Glycosylation from the Non-reducing End Using a Combination of Thioglycoside and Glycosyl Sulfoxide as the Glycosyl Donor and the Acceptor

Tetsuya KAJIMOTO,*[,a] Kenji ARIMITSU,[b] Minoru OZEKI,[b] and Manabu NODE*[,b]

[a] *Osaka University of Pharmaceutical Sciences; 4–1–20 Nasahara, Takatsuki, Osaka 569–1094, Japan: and* [b] *Kyoto Pharmaceutical University; 1 Shichono-cho, Misasagi, Yamashina-ku, Kyoto 607–8412, Japan.*
Received February 1, 2010; accepted March 2, 2010; published online March 5, 2010

A glycosylation reaction was performed using a combination of thioglycoside and glycosyl sulfoxide, which were prepared with odorless *p*-octyloxybenzenethiol, as a glycosyl donor and an acceptor, respectively. Promising results were obtained when *p*-octyloxylphenyl *N*-phthaloyl-D-*thio*-glucosaminide was activated with *N*-iodosuccinimide (NIS) and triflic acid (TfOH) for glycosylation of the hydroxyl group of the C-6 position of derivatives of D-glucosyl sulfoxide. Successive reduction of the resulting disaccharyl sulfoxides provided the corresponding thioglycosides, which could be used as the glycosyl donors in another glycosylation reaction to afford trisaccharides in good yield. The present method would be useful for the block synthesis of glycosyl donors in the total synthesis of blanched oligosaccharides, especially when *N*-acetylglucosamines are presented at the non-reducing ends.

Key words glycosylation; glycosyl sulfoxide; thioglycoside; odorless benzenethiol

In 1989, Kahne and his colleagues reported that phenyl glycosyl sulfoxides could act as excellent glycosyl donors in the presence of triflic acid (TfOH) or triflic anhydride.[1)] Later, they applied the method to the one-pot synthesis of the trisaccharide of ciclamycin, with glycosyl phenyl sulfoxides and glycosyl *p*-methoxyphenyl sulfoxides employed as glycosyl donors and phenyl thioglycoside as an acceptor.[2)] However, a glycosylation reaction using glycosyl sulfoxide as the acceptor with thioglycoside as the donor has not been reported to date.

Meanwhile, we recently reported the usefulness of aryl thioglycosides **1**, **2** prepared with odorless benzenethiol **3**, **4**[3,4)] as glycosyl donors in a glycosylation reaction, with *N*-iodosuccinimide (NIS) and TfOH as the activator,[3,4)] as part of our study on the development of odorless thiols and their application in organic synthesis (Fig. 1).[5—17)]

Against this background, we were interested that *p*-octyloxyphenyl glycosyl sulfoxides (**5**) could be easily prepared from **2** by selective oxidation of the sulfide group. Since the resulting oligoglycosyl sulfoxide **6** by the glycosylation reaction, using **2** and **5** as the glycosyl donor and acceptor, respectively, could be reduced to the corresponding aryl thioglycoside **7**, which would be available as the oligoglycosyl donor in the next step, the strategy provides a useful method for the synthesis of oligosaccharides from the non-reducing end (Chart 1).

Thus, in the present paper, we report the results of the glycosylation reaction using a combination of **5** and **2** as the glycosyl acceptor and donor, respectively, and its application for the synthesis of trisaccharides from the non-reducing-end.

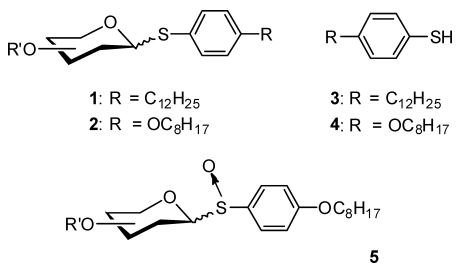


Fig. 1. Structures of Odorless Benzenethiols, Thioglycoside and Glycosyl Sulfoxide

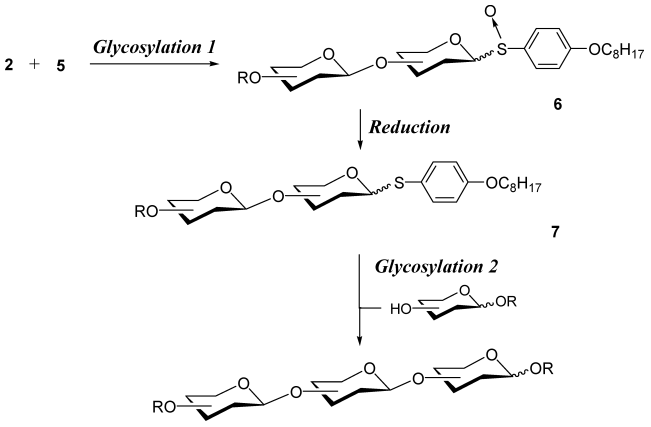


Chart 1. Glycosylation Using Thioglycoside **2** and Glycosyl Sulfoxide **5**

Results and Discussion

First, aryl thioglycosides **2a**, **2b**, which were prepared from *p*-octyloxyphenyl 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranose (**2c**) in 4 steps, and **2d**[3,4)] were oxidized with *m*-chloroperbenzoic acid (*m*-CPBA) to afford the corresponding glycosyl sulfoxides **5a**—**c** (Chart 2).

Using **5a**—**c** as the glycosyl acceptor, glycosylation reactions where thioglycosides **2c** and **2e**—**g** were employed as glycosyl donors were performed in the presence of NIS and TfOH in dichloromethane at −50 °C (Table 1). Interestingly, satisfactory results were obtained only when *N*-phthaloylglucosamine derivative **2e** and glucose derivatives **5a**, **5b** were employed as the donor and acceptor substrates, respectively (Table 1, entries 2—4). It is noteworthy to emphasize that use of a mixture of two diastereoisomers of sulfoxide **5b** gave an almost same result comparing with the reaction using the single isomer (Table 1, entries 3, 4). Therefore, it is unnecessary

* To whom correspondence should be addressed. e-mail: kajimoto@gly.oups.ac.jp

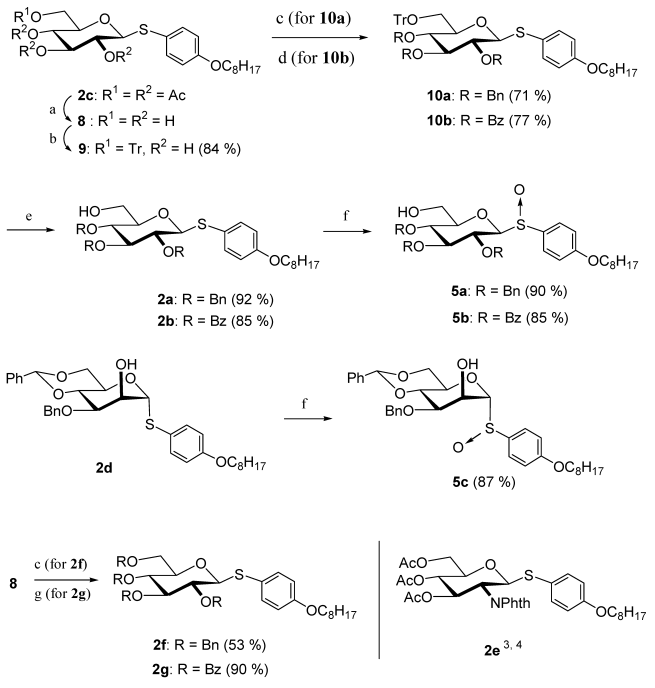


Chart 2. Structures and Preparation of **2a**—**f** and Glycosyl Sulfoxide **5a**—**c**

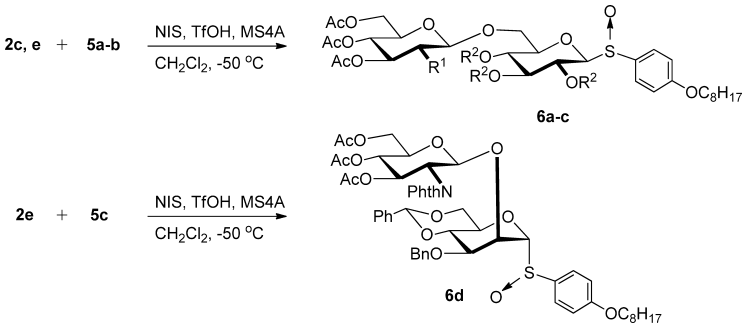
to separate two diastereomers of the acceptors for practical application of the glycosylation. Other combinations of the glycosyl donor and acceptor, *e.g.*, **2c** and **5b**, gave unsatisfied yields (<5%). In addition, the glycosylation of **5b** with **2f**—**g** did not yield the desired product at all and donors **2f**, **g** were recovered in good yield (66% and 99%, respectively) while complete consumption of the acceptor substrate **5b** was observed on monitoring the reaction.

Herein, we challenged the synthesis of a trisaccharide by taking advantage of the reaction of **2e** and **5a**, **b** (Table 1, entries 2—4). In order to apply the synthesis of disaccharides **6b**, **c** to further glycosylation, the sulfoxide group had to be reduced to the sulfide group. After several attempts, the combination of triphenylphosphine and carbon tetrachloride under the refluxed condition of acetonitrile[18] could convert **6b** and **6c** to the appropriate sulfides **11a** and **11b**, respectively, in good yield (82%, 84%). Glycosylation of methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **12** using **11a**, **b** as the glycosyl donor was also achieved to afford trisaccharides **13a**, **b** in satisfactory yield (50%, 76%), although a mixture of α and β isomers (1 : 2.5) was produced in the former reaction (Chart 3).

Conclusion

In conclusion, we found that the combination of *p*-octyloxylphenyl *N*-phthaloyl-D-*thio*-glucosaminide and *p*-

Table 1. Glycosylation Reaction of **2** and **5**



Entry	Donor	Acceptor	Time (min)	Product			Yield	$\beta : \alpha$	Recovery
					R^1	R^2			
1	**2c**	**5a**[a)]	40	**6a**	OAc	Bn	35%	1 : 0	**5a** (40%)
2	**2e**	**5a**[a)]	15	**6b**	NPhth	Bn	73%	1 : 0	—
3	**2e**	**5b**[a)]	15	**6c**	NPhth	Bz	66%	1 : 0	—
4	**2e**	**5b**[b)]	15	**6c**+**6c′**[c)]	NPhth	Bz	59%	1 : 0	—
5	**2e**	**5c**[a)]	15	**6d**	—	—	21%	1 : 0	**5c** (46%)

a) The less polar diastereomer on the sulfur atom was used. *b*) A mixture of two diastereomer was used. *c*) The more polar product than **6c**.

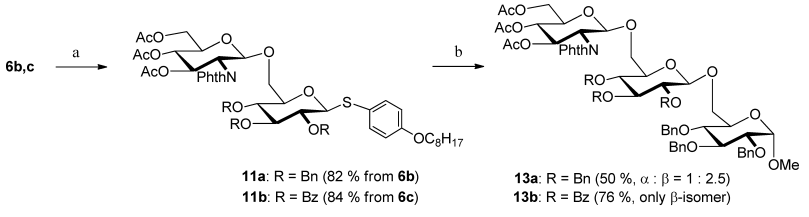


Chart 3. Synthesis of Trisaccharides **13a**, **b**

octyloxylphenyl D-glucosyl sulfoxide derivatives provided a compatible set of glycosyl donor and acceptor in the glycosylation reaction, where NIS and TfOH were the activating agents. When treated with triphenyl phosphine and carbon tetrachloride, the resulting disaccharyl sulfoxide could be easily converted to the corresponding thioglycoside, which was available as the glycosyl donor in other glycosylation. Since our strategy could be repeated in further steps, it provides a novel practical method for the block synthesis of glycosyl donors in the total synthesis of blanched oligosaccharides, especially, in which *N*-acetylglucosamines are presented at the non-reducing ends.

