A Novel Glycosidation Promoted by the Combination of Trimethylsilyl Halide and Zinc Triflate

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A novel glycosidation method has been developed which utilizes a trimethylsilyl halide–zinc triflate catalyst system to activate various benzyl-protected fucosyl, glucosyl and galactosyl esters. The promoter system was extended to use benzyl-protected alkyl glycosides and *N*-2,2,2,-trichloroethoxycarbonyl-protected glucosaminyl and galactosaminyl acetates as glycosyl donors.

Keywords glycosidation; trimethylsilyl chloride; trimethylsilyl bromide; zinc triflate; activator; glycosyl donor; glycosyl ester; glycosaminyl acetate; alkyl glycoside; steroidal glycoside

The very high abundance and paramount biological importance of oligosaccharides and glycoconjugates necessitate the development of new methods for the efficient and stereocontrolled construction of glycosidic linkages.[1,2] Recently, we have developed a glycosidation, catalyzed by a combination of trimethylsilyl bromide (TMSBr) and zinc bromide ($ZnBr_2$) using simple *O*-glycosides of glucosamine derivatives directly as glycosyl donors.[3] This methodology was also applicable to acetyl-protected glucopyranosides other than glucosamine, though low conversion to the glycosidation product was encountered with such substrates. As an extension of the studies on glycosidation by the combined use of trimethylsilyl halide (TMSX) and Lewis acid as activators, in this paper, we describe an improved glycosidation, promoted by the combination of TMSX and zinc triflate ($Zn(OTf)_2$) using various 1-*O*-acyl[4] and 1-*O*-alkyl glycopyranosides[5] as glycosyl donors.

The glycosyl esters (**1**, **2**, **5**, **6**, **8**—**10**) and alkyl glycosides (**3**, **4**, **7**) used here as glycosyl donors for this glycosidation are shown in Chart 1. These compounds were easily prepared according to published procedures and could be stored at 5 °C for at least several weeks without detectable deterioration.

First, we evaluated the catalyst system generated from the TMSX–Lewis acid type species in a glycosidation using benzyl-protected fucose derivatives (**1**—**4**) having an acyloxy or alkoxy moiety at the anomeric position as a leaving group.[6] Since the combined use of TMSBr and $ZnBr_2$ was presumed to cleave the benzyl ether bond, we postulated that the Lewis acid $Zn(OTf)_2$, would be the preferred reagent. Initially the glycosidation reactions were investigated with 3β-cholestanol (**11a**) as a model acceptor and benzyl-protected fucopyranosyl *p*-nitrobenzoate (**1**) as a donor.[7] After surveying a variety of conditions, coupling of the *p*-nitrobenzoate (**1**,[8] a 36 : 64 anomeric mixture of **1**α : **1**β) with 3β-cholestanol (**11a**) (2.0 eq) in dichloromethane in the presence of trimethylsilyl chloride (TMSCl) (1.5 eq) and $Zn(OTf)_2$ (1.5 eq) with ice cooling for 1 h was found to proceed smoothly to give the steroidal glycoside (**12a**) with the $\alpha : \beta$ ratio of 55 : 45 in 60% combined yield (Table I, run 1). It should be noted that no reaction occurred when $Zn(OTf)_2$ alone was used as an activator, indicating that the presence of both TMSCl and $Zn(OTf)_2$ is necessary for this glycosidation to proceed. Glycosidation of the steroidal alcohol (**11a**) with α-anomer (**1**α) or β-anomer (**1**β) under the above conditions furnished the glycoside (**12a**) with the $\alpha : \beta$ ratio of 47 : 53 in 65% yield and 70 : 30 in 55% yield, respectively (runs 2 and 3). When TMSBr was used instead of TMSCl, **12a** was obtained with the $\alpha : \beta$ ratio of 81 : 19 in 53% yield (run 7). In an effort to enhance the yield and the stereoselectivity, we focused on the effect of solvents.[9] The glycosidation of **11a** with **1** in dichloromethane in the presence of small amounts of ethers (5.0 eq) such as monoglyme, diglyme or tetraglyme required longer reaction times than the original method, but the yield of **12a** was improved to over 79% with the $\alpha : \beta$ ratio ranging from 51 : 49 to 75 : 25 (runs 4—6).

To ascertain the improvements in stereoselectivity and yield from using diglyme as an additive, glycosidation of 3β-cholestanol (**11a**) with other glycosyl donors such as

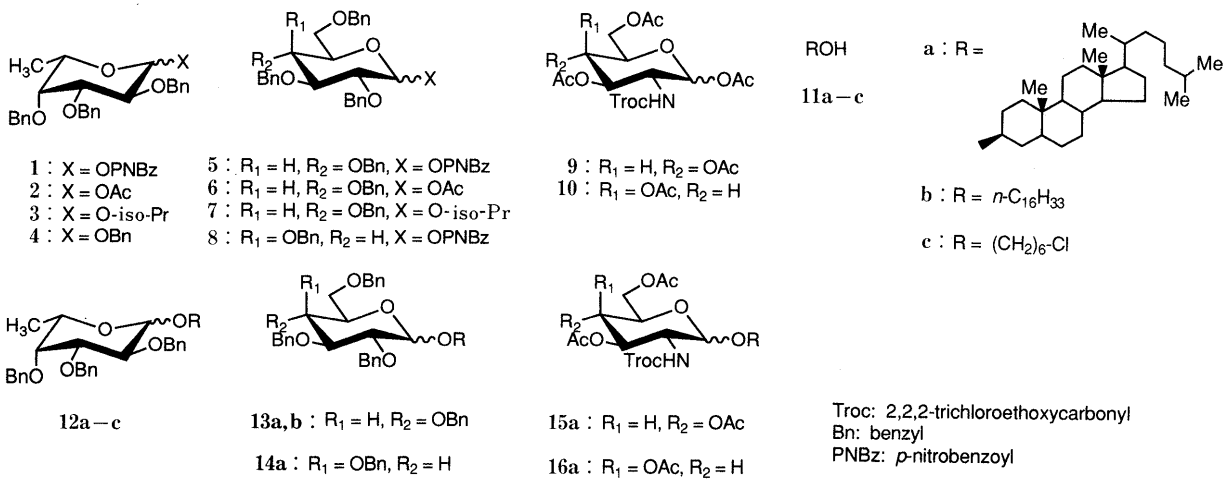

Chart 1

TABLE I. Glycosidation Promoted by the Combination of Trimethylsilyl Halide and Lewis Acid Using 1-*O*-Acyl (**1**, **2**, **5**, **6**, **8**—**10**) or 1-*O*-Alkyl Glycosides (**3**, **4**, **7**) as Glycosyl Donors

