Carbohydrate Research 361 (2012) 41–48

Contents lists available at SciVerse ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Reaction of glycal derivatives with alcohols in the presence of *N*-bromosuccinimide and diphenyldiselenide: preparation of 2-deoxy-2-phenylselenyl glycosides

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ARTICLE INFO

Article history:
Received 12 June 2012
Received in revised form 10 August 2012
Accepted 14 August 2012
Available online 21 August 2012

Keywords:
Glycoside
Diphenyl diselenide
2-Deoxy-2-phenylselenyl sugar
N-Bromosuccinimide
Glycal

ABSTRACT

Reaction of glycal derivatives with alcohols or glycosyl acceptors in the presence of *N*-bromosuccinimide (NBS) and diphenyldiselenide resulted in the formation of alkyl 2-deoxy-2-phenylselenyl glycosides or disaccharide derivatives in excellent yield. The reactions are reasonably fast and considerable stereoselectivity was observed in the preparation of disaccharide derivatives.

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1. Introduction

Glycal derivatives are important intermediates in the preparation of several biologically important molecules.[1–3] They can be transformed to 2-substituted carbohydrate derivatives exploiting their enol ether functionalities. Because of the significant role of the 2-deoxy sugars in the medicinally useful molecules, a number of attempts were made in the past to synthesize them. 2-Deoxy glycosides can be conveniently synthesized from glycal derivatives through the formation of 2-halo,[4–7] 2-sulfo,[8–12] and 2-seleno glycosides.[13–15] Since 2-seleno group can be removed easily by reductive as well as oxidative conditions, 2-seleno glycosides can be considered as most convenient precursors of 2-deoxy glycosides than others. As a consequence, a number of reports appeared in the past to synthesize 2-deoxyglycosides from glycal derivatives via the formation of 2-selenoglycosides.[13–17] In this context, it is worth mentioning that although 2-seleno glycosides can act as precursors of 2-deoxy glycosides, which are essential components of many bioactive molecules, selenium compounds showed toxicity in the human neuronal cell line through the increase of reactive oxygen species (ROS)/RNS and apoptosis.[18] Conventionally, 2-selenoglycosides were prepared in a two step process: (a) generation of phenylselenyl cation ($PhSe^+$) and its addition to the double bond of the glycal derivative to form an episelenonium ion reaction intermediate; (b) attack of a nucleophile to the episelenonium ion to furnish 2-seleno glycosides as anti-addition products. In most of the cases two isomeric anti-addition products were obtained depending on the stereochemistry of the episelenonium ion. For the synthesis of 2-selenoglycosides, phenylselenyl halides have been used as the source of phenylselenyl cation in the presence of silver salt.[13–17] Earlier, diphenyl diselenide has also been used as the source of phenylselenyl moiety in combination with azide salts to generate 2-azido selenides or 2-azido selenoglycosides from alkenes and glycal derivatives respectively in the presence of (diacetoxyiodo)benzene[19–21] or by electrochemical methods.[22,23] In our attempt to prepare alkyl 2-deoxy-2-phenylselenyl glycosides, we sought to explore the reaction of glycal derivatives with alcohols in the presence of a combination of *N*-bromosuccinimide (NBS) and diphenyl diselenide. Earlier NBS has been used in the carbohydrate chemistry to transform glycal derivatives into a variety of useful intermediates.[24–27] It was envisaged that NBS could react with diphenyl diselenide in an oxidative mechanism [by generating bromonium ion (Br^+)] to produce phenylselenyl bromide in situ, which could react with glycal derivative in the presence of an alcohol or sugar acceptor to furnish 2-deoxy-2-phenylselenyl glycoside. We report herein the reaction of glycal derivatives with alcohols in the presence of a combination of NBS and diphenyl diselenide toward the preparation of alkyl 2-deoxy-2-phenylselenyl glycosides (Scheme 1).

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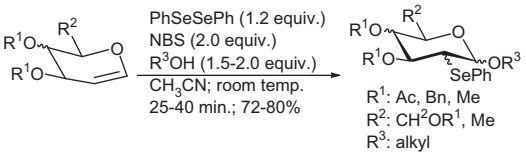
http://dx.doi.org/10.1016/j.carres.2012.08.009



Scheme 1. Reaction of glycal derivatives with alcohol or glycosyl acceptor in the presence of a combination of diphenyl diselenide and NBS.

2. Results and discussion

In a set of initial experiments, tri-*O*-acetyl-D-glucal (**1**) was allowed to react with a varied quantity of diphenyl diselenide (0.8–1.5 equiv) and methanol (1.2–3.0 equiv) in CH_3CN in the presence of a different quantity of NBS (1.0–2.0 equiv) at room temperature. After a series of experimentation it was observed that reaction of **1** with 1.2 equiv of diphenyl diselenide and 2.0 equiv of methanol in the presence of 1.5 equiv of NBS in CH_3CN furnished methyl 2-deoxy-2-phenylselenyl glycoside as a mixture of two isomer (β-D-gluco-(**7**)/α-D-manno-(**8**) = 1:3) in excellent yield (82%) at room temperature in 25 min. Among the most commonly used organic solvents for example CH_3CN, CH_2Cl_2, Et_2O, toluene, THF, and 1,2-$(CH_2)_2Cl_2$ the best results were obtained using CH_3CN as the reaction medium. To establish the generality of the reaction condition, a series of D-glucal derivatives (containing acetoxy, benzoxy, and methoxy functionalities) were allowed to react with a combination of diphenyl diselenide and NBS in a variety of alcohols at room temperature. Excellent yield of the products were obtained in all reactions, which is presented in Table 1. D-galactal and L-rhamnal derivatives also furnished 2-deoxy-2-phenylselenyl and 2,6-dideoxy-2-phenylselenyl-glycosides, respectively in excellent yield under similar reaction conditions. The reaction condition has been further extended toward the preparation of disaccharide derivatives. In order to establish the requirement of NBS in the reaction medium, a control experiment has been carried out without using NBS and it was observed that the reaction did not take place even after 24 h at room temperature, which confirmed the involvement of NBS in the reaction. The reaction of monosaccharide acceptors with glycal derivatives under similar reaction condition furnished 2-deoxy-2-phenylselenyl disaccharide derivatives in excellent yield. Although the reaction of primary sugar alcohols gave satisfactory yield of the products, the reaction did not proceed with the secondary sugar alcohols and degradation of starting materials was observed with time, which could be explained by considering the steric crowding around the episelenonium transition state which inhibits the approach of a secondary sugar alcohol. An isomeric mixture of the products was formed in most of the cases, the disaccharide derivatives and D-galactal derived products were obtained mostly as one major or exclusive product (α-D-manno/(α-D-talo isomer). Various functional groups used in the protection of carbohydrates remained unaffected under the reaction condition. The structure of the products was confirmed from their NMR spectral analysis. It is presumed that the reaction proceeds through the formation of a episelenonium transition state[22] which becomes trapped with alcohols to furnish two isomers of 2-phenylselenyl glycosides (α-D-manno/talo isomer as major and β-D-gluco-/galacto– as minor products). The formation of episelenonium species may be possible in two ways as presented in the plausible mechanisms in Figure 1 and Figure 2. According to path A (Fig. 1), diphenyl diselenide reacts with *N*-bromosuccinimide (NBS) to generate phenylselenyl bromide which adds to the double bond of glycal derivative to give an isomeric mixture of episelenonium species. 1,2-*Trans* opening of the episelenonium transition states lead to the formation of an isomeric mixture of 2-deoxy-2-phenylselenyl glycosides as major and minor products. According to path B (Fig. 2), NBS generates bromonium ion (Br^+) in the first step, which adds to the double bond of the glycal derivative to form glycal 1,2-bromonium ion adduct, which opens up by diphenyl diselenide to form *trans* 2-bromo-1-selenophenyl glycoside in situ. Recyclization of *trans* 2-bromo-1-phenylselenyl glycoside in the second step forms episelenonium ion species, which becomes trapped by the alcohol by *trans* addition to furnish an isomeric mixture of 2-deoxy-2-phenylselenyl glycosides as major and minor products.

