RARE EARTH SALTS PROMOTED GLYCOSIDATION OF GLYCOSYL FLUORIDES†

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Abstract - A glycosidation reaction of glycosyl fluorides with free alcohol acceptors has been found to be promoted effectively by using rare earth metal salts, with or without the requirement of usual Lewis acids such as $ZnCl_2$ and $Ba(ClO_4)_2$. Moreover, a glycosidation reaction of glycosyl fluorides with trimethylsilyl ethers has been found to be promoted more effectively by using a catalytic amount of rare earth metal perchlorates.

INTRODUCTION

Development of stereoselective glycosylation reactions is one of important topics in carbohydrate chemistry. Hence a variety of glycosylation methods[1a] have been exploited since the first use of the classical Königs-Knorr synthesis.[1b] Of many methods so far developed, glycosyl fluorides as a donor have been employed most frequently in the synthesis of rather complex sugar chains.[2] These fluorides have been glycosidated in the presence of various Lewis acids such as $SnCl_2$-$AgClO_4$,[3a] Cp_2MCl_2-$AgClO_4$ (M = Ti, Zr, Hf),[3b] SiF_4,[3c] Me_3SiOTf,[3c] BF_3•Et_2O,[3d] Me_2GaX (X = Cl, OTf),[3e] TiF_4,[3f] and Tf_2O.[3g] Amongst these it appears that either $SnCl_2$-$AgClO_4$ or Cp_2MCl_2-$AgClO_4$ have been utilized most frequently. We have developed a more cost-effective and powerful method for the glycosidation reaction using glycosyl fluorides, which has allowed us to achieve several notable glycosylation reactions. This

† Dedicated to the memory of Professor Yoshio Ban.

method uses rare earth metal salts, glycosyl fluorides, and glycosyl acceptors, with or without usual Lewis acids such as $ZnCl_2$ and $Ba(ClO_4)_2$.[4a] The basic idea evolved from the realization that the rare earth metal-fluorine bond has a large bond dissociation energy.[5,6] Moreover, in an attempt to improve the new glycosylation reaction, we have found[4b] that a catalytic amount of rare earth perchlorate more effectively promotes the condensation of appropriately protected glycosyl fluorides and trimethylsilyl ethers[7] than does the stoichiometric method. A possible mechanism for the catalytic procedure is also discussed based on ^{19}F nmr spectral data.

RESULTS AND DISCUSSION

We began with an examination of the fluorophilicity of rare earth metal salts by carrying out the reaction of the glucose derivative (**1**)[8] with cyclohexanol (**2a**) under a variety of conditions (Figure 1). We were

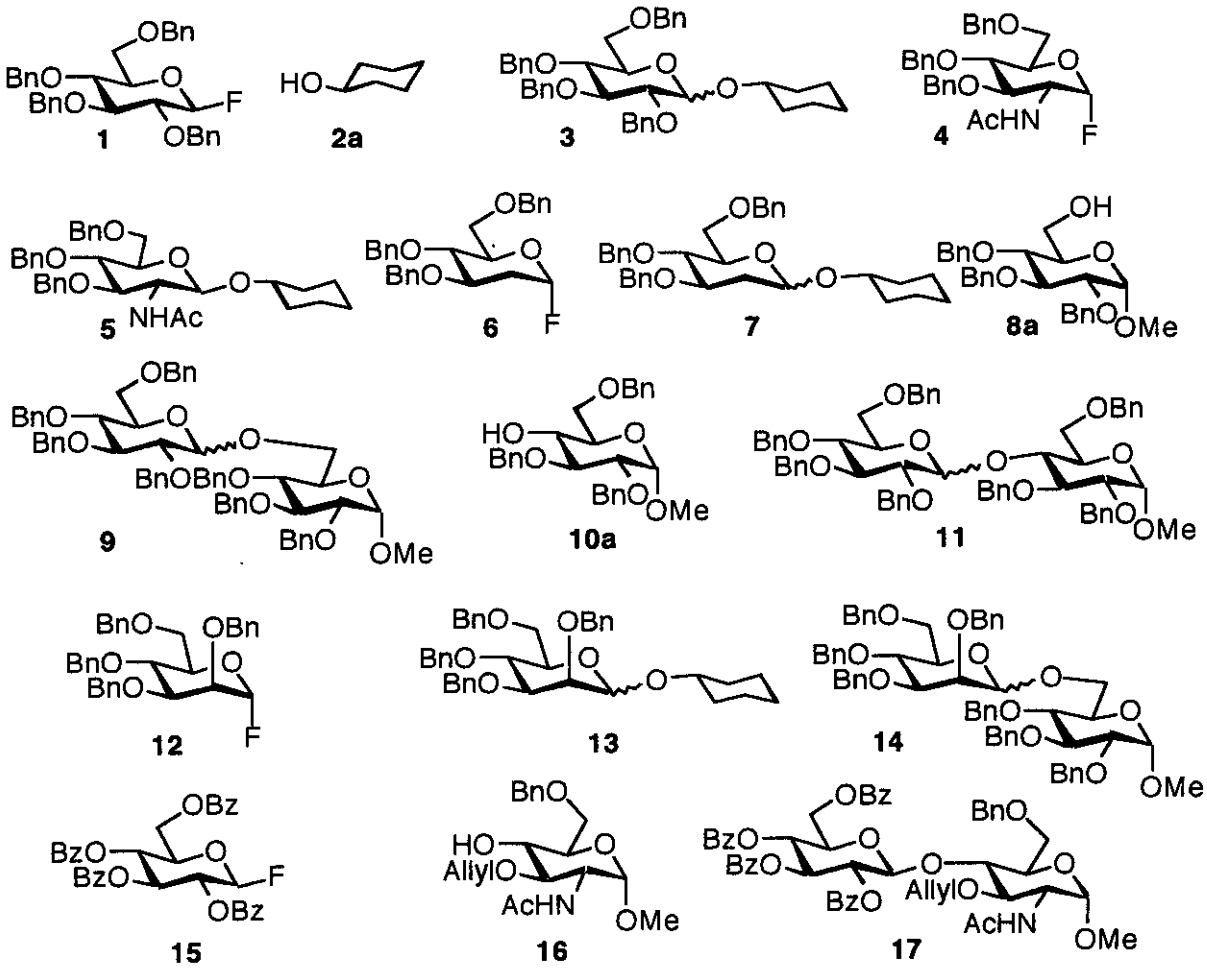


Figure 1. Glycosyl Donors, Acceptors and Synthesized Glycosides.

