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# Di-*tert*-butylsilylene-directed α-selective synthesis of *p*-nitrophenyl T-antigen analogues

**Tetsuro Sato · Akihiro Imamura · Hiromune Ando · Hideharu Ishida · Makoto Kiso**

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**Abstract** Seven analogues of *p*-nitrophenyl T-antigen [Galβ(1→3)GalNAcα(1→*O*)PNP] have been synthesized as potential substrates for elucidation of the substrate specificity of *endo*-α-*N*-acetylgalactosaminidase. These compounds, which are commercially unavailable, include: GlcNAcβ(1→3){GlcNAcβ(1→6)}GalNAcα(1→*O*)PNP [core 4 type], GalNAcα(1→3)GalNAcα(1→*O*)PNP [core 5 type], GlcNAcβ(1→6)GalNAcα(1→*O*)PNP [core 6 type], GalNAcα(1→6)GalNAcα(1→*O*)PNP [core 7 type], Galα(1→3)GalNAcα(1→*O*)PNP [core 8 type], Glcβ(1→3)GalNAcα(1→*O*)PNP and GalNAcβ(1→3)GalNAcα(1→*O*)PNP. The assembly of these synthetic probes was accomplished efficiently, based on di-*tert*-butylsilylene (DTBS)-directed α-galactosylation as a key reaction.

**Keywords** Glycosylation · *p*-nitrophenyl glycoside · Di-*tert*-butylsilylene group · Stereoselectivity · *Endo*-α-*N*-acetylgalactosaminidase

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## Introduction

*Endo*-α-*N*-acetylgalactosaminidase, which hydrolyzes the *O*-glycosidic α-linkage between T-antigen and a serine or threonine residue in mucin-type glycoproteins, is a glycosidase of widespread occurrence in the bacterial kingdom [1, 2]. Recently, a similar *endo*-α-*N*-GalNAcase was isolated from an enterobacterial genus *Bifidobacterium* by Yamamoto *et al.* [3]. They suggested that the enzyme may play an important role in the degradation and utilization of mucins having core 1 *O*-glycans through the pathway that the released disaccharide may be transported into the cytosol of bacterial cells through an ABC-type transporter and metabolized by phosphorylase and kinase in the cytosol. It is well known that bifidobacteria have many beneficial effects on human health [4]. There is now an interest in modulating the composition of intestinal flora, such as via prebiotics and probiotics, which function as bifidogenic growth stimulators. We can contribute to the maintenance of better health or to recovery from illness by coordinating the constitution of intestinal flora through clarification of a substrate that multiplies only useful bacteria such as *Bacillus bifidus*. To elucidate the substrate specificity of the enzyme, or to screen new species from other living organisms, sensitive synthetic fluorogenic T-antigen probes are intensively sought.

*p*-Nitrophenyl (PNP) glycosides are popular fluorogenic probes for hydrolases, because of the potent fluorometric property of the phenolic moiety liberated by enzymatic hydrolysis [5]. However, PNP glycoside synthesis is generally difficult. In particular, the synthesis of α-glycosaminides such as the title compound is extremely arduous in order to circumvent the participating effects of the *N*-acetyl group. Recently, we have developed the efficient α-galactosylation method which utilizes a di-*tert*-butylsilylene

(DTBS) group mounted on the C-4 and -6 hydroxyl groups of the glycosyl donor as an α-directing element [7, 8, 9]. We demonstrate the successful extension of DTBS-directed galactosylation to the facile syntheses of *p*-nitrophenyl T-antigen [Galβ(1→3)GalNAcα(1→*O*)PNP] analogues as substrates for *endo*-α-*N*-acetylgalactosaminidase.

## Results and discussion

As illustrated in Fig. 1, mucin-type core glycans and their analogues bearing structural similarities to T-antigen were designed as substrates for *endo*-α-GalNAcase, except for commercially available cores 1 [T-antigenα(1→*O*)PNP], 2 [Galβ(1→3){GlcNAcβ(1→6)}GalNAcα(1→*O*)PNP] and 3 [GlcNAcβ(1→3) GalNAcα(1→*O*)PNP]. To date, many efforts for the formation of T-antigenα(1-*O*)Ser/Thr using chemical [10, 11] and chemoenzymatic [12] method have been reported. However, the construction of an α-GalNAc linkage during the chemical syntheses of the presented target compounds would emerge as a key step. Hitherto, 2-azido derivatives have generally been used as glycosyl donors for the chemical synthesis of α-galactosaminide [13]. After glycosylation, the azide functionality must undergo reduction procedures, such as hydrogenolysis, and is converted into the corresponding acetamide group. Therefore, the introduction of an additional reductive-labile nitro group onto the phenyl group must follow reduction of the azide group. In contrast to the above strategy, the compatibility of DTBS-directed α-galactosylation with C2-participating groups allows the use of orthogonal amino protection by a nitro group, such as phthaloyl [14]. Therefore, we envisaged that DTBS-directed α-galactosylation would likely be the most effective method of achieving efficient synthesis of the target compounds.

Consequently, the following systematic synthetic scheme was forged in this study: (1) Starting with DTBS-protected galactosamine **8** as a key material, α-selective glycosidation with *p*-nitrophenol **9**; (2) Conversions into 3-OH acceptor **10** and 6-OH acceptor **11** as key glycosyl acceptors; and (3) Final glycosylations with proper carbohydrate coupling partners and deprotections to afford the target compounds (Scheme 1).

The feasibility of the DTBS-directed α-galactosylation procedure was first established by the assembly of aryl glycoside **14**, which proceeded with extremely high efficiency (Scheme 2). Initially, thioglycoside **12** [7] was used as a glycosyl donor for glycosidation with *p*-nitrophenol **9**.

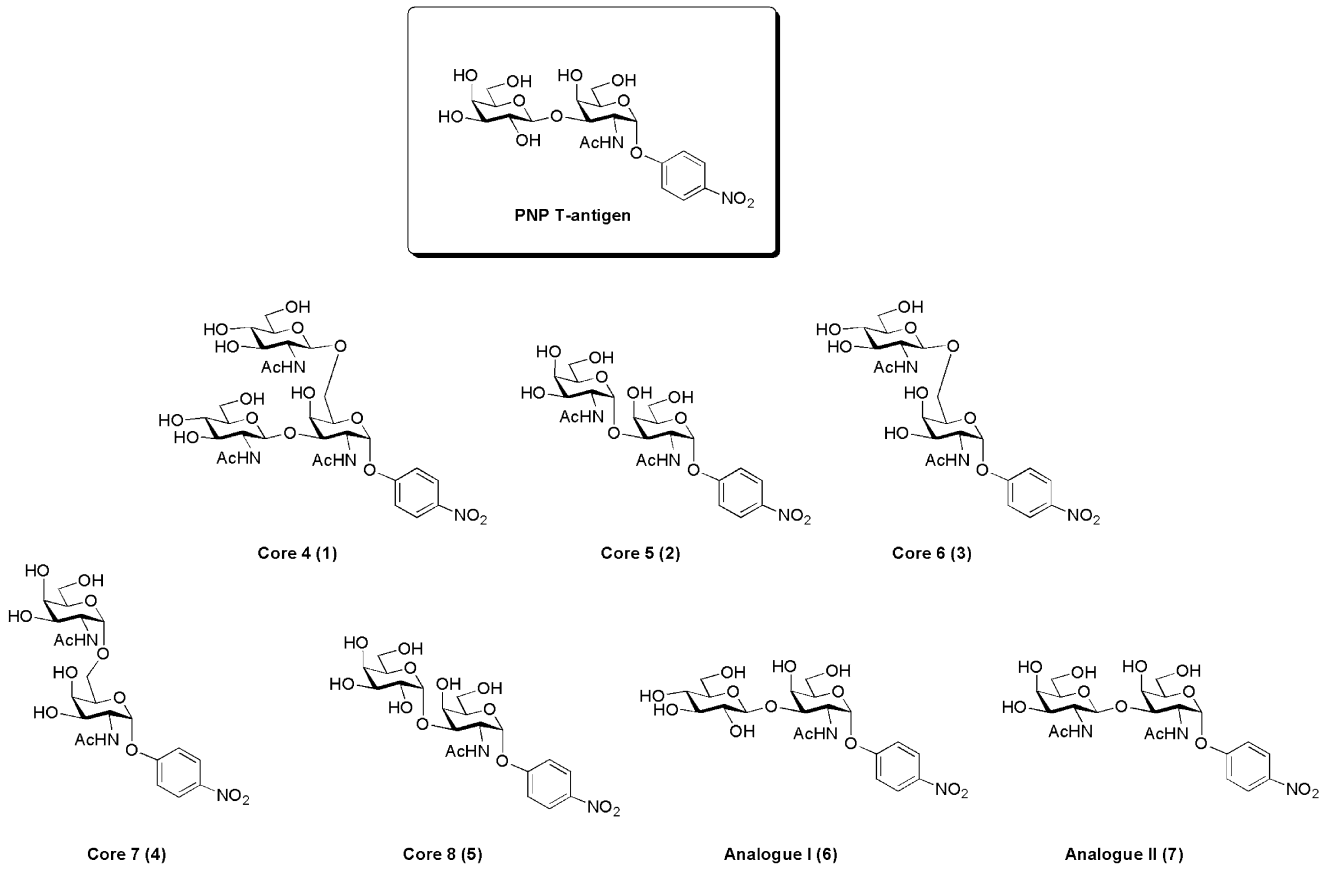
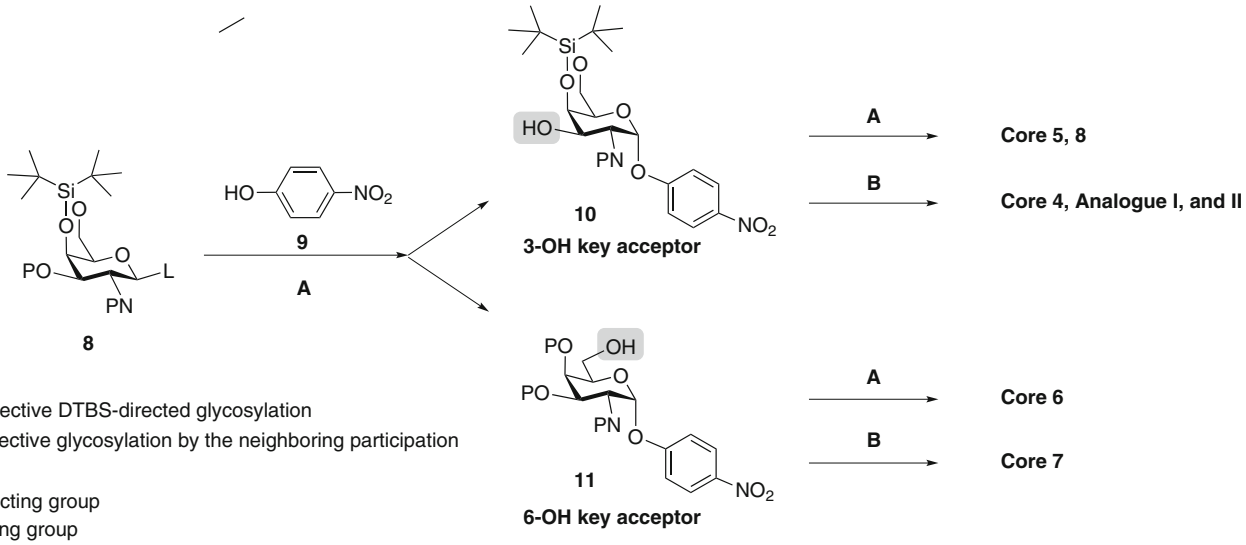



**Fig. 1** Structure of target compounds, PNP T-antigen analogues

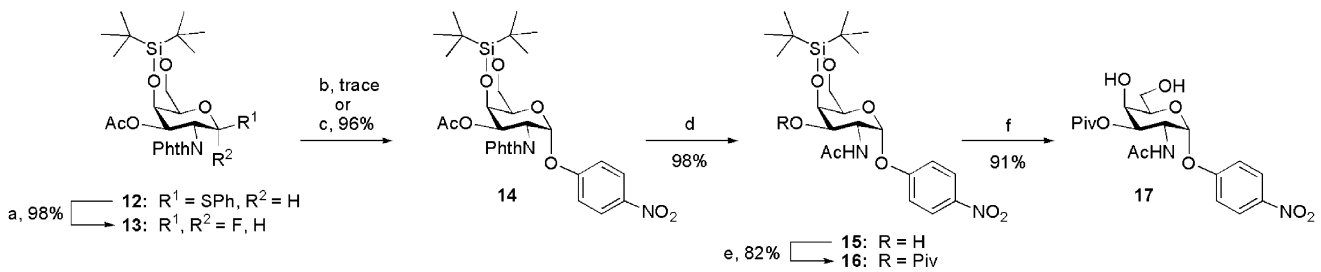



**Scheme 1** Systematic synthetic scheme for preparation of target compounds

However, the desired PNP glycoside **14** was not obtained, even though **12** had been a successful donor for α-galactosylation in our previous study [7]. Next, fluoride donor [15] **13**, which was transformed from **12**, was subjected to aryl glycosidation with **9** in the presence of $BF_3{\cdot}OEt_2$ and $NEt_3$ [16, 17] in $CH_2Cl_2$ at 0°C to afford **14** as a sole product in excellent yield (96%). This result clearly demonstrates the applicability of DTBS-directed α-galactosylation to the synthesis of aryl glycosides. Furthermore, to our knowledge, the yield and stereoselectivity are the highest reported, even for aryl glycosylation of GalNAc residues.