Experimental

General Melting points were taken on a micro hot-stage apparatus (Yanagimoto) and were uncorrected. Infrared (IR) spectra were recorded on a Shimadzu FT-IR-8300 diffraction grating infrared spectrophotometer, and ^{1}H-NMR spectra were obtained on a Varian Unity INOVA-400 spectrometer with tetramethylsilane as the internal standard. ^{13}C-NMR spectra were obtained on a Varian Unity INOVA-400 spectrometer with C_5D_5N as the internal standard. Mass spectra (MS) were determined on a JEOL JMS-SX 102A QQ or a JEOL JMS-GC-mate mass spectrometer. Combustion analysis was performed on a Perkin Elmer Series II CHNS/O Analyzer 2400. Specific rotations were recorded on a Horiba SEPA-200 automatic digital polarimeter. Flash column chromatography was performed with Silica Gel 60N (Kanto Chemical Co., Inc.). Kieselgel 60 F-254 plates (Merk) were used for thin layer chromatography (TLC). Preparative TLC (PTLC) was performed with a Silica gel 60 F-254 plate (0.5 mm, Merk). When necessary, compounds were further purified using a recycled HPLC (JAI LC-908) on a GPC column (JAIGEL 1H and 2H) after purification on silica gel.

Materials Most reagents were obtained from Wako Pure Chemical Industries, Ltd., Nakalai Tesque, Inc., and Aldrich Chemical Inc.

***p*-Octyloxyphenyl 2,3,4-Tri-*O*-benzyl-1-*thio*-β-D-glucopyranoside (2a)** A solution of 4 M hydrochloric acid in 1,4-dioxane (5.0 ml) was added to a solution of **10a** (2.53 g) in 1,4-dioxane (50 ml) and the reaction mixture was stirred for 22 h at room temperature. After the reaction, the reaction mixture was neutralized with a saturated aqueous solution of sodium bicarbonate. The mixture was then extracted with ethyl acetate and the organic layer was washed with brine, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate=10 : 1 to 5 : 1) to afford compound **2a** (1.71 g, 92%). $[\alpha]_D=+5.6°$ (c=1.16, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.83 (3H, t, J=6.5 Hz), 1.22 (8H, m), 1.35 (2H, m), 1.68 (2H, quint., J=7.0 Hz), 3.69 (1H, ddd, J=2.5, 4.0, 9.0 Hz, H-5), 3.74 (1H, t, J=9.0 Hz, H-2), 3.86 (2H, t, J=7.0 Hz, OCH_2), 3.99 (1H, t, J=9.0 Hz, H-3), 4.06 (1H, t, J=9.0 Hz, H-4), 4.14 (1H, ddd, J=4.0, 6.5, 12.0 Hz, H-6), 4.27 (1H, dd, J=6.5, 12.0 Hz, H-6), 4.96, 4.98, 5.02, 5.03, 5.05, 5.10 (each 1H, d, J=10.0 Hz, OBn), 5.04 (1H, d, J=9.0 Hz, H-1), 6.81 (1H, t, J=6.5 Hz, OH), 6.98 (2H, d, A part of AB type, J=8.8 Hz), 7.24—7.41 (9H, m), 7.43—7.49 (4H, m), 7.60 (2H, d, J=7.0 Hz), 7.79 (2H, d, B part of AB type, J=8.8 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.2, 22.9, 26.3, 29.4 (2C), 29.5, 32.0, 61.4 (C-6), 68.3 (OCH_2), 75.0 (OBn), 75.2 (OBn), 75.6 (OBn), 78.4 (C-4), 81.2 (C-5), 81.5 (C-2), 87.0 (C-3), 88.7(C-1), 115.6 (2C), 124.7, 127.8, 127.9, 127.98, 128.1(2C), 128.2 (2C), 128.4 (2C), 128.7 (6C), 134.8 (2C), 139.3, 139.4, 139.6, 159.7. IR ($CHCl_3$) ν: 3589, 3007, 2930, 2860, 1593, 1495, 1470, 1454 cm^{-1}. HR-MS *m*/*z*: 693.3223 (Calcd for $C_{41}H_{50}O_6SNa$: 693.3226).

***p*-Octyloxyphenyl 2,3,4-Tri-*O*-benzoyl-1-*thio*-β-D-glucopyranoside (2b)** A solution of 4 M hydrochloric acid in 1,4-dioxane (0.3 ml) was added to a solution of **10b** (30.3 mg, 0.032 mmol) in 1,4-dioxane (2 ml) and the reaction mixture was stirred for 5 h at room temperature. After the reaction, the reaction mixture was neutralized with a saturated aqueous solution of sodium bicarbonate. The mixture was then extracted with ethyl acetate and the organic layer was washed with brine, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified by preparative thin layer chromatography on silica gel (*n*-hexane : ethyl acetate=2 : 1) to afford compound **2b** (19.2 mg, 85%). $[\alpha]_D=-13.2°$ (c=1.18, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.83 (3H, t, J=7.0 Hz), 1.18 (8H, m), 1.35 (2H, m), 1.67 (2H, quint., J=6.6 Hz), 3.84 (2H, t, J=6.6 Hz, OCH_2), 4.17 (1H, dd, J=5.0, 12.5 Hz, H-6), 4.27 (1H, dd, J=2.2, 12.5 Hz, H-6), 4.44 (1H, ddd, J=2.2, 5.0, 9.9 Hz, H-5), 4.95 (1H, br, OH), 5.62 (1H, d, J=9.9 Hz, H-1), 6.01 (1H, t, J=9.9 Hz, H-2), 6.19 (1H, t, J=9.9 Hz, H-4), 6.51 (1H, t, J=9.9 Hz, H-3), 6.96 (2H, d, J=8.8 Hz), 7.12 (2H, br tt, J=1.5, 7.3 Hz), 7.24 (3H, tt, J=1.5, 7.3 Hz), 7.31 (2H, tt, J=1.5, 7.3 Hz), 7.37 (1H, tt, J=1.5, 7.3 Hz), 7.42 (1H, tt, J=1.5, 7.3 Hz), 7.73 (2H, d, J=8.8 Hz), 7.99 (2H, dt, J=1.5, 7.3 Hz), 8.06 (2H, dt, J=1.5, 7.3 Hz), 8.18 (2H, dt, J=1.5, 7.3 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.2, 22.9, 26.3, 29.43, 29.45, 29.5, 32.0, 61.6 (C-6), 68.3 (OCH_2), 70.2 (C-4), 71.7 (C-2), 75.8 (C-3), 80.3 (C-5), 86.9 (C-1), 115.6 (2C), 122.6, 128.7 (2C), 128.8 (2C), 128.9 (2C), 129.6, 129.8, 129.95 (2C), 129.99 (3C), 130.1 (2C), 133.5, 133.6, 133.7, 135.9 (2C), 160.2, 165.60, 165.64, 166.3. IR ($CHCl_3$) ν: 3526, 3071, 2930, 2856, 1732, 1595, 1493, 1452, 1281, 1261 cm^{-1}. HR-MS *m*/*z*: 735.2608 (Calcd for $C_{41}H_{44}O_9SNa$: 735.2604).

***p*-Octyloxyphenyl 2,3,4,6-Tetra-*O*-acetyl-1-*thio*-β-D-glucopyranoside (2c)** *p*-Octyloxybenzenethiol (**4**)[3,4] (6.61 g, 27.7 mmol) and boron trifluoride etherate (3.5 ml, 27.6 mmol) were successively added to a solution of 1,2,3,4,6-penta-*O*-acetyl-D-glucopyranose (4.95 g, 12.7 mmol) in dichloromethane (50 ml) at 0 °C and the reaction mixture was stirred for 12.5 h at room temperature. The reaction was quenched by adding distilled water and the mixture was extracted with ethyl acetate. The organic layer was washed with a saturated aqueous solution of sodium bicarbonate and brine, successively, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate=3 : 1) to afford **2c** (6.44 g, 89%). $[\alpha]_D=-28.0°$ (c=1.05, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.83 (3H, t, J=7.1 Hz), 1.22 (8H, m), 1.36 (2H, m), 1.71 (2H, quint., J=6.6 Hz), 1.978, 1.982, 2.02, 2.13 (each 3H, s), 3.90 (2H, t, J=6.6 Hz, –OCH_2–), 4.13 (1H, ddd, J=10.1, 4.9, 2.4 Hz, H-5), 4.41 (1H, dd, J=12.3, 2.4 Hz, H-6), 4.50 (1H, dd, J=12.3, 4.9 Hz, H-6), 5.18 (1H, d, J=10.0 Hz, H-1), 5.40 (1H, dd, J=10.0, 9.5 Hz, H-2), 5.43 (1H, t, J=9.5 Hz, H-4), 5.77 (1H, t, J=9.5 Hz, H-3), 7.04, 7.75 (each 2H, d, AB type, J=8.8 Hz, Ar). ^{13}C-NMR (C_5D_5N) δ: 14.2, 20.38, 20.41, 20.6, 20.7, 22.9, 26.2, 29.42, 29.43, 29.5, 32.0, 62.5 (C-6), 68.3 (OCH_2), 68.9 (C-4), 70.7 (C-2), 74.6 (C-3), 76.1 (C-5), 86.1 (C-1), 115.5 (2C), 121.8, 136.5 (2C), 160.4, 169.6, 169.7, 170.3, 170.4. IR ($CHCl_3$) ν: 3038, 2930, 2856, 1753, 1493, 1369, 1283, 1252 cm^{-1}. HR-MS *m*/*z*: 591.2234 (Calcd for $C_{28}H_{40}O_{41}SNa$: 591.2240).

***p*-Octyloxyphenyl 2,3,4,6-Tetra-*O*-benzyl-1-*thio*-β-D-glucopyranoside (2f)** Sodium hydride (55% in mineral oil, 209 mg, 4.78 mmol) was added to a solution of compound **8** in *N*,*N*-dimethylformamide (9.0 ml) and the mixture was stirred at 0 °C for 10 min. Keeping the temperature, benzyl bromide (567 μl, 4.78 mmol) was added drop wise to the reaction mixture, which was stirred for 6 h at room temperature. After the reaction, the reaction mixture was poured into ice water, which was extracted with diethyl ether. The organic layer was successively washed with small amount of distilled water, a saturated aqueous solution of sodium thiosulfate, and brine, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate=10 : 1) to afford **2f** (388 mg, 53%). $[\alpha]_D=-4.9°$ (c=1.10, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.84 (3H, t, J=7.4 Hz), 1.20 (8H, m), 1.38 (2H, m), 1.70 (2H, quint., J=6.5 Hz), 3.72 (1H, dd, J=8.8, 9.7 Hz, H-2), 3.75 (1H, ddd, J=2.0, 4.2, 9.5 Hz, H-5), 3.86 (1H, t, J=8.8 Hz, H-4), 3.88 (2H, t, J=6.5 Hz, OCH_2), 3.91 (1H, dd, J=4.2, 8.8 Hz, H-6), 3.94 (1H, dd, J=2.0, 8.8 Hz, H-6), 3.95 (1H, t, J=8.8 Hz, H-3), 4.59, 4.66 (each 1H, d, AB type, J=11.9 Hz, OBn), 4.76 (1H, d, J=11.0 Hz, OBn), 4.96 (1H, d, J=11.0 Hz, OBn), 4.97 (1H, d, J=9.7 Hz, H-1), 4.97, 4.98, 5.04, 5.12 (each 1H, d, J=11.0 Hz, OBn), 6.99 (2H, d, J=9.0 Hz), 7.25—7.43 (14H, m), 7.46, 7.50, 7.60 (each 2H, dt, J=1.5, 8.0 Hz), 7.84 (2H, d, J=9.0 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.3, 22.9, 26.3, 29.5 (2C), 29.6, 32.0, 68.3 (OCH_2), 69.7 (C-6), 73.5, 75.0, 75.2, 75.6 (4×OBn), 78.4 (C-4), 79.4 (C-5), 81.3 (C-2), 87.0 (C-3), 88.2 (C-1), 115.6 (2C), 124.1, 127.9 (2C), 127.97, 128.01, 128.06 (2C), 128.12 (2C), 128.2 (2C), 128.4 (2C), 128.7 (6C), 128.8 (2C), 135.3 (2C), 139.17, 139.22, 139.3, 139.5, 159.8. IR ($CHCl_3$) ν: 3067, 3038, 2928, 2858, 1593, 1495, 1470, 1454, 1088, 1069 cm^{-1}. HR-MS *m*/*z*: 783.3692 (Calcd for $C_{48}H_{56}O_6SNa$: 783.3695).

