

Odorless Eco-Friendly Synthesis of Thio- and Selenoglycosides in Ionic Liquid

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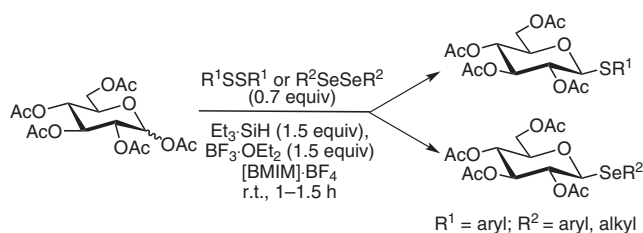
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Abstract: An environmentally benign odorless methodology for the preparation of 1,2-*trans*-thio- and selenoglycosides is reported. In a one-pot condition, the reductive cleavage of disulfides and diselenides using triethylsilane and borontrifluoride diethyletherate combination followed by the reaction of the in situ generated thiolate and selenoates with glycosyl acetate derivatives in recyclable room-temperature ionic liquid, [BMIM]-BF₄ resulted in excellent yields of thio- and selenoglycosides avoiding the use of obnoxious thiols/selenols and metallic catalysts.

Key words: thioglycoside, selenoglycoside, disulfide, diselenide, triethylsilane, ionic liquid

Thioglycosides are useful intermediates for the synthesis of complex oligosaccharides as well as natural products.^{1,2} They have been widely used as effective and stable glycosyl donors in the synthetic carbohydrate chemistry where a wide range of protecting-group manipulations are involved.³ They also act as practical precursors for the preparation of glycosyl fluorides,⁴ sulfoxides, and sulfones, which have applications in the O- and C-glycosylations as glycosyl donors.^{5,6} Besides their important roles in the glycosylations, thioglycosides have been evaluated as effective inhibitors of several glycosidase enzymes because of their structural similarities to the O-glycosides.^{7,8} Thioglycosides can serve as orthogonal glycosyl donors by acting as donors as well as acceptors depending on the reaction conditions.⁹ Conventionally, per-O-acetylated thioglycosides are prepared by the treatment of glycosyl acetates with obnoxious thiols¹⁰ or trimethylsilylthiol derivatives in the presence of a Lewis acid.¹¹ Use of malodorous and toxic thiols, formation of anomerized products, and requirement of large quantity of chlorinated organic solvents are major drawbacks of these methods. Few other comparatively odorless conditions have also been developed in the recent past, which include (a) zinc-mediated cleavage of disulfides and reaction of the in situ generated thiolates with glycosyl bromides,¹² and (b) preparation of *S*-glycosylisothiuronium salts followed by treatment with alkyl halides under mild basic conditions.¹³ Besides their usefulness, they have serious limitations including the use of metallic salts, unstable glycosyl bromides and organic solvents, pregeneration of *S*-glycosyl isothiuronium salts from unstable glycosyl halides, etc.

Similar to the thioglycosides, selenoglycosides have also been used in carbohydrate chemistry for the preparation of oligosaccharides, C-glycosides, glycoconjugates, etc.¹⁴ Selenoglycosides can be selectively activated in the presence of thioglycosides and hence become attractive intermediates in the oligosaccharide synthesis.¹⁵ Selenoglycosides are usually prepared by treating glycosyl halides with selenium under sodium borohydride reduction conditions¹⁶ or by treating glycosyl acetate with arylselenol derived from the reduction of phenyldiselenide in the presence of BF₃·OEt₂.¹⁷ Resembling the thioglycosides, preparation of selenoglycosides also suffers from a number of shortcomings including the use of malodorous reagents, incompatibility of base-labile protecting groups, and use of organic solvents. Therefore, there is a constant need to develop an odorless, environmentally benign reaction protocol for the preparation of thio- and selenoglycosides. It was envisaged that reduction of disulfides and diselenides under a metal-free condition followed by the treatment with glycosyl acetates in one-pot in room-temperature ionic liquid (RTIL) could provide a green protocol for the preparation of thio- and selenoglycosides avoiding malodorous thiols. Since combination of triethylsilane and borontrifluoride diethyletherate (BF₃·OEt₂) has been found as useful reducing agent in the regioselective ring opening of acetal ring in carbohydrate derivatives,¹⁸ we sought to explore this reagent in the reduction of disulfides/diselenides. We also presumed that BF₃·OEt₂ present in the reaction medium could activate the glycosyl acetates to react with in situ generated thiolates/selenoates in one pot. In the current scenario, RTIL appeared to be the most attractive reaction solvents for the development of green methodologies.¹⁹ A number of organic transformations useful in the synthetic carbohydrate chemistry have been successfully carried out in ionic liquids (IL).²⁰ In this communication, we wish to report our findings on the treatment of disulfides/diselenides with a combination of triethylsilane and BF₃·OEt₂