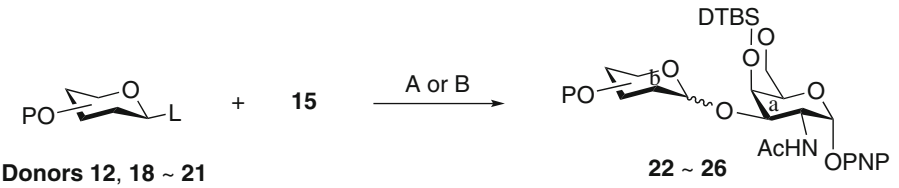
The concomitant removal of the *N*-phthaloyl group and the acetyl group at the C-3 position of **14** in the presence of hydrazine monohydrate and subsequent selective *N*-acetylation gave key acceptor **15** in this study. After pivaloylation of the hydroxyl group, cleavage of the DTBS group was executed using tri-*n*-butylammonium hydrogenfluoride (TBAHF) [18] to afford another key acceptor, **17**, in good yield.

As summarized in Table 1, the key acceptor bearing a 3-OH group **15** was glycosylated with various glycosyl donors under conditions of either: (A) *N*-iodosuccinimide (NIS)−trifluoromethanesulfonic acid (TfOH) [19] as a promoter system in $CH_2Cl_2$ at 0°C, or (B) trimethylsilyl trifluoromethanesulfonate (TMSOTf) [20] in $CH_2Cl_2$ at 0°C. For the synthesis of target compounds **2** and **5**, which involve α-GalNAc and α-Gal structures at the non-reducing terminal, respectively, DTBS-directed glycosylation was again employed. Thus, the aforementioned galactosaminyl donor **12** was subjected to glycosidation with **15** under conditions (A) to afford α-glycoside **22** exclusively in 98% yield (entry 1). Similarly, access to α-galactoside **23** was accomplished using glycosyl imidate donor **18** [6] under conditions (B) (entry 2). Interestingly, when phenyl 2,3-di-*O*-benzoyl-4,6-*O*-di-*tert*-butylsilylene-1-thio-β-D-galactopyranoside was used as an alternative glycosyl donor in this reaction, any adverse side reactions, which probably involved the formation of an orthoester, resulted in a complex mixture of products, including 3-*O*-benzoylated **15** derived from the orthoester (data not shown). Although the reason is not clear at present, DTBS-tethered thiogalactosyl donors may have a tendency




**Scheme 2** Preparation of key acceptors **15** and **17**. Reagents and conditions: *a* DAST, NBS, $CH_2Cl_2$, −15°C; *b* **12**, **9**, NIS, TfOH, MS3Å, $CH_2Cl_2$, 0°C; *c* **13**, **9**, $BF_3{\cdot}OEt_2$, $NEt_3$, MS3Å, $CH_2Cl_2$, 0°C; *d* (1) $NH_2NH_2{\cdot}H_2O$, EtOH, reflux, (2) $Ac_2O$, MeOH; *e* PivCl, Py; *f* TBAHF, THF, $H_2O$

**Table 1** Glycosylations of key acceptor 15 with various glycosyl donors 12, 18 ~ 21

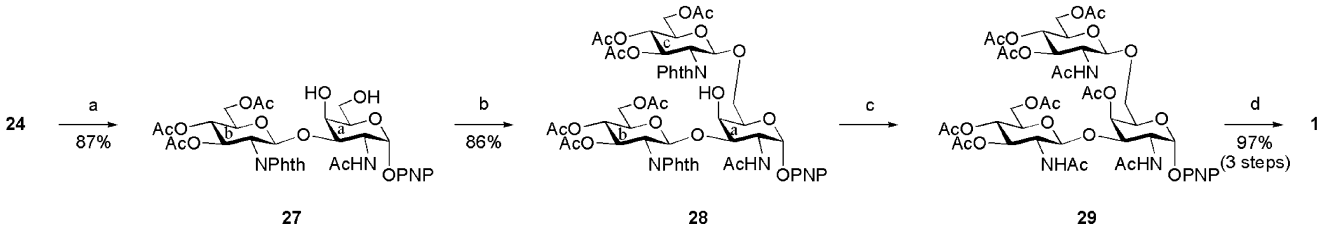



**Donors 12, 18 ~ 21** **22 ~ 26**

| Entry | Donor | Condition[a] | Product | % Yield[b] |
|---|---|---|---|---|
| 1 | **12** | A | **22** | 98 |
| 2 | **18** | B | **23** | 64 |
| 3 | **19** | A | **24** | 96 |
| 4[c] | **20** | B | **25** | 64 |
| 5 | **21** | A | **26** | 81 |

[a] (A) NIS, TfOH, MS4Å, $CH_2CI_2$, 0°C; (B) TMSOTf, AW-300, $CH_2CI_2$, 0°C
[b] Isolated yield
[c] The reaction was conducted at room temperature

to form the corresponding orthoester intermediates, compared with DTBS-Gal donors bearing other leaving groups, such as trichloroacetimidate and fluoride. The latter entries in Table 1 showed β-selective glycosylation of **15** with suitably protected glycosyl donors with the well-known neighboring participating effect. For example, glucosaminyl thioglycoside **19** [21] and galactosaminyl thioglycoside **21** [22], both possessing phthaloyl groups, were coupled with **15** to yield the corresponding disaccharides **24** and **26** with complete stereoselectivity, respectively (entries 3 and 5). On the other hand, the coupling reaction of **15** with phenylthioglycoside of per-benzoylated glucose provided **25** in low yield with inseparable byproducts, in preliminary experiments. Therefore imidate donor **20** [23] was chosen as a glycosyl donor for the assembly of β-glucoside. When the coupling reaction of **20** and **15** was conducted at room temperature, the desired disaccharide **25** was obtained in rewarding 64% yield.



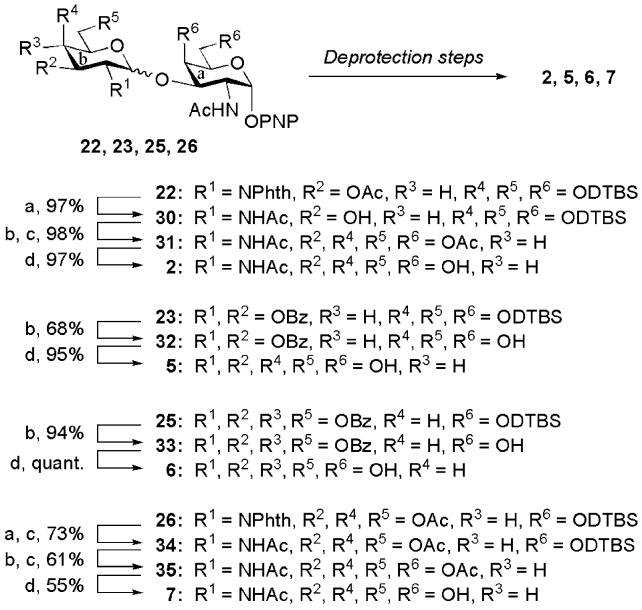

**Scheme 3** Synthesis of core 4 analogue (**1**). Reagents and conditions: *a* TBAHF, THF, $H_2O$; *b* **19**, NIS, TfOH, MS4Å, $CH_2Cl_2$, r.t.; *c* (1) $NH_2NH_2{\cdot}H_2O$, EtOH, reflux, (2) $Ac_2O$, Py; *d* NaOMe, MeOH

The disaccharide **24** was employed to obtain the branched trisaccharide *1*. To incorporate GalNAc residue into the C6-hydroxyl of **24**, selective cleavage of the DTBS group was achieved by treatment of TBAHF, yielding the diol acceptor **27** in good yield. Following the same procedure as for the synthesis of *24*, diol *27* was glycosylated with glucosaminyl donor *19* to provide trisaccharide **28** in 86% yield with complete regio- and stereoselectivity. Then, the phthaloyl and acetyl groups were simultaneously removed using hydrazine monohydrate under reflux conditions, followed by the concomitant introduction of the *N*-acetyl and *O*-acetyl groups by the action of acetic anhydride in pyridine to afford per-protected **29**. Subsequently, global deprotection was efficiently accomplished under conventional Zemplén conditions to provide **1** in almost quantitative yield over the three steps (Scheme 3).

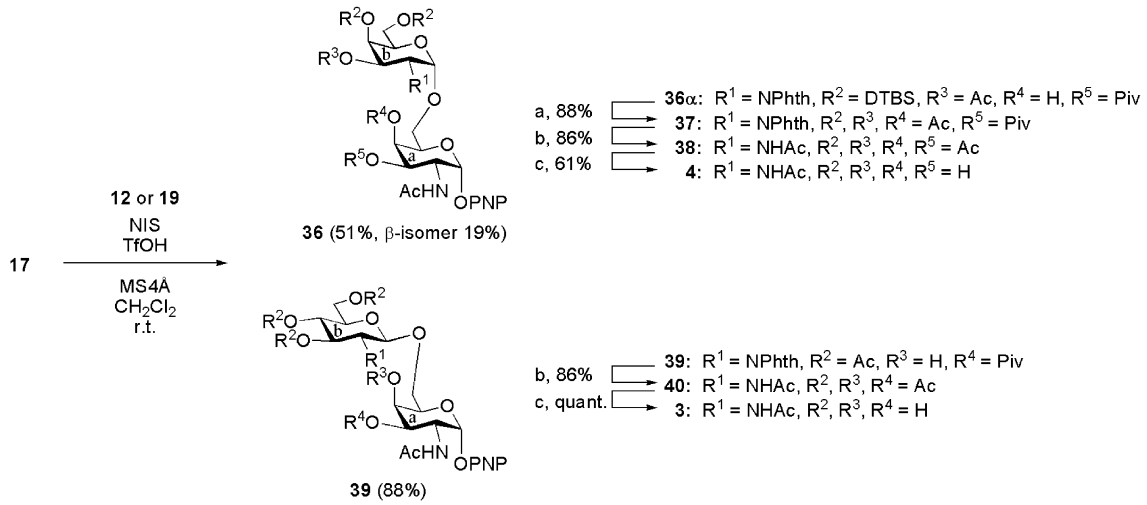
As illustrated in Scheme 4, the conversions of **22**, **23**, **25**, and **26** into targets **2**, **5**, **6**, and **7** were carried out by using similar procedures to those used in the synthesis of **1**. For target **2**, cleavage of the phthaloyl and acetyl groups was accomplished using hydrazine monohydrate, followed by selective *N*-acetylation of the liberated amine with $Ac_2O$ in MeOH to give **30** in excellent yield. After removal of DTBS groups, acetylation of the resulting hydroxyls was executed by the action of $Ac_2O$ in pyridine to afford **31** in almost quantitative yield. In view of the synthetic technique, *O*-acetylation was critical for the complete purification of precursor *31* to obtain high purity of the deprotected structure. Finally, acyl-protected derivative **31** was deprotected to provide target **2** in 97% yield. Both **23** and **25**, which possess similar protecting groups, gave rise to target molecules **5** and **6**, respectively, through the same reaction sequences: removal of the DTBS group and subsequent debenzoylation led to effective conversion of **23** and **25** into **5** and **6** in good yields. Next, the use of hydrazine monohydrate in **26** exposed an amine and three hydroxyls. After selective *N*-acetylation in neutral MeOH, *O*-acetylation under basic conditions allowed us to easily separate **34** from the reaction mixture. Deprotection of the DTBS group and subsequent acetylation gave per-protected compound **35**. The final deprotection step yielded target **7**.

Scheme 5 shows the synthesis of C6-branched compounds **3** and **4**. First, key acceptor **17** bearing diols at the C4 and C6 positions was subjected to glycosylation with **12** in the presence of NIS−TfOH in $CH_2Cl_2$ at room temperature, affording the corresponding disaccharide **36** in 70% yield. Unexpectedly, the desired α-glycoside **36α** was obtained in only 51% yield, despite the presence of DTBS-tethering, and was accompanied by the corresponding β-isomer **36β** in 19% yield. Stereoselectivity was not improved appreciably, when the reaction was conducted at 0°C. Next, the conversion of **36α** into target **4** was efficiently executed according to the above-mentioned procedures. Deprotection of the DTBS group in **36α** and subsequent acetylation gave compound **37** from which phthaloyl and acyl groups, including the pivaloyl group, were simultaneously cleaved before per-acetylation to provide **38** in good yield. The final deprotection of all *O*-acetyl groups gave target **4**.

On the other hand, in the hope of capitalizing on neighboring group participating effects to produce a β-glycosyl linkage, compound **19** was employed as the glycosyl donor in a glycosidation step with **17**. As




**Scheme 4** Conversion of **22**, **23**, **25**, and **26** into target **2**, **5**, **6**, and **7**, respectively. Reagents and conditions: *a* (1) $NH_2NH_2{\cdot}H_2O$, EtOH, reflux, (2) $Ac_2O$, MeOH; *b* TBAHF, THF, $H_2O$; *c* $Ac_2O$, Py; *d* NaOMe, MeOH




**Scheme 5** Glycosylation of **17** with **12** and **19** and subsequent deprotection to afford **4** and **3**, respectively. Reagents and conditions: *a* (1) TBAHF, THF, $H_2O$, (2) $Ac_2O$, Py; *b* (1) $NH_2NH_2{\cdot}H_2O$, EtOH, reflux, (2) $Ac_2O$, Py; *c* NaOMe, MeOH

expected, the desired β-glycoside **39** was obtained in good yield. Finally, through deprotection of the phthaloyl and acyl groups, subsequent acetylation and global deprotection, **39** was converted into target **3** in good yield (86% over the three steps).