Run	Donor	Acceptor[a]	Activator[b]	Additive[c]	Time[d] (h)	Yield[e] (%)	$\alpha:\beta$[f]
1	**1**	**11a**	A	—	1	60	55:45
2	**1α**	**11a**	A	—	1	65	47:53
3	**1β**	**11a**	A	—	1	55	70:30
4	**1**	**11a**	A	Monoglyme	16	79	75:25
5	**1**	**11a**	A	Diglyme	15	90	65:35
6	**1**	**11a**	A	Tetraglyme	15	85	51:49
7	**1**	**11a**	B	—	1	53	81:19
8	**1**	**11a**	B	Diglyme	16	81	61:39
9	**2**	**11a**	A	—	2	70	73:27
10	**2**	**11a**	A	Diglyme	20	88	71:29
11	**2**	**11a**	B	—	1	65	85:15
12	**3**	**11a**	B	—	4.5	50[g]	78:22
13	**3**	**11a**	B	Diglyme	15	65[h]	71:29
14	**4**	**11a**	B	Diglyme	18	39[i]	72:28
15	**1**	**11b**	B	—	1	58	50:50
16	**1**	**11b**	B	Diglyme	17	84	52:48
17	**2**	**11b**	B	—	0.5	75	37:63
18	**2**	**11b**	B	Diglyme	18	93	61:39
19	**3**	**11b**	B	—	2	69[j]	61:39
20	**3**	**11b**	B	Diglyme	16	79[k]	65:35
21	**1**	**11c**	A	—	1.5	87	70:30
22	**1**	**11c**	A	Diglyme	19	93	69:31
23	**5α**	**11a**	B	—	3	51	67:33
24	**5α**	**11a**	B	Diglyme	3[l]	85	68:32
25	**6**	**11a**	B	Diglyme	2.5[l]	63	65:35
26	**5α**	**11b**	B	Diglyme	19	77	44:56
27	**7β**	**11b**	B	Diglyme	24[l]	71[m]	65:35
28	**8α**	**11a**	B	—	0.5	37	87:13
29	**8α**	**11a**	B	Diglyme	15	98	49:51
30	**9**	**11a**	A	—	40[l]	75	>99:1
31	**9**	**11a**	B	—	3[l]	81	>99:1
32	**9**	**11a**	C	—	22[l]	61	>99:1
33	**10**	**11a**	B	—	2[l]	82	>99:1

a) Two equivalent amounts of acceptor were used in each case. *b*) A, TMSCl (1.5 eq)–$Zn(OTf)_2$(1.5 eq); B, TMSBr (1.5 eq)–$Zn(OTf)_2$(1.5 eq); C, TMSCl (1.5 eq)–$ZnCl_2$(1.5 eq). *c*) Five equivalent amounts of additive were used. *d*) All reactions were carried out in dichloromethane with ice cooling unless otherwise noted. *e*) Isolated total yield. *f*) The $\alpha:\beta$ ratios were determined by ^{1}H-NMR analysis. *g*) The starting material (**3**) was recovered in 15% yield. *h*) The starting material (**3**) was recovered in 14% yield. *i*) The starting material (**4**) was recovered in 54% yield. *j*) The starting material (**3**) was recovered in 9% yield. *k*) The starting material (**3**) was recovered in 10% yield. *l*) Performed at room temperature. *m*) The starting material (**7**) was recovered in 13% yield.

fucopyranosyl acetate (**2**), isopropyl fucopyranoside (**3**) and benzyl fucopyranoside (**4**) using the catalyst system in both the absence and presence of diglyme was carried out. Fucopyranosyl acetate (**2**, an 88:12 anomeric mixture of **2α**:**2β**) was also found to be reactive as a glycosyl donor (runs 9—11). When isopropyl fucopyranoside (**3**, a 47:53 anomeric mixture of **3α**:**3β**) was used as a glycosyl donor, results similar to those with fucopyranosyl esters (**1**, **2**) were obtained (runs 12, 13), whereas the reaction using benzyl fucopyranoside (**4**, a 30:70 anomeric mixture of **4α**:**4β**) resulted in the recovery of the starting material in a substantial quantity and the yield of the steroidal glycoside (**12a**) was 39% (run 14).

We then investigated the reactions of fucose derivatives (**1**—**3**) with one of the other alcohols (**11b**, **c**). All the reactions resulted in the formation of the corresponding glycosides (**12b**, **c**) in good yields (runs 15—22).

Furthermore, the generality of this method was demonstrated for a range of differently protected glycosyl donors prepared from glucose (**5**—**7**), galactose (**8**), glucosamine (**9**) and galactosamine derivatives (**10**) by use of the acceptors (**11a**, **b**) (runs 23—33). The results are summarized in Table I. Glycosidation of 3β-cholestanol (**11a**) with glucopyranosyl *p*-nitrobenzoate (**5α**),[10] glucopyranosyl acetate (**6**,[11]) an 88:12 anomeric mixture of **6α**:**6β**) or galactopyranosyl *p*-nitrobenzoate (**8α**)[12] using the combination of TMSBr and $Zn(OTf)_2$ as an activator in the presence of diglyme afforded the corresponding steroidal glycosides (**13a**,[13] **14a**) in good yields (runs 24, 25, 29). Isopropyl glucopyranoside (**7β**)[14] was found to be applicable as a glycosyl donor (run 27). Apart from benzyl-protected glycopyranoses, the method could advantageously be extended to *N*-2,2,2-trichloroethoxycarbonyl (Troc)-protected glycosaminyl acetates (**9**, **10**). It should be noted that the reactions using *N*-Troc-protected glycosaminyl acetates **9**,[15] (an 83:17 anomeric mixture of **9α**:**9β**) and **10** (a 36:64 anomeric mixture of **10α**:**10β**) as glycosyl donors resulted in the stereoselective formation of α-glycosides **15aα**[16] and **16aα**, which are thought to be difficult to obtain in good yields, because the neighboring-group participation in principle would lead predominantly to the β-glycoside (runs 30—33).

In summary we have demonstrated that the combination of TMSX and $Zn(OTf)_2$ can serve as a potential activator in glycosidation using glycosyl esters or alkyl glycosides as glycosyl donors. Further extension of this method to other glycopyranoses is currently under investigation.

Experimental

Melting points were determined on a Yanagimoto melting point apparatus, and are uncorrected. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained in deuteriochloroform on a Varian VXR-500S spectrometer (500 MHz). Chemical shifts are reported in parts per million relative to tetramethylsilane (δ units) as an internal standard. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. Column chromatography was performed with Merck Silica gel 60 (230—400 mesh).