Scheme 1 One-pot preparation of thio- and selenoglycosides by the reduction of disulfides/diselenides using triethylsilane and BF₃·OEt₂ followed by reaction with glycosyl acetates in [BMIM]·BF₄.

followed by reaction with glycosyl acetates in one pot in IL to furnish thio- and selenoglycosides under environmentally benign odorless reaction conditions (Scheme 1).

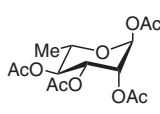
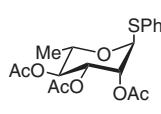
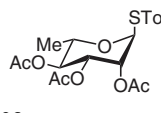
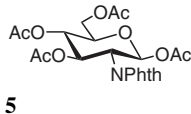
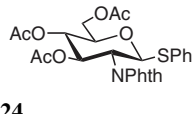
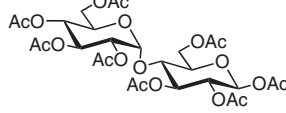
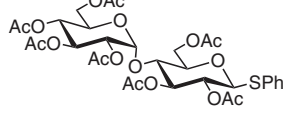
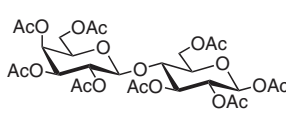
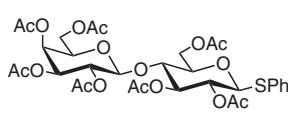
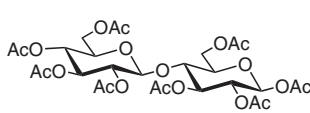
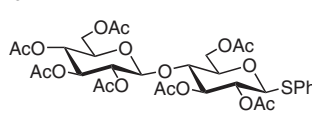
In a set of initial experiments, a mixture of β -D-glucose pentaacetate (**1**) and phenyl disulfide (0.5–1.5 equiv) was treated with triethylsilane (1.0–2.0 equiv of phenyl disulfide) and $\text{BF}_3 \cdot \text{OEt}_2$ (1.0–2.5 equiv of phenyl disulfide) in 1-butyl-3-methylimidazolium tetrafluoroborate {[BMIM] $\cdot\text{BF}_4$; 0.5–2.0 mL per mmol of substrate} at room temperature. To our satisfaction, the reaction proceeds well and resulted in the formation of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-glucopyranoside (**13**) in one

hour. After experimentation, it was observed that treatment of compound **1** with phenyl disulfide (0.7 equiv), triethylsilane (1.5 equiv of phenyl disulfide), and $\text{BF}_3 \cdot \text{OEt}_2$ (1.5 equiv of phenyl disulfide) in [BMIM] $\cdot\text{BF}_4$ (1.0 mL per mmol of substrate) furnished 85% yield of compound **13** together with minor quantity (ca. 5%) of α -isomer in one hour at room temperature. Following similar reaction conditions a series of thioglycosides have been prepared from different sugar acetates using phenyl disulfide, tolyl disulfide, naphthyl disulfide, etc. in excellent yield (Table 1).

Table 1 Preparation of Thioglycosides by Reductive Cleavage of Disulfides Using $\text{Et}_3\text{SiH} \cdot \text{BF}_3 \cdot \text{OEt}_2$ Followed by Reaction with Glycosyl Acetates in [BMIM] $\cdot\text{BF}_4$ at Room Temperature

Entry	Glycosyl acetate	Disulfides ^a	Thioglycosides	Time (h)	Yield (%) ^b
1	1	PhSSPh (9)	13	1.0	85 ^{c,21}
2		TolSSTol (10)	14	1.0	86 ^{d,10g}
3		NapSSNap (11)	15	1.2	88 ²²
4		PNPSSPNP (12)	16	1.5	80
5	2	PhSSPh (9)	17	1.0	86 ²³
6		TolSSTol (10)	18	1.0	85 ^{10g}
7	3	PhSSPh (9)	19	1.0	78 ^{e,24}
8		TolSSTol (10)	20	1.0	76 ^{10g}
9		NapSSNap (11)	21	1.2	75 ²²