In conclusion, seven types of *p*-nitrophenyl T-antigen analogues were efficiently synthesized using a combination of DTBS-directed α-galactosylation for the assembly of α-galactoside and neighboring acyl group participation for β-glycoside. These results demonstrate that DTBS-directed α-galactosylation can be applied for the synthesis of oligosaccharides, including α-Gal and/or α-GalNAc structures. Synthesized PNP T-antigen probes will undergo evaluation for *endo*-α-*N*-acetylgalactosaminidase.

## Experimental

### General procedures

Optical rotations were determined with a Horiba SEPA-300 high-sensitive polarimeter. $^1$H and $^{13}$C NMR spectra were taken by Varian INOVA 400 (400 MHz) and 500 (500 MHz). Chemical shifts are expressed in ppm ($\delta$) relative to the signal of $Me_4Si$, adjusted to $\delta$ 0.00 ppm. 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 a 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). Compounds detection were either by exposure to UV light (2536Å) or by spraying with a solution of 10% $H_2SO_4$ in ethanol. 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. A 1M solution of tri-*n*-butylammonium hydrogenfluoride·1.25 $H_2O$ (TBAHF) was prepared according to the literature [18]

*3-O-Acetyl-1,2-dideoxy-4,6-O-di-tert-butylsilylene-2-phthalimido-D-galactopyranosyl Fluoride* **(13)** To a solution of compound **12** (4.9 g, 8.4 mmol) in $CH_2Cl_2$ (84 ml) were added (diethylamino)sulfur trifluoride (1.7 ml, 12.7 mmol) and *N*-bromosuccinimide (2.0 g, 11.0 mmol) at −15°C under argon atmosphere. The mixture was stirred for 46 h, as the proceeding of the reaction was monitored by TLC ($CHCl_3$/MeOH=200/1 twice). The reaction mixture was diluted with $CHCl_3$ and ice-cooled sat $Na_2CO_3$ aq. was added. The mixture was vigorously stirred for 5 min. The organic layer was washed with $H_2O$ and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel ($PhCH_3$/EtOAc=100/1) to give **13** (4.1 g, 98%: α:β 1:1): **13α** $[\alpha]_D$=+155.5° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 7.88–7.75 (m, 4 H, Ph) 6.27 (dd, 1 H, $J_{2,3}$=11.9 Hz, $J_{3,4}$=2.6 Hz, H-3) 5.79 and 5.68 (2 d, 1 H, $J_{1,2}$=2.6 Hz, $J_{1,F}$=53.9 Hz, H-1) 5.08 and 5.02 (2 dd, 1 H, $J_{1,2}$=2.6 Hz, $J_{2,3}$=11.9 Hz, H-2) 4.99 (d, 1 H, $J_{3,4}$=2.6 Hz, H-4) 4.32 (near d, 1 H, $J_{gem}$=12.7 Hz, H-6) 4.26 (near d, 1 H, $J_{gem}$=12.7 Hz, H-6') 4.15 (s, 1 H, H-5) 2.00 (s, 3 H, Ac) 1.12 and 1.04 (2 s, 18 H, 2 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 169.9, 134.3, 123.5, 107.7, 105.5, 69.6, 69.6, 69.3, 67.0, 66.6, 49.1, 48.9, 27.5, 27.1, 23.2, 20.7; MALDI MS: *m/z*: calcd for $C_{24}H_{32}FNO_7$-SiNa: 516.18; found: 516.23 $[M + Na]^+$; **13β** $[\alpha]_D$=+57.5° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 7.89–7.76

(m, 4 H, Ph), 6.02 and 5.91 (2 d, 1 H, $J_{1,2}$=8.0 Hz, $J_{1,F}$= 53.4 Hz, H-1), 5.57 and 5.54 (2 dd, 1 H, H-3), 4.91 and 4.89 (2 t, 1 H, $J_{1,2}$=8.0 Hz, H-2), 4.82 (t, 1 H, H-4), 4.35 (d, 2 H, H-6, H-6'), 3.77 (s, 1 H, H-5), 1.97 (s, 3 H, Ac), 1.15 and 1.04 (2 s, 18 H, 2 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 170.2, 134.3, 131.4, 123.5, 105.9, 103.8, 71.4, 71.4, 70.0, 69.9, 68.8, 66.5, 50.4, 50.2, 27.6, 27.6, 27.4, 27.3, 23.2, 20.8, 20.6; MALDI MS: *m/z*: calcd for $C_{24}H_{32}FNO_7SiNa$: 516.18; found: 516.23 $[M + Na]^+$.

*p-Nitrophenyl 3-O-acetyl-2-deoxy-4,6-O-di-tert-butylsilylene-2-phthalimido-α-D-galactopyranoside* **(14)** To a solution of compound **13** (3.0 g, 6.1 mmol) and **9** (563 mg, 4.1 mmol) in $CH_2Cl_2$ (120 ml) was added molecular sieves 3Å (3.6 g) under argon atmosphere. The suspension was stirred for 1 h and cooled to 0°C. To the mixture was added triethylamine (424 μl, 3.0 mmol) and $BF_3{\cdot}OEt_2$ (1.9 ml, 15.2 mmol), and stirring was continued at 0°C for 17 h. The termination of the reaction was confirmed by TLC (EtOAc/hexane=1/3 twice). The reaction was quenched by sat $Na_2CO_3$ aq. and filtered through Celite. The combined filtrate and washings was extracted with $CHCl_3$, and the organic layer was washed with $H_2O$ and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel ($PhCH_3$/acetone=200/1) to give **14** (2.4 g, 96%): $[\alpha]_D$=+160.0° (*c* 0.2, $CHCl_3$); $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.13 (m, 2 H, $OC_6H_4NO_2$), 7.87–7.73 (m, 4 H, Ph), 7.12 (m, 2 H, $OC_6H_4NO_2$), 6.46 (dd, 1 H, $J_{2,3}$=12.0 Hz, $J_{3,4}$= 2.5 Hz, H-3), 5.78 (d, 1 H, $J_{1,2}$=3.3 Hz, H-1), 5.22 (dd, 1 H, $J_{1,2}$=3.3 Hz, $J_{2,3}$=12.0 Hz, H-2), 5.00 (d, 1 H, $J_{3,4}$=2.5 Hz, H-4), 4.26 (near d, 1 H, $J_{gem}$=12.8 Hz, H-6), 4.13 (near d, 1 H, $J_{gem}$=12.8 Hz, H-6'), 3.96 (s, 1 H, H-5), 2.02 (s, 3 H, Ac), 1.17 and 1.04 (2 s, 18 H, 2 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 170.0, 161.0, 142.6, 134.3, 125.7, 123.4, 116.2, 96.6, 69.4, 68.6, 67.3, 66.7, 49.1, 31.8, 30.2, 29.6, 29.6, 29.3, 27.5, 27.1, 23.2, 22.6, 20.8, 20.7, 14.0; MALDI MS: *m/z*: calcd for $C_{30}H_{36}N_2O_{10}SiNa$: 635.20; found: 635.06 $[M + Na]^+$.

*p-Nitrophenyl 2-acetamido-2-deoxy-4,6-O-di-tert-butylsilylene-α-D-galactopyranoside* **(15)** To a solution of compound **14** (100 mg, 0.2 mmol) in EtOH (8.2 ml) was added $NH_2NH_2{\cdot}H_2O$ (237 μl, 4.9 mmol), and the mixture was stirred under reflux for 1 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=10/1). The reaction mixture was concentrated. The residue was dissolved in MeOH (8.2 ml), and acetic anhydride (461 μl, 4.9 mmol) was added to the solution at room temperature. The mixture was stirred for 10 min. The termination of reaction was confirmed by TLC (EtOAc/hexane=3/1). The reaction mixture was concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=1/1) to give **15** (77 mg, 98%): $[\alpha]_D$=177.5° (*c* 0.2, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.20 (m, 2 H, $OC_6H_4NO_2$), 7.17 (m, 2 H, $OC_6H_4NO_2$), 5.80 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1), 5.78 (d, 1 H, $J_{2,NH}$=8.5 Hz, NH), 4.65 (m, 1 H, $J_{1,2}$= 3.4 Hz, $J_{2,3}$=10.9 Hz, $J_{2,NH}$=8.5 Hz, H-2), 4.52 (d, 1 H, $J_{3,4}$=3.1 Hz, H-4), 4.24 (near d, 1 H, $J_{gem}$=12.7 Hz, H-6), 4.09 (near d, 1 H, $J_{gem}$=12.7 Hz, H-6'), 3.91 (dt, 1 H, $J_{2,3}$= 10.9 Hz, $J_{3,4}$=3.17 Hz, H-3), 3.74 (s, 1 H, H-5), 2.67 (d, 1 H, OH), 2.05 (s, 3 H, Ac), 1.11 and 1.07 (2 s, 18 H, 2 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 171.0, 161.0, 142.7, 125.8, 116.2, 69.7, 72.3, 69.1, 68.8, 66.5, 49.7, 27.5, 27.3, 23.3, 20.7; MALDI MS: *m/z*: calcd for $C_{22}H_{34}N_2O_8SiNa$: 505.20; found: 505.12 $[M + Na]^+$.

*p-Nitrophenyl 2-acetamido-2-deoxy-4,6-O-di-tert-butylsilylene-3-O-pivaloyl-α-D-galactopyranoside* **(16)** To a solution of compound **15** (337 mg, 0.7 mmol) in pyridine (7.0 ml) was added pivaloyl chloride (172 μl, 1.4 mmol) at 0°C under argon atmosphere, and the mixture was stirred at room temperature for 4 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=1/1). The reaction mixture was coevaporated with toluene and extracted with EtOAc. The organic layer was washed with 2M HCl, $H_2O$, sat $Na_2CO_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=1/3) to give **16** (324 mg, 82%): $[\alpha]_D$=+141.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.22 (m, 2 H, $OC_6H_4NO_2$), 7.17 (m, 2 H, $OC_6H_4NO_2$), 5.77 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1), 5.68 (d, 1 H, $J_{2,NH}$=9.2 Hz, NH), 5.18 (dd, 1 H, $J_{2,3}$=11.2 Hz, $J_{3,4}$= 2.9 Hz, H-3), 5.03 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,3}$=11.2 Hz, $J_{2,NH}$=9.2 Hz, H-2), 4.63 (d, 1 H, $J_{3,4}$=2.9 Hz, H-4), 4.21 (near d, 1 H, $J_{gem}$=12.7 Hz, H-6), 4.07 (near d, 1 H, $J_{gem}$= 12.7 Hz, H-6'), 3.75 (s, 1 H, H-5), 1.96 (s, 3 H, Ac), 1.24, 1.12 and 1.03 (3 s, 27 H, 3 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 179.1, 169.8, 160.9, 142.8, 125.9, 116.2, 96.8, 77.1, 70.0, 69.9, 68.6, 66.6, 46.8, 39.0, 27.5, 27.1, 26.9, 23.3, 23.1, 20.7; MALDI MS: *m/z*: calcd for $C_{27}H_{42}N_2O_9$-SiNa: 589.26; found: 589.32 $[M + Na]^+$.

*p-Nitrophenyl 2-acetamido-2-deoxy-3-O-pivaloyl-α-D-galactopyranoside* **(17)** A 1M TBAHF solution (13 ml) was added to a flask containing compound *16* (733 mg, 1.3 mmol), and the mixture was stirred at room temperature for 30 min. The termination of reaction was confirmed by TLC (EtOAc/hexane=3/1). The reaction mixture was extracted with EtOAc, and the organic layer was washed with 2M HCl, $H_2O$, sat $Na_2CO_3$ aq. and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=5/1) to give **17** (504 mg, 91%): $[\alpha]_D$=+150.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.22 (m, 2 H, $OC_6H_4NO_2$), 7.19 (m, 2 H, $OC_6H_4NO_2$), 5.82 (d, 1 H, $J_{2,NH}$=9.5 Hz, NH), 5.76 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1), 5.34 (dd, 1 H, $J_{2,3}$=

11.4 Hz, H-3), 4.97 (m, 1 H, $J_{1,2}$=3.6 Hz, $J_{2,3}$=11.4 Hz, $J_{2,NH}$=11.4 Hz, H-2), 4.26 (d, 1 H, H-4), 3.92–3.84 (m, 3 H, H-5, H-6, H-6'), 3.23 (s, 1 H, OH), 2.60 (s, 1 H, OH), 1.96 (s, 3 H, Ac), 1.24 (s, 3 H, $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 178.9, 170.1, 160.8, 142.9, 125.9, 116.3, 96.6, 77.2, 71.0, 69.8, 68.6, 62.7, 47.4, 39.1, 27.0, 23.1; MALDI MS: *m/z*: calcd for $C_{19}H_{26}N_2O_9Na$: 449.15; found: 449.42 $[M + Na]^+$.