1-*O*-Acetyl-2,3,4-tri-*O*-benzyl-L-fucopyranose (2) 2,3,4-Tri-*O*-benzyl-L-fucopyranose[8] (4.27 g, 9.83 mmol) was dissolved in pyridine (13 ml) and acetic anhydride (10 ml) was added to this solution under ice-cooling. The reaction mixture was allowed to warm to room temperature and stirring was continued for 15 h at room temperature. The reaction mixture was diluted with AcOEt, washed with water, 10% citric acid, water, 5% $NaHCO_3$ and water, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel (200 g) with chloroform to give an inseparable 82:12 anomeric mixture (4.68 g, quant.) of **2α** and **2β** as a colorless powder.

Isopropyl 2,3,4-Tri-*O*-benzyl-L-fucopyranoside (3) A mixture of 2,3,4-tri-*O*-benzyl-L-fucopyranose (2.00 g, 4.60 mmol) and Dowex 50W-X8 (7.00 g) in isopropyl alcohol (100 ml) was heated under reflux for 24 h. After cooling, the resin was removed by filtration, and solution was concentrated under reduced pressure. The residue was chromatographed on silica gel (50 g) with chloroform to give a 47:53 anomeric mixture (2.19 g, quant.) of **3α** and **3β**. Analytical samples of **3α** and **3β** were prepared by repeated silica gel (50 g) column chromatography with hexane–chloroform (1:1).

3α: A colorless oil. $[\alpha]_D$ −48.2° (c=0.85, $CHCl_3$). *Anal.* Calcd for $C_{30}H_{36}O_5$: C, 75.60; H, 7.61. Found: C, 75.19; H, 7.71. ^{1}H-NMR δ: 1.06 (3H, d, J=6.4 Hz, CH_3), 1.13 (3H, d, J=6.4 Hz, CH_3), 1.17 (3H, d, J=6.4 Hz, CH_3), 3.63 (1H, d, $J_{4,3}$=2.9 Hz, H-4), 3.83 (1H, heptet, J=6.4 Hz, $CH(CH_3)_2$), 3.89 (1H, q, $J_{5,6}$=6.4 Hz, H-5), 3.90 (1H, dd, $J_{3,4}$=2.9 Hz, $J_{3,2}$=10.0 Hz, H-3), 3.97 (1H, dd, $J_{2,1}$=3.7 Hz, $J_{2,3}$=10.0 Hz, H-2), 4.61 (1H, d, J=11.5 Hz, $ArCH_2$), 4.63 (1H, d, J=12.0 Hz, $ArCH_2$), 4.69 (1H, d, J=11.7 Hz, $ArCH_2$), 4.75 (1H, d, J=12.0 Hz, $ArCH_2$), 4.84 (1H, d, J=11.7 Hz, $ArCH_2$), 4.86 (1H, d, $J_{1,2}$=3.7 Hz, H-1), 4.94 (1H, d, J=11.5 Hz, $ArCH_2$), 7.24—7.40 (15 Hz, m, ArH).

3β: A colorless oil. $[\alpha]_D$ +7.7° (c=0.94, $CHCl_3$). *Anal.* Calcd for $C_{30}H_{36}O_5$: C, 75.60; H, 7.61. Found: C, 75.28; H, 7.70. ^{1}H-NMR δ: 1.16 (3H, d, J=6.4 Hz, CH_3), 1.21 (3H, d, J=6.1 Hz, CH_3), 1.26 (3H, d, J=6.1 Hz, CH_3), 3.42 (1H, dq, $J_{5,4}$=0.7 Hz, J=6.4 Hz, H-5), 3.49 (1H, dd, $J_{3,4}$=2.9 Hz, $J_{3,2}$=9.8 Hz, H-3), 3.53 (1H, dd, $J_{4,5}$=0.7 Hz, $J_{4,3}$=2.9 Hz, H-4), 3.77 (1H, dd, $J_{2,1}$=7.6 Hz, $J_{2,3}$=9.8 Hz, H-2), 3.98 (1H,

heptet, $J=6.1$ Hz, $CH(CH_3)_2$), 4.38 (1H, d, $J_{1,2}=7.6$ Hz, H-1), 4.70 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.71 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.74 (1H, d, $J=10.8$ Hz, $ArCH_2$), 4.79 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.95 (1H, d, $J=10.8$ Hz, $ArCH_2$), 4.96 (1H, d, $J=11.7$ Hz, $ArCH_2$), 7.25—7.38 (15H, m, ArH).

Benzyl 2,3,4-Tri-*O*-benzyl-L-fucopyranoside (4) A mixture of 2,3,4-tri-*O*-benzyl-L-fucopyranose (3.07 g, 7.07 mmol) and 2.8 M HCl–dioxane (10 ml) in benzyl alcohol (50 ml) was stirred for 2 h at 100 °C. After cooling, the reaction mixture was concentrated under reduced pressure and the residue was partitioned between AcOEt and water. The separated organic layer was washed with 5% $NaHCO_3$ and water, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel (150 g) with hexane–AcOEt (12 : 1) to give **4α** (2.10 g, 57%) and a 30 : 70 anomeric mixture (1.50 g, 40%) of **4α** and **4β**.

4α: mp 100—104 °C. $[\alpha]_D$ −58.8° ($c=1.52$, $CHCl_3$). *Anal.* Calcd for $C_{34}H_{36}O_5$: C, 77.83; H, 6.92. Found: C, 77.69; H, 7.01. ^{1}H-NMR δ: 1.07 (3H, d, $J=6.4$ Hz, CH_3), 3.66 (1H, d, $J_{4,3}=2.7$ Hz, H-4), 3.88 (1H, q, $J=6.4$ Hz, H-5), 3.99 (1H, dd, $J_{3,4}=2.7$ Hz, $J_{3,2}=10.0$ Hz, H-3), 4.03 (1H, dd, $J_{2,1}=3.7$ Hz, $J_{2,3}=10.0$ Hz, H-2), 4.57 (1H, d, $J=12.2$ Hz, $ArCH_2$), 4.58 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.64 (1H, d, $J=11.5$ Hz, $ArCH_2$), 4.67 (1H, d, $J=12.2$ Hz, $ArCH_2$), 4.73 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.75 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.87 (1H, d, $J_{1,2}=3.7$ Hz, H-1), 4.88 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.98 (1H, d, $J=11.5$ Hz, $ArCH_2$), 7.23—7.41 (20H, m, ArH).