3. Conclusion

In conclusion, a straightforward reaction condition for the preparation of 2-deoxy-2-selenoglycosides has been developed from glycal derivatives using a combination of diphenyl diselenide and NBS. A series of disaccharide derivatives have also been synthesized with high stereoselectivity. The reaction condition has several noteworthy features to be considered as a useful alternative to the other existing methods such as, operational simplicity, significantly fast, mild, and less hazardous reaction condition avoiding the use of highly reactive phenylselenyl chloride and high yield.

4. Experimental

4.1. General methods

All reactions were monitored by thin layer chromatography over silica gel coated TLC plates. The spots on TLC were visualized by warming ceric sulfate (2% $Ce(SO_4)_2$ in 2 N H_2SO_4) sprayed plates in hot plate. Silica gel 230–400 mesh was used for column chromatography. ^1H and ^{13}C NMR spectra were recorded on Brucker Avance 200 and 500 MHz spectrometers using $CDCl_3$ as solvent and TMS as internal reference unless stated otherwise. Chemical shift value is expressed in δ ppm. ESI-MS were recorded on a Micromass mass spectrometer. Commercially available grades of organic solvents of adequate purity are used in all reactions.

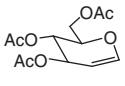
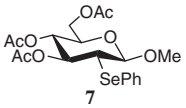
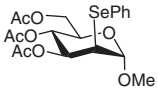
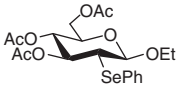
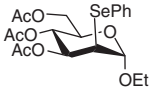
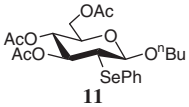
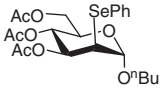
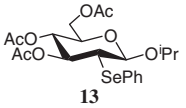
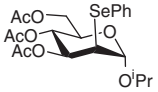
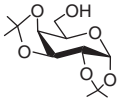
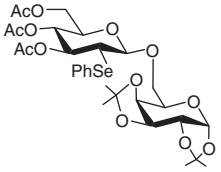
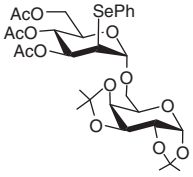
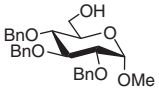
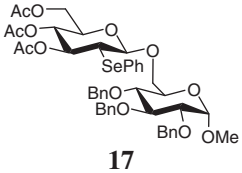
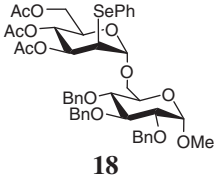
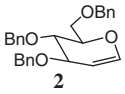
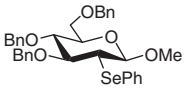
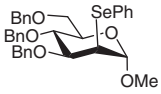
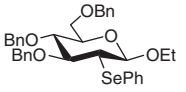
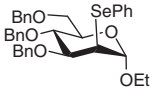
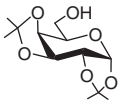
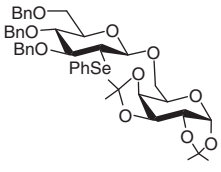
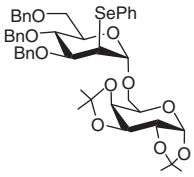
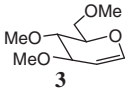
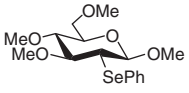
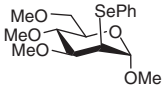
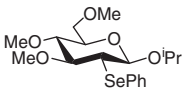
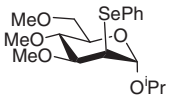
4.2. Typical experimental condition

To a solution of tri-*O*-acetyl-D-glucal (**1**; 545 mg, 2.0 mmol) in CH_3CN (5 mL) were added alcohol (4.0 mmol) or monosaccharide acceptor (2.5 mmol), diphenyl diselenide (750 mg, 2.40 mmol), and NBS (550 mg, 3.09 mmol) and the reaction mixture was allowed to stir at room temperature for appropriate time as mentioned in Table 1. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was successively washed with satd. $NaHCO_3$, water, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane–EtOAc as eluant to give pure individual isomer. Spectral data of the isolated products are presented below.

4.2.1. Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-β-D-glucopyranoside (7)

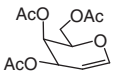
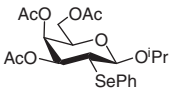
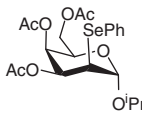
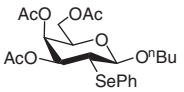
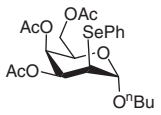
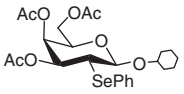
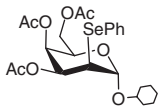
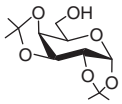
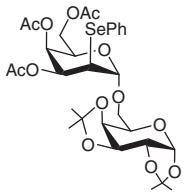
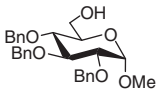
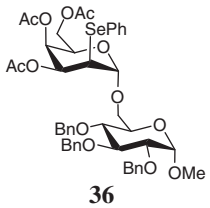
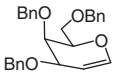
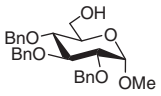
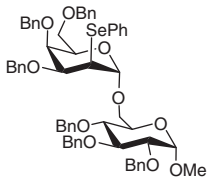
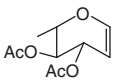
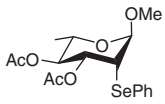
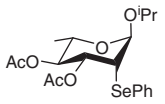
Colorless oil; $[\alpha]_D^{25}$ +66 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.66–7.28 (m, 5H, Ar-H), 5.13 (t, *J* = 9.0 Hz each, 1H, H-3), 4.97 (t, *J* = 9.0 Hz each, 1H, H-6_a), 4.13 (d, *J* = 8.5 Hz, 1H, H-1), 4.08 (dd, *J* = 12.5, 2.5 Hz, 1H, H-6_b), 3.54–3.51 (m, 1H, H-5), 3.50 (s, 3H, OC*H*$_3$), 3.09 (t, *J* = 9.0 Hz each, 1H, H-2), 2.09, 2.06, 2.03, (3 s, 9H, 3 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.7, 170.4, 170 (3 *C*OCH$_3$), 136.4–128.7 (Ar-C), 103.2 (C-1), 72.7 (C-3), 71.5 (C-5), 69.8 (C-4), 62.1 (C-6), 57.1 (O*C*H$_3$), 47.1 (C-2), 20.8, 20.7, 20.6 (3 *C*OCH$_3$); ESI-MS: 483.0 $[M+Na]^+$; Anal. Calcd for $C_{19}H_{24}O_8Se$ (460.06): C, 49.68; H, 5.27. Found: C, 49.52; H, 5.50.

Table 1
Reaction of glycal derivatives with alcohols in the presence of a combination of diphenyl diselenide and NBS to furnish 2-deoxy-2-phenylselenyl glycosides[a]

Sl. No.	Glycal	Alcohol	Product		Time (min)	Yield[b] (%)	Ratio
			β-Gluco–/Galacto–	α-Manno–/Talo–			
1	 **1**	MeOH	 **7**	 **8**	25	82	1:3
2	**1**	EtOH	 **9**[28]	 **10**[28]	30	80	1:4
3	**1**	^{n}BuOH	 **11**	 **12**	40	82	1:3
4	**1**	^{i}PrOH	 **13**	 **14**	40	84	1:3
5	**1**		 **15**	 **16**	45	78	1:17
6	**1**		 **17**	 **18**	40	75	1:18
7	 **2**	MeOH	 **19**	 **20**	25	76	1:5
8	**2**	EtOH	 **21**	 **22**	30	74	2:7
9	**2**		 **23**	 **24**	45	72	1:15
10	 **3**	MeOH	 **25**	 **26**	25	86	1:4
11	**3**	^{i}PrOH	 **27**	 **28**	25	85	2:7

(*continued on next page*)

Table 1 (*continued*)

Sl. No.	Glycal	Alcohol	Product		Time (min)	Yield[b] (%)	Ratio
			β-Gluco–/Galacto–	α-Manno–/Talo–			
12	 **4**	^{i}PrOH	 **29**	 **30**	25	77	1:15
13	**4**	^{n}BuOH	 **31**	 **32**	25	74	1:16
14	**4**	Cyclo-hexanol	 **33**	 **34**	25	75	1:15
15	**4**		–	 **35**	40	72	–
16	**4**		–	 **36**	40	70	–
17	 **5**		–	 **37**	40	72	–
18	 **6**	MeOH	 **38**	 **39**	25	82	2:7
19	**6**	^{i}PrOH	 **40**	 **41**	25	84	2:9

[a] All reactions are carried out at room temperature.
[b] Isolated yield.