***p*-Octyloxyphenyl 2,3,4,6-Tetra-*O*-benzoyl-1-*thio*-β-D-glucopyranoside (2g)** Benzoic anhydride (1.21 g, 5.35 mmol) and *N*,*N*-dimethyl-4-aminopyridine (0.1 mg) were added to a solution of compound **8** (379 mg, 0.894 mmol) in pyridine (10.0 ml) and the mixture was stirred at room temperature for 17 h. The reaction mixture was poured into ice water, which was extracted with ethyl acetate. The organic layer was washed with 1 M hydrochloric acid, a saturated aqueous solution of sodium bicarbonate, brine, successively, and dried over magnesium sulfate, then evaporated. The residue was purified by silica gel column chromatography (*n*-hexane : ethyl acetate=8 : 1) to afford **2g** (655 mg, 90%). $[\alpha]_D=+20.9°$ (c=0.80, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.85 (3H, t, J=7.0 Hz), 1.23 (8H, m), 1.38 (2H, m), 1.70 (2H, quint., J=6.6 Hz), 3.80, 3.81 (each 1H, dt, J=6.4, 9.2 Hz, OCH_2), 4.69 (1H, ddd, J=2.5, 5.0, 10.0 Hz, H-5), 4.82 (1H, dd, J=5.0, 12.2 Hz, H-6), 5.03 (1H, dd, J=2.5, 12.2 Hz, H-6), 5.62 (1H, d, J=9.9 Hz, H-1), 6.02 (1H, t, J=

9.6 Hz, H-2), 6.17 (1H, t, *J*=9.6 Hz, H-4), 6.55 (1H, t, *J*=9.6 Hz, H-3), 6.87 (2H, d, *J*=11.0 Hz), 7.10 (2H, tt, *J*=1.5, 7.5 Hz), 7.23 (3H, tt, *J*=1.5, 7.5 Hz), 7.30 (2H, tt, *J*=1.5, 7.5 Hz), 7.37 (1H, tt, *J*=1.5, 7.5 Hz), 7.43 (3H, tt, *J*=1.5, 7.5 Hz), 7.55 (1H, tt, *J*=1.5, 7.5 Hz), 7.75 (2H, d, *J*=11.0 Hz), 7.95, 8.05, 8.18, 8.27 (each 2H, dt, *J*=1.5, 7.5 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.3, 22.9, 26.3, 29.45, 29.48, 29.6, 32.0, 63.3 (C-6), 68.3 (OCH_2), 70.0 (C-4), 71.3 (C-2), 75.3 (C-3), 76.5 (C-5), 86.1 (C-1), 115.5 (2C), 121.5, 128.8 (2C), 128.88 (2C), 128.93 (2C), 128.97 (2C), 129.39, 129.43, 129.9 (2C), 130.06 (2C), 130.15 (2C), 130.20 (3C), 130.4, 133.5, 133.6, 133.8 (2C), 136.8 (2C), 160.4, 165.6, 165.7, 166.2 (2C). IR ($CHCl_3$) ν: 3067, 2930, 2856, 1732, 1595, 1493, 1273, 1109 cm^{-1}. HR-MS *m*/*z*: 839.2861 (Calcd for $C_{48}H_{48}O_{10}SNa$: 839.2866).

***p*-Octyloxyphenyl 2,3,4-Tri-*O*-benzyl-β-D-glucopyranosyl Sulfoxide (5a)** *m*-Chloroperbenzoic acid (77%, 304.9 mg, 1.36 mmol) was added to a solution of **2a** (0.87 g, 1.30 mmol) in dichloromethane (15 ml) at 0 °C and the reaction mixture was stirred for 0.5 h with keeping the temperature. After the reaction, the reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate, which was extracted with ethyl acetate. The organic layer was successively washed with a saturated aqueous solution of sodium thiosulfate, a saturated aqueous solution of sodium bicarbonate, and brine, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified column chromatography on silica gel (chloroform) to afford compound **5a** (797.8 mg, 90%).

Less polar (major) component, $[\alpha]_D=-130.0°$ (c=0.74, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.84 (3H, t, *J*=7.0 Hz), 1.19 (8H, m), 1.34 (2H, m), 1.67 (2H, quint., *J*=6.6 Hz), 3.55 (1H, dt, *J*=2.5, 9.0 Hz, H-5), 3.85 (2H, t, *J*=6.6 Hz, OCH_2), 4.03 (2H, br s, H_2-6), 4.12 (1H, t, *J*=9.0 Hz, H-3), 4.21 (1H, t, *J*=9.0 Hz, H-4), 4.45 (1H, t, *J*=9.0 Hz, H-2), 4.52 (1H, d, *J*=9.0 Hz, H-1), 5.02, 5.08 (each 2H, s, OBn), 5.19, 5.27 (each 1H, d, AB type, *J*=10.8 Hz, OBn), 6.65 (1H, br s, OH), 7.08 (2H, d, A part of AB type, *J*=8.8 Hz), 7.21—7.45 (11H, m), 7.48, 7.60 (each 2H, d, *J*=7.0 Hz), 7.89 (2H, d, B part of AB type, *J*=8.8 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.2, 22.9, 26.2, 29.3, 29.4, 29.5, 31.9, 61.0 (C-6), 68.4 (OCH_2), 75.0 (OBn), 75.4 (OBn), 75.6 (OBn), 77.9 (C-2), 78.1 (C-4), 81.9 (C-5), 86.7 (C-3), 93.8 (C-1), 115.2 (2C), 127.9 (2C), 128.0 (2C), 128.08, 128.14, 128.2 (2C), 128.5 (2C), 128.7 (2C), 128.75 (3C), 128.78 (2C), 131.8, 138.9, 139.3, 139.4, 161.9. IR ($CHCl_3$) ν: 3352, 2928, 2858, 1593, 1497, 1454, 1256, 1101, 1088 cm^{-1}. HR-MS *m*/*z*: 709.3179 (Calcd for $C_{41}H_{50}O_7SNa$: 709.3175).

More polar (minor) component, $[\alpha]_D=-35.4°$ (c=0.67, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.84 (3H, t, *J*=7.0 Hz), 1.22 (8H, m), 1.38 (2H, m), 1.70 (2H, quint., *J*=7.0 Hz), 3.82, 3.84 (each 1H, dt, AB type, *J*=2.5, 9.5 Hz, OCH_2), 3.90 (1H, ddd, *J*=2.0, 4.0, 9.0 Hz, H-5), 4.06 (1H, t, *J*=9.0 Hz, H-4), 4.14 (1H, t, *J*=9.0 Hz, H-3), 4.15 (1H, m, H-6), 4.27 (1H, ddd, *J*=4.0, 6.0, 12.0 Hz, H-6), 4.38 (1H, t, *J*=9.0 Hz, H-2), 4.89 (1H, d, *J*=11.0 Hz, OBn), 4.95 (1H, d, *J*=12.0 Hz, OBn), 4.98 (1H, d, *J*=11.0 Hz, OBn), 4.99 (1H, d, *J*=12.0 Hz, OBn), 5.00 (1H, d, *J*=9.0 Hz, H-1), 5.01, 5.08 (each 1H, d, *J*=11.5 Hz, OBn), 6.86 (1H, t, *J*=6.0 Hz, OH), 6.98 (2H, d, *J*=8.8 Hz), 7.21—7.35 (11H, m), 7.39, 7.43 (each 2H, br d, *J*=7.0 Hz), 7.84 (2H, d, *J*=8.8 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.3, 22.9, 26.3, 29.4, 29.46, 29.54, 32.0, 61.3 (C-6), 68.4 (OCH_2), 73.6 (OBn), 74.8 (OBn), 75.2 (OBn), 76.2 (C-2), 78.0 (C-4), 81.5 (C-5), 86.8 (C-3), 96.5 (C-1), 115.3 (2C), 127.1 (2C), 127.51, 127.53 (2C), 127.88, 127.93, 128.0 (2C), 128.2 (2C), 128.4 (2C), 128.70 (2C), 128.71 (2C), 132.8, 139.1, 139.17, 139.20, 161.6. IR ($CHCl_3$) ν: 3314, 2930, 2856, 1593, 1497, 1468, 1456, 1258, 1132, 1092 cm^{-1}. HR-MS *m*/*z*: 709.3170 (Calcd for $C_{41}H_{50}O_7SNa$: 709.3175).

***p*-Octyloxyphenyl 2,3,4-Tri-*O*-benzoyl-β-D-glucopyranosyl Sulfoxide (5b)** *m*-Chloroperbenzoic acid (77%, 549 mg, 2.45 mmol) was added to a solution of **2b** (1.65 g, 2.31 mmol) in dichloromethane (50 ml) at 0 °C and the reaction mixture was stirred for 1 h with keeping the temperature. After the reaction, the reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate, which was extracted with chloroform. The organic layer was successively washed with a saturated aqueous solution of sodium thiosulfate, a saturated aqueous solution of sodium bicarbonate, and brine, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified column chromatography on silica gel (*n*-hexane : ethyl acetate = 1 : 1) to afford compound **5b** (1.44 g, 85%).

Less polar (major) component, $[\alpha]_D=-48.8°$ (c=1.16, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.84 (3H, t, *J*=7.0 Hz), 1.21 (8H, m), 1.34 (2H, m), 1.66 (2H, quint., *J*=6.5 Hz), 3.77, 3.82 (each 1H, dt, *J*=6.5, 9.5 Hz), 4.11 (1H, dd, *J*=5.0, 12.5 Hz, H-6), 4.20 (1H, br d, *J*=2.5, 12.5 Hz, H-6), 4.41 (1H, ddd, *J*=2.5, 5.0, 9.5 Hz, H-5), 5.36 (1H, d, *J*=9.5 Hz, H-1), 6.29 (1H, t, *J*=9.5 Hz, H-4), 6.49 (1H, t, *J*=9.5 Hz, H-2), 6.55 (1H, t, *J*=9.5 Hz, H-3), 7.00 (1H, br s, OH), 7.06 (2H, d, *J*=9.0 Hz), 7.15 (2H, tt, *J*=1.5, 7.0 Hz), 7.22 (2H, br t, *J*=7.0 Hz), 7.25 (1H, dd, *J*=7.0, 1.5 Hz), 7.29 (2H, tt, *J*=1.5, 7.0 Hz), 7.36, 7.42 (each 1H, tt, *J*=1.5, 7.0 Hz), 7.96 (2H, d, *J*=9.0 Hz), 8.01 (4H, tt, *J*=1.5, 7.0 Hz), 8.10 (2H, dd, *J*=1.5, 7.0 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.2, 22.9, 26.2, 29.3, 29.4, 29.5, 32.0, 61.2 (C-6), 68.4 (OCH_2), 69.3 (C-2), 69.7 (C-4), 75.8 (C-3), 80.7 (C-5), 91.8 (C-1), 115.4 (2C), 128.4 (2C), 128.7 (2C), 128.8 (4C), 129.5, 129.6, 129.8, 129.97 (2C), 130.01 (2C), 130.2 (2C), 131.3, 133.6 (2C), 133.8, 162.4, 165.3, 165.5, 166.3. IR ($CHCl_3$) ν: 3364, 2930, 2856, 1738, 1593, 1497, 1452, 1279, 1259 cm^{-1}. HR-MS *m*/*z*: 751.2550 (Calcd for $C_{41}H_{44}O_{10}SNa$: 751.2553).