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-D-galactopyranose (10) Trichloroethoxycarbonyl chloride (7.35 g, 34.7 mmol) was added to a solution of D-(+)-galactosamine hydrochloride (5.00 g, 23.2 mmol) and $NaHCO_3$ (5.00 g, 59.5 mmol) in water (70 ml) under ice-cooling. The reaction mixture was allowed to warm to room temperature and stirring was continued for 48 h at room temperature. The precipitate was collected by filtration, washed with ice-cold water and dried to give crude 2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-D-galactopyranose. The filtrate and washings were combined and concentrated under reduced pressure and the resulting precipitate was collected by filtration, washed with ice-cold water and dried. 2-Deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-D-galactopyranose (6.45 g) thus obtained was dissolved in pyridine (26 ml) and acetic anhydride (20 ml) was added to this solution under ice-cooling. The reaction mixture was allowed to warm to room temperature and stirring was continued for 20 h at room temperature. The reaction mixture was diluted with AcOEt, washed with water, 10% citric acid, water, 5% $NaHCO_3$ and water, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel (250 g) with hexane–AcOEt (3 : 1) to give a 36 : 64 anomeric mixture (9.27 g, 76%) of **10α** and **10β** as a colorless powder.

Typical Procedure for the Reaction between Glycosyl Esters (1, 2, 5, 6, 8, 9) or Alkyl Glycosides (3, 4, 7) and Alcohols (11a—c) TMSCl (72 mg, 0.66 mmol) was added to a solution of **1** (257 mg, 0.44 mmol), **11a** (342 mg, 0.88 mmol), diglyme (295 mg, 2.2 mmol) and $Zn(OTf)_2$ (240 mg, 0.66 mmol) in dichloromethane (20 ml) under ice-cooling. After being stirred for 15 h at the same temperature, the reaction mixture was diluted with AcOEt, washed with 5% $NaHCO_3$ and water, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel (60 g) with chloroform to give a 65 : 35 anomeric mixture (318 mg, 90%) of **12aα** and **12aβ** as a colorless foam. Analytical samples of **12aα** and **12aβ** were prepared by repeated silica gel (40 g) column chromatography with hexane–AcOEt (8 : 1).

Analytical data for the glycosides (**12a—c**, **13a**, **b**, **14a—16a**) thus obtained are as follows.

12aα: mp 111—112 °C. $[\alpha]_D$ −30.9° ($c=0.90$, $CHCl_3$). *Anal.* Calcd for $C_{54}H_{76}O_5$: C, 80.55; H, 9.51. Found: C, 80.16; H, 9.45. ^{1}H-NMR δ: 0.64 (3H, s, CH_3), 0.80 (3H, s, CH_3), 0.86 (3H, d, $J=6.6$ Hz, CH_3), 0.87 (3H, d, $J=6.6$ Hz, CH_3), 0.89 (3H, d, $J=6.6$ Hz, CH_3), 1.08 (3H, d, $J=6.6$ Hz, CH_3), 3.48 (1H, m, OCH), 3.65 (1H, d, $J_{4,3}=2.5$ Hz, H-4), 3.93 (1H, dd, $J_{3,4}=2.5$ Hz, $J_{3,2}=10.0$ Hz, H-3), 3.94 (1H, q, $J=6.6$ Hz, H-5), 4.00 (1H, dd, $J_{2,1}=3.7$ Hz, $J_{2,3}=10.0$ Hz, H-2), 4.65 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.67 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.73 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.78 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.88 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.94 (1H, d, $J_{1,2}=3.7$ Hz, H-1), 4.97 (1H, d, $J=11.7$ Hz, $ArCH_2$), 7.24—7.40 (15H, m, ArH).

12aβ: mp 155—157 °C. $[\alpha]_D$ +13.9° ($c=0.92$, $CHCl_3$). *Anal.* Calcd for $C_{54}H_{76}O_5$: C, 80.55; H, 9.51. Found: C, 80.23; H, 9.20. ^{1}H-NMR δ: 0.64 (3H, s, CH_3), 0.82 (3H, s, CH_3), 0.86 (3H, d, $J=6.6$ Hz, CH_3), 0.88 (3H, d, $J=6.6$ Hz, CH_3), 0.89 (3H, d, $J=6.6$ Hz, CH_3), 1.16 (3H, d, $J=6.4$ Hz, CH_3), 3.42 (1H, q, $J=6.4$ Hz, H-5), 3.48 (1H, dd, $J_{3,4}=2.7$ Hz, $J_{3,2}=9.5$ Hz, H-3), 3.53 (1H, d, $J_{4,3}=2.7$ Hz, H-4), 3.61 (1H, m, OCH), 3.77 (1H, dd, $J_{2,1}=7.8$ Hz, $J_{2,3}=9.5$ Hz, H-2), 4.42 (1H, d, $J_{1,2}=7.8$ Hz, H-1), 4.69 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.70 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.74 (1H, d, $J=10.8$ Hz, $ArCH_2$), 4.79 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.96 (1H, d, $J=10.8$ Hz, $ArCH_2$), 4.96 (1H, d, $J=11.7$ Hz, $ArCH_2$), 7.24—7.38 (15H, m, ArH).

12bα: mp 34 °C. $[\alpha]_D$ −30.6° ($c=1.48$, $CHCl_3$). *Anal.* Calcd for $C_{43}H_{62}O_5$: C, 78.37; H, 9.49. Found: C, 78.38; H, 9.69. ^{1}H-NMR δ: 0.88 (3H, t, $J=6.8$ Hz, CH_3), 1.10 (3H, d, $J=6.6$ Hz, CH_3), 1.20—1.38 (26H, m, $CH_2\times13$), 1.58—1.65 (2H, m, CH_2), 3.43 (1H, m, OCH_2), 3.58 (1H, m, OCH_2), 3.65 (1H, d, $J_{4,3}=2.9$ Hz, H-4), 3.87 (1H, q, $J=6.6$ Hz, H-5), 3.94 (1H, dd, $J_{3,4}=2.9$ Hz, $J_{3,2}=10.0$ Hz, H-3), 4.02 (1H, dd, $J_{2,1}=3.7$ Hz, $J_{2,3}=10.0$ Hz, H-2), 4.65 (1H, d, $J=11.5$ Hz, $ArCH_2$), 4.67 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.74 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.78 (1H, d, $J_{1,2}=3.7$ Hz, H-1), 4.81 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.88 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.98 (1H, d, $J=11.5$ Hz, $ArCH_2$), 7.24—7.41 (15H, m, ArH).