4.2.2. Methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-α-D-mannopyranoside (8)

Colorless oil; $[\alpha]_D^{25}$ +75 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.57–7.25 (m, 5H, Ar-H), 5.43 (t, *J* = 9.5 Hz each, 1H, H-4), 5.39 (dd, *J* = 9.5, 4.5 Hz, 1H, H-3), 5.07 (br s, 1H, H-1), 4.21–4.14 (m, 2H, H-6_{ab}), 3.96–3.93 (m, 1H, H-5), 3.90 (dd, *J* = 4.5, 1.5 Hz, 1H, H-2), 3.37 (s, 3H, O*CH*$_3$), 2.13, 2.03, 1.68 (3 s, 9H, 3 CO*CH*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 170.2, 169.6 (3 *C*OCH$_3$), 134.3–127.8 (Ar-C), 101.5 (C-1), 70.9 (C-3), 68.7 (C-4), 67.2 (C-5), 62.6 (C-6), 55.2 (O*CH*$_3$), 47.9 (C-2), 20.8, 20.7, 20.3 (3 CO*CH*$_3$); ESI-MS: 483.0 $[M+Na]^+$; Anal. Calcd for $C_{19}H_{24}O_8Se$ (460.06): C, 49.68; H, 5.27. Found: C, 49.50; H, 5.47.

4.2.3. Ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-β-D-glucopyranoside (9)

Colorless oil; $[\alpha]_D^{25}$ +56 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.57–7.25 (m, 5H, Ar-H), 5.11 (t, *J* = 9.0 Hz each, 1H, H-3), 4.94 (t, *J* = 9.0 Hz each, 1H, H-4), 4.25 (d, *J* = 9.0 Hz each, 1H, H-1), 4.22 (dd, *J* = 12.0, 5.0 Hz, 1H, H-6_a), 4.03 (dd, *J* = 12.0, 2.5 Hz, 1H, H-6_b), 3.89–3.85 (m, 1H, O*CH*$_{2a}$), 3.54–3.51 (m, 1H, H-5), 3.50–3.46 (m, 1H,

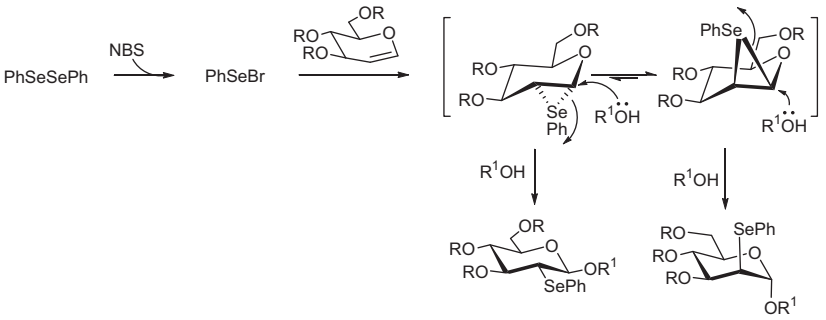


Figure 1. Plausible mechanism for the formation of 2-deoxy-2-phenylselenyl glycoside (Path A).

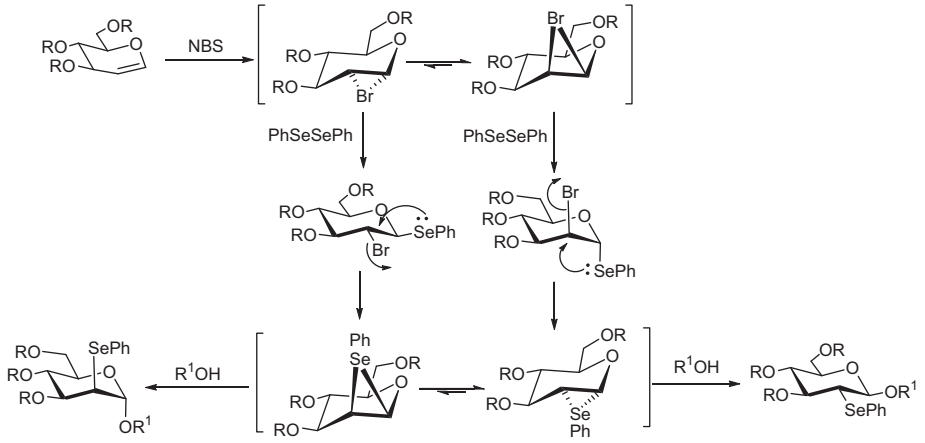


Figure 2. Plausible mechanism for the formation of 2-deoxy-2-phenylselenyl glycoside (Path B).

OCH_{2b}), 3.10 (t, J = 9.0 Hz each, 1H, H-2), 2.02, 2.00, 1.98 (3 s, 9H, 3 COCH_3), 1.20 (t, J = 7.0 Hz each, 3H, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.7, 170.2, 169.6 (3 COCH$_3$), 136.0–128.4 (Ar-C), 102.6 (C-1), 72.7 (C-3), 71.4 (C-5), 69.8 (C-4), 65.8 (OCH_2CH$_3$), 62.2 (C-6), 47.7 (C-2), 20.8, 20.7, 20.6 (3 COCH_3), 14.9 (CH_2CH_3); ESI-MS: 497.0 [M+Na]$^+$; Anal. Calcd for $C_{20}H_{26}O_8Se$ (474.07): C, 50.74; H, 5.54. Found: C, 50.55; H, 5.77.

4.2.4. Ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-α-D-mannopyranoside (10)

Colorless oil; $[\alpha]_D^{25}$ +62 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58–7.25 (m, 5H, Ar-H), 5.44–5.43 (m, 2H, H-3, H-4), 5.19 (br s, 1H, H-1), 4.21 (dd, J = 12.0, 5.0 Hz, 1H, H-6$_a$), 4.14 (dd, J = 12.0, 2.5 Hz, 1H, H-6$_b$), 3.99–3.96 (m, 1H, H-5), 3.90 (br s, 1H, H-2), 3.72–3.68 (m, 1H, CH_{2a}), 3.53–3.49 (m, 1H, CH_{2b}), 2.13, 2.04, 1.68 (3 s, 9H, 3 COCH_3), 1.25 (t, J = 7.0 Hz each, 3H, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 170.2, 169.7 (3 COCH$_3$), 134.2–127.8 (Ar-C), 100.3 (C-1), 71.0 (C-3), 68.7 (C-4), 67.4 (C-5), 63.7 (OCH_2CH$_3$), 62.6 (C-6), 48.2 (C-2), 20.8, 20.7, 20.3 (3 COCH_3), 14.9 (CH_2CH_3); ESI-MS: 497.0 [M+Na]$^+$; Anal. Calcd for $C_{20}H_{26}O_8Se$ (474.07): C, 50.74; H, 5.54. Found: C, 50.53; H, 5.76.