*p-Nitrophenyl 3-O-acetyl-2-deoxy-4,6-O-di-tert-butylsilylene-2-phthalimido-α-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-O-di-tert-butylsilylene-α-D-galactopyranoside* **(22)** To a solution of compound **12** (242 mg, 0.41 mmol) and compound **15** (100 mg, 0.21 mmol) in $CH_2Cl_2$ (6.2 ml) was added molecular sieves 4Å (342 mg) under argon atmosphere. The suspension was stirred at room temperature for 1 h. To the suspension were added NIS (186 mg, 0.83 mmol) and TfOH (7.3 μl, 0.08 mmol). The stirring was continued at room temperature for 1.5 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=1/1). The reaction mixture was filtered through Celite. The combined filtrate and washings was extracted with $CHCl_3$, and the organic layer was washed with sat $Na_2CO_3$ aq., sat $Na_2S_2O_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/$PhCH_3$=1/2) to give **22** (195 mg, 98%): $[\alpha]_D$=+262.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.18 (m, 2 H, $OC_6H_4NO_2$), 7.80–7.68 (m, 4 H, Phth), 7.12 (m, 2 H, $OC_6H_4NO_2$), 6.32 (dd, 1 H, H-3b), 5.95 (d, 1 H, $J_{1,2}$=3.1 Hz, H-1a), 5.63 (d, 1 H, NH), 5.59 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1b), 5.09 (dd, 1 H, $J_{1,2}$=3.6 Hz, H-2b), 4.96 (d, 1 H, H-4b), 4.79 (d, 1 H, H-4a), 4.42 (m, 1 H, $J_{1,2}$=3.1 Hz, H-2a), 4.37 (near d, 1 H, $J_{gem}$=12.4 Hz, H-6a), 4.25 (near d, 1 H, $J_{gem}$=12.4 Hz, H-6'a), 4.19 (near d, 1 H, $J_{gem}$=10.9 Hz, H-6b), 4.02 (near d, 1 H, $J_{gem}$=10.9 Hz, H-6'b), 3.98 (dd, 1 H, H-3a), 3.97 (s, 1 H, H-5a), 3.65 (s, 1 H, H-5b), 2.15 and 2.03 (2 s, 6 H, 2 Ac), 1.14, 1.05, 0.97 and 0.70 (4 s, 36 H, 4 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): δ 171.3, 170.4, 161.4, 142.6, 125.8, 116.4, 96.4, 93.0, 70.1, 69.7, 68.4, 68.2, 67.8, 67.6, 67.0, 66.8, 48.7, 48.6, 27.5, 27.3, 27.2, 27.1, 26.7, 23.4, 23.3, 23.0, 20.8, 20.7, 20.3; MALDI MS: *m/z*: calcd for $C_{46}H_{65}N_3O_{15}Si_2Na$: 978.39; found: 978.43 $[M + Na]^+$.

*p-Nitrophenyl 2,3-di-O-benzoyl-4,6-O-di-tert-butylsilylene-α-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-O-di-tert-butylsilylene-α-D-galactopyranoside* **(23)** To a solution of compound **18** (465 mg, 0.69 mmol) and compound **15** (164 mg, 0.34 mmol) in $CH_2Cl_2$ (10.3 ml) was added molecular sieves 4Å AW-300 (630 mg). The suspension was stirred at room temperature for 3 h. To the suspension was added TMSOTf (2.5 μl, 14 μmol), and the stirring was continued for 18 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=1/2). The reaction mixture was filtered through Celite. The combined filtrate and washings was extracted with $CHCl_3$, and the organic layer was washed with sat $Na_2CO_3$ aq. and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=1/3) to give **23** (218 mg, 64%): $[\alpha]_D$=+270.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$), mixture of rotamers **23a** and **23b** (a/b=4/1): $\delta$ 8.22 (m, 2 H, $OC_6H_4NO_2$), 8.02–7.33 (m, 10 H, 2 Ph), 7.15 (m, 2 H, $OC_6H_4NO_2$), 5.81–5.78 (m, 2 H, $J_{1,2}$=3.6 Hz, H-1a, H-3b), 5.64 (d, 1 H, NH), 5.63 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1b), 5.60 (dd, 1 H, $J_{1,2}$=3.6 Hz, H-2b), 4.96 (m, 1 H, $J_{1,2}$=3.6 Hz, H-2a), 4.94 (d, 1 H, H-4b), 4.60 (d, 1 H, H-4a), 4.39 (near d, 1 H, $J_{gem}$=12.7 Hz, H-6b), 4.29 (near d, 1 H, $J_{gem}$=12.7 Hz, H-6'b), 4.09 (near d, 1 H, $J_{gem}$=12.9 Hz, H-6a), 4.03 (s, 1 H, H-5b), 3.99 (near d, 1 H, $J_{gem}$=12.9 Hz, H-6'a), 3.89 (dd, 1 H, H-3a), 3.59 (s, 1 H, H-5a), 4.12 (s, 3 H, Ac), 1.14, 0.98, 0.93 and 0.90 (4 s, 36 H, 4 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 170.0, 166.4, 166.0, 161.0, 142.7, 133.3, 133.0, 130.0, 129.9, 129.8, 129.6, 129.2, 128.4, 128.3, 125.9, 125.8, 116.3, 96.9, 95.6, 75.0, 71.2, 70.5, 69.5, 68.8, 68.6, 68.0, 66.8, 66.6, 47.6, 27.5, 27.5, 27.3, 27.3, 27.2, 27.0, 26.9, 23.6, 23.2, 23.1, 20.7, 20.5; MALDI MS: *m/z*: calcd for $C_{50}H_{68}N_2O_{15}Si_2Na$: 1015.41; found: 1015.48 $[M + Na]^+$.

*p-Nitrophenyl 3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-O-di-tert-butylsilylene-α-D-galactopyranoside* **(24)** To a solution of compound **19** (149 mg, 0.28 mmol) and compound **15** (100 mg, 0.24 mmol) in $CH_2Cl_2$ (5.0 ml) was added molecular sieves 4 Å (250 mg) under argon atmosphere. The suspension was stirred at room temperature for 1 h. To the suspension were added NIS (127 mg, 0.56 mmol) and TfOH (5 μl, 0.06 mmol), and the stirring was continued for 1 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=2/1). The reaction mixture was filtered through Celite. The combined filtrate and washings was extracted with $CHCl_3$, and the organic layer was washed with sat $Na_2CO_3$ aq., sat $Na_2S_2O_3$ aq. and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=2/1) to give **24** (207 mg, 96%): $[\alpha]_D$=+89.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.19 (m, 2 H, $OC_6H_4NO_2$), 7.88–7.75 (m, 4 H, Phth), 7.14 (m, 2 H, $OC_6H_4NO_2$), 5.80 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.77 (d, 1 H, $J_{1,2}$=8.5 Hz, H-1b), 5.64 (dd, 1 H, $J_{2,3}$=10.7 Hz, H-3b), 5.44 (d, 1 H, $J_{2,NH}$=7.5 Hz, NH), 5.23 (dd, 1 H, H-4b), 4.73 (d, 1 H, H-4a), 4.66 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,NH}$=7.5 Hz, H-2a), 4.44 (dd, 1 H, $J_{1,2}$=8.5 Hz, $J_{2,3}$=10.7 Hz, H-2b), 4.26 (dd, 1 H, $J_{gem}$=12.4 Hz, H-6b), 4.21 (dd, 1 H, $J_{gem}$=12.4 Hz, H-6'b), 4.15 (near d, 1 H, $J_{gem}$=12.7 Hz, H-6a), 4.03 (near d, 1 H, $J_{gem}$=

12.7 Hz, H-6'a), 3.93 (dd, 1 H, H-3a), 3.92 (m, 1 H, H-5b), 3.65 (s, 1 H, H-5a), 2.09, 2.05, 1.86 and 1.42 (4 s, 12 H, 4 Ac), 1.05 and 1.01 (2 s, 18 H, 2 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 170.3, 170.2, 169.7, 169.2, 161.3, 142.7, 134.5, 131.3, 125.8, 116.3, 99.5, 96.5, 77.2, 72.3, 72.1, 71.0, 68.8, 68.5, 66.7, 62.1, 54.5, 47.6, 27.5, 27.2, 27.1, 23.2, 22.4, 20.7, 20.6, 20.5, 20.3; MALDI MS: *m*/*z*: calcd for $C_{42}H_{53}N_3O_{17}SiNa$: 922.30; found: 922.34 $[M + Na]^+$.

*p-Nitrophenyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl-(1→3)-2-acetamido-4,6-O-di-tert-butylsilylene-2-deoxy-α-D-galactopyranoside* **(25)** To a solution of compound **20** (1.0 g, 1.35 mmol) and compound *15* (521 mg, 1.08 mmol) in $CH_2Cl_2$ (24.3 ml) was added molecular sieves 4Å AW-300 (2.5 g). The suspension was stirred at room temperature for 3 h. To the suspension was added TMSOTf (9.8 μl, 0.05 mmol), and the stirring was continued for 19 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=1/1). The reaction mixture was filtered through Celite. The combined filtrate and washings was extracted with $CHCl_3$, and the organic layer was washed with sat $Na_2CO_3$ aq. and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/$PhCH_3$=1/3) to give **25** (732 mg, 64%): $[\alpha]_D$=+111.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.13 (m, 2 H, $OC_6H_4NO_2$), 8.04–7.26 (m, 20 H, 4 Ph), 6.99 (m, 2 H, $OC_6H_4NO_2$), 5.96 (t, 1 H, $J_{2,3}$=9.5 Hz, $J_{3,4}$=9.7 Hz, H-3b), 5.91 (d, 1 H, H-1a), 5.81 (d, 1 H, NH), 5.77 (t, 1 H, $J_{3,4}$=9.7 Hz, H-4b), 5.62 (t, 1 H, $J_{1,2}$=8.0 Hz, $J_{2,3}$=9.5 Hz, H-2b), 5.38 (d, 1 H, $J_{1,2}$=8.0 Hz, H-1b), 4.80 (m, 1 H, H-2a), 4.75 (d, 1 H, H-4a), 4.72 (d, 1 H, H-6b), 4.48 (dd, 1 H, H-6'b), 4.28 (m, 1 H, H-5b), 4.12 (dd, 1 H, H-3a), 4.02 (near d, 1 H, $J_{gem}$=12.7 Hz, H-6a), 3.96 (near d, 1 H, $J_{gem}$=12.7 Hz, H-6'a), 3.58 (s, 1 H, H-5a), 1.46 (s, 3 H, Ac), 1.07 and 0.89 (2 s, 18 H, 2 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 170.4, 166.0, 165.7, 165.0, 165.0, 161.2, 142.5, 133.5, 133.5, 133.3, 133.3, 129.9, 129.7, 129.6, 129.6, 129.2, 128.8, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 125.6, 116.3, 101.4, 96.5, 76.1, 73.0, 72.7, 72.1, 71.8, 69.0, 68.8, 66.5, 62.9, 47.7, 27.3, 27.1, 23.0, 22.2, 20.6; MALDI MS: *m*/*z*: calcd for $C_{56}H_{60}N_2O_{17}SiNa$: 1083.36; found: 1083.31 $[M + Na]^+$.

*p-Nitrophenyl 3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-O-di-tert-butylsilylene-α-D-galactopyranoside* **(26)** To a solution of compound **21** (218 mg, 0.41 mmol) and compound **15** (100 mg, 0.21 mmol) in $CH_2Cl_2$ (6.2 ml) was added molecular sieves 4Å (318 mg) under argon atmosphere. The suspension was stirred at room temperature for 1 h. To the suspension were added NIS (186 mg, 0.83 mmol) and TfOH (7.3 μl, 0.08 mmol), and the stirring was continued for 1 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=2/1). The reaction mixture was filtered through Celite. The combined filtrate and washings was extracted with $CHCl_3$, and the organic layer was washed with sat $Na_2CO_3$ aq., sat $Na_2S_2O_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=1/1) to give **26** (151 mg, 81%): $[\alpha]_D$=+130.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.19 (m, 2 H, $OC_6H_4NO_2$), 7.90–7.77 (m, 4 H, Phth), 7.12 (m, 2 H, $OC_6H_4NO_2$), 5.77 (d, 1 H, $J_{1,2}$=3.3 Hz, H-1a), 5.71 (d, 1 H, NH), 5.64 (dd, 1 H, H-3b), 5.47 (d, 1 H, H-4b), 5.36 (d, 1 H, $J_{1,2}$=8.0 Hz, H-1b), 4.79 (d, 1 H, $J_{3,4}$=2.5 Hz, H-4a), 4.68–4.63 (m, 2 H, $J_{1,2}$=3.3 Hz, $J_{1,2}$=8.0 Hz, H-2a, H-2b), 4.21–4.02 (m, 5 H, H-6a, H-6'a, H-5b, H-6b, H-6'b), 3.91 (dd, 1 H, $J_{3,4}$=2.5 Hz, H-3a), 3.65 (s, 1 H, H-5a), 2.21, 2.05, 1.86 and 1.30 (4 s, 12 H, 4 Ac), 1.07 (s, 18 H, 2 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 170.4, 170.3, 170.1, 169.8, 161.4, 142.8, 126.0, 116.5, 100.0, 96.7, 77.4, 72.2, 71.2, 68.9, 68.6, 67.0, 66.7, 61.7, 51.6, 47.8, 27.7, 27.6, 27.4, 27.3, 23.5, 22.5, 20.9, 20.8, 20.8, 20.7; MALDI MS: *m*/*z*: calcd for $C_{42}H_{53}N_3O_{17}SiNa$: 922.30; found: 922.32 $[M + Na]^+$.

