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GLYCOSIDATION REACTIONS OF BENZYL-TYPE SELENOGLYCOSIDE DONORS

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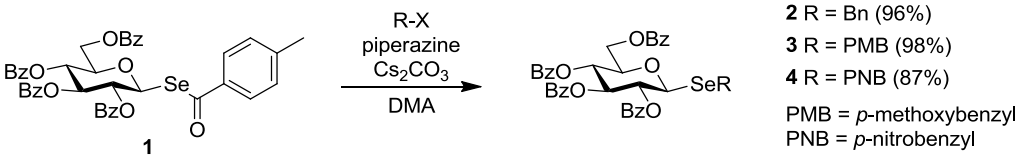
Abstract – *p*-Methoxybenzyl (PMB), and *p*-nitrobenzyl (PNB) selenoglycosides of glucose were synthesized, and their glycosidation reactions were investigated. The Bn and PNB derivatives were successfully activated with IBr-$AgClO_4$ to provide the glycosylated products in high yields. The glycosidation with the PMB derivatives required promotion with a metal triflate, such as $(CuOTf)_2$·PhMe or $In(OTf)_3$, and afforded the glycosylated products in medium to high yields.

Selenoglycosides are attractive potential glycosyl donors.[1] The soft, highly nucleophilic selenium atom means that selenoglycosides can be activated by a wide range of soft electrophiles, and preferentially activated over thioglycosides.[2] However, the lack of methods for the synthesis of selenoglycosides has limited their use as glycosyl donors.[3] Namely, only phenylselenoglycoside donors have been utilized in the synthesis of carbohydrates. Previously, we have reported a facile synthetic method for alkyl selenoglycosides,[4] which features the in situ chemoselective generation of an anomeric selenolate anion from β-*p*-methylbenzoyl selenoglycoside. Here, as a part of exploration of selenoglycoside donors, we report the glycosidation reactions of a benzyl selenoglycoside donor and its *para*-substituted analogues.

Three types of benzyl selenoglycosides (**2**-**4**) were synthesized according to our previously reported

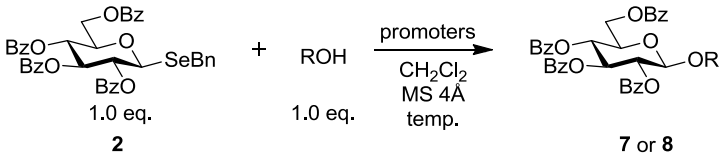
method.[4] *p*-Methylbenzoyl 2,3,4,6-tetra-*O*-benzoyl-1-seleno-β-D-glucopyranoside (**1**) was reacted with the corresponding benzyl halide in the presence of piperazine and Cs_2CO_3 to afford selenoglycosides **2**-**4** in high yields (Scheme 1).



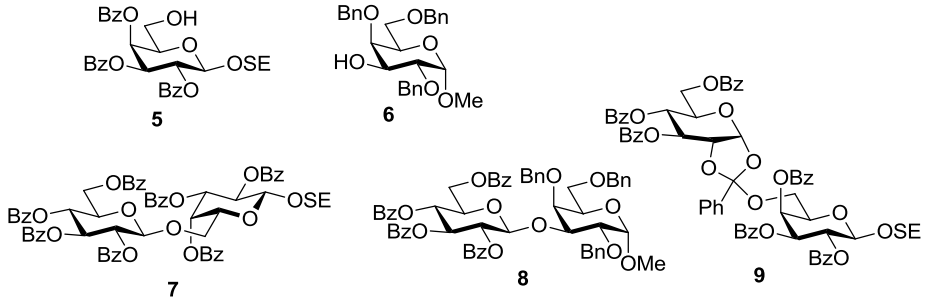
Scheme1. Synthesis of selenoglycoside donors

We examined the glycosidation reactions of the selenoglycoside donors with various glycosyl acceptors and promoters. Initially, the glycosidation with benzyl selenoglycoside **2** was attempted using various glycosylation promoters in the presence of 4 Å molecular sieves in CH_2Cl_2 (Table 1). The glycosidation promoted by PhSeOTf at -80 °C was sluggish and provided only a marginal yield of disaccharide **7** (45%, entry 1). The coupling yield was not improved by raising the reaction temperature. MeOTf required a higher temperature for the glycosylation, and produced **7** in low yield (36%) with orthoester **9** as a byproduct (entry 2). Surprisingly, NIS-TfOH generated orthoester **9** as the single major product (entry 3). However, IBr-$AgClO_4$[5] provided the best yield of **7** (63%) at -80 °C (entry 4). For the reaction with the electron-rich hydroxyl group of compound **6**, the yield of disaccharide **8** was 85% (entry 5).