4.2.5. ″Butyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-β-D-glucopyranoside (11)

Colorless oil; $[\alpha]_D^{25}$ +7 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64–7.27 (m, 5H, Ar-H), 5.11 (t, J = 9.0 Hz each, 1H, H-3), 4.95 (t, J = 9.5 Hz each, 1H, H-4), 4.27 (d, J = 9.0 Hz, 1H, H-1), 4.25 (dd, J = 12.0, 4.5 Hz, 1H, H-6$_a$), 4.04 (dd, J = 12.0, 2.5 Hz, 1H, H-6$_b$), 3.87–3.82 (m, 1H, OCH_{2a}), 3.55–3.51 (m, 1H, H-5), 3.46–3.42 (m, 1H, OCH_{2b}), 3.12 (t, J = 9.0 Hz each, 1H, H-2), 2.04, 2.02, 2.00 (3 s, 9H, 3 COCH_3), 1.60–1.58 (m, 2H, –CH_2–), 1.40–1.33 (m, 2H, –CH_2–), 0.92 (t, J = 7.0 Hz each, 3H, –CH_3–); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.7, 170.6, 170.0 (3 COCH$_3$), 135.8–128.2 (Ar-C), 102.7 (C-1), 72.8 (C-3), 71.4 (C-4), 69.9 (C-5), 69.8 (OCH_2), 62.1 (C-6), 47.8 (C-2), 29.6 (CH_2), 22.7 (CH_2), 20.7, 20.6 (2 C), (3 COCH_3), 14.1 (CH_3); ESI-MS: 525.1 [M+Na]$^+$; Anal. Calcd for $C_{22}H_{30}O_8Se$ (502.11): C, 52.70; H, 6.03. Found: C, 52.52; H, 6.20.

4.2.6. ″Butyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-α-D-mannopyranoside (12)

Colorless oil; $[\alpha]_D^{25}$ +80 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58–7.24 (m, 5H, Ar-H), 5.44–5.38 (m, 2H, H-3, H-4), 5.14 (br s, 1H, H-1), 4.19 (dd, J = 12.0, 5.0 Hz, 1H, H-6$_a$), 4.13 (dd, J = 12.0, 2.5 Hz, 1H, H-6$_b$), 3.97–3.94 (m, 1H, H-5), 3.90–3.89 (m, 1H, H-2), 3.66–3.62 (m, 1H, OCH_{2a}), 3.46–3.43 (m, 1H, OCH_{2b}), 2.12, 2.04, 1.67 (3 s, 9H, 3 COCH_3), 1.60–1.53 (m, 2H, –CH_2–), 1.39–1.33 (m, 2H, –CH_2–), 0.94 (t, J = 7.0 Hz each, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.6, 170.6, 169.5 (3 COCH$_3$), 143.3–127.7 (Ar-C), 100.4 (C-1), 71.1 (C-3), 68.8 (C-4), 67.9 (C-5), 67.3 (–OCH_2–), 62.6 (C-6), 48.0 (C-2), 29.7 (–CH_2–), 20.8, 20.7, 20.3 (3 COCH_3), 19.4 (–CH_2–), 13.8 (–CH_3–); ESI-MS: 525.1 [M+Na]$^+$; Anal. Calcd for $C_{22}H_{30}O_8Se$ (502.11): C, 52.70; H, 6.03. Found: C, 52.50; H, 6.25.

4.2.7. 2-Propyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-β-D-glucopyranoside (13)

Colorless oil; $[\alpha]_D^{25}$ +10 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 763–7.24 (m, 5H, Ar-H), 5.14, (t, J = 9.0 Hz each, 1H, H-3), 4.96 (t, J = 9.5 Hz each, 1H, H-4), 4.48 (d, J = 9.5 Hz, 1H, H-1), 4.26 (dd, J = 12.0, 5.5 Hz, 1H, H-6$_a$), 4.09 (dd, J = 12.0, 2.5 Hz, 1H, H-6$_b$), 3.98–3.93 (m, 1H, CH(CH$_3$)$_2$), 3.62–3.58 (m, 1H, H-5), 3.18 (t, J = 9.0 Hz each, 1H, H-2), 2.05, 2.00, 1.99 (3 s, 9H, 3 COCH_3), 1.22 (d, J = 6.5 Hz, 3H, CH_3), 1.83 (d, J = 6.0 Hz, 3H, CH_3); ^{13}C NMR

($CDCl_3$, 125 MHz): δ 170.7, 170.2, 169.7 (3 $COCH_3$), 135.0–127.9 (Ar-C), 101.7 (C-1), 73.0 (C-3), 72.9 (C-5), 71.4 (C-4), 70.0 ($CH(CH_3)_2$), 62.4 (C-6), 48.8 (C-2), 23.2 (CH_3), 21.8 (CH_3), 20.8, 20.7, 20.6 (3 $COCH_3$); ESI-MS: 511.0 $[M+Na]^+$; Anal. Calcd for $C_{21}H_{28}O_8Se$ (488.09): C, 51.75; H, 5.79. Found: C, 51.58; H, 6.00.

4.2.8. 2-Propyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-α-D-mannopyranoside (14)

Colorless oil; $[\alpha]_D^{25}$ +97 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.58–7.25 (m, 5H, Ar-H), 5.44–5.43 (m, 2H, H-3, H-4), 5.27 (br s, 1H, H-1), 4.19 (dd, *J* = 12.0, 5.0 Hz, 1H, H-6_a), 4.13 (dd, *J* = 12.0, 2.5, Hz, 1H, H-6_b), 4.06–4.02 (m, 1H, H-5), 3.91–3.87 (m, 1H, C*H*(CH_3)$_2$), 3.86–3.85 (m, 1H, H-2), 2.11, 2.04, 1.67 (3 s, 9H, 3 COC*H*$_3$), 1.22 (d, *J* = 6.0 Hz, 3H, C*H*$_3$), 1.15 (d, *J* = 6.0 Hz, 3H, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 170.2, 169.7 (3 *C*OCH$_3$), 134.1–127.7 (Ar-C), 98.7 (C-1), 71.1 (C-3), 70.5 (C-5), 68.8 (*C*H(CH_3)$_2$), 67.5 (C-5), 62.7 (C-6), 48.6 (C-2), 23.1 (*C*H$_3$), 21.5 (*C*H$_3$), 20.8, 20.7, 20.3 (3 COCH$_3$); ESI-MS: 511.0 $[M+Na]^+$; Anal. Calcd for $C_{21}H_{28}O_8Se$ (488.09): C, 51.75; H, 5.79. Found: C, 51.54; H, 6.06.

4.2.9. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phenylselenyl-α-D-mannopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (16)

Colorless oil; $[\alpha]_D^{25}$ −2 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.57–7.24 (m, 5H, Ar-H), 5.49 (d, *J* = 4.0 Hz, 1H, H-1_A), 5.40 (t, *J* = 9.5 Hz each, 1H, H-4_B), 5.37 (dd, *J* = 9.5, 3.0 Hz, 1H, H-3_B), 5.20 (br s, 1H, H-1_B), 4.59 (dd, *J* = 8.0, 2.5 Hz, 1H, H-4_A), 4.30–4.29 (m, 1H, H-2_A), 4.24–4.18 (m, 2H, H-3_A, H-6_{aB}), 4.14–4.10 (m, 1H, H-6_{bB}), 4.08–4.05 (m, 1H, H-5_B), 3.96–3.91 (m, 2H, H-2_B, H-5_A), 3.76 (dd, *J* = 10.5, 6.5 Hz, 1H, H-6_{aA}), 3.70 (dd, *J* = 10.5, 6.5 Hz, 1H, H-6_{bA}), 2.12, 2.03, 1.68 (3 s, 9H, 3 COC*H*$_3$), 1.53, 1.41, 1.33, 1.31, (4 s, 12H, 4 C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.5, 169.9, 169.4 (3 *C*OCH$_3$), 134.3–127.7 (Ar-C), 109.3 (*C*(CH_3)$_2$), 108.6 (*C*(CH_3)$_2$), 100.5 (C-1_B), 96.2 (C-1_A), 71.0 (C-3_B), 70.9 (C-4_B), 70.6 (C-2_A), 70.5 (C-3_A), 68.9 (C-4_A), 67.0 (C-5_B), 66.9 (C-6_A), 66.3 (C-5_A), 62.4 (C-6_B), 47.9 (C-2_B), 26.1, 26.0, 24.9, 24.5 (4 *C*H$_3$), 20.9, 20.7, 20.3 (3 COCH$_3$); ESI-MS: 711.1 $[M+Na]^+$; Anal. Calcd for $C_{30}H_{40}O_{13}Se$ (688.16): C, 52.40; H, 5.86. Found: C, 52.18; H, 6.06.