Table 1 Preparation of Thioglycosides by Reductive Cleavage of Disulfides Using $\text{Et}_3\text{SiH}-\text{BF}_3\cdot\text{OEt}_2$ Followed by Reaction with Glycosyl Acetates in $[\text{BMIM}]\cdot\text{BF}_4$ at Room Temperature (continued)

Entry	Glycosyl acetate	Disulfides ^a	Thioglycosides	Time (h)	Yield (%) ^b
10		PhSSPh (9)		1.0	92 ²⁵
11	4	TolSSTol (10)		1.0	88 ^{10g}
12		PhSSPh (9)		1.5	80 ²⁶
13		PhSSPh (9)		1.5	85 ²⁷
14		PhSSPh (9)		1.5	84 ²⁷
15		PhSSPh (9)		1.5	82 ²⁷
	8		27		

^a Ph: phenyl; Tol: 4-methylphenyl, Nap: 2-naphthyl, PNP: 4-nitrophenyl.

^b Isolated yield.

^c Together with some α -isomer (ca. 5%).

^d Together with some α -isomer (ca. 10%).

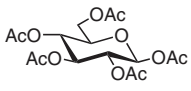
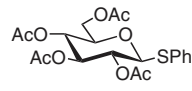
^e Together with some α -isomer (ca. 10%).

In a comparative study, a number of imidazolium IL, for example, $[\text{BMIM}]\cdot\text{PF}_6$, $[\text{BMIM}]\cdot\text{OTf}$, and $[\text{BMIM}]\cdot\text{Cl}$ were also examined as reaction solvent. The best results were obtained using $[\text{BMIM}]\cdot\text{BF}_4$ in terms of solubility of the substrates and yield of the products obtained (Table 2). After successful preparation of thioglycosides, the reaction conditions have been applied for the preparation selenoglycosides using phenyl diselenide, benzyl diselenide, etc. in place of disulfides. Excellent yield of selenoglycosides were achieved under similar reaction conditions. In the preparation of selenoglycosides, benzyl

diselenide took slightly longer time in comparison to the phenyl diselenide.

The findings on the cleavage of diselenides using a combination of triethylsilane and $\text{BF}_3\cdot\text{OEt}_2$ followed by reaction with glycosyl acetates in $[\text{BMIM}]\cdot\text{BF}_4$ are listed in Table 3. The products were obtained by aqueous workup and extraction with ethyl acetate. In most of the cases, exclusive 1,2-*trans* thio- and selenoglycoside derivatives were obtained. All known compounds gave acceptable ^1H NMR and ^{13}C NMR spectra that matched the reported data. The recycling property of the IL was evaluated by per-

Table 2 Preparation of Thioglycoside **13** Using Phenyl Disulfide and $\text{Et}_3\text{SiH}-\text{BF}_3\cdot\text{OEt}_2$ followed by Reaction with Glycosyl Acetate **1** in Different Ionic Liquids at Room Temperature

Entry	Glycosyl acetate	Thioglycoside	IL	Time (h)	Yield (%)
1			$[\text{BMIM}]\cdot\text{BF}_4$	1.0	85
2			$[\text{BMIM}]\cdot\text{PF}_6$	3.5	76
3			$[\text{BMIM}]\cdot\text{OTf}$	7.0	55
4			$[\text{BMIM}]\cdot\text{Cl}$	10.0	40
	1	13			

forming the reaction in recovered [BMIM]·BF₄. The recovered IL was reused at least four times without significant loss of efficiency providing almost similar yield of selenoglycoside derivative (Table 3, entry 1).

In summary, an odorless, environmentally benign, high-yielding methodology has been developed for the preparation of a series of 1,2-*trans*-thio- and -selenoglycosides through triethylsilane–BF₃·OEt₂-mediated reduction of

disulfides and diselenides followed by the reaction of in situ generated thiolates and selenoates with glycosyl acetates in IL [BMIM]·BF₄. Operational simplicity, green, stereoselective formation of 1,2-*trans*-thio- and -selenoglycosides in recyclable IL avoiding the use of malodorous thiols/selenols make this protocol better to the existing methodologies in this area.