Table 1. Glycosidation Reactions[a] Using Rare Earth Metal Salts

Entry	Glycosyl Donor	Glycosyl Acceptor[b]	Glycoside	Rare Earth Metal Salt[c]	Solvent	Base[d]	Additive[e]	Temp (°C)	Time (h)	Yield (%)	α : β
1	**1**	**2a**	**3**	$Yb(OTf)_3$	MeCN	K_2CO_3		-15	3.5	63	6 : 94
2	**1**	**2a**	**3**	$Y(OTf)_3$	Et_2O	$CaCO_3$		RT	22	96	94 : 6
3	**1**	**2a**	**3**	$YbCl_3$	Et_2O	$CaCO_3$		RT	17	98	97 : 3
4	**1**	**2a**	**3**	$La(OTf)_3$	MeCN	K_2CO_3		RT	43	36	β
5	**1**	**2a**	**3**	$La(OTf)_3$	Et_2O	$CaCO_3$		RT	72	67	α
6	**4**	**2a**	**5**	$Yb(OTf)_3$	MeCN			RT	14	70	β
7	**6**	**2a**	**7**	$Yb(OTf)_3$	MeCN	K_2CO_3		-15	2	73	19 : 81
8	**6**	**2a**	**7**	$YbCl_3$	Et_2O	$CaCO_3$		RT	4	88	50 : 50
9	**1**	**8a**	**9**	$Yb(OTf)_3$	MeCN	K_2CO_3		-15	3.5	68	12 : 88
10	**1**	**8a**	**9**	$Y(OTf)_3$	Et_2O	$CaCO_3$		RT	17	88	80 : 20
11	**1**	**10a**	**11**	$Yb(OTf)_3$	MeCN	K_2CO_3		RT	21	50	30 : 70
12	**1**	**10a**	**11**	$Yb(OTf)_3$	MeCN	K_2CO_3	$ZnCl_2$	RT	0.5	77	38 : 62
13	**1**	**10a**	**11**	$Yb(OTf)_3$	MeCN	K_2CO_3	$Ba(ClO_4)_2$	RT	0.5	79	39 : 61
14	**1**	**10a**	**11**	$Yb(OTf)_3$	MeCN	K_2CO_3	$ZnCl_2$	-15	38	61	22 : 78
15	**1**	**10a**	**11**	$Yb(OTf)_3$	MeCN	K_2CO_3	$Ba(ClO_4)_2$	-15	38	81	23 : 77
16	**1**	**10a**	**11**	$Y(OTf)_3$	Et_2O	$CaCO_3$		RT	41	66	74 : 26
17	**12**	**2a**	**13**	$Yb(OTf)_3$	Toluene	K_2CO_3		RT	37	94	35 : 65
18	**12**	**2a**	**13**	$Yb(OTf)_3$	Toluene	K_2CO_3	$ZnCl_2$	RT	2	100	39 : 61
19	**12**	**8a**	**14**	$Yb(OTf)_3$	Toluene	K_2CO_3	$ZnCl_2$	RT	42	94	60 : 40
20	**12**	**8a**	**14**	$Y(OTf)_3$	Toluene	$CaCO_3$		RT	87	74	58 : 42
21	**15**	**16**	**17**	$Yb(OTf)_3$	MeCN	K_2CO_3[f]	$Ba(ClO_4)_2$	55	14	52	β
22	**15**	**16**	**17**	$La(ClO_4)_3$[g]	MeCN	K_2CO_3		-15	38	73	β

[a] All reactions were carried out in the presence of MS4A. [b,c] 1.2 mol equiv was used.
[d] 4 mol equiv was used. [e] $ZnCl_2$, $Ba(ClO_4)_2$; 0.6 mol equiv was used.
[f] 3 mol equiv was used. [g] 2.4 mol equiv of $La(ClO_4)_3 \cdot 7H_2O$ was used.

pleased to find that several rare earth metal salts were highly efficient in this reaction. For β-selectivity, the use of $Yb(OTf)_3$, K_2CO_3 and MS 4A in MeCN was found to be the most effective (Entry 1). Less satisfactory results were obtained in the absence of MS 4A.[9]

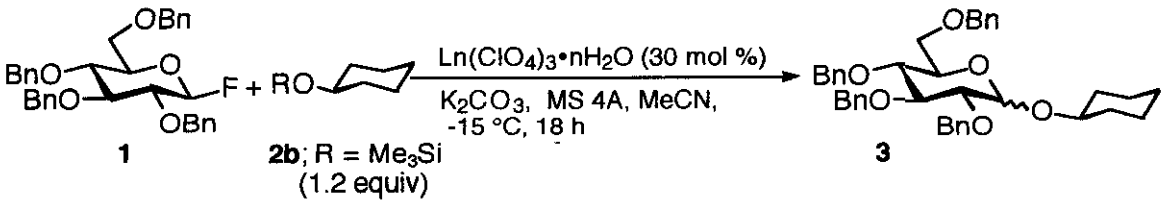
On the other hand, for α-selectivity, the utilization of either $Y(OTf)_3$ or $YbCl_3$ in ether, containing $CaCO_3$ and MS 4A, gave the best result (Entries 2, 3). Under these conditions the β- and α-glycosides (**3β**) and (**3α**), respectively, were obtained in a highly stereocontrolled manner. The structures of two isomers, α- and β-anomer, were determined by ^1H- and ^{13}C-nmr after silica gel column separation. We assume that the mechanism of these glycosidation reactions proceed *via* an oxonium cation intermediate,[10] since use of MeCN as a solvent gave β-selectivity and use of Et_2O gave α-selectivity. The use of $La(OTf)_3$ as a promoter gave less satisfactory results (Entries 4, 5). We then turned our attention to the synthesis of 2-acetamido-2-deoxy-β-glycoside of the type (**5**). 2-Acetamido-2-deoxy-β-glycosides are very important components of peptidoglycans, glycoproteins, mucopolysaccharides, and blood group determinants. To the best of our knowledge, no direct glycosidation reaction using glycosyl fluorides with the 2-acetamide moiety has been reported. Thus, it was noteworthy that treatment of **4**[8] with cyclohexanol (**2a**) (1.2 equiv) in MeCN, containing $Yb(OTf)_3$ (1.2 equiv) and MS 4A, gave only the β-glycoside (**5**) in 70% yield (Entry 6). Interestingly, when this glycosidation reaction was carried out in the presence of K_2CO_3, only the corresponding oxazoline was formed. Next the reaction was applied with the 2-deoxy sugar (**6**) as a glycosyl donor. Until now few experiments with 2-deoxy glycosyl fluorides have been reported, probably due to difficulties with control of reaction at the anomeric center.[11] It was found that exposure of **6**[8] to cyclohexanol (**2a**) (1.2 equiv), $Yb(OTf)_3$ (1.2 equiv), K_2CO_3 (4.0 mol equiv), and MS 4A in MeCN at -15 °C for 2 h gave **7** in 73% yield (α : β = 19 : 81) (Entry 7), while treatment of **6** with cyclohexanol (**2a**) (1.2 equiv) in Et_2O, in the presence of $YbCl_3$ (1.2 equiv), $CaCO_3$ (4.0 mol equiv), and MS 4A at room temperature for 4 h, afforded **7** in 88% yield (α : β = 50 : 50) (Entry 8). Moreover, the glycosylation reaction was successfully applied to the synthesis of **9β** and **9α**. As shown in Table 1, **1** was stereoselectively converted to **9β** in 68% yield (α : β = 12 : 88 Entry 9), while **1** was also transformed into **9α** stereoselectively in 88% yield (α : β = 80 : 20 Entry 10). Likewise, the glycosyl fluoride (**1**) was converted to **11** (α : β = 30 : 70), albeit in modest yield (50%, Entry 11). We have found that addition of the usual Lewis acids such as $ZnCl_2$ and $Ba(ClO_4)_2$ greatly accelerates the glycosylation reaction and also improves the chemical yield (Entries 12~15). When **11β** was reexposed to the various reaction conditions we employed, but in the absence of glycosyl fluoride, unchanged **11β** could be fully recovered. This