*p-Nitrophenyl 3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside* **(27)** A 1M TBAHF solution (1.8 ml) was added to a flask containing compound *24* (160 mg, 0.18 mmol), and the mixture was stirred at room temperature for 1.5 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 2M HCl, $H_2O$, sat $Na_2CO_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH=20/1) to give **27** (117 mg, 87%): $[\alpha]_D$=+194.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.19 (m, 2 H, $OC_6H_4NO_2$), 7.90–7.77 (m, 4 H, Phth), 7.13 (m, 2 H, $OC_6H_4NO_2$), 5.71 (near t, 1 H, $J_{2,3}$=10.7 Hz, $J_{3,4}$=9.0 Hz, H-3b), 5.67 (d, 1 H, $J_{1,2}$=8.5 Hz, H-1b), 5.65 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.31 (d, 1 H, $J_{2,NH}$=9.0 Hz, NH), 5.18 (dd, 1 H, $J_{3,4}$=9.0 Hz, H-4b), 4.62 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,NH}$=9.0 Hz, H-2a), 4.41 (near t, 1 H, $J_{1,2}$=8.5 Hz, $J_{2,3}$=10.7 Hz, H-2b), 4.35 (dd, 1 H, $J_{gem}$=12.4 Hz, H-6b), 4.32 (s, 1 H, H-4a), 4.20 (dd, 1 H, $J_{gem}$=12.4 Hz, H-6'b), 3.95–3.91 (m, 2 H, H-3a, H-5b), 3.84–3.81 (m, 3 H, H-5a, H-6a, H-6'a), 2.85 (s, 1 H, OH), 2.51 (d, 1 H, OH), 2.12, 2.06, 1.87 and 1.33 (4 s, 12 H, 4 Ac); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 170.7, 170.1, 169.4, 169.3, 160.8, 142.8, 134.6, 131.2, 125.8, 116.3, 99.0, 96.4, 78.3, 77.1, 72.3, 70.5, 70.4, 68.6, 68.6, 62.1, 61.6, 54.4, 47.4, 22.3, 20.7, 20.5, 20.3; MALDI MS: *m*/*z*: calcd for $C_{34}H_{57}N_3O_{17}Na$: 782.20; found: 782.33 $[M + Na]^+$.

*p-Nitrophenyl 3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→3)-[3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-D-galactopyranoside* **(28)** To a solution of compound *19* (83 mg, 0.16 mmol) and compound **27** (100 mg, 0.13 mmol) in $CH_2Cl_2$ (3.0 ml) was added molecular sieves 4Å (183 mg) under argon atmosphere. The suspension was stirred at room temperature for 1 h. To the suspension were added NIS (71 mg, 0.32 mmol) and TfOH (3 μl, 0.03 mmol), and the stirring was continued for 4 h. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH=20/1). The reaction mixture was filtered through Celite. The combined filtrate and washings was extracted with $CHCl_3$, and the organic layer was washed with sat $Na_2CO_3$ aq., sat $Na_2S_2O_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=5/1) to give **28** (134 mg, 86%): $[\alpha]_D$=+107.5° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.13 (m, 2 H, $OC_6H_4NO_2$), 7.88–7.76 (m, 8 H, 2 Phth), 6.97 (m, 2 H, $OC_6H_4NO_2$), 5.70 (t, 1 H, $J_{3,4}$=9.0 Hz, H-3c), 5.67 (near t, 1 H, $J_{2,3}$=10.7 Hz, $J_{3,4}$=9.0 Hz, H-3b), 5.56 (d, 1 H, $J_{1,2}$=8.3 Hz, H-1b), 5.37 (d, 1 H, $J_{1,2}$=8.5 Hz, H-1c), 5.37 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.26 (d, 1 H, $J_{2,NH}$=8.7 Hz, NH), 5.14 (t, 1 H, $J_{3,4}$=9.0 Hz, H-4b), 5.06 (t, 1 H, $J_{3,4}$=9.0 Hz, H-4c), 4.46 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,NH}$=8.7 Hz, H-2a), 4.36 (dd, 1 H, $J_{1,2}$=8.3 Hz, $J_{2,3}$=10.7 Hz, H-2b), 4.30–4.11 (m, 6 H, $J_{1,2}$=8.5 Hz, H-4a, H-6b, H-6'b, H-2c, H-6c, H-6'c), 4.00 (dd, 1 H, $J_{gem}$=10.2 Hz, H-6a), 3.89 (t, 1 H, H-5a), 3.84 (dd, 1 H, H-3a), 3.83–3.77 (m, 2 H, H-5b, H-5c), 3.73 (dd, 1 H, $J_{gem}$=10.2 Hz, H-6'a), 2.68 (d, 1 H, OH), 2.12, 2.11, 2.05, 2.02, 1.85, 1.84 and 1.35 (7 s, 21 H, 7 Ac); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 170.4, 170.1, 170.0, 169.3, 169.3, 169.1, 161.1, 142.8, 134.5, 134.4, 131.1, 125.7, 123.5, 116.7, 98.9, 98.1, 96.8, 77.8, 72.2, 71.9, 70.5, 70.4, 69.6, 68.8, 68.7, 68.6, 67.6, 62.0, 61.7, 54.4, 54.3, 47.6, 22.3, 20.7, 20.6, 20.6, 20.5, 20.3; MALDI MS: *m/z*: calcd for $C_{54}H_{56}N_4O_{26}Na$: 1199.31; found: 1199.35 $[M + Na]^+$.

*p-Nitrophenyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→3)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-D-galactopyranoside* **(1)** To a solution of compound **28** (83 mg, 0.07 mmol) in EtOH (3.5 ml) was added $NH_2NH_2{\cdot}H_2O$ (103 μl), and the mixture was stirred under reflux for 1 h. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH=10/1). The reaction mixture was concentrated. The residue was dissolved in pyridine (1.5 ml), and acetic anhydride (660 μl, 7.0 mmol) was added to the solution at room temperature. The mixture was stirred for 4 h. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH=10/1). The reaction mixture was concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH=50/1) to give a mixture of *29* with trace amounts of inseparable byproducts, which was exposed to high vacuum.

To a solution of the mixture (72 mg) in MeOH (1.0 ml) was added catalytic amounts of sodium methoxide (28% solution in MeOH) at 0°C under argon atmosphere. The reaction mixture was stirred at room temperature for 30 min. The termination of reaction was confirmed by TLC (*n*-BuOH/MeOH/5% $CaCl_2$ aq.=2/1/1). The reaction mixture was neutralized with Dowex ($H^+$) resin and filtered. The resin was washed with MeOH, and the combined filtrate and washings was concentrated. The residue was purified by gel filtration chromatography on Sephadex LH-20 ($H_2O$) to give **1** (50 mg, 97%): $[\alpha]_D$=+65.0° (*c* 1.0, $H_2O$); $^1$H-NMR (500 MHz, $D_2O$): $\delta$ 8.23 (m, 2 H, $OC_6H_4NO_2$), 7.20 (m, 2 H, $OC_6H_4NO_2$), 5.70 (d, 1 H, $J_{1,2}$=3.9 Hz, H-1a), 4.59 (d, 1 H, $J_{1,2}$=8.5 Hz, H-1b), 4.43 (dd, 1 H, $J_{1,2}$=3.9 Hz, $J_{2,3}$=10.9 Hz, H-2a), 4.39 (d, 1 H, $J_{1,2}$=8.0 Hz, H-1c), 4.24 (d, 1 H, $J_{3,4}$=3.1 Hz, H-4a), 4.18 (dd, 1 H, $J_{2,3}$=10.9 Hz, $J_{3,4}$=3.1 Hz, H-3a), 4.13–3.21 (m, 15 H, H-5a, H-6a, H-6'a, H-2b, H-3b, H-4b, H-5b, H-6b, H-6'b, H-2c, H-3c, H-4c, H-5c, H-6c, H-6'c), 1.98, 1.97 and 1.85 (3 s, 9 H, 3 Ac); $^{13}$C-NMR (125 MHz, $D_2O$): $\delta$ 181.6, 174.6, 174.3, 174.0, 168.5, 161.6, 142.5, 126.3, 116.9, 116.8, 102.7, 101.3, 96.1, 76.3, 76.1, 76.0, 74.2, 73.7, 70.8, 70.1, 70.0, 69.3, 68.9, 61.0, 60.7, 55.8, 55.5, 48.2, 23.4, 22.4, 22.2, 22.1; MALDI MS: *m/z*: calcd for $C_{30}H_{44}N_4O_{18}Na$: 771.25; found: 771.35 $[M + Na]^+$.

*p-Nitrophenyl 2-acetamido-2-deoxy-4,6-O-di-tert-butylsilylene-α-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-O-di-tert-butylsilylene-α-D-galactopyranoside* **(30)** To a solution of compound **22** (274 mg, 0.29 mmol) in EtOH (14.4 ml) was added $NH_2NH_2{\cdot}H_2O$ (418 μl, 8.61 mmol), and the mixture was stirred under reflux for 4 h. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH=10/1). The reaction mixture was concentrated. The residue was dissolved in MeOH (14.4 ml), and acetic anhydride (812 μl, 8.61 mmol) was added to the solution at room temperature. The mixture was stirred for 13 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=5/1). The reaction mixture was concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=3/1) to give **30** (230 mg, 97%): $[\alpha]_D$=+254.0° (*c* 1.0, $CHCl_3$/MeOH=1/1); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.20 (m, 2 H, $OC_6H_4NO_2$), 7.18 (m, 2 H, $OC_6H_4NO_2$), 6.40 (d, 1 H, NH), 5.75 (d, 1 H, NH), 5.71 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.34 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1b), 5.01 (dt, 1 H, $J_{1,2}$=3.4 Hz, H-2a), 4.79 (d, 1 H, H-4a), 4.59 (dt, 1 H, $J_{1,2}$=3.6 Hz, H-2b), 4.44 (d, 1 H, H-4b), 4.32 (near d, 1 H, H-6b), 4.25 (near d, 1 H, H-6a), 4.21 (near d, 1 H, H-6'b), 4.09 (near d, 1 H, H-6'a), 3.95 (dd, 1 H, H-3a), 3.76 (s, 1 H, H-5b), 3.72 (s, 1 H, H-5a), 3.59 (t, 1 H, H-3b), 2.77 (d, 1 H, OH), 2.05

and 2.02 (2 s, 6 H, 2 Ac), 1.11, 1.08, 1.07 and 1.04 (4 s, 36 H, 4 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 171.4, 170.3, 160.7, 142.8, 125.8, 116.2, 97.0, 94.0, 77.1, 72.9, 72.4, 70.6, 68.7, 68.4, 68.2, 67.0, 66.7, 60.3, 48.9, 47.1, 27.4, 27.4, 27.2, 27.2, 23.4, 23.3, 23.2, 20.9, 20.7, 20.7, 14.1; MALDI MS: *m/z*: calcd for $C_{38}H_{63}N_3O_{13}Si_2Na$: 848.38; found: 848.52 $[M + Na]^+$.

*p-Nitrophenyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-O-acetyl-2-deoxy-α-D-galactopyranoside* **(31)** A 1M TBAHF solution (2.0 ml) was added to a flask containing compound **30** (140 mg, 0.17 mmol), and the mixture was stirred at room temperature for 30 min. The termination of reaction was confirmed by TLC (*n*-BuOH/MeOH/5% $CaCl_2$ aq.=2/1/1). The reaction mixture was concentrated. The residue was dissolved in pyridine (2.0 ml), and acetic anhydride (797 μl, 8.45 mmol) was added to the solution at room temperature. The mixture was stirred for 6 h. The termination of reaction was confirmed by TLC (*n*-BuOH/MeOH/5% $CaCl_2$ aq.= 2/1/1). The reaction mixture was coevaporated with toluene and extracted with EtOAc. The organic layer was washed with 2M HCl, $H_2O$, sat $Na_2CO_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH=40/1) to give **31** (125 mg, 98%): $[\alpha]_D$=+175.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.23 (m, 2 H, $OC_6H_4NO_2$), 7.23 (m, 2 H, $OC_6H_4NO_2$), 6.37 (d, 1 H, $J_{2,NH}$=9.7 Hz, NH), 6.26 (d, 1 H, $J_{2,NH}$=9.5 Hz, NH), 5.71 (d, 1 H, $J_{1,2}$= 3.4 Hz, H-1a), 5.48 (d, 1 H, H-4a), 5.38 (d, 1 H, $J_{3,4}$= 2.9 Hz, H-4b), 5.14 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1b), 4.97 (dd, 1 H, $J_{3,4}$=2.9 Hz, H-3b), 4.83 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,NH}$= 9.5 Hz, H-2a), 4.67 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,NH}$=9.7 Hz, H-2b), 4.33 (m, 1 H, H-5a), 4.24–4.14 (m, 4 H, H-3a, H-6a, H-5b, H-6b), 4.08–4.03 (m, 2 H, H-6'a, H-6'b), 2.24, 2.19, 2.11, 2.02, 2.00, 1.99 and 1.94 (7 s, 21 H, 7 Ac); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 171.5, 170.5, 170.4, 170.3, 170.1, 170.0, 160.9, 143.0, 125.7, 116.6, 97.0, 96.8, 72.3, 68.3, 67.6, 66.4, 66.1, 65.8, 61.3, 61.3, 47.9, 46.9, 22.9, 22.8, 20.8, 20.6, 20.6, 20.5, 20.4; MALDI MS: *m/z*: calcd for $C_{32}H_{41}N_3O_{18}Na$: 778.23; found: 778.31 $[M + Na]^+$.

