265.44**;** found: 2265.48 $[M+Na]^+$; **40**β: $[\alpha]_D$=+44.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68 (m, 23H, Ph), 6.41 (d, 1H, NHa), 6.27 (d, 1H, NHd), 5.62 (m, 1H, H-8c), 5.50 (m, 2H, H-4d, H-7d), 5.44 (t, 1H, H-2b), 5.35 (m, 1H, H-8d), 5.29 (d, 1H, H-4b), 5.18 (m, 3H, H-7c, PhCH_2), 4.99 (d, 1H, H-1b), 4.96 (d, 1H, NHc), 4.86 (m, 2H, H-3b, OCH_2CCl_3), 4.83 (d, 1H, $J_{1,2}$=2.7 Hz, H-1a), 4.73 (m, 4H, NHa, H-4c, H-9d, CH^{Ser}), 4.36 (m, 3H, H-9d, CH_2 and CH of Fmoc), 4.32 (td, 1H, $J_{1,2}$=2.7 Hz, H-2a), 4.24 (s, 3H, H-4a, H-6b, H-6′b), 4.14 (m, 4H, H-6d, H-9′d, OCH_2CCl_3), 4.06 (t, 1H, H-5b), 4.02 (dd, 1H, CH_2^{Ser}), 3.95 (d, 1H, OCH_2CCl_3), 3.91 (dd, 1H, H-9′c), 3.87 (s, 3H, COOMe), 3.79 (m, 5H, H-3a, H-6a, H-6′a, H-5c, CH_2^{Ser}), 3.71 (s, 3H, COOMe), 3.65 (m, 2H, H-5a, H-6c), 2.93 (s, 1H, OH), 2.59 (dd, 1H, H-3$_{eq}$d), 2.46 (dd, 1H, H-3$_{eq}$c), 1.96 (10s, 30H, 10 Ac), 1.78 (t, 1H, H-3$_{ax}$d), 1.65 (t, 1H, H-3$_{ax}$c); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 170.9, 170.8, 170.7, 170.2, 170.1, 170.0, 169.9, 168.2, 166.8, 166.0, 165.3, 156.1, 154.5, 154.0, 143.7, 141.3, 141.2, 137.8, 133.5, 133.4, 130.1, 130.0, 129.0, 128.7, 128.7, 128.6, 128.5, 128.2, 128.2, 127.9, 127.8, 127.7, 127.1, 127.1, 125.4, 125.3, 125.3, 125.2, 125.2, 120.3, 119.9, 100.8, 98.7, 98.2, 96.7, 95.6, 95.5, 78.0, 77.2, 74.2, 74.0, 72.1, 71.6, 71.4, 71.2, 71.0, 70.9, 69.1, 68.8, 68.4, 67.8, 67.6, 67.5, 66.7, 62.5, 61.9, 54.2, 53.3, 52.7, 51.0, 50.0, 48.8, 46.9, 37.5, 37.3, 37.1, 31.9, 30.0, 29.7, 29.3, 27.1, 23.1, 22.7, 21.5, 20.9, 20.8, 20.8, 20.7, 20.6, 20.5, 14.1; MALDI MS: *m*/*z*: calcd for $C_{97}H_{108}Cl_6N_4O_{44}Na$: 2265.44; found: 2265.36 $[M+Na]^+$.