proved that our reaction conditions did not promote isomerization. As expected, **1** remained unchanged by treatment only with the usual Lewis acids, MS 4A, and K_2CO_3 in MeCN, strongly suggesting that $Yb(OTf)_3$ was activated by the interaction with the usual Lewis acids, especially $Ba(ClO_4)_2$ in the above case.[12] On the other hand, exposure of **1** to **10a**, $Y(OTf)_3$ (1.2 equiv), $CaCO_3$ (4.0 mol equiv), and MS 4A in Et_2O at room temperature for 41 h afforded **11**α selectively in 66% yield (α : β = 74 : 26, Entry 16). Further we examined the glycosidation reaction with the mannose derivative (**12**). Mannose is a very important component in sugar chains, where a part of mannose residues has a β-linkage at their anomeric centers.[13] Although mannosylation reactions are essential in order to synthesize sugar chains, a major problem still exists with construction of the β-linkage. We were pleased to find that treatment of **12**[8] with cyclohexanol (**2a**) (1.2 equiv), $Yb(OTf)_3$ (1.2 equiv), MS 4A and K_2CO_3 (4.0 mol equiv), in toluene at room temperature for 37 h, provided **13**β selectively in 94% yield (α : β = 35 : 65, Entry 17). This reaction was found to be also accelerated by the addition of $ZnCl_2$ (0.6 equiv) as shown in Table 1 (Entry 18). Similar reaction conditions were next applied to the mannosylation reaction using **8a** as a glycosyl acceptor, giving **14** in 94% yield (α : β = 60 : 40, Entry 19).

Finally, the glycosidation reaction using **15**[8] and **16** was investigated under a variety of reaction conditions. It was found that this reaction did not proceed in the absence of $Ba(ClO_4)_2$. Exposure of **15** to **16** (1.2 equiv), $Yb(OTf)_3$ (1.2 equiv), $Ba(ClO_4)_2$ (0.6 equiv), K_2CO_3(3 mol equiv), and MS 4A, in MeCN at 55 °C for 14 h gave only **17**β in 52% yield (Entry 21). We also examined the glycosidation reaction of **15** and **16** using $La(ClO_4)_3{\cdot}nH_2O$ as a promoter since the naked environment of the metal in lanthanum perchlorate[14] was expected to facilitate the glycosylation reaction more effectively. In fact, under these conditions we obtained only **17**β in 73% yield (Entry 22). Quite interestingly, the reaction did not proceed by the use of $Yb(ClO_4)_3{\cdot}nH_2O$ as a promoter. This result bodes well for the new method, since treatment of **15** with **16** (1.5 equiv), $SnCl_2$ (2.4 equiv), $AgClO_4$ (2.4 equiv) and MS 4A in MeCN at room temperature for 20 h[2a,3a] afforded **17**β in only 43% yield.

With these excellent results in hand, we then turned our attention to the glycosidation reaction of the glucose derivative (**1**) and cyclohexyl trimethylsilyl ether (**2b**) by using a catalytic amount of rare earth salts. Of the many types of rare earth salts available, we chose rare earth perchlorates because of the increased fluorophilicity of the metal cations as described above.[14] We were pleased to find that several rare earth perchlorates were highly efficient in promoting this type of reaction. For β-selectivity, the use of 30 mol % of $La(ClO_4)_3{\cdot}nH_2O$, $Ce(ClO_4)_3{\cdot}nH_2O$ or $Pr(ClO_4)_3{\cdot}nH_2O$, in the presence of K_2CO_3 (4 mol

equiv) and MS 4A in MeCN was found to be most effective (Table 2, Entries 1~3). Under these conditions the β-glycoside (**3**) was obtained in a highly stereocontrolled manner more efficiently than the stoichiometric procedure, which gave **3** in 63% yield (Table 1, Entry 1, α : β = 6 : 94). We also found that the α-glycoside was obtained exclusively (94%) on treatment of **1** with **2b**, $La(ClO_4)_3 \cdot nH_2O$ (30 mol %), $CaCO_3$ (4 mol equiv), MS 4A in Et_2O (Table 3, Entry 1). In addition, the glycosidation reaction of **1** with **2b** by 20 mol % of $La(ClO_4)_3 \cdot nH_2O$, K_2CO_3 and MS 4A in MeCN at room temperature also gave the product in 95% yield (Table 2, Entry 2, α : β = 24 : 76). To better understand the mechanism of this



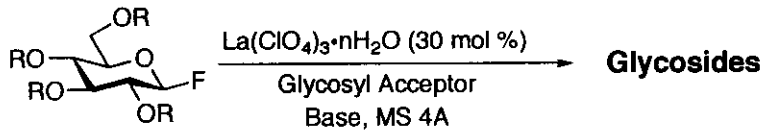
1 **2b**; R = Me_3Si (1.2 equiv) **3**

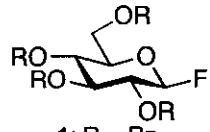
Table 2. Glycosidation Reactions Using Rare Earth Perchlorates

Entry	$Ln(ClO_4)_3 \cdot nH_2O$	R	Yield (%)	α : β
1	$La(ClO_4)_3 \cdot nH_2O$	Me_3Si	82	8 : 92
2	$La(ClO_4)_3 \cdot nH_2O$[a]	Me_3Si	95	24 : 76
3	$Ce(ClO_4)_3 \cdot nH_2O$	Me_3Si	89	β[b]
4	$Pr(ClO_4)_3 \cdot nH_2O$	Me_3Si	80	β[b]
5	$Eu(ClO_4)_3 \cdot nH_2O$	Me_3Si	61	15 : 85
cf[c]	$Yb(OTf)_3$	H	63	6 : 94

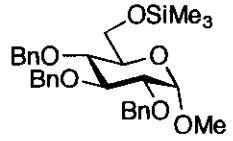
[a] 20 mol % of $La(ClO_4)_3 \cdot nH_2O$ was used at room temperature.
[b] α-Anomer was not detectable by ^1H nmr analysis.
[c] See Table 1, Entry 1.

glycosylation reaction, we obtained the ^{19}F nmr spectrum of the reaction mixture in acetonitrile-d_3, and only trimethylsilyl fluoride was observed.[15] This result suggests that the interaction of the glycosyl fluoride with the rare earth perchlorate produces an oxonium cation intermediate, which then reacts with the trimethylsilyl ether to form the glycoside, trimethylsilyl fluoride, and rare earth perchlorate, thereby making possible the catalytic cycle. Furthermore, it is noteworthy that the glycosidation does not proceed in the presence of rare earth perchlorates such as $Gd(ClO_4)_3 \cdot nH_2O$, $Ho(ClO_4)_3 \cdot nH_2O$, $Yb(ClO_4)_3 \cdot nH_2O$, $Y(ClO_4)_3 \cdot nH_2O$, suggesting that only rare earth metals with a certain range of ionic radii are effective for this type of glycosidation. On the basis of the above results, we have selected $La(ClO_4)_3 \cdot 7H_2O$ as an economical catalyst for this reaction.[16]