*p-Nitrophenyl 2-acetamido-2-deoxy-α-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside* **(2)** To a solution of compound **31** (10 mg, 13 μmol) in MeOH (1.0 ml) was added catalytic amounts of sodium methoxide (28% solution in MeOH) at 0°C under argon atmosphere, and the mixture was stirred at room temperature for 1 h. The termination of reaction was confirmed by TLC (*n*-BuOH/ MeOH/5% $CaCl_2$ aq.=2/1/1). The reaction mixture was neutralized with Dowex ($H^+$) resin and filtered through cotton. The resin was washed with MeOH, and the combined filtrate and washings was concentrated. The residue was purified by gel filtration chromatography on Sephadex LH-20 ($H_2O$) to give **2** (7 mg, 97%): $[\alpha]_D$=+181.0° (*c* 1.0, DMSO); $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.15 (m, 2 H, $OC_6H_4NO_2$), 7.24 (m, 2 H, $OC_6H_4NO_2$), 5.60 (d, 1 H, $J_{1,2}$= 3.4 Hz, H-1a), 4.88 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1b), 4.48 (dd, 1 H, $J_{1,2}$=3.4 Hz, H-2a), 4.07 (dd, 1 H, $J_{1,2}$=3.6 Hz, H-2b), 4.00 (dd, 1 H, $J_{3,4}$=2.6 Hz, H-3a), 3.95 (d, 1 H, $J_{3,4}$=2.6 Hz, H-4a), 3.76 (d, 1 H, H-4b), 3.72 (t, 1 H, H-5b), 3.66-3.54 (m, 4 H, H-5a, H-3b, H-6b, H-6'b), 3.49 (d, 2 H, H-6a, H-6'a), 1.87 and 1.86 (2 s, 6 H, 2 Ac); $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ 169.8, 169.6, 161.9, 141.8, 125.6, 117.2, 96.9, 96.8, 74.8, 72.5, 71.5, 68.1, 67.5, 65.0, 60.4, 59.8, 49.3, 46.9, 39.9, 39.7, 22.7, 22.5; MALDI MS: *m/z*: calcd for $C_{22}H_{31}N_3O_{13}Na$: 568.18; found: 568.36 $[M + Na]^+$.

*p-Nitrophenyl 2,3-di-O-benzoyl-α-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside* **(32)** A 1M TBAHF solution (1.8 ml) was added to a flask containing compound **23** (180 mg, 0.18 mmol), and the mixture was stirred at room temperature for 3 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 2M HCl, $H_2O$, sat $Na_2CO_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH=30/1) to give **32** (88 mg, 68%): $[\alpha]_D$=+332.0° (*c* 1.0, $CHCl_3$/MeOH=1/1); $^1$H-NMR (500 MHz, $CD_3OD$): $\delta$ 8.20 (m, 2 H, $OC_6H_4NO_2$), 8.01–7.36 (m, 10 H, 2 Ph), 7.31 (m, 2 H, $OC_6H_4NO_2$), 5.77 (dd, 1 H, $J_{1,2}$=3.9 Hz, $J_{2,3}$=10.7 Hz, H-2b), 5.69 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.62 (dd, 1 H, $J_{2,3}$=10.7 Hz, $J_{3,4}$= 3.1 Hz, H-3b), 5.52 (d, 1 H, $J_{1,2}$=3.9 Hz, H-1b), 4.82 (dd, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,3}$=11.2 Hz, H-2a), 4.38 (d, 1 H, $J_{3,4}$= 3.1 Hz, H-4b), 4.23 (t, 1 H, H-5b), 4.20 (dd, 1 H, $J_{2,3}$= 11.2 Hz, H-3a), 4.08 (d, 1 H, H-4a), 3.91 (dd, 1 H, $J_{gem}$= 11.2 Hz, H-6b), 3.80 (dd, 1 H, $J_{gem}$=11.2 Hz, H-6'b), 3.75 (t, 1 H, H-5a), 3.62 (dd, 1 H, $J_{gem}$=11.7 Hz, H-6a), 3.53 (dd, 1 H, $J_{gem}$=11.7 Hz, H-6'a), 2.09 (s, 3 H, Ac); $^{13}$C-NMR (100 MHz, $CD_3OD$): $\delta$ 174.0, 167.6, 167.4, 163.1, 144.0, 134.5, 134.3, 131.0, 130.8, 130.7, 130.6, 129.5, 129.4, 126.6, 118.0, 98.2, 96.3, 75.8, 73.8, 73.0, 73.0, 70.2, 68.8, 66.8, 62.6, 62.3, 49.3, 22.8; MALDI MS: *m/z*: calcd for $C_{34}H_{36}N_2O_{15}Na$: 735.20; found: 735.22 $[M + Na]^+$.

*p-Nitrophenyl α-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside* **(5)** To a solution of compound **32** (88 mg, 0.12 mmol) in MeOH (1.2 ml) was added catalytic amounts of sodium methoxide (28% solution in MeOH) at 0°C under argon atmosphere, and the mixture was stirred at room temperature for 12 h. The termination of reaction was confirmed by TLC (*n*-BuOH/ MeOH/5% $CaCl_2$ aq.=2/1/1). The reaction mixture was neutralized with Dowex ($H^+$) resin and filtered. The resin

was washed with MeOH, and the combined filtrate and washings was concentrated. The residue was purified by gel filtration chromatography on Sephadex LH-20 (MeOH) to give **5** (59 mg, 95%): $[\alpha]_D$=+334.0° (*c* 1.0, MeOH/$H_2O$=1/1); $^1$H-NMR (500 MHz, $CD_3OD/D_2O$=1/1): $\delta$ 8.21 (m, 2 H, $OC_6H_4NO_2$), 7.30 (m, 2 H, $OC_6H_4NO_2$), 5.73 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1a), 5.15 (d, 1 H, $J_{1,2}$=3.9 Hz, H-1b), 4.62 (dd, 1 H, $J_{1,2}$=3.6 Hz, H-2a), 4.24 (dd, 1 H, H-3a), 3.95–3.70 (m, 10 H, H-4a, H-5a, H-6a, H-6'a, H-2b, H-3b, H-4b, H-5b, H-6b, H-6'b), 2.04 (s, 3 H, Ac); $^{13}$C-NMR (100 MHz, $CD_3OD/D_2O$=1/1): $\delta$ 174.9, 162.6, 143.4, 126.8, 117.7, 97.3, 96.9, 74.3, 73.0, 72.7, 70.7, 70.5, 69.2, 65.9, 62.3, 61.9, 48.8, 22.8; MALDI MS: *m*/*z*: calcd for $C_{20}H_{28}N_2O_{13}Na$: 527.15; found: 527.26 $[M + Na]^+$.

*p-Nitrophenyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside* **(33)** A 1M TBAHF solution (5.5 ml) was added to a flask containing compound **25** (580 mg, 0.55 mmol), and the mixture was stirred at room temperature for 2 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=2/1). The reaction mixture was extracted with EtOAc, and the organic layer was washed with 2M HCl, $H_2O$, sat $Na_2CO_3$ aq. and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=3/1) to give **33** (472 mg, 94%): $[\alpha]_D$=+143.5° (*c* 1.0, $CHCl_3$); $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.16 (m, 2 H, $OC_6H_4NO_2$), 8.08–7.26 (m, 20 H, 4 Ph), 7.05 (m, 2 H, $OC_6H_4NO_2$), 5.96 (t, 1 H, $J_{2,3}$=9.8 Hz, $J_{3,4}$=9.5 Hz, H-3b), 5.81 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1a), 5.65 (t, 1 H, $J_{3,4}$=9.5 Hz, H-4b), 5.52 (t, 1 H, $J_{1,2}$=8.0 Hz, $J_{2,3}$=9.8 Hz, H-2b), 5.35 (d, 1 H, NH), 5.12 (d, 1 H, $J_{1,2}$=8.0 Hz, H-1b), 4.85 (dd, 1 H, $J_{gem}$=11.0 Hz, H-6b), 4.68 (m, 1 H, $J_{1,2}$=3.6 Hz, H-2a), 4.43 (dd, 1 H, $J_{gem}$=11.0 Hz, H-6'b), 4.30 (s, 1 H, H-4a), 4.24 (m, 1 H, H-5b), 4.01 (dd, 1 H, H-3a), 3.71–3.59 (m, 3 H, H-5a, H-6a, H-6'a), 2.93 (s, 1 H, OH), 2.28 (s, 1 H, OH), 1.41 (s, 3 H, Ac); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 170.3, 166.2, 165.7, 165.1, 164.8, 161.0, 142.6, 133.6, 133.4, 129.8, 129.7, 129.6, 129.1, 128.7, 128.6, 128.4, 128.3, 125.7, 116.4, 101.4, 96.4, 78.2, 77.2, 72.8, 72.3, 72.0, 70.7, 69.1, 68.2, 62.4, 62.0, 47.9, 29.6, 26.6, 22.2; MALDI MS: *m*/*z*: calcd for $C_{48}H_{44}N_2O_{17}Na$: 943.25; found: 943.16 $[M + Na]^+$.

*p-Nitrophenyl β-D-glucopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside* **(6)** To a solution of compound **33** (242 mg, 0.24 mmol) in MeOH (2.4 ml) was added catalytic amounts of sodium methoxide (28% solution in MeOH) at 0°C under argon atmosphere, and the mixture was stirred at room temperature for 6 h. The termination of reaction was confirmed by TLC (*n*-BuOH/MeOH/5% $CaCl_2$ aq.=2/1/1). The reaction mixture was neutralized with Dowex ($H^+$) resin and filtered. The resin was washed with MeOH, and the combined filtrate and washings was concentrated. The residue was purified by gel filtration chromatography on Sephadex LH-20 (MeOH/$H_2O$=1/1) to give **6** (122 mg, quant.): $[\alpha]_D$=+133.0° (*c* 1.0, $H_2O$); $^1$H-NMR (400 MHz, $D_2O$): $\delta$ 8.23 (m, 2 H, $OC_6H_4NO_2$), 7.26 (m, 2 H, $OC_6H_4NO_2$), 5.81 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1a), 4.61 (d, 1 H, $J_{1,2}$=8.0 Hz, H-1b), 4.58 (dd, 1 H, $J_{1,2}$=3.6 Hz, H-2a), 4.32–4.27 (m, 2 H, H-3a, H-4a), 4.02 (m, 1 H, H-5a), 3.92 (dd, 1 H, H-6b), 3.77–3.67 (m, 3 H, H-6a, H-6'b, H-6'a), 3.53–3.42 (m, 3 H, H-3b, H-5b, H-4b), 3.34 (t, 1 H, $J_{1,2}$=8.0 Hz, H-2b), 2.02 (s, 3 H, Ac); $^{13}$C-NMR (100 MHz, $D_2O$): $\delta$ 174.8, 161.4, 142.4, 126.1, 116.7, 104.4, 96.0, 77.1, 75.9, 75.7, 73.0, 72.1, 69.6, 68.6, 61.0, 60.6, 48.3, 22.1; MALDI MS: *m*/*z*: calcd for $C_{20}H_{28}N_2O_{13}Na$: 527.15; found: 527.19 $[M + Na]^+$.

*p-Nitrophenyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-O-di-tert-butylsilylene-α-D-galactopyranoside* **(34)** To a solution of compound **26** (115 mg, 0.13 mmol) in EtOH (6.4 ml) was added $NH_2NH_2{\cdot}H_2O$ (186 μl, 3.84 mmol), and the mixture was stirred under reflux for 3 h. The termination of the reaction was confirmed by TLC (EtOAc/hexane=4/1). The reaction mixture was concentrated. The residue was dissolved in MeOH (6.4 ml) and acetic anhydride (362 μl, 3.84 mmol) was added to the solution at room temperature. The mixture was stirred for 18 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=4/1). The reaction mixture was concentrated. The residue was dissolved in pyridine (2.6 ml), and acetic anhydride (145 μl, 1.54 mmol) was added to the solution at room temperature. The mixture was stirred for 20 h. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH=10/1). The reaction mixture was coevaporated with toluene and extracted with EtOAc. The organic layer was washed with 2M HCl, $H_2O$, sat $Na_2CO_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH=50/1) to give **34** (76 mg, 73%): $[\alpha]_D$=+222.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.20 (m, 2 H, $OC_6H_4NO_2$), 7.17 (m, 2 H, $OC_6H_4NO_2$), 6.24 (d, 1 H, $J_{2,NH}$=7.5 Hz, NH), 6.15 (d, 1 H, NH), 5.91 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.55 (dd, 1 H, H-3b), 5.40–5.36 (m, 2 H, H-1b, H-4b), 4.80 (d, 1 H, H-4a), 4.77 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,NH}$=7.5 Hz, H-2a), 4.20–3.96 (m, 6 H, H-3a, H-6a, H-6'a, H-5b, H-6b, H-6'b), 3.69–3.68 (m, 2 H, H-5a, H-2b), 2.15, 2.02, 2.00, 1.99 and 1.98 (5 s, 15 H, 5 Ac), 1.10 and 1.07 (2 s, 18 H, 2 $^t$Bu); $^{13}$C-NMR (125 MHz, $CDCl_3$): $\delta$ 171.0, 170.4, 170.2, 170.1, 170.0, 161.3, 142.6, 125.8, 116.3, 100.7, 96.7, 76.8, 71.9, 70.6, 68.9, 68.7, 66.8, 66.6, 61.4, 53.2, 47.7, 29.6, 27.4, 27.1, 23.6, 23.2, 23.2, 20.6, 20.5; MALDI MS: *m*/*z*: calcd for $C_{36}H_{53}N_3O_{16}SiNa$: 834.31; found: 834.56 $[M + Na]^+$.