***N*-(9-Fluorenylmethoxycarbonyl)-*O*-[{(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-(6-*O*-acetyl-2,4-di-*O*-benzoyl-β-D-galactopyranosyl}-(1→3)-{(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)}-4-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbamoyl)-α-D-galactopyranosyl]-L-serine benzyl ester (41)**: Zinc powder (280 mg) was added to a solution of compound **40**α (28 mg, 12.5 μmol) in AcOH (0.2 mL). The suspension was stirred for 3 h at 40 °C. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH/$PhCH_3$ 10:1:1). The reaction mixture was filtered through Celite. The combined filtrate and washings were extracted with $CHCl_3$, and the organic layer was washed with satd. aq. Na_2CO_3 and brine, dried over Na_2SO_4 and concentrated. To the residue in pyridine (0.4 mL) was added acetic anhydride (47 μL) at 0 °C under argon atmosphere, and the mixture was stirred for 11 h at ambient temperature. The reaction mixture was coevaporated with toluene and extracted with $CHCl_3$. The organic phase was washed with 2 M HCl, H_2O, satd. aq. Na_2CO_3 and brine, dried (Na_2SO_4) and concentrated. The residue was purified by chromatography on silica gel ($CHCl_3$/MeOH/$PhCH_3$ 35:1:3.5) to give **41** (17 mg, 68 %). $[\alpha]_D$=+44.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (m, 23H, Ph), 6.11 (d, 1H, NH^{Ser}), 5.69 (m, 1H, H-8c), 5.45 (d, 1H, NHa), 5.40 (s, 1H, H-4a), 5.34 (t, 1H, $J_{1,2}$=7.8 Hz, H-2b), 5.32 (m, 2H, H-7d, H-8d), 5.22 (d, 1H, $J_{3,4}$=3.2 Hz, H-4b), 5.21, 5.02 (2 d, 2H, PhCH_2), 5.15 (dd, 1H, H-7c), 5.11 (d, 1H, NHc), 4.96 (d, 1H, NHc), 4.91 (d, 1H, $J_{1,2}$=7.8 Hz, H-1b), 4.87 (d, 1H, $J_{1,2}$=2.9 Hz, H-1a), 4.84 (m, 1H, H-4d), 4.77 (dd, 1H, H-4c), 4.75 (dd, 1H, $J_{3,4}$=3.2 Hz, H-3b), 4.57 (m, 1H, CH^{Ser}, 4.41 (m, 5H, $J_{1,2}$=2.9 Hz, H-2a, H-6b, H-6′b, H-9d, CH of Fmoc), 4.26 (m, 2H, H-5b, H-9d), 4.07 (m, 6H, H-3a, H-5d, H-6d, H-9′d, CH_2 of Fmoc), 3.92 (m, 5H, H-5a, CH_2^{Ser}, CO(O)CH_3), 3.79 (m, 7H, H-6a, H-5c, H-9′c, CH_2^{Ser}, CO(O)CH_3), 3.61 (dd, 1H, H-6c), 3.37 (dd, 1H, H-6′a), 2.55 (dd, 1H, H-3$_{eq}$d), 2.47 (dd, 1H, H-3$_{eq}$c), 1.99 (13s, 39H, Ac), 1.97 (t, 1H, H-3$_{ax}$d), 1.63 (t, 1H, H-3$_{ax}$c); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.1, 170.9, 170.8, 170.6, 170.3, 170.2, 170.1, 170.0, 169.9, 169.6, 168.2, 167.8, 165.7, 164.8, 156.1, 143.8, 143.7, 141.3, 134.9, 133.4, 133.3, 130.3, 130.2, 130.1, 129.4, 128.9, 128.8, 128.5, 128.4, 127.8, 127.1, 125.1, 120.0, 117.1, 116.9, 116.6, 100.8, 99.9, 98.6, 96.8, 75.0, 72.6, 71.9, 71.3, 71.2, 71.0, 69.3, 69.1, 68.9, 68.5, 68.2, 67.4, 67.2, 67.1, 64.2, 63.0, 62.2, 61.8, 54.6, 53.3, 52.8, 49.3, 48.9, 48.7, 47.1, 37.5, 37.2, 37.1, 32.8, 31.9, 30.4, 30.0, 29.7, 29.4, 27.5, 27.1, 23.2, 23.1, 22.7, 22.2, 21.5, 21.1, 21.0, 20.8, 20.7, 20.6, 20.3, 14.1; MALDI MS: *m*/*z*: calcd for $C_{97}H_{112}N_4O_{43}Na$: 2043.66; found: 2043.67 $[M+Na]^+$.

Acknowledgements

This work was financially supported in part by MEXT of Japan (Grant-in-Aid for Scientific Research to H.A., no. 16780083, H.I., no. 16580086, and M.K., no. 1701007), and Mitsubishi Chemical Corporation Fund (H.A.). We thank Ms. Kiyoko Ito for technical assistance.

[1] A. Varki, *Glycobiology* **1993**, *3*, 97–130.

[2] Recent reviews: a) H. Herzner, T. Reipen, M. Schultz, H. Kuntz, *Chem. Rev.* **2000**, *100*, 4495–4537; b) K. C. Nicolaou, H. J. Mitchell, *Angew. Chem.* **2001**, *113*, 1624–1672; *Angew. Chem. Int. Ed.* **2001**, *40*, 1576–1624; c) A. V. Demchenko, *Synlett* **2003**, 1225–1240; recent papers on α-galactosyl or galacatosamyl glycan synthesis: d) H. Tanaka, H. Sakamoto, A. Sano, S. Nakamura, M. Nakajima, S. Hashimoto, *Chem. Commun.* **1999**, 1259–1260; e) D. K. Baeschlin,