12bβ: mp 48—49 °C. $[\alpha]_D$ +9.4° ($c=0.97$, $CHCl_3$). *Anal.* Calcd for $C_{43}H_{62}O_5$: C, 78.37; H, 9.49. Found: C, 78.05; H, 9.61. ^{1}H-NMR δ: 0.88 (3H, t, $J=6.6$ Hz, CH_3), 1.17 (3H, d, $J=6.4$ Hz, CH_3), 1.20—1.42 (26H, m, $CH_2\times13$), 1.57—1.69 (2H, m, CH_2), 3.43 (1H, q, $J=6.4$ Hz, H-5), 3.46 (1H, m, OCH_2), 3.50 (1H, dd, $J_{3,4}=2.9$ Hz, $J_{3,2}=9.5$ Hz, H-3), 3.54 (1H, d, $J_{4,3}=2.9$ Hz, H-4), 3.79 (1H, dd, $J_{2,1}=7.8$ Hz, $J_{2,3}=9.5$ Hz, H-2), 3.92 (1H, m, OCH_2), 4.30 (1H, d, $J_{1,2}=7.8$ Hz, H-1), 4.69 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.72 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.76 (1H, d, $J=10.8$ Hz, $ArCH_2$), 4.79 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.94 (1H, d, $J=10.8$ Hz, $ArCH_2$), 4.97 (1H, d, $J=11.7$ Hz, $ArCH_2$), 7.24—7.38 (15H, m, ArH).

12cα: A colorless oil. $[\alpha]_D$ −42.4° ($c=0.88$, $CHCl_3$). *Anal.* Calcd for $C_{33}H_{41}ClO_5$: C, 71.65; H, 7.47. Found: C, 71.20; H, 7.68. ^{1}H-NMR δ: 1.11 (3H, d, $J=6.6$ Hz, CH_3), 1.32—1.40 (2H, m, CH_2), 1.40—1.48 (2H, m, CH_2), 1.56—1.68 (2H, m, CH_2), 1.76 (2H, m, CH_2), 3.43 (1H, m, OCH_2), 3.51 (2H, t, $J=6.6$ Hz, CH_2Cl), 3.60 (1H, m, OCH_2), 3.66 (1H, d, $J_{4,3}=2.9$ Hz, H-4), 3.86 (1H, q, $J=6.6$ Hz, H-5), 3.93 (1H, dd, $J_{3,4}=2.9$ Hz, $J_{3,2}=10.0$ Hz, H-3), 4.02 (1H, dd, $J_{2,1}=3.7$ Hz, $J_{2,3}=10.0$ Hz, H-2), 4.65 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.67 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.74 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.78 (1H, d, $J_{1,2}=3.7$ Hz, H-1), 4.81 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.88 (1H, d, $J=11.7$ Hz, $ArCH_2$), 4.98 (1H, d, $J=11.7$ Hz, $ArCH_2$), 7.24—7.41 (15H, m, ArH).

12cβ: A colorless oil. $[\alpha]_D$ +8.8° ($c=1.29$, $CHCl_3$). *Anal.* Calcd for $C_{33}H_{41}ClO_5$: C, 71.65; H, 7.47. Found: C, 71.28; H, 7.71. ^{1}H-NMR δ: 1.17 (3H, d, $J=6.6$ Hz, CH_3), 1.32—1.44 (4H, m, $CH_2\times2$), 1.58—1.68 (2H, m, CH_2), 1.70—1.76 (2H, m, CH_2), 3.44 (1H, q, $J=6.4$ Hz, H-5), 3.46 (1H, m, OCH_2), 3.49 (2H, t, $J=6.6$ Hz, CH_2Cl), 3.51 (1H, dd, $J_{3,4}=2.7$ Hz, $J_{3,2}=9.5$ Hz, H-3), 3.55 (1H, d, $J_{4,3}=2.7$ Hz, H-4), 3.79 (1H, dd, $J_{2,1}=7.6$ Hz, $J_{2,3}=9.5$ Hz, H-2), 3.93 (1H, m, OCH_2), 4.30 (1H, d, $J_{1,2}=7.6$ Hz, H-1), 4.70 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.72 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.77 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.79 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.93 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.98 (1H, d, $J=12.0$ Hz, $ArCH_2$), 7.25—7.35 (15H, m, ArH).

13aα: mp 119—120 °C. [lit.[13] mp 117.5—119.0 °C]. $[\alpha]_D$ +60.6° ($c=0.94$, $CHCl_3$). [lit.[13] $[\alpha]_D$ +65.1° ($c=1.06$, $CHCl_3$)]. ^{1}H-NMR δ: 0.65 (3H, s, CH_3), 0.80 (3H, s, CH_3), 0.86 (3H, d, $J=6.6$ Hz, CH_3), 0.87 (3H, d, $J=6.6$ Hz, CH_3), 0.90 (3H, d, $J=6.6$ Hz, CH_3), 3.52 (1H, m, OCH), 3.54 (1H, dd, $J_{2,1}=3.7$ Hz, $J_{2,3}=9.3$ Hz, H-2), 3.61 (1H, dd, $J_{4,3}=9.3$ Hz, $J_{4,5}=10.0$ Hz, H-4), 3.63 (1H, dd, $J_{6,5}=2.0$ Hz, $J_{6,6'}=10.8$ Hz, H-6), 3.72 (1H, dd, $J_{6',5}=3.7$ Hz, $J_{6',6}=10.8$ Hz, H-6'), 3.88 (1H, ddd, $J_{5,6}=2.0$ Hz, $J_{5,6'}=3.7$ Hz, $J_{5,4}=10.0$ Hz, H-5), 3.99 (1H, t, $J_{3,2}=J_{3,4}=9.3$ Hz, H-3), 4.46 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.46 (1H, d, $J=11.0$ Hz, $ArCH_2$), 4.60 (1H, d, $J=12.2$ Hz, $ArCH_2$), 4.65 (1H, d, $J=12.2$ Hz, $ArCH_2$), 4.75 (1H, d, $J=12.0$ Hz, $ArCH_2$), 4.80 (1H, d, $J=11.2$ Hz, $ArCH_2$), 4.83 (1H, d, $J=11.2$ Hz, $ArCH_2$), 4.93 (1H, d, $J_{1,2}=3.7$ Hz, H-1), 5.00 (1H, d, $J=11.0$ Hz, $ArCH_2$), 7.12—7.36 (20H, m, ArH).