Table 3 Preparation of Selenoglycosides by Reductive Cleavage of Diselenides Using Et₃SiH–BF₃·OEt₂ Followed by Reaction with Glycosyl Acetates in [BMIM]·BF₄ at Room Temperature

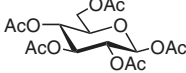
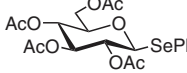
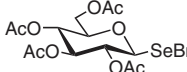
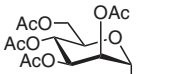
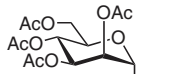
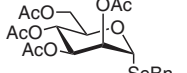
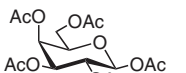
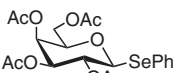

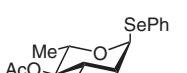
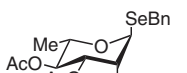
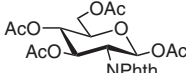
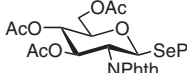
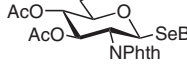
Entry	Glycosyl acetate	Diselenides	Thioglycosides	Time (h)	Yield (%) ^a
1		PhSeSePh (28)		1.0	88 ^{b,15a} 87 ^{c,15a} 82 ^{d,15a} 80 ^{e,15a}
	1		30		
2		BnSeSeBn (29)		1.0	82
			31		
3		PhSeSePh (28)		1.0	85 ^{14a}
	2		32		
4		BnSeSeBn (29)		1.0	80
			33		
5		PhSeSePh (28)		1.0	86 ^{12a}
	3		34		
6		PhSeSePh (28)		1.0	90 ^{15a}
	4		35		
7		BnSeSeBn (29)		1.0	82
			36		
8		PhSeSePh (28)		1.2	88 ^{15a}
	5		37		
9		BnSeSeBn (29)		1.5	82 ²⁸
			38		

Table 3 Preparation of Selenoglycosides by Reductive Cleavage of Diselenides Using Et₃SiH–BF₃·OEt₂ Followed by Reaction with Glycosyl Acetates in [BMIM]·BF₄ at Room Temperature (continued)

Entry	Glycosyl acetate	Diselenides	Thioglycosides	Time (h)	Yield (%) ^a
10		BnSeSeBn (29)		1.5	72
11		PhSeSePh (28)		1.5	75
12		BnSeSeBn (29)		1.5	70

^a Isolated yield.^b Fresh [BMIM]·BF₄.^c 1st recycled [BMIM]·BF₄.^d 2nd recycled [BMIM]·BF₄.^e 3rd recycled [BMIM]·BF₄.**Typical Experimental Conditions**

To a mixture of penta-*O*-acetyl- β -D-glucopyranose (**1**, 390.0 mg; 1.0 mmol), phenyl disulfide (155.0 mg, 0.71 mmol) or phenyl diselenide (220.0 mg, 0.70 mmol), and TES (170.0 μ L, 1.06 mmol) in [BMIM]·BF₄ (1.0 mL) was added BF₃·OEt₂ (130.0 μ L, 1.05 mmol), and the reaction mixture was allowed to stir at 20 °C for 1 h (Tables 1 and 3). After completion, the reaction mixture was poured into H₂O and extracted with EtOAc. The organic layer was successively washed with sat. NaHCO₃ and H₂O, dried (Na₂SO₄), and concentrated under reduced pressure to give the crude product, which was purified by crystallization from EtOH or by column chromatography using hexane–EtOAc (5:1) as eluent to furnish pure compound **13** or **30** (Tables 1 and 3).²⁹ The aqueous layer was evaporated to dryness, and the crude mass was passed through a short pad of SiO₂ using EtOAc as eluent to furnish [BMIM]·BF₄, which was dried at 70–80 °C under reduced pressure before its reuse.

Supporting Information for this article is available online at <http://www.thieme-connect.com/ejournals/toc/synlett>.