4.2.10. Methyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-α-D-mannopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (18)

Colorless oil; $[\alpha]_D^{25}$ +82 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.55–7.20 (m, 20 H, Ar-H), 5.40–5.35 (m, 2H, H-3_B, H-4_B), 5.18 (br s, 1H, H-1_B), 4.97–4.58 (m, 6H, 3 PhC*H*$_2$), 4.53 (d. *J* = 3.5 Hz, 1H, H-1_A), 4.06–4.01 (m, 2H, H-6_{abB}), 3.98–3.95 (m, 1H, H-5_A), 3.92–3.90 (m, 2H, H-2_B, H-4_A), 3.77–3.72 (m, 2H, H-5_B, H-6_{aA}), 3.63 (d, *J* = 10.5 Hz, 1H, H-6_{bA}), 3.49–3.42 (m, 2H, H-2_A, H-3_A), 3.35 (s, 3H, OC*H*$_3$), 2.09, 2.01, 1.69 (3 s, 9H, 3 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.1, 170.0, 169.9 (3 *C*OCH$_3$), 145.6–127.4 (Ar-C), 100.5 (C-1_B), 97.8 (C-1_A), 82.2 (C-5_A), 80.1 (C-2_A), 77.6 (C-3_A), 75.7 (PhCH$_2$), 74.8 (PhCH$_2$), 73.3 (PhCH$_2$), 70.9 (C-3_B), 69.7 (C-4_A), 68.9 (C-5_B), 67.0 (C-4_B), 66.3 (C-6_A), 62.3 (C-6_B), 55.1 (OCH$_3$), 47.7 (C-2_B), 20.7, 20.6, 20.3 (3 COCH$_3$); ESI-MS: 915.2 $[M+Na]^+$; Anal. Calcd for $C_{46}H_{52}O_{13}Se$ (892.25): C, 61.95; H, 5.88. Found: C, 61.74; H, 6.11.

4.2.11. Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-phenylselenyl-β-D-glucopyranoside (19)

Colorless oil; $[\alpha]_D^{25}$ +51 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.67–7.16 (m, 20 H, Ar-H), 5.05 (d, *J* = 10.5 Hz, 1H, PhC*H*$_2$), 4.88 (d, *J* = 10.5 Hz, 1H, PhC*H*$_2$), 4.80 (d, *J* = 11.0 Hz, 1H, PhC*H*$_2$), 4.62–4.46 (m, 3H, PhC*H*$_2$), 4.20 (d, *J* = 9.0 Hz, 1H, H-1), 3.74–3.67 (m, 2H, H-6_{ab}), 3.59 (t, *J* = 9.0 Hz each, 1H, H-3), 3.57 (t, *J* = 9.0 Hz each, 1H, H-4), 3.47 (s, 3H, OC*H*$_3$), 3.39–3.36 (m, 1H, H-5), 3.15 (t, *J* = 9.0 Hz each, 1H, H-2); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.2–127.6 (Ar-C), 103.7 (C-1), 82.9 (C-3), 79.7 (PhCH$_2$), 75.6 (C-5), 74.9 (PhCH$_2$), 74.7 (PhCH$_2$),, 73.5 (C-4), 68.9 (C-6), 56.9 (OCH$_3$), 50.4 (C-2); ESI-MS: 627.1 $[M+Na]^+$; Anal. Calcd for $C_{34}H_{36}O_5Se$ (604.17): C, 67.65; H, 6.01. Found: C, 67.46; H, 6.20.

4.2.12. Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-phenylselenyl-α-D-mannopyranoside (20)

Colorless oil; $[\alpha]_D^{25}$ +17 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.64–7.16 (m, 20 H, Ar-H), 4.98 (br s, 1H , H-1), 4.88 (d, *J* = 10.5 Hz, 1H, PhC*H*$_2$), 4.69 (d, *J* = 12.5 Hz, 1H, PhC*H*$_2$), 4.58–4.48 (m, 4H, PhC*H*$_2$), 4.19–4.16 (m, 1H, H-5), 3.84 (t, *J* = 9.0 Hz each, 1H, H-4), 3.81 (br s, 1H, H-2), 3.80–3.70 (m, 3H, H-3, H-6_{ab}), 3.29 (s, 3H, OC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.8–127.5 (Ar-C), 101.6 (C-1), 78.9 (C-3), 75.7 (PhCH$_2$), 75.0 (C-5), 73.4 (PhCH$_2$), 71.6 (PhCH$_2$), 71.4 (C-4), 69.2 (C-6), 54.8 (OCH$_3$), 49.4 (C-2); ESI-MS: 627.1 $[M+Na]^+$; Anal. Calcd for $C_{34}H_{36}O_5Se$ (604.17): C, 67.65; H, 6.01. Found: C, 67.48; H, 6.22.

4.2.13. Ethyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-phenylselenyl-β-D-glucopyranoside (21)

Colorless oil; $[\alpha]_D^{25}$ +11 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.64–7.13 (m, 20 H, Ar-H), 4.99 (d, *J* = 10.5 Hz, 1H, PhC*H*$_2$), 4.83 (d, *J* = 10.5 Hz, 1H, PhC*H*$_2$), 4.78 (d, *J* = 11.0 Hz, 1H, PhC*H*$_2$), 4.57–4.48 (m, 3H, PhC*H*$_2$), 4.30 (d, *J* = 9.0 Hz, 1H, H-1), 3.89–3.80 (m, 1H, –C*H*$_{2a}$–), 3.70 (dd, *J* = 12.0, 2.0 Hz, 1H, H-6_a), 3.67 (dd, *J* = 12.0, 5.0 Hz, 1H, H-6_b), 3.57 (t, *J* = 9.0 Hz, each, 1H, H-3), 3.54 (t, *J* = 9.0 Hz, each, 1H, H-4), 3.50–3.42 (m, 1H, –C*H*$_{2b}$–), 3.38–3.35 (m, 1H, H-5), 3.16 (t, *J* = 9.0 Hz each, 1H, H-2), 1.13 (t, *J* = 7.0 Hz each, 3H, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.2–127.6 (Ar-C), 103.1 (C-1), 82.9 (C-3), 79.8 (C-5), 75.7 (PhCH$_2$), 74.9 (PhCH$_2$), 74.8 (C-4), 73.5 (PhCH$_2$), 69.0 (CH_2CH_3), 65.4 (C-6), 50.9 (C-2), 14.9 (CH_3CH_2); ESI-MS: 641.1 $[M+Na]^+$; Anal. Calcd for $C_{35}H_{38}O_5Se$ (618.18): C, 68.06; H, 6.20. Found: C, 67.85; H, 6.42.

4.2.14. Ethyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-phenylselenyl-αD-mannopyranoside (22)

Colorless oil; $[\alpha]_D^{25}$ +44 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.61–7.13 (m, 20 H, Ar-H), 5.09 (br s, 1H, H-1), 4.87 (d, *J* = 10.5 Hz, 1H, PhC*H*$_2$), 4.66 (d, *J* = 12.5 Hz, 1H, PhC*H*$_2$), 4.56–4.45 (m, 4H, PhC*H*$_2$), 4.21–4.18 (m, 1H, H-5), 3.85 (t, *J* = 9.0 Hz each, 1H, H-4), 3.89–3.79 (m, 2H, H-6_{ab}), 3.75 (dd, *J* = 9.0, 4.0 Hz, 1H, H-3), 3.69 (br s, 1H, H-2), 3.67–3.63 (m, 1H, –C*H*$_{2a}$–), 3.39–3.35 (m, 1H, –C*H*$_{2b}$–), 1.20 (t, *J* = 7.0 Hz each, 1H, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.5–127.5 (Ar-C), 100.3 (C-1), 79.1 (C-3), 75.8 (C-4), 75.1 (PhCH$_2$), 73.4 (PhCH$_2$), 71.7 (C-5), 71.5 (PhCH$_2$), 69.2 (CH_2CH_3), 63.1 (C-6), 49.8 (C-2), 15.0 (CH_3CH_2); ESI-MS: 641.1 $[M+Na]^+$; Anal. Calcd for $C_{35}H_{38}O_5Se$ (618.18): C, 68.06; H, 6.20. Found: C, 67.83; H, 6.45.