More polar (minor) component, $[\alpha]_D=-65.1°$ (c=1.23, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.85 (3H, t, *J*=7.0 Hz), 1.23 (8H, m), 1.37 (2H, m), 1.64 (2H, quint., *J*=7.0 Hz), 3.56, 3.68 (each 1H, dt, AB type, *J*=9.1, 7.0 Hz, OCH_2), 4.19 (1H, dt, *J*=6.0, 12.6 Hz, H-6), 4.27 (1H, ddd, *J*=3.5, 7.0, 12.6 Hz, H-6), 4.58 (1H, ddd, *J*=2.5, 5.0, 9.5 Hz, H-5), 5.57 (1H, d, *J*=9.5 Hz, H-1), 6.19 (1H, t, *J*=9.5 Hz, H-4), 6.52 (1H, t, *J*=9.5 Hz, H-3), 6.68 (1H, t, *J*=9.5 Hz, H-2), 6.84 (2H, d, *J*=9.0 Hz), 7.12 (2H, t, *J*=7.5 Hz), 7.17—7.28 (6H, m), 7.37, 7.40 (each 1H, tt, *J*=1.5, 7.5 Hz), 7.73 (2H, dd, *J*=1.5, 7.5 Hz), 7.78 (2H, d, *J*=9.5 Hz), 8.00 (4H, td, *J*=7.5, 1.5 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.2, 22.9, 26.2, 29.3, 29.4, 29.5, 32.0, 61.4 (C-6), 67.0 (C-2), 68.1 (OCH_2), 69.5 (C-4), 76.0 (C-3), 80.8 (C-5), 93.9 (C-1), 115.4 (2C), 126.3 (2C), 128.4 (2C), 128.7 (2C), 128.8 (2C), 129.5, 129.6, 129.7, 129.89 (2C), 129.96 (2C), 130.00 (2C), 131.1, 133.3, 133.6, 133.7, 161.6, 164.8, 165.5, 166.2. IR ($CHCl_3$) ν: 3344, 3072, 2930, 2856, 1736, 1593, 1452, 1277, 1259 cm^{-1}. HR-MS *m*/*z*: 751.2546 (Calcd for $C_{41}H_{44}O_{10}SNa$: 751.2553).

***p*-Octyloxyphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl Sulfoxide (5c)** *m*-Chloroperbenzoic acid (77%, 40.6 mg, 0.181 mmol) was added to a solution of **2d**[3,4] (100.6 mg, 0.174 mmol) in dichloromethane (4.0 ml) at 0 °C and the reaction mixture was stirred for 1 h with keeping the temperature. After the reaction, the reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate, which was extracted with chloroform. The organic layer was successively washed with a saturated aqueous solution of sodium thiosulfate, a saturated aqueous solution of sodium bicarbonate, and brine, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified column chromatography on silica gel ($CHCl_3$) to afford compound **5c** (90.3 mg, 87%).

Less polar (major) component, $[\alpha]_D=-12.7°$ (c=0.72, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.83 (3H, t, *J*=7.0 Hz), 1.20 (8H, m), 1.37 (2H, m), 1.71 (2H, quint., *J*=6.6 Hz), 3.89 (1H, t, A part of AB type, *J*=10.0 Hz, H-6), 3.91 (2H, t, *J*=6.6 Hz, OCH_2), 4.42 (1H, dd, B part of AB type, *J*=5.0, 10.0 Hz, H-6), 4.56 (1H, dt, *J*=5.0, 10.0 Hz, H-5), 4.72 (1H, dd, *J*=10.0, 3.5 Hz, H-3), 4.89 (1H, t, *J*=10.0 Hz, H-4), 4.90, 5.03 (each 1H, d, AB type, *J*=12.0 Hz, OBn), 5.16 (1H, d, *J*=1.0 Hz, H-1), 5.39 (1H, ddd, *J*=1.0, 3.5, 4.5 Hz, H-2), 5.84 (1H, s, PhCH<), 7.16 (2H, d, *J*=9.0 Hz), 7.22—7.31 (3H, m), 7.36 (1H, tt, *J*=1.5, 9.0 Hz), 7.42 (2H, tt, *J*=1.0, 9.0 Hz), 7.47 (2H, dd, *J*=9.0, 1.5 Hz), 7.75 (2H, dd, *J*=9.0, 1.0 Hz), 7.88 (2H, d, *J*=9.0 Hz), 7.95 (1H, d, *J*=4.5 Hz, OH). ^{13}C-NMR (C_5D_5N) δ: 14.3, 22.9, 26.3, 29.40, 29.45, 29.54, 32.0, 66.0 (C-2), 68.5, 68.7 (OCH_2 and C-6), 70.5 (C-5), 72.9 (OBn), 77.5 (C-3), 78.8 (C-4), 101.1 (C-1), 102.1 (PhCH<), 115.8 (2C), 126.9 (2C), 127.0 (2C), 127.9 , 128.3 (2C), 128.56 (2C), 128.62 (2C), 129.3, 133.5, 138.6, 139.3, 162.3. IR ($CHCl_3$) ν: 3564, 2930, 2856, 1593, 1497, 1468, 1373, 1258 cm^{-1}. HR-MS *m*/*z*: 617.2546 (Calcd for $C_{34}H_{42}O_7SNa$: 617.2549).

More polar (minor) component, $[\alpha]_D=+113.4°$ (c=0.72, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.84 (3H, t, *J*=7.0 Hz), 1.21 (8H, m), 1.37 (2H, m), 1.72 (2H, quint., *J*=6.5 Hz), 3.84 (1H, t, A part of AB type, *J*=10.0 Hz, H-6), 3.92 (2H, td, *J*=6.5, 1.5 Hz, OCH_2), 4.41 (1H, dd, *J*=10.0, 5.0 Hz, H-6), 4.72 (1H, dd, *J*=9.5, 3.5 Hz, H-3), 4.86 (1H, t, *J*=9.5 Hz, H-4), 4.89 (1H, d, A part of AB type, *J*=12.0 Hz, OBn), 4.89 (1H, dd, *J*=3.5, 1.0 Hz, H-2), 4.98 (1H, dt, *J*=10.0, 5.0 Hz, H-5), 5.03 (1H, d, B part of AB type, *J*=12.0 Hz, OBn), 5.19 (1H, d, *J*=1.0 Hz, H-1), 5.81 (1H, s, PhCH<), 7.15 (2H, d, *J*=9.0 Hz), 7.25—7.37 (4H, m), 7.40 (2H, tt, *J*=7.5, 1.5 Hz), 7.46 (2H, dd, *J*=7.5, 2.0 Hz), 7.72 (2H, dt, *J*=7.5, 2.0 Hz), 7.81 (2H, d, *J*=9.0 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.3, 22.9, 26.2, 29.4, 29.45, 29.54, 32.0, 68.48, 68.51 (C-2 and OCH_2), 68.9 (C-6), 70.5 (C-5), 73.0 (OBn), 77.4 (C-3), 79.2 (C-4), 99.6 (C-1), 102.1 (PhCH<), 115.8 (2C), 126.9 (2C), 127.4 (2C), 127.9, 128.4 (2C), 128.5 (2C), 128.7 (2C), 129.2, 132.7, 138.7, 139.3, 162.2. IR ($CHCl_3$) ν: 3558, 2855, 1593, 1497, 1468, 1375, 1256 cm^{-1}. HR-MS *m*/*z*: 617.2545 (Calcd for $C_{34}H_{42}O_7SNa$: 617.2549).

2,3,4,6-Tetra-*O*-acetyl-D-glucopyranosyl-β(1—6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosyl *p*-Octyloxyphenyl Sulfoxide (6a) *N*-Iodosuccinimide (20.1 mg, 0.089 mmol) and a quite small amount of triflic acid (1 drop with a capillary) were added to a suspension of **2c** (21.9 mg, 0.039 mmol), **5a** (the less polar isomer) (24.0 mg, 0.035 mmol), and molecular sieves 4A (MS 4A) (150 mg) in dichloromethane (3 ml) at −50 °C. After stirring the mixture for

2 h while keeping the temperature, the reaction mixture was filtered through Hyflo super® which was washed with ethyl acetate. The filtrate was diluted with an aqueous solution of sodium bicarbonate and sodium thiosulfate, and extracted with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate=2 : 1) to afford **6a** (12.3 mg, 35%). $[\alpha]_D=-38.2°$ ($c=0.30$, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.84 (3H, t, $J=6.8$ Hz), 1.22 (8H, m), 1.43 (2H, m), 1.78 (2H, quint., $J=6.5$ Hz), 2.01 (6H, s, 2×Ac), 2.02, 2.04 (each 3H, s, Ac), 3.72 (1H, dt, $J=3.5$, 9.5 Hz, sulfox-Glc-5), 3.92 (1H, t, $J=9.5$ Hz, sulfox-Glc-4), 4.00—4.12 (5H, m, sulfox-Glc-6, sulfox-Glc-3, OCH_2), 4.18 (1H, ddd, $J=2.8$, 4.3, 9.5 Hz, Glc-5), 4.40 (1H, t, $J=9.5$ Hz, sulfox-Glc-2), 4.49 (1H, d, $J=9.5$ Hz, sulfox-Glc-1), 4.53 (1H, dd, $J=2.8$, 12.2 Hz, Glc-6), 4.58 (1H, dd, $J=4.3$, 12.2 Hz, Glc-6), 4.79 (1H, d, $J=11.0$ Hz, OBn), 4.97 (1H, d, $J=8.0$ Hz, Glc-1), 4.98 (1H, d, $J=10.8$ Hz, OBn), 5.01, 5.06 (each 1H, d, $J=11.5$ Hz, AB type, OBn), 5.17, 5.26 (each 1H, d, $J=10.9$ Hz, AB type, OBn), 5.42 (1H, dd, $J=8.0$, 9.5 Hz, Glc-2), 5.48 (1H, t, $J=9.5$ Hz, Glc-4), 5.69 (1H, t, $J=9.5$ Hz, Glc-3), 7.27—7.42 (13H, m), 7.47, 7.59 (each 2H, br d, $J=7.5$ Hz), 7.97 (2H, d, $J=8.8$ Hz). ^{13}C-NMR (C_5D_5N) δ: 14.3, 20.47, 20.50, 20.6, 20.7, 22.9, 26.3, 29.5 (2C), 29.6, 32.0, 62.6 (Glc-6), 68.5, 68.97, 69.01 (sulfox-Glc-6, Glc-4, OCH_2), 72.3 (2C) (Glc-2 and 5), 73.7 (Glc-3), 75.0, 75.4, 75.6 (OBn), 77.7 (sulfox-Glc-2), 78.1 (sulfox-Glc-4), 80.0 (sulfox-Glc-5), 86.5 (sulfox-Glc-3), 93.3 (sulfox-Glc-1), 101.4 (Glc-1), 115.4 (2C), 128.0, 128.06 (3C), 128.15 (2C), 128.24 (3C), 128.5 (3C), 128.8 (5C), 131.6, 138.8, 138.9, 139.1, 162.1, 169.7, 169.8, 170.3, 170.6. IR ($CHCl_3$) ν: 1755, 1593, 1497, 1366, 1258, 1097 cm^{-1}. HR-MS *m/z*: 1039.4132 (Calcd for $C_{55}H_{68}O_{16}SNa$: 1039.4126).