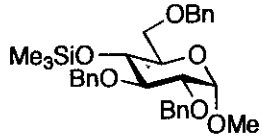




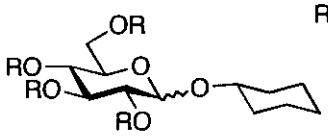
1; R = Bn
15; R = Bz
18; R = Ac



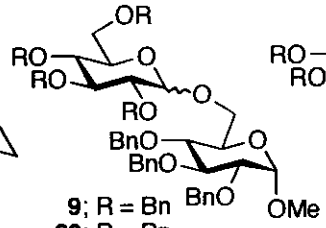
8b



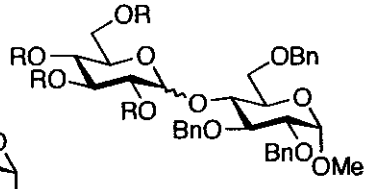
10b



3; R = Bn
19; R = Bz



9; R = Bn
20; R = Bz
21; R = Ac

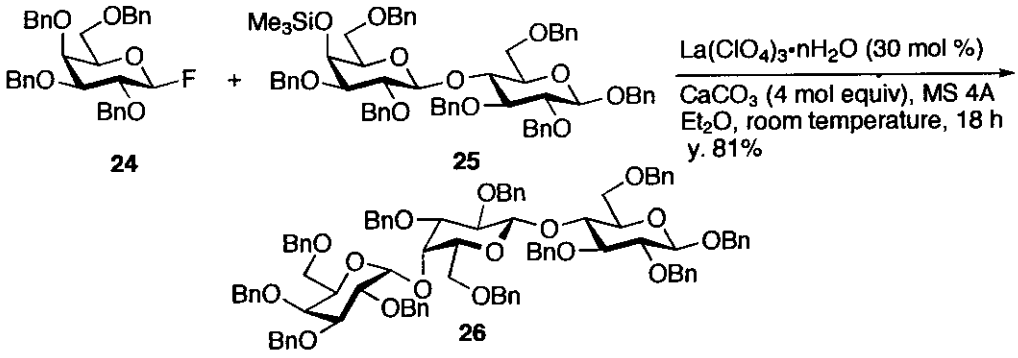


11; R = Bn
22; R = Bz
23; R = Ac

Table 3. Glycosidation Reactions by $La(ClO_4)_3 \cdot nH_2O$ (30 mol %)

Entry	Glycosyl Donor	Glycosyl Acceptor[a]	Solv.	Base[b]	Temp. (°C)	Time (h)	Glycosides	Yield (%)	α : β
1	**1**	**2b**	Et_2O	$CaCO_3$	rt	18	**3**	94	α[d]
2	**15**	**2b**	MeCN	K_2CO_3	0	2	**19**	94	β
3	**1**	**8b**	MeCN	K_2CO_3	-15	38	**9**	85	9 : 91
4	**1**	**8b**	Et_2O	$CaCO_3$	rt	18	**9**	94	75 : 25
5	**15**	**8b**	MeCN	K_2CO_3	rt	2	**20**	93	β
6	**18**	**8b**	MeCN	K_2CO_3	5	1	**21**	80	β
7	**1**	**10b**	MeCN	K_2CO_3	-15	38	**11**	75	23 : 77
8	**1**	**10b**	Et_2O	$CaCO_3$	rt	24	**11**	63	78 : 22
9	**15**	**10b**[c]	MeCN	K_2CO_3	rt	1	**22**	99	β
10	**18**	**10b**	MeCN	K_2CO_3	5	1	**23**	75	β

[a] 1.2 equiv was used [b] 4 mol equiv was used. [c] 1 5 equiv was used [d] β-Anomer was not detectable by ^{1}H-nmr analysis.



24

25

26

Next we examined the glycosidation of **1** with the 2,3,4- and 2,3,6-benzyl protected glucopyranoside derivatives (**8b**) and (**10b**). As shown in Table 3, these reactions were found to proceed smoothly, giving **9** (Entry 3, 85%, $\alpha : \beta = 9 : 91$), **9** (Entry 4, 94%, $\alpha : \beta = 75 : 25$), **11** (Entry 7, 75%, $\alpha : \beta = 23 : 77$), and **11** (Entry 8, 63%, $\alpha : \beta = 78 : 22$). Also in these cases, improved results were obtained in comparison with the stoichiometric procedure (See Table 1, Entry 9). Some other examples of the $La(ClO_4)_3$ catalyzed glycosidation reactions using benzoyl or acetyl protected glycosyl fluorides[17] are also summarized in Table 3. The reactions were found to proceed quite smoothly, affording only the β-glycosides (**20**),[18] (**21**),[19] (**22**),[18] and/or (**23**)[19] in good to excellent yields. Particularly noteworthy are the glycosidations using 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl fluoride (**18**) (Entries 6 and 10), because no reaction had occurred using the stoichiometric procedure.

Finally, this glycosylation method was applied in the synthesis of the trisaccharide of an intermediate leading to globotriaosyl ceramide.[20] It has been well established that glycosphingolipides are molecules of considerable biological significance within the area of cellular recognition. We were pleased to find that the $La(ClO_4)_3$ catalyzed glycosidation reaction of the galactosyl fluoride (**24**) with the lactosyl derivative (**25**)[20] proceeded efficiently to give the α-trisaccharide (**26**) exclusively in 81% yield. The stoichiometric procedure gave **26** in 75% yield.

In conclusion, we have succeeded in developing a glycosylation reaction using rare earth metal salts with or without the requirement of the usual Lewis acids such as $ZnCl_2$, and $Ba(ClO_4)_2$ and also an improved rare earth perchlorate catalyzed glycosidation of glycosyl fluorides with trimethylsilyl ethers. We believe that this glycosylation reaction could play a key role in glycosidations using glycosyl fluorides as a glycosyl donor. Moreover, the results described herein should be quite instructive for future research utilizing rare earth metals in organic synthesis.

EXPERIMENTAL

^1H- Nmr and ^{13}C-nmr spectra were recorded on a JEOL JNM-EX 270 spectrometer with tetramethylsilane as a internal standard and ir spectra were measured on a PERKIN-ELMER 1600 Series FTIR spectrophotometer. Optical rotations were measured with a JASCO DIP-140 digital polarimeter. Mass spectra were obtained on JEOL-DX 303 mass spectrometer. Merck Kieselgel 60 F 254 was employed for column chromatography.