A. R. Chaperon, L. G. Green, M. G. Hahn, S. J. Ince, S. V. Ley, *Chem. Eur. J.* **2000**, *6*, 172–186; f) H. Dohi, Y. Nishida, H. Tanaka, K. Kobayashi, *Synlett* **2001**, 1446–1448; g) F. Burkhart, Z. Zhang, S. Wacowich-Sgarbi, C. H. Wong, *Angew. Chem.* **2001**, *113*, 1314–1317; *Angew. Chem. Int. Ed.* **2001**, *40*, 1274–1277; h) Y. P. Cheng, H. T. Chen, C. C. Lin, *Tetrahedron Lett.* **2002**, *43*, 7721–7723; i) C. C. Wang, J. C. Lee, S. Y. Luo, H. F. Fan, C. L. Pai, W. C. Yang, L. D. Lu, S. C. Hung, *Angew. Chem.* **2002**, *114*, 2466–2468; *Angew. Chem. Int. Ed.* **2002**, *41*, 2360–2362; j) Y. Nishida, Y. Shingu, H. Dohi, K. Kobayashi, *Org. Lett.* **2003**, *5*, 2377–2380; k) L. Chen, F. Kong, *Tetrahedron Lett.* **2003**, *44*, 3691–3695; l) Y. Wang, X. Huang, L. H. Zhang, X. S. Ye, *Org. Lett.* **2004**, *6*, 4415–4417; m) N. Shao, Z. Guo, *Org. Lett.* **2005**, *7*, 3589–3592; n) T. Buskas, S. Ingale, G. J. Boons, *Angew. Chem.* **2005**, *117*, 6139–6142; *Angew. Chem. Int. Ed.* **2005**, *44*, 5985–5988; o) H. Hojo, Y. Matsumoto, Y. Nakahara, E. Ito, Y. Suzuki, M. Suzuki, A. Suzuki, Y. Nakahara, *J. Am. Chem. Soc.* **2005**, *127*, 13720–13725.

[3] G. A. Winterfeld, R. R. Schmidt, *Angew. Chem.* **2001**, *113*, 2718–2721; *Angew. Chem. Int. Ed.* **2001**, *40*, 2654–2657.

[4] J. H. Kim, H. Yang, J. Park, G. J. Boons, *J. Am. Chem. Soc.* **2005**, *127*, 12090–12097.

[5] a) A. Imamura, H. Ando, S. Korogi, G. Tanabe, O. Muraoka, H. Ishida, M. Kiso, *Tetrahedron Lett.* **2003**, *44*, 6725–6728; b) A. Imamura, H. Ando, H. Ishida, M. Kiso, *Org. Lett.* **2005**, *7*, 4415–4418.

[6] a) E. J. Corey, P. B. Hopkins, *Tetrahedron Lett.* **1982**, *23*, 4871–4874; b) K. Furusawa, K. Ueno, T. Katsura, *Chem. Lett.* **1990**, 97–100.

[7] M. Numata, M. Sugimoto, K. Koike, T. Ogawa, *Carbohydr. Res.* **1987**, *163*, 209–225.

[8] For the synthesis, see Supporting Information.

[9] a) G. H. Veeneman, S. H. van Leeuwen, J. H. van Boom, *Tetrahedron Lett.* **1990**, *31*, 1331–1334; b) P. Konradsson, U. E. Udodong, B. Fraser-Reid, *Tetrahedron Lett.* **1990**, *31*, 4313–4316.

[10] S. Hashimoto, M. Hayashi, R. Noyori, *Tetrahedron Lett.* **1985**, *26*, 1379–1382.

[11] F. Dasgupta, P. J. Garegg, *Carbohydr. Res.* **1990**, *202*, 225–238.

[12] T. Mukaiyama, Y. Murai, S. Shoda, *Chem. Lett.* **1981**, 431–432.

[13] K. Suzuki, H. Maeta, T. Suzuki, T. Matsumoto, *Tetrahedron Lett.* **1989**, *30*, 6879–6882.

[14] R. R. Schmidt, *Angew. Chem.* **1986**, *98*, 213; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 212–235.

[15] C. A. A. van Boeckel, T. Beetz, S. F. van Aelst, *Tetrahedron*, **1984**, *40*, 4097–4107.

[16] M. Yamaguchi, A. Horiguchi, A. Fukuda, T. Minami, *J. Chem. Soc. Perkin Trans. 1* **1990**, 1079–1082.

[17] Recent papers on α-Gal-Cer synthesis: a) G. T. Fan, Y. S. Pan, K. C. Lu, Y. P. Cheng, W. C. Lin, S. Lin, C. H. Lin, C. H. Wong, J. M. Fang, C. C. Lin, *Tetrahedron* **2005**, *61*, 1855–1862; b) W. Du, J. Gervay-Hague, *Org. Lett.* **2005**, *7*, 2063–2065.

[18] K. Furusawa, *Chem. Lett.* **1989**, 509–510.

[19] H. Ando, Y. Koike, H. Ishida, M. Kiso, *Tetrahedron Lett.* **2003**, *44*, 6883–6886.

[20] First report on the synthesis of glycophorin A: Y. Nakahara, H. Iijima, T. Ogawa, *Tetrahedron Lett.* **1994**, *35*, 3321.

Received: June 14, 2006
Published online: August 22, 2006