13aβ: mp 96—97 °C. [lit.[13] mp 93.5 °C]. $[\alpha]_D$ +17.9° ($c=0.91$, $CHCl_3$). [lit.[13] $[\alpha]_D$ +20.2° ($c=1.04$, $CHCl_3$)]. ^{1}H-NMR δ: 0.65 (3H, s, CH_3), 0.82 (3H, s, CH_3), 0.86 (3H, d, $J=6.6$ Hz, CH_3), 0.87 (3H, d, $J=6.6$ Hz, CH_3), 0.90 (3H, d, $J=6.4$ Hz, CH_3), 3.43 (1H, dd, $J_{2,1}=8.1$ Hz, $J_{2,3}=9.0$ Hz, H-2), 3.45 (1H, ddd, $J_{5,6}=1.7$ Hz, $J_{5,6'}=5.4$ Hz, $J_{5,4}=9.8$ Hz, H-5), 3.53 (1H, dd, $J_{4,3}=8.8$ Hz, $J_{4,5}=9.8$ Hz, H-4), 3.62 (1H, dd, $J_{3,4}=8.8$ Hz, $J_{3,2}=9.0$ Hz, H-3), 3.65 (1H, dd, $J_{6,5}=5.4$ Hz, $J_{6,6'}=10.8$ Hz, H-6), 3.66 (1H, m, OCH), 3.74 (1H, dd, $J_{6',5}=1.7$ Hz, $J_{6',6}=10.8$ Hz, H-6'), 4.51 (1H, d, $J_{1,2}=8.1$ Hz, H-1), 4.53 (1H, d, $J=10.8$ Hz, $ArCH_2$), 4.55 (1H, d, $J=12.2$ Hz, $ArCH_2$), 4.60 (1H, d, $J=12.2$ Hz, $ArCH_2$), 4.71 (1H, d, $J=11.0$ Hz, $ArCH_2$), 4.77 (1H, d, $J=11.0$ Hz, $ArCH_2$), 4.81 (1H, d, $J=11.0$ Hz, $ArCH_2$), 4.91 (1H, d, $J=11.0$ Hz, $ArCH_2$), 4.96 (1H, d, $J=10.8$ Hz, $ArCH_2$), 7.16—7.36 (20H, m, ArH).

13bα: mp 29—30 °C. $[\alpha]_D$ +29.5° (c=1.22, $CHCl_3$). *Anal.* Calcd for $C_{50}H_{68}O_6$: C, 78.49; H, 8.96. Found: C, 78.21; H, 9.10. ^{1}H-NMR δ: 0.88 (3H, t, J=6.8 Hz, CH_3), 1.20—1.38 (26H, m, $CH_2\times13$), 1.62 (2H, m, CH_2), 3.42 (1H, m, OCH_2), 3.55 (1H, dd, $J_{2,1}$=3.7 Hz, $J_{2,3}$=9.3 Hz, H-2), 3.61 (1H, m, OCH_2), 3.62 (1H, dd, $J_{6,5}$=2.0 Hz, $J_{6,6'}$=10.8 Hz, H-6), 3.63 (1H, dd, $J_{4,3}$=9.3, $J_{4,5}$=10.0 Hz, H-4), 3.72 (1H, dd, $J_{6',5}$=3.7 Hz, $J_{6',6}$=10.8 Hz, H-6'), 3.77 (1H, ddd, $J_{5,6}$=2.0 Hz, $J_{5,6'}$=3.7 Hz, $J_{5,4}$=10.0 Hz, H-5), 3.99 (1H, t, $J_{3,2}=J_{3,4}$=9.3 Hz, H-3), 4.46 (1H, d, J=10.8 Hz, $ArCH_2$), 4.47 (1H, d, J=12.2 Hz, $ArCH_2$), 4.61 (1H, d, J=12.2 Hz, $ArCH_2$), 4.65 (1H, d, J=12.2 Hz, $ArCH_2$), 4.75 (1H, d, $J_{1,2}$=3.7 Hz, H-1), 4.78 (1H, d, J=12.2 Hz, $ArCH_2$), 4.81 (1H, d, J=10.8 Hz, $ArCH_2$), 4.83 (1H, d, J=10.8 Hz, $ArCH_2$), 4.99 (1H, d, J=10.8 Hz, $ArCH_2$), 7.11—7.36 (20H, m, ArH).

13bβ: mp 42—44 °C. $[\alpha]_D$ +4.4° (c=1.46, $CHCl_3$). *Anal.* Calcd for $C_{50}H_{68}O_6$: C, 78.49; H, 8.96. Found: C, 78.15; H, 9.13. ^{1}H-NMR δ: 0.88 (3H, t, J=6.8 Hz, CH_3), 1.18—1.44 (26H, m, $CH_2\times13$), 1.60—1.71 (2H, m, CH_2), 3.45 (1H, dd, $J_{2,1}$=7.8 Hz, $J_{2,3}$=9.0 Hz, H-2), 3.46 (1H, ddd, $J_{5,6}$=1.7 Hz, $J_{5,6'}$=5.1 Hz, $J_{5,4}$=9.5 Hz, H-5), 3.56 (1H, m, OCH_2), 3.57 (1H, dd, $J_{4,3}$=9.0 Hz, $J_{4,5}$=9.5 Hz, H-4), 3.64 (1H, t, $J_{3,2}=J_{3,4}$=9.0 Hz, H-3), 3.67 (1H, dd, $J_{6,5}$=5.1 Hz, $J_{6,6'}$=10.8 Hz, H-6), 3.74 (1H, dd, $J_{6',5}$=1.7 Hz, $J_{6',6}$=10.8 Hz, H-6'), 3.96 (1H, m, OCH_2), 4.40 (1H, d, $J_{1,2}$=7.8 Hz, H-1), 4.52 (1H, d, J=10.8 Hz, $ArCH_2$), 4.56 (1H, d, J=12.2 Hz, $ArCH_2$), 4.62 (1H, d, J=12.2 Hz, $ArCH_2$), 4.72 (1H, d, J=11.0 Hz, $ArCH_2$), 4.79 (1H, d, J=11.0 Hz, $ArCH_2$), 4.81 (1H, d, J=10.8 Hz, $ArCH_2$), 4.93 (1H, d, J=11.0 Hz, $ArCH_2$), 4.96 (1H, d, J=11.0 Hz, $ArCH_2$), 7.14—7.35 (20H, m, ArH).

14aα: A colorless oil. $[\alpha]_D$ +41.2° (c=0.26, $CHCl_3$). *Anal.* Calcd for $C_{61}H_{82}O_6\ 2H_2O$: C, 77.34; H, 9.15. Found: C, 77.72; H, 9.20. ^{1}H-NMR δ: 0.65 (3H, s, CH_3), 0.80 (3H, s, CH_3), 0.87 (3H, d, J=6.6 Hz, CH_3), 0.87 (3H, d, J=6.6 Hz, CH_3), 0.91 (3H, d, J=6.6 Hz, CH_3), 3.48—3.68 (3H, m), 3.93—3.97 (2H, m), 4.01 (1H, dd, $J_{2,1}$=3.7 Hz, $J_{2,3}$=9.8 Hz, H-2), 4.04 (1H, t, J=6.0 Hz), 4.41 (1H, d, J=11.7 Hz, $ArCH_2$), 4.49 (1H, d, J=11.7 Hz, $ArCH_2$), 4.57 (1H, d, J=11.5 Hz, $ArCH_2$), 4.68 (1H, d, J=12.0 Hz, $ArCH_2$), 4.73 (1H, d, J=11.5 Hz, $ArCH_2$), 4.79 (1H, d, J=12.0 Hz, $ArCH_2$), 4.86 (1H, d, J=11.5 Hz, $ArCH_2$), 4.96 (1H, d, J=11.5 Hz, $ArCH_2$), 4.99 (1H, d, $J_{1,2}$=3.7 Hz, H-1), 7.24—7.40 (20H, m, ArH).