Acknowledgment

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References and Notes

- (1) (a) Oscarson, S. In *Carbohydrates in Chemistry and Biology*, Vol. 1; Ernst, B.; Hart, G. W.; Sinay, P., Eds.; Wiley-VCH: Weinheim, **2000**, 93–116. (b) Nicolaou, K. C.; Ueno, H. In *Preparative Carbohydrate Chemistry*; Hanessian, S., Ed.; Marcel Dekker: New York, **1997**, 313–338.
- (2) (a) Tsai, T. Y. R.; Jin, H.; Wiesner, K. *Can. J. Chem.* **1984**, *62*, 1403. (b) Wuts, P. G. M.; Bigelow, S. S. *J. Org. Chem.* **1983**, *48*, 3489. (c) Lear, M. J.; Yoshimura, F.; Hiram, M. *Angew. Chem. Int. Ed.* **2001**, *40*, 946. (d) Nicolaou, K. C.; Dolle, R. E.; Papahatjis, D. P.; Randall, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4189. (e) Dolle, R. E.; Nicolaou, K. C. *J. Am. Chem. Soc.* **1985**, *107*, 1691. (f) Nicolaou, K. C.; Bockovich, N. J.; Carcanague, D. R.; Hummel, C. W.; Even, L. F. *J. Am. Chem. Soc.* **1992**, *114*, 8701.
- (3) (a) Codee, J. D. C.; Litjens, R. E. J. N.; van den Bos, L. J.; Overkleeft, H. S.; van der Marel, G. A. *Chem. Soc. Rev.* **2005**, *34*, 769. (b) Garegg, P. J. *Adv. Carbohydr. Chem. Biochem.* **1997**, *52*, 179. (c) Fugedi, P.; Garegg, P. J.; Lohn, H.; Norberg, T. *Glycoconjugate J.* **1987**, *4*, 97. (d) Toshima, K.; Tatsuta, K. *Chem. Rev.* **1993**, *93*, 1503. (e) Ferrier, R. J.; Furneaux, R. H. *Methods Carbohydr. Chem.* **1980**, *8*, 251. (f) Kartha, K. P. R.; Field, R. A. In *Best Synthetic Methods: Carbohydrates*; Osborn, H. M. I., Ed.; Academic Press: Oxford, **2003**, 121–145.
- (4) (a) Rosenbrook, W.; Riley, D. A.; Lartey, P. A. *Tetrahedron Lett.* **1985**, *26*, 3. (b) Posner, G. H.; Haines, S. R. *Tetrahedron Lett.* **1985**, *26*, 5. (c) Nicolaou, K. C.; Dolle, R. E.; Papahatjis, D. P.; Randall, L. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1155.
- (5) (a) Kahne, D.; Walker, S.; Cheng, Y.; van Engen, D. *J. Am. Chem. Soc.* **1989**, *111*, 6881. (b) Raghavan, S.; Kahne, D. *J. Am. Chem. Soc.* **1993**, *115*, 1580. (c) Yan, L.; Kahne, D. *J. Am. Chem. Soc.* **1996**, *118*, 9239. (d) Crich, D.; Sun, S. *J. Org. Chem.* **1997**, *62*, 1198.
- (6) (a) Brown, D. S.; Ley, S. V.; Vile, S. *Tetrahedron Lett.* **1988**, *29*, 4873. (b) Brown, D. S.; Ley, S. V.; Vile, S.; Thompson, M. *Tetrahedron* **1991**, *47*, 1329. (c) Chang, G. X.; Lowary, T. L. *Org. Lett.* **2000**, *2*, 1505. (d) Vlahov, I. R.; Vlahova, P. I.; Linhardt, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 1480.
- (7) (a) Khan, S. H.; Hindsgaul, O. In *Molecular Glycobiology*; Fukuda, M.; Hindsgaul, O., Eds.; IRL: Oxford, **1994**, 206. (b) Norberg, T. In *Modern Methods in Carbohydrate Synthesis, Frontiers in Natural Product Research Series*, Vol. 1; Khan, S. H.; O'Neill, R. A., Eds.; Harwood Academic Publishers: Amsterdam, **1995**, 82–106.
- (8) (a) Varki, A. *Glycobiology* **1993**, *3*, 97. (b) Witczak, Z. J. *Curr. Med. Chem.* **1999**, *6*, 165.