A typical stoichiometric procedure: An activator (a rare earth metal salt, 1.2 mol equiv to a glycosyl donor), an inorganic base (K_2CO_3 or $CaCO_3$, 4.0 mol equiv) and MS 4A (*ca.* 100 mg) were dried at *ca.* 110 °C *in vacuo* for 2 h. A solution (1 ml) of a well-dried glycosyl fluoride(**1**)(30 mg, 0.055 mmol) and

glycosyl acceptor (1.2 equiv) was then added. After the reaction was complete, saturated aq. $NaHCO_3$ was added. Filtration to remove inorganic materials and usual work up gave a product which was purified by silica gel column chromatography.

A typical catalytic procedure: First $La(ClO_4)_3 \cdot 7H_2O$ (30 mol % to a glycosyl donor), an inorganic base (K_2CO_3 or $CaCO_3$, 4.0 mol equiv) and MS 4A (*ca.* 50 mg) were dried at *ca.* 180 °C *in vacuo* for 2 h, leaving about two waters of hydration. A solution (2 ml) of the glycosyl fluoride(**1**)(54.2 mg, 0.1 mmol) and the glycosyl acceptor (1.2 equiv) was then added. After the reaction was complete, saturated aq. $NaHCO_3$ was added. Filtration to remove inorganic compounds and usual work up gave a product which was purified by silica gel column chromatography.

Spectral and Analytical Data

Cyclohexyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranoside (3α) : $[\alpha]_D^{25}$ +24.8° (*c* 1.0, $CHCl_3$); ir (neat) 3087, 3063, 3029, 2931, 2857, 1737, 1496, 1453, 1359, 1159, 1072, 1028, 736, 697 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.38-7.12 (m, 20 H, aromatic), 5.02-4.43 (m, 8 H, benzyl), 4.95 (d, 1 H, *J* = 3.7 Hz, H-1), 4.00 (t, 1 H, *J* = 9.0 Hz, H-4), 3.88 (ddd, 1 H, *J* = 2.0, 3.5, 9.0 Hz, H-5), 3.74 (dd, 1 H, *J* = 3.5, 10.5 Hz, H-6a), 3.63 (dd, 1 H, *J* = 9.0, 9.5 Hz, H-3), 3.62 (dd, 1 H, *J* = 2.0, 10.5 Hz, H-6b), 3.55 (dd, 1 H, *J* = 3.7, 9.5 Hz, H-2), 3.54 (m, 1 H), 1.18-1.95 (m, 10 H); ^{13}C-nmr ($CDCl_3$) δ 139.9, 139.3, 139.2, 138.9, 129.7-128.4 (20 C), 95.6, 83.0, 80.9, 78.8, 76.6, 76.2, 76.0, 74.3, 73.9, 71.0, 69.5, 34.3, 32.4, 26.5, 25.4, 25.1; ms *m/z* 531 (M^+-Bn); Anal. Calcd for $C_{40}H_{46}O_6$: C, 77.14; H, 7.44. Found: C, 76.86; H, 7.44.

Cyclohexyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranoside (3β) : $[\alpha]_D^{25}$ +12.2° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 3018, 2934, 2859, 1716, 1453, 1362, 1277, 1216, 1069, 758, 668 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.38-7.15 (m, 20 H, aromatic), 5.04-4.51 (m, 8 H, benzyl), 4.53 (d, 1 H, *J* = 8.0 Hz, H-1), 3.77 (dd, 1 H, *J* = 1.8, 11 Hz, H-6a), 3.72 (m, 1 H), 3.67 (dd, 1 H, *J* = 4.9, 11 Hz, H-6b), 3.66 (t, 1 H, *J* = 9.0 Hz), 3.56 (t, 1 H, *J* = 9.0 Hz), 3.48 (ddd, 1 H, *J* = 1.8, 4.9, 9.0 Hz, H-5), 3.47 (dd, 1 H, *J* = 8.0, 9.0 Hz, H-2), 2.07-1.20 (m, 10 H); ^{13}C-nmr ($CDCl_3$) δ 138.7, 138.6, 138.3, 138.2, 128.3-127.5 (20 C), 102.0, 84.9, 82.3, 78.0, 77.8, 75,7, 75.0, 74.8 (2 C), 73.4, 69.2, 33.8, 32.0, 25.6, 24.1, 24.0; Anal. Calcd for $C_{40}H_{46}O_6$: C, 77.14; H, 7.44. Found: C, 76.84; H, 7.60.

Cyclohexyl 2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (5) : $[\alpha]_D^{25}$ +15.1° (*c* 0.5, $CHCl_3$); ir ($CHCl_3$) 3018, 2935, 1676, 1518, 1215, 1066, 756, 669 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.38-7.12 (m, 15 H, aromatic), 5.51 (d, 1 H, *J* = 7.5 Hz, NH), 4.92 (d, 1 H, *J* = 8.0 Hz, H-1), 4.78-4.46 (m, 6 H, benzyl), 4.18 (m, 1 H), 3.71-3.48 (m, 5 H), 3.12 (dt, 1 H, *J* = 8.0, 10.0 Hz), 1.78 (s, 3 H, Ac), 1.91-1.05 (m, 10 H); ^{13}C-nmr ($CDCl_3$) δ 170.4, 138.6, 138.3, 138.1, 128.4-127.5 (15 C), 97.9, 80.3, 79.0, 77.3 (2 C), 74.7 (2 C), 74.6, 73.4, 58.2, 33.5, 31.9, 25.6, 24.1, 23.9, 23.6; ms *m/z* 574 (M^+); Anal. Calcd for $C_{35}H_{43}NO_6$: C, 73.27; H, 7.55; N, 2.44. Found: C, 72.98; H, 7.72; N, 2.52.

Cyclohexyl 2-Deoxy-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7α) : $[\alpha]_D^{25}$ +11.5° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 3016, 2935, 2858, 1496, 1453, 1364, 1216, 1099, 1049, 1028, 998, 756, 698, 668

cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.40-7.15 (m, 15 H, aromatic), 5.12 (dd, 1 H, *J* = 0.9, 2.7 Hz, H-1), 4.91-4.48 (m, 6 H, benzyl), 4.02 (ddd, 1 H, *J* = 5.0, 9.0, 12.0 Hz, H-3), 3.88 (ddd, 1 H, *J* = 1.5, 3.5, 9.5 Hz, H-5), 3.80 (dd, 1 H, *J* = 3.5, 10.0 Hz, H-6a), 3.67 (dd, 1 H, *J* = 1.5, 10.0 Hz, H-6b), 3.61 (t, 1 H, *J* = 9.0, 9.5 Hz, H-4), 3.55 (m, 1 H), 2.24 (ddd, 1 H, *J* = 0.9, 5.0, 13.0 Hz, H-2eq), 1.92-1.10 (m, 11 H); ^{13}C-nmr ($CDCl_3$) δ 138.8, 138.5, 138.2, 128.3-127.5 (15 C), 95.0, 78.5, 77.8, 75.0, 74.3, 73.4, 71.7, 70.7, 69.0, 36.0, 33.4, 31.4, 25.7, 24.3, 24.0; ms *m/z* 516 (M^+), 425 (M^+-Bn).