4.2.15. 3,4,6-Tri-*O*-benzyl-2-deoxy-2-phenylselenyl-α-D-mannopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-αD-galactopyranose (24)

Colorless oil; $[\alpha]_D^{25}$ +7 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.61–7.14 (m, 20 H, Ar-H), 5.48 (d, *J* = 4.5 Hz, 1H, H-1_A), 5.18 (br s, 1H, H-1_B), 4.87, 4.68, (2 d, *J* = 10.5 Hz each, PhC*H*$_2$), 4.58–4.56 (m, 1H, H-4_A), 4.55–4.47 (m, 4H, PhC*H*$_2$), 4.28–4.26 (m, 1H, H-2_A), 4.20–4.16 (m, 1H, H-5_B), 4.14 (dd, *J* = 8.0, 2.0 Hz, 1H, H-3_A), 3.92–3.88 (m, 1H, H-5_A), 3.87–3.84 (m, 2H, H-3_B, H-4_B), 3.82 (dd, *J* = 4.5, 1.5 Hz, 1H, H-2_B), 3.78–3.61 (m, 4H, H-6_{abA}, H-6_{abB}), 1.52, 1.47, 1.29 (3 s, 12H, 2 C(C*H*$_3$)$_2$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.5–127.4 (Ar-C), 109.3, 108.5, (2 *C*(CH_3)$_2$), 100.5 (C-1_B), 96.3 (C-1_A), 78.9 (C-5_B), 75.5 (C-4_A), 74.9 (PhCH$_2$), 73.4 (PhCH$_2$), 72.0 (C-3_B), 71.5 (PhCH$_2$), 70.9 (C-4_B), 70.7 (C-3_A), 70.6 (C-2_A), 69.0 (C-6_B), 65.8 (C-6_A), 65.7 (C-5_A), 49.6 (C-2_B), 26.1, 26.0, 24.9, 24.6

(CH_3); ESI-MS: 855.2 $[M+Na]^+$; Anal. Calcd for $C_{45}H_{52}O_{10}Se$ (832.27): C, 64.97; H, 6.30. Found: C, 64.74; H, 6.46.

4.2.16. Methyl 3,4,6-tri-*O*-methyl-2-deoxy-2-phenylselenyl-β-D-glucopyranoside (25)

Colorless oil; $[\alpha]_D^{25}$ +30 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.66–7.23 (m, 5H, Ar-H), 4.12 (d, *J* = 9.0 Hz, 1H, H-1), 3.64 (s, 3H, OCH_3), 3.60–3.54 (m, 2H, H-6_{ab}), 3.53 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 3.39 (s, 3H, OCH_3), 3.21–3.16 (m, 2H, H-3, H-5), 3.13 (t, *J* = 9.0 Hz each, 1H, H-4), 2.97 (t, *J* = 9.0 Hz each, 1H, H-2); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.7–127.8 (Ar-C), 103.7 (C-1), 84.4 (C-3), 81.1 (C-5), 74.5 (C-4), 71.2 (C-6), 60.5 (OCH_3), 60.2 (OCH_3), 59.3 (OCH_3), 56.8 (OCH_3), 49.8 (C-2); ESI-MS: 399.0 $[M+Na]^+$; Anal. Calcd for $C_{16}H_{24}O_5Se$ (376.07): C, 51.20; H, 6.45. Found: C, 51.0; H, 6.67.

4.2.17. Methyl 3,4,6-tri-*O*-methyl-2-deoxy-2-phenylselenyl-α-D-mannopyranoside (26)

Colorless oil; $[\alpha]_D^{25}$ +4 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.62–7.22 (m, 5H, Ar-H), 4.88 (br s, 1H, H-1), 3.77–3.72 (m, 2H, H-6_{ab}), 3.64–3.53 (m, 3H, H-2, H-3, H-5), 3.53 (s, 3H, OCH_3), 3.43 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3), 3.33 (t, *J* = 9.0 Hz each, 1H, H-4), 3.29 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.8–127.6 (Ar-C), 101.5 (C-1), 80.4 (C-3), 77.4 (C-4), 71.8 (C-6), 71.3 (C-5), 60.6 (OCH_3), 59.3 (OCH_3), 56.8 (OCH_3), 54.8 (OCH_3), 48.7 (C-2); ESI-MS: 399.0 $[M+Na]^+$; Anal. Calcd for $C_{16}H_{24}O_5Se$ (376.07): C, 51.20; H, 6.45. Found: C, 51.02; H, 6.70.

4.2.18. 2-Propyl 3,4,6-tri-*O*-methyl-2-deoxy-2-phenylselenyl-β-D-glucopyranoside (27)

Colorless oil; $[\alpha]_D^{25}$ +34 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.63–7.20 (m, 5H, Ar-H), 4.42 (d, *J* = 9.0 Hz, 1H, H-1), 3.94–3.89 (m, 1H, CH(CH_3)$_2$), 3.60 (s, 3H, OCH_3), 3.59–3.53 (m, 2H, H-6_{ab}), 3.52 (s, 3H, OCH_3), 3.39 (s, 3H, OCH_3), 3.23–3.20 (m, 1H, H-5), 3.17 (t, *J* = 9.0 Hz each, 1H, H-3), 3.12 (t, *J* = 9.0 Hz each, 1H, H-4), 3.04 (t, *J* = 9.0 Hz, each 1H, H-2), 1.14 (d, *J* = 6.0 Hz, 3H, CH_3), 1.10 (d, *J* = 6.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.4–127.1 (Ar-C), 101.9 (C-1), 84.5 (C-3), 81.2 (C-5), 74.5 (C-4), 71.8 (CH(CH_3)$_2$), 71.5 (C-6), 60.4 (OCH_3), 60.2 (OCH_3), 59.3 (OCH_3), 51.0 (C-2), 23.4 (CH_3), 21.6 (CH_3); ESI-MS: 427.1 $[M+Na]^+$; Anal. Calcd for $C_{18}H_{28}O_5Se$ (404.11): C, 53.60; H, 7.00. Found: C, 53.42; H, 7.20.

4.2.19. 2-Propyl 3,4,6-tri-*O*-methyl-2-deoxy-2-phenylselenyl-α-D-mannopyranoside (28)

Colorless oil; $[\alpha]_D^{25}$ +28 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.61–7.23 (m, 5H, Ar-H), 5.09 (br s, 1H, H-1), 3.85–3.81 (m, 1H, CH(CH_3)$_2$), 3.80–3.77 (m, 1H, H-5), 3.71–3.67 (m, 2H, H-6_{ab}), 3.60 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H, H-3), 3.56 (br s, 1H, H-2), 3.53 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3), 3.35 (t, *J* = 9.0 Hz each, 1H, H-4), 1.55 (d, *J* = 6.0 Hz, 3H, CH_3), 1.03 (d, *J* = 6.0 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.4–127.4 (Ar-C), 98.1 (C-1), 80.5 (C-3), 77.6 (C-5), 71.8 (C-6), 71.3 (CH(CH_3)$_2$), 68.9 (C-4), 60.5 (OCH_3), 59.3 (OCH_3), 56.9 (OCH_3), 49.2 (C-2), 23.2 (CH_3), 21.2 (CH_3); ESI-MS: 427.1 $[M+Na]^+$; Anal. Calcd for $C_{18}H_{28}O_5Se$ (404.11): C, 53.60; H, 7.00. Found: C, 53.45; H, 7.22.