- (9) Kanie, O.; Ito, Y.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 12073.
- (10) (a) Ferrier, R. J.; Hay, R. W.; Vethaviyasar, N. *Carbohydr. Res.* **1973**, *27*, 55. (b) Lemieux, R. U. *Can. J. Chem.* **1951**, *29*, 1079. (c) Lönn, H. *Carbohydr. Res.* **1985**, *139*, 105. (d) Das, S. K.; Roy, N. *Carbohydr. Res.* **1996**, *296*, 1079. (e) Kihlberg, J. O.; Leigh, D. A.; Bundle, D. R. *J. Org. Chem.* **1990**, *55*, 2860. (f) Agnihotri, G.; Tiwari, P.; Misra, A. K. *Carbohydr. Res.* **2005**, *340*, 1393. (g) Tai, C. A.; Kulkarni, S. S.; Hung, S. C. *J. Org. Chem.* **2003**, *68*, 8719. (h) Weng, S. S.; Lin, Y. D.; Chen, C. T. *Org. Lett.* **2006**, *8*, 5633.
- (11) (a) Hanesian, S.; Guindon, Y. *Carbohydr. Res.* **1980**, *86*, C3. (b) Pozsgay, V.; Jennings, H. J. *Tetrahedron Lett.* **1987**, *28*, 1375. (c) Kameyama, A.; Ishida, H.; Kiso, M.; Hasegawa, A. *J. Carbohydr. Chem.* **1991**, *10*, 549.
- (12) (a) Mukherjee, C.; Tiwari, P.; Misra, A. K. *Tetrahedron Lett.* **2006**, *47*, 441. (b) Zhao, X.; Yu, Z.; Yan, S.; Wu, S.; Liu, R.; He, W.; Wang, L. *J. Org. Chem.* **2005**, *70*, 7338.
- (13) (a) Tiwari, P.; Agnihotri, G.; Misra, A. K. *J. Carbohydr. Chem.* **2005**, *24*, 723. (b) Ibatullin, F. M.; Shabalin, K. A.; Janis, J. V.; Shavva, A. G. *Tetrahedron Lett.* **2003**, *44*, 7961.
- (14) (a) Randell, K. D.; Johnston, B. D.; Brown, P. N.; Pinto, B. M. *Carbohydr. Res.* **2000**, *325*, 253. (b) Jiaang, W.-T.; Chang, M.-Y.; Tseng, P.-H.; Chen, S.-T. *Tetrahedron Lett.* **2000**, *41*, 3127.
- (15) (a) Mehta, S.; Pinto, B. M. *J. Org. Chem.* **1993**, *58*, 3269. (b) Mehta, S.; Pinto, B. M. *Tetrahedron Lett.* **1991**, *32*, 4435.
- (16) (a) Crich, D.; Suk, D.-H.; Sun, S. *Tetrahedron: Asymmetry* **2003**, *14*, 2861. (b) Witczak, Z. J.; Whistler, R. L. *Heterocycles* **1982**, *19*, 1719.
- (17) (a) Gerz, M.; Matter, H.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 269. (b) Aloui, M.; Chambers, D. J.; Cumpstey, I.; Fairbanks, A. J.; Redgrave, A. J.; Seward, C. M. P. *Chem. Eur. J.* **2002**, *8*, 2608.
- (18) (a) Debenham, S. D.; Toone, E. J. *Tetrahedron: Asymmetry* **2000**, *11*, 385. (b) Aravind, A.; Baskaran, S. *Tetrahedron Lett.* **2005**, *46*, 743. (c) Aravind, A.; Mohanty, S. K.; Pratap, T. V.; Baskaran, S. *Tetrahedron Lett.* **2005**, *46*, 2965.
- (19) (a) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015. (b) Murugesan, S.; Linhardt, R. J. *Curr. Org. Synth.* **2005**, *2*, 437.
- (20) (a) Pakulski, Z. *Synthesis* **2003**, 2074. (b) Galan, M. C.; Jouvin, K.; Alvarez-Dorta, D. *Carbohydr. Res.* **2010**, *345*, 45. (c) Park, T.-J.; Weiwer, M.; Yuan, X.; Baytas, S. N.; Munoz, E. V.; Murugesan, S.; Linhardt, R. J. *Carbohydr. Res.* **2007**, *342*, 614. (d) Rencurosi, A.; Lay, L.; Russo, G.; Caneva, E.; Poletti, L. *J. Org. Chem.* **2005**, *70*, 7765. (e) Forsyth, S. A.; MacGarlane, D. R.; Thomson, R. J.; von Itzstein, M. *Chem. Commun.* **2002**, 714. (f) Zhang, J.; Ragauskas, A. J. *Carbohydr. Res.* **2005**, *340*, 2812.
- (21) Dasgupta, F.; Garegg, P. J. *Acta Chem. Scand.* **1989**, *43*, 471.
- (22) Mukherjee, C. M.; Misra, A. K. *J. Carbohydr. Chem.* **2007**, *26*, 213.
- (23) Martin-Lomas, M.; Khiar, N.; Garcia, S.; Koessler, J.-L.; Nieto, P. M.; Rademacher, T. W. *Chem. Eur. J.* **2000**, *6*, 3608.
- (24) Khiar, N.; Martin-Lomas, M. *J. Org. Chem.* **1995**, *60*, 7017.
- (25) Pozsgay, V.; Jennings, H. J. *J. Org. Chem.* **1988**, *53*, 4042.
- (26) Chowdhury, U. S. *Tetrahedron* **1996**, *52*, 12775.
- (27) Tropper, F. D.; Andersson, F. O.; Grand-Maitre, C.; Roy, R. *Synthesis* **1991**, 734.
- (28) Tiwari, P.; Misra, A. K. *Tetrahedron Lett.* **2006**, *47*, 2345.
- (29) Spectral data of products, which have not been reported earlier, are presented below.