Cyclohexyl 2-Deoxy-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (7β) : $[\alpha]_D^{25}$ +42.2° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 3018, 2935, 2859, 1496, 1454, 1365, 1216, 1096, 768, 669 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.40-7.15 (m, 15 H, aromatic), 4.91 (d, 1 H, *J* = 11 Hz, benzyl), 4.70 (d, 1 H, *J* = 11.5 Hz, benzyl), 4.62-4.55 (m, 5 H, 4 benzyl and H-1), 3.78 (dd, 1 H, *J* = 2.0, 11 Hz, H-6a), 3.69 (dd, 1 H, *J* = 5.0, 11 Hz, H-6b), 3.72-3.62 (m, 2 H, H-3 and c-hexyl), 3.48 (t, 1 H, *J* = 9.5 Hz, H-4), 3.42 (ddd, 1 H, *J* = 2.0, 5.0, 9.5 Hz, H-5), 2.32 (ddd, 1 H, *J* = 2.0, 5.0, 12.5 Hz, H-2eq), 2.07-1.10 (m, 11 H); ^{13}C-nmr ($CDCl_3$) δ 138.54, 138.45, 138.4, 128.3-127.5 (15 C), 97.7, 79.7, 78.2, 76.6, 75.1, 75.0, 73.4, 71.3, 69.5, 37.3, 33.7, 32.0, 25.6, 24.3, 24.2; ms *m/z* 425 (M^+-Bn).

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (9α) : $[\alpha]_D^{25}$ +44.8° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 3019, 1216, 771 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.40-7.10 (m, 35 H, aromatic), 4.98-4.39 (m, 14 H, benzyl), 4.97 (d, 1 H, *J* = 3.7 Hz, H-1'), 4.56 (d, 1 H, *J* = 3.5 Hz, H-1), 3.99 (t, 1 H, *J* = 9.0 Hz), 3.96 (t, 1 H, *J* = 9.0 Hz), 3.86-3.71 (m, 4 H), 3.70-3.60 (m, 3 H), 3.60-3.51 (m, 2 H), 3.44 (dd, 1 H, *J* = 3.5, 9.5 Hz), 3.35 (s, 3 H, OMe); ^{13}C-nmr ($CDCl_3$) δ 139.1-138.3 (7 C), 128.7-127.9 (35 C), 98.3, 97.6, 82.4, 82.0, 80.5, 80.3, 78.1, 77.9, 76.0, 75.8, 75.3, 75.2, 73.7 (2 C), 72.7, 70.7, 70.5, 68.8, 66.3, 55.5; ms *m/z* 895 (M^+-Bn), 864 (M^+-Bn-OMe); Anal. Calcd for $C_{62}H_{66}O_{11}$ C, 75.43; H, 6.74. Found: C, 75.13; H, 7.02.

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (9β) : $[\alpha]_D^{25}$ +23.5° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 3019, 1215, 929, 756, 668 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.37-7.13 (m, 35 H, aromatic), 5.00-4.48 (m, 14 H, benzyl), 4.60 (d, 1 H, *J* = 3.6 Hz, H-1), 4.34 (d, 1 H, *J* = 7.7 Hz, H-1'), 4.18 (dd, 1 H, *J* = 1.4, 9.9 Hz), 3.98 (t, 1 H, *J* = 9.0 Hz), 3.82 (ddd, 1 H, *J* = 0.9, 4.5, 9.9 Hz), 3.71-3.40 (m, 8 H), 3.59 (t, 1 H, *J* = 9.0 Hz), 3.32 (s, 3 H, OMe); ^{13}C-nmr ($CDCl_3$) δ 138.8-138.1 (7 C), 128.4-127.5 (35 C), 103.8, 98.0, 84.7, 82.0, 81.9, 79.7, 78.0, 77.9, 75.7 (2 C), 75.0 (2 C), 74.8 (2 C), 73.4, 73.3, 69.8, 69.0, 68.5, 55.2; ms *m/z* 895 (M^+-Bn), 879 (M^+-OBn); Anal. Calcd for $C_{62}H_{66}O_{11}$: C, 75.43 H, 6.74. Found: C, 75.21; H, 6.90.

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (11α) : $[\alpha]_D^{25}$ +47.5° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 3018, 1216, 1049, 757, 668 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.30-7.05 (m, 35 H, aromatic), 5.69 (d, 1 H, *J* = 3.6 Hz, H-1'), 5.03 (d, 1 H, *J* = 12 Hz, benzyl), 4.88 (d, 1 H, *J* = 11 Hz, benzyl), 4.82-4.75 (m, 3 H, benzyl), 4.69 (d, 1 H, *J* = 12 Hz, benzyl), 4.62-4.49 (m, 7 H, 6 benzyl and H-1), 4.42 (d, 1 H, *J* = 11 Hz, benzyl), 4.27 (d, 1 H, *J* = 12

Hz, benzyl), 4.12-4.00 (m, 2 H), 3.94-3.80 (m, 3 H), 3.74-3.57 (m, 4 H), 3.49-3.40 (m, 3 H), 3.37 (s, 3 H) ; ^{13}C-nmr ($CDCl_3$) δ 138.9-137.9 (7 C), 128.4-126.7 (35 C), 97.7, 96.6, 82.0 (2 C), 80.2, 79.4, 77.6, 75.5, 74.9, 74.4, 73.42, 73.35, 73.2, 73.1, 72.3, 70.9, 69.5, 69.0, 68.1, 55.1 ; ms *m/z* 895 (M^+-Bn).

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (11β) : $[\alpha]_D^{25}$ +20.7° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 3028, 2926, 1652, 1636, 1558, 1540, 1506, 1496, 1455, 1362, 1216, 1070, 757, 699 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.45-7.17 (m, 35 H, aromatic), 5.09 (d, 1 H, *J* = 11 Hz, benzyl), 4.87 (d, 1 H, *J* = 11 Hz, benzyl), 4.82-4.71 (m, 6 H, benzyl), 4.62-4.53 (m, 3 H, benzyl), 4.55 (d, 1 H, *J* = 3.0 Hz, H-1), 4.46-4.35 (m, 3 H, benzyl), 4.40 (d, 1 H, *J* = 7.0 Hz, H-1'), 3.97 (t, 1 H, *J* = 9.5 Hz), 3.85 (m, 2 H), 3.71 (dd, 1 H, *J* = 1.5, 11 Hz), 3.63-3.53 (m, 3 H), 3.50-3.43 (m, 4 H), 3.36 (s, 3 H), 3.33-3.27 (m, 1 H); ^{13}C-nmr ($CDCl_3$) δ 139.6-137.8 (7 C), 128.7-127.0 (35 C) 102.4, 98.4, 84.8, 82.8, 80.4, 78.8, 78.0, 75.5, 75.3, 75.1, 74.9, 74.7, 73.6, 73.3 (2 C), 69.9, 69.0, 67.8, 55.3 ; ms *m/z* 895 (M^+-Bn).