Table 1. Glycosidation of benzyl selenoglycoside **2**

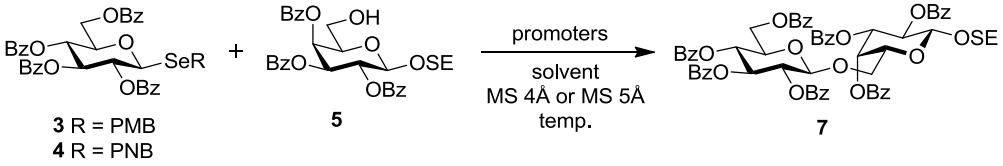


Entry	ROH	Promoters	Temp.	Time	Product & Yield
1	**5**	PhSeBr (2.0 eq.) AgOTf (3.0 eq.)	-80 °C	45 h	**7** (45%)
2	**5**	MeOTf (2.0 eq.)	25 °C	24 h	**7** (36%), **9** (4%)
3	**5**	NIS (2.0 eq.) TfOH (0.1 eq.)	-80 °C	27 h	**9** (31%)
4	**5**	IBr (2.0 eq.) $AgClO_4$ (3.0 eq.)	-80 °C	5 h	**7** (63%)
5	**6**	IBr (2.0 eq.) $AgClO_4$ (3.0 eq.)	-40 °C	15 min	**8** (85%)

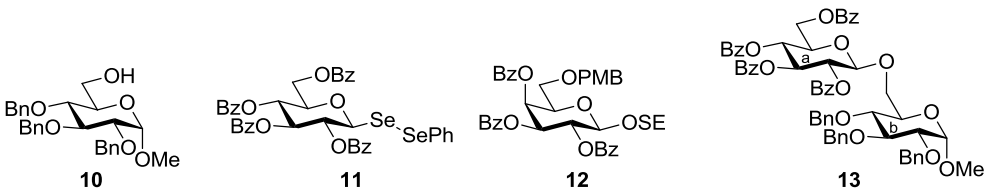


Next, we compared the glycosidation of **5** with *p*-methoxybenzyl (PMB) selenoglycoside **3** with that of *p*-nitrobenzyl (PNB) selenoglycoside **4** (Table 2). NIS-TfOH did not produce disaccharide **7**, whereas a good yield was obtained with IBr-$AgClO_4$ for the PNB derivative **4** (entries 1-4). Although PhSeOTf

Table 2. Glycosidation of *p*-substituted benzyl selenoglycosides **3** and **4**



Entry	Donor	ROH	Promoters	Solvent	Temp.	Time	Product & Yield
1	**3**	**5**	NIS (2.0 eq.) TfOH (0.1 eq.)	CH_2Cl_2	-80 °C	78 h	**7** (0%), **9** (trace)
2	**4**	**5**				54 h	**7** (0%), **9** (72%)
3	**3**	**5**	IBr (2.0 eq.) $AgClO_4$ (3.0 eq.)	CH_2Cl_2	-80 °C	3 h	**9** (12%)
4	**4**	**5**				24 h	**7** (83%)
5	**3**	**5**	PhSeBr (2.0 eq.) AgOTf (3.0 eq.)	CH_2Cl_2	-80 °C	6 h	**7** (36%)
6	**4**	**5**				2 h	**7** (30%)
7	**3**	**5**	MeOTf (2.0 eq.)	CH_2Cl_2	25 °C	72 h	complex mixture
8	**4**	**5**				72 h	**7** (69%)
9	**3**	**5**	AgOTf (2.0 eq.)	CH_2Cl_2	25 °C	36 h	**7** (8%)
10	**4**	**5**				72 h	trace
11	**3**	**5**	$Zn(OTf)_2$ (2.0 eq.)	1,2-DCE	40 °C	96 h	No reaction
12	**4**	**5**				96 h	No reaction
13	**3**	**5**	$Cu(OTf)_2$ (2.0 eq.)	1,2-DCE	40 °C	96 h	Complex mixture
14	**4**	**5**				114 h	trace
15	**3**	**5**	$(CuOTf)_2$·PhMe (1.0 eq.)	CH_2Cl_2-PhMe	25 °C	48 h	**7** (54%)
16	**4**	**5**				96 h	trace
17	**3**	**10**	$In(OTf)_3$ (2.0 eq.)	1,2-DCE	40 °C	48 h	**13** (88%)
18	**4**	**10**				72 h	**13** (2%)