14aβ: mp 99—100 °C. $[\alpha]_D$ +5.0° (c=0.46, $CHCl_3$). *Anal.* Calcd for $C_{61}H_{82}O_6H_2O$: C, 78.84; H, 9.11. Found: C, 79.09; H, 9.35. ^{1}H-NMR δ: 0.64 (3H, s, CH_3), 0.80 (3H, s, CH_3), 0.86 (3H, d, J=6.6 Hz, CH_3), 0.86 (3H, d, J=6.6 Hz, CH_3), 0.90 (3H, d, J=6.6 Hz, CH_3), 3.47—3.52 (2H, m), 3.57 (2H, d, J=6.1 Hz, H-6 and H-6'), 3.59—3.66 (1H, m, OCH), 3.79 (1H, dd, $J_{2,1}$=7.8 Hz, $J_{2,3}$=9.8 Hz, H-2), 3.86 (1H, d, $J_{4,3}$=2.7 Hz, H-4), 4.41 (1H, d, J=11.7 Hz, $ArCH_2$), 4.44 (1H, d, J=11.7 Hz, $ArCH_2$), 4.46 (1H, d, $J_{1,2}$=7.8 Hz, H-1), 4.61 (1H, d, J=11.7 Hz, $ArCH_2$), 4.70 (1H, d, J=12.0 Hz, $ArCH_2$), 4.75 (1H, d, J=10.5 Hz, $ArCH_2$), 4.75 (1H, d, J=12.0 Hz, $ArCH_2$), 4.92 (1H, d, J=11.7 Hz, $ArCH_2$), 4.94 (1H, d, J=10.5 Hz, $ArCH_2$), 7.24—7.38 (20H, m, ArH).

15aα: mp 178—180 °C. [lit.[16] mp 180—182 °C]. $[\alpha]_D$ +79.0 °C (c=0.94, $CHCl_3$). [lit.[16] $[\alpha]_D$ +79.1° (c=0.43, $CHCl_3$)]. ^{1}H-NMR δ: 0.65 (3H, s, CH_3), 0.82 (3H, s, CH_3), 0.86 (3H, d, J=6.6 Hz, CH_3), 0.86 (3H, d, J=6.6 Hz, CH_3), 0.90 (3H, d, J=6.6 Hz, CH_3), 2.00 (3H, s, CH_3CO), 2.03 (3H, s, CH_3CO), 2.09 (3H, s, CH_3CO), 3.54 (1H, m, OCH), 4.02 (1H, ddd, $J_{2,1}$=3.7 Hz, $J_{2,NH}$=9.8 Hz, $J_{2,3}$=10.0 Hz, H-2), 4.05—4.12 (2H, m, H-5 and H-6), 4.23 (1H, dd, $J_{6',5}$=4.6 Hz, $J_{6',6}$=12.2 Hz, H-6'), 4.66 (1H, d, J=12.0 Hz, CH_2CCl_3), 4.78 (1H, d, J=12.0 Hz, CH_2CCl_3), 5.01 (1H, d, $J_{1,2}$=3.7 Hz, H-1), 5.08 (1H, t, $J_{4,3}=J_{4,5}$=10.0 Hz, H-4), 5.19 (1H, d, $J_{NH,2}$=9.8 Hz, NH), 5.24 (1H, t, $J_{3,2}=J_{3,4}$=10.0 Hz, H-3).

16aα: mp 92—97 °C. $[\alpha]_D$ +75.6° (c=0.99, $CHCl_3$). *Anal.* Calcd for $C_{42}H_{66}Cl_3NO_{10}$: C, 59.25; H, 7.81; N, 1.65. Found: C, 58.94; H, 7.50; N, 1.62. ^{1}H-NMR δ: 0.65 (3H, s, CH_3), 0.82 (3H, s, CH_3), 0.86 (3H, d, J=6.6 Hz, CH_3), 0.86 (3H, d, J=6.6 Hz, CH_3), 0.90 (3H, d, J=6.6 Hz, CH_3), 1.97 (3H, s, CH_3CO), 2.04 (3H, s, CH_3CO), 2.16 (3H, s, CH_3CO), 3.54 (1H, m, OCH), 4.06 (1H, dd, $J_{6,5}$=7.1 Hz, $J_{6,6'}$=11.2 Hz, H-6), 4.12 (1H, dd, $J_{6',6}$=6.1 Hz, $J_{6',6}$=11.2 Hz, H-6'), 4.25 (1H, ddd, $J_{2,1}$=3.7 Hz, $J_{2,NH}$=10.0 Hz, $J_{2,3}$=11.2 Hz, H-2), 4.28 (1H, dd, $J_{5,6'}$=6.1 Hz, $J_{5,6}$=7.1 Hz, H-5), 4.65 (1H, d, J=12.2 Hz, CH_2CCl_3), 4.80 (1H, d, J=12.2 Hz, CH_2CCl_3), 5.04 (1H, d, $J_{1,2}$=3.7 Hz, H-1), 5.08 (1H, d, $J_{NH,2}$=10.0 Hz, NH), 5.15 (1H, dd, $J_{3,4}$=3.2 Hz, $J_{3,2}$=11.2 Hz, H-3), 5.38 (1H, d, $J_{4,3}$=3.2 Hz, H-4).