Cyclohexyl 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranoside (13α) : $[\alpha]_D^{25}$ +26.9° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 3018, 2934, 1453, 1215, 1062, 1028, 760, 669 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.36-7.15 (m, 20 H, aromatic), 4.99 (d, 1 H, *J* = 1.65 Hz, H-1), 4.89-4.48 (benzyl, 8 H), 3.99 (t, 1 H, *J* = 8.9 Hz, H-4), 3.93 (dd, 1 H, *J* = 3.0, 8.9 Hz, H-6a), 3.86 (ddd, 1 H, *J* = 3.0, 4.6, 8.9 Hz, H-5), 3.80 (dd, 1 H, *J* = 4.6, 10.6 Hz, H-6b), 3.72 (dd, 1 H, *J* = 1.65, 4.6 Hz, H-2), 3.73 (dd, 1 H, *J* = 4.6, 8.9 Hz, H-3), 3.64-3.50 (m, 1 H), 1.88-1.09 (m, 10 H); ^{13}C-nmr ($CDCl_3$) δ 138.7-138.5 (4 C), 128.3-127.4 (20 C), 97.5, 80.3, 75.4, 75.2 (2 C), 74.7, 73.3, 72.6, 72.2, 71.8, 69.4, 33.2, 31.3, 25.6, 24.0, 23.8 ; ms *m/z* 531 (M^+-Bn).

Cyclohexyl 2,3,4,6-Tetra-*O*-benzyl-β-D-mannopyranoside (13β) : $[\alpha]_D^{25}$ -40.5° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 2932, 1558, 1506, 1456, 1216, 1109, 756 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.50-7.16 (m, 20 H, aromatic), 5.04-4.89 and 4.56-4.40 (m, 8 H, benzyl), 4.61 (d, 1 H, *J* = 1.0 Hz, H-1), 3.84 (t, 1 H, *J* = 9.0 Hz, H-4), 3.86 (dd, 1 H, *J* = 3.0, 1.0 Hz, H-2), 3.83 (dd, 1 H, *J* = 1.8, 10.5 Hz, H-6a), 3.73 (dd, 1 H, *J* = 6.0, 10.5 Hz, H-6b), 3.77-3.66 (m, 1 H), 3.50 (dd, 1 H, *J* = 3.0, 9.0 Hz, H-3), 3.44 (ddd, 1 H, *J* = 1.8, 6.0, 9.8 Hz, H-5), 2.02-1.20 (m, 10 H); ^{13}C-nmr ($CDCl_3$) δ 138.7-138.5 (4 C), 128.3-127.4 (20 C), 99.5, 82.6, 76.7, 75.9, 75.1, 75.0, 74.1, 73.7, 73.4, 71.4, 69.9, 33.5, 31.6, 25.7, 23.8, 23.7 ; ms *m/z* 531 (M^+-Bn) ; Anal. Calcd for $C_{40}H_{46}O_6$: C, 77.14; H, 7.44. Found: C, 76.94; H, 7.73.

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (14α) : $[\alpha]_D^{25}$ +37.5° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 3018, 2928, 1754, 1665, 1596, 1496, 1454, 1360, 1215, 1088, 756, 698, 669 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.39-7.11 (m, 35 H, aromatic), 4.98-4.43 (m, 14 H, benzyl), 4.97 (d, 1 H, *J* = 1.95 Hz, H-1'), 4.89 (d, 1 H, *J* = 10.6 Hz), 3.99 (t, 1 H, *J* = 9.8 Hz, H-4'), 3.97 (t, 1 H, *J* = 9.8 Hz, H-3), 3.87-3.81 (m, 2 H), 3.78 (dd, 1 H, *J* = 1.95, 2.2 Hz, H-2'), 3.72-3.57 (m, 5 H), 3.45 (dd, 1 H, *J* = 3.4, 9.8 Hz, H-2), 3.39 (t, 1 H, *J* = 9.8 Hz, H-4), 3.30 (s,

3H, OMe); ^{13}C-nmr ($CDCl_3$) δ 138.7-138.1 (7 C), 128.5-127.4 (35 C), 98.3, 97.8, 82.1, 80.0, 79.6, 77.6 (2 C), 75.8, 75.0, 74.9, 74.7, 73.2 (2 C), 72.5, 72.0, 71.9, 69.8, 69.1, 65.8, 55.1; ms *m/z* 895 (M^+-Bn).

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-β-D-mannopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (14β) : $[\alpha]_D^{25}$ -18.1° (*c* 0.25, $CHCl_3$); ir ($CHCl_3$) 2948, 1453, 1383, 1094, 910, 731, 651 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.43-7.15 (m, 35 H, aromatic), 5.04-4.50 (m, 14 H, benzyl), 4.58 (d, 1 H, *J* = 3.0 Hz, H-1), 4.16 (dd, 1 H, *J* = 1.6, 10.5 Hz), 4.13 (d, 1 H, *J* = 0 Hz, H-1"), 4.02 (t, 1 H, *J* = 9.0 Hz), 3.88-3.68 (m, 5 H), 3.54-3.35 (m, 5 H), 3.33 (s, 3H, OMe); ^{13}C-nmr ($CDCl_3$) δ 138.8-138.1 (7 C), 128.4-127.4 (35 C), 101.5, 97.8, 82.3, 82.1, 79.9, 77.6, 77.2, 76.0, 75.7, 75.1, 75.0, 74.7, 73.6, 73.5, 73.3, 71.6, 69.8, 69.7, 68.3, 55.0; ms *m/z* 895 (M^+-Bn).

Methyl *O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→4)-(2-deoxy-2-*N*-acetyl-amino)-3-allyl-6-*O*-benzyl-α-D-glucopyranoside(17): $La(ClO_4)_3 \cdot 7H_2O$ (2.4 mol equiv to **15**), K_2CO_3 (4.0 mol equiv) and MS 4A (*ca.* 190 mg) were dried at *ca.* 180 °C *in vacuo* for 2 h. A CH_3CN solution (1 ml) of the glycosyl fluoride (**15**) (30 mg, 0.055 mmol) and the glycosyl acceptor (**16**) (1.2 equiv) was then added at -15 °C. After the reaction was complete, saturated aq. $NaHCO_3$ was added. Filtration to remove inorganic materials and usual work up gave a product which was purified by silica gel column chromatography. $[\alpha]_D^{25}$ +48.9° (*c* 0.5, $CHCl_3$); ir ($CHCl_3$) 2925, 1732, 1666, cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.88 (m, 8 H), 7.42 (m, 17 H), 5.86-5.43 (m, 5 H, allyl, H-4', H-3', H-2', NH), 5.07 (dd, *J* = 11.2, 15.8 Hz, 2 H, allyl), 4.80 (d, 1 H, *J* = 8.2 Hz, H-1'), 4.73 (d, 1 H, *J* = 12.2 Hz, allyl), 4.68 (d, 1 H, *J* = 3.6 Hz, H-1), 4.61 (dd, 1 H, *J* = 7.9, 12.2 Hz, allyl), 4.40 (m, 3 H, H-6', H-6, benzyl), 4.17 (m, 1 H, H-2), 4.40 (m, 2 H, H-4, benzyl), 3.84 (m, 1 H, H-5'), 3.68 (dd, 1 H, H-5), 3.45 (m, 3 H, H-3, H-6a,b), 3.24 (s, 3 H), 1.97 (s, 3 H); ^{13}C-nmr ($CDCl_3$) ppm 169.8, 166.2, 165.7, 165.1, 164.9, 138.1, 133.4, 133.3, 129.8, 129.6, 129.0, 128.9, 128.8, 128.5, 128.4, 128.3, 128.1, 116.4, 100.5, 98.5, 77.8, 77.4, 73.5, 73.2, 73.1, 72.3, 71.9, 70.2, 69.6, 67.5, 62.8, 55.1, 52.3, 23.4; ms *m/z* 944 (M^+), 912 (M^+-OMe), 886 (M^+-NHAc), 597, 105 ; Anal. Calcd for $C_{53}H_{53}NO_{15}$: C, 67.43; H, 5.66; N, 1.48. Found: C, 67.46; H, 5.78; N, 1.42.