showed a better affinity for **3** and **4**, the glycosidation yields remained low (entries 5 and 6). The reaction of **3** and PhSeOTf also produced asymmetric diselenide **11** and 6-*O*-*p*-methoxybenzylated compound **12** (entry 5) because of the preferential generation of the PMB cation instead of the oxocarbenium ion. When the reaction was promoted with MeOTf, PNB derivative **4** afforded an acceptable yield of **7**, whereas PMB derivative **3** gave a complex mixture of products (entries 7 and 8).

The glycosidation of **3** and **4** was attempted in the presence of various metal triflates. Although electron-rich glycosyl donor **3** could be activated with AgOTf,[6] $Cu(OTf)_2$,[7] and $(CuOTf)_2$·PhMe, almost no product was observed for AgOTf, $Cu(OTf)_2$. A moderate yield was observed for $(CuOTf)_2$·PhMe (entries 9, 13, and 15). However, electron-deficient glycosyl donor **4** was not affected by any of the metal triflates (entries 10, 12, 14, 16, and 18). In contrast to **4**, $In(OTf)_3$ promoted the glycosidation of **3** with **10** to give disaccharide **13**[8] in 88% yield.

In conclusion, we have synthesized three types of benzyl selenoglycosides (**2**-**4**). The Bn and PNB selenoglycoside donors were activated with IBr-$AgClO_4$ or MeOTf, and afforded the corresponding glycoside in good yields. In addition, $In(OTf)_3$ promoted the glycosidation with the PMB selenoglycoside donor **3**, implying a possibility of the chemoselective activation of **3** over other selenoglycosides.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded with JEOL JNM-ECX400P, JNM-ECA500, and JNM-ECA600 spectrometers. Chemical shifts in the ^1H NMR spectra are expressed in ppm (δ) relative to the Me_4Si signal adjusted to δ 0.00 ppm. COSY methods were used to confirm the NMR peak assignments. Specific rotations were determined with a Horiba SEPA-300 high sensitivity polarimeter. High-resolution mass spectrometry (HRMS) was conducted with a Bruker Daltonics micrOTOF (ESI-TOF) system. Molecular sieves were purchased from Wako Chemicals Inc. and dried at 300 °C for 2 h in a muffle furnace prior to use. Solvents used in reactions were dried over molecular sieves and used without purification. TLC analysis was performed on Merck glass TLC plates (silica gel $60F_{254}$). Compounds were detected with UV light (253 nm) or by soaking in a 10% solution of H_2SO_4 in ethanol followed by heating. Silica gel (80 and 300 mesh) manufactured by Fuji Silysia Chemical Ltd. was used for flash column chromatography. The amount of silica gel was usually about 150- to 200-fold the weight of the sample. Solvent systems in chromatography are specified as volume ratios. Evaporation and condensation were carried out in vacuo.

Typical procedure of benzyl selenoglycosides: Piperazine (1.5 eq.) was added to a suspension of *p*-methylbenzoyl 2,3,4,6-tetra-*O*-benzoyl-1-seleno-β-D-glucopyranoside **1** (1.0 eq.), Cs_2CO_3 (2.0 eq.), and

alkyl halide (2.0 eq.) in degassed DMA (50 mM) under Ar stream at ambient temperature. The reaction was monitored by TLC (*n*-Hexane/EtOAc = 2/1, developed twice). After stirred for 1 h, the reaction mixture was extracted with EtOAc. Then the organic layer was successively washed with H_2O, 2 M HCl, satd. aq. $NaHCO_3$, and brine. The organic solution was dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (*n*-Hexane/EtOAc = 5/1)