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References and Notes

1) For recent reviews, see: *a*) H. Paulsen, *Angew. Chem., Int. Ed. Engl.*, **21**, 155 (1982); *b*) *Idem*, *Chem. Soc. Rev.*, **13**, 15 (1984); *c*) R. R. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **25**, 212 (1986); *d*) H. Kunz, *ibid.*, **26**, 294 (1987); *e*) R. R. Schmidt, *Pure Appl. Chem.*, **61**, 1257 (1989); *f*) H. Paulsen, *Angew. Chem., Int. Ed. Engl.*, **29**, 823 (1990).
2) For recent papers, see: *a*) S. Hashimoto, T. Honda, and S. Ikegami, *J. Chem. Soc., Chem. Commun.*, **1989**, 685; *b*) G. V. Reddy, V. R. Kulkarni, and H. B. Mereyala, *Tetrahedron Lett.*, **30**, 4283 (1989); *c*) D. Kahne, S. Walker, Y. Cheng, and D. V. Engen, *J. Am. Chem. Soc.*, **111**, 6881 (1989); *d*) K. Suzuki, H. Maeta, and T. Matsumoto, *Tetrahedron Lett.*, **30**, 4853 (1989); *e*) N. K. Kochetkov, E. M. Klimov, and N. N. Malysheva, *ibid.*, **30**, 5459 (1989); *f*) P. Konradsson, D. R. Mootoo, R. E. McDevitt, and B. Fraser-Reid, *J. Chem. Soc., Chem. Commun.*, **1990**, 270; *g*) G. H. Veeneman and J. H. van Boom, *Tetrahedron Lett.*, **31**, 275 (1990); *h*) R. R. Schmidt, H. Gaden, and H. Jatzke, *ibid.*, **31**, 327 (1990); *i*) G. H. Veeneman, S. H. van Leeuwen, and J. H. van Boom, *ibid.*, **31**, 1331 (1990); *j*) S. Kobayashi, K. Koide, and M. Ohno, *ibid.*, **31**, 2435 (1990); *k*) C. Amatore, A. Jutand, J.-M. Mallet, G. Meyer, and P. Sinay, *J. Chem. Soc., Chem. Commun.*, **1990**, 718; *l*) T. Yamanoi and T. Inazu, *Chem. Lett.*, **1990**, 849.
3) K. Higashi, K. Nakayama, E. Shioya, and T. Kusama, *Chem. Pharm. Bull.*, **40**, 1042 (1992).
4) For some glycosidations using glycosyl esters directly as the glycosyl donor, see: *a*) T. Mukaiyama, S. Kobayashi, and S. Shoda, *Chem. Lett.*, **1984**, 907; *b*) *Idem*, *ibid.*, **1984**, 1529; *c*) Y. Shibata and S. Ogawa, *Carbohydr. Res.*, **189**, 309 (1989); *d*) T. Mukaiyama, T. Shimpuku, T. Takashima, and S. Kobayashi, *Chem. Lett.*, **1989**, 145; *e*) T. Mukaiyama, T. Takashima, M. Katsurada, and H. Aizawa, *ibid.*, **1991**, 533; *f*) T. Mukaiyama, M. Katsurada, and T. Takashima, *ibid.*, **1991**, 985; *g*) J. C. Lopez and B. Fraser-Reid, *J. Chem. Soc., Chem. Commun.*, **1991**, 159; *h*) K. Koide, M. Ohno, and S. Kobayashi, *Tetrahedron Lett.*, **32**, 7065 (1991).
5) *a*) D. R. Mootoo, P. Konradsson, U. Udodong, and B. Fraser-Reid, *J. Am. Chem. Soc.*, **110**, 5583 (1988); *b*) B. Fraser-Reid, P. Konradsson, D. R. Mootoo, and U. Udodong, *J. Chem. Soc., Chem. Commun.*, **1988**, 823.
6) For recent fucosylations, see: *a*) S. Hashimoto, T. Honda, and S. Ikegami, *Tetrahedron Lett.*, **31**, 4769 (1990); *b*) R. R. Schmidt and A. Toepfer, *ibid.*, **32**, 3353 (1991); *c*) K. C. Nicolaou, C. W. Hummel, N. J. Bockovich, and C.-H. Wong, *J. Chem. Soc., Chem. Commun.*, **1991**, 870; *d*) A. Kameyama, H. Ishida, M. Kiso, and A. Hasegawa, *Carbohydr. Res.*, **209**, c1 (1991); *e*) V. Vill, T. K. Lindhorst, and J. Thiem, *J. Carbohydr. Chem.*, **10**, 771 (1991); *f*) P. Smid, G. A. de Ruiter, G. A. van der Marel, F. M. Rombouts, and J. H. van Boom, *ibid.*, **10**, 833 (1991); *g*) H. Baumann, P.-E. Jansson, and L. Kenne, *J. Chem. Soc., Perkin Trans. 1*, **1991**, 2229; *h*) T. Peters and T. Weimar, *Justus Liebigs Ann. Chem.*, **1991**, 237.
7) For some glycosidation using *p*-nitrobenzoate as a glycosyl donor in the presence of trimethylsilyl trifluoromethanesulfonate, see: *a*) Y. Kimura, M. Suzuki, M. Matsumoto, R. Abe, and S. Terashima, *Chem. Lett.*, **1984**, 501; *b*) *Idem*, *Bull. Chem. Soc. Jpn.*, **50**, 423 (1986).
8) D. Juszynski and H. M. Flowers, *Charbohydr. Res.*, **18**, 219 (1971).
9) For some selective glycosidations by using solvent effect, see: *a*) R. R. Schmidt, M. Behrendt, and A. Toepter, *Synlett*, **1990**, 694, and references cited therein; *b*) S. Hashimoto, M. Hayashi, and R. Noyori, *Tetrahedron Lett.*, **25**, 1379 (1984); *c*) K. C. Nicolaou, T. Ladduwahetty, J. L. Randall, and A. Chucholowski, *J. Am. Chem. Soc.*, **108**, 2466 (1986); *d*) T. Matsumoto, H. Maeta, K. Suzuki, and G. Tsuchihashi, *Tetrahedron Lett.*, **29**, 3567 (1988); *e*) M. Perez and J.-M. Beau, *ibid.*, **30**, 75, (1989); *f*) K. Suzuki, H. Maeta, T. Suzuki, and T. Matsumoto, *ibid.*, **30**, 6879 (1989); *g*) K. Toshima, Y. Nozaki, and K. Tatsuta, *ibid.*, **32**, 6887 (1991).
10) C. P. J. Glaudemans and H. G. Fletcher, Jr., *Methods Carbohydr. Chem.*, **6**, 373 (1972).
11) M. Chmielewski and J. N. BeMiller, *Carbohydr. Res.*, **96**, 73 (1981).
12) H. H. Baer, J. M. J. Frechet and U. Williams, *Can. J. Chem.*, **52**, 3337 (1974).
13) T. Mukaiyama, T. Nakatsuka, and S. Shoda, *Chem. Lett.*, **1979**, 487.
14) K. Jansson, G. Noori, and G. Magnusson, *J. Org. Chem.*, **55**, 3181 (1990).
15) M. Imoto, H. Yoshimura, T. Shimamoto, N. Sakaguchi, S. Kusumoto, and T. Shiba, *Bull. Chem. Soc. Jpn.*, **60**, 2205 (1987).
16) K. Higashi, K. Nakayama, T. Soga, E. Shioya, K. Uoto, and T. Kusama, *Chem. Pharm. Bull.*, **38**, 3280 (1990).