Methyl *O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (20) : $[\alpha]_D^{25}$ +21.7° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 2929, 1733, 1451, 1265, 1092, 1069, 1027, 709 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.80-8.05 (m, 8 H), 7.01-7.52 (m, 27 H), 5.89 (t, *J* = 9.6 Hz,1 H), 5.68 (t, *J* = 9.6 Hz, 1 H), 5.60 (dd, 1 H, *J* = 7.9, 9.6 Hz), 4.85 (d, 1 H, *J* = 9.6 Hz), 4.51 (d, 1 H, *J* = 3.3 Hz), 4.27-4.91 (m, 7 H), 4.12 (m, 2 H), 3.89 (t, *J* = 9.2 Hz, 1 H), 3.74 (m, 2 H), 3.44 (m, 2 H), 3.21 (s, 3 H, OMe); ^{13}C-nmr ($CDCl_3$) δ 164.9-166.0 (4 C), 127.4-138.7 (42 C), 101.3, 97.9, 81.8, 79.7, 77.3, 75.4, 74.6, 73.3, 72.8, 72.1, 71.8, 69.7, 69.4, 68.2, 63.2, 54.9; ms *m/z* 951 (M^+-Bn).

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (21) : $[\alpha]_D^{25}$ +6.8° (*c* 0.5, $CHCl_3$); ir ($CHCl_3$) 2924, 1730, 1360, 1187, 1034 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.36 (m, 15 H), 5.22 (t, 1 H, *J* = 9.2 Hz), 5.16 (t, 1 H, *J* = 7.9 Hz), 5.04 (m, 2 H),

4.86 (m, 3 H), 4.65 (m, 2 H), 4.60 (d, 1 H, J = 3.6 Hz), 4.54 (d, 1 H, J = 7.6 Hz), 4.27 (dd, 1 H, J = 4.6, 12.5 Hz), 4.07 (m, 3 H), 3.75 (m, 3 H), 3.59 (dd, 1 H, J = 3.6, 3.3 Hz), 3.47 (t, 1 H, J = 9.2 Hz), 3.39 (s, 3 H), 2.04 (s, 3H), 2.01 (s, 3 H), 1.99 (s, 3 H), 1.95 (s, 3 H); ^{13}C-nmr ($CDCl_3$) δ 171.1, 170.8, 169.8, 169.5, 128.1-139.2 (18 C), 101.2, 98.5, 82.4, 80.3, 78.1, 77.6, 77.3, 76.2, 75.3, 73.9, 73.4, 72.2, 71.7, 70.1, 68.8, 68.7, 62.4, 55.6, 21.0 (4 C); ms *m/z* 703 (M^+-Bn).

Methyl *O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (22) : $[\alpha]_D^{25}$ +1.0° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 2938, 1730, 1601, 1451, 1263, 1176, 1092, 709 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.75-7.99 (m, 8 H), 7.05-7.53 (m, 27 H), 5.43-5.66 (m, 3 H), 5.07 (d, 1 H, J = 11.2 Hz), 4.74 (d, 1 H, J = 9.2 Hz), 4.55 (d, 1 H, J = 3.9 Hz), 4.31-4.82 (m, 5 H), 4.40 (dd, J = 3.3, 12.2 Hz, 1 H), 4.25 (dd, J = 4.9, 12.2 Hz, 1 H), 3.92 (m, 2 H), 3.72 (m, 2 H), 3.48 (m, 3 H), 3.27 (s, 3 H); ^{13}C-nmr ($CDCl_3$) δ 164.7-165.9 (4 C), 127.1-139.2 (42 C) 100.3, 98.4, 79.9, 78.7, 77.2, 75.3, 73.6, 73.5, 73.1, 72.2, 71.8, 69.8, 69.4, 67.5, 63.1, 55.3 ; ms *m/z* 951 (M^+-Bn).

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (23) : $[\alpha]_D^{25}$ -6.3° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 2924, 1757, 1452, 1366, 1220, 1039 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 7.29 (m, 15 H), 4.95 (m, 4 H), 4.74 (m, 3 H), 4.56 (d, 1 H, J = 3.6 Hz), 4.49 (d, 1 H, J = 7.6 Hz), 4.60-4.39 (m, 2 H), 4.13 (dd, 1 H, J = 3.9, 12.2 Hz), 3.85 (m, 4 H), 3.60 (m, 2 H), 3.47 (dd, J = 3.6, 9.6 Hz, 1 H), 3.36 (s, 3 H), 3.28 (m, 1 H), 2.01, 1.99, 1.98, 1.97 (4s, 12 H); ^{13}C-nmr ($CDCl_3$) δ 170.6, 170.2, 169.3, 169.0, 127.2-139.3 (18 C), 100.0, 98.4, 79.9, 78.8, 77.2, 75.1, 73.7, 73.5, 73.2, 71.9, 71.4, 69.5, 68.1, 67.5, 61.6, 55.4, 20.6 (4 C); ms *m/z* 793 (M^+), 703 (M^+-Bn).

Benzyl O-(2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (26): $[\alpha]_D^{25}$ +71.3° (*c* 1.0, $CHCl_3$); ir ($CHCl_3$) 2925, 2867, 1724, 1603, 1497, 1453, 1364, 1274, 1052, 750, 698 cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 4.73 (d, 1 H, J = 3.3 Hz), 4.44 (d, 1 H, J = 6.6 Hz), 4.24 (d, 1 H, J = 6.2 Hz), 3.81 (dd, 1 H, J = 4.4, 10.9 Hz), 3.15 (dd, 1 H, J = 4.8, 4.4 Hz); ^{13}C-nmr ($CDCl_3$) ppm 133.9-132.4 (11C), 123.3-121.4 (55C), 102.8, 102.5, 100.7, 82.7, 79.4, 77.2, 75.2, 75.1, 75.0, 74.9, 73.7, 73.3, 73.2, 73.0, 72.4, 72.1, 70.9, 69.4, 68.3, 67.8, 67.7.

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16. Purchased from Soekawa Chemical Co., Ltd., Tokyo, Japan ($La(ClO_4)_3 \cdot 7H_2O$ is cheaper than $Ce(ClO_4)_3 \cdot 8H_2O$ and $Pr(ClO_4)_3 \cdot 6H_2O$).

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