p-Nitrophenyl 2,3,4,6-Tetra-O-acetyl-1-thio-β-D-glucopyranoside (16)

Yellow solid; mp 180–182 °C; $[\alpha]_D^{25}$ –32.7 (*c* 1.2, CHCl₃). IR (KBr): 2923, 2368, 1753, 1344, 1220, 1042, 770 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 8.16 (d, *J* = 8.9 Hz, 2 H), 7.59 (d, *J* = 8.8 Hz, 2 H), 5.28 (t, *J* = 9.2 Hz each, 1 H, H-3), 5.08 (t, *J* = 9.7 Hz each, 1 H, H-2), 5.04 (t, *J* = 9.6 Hz each, 1 H, H-4), 4.89 (d, *J* = 10.0 Hz, 1 H, H-1), 4.25–4.21 (m, 2 H, H-6_{a,b}), 3.85–3.80 (m, 1 H, H-5), 2.10, 2.08, 2.04, 2.0 (4 s, 12 H, 4 COCH₃). ¹³C NMR (50 MHz, CDCl₃): δ = 170.2, 169.9, 169.2, 169.0, 147.6, 141.6, 131.7 (2 C), 124.1 (2 C), 84.6, 76.6, 74.0, 70.0, 68.3, 62.2, 21.0, 20.9, 20.8 (2 C). ESI-MS: *m/z* = 508.1 [M + Na]⁺. Anal. Calcd for C₂₀H₂₃NO₁₁S (485.10): C, 49.48; H, 4.78. Found: C, 49.25; H, 5.0.

Benzyl 2,3,4,6-Tetra-O-acetyl-1-seleno-β-D-glucopyranoside (31)

Yellow oil; $[\alpha]_D^{25}$ –30 (*c* 1.5, CHCl₃). IR (neat): 2934, 1769, 1357, 1242, 1074, 764 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.40–7.21 (m, 5 H, ArH), 5.88 (d, *J* = 8.5 Hz, 1 H), 5.27 (t, *J* = 9.5 Hz each, 1 H), 5.06–4.89 (m, 2 H), 4.34–4.19 (m, 2 H), 3.90 (d, *J* = 11.1 Hz, 1 H), 3.83–3.67 (ABq, *J* = 12.0 Hz, 2 H), 2.08, 2.02, 1.99 (3 s, 12 H, 4 COCH₃). ¹³C NMR (50 MHz, CDCl₃): δ = 171.0, 170.8, 169.9 (2 C), 135.0–127.0 (ArC), 78.8, 76.3, 71.7, 71.2, 69.9, 68.6, 62.0, 26.6, 21.0, 20.9 (2 C). ESI-MS: *m/z* = 525.0 [M + Na]⁺. Anal. Calcd for C₂₁H₂₆O₉Se (502.07): C, 50.31; H, 5.23. Found: C, 50.08; H, 5.50.

Benzyl 2,3,4,6-Tetra-O-acetyl-1-seleno-α-D-mannopyranoside (33)

Yellow oil; $[\alpha]_D^{25}$ +126.8 (*c* 1.0, CHCl₃). IR (neat): 2972, 2362, 1742, 1598, 1373, 1246, 1107, 1050, 977, 756 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 7.28–7.09 (m, 5 H, ArH), 5.35 (br s, 1 H, H-2), 5.24 (br s, 1 H, H-1), 5.20–5.16 (m, 2 H, H-3 and H-4), 4.24–4.20 (m, 2 H, H-6_{ab}), 3.91–3.85 (m, 1 H, H-5), 3.77–3.73 (ABq, *J* = 12.0 Hz, 2 H, CH₂Ph), 2.07, 2.03, 1.98, 1.90 (4 s, 12 H, 4 COCH₃). ¹³C NMR (50 MHz, CDCl₃): δ = 170.2, 169.4 (2 C), 169.3, 137.6, 128.6 (2 C), 128.3 (2 C), 126.8, 77.6, 71.4, 70.6, 69.7, 65.8, 61.8, 27.4, 20.5, 20.4, 20.3, 20.2. ESI-MS: *m/z* = 525 [M + Na]⁺. ESI-MS: *m/z* = 525.0 [M + Na]⁺. Anal. Calcd for C₂₁H₂₆O₉Se (502.07): C, 50.31; H, 5.23. Found: C, 50.09; H, 5.52.