*p-Nitrophenyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-di-O-acetyl-α-D-galactopyranoside* **(35)** A 1M TBAHF solution (1.0 ml) was added to a flask containing compound **34** (76 mg, 0.09 mmol), and the mixture was stirred at room temperature for 2 h. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH=10/1). The reaction mixture was concentrated. The residue was dissolved in pyridine (1.0 ml), and acetic anhydride (355 μl, 3.76 mmol) was added to the solution at room temperature. The mixture was stirred for 2 h. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH=10/1). The reaction mixture was coevaporated with toluene and extracted with EtOAc. The organic layer was washed with 2M HCl, $H_2O$, sat $Na_2CO_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH=30/1) to give **35** (43 mg, 61%): $[\alpha]_D$=+110.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.22 (m, 2 H, $OC_6H_4NO_2$), 7.14 (m, 2 H, $OC_6H_4NO_2$), 6.55 (d, 1 H, $J_{2,NH}$=6.1 Hz, NH), 6.01 (d, 1 H, NH), 6.00 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.54 (d, 1 H, H-4a), 5.38 (dd, 1 H, $J_{3,4}$=3.4 Hz, H-4b), 5.30 (dd, 1 H, $J_{3,4}$=3.4 Hz, H-3b), 4.97 (d, 1 H, $J_{1,2}$=8.0 Hz, H-1b), 4.54 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,NH}$=6.1 Hz, H-2a), 4.22–4.10 (m, 5 H, H-3a, H-5a, H-6a, H-5b, H-6b), 4.00–3.94 (m, 3 H, $J_{1,2}$=8.0 Hz, H-6'a, H-2b, H-6'b), 2.18, 2.16, 2.06, 2.04, 2.03, 2.03 and 1.92 (7 s, 21 H, 7 Ac); $^{13}$C-NMR (125 MHz, $CDCl_3$): $\delta$ 174.4, 171.1, 170.6, 170.4, 170.2, 170.0, 169.9, 161.1, 142.8, 125.7, 116.6, 99.4, 96.0, 72.7, 71.3, 69.6, 68.4, 67.3, 66.4, 62.2, 61.4, 52.0, 49.3, 29.6, 23.6, 23.0, 20.6, 20.5; MALDI MS: *m/z*: calcd for $C_{32}H_{41}N_3O_{18}Na$: 778.23; found: 778.29 $[M + Na]^+$.

*p-Nitrophenyl 2-acetamido-2-deoxy-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside* **(7)** To a solution of compound **35** (40 mg, 0.05 mmol) in MeOH (1.0 ml) was added catalytic amounts of sodium methoxide (28% solution in MeOH) at 0°C under argon atmosphere, and the mixture was stirred at room temperature for 2 h. The termination of reaction was confirmed by TLC (*n*-BuOH/MeOH/5% $CaCl_2$ aq.=2/1/1). The reaction mixture was neutralized with Dowex ($H^+$) resin and filtered. The resin was washed with MeOH, and the combined filtrate and washings was concentrated. The residue was purified by gel filtration chromatography on Sephadex LH-20 ($H_2O$) to give **7** (16 mg, 55%): $[\alpha]_D$=+318.5° (*c* 1.0, DMSO); $^1$H-NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.21 (m, 2 H, $OC_6H_4NO_2$), 7.86 (d, 1 H, $J_{2,NH}$=7.8 Hz, NH), 7.69 (d, 1 H, NH), 7.27 (m, 2 H, $OC_6H_4NO_2$), 5.65 (d, 1 H, $J_{1,2}$= 3.6 Hz, H-1a), 4.63 (d, 1 H, $J_{1,2}$=8.3 Hz, H-1b), 4.34 (m, 1 H, $J_{1,2}$=3.6 Hz, $J_{2,NH}$=7.8 Hz, H-2a), 4.11 (d, 1 H, H-4a), 3.95 (dd, 1 H, H-3a), 3.73–3.64 (m, 3 H, $J_{1,2}$=8.3 Hz, H-5a, H-2b, H-6b), 3.58–3.49 (m, 4 H, H-6a, H-3b, H-4b, H-6'b), 3.42–3.32 (m, 2 H, H-6'a, H-5b), 1.85 and 1.84 (2 s, 6 H, 2 Ac); $^{13}$C-NMR (125 MHz, DMSO-$d_6$): $\delta$ 170.1, 169.7, 162.0, 141.7, 125.7, 117.0, 102.2, 96.4, 76.1, 75.3, 72.8, 72.2, 67.4, 67.0, 60.4, 60.2, 52.7, 47.9, 39.9, 39.7, 23.0, 22.5; MALDI MS: *m/z*: calcd for $C_{22}H_{31}N_3O_{13}Na$: 568.18; found: 568.31 $[M + Na]^+$.

*p-Nitrophenyl 3-O-acetyl-2-deoxy-4,6-O-di-tert-butylsilylene-2-phthalimido-α-D-galactopyranosyl-(1→6)-2-acetamido-2-deoxy-3-O-pivaloyl-α-D-galactopyranoside* **(36)** To a solution of compound **12** (165 mg, 0.28 mmol) and compound **17** (100 mg, 0.24 mmol) in $CH_2Cl_2$ (5.2 ml) was added molecular sieves 4Å (265 mg) under argon atmosphere. The suspension was stirred at room temperature for 1 h. To the suspension were added NIS (127 mg, 0.56 mmol) and TfOH (5 μl, 0.06 mmol), and the stirring was continued for 1 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=2/1). The reaction mixture was filtered through Celite. The combined filtrate and washings was extracted with $CHCl_3$, and the organic layer was washed with sat $Na_2CO_3$ aq., sat $Na_2S_2O_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=1/1) to give *36* (109 mg, 51%) and its β-isomer **36β** (40 mg, 19%): **36*α***: $[\alpha]_D$=+201.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.21 (m, 2 H, $OC_6H_4NO_2$), 7.87–7.73 (m, 4 H, Ph), 7.00 (m, 2 H, $OC_6H_4NO_2$), 6.10 (dd, 1 H, $J_{2,3}$=11.9 Hz, H-3b), 5.77 (d, 1 H, $J_{2,NH}$=9.2 Hz, NH), 5.41 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.25 (dd, 1 H, $J_{2,3}$=11.2 Hz, $J_{3,4}$=2.9 Hz, H-3a), 4.99 (dd, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,3}$=11.9 Hz, H-2b), 4.96 (d, 1 H, $J_{1,2}$= 3.4 Hz, H-1b), 4.89 (dd, 1 H, H-4b), 4.77 (m, 1 H, $J_{1,2}$= 3.4 Hz, $J_{2,3}$=11.2 Hz, $J_{2,NH}$=9.2 Hz, H-2a), 4.26 (dd, 1 H, $J_{gem}$=12.4 Hz, H-6b), 4.15 (dd, 1 H, $J_{gem}$=12.4 Hz, H-6'b), 4.01 (d, 1 H, $J_{3,4}$=2.9 Hz, H-4a), 3.94 (t, 1 H, H-5a), 3.87 (s, 1 H, H-5b), 3.86 (dd, 1 H, H-6a), 3.51 (dd, 1 H, H-6'a), 2.52 (d, 1 H, OH), 1.97 and 1.91 (2 s, 6 H, 2 Ac), 1.21, 1.11 and 1.01 (3 s, 27 H, 3 $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 178.7, 170.0, 169.8, 160.8, 143.0, 134.2, 125.9, 123.2, 116.3, 98.9, 96.5, 69.7, 67.5, 67.3, 66.9, 49.4, 47.5, 39.0, 29.5, 27.6, 27.6, 27.4, 27.1, 27.0, 23.2, 23.1, 20.7, 20.7; MALDI MS: *m/z*: calcd for $C_{43}H_{57}N_3O_{16}SiNa$: 922.34; found: 922.37 $[M + Na]^+$; *36β*: $[\alpha]_D$=+64.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.16 (m, 2 H, $OC_6H_4NO_2$), 7.87–7.73 (m, 4 H, Ph), 7.07 (m, 2 H, $OC_6H_4NO_2$), 5.75 (d, 1 H, $J_{2,NH}$=9.2 Hz, NH), 5.57 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.44 (dd, 1 H, $J_{2,3}$=11.2 Hz, $J_{3,4}$= 2.9 Hz, H-3b), 5.30 (dd, 1 H, $J_{2,3}$=11.4 Hz, $J_{3,4}$=3.1 Hz, H-3a), 5.28 (d, 1 H, $J_{1,2}$=8.7 Hz, H-1b), 4.83 (m, 1 H, $J_{1,2}$= 3.4 Hz, $J_{2,3}$=11.4 Hz, $J_{2,NH}$=9.2 Hz, H-2a), 4.78 (d, 1 H, $J_{3,4}$=2.9 Hz, H-4b), 4.68 (dd, 1 H, $J_{1,2}$=8.7 Hz, $J_{2,3}$= 11.2 Hz, H-2b), 4.33 (dd, 1 H, $J_{gem}$=12.4 Hz, H-6b), 4.26 (dd, 1 H, $J_{gem}$=12.4 Hz, H-6'b), 4.10 (t, 1 H, $J_{3,4}$=3.1 Hz,

H-4a), 3.96 (t, 1 H, $J_{gem}$=9.2 Hz, H-6a), 3.88 (s, 1 H, H-5b), 3.68 (t, 1 H, H-5a), 3.63 (dd, 1 H, $J_{gem}$=9.2 Hz, H-6'b), 2.65 (d, 1 H, OH-4a), 1.93 and 1.91 (2 s, 6 H, 2 Ac), 1.24, 1.05 and 1.02 (3 s, 27 H, 3 $^{t}$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 179.0, 170.3, 169.8, 161.0, 142.7, 134.2, 131.4, 125.8, 123.5, 123.4, 116.3, 98.3, 96.6, 77.1, 71.5, 70.7, 69.7, 69.2, 68.9, 66.8, 66.4, 65.9, 60.3, 50.0, 47.7, 39.0, 29.6, 27.4, 27.2, 27.1, 23.2, 23.1, 21.0, 20.6, 20.6, 14.1; MALDI MS: *m/z*: calcd for $C_{43}H_{57}N_3O_{16}SiNa$: 922.34; found: 922.28 $[M + Na]^+$.

*p-Nitrophenyl 3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-α-D-galactopyranosyl-(1→6)-2-acetamido-4-O-acetyl-2-deoxy-3-O-pivaloyl-α-D-galactopyranoside* **(37)** A 1M TBAHF solution (1.0 ml) was added to a flask containing compound **36** (105 mg, 0.12 mmol), and the mixture was stirred at room temperature for 4 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=2/1). The reaction mixture was concentrated. The residue was dissolved in pyridine (1.0 ml), and acetic anhydride (221 μl, 2.34 mmol) was added to the solution at room temperature. The mixture was stirred for 1 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=2/1). The reaction mixture was coevaporated with toluene and extracted with EtOAc. The organic layer was washed with 2M HCl, $H_2O$, sat $Na_2CO_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=1/1) to give **37** (92 mg, 88%): $[\alpha]_D$=+175.5° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.32 (m, 2 H, $OC_6H_4NO_2$), 7.80–7.67 (m, 4 H, Phth), 7.18 (m, 2 H, $OC_6H_4NO_2$), 6.29 (dd, 1 H, $J_{2,3}$=12.2 Hz, H-3b), 5.76 (d, 1 H, $J_{2,NH}$=9.2 Hz, NH), 5.66 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.55 (d, 1 H, H-4b), 5.29 (dd, 1 H, H-3a), 5.19 (d, 1 H, H-4a), 4.82 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1b), 4.74 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,NH}$=9.2 Hz, H-2a), 4.69 (dd, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,3}$=12.2 Hz, H-2b), 4.25 (t, 1 H, H-5b), 4.18–4.13 (m, 2 H, H-5a, H-6b), 4.05 (dd, 1 H, H-6'b), 3.64 (dd, 1 H, $J_{gem}$=10.0 Hz, H-6a), 3.24 (dd, 1 H, $J_{gem}$=10.0 Hz, H-6'a), 2.14, 2.05, 2.03, 1.93 and 1.83 (5 s, 15 H, 5 Ac), 1.02 (s, 9 H, $^{t}$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 177.8, 170.3, 170.0, 169.9, 169.2, 169.2, 160.5, 143.3, 133.7, 131.7, 126.1, 123.2, 116.4, 98.05, 96.4, 68.8, 67.4, 67.2, 66.9, 65.5, 64.6, 61.7, 49.8, 47.9, 38.7, 26.7, 23.0, 20.6, 20.5, 20.4, 20.4; MALDI MS: *m/z*: calcd for $C_{41}H_{47}N_3O_{19}Na$: 908.27; found: 908.38 $[M + Na]^+$.