4.2.20. 2-Propyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-α-D-talopyranoside (30)

Colorless oil; $[\alpha]_D^{25}$ +33 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.52–7.25 (m, 5H, Ar-H), 5.45 (dd, *J* = 5.0, 3.0 Hz, 1H, H-3), 5.31 (br s, 1H, H-4), 5.42 (br s, 1H, H-1), 4.30–4.28 (m, 1H, H-5), 4.17–4.09 (m, 2H, H-6_{ab}), 3.86–3.81 (m, 1H, CH(CH_3)$_2$), 3.48–3.47 (m, 1H, H-2), 2.22, 2.08, 2.04 (3 s, 9H, 3 COCH_3), 1.19, 1.40 (2 d, *J* = 6.0 Hz each, 1H, 2 CH_3); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 170.2, 169.9, 169.8 (3 COCH$_3$), 133.6–127.6 (Ar-C), 100.1 (C-1), 70.3 (C-5), 67.2 (C-3), 66.7 (C-4), 66.5 (C(CH_3)$_2$, 62.1 (C-6), 46.7 (C-2), 23.1, 21.5, (2 CH_3), 21.0, 20.9, 20.6 (3 COCH$_3$); ESI-MS: 511.1 $[M+Na]^+$; Anal. Calcd for $C_{21}H_{28}O_8Se$ (488.09): C, 51.75; H, 5.79. Found: C, 51.59; H, 6.0.

4.2.21. ^{n}Butyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-α-D-talopyranoside (32)

Colorless oil; $[\alpha]_D^{25}$ +27 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.53–7.36 (m, 5H, Ar-H), 5.44 (dd, *J* = 5.0, 3.0 Hz, 1H, H-3), 5.31 (br s, 1H, H-4), 5.15 (br s, 1H, H-1), 4.22–4.20 (m, 1H, H-5), 4.19–4.10 (m, 2H, H-6_{ab}), 3.63–3.58 (m, 1H, O–CH_2–), 3.51–3.50 (m, 1H, H-2), 3.39–3.35 (m, 1H, O–CH_2–), 2.22, 2.08, 2.07 (3 s, 9H, 3 COCH_3), 1.56–1.49 (m, 2H, –CH_2–), 1.34–1.25 (m, 2H, –CH_2–), 0.89 (t, *J* = 7.4 Hz each, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.2, 169.8, 169.7 (3 COCH$_3$), 133.8–127.6 (Ar-C), 101.8 (C-1), 67.8 (C-5), 67.2 (C-3), 66.6 (C-4), 66.4 (–OCH_2–), 62.1 (C-6), 46.4 (C-2), 31.4 (CH_2), 21.0, 20.9, 20.7 (3 COCH$_3$), 19.3 (CH_2), 13.8 (CH_3); ESI-MS: 525.1 $[M+Na]^+$; Anal. Calcd for $C_{22}H_{30}O_8Se$ (502.11): C, 52.70; H, 6.03. Found: C, 52.52; H, 6.22.

4.2.22. Cyclohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-α-D-talopyranoside (34)

Colorless oil; $[\alpha]_D^{25}$ +48 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.52–7.25 (m, 5H, Ar-H), 5.47–5.45 (dd, *J* = 5.0, 3.0 Hz, 1H, H-3), 5.32 (br s, 1H, H-4), 5.28 (br s, 1H, H-1), 4.32–4.30 (m, 1H, H-5), 4.18–4.08 (m, 2H, H-6_{ab}), 3.52–3.50 (m, 1H, –CH–), 3.49–3.48 (m, 1H, H-2), 2.22, 2.05, 2.04, (3 s, 9H, 3 COCH_3), 1.73–1.64 (m, 4H), 1.36–1.18 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.1, 169.9, 169.6 (3 COCH$_3$), 133.5–127.5 (Ar-C), 99.9 (C-1), 77.1 (–CH–), 67.2 (C-5), 66.7 (C-3), 66.5 (C-4), 62.2 (C-6), 46.7 (C-2), 33.2, 31.5, 25.5, 24.2, 23.8, 21.0, 20.9, 20.6 (3 COCH$_3$); ESI-MS: 551.1 $[M+Na]^+$; Anal. Calcd for $C_{24}H_{32}O_8Se$ (528.12): C, 54.65; H, 6.11. Found: C, 54.48; H, 6.30.

4.2.23. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phenylselenyl-α-D-talopyranosyl-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (35)

Colorless oil; $[\alpha]_D^{25}$ +1 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.53–7.24 (m, 5H, Ar-H), 5,46 (d, *J* = 5.0 Hz, 1H, H-1_A), 5.43 (dd, *J* = 5.0, 3.0 Hz, 1H, H-3_B), 5.33 (br s, 1H, H-4_B), 5.22 (br s, 1H, H-1_B), 4.54 (dd, *J* = 7.5, 2.0 Hz, 1H, H-4_A), 4.35–4.33 (m, 1H, H-5_B), 4.27–4.26 (m, 1H, H-2_A), 4.20–4.16 (m, 1H, H-6_{aB}), 4.13–4.09 (m, 2H, H-3_A, H-6_{bB}), 3.91–3.86 (m, 1H, H-5_A), 3.76–3.61 (m, 2H, H-6_{abA}), 3.56–3.55 (m, 1H, H-2_B), 2.22, 2.08, 2.07 (3 s, 9H, 3 COCH_3), 1.48, 1.34, 1.30, 1.24 (4 CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.1, 169.9, 169.7 (3 COCH$_3$), 133.7–127.6 (Ar-C), 109.3, 108.6 (2 C(CH_3)$_2$), 101.8 (C-1_B), 96.1 (C-1_A), 70.9 (C-3_A), 70.6 (C-4_A), 70.5 (C-2_A), 76.1 (C-3_B), 66.9 (C-5_B), 66.5 (C-4_B), 66.4 (C-5_A), 66.2 (C-6_A), 62.0 (C-6_B), 46.2 (C-2_B), 26.1, 25.9, 24.9, 24.5, (4 CH_3), 21.0, 20.9, 20.7 (3 COCH$_3$); ESI-MS: 551.1 $[M+Na]^+$; Anal. Calcd for $C_{30}H_{40}O_{13}Se$ (688.16): C, 52.40; H, 5.86. Found: C, 52.22; H, 6.10.

4.2.24. Methyl (3,4,6-tri-*O*-acetyl-2-deoxy-2-phenylselenyl-α-D-talopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (36)

Colorless oil; $[\alpha]_D^{25}$ +7 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.57–7.19 (m, 20 H, Ar-H), 5.38 (dd, *J* = 5.0, 3.0 Hz, 1H, H-3_B), 5.28 (br s, 1H, H-4_B), 5.22 (br s, 1H, H-1_B), 4.95–4.54 (6 d, *J* = 11.0 Hz each, 6H, PhCH_2), 4.41 (d, *J* = 3.5 Hz, 1H, H-1_A), 4.17–4.15 (m, 1H, H-5_B), 4.12–4.00 (m, 2H, H-6_{abB}), 3.92 (t, *J* = 9.5 Hz each, 1H, H-4_A), 3.69–3.61 (m, 3H, H-5_A, H-6_{abA}), 3.49–3.48 (m, 1H, H-2_B), 3.36–3.32 (m, 2H, H-2_A, H-3_A), 3.30 (s, 3H, OCH_3), 2.20, 2.08, 1.97 (3 s, 9H, 3 COCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.1, 169.9, 169.8, (3 COCH$_3$), 138.6–127.6 (Ar-C), 101.9 (C-1_B), 97.7 (C-1_A), 82.1 (C-4_A), 80.1 (C-3_A), 77.6 (C-2_A), 75.7 (PhCH$_2$), 74.8 (PhCH$_2$),

73.2 (PhCH$_2$), 69.7 (C-5$_A$), 66.9 (C-3$_B$), 66.7 (C-4$_B$), 66.4 (C-5$_B$), 66.0 (C-6$_A$), 62.0 (C-6$_B$), 55.0 (OCH$_3$), 46.2 (C-2$_B$), 21.0, 20.9, 20.6 (3 COCH$_3$); ESI-MS: 915.2 [M+Na]$^+$; Anal. Calcd for $C_{46}H_{52}O_{13}Se$ (892.25): C, 61.95; H, 5.88. Found: C, 61.76; H, 6.10.