***p*-Methoxybenzyl 2,3,4,6-tetra-*O*-benzoyl-1-seleno-β-D-glucopyranoside (3)**: $[\alpha]_D$ -22.5 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05-6.76 (m, 22 H, Ar), 5.82 (dd, 1 H, $J_{2,3}$ = 8.9 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 5.67 (dd, 1 H, $J_{4,5}$ = 10.3 Hz, H-4), 5.63 (dd, 1 H, $J_{1,2}$ = 10.3 Hz, H-2), 4.82 (d, 1 H, H-1), 4.64, (dd, 1 H, $J_{5,6a}$ = 2.8 Hz, J_{gem} = 12.4 Hz, H-6a), 4.51 (dd, 1 H, $J_{5,6b}$ = 5.5 Hz, H-6b), 4.04 (m, 2 H, H-5, SeCH_2), 3.91 (d, 1 H, J_{gem} = 11.7 Hz, SeCH_2), 3.79 (s, 3 H, OCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 165.8, 165.3, 165.2, 158.6, 133.4, 133.3, 133.2, 130.2, 129.9, 129.8, 129.7, 129.6, 129.6, 129.1, 128.8, 128.4, 128.3, 128.3, 114.0, 77.4, 77.1, 74.0, 71.4, 69.7, 63.5, 55.2, 26.3; ^{77}Se-NMR (95 MHz, $CDCl_3$) δ 377.4; HRMS (ESI): found $[M+Na]^+$ 803.1370, $C_{42}H_{36}O_{10}Se$ calcd. for $[M+Na]^+$ 803.1371.

***p*-Nitrobenzyl 2,3,4,6-tetra-*O*-benzoyl-1-seleno-β-D-glucopyranoside (4)**: $[\alpha]_D$ -48.5 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06-7.25 (m, 25 H, Ar), 5.88 (dd, 1 H, $J_{2,3}$ = 9.0 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 5.71 (dd, 1 H, $J_{4,5}$ = 10.3 Hz, H-4), 5.65 (dd, 1 H, $J_{1,2}$ = 9.7 Hz, H-2), 4.93 (d, 1 H, H-1), 4.68 (dd, 1 H, $J_{5,6a}$ = 3.5 Hz, J_{gem} = 12.4 Hz, H-6a), 4.53 (dd, 1 H, $J_{5,6b}$ = 5.5 Hz, H-6b), 4.13 (m, 2 H, H-5, SeCH_2), 4.00 (d, 1 H, J_{gem} = 11.7 Hz, SeCH_2); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 165.7, 165.3, 165.2, 146.8, 146.0, 133.5, 129.8, 129.6, 129.4, 128.7, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 123.8, 76.8, 73.7, 71.3, 69.4, 63.1, 60.3, 25.5, 21.0, 14.1; ^{77}Se-NMR (95 MHz, $CDCl_3$) δ 388.1; HRMS (ESI): found $[M+Na]^+$ 818.1113, $C_{41}H_{33}O_{11}Se$ calcd. for $[M+Na]^+$ 818.1117.

Typical procedure for the glycosidation: A mixture of donor (1.0 eq.), acceptor (1.0 eq.), and desiccant (MS 4 Å or MS 5 Å, 100 mg/mL for solvent) in CH_2Cl_2 (40 mM) was stirred under Ar atmosphere at ambient temperature. Then, glycosylation promotor was added to the mixture at corresponding temperature. The completion of the reaction was monitored by TLC (toluene/EtOAc = 10/1). The reaction mixture was diluted with EtOAc. The mixture was then neutralized with satd. aq. $NaHCO_3$. The mixture was filtered through a pad of celite and the filtrate was extracted with EtOAc. The organic layer was washed with H_2O and brine, and dried over Na_2SO_4, and concentrated. The resulting residue was purified by silica gel column chromatography (toluene/EtOAc = 20/1).