*p-Nitrophenyl 3,4,6-tri-O-acetyl-2-acetamido-2-deoxy-α-D-galactopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-α-D-galactopyranoside* **(38)** To a solution of compound **37** (94 mg, 0.11 mmol) in EtOH (5.0 ml) was added $NH_2NH_2{\cdot}H_2O$ (154 μl, 3.18 mmol), and the mixture was stirred under reflux for 2 h. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH=20/1). The reaction mixture was concentrated. The residue was dissolved in pyridine (2.0 ml), and acetic anhydride (1.04 ml, 11.0 mmol) was added to the solution at room temperature. The mixture was stirred for 15 h. The termination of reaction was confirmed by TLC ($CHCl_3$/MeOH=20/1). The reaction mixture was concentrated. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH=50/1) to give **38** (69 mg, 86%): $[\alpha]_D$=+175.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.26 (m, 2 H, $OC_6H_4NO_2$), 7.20 (m, 2 H, $OC_6H_4NO_2$), 5.82 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1a), 5.78 (d, 1 H, $J_{2,NH}$=9.2 Hz, NH), 5.57 (d, 1 H, $J_{2,NH}$=10.0 Hz, NH), 5.55 (d, 1 H, $J_{3,4}$=3.1 Hz, H-4a), 5.47 (dd, 1 H, $J_{2,3}$=11.4 Hz, $J_{3,4}$=3.1 Hz, H-3a), 5.31 (d, 1 H, H-4b), 4.85 (dd, 1 H, $J_{2,3}$=11.2 Hz, H-3b), 4.80 (m, 1 H, $J_{1,2}$=3.6 Hz, $J_{2,3}$=11.4 Hz, $J_{2,NH}$=9.2 Hz, H-2a), 4.72 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1b), 4.56 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,3}$=11.2 Hz, $J_{2,NH}$=10.0 Hz, H-2b), 4.17–4.14 (m, 2 H, H-5a, H-6b), 4.08 (t, 1 H, H-5b), 3.94 (dd, 1 H, H-6'b), 3.70 (dd, 1 H, $J_{gem}$=9.2 Hz, H-6a), 3.34 (dd, 1 H, $J_{gem}$=9.2 Hz, H-6'a), 2.21, 2.15, 2.08, 1.99, 1.97, 1.96 and 1.92 (7 s, 21 H, 7 Ac); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 171.0, 170.8, 170.4, 170.3, 170.2, 170.2, 160.4, 143.2, 125.9, 116.2, 97.5, 95.8, 77.1, 68.6, 68.0, 67.4, 67.2, 67.1, 67.0, 64.5, 62.1, 48.1, 47.2, 37.0, 31.9, 30.0, 29.6, 29.3, 23.2, 22.9, 20.7, 20.6, 20.6, 20.5; MALDI MS: *m/z*: calcd for $C_{32}H_{41}N_3O_{18}Na$: 778.23; found: 778.51 $[M + Na]^+$.

*p-Nitrophenyl 2-acetamido-2-deoxy-α-D-galactopyranosyl-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside* **(4)** To a solution of compound **38** (39 mg, 0.05 mmol) in MeOH (1.0 ml) was added catalytic amounts of sodium methoxide (28% solution in MeOH) at 0°C under argon atmosphere, and the mixture was stirred at room temperature for 2 h. The termination of reaction was confirmed by TLC (*n*-BuOH/MeOH/5% $CaCl_2$ aq.=2/1/1). The reaction mixture was neutralized with Dowex ($H^+$) resin and filtered. The resin was washed with MeOH, and the combined filtrate and washings was concentrated. The residue was purified by gel filtration chromatography on Sephadex LH-20 ($H_2O$) to give **4** (17 mg, 61%): $[\alpha]_D$=+169.0° (*c* 1.0, $H_2O$); $^1$H-NMR (500 MHz, $D_2O$): $\delta$ 8.27 (m, 2 H, $OC_6H_4NO_2$), 7.29 (m, 2 H, $OC_6H_4NO_2$), 5.89 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1a), 4.79 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1b), 4.41 (dd, 1 H, $J_{1,2}$=3.6 Hz, H-2a), 4.21–4.18 (m, 2 H, H-3a, H-5a), 4.09 (d, 1 H, H-4a), 4.05 (dd, 1 H, $J_{1,2}$=3.6 Hz, $J_{2,3}$=10.9 Hz, H-2b), 3.91 (d, 1 H, H-4b), 3.87 (t, 1 H, H-5b), 3.82 (dd, 1 H, $J_{gem}$=10.7 Hz, H-6a), 3.74–3.72 (m, 2 H, H-6b, H-6'b), 3.66 (dd, 1 H, $J_{gem}$=10.7 Hz, H-6'a), 3.46 (dd, 1 H, $J_{2,3}$=10.9 Hz, H-3b), 2.04 and 1.92 (2 s, 6 H, 2 Ac); $^{13}$C-NMR (100 MHz, $D_2O$): $\delta$ 175.0, 174.6, 161.5, 132.8, 126.2, 117.0, 96.5, 95.5, 71.2, 70.5, 68.9, 68.6, 68.1, 67.7, 66.6, 61.3, 49.9, 49.6, 22.1; MALDI MS:

*m/z*: calcd for $C_{22}H_{31}N_3O_{13}Na$: 568.18; found: 568.20 [$M$ + Na]$^+$.

*p-Nitrophenyl 3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-3-O-pivaloyl-α-D-galactopyranoside* **(39)** To a solution of compound **19** (149 mg, 0.28 mmol) and compound **17** (100 mg, 0.24 mmol) in $CH_2Cl_2$ (5.2 ml) was added molecular sieves 4Å (249 mg) under argon atmosphere. The suspension was stirred at room temperature for 1 h. To the suspension were added NIS (127 mg, 0.56 mmol) and TfOH (5 μl, 0.06 mmol), and the stirring was continued for 1 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=2/1). The reaction mixture was filtered through Celite. The combined filtrate and washings was extracted with $CHCl_3$, and the organic layer was washed with sat $Na_2CO_3$ aq., sat $Na_2S_2O_3$ aq., and brine, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=2/1) to give *39* (175 mg, 88%): $[\alpha]_D$=+125.0° (*c* 1.0, $CHCl_3$): $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.15 (m, 2 H, $OC_6H_4NO_2$), 7.84–7.73 (m, 4 H, Ph), 7.05 (m, 2 H, $OC_6H_4NO_2$), 5.78 (d, 1 H, $J_{2,NH}$=9.2 Hz, NH), 5.72 (t, 1 H, $J_{2,3}$=10.7 Hz, H-3b), 5.56 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.41 (d, 1 H, $J_{1,2}$=8.5 Hz, H-1b), 5.25 (dd, 1 H, $J_{2,3}$= 11.2 Hz, $J_{3,4}$=3.1 Hz, H-3a), 5.08 (t, 1 H, H-4b), 4.84 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,3}$=11.2 Hz, H-2a), 4.30 (dd, 1 H, $J_{gem}$= 12.2 Hz, H-6b), 4.21 (t, 1 H, $J_{1,2}$=8.5 Hz, $J_{2,3}$=10.7 Hz, H-2b), 4.15 (dd, 1 H, $J_{gem}$=12.2 Hz, H-6'b), 4.09 (t, 1 H, $J_{3,4}$= 3.1 Hz, H-4a), 4.00 (dd, 1 H, $J_{gem}$=9.7 Hz, H-6a), 3.91–3.86 (m, 2 H, H-5a, H-5b), 3.66 (dd, 1 H, $J_{gem}$=9.7 Hz, H-6'a), 2.93 (d, 1 H, OH), 2.13, 2.04, 1.91 and 1.84 (4 s, 12 H, 4 Ac), 1.23 (s, 9 H, $^t$Bu); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 178.8, 170.6, 170.0, 169.8, 169.3, 161.0, 142.7, 134.4, 131.1, 125.7, 123.5, 116.3, 98.1, 96.5, 72.0, 70.4, 69.8, 69.4, 68.7, 67.4, 65.8, 61.9, 54.3, 47.5, 38.9, 26.9, 26.8, 23.0, 20.6, 20.5, 20.3; MALDI MS: *m/z*: calcd for $C_{39}H_{45}N_3O_{18}Na$: 866.26; found: 866.29 [$M$ + Na]$^+$.

*p-Nitrophenyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-O-acetyl-2-deoxy-α-D-galactopyranoside* **(40)** To a solution of compound **39** (100 mg, 0.12 mmol) in EtOH (5.0 ml) was added $NH_2NH_2{\cdot}H_2O$ (173 ml, 3.57 mmol), and the mixture was stirred under reflux for 1 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=2/1). The reaction mixture was concentrated. The residue was dissolved in pyridine (2.0 ml), and acetic anhydride (674 μl, 7.14 mmol) was added to the solution at room temperature. The mixture was stirred for 2 h. The termination of reaction was confirmed by TLC (EtOAc/hexane=2/1). The reaction mixture was concentrated. The residue was purified by column chromatography on silica gel (EtOAc/hexane=5/1) to give **40** (77 mg, 86%): $[\alpha]_D$=+87.0° (*c* 1.0, $CHCl_3$); $^1$H-NMR (500 MHz, $CDCl_3$): $\delta$ 8.27 (m, 2 H, $OC_6H_4NO_2$), 7.19 (m, 2 H, $OC_6H_4NO_2$), 5.79 (d, 1 H, $J_{2,NH}$=9.0 Hz, NH), 5.71 (d, 1 H, $J_{1,2}$=3.4 Hz, H-1a), 5.48 (d, 1 H, $J_{2,NH}$=8.3 Hz, NH), 5.46 (d, 1 H, H-4a), 5.38 (dd, 1 H, $J_{2,3}$=11.4 Hz, H-3a), 5.28 (t, 1 H, $J_{2,3}$=10.5 Hz, H-3b), 4.91 (t, 1 H, H-4b), 4.76 (m, 1 H, $J_{1,2}$=3.4 Hz, $J_{2,3}$=11.4 Hz, $J_{2,NH}$=9.0 Hz, H-2a), 4.72 (d, 1 H, $J_{1,2}$=8.3 Hz, H-1b), 4.20 (t, 1 H, H-5a), 4.18 (dd, 1 H, $J_{gem}$=12.2 Hz, H-6b), 4.06 (dd, 1 H, $J_{gem}$=12.2 Hz, H-6'b), 3.77 (dd, 1 H, H-6a), 3.66–3.60 (m, 2 H, H-6'a, H-5b), 3.54 (dt, 1 H, $J_{1,2}$=8.3 Hz, $J_{2,3}$=10.5 Hz, $J_{2,NH}$=8.3 Hz, H-2b), 2.18, 2.06, 2.05, 2.01, 2.00, 1.98 and 1.89 (7 s, 21 H, 7 Ac); $^{13}$C-NMR (125 MHz, $CDCl_3$): $\delta$ 171.0, 170.6, 170.5, 170.3, 170.2, 170.1, 169.4, 161.0, 143.1, 126.0, 116.7, 99.8, 96.5, 71.8, 71.7, 69.0, 68.4, 67.8, 67.0, 66.2, 61.9, 55.0, 48.0, 29.7, 23.2, 23.2, 20.7, 20.7, 20.6, 20.6; MALDI MS: *m/z*: calcd for $C_{32}H_{41}N_3O_{18}Na$: 778.23; found: 778.35 [$M$ + Na]$^+$.

*p-Nitrophenyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-α-D-galactopyranoside* **(3)** To a solution of compound **40** (20 mg, 0.03 mmol) in MeOH (2.0 ml) was added catalytic amounts of sodium methoxide (28% solution in MeOH) at 0°C under argon atmosphere, and the mixture was stirred at room temperature for 1 h. The termination of reaction was confirmed by TLC (*n*-BuOH/MeOH/5% $CaCl_2$ aq.=2/1/1). The reaction mixture was neutralized with Dowex ($H^+$) resin and filtered. The resin was washed with MeOH, and the combined filtrate and washings was concentrated. The residue was purified by gel filtration chromatography on Sephadex LH-20 ($H_2O$) to give **3** (14 mg, quant.): $[\alpha]_D$=+19.0° (*c* 1.0, $H_2O$): $^1$H-NMR (500 MHz, $D_2O$): $\delta$ 8.30 (m, 2 H, $OC_6H_4NO_2$), 7.27 (m, 2 H, $OC_6H_4NO_2$), 5.80 (d, 1 H, $J_{1,2}$=3.6 Hz, H-1a), 4.46 (d, 1 H, $J_{1,2}$=8.5 Hz, H-1b), 4.38 (dd, 1 H, $J_{1,2}$=3.6 Hz, H-2a), 4.18–3.31 (m, 11 H, H-3a, H-4a, H-5a, H-6a, H-6'a, H-2b, H-3b, H-4b, H-5b, H-6b, H-6'b), 2.03 and 1.92 (2 s, 6 H, 2 Ac); $^{13}$C-NMR (100 MHz, $D_2O$): $\delta$ 174.7, 174.2, 161.6, 142.3, 126.1, 116.7, 101.1, 95.9, 75.8, 73.9, 70.6, 69.8, 68.6, 68.2, 67.2, 60.7, 55.3, 49.4, 22.0, 21.8; MALDI MS: *m/z*: calcd for $C_{22}H_{31}N_3O_{13}Na$: 568.18; found: 568.19 [$M$ + Na]$^+$.

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