3,4,6-Tri-*O*-acetyl-2-*N*-phthaloyl-β(1—6)-D-glucosaminyl-2,3,4-tri-*O*-benzyl-β-D-glucopyranosyl *p*-Octyloxyphenyl Sulfoxide (6b) *N*-Iodosuccinimide (22.6 mg, 0.10 mmol) and a quite small amount of triflic acid (1 drop with a capillary) were added to a suspension of **2e** (33.0 mg, 0.053 mmol), **5a** (the less polar isomer) (26.2 mg, 0.038 mmol), and molecular sieves 4A (MS 4A) (150 mg) in dichloromethane (3 ml) at −50 °C. After stirring the mixture for 15 min. while keeping the temperature, the reaction mixture was filtered through Hyflo super® which was washed with ethyl acetate. The filtrate was diluted with an aqueous solution of sodium bicarbonate and sodium thiosulfate, and extracted with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate=2 : 1) to afford **6b** (30.8 mg, 73%). $[\alpha]_D=-32.2°$ ($c=0.62$, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.83 (3H, t, $J=7.0$ Hz), 1.23 (8H, m), 1.44 (2H, m), 1.80 (2H, quint., $J=7.0$ Hz), 1.83, 1.98, 2.10 (each 3H, s, OAc), 3.58 (1H, br d, $J=9.0$ Hz, Glc-5), 3.96—4.16 (6H, m), 4.38 (1H, br q, $J=9.5$ Hz, GlcN-5), 4.41 (1H, d, $J=9.5$ Hz, Glc-1), 4.41 (1H, m), 4.64 (1H, d, $J=11.0$ Hz, OBn), 4.70, 4.74 (each 1H, d, AB type, $J=9.0$ Hz, GlcN-6H$_2$), 4.76 (1H, d, $J=11.0$ Hz, OBn), 4.85 (1H, dd, $J=8.5$, 9.0 Hz, GlcN-2), 4.94, 5.01 (each 1H, d, AB type, $J=11.5$ Hz, OBn), 5.15, 5.26 (each 1H, d, AB type, $J=11.0$ Hz, OBn), 5.63 (1H, t, $J=10.0$, 9.5 Hz, GlcN-4), 5.97 (1H, d, $J=8.5$ Hz, GlcN-1), 6.35 (1H, dd, $J=10.0$, 9.0 Hz, H-3, GlcN), 7.17—7.44 (14H, m), 7.51 (2H, dd, $J=3.0$, 5.5 Hz), 7.57 (3H, br t, $J=7.5$ Hz), 7.80 (2H, dd, $J=5.0$, 3.0 Hz), 8.02 (2H, d, $J=9.0$ Hz). ^{13}C-NMR (C_5D_5N) δ: 14.2, 20.3, 20.5, 20.8, 22.9, 26.3, 29.48, 29.53, 29.6, 32.0, 55.7 (GlcN-2), 62.6 (GlcN-6), 68.6 (OCH_2), 69.5 (2C) (GlcN-4 and Glc-6), 71.6 (GlcN-3), 72.6 (GlcN-5), 74.9 (OBn), 75.3 (OBn), 75.6 (OBn), 77.6 (Glc-2), 77.9 (Glc-4), 79.6 (Glc-5), 86.5 (Glc-3), 93.4 (Glc-1), 99.5 (GlcN-1), 115.4 (2C), 127.88, 127.91, 127.98 (3C), 128.10 (3C), 128.14, 128.4, 128.5 (3C), 128.6 (3C), 128.7 (3C), 128.8 (3C), 131.6, 131.7, 134.7 (2C), 138.7, 138.8, 139.2, 162.2, 169.8, 170.5, 170.7. IR ($CHCl_3$) ν: 1747, 1719, 1593, 1497, 1387, 1366, 1252 cm^{-1}. HR-MS *m/z*: 1126.4229 (Calcd for $C_{61}H_{69}NO_{16}SNa$: 1126.4235).

3,4,6-Tri-*O*-acetyl-2-*N*-phthaloyl-β(1—6)-D-glucosaminyl-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl *p*-Octyloxyphenyl Sulfoxide (6c) *N*-Iodosuccinimide (23.8 mg, 0.106 mmol) and a quite small amount of triflic acid (1 drop with a capillary) were added to a suspension of **2e** (41.6 mg, 0.063 mmol), **5b** (the less polar diastereomer) (30.7 mg, 0.042 mmol), and molecular sieves 4A (MS 4A) (150 mg) in dichloromethane (3 ml) at −50 °C. After stirring the mixture for 15 min while keeping the temperature, the reaction mixture was filtered through Hyflo super® which was washed with ethyl acetate. The filtrate was diluted with an aqueous solution of sodium bicarbonate and sodium thiosulfate, and extracted with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate=1 : 1) and preparative thin layer chromatography (*n*-hexane/ethyl acetate=1 : 1) to afford **6c** (32.1 mg, 66%). $[\alpha]_D=-57.8°$ ($c=0.87$, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.85 (3H, t, $J=7.0$ Hz), 1.23 (8H, m), 1.44 (2H, m), 1.78 (2H, quint., $J=6.6$ Hz), 1.85, 1.98, 2.14 (each 3H, s, OAc), 4.00, 4.02 (each 1H, dt, AB type, $J=6.6$, 9.3 Hz, OCH_2), 4.09 (1H, dd, $J=5.5$, 11.8 Hz, Glc-6), 4.25 (1H, ddd, $J=2.5$, 4.5, 9.5 Hz, GlcN-5), 4.30 (1H, dd, $J=2.0$, 11.8 Hz, Glc-6), 4.51 (1H, dd, $J=2.5$, 12.5 Hz, GlcN-6), 4.53 (1H, ddd, $J=2.0$, 5.5, 9.5 Hz, Glc-5), 4.60 (1H, dd, $J=4.5$, 12.5 Hz, GlcN-6), 4.84 (1H, dd, $J=8.4$, 10.0 Hz, GlcN-2), 5.31 (1H, d, $J=9.5$ Hz, Glc-1), 5.54 (1H, t, $J=9.5$ Hz, GlcN-4), 5.91 (1H, t, $J=9.5$ Hz, Glc-4), 6.01 (1H, d, $J=10.0$ Hz, GlcN-1), 6.28 (1H, dd, $J=8.4$, 9.5 Hz, GlcN-3), 6.30 (1H, t, $J=9.5$ Hz, Glc-2), 6.43 (1H, t, $J=9.5$ Hz, Glc-3), 7.08 (2H, t, $J=8.0$ Hz), 7.15—7.28 (5H, m), 7.32 (2H, d, $J=9.0$ Hz), 7.34 (1H, tt, $J=1.3$, 7.5 Hz), 7.39 (1H, tt, $J=1.3$, 7.5 Hz), 7.56 (2H, dd, $J=3.0$, 5.5 Hz), 7.79 (2H, dd, $J=1.3$, 8.2 Hz), 7.87 (2H, dd, $J=1.3$, 7.5 Hz), 7.87 (2H, m), 8.04 (2H, d, $J=9.0$ Hz), 8.07 (2H, dt, $J=1.3$, 7.5 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.3, 20.2, 20.4, 20.8, 22.9, 26.3, 29.5 (2C), 29.6, 32.0, 55.4 (GlcN-2), 62.5 (GlcN-6), 68.6 (Glc-6), 69.0 (Glc-2 and OCH_2), 69.4 (Glc-4), 69.5 (GlcN-4), 71.5 (GlcN-3), 72.5 (GlcN-5), 75.3 (Glc-3), 78.2 (Glc-5), 90.3 (Glc-1), 98.9 (GlcN-1), 115.5 (2C), 128.7 (6C), 128.77 (4C), 128.80 (3C), 129.2, 129.3, 129.7, 129.9 (2C), 130.0 (2C), 130.2 (2C), 130.8, 132.1, 133.6, 133.7 (2C), 134.6 (2C), 162.6, 165.2, 165.3, 166.2, 169.8, 170.4, 170.6. IR ($CHCl_3$) ν: 1740, 1720, 1593, 1495, 1452, 1389, 1367, 1279, 1259 cm^{-1}. HR-MS *m/z*: 1168.3617 (Calcd for $C_{61}H_{63}NO_{19}SNa$: 1168.3613).

3,4,6-Tri-*O*-acetyl-2-*N*-phthaloyl-β(1—6)-D-glucosaminyl-2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl *p*-Octyloxyphenyl Sulfoxide (6c′) *N*-Iodosuccinimide (24.4 mg, 0.109 mmol) and a quite small amount of triflic acid (1 drop with a capillary) were added to a suspension of **2e** (42.8 mg, 0.065 mmol), **5b** (a mixture of two diastereomers on the sulfur atom) (31.6 mg, 0.043 mmol), and molecular sieves 4A (MS 4A) (150 mg) in dichloromethane (3 ml) at −50 °C. After stirring the mixture for 15 min. while keeping the temperature, the reaction mixture was filtered through Hyflo super® which was washed with ethyl acetate. The filtrate was diluted with an aqueous solution of sodium bicarbonate and sodium thiosulfate, and extracted with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate=2 : 1) to afford **6c** (16.3 mg) and more polar component **6c′** (12.9 mg) (Total 59%). $[\alpha]_D=+20.7°$ ($c=0.78$, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.85 (3H, t, $J=7.0$ Hz), 1.24 (8H, m), 1.39 (2H, m), 1.69 (2H, quint., $J=6.6$ Hz), 1.83, 1.99, 2.08 (each 3H, s, OAc), 3.65, 3.78 (each 1H, dt, AB type, $J=6.6$, 9.0 Hz, OCH_2), 4.09 (1H, dd, $J=6.6$, 11.5 Hz, Glc-6), 4.18 (1H, ddd, $J=2.5$, 4.5, 10.0 Hz, GlcN-5), 4.37 (1H, dd, $J=2.0$, 11.5 Hz, Glc-6), 4.39 (1H, dd, $J=2.5$, 12.3 Hz, GlcN-6), 4.60 (1H, ddd, $J=2.0$, 6.6, 9.2 Hz, Glc-5), 4.62 (1H, dd, $J=4.5$, 12.3 Hz, GlcN-6), 4.90 (1H, dd, $J=8.5$, 10.8 Hz, GlcN-2), 5.36 (1H, d, $J=9.2$ Hz, Glc-1), 5.57 (1H, t, $J=10.0$ Hz, GlcN-4), 5.81 (1H, t, $J=9.2$ Hz, Glc-4), 6.05 (1H, d, $J=8.5$ Hz, GlcN-1), 6.34 (1H, dd, $J=9.2$, 10.0 Hz, GlcN-3), 6.38 (1H, t, $J=9.2$ Hz, Glc-3), 6.50 (1H, t, $J=9.2$ Hz, Glc-2), 6.92 (2H, d, $J=9.0$ Hz), 7.10 (2H, br t, $J=7.3$ Hz), 7.17—7.25 (5H, m), 7.35, 7.38 (each 1H, tt, $J=1.3$, 7.5 Hz), 7.55 (2H, dd, $J=3.5$, 5.5 Hz), 7.68 (2H, d, $J=9.0$ Hz), 7.71 (2H, dd, $J=1.3$, 8.5 Hz), 7.82 (2H, dd, $J=1.3$, 8.5 Hz), 7.89 (2H, dd, $J=1.3$, 8.5 Hz), 7.92 (2H, dt, $J=3.1$, 8.5 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.3, 20.2, 20.4, 20.7, 22.9, 26.3, 29.4, 29.5, 29.6, 32.0, 55.4 (GlcN-2), 62.4 (GlcN-6), 67.0 (Glc-2), 68.3 (OCH_2), 68.6 (Glc-6), 69.3 (Glc-4), 69.5 (GlcN-4), 71.4 (GlcN-3), 72.4 (GlcN-5), 75.4 (Glc-3), 78.3 (Glc-5), 93.7 (Glc-1), 98.9 (GlcN-1), 115.4 (2C), 123.9, 124.0, 126.5 (2C), 128.4 (2C), 128.7 (2C), 128.8 (2C), 129.2, 129.3, 129.6, 129.9 (6C), 130.0 (3C), 131.1, 132.1, 133.4, 133.6, 133.7, 134.7 (2C), 161.7, 164.7, 165.3, 166.1, 169.8, 170.4, 170.5. IR ($CHCl_3$) ν: 1740, 1720, 1595, 1495, 1452, 1389, 1367, 1277, 1259 cm^{-1}. HR-MS *m/z*: 1168.3618 (Calcd for $C_{61}H_{63}NO_{19}SNa$: 1168.3613).