2-(Trimethylsilyl)ethyl (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-

D-galactopyranoside (7): $[\alpha]_D$ +80.0 (c 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13-7.29 (m, 35 H, Ar), 6.00 (d, 1 H, $J_{3,4}$ = 4.8 Hz, H-4^{Gal}), 5.97 (dd, 1 H, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 9.6 Hz, H-3^{Glc}), 5.81 (dd, 1 H, $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 10.3 Hz, H-2^{Gal}), 5.76 (t, 1 H, $J_{4,5}$ = 9.6 Hz, H-4^{Glc}), 5.64-5.61 (m, 2 H, H-3^{Gal}, H-2^{Glc}), 5.04 (d, 1 H, $J_{1,2}$ = 8.3 Hz, H-1^{Glc}), 4.78 (d, 1 H, H-1^{Gal}), 4.70 (dd, 1 H, $J_{5,6a}$ = 2.8 Hz, J_{gem} = 11.7 Hz, H-6a^{Glc}), 4.42 (dd, 1 H, $J_{5,6b}$ = 4.8 Hz, H-6b^{Glc}), 4.27 (dd, 1 H, $J_{5,6a}$ = 4.8 Hz, H-5a^{Gal}), 4.21-4.17 (m, 2 H, H-5^{Glc}, H-6a^{Gal}), 4.02 (m, 2 H, H-6b^{Gal}, OCH_2CH_2Si), 3.55 (m, 1 H, OCH_2CH_2Si), 0.91, 0.82 (m, 2 H, OCH_2CH_2Si), 0.00 (s, 9 H, 3 CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 165.7, 165.5, 165.4, 165.2, 165.1, 164.9, 133.4, 133.2, 133.1, 133.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.2, 129.1, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 101.1, 100.8, 73.1, 72.8, 72.3, 71.9, 71.8, 69.9, 69.4, 68.7, 68.3, 67.5, 62.7, 17.7, -1.5; HRMS (ESI): found $[M+Na]^+$ 1193.3594, $C_{66}H_{62}O_{18}Si$ calcd. for $[M+Na]^+$ 1193.3598.

Methyl (2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-β-D-galacto-pyranoside (8): $[\alpha]_D$ -19.4 (c 1.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-7.00 (m, 35H, Ar), 5.93 (t, 1 H, H-3^{Glc}, $J_{2,3}$ = $J_{3,4}$ = 9.8 Hz), 5.71 (t, 1 H, H-4^{Glc}, $J_{4,5}$ = 9.8 Hz), 5.67 (dd, 1 H, H-2^{Glc}, $J_{1,2}$ = 8.0 Hz), 5.30 (d, 1 H, H-1^{Glc}), 5.01 (d, 1 H, OCH_2Ph, J_{gem} = 11.3 Hz), 4.65 (dd, 1H, H-6a^{Glc}, J_{gem} = 12.1 Hz, $J_{5,6a}$ = 3.1 Hz), 4.53 (dd, 1 H, H-6b^{Glc}, $J_{5,6b}$ = 5.7 Hz), 4.52 (d, 1 H, OCH_2Ph, J_{gem} = 11.3 Hz), 4.44 and 4.43 (2 d, 2 H, 2 OCH_2Ph, J_{gem} = 11.3 Hz), 4.36 (d, 1 H. H-1^{Gal}, $J_{1,2}$ = 3.7 Hz), 4.35 (d, 1 H, OCH_2Ph, J_{gem} = 11.4 Hz), 4.19 (dd, 1 H, H-3^{Gal}, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 3.0 Hz), 4.14 (ddd, 1 H ,H-5^{Glc}), 4.09 (d, 1 H, OCH_2Ph, J_{gem} = 12.5 Hz), 3.98 (d, 1 H, H-4^{Gal}), 3.79 (dd, 1 H, H-5^{Gal}, $J_{5,6a}$ = 6.5 Hz, $J_{5,6b}$ = 5.7 Hz), 3.77 (dd, 1 H, H-2^{Gal}), 3.47 (dd, 1 H, H-6a^{Gal}, J_{gem} = 9.7 Hz), 3.37 (dd, 1 H, H-6b^{Gal}) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 165.8, 165.2, 165.0, 138.6, 138.3, 138.1, 133.4, 133.2, 133.2, 133.1, 129.8, 129.7, 129.5, 129.2, 129.0, 128.8, 128.7, 128.6, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 127.7, 127.6, 127.5, 127.4, 125.3, 101.9, 98.5, 78.1, 77.3, 77.2, 76.3, 75.0, 73.8, 73.3, 72.9, 72.2, 72.1, 69.7, 69.3, 69.2, 62.7, 55.1; HRMS (ESI): found $[M+Na]^+$ 1065.3667, $C_{62}H_{58}O_{15}$ calcd. for $[M+Na]^+$ 1065.3668.