Benzyl 2,3,4-Tri-O-acetyl-1-seleno-α-L-rhamnopyranoside (36)

Yellow oil; $[\alpha]_D^{25}$ –114 (*c* 1.2, CHCl₃). IR (neat): 2367, 1756, 1600, 1366, 1230, 955 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 7.28–7.14 (m, 5 H, ArH), 5.34 (br s, 1 H, H-1), 5.32–5.30 (m, 1 H, H-2), 5.18 (dd, *J* = 9.7, 3.0 Hz, 1 H, H-3), 5.04 (t, *J* = 9.7 Hz each, 1 H, H-4), 4.12–4.02 (m, 1 H, H-5), 3.83 (ABq, *J* = 12.2 Hz, 2 H, PhCH₂), 2.08, 2.01, 1.93 (3 s, 9 H, 3 COCH₃), 1.18 (d, *J* = 6.2 Hz, 1 H, CCH₃). ESI-MS: *m/z* = 467.0 [M + Na]⁺. Anal. Calcd for C₁₉H₂₄O₇Se (444.07): C, 51.47; H, 5.46. Found: C, 51.25; H, 5.70.

Benzyl 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-acetyl-1-seleno-β-D-glucopyranoside (39)

Yellow oil; $[\alpha]_D^{25}$ +51 (*c* 1.0, CHCl₃). IR (neat): 3023, 1764, 1418, 1257, 1086, 769 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.32–7.20 (m, 5 H, ArH), 5.40–5.23 (m, 2 H), 5.18–5.09 (m, 1 H), 5.06–4.88 (m, 2 H), 4.86–4.76 (m, 1 H), 4.54–4.49 (m, 1 H), 4.46–4.38 (m, 1 H), 4.26–4.16 (m, 2 H), 4.06–3.82 (m, 5 H), 3.58–3.49 (m, 1 H), 2.13, 2.07, 1.99, 1.96, 1.95, 1.94 (6 s, 21 H, 7 COCH₃). ESI-MS: *m/z* = 813.1 [M + Na]⁺. Anal. Calcd for C₃₃H₄₂O₁₇Se (790.16): C, 50.19; H, 5.36. Found: C, 50.0; H, 5.60.

Phenyl 2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-acetyl-1-seleno-β-D-glucopyranoside (40)

Yellow oil; $[\alpha]_{\text{D}}^{25} +9$ (*c* 1.0, CHCl_3). IR (neat): 3036, 1790, 1432, 1276, 1094, 766 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 7.56\text{--}7.26$ (m, 5 H, ArH), 5.30–5.28 (m, 1 H), 5.16 (t, $J = 9.1$ Hz each, 1 H), 5.05 (dd, $J = 7.3$ Hz each, 1 H), 4.94–4.82 (m, 3 H), 4.51–4.46 (m, 1 H), 4.42 (d, $J = 7.9$ Hz, 1 H), 4.12–4.02 (m, 3 H), 3.85–3.81 (m, 1 H), 3.70 (t, $J = 9.1$ Hz each, 1 H), 3.62–3.56 (m, 1 H), 2.13, 2.07, 2.05, 2.01, 2.0, 1.94 (6 s, 21 H, 7 COCH_3). ESI-MS: $m/z = 799.1$ $[\text{M} + \text{Na}]^+$. Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{O}_{17}\text{Se}$ (776.14): C, 49.55; H, 5.20. Found: C, 49.32; H, 5.50.

Benzyl 2,3,4,6-Tetra-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-2,3,6-tri-*O*-acetyl-1-seleno- β -D-glucopyranoside (41)

Yellow oil; $[\alpha]_{\text{D}}^{25} +21$ (*c* 1.0, CHCl_3). IR (neat): 3023, 1767, 1424, 1281, 1089, 769 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): $\delta = 7.30\text{--}7.27$ (m, 5 H, ArH), 5.40–5.28 (m, 2 H), 5.20–4.88 (m, 4 H), 4.54–4.44 (m, 2 H), 4.22–4.06 (m, 4 H), 4.02–3.86 (m, 2 H), 3.82–3.70 (m, 1 H), 3.56–3.48 (m, 1 H), 2.17, 2.15, 2.14, 2.06, 2.03, 2.0, 1.97 (7 s, 21 H, 7 COCH_3). ESI-MS: $m/z = 813.1$ $[\text{M} + \text{Na}]^+$. Anal. Calcd for $\text{C}_{33}\text{H}_{42}\text{O}_{17}\text{Se}$ (790.16): C, 50.19; H, 5.36. Found: C, 50.0; H, 5.58.