4.2.25. Methyl (3,4,6-tri-*O*-benzyl-2-deoxy-2-phenylselenyl-α-D-talopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (37)

Colorless oil; $[\alpha]_D^{25}$ +10 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59–7.18 (m, 35H, Ar-H), 5.27 (br s, 1H, H-1$_B$), 5.11–4.47 (10 d, *J* = 11.0 Hz each, 10 H, PhCH$_2$), 4.45 (d, *J* = 3.0 Hz, 1H, H-1$_A$), 4.40, 4.34 (2 d, *J* = 11.0 each, 2H, PhCH$_2$), 4.11–4.09 (m, 1H, H-3$_B$), 3.96–3.94 (m, 1H, H-5$_B$), 3.93 (t, *J* = 9.0 Hz, 1H, H-4$_A$), 3.85 (br s, 1H, H-4$_B$), 3.74–3.61 (m, 4H, H-6$_{abA}$, H-6$_{abB}$), 3.58–3.55 (m, 2H, H-2$_B$, H-5$_A$), 3.38 (dd, *J* = 9.5, 3.0 Hz, 1H, H-2$_A$), 3.35 (t, *J* = 9.5 Hz each, 1H, H-3$_A$), 3.21 (s, 3H, OCH$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.7–127.2 (Ar-C), 102.2 (C-1$_B$), 97.6 (C-1$_A$), 82.0 (C-4$_A$), 80.1 (C-2$_A$), 77 8 (C-3$_A$), 75.8 (PhCH$_2$), 74.9 (PhCH$_2$), 74.6 (PhCH$_2$), 74.5 (C-3$_B$), 73.7 (C-4$_B$), 73.4 (PhCH$_2$), 73.2 (PhCH$_2$), 70.1 (C-5$_B$), 69.8 (C-5$_A$), 69.7 (PhCH$_2$), 69.2 (C-6$_A$), 65.7 (C-6$_B$), 54.9 (OCH$_3$), 47.1 (C-2$_B$); ESI-MS: 1059.3 [M+Na]$^+$; Anal. Calcd for $C_{61}H_{64}O_{10}Se$ (1036.36): C, 70.71; H, 6.23. Found: C, 70.50; H, 6.46.

4.2.26. Methyl 3,4-di-*O*-acetyl-2,6-dideoxy-2-phenylselenyl-β-L-glucopyranoside (38)

Colorless oil; $[\alpha]_D^{25}$ −92 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.65–7.24 (m, 5H, Ar-H), 5.07 (t, *J* = 9.0 Hz each, 1H, H-4), 4.68 (t, *J* = 9.0 Hz each, 1H, H-3), 4.08 (d, *J* = 9.0 Hz, 1H, H-1), 3.48 (s, 3H, OCH$_3$), 3.40–3.35 (m, 1H, H-5), 3.05 (t, *J* = 9.0 Hz each, 1H, H-2), 2.02, 2.01 (2 s, 6H, 2 COCH$_3$), 1.21 (d, *J* = 6.0 Hz, 3H, CCH$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.4, 169.9 (2 COCH$_3$), 136.3–128.4 (Ar-C), 102.8 (C-1), 74.9 (C-3), 72.8 (C-5), 69.5 (C-4), 56.8 (OCH$_3$), 47.5 (C-2), 20.8, 20.7 (2 COCH$_3$), 17.4 (CCH$_3$); ESI-MS: 425.0 [M+Na]$^+$; Anal. Calcd for $C_{17}H_{22}O_6Se$ (402.05): C, 50.88; H, 5.53. Found: C, 50.70; H, 5.70.

4.2.27. Methyl 3,4-di-*O*-acetyl-2-deoxy-2-phenylselenyl-α-L-rhamnopyranoside (39)

Colorless oil; $[\alpha]_D^{25}$ −57 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.56–7.24 (m, 5H, Ar-H), 5.31 (dd, *J* = 9.5, 4.5 Hz, 1H, H-3), 5.18 (t, *J* = 9.0 Hz each, 1H, H-4), 4.96 (br s, 1H, H-1), 3.90 (br s, 1H, H-2), 3.85–3.80 (m, 1H, H-5), 3.35 (s, 3H, OCH$_3$), 2.02, 1.67 (2 s, 6H, 2 COCH$_3$), 1.21 (d, *J* = 6.0 Hz, 3H, CCH$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.7, 170.0 (2 COCH$_3$), 134.3–127.6 (Ar-C), 101.3 (C-1), 72.2 (C-3), 71.0 (C-5), 66.5 (C-4), 54.9 (OCH$_3$), 48.1 (C-2), 20.8, 20.3 (2 COCH$_3$), 17.7 (CCH$_3$); ESI-MS: 425.0 [M+Na]$^+$; Anal. Calcd for $C_{17}H_{22}O_6Se$ (402.05): C, 50.88; H, 5.53. Found: C, 50.72; H, 5.75.

4.2.28. 2-Propyl 3,4-di-*O*-acetyl-2,6-dideoxy-2-phenylselenyl-β-L-glucopyranoside (40)

Colorless oil; $[\alpha]_D^{25}$ −10 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61–7.22 (m, 5H, Ar-H), 5.06 (t, *J* = 9.0 Hz each, 1H, H-3), 4.69 (t, *J* = 9.0 each, 1H, H-4), 4.41 (d, *J* = 9.0 Hz, 1H, H-1), 3.97–3.92 (m, 1H, CH(CH$_3$)$_2$), 3.47–3.44 (m, 1H, H-5), 3.15 (t, *J* = 9.0 Hz each, 1H, H-2), 2.00, 1.97 (2 COCH$_3$), 1.19 (d, *J* = 6.0 Hz, 3H, CH$_3$), 1.15 (d, *J* = 6.0 Hz, 3H, CH$_3$), 1.13 (d, *J* = 6.0 Hz, 3H, CH$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.1, 169.7 (2 COCH$_3$), 134.9–127.7 (Ar-C), 101.2 (C-1), 74.9 (C-3), 73.0 (C-5), 72.2 (CH(CH$_3$)$_2$), 69.4 (C-4), 49.2 (C-2), 23.4 (CH$_3$), 21.7 (CH$_3$), 20.7 (2 C, COCH$_3$), 17.5 (CH$_3$); ESI-MS: 453.0 [M+Na]$^+$; Anal. Calcd for $C_{19}H_{26}O_6Se$ (430.08): C, 53.15; H, 6.10. Found: C, 53.0; H, 6.27.

4.2.29. 2-Propyl 3,4-di-*O*-acetyl-2-deoxy-2-phenylselenyl-α-L-rhamnopyranoside (41)

Colorless oil; $[\alpha]_D^{25}$ −78 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.56–7.22 (m, 5H, Ar-H), 5.35 (dd, *J* = 9.0, 4.5 Hz, 1H, H-3), 5.18 (t, *J* = 9.0 Hz each, 1H, H-4), 5.16 (br s, 1H, H-1), 3.92–3.88 (m, 1H, H-5), 3.87–3.83 (m, 2H, H-2, (CH(CH$_3$)$_2$), 2.03, 1.66 (2 s, 6H, 2 COCH$_3$), 1.20, 1.18, 1.13 (3 d, *J* = 6.0 Hz each, 9H, 3 CH$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.1, 169.7 (2 COCH$_3$), 134.1–127.5 (Ar-C), 98.2 (C-1), 72.5 (C-3), 71.1 (C-5), 69.7 (C-4), 66.6 (CH(CH$_3$)$_2$), 48.8 (C-2), 23.2 (CH$_3$), 21.4 (CH$_3$), 20.8, 20.3 (2 COCH$_3$), 17.6 (CH$_3$); ESI-MS: 453.0 [M+Na]$^+$; Anal. Calcd for $C_{19}H_{26}O_6Se$ (430.08): C, 53.15; H, 6.10. Found: C, 53.0; H, 6.27.

Acknowledgements

A.S. thanks CSIR, New Delhi for providing a Senior Research Fellowship. This work was funded by the Department of Science and Technology (DST), New Delhi (SR/S1/OC-83/2010) and Bose Institute, Kolkata.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2012.08.009.

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