3,4,6-Tri-*O*-acetyl-2-*N*-phthaloyl-β(1—2)-D-glucosaminyl-3-*O*-benzyl-(4,6)-benzylidene-β-D-mannopyranosyl *p*-Octyloxyphenyl Sulfoxide (6d) *N*-Iodosuccinimide (19.8 mg, 0.088 mmol) and a quite small amount of triflic acid (1 drop with a capillary) were added to a suspension of **2e** (35.0 mg, 0.053 mmol), **5c** (the less polar isomer) (21.1 mg, 0.036 mmol), and molecular sieves 4A (MS 4A) (150 mg) in dichloromethane (3 ml) at −50 °C. After stirring the mixture for 2 h while keeping the temperature, the reaction mixture was filtered through Hyflo super® which was washed with ethyl acetate. The filtrate was diluted with an aqueous solution of sodium bicarbonate and sodium thiosulfate, and extracted with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and evaporated. The residue was purified by preparative silica gel thin layer chromatography (*n*-hexane/ethyl acetate=2 : 1, 5 times development) to afford **6d** (7.4 mg, 21%). $[\alpha]_D=+30.5°$ ($c=0.15$, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.85 (3H, t, $J=7.0$ Hz), 1.24 (8H, m), 1.45 (2H, m), 1.80 (2H, quint., $J=6.6$ Hz), 1.83, 2.01, 2.06 (each 3H, s, OAc), 3.26 (1H, t, $J=9.5$ Hz, Man-6), 3.88 (1H, ddd, $J=2.3$, 4.5, 9.6 Hz, GlcN-5), 4.01 (1H, m, Man-6), 4.02 (1H, t, $J=7.0$ Hz, OCH_2), 4.06 (1H, dd, $J=6.5$, 9.5 Hz, Man-6), 4.29 (1H, dd, $J=2.3$, 12.2 Hz,

GlcN-6), 4.35 (1H, t, J=10.2 Hz, Man-4), 4.35 (1H, m, Man-5), 4.57 (1H, dd, J=4.5, 12.2 Hz, GlcN-6), 4.69 (1H, dd, J=3.6, 9.7 Hz, Man-3), 4.78 (1H, br s, Man-1), 4.79 (1H, d, J=11.7 Hz, OBn), 4.92 (1H, dd, J=8.5, 10.7 Hz, GlcN-2), 5.02 (1H, d, J=11.7 Hz, OBn), 5.22 (1H, dd, J=3.6, 0.5 Hz, Man-2), 5.50 (1H, s, PhCH<), 5.58 (1H, t, J=9.6 Hz, GlcN-4), 5.82 (1H, d, J=8.5 Hz, GlcN-1), 6.32 (1H, dd, J=9.6, 10.7 Hz, GlcN-3), 7.25 (1H, tt, J=2.0, 7.5 Hz), 7.26 (2H, d, J=8.6 Hz), 7.32 (3H, tt, J=7.0, 2.0 Hz), 7.35 (3H, tt, J=2.3, 7.5 Hz), 7.54 (3H, m), 7.58 (4H, m), 7.79 (2H, d, J=8.6 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.3, 20.2, 20.4, 20.6, 22.9, 26.3, 29.4, 29.5, 29.6, 32.0, 55.2 (GlcN-2), 62.1 (GlcN-6), 68.2 (Man-6), 68.8 (OCH_2), 69.4 (GlcN-4), 70.2 (Man-5), 71.1 (GlcN-3), 71.4 (OBn), 72.2 (Man-2), 72.9 (GlcN-5), 75.3 (Man-3), 77.9 (Man-4), 96.9, 97.0 (GlcN-1 and Man-1), 102.1 (PhCH<), 116.0 (2C), 126.8 (2C), 126.9 (3C), 127.9, 128.4 (3C), 128.5 (3C), 128.6 (3C), 129.3, 131.8, 132.8, 134.7 (2C), 138.2, 139.0, 162.5 (2C), 169.7, 170.4, 170.5. IR ($CHCl_3$) ν: 1749, 1719, 1593, 1497, 1367, 1258, 1107 cm^{-1}. HR-MS m/z: 1034.3606 (Calcd for $C_{54}H_{61}NO_{16}SNa$: 1034.3609).

***p*-Octyloxyphenyl 6-*O*-Trityl-1-*thio*-β-D-glucopyranoside (9)** Trityl chloride (2.49 g, 8.93 mmol) and *N*,*N*-dimethylaminopyridine (10.0 mg) were added to a solution of **8**[3,4] (3.53 g) in pyridine (40 ml) and the mixture was stirred at the reflux temperature for 5.5 h. After the reaction, distilled water was added to the reaction mixture, which was then extracted with chloroform. The organic layer was washed with brine, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate=1 : 2) to afford compound **9** (3.33 g, 84%). $[\alpha]_D$=−17.3° (c=1.03, $CHCl_3$). ^{1}H-NMR (C_5D_5N+D_2O) δ: 0.84 (3H, t, J=7.0 Hz), 1.21 (8H, m), 1.38 (2H, m), 1.71 (2H, quint., J=6.5 Hz), 3.73 (1H, dd, J=4.0, 9.5 Hz, H-6), 3.87 (2H, t, J=6.5 Hz, OCH_2), 3.91 (1H, br d, J=9.5 Hz, H-6), 4.00 (1H, t, J=9.5 Hz, H-4), 4.02 (1H, d, J=4.0 Hz, H-5), 4.08 (1H, t, J=9.5 Hz, H-2), 4.21 (1H, t, J=9.5 Hz, H-3), 5.24 (1H, dd, J=0.5, 9.5 Hz, H-1), 7.02 (2H, d, J=9.0 Hz), 7.24 (3H, tt, J=1.3, 7.3 Hz), 7.33 (6H, br t, J=7.3 Hz), 7.54 (6H, br d, J=7.3 Hz), 8.04 (2H, d, J=9.0 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.2, 22.9, 26.3, 29.46 (2C), 29.54, 32.0, 65.0 (C-6), 68.2 (OCH_2), 71.5 (C-4), 73.8 (C-2), 80.3 (C-3), 80.5 (C-5), 86.8 (Ph_3C), 90.0 (C-1), 115.5 (2C), 125.1, 127.3 (2C), 128.2 (6C), 129.3 (6C), 135.1 (3C), 145.1 (3C), 159.5. IR ($CHCl_3$) ν: 3584, 3065, 2930, 2856, 1593, 1493, 1285, 1248 cm^{-1}. HR-MS m/z: 665.2918 (Calcd for $C_{39}H_{46}O_6SNa$: 665.2913).

***p*-Octyloxyphenyl 2,3,4-Tri-*O*-benzyl-6-*O*-trityl-1-*thio*-β-D-glucopyranoside (10a)** Sodium hydride (55% in mineral oil, 1.57 g, 36.0 mmol) was added to a solution of compound **9** in *N*,*N*-dimethylformamide (30 ml) and the mixture was stirred at 0 °C for 30 min. Keeping the temperature, benzyl bromide (2.0 ml, 16.8 mmol) was added drop wise to the reaction mixture, which was stirred for 20 h at room temperature. After the reaction, the reaction mixture was poured into ice water, which was extracted with diethyl ether. The organic layer was successively washed with small amount of distilled water, a saturated aqueous solution of sodium thiosulfate, and brine, dried over magnesium sulfate, and condensed *in vacuo*. The residue was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate=30 : 1) to afford compound **10a** (2.84 g, 71 %). $[\alpha]_D$=−12.1° (c=1.25, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.83 (3H, t, J=7.0 Hz), 1.20 (8H, m), 1.38 (2H, m), 1.71 (2H, quint., J=6.5 Hz), 3.46 (1H, dd, J=5.0, 10.5 Hz, H-6), 3.75 (2H, br d, J=9.0 Hz, H-5 and H-6), 3.83 (1H, t, J=9.0 Hz, H-2), 3.88, 3.90 (each 1H, q, AB type, J=6.5 Hz, OCH_2), 3.93 (1H, t, J=9.0 Hz, H-3), 3.98 (1H, t, J=9.0 Hz, H-4), 4.52 (1H, d, J=10.5 Hz, OBn), 4.87 (1H, d, J=10.5 Hz, OBn), 4.97 (1H, d, J=11.0 Hz, OBn), 4.99 (1H, d, J=11.0 Hz, OBn), 5.02 (1H, d, J=11.0 Hz, OBn), 5.05 (1H, d, J=9.0 Hz, H-1), 5.14 (1H, d, J=11.0 Hz, OBn), 7.06 (2H, d, J=8.8 Hz), 7.07 (2H, m), 7.24—7.42 (18H, m), 7.45 (2H, br d, J=8.0 Hz), 7.63 (2H, br d, J=8.0 Hz), 7.75 (6H, br d, J=8.0 Hz), 7.98 (2H, d, J=8.0 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.2, 22.9, 26.3, 29.5 (2C), 29.6, 32.0, 63.3 (C-6), 68.3 (OCH_2), 75.0 (OBn), 75.2 (OBn), 75.7 (OBn), 78.5 (C-4), 79.2 (C-5), 81.4 (C-2), 86.9 (Ph_3C-), 87.1 (C-3), 88.4 (C-1), 115.7 (2C), 124.4, 127.5 (2C), 127.88, 127.91, 128.0, 128.1 (3C), 128.37 (9C), 128.40 (3C), 128.6 (3C), 128.7 (4C), 129.3 (6C), 138.7, 139.3, 139.4, 144.7 (2C), 159.9. IR ($CHCl_3$) ν: 3065, 2930, 2858, 1593, 1493, 1470, 1450 cm^{-1}. HR-MS m/z: 935.4317 (Calcd for $C_{60}H_{64}O_6SNa$: 935.4321).

***p*-Octyloxyphenyl 2,3,4-Tri-*O*-benzoyl-6-*O*-trityl-1-*thio*-β-D-glucopyranoside (10b)** Benzoyl chloride (34 μl, 0.29 mmol) and *N*,*N*-dimethyl-4-aminopyridine (0.1 mg) were added to a solution of compound **9** (46.7 mg, 0.073 mmol) in pyridine (2.0 ml) and the mixture was stirred at 50 °C for 6 h. After removing the organic solvent *in vacuo*, the residue was extracted with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and evaporated. The residue was purified by silica gel column chromatography (*n*-hexane : ethyl acetate=8 : 1) to afford **10b** (53.2 mg, 77%). $[\alpha]_D$=+16.1° (c=1.01, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.84 (3H, t, J=7.0 Hz), 1.22 (8H, m), 1.38 (2H, m), 1.71 (2H, quint., J=6.6 Hz), 3.45 (1H, dd, J=4.2, 10.6 Hz, H-6), 3.70 (1H, dd, J=1.8, 10.6 Hz, H-6), 3.87 (2H, t, J=6.6 Hz, OCH_2), 4.41 (1H, ddd, J=1.8, 4.2, 9.9 Hz, H-5), 5.59 (1H, d, J=9.9 Hz, H-1), 6.09 (1H, t, J=9.9 Hz, H-2), 6.25 (1H, t, J=9.9 Hz, H-4), 6.43 (1H, t, J=9.9 Hz, H-3), 7.05—7.26 (16H, m), 7.31 (2H, br t, J=7.5 Hz), 7.39 (1H, tt, J=1.5, 7.5 Hz), 7.43 (1H, tt, J=1.5, 7.5 Hz), 7.69 (6H, dt, J=1.5, 7.5 Hz), 7.85 (2H, dt, J=1.5, 7.5 Hz), 7.95 (4H, dt, J=1.5, 7.5 Hz), 8.18 (2H, dt, J=1.5, 7.5 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.3, 22.9, 26.3, 29.5 (2C), 29.6, 32.0, 62.5 (C-6), 68.3 (OCH_2), 69.5 (C-4), 71.6 (C-2), 75.8 (C-3), 78.1 (C-5), 86.3 (C-1), 87.0 (CPh_3), 115.7 (2C), 121.7, 127.4 (3C), 128.3 (6C), 128.69 (2C), 128.72 (2C), 129.0 (2C), 129.1 (6C), 129.5, 129.7, 129.97 (2C), 130.0 (3C), 130.2 (2C), 133.6 (3C), 133.8, 136.9 (2C), 144.4 (2C), 160.5, 165.3, 165.6, 166.2. IR ($CHCl_3$) ν: 3065, 2930, 2856, 1732, 1595, 1493, 1450, 1281, 1261 cm^{-1}. HR-MS m/z: 977.3693 (Calcd for $C_{60}H_{58}O_9SNa$: 977.3699).