3,4,6-Tri-*O*-benzoyl-α-D-glycopyranose 1,2-[2-(trimethylsilyl)ethyl 2,3,4-tri-*O*-benzoyl-β-D-galacto-pyranosid-6-yl orthobenzoate] (9): $[\alpha]_D$ -60.4 (c 2.6, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18-7.29 (m, 35 H, Ar), 6.01 (d, 1 H, $J_{1,2}$ = 3.2 Hz, H-1^{Glc}), 5.93 (dd, 1 H, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 1.4 Hz, H-3^{Glc}), 5.77 (m, 2 H, H-2^{Gal}, H-4^{Gal}), 5.61 (dd, 1 H, $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 3.2 Hz, H-3^{Gal}), 5.51 (dd, 1 H, $J_{4,5}$ = 8.7 Hz, H-4^{Glc}), 4.87 (dd, 1 H, H-2^{Glc}), 4.83 (d, 1 H, $J_{1,2}$ = 7.7 Hz, H-1^{Glc}), 4.53 (dd, 1 H, $J_{5,6a}$ = 3.2 Hz, J_{gem} = 11.9 Hz, H-6a^{Glc}), 4.39 (dd, 1 H, $J_{5,6b}$ = 5.0 Hz, H-6b^{Gal}), 4.11 (m, 3 H, H-5^{Glc}, H-6a^{Gal}, OCH_2CH_2Si), 3.64 (m, 3 H, H-5^{Gal}, H-6b^{Gal}, OCH_2CH_2Si), 0.96 (m, 2 H, OCH_2CH_2Si), 0.00 (s, 9 H, 3 CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 165.6, 165.5, 165.2, 165.1, 164.5, 134.4, 133.6, 133.4, 133.4, 133.1, 132.9,

130.1, 129.9, 129.9, 129.7, 129.7, 129.6, 129.6, 129.2, 129.1, 129.0, 128.9, 128.5, 128.4, 128.3, 128.2, 128.2, 126.1, 121.0, 101.0, 97.5, 77.2, 72.2, 71.9, 71.7, 69.9, 68.9, 68.3, 67.9, 67.7, 67.5, 64.0, 61.3, 29.7, 18.0, -1.5; HRMS (ESI): found $[M+Na]^+$ 1193.3597, $C_{66}H_{62}O_{18}Si$ calcd. for $[M+Na]^+$ 1193.3598.

2-(Trimethylsilyl)ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-*p*-methoxybenzyl-β-D-galactopyranoside (12): $[\alpha]_D$ +96.0 (c 0.5, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 8.03-6.74 (m, 19 H, Ar), 5.93 (d, 1 H, $J_{3,4}$ = 3.4 Hz, H-4), 5.73 (dd, 1 H, $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 8.6 Hz, H-2), 5.54 (dd, 1 H, H-3), 4.78 (d, 1 H, H-1), 4.47 and 4.35 (2 d, 2 H, J_{gem} = 11.0 Hz, O*CH*$_2$Ar), 4.10 (m, 2 H, H-6a, OC*H*$_2$CH$_2$Si), 3.71 (s, 3 H, OCH_3), 3.65 (m, 3 H, H-5, H-6b, OC*H*$_2$CH$_2$Si), 0.92 (m, 2 H, OCH_2CH_2Si), -0.06 (s, 9 H, 3 CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 165.5, 165.2, 159.2, 133.3, 133.1, 133.0, 129.9, 129.7, 129.7, 129.6, 129.5, 129.5, 129.3, 128.9, 128.4, 128.2, 128.2, 113.7, 101.0, 73.2, 72.7, 72.0, 70.0, 68.4, 67.7, 67.5, 55.1, 18.0, -1.5; HRMS (ESI): found $[M+Na]^+$ 735.2597, $C_{42}H_{36}O_{10}Se$ calcd. for $[M+Na]^+$ 735.2596.

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