***p*-Octyloxyphenyl 3,4,6-Tri-*O*-acetyl-2-*N*-phthaloyl-β(1—6)-D-glucosaminyl-1-*thio*-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (11a)** A solution of triphenylphosphine (68.8 mg, 0.26 mmol) in carbon tetrachloride (1.0 ml) was added to a solution of **6b** (29.0 mg, 0.026 mmol) in acetonitrile (2.0 ml), which was stirred for 2 h under refluxing condition. After the reaction, the reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate and extracted with ethyl acetate. The organic layer was extracted with ethyl acetate, washed with brine, dried over magnesium sulfate, and evaporated. The residue was purified by preparative silica gel thin layer chromatography (*n*-hexane : ethyl acetate=3 : 1) to afford **11a** (23.3 mg, 82%). $[\alpha]_D$=+6.3° (c=0.73, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.83 (3H, t, J=7.0 Hz), 1.20 (8H, m), 1.42 (2H, m), 1.76 (2H, quint., J=6.6 Hz), 1.83, 2.01, 2.05 (each 3H, s, 3×Ac), 3.55 (1H, t, J=9.5 Hz, Glc-2), 3.61 (1H, t, J=9.5 Hz, Glc-4), 3.74 (1H, ddd, J=1.8, 4.7, 9.5 Hz, Glc-5), 3.83 (1H, t, J=9.5 Hz, Glc-3), 3.98—4.09 (3H, m, Glc-6 and A part of AB type, OCH_2), 4.15 (1H, ddd, J=2.4, 4.6, 10.0 Hz, GlcN-5), 4.42 (1H, dd, J=1.8, 10.8 Hz, B part of AB type, OCH_2), 4.44 (1H, dd, J=2.4, 12.2 Hz, GlcN-6), 4.55 (1H, d, J=10.5 Hz, OBn), 4.60 (1H, dd, J=4.6, 12.2 Hz, GlcN-6), 4.71 (1H, d, J=10.5 Hz, OBn), 4.81 (1H, d, J=10.8 Hz, OBn), 4.83 (1H, d, J=9.5 Hz, Glc-1), 4.84 (1H, d, J=11.5 Hz, OBn), 4.92 (1H, d, J=11.5 Hz, OBn), 4.95 (1H, dd, J=8.5, 10.5 Hz, GlcN-2), 5.01 (1H, d, J=10.8 Hz, OBn), 5.61 (1H, dd, J=9.2, 10.0 Hz, GlcN-4), 6.00 (1H, d, J=8.5 Hz, GlcN-1), 6.36 (1H, dd, J=9.2, 10.5 Hz, GlcN-3), 7.18 (2H, d, J=8.8 Hz), 7.23—7.38 (14H, m), 7.46 (2H, dd, J=3.1, 5.5 Hz), 7.54 (2H, br d, J=1.3, 8.4 Hz), 7.75 (2H, dd, J=3.2, 5.2 Hz), 7.80 (2H, d, J=8.8 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.3, 20.2, 20.5, 20.7, 22.9, 26.3, 29.5, 29.56, 29.59, 32.0, 55.4 (GlcN-2), 62.5 (GlcN-6), 68.3 (Glc-6), 68.8 (OCH_2), 69.6 (GlcN-4), 71.4 (GlcN-3), 72.5 (GlcN-5), 74.8 (OBn), 75.1 (OBn), 75.4 (OBn), 78.2 (Glc-4), 78.3 (Glc-5), 80.9 (Glc-2), 86.7 (Glc-3), 87.7 (Glc-1), 98.7 (GlcN-1), 115.7 (2C), 123.9 (2C), 127.8, 127.9 (4C), 128.0, 128.1 (3C), 128.3 (3C), 128.7 (7C), 131.7, 134.7 (2C), 135.3 (2C), 138.8, 139.2, 139.3, 159.9, 169.8, 170.4, 170.6. IR ($CHCl_3$) ν: 2930, 2856, 1747, 1720, 1593, 1495, 1387, 1366 cm^{-1}. HR-MS m/z: 1110.4282 (Calcd for $C_{61}H_{69}NO_{15}SNa$: 1110.4286).

***p*-Octyloxyphenyl 3,4,6-Tri-*O*-acetyl-2-*N*-phthaloyl-β(1—6)-D-glucosaminyl-1-*thio*-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (11b)** A solution of triphenylphosphine (66.1 mg, 0.256mmol) in carbon tetrachloride (1.0 ml) was added to a solution of a mixture of **6c** and **6c′** (29.2 mg, 0.026 mmol) in acetonitrile (2.0 ml), which was stirred for 2 h under refluxing condition. After the reaction, the reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate and extracted with ethyl acetate. The organic layer was extracted with ethyl acetate, washed with brine, dried over magnesium sulfate, and evaporated. The residue was purified by preparative silica gel thin layer chromatography (*n*-hexane : ethyl acetate=1 : 1) to afford **11b** (24.3 mg, 84%). $[\alpha]_D$=−6.7° (c=0.80, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 0.84 (3H, t, J=7.0 Hz), 1.22 (8H, m), 1.41 (2H, m), 1.75 (2H, quint., J=6.6 Hz), 1.83, 1.98, 2.03 (each 3H, s, 3×Ac), 3.99 (2H, t, J=6.6 Hz, OCH_2), 4.05 (1H, dd, J=6.0, 11.3 Hz, Glc-6), 4.13 (1H, ddd, J=2.5, 4.8, 10.0 Hz, GlcN-5), 4.35 (1H, dd, J=2.5, 12.2 Hz, GlcN-6), 4.43 (1H, dd, J=2.0, 11.3 Hz, Glc-6), 4.47 (1H, ddd, J=2.0, 6.0, 9.5 Hz, Glc-5), 4.56 (1H, dd, J=4.8, 12.2 Hz, GlcN-6), 4.93 (1H, dd, J=8.5, 10.8 Hz, GlcN-2), 5.38 (1H, d, J=9.5 Hz, Glc-1), 5.56 (1H, dd, J=9.3, 10.0 Hz, GlcN-4), 5.80, 5.81 (each 1H, t, J=9.5 Hz, Glc-2 and 4), 6.01 (1H, d, J=8.5 Hz, GlcN-1), 6.33 (1H, dd, J=9.3, 10.8 Hz, GlcN-3), 6.36 (1H, t, J=9.5 Hz, Glc-3), 7.06 (2H, br t, J=7.5 Hz), 7.15 (2H, d, J=9.0 Hz), 7.17—7.30 (5H, m), 7.36 (1H, tt, J=1.5, 7.3 Hz), 7.39 (1H, tt, J=1.5, 7.3 Hz), 7.54 (2H, dd, J=3.1, 5.4 Hz), 7.73 (2H, d, J=8.0 Hz), 7.82—7.90 (6H, m), 8.10 (2H, dt, J=1.5, 7.3 Hz). ^{13}C-NMR (C_5D_5N) δ: 14.3, 20.2, 20.4, 20.6, 22.9, 26.3, 29.48, 29.53, 29.59, 32.0, 55.4 (GlcN-2), 62.4 (GlcN-6), 68.3 (OCH_2), 68.8 (Glc-

6), 69.5 (GlcN-4), 69.9 (Glc-4), 71.2 (Glc-2), 71.4 (GlcN-3), 72.4 (GlcN-5), 75.3 (Glc-3), 77.5 (Glc-5), 85.9 (Glc-1), 98.9 (GlcN-1), 115.6 (2C), 121.7, 128.7 (3C), 128.8 (3C), 128.9 (3C), 129.3, 129.4, 129.87 (3C), 129.95 (3C), 130.1 (3C), 132.1, 133.5, 133.7 (2C), 134.6 (2C), 136.6 (2C), 160.4, 165.37, 165.40, 166.1, 169.8, 170.4, 170.5. IR ($CHCl_3$) *v*: 1738, 1722, 1595, 1495, 1389, 1367, 1281, 1259, 1109, 1092 cm^{-1}. HR-MS *m/z*: 1152.3667 (Calcd for $C_{61}H_{63}NO_{18}SNa$: 1152.3664).

Methyl [(3,4,6-Tri-*O*-acetyl-2-*N*-phthaloyl-D-glucosaminyl)-β(1—6)-2,3,4-tri-*O*-benzyl-D-glucopyranosyl]-β(1—6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (13a) *N*-Iodosuccinimide (15.2 mg, 0.068 mmol) and a quite small amount of triflic acid (1 drop with a capillary) were added to a suspension of **11a** (29.4 mg, 0.027 mmol), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**12**) (12.7 mg, 0.027 mmol), and molecular sieves 4A (MS 4A) (150 mg) in dichloromethane (3 ml) at −50 °C. After stirring the mixture for 1 h while keeping the temperature, the reaction mixture was filtered through Hyflo super® which was washed with ethyl acetate. The filtrate was diluted with an aqueous solution of sodium bicarbonate and sodium thiosulfate, and extracted with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and evaporated. The residue was purified by preparative silica gel thin layer chromatography (*n*-hexane/ethyl acetate=3 : 2) to afford **13a** (a mixture of α- and β-isomers, α : β=1 : 2.5) (17.9 mg, 50%).

β-Isomer: $[\alpha]_D$=+15.0° (*c*=0.44, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.81, 2.00, 2.01 (each 3H, s, OAc), 3.44 (3H, s, OMe), 3.57 (1H, dd, *J*=7.8, 9.0 Hz, β-Glc-2), 3.61 (1H, dd, *J*=8.5, 9.0 Hz, β-Glc-4), 3.67 (1H, ddd, *J*=1.5, 4.7, 9.9 Hz, β-Glc-5), 3.78 (1H, t, *J*=9.0 Hz, β-Glc-3), 3.84 (1H, *J*=3.5, 9.2 Hz, MeO-Glc-2), 3.87 (1H, *J*=9.2, 9.8 Hz, MeO-Glc-4), 3.87 (1H, *J*=3.5, 10.0 Hz, MeO-Glc-6), 4.02 (1H, ddd, *J*=1.5, 3.5, 9.8 Hz, MeO-Glc-5), 4.04 (1H, dd, *J*=4.7, 11.2 Hz, β-Glc-6), 4.17 (1H, ddd, *J*=2.4, 4.5, 10.2 Hz, GlcN-5), 4.30 (1H, t, *J*=9.2 Hz, MeO-Glc-3), 4.37 (1H, dd, *J*=1.5, 11.2 Hz, β-Glc-6), 4.41 (1H, dd, *J*=1.5, 10.0 Hz, MeO-Glc-6), 4.43 (1H, dd, *J*=2.4, 12.2 Hz, GlcN-6), 4.53 (1H, d, *J*=11.0 Hz, OBn), 4.62 (1H, dd, *J*=4.6, 12.3 Hz, GlcN-6), 4.64 (1H, d, *J*=7.8 Hz, β-Glc-1), 4.73 (1H, d, *J*=11.0 Hz, OBn), 4.83 (5H, br d, *J*=11.0 Hz, OBn), 4.91 (1H, dd, *J*=8.5, 10.8 Hz, GlcN-2), 4.93 (1H, d, *J*=11.0 Hz, OBn), 4.99, 5.00 (each 1H, d, *J*=11.0 Hz, OBn), 5.05 (1H, d, *J*=3.5 Hz, MeO-Glc-1), 5.14, 5.18 (each 1H, d, *J*=11.0 Hz, OBn), 5.58 (1H, dd, *J*=9.2, 10.2 Hz, GlcN-4), 5.97 (1H, d, *J*=8.5 Hz, GlcN-1), 6.38 (1H, dd, *J*=9.2, 10.8 Hz, GlcN-3), 7.22—7.43 (25H, m), 7.45—7.53 (9H, m). ^{13}C-NMR (C_5D_5N) δ: 20.2, 20.5, 20.7, 55.2 (OMe), 55.4 (GlcN-2), 62.4 (GlcN-6), 68.6 (2C) (MeO-Glc-6 and β-Glc-6), 69.6 (GlcN-4), 70.6 (MeO-Glc-5), 71.2 (GlcN-3), 72.4 (GlcN-5), 72.8 (OBn), 74.7 (2C) and 74.9 (2C) (3×OBn and β-Glc-4), 75.3 and 75.5 (2×OBn), 78.3 and 78.5 (β-Glc-5 and MeO-Glc-4), 81.1 (MeO-Glc-2), 82.3 (MeO-Glc-3), 82.6 (β-Glc-2), 84.8 (β-Glc-3), 99.2 (MeO-Glc-1), 98.7 (GlcN-1), 104.0 (β-Glc-1), 127.77 (3C), 127.83, 128.0 (9C), 128.1 (8C), 128.2 (2C), 128.62 (2C), 128.66 (2C), 128.68 (2C), 128.70 (2C), 128.73 (2C), 128.74 (2C), 131.7, 134.8 (2C), 138.8, 139.3 (2C), 139.45, 139.48, 139.8, 169.8, 170.4, 170.6. IR ($CHCl_3$) *v*: 1749, 1720, 1387, 1366, 1159, 1086, 1072 cm^{-1}. HR-MS *m/z*: 1336.5096 (Calcd for $C_{75}H_{79}NO_{20}SNa$: 1336.5093).

α-Isomer: $[\alpha]_D$=+41.8° (*c*=0.20, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.82, 2.00, 2.04 (each 3H, s, Ac), 3.41 (3H, s, OMe), 3.58 (1H, dd, *J*=3.3, 9.5 Hz, α-Glc-2), 3.59 (1H, t, *J*=9.5 Hz, α-Glc-4), 3.66 (1H, dd, *J*=3.5, 9.5 Hz, MeO-Glc-2), 3.77 (1H, br d, *J*=11.5 Hz, α-Glc-6), 3.92 (1H, br dd, *J*=4.0, 10.0 Hz, MeO-Glc-5), 3.95 (1H, dd, *J*=4.0, 11.0 Hz, MeO-Glc-6), 3.96 (1H, t, *J*=10.0 Hz, MeO-Glc-4), 4.02 (1H, dd, *J*=3.8, 11.5 Hz, α-Glc-6), 4.10 (1H, ddd, *J*=1.0, 3.0, 9.5 Hz, α-Glc-5), 4.16 (1H, ddd, *J*=2.5, 4.5, 10.5 Hz, GlcN-5), 4.22 (1H, t, *J*=9.5 Hz, α-Glc-3), 4.23 (1H, dd, *J*=9.5, 10.0 Hz, MeO-Glc-3), 4.40 (1H, dd, *J*=2.5, 12.3 Hz, GlcN-6), 4.41 (1H, dd, *J*=1.5, 11.0 Hz, MeO-Glc-6), 4.48 (1H, *J*=11.0 Hz, OBn), 4.62 (1H, d, *J*=11.0 Hz, OBn), 4.63 (1H, dd, *J*=4.5, 12.3 Hz, GlcN-6), 4.68, 4.73, 4.74, 4.75, 4.83 (each 1H, d, *J*=11.0 Hz, OBn), 4.91 (2H, d, *J*=11.0 Hz, OBn), 4.91 (1H, dd, *J*=8.5, 10.5 Hz, GlcN-2), 4.98 (1H, d, *J*=3.5 Hz, MeO-Glc-1), 5.03, 5.10, 5.12 (each 1H, d, *J*=11.0 Hz, OBn), 5.12 (1H, d, *J*=3.3 Hz, α-Glc-1), 5.60 (1H, dd, *J*=9.0, 10.5 Hz, GlcN-4), 5.93 (1H, d, *J*=8.5 Hz, GlcN-1), 6.41 (1H, dd, *J*=9.0, 10.5 Hz, GlcN-3), 7.22—7.40 (22H, m), 7.43—7.52 (10H, m), 7.78 (2H, dd, *J*=3.2, 5.3 Hz). ^{13}C-NMR (C_5D_5N) δ: 20.2, 20.4, 20.6, 55.1 (OMe), 55.4 (GlcN-2), 62.3 (GlcN-6), 66.2 (α-Glc-6), 68.9 (MeO-Glc-6), 69.5 (GlcN-4), 70.3 (α-Glc-5), 70.9 (MeO-Glc-5), 71.2 (GlcN-3), 72.2 (OBn), 72.4 (GlcN-5), 72.8, 74.8, 75.0, 75.1, 75.5 (5×OBn), 78.1 and 78.2 (MeO-Glc-4, α-Glc-4), 80.8 (MeO-Glc-2), 81.1 (α-Glc-2), 81.7 (α-Glc-3), 82.4 (MeO-Glc-3), 97.1 (α-Glc-1), 98.2 (MeO-Glc-1), 98.9 (GlcN-1), 127.6, 127.7, 127.82, 127.86, 127.89 (3C), 127.95 (3C), 127.98 (3C), 128.05 (3C), 128.08 (3C), 128.2 (2C), 128.56 (3C), 128.62 (4C), 128.68 (3C), 128.71 (3C), 128.74 (3C), 131.7, 138.9, 139.2 (2C), 139.4, 139.6, 139.7, 169.8, 170.5, 170.6. IR ($CHCl_3$) *v*: 1747, 1720, 1387, 1366, 1163, 1084, 1074 cm^{-1}. HR-MS *m/z*: 1336.5098 (Calcd for $C_{75}H_{79}NO_{20}SNa$: 1336.5093).

Methyl [(3,4,6-Tri-*O*-acetyl-2-*N*-phthaloyl-D-glucosaminyl)-β(1—6)-2,3,4-tri-*O*-benzoyl-D-glucopyranosyl]-β(1—6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (13b) *N*-Iodosuccinimide (12.0 mg, 0.053 mmol) and a quite small amount of triflic acid (1 drop with a capillary) were added to a suspension of **11b** (24.3 mg, 0.022 mmol), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**12**) (10.0 mg, 0.022 mmol), and molecular sieves 4A (MS 4A) (150 mg) in dichloromethane (3 ml) at −50 °C. After stirring the mixture for 25 min while keeping the temperature, the reaction mixture was filtered through Hyflo super® which was washed with ethyl acetate. The filtrate was diluted with an aqueous solution of sodium bicarbonate and sodium thiosulfate, and extracted with ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate, and evaporated. The residue was purified by preparative silica gel thin layer chromatography (*n*-hexane/ethyl acetate=1 : 1) to afford **13b** (22.3 mg, 76%). $[\alpha]_D$=+3.1° (*c*=0.78, $CHCl_3$). ^{1}H-NMR (C_5D_5N) δ: 1.78, 1.98, 2.06 (each 3H, s, OAc), 3.35 (3H, s, OMe), 3.66 (1H, dd, *J*=3.5, 9.5 Hz, α-Glc-2), 3.77 (1H, t, *J*=9.0 or 9.5 Hz, α-Glc-4), 3.93—4.00 (2H, m, α-Glc-5 and 6), 4.11—4.23 (3H, m, α-Glc-3, GlcN-5, β-Glc-6), 4.36—4.47 (4H, m, β-Glc-5, β-Glc-6, α-Glc-6, GlcN-6), 4.59 (1H, dd, *J*=4.8, 12.5 Hz, GlcN-6), 4.67 (1H, d, *J*=11.3 Hz, OBn), 4.72 (2H, s, OBn), 4.79 (1H, d, *J*=11.3 Hz, OBn), 4.83 (1H, d, *J*=11.4 Hz, OBn), 4.89 (1H, dd, *J*=8.4, 10.5 Hz, GlcN-2), 4.92 (1H, d, *J*=3.5 Hz, α-Glc-1), 5.04 (1H, d, *J*=11.4 Hz, OBn), 5.22 (1H, d, *J*=7.7 Hz, β-Glc-1), 5.54 (1H, dd, *J*=9.0, 10.0 Hz, GlcN-4), 5.90 (1H, t, *J*=9.5 Hz, β-Glc-4), 5.96 (1H, dd, *J*=7.7, 9.5 Hz, β-Glc-2), 6.00 (1H, d, *J*=8.4 Hz, GlcN-1), 6.34 (1H, t, *J*=9.5 Hz, β-Glc-3), 6.34 (1H, dd, *J*=9.5, 10.5 Hz, GlcN-3), 7.06 (2H, br t, *J*=7.5 Hz), 7.16—7.47 (22H, m), 7.55 (2H, dd, *J*=3.0, 5.5 Hz), 7.86—7.93 (6H, m), 8.08 (2H, dt, *J*=1.5, 7.5 Hz). ^{13}C-NMR (C_5D_5N) δ: 20.2, 20.4, 20.7, 55.1 (OMe), 55.4 (GlcN-2), 62.4 (GlcN-6), 67.9 (β-Glc-6), 68.6 (α-Glc-6), 69.6 (GlcN-4), 70.1 (β-Glc-4), 70.3 (α-Glc-5), 71.2 (GlcN-3), 72.4 (GlcN-5), 72.8 (β-Glc-2 and OBn), 74.0 (β-Glc-3, 5), 74.7 (OBn), 75.3 (OBn), 78.0 (α-Glc-4), 81.0 (α-Glc-2), 82.2 (α-Glc-3), 98.1 (α-Glc-1), 98.6 (GlcN-1), 101.4 (β-Glc-1), 127.7, 127.84, 127.87 (3C), 127.9, 128.08 (3C), 128.13 (3C), 128.6 (3C), 128.7 (8C), 128.8 (2C), 128.9 (2C), 129.36, 129.41, 129.8 (2C), 129.9, 129.98 (2C), 130.01 (2C), 133.56, 133.61, 133.7, 134.7 (2C), 139.31, 139.35, 139.7, 165.5 (2C), 166.1, 169.8, 170.4, 170.5. IR ($CHCl_3$) *v*: 3065, 1738, 1722, 1603, 1452, 1389, 1367, 1281, 1261 cm^{-1}. HR-MS *m/z*: 1378.4469 (Calcd for $C_{75}H_{73}NO_{23}Na$: 1378.4471).

Acknowledgements We are grateful for the support of a Grant-in-Aid (No. 20590022) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

1) Kahne D., Walker S., Chen Y., van Engen D., *J. Am. Chem. Soc.*, **111**, 6881—6882 (1989).
2) Raghavan S., Kahne D., *J. Am. Chem. Soc.*, **115**, 1580—1581 (1993).
3) Kajimoto T., Ishioka Y., Katoh T., Node M., *Bioorg. Med. Chem. Lett.*, **16**, 5736—5739 (2006).
4) Kajimoto T., Ishioka Y., Katoh T., Node M., *J. Carbohydr. Chem.*, **26**, 469—495 (2007).
5) Nishide K., Ohsugi S., Shiraki H., Tamakita H., Node M., *Org. Lett.*, **3**, 3121—3124 (2001).
6) Node M., Kumar K., Nishide K., Ohsugi S., Miyamoto T., *Tetrahedron Lett.*, **42**, 9207—9210 (2001).
7) Nishide K., Ohsugi S., Fudesaka M., Kodama S., Node M., *Tetrahedron Lett.*, **43**, 5177—5179 (2002).
8) Nishide K., Miyamoto T., Kumar K., Ohsugi S., Node M., *Tetrahedron Lett.*, **43**, 8569—8573 (2002).
9) Ohsugi S., Nishide K., Node M., *Tetrahedron*, **59**, 1859—1871 (2003).
10) Ohsugi S., Nishide K., Oono K., Okuyama K., Fudesaka M., Kodama S., Node M., *Tetrahedron*, **59**, 8393—8398 (2003).
11) Nishide K., Ohsugi S., Miyamoto T., Kumar K., Node M., *Monatsh. Chem.*, **135**, 189—200 (2004).
12) Nishide K., Pranab K. P., Matoba M., Shanmugasundaram K., Node M., *Green Chem.*, **6**, 142—146 (2004).
13) Pranab K. P., Nishide K., Fuji K., Node M., *Synthesis*, **2004**, 1003—1006 (2004).
14) Matoba M., Kajimoto T., Nishide K., Node M., *Chem. Pharm. Bull.*, **54**, 141—146 (2006).
15) Node M., Kajimoto T., *Heteroatom Chem.*, **18**, 572—583 (2007).
16) Matoba M., Kajimoto T., Node M., *Synlett*, **2007**, 1930—1934 (2007).
17) Matoba M., Kajimoto T., Node M., *Syn. Comm.*, **38**, 1194—1200 (2008).
18) Castrillón J. P. A., Szmant H., *J. Org. Chem.*, **30**, 1338—1